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Gold(I)-Catalyzed Indole Synthesis through Aza-Nazarov-Type Cyclization of α-Imino Gold Carbene Complexes and Arenes

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Abstract: Here we report a gold(I)-catalyzed and atom-economical *ortho*-*N*-indolyl-*N*-pyrazolylbenzene synthesis from 1,2,3-triazapentalenes and ynamides. The reaction occurs through the cleavage of the triazole ring and formation of a α-imino gold carbene intermediate. An aza-Nazarov-type cyclization with participation of an arene ring is involved. The reaction consists in a formal [4+1] heterocycloaddition where the four-carbon synthon is provided by the ynamide. Finally, indole synthesis could also be performed in a one-pot procedure from their 1-propargyl-1*H*-benzotrizaole precursors.

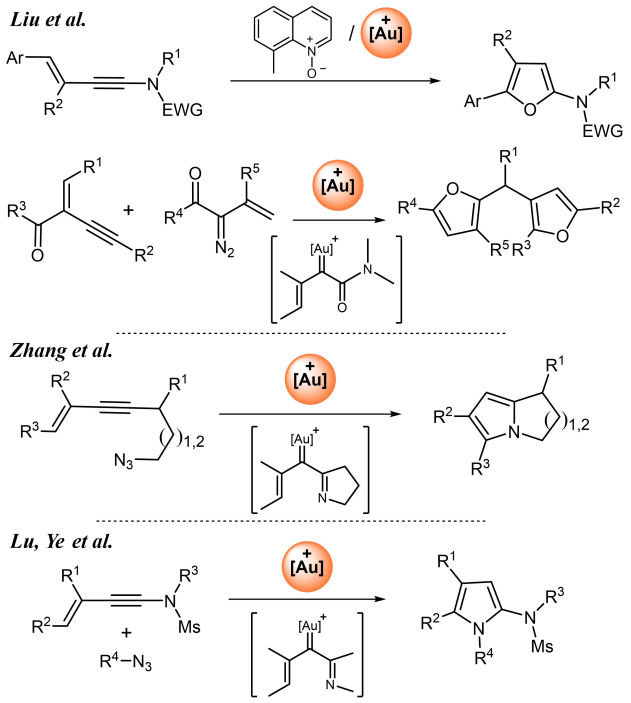
Keywords: Gold; Ynamides; Carbenes; Nazarov; Indoles

Gold carbene complexes[1] have played a key role as intermediates in a large number of reactions in the field of homogeneous gold catalysis.[2] Among them, α-oxo gold carbene complexes[3] have been extensively studied. Related to their nitrogenated analogues, such as α-imino gold carbene complexes, they have emerged in recent years, as important *N*-heterocyclic precursors,[4] since seminal work described by Toste and co-workers in 2005.[5] These intermediates can be generated from a nitrene transfer to gold activated alkynes. For that purpose several nitrenoid precursors[4] as azides, 2*H*-azirines, isoxazoles, 1,2,4-oxadiazoles, 1,4,2-dioxazoles, 4,5-dihydro-1,2,4-oxadiazoles, 2,1-benzoisoxazoles, 1,2-benzisoxazoles, aza-ylides, sulphur-ylides, pyrido[1,2-*b*]indazoles, have been employed. In this field, our research group has recently reported the use of 1,2,3-triazapentalenes-easily accessible from 1*H*-propargylbenzotriazoles- as nitrenoid precursors.[6]

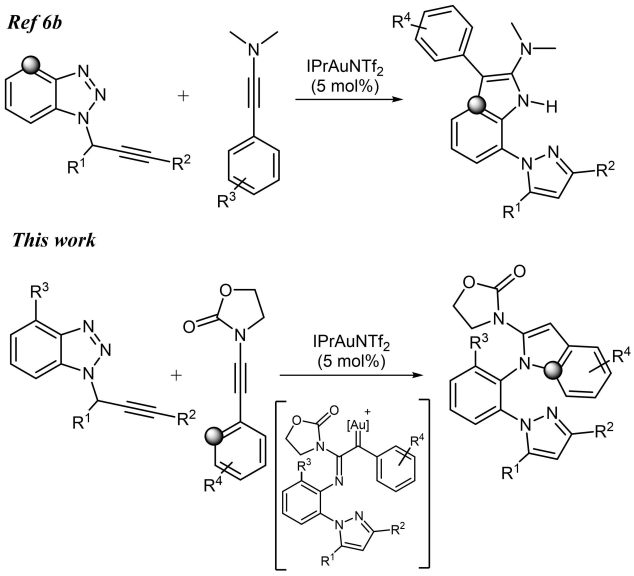
For the vast majority of the examples, the α-imino gold carbene formation resulted from an intramolecular procedure. Focussing on the limited cases of intermolecular methodologies, only a few examples by Lu and Ye et al.,[7] and Hashmi and coworkers[8] have been reported to date of carbene reaction by a position originally belonging to the alkyne derivative instead of the nitrene transferor. Moreover, a single example by Lu and Ye and coworkers[9] involves a group directly attached to the triple bond.

On the other hand, participation of gold carbene complexes in Nazarov-type cyclizations has been scarcely documented.[10] Moreover, related to the participation of these complexes in Nazarov-type heterocyclizations,[11] two examples of oxa-Nazarov[12] have been reported, by Liu and co-workers (Scheme 1; *top*). Additionally, Zhang[13] and Lu and Ye[9] groups described the only reported to date reactions involving α-imino gold carbene complexes, generated from azides, in respective intra- and intermolecular aza-Nazarov-type reactions (Scheme 1; *middle and bottom*). However, in all cases, heterocyclizations involved participation of alkenes and no examples implicating arene rings in the 4π-electrons cyclization step, have been reported to date.

In the course of our investigations in the field of gold catalysis using 1,2,3-triazapentalenes as nitrene transfers, we previously described an efficient and atom-economical indole synthesis through intramolecular closure of a α-imino gold carbene complex. 1,2,3-Triazapentalenes could be readily synthesized from the corresponding 1*H*-propargylbenzotriazole precursors or directly utilized in situ, in a one-pot procedure (Scheme 2: *top*). At this point, in order to explore new reactive possibilities, we decided to block C4-position at the benzotriazole skeleton. In fact, this modification allowed us to achieve a new gold-catalyzed formal [4+1] heterocycloaddition of ynamides with incorpo-



Scheme 1. Gold-catalyzed hetero-Nazarov-type reactions.



Scheme 2. Previous work and working hypothesis for gold-catalyzed indole synthesis.

ration of the nucleophilic nitrogen atom of the triazapentalene.

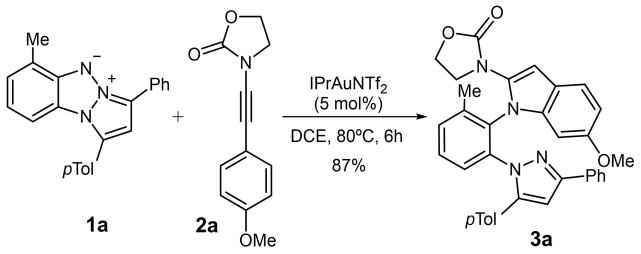
Here we report a new indole synthesis[14] that represents the first example of a gold-catalyzed heterocyclization through an aza-Nazarov-type reaction with participation of α-imino gold carbene complexes and arene rings (Scheme 2; *bottom*).

We initiated our study from benzo-fused 1,2,3-triazapentalene **1a**, bearing a methyl group to block a potential reaction of the carbene intermediate at the arene ring of the tiazapentalene. Thus, gold-catalyzed reaction of this dipolar compound **1a**, with ynamide **2a**, derived from 2-oxazolidinone, resulted in the formation of *N*-arylindole **3a**. For this initial reaction, 5 mol% of $IPrAuNTf_2$ (IPr = 1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-imidazol-2-ylidene) was used as the gold catalyst and the reaction performed in 1,2-dichloroethane at 80 °C, for 6 hours. Under these conditions, *ortho*-*N*-indolyl-*N*-pyrazolylbenzene **3a** was obtained in 87% yield, after chromatographic purification (Scheme 3).

The structure of compound **3a** could be determined by mono and bidimensional NMR experiments and unambiguously confirmed by a X-ray diffraction analysis[15] performed on a single crystal obtained from a methylene chloride-hexane solution (Figure 1).

At this point, we decided to explore the capability of different gold catalysts to accomplish the reported indole **3** formation. From Scheme 4 it can be inferred that formation of indole **3a** is only performed, in a satisfactory way, using $IPrAuNTf_2$ as the gold catalyst.

Next, we focussed our efforts on exploring the scope of the reaction in terms of triazapentalene **1** and ynamide **2** substitution patterns. As it is shown in Scheme 5, *N*-arylindoles with different combination of substituents at the reagents could be accomplished. Thus, aliphatic groups, aromatic substituents with electron donating (**3j**,**k**) or electron-withdrawing



Scheme 3. Reaction of triazapentalene **1a** with ynamide **2**.

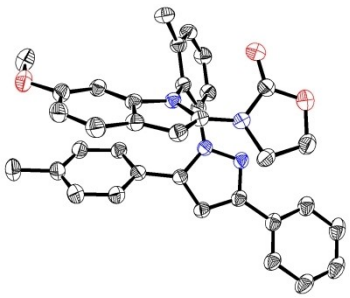
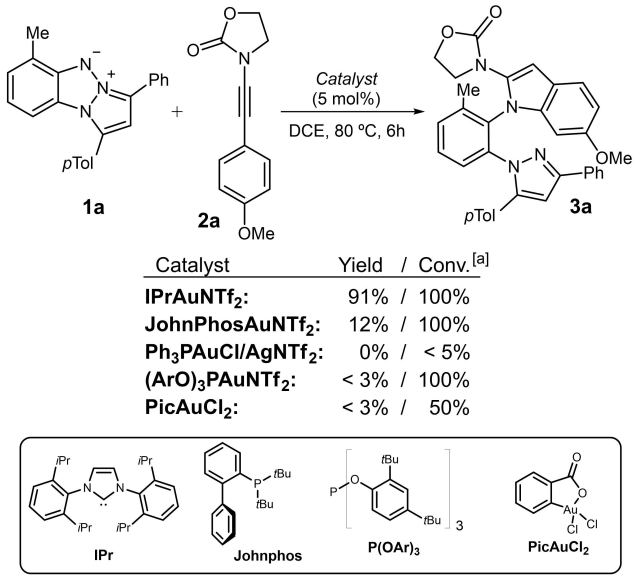


Figure 1. X-ray crystal structure for compound **3a**. Hydrogen atoms were removed for clarity.

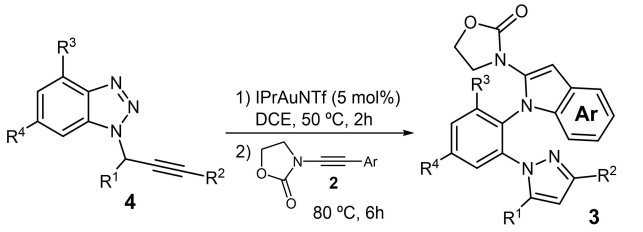


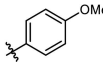
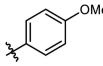
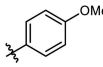
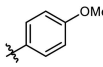
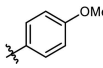
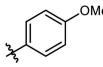
Scheme 4. Ligand screening for indole **3a** formation. [a] Yields and conversions were determined by NMR spectroscopy using dibromomethane, as internal standard.

groups (**3l**) and even halogens (**3m–o**) can be placed at the benzo-fused ring of the triazapentalene **1**. On the other hand, pyrazolyl group could also be obtained with an aliphatic substituent in its skeleton. In addition, as a representative example, indole **3s**, with an imidazolidin-2-one moiety, could also be synthesized. Finally, related to the electronic nature of the arene ring of the ynamides, the presence of electron-donating groups, seems to be very relevant for the indole formation.

Going one step further, formation of indoles **3** could also be accomplished starting from 1-propargyl-1*H*-benzotriazole precursors **4** in a one-pot procedure, involving two catalytic cycles (Table 1). However, incorporation of a substituent at the position 4 of propargylbenzotriazoles **4** seems to slow down its gold-catalyzed transformation into corresponding of triazapentalenes **1**. On the other hand, probably due to interferences between both gold-catalyzed reactions – triazapentalene formation and consecutive transformation – we observed a dramatical decline in the reaction yield. Taking this into account, previously to the addition of the ynamide **2** to the reaction mixture, benzotriazole **4** was stirred in 1,2-dichloroethane at 50 °C for two hours in the presence of the gold catalyst ($IPrAuNTf_2$). After that period, ynamide **2** was added to the reaction vessel and the mixture stirred for 6 h, under the previously mentioned standard reaction conditions. Following this methodology, *ortho*-*N*-indolyl-*N*-pyrazolylbenzenes **3** were obtained without significant differences, further than a slightly lowering in the overall yield of the reaction.

Table 1. One-pot synthesis of indoles **3**.

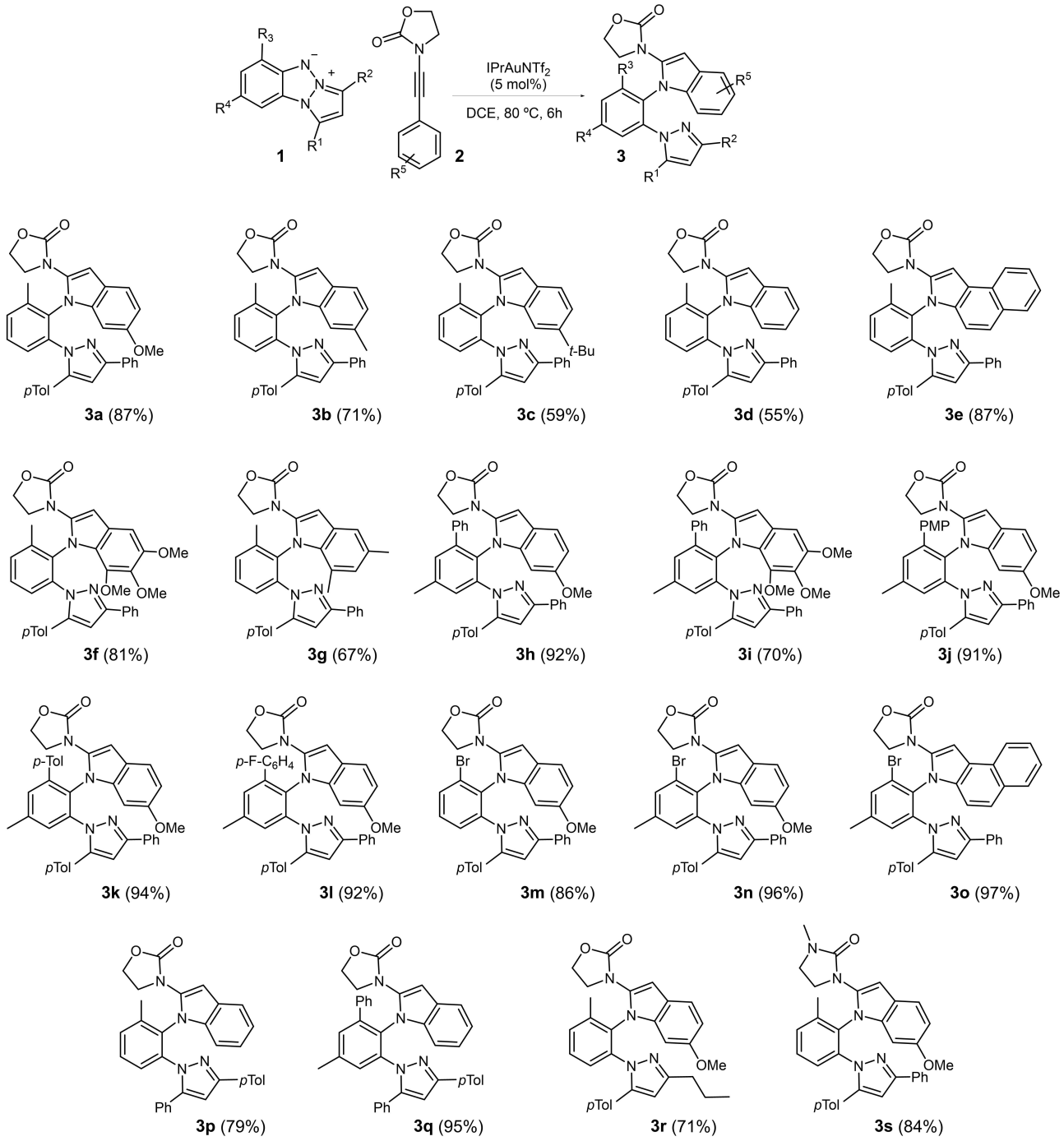


3	R^1	R^2	R^3	R^4	Ar	Yield[a] [%]
3a	*p*Tol	Ph	Me	H		81
3b	*p*Tol	Ph	Me	H		65
3d	*p*Tol	Ph	Me	H		50
3e	*p*Tol	Ph	Me	H		89
3g	*p*Tol	Ph	Me	H		62
3h	*p*Tol	Ph	Ph	Me		84
3n	*p*Tol	Ph	Br	Me		90
3l	*p*Tol	Ph	*p*FC_6H_4	Me		86
3q	Ph	*p*Tol	Ph	Me		93
3r	*p*Tol	Pr	Me	H		69

[a] Isolated yields.

Finally, also as an indicative of the robustness of the described methodology, the one-pot synthesis of *N*-arylindoles **3** could be performed at a gram scale. Thus, starting from 2.5 mmol of the corresponding benzotriazole and ynamide **2a** and following the standard one-pot reaction conditions, 1.31 g of compound **3h** (Figure 2) were obtained without any significant variation in the overall yield of the reaction (83%).

Once the versatility of the reaction, in terms of the substitution pattern, has been proven, a mechanistic proposal for the formation of *N*-indolyl-*N*-pyrazolyl-



Scheme 5. *o*-*N*-Indolyl-*N*-pyrazolylbenzenes **3** synthesized from triazapentalenes **1** and ynamides **2** and isolated yields.

benzenes **3** could be stablished and it is outlined in Scheme 6. Initially, formation of dipolar benzo-fused 1,2,3-triazapentalene **1** occurs through a previously described intramolecular 5-*endo*-*dig* gold(I)-catalyzed cyclization.[6] Next, a new catalytic cycle could be initiated by a nucleophilic attack from triazapentale **1** to the gold(I) activated ynamide **III**,[16] giving rise to the formation of intermediate **IV**. This new intermediate **IV** could evolve to the formation of α-imino gold carbene intermediate **Va** triggered by the formation of the pyrazole ring. At this point, it is worth to mention that in consonance with the experimental results of higher yields for the indole formation using ynamides with electron-donating groups at the aromatic ring, the mesomeric cationic form **Vb** could be favoured. Taking this into account, intermediate **V** could evolve through a formal aza-Nazarov-type reaction to the formation of the pyrrolidinium ring of intermediate **VI**.

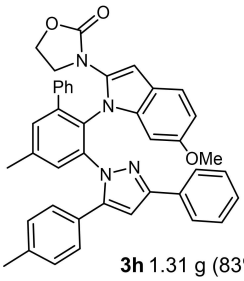


Figure 2. *N*-indolyl-*N*-pyrazolylbenzene **3h** synthesized at gram-scale.

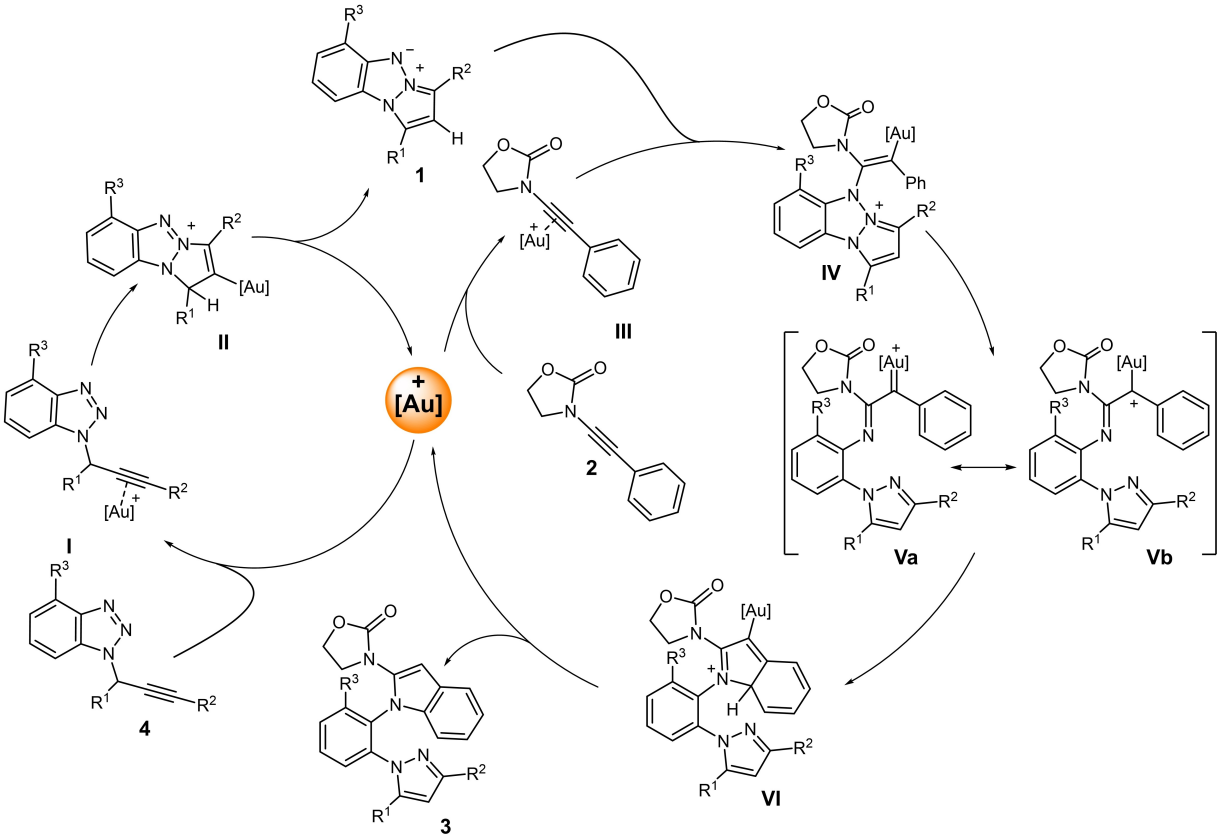
Finally, *N*-indolyl-*N*-pyrazolylbenzenes **3** could be accessed by consecutive rearomatization and proto-deauration steps.

In summary, in this work an atom-economical and one-pot gold-catalyzed formal [4 + 1] heterocyclization from benzotriazole derivatives and ynamides is described. The reaction takes place involving the participation of a α-imino gold carbene complex – with a 1,2,3-triazapentalene acting a nitrene transferor – and its evolution occurs through an aza-Nazarov-type reaction. Relevantly, this result represents an example of a Nazarov-type heterocyclization with the participation of gold carbene intermediates and arene rings. On the other hand, this result, together with the example reported by Lu and Ye *et al.*,[9] are the only two examples, reported to date, of capture of α-imino gold carbene complexes at a position next to the alkyne moiety. Finally, as the result of this methodology, *ortho*-*N*-indolyl-*N*-pyrazolylbenzenes are obtained, as the triazole ring is broken up into two new heterocycles. From the synthetic point of view, the use of easily accessible propargyl benzotriazoles,[17] allows the access to an interesting unit as the 2-aminoindole skeleton in present in a number of alkaloids[18] and other pharmacologically active compounds.[19] In this sense, the synthesis of 2-aminoindoles is been a pursued target and diverse methodologies have been employed focused on this objective.[20,21]

Experimental Section

Synthesis of *N*-Indolyl-*N*-Pyrazolylbenzenes 3

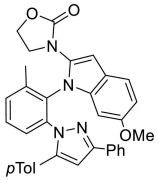
From triazapentalenes 1: To a solution of 0.2 mmol of 1,2,3-triazapentalene **1** in 1 mL of 1,2-dichloroethane, 0.21 mmol (1.05 eq) of the corresponding ynamide **2** and 8.7 mg (0.01 mmol, 5 mol%) of $IPrAuNTf_2$ were added. The mixture was heated at 80 °C for 6 hours. After that time, the reaction was allowed to cool down and the solvent removed under



Scheme 6. Mechanistic proposal.

vacuum. The residue was purificated by chromatographic column, obtaining the corresponding *N*-indolyl-*N*-pyrazolylbenzene **3** as pure compound.

From 1-propargyl-1H-benzotriazoles 4: To a solution of 0.2 mmol of propargyl-1*H*-benzotriazole **4** in 1 mL of 1,2-dichloroethane, 0.01 mmol (5 mol%) of the gold catalyst ($IPrAuNTf_2$) was added. The mixture was stirred for 2 hours at 50 °C. After that period, the heating bath was removed and 0.21 mmol (1.05 eq) of the corresponding ynamide **2** was added to the mixture. From this point, same reaction conditions (80 °C) described in the procedure starting from 1,2,3-triazapentalenes were followed to obtain *N*-indolyl-*N*-pyrazolylbenzene **3** as pure compounds.



3-(6-Methoxy-1-(2-methyl-6-(3-phenyl-5-*(p*-tolyl)-1*H*-pyrazol-1-yl)phenyl)-1*H*-indol-2-yl)oxazolidin-2-one (3 a): Yield: 87%; 97 mg (From triazapentalene **1 a**); 81%; 91 mg (From benzotriazole **4 a**). Yellow solid; m.p.: 128 °C (dec.). Rf: 0.38 (Hexanes/Dichloromethane/Ethyl acetate (3:1:1)); ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm) = 7.69 (d, *J*(H,H) = 7.4 Hz, 2H), 7.62-7.58 (m, 1H), 7.57-7.48 (m, 2H), 7.45-7.28 (m, 4H), 6.84 (d, *J*(H,H) = 7.8 Hz, 2H), 6.76-6.67 (m, 3H), 6.52 (s, 1H), 6.19 (s, 1H), 5.69 (s, 1H), 4.24-3.99 (m, 2H), 3.75-3.64 (m, 1H), 3.64 (s, 3H), 3.15 (dt, *J*(H,H) = 8.1 and 3.9 Hz, 1H), 2.30 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ(ppm) = 156.4 (C), 155.8 (C), 151.7 (C), 145.7 (C), 140.7 (C), 138.3 (C), 138.2 (C), 135.6 (C), 132.9 (C), 132.3 (C), 131.7 (CH), 131.7 (C), 129.0 (CH), 128.9 (2 x CH), 128.7 (2 x CH), 128.0 (CH), 127.4 (2 x CH), 127.0 (CH), 126.5 (C), 125.5 (2 x CH), 120.5 (CH), 120.4 (C), 109.5 (CH), 103.6 (CH), 94.5 (CH), 93.8 (CH), 62.4 (CH_2), 55.0 (CH_3), 47.8 (CH_2), 21.1 (CH_3), 18.8 (CH_3). HRMS (EI) for $C_{35}H_{31}N_4O_3$ [M + 1]: Calc: 555.2391; found: 555.2393.

Acknowledgements

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