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Gold-catalyzed cyclization of propargylic diynes: Ethers *vs* acetates – Related products but different pathways

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Dedicated to Prof. Hubert Schmidbaur on the occasion of his 80th birthday.

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ABSTRACT

Diyne substrates bearing one propargylic ether instead of the previously published propargylic acetates were subjected to a gold catalyst. α–Naphthol derivatives were obtained as products of the cycloisomerization. The close relationship of the products to the corresponding cyclizations implicated a related mechanistic scenary at first, but further studies favour a mechanistic pathway that is completely different.

1. Introduction

In the highly active field of homogeneous gold catalysis [1], diynes are gaining importance as starting materials for gold-catalyzed transformations. The common reaction principles are dual gold-catalyzed transformations [2], reactions in which one of the alkynes is transferred into a nucleophilic part which then undergoes a subsequent cyclization with the remaining alkyne [3] and carbene transfer reactions in which an alkyne-derived gold carbenoid is transferred over a pendant alknye followed by classical carbenoid transformations as terminating step [4].

During our studies on the gold-catalyzed transformation of 1,6-diynes **1** and **3**, we observed a completely different reactivity which depended on the oxygen functionalities (Scheme 1). While in the case of an unprotected propargylic alcohol a complex cascade, that is most probably initiated by an attack of the nucleophilic oxygen onto the triple bond, delivered β-keto-naphtalines **2** as the products [5], a completely different picture was obtained for the corresponding acetate derivatives [4c,d,g]. In this case an initial 1,2-migration of the acetal and a subsequent transfer of the so formed gold carbenoid delivered β-naphtole derivates **4** as final products of the reaction cascade. Inspired by this strong influence of the oxygen functionality in the precursors, we considered the incorporation of ether moieties in the starting materials **5** as well. As these precursors are not known to deliver gold carbenoids and in addition due to the increased sterical bulkiness of the methoxy group a nucleophilic addition pathway should be less favoured, we were curious if an alternative reaction pathway might be opened for this type of reactants. The results of our studies will be discussed in this contribution.

2. Results and discussion

Appropriate starting materials for our investigations were prepared via Sonogashira coupling of the corresponding bromoaldehydes, addition of an ethynyl Grignard reagent to the aldehyde and alkylation of the obtained propargylic alcohols (see SI for further details). Initial tests were conducted with model diyne **5a**. The results with different catalyst are summarized in Table 1. With the well established $IPrAuNTf_2$ catalyst, complete conversion was monitored and 88% yield of a single product could be obtained

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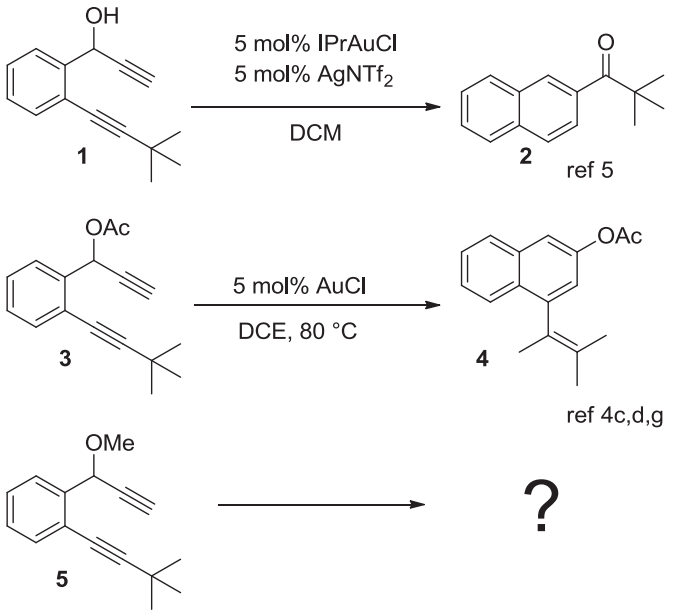
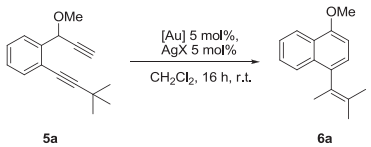
0022-328X/



Scheme 1. Known reactivity patterns for oxygen-substituted diynes **1** and **3** and our planned investigation.

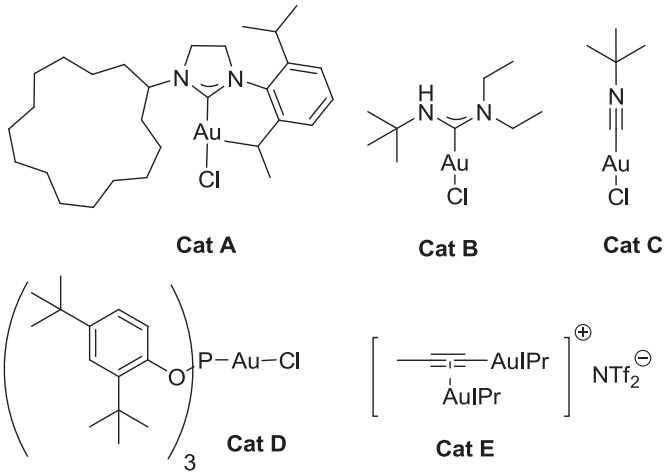
(Entry 1). NMR analysis revealed that no migration of the methoxy group had taken place and an α-naphthol **6a** was obtained as product. The structure of the cycloisomerized product shows a strong relationship to that of carbene migration products **4**. Like in the case of substrates **3**, a methyl group migration also takes place in this case which finally delivers a tetra-substituted double bond in the products. Further experiments revealed that simple AuCl and $NaAuCl_4$ cannot efficiently catalyze the transformation (Entries 2 and 3). Much better results were obtained with **Cat A** [6] (Scheme 2), a NHC complex with a large 15-membered ring

Table 1
Catalyst screening.



Entry[a]	[Au]	AgX	Conversion [%]	Yield [%]
1	$IPrAuNTf_2$		100	88
2	AuCl		49	18
3	$NaAuCl_4$		29	0
4	**Cat A**	$AgNTf_2$	100	80
5	**Cat B**	$AgNTf_2$	95	59
6	**Cat C**	$AgNTf_2$	70	27
7	SPhosAuCl	$AgNTf_2$	100	88
8	XPhosAuCl	$AgNTf_2$	100	80
9	PPh_3AuNTf_2		37	0
10	**Cat D**	$AgNTf_2$	100	74
11	**Cat E**		37	0
12		$AgNTf_2$	43	6
13	$IPrAuNTf_2$		100	38[b]
14	IPrAuCl	$AgPF_6$	100	15
15	IPrAuCl	$AgSbF_6$	19	1
16	IPrAuCl	$AgBF_4$	53	15
17	IPrAuCl	AgOTf	16	2

[a] 80 μmol **5a**, 5 mol% gold catalyst and 5 mol% silver salt were stirred in CH_2Cl_2 (4 ml) at rt; after 16 h conversions and yield were determined by GC using *n*-dodecan as internal standard.
[b] tenfold concentration (0.2 M).



Scheme 2. Applied catalysts.

besides the one IPr-substituent (Entry 4). A simpler NAC complex (**Cat B**) [7] only delivered moderate yield (Entry 5) and isonitrile complex **Cat C** showed no full conversion (Entry 6). In a series of phosphane ligands very good results were obtained with sterically shielded Buchwald type ligands SPhos and XPhos (Entries 7 and 8), while simple $Ph_3PAuNTf_2$ turned out to be inefficient (Entry 9). The phosphite complex **Cat D** also catalyzed the transformation but yields were only moderate (Entry 10). As due to the terminal alkyne in the substrate a dual activation pathway cannot be ruled out, a test reaction was conducted in the presence of dual activation catalyst **Cat E** (Entry 11) [8]. The poor result for this catalyst class gives a clear hint that a dual activation pathway is unlikely for this transformation. A control experiment with only $AgNTf_2$ showed only low conversion and only a trace of the desired product was obtained (Entry 12). A tenfold increase of the substrate concentration led to a significant drop in yield (Entry 13) and a screening of different counter ions in combination with the IPr complex was unsuccessful (Entries 14–17).

With the optimized conditions in hand we turned our focus on the evaluation of the substrate scope of the cycloisomerization (Table 2). A preparative scale of the reaction with diyne **5a** delivered the corresponding naphthol derivate **6a** in 78% yield (Entry 1). The installation of two electron-donating methoxy groups in the aromatic backbone of starting material **5b** led to a significant drop in yield and the corresponding product was only obtained in 47% yield (Entry 2). Fortunately, we were able to obtain crystals suitable for X-ray crystal structure analysis. The obtained solid state molecular structure unambiguously verifies the assignment of the obtained α-naphthol structure bearing a tetra-substituted double bond in *peri*-position (Fig. 1). Substrates **5c** and **5d** with only one donating methoxy or methyl group in the backbone delivered good to excellent results again (Entry 3 and 4), while only a low yield was obtained with acetal protected starting material **5e** (Entry 5). Electron-withdrawing groups were tolerated well, no matter if nitro or fluoro groups were installed in the backbone (Entries 6 and 7). As a next step we tested heteroaromatic and nonaromatic backbones. Probably due to the strong coordinating properties of the pyridine no reaction took place for starting material **5h** (Entry 8). The conversion of thiophene substrate **5i** only led to an inseparable mixture of products. In the case of substrates **5j** and **5k** with cyclic aliphatic backbones, the 5-membered ring turned out to be completely unreactive even at 80 °C (Entry 10), while in the case of the 6-membered homologue, a slow conversion delivered the desired product **6k** in low yield (Entry 11). Next we probed the possibility to vary the non-terminal alkyne substituent but none of

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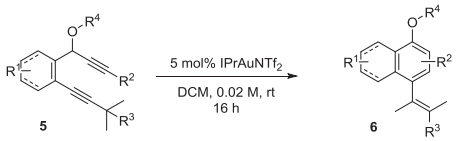
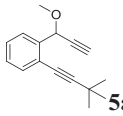
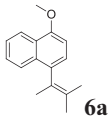
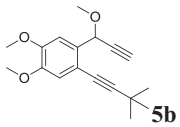
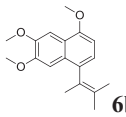
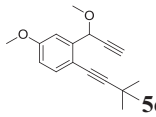
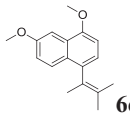
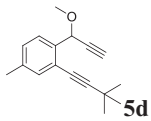
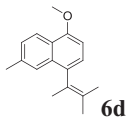
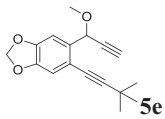
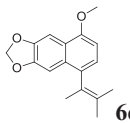
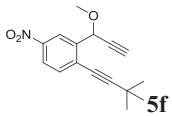
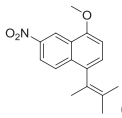
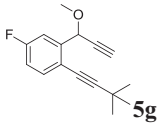
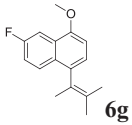
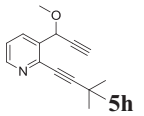
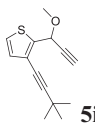
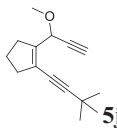
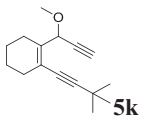
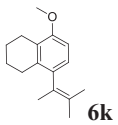
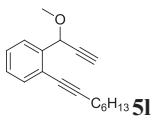
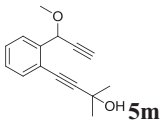
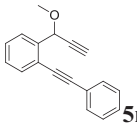
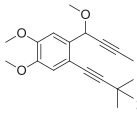
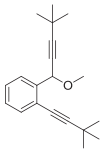
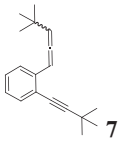
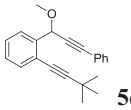
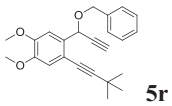
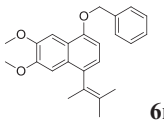
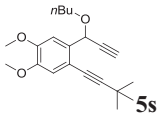
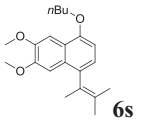
Table 2
Substrate scope.



Entry	Starting material	Product	Yield [%][a]	^{1}H NMR data for **6** in $CDCl_3$ (ppm values)
1	 **5a**	 **6a**	78	1.40 (s, 3H), 1.92 (s, 3H), 2.00 (s, 3H), 4.00 (s, 3H), 6.79 (d, 7.8 Hz, 1H), 7.09 (d, 7.8 Hz, 1H), 7.43–7.48 (m, 2H), 7.72–7.75 (m, 1H), 8.27–8.29 (m, 1H).
2	 **5b**	 **6b**	47	1.42 (s, 3H), 1.93 (s, 3H), 2.00 (s, 3H), 3.94 (s, 3H), 3.99 (s, 3H), 4.02 (s, 3H), 6.70 (7.8 Hz, 1H), 6.96 (d, 7.8 Hz, 1H), 7.02 (s, 1H), 7.56 (s, 1H).
3	 **5c**	 **6c**	74	1.31 (s, 3H), 1.82 (s, 3H), 1.90 (s, 3H), 3.87 (s, 3H), 3.92 (s, 3H), 6.70 (d, 7.9 Hz, 1H), 6.78 (d, 7.9 Hz, 1H), 7.04 (dd, 9.0 Hz, 2.4 Hz, 1H), 7.49 (d, 2.4 Hz, 1H), 7.57 (d, 1H).
4	 **5d**	 **6d**	90	1.42 (s, 3H), 1.94 (s, 3H), 2.00 (s, 3H), 2.50 (s, 3H), 3.99 (s, 3H), 6.72 (d, 7.7 Hz, 1H), 7.05 (d, 7.7 Hz, 1H), 7.29 (dd, 8.5 Hz, 1.6 Hz, 1H), 7.48 (d, 1.6 Hz, 1H), 8.18 (d, 8.5 Hz, 1H).
5	 **5e**	 **6e**	40	1.40 (s, 3H), 1.89 (s, 3H), 1.95 (s, 3H), 3.96 (s, 3H), 6.01 (s, 2H), 6.70 (d, 7.8 Hz, 1H), 6.94 (d, 7.8 Hz, 1H), 7.04 (s, 1H), 7.57 (s, 1H).
6	 **5f**	 **6f**	87	1.37 (s, 3H), 1.93 (s, 3H), 1.98 (s, 3H), 4.04 (s, 3H), 6.90 (d, 7.9 Hz, 1H), 7.29 (d, 7.9 Hz, 1H), 7.82 (d, 9.2 Hz, 1H), 8.18 (dd, 9.2 Hz, 2.4 Hz, 1H), 9.23 (d, 2.4 Hz, 1H).
7	 **5g**	 **6g**	83	1.38 (s, 3H), 1.91 (s, 3H), 1.98 (s, 3H), 3.99 (s, 3H), 6.81 (d, 7.8 Hz, 1H), 7.04 (d, 7.8 Hz, 1H), 7.21 (ddd, 10.8 Hz, 9.2 Hz, 2.7 Hz, 1H), 7.72 (dd, 9.2 Hz, 5.7 Hz, 1H), 7.87 (dd, 10.7 Hz, 2.7 Hz, 1H).
8	 **5h**	-	no reaction	_
9	 **5i**	-	unselective	_
10	 **5j**	-	no reaction	_
11	 **5k**	 **6k**	32[b]	1.41 (s, 3H), 1.68–1.78 (m, 4H), 1.79 (s, 3H), 1.84 (s, 3H), 2.50 (t, 2H), 2.68 (t, 6.4 Hz, 2H), 3.81 (s, 3H), 6.64 (d, 8.2 Hz, 1H), 6.77 (d, 8.2 Hz, 1H).
12	 **5l**	-	unselective	_

(*continued on next page*)

Table 2 (*continued*)

Entry	Starting material	Product	Yield [%][a]	^{1}H NMR data for **6** in $CDCl_3$ (ppm values)
13	 **5m**	-	unselective	_
14	 **5n**	-	unselective	_
15	 **5o**	-	unselective	_
16	 **5p**	 **7**	20[c]	_
17	 **5q**	-	unselective	_
18	 **5r**	 **6r**	15	1.43 (s, 3H), 1.92 (s, 3H), 2.00 (s, 3H), 3.94 (s, 3H), 4.00 (s, 3H), 5.25 (s, 2H), 6.77 (d, 7.8 Hz, 1H), 6.95 (d, 7.8 Hz, 1H), 7.04 (s, 1H), 7.35 (t, 7.2 Hz, 1H), 7.42 (t, 7.2 Hz, 2H), 7.53 (d, 7.2 Hz, 2H), 7.64 (s, 1H).
19	 **5s**	 **6s**	51	1.03 (t, J = 7.4 Hz, 3H), 1.41 (s, 3H), 1.52–1.61 (m, 2H), 1.88–1.93 (m, 5H), 1.99 (s, 3H), 3.93 (s, 3H), 4.01 (s, 3H), 4.13 (t, 6.3 Hz, 2H), 6.69 (d, 7.8 Hz, 1H), 6.92 (d, 7.8 Hz, 1H), 7.01 (s, 1H), 7.58 (s, 1H).

[a] Isolated yield.
[b] Reaction in DCE at 80 °C.
[c] Product mixture with allene **7** as main product.

the substrates showed a selective reaction course (Entries 12–14). Unfortunately this was also the case for substrates bearing non-terminal alkynes at the propargylic moiety (Entries 15–17). In this case the only product that could be identified was allene **7** that can be explained by a 1,5-hydride shift with subsequent elimination of formaldehyde, a sequence that is in analogy to an allene synthesis reported by the Gagosz group [9]. Finally the role of the ether substituent was investigated. A lower yield was obtained with benzylic ether **5r** which might be explained by competing hydride shift pathways that are favoured in the case of a benzylic position (Entry 18). Substrate **5s** with a butyl ether moiety delivered comparable yields to its methyl ether derivative **5b** again (Entry 19).

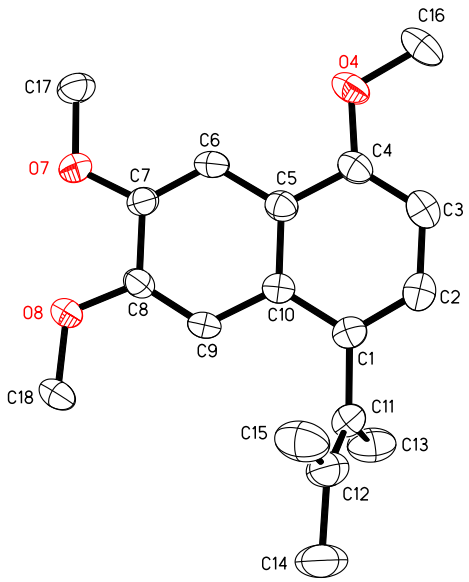


Fig. 1. Solid state molecular structure of compound **6b**.

As the obtained product of the transformation strongly resembled the structure of the carbene transfer products **4** derived from propargylic acetates (compare Scheme 1), we considered that a related pathway might have taken place for methoxy substituted diynes as well (Scheme 3, upper part). Coordination to the terminal triple bond by the gold catalyst and a subsequent hydride shift [10] might deliver acceptor-substituted vinyl gold species **IIa** which in another mesomeric form can be regarded as carbenoid **IIb** [11]. The subsequent steps (carbene transfer and 1,2-methylshift) would be in complete accordance to our previous results with the acetate precursors [4c]. Even if this mechanistic picture cannot be completely ruled out, it is not explainable that starting materials like substrate **5m**, which formed the corresponding products in the case of a propargylic acetates [4g], turned out to be unsuitable for this reaction. Besides the limitation to a *tert*-butyl substituent at the alkyne, it is not explainable that substrates bearing two non-

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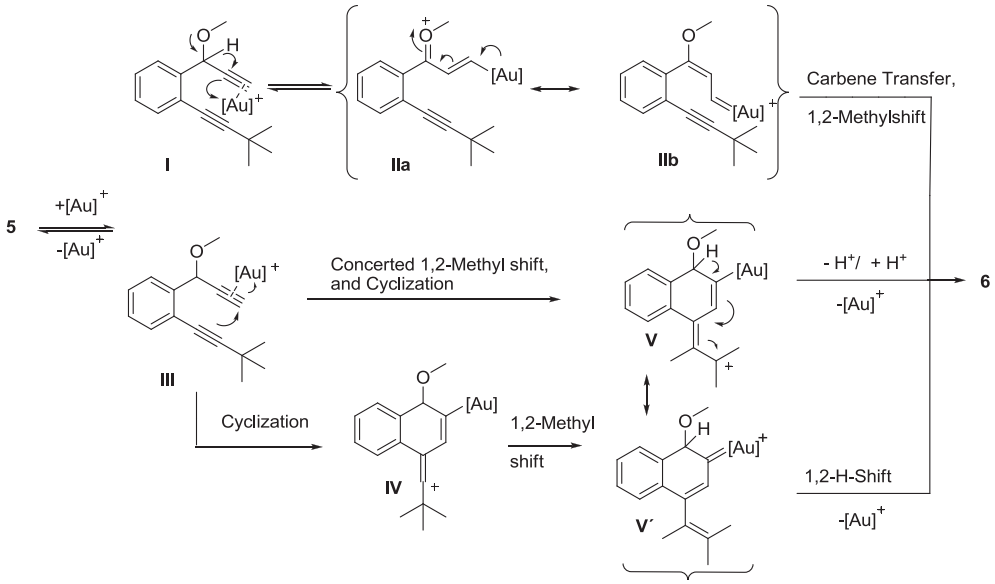
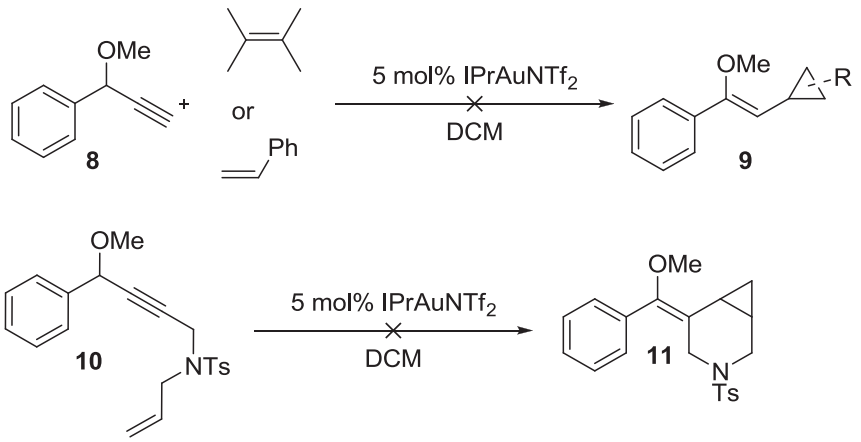


Scheme 3. Possible mechanistic scenarios.



Scheme 4. Control experiment with propargylic ethers **8** and **10**.

terminal alkyne substituents were unsuitable substrates as well. To evaluate if a carbenoid species can be generated from propargylic ethers, we converted methyl-propargylicether **8** under the reaction conditions in the presence of externally offered alkenes (Scheme 4, upper part). No cyclopropanation products **9** could be obtained which makes it unrealistic that carbenoids can be formed by this precursors [12]. Even the intramoleculary offered alkene in compound **10** did not deliver any cyclopropanation product under the standard conditions (Scheme 4, upper part). Based on this finding, we postulate a mechanism in which the *tert*-butyl alkyne reacts as a nucleophile under generation of vinyl cation **III** that can be stabilized by the attached *tert*-butyl group by hyperconjugation. A subsequent 1,2-methyl shift followed by rearomatization of intermediate **IV** would then deliverer the product after protodemetalation of the gold fragment. Besides the stepwise formation of intermediate **V**/**V′** a concerted pathway including 1,2-methyl shift and cyclization is also a reasonable alternative.

3. Conclusion

In conclusion we could demonstrate that propargylic ethers can be applied as substrates for diyne cylizations, too. Despite the strong relationship of the products to the corresponding acetate starting materials, the scope for this transformation is not that broad. This might be explained by a completely different reaction pathway that is based on the nucleophilic addition of the second alkyne moiety instead of a carbene transfer pathway. This might open up new possibilities for the design of new gold-catalyzed reactions.

4. Experimental Section (see SI for further informations)

All reagents and solvents were obtained from Acros, ABCR, Alfa Aesar, Sigma–Aldrich or VWR and were used without further purification unless otherwise noted. Deuterated solvents were purchased from Euriso-Top. Absolute solvents were dried by a MB SPS-800 with the aid of drying columns. Preparation of air- and moisture-sensitive materials was carried out in flame dried flasks under an atmosphere of nitrogen using Schlenk-techniques. Thin layer chromatography (TLC) was performed using Polygram precoated plastic sheets SIL G/UV_{254} (SiO_2, 0.20 mm thickness) from Macherey–Nagel. Column chromatography was performed using silica gel (40.0–63.0 nm particle size) from Macherey–Nagel. NMR spectra were recorded on Bruker Avance 500, Bruker Avance 300

and Bruker ARX-250 spectrometers. *Chem*ical shifts (in ppm) were referenced to residual solvent protons [13]. Signal multiplicity was determined as s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet). ^{13}C assignment was achieved via DEPT90 and DEPT135 or HSQC-me spectra. MS spectra were recorded on a Vakuum Generators ZAB-2F, Finnigan MAT TSQ 700 or JEOL JMS-700 spectrometer. GC spectra were recorded on HP Agilent 5890 Series II Plus with FID analyser. IR spectra (in cm^{-1}) were recorded on a Bruker Vector 22 FT-IR. Crystal structure analysis was accomplished on a Bruker APEX II Quazar diffractometer [14]. Elemental analysis was performed on an Elementar Vario EL.

Representative Synthesis of **6a**; other products were obtained in a similar fashion (see SI and Table 2).

300 mg (1.32 μmol) **5a** were dissolved in 70 ml DCM. To this solution were added $IPrAuNTf_2$ (57.0 mg, 66.0 μmol, 5 mol%). The reaction mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure. After purification by flash column chromatography (SiO_2, PE), 232 mg (1.03 mmol, 78%) of **6a** were obtained as an yellow oil.

R_f (PE) = 0.37; IR (reflection): $\tilde{\nu}$ = 3064, 2985, 2911, 2855, 1586, 1461, 1421, 1389, 1372, 1323, 1293, 1255, 1236, 1219, 1164, 1081, 1025, 817, 765 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.40 (d, J = 1.3 Hz, 3H), 1.92 (s, 3H), 2.00 (s, 3H), 4.00 (s, 3H), 6.79 (d, J = 7.8 Hz, 1H), 7.09 (d, J = 7.8 Hz, 1H), 7.43–7.48 (m, 2H), 7.72–7.75 (m, 1H), 8.27–8.29 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.0 (q), 21.2 (q), 22.0 (q), 55.4 (q), 103.5 (d), 122.2 (d), 124.8 (d), 124.9 (d), 125.5 (d), 125.7 (s), 126.1 (d), 128.0 (s), 128.9 (s), 132.1 (s), 135.1 (s), 153.8 (s) ppm; MS (EI (+), 70 eV): m/z (%) = 226 (100) $[M]^+$, 211 (75) $[M-CH_3]^+$; HRMS (EI (+), 70 eV): $C_{16}H_{18}O$ calc.: 226.1358, found: 226.1339.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.04.053.

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