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**Supporting Information** 

# Designing a new basic ionic liquid [DHIM][OH] as a task specific bifunctional catalyst for facile microwave assisted metal free synthesis of 5-amino-1,2,3-triazoles

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#### 1) General information

All reactions were carried out in oven dried glassware under atmospheric conditions otherwise noted. Starting materials and solvents were obtained from common commercial sources and used without further purification. All reported yields are isolated yields. TLC was carried out using aluminium sheets pre-coated with silica gel 60F<sub>254</sub> (Merck) and was visualized under 254 nm UV light. Melting points were obtained by an open capillary method and are uncorrected. Infrared spectra were measured using potassium bromide (KBr) pellets on a Perkin-Elmer FT-IR-2000 spectrophotometer and absorptions are reported in cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C NMR (125 MHz) were recorded on a Bruker Avance 500 MHz spectrometer using TMS as an internal standard. <sup>1</sup>F NMR (471 MHz) was recorded on Bruker Avance 500 MHz FT-NMR spectrometer. Chemical shifts are reported in parts per million (ppm), downfield from residual solvents peaks and coupling constants are reported as Hertz (Hz).). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), br (broad) and m (multiplet, for unresolved lines). The mass spectra were recorded on a Q-TOF micromass (YA-105) spectrometer in ESI (electrospray ionization) mode. Thermo gravimetric Analysis (TGA) was performed from 30-800 °C at scanning rate of 10 °C/min with TGA/SDTA851 Mettler Toledo instrument under a nitrogen atmosphere. The reactions were carried out in closed glass tube in anton Paar monowave 400 microwave synthesis reactor.

#### 2) General procedure for synthesis of 5-amino-1,2,3-triazole derivatives

2-Phenylacetonitrile derivatives (1 mmol), phenyl azide derivatives (1.5 mmol) and [DHIM][OH] (15 mol%) were subjected to microwave irradiation in 70W (130 °C) for 2 minutes. The progress of the reaction was monitored by TLC under UV light. After completion of the reaction the mixture was extracted with ethyl acetate (3 x 10 mL) and washed with water (3 x 10 mL). The combined

extract was dried over anhydrous  $Na_2SO_4$ . The filtrate was concentrated under reduced pressure. The product was purified by column chromatography over silica gel using n-hexane/ethyl acetate (3:1 v/v) as eluent to get the purified product. The products were then characterized by ESI-MS, <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra.

#### 3) Synthesis and characterization of [DHIM][OH]

The basic ionic liquid [DHIM][OH] was also prepared through microwave irradiation. Initially, a glass tube equipped with magnetic stirring bar was charged with imidazole (1g, 14.69 mmol), 1bromohexadecane (9.87g, 32.33 mmol) and 10mL of 10% aqueous NaOH solution and the mixture was subjected to microwave irradiation at 110 °C for 10 minutes until the mixture solidified. After completion of the reaction, 20 mL water was added and organic part was extracted with ethyl acetate to obtain 1,3-dihexadecyl-1H-imidazol-3-ium bromide ([DHIM][Cl]) as yellow sticky liquid. The synthesized IL was dried under vacuum to obtain yellow solid. Thereafter, [DHIM][Cl] (3g, 5.79 mmol) and KOH (0.39g, 6.95 mmol) in anhydrous ethanol was stirred for 24 hours at room temperature. The mixture was then centrifuged to remove KBr as white solid. After removal of ethanol the new basic ionic liquid 1,3-dihexadecyl-1H-imidazol-3-ium hydroxide was obtained as yellow solid and labelled as [DHIM][OH]. The ionic liquid is characterized by <sup>1</sup>H and <sup>13</sup>C NMR, HRMS, FT-IR and TGA analysis.

#### Characterization of prepared ionic liquid (IL):

#### IR analysis:

For the characterization of prepared ionic liquid, [DHIM][OH], FT-IR analysis was carried out as shown in Figure 2. The band at 3422 cm<sup>-1</sup> is assigned for stretching vibration of O-H caused by residual ethanol. The two bands observed at 2952 cm<sup>-1</sup> and 2850 cm<sup>-1</sup> are observed for the C-H stretching of the alkane. Two bands due to C=N and C=C stretching of the imidazolium ring were

obtained at 1660 cm<sup>-1</sup> and 1563 cm<sup>-1</sup>. The characteristic peaks at 1459 cm<sup>-1</sup> and 1160 cm<sup>-1</sup> can be ascribed to  $-CH_2$  deformation vibration in alkane and C-N-C stretching respectively. The band observed at 718 cm<sup>-1</sup> is due to the bending vibration of long chain alkanes in [DHIM][OH].



**Molecular mass analysis**: Mass Spectroscopy of the ionic liquid is done in methanol solvent with MicroMass Q-TOF.

For [DHIM][OH]: LC-MS (ESI-Positive) m/z: 517.5455 calculated for  $C_{35}H_{29}N^{2+}$  and found 517.5636; 293.2951 calculated for  $C_{19}H_{37}N^{2+}$  i.e., for the breaking of C-N bond and found 293.2953.



Fig. 1 Mass Spectra of [DHIM][OH]

## NMR data of prepared ionic liquid:

<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  9.25 (s, 1H), 7.81 (d, *J* = 1.6 Hz, 2H), 4.17 (t, *J* = 7.0 Hz, 2H), 3.51 (t, *J* = 6.7 Hz, 2H), 1.97 – 1.57 (m, 4H), 1.24 (d, *J* = 2.1 Hz, 52H), 0.86 (t, *J* = 6.9 Hz, 6H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  135.88, 122.41, 60.41, 48.79, 31.19, 28.94, 25.33, 21.97, 13.82.

## NMR spectra of prepared ionic liquid:

## <sup>1</sup>H and <sup>13</sup>C NMR spectra of [DHIM][OH]:



### 4) Spectral data of products

1-(3-chlorophenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table2, 6a1)



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 (d, J = 7.3 Hz, 2H), 7.70 (s, 1H), 7.56 (t, J = 1.7 Hz, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.49 (d, J = 7.8 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 4.16 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  137.26, 135.60, 131.09, 130.89, 130.07, 129.40, 129.00, 127.18, 125.66, 124.34, 122.11.

#### 1-(4-chlorophenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a2)



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, J = 5.2 Hz, 2H), 7.79 – 7.30 (m, 7H), 4.10 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  137.24, 135.30, 133.57, 131.14, 130.10, 129.00, 127.16, 125.64, 125.44.

#### 1-(4-methoxyphenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a3)

OMe



<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  7.80 (d, *J* = 7.4 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 8.8 Hz, 2H), 5.66 (s, 2H), 3.86 (s, 3H).<sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  159.88, 139.67, 132.42, 128.93, 128.43, 127.63, 126.85, 126.29, 125.19, 56.00.

#### 1-(4-fluorophenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a4)



<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  7.81 (d, J = 7.9 Hz, 2H), 7.67 (d, J = 13.4 Hz, 2H), 7.53 – 7.40 (m, 3H), 7.27 (t, J = 7.4 Hz, 2H), 5.80 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  161.32, 139.80, 132.14, 128.95, 127.65, 126.41, 125.28, 116.90.

#### 4-phenyl-1-(p-tolyl)-1H-1,2, 3-triazol-5-amine (Table 2, 6a5)



<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  7.82 (d, J = 12.1 Hz, 2H), 7.50 – 7.42 (m, 5H), 7.27 (t, J = 6.7 Hz, 2H), 5.70 (s, 2H), 2.42 (s, 3H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  139.20, 133.19, 132.34, 130.45, 129.86, 128.94, 126.35, 125.27, 124.90, 123.45, 21.09.

1-(4-(methylthio)phenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (table 2, 6a6)



<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  7.81 (d, *J* = 7.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.39 (m, 3H), 7.27 (t, *J* = 7.1 Hz, 2H), 5.76 (s, 2H), 3.35 (s, 3H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  139.59, 132.34, 128.41,135.6, 127.87, 126.90, 126.38, 125.56, 125.28, 14.97.

1-(4-(difluoromethoxy)phenyl)-4-phenyl-1H-1,2,3-triazol-5-amine(Table 2, 6a7)



<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  7.85 (d, *J* = 7.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.31 (s, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 5.99 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  168.61, 159.32, 140.97,136.36, 131.50, 131.50, 128.79, 127.72, 125.24, 119.54

#### 1-(naphthalen-2-yl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a8)



<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.25 (d, *J* = 8.5 Hz, 2H), 8.15 (d, *J* = 8.6 Hz, 2H), 8.01 (d, *J* = 10.9 Hz, 1H), 7.92 (d, *J* = 7.4 Hz, 2H), 7.70 (s, 1H), 7.69 (t, 2H), 7.64 (t, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 6.46 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  140.60, 138.13, 134.41, 129.36, 128.28, 127.95, 126.84, 126.72, 126.42, 123.10, 121.50

#### 1,4-diphenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a9)



<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  7.95 (d, J = 7.4 Hz, 2H), 7.88 (d, J = 8.1 Hz, 2H), 7.74 – 7.38 (m, 6H), 5.99 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  140.56, 137.08, 129.91, 129.68, 128.61, 125.33, 123.84, 120.51.

1-(3,4-difluorophenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a11)



<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  7.80 (d, J = 7.1 Hz, 2H), 7.75 – 7.68 (m, 3H), 7.44 (d, J = 7.8 Hz, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.28 (s, 1H), 5.91 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  148.73, 139.94, 137.08, 132.09, 128.97, 127.71, 126.48, 125.31, 122.79, 118.74.

#### 1-(4-nitrophenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a12)

JO2



<sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  8.41 (d, *J* = 9.0 Hz, 2H), 8.21 (d, *J* = 9.1 Hz, 2H), 7.94 (d, *J* = 7.5 Hz, 2H), 7.63(t, *J* = 6.4 Hz, 2H), 7.44(t, *J* = 6.9 Hz, 1H), 5.61 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  151.94, 146.54, 140.36, 133.40, 129.60, 129.32, 128.39, 127.65, 123.89, 123.65.

4-(4-bromophenyl)-1-(3-chlorophenyl)-1H-1,2,3-triazol-5-amine (Table 2, 6a13)



Br' <sup>1</sup>H NMR (500 MHz, DMSO) δ 7.75 (s, 1H), 7.73 (d, J = 1.9 Hz, 2H), 7.64 (d, J = 2.0 Hz, 3H), 7.63 (d, J = 3.3 Hz, 1H), 7.61 (t, J = 2.3 Hz, 1H), 6.01 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO) δ 140.01, 136.74, 134.17, 131.75, 131.34, 129.33, 127.26, 126.87, 125.01, 123.86, 119.25

1-(3-chlorophenyl)-4-(1H-indol-3-yl)-1H-1,2,3-triazol-5-amine (Table2, 6a18)



H <sup>1</sup>H NMR (500 MHz, DMSO) δ 12.13 (s, 1H), 8.80 (s, 1H), 8.29 (d, J = 3.1 Hz, 1H), 8.09 (d, J = 7.9 Hz, 1H), 7.51 (d, J = 8.1 Hz, 2H), 7.28 – 7.15 (m, 4H), 5.98 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 140.36, 137.61, 136.76, 129.60, 129.01, 128.39, 123.89, 123.65, 122.45, 121.21, 112.91.

#### 4-(4-bromophenyl)-1-(4-chlorobenzyl)-1H-1,2,3-triazol-5-amine (Table 2, 6a19)

Cl



Br' <sup>1</sup>H NMR (500 MHz, DMSO) δ 7.92 (d, J = 8.4 Hz, 2H), 7.55 (t, J = 7.0 Hz, 3H), 7.39 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 5.50 (s, 2H), 4.46 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO) δ 138.88, 136.51, 133.26, 131.70, 129.51, 128.78, 128.59, 42.42.

#### 1-(4-bromobenzyl)-4-(4-bromophenyl)-1H-1,2,3-triazol-5-amine (Table 2, 6a20)



Br' <sup>1</sup>H NMR (500 MHz, DMSO) δ 7.74 (d, J = 7.3 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.40 (t, J = 7.7 Hz, 3H), 7.20 (d, J = 8.3 Hz, 2H), 5.88 (s, 2H), 5.46 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO) δ 138.58, 135.08, 131.62, 130.86, 128.99, 127.88, 126.62, 125.13, 123.89, 120.18.

## 5)Copies of <sup>1</sup>H NMR and <sup>13</sup>C NMR of the products

<sup>1</sup>H spectrum of 1-(3-chlorophenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a1)



<sup>13</sup>C spectrum of 1-(3-chlorophenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a1)



# <sup>1</sup>H spectrum of 1-(4-chlorophenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a2)



<sup>13</sup>C spectrum of 1-(4-chlorophenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a2)

#### 137.24 135.30 131.14 131.14 131.14 131.14 131.14 132.16 127.16 125.44





<sup>1</sup>H spectrum of 1-(4-methoxyphenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a3)

<sup>13</sup>C spectrum of 1-(4-methoxyphenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a3)



## <sup>1</sup>H spectrum of 1-(4-fluorophenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a4)



# <sup>13</sup>C spectrum of 1-(4-fluorophenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a4)



<sup>1</sup>H spectrum of 4-phenyl-1-(p-tolyl)-1H-1,2, 3-triazol-5-amine (Table 2, 6a5)



<sup>13</sup>C spectrum of 4-phenyl-1-(p-tolyl)-1H-1,2, 3-triazol-5-amine (Table 2, 6a5)



<sup>1</sup>H spectrum of 1-(4-(methylthio)phenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (table 2, 6a6)



<sup>13</sup>C spectrum of 1-(4-(methylthio)phenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (table 2, 6a6)



<sup>1</sup>H spectrum of 1-(4-(difluoromethoxy)phenyl)-4-phenyl-1H-1,2,3-triazol-5-amine(Table 2, 6a7)



<sup>13</sup>C spectrum of 1-(4-(difluoromethoxy)phenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a7)







<sup>13</sup>C spectrum of 1-(naphthalen-2-yl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a8)



## <sup>1</sup>H spectrum of 1,4-diphenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a9)



<sup>13</sup>C spectrum of 1,4-diphenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a9)



<sup>1</sup>H spectrum of 1-(3,4-difluorophenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a11)



<sup>13</sup>C spectrum of 1-(3,4-difluorophenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a11)



<sup>1</sup>H spectrum of 1-(4-nitrophenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a12)



<sup>13</sup>C spectrum of 1-(4-nitrophenyl)-4-phenyl-1H-1,2,3-triazol-5-amine (Table 2, 6a12)



<sup>1</sup>H spectrum of 4-(4-bromophenyl)-1-(3-chlorophenyl)-1H-1,2,3-triazol-5-amine (Table 2, 6a13)



<sup>13</sup>C spectrum of 4-(4-bromophenyl)-1-(3-chlorophenyl)-1H-1,2,3-triazol-5-amine (Table 2, 6a13)



<sup>1</sup>H spectrum of 1-(3-chlorophenyl)-4-(1H-indol-3-yl)-1H-1,2,3-triazol-5-amine (Table2, 6a18)



<sup>13</sup>C spectrum of 1-(3-chlorophenyl)-4-(1H-indol-3-yl)-1H-1,2,3-triazol-5-amine (Table2,



<sup>1</sup>H spectrum of 4-(4-bromophenyl)-1-(4-chlorobenzyl)-1H-1,2,3-triazol-5-amine (Table 2, 6a19)



<sup>13</sup>C spectrum of 4-(4-bromophenyl)-1-(4-chlorobenzyl)-1H-1,2,3-triazol-5-amine (Table 2, 6a19)



<sup>1</sup>H spectrum of 1-(4-bromobenzyl)-4-(4-bromophenyl)-1H-1,2,3-triazol-5-amine (Table 2, 6a20)



<sup>13</sup>C spectrum of 1-(4-bromobenzyl)-4-(4-bromophenyl)-1H-1,2,3-triazol-5-amine (Table 2, 6a20)



6) E-factor data of products

E factor is an important parameter in determining greenness of a transformation which can be calculated as E factor = Amount of organic waste/ Amount of Product. The calculated E-factor for our products are given in the table below.

Products	E-factor	Products	E-factor
6a1	0.587	6a11	0.668
6a2	0.587	6a12	0.681
6a3	0.589	6a13	0.455
6a4	0.587	6a14	0.696
6a5	0.588	6a15	0.682
6a6	0.610	6a16	0.668
6a7	0.617	6a17	0.583
6a8	0.635	6a18	0.737
6a9	0.598	6a19	0.610
6a10	0.587	6a20	0.574

E-factors for all the reactions of our protocol lies within the range of 0.455-0.737 which indicates that the negligible amount of waste is generated for this protocol.