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Experimental and theoretical approving of anomeric based oxidation in the preparation of 2-sbstituted benz-(imida, oxa and othia)-zoles using $[2,6\text{-DMPy-NO}_2]C(NO_2)_3$ as a novel nano molten salt catalyst†

Mohammad Ali Zolfigol,*[a] Ardeshir Khazaei,*[a] Saied Alaie,[a] Saeed Baghery,[a] Farahnaz Maleki,[a] Yadollah Bayat[b] and Asiye Asgari[b]

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The synthesis of 2-sbstituted benz-(imida, oxa and othia)-zole derivatives were occurred in the presence of 2,6-dimethyl-1-nitropyridin-1-ium trinitromethanide $[2,6\text{-DMPy-NO}_2]C(NO_2)_3$ *via* the condensation reaction between 1,2-phenylenediamine or 2-aminophenol or 2-aminothiophenol and corresponding aldehyde at room temperature under solvent-free conditions respectively. $[2,6\text{-DMPy-NO}_2]C(NO_2)_3$ as a nano molten salt (NMS) catalyst was fully characterized by Fourier transform infrared (FT-IR), nuclear magnetic resonance (^{1}H NMR and ^{13}C 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 described reactions are in close agreement with the green chemistry disciplines and their major advantages are good yields, short reaction time and ease of separation. Our recently new introduced concept entitled "anomeric based oxidation" was proposed for the final step of the described synthesis and it was also approved using theoretical studies.

Introduction

2-Substituted benz-(imida, oxa and othia)-zoles have received remarkable attention in heterocyclic chemistry.[1] These heterocyclic compounds display biological and pharmacological activities such as: antimicrobial,[2] antiparkinson,[3] antiviral,[4] antifungal,[5] antibiotic[6] and anticancer.[7] These compounds are also used as ligands for asymmetric transformations.[8] Synthetic methods that are common for the preparation of these compounds usually include the reaction of a carboxylic acid or its derivatives with an appropriate 1,2-phenylenediamine, 2-aminophenol or 2-aminothiophenol using a strong acid at high temperatures.[9] Various synthetic processes and catalysts have been developed for the synthesis of 2-substituted benz-(imida, oxa and othia)-zoles such as cetylpyridinium bromide,[10] PEG 400,[11] DDQ,[12] NiO_2,[13] $Ba(MnO_4)_2$,[14] PCC,[15] $ZrOCl_2\cdot 8H_2O$,[16] TMSCl[17] and CAN[18] because of the importance of this type of compounds.

Ionic liquids (ILs) and molten salts (MSs) are materials that are completely composed of ions and can be synthesized for different purposes. Attention to these compounds, often is attracted as the green, technological media of the future is still increasing quickly[19] and stems from their near-zero vapour pressure,[20] their thermal stability[21] and their broadly harmonic properties as hydrophobicity, polarity and solvent miscibility behaviour by suitable modification of the cation and the anion. Mainly, ILs and MSs are defined as those fused salts with a melting point less than 100 °C, with salts with higher melting points mentioned to as molten salts (melting point more than 100 °C).[22] Combination of various cations and anions allow a wide range of chemical and physical characteristics to be attained, including volatile[23] and involatile systems, and thus the terms "designer" and "task-specific" ILs and MSs have been developed.[24,25] Most recently, Atkin *et al.* have extensively reviewed the chemical and physical properties of nanostructured ILs and MSs.[26] Since the energetic materials have attracted interest over the past decades,[27] we decided to design and synthesize novel and recyclable NMS catalyst. For this purpose, we have prepared 2,6-dimethyl-1-nitropyridin-1-ium trinitromethanide $[2,6\text{-DMPy-NO}_2]C(NO_2)_3$ as a naval and recyclable nanostructured molten salt (NMS) (Scheme 1). In our previous works we reported some theoretical studies that all supported the anomeric-based oxidation mechanism.[28,29] Herein we also report a theoretical study on above mechanism for the synthesis of compounds reported here.

[a]*Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran. E-mail: zolfi@basu.ac.ir; mzolfigol@yahoo.com; Khazaei_1326@yahoo.com; Fax: +98 8138257407*

[b]*Faculty of Chemistry and Chemical Engineering, Malek Ashtar University of Technology, Tehran, Iran*

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Scheme 1 Synthesis of 2,6-dimethyl-1-nitropyridin-1-ium trinitromethanide [2,6-DMPy-NO_2]$C(NO_2)_3$ as a NMS catalyst.

Experimental

The materials were purchased from Merck, Fluka and Sigma-Aldrich and were used without any additional purification. All reactions were tested by thin layer chromatography (TLC) on gel F254 plates. Spectrometer (^{1}H NMR 400 MHz and ^{13}C NMR 100) in pure deuterated DMSO with tetramethylsilane (TMS) was studied as the internal standard. The prepared NMS catalyst was known by FT-IR, ^{1}H NMR, ^{13}C NMR, mass, X-ray diffraction patterns (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal gravimetric (TG) and derivative thermal gravimetric (DTG) analysis. X-ray diffraction (XRD) patterns of catalyst were attained on a APD 2000, Ital structure with Cu Kα radiation (k = 0.1542 nm) operating at 50 kV and 20 mA in a 2 h range of 5–90° with step size 0.01° and time step 1.0 s to assess the crystallinity of the catalyst. Fourier transform-infrared spectra of the samples were recorded on a Perkin-Elmer FT-IR spectrometer 17259 using KBr disks. Thermal gravimetric analyses by a Perkin-Elmer TGA were achieved on catalyst. The SEM analyses were performed with a TESCAN/MIRA and a maximum acceleration voltage of the primary electrons between 10 and 15 kV. Transmission electron microscope (TEM) measurements were carried out on a Philips CM10 analyzer.

General procedure for the synthesis of 2,6-dimethyl-1-nitropyridin-1-ium trinitromethanide [2,6-DMPy-NO_2]$C(NO_2)_3$ as nano structure molten salt (NMS) catalyst

To a round-bottomed flask (50 mL) containing 2,6-dimethylpyridine (3 mmol; 0.322 g) in CH_3CN (5 mL), was added tetranitromethane (3 mmol; 0.588 g) drop wise and stirred over a period of 120 min at room temperature. Then, the solvent was removed by distillation under reduced pressure and the product was dried under vacuum at 80 °C for 120 minutes. The yellow solid product was filtered, washed with diethyl ether for three times, and then dried under vacuum conditions. [2,6-DMPy-NO_2]$C(NO_2)_3$ was identified by FT-IR, ^{1}H NMR, ^{13}C NMR, mass, thermal gravimetry (TG), derivative thermal gravimetric (DTG), X-ray diffraction patterns (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis (Scheme 1).

2,6-Dimethyl-1-nitropyridin-1-ium trinitromethanide [2,6-DMPy-NO_2]$C(NO_2)_3$. Yellow solid; mp: 145–147 °C; yield: 96% (0.873 g); IR (KBr): ν 3511, 3090, 3000, 1662, 1389, 1350, 1175, 829 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} 2.70 (s, 6H, –CH_3), 7.75 (d, 2H, ArH, J = 8.0 Hz), 8.39 (t, 1H, ArH, J = 7.8 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ_{ppm} 18.1, 97.4, 139.3, 160.0, 165.9; MS: m/z = 303 [M]$^+$.

General procedure for the synthesis of 2-aryl benz-(imida, oxa and othia)-zole derivatives

To a mixture of aromatic aldehydes (1 mmol) and one of the 1,2-phenylenediamine (1 mmol; 0.108 g), 2-aminophenol (1 mmol; 0.109 g) or 2-aminothiophenol (1 mmol; 0.125 g) in a round bottom flask, 1 mol% (0.003 g) of [2,6-DMPy-NO_2]$C(NO_2)_3$ NMS was added as a catalyst and stirred at room temperature under solvent-free conditions for appropriate time (Table 3). After completion of the reaction as detected by thin layer chromatography (TLC) (*n*-hexane/ethyl acetate: 5/2), ethyl acetate (10 mL) was added to reaction mixture and stirred under reflux condition for 10 minutes. Then, the resulting mixture was washed with water (10 mL) and decanted to separate catalyst from other materials (the reaction mixture was soluble in hot ethyl acetate and NMS catalyst was soluble in water). The aqueous layer was decanted, separated and its water was removed to provide the catalyst for another reaction. The solvent of organic layer was removed and the crude product was purified by recrystallization from ethanol (95%). More purification can be performed by recrystallization in *n*-hexane. In this study, NMS catalyst was recycled and reused for five times without significant loss of its catalytic activity.

Spectral data analysis for compounds

2-(1-Phenylprop-1-en-2-yl)-1*H*-benzo[*d*]imidazole (Table 3, entry 2). Orange solid; mp: 229–231 °C; yield: 87%; IR (KBr): ν 3417, 3067, 2994, 2973, 1636, 1619, 1449, 1417, 1279 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} 2.41 (s, 3H, –CH_3), 3.40 (s, 1H, –CH), 7.23 (t, 3H, J = 7.6 Hz, ArH), 7.38 (d, 1H, J = 7.6 Hz, ArH), 7.48 (t, 2H, J = 7.6 Hz, ArH), 7.52 (d, 2H, J = 7.6 Hz, ArH), 7.58 (s, 1H, –NH), 7.63 (d, 1H, J = 7.6 Hz, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ_{ppm} 15.1, 110.9, 111.0, 118.7, 121.4, 122.5, 127.4, 127.5, 128.1, 128.5, 128.8, 129.2, 130.2, 136.3, 143.4; MS: m/z = 234 [M]$^+$.

2-([1,1′-Biphenyl]-4-yl)-1*H*-benzo[*d*]imidazole (Table 3, entry 3). Yellow solid; mp: 213–215 °C; yield: 94%; IR (KBr): ν 3462, 3366, 3025, 1595, 1486, 1371, 1265, 1135 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} 6.59 (t, 1H, J = 7.6 Hz, ArH), 6.74 (d, 1H, J = 6.8 Hz, ArH), 7.00 (t, 1H, J = 8.4 Hz, ArH), 7.17 (d, 1H, J = 8.0 Hz, ArH), 7.43 (t, 1H, J = 7.4 Hz, ArH), 7.53 (t, 2H, J = 7.4 Hz, ArH), 7.77 (d, 2H, J = 8.0 Hz, ArH), 7.83 (d, 2H, J = 8.4 Hz, ArH), 8.09 (d, 2H, J = 8.4 Hz, ArH), 8.71 (s, 1H, –NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ_{ppm} 114.6, 116.1, 116.9, 126.7, 126.8, 127.6, 127.9, 129.0, 129.1, 135.6, 139.3, 142.3, 143.8, 155.7; MS: m/z = 270 [M]$^+$.

4-(1*H*-Benzo[*d*]imidazol-2-yl)-2-ethoxyphenol (Table 3, entry 5). White solid; mp: 208–210 °C; yield: 85%; IR (KBr): ν 3350, 3050, 2981, 1593, 1501, 1452, 1271 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} 3.94 (t, 3H, J = 7.6 Hz, –CH_3), 3.94 (q, 2H, J = 7.2 Hz, –CH_2), 5.42 (s, 1H, –OH), 6.39 (d, 1H, J = 8.0 Hz, ArH), 6.63 (s, 1H, ArH), 6.68 (t, 1H, J = 8.2 Hz, ArH), 6.94 (d, 1H, J = 8.0 Hz,

ArH), 7.17 (s, 1H, –NH), 7.22 (d, 1H, $J = 7.6$ Hz, ArH), 7.48 (d, 1H, $J = 7.6$ Hz, ArH), 7.67 (t, 1H, $J = 9.2$ Hz, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ_{ppm} 14.5, 63.7, 110.8, 111.9, 114.0, 115.5, 118.5, 122.0, 127.8, 135.9, 142.5, 146.5, 146.6, 148.2, 153.4; MS: $m/z = 254$ $[M]^+$.

2-(1*H*-Indol-3-yl)-1*H*-benzo[*d*]imidazole (Table 3, entry 6). Brown solid; mp: 299–301 °C; yield: 83%; IR (KBr): ν 3484, 3167, 3113, 3042, 2979, 1634, 1576, 1497, 1393, 1243 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} 7.20 (s, 1H, ArH), 7.29 (t, 4H, $J = 7.2$ Hz, ArH), 7.52 (d, 2H, $J = 7.6$ Hz, ArH), 8.10 (d, 2H, $J = 7.2$ Hz, ArH), 8.29 (s, 1H, –NH), 9.93 (s, 1H, –NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ_{ppm} 114.6, 116.1, 116.9, 123.8, 126.7, 127.4, 127.8, 128.2, 128.5, 130.6, 132.7, 134.2, 134.3, 135.0, 144.0; MS: $m/z = 233$ $[M]^+$.

2-(Pyridin-4-yl)-1*H*-benzo[*d*]imidazole (Table 3, entry 8). Orange solid; mp: 203–205 °C; yield: 87%; IR (KBr): ν 3350, 3050, 2981, 1593, 1501, 1452, 1271 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} 6.06 (d, 3H, $J = 6.0$ Hz, ArH), 7.22 (d, 3H, $J = 9.2$ Hz, ArH), 7.27 (t, 1H, $J = 6.0$ Hz, ArH), 7.79 (t, 1H, $J = 6.8$ Hz, ArH), 8.81 (s, 1H, –NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ_{ppm} 111.8, 113.6, 114.4, 116.3, 117.2, 118.5, 127.1, 127.3, 139.3, 152.3, 162.7; MS: $m/z = 195$ $[M]^+$.

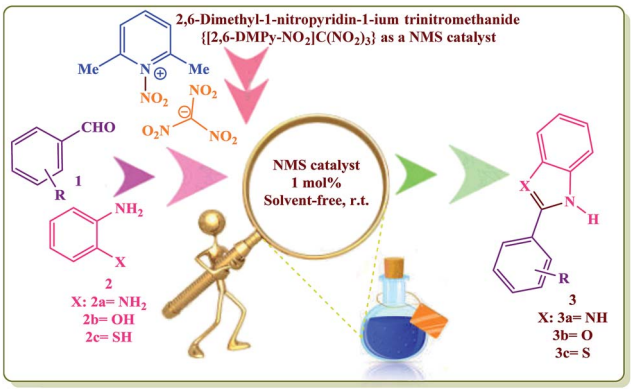
4-(1*H*-Benzo[*d*]imidazol-2-yl)benzene-1,2-diol (Table 3, entry 9). Pink solid; mp: 243–245 °C; yield: 85%; IR (KBr): ν 3412, 1693, 1610, 1451, 1285 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} 5.35 (s, 1H, –NH), 6.35 (d, 1H, $J = 8.0$ Hz, ArH), 6.39 (s, 1H, ArH), 6.65 (d, 1H, $J = 8.0$ Hz, ArH), 6.85 (d, 1H, $J = 8.4$ Hz, ArH), 7.00 (d, 1H, $J = 8.0$ Hz, ArH), 7.20 (t, 2H, $J = 7.6$ Hz, ArH), 7.35 (s, 1H, –OH), 7.65 (s, 1H, –OH); ^{13}C NMR (100 MHz, DMSO-d_6): δ_{ppm} 110.9, 113.4, 115.4, 115.5, 116.5, 116.6, 117.0, 118.7, 120.3, 121.8, 122.0, 127.7, 132.2; MS: $m/z = 226$ $[M]^+$.

Computational details

Computations were performed using the Gaussian09 program.[30] Density functional theory has been used to investigate the reactions of 2-phenyl benz-(imida, oxa and othia)-zole compounds (7) in the presence of HNO_3 and $CH(NO_2)_3$ which *in situ* have been generated from NMS catalyst. All geometry optimizations were performed at B3LYP/TZVP level of theory. Frequency calculations at the same level of theory have also been performed to identify all of the stationary points as minima with no imaginary frequencies or transition structures with one imaginary frequency. In addition, the nature of transition structures was confirmed by intrinsic reaction coordinates (IRC).[31] In order to investigate the mechanism we used the total electronic energy (E_{el} + ZPE) and the Gibbs free energies. The intramolecular interactions were calculated on the basis of natural bond orbital (NBO)[32] analyses.

Results and discussion

In continuation of our studies on development of nano-structured ionic liquids (NILs),[33] molten salts (NSMSs)[34,35] in organic synthesis, herein we wish to introduce a novel nano molten salt catalyst, namely 2,6-dimethyl-1-nitropyridin-1-ium trinitromethanide [2,6-DMPy-NO_2]C(NO_2)$_3$ (Scheme 1) for the synthesis of 2-sbstituted benz-(imida, oxa and othia)-zoles. Reaction was proceeded by using 1,2-phenylenediamine or 2-aminophenol or 2-aminothiophenol and corresponding aldehydes at room temperature under solvent-free conditions respectively (Scheme 2).



Scheme 2 Synthesis of 2-substituted benz-(imida, oxa and othia)-zoles by [2,6-DMPy-NO_2]C(NO_2)$_3$ as a NMS catalyst.

Characterization of 2,6-dimethyl-1-nitropyridin-1-ium trinitromethanide [2,6-DMPy-NO_2]C(NO_2)$_3$ as a NMS catalyst

Characterization of [2,6-DMPy-NO_2]C(NO_2)$_3$ as a nano molten salt catalyst was approved using FT-IR, ^{1}H NMR, ^{13}C NMR, mass, TG, DTG, XRD, SEM and TEM analysis.

In the FT-IR spectrum of [2,6-DMPy-NO_2]C(NO_2)$_3$ the absorption bond at 1662 cm^{-1} and 1389 cm^{-1} is connected to vibrational modes of –NO_2 bonds. Furthermore, the known peak at 3090 cm^{-1} related to C–H stretching group on 2,6-dimethyl-1-nitropyridin-1-ium ring. Also, the known peak at 3000 cm^{-1} linked to C–H stretching of methyl group on 2,6-dimethyl-1-nitropyridin-1-ium ring. The IR spectrum changes of [2,6-DMPy-NO_2]C(NO_2)$_3$ in comparison with 2,6-dimethylpyridin and tetranitromethane displayed formation of NMS catalyst (Fig. 1).

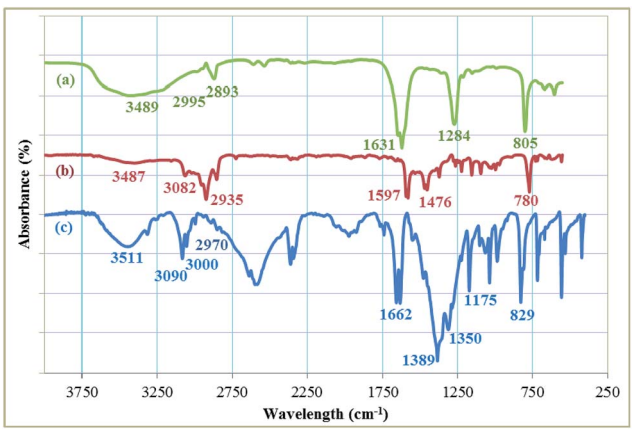


Fig. 1 The IR spectrum of tetranitromethane (a), 2,6-dimethylpyridine (b) and [2,6-DMPy-NO_2]C(NO_2)$_3$ (c).

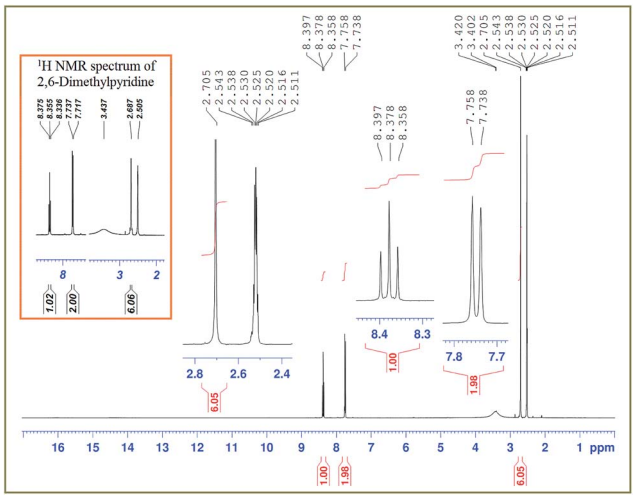


Fig. 2 The ^{1}H NMR spectrum of [2,6-DMPy-NO_2]$C(NO_2)_3$.

The ^{1}H NMR spectrum of the [2,6-DMPy-NO_2]$C(NO_2)_3$ shows a triplet at 8.39 ppm and a doublet at 7.75 ppm related to hydrogens on the aromatic ring of 2,6-dimethyl-1-nitropyridin-1-ium. Also a singlet at 2.70 ppm linked to hydrogens methyl group on the aromatic ring of 2,6-dimethyl-1-nitropyridin-1-ium. The ^{1}H NMR chemical shift changes of [2,6-DMPy-NO_2]$C(NO_2)_3$ in comparison with 2,6-dimethylpyridine displayed creation of described NMS catalyst (Fig. 2).

Appearance of five signals in the ^{13}C NMR spectrum is in accordance with the [2,6-DMPy-NO_2]$C(NO_2)_3$ structure. The important peak of ^{13}C NMR spectra of NMS catalyst is related to the $-C(NO_2)_3$ group on trinitromethanide counter ion which is identified at $\delta = 97.4$ ppm and corresponded peaks at 139.3, 160.0 and 165.9 ppm are linked to aromatic carbons of 2,6-dimethyl-1-nitropyridin-1-ium ring. Also a peak at 18.2 ppm connected to methyl group on the aromatic ring of 2,6-dimethyl-1-nitropyridin-1-ium. Furthermore the ^{13}C NMR chemical shift

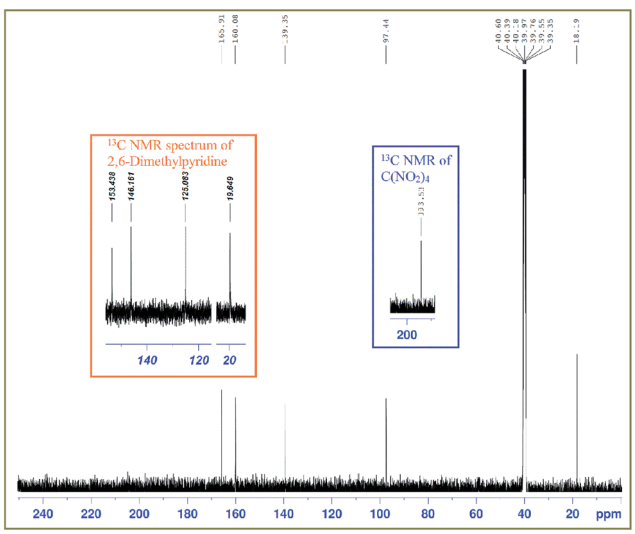


Fig. 3 The ^{13}C NMR spectrum of [2,6-DMPy-NO_2]$C(NO_2)_3$.

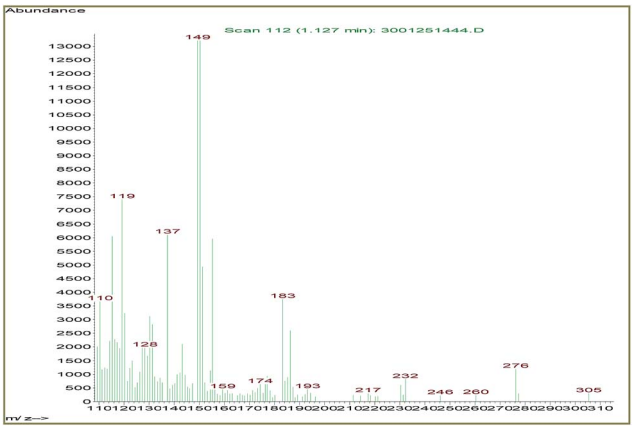


Fig. 4 The mass spectrum of [2,6-DMPy-NO_2]$C(NO_2)_3$.

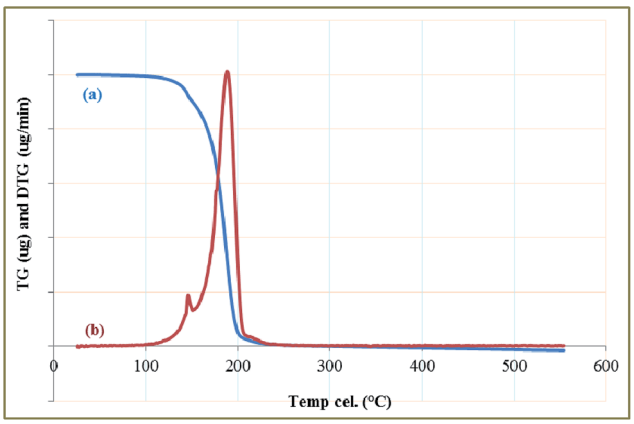


Fig. 5 The thermal gravimetric (TG) (a) and derivative thermal gravimetric (DTG) (b) analysis of [2,6-DMPy-NO_2]$C(NO_2)_3$.

changes of [2,6-DMPy-NO_2]$C(NO_2)_3$ in comparison with 2,6-dimethylpyridine and tetranitromethane obviously revealed preparation of the synthesized NMS catalyst (Fig. 3).

The mass spectrum of the [2,6-DMPy-NO_2]$C(NO_2)_3$ is in agreement with the structure of the NMS catalyst and showed

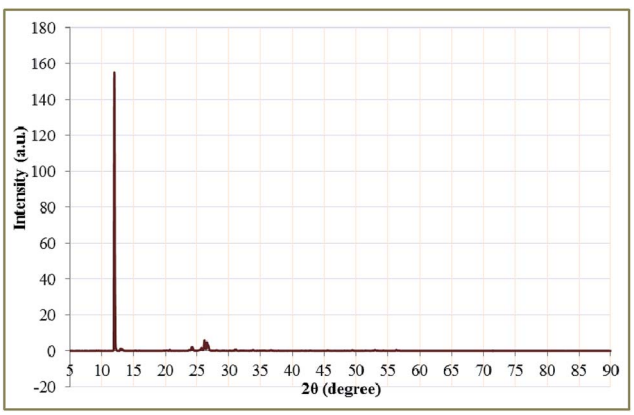


Fig. 6 The XRD pattern of {[2,6-DMPy-NO_2]$C(NO_2)_3$}.

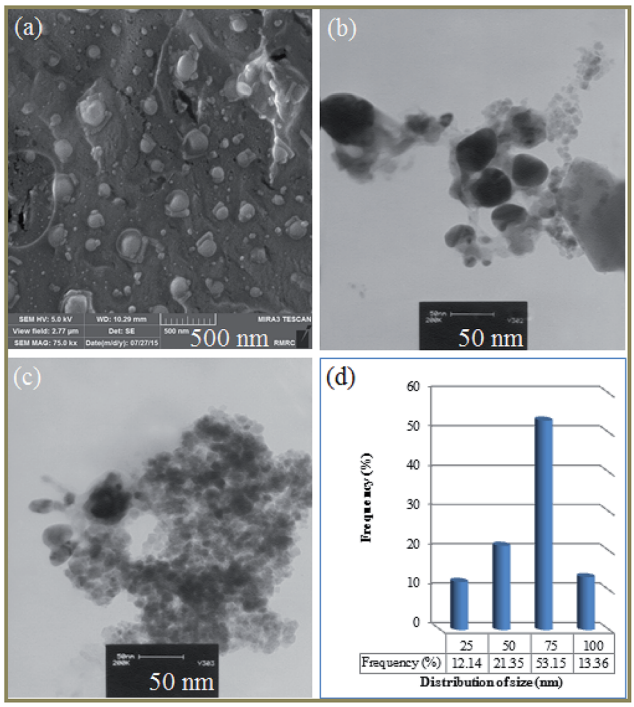


Fig. 7 Scanning electron microscopy (SEM) (a), transmission electron microscopy (TEM) (b and c) and TEM histogram (d) of [2,6-DMPy-NO_2]$C(NO_2)_3$.

Table 1 Optimization reaction between biphenyl-4-carbaldehyde and 1,2-phenylenediamine[a]

Entry	Catalyst amount (mol%)	Temperature (°C)	Time (min)	Yield[b] (%)
1	—	r.t.	120	7
2	—	100	120	11
3	0.5	r.t.	30	71
4	0.5	100	30	71
5	1	r.t.	15	94
6	1	50	15	94
7	1	75	15	94
8	1	100	15	94
9	2	r.t.	15	94
10	2	100	15	94
11	5	r.t.	15	94
12	5	100	15	94

[a] Reaction condition: biphenyl-4-carbaldehyde (1 mmol, 0.182 g), 1,2-phenylenediamine (1 mmol, 0.108 g). [b] Reaction condition: isolated yield.

the parent peak at 303 m/z. The noteworthy peak of mass spectrum of NMS catalyst is linked to trinitromethanide counter ion which is known at 150 m/z and connected peak at 153 m/z is related to 2,6-dimethyl-1-nitropyridin-1-ium ring (Fig. 4).

The thermal gravimetric (TG) analysis and derivative thermal gravimetric (DTG) of [2,6-DMPy-NO_2]$C(NO_2)_3$ as a NMS catalyst were also studied at range of 25 to 550 °C, with a temperature increase rate of 10 °C min^{-1} in a nitrogen atmosphere. The linked diagrams are displayed in Fig. 5. The first weight loss curve around 90–110 °C (3%) is related to the residual physisorbed water and organic solvents, which were applied in the catalyst synthesis. The significant weight loss of the NMS catalyst was occurred above 187 °C, which can be suitable for the catalytic uses in organic synthesis. The considerable weight loss happened in the range of 110–187 °C, is the main loss of [2,6-DMPy-NO_2]$C(NO_2)_3$. The thermal gravimetric (TG) analysis and derivative thermal gravimetric (DTG) of the NMS catalyst presented important loss in one step, and decomposed above 187 °C.

Size, shape and morphology of 2,6-dimethyl-1-nitropyridin-1-ium trinitromethanide [2,6-DMPy-NO_2]$C(NO_2)_3$ as a mild NMS catalyst was investigated by X-ray diffraction (XRD) pattern (Fig. 6), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. 7). To confirm the structure of [2,6-DMPy-NO_2]$C(NO_2)_3$, initially its XRD pattern was considered. As shown in Fig. 6, the XRD patterns of NMS catalyst expose peaks at $2\theta \approx 12.00°$, which was approved using the described value of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. 7). Peak width (FWHM), size and inter planer distance related to XRD pattern of [2,6-DMPy-NO_2]$C(NO_2)_3$ were investigated in the 12.00° degree. The average crystallite size D was studied by the Scherrer formula: $D = K\lambda/(\beta \cos \theta)$, where K is the Scherrer constant, λ being the X-ray wavelength, β is the half-maximum peak width, and θ is the Bragg diffraction angle. Consequently, the average size of the NMS catalyst achieved from this equation was found to be about 79.91 nm ($2\theta = 12.00°$; peak width [FWHM] = 0.10 degree; size = 79.91 nm; inter planer distance = 0.736645 nm), which is mainly in a good accordance with the scanning electron microscopy and transmission electron microscopy (Fig. 7). The results of TEM histogram of [2,6-DMPy-NO_2]$C(NO_2)_3$ clearly shows that particle size of NMS catalyst is scattered mainly between 50 and 75 nm.

Catalytic application of 2,6-dimethyl-1-nitropyridin-1-ium trinitromethanide [2,6-DMPy-NO_2]$C(NO_2)_3$ as a NMS catalyst

Initially, to optimize the reaction conditions, the condensation reaction between biphenyl-4-carbaldehyde and 1,2-phenylenediamine was selected as a model and different amounts of

Table 2 Solvent effect in the reaction between biphenyl-4-carbaldehyde and 1,2-phenylenediamine[a]

Solvent	Solvent-free	H_2O	C_2H_5OH	CH_3CN	CH_2Cl_2	CH_3CO_2Et	*n*-Hexane
Reaction time (min)	15	30	15	30	30	45	60
Yield (%)[b]	94	91	94	93	89	83	74

[a] Reaction condition: biphenyl-4-carbaldehyde (1 mmol, 0.182 g), 1,2-phenylenediamine (1 mmol, 0.108 g), NMS catalyst (1 mol%, 0.003 g), solvent (2 mL). [b] Reaction condition: isolated yield.

Table 3 Synthesis of 2-aryl benz-(imida, oxa and othia)-zole derivatives by using [2,6-DMPy-NO_2]$C(NO_2)_3$ as an efficient catalyst under solvent-free conditions[a]

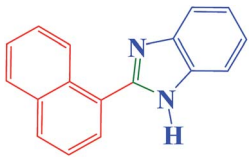
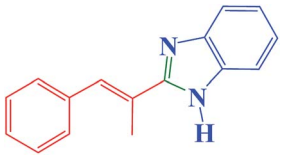
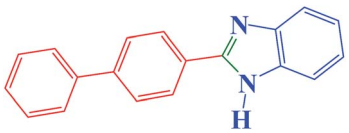
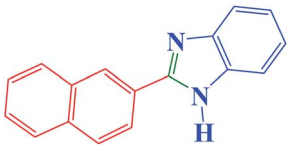
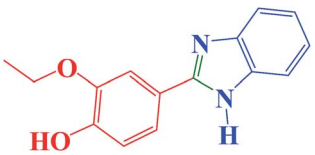
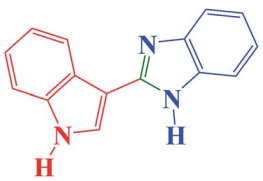
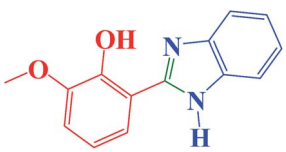
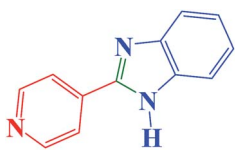
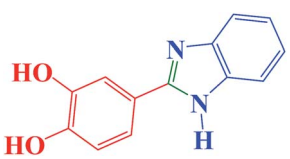
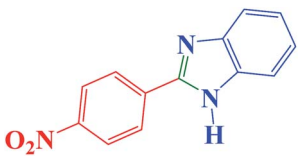
Entry	Product	Time (min)	Yield[b] (%)	Mp (°C) [Lit.][Ref.]
1		15	94	263–265 [270–272][36a] (orange solid)
2		25	87	229–231 (orange solid)
3		15	94	213–215 (yellow solid)
4		15	93	159–161 (ref. 36*b*) (yellow solid)
5		30	85	208–210 (white solid)
6		30	83	299–301 (brown solid)
7		30	85	278–280 (ref. 36*c*) (yellow solid)
8		25	87	203–205 (orange solid)
9		30	85	243–245 (pink solid)
10		10	96	313–315 [315–317][36d] (yellow solid)

Table 3 (*Contd.*)

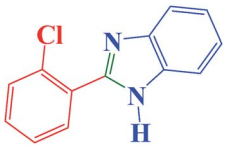
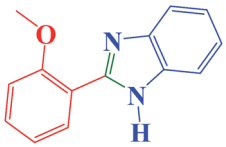
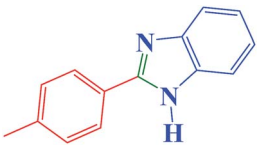
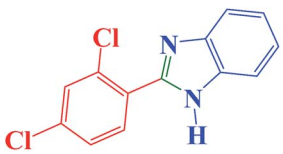
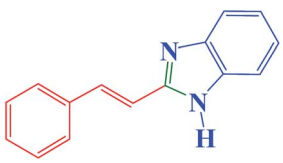
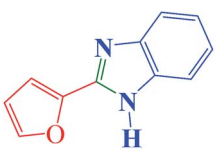
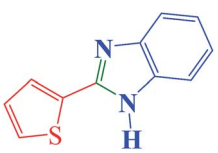
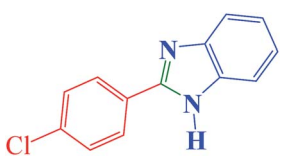
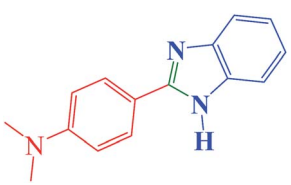
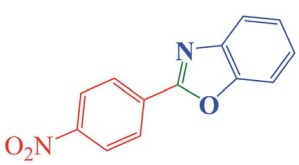
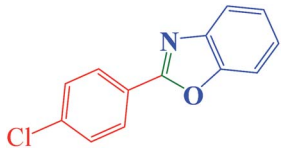
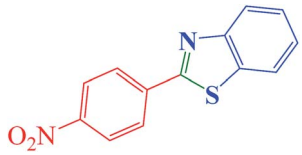
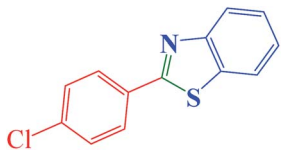
Entry	Product	Time (min)	Yield[b] (%)	Mp (°C) [Lit.][Ref.]
11		20	92	225–227 [231–233][36d] (grey solid)
12		25	90	173–175 [175–177][36e] (brown solid)
13		20	92	267–269 [268–270][36d] (yellow solid)
14		20	92	237–239 (ref. 36*b*) (yellow solid)
15		25	88	203–205 [200–201][36f] (yellow solid)
16		25	87	290–292 [283–285][36g] (yellow solid)
17		25	87	342–344 [>300][36f] (yellow solid)
18		15	95	291–293 [290–292][36d] (yellow solid)
19		25	88	235–237 [238–240][36g] (yellow solid)
20		20	93	261–263 [265–267][36h] (yellow solid)

Table 3 (*Contd.*)

Entry	Product	Time (min)	Yield[b] (%)	Mp (°C) [Lit.][Ref.]
21		25	91	147–149 [143–145][36h] (yellow solid)
22		25	91	221–223 [224–225][36i] (yellow solid)
23		30	90	121–123 [116–118][36i] (yellow solid)

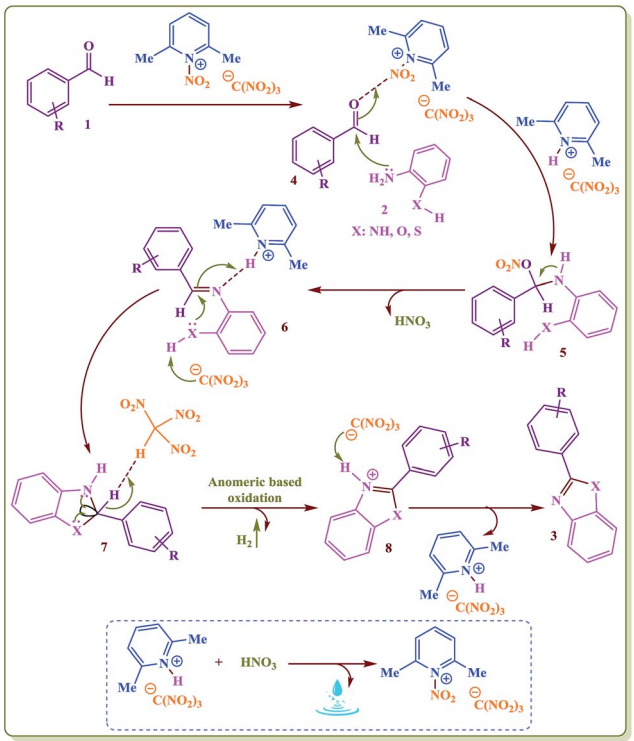
[a] Reaction condition: aldehyde (1 mmol), 1,2-phenylenediaime or 2-aminophenol or 2-aminothiophenol (1 mmol), NMS catalyst (1 mol%). [b] Reaction condition: isolated yield.

NMS catalyst at range of room temperature up to 100 °C were investigated under solvent-free conditions (Table 1). As displayed in Table 1, the best results were attained when the reaction was achieved using 1 mol% of NMS catalyst at room temperature (Table 1, entry 5). No improvement was identified in the yield of reaction *via* increasing the amount of the NMS catalyst and temperature (Table 1, entries 6–12). Table 1 clearly shows that in the absence of NMS catalyst, the product was attained in low yield after 120 min (Table 1, entries 1 and 2).

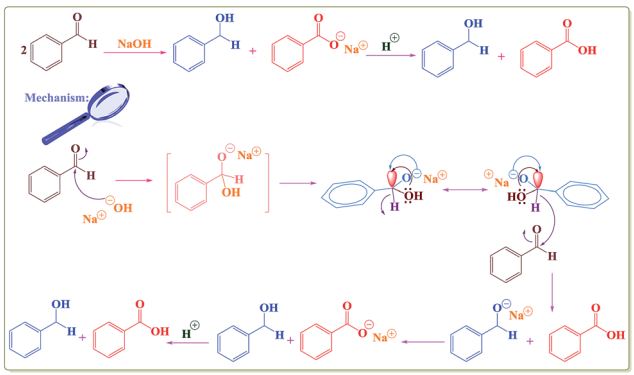
Also, to compare the result of the solution in comparison with solvent-free conditions, a mixture of biphenyl-4-carbaldehyde and 1,2-phenylenediamine as a typical reaction, by 1 mol% of NMS catalyst in various solvents for example H_2O, C_2H_5OH, CH_3CN, CH_2Cl_2, CH_3CO_2Et and *n*-hexane were studied at room temperature. From Table 2 it can be identified that this reaction under solvent-free conditions is obviously the best choice. However, in this research solvent-free condition is preferred to water and/or ethanol since solvent-free condition is green, mild, safe and cheap in comparison with solution. The obtained results (yield of product and reaction time) in polar solvent were more enhanced than nonpolar solvent due to ionic structure of NMS catalyst (the catalytic activity of NMS catalyst was improved).

After finding the optimized reaction conditions, the investigation was proceeded by completing the reaction between a series of aromatic aldehydes and 1,2-phenylenediaime or 2-aminophenol or 2-aminothiophenol. To show the common applicability of this procedure, various aromatic and hetero-aromatic aldehydes were capably reacted in the same conditions. These results stimulated us to study briefly the capability of this new process for several aromatic and hetero-aromatic aldehydes under optimized conditions. As shown in Table 3, a series of aromatic aldehydes underwent electrophilic substitution reaction with varied range of 2-aryl benz-(imida, oxa and othia)-zole derivatives in good to excellent yields. The nature and electronic properties of the substituents on the aromatic ring affect the conversion rate, and aromatic aldehydes counting electron-withdrawing groups on the aromatic ring react faster than electron-releasing groups.

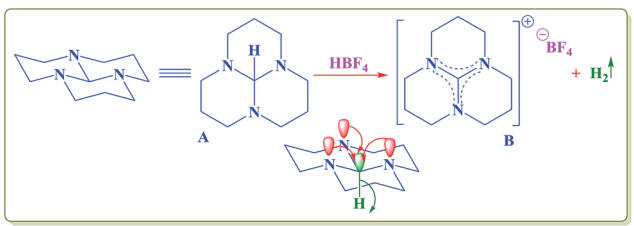
According to the previously reported method,[28,29,35] an appropriate mechanism for the synthesis of 2-aryl benz-(imida, oxa and othia)-zole derivatives (3) using [2,6-DMPy-NO_2]C(NO_2)$_3$ as a NMS catalyst was suggested (Scheme 3). Firstly, 1,2-phenylenediaime or 2-aminophenol or 2-aminothiophenol (2) attack to aldehyde (4), which is activated with the [2,6-DMPy-NO_2]C(NO_2)$_3$ as a NMS catalyst to form imine intermediate (6) by removing one molecule of HNO_3. Then, intermediate (7) is produced *via* intra-molecular cyclization and proton exchange of imine intermediate (6). Finally, intermediate (7) *via* anomeric based oxidation was transferred to 2-aryl benz-(imida, oxa and othia)-zoles (3).[36] Previous studies have proposed aerobic auto oxidation for conversion of intermediate (7) to its corresponding 2-aryl benz-(imida, oxa and othia)-zoles (3).[37] In contrast to the previously reported mechanistic explanation for the final step of the above described organic synthesis,[37] we believed that, this step might be a progress by uncommon hydride transfer as well as Cannizzaro reaction (Scheme 4)[38] and H_2 releasing from tricyclic orthoamide (Scheme 5).[39] Recently, we have suggested an anomeric based oxidation for the final step for the synthesis of 1,4-dihydropyrano-[2,3-*c*]-pyrazole,[28a] 2,4,6-triarylpyridine derivatives[28b] and 2-amino-3-cyanopyridines[29] (Schemes 6–8). To achieve this goal, reaction was performed under nitrogen atmosphere and in the absence of any molecular oxygen. We observed that, the reaction progressed in the



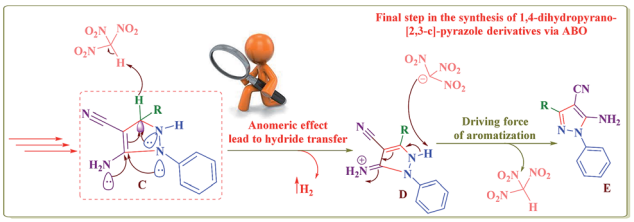
Scheme 3 The proposed mechanism for the synthesis of 2-aryl benz-(imida, oxa and othia)-zole derivatives by {[2,6-DMPy-NO_2]$C(NO_2)_3$} as a NMS catalyst.



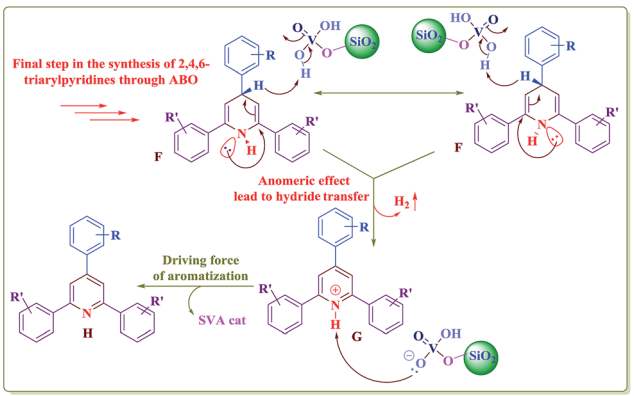
Scheme 4 The proposed mechanism for the *in situ* oxidation–reduction in Cannizzaro reaction through unusual hydride transfer *via* ABO.[38]



Scheme 5 A striking example which had been observed for an unusual hydride transfer from tricyclic orthoamide (A) through ABO.[39]

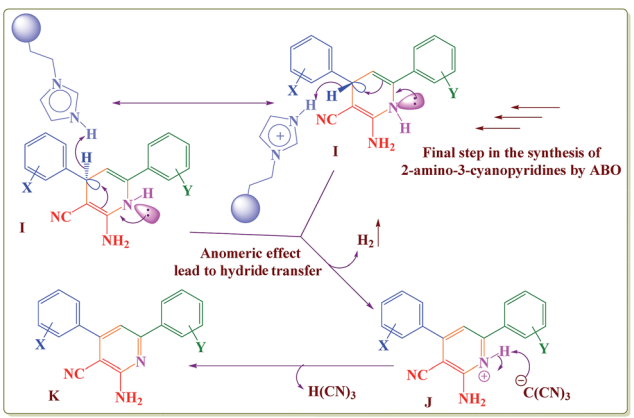


Scheme 6 Synthesis of 1,4-dihydropyrano-[2,3-*c*]-pyrazole derivatives *via* ABO.[28a]

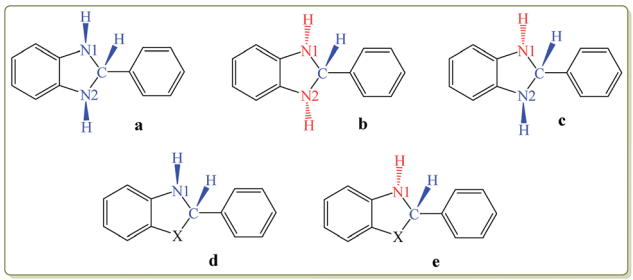


Scheme 7 The synthesis of 2,4,6-triarylpyridines through ABO.[28b]

absence of any oxygen molecules and under nitrogen atmosphere. This fact approves that the oxidation of intermediate (7) to its corresponding 2-aryl benz-(imida, oxa and othia)-zoles (3) did not need the oxygen in the air. By studying the above-mentioned evidence, conversion of intermediate (7) to its corresponding products (3) might be carried out using unusual hydride transfer and releasing of molecular hydrogen (H_2). The C–H bond is so weakened *via* electron donation from the nitrogen's lone pairs into the anti-bonding of C–H (σ^*_{C-H} orbital) which can be broken *via* reaction with a proton to afford molecular hydrogen. Most recently, we introduced a new term for this phenomenon entitled "anomeric based oxidation"



Scheme 8 The synthesis of 2-amino-3-cyanopyridines by ABO.[29]



Scheme 9 Different conformers considered for 2-phenyl benz-(imida, oxa and othia)-zole intermediates 7.

(ABO). The major reason of ABO is driving force of aromatization which will be supported *via* stereo electronic and/or anomeric effect.

Density functional theory has been used to investigate the "anomeric based oxidation" (ABO) for the final step in mechanistic process for the synthesis of 2-phenyl benz-(imida, oxa and othia)-zole. Starting from 7, three different orientations of two N–H and adjacent C–H groups on imidazole intermediate 7 with respect to each other and also two different orientations of adjacent N–H and C–H groups on oxazole and thiazole intermediates 7 give a to e conformers (Scheme 9). Our calculations show that the difference in stability between the conformers of one defined structure is less than 0.6 kcal mol^{-1} for all of the compounds (for more details see ESI†). So, Fig. 8 shows energy profile only for conformer a of imidazole intermediate 7 and d of oxazole and thiazole intermediates 7. As illustrated in Fig. 8, by addition of $CH(NO_2)_3$ moiety of NMS catalyst through the formation of transition structures, TS-N, TS-O and TS-S, and then removing the molecular hydrogen (H_2) the intermediate 8 will be formed for all of 2-phenyl benz-(imida, oxa and othia)-zole compounds 3. According to values of calculated Gibbs free energies, this reaction for intermediate 8 is about −2.68 kcal mol^{-1} exothermic but for oxazole and thiazole intermediates 8 are respectively 8.32 and 11.32 kcal mol^{-1} endothermic.

In the final step of the reaction the intermediate 8 converts into 2-phenyl benz-(imida, oxa and othia)-zole (3) through an exothermic process (ΔG = −13.00, −19.75 and −20.93 kcal mol^{-1} for benzimidazole, benzoxazole and benzothiazole, respectively). In conclusion, the whole process of conversion of 7 to 3 through the releasing molecular hydrogen for all of 2-phenyl benz-(imida, oxa and othia)-zole is exothermic (ΔG = −15.92, −11.44 and −9.81 kcal mol^{-1}, respectively).

Intriguingly, we found that the released HNO_3 during the formation of intermediate 6, operates similar to $CH(NO_2)_3$ moiety of NMS catalyst, so the formation of 2-phenyl benz-(imida, oxa and othia)-zole compounds occurs using release of hydrogen molecule (Fig. 9). Comparison of the energy profiles given in Fig. 8 and 9 shows that there are similar amounts of $\Delta G^{\ddagger}$ for both $CH(NO_2)_3$ and HNO_3 groups in all reactions. However, in the presence of HNO_3, in contrast to $CH(NO_2)_3$, the final step that corresponds to the formation of 2-phenyl benz-(imida and oxa)-zole 3 through intermediate 8 is endothermic (ΔG = 1.89, 0.11 and −1.89 kcal mol^{-1} for benzimidazole, benzoxazole and benzothiazole, respectively).

The important step of anomeric based oxidation is the direct elimination of H_2 molecule from intermediate 7 and $CH(NO_2)_3$ or HNO_3 catalyst (Fig. 8 and 9) in which the C–H bond in

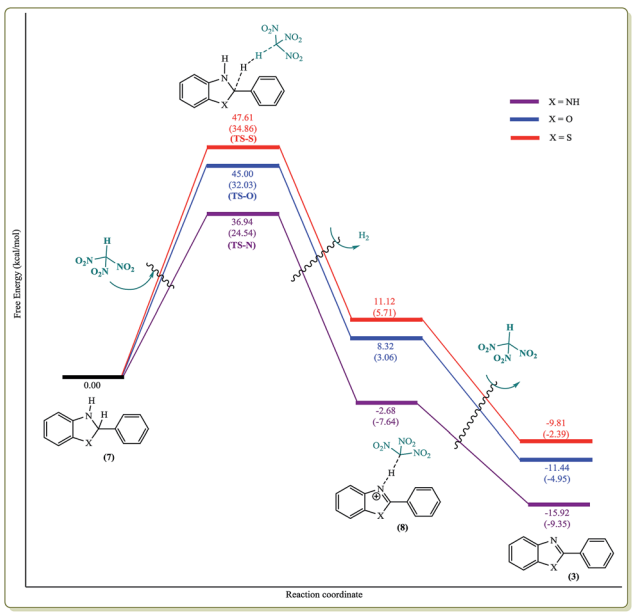


Fig. 8 Energy profile calculated for synthesis of 2-phenyl benz-(imida, oxa and othia)-zole (3) by $CH(NO_2)_3$ moiety of NMS catalyst beginning from compound 7 (see Scheme 4). The relative Gibbs free energies and the total electronic energies (E_{el} + ZPE, figures in parentheses) obtained from the B3LYP/TZVP calculations both are given in kcal mol^{-1}.

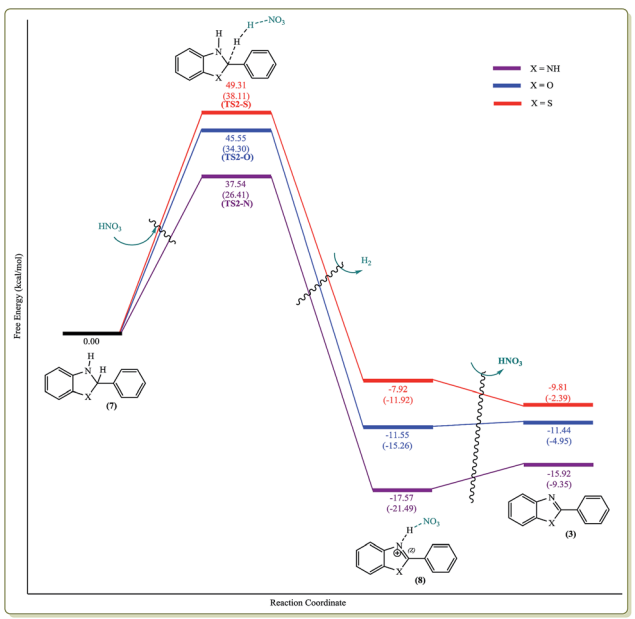
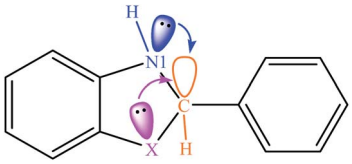


Fig. 9 Energy profile calculated for synthesis of 2-phenyl benz-(imida, oxa and othia)-zole (3) by HNO_3 beginning from compound 7 (see Scheme 4). The relative Gibbs free energies and the total electronic energies (E_{el} + ZPE, figures in parentheses) obtained from the B3LYP/TZVP calculations both are given in kcal mol^{-1}.

Table 4 The main second order perturbation energies (kcal mol^{-1}) calculated for different conformers of imidazole, oxazole and thiazole intermediates 7

Compounds	Conformer	LP N1 → σ^*_{C-H}	LP X → σ^*_{C-H} X = N, O and S	Total
	a	6.35	6.35	12.70
Imidazole	b	4.92	4.92	9.84
	c	5.09	4.84	9.95
Oxazole	d	5.84	7.06	12.90
	e	4.39	6.30	10.69
Thiazole	d	7.48	3.88	11.36
	e	5.09	3.18	8.27



compound 7 is so weakened due to the delocalization of lone pair of X atoms (X = N, O or S atoms) to σ^*_{C-H} bond (the anomeric effect) and therefore the activation energy is relatively minor. The NBO analysis of donor–acceptor interactions which are shown in Table 4 identified that the anomeric effect due to delocalization of lone pair of X atoms to σ^*_{C-H} bond for conformer a of imidazole and conformer d of oxazole and thiazole intermediates 7 are maximum and are 12.70, 12.90 and 11.36 kcal mol^{-1}, respectively.

Thus the above theoretical studies support our suggested mechanism and shows that releasing molecular hydrogen (H_2) is quite possible in such systems. The Cartesian atomic coordinates of all compounds involved in our suggested mechanism are available in ESI.† In theoretical calculations, the solvent effect was not investigated, because the reaction was performed under solvent-free conditions.

The reusability of the [2,6-DMPy-NO_2]C(NO_2)$_3$ as a NMS catalyst is an important advantage for any catalytic system. For this purpose, the reaction between biphenyl-4-carbaldehyde and 1,2-phenylenediamine was selected as a typical reaction by NMS catalyst. After completion of the reaction (identified by TLC), ethyl acetate was added to the reaction mixture and heated to extract product from remained starting materials. This solution was washed with water to separate NMS catalyst from other materials (the product is soluble in hot ethyl acetate and NMS catalyst is soluble in water). The aqueous layer was decanted, separated and applied for alternative reaction after removing water. It is recognized that the catalytic activity of the NMS catalyst was restored within the limits of the experimental errors for five continuous runs. The recycled catalyst was also characterized by FT-IR spectrum after its application in the reaction. This spectrum was the same as those of the fresh catalyst. The deactivation of the NMS catalyst is low. The reaction was scaled up to 10 mmol of biphenyl-4-carbaldehyde and 1,2-phenylenediamine using 10 mol% of NMS catalyst at room temperature. The yield of the reaction was 94% after 15 min and 84% after the fourth run. The results were summarized in Fig. 10.

Also in using [2,6-DMPy-NO_2]C(NO_2)$_3$ as a NMS catalyst in the synthesis of benzimidazole (a), benzoxazole (b) and benzothiazole (c) derivatives, we investigated the efficacy of various catalysts for approving suggested mechanism and ABO. To optimize the reaction conditions, the reaction between 4-chlorobenzaldehyde and 1,2-phenylenediaime or 2-aminophenol or 2-aminothiophenol under N_2 atmosphere at room temperature was applied as a typical procedure (Table 5).

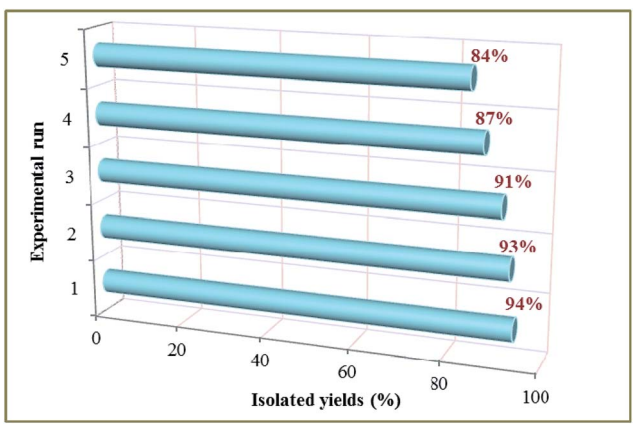


Fig. 10 Reusability investigations of [2,6-DMPy-NO_2]C(NO_2)$_3$ as a NMS catalyst for the reaction between biphenyl-4-carbaldehyde and 1,2-phenylenediamine in 15 min.

Table 5 The synthesis of benzimidazole, benzoxazole and benzothiazole derivatives by various catalysts for approving of suggested mechanism and ABO[a]

Entry	Catalyst	Catalyst loading	Time (min) a	Time (min) b	Time (min) c	Yield[b] (%) a	Yield[b] (%) b	Yield[b] (%) c
1	NMS catalyst	1 mol%	15	25	30	95	91	90
2	HBF_4	5 mol%	30	45	60	87	72	70
3	$Fe(HSO_4)_3$	10 mol%	30	45	60	73	55	51
4	$Ca(HSO_4)_2$	10 mol%	30	45	60	45	31	28
5	$Zn(HSO_4)_2$	10 mol%	30	45	60	51	37	33
6	Oxone	5 mol%	30	45	60	57	42	40
7	$Ce(HSO_4)_3 \cdot 7H_2O$	10 mol%	30	45	60	63	47	45
8	$Al(HSO_4)_3$	10 mol%	30	45	60	58	44	41
9	$Bi(HSO_4)_3$	10 mol%	30	45	60	48	35	30
10	CeO_2	10 mol%	30	45	60	67	53	49
11	PbO_2	10 mol%	30	45	60	41	36	32

[a] Reaction conditions: 4-chlorobenzaldehyde (1 mmol) and 1,2-phenylenediaime, 2-aminophenol and 2-aminothiophenol (1 mmol), under N_2 atmosphere, r.t. [b] Reaction conditions: isolate yield.

Table 6 Comparison of the results in the synthesis of typical product by [2,6-DMPy-NO_2]C$(NO_2)_3$ as a NMS catalyst with those reported catalysts in the literature

Entry	Reaction condition	Catalyst loading	Time (min)	Yield (%)	Ref.
1	NMS catalyst, solvent-free, r.t.	1 mol%	15	95	This work
2	[Msim]Cl, EtOAc, 60 °C	10 mol%	13	89	36*d*
3	[Dsim]Cl, EtOAc, 60 °C	10 mol%	8	93	36*d*
4	Boric acid, H_2O, r.t.	0.1 g	15	93	36*b*
5	$BF_3 \cdot OEt_2$, r.t.	0.1 mmol	30	89	40*a*
6	Cu/C, EtOH, r.t.	5 mol%	300	90	40*b*
7	TBAF, H_2O, ultrasonic irradiation	5 mol%	45	88	36*a*
8	Glycerol : H_2O, 90 °C	5 : 2 mL	180	75	40*c*
9	Scolecite, EtOH, 90 °C	3 wt%	60	94	36*f*
10	CAN, PEG, 50 °C	5 mol%	90	94	36*c*
11	$CuSO_4$, EtOH, 60 °C	0.01 mmol	60	78	40*d*
12	H_5IO_6–SiO_2, CAN, r.t.	0.2 mmol	20	84	40*e*
13	Acetic acid, reflux	20 mL	240	46	40*f*

To compare the efficiency of described catalyst with some of those reported catalysts by other researchers in the literature for the synthesis of benzimidazole derivatives, we have presented the results of those reported catalysts for the condensation of 4-chlorobenzaldehyde and 1,2-phenylenediaime in Table 6. As Table 6 presents, the [2,6-DMPy-NO_2]C$(NO_2)_3$ as a NMS catalyst has significantly improved the synthesis of product in different terms.

Conclusion

In summary, naval, mild and recyclable 2,6-dimethyl-1-nitropyridin-1-ium trinitromethanide [2,6-DMPy-NO_2]C$(NO_2)_3$ as nanostructured molten salt (NMS) was designed, synthesized and fully characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, mass, thermal gravimetric (TG), derivative thermal gravimetric (DTG), X-ray diffraction patterns (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis. Catalytic application of [2,6-DMPy-NO_2]C$(NO_2)_3$ was studied in the synthesis of 2-aryl benz-(imida, oxa and othia)-zole derivatives *via* the condensation reaction between various aromatic aldehyde and 1,2-phenylenediamine or 2-aminophenol or 2-amino-thiophenol at room temperature under solvent-free conditions. The advantages of this investigation are simplicity of product isolation, cleaner reaction profile, short reaction time, high yield, reusability of the NMS catalyst. A mechanistic method was also suggested for the final step of 2-aryl benz-(imida, oxa and othia)-zoles synthesis which was supported by theoretical investigations.

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