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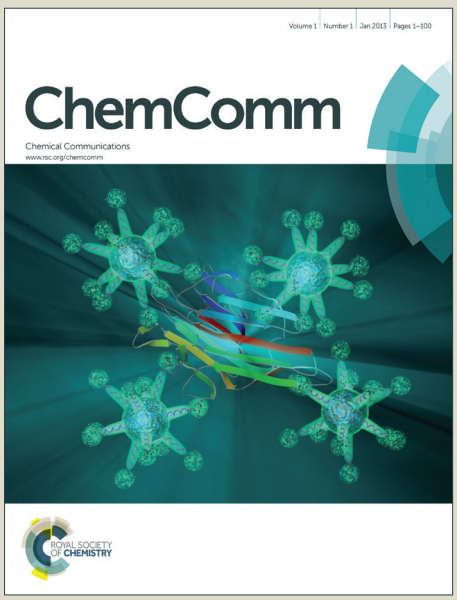

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Gold(I)-Catalysed Cascade Reactions in the Synthesis of 2,3-Fused Indole Derivatives

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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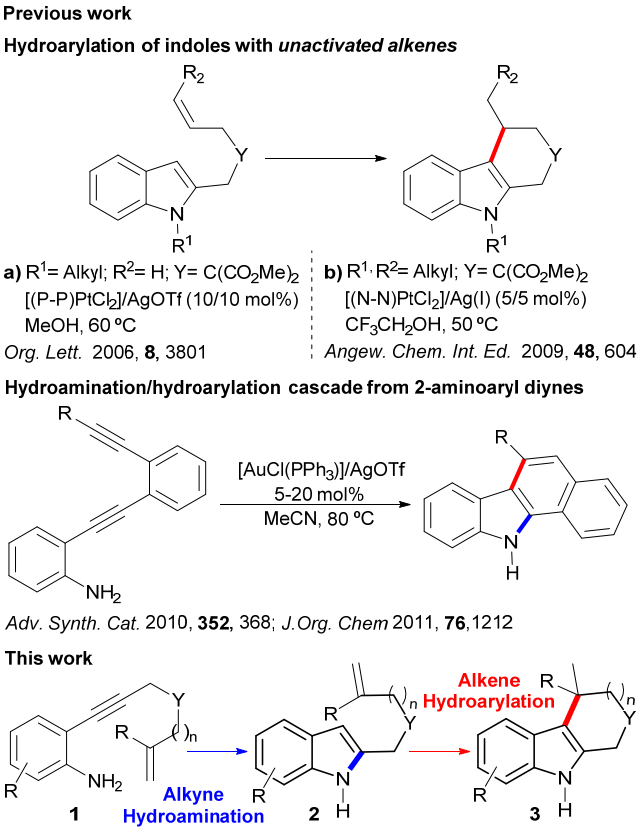
A gold(I)-catalysed hydroaminative/arylative cascade for the efficient synthesis of a variety of indole-fused skeletons has been developed. Factors controlling the catalyst loading required in these transformations involving 1,3-unsubstituted indole intermediates have been revealed allowing isolation of an unprecedented 1,3-dimetallated 3*H*-indole gold complex characterized by X-ray diffraction

Synthetic approaches developed for polycyclic indole derivatives, a class of compounds present in many natural bioactive alkaloids, common drugs and agrochemicals,[1] often consist in the annulation of previously functionalized indole rings.[2] Attractive methodologies to synthesize the 2,3-fused indole core with high atom and step economy would be transition metal catalysed hydroamination/hydroarylation tandem protocols involving just one chemical transformation.[3] In particular, Au(I)-catalysed hydroarylation of indoles with alkynes and allenes[4] and Pt(II)- catalysed hydroarylation of indoles with alkenes[5]are well documented. By contrast, unactivated alkenes are reluctant in taking part in hydroarylation reactions requiring high temperatures, prolonged reaction times and high loading of catalyst.[6] Moreover, alkyne hydroarylation of 1,3-unsubstituted indole rings is particularly challenging requiring in cascade reactions up to 20 mol% catalyst.[7] However those performed with alkynes and C3-substituted indoles utilize 5 mol% or less gold(I) catalyst.[8] The usefulness of these processes[9] prompted us to explore the gold-catalysed hydroaminative[10]/arylative cascade cyclization (Scheme 1) of 2-aminoaryl 1,X-enynes (n = 0, 1 or 2) **1** as an expeditious route to 2,3-fused indole rings **3** in a process taking place with unactivated alkenes and 1,3-unsubstituted indole intermediates **2**. Tetrahydrocarbazole and related partners **3** were obtained through tandem 5-*endo*-dig hydroamination/X-*exo*-(or *endo*-)trig hydroarylation reactions. Aurated indole complexes have been characterized and/or isolated along these reactions.

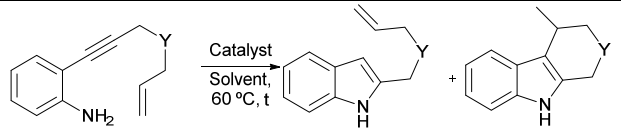


Scheme 1. Gold(I) catalysed reactions in the construction of 2,3-fused indole rings.

The transformation of **1a** into **3a** was first explored by using 5 mol% [AuCl(IPr)] /7.5 mol% $AgSbF_6$ or 5 mol% [Au(JohnPhos) as gold source under different conditions.
(MeCN)]SbF_6. The best yield was obtained with the second catalyst in DMF solution. The cyclization of **1a** proceeded satisfactorily also in a polar protic solvent like EtOH (Table 1, entry 5). Conversely, a mixture of **2a** and **3a** was obtained in DCM or toluene solution

(entries 6 and 7, Table 1). Complexes [Au(JohnPhos)]NTf_2 and the mixture 5 mol%)[AuCl(PPh_3)]/(7.5 mol%) $AgSbF_6$ were less efficient in this transformation. Compound **1a** was recovered unaltered when Brönsted acids or bases[11] were assayed as catalysts in control experiments (Table 1, entries 8-10).

Table 1. Gold-Catalysed Annulation of **1a**. Optimization Experiments



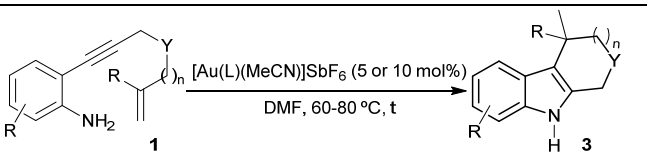
1a, Y = $CH_2(CO_2Me)_2$ **2a** **3a**

Entry	5 mol% Catalyst[a]	Solvent	t(h)	**2a**(%)[c]	**3a**(%)[c]
1	[Au(IPr)]SbF_6	DMF	16	8	90
2	[Au(L)(MeCN)]SbF_6	DMF	1.5	-	≥95
3	[Au(JohnPhos)]NTf_2	DMF	44	>95	-
4	[Au(PPh_3)]SbF_6	DMF	38	50	18
5	[Au(L)(MeCN)]SbF_6	EtOH	3	10	88
6	[Au(L)(MeCN)]SbF_6	DCM	17	90	9
7	[Au(L)(MeCN)]SbF_6	PhMe	17	65	35
8	TfOH[c)]	DMF	15	-	-
9	TfOH[c)]	PhMe	38	-	-
10	*t*BuOK[d)]	NMP	15	-	-

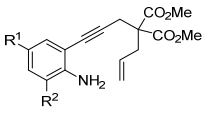
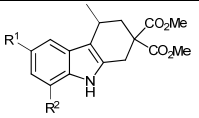
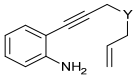
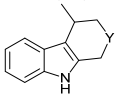
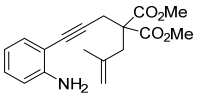
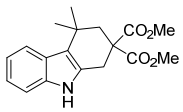
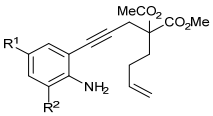
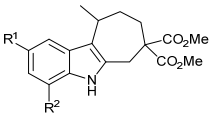
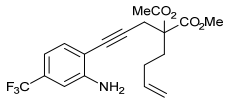
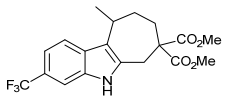
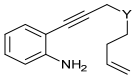
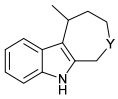
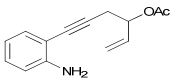
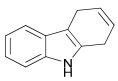
[a)] L = JohnPhos. [c)] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c)] 20 mol% of TfOH was used. [d)] 2.5 eq. of the base were employed.

Encouraged by these results we decided to explore the scope and limits of the [Au(L)(MeCN)]SbF_6 catalyzed cascade transformation of a series of compounds **1**. The effect of the substituents on the aromatic ring, the nature of the connector fragment (Y) and the length of the enyne chain (n=0,1,2) were evaluated. The cascade cyclization of 2-aminoaryl enynes **1a-p** in DMF was revealed as a robust procedure for the facile preparation of a variety of indole-fused ring systems **3a-p** through the corresponding 1,3-unsubstituted indole intermediates **2a-p**. Disappointingly, the synthesis of compounds **3** with high yield required in many cases portion wise addition of 10mol% of catalyst[†] (see Table 2). The hydroarylation step was found to be slower than the initial hydroaminative cyclization in the formation of compounds **3**. Noteworthy, carbazoles **3a-d** and **3i** (entries 1-4 and 9, Table 2), obtained by 6-*exo*-trig hydroarylation of plain or electron deficient intermediate indoles **2a-d** or the more reactive 2-metyl substituted alkenyl indol **2i** respectively, were formed with high yield by using only 5 mol% of gold catalyst in a single portion. According with this, the hydroarylation step seems to be less demanding with these latter substrates. By the contrary, complete conversion of the methoxy substituted intermediate indole **2e**, apparently activated towards the hydroarylation reaction, into **3e** (entry 5, Table 2), required 10 mol% catalyst load. In the same sense, formation of polycyclic indoles **3j** and **3p** (entries 10 and 16, Table 2), obtained by 7-*exo*-trig hydroarylation of the intermediate **2j** or S_N2' type 6-*endo*-trig hydroarylation[12] of **2p** respectively, also required 10 mol% gold catalyst load in two portions. These puzzling results attracted our attention and the loss of catalytic activity during the reaction with some substrates was investigated using the transformation **1j** into

Table 2. Gold(I)-Catalysed Synthesis of 2,3-Fused Indole Derivatives **3**.



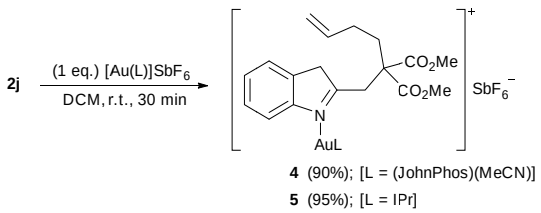
1 **3**

Run	aminoaryl enyne **1**	T (ºC)	t (h)	Yield **3** (%)[a]
				
1	**1a**, $R^1 = R^2 = H$	60	1.5	**3a** (91)[b]
2	**1b**, R^1 = Me, R^2 = Br	60	19	**3b** (75)[b]
3	**1c**, R^1 = Cl, $R^2 = H$	60	6	**3c** (81),[b] (82)[c]
4	**1d**, R^1 = *i*Pr, $R^2 = H$	60	6	**3d** (78)[b]
5	**1e**, R^1 = OMe, $R^2 = H$	60	23	**3e** (90)[d]
				
6	**1f**, Y = NTs	80	28	**3f** (90),[d] (92)[c]
7	**1g**, Y = CH_2	60	28	**3g** (91)[d]
8	**1h**, Y = O	80	31	**3h** (48)[d]
				
9	**1i**	60	22	**3i** (80)[b]
				
10	**1j**, $R^1 = R^2 = H$	80	24	**3j** (90),[d] (95)[c,e]
11	**1k,** R^1 = Me, R^2 = Br	80	20	**3k** (80)[d]
12	**1l**, R^1 = Cl, $R^2 = H$	80	44	**3l** (77)[d]
13	**1m**, R^1 = OMe, $R^2 = H$	80	20	**3m** (82)[d]
				
14	**1n**	80	44	**3n** (76),[c] (78)[e]
				
15	**1o**, Y = NTs	80	21	**3o** (80)[c]
				
16	**1p**	80	24	**3p** (81)[c]

[a)]Isolated yield. [b)]5 mol% [Au(JohnPhos)(MeCN)]SbF_6 [c)] 5 mol% catalyst load in 1:1 DMF/HFIP as solvent; reaction time 30 h. [d)] 10 mol% catalyst load in two portions [e)]5 mol% [Au(JohnPhos)(MeCN)]SbF_6/7.5 mol% *p*-$NO_2C_6H_4CO_2H$ as catalyst; reaction time 44 h

cycloheptaindole **3j** as a model. The initial step involving the hydroamination of the alkyne moiety with formation of the indole ring is a straightforward process[13] that takes place with a low load of catalyst. The hydroarylation, second step of the cascade, is more demanding with regard to the amount of catalyst needed although it

proceeds readily in the case on intermediate indoles **2a-d** and **2i**. To get further insight in this step we studied the stoichiometric reaction of **2j** with complexes [Au(JohnPhos)(MeCN)]SbF_6 and [Au(IPr)]SbF_6. These experiments revealed the formation of stable gold species not detected under our catalytic conditions.[‡] DCM was used as solvent in this study due to the slow reaction rate in this medium (entry 6, Table1). New stable metallated indoles **4** and **5** in the 3*H*-indole form could be fully characterized after 30 min at room temperature. (Scheme 2).[14,15] Formation of cycloheptaindole **3j** was not observed under these conditions.



Scheme 2. Formation of 3*H*-indole complexes **4** and **5** in the stoichiometric reaction between indole **2j** and [Au(L)]SbF_6.

All attempts to obtain suitable single crystals from complexes **4** or **5** for X-ray analysis were unsuccessful. However, in the crystallization from a dichloromethane-pentane solution at low temperature, a new diaurated species **6** (derived from [Au(IPr)]SbF_6) could be isolated.

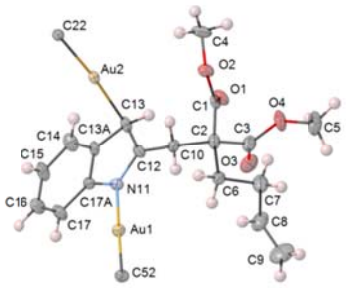
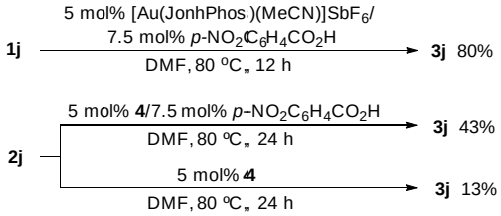


Figure 1. Thermal ellipsoid plot (50% probability level) for **6**, IPr ligands (C22 and C52) have been omitted.

The structure of [**6**][SbF_6]·1.5(CH_2Cl_2) was unambiguously determined by single crystal X-ray diffraction as a 6π 3*H*-indole motif containing two metal fragments at the N-1 and C-3 positions respectively (Figure 1).[16] This is the first example of 3H-indole dimetallated gold structure.[17]

These findings suggest that the indole ring could act in the catalytic reaction as an effective gold sponge with formation of a new gold complex.[18] 3*H*-Indole complex **4** was assayed as catalyst in the hydroarylation reaction of **2j** showing a very limited activity giving cycloheptaindole **3j** in only 13% yield after 24 h at 80 °C in DMF (Scheme 3). Unfortunately, complex **6** was highly unstable and its possible role in the catalytic reaction could not be assessed. The solvent effect on the cascade cyclization was next examined by carrying out reactions in different solvents at 80 °C for 30 h (see Table 3 in ESI). The hydroarylation step failed in neat non-coordinating aprotic solvents (entries 1-3, Table 3 in ESI) but proceeded in non-protic coordinating solvents and the yield of this step increased with the coordinating ability. (entries 4-6, Table 3 in ESI). The hydroarylation step was slightly less efficient in ethanol, a low coordinating protic solvent, than in DMF solution but failed in hexafluoro-2-propanol (HFIP), a less-coordinating but acidic alcohol. These results suggest that use of a solvent both coordinating and protic is necessary for the success of the cascade reaction. Indeed, the reaction performed in a 1:1 DMF/HFIP mixture gave **3j** with 95% yield. To test this idea, we decided to perform the cascade reaction by using as catalyst a mixture of 5 mol% [Au(JohnPhos)(MeCN)]SbF_6 and 7.5 mol% of an acid additive in DMF as solvent. The amount of cycloheptaindole **3j** formed depends in this case of the pKa of the acid additive. Use of strong acids like TfOH or *p*-TsOH gave poor results and nearly equimolecular mixtures of **2j** and **3j** were obtained. However carboxylic acids were found to be effective additives (entries 10-11, Table 3 in ESI) and addition of *p*-nitrobenzoic acid allowed the complete conversion of **1j** into the polycyclic indole **3j** after 45 h (entry 12, Table 3 in ESI).



Scheme 3. Influence of the acid addititive and the catalyst in the preparation of polycyclic indole **3j**.

These observations suggest that the afore mentioned low catalytic activity of the aurated 3*H*-indole **4** should be enhanced in presence of acid in the reaction medium. As expected, the cyclization of **2j** in DMF at 80 ºC with a mixture of 5 mol% **4** and 7.5 mol% *p*-nitrobenzoic acid as catalyst in DMF solution gave cycloheptaindole **3j** with 43% yield after 24 h (see Scheme 3) revealing the release of the metal from compound **4** by protodemetallation.[19] Direct conversion of **1j** into **3j** catalysed by the mixture 5 mol% [Au(JohnPhos)(MeCN)]SbF_6/7.5 mol% *p*-$NO_2C_6H_4CO_2H$ was faster than the conversion of **2j** into **3j** catalysed by the mixture complex **4**/*p*-$NO_2C_6H_4CO_2H$. This means that **4** is not the actual catalyst in the direct cascade reaction but a complex with very low catalytic activity resulting from partial trapping of [Au(JohnPhos)(MeCN)]SbF_6 by the intermediate indol **2** in a process competing with the hydroarylation step.

Conclusions

The [Au(JohnPhos)(MeCN)]SbF_6 catalysed 5-*endo*-dig hydroamination/X-*exo*-(or *endo*-)trig hydroarylation tandem reactions of readily available 2-aminoaryl enynes **1** is a robust procedure for the facile preparation of a variety of indole-fused ring systems. The wide scope of the method allows the presence of both EDG and EWG substituents at the aniline aromatic ring and tolerates well the presence of NTs, O, CH_2 and gem-disubstituted enyne linkers. The indole ring formed in the initial hydroamination step can act in the cyclization of 2-aminoaryl-1,7-enynes as an effective gold(I) sponge by forming stable non-catalytic aurated species. Complete conversion of compounds **1** into **3** requires a second portion of 5 mol%

catalyst, a protic solvent or an acid additive unless i) a less nucleophilic intermediate indole ring 2, ii) an activated akene towards the electrophilic attack or iii) formation of a six member ring are involved in the hydroamination step facilitating the cascade reaction.

The financial support from Spanish Ministerio de Ciencia e Innovación and European Community Founds (FEDER) Grant Consolider-Ingenio 2010 (CSD2007-00006) are gratefully acknowledged. We thank the SCSIE (Universidad de Valencia) for access to instrumental facilities.

Notes and references

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† A second portion of 5 mol% [Au(JohnPhos)(MeCN)]SbF_6 was added after 8 h since the beginning of the reaction. When the amount of catalyst was increased up to 10 mol% added at once the result was also unsatisfactory.

‡ The thermal stability of [Au(JohnPhos)(MeCN)]SbF_6 in DMF was ascertained by heating of the complex at 80 ºC for 15 h.

Electronic Supplementary Information (ESI) available: [Detailed experimental procedures and copies of NMR spectra]. See DOI: 10.1039/c000000x/

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