



NANO BISMUTH MOLYBDATE FOR PHOTO-CATALYTIC SYNTHESIS OF IMIDAZO [1, 2-A] PYRIDINES USING 2-AMINOPYRIDINES AND PHENACYL BROMIDE IN AQUEOUS CONDITIONS

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ABSTRACT

An efficient and green method for synthesis of imidazo[1,2-a]pyridines from 2-aminopyridines and ketones has been developed using a nano photo-catalyst, Bi_2MoO_6 , under UV and visible light illumination in the absence of any ligands and additives. This strategy was compatible with a large range of substrates, including unactivated aryl ketones and unsaturated ketones and went through the C–H bond functionalization mechanism instead of Γ -assisted Ortoleva-King reaction to provide the corresponding imidazo[1,2-a]pyridines in good yields with low catalyst loading (1.2 mol%). Moreover, the heterogeneous catalyst can be successfully employed in gram-scale synthesis and reused many times without the significant loss of catalytic activity.

Key words: Imidazo[1,2-a]pyridines, Nano particles, Bismuth Molybdate, Phenacyl bromide, Amino pyridine, Photo-catalyst

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1. INTRODUCTION

Natural Products containing Imidazo[1,2-a]pyridine ring system has very important role in medicinal Chemistry. Imidazo[1,2-a]pyridine is a bicyclic system with a bridgehead nitrogen atom. It was first described by Chichibabin in 1925 [1]. Imidazo[1,2-a]pyridine is currently the object of renewed interest as demonstrated by the number of recent patents concerning this series. Imidazo[1,2-a]pyridines (IPs) have received considerable interest from the

pharmaceutical industry because of their interesting therapeutic properties [2], including antibacterial [3], antifungal [4], antiviral [5], antiulcer [6] and anti-inflammatory behavior [7]. They have also been characterized as selective cyclin-dependent kinase inhibitors [8], calcium channel blockers [9], β -amyloid formation inhibitors [10] and benzodiazepine receptor agonists [11] and they constitute a novel class of orally active nonpeptide bradykinin B2 receptor antagonists [12]. Among the commercialized Imidazo[1,2-*a*]pyridines, some are given in Fig 1. Zolpidem 1 was the first reaching the market as a hypnotic drug. This compound is the most widely used in treating insomnia in the world [13]. Alpidem 2, a peripheral benzodiazepine receptor ligand, was marketed as an anxiolytic agent [14]. Zolimidine 3 was marketed notably as an anti-ulcer agent [15]. Olprinone 4, a phosphodiesterase 3 (PDE 3) inhibitor is used for treating acute heart failure [16]. SCH 28080 5 has been described as a reversible proton pump inhibitor [17].

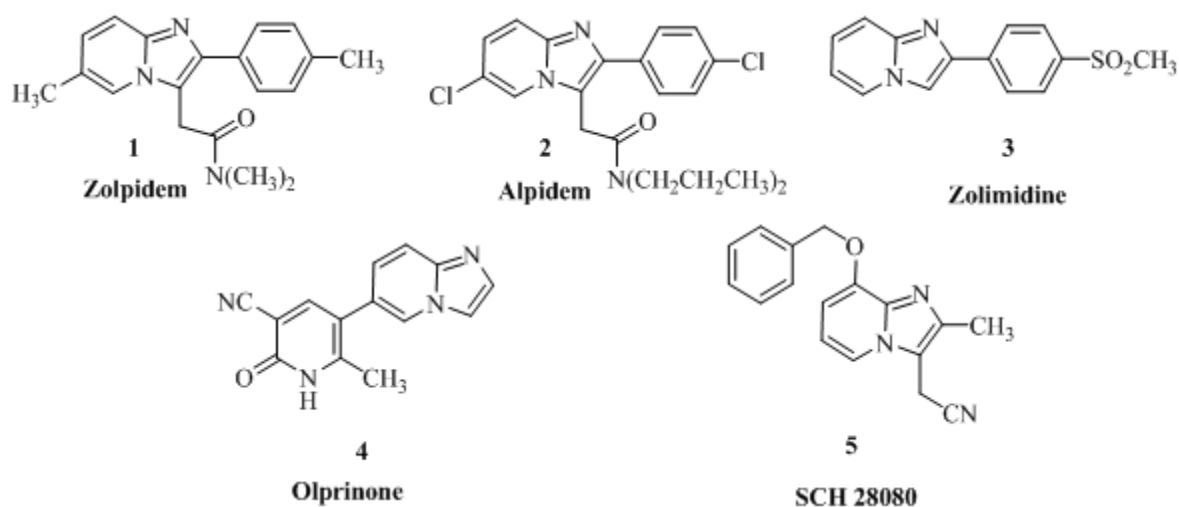


Figure 1 Some of the commercially available Imidazo[1,2-*a*]pyridines as drugs

Many approaches were adopted to synthesize a variety of Imidazo[1,2-*a*]pyridines. Some of those strategies involved the use of catalysts [18] while others employed catalyst free conditions [19]. An efficient method to prepare 2,3-diarylimidazo[1,2-*a*]pyridines which involves a Suzuki cross-coupling reaction followed by a direct arylation at position 3 was reported by S. Marhadour et. al. [20]. A direct preparation of imidazo[1,2-*a*]pyridines from alcohols in good to moderate yields by the successive treatment with iodosylbenzene and *p*-toluenesulfonic acid monohydrate, followed by 2-aminopyridine, respectively [21]. Adib, Mehdi et al reported [22] novel and efficient synthesis of imidazo[1,2-*a*]pyridines from the addition of pyridines to α -bromoketones, by nucleophilic addition of ammonium acetate under microwave irradiation and solvent-free conditions to afford the corresponding imidazo[1,2-*a*]pyridines in excellent yields.

The ready availability, relative stability and facile decomposition of α -bromocarbonyl compounds under thermal, photochemical, acid, base and transition metal catalysis conditions make them useful intermediates in organic synthesis [21]. These reactions are chemoselective, which allow new carbon-carbon and carbon-hetero atom bond formation under mild conditions [22]. Here we report an efficient method for the synthesis of substituted Imidazo[1,2-*a*]pyridines via the coupling of 2-aminopyridines and α -Bromoketones using a nano photo-catalyst (Bismuth Molybdate) and water as solvent under UV or Visible light illumination, as per scheme 1 (Fig.2).

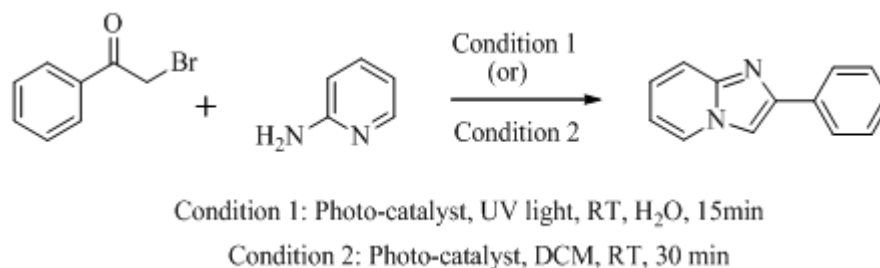


Figure 2 Scheme for the synthesis of Imidazo[1,2-*a*]pyridines

2. EXPERIMENTAL METHODS

2.1. Preparation of Nano sized Bismuth Molybdate: Bi₂MoO₆ was synthesized by the solution combustion method using citric acid (S.D. Fine-Chem Ltd., India, 99%) as a fuel. Bi(NO₃)₃·6H₂O and (NH₄)₆Mo₇O₂₄·4H₂O (S.D. Fine-Chem Ltd., India, 99%) were taken as the precursors. Bi(NO₃)₃·6H₂O and Eu₂O₃ were dissolved in 5(M) nitric acid to make clear solution and (NH₄)₆Mo₇O₂₄·4H₂O was dissolved in double distilled water. Both were mixed in a beaker and stirred with magnetic stirrer. Stoichiometric amount of fuel was added to the clear solution and the resulting mixture was kept in a hot plate maintained at 300 °C. When citric acid undergoes combustion with precursors, it produces heat that is absorbed by the precursors leading to better chemical reaction. After the combustion reaction, the product was sintered in a muffle furnace at 500, 600 & 700 °C for 5 h each to obtain pure γ(L)-Bi₂MoO₆.

2.2. Synthesis of Imidazo[1, 2-*a*]pyridines: A mixture of α-bromo acetophenone (1 mmol, 197mg), 2-amino pyridine(1.1 mmol, 103 mg) and the nano-catalyst (100 mg) were mixed together in a round flask in water or DCM (5 mL). The reaction was carried out by illuminating (i) UV light at RT for 15 min. or (ii) Visible light at RT for 30 min. After being illuminated by desired lamp sources the stirred reaction mixture was allowed to settle down, by switching off the corresponding lamp. The solid precipitate was isolated by filtration and the resulting product was purified by column chromatography (60–120 silica gel mesh) using EtOAc:hexane mixture to afford pure imidazo[1,2-*a*]pyridine. The recovered filtrate was tested for reuse for subsequent reactions.

3. CHARACTERIZATION

The as prepared Bi₂MoO₆ nano catalyst was characterized by powder XRD for detecting the phase formation. Powder XRD patterns show, phase pure orthorhombic γ(L)-Bi₂MoO₆ formation without any impurities. The morphology and particle size of Bi₂MoO₆ was further contemplated by examining the SEM images of the sample. The SEM pictures of nano-particles plainly demonstrate that Bi₂MoO₆ nano-particles have flake like structure. A representative SEM image is shown in Fig. 3.

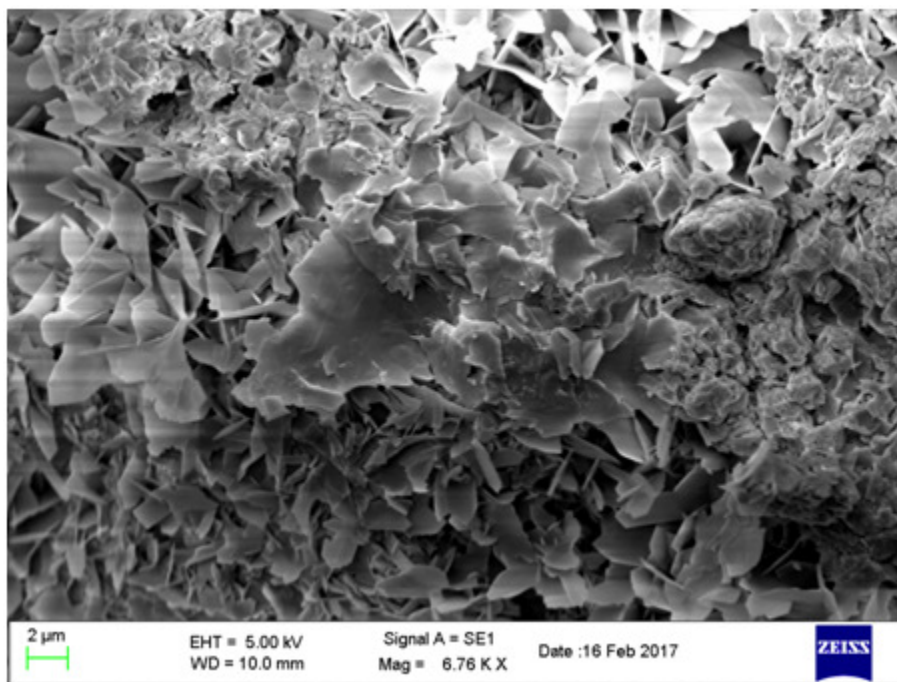


Figure 3 SEM image of nano-photocatalyst Bi_2MoO_6 with flake like morphology

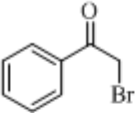
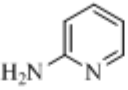
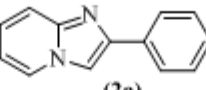
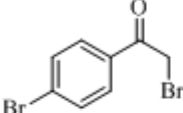
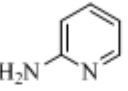
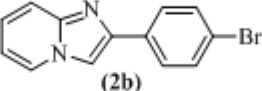
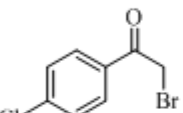
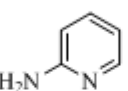
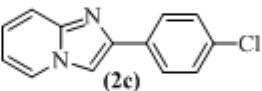
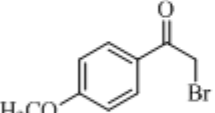
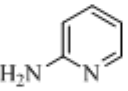
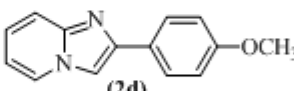
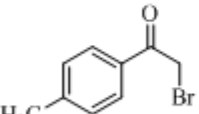
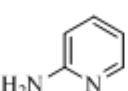
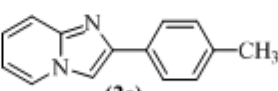
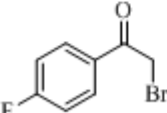
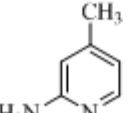
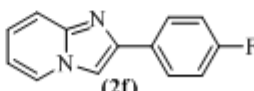
The resulting compounds obtained as per scheme 1, were characterized by IR, ^1H NMR and mass spectral data. The catalyst was also characterized before reuse.

4. RESULTS AND DISCUSSION

In our study, various α -bromo ketones reacted smoothly with several 2-aminopyridines to give the corresponding 2-aryl Imidazo[1,2-a]pyridine derivatives as the products (Table 1) of nitrogen insertion. The structures of the products were established by ^1H NMR, ^{13}C NMR, IR and high resolution mass spectroscopy (HRMS). In the absence of photo-catalyst, the reaction proceeded very slowly and by carrying out the experiment at 80°C for 80 min. gave only nearly 40 % yield (reaction between phenacyl bromide and 2-amino pyridine). In the presence of photo-catalyst (nano-Bismuth molybdate), in all cases (entries 1-6 in Table 1), the reactions proceeded efficiently in the above conditions and the products were obtained in high yields with high selectivity.

Interestingly, the reaction condition 1 (UV light, RT and Water as solvent) resulted in quick product formation with a reaction time of 15 min. for the percentage yields of nearly 90 to 95 %, while the reaction condition 2 (Visible light, RT and DCM as solvent) took little more time i.e. around 30 min. for nearly the same percentage yield. Paplal et al. [23,24] have used Bi_2WO_6 nanoparticle as heterogeneous catalysts, for the synthesis of functionalized dihydropyridines, polyhydroquinolines, 4H-chromenes and 1,2,3-triazoles etc. at ambient temperature in aqueous medium and reported good to excellent yields in 10-45 min. in the presence of the catalyst.

Table 1 Products formed from α -Bromo ketones & 2-amino pyridines under conditions 1 & 2 with their time of reaction and corresponding yields

S.No.	α -Bromo Ketone	2-Amino Pyridine	Product ^a	Condition 1 Time(min) Yield(%) ^b	Condition 2 Time(min) Yield(%) ^b
(1)			 (2a)	15 98	30 96
(2)			 (2b)	16 98	32 97
(3)			 (2c)	15 91	31 90
(4)			 (2d)	15 96	33 96
(5)			 (2e)	17 97	30 94
(6)			 (2f)	15 92	32 91

^aAll products were characterized by IR, ¹H NMR and mass spectroscopy.^bYield refers to pure products after column chromatography.Condition 1: Photo-catalyst, H₂O, UV-light, RT, 15 min

Condition 2: Photo-catalyst, DCM, RT, 30 min

The products were analyzed by IR, ¹H NMR and mass spectral data. The ¹H NMR and mass spectral data of the products is presented below.

4.1. 2-Phenylimidazo[1,2-a]pyridine (2a): White colour solid; mp 131–133 °C; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 6.74 (t, 1H, J = 6.7 Hz, Ar-H), 7.14 (dd, 1H, J = 6.7, 9.0 Hz, Ar-H), 7.30 (d, 1H, J = 7.5 Hz, Ar-H), 7.40 (t, 2H, J = 7.5 Hz, Ar-H), 7.63 (d, 1H, J = 9.0 Hz, Ar-H), 7.82 (s, 1H), 7.91 (d, 2H, J = 7.5 Hz, Ar-H), 8.09 (d, 1H, J = 6.7 Hz, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 108.1, 116.2, 117.4, 124.7, 125.5, 126.0, 127.9, 128.7, 131.9, 145.6; MS (ESI) m/z : 195 (M+H)⁺; HRMS (ESI) Calcd for C₁₃H₁₁N₂ (M+H)⁺: 195.0922; found, 195.0924.

4.2. 2-(4-Bromophenyl)imidazo[1,2-a]pyridine (2b): White colour solid; mp 210–212 °C; ¹H NMR (CDCl₃) δ (ppm) 6.80 (dt, 1H, J = 1.2, 6.8 Hz, Ar-H), 7.19 (t, 1H, J = 8.0 Hz, Ar-H), 7.54–7.58 (m, 2H, Ar-H), 7.63 (dd, 1H, J = 0.8, 9.2 Hz, Ar-H), 7.81–7.85 (m, 2H, Ar-H), 7.86 (s, 1H, Ar-H), 8.12 (td, 1H, J = 1.2, 6.8 Hz, Ar-H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 108.2, 112.6, 117.5, 121.9, 125.0, 125.6, 127.5, 131.8, 132.5, 144.5, 145.6; MS (ESI) m/z 274

(M+2H)⁺, 272 (M+H)⁺; HRMS (ESI) Calcd for C₁₃H₁₀BrN₂ (M+H)⁺: 273.0022; found, 271.0029.

4.3. 2-(4-Chlorophenyl)imidazo[1,2-a]pyridine (2c): White colour solid; mp 204-207 °C; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 6.77 (dt, 1H, J₁=6.8, J₂=1.5, Ar-H), 7.11-7.20 (m, 1H, Ar-H), 7.23-7.29 (m, 1H, Ar-H), 7.30-7.37 (m, 1H, Ar-H), 7.61 (1H, J =9.1, Ar-H), 7.77-7.85 (m, 2H, Ar-H), 7.90-7.93 (m, 1H, Ar-H), 8.10 (d, 1H, J=6.8, Ar-H); ¹³CNMR (75 MHz, CDCl₃) δ (ppm) 108.1, 112.5, 117.4, 124.9, 125.5, 127.2, 128.8, 132.1, 133.6,144.5, 145.6; MS (ESI) m/z 229 (M+H)⁺; HRMS (ESI) Calcd for C₁₃H₁₀ClN₂ (M+H)⁺: 229.0533; found, 229.0545.

4.4 2-(4-Methoxyphenyl)imidazo[1,2-a]pyridine (2d) : Yellow colour solid; mp 137-138 °C; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 3.84 (s, 3H), 6.74 (dt, 1H, J = 0.8, 6.8 Hz, Ar-H), 6.97 (d, 2H, J = 9.2 Hz, Ar-H), 7.14 (t, 1H, J = 6.8 Hz, Ar-H), 7.60 (d, 1H, J = 9.0 Hz, Ar-H), 7.76 (s, 1H, Ar-H), 7.88 (d, 2H, J = 9.6 Hz, Ar-H), 8.08 (td, 1H, J = 1.2, 6.8 Hz, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 55.2, 107.1, 112.1, 114.1, 117.2, 124.3, 125.4, 126.4, 127.2, 145.6, 159.5; MS (ESI) m/z 225 (M+H)⁺; HRMS (ESI) Calcd for C₁₄H₁₃N₂O (M+H)⁺: 225.1022; found, 225.1027.

4.5. 2-p-Tolylimidazo[1,2-a]pyridine (2e): White colour solid; mp 144-145 °C; ¹H NMR (300MHz, CDCl₃) δ (ppm) 2.38 (s, 3H, Ar-CH₃), 6.73 (t, J = 6.9 Hz, 1H, Ar-H), 7.13 (t, J = 7.8 Hz, 1H, Ar-H), 7.24 (d, J = 8.4 Hz, 2H, Ar-H), 7.6 (d, J = 9.0 Hz, 1H, Ar-H), 7.79 (s, 1H, Ar-H), 7.84 (d, J = 8.4 Hz, 2H, Ar-H), 8.06 (d, J = 7.8 Hz, 1H, Ar-H); ¹³C NMR δ (ppm) 21.3, 107.7, 112.2, 117.3, 124.5, 125.4, 125.8, 129.4, 130.8, 137.7, 145.5,145.8; MS (ESI) m/z 209 (M+H)⁺; HRMS (ESI) Calcd for C₁₄H₁₃N₂ (M+H)⁺: 209.1073; found, 209.1072.

4.5. 2-(4-Fluorophenyl)imidazo[1,2-a]pyridine (2f): Yellow colour solid; mp 159-162 °C; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 6.82 (dt, J = 0.8, 6.8 Hz, 1H, Ar-H), 7.10-7.16 (m, 2H, Ar-H), 7.19-7.24 (m, 1H, Ar-H), 7.68 (d, J = 9.2 Hz, 1H, Ar-H), 7.81 (s, 1H, Ar-H), 7.91-7.96 (m, 2H, Ar-H), 8.13 (td, J = 1.2, 6.8 Hz, 1H, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 107.52, 111.96, 115.61, 117.52, 124.74, 126.08, 127.58, 128.61, 143.92, 145.88, 163.94; MS (ESI) m/z 213 (M+H)⁺; HRMS (ESI) Calcd for C₁₃H₁₀FN₂ (M+H)⁺: 213.0822; found, 213.0825.

5. CONCLUSION

In summary, we described a novel and efficient protocol for the synthesis of 2-aryl Imidazo[1,2-a]pyridines via the coupling of α-Bromoketones with 2-aminopyridines by use of a visible light active photo-catalyst, Bi₂MoO₆, in extremely short reaction times. In addition to its simplicity and green reaction conditions, this method provides high yields of products with high selectivity making it a useful and attractive strategy for the preparation of biologically relevant 2-susbtituted Imidazo[1,2-a]pyridines in a single step operation.

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