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Synthesis of novel phenol based 1, 2, 3-triazole by using the magnetically active Fe_3O_4.Cu_2O nanocatalyst

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Synthesis of Novel Phenol based 1, 2, 3- Triazole by Using the Magnetically Active $Fe_3O_4.Cu_2O$ Nanocatalyst

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Abstract. Substituted Phenol based novel 1,2,3- triazole derivatives were synthesized via click chemistry approach efficiently by using the magnetically active $Fe_3O_4.Cu_2O$ nanocatalyst and characterized by the ^1H NMR, ^{13}C NMR, HRMS and IR spectroscopy. The catalyst has been used in lower concentration for the completion of reaction. $Fe_3O_4.Cu_2O$ nanocatalyst can promote the yields and reaction times over five runs without significant loss in its efficiency. This methodology has advantages such as simplicity, excellent yields and shorter reaction time. The catalyst was characterized by powder XRD, TEM, SEM and IR spectroscopy.

INTRODUCTION

Functionalized fused N-heteroaromatics have played a key role in the early stage of drug discovery [1, 2]. Phenol and their derivative have significant importance in biological activity. It has been observed that, synthesis of 1,2,3-triazoles from phenols and acids performed through multicomponent methodology [3]. Phenol based 1,4-disubstituted-1,2,3-triazole derivatives are potent against glioblastoma cells [4]. It is well known that heterogeneous catalysts possess intrinsic advantages over homogeneous catalysts. The number of organic transformations is carried out by using heterogeneous catalytic systems due to mild reaction conditions, thermal stability of catalysts, easy of handling, simple reaction workup, reusability and recyclability of catalysts [5]. Recently number of heterogeneous catalyst employed such as CuO [6], Copper-doped silica cuprous sulfate (CDSCS) [7], Nanoporous titania supported gold nanoparticles [8], graphene oxide/Fe_3O_4 [9], hydroxyapatite-encapsulated α-Fe_2O_3 as organic–inorganic hybrid nanocatalys [10], Copper Supported on MWCNT-Guanidine Acetic Acid@Fe_3O_4 [11] have been successfully used to catalyze [3+2] cycloaddition reaction between substituted azide and different alkynes for the synthesis of variety of substituted 1,2,3-Triazole.

Fe_3O_4 nano material have potential catalytic activity. Fe_3O_4 nanocatlyast and their composite have been used in synthesis of Polyhydroquinolines in water [12], bis-coumarin derivatives[13], Enhanced Performance for Fischer–Tropsch Synthesis[14], quinolines[15], 1-substituted 1H-1, 2, 3, 4-tetrazoles [16], dihydropyrano[2,3-c]pyrazole [17]. Considering the use of mix metal oxide nanoparticles for organic transformations, herein we reported the simple and efficient route for the synthesis of novel phenol based 1,2,3-triazole derivative by using reusable $Fe_3O_4.Cu_2O$ catalyst.

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EXPERIMENTAL SECTION

General procedure for the preparation of Fe_3O_4 and Fe_3O_4.Cu_2O nanocatalyst:

Magnetic Fe_3O_4 nanocatalyst were synthesized by a wet impregnation method according to reported method. In a procedure, 0.54 g $FeCl_3.6H_2O$ and 1.20g $NaAc.3H_2O$ were added to 30 ml ethylene glycol, after vigorous stirring at normal room temperature. After formation of colloidal mixture, the mixture was sealed in the Teflon-lined stainless steel autoclave. Then, autoclave heated at 150^0C for 30 hours, then cooled at room temperature, the black powder product was formed. It washes with several times with absolute ethanol and dried at 60^0C.

The magnetic $Fe_3O_4.Cu_2O$ nanocatalyst was prepared according to reported literature. The black powder Fe_3O_4 (0.322 g) were dispersed in 80 ml of deionized water. Followed by addition of 5 ml of 0.1 mol/lit $CuCl_2$ solution were added into the aqueous solution of Fe_3O_4 with vigorous stirring. After sonicated for 15 min, 1.8 ml of 1.0 mol/lit NaOH solution was drop by drop added into the solution under sonication. The solution turns light blue immediately, indicating that formation of $Cu(OH)_2$ precipitate. After sonication 12 ml of 0.1 mol/lit $NH_2OH.HCl$ were added immediately. After that solution were kept into the water bath for 1 hour for growth of nano crystal. Then solution was centrifuged and obtained precipitate wash with absolute alcohol and de-ionized water 3 times and finally dried at 100^0C for 3 hours.

General Procedure

General procedure for the synthesis of alkyne intermediate

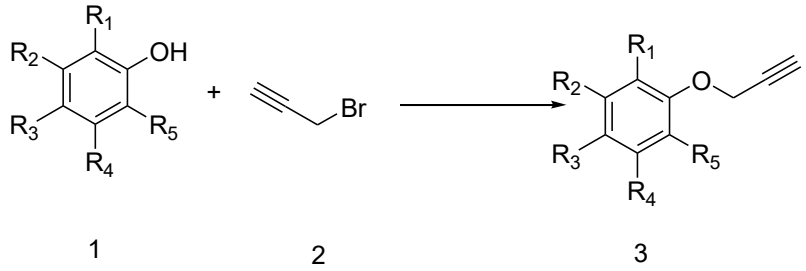

FIGURE 1. Alkyne 3 from propargyl bromide 2 and substituted phenol 1

To a solution of substituted/unsubstituted phenol (1 eq) in dry acetone (10 vol) was added potassium carbonate (1.3 eq), stirred at ambient temperature for 15 min. Then propargyl bromide (1.2 eq) was added drop wise and content were stirred at 60°C for 4-6h. Progress of reaction was monitored by TLC. After completion of reaction filter the unreacted base and solvent was evaporated till dryness (Fig 1). Then reaction was quenched by addition of water and extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulphate and evaporated to get title alkyne intermediate and recorded yield 80-95%

General procedure of Click chemistry

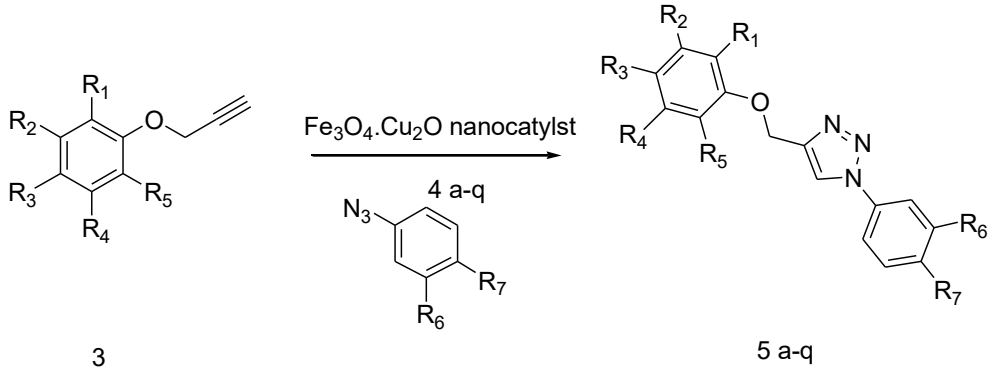

FIGURE 2. Substituted isoxazole 5 from substituded alkyne 3

To a solution of alkyne intermediate (1 eq) and corresponding aryl/ benzyl azide (1 eq) in ethanol: water (7:3) was added $Fe_3O_4.Cu_2O$ (0.05 eq). Contents were heated at 60°C for 1h. Reaction was monitored by TLC. Reaction mass was cooled down to room temperature gradually (Fig 2). Solid was precipitated out. Solvent was evaporated on rotary evaporator, water was added and extracted with ethyl acetate. Organic layer was dried on anhydrous sodium sulfate and evaporated. Crude compound was purified by column chromatography (60-120 mesh silica gel) using ethyl acetate: hexane as eluent.

RESULT AND DISCUSSION

Characterization of Fe_3O_4 Nanocatalyst

Based on the observation $Fe_3O_4.Cu_2O$ nanocatalyst is black in colour appearance and showed the magnetic properties. In FTIR, the characteristic peak at 554 cm^{-1} is the bond vibration of Fe-O bond stretching in Fig.3. The crystal geometry of the $Fe_3O_4.Cu_2O$ nanocatalyst were confirmed by X-ray diffraction pattern and is shown in Fig 4. All diffraction peaks of the samples are indexed to $Fe_3O_4.Cu_2O$. The diffraction peaks for pure $Fe_3O_4.Cu_2O$ nanocatalyst at $2\theta = 30.119^\circ$, 37.118°, 41.577°, 54.311, 61.498°, 75.701° and 78.589° corresponds to the crystal planes of 110, 111, 200, 211, 220, 311 and 222 of crystalline Cu_2O, respectively (JCPDS card no. 05-0667). While diffraction peaks for Fe_3O_4 nanoparticles at $2\theta = 31.513^\circ$, 35.255°, 43.089°, 57.519° and 63.621° corresponds to the 220, 311, 400, 511, 422 respectively (JCPDS card no. 65-19-0629). The seven distinguishable peaks in the XRD pattern of Cu_2O confirms the rhombic dodecahedral crystals in the cubic phase with a cuprite structure. XRD patterns of Fe_3O_4 five distinguishable peaks in the XRD pattern of confirms suggests the cubic phase structure.

The morphology of the prepared $Fe_3O_4.Cu_2O$ sample was recorded by field emission scanning electron microscopy (FESEM) and is shown in Fig. 5. FESEM images confirms the cubic-like morphology of samples with variable sizes. In order to confirm the elements in the sample, the energy dispersive X-ray (EDS) spectrum of the $Fe_3O_4.Cu_2O$ nanocomposite was recorded and shown in Fig 7. The EDS spectra confirms the purity of samples as there is no other elements other than Cu, Fe and O. The size and morphology of the $Fe_3O_4.Cu_2O$ nanoparticles analyzed by TEM and shown in Fig. 6. The TEM images confirm cubic morphology of samples.

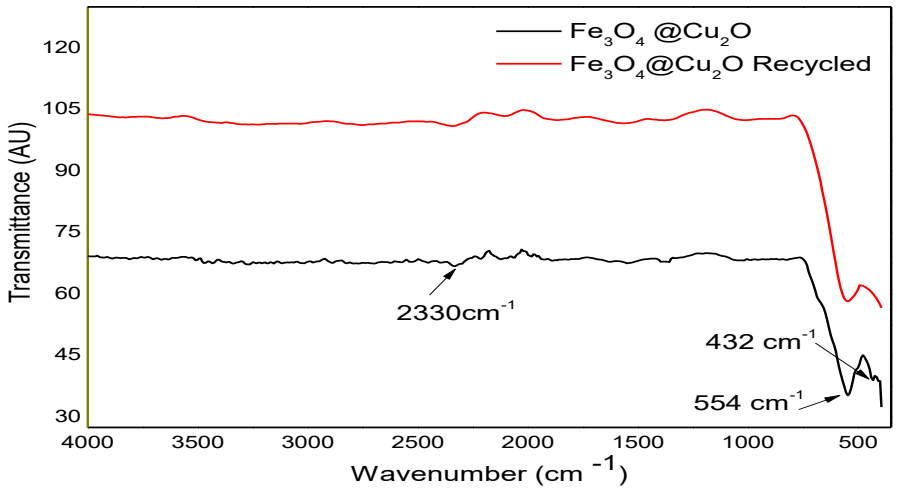

FIGURE 3: (FTIR) of $Fe_3O_4.Cu_2O$

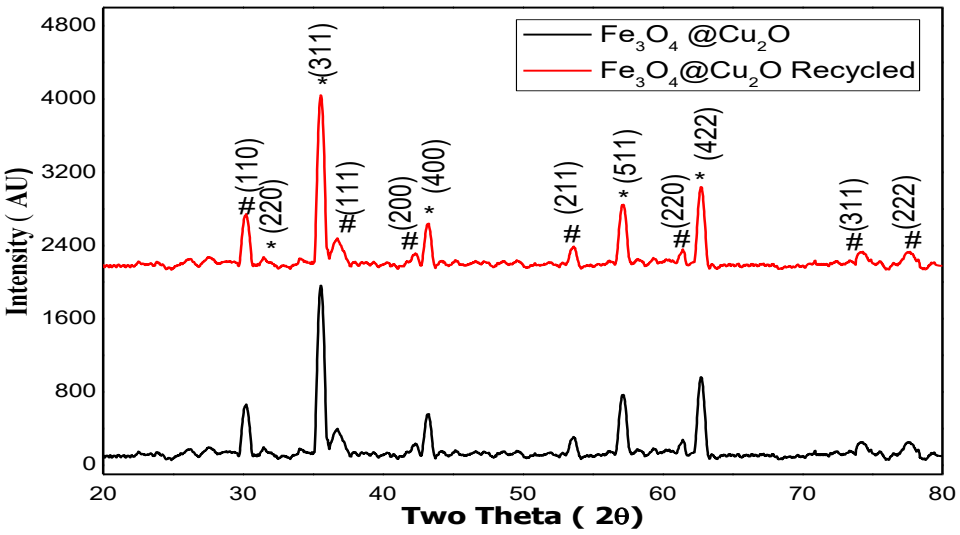

FIGURE 4: XRD pattern of Fe_3O_4.Cu_2O

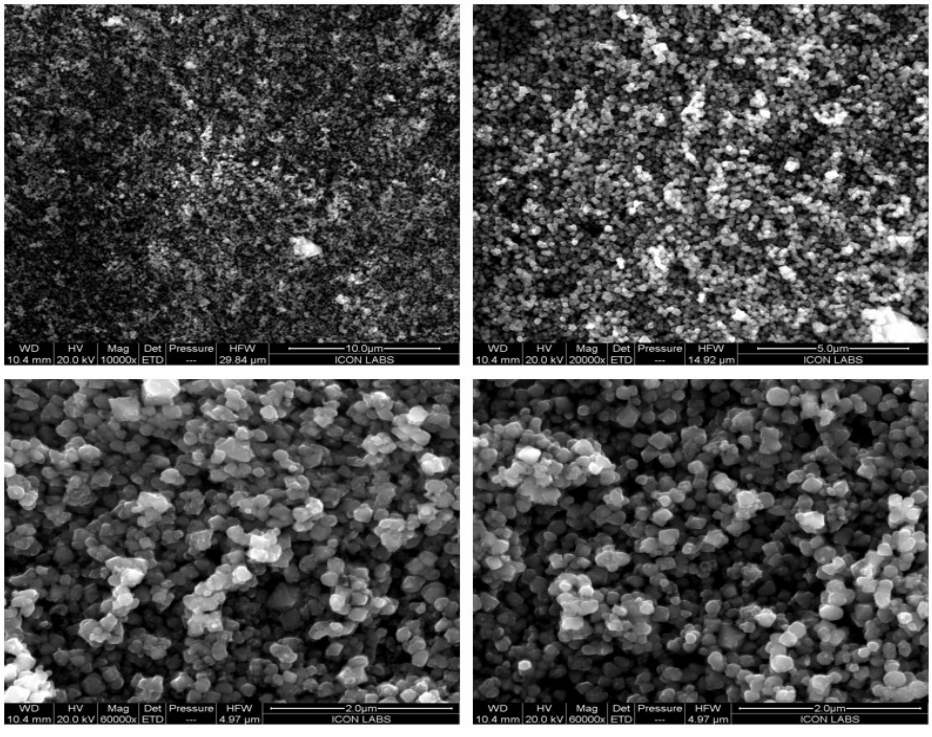

FIGURE 5: SEM images of Fe_3O_4.Cu_2O

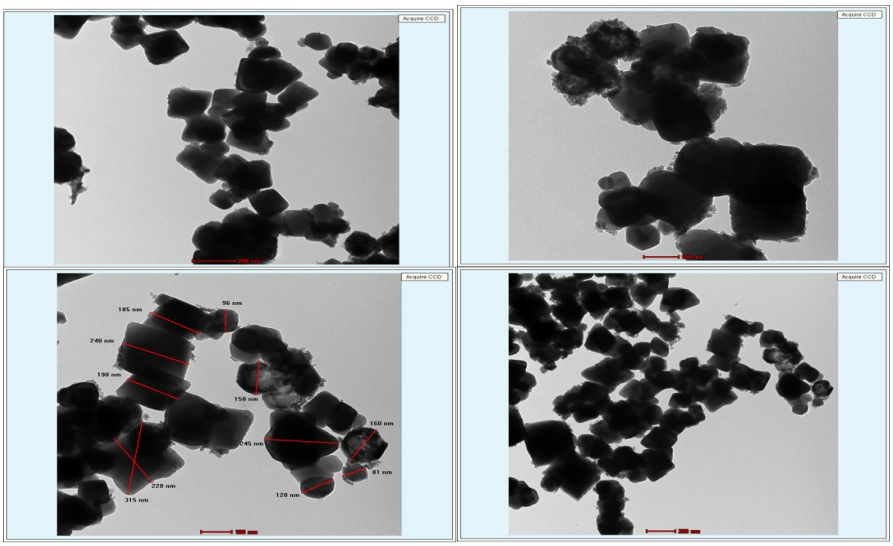

FIGURE 6: TEM images of $Fe_3O_4.Cu_2O$

Reaction Between The Alkyne Intermediate And Substituted Azide (5a-5q)

The alkyne intermediate and corresponding aryl/ benzyl azide in presence of $Fe_3O_4.Cu_2O$ catalyst in ethanol: water system at 60°C for 1 hour gets triazole moieties. The overall observations of alkyne intermediate and corresponding aryl/ benzyl azide works well in ethanol: water combination for the reaction. After completion of the reaction just filtered the catalyst through celite bed (keeping filter paper on celite bed for recovery of the catalyst) and filtrate evaporated. The crude material after water work up was purified by column chromatography using Ethyl acetae: Hexane system. All compounds obtained are solid in nature. The recovered catalyst again reused for the further reactions and there is no loss of yield is observed. It works well for further reactions.

TABLE 1: *In compound 8d and 8h, Azide used = 1-napthyl azide

Entry	R1	R2	R3	R4	R5	R6	R7	Product	M.P. (^{0}C)	Yield (%)
1	-H	-H	-H	-H	-H	-H	$-NO_2$	5a	90-91	93
2	-H	-H	-H	-H	-H	-H	$-OCH_3$	5b	135-136	81
3	-H	-H	-H	-H	-H	$-CF_3$	-H	5c	83-85	71
4	-H	-H	-H	-H	-H	-Ph	-Ph	5d	72-73	65
5	-H	-H	-H	-H	-H	-Cl	-H	5e	101-102	90
6	-H	-H	-H	-H	-H	$-OCH_3$	-Cl	5f	152-153	72
7	-H	-H	-Cl	-H	-H	-H	-I	5g	84-85	66
8	-H	-H	-H	-H	-H	-H	-I	5h	52-54	70
9	-Cl	-H	-H	-H	-Cl	-H	-I	5i	119-120	88
10	-H	-H	-H	-H	-H	$-CF_3$	-H	5j	94-95	71
11	-Cl	-H	-Cl	$-NHCOCH_3$	-H	$-CF_3$	-H	5k	60-61	73
12	-H	-H	-H	$-CF_3$	-H	-Cl	-F	5l	78-79	78
13	-Cl	-H	-Cl	$-NHCOCH_3$	-H	-Cl	-F	5m	68-69	91
14	-Cl	-H	-H	-H	-Cl	-H	-F	5n	111-112	82
15	-H	-H	-Cl	-H	-H	-H	-CN	5o	143-144	93
16	-H	$-CF_3$	-H	-H	-H	-H	-H	5q	88-89	86
17	-Cl	-H	-H	-H	-Cl	-H	-H	5r	120-121	87

Recyclability of $Fe_3O_4.Cu_2O$

To study the recyclability of $Fe_3O_4.Cu_2O$ catalyst substituted alkyne 3a and substituted azide 7a were used as substrate. After every run, nanocatalyst was washed several times with absolute alcohol and de-ionized water and dried at 120^0C for 1 hour in oven. Finally, it was reused for another four reaction cycles. It was found that no significant drop in yield after fifth cycle.

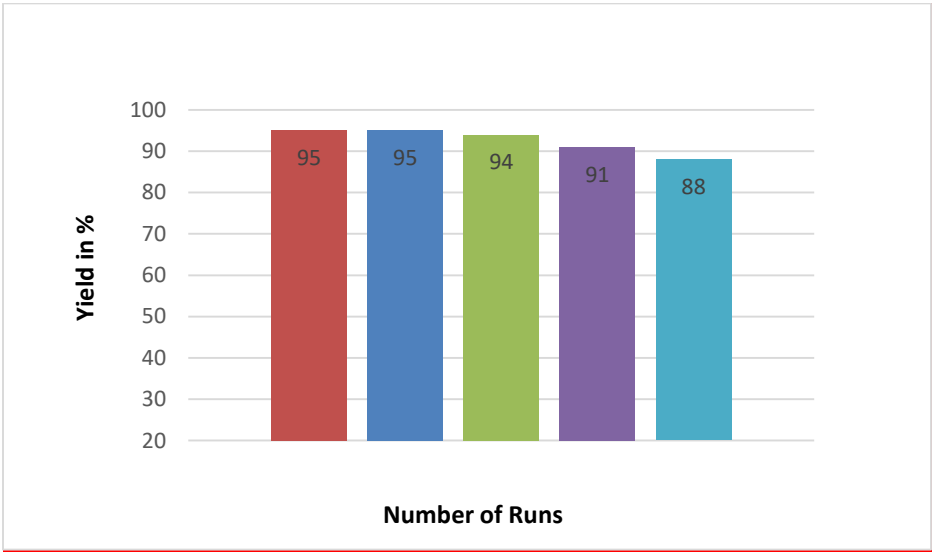

FIGURE 7: Re-cyclability study of nanocatalyst $Fe_3O_4.Cu_2O$

Spectral Analysis of 5a-5q

1-(4-nitrophenyl)-4-(phenoxymethyl)-1H-1,2,3-triazole (5a):
Yield: 79%, **^{1}H NMR (500 MHz, DMSO d$_6$)** δ ^{1}H NMR (500 MHz, DMSO) δ 9.18 (s, 1H), 8.50 – 8.43 (m, 2H), 8.29 – 8.22 (m, 2H), 7.36 – 7.30 (m, 2H), 7.09 (dd, *J* = 8.7, 0.9 Hz, 2H), 6.98 (dd, *J* = 10.6, 4.1 Hz, 1H), 5.27 (s, 2H). **^{13}C NMR (126 MHz, DMSO d$_6$)** δ 158.40, 147.25, 145.10, 141.26, 130.05, 126.05, 123.75, 121.52, 121.16, 115.19, 61.30. **HRMS m/z [M+H]$^+$** calcd for $C_{15}H_{13}N_4O_3$ 297.0988, found 297.0981.
1-(4-methoxyphenyl)-4-(phenoxymethyl)-1H-1,2,3-triazole (5b):
^{1}H NMR (500 MHz, DMSO d$_6$) δ 8.84 (s, 1H), 7.84 – 7.80 (m, 2H), 7.35 – 7.30 (m, 2H), 7.16 – 7.13 (m, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 5.22 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 159.80, 158.49, 144.16, 130.47, 130.02, 123.28, 122.29, 121.41, 115.37, 115.18, 61.41, 56.04. **HRMS m/z [M+H]$^+$** calcd for $C_{16}H_{16}N_3O_2$ 282.1243, found 282.1240.
4-(phenoxymethyl)-1-(3-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (5c):
^{1}H NMR (500 MHz, DMSO d$_6$) δ 9.15 (s, 1H), 8.34 – 8.25 (m, 2H), 7.92 – 7.83 (m, 2H), 7.37 – 7.29 (m, 2H), 7.09 (dt, *J* = 9.2, 1.8 Hz, 2H), 7.01 – 6.94 (m, 1H), 5.27 (s, 2H).). ^{13}C NMR (126 MHz, DMSO) δ 158.44, 144.76, 137.51, 131.81, 130.04, 124.53, 123.63, 121.48, 117.30, 117.27, 115.19, 61.39. **HRMS m/z [M+H]$^+$** calcd for $C_{16}H_{13}F_3N_3O$ 320.1011, found 320.0868.
1-**(naphthalen-1-yl)-4-(phenoxymethyl)-1H-1,2,3-triazole (5d):**
^{1}H NMR (500 MHz, DMSO d$_6$) δ 8.79 (s, 1H), 8.21 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 7.78 – 7.59 (m, 4H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.38 – 7.30 (m, 2H), 7.12 (dd, *J* = 8.7, 0.9 Hz, 2H), 6.99 (dd, *J* = 10.5, 4.1 Hz, 1H), 5.30 (s, 2H). **HRMS m/z [M+H]$^+$** calcd for $C_{19}H_{16}N_3O$ 302.1293, found 302.1302.
1-**(3-chlorophenyl)-4-(phenoxymethyl)-1H-1,2,3-triazole (5e):**
^{1}H NMR (500 MHz, DMSO d$_6$) δ 9.04 (s, 1H), 8.07 (t, *J* = 2.0 Hz, 1H), 7.94 (ddd, *J* = 8.1, 2.1, 1.0 Hz, 1H), 7.64 (t, *J* = 8.1 Hz, 1H), 7.58 (ddd, *J* = 8.1, 2.0, 1.0 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.13 – 7.05 (m, 2H), 6.97 (tt, *J* = 7.5, 1.0 Hz, 1H), 5.24 (s, 2H). **HRMS m/z [M+H]$^+$** calcd for $C_{15}H_{13}ClN_3O$ 286.0747, found 286.0741.
1-**(4-chloro-3-methoxyphenyl)-4-(phenoxymethyl)-1H-1,2,3-triazole (5f):**

^{1}H NMR (500 MHz, DMSO d$_6$) δ 8.93 (s, 1H), 8.04 (d, *J* = 2.6 Hz, 1H), 7.88 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.38 – 7.30 (m, 3H), 7.09 – 7.06 (m, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 5.22 (s, 2H), 3.94 (s, 3H). **HRMS m/z [M+H]$^+$** calcd for $C_{16}H_{15}ClN_3O_2$ 316.0853, found 316.0847.

5-**((4-chlorophenoxy)methyl)-1-(4-iodophenyl)-1H-1,2,3-triazole (5g):**

IR (KBr, υ$_{max}$/cm^{-1}): 3136, 1485, 1372, 1229, 1167, 1093, 1051, 1030, 1003, 981, 823, 647, 524. **^{1}H NMR (500 MHz, DMSO d$_6$)** δ 8.98 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 5.24 (s, 2H). **^{13}C NMR (126 MHz, DMSO d$_6$) δ** 157.26, 144.35, 139.23, 136.83, 129.77, 125.20, 123.46, 122.62, 117.22, 94.94, 61.76. **HRMS m/z [M+H]$^+$** calcd for $C_{39}H_{59}ClN_3O_3$ 652.4245, found 622.4246

1-**(4-iodophenyl)-4-((phenylthio)methyl)-1H-1,2,3-triazole (5h):**

IR (KBr, υ$_{max}$/cm^{-1}): 3126, 3088, 1578, 1490, 1230, 1042, 978, 88, 732, 687, 517. **^{1}H NMR (500 MHz, DMSO d$_6$)** δ 8.71 (s, 1H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.40 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 4.37 (s, 2H). **^{13}C NMR (126 MHz, DMSO d$_6$)** δ 145.47, 139.12, 136.65, 136.11, 129.60, 128.77, 126.60, 122.28, 121.84, 94.76. **HRMS m/z [M+H]$^+$** calcd for $C_{15}H_{13}IN_3S$ 393.9875, found 393.9870.

4-**((2,6-dichlorophenoxy)methyl)-1-(4-iodophenyl)-1H-1,2,3-triazole (5i):**

^{1}H NMR (500 MHz, DMSO d$_6$) δ 9.03 (s, 1H), 7.97 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 5.21 (s, 2H). **^{13}C NMR (126 MHz, DMSO d$_6$)** δ 150.55, 143.79, 139.20, 136.66, 129.91, 129.42, 127.07, 123.93, 122.51, 94.94, 66.27. **HRMS m/z [M+H]$^+$** calcd for $C_{15}H_{13}IN_3S$ 393.9875, found 411.9708. **HRMS m/z [M+H]$^+$** calcd for $C_{15}H_{11}Cl_2IN_3O$ 445.9324, found 445.9320. **IR (KBr, υ$_{max}$/cm^{-1})**:3139, 3072, 1739, 1559, 1493, 1457, 1434, 1244, 1224, 1205, 1044, 1020, 938, 823, 772, 560.

5-**((phenylthio)methyl)-1-(3-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (5j):**

IR (KBr, υ$_{max}$/cm^{-1}): 3141, 3074, 1581, 1481, 1459, 1319, 1290, 1166, 1114, 1092, 1069, 801, 737, 692, 648.

^{1}H NMR (500 MHz, DMSO d$_6$) δ 8.91 (s, 1H), 8.30 – 8.18 (m, 2H), 7.90 – 7.79 (m, 2H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 4.40 (s, 2H). **^{13}C NMR (126 MHz, DMSO d$_6$)** δ 145.67, 137.45, 136.03, 131.74, 129.52, 128.79, 126.50, 124.25, 122.21, 117.08, 27.77. **HRMS m/z [M+H]$^+$** calcd for $C_{16}H_{12}F_3N_3S$ 336.0782, found 336.0787.

N-**(2,4-dichloro-5-((1-(3-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-4yl)methoxy)phenyl)acetamide (5k):**

IR (KBr, υ$_{max}$/cm^{-1}): 3292, 3093, 1666, 1586, 1526, 1477, 1429, 1394, 1331, 1287, 1252, 1120, 1090, 1071, 1000, 870, 796, 870, 796, 692. **^{1}H NMR (500 MHz, DMSO d$_6$)** δ 9.67 (s, 1H), 9.16 (s, 1H), 8.31 (d, *J* = 26.2 Hz, 2H), 7.85 (d, *J* = 32.9 Hz, 3H), 7.64 (s, 1H), 5.36 (s, 2H), 2.14 (s, 3H). **HRMS m/z [M+H]$^+$** calcd for $C_{18}H_{14}Cl_2F_3N_4O_2$ 445.0446, found 445.0443.

1-**(3-chloro-4-fluorophenyl)-4-((3-(trifluoromethyl)phenoxy)methyl)-1H-1,2,3-triazole (5l):**

^{1}H NMR (500 MHz, DMSO d$_6$) δ 9.02 (s, 1H), 8.24 (s, 1H), 7.99 (s, 1H), 7.78-7.30 (m,, 5H), 5.36 (s, 2H). **^{13}C NMR (126 MHz, DMSO d$_6$)** δ 158.81, 144.19, 134.40, 131.25, 123.99, 123.04, 121.65, 121.46, 119.44, 118.67, 118.49, 118.03, 112.00, 61.78. **HRMS m/z [M+H]$^+$** calcd for $C_{16}H_{11}ClF_4N_3O$ 372.0527, found 372.0533. **IR (KBr, υ$_{max}$/cm^{-1})**: 1591, 1503, 1453, 1409, 1264, 1228, 1149, 1057, 1041, 1003, 851, 785, 743, 712, 694, 656.

O-**(2,4-dichloro-5-((1-(3-chloro-4-fluorophenyl)-1H-1,2,3-triazol-4-yl)methoxy)phenyl)acetamide (5m):**

IR (KBr, υ$_{max}$/cm^{-1}): 3091, 2125, 1736, 1600, 1563, 1335, 1314, 1235, 1179, 1123, 904, 852, 815, 791, 743, 695, 655, 518. **^{1}H NMR (500 MHz, DMSO d$_6$)** δ 9.00 (s, 1H), 7.97 (d, *J* = 8.6 Hz, 2H), 7.75 (d, *J* = 8.6 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 1H), 5.35 (s, 2H).

4-**((2,6-dichlorophenoxy)methyl)-1-(4-fluorobenzyl)-1H-1,2,3-triazole (5n):**

IR (KBr, υ$_{max}$/cm^{-1}): 3097, 1738, 1603, 1563, 1510, 1437, 1241, 1220, 976, 842, 770, 526. **^{1}H NMR (500 MHz, DMSO d$_6$)** δ 8.33 (s, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.37 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.20 (dt, *J* = 13.9, 8.5 Hz, 3H), 5.61 (s, 2H), 5.13 (s, 2H). **^{13}C NMR (126 MHz, DMSO d$_6$)** δ 163.38, 161.43, 150.43, 142.90, 132.78, 130.65, 130.58, 129.73, 129.35, 126.75, 125.76, 116.11, 115.94, 66.38, 52.47. **HRMS m/z [M+H]$^+$** calcd for $C_{16}H_{13}Cl_2FN_3O$ 352.0420, found 352.0423

5-**(4-((4-chlorophenoxy)methyl)-1H-1,2,3-triazol-1-yl)benzonitrile (5o):**

IR (KBr, υ$_{max}$/cm^{-1}): 3147, 3117, 2233, 1667, 1606, 1517, 1488, 1458, 1406, 1287, 1234, 1169, 1042, 821, 655, 513.

^{1}H NMR (500 MHz, DMSO d$_6$) δ 9.12 (s, 1H), 8.17 (d, *J* = 8.9 Hz, 2H), 8.12 (d, *J* = 8.9 Hz, 2H), 7.36 (d, *J* = 9.0 Hz, 2H), 7.11 (d, *J* = 9.0 Hz, 2H), 5.27 (s, 2H). **HRMS m/z [M+H]$^+$** calcd for $C_{16}H_{12}ClN_4O$ 311.0700, found 311.0699.

1-**benzyl-4-((3-(trifluoromethyl)phenoxy)methyl)-1H-1,2,3-triazole (5q):**

IR (KBr, υ$_{max}$/cm^{-1}): 3137, 3092, 1739, 1588, 1492, 1453, 1434, 1366, 1287, 1154, 1117, 1009, 988, 885, 790, 739, 696, 579. **^{1}H NMR (500 MHz, DMSO d$_6$)** δ 8.30 (s, 1H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.43 – 7.26 (m, 8H), 5.62 (s, 2H), 5.24 (s, 2H).

1-**benzyl-4-((2,6-dichlorophenoxy)methyl)-1H-1,2,3-triazole (5r):**

IR (KBr, υ_{max}/cm^{-1}): 3147, 3101, 1489, 1238, 1221, 1030, 992, 858, 830, 814, 764, 719, 704, 648, 580, 513. **^{1}H NMR (500 MHz, DMSO d_6)** δ 8.28 (s, 1H), 7.39-7.29 (m, 7H), 7.05 (d, *J* = 8.6 Hz, 2H), 5.61 (s, 2H), 5.13 (s, 2H). **HRMS m/z [M+H]$^+$** calcd for $C_{16}H_{14}Cl_2N_3O$ 336.0782, found 336.0787.

CONCLUSION

$Fe_3O_4.Cu_2O$ nanoparticle catalyst is magnetically active nanocatalyst. The alkyne-azide coupling reaction using $Fe_3O_4.Cu_2O$ catalyst worked well. The formed indole based novel 1,2,3-triazole molecules isolated having overall yield ~ 75%. $Fe_3O_4.Cu_2O$ nanocatalyst preparation is easy, simple preparation condition and reusable. The nanocatalyst used for the reaction shows good result within short time, better yield with moderate temperature. $Fe_3O_4.Cu_2O$ nanocatalyst recycled four times after the reaction and showed the optimum result without changes the catalytic activity.

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