# APPLICATIONS OF Au & Ag NANOPARTICLES IN THE SYNTHESIS OF HETEROCYCLIC COMPOUNDS

## Abstract

Role of Nano catalyst is between homogenous and heterogeneous catalyst. They are useful from the point of their activity, selectivity, efficiency and reusability, Noble metal nanoparticles such as Au, Ag and Pt with high surface area and more active sites gives faster reactions and increase yield of product. Some of the applications in the synthesis of heterocyclic scaffold using Au and Ag nanoparticles is discussed herewith.

**Keywords:** Nanoparticles, AgNPs, AuNPs, Quinoxalines, chemo-selective reduction.

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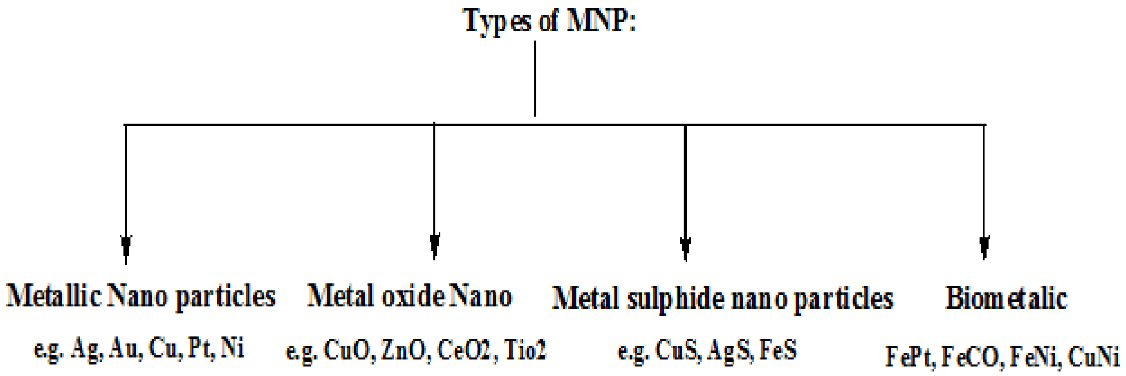
## I. INTRODUCTION

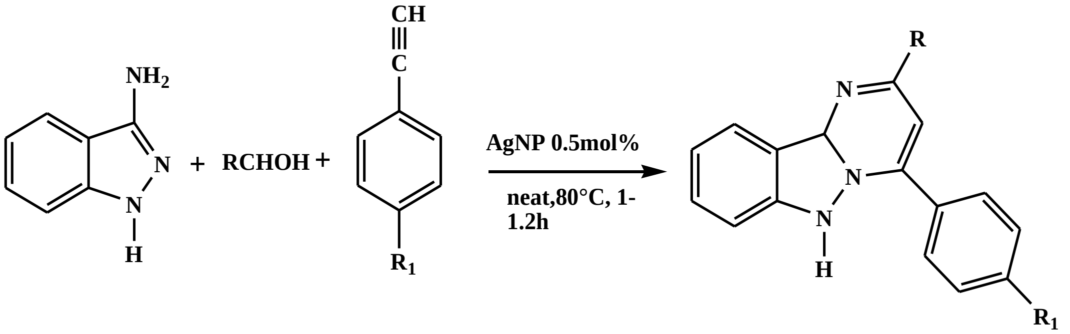
Heterocyclic compounds have wide range of applications they are used in the preparations pharmaceuticals, agrochemicals and veterinary products .They are important part of many drugs, agrochemicals and veterinary products.

Synthesis of new heterocycles is challenging for research's but due to wide range of applications of nanotechnology numerous metal nanoparticles were used for the synthesis of heterocyclic moieties .The metal nanoparticles used in the synthesis involves Ag, Au, Co, Cu, Fe, Ni, Pd, Pt, Rh, Ru, Si, Ti and Zn. Among this noble metallic nanoparticles are AuNPs, AgNPs PtNPs, which are commonly used in synthesis of heterocyclic scaffold [1,2] as it offers high stability. Metallic nanoparticles have metal core having inorganic metal or metal oxide which is covered with a shell made of inorganic or organic metal oxide.



MNP used in organic synthesis are safest as it keeps clean reaction and do not affect the environment .Number of organic transformations are brought by Nano particles but here we will discuss few synthesis of heterocycles by using nanoparticles.

1. **AgNP-Catalyzed synthesis of heterocycles:** Synthesis of pyrimido [1,2-b]imidazole derivatives was carried by Balwea et al[3].using silver nanoparticles (AgNPs) extracted from plant *Radix pueraiae*.

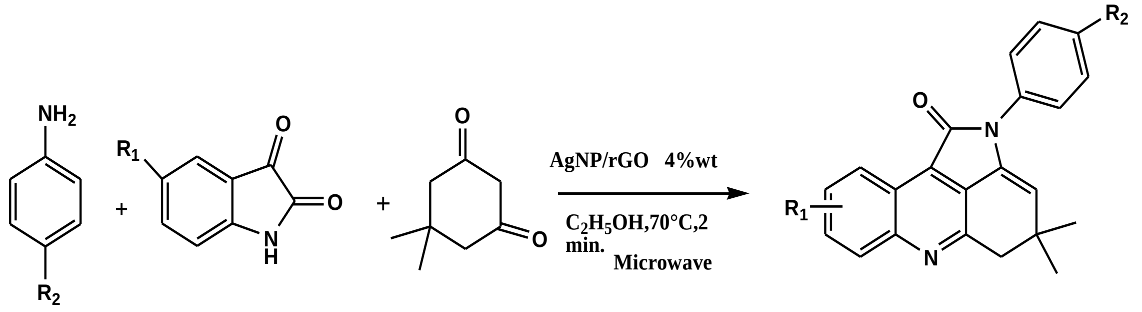


R=$C_6H_4$, 2-OMe-$C_6H_4$, 4-OMe-$C_6H_4$, 2-OET-$C_6H_4$, 4-Bu-$C_6H_4$, 2,5-$(Me)_2$, 2-ClF$C_6H_3$, 4-Cl-$C_6H_4$, 4-F-$C_6H_4$, 3-Cl-$C_6H_4$, 4-Br$C_6H_4$, 3-F-$C_6H_4$, 2-F-$C_6H_4$, 2-Cl-$C_6H_4$, 3-Br$C_6H_4$, 2-thienyl, 2-furanyl,2-naphthy-l,2-cyclohexyl R1=H, Me

**Scheme 1: Synthesis of pyrimido [1,2-b]imidazole derivatives**

The synthesis of pyrimido [1,2-b]imidazole derivatives was carried using 3-aminoimidazole aldehyde which may be aryl, heteraryl, allylic and substituted phenyl acetate using AgNPs in 0.5mol%. The reaction was carried at 80°Cfor 1 hr.in solvent free condition. Yield of reaction is 90%. The catalyst is recovered after the reaction, washed with water and used for three consecutive reactions.

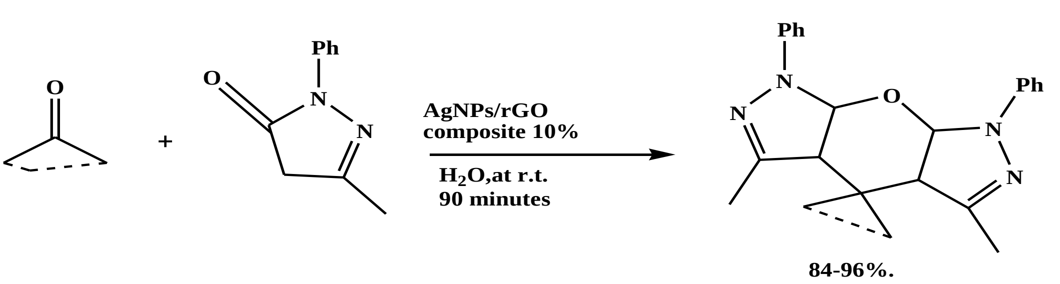
Synthesis of Pyrrolo[2,3,4-*kl*]acridin-1ones was reported by Dandia et al[4]. using silver nanoparticles decorated reduced grapheme oxide (AgNP/rGO) involves simultaneous reduction of graphene oxide (GO). The structure of these nanoparticles were confirmed by using TEM, XRD, SEM, XPS, EDX, UV-VIS spectroscopy, cyclic voltammetry, Raman and FTIR spectroscopy. Synthesis of Pyrrolo[2,3,4-*kl*]acridin-1-ones was carried by treating substituted isatin, anilines and dimedones in ethanol under microwave reduction at 70°Cfor 2 minutes in 89-93%yield. Ethanol is suitable solvent among all due to higher dispersion of catalyst and reactants. The catalyst recovered from reaction was used for seven catalytic cycles without loss of product yield.



**$R_1$=H, Br, F, $NO_2$ ,Me $R_2$=H, F, Cl,Br,,Me**

**Scheme 2: Synthesis of Pyrrolo[2,3,4-*kl*]acridin-1ones**

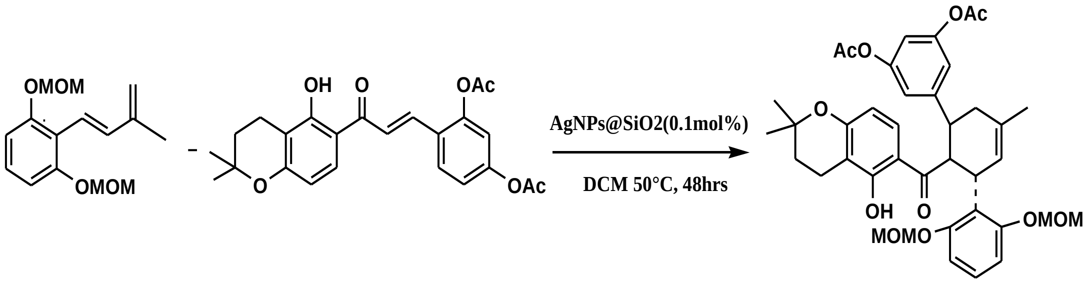
Synthesis of Pyrano [2,3-c6,5c]dipyrazol-2-ones was reported by Dandia et al[5] by using AgNP decorated GO(grapheme oxide) as catalyst on water in excellent yield. Here AgNPs role is as Lewis acid which is able to proceed through Knoevenagel than Michael addition and further cyclization. The catalyst recovered from reaction was found to be as effective for seven catalytic cycles.



Aldehyde $C_6H_5$, 4-Me-$C_6H_4$, 4-OMe-$C_6H_4$, 3,4,5-$(OMe)_3$ $C_6H_2$, 3-OPh-$C_6H_4$, 4-$FeC_6H_4$, 4-$ClC_6H_4$, 4-$NO_2C_6H_4$, Indole -3-yl, thiophene-2-yl , Ketones 1,2-Acenaphthoquinones, isatin

**Scheme 3: Synthesis of Pyrano [2,3-c6,5c]dipyrazol -2-ones**

Diels-Alder [4+2] cycloaddition reaction by using AgNPs was reported by Porco et al[6]. The reaction was carried by using chalcone and diene to give cycloadduct which gives endo and exo diasteroisomers in 2:1 ratio. The AgNPs were prepared via the reduction of silver tetrafluroborate (AgFB4) with silica gel in dichloromethane.



Endo :Exo=2:1 90%

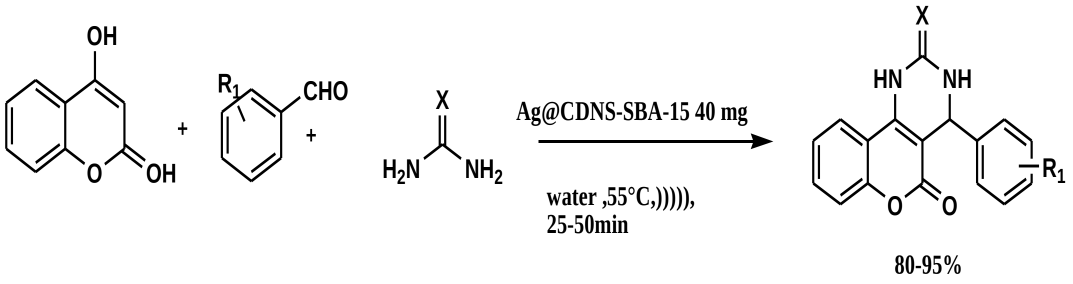
Scheme 4: Diels-Alder reaction

Chemo selective reduction of tetrazoles containing nitroarenes was reported by Lykakis[7] by using AgNP-supported mesoporous silica (Ag/HMS).

$R_1$=ipr, cyclopentyl, cyclohexyl, C(Me)-2-COOMe, $CH_2CH_2COOMe$,CHMeCOOMe
$CH(CH_2iPr)COOMe$, CH(iPr)COOMe, 4-$OMeC_6H_4$-$CH_2$, 4-$MeC_6H_4$
$R_2$=H, 2-Me, 4-Cl, $R_3$ = t-Bu, $CH(Me)_2$, $CH_2$ t-Bu, OMe

Scheme 5: Chemo-selective reduction of tetrazole

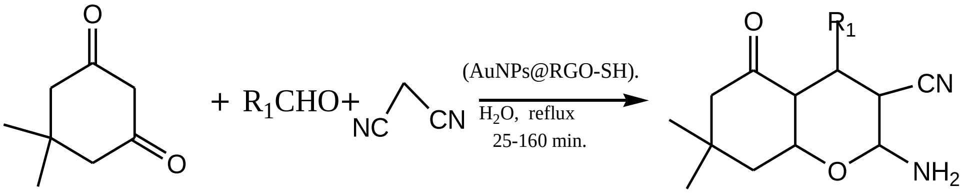
Catalytic use of bio-assisted AgNPs supported on an SBA-15/cyclodextrin nanosponge adduct was reported by Heravi et. al[8]. The reaction was carried under ultrasonication. Here benzopyranopyrimidine was synthesized from 4-hydroxycoumarins, substituted benzaldehydes and urea or thiourea. Here cyclodextrin plays important key role it brings reagents in close proximity of AgNPs. The catalyst was used again four times with the same catalytic activity



X= O, S; $R_1$=H, 2-OH, 4-OMe, 4-$NMe_2$, 2-Cl, 4-Cl, 3-$NO_2$

**Scheme 6: Synthesis of benzopyranopyrimidine**

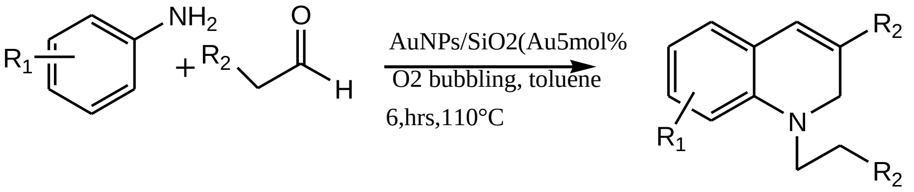
2. **AuNPs catalyzed synthesis of heterocycles:** Naeimi et al[9]. reported the synthesis of tetrahydro -4H-chromones by using gold nanoparticles supported on thiol functionalized reduced grapheme oxide (AuNPs@RGO-SH).These nanoparticles are treated to benzaldehyde, malono nitrile in aqueous medium under reflux.The catalytic activity of catalyst remains even after sixth catalytic run, yielding 90% of the product.



$R_1$= nPr, n-Bu ,$C_6H_5$,4-N$(Me)_2$-$C_6H_4$,2Cl-$C_6H_4$, 4-Cl-$C_6H_4$ ,2,
4-(Cl) $C_6H_3$, 3-Br-$C_6H_4$, 4-Br-$C_6H_4$, 4-F-$C_6H_4$,
4-(OMe)-$C_6H_4$, 3-(OMe)-$C_6H_4$, 2-OH-5-Br-$C_6H_3$, thiophenel-2-yl

**Scheme 7: Synthesis of tetrahydro-4H-chromens**

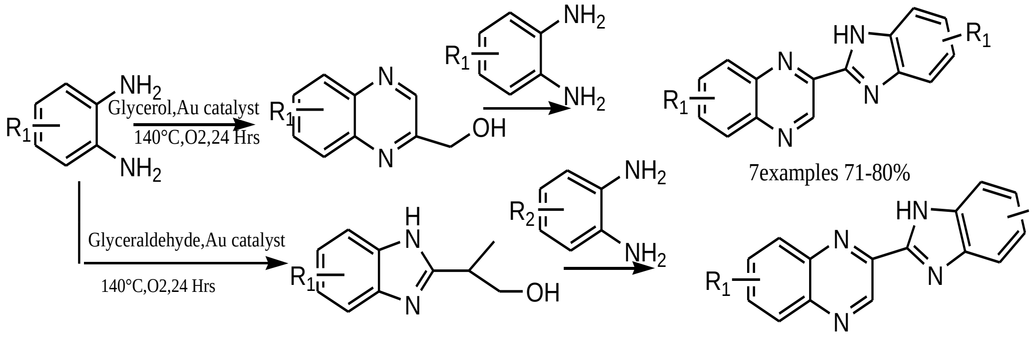
Polysubstituted Quinolines were synthesized by Che et al[10] from substituted anilines and aryl/alkyl aldehydes by using Sio2 supported AuNPs under oxygenated environment. The structure of synthesized nanoparticles were characterized by XRD, XPS, TEM, SAED analysis EDX And ICPMS



$R_1$= H, 2-Me, 3-Me, 4-Me, 2,3-$(Me)_2$ , 2,4-$(Me)_2$ , 2,5-$(Me)_2$, 4-ipr, 3-OMe, 4-OMe,
3,4,5-trimethoxy, 4-Cl-2Ph $R_2$=ethyl, n-butyl, n-decoyl

**Scheme 8: Synthesis of polysubstituted Quinolines**

Synthesis of poly substituted benzimidazolyl quinolines from o-phenelyne diamine, glycerol and glycealdehyde was carried by Climent et al[11] by using gold nanoparticles immobilized on Nano particulate CeO2in catalytic amount in the presence of air.



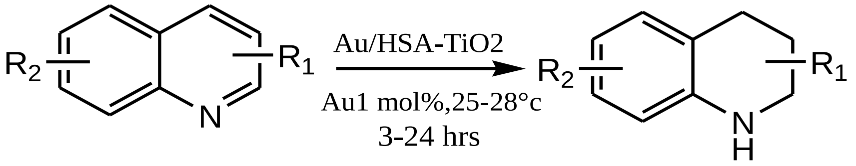
7examples 71-80%

12 examples 63-79%

$R_1$, $R_2$= H, Me, 4-OMe, 4-Cl, 4-$NO_2$, 4-CN,-$(CH_4)_2$

**Scheme 9: Synthesis of poly substituted benzimidazolyl quinolines**

Renet al[12] carried chemoselective reductions of substituted quinilines by using AuNPs supported on high surface area of TiO2 (Au/HAS-TiO2) at 25-28°C synthesized nanoparticles were were charactarised by XPS, DRIFTS, XANEs, yield of reactions was 100%

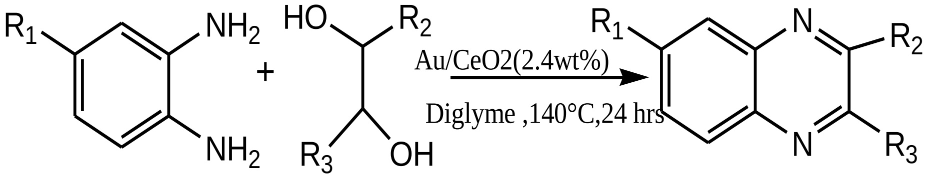


12 examples71-100%

$R_1$=2-Me, 4-Me, $R_2$=6-OMe, 8-$NH_2$, 8-OH, 5-Cl-8-OH, 6-F, 6-Cl, 6-COMe, 7-CH=$CH_2$

**Scheme 10: Hydrogenation of Quinilines catalyzed by AuNPs**

Synthesis of Quinoxalines was reported by Iborra et al[13].These authors condensed a pheylene diamide with biomass derived substituted glycol or Vicinol diols using AuNPs supported on CeO2 catalyst and dimethyl glyoxmie as solvent at 140 °C without base.The catalytic activity of catalyst remais same upto 4th cycle.

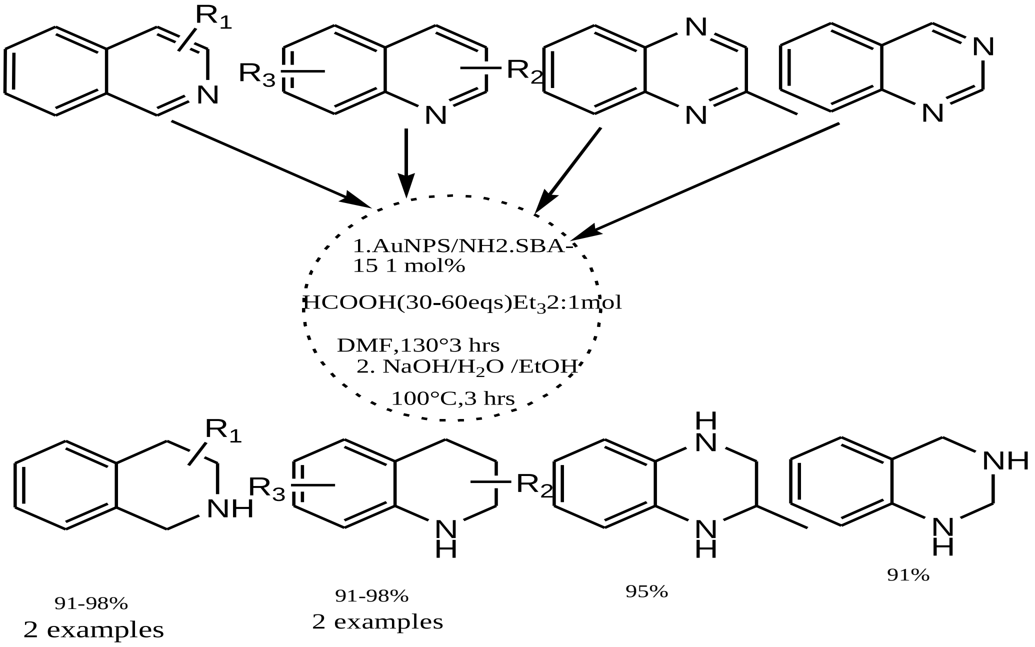


14 examples 35-91%

$R_1$= H, Me, OMe, Cl, CN, $NO_2$,    $R_2$= H, Me, Ph    $R_3$= H, Me, Et, nPr, n-Bu

**Scheme 11 Synthesis of Quinoxalines**

Silver nano particles AuNPs supported on 3-amino propyl functionalized silica (AuNPs/NH2/3-SBA- s) as catalyst in anhydrous DMF in formic acid[14] was shown to be effective for hydrogenation of N- heterocyclic compounds such as isoquinolines, quinolines quinoxalines and quinazoline.

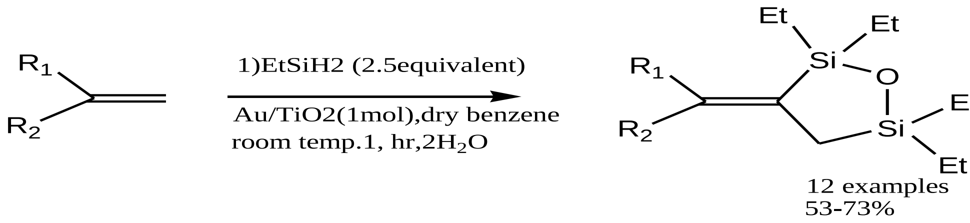


$R_1$=H, 3-Me, 8-Ph, $R_2$ =H, 2-Me, $R_3$=H, 6-OMe, 7-$CF_3$, 8-F, 8-Me

**Scheme 12: Hydrogenation of N-heterocyclic compounds**

The same reaction was also showed for the reduction of acridine, 1,10-phenanthroline, phenanthridine and benzo quinoline. The reaction proceeds via protonation using formic acid which underwent 1,2 addition followed by dis propitiation to give the hydrogenated product.

Synthesis of 3-alkylidene 1,2,5-oxadisilolanes was reported by Stratakis et.al[15] from AuNPs supported TiO2(Au/TiO2) catalyzed regioselective dehydrogenative 1,2-desilyation from allenesand diethyl dihydrosilane.



$R_1$=H, Me, Bn, $R_2$=Me, OMe, cyclohexyl, Ph, 4-Me-$C_6H_4$, 4-Cl-$C_6H_4$, Bn, 2-naphthyl

**Scheme 13 Synthesis of 3-alkylidene 1,2,5-oxadisilolanes**

## II. CONCLUSION

Synthesis of heterocyclic compounds with nitrogen and oxygen using metal Nano catalyst plays a vital role by increasing the surface area of catalyst, bringing the electrophiles and nucleophiles in vicinity, reducing the energy gap between reactant and product. Metal nano particles have been used for the synthesis of five, six or seven membered monocyclic, bicyclic tricyclic and tetracyclic heteroaromatic scaffolds. AuNPs are generally used for the synthesis of substituted Quinolines, and Quinoxalines. AgNPs are generally used for the synthesis of imidazole derivatives, Pyrrolo[2,3,4-kl]acridin-1ones, Chemo selective reduction of tetrazole and various reactions. The use of metal nanoparticles such as Au and Ag led to significant advancement in the synthesis of heterocyclic moieties.

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