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## Gold-catalyzed [4+1]-Annulation Reactions between Anthranils and 4-Methoxy-1,2-dienyl-5-ynes Involving a 1,2-Allene Shift

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Gold-catalyzed [4+1]-annulations of 4-methoxy-1,2-dienyl-5-ynes with anthranils are described. The mechanism of these annulations involves nitrene formation of  $\alpha$ -imino gold carbenes that undergo a 1,2-allene shift to form (pyrrol-2-yl)methylgold intermediates. With allenyl ester substrates, these gold intermediates become enolate species to enable intramolecular aldol reactions to form useful pyrrolo[1,2-*a*]quinoline derivatives.

Interest in the N,O-functionalizations of alkynes with isoxazoles and anthranils is rapidly increasing in gold catalysis because of their efficient generations of versatile  $\alpha$ -imino gold carbenes under ambient conditions.<sup>1</sup> The current work focuses intensively on activated alkynes such as ynamides and propiolate derivatives.<sup>2-3</sup> The *N*,*O*-functionalizations of unactivated alkynes with these aromatic nitroxy species are highly desirable. The high reactivity of 1,4-diyn-3-ols toward gold-catalyzed nucleophilic attack is notable.<sup>4</sup> We believe that these 1,4-diyn-3-ols possess two adjacent alkynes toward gold catalysts, thus increasing their electrophilic reactions. Hashmi reported<sup>4a</sup> gold-catalyzed oxidations of 1,4-diyn-3-ols with pyridine-based oxides to generate  $\alpha$ -oxo gold carbenes In-1 that underwent a subsequent 1,2-alkyne shift to give 3formylfuran derivatives. We reported<sup>4b</sup> catalytic [4+1]annulations of 1,4-diyn-3-ols with isoxazoles or anthranils to generate  $\alpha$ -imino gold carbenes **In-2**, resulting in a 1,2-alkyne shift before proceeding to N-enonyl 3-formylpyrrole products (eq 2). Apart from 1,4-diyn-3-ols, the present work reports regioselective N,O-funtionalizations of 4-methoxy-1,2-dienyl-5ynes  $(1)^5$  with anthranils; we postulate that the binding ability of allenes and alkynes with a gold complex are of comparable affinity.<sup>6</sup> Herein, anthranils attack initially at a  $\pi$ -acid activated alkyne to form  $\alpha$ -imino gold carbenes **In-3**, which undergo a

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yl)methylgold intermediates **In-4**. A subsequent aldol reaction of these gold enolates delivers useful pyrrolo[1,2-*a*]quinoline derivatives when allenyl esters were used (R' = CO<sub>2</sub>Et). In mechanistic aspect, we are aware of no examples for a 1,2allene migration into metal carbene moieties. The significance of this work is to provide an easy access to pyrrolo[1,2*a*]quinoline frameworks<sup>7</sup> that are commonly found in many bioactive molecules; the representatives **I-IV** are shown in Figure 1. Among them, compounds I and II are found to be highly active in human-breast cancer cells T47D<sup>8</sup> and compound III exhibits bacteriostatic or fungistatic activity.<sup>9</sup> Species IV can decrease the sensitivity to the toxicity of anthrax.<sup>10</sup>

subsequent 1,2-allene migration to form interesting (pyrrol-2-

Previous work: 1,2-alkyne shift



Table 1 shows optimizations of conditions between 4methoxy-1,2-dienyl-5-ynes **1a** with anthranil **2a**. Our initial tests employed IPrAuCl/AgNTf<sub>2</sub> (10 mol %) to catalyze the reactions of 1,2-dienyl-5-yne **1a** with anthranil **2a** in

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dichloroethane (DCE, 70 °C, 18 h), affording pyrrole 3a in 12% yield (entry 1). Under this condition, a high loading (4.0 equiv.) of anthranil 2a gave 3a in a slightly increased yield, ca. 19%; an alcohol derivative 4a was isolated in 13% yield (entry 2). A switch of catalyst to LAuCl/AgNTf<sub>2</sub> (10 mol %, L =  $P(t-Bu)_2(o-t)$ biphenyl), rendered the desired product 3a in only 10% yield (entry 3). We observed no reactivity with PPh<sub>3</sub>AuCl/AgNTf<sub>2</sub> (entry 4). Among other silver salts (AgX, X = OTf, SbF<sub>6</sub> and CO<sub>2</sub>CF<sub>3</sub>), only AgCO<sub>2</sub>CF<sub>3</sub> gave an increased yield of compound 3a with 27% (entries 5-7). Notably, we employed a high loading (15 mol %) of IPrAuCl/AgCO<sub>2</sub>CF<sub>3</sub> to increase compound 3a to 30% yield (entry 8); an increased amount of AgCO<sub>2</sub>CF<sub>3</sub> (50 mol %) gave compound 3a up to 65% yield (entry 9). In the presence of CF<sub>3</sub>CO<sub>2</sub>Li (35 mol %) additive, this 15 % IPrAuCl /AgCO<sub>2</sub>CF<sub>3</sub> system became much less active (entry 10). The use of IPrAuCl(15 mol %)/AgNTf<sub>2</sub>(50 mol %) gave the desired products **3a** and **4a** in small proportions (< 5%) (entry 11). AgCO<sub>2</sub>CF<sub>3</sub> (50%) alone was catalytically inactive (entry 12). The performance of IPrAuCl/AgCO2CF3 in a 15/50 molar ratio was also examined in toluene, 1,4-dioxane, and DMF; only toluene showed a moderate efficiency to deliver desired 3a in 48% yield (entries 13-15). The molecular structures of compound 3a and 4a were characterized with X-ray diffraction study.<sup>11</sup>

We assess the scope of these [4+1]-annulation reactions with various 4-methoxy-1,2-dienyl-5-ynes **1** and anthranil **2a** using IPrAuCl (15 mol %)/AgCO<sub>2</sub>CF<sub>3</sub> (50 mol %) in DCE; the results are summarized in Table 2. For 1,2-dien-5-ynes bearing 4-substituted phenylalkynyl species (**1b-f**;  $R = 4-XC_6H_4$ , X = Cl, Br, OMe, Me, *t*-Bu), their gold-catalyzed reactions yielded

Table 1. Catalytic reactions with various metal catalysts

h 1:	$\frac{DMe}{h} + \frac{C}{N} \frac{catal}{solvent}$	lyst ., 70 ' ne			Ph. O	LN 4a	Учон
					Yield <sup>a</sup> (%)		
Entry	Catalyst ( mol% )	n	Solvent	Time (h)	1a	3a	4a
1	IPrAuCl (10) /AgNTf <sub>2</sub> (10) <sup>b</sup>	2	DCE	18	30	12	trace
2	IPrAuCl (10) /AgNTf <sub>2</sub> (10)	4	DCE	14	-	19	13
3	LAuCl (10)/AgNTf <sub>2</sub> (10) <sup>c</sup>	4	DCE	20	12	10	-
4	Ph <sub>3</sub> PAuCl (10)/AgNTf <sub>2</sub> (10)	4	DCE	24	60	-	-
5	IPrAuCl (10)/AgCO <sub>2</sub> CF <sub>3</sub> (10)	4	DCE	48	33	27	-
6	IPrAuCl (10)/AgOTf (10)	4	DCE	48	21	11	-
7	IPrAuCl (10)/AgSbF <sub>6</sub> (10)	4	DCE	32	6	24	-
8	IPrAuCl (15)/AgCO <sub>2</sub> CF <sub>3</sub> (15)	4	DCE	34	10	30	-
9	IPrAuCl (15)/AgCO <sub>2</sub> CF <sub>3</sub> (50)	4	DCE	30	-	65	-
10	IPrAuCl (15)/AgCO <sub>2</sub> CF <sub>3</sub> (15) <sup>d</sup>	4	DCE	47	40	25	-
11	IPrAuCl (15)/AgNTf <sub>2</sub> (50)	4	DCE	40	-	2	5
12	$AgCO_2CF_3$ (50)	4	DCE	72	95	-	-
13	IPrAuCl (15)/AgCO <sub>2</sub> CF <sub>3</sub> (50)	4	toluene	20	-	48	-
14	IPrAuCl (15)/AgCO <sub>2</sub> CF <sub>3</sub> (50)	4	1,4-dioxane	48	11	-	-
15	IPrAuCl (15)/AgCO <sub>2</sub> CF <sub>3</sub> (50)	4	DMF	48	55	-	-

**1a** (0.14 M, 1.0 equiv.) <sup>*a*</sup> Product yields are obtained after purification from a silica column, <sup>*b*</sup> IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene, <sup>*c*</sup> L = P(*t*-Bu)<sub>2</sub>(*a*-biphenyl), Tf = trifluoromethanesulfonyl. <sup>*d*</sup> LiCF<sub>3</sub>CO<sub>2</sub> (35 mol %) was added



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1 (0.14 M, 1.0 equiv.) <sup>*a*</sup> Product yields are obtained after purification from a silica column. <sup>*b*</sup> IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene.

desired **3b–3f** in 54-66% yields (entries 1–5). To our delight, these annulations were applicable also to various alkylsubstituted 1,2-dienyl-5-ynes (**1g-i**; R = isopropyl, cyclopropyl and *n*-butyl), further affording the desired products **3g-3i** in 61-75% yields (entries 6-8). For 2-thienyl-substituted 1,2dienyl-5-yne **1j**, its corresponding product **3j** was obtained in 41% yield (entry 9). We tested the reaction on 3-allenyl-5-yne **1k**, but yielding a complicated mixture of product (entry 10).

We also prepared various anthranils **2b-2l** to test their efficiencies with these gold catalyzed reactions. For species **2b-2f** bearing various 5-substituted anthranils (X = Cl, Br, Me, OMe and OAc), their gold catalyzed reactions rendered the desired products **3b'-3f'** in 59-74% yields (Table 3, entries 1-5). In the case of 6-substituted anthranils **2g-2j** (X = Cl, Br, Me, and OMe), their resulting products **3g'-3j'** were obtained in 62-71% yields (entries 6-9). Under the standard conditions, dioxolo-substituted anthranil **2k** delivered compound **3k'** in

### Table 3. Catalytic Reactions with various anthranils



**1a** (0.14 M, 1.0 equiv.) <sup>o</sup> Product yields are obtained after purification from a silica column. <sup>b</sup> IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene.

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68% yield (entry 10). We examined the reaction on 3methylanthranil **2I**, yielding compound **3I'** in 76% yield (entry 11).

The presence of the minor byproduct **4a** in Table 1 (entry 2) inspires us to prepare an allenyl ester derivative **1a'** to facilitate a possible aldol reaction. Among different silver salts ( $X = NTf_2$ , SbF<sub>6</sub> and CO<sub>2</sub>CF<sub>3</sub>), IPrAuCl/AgNTf<sub>2</sub> (15 mol %) was the most productive, delivering an aldol product **4b** in 78% yield with dr = 1.6:1. In the presence of DBU (1 equiv.), this aldol product was efficiently converted to pyrrolo[1,2-*a*]quinoline **5a** in 85% yield (eq 4). The molecular structure of compound **5a** was characterized by X-ray diffraction.<sup>11</sup>



We assess the scope of the pyrrolo[1,2-a]quinoline synthesis with various aryl- substituted allenyl esters 1b'-1k' via one-pot two-step operations; the results were summarized in Table 4. Treatment of 4-methoxy-1,2-dienyl-5-ynes 1' with anthranil 2a (4 equiv.) and IPrAuCl/AgNTf<sub>2</sub> (15 mol %) in hot DCE (70 °C, 42-45 h) afforded the intermediate 4 that was converted to pyrrolo[1,2-a]quinolines with DBU (1.0 equiv.) in DCE at 25 °C. We prepared 4-substituted phenyl derivatives 1b'-1d' (X = OMe, Me and Cl) that afforded the desired products 5b-5d in 52-80% yields (entries 1-3); as we expected, electron-rich arylalkyne derivatives (X = OMe and Me) were efficient with these annulations. We tested the reactions also on 3- and 2phenyl analogues 1e'-1h' bearing OMe and Cl substituents (entries 5-8), their resulting products 5e-5h were obtained in high yields (> 74%) except compound 5f that was obtained in 47% (entry 6). For 2-thienyl substituted analogue 1i', its corresponding product 5i was produced in 34% yield (entry 9). We tested the reactions on alkyl substituted analogues 1j' and 1k' that afforded compounds 5j and 5k in 76% and 60% yields respectively (entries 10-11). Such pyrrolo[1,2-a]quinoline synthesis was also operable with 5-substituted anthranils (R<sup>2</sup> = Cl, OCO<sub>2</sub>Me; R<sup>3</sup> = H), affording the desired compounds **5b'** and 5c' in 58% and 27% yields respectively (entries 12-13). For 6substituted anthranils ( $R^2 = H$ ;  $R^3 = Cl$  and Me), their corresponding products 5d' and 5e' were produced in 41% and 73% yields respectively (entries 14-15). 5,6-Disubstituted anthranils ( $R^2 = R^3 = OMe \text{ or } R^2, R^3 = -OCH_2O$ -) led to formation of pyrrolo[1,2-a]quinoline 5f' and 5g' species in high yields (70-89% entries 16-17).

As shown in Scheme 1, we found that 15% IPrAuCL/30%  $AgNTf_2$  gave cyclic alcohol **4a** in a notable 18% yield (eq 5). But this condition failed to convert pyrrole **3a** to the alcohol derivative **4a** at all (eq 6). We also tested a running condition in Table 4. With a mixture of allenyl ester **1j'** (1 equiv.), anthranil **2a** (4 equiv.) and pyrrolyl species **3a**, we obtained only pyrrolo[1,2-*a*]quinoline **5j** in 71% yield whereas another



Table 4. One-pot synthesis of pyrrolo[1,2-a]quinolines

1' (0.10 M, 1.0 equiv.) <sup>*a*</sup> Product yields are obtained after purification from a silica column. <sup>*b*</sup> IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene. Tf = trifluoromethanesulfonyl.

cyclized product **4a** was completely absent (eq 7). This information indicated that (pyrrol-2-yl)methylgold species **In-Au** likely formed cyclized product **4a**, although species **In-Au** was more active toward hydrodeauration to form 3-formylpyrrole product **3a**. We also prepared species **1a** with <sup>13</sup>C-enriched at the C(4)- carbon; the gold-catalyzed reaction gave pyrrolyl product **3a** with the <sup>13</sup>C-enrichment at the formyl carbon.

We postulate a mechanism in Scheme 2 involving goldcontaining intermediates In-Au that are inferred by our data in Scheme 1. The nitrogen of anthranil is generally more nucleophilic than its adjacent oxygen atom; this N-attack occurs preferably at the alkynyl rather than at the allene moiety. After a nitrene transfer, the resulting  $\alpha$ -imino gold-





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carbenes undergoes a 1,2-allene shift rather than a 1,2hydrogen shift, subsequently yielding Au- $\pi$ -allene species **D**; we postulate that this allene migration is probably due to an efficient overlap through space between the  $\pi$ -orbitals of the C(3) and C(5) carbons in species **B**. An intramolecular cyclization of intermediate **D** generates gold-containing pyrrole species **E** in which the oxonium moiety is attacked by water to yield a key intermediate **In-Au**. For unsubstituted 1,2-dienyl-5yne **1a** (R = H), most of species **In-Au** is protonated to give the observed product **3a**. In the case of an ester derivative (**1a**'), species **In-Au** bearing a stable enolate (R = CO<sub>2</sub>Et) undergoes an aldol reaction to afford compounds **4b** efficiently.

Catalytic N,O-functionalizations of alkynes with isoxazoles and anthranils were studied intensively on activated alkynes. In seeking unactivated alkynes, we report gold catalyzed [4+1]annulations of 4-methoxy-1,2-dienyl-5-ynes with anthranils.12,13 The mechanism of these annulations involves initial formation of  $\alpha$ -imino gold carbenes that undergo a subsequent 1,2-allene shift before forming (pyrrol-2yl)methylgold intermediates. With organogold these intermediates, we performed one-pot synthesis of pyrrolo[1,2a]quinoline products 5 using allenyl ester substrates; the key step involves intramolecular aldol reactions.14

### **Conflicts of interest**

There are no conflicts to declare.

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- 14 The results in Table 1 (entries 9-12), indicated that both  $Ag^+$ and  $CF_3CO_2^-$  play important roles for the annulations of nonallenyl esters **1**. Allenyl esters **1'** did not require extra  $AgNTf_2$ because the cyclization of intermediate **D** proceeds through a Michael-type reaction. For unactivated allenes **1**, we speculate that this process requires additional  $Ag^+$  to form Ag(I)- $\pi$ -allene to facilitate the cyclization.  $CF_3CO_2^-$  possibly stabilizes oxonium intermediates **E** via a complexation as depicted below.



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Gold catalyzed [4+1]-annulations of 4-methoxy-1,2-dien-5-ynes with anthranils are described; the reaction mechanism involves initial formation of  $\alpha$ -imino gold carbenes, followed by a subsequent 1,2-allene shift.