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Research Article

Microwave Assisted Expeditious and Green Cu(II)-Clay Catalyzed Domino One-Pot Three Component Synthesis of 2H-indazoles

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Abstract

A simple and efficient synthesis of 2H-indazoles is achieved from 2-primary amines, bromobenzaldehydes and sodium azide through domino condensation, C–N and N–N bond formations, catalyzed by a heterogeneous Cu(II)-Clay catalyst. The recyclable heterogeneous Cu(II)-Clay catalyst exhibited a remarkable activity for the title reaction without any additives. An assortment of structurally diverse 2H-indazoles were prepared in good to excellent yields from easily available starting materials by using this protocol. The Cu(II)-Clay catalyst was characterized by using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Brunauer-Emmett-Teller (BET) techniques. Copyright © 2018 BCREC Group. All rights reserved

Keywords: 2H-indazoles; Copper catalyst; Multi-component reaction; Green synthesis; Neat protocol

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1. Introduction

The importance of indazole derivatives as pharmacophores in drug discovery is well exemplified by its broad application in antitumor, [1] anti-HIV [2], antidepressant [3], antimicrobial [4], anti-angiogenic [5], and anti-pyretic [6]. In addition, indazoles are widely used as precursors in the synthesis of many natural products like nigellcine and nigellidine [7]. Owing to their importance as pharmaceuticals, agrochemicals, and novel materials a plethora of methods have been developed for their synthesis, such as: Cadogan indazole synthesis [8], cyclization reactions to selectively generate 2H-indazoles [9], reductive cyclization of ortho-imino-nitrobenzenes mediated by triethyl phosphite, transition metal catalyzed reductive cyclizations of iminonitroaromatic [10], sydnone/benzyne cycloaddition [11], zincate addition to diazonium salts [12], intramolecular aminations [13], and condensation of benzaldehydes with hydrazine [14].

Many of these methods suffer with drawbacks in terms of substrate scope, reaction conditions, reaction time, unsatisfactory yields, elevated temperatures, and/or protected syntheses of substrates. Consequently, there is a need to develop environment friendly, operationally simple and mild methods to obtain this privileged pharmacophore from a broad class of readily available synthetic reagents.

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Clays are considered to be potentially the most cost-effective and environmentally benign catalysts for organic reactions [15]. The metal doped clays can be the hybrid materials with combined catalytic rewards of metal salts and clay catalysts. Thus, in continuation of our interests [16-21], we herein report synthesis of 2H-indazoles from readily available 2-primary amines, bromobenzaldehydes and sodium azide using a heterogeneous Cu(II)/Montmorillonite-clay catalyst. The advantages of the system include, short reaction times, catalyst recyclability, neat conditions, remarkable activity without any additives and amenable for synthesis of diverse 2H-indazoles.

2. Materials and Methods

2.1 Preparation of the catalyst

Cu(II)-clay catalyst was prepared by introducing of calculated amount of aqueous Copper oligomer (prepared from copper(II) chloride precursor) to form a 10 wt.% copper loading (pre-optimized loading) on to Montmorillonite KSF clay (purchased from Sigma-Aldrich) and the system was stirred for 15 h followed by filtration and then washed with distilled water several times to remove chlorides. The cake so formed was dried at room temperature, kept overnight in air oven at 110 ^{o}C and then powdered and calcined in air at 425 ^{o}C for 3 h. The calcined product is referred to as Cu(II) doped clay catalyst (CDC 2) and the catalyst so formed was used in the experiments without further activation.

2.2 Procedure for the preparation of 2H-indazoles

Reaction mixture (in a typical reaction 1.0 mmol 2-bromobenzaldehyde, 1.2 mmol aniline, 1.8 mmol sodium azide, and 5 mg Cu-Clay catalyst were taken into a Scientific Microwave Synthesizer CATA - R I operating at 300 watts, and irradiated for 8 minutes. On completion of the reaction, followed by thin layer chromatography (TLC) examination, the mixture was cooled to room temperature, dissolved in ethyl acetate and filtered to separate the catalyst. The filtrate was concentrated under high vacuum. The crude products were purified by crystallization and the pure products were characterized by nuclear magnetic resonance spectroscopy (NMR) and mass analysis and the characterization data of the synthesized compounds was compared with the literature reports.

2.3 Catalyst characterization

The XRD analysis of Cu(II)-clay catalyst was done by recording X-ray powder diffraction patterns on a Rigaku Miniflex diffractometer, using Ni-filtered Cu-Ka (0.15418 nm) radiation source (Figure 1). The sample was scanned over the range 5.00-70.99 on 2u scale with steps 0.0118 and step time 13.6 s. To study the morphology, a SEM of the catalyst was carried out using JEOL JEM100CXII ELECTRON MICROSCOPE with ASID Accelerating Voltage 40.0 KV. The BET surface area of the catalyst was determined using the instrument SMART SORB 92/93 under the liquid nitrogen.

3. Results and Discussion

In this protocol, we used Cu(II)-clay catalyst with 10 wt.% copper loading, which was pre-optimized. The best yield was found by 10 wt.% copper loading may be due to its optimum nano size of the catalyst and hence increased number of active catalytic sites are produced. Higher copper loading may direct increased in the particle size formation of CuO and hence lesser surface area and lesser number of active

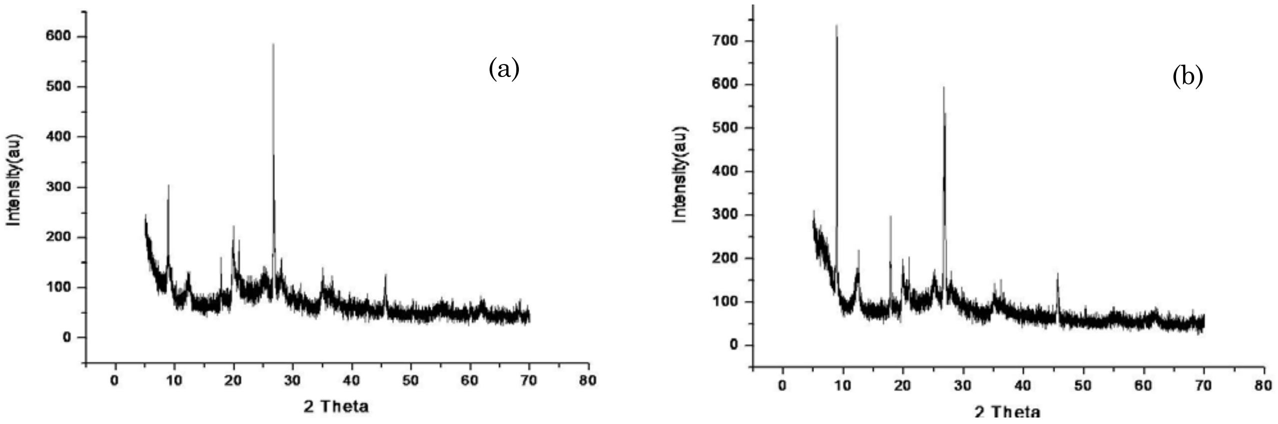


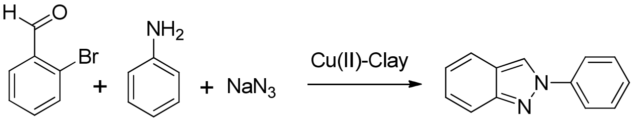
Figure 1. XRD peaks of fresh Cu(II)-clay

sites. Lower copper loading leads to lower active catalyst quantity.

This catalyst was characterized by using different instrumental techniques to support our results. The XRD patterns of the fresh Cu(II)-clay catalyst are shown in Figure 1a. The 2θ at 8.4° is commonly assigned to the characteristic peak of basal spacing (*d* 001) (2:1 TOT) of montomorillonite-KSF; the basal reflection represents the distance between two clay layers, including the thickness of one of the layers [22]. The presence of very low intensity diffraction peaks at 2θ of 36.1, 37.7, 38.9, 48.8, 53.60, and 58.7 which attributing to (110), (002), (111), (202) of CuO indicates that there are no sharp crystalline phases thus CuO being supported on MKSF in the form highly dispersed fine particles [23]. Peaks at 2θ of 20.9, 26.9, 36.5, 39.2, 48.6, 50.0, and 59.6 are due to reflection of the quartz (SiO_2) impurities [24]. Other peaks for montomorillonite appear at 2θ of 20.0, 24.3, 29.8 and 35.5. A sharp peak observed at 2θ of 17.8 along with some small peaks at 30.1, 36.0 and 47.2 correspond to the presence of Melanothallite [Cu_2OCl_2]. Presence of Kaolinite is implied to a sharp peak at 12.0 which corresponds to (001) and other peaks for this material appear at 24.1, 32.3, 38.0, and 42.7. There are two additional humps one at 55.0 and other at 61.9 which are due to montomorillonite and CuO in bulk, respectively [25]. Comparison of XRD patterns of the fresh catalyst with that of used catalyst (Figure 1b), clearly shows that there is almost no change in catalyst texture after use, which guarantees robustness and recyclability of the catalyst.

The SEM images of the Montmorilonite-KSF and Cu(II)-clay with 20000 magnifications are displayed in Figure 2. The montmorilonite-KSF without CuO (Figure 2a) possess smooth surface without any scrap but turns crumby after loading of CuO. Figure 2b clearly shows that CuO particles are highly dispersed over the support surface in the form of nano aggregates which in agreement with the XRD pattern. The nanosized CuO distributed in mosaic form on the surface of the clay leads to coarse surface (thus elevated surface area). From the SEM (EDAX) elemental analysis it was found that the catalyst prepared contains 9.21 % of copper loaded. The surface area of the catalyst is 96.4551 m^2/g, where as that of montmorillonite-KSF clay support only is 37.35 m^2/g. The increase in specific surface area of the catalyst may be due to mesopores formed by delamination of support during the process of catalyst preparation.

We began our efforts with the reaction of 2-bromobenzaldehyde, aniline, and sodium azide (1 mmol each) in toulene at room temperature which only to find no product formation (Table 1 entry 1). This led us to increase the reaction temperature to 120 °C, which to our delight gave corresponding indazole in about 12 % yields. While operating at this temperature, we changed ratio of the reactants from 1:1:1 to 1:1.2:1, respectively, the product yield did no change by more than 2 %. By using ratio of 1:1.2:1.2 of the reactants, the product yield increased to approximately 21 % and at ratio of 1:1.2:1.5, it raised to 30 %. When the ratio was changed to 1:1.2:1.8, product yield increased slightly, i.e. to 34 % (Table 1 entry 2 based Scheme 1). These results warranted optimization of the reaction conditions.



Scheme 1. Synthesis of 2H-indazoles using Cu-Clay catalyst

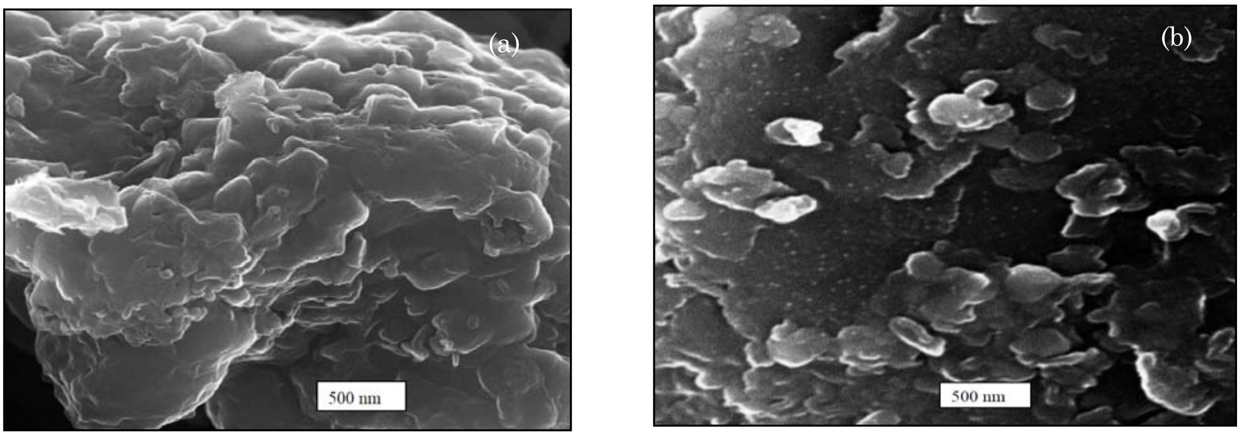
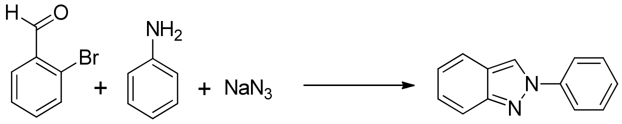


Figure 2. SEM image of Montmorilonite-KSF (a) and Cu(II)-Clay (b)

We therefore examined the feasibility of reaction in other solvents, such as: acetonitrile, methanol, ethanol, DMF, and THF. The reaction was equally feasible ion other solvents as well, wherein use of acetonitrile, methanol, ethanol, and DMF gave the product in almost comparable yields, however, DMSO as a solvent significantly increased the reaction yields to 81 % which may be attributed to the polar non-protic nature of DMSO. The reaction without the use of a solvent led to significant drops of product yields. We also investigated the reaction under sonication and microwave conditions. To our delight the reaction in microwave resulted in quantitative conversion to the products under solvent free condition in a matter of minutes. The identification of the optimum catalyst loading was another important aspect of the reaction strategy. Decreasing the amount of catalyst to even 3 mg resulted in product formation in as much as 98 % yields.

We were further intrigued to investigate the impact of other clay catalysts on the present reactions (Table 2). The catalysts such as Kaoline, Montmorillonite-KSF, Montmorillonite-K10, and bentonite did not give any product formation. The Pd/Montmorillonite-KSF though gave corresponding product albeit in low yields. The other montmorillonite based catalysts viz., Ni/Montmorillonite-KSF, Co/Montmorillonite-KSF, Sn/Montmorillonite-KSF, and Zn/Montmorillonite-KSF gave the products in trace amounts. Furthermore, the use of $PdCl_2$ and CuO as well did not offer any increased yield of product formation. The Cu(II) doped clay catalyst was found to show much better results than commercially available CuO for the model reaction under optimized conditions. This may be attributed to the high dispersion and the nano-sized character of Cu(II) ions on clay support [21].

After investigating the various reaction procedures, the best reaction conditions obtained was identified: 5 mg Cu-Clay catalyst 2-bromobenzaldehyde (1.0 mmol), aniline (1.2 mmol), sodium azide (1.8 mmol), and catalyst



Scheme 2. Reaction in the presence of various catalysts

Table 1. Synthesis of 2H-indazoles using Cu-Clay catalyst under different reaction conditions (Scheme 1)

Entry	Condition	Solvent	Time	Catalyst (mg)	Yield[a] (%)
1.	Stirring at room T	Toluene	2 h	15	N.R.
2.	Stirring at 120 °C	Toluene	2 h	15	34
3.	Stirring at 120 °C	Acetonitrile	2 h	15	59
4.	Stirring at 120 °C	Methanol	2 h	15	66
5.	Stirring at 120 °C	Ethanol	2 h	15	51
6.	Stirring at 120 °C	DMF	2 h	15	62
7.	Stirring at 120 °C	DMSO	2 h	15	81
8.	Stirring at 120 °C	THF	2 h	15	45
9.	Stirring at 120 °C	Solvent free	2 h	15	13
10.	Microwave	Solvent free	10 min.	15	98
11.	Microwave	Solvent free	8 min.	15	98
12.	Microwave	Solvent free	6 min.	15	73
13.	Microwave	Solvent free	8 min.	10	98
14.	Microwave	Solvent free	8 min.	5	98
15.	Microwave	Solvent free	8 min.	3	78
16.	Microwave	Solvent free	10 min	No catalyst	N. R.

[a]= isolated yield

(5 mg) under microwave and solvent free conditions.

Using the optimized reaction conditions, the substrate scope of the condensation reaction was then examined for the synthesis of substituted *2H*-indazoles. Substituted anilines were well tolerated to reaction conditions. Substituted halogens were found to be the good substrates for heterocyclization. Electron donating groups, e.g. methoxy, as well as electro withdrawing groups, e.g. nitro and triflouromethoxy groups, have no significant effect on the reaction yields. Also, the halogen substitution a tortho position gave the product formation in excellent yields.

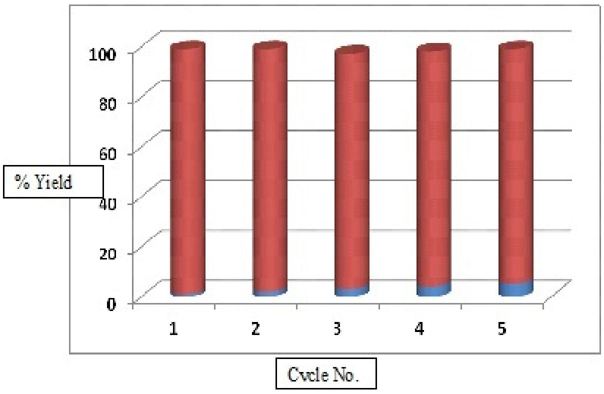


Figure 3. Recyclability of the catalyst for on pot synthesis of 2H-indazole[a] ([a]= model reaction, red bars indicate product yield and blue bars indicate decrease in yield

Recyclability of the catalyst was investigated using model reaction between bromobenzaldehyde (1.0 mmol), aniline (1.2 mmol), sodium azide (1.8 mmol), and catalyst (5 mg) under microwave and solvent free conditions. This experiment proved excellent recycling capability of the catalyst without significant loss of activity and the catalyst could be easily recovered by simple filtration and reused, leading to corresponding 2H-indazole in quantitative yield even up to five consecutive cycles (Figure 3).

On the basis of previous studies [26] a probable mechanism is shown in Scheme 3. The multicomponent one-pot coupling reaction first engages the formation of the N-(2-bromobenzylidene) amine intermediate. The bromide is substituted with azide in the presence of the Cu (II)-Clay catalyst in the next stage with the outcome of N-(2-azidobenzylidene) amine. The azide in the intermediate thus formed, undergoes activation by the Cu (II)-Clay catalyst which leads to the desired 2H-indazole product formation via intramolecular cyclization with N-N bond formation.

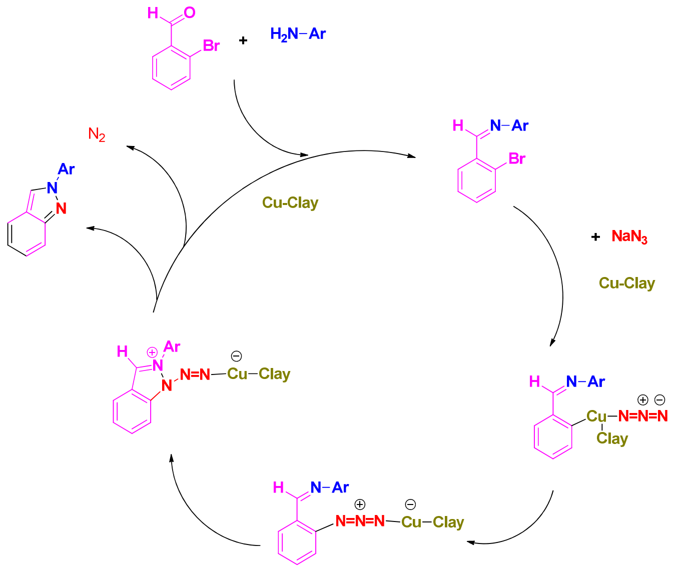
4. Conclusions

In conclusion, a microwave assisted and solvent-free synthesis of 2H-indazoles using Cu(II)-Clay is an efficient heterogeneous catalyst. This protocol is novel, simple, and proficient for three component consecutive conden-

Table 2. Reaction in the presence of various catalysts (Scheme 2)

Entry	Catalyst	Catalyst loading (mg)	Yield[a] (%)
1.	Kaoline	5	NR
2.	Montmorillonite-KSF	5	NR
3.	Montmorillonite-K10	5	NR
4.	Bentonite	5	NR
5.	Pd/ Montmorillonite-KSF	5	47
6.	Cu/ Montmorillonite-KSF	5	98
7.	Ni/Montmorillonite-KSF	5	11
8.	Co/Montmorillonite-KSF	5	13
9.	Sn/Montmorillonite-KSF	5	traces
10.	Zn/Montmorillonite-KSF	5	traces
11.	$PdCl_2$	5	Traces
12.	CuO	5	53
13.	No Catalyst	---	NR

Reaction time 8 min, [a] = isolated yield; NR: No Reaction



Scheme 3. A possible reaction mechanism for Cu (II)-Clay catalysed 2H-indazoles formation

sation, C–N and N–N bond formations as a one-pot MCR. The catalyst was easy to prepare, environmentally friendly, highly stable, leaching-free, and can be recycled several times without significant loss of activity. Moreover, being fast and high yielding, this protocol will be highly useful for economical synthesis of 2H-indazoles.

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Appendices

Spectral data of some representative compounds

2-Phenyl-2*H*-indazole: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 1.2 Hz, 1H), 7.97-7.93 (m, 2H), 7.86-7.83 (m, 1H), 7.77-7.74 (m, 1H), 7.60-7.54 (m, 2H), 7.47-7.42 (m, 1H), 7.40-7.34 (m, *J* = 8.4, 6.6, 0.9 Hz, 1H), 7.16 (m, *J* = 8.4, 6.6, 0.9 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 150.1, 140.8, 129.9, 128.2, 127.1, 123.0, 122.7, 121.3, 120.7 (2C), 118.2; MS (EI) *m/z*: 195 [M^+ +1].

2-*p*-Tolyl-2*H*-indazole: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 0.9 Hz, 1H), 7.81-7.75 (m, 3H), 7.70 (m, 8.4, 0.9 Hz, 1H), 7.34-7.29 (m, 3H), 7.13-7.08 (m, *J* = 8.7, 6.6, 0.9Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 138.2, 137.9, 130.06, 126.6, 122.7, 122.3, 120.8 (2C), 120.3, 117.8, 21.0; MS (EI) *m/z*: 209 [M^+ +1].

2-(4-chlorophenyl)-2*H*-indazole: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 0.9 Hz, 1H), 7.86-7.71 (m, 2H), 7.78-7.75 (m, 1H), 7.68 (m, *J* = 8.7, 0.9 Hz, 1H), 7.50-7.49 (m, 2H), 7.32 (m, 8.7, 6.6, 1.2 Hz, 1H), 7.11 (m, *J* = 8.4, 6.6, 0.9Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 138.9, 133.5, 129.6, 127.1, 122.8, 122.7, 121.9, 120.3, 120.2, 117.8; MS (EI) *m/z*: 230 [M^+ +1].