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ARTICLE TYPE

Design of 1-methylimidazolium tricyanomethanide as the first nanostructured molten salt and its catalytic application on the condensation reaction of various aromatic aldehydes, amide and β -naphthol compared with tin dioxide nano particles

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1-Methylimidazolium tricyanomethanide {[HMIM]C(CN)₃} as a novel, green and nano molten salt catalyst was designed ¹⁰ and fully identified by IR, ¹H NMR, ¹³C NMR, mass, thermal gravimetric (TG), derivative thermal gravimetric (DTG), x-ray diffraction patterns (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis. The catalytic application of {[HMIM]C(CN)₃} was studied on ¹⁵ the preparation of 1-amidoalkyl-2-naphthols by the one-pot three-component condensation reaction of various aromatic aldehydes, amide and β -naphthol at room temperature under solvent-free conditions in comparison with nano SnO₂. In the presented investigations, some products were produced and ²⁰ reported for the first time.

Introduction

Room-temperature molten salts (RTMSs), termed as room-temperature ionic liquids, (RTILs), which are immiscible or only partially miscible with water, have 25 been revealed to be promising as replacements to common organic solvents. Molten salts (MSs) have important potential as electrolyte materials. The molten salts, lately called ionic liquids, have possessed very attention in various scientific fields.¹ Generally, MSs refer to inorganic 30 MSs and RTILs to organic onium salts molten below 100 °C. MSs are an attractive class of liquids due to their incomparable ionic interactions and their varied number of scientific usages.^{2, 3} Molten salts and ILs can be applied as a GC stationary phases for both packed and open-tubular 35 columns.⁴⁻⁷

The nano sciences have lately developed as a main study path of our modern society resulting from a continuing attempt to miniaturize at the nano scale operations that currently use microsystems. To this end, it 40 is well known that the bottom-up method should now change the classic top-down one, a strategic move that is common to various areas of nano sciences containing sensing, medicine, opto-electronics and catalysis.⁸ More lately, there have been developments towards biological 45 and medical usages of nanoparticles. The entrapment of anticancer drugs in nanoparticles, and the decoration of the particles with molecular ligands for the affecting of cancerous cells, offers the outlook of more efficient cancer treatment with reduced side-effects.9 A different strategy 50 for the use of nanoparticles in cancer therapy is photothermal tumor ablation.¹⁰ Tin oxide (SnO₂) is an significant material because of its properties for example low operating temperature, strong physical and chemical interaction with adsorbed species, high degree of 55 transparency in the visible spectrum and strong thermal stability in air (up to 500 °C).¹¹ Tin dioxide, an *n*-type semiconductor with a broad band gap (Eg = 3.6 eV, at 300 K), is a main functional material that has been widely applied for optoelectronic devices.¹² Tin oxide received 60 little consideration in the catalysis field compared to other metal oxides.¹³ Although, tin oxide supported catalysts have been described to be active for oxidative dehydrogenation of propane, CO oxidation and esterification reaction.14 65

Multicomponent reactions (MCRs) making heterocyclic compounds are influential tools in the drug-discovery process as they can offer appropriate synthesis of libraries of druglike compounds in a single procedure.¹⁵ The onepot multi-component condensation reaction between 70 aromatic aldehydes with β -naphthol and amide derivatives has been offered as a suitable synthetic method toward 1amidoalkyl-2-naphthols.¹⁶⁻²³ 1-Amidoalkyl-2-naphthols are imperative intermediates which can be effortlessly transformed into biologically active aminoalkyl naphthols 75 derivatives via amide hydrolysis. The hypertensive and bradycardiac properties of these compounds have been expected.^{24, 25} Several catalysts have been applied to achieve this reaction, including boric acid,¹⁶ trityl chloride,17 saccharin sulfonic acid (SASA),18 [Et₃N- 80 SO₃H]Cl,¹⁹ nano-S (S8-NP),²⁰ [Msim]Cl, [Dsim]Cl, [Msim]AlCl₄,²¹ Fe(HSO₄)₃²² and [2-MPyH]OTf.²³ In this work, we have prepared a novel molten salt and

catalyst, namely 1-methylimidazolium tricyanomethanide $\{[HMIM]C(CN)_3\}$ (Scheme 1) and used it for the ss synthesis of 1-amidoalkyl-2-naphthol derivatives under

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solvent-free reaction conditions (Scheme 2). Also, to compare the catalytic activity of $[HMIM]C(CN)_3$ in nano scale, SnO_2 nanoparticles were applied instead of it in the synthesis of 1-amidoalkyl-2-naphthol derivatives in similar conditions.



Scheme 1. The synthesis of 1-methylimidazolium tricyanomethanide {[HMIM]C(CN)₃} as a nano molten salt catalyst



Scheme 2. The synthesis of 1-amidoalkyl-2-naphthol derivatives in the 20 presence of {[HMIM]C(CN)₃} as nano molten salt (a) and SnO₂ nano particles (b) as green nano catalytic systems

Results and discussion

Characterization of 1-methylimidazolium tricyanomethanide {[HMIM]C(CN)₃] as a nano molten salt catalyst 25 The structure of 1-methylimidazolium tricyanomethanide as a novel nano malten salt catalyst was studied and identified by FT-IR, ¹H NMR, ¹³C NMR, mass, TG, DTG, XRD, SEM and TEM analysis.

The IR spectrum of the nano molten salt displayed a $_{30}$ special peak at 3417 cm⁻¹ which can be related to N–H stretching group on imidazolium ring. Furthermore, the two peaks detected at 2170 cm⁻¹ and 2081 cm⁻¹ related to vibrational modes of –CN bonds (Fig. 1).



Fig. 1. The IR spectrum of 1-methylimidazolium tricyanomethanide (a); tricyanomethane (b); 1-methylimidazole (c)

Additionally, the ¹H NMR and ¹³C NMR spectra of the 1-methylimidazolium tricyanomethanide in DMSO- d_6 are demonstrated in Figures 2 and 3, respectively. As Figures ⁵⁵ 2 and 3, indicate that, the main peak of ¹H NMR spectra of nano molten salt catalyst is related to N–H group on methyl imidazolium ring of {[HMIM]C(CN)₃} which is observed in δ = 11.95 ppm. The peak related to methyl group is appeared at 2.5 ppm and the peaks related to ⁶⁰ imidazolium ring are depicted at 7.0 and 7.8 ppm respectively. Also, the important peak of ¹³C NMR spectra of nano molten salt catalyst is linked to the –CN group on tricyanomethanide anion which is detected at δ = 74.8 ppm and corresponded peaks at 119.7 and 134.8 ppm are ⁶⁵ related to carbons of imidazolium ring.









Thermal gravimetric (TG) and derivative thermal gravimetric (DTG) analysis of 1-methylimidazolium tricyanomethanide was investigated at range of 25 to 600 °C, with a temperature increase rate of 10 °C.min⁻¹ in a nitrogen atmosphere. The results are depicted in Figures 4 ¹⁰⁵ and 5. The thermal gravimetric (TG) and derivative thermal gravimetric (DTG) analysis of the nano molten salt catalyst showed importance losses in one step, and decomposed after 320 °C.

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Fig. 4. The thermal gravimetric (TG) analysis of nano molten salt catalyst



Fig. 5. The derivative thermal gravimetric (DTG) analysis of nano molten salt catalyst

Size, shape and morphology of 1-methylimidazolium tricyanomethanide as the nano molten salt catalyst were 30 studied by x-ray diffraction (XRD) pattern, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) imaging demonstrations. XRD patterns of the catalyst {[HMIM]C(CN)₃} was considered in a domain of 10-90 degree (Figure 6). As it is shown at 35 Figure 6, XRD patterns showed diffraction lines of high crystalline nature at $2\theta \approx 27.20^{\circ}$, 38.90° and 50.90° . Peak width (FWHM), size and inter planer distance related to XRD pattern of {[HMIM]C(CN)₃} were investigated in the 27.20° to 50.90° degree and the obtained results have 40 been summarized in Table 1. For example, assignments for the highest diffraction line 27.20° offered that an FWHM of 0.26 a crystallite size of the catalyst of ca. 31.44 nm via the Scherrer equation $[D = K\lambda/(\beta \cos\theta)]$ (Where D is the crystallite size, K is the shape factor, 45 being corresponding to 0.9, λ is the x-ray wavelength, β is the full width at half maximum of the diffraction peak, and θ is the Bragg diffraction angle in degree) and an inter planer distance of 0.327462 nm (sing the similar highest diffraction line at 27.20°) was calculated via the Bragg 50 equation: dhkl = $\lambda/(2\sin\theta)$, (λ : Cu radiation (0.154178) nm) were achieved. Obtaining crystallite sizes from various diffraction lines using the Scherrer equation were found to be in the nanometer range (29.06-47.31 nm), which is principally in a good agreement with the 55 scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Figures 7 and 8).



Fig. 6. The x-ray diffraction (XRD) pattern of the 1-methylimidazolium tricyanomethanide as a nano molten salt catalyst

Table 1. X-ray diffraction (XRD) data for the 1-methylimidazolium tricvanomethanide as a nano molten salt catalyst

Entry	ry 2θ Peak width [FW] (degree)		Size [nm]	Inter planer distance [nm]
1	27.20	0.26	31.44	0.327462
2	38.90	0.29	29.06	0.231242
3	50.90	0.17	47.31	0.179181



Fig. 7. Scanning electron microscopy (SEM) of the 1-methylimidazolium tricyanomethanide as a nano molten salt catalyst



Fig. 8. Transmission electron microscopy (TEM) of the 110 1-methylimidazolium tricyanomethanide as a nano molten salt catalyst

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Characterization of tin dioxide (SnO_2) as a nano particle catalyst

The SnO₂ nano particles (NPs) were synthesized and investigated according to previous literature.^{13,14,26,27} Size, shape and morphology of the SnO2 NPs catalyst were 5 investigated using XRD patterns, FE-SEM and TEM imaging approaches. The x-ray diffraction (XRD) pattern of SnO₂ NPs is presented in Figure 9. The peaks at 2θ values of 26.50°, 33.75°, 37.80°, 51.60°, and 54.85° can be observed. The SnO₂ product displays tetragonal 10 structure. With respect to the intensity ratio of major peak detected at 2θ equal to 51.60°, the crystalline structure of the catalyst can noticeably be recognized. The average crystallite size was proposed using width line of the diffraction peak in radians (β), Bragg angle in degrees (θ), 15 and Debye-Scherrer equation (Figure 9 and Table 2). The average size of the catalyst, consequently, achieved from this equation that was established to be in the nanometer range (28.73-36.66 nm), which is basically in agreement with the FE-SEM and TEM (Fig. 10 and Fig. 11).





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Entry	20	Peak width [FWHM] (degree)	Size [nm]	Inter planer distance [nm]		
1	26.50	0.24	33.88	0.336245		
2	33.75	0.25	32.92	0.265517		
3	37.80	0.29	28.73	0.237654		
4	51.60	0.24	36.66	0.177012		
5	54.85	0.30	30.02	0.167028		



Fig. 10. Field emission scanning electron microscopy (FE-SEM) of the SnO₂ 50 NPs catalyst



Fig. 11. Transmission electron microscopy (TEM) of the SnO₂ NPs catalyst

Application of 1-methylimidazolium tricyanomethanide nano MS and SnO_2 NPs as a catalyst.

At first, to optimize the reaction conditions, the condensation reaction of naphthalene-1-carbaldehyde, 70 β -naphthol and acetamide was selected as a model and different amounts of nano catalyst at range of 25-125 °C were tested on it under solvent-free conditions (Table 3). As shown in Table 3, the best results were attained when the reaction was achieved in the presence of 1 mol% of 75 nano molten salt and SnO2 nanoparticles at room temperature (Table 3, entry 5). No improvement was observed in the yield of reaction by increasing the amount of the nano catalysts and the temperature (Table 3, entries 6-13). Table 3 clearly demonstrates that in the absence of 80 nano catalyst, the product was not prepared. A slight excess of the amide was established to be favorable and hence the molar ratio of β -naphthol and aromatic aldehyde to amide was considered at 1:1:1.2.

Table 3. Result of amount of the catalyst and temperature on the ss condensation reaction of naphthalene-1-carbaldehyde, β -naphthol and acetamide under solvent-free conditions

Entry	Amount of	Reaction	Reacti	Reaction time		(%)
	catalyst (mol%)	temperature (°C)	(min)			
			Molten	Nano	Molten	Nano
			salt	SnO_2	salt	SnO_2
1	_	r.t.	75	75	_	_
2	_	100	75	75	_	_
3	0.5	r.t.	60	60	37	25
4	0.5	100	60	60	37	25
5	1	r.t.	7	17	96	87
6	1	50	7	17	96	87
7	1	75	7	17	96	87
8	1	100	7	17	96	87
9	1	125	7	17	93	85
10	2	r.t.	7	17	96	87
11	2	100	7	17	96	87
12	5	r.t.	10	20	95	86
13	5	100	10	20	95	86

To compare the effect of the solution in comparison with solvent-free conditions, a mixture of naphthalene-1carbaldehyde, β -naphthol and acetamide as model reaction, in the presence of 1 mol% of nano molten salt and nano SnO₂ as a catalyst in several solvents such as 5 H₂O, C₂H₅OH, CH₃CN, CH₃CO₂Et, CH₂Cl₂ and toluene was considered at room temperature. The results are depicted in Table 4. As it can be shown in Table 4, solvent-free condition was the best condition in this reaction. 10

Table 4. The effect of different solvents on the reaction of naphthalene-1carbaldehyde, β -naphthol and acetamide catalyzed by of nano molten salt (1 mol%) and SnO₂ NPs (1 mol%) at room temperature

Entry	Solvent	Reaction	time (min)	Yield (%)		
		Molten salt	Nano SnO ₂	Molten salt	Nano SnO ₂	
1	Solvent-free	7	17	96	87	
2	H_2O	30	30	25	15	
3	C ₂ H ₅ OH	30	30	25	25	
4	CH ₃ CN	30	30	20	20	
5	CH ₃ CO ₂ Et	60	60	10	10	
6	CH_2Cl_2	75	75	_	_	
7	Toluene	120	120	_	_	

After optimization of the reaction conditions, to explore the efficiency and the scope of the presented protocol, several 15 1-amidoalkyl-2-naphthol derivatives were synthesized by the three-component condensation reaction of various aromatic aldehydes, β -naphthol and different amides in the presence of a catalytic amount of 1-methylimidazolium tricyanomethanide { $[HMIM]C(CN)_3$ } as a nano molten 20 salt catalyst and SnO₂ as nano particles catalyst under solvent-free reaction conditions. The results have been represented in Table 5. The effect of substituents on the aromatic ring were indicated estimated strong effects in terms of yields under these reaction conditions. All 25 aromatic aldehydes including benzaldehyde and aldehydes containing electron-releasing substituents, electronwithdrawing substituents on their aromatic ring afforded the related products in high to excellent yields in short reaction times. The reaction times of aromatic aldehydes 30 having electron withdrawing groups were rather faster than electron donating groups. Also, amide derivatives similarly experienced well to the transformation. Moreover, in this reaction condition acetamide was reacted faster than benzamide and urea. Particularly, the 35 obtained results displayed that the nano molten salt (a) as a catalyst was more successful than nanoparticles (b) in this reaction conditions.

In Scheme 3, we have suggested a possible mechanism for the synthesis of 1-amidoalkyl-2-naphthol derivatives in 40 the presence of $\{[HMIM]C(CN)_3\}$ as a nano molten salt catalyst and SnO₂ nano particles as catalyst. The reaction of aromatic aldehydes with β -naphthol in the presence of nano catalyst is predictable to generate ortho-quinone methides (o-QMs). The prepared o-QMs, have been 45 reacted with amide derivatives to give 1-amidoalkyl-2naphthol derivatives. A practical description for this result can be given by considering the nucleophilic addition of amide to o-QMs intermediate and lastly the desired

product was obtained after aromatization.17-22, 28,29 50

Table 5. Synthesis of 1-amidoalkyl-2-naphthol derivatives using 1-methylimidazolium tricyanomethanide nano molten salt (1 mol%) and SnO₂ nano particles (1 mol%) as a catalyst

Entry	Aldehyde	R'	Time	Time (min)		Yield (%)	
			Molten	Nano	Molten	Nano	[Ref.]
			salt	SnO_2	salt	SnO_2	
1	Benzaldehyde	NH ₂	25	35	90	81	177-179
							[23]
2	4-Nitrobenzaldehyde	NH_2	15	25	94	85	200-202
							[23]
3	4-Chlorobenzaldeyhe	$\rm NH_2$	20	29	92	83	161-163
							[23]
4	2,5-	$\rm NH_2$	23	31	91	83	206-208
	Dimethoxybenzaldehyde						
5	Furfural	NH_2	25	35	90	80	140-142
							[23]
6	Thiophene-2-	NH_2	25	35	90	80	152-154
	carbaldehyde						[23]
7	Naphthalene-1-	NH_2	18	27	93	84	195-197
	carbaldehyde						[23]
8	α-	NH ₂	30	35	90	80	279-281
	Methylcinnamaldehyde		_				
9	4-Nitrobenzaldehyde	CH ₃	5	15	97	88	248-250
							[23]
10	4-Chlorobenzaldeyhe	CH ₃	10	20	95	85	258-260
	2.5		10	20	05	0.5	[23]
11	2,5-	CH ₃	12	20	95	85	280-282
12	Norbtholong 1	CII	7	17	06	07	[23]
12	Naphthalene-1-	СП3	/	17	90	07	203-207
12	Cinnomoldohydo	CU	15	25	02	07	220 222
15	Chinanaldenyde	СП3	15	23	95	85	[16]
14	Nanhthalene-2-	CH.	7	17	96	86	256-258
11	carbaldebyde	cn3	,	17	70	00	[20]
15	a-	CH	20	27	92	83	223-225
	Methylcinnamaldehyde	0113	20	27	/2	02	220 220
16	Biphenyl-4-	CH₃	8	15	96	88	244-246
	carbaldehvde	,					
17	4-Nitribenzaldeyhe	Ph	8	20	96	87	253-255
	2						[23]
18	4-Chlorobenzaldeyhe	Ph	15	25	94	83	205-207
							[23]
19	2,5-	Ph	18	25	93	83	271-273
	Dimethoxybenzaldehyde						
20	Naphthalene-1-	Ph	10	23	95	85	293-295
	carbaldehyde						
21	Cinnamaldehyde	Ph	18	30	92	82	201-203
22	Naphthalene-2-	Ph	10	23	95	85	264-266
	carbaldehyde						
23	α-	Ph	25	30	92	81	244-246
	Methylcinnamaldehyde						
24	Biphenyl-4-	Ph	10	30	96	86	281-283
	carbaldehyde						

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Scheme 3. Proposed mechanism for the synthesis of 1-amidoalkyl-2- naphthol 20 derivatives in the presence of {[HMIM]C(CN)₃} as a nano MS and SnO₂ as a NPs catalyst.

Furthermore, reusability of the catalyst was investigated upon the condensation between naphthalene-1-carbaldehyde, β naphthol and acetamide. After the completion of the 25 reaction, ethyl acetate was added to the reaction mixture and stirred and heated to separate product and remained starting materials from the catalyst. This solution was washed with water to separate catalyst from other materials (the product and starting materials are soluble in 30 hot ethyl acetate and nano molten salt catalyst is soluble in water). The aqueous layer was decanted and separated and the catalyst was reused for alternative reaction after removing of water. The catalytic activity of the catalyst was restored within the limits of the experimental errors 35 for four continuous runs (Figure 12). For recycling of SnO₂ NPs, at the end of reaction, warm ethyl acetate was added to the reaction mixture, stirred and heated to separate product and remained starting materials from the catalyst. Afterward, the obtained mixture, was centrifuged 40 to separate catalyst (SnO2 NPs catalyst is insoluble in ethyl acetate and the reaction mixture is soluble in ethyl acetate). The structure of reused [HMIM]C(CN)₃ was also confirmed by IR, ¹H NMR and ¹³C NMR spectra after its application in the reaction. These presented spectra are in 45 a very good accordance with the spectra of fresh catalyst (Figures S3, S4 and S5). Moreover, the size and morphology of reused catalysts were studied by SEM and TEM analysis. These studies were shown that the catalysts were recovered in nano size (Figures S6 and S7). 50



Fig. 12. Reusability of the nano MS catalyst in 7 minutes and nano NPs catalyst in 17 minutes

To compare the efficiency of our catalyst with some reported 65 catalysts for the synthesis of 1-amidoalkyl-2- naphthols, we have tabulated the results of these catalysts to perform the condensation of 4-chlorobenzaldehyde, β -naphthol and acetamide, in Table 6. As Table 6 indicates, [HMIM]C(CN)₃ has remarkably improved the synthesis of 1-amidoalkyl-2- 70 naphthols in different terms {reaction time, yield and turn-over frequency (TOF)}. The TOF values were calculated by the equation TOF = Yield (%)/[Time (min)×Catalyst amount (mol%)]. The reaction times were shorter, and the yields and TOFs were higher when our catalysts were utilized. 75

Table 6. Comparison of the results on the condensation reaction of 4-chlorobenzaldehyde, β -naphthol and acetamide catalyzed by [HMIM]C(CN)₃ with those obtained by the recently reported catalysts.

Reaction Condition	Catalyst loading	Time (min)	Yield ^a (%)	TOF ^b (min ⁻	Ref.	
Cu _{1.5} PW ₁₂ O ₄₀ , 100 °C	2 mol%	90	78	0.433	[30 a]	
Fe(HSO ₄) ₃ , 85 °C	5 mol%	45	88	0.125	[22]	
Sulfamic acid, ultrasound, 28-30 °C	51.5 mol%	120	92	0.015	[30 b]	
I ₂ , r.t.	5 mol%	690	90	0.026	[30 c]	
Cyanuric chloride, 100 °C	10 mol%	10	90	0.900	[30 d]	
H ₃ PW ₁₂ O ₄₀ , 100 °C	2 mol%	80	88	0.550	[30 e]	
4-(1-Imidazolium) butane sulfonate, 80 °C	10 mol%	120	85	0.070	[30 f]	
N-(4-sulfonic acid)butyl triethylammonium hydrogensulfate,	5	10	85	1.7	[30 g]	
[HMIM]C(CN) ₃ , r.t.	1 mol%	10	95	9.5	- ^c	

^a Isolated yield; ^b Turn-over frequency; ^c Our work

The efficacy of SnO₂ nano particles on the synthesis of 1amidoalkyl-2- naphthols was also studied in comparison with some other dioxide catalysts such as CeO₂, PbO₂, TiO₂, Ag-TiO₂ and ZrO₂. For this purpose, the reaction of 4-chlorobenzaldehyde, β -naphthol and acetamide was ss investigated in the persence of these catalysts (Table 7). As shown in Table 7, synthesis of 1-amidoalkyl-2- naphthols in

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the presence of SnO_2 NPs as a catalyst was the best conditions (dioxide catalyst) in this reaction.

 Table 7. Comparison synthesis of 1-amidoalkyl-2-naphthols using different dioxide catalyst under solvent-free conditions at room temperature^a

Dioxide	Catalyst loading	Time (min)	Yield ^b (%)
Nano-SnO ₂	1 mol%	20	85
CeO ₂	1 mol%	60	15
PbO ₂	2 mol%	120	_
Nano-TiO ₂	1 mol%	30	30
Nano-Ag-TiO ₂	2 mol%	60	5
ZrO_2	1 mo1%	30	45

Reaction condition: ^a 4-chlorobenzaldehyde (1 mmol), β -naphthol (1 mmol), 5 acetamide (1.2 mmol); ^b Isolated yields.

Conclusion

In summary, a novel, green and efficient nano molten salt catalyst namely 1-Methyl imidazolium tricyanomethanide $\{[HMIM]C(CN)_3\}$ was designed and completely 10 characterized by IR, ¹H NMR, ¹³C NMR, mass, thermal gravimetric (TG) and derivative thermal gravimetric (DTG), x-ray diffraction patterns (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis. Catalytic application of {[HMIM]C(CN)₃] 15 was studied on the synthesis of 1-amidoalkyl-2-naphthol derivatives by the three-component condensation reaction of various aromatic aldehydes, β -naphthol and several amide at room temperature under solvent-free conditions. Moreover, to compare the catalytic activity of the catalyst in similar 20 conditions nano SnO₂ was used instead of $\{[HMIM]C(CN)_3\}$ in the synthesis of 1-amidoalkyl-2-naphthol derivatives. Generally, the achieved results showed that the {[HMIM]C(CN)₃} nano molten salt was more successful than SnO2 nanoparticles as a catalyst (due to formation of products 25 higher yields and shorter reaction with time. $\{[HMIM]C(CN)_3\}$ as a nano molten salt catalyst is better than SnO₂ nanoparticles as a catalyst). Additional studies indicated that the nano molten salt basicity plays a main role in the dual-catalyzed reactions. Various important advantages of 30 this study are relatively short reaction time, high yield, cleaner reaction profile, low cost, simplicity of product isolation, reusability of the nano catalyst and compliance with the green chemistry protocols.

Experimental

General procedure for the preparation of nano molten salt catalyst: 1-methylimidazolium tricyanomethanide

1-Methylimidazole (3 mmol: 0.246 g) was added to 5 mL an aqueous solution of tricyanomethane (3 mmol: 0.273 g) and stirred at room temperature for 60 minutes. ⁴⁰ Subsequently the solvent was removed by distillation under reduced pressure; the white residue was dried under vacuum at 100 °C for 3 h. A pale pink solid formed which was filtered, washed with diethyl ether three times, and then dried under vacuum (a pale pink solid was insoluble ⁴⁵ in diethyl ether) and which was characterized by IR, ¹H NMR, ¹³C NMR, mass, thermal gravimetric (TG) and derivative thermal gravimetric (DTG), x-ray diffraction patterns (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis and ⁵⁰ (s, 51, —C113), 7.00 (s, 211, —C11), 7.05 (s, 111, —C11), 11.95 (brs, 1H, —NH); ¹³C NMR (100 MHz, DMSO- d_6): δ 46.4, 67.2, 74.8, 119.8, 134.9, 160.2; MS: m/z = 173 [M]⁺, 174 [M+H]⁺.

General procedure for the preparation of tin dioxide nano 60 particles catalyst

SnO₂ NPs were prepared using dissolving of 0.1 M: 2 g stannous chloride dehydrate (SnCl₂.2H₂O) in 50 ml distilled water. Afterward complete dissolution, ammonia solution was added drop wise to the above solution and 65 stirred. The resulting gels were filtered and dried at 80 °C for 24 h in order to remove water. In conclusion, SnO₂ NPs were formed at 600 °C for 2h and which was considered by x-ray diffraction patterns (XRD), field emission scanning electron microscopy (FE-SEM) and 70 transmission electron microscopy (TEM) analysis.^{13,14,26,27} *General procedure for the synthesis of 1-amidoalkyl-2-naphthol derivatives*

To a mixture of aromatic aldehydes (1mmol), β -naphthol (1mmol) and amide derivatives (1.2 mmol) in a round 75 bottom flask connected to condenser, 1 mol% of {[HMIM]C(CN)₃} nano molten salt or SnO₂ nano particles was added as catalyst and the resulting mixture was firstly stirred magnetically under solvent-free conditions at room temperature for appropriate time. After completion of the 80 reaction as monitored by TLC (n-hexane/ethyl acetate: 5/1), ethyl acetate (10 mL) was added to reaction mixture, stirred and refluxed for 5 min, and then washed with water (10 mL) and decanted to separate catalyst from the other materials (the reaction mixture was soluble in hot ethyl 85 acetate and nano molten salt catalyst was soluble in water). The aqueous layer was decanted, separated and after removing of water the remained catalyst was used for alternative reaction. The solvent of organic layer was removed and the crude product was purified by 90 recrystallization from ethanol (95%). Note: In another procedure, for the recycle of SnO2 NPs, at the end of reaction, warm ethyl acetate was added to the reaction mixture and centrifuged to separate product and starting materials from the catalyst (SnO₂ NPs catalyst is insoluble 95 in ethyl acetate). In this work, nano molten salt and SnO_2 nano particles as catalyst were recycled and reused for four times without significant loss of its catalytic activity. Spectral data analysis for compounds

1-((2-Hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl)urea ¹⁰⁰ (*Table 3, entry 2*): Yellow solid; M.p: 200-202 °C; Yield: (nano molten salt: 94%, nano SnO₂: 85%); IR (KBr): v 3484, 3457, 3316, 3074, 1655, 1604, 1516, 1348 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ 6.94 (brs, 1H, —OH), 7.48 (brs, 2H, —NH₂), 7.61 (d, 1H, *J* = 9.2 Hz, —CH ¹⁰⁵ aliphatic), 7.68 (d, 2H, *J* = 7.2 Hz, ArH), 7.94 (d, 2H, *J* = 8.8 Hz, ArH), 7.99 (t, 4H, *J* = 9.0 Hz, ArH), 8.04 (d, 2H, *J* = 8.8 Hz, ArH), 8.71 (d, 1H, *J* = 8.4 Hz, —NH); ¹³C NMR

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(100 MHz, DMSO-*d*₆): δ 36.7, 116.6, 118.2, 123.6, 124.2, 125.2, 127.7, 129.2, 129.5, 130.1, 131.1, 131.2, 146.3, 148.5, 153.1, 196.3.

1-((2,5-Dimethoxyphenyl)(2-hydroxynaphthalen-1yl)methyl)urea (Table 3, entry 4): Pale yellow solid; M.p: 5 206-208 °C; Yield: (nano molten salt: 91%, nano SnO₂: 83%); IR (KBr): v 3493, 3386, 3082, 2994, 1662, 1529, 1495, 1271 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ 3.50 (s, 3H, -OCH₃), 3.66 (s, 3H, -OCH₃), 4.30 (brs, 2H, -NH₂), 6.75 (s, 1H, ArH), 6.81 (d, 1H, J = 9.2 Hz, --CH 10 aliphatic), 7.13 (d, 2H, J = 8.4 Hz, ArH), 7.19 (d, 1H, J = 8.4 Hz, ArH), 7.27 (t, 1H, J = 7.4 Hz, ArH), 7.44 (t, 1H, J = 7.6 Hz, ArH), 7.69 (d, 1H, J = 8.8 Hz, ArH), 7.76 (d, 1H, J = 8.0 Hz, ArH), 8.18 (d, 1H, J = 8.8 Hz, ArH), 8.35 (d, 1H, J = 8.4 Hz, -NH), 9.83 (brs, 1H, -OH); ¹³C 15 NMR (100 MHz, DMSO-d₆): δ 44.9, 55.7, 56.4, 111.5, 112.3, 116.3, 119.1, 119.3, 122.6, 123.8, 126.3, 128.6, 128.7, 129.2, 132.1, 133.0, 151.2, 153.2, 153.7, 168.8; MS: $m/z = 352 [M]^+$.

I-((2-Hydroxynaphthalen-1-yl)(naphthalen-1yl)methyl)urea (Table 3, entry 7): Pale yellow solid; M.p.: 195-197 °C; Yield: (nano molten salt: 93%, nano SnO₂: 84%); IR (KBr): v 3432, 3333, 3220, 2974, 1650, 1629, 1538, 1515 cm⁻¹; ¹H NMR (400 MHz, DMSO- d_6): δ 5.40 (brs, 2H, —NH₂), 5.70 (brs, 1H, —OH), 7.04 (d, 1H, J = 258.4 Hz, —CH aliphatic), 7.26 (d, 2H, J = 8.8 Hz, ArH), 7.35 (t, 1H, J = 7.4 Hz, ArH), 7.49 (t, 2H, J = 9.9 Hz, ArH), 7.54 (d, 2H, J = 6.4 Hz, ArH), 7.77 (d, 2H, J = 8.8Hz, ArH), 7.80 (d, 2H, J = 8.4 Hz, ArH), 7.95 (t, 2H, J =7.0 Hz, ArH), 8.23 (d, 1H, J = 7.6 Hz, —NH); ¹³C NMR ³⁰ (100 MHz, DMSO- d_6): δ 47.8, 119.2, 119.8, 122.8, 123.0, 124.3, 125.2, 125.4, 125.5, 125.8, 126.0, 126.3, 126.8, 127.7, 128.9, 129.0, 129.1, 129.5, 131.4, 133.0, 134.0, 158.4.

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1-(1-(2-Hydroxynaphthalen-1-yl)-2-methyl-3- 35 *phenylallyl)urea (Table 3, entry 8)*: Yellow solid; M.p: 279-281 °C; Yield: (nano molten salt: 90%, nano SnO₂: 80%); IR (KBr): v 3513, 3383, 3271, 3064, 2969, 1659, 1600, 1230 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.11 (s, 3H, —CH₃), 4.53 (s, 1H, —CH), 5.41 (brs, 1H, —OH), 40 5.53 (d, 1H, *J* = 5.2 Hz, —CH aliphatic), 5.85 (brs, 2H, —NH₂), 6.96 (d, 1H, *J* = 5.0 Hz, ArH), 7.12 (t, 1H, *J* = 7.2 Hz, ArH), 7.20 (t, 2H, *J* = 7.4 Hz, ArH), 7.30 (d, 5H, *J* = 5.8 Hz, ArH), 7.42 (d, 1H, *J* = 6.4 Hz, —NH), 7.83 (t, 2H, *J* = 9.0 Hz, ArH); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 13.5, 45 46.2, 75.9, 112.5, 119.0, 123.4, 123.5, 126.9, 128.7, 128.9, 129.0, 129.4, 129.6, 133.2, 146.2, 152.6, 157.8; MS: m/z = 332 [M]⁺.

N-((4-chlorophenyl)(2-hydroxynaphthalen-1-

yl)methyl)acetamide (*Table 3, entry 10*): White solid; ⁵⁰ M.p: 258-260 °C; Yield: (nano molten salt: 95%, nano SnO₂: 85%); IR (KBr): v 3392, 3053, 2965, 1638, 1623, 1580, 1515, 1244 cm⁻¹; ¹H NMR (400 MHz, DMSO- d_6): δ 2.30 (s, 3H, —CH₃), 6.76 (d, 1H, J = 7.2 Hz, —CH aliphatic), 7.22 (brs, 1H, —OH), 7.47 (d, 2H, J = 7.2 Hz, s⁵⁵ ArH), 7.58 (d, 2H, J = 9.2 Hz, ArH), 7.66 (t, 4H, J = 8.4Hz, ArH), 7.95 (d, 2H, J = 8.8 Hz, ArH), 8.68 (d, 1H, J =8.4 Hz, —NH); ¹³C NMR (100 MHz, DMSO- d_6): δ 36.2, 47.5, 118.1, 123.8, 125.1, 127.5, 128.7, 128.8, 128.9, 129.0, 129.1, 129.2, 129.7, 130.1, 131.1, 131.2, 131.4, 60 144.9, 148.4, 191.5.

N-((2-hydroxynaphthalen-1-yl)(naphthalen-1-

st (12 *n*)*arosynaprimation 1 y*(*naprimation 1 y*(*maprimation 1 y*(*naprimation 1 y*(*maprimation 1 y*(*naprimation 1 y*(*maprimation 1*) *y*(*maprimation 1*) *y*(*matrial*) *y*(*matrialled*) *y*(*mat*

N-(*1*-(2-hydroxynaphthalen-1-yl)-3-phenylallyl)acetamide (*Table 3, entry 13*): Yellow solid; M.p: 230-232 °C; Yield: (nano molten salt: 93%, nano SnO₂: 83%); IR (KBr): υ so 3417, 3175, 3065, 3023, 1657, 1642, 1515, 1439, 1270 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.90 (s, 3H, — CH₃), 6.49 (d, 1H, *J* = 7.8 Hz, ArH), 6.60 (t, 1H, *J* = 7.4 Hz, —CH aliphatic), 6.67 (d, 1H, *J* = 5.6 Hz, ArH), 7.22 (t, 2H, *J* = 8.4 Hz, ArH), 7.31 (t, 3H, *J* = 7.2 Hz, ArH), ss 7.36 (d, 2H, *J* = 8.4 Hz, ArH), 7.47 (t, 1H, *J* = 7.2 Hz, ArH), 7.75 (d, 1H, *J* = 8.4 Hz, ArH), 7.81 (d, 1H, *J* = 7.6 Hz, ArH), 8.14 (d, 1H, *J* = 8.4 Hz, ArH), 8.40 (d, 1H, *J* = 7.6 Hz, —NH), 10.04 (brs, 1H, —OH); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 23.1, 47.8, 118.8, 119.0, 122.9, 126.5, 90 126.7, 127.7, 128.9, 129.0, 129.1, 129.2, 129.5, 131.1, 132.5, 137.1, 153.5, 169.2.

N-((2-hydroxynaphthalen-1-yl)(naphthalen-2-

yl)methyl)acetamide (Table 3, entry 14): White solid; M.p: 256-258 °C; Yield: (nano molten salt: 96%, nano SnO₂: 95 86%); IR (KBr): v 3407, 3153, 3060, 3011, 1644, 1629, 1514, 1271 cm⁻¹; ¹H NMR (400 MHz, DMSO- d_6): δ 2.05 (s, 3H, —CH₃), 7.26 (d, 1H, J = 8.8 Hz, —CH aliphatic), 7.29 (d, 2H, J = 5.6 Hz, ArH), 7.34 (t, 2H, J = 5.6 Hz, ArH), 7.47 (t, 2H, J = 5.6 Hz, ArH), 7.53 (d, 3H, J = 5.6 Io0 Hz, ArH), 7.83 (t, 3H, J = 7.6 Hz, ArH), 7.90 (s, 1H, ArH), 8.59 (d, 1H, J = 8.4 Hz, —NH), 10.05 (brs, 1H, —OH); ¹³C NMR (100 MHz, DMSO- d_6): δ 23.2, 48.4, 119.0, 119.2, 122.9, 123.8, 124.2, 125.5, 125.9, 126.5, 126.8, 127.8, 128.0, 128.1, 129.0, 129.1, 129.9, 132.2, 132.9, 105 133.2, 140.8, 153.7, 169.9.

N-(*1*-(2-hydroxynaphthalen-1-yl)-2-methyl-3phenylallyl)acetamide (Table 3, entry 15): White solid; M.p: 223-225 °C; Yield: (nano molten salt: 92%, nano SnO₂: 83%); IR (KBr): v 3395, 3055, 3023, 2965, 1627, ¹¹⁰ 1524, 1515, 1371, 1274 cm⁻¹; ¹H NMR (400 MHz, DMSOd₆): δ 1.67 (s, 3H, —CH₃), 1.94 (s, 3H, —CH₃), 6.45 (s, 1H, ArH), 6.53 (d, 1H, J = 8.4 Hz, —CH aliphatic), 7.22 (t, 4H, J = 8.8 Hz, ArH), 7.28 (d, 1H, J = 6.8 Hz, ArH), 7.34 (d, 2H, J = 7.6 Hz, ArH), 7.45 (t, 1H, J = 7.2 Hz, ¹¹⁵ ArH), 7.76 (d, 1H, J = 8.8 Hz, ArH), 7.81 (d, 1H, J = 7.6 Published on 21 April 2015. Downloaded by Fudan University on 02/05/2015 19:58:28.

Hz, ArH), 8.13 (d, 1H, J = 8.4 Hz, ArH), 8.28 (d, 1H, J = 8.4 Hz, —NH), 9.95 (brs, 1H, —OH); ¹³C NMR (100 MHz, DMSO- d_6): δ 16.7, 23.1, 51.4, 117.8, 119.0, 122.8, 123.5, 123.6, 126.6, 126.7, 128.6, 128.9, 129.0, 129.1, 129.6, 133.4, 138.2, 138.5, 153.8, 169.5; MS: m/z = 331 s [M]⁺.

N-(biphenyl-4-yl(2-hydroxynaphthalen-1-

yl)methyl)acetamide (Table 3, entry 16): White solid; M.p: 244-246 °C; Yield: (nano molten salt: 96%, nano SnO₂: 88%); IR (KBr): v 3395, 3156, 3060, 3030, 3011, 1643, ¹⁰ 1516, 1335 cm⁻¹; ¹H NMR (400 MHz, DMSO- d_6): δ 2.00 (s, 3H, —CH₃), 7.17 (d, 1H, J = 8.4 Hz, —CH aliphatic), 7.24 (t, 2H, J = 8.8 Hz, ArH), 7.27 (d, 1H, J = 8.8 Hz, ArH), 7.34 (d, 2H, J = 7.6 Hz, ArH), 7.45 (t, 2H, J = 7.6 Hz, ArH), 7.61 (d, 2H, J = 15 7.2 Hz, ArH), 7.79 (d, 1H, J = 8.8 Hz, ArH), 7.83 (d, 2H, J = 7.6 Hz, ArH), 7.89 (t, 1H, J = 7.0 Hz, ArH), 8.51 (d, 1H, J = 8.4 Hz, —NH), 10.06 (brs, 1H, —OH); ¹³C NMR (100 MHz, DMSO- d_6): δ 23.1, 48.1, 118.9, 119.2, 122.9, 126.8, 127.0, 127.1, 127.7, 128.9, 129.0, 129.3, 129.8, ²⁰ 132.8, 138.5, 140.4, 142.4, 153.6, 169.8; MS: m/z = 367 [M]⁺.

N-((2-hydroxynaphthalen-1-yl)(4-

nitrophenyl)methyl)benzamide (Table 3, entry 17): Yellow solid; M.p: 253-255 °C; Yield: (nano molten salt: 96%, 25 nano SnO₂: 87%); IR (KBr): v 3435, 3415, 3181, 3082, 3069, 1637, 1600, 1577, 1516, 1345 cm⁻¹; ¹H NMR (400 MHz, DMSO- d_6): δ 5.75 (brs, 1H, —OH), 7.29 (d, 1H, J = 8.8 Hz, —CH aliphatic), 7.34 (d, 1H, J = 7.6 Hz, ArH), 7.43 (d, 1H, J = 7.6 Hz, ArH), 7.50 (t, 1H, J = 7.4 Hz, 30 ArH), 7.61 (t, 2H, J = 7.6 Hz, ArH), 7.74 (dd, 2H, J = 8.0 Hz, ArH), 7.87 (dd, 2H, J = 8.0 Hz, ArH), 7.92 (d, 2H, J = 7.2 Hz, ArH), 8.10 (d, 2H, J = 8.0 Hz, ArH), 9.18 (d, 2H, J = 8.0 Hz, ArH), 10.50 (brs, 1H, —NH); ¹³C NMR (100 MHz, DMSO- d_6): δ 49.4, 121.4, 122.1, 123.0, 123.3, 35 127.5, 127.9, 128.0, 128.7, 128.8, 128.9, 129.2, 129.6, 130.0, 130.2, 130.5, 131.7, 132.1, 132.7, 133.8, 134.4, 135.0, 145.0, 193.7.

N-((2,5-dimethoxyphenyl)(2-hydroxynaphthalen-1-

yl)methyl)benzamide (Table 3, entry 19): Yellow solid; 40 M.p: 271-273 °C; Yield: (nano molten salt: 93%, nano SnO₂: 83%); IR (KBr): v 3420, 3160, 3065, 2993, 1640, 1577, 1526, 1492, 1275 cm⁻¹; ¹H NMR (400 MHz, DMSO d_6): δ 3.61 (s, 3H, -CH₃), 3.66 (s, 3H, -CH₃), 6.80 (d, 1H, J = 3.2 Hz, ArH), 6.91 (d, 1H, J = 8.8 Hz, --CH 45 aliphatic), 7.09 (s, 1H, ArH), 7.20 (d, 1H, J = 8.8 Hz, ArH), 7.30 (t, 1H, J = 7.4 Hz, ArH), 7.47 (t, 4H, J = 6.4 Hz, ArH), 7.52 (d, 1H, J = 7.2 Hz, ArH), 7.74 (d, 1H, J = 8.8 Hz, ArH), 7.80 (d, 1H, J = 8.4 Hz, ArH), 7.85 (d, 2H, J = 7.2 Hz, ArH), 8.27 (d, 1H, J = 8.8 Hz, ArH), 8.84 (d, 50 1H, J = 8.0 Hz, —NH), 10.17 (brs, 1H, —OH); ¹³C NMR (100 MHz, DMSO-d₆): δ 45.8, 55.7, 56.6, 112.0, 112.5, 116.5, 119.0, 119.2, 123.0, 123.7, 126.6, 127.6, 128.7, 128.8, 128.9, 129.4, 131.4, 131.6, 133.0, 135.0, 151.4, 153.3, 153.7, 165.5; MS: $m/z = 413 [M]^+$. 55

N-((2-hydroxynaphthalen-1-yl)(naphthalen-1-

yl)methyl)benzamide (Table 3, entry 20): White solid; M.p: 293-295 °C; Yield: (nano molten salt: 95%, nano SnO₂: 85%); IR (KBr): υ 3424, 3128, 3031, 1629, 1536, 1342, 1250 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.28 ⁶⁰ (d, 1H, *J* = 3.6 Hz, —CH aliphatic), 7.30 (d, 1H, *J* = 5.2 Hz, ArH), 7.40 (t, 3H, *J* = 6.0 Hz, ArH), 7.44 (d, 2H, *J* = 7.6 Hz, ArH), 7.51 (t, 1H, *J* = 7.2 Hz, ArH), 7.57 (d, 2H, *J* = 8.0 Hz, ArH), 7.85 (t, 4H, *J* = 8.2 Hz, ArH), 7.90 (d, 1H, *J* = 7.2 Hz, ArH), 7.95 (d, 1H, *J* = 8.0 Hz, ArH), 7.99 (d, 65 1H, *J* = 8.0 Hz, ArH), 8.09 (d, 1H, *J* = 7.6 Hz, ArH), 8.27 (d, 1H, *J* = 8.0 Hz, ArH), 9.26 (d, 1H, *J* = 8.4 Hz, —NH), 10.22 (brs, 1H, —OH); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 48.4, 118.3, 119.2, 122.9, 123.9, 125.7, 126.1, 126.5, 126.9, 127.9, 128.4, 128.7, 129.0, 129.1, 129.2, 129.8, 70 131.7, 131.8, 133.3, 134.1, 134.7, 136.7, 154.1, 165.8; MS: m/z = 403 [M]⁺.

N-(1-(2-hydroxynaphthalen-1-yl)-3-phenylallyl)benzamide (Table 3, entry 21): Yellow solid; M.p: 201-203 °C; Yield: (nano molten salt: 92%, nano SnO2: 82%); IR (KBr): v 75 3413, 3180, 3062, 3027, 1634, 1516, 1341, 1277 cm⁻¹; ¹H NMR (400 MHz, DMSO- d_6): δ 6.56 (d, 2H, J = 7.8 Hz, ArH), 6.78 (t, 1H, J = 9.6 Hz, --CH aliphatic), 6.84 (t, 1H, J = 6.0 Hz, ArH), 7.21 (t, 2H, J = 6.2 Hz, ArH), 7.28 (t, 3H, J = 7.6 Hz, ArH), 7.39 (d, 2H, J = 7.2 Hz, ArH), 80 7.51 (t, 3H, J = 9.2 Hz, ArH), 7.76 (d, 1H, J = 8.8 Hz, ArH), 7.83 (d, 1H, J = 8.4 Hz, ArH), 7.86 (d, 2H, J = 7.6 Hz, ArH), 8.30 (d, 1H, J = 8.4 Hz, ArH), 8.95 (d, 1H, J = MHz, DMSO-d₆): δ 49.2, 118.7, 119.1, 123.0, 123.3, 85 126.7, 126.9, 127.6, 127.6, 128.8, 129.0, 129.5, 129.8, 130.1, 131.7, 132.4, 134.9, 137.1, 153.6, 165.7, 182.9; MS: $m/z = 379 [M]^+$.

N-((2-hydroxynaphthalen-1-yl)(naphthalen-2-

yl)methyl)benzamide (Table 3, entry 22): Yellow solid; 90 M.p: 264-266 °C; Yield: (nano molten salt: 95%, nano SnO₂: 85%); IR (KBr): v 3419, 3062, 3029, 1629, 1535, 1344, 1275 cm⁻¹; ¹H NMR (400 MHz, DMSO- d_6): δ 7.29 (d, 1H, J = 9.2 Hz, —CH aliphatic), 7.33 (d, 1H, J = 7.6Hz, ArH), 7.46 (d, 4H, J = 9.6 Hz, ArH), 7.48 (s, 1H, 95 ArH), 7.52 (d, 2H, J = 7.6 Hz, ArH), 7.58 (t, 1H, J = 7.2Hz, ArH), 7.86 (t, 6H, J = 6.4 Hz, ArH), 7.93 (d, 2H, J =7.2 Hz, ArH), 8.17 (d, 1H, J = 8.8 Hz, ArH), 9.15 (d, 1H, J = 8.8 Hz, —NH), 10.38 (brs, 1H, —OH); ¹³C NMR (100 MHz, DMSO- d_6): δ 49.9, 118.7, 119.2, 123.2, 123.3, 100 124.9, 125.8, 126.1, 126.6, 127.3, 127.7, 127.8, 127.9, 128.2, 128.3, 128.9, 129.0, 129.1, 130.0, 131.9, 132.4, 132.9, 133.2, 134.8, 140.1, 153.8, 166.5; MS: m/z = 403 [M]⁺.

N-(1-(2-hydroxynaphthalen-1-yl)-2-methyl-3-

phenylallyl)benzamide (Table 3, entry 23): Yellow solid; M.p: 244-246 °C; Yield: (nano molten salt: 92%, nano SnO₂: 81%); IR (KBr): v 3419, 3065, 3026, 2905, 1629, 1514, 1340, 1272 cm⁻¹; ¹H NMR (400 MHz, DMSO- d_6): δ 1.88 (s, 3H, —CH₃), 6.41 (s, 1H, —CH), 6.75 (d, 1H, J = 1108.4 Hz, —CH aliphatic), 7.20 (t, 3H, J = 7.0 Hz, ArH), 7.25 (d, 1H, J = 8.8 Hz, ArH), 7.32 (t, 3H, J = 5.8 Hz, ArH), 7.47 (d, 2H, J = 7.2 Hz, ArH), 7.56 (d, 2H, J = 7.2Hz, ArH), 7.82 (t, 2H, J = 9.6 Hz, ArH), 7.87 (d, 2H, J =7.2 Hz, ArH), 8.23 (d, 1H, J = 8.4 Hz, ArH), 8.83 (d, 1H, 115 J = 8.4 Hz, —NH), 10.21 (brs, 1H, —OH); ¹³C NMR (100 MHz, DMSO- d_6): δ 16.7, 53.1, 117.5, 119.1, 123.0, 123.4, 124.9, 126.7, 127.0, 127.6, 128.6, 128.8, 128.9, 129.0, 129.2, 129.7, 131.8, 133.3, 135.0, 137.8, 137.9, 153.9, 166.2; MS: m/z = 393 [M]⁺.

N-(biphenyl-4-yl(2-hydroxynaphthalen-1yl)methyl)benzamide (Table 3, entry 24): White solid; M.p: 281-283 °C; Yield: (nano molten salt: 96%, nano SnO₂: 86%); IR (KBr): v 3414, 3071, 3026, 2940, 1631, 1538, 1342 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.28 (d, 1H, J = 8.8 Hz, —CH aliphatic), 7.33 (d, 2H, J = 7.2 10 Hz, ArH), 7.38 (t, 3H, J = 7.4 Hz, ArH), 7.45 (t, 2H, J = 7.6 Hz, ArH), 7.51 (t, 3H, J = 7.4 Hz, ArH), 7.61 (d, 5H, J = 8.8 Hz, ArH), 7.83 (d, 1H, J = 8.8 Hz, ArH), 7.87 (d, 1H, J = 7.62 Hz, ArH), 7.90 (d, 2H, J = 8.4 Hz, ArH), 8.15 (d, 1H, J = 8.4 Hz, ArH), 9.10 (d, 1H, J = 8.8 Hz, --- 15 NH), 10.41 (brs, 1H, -OH); ¹³C NMR (100 MHz, DMSO-d₆): δ 49.5, 118.7, 119.1, 123.2, 127.0, 127.1, 127.3, 127.5, 127.6, 127.8, 128.8, 129.0, 129.1, 129.4, 129.9, 131.9, 132.8, 134.7, 139.0, 140.4, 141.7, 153.7,166.2; MS: m/z = 429 [M]⁺. 20

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Abstract

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Design of 1-methylimidazolium tricyanomethanide as the first nanostructured molten salt and its catalytic application on the condensation reaction of various aromatic aldehydes, amide and β -naphthol compared with tin dioxide nano particles 25



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1-Methyl imidazolium tricyanomethanide $\{[HMIM]C(CN)_3\}$ as a novel nano molten salt (MS) was synthesized and applied for the synthesis of 1-amidoalkyl-2-naphthols in comparison with tin dioxide (SnO₂) nano particles.

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