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Graphical Abstract

Role of basicity and catalytic activity of KOH loaded MgO and hydrotalcite as catalysts for efficient synthesis of 1-[(2-benzothiazolylamino)arylmethyl]-2-

naphthalenols

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Role of basicity and catalytic activity of KOH loaded MgO and hydrotalcite as catalysts for efficient synthesis of 1-[(2-benzothiazolylamino)arylmethyl]-2-naphthalenols

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Abstract

Published on 30 July 2015. Downloaded by University of Sussex on 07/08/2015 14:59:11.

Novel KOH-loaded MgO and hydrotalcite as basic catalysts have been synthesized and were characterized by XRD, SEM and basicity. Effects of KOH wt %, reaction time, basicity and catalyst loading have been investigated in three component reaction of aldehydes, 2-amino benzothiazole and 2-naphthol. Present studies revealed that loading of KOH and reaction time greatly appreciated. Best conversion and yield at 70 °C were obtained as 93% and 88%, respectively. Hydrotalcite could be reused four times without loss of catalytic efficiency. Present catalytic systems have required short reaction time, non toxic, easy to workup, good catalytic activity and gives high efficiency.

Keywords: KOH-loaded MgO, Catalytic Activity, Hydrotalcite, Reusability, Multi-component Synthesis.

1. Introduction

The scaffold decoration of bioactive molecules represents one of the most exciting research areas in organic chemistry and has a rich history within the realm of fragment-based drug design. o-Quinone methides (o-QMs) are highly reactive, transient species that have been applied as

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intermediates in the synthesis of several natural compounds including flavonoids, isoflavans, chromenes and benzopyranes.¹⁻⁴ Multi-component reactions (MCRs) are powerful tool and have attracted much attention of synthetic organic chemists because of building of complex molecules with diverse range of complexity which can easily be achieved from readily available starting materials.⁵ Such processes enable the rapid elaboration of complex structures in a highly efficient, higher yield than almost any sequential synthesis of the same target, a single purification step, time and energy saving, low expenditures, easy adaptation to combinatorial synthesis and modular manner.⁶ However, researchers have synthesized the 2-aminobenzothiazolomethyl naphthol derivatives with many drawbacks such as long reaction time, higher catalyst loading, low yield, higher reaction temperature and no reusability of catalyst.^{7,8}

In recent year, due to increasing concern about environmental impact, tremendous effort has been made towards the development of new processes that minimize pollution in chemical synthesis. For this reason and others (catalyst removal, recovery, and recycling), heterogeneous catalysis is clearly on the rise in industry.⁹ Heterogeneous catalysts have separated easily from the reaction mixture by filtration and then reused. In recent year, hydrotalcite and metal loaded catalysts have been investigated more for biodiesel production.^{10, 11} Hydrotalcites can be involved in the preparation of catalysts dedicated to the production of H_2 ,¹² wide range of organic compounds.¹³ hydrotalcite has also been used as catalyst other than from reactions¹⁴ and showed good catalytic efficiency, recyclability, reaction time, yield etc.

However KOH loaded MgO and hydrotalcite have not been used as catalyst in synthesis of 2-aminobenzothiazolomethyl naphthols by multi-component reaction. So in present study, we have used KOH loaded MgO as catalyst in multi-component reaction of 2-amino benzothiazole,

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aldehydes and 2-naphthol and found good yield. But due to low catalytic efficiency of recycled catalyst, this catalyst failed to produce better yield. Further, for removing this problem, hydrotalcite was used as catalyst and found good catalytic activity and recyclability. Synthesis was tried with hydrotalcite which is rapid, low reactor corrosive, easy to separate, inexpensive and highly efficient.¹⁵ Herein, first time, we report the synthesis of 2-aminobenzothiazolomethyl naphthols by three-component reaction of aldehydes, 2-amino benzothiazole and 2-naphthol using KOH-loaded MgO and hydrotalcite as novel catalysts under solvent free conditions (Scheme 1).





2. Experimental section

General

The ¹H NMR spectra were measured by BRUKER AVANCE II 400 NMR spectrometer with tretramethylsilane as an internal standard at 20-25 °C; data for ¹H NMR are reported as follow: chemical shift (ppm), integration, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and br, broad), coupling constant (Hz). IR spectra were recorded by SHIMADZU, IR spectrometer of sample dispersed in KBr pellet and are reported in terms of frequency of absorption (cm⁻¹). E-Merck pre-coated TLC plates and RANKEM silica gel G were used for preparative thin-layer chromatography. Melting points were determined on electrical melting point apparatus in open capillary and were uncorrected. 2-Amino benzothiazole was purchased

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from Sigma Aldrich and other chemicals were purchased from Himedia, Mumbai India and used without any further purification.

HPLC separations were carried out using an HPLC system (Water alliance e2695, separation module, USA) composed a detector (2489 UV/Vis detector), vacuum degasser, a quaternary pump, injector with 50 μ L sample loop, variable wavelength detector (VWD). The packing materials were dispersed in ethanol and packed in the column under 35 MPa with ethanol. The HPLC phase consisted of acetonitrile/10mM ammonium acetate buffer pH 4.0 (30/70, v/v). The flow rate was set at 0.25 mL/min and analysis was performed in isocratic mode.

The surface area of hydrotalcite samples was determined from the N_2 adsorption data measured at 77 K using Micromeritics, ASAP 2010. The samples were activated at 80 °C for 4 h under vacuum prior to N_2 adsorption measurements. The specific surface area of the samples was calculated from the N_2 adsorption isotherms according to the BET method.

KOH-loaded catalyst preparation

The catalyst was prepared by magnesia with an aqueous solution of KOH. The catalysts were dried at 393 K for 16 h and calcined at 773 K for 5 h. X-ray powder diffraction patterns were obtained from calcined catalyst samples with a PC X-ray diffractometer using Cu K α radiation at 40 kV and 40 mA and a scan speed of 2 °C/min. The surface morphology of the prepared catalysts was investigated by a scanning electron microscope (SEM).

Preparation of hydrotalcite

The catalyst hydrotalcite was synthesized using literature procedure.¹⁶

Typical procedure. One-pot hydrothermal reactions at higher temperature and autogenous pressure in aqueous media were carried out to obtain small and high surface area particles. In a typical reaction Mg^{2+} and Al^{3+} hydroxide (metallic ratio of 3:1) were taken and corresponding

ratio of sodium bicarbonate was added to maintaining the pH 8.5. After aging the slurry, the precipitate was filtered, washed, and dried.

One-pot three component reaction

<u>Typical procedure with KOH-loaded MgO</u>. A mixture of aldehydes (2 mmol), 2-naphthol (2 mmol) and 2-amino benzothiazole (2 mmol) were heated at 70 °C under solvent free conditions using KOH-loaded MgO as a catalyst. The time taken by different aldehydes in reaction has mentioned in table 2. After completion of the reaction (TLC analysis), the reaction mixture was cooled to room temperature and filtered. Solid cake was washed with ethyl acetate. Filtrate having product was washed with water and extracted with ethanol and concentrated the ethanol to crystallize the product. Recycled KOH/MgO catalyst was washed with ethyl acetate to remove organic impurity.

<u>Typical procedure using Hydrotalcite.</u>

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A mixture of aldehydes (2 mmol), 2-naphthol (2 mmol) and 2-amino benzothiazole (2 mmol) were heated at 70 °C under solvent free conditions using hydrotalcite (Mg-Al-CO₃, 80 mg) as a catalyst. The time taken by different aldehydes in reaction has mentioned in table 2. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and poured in cold water. The solid mass was filtered and dissolved in ethanol then filtered again so that product was dissolved in ethanol and hydrotalcite has been separated and concentrated the ethanol to crystallize the product. Recycled hydrotalcite was washed with ethanol to remove organic impurity.

3. Results and discussion

The powder X-ray diffraction spectra of KOH/MgO catalyst has been prepared are shown in the figure 1 (A). From figure 1 (A) it can be seen that there are typical characteristic peaks both

at 37.0°, 43.0°, and 62.3°, which can be signed to the characteristic peaks of MgO crystalline.¹⁷ The XRD analysis of the 1wt % KOH/MgO sample shows the crystalline phase corresponding to magnesia. This interaction is the main difference between the homogeneous KOH catalyst and KOH/MgO catalyst. Small crystallite of KOH was also observed at 4 wt % KOH/MgO catalyst (figure 2).

Fig 1. Effect of different loading amounts on catalyst 1%, (b) 2%, (c) 3%, (d) 4%



Fig 2. SEM images of catalysts



Model reaction starting from benzaldehyde, 2-naphthol and 2-amino benzothiazole have proved to be a facile method for preparation of 2-aminobenzothiazolo-phenylmethyl-2-naphthol derivatives. To optimize the reaction conditions, first of all we have investigated different catalysts for synthesis of 2-aminobenzothiazolo-phenylmethyl-2-naphthol derivatives. Table 1 suggests that without catalyst longer reaction time was necessary (24 hours) with poor yield. The best result was obtained when KOH-loaded MgO used with maximum yield (Table 1, entry 2). Other metal catalysts give moderately to significant yield.

Table 1. Screening of catalysts^a

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Entry	Catalyst (in mole)	Time (hrs)	Yield% of 1a
1	Without catalyst	24	15
2	KOH/MgO	3.0	88
	(40 mg KOH per gram support)		
3	AlCl ₃ (0.001)	4.5	71
4	MgCl ₂ (0.001)	5.0	49
5	Mg(OH) ₂ (0.001)	4.5	57
6	Al(OH) ₃ (0.001)	6.0	61
07	Ca(OH) ₂ (0.001)	5.0	52
8	MgO (0.001)	5.5	69
9	Al ₂ O ₃ (0.001)	4.0	42
10	CaO (0.001)	4.5	43

^aReaction conditions: benzaldehyde (2 mmol), 2-naphthol (2 mmol) and 2-amino benzothiazole (2 mmol) in presence of various catalysts under solvent free conditions.

Table 2. Synthesis of 2-annihobenzounazorometry napititor derivative	Table 2	2. Synthesis	of 2-aminober	zothiazolomethy	l naphthol	derivatives
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Entry	Aldehydes	Product	КО	H/MgO	Hydrota	lcite	M.P. (°C	<u>(</u>)
			Time (h)	Yield (%)	Time (h)	Yield (%)	Found	Reported ^(ref.)
1	СНО	1a	2.5	88	2.8	92	203-204	202-204 ^{8(c)}
2	OH OCH ₃ CHO	1b	3.0	90	3.0	90	194-175	173-175 ^{8(f)}

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3	CH ₃ CH ₃	1c	3.5	85	2.6	89	192-194 192-194 ^{8(g)}
4		1d	3.0	91	2.6	91	190-192 189-191 ^{8(a)}
5	СНО	1e	2.5	88	2.6	87	162-163 160-161 ^{8(f)}
6	осн _з	1f	2.5	90	2.8	92	172-173 172-173 ^{8(c)}
7	СНО СН3 СНо	1g	2.5	89	2.6	92	180-181 183-184 ^{8(c)}
8	СІ	1h	3.0	92	2.8	93	208-209 208-209 ^{8(f)}
9	ОН	1i	3.0	73	3.0	78	188-190 188-190 ^{8(g)}
10	СІ СНО	1j	2.5	84	2.4	88	>250 242(Dec.) ^{8(f)}



^aReaction conditions: 2-amino benzothiazole (2 mmol), 2-naphthol (2 mmol) and benzaldehyde (2 mmol), hydrotalcite or KOH/MgO under solvent free conditions.

To optimize the effect of reaction time on the yield of target product, a model reaction was carried out at different time under solvent free conditions using KOH-loaded MgO at 70 °C. The reaction time 3.0 h was found to be optimum time and highest conversion (from 35-93%) and yield (from 31-88%) was obtained (figure 3). Conversion of starting materials to product was measured by HPLC analysis. When the loading of catalyst was not enough, the maximum yield could not be reached. To avoid this kind of problem, an optimum amount of catalyst loading had to be investigated. For this study, model reaction has been carried out in the presence of different amount of prepared catalyst (10 mg, 20, mg, 50 mg, 80 mg, 100 mg) respectively (table 3). Highest yield was obtained with 50 mg of KOH-loaded MgO catalyst. The catalyst loading 50 mg was found to be the optimal quantity and used for further studies.





Table 3. Effect of catalyst loading on yield^a

Entry	Catalyst loading (mg)	Yield
1	10	60
2	20	76
3	50	88
4	80	88
5	100	88

^aReaction conditions: benzaldehyde (2 mmol), 2-naphthol (2 mmol) and 2-amino benzothiazole (2 mmol) in presence of KOH/MgO catalysts under solvent free conditions.

The reaction temperature can influence the reaction rate and yield because the intrinsic rate constants are strong functions of temperature.¹⁸ In this study, the effects of the reaction temperature were investigated at four different reaction temperatures, such as room temperature, 50, 70 and 100 °C temperatures. The catalyst used in this experiment was 4 wt % KOH/MgO. The results are shown in figure 4. Best conversion and yield at 70 °C were obtained as 93% and 88%, respectively.





To gain the effect of KOH loadings of catalysts on their catalytic activities, different loadings of KOH ranging from 1 to 5 wt % were studied with model reaction. The results are demonstrated in figure 5. As loading of KOH was raised from 1 to 4 wt %, the conversion of starting material was increased. However, by increasing the amount of KOH from 4 to 5 wt %, a significant change in conversion and yield were not observed. Highest yield was obtained with loading of KOH of 4 wt % on MgO. It is obvious that change in their catalytic activity was well

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correlated to change their basicity as shown in table 4. These results are also in agreement with the results obtained by D'Cruz et al.¹⁹



Fig 5. Effect of KOH loading on conversion and yield

Basicity of the catalyst was determined using Hammett indicator and benzoic acid titration method.²⁰⁻²² Model reaction was carried out in the presence of KOH-loaded MgO catalyst. Excellent catalytic activity has showed using different substituted aromatic aldehydes. We have studied the different amount of KOH loading on metal and correlate with the basicity of catalyst. As evident from Table 4, KOH loading on the surface of MgO could induce the basicity of catalyst. As loadings of KOH were raised from 1 to 4 wt %, the yield of target product was increased and yield was 88%. Moreover as seen in Table 4, basicity play an important role in catalytic activity of the catalyst prepared. BET surface area has been demonstrated in table 4 which shows that as KOH loading increases, surface area was decrease.

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Entry	Samples	Time (h)	Yield (%)	Basicity (mmol/g)	BET area (m ² /g)
1	1% wt KOH/MgO	6.0	57	1.065	22.52
2	2% wt KOH/MgO	4.5	74	1.096	20.01
3	3% wt KOH/MgO	3.5	81	1.117	18.21
4	4% wt KOH/MgO	3.0	88	1.187	17.13
5	5% wt KOH/MgO	3.0	88	1.010	15.50

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The dependence of the activity of KOH/MgO catalysts on the loading amount of KOH has been investigated with effect of basicity. The most basic properties of catalysts arise when an alkali base is loaded onto a support. The presence of alkali cations enhances the electron density of the framework oxygen, thus acting as basic sites. The data clearly demonstrate the involvement of potassium in the activity and basicity. The incorporation of potassium increased the basic strength of the pure MgO, resulting in an increase the yield. The results in Table 4 show that the activity increased by increasing the KOH content (4%) due to presence of highest number of basic sites or suggesting that basic sites have a very specific environment. But basic sites may be cover by exceeded KOH when the amount of loaded KOH was from 4-5 wt %, resultant basic strength and the basic site of the catalyst were not raised, and lower the surface areas of active components and lower the catalytic activity. At a low loading of KOH, the active sites are more dispersed on the pure MgO surface and cannot disperse properly with too much KOH.

The recyclability of the catalyst was also investigated for 4 wt % KOH/MgO catalyst, which gives the highest yield of 88%. After the reaction, catalyst was separated by filtration and then reused in the model reaction. It was shown that the reaction catalyzed by a used catalyst provided 70% yield, which was lower than the yield over the fresh catalyst. This indicated that the spent catalyst was slightly deactivated. Thus, the decrease in catalytic activity probably resulted from the leaching of the some potassium content. This low activity may be explained by dissolution of K species in the heterogeneous KOH/MgO catalyst.²³

Thus, we have further synthesized and used hydrotalcite (Mg:Al; 3:1) as new heterogeneous catalyst to removing the drawback of recyclability or leaching of catalyst which overcome with KOH/MgO catalyst. Mg:Al atomic ratio was measured using X-ray

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microanalysis and found 3.16, which is in good agreement with the metallic ratio (3.0) taken in solution. The value of x [x = $M^{III}/M^{II} + M^{III}$] was found to 0.24, which suggest the purity of hydrotalcite.²⁴ Powder X-ray diffraction (P-XRD) pattern for sample Mg-Al-CO₃ is shown in figure 6. The presence of CO₃²⁻ anion in the interlayer gallery of the hydrotalcite is confirmed by the characteristic basal spacing $d_{003} = 7.76 \text{ A}^{\circ}$. This indicates a gallery height of 2.96 A^o (assuming a thickness of 4.8 A^o for the cationic sheets). The material is reasonably crystalline and suggests a relatively well-ordered sheet arrangement.²⁵ Diffraction peaks of the (003) basal plane that gives the distance between the layers became sharper which indicates higher crystallinity and order. This fact is supported by the increase in the ratio of the intensities of the diffraction from the (006) basal plane to that of the (003) one. The crystallite size of this sample was found 24.87 nm as calculated using Scherrer formula.²⁶ More intensive and sharper reflections of the (003) and (006) planes has found at low 2θ values (11-23°).





XRD pattern Mg-Al- 3:1



SEM image Mg-Al- 3:1

A typical SEM image of Mg-Al-CO₃ hydrotalcite is shown below in figure 6. This figure indicates the existence of lamellar particles looks like rounded hexagonal shape and typical of hydrotalcite like material. The material was found mesoporous with the surface area 90 m²/g.

Basicity of hydrotalcite is a key for the preparation of material with high performance.²⁷ It can be achieved by changing the nature of M²⁺/M³⁺ metals.²⁸ As far as Mg-Al mixed oxides of hydrotalcite is concerned, a correlation can be established between the composition and the basicity; when the amount of Al increases, the total number of basic sites decreases.^{15, 29} The decrease in basic site density observed in Mg-Al mixed oxide derived from hydrotalcites when increasing the Al content is reported to be the reason for decreasing activity in the Knoevenagel condensation reaction between glyceraldehydes acetonide and ethyl acetoacetate.³⁰ The performance of Mg-Al mixed oxide in the methanolysis of soyabean oil was shown to be dependent on the Mg/Al ratio.^{11(g)} Numerous authors have tried to identify the best composition of Mg-Al mixed oxide catalysts in the case of various reactions. A set of Mg-Al hydrotalcite-like precursors with different Mg/Al atomic ratios were studied by Diez et al.³¹ The optimum Mg/Al molar ratio is dependent on the target reaction and more precisely, on the basic strength needed

to activate the reactant. By encouraging from previous results,³² it is clear that among the all metallic ratio of hydrotalcites, 3:1 ratio of hydrotalcite (Mg-Al-CO₃) gives better results. Resultant, in this communication we have synthesized hydrotalcite catalyst (Mg-Al-CO₃, 3:1) and used in present reaction.

In order to evaluate the appropriate catalyst loading, reaction of benzaldehyde (2 mmol), 2amino benzothiazole (2 mmol) and 2-naphthol (2 mmol) was carried out using 20 mg, 50 mg, 80 mg, 100 mg and 120 mg of hydrotalcite as catalyst at 70 °C under solvent free conditions. The catalyst loading 80 mg was found to be the optimal quantity (Table 5). Catalyst was reused and the results show that the hydrotalcite (Mg-Al-CO₃) can be reused as such without significant loss in yield (Table 6). A variety of electron donating and electron withdrawing groups on aromatic aldehydes have been studied (Table 2). It was found that meta substituted aldehyde give the lower yield as compared to ortho and para substituents (Table 2, entry 9, 11).

 Table 5. Effect of Catalyst [Mg-Al-HT (Mg/Al=3:1)] Loading^a

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Entry	Catalyst loading (mg)	Time (min)	Yield (%)	
1	20	180	40	
2	50	170	76	
3	80	160	92	
4	100	160	92	
5	120	160	92	
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^aReaction conditions: Benzaldehyde (0.0025), 2-amino benzothiazole (0.0025 mol) and 2-naphthol (0.0025 mol), hydrotalcite (80 mg), temp. at 70 °C.

Table 6. Recyclability of hydrotalcite [Mg-Al-HT (Mg/Al=3:1)]^a

Product	Fresh HT	Reuse (I)	Reuse (II)	Reuse (III)	Reuse (IV)
1a	92	92	91	90	90

^aReaction conditions: benzaldehyde (0.0025 mol), 2-amino benzothiazole (0.0025 mol) and 2-naphthol (0.0025 mol), hydrotalcite (80 mg), temp. at 70 °C.

A model reaction has been carried out using of benzaldehyde (0.0025 mol), 2-amino benzothiazole (0.0025 mol) and 2-naphthol (0.0025 mol) for recyclability and reusability of

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hydrotalcite as catalyst by incorporating 80 mg of catalyst. After completion of reaction, the contents were filtered to recycle the hydrotalcite catalyst through whatman filter 42. Recycled hydrotalcite washed with 5 ml ethanol to remove organic impurities. Hydrotalcite catalyst can be readily recovered and reused for at least four runs without any significant loss of activity.





XRD data of recovered hydrotalcite (figure 7) which showed the similar profile as fresh catalyst which confirmed that layered structure of hydrotalcite was maintained after the reaction.

4. Conclusion

In conclusion, 4 wt. % KOH/MgO and hydrotalcite as catalysts, which have the highest yield of target product and gave the best catalytic activity for multi-component reaction of substituted aldehydes, 2-amino benzothiazole and 2-naphthol at 70 °C under solvent free conditions. Loading of KOH with 4 wt % gave the highest basicity and best catalytic activity. Highest conversion and yield of product were obtained at 3.0 h of reaction time. After recycling, KOH/MgO could not better perform than fresh catalyst due to leaching of basic sites but this drawback has been removed by using hydrotalcite as catalyst. Morphology and characterization of catalysts are characterized by XRD and SEM. Hydrotalcite and KOH-loaded MgO have showed better results as compared to simple metal catalysts used. Present methodology involves the operational simplicity, short reaction times, simple catalyst system, higher yield and ease of work-up procedure.

Characterization data

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1-[(2-Benzothiazolylamino)phenylmethyl]-2-naphthalenol (1a)

White powder, mp 203-204°C; IR (KBr) (ν_{max} , cm⁻¹): 3381 (OH_{str}), 1599 (C=C_{str}), 1542 (N-H_{ben}), 1515 (C-H_{ben}), 1449 (C-H_{ben}); ¹H NMR (400 MHz, DMSO): δ_{H} 6.69-7.93 (16H, m, 15H-arom and 1H-CH), 8.67 (1H, s, NH), 10.11 (1H, s, OH); ¹³C NMR (100 MHz, DMSO): 53.36, 118.02, 118.57, 118.81, 120.49, 120.84, 122.27, 123.58, 125.23, 126.04, 127.83, 128.34, 128.56, 129.28, 130.59, 132.12, 142.25, 151.96, 153.19, 166.33; ESI-MS: m/z Calculated for C₂₄H₁₈N₂OS 382; Found [M+H]⁺ 283.3.

1-[(2-Benzothiazolylamino)(4-nitrophenyl)methyl]-2-naphthalenol (1d)

White powder, mp 120-122°C; IR (KBr) (v_{max} , cm⁻¹): 3348 (OH_{str}), 2933 (C-H_{str}), 1625 (C=C_{str}), 1510 (N-H_{ben}), 1267(C-N_{str}), 962-812 (C-H_{def}); ¹H NMR (400 MHz, DMSO): $\delta_{\rm H}$ 6.88-7.75 (15H, m, 14H-arom and -CH), 8.65 (1H, s, NH), 10.00 (1H, s, OH); ¹³C NMR (100 MHz, DMSO): 53.43, 117.81, 118.31, 118.58, 119.59, 120.41, 121.46, 122.54, 122.91, 123.24, 122.98, 125.20, 125.33, 126.65, 127.32, 128.57, 128.98 129.89, 145.99, 150.68, 153.38, 166.69; ESI-MS: m/z Calculated for C₂₄H₁₇N₃O₃S 427.2 Found [M+H]⁺ 428.1.

1-[(2-Benzothiazolylamino)(2-hydroxyphenyl)methyl]-2-naphthalenol (1e)

Off white powder, mp 162-163°C; IR (KBr) (v_{max} , cm⁻¹): 3504 (OH_{str}), 2941 (C-H_{str}), 1627 (C=C_{str}), 1508 (N-H_{ben}), 1280 (C-N_{str}), 962-813 (C-H_{def}); ¹H NMR (400 MHz, DMSO): $\delta_{\rm H}$ 6.68-7.49 (15H, m, 14H-arom and -CH), 8.68 (1H, s, NH), 10.04 (1H, s, OH), 10.34 (1H, s, OH); ¹³C NMR (100 MHz, DMSO): 51.82, 116.74, 116.95, 117.76, 118.84, 119.40, 120.60, 121.11,

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121.24, 125.54, 122.52, 126.31, 128.20, 128.98, 129.80, 131.73, 132.12, 136.31, 150.86, 152.65,

154.47, 160.83, 166.54; ESI-MS: m/z Calculated for $C_{24}H_{18}N_2O_2S$ 398.2 Found $[M+H]^+$ 399.1.

1-[(2-Benzothiazolylamino)(4-methoxyphenyl)methyl]-2-naphthalenol (1f)

Off white powder, mp 172-173°C; IR (KBr) (ν_{max} , cm⁻¹): 3510 (OH_{str}), 3012 (C-H_{str}), 2922 (C-H_{str}), 1625 (C=C_{str}), 1500 (N-H_{ben}), 1278 (C-N_{str}); ¹H NMR (400 MHz, DMSO): $\delta_{\rm H}$ 3.69 (3H, s, OCH₃), 6.69-7.87 (15H, m, 14H-arom and -CH), 8.51 (1H, s, NH), 10.53 (1H, s, OH); ¹³C NMR (100 MHz, DMSO): 54.81, 59.12, 113.33, 118.11, 119.03, 119.12, 120.58, 122.53, 125.52, 126.22, 127.42, 128.47, 128.79, 129.38, 130.22, 132.16, 133.56, 151.69, 153.35, 158.00, 166.84; ESI-MS: m/z Calculated for C₂₅H₂₀N₂O₂S 412.2 Found [M+H]⁺ 413.1.

1-[(2-Benzothiazolylamino)(4-methylphenyl)methyl]-2-naphthalenol (1g)

White powder, mp 180-181°C; IR (KBr) (ν_{max} , cm⁻¹): 3007 (C-H_{str}), 2922 (C-H_{str}), 1625 (C=C_{str}), 1510 (N-H_{ben}), 1267 (C-N_{str}); ¹H NMR (400 MHz, DMSO): $\delta_{\rm H}$ 2.23 (3H, s, CH₃), 6.75-7.80 (15H, m, 14H-arom and -CH), 8.66 (1H, s, NH), 10.14 (1H, s, OH); ¹³C NMR (100 MHz, DMSO): 20.60, 53.33, 118.00, 118.66, 118.92, 120.51, 120.85, 122.27, 125.26, 126.03, 128.34, 128.50, 128.60, 129.22, 130.55, 132.13, 135.17, 139.13, 151.97, 153.20, 166.39; ESI-MS: m/z Calculated for C₂₅H₂₀N₂OS 396.2 Found [M]⁺ 396.1.

1-[(2-Benzothiazolylamino)(4-chlorophenyl)methyl]-2-naphthalenol (1h)

White powder, mp 208-209 °C; IR (KBr) (ν_{max} , cm⁻¹): 3504 (OH_{str}), 1627 (C=C_{str}), 1267 (C-N_{str}), 1122 (C-H_{ben}); ¹H NMR (400 MHz, DMSO): $\delta_{\rm H}$ 6.97-7.98 (15H, m, 14H-arom and -CH), 8.57 (1H, s, NH); ¹³C NMR (100 MHz, DMSO): 53.48, 117.71, 118.13, 118.44, 118.96, 120.95, 121.12, 122.43, 122.47, 125.81, 126.82, 127.30, 127.78, 128.22, 129.54, 130.32, 131.39, 134.52, 138.16, 151.61, 153.28, 155.11, 166.89; ESI-MS: m/z Calculated for C₂₄H₁₇N₂OCIS 416.4 Found [M+H]⁺ 417.2.

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Acknowledgements

We are grateful thanks to Punjab University, Chandigarh for spectral analytical data.

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Figure Legends

- **Fig 1**. XRD pattern of KOH/MgO with different loading amounts: 1%, (b) 2%, (c) 3%, (d) 4%
- Fig 2. SEM images of catalysts
- Fig 3. Effect of reaction time on yield of target product
- Fig 4. Effect of temperature on conversion and yield of product
- Fig 5. Effect of KOH loading on conversion and yield
- Fig 6. P-XRD pattern and SEM image of hydrotalcite (Mg-Al-3:1)
- Fig 7. XRD pattern of recovered hydrotalcite

Scheme Captions

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Scheme 1. Synthesis using hydrotalcite or KOH/MgO at 70 °C.