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# Gold *versus* silver catalyzed intramolecular hydroarylation reactions of [(3-arylprop-2-ynyl)oxy]-benzene derivatives†

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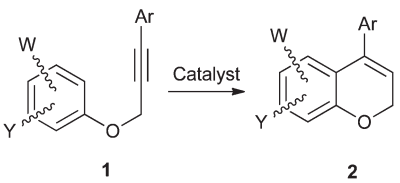
The scope and the generality of gold *versus* silver catalyzed intramolecular hydroarylation reactions of 3-[(3-arylprop-2-ynyl)oxy]benzene derivatives in terms of rings substitution were investigated. Only products deriving from *6-endo* cyclization were exclusively formed. The features of substituents had a considerable effect on the reaction outcome in the presence of silver catalysis, whereas gold catalysis revealed a unique blend of reactivity and selectivity and represented the only choice for the intramolecular hydroarylation reaction of the starting substrates bearing electron deficient arenes.



## Introduction

Development of new approaches for the synthesis of heterocycles, employing efficient and atom-economical routes, is currently a popular research area. Among the many new synthetic transformations, gold and silver-catalyzed reactions are very attractive.[1] The use of environmentally benign gold and silver catalysts in the direct functionalisation of C–H bonds represents an increasingly viable alternative to the multi-step strategies traditionally adopted for such transformation and highlights their remarkable reactivity leading to a significant increase in their utilisation.[2] In particular intra- as well as intermolecular addition of arenes to alkynes is a well-established process promoted by late transition metal catalysts, and gold brought new perspective in the field.[3] The intramolecular gold-catalyzed hydroarylation reaction resulted in a powerful tool for the formation of a variety of heterocycle derivatives such as pyrrolo-pyridines,[4] dihydroquinolines,[5] quinolines,[6] 4-*exo*-methylene-1,2-dihydrocinnolines,[7] azaanthraquinones,[8] coumarins,[5c,9] benzofurans,[5c] 2*H*-chromenes,[5c,10] and seven-membered heterocyclic rings anellated to furans.[11] Rapid access to chroman-3-ones was achieved through gold-catalyzed oxidations of propargyl aryl ethers.[12] Many of these latter processes require a co-catalyst, usually in the form of a silver salt, to activate the gold species that is used. On the other hand, silver catalysis alone has been reported to efficiently promote the synthesis of annulated quinoline and pyridine derivatives by promoting intramolecular hydroarylative processes.[13] Interestingly, AgOTf catalyzed the intramolecular alkyne hydroarylation reaction leading to the formation of methyl 5-amino-2*H*-1-benzopyran-8-carboxylate derivatives.[10d] It was suggested that the AgOTf-catalyzed reaction proceeded, at least in part, *via* the Claisen-like [3,3] sigmatropic rearrangement[14] rather than the electrophilic hydroarylation pathway proposed for a variety of gold-catalyzed processes.[15] It was also shown that silver-tetrafluoroborate (or trifluoroacetate)-catalyzed rearrangement of propargyl-phenylethers to 2*H*-chromenes occurs at lower temperature (20–80 °C) than the thermal one (about 200 °C).[16] Yet, the Ag(I) catalyzed pathway could lead to the formation of dimeric and benzofuran[10d,3i] derivative byproducts. Our ongoing studies[17] on diversity in gold- and silver-catalysis in organic synthesis[18] prompted us to focus on the intramolecular hydroarylation of [(3-arylprop-2-yn-1-yl)oxy]benzene derivatives **1** as a viable approach to the synthesis of 4-aryl-substituted-2*H*-chromenes **2** (Scheme 1).

In spite of the several examples of 2*H*-chromenes synthesis *via* metal-catalyzed alkyne hydroarylation,[3i,10] only two specific




**1** **2**

**Scheme 1**

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†Electronic supplementary information (ESI) available: Preparation and characterizations of compounds **1a–t**; copies of the $^{1}$H NMR and $^{13}$C NMR for the new compounds. See DOI: 10.1039/c2ob26763b

examples of respectively Pt-[19] and Pd-catalyzed[20] cyclization of [(3-phenylprop-2-yn-1-yl)oxy]benzene into 4-aryl-2*H*-1-chromene derivative in moderate yield have been reported so far. The generality, scope and limitations, as well as the product selectivity in the cyclization of readily available aryl-substituted propargylic aryl ethers[21] **1** have not been previously investigated. Applications of this key reaction can be relevant in natural product synthesis of the 2*H*-chromene moiety which appears in a vast number of naturally occurring and pharmaceutically relevant substrates.[10a]

Hereafter we show the results of our study.

## Results and discussion

As part of a program devoted to the chemical valorization of widespread diffused molecules in renewable sources,[22] we became interested in the preparation of 2*H*-chromene derivatives by using as starting material the 4-(2-hydroxyethyl)phenol (tyrosol), a naturally occurring bioactive molecule found in extra virgin olive oil and agricultural wastewater.[23]

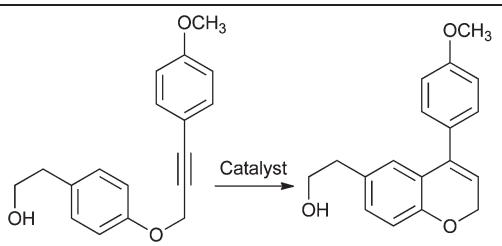
Its 2-(4-{[3-(4-methoxyphenyl)prop-2-yn-1yl]oxy}phenyl)ethan-1-ol derivative **1a** was used as a model substrate for our initial studies of the intramolecular hydroarylation (IMHA) of aryl-substituted propargylic aryl ethers under a spectrum of metal salts and complexes.[24] Some of our results of the screening of the reaction conditions are summarized in Table 1.

In a preliminary experiment, no IMHA of **1a** was observed by using the catalyst **A** (2 mol%) in a $CH_2Cl_2$ solution[5c] maintained at room temperature for 48 h (Table 1, entry 1). Increasing the reaction temperature to over 60 °C gave **2a** in about quantitative yield (Table 1, entries 2, 3). Surprisingly, the formation of **2a** did not occur (Table 1, entry 4) in the presence of $Ph_3PAuNTf_2$, which was a superior catalyst for the selective synthesis of 4-unsubstituted-2*H*-chromenes.[10a] The importance of both the ligand and the non-nucleophilic anion in the gold catalyst is also pointed out by the failure of the formation of **2a** in the presence of the chloride **B** as the catalyst (Table 1, entries 5–7). By contrast with the results observed in the annulation reactions of propargylic anilines,[24] $NaAuCl_4{\cdot}2H_2O$ was not effective in the IMHA of **1a** both in ethanol and $CH_2Cl_2$ (Table 1, entries 8–10). Analogously, under copper catalysis **1a** was recovered unchanged (Table 1, entries 11–12). AgOTf alone catalyzed the reaction although a little more slowly and less efficiently (Table 1, entry 13). Note that the (2-biphenyl)di-*tert*-butylphosphine Buchwald-type ligand hampered the catalytic activity of $AgSbF_6$ (Table 1, entry 14). We continued to establish the scope and the generality of gold *versus* silver catalyzed IMHA reactions of aryl-substituted propargylic aryl ethers **1** in terms of rings substitution. To that end a range of readily accessible derivatives **1** was prepared and then subjected to the same reaction conditions in the presence of gold catalyst **A** or AgOTf.

The outcomes of such studies are shown in Table 2.

By using the catalyst **A** (2 mol%) in $CH_2Cl_2$, the cyclization of derivatives **1a–o** was quite general and proceeded smoothly at 60 °C to give exclusively the 4-aryl-substituted-2*H*-chromenes **2a–o** in excellent yields. In contrast, the introduction of

**Table 1** Screening optimal conditions




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

| Entry | Catalyst (2 mol%) | Solvent | Temperature (°C) | Time (h) | **2a** Yield[a,b] (%) |
|---|---|---|---|---|---|
| 1 | **A** | $CH_2Cl_2$ | r.t. | 48 | –(100) |
| 2 | **A** | $CH_2Cl_2$ | 60 | 1 | >98[c] |
| 3 | **A** | $CH_2Cl_2$ | 80 | 0.2 | >99 |
| 4 | $Ph_3PAuNTf_2$ | $CH_2Cl_2$ | 60 | 24 | –(100) |
| 6 | **B** | $CH_2Cl_2$ | 80 | 24 | –(100) |
| 7 | **B** | $CH_2Cl_2$ | 100 | 24 | –(100) |
| 8 | $NaAuCl_4{\cdot}2H_2O$ | EtOH | 60 | 24 | –(100) |
| 9 | $NaAuCl_4{\cdot}2H_2O$ | EtOH | 80 | 24 | 18 (82) |
| 10 | $NaAuCl_4{\cdot}2H_2O$ | $CH_2Cl_2$ | 80 | 24 | 4 (96) |
| 11 | CuCl[d] | Dioxane | 60 | 24 | –(100) |
| 12 | CuI[d]/L-proline[e] | Toluene | 80 | 24 | –(100) |
| 13 | AgOTf | $CH_2Cl_2$ | 60 | 3 | 83[c] |
| 14 | **C** | $CH_2Cl_2$ | 60 | 24 | 4 (96) |

[a] If not otherwise stated, yields refer to single run and are for pure isolated products. [b] Figures in brackets refer to the recovered **1a**. [c] Average yield referred to three runs. [d] 5 mol%. [e] 10 mol%.

**Table 2** Scope of gold *versus* silver catalyzed IMHA reactions of aryl-substituted propargylic aryl ethers **1**

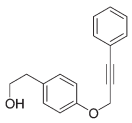
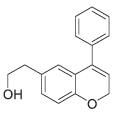
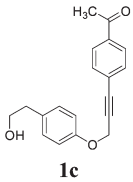
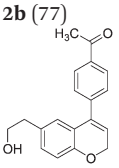
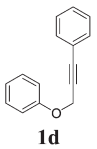
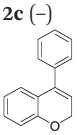
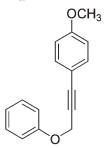
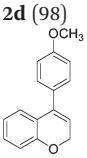
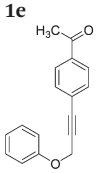
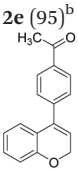
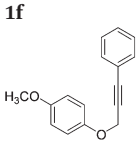
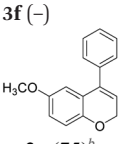
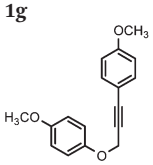
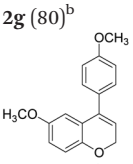
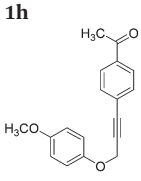
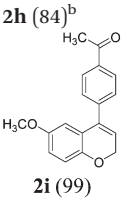
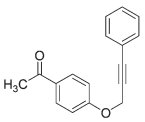
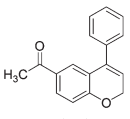
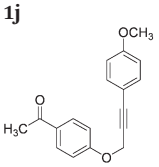
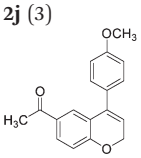
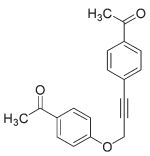
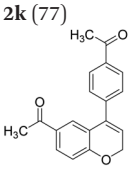
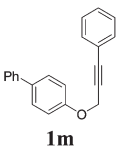
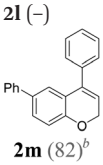
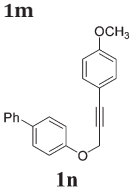
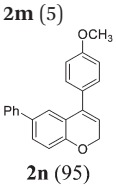
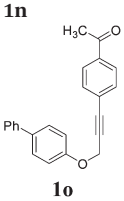
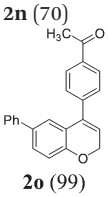
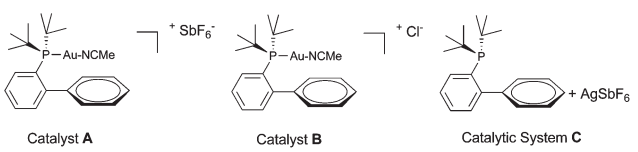
| Entry | 1 | Catalyst | Time (h) | 2 (% yield)[a] |
|---|---|---|---|---|
| 1 |  **1b** | **A** | 1 |  **2b** (99) |
| 2 | **1b** | AgOTf | 1 | **2b** (77) |
| 3 |  **1c** | **A** | 1 |  **2c** (96) |
| 4 | **1c** | AgOTf | 1 | **2c** (–) |
| 5 |  **1d** | **A** | 1 |  **2d** (56) |
| 6 | **1d** | AgOTf | 1 | **2d** (98) |
| 7 |  **1e** | **A** | 1 |  **2e** (75) |
| 8 | **1e** | AgOTf | 1 | **2e** (95)[b] |
| 9 |  **1f** | **A** | 1 |  **2f** (73)[b] |
| 10 | **1f** | AgOTf | 3 | **3f** (–) |
| 11 |  **1g** | **A** | 1 |  **2g** (75)[b] |
| 12 | **1g** | AgOTf | 3 | **2g** (80)[b] |
| 13 |  **1h** | **A** | 3 |  **2h** (97)[b] |
| 14 | **1h** | AgOTf | 2 | **2h** (84)[b] |
| 15 |  **1i** | **A** | 1 |  **2i** (99) |
| 16 | **1i** | AgOTf | 3 | **2i** (24) |

**Table 2** *(Contd.)*

| Entry | 1 | Catalyst | Time (h) | 2 (% yield)[a] |
|---|---|---|---|---|
| 17 |  **1j** | **A** | 3 |  **2j** (99) |
| 18 | **1j** | AgOTf | 3 | **2j** (3) |
| 19 |  **1k** | **A** | 15 |  **2k** (99) |
| 20 | **1k** | AgOTf | 3 | **2k** (77) |
| 21 |  **1l** | **A** | 1 |  **2l** (98)[b] |
| 22 | **1l** | AgOTf | 3 | **2l** (–) |
| 23 |  **1m** | **A** | 2 |  **2m** (82)[b] |
| 24 | **1m** | AgOTf | 3 | **2m** (5) |
| 25 |  **1n** | **A** | 1 |  **2n** (95) |
| 26 | **1n** | AgOTf | 3 | **2n** (70) |
| 27 |  **1o** | **A** | 22 |  **2o** (99) |
| 28 | **1o** | AgOTf | 7 | **2o** (22) |

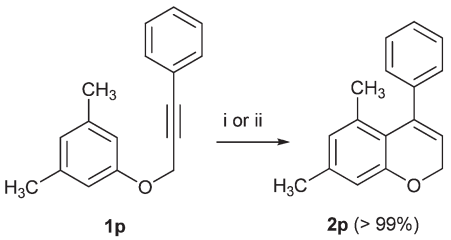
[a] If not otherwise stated, yields refer to single run and are for pure isolated products. [b] Average yield referred to three runs.

substituents on the aryl groups had a considerable effect on the yield of the reaction in the presence of the silver catalysis.




Catalyst **A** Catalyst **B** Catalytic System **C**

Substituents were first introduced onto the aromatic ring attached to the alkyne. Whereas the presence of the electron-donating group MeO in the *para* position and the absence of any substituent (Table 2, entry 2) allowed the formation of the




**1p** **2p** (> 99%)

i = $CH_2Cl_2$, A, 60°C, 1h

ii = $CH_2Cl_2$, AgOTf, 60°C, 4h

**Scheme 2**



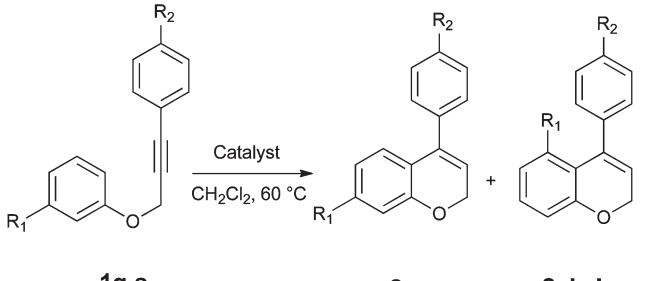
corresponding 2*H*-chromene **2a–b** in good yield, the introduction of the electron-withdrawing carbonyl group resulted in the failure of the formation of the product **2c** (Table 2, entry 4). The introduction of substituents onto the aromatic ring attached to the oxygen moiety also had a pronounced effect. The silver-catalyzed formation of the target 4-aryl-2*H*-chromene derivative **2** occurred only by the introduction of an electron-donating group on the phenyl ring *para* to the oxygen (Table 2, entries 12, 14), while the presence of the acyl or the phenyl groups on the same position hampered the IMHA reaction (Table 2, entries 18, 24). As expected, the introduction of an electron-donating group in the *para* position of both aromatic rings of the starting aryl-substituted propargylic aryl ethers efficiently promoted the silver-catalyzed process which proceeded only in the presence of at least an electron-donating group on the *para* position of one of the aromatic rings of the starting substrate when an electron-withdrawing group was attached to the *para* position of the other aromatic moiety (Table 2, entries 14, 16, 20). It is worth emphasizing that in the presence of the gold catalyst **A** the IMHA is allowed in almost quantitative yield even in the presence of a withdrawing carbonyl in the *para* position of both aryl groups of the reactant **1l** (Table 2, entry 21).

In absolute agreement with previous considerations of the positive effect of electronic releasing groups on the silver-catalyzed IMHA of the substrates **1**, substrate **1p** bearing two methyl groups on the same benzene nucleus was smoothly converted to the corresponding 4-phenyl-2*H*-chromene **2p** in about quantitative yield either by the gold or silver catalyzed reaction (Scheme 2).

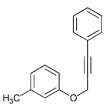
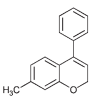
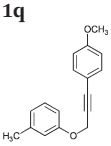
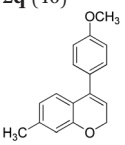
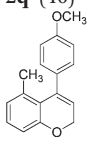
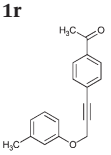
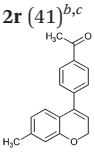
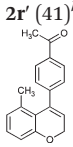
In the case of *meta*-methyl derivatives **1q–s**, the gold-catalyzed annulation of **1q–s** afforded almost only regioisomers **2q–s** derived from the IMHA at the *para*-position to the methyl group (Table 3, entries 1, 3, 5).[10a,c,f] By contrast, under silver catalysis the formation in a 1 : 1 ratio of both regioisomers derived from the IMHA at the *para*- and the *ortho*-position to the methyl group was observed (Table 3, entries 2, 4, 6).

Some trends have emerged from the current study regarding the comparison of gold with silver catalyzed IMHA of substrates **1**. Reactions can be carried out in air and rigorous exclusion of moisture is unnecessary since reactions are compatible with a small amount of water. Furthermore, products derived from *6-endo* cyclization of substrate **1** are formed

**Table 3** Investigation on the regioselectivity of the IMHA

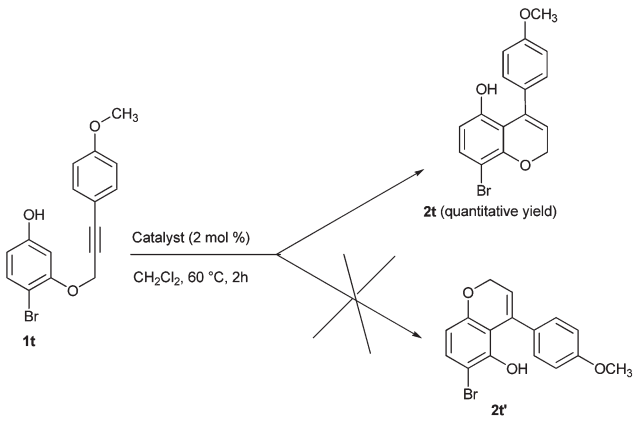



**1q-s** **2q-s** **2q'-s'**

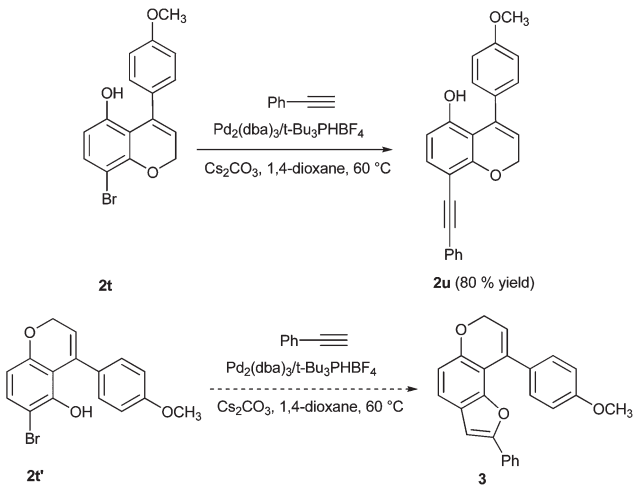
| Entry | Substrate **1** | Catalyst/ time (h) | Product **2** (% yield) | Product **2′** (% yield) |
|---|---|---|---|---|
| 1 |  **1q** | **A**/3 |  **2q** (99)[a] |  **2q'** (-) |
| 2 | **1q** | AgOTf/3 | **2q** (40)[b] | **2q′** (40)[b] |
| 3 |  **1r** | **A**/1.5 |  **2r** (95)[c] |  **2r'** (-) |
| 4 | **1r** | AgOTf/4 | **2r** (41)[b,c] | **2r′** (41)[b,c] |
| 5 |  **1s** | **A**/1.5 |  **2s** (94)[a] |  **2s'** (5) |
| 6 | **1s** | AgOTf/4 | **2s** (8)[b] | **2s′** (8)[b] |

[a] Yields refer to single run and are for pure isolated products. [b] The ratio of the regioisomers was determined by $^1$H NMR. [c] Average yield referred to three runs.

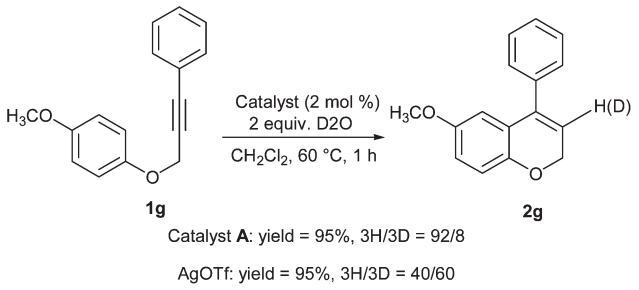
exclusively. The undesired formation of a 4-aryl-4*H*-chromene isomer reported to occur though the Pt(IV)-catalyzed cyclization of **1d** was not observed in our cases.[19] Analogously, the formation of saturated benzopyran derivatives produced according to the $Pd(OAc)_2$/TFA based protocol[20] is avoided under the present reaction conditions. Striking improvements over the previous methodology are due to the suppression of the depropargylation reaction.[10a–d] No dimeric 2*H*-chromene derivatives[10] as well as benzofuran by-products[5c,10] were detected during the cycloisomerization reactions. Notably, the drawbacks due to the competing Au-catalyzed hydration of the alkyne moiety[25] leading to the corresponding ketone derivative[10a,c,d] are overcome because of the faster rate of the Au-catalyzed cyclization reaction of substrate **1** promoted by catalyst **A**. The activity of catalyst **A** and AgOTf was comparable toward substrates containing arene rings with electron-donating substituents. From a practical standpoint the AgOTf catalyzed cyclization is more attractive because AgOTf is cheaper than catalyst **A**. Nevertheless it appears that the gold catalyst **A**



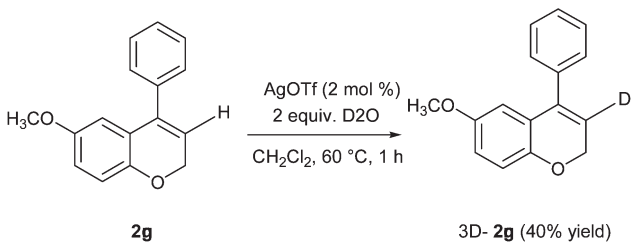

Scheme 3



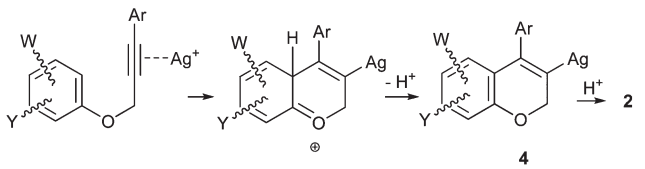

Scheme 4




Scheme 5




Scheme 6




Scheme 7

possesses a unique blend of reactivity and selectivity. Our results revealed that **A** might be a general catalyst for the cyclization of aryl-substituted-arylpropargyl ethers **1** to the corresponding 4-aryl-2*H*-chromenes **2** and represent up to now the only choice to efficiently achieve the annulation reaction of substrates **1** bearing electron deficient arenes.

Transition metal-catalyzed IMHA[26] approaches have been reported to involve multiple mechanistic possibilities. These alternative mechanistic routes include multiple bond activation–electrophilic substitution,[27] metal-catalyzed Claisen rearrangement,[16,28] arene metallation–Heck type addition.[29] Examples of phenol synthesis in which furan-ynes are used as substrates have been reported to involve the formation of metal cyclopropyl carbene intermediates.[30] Another mechanistic possibility involves hydrometallation of the triple carbon–carbon bond, generating an alkenyl metal species, followed by intramolecular substitution of the arene ring.[31] In our procedure the formation of the only isomer **2t** in about quantitative yield from the substrate **1t** in the presence of 2 mol% of either catalyst **A** or AgOTf in $CH_2Cl_2$ at 60 °C should rule out that the cyclization of derivatives **1** proceeds *via* the Claisen rearrangement (Scheme 3).

The structure of **2t** has been unambiguously assigned by NMR spectroscopy and chemical evidence. Indeed, the isolation of the alkynyl derivative **2u** (80% yield) under Sonogashira modified conditions provided further evidence about the assignment of the structure of the product of the cyclization of **1t** (Scheme 4).

The formation of the benzo[*b*]furan derivative **3** which should be generated from the isomer **2t′** under the reaction conditions above was not observed.[32]

The cyclization of the substrate **1g** in the presence of 2 equiv. of $D_2O$ (Scheme 5) revealed that the deuterium atom is significantly incorporated into product **2g** at the C3 position as judged by $^1H$ NMR only under silver catalysis.

Interestingly, also the vinyl proton of the 2*H*-chromene derivative **2g** was deuterated in the presence of AgOTf under similar conditions (Scheme 6).[33]

By contrast the formation of the C3-deuterated **2g** did not occur under the gold catalysis. These results suggest that the silver catalyzed cyclization of the aryl-substituted arylpropargylic ethers **1** is in accordance with a Friedel–Crafts type reactivity. Coordination of AgOTf activates the carbon–carbon triple bond for interception by the benzene ring (Scheme 7). The following electrophilic attack determines the release of the proton of the arene into the solvent along the reaction path and the final hydroarylation product is generated by the

intermediacy of the vinyl silver intermediate **4** by some type of reversible protonation event.

Different C–H activation of arenes has been reported to occur under gold catalysis *via* σ-bond metathesis[34] or electrophilic auration,[35] but in our cases both seem very unlikely. An oxidative addition mechanism[36] for the gold-catalyzed annulation reaction of substrates **1**, where a transient Au(III) hydride species is formed, would be, also, discarded since 5-*exo-dig* cyclization on the exclusive *cis*-selectivity can be expected for that intermediate. However, further studies are needed to unambiguously establish the reaction mechanism for the Au(I)-catalyzed process.

## Conclusions

In summary, the generality, scope and limitations, as well as the product selectivity in the cyclization of readily available aryl-substituted propargylic aryl ethers by means of gold and silver catalysis have been investigated. Products deriving from *6-endo* cyclization of the starting substrate are formed exclusively. The study of the comparison of the gold *vs.* silver catalysis for the IMHA process showed that the silver-catalyzed process can be efficiently applied only to aryl-substituted aryl-propargylic ethers containing arene rings bearing electron-donating substituents in accordance with a Friedel–Crafts type reactivity. The results observed in the gold-catalyzed IMHA reaction revealed that gold(I) catalysis might represent up to now the only choice possible to efficiently achieve the synthesis of 4-aryl-2*H*-chromenes through the annulation reaction of starting substrates bearing electron deficient arenes. The gold-catalyzed IMHA reaction seems to proceed by a different mechanism that determines the unique properties of gold catalysis in terms of reactivity and product selectivity control. This unusual mechanistic behaviour should provide new insight into the burgeoning field of gold catalysis.

## Experimental

Typical procedures for the gold- and silver-catalyzed synthesis of 4,6-, or 4,7- or 4,8-disubstituted-2*H*-chromenes (2): preparation of 6-methoxy-4-(4-methoxyphenyl)-2*H*-chromene (2H). A solution of 4-methoxy-*O*-(4-methoxyphenyl)prop-2-ynylphenol (**1h**) (0.107 g, 0.40 mmol, 1 equiv.) in $CH_2Cl_2$ (4 mL) was treated with (acetonitrile)((2-biphenyl)di-*tert*-butylphosphine)gold(I) hexafluoroantimonate (0.0061 g, 0.008 mmol, 0.02 equiv.) or with AgOTf (0.0021 g, 0.008 mmol, 0.02 equiv.). The resulting solution was stirred at 60 °C for 1 h until determined to be complete by TLC and then concentrated under reduced pressure. The product was subjected to flash column chromatography ($SiO_2$ 50 g), eluting with *n*-hexane–ethyl acetate 95 : 5 v/v to afford the product (**2h**) as a yellow oil (0.106 g, 99% (catalyst **A**) or 0.0909 g, 85% (AgOTf)).

4-(4-Methoxyphenyl)-6-(2-hydroxyethyl)-2*H*-chromene (2A). (0.1117 g, 99% [catalyst **A**]; 0.0936 g, 83% [AgOTf]). Oil. Found C, 76.62; H, 6.44. Anal calcd for $C_{18}H_{18}O_3$, C, 76.57; H, 6.43. IR (KBr): $\nu_{max}/cm^{-1}$ 3431, 2924, 1608, 1512, 1248, 1034, 837, 804. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.29 (d, $J$ = 8.4 Hz, 2H), 7.03 (d, $J$ = 8.3 Hz, 1H), 6.96 (d, $J$ = 8.4 Hz, 2H), 6.92 (s, 1H), 6.87 (d, $J$ = 8.2 Hz, 1H), 5.78 (t, $J$ = 4.0 Hz, 1H), 4.82 (d, $J$ = 4.0 Hz, 2H), 3.87 (s, 3H), 3.75 (t, $J$ = 6.7 Hz, 2H), 2.73 (t, $J$ = 6.7 Hz, 2H), 1.93 (bs, 1H). $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 159.3, 153.5, 136.6, 131.1, 130.6, 129.7, 129.6, 126.3, 124.0, 119.6, 116.3, 113.9, 65.2, 63.8, 55.3, 38.5. MS (relative intensity): $m/z$ 282 ($M^+$, 29), 251 (14), 207 (16), 77 (10), 45 (17).

4-Phenyl-6-(2-hydroxyethyl)-2*H*-chromene (2B). (0.0997 g, 99% [catalyst **A**]; 0.0775 g, 77% [AgOTf]). Oil. Found C, 80.98; H, 6.40. Anal calcd for $C_{17}H_{16}O_2$, C, 80.93; H, 6.39. IR (KBr): $\nu_{max}/cm^{-1}$ 3396, 2924, 1630, 1491, 1444, 1228, 1032, 744, 702. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.46–7.37 (m, 5H), 7.05 (d, $J$ = 8.0 Hz, 1H), 6.89 (m, 2H), 5.83 (t, $J$ = 4.0 Hz, 1H), 4.85 (d, $J$ = 4.0 Hz, 2H), 3.74 (t, $J$ = 6.7 Hz, 2H), 2.73 (t, $J$ = 6.7 Hz, 2H), 1.85 (bs, 1H). $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 153.4, 138.3, 137.1, 131.2, 129.7, 128.6, 128.5, 127.9, 126.3, 123.8, 120.3, 116.3, 65.3, 63.8, 38.5. MS (relative intensity): $m/z$ 252 ($M^+$, 45), 221 (39), 207 (21), 175 (22), 77 (32).

4-(4-Acetylphenyl)-6-(2-hydroxyethyl)-2*H*-chromene (2C). (0.1129 g, 96% [catalyst **A**]). Mp: 92–95 °C. Found C, 77.45; H, 6.16. Anal calcd for $C_{19}H_{18}O_3$, C, 77.53; H, 6.16. IR (KBr): $\nu_{max}/cm^{-1}$ 3425, 2864, 1685, 1601, 1489, 1257, 1059, 827, 802. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.99 (d, $J$ = 8.4 Hz, 2H), 7.44 (d, $J$ = 8.4 Hz, 2H), 7.06 (d, $J$ = 8.2 Hz, 1H), 6.89 (d, $J$ = 8.2 Hz, 1H), 6.82 (s, 1H), 5.86 (t, $J$ = 4.0 Hz, 1H), 4.82 (d, $J$ = 4.0 Hz, 2H), 3.76 (t, $J$ = 6.1 Hz, 2H), 2.73 (t, $J$ = 6.1 Hz, 2H), 2.66 (s, 3H), 1.57 (bs, 1H). $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 197.8, 153.3, 143.1, 136.5, 136.4, 131.4, 130.0, 128.8, 128.6, 126.1, 123.1, 121.4, 116.4, 65.1, 63.7, 38.5, 26.6. MS (relative intensity): $m/z$ 294 ($M^+$, 16), 263 (6), 175 (5), 77 (6), 45 (7), 43 (100).

4-Phenyl-2*H*-chromene (2D). (0.0732 g, 88% [catalyst **A**]; 0.0815 g, 98% [AgOTf]). Oil. Found C, 86.45; H, 5.82. Anal calcd for $C_{15}H_{12}O$, C, 86.51; H, 5.81. IR (KBr): $\nu_{max}/cm^{-1}$ 1603, 1485, 1448, 1225, 758, 700. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.47–7.37 (m, 4H), 7.21 (t, $J$ = 7.8 Hz, 1H), 7.08 (d, $J$ = 8.2 Hz, 1H), 6.97 (d, $J$ = 8.2 Hz, 1H), 6.91 (t, $J$ = 7.8 Hz, 1H), 5.85 (t, $J$ = 4.0 Hz, 1H), 4.90 (d, $J$ = 4.0 Hz, 2H). $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 154.8, 138.3, 137.2, 129.3, 128.7, 128.4, 127.8, 125.9, 123.7, 121.2, 120.0, 116.3, 65.3. MS (relative intensity): $m/z$ 208 ($M^+$, 53).

4-(4-Methoxyphenyl)-2*H*-chromene (2E). (0.0714 g, 75% [catalyst **A**]; 0.0904 g, 95% [AgOTf]). Mp: 90–91 °C. Found C, 80.72; H, 5.90. Anal calcd for $C_{16}H_{14}O_2$, C, 80.65; H, 5.92. IR (KBr): $\nu_{max}/cm^{-1}$ 2837, 1606, 1572, 1508, 1456, 1244, 1032, 839, 804. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.30 (d, $J$ = 8.8 Hz, 2H), 7.18 (t, $J$ = 7.6 Hz, 1H), 7.05 (d, $J$ = 7.6 Hz, 1H), 6.95 (d, $J$ = 8.8 Hz, 2H), 6.92 (d, $J$ = 7.5 Hz, 1H), 6.88 (t, $J$ = 7.5 Hz, 1H), 5.79 (t, $J$ = 4.0 Hz, 1H), 4.86 (d, $J$ = 4.0 Hz, 2H), 3.87 (s, 3H). $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 159.4, 154.9, 136.7, 130.7, 129.8, 129.2, 125.9, 124.0, 121.1, 119.2, 116.2, 113.8, 65.3, 55.3. MS (relative intensity): $m/z$ 238 ($M^+$, 22), 77 (12).

4-(4-Acetylphenyl)-2*H*-chromene (2f). (0.099 g, 99% [catalyst **A**]). Mp: 110–112 °C. Found C, 81.43; H, 5.66. Anal calcd for $C_{17}H_{14}O_2$, C, 81.58; H, 5.64. IR (KBr): $\nu_{max}/cm^{-1}$ 1682, 1603, 1487, 1259, 1016, 849, 779. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 8.01 (d, $J$ = 8.4 Hz, 2H), 7.46 (d, $J$ = 8.4 Hz, 2H), 7.19 (t, $J$ = 7.6 Hz, 1H), 6.97 (d, $J$ = 7.6 Hz, 1H), 6.93 (d, $J$ = 7.6 Hz, 1H), 6.88 (t, $J$ = 7.6 Hz, 1H), 5.87 (t, $J$ = 4.0 Hz, 1H), 4.87 (d, $J$ = 4.0 Hz, 2H), 2.65 (s, 3H). $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 197.6, 154.7, 143.1, 136.5, 136.4, 129.6, 128.8, 128.5, 125.6, 123.1, 121.3, 121.1, 116.4, 65.1, 26.6. MS (relative intensity): $m/z$ 250 ($M^+$, 36), 207 (17), 131 (30), 77(5), 43 (100).

6-Methoxy-4-phenyl-2*H*-chromene (2g). (0.0714 g, 75% [catalyst **A**]; 0.0762 g, 80% [AgOTf]). Mp: 60–64 °C. Found C, 80.76; H, 5.95. Anal calcd for $C_{16}H_{14}O_2$, C, 80.65; H, 5.92. IR (KBr): $\nu_{max}/cm^{-1}$ 2829, 1608, 1491, 1209, 1038, 762, 700. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.44–7.39 (m, 5H), 6.90 (d, $J$ = 8.8 Hz, 1H), 6.77 (dd, $J_1$ = 8.8 Hz, $J_2$ = 2.8 Hz, 1H), 6.65 (d, $J$ = 2.8 Hz, 1H), 5.89 (t, $J$ = 4.0 Hz, 1H), 4.83 (d, $J$ = 4.0 Hz, 2H), 3.71 (s, 3H); $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 154.0, 148.7, 138.2, 137.3, 128.6, 128.4, 127.8, 124.5, 120.9, 116.7, 114.2, 111.7, 65.2, 55.7. MS (relative intensity): $m/z$ 238 ($M^+$, 100), 207 (23), 161 (31), 77 (19).

6-Methoxy-4-(4-methoxyphenyl)-2*H*-chromene (2h). (0.1061 g, 99% [catalyst **A**]; 0.0911 g, 85% [AgOTf]). Oil. Found C, 76.18; H, 6.03. Anal calcd for $C_{17}H_{16}O_3$, C, 76.10; H, 6.01. IR (KBr): $\nu_{max}/cm^{-1}$ 2825, 1608, 1489, 1248, 1034, 837, 806. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.32 (d, $J$ = 8.8 Hz, 2H), 6.97 (d, $J$ = 8.8 Hz, 2H), 6.89 (d, $J$ = 8.8 Hz, 1H), 6.76 (dd, $J_1$ = 8.8 Hz, $J_2$ = 2.8 Hz, 1H), 6.66 (d, $J$ = 2.8 Hz, 1H), 5.84 (t, $J$ = 4.0 Hz, 1H), 4.80 (d, $J$ = 4.0 Hz, 2H), 3.88 (s, 3H), 3.71 (s, 3H); $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 159.4, 154.0, 148.8, 136.8, 130.5, 129.8, 124.8, 120.1, 116.6, 114.1, 113.9, 111.6, 65.2, 55.7, 55.3. MS (relative intensity): $m/z$ 268 ($M^+$, 100), 237 (15), 161 (17).

6-Methoxy-4-(4-acetylphenyl)-2*H*-chromene (2i). (0.1109 g, 99% [catalyst **A**]; 0.0269 g, 24% [AgOTf]). Mp: 95–98 °C. Found C, 77.21; H, 5.77. Anal calcd for $C_{18}H_{16}O_3$, C, 77.12; H, 5.75. IR (KBr): $\nu_{max}/cm^{-1}$ 2825, 1678, 1601, 1578, 1485, 1427, 1265, 1063, 856, 814. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 8.00 (d, $J$ = 8.4 Hz, 2H), 7.46 (d, $J$ = 8.4 Hz, 2H), 6.88 (d, $J$ = 8.7 Hz, 1H), 6.75 (dd, $J_1$ = 8.8 Hz, $J_2$ = 2.8 Hz, 1H), 6.53 (d, $J$ = 2.8 Hz, 1H), 5.92 (t, $J$ = 4.0 Hz, 1H), 4.80 (d, $J$ = 4.0 Hz, 2H), 3.68 (s, 3H), 2.64 (s, 3H); $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 197.5, 154.1, 148.6, 143.0, 136.6, 136.5, 128.8, 128.5, 123.8, 122.0, 116.9, 114.5, 111.4, 65.0, 55.7, 26.6. MS (relative intensity): $m/z$ 280 ($M^+$, 46), 237 (12), 161 (14), 77 (3), 43 (100).

4-Phenyl-6-acetyl-2*H*-chromene (2j). (0.0990 g, 99% [catalyst **A**]; 0.0031 g, 3% [AgOTf]). Oil. Found C, 81.43; H, 5.66. Anal calcd for $C_{17}H_{14}O_2$, C, 81.58; H, 5.64. IR (KBr): $\nu_{max}/cm^{-1}$ 2835, 1676, 1601, 1491, 1246, 1014, 766, 702. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.81 (dd, $J_1$ = 8.4 Hz, $J_2$ = 2.0 Hz, 1H), 7.68 (d, $J$ = 2.0 Hz, 1H), 7.44–7.34 (m, 5H), 6.93 (d, $J$ = 8.4 Hz, 1H), 5.82 (t, $J$ = 4.0 Hz, 1H), 4.97 (d, $J$ = 4.0 Hz, 2H), 2.45 (s, 3H); $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 196.7, 159.0, 137.6, 136.4, 130.8, 130.2, 128.7, 128.4, 128.2, 126.3, 123.0, 120.4, 116.2, 65.9, 26.3. MS (relative intensity): $m/z$ 250 ($M^+$, 17), 207 (5), 173 (5), 77 (5), 43 (100).

4-(4-Methoxyphenyl)-6-acetyl-2*H*-chromene (2k). (0.1109 g, 99% [catalyst **A**]; 0.0862 g, 77% [AgOTf]). Oil. Found C, 77.18; H, 5.76. Anal calcd for $C_{18}H_{16}O_3$, C, 77.12; H, 5.75. IR (KBr): $\nu_{max}/cm^{-1}$ 2835, 1676, 1601, 1512, 1250, 1032, 837, 804. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.81 (dd, $J_1$ = 8.3 Hz, $J_2$ = 2.0 Hz, 1H), 7.70 (d, $J$ = 2.0 Hz, 1H), 7.28 (d, $J$ = 8.7 Hz, 2H), 6.97 (d, $J$ = 8.7 Hz, 2H), 6.92 (d, $J$ = 8.3 Hz, 1H), 5.78 (t, $J$ = 4.0 Hz, 1H), 4.95 (d, $J$ = 4.0 Hz, 2H), 3.87 (s, 3H), 2.47 (s, 3H); $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 196.7, 159.6, 159.1, 136.0, 130.7, 130.1, 129.9, 129.6, 126.4, 123.2, 119.6, 116.2, 114.1, 65.9, 55.3, 26.3. MS (relative intensity): $m/z$ 280 ($M^+$, 55), 237 (8), 43 (100).

4-(4-Acetylphenyl)-6-acetyl-2*H*-chromene (2l). (0.1156 g, 99% [catalyst **A**]). Mp: 109–112 °C. Found C, 78.12; H, 5.54. Anal calcd for $C_{19}H_{16}O_3$, C, 78.06. IR (KBr): $\nu_{max}/cm^{-1}$ 1674, 1603, 1568, 1495, 1254, 1080, 829, 806. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.99 (d, $J$ = 8.0 Hz, 2H), 7.78 (dd, $J_1$ = 8.4 Hz, $J_2$ = 2.0 Hz, 1H), 7.58 (d, $J$ = 2.0 Hz, 1H), 7.42 (d, $J$ = 8.0 Hz, 2H), 6.91 (d, $J$ = 8.4 Hz, 1H), 5.86 (t, $J$ = 4 Hz, 1H), 4.95 (d, $J$ = 4 Hz, 2H), 2.62 (s, 3H), 2.43 (s, 3H); $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 197.5, 196.5, 158.9, 142.3, 136.7, 135.7, 130.8, 130.6, 128.7, 128.6, 125.9, 122.4, 121.5, 116.4, 65.7, 26.7, 26.3. H, 5.52. MS (relative intensity): $m/z$ 292 ($M^+$, 10), 206 (3), 173 (6), 43 (100).

4,6-Diphenyl-2*H*-chromene (2m). (0.0943 g, 83% [catalyst **A**]; 0.0057 g, 5% [AgOTf]). Mp: 133–136 °C. Found C, 88.77; H, 5.68. Anal calcd for $C_{21}H_{16}O$, C, 88.70; H, 5.67. IR (KBr): $\nu_{max}/cm^{-1}$ 1599, 1479, 1230, 1061, 766, 698. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.53–7.34 (m, 12H), 7.08 (d, $J$ = 8.4 Hz, 1H), 5.91 (t, $J$ = 4 Hz, 1H), 4.97 (d, $J$ = 4 Hz, 2H). $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 154.5, 146.6, 140.9, 138.2, 137.2, 134.4, 128.8, 128.7, 128.6, 128.0, 127.9, 126.8, 124.6, 123.9, 120.4, 116.6, 65.5. MS (relative intensity): $m/z$ 284 ($M^+$, 100), 207 (22), 77 (57).

4-(4-Methoxyphenyl)-6-phenyl-2*H*-chromene (2n). (0.1193 g, 95% [catalyst **A**]; 0.0879 g, 70% [AgOTf]). Mp: 108–110 °C. Found C, 84.12; H, 5.78. Anal calcd for $C_{22}H_{18}O_2$, C, 84.05; H, 5.77. IR (KBr): $\nu_{max}/cm^{-1}$ 2924, 2841, 1606, 1508, 1479, 1225, 1026, 845, 806, 762, 700. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.51–7.32 (m, 9H), 7.04–6.98 (m, 3H), 5.85 (t, $J$ = 4 Hz, 1H), 4.92 (d, $J$ = 4 Hz, 2H), 3.89 (s, 3H); $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 159.4, 154.5, 149.7, 140.9, 136.7, 134.3, 130.6, 129.8, 128.7, 127.9, 126.8, 124.6, 124.1, 119.6, 116.6, 114.0, 65.4, 55.3. MS (relative intensity): $m/z$ 314 ($M^+$, 69), 283 (16), 207 (36), 77 (47).

4-(4-Acetylphenyl)-6-phenyl-2*H*-chromene (2o). (0.1291 g, 99% [catalyst **A**]; 0.0287 g, 22% [AgOTf]). Mp: 146–148 °C. Found C, 84.71; H, 5.54. IR (KBr): $\nu_{max}/cm^{-1}$ 2922, 1678, 1603, 1481, 1259, 1016, 824, 804, 762, 700. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 8.03 (d, $J$ = 8.2 Hz, 2H), 7.52 (d, $J$ = 8.2 Hz, 2H), 7.48–7.43 (m, 3H), 7.39 (t, $J$ = 7.4 Hz, 2H), 7.30 (t, $J$ = 7.3 Hz, 1H), 7.22 (d, $J$ = 2.0 Hz, 1H), 7.03 (d, $J$ = 8.4 Hz, 1H), 5.93 (t, $J$ = 4.0 Hz, 1H), 4.93 (d, $J$ = 4.0 Hz, 2H), 2.67 (s, 3H). $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 197.6, 154.4, 143.0, 140.7, 136.7, 136.5, 134.5, 128.8, 128.7, 128.6, 128.3, 126.9, 126.7, 124.3, 123.3, 121.5, 116.8, 65.3, 26.6. Anal calcd for $C_{23}H_{18}O_2$, C, 84.64; H, 5.56. MS (relative intensity): $m/z$ 326 ($M^+$, 26), 283 (5), 207 (8), 77 (10), 43 (100).

5,7-Dimethyl-4-(4-methoxyphenyl)-2*H*-chromene (2p). (0.1053 g, 99% [catalyst **A**]; 0.1053 g, 99% [AgOTf]). Oil. Found C, 81.24;

H, 6.80. Anal calcd for $C_{18}H_{18}O_2$, C, 81.17; H, 6.81. IR (KBr): $\nu_{max}/cm^{-1}$ 2833, 1608, 1518, 1458, 1246, 1034, 837, 806. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.20 (d, $J$ = 8.4 Hz, 2H), 6.92 (d, $J$ = 8.4 Hz, 2H), 6.75 (s, 1H), 6.63 (s, 1H), 5.86 (t, $J$ = 4.8 Hz, 1H), 4.59 (d, $J$ = 4.8 Hz, 2H), 3.87 (s, 3H), 2.34 (s, 3H), 1.81 (s, 3H). $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 159.0, 156.6, 138.8, 138.0, 135.7, 134.0, 128.7, 125.9, 121.2, 120.6, 114.5, 113.8, 64.4, 55.3, 22.4, 21.2. MS (relative intensity): $m/z$ 266 ($M^+$, 100), 235 (13), 159 (10), 108 (8), 77 (16).

7-Methyl-4-phenyl-2*H*-chromene (2Q). (0.0879 g, 99% [catalyst **A**]). oil. Found C, 86.52; H, 6.36. Anal calcd for $C_{16}H_{14}O$, C, 86.45; H, 6.35. Found C, 86.52; H, 6.36. IR (KBr): $\nu_{max}/cm^{-1}$ 2922, 1618, 1491, 1446, 1255, 1039, 764, 702. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.46–7.41 (m, 5H), 6.98 (d, $J$ = 7.5 Hz, 1H), 6.82 (s, 1H), 6.74 (d, $J$ = 7.5 Hz, 1H), 5.80 (t, $J$ = 4.0 Hz, 1H), 4.89 (d, $J$ = 4.0 Hz, 2H), 2.38 (s, 3H).). $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 154.8, 139.6, 138.5, 137.2, 128.7, 128.4, 127.8, 125.7, 121.9, 121.1, 118.9, 116.8, 65.3, 21.4 MS (relative intensity): $m/z$ 222 ($M^+$, 100).

7-Methyl-4-(4-methoxyphenyl)-2*H*-chromene (2R). (0.0958 g, 95% [catalyst **A**]). Oil. Found C, 80.99; H, 6.37. Anal calcd for $C_{17}H_{16}O_2$, C, 80.93; H, 6.39. IR (KBr): $\nu_{max}/cm^{-1}$ 2924, 1610, 1450, 1263, 1022, 873. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.32 (d, $J$ = 8.4 Hz, 2H), 6.98–6.82 (m, 3H), 6.78 (s, 1H), 6.72 (d, $J$ = 7.6 Hz, 1H), 5.74 (t, $J$ = 4.0 Hz, 1H), 4.85 (d, $J$ = 4.0 Hz, 2H), 3.89 (s, 3H), 2.36 (s, 3H). $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 159.3, 154.8, 139.5, 136.7, 130.9, 129.7, 125.7, 121.9, 121.3, 118.1, 116.8, 113.8, 65.3, 55.3, 21.3. MS (relative intensity): $m/z$ 252 ($M^+$, 92), 205 (81), 145 (87).

7-Methyl-4-(4-acetylphenyl)-2*H*-chromene (2S). (0.0993 g, 94% [catalyst **A**]; 0.008 g, 8% [AgOTf]). Mp: 91–93 °C. Found C, 81.85; H, 6.11. Anal calcd for $C_{18}H_{16}O_2$, C, 81.79; H, 6.10. IR (KBr): $\nu_{max}/cm^{-1}$ 2841, 1684, 1604, 1560, 1502, 1462, 1261, 1016, 841, 806. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 8.00 (d, $J$ = 8.4 Hz, 2H), 7.45 (d, $J$ = 8.4 Hz, 2H), 6.86 (d, $J$ = 7.6 Hz, 1H), 6.76 (s, 1H), 6.70 (d, $J$ = 7.5 Hz, 1H), 5.81 (t, $J$ = 4.0 Hz, 1H), 4.84 (d, $J$ = 4.0 Hz, 2H), 2.64 (s, 3H), 2.32 (s, 3H). $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 197.6, 154.7, 143.3, 140.0, 136.4, 128.8, 128.5, 125.4, 122.1, 120.4, 120.0, 117.0, 65.2, 26.6, 21.4. MS (relative intensity): $m/z$ 264 ($M^+$, 65), 145 (50), 43 (100).

8-Bromo-5-hydroxy-4-(4-methoxyphenyl)-2*H*-chromene (2T). (0.1265 g, 95%; [catalyst **A**]; 0.1066 g, 80% [AgOTf]). Oil. Found C, 57.73; H, 3.92. Anal calcd for $C_{16}H_{13}BrO_3$, C, 57.78; H, 3.93; Br, 23.98. IR (KBr): $\nu_{max}/cm^{-1}$ 3483, 2841, 1604, 1558, 1508, 1464, 1248, 1030, 839, 802, 557. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.33–7.30 (m, 3H), 6.99 (d, $J$ = 8.8 Hz, 2H), 6.42 (d, $J$ = 8.8 Hz, 1H), 5.82 (t, $J$ = 4.0 Hz, 1H), 4.77 (d, $J$ = 4.0 Hz, 2H), 3.87 (s, 3H); $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 160.4, 152.7, 152.4, 133.8, 133.2, 129.2, 128.8, 121.6, 114.9, 112.5, 111.9, 101.1, 65.2, 55.4. MS (relative intensity): $m/z$ 333 ($M^+$, 72), 286 (46), 223 (53).

8-Phenylethynyl-5-hydroxy-4-(4-methoxyphenyl)-2*H*-chromene (2U). (0.0685 g, 80%; Oil. Found C, 81.27; H, 5.11, Br, 23.92. Anal calcd for $C_{24}H_{18}O_3$, C, 81.34; H, 5.12. IR (KBr): $\nu_{max}/cm^{-1}$ 3487, 2927, 2150, 1510, 1243, 1033, 1248, 835. $\delta_H$ (400 MHz; $CDCl_3$; $Me_4Si$) 7.57 (d, $J$ = 6.8 Hz, 2H), 7.36–7.30 (m, 6H), 6.96 (d, $J$ = 8.4 Hz, 2H), 6.45 (d, $J$ = 8.4 Hz, 1H), 5.81 (t, $J$ = 3.6 Hz, 1H), 4.78 (d, $J$ = 3.6 Hz, 2H), 3.93 (bs, 1H), 3.79 (s, 3H); $\delta_C$ (100.6 MHz; $CDCl_3$; $Me_4Si$) 160.1, 157.5, 153.9, 148.0, 133.9, 133.8, 131.6, 129.7, 129.1, 128.2, 127.8, 123.9, 121.0, 114.6, 111.3, 110.7, 103.1, 91.9, 85.6, 65.1, 55.4. MS (relative intensity): $m/z$ 354 ($M^+$, 100).

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