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Regiodivergent Control in the Gold(I) Catalyzed Synthesis of 7-Pyrazolylindoles from 1-Propargyl-1*H*-benzotriazoles and Ynamides through α-Imino Gold(I) Carbene Complexes

Darío Allegue, Jairo González, Sergio Fernández, Javier Santamaría* and Alfredo Ballesteros*

Instituto Universitario de Química Organometálica "Enrique Moles" and Departamento de Química Orgánica e Inorgánica
Universidad de Oviedo
c/ Julián Clavería 8, 33007, Oviedo (Spain)
E-mail: abg@uniovi.es, jsv@uniovi.es

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Abstract. A smooth, gold catalyzed, atom-economical and regioselective synthesis of indoles is reported here. The reaction occurs from a nucleophilic attack of *in situ* synthesized triazapentalenes to gold activated ynamides and involves the participation of α-imino gold carbene complexes. The use of sulfonyl ynamides drives the reaction to the formation of 2-amidosubstituted indoles. However, the employment of 2-oxazolidinolylynamides allows the formation of both isomers, such as, 2-amido- and 3-amidosubstituted indoles. In this case, the regioselection could be controlled by a correct choice of the catalyst ligand and the electron-donating capability of the aryl substituent of the ynamide. A correct control in both parameters permits a totally regioselective synthesis of one or the other regioisomer. Isolation of key intermediates and X-ray analysis allowed for a plausible explanation for this behavior.

Keywords: Catalysis; Gold; Carbenes; Ynamides; Heterocycles

Introduction

Homogeneous gold catalysis has experimented a great development, in the last decade, as a powerful tool in the discovery of new selective organic reactions.[1] Among them, procedures involving gold carbene intermediates have been widely reported.[2] In this field, a large number of reactions involving α-oxo gold carbenes have been described.[3] However, since the pioneering work by Toste et al. in 2005 using azides,[4] methodologies invoking the participation of α-imino gold carbene complexes have not received attention until recently.[5] In addition to the use of azides, other procedures involving intra- or intermolecular attacks to gold activated alkyne derivatives have been performed. Thus, pyridine-*N*-aminides,[6] 2*H*-azirine derivatives,[7] isoxazoles,[8] oxadiazoles,[9] dioxazoles,[10] indazoles[11] or directly from a gold-catalyzed decomposition of diazo compounds[12] have demonstrated to be alternatives. On the other hand, we have recently reported in this field an efficient procedure for the synthesis of 2-imidazolyl-1-pyrazolylbenzenes from propargylbenzotriazoles, alkynes and nitriles (Figure 1),[13] with the participation of isolable triazapentalenes as nucleophiles. Exploration of this reaction in absence of the nitrile compounds resulted in the decomposition of the starting materials. However, the use of heteroatom activated alkynes, such as ynamides, allowed us the formation of a new compound with two very valuable heterocyclic moieties: indole[14] and pyrazole[15].

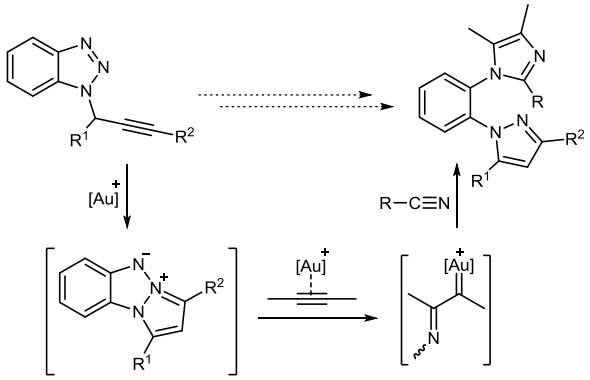


Figure 1. Previous work.

Furthermore, the use of ynamide derivatives have reached, in the last two decades, a great development in the synthesis of carbo- and heterocyclic compouds.[16] Among these reactions, gold activated ynamides have emerged as useful counterparts in the course of intermolecular reactions involving α-imino gold carbene complexes.[5] However, with the exception of the work reported by Huang *et al.*,[11] these compounds react following the usual reactivity pattern, through a nucleophilic attack to the α-position of the metal-activated ynamide (Figure 2).

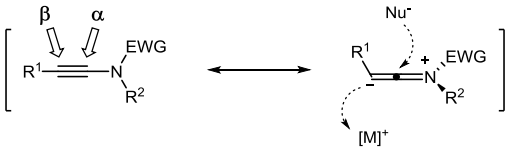


Figure 2. Common reactivity pattern of ynamides.

Related to metal-activated ynamide reactivity through a nucleophilic attack at the α-position, scarce examples have been reported to date. In this sense, only few examples, involving a metal chelating effect with copper[17] or rhodium[18] acting as directing groups, have been reported. Finally, of special interest in this field are the results by Hashmi[19] and Gagosz[20] involving a gold catalyzed intramolecular attack of carbamate ynamides or a very recent work by Ye *et al.* of pyrrole formation from *N*-propargyl ynamides.[21]

Here we present an efficient, atom-economical and regioselective gold(I) catalyzed synthesis of 7-pyrazolylindoles from ynamides and benzotriazole derivatives. The reaction can be justified through the participation of α-imino gold(I) carbene intermediates and the regioselectivity can be controlled by a combination of the nature of the gold ligand and the substitution pattern of the ynamide (Figure 3).

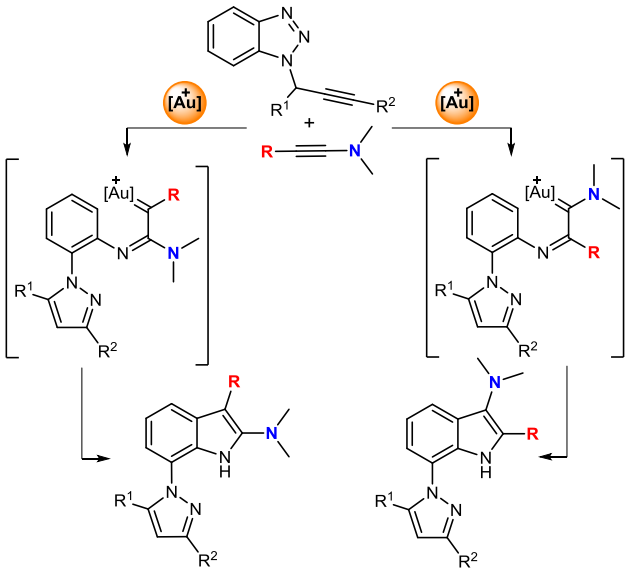
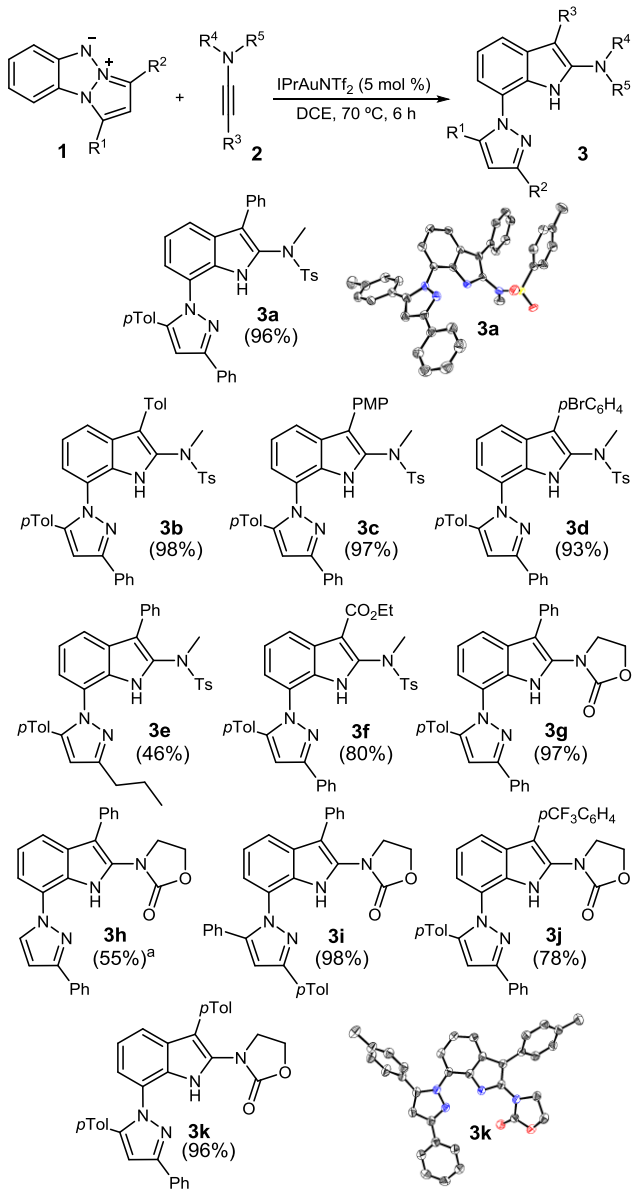


Figure 3. Indole syntheses from 1-propargyl-1*H*-benzotriazoles.

Results and Discussion

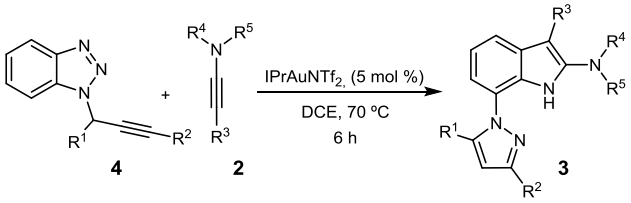
We started our study using benzofused triazapentalene **1a** (R^1 = *p*Tol; R^2 = Ph), easily accessible from the corresponding 1-propargyl-1*H*-benzotriazole,[13] and *N*-methyl-*N*-tosylynamide **2a** (R^3 = Ph), as the starting materials (Scheme 1). The reaction was performed at 70 °C, in 1,2-dichloroethane (DCE) and using $IPrAuNTf_2$ (IPr = 1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-imidazol-2-ylidene) as the gold catalyst. After 6 hours of reaction, removal of the solvent and chromatographic purification, 7-pyrazolylindole **3a** was obtained in high yield and as a single regioisomer. The structure of the indole **3a** was determined by NMR experiments and unambiguously confirmed by an X-ray analysis.[22] Next, this methodology was extended to other substitution patterns. As it is shown in Scheme 1, the reaction works very satisfactorily with donor groups in the aromatic ring of the ynamide (**3b-c,k**), acceptors in that position (**3d,j**) and even with an ester directly bound to the triple bond (**3f**). Regarding to the structure of the triazapentalene **1**, different substitution patterns were also tolerated. Finally, it is worth to mention that, in addition to sulfonylynamides (**3a-f**), 7-pyrazolylindoles were also accessible from triazapentalenes **1** and ynamides derived from carbamates (**3g-k**). In this sense, to banish any kind of doubt related to the structure of these compounds, an X-ray analysis was also performed on a monocrystal of compound **3k**. This analysis revealed that indoles **3g-k** were formed without the observation of any relevant change in terms of the structure of the compounds or the regioselectivity of the reaction.



Scheme 1. Synthesis of 7-pyrazolylindoles **3** from triazapentalenes **1** and ynamides **2**. Ortep view for indoles **3a** and **3k**. Thermal ellipsoids are plotted at the 50% level and the hydrogens were removed for clarity. [a)]Performed at 100 °C for 3 h.

As the next step, taking into account that triazapentalenes **1** can be efficiently synthesized from the corresponding 1-propargyl-1*H*-benzotriazoles **4**,[13] we decided to attempt the pyrazolylindole synthesis directly from these compounds, in a one-pot procedure that should involve two consecutive catalytic cycles. After a preliminary screening of the catalyst ligands (*see Supporting Information for details*; Figure S1) we selected $IPrAuNTf_2$ as the optimal reaction catalyst and performed the reaction under the standard conditions. The results are shown in Table 1 and no significant differences were observed in comparison to the use of triazapentalenes **1** as the starting materials.

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



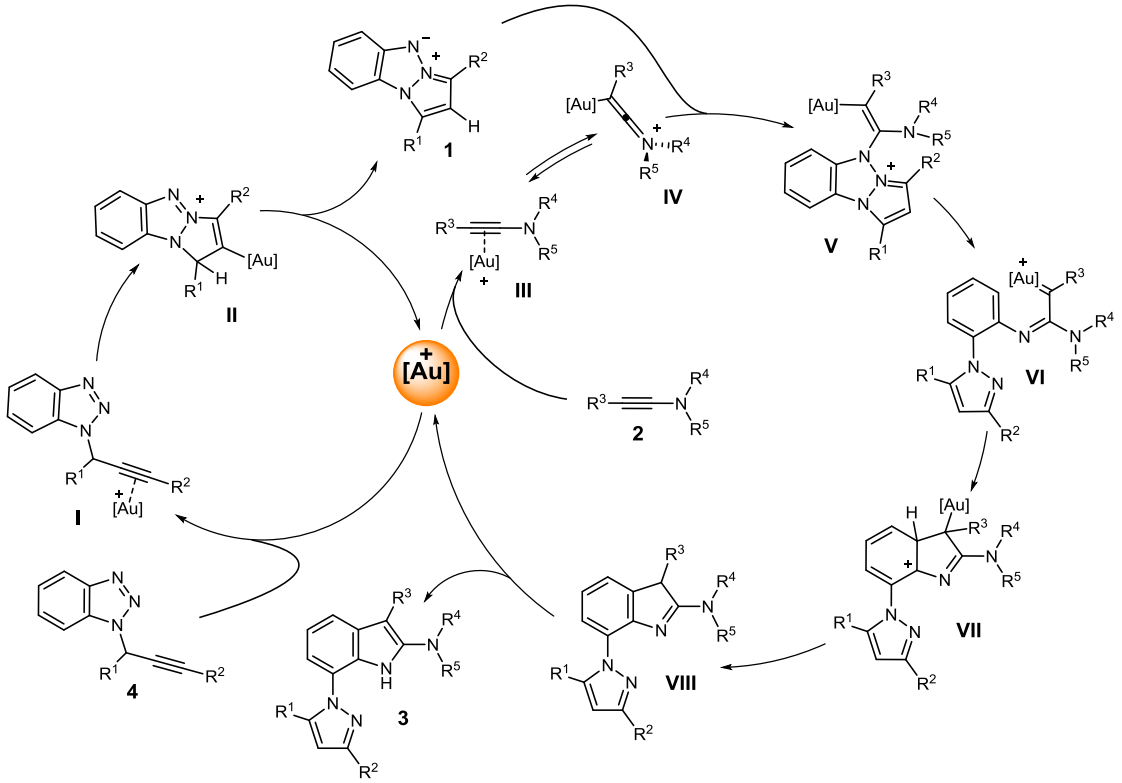
Compound	R^1	R^2	R^3	R^4	R^5	Yield [%][a)]
3a	*p*Tol	Ph	Ph	Me	Ts	93
3b	*p*Tol	Ph	*p*Tol	Me	Ts	95
3c	*p*Tol	Ph	*p*MeOC$_6$H$_4$	Me	Ts	95
3d	*p*Tol	Ph	*p*BrC$_6$H$_4$	Me	Ts	94
3f	*p*Tol	Ph	CO_2Et	Me	Ts	73
3g	*p*Tol	Ph	Ph			96
3i	Ph	*p*Tol	Ph			91
3k	*p*Tol	Ph	*p*Tol			89
3l	*p*Tol	Ph	*p*MeOC$_6$H$_4$			93
3m	*p*Tol	Ph	*p*BrC$_6$H$_4$			89
3n	*p*Tol	Ph	3,4,5-(MeO)$_3$C$_6$H$_2$			89

[a)]Isolated yields; Ts = *p*Toluenesulfonyl

Finally, as a proof of the goodness of this methodology, compound **3a** was also obtained in a gram scale from the corresponding benzotriazole. Thus, when the reaction was performed in a 3 mmol scale, 1.63 g (89%) of 3-phenyl-7-pyrazolylindole **3a** were obtained without any significant change in the global yield of the reaction.

The mechanistic proposal for the formation of the indole derivatives **3** is outlined in Scheme 2. Thus, as it has been previously reported,[13] the reaction is initiated by a gold catalyzed 5-*endo-dig* cycloisomerization of the propargylbenzotriazole **4** to form triazapentalene **1**. Triazapentalene **1** can be isolated or, in the presence of the ynamide **2**, could enter in a second catalytic cycle. Next, the formation of the indole derivatives from compound **1** could be explained in a similar way to separate procedures recently reported by Ye[4f] and Hashmi.[8d] Accordingly, ynamide **2**, activated by the gold catalyst liberated from the first catalytic cycle, could receive a regioselective nucleophilic attack by triazapentalene **1**, with formation of intermediate **V**. This intermediate **V** could evolve

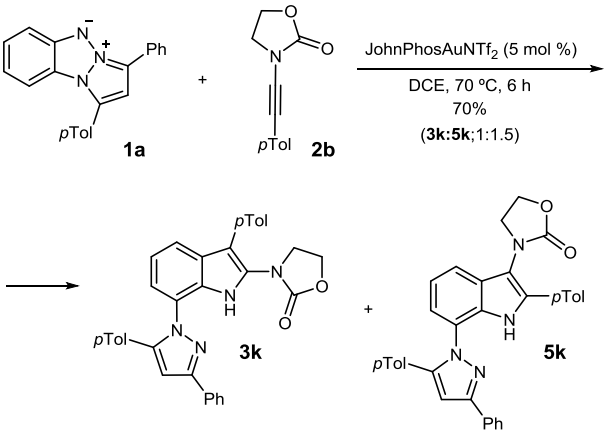
through the formation of a new intermediate with the structure of an α-imino gold(I) carbene complex **VI**, triggered by the breakage of the triazole and formation of the pyrazole ring. Finally, complex **VI**, in absence of any external nucleophile, would evolve through a C-H functionalization of the arene ring and formation of the indole skeleton **VII**. Final rearomatization and protodeauration would raise the formation of the 7-pyrazolylindoles **3**, as the reaction products.



Scheme 2. Mechanistic proposal for the synthesis of 7-pyrazolylindoles **3**.

As a summary of this part, it is worth to mention that it was possible to accomplish an intermolecular, regioselective and high yielding synthesis of 7-pyrazolylindoles, in a process that involves two catalytic cycles and a total atom economy. In addition, the procedure globally implies the breakage of one heterocycle into two linked new ones, as benzotriazole derivatives are transformed into indole and pyrazole rings.

Interestingly, during the course of our study of the formation of the indoles we made an interesting observation employing ynamides derived from 2-oxazolidinone. Although no differences were observed, in terms of the regioselectivity, during the screening of the gold ligands in the reaction of benzotriazole **4** with sulfonyl ynamides (*see Supporting Information*; Figure S1), significant differences were observed with the use of ynamides derived from 2-oxazolidinone. Thus, when JohnPhos was selected as the gold ligand, the reaction between triazapentalene **1a** and ynamide **2b**, under the standard reaction conditions, resulted in the formation of the 7-pyrazolylindoles in high yield but as a mixture of two regioisomers, such as **3k** and **5k** (Scheme 3). Both regioisomers could be satisfactorily isolated by a chromatographic column and independently characterized.



Scheme 3. Synthesis of 7-pyrazolylindoles **3** and **5**, as a mixture of regioisomers.

The structure of both regioisomeric indoles **3k** (*vide supra*) and **5k** were determined by NMR experiments and X-ray analysis. Figure 4 shows an X-ray crystal structure for regioisomer **5k**.

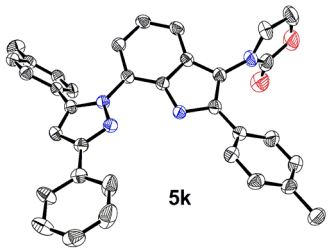


Figure 4. X-ray crystal structure for compound **5k**. Thermal ellipsoids are plotted at the 50% level and the hydrogens were removed for clarity.

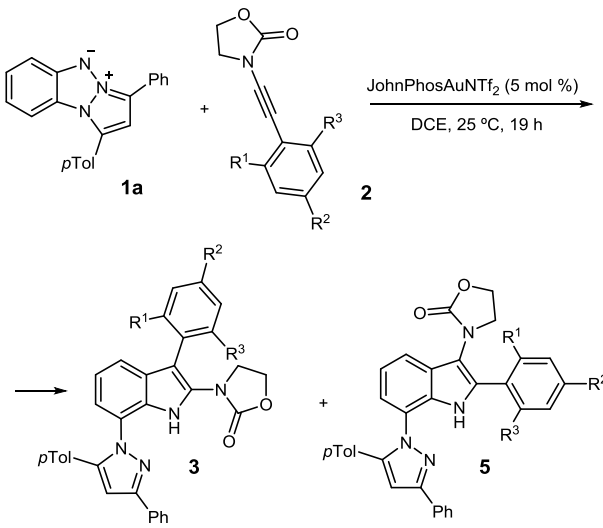
Although Huang *et al.* reported a similar behaviour for these ynamides, in terms of its unexpected reactivity through their β-position,[11] this is the first time that both regioisomers can be obtained in a single reactive process.

With this encouraging result in hands we decided to perform a deep screening of the reaction conditions in terms of temperature, solvent and catalyst ligand, in order to stablish the influence of these factors in the regioselectivity of the reaction (Table 2; *see below*, *next page*).

An increase in the regioselectivity was observed when the temperature was progressively lowered from 70 to 10 °C (entries 1-4), favoring the formation of the major isomer **5k**. Although the best results were obtained at 10 °C, non-significant differences were observed at 25 °C (1:2.7 *vs*. 1:2.5) and, for operative reasons, we decided to select 25 °C as the optimal reaction temperature. Next, we investigated the use of different solvents (entries 5-13) without the observation of any improvement, resulting 1,2-dichloroethane (DCE) as the best choice. Finally, taking into account the ligand nature, we observed that only with the use of JohnPhos as the gold ligand, the regioisomer **5k** is majority over the other isomer. This particular effect was not observed with ligands with higher or lower donating capability over the gold atom and smaller or bigger size in terms of steric hindrance. In addition, no differences were appreciated related to the nature of the anion of the gold complexes (entries 3 and 22).

As the results of the screening, we selected JohnPhosAuNTf$_2$ as the gold catalyst and 1,2-dichloroethane and 25 °C as the optimal reaction conditions. Under these conditions we next evaluated the influence of the substitution pattern of the aromatic ring of the ynamide, in terms of its electronical contribution. Thus, we performed the reaction of the model triazapentalene **1a** with different ynamides **2** and we observed a good trend in the experimental results (Table 3). To our delight, it was possible to selectively move from the synthesis of one to the other regioisomeric pyrazolylindole, under the same reaction conditions, and with a simple modification in the substitution pattern of the ynamide **2**.

Table 3. Ynamide influence in the regiosectivity.

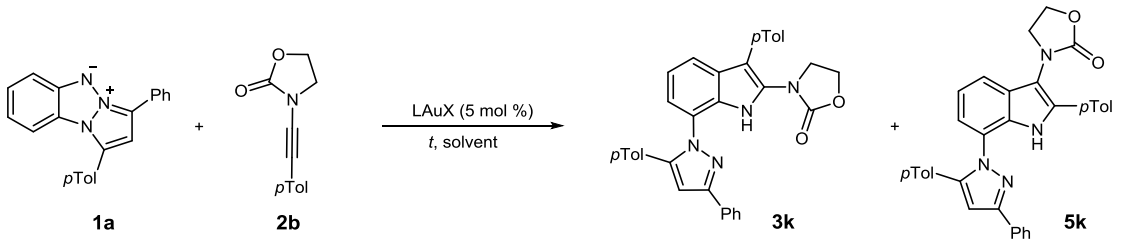


Entry	R^1	R^2	R^3	**3**	**5**	**3:5**	Yield [%][a]
1	H	CF_3	H	**3j**	**5j**	>20:1	43[b]
2	H	Br	H	**3m**	**5m**	2.7:1	70
3	H	F	H	**3o**	**5o**	1.5:1	83
4	H	H	H	**3g**	**5g**	1.1:1	88
5	H	Me	H	**3k**	**5k**	1:2.5	90
6	H	OMe	H	**3l**	**5l**	1:10	86
7	OMe	OMe	H	**3p**	**5p**	1:20	83
8	OMe	OMe	OMe	**3q**	**5q**	1:>20	71[c]
9	H	NMe_2	H	**3r**	**5r**	1:>20	71

[a]Isolated yields; [b]Conversion of 73% determined by NMR, using dibromomethane as internal standard. [c]24h of reaction.

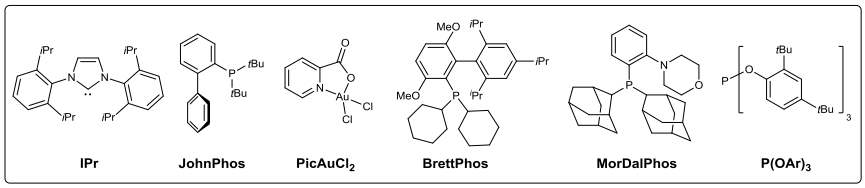
Thus, from Table 3 can be inferred that, under the reaction conditions, a phenyl ynamide raises both indoles in almost equimolecular amount (entry 4). However, the presence of electron-donating groups favours preferentially the formation of the 3-amidoindole compound **5** (entries 5-9). Additionally, this effect correlates very well with the donation capability of the substituents, ranging from a low effect for the methyl group (entry 5) to an almost exclusive formation of regioisomer **5** in other cases (entries 7-9). On the other hand, the presence of electron-withdrawing groups drives the reaction to the preferential formation of 2-amidoindole **3**, that is exclusively formed with 4-trifluoromethylphenyl ynamide. In addition, in all cases, both regioisomeric indoles **3** and **5** could be independently isolated by chromatographic column and characterized.

Table 2. Reaction screening for the regioselectivity in the formation of 7-pyrazolylindoles **3k** and **5k**.



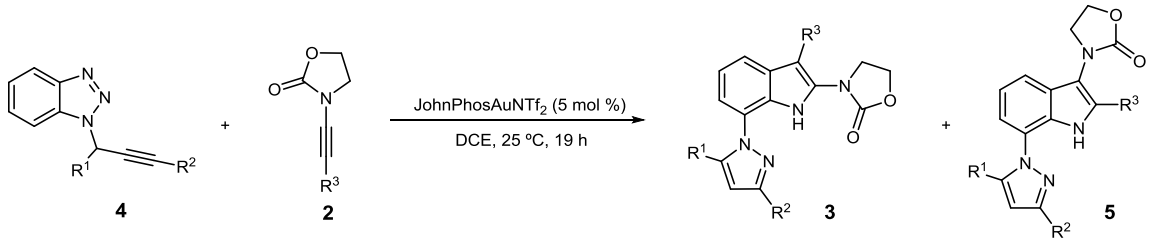
Entry	t [°C]	Solvent [0.2M]	Catalyst	Yield/Conv [%]	**3k : 5k**[a]
1	70	DCE	JohnPhosAuNTf$_2$	70/100	1 : 1.5
2	50	DCE	JohnPhosAuNTf$_2$	73/93	1 : 2
3	25	DCE	JohnPhosAuNTf$_2$	90/100	1 : 2.5
4	10	DCE	JohnPhosAuNTf$_2$	77/92	1 : 2.7
5	25	Toluene	JohnPhosAuNTf$_2$	99/100	2.6 : 1
6	25	Dioxane	JohnPhosAuNTf$_2$	99/100	1.6 : 1
7	25	PhCl	JohnPhosAuNTf$_2$	91/100	1 : 1
8	25	$CHCl_3$	JohnPhosAuNTf$_2$	74/100	1 : 1.2
9	25	THF	JohnPhosAuNTf$_2$	99/100	1 : 1.3
10	25	$MeNO_2$[b]	JohnPhosAuNTf$_2$	81/97	1 : 1.3
11	25	DMF[b]	JohnPhosAuNTf$_2$	31/12	1 : 1.4
12	25	DCE[c]	JohnPhosAuNTf$_2$	88/100	1 : 1.9
13	25	CH_2Cl_2	JohnPhosAuNTf$_2$	99/100	1 : 2.3
14	70	DCE	IPrAuNTf$_2$	98/100	1 : 0
15	25	DCE	PicAuCl$_2$	33/54	15 : 1
16	25	DCE	BrettPhosAuNTf$_2$	97/100	8.7 : 1
17	25	DCE	MorDalPhosAuNTf$_2$	81/100	1.9 : 1
18	50	DCE	$(ArO)_3PAuNTf_2$	5/35	1.5 : 1
19	25	DCE	$PPh_3AuCl/AgNTf_2$	23/93	1.3 : 1
20	25	DCE	JohnPhosAuNTf$_2$[d]	69/95	1 : 2
21	25	DCE	JohnPhosAuNTf$_2$[e]	91/100	1 : 2.3
22	25	DCE	JohnPhosAu(MeCN)SbF$_6$	94/100	1 : 2.5

[a]Yields, conversions and regioisomeric ratios were determined by NMR analysis using dibromomethane as internal standard; [b]0.15M; [c]0.1M; [d]2.5 mol %; [e]10 mol %.



Similarly to the synthesis of 2-amidoindoles **3** using IPrAuNTf$_2$ in a one-pot procedure from 1-propargyl-1*H*-benzotriazoles **4** (*vide supra*; Scheme 2), a one-pot JohnPhosAuNTf$_2$ catalyzed reaction, focused towards the synthesis of 3-amidoindoles **5**, could also been attempted. Thus, we tested this possibility, which should involve two consecutive catalytic cycles. To our delight, several 3-amidoindoles **5** were synthesized without any significant differences in terms of yield and regioselectivity compared with the results obtained starting from triazapentalenes **1** (Table 4).

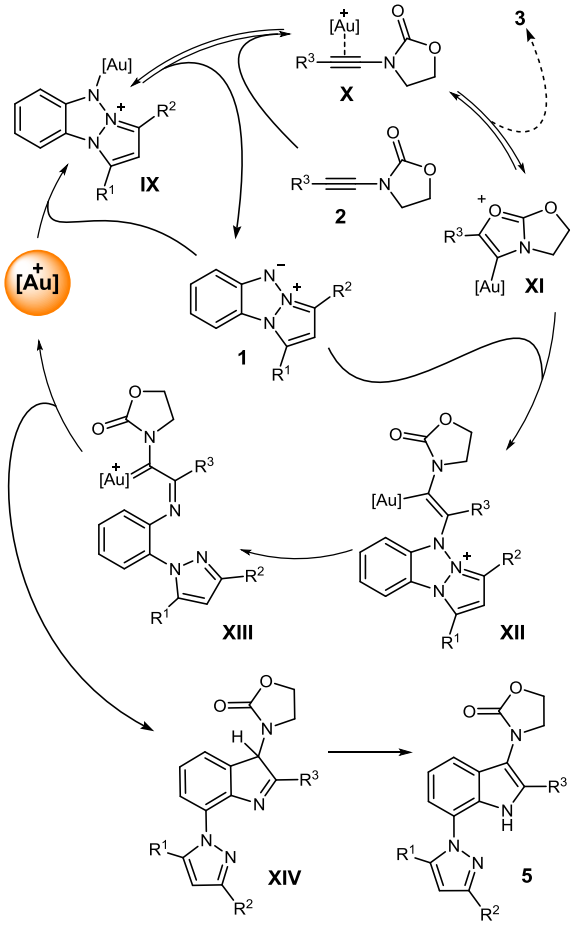
Table 4. One-pot synthesis of indoles **3** and **5** from propargylbenzotriazoles **4**.



Entry	R^1	R^2	R^3	**3**	**5**	**3 : 5**	Yield[%][a]
1	*p*Tol	Ph	*p*MeOC$_6$H$_4$	**3l**	**5l**	1 : 10	87
2	*p*Tol	Ph	2,4,6-(MeO)$_3$C$_6$H$_2$	**3q**	**5q**	1 : >20	72[b]
3	*p*Tol	Ph	*p*Me$_2$NC$_6$H$_4$	**3r**	**5r**	0 : 1	75
4	Ph	*p*Tol	2,4,6-(MeO)$_3$C$_6$H$_2$	**3s**	**5s**	1 : >20	69[b]
5	Ph	*p*Tol	*p*Me$_2$NC$_6$H$_4$	**3t**	**5t**	0 : 1	66

[a]Isolated yields. [b]24h of reaction.

Formation of regioisomers **5** could be explained through the participation of a key intermediate derived from an intramolecular attack of the carbonyl oxygen of the ynamide to the gold activated triple bond. With this premise in mind, a mechanistic proposal could be formulated and it is outlined in Scheme 4. Thus, the reaction would begin with the formation of intermediate **IX** as the result of the coordination of the gold catalyst to the nucleophilic dipolar triazapentalene **1**. This intermediate **IX** could be identified in a stoichiometric experiment (*see Supporting Information*). Next, after migration of the gold complex to the ynamide, the gold activated ynamide **X** could directly react with the nucleophilic triazapentalene **1**, evolving through the mechanistic proposal previously described in Scheme 2 (*vide supra*) for the formation of 7-pyrazolylindoles **3**. However, for gold activated ynamides derived from 2-oxazolidinone, an intramolecular attack of the oxygen of the carbamate could occur, with formation of the cationic intermediate **XI**. Formation of intermediate **XI** have also been reported by Huang *et al.*[11] and their existence was demonstrated through several X-ray analysis (*vide infra*). Next, the reaction could evolve through a nucleophilic attack of the triazapentalene **1** to the intermediate **XI**, resulting in the formation of **XII**. This intermediate **XII** could be transformed into the α-imino gold carbene complex **XIII** triggered by the formation of the pyrazole ring. Finally, carbene complex **XIII** would raise 7-pyrazolylindole **5**, in a reaction pathway that involves consecutive cyclization and tautomerization-aromatization steps.



Scheme 4. Mechanistic proposal for the synthesis of 7-pyrazolylindoles **5**.

At this time, we focused our efforts in the key intermediate **XI**, trying to find out a reasonable explanation for the reaction behaviour. For this purpose, we performed a number of

stoichiometric experiments that were analysed by NMR (*See Supporting Information for details*). First, in two separate experiments, to a solution in deuterated methylene chloride of the corresponding catalysts, $IPrAuNTf_2$ and $JohnPhosAuNTf_2$, phenyl ynamide **2c** was added in equimolecular amount. Both experiments resulted in the almost exclusive formation of compounds that could be identified by NMR as intermediates **XI**. Next, addition of one equivalent of dipolar nucleophilic triazapentalene **1a** to the solutions triggers the instantaneous disappearance of bicyclic intermediate **XI** and initiates the formation of the indole derivatives. The disappearance of intermediates **XI** and formation of triazapentalene gold complexes **IX**, which progressively evolve to the indole derivatives, indicates the existence of equilibrium between species **IX**, **X** and **XI**, as it is outlined in Scheme 4. Next, after a short period of time, two N-H indole signals were observed, in the experiment that involves $IPrAuNTf_2$ as the gold catalyst, and four signals for the solution containing $JohnPhosAuNTf_2$. These signals could be identified as indoles **3g** and **5g** and their corresponding gold(I) coordinated complexes. Finally, after a triphenylphosphine treatment we observed, in both cases, the disappearance of half of the signals and the procurance of indole **3a** or a mixture of regioisomers **3a** and **5a**, respectively.

In an effort to elucidate the differences in the behavior between both catalysts, intermediates **XI-IPr** and **XI-JohnPhos** in addition to the JohnPhos complex with *p*-methoxyphenyl ynamide **2d** (**XI-(MeO)-JohnPhos**), were isolated and characterized. Additionally, X-ray analyses were performed on the corresponding monocrystals of the three compounds (Figure 5).

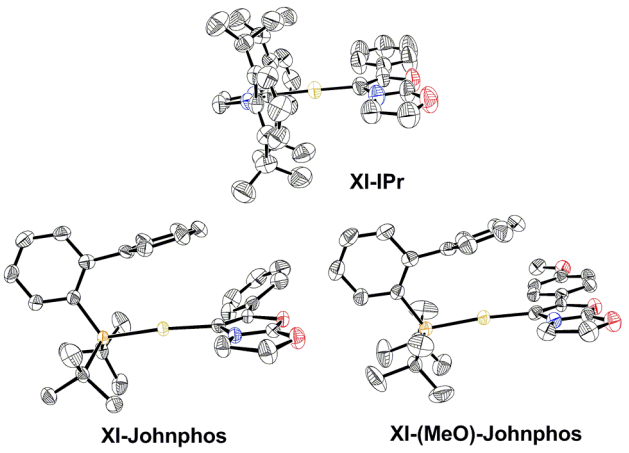


Figure 5. X-ray crystal structure for intermediates **XI-IPr** (top), **XI-JohnPhos** (bottom-left) and **XI-(MeO)-JohnPhos** (botton-right). For all the structures, thermal ellipsoids are represented at the 50% level and the hydrogen atoms and counterions were removed for clarity.

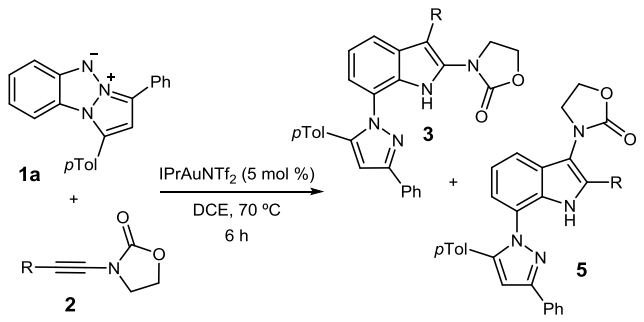
Comparing the crystal structures of **XI-IPr** and **XI-JohnPhos**, a clear structural difference can be observed pointing to a different stability and consequently different behavior. Thus, for the JohnPhos ligand, its conformation, with the phenyl ring on the top of the gold atom due to a weak interaction gold-phenyl ring,[23] can be the clue for its particular behaviour. The proximity of the phenyl ring to the cationic intermediate could provide an extra degree of stabilization[24] facilitating its posterior evolution through a nucleophilic attack. In this sense, from the solid state can be observed that the phenyl ring of the ligand is slightly deviated towards the reactive ring of the intermediate **XI-JohnPhos** (dihedral angle (Au-P-C-C) = 17.7°). Additionally, a measure of spatial distances revealed that both carbons of the double bond of that ring are placed at distances ranging from 3,4 to 3,8 Å from the external rim of the phenyl ring of the ligand. These distances lay into the values considered, by several authors,[25] at the upper limit for a π-stacking interaction between two phenyl rings. That interaction is not possible for intermediate **XI-IPr** and similarly for intermediates with other ligands (Table 2). In this sense, the presence of isopropyl groups in a ligand with structural similarities, such as BrettPhos, could difficult the approximation of the phenyl ring.

In addition, the electronic influence of the substituents of the aromatic ring of the ynamides could also be correlated in terms of the stability of intermediates **XI**. Thus, crystal structure of intermediate **XI-(MeO)-JohnPhos** (Figure 5) shows an almost complete planarity of the aromatic ring with the bicyclic skeleton, indicating a high degree of conjugation. This planarity is not observed for **XI-JohnPhos** (dihedral angle (C-C-C-C)= -30.3°). The planarity in **XI-(MeO)-JohnPhos** evidences that electron-donating groups should stabilize the cationic intermediate ring by conjugation, in a progressive effect that correlates very well with the electron-donating capability of the aromatic ring of the ynamide. On the contrary, the presence of electron-withdrawing groups operates in the opposite direction, diminishing the formation of indole **5** (almost negligible for CF_3) through an unstabilization of the cationic intermediate **XI**.

Finally, in order to corroborate this hypothesis of a double, but independent, contribution of the nature of the gold ligand and the substitution pattern of the ynamide, three more experiments were attempted (Table 5). Thus, the reaction of formation of indoles was performed, under the standard reaction conditions, using $IPrAuNTf_2$ and ynamides with highly activated aryl groups

such as 2,4-dimethoxyphenyl, 2,4,6-trimethoxyphenyl or 4-dimethylaminophenyl. To our delight, in all cases, the presence of the strongly electron-donating groups allows for a partial formation of 3-amidoindoles **5**, regioisomers that have never been previously observed using that catalyst. These results indicate that the high stabilizing effect of the substituents overcomes the lack of effect due to the gold ligand. In addition, the use of a very electron-donating group such as dimethylamino (entry 3) is able to form regioisomer **5** as the slightly majority product.

Table 5. Synthesis of both regioisomers using $IPrAuNTf_2$.



Entry	R	3	5	3 : 5	Yield[%][a)]
1	2,4-$(MeO)_2C_6H_3$	**3p**	**5p**	3:1	80
2	2,4,6-$(MeO)_3C_6H_2$	**3q**	**5q**	1.8:1	91
3	*p*$Me_2NC_6H_4$	**3r**	**5r**	1:1.5	63

[a)]Isolated yields.

The results shown in Table 5 represent the only example reported to date of use of an IPr ligand in a procedure involving a gold catalyzed nucleophilic attack through the β-position of an ynamide. On the other hand, these results allow us affirming that gold ligand and substitution pattern or the ynamide independently contribute to the stability of the key intermediate of the reaction.

Conclusions

In conclusion, here is reported a simple, high yielding, atom-economical and catalytic regioselective synthesis of 7-pyrazolylindoles from a nucleophilic attack of a triazapentalene, as an isolable intermediate, to a gold activated ynamide. The reaction presumably occurs with the participation of an α-imino gold carbene complex and involves two consecutive catalytic cycles. As the result, one heterocycle, a benzotriazole, is broken into two new connected ones, such as indole and pyrazole. More relevantly, the regioselectivity of the reaction can be controlled, or even reversed, by an appropriated selection of the ynamide structure and the gold catalyst. Thus, sulfonyl ynamides drive the reaction to the formation of 2-amidoindoles through the usual nucleophilic attack to the α-position of the ynamide, regardless of the nature of the gold catalyst. However, the employment of ynamides derived from 2-oxazolidinone, in combination with the use of JohnPhos as the gold ligand, allows for the formation of both regioisomers, 2- or 3-amidoindoles. The formation of the unusual 3-amido regioisomer, as the results of an attack to the β-position of the ynamide, can be controlled by the electron-donating capability of an arene group in the ynamide skeleton. This regioselectivity ranges from negligible to the exclusive formation of one or the other isomer. Although a single example of gold catalyzed intermolecular attack to the β-position of an ynamide has been previously reported,[11] this is the first example to date where the reaction can be driven to one or the other regioisomeric attack, on demand.

Experimental Section

General Methods

All operations were carried out under argon atmosphere using conventional Schlenck techniques. All common reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Tetrahydrofuran (THF) was distilled from sodium-benzophenone and 1,2-dichloroethane from calcium hydride, prior to use. Ethyl acetate, methanol and methylene chloride were used from commercial suppliers. TLC was performed on aluminium-backed plates coated with silica gel 60, with F254 indicator or neutral aluminium oxide. Flash chromatographic columns were carried out on silica gel 60 (230-400 mesh). High-resolution mass spectra were determined on a Finnigan MAT95 spectrometer. NMR spectra were run on Bruker AV-300, DPX-300, AV-400 or AMX-400 spectrometer using $CDCl_3$ or CD_2Cl_2 as solvents. Melting points were measured in a Büchi-Tottoli apparatus and were not corrected.

Experimental procedure for the synthesis of 7-pyrazolylindoles 3 and 5.

Using $IPrAuNTf_2$ as catalyst

*From triazapentalenes **1***

To a solution of 0.2 mmol of 1,2,3-triazapentalene **1** in 1 mL of 1,2-dichloroethane, 0.2 mmol of the corresponding ynamide **2**, and 8.7 mg (0.01 mmol; 5 mol %) of gold catalyst were added. The mixture was heated at 70 ºC and stirred for 6 hours. After that period of time, the mixture

was allowed to cool down and the solvents evaporated under vacuum. Finally, after purification of the residue under chromatographic column, the corresponding 7-pyrazolylindoles **3a-k**, **3p-r** and **5p-r** were obtained as pure compounds.

*From propargylbenzotriazoles **4***

The experimental procedure for the synthesis of 7-pyrazolylindoles **3** and **5** starting from 1-propargyl-1*H*-benzotriazoles **4**, follows the same reaction conditions described from triazapentalenes **1**. Under these conditions, 7-pyrazolylindoles **3a-d**, **3f-g**, **3i** and **3k-n** were obtained as pure compounds.

Using JohnPhosAuNTf$_2$ as catalyst

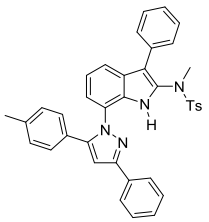
*From triazapentalenes **1***

For the synthesis of 7-pyrazolylindoles **3** and **5**, using JohnPhosAuNTf$_2$ instead of IPrAuNTf$_2$, the same experimental procedure can be followed but stirring the mixture for 19 hours (24 hours for **3s** and **5s**) at 25 ºC. Under this procedure, pure **3g**, **3j**, **3k-m**, **3o-r**, **5g**, **5k-m** and **5o-r** were obtained.

*From propargylbenzotriazoles **4***

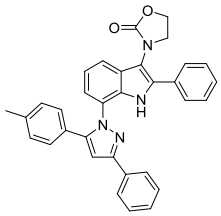
Previously to the addition of the ynamide **2**, 1-propargyl-1*H*-benzotriazole **4** (0.02 mmol) and gold catalyst (7.8 mg, 0.01 mmol; 5 mol %) was stirred in 1 mL of 1,2-dichloroethane, at room temperature, for one hour and a half. After that period, 0.02 mmol of the ynamide **2** was added and, from this point, the experimental procedure follows the same methodology described starting from triazapentalenes 1. Pure 7-pyrazolylindoles **3l**, **5l**, and **5q-t** were obtained.

_N_,4-Dimethyl-_N_-(3-phenyl-7-(3-phenyl-5-(_p_-tolyl)-1_H_-pyrazol-1-yl)-1_H_-indol-2-yl)benzenosulfonamide (3a)



Yield: 96%, 122 mg (From triazapentalene **1a**); 93%, 113 mg (From benzotriazole **4a**). Yellow solid; m.p.: 221-223 ºC. Rf = 0.64 (Hexanes/Methylene chloride/Ethyl acetate, (20:10:1)). ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS): δ (ppm) 9.81 (s, 1H), 8.04 (d, *J* =7.5 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.55-7.40 (m, 4H), 7.35-7.15 (m, 9H), 7.02-6.80 (m, 3H), 6.91 (s, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 3.12 (s, 3H), 2.42 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ (ppm) 152.3 (C), 145.0 (C), 144.3 (C), 138.6 (C), 134.6 (C), 133.0 (C), 132.8 (C), 131.5 (C), 129.9 (2 x CH), 129.4 (2 x CH), 129.3 (2 x CH), 128.9 (CH), 128.8 (2 x CH), 128.7 (2 x CH), 128.3 (2 x CH), 128.3 (CH), 127.7 (C), 127.6 (2 x CH), 127.2 (C), 126.9 (CH), 125.9 (2 x CH), 124.2 (C), 119.6 (CH), 118.4 (CH), 118.0 (CH), 112.1 (C), 105.4 (CH), 38.5 (CH_3), 21.5 (CH_3), 21.4 (CH_3). HRMS (EI) for $C_{38}H_{33}N_4O_2S$ [M+1]: Calc: 609.2319; found: 609.2310.

_N_-(2-Phenyl-7-(3-Phenyl-5-(_p_-tolyl)-1_H_-pyrazol-1-yl)-1_H_-indol-3-yl)oxazolidin-2-one (5g)



Yield: 42%, 43 mg. White solid; m.p.: 239 ºC (dec.). Rf = 0.22 (Hexanes/Methylene chloride/Ethyl acetate, (10:10:1)). ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS) δ (ppm) 9.72 (s, 1H), 8.04-7.89 (m, 2H), 7.73 (d, *J* = 7.1 Hz, 2H), 7.58-7.33 (m, 7H), 7.33-7.23 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.88 (s, 1H), 6.75 (d, *J* = 7.5 Hz, 1H), 4.56 (t, *J* = 8.0 Hz, 2H), 3.88 (t, *J* = 8.0 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ (ppm) 158.0 (C), 152.2 (C), 145.3 (C), 138.8 (C), 134.9 (C), 132.8 (C), 130.6 (C), 129.3 (2 x CH), 129.3 (2 x CH), 128.8 (2 x CH), 128,8 (CH), 128.7 (2 x CH), 128.4 (C), 128.3 (CH), 127.4 (C), 127.4 (C), 127.1 (2 x CH), 125.7 (2 x CH), 124.7 (C), 120.1 (CH), 118.0 (CH), 116.9 (CH), 110.9 (C), 105.4 (CH), 62.7 (CH_2), 47.5 (CH_2), 21.4 (CH_3). HRMS (EI) for $C_{33}H_{27}N_4O_2$ [M+1]: Calc: 511.2129; found: 511.2128.

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Darío Allegue, Jairo González, Sergio Fernández, Javier Santamaría* and Alfredo Ballesteros*