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ARTICLE TYPE

Synthetic application of gold nano particles and auric chloride for the synthesis of 5-substituted 1-*H* tetrazoles

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An effective one-pot, convenient gold catalyzed synthesis of 5-substituted 1*H*-tetrazoles has been discussed. The study demonstrated the comparative overview for utilization of gold (III) and gold nano-particles (spheres) as a catalyst. Detailed understandings of the mechanism, surface area effect (in reference of nanoparticles) of gold in the activation of nitriles for nucleophilic (3+2) cycloaddition of sodium azide to give product have also been studied.

1. Introduction

The 1*H*-tetrazole functional group is a versatile moiety in organic synthesis and found quite stable in a broad pH range, and well tolerated against various oxidizing and reducing agents.[1] It is important pharmacophore in the field of medicinal chemistry[2] and its pharmaceutical applications are vastly explored and comprehensively documented in the literature.[3] The tetrazole-based drug candidates possess anticonvulsants,[4] antihypertensive, antiallergic and antibiotic activities,[5] and have shown promising results in treatment of dreaded diseases, such as cancer and AIDS.[6] Besides, tetrazoles are broadly used in agriculture as herbicides and fungicides.[7] It is also reported that biphenyltetrazoles stimulate the release of growth hormones,[8] and thus widely used to synthesize sartan family drugs.[9] Furthermore, tetrazoles are also used in photography and photo-imaging as stabilizers.[2] The tetrazoles are lipophilic, metabolically stable compounds[10] and can be considered for carboxylic acid bioisosteres,[11] cis-amide isosteres in peptide chemistry[12] as well as in material sciences.[13] Owing to the high enthalpy of formation, their derivatives have been explored in various explosives and propellant components.[14] Further, tetrazoles have low molecular weight and possess high nitrogen content,[15] and can possess various substituents to form stable complexes with several metal ions,[16] which makes it important intermediate in coordination chemistry.[17] Tetrazoles are selectively synthesized by (3+2) dipolar cycloaddition of an azide moiety over nitrile through a concerted and regioselective[18] manner to give 5-substituted 1-*H* tetrazoles. 5-Substituted 1*H*-tetrazoles synthesis is fascinating field in organic synthesis, and several new methods have emerged since its synthesis by Finnegan, which are either revision of existing processes or new catalytic protocols.[19] The synthesis involves the influence of several efficient catalysts and different solvent conditions. Till date, several new catalysts have also been investigated. These catalysts, which serve the aforementioned purpose, are copper triflates,[20] zinc(II) salts,[21] $Fe(OAc)_2$,[22] Lewis acids, such as $FeCl_3$,[23] TBAF,[24] $AlCl_3$,[25] BF_3-OEt_2,[26] heterogeneous catalysis, CoY zeolites,[27] mesoporous ZnS nanospheres,[28] Cu_2O[29] and $CuFe_2O_4$ nano particles.[30] Acid catalysts are also used for the synthesis of tetrazoles via cycloaddition.[31] However, majority of previously reported procedures, which involve Lewis acids, were found poor catalysts for the synthesis of aliphatic tetrazoles or they have not included the synthesis of aliphatic tetrazole.[19] Furthermore, they were found riddled with several potential drawbacks like long reaction time, elevated temperature conditions (120-190 °C),[32] low yield, use of toxic metals. In addition to this, some cases show formation of toxic hydrazoic acid,[33] involvement of alkyltin based reagents which warrant the safety of the procedure. The importance of tetrazoles in the field of medicinal chemistry demands newer, safe and sustainable protocols for the synthesis of tetrazoles with minimal drawbacks associated with previous methods. Thus, the choice of catalyst is one of the most crucial steps to achieve good results.

Over the past few decades, transition metals have attracted the attention of chemists, and consequently several reports have shown the utility of transition elements and their salts as a catalyst in organic synthesis. Being a soft Lewis acid,[34] gold has attracted considerable attention of chemists for its potential use as catalysis. The potential catalytic property of gold is attributed to its well known π-acidity[35] and thus exploited well in recent years to influence a range of transformations. Many organic transformations, such as coupling reactions,[36] Friedel Crafts type,[37] cycloaddition reactions,[38] cyclization of allenol and alkynol,[39] carbon-carbon bond formation,[36] C-H activation,[40] from C-X (X = O, N) bond formation are known to be catalyzed by Au(III) state, and this enhanced catalytic activity is attributed to their Lewis acidity.[41] Similarly, AuNPs feature a wide range of potential applications in various fields such as catalysis,[42] biotechnology,[43] and medicine,[44] and are thus may be explored as the most powerful tool for studying nanoscale materials. This

broad range of applicability of gold encourages us to use it as a catalyst for the synthesis of 5-substituted 1-*H* tetrazoles. The extensive literature survey reveals that till date, neither AuNPs nor $HAuCl_4.3H_2O$ as catalysts have been used in the synthesis of 5-substituted 1*H*-tetrzole. Herein, we are going to report the utility of Gold Nano Particles and Auric Chloride for one pot synthesis of 5-substituted 1*H*-tetrazoles via (3+2) cycloaddition with high yields. Our research is focused on design and synthesis of biologically active molecules[45] and X-rays analysis of small molecules.[46] In diversification of our ongoing research, we recently reported new catalytic method for synthesis of carboxylic acids[47] and tetrazoles.[48]

2. Experimental

2.1 General experimental condition for $HAuCl_4.3H_2O$ catalysed reaction:

The representative tetrazole 1b was synthesized via following procedure: Sodium azide (1.5 mmol) was added to a solution of nitrile 1a (1mmol) and $HAuCl_4.3H_2O$ (10 mmol %) in dry DMF (2 ml) and reaction mixture was stirred for 0.45 h at 110 °C under nitrogen atmosphere. After consumption of 1a as seen by TLC, the reaction mixture was cooled to room temperature and the DMF was evaporated under reduced pressure. The crude reaction mixture was dissolved in ethyl acetate (30mL) and washed with acidified water (20mL, 4N HCl) twice. The organic layer was separated and washed with brine solution, dried over anhydrous Na_2SO_4, and solvent was evaporated till dryness to obtained tetrazole 1b as a white crystalline solid in 90% yield.

2.2 General experimental condition for Au nano-spheres (AuNPs) catalysed reaction:

Sodium azide (1.5 mmol) was added to a solution of nitrile 1a (1mmol) and AuNPs (2 mmol %) in anhydrous DMF (2 ml). The reaction mixture was stirred for 0.3 h at 80 °C under nitrogen atmosphere. After consumption of 1a as seen by TLC, the reaction mixture was cooled to room temperature and solvent evaporated under reduced pressure. The crude reaction mixture was dissolved in ethyl acetate (30mL) and washed with acidified water (20mL, 4N HCl) twice. The organic layer was separated and washed with brine solution dried over anhydrous Na_2SO_4, and solvent was evaporated to obtained tetrazole 1b as a white crystalline solid in 95% yield. All synthesized compounds were characterized by using various analytical techniques viz. melting point measurements, ^1H, ^{13}C NMR, IR and X-rays (12b Au (III) as a catalyst and 14b by using AuNPs catalysed procedure) crystallography study (Fig. 1) and the data were found comparable with the literature reported data.

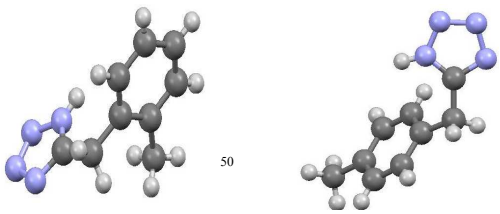


Fig. 1. ORTEP diagram for compound 12b and 14b (Proposed method is validated by X-ray crystallographic analysis of product 12b and 14b synthesized by gold(III) chloride and gold(0) naoparticles respectively).

2.3 General experimental procedure for synthesis of Au nano-spheres (AuNPs):

Gold nano particles were synthesized according to the reported literature procedure.[49] Its morphology and particles size was determined by using UV-vis absorption spectrum, DLS and TEM, techniques (Fig. 2-5). UV-vis absorption spectrum of the synthesized AuNPs exhibited a strong absorption peak around 526 nm, which was found dependent on the size and shape of particles (Fig. 3). Size distribution analysis by DLS showed average particle size around 26.33 nm (Fig. 4). Furthermore, the size and shape analysis of AuNPs by TEM imagaing technique showed uniform distribution with predominantly spherical morphology with their average size of about 26±3 nm (Fig. 2).

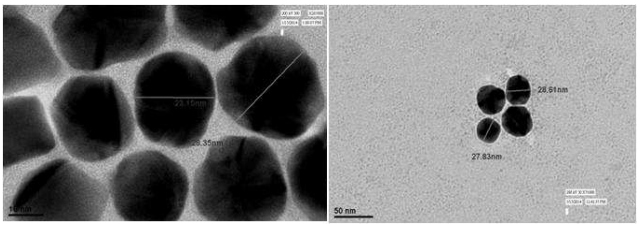


Fig. 2. Transmission electron microscopy (TEM) Image for Gold nanoparticles.

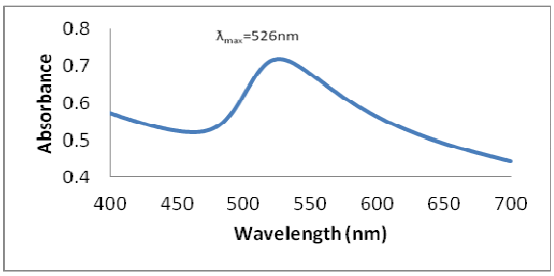


Fig. 3. UV- vis spectra of Gold nanoparticle in H_2O.

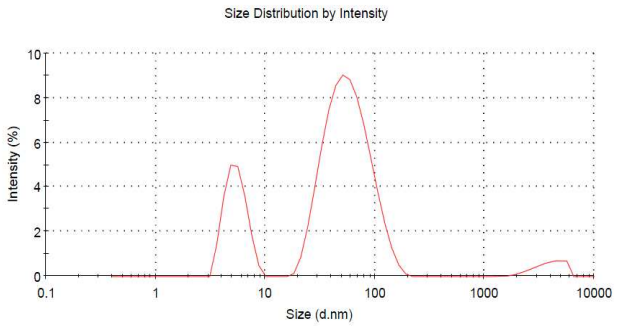


Fig. 4. Average size (d. nm) 26.33

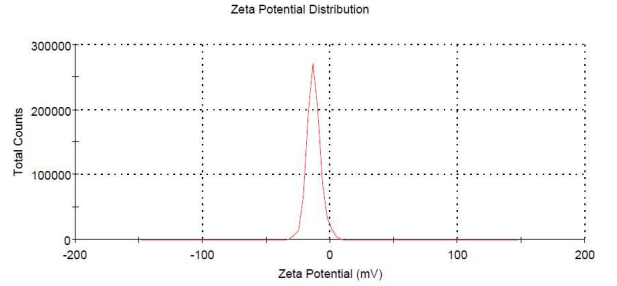


Fig. 5. Zeta Potential (mV): -12.9

To ascertain the oxidation state of Au(0) in AuNPs, we performed XPS experiment. Briefly, X-rays photo electron spectroscopic measurements were carried out by using VG Micro Tech ESCA-3000. AlKα X-ray radiation (hυ = 1486.6eV) with a spectral resolution of 0.4eV. Analyzer- mode passes energy of 50eV. The spectrum was charge calibrated with respect to the adventitious C 1s peak at 285.0 eV.

The XPS analysis of AuNPs confirmed that the Au is in zero oxidation state (Fig. 6). The values exactly match with earlier reported spectra of Au(0)[50]. Interpretation of spectra reveals two peaks at binding energy 84.0eV and 87.7eV corresponding to $Au4f_{7/2}$ and $Au4f_{5/2}$, respectively. The Au4f region has well separated spin-orbit coupling components with binding energy difference of 3.7eV, which is a characteristic of Au (0).

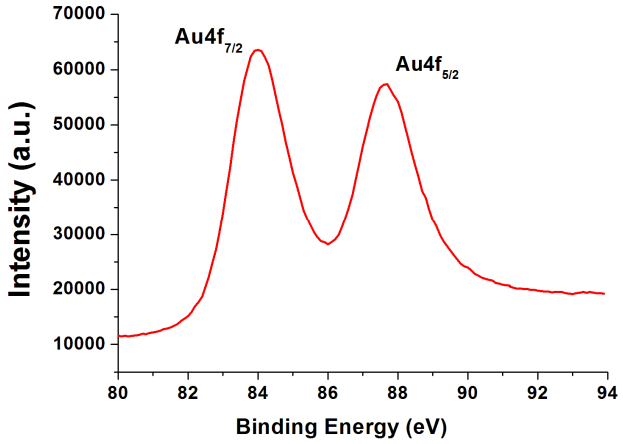
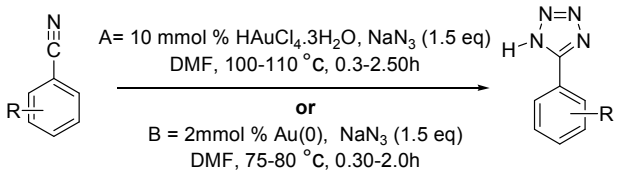


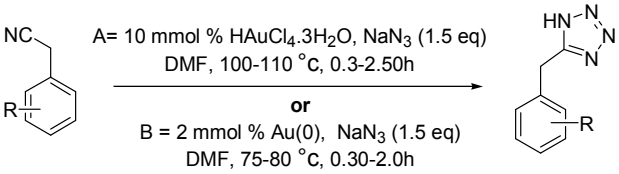
Fig.6. X-rays photo electron spectrum of AuNPs (Au4f)

3. Results and discussion

The broad spectrum of utilities of gold in chemical transformations plays major role in catalysis. This catalytic activity is supposedly attributed to its ability of activation of a particular functionality via coordination, which selectively affords the reactivity of the molecule. For example, our result explicitly shows involvement of activation of nitrile functionality of cyanobenzene by an Au (III or 0) state of catalyst. The pre-coordination of nitrile functional group with Au (III or 0) state, activates nitrile moiety for the (3+2) cycloaddition nucleophilic reaction with sodium azide. This enhanced activation of nitrile with Au (III) is probably due to its Lewis acid behaviour. Furthermore, the Au (0) state, in case of AuNPs, facilitates the same coordination chemistry owing to its negative zeta potential (Fig. 5) which, along with its large surface area available for coordination, enhance its Lewis acidity and therefore, leads to substantial yield of tetrazole formation. Functional compatibility of Au (III and 0) catalysts, for several functional groups like halides, alkoxy, amines, nitro, methyl, hydroxy and aldehydes were found well tolerated and preserved during the tetrazole formation. Besides, the AuNPs catalysed reaction shows better yield which may be the outcome of large surface area. This may also be accounted for the small reaction time and comparatively low temperature requirements (75 °C) with low catalyst loading (2 mmol %).



Scheme 1. Reaction of benzonitrile with sodium azide in DMF



Scheme 2. Reaction of benzylnitrile with sodium azide in DMF

In the current study, we investigated the effect of other solvents, such as DMF, NMP, DMSO, DCM, acetonitrile, chloroform, acetone, 1,4-dioxane, and EtOH, on account of their solubility, ease of product formation, effect on yield and environmental compatibility. Among the solvents tested, DMF was found most efficient solvent on many aspects, (Table 1, entries 1-4), while no detectable reaction was observed in chloroform, DCM, 1,4-dioxane and acetone even after prolonged heating under optimized conditions of catalyst (Table 1, entries 11-14). Further, in acetonitrile and ethanol, only small amount of product formed (5-7%, Table 1, entries 9,10) and, in case of DMSO, NMP and toluene conversion was achieved up to 56-60% at elevated temperature under optimized conditions of catalyst (10 mmol % and 110 °C) (Table 1, entries 5,6 and 8).

The optimization of catalysts were achieved by setting a number of experiments via varying the quantity of $HAuCl_4.3H_2O$ and AuNPs, using 1a as a starting material, shown in Table 1 and Table 2 respectively. The best yield (93%) was obtained in conversion of 1a to 1b with 15 mmol % of $HAuCl_4.3H_2O$ in DMF as a catalyst (Table 1 entry 4), while conversion reduced to 75% at 5 mmol % catalyst (Table 1, entry 1). Further, setting the reaction with amount of $HAuCl_4.3H_2O$ up to 10 mmol % resulted in small decrease in yield (90%) with almost neglible effect (Table 1, entry 2). Moreover, prolonged heating (1.3 hour) does not show significant increase in the yield (91%, Table 1, entry 3). Optimization of reaction temperature, to achieve maximum yield, was found out by carrying reaction at various temperatures, and eventually (100-110 °C with Au(III) and 75-80 °C with Au(0) were found optimal temperature. DMF was found best solvent with respect to temperature, time and catalyst loading parameters. This optimized protocol (1 eq. nitrile, 1.5 eq. NaN_3, and 10 mmol % of $HAuCl_4.3H_2O$ in DMF at 100-110 °C while in case of AuNPs it was 2 mmol % at 75-80 °C) consistently yielded good amount of products in all cases (Table 3). Furthermore, the protocol was also found applicable for aliphatic tetrazole formation in appreciable good yield (Scheme 1, and 2).

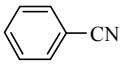
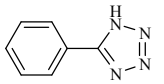
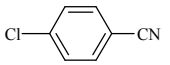
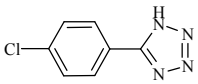
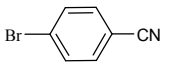
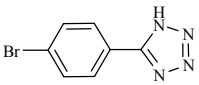
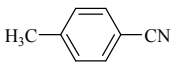
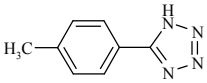
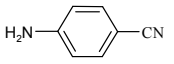
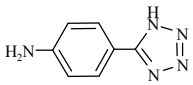
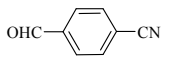
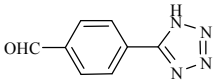
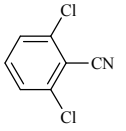
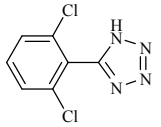
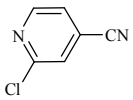
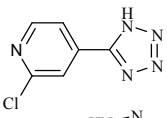
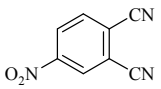
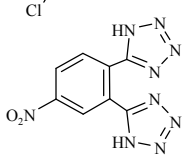
Table 1: Effect of $HAuCl_4.3H_2O$ (with 49 % purity) as catalyst and solvent on the formation of tetrazole 1b from 1a.

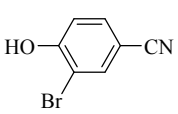
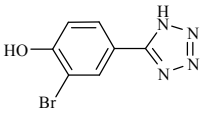
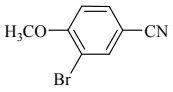
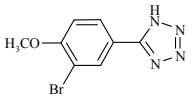
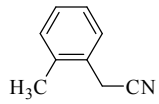
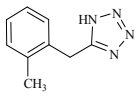
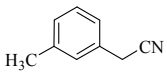
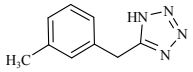
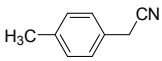
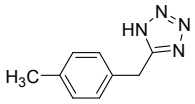
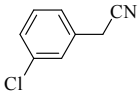
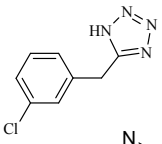
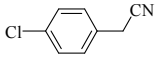
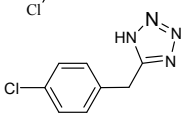
Entry	Catalyst (mmol%)	Solvent	Temp. (°C)	Time (h)	Yield (%)1b
1	5	DMF	110	1.00	75
2	10	DMF	110	0.45	90
3	10	DMF	110	1.30	91
4	15	DMF	110	1.30	93
5	10	DMSO	110	8.00	56
6	10	NMP	110	3.00	60
7	15	NMP	110	3.00	60
8	10	Toluene	110	3.00	58
9	10	CH_3CN	80	22.0	7
10	10	EtOH	78	12.0	5
11	10	$CHCl_3$	61	24.0	0
12	10	DCM	39	24.0	0
13	10	1,4-Dioxane	100	24.0	0
14	10	Acetone	56	24.0	0

Table 2: Effect of Au nanoparticles as a catalyst loading on the formation of tetrazole 1b from 1a in DMF.

Enry	Catalyst AuNPs (Fig. 2-5)	Temp (°C)	Time (h)	Yield (%)
1.	Au(0) (1 mmol %)	80	1.30	80
2.	Au(0) (2 mmol %)	80	0.30	95
3.	Au(0) (5 mmol %)	80	1.00	95
4.	Au(0) (10mmol %)	80	1.30	96

Table 3: $HAuCl_4.3H_2O$ (with 49% purity) & Au nanoparticle-catalyzed synthesis of 5-substituted 1*H*-tetrazoles.

S.No.	Nitriles [a]	Tetrazoles [b]	Temp (°C) Au(III)/ Au(0)	Time (h) Au(III)/ Au(0)	% Yields Au(III) [c]	% Yields Au(0) [d]
1			110/80	0.45/0.30	90	95
2			100/75	1.30/1:20	90	91
3			100/80	2.5/2.00	90	92
4			110/80	2/1.50	96	98
5			100/80	1.10/1.00	98	99
6			100/80	0.55/0.45	89	91
7			110/80	1.00/1.00	92	93
8			110/80	1.00/1.00	95	96
9[e]			110/80	1.30/1.20	94	96

10			100/80	1.40/1.30	89	94
11			110/80	0.30/0.30	92	94
12[f]			110/80	1.00/1.00	82	84
13			110/80	1.00/1.00	86	85
14[g]			110/80	1.00/1.00	85	87
15			110/80	1.00/1.00	82	83
16			100/80	1.20/1.10	84	84

[a] Nitriles 1(1a-16a except 9a) and NaN_3 (1.5 equiv) were subjected to react in dry DMF containing 10 mmol % of $HAuCl_4.3H_2O$/2 mmol % AuNPs, at given temperature and time details are given in the Table 3.

[c & d] Experimental yield.

[e] Nitriles 9a was reacted with NaN_3 (3.0 equiv) in dry DMF containing 20 mmol % of $HAuCl_4.3H_2O$/4 mmol % AuNPs at given temperature and time.

[f & g] Fig. 1.

The results of DMF mediated (3+2) cycloaddition reaction of various nitriles [a] with NaN_3, using 10 mmol % $HAuCl_4.3H_2O$ (with 49% purity) or 2 mmol % AuNPs as a catalyst for the formation of their respective tetrazoles are summarized in Table 3. It is observed that the reactions of the aryl nitriles 4a and 5a, bearing an electron-donating group at the para-position of the aromatic ring possess better yield (Table 3, entries 4 and 5) than electron withdrawing (Table 3, entry 6) group when present at para position. The effect of slightly deactivating group were also studied and found only small drop in yield (Table 3, entries 2 and 3). Further, steric crowding has no significant effect in the synthesis of tetrazoles (Table 3, entry 7). This method is also significant for hetroaromatic tetrazole formation from their corresponding heteroaromatic nitriles (Table 3, entry 8). In addition to this, it is also found applicable for aliphatic nitrile transformation (Table 3, entries 12-16). Dicyano derivative also converted into ditetrazole without any selectivity (Table 3, entry 9). Besides, the reaction is also tested on disubstituted nitriles, and the results indicate that meta substituent has no role while para substitution with electron releasing group to gives intermediate yield (Table 3, entries 10, 11). The above results stipulate that the tetrazole ring formation via (3+2) cycloaddition reaction involving Au(III) and Au(0) do not affect the other substituents and functional group and it is well tolerable irrespective of their electronic behaviour, positions and independent of the type of aromatic or aliphatic ring.

Leaching experiment

For getting the best results and to avoid any discrepancy, three parallel reactions were performed in separate apparatus, but at the same time and under similar reaction conditions. In first reaction mixture, the tetrazole synthesis was conducted at 80 °C for 20 minutes in the presence of catalyst which yielded 72 % of product after usual work up.

Simultaneously in second reaction, the reaction was conducted for 20 minutes and the AuNPs were removed from the reaction mixture by filtration. The reaction mixture was allowed to run for another 30 minutes at 80 °C. No progress of the reaction in this span was observed as the yield remains constant after work up (72 %).

In the third experiment, the reaction was followed the same protocol up to 50 min as mentioned in 2nd experiment then, AuNPs were added in desired catalytic amount to the reaction mixture and reaction was allowed to stir for another 10 minutes which gave quantitative yield of product after workup (95%) (Scheme 1, Fig.7).

These experiments confirmed that AuNPs are essential for completion of reaction. The heterogeneous nature of the catalyst was confirmed by ICP-OES analysis (Spectro Arcos, FHS-12).

No leaching of Au metal was detected in the ICP analysis of reaction mixtures. We conclude that AuNPs in reaction medium

act as heterogeneous catalyst. ICP data analysis is shown in Table 5 in supplementary file.

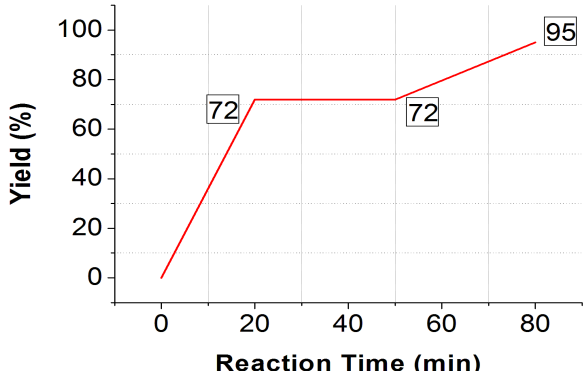


Fig.7. Leaching Test

In order to establish superior approach for the tetrazoles synthesis, we compared with other well known existing method for tetrazoles synthesis. It is evident from Table 4 that use of AuNPs/ $HAuCl_4.3H_2O$ gave high yield at lower temperature and in lesser reaction time as compared to others. Thus we can conclude that AuNPs/ $HAuCl_4.3H_2O$ are better catalyst for tetrazoles synthesis.

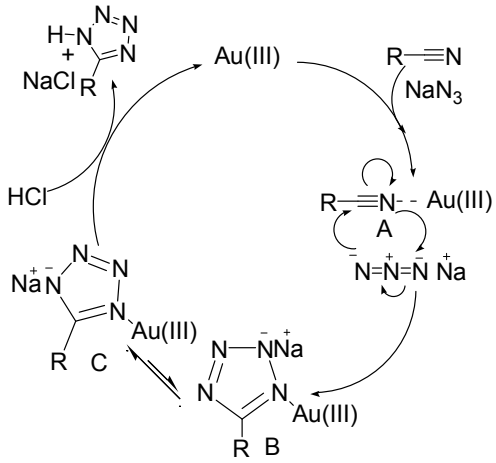
Table 4: Comparison of various catalysts used in synthesis of 5-substituted 1*H* tetrazole from benzonitrile.

S.No.	Catalyst	Reaction Time (h)	Temperature (°C)	Yield (%)
1	$HAuCl_4.3H_2O$[a]	0.45	110	90
2	AuNPs[a]	0.30	80	95
3	Cu-Zn alloy nanopowder[15]	10	120	95
4	$ZnBr_2$[21]	24	reflux	76
5	$Fe(OAc)_2$[22]	24	80	56
6	$FeCl_3$-SiO_2[23]	12	120	79
7	$TMSN_3.TBAF.3H_2O$[24]	18	85	86
8	CoY Zeolite[27]	14	120	90
9	Mesoporous ZnS nanospheres[28]	36	120	96
10	$CuFe_2O_4$[30]	12	120	82
11	SiO_2-H_2SO_4[31]	12	130	88
12	Amberlyst-15[33]	12	85	85

[a]present method.

5. Mechanism

The uses of gold in catalytic organic transformations are well known because of its electrophilic activation. The π-electron-containing compounds, such as alkenes, alkynes, allenes, facilitate this auration[51]. Here in this report, the given starting molecule is supposed to be activated via the auration of nitrile functionality for transformation into respective tetrazole. A plausible mechanism for the synthesis of 5-substituted 1*H*-tetrazole as shown in scheme 3, is Au(III) coordinate initially with nitrile group through its π-electron-cloud which assist to activate C-N functionality to form intermediate [A] for nucleophilic addition with NaN_3, which generates the intermediate [B]. The reaction proceeds via (3+2) cycloaddition between the C–N bond of nitrile and NaN_3. The complex [B] rearranges to produce more stable [C] which on protonolysis by 35% HCl (pH of solution was adjusted in between 2-3) affords the desired product 5-substituted 1*H*-tetrazole and Au(III) at the end of the reaction. Similar mechanism is expected for Au(0) nanoparticle catalysed reaction, the enhanced reactivity of Au nanoparticles might be due to large surface area which facilitates more coordination between C-N of nitrile and Au(0).



Scheme 3. Plausible mechanism for the synthesis of tetrazoles

Conclusions

We developed a newer highly efficient method for the synthesis of 5-substituted 1*H*-tetrazoles by treatment of sodium azide with various functionalized nitriles. This functionalization of nitriles was achieved by using auric chloride in gold(III) state and gold nanospheres as gold(0) state for catalysis. In addition to aromatic and heteroaromatic tetrazole synthesis, the protocol is found working efficiently for the aliphatic tetrazoles synthesis with good yield, which shows its superiority over other previously reported procedures. In the previously reported cases, low loading of the gold catalyst is sufficient for catalysis and the requirement of short reaction time is competitive with the cost-effective alternatives. The significant advantages of this methodology include simple work-up procedure, easy preparation and handling of the catalyst, high yields, elimination of dangerous and harmful hydrazoic acid formation and no column chromatography of the final product. This report may open a new avenue of reactivity in synthetic organic chemistry.

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†Electronic Supplementary Information (ESI) available: [All spectroscopic data of compounds are attached as supplementary information file, and crystallographic data for the compound 12b and 14b have been deposited in the Cambridge Crystallographic Data Centre with CCDC 929716 and CCDC 951458 respectively. Copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.-cam.ac.Uk). All these information associated with this article can be found, in the online version.]. See DOI: 10.1039/b000000x/

X-ray Crystallographic Study

X-Rays data were collected on Crysalis PRO (Oxford Diffraction, 2009) with graphite mono75 chromate Mo K_α radiation (λ = 0.71073 Å) at 298 (2) K. The structure was solved by a direct method using SHELXL-97 and refined by full matrix least-squares method on F^2 (SHELXL-97).

12b Crystal data for shelxl: $C_9H_{10}N_4$, M = 174.21, monoclinic, a = 7.8232(8) Å, b = 11.9434(14) Å, c = 9.8716(9) Å, α = 90.00°, β = 96.825(8)°, γ = 90.00°, V = 915.82(17) $Å^3$, T = 298(2) K, space group P21/c, Z = 4, μ(MoKα) = 0.082 mm^{-1}, 6368 reflections measured, 1788 independent reflections (R_{int} = 0.0221). The final R^1 values was 0.0619 (I > 2σ(I)). The final wR(F^2) values was 0.1981 (I > 2σ(I)). The final R^1 values was 0.0734 (all data). The final wR(F^2) values was 0.2061 (all data). The goodness of fit on F^2 was 1.450.

14b Crystal data for shelxl: $C_9H_{10}N_4$, M = 174.21, monoclinic, a = 14.907(2) Å, b = 4.9488(5) Å, c = 12.804(2) Å, α = 90.00°, β = 108.31(2)°, γ = 90.00°, V = 896.8(2) $Å^3$, T = 298(2) K, space group P21/c, Z = 4, μ(MoKα) = 0.084 mm^{-1}, 4341 reflections measured, 2427 independent reflections (R_{int} = 0.0312). The final R^1 values were 0.0759 (I > 2σ(I)). The final wR(F^2) values were 0.2288 (I > 2σ(I)). The final R^1 values was 0.1224 (all data). The final wR(F^2) values was 0.2931 (all data). The goodness of fit on F^2 was 0.923.

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Graphical Abstract