



**A RAPID AND GREEN METHOD FOR SOLVENT-FREE CLICK SYNTHESIS OF  
CARBAMATOALKYL NAPHTHOLS USING Ce(SO<sub>4</sub>)<sub>2</sub>.4H<sub>2</sub>O AS NOVEL AND  
REUSABLE INORGANIC CATALYST**

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**Abstract:** In the absence of any solvent, the reaction of  $\beta$ -naphthol with aromatic aldehydes and methyl or benzyl carbamate catalyzed by cerium (IV) sulfate tetrahydrate, Ce(SO<sub>4</sub>)<sub>2</sub>.4H<sub>2</sub>O, as an effective and novel inorganic solid acid catalyst under thermal heating conditions smoothly afforded carbamatoalkyl naphthols in high yields. The catalyst is inexpensive and readily available and can be recovered conveniently and reused efficiently such that a considerable catalytic activity still could be achieved after fifth run. Other advantages of this protocol are short reaction times, easy work-up and absence of any volatile and hazardous organic solvents.

**Keywords:** Carbamatoalkyl naphthols, Ce(SO<sub>4</sub>)<sub>2</sub>.4H<sub>2</sub>O, Solvent-free conditions

**Introduction**

Organic syntheses involving greener process have been investigated world wide due to stringent environment and economic regulations. In addition, with increasing environmentally concerns and the regulatory constraints faced in the chemical and pharmaceutical industries, development of environmentally benign organic reactions has become a crucial and demanding research area in modern organic chemical research<sup>i-iv</sup>. Multi-component reactions (MCRs) are a promising and vital field of chemistry because the synthesis of complicated molecules can be achieved in a very fast, efficient, and time saving manner without the isolation of any intermediates and hence it has drawn the attraction of organic chemists to develop novel MCRs and or to improve known MCRs<sup>v-vii</sup>. One such reaction is the synthesis of carbamatoalkyl naphthols. These compounds can be converted to important biologically active 1-aminomethyl-2-naphthol derivatives by carbamate hydrolysis. The hypotensive and bradycardiac effects of later compounds have been evaluated<sup>viii,ix</sup>. A literature survey revealed

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7.35 (m, 7H, arom-H), 7.40 (t, 1H,  $J = 7.2$  Hz, arom-H), 7.69 (br, 1H, NH), 7.78 (d, 1H,  $J = 8.8$  Hz, arom-H), 7.82 (d, 1H,  $J = 8.0$  Hz, arom-H), 7.93 (d, 1H,  $J = 8.0$  Hz, arom-H), 10.14 (s, 1H, OH); IR (KBr disc):  $\nu$  3422 (NH), 3198 (OH), 1677 (C=O)  $\text{cm}^{-1}$ .

**Methyl [(2-hydroxynaphthalen-1-yl)(3-nitrophenyl)methyl]carbamate 4e (R = 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, R' = Me):** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  3.61 (s, 3H, OCH<sub>3</sub>), 6.97 (d, 1H,  $J = 8.0$  Hz, CH), 7.23 (d, 1H,  $J = 8.8$  Hz, arom-H), 7.31 (t, 1H,  $J = 7.6$  Hz, arom-H), 7.44 (t, 1H,  $J = 7.6$  Hz, arom-H), 7.57 (t, 1H,  $J = 8.0$  Hz, arom-H), 7.64 (d, 1H,  $J = 8.0$  Hz, arom-H), 7.31 (t, 2H,  $J = 9.2$  Hz, arom-H), 7.96 (br, 2H, NH & arom-H), 8.08 (d, 1H,  $J = 8.4$  Hz, arom-H), 8.13 (s, 1H, arom-H), 10.26 (s, 1H, OH); IR (KBr disc):  $\nu$  3388 (NH), 3286 (OH), 1686 (C=O), 1526 & 1348 (NO<sub>2</sub>)  $\text{cm}^{-1}$ .

**Methyl [(2-hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl]carbamate 4f (R = 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, R' = Me):** <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  3.59 (s, 3H, OCH<sub>3</sub>), 6.93 (d, 1H,  $J = 8.4$  Hz, CH), 7.20 (d, 1H,  $J = 8.8$  Hz, arom-H), 7.29 (t, 1H,  $J = 7.4$  Hz, arom-H), 7.41 (t, 1H,  $J = 7.1$  Hz, arom-H), 7.46 (d, 2H,  $J = 8.6$  Hz, arom-H), 7.77-7.85 (m, 3H, arom-H), 7.88 (br, 1H, NH), 8.14 (d, 2H,  $J = 8.8$  Hz, arom-H), 10.18 (s, 1H, OH); IR (KBr disc):  $\nu$  3423 (NH), 3258 (OH), 1682 (C=O), 1516 & 1346 (NO<sub>2</sub>)  $\text{cm}^{-1}$ .

**Benzyl [(2-hydroxynaphthalen-1-yl)(3-nitrophenyl)methyl]carbamate 4h (R = 3-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, R' = CH<sub>2</sub>Ph):** <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  5.06 (d,  $J = 12.6$  Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 5.14 (d,  $J = 12.6$  Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 6.98 (d, 1H,  $J = 8.6$  Hz, CH), 7.22 (d, 1H,  $J = 8.8$  Hz, arom-H), 7.25-7.45 (m, 7H, arom-H), 7.55 (t, 1H,  $J = 7.9$  Hz, arom-H), 7.62 (d, 1H,  $J = 7.7$  Hz, arom-H), 7.81 (d, 1H,  $J = 9.0$  Hz, arom-H), 7.83 (d, 1H,  $J = 8.5$  Hz, arom-H), 7.95 (br, 1H, NH), 8.07 (d, 2H,  $J = 8.0$  Hz, arom-H), 8.13 (s, 1H, arom-H), 10.22 (s, 1H, OH); IR (KBr disc):  $\nu$  3385 (NH), 3350 (OH), 1694 (C=O), 1528 & 1349 (NO<sub>2</sub>)  $\text{cm}^{-1}$ .

**Benzyl [(2-hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl]carbamate 4i (R = 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, R' = CH<sub>2</sub>Ph):** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  5.07 (d,  $J = 12.4$  Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 5.13 (d,  $J = 12.4$  Hz, 1H, one proton of diastereotopic protons in CH<sub>2</sub>), 6.99 (d, 1H,  $J = 8.4$  Hz, CH), 7.22 (d, 1H,  $J = 8.8$  Hz, arom-H), 7.25-7.55 (m, 10H, arom-H), 7.83 (t, 2H,  $J = 8.0$  Hz, arom-H), 7.89 (br, 1H, NH), 8.16 (d, 2H,  $J = 8.8$  Hz, arom-H), 10.23 (s, 1H, OH); IR (KBr disc):  $\nu$  3413 (NH), 3294 (OH), 1686 (C=O), 1516 & 1347 (NO<sub>2</sub>)  $\text{cm}^{-1}$ .

## Results and discussion

Our efforts to develop an efficient and environmentally benign methodology for the synthesis of carbamatoalkyl naphthols focused initially on the three-component condensation of  $\beta$ -naphthol (1 mmol), 4-chlorobenzaldehyde (1 mmol), and methyl carbamate (1.1 mmol), as a model reaction for the synthesis of compound **4c**. Because of the reactions under solvent-free conditions offer several advantages in preparative procedures such as environmental compatibility, simplification of work-ups, formation of cleaner products, enhanced selectivity, reduction of by-products, a reduction in waste produced, and much improved reaction rates, we decided to investigate the efficiency of Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O in the synthesis of carbamatoalkyl naphthols under solvent-free conditions. In order to get the effective reaction conditions, the reaction was optimized in terms of catalyst composition and influence of temperature. The results are summarized in Table 1. First, the reaction was carried out without any catalyst at high temperature under solvent-free conditions. Only a trace amount of product was observed even after prolonged reaction time (entry 1). The best result was conducted at 90 °C in the presence of 7 mol% of Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O (entry 10). An increase in

the reaction temperature and amount of the catalyst did not change the yields significantly (entries 11 and 12).

Next, the reaction was performed in the presence of 7 mol% of  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  in different solvents including EtOH, MeOH,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{CO}_2\text{Et}$ . As shown, the product yield in refluxing  $\text{H}_2\text{O}$  was low even after 60 min of reaction (entry 15), whereas relatively good to high yields were obtained in other tested solvents. Although, there is no significant difference in yield between solvent-free conditions and solvents including EtOH,  $\text{CH}_3\text{CN}$ , and  $\text{CH}_3\text{CO}_2\text{Et}$ , the reaction under solvent-free conditions has shorter reaction time. On the other hand, in solvent-free condition, the catalyst can be readily recovered from the reaction mixture and subsequently reused several times. Consequently, all subsequent reactions were carried out in the presence of 7 mol% of the catalyst at 90 °C under solvent-free conditions.

**Table 1.** Optimization of reaction conditions for synthesis of compound **4c** catalyzed by  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ <sup>a</sup>

Entry	Catalyst (mol%)	Solvent	T (°C)	Time (min)	Isolated Yield (%)
1	None	----	120	120	trace
2	2	----	50	30	56
3	2	----	70	18	72
4	2	----	90	12	77
5	5	----	50	28	60
6	5	----	70	15	77
7	5	----	90	5	84
8	7	----	50	20	68
9	7	----	70	12	82
10	7	----	90	5	95
11	7	----	120	5	95
12	10	----	90	5	96
13	7	EtOH	Reflux	30	90
14	7	MeOH	Reflux	30	71
15	7	$\text{H}_2\text{O}$	Reflux	60	15
16	7	$\text{CH}_3\text{CN}$	Reflux	30	90
17	7	$\text{CHCl}_3$	Reflux	30	70
18	7	$\text{CH}_3\text{CO}_2\text{Et}$	Reflux	30	88

<sup>a</sup>Reaction conditions:  $\beta$ -naphthol (1 mmol), 4-chlorobenzaldehyde (1 mmol), and methyl carbamate (1.1 mmol).

Encouraged by the remarkable results obtained with the above reaction conditions, and in order to show the generality and scope of this new protocol, a range of carbamatoalkyl naphthols were prepared by the reaction of  $\beta$ -naphthol, aromatic aldehydes, and methyl or benzyl carbamate in the presence of  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  under optimized reaction conditions and the results are summarized in Table 2. As shown, all reactions proceed very clean to give the corresponding carbamatoalkyl naphthol products **4a-i** in high yields over short reaction times and no undesirable side-products were observed. Under the same conditions, this reaction did not proceed when aliphatic aldehydes such as propionaldehyde or isobutyraldehyde (entries 10 and 11) were used as the starting material.

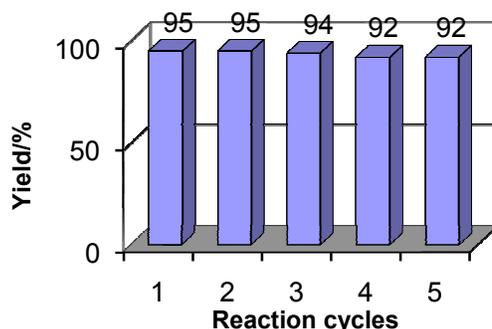
The principle advantage of the use of solid catalysts in organic transformations is their reusability. Thus, the reusability of  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  was explored using the model reaction system under the optimized conditions. The catalyst was readily recovered from the reaction mixture using the procedure outlined in the experimental section. The separated catalyst was washed with hot ethanol and subsequently dried at 60 °C under vacuum for 2 h before being reused in a similar reaction. The catalyst could be used at least five times without significant reduction in its activity (Fig. 1). Furthermore, retention of the structure of the catalyst was confirmed by comparing the FT-IR spectra of the recovered catalyst after fifth run (Fig. 2b)

with that of the fresh catalyst (Fig. 2a) for the model reaction. As shown, these spectra are almost identical.

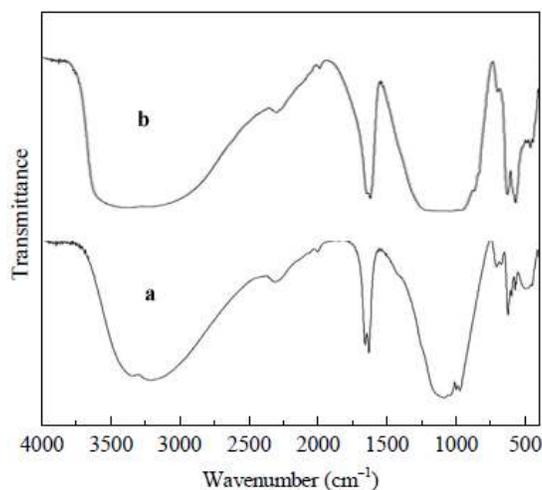
**Table 2.** Synthesis of carbamatoalkyl naphthols **4a-i** using  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  as catalyst<sup>a</sup>

Entry	R	R'	Product	Time (min)	Isolated Yields (%)	m.p. (°C)	
						Found	Reported
1	C <sub>6</sub> H <sub>5</sub>	Me	<b>4a</b>	5	91	220-222	217-219 <sup>[xi]</sup>
2	4-BrC <sub>6</sub> H <sub>4</sub>	Me	<b>4b</b>	8	87	204-207	195-197 <sup>[xi]</sup>
3	4-ClC <sub>6</sub> H <sub>4</sub>	Me	<b>4c</b>	5	95	208-210	202-204 <sup>[xiii]</sup>
4	2-ClC <sub>6</sub> H <sub>4</sub>	Me	<b>4d</b>	5	92	191-193	182-184 <sup>[xi]</sup>
5	3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Me	<b>4e</b>	5	96	252-254	252 <sup>[xi]</sup>
6	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Me	<b>4f</b>	5	92	206-207	205-207 <sup>[xi]</sup>
7	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> Ph	<b>4g</b>	6	90	174-176	179-180 <sup>[xi]</sup>
8	3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> Ph	<b>4h</b>	5	91	200-202	206-208 <sup>[xiii]</sup>
9	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> Ph	<b>4i</b>	5	92	197-199	202-204 <sup>[xiii]</sup>
10	CH <sub>3</sub> CH <sub>2</sub>	Me	None	40	----	----	----
11	(CH <sub>3</sub> ) <sub>2</sub> CH	Me	None	40	----	----	----

<sup>a</sup>Reaction conditions:  $\beta$ -naphthol (1 mmol), aromatic aldehyde (1 mmol), methyl or benzyl carbamate (1.1 mmol), and  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  (0.07 mmol, 7 mol%) at 90 °C under solvent-free conditions.

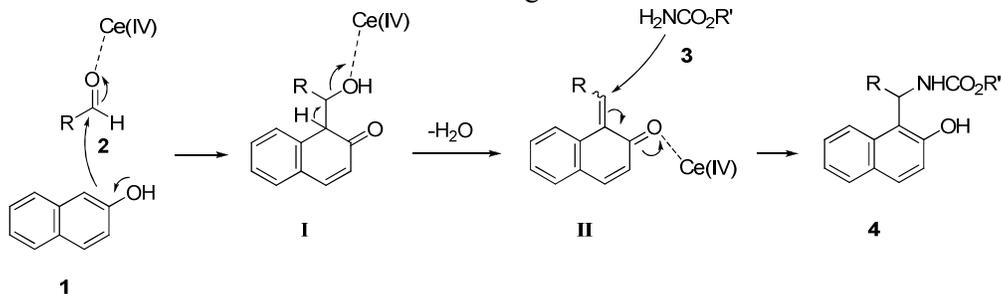


**Fig. 1.** Reusability of  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  for the synthesis of compound **4c**



**Fig. 2.** FT-IR spectra of fresh catalyst  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  (a), and recovered catalyst after fifth run (b) for synthesis of compound **4c**.

Although we did not investigate the reaction mechanism, to show the catalyst's role, a plausible mechanism for the present reaction may proceed as depicted in Scheme 2. It is proposed that the reaction occurs *via* initial formation of the *ortho*-quinone methide (*o*-QM) intermediate [II], prepared by condensation of  $\beta$ -naphthol **1** with aryl aldehydes **2** *via* the intermediate [I]. Subsequent Michael addition of the *o*-QM intermediate [II] with amino group in carbamate **3** afforded final products **4**. As shown in Scheme 2, we propose that the catalyst  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} \equiv \text{Ce}(\text{IV})$  activate the carbonyl group in aryl aldehydes and also the intermediates [I] and [II] in this reaction. Under these conditions, attempts to isolate the intermediates failed even after careful monitoring of the reactions.



**Scheme 2.** Plausible mechanism for the formation of carbamatoalkyl naphthols in the presence of  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} \equiv \text{Ce}(\text{IV})$  as catalyst

### Conclusion

We showed that  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , as a novel inorganic solid acid catalyst, efficiently catalyzed the synthesis of carbamatoalkyl naphthols by one-pot three-component condensation reaction of  $\beta$ -naphthol, aryl aldehydes, with methyl or benzyl carbamate under solvent-free conditions. Aromatic aldehydes reacted successfully and gave the expected products in high yields while no product could be detected using aliphatic aldehydes. The method was fast and high yielding, and the work-up was easy. Furthermore, the catalyst could be recycled after a simple work-up, and used at least five times without significant reduction in its catalytic activity. The procedure is also advantageous in the sense that it is a solvent-free reaction and therefore operates under environmentally friendly conditions.

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