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Research Article

Gold-Catalyzed Ascorbic Acid-Induced Arylative Carbocyclization of Alkynes with Aryldiazonium Tetrafluoroborates

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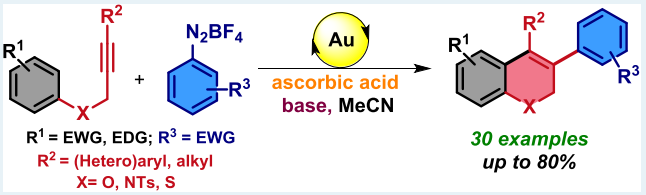
ABSTRACT: We describe, herein, arylative carbocyclization of alkynes catalyzed by gold. In this process, Au(I) is oxidized to Au(III) with aryldiazonium tetrafluoroborates following a photosensitizer-free and irradiation-free protocol. Ascorbic acid acts as a radical initiator, generating aryl radicals. According to DFT calculations, these radicals are added to Au(I), leading to a Au(II) species that is further oxidized to Au(III) with the assistance of a tetrafluoroborate anion. The overall arylative carbocyclization process is very energetically favorable, transforming arylpropargyl ethers into valuable 3,4-diaryl-2*H*-chromenes in a completely regio- and stereoselective fashion. Furthermore, we show that one of the synthesized 3,4-diaryl-2*H*-chromenes exhibits polymorphism with marked differences in the color of its crystals, a property that could lead to the development of colored derivatives in the future.



KEYWORDS: *arylative carbocyclization, gold, ascorbic acid, aryldiazonium salts, polymorphism*

I. INTRODUCTION

Tetrasubstituted olefins are important structural motifs present in biologically active compounds,[1] molecular switches, molecular motors, organic light-emitting diodes, and bioimaging.[2] However, the synthesis of stereodefined tetrasubstitued olefins is far from trivial.[3] It is well known that traditional methodologies such as elimination,[4] Wittig reactions,[5] the McMurry coupling,[6] and even olefin metathesis[7] suffer from poor values of regio- and/or stereoselectivity. On the other hand, multicomponent reactions like Cattellani type reactions have reached high levels of regio- and stereoselectivity in some cases,[8] although the most widely used method for the synthesis of stereodefined tetraolefins is the carbometallation of alkynes.[9] This approach involves the formation of a nucleophilic vinyl metal species that is transformed stepwise or in situ into the desired olefin. Complementary alkynes can be transformed into tetrasubstitued olefins by a less explored metal-catalyzed electrophilic carbofunctionalization (Figure 1).[10] It was initially described by Greany[10a] using a palladium catalyst and aryliodonium salt as an electrophile and was later extended by Gaunt, who used a copper source.[10] Other metals like iron, calcium, indium, or borderline bismuth have been shown to be active in this transformation, and along with aryliodonium salts, alcohols, acetals, and acrylates have been used as an electrophilic source. In this context, we were intrigued by exploring the synthesis of tetrasubstituted alkenes using a gold-catalyzed electrophilic carbofunctionalization. Our group has been focused on the development of gold redox processes with aryldiazonium salts. In particular, we have been interested in processes where the diazonium salt is thermally or chemically activated.[11] Initial reports on catalytic redox processes of Au(I) with aryldiazonium salts required the use of a cocatalyst and light irradiation to promote the formation of Au(III) species, but later studies manifested that, in some cases, just light, heat, or certain ligands and bases are enough to promote this process.[12,13] Recently, we evidenced that ascorbic acid, a natural reducing agent, is able to promote the oxidative addition of Au(I) with aryldiazonium chlorides, and used this protocol for the arylation of *N*-methyl indoles.[11c] In that transformation, we needed to use a stoichiometric amount of gold because of the competitive formation of *N*-methylindol-diazo coupling derivatives. In this paper, we show that ascorbic acid in combination with aryldiazonium tetrafluoroborates is able to promote arylative carbocyclization of alkynes using a catalytic amount of gold in the absence of a cocatalyst or an external irradiating source. The products obtained are tetrasubstituted alkenes with total control of regio- and stereoselectivity.

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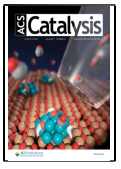

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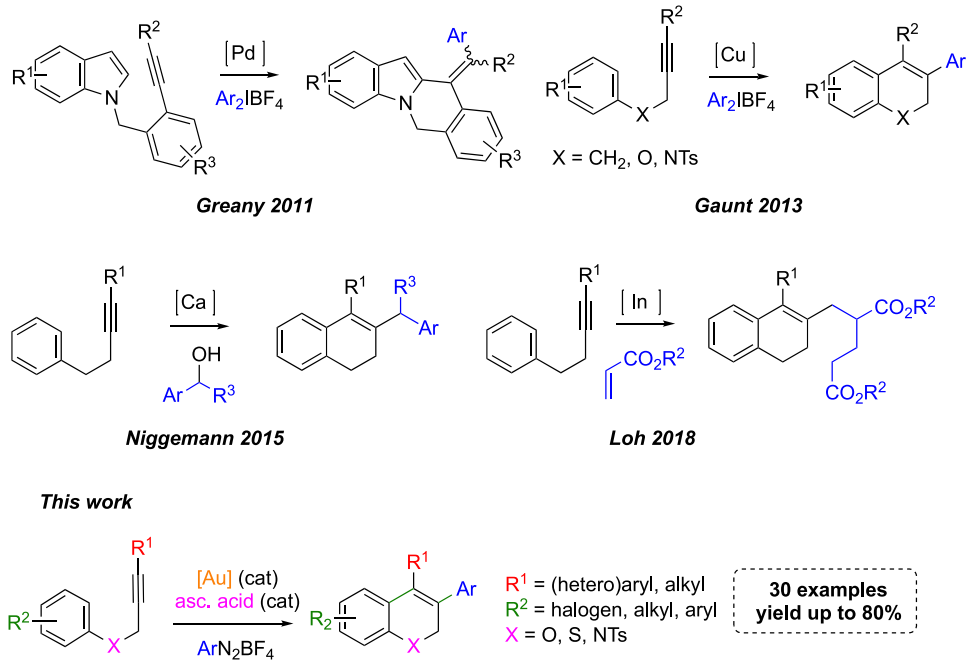
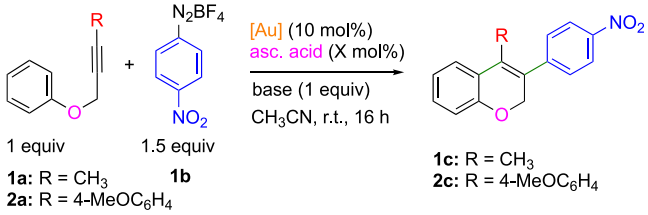


Figure 1. State-of-the-art of electrophilic arylative carbocyclizations for the synthesis of tetrasubstituted alkenes in this work.

II. RESULTS AND DISCUSSION

To perform our study, we chose arylpropargyl ethers as alkyne models because of the easy access to a variety of skeletal scaffolds and the biological significance of chromene derivatives.[14] We first synthesized arylpropargyl ethers **1a** and **2a** containing methyl and *p*-methoxyphenyl, respectively (Table 1), with the aim of enriching the electron density onto the alkyne. As an aryldiazonium model, we took *p*-nitrobenzendiazonium tetrafluoroborate, as we have already observed that the nitro group confers special reactivity toward Au(I) because of its electron-withdrawing character. In our precedent work related to the arylation of indoles, we noticed that the nature of the counteranion of the diazonium salt has a significant influence on the oxidative addition step.[11c] In that case, we found that chloride was the best counteranion to attain high arylation yields. Nonetheless, this time we replaced chloride with tetrafluoroborate, with the purpose of creating a coordination vacancy on the gold coordination sphere, which facilitates the coordination of the alkyne. With this in mind, we examined the reaction of **1a** with *p*-nitrobenzendiazonium tetrafluoroborate using Ph_3PAuCl (10 mol %) as a gold source in the presence of ascorbic acid (5 mol %). After stirring in acetonitrile at rt for 16 h, the desired 2*H*-chromene **1c** was gratifyingly formed although in a modest yield (23%, Table 1, entry 1). Decreasing the amount of ascorbic acid to 1 and to 0.5 mol % increased the yield up to 55% and 57%, respectively (entries 2 and 5). The latter can be understood because a decrease in the amount of ascorbic acid decreases the rate at which radicals are being formed, avoiding competing decomposition pathways. Soon after, we examined the effect of replacing a Ph_3P ligand with a more electron-donating ligand like carbene *I*Pr and by the electron-withdrawing phosphite $(2,4\text{-}t\text{Bu}_2\text{PhO})_3P$ (entries 3 and 4). In both cases, the yield decreased below 5%. Using the more electron-rich arylproprargyl ether **2a** (entry 6) under the conditions depicted in entry 5, 2*H*-chromene **2c** was isolated in a similar yield (55%). With this arylpropargyl ether, we tested the addition of inorganic bases like Cs_2CO_3 and Li_2CO_3, which increased the yield up to 65% and 70%, respectively (entries 7

Table 1. Optimization of the Reaction Conditions[a]



	substrate	[Au]	ascorbic acid	base	yield[b]
1	**1a**	Ph_3PAuCl	5		23%
2	**1a**	Ph_3PAuCl	1		55%
3	**1a**	IPrAuCl	1		<5%
4[c]	**1a**	$(ArO)_3PAuCl$[c]	1		<5%
5	**1a**	Ph_3PAuCl	0.5		57%
6	**2a**	Ph_3PAuCl	0.5		55%
7	**2a**	Ph_3PAuCl	0.5	Li_2CO_3	70%
8	**2a**	Ph_3PAuCl	0.5	Cs_2CO_3	65%
9	**2a**	Ph_3PAuCl	0.5	DBU	42%
10	**2a**	Ph_3PAuCl	0.5	DTBPy	80%
11	**1a**	Ph_3PAuCl	0.5	DTBPy	64%
12	**2a**	Ph_3PAuCl	0.5	BPy	nr
13	**2a**	Ph_3PAuCl		BPy	nr
14	**2a**	$(p\text{CF}_3\text{C}_6\text{H}_4)_3PAuCl$	0.5	DTBPy	29%
15	**2a**	JhonphosAuCl	0.5	DTBPy	nr
16	**2a**	$Ph_3PAuNTf_2$[d]	0.5	DTBPy	nr
17	**2a**	Ph_3PAuCl		DTBPy	47%
18	**2a**		0.5	DTBPy	nr
19	**2a**	Ph_3PAuCl[e]		DTBPy	47%
20	**2a**	Ph_3PAuCl[f]		DTBPy	32%

[a][**1a** or **2a**] = 0.1 M. [b]Isolated yield. [c]Ar = 2,4-$t\text{Bu}_2$Ph. [d]Reaction carried out with chloride as a counteranion of the diazonium salt. [e]Reaction carried out under irradiation with blue LEDs. [f]Reaction carried out with $[Ru(bpy)_3](PF_6)_2$ (2.5 mol %) as a cocatalyst and under irradiation with blue LEDs.

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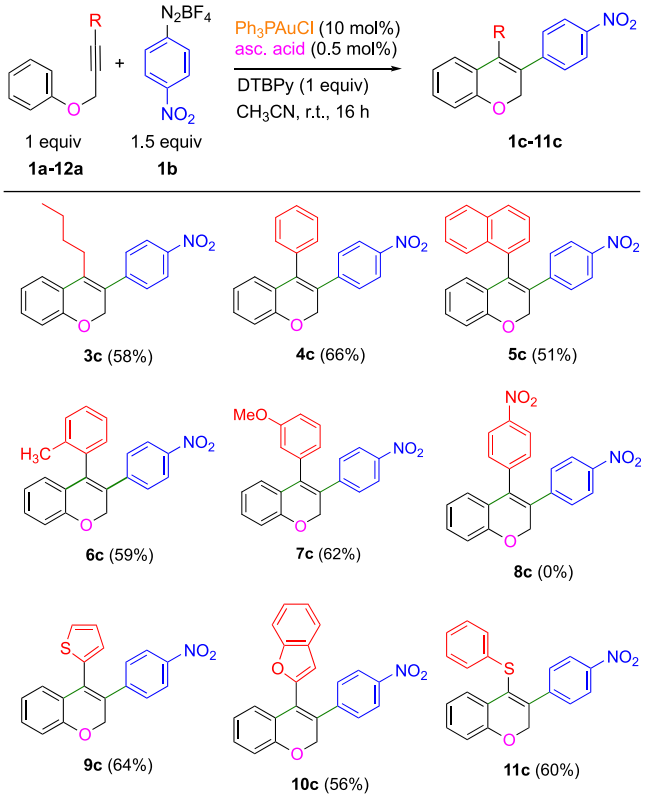
and 8). Otherwise, the addition of an organic base like DBU was detrimental, **2c** being recovered in 40% (entry 9). On the contrary, DTBPy had a marked positive effect, increasing the yield to 80% (entry 10). Satisfyingly, we confirmed that this base also increased the reaction yield of substrate **1a** (64%, entry 11). Next, we tested the effect of the chelating BPy ligand, which has been successfully used in ligand-promoted oxidative addition of Au(I) with aryldiazonium salts;[12d] however, in our case, no reaction was observed (entries 12 and 13). Using DTBPy as a base, we also evaluated the performance of $(p\mathrm{CF_3C_6H_4})_3\mathrm{PAuCl}$ and JhonphosAuCl (entries 14 and 15). In the first case, the yield was 29%, whereas, in the second, no reaction took place. Additionally, we examined the reactivity of *p*-nitrobenzendiazonium chloride and **2a** in the presence of the cationic gold complex $\mathrm{Ph_3PAuNTf_2}$, but under these conditions, **2a** was recovered unchanged (entry 16). To summarize, the best results were obtained using $\mathrm{Ph_3PAuCl}$(10 mol %) as a catalyst in the presence of ascorbic acid (0.5 mol %) and DTBPy (1 equiv) as a base. Phosphines bearing electron-withdrawing bulky groups inhibited the reaction. We performed some control experiments to verify the influence of the gold catalyst and ascorbic acid. In the absence of the latter, the yield of the reaction of **2a** with *p*-nitrobenzendiazonium tetrafluoroborate dropped to 47% (entry 17), whereas, in the absence of $\mathrm{Ph_3PAuCl}$, no reaction took place (entry 18). These results confirmed that both ascorbic acid and $\mathrm{Ph_3PAuCl}$ are essential for the reaction to proceed in a good yield. Finally, to compare the efficiency of the arylative cabocyclization of **2a** under the optimized conditions encountered by us (entry 10) versus previously reported protocols, we studied the reactivity of **2a** under irradiation with blue LEDs and in the presence of $[\mathrm{Ru(bpy)_3}](\mathrm{PF_6})_2$ (2.5 mol %) as a cocatalyst under irradiation with blue LEDs. As shown in entries 19 and 20, the yield was lower in both cases (47 and 32%, respectively), evidencing the major performance of our optimized conditions.

With the best reaction conditions encountered, we next studied the effect of a terminal substituent onto an alkyne (Table 2). Compound **3a** bearing an *n*-butyl group gave 2*H*-chromene **3c** in a 58% yield. We were pleased by this result since the arylative carbocyclization methods described so far have not been applied to alkynes containing an alkyl group at the terminal position.[10] Compounds **4a** and **5a** with a phenyl and a naphthyl group reacted with a 66% and 51% yield, respectively. Compound **6a** with a methyl group at the ortho position reacted in a 59% yield, whereas compound **7a** bearing a *p*-methoxy group reacted in a 62% yield. The presence of a *p*-nitro group at the aryl moiety completely inhibited the reaction with **8c** not being formed. This is probably due to the less nucleophilic character of the alkyne. We inspected the effect of electron-rich heteroarenes such as thiophene (**9a**) and benzofurane (**10a**). In the first case, the yield was 64%, whereas, in the second, the yield was 54%. Compound **11a** with a phenylsulfanyl group attached to the alkyne reacted in a 64% yield. It is important to note that the reaction was not inhibited even in the presence of a pendant sulfur atom, which may strongly coordinate gold. To end, we examined the behavior of a terminal alkyne **12a** (R = H). This compound reacted to give the Sonogashira type coupling product **8a** in a 42% yield; however, the product from arylative carbocyclization was not observed from arylative carbocyclization. The results given in Table 2 show that the reaction is sensitive to both electronic properties and steric hindrance of the group

Table 2. Influence of the Terminal Substituent on the Alkyne[a]



[a] [**1a-12a**] = 0.1 M; = Isolated yield. For R =H, **12c** was not observed, on its place was formed the Sonogashira type coupling product:

attached at the terminal position of the alkyne. Thus, electron-withdrawing groups can inhibit the reaction, and steric hindrance decreases the yields.

Thereafter, we focused our attention on exploring the effect of modifying the nucleophilic character of the phenol moiety (Table 3). Electron-donating groups such as MeO-, *t*-Bu, -OBn, and -Ph at the para position of a propargyl ether link maintained yields in the range of 55−77%. As expected, substrates containing electron-withdrawing groups reacted more sluggishly and required an increase in the amount of the diazonium salt to achieve better yields. Thus, substrates containing halogens atoms such us *p*-Br (**17a**) and *o*-I (**18a**) reacted in a 44 and 45% yield, respectively, using 2 equiv of **1b**, whereas the substrate containing *p*-$\mathrm{CH_3CO}$ (**19a**) required 3.5 equiv of **1b** to form **19c** in a 34% yield. It is important to note the good compatibility of this arylative carbocyclization protocol with C-halogen bonds, enabling further functionalization of halogenated 2*H*-chromenes. We also replaced the oxygen link by an atom of sulfur (**20a**) and by a NTs (Ts =Tosyl) group (**21a**). Arylative carbocyclization of substrate **20a** took place in a 18% yield. We suspect that, in this case, diazo coupling is a competing reaction because when substrate **20a** was mixed with **1b**, the solution turned its color, and a second polar compound was observed by TLC at the end of

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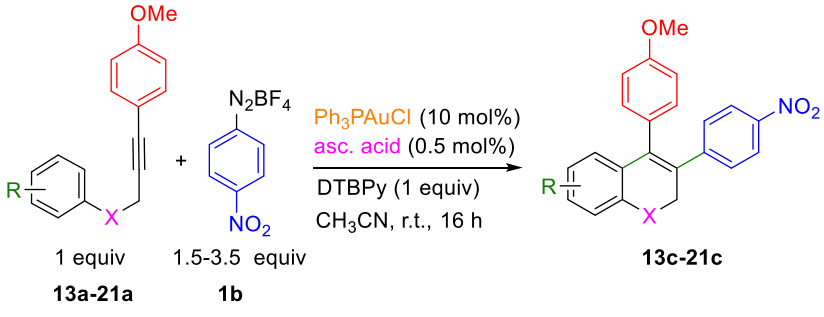
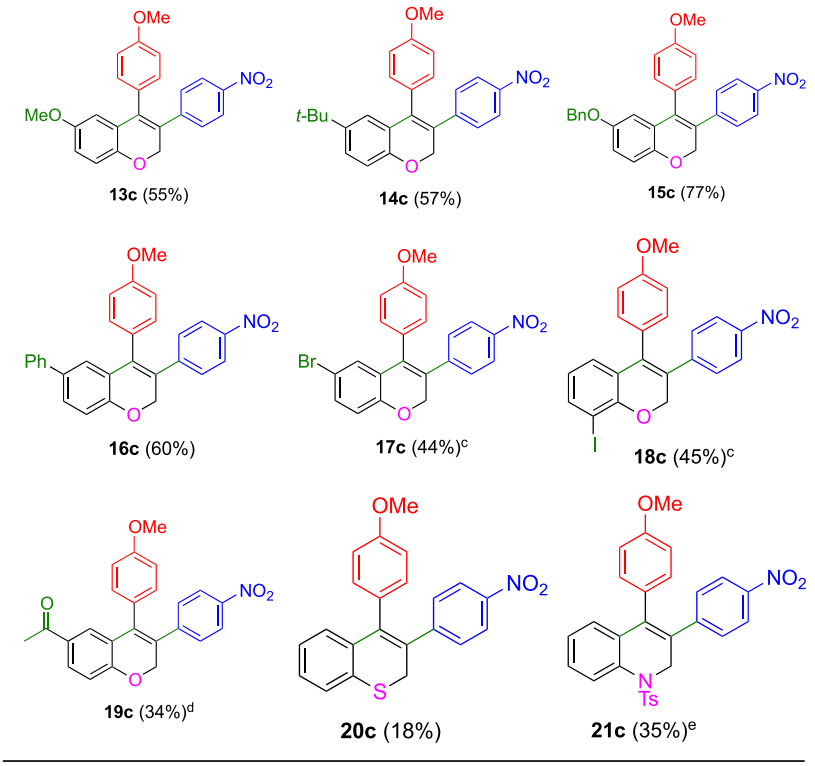
Table 3. Effect of the Nature of Substituents on the Phenol Moiety[a,b]





[a][13a−21a] = 0.1 M, 1.5 equiv of **1b**. [b]Isolated yield. [c]2 equiv of **1b**. [d]2.5 equiv of **1b**. [e]3.5 equiv of **1b**.

the reaction, which we were not able to characterize. Substrate **21a** bearing a NT group reacted in a 35% yield, which shows the lower nucleophilic character of the aryl ring by means of the NTs (Ts =Tosyl) group.

Lastly, we explored the scope of the reaction over a variety of aryldiazonium salts (Table 4). We began by examining the effect of electron-withdrawing substituents at the para position. Aryldiazonium salts containing halogen substituents (**2b** = *p*-Cl, **3b** = *p*-Br, and **4b** = *p*-F) reacted in a 68−44% yield, the lower yield being obtained with *p*-fluorobenzendiazonium tetrafluoroborate. The introduction of an ester moiety in the aryldiazonium ring led to the corresponding 2*H*-chromene (**25c**) in a 49% yield. A bulky group, such as *p*-benzophenone led to the desired 2*H*-chromene **26c** in a 46% yield, whereas nitrile increased the yield up to 74% (compound **27c**). Next, we examined the influence of placing certain groups at the meta and the ortho positions of the aryldiazonium salt (**8b** = *m*-NO_2, **9b** = *m*-CN and **10b** = *m*-Cl, and **11b** = *o*-NO_2). These types of couplings are challenging because of steric reasons, and although the yields were comparatively lower, the corresponding 3,4-diaryl 2*H*-chromenes were obtained in a satisfactory 41−60% yield. Concerning electron-donating groups, we examined the reactivity of benzendiazonium tetrafluoroborate, *p*-methylbenzendiazonium tetrafluoroborate, and *p*-methoxybenzendiazonium tetrafluoroborate toward **2a**, but in all cases, we recovered the arylpropargyl ether or it was decomposed. So this arylative carbocyclization protocol is limited to aryldiazonium salts bearing electron-withdrawing groups.

After a thorough examination of the reaction scope, we turned our attention to the reaction mechanism.[15] In our previous study on the arylation of indoles with aryldiazonium chlorides,[11c] we confirmed by EPR and electrochemical experiments that ascorbic acid generates aryl radicals. In addition, DFT calculations showed that these radicals are added barrierless to Au(I), generating an arylAu(II) species that is lastly oxidized by a reaction with a second equivalent of aryldiazonium chloride. Surprisingly, this reaction is also barrierless, and it is triggered by the high affinity of a Cl^- anion to the Au(II) center. In the present case, we wondered if a fluoride atom from the BF_4^- anion would be able to display a similar role to chloride, inducing Au(II)/Au(III) oxidation. We were also interested in calculating the overall energetic profile of the arylative carbocyclization reaction. Figure 2 shows the

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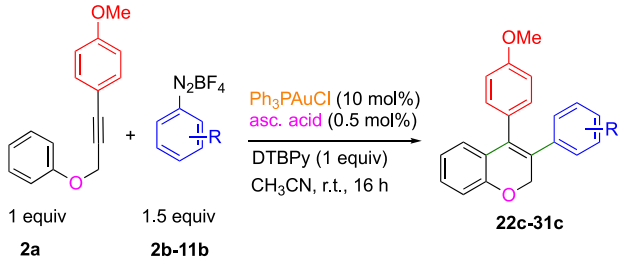
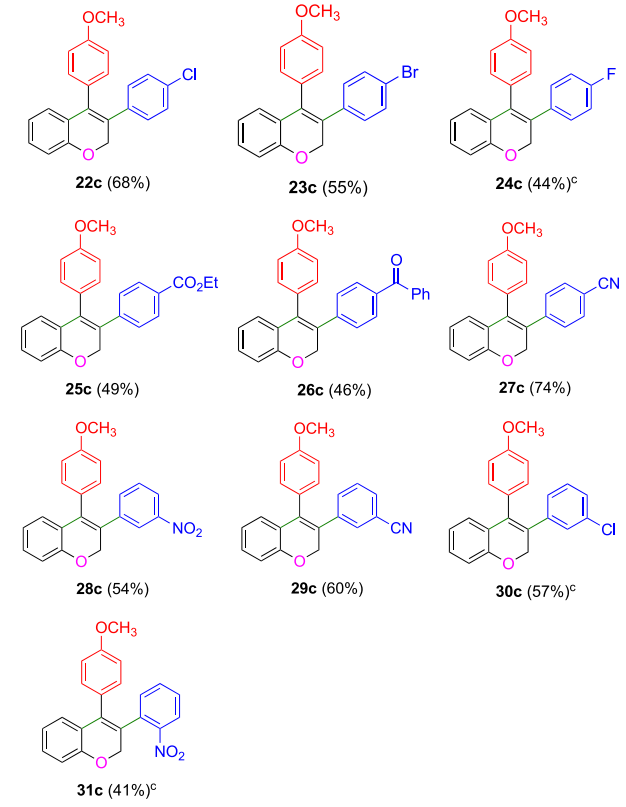
Table 4. Scope over Aryldiazonium Tetrafluoroborate[a,b]





[a][2a] = 0.1 M. [b]Isolated yield. [c]reaction at 50 °C.

energy profile of a proposed reaction mechanism. The energy of the proposed intermediates was calculated at the M06/Def2TZVP level of theory. To simplify the system, we replaced triphenylphosphine with trimethyl phosphine as a ligand. To our delight, it was confirmed that Au(I)/Au(III) oxidation with 4-$NO_2C_6H_4BF_4$ proceeds by a similar pathway as that shown by 4-$NO_2C_6H_4Cl$. First, Me_3PAuCl is barrierlessly oxidized to a 4-$NO_2C_6H_4Au$(II) species by a 4-$NO_2C_6H_4$· radical. Next, gold is further oxidized to 4-$NO_2C_6H_4Au$(III) by a reaction with another equivalent of the aryldiazonium salt. This step is assisted by a BF_4^- anion of the diazonium salt, which accesses the coordination sphere of the metal. The metal−BF_4^- interaction is strong enough to significantly elongate the B−F bond that is in the coordination sphere (1.55 Å). However, this F−BF_3 bond is still energetically enough to pyrimidalize the BF_3 moiety. Notably, the oxidation of Au(II) by a penetrating anion was observed in our precedent study with Cl^-, and as previously noticed, this step is barrierless. The energy difference between the arylAu(II) and the arylAu(III) species ($E_{Au(III)} - E_{Au(II)}$) was −7.19 kcal/mol. Comparatively, this energy difference was much higher when the oxidizing anion was Cl^- (−16.63 kcal/mol in the gas phase). The larger energy value indicates that the formation of a Cl−Au(III) bond is more favorable than the F_3B−F−Au(III) interaction.[16]

Once the arylAu(III) complex is generated, it coordinates to the alkyne, leading to an arylAu(III)-alkyne adduct, in which the carbon placed at the β position to the oxygen is more strongly bonded to the metal (2.36 Å) than the carbon placed at the γ position (2.51 Å). The latter carbon is also relatively close to the ortho carbon of the aryl ring, which facilitates the cyclization step. In fact, the LUMO of this intermediate is located both on the metal center and on the alkyne carbon placed at the γ position to the oxygen (Figure 3). This acid carbon can then easily react with the π electrons of the aryl group (HOMO). These MOs explain the low activation barrier for the cyclization step, only 10.28 kcal/mol. The bicyclic compound formed after cyclization is further stabilized by rearomatization. The transition state (TS) of the rearomatization has very low energy, such that once the entropy is added, the activation free energy ($\Delta G^{\ddagger}$) became slightly negative. The last step is also very favorable. The reductive elimination proceeds through TS5 with relatively low energy (7.54 kcal/mol), leading to the final 2*H*-chromene product and the initial Au(I) complex. The low energy barrier of the reductive elimination step is remarkable, considering that protodeauration is frequently a strong competitive reaction in vinyl-gold(III) complexes. In our precedent study, we found that the formation of arylAu(II) and arylAu(III) species proceeds without the energy barrier for both NO_2 and OMe groups at the aryl moiety,[11c] and now a similar trend is expected. This time to better understand the lack of reactivity of aryldiazonium salts containing electron-donating groups, we studied if there is a significant difference in the energy barrier of the carbocyclization step (TS4) depending on the nature of the substituent at the aryl ring. However, the energy values for TS4 when the aryl ring bears an OMe group or a NO_2 group are very similar (Figure 4). Considering these results, the lack of reactivity of aryldiazonium salts containing electron-donating groups must come from potential decomposition of the aryl-generated radicals due to stability reasons. A similar trend has been observed recently in gold-catalyzed aryl couplings under light irradiations.[12s] Detailed mechanistic studies evidenced that aryldiazonium salts with electron-donating substituents are harder to react.[12s]

In summary, all of the TSs and the intermediaries depicted in the reaction mechanism (Figure 2) are of relatively low energy, which shows the plausibility of the proposed reaction path. Importantly, the results derived from the DFT calculations further support that under our conditions, Au(I) oxidation with aryldiazonium salts can be accessed in the absence of a cocatalyst or an external irradiating source, being simply triggered by the affinity of the counteranion of the diazonium salt to the Au(II) center. The counteranion thus releases electron density onto Au(II), assisting the transfer of one electron from Au(II) to the aryldiazonium cation. This lastly leads to a Au(III) complex and an aryldiazonium radical, which regenerates the initial aryl radical by losing nitrogen.

After the examination of the reaction scope and the mechanism, we became interested in analyzing in detail the highly noticeable chromism exhibited in the solid state of some 2*H*-chromenes derivatives, especially **2c**. When this compound was isolated after purification by column chromatography, the evaporation of the fractions in hexane at room temperature

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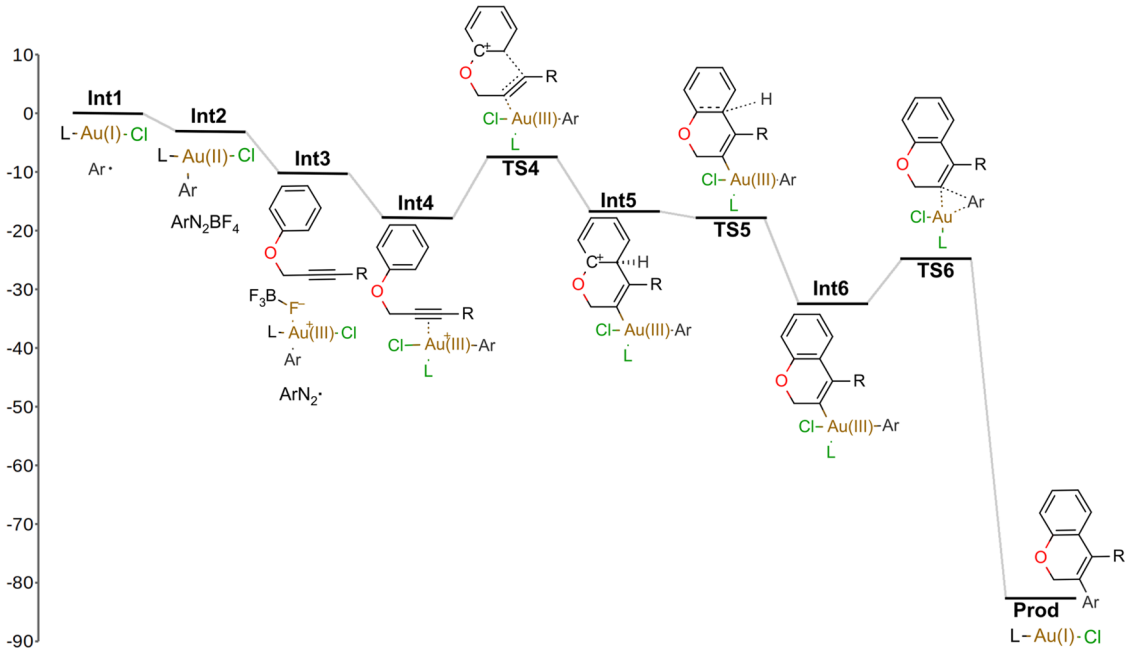

Figure 2. Relative energy of the intermediaries and transition states of the reaction mechanism of catalytic arylative carbocyclization of alkynes. The L and R groups used for the DFT calculations were $P(CH_3)_3$ and CH_3, respectively, Ar═4-$NO_2C_6H_4$. Energies are given in kcal/mol.

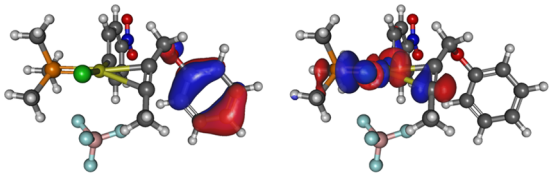

Figure 3. HOMO and LUMO of the Au(III)-alkyne adduct.

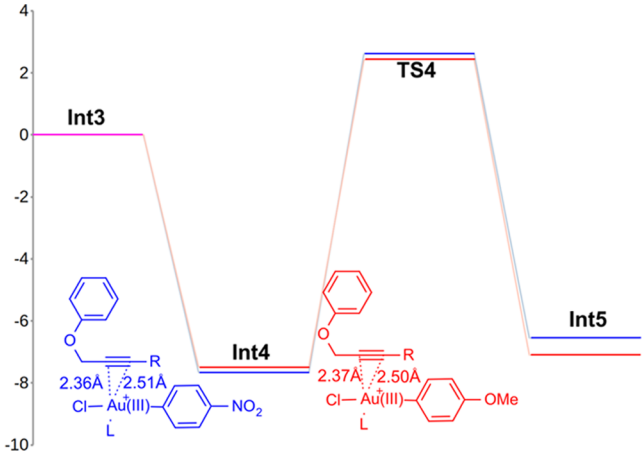

Figure 4. Relative energy to **Int3** of the carbocyclization step with a electron-withdrawing group (NO_2, blue) and with an electron-donating group (OMe, red). Energies are given in kcal/mol.

yielded a mixture of dark orange and yellow solids. Later, it was found that when the solution was evaporated at 60 °C, the dark orange solid **2c(I)** was exclusively obtained, while if the evaporation was carried out near 10 °C, the obtained solid acquired a yellow color **2c(II)**. This behavior strongly suggested crystal polymorphism[17,18] because the eluates were pure, as indicated by ^{1}H NMR in solution. Thus, we employed several solid-state techniques to gain further insights into this phenomenon.

Considering the abovementioned, we grew and diffracted suitable crystalline specimens of both solids at the mentioned temperatures. Their diffraction patterns were indexed and refined in triclinic $P\bar{1}$ or monoclinic $P2_1$ spatial groups, respectively. Careful examination of their crystalline molecular structures showed that there are significant differences (ca. 5 and 10°) for the dihedral angles φ_1 and φ_2 formed between aromatic substituents and the *2H*-chromene framework, as shown in Figure 5a,b. Furthermore, it was possible to recognize the formation of π-stacking interactions between adjacent nitroaromatic rings with a centroid−centroid distance of 4.046 Å (Figure 5c). Otherwise, the crystal arrangement of **2c(II)** is governed by an O···$\pi(N)_{NO2}$ interaction, with a distance of 2.944 Å (Figure 5d), which is within the range reported for this contact in organic crystals (2.939−3.006 Å).[28]

Large batches of both solids were prepared for further analysis, and the resulting phase purity was confirmed by PXRD analyses (Figures S1 and S2). To complement the structural diffraction results, we carried out ^{13}C CPMAS NMR experiments at 298 K (Figures S3 and S4). Particularly, in the case of the spectrum from **2c(II)**, the data confirmed the presence of two molecules with different crystallographic environments ($Z' = 2$), as obtained by single-crystal X-ray diffraction. To determine the thermal stability of these crystalline solids, we carried out differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA). It was confirmed that their crystalline structure is unaffected by heating and that both compounds melt without interconversion of their forms, with distinctive melting points of 157 °C for **2c(I)** and 153 °C for **2c(II)** (Figures S5 and S6).

These results demonstrated that the orange and yellow solids obtained for **2c** represent a case of conformational dimorphism.[19] After studying the X-ray structure of each form, we can conclude that the color change is due to the different molecular conformations, which modify the π-extension of the chromophore and therefore, the energetic gap between basal and excited states. We consider that the torsion of the angle $\varphi 2$

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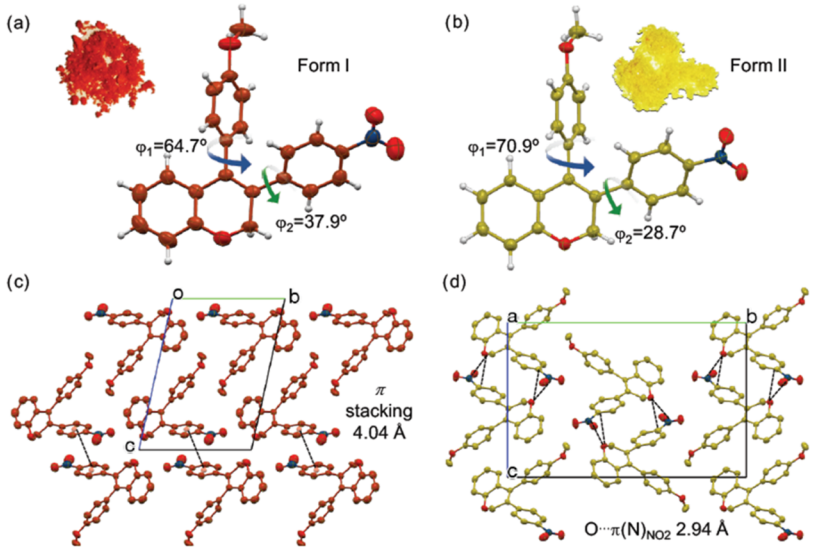

Figure 5. (a and b) ORTEP diagrams of solid forms 2c(I) and 2c(II) highlighting dihedral angles φ_1 and φ_2. (c and d) Intermolecular interactions in crystalline packing of polymorphic solids (hydrogens are omitted for clarity).

is decisive in the resulting color. Additionally, the lower melting point, the high value of molecules in the asymmetric unit ($Z' = 2$), and the unusual O···π(N) interactions allowed us to infer that the yellow solid 2c(II) corresponds to the kinetic state. The solid-state behavior of these chromenes is very interesting and it could be explored in other derivatives in the future.

III. CONCLUSIONS

In conclusion, we have shown that Au(I) is able to catalyze arylative carbocyclization of alkynes with aryldiazonium tetrafluoroborates.[20] The role of ascorbic acid is to generate aryl radicals that are added to Au(I), forming an electrophilic arylAu(II) species, which is further oxidized to Au(III) with the assistance of a BF_4^- anion. Notably, in this work, it is further evidenced that the counteranion of the aryldiazonium salt has a key role in the reaction, assisting the oxidation of the ArAu(II) species into ArAu(III). This breakthrough sheds light on the mechanism underlying the oxidative addition of Au(I) with aryldiazonium salts. The results encountered will help in the development of new catalytic processes involving the redox pair Au(I)/Au(III), which will not require the use of a cocatalyst or an irradiating source to achieve the desired oxidation of Au(I), thus making these type of transformations broadly accessible. Moreover, the protocol described allows the regio- and stereoselective synthesis of 3,4-diaryl-2*H*-chromenes, which can exhibit drastic changes in the appearance of the solids, a property that could be explored in future studies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c01826.

Experimental procedures, characterization of new compounds, NMR spectra, X-ray data, and the crystal structure of 2c(I) and 2c(II) (PDF)

(CIF)

(CIF)

(PDF)

(PDF)

(ZIP)

Accession Codes

CCDC 2046490 and CCDC 2046491 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/dat_request/cis, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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