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Gold(I)-Catalyzed Intermolecular Formal [4+2] Cycloaddition of *O*-Aryl Ynol Ethers and Enol Ethers: Synthesis of Chromene Derivatives

Tatiana Suárez-Rodríguez,[a] Ángel L. Suárez-Sobrino,[a] and Alfredo Ballesteros*[a]

Abstract: Gold(I)-catalyzed formal [4+2] cycloaddition of *O*-aryl ynol ethers **1** and enol ethers **2** is described. This intermolecular reaction between two electron-rich unsaturated systems takes place, under mild conditions, in the presence of 5 mol% $[IPrAu(CH_3CN)]SbF_6$ as catalyst giving chromene derivatives with good yields. The cycloaddition is completely regio- and stereoselective, as well as versatile for both reactives. Silyl enol ethers can also react in the same way and under the same reaction conditions with quantitative yields. A plausible mechanism through a selective addition of the enol ether to the alkyne gold activated complex followed by an intramolecular aromatic electrophilic substitution is proposed. Several experimental results support the presence of a cationic oxonium intermediate prior to the aromatic substitution. The reaction represents a new entry to the chromene core.

Introduction

Gold(I) catalysis in alkynes has demonstrated to be an useful tool in organic synthesis.[1] For instance, the gold-promoted cycloisomerization of enynes has been widely studied in the past years.[1e,2] This reaction provides diverse and, in many cases, unusual carbo and heterocyclic compounds in mild conditions, being extensively applied for the synthesis of a variety of natural products.[2c,3]

Despite the achievements of this intramolecular cyclization between an alkyne and an alkane, the intermolecular version has not received much attention.[2c,4] One of the potential problems in these reactions is the coordinative competition of the alkene to the catalyst, that could further lead to olefin isomerization or polymerization.

These drawbacks were successfully overcome by Echavarren group by the use of more selective gold(I) complexes bearing either bulky phosphine or N-heterocycle carbenes (NHC) as ligands,[5] allowing [2+2] and [2+2+2] cycloaddition reactions of terminal arylacetylenes with substituted alkenes[6] and oxoalkenes[7] respectively; furthermore, furans also underwent intermolecular cycloaddition with arylacetylenes to obtain phenols.[8] (Figure 1a). The role of the gold(I) counterion in this

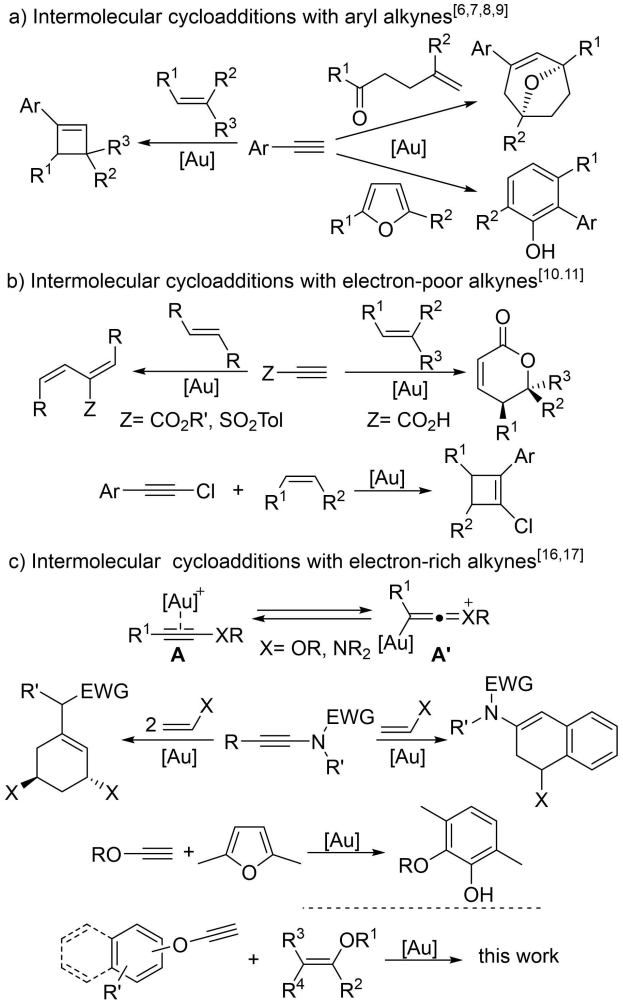

Figure 1. Gold(I)-catalyzed intermolecular cycloadditions of alkynes.

[a] *Dr. T. Suárez-Rodríguez, Prof. Dr. Á. L. Suárez-Sobrino, Prof. Dr. A. Ballesteros*
Departamento de Química Orgánica e Inorgánica
Instituto de Química Organometálica "Enrique Moles"
Universidad de Oviedo
Julián Clavería,Oviedo, 8, 33006-Oviedo (Spain)
E-mail: abg@uniovi.es

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transformation was further demonstrated when no coordinating tetrakis[3,5]-bis(triflluoromethy)phenyl]borate (BARF) was used, avoiding presumably the formation of unproductive α,π-(alkyne)digold(I) complexes.[9]

Other problem regarding the intermolecular version arises from the absence of a tether that makes difficult the regio- and stereoselective control of the reaction. In this regard, the use of electronically polarized alkynes can facilitate the intermolecular reaction with selective control.[1f] Thus, Shin and coworkers described a selective [4+2] cycloaddition and a enyne cross metathesis involving propiolic acid derivatives and alkenes.[10] More recently, Zhang used the electronic polarized chloroalkynes to achieve a [2+2] cycloaddition with inactivated alkenes (Figure 1b).[11]

Electron-rich alkynes such as ynamides[12,13] or ynol ethers[14,15] are attracting substrates by its high nucleophilic reactivity and its strongly polarized triple bond that facilitates the regioselective control of the process. In the case of gold catalyzed reaction, the ketene-like structure **A'** of the metal complex intermediate supports this idea (Figure 1c). In this way, electron-rich alkenes proved to be good partners in gold catalyzed [4+2] cycloadditions of aryl substituted ynamides after the participation of the aryl moiety; furthermore, enol ethers take part in [2+2+2] cycloadditions with terminal ynamides[16] On the other hand, Hashmi has recently described a furan-yne cyclization using terminal ynol ethers, the sole example of this kind of compounds in intermolecular gold catalysis.[17]

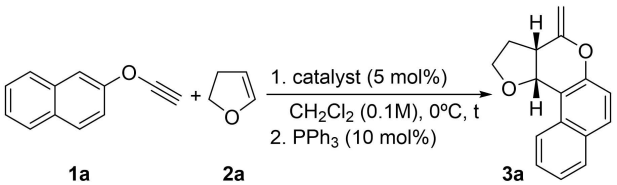
With all of this in mind, we found interesting to study the efficiency and selectivity of gold catalysis employing two electron-rich unsaturated substrates such as *O*-aryl ynol ethers **1** and enol ethers **2** in an intermolecular process (Figure 1c)

Results and Discussion

Our initial studies focused on the reaction between 2-(ethynyloxy)naphtalene **1a** (1 equiv) and 2,3-dihydrofuran **2a** (3 equiv) employing various gold(I) complexes and other metal salts as catalyst in CH_2Cl_2 (0.1 M) at 0 °C (Table 1). Thus, when $IPrAuNTf_2$ (IPr = 1,3-bis(diisopropylphenyl)imidazole-2-ylidene, Tf = trifluoromethanesulfonate) was used as catalyst (5 mol%), the reaction was completed in 1.5 h after NMR signals of **1a** disappearance (Table 1, entry 1). Quenching with 10 mol% PPh_3, reaction work up. and purification of the crude (SiO_2, hexane/ethyl acetate 10:1) gave product **3a**, resulting from a formal [4+2] cycloaddition, in an 80% isolated yield. The 1*H*-2,3-dihydrobenzo[f]chromene structure of compound **3a** was elucidated by mono and bidimensional NMR experiments.

Our first attempts to optimize the reaction started with the use of other ligands; thus, JohnPhos (2-biphenyl)di-*tert*-butylphosphine) allowed to complete the reaction in 1 h but with a lower yield (Table 1, entry 2); on the other hand, room temperature was necessary to complete the reaction with 2,4-di*t*Bu$C_6H_3O)_3P$ as ligand affording only 32% (determined by NMR) of compound **3a** (Table 1, entry 3). The use of hexafluoro antimoniate (SbF_6^-) as counterion, clearly improved the reaction

Table 1. Optimization experiments for the reaction of ynol ether **1a** and enol ether **2a**.



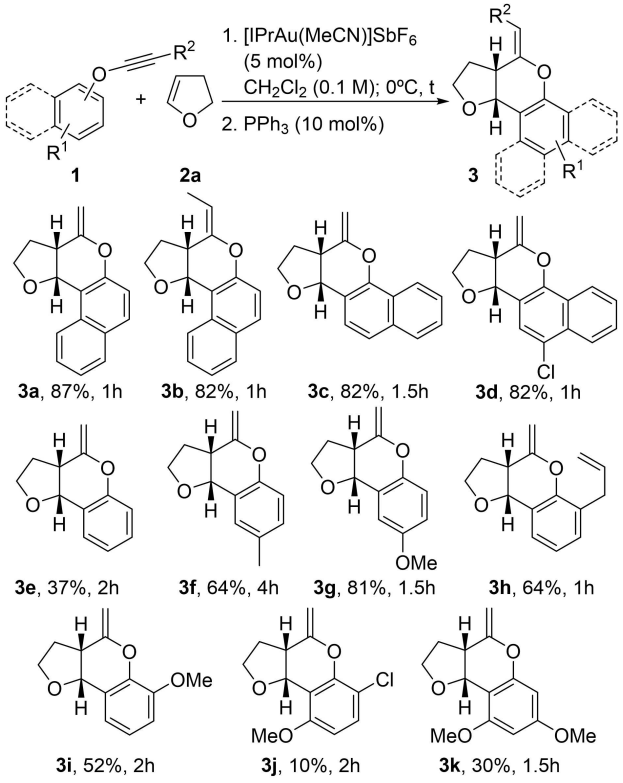
1a **2a** **3a**

Entry[a]	catalyst	t [h]	Yield [%][b]
1	$iPrAuNTf_2$	1.5	83 (80)
2	$JohnPhosAuNTf_2$	1	72
3[c]	$(ArO)_3PAuNTf_2$	1	32
4	$[IPrAu(CH_3CN)]SbF_6$	1	93(87)
5	$[(ArO)_3PAu(CH_3CN)]SbF_6$	1	20
6	$[JohnPhosAu(CH_3CN)]SbF_6$	1	80
7	$[IPrAu(CH_3CN)]BARF$	1	85
8[c]	–	1	0
9[c,d]	$HBF_4.Et_2O$	7	0
10[c,d]]	PTSA	7	0
11[c,d]	HOTf	0.5	0
12[c,d]	$AgNTf_2$	7	7
13[c,d]	$Zn(OTf)_2$	6	20
14[c,d]	$[RuCl_2(CO)_3]_2$	7	24

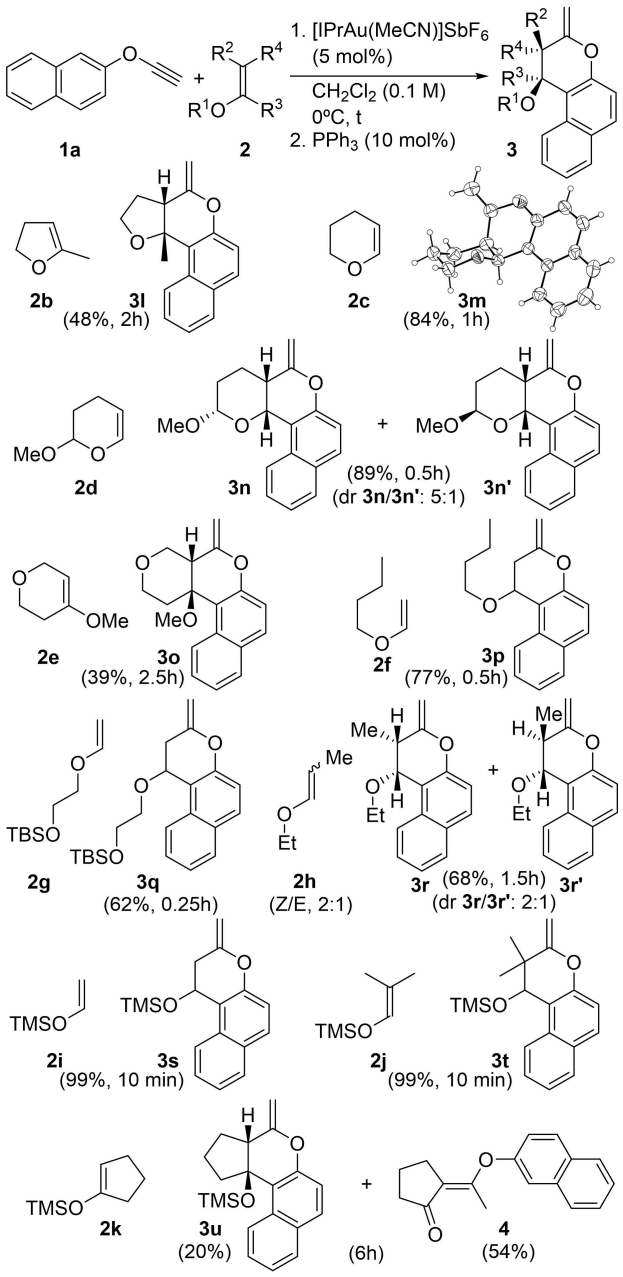
[a] Reaction conditions: **1a** (2 mmol, 1 equiv), **2a** (6 mmol, 3 equiv); 5 mol% of the catalyst, CH_2Cl_2 (0.1 M), 0 °C. [b] Yields determined by ^1H NMR using CH_2Br_2 as internal standard. Yields of the isolated products are given in parenthesis. [c] Reaction performed at room temperature. [d] 10 mol% of the catalyst. IPr: 1,3-bis(diisopropylphenyl)-imidazol-2-ylidene, JohnPhos: (2- biphenyl)di-*tert*-butylphosphine; Ar: 2,4-di*t*BuC_6H_3; BARF: tetrakis[3,5-bis(trisfluoromethyl)phenyl]borate.

with IPr as ligand, leading to **3a** with a 87% isolated yield in a shorter reaction time (1 h) (Table 1, entry 4), this applies also for other ligands but without bigger improvements (Table 1, entries 5,6). Surprisingly, less coordinating counterion BARF did not improved the yield (Table 1, entry 7). Furthermore, the reaction did not work in the absence of catalyst (Table 1, entry 8) or in the presence of catalytic Bronsted acid at room temperature (Table 1, entries 9–11), inducing the complete decomposition of the enol ether **2a**. Finally, poor yields of **3a** were obtained when other metal salts like $AgNTf_2$ and $Zn(TfO)_2$ or complex $[RuCl_2(CO)_3]_2$ were used as catalyst even at room temperature and higher catalyst loadings (Table 1, entries 12–14).

The scope of the reaction was examined next; we employed different *O*-aryl ynol ethers **1**, and 2,3-dihydrofuran **2a** (3 equiv) as reaction partner using the previous optimized conditions, $[IPrAu(MeCN)]SbF_6$ as catalyst in CH_2Cl_2 at 0 °C, (Scheme 1). First, the synthesis of the *E*-isomer of **3b** (R^2 = Me) as a sole diastereoisomer in 82% yield demonstrated that the reaction can selectively work with internal ynol ethers. The reaction also was carried out with *O*-1-naphtyl substituted ynol ethers giving rise to chromenes **3c** and **3d** with good yields. *O*-Phenyl ynol ethers bearing different substituents in the phenyl group were tried next; in this case, the lower yield obtained for the parent ethynyl phenyl ether (R^1 = H, **3e**, 37%) could be definitely improved by the presence of an electron-donor substituent at the phenyl moiety either in *para* (**3f**, R^1 = *p*-Me, 64%; **3g**, R^1 = *p*-OMe, 81%) or *ortho* (**3h**, R^1 = *o*-allyl, 64%; **3i**, R^1 = *o*-MeO, 52%)



Scheme 1. Gold(I)-catalyzed [4 + 2] intermolecular cycloaddition of aryl ynol ethers **1** and 2,3-dihydrofuran **2a**.



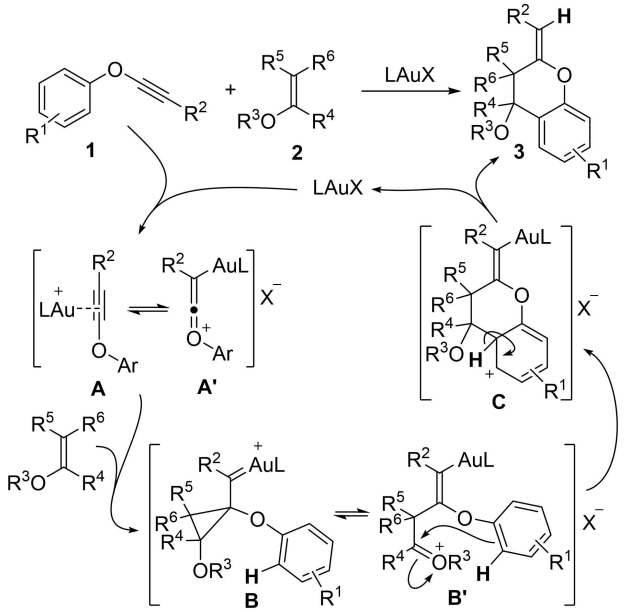
Scheme 2. Gold(I)-catalyzed [4 + 2] intermolecular cycloaddition of 2-naphtyl ynol ether **1a** and enol ethers **2**.

positions. Disubstitution at the phenyl moiety could also be possible but with poorer yields (**3j**, 10%; **3k**, 30%).

We also studied the reaction of 2-naphtyl ethynyl ether **1a** with different enol ethers **2** under the same reaction conditions (Scheme 2). Thus, the α-substituted enol ether, 2-methyl-3,4-dihydrofuran **2b** gave adduct **3l** in moderate yield (48%). On the other hand, 3,4-dihydro-2*H*-pyrane **2c** led to good results, giving rise to chromene derivative **3m** (84%), the structure of this compound was further confirmed by X-ray diffraction.[18] Interestingly, the racemic ketal-functionalized enol ether **2d** gave, in shorter reaction time (0.5 h) and excellent yield (89%), a 5:1 mixture of diastereoisomers **3n** and **3n'** (see below). Moreover, α,β-disubstituted enol ether 3-methoxy-5-dihydro-2*H*-dihydropyrane **2e** was also employed, giving cycloadduct **3o** (39%) with complete diastereoselectivity.

Additionally, the reaction appears to be faster when unsubstituted enol ethers were used; thus, *n*-butyl vinyl ether **2f** and silyloxy enol ether **2g** gave the corresponding [4 + 2] adducts **3p,q** in just 0.5 h and in good yields (77% and 62% respectively). On the other hand, the 2:1 *Z/E* mixture of β-substituted enol ether **2h** led diastereoisomers **3r-r'** in the same 2:1 ratio (68%). Additionally, when *O*-trimethyl silyl enol ethers **2i** and **2j** were employed, under the same reaction conditions, the reaction was completed in 10 min to give quantitatively the corresponding silyloxy chromanes **3s** and **3t**. On the other hand, when silyl enol ether derived from cyclopentanone **2k** was used, the reaction needed 6 h to be completed, leading to the expected [4 + 2] adduct **3u** as minor reaction product (20% yield) along with major cyclopentanone derivative **4** (54% yield) resulting from the addition of **2k** to the triple bond of the ynol ether **1a**. It is worth mentioning the variety of products obtained in this reaction that contain the chromene scaffold which is present in many natural and medical compounds.[19]

Scheme 3 depicts our proposed mechanism for this transformation; thus, the reaction would start from the regioselective attack of the enol ether **2** to the gold(I) ynol ether complex.[16,17] According to previous mechanism studies in gold catalyzed alkyne cycloaddition reactions,[2b,20] this attack would form the

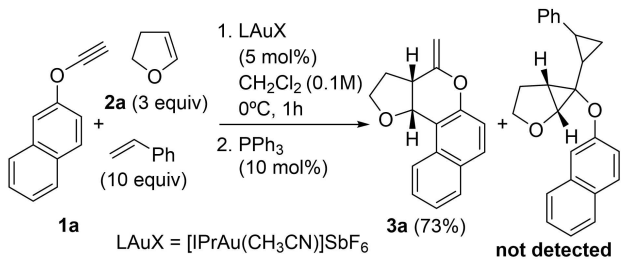


Scheme 3. Proposed mechanism.

cyclopropyl gold carbene intermediate **B**, or the oxonium ion intermediate **B′**.[21] In this case, the carbocation stabilized by the alkoxy group would favor a major contribution of structure **B′**;[22] then, intramolecular electrophilic aromatic substitution in the aryl group would form cyclic intermediate **C**, that after a stereoselective protodeauration at the *cis* position to the alkoxy group would form the final chromene derivatives **3**.

In order to provide evidence of the mechanism that operates in this transformation, we carried out the reaction in the presence of styrene with the purpose to confirm the participation of carbene intermediate **B**. Thus, ynol ether **1a** and enol ether **2a** were reacted in the presence of 10 equiv. of styrene in the same reaction conditions.[23] In this case any significant change in the reaction outcome was observed (73% yield instead of 87% in the absence of styrene), and the corresponding cyclopropanation product was not detected (Scheme 4); this could demonstrate the low contribution of carbene structure **B** in the gold intermediate.

Some other experimental results could support our mechanistic hypothesis in the direction of structure **B′** as intermediate;

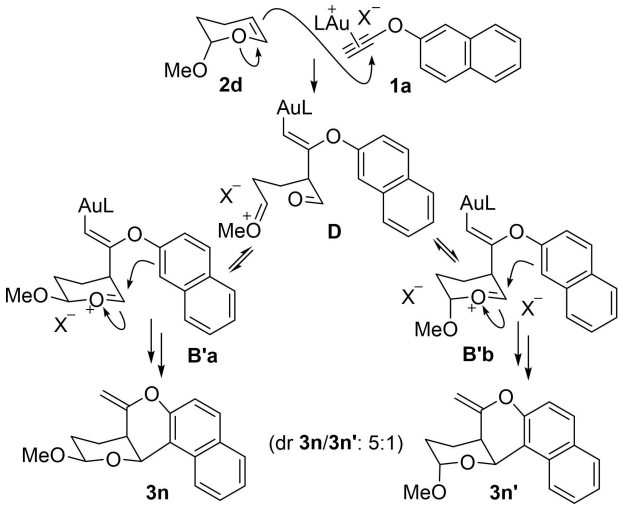


Scheme 4. Reaction of ynol ether **1a** and enol ether **2a** in the presence of styrene.

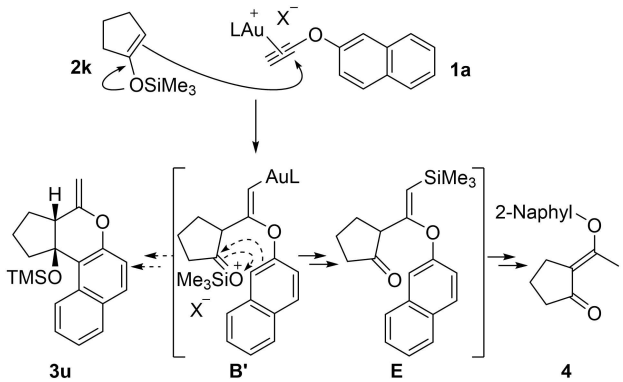
thus, the formation of a 5:1 mixture of adducts **3n** and **3n′** from racemic acetal **2d** can be explained by the major contribution of oxonium intermediates **B′** (Scheme 3); in this case, the **3n**/**3n** relationship can be justified through an equilibrium between oxonium intermediates **B′a** and **B′b** through the open cation **D** (Scheme 5).

Additionally, the major formation of the acyclic product **4** when cyclopentanone-derived silyl enol ether **2k** was used can also confirm the preference for oxonium intermediates **B′** (Scheme 6) Thus, silyl oxonium intermediate **B′** can evolve to the [4+2] cycloaddition product **3**, or through an alternative pathway, involving silyldeauration,[24] leading to vinyl silane **E** that in the work up conditions would undergo protodesilylation and double bond isomerization to give the acyclic cyclopentanone derivative **4**.

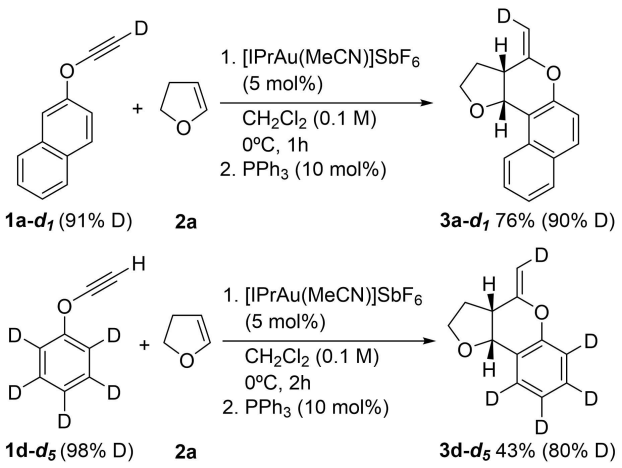
Next, we addressed the study concerning the complete *E*-selectivity observed when **3b** was obtained from the corresponding internal *O*-(2-naphtyl) ynol ether (Scheme 2), in addition to a revision related to the process of protodeauration of intermediate **C** (Scheme 3). These experiments were carried out with the isotopically-labeled compounds shown in Scheme 7.[25] Thus, *E*-selectivity was confirmed with the reaction



Scheme 5. Formation of the 5:1 mixture of **3n** and **3n′**.



Scheme 6. Formation of compounds **3u** and **4**.



Scheme 7. Deuterium-labelling experiments.

of deuterated *O*-(2–naphthyl) ynol ether **1a-d$_1$** (91% D) giving exclusively **3a-d$_1$** (90% D) and maintaining the deuterium atom in the same carbon atom, *trans* to the oxygen atom of the chromene. On the other hand, deuterated *O*-phenyl ynol ether **1e-d$_5$** (98% D) led exclusively to **3e-d$_5$** with good deuterium incorporation, (80% D) and indicates that the proton used for the final protodeauration process, proceeds from the aromatic ring involved in the intramolecular aromatic electrophilic substitution step. Moreover, the presence of the gold moiety in intermediate **C** *cis* to the alkoxy substituent determines the selectivity of the reaction.

Conclusion

In conclusion, we have described a new formal [4+2] intermolecular cycloaddition between two electron-rich unsaturated substrates such as *O*-aryl ynol ethers **1** and enol ethers **2** catalyzed by gold(I) complex [IPrAu(CH$_3$CN)]SbF$_6$. The cycloaddition proceeds for a variety of ynol and enol ethers with a complete regio- and stereoselectivity under mild conditions and good to moderate yields to give chromene derivatives. Optimization studies demonstrated poor or no effectiveness of other transition metals or Bronsted acids to catalyze this reaction. Additionally, silyl enol ethers can also participate in this reaction leading to the corresponding cycloadducts in quantitative yields. A plausible mechanism consists in a regioselective addition of the enol ether to the gold-alkyne complex followed by an intramolecular electrophilic aromatic substitution of the oxonium intermediate **B'** and final protodeauration. The reaction represents a new easy and selective entry to the chromene core.

Experimental Section

Typical procedure

Preparation of chromane 3a: Ynol ether **1a** (33,64 mg, 0.2 mmol, 1 equiv) and enol ether **2a** (42,11 mg, 0.6 mmol, 3 equiv) were dissolved, under inert atmosphere, in 2 mL CH_2Cl_2 at 0 °C. Then, the catalyst [IPrAu(CH$_3$CN)]SbF$_6$ (8.6 mg, 0.01 mmol, 5 mol%) was added and the mixture was stirred until the consumption of **1a**. Then, PPh_3 (5.2 mg, 0.02 mmol, 10 mol%) was added and the solvent removed. The crude was purified by column chromatography (SiO_2, hexane/EtAcO, 10:1). The product was obtained in 87% yield (41,5 mg) as a white solid. R_f = 0.42 (hexane/EtAcO 10:1); m.p. 60–62 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, ^3J = 8.5, 1H), 7.82–7.71 (m, 2H), 7.59–7.50 (m, 1H), 7.44–7.36 (m, 1H), 7.14 (d, ^3J = 9.0, 1H), 5.46 (d, ^3J = 6.7, 1H), 4.86 (brs, 1H), 4.59 (brs, 1H), 4.09–3.87 (m, 2H), 3.38 (q, ^3J = 6.9, 1H), 2.48–2.29 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.7 (C), 151.0 (C), 133.4 (C), 130.9 (CH), 130.2 (C), 128.6 (CH), 127.3 (CH), 124.4 (CH), 124.3 (CH), 118.0 (CH), 113.1 (C), 93.5 (CH_2), 72.8 (CH), 66.5 (CH_2), 40.6 (CH), 31.4. (CH_2); HRMS (ESI): *m/z* calcd for $C_{16}H_{14}NaO_2$: 261.0891 $[M+Na]^+$; found: 261.0886.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: alkenes · alkynes · chromenes · cycloaddition · gold · homogeneous catalysis

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