

Friedel-crafts alkylation of indoles with epoxides using PW₁₂-APTES@SBA-15

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Abstract

H₃PW₁₂O₄₀ (PW₁₂) was immobilized over mesoporous alumina through the reaction of mesoporous alumina functionalized 3-aminopropyl triethoxy silane (3-APTES) and PW₁₂. The surface properties of the functionalized nanocomposite was analyzed by a series of characterization techniques like elemental analysis, FTIR and XRD. XRD and adsorption-desorption analysis show that the mesostructure of silica remains intact after various modifications, while spectral technique show the successful grafting of the neat PW₁₂ inside the porous silica support. 3-Alkylindole derivatives were produced by ring opening of epoxides in the presence of PW₁₂-APTES@ SBA-15 nanocomposites as an efficient catalyst. The catalyst can be reused for several times but it will be less active.

Keywords: Friedel-crafts alkylation; indole; epoxide; SBA-15; heterogeneous catalysis; polyoxotungstate.

Introduction

After the discovery of silica based ordered mesoporous materials of M41S family by researchers at Mobil Corporation in 1992 [1], much attention had been focused to the synthesis of non-siliceous mesoporous materials due to their potential applications in the field of separation science, nano science, catalysis, etc. Huo et al. [2] and Sayari and Liu [3] demonstrated the synthesis of a variety of non-siliceous mesoporous materials, among them, only a few exhibit better stability and increased mesostructural ordering after the removal of the structure directors which limits its use as a catalyst or catalyst support. Hence, the synthesis of non-siliceous mesoporous materials with better stability remains a challenge

because when compared to its oxide form, the mesoporous materials possess high surface areas and variable pore sizes and hence can be finely tuned for specific applications like selective adsorption process by the suitable anchoring of various organic pendant groups [4]. Thus, the synthesis of various organic-inorganic hybrid mesoporous materials emerges as a potential tool to anchor various homogenous metal salts/complexes and it is interesting to probe the stability of such materials during various modification processes.

Heterogenization of homogenous catalysts has been an interesting area of research in an academic and in an industrial point of view, as this method can provide an ideal way for combining

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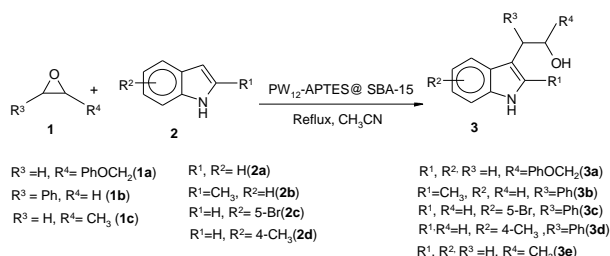
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the advantages of homogenous catalysts and simultaneously avoiding its disadvantages like handling and reusability [5,6].

Indole derivatives are found abundantly in a variety of natural plants and exhibit various physiological properties and are potentially bioactive compounds [7-10]. Friedel-Crafts alkylation of indoles with α,β -unsaturated N-acylbenzotriazoles [11] and with nitroalkenes [12] have been reported. However, epoxides are one of the most usable compounds in alkylation of indoles. Numerous methods describing ring opening of epoxides with indoles has been reported in the literature using Lewis acids such as $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ [13], sulfated zirconia [14], $\text{SbCl}_3/\text{K-10}$ [15], LiClO_4 [16-19], $\text{Ln}(\text{OTf})_3$ [20], InCl_3 [21], InBr_3 [22],

$\text{HBF}_4 \cdot \text{SiO}_2$ [23], silicagel [24], nano MgO [25], Cu(I) [26], Br_2 [27], ultrasound irradiation [28], and Chiral Phosphoric acid [29-31]. Furthermore the ring opening of epoxides with indoles has been reported using high pressure conditions [32,33], or ionic liquid [34]. Most of these methods suffer from some disadvantages such as large excess amount of reagents, high pressure, low yields, poor regioselectivity, and special efforts are needed to prepare the catalyst.

As part of a continuing effort to understand catalytic properties of heteropoly acids, (HPAs) [35-37], herein, we wish to report $\text{PW}_{12}\text{-APTES@SBA-15}$ nanosized mesoporous composites as highly efficient catalyst for the Friedel-Crafts alkylation of indoles (Scheme 1).



Scheme 1. Friedel-crafts alkylation of indoles by epoxides by $\text{PW}_{12}\text{-APTES@SBA-15}$ nanocomposites

Experimental

All materials were commercial reagent grade. Infrared spectra ($400\text{--}4000\text{ cm}^{-1}$) were recorded from KBr pellets on a PerkinElmer Spectrum 65 spectrometer. The X-ray powdered diffraction patterns were performed on a Bruker-D8ADVANCE with automatic control. The patterns were run with monochromatic $\text{Cu K}\alpha$ (1.5406 \AA) radiation with a scan rate of 2° min^{-1} . Nitrogen adsorption measurements were performed at -196°C using an ASAP 2010M surface analyzer, and the pretreatment temperature was 180°C . Transmission electron micrographs (TEM) were obtained on a Joel JEM

2010 scan-transmission electron microscope. The sample for the TEM measurement was suspended in ethanol and supported on a carbon coated copper grid.

Preparation of SBA-15

SBA-15 was first synthesized by Zhao et al. in 1998 [38], using amphiphilic triblock copolymers, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (Pluronic P123), as template. In a typical synthesis, 1.00 g of P123 was dissolved in a mixture of $\text{HCl}/\text{H}_2\text{O}$ (30.00 g of 2 M HCl to 7.50 g H_2O). Then, 2.08 g of tetraethyl orthosilicate (TEOS) was added. The slurry was hydrothermally treated at 100°C for 48

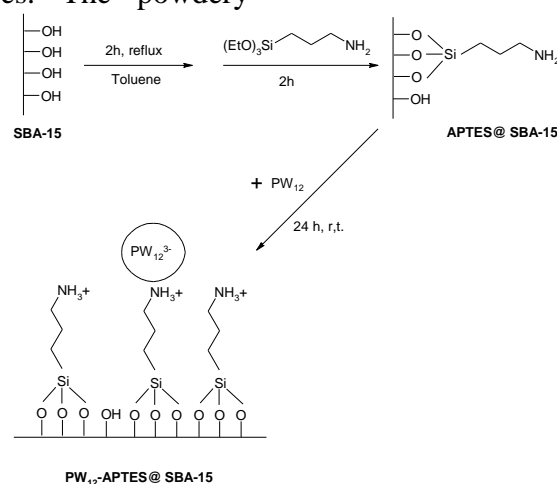
h after stirring at 40 °C for 16 h. The product was filtered off and dried at 80 °C for 10 h.

Preparation of PW₁₂-APTES@SBA-15

Scheme 2 shows the procedures for the surface modification of mesoporous silica sample and the subsequent immobilization of H₃PW₁₂O₄₀ (PW₁₂) on the surface modified mesoporous silica (APTES@SBA-15). Surface modification of mesoporous silica were done by a grafting method [39].

To a suspension of 10 g of calcined SBA-15 in 50 mL dry toluene, 2.68 g of 3-aminopropyl triethoxy silane was added slowly and heated to reflux with continuous stirring for 8 h under nitrogen atmospheres. The powdery

sample containing amino groups was filtered, washed with acetone and then soxhlet extracted using a solution mixture of diethyl ether and dichloromethane (1:1) to remove unreacted APTES for 24 h and dried under vacuum. It was finally calcined at 180 °C for 2 h to yield the APTES@SBA-15. Immobilization of PW₁₂ on the APTES@SBA-15 was achieved as following. APTES@SBA-15 (1.0 g) was added into the acetonitrile solution containing 0.5 g of PW₁₂ with vigorous stirring at room temperature, and the resulting solution was maintained at room temperature for 24 h. The solid product was filtered, and then it was dried overnight at 80 °C to yield the PW₁₂/APTES@SBA-15 silica [33].



Scheme 2. The procedures for the surface modification of SBA-15 and the subsequent immobilization of PW₁₂ on the surface modified SBA-15

General procedure for the Friedel-Crafts alkylation of indole using PW₁₂/APTES@SBA-15

A mixture of epoxide (1 mmol), indole derivatives (1 mmol), and PW₁₂/APTES@SBA-15 (0.1 g, 3 mol%) was stirred at reflux condition in CH₃CN. When the reaction was completed (monitored by TLC or GC chromatography), the mixture was extracted with ethylacetate (three times). Then the product was purified by column chromatography.

Spectral data

1-(1H-indol-3-yl)-3-phenoxy-2-propanol (3a): Purple solid; M.p 81-83°C; IR (KBr) ν (cm⁻¹): 3054, 3323, 3419, 3543; ¹H NMR (CDCl₃, 250 MHz) δ : 2.62 (s, 1H, -OH), 3.15 (m, 2H, Ar-CH₂-), 3.97 (m, 2H, PhO-CH₂-), 4.35 (m, 1H, -CH(OH)-), 6.92-7.37 (m, 9H, Ar-H), 7.66 (s, 1H, Ar-H), 8.20 (s, 1H, -N(H)-); ¹³C NMR (CDCl₃, 62.9 MHz) δ : 29.37, 70.12, 71.12, 111.19, 114.59, 118.80, 119.61, 121.04, 122.24, 122.92, 127.15, 129.49, 136.52, 158.20.

2-(2-Methyl-1H-indol-3-yl)-2-phenylethanol (3b)

Dark yellow oil; IR (neat) ν (cm^{-1}): 2983, 3048, 3371, 3452; ^1H NMR (CDCl_3 , 250 MHz) δ : 2.20 (s, 3H, Ar- CH_3), 2.55 (s, 1H, -OH), 4.01 (m, 2H, - CH_2 -OH), 4.30 (t, 1H, Ph-C(H)-, $J = 6.6$ Hz), 6.90-7.74 (m, 9H, Ar-H), 8.16 (s, 1H, -N(H)-); ^{13}C NMR (CDCl_3 , 62.9 MHz) δ : 21.05, 45.57, 66.37, 111.31, 115.73, 119.32, 119.42, 122.08, 125.99, 126.74, 127.03, 128.34, 128.61, 129.64, 136.52, 141.81, 142.31.

2-(5-Bromo-1H-indol-3-yl)-2-phenylethanol (3c)

Brown oil; IR (neat) ν (cm^{-1}): 3098, 3376, 3450; ^1H NMR (CDCl_3 , 250 MHz) δ : 2.69 (s, 1H, -OH), 4.10 (m, 2H, - CH_2 -OH), 4.39 (t, 1H, Ph-C(H)-, $J = 6.6$ Hz), 6.70 (s, 1H, Ar-H), 7.20-7.74 (m, 8H, Ar-H), 8.37 (s, 1H, -N(H)-); ^{13}C NMR (CDCl_3 , 62.9 MHz) δ : 45.57, 66.37, 111.33, 115.73, 118.52, 119.43, 122.11, 122.17, 126.23, 126.75, 127.15, 128.35, 128.62, 136.51, 141.82, 142.28.

2-(4-Methyl-1H-indol-3-yl)-2-phenylethanol (3d)

Dark yellow oil; IR (KBr) ν (cm^{-1}): 3084, 3329, 3446; ^1H NMR (CDCl_3 , 250MHz) δ : 2.35 (s, 3H, Ar- CH_3), 2.55 (s, 1H, -OH), 4.11 (m, 2H, - CH_2 -OH), 4.40 (t, 1H, Ph-C(H)-, $J = 6.7$ Hz), 6.78 (s, 1H, Ar-H), 6.83- 7.82 (m, 8H, Ar-H), 8.45 (s, 1H, -N(H)-); ^{13}C NMR (CDCl_3 , 62.9 MHz) δ : 22.51, 45.61, 66.41, 108.53, 111.42, 115.44, 119.44, 120.62, 122.90, 126.32, 127.04, 127.24, 127.83, 128.65, 131.44, 136.41, 142.05.

Results and discussion**Structural characterization****FTIR**

Figure 1 presents the FTIR spectra in the skeletal region of 4000–400 cm^{-1} for the bare and modified mesoporous

SBA-15 materials. A band at 1624–1641 cm^{-1} observed in all samples can be assigned to the –OH vibration of physisorbed H_2O . In the case of unmodified SBA-15, the Si–O–Si bands originated from silicas were observed at around 1000–1250, 805–820, and 461–475 cm^{-1} . The amino functionalization followed by succinylation of the mesoporous SBA-15 silica were analyzed by FTIR spectroscopy. The broad band at 3600–3000 cm^{-1} for hydrogen bonded silanol [40,41] was appreciably reduced in the modified samples. The organosilane presence was identified by the absorbance of the band 2950–2850 cm^{-1} for the propyl chain [42] and the deformation bands at 1455–1410 cm^{-1} [35]. The N-H absorption band overlapped with O-H bands at 3300–3500 cm^{-1} [43,44]. The successful immobilization of the PW_{12} catalyst on the aminopropyl-functionalized mesoporous silicas was confirmed by FT-IR analyses as shown in Figure 1. The primary structure of unsupported PW_{12} can be identified by the four characteristic IR bands appearing at 1080 cm^{-1} (P–O band), 990 cm^{-1} (W=O band), 890 and 810 cm^{-1} (W–O–W bands) [45]. The characteristic IR bands of PW_{12} in the $\text{PW}_{12}/\text{APTES}@$ SBA-15 were different from those of unsupported PW_{12} . The P–O band in the $\text{PW}_{12}/\text{APTES}@$ SBA-15 sample was not clearly identified due to overlap by the broad Si–O–Si band. However, W=O and W–O–W bands of PW_{12} in the $\text{PW}_{12}/\text{APTES}@$ SBA-15 appeared at slightly shifted positions compared to those of the unsupported PW_{12} , indicating a strong interaction between PW_{12} and $\text{APTES}@$ silica [46].

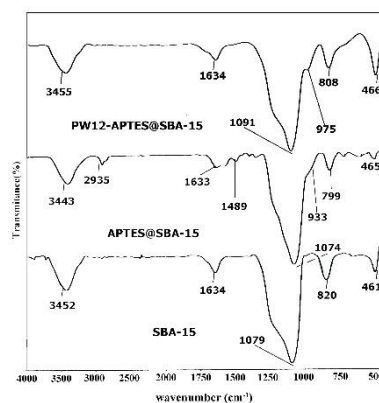


Figure 1. FTIR spectra of SBA-15 materials

XRD

Figure 2 shows the XRD patterns of the PW₁₂/APTES@ SBA-15 within the 2θ range of 0.7–5° (Figure 2a) and 10–80° (Figure 2b). There was no significant peak observed for SBA-15 [47]. After immobilization of PW₁₂-APTES, the intensities of the reflections decrease, which could be assigned to the decrease in electron density contrast upon introduction of PW₁₂-APTES into the mesoporous of the silica host materials.

Figure 2b shows the XRD patterns of PW₁₂/ APTES@ SBA-15 in (2θ = 10–80°). What is interesting is that all samples showed no characteristic XRD pattern, even though 35% wt% PW₁₂ was loaded on the mesoporous silicas. This indicates that the PW₁₂ species were not in a crystal state but in an amorphous-like state, demonstrating that Keggin species are finely and molecularly dispersed on the mesoporous silicas.

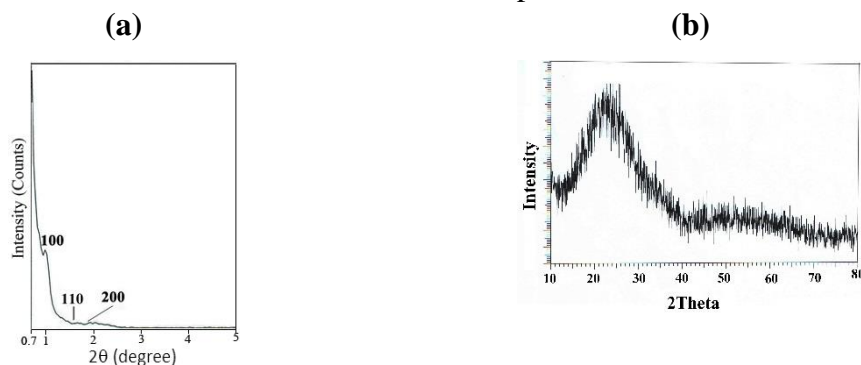


Figure 2. XRD patterns of PW₁₂-APTES@SBA-15 (a) 2θ=0.7-5; (b) 2θ=10-80

Friedel-Crafts alkylation of indoles with epoxides using PW₁₂/APTES@ SBA-15

The catalytic activity of the prepared catalyst was tested using glycidyl phenyl ether (1a) as reference epoxide. Alkylation was carried out between glycidyl phenyl ether (1a) and indole (2a) in the presence of catalytic amounts of PW₁₂-APTES@ SBA-15 and its behavior was studied under a variety of conditions *via* GC and NMR

spectroscopy (Table 2). In the catalytic reactions the choice of solvent is crucial. The influence of the various solvent on the yield of the reaction was investigated. From these studies it was concluded that CH₂Cl₂ was the most favorable solvent (Table 1). The performance of the PW₁₂-APTES@ SBA-15 composite and SBA-15 (bare) are shown in Table 1. It is important that PW₁₂-APTES grafting caused the increase of reactivity.

Table 1. Effect of different conditions in the Friedel-Crafts alkylation of indoles with epoxides using PW₁₂/ APTES@ SBA-15 after 6 h

Entry	Solvent	PW ₁₂ / APTES@ SBA-15 (mol %)	Yield% ^b
1	H ₂ O	3	20
2	CH ₃ CN	3	25
3	CH ₂ Cl ₂	3	90
4	EtOH	3	53
5	MeOH	3	28
6	CH ₃ Cl	3	40
7	CH ₂ Cl ₂ (25°C)	3	68
8	CH ₂ Cl ₂	4	87
9	CH ₂ Cl ₂	2	63
10	CH ₂ Cl ₂	3 (bare SBA-15)	9



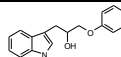

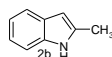
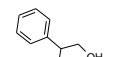


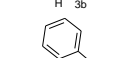


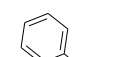


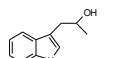
^aReaction condition: glycidyl phenyl ether(1a): (1 mmol), indole (2a): (1 mmol), PW₁₂/ APTES@ SBA-15, solvent (3 mL). ^bIsolated yield.

To study the scope of this procedure the alkylation of other indols was next studied (Table 2).

Aromatic (Table 2, Entries 1-4) and aliphatic (Table 2, Entry 5) epoxides reacted with indoles in the presence of PW₁₂-APTES@ SBA-15 to give good yields of substitution products with

high regioselectivity. The regioselectivity was determined by ¹H NMR spectral data. In the case of 4-methyl indole 2d with a group located at the 4-position reacted with 1a smoothly to give regioselectively the corresponding alkylated indoles 3d (Table 2, Entry 4).

Table 2. Friedel-Crafts alkylation of indoles with epoxides using PW₁₂/ APTES@ SBA-15 under reflux condition^a

Entry	Epoxide (1)	Indole (2)	Product	Time (h):yield (%) ^b
1				6:90
2				6:87
3				7:78
4				12:80
5 ^c				12:75

^aReaction conditions: epoxide (1 mmol), indole derivatives (1 mmol), PW₁₂/ APTES@ SBA-15 (0.1 g, 3 mol%), CH₂Cl₂(3 mL), reflux condition. ^bYields were determined by GC.

^cDue to its low boiling point, excess amount of 2-methyloxirane was used at room temperature.

The recovery and reusability of the catalyst were investigated (Table 4). We have noticed that after the addition of CH₂Cl₂ to the reaction mixture, this catalyst can be easily recovered quantitatively by simple filtration. The

wet catalyst was recycled (the nature of the recovered catalysts was followed by ICP, (Table 3)) and no appreciable change in activity was noticed after three cycles.

Table 3. Investigation of the feasibility of reusing of PW₁₂-APTES@ SBA-15 in the Friedel-Crafts alkylation of indoles with epoxides^a

Run	Yield (%) ^b	Amount of W leached (%) ^c
1	90	-
2	90	-
3	85	0.02
4	86	0.02
5	38	0.13

^aReaction conditions: glycidyl phenyl ether(1a): (1 mmol), indole (2a): (1 mmol), PW₁₂/ APTES@ SBA-15 (0.1 g, 3 mol%), CH₃CN (3 mL), reflux condition.

^bYields were determined by GC.

^cDetermined by ICP.

In order to show the merit of the present work in comparison with recently reported protocols, we compared the results with respect to the amounts of the catalysts used, reaction times and yields of the products (Table 3). Comparison of PW₁₂/ APTES@

SBA-15 with these catalysts for Friedel-Crafts alkylation of indoles with epoxides show that activity of PW₁₂/ APTES@ SBA-15 seems to be higher than or equal to other known catalysts (Table 4).

Table 4. Comparison of PW₁₂/ APTES@ SBA-15 with other catalysts for Friedel-Crafts alkylation of indoles with glycidyl phenyl ether

Time (h): Yield (%): temperature (°C)				
Nano-MgO [25]	Sulfated zirconia [14]	SbCl ₃ /K10 [15]	Nano-TiO ₂ [24]	PW ₁₂ / APTES@ SBA-15 (This work)
8:70:100	4.5:44:rt	1:58:rt	12:0:rt	6:90:40

Conclusion

The results of this research demonstrated that PW₁₂-APTES@ SBA-15 is affecting catalysts for Friedel-Crafts alkylation of indoles with epoxides. The advantages of this catalytic system is mild reaction conditions, short reaction times, moderate to good product yields, easy preparation of the catalysts, non-toxicity of the catalysts, simple and clean work-up of the desired products.

Acknowledgements

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References

- [1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature*, **1992**, 359, 710-712.
- [2] Q. Huo, D.I. Margolese, V. Ciesla, P. Feng, T.E. Gier, P. Sieger, R. Leon, P.M. Petroff, F. Schuth, G.D. Stucky, *Nature*, **1994**, 368, 317-321.
- [3] A. Sayari, P. Liu, *Microporous Mater.*, **1997**, 12, 149-296.

- [4] M. Chidambaram, D.C. Ferre, A.P. Singh, B.G. Anderson, *J. Catal.*, **2003**, 220, 442-456.
- [5] Y. Iwasawa, *Tailored Metal Catalysts*, Springer, Reidel, Holand, **1986**, 141-182
- [6] A. Kozlov, K. Asakura, Y. Iwasawa, *Microporous Mesoporous Mater.*, **1998**, 21, 571-579.
- [7] J.T. Li, H.G. Dai, Z.P. Lin, *Prog. Chem.*, **2007**, 19, 751-761.
- [8] Y. Tomioka, K. Ohkubo, H.J. Maruoka, *Heterocycl. Chem.*, **2007**, 44, 419-424.
- [9] C. Unaleroglu, C.; Aytac, S.; Temelli, B. *Heterocycles*, **2007**, 71, 2427-2440.
- [10] J.W. Huffman, L.W. Padgett, M.L. Isherwood, J.L. Wiley, B.R. Martin, *Bioorg. Med. Chem. Lett.*, **2006**, 16, 5432-5435.
- [11] X. Zou, X. Wang, C. Cheng, L. Kong, H. Mao, *Tetrahedron Lett.*, **2006**, 47, 3767-3771.
- [12] S. Lin, T. You, *Tetrahedron*, **2009**, 65, 1010-1016.
- [13] K. Tabatabaeian, M. Mamaghani, N.O. Mahmoodi, A. Khorshidi, *Tetrahedron Lett.*, **2008**, 49, 1450-1454.
- [14] B. Das, P. Thirupathi, R.A. Kumar, K.R. Reddy, *Catal. Commun.*, **2008**, 9, 635-638.
- [15] Y.H. Liu, Q.S. Liu, Z.H. Zhang, *Tetrahedron Lett.*, **2009**, 50, 916-921.
- [16] N. Azizi, S. Mehrazma, M.R. Saidi, *Can. J. Chem.*, **2006**, 84, 800-803.
- [17] A. Heydari, M. Mehrdad, A. Maleki, N. Ahmadi, *Synthesis*, **2004**, 10, 1557-1558.
- [18] J.S. Yadav, B.V.S. Reddy, G.J. Parimala, *Chem. Res. Synop.*, **2003**, 2, 78-81.
- [19] M. Westermaier, H. Mayr, *Chem. Eur. J.*, **2008**, 14, 1638-1647.
- [20] H. Kotsuki, M. Teraguchi, N. Shimomoto, M. Ochi, *Tetrahedron Lett.*, **1996**, 37, 3727-3730.
- [21] J.S. Yadav, B.V.S. Reddy, S. Araham, G. Sabitha, *Synlett*, **2002**, 9, 1550-1552.
- [22] M. Bandini, P.G. Cozzi, P. Melchiorre, A.U. Ronchi, *J. Org. Chem.*, **2002**, 67, 5386-5389.
- [23] B.P. Bandgar, A.V. Patil, *Tetrahedron Lett.*, **2007**, 48, 173-176.
- [24] T. Hudlicky, U. Rinner, K.J. Finn, I. Ghiviriga, *J. Org. Chem.*, **2005**, 70, 3490-3499.
- [25] M.H. Sarvari, G. Parhizgar, *Green Chem. Lett. Rev.*, **2012**, 1-11.
- [26] C. Ge, R. R. Liu, J.R. Gao, Y.X. Jia, *Org. Lett.* **2016**, DOI: 0.1021/acs.orglett.6b01317
- [27] D. Lianga, X. Lia, W. Zhanga, Y. Lia, M. Zhanga, P. Chengb *Tetrahedron Lett.*, **2016**, 57, 1027-30.
- [28] M.M. Nasefab, M. Zakeria, J. Asadic, E. A. Lotfab, A. Ahmada, R. Malakootid *Green Chemistry Letters and Reviews*, **2016**, 9, 76-84.
- [29] A. Taheri, B. Lai, C. Chenga, Y. Gu, *Green Chem.*, **2015**, 17, 812-816.
- [30] B. Bi, Q.X. Lou, Y.Y. Ding, S.W. Chen, S.S. Zhang, W.H. Hu, J.L. Zhao, *Org. Lett.*, **2015**, 17, 540-543
- [31] T. Courant, S. Kumarn, L. He, P. Retailleau1, G. Masson, *Adv. Synth. Catal.*, **2013**, 355, 836-840.
- [32] H. Kotsuki, K. Hayashida, T. Shimanouchi, H. Nishizawa, *J. Org. Chem.*, **1996**, 61, 984-990.
- [33] H. Kotsuki, M. Nishiuchi, S. Kobayashi, H. Nishizawa, *J. Org. Chem.*, **1990**, 55, 2969-2972.
- [34] M.L. Kantam, R. Chakravarti, B. Sreedhar, S. Bhargava, *Synlett*, **2008**, 10, 1449-1454.
- [35] R. Fazaeli, S. Tangestaninejad, H. Aliyan, *Appl. Catal. A.*, **2007**, 318, 218-226.
- [36] R. Fazaeli, H. Aliyan, *Appl. Catal. A.*, **2007**, 331, 78-83.

- [37] R. Fazaeli, H. Aliyan, *Appl. Catal. A.*, **2009**, *353*, 74-79.
- [38] M. Sun, J.Z. Zhang, C.J. Cao, Q.H. Zhang, Y. Wang, H.L. Wan. *Appl. Catal. A.*, **2008**, *349*, 212-221.
- [39] V.D. Chaube, S. Shylesh, A.P. Singh, *J. Mol. Catal: Chem.*, **2005**, *241*, 79-87.
- [40] I. Diaz, C. Marquez-Alvarez, F. Mahino, J. Perez-Periente, E. Sastre, *J. Catal.*, **2000**, *193*, 283-294.
- [41] B.H. Wouters, T. Chen, M. Dewilde, P.J. Grobet, *Micropor. Mesopor. Mater.*, **2001**, *45*, 453-457.
- [42] A.B. Jarzebski, K. Szyman'ska, J. Bryjak, J. Mrowiec-Bialon', *Catal. Today*, **2007**, *124*, 2-10.
- [43] Y. Guo, D. Li, C. Hu, Y. Wang, E. Wang, Y. Zhou, S. Feng, *Appl. Catal. B: Env.*, **2001**, *30*, 337-349.
- [44] J. Aburto, M. Ayala, I. Bustos-Jaimes, C. Montiel, E. Terre's, J.M. Domínguez, E. Torres, *Micropor. Mesopor. Mater.*, **2005**, *83*, 193-200.
- [45] I.V. Kozhevnikov, *Catalysis by Polyoxometalates*, Wiley, England, **2002**.
- [46] V.D. Chaube, S. Shylesh, A.P. Singh, *J. Mol. Catal. A: Chem.*, **2005**, *241*, 79-87.
- [47] K. Kannan, R.V. Jasra, *J. Mol. Catal. B: Enzym.*, **2009**, *56*, 34-40.

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