Green Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

Green Chemistry

RSCPublishing

PAPER

β-Cyclodextrin-butane sulfonic acid: an efficient and reusable catalyst for the multicomponent synthesis of 1-amidoalkyl-2-naphthols under solvent-free conditions

Cite this: DOI: 10.1039/xoxxoooooox

Received ooth February 2015,
Accepted ooth February 2015

DOI: 10.1039/xoxxoooooox

www.rsc.org/

Kai Gong*[a], Hualan Wang,[b] Xiaoxue Ren,[a] Ying Wang[a] and Jinghua Chen[a]

A β-cyclodextrin-butane sulfonic acid is reported as an efficient catalyst for the one-pot synthesis of 1-amidoalkyl-2-naphthols by the multicomponent condensation of aromatic aldehydes, β-naphthol and amides under solvent-free conditions. The present methodology offers several advantages such as shorter reaction time, mild reaction conditions, simple operational procedure, using of recyclable catalyst.

1. Introduction

Recently, development of new processes that minimize pollution in chemical industry has received considerable attention due to growing environmental concerns. In this direction, heterogeneous catalysis has emerged as a useful tool to reduce waste production with regard to simplicity of the process, lower contamination of the products with the active catalytic species, avoiding the use of toxic solvents, separation and recycling of the catalysts.[1] For this purpose, some catalytic active centers have been often immobilized on inorganic materials, synthetic organic polymers or hybrid materials.[2] Biopolymers such as starch, cellulose, chitosan or wool are emerging as green and sustainable supports in heterogeneous catalysis.[3] Among these, cyclodextrin (CD) has also drawn much attention due to its water-solubility and special hydrophobic cavity. By using these properties, cyclodextrins and cyclodextrin derivatives have been used as catalysts in organic synthesis.[4] However, further efforts are necessary in the design of new heterogeneous catalysts using cyclodextrins as green and biodegradable supports, to achieve excellent catalytic activity and selectivity.

Multi-component reactions (MCRs) have been proven remarkably successful in generating molecular complexity in a single synthetic operation, and have shown simple procedures, high atom-economy and high selectivity due to the formation of carbon-carbon and carbon-heteroatom bonds in one-pot.[5] Therefore, researchers have made great efforts to find and develop new MCRs.

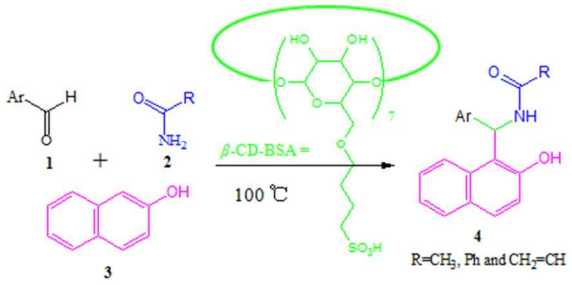
The synthesis of 1-amidoalkyl-2-naphthols is important as 1,3-amino-oxygenated moiety is ubiquitous to a variety of biologically compounds.[6] 1-Amidoalkyl-2-naphthols can be prepared by multicomponent condensation of aldehydes, β-naphthol and acetonitrile or amides in the presence of Brønsted or Lewis acids, such as *p*-TSA,[7] $Fe(HSO_4)_3$,[8] P_2O_5,[9] acid ionic liquid or supported acidic ionic liquid,[10] nano-Fe_3O_4-SO_3H,[11] cellulose-SO_3H,[12] Carbon-SO_3H,[13] MCM-41-*N*-propylsulfamic acid,[14] $HClO_4$-SiO_2,[15] $H_4SiW_{12}O_{40}$,[16] montmorillonite K10,[17] $FeCl_3$-SiO_2,[18] I_2,[19] MoO_3-ZrO_2,[20] $K_5CoW_{12}O_{40}\cdot H_2O$,[21] nano-$S_8$[22] and zwitterionic salts[23]. 1-Amidoalkyl-2-naphthols have also been synthesized under microwave[24] and ultrasound irradiations[25]. However, these methodologies suffer from one or more shortcomings such as low yield, prolonged reaction time, use of toxic organic solvents, requirement of excess of reagents or catalysts and harsh reaction conditions. Therefore, introducing clean processes and utilizing eco-friendly catalysts which can be simply recycled at the end of reactions have been under permanent attention. The demand for environmentally benign procedure with heterogeneous and reusable catalyst promoted us to develop a safe alternate method for the synthesis of 1-amidoalkyl-2-naphthols.

Having the above points in mind, we wish to report the synthesis of a β-cyclodextrin-butane sulfonic acid (β-CD-BSA),

[a] School of Pharmaceutical Science, Jiangnan University, Wuxi, 214122, China.
[b] Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Normal University, Hangzhou, 311121, China.

† Electronic Supplementary Information (ESI) available: The FT-IR, ^{1}H NMR and ^{13}C NMR for β-CD-BSA and some compounds. See DOI: 10.1039/b000000x/

from available and inexpensive starting materials, and its application as a highly efficient and green catalyst for the one-pot, three-component synthesis of 1-amidoalkyl-2-naphthols in excellent yields (Scheme 1). To the best of our knowledge, the synthesis of 1-amidoalkyl-2-naphthols catalyzed by *β*-CD-BSA is not yet reported.

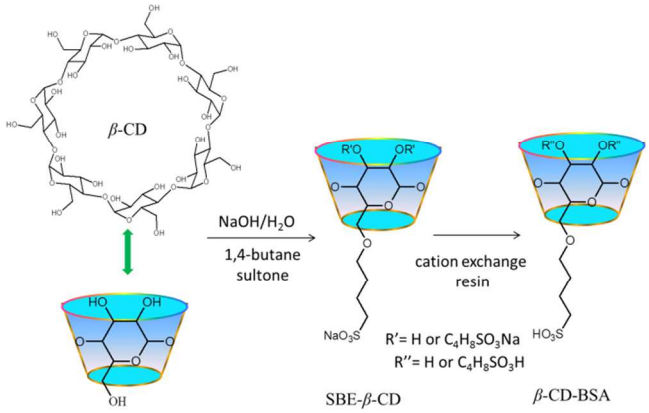


Scheme 1 Synthesis of 1-amidoalkyl-2-naphthols

2. Results and discussion

2.1 Preparation and characterization of *β*-CD-BSA

The detailed preparation for *β*-CD-BSA is shown in Scheme 2. First, commercially available *β*-CD was reacted with 1,4-butane sultone in NaOH solution to afford sulfobutyl ether *β*-cyclodextrin (SBE-*β*-CD), which was further treated with acidic resin to give *β*-CD-BSA.



Scheme 2 Synthesis of *β*-CD-BSA

β-CD-BSA was characterized by FT-IR spectroscopy and ^{1}H NMR. The FT-IR spectra of *β*-CD and *β*-CD-BSA are shown in Figure 1. The O-H stretching vibration at 3400 cm^{-1}, the C-H stretching vibration at 2925 cm^{-1}, the C-OH stretching vibration cm^{-1} and other adsorption peaks in the spectrum of *β*-CD also appeared nearly at the same wavenumbers in the spectrum of *β*-CD-BSA, indicating that *β*-CD-BSA are made up chiefly by *β*-CD units. Compared with *β*-CD, *β*-CD-BSA exhibited a broader O-H stretching vibration (at 3410 cm^{-1}) and a stronger O-H deformation vibration (at 1643 cm^{-1}), probably because O-H bonds in *β*-CD-BSA were influenced by the introduced sulfonate groups. The characteristic adsorption peaks of sulfonate groups (S=O stretching vibration at 1158 and 1043 cm^{-1}) were absent in the spectrum of *β*-CD-BSA, illustrating the success graft of butane sulfonic acid functionality onto *β*-CD, which was further verified from ^{1}H NMR result.

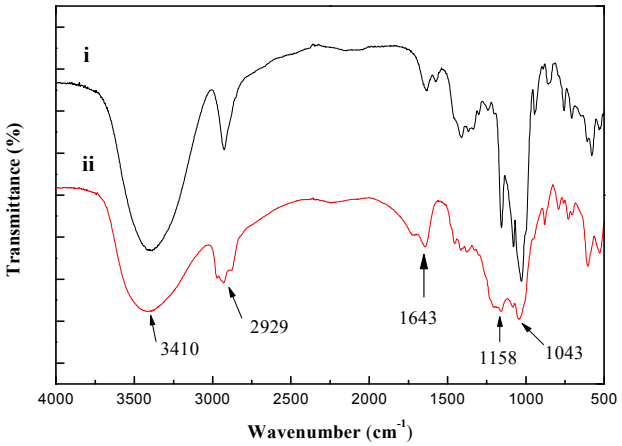


Figure 1 FT-IR spectra of *β*-CD (i) and *β*-CD-BSA (ii) in KBr

The proton chemical shifts for *β*-CD and *β*-CD-BSA are shown in Figure 2. Two important peaks at 2.88 ppm (-OCH_2CH_2-CH_2*CH_2*SO_3H) and 1.70 ppm (-OCH_2 *CH_2CH_2*CH_2SO_3H) are observed. The C1-H was split into two peaks at 5.01 ppm and 5.14 ppm, due to the distribution of the butane sulfonic acid among the C2-OH and C6-OH. The significant distinguish for ^{1}H NMR spectra strongly confirmed that the butane sulfonic acid was successfully grafted onto the *β*-CD by covalent bonds. The degree of substitution for butane sulfonic acid was calculated according to previous described method,[26] and it was about 7. The average substitution degree was also estimated from the elemental analysis. The elemental compositions of C, H, and S, are 37.85%, 6.42% and 10.18%, respectively. The radio of C/S was used to calculate the average degree of substitution. It was 7.10. The results from different methods are in agreement with each other.

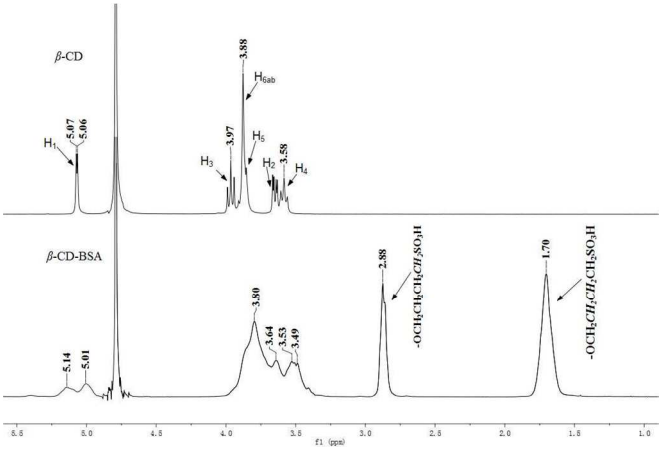


Figure 2 ^{1}H NMR spectra of *β*-CD and *β*-CD-BSA in D_2O

Thermal gravimetric (TG) and derivative thermal gravimetric (DTG) analysis of *β*-CD-BSA was investigated at the range of 30 to 800 ℃, with a temperature increase rate of 10 ℃/min in a nitrogen atmosphere (Figure 3). According to TG and DTG

diagrams, the weight loss processes of *β*-CD-BSA could be divided into three stages. The first weight loss in the range of 40-120 ℃ was attributed to the release of water molecules, including complexed water inside the cavity of *β*-CD-BSA and uncomplexed water outside the cavity of *β*-CD-BSA. The second weight loss in the range of 150-300 ℃ was due to that the sulfonate groups were degraded. The third weight loss in the range of 320-400 ℃ was attributed to the decomposition of *β*-CD framework. Therefore, *β*-CD-BSA is stable below about 150 ℃, which is enough for constant during the catalysis procedure of our experiments.

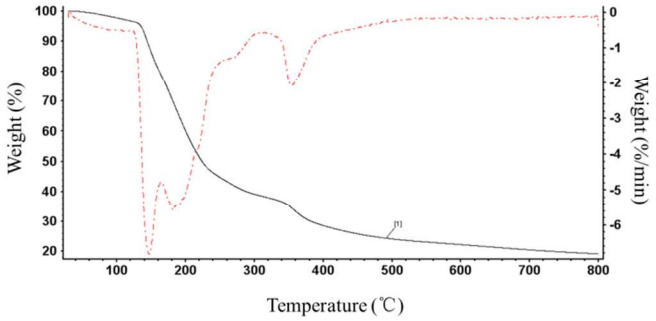
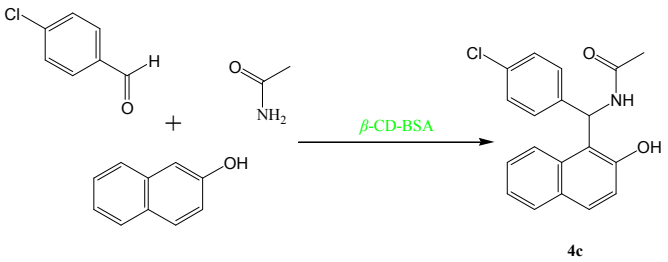


Figure 3 The TG and DTG diagrams of *β*-CD-BSA

2.2 Synthesis of 1-amidoalkyl-2-naphthols

Preliminary investigation of the title reaction was carried out using *β*-CD-BSA as catalyst, while MCRs of *p*-chlorobenzaldehyde, *β*-naphthol and acetamide were chosen as a model reaction to optimize the reaction conditions (Scheme 3). The results are summarized in Table 1. All of the reactions were performed in the optimized experimental procedure given in the Experimental Section. The reaction did not proceed in absence of catalyst at room temperature under neat condition (Table 1, entry 1). Stirring the mixture at 50/100/120 ℃ also could not form product after prolonging reaction time (Table 1, entry 2-4). These negative results indicated the necessity of a catalyst. Next, we investigated the reaction by using *β*-CD-BSA (1 mol%) under solvent-free condition at 100 ℃. To our surprise, *β*-CD-BSA showed outstanding activity in the formation of desired product in excellent yield within much shorter time (Table 1, entry 5). The reaction was very clean with no side product formation. A further increase in catalyst amount did not improve the product yields (Table 1, entry 6). *β*-CD and SBE-*β*-CD were used as catalysts in the same conditions for comparison, however, no reaction occurred or giving poor yields (Table 1, entry 7-8). In order to check the effect of solvents (if any) in the reaction, several solvents were screened. The reactions were sluggish and gave poor yields with longer reaction time (Table 1, entry 9-14). In a word, the optimal conditions were determined as that the reaction was catalyzed by 1 mol% of *β*-CD-BSA under solvent-free condition at 100 ℃.



Scheme 3 Model reaction for synthesis of **4c**

Table 1. Optimization of reaction conditions for the synthesis of **4c**[a]

Entry	Solvents	T (℃)	Catalyst(mol%)	Time(min)	Yield(%)[b]
1	Solvent-free	rt	none	120	NR[c]
2	Solvent-free	50	none	120	NR[c]
3	Solvent-free	100	none	120	NR[c]
4	Solvent-free	120	none	120	NR[c]
5	Solvent-free	100	*β*-CD-BSA (1)	10	90
6	Solvent-free	100	*β*-CD-BSA (2)	10	90
7	Solvent-free	100	*β*-CD (1)	10	NR[c]
8	Solvent-free	100	SBE-*β*-CD (1)	10	40
9	H_2O	100	*β*-CD-BSA (1)	100	65
10	CH_3CH_2OH	reflux	*β*-CD-BSA (1)	60	81
11	$ClCH_2CH_2Cl$	reflux	*β*-CD-BSA (1)	150	78
12	EtOAc	reflux	*β*-CD-BSA (1)	150	38
13	THF	reflux	*β*-CD-BSA (1)	150	32
14	Toluene	100	*β*-CD-BSA (1)	150	26

[a] Reaction condition: *p*-chlorobenzaldehyde (2 mmol), *β*-naphthol (2 mmol) and acetamide (2 mmol), solvent-free or solvent (5 mL). [b] Isolated yield. [c]No reaction was observed.

Table 2 Synthesis of 1-amidoalkyl-2-naphthols catalyzed by β-CD-BSA under solvent-free conditions[a]

Entry	Ar	R	Compound	Time / min	Yield / %[b]	TOF / min^{-1}
1	C_6H_5	CH_3	**4a**	6	90	210.0
2	2-Cl-C_6H_4	CH_3	**4b**	10	90	126.0
3	4-Cl-C_6H_4	CH_3	**4c**	10	94	131.6
4	2,4-Cl_2-C_6H_4	CH_3	**4d**	10	93	130.2
5	4-Br-C_6H_4	CH_3	**4e**	8	92	161.0
6	2-NO_2-C_6H_4	CH_3	**4f**	14	90	90.0
7	3-NO_2-C_6H_4	CH_3	**4g**	12	91	106.2
8	4-NO_2-C_6H_4	CH_3	**4h**	7	95	190.0
9	4-CH_3-C_6H_4	CH_3	**4i**	10	90	126.0
10	4-CH_3O-C_6H_4	CH_3	**4j**	20	87	60.9
11	4-OH-C_6H_4	CH_3	**4k**	12	89	103.8
12	C_6H_5	CH_2=CH	**4l**	6	86	200.7
13	2-Cl-C_6H_4	CH_2=CH	**4m**	10	90	126.0
14	4-Cl-C_6H_4	CH_2=CH	**4n**	8	92	161.0
15	2,4-Cl_2-C_6H_4	CH_2=CH	**4o**	10	90	126.0
16	4-F-C_6H_4	CH_2=CH	**4p**	10	94	131.6
17	2-NO_2-C_6H_4	CH_2=CH	**4q**	12	88	102.7
18	3-NO_2-C_6H_4	CH_2=CH	**4r**	8	91	159.3
19	4-NO_2-C_6H_4	CH_2=CH	**4s**	10	93	130.2
20	4-CH_3-C_6H_4	CH_2=CH	**4t**	10	92	128.8
21	4-CH_3O-C_6H_4	CH_2=CH	**4u**	10	89	124.6
22	4-OH-C_6H_4	CH_2=CH	**4v**	10	90	126.0
23	C_6H_5	C_6H_5	**4w**	6	88	205.3
24	2-Cl-C_6H_4	C_6H_5	**4x**	10	90	126.0
25	4-Cl-C_6H_4	C_6H_5	**4y**	10	93	130.2
26	2,4-Cl_2-C_6H_4	C_6H_5	**4z**	10	91	127.4
27	4-F-C_6H_4	C_6H_5	**4A**	6	90	210.0
28	2-NO_2-C_6H_4	C_6H_5	**4B**	5	88	246.4
29	3-NO_2-C_6H_4	C_6H_5	**4C**	7	91	182.0
30	4-NO_2-C_6H_4	C_6H_5	**4D**	10	94	131.6
31	4-CH_3-C_6H_4	C_6H_5	**4E**	8	91	159.3
32	4-CH_3O-C_6H_4	C_6H_5	**4F**	10	88	123.2
33	4-OH-C_6H_4	C_6H_5	**4G**	9	90	140.0

[a] Reaction conditions: aldehydes (2 mmol), β-naphthol (2 mmol) and amide (2 mmol), β-CD-BSA (0.02 mmol), 100 ℃, solvent-free condition. [b] Isolated yield.

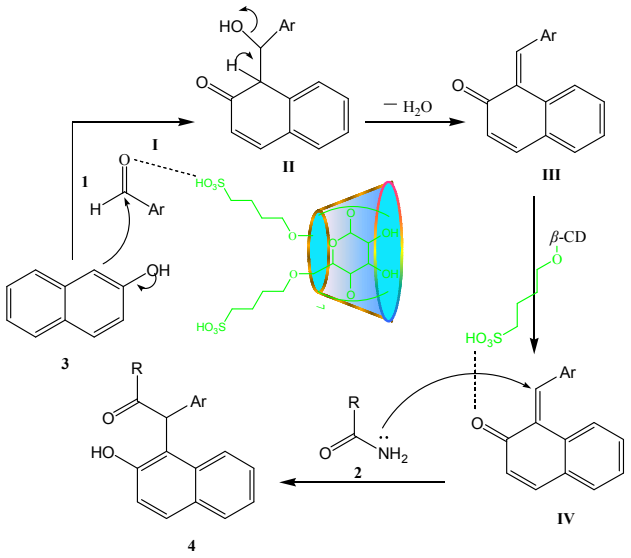
Encouraged by the remarkable results obtained with the above reaction conditions, and to show the generality and scope of this new protocol, a range of amidoalkyl naphthols were prepared in *β*-CD-BSA under optimized conditions, with the results shown in Table 2. Most of the reactions proceeded very efficiently and no-byproducts were observed. As can be seen from Table 2, aromatic aldehydes bearing either electron-donating or electron-withdrawing substituents reacted successfully with *β*-naphthol and amides to give the corresponding amidoalkyl naphthols in high yields with a high TOF in the range 60.9-246.4 min^{-1} and in short reaction time. The results also show that the aromatic aldehydes with electron-withdrawing react more quickly and produce higher yields compared to the aromatic aldehydes with electron-donating groups. We find that, when the electron-withdrawing substituents of aromatic aldehydes are nitro and halogen, the yields vary with the substituent positions and follow the rule: *ortho* < *meta* < *para*, no matter what kind of substituent R in amides. Different amides, such as acetamide, acrylamide and benzamide worked approximately equally. As one can see, after the introduction of *β*-CD-BSA as homogeneous catalyst, such kind of MCRs can be carried out rapidly in 5-20 min with high yields ranging from 86% to 95%，no matter what type the substituents are and how the substituent position changes. Thus, we realized the high efficient synthesis of 1-amidoalkyl-2-naphthols through green process, which conforms to the requirements for the development of green chemistry.

To compare the efficiency of our catalyst with the reported catalysts for the synthesis of 1-amidoalkyl-2-naphthols, we have tabulated the results of these catalysts to promote the synthesis of compounds **4a** from benzaldehyde, *β*-naphthol and acetamide. The results are summarized in Table 3. Obviously, *β*-CD-BSA showed a much higher catalytic activity in terms of very short reaction time and mild conditions.

Table 3 Comparison of *β*-CD-BSA with the reported catalysts for synthesis of **4a**

Entry	Catalyst	Condition	Time	Yield(%)	Ref.
1	*β*-CD-BSA	solvent-free/100 ℃	6 min	90	This work
2	Carbon-SO_3H	solvent-free/130 ℃	5 min	86	13
3	nano-Fe_3O_4-SO_3H	solvent-free/100 ℃	10 min	93	11
4	MCM-41-*N*-propylsulfamic acid	solvent-free/130 ℃	120 min	97	14
5	cellulose-SO_3H	H_2O/80 ℃	1.5 h	90	12
6	[TEBSA][HSO_4]	solvent-free/110 ℃	10 min	87	10a
7	Silica-ionic liquid	solvent-free/85 ℃	5 min	90	10d
8	[Dsim]HSO_4	solvent-free/80 ℃	9 min	98	10b
9	*p*-TSA	solvent-free/125 ℃	5 h	85	7
10	$H_4SiW_{12}O_{40}$	solvent-free/110 ℃	20 min	92	16
11	$K_5CoW_{12}O_{40}·H_2O$	solvent-free/125 ℃	2 h	90	21
12	I_2	solvent-free/125 ℃	5.5 h	85	19
13	$Fe(HSO_4)_3$	solvent-free/85 ℃	65 min	83	8
14	nano-S_8	solvent-free/50 ℃	30 min	95	22
15	$FeCl_3$-SiO_2	solvent-free/120 ℃	11 min	86	18
16	montmorillonite K10	solvent-free/125 ℃	1.5 h	89	17

The plausible reaction mechanism for the synthesis of 1-amidoalkyl-2-naphthols mediated by *β*-CD-BSA is outlined in Scheme 4. Considering the protonic acid nature of *β*-CD-BSA, we propose that the aromatic is activated by *β*-CD-BSA to give **I**. Then, *β*-naphthol attacks the carbonyl group of the activated aldehyde, and affords intermediate **II**. Next, *ortho*-quinone methides (*o*-QMs, **III**) is formed by removing H_2O from **II**. The intermediate **III** is activated by *β*-CD-BSA to form **IV** as a Michael acceptor. Afterward, Michael addition of amide to intermediate affords the expected 1-amidoalkyl-2-naphthols. The high reaction rate observed in the present method could be attributed to the fact that the acidic sites of *β*-CD-BSA for activating aldehydes efficiently and the hydrophobic central cavities of *β*-CD units in the *β*-CD-BSA as a micro-vessel. In addition, the hydrophilic exterior due to the outer -OH of the *β*-CD-BSA cavity promoted the reaction *via* hydrogen bonding.



Scheme 4 Proposed mechanism for the synthesis of 1-amidoalkyl-2-naphthols catalysed by *β*-CD-BSA

2.3 Reusability of *β*-CD-BSA

The recovery and reuse of catalysts is highly preferable for a green process. Thus, the reusability of the catalyst was investigated by using *p*-chlorobenzaldehyde, *β*-naphthol and acetamide as model substrates. The catalyst was easily recovered by filtration after the reaction and washing with acetone. The filtrates were vacuumed and the resulting catalyst was reused directly for the next run. The procedure was repeated and the results indicated that the catalyst could be recycled five times with a slight loss of catalyst activity. The reason for decreased yields may be that the catalyst partly lost when it was reused. The recovering ratio of the catalyst is 88% after recycling five times.

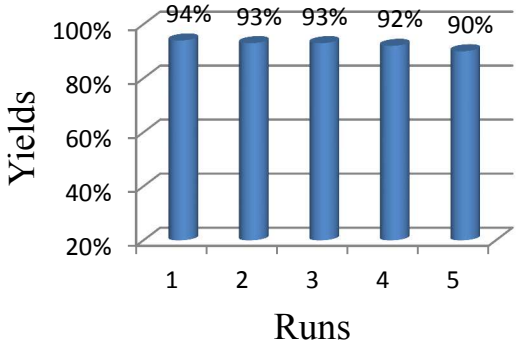


Figure 4 Recycling experiment of *β*-CD-BSA

3. Conclusion

In summary, *β*-CD-BSA have been synthesized and evaluated as catalyst for the one-pot synthesis of 1-amidoalkyl-2-naphthols *via* a three-component condensation reaction of aldehydes, *β*-naphthol and amides under solvent-free conditions. The notable advantages of this method are high catalytic activity, short reaction time, excellent yields, reusable catalyst, simple work-up and mild reaction conditions. Thus, this procedure is a better and more practical alternative for green chemistry.

4. Experimental

4.1 General

Melting points were determined on an X6-data microscopic melting points apparatus and were uncorrected. FT-IR spectra were recorded on a BRUKER VECTER 22 (KBr). NMR spectra were obtained from solution D_2O or DMSO-d_6 with TMS as internal standard using a BRUKER AVANCE III (400 MHz) spectrometer. Elemental analysis was performed on an Elementar VARIOEL III spectrometer. Thermogravimetric analysis was carried out in nitrogen using a Netzsch TG209 thermal analyser.

4.2 Synthesis of *β*-CD-BSA

First, *β*-CD (2 g) was dissolved in NaOH solution (5M, 20 mL) in a 50 ml round bottom flask at 75 ℃. To the solution, 1,4-butane sultone (2.4 g) was added dropwise. Then the mixture was stirred for 3 h. The reaction solution was cooled to room temperature, which was adjusted to neutral using HCl solution (3 M). The mixture was dropped in ethanol to afford sulfobutyl ether *β*-cyclodextrin (SBE-*β*-CD).

Second, the acidic resin was activated in a saturated aqueous solution of NaCl for 1 day, followed by the treatment of 2.5 wt % NaOH aqueous solution for 80 min, and then washed with distilled water until pH 7.0, and finally it was treated with 5.0 wt % HCl aqueous solution for 12 h. Afterward, the resin was transferred to a column and washed with deionized water until the eluent reached pH 7.0.

Lastly, the sodium salt of SBE-*β*-CD (1.0 g) was dissolved in water (100 mL), and the solution was allowed to flow through the acidic resin column at a speed of 20 drops per minute. The acidic eluent was collected and then freeze-dried for 12 h to obtain *β*-CD-BSA product.

FT-IR (KBr, cm^{-1}): 3410, 2929, 1643, 1455, 1416, 1377, 1158, 1043, 879, 604, 531. ^{1}H NMR (400 MHz, D_2O): δ (ppm) 1.70 (s, -$OCH_2CH_2CH_2CH_2SO_3H$), 2.88 (s, -OCH_2 $CH_2CH_2CH_2$-SO_3H), 3.49-3.8 (m, -$OCH_2CH_2CH_2CH_2SO_3H$ and C*H*), 5.01-5.14 (m, C_1-H). ^{13}C NMR (400 MHz, D_2O,): δ (ppm) 20.50, 20.89, 27.47, 27.99, 50.62, 60.32, 68.72, 70.58, 71.52, 72.08, 79.83. Anal. Found: C 37.85, H 6.42, S 10.15.

4.3 Typical procedure for the synthesis of 1-amidoalkyl-2-naphthols

The mixture of the aromatic aldehyde **1** (2 mmol), 2-naphthol (2 mmol), amide (2 mmol), and *β*-CD-BSA (0.02 mmol) was stirred at 100 ℃ for the appropriate time (monitored by TLC). Then, acetone (15 mL) was added and the reaction mixture was filtered. The solid catalyst was washed with acetone (2×10 mL) and dried under vacuum. Pure 1-amidoalkyl-2-naphthols were afforded by evaporation of the solvent followed by

recrystallization from ethanol. All products were characterized by spectral data and compared with their physical data with the literature.

The spectral (FT-IR, ^{1}H NMR, ^{13}C NMR) and analytical data for some selected 1-amidoalkyl-2-naphthols are presented below:

N-[(2-Hydroxynaphthalen-1-yl)-phenylmethyl]acetamide (Table 2, entry 1): White solid; mp 227-229 ℃; FT-IR (KBr, cm^{-1}): 3400, 3248, 3062, 1640, 1583, 1513, 1437, 1372, 1337, 1304, 1277, 1252, 1235, 1208, 1168, 1103, 1061, 1029, 987, 933, 877, 838, 807, 742, 697, 659, 625, 569; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.97 (s, 3H, CH_3), 7.11-7.16 (m, 4H, ArH), 7.20-7.27 (m, 4H, ArH), 7.35 (t, *J=7.4 Hz*, 1H, ArH), 7.75-7.81 (m, 3H, ArH and CH), 8.44 (d, *J=8.4 Hz*, 1H, NH), 9.98 (s, 1H, ArOH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 23.13, 48.26, 118.93, 119.31, 122.85, 126.50, 126.76, 128.45, 128.92, 129.00, 129.70, 132.79, 143.09, 153.61, 169.69.

N-((4-Chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl)acrylamide (Table 2, entry 14): White solid; mp 212-213 ℃; IR (KBr, cm^{-1}): 3410, 3160, 1656, 1624, 1582, 1514, 1489, 1438, 1403, 1333, 1316, 1300, 1272, 1221, 1183, 1170, 1144, 1090, 1068, 1014, 978, 931, 877, 846, 817, 749, 721, 677, 627, 543; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 5.61-5.64 (dd, 1H, CH_2), 6.12-6.17 (dd, 1H, CH_2), 6.57-6.63 (dd, 1H, CH), 7.14-7.41 (m, 8H, ArH and CH), 7.78-7.83 (m, 3H, ArH), 8.74 (d, *J=8.8 Hz*, 1H, NH), 10.08 (s, 1H, ArOH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 48.06, 118.52, 118.90, 112.96, 123.56, 126.32, 126.98, 128.40, 128.47, 128.91, 129.10, 130.07, 131.19, 132.07, 132.69, 141.86, 153.77, 165.06.

N-((2-Hydroxynaphthalen-1-yl)(p-tolyl)methyl)benzamide (Table 2, entry 31): Light yellow solid; mp 206-207 ℃; IR (KBr, cm^{-1}): 3410, 3153, 3062, 1632, 1575, 1538, 1515, 1487, 1436, 1413, 1344, 1278, 1212, 1281, 1145, 1074, 1054, 1025, 940, 876, 815, 751, 703, 688, 586, 509; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 2.24 (s, 3H, CH_3), 7.08 (d, *J=7.1 Hz*, 2H, ArH), 7.18 (d, *J=7.1 Hz*, 2H, ArH), 7.24-7.31 (m, 3H, ArH and CH), 7.44-7.57 (m, 4H, ArH), 7.79-7.87 (m, 4H, ArH), 8.08 (d, *J=8.0 Hz*, 1H, NH), 9.01 (d, *J=8.0 Hz*, 2H, ArH), 10.33 (s, 1H, ArOH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 21.04, 49.54, 118.92, 119.17, 123.14, 126.90, 127.19, 127.58, 128.85, 128.99, 129.08, 129.22, 129.76, 131.88, 132.77, 134.86, 136.09, 139.47, 153.60, 166.12.

Acknowledgements

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (NO. 51303069), the Fundamental Research Funds for the Central Universities (JUSRP11236).

References

1 (a) J. M. Thomas and W. J. Thomas, Principles and Practice of Heterogeneous Catalysis, Wiley-VCH, Weinheim, 1996; (b) G. V. Smith and F. Notheisz, Heterogeneous Catalysis in Organic Chemistry, Elsevier, 2000.

2 (a) A. Gniewek, J. J. Ziółkowski, A. M. Trzeciak, M. Zawadzki, H. Grabowska and J. Wrzyszcz, *J. Catal.*, 2008, **254**, 121-130; (b) L. C. Li, Y. D. Zhu, X. H. Lu, M. J. Wei, W. Zhuang, Z. H. Yang and X. Feng, *Chem. Commun.*, 2012, **48**, 11525-11527; (c) X. L. Shi, X. L. Xing, H. K. Lin and W. Q. Zhang, *Adv. Synth. Catal.*, 2014, **356**, 2349-2354.

3 (a) J. Ren, C. J. Guo, L. L. Yang and Z. Li, *Chin. J. Catal.*, 2013, **34**, 1734-1744; (b) A. Rajack, K. Yuvaraju, C. Praveen and Y. L. N. Murthy, *J. Mol. Catal. A: Chem.*, 2013, **370**, 197-204; (c) M. G. Dekamin, M. Azimoshan and L. Ramezani, *Green Chem.*, 2013, **15**, 811-820; (d) S. Wu, H. C. Ma, X. J. Jia, Y. M. Zhong and Z. Q. Lei, *Tetrahedron*, 2011, **67**, 250-256.

4 (a) F. Hapiot, H. Bricout, S. Menuel, S. Tilloy and E. Monflier, *Catal. Sci. Technol.*, 2014, **4**, 1899-1908; (b) G. F. Zhang, Y. X. Luan, X. W. Han, Y. Wang, X. Wen, C. R. Ding and J. R. Gao, *Green Chem.*, 2013, **15**, 2081-2085; (c) J. A. Shin, Y. G. Lim and K. H. Lee, *J. Org. Chem.*, 2012, **77**, 4117-4122; (d) J. Wu, X. L. Du, J. Ma, Y. P. Zhang, Q. C. Shi, L. J. Luo, B. A. Song, S. Yang and D. Y. Hu, *Green Chem*., 2014, **16**, 3210-3217; (e) P. Blach, D. Landy, S. Fourmentin, G. Surpateanu, H. Bricout, A. Ponchel, F. Hapiot and E. Monflier, *Adv. Synth. Catal.*, 2005, **347**, 1301-1307.

5 (a) J. Zhu, H. Bienaymé, Multicomponent Reactions, Wiley-VCH, Weinheim, 2005; (b) C. Graaff, E. Ruijter and R. V. A. Orru, *Chem. Soc. Rev.*, 2012, **41**, 3969-4009; (c) A. Dömling, *Chem. Rev.*, 2006, **106**, 17-89.

6 (a) H. R. Shaterian, H. Yarahmadi and M. Ghashang, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 788-792; (b) D. Seebach and J. L. Matthews, *Chem. Commun.*, 1997, **21**, 2015-2022; (c) Dingermann, T.; Steinhilber, D.; Folkers, G. In Molecular Biology in Medicinal Chemistry, Wiley-VCH, 2004.

7 M. M. Khodaei, A. R. Khosropour and H. Moghanian, *Synlett*, 2006, **6**, 916-920.

8 H. R. Shaterian, H. Yarahmadi and M. Ghashang, *Bioorg. Med. Chem. Lett.* , 2008, **18**, 788-792.

9 G. C. Nandi, S. Samai, R. Kumar and M. S. Singh, *Tetrahedron Lett.*, 2009, **50**, 7220-7222.

10 (a) A. R. Hajipour, Y. Ghayeb, N. Sheikhan and A. E. Ruoho, *Tetrahedron Lett.*, 2009, **50**, 5649-5651; (b) A. Zare, T. Yousofi and A. R. Moosavi-Zare, *RSC Adv.*, 2012, **2**, 7988-7991; (c) M. A. Zolfigol, A. Khazaei, A. R. Moosavi-Zare, A. Zare, V. Khakyzadeh, Appl. Catal. A: Gen., 2011, **400**, 70-81; (d) Q. Zhang, J. Luo and Y. Y. Wei, *Green Chem.*, 2010, **12**, 2246-2254.

11 J. Safari and Z. Zarnegar, J. Mol. Catal. A: Chem., 2013, **379**, 269-276.

12 A. Kumar, M. K. Gupta and M. Kumar, *RSC Adv.*, 2012, **2**, 7371-7376.

13 Davoodni, R. Mahjoobin and N.Tavakoli□Hoseini, *Chin. J.Catal.*, 2014, 35, 490-495.

14 M. Hajjami, F. Ghorbani and F. Bakhti*, Appl. Catal. A: Gen.,* 2014, 470: 303-310.

15 H. R. Shaterian, H. Yarahmadi and M. Ghashang, *Tetrahedron*, 2008, **64**, 1263-1269.

16 A. Supale and G. S. Gokavi, *J. Chem. Sci.*, 2010, **122**, 189-192.

17 S. Kantevari, S. V. N. Vuppalapati and L. Nagarapu, *Catal.Commun.*, 2007, **8**, 1857-1862.

18 H. R. Shaterian and H. Yarahmadi, *Tetrahedron Lett.*, 2008, **49**, 1297-1300.

19 B. Das, K. Laxminarayana, B. Ravikanth and R. Rao, *J. Mol. Catal. A: Chem*., 2007, **261**, 180-183.

20 S. Samantaray, G. Hota and B.G. Mishra, *Catal. Commun.*, 2011, **12**, 1255-1259.

21 L. Nagarapu, M. Baseeruddin, S. Apuri and S. Kantevari, *Catal. Commun.*, 2007, **8**, 1729-1734.

22 D. Kundu, A. Majee and A. Hajra, *Catal. Commun.*, 2010, **11**, 1157-1159.

23 V. K. Das, M. Borah, and A. J. Thakur, *J. Org. Chem.*, 2013, **78**, 3361-3366.

24 J. Safari and Z. Zarnegar, *J. Ind. Eng. Chem.,* 2014, **20**, 2292-2297.

25 (a) B. Datta and M.A. Pasha, *Ultrason. Sonochem.*, 2011, **18**, 624-628; (b) J. Safari and Z. Zarnegar, *Ultrason. Sonochem.*, 2014, **21**, 1132-1139.

26 (a) A. J. Song, J. H. Wang, C. D. Liu and L. H. Deng, *Chin. Sci. Bull,* 2009, **54**, 1362-1373; (b) Q. Qu, E. Tucker and S. D. Christian, *J. Incl. Phenom. Macro.*, 2002, **43**, 213-221.

β-Cyclodextrin-butane sulfonic acid: an efficient and reusable catalyst for the multicomponent synthesis of 1-amidoalkyl-2-naphthols under solvent-free conditions

Kai Gong*[,a], Hualan Wang [b], Xiaoxue Ren [a], Ying Wang [a] and Jinghua Chen [a]

[a] School of Pharmaceutical Science, Jiangnan University, Wuxi, 214122, China

[b]Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Normal University, Hangzhou, 311121, China

β-Cyclodextrin-butane sulfonic acid (*β*-CD-BSA) efficiently catalyzed the synthesis of 1-amidoalkyl-2-naphthols by a one-pot three component condensation of aromatic aldehydes, *β*-naphthol and amides at 100 ℃ under solvent-free conditions.