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# Beyond protodeauration: Vinyl-gold as nucleophilic platforms in gold catalysis

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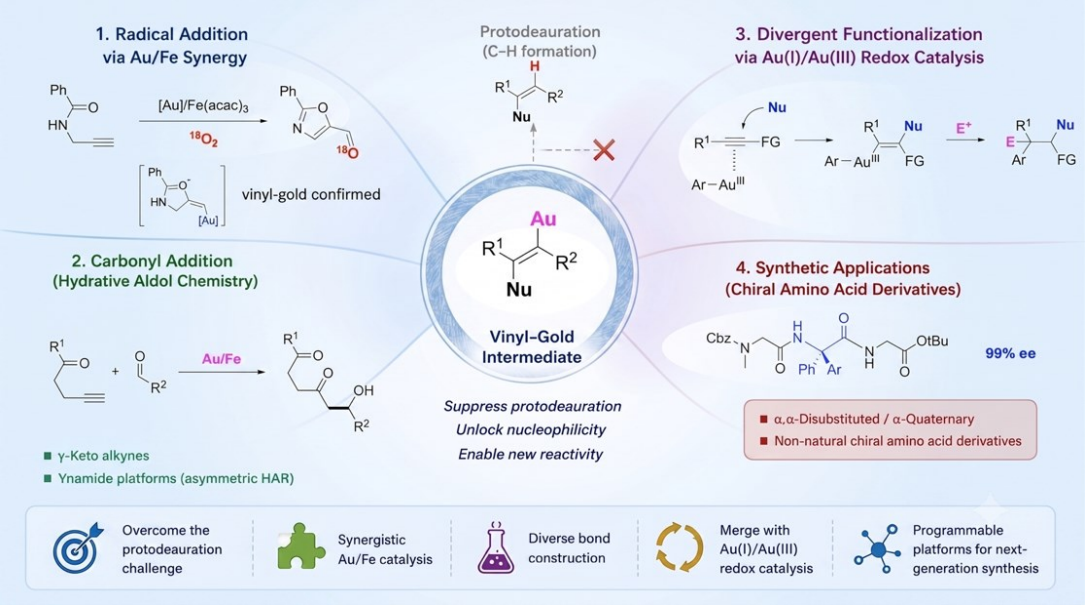
## Abstract

Gold-catalyzed alkyne and allene transformations often generate vinyl-gold intermediates, but their broader organometallic reactivity is limited by rapid protodeauration. This review summarizes our efforts to redirect these transient species into nucleophilic platforms for bond construction. Synergistic Au/Fe catalysis suppresses competitive protonation and enables radical addition, carbonyl addition and stereoselective hydrative aldol reactions, including ynamide variants. Further merger with Au(I)/Au(III) redox catalysis allows divergent alkyne functionalization and multiple bond formation in one operation. Together, these studies establish vinyl-gold intermediates as tunable and programmable organogold species for next-generation gold catalysis.




**Keywords:** Gold catalysis, vinyl-gold intermediates, protodeauration, hydrative aldol reaction, Au(I)/Au(III) redox catalysis

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## 1. Introduction

Homogeneous gold catalysis has become a powerful platform for the activation of alkynes and allenes in organic synthesis.[1,2] Unlike many conventional Lewis acidic or transition-metal systems, cationic gold complexes can engage C–C π-bonds under mild conditions with high functional-group tolerance and distinctive chemoselectivity.[3,4] This reactivity has enabled a broad range of transformations in which alkynes are converted into structurally complex, alkene-containing products without extensive overactivation of the newly formed C=C bond.[5,6]

A central feature of many gold-catalyzed alkyne and allene reactions is the formation of vinyl-gold intermediates.[7,8] In a typical sequence, coordination of a cationic gold species to an alkyne generates an activated π-complex, followed by nucleophilic addition to give a defined C–Au-containing vinyl-gold species. In most classical gold-catalyzed transformations, this intermediate undergoes rapid protodeauration, converting the C–Au bond into a C–H bond and delivering the corresponding alkene product.[9,10] As a result, protodeauration has long been viewed as the dominant and often inevitable termination step in gold π-activation chemistry.[9]

From a synthetic perspective, however, the vinyl-gold intermediate represents a much broader opportunity. The presence of a polarized C–Au bond suggests that, if protonation can be suppressed or redirected, vinyl-gold species could be used as productive organometallic partners for further bond construction. This possibility is especially attractive because it would move gold catalysis beyond simple π-activation/protodeauration manifolds and allow vinyl-gold intermediates to participate in C–C and C–heteroatom bond-forming processes.[8,11] The key challenge is therefore not merely to generate vinyl-gold intermediates, which is common in gold catalysis, but to control their fate before rapid protodeauration occurs.

Our research program has focused on addressing this challenge by developing strategies that convert vinyl-gold intermediates from short-lived spectators into nucleophilic platforms. One approach relies on synergistic Au/Fe catalysis, in which the iron component suppresses protonation pathways and allows vinyl-gold species to engage in radical addition and carbonyl addition.[12] This strategy enabled the development of hydrative aldol-type reactions under mild conditions, providing direct access to β-hydroxy carbonyl products through productive vinyl-gold nucleophilicity.[12] Further tuning of the alkyne substrate, particularly through the use of electron-rich ynamides, expanded this concept beyond carbonyl-directed systems and enabled highly stereoselective and asymmetric intermolecular additions.[13,14]

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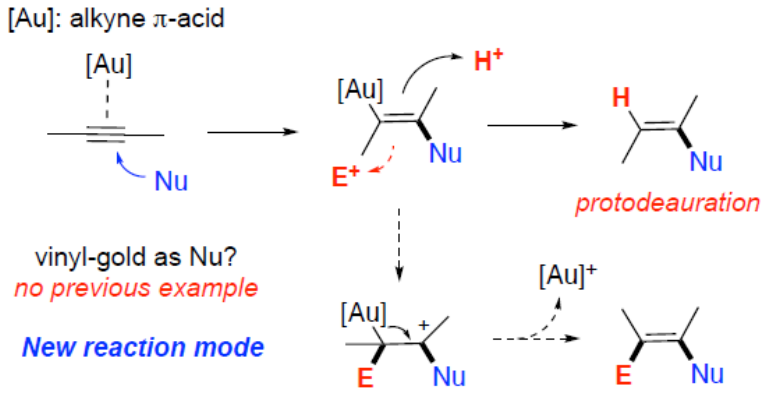
A second direction emerged from the integration of vinyl-gold nucleophilicity with Au(I)/Au(III) redox catalysis. In this manifold, vinyl-gold intermediates are not simply protected from protodeauration; instead, they are incorporated into a redox-active catalytic sequence involving oxidation, nucleophilic trapping and reductive elimination. This merger enables divergent alkyne functionalization and multiple bond-forming events in a single operation, further highlighting the programmable reactivity of vinyl-gold species.[11,15,16]

In this review, we summarize these developments from the perspective of overcoming protodeauration. The discussion is organized around three stages: the initial discovery that vinyl-gold intermediates can be intercepted under Au/Fe cooperative conditions, the development of hydrative aldol chemistry based on vinyl-gold nucleophilicity, and the merger of vinyl-gold reactivity with Au(I)/Au(III) redox catalysis. Together, these studies establish vinyl-gold intermediates as versatile nucleophilic platforms and provide a foundation for the design of new gold-catalyzed transformations.[12,13,16]

## 2. Vinyl-Gold Intermediates as Nucleophilic Platforms

The common presence of vinyl-gold intermediates in gold-catalyzed π-activation chemistry provides an attractive opportunity for reaction design, but their productive use requires a pathway that can compete with rapid protodeauration. As outlined in Scheme 1, the central challenge is to redirect these intermediates away from simple C–H bond formation and toward productive C–C or C–heteroatom bond construction.[8,9] Our initial progress in this area came from synergistic Au/Fe catalysis, which revealed that vinyl-gold intermediates could be intercepted under properly designed reaction conditions and converted into useful nucleophilic organometallic partners.[12]




**Scheme 1.** Conceptual framework for redirecting vinyl-gold intermediates from protodeauration toward nucleophilic bond construction.

### 2.1. Intercepting vinyl-gold intermediates through Au/Fe cooperative catalysis

The origin of this program was an accidental discovery made during our efforts to merge gold catalysis with radical chemistry. At that time, our goal was to identify radical conditions that would be compatible with Au(I)-mediated π-activation and might eventually connect gold π-acid catalysis with redox processes. Propargyl amides were selected as model substrates because their gold-catalyzed cyclization provides a reliable and well-defined route to vinyl-gold intermediates.[12] Most radical-generating systems, however, were not compatible with this process and led to complex mixtures or unproductive reaction pathways.

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A key breakthrough was achieved when $Fe(acac)_3/O_2$ was identified as a uniquely compatible radical-generating system. Under these conditions, gold-catalyzed cyclization of propargyl amides **1** generated vinyl-gold intermediate **3** that could be intercepted before protodeauration, leading to the formation of oxazole aldehydes **2** under mild conditions (Scheme 2A).[12] This result was important because it showed that vinyl-gold species, although often treated as short-lived intermediates en route to protonation, can persist long enough to participate in productive bond-forming chemistry when an appropriate competing pathway is available.

Mechanistic studies supported direct interception of the vinyl-gold intermediate rather than a simple stepwise sequence involving protodeauration followed by oxidation of the alkene product **4**. Kinetic analysis showed that product formation under the cooperative Au/Fe conditions ($\mathbf{k_1}$) was faster than independent gold-catalyzed cyclization ($\mathbf{k_2}$) followed by $Fe/O_2$-mediated oxidation of the corresponding alkene ($\mathbf{k_3}$).[12] This observation indicated that the vinyl-gold intermediate **3** was more reactive toward the iron-mediated oxygen radical pathway than the alkene product and provided the first key evidence that the C–Au bond could be preserved and exploited under carefully matched catalytic conditions.[12]

The mechanistic lesson from this discovery was broader than the radical reaction itself. It suggested that protodeauration, although fast, is not necessarily unavoidable. If the protonation pathway can be slowed or if a productive trapping pathway can be made sufficiently competitive, vinyl-gold intermediates can be redirected toward new reactivity.[10,12] This idea became the foundation for our subsequent design of Au/Fe cooperative catalysis as a strategy to unlock the nucleophilic character of vinyl-gold species.

This concept was next translated into carbonyl addition chemistry.[12] We designed γ-keto alkynes **5** as substrates in which gold-catalyzed alkyne activation and water addition would generate a vinyl-gold intermediate positioned near a carbonyl group or hemiacetal-like structure **6**. The goal was to extend the lifetime of the vinyl-gold species and allow it to react with an external aldehyde or ketone to form **7** before protonation. In the absence of the iron component, however, gold catalysis mainly led to simple hydration/protodeauration, giving the corresponding ketone **8** as the major product. The introduction of $Fe(acac)_3$ changed the reaction outcome and enabled formation of the desired hydrative aldol product (Scheme 2B).[12]

Further optimization identified an effective Au/Fe catalytic system using CyJohnPhosAu(TA-Me)OTf, $Fe(acac)_3$, $LiClO_4$, and water in ethyl acetate at room temperature. Under these mild and neutral conditions, the hydrative aldol product was obtained in high yield, demonstrating that a vinyl-gold intermediate generated in the presence of water could be redirected toward carbonyl addition rather than conventional hydration/protodeauration. This transformation provided the first clear example in which vinyl-gold intermediates were used as nucleophilic organometallic species for intermolecular carbonyl addition.[12]

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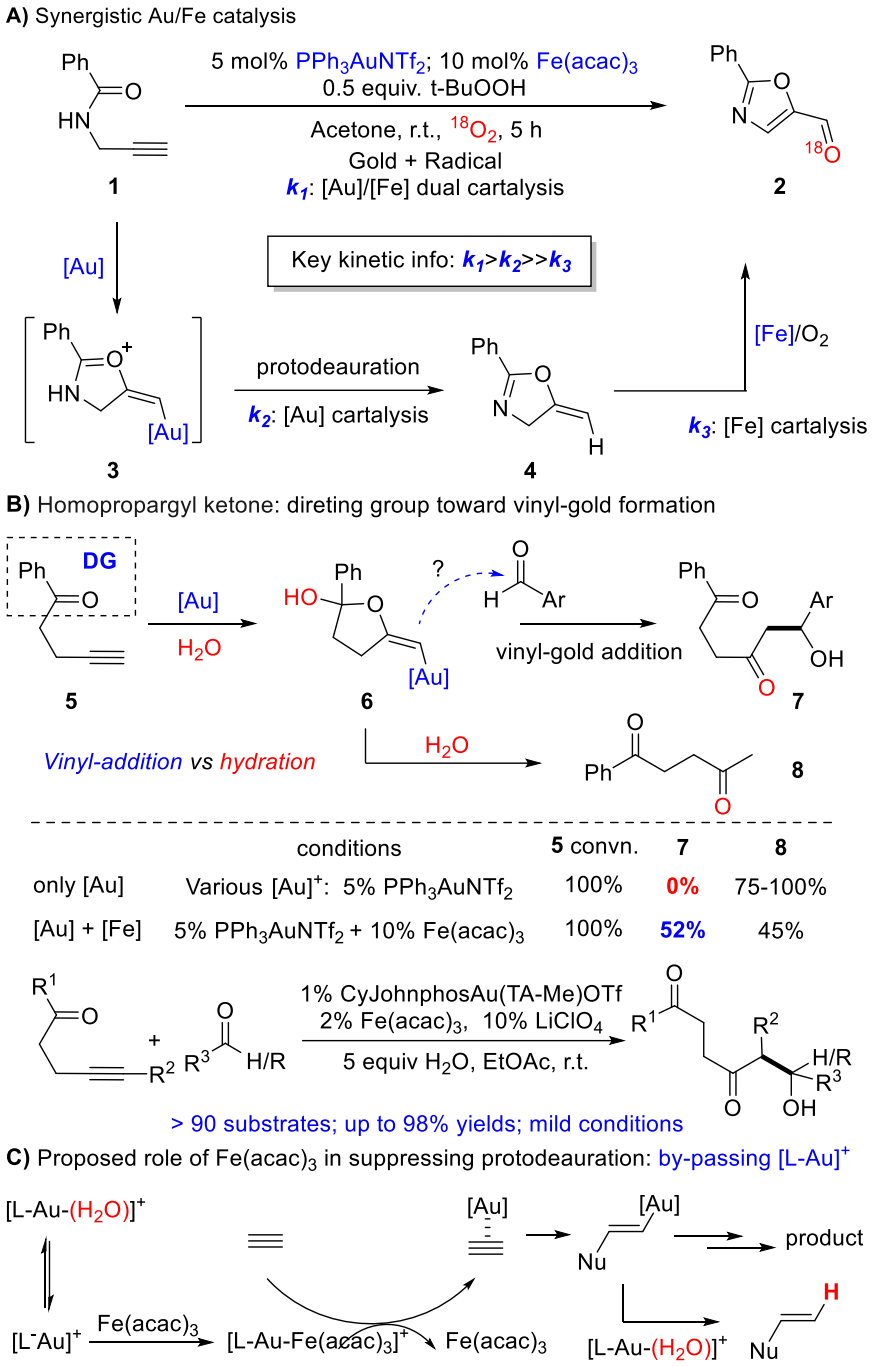


**Scheme 2.** Conceptual development of Au/Fe cooperative catalysis for redirecting vinyl-gold intermediates from protodeauration to bond construction.

Together, these studies established Au/Fe cooperative catalysis as a practical strategy for controlling the fate of vinyl-gold intermediates. The initial radical interception experiment revealed that these intermediates could be trapped before protonation, while the hydrative aldol reaction demonstrated that the same principle could be developed into a synthetically useful C–C bond-forming process. More broadly, this work provided the first step toward treating vinyl-gold species not merely as transient intermediates in gold π-activation chemistry, but as nucleophilic platforms whose reactivity can be tuned through catalyst cooperation and substrate design.[12]

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### 2.2 . Extending vinyl-gold nucleophilicity beyond directing-group control

The carbonyl-directed hydrative aldol reaction established that vinyl-gold intermediates could be converted into carbon nucleophiles under Au/Fe cooperative catalysis. However, this first-generation system also raised an important question: was the γ-carbonyl group essential for organizing and stabilizing the reactive vinyl-gold intermediate, or could this reactivity be generalized through a different design principle? In other words, if protodeauration could be slowed by the Au/Fe cooperative system, could a non-directed alkyne still generate a vinyl-gold species sufficiently nucleophilic to react with an external carbonyl electrophile?

Initial studies with simple alkynes showed that this challenge was nontrivial. A series of non-directed alkynes, including substrates bearing hydrogen, ester, bromo, enyne and diyne substituents, mainly underwent hydration under Au/Fe conditions and failed to deliver the desired hydrative aldol products. These results indicated that suppressing protodeauration alone was not sufficient. For vinyl-gold intermediates to participate in intermolecular carbonyl addition, the substrate must also generate a sufficiently polarized and electron-rich C–Au species capable of acting as a carbon nucleophile before protonation or simple hydration occurs. This observation led us to consider substrate electronics as a second control element for vinyl-gold nucleophilicity. Among possible alkyne classes, ynamides were particularly attractive because the nitrogen substituent can donate electron density into the alkyne π-system and strongly polarize the resulting vinyl-gold intermediate after gold-catalyzed hydration.[13,14] We envisioned that such an electronically activated vinyl-gold species would possess enhanced nucleophilic character at the carbon terminus involved in C–C bond formation and could therefore be intercepted by aldehydes without the need for a built-in γ-carbonyl directing group. In this way, the role of the directing group in the first-generation system could be replaced, at least in part, by electronic activation of the alkyne substrate.[14,17]

This design proved effective. In contrast to simple alkynes **9**, ynamide substrates **11** displayed distinct reactivity under Au/Fe cooperative conditions and produced hydrative aldol products **12** through intermolecular addition to aldehydes. After optimization, RuPhosAuNTf$_2$ and Fe(acac)$_3$ in toluene provided an efficient catalytic system for this transformation, delivering β-hydroxy amide products **12** in high yield and with excellent *syn* selectivity. These results demonstrated that productive vinyl-gold nucleophilicity could be achieved beyond carbonyl-directed substrates when three factors were properly balanced: suppression of protonation by the Au/Fe system, electronic activation of the alkyne through the ynamide substituent, and efficient trapping by an external aldehyde electrophile (Scheme 3).[13]

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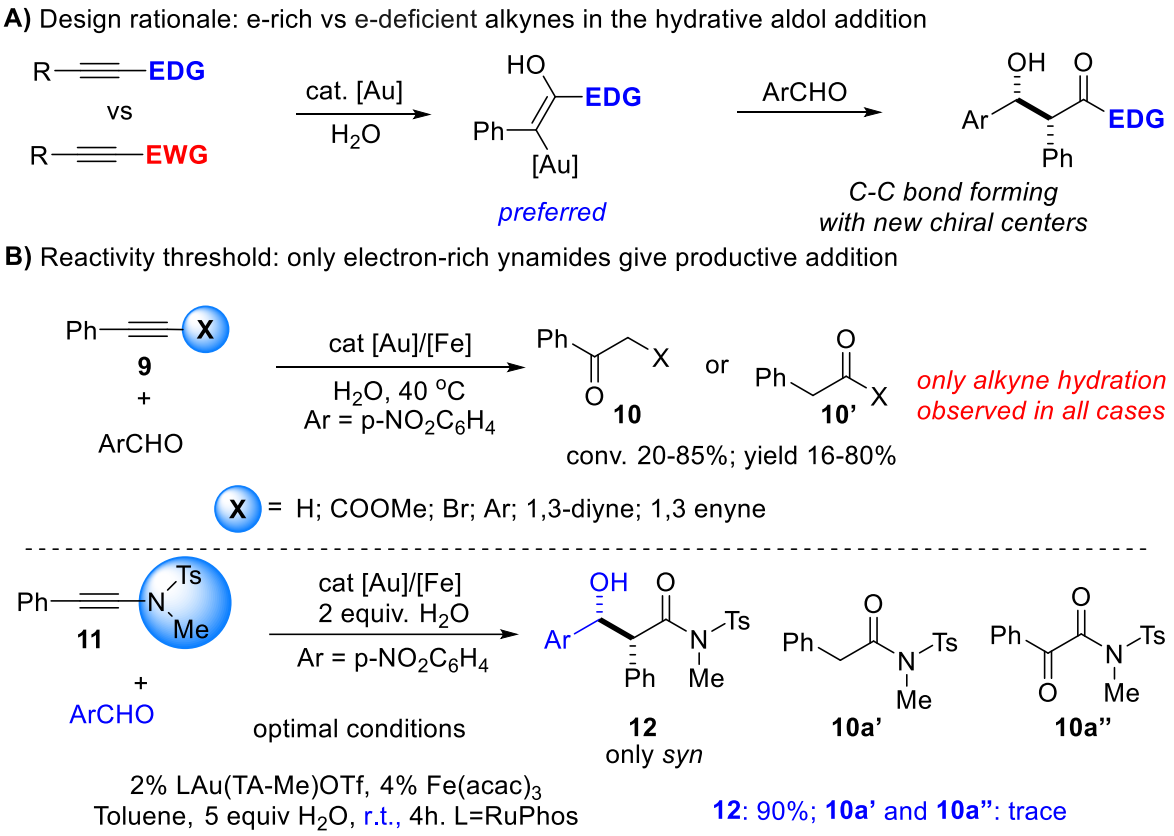


**Scheme 3.** Extending vinyl-gold nucleophilicity beyond carbonyl-directed substrates.

The synthetic performance of the ynamide hydrative aldol reaction further highlighted the value of this design. A broad range of aldehydes and ynamides participated smoothly, affording *syn*-β-hydroxy amides in good to excellent yields and high diastereoselectivity.[13] Importantly, the reaction proceeded under mild conditions without the need for strong bases, stoichiometric metal enolates or harsh Lewis acidic conditions. This feature is mechanistically significant because conventional aldol-type methods often rely on preformed or reversibly generated enolates, which can lead to erosion of stereochemical control through enolate isomerization or product epimerization. In contrast, the high *syn* selectivity observed in this system is consistent with a well-defined vinyl-gold addition pathway.[18]

The practicality of this reaction was also demonstrated on preparative scale. The ynamide hydrative aldol reaction could be performed on a 30 mmol scale, providing the corresponding β-hydroxy amide product in high yield while maintaining excellent stereochemical control.[13] This result is important because it shows that the Au/Fe cooperative strategy is not limited to small-scale mechanistic demonstrations, but can provide useful quantities of stereodefined products under operationally simple conditions.

The method was further extended to asymmetric synthesis by using chiral auxiliary-containing ynamides.[13] In these cases, the electronically activated ynamide platform not only enabled productive vinyl-gold carbonyl addition, but also allowed efficient stereochemical induction in the C–C bond-forming step. A series of enantioenriched β-hydroxy amide products were obtained with excellent stereocontrol, including examples with up to 99% ee. X-ray crystallographic analysis of representative products supported the assigned relative configuration and provided further evidence for the highly organized nature of the vinyl-gold addition process (Scheme 4).

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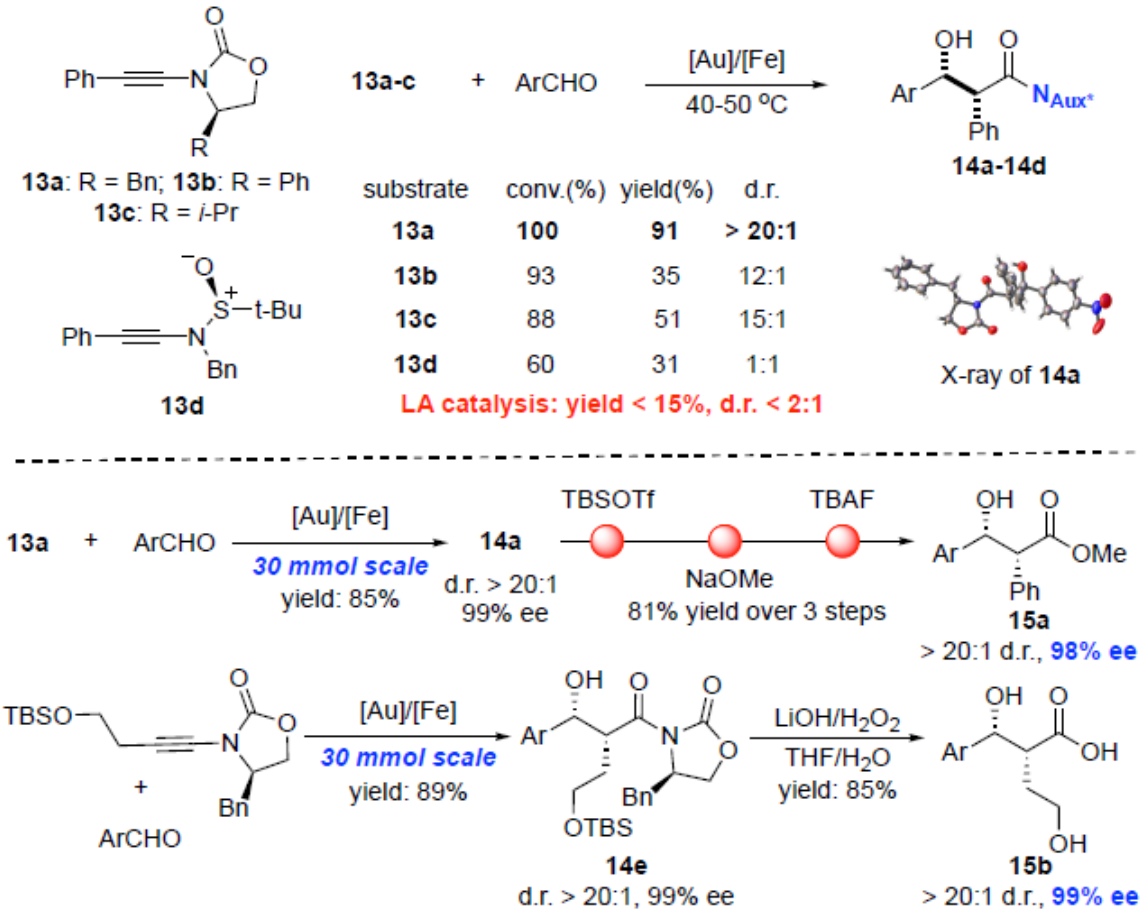


**Scheme 4.** Scope and asymmetric extension of the Au/Fe-catalyzed ynamide hydrative aldol reaction.

Overall, the ynamide hydrative aldol reaction represented an important expansion of vinyl-gold nucleophilic chemistry. Compared with the carbonyl-directed γ-keto alkyne system, this work showed that a built-in directing group is not always required when the electronic properties of the alkyne are properly tuned. More broadly, it established that vinyl-gold intermediates can be designed as tunable nucleophilic organometallic species through a combination of catalyst cooperation and substrate electronic control. This principle significantly broadened the scope of Au/Fe cooperative catalysis and provided a foundation for developing stereoselective C–C bond-forming reactions based on vinyl-gold reactivity.

### 2.3. Merging vinyl-gold nucleophilicity with Au(I)/Au(III) redox catalysis

The Au/Fe cooperative strategy established that vinyl-gold intermediates could be protected from rapid protodeauration and redirected toward productive nucleophilic addition. However, this approach still relied on preserving the reactivity of vinyl-gold species within an Au(I)-centered manifold. A more ambitious question was whether vinyl-gold nucleophilicity could be integrated into a redox-active Au(I)/Au(III) catalytic cycle.[11,15] Such a merger would move vinyl-gold chemistry beyond simple interception of an Au(I) intermediate and would allow vinyl-gold species to participate in more complex sequences involving oxidation, nucleophilic trapping, and reductive elimination.

This idea raised several important challenges. First, the oxidative conditions required to access Au(III) species had to be compatible with alkyne π-activation, water addition, and vinyl-gold formation. Second, it was

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unclear whether a vinyl-gold intermediate in a higher-valent Au(III) manifold would retain sufficient nucleophilic character to participate in bond formation.[8,19] Previous Au/Fe studies had shown that vinyl-gold(I) species could behave as carbon nucleophiles when protonation was suppressed, but whether analogous vinyl-gold(III) species could support nucleophilic addition remained uncertain. These questions defined the central challenge for merging vinyl-gold nucleophilicity with redox gold catalysis (Scheme 5A).

Our earlier studies on ligand-assisted gold-catalyzed cross-coupling with aryldiazonium salts provided an important starting point. In that work, diazonium salts served as mild oxidants capable of converting organogold(I) species into Au(III) intermediates without the need for strong external oxidants or photocatalysts. The resulting Au(III) species could then undergo reductive elimination to forge C–C bonds. This precedent suggested that diazonium salts might provide a compatible entry into redox-active gold catalysis, while also serving as functional group sources in reactions involving vinyl-gold intermediates.[16]

Initial attempts to combine vinyl-gold addition with Au(I)/Au(III) redox catalysis highlighted the difficulty of this design. Under several oxidative gold-catalytic conditions, γ-keto alkynes mainly underwent simple hydration or unproductive decomposition, rather than productive vinyl-gold trapping and reductive elimination.[16] These results showed that merely generating a vinyl-gold(I) intermediate and then attempting oxidation was not sufficient. The order of elementary steps had to be carefully controlled so that π-activation, vinyl-gold formation, oxidation state change, nucleophilic addition and reductive elimination could operate within one compatible catalytic sequence.

The effective solution came from reversing the sequence of events. Instead of first forming a vinyl-gold(I) intermediate and then oxidizing it, an inactive Au(I) precatalyst could be oxidized under diazonium conditions to generate a catalytically competent Au(III) species.[16] This Au(III) complex could then activate the alkyne and promote formation of a vinyl-gold(III) intermediate. Remarkably, this higher-valent vinyl-gold species retained sufficient nucleophilic character to react with the diazonium-derived electrophilic partner, forming a new C–N bond. Subsequent reductive elimination from Au(III) forged the C–C bond and regenerated the Au(I) catalyst. In this way, π-acid activation, vinyl-gold nucleophilic addition, and Au(I)/Au(III) redox cycling were combined in a single catalytic manifold (Scheme 5B).

This strategy enabled a divergent alkyne trifunctionalization reaction in which C–O, C–N and C–C bonds were constructed in one operation from an alkyne substrate.[16] The γ-keto directing group remained important for organizing the reaction sequence, while the diazonium salt played a dual role as both an electrophilic nitrogen source and an oxidizing aryl source. The reaction proceeded under mild conditions and displayed broad substrate compatibility, providing access to densely functionalized products in high yields. More importantly, this work provided the first clear demonstration that vinyl-gold chemistry could be integrated into a complete Au(I)/Au(III) catalytic cycle. Rather than being limited to protodeauration or simple nucleophilic addition, vinyl-gold intermediates could now function within a multistep redox sequence involving oxidation, nucleophilic trapping and reductive elimination.

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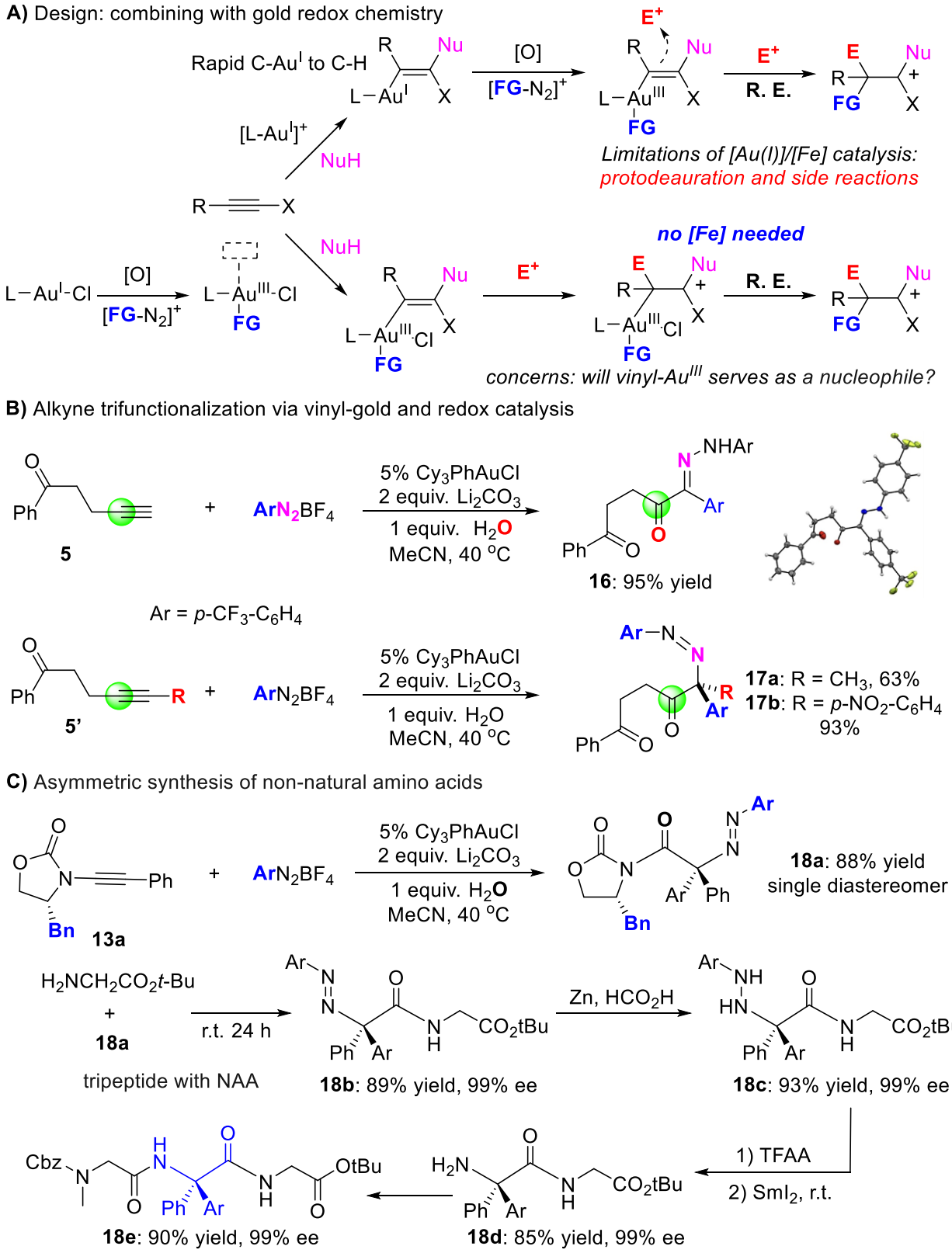


**Scheme 5.** Merging vinyl-gold nucleophilicity with Au(I)/Au(III) redox catalysis.

The synthetic value of this redox-active vinyl-gold manifold was further demonstrated by its application to the synthesis of non-natural chiral amino acid derivatives. As shown in Scheme 5C, when the divergent gold-

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catalyzed trifunctionalization was combined with a chiral auxiliary-containing substrate **13a**, the reaction provided an efficient route to enantioenriched amino acid derivatives bearing an α-quaternary stereocenter. Such α-quaternary amino acid motifs are valuable structural units but remain challenging to access by conventional methods because their synthesis requires simultaneous control of C–C bond formation, nitrogen incorporation, and stereochemical induction at a congested α-carbon center. This example therefore illustrates a key advantage of the vinyl-gold/Au(I)/Au(III) redox strategy: it enables not only formal alkyne trifunctionalization, but also the construction of stereochemically defined, highly substituted chiral building blocks.

Overall, this work substantially expanded the conceptual scope of vinyl-gold chemistry. The Au/Fe studies described above established that vinyl-gold(I) intermediates can be redirected from protodeauration and used as nucleophilic partners under cooperative catalytic conditions. The redox gold platform further showed that vinyl-gold reactivity can be incorporated into Au(I)/Au(III) catalysis when the reaction sequence is properly designed. This advance transformed vinyl-gold intermediates from protected Au(I) nucleophiles into programmable organogold platforms capable of supporting divergent alkyne functionalization, multiple bond formation, and the synthesis of synthetically valuable chiral architectures.

## 3. Conclusions

The studies summarized in this review show that vinyl-gold intermediates can be redirected from rapid protodeauration and developed into productive nucleophilic platforms for bond construction. Through Au/Fe cooperative catalysis, vinyl-gold species can be intercepted before protonation and used in radical addition and hydrative aldol reactions, establishing a practical strategy for controlling the fate of the C–Au bond.

Further development demonstrated that this reactivity is not limited to carbonyl-directed substrates. Electronically activated ynamides generate more polarized vinyl-gold intermediates, enabling stereoselective hydrative aldol reactions and asymmetric access to β-hydroxy amide products. Finally, integration of vinyl-gold nucleophilicity with Au(I)/Au(III) redox catalysis expanded this chemistry into divergent alkyne trifunctionalization, including applications to α-quaternary non-natural chiral amino acid derivatives.

Together, these advances transform vinyl-gold intermediates from transient species into tunable organogold platforms that connect π-activation, nucleophilic reactivity, cooperative catalysis, and redox chemistry.[12,13,16] Continued development of ligand control, asymmetric variants and new electrophile classes should further broaden the synthetic impact of vinyl-gold chemistry.

## 4. Acknowledgements

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