

## [2-(Sulfooxy) ethyl] sulfamic acid (SESA): an efficient heterogeneous recyclable catalyst promoted green synthesis of $\beta$ -amido carbonyl compounds derivatives by multi-component reactions (MCRS)

M. Hadizadeh, M. H. Mosslemin\*, B. Sadeghi

Department of Chemistry, Yazd Branch, Islamic Azad University, Yazd, Iran

Submitted March 24, 2016; Accepted August 8, 2016

Easily synthesized [2-(sulfooxy) ethyl] sulfamic acid (SESA) as a novel catalyst efficiently promoted the synthesis of  $\beta$ -acetamido carbonyl compounds derivatives via condensation of enolizable ketones with various aryl aldehydes at room temperature conditions in acetonitrile and acetyl chloride. This research provides a new way for the synthesis of  $\beta$ -acetamido carbonyl compounds in good to excellent yields of products with easy work up. The catalyst could be recycled and reused several times without any loss of efficiency.

**Keywords:** Multi-component reactions, [2-(sulfooxy) ethyl] sulfamic acid,  $\beta$ -acetamido carbonyl compounds, Green chemistry

### INTRODUCTION

Multi component reactions (MCRs) are significant for their unique characteristic. These reactions due to one-pot essence, not only they don't have extra expense to separate and purify of middle process, but also final process has better selectivity [1-3]. They also have more speed, economy advantage, and higher profit than continuous linear and usual way, thus they have excess importance in organic chemistry, medicinal, as well as agriculture and industry researchers [4].  $\beta$ -acetamido ketones due to having their polyfunctional nature are used as an important intermediate and versatile in synthesis of many organic components and medicinal as well as biological [5]. They are usually prepared through acylation of  $\beta$ -aminoketones [6], Michael addition to  $\alpha$ ,  $\beta$ -unsaturated ketones [7] or photoisomerisation of phthalimides [8]. Several  $\beta$ -acetamido ketones/esters were synthesized as they are potential core structures for mechanism based inhibitors for various proteases. The  $\beta$ -acetamido esters are also useful precursors to  $\beta$ -aryl homoisothreonine derivatives which can be incorporated in an amino acid residue to afford the corresponding dipeptide isosteres. Reduction of these groups of compounds to 1, 3-amino alcohols with the simplest way is possible [9, 10].

1, 3-amino alcohols are also considered as manufacturing units many antibiotics such as nikkomycins and neopolyoxines [11, 12]. One-pot reaction involves the condensation of enolizable ketones/esters, aryl aldehydes, and acetyl chloride in acetonitrile in the presence of suitable catalyst is

considered as a most efficient route for synthesis of  $\beta$ -carbonyl compounds. The conventional way for the preparation of these compounds is the Dakin-west reaction that for the first time is reported by Iqbal and co-workers [13, 14]. Although a lot of catalyst including  $\text{CoCl}_2$  [15],  $\text{Cu}(\text{OTf})_3/\text{Sc}(\text{OTf})_3$  [16], montmorillonitk-10 clay [17],  $\text{CuO}$ ,  $\text{Fe}_2\text{O}_3$  [18] and  $\text{MgCl}_2$  [19] reported so far, but some of these way have difficulties such as long reaction times, the use of large amounts of catalysts, high temperatures, low yields and the use of toxic or expensive catalyst. The catalyst, [2-(sulfooxy) ethyl] sulfamic acid (SESA) a bronsted acid, works under heterogeneous conditions for the one-pot synthesis of  $\beta$ -acetamido ketones. Some of the important benefits of this catalyst are environmentally friendly, reusability, great selectivity, cheap and non-toxic. Recently, [2-(sulfooxy) ethyl] sulfamic acid has emerged as medium and as well as catalyst in various organic transformation, including synthesis of xanthen derivatives [20], quinoxaline derivatives [21] and region selective thiocyanation of aromatic and heteroaromatic compounds [22, 25]. Herein, we describe simple, eco-friendly and effective procedure for synthesis of  $\beta$ -acetamido carbonyl compounds with enolizable Ketones, aryl aldehydes, acetyl chlorid and acetonitrile in the presence of [2-(sulfooxy) ethyl] sulfamic acid at room temperature.

### RESULTS AND DISCUSSION

At the first, to show the fairly advantages of using SESA as a catalyst in the synthesis of  $\beta$ -acetamido ketones our protocol was compared with

\* To whom all correspondence should be sent:  
E-mail: mhmossemine@iauyazd.ac.ir

previously reported methods (Table 1).

**Table 1.** Evaluation of the activity of different catalysts for the condensation of benzaldehyde, acetophenone, acetyl chloride and acetonitrile in presence of SESA

Entry	Catalyst (mol %)	Time(h)	Temperature (°C)	Yield (%) <sup>ref.</sup>
1	Bi (OTf) <sub>3</sub> (10)	30	RT	69 [16]
2	MgCl <sub>2</sub> (20)	20	RT	30 [19]
3	Fe <sub>2</sub> O <sub>3</sub> (50)	20	80	65 [18]
4	CuO (50)	20	80	40 [18]
5	TiO <sub>2</sub> (50)	18	80	20 [18]
6	ZrCl <sub>4</sub> (20)	5	RT	80 [19]
7	ZnO (50)	6	80	90 [18]
8	SESA (20)	1.5	RT	91 <sup>a</sup>

<sup>a</sup> This work

**Table 2.** Optimization of the SESA catalyzed multi-component reaction

Entry	Catalyst (mol %)	Time(h)	Yield <sup>a</sup> (%)
1	0	24	25
2	2	1.5	45
3	5	1.5	65
4	10	1.5	69
5	20	1.5	91
6	30	1.5	92

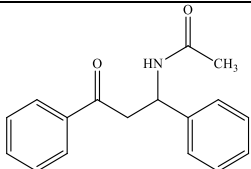
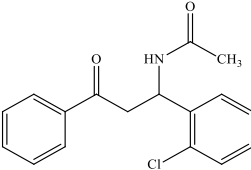
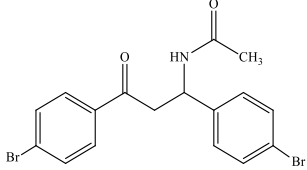
<sup>a</sup>Isolated yields

We optimized the amount of SESA in the reaction between benzaldehyde, acetophenone, acetyl chloride and acetonitrile (Table 2).

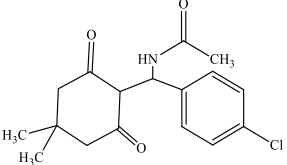
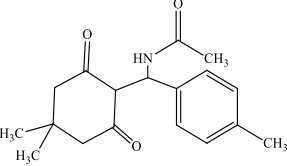
In the absence of the catalyst, the reaction was not completed even after 24 hours. The best condition to preparation the  $\beta$ -acetamido carbonyl compounds were obtained using 20 mol% of SESA in 91% yield. Under optimal conditions, in order to show generality and scope of this method, we used various substituted aryl aldehydes with the

enolizable ketones such as acetophenone, acetyl acetone, benzoyl acetone and dimedone for the preparation of  $\beta$ -acetamido carbonyl compounds. In all cases, aryl aldehydes with substituents carrying either electron-donating or electron-withdrawing group reacted successfully and gave the expected products in good to excellent yields without the formation of any side products. A series of  $\beta$ -acetamido ketones were prepared and the results obtained are summarized in (Table 3).

**Table 3.** SESA catalyzed for the synthesis of  $\beta$ -acetamido carbonyl compounds from aldehydes and enolizable ketones in the presence of acetonitrile and acetyl chloride.

Entry	Product	Time(h)	Yield <sup>a</sup> (%)	m.p (°C), Found	m.p (°C), Reported <sup>ref.</sup>
1		1.5	91	104-105	104-106[24]
2		1	90	136-137	134-136[24]
3		1	92	142-145	142-145[19]

4		1	90	160-161	161-162[19]
5		1.5	85	179-180	176-179[19]
6		2	85	135-137	New
7		2	90	131-133	new
8		2	93	130-132	New
9		2.5	95	120-122	121-122[23]
Entry	Product	Time(h)	Yield <sup>a</sup> (%)	m.p (°C), Found	m.p (°C), Reported <sup>ref.</sup>
10		3	82	198-200	200[26]
11		2	90	164-166	165-167[27]
12		2	92	197-198	198[26]
13		3	80	175-176	173[26]

14		2	89	194-195	195[26]
15		3	85	103-104	105[26]

<sup>a</sup>Isolated yields

The compounds were characterised by their elemental analyses and by their <sup>1</sup>H, <sup>13</sup>C NMR and IR spectral data.

In summary, the simple experimental procedure combined with the easy workup and excellent yields of products and mild reaction conditions prominent features of the method presented herein. After completion of the reaction the heterogeneous catalyst was recovered by filtration. Then, the residue solution was poured into 50 mL ice-water and extracted with dichloromethane and washed with water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was evaporated under reduced pressure and the residue was stirred with diethyl ether (5 mL). The precipitated solid was filtered and dried to afford

pure product. For the synthesis of β-acetamido carbonyl compounds, no significant loss the product yield was observed when SESA catalyst was used after fifth times recycling (Table 4). In every experiment whole of the SESA was easily recovered from the reaction mixture. The reusability catalyst is one of the most important benefits and makes them useful for commercial applications. Thus the recovery and reusability of SESA was investigated. The separated catalyst can be reused after washing with CH<sub>2</sub>Cl<sub>2</sub> and drying. The reusability of the catalyst was checked by the reaction of benzaldehyde and acetophenone in the presence of acetyl chloride and acetonitrile using 20 mol% of SESA at room temperature.

**Table 4.** Recovery and reusable of catalyst

Entry	Reaction	Yield <sup>a</sup> (%)
1	First	91
2	Second	90
3	Third	89
4	Forth	87
5	Fifth	85

<sup>a</sup>Isolated yields

We also tried to use benzoyl chloride and acetic anhydride instead of acetyl chloride in the model reaction. Unfortunately, our attempts to carry out the reaction in the presence of these reagents failed. For further improvement of yield and reaction time, reaction was checked using microwave irradiation. Using microwave, in the presence of acetyl chloride, the yield of product was reduced to 25%

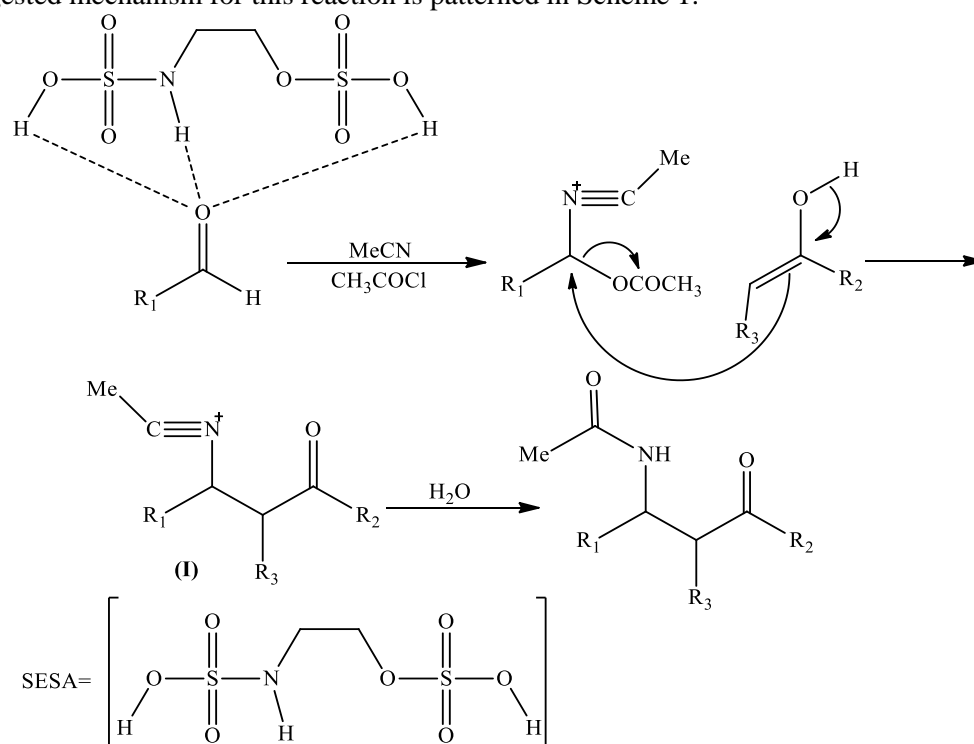
and in the absence of acetyl chloride reaction was not accomplished. The effect of temperature was also studied by carrying out the model reaction in the presence of acetyl chloride at room temperature (25 °C) and 80 °C. At room temperature and reflux in the presence or absence of acetyl chloride, the reaction yield was found to be decrease. (Table 5)

**Table 5.** Reaction of benzaldehyd (1 mmol), acetophenone (1 mmol), acetonitrile and acetyl chloride in the presence of SESA under various reaction conditions.

Entry	Reaction conditions	Time(h)	Yield <sup>a</sup> (%)
1	CH <sub>3</sub> COCl / R.T	1.5	91
2	- / R.T	12	10
3	CH <sub>3</sub> COCl / Reflux	1.5	30
4	- / Reflux	12	10
5	CH <sub>3</sub> COCl / MW	30 (min)	25
6	- / MW	30 (min)	0
7	PhCOCl or Ac <sub>2</sub> O / R.T	12	0

<sup>a</sup>Isolated yields

The suggested mechanism for this reaction is patterned in Scheme 1.



## EXPERIMENTAL

**General:** Melting points were determined with an Electro thermal 9100 apparatus. IR spectra were recorded on a Perkin Elmer FT-IR spectrophotometer. The <sup>1</sup>H NMR (300MHz) and <sup>13</sup>C NMR (75MHz) in CDCl<sub>3</sub> solutions and <sup>1</sup>H NMR (400MHz) and <sup>13</sup>C NMR (100MHz) in DMSO solutions were measured on a Bruker DRX-300 Avance spectrometer and Bruker DRX-400 Avance spectrometer, respectively. The compound [2-(Sulfooxy) ethyl] sulfamic acid was synthesized according to previous reported.<sup>20</sup>

**General procedure for the synthesis of β-amido carbonyl compound:** At temperature a mixture of aryl aldehyde (1 mmol), enolizable ketones (1mmol), acetyl chloride (4 mL) in acetonitrile (3 mL) was treated whit a catalytic amount of [2-(Sulfooxy) ethyl] sulfamic Acid (20 mol %). The progression of the reaction was followed by TLC (eluent:*n*-hexane:ethylacetate). After completion of the reaction, the reaction mixture was filtered and the heterogeneous catalyst was recovered. Then, the residue solution was poured into 50 mL ice-water and extracted with dichloromethane to remove any residual starting materials and washed with water (3×10 mL).The organic layer was dried over

anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was evaporated under reduced pressure and the residue was stirred with diethyl ether (4 mL). The precipitated solid was filtered and dried to afford pure product.

N-(1, 3-Diphenyl-3-oxopropyl) acetamide (Entry1)

FT-IR (KBr, cm<sup>-1</sup>): 3297 (NH amide), 3071 (CH<sub>str</sub>), 1690 (C=O ketone), 1651 (C=O amide). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ= 2.03 (3H, s, CH<sub>3</sub>), 3.46 (1H, dd, J = 6.0 and 16.9 Hz, CH), 3.75 (1H, dd, J= 5.3 and 16.9 Hz, CH), 5.54- 5.61 (1H, m, CH), 6.94 (1H, d, J = 6.9 Hz, NH), 7.24-7.36 (5H, m, CH<sub>arom</sub>), 7.45 (2H, t, J = 7.0 Hz, CH<sub>arom</sub>), 7.57 (1H, t, J =7.0 Hz, CH<sub>arom</sub>), 7.92 (2H, d, J = 7.5 Hz, CH<sub>arom</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ= 23.34, 43.19, 50, 126.51, 127.5, 128.13, 128.68, 128.72, 133.56, 136.56, 140.9, 169.72, 198.52 ppm.

N-[3-(2-Chlorophenyl)-1-phenyl-3-oxopropyl] acetamide (Entry2)

FT-IR (KBr, cm<sup>-1</sup>): 3290 (NH amide), 3080(CH<sub>str</sub>), 1692 (C=O ketone), 1653 (C=O amide).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ= 2.04 (3H, s, CH<sub>3</sub>), 3.47 (1H, dd, J = 5.5 and 16.7 Hz, CH), 3.76 (1H,dd, J = 5.9 and 16.7 Hz, CH), 5.80-5.87 (1H, m, CH),7.14-7.22 (5H, m, CH<sub>arom</sub>, NH), 7.28-7.89 (3H, m, CH<sub>arom</sub>), 7.90 (2H, d, J = 7.2 Hz, CH<sub>arom</sub>) ppm.

N-[3-(4-Bromophenyl)-1-(4-bromophenyl)-3-oxopropyl] acetamide (Entry3)

FT-IR (KBr, cm<sup>-1</sup>): 3270 (NH amide), 3061(CH<sub>str</sub>), 1684 (C=O ketone), 1638 (C=O amide). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ= 2.03 (3H, s, CH<sub>3</sub>), 3.35 (1H, dd, J = 6.0 and 17.0 Hz, CH), 3.71 (1H, dd, J = 5.3 and 17.0 Hz, CH), 5.47- 5.53 (1H, m, CH), 6.89 (1H, d, J = 7.7 Hz, NH), 7.21 (2H, d, J = 8.3 Hz, CH<sub>arom</sub>), 7.44 (2H, d, J = 8.3 Hz, CH<sub>arom</sub>), 7.60 (2H, d, J = 8.7 Hz, CH<sub>arom</sub>), 7.76 (2H, d, J = 8.5 Hz, CH<sub>arom</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ= 23.32, 42.9, 49.4, 121.47, 128.3, 129.05, 129.60, 131.80, 132.12, 135.07, 139.73, 169.77, 197.23 ppm.

N-[3-(2-Methoxyphenyl)-1-(4-bromophenyl)-3-oxopropyl] acetamide (Entry4)

FT-IR (KBr, cm<sup>-1</sup>): 3310(NH amide), 3074(CH<sub>str</sub>), 1694(C=O ketone), 1648(C=O amide). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ= 2.02 (3H, s, CH<sub>3</sub>), 3.43 (1H, dd, J = 6.7 and 15.7 Hz, CH), 3.55 (1H, dd, J = 6.0 and 15.8 Hz, CH), 3.89 (3H, s, OCH<sub>3</sub>), 5.71 (1H, m, CH), 6.86-7.29 (5H, m,

CH<sub>arom</sub>, NH), 7.57 (2H, d, J = 8.5 Hz, CH<sub>arom</sub>), 7.79 (2H, d, J = 8.4 Hz, CH<sub>arom</sub>) ppm.

N-[3-(4-Nitrophenyl)-1-(4-nitrophenyl)-3-oxopropyl] acetamide (Entry5)

FT-IR (KBr, cm<sup>-1</sup>):3274 (NH amide), 3083 (CH<sub>str</sub>), 1696 (C=O ketone), 1663 (C=O amide). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ= 2.02 (3H, s, CH<sub>3</sub>), 3.58 (1H, dd, J = 5.7 and 17.3 Hz, CH), 3.90 (1H, dd, J = 4.8 and 17.7 Hz, CH), 5.65- 5.71 (1H, m, CH), 6.74 (1H, d, J = 7.6 Hz, NH), 7.54 (2H, d, J = 8.6 Hz, CH<sub>arom</sub>), 8.09 (2H, d, J = 8.7 Hz, CH<sub>arom</sub>), 8.20 (2H, d, J = 8.6 Hz, CH<sub>arom</sub>), 8.32 (2H, d, J = 8.7 Hz, CH<sub>arom</sub>) ppm. <sup>13</sup>CNMR (75 MHz, CDCl<sub>3</sub>): δ= 23.4, 43.36, 49.15, 124, 124.09, 127.52, 129.18, 140.33, 147.3, 147.77, 150.53, 169.83, 196.34 ppm.

N-[2-acetyl-3-oxo-1-(p-tolyl) butyl] acetamide (Entry6)

FT-IR (KBr, cm<sup>-1</sup>): 3301(NH amide), 3092(CH<sub>str</sub>), 1721(C=O ketone), 1643(C=O amide). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ= 1.75 (3H, s, CH<sub>3</sub>), 1.95 (3H, s, CH<sub>3</sub>), 2.18 (3H, s, CH<sub>3</sub>), 2.24 (3H, s, CH<sub>3</sub>), 4.45 (1H, d, J= 10 Hz, CH), 5.47 (1H, t, J = 9.9 Hz, CH), 7.27 (2H, d, J = 7.9 Hz, CH<sub>arom</sub>), 7.36 (2H, d, J = 8 Hz, CH<sub>arom</sub>), 8.37 (1H, d, J = 9.2 Hz, NH) ppm. <sup>13</sup>CNMR (100 MHz, DMSO-d<sub>6</sub>): δ=20.59, 22.57, 29.55, 30.66, 51.45, 71.85, 128.85, 129.66, 136.45, 140.75, 160.20, 201.72, 202.89.

N-[2-acetyl-1-(4-bromophenyl)-3-oxobutyl] acetamide (Entry7)

FT-IR (KBr, cm<sup>-1</sup>): 3295 (NH amide), 3063 (CH<sub>str</sub>), 1715 (C=O ketone), 1652 (C=O amide).

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ= 1.86 (3H, s, CH<sub>3</sub>), 2.08 (3H, s, CH<sub>3</sub>), 2.28 (3H, s, CH<sub>3</sub>), 4.59 (1H, d, J= 10.7 Hz, CH), 5.47 (1H, t, J = 10.2 Hz, CH), 7.06 (2H, d, J = 8.2 Hz, CH<sub>arom</sub>), 7.37 (2H, d, J = 8.2 Hz, CH<sub>arom</sub>), 8.50 (1H, d, J = 9.0 Hz, NH) ppm. <sup>13</sup>CNMR (100 MHz, DMSO-d<sub>6</sub>): δ=22.53, 29.77, 30.60, 51.05, 71.29, 120.42, 129.51, 131.20, 140.03, 168.44, 201.59, 201.67.

N-[2-acetyl-1-(4-chlorophenyl)-3-oxobutyl] acetamide (Entry8)

FT-IR (KBr, cm<sup>-1</sup>): 3289 (NH amide), 3064 (CH<sub>str</sub>), 1727 (C=O ketone), 1652 (C=O amide). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ= 1.77 (3H, s, CH<sub>3</sub>), 1.98 (3H, s, CH<sub>3</sub>), 2.19 (3H, s, CH<sub>3</sub>), 4.50 (1H, d, J= 10.6 Hz, CH), 5.49 (1H,t, J = 9.3 Hz, CH), 7.47 (2H,d, J = 8.6 Hz, CH<sub>arom</sub>), 7.54(2H,d, J = 8.6 Hz, CH<sub>arom</sub>), 8.41 (1H, d, J = 9.1 Hz, NH) ppm. <sup>13</sup>CNMR (100 MHz, DMSO-d<sub>6</sub>): δ= 22.53, 29.74, 30.61, 51, 71.38, 128.27, 129.11, 135.18,

139.60, 168.44, 201.60, 201.67 ppm.

N-[2-benzoyl-3-oxo-1-phenylbutyl] acetamide (Entry9)

FT-IR (KBr,  $\text{cm}^{-1}$ ): 3304 (NH amide), 3072 ( $\text{CH}_{\text{str}}$ ), 1727 (C=O ketone), 1658 (C=O amide).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ = 1.81 (3H, s,  $\text{CH}_3$ ), 2.20 (3H, s,  $\text{CH}_3$ ), 5.56 (1H, d, J = 9.4 Hz, CH), 5.68-5.81 (1H, m, CH), 7.12-7.68 (10H, m,  $\text{CH}_{\text{arom}}$ ), 8.56(1H, d, J = 9.4 Hz, NH) ppm.  $^{13}\text{C}$ NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ =22.65, 28.11, 52.33, 66.86, 127.29, 127.34, 128.25, 128.89, 129, 134.01, 135.90, 140.56, 168.38, 193.34, 201.65 ppm.

N-[(4, 4-dimethyl-2, 6-dioxocyclohexyl) (phenyl) methyl] acetamide (Entry10)

FT-IR (KBr,  $\text{cm}^{-1}$ ): 3397 (NH amide), 3091 ( $\text{CH}_{\text{str}}$ ), 1658 (C=O ketone), 1631 (C=O amide).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ = 0.98 (6H, s, 2 $\text{CH}_3$ ), 1.92 (3H, s,  $\text{CH}_3$ ), 2.25 (4H, brs, 2 $\text{CH}_2$ ), 6.30 (1H, d, J = 9.0 Hz, CH), 7.19-7.24 (5H, m,  $\text{CH}_{\text{arom}}$ ), 7.94 (1H, d, J = 9.1 Hz, CH), 10.14(1H, brs, NH) ppm.  $^{13}\text{C}$ NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ =22.80, 27.86, 31.74, 45.74, 50, 73.99, 125.78, 126.14, 127.67, 143.05, 168.41, 195.97 ppm.

N-[(4, 4-dimethyl-2, 6-dioxocyclohexyl) (4-methoxyphenyl) methyl] acetamide (Entry11)

FT-IR (KBr,  $\text{cm}^{-1}$ ): 3404 (NH amide), 2961 ( $\text{CH}_{\text{str}}$ ), 1679 (C=O ketone), 1664 (C=O amide).

$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ = 0.98 (6H, s, 2 $\text{CH}_3$ ), 1.89 (3H, s,  $\text{CH}_3$ ), 2.24 (4H, brs, 2 $\text{CH}_2$ ), 3.69 (3H, s,  $\text{OCH}_3$ ), 6.21 (1H, d, J = 9.1 Hz, CH), 6.80 (2H, d, J = 8.6 Hz,  $\text{CH}_{\text{arom}}$ ), 7.10 (2H, d, J = 8.5 Hz,  $\text{CH}_{\text{arom}}$ ), 7.91 (1H, d, J = 9.1 Hz, CH), 10.08(1H, brs, NH) ppm.  $^{13}\text{C}$ NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ =22.83, 27.85, 31.82, 45.28, 50.01, 54.94, 73.10, 126.91, 128.96, 135.02, 157.48, 168.24, 196.05 ppm.

N-[(4-bromophenyl) (4, 4-dimethyl-2, 6-dioxocyclohexyl) methyl] acetamide (Entry12)

FT-IR (KBr,  $\text{cm}^{-1}$ ): 3404 (NH amide), 2961 ( $\text{CH}_{\text{str}}$ ), 1658 (C=O ketone), 1628 (C=O amide).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ = 0.90 (6H, s, 2 $\text{CH}_3$ ), 1.92 (3H, s,  $\text{CH}_3$ ), 2.24 (4H, brs, 2 $\text{CH}_2$ ), 6.22 (1H, d, J = 8.7 Hz, CH), 7.13 (2H, d, J = 7.9 Hz,  $\text{CH}_{\text{arom}}$ ), 7.42 (2H, d, J = 8.0 Hz,  $\text{CH}_{\text{arom}}$ ), 7.95 (1H, d, J = 8.7 Hz, CH), 9.21(1H, brs, NH) ppm.  $^{13}\text{C}$ NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ =22.71, 27.84, 31.73, 45.32, 49.93, 68.63, 118.73, 128.03, 130.51, 142.70, 168.57, 196.03 ppm.

N-[(4, 4-dimethyl-2, 6-dioxocyclohexyl) (4-nitrophenyl) methyl] acetamide (Entry13)

FT-IR (KBr,  $\text{cm}^{-1}$ ): 3394 (NH amide), 3099 ( $\text{CH}_{\text{str}}$ ), 1709 (C=O ketone), 1664 (C=O amide).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ = 0.97 (6H, s, 2 $\text{CH}_3$ ), 1.91 (3H, s,  $\text{CH}_3$ ), 2.24 (4H, brs, 2 $\text{CH}_2$ ), 6.25 (1H, d, J = 8.8 Hz, CH), 7.03-7.21 (4H, m,  $\text{CH}_{\text{arom}}$ ), 7.96 (1H, d, J = 8.9 Hz, CH), 9.17(1H, brs, NH) ppm.  $^{13}\text{C}$ NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ = 22.74, 27.83, 31.74, 45.22, 49.94, 74.43, 127.53, 129.61, 139.22, 159.36, 168.47, 196.05 ppm.

N-[(4-chlorophenyl) (4, 4-dimethyl-2, 6-dioxocyclohexyl) methyl] acetamide (Entry14)

FT-IR (KBr,  $\text{cm}^{-1}$ ): 3410 (NH amide), 3087 ( $\text{CH}_{\text{str}}$ ), 1685 (C=O ketone), 1640 (C=O amide).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ = 0.97 (6H, s, 2 $\text{CH}_3$ ), 1.92 (3H, s,  $\text{CH}_3$ ), 2.24 (4H, brs, 2 $\text{CH}_2$ ), 6.24 (1H, d, J = 8.5 Hz, CH), 7.19 (2H, d, J = 7.6 Hz,  $\text{CH}_{\text{arom}}$ ), 7.29 (2H, d, J = 7.6 Hz,  $\text{CH}_{\text{arom}}$ ), 7.95 (1H, d, J = 8.4 Hz, CH), 9.21(1H, brs, NH) ppm.  $^{13}\text{C}$ NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ = 22.71, 27.84, 31.74, 45.25, 49.92, 73.71, 127.60, 129.89, 130.29, 142.23, 168.58, 196.04 ppm.

N-[(4, 4-dimethyl-2, 6-dioxocyclohexyl) (p-tolyl) methyl] acetamide (Entry15)

FT-IR (KBr,  $\text{cm}^{-1}$ ): 3401 (NH amide), 3085 ( $\text{CH}_{\text{str}}$ ), 1661 (C=O ketone), 1631 (C=O amide).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ = 0.97 (6H, s, 2 $\text{CH}_3$ ), 1.90 (3H, s,  $\text{CH}_3$ ), 2.20 (3H, s,  $\text{CH}_3$ ), 2.23 (4H, brs, 2 $\text{CH}_2$ ), 6.23 (1H, d, J = 8.9 Hz, CH), 7.02-7.08 (4H, m,  $\text{CH}_{\text{arom}}$ ), 7.89 (1H, d, J = 8.9 Hz, CH), 9.10(1H, brs, NH) ppm.  $^{13}\text{C}$ NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ = 20.52, 22.82, 27.84, 31.83, 45.48, 49.99, 74.10, 125.69, 128.23, 134.68, 140.06, 168.30, 196 ppm.

## CONCLUSION

In conclusion, a novel, heterogeneous, strong and highly effective acid catalyst for the synthesis of  $\beta$ -acetamido carbonyl compounds has been reported. The major advantage of this method is the easy of the work-up. The products can be isolated without chromatography. The method also offers some other advantages such as clean reaction, low loading of catalyst, reusability, efficiency, generality, and excellent yields of products, simplicity and short reaction time.

**ACKNOWLEDGEMENTS.** *The Research Council of the Islamic Azad University of Yazd is gratefully acknowledged for the financial support for this work.*

## REFERENCES

1. M. Khodaei, A. R. Khosropour, P. Fattahpour, *Tetrahedron Lett.*, **46**, 2105 (2005).

- M.H. Mosslemin, N. Shams, H. Anaraki-Ardakani and A. Yazdani, *J. Chem. Res.*, 668 (2013).
- N. Shams, M.H. Mosslemin, H. Anaraki-Ardakani and E. Zarenezhad, *J. Chem. Res.*, **39**, 270 (2015).
- I. Ugi, B. Werner, A. Domling, *Molecules*, **8**, 53 (2003).
- J.R. Casimir, C. Turetta, L. Ettouati, J. Paris, *Tetrahedron Lett.*, **36**, 4797 (1995).
- P. Dallemagne, S. Rault, K.M. Hassan, M. Robba, *Tetrahedron Lett.*, **27**, 2607 (1986).
- P.W. Jeffs, R. Redfearn, J. Wolfram, *J. Org. Chem.*, **48**, 3861 (1983).
- M.R. Paleo, D. Dominguez, L. Castedo, *Tetrahedron Lett.*, **34**, 2369 (1993).
- J. Barluenga, A.L. Viado, E. Aguilar, S. Fustero, B. Olano, *J. Org. Chem.*, **58**, 5972 (1993).
- D. Enders, M. Moser, G. Gelibel, M.C. Laufe, *Synthesis*, **12**, 2040 (2004).
- K. Kobinata, M. Vramoto, M. Nshii, H. Kusakabee, G. Nakamura, *Agric Biol Chem.*, **44**, 1709 (1980).
- U. Dahn, H. Hagemmaier, H. Hohne, W.A. Konig, G. Wolf, H. Zahner, *Arch. Microbiol.*, **107**, 143 (1976).
- B. Bhatia, M.M. Reddy, J. Iqbal, *J. Chem. Soc. Chem. Commun.*, 713 (1994).
- I. N. Rao, E. N. Prabhakaran, S. K. Das, J. Iqbal, *J. Org. Chem.*, **68**, 4079 (2003).
- M. M. Reddy, B. Bhatia, J. Iqbal, *Tetrahedron Lett.*, **36**, 4877 (1995).
- G. Pandey, R. P. Singh, A. Garg and V.K. Singh, *Tetrahedron Lett.*, **46**, 2137 (2005).
- D. Bahulayan, S.K. Das, J. Iqbal, *J. Org. Chem.*, **68**, 5735 (2003).
- M.T. Maghsoodlou, A. Hassan Khani, H. R. Shaterian, S.M.Habib- Khorasani, E. Mossaddegh, *Tetrahedron Lett.*, **48**, 1729 (2007).
- A.R. Momeni, M. Sadeghi, M. Hadizadeh, *Turk. J. Chem.*, **33**, 751 (2009).
- S. Sajjadifar, M. Fadaeian, M. Bakhtiyari, S. Rezayati, *Chem. Sci Trans.*, **3**, 107 (2014).
- S. Sajjadifar, H. Noorizadeh, H. Veisi, O. Louie, M. Mansouji Avval, S. Rezayati, *J. Pharm., Biol., Chem., Sci.*, **4**, 907 (2013).
- S. Sajjadifar, S. Karimian, H. Noorizadeh, H. Veisi, *J. Catal.* **2013**, (2013).
- J.S. Yadav, B.V. S. Reddy, K. S. Shankar, K. Premalatha, *Org. Commun.*, **1:4**, 76 (2008).
- N.P. Selvam, P.T. Perumal, *Arkivoc.* **X**, 265 (2009).
- M. M. Heravi, L. Ranjbar, F. Derikvand, *J. Mol. Catal. A: Chem.*, **276**, 226 (2007).
- H.A. Oskooie, M.M. Heravi, L. Tahershamsi, S. Sadjadi, M. Tajbakhsh, *Synth. Commun.*, **40**, 1772 (2010).
- M. Anary-Abbasinejad, A. Hassanabadi, K. Charkhati, *Synth Commun.*, **39**, 4289 (2009).