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Development of 1,2,3-Triazoles employing Copper Oxide/Reduced Graphene Oxide Nanocomposite

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Abstract

A one-pot approach was studied for synthesising 1,2,3-triazole derivatives with alkyne and sodium azide over reduced copper oxide and graphene oxide catalysts. The catalyst is synthesised in one pot using the ultrasonication process. The characterization of prepared catalyst was done using PXRD, FTIR, FESEM, EDX/EDS, TGA and TEM. The product was separated by simply washing the crude reaction residue with ethanol, then evaporating the solvent.

The catalyst was recycled for use in future reactions. The azides are created in situ, hence this technique eliminates the need to handle dangerous azides. This procedure provides broad access to a wide range of 1,2,3-triazoles with various substituents.

Keywords: 1,2,3-Triazoles, Copper oxide, Graphene oxide, Nanocomposite.

Introduction

Most important classes of N-containing heterocyclic compounds, 1,2,3-triazoles have drawn a lot of interest as functional materials as well as biologically active pharmaceuticals[6,7,24,28,39,41,42]. Furthermore, the usage of these compounds in a variety of industries including organic semiconductors, dyes, dehydroannulenes and electroluminescent materials, is drawing a lot of attention[9,13,16,17,20,22,23,26,27,31,43,47]. Numerous techniques have been devised for the manufacture of 1,2,3-triazoles because of their inherent significance. One of the most effective synthetic application tools in organic synthesis is Huisgen's 1,3-dipolar cycloaddition reaction of terminal alkynes and organic azides, catalysed by homogeneous CuI salts (CuAAC).

Because organic azides are poisonous and dangerous, handling them is not safe. Alkyl azides can be readily synthesised via the displacement reaction of sodium azide with alkyl halides, although in some circumstances, separation and purification might be difficult. However, the process of making aryl azides from aromatic amines is more complicated. As a result, for triazole synthesis, a one-pot procedure comprising the reaction of azides generated *in situ* from the suitable precursors and alkynes is very desirable. Recently, a number of these one-pot reactions catalysed by different Cu compounds have been reported[8,15]. Heterogeneous copper, which is achieved by immobilising copper nanoparticles on a variety of heterogeneous organic and inorganic substrates, may also catalyse the click reaction[14]. However, this click reaction requires a large catalyst loading with bases and is relatively sluggish when copper metal alone is used as the catalyst. Without the need for additional bases or supports, Jin and colleagues recently created an intriguing monolithic nanoporous Cu catalyst whose nanoporosity structure of Cu surface led to a considerable improvement of catalytic activity in click chemistry[45].

As a consequence, developing a nanostructure on the surface of monolithic copper is not only useful for producing high-catalytic activity catalysts for use in click chemistry, but it also simplifies the catalyst project's recovery procedure. Research into the development and manufacturing of catalysts with enhanced catalytic activity is becoming increasingly important.

Because of their increased surface/volume ratio, nanoparticles have attracted a lot of interest as catalysts. Graphene oxide presents intriguing mechanical, electrical and thermal characteristics. Its enormous surface area and diverse functional groups allow for chemical changes, making graphene oxide a valuable study target[32]. It also serves as a useful catalyst support.

Consequently, researchers doped NPs on the GO. This prevented the requirement for an additional stabilising agent by internally stabilising the NPs. Metal/graphene oxide nanocomposites are critical in a wide range of research domains including catalysis, sensors, photocatalysis, organic synthesis reduction, toxic metal ion elimination, cellular imaging, drug administration and many more properties recorded in literature[25]. Copper, a cheap metal, has a wide variety of catalytic activity, from heterocycle production to C-C coupling[19,25,29]. We were inspired to develop a copper oxide/reduced graphene oxide nanocomposite (CuO/rGO) for catalysis. Our study presents a CuO/rGO nanocomposite catalyst that is efficient, green and sustainable for triazole production. Using various ethynylbenzene derivatives and sodium azide, we were able to synthesise several di-substituted 1,2,3-triazoles in large quantities.

Material and Methods

The materials used were purchased from Sigma Aldrich like sodium boric acid, potassium permanganate, graphite flakes, hydrogen peroxide and 4-nitrophenol. Cu K radiation with a wavelength of 0.15418 nm is used in PXRD to detect the powder characteristics of the manufactured material.

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Furthermore, FT-IR analysis was performed on the generated materials to track and to identify the peaks of different functional groups. Thermo-Gravimetric measurements were performed at a heating rate of 10^0C in a nitrogen environment using the Perkin Elmer STA 6000. With a point resolution of 0.24, the 200 Kv Tecnai G2 20 S-TWIN [FEI] TEM provides excellent resolution. EDS/EDX provides the elemental composition of the sample. The synthetic material's morphology was investigated through the use of Field Emission Scanning Electron Microscopy.

Preparation of Metal Oxide decorated reduced Graphene Oxide Nanoparticles: Graphene oxide is prepared as reported earlier[11]. 1g of graphene oxide is added to 200ml of distilled water in a beaker. Then, it was sonicated for 10 min. After that, CuO (400 mg) and distilled water (100 ml) were added to another beaker and sonicated for 10 minutes. After sonication, both solutions were mixed with the addition of sodium borohydride (20mg). The reaction mixture was left to stir for 4 hours at room temperature. After that, it was filtered, washed multiple times with ethanol and dried in an oven for 8 to 10 hours at 80°C to produce copper-decorated reduced graphene oxide (rGO-CuO)[3,48].

Catalytic Reaction of prepared material: In a round bottom flask, 1-chloro-4-ethynylbenzene(100mg) and methanol (10ml) are added and stirred for some time. Then, sodium azide (57mg) is added followed by addition of catalyst (10mg). The reaction mixture is stirred at 50-60° C for 16h. The reaction crude was extracted with dichloromethane and distilled water. After drying over $MgSO_4$, the mixture was poured into a celite pad. The solvent was evaporated under reduced pressure. For the structural analysis of desired products, the crude products were purified by recrystallization with chloroform and hexane to get off white solid. Similarly with different derivatives of 1-chloro-4-ethynylbenzene(1-ethynyl-4-methoxybenzene, 5-ethynyl-2-fluoropyridine, ethynylbenzene, 1-(4-ethynylphenyl)-1H-pyrazole, 6-ethynyl-2-methylbenzo[d]thiazole, 2-ethynyl-5-fluoropyridine, 7-ethynylindolin-2-one,methyl 2-ethynylisonicotinate), same procedure reaction is performed.

Results and Discussion

Fourier Transform Infrared of the prepared catalyst is observed to examine the different functional groups in the catalyst (Figure 1). The peaks present in graphene oxide are 1264 cm^{-1} (C-O epoxy), 1067 cm^{-1} (C-O alkoxy) and 1721 cm^{-1} (C=O carbonyl). In the nanocomposite catalyst, the peaks of the OH functional group and the C=C double bond vanished and the intensity of the C=O, C-OH and C=O peaks decreased, confirming the reduction of graphene oxide during preparation. This suggests that graphene oxide will be reduced in addition to the nanocomposite's synthesis[10,30,34]. Powder X-ray diffraction patterns of the prepared catalyst (Figure 2) shows a broad peak at $2\theta=25°$. Then, diffraction peaks at 2θ = 28.72°(002), 38.99°(111), 42.41°(111), 46.47°(200), 50.53°(202), 53.46°(020), 60.09°(202), 64.06°(220), 66.82°(022), 69.82°(113) and 72.90°(311) are almost similar to the standard XRD data (JCPDS card no. 89-2530).

Thermogravimetric analysis (Figure 3) is used to check the thermal stability of prepared catalyst in the temperature range of 10°/min to 900°C. It is observed that approx. 12 % weight loss occurred till 150°C. The elemental composition of prepared catalyst was examined using Energy Dispersive Spectroscopy. The mapping gives a clear confirmation about proper arrangement of CuO on rGO sheets. The elemental composition of the nano-composite is carbon 78.08 wt%, copper 15.70 wt% and oxygen 6.22 wt %[30]. The surface morphology of prepared catalyst is examined using Field Emission Scanning Electron Microscopy (Figure 4a, 4b).

It is clearly shown in the images that copper oxide particles are attached on the fringes of graphene oxide. The diameter of CuO is between 6nm and 10nm[47,48]. The generated catalyst's shape and size are depicted in the transmission electron microscopy pictures. The TEM image (Figure 5a,5b) at high magnification clearly shows the spherical form of copper oxide. The interplanar lattice shown in the lattice fringes correlates to 111 atomic planes in the monoclinic CuO lattice. It was found that the particle size ranged from 18 to 45 nm.

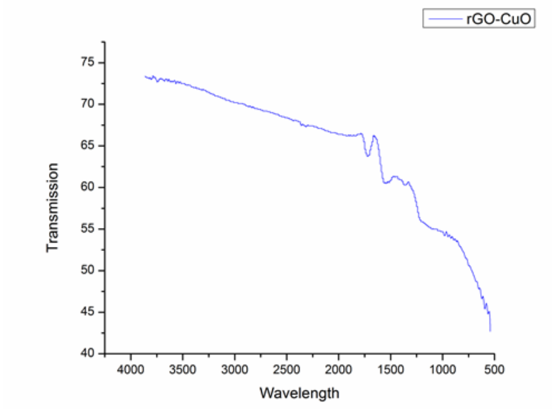


Figure 1: FTIR of catalyst

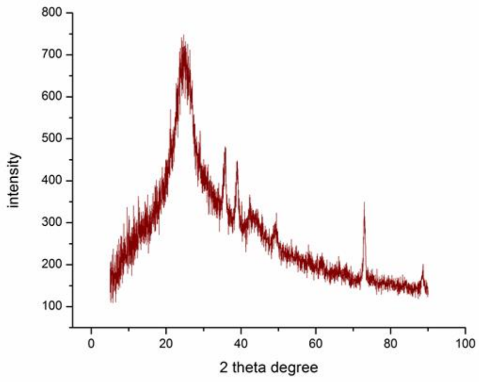


Figure 2: PXRD of catalyst

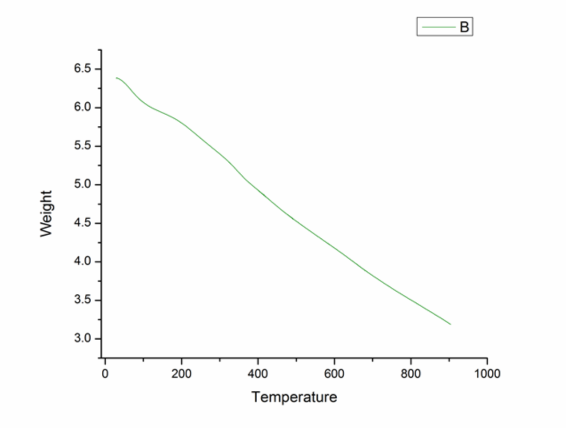


Figure 3: TGA of catalyst

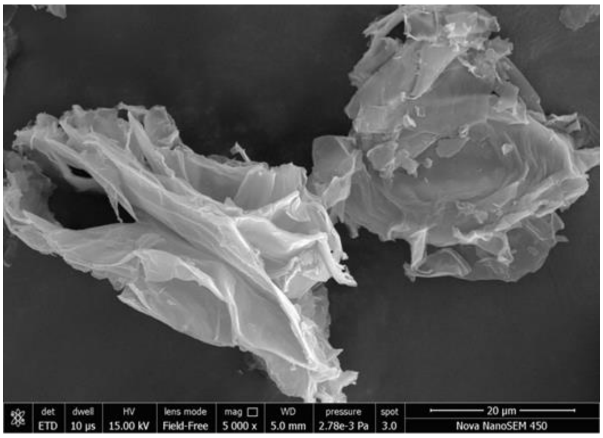


Figure 4a: SEM

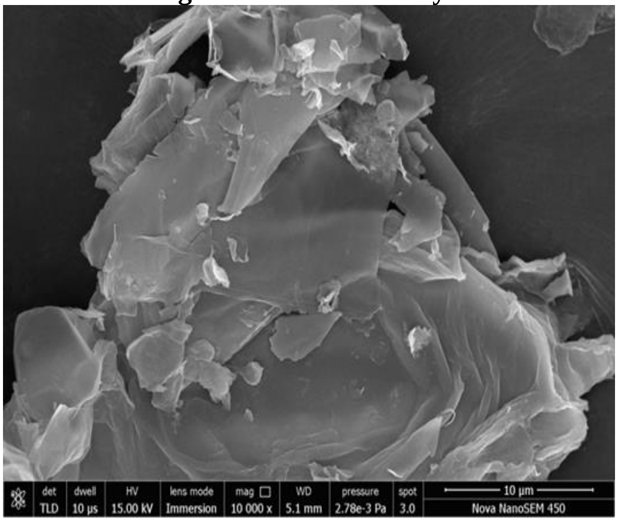


Figure 4b: SEM

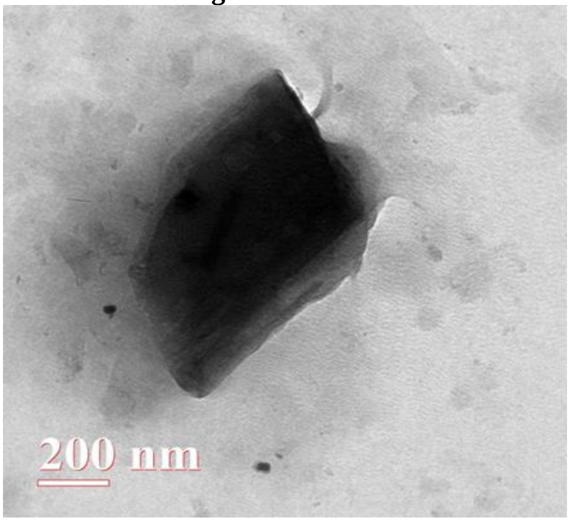


Figure 5a: TEM

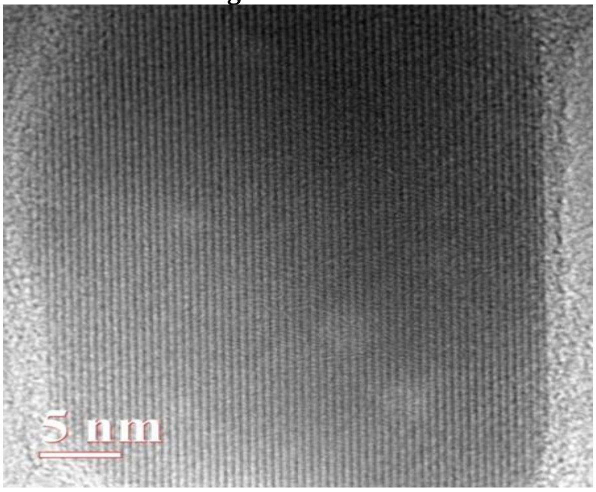
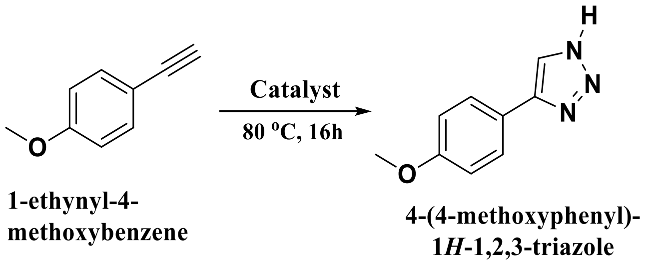


Figure 5b: TEM

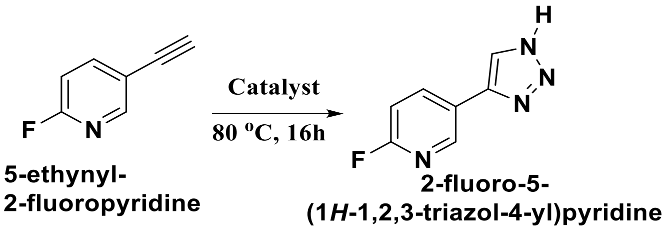
Catalytic Reactions: To optimize the reaction conditions, a series of experiments were carried out using different derivatives of 1-ethynyl-4-methoxy benzene, sodium azide and methanol as a solvent. It was found that with methyl 2-ethynylisonicotinate and sodium azide (entry-11), the reaction gives better results (79%) (Tables 1 and 2). Using derivatives 1-ethynyl-4-methoxybenzene (entry 1), 5-ethynyl-2-fluoropyridine (entry 2), 6-ethynyl-2-methylbenzo[d]thiazole (entry 6), 2-ethynyl-5-fluoropyridine (entry 7) and in entries 9, 10, the yields are considerable i.e. more than 60%. It was found that with 7-ethynylindolin-2-one(entry-8) and sodium azide, no desired product was formed.

a) Synthesis of 4-(4-methoxyphenyl)-1H-1,2,3-triazole: 100 mg of 1-ethynyl-4-methoxybenzene is taken with 10 ml methanol and 57 mg sodium azide followed by addition of catalyst (10 mg) (Scheme 1). NMR-1H NMR (400 MHz, DMSO-d6) δ 3.79(s, 3H), 7.02 (d, J = 8.55, Hz, 1H), 7.78 (d, J = 8.55, 2H), 8.21 (s, 1H), 14.95 (br s, 1H).



Scheme 1: Synthesis of 4-(4-methoxyphenyl)-1H-1,2,3-triazole

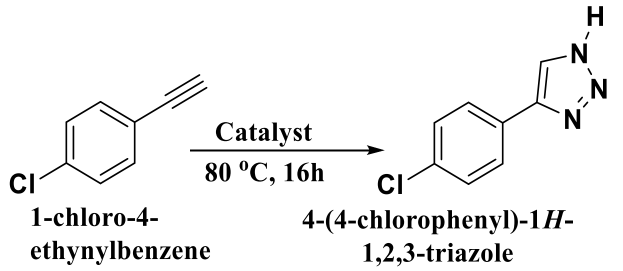
b) Synthesis of 2-fluoro-5-(1H-1,2,3-triazol-4-yl) pyridine: 100 mg of 5-ethynyl-2-fluoropyridine is taken with 10 ml methanol and 57 mg sodium azide followed by addition of catalyst (10 mg) (Scheme 2). NMR-1H NMR (400 MHz, DMSO-d6) δ 7.31(dd, J = 8.56, 2.81Hz, 1H), 8.39-8.46 (m, 2H), 8.73-8.75 (m, 1H), 15.31 (br s, 1H).



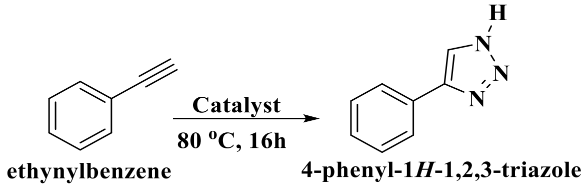
Scheme 2: Synthesis of 2-fluoro-5-(1H-1,2,3-triazol-4-yl)pyridine

c) Synthesis of 4-(4-chlorophenyl)-1H-1,2,3-triazole: 100 mg of 1-chloro-4-ethynylbenzene is taken with 10 ml methanol and 57 mg sodium azide followed by addition of catalyst (10 mg) (Scheme 3). NMR-1H NMR (400 MHz, DMSO-d6) δ 7.52(dd, J = 8.56Hz, 2H), 7.64(dd, J = 8 Hz, 2.81Hz, 1H), 7.89(d, 12Hz, 1H), 8.31 (s, 1H), 15.31 (br s, 1H).

d) Synthesis of 4-phenyl-1H-1,2,3-triazole: 100 mg of ethynylbenzene is taken with 10 ml methanol and 57 mg sodium azide followed by addition of catalyst (10 mg) (Scheme 4). NMR-1H NMR (400 MHz, DMSO-d6) δ 7.36-7.42(m, 1H), 7.44-7.50(m, 2H), 7.88(d, J=21Hz, 2H), 8.26 (br s, 1H), 14.96 (br s, 1H).



Scheme 3: Synthesis of 4-(4-chlorophenyl)-1H-1,2,3-triazole

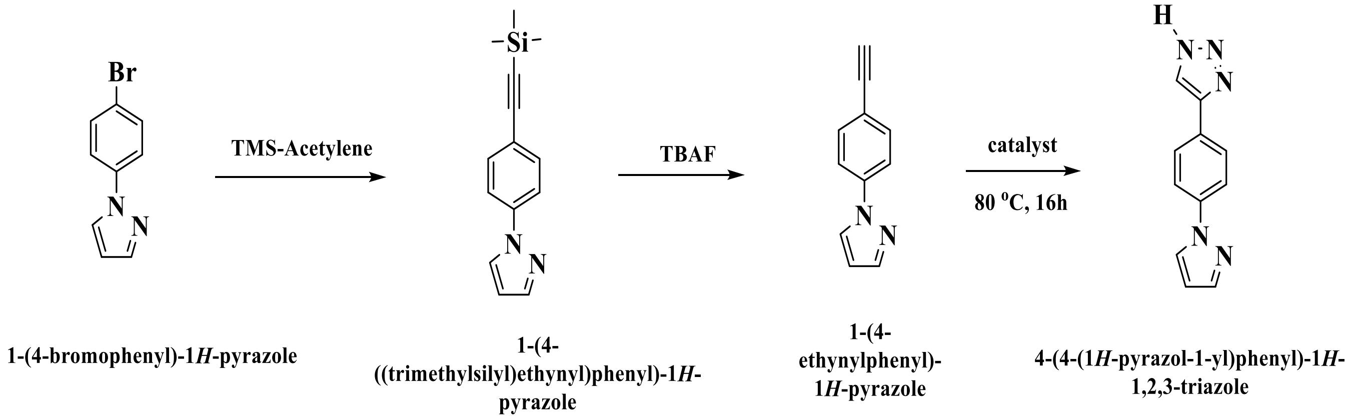


Scheme 4: Synthesis of 4-phenyl-1H-1,2,3-triazole

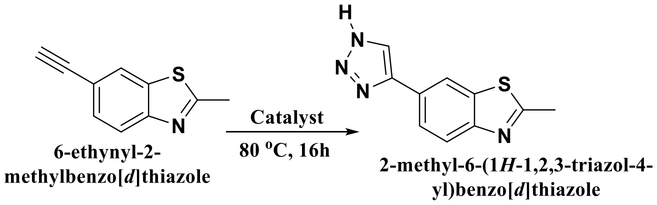
e) Synthesis of 4-(4-(1H-pyrazol-1-yl)phenyl)-1H-1,2,3-triazole: 100 mg of 1-(4-ethynylphenyl)-1H-pyrazole is taken with 10 ml methanol and 57 mg sodium azide followed by addition of catalyst (10 mg) (Scheme 5). ^{1}H NMR (400 MHz, DMSO-d6) δ 6.56 (s, 1H), 7.76 (s, 1H), 7.76-7.99 (m, 4H), 8.43 (s, 1H),8.54-8.55(d, J=4Hz, 1H), 14.12 (br,s, 1H).

f) Synthesis of 2-methyl-6-(1H-1,2,3-triazol-4-yl)benzo [d]thiazole: 100 mg of 6-ethynyl-2-methylbenzo[d]thiazole is taken with 10 ml methanol and 57 mg sodium azide followed by addition of catalyst (10 mg) (Scheme 6). ^{1}H NMR (400 MHz, DMSO-d6) δ 2.81 (s, 3H), 7.97 (s, 2H), 8.32 (s, 1H), 8.52 (m, 1H), 15.06 (br s, 1H).

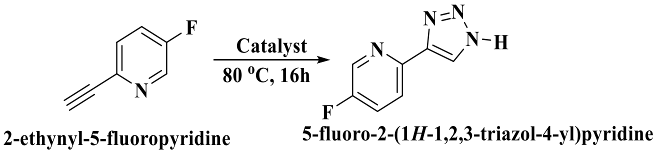
g) Synthesis of 5-fluoro-2-(1H-1,2,3-triazol-4-yl) pyridine: 100 mg of 2-ethynyl-5-fluoropyridine is taken with 10 ml methanol and 57 mg sodium azide followed by addition of catalyst (10 mg) (Scheme 7). ^{1}H NMR (400 MHz, DMSO-d6) δ 7.30 (br t,J=8.71 2H),7.88-7.91 (m, 2H), 8.33 (d, , J = 8 Hz 1H,) (15.05 (br s,1H).



Scheme 5: Synthesis of 4-(4-(1H-pyrazol-1-yl)phenyl)-1H-1,2,3-triazole



Scheme 6: Synthesis of 2-methyl-6-(1H-1,2,3-triazol-4-yl)benzo[d]thiazole



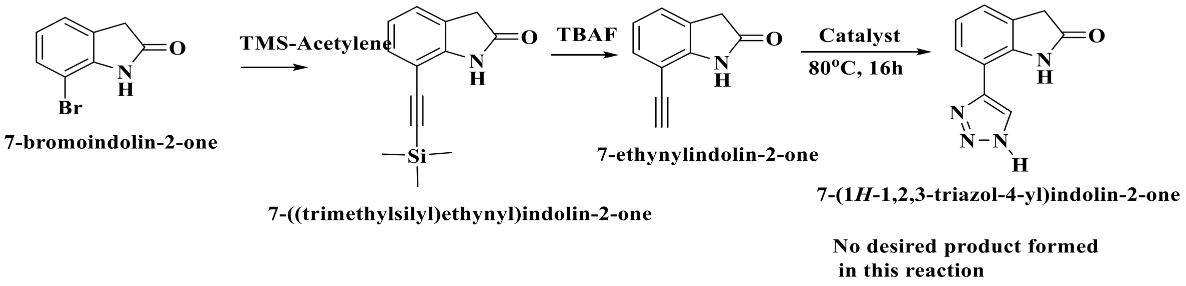
Scheme 7: Synthesis of 5-fluoro-2-(1H-1,2,3-triazol-4-yl) pyridine

h) Synthesis of 7-(1H-1,2,3-triazol-4-yl)indolin-2-one: 100 mg of 7-ethynylindolin-2-one is taken with 10 ml methanol and 57 mg sodium azide followed by addition of catalyst (10 mg) (Scheme 8). NMR- NA (No desired product formed).

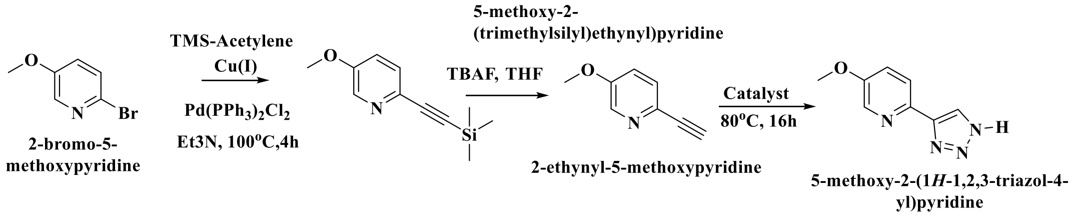
i) Synthesis of 5-methoxy-2-(1H-1,2,3-triazol-4-yl) pyridine: 100 mg of 2-ethynyl-5-methoxypyridine is taken with 10 ml methanol and 57 mg sodium azide followed by addition of catalyst (10 mg) (Scheme 9). 1H NMR (400 MHz, DMSO-d6) δ 3.87 (s, 3H), 7.49-7.51 (d, J = 8 Hz, 1H), 7.91-7.93 (d, J=8Hz, 1H), 8.23 (s, 1H), 8.33(s, 1H), 15.36 (br s,1H).

j) Synthesis of methyl 5-(1H-1,2,3-triazol-4-yl) nicotinate: 100 mg methyl 5-(1H-1,2,3-triazol-4-yl) nicotinate is taken with 10 ml methanol and 57 mg sodium azide followed by addition of catalyst (10 mg) (Scheme 10). 1H NMR (400 MHz, DMSO-d6) δ 3.93 (s, 3H), 8.65-8.69 (d, J=18.8Hz, 2H), 9.05 (s, 1H), 9.32(s,1H), 15.44 (br s,1H).

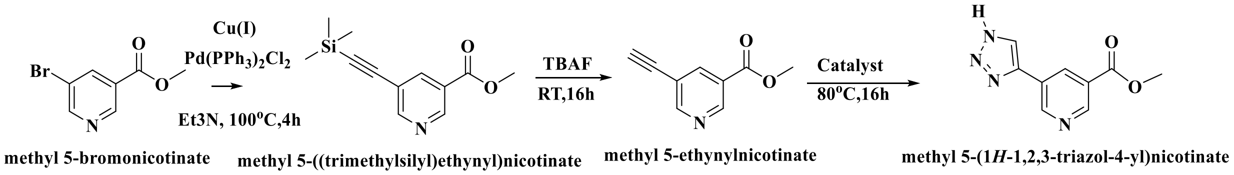
k) Synthesis of methyl 2-(1H-1,2,3-triazol-4-yl) isonicotinate: 100 mg of methyl 2-ethynylisonicotinate is taken with 10 ml methanol and 57 mg sodium azide followed by addition of catalyst (10 mg) (Scheme 11). NMR-1H NMR (400 MHz, DMSO-d6) δ 3.94 (s, 3H), 7.79-7.80 (d, J = 4.0 Hz, 1H), 8.35-8.61 (m, 2H), 8.84 (d, J = 4.98 Hz, 1H), 15.36 (br s,1H).



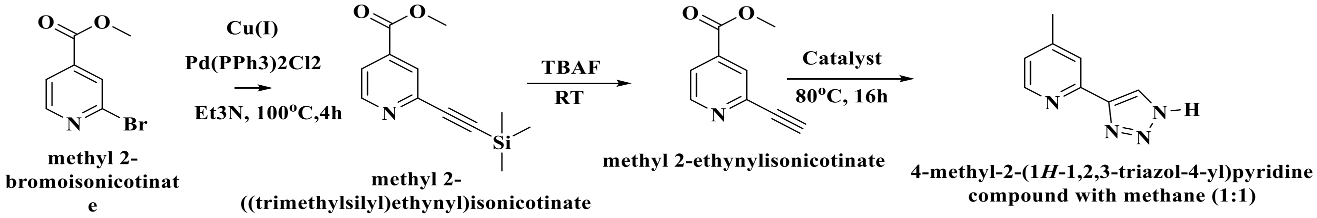
Scheme 8: Synthesis of 7-(1H-1,2,3-triazol-4-yl)indolin-2-one



Scheme 9: Synthesis of 5-methoxy-2-(1H-1,2,3-triazol-4-yl)pyridine



Scheme 10: Synthesis of methyl 5-(1H-1,2,3-triazol-4-yl)nicotinate



Scheme 11: Synthesis of methyl 2-(1H-1,2,3-triazol-4-yl)isonicotinate

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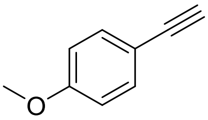
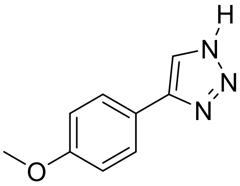
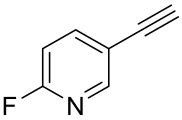
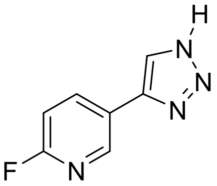
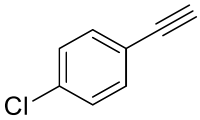
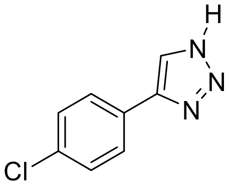
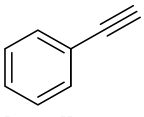
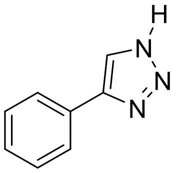
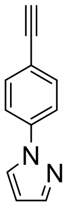
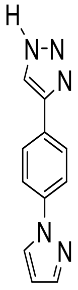
Table 1
Optimization of synthesis of different derivatives of 1,2,3- triazole

S.N.	Alkyne	Azide	Product	Solvent	Time	Catalyst (mg) 10 W %	Yield (%)
1	 1-ethynyl-4-methoxybenzene Molecular Weight: 132.16	NaN_3 Sodium azide	 4-(4-methoxyphenyl)-1H-1,2,3-triazole Molecular Weight: 175.19	MeOH	16h	10 mg	80 mg 60%
2	 5-ethynyl-2-fluoropyridine Molecular Weight: 121.11	NaN_3 Sodium azide	 2-fluoro-5-(1H-1,2,3-triazol-4-yl)pyridine Molecular Weight: 164.14	MeOH	16h	10 mg	81 mg 62%
3	 1-chloro-4-ethynylbenzene Molecular Weight: 136.58	NaN_3 Sodium azide	 4-(4-chlorophenyl)-1H-1,2,3-triazole Molecular Weight: 179.61	MeOH	16h	10 mg	71 mg 53%
4	 ethynylbenzene Molecular Weight: 102.14	NaN_3 Sodium azide	 4-phenyl-1H-1,2,3-triazole Molecular Weight: 145.17	MeOH	16h	10 mg	80 mg 56%
5	 1-(4-ethynylphenyl)-1H-pyrazole Molecular Weight: 168.20	NaN_3 Sodium azide	 4-(4-(1H-pyrazol-1-yl) phenyl)-1H-1,2,3-triazole Molecular Weight: 211.23	MeOH	16h	10 mg	90 mg 72%

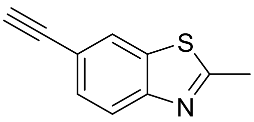
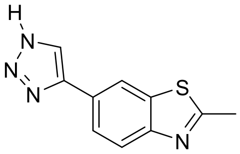
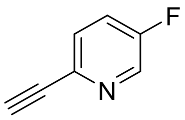
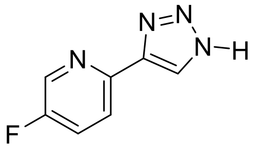
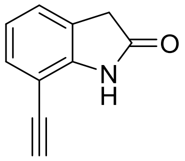
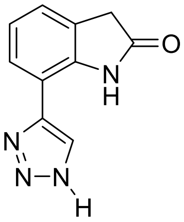
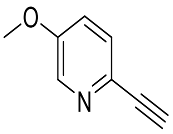
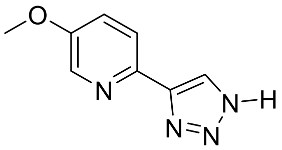
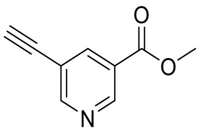
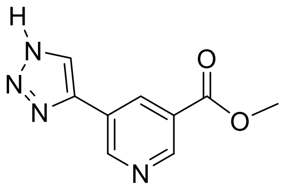
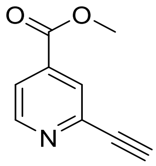
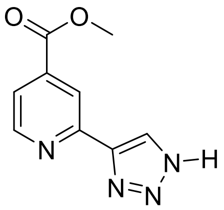
6	 6-ethynyl-2-methylbenzo[d]thiazole Molecular Weight: 173.23	NaN_3 Sodium azide	 2-methyl-6-(1H-1,2,3-triazol-4-yl)benzo [d]thiazole Molecular Weight: 216.26	MeOH	16h	10 mg	85mg 68%
7	 2-ethynyl-5-fluoropyridine Molecular Weight: 121.11	NaN_3 Sodium azide	 5-fluoro-2-(1H-1,2,3-triazol-4-yl) pyridine Molecular Weight: 164.14	MeOH	16h	10 mg	62.96 mg 62%
8	 7-ethynylindolin-2-one Molecular Weight: 157.17	NaN_3 Sodium azide	 7-(1H-1,2,3-triazol-4-yl) indolin-2-one Molecular Weight: 200.20	MeOH	16h	10 mg	XX g XX % No desired product formed in this reaction
9	 2-ethynyl-5-methoxypyridine Exact Mass: 133.05 Molecular Weight: 133.15	NaN_3 Sodium azide	 Molecular Weight: 176.18	MeOH	16h	10 mg	86 mg 65%
10	 methyl 5-ethynylnicotinate Exact Mass: 161.05 Molecular Weight: 161.16	NaN_3 Sodium azide	 Molecular Weight: 204.19	MeOH	16h	10 mg	90 mg 71%
11	 methyl 2-ethynylisonicotinate Molecular Weight: 161.16	NaN_3 Sodium azide	 methyl 2-(1H-1,2,3-triazol-4-yl)isonicotinate Molecular Weight: 204.19	MeOH	16h	10 mg	100mg 79%

Table 2
Optimization of synthesis of different derivatives of 1,2,3- triazole with different solvents

S.N.	Catalyst	Temperature	Solvent	Time	Reaction monitoring data in %
1	rGO-CuO	80°C	MeOH	16h	35%
2	rGO-CuO	80°C	DMF	16h	1.28%
3	rGO-CuO	80°C	WATER	16h	2.3%
4	rGO-CuO	80°C	ACETONE	16h	1.6%
5	rGO-CuO	80°C	DMSO	16h	No product
6	rGO-CuO	80°C	ACN	16h	6.24%
7	rGO-CuO	80°C	tBuOH	16h	25%
8	rGO-CuO	80°C	IPA	16h	30%

Conclusion

We have synthesised 1,2,3-triazole derivatives by using alkyne and sodium azide using reduced copper oxide and graphene oxide catalyst. The characterization of prepared catalyst is done using PXRD, FTIR, FESEM, EDX/EDS, TGA and TEM. It was found that with methyl 2-ethynylisonicotinate and sodium azide, the reaction gives better results (79%). Using derivatives 1-ethynyl-4-methoxybenzene, 5-ethynyl-2-fluoropyridine, 6-ethynyl-2-methylbenzo[d]thiazole, 2-ethynyl-5-fluoropyridine (entry-7), the yields are considerable, more than 60%.

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