How to cite: *Angew. Chem. Int. Ed.* **2025**, *64*, e202420360
doi.org/10.1002/anie.202420360

Gold Catalysis

Gold-Catalysed Intramolecular Reaction of Alkynes with Sulfoximines Acting as N- and O-Transfer Reagents

*Alexandra V. Mackenroth, Patrick W. Antoni, Farshad Shiri, Christoph Bendel, Christian Mayer, Jürgen H. Gross, Frank Rominger, Matthias Rudolph, Alireza Ariafard, and A. Stephen K. Hashmi**

Abstract: Among the nucleophilic oxidants employed in the gold-catalysed oxidation of alkynes, sulphur-based reagents have played a substantial role since the beginning, granting access to the respective gold carbene intermediates. Herein, we describe the first example of the substance class of sulfoximines being used as atom transfer reagents to alkynes in gold catalysis. Based on the transformation of *N*-(2-alkynylphenyl) sulfoximines to 3*H*-indol-3-ones, it is demonstrated that the sulfoximine functionality is capable of selectively transferring first its nitrogen moiety to the alkyne, forming the α-imino gold carbene, which is then oxidised by the released sulfoxide moiety in a second step *via* a *pseudo-intramolecular* mechanism—a distinctive feature that differentiates this work mechanistically from earlier studies. A combination of extensive experimental and theoretical studies provides evidence for this mechanistic rationale. As no external reagents for the 1,2-difunctionalisation of the alkyne unit are required, a wide variety of functional groups are tolerated in the transformation, affording the desired 3*H*-indol-3-ones in mostly good yields. It was further also showcased that it is possible to combine our methodology with additional transformations of the 3*H*-indol-3-one core in one-pot procedures, allowing facile access to C2-quaternary indolin-3-one structures.

Introduction

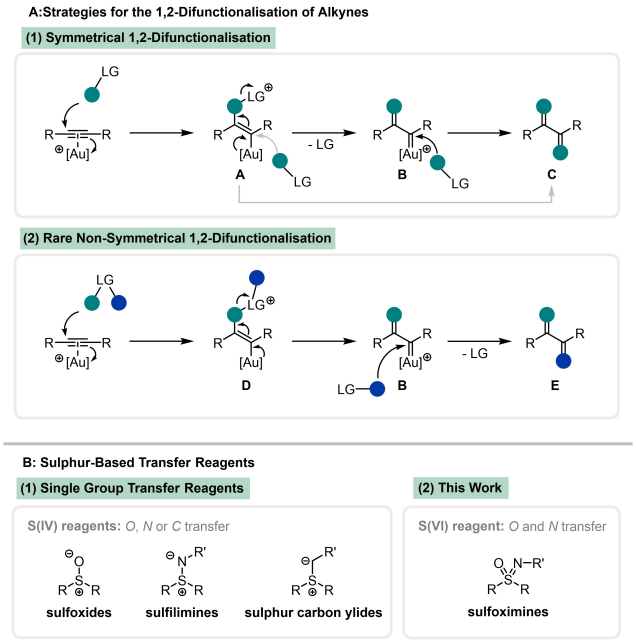
The gold-catalysed 1,2-difunctionalisation of alkynes constitutes an efficient and elegant way of accessing complex structural motifs.[1] For instance, for the gold-catalysed transformation of alkynes to glyoxals,[2] the π-activated alkyne[3] is attacked by the nucleophilic oxidant to give alkenyl gold species **A** (Scheme 1A).[4] Following elimination of the leaving group (LG), α-oxo gold carbene **B** can be formed, which can then be oxidised by a second equivalent of the respective oxidant, affording the desired 1,2-dicarbonyl **C**.[5] It is also possible that vinyl gold species **A** is directly attacked by the second oxidant molecule, leading to product **C** without the formation of a carbene-type intermediate.[2b] In order to achieve an N-/O-functionalisation of the triple bond *via* the same strategy, the presence of two different oxidants would be required—one transferring the oxygen atom, the other one providing the nitrogen moiety—a combination that is prone to lead to the formation of a mixture of different reaction products. To circumvent this problem, it is highly desirable to make use of a single oxidant that is capable of selectively transferring both units in a successive manner. The attack of the first moiety would lead to the formation of alkenyl gold intermediate **D**, which can then fragment to the respective α-oxo or α-imino gold carbene **B** under elimination of the leaving group. Subsequently, the leaving group, i.e. the reduced form of the former oxidant, could potentially transfer the second unit, oxidising the carbene centre to furnish oxoimination product **E**.

[*] A. V. Mackenroth, Dr. P. W. Antoni, C. Bendel, C. Mayer, Dr. J. H. Gross, Dr. F. Rominger, Dr. M. Rudolph, Prof. Dr. A. S. K. Hashmi
Organisch-Chemisches Institut
Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
E-mail: hashmi@hashmi.de

Dr. F. Shiri
Department of Chemistry
The Hong Kong University of Science and Technology
Clear Water Bay, Kowloon, Hong Kong 999077, China

Dr. A. Ariafard
Research School of Chemistry
Australian National University
Canberra, ACT 2601, Australia

Prof. Dr. A. S. K. Hashmi
Chemistry Department, Faculty of Science
King Abdulaziz University
Jeddah 21589, Saudi Arabia



Scheme 1. a) Symmetrical and non-symmetrical gold-catalysed 1,2-difunctionalisation of alkynes and b) the established S(IV) transfer reagents in contrast to the herein presented sulfoximines.

With regard to N- and O-transfer reagents to alkynes in gold catalysis, Shin *et al.*[6] and Liu *et al.*[7] have made use of nitrones, which initially attack the alkyne with their oxygen atom to form the α-oxo gold carbene, which is then trapped by the transiently formed imine to give the oxoamination product after hydrolysis. The oxoimination product can be obtained by using nitrosobenzene, although not *via* the aforementioned reaction sequence, but by means of an alkyne/nitroso metathesis mechanism.[7] Nitro groups can be used in conjunction with alkynes to first form the α-oxo gold carbene, which subsequently reacts with the remaining nitroso group to form the oxoimination *N*-oxide.[1a,8]

Among a variety of other types of oxidants, sulphur-based reagents have always played a critical role in this type of gold-catalysed oxidation of alkynes (Scheme 1B).[9] Sulfoxides were the first reagents to be used for this kind of approach[10] and have since then served as a versatile source of α-oxo gold carbenes, giving rise to many different transformations and structural motifs. Their nitrogen analogues, sulfilimines, were explored more recently and were shown to give access to α-imino gold carbenes.[11] A few examples have also been reported that make use of sulphur carbon ylides acting as carbene transfer reagents in gold-catalysed conversions of alkynes.[12] Despite this frequent use of S(IV) reagents, the reactivity of the S(VI) compound class of sulfoximines—which can be regarded as a fusion of sulfoxides and sulfilimines—in gold-catalysed reactions remains virtually unexplored. The synthesis and reactivity of sulfoximines is fairly well known,[13] as they have shown to exhibit properties that give rise to many valuable applications in medicinal chemistry[14] as well as crop protection.[15] They have further been shown to be of a high synthetic value, for instance serving as ligands,[16] directing groups,[17] chiral auxiliaries[18] or reagents[19] in a variety of chemical transformations. A very recent report features sulfoximines being used as reactants in a gold-catalysed transformation of enynone systems, however, in that case, no reaction between the sulfoximine and the alkyne takes place. Instead, the sulfoximine's nitrogen atom acts as a nucleophile, trapping a carbocation generated in a preceding intramolecular gold-catalysed cyclisation reaction, with the sulfoximine entity remaining intact.[20]

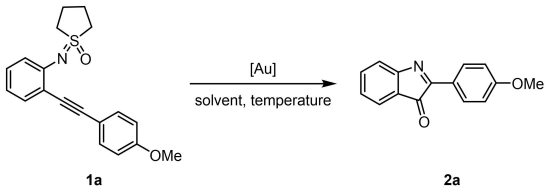
Results and Discussion

We envisioned that, in gold catalysis, sulfoximines have the potential to act as N- and O-transfer reagents, first transferring one of the units to the alkyne, forming the respective gold carbene, which can then in turn be trapped by the remaining sulfoxide or sulfilimine moiety. This strategy would enable a facile 1,2-N,O-difunctionalisation of alkynes in one step without the need for the addition of any further reagents. In order to test our hypothesis, we chose to construct intramolecular system **1a**, that incorporates both the alkyne and the sulfoximine unit and can be accessed *via* a two-step sequence consisting of a Sonogashira coupling and a successive Buchwald Hartwig amination using the conditions developed by Bolm *et al.*[21] The employed tetrahydrothiophene-based sulfoximine building block is both commercially available and can be readily synthesised on a multi-gram scale.[22] Following a successful synthesis of the desired system, we reacted **1a** with IPrAuCl/$AgNTf_2$ in benzene at room temperature (rt) and observed the formation of two main species, one of them clearly being tetrahydrothiophene. Upon careful spectroscopic assessment, we were able to assign the second species to be 3*H*-indol-3-one **2a**, showcasing that the sulfoximine did indeed transfer both the nitrogen and the oxygen atom to the alkyne unit, releasing the sulfide as the by-product.

3*H*-Indol-3-ones themselves have been shown to constitute interesting structures due to their antimalarial properties.[23] Beyond this, they primarily serve as substrates for the construction of indolin-3-ones with a quaternary C2-atom. As this structural motif is present in countless natural products exhibiting various promising biological activity,[24] a multitude of transformations accessing the 2,2-disubstituted indolin-3-one core from 3*H*-indol-3-one building blocks have been developed.[25] In this regard, a very recent work published by Li and Wu *et al.* is particularly noteworthy, which combines a gold-catalysed synthesis of 3*H*-indol-3-ones from 2-alkynyl arylazides with a subsequent enantioselective organocatalytic transformation to the respective C2-quaternary indolin-3-ones in a one-pot procedure.[26]

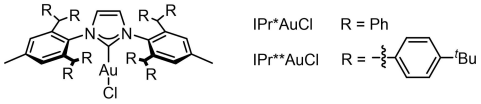
Despite the reaction showing full conversion of sulfoximine **1a**, the yield of **2a** only constituted 40 % as determined by ^{1}H NMR spectroscopy. Therefore, we turned to screen the reaction conditions for the underlying transformation (Table 1). Switching from the NHC-based Au(I) catalyst to phosphine- or phosphite-based Au(I) catalysts led to a decrease of the yield to 22 % and 16 %, respectively

Table 1: Screening of the reaction conditions for the gold-catalysed conversion of *N*-(2-alkynylphenyl) sulfoximine **1a** to 3*H*-indol-3-one **2a**.[a]



1a **2a**

Entry	Catalyst	Solvent	T [°C]	Conversion of **1a**	Yield of **2a**
1	IPrAuCl/$AgNTf_2$	benzene	rt	100%	40%
2	$Ph_3PAuCl/AgNTf_2$	benzene	rt	100%	22%
3	Phosphite[b]AuCl/$AgNTf_2$	benzene	rt	100%	16%
4	$picAuCl_2$	benzene	rt	100%	7%
5	SIPrAuCl/$AgNTf_2$	benzene	rt	75%	22%
6	IPr*AuCl/$AgNTf_2$	benzene	rt	60%	54%
7	IPr**AuCl/$AgNTf_2$	benzene	rt	67%	62%
8	IPr**AuCl/$AgSbF_6$	benzene	rt	37%	34%
9	IPr**AuCl/$NaBArF_{24}$	benzene	rt	48%	43%
10	**IPr**AuNTf$_2$**	**benzene**	**rt**	**86%**	**76%**
11	IPr**AuNTf$_2$	benzene	80	78%	63%
12	IPr**AuNTf$_2$	1,2-DCE	rt	38%	27%
13	IPr**AuNTf$_2$	toluene	rt	96%	76%

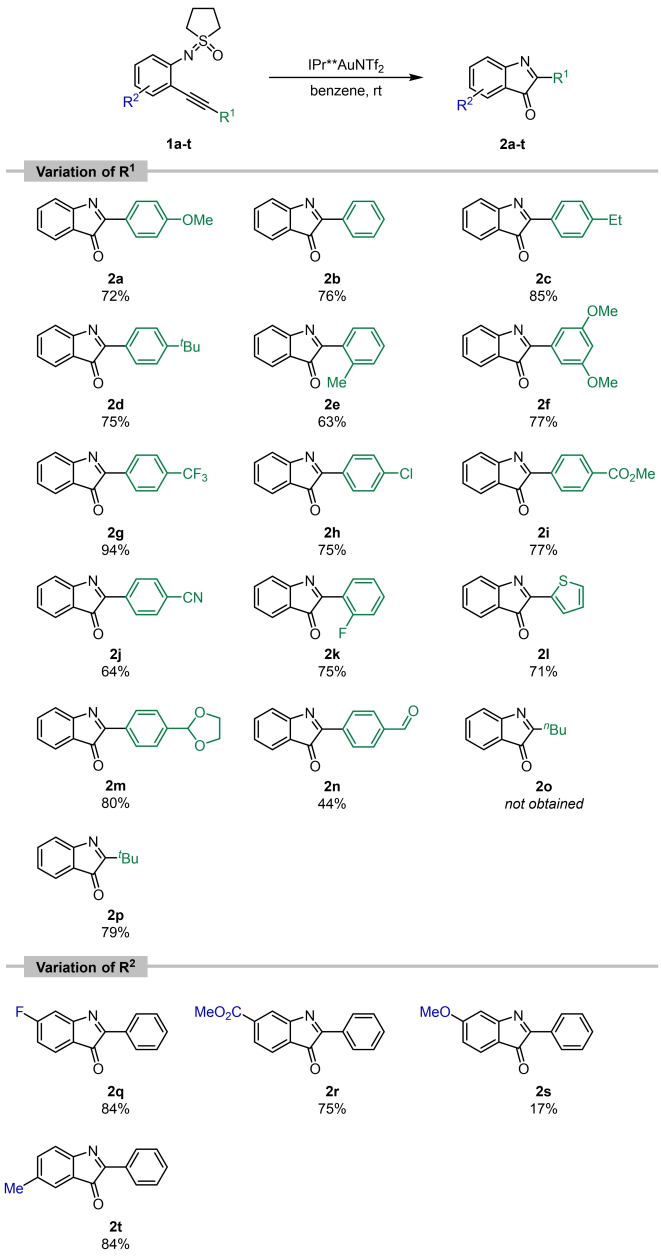


[a] The reactions were run on a 30.7 μmol scale in 0.3 mL solvent in the presence of 5.00 mol% of the gold catalyst and 5.00 mol% of the silver salt. The yield was determined by ^{1}H NMR spectroscopy using hexamethylbenzene as internal standard. [b] Tris(2,4-di-*tert*-butylphenyl) phosphite.

(entries 2 and 3). Equally, the use of the Au(III) catalyst $picAuCl_2$ gave very poor results (entry 4), although it had been shown to be superior to Au(I) catalysts in many cases of sulfilimines being used as nitrene transfer reagents.[2a–d] In light of these results, we assessed the performance of different NHC Au(I) catalysts in the reaction. SIPr, the saturated version of IPr, also gave an inferior result of 22% (entry 5). Employing the sterically significantly more demanding IPr*, on the other hand, increased the yield to 54% (entry 6). Further increasing the steric bulk on the NHC ligand by switching to IPr** increased the yield of **2a** to promising 62% (entry 6). Using the IPr** ligand but varying the counter anion from NTf_2^- to SbF_6^- or $BArF_{24}^-$ lowered the yield to 34% and 43% (entries 8 and 9). Using the pre-activated IPr**AuNTf$_2$ catalyst in the absence of silver cations, on the other hand, improved the yield to satisfactory 76% with 86% conversion (entry 10). Lastly, neither changing the reaction temperature to 80°C (entry 11), nor switching the solvent from benzene to 1,2-dichloroethane (1,2-DCE, entry 12) had a positive impact on the reaction outcome. It was however possible to replace benzene by the less hazardous toluene without any negative impact on the yield of 3*H*-indol-3-one **2a** (entry 13).

With these conditions at hand, we proceeded to evaluate the scope of the reaction, starting with the alkyne unit (Scheme 2). Example **2a**, featuring a methoxy group in the *para*-position on the aryl ring of the alkyne unit, was isolated with a yield of 72%. Other electron-donating groups in the *para*-position were shown to produce similarly good or even superior results, as shown by example **2c** for an ethyl group (85%) or example **2d** for a *tert*-butyl substituent (75%). 3*H*-Indol-3-one **2f**, with a very electron-rich aryl unit carrying two methoxy groups in the *meta*-positions, was obtained in a good yield of 77%. A methyl group in the *ortho*-position gave a slightly decreased yield of 63% (**2e**), possibly due to the high steric demand of the gold catalyst interfering with the methyl group in close proximity. Sulfoximine **1b** with an unsubstituted phenyl ring on the alkyne gave the corresponding 3*H*-indol-3-one **2b** in a satisfactory yield of 76%. An electron-withdrawing trifluoromethyl group in the *para*-position produced an excellent yield of 94% (**2g**). Halide substituents resulted in a yield of 75% for both cases of fluoride (**2k**) and chloride (**2h**). Example **2l** shows that heteroaryl units on the alkyne, in this case thiophene, also result in good yields (71%). Some of the known strategies of synthesising 3*H*-indol-3-ones require the presence of a strong base.[27] Therefore, we assessed whether our method is efficient in the presence of base-labile functional groups and were able to show that good yields of 77% and 64% were obtained for substrates carrying an ester group (**2i**, the solid state structure is depicted in Figure 1)[28] or a nitrile group (**2j**).

Other known methods of accessing 3*H*-indol-3-one cores involve the participation of strong acids,[29] which prompted us to evaluate whether our approach is equally feasible with acid-labile functional groups. Indeed, conducting the reaction with acetal-substituted substrate **1m** gave the desired product in an excellent yield of 80%. When using alkynyl nitroarenes for the transition metal-catalysed synthesis of 3*H*-indol-3-ones, the reaction first affords the corresponding



Scheme 2. Substrate scope. [a] Reaction conditions: The reactions were run on a 170 µmol scale with respect to the sulfoximine in the presence of 5.00 mol% of IPr**AuNTf$_2$ in benzene (1.7 mL). The yields constitute isolated yields after column chromatography.

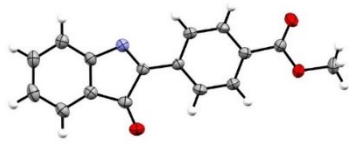
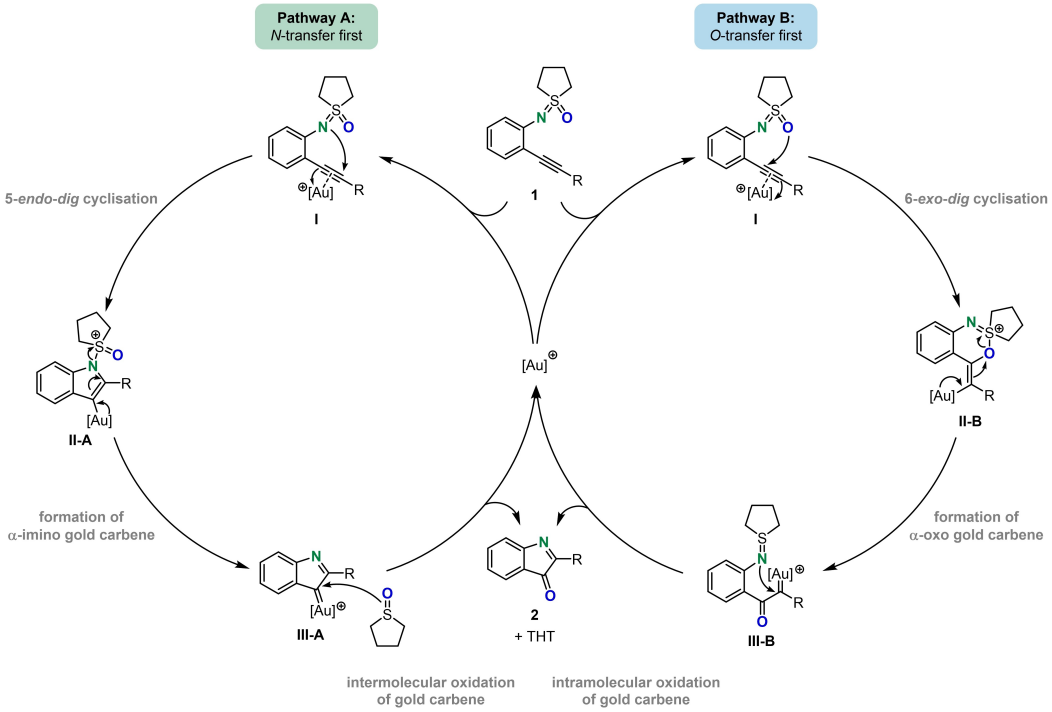


Figure 1. Solid state molecular structure of **2i**, thermal ellipsoids are shown at a 50% probability level.[28]

isatogens that then need to be reduced by an external reducing agent.[30] In our case, functional groups that are prone to undergo reduction are also tolerated as illustrated by the example of aldehyde **2n**, although in a decreased yield of 44%. Next, we wanted to assess whether the aryl unit on the distal end of the alkyne can be exchanged for an alkyl chain. Unfortunately, when subjected to the reaction conditions, sulfoximine **1o** with an *n*-butyl residue gave a complex mixture of different products that seem to be the result of further reactions of temporarily formed 3*H*-indol-3-one **2o** (see Supporting Information, Scheme S1). The *t*-butyl equivalent **1p**, however, with no protons in α-position to the alkyne, delivered the desired reaction product in 79% yield. Next, we evaluated the possibility of introducing substituents on the backbone of the system and were able to demonstrate that the presence of a fluoride (**2q**) or an ester group (**2r**) in the 5-position of the backbone provides excellent yields of 84% and 75%, respectively. Equally pleasing, product **2t** with a methyl group in the 4-position was isolated with 84%. Merely a methoxy group in the 5-position proved to be problematic as the corresponding 3*H*-indol-3-one **2s** was only obtained with a disappointing yield of 17% due to an incomplete conversion of the sulfoximine even after a significantly prolonged reaction time.

From a mechanistic point of view,[31] the reaction can proceed *via* two different pathways (Scheme 3). Both arise from the π-coordination of the Lewis acidic cationic Au(I) complex to the alkyne moiety of substrate **1**, leading to the formation of complex **I**. From this point, a nucleophilic attack on the activated alkyne can occur from either the nitrogen or the oxygen atom. For the case of the nitrogen atom (Scheme 3, pathway A), a 5-*endo-dig* cyclisation occurs, forming vinyl gold species **II-A**, which then forms α-imino gold carbene **III-A** by elimination of tetrahydrothiophene oxide. The sulfoxide can then, in turn, oxidise gold carbene **III-A** intermolecularly to give product **2** after release of the gold catalyst, generating tetrahydrothiophene as a by-product. Alternatively, starting from π-complex **I**, the oxygen atom can attack the alkyne, resulting in a 6-*exo-dig* cyclisation to form vinyl gold species **II-B** (Scheme 3, pathway B). This could then lead to a cleavage of the S–O bond and the formation of α-oxo gold carbene **III-B** with a tethered sulfilimine unit. The sulfilimine nitrogen atom could then trap the carbene, in this case furnishing product **2** in an intramolecular manner.

In order to obtain a first idea about the reaction pathway, we monitored the gold-catalysed conversion of substrate **1a** by means of positive-ion electrospray ionisation mass spectrometry (ESI-MS). The ESI mass spectrum exhibited a prominent peak at m/z 1883.0258, the occurrence of which corresponds to an ion $[C_{120}H_{139}AuN_3O_2S]^+$ (calc. m/z 1883.0248) which is equivalent to the combined mass of sulfoximine **1a** and cationic gold complex [IPr**Au]$^+$ (see Supporting Information, Figure S1 and Table S1). Further study of the ion by tandem mass spectrometry using collision-induced dissociation (CID, collision offset voltage 80 V) showed that it delivered three fragment ions at m/z 1557.9101, 1778.9937, and 1794.9887 (see Supporting Information, Figure S2 and Table S2). Based on the accurate mass data, these can be assigned to the formulas $[C_{101}H_{120}AuN_2]^+$ (calc. m/z 1557.9112), $[C_{116}H_{131}AuN_3O]^+$



Scheme 3. Two possible mechanistic pathways A and B for the gold-catalysed conversion of sulfoximines **1** to 3*H*-indol-3-ones **2**.

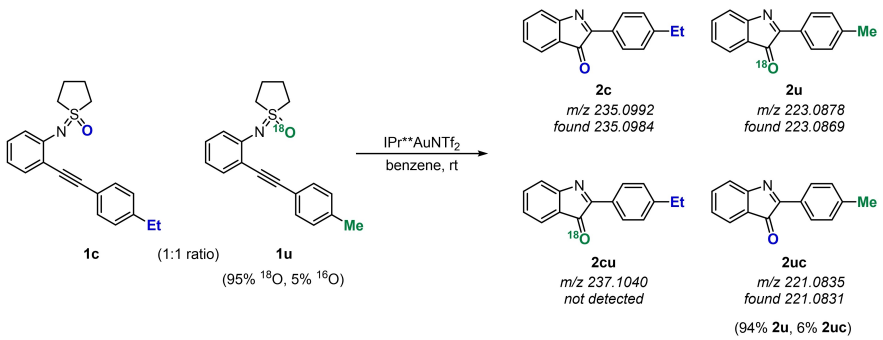
(calc. m/z 1778.9952), and $[C_{116}H_{131}AuN_3O_2]^+$ (calc. m/z 1794.9902), respectively. Thus, two of these correspond to the loss of tetrahydrothiophene and tetrahydrothiophene 1-oxide, respectively, while the third indicates the free cationic gold catalyst.

Next, we conducted a series of mechanistic experiments to gain further insight into the underlying mechanism. First, competing carbene trapping reagents were added to the reaction in order to assess whether they could react with any potential intermediate gold carbenes. Especially if the reaction were to proceed *via* the intermolecular pathway A, one would expect to observe a competition between the transiently formed sulfoxide and the added reagents. However, neither the addition of an excess of 1,3,5-trimethoxybenzene nor the addition of an excess of 4-fluorostyrene showed the formation of reaction products resulting from a nucleophilic trapping or a cyclopropanation of a potential gold carbene intermediate (see Supporting Information, Scheme S2), as observed by NMR spectroscopy. Next, we assessed whether adding a sulfoxide as similar as possible to tetrahydrothiophene 1-oxide to the reaction could lead to a competing oxidation of potential α-imino gold carbene **III-A**. To this end, we selected a tetrahydrothiophene-based sulfoxide featuring two methyl groups on the rear end of the five-membered ring, which should not be expected to alter its reactivity from a steric or electronic point of view. Whereas one could clearly see the formation of both reaction product **2a** and unsubstituted tetrahydrothiophene when monitoring the reaction by ^{1}H NMR spectroscopy, no formation of the corresponding dimethyl-substituted tetrahydrothiophene, which would be an inevitable by-product of a competing oxidation, was observed (see Supporting Information, Schemes S3 and S4).

Lastly, we performed a crossover experiment to further distinguish between an inter- and an intramolecular process (Scheme 4). As the oxygen atom is the only component that could potentially be exchanged, we synthesised ^{18}O-labelled sulfoximine **1u**, substituted with a methyl group on the phenyl acetylene unit, and reacted it in a 1:1 mixture with non-^{18}O-labelled sulfoximine **1c**, carrying an ethyl group in the same position.

The formation of mainly non-crossover products **2c** and **2u** was observed by high resolution mass spectrometry. A small share of crossover product **2uc** was found, yet this cannot be attributed to an exchange between substrates **1c** and **1u**, but rather is the result of an incomplete ^{18}O-labelling of sulfoximine **1u** (5 % ^{16}O content as determined by mass spectrometry). Most importantly, the opposing crossover product **2cu** could not be detected, indicating that no exchange of the oxygen atom can take place in the course of the mechanism, therefore pointing to the reaction occurring intramolecularly (see Supporting Information, Figure S3).

All the gathered experimental evidence points to an intramolecular reaction mechanism, which would be in favour of pathway B. However, we decided to further examine the reaction from a computational chemistry point of view and conducted density functional theory (DFT) calculations at the SMD/wB97XD/def2-TZVP//SMD/wB97XD/6-31G(d), SDD level of theory in benzene. As shown in the free energy profile depicted in Figure 2a, π-complex **I** serves as a branching point for both pathways A and B. Pathway A begins with the nucleophilic attack of the



Scheme 4. A crossover experiment carried out in order to distinguish between the possible reaction pathways A and B.

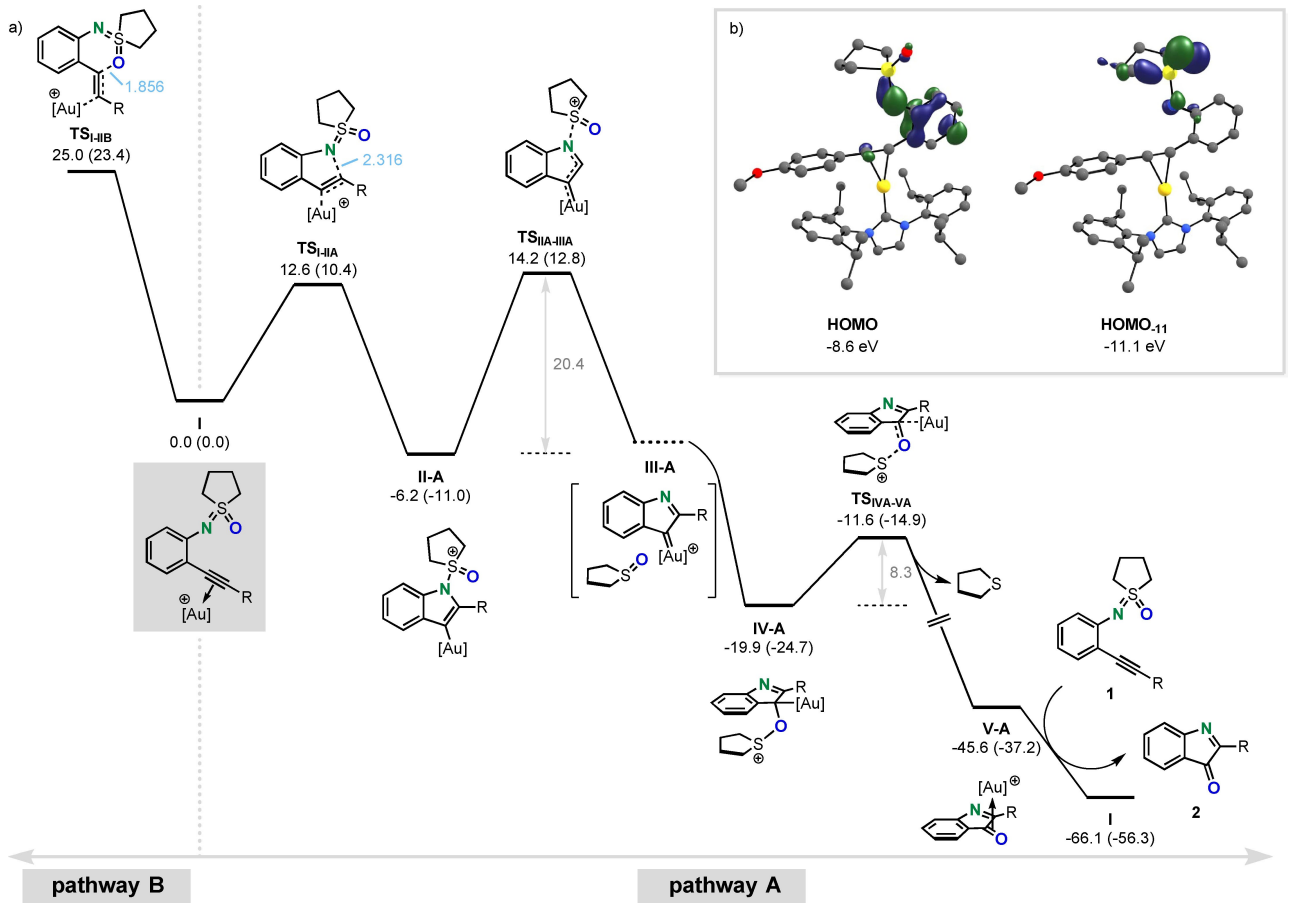


Figure 2. (a) The calculated free energy profile for the cyclisation of sulfoximines **1** to 3*H*-indol-3-ones **2**. The pale blue values indicate the length of selected bonds in Å. The relative Gibbs free energies and relative electronic energies (in parentheses) are given in kcal mol^{-1}. (b) Analysis of the Kohn–Sham orbitals of complex **I**, in particular the HOMO and HOMO$_{-11}$.

nitrogen atom on the Au-activated π-bond *via* transition structure $\mathbf{TS_{I\text{-}IIA}}$, whereas pathway B commences with the nucleophilic attack of the oxygen atom on the Au-activated π-bond *via* transition structure $\mathbf{TS_{I\text{-}IIB}}$. $\mathbf{TS_{I\text{-}IIA}}$, having a relative free energy of 12.6 kcal mol^{-1}, is calculated to be 12.4 kcal mol^{-1} lower in energy compared to $\mathbf{TS_{I\text{-}IIB}}$, which possesses a relative free energy of 25.0 kcal mol^{-1}. This implies that the nitrogen atom is more nucleophilic than the oxygen atom, which is confirmed by the analysis of the Kohn–Sham orbitals of complex **I** (Figure 2b). Specifically, the HOMO of complex **I**, with an energy of −8.6 eV, is primarily composed of the nitrogen lone pair, while the HOMO$_{-11}$, having an energy of −11.1 eV, is predominantly constituted by the oxygen lone pair. This indicates that the nitrogen lone pair lies significantly higher in energy, thereby making it more nucleophilic than the oxygen atom.

The nucleophilic attack of the nitrogen atom generates intermediate **II-A**, from which product **2** is formed after

undergoing several chemical sequences, as outlined in Figure 2a. Accordingly, all the transition structures involved in pathway A are considerably lower in energy than transition structure $\mathbf{TS_{I\text{-}IIB}}$, suggesting that pathway A is energetically much more favourable. Therefore, we chose not to investigate pathway B computationally in its entirety.

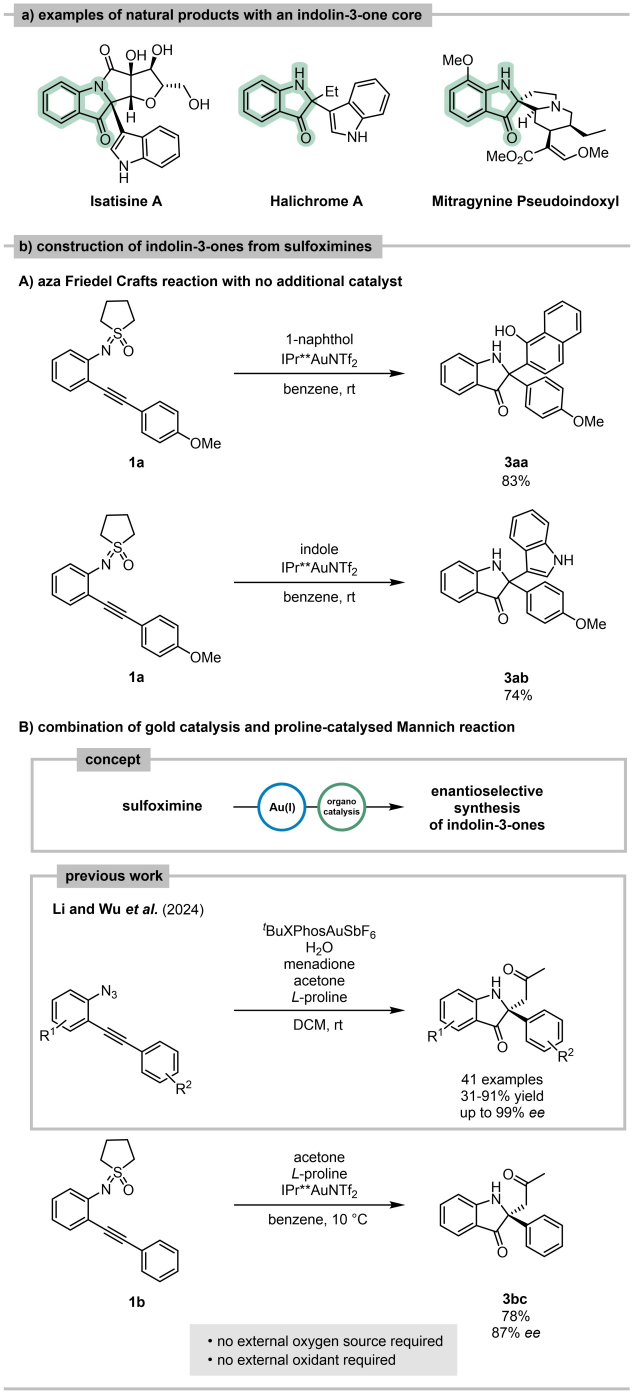
Upon the formation of complex **II-A**, it releases the sulfoxide *via* transition structure $\mathbf{TS_{IIA\text{-}IIIA}}$. This transition structure was anticipated to lead to the formation of outer-sphere complex **III-A**; however, IRC calculations revealed that this outer-sphere complex is not a local minimum, and it prefers to yield complex **IV-A** by a barrierless recombination of the carbene complex and the sulfoxide within complex **III-A**. It is worth noting that our additional attempts to isolate outer-sphere complex **III-A** as a distinct species were also unsuccessful, invariably resulting in the formation of **IV-A**. The recombination of the fragments in **III-A** occurs *via* a nucleophilic attack of the sulfoxide onto the electrophilic carbon atom of the carbene. This observation indicates that while the formation of **IV-A** occurs through an *inter*molecular reaction, the interaction between the carbene complex and the sulfoxide is so immediate that the sulfoxide cannot escape the solvent cage. Hence, we propose classifying the transformation as a *"pseudo-intramolecular"* reaction rather than an intermolecular reaction. This computational evidence provides a clear explanation for why all the aforementioned mechanistic experiments suggest that the reaction proceeds intramolecularly, despite it actually following intermolecular pathway A.

Subsequently, the interaction between the Au–C σ orbital and the S–O σ* orbital in intermediate **IV-A** leads to the cleavage of the S–O bond with an activation energy of 8.3 kcal mol^{-1}. This results in the formation of the final product, which remains coordinated to the gold centre in intermediate **V-A**, accompanied by the concurrent liberation of tetrahydrothiophene. Ultimately, the ligand exchange between intermediate **V-A** and substrate **1** results in the liberation of product **2** and the regeneration of **I**, all within an exergonic process.

For the sake of completeness, we also investigated the formation of intermediate **IV-A** from **II-A** *via* an asynchronous [2,3]-sigmatropic rearrangement computationally. However, attempts to locate the transition state for this pathway resulted in complete cleavage of the N–S bond. This result suggests that the asynchronous rearrangement is unlikely to be feasible, making the stepwise mechanism outlined in Figure 2 the most likely operative pathway.

As mentioned previously, 3*H*-indol-3-ones are mainly employed as substrates for the construction of indolin-3-ones with a quaternary C2-atom as this substructure is present in a variety of biologically active natural products, a selection of which is depicted in Scheme 5a.[24]

In light of this, we contemplated whether our methodology could be combined with a subsequent conversion of the emerging 3*H*-indol-3-ones to produce the highly desired indolin-3-ones directly from sulfoximines **1** in a one-pot procedure (Scheme 5b). First, we assessed whether adding electron-rich aryl systems to the reaction could lead to an aza Friedel Crafts reaction with the ketimine system of the



Scheme 5. a) A selection of natural products that incorporate an indolin-3-one core and b) an extension of our methodology to synthesise indolin-3-ones from sulfoximines in one-pot procedures.

3*H*-indol-3-one. To our delight, when adding 1.00 eq. of 1-naphthol to **1a** using our standard reaction conditions, the envisioned product **3aa** was obtained in an excellent yield of 83 %.[25i] Due to the Lewis acidity of Au(I), no additional catalyst was required to enable the Friedel Crafts reaction. Equally, replacing 1-naphthol with indole gave the corresponding product **3ab** in a yield of 74 %.[25c]

Alternatively, in the hope of constructing the chiral centre with enantioselectivity, we sought to combine the gold catalysis with a consecutive organocatalysis using a chiral catalyst. In the course of the completion of the underlying project, Li and Wu *et al.* have published a very similar strategy starting from 2-alkynyl arylazides.[26] In that case, they combined the gold-catalysed synthesis of the 3*H*-indol-3-one core with a previously reported proline-catalysed asymmetric Mannich reaction.[32] Albeit excellent results, their approach requires the presence of water as the oxygen source and an excess of an external oxidant for the construction of the 3*H*-indol-3-one,[26] which constitutes a significant limitation to the substrate scope. By replacing the azide functionality with a sulfoximine moiety, the addition of an external oxygen source as well as an external oxidant could be circumvented which would be highly beneficial to the applicability of the reaction. Therefore, we reacted sulfoximine **1b** with IPr**AuNTf$_2$, *L*-proline and acetone in benzene and were able to isolate the desired indolin-3-one **3bc** in 78 % yield with 87 % *ee*.

Conclusion

To conclude, we have showcased that sulfoximines can be used as highly efficient N- and O-transfer reagents to alkynes in gold catalysis with the example of the conversion of *N*-(2-alkynylphenyl) sulfoximines to 3*H*-indol-3-ones. Extensive experimental and theoretical investigations of this 1,2-difunctionalisation of the alkyne have shown that the nitrogen moiety is transferred first, resulting in the formation of the α-imino gold carbene, which is then oxidised by the transiently formed sulfoxide *via* a *pseudo-intramolecular* mechanism. The presented methodology exhibits an excellent functional group tolerance and gives the desired products in mostly high yields. Furthermore, we have demonstrated that it can easily be combined with further transformations in one-pot procedures, giving access to a high level of molecular complexity in a single step. Sulfoximines in general constitute an easily accessible and safe-to-handle substance class and we believe that due to their favourable properties and the synthetic variability, they possess an immense potential to act as N- and O-transfer reagents in a multitude of gold-catalysed conversions. Further work on the expansion of this methodology to other systems is currently ongoing in our laboratories.

Supporting Information

The authors have cited additional references within the Supporting Information.[33–63]

Acknowledgements

Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Alkyne Oxidation · Alpha Imino Gold Carbenes · Gold Catalysis · Sulfoximines · Transfer Reagents

[1] a) D. B. Huple, S. Ghorpade, R.-S. Liu, *Adv. Synth. Catal.* **2016**, *358*, 1348–1367; b) L.-W. Ye, X.-Q. Zhu, R. L. Sahani, Y. Xu, P.-C. Qian, R. -S Liu, *Chem. Rev.* **2021**, *121*, 9039–9112.
[2] a) C.-F. Xu, M. Xu, Y.-X. Jia, C.-Y. Li, *Org. Lett.* **2011**, *13*, 1556–1559; b) S. Shi, T. Wang, W. Yang, M. Rudolph, A. S. K. Hashmi, *Chem. Eur. J.* **2013**, *19*, 6576–6580; c) A. Y. Dubovtsev, D. V. Dar'in, M. Krasavin, V. Y. Kukushkin, *Eur. J. Org. Chem.* **2019**, 1856–1864; d) A. Y. Dubovtsev, N. V. Shcherbakov, D. V. Dar'in, V. Y. Kukushkin, *J. Org. Chem.* **2020**, *85*, 745–757.
[3] M. Pernpointner, A. S. K. Hashmi, *J. Chem. Theory Comput.* **2009**, *5*, 2717–2725.
[4] a) A. S. K. Hashmi, A. Schuster, F. Rominger, *Angew. Chem. Int. Ed.* **2009**, *48*, 8247–8249; *Angew. Chem.* **2009**, *121*, 8396–8398; b) A. S. K. Hashmi, *Gold Bull.* **2009**, *42*, 275–279.
[5] Z. Zheng, X. Ma, X. Cheng, K. Zhao, K. Gutman, T. Li, L. Zhang, *Chem. Rev.* **2021**, *121*, 8979–9038.
[6] a) H.-S. Yeom, J.-E. Lee, S. Shin, *Angew. Chem. Int. Ed.* **2008**, *47*, 7040–7043; *Angew. Chem.* **2008**, *120*, 7148–7151; b) H. -S Yeom, Y. Lee, J.-L. Lee, S. Shin, *Org. Biomol. Chem.* **2009**, *7*, 4744–4752.
[7] A. Mukherjee, R. B. Dateer, R. Chaudhuri, S. Bhunia, S. N. Karad, R.-S. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 15372–15375.
[8] N. Asao, K. Sato, Y. Yamamoto, *Tetrahedron Lett.* **2003**, *44*, 5675–5677.
[9] a) L. Zhang, *Acc. Chem. Res.* **2014**, *47*, 877–888.
[10] a) N. D. Shapiro, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 4160–4161; b) G. Li, L. Zhang, *Angew. Chem. Int. Ed.* **2007**, *46*, 5156–5159; *Angew. Chem.* **2007**, *119*, 5248–5251.
[11] a) X. Tian, L. Song, A. S. K. Hashmi, *Chem. Eur. J.* **2020**, *26*, 3197–3204; b) X. Tian, L. Song, M. Rudolph, F. Rominger, T. Oeser, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2019**, *58*, 3589–3593; *Angew. Chem.* **2019**, *131*, 3627–3631; c) X. Tian, L. Song, M. Rudolph, Q. Wang, X. Song, F. Rominger, A. S. K. Hashmi, *Org. Lett.* **2019**, *21*, 1598–1601; d) X. Tian, L. Song, C. Han, C. Zhang, Y. Wu, M. Rudolph, F. Rominger, A. S. K. Hashmi, *Org. Lett.* **2019**, *21*, 2937–2940; e) X. Tian, L. Song, M. Rudolph, F. Rominger, A. S. K. Hashmi, *Org. Lett.* **2019**, *21*, 4327–4330; f) X. Zhao, M. Rudolph, A. M. Asiri, A. S. K. Hashmi, *Front. Chem. Sci. Engin.* **2020**, *14*, 317–349; g) A. V. Mackenroth, P. W. Antoni, F. Rominger, M. Rudolph, A. S. K. Hashmi, *Org. Lett.* **2023**, *25*, 2907–2912; h) Q. Sun, C. Hüßler, J. Kahle, A. V. Mackenroth, M. Rudolph, P. Krämer, T. Oeser, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2024**, *63*, e202313738; *Angew. Chem.* **2024**, *136*, e202313738; for sulfilimines being used as nitrene transfer reagents in non-gold-catalysed reactions, see for example i) P. W. Antoni, A. V. Mackenroth, F. F. Mulks, M. Rudolph, G. Helmchen, A. S. K. Hashmi, *Chem. Eur. J.* **2020**, *26*, 8235–8238; j) X. Tian, L. Song, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2020**, *59*, 12342–12346; *Angew. Chem.* **2020**, *132*, 12441–12445.

[12] a) S. Kramer, T. Skrydstrup, *Angew. Chem. Int. Ed.* **2012**, *51*, 4681–4684; *Angew. Chem.* **2012**, *124*, 4759–4762; b) X. Huang, B. Peng, M. Luparia, L. F. R. Gomes, L. F. Veiros, N. Maulide, *Angew. Chem. Int. Ed.* **2012**, *51*, 8886–8890; *Angew. Chem.* **2012**, *124*, 9016–9020.

[13] a) V. Bizet, C. M. M. Hendriks, C. Bolm, *Chem. Soc. Rev.* **2015**, *44*, 3378–3390; b) M. Andresini, A. Tota, L. Degennaro, J. A. Bull, R. Luisi, *Chem. Eur. J.* **2021**, *27*, 17293–17321; c) W. Zheng, X. Chen, F. Chen, Z. He, Q. Zeng, *Chem. Rec.* **2021**, *21*, 396–416.

[14] a) U. Lücking, *Angew. Chem. Int. Ed.* **2013**, *52*, 9399–9408; b) M. Frings, C. Bolm, A. Blum, C. Gnamm, *Eur. J. Med. Chem.* **2017**, *126*, 225–245; c) P. Mäder, L. Kattner, *J. Med. Chem.* **2020**, *63*, 14243–14275; d) Y. Han, K. Xing, J. Zhang, T. Tong, Y. Shi, H. Cao, H. Yu, Y. Zhang, D. Liu, L. Zhao, *Eur. J. Med. Chem.* **2021**, *209*, 112885–112898; e) D. Strobbe, R. Pecorari, O. Conte, A. Minutolo, C. M. M. Hendriks, S. Wiezorek, D. Faccenda, R. Abeti, C. Montesano, C. Bolm, M. Campanella, *Br. J. Pharmacol.* **2021**, *178*, 298–311; f) U. Lücking, *Chem. Eur. J.* **2022**, *28*, e202201993.

[15] a) T. C. Sparks, G. B. Watson, M. R. Loso, C. Geng, J. M. Babcock, J. D. Thomas, *Pestic. Biochem. Physiol.* **2013**, *107*, 1–7; b) K. E. Arndt, D. C. Bland, N. M. Irvine, S. L. Powers, T. P. Martin, J. R. McConnell, D. E. Podhorez, J. M. Renga, R. Ross, G. A. Roth, B. D. Scherzer, T. W. Toyzan, *Org. Process Res. Dev.* **2015**, *19*, 454–462.

[16] a) C. Bolm, O. Simić, *J. Am. Chem. Soc.* **2001**, *123*, 3830–3831; b) M. Langner, C. Bolm, *Angew. Chem. Int. Ed.* **2004**, *43*, 5984–5987; *Angew. Chem.* **2004**, *116*, 6110–6113; c) S.-M. Lu, C. Bolm, *Adv. Synth. Catal.* **2008**, *350*, 1101–1105.

[17] a) M. R. Yadav, R. K. Rit, A. K. Sahoo, *Chem. Eur. J.* **2012**, *18*, 5541–5545; b) K. Ghosh, M. Shankar, R. K. Rit, G. Dubey, P. V. Bharatam, A. K. Sahoo, *J. Org. Chem.* **2018**, *83*, 9667–9681; c) K. Ghosh, A. Ghosh, K. Mukherjee, R. K. Rit, A. K. Sahoo, *J. Org. Chem.* **2020**, *85*, 8618–8626.

[18] a) S. Koep, H.-J. Gais, G. Raabe, *J. Am. Chem. Soc.* **2003**, *125*, 13243–13251; b) D. Craig, F. Grellepois, A. J. P. White, *J. Org. Chem.* **2005**, *70*, 6827–6832; c) S. Sau, K. Mukherjee, K. Kondalarao, V. Gandon, A. K. Sahoo, *Org. Lett.* **2023**, *25*, 7667–7672.

[19] a) W. Zhang, F. Wang, J. Hu, *Org. Lett.* **2009**, *11*, 2109–2112; b) K. Matsui, M. Shibuya, Y. Yamamoto, *Commun. Chem.* **2018**, *1*, 1–8; c) Y. -F Zhang, X.-Y. Dong, J.-T. Cheng, N.-Y. Yang, L.-L. Wang, F.-L. Wang, C. Luan, J. Liu, Z.-L. Li, Q.-S. Gu, X.-Y. Liu, *J. Am. Chem. Soc.* **2021**, *143*, 15413–15419; d) X. Wang, M. Frings, K. Rissanen, C. Bolm, *J. Org. Chem.* **2023**, *88*, 2666–2669; e) T. Koike, *Chem. Rec.* **2023**, *23*, e202300032.

[20] A. A. H. Mercy, V. R. P. Priya, R. Hariprasad, K. Gayathri, S. Ravindra, G. C. Nandi, R. Kataria, *Org. Biomol. Chem.* **2024**, *22*, 945–949.

[21] C. Bolm, J. P. Hildebrand, *J. Org. Chem.* **2000**, *65*, 169–175.

[22] M. Zenzola, R. Doran, L. Degennaro, R. Luisi, J. A. Bull, *Angew. Chem. Int. Ed.* **2016**, *55*, 7203–7207; *Angew. Chem.* **2016**, *128*, 7319–7323.

[23] a) E. Najahi, A. Valentin, P.-L. Fabre, K. Reybier, F. Nepveu, *Eur. J. Med. Chem.* **2014**, *78*, 269–274; b) N. V. Rakotoarivelo, P. Perio, E. Najahi, F. Nepveu, *J. Phys. Chem. B* **2014**, *118*, 13477–13485.

[24] a) A. Karadeolian, M. A. Kerr, *Angew. Chem.* **2010**, *49*, 1133–1135; *Angew. Chem.* **2010**, *122*, 1151–1153; b) T. Abe, A. Kukita, K. Akiyama, T. Naito, D. Uemura, *Chem. Lett.* **2012**, *41*, 728–729; c) P. Angyal, K. Hegedüs, B. B. Mészáros, J. Daru, Á. Dudás, A. R. Galambos, N. Essmat, M. Al-Khrasani, S. Varga, T. Soós, *Angew. Chem. Int. Ed.* **2023**, *62*, e202303700; *Angew. Chem.* **2023**, *135*, e202303700.

[25] a) A. Parra, R. Alfaro, L. Marzo, A. Moreno-Carrasco, J. L. García Ruano, J. Alemán, *Chem. Commun.* **2012**, *48*, 9759–9761; b) J.-S. Li, Y.-J. Liu, S. Li, J.-A. Ma, *Chem. Commun.* **2018**, *54*, 9151–9154; c) M. Rueping, S. Raja, A. Núñez, *Adv. Synth. Catal.* **2011**, *353*, 563–568; d) S. Nakamura, N. Matsuda, M. Ohara, *Chem. Eur. J.* **2016**, *22*, 9478–9482; e) X. Yuan, X. Wu, F. Peng, H. Yang, C. Zhu, H. Fu, *Chem. Commun.* **2020**, *56*, 12648–12651; f) Q.-X. Zhang, Y. Li, J. Wang, C. Yang, C.-J. Liu, X. Li, J.-P. Cheng, *Angew. Chem. Int. Ed.* **2020**, *59*, 4550–4556; *Angew. Chem.* **2020**, *132*, 4580–4586; g) Q. Zhao, Y. Li, Q.-X. Zhang, J.-P. Cheng, X. Li, *Angew. Chem. Int. Ed.* **2021**, *60*, 17608–17614; *Angew. Chem.* **2021**, *133*, 17749–17755; h) J. Yadav, A. J. Dolas, E. Iype, K. Rangan, J. Ohshita, D. Kumar, I. Kumar, *J. Org. Chem.* **2021**, *86*, 17213–17225; i) T. Ma, Y. He, X.-X. Qiao, C.-P. Zou, X.-X. Wu, G. Li, X.-J. Zhao, *Org. Biomol. Chem.* **2023**, *21*, 489–493; j) X.-X. Qiao, Y. He, T. Ma, C.-P. Zou, X.-X. Wu, G. Li, X.-J. Zhao, *Chem. Eur. J.* **2023**, *29*, e202203914; k) C.-P. Zou, T. Ma, X.-X. Qiao, X.-X. Wu, G. Li, Y. He, X.-J. Zhao, *Org. Biomol. Chem.* **2023**, *21*, 4393–4397; l) X.-X. Wu, Y. He, X.-X. Qiao, T. Ma, C.-P. Zou, G. Li, X.-J. Zhao, *J. Org. Chem.* **2023**, *88*, 6599–6610; m) X.-X. Wu, T. Ma, X.-X. Qiao, C.-P. Zou, G. Li, Y. He, X.-J. Zhao, *Chem. Asian J.* **2023**, *18*, e202300526.

[26] W.-B. Wang, J.-C. Lu, H. Bai, Y.-M. Fu, L.-J. Cheng, C.-F. Zhu, Y.-G. Li, X. Wu, *Org. Lett.* **2024**, *26*, 1792–1796.

[27] a) A. C. Lindsay, I. K. H. Leung, J. Sperry, *Org. Lett.* **2016**, *18*, 5404–5407; b) J.-S. Li, Y.-J. Liu, G.-W. Zhang, J.-A. Ma, *Org. Lett.* **2017**, *19*, 6364–6367.

[28] Deposition numbers CCDC 2388227 (for **2i**), CCDC 2388228 (for **S11**), CCDC 2388229 (for **S12**) and CCDC 2388230 (for **S13**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data centre via www.ccdc.cam.a-c.uk/structures.

[29] W. Yong, P. Li, R. Sheng, W. Rao, X. Zhang, *ChemistrySelect* **2018**, *3*, 11696–11699.

[30] H. Peng, J. Ma, L. Duan, G. Zhang, B. Yin, *Org. Lett.* **2019**, *21*, 6194–6198.

[31] a) A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2010**, *49*, 5232–5241; *Angew. Chem.* **2010**, *122*, 5360–5369; b) T. Lauterbach, A. M. Asiri, A. S. K. Hashmi, *Adv. Organomet. Chem.* **2014**, *62*, 261–297.

[32] L. Li, M. Han, M. Xiao, Z. Xie, *Synlett* **2011**, *12*, 1727–1730.

[33] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.

[34] W. L. Mock, R. M. Nugent, *J. Am. Chem. Soc.* **1975**, *97*, 6526–6529.

[35] A. K. Verma, T. Kesharwani, J. Singh, V. Tandon, R. C. Larock, *Angew. Chem. Int. Ed.* **2009**, *48*, 1138–1143; *Angew. Chem.* **2009**, *121*, 1158–1163.

[36] D. L. J. Clive, D. C. Cole, *J. Chem. Soc. Perkin Trans. 1* **1991**, *12*, 3263–3270.

[37] A. K. Verma, R. R. Jha, R. Chaudhary, R. K. Tiwari, K. S. K. Reddy, A. Danodia, *J. Org. Chem.* **2012**, *77*, 8191–8205.

[38] Z. U. Levi, T. D. Tilley, *J. Am. Chem. Soc.* **2009**, *131*, 2796–2797.

[39] M. Kuhn, F. C. Falk, J. Paradies, *Org. Lett.* **2011**, *13*, 4100–4103.

[40] P. S. Shinde, A. C. Shaikh, N. T. Patil, *Chem. Commun.* **2016**, *52*, 8152–8155.

[41] L.-C. Campeau, M. Parisien, A. Jean, K. Fagnou, *J. Am. Chem. Soc.* **2006**, *128*, 581–590.

[42] A. Orita, K. Miyamoto, M. Nakashima, F. Ye, J. Otera, *Adv. Synth. Catal.* **2004**, *346*, 767–776.

[43] K. Naveen, P. T. Perumal, D.-H. Cho, *Org. Lett.* **2019**, *21*, 4350–4354.

[44] T. Morishita, H. Yoshida, J. Ohshita, *Chem. Commun.* **2010**, *46*, 640–642.
[45] T. Sanji, K. Shiraishi, T. Kashiwabara, M. Tanaka, *Org. Lett.* **2008**, *10*, 2689–2692.
[46] X. Yang, Z. Li, J. Zhi, J. Ma, A. Hu, *Langmuir* **2010**, *26*, 11244–11248.
[47] M. L. N. Rao, P. Dasgupta, S. S. Islam, *Org. Chem. Front.* **2017**, *4*, 335–342.
[48] H. Sashida, K. Sadamori, T. Tsuchiya, *Synth. Commun.* **1998**, *28*, 713–727.
[49] K. Hirano, Y. Inaba, K. Takasu, S. Oishi, Y. Takemoto, N. Fujii, H. Ohno, *J. Org. Chem.* **2011**, *76*, 9068–9080.
[50] V. Guilarte, M. A. Fernández-Rodríguez, P. García-García, E. Hernando, R. Sanz, *Org. Lett.* **2011**, *13*, 5100–5103.
[51] T. Watanabe, H. Abe, Y. Mutoh, S. Saito, *Chem. Eur. J.* **2018**, *24*, 11545–11549.
[52] M. Chen, N. Su, T. Deng, D. J. Wink, Y. Zhao, T. G. Driver, *Org. Lett.* **2019**, *21*, 1555–1558.
[53] Q. Liu, P. Chen, G. Liu, *ACS Catal.* **2013**, *3*, 178–181.
[54] A. A. Vasil'ev, L. Engman, E. P. Serebryakov, *J. Chem. Soc. Perkin Trans. 1* **2000**, 2211–2216.
[55] Y.-L. Zhu, Y.-F. Dong, S.-R. Wang, Y.-G. Li, X. Wu, L.-W. Ye, *Org. Lett.* **2024**, *26*, 631–635.
[56] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, in *Gaussian 16 Rev. C.01*, Wallingford, CT **2016**.
[57] J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.
[58] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Chem. Theory Comput.* **2013**, *9*, 609–620.
[59] a) A. Bergner, M. Dolg, W. Küchle, H. Stoll, H. Preuß, *Mol. Phys.* **1993**, *80*, 1431–1441; b) M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.* **1987**, *86*, 866–872; c) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213–222.
[60] X. Li, M. J. Frisch, *J. Chem. Theory Comput.* **2006**, *2*, 835–839.
[61] K. Fukui, *Acc. Chem. Res.* **1981**, *14*, 363–368.
[62] F. Weigend, F. Furche, R. Ahlrichs, *J. Chem. Phys.* **2003**, *119*, 12753–12762.
[63] C. J. Cramer, *Essentials of computational chemistry: theories and models*, John Wiley & Sons **2013**.

Manuscript received: October 21, 2024
Accepted manuscript online: December 11, 2024
Version of record online: January 13, 2025