Synthetic Methods

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Gold Catalysis: Switching the Pathway of the Furan-Yne Cyclization

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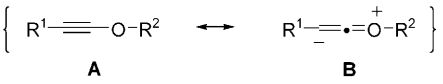
The use of gold compounds as homogeneous catalysts for the conversion of many organic substrates is one of the fastest growing areas in organic chemistry today.[1] Among these transformations, the cyclization of ene–ynes is playing a major role.[2] We developed the gold-catalyzed synthesis of highly substituted phenols, starting from furan–alkyne systems. In this case, as in most of the common ene–yne systems, the first step of the reaction is also initiated by a 5-*exo-dig* cyclization, but because of the furan moiety, a series of subsequent steps (ring opening of the furan system, oxepine-formation, and rearrangement) finally leads to phenolic systems.[3]

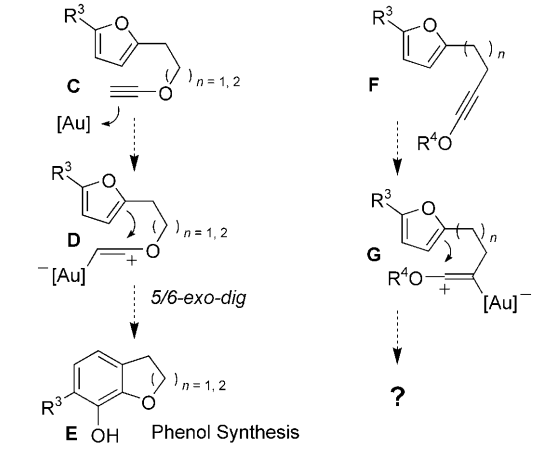
Recently, we investigated the use of ynamide- and alkynylether moieties in the side chain of these systems, which led to a dramatic increase in reaction rates and to higher selectivities (see Scheme 2, left side).[4,5] These effects stem from the highly polarized triple bond that can be formulated as the ketene-like mesomer **B** in Scheme 1.



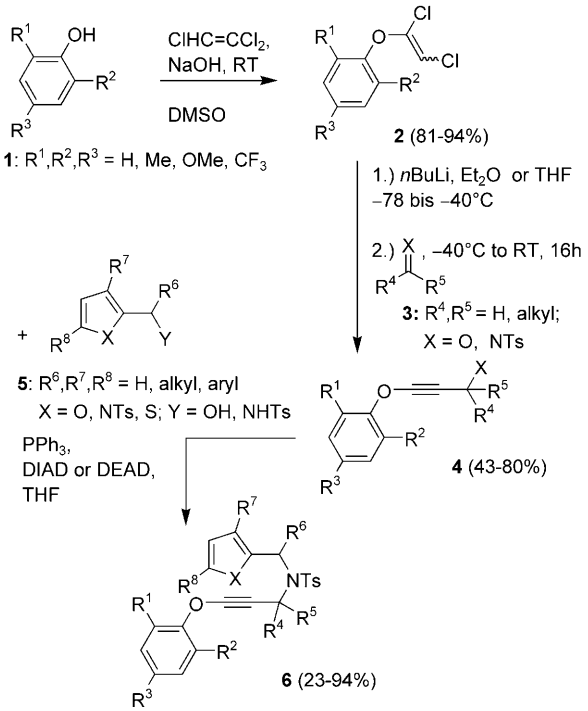
Scheme 1. The highly polarized triple bond of alkynylethers.

As these ether oxygen atom could potentially be used as a directing element to initiate a bonding of the metal atom to the other end of the alkyne moiety in substrates of type **F**, we were eager to explore if this could lead to a totally different reaction pathway, initiated by an *endo-dig*-cyclization in the first reaction step (Scheme 2, right side).

In a highly convergent three-step synthesis, starting from commercially available substrates, we were able to produce a small library of test substrates **6** (Scheme 3). Substituted phenols **1** were converted into the dichlorovinylethers **2**,[6]



Scheme 2. Alkynyl ethers as possible switches for different cyclization modes.



Scheme 3. Preparation of substrates **6**. DMSO = dimethylsulfoxide, DIAD = diisopropylazodicarboxylate, DEAD = diethylazodicarboxylate, Ts = tosylate = *p*-toluenesulfonyl.

transformed into the lithiated alkynes, which were added to carbonyl compounds or imines to deliver propargylamides/alcohols **4**;[7] these were coupled to the heterocyclic products **5** under Mitsunobu conditions.[8]

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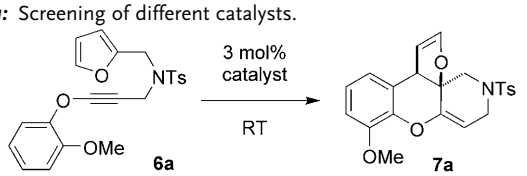
In a catalyst screening, model substrate **6a** could be converted into the tetracyclic system **7a** within minutes by the use of the air-stable $[Mes_3PAu]NTf_2$ catalyst in chloroform (Mes = mesityl, Tf = triflyl; the X-ray crystal-structure analysis[9] of this complex is shown in the Supporting Information). The use of $AuCl_3$ or $[Ad_2(n\text{Bu})PAu]NTf_2$[10] (Ad = adamantyl) led to decomposition, whereas silver tetrafluoroborate and *para*-toluenesulfonic acid did not show any conversion (Table 1). The structure of the tetracyclic product **7a** could be unambiguously determined by X-ray crystal-structure analysis (Figure 1).[9]

Table 1: Screening of different catalysts.



Entry	Catalyst	*t*	Solvent	Yield of **7a**
1	$AuCl_3$	10 min	CH_3CN	–[a]
2	$[Ad_2(n\text{Bu})PAu]NTf_2$	10 min	CH_2Cl_2	–[a]
3	$[Mes_3PAu]NTf_2$	10 min	$CHCl_3$	54%
4	$[Mes_3PAu]NTf_2$	3 h	CH_2Cl_2	44%
5	*p*-TsOH	1 day	$CHCl_3$	–
6	$AgBF_4$	1 day	CH_2Cl_2	–

[a] Decomposition of the starting material.

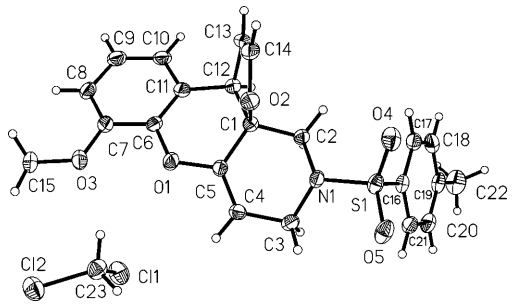


Figure 1. Ortep plot of the solid-state structure of **7a**.

Encouraged by this result, we examined the conversion of substrates **6b**–**6q** under the optimized reaction conditions (Table 2). Even without the activating methoxy group on the phenyl ring of **6a** the cycloisomerization readily proceeds, as demonstrated by the reaction of **6b** (Table 2, entry 1). On the other hand, the electron-withdrawing CF_3 group on the phenyl group of **6c** (Table 2, entry 2) led to a decomposition of the starting material. Not unexpectedly, the blocking of both *ortho*-positions of the phenyl group **6d** (Table 2, entry 3) also led to a decomposition of the substrate. Further limits are electron-rich furan derivatives, such as **6e** (Table 2, entry 4), which like **6a** have the activating methoxy group on the phenyl group but in addition a methyl-donor on the 5-position of the furan ring.

Returning to a monosubstituted furan ring and shifting the activating methoxy group on the phenyl group to the *para*-position in **6f** (Table 2, entry 5) delivered **7f** in good yield. Again, as with **6e**, adding an electron-donating methyl group on the 5-position of the furan ring of **6g** prevented the formation of **7g** (Table 2, entry 6).

Thus we returned to substrates with monosubstituted furan rings, used the *para*-methoxyphenyl group as in **6f** but added a chiral center in propargylic positions. For the small propargylic methyl group in **6h** these 1,4-inductions only led to a diastereoselectivity of 71:29 in **7h** (Table 2, entry 7). With the larger ethyl group in **6i**, as expected, the diastereoselectivity increased to 90:10 for **7i** (Table 2, entry 8), but then unexpectedly with the *tert*-butyl substituent in **6j** dropped to 80:20 for **7j** (Table 2, entry 9). Fortunately, for both diastereomers of **7j** crystals suitable for X-ray structure analysis could be grown (Figure 2).[9] The main diastereomer shows a *trans*-arrangement of the *tert*-butyl group and the dihydrofuran ring.

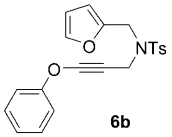
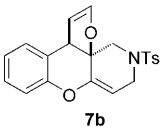
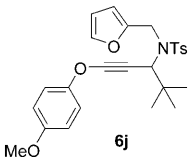
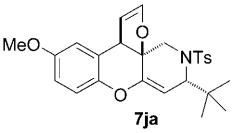
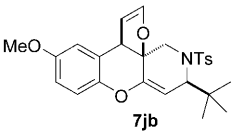
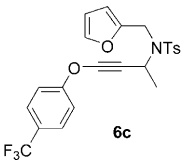
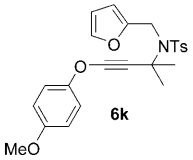
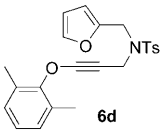
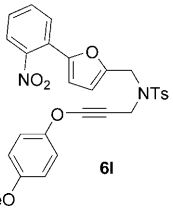
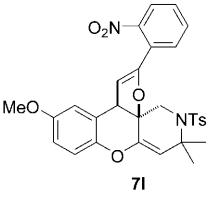
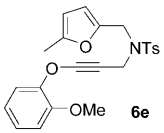
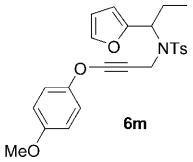
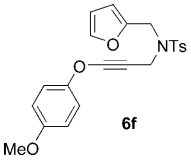
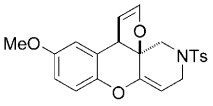
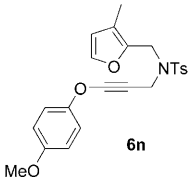
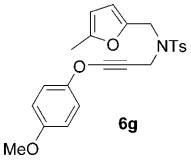
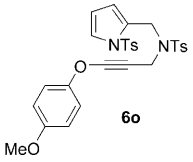
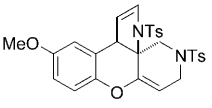
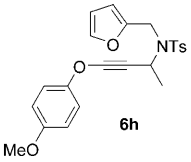
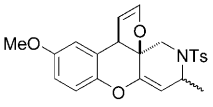
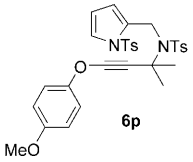
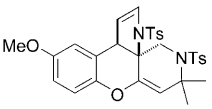
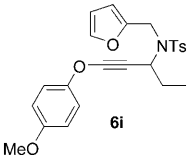
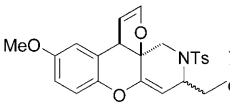
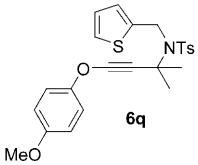
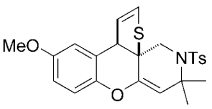
For the furan systems discussed above, the conversions were complete in minutes, but in the case of the disubstituted propargylic position in **6k**, the substrate decomposed (Table 2, entry 10). On the other hand, combining this propargylic disubstitution with a sterically demanding *ortho*-nitrophenyl group at the R^8-position in substrate **6l** led to a successful conversion, however, the reaction time increased to 4 h (Table 2, entry 11). Substrate **6m** which contains a stereogenic center in the furyl position for the investigation of a potential 1,2-induction, also led to a decomposition of the substrate. The higher stability of a secondary propargylic cation might account for this observation (Table 2, entry 12). The only substrate that showed no conversion at all was substrate **6n** (Table 2, entry 13). In this case, the methyl group in the 3-position of the furan (which is very close to the evolving spiro center and at the position which then has to attack the phenyl group) seems to be a steric problem.

γ-Alkynylpyrroles without an ether moiety on the alkyne undergo a hydroarylation reaction rather than the phenol synthesis.[3h] With the arylether group, even for the *N*-tosylpyrroles **6o** and **6p**, a formation of the desired tetracyclic systems **7o** and **7p** was observed in high yields (Table 2, entries 14 and 15). Even the thiophene substrate **6q** could be perfectly converted without any sign of catalyst deactivation (Table 2, entry 16). This is one of the few conversions of low-valent sulfur-containing compounds in gold catalysis,[11] and it is remarkable that in the course of the reaction the aromaticity is broken, not only in the furan ring with its low aromatic character, but also in the pyrrole, and even the thiophene ring.[12]

We could extend this method to non-heterocyclic, olefinic systems. Substrate **8** with a prenyl side-chain delivered the tricyclic heterocycle **9** in good yield (Scheme 4).

A mechanistic proposal for this reaction is given in Scheme 5. As a result of the electronic properties of the alkynylether moiety, the initiation step is a 6-*endo*-*dig* cyclization, leading to the stabilized cation **H** (which potentially could also be a carbenoid system **I**; there is an ongoing discussion on the nature of these intermediates).[13] The reaction cascade continues by a Friedel–Crafts-like arylation,[14] followed by protodemetallation to form the products **7**. The failure of the methyl-substituted furans **6e** and **6g** to undergo a selective cyclization (Table 2, entries 4 and 6) might

Table 2: Gold-catalyzed conversions of substrates **6** into **7** in $CHCl_3$ at room temperature.

Entry	Substrate	*t*	Product	Yield [%]	Entry	Substrate	*t*	Product	Yield [%]
1	 **6b**	10 min	 **7b**	52	9	 **6j**	5 min	 **7ja**  **7jb**	79 **7ja**/**7jb** d.r. = 80:20[b]
2	 **6c**	10 min	–[a]	–	10	 **6k**	16 h	–[a]	–
3	 **6d**	30 min	–[a]	–	11	 **6l**	4 h	 **7l**	89[c]
4	 **6e**	10 min	–[a]	–	12	 **6m**	5 min	–[a]	–
5	 **6f**	5 min	 **7f**	74	13	 **6n**	1 d	–[a]	–
6	 **6g**	10 min	–[a]	–	14	 **6o**	5 min	 **7o**	79
7	 **6h**	5 min	 **7h**	83 d.r. = 71:29[b]	15	 **6p**	4 h	 **7p**	97[c]
8	 **6i**	5 min	 **7i**	75 d.r. = 90:10[b]	16	 **6q**	1 h	 **7q**	97[c]

[a] Decomposition of the starting material. [b] From integration of NMR spectra. [c] See Supporting Information for crystal structure.[9]

originate from the additional stabilization of the carbocationic form **H**, the resulting reduced electrophilicity then makes the next step less efficient and leads to unspecific side-reactions.

Finally, we investigated if for the nonpolarized alkynes **10a/b** (Scheme 6, which also comprise an aromatic system as potential nucleophile), a similar reaction pathway could take place. Unfortunately, these substrates showed either no

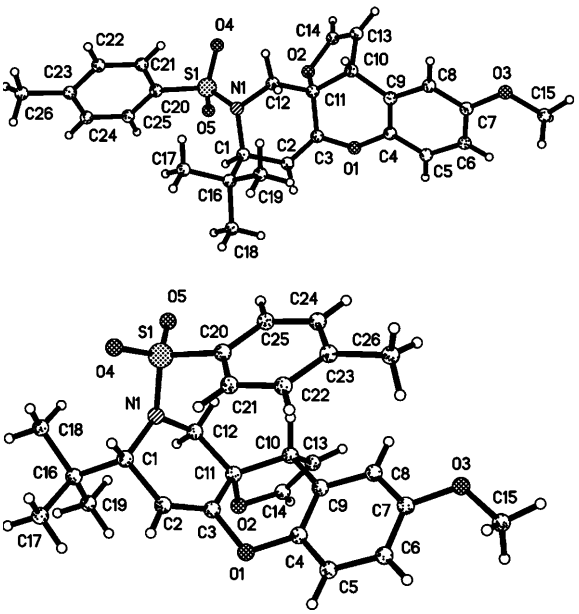
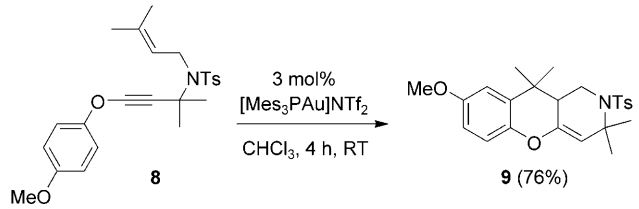
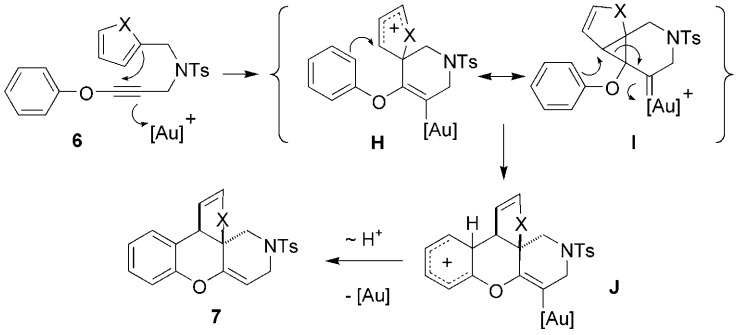


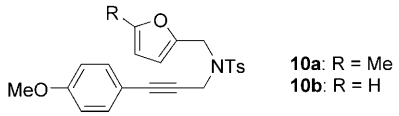
Figure 2. Solid-state structures of the major diastereomer **7ja** and the minor diastereomer **7jb**.



Scheme 4. Conversion of the prenyl substrate **8**.



Scheme 5. Mechanistic proposal for the conversion of **6**.



Scheme 6. The reaction fails with substrate **10** which does not have the alykynylether substructure.

conversion (**10b**, both at room temperature and at 60 °C), or a fast decomposition reaction (**10a**, both at −40 °C and at room temperature). Clearly, the directing property of the heteroatom directly attached to the alkyne moiety is crucial for the switch from the phenol synthesis to this newly discovered reactivity pattern.

In summary, we were able to use an alkynylether moiety to trigger a new reaction mode of the gold-catalyzed furanyne cyclization, delivering a new class of tetracyclic systems rather than phenols. In these new reactions the aromatic character of the heteroaromatic system is lost, and tetracyclic systems, with two new stereocenters, can be prepared from easy available and highly modular starting materials under very mild reaction conditions. Owing to the lower substitution of the enol ether, enamine, or enthiol ether in the five-membered heterocycle of the products **7**, this unit is chemically differentiable from the enol ether in the six-membered heterocycle and thus further chemical manipulation is possible, which could for example, open a way to the broad class of anellated chromanes and chromenes. An extension of the scope of this reaction to other heterocycles and to non-heterocyclic ene units and enantioselective versions of this reaction will be investigated and will be reported in due course.

Experimental Section

Representative procedure for the gold-catalyzed transformations: Compound **6a** 100 mg (243 μmol) was dissolved in $CHCl_3$ (5 mL). After the addition of $[Mes_3PAu]NTf_2$ (6.31 mg; 7.29 μmol) the reaction mixture was stirred for 10 min at room temperature. After evaporation of the solvent, the crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 5:1). 54.0 mg (131 μmol, 54 %) of **7a** were obtained as a colorless solid. M.p.: 162 °C. R_f (petroleum ether/ethyl acetate 20:1) = 0.21. IR (film): $\tilde{\nu}$ = 2382, 1727, 1692, 1618, 1479, 1457, 1439, 1369, 1342, 1268, 1247, 1221, 1161, 1146, 1114, 1050, 969, 943, 861, 817, 765, 710, 663 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 2.42 (s, 3H), 2.60 (d, ^2J = 12.5 Hz, 1H), 3.44 (dd, ^2J = 16.5 Hz, ^3J = 2.4 Hz, 1H), 3.68 (m, 1H), 3.87 (s, 3H), 4.21 (dd, ^2J = 16.5 Hz, ^3J = 4.7 Hz, 1H), 4.23 (d, ^2J = 12.5 Hz, 1H), 5.14 (t, ^3J = 2.8 Hz, 1H), 5.70 (dd, ^3J = 4.7 Hz, ^3J = 2.4 Hz, 1H), 6.28 (dd, ^3J = 2.8 Hz, ^4J = 1.8 Hz, 1H), 6.62 (ddd, ^3J = 8.0 Hz, ^4J = 1.3 Hz, ^4J = 0.6 Hz, 1H), 6.73 (dd, ^3J = 8.0 Hz, ^4J = 1.3 Hz, 1H), 6.86 (t, ^3J = 8.0 Hz, 1H), 7.31 (d, ^3J = 8.3 Hz, 2H), 7.73 ppm (d, ^3J = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.67 (q), 43.52 (t), 43.65 (d), 52.54 (t), 56.22 (q), 79.92 (s), 104.63 (d), 107.22 (d), 110.29 (d), 119.65 (d), 122.55 (d), 123.23 (s), 127.87 (d, 2C), 129.81 (d, 2C), 134.04 (s), 141.18 (s), 143.91 (s), 144.42 (s), 145.04 (d), 148.18 ppm (s). MS (ESI (+): *m/z* (%): 434 (100) $[M+Na]^+$. $C_{22}H_{21}NO_5S$ (411.47): calcd (%) C 64.22, H 5.14, N 3.40; found C 64.35, H 5.44, N 3.19.

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