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ARTICLE TYPE

Gold nanoparticles catalyzed intramolecular C-S bond formation/ C-H bond functionalization/Cyclization Cascades

Prasanta Gogoi,*Bappi Paul, Sukanya Hazarika and Pranjit Barman

An efficient synthesis of 2-(N-aryl) aminobenzo [d]-1, 3-thiazoles via intramolecular C-S bond formation/C-H bond functionalization utilizing an unusual cocatalytic Au NPs/$KMnO_4$ system under an oxygen atmosphere at 80 °C. 10 Au-NPs can be easily prepared by using $HAuCl_4$ with reductive potential of *Kayea assamica* (sia nahor) aqueous fruit extract. The catalyst can be easily separated and recycled for eight times without any appreciable loss of activity.

15 Introduction

The formation of C–S bond is prevalent in the synthesis of a broad range of biologically active molecules and functional materials. In traditional methods, the cross-coupling of aryl halides with thiols/disulfides has become one of the dominant 20 methods for the construction of C–S bonds. However, the pre-functionalization of the starting materials in this protocol limited its application. More recently, combination of selective, catalytic activation of C-H bonds with functionalization to form C-S bonds has been a subject of particular interest in recent years.Various 25 catalytic systems based on copper,[11] palladium,[12-15] ruthenium[16-19] and rhodium[17-23]catalyzed C–S bond formation from thioamides via C–H functionalization has been realized. In this particular area, gold catalyzed intramolecular C-H functionalization has been less studied. Most of the systems 30 involve a homogeneous process, and the problems associated with the removal of metal-residues from reaction products.

The use of Gold nanoparticles as catalysts inorganic reactions has attracted considerable interest as nanoparticles provide a larger number of active sites per unit area compared to their 35 homogeneous counterparts. Furthermore, the nanomaterial catalyzed reactions provide the advantages of high atom efficiency, simplified isolation of product, and easy recovery and recyclability of the catalysts. Here we demonstrate a unique strategy for C-S bond construction through AuNPs catalyzed 40 oxidative C-H bond activation. To best of our knowledge, this is first example of Gold nanoparticles catalyzed intramolecular C-S bond formation via C-H bond functionalization.

Results and discussion

45 Synthesis of Gold nanoparticles

The use of plant systems has been measured as a green route and a consistent method for the biosynthesis of nanoparticles remaining to its environmental friendly nature.[26-27] The AuNPs were synthesized by using $HAuCl_4$ with reductive potential of 50 *Kayea assamica,* (*K. assamica*) King & Prain (Clusiaceae) aqueous fruit extract (Fig.1, SI). *K. assamica* is a medicinally important plant. Its extract of flower (kayeassamins CI) has potential anticancer activity[28] and the fruit of this species is used to kill fishes. The use of fruit extracts has more advantages than 55 aqueous leaf extracts because later contains undesirable components like fats, chlorophyll and less polar compounds.[29]

In a typical procedure, 10 ml of fruit extract was added to 90 ml (10^{-3} M) aqueous solution of chloroauric acid and was stirred for 20 minutes. The progress of the reaction was routinely monitored 60 by observing colour change as well as recording UV-visible spectrum (ESI). The initial light-yellow solution turned to purple, indicating formation of colloidal gold. The supernatant containing Au-NPs was collected by centrifugation at 10,000 rpm. The solution was dried in a vacuum desiccator and the solid Au-NPs 65 were collected for characterization. The XRD pattern of the prepared gold nanoparticles is shown in Fig. 2. The XRD pattern thus clearly shows that the gold nanoparticles were essentially crystalline. The result was consistent with TEM which shows a

size distribution between 1 and 20 nm (Fig. 3). The five diffraction peaks at 38.1, 44.5, 64.8, 78.8 and 81.5° are indexed to the (111), (200), (220), (311) and (222) (JCPDS file, no. 89-3697) planes, respectively.
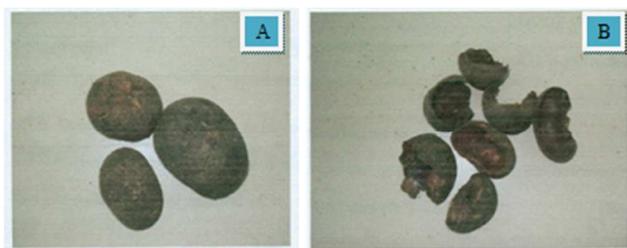

Fig. 1: **(A)** *K. assamica* fruit (Before drying) **(B)** *K. assamica* fruit peel (After drying)
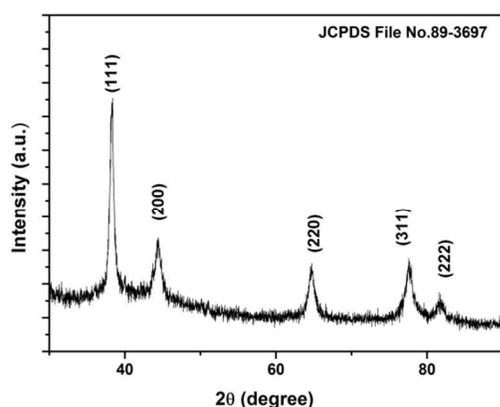

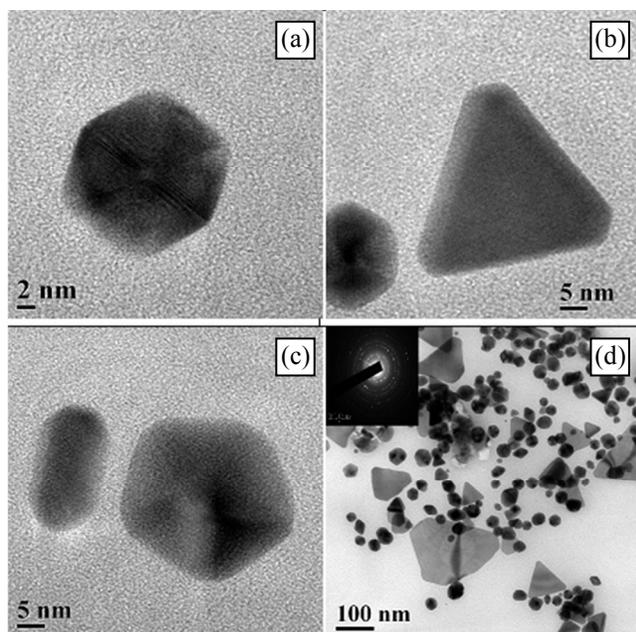**Fig. 2** X-ray powder diffraction spectrum of as-prepared gold nanoparticles

Fig. 3 (a-d) TEM images of Au-NPs **d)** ED-pattern (inset) of Au-NPs

Catalytic activity

Initial optimization studies using model substrate **1a** under catalytic Au-NPs usually not encouraging. Because typically Pd(0) afforded good activity.[30-31] However, to standardize the reaction conditions, a series of experiments was performed with variation of different reaction parameters such as solvent, temperature, time and best results was obtained using 3 mol% Au-NPs in CH_2Cl_2 solvent in the presence of 10 mol% $KMnO_4$ at 80 °C under an O_2 atmosphere gave a 90% yield of **2a** after 4h (Table 1, entry 3).

Table1 Reaction optimization [a]
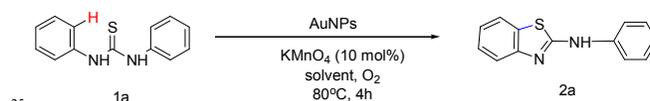
entry	Au-NPs (mol%)	solvent	yield (%)[b]
1	--	CH_2Cl_2	Nr
2	**3**	**CH_2Cl_2**	**90**
3	5	CH_2Cl_2	90
4	5	DMF	55
5	3	H_2O	20
6	3	THF	30
7[c]	3	CH_2Cl_2	20
8[d]	3	CH_2Cl_2	10
9	5	CH_3CN	45
10[e]	3	CH_2Cl_2	55
11[f]	3	CH_2Cl_2	87

[a]Reaction conditions: diphenyl thiourea (1 mmol), Au-NPs (3 mol%), $KMnO_4$ (10 mol %), in solvent(2.0 mL) under air for 4h. [b]Isolated yield. [c]For 10 h argon atmosphere. [d]For 10 h nitrogen atmosphere. [e]Room temperature. [f]K_2CO_3(1.5 mmol)

Under optimized reaction conditions (Table 2), we explored the substrate scope of this transformation. Arylthiourea containing methyl and methoxy groups on the aryl ring afforded desired product with excellent yields (**2b, 2i**). *Para*-cyano, -chloro, -

bromo, and iodo groups were well-tolerated, furnishing amino benzothiazole derivatives in yields from 69% to 90%.When arylisothiocyanates (Table 2, **2k-m**) were treated with morpholine, the resultant intermediate aryl thioureas (insitu) underwent the intramolecular heteroarylation reaction well in the presence of the catalyst.The strong electron donating group gives the maximum yield 95% (**2l**) while electron withdrawing group give least 75% (**2k**).

The mechanism of nanoparticle catalysed reactions is not easy to understand. However on the basis of previous studies, [34]a catalytic cycle is proposed for the gold nanoparticle catalyzed intramolecular C-S bond formation via C-H bond functionalization (Fig. 5). In this scenario, thiourea **1** reacts with molecular oxygen in presence of catalytic amount of gold nanoparticles to form intermediate **A**. The intermediate **A** upon releasing H_2O_2 to gives intermediate **B,** which immediately gives the final product and regenerates the catalyst for the next catalytic cycle. The catalytic activity remains constant on addition of potassium permanganate. The catalyst was easily separated [32-33] and was reused for 8th catalytic cycle without loss of its activity (Fig. 4).
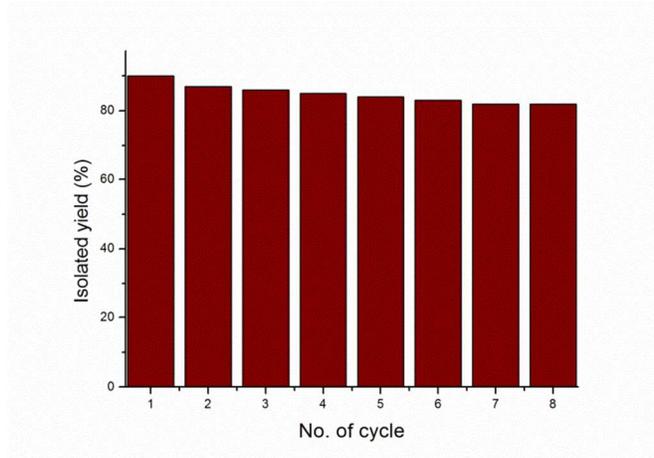

Fig. 4 Recycling of Au-Nanoparticles

Table 2 Synthesis of 2-aminobenzothiazoles

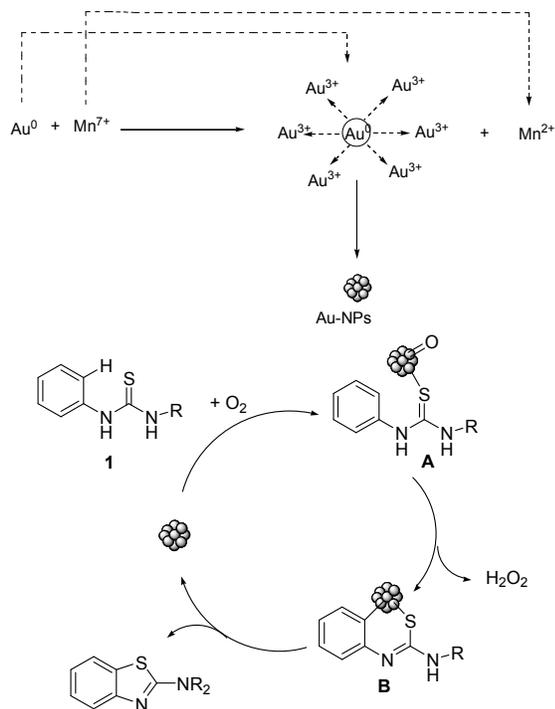| entry	substrate (1)	product (2)	Yield(%)[a]
1	**1a**	**2a**	90
2	**1b**	**2b**	96
3	**1c**	**2c**	90
4	**1d**	**2d**	86
5	**1e**	**2e**	85
6	**1f**	**2f**	90
7	**1g**	**2g**	78
8	**1h**	**2h**	75
9	**1i**	**2i**	98
10	**1j**	**2j**	69
11	**1k**	**2k**	75
12	**1l**	**2l**	95
13	**1m**	**2m**	80

[a]Isolated yield

Fig. 5 Plausible mechanism

To conclude, we report herein a simple method for the synthesis of Au-NPs by using *K. assamica aqueous fruit* extract solution. Au-NPs with size between 1-20 nm and different shapes were confirmed by TEM & XRD analysis. The present procedure using catalytic amount Au-NPs provides a very efficient and convenient methodology for the synthesis of 2-aminobenzothiazoles by oxidative C-H bond functionalization.The notable advantages offered by this procedure are operational simplicity.

Notes and references

Department of Chemistry, National Institute of Technology, Silchar 788010, Assam, India
E-mail: prasantanits.11@gmail.com
Electronic Supplementary Information (ESI) available

1. E. Boisselier and D. Astruc, *Chem. Soc. Rev.*, 2009, **38,** 1759−1782.
2. K. Saha, S. S. Agasti, C. Kim, X. Li and V. M. Rotello*Chem. Rev.,* 2012, **112,** 2739−2779.
3. E. C. Dreaden, A. M. Alkilany, X. Huang, C. J. Murphy and M. A. ElSayed, *Chem. Soc. Rev.,* 2012, **41,** 2740−2779.
4. P. Ghosh, G. Han, M. De, C. K. Kim and V. M. Rotello, *Adv. Drug Delivery Rev.*, 2008, **60,** 1307−1315.
5. D. A. Giljohann, D. S. Seferos, W. L. Daniel, M. D.Massich, P. C. Patel and C. A. Mirkin, *Angew. Chem.Int. Ed.,* 2010, **49,** 3280−3294.
6. Y. Zhang, X. Cui, F. Shi, and Y. Deng, *Chem. Rev.,* 2012, **112,** 2467-2505.
7. P. V. Kamat, *J. Phys. Chem. B* 2002, **106,** 7729−7744.
8. M.-C. Daniel, D. Astruc, *Chem.Rev.* 2004, **104,** 293−346.
9. R. Skouta and C.-J. Li, *Tetrahedron,* 2008, **64,** 4917-4938.
10. K. Inamoto, C. Hasegawa, K. Hiroya and T. Doi, *Org. Lett.,* 2008, **10,** 5147-5155.
11. X. Chen, X. S Hao, C. E. Goodhue and J. Q. Yu, *J. Am. Chem. Soc.,* 2006, **128,** 6790-6791.
12. E. M. Beck, N. P. Grimster, R. Hatley, and M. J. Gaunt, *J. Am. Chem. Soc.,* 2006, **128,** 2528-2529.
13. T. A. Dwight, N. R. Rue, D. Charyk, R. Josselyn, and B. DeBoef, *Org. Lett.*, 2007, **9,** 3137-3139.
14. A. R. Dick, K. L. Hull and M. S. Sanford, *J. Am. Chem. Soc.,*2004, **126,** 2300-2301.
15. T. W. Lyons and M. S. Sanford, 2010, *Chem. Rev.,* **110,** 1147-1169.
16. V. Ritleng, C. Sirlin, and M. Pfeffer, 2002, *Chem. Rev.,* **102,** 1731-1770.
17. P. B. Arockiam, C. Bruneau, and P. H. Dixneuf, *Chem. Rev.,*2012, **112,** 5879-5918.
18. L. Ackermann, L. Wang, R. Wolfram, and A. V. Lygin,*Org. Lett.*, 2012, **14,** 728-731.
19. L. Ackermann, and S.Fenner, *Org. Lett.*, 2011, **13,** 6548-6551.
20. D. A. Colby, R. G. Bergman and J. A. Ellman, *Chem. Rev.,* 2009, **110,** 624-655.
21. D. A. Colby, A. S. Tsai, R. G. Bergman and J. A. Ellman, *Acc. Chem. Res.*, 2011, **45,** 814-825.
22. A. S. Tsai, M. E. Tauchert, R. G. Bergman and J. A. Ellman, *J. Am. Chem. Soc.,* 2011, **133,** 1248-1250.
23. G. Song, F. Wang and X. Li, *Chem. Soc. Rev.,*2012, **41,** 3651-3678.
24. Z. Shi and C. He, *J. Org. Chem.*, 2004, **69,** 3669-3671.
25. Xie, J., Li, H., Zhou, J., Cheng, Y. and Zhu, C. *Angew. Chem.*, 2012, **124,** 1278-1281.
26. S. Iravani, *Green Chem.,*2011, **13,** 2638-2650.
27. V. Kumar and S. K. Yadav, *J. Chem. Technol. Biotechnol.,* 2009, **84,** 151-157.
28. N. N. Win, S. Awale, H. Esumi, Y. Tezuka and S. Kadota, *Bioorg. Med. Chem.*, 2008, **16,** 8653-8660.
29. Kumar, V., Yadav, S. C., &Yadav, S. K. *J. Chem. Technol. Biotechnol.,*2010, **85,** 1301-1309.
30. X. Zhao, E. Dimitrijevic and V. M. Dong, *J. Am. Chem. Soc.,* 2009, **131,** 3466-3467.
31. L. L. Joyce and R. A. Batey, *Org. Lett.*, 2009, **11,** 2792-2795.

32.   D. Astruc, F. Lu and J.R. Aranzaes,*Angew. Chem. Int. Ed.*, 2005, **44,** 7852-7872.

33.   S. Praharaj, S. Nath, S.K. Ghosh, S. Kundu and T. Pal, *Langmuir,* 2004, **20,** 9889-9892.

5   34.   A.Monga and B. Pal*ParticulSci Technol.*, 2015, **33,** 159-165.