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Gold-Catalyzed Cyclisation by 1,4-Dioxidation: Synthesis of

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[+] Crystallographic investigation

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Abstract:

Amide-substituted diynes were cyclized in the presence of a cationic gold catalyst and an external nucleophile leading to 1-indenones and 1-iminoindenones. The electron-donating features of the nitrogen atom enable the formation of a reactive ketene iminium ion, which can be trapped by either diphenyl sulfoxide or anthranil as nucleophiles in a subsequent oxidation step, providing substituted inden-1-on-3-carboxamides.

In the highly active field of gold catalysis,[1] reactions applying diyne systems as starting materials have become increasingly important.[2] The most common reactivity pattern includes the intermolecular or intramolecular attack of a nucleophile on one of the triple bonds activated by a π-coordinated gold complex. The resulting intermediates can undergo valuable cascade reactions to form highly interesting products.[3] If the diyne contains at least one terminal alkyne, it can additionally be activated by a σ-bonded gold complex in the so-called dual activation mode.[1c] This leads to the formation of highly reactive gold vinylidenes which can undergo further transformations (Scheme

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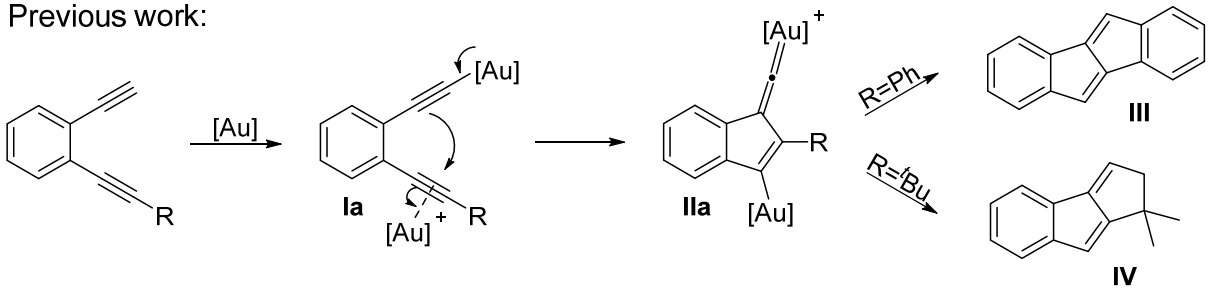
1).[4] The highly electrophilic *sp*-carbon center of the vinylidene can for example be trapped by an intramolecular nucleophilic attack of an phenyl ring to form a dipenzopentalene (**III**) or by an C(sp^3)-H bond insertion leading to benzofulvene substrates (**IV**).

We envisioned that if we substitute the gold acetylide by an ynamide, we could form a ketene iminium ion instead, which can then likewise can be attacked by different intramoleculary offered nucleophiles (Scheme 2). Ynamides, with their polarized structure due to the electron-donating features of the nitrogen atom, are highly reactive and together with the distinction of the two *sp*-carbon atoms they show interesting reactivities.[5] To our surprise, when we conducted our initial experiments, we always obtained a product with two additional oxygen atoms[6] in place of the desired substituted dibenzopentalene (Scheme 3). It seems that the ketene iminium ion intermediate is way more stable and the electrophilicity of the *sp*-carbon is significantly lowered. Therefore, the intermediate can be attacked by an external *O*-nucleophile, which in this case could be the oxygen of a tosyl group of another substrate molecule, leading to an interesting substituted 1-indenone structure in the further reaction.

Functional 1-indenones are wide spread structural motifs in natural products and highly bioactive molecules.[7] Furthermore, they are important intermediates in the synthesis of natural products and pharmaceuticals.[8] Especially 2-aryl-substituted 1-indenones show outstanding pharmaceutical and biological features.[9] Since these structures are so highly favorable, there are already many protocols for their synthesis published in the last decades.[10] Nevertheless, a mild procedure for the synthesis of functionalized indenones with readily available starting materials is still of high interest. There is only one example known for a gold-catalyzed protocol starting from 2-alkynylarylketones.[11] That procedure still lacks selectivity as the corresponding isoquinoline is obtained as a side product only, isolated in low yields. Protocols for the synthesis of 2-aryl-3-carboxamide indenones are not known at all. Therefore, we present a direct and mild gold(I)-catalyzed oxidative cyclization of tosylamide-substituted diynes leading to substituted 1-indenones.[12]



Scheme 1. Dual activation of diynes and further reactions

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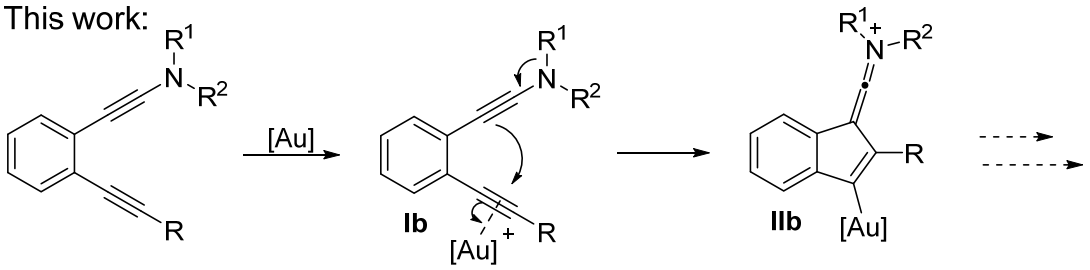
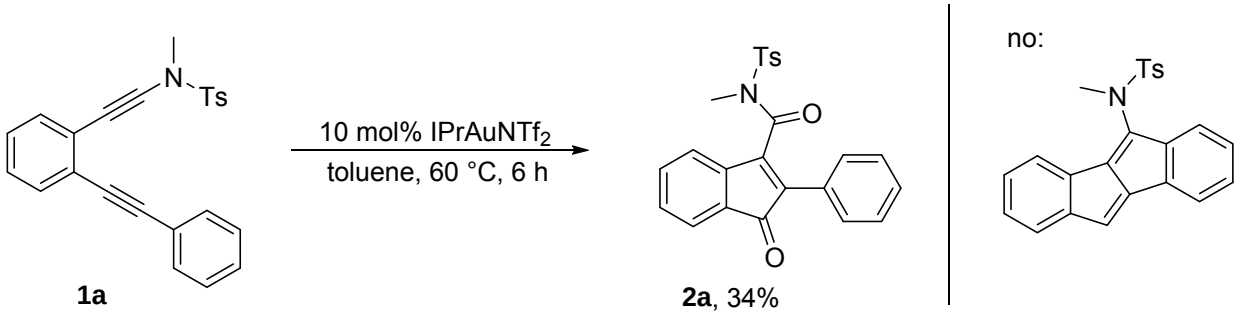


Scheme 2. Formation of a ketene iminium ion



Scheme 3. Initial experiment

Triggered by the results in our initial experiments, we first conducted a screening with diyne **1a** and different external oxygen donors (Table 1). First we used 3,5-dibromopyridine-*N*-oxide as an oxidant and could selectively obtain the diketone **3a** as a major product, the desired product **2a** was observed only in traces (entry 2). It is known, that pyridine-*N*-oxides can generate α-oxo gold carbene intermediates with alkynes in the presence of a gold catalyst.[13] Oxidation of the carbene with a second molecule of *N*-oxide can then lead to the formation of the diketone moiety.[14] Therefore we tested different catalyst/oxidant/solvent combinations, which are already known to avoid the formation of the undesired diketone.[15] But neither changing the oxidant to the sterically more hindered 8-ethylquinoline- and 8-isopropylquinolin-*N*-oxide, nor replacing the IPr ligand by the more bulky JohnPhos (entry 5) or XPhos ligand (entry 4), provided a higher yield. Next, we used the diphenyl sulfoxide as an oxidant and could achieve a significant increase of the yield of **2a** and no undesired 1,2-diketone was observed (entry 7), although this undesired side-reaction is known.[16] Now we changed the counter ion to the SbF_6^- anion and obtained the product in an excellent yield (entry 8). When we applied the same catalyst in combination with an *N*-oxide instead of the diphenyl sulfoxide, exclusively the diketone was obtained in excellent yields. When conducting the reaction at room temperature, a small decrease of yield was observed. However, increasing the amount of the oxidant did not lead to any improvement.

Table1. Optimization of the Reaction Conditions

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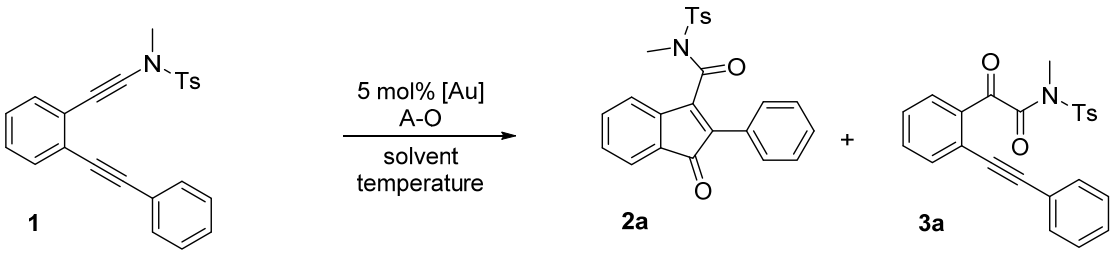
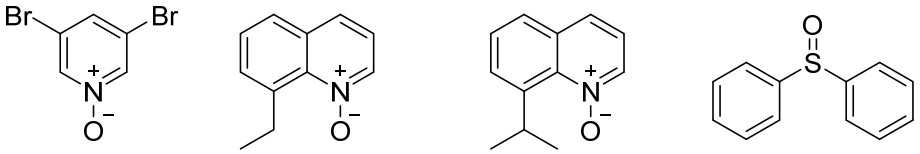


Entry	Catalyst	A-O	Solvent	T	Yield **2a**	Yield **3a**
1	$IPrAuNTf_2$[b]	----	toluene	60 °C	34%	0%
2	$IPrAuNTf_2$[b]	2 eq. **4a**	toluene	60 °C	trace	79%
3	$IPrAuNTf_2$	2 eq. **4b**	H_2O	80 °C	0%	0%
4	$XPhosAuCl/AgNTf_2$	2 eq. **4b**	DCE	rt	0%	81%
5	$JohnPhosAuCl/AgNTf_2$	2 eq. **4b**	DCE	rt	0%	89%
6	$JohnPhosAuCl/AgNTf_2$	2 eq. **4c**	DCE	rt	0%	83%
7	$IPrAuNTf_2$	2 eq. **4d**	DCM	40 °C	76%	0%
8	$[(IPr)Au(NCMe)]SbF_6$	2 eq**. 4d**	DCM	40 °C	91%[c]	0%
9	$[(IPr)Au(NCMe)]SbF_6$	2 eq. **4a**	DCM	rt	0%	95%
6	$[(IPr)Au(NCMe)]SbF_6$	2 eq. **4d**	DCM	rt	86%	0%
7	$[(IPr)Au(NCMe)]SbF_6$	3 eq. **4d**	DCM	40 °C	90%	0%

[a] Reactions were run on a 250 mmol scale. Yields were determined by ^1H NMR spectroscopy; hexamethylbenzene was used as an internal standard, if not stated otherwise. [b] 10 mol% of the catalyst was used. [c] Isolated yield.



4a **4b** **4c** **4d**

After optimizing the reaction conditions, we focused on the scope of the reaction (Table 2). First, we varied the aryl unit connected to one of the two alkynes. To our delight, electron-donating groups, such as *tert*-butyl (**2b**) and methoxy (**2d**) groups in *para*-position were tolerated well. Changing to a mesityl group (**2c**) lead to a significant decrease of the yield, probably caused by a higher steric hindrance. If a fluorine in para position as an electron-withdrawing group is applied, the product was obtained in an excellent yield (**2e**). A 2-thienyl group (**2f**) as model for an electron-rich heterocycle and the 1-naphthyl group (**2g**) were also tolerated in the reaction. When we tested aliphatic groups, the product could be obtained in moderate yields using an *n*-hexyl group (**2h**), whereas a *tert*-butyl group (**2i**) leads to the decomposition of the starting material. As a next step, we varied the backbone of the diyne. If a [1,3]-dioxole backbone is applied, decomposition of the starting material was observed (**2j**). When

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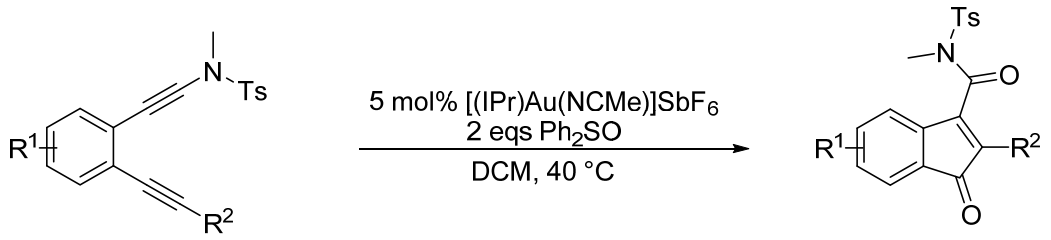
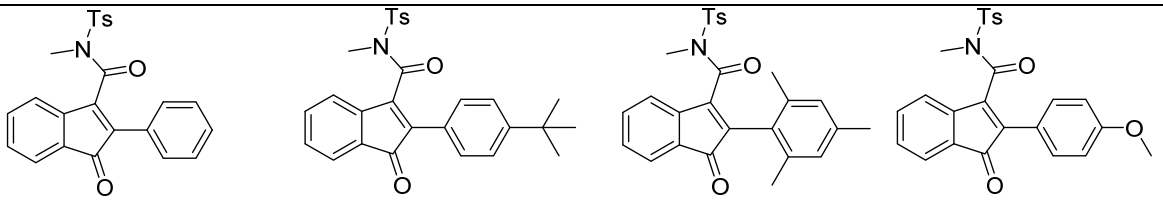
using an additional methoxy (**2k**) or fluorine group (**2l**) in the backbone, the reaction was proceeding well and excellent yields could be obtained.

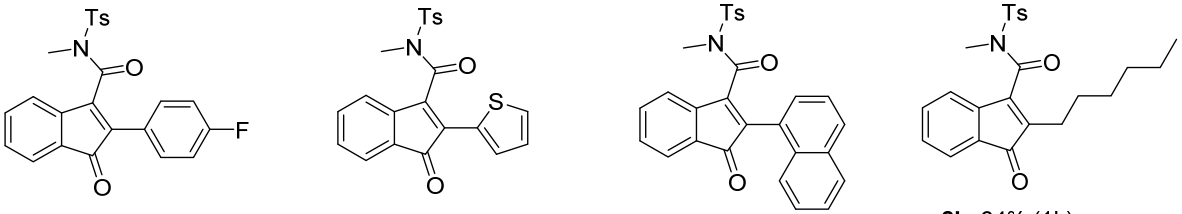
Table 2. Scope with respect to the *N*-methyltosylynamides



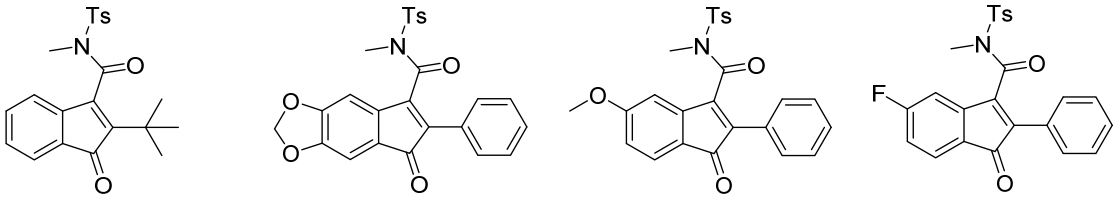
1a-l **2a-l**



2a, 91% (1h) **2b**, 57% (2h) **2c**, 31% (10h) **2d**, 78% (1h)



2e, 90% (1h) **2f**, 79% (1h) **2g**, 56% (2h) **2h**, 64% (1h)



2i, 0% decomposition **2j**, 0% decomposition **2k**, 94% (1h) **2l**, 92% (2h)

Furthermore, we extended the scope by varying the amide (Table 3). Since, for reasons of stability, an electron-withdrawing group is needed, we started by switching from a methyl group to a benzyl group, which was tolerated extremely well; **2m** was obtained in excellent yield. In order to verify the connectivity of the indenone structure, we conducted an X-ray crystal structure analysis of a single crystal of **2m** (Figure 1).[17] A thiophen-2-ylmethyl group (**2n**) only led to a decomposition of the starting material. However, a cyclopropyl group (**2o**) was tolerated well, delivering a good yield of the corresponding indenone. Changing the electron-withdrawing group to a nosyl group (**2p**), provided a good yield, too. An oxazolidinone group was also tolerated, **2q** was obtained in moderate yields.

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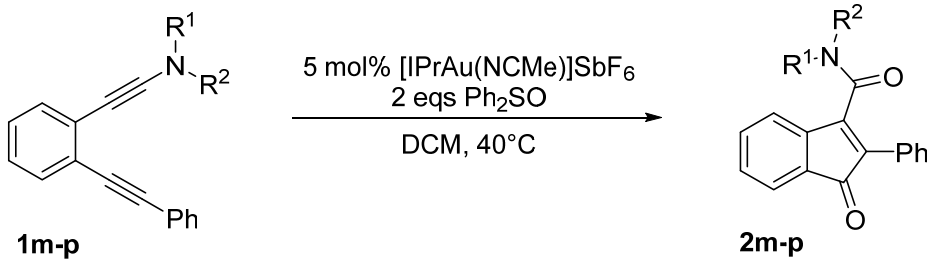
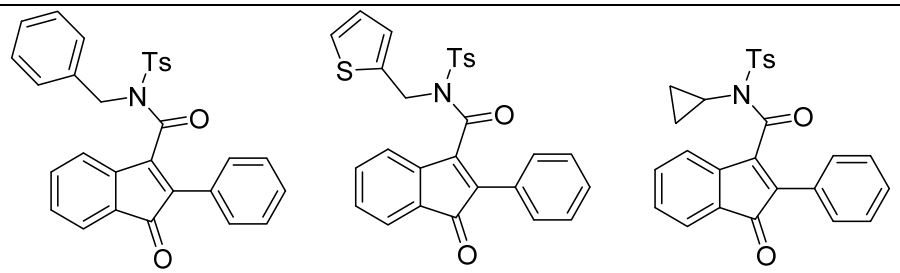
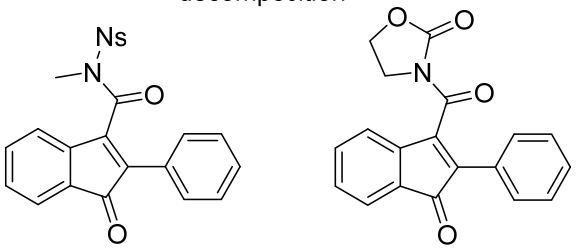
Table 3. Scope with respect to the amide



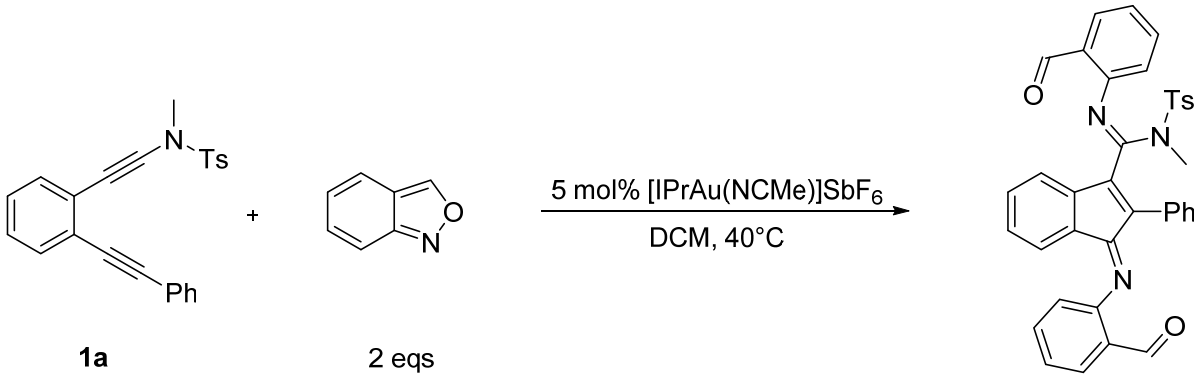
1m-p **2m-p**



2m, 95% (1 h) **2n**, 0% decomposition **2o**, 81% (1 h)



2p, 70% (2 h) **2q**, 55% (30 h)



1a 2 eqs **5a**, 63% (**1h**)

Scheme 4. Reaction with anthranil as a weak nucleophile

To extend this new reactivity, we also varied the external nucleophile. Since anthranil is known to react as a nitrene donor,[18] comparable to the oxygen atom transfer from

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diphenyl sulfoxide, we decided to apply this nucleophile together with our standard diyne **1a**. To our delight, the reaction proceeded well and the corresponding diimine **5a** could be obtained in moderate yields. We also proved the structure of the product by single crystal X-ray structure analysis (Figure 1).[17]

As mentioned, the reaction most likely[19] is initiated by a nucleophilic attack of the β-carbon of the amide-substituted alkyne at the π-activated alkyne in a 5-*endo*-*dig* fashion, promoted by the electron donating features of the nitrogen atom (Scheme 5). This leads to the formation of the ketene iminium ion **IIb**. This intermediate can be attacked at the electrophilic *sp*-carbon by the oxygen atom of diphenyl sulfoxide, giving rise to intermediate **IIIb**. In the next step, the gold carbene intermediate **IVb** is formed and diphenyl sulfide is released. The gold carbene **IVb** can be attacked by a second diphenyl sulfoxide molecule, leading to the desired indenone product **2** by releasing another diphenyl sulfide molecule. An alternative pathway via a gold α-oxo carbene is also possible. To proof our mechanistic proposal, we intended to trap the different carbene species with an alkene function in a cyclopropanation reaction. Trapping the gold carbene **IVb** with an alkene function in appropriate distance proceeded well and the corresponding cyclopropanation product **6q** was obtained in moderate yields (Scheme 4).

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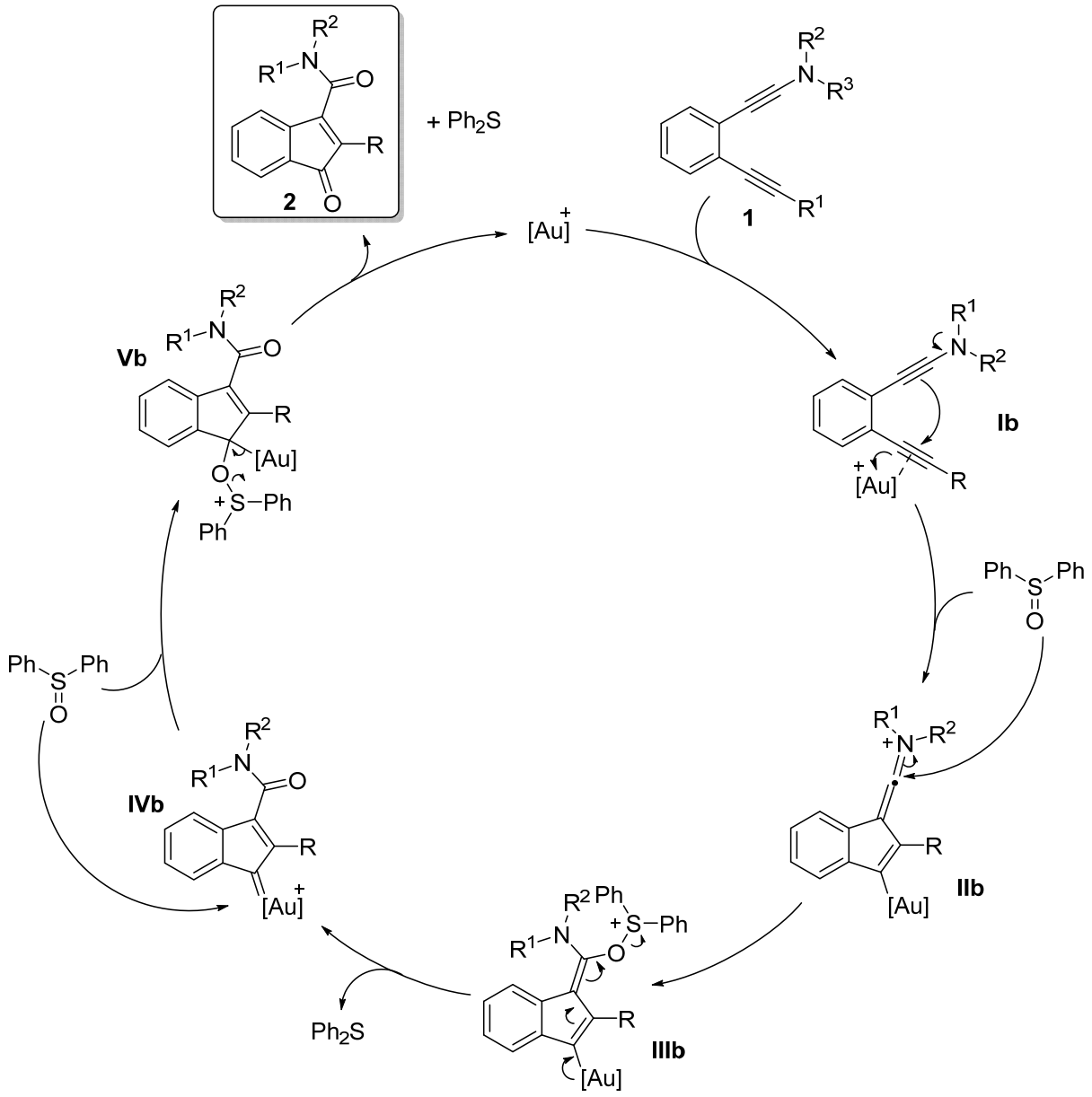

Scheme 5. Proposed reaction mechanism

However, proving that no α-oxo carbene (of type **VI**) is involved, is significantly more challenging. Nevertheless, diphenyl sulfoxide is not known for forming gold α-oxo carbenes in intermolecular alkyne oxidation reaction pathways.[13] We synthesized an diyne substrate **1r**, which offers an alkene function in the right distance for trapping a possible α-oxo-carbene. To our delight it was possible to isolate the corresponding indenone **2r** in a good yield with respect to the oxidant, the alkene function remained untouched, no **7r** was detected (Scheme 7). In our screening we always obtained the diketone as a main product when using an *N*-oxide, thus we assumed that with these oxidants the reactions proceeded via the α-oxo carbene. To show that the carbene can be trapped by the alkene, we tried the same reaction with the *N*-oxides **4a**-**4c**. The gold-catalyzed cyclopropanation reaction of a similar system is already known from simple en-ynamide-type substrates.[14e] Unfortunately, we only obtained complex product mixtures and the desired cyclopropanation product could not be isolated. As there are many different functional groups in our system, the unselective reaction can easily be explained.

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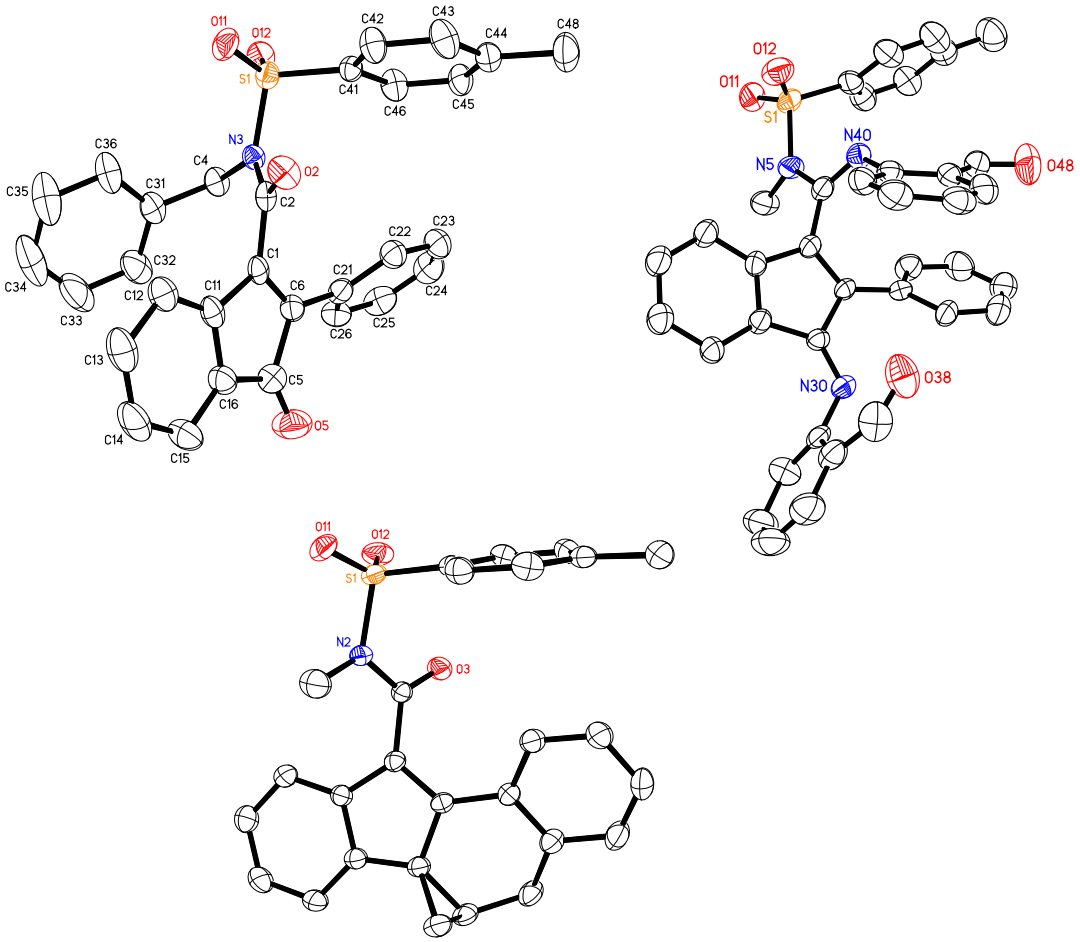
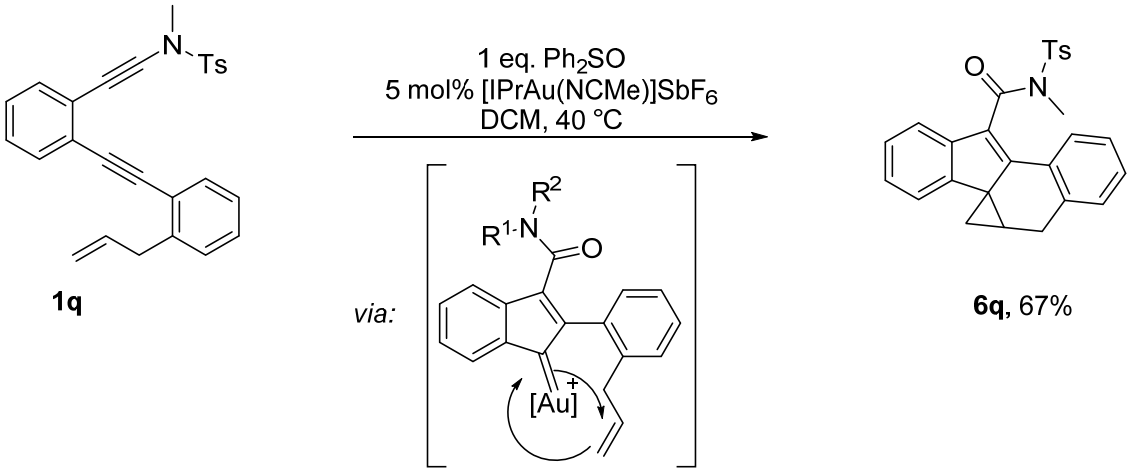


Figure 1. Solid state molecular structures of **2m** (*left*), **3a** (*right*) and **6q** (*bottom*)



1q

6q, 67%

Scheme 6. Trapping the gold carbene by a cyclopropanation reaction

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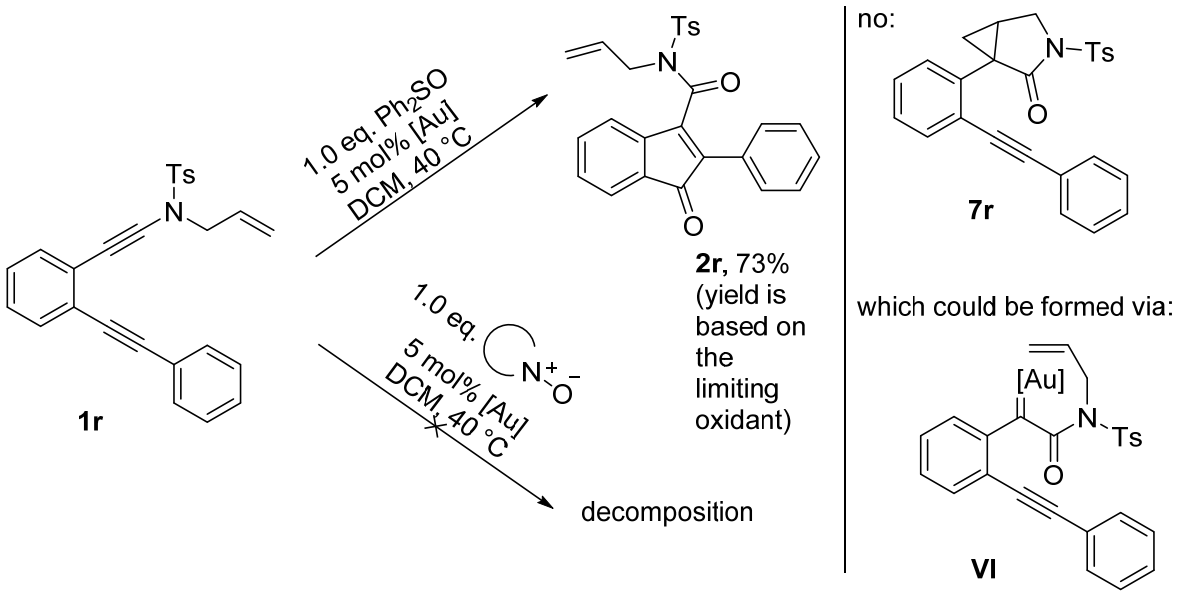

Scheme 7. Mechanistic studies

In conclusion, we developed a mild and simple gold-catalyzed protocol for the synthesis of functionalized 1-indenones. The gold-catalyzed cyclization of the amide-substituted diyne to the indenone products most likely proceeds as predicted, i.e. *via* the ketene iminium ion intermediate. However, the *sp*-carbon of this intermediate is by far not electrophilic enough to be trapped by an aryl or *tert*-butyl group like it is known for gold vinylidenes.[20] But we were able to trap the ketene iminium ion with external nucleophiles giving rise to highly desirable 1-indenone and 1-iminoindenone structures. To the best of our knowledge, there is no synthesis established for achieving this specific substitution pattern. The reaction is tolerant to most of the tested functional groups and leads to a broad range of products. For further applications the biological activity of those products should be distinguished.

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