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Synthesis of pyrano[2,3-*f*]chromen-2-ones *vs.* pyrano[3,2-*g*]chromen-2-ones through site controlled gold-catalyzed annulations†

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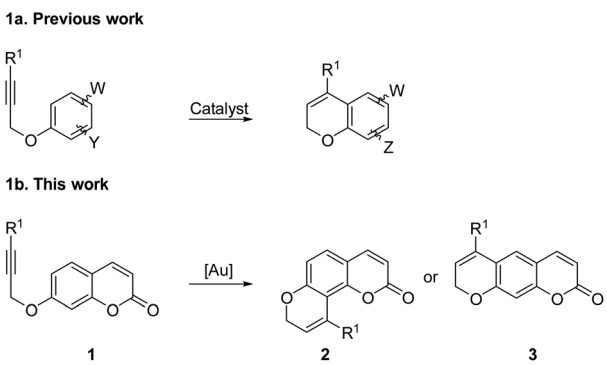
Regioselective access to 10-substituted-2*H*,8*H*-pyrano[2,3-*f*]chromen-2-ones through the gold-catalyzed intramolecular hydroarylation of readily available 7-(prop-2-yn-1-yloxy)-2*H*-chromen-2-one derivatives at their C-8 congested position was investigated by tuning the electronic and steric properties of the ligand on the gold complex. On the other hand, the combination of the JohnPhosAu(MeCN)SbF_6 catalyzed intramolecular hydroarylation of 8-iodo-7-(prop-2-yn-1-yloxy)-2*H*-chromen-2-one derivatives followed by selective palladium/formate C–I reduction allows for the exclusive formation of 2*H*,8*H*-pyrano[3,2-*g*]chromen-2-one regioisomers. The development of these two protocols provides versatile synthetic tools required for exploring the biological activities of these new pyranocoumarin derivatives.

Umbelliferone (7-hyroxycoumarine), a phenolic metabolite found in many familiar plants, and its derivatives exhibit various pharmacological properties including anti-inflammatory,[1,2] antioxidant,[3] anti-metastatic,[4] proapoptotic,[5] and neuroprotective activities.[6] Umbelliferone glycosides show antidiabetic and antihyperlipidemic properties[7] and have been found to prevent serum deprivation-induced PC12 cell damage.[8] Furthermore, 7-substituted umbelliferone derivatives resulted in androgen receptor antagonists for the potential treatment of prostate and breast cancer[9] and showed antifungal and antibacterial activities.[10] Structure–activity relationship (SAR) studies drove forward suitable umbelliberone modifications for the identification of biologically active compounds.[11–13] Also, researchers are extensively exploring the synthesis of various umbelliferone derivatives as a source of potential candidates in drug development.[14–19] The insertion of a C–C triple bond directly into a C–H bond of aromatic compounds represents an attractive alternative to the traditionally adopted Heck and cross coupling reactions, and can be performed in an inter- or intramolecular fashion with variable regio- and stereoselectivity depending on the reaction partners, the catalyst, and the reaction conditions.[20–22] Gold-catalyzed intramolecular hydroarylation (IMHA) of alkynes provides a powerful tool for the construction of polyheterocycles.[23–29] As part of our ongoing interest in the development of new approaches for the synthesis of heterocycles employing efficient and atom-economical routes, we previously investigated the IMHA of reactions of 3-[(3-arylprop-2-ynyl)oxy]benzene derivatives and showed that gold catalysis exhibits a unique blend of reactivity and selectivity making it the only choice for the IMHA of substrates bearing electron-deficient arenes (Scheme 1a).[30] Subsequently, we envisaged to investigate the intramolecular gold-catalyzed hydroarylation of the readily available 7-(prop-2-yn-1-yloxy)-2*H*-chromen-2-one



Scheme 1 (a) IMHA of 3-[(3-arylprop-2-ynyl)oxy]benzene derivatives; (b) work hypothesis.

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†Electronic supplementary information (ESI) available: Experimental details, characterization data of all compounds, and copies of ^{1}H and ^{13}C NMR spectra (PDF). See DOI: 10.1039/c9ob01695c

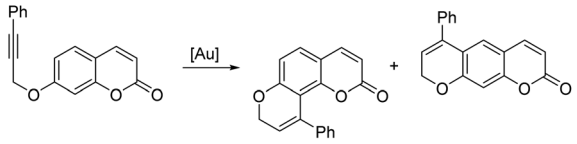
derivatives **1** to selectively afford the corresponding 10-substituted-2*H*,8*H*-pyrano[2,3-*f*]chromen-2-ones **2** or the 6-substituted-2*H*,8*H*-pyrano[3,2-*g*]chromen-2-ones **3** (Scheme 1b). Pyranocoumarin derivatives show a variety of biological activities[31,32] and this aspect may justify our efforts to develop a new and efficient protocol for their preparation.

Hereafter we report the results of our investigation.

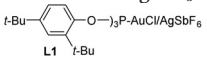
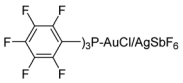
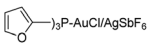
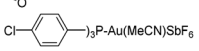
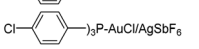
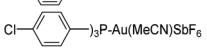
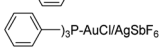
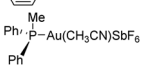
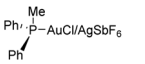
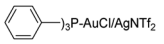
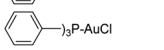
Results and discussion

We started our study using the reaction of 7-((3-phenylprop-2-ynil)oxy)-2*H*-chromen-2-one **1a** as a probe for evaluating the feasibility of the reaction. On the basis of our previous work,[30] we carried out some preliminary experiments using the commercially available gold catalyst JohnPhosAu(CH_3CN)SbF_6. No evidence of reaction products was obtained by performing the reaction in DMSO and in DMF at 60 °C (Table 1 entries 1 and 2), whereas the use of CH_2Cl_2 as a solvent gave, in about quantitative yield, a mixture of regioisomers **2a** and **3a** in a relative product ratio **2a**/**3a** of 60/40 (Table 1, entry 4). This result is similar to a previous report in which the $Ph_3PAuNTf_2$ catalyzed IMHA of 7-((2-methylbut-3-yn-2-yl)oxy)-2*H*-chromen-2-one led to the formation of a 60 : 40 mixture of the corresponding pyranocoumarins seselin and xanthyletin.[33] Switching to the less polar solvents such as $CHCl_3$ and 1,4-

Table 1 Screening optimal conditions for the IMHA of 7-((3-phenylprop-2-ynil)oxy)-2*H*-chromen-2-one **1a**[a]

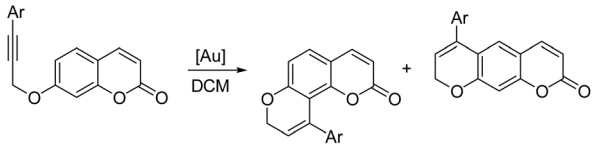


1a **2a** **3a**

Entry	Catalyst (mol %)	Solvent	*T* (°C)	Time (h)	Yield[b] (%)	Ratio[c] **2a**/**3a**
1	JohnPhosAu(MeCN)SbF_6	DMSO	60	24	—[d]	—
2	JohnPhosAu(MeCN)SbF_6	DMF	60	24	—[d]	—
3	JohnPhosAu(MeCN)SbF_6	CH_2Cl_2	r.t.	8	-	—
4	JohnPhosAu(MeCN)SbF_6	CH_2Cl_2	60	2	99	60/40
5	JohnPhosAu(MeCN)SbF_6	$CHCl_3$	60	4	99	62/38
6	JohnPhosAu(MeCN)SbF_6	1,4-Dioxane	60	3	99	76/24
7	CyJohnPhosAuCl/$AgSbF_6$	CH_2Cl_2	r.t	3.0	—[d]	—
8	CyJohnPhosAuCl/$AgSbF_6$	CH_2Cl_2	60	2.0	99	72/28
9	XPhosAuCl/$AgSbF_6$	CH_2Cl_2	r.t.	2.0	99	67/33
10	SPhosAuCl/$AgSbF_6$	CH_2Cl_2	r.t.	3.0	99	70/30
11	RuPhosAuCl/$AgSbF_6$	CH_2Cl_2	r.t.	3.0	99	70/30
12	 **L1**	CH_2Cl_2	r.t.	1	98	93/7
13		CH_2Cl_2	r.t.	24	—	—
14		CH_2Cl_2	r.t.	24	—[d]	—
15		CH_2Cl_2	r.t.	14	96	95/5
16		CH_2Cl_2	r.t.	24	32	90/10
17		CH_2Cl_2	60	1.5	87	90/10
18		CH_2Cl_2	r.t.	6	96	95/5
19		CH_2Cl_2	r.t	24	93	92/8
20		CH_2Cl_2	r.t	1.5	96	90/10
21		CH_2Cl_2	r.t.	24	57[e]	91/9
22		CH_2Cl_2	r.t.	24	—[d]	—
23	$AgSbF_6$	CH_2Cl_2	60	4	—[d]	—
24	$AgSbF_6$/PPh_3	CH_2Cl_2	60	4	—[d]	—
25	$PdCl_2(MeCN)_2$	MeCN	80	24	—[d]	—
26	$NaAuCl_4$ H_2O	$BMIMBF_4$	120	48	—[d]	—

[a] Unless otherwise stated, reactions were carried out on a 0.3 mmol scale using 0.02 equiv. of catalyst in 2.0 mL of solvent. [b] Overall yield values are related to a mixture of the two isomers obtained after filtration on a SiO_2 pad. [c] Isomeric ratios were calculated from the ^{1}H NMR analyses. [d] Starting alkyne recovered in almost quantitative yield. [e] The starting alkyne was recovered in 43% yield.

Table 2 Au(I)-Catalyzed intramolecular hydroarylation of 7-(prop-2-yn-1-yloxy)-2*H*-chromen-2-one derivatives[a]



1 2 3

[Au] = JohnPhosAu(MeCN)SbF_6 = **A** (2 mol %)

[Au] = PPh_3AuCl + $AgSbF_6$ = **B** (2 mol %)

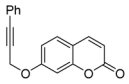
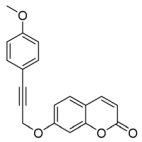
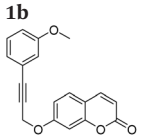
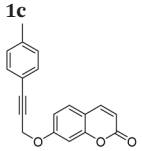
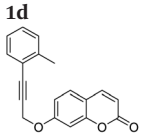
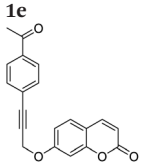
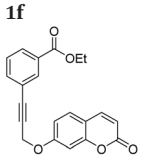
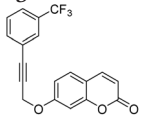
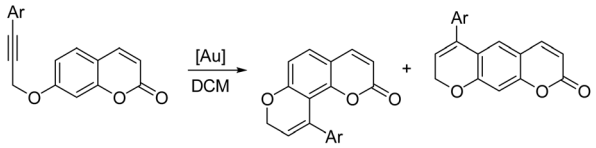
Entry	Starting **1**	Catalyst	*T* (°C)	Time (h)	Yield[b] (%)	Ratio[c] **2**/**3**
1	 **1a**	**A**	60	3	99	60/40
2	**1a**	**B**	r.t.	3	96	95/5
3	 **1b**	**A**	60	1	99	15/85
4	**1b**	**B**	r.t.	5	99	77/23
5	 **1c**	**A**	60	1	99	80/20
6	**1c**	**B**	r.t.	8	90	92/8
7	 **1d**	**A**	60	24	99	43/57
8	**1d**	**B**	r.t.	2	93	86/14
9	 **1e**	**A**	60	48	26[d]	85/15
10	**1e**	**B**	r.t.	3	99	84/16
11	 **1f**	**A**	60	3	92	85/15
12a	**1f**	**B**	r.t.	5	94	85/15
12b[e]	**1f**	**B**	r.t.	12	70	75/25
13	 **1g**	**A**	60	1	99	80/20
14	**1g**	**B**	r.t.	5	95	88/12
15	 **1h**	**A**	60	24	99	77/23

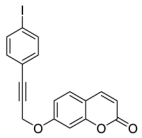
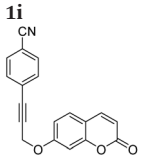
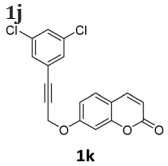
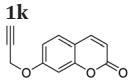
Table 2 *(Contd.)*



1 2 3

[Au] = JohnPhosAu(MeCN)SbF_6 = **A** (2 mol %)

[Au] = PPh_3AuCl + $AgSbF_6$ = **B** (2 mol %)

Entry	Starting **1**	Catalyst	*T* (°C)	Time (h)	Yield[b] (%)	Ratio[c] **2**/**3**
16	**1h**	**B**	r.t	2	93	94/6
17	 **1i**	**A**	60	48	67[f]	65/35
18	**1i**	**B**	r.t.	3	99	90/10
19	 **1j**	**A**	60	48	92	85/15
20	**1j**	**B**	r.t.	24	15[g]	85/15
21	 **1k**	**A**	60	3	97	84/16
22	**1k**	**B**	r.t.	3	99	84/16
23	 **1l**	**A**	60	1	99	63/37
24	**1l**	**B**	r.t.	24	65[h]	65/35

[a] Unless otherwise stated, reactions were carried out on a 0.3 mmol scale using 0.02 equiv. of a catalyst in 2.0 mL of CH_2Cl_2. [b] Overall yield values are related to a mixture of the two isomers obtained after filtration on a SiO_2 pad. [c] Isomeric ratios were calculated from the ^{1}H NMR analyses. [d] The starting alkyne was recovered in 73% yield. [e] Reaction carried out in 2 mL of $CHCl_3$. [f] The starting alkyne was recovered in 30% yield. [g] The starting alkyne was recovered in 90% yield. [h] The starting alkyne was recovered in 10% yield.

dioxane a slight increase in the ratio **2a**/**3a** was observed (Table 1, entries 5 and 6).

In order to enhance the regioselective control, we decided to explore various cationic Au(I) catalysts.[25,34]

A variety of Au(I)complexes have been screened generating *in situ* the active catalysts by the combined use of LAuCl (L = dialkylbiaryl phosphine ligands or alkyldiaryl phosphine ligands or triarylphosphine ligands) and $AgSbF_6$. In the presence of different dialkylbiaryl phosphine Au(I) complexes, almost similar results were reported (Table 1, entries 7–11). Switching to the electron-deficient tris(2,4-di-*tert*-butylphenyl) phosphite ligand led to selective cyclization at the C-8 position of the starting umbelliferone derivative (Table 1, entry 12) giving 98% yield. This result suggested that the electron-deficient ligand might favor IMHA in accordance with a Friedel–Crafts type reactivity by enhancing the electrophilic nature of the gold center.[35] Surprisingly, the reaction completely failed both with tris-(pentafluorophenyl)phosphine gold(I) chloride/$AgSbF_6$ (Table 1, entry 13) and with tri(furan-2-yl) phosphine gold chloride/$AgSbF_6$ (Table 1, entry 14). By contrast, the formation of 10-phenyl-2*H*,8*H*-pyrano[2,3-*f*]-2-one **2a** was observed in high yield and with good regioselectivity with the gold(I) catalyst bearing tris-(4-chlorophenyl)-phosphine, triphenylphosphine, and methyldiphenylphosphine (Table 1, entries 15–20). Particularly, the $Ph_3PAuCl/AgSbF_6$ catalytic system revealed remarkable applicability for the regioselective formation of complex coumarins useful as neuroimaging agents.[36] Moreover, triphenylphosphine-gold(I) catalysis provided better results in terms of yield and selectivity compared to the platinum-catalyzed IMHA of functionalised propargyl ethers.[37]

Further optimization studies revealed that worse results are obtained by replacing $AgSbF_6$ with $AgNTf_2$, as the activator of the gold precatalyst (Table 1, entry 21). Control experiments

with either the gold catalyst alone or the silver salt showed no conversions (Table 1, entries 22–24).

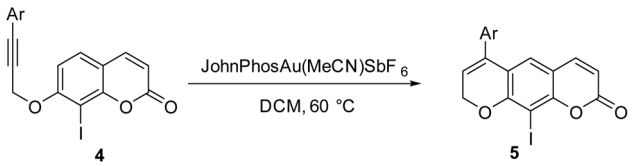
IMHA failed in the presence of $NaAuCl_4$ $2H_2O$ using [bmin] BF_4 as the reaction medium (Table 1, entries 26).[38] Also the activity of other metal catalysts was evaluated. The reaction conducted in the presence of a Pd(II) catalyst did not provide any product, and the starting materials were quantitatively recovered after 4 h in MeCN at 80 °C (Table 1, entry 16).[39,40]

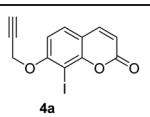
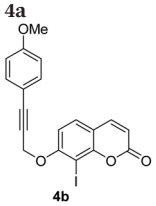
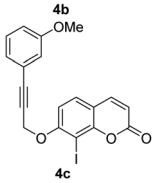
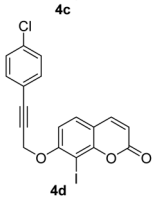
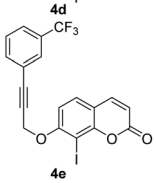
We next compared the effect of JohnPhosAu(MeCN)SbF_6 (**A**) and $Ph_3PAuCl/AgSbF_6$ (**B**) catalytic systems on the control of the regioselective outcome of the IMHA reaction of a variety of 7-((3-arylprop-2-yn-1-yl)oxy)-2*H*-chromen-2-ones **1** in terms of aryl ring substitution (Table 2). In agreement with the gold(I)-catalyzed IMHA of [(3-arylprop-2-ynyl)oxy]-benzene derivatives,[32] reactions were carried out under air, and rigorous exclusion of moisture was unnecessary. It is worth noting that only products derived from the 6-*endo* cyclization of substrate **1** were observed: in fact, no benzofuran by-products[41] and dimeric derivatives[42] were detected during the cycloisomerization reactions. By using catalyst **A** (2 mol%), the cyclization of derivatives **1a–l** was quite general and proceeded smoothly at 60 °C in excellent yields, while the presence of *ortho*-methyl group was detrimental to furnishing the IMHA products in 25% overall yield (Table 2, entry 9). Only substrate **1b** bearing an Ar substituted with the –OMe group at the *para* position showed the prevalent formation of 6-substituted-2*H*,8*H*-pyrano[3,2-*g*]chromen-2-ones **3b** (Table 2, entry 3). Conversely, regioisomer **2b** was isolated with good regioselectivity in the presence of catalytic system **B** (Table 2, entry 4). It was previously shown that ion pairing to a small noncoordinating counter ion such as SbF_6^- can influence the regioselective outcome of the gold-catalyzed IMHA reactions.[43] Considering that Au(I) complexes were reported to form tight ion pairs with their counterions in solvents with $\varepsilon \leq 5$,[44,45] we carried out the catalytic IMHA with catalyst **B** of **1c** also in $CHCl_3$ with surprisingly disappointing results (Table 1, entry 5 and Table 2, entry 12b). For the purpose of exploring the scope of the gold–silver system **B**, we employed milder room temperature conditions with a 2 mol% loading. The catalytic IMHA of substrates **1a–k** showed excellent tolerance for both the functional groups and steric hindrance. The cyclization of substrate **1** proceeded generally with good regioselectivity affording the more sterically congested product **2**.[46] Better selectivity was observed in the presence of electron-withdrawing substituents in the aryl moiety, although a low yield occurred with the *p*-CN substituent (Table 2, entry 20).

The regioselective outcome of substrates containing *ortho*-substituted aryl rings, as well as of the unsubstituted propargylic aryl ether **1l**, was comparable to both the catalytic systems **A** and **B** (Table 2, entries 9–10 and 23–24). The formation of isomer **2** increases with the increased electron-withdrawing effect of the substituents on the aryl moiety (Table 2 entries 1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21 and 23). By using the less hindered PPh_3 ligand, isomer **2** formation significantly prevails on isomer **3** in all the cases. These data seem to indicate that under these conditions, the coumarin ring reacts according to its natural reactivity being more nucleophilic at C8, as for example observed in the regioselective C8 umbelliferone iodination.[47] Furthermore, this view is supported by the ^{13}C NMR spectra of compounds **1a–l** in which the signal of C8 appears more shielded than the C6 signal.[48]

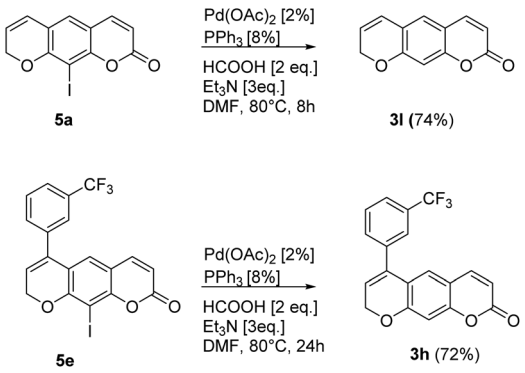
To examine the limits of this hydroarylative cyclization and to force the formation of regioisomer **3**, we prepared 8-iodo-2*H*-chromen-2-one derivatives **4a–e**. Their IMHA with catalyst **A** under the optimized conditions led to the corresponding 10-iodo-2*H*,8*H*-pyrano[3,2-*g*] chromen-2-one derivatives **5a–e** in high yields, (Table 3). To evaluate the possible use of the cheaper PPh_3 ligand, we compared the efficiency of both catalysts **A and B** in the annulation reaction of **4a**. The formation

Table 3 IMHA of 8-iodo-7-(prop-2-yn-1-yloxy)-2*H*-chromen-2-one derivatives[a]



Entry	Starting **4**	Time (h)	Yield[b] (%)
1	 **4a**	1	90
2	**4a**	6	70[c]
3	 **4b**	3.5	98
4	 **4c**	3	99
5	 **4d**	5	96
6	 **4e**	6	98

[a] Unless otherwise stated, reactions were carried out on a 0.3 mmol scale using 0.02 equiv. of JohnPhosAu(MeCN)SbF_6 in 2.0 mL of CH_2Cl_2 at 60 °C. [b] Yields refer to the isolated products. [c] Reaction was carried out using $Ph_3PAuCl/AgSbF_6$ as a catalyst (catalyst **B**); the starting **4a** was recovered in 28% yield.



Scheme 2 Pd-Catalyzed reduction of the C–I bond of **5a** and **5e**.

of **5a** occurred in a lower yield when catalyst **B** was used instead of A at 60 °C, while no interconversion of **4a** was observed with this latter catalyst at r.t. (Table 3, entries 1 and 2).

The following palladium-catalyzed selective reduction of the C–I bond by ammonium formate, carried out on **5a** and **5e** derivatives, led to the desired 2*H*,8*H*-pyrano[3,2-*g*] chromen-2-one derivatives in good yields (Scheme 2).[49]

Conclusions

In conclusion, we have developed a regioselective intramolecular hydroarylation of 7-(prop-2-yn-1-yloxy)-2*H*-chromen-2-one derivatives to afford 10-substituted-2*H*,8*H*-pyrano[2,3-*f*] chromen-2-ones by means of Au(I) catalysis. The regioselective outcome of the cyclization is established through fine-tuning the electronic and steric effects of the ligands of gold complexes. The $Ph_3PAuCl/AgSbF_6$ catalytic system accomplished the formation of the 10-substituted-2*H*,8*H*-pyrano[2,3-*f*] chromen-2-ones in general in good to excellent yields under mild conditions with compatibility with many functional groups, although the procedure was found to be sensitive to some extent to the electronic and steric effects of the arene substituents. The exclusive formation of the 2*H*,8*H*-pyrano[3,2-*g*]chromen-2-one regioisomers was allowed by combining the JohnPhosAu(MeCN)SbF_6 catalyzed intramolecular hydroarylation of 8-iodo-7-(prop-2-yn-1-yloxy)-2*H*-chromen-2-one derivatives with selective C–I reduction by the palladium/formate system.

Experimental

A list of chemicals and instrumentation is provided in the ESI.†

Typical procedure for the preparation of 7-(3-phenylprop-2-ynyloxy)-2*H*-chromen-2-one 1a

A flask equipped with a magnetic stirring bar was charged with $PdCl_2(PPh_3)_2$ (49 mg, 0.07 mmol, 0.02 equiv.) and CuI (26.5 mg, 0.14 mmol, 0.04 equiv.) dissolved in diisopropylamine (7 mL) and *N*,*N*-dimethylformamide (5 mL). The resultant solution was stirred under nitrogen at room temperature for 10 minutes before adding iodobenzene (714 mg, 3.5 mmol, 1.0 equiv.) in diisopropylamine (3 mL) and 7-(prop-2-ynyloxy)-2*H*-chromen-2-one (841 mg, 4.2 mmol, 1.2 equiv.) and stirred for 3 hours at room temperature. After this, the reaction mixture was diluted with Et_2O and washed with a saturated NH_4Cl solution and with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by chromatography on SiO_2 (25–40 μm), eluting with an 80/20 (v/v) *n*-hexane/AcOEt mixture (R_f = 0.24) to obtain 870 mg (90% yield) of 7-(3-phenylprop-2-ynyloxy)-2*H*-chromen-2-one **1a**.

1a[50]: white solid; mp: 140–142 °C; IR (KBr): 2963, 2219, 1711, 1615, 1506, 1488, 1209 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.67 (d, J = 9.5 Hz, 1 H), 7.47–7.28 (m, 6 H), 7.03 (d, J = 2.4 Hz, 1 H), 6.98 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 6.29 (d, J = 9.5 Hz, 1 H), 5.00 (s, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 161.1, 160.9, 155.7, 143.3, 131.9, 129.0, 128.8, 128.4, 121.8, 113.5, 113.2, 113.1, 102.2, 88.2, 82.6, 57.1; MS (EI ion source): *m*/*z* (%) = 276 (100, [M^+]), 247 (32), 199(15), 63.00 (43).

Typical procedure for the preparation of 2a/3a

A flask equipped with a magnetic stirring bar was charged with 7-(3-phenylprop-2-ynyloxy)-2*H*-chromen-2-one (82.9 mg, 0.3 mmol, 1 equiv.) and CH_2Cl_2 (2 mL) before adding catalyst **A** or catalyst **B** (catalyst **A**: JohnPhosAu(MeCN)SbF_6 4.6 mg, 0.006 mmol, 0.02 equiv.; catalyst **B**: Ph_3PAuCl 3.0 mg, 0.006 mmol, 0.02 equiv. and $AgSbF_6$ 2.1 mg, 0.006 mmol, 0.02 equiv.). The resulting mixture was stirred for 3 hours, then it was concentrated under reduced pressure and the residue was filtered on a pad of SiO_2 to afford 81.8 mg of **2a** + **3a** (99% overall yield) using catalyst **A** or 79.5 mg of **2a** + **3a** (96% overall yield) using catalyst **B**. The **2a**/**3a** ratio was calculated from the ^1H NMR analyses. Afterwards, the two isomers were separated by semi-preparative HPLC to obtain suitable NMR spectra of each compound.

Overall yield (catalyst **A**): 99% (81.8 mg); **2a**/**3a** = 60/40

Overall yield (catalyst **B**): 96% (79.5 mg); **2a**/**3a** = 95/5

2a: white solid; mp: 170–172 °C; IR (KBr): 3060, 2922, 1702, 1593, 1480, 1402, 1343, 1232 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.59 (d, J = 9.5 Hz, 1 H), 7.40–7.39 (m, 3 H), 7.34 (d, J = 8.4 Hz, 1 H), 7.28–7.26 (m, 2 H), 6.96 (d, J = 8.4 Hz, 1 H), 6.15 (d, J = 9.5 Hz, 1 H), 5.96 (t, J = 4.5 Hz, 1 H), 4.81 (d, J = 4.5 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.6, 159.2, 150.9, 143.6, 139.2, 135.1, 128.6, 128.1, 127.7, 127.2, 121.9, 113.9, 113.5, 113.2, 112.3, 65.3; MS (EI ion source): *m*/*z* (%) = 276 (21 [M^+]), 207 (16), 135 (11), 73 (100); HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{10}N$: 180.0808; found: 180.0808.

3a: solid; mp: 163–164 °C; IR (KBr): 3076, 2818, 1734, 1620, 1487, 1401 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.51–7.43 (m, 4 H), 7.36–7.34 (m, 2 H), 7.06 (s, 1 H), 6.83 (s, 1 H), 6.22 (d, J = 9.5 Hz, 1 H), 5.83 (t, J = 3.8 Hz, 1 H), 5.01 (d, J = 3.8 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 161.0, 158.3, 155.3, 143.5, 137.6, 135.6, 128.7, 128.5, 128.3, 124.6, 120.7, 120.3, 113.4, 113.0, 104.4, 66.1; MS (EI ion source): *m*/*z* (%) = 276

(7 [M^+]), 207 (16), 135 (11) 73 (100); HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{10}N$: 180.0808; found: 180.0808.

Conflicts of interest

There are no conflicts to declare.

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