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One-pot oxidative Ugi-type three-component reaction of aromatic hydrocarbons of petroleum naphtha: comparing catalytic effect of cellulose- and wool–SO_3H supported with manganese dioxide nanostructures

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A novel domino oxidative Ugi-type three-component reaction of aromatic hydrocarbons (OU-3CR) has been investigated with aromatic hydrocarbons of petroleum naphtha using two biopolymer supported MnO_2 nanostructured catalysts, MnO_2@cellulose–SO_3H and MnO_2@wool–SO_3H, for the synthesis of α-amino amides, 3,4-dihydroquinoxalin-2-amine, 4*H*-benzo[*b*][1,4]thiazin-2-amine, and cyanophenylamino-acetamide derivatives. Nano-MnO_2@cellulose–SO_3H and nano-MnO_2@wool–SO_3H were used as biodegradable oxidation and solid acid catalysts. The best results for oxidation and condensation processes are obtained with MnO_2@cellulose–SO_3H and MnO_2@wool–SO_3H, respectively. To the best of our knowledge this approach can be considered as the first example of OU-3CR of alkyl arenes with a nano-MnO_2 catalyst which would be very useful from a practical point of view.

1. Introduction

The mixtures of benzene, toluene, and the three xylene isomers, BTX, are very important petrochemical materials. BTX can be made by various processes. However, most BTX production is based on the recovery of aromatics derived from the catalytic reforming of naphtha in petroleum refineries. Among the BTX family members, toluene and xylenes (TXs) were modified by chemical processing and a large number of fine chemicals and petrochemicals were produced from them.[1]

Multicomponent reactions (MCRs)[2,3] and specially isocyanide based MCRs (IMCRs)[4,5] are powerful tools for the synthesis of biologically heterocyclic molecules and have enormous applications in the field of drugs and pharmaceutical industries. One of the most important reactants in IMCRs is carbonyl compounds which unfortunately this limits the versatility of these reactions. To solving this issue, one-pot oxidative MCRs protocol can be done by transforming an inert substance into a reactive substrate of the IMCRs. These transformations involve *in situ* oxidation of one reagent or the oxidation is performed as a separate step.[6] Very recently it has been shown that the direct use of alcohols and *N*-alkyl amines in Passerini and Ugi reactions, respectively, could significantly widen the versatility and the scope of well-known aldehyde-based multicomponent.[7–18] Since, the oxidation of alkyl arenes is among the most important transformations in chemistry and industry to introduce and modify functional groups,[19] this useful strategy (domino aerobic oxidation/MCRs) can be developed with either primary or secondary alkyl arenes instead of their corresponding aldehydes or ketones in the IMCRs. To the best of our knowledge, there is currently no report of employing alkyl arenes in one-pot oxidative Ugi-type multi-component reactions (OU-MCRs).

In our previous reports evidenced that the prepared MnO_2@cellulose and MnO_2@wool catalysts showed high selectivity in the oxidation of the alkyl arenes to the related aldehydes or ketones.[20,21] In this work, we used MnO_2@cellulose–SO_3H and MnO_2@wool–SO_3H as two biopolymer based catalysts in OU-3CR with the toluene and three xylene isomers. The double nature of the prepared catalysts (oxidation capability and acidic property) was made capable us to use these catalysts in the both oxidation and synthetic sections of the reactions.

2. Materials and methods

2.1. General

All reagents were obtained from Aldrich or Merck and used without further purification. Scanning electron microscopy (SEM) observations were carried out on an electron microscopy Philips XL-30 ESEM. All samples were sputtered with gold before observation. Mn(IV) determination was carried out on an FAAS (Shimadzu model AA-680 flame atomic absorption spectrometer) with a Mn hollow cathode lamp at 279.5 nm, using an air–acetylene flame. Thermogravimetric analysis (TGA) was

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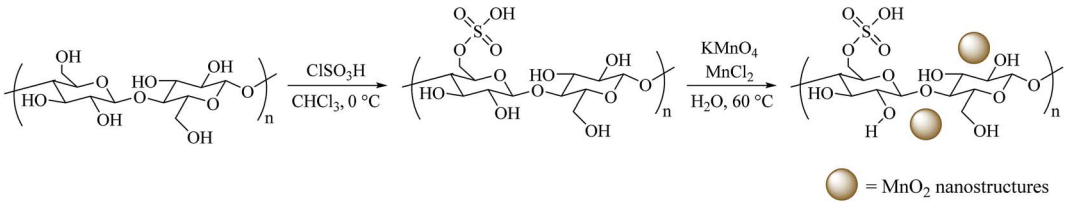
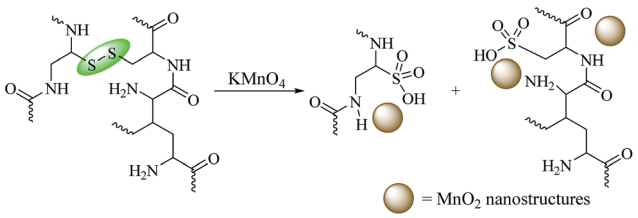


Scheme 1 Preparation of MnO_2@cellulose–SO_3H catalyst.



Scheme 2 Preparation of MnO_2@wool–SO_3H catalyst.

carried out using STA 1500 instrument at a heating rate of 10 °C min^{-1} in air. X-ray diffraction (XRD) pattern of product was recorded on a STOE STADI P with scintillation detector, secondary monochromator using Cu Kα radiation ($\lambda = 0.1540$ nm). Products were analyzed using a Varian 3900 GC. Melting points were measured on an Electrothermal 9200 apparatus. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^1H NMR spectra were recorded on a Bruker DRX-300 Avance spectrometer 300.13 MHz; chemical shifts are reported in parts per million (ppm). The ^{13}C NMR spectra were recorded at 75.47 MHz; chemical shifts are reported in parts per million (ppm). The elemental analyses were performed with an Elementar Analysen systeme GmbH VarioEL.

2.2. Preparation of catalysts

2.2.1. Preparation of MnO_2@cellulose–SO_3H. According to our previous works,[22–24] chlorosulfonic acid (0.40 g, 3.60 mmol) was added dropwise to a magnetically stirred mixture of cellulose (1.00 g) in $CHCl_3$ (20 mL) at 0 °C during 2 h. Then, the mixture was stirred for 3 h at room temperature until HCl was

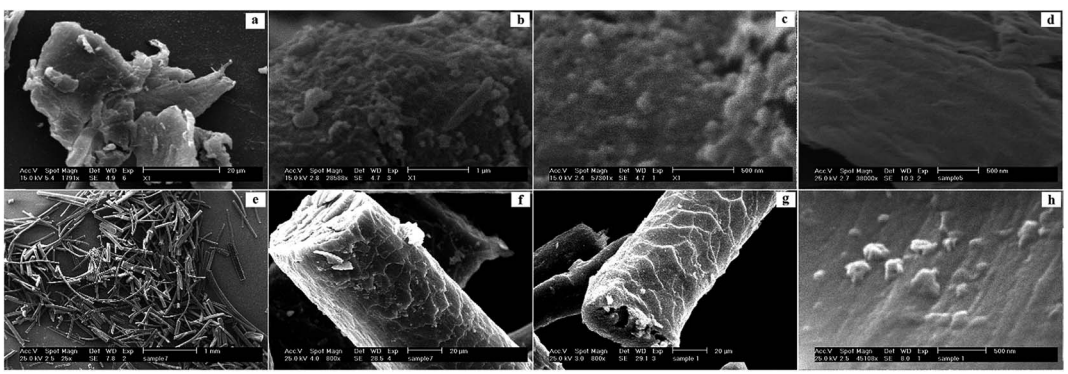


Fig. 1 SEM images of MnO_2@cellulose–SO_3H (a–c) in different scales, cellulose (d), wool (e and f), and MnO_2@wool–SO_3H (g and h) in different scales.

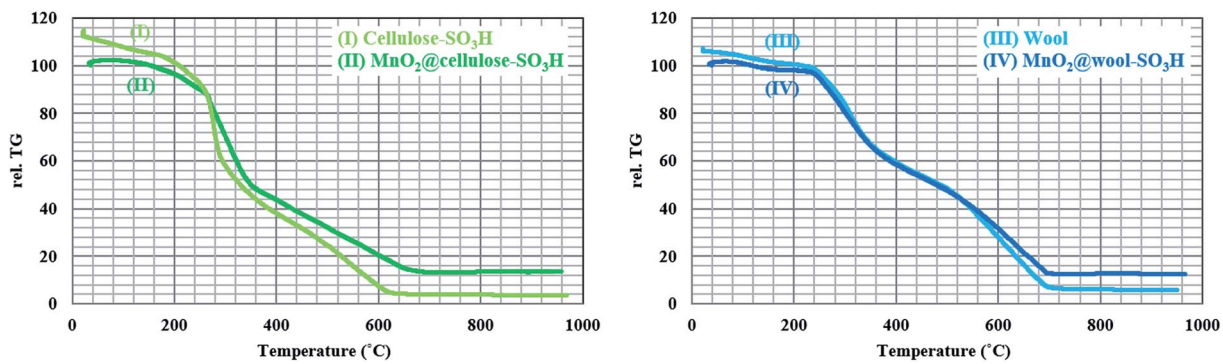


Fig. 2 TG curves of cellulose–SO_3H (I), MnO_2@cellulose–SO_3H (II), wool (III), and MnO_2@wool–SO_3H (IV) in air.

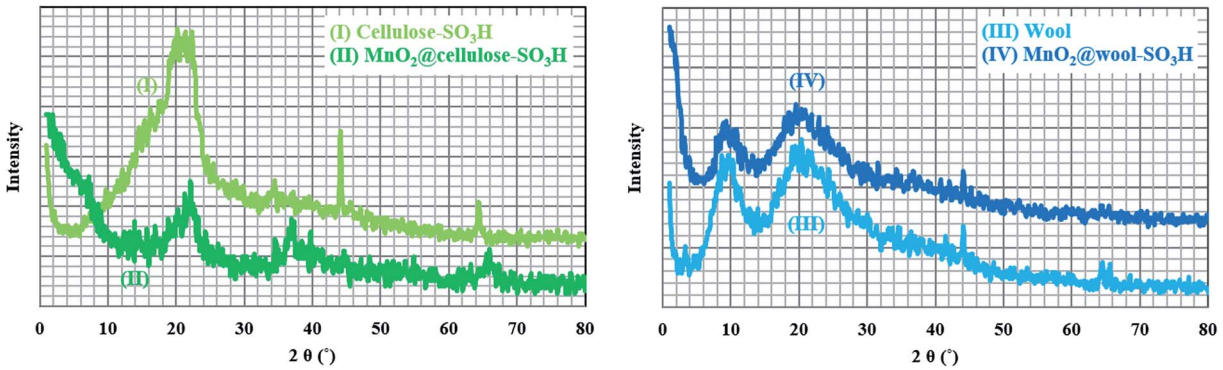


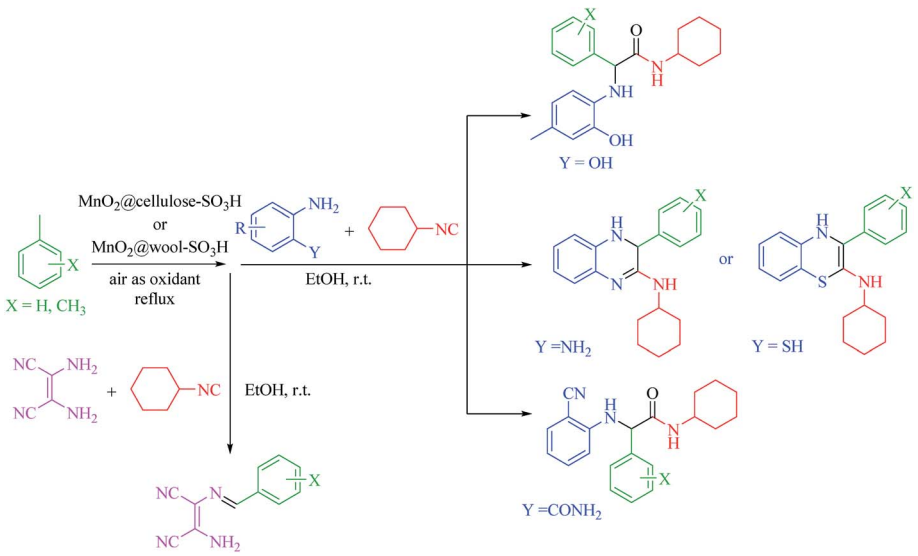
Fig. 3 XRD patterns of cellulose–SO_3H (I) and wool (III), nano-MnO_2@cellulose–SO_3H (II), and nano-MnO_2@wool–SO_3H (IV).

removed from the reaction vessel. The mixture was filtered and washed with methanol (5 × 10 mL). The product was dried at room temperature to obtain cellulose sulfuric acid as white powder. Manganese dioxide nanostructures on sulfonated cellulose fibers was prepared according to the our previous report to synthesis of MnO_2@cellulose.[20] A solution of $KMnO_4$ (0.01 M, 90 mL) at 60 °C, and a solution of $MnCl_2$ (0.02 M, 75 mL) at 70 °C were added dropwise to a mixture of sulfonated cellulose (1.00 g) in 50 mL of H_2O at 60 °C for 12 h. The mixture was stirred for 24 h at room temperature. Then, the reaction mixture was filtered, washed and dried under vacuum at 70 °C (Scheme 1).

2.2.2. Preparation of MnO_2@wool–SO_3H. Natural white wool (sheep of Kangavar/Iran) was washed with NaOH solution (0.01 M), distilled water, methanol, and ethanol, then cut with scissors to very short pieces (about 50–500 μm, based on SEM images). A solution of $KMnO_4$ (0.01 M, 180 mL) was added dropwise to a magnetically stirred suspention of the wool pieces (1.00 g) in 100 mL of H_2O during 12 h at room temperature. The stirring was continued at room temperature for 24 h. The mixture was filtered and washed with acetone (3 × 10 mL) and EtOH (3 × 10 mL), successively and dried under vacuum at 60 °C for 24 h to give MnO_2@wool–SO_3H (Scheme 2).[21]

2.3. General procedure for the preparation of products 4a–c, 5a–d, 6a–c, 7a–c, and 8a–d

In a typical reaction, an aromatic hydrocarbon (2.00 mL) was added to a two-necked flask containing catalyst (0.09 g, 10 mol% for MnO_2@cellulose–SO_3H or 0.10 g, 10 mol% for MnO_2@wool–SO_3H catalyst) and stirred under reflux conditions and air blowing. The progress of the reaction was followed by GC method. After the indicated time in Table 2, the mixture of reaction was cooled. Amine (1.00 mmol), isocyanide (1.00 mmol), and 5 mL of ethanol 96% was added to the reaction media and stirred at room temperature. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was filtered off and washed with ethanol, and then the precipitation of filtrate was done to give products **4a–c**, **5a–d**, **6a–c**, **7a–c**, and **8a–d**.



Scheme 3 Synthesis of α-amino amide, 3,4-dihydroquinoxalin-2-amine, 4*H*-benzo[*b*][1,4]thiazin-2-amine, and cyanophenylamino-acetamide derivatives.

2.4. Caracterization of catalyst

The MnO_2@cellulose–SO_3H and MnO_2@wool–SO_3H were characterized by scanning electron microscopy (SEM), flame atomic absorption spectrometer (FAAS), thermogravimetric analysis (TGA), and X-ray diffraction (XRD). From the Fig. 1a–d it is evident that the sulfunation of cellulose with chlorosulfonic acid have not been altered the morphology of the cellulose support. Also, Fig. 1e–h shows SEM images of wool (Fig. 1e and f) and the synthesized MnO_2@wool–SO_3H (Fig. 1g and h) which indicated the relatively retained morphology of wool after functionalizing with oxidation of –S–S– bonds to –SO_3H groups. As predicted, MnO_2 nanostructures were well dispersed on the surface of cellulose–SO_3H and wool–SO_3H fibers (Fig. 1c and h, respectively).

The Mn(IV) contents of the MnO_2@cellulose–SO_3H and MnO_2@wool–SO_3H catalysts was determined using FAAS method. The amounts of MnO_2 in the MnO_2@cellulose–SO_3H and MnO_2@wool–SO_3H were determined 9.13% and 8.82%, respectively.

In continue, these catalysts were characterized by thermogravimetric analysis (TGA) that confirmed functionalization of supports and the presence of MnO_2 in the supports. Fig. 2 shows the thermal behavior of cellulose–SO_3H (I), MnO_2@cellulose–SO_3H (II), wool (III), and MnO_2@wool–SO_3H (IV). The thermogram of cellulose–SO_3H and MnO_2@cellulose–SO_3H show a weight loss of around 100% and 90% at temperature higher than 700 °C, respectively. In the case of MnO_2@cellulose–SO_3H, the decreased 10% weight loss is directly related to the presence of the MnO_2. In the case of the MnO_2@wool–SO_3H at the temperature higher than 720 °C a lose in weight about 91% is observable; the remaining weight is related to the MnO_2 loaded on the catalyst.

The XRD patterns of cellulose–SO_3H and wool fibers and MnO_2@cellulose–SO_3H and MnO_2@wool–SO_3H catalysts were employed to investigate the structures of the synthetic catalysts (Fig. 3). In the XRD patterns I and II the characters of cellulose–SO_3H and MnO_2@cellulose–SO_3H were observable, respectively. The XRD pattern of wool fibers and MnO_2@wool–SO_3H is shown in XRD patterns III and IV. The peaks related to MnO_2 (2θ = 13.90°, 24.28°, 34.60°, and 65.26°) can be ascribed to the MnO_2 nanostructures dispersed onto the surface of support fibers.

3. Results and discussion

During the course of our studies toward the development of new routes to the synthesis of organic compounds using green reaction media[25–28] and introduction of wool–SO_3H and cellulose–SO_3H for the first time as a biopolymer solid acid catalyst,[22–24] and using nano-MnO_2@cellulose and nano-MnO_2@wool for the oxidation of the alkyl arenes,[20,21] herein, we report the one-pot OU-3CR with the TXs to synthesis of α-amino amides, 3,4-dihydroquinoxalin-2-amine, 4*H*-benzo[*b*][1,4]thiazin-2-amine, and cyanophenylamino-acetamide derivatives in the presence of MnO_2@cellulose–SO_3H and MnO_2@wool–SO_3H as biodegradable oxidation and solid acid catalysts (Scheme 3).

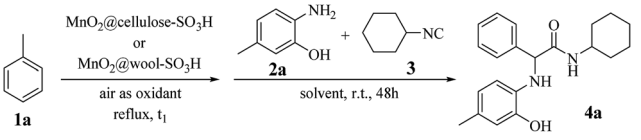
In order to obtain the optimum reaction conditions, toluene has been oxidized in the presence of the MnO_2@cellulose–SO_3H or MnO_2@wool–SO_3H catalyst in the reflux reaction conditions at the reaction times which have been presented in the Table 1. After cooling the reaction media 2-amino-5-methylphenol (**2a**) and cyclohexyl isocyanide (**3**) in various organic solvents and water were allowed to react at room temperature. As can be seen from Table 1, commercially available ethanol 96% is the best solvents for the synthesis of compound *N*-cyclohexyl-2-((2-hydroxy-4-methylphenyl)amino)-2-phenylacetamide (**4a**) respect to yield and reaction times. In order to find the best conditions, toluene and the three xylene isomers (**1a–d**) and various amines (**2a–e**) were examined in this reaction. The results have been shown in Table 2.

The successfully carrying out of the reactions had confirmed the usability of the synthesized catalyst for the first-(aerobic oxidation) and second-step (solid acid catalyst), as it has been designed.

In order to investigate the scope and limitations of this reaction, we extended it to *o*-phenylenediamine (**2b**), 2-aminothiophenol (**2c**), 2-aminobenzamide (**2d**), and 2,3-diaminomaleonitrile (**2e**) instead of 2-amino-5-methylphenol (**2a**). Due to intramolecular nucleophilic attack of NH and SH groups to the activated nitrile moiety, interesting products such as 3,4-dihydroquinoxalin-2-amines **4a–c** and 4*H*-benzo[*b*][1,4]thiazin-2-amines **5a–d** were obtained but in the case of using 2-amino-5-methylphenol (**2a**) and 2-aminobenzamide (**2d**) the cyclyzation product was not obtained (Table 2).

The reaction of 2,3-diaminomaleonitrile, aldehyde, and isocyanide was known to produce Schiff base and nucleophilic attack by isocyanide does not occur.[28] So, the isolated compounds were intermediates **8a–d**. Unfortunately, in the case of using *m*-xylene as an alkyl arene, the yield of reactions was

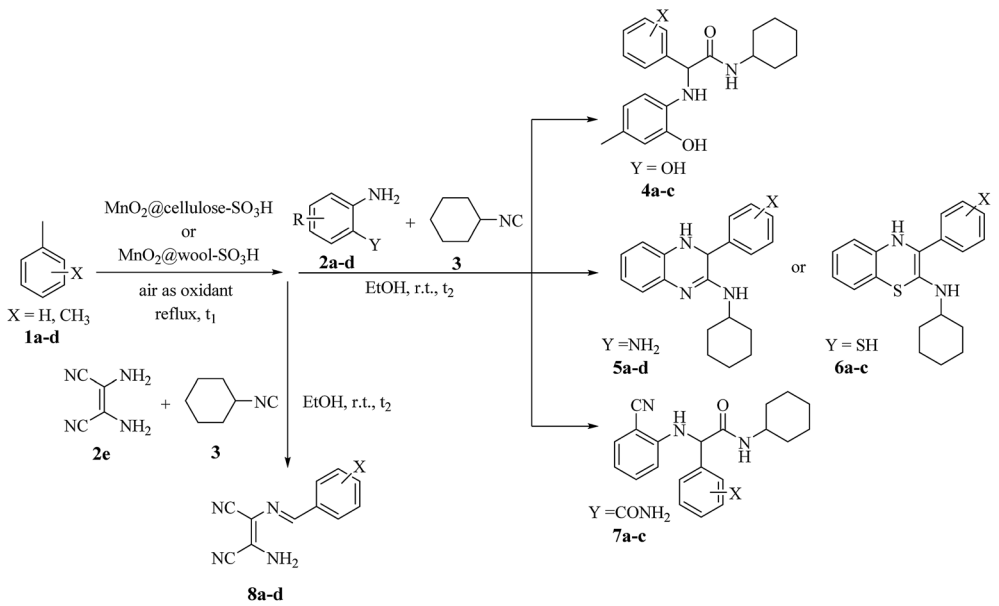
Table 1 Optimization of the reaction conditions for the synthesis of compound *N*-cyclohexyl-2-((2-hydroxy-4-methylphenyl)amino)-2-phenylacetamide (**4a**) by MnO_2@cellulose–SO_3H and MnO_2@wool–SO_3H catalysts[a]



Entry	Catalyst (MnO_2 content/mol%)	t_1 (h)	Solvent	Yield[b] (%)
1	MnO_2@cellulose–SO_3H (10)	8	MeOH	56
2	MnO_2@wool–SO_3H (10)	10	MeOH	78
3	MnO_2@cellulose–SO_3H (10)	8	EtOH	91
4	MnO_2@wool–SO_3H (10)	10	EtOH	96
5	MnO_2@cellulose–SO_3H (10)	8	H_2O	Trace
6	MnO_2@wool–SO_3H (10)	10	H_2O	Trace
7	MnO_2@cellulose–SO_3H (10)	8	—	Trace
8	MnO_2@woolSO_3H (10)	10	—	Trace

[a] Reaction conditions: first step: toluene (2.00 mL), air as oxidant; second step: 2-amino-5-methylphenol (1.00 mmol), cyclohexyl isocyanide (1.00 mmol), solvent (5.00 mL). [b] Isolated yield.

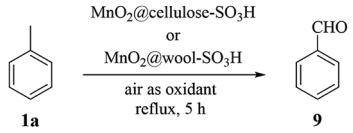
Table 2 The synthesis of α-amino amides, 3,4-dihydroquinoxalin-2-amine, 4*H*-benzo[*b*][1,4]thiazin-2-amine, cyanophenylamino-acetamide derivatives by MnO_2@cellulose–SO_3H and MnO_2@wool–SO_3H catalysts[a]



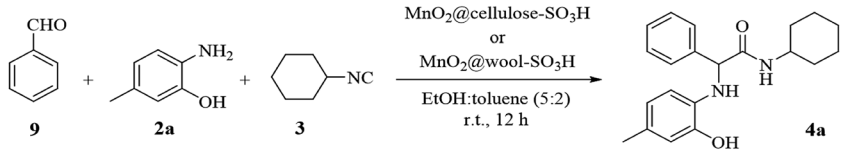
Entry	Arenes	Amines	Catalyst	t_1 (h)	t_2 (h)	Yield[b] (%)		Mp (°C) Found	Mp (°C) Reported
1	Toluene	2-Amino-5-methylphenol	MnO_2@cellulose–SO_3H	8	48	**4a**	**91**	261–263	260–261 (ref. 29)
			MnO_2@wool–SO_3H	10	48		**96**		
2	Toluene	*o*-Phenylenediamine	MnO_2@cellulose–SO_3H	8	12	**5a**	**88**	186–187	185–187 (ref. 25 and 30)
			MnO_2@wool–SO_3H	10	12		**87**		
3	Toluene	2-Aminothiophenol	MnO_2@cellulose–SO_3H	8	48	**6a**	**76**	190–192	192 (ref. 24 and 31)
			MnO_2@wool–SO_3H	10	48		**74**		
4	Toluene	2-Aminobenzamide	MnO_2@cellulose–SO_3H	8	48	**7a**	**77**	141–143	142–144 (ref. 26)
			MnO_2@wool–SO_3H	10	48		**70**		
5	Toluene	2,3-Diaminomaleonitrile	MnO_2@cellulose–SO_3H	8	12	**8a**	**91**	205–206	205–207 (ref. 28)
			MnO_2@wool–SO_3H	10	12		**93**		
6	*o*-Xylene	2-Amino-5-methylphenol	MnO_2@cellulose–SO_3H	6	48	**4b**	**92**	195–196 (ref. 32)	—
			MnO_2@wool–SO_3H	7	48		**88**		
7	*o*-Xylene	*o*-Phenylenediamine	MnO_2@cellulose–SO_3H	6	12	**5b**	**87**	216–217 (ref. 32)	—
			MnO_2@wool–SO_3H	7	12		**85**		
8	*o*-Xylene	2-Aminothiophenol	MnO_2@cellulose–SO_3H	6	48	**6b**	**80**	156–157 (ref. 32)	—
			MnO_2@wool–SO_3H	7	48		**76**		
9	*o*-Xylene	2-Aminobenzamide	MnO_2@cellulose–SO_3H	6	48	**7b**	**73**	170–173 (ref. 32)	—
			MnO_2@wool–SO_3H	7	48		**75**		
10	*o*-Xylene	2,3-Diaminomaleonitrile	MnO_2@cellulose–SO_3H	6	12	**8b**	**91**	186–187 (ref. 32)	—
			MnO_2@wool–SO_3H	7	12		**90**		
11	*p*-Xylene	2-Amino-5-methylphenol	MnO_2@cellulose–SO_3H	6	48	**4c**	**90**	>290	>290 (ref. 29)
			MnO_2@wool–SO_3H	7	48		**94**		
12	*p*-Xylene	*o*-Phenylenediamine	MnO_2@cellulose–SO_3H	6	12	**5c**	**85**	200–202	201 (ref. 25 and 30)
			MnO_2@wool–SO_3H	7	12		**81**		
13	*p*-Xylene	2-Aminothiophenol	MnO_2@cellulose–SO_3H	6	48	**6c**	**80**	205–206	205 (ref. 24 and 31)
			MnO_2@wool–SO_3H	7	48		**83**		
14	*p*-Xylene	2-Aminobenzamide	MnO_2@cellulose–SO_3H	6	48	**7c**	**79**	178–180	178–180 (ref. 26)
			MnO_2@wool–SO_3H	7	48		**77**		
15	*p*-Xylene	2,3-Diaminomaleonitrile	MnO_2@cellulose–SO_3H	6	12	**8c**	**90**	234–235 (ref. 32)	—
			MnO_2@wool–SO_3H	7	12		**86**		
16	*m*-Xylene	*o*-Phenylenediamine	MnO_2@cellulose–SO_3H	9	48	**5d**	**15**	189–192 (ref. 32)	—
			MnO_2@wool–SO_3H	10	48		**18**		
17	*m*-Xylene	2,3-Diaminomaleonitrile	MnO_2@cellulose–SO_3H	9	48	**8d**	**20**	214–217 (ref. 32)	—
			MnO_2@wool–SO_3H	10	48		**27**		

[a] Reaction conditions: first step: arene (2.00 mL), air as oxidant; second step: amine (1.00 mmol), cyclohexyl isocyanide (1.00 mmol), catalyst (0.09 g for MnO_2@cellulose–SO_3H and 0.10 g MnO_2@wool–SO_3H), EtOH (5.00 mL). [b] Isolated yield.

Table 3 Comparison of the efficiency of the obtained catalysts in same time for the synthesis of compound **4a**



Entry[a]	Catalyst	Conversion of **9**[b] (%)
1	MnO_2@cellulose–SO_3H	17
2	MnO_2@wool–SO_3H	10



Entry[c]	Catalyst	Yield of **4a**[d] (%)
1	MnO_2@cellulose–SO_3H	40
2	MnO_2@wool–SO_3H	61

[a] Reaction conditions: arene (2.00 mL), catalyst (0.09 g for MnO_2@cellulose–SO_3H and 0.10 g MnO_2@wool–SO_3H), air as oxidant. [b] Conversion determined by GC analysis. [c] Reaction conditions: benzaldehyde (1.00 mmol), 2-amino-5-methylphenol (1.00 mmol), cyclohexyl isocyanide (1.00 mmol), catalyst (0.09 g for MnO_2@cellulose–SO_3H and 0.10 g MnO_2@wool–SO_3H). [d] Isolated yield.

very low and only **4d** and **8d** products have been separated from reaction media.

To select the best catalyst from reaction yield point of view, the synthesis of compound *N*-cyclohexyl-2-((2-hydroxy-4-methylphenyl)amino)-2-phenylacetamide (**4a**) has been studied. The reactions have been studied in the same reaction time. The reactions and obtained results have been presented in the Table 3. From the data it has been clearefied that MnO_2@cellulose–SO_3H acts as the better catalyst for the oxidation processes in the step 1 while the MnO_2@wool–SO_3H catalyst acts as the better acid catalyst in the step 2.

Recyclability of the catalysts in the both oxidation and solid-acid-catalyzed steps were examined. The catalysts which were recovered from OU-3CR between toluene, 2-amino-5-methylphenol, and cyclohexyl isocyanide by filtration, dried and reused for five times. Results are shown in Fig. 4. It is clear that by successive use of catalysts their activity and performance have not been decreased in a considerable amount (Fig. 4).

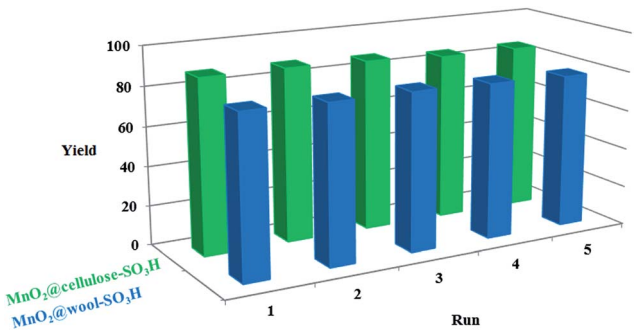


Fig. 4 Successive use of the prepared catalysts for the synthesis of compound *N*-cyclohexyl-2-((2-hydroxy-4-methylphenyl)amino)-2-phenylacetamide (**4a**).

4. Conclusion

In conclusion, we have developed a novel domino, aerobic, oxidative Ugi-type three-component reaction of aromatic hydrocarbons using biodegradable catalysts. The MnO_2@cellulose–SO_3H and MnO_2@wool–SO_3H catalysts have been used successfully to oxidize the low-price aromatic hydrocarbons (toluene and xylenes) to valuable aldehydes. The double nature of the prepared catalysts (oxidation capability and acidic property) was made capable us to use the same catalyst in the synthetic section of the reactions, as well. The green aspect of the catalysts is increasing the usability of the catalyst in the situation which environment pollutant materials are restricted to be used.

Acknowledgements

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References and notes

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32 Spectral data of new compounds: *N*-Cyclohexyl-2-((2-hydroxy-4-methylphenyl)amino)-2-(*o*-tolyl)acetamide (**4b**): cream powder; mp 195–196 °C; IR (KBr, cm^{-1}) 3362, 3038, 2927, 2854, 2427, 1582, 1517, 1450; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 1.10–1.99 (10H, m, $5CH_2$ of cyclohexyl), 2.05 (3H, s, CH_3), 2.12 (3H, s, CH_3), 4.10 (1H, br s, CH–NH), 5.27 (1H, s, CH–Ph), 6.37–7.25 (9H, m, H–Ar and 2NH), 9.47 (1H, br s, OH). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ 20.8, 21.1, 21.3, 25.1, 25.2, 25.7, 32.2, 49.0, 85.8, 114.3, 115.7, 116.9, 119.7, 123.0, 123.9, 126.4, 127.5, 129.7, 131.1, 139.2, 143.2, 154.0. Anal. calcd for $C_{22}H_{28}N_2O_2$: C, 74.97; H, 8.01; N, 7.95. Found C, 74.82; H, 7.85; N, 7.99. *N*-Cyclohexyl-3-(*o*-tolyl)-3,4-dihydroquinoxalin-2-amine (**5b**): cream powder; mp 216–217 °C; IR (KBr, cm^{-1}) 3740, 3433, 2929, 2857, 1646, 1507, 1448; ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 1.12–2.13 (10H, m, $5CH_2$ of cyclohexyl), 2.78 (3H, s, CH_3), 4.20 (1H, br s, CH–NH), 5.42 (1H, s, CH–Ph), 5.88 (1H, br s, NH), 6.53–7.40 (9H, m, H–Ar and NH). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 18.2, 20.0, 20.9, 21.3, 48.0, 52.9, 125.8, 128.6, 129.2, 129.5, 130.2, 130.7, 134.0, 134.3, 137.5, 140.0, 141.6, 142.3, 150.3. Anal. calcd for $C_{21}H_{25}N_3$: C, 78.96; H, 7.89; N, 13.15. Found C, 78.79; H, 7.96; N, 12.98. *N*-Cyclohexyl-3-(*m*-tolyl)-3,4-dihydroquinoxalin-2-amine (**5d**): cream powder; mp 189–192 °C; IR (KBr, cm^{-1}) 3244, 3046, 2931, 2855, 1654, 1598, 1504, 1449; ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 0.91–2.17 (10H, m, $5CH_2$ of cyclohexyl), 2.31 (3H, s, CH_3), 4.78 (1H, br s, CH–NH), 5.16 (1H, s, CH–Ph), 6.67–8.07 (10H, m, H–Ar and 2NH). Anal. calcd for $C_{21}H_{25}N_3$: C, 78.96; H, 7.89; N, 13.15. Found C, 79.01; H, 7.95; N, 13.02. *N*-Cyclohexyl-3-(*o*-tolyl)-4*H*-benzo[*b*][1,4]thiazin-2-amine (**6b**): yellow powder; mp 156–157 °C; IR (KBr, cm^{-1}) 3056, 2938, 2861, 2608, 2551, 2049, 1673, 1536, 1456; ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 1.00–1.92 (10H, m, $5CH_2$ of cyclohexyl), 2.40 (3H, s, CH_3), 2.86 (1H, br s, CH–NH), 7.21–7.79 (10H, m, H–Ar and 2NH). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 21.4, 24.3, 24.6, 30.6, 50.7, 125.7, 125.8, 126.1, 126.2, 126.2, 126.8, 128.6, 128.7, 128.9, 128.9, 129.1, 129.9, 140.7, 141.4. Anal. calcd for $C_{21}H_{24}N_2S$: C, 74.96; H, 7.19; N, 8.33. Found C, 75.03; H, 7.12; N, 8.27. 2-((2-Cyanophenyl)amino)-*N*-cyclohexyl-2-(*o*-tolyl)acetamide (**7b**): cream powder; mp 170–173 °C; IR (KBr, cm^{-1}) 3470, 3396, 3062, 2925, 2846, 2202, 1645, 1588, 1506, 1327; ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 1.26–2.38 (13H, m, $5CH_2$ of cyclohexyl and CH_3), 3.24 (1H, br s, CH–NH), 3.52 (1H, br s, NH), 4.48 (1H, s, CH–Ph), 6.96–8.66 (9H, m, H–Ar and NH). Anal. calcd for $C_{22}H_{25}N_3O$: C, 76.05; H, 7.25; N, 12.09. Found C, 76.12; H, 7.35; N, 12.15. 2-Amino-3-(((*E*)-2-methylbenzylidene)amino) maleonitrile (**8b**): yellow powder; mp 186–187 °C; IR (KBr, cm^{-1}) 3430, 3316, 3160, 2239, 2199, 1604, 1447, 1373; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 2.50 (3H, s, CH_3), 7.25–7.40 (3H, m, H–Ar), 7.92 (2H, br s, NH_2), 8.24 (1H, d, ^{3}JHH = 7.5 Hz, H–Ar), 8.50 (1H, s, CH). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ 19.2, 103.8, 114.2, 114.9, 126.6, 127.1, 128.1, 131.4, 131.7, 133.5, 139.0, 153.4. Anal. calcd for $C_{12}H_{10}N_4$: C, 68.56; H, 4.79; N, 26.65. Found C, 68.51; H, 4.72; N, 26.73. 2-Amino-3-(((*E*)-4-methylbenzylidene)amino)maleonitrile (**8c**): yellow powder; mp 234–235 °C; IR (KBr, cm^{-1}) 3413, 3301, 2902,

2230, 2196, 1908, 1611, 1374; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 2.96 (3H, s, CH_3), 7.28 (2H, d, ^{3}JHH = 7.8 Hz, H–Ar), 7.80 (2H, br s, NH_2), 7.91 (2H, d, ^{3}JHH = 7.8 Hz, H–Ar), 8.22 (1H, s, CH). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ 21.7, 103.3, 114.2, 114.9, 127.0, 129.5, 129.8, 133.4, 142.2, 155.5. Anal. calcd for $C_{12}H_{10}N_4$: C, 68.56; H, 4.79; N, 26.65. Found C, 68.62; H, 4.74; N, 26.70. 2-Amino-3-(((*E*)-3-methylbenzylidene)amino) maleonitrile (**8d**): yellow powder; mp 214–217 °C; IR (KBr, cm^{-1}) 3460, 3334, 3104, 2924, 2197, 1950, 1688, 1594, 1518, 1334; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ 2.63 (3H, s, CH_3), 7.22-7.25 (2H, m, H–Ar), 7.37–7.40 (2H, m, H–Ar and CH), 7.61 (2H, br s, NH_2), 7.74 (1H, d, ^{3}JHH = 6.9 Hz, H–Ar). ^{13}C NMR (75.47 MHz, DMSO-d_6) δ 21.5, 122.4, 126.0, 126.4, 128.6, 129.8, 129.9, 130.4, 131.7, 137.5, 138.3, 152.3. Anal. calcd for $C_{12}H_{10}N_4$: C, 68.56; H, 4.79; N, 26.65. Found C, 68.50; H, 4.65; N, 26.75.