IRANIAN JOURNAL OF CATALYSIS

Using of modified sugarcane bagasse as a green and inexpensive catalyst for the synthesis of indeno[1,2-b]quinolin-8-one derivatives

Samaneh Hamidi Zare*, Esmael Rostami

Department of chemistry, Payame Noor University, PO BOX 19395-3697 Tehran, Iran.

Received 4 January 2020; received in revised form 6 October 2020; accepted 10 October 2020

ABSTRACT

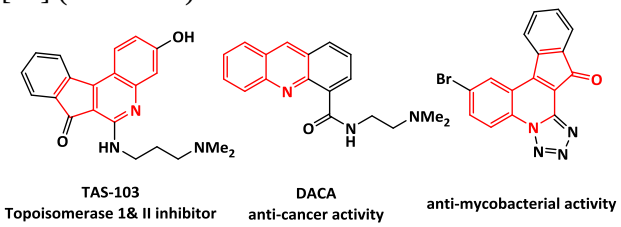
Chemical grafting of 3-aminipropyl triethoxysilane to carbonized bagasse and acidification of amino groups leads us to introduce a new, efficient and green solid acid catalyst. We used the Fourier-transform infrared spectroscopy (FT-IR), X-Ray Diffraction (XRD), Thermogravimetric analysis (TGA), Field Emission Scanning Electron Microscope (FE-SEM), elemental-mapping and Energy Dispersive X-ray spectroscopy (EDX) for the characterization of the catalyst. This novel catalyst efficiently used to the synthesis of benzo[h]indenoquinolin derivatives and the products were obtained with 80–95% of yields at 3-5 h with high purity. All of the products were characterized by FT-IR, ^{1}H and ^{13}CNMR spectroscopies and compared with authentic samples. Our protocol offers several significant advantages, such as easy preparation of catalyst, green nature of catalyst and reaction media, high yields, good reaction times and easy workup.

***Keywords**: Sugarcane bagasse, Solid acid catalyst, Heterogeneous catalyst, Indenoquinolin.*

1. Introduction

A very powerful method in organic chemistry is multicomponent reactions (MCRs), which can simplify complex reactions for preparing a wide variety of organic molecules in a single operation. Other remarkable advantages of MCRs include a reduction in the number of purification steps and the minimization of byproducts and impurities, rendering the transformations green.

Among the ubiquitous nitrogen-containing heterocycles, indenoquinolines showed important and diverse biological properties such as topoisomerase I/II inhibitors [1, 2], anti-osteoclastogenic activators [3], anti-cancer properties [4-6], anti-mycobacterials [7, 8], acetylcholonesterase inhibitors [9], and antimalarials [10] (**Scheme 1**).



Scheme 1. Typical indenoquinoline drugs.

Recently, various catalysts have been used to promote the synthesis of indenoquinolines by MCRs, some of which are: *p*-toluenesulfonic acid (*p*-TSA) [11], tribromomelamine [12], melamine trisulfonic acid [13], Au (I) [14], $FeCl_3$ [15], $La(OTf)_3$ [16] and TBAI/TBHP [17].

To the best of our knowledge, among the different kinds of indenoquinolines there are few reports about the synthesis of indeno[1,2-b]quinolin-8-ones. Some of the conditions and catalysts used for the synthesis of them including reflux in ethanol without the catalyst [18], ultrasound [19], poly(4-vinylpyridinium) hydrogen sulfate [20], tribromomelamine [21], Fe_3O_4@cellulose-OSO_3H [22] and Fe_3O_4@urea/HITh-SO_3H [23]. Although these protocols are very efficient in the synthesis of these compounds, in some cases long reaction times and difficult separation conditions of products are observed. Therefore, designing of new methods and catalysts for the synthesis of these compounds are still in demand.

The main constituent of all plant materials is cellulose, which has attracted the interest of many scientists in different fields due to its abundant renewability.

*Corresponding author:
E-mail address: *hamidizare.samaneh@gmail.com*
(S. Hamidi Zare)

In chemistry, plants are important from different aspects one of is using them as carbon beds for the synthesis of catalysts. Researchers working on catalysts in different parts of worlds always look for green, inexpensive and renewable materials as beds for synthesis of their catalysts [24-36].

Among the plant-based materials sugarcane bagasse is one of the plants that have good potential for the synthesis of solid acids. Sugarcane bagasse is a by-product in the sugar and alcohol industries and annually several million tons of that will be burnt [37]. There are many reports about the application of sugarcane bagasse in different industries and scientific fields, but to the best of our knowledge the use of it as a catalyst for the synthesis of chemicals (not biodiesel) has received less attention. In this work we prepared a new solid acid catalyst by the modification of the surfaces of pre-pyrolysis sugarcane bagasse using the immobilization of hydrogen sulfate moieties. Then, the heterogeneous catalysts are efficiently used in accelerating the preparation of benzo[h]indeno[1,2-b]quinolins.

2. Experimental

2. 1. Material and instrumentation

The chemicals were purchased from Merck, Aldrich and Fluka in high purity. Bagasse was provided from a local factory in Khuzestan Province in Iran and after washing with distilled water, it was dried in sunlight. The dried sugarcane pulp was smashed and sieved, and its 60 mesh size was separated to continue the preparation process. 11 g of obtained bagasse powder was immersed in 100 mL of concentrated potassium hydroxide for overnight at 80 ˚C. The reaction mixture was then filtered and washed several times with water and dried overnight at 100 ° C. Pre-carbonized bagasse was prepared by heating in a tubular furnace at 400°C for 4 h in N_2 atmosphere.

The instruments used in this work are listed below: FT-IR: Thermo/Nicolet Avatar 360 in KBr matrix. XRD: PHILIPS PW1730 X-ray diffractometer using Ni-filtered Cu-Kα radiation (λ=0.15418 nm). FE-SEM: TESCAN MIRA instrument. TGA: PT1000 Linseis thermoanalyzer. ^{1}HNMR and ^{13}CNMR: Bruker Avance 400 spectrometer.

2.2. Preparation of catalyst

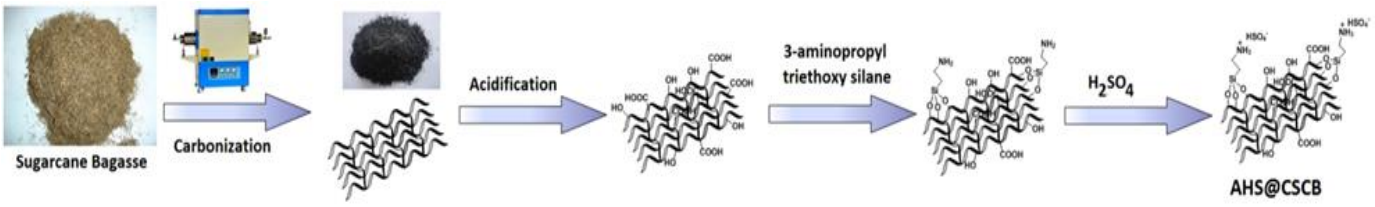
For the synthesis of the catalyst [38], firstly the prepared bagasse was immersed in the concentrated nitric acid solution for 24 h and washed with distillated water. Then, in a 250 mL round bottomed flask containing 100 mL of ethanol/water solution with the ratio of 75/25, 10 grams of activated bagasse and 3 g of 3-(triethoxysilyl) propylamine was mixed at 80 °C for 12h. After this time, the solid content was filtered and washed several times by water/ethanol mixture and dried at 100 °C for 5 h. After the preparation of aminated bagasse, 2.3 g of that was dispersed in 10 mL of CH_2Cl_2 and 0.5 g of concentrated sulfuric acid was inserted drop wise to the reaction vessel and refluxed for 8 h. Finally, the catalyst (AHS@CSCB) was obtained from the residue separated by filtration, washing with distillated water and drying at 100°C.

2.3. Typical procedure for the preparation of indenoquinolines

The amount of one mmol of each of the compounds of aldehyde, 1-naphthylamine and indanedione and 20 mg of AHS@CSCB was refluxed in ethanol for appropriate time. After the completion of reaction (monitored by TLC) the mixture was filtered and allowed to reach room temperature. After the evaporation of ethanol and recrystallization of the solid residue in chloroform, the considered indenoquinolines was obtained in high yields. ^{1}H NMR and ^{13}C NMR spectra (see supplementary information) were consistent with the assigned structures and by comparison with those reported in the literature [19].

3. Results and Discussion

After the synthesis and characterization of the catalyst [38] (**Scheme 2**), and to investigation the catalyst efficiency in the promotion of the organic reactions, we decided to check the synthesis of indeno[1,2-b]quinolin-8-one derivatives by the reaction between 1-naphthylamine, indanedione, and various arylaldehydes in the presence of AHS@CSCB.



Scheme 2. Preparation of catalyst

For the optimization of the reaction conditions based on previous reports, the reaction of 1 mmol of 4-chlorobenzaldehyde, 1 mmol of indanedione and 1 mmol of 1-naphthylamine in the presence of 30 mg of catalyst in ethanol and reflux conditions was performed. The product after 3 h and with 80% yield was obtained. The amounts of chemicals were sufficient and the conditions were green so for gained the optimum amount of catalyst, reaction was run in the presence of 25 and 20 mg of catalyst and the results was not changed. With more decreasing of catalyst to 15 and 10 mg the yield of products reduced to 73 and 70 percent in 3.5 and 4 h (**Fig. 1**). Therefore, the optimized condition was selected as shown in **Scheme 3**.

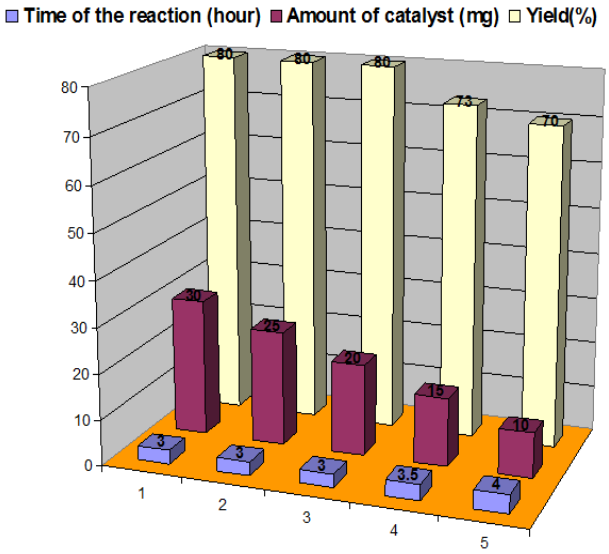
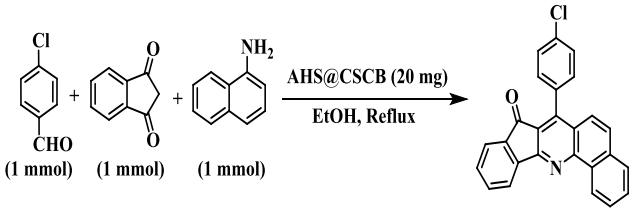


Fig. 1. Optimization of the reaction conditions.

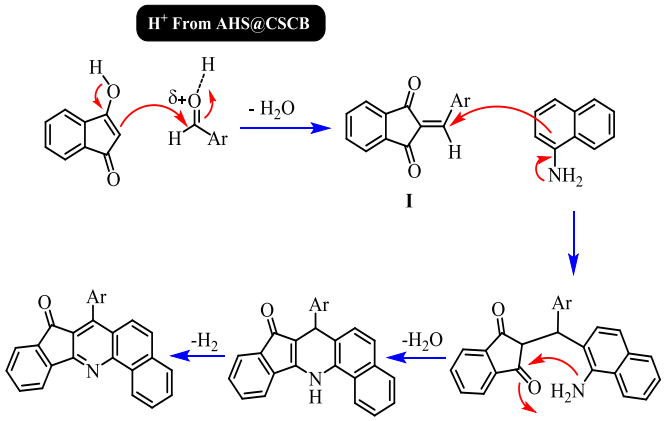


Scheme 3. Optimum condition.

After the optimization of reaction conditions, various aldehydes containing electron donating and electron withdrawing groups were selected for the preparation of indenoquinolin derivatives (**Table 1**). Aromatic aldehydes with electron withdrawing groups yielded the products in a shorter time compared to electron-donating ones. Also, the hindered aldehyde with an ortho substituent (**Table 1**, entry 10) gave the required product in longer time with good yield.

In all cases products were obtained with high yield (84-95%) between 3 to 5 h. The structures of all products were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy.

As shown in proposed mechanism (**Scheme 4**), Bronsted acidic nature of catalyst leads to preparing of aldehyde for nucleophilic attack by indenoquinoline and produced the intermediate **I**. Existence of the electron withdrawing groups on the aldehyde made the carbonyl of aldehyde more susceptible for the nucleophilic attack by indenoquinoline and faster production of intermediate **I** (step 1 in the mechanism). Then the reaction of intermediate **I** with 1-naphtylamine and followed by the elimination of H_2O and oxidation resulted in the desired product and the generation of AHS@CSCB in the reaction mixture.



Scheme 4. Proposed mechanism.

The reusability of AHS@CSCB was investigated in the synthesis of 7-(4-Chlorophenyl)-8*H*-benzo [h]indeno [1,2-b]quinolin-8-one (**Table 1**, Entry 2). After the first run, the catalyst was separated by filtration and washed with chloroform and dried at 100 °C. The process was carried out for three runs and the results showed that the catalyst preserved the same efficiency after three runs (**Fig. 2**).

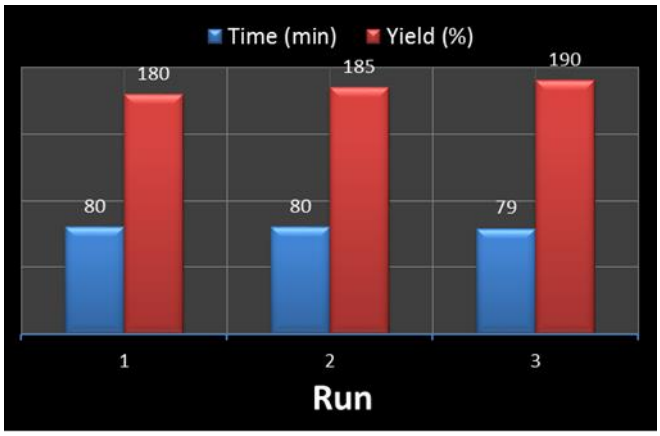


Fig. 2. Reusability of catalyst in the synthesis of 7-(4-Chlorophenyl)-8*H*-benzo[h]indeno[1,2-b]quinolin-8-one.

Table 1. Preparation of 7-aryl-8*H*-benzo[h]indeno[1,2-b]quinolin-8-ones in the presence of AHS@CSCB.

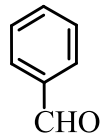
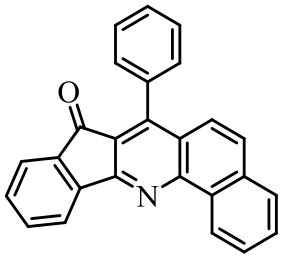
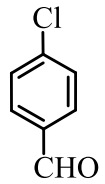
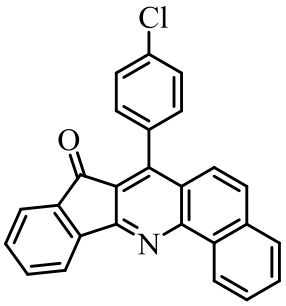
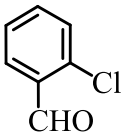
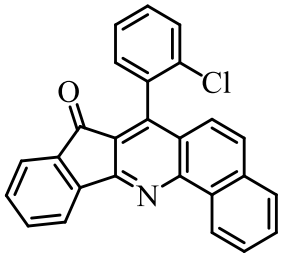
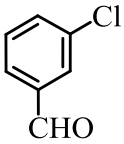
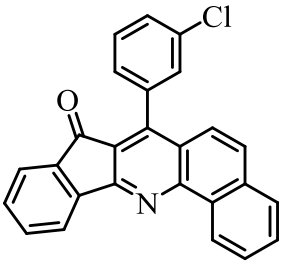
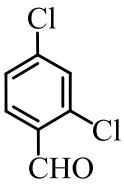
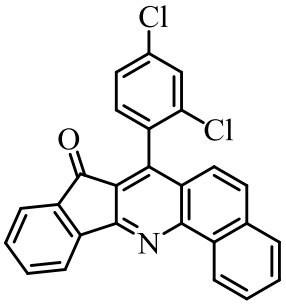
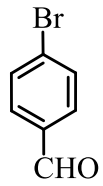
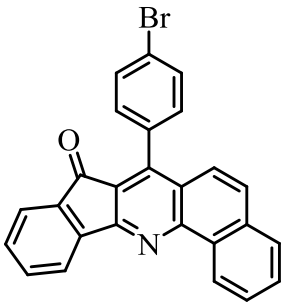
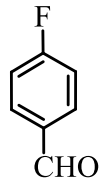
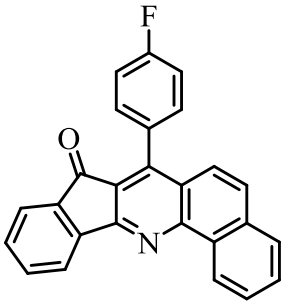
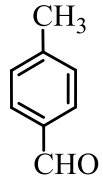
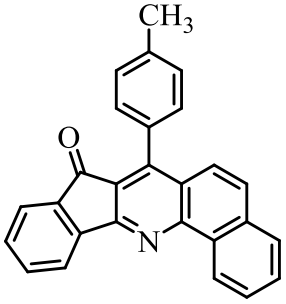
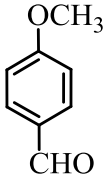
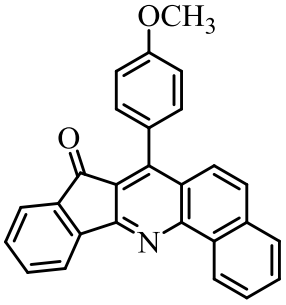
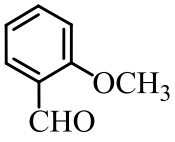
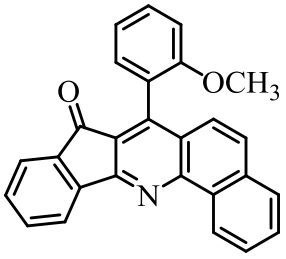
Entry	Aldehyde	product	Time (h)	Yield(%)[a]	M.P. (°C)	
					Obs.	Rep. [16]
1			3	86	223-225	224-226
2			3	80	260-263	259-261
3			3.5	89	290-292	289-291
4			3	90	270-273	274-276
5			4	92	235-237	234-236

Table 1. *Continued*

6			3.5	95	259-260	258-260
7			3	91	232-234	231-235
8			4	89	257-261	256-260
9			4.5	84	279-280	278-281
10			5	87	249-250	246-248

a: Isolated yield.

4. Conclusions

In conclusion, the results obtained in this work demonstrate that AHS@CSCB can be used as an efficient heterogeneous catalyst for the one-pot synthesis of indenoquinolines derivatives. Our protocol offers several significant advantages, such as the easy preparation of catalyst, the green nature of catalyst and reaction media, high yields, good reaction times and easy workup. Further work to explore this novel catalyst in other multicomponent reactions is in progress.

Acknowledgements

The financial support of this work by Payame Noor University (PNU) Research Council is acknowledged.

References

[1] C. H. Tseng, C. C. Tzeng, C. L. Yang, P. J. Lu, Y. P. Liu, H. L. Chen, C. Y. Chen, C. N. Yang, Y. L. Chen, Mol. Divers, 17 (2013) 781–799.
[2] C. H. Tseng, C. C. Tzeng, C. L. Yang, P. J. Lu, H. L.Chen, H. Y. Li, Y. C. Chuang, C. N. Yang, Y. L.Chen, J. Med. Chem. 53 (2010) 6164–6179.
[3] C. H. Tseng, R. W. Lin, Y. L.Chen, G. J. Wang, M. L. Ho, C. C. Tzeng, J. Med. Chem. 54 (2011) 3103–3107.
[4] T. Utsugi, K. Aoyagi, T. Asao, S. Okazaki, Y. Aoyagi,M. Sano, K. Wierzba, Y. Yamada, Jpn. J. Cancer Res. 88 (1997) 992–1002.
[5] M. Yamato, Y. Takeuchi, K. Hashigaki, Y. Ikeda, C. Ming-rong, K. Takeuchi, M. Matsushima, T. Tsuruo, T. Tashiro, J Med Chem. 32 (1989) 1295 - 1300.
[6] A. Rampa, A. Bisi, F. Belluti, S. Gobbi, P. Valenti, V. Andrisano, V. Cavrini, A. Cavalli, M. Recanatini, Bioorg Med Chem, 8 (2000) 497-506.
[7] R. S. Upadhayaya, P. D. Shinde, A. Y. Sayyed, S. A. Kadam, A. N. Bawane, A. Poddar, O. Plashkevych, A. Foldesic, J. Chattopadhyaya, Org. Biomol. Chem. 8 (2010) 5661–5673.
[8] R. S. Upadhayaya, S. V. Lahore, A. Y. Sayyed, SS. Dixit, P. D. Shinde, J. Chattopadhyaya, Org. Biomol. Chem. 8 (2010) 2180–2197.
[9] L. W. Deady, J. Desneves, A. J. Kaye, G. J. Finlay, B. C. Baguley, W. A. Denny. Bioorg Med Chem. 8 (2000) 977-984.
[10] X. Lu, J. L. Petersen, K. K. Wang. Org Lett. 5 (2003) 3277-3280.
[11] K. Ahmed, B. Dubey, S. Nadeem, B. Shrivastava, P. Sharma, Chin. Chem. Lett. 27 (2016) 721-725.
[12] PN. Sudhan, M. Ghashang, S. S. Mansoor, Iran J Sci. Technol. Trans Sci. 42 (2018) 1895–1904.
[13] F. Shirini, S. Sarvi Beigbaghlou, S. V. Atghia, S. A. Mousazadeh, Dyes Pigm. 97 (2013) 19-25.
[14] C. Jiang, Z. Xiong, S. Jin, P. Gao, Y. Tang, Y. Wang, C. Du, X. Wang, Y. Liu, B. Lin, Y. Liu, M. Cheng, Chem. Commun., 52 (2016) 11516-11519.
[15] A. Mondal, C. Mukhopadhyay, ACS Comb. Sci. 17 (2015) 404–408.
[16] S. Kumari, M. Rajeswari, J. M. Khurana, Synth. Commun, 46 (2016) 387-394.
[17] J. Meesin, M. Pohmakotr, V. Reutrakul, D. Soorukram, P. Leowanawat, S. Saithong, C. Kuhakarn, Org. Lett. 19 (2017) 6546–6549.
[18] N. G. Kozlov, K. N. Gusak, Russ. J. Org. Chem. 42 (2006) 1668−1674.
[19] M. Mamaghani, T. Hosseyni Larghani, J. Chem. Res. 36 (2012) 235-237.
[20] N. Ghaffari Khaligh, Chinese J. Catal. 35 (2014) 474–480.
[21] S. S. Mansoor, M. Ghashang, K. Aswin, Res. Chem. Intermed. 41 (2015) 6907–6926.
[22] A. Maleki, N. Nooraie Yeganeh, Appl. Organometal. Chem. 31 (2017) e: 3814.
[23] S. Jiang, M. Shen, F. R. Sheykhahmad, Open Chemistry, 18 (2020) 648–662.
[24] B.B. F. Mirjalili, R. Zare Reshquiyea, RSC. Adv. 5 (2015) 15566-15571.
[25] B. Sadeghi, I. Zarepour, J. Nanostruct. Chem. 5 (2015) 305-311.
[26] S. Dehghanpoor, B. Sadeghi, M. Mosslemin, Bulg. Chem. Commun. 50 (2018) 18-22.
[27] F.Shirini, S. Akbari Dadamahaleh, A. Mohammad Khah, A. R. Aliakbar, C. R. Chimie.16 (2013) 207–216.
[28] M. Seddighi, F. Shirini, O. Goli Jolodar, RSC. Adv. 6 (2016) 23564-23570.
[29] W. Yu , L. Wei, C. Xiu-Mei , S. Yang , X. Hai-Qiang, X. Hua-Hong, Y. Rui, P.Li-Ling , M.Rui, Y. Cai Hui, Y. Wei, B. Rong Cheng, W. Hui, Lett. Org. Chem.6 (2009) 456-461.
[30] C. Guo, F. Baishan, Bioresource. Technol. 102 (2011) 2635–2640.
[31] Y.Shang, Y. Jiang, Gao, J. Energ. Source. Part. A 37 (2015) 1039–1045.
[32] D. Yong-Ming, C. Kung Tung, W. YuJie, C. Chiing Chang, Int. J. Chem. Eng. 5 (2014) 276-280.
[33] Z. Danlin, L. Shenglan, G. Wanjun, W. Guanghui, Q. Jianghua, C. Hongxiang, Appl. Catal. A. Gen 469 (2014) 284–289.
[34] S.Molaei, S. Javanshir, Green. Chem. Lett. Rev. 11 (2018) 275–285.
[35] S. Mengxiao, L. Tianhang, Z. Zhaoyuan, W. Nana, X. Aming, L. Xuliang, W. Yuan, W. Fan, W. Mingyang, RSC. Adv. 5 (2015) 84406-84409.
[36] S. Sarvi Beigbaghlou, R. Javad Kalbasi, K. Marjani, A. Habibi, Catal. Lett.148 (2018) 2446–2458.
[37] A. K. Chandel, S. S. Da Silva, W. Carvalho, O. V. Singh, J. Chem. Technol. Biotechnol. 87 (2012) 11–20.
[38] E. Rostami, S. Hamidi Zare, ChemistrySelect, 4 (2019), 13295 – 13303.