Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2016, 8(4):1093-1099

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis and Characterization of Au(III)-IsatinThiosemicarbazone Complexes as potential Anticancer Drugs

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ABSTRACT

Thiosemicarbazones with their good chelatogenic properties and varied antimicrobial activities are thought of producing potentially beneficial molecules when derived from isatin for pharmaceutical applications. studies were initiated to complex Au(III) with N^4 substituted thiosemicarbazones derived from isatin. the synthesis, spectral investigations and biolological activity of Au(III) Isatin N4substituted thiosemicarbazone complexes. The synthesized compounds were evaluated for antimicrobial activity against several gram negative and gram positivebacterium strains

Key words:schiff's bases,isatin,antimicrobial activity**.**

INTRODUCTION

Isatinis a synthetically versatile molecule and this property has been made use extensively in organic synthesis. Isatin participates in a wide range of central nervous system activities. Isatin derivatives were reported for a variety of biological activities such as anti bacterial, anti-fungal and anti HIV properties[1-5]. Thiosemicarbazones with their good chelatogenic properties and varied antimicrobial activities are thought of producing potentially beneficial molecules when derived from isatin for pharmaceutical applications. Studies have been reported on substitution at N^4-position of the thiosemicarbazone moiety derived from isatin, N^4-2-pyridyl- [6], N^4-phenyl- [7], N^4-ethyl-[8] and N^4-dimethyl[9] in metal complexes. Although it was found that substitution at N^4-position of the thiosemicarbazone moiety could reduce anti-smallpox activity of isatinthiosemicarbazones[6], two butyl groups attached at the N^4-position provided the molecule with enhanced activities against Ectromelia(vaccina virus) and also against type 2 polio[10]. Recently Copper(II) complexes of N^4-substituted thiosemicarbazones of isatin[11] and N^4-hexa-methyleneiminylthiosemi-carbazone of isatin have been reported[12]. A number of metal complexes of isatinthiosemicarbazones appeared in the literature but none on Au(III) complexes. Sulphur containing ligands and their platinum complexes were found to have inhibitory action against tumours. Taking a note on the fact that gold is a structural analogue of platinum and that gold complexes may become alternatives to platinum complexes in pharmaceutical applications, studies were initiated to complex Au(III) with N^4 substituted thiosemicarbazones derived from isatin. This chapter describes the synthesis, spectral investigations and biolological activity of Au(III) Isatin N^4substituted thiosemicarbazone complexes.

EXPERIMENTAL SECTION

Chloroauric acid, $HAuCl_4 H_2O$ and Isatin were purchased from LOBA and Merck respectively and used as received. All other reagents were of high purity and used as received without any further purification.

Synthesis of ligands

IsatinTsc and Isatin N^4-substituted Tscs' were synthesized by condensing equimolar (0.01M) solutions of Isatin and Tsc/N^4-substituted Tsc as per reported procedures[13]

Synthesis of IsatinthiosemicarbazoneAu(III) complexes

Au(III) complexes of Isatinthiosemicarbazones were synthesized by the reported procedures[14]. Modifications were carried out in the reported procedures with respect to refluxing time and solvents used depending on the solubility of ligands and % of yield.Equimolar solutions(0.001M) of $HAuCl_2 H_2O$ and IsatinTsc in methanol were mixed in 1:1 ratio and a few drops of acetic acid were added. Immediate formation of an orange colored precipitate was observed. The contents were refluxed on water bath for 1hr. On cooling, orange colored compound separated out, which was filtered and washed with 50% ethanol and dried.

Antibacterial activity

Isatinthiosemicarbazone ligands with N4-methyl/ ethyl/ isopropyl/ benzyl/ p-tolyl/ cyclohexyl substituents synthesized in our laboratory were complexed with Au(III) metal ions. The antibacterial activities of these complexes were tested by well diffusion method for five bacterial species, *Staphylococcus aureus, Bacillus cereus, Pseudomonas aeruginosa, Bacillus subtilis* and *Staphylococcus epidermidis*.

RESULTS AND DISCUSSION

Synthesized Au(III) complexes of Isatinthiosemicarbazones and isatin N^4-substituted thiosemicarbazones were variously coloured as shown above. Melting points measured for the complexes exhibited a close range from 248^{o}C to 220^{o}C except for one value ie., 121^{o}C for N^4-p-tolylderivative. N^4-isopropyl derivative recorded a maximum temperature of 248^{o}C and N^4-p-tolyl derivative recorded a minimum of 121^{o}C, indicating that the complexes were fairly stable thermally. The complexes were insoluble in common organic solvents but soluble in DMF and DMSO. Analytical data obtained from CHN analysis (Table 1) for all the synthesized complexes were in agreement with the proposed stoichiometries of 1:1 Metal: Ligand ratio and with the proposed molecular formulae. Molar conductances for the complexes were recorded and the values were obtained in the range 75 to 95$\Omega^{-1}cm^{-1}mol^{-1}$ indicating 1:1 electrolytic behaviour[15] with a general formula for the complex as $[Au(L)Cl_2]Cl$.

Table1:Stoichiometries and partial elemental analysis of IsatinTsc complexes

S.No	Compound	Molecular Formula	Mol.Wt	Colour	%Elementalanalysis Found (cal)		
					C	H	N
1.	IT Au	$C_9H_8N_4OS\ Au\ Cl_3$	523.50	Orange	20.57 (20.55)	1.51 (1.49)	10.73 (10.71)
2.	ImTAu	$C_{10}H_{10}N_4OS\ Au\ Cl_3$	535.27	Reddish brown	22.50 (22.45)	1.66 (1.65)	10.33(1.31)
3.	IeTAu	$C_{11}H_{12}N_4OS\ Au\ Cl_3$	549.30	Red	23.90 (23.85)	2.10 (2.09)	10.30 (10.25)
4.	IiprT Au	$C_{12}H_{15}N_4OS\ Au\ Cl_3$	564.33	Orange	25.35 (25.32)	2.45 (2.41)	9.81 (9.79)
5.	IbzT Au	$C_{16}H_{14}N_4OS\ Au\ Cl_3$	611.33	Brown	31.05 (31.45)	2.39 (2.38)	9.36 (9.31)
6.	IptT Au	$C_{16}H_{15}N_4OS\ Au\ Cl_3$	612.33	Deep red	31.47 (31.45)	2.46 (2.41)	9.25 (9.22)
7.	IcyT Au	$C_{15}H_{18}N_4OS\ Au\ Cl_3$	603.38	Yellow	31.29 (31.25)	3.15 (3.11)	8.91 (8.89)

IR Spectral Analysis

IR Spectral assignments establish the structural identity of the molecule in almost all the cases. Important Infra Red frequencies along with their assignments for the groups in the complex are listed in (Table 2). In the case of uncomplexed ligand Isatinthiosemicarbazone, the absence of band in the region 2500-2600cm^{-1}, characteristic of thiol group (C-SH), indicated stable thione form of the ligand. Band assigned for (N^4-H) in thiosemicarbazide at 3370cm^{-1} shifted in the ligand, indicating substitution at N^4 position[16] and the same result was observed depending on the nature of the substituent in all the synthesized Isatin N^4 substituted thiosemicarbazone ligands from IT_1 to IT_7. The band at 1620cm^{-1} corresponding to the carbonyl $\upsilon(C^3{=}O)$ stretching vibration in isatin was found to be absent in the ligand. New bands were observed at a lower frequency in the range 1590cm^{-1} to 1611cm^{-1} in all the ligands from IT_1 to IT_7 and were assigned to the formation of (C=N) at N^1 position of thiosemicarbazide which was in agreement with earlier reports of N^4-substituted thiosemicarbazones[17]. The (C^2=O) band, originally at 1740cm^{-1} shifted to a range from 1671cm^{-1} to 1699cm^{-1} in the Isatinthiosemicarbazone ligands [18]. The four

bands that appeared in the ligands for thioamide group vibrations at 1450cm^{-1}, 1340cm^{-1}, 1196cm^{-1} and 788cm^{-1} were due to mixed contributions of ν(N-H),ν(C-N), ν(C-**S)** and δ(C-H)[19-21] and ν(C=S) vibration was obtained at 885cm^{-1} in N^4-unsubstituted ligand while 838cm^{-1} to 884cm^{-1} range was obtained in the N^4 substituted ligands for the same group[22].

The band at 3414cm^{-1} due to N^4-H in the ligand remained almost same in the unsubstituted (IT$_1$-Au) complex, indicating the non-coordination of N^{4}H's nitrogen atom with the Au(III) metal ion. The band at 3144cm^{-1} for ring NH stretching vibration was absent in the complex[18], indicating the coordination of C-O and simultaneous formation of (C=N) linkage. This was further confirmed by the appearance of a new band at 1620cm^{-1} in the complex assigned to ν(C^2-O), which could also be due to shifting of 1670cm^{-1} bandin the ligand. This observation confirmed the coordination of carbonyl oxygen to the Au(III)metal ion[23]. ν(C=S) vibration band in the ligand shifted to lower frequency in the complexes, indicating the coordination of thionesulphur with the Au(III) metal ion. This was further supported by the appearance of bands in the far IR region at 480cm^{-1} assigned to (Au-O), 320cm^{-1} assigned to (Au-S) and still lower value at 279cm^{-1} assigned to(Au-Cl). The bonding modes confirmed that the ligand behaved as a bidentate ligand, coordinating through sulphurof thiosemicarbazide moiety and carbonyl oxygen of isatin moiety.

All the other complexes followed more or less the same trend in their IR frequencies confirming the bonding of the metal ion with the donor groups of the ligands ie., Compared to N^4-H value of thiosemicarbazide (3370cm^{-1}), there was a small decrease in the value for N^4-methyl substitution (3363cm^{-1}) on the ligand, where as increase in the values were recorded for ethyl and isopropyl groups i.e., ethyl at 3434cm^{-1} and isopropyl at 3451cm^{-1}. The bands in the range from 3144cm^{-1} to 3056cm^{-1} for ring NH stretching vibrations were absent in the complexes IT$_2$-Au to IT$_7$-Au, indicating the formation of (C=N)group. This was further confirmed by the appearance of new bands in the region 1620cm^{-1}-1615cm^{-1} assigned to ν(C=O) in the complexes which were shifted from 1699cm^{-1}-1671cm^{-1} range in the ligands[23].

In N^4-substituted complexes,the coordination of oxygen of (C=O) was confirmed by the appearance of bands in far IR region for (Au-O) in the range 460-420cm^{-1}.The ν(C=S) vibrations present in the ligands at 885cm^{-1} was shifted to a lower frequency, 845cm^{-1} in complexes, indicating the coordination of thionesulphur. This was further supported by the presence of bands in far IR region at 320cm^{-1} assigned to (Au-S) vibrations in unsubstituted complex while the bands in the region 380-320cm^{-1} appeared for N^4-substituted complexes. The lower values in the range 276cm^{-1} - 298cm^{-1} were assigned to (Au-Cl) in substituted complexes compared to a value of 279cm^{-1} in N^4 un substituted complex. In conclusion the ligand behaved as a bidentate ligand coordinating through thiol sulphur and carbonyloxygen

Table2:IR spectral data of Au(III) isatinthiosemicarbazone complexes.(in cm^{-1})

S.NO	Compound	ν(NH)	ν(C^2=0)	ν(C=N)	ν(C=S)	(M-O)	(M-S)	(M-Cl)
1.	IT-Au	3153	1620	1604	845	422	320	279
2.	ImT-Au	3485	1620	1606	860	421	323	278
3.	IeT-Au	3403	1618	1600	818	420	321	276
4.	IiprT-Au	3428	1619	1602	797	420	320	288
5.	IbzT-Au	3188	1615	1591	838	423	321	289
6.	IptT-Au	3155	1616	1597	788	421	320	298
7.	IcyT-Au	3429	1619	1565	835	421	321	280

^{1}HNMR Spectral analysis

The ^{1}HNMR spectra of IT$_1$ and IT$_1$-Au complexes data in (Table3)^{1}H NMR of ligand showed a resonance peak at 9.32 ppm for N^{4}H and another peak at 12.58 for N^{2}H resonance. Ring NH proton signal appeared at 11.2 ppm. The aromatic region of ligand showed peaks in the region 7.8 - 8.2 ppm and the values were in agreement with the reported values for IsatinTsc compounds[24]. The peak observed for N^{4}H in the ligand at 9.3 was shifted downfield in the complex to 9.5 ppm and N^{2}H resonance at 12.58 ppm in the ligand was unchanged in the complex. The aromatic region shifted upfield in the complexes to 7.6-7.0 ppm and this may be due to decrease in the electron density of aromatic ring due to the formation of the complex[25*]. Ring NH proton signal observed at 11.2 ppm in the ligand was found to be absent in the complex indicating the coordination of carbonyl oxygen to the Au(III)metal ion. For substituted ligands from IT$_2$ to IT$_7$, peaks were observed in the range 9.8- 9.5 ppm for the hydrogen of N^{4}H and these peaks were shifted downfield to a range 9.50 - 9.58 ppm in their complexes. N^{2}H

resonances in the range 12.63 -12.80 ppm in the substituted ligands were unchanged in their complexes. The aromatic region shifted upfield in the complexes from 7.5 to 7.0 ppm due to the formation of complex. Ring NH proton signals observed in the range 11.7 to 11.8 ppm in the N^4 substituted ligands were found to be absent in their the complexes [25] indicating carbonyl oxygen coordination to the metal.

Table 3 : ^{1}HNMR Spectral data for Isatinthiosemicarbazone Au(III)complexes(ppm)

Ligand/Complex	N^4 H	N^2 H	Ring NH	Aromatic ring
IT	9.32	12.63	11.2	7.8-8.2
IT-Au	9.5	12.64	-	7.4-8.0
ImT	9.4	12.68	11.5	7.5-7.0
ImT-Au	9.44	12.68	-	7.0-7.2
IeT	9.38	12.63	11.4	7.2-7.7
IeT-Au	9.4	12.66	-	7.0-7.9
IiprT	9.46	12.69	11.8	7.2-7.5
IiprT-Au	9.49	12.7	-	7.2-7.7
IbzT	9.5	12.77	11.62	7.5-7.8
IbzT-Au	9.54	12.79	-	7.6-7.9
IptT	9.8	12.8	11.55	7.6-7.9
IptT-Au	9.82	12.8	-	7.3-7.6
IcyT	9.62	12.75	11.63	7.3-7.8
IcyT- Au	9.65	12.72	-	7.3-7.9

^{13}C NMR Spectral analysis

The ^{13}C NMR spectra of IT and IT-Au complexes were recorded in DMSO and presented in Table 4 The IT_1 ligand recorded a peak at 165.0ppm for (C^3=N), at 155.0ppm for (C^9=S) and at 135.0ppm for (C^2=O) which were in agreement with earlier reports.In the complexes these peaks shifted to high field, (C^9=S) shifted to 147.8 ppm and (C^2=O) shifted to 122 ppm may be due to the involvement of these groups in coordination[26,27]. In the N^4 substituted ligands, the values recorded for (C^9=S) in the range 145 to 147.6ppm shifted to 147.8 to 149.0 ppm range in their complexes from IT_2 to IT_7. The peaks observed for (C^2=O) in the range 130.0 to 131.7 ppm in substituted ligands shifted upfield to 122.0 to 127.0 ppm range in their complexes. The signal recorded for (C^3=N) at 165.0ppm in the substituted ligands was unchanged in the complexes, suggesting the Metal–Ligand coordination through sulphur and oxygen.

UV-VIS Spectral analysis

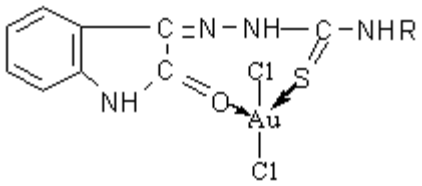
The electronic spectra of isatinthiosemicarbazone ligands and their Au(III) complexes were recorded in DMF solutions and presented in Fig. 4.16 to Fig. 4.18. Bands located above 350nm resulted from $\pi-\pi^*$ transitions of aromatic ring system[28]. The electronic spectra of ligand showed three electronic spectral bands at 280nm, 330nm and 375nm due to $\pi-\pi^*$ and $n-\pi^*$ transitions in the ligands.The bands between 250nm and 380nm were assigned to $\pi-\pi^*$ transitions of thiosemicarbazones [29]. The band located at 280nm in the IT1 ligand disappeared in the spectrum of IT1-Au complex and the appearance of band at 435nm indicated LMCT type of charge transfers between sulfur - metal bond formation [19*]. The band at 805nm with low intensity hump could be assigned to a d-d tranisition in the IT1 –Au complexes.[30]

Table 4 : ^{13}C NMR Spectral data for Isatinthiosemicarbazone Au(III)complexes

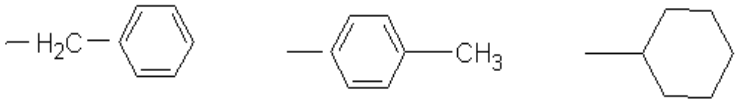
Ligand/complex	C^2= O	C^3= N (unchanged)	C^9=S
IT	135.0	165.0	155.0
IT-Au	122.0	165.1	147.8
ImT	132.0	164.0	154.1
ImT-Au	122.5	164.2	148.6
IeT	131.0	165.2	155.0
IeT-Au	125.1	164.2	147.0
IiprT	130.1	165.0	157.4
IiprT-Au	127.0	164.4	149.2
IbzT	130.5	164.2	154.8
IbzT-Au	124.5	165.0	148.5
IptT	131.6	164.6	156.4
IptT-Au	126.0	164.2	149.0
IcyT	131.7	165.2	155.5

IcyT-Au	123.2	165.0	147.6

Based on the above studies the structure of the Isatin[4]Nsubstituted thiosemicarbazone Au(III) complex was proposed as



R = $-CH_3$ $-C_2H_5$ $-C_3H_7$



Antibacterial activity of Au(III)isatinthiosemicarbazone complexes

Antibacterial activity of all the synthesized complexes were recorded against five bacterial species: *Staphylococcu aureus, Bacillus cereus, Pseudomonas aeruginosa, Bacillus subtilis* and *Staphylococcus epidermidis*.

In the series of Isatin complexes IptT-Au showed highest activity against B.cereus. Among all the complexes N^4 substitution by paratolyl, benzyl and cyclohexyl exhibited highest activity and all the complexes showed moderate activity against Bacillus subtilis, Bacillus cereus, Staphylococcus aureus species. For Staphylococcus epidermidis and Pseudomonas aeruginosa, N^4-substitution by ethyl group (IeT-Au) showed the highest activity**.**

For Bacillus subtilis

N^4-p-tolyl complex (IptT-Au) exhibited the highest activity, N^4-benzyl complex (IbzT-Au), N^4-cyclohexyl(IcyT-Au) equal activity while .N^4isopropyl (IiprT-Au) substitution the least activity against the organisms.

For Bacillus cereus

N^4-p-tolyl(IptT-Au), N^4-ethyl(IeT-Au), substitutions exhibited equal and highest activity while N^4-isopropyl(IiprT-Au), the least activity.

For Staphylococcus aureus

N^4-p-tolyl(IptT-Au) exhibited highest activity while N^4-isopropyl (IiprT-Au), the least.

For Staphylococcus epidermidis

N^4-ethyl(IeT-Au) substitution exhibited the highest activity against the organisms while the least was for N^4-ununsubstituted complex.

For Pseudomonas aeruginosa

N^4-ethyl(IeT-Au), N^4-p-tolyl(IptT-Au) exhibited highest activities against the organisms. while the least activity was recorded for N^4-methyl(ImT-Au) complex.

In the series of Au(III) isatinthiosemcarbazone complexes, N^4-p-tolyl(IptT-Au) showed highest activity against B.cereus. N^4-p-tolyl, N^4-benzyl and N^4- cyclohexyl exhibited the highest activity and the remaining complexes showed moderate activit against Bacillus subtilis, Bacillus cereus and Staphylococcus aureus.. For Staphylococcus epidermidis, Pseudomonas aeruginosa ,N^4 substitution by ethyl group (IeT-Au) showed the highest activity.

Table: 5 Antibacterial Activity of Au(III) Isatinthiosemicarbazone complexes

S.No	Compound	Zone diameter in millimeters.				
		B.subtilis	B.cereus	S.aureus	S.epidermidis	P.aureginosa
1	I TAu	15 mm	11 mm	15 mm	7 mm	11 mm
2	ImTAu	18 mm	12 mm	14 mm	10 mm	9 mm
3	I eT Au	21 mm	22 mm	16 mm	30 mm	21 mm
4	IiprT Au	10 mm	10 mm	9 mm	15 mm	10 mm
5	IbzTAu	20 mm	16 mm	13 mm	17 mm	15 mm
6	IptT Au	31 mm	22 mm	19 mm	21 mm	18 mm
7	IcyT Au	20 mm	13 mm	15 mm	16 mm	14 mm

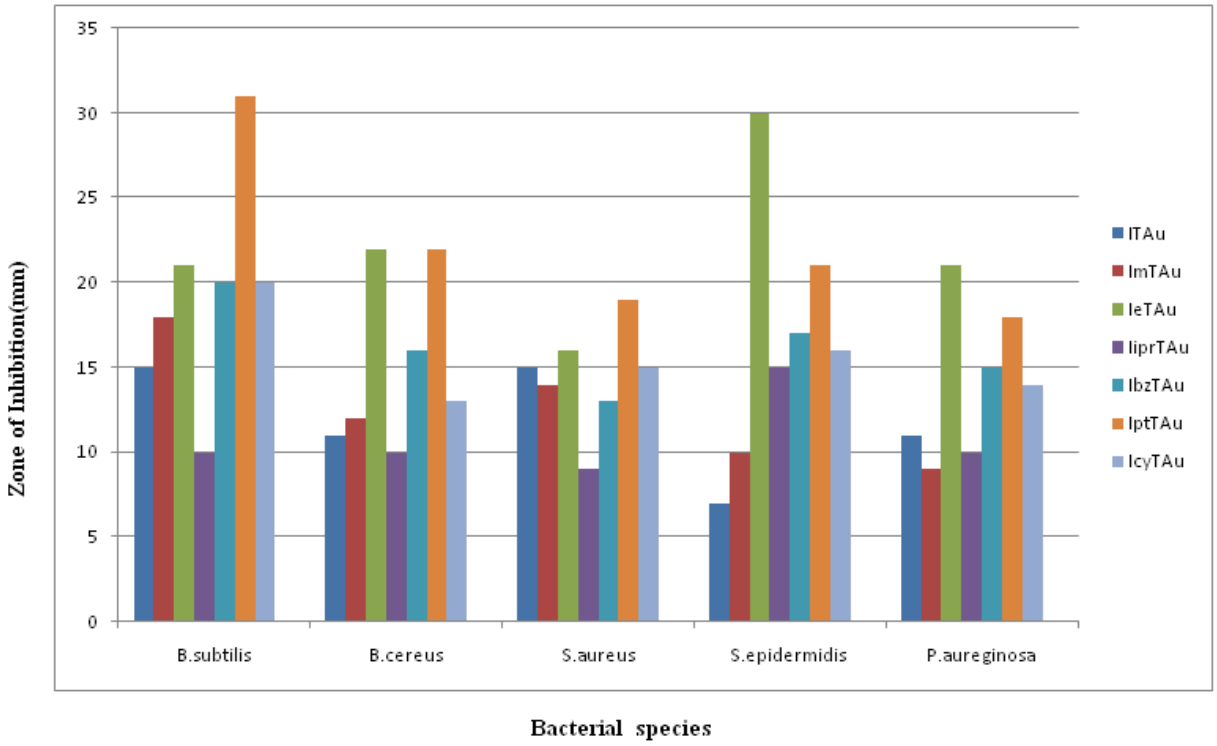


Fig. Graphical representation of zone of inhibition of Au(III) Isatinthiosemicarbazonecomplexes

CONCLUSION

This paper describes the successful synthesis and characterization of isatinthiosemicarbazoneAu(III) complexes. Isatinthiosemicarbazone and Isatin[4]N-substituted thiosemicarbazones were complexed with Au(III) ion and stable complexes were obtained by coordination of C=O and C=S of the ligands in a bidentate manner with the metal ions. Based on elemental analysis and spectral data square planar structures were proposed for the complexes. The metal complexes were screened for their antibacterial activities and the order of activity of the complexes was presented. In the series of Isatin complexes IptT-Au showed highest activity against B.cereus. Among all the complexes N4 substitution by paratolyl, benzyl and cyclohexyl exhibited highest activity and all the complexes showed moderate activity against Bacillus subtilis, Bacillus cereus, Staphylococcus aureus species. For Staphylococcus epidermidis and Pseudomonas aeruginosa, N4-substitution by ethyl group (IeT-Au) showed the highest activity

Acknowledgements
Author YASJ Prasannakumari thankful to SERO Hyderabad for financial assistance and sanction of leave through FDP program for the up liftment of research,And also thankful to the SS&N college Management for help us in improving our academic career.

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