Gold Redox Catalysis with a Selenium Cation as Mild Oxidant

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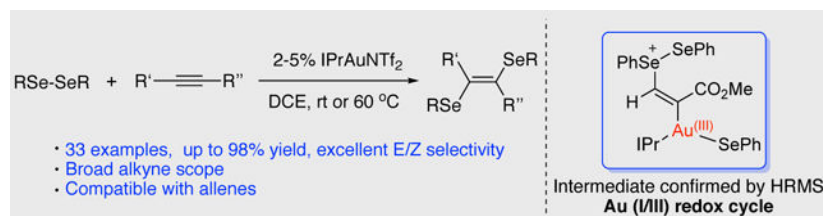[3]University of South Florida, Chemistry, UNITED STATES.

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Abstract

Gold-catalyzed alkyne and allene diselenations were developed. Excellent regioselectivity (trans) and good to excellent yields were achieved (up to 98% with 2% catalyst loading) with a wide range of substrates. Mechanistic investigation revealed the formation of a vinyl gold(I) intermediate followed by an intermolecular selenium cation migration, suggesting that a gold (I/III) redox process was successfully implemented under mild conditions.

Graphical Abstract

- 33 examples, up to 98% yield, excellent E/Z selectivity
- Broad alkyne scope
- Compatible with allenes

Intermediate confirmed by HRMS
Au (I/III) redox cycle

Keywords

gold redox catalysis; deselenation; mild oxidant; alkyne; allene

The past two decades have witnessed tremendous growth in homogeneous gold catalysis.[1] The unique capability of the gold cation as a carbophilic Lewis acid[2] has rendered it a

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superior catalyst in nucleophilic addition reactions towards alkenes, allenes, and alkynes.[3] On the other hand, the redox chemistry of gold(I) catalyst is largely neglected, mainly due to the high oxidation potential (AuI/III = 1.4 eV).[4] Thanks to the pioneering work from Zhang, Hashmi, Toste and other groups, this challenge has been successfully overcome by utilizing external strong oxidants such as selecfluor, hypervalent iodine reagents, aryldiazonium salts and even alkynyl bromides.[5] Another significant observation in this regard was reported by Glorius' group, who first indentified that diazonium salt could be used as a mild oxidant for gold (I) oxidation in the presence of an additional ruthenium-based photoredox catalyst(Scheme 1A).[6] Despite of these progresses, the necessity of using an external oxidant impedes further development of this methodology with only limited reaction scope. More recently, direct oxidative addition at a gold(I) complex emerged.[7] However, the reported examples so far either requires highly-strained starting materials in the case of X-X oxidative addition (X=Si or C) or a delicate catalyst design to activate allyl or aryl halides. Thus, developing a novel and effective approach to accomplish gold redox catalysis is not only important for enhancing the basic understanding of this rapidly-growing field, but also holds promise for generating synthetically valuable building blocks.

Recently, we reported a highly efficient and stereoselective thioallylation of electron-deficient alkynes (Scheme 1B).[8] Mechanistic study suggested that this reaction was initiated by sulfur nucleophilic addition to form a vinyl gold intermediate, which underwent a sequential allyl transfer via Au(I/III) cycle. Notably, we for the first time propose the allyl sulfonium cation functions as a mild internal oxidant to accomplish the Au(I/III) oxidation, which represents a powerful strategy to combine the excellent π-acid reactivity of Au(I) complexes with gold redox catalysis.

Although we have successfully observed Au(III) species via Mass Spectrometry in the thioallylation of alkynes, we could not completely rule out a possible [3,3]-rearrangement pathway[9] which doesn't involve Au(I) oxidation. Moreover, only electron deficient alkynes (EWG modified alkynes) successfully participated in this transformation, which greatly limited the reaction scope. Other alkynes and allenes, which are typical substrates in gold catalysis, did not give the desired products. Therefore, it is important to conduct a more detailed investigations regarding detailed reaction mechanism and further extend the reaction to a broader scope. Herein, we report our efforts on facilitating RXXR addition toward alkynes and allenes under gold-catalyzed conditions (Scheme 1C). Notably, regioselective gold-catalyzed alkyne and allene diselenations were successfully achieved. The transformation took place under mild conditions with high efficiency, giving desired products in good to excellent yields and excellent regioselectivity. Mechanistic investigations confirmed Au(I/III) redox cycle, which validates the great potential of applying selenium cation as an effective mild oxidant to promote gold redox catalysis in future. What's more, the diselenation product can be further derived into value-added synthetic intermediates.[10]

As suggested in Scheme 1C, compounds with RXXR moiety could be of interest in performing sequential nucleophilic addition and redox chemistry with a single Au(I) catalyst. Unlike thioallylation, [3,3]-rearrangement path is not available in this alkyne difuntionalization reaction, which provides a simple model for studying gold redox catalytic

cycle. Notably, with a relatively weak X-X bond, it has been reported in literature that RXXR type compounds could form RX radical and proceed aforementioned transformation via a radical path.[11] As a result, poor regioselectivity was often observed. The proposed gold catalytic route, if successful, will not only provide an alternative approach for RXXR activation, but also likely accomplish the reaction with much better stereo-outcome. Potential challenges can be 1) reduced [LAu]$^+$ reactivity caused by X-Au coordination and 2) slow C-X reductive elimination (relative to C-C), which could lead to competing protodeauration as the major byproduct. To initiate our investigation, we first attempted using ROOR, RNNR and RSSR as nucleophiles to react with alkynes. The results are summarized in Figure 1.

Treating alkyne **1a** with peroxide or peracid gave 100% conversion. However, desired product **3** or byproduct **3'** was not obtained based on crude NMR. Reaction with tetramethyl hydrazine gave almost no alkyne conversion, likely due to catalyst poisoning. Interestingly, reaction of disulfide **2a** (PhSSPh) gave the desired dithiolation product **3a** in 58% yield (80% conversion). As expected, hydrothiolation product **3a'** was observed (22%) as the byproduct. It is important to note that both **3a** and **3a'** were observed as single isomer (*E/Z* > 100:1). The alkene geometry was later confirmed by X-ray crystallography (*vide infra*). These results are exciting, since they suggested that the proposed combination of gold π-acid activation and redox catalysis is valid.

In theory, protodeauration could occur form both gold(I) intermediate (vinyl gold) or gold(III) intermediate.[12] Considering gold(III) reductive elimination is a rather rapid process, we postulate that stronger oxidants may help to avoid protodeauruation by promoting the reaction with faster gold (I) oxidation. Thus, we turned our attention to diselenides based on 1) Se as better nucleophile over S and 2) selenium cation as a stronger oxidant. To our delight, the desired diselenation product **3b** was formed in excellent yield (90%). Further catalyst screening revealed that electron-rich gold catalyst IPrAuNTf$_2$ gave the best yield and DCE was identified as the optimal solvent. The catalyst loading can be reduced to 2% without sacrificing the yield or regioselectivity. Other metal catalysts including Pt, Ag, Cu, Fe gave inferior results (see SI for details). Reduced yield was observed when using PhTeTePh (**3c**), which is likely due to a stronger coordination between Te and gold catalyst, comparing to Se or S, that leads to slower reaction. Comparisons of the optimal conditions with some alternative conditions are summarized in Table 1.

With the optimal conditions in hand, we next explored the reaction scope as shown in Table 2. Most aryl diselenides with either electron-donating or electron-withdrawing substituents proved to be suitable for this transformation, giving good to excellent yields when reacting with methyl propiolate (**3a**-**3g**). One exception is *para*-CF$_3$ substituted aryl deselenides, which only provided **3h** with moderate yield due to sluggish nucleophilic addition step. Alkyl diselenides participated in this reaction smoothly as well, realizing **3j** and **3k** in satisfactory yields. Other carbonyl-activated alkynes, including esters (**3l** and **3m**), ketone (**3q**) and acetylene diester (**3r**) all underwent diselenation successfully with excellent yields; amides (**3n**-**3p**) on the other hand gave lower yields presumably due to substrate coordination. We next turned our attention to a broader scope of alkynes. First, various bromoalkynes with either aryl or alkyl group connecting to the C-C triple bond reacted with

phenyl diselenide and provided desired products in moderate to excellent yields (**3s-3z**); other diselenides were also compatible with bromoalkynes (**3aa-3ae**) The fact that no cyclopropyl ring opening product was observed ruled out a radical reaction pathway (**3z**). Chloroalkyne was a valid substrate for this reaction as expected (**3af**). We were pleased to find out that electron-rich alkynes such as ynamides underwent diselenation successfully, giving desired products in moderate yields (**3aq**). Encouraged by this result, we tested both terminal and internal alkynes without electronic biases. We are delighted to find out that desired products **3ah** and **3ai** were formed in moderate yield under gold-catalyzed conditions, which further showcased the broad scope of this transformation. It is worthwhile to mention that in all cases diselenation products were formed as essentially one alkene isomer, and their *E*-geometry were ambiguously identified by X-ray crystallography of product **3t**.

Encouraged by the successful diselenation of alkynes, we wondered if this transformation can be further extended to allenes, which were not suitable substrates in previous thioallylation studies. After detailed reaction optimization, we were pleased to find out that allene diselenation products could also be formed smoothly via this protocol. As shown in Table 3, when treating 1,1-diphenyl allene with different diselenides, desired products were formed in good to excellent yields (**5a-5e**). 1,1-dimethyl allene could also give the desired products in excellent yield (**5f**). Trisubstituted allenes underwent diselenation reaction uneventfully, providing desired product **5g** in moderate yield. Monosubstituted allenes also provided excellent yields, although only moderate *E/Z* selectivity were observed (**5i-5k**). The structure of *E/Z* isomers were unambiguously assigned by X-ray crystallography (*E*-**5i**).

To better elucidate the mechanism,[13] a series of experiments were carried out. First, cross-over experiment clearly supported an intermolecular selenium transfer mechanism (Figure 2A). In addition, direct oxidative addition of phenyl diselenide with gold(I) catalyst was not observed (see SI). When using more electron-rich styrene, such reaction didn't occur, which ruled out a Au(I)-assisted selenium cation formation pathway. Based on these results, we propose a mechanism which includes gold-catalyzed nucleophilic addition of diselenides and subsequent selenium transfer via gold redox catalysis, and attempted to trap the key intermediates with Mass spectrometry (Figure 2B). A mass corresponding to vinyl gold intermediate **A** was clearly detected. In addition, CID experiment of m/z of intermediate **A** suggested a Au(II)-SePh$^+$ fragment, which most likely came from a Au(III) intermediate **B** that possesses the same mass as intermediate **A**. Another Au(III) intermediate **C** which contains a similar composition as in the thioallylation case was also observed, and CID confirmed the existence of a Au(III) fragment too. The Mass study thus strongly supported that Au(I/III) redox cycle is plausible for this transformation.

While 1,2-diselenide products **3** are interesting building blocks, they can be readily converted into other compounds through simple transformations. As shown in Figure 2C, treating **3r** under standard Suzuki coupling conditions gave desired couping product **6** in 75% yield. Interestingly, although excess amount ArB(OH)$_2$ were used, only single isomer with mono-substitution product was obtained with structure confirmed by X-ray crystallography (see SI). This result suggested a Heck-type mechanism might occurred with this substrate instead of direct CSe bond oxidative addition as proposed in literature.[10a]

This excellent chemo and stereoselectivity greatly highlighted the potential synthetic utility of these 1,2-diselenide compounds under this new and mild gold redox conditions.

In conclusion, we herein reported a gold-catalyzed diselenation reaction of alkynes and allenes. Excellent yields and stereoselectivity as well as broad reaction scope were achieved for this transformation. Au(I/III) mechanism was proposed based on the cross-over experiment, control experiments and in-situ MS results. Other mild oxidants are currently under investigation in our lab.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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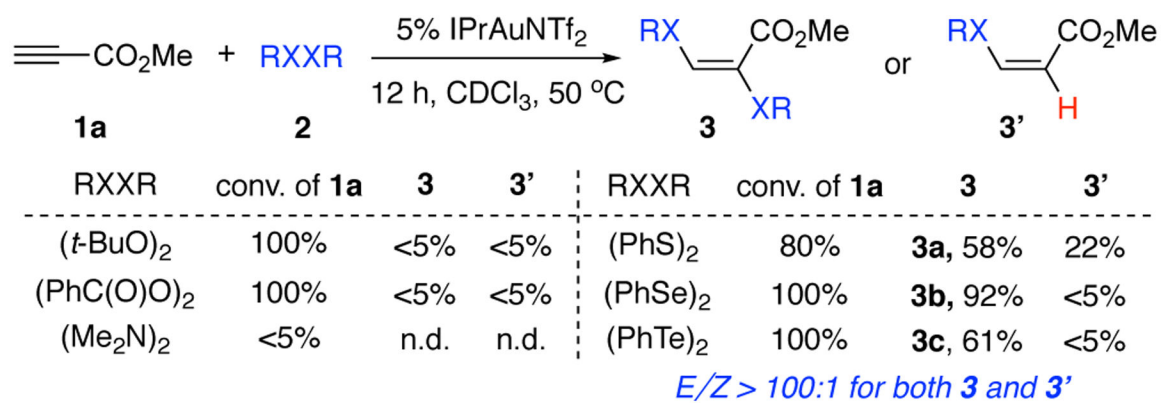[13]. Hashmi ASK, Angew. Chem. Int. Ed 2010, 49, 5232–5241.

Figure 1.
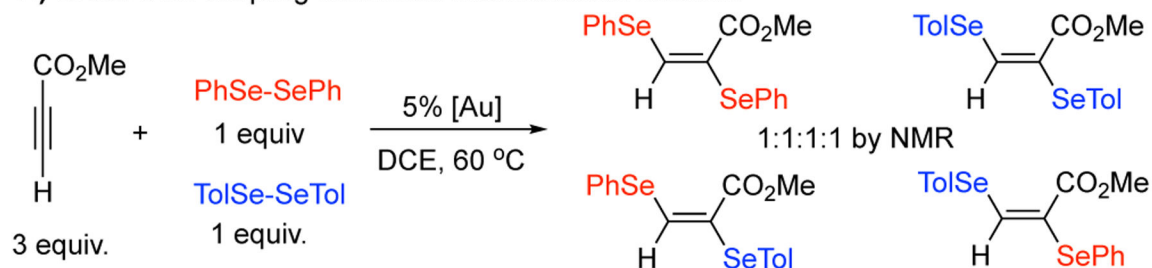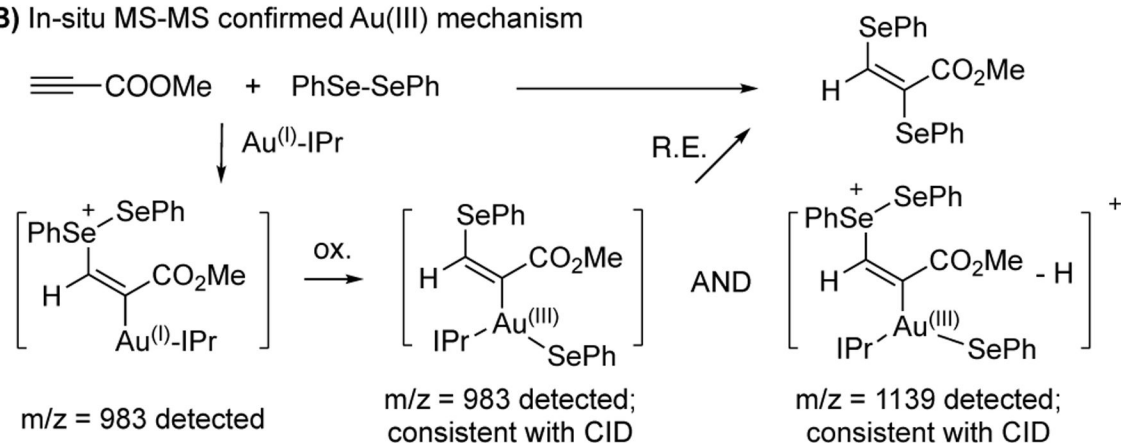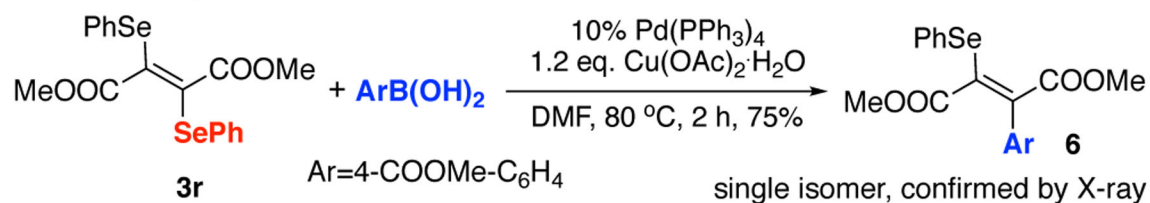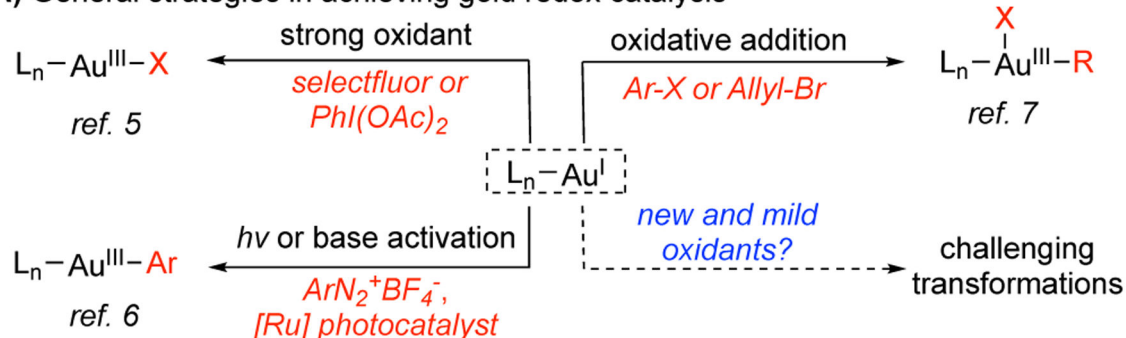Gold-catalyzed RXXR addition to alkynes

Figure 2.
Mechanistic investigations and **3r** conversion

A) General strategies in achieving gold redox catalysis

$L_n-Au^{III}-X$

ref. 5

strong oxidant

selectfluor or PhI(OAc)$_2$

L_n-Au^I

oxidative addition

Ar-X or Allyl-Br

$L_n-Au^{III}-R$ (X)

ref. 7

hv or base activation

ArN$_2^+$BF$_4^-$, [Ru] photocatalyst

$L_n-Au^{III}-Ar$

ref. 6

new and mild oxidants?

challenging transformations

B) Recent example from our lab: *alkyne thioallylation*

PhS

+

$\equiv$—CO$_2$Me

$[L-Au]^+$

$\begin{bmatrix} PhS^+ \diagup \\ H \diagdown \text{CO}_2\text{Me} \\ Au^I\text{-L} \end{bmatrix}$

3,3-rearrang.

or Au^{III} ?

SPh

H   CO$_2$Me
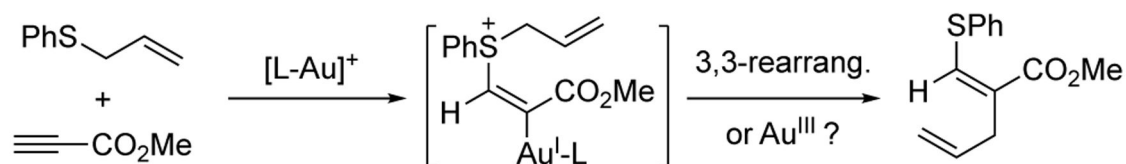
Concerns: 1) only works for *EWG* activated *alkynes*;
2) plausible 3,3-rearrangement, *not gold redox catalysis?*

C) *This work*: Exploring RX-XR as plausible Nu and oxidant for gold redox catalysis

RX-XR
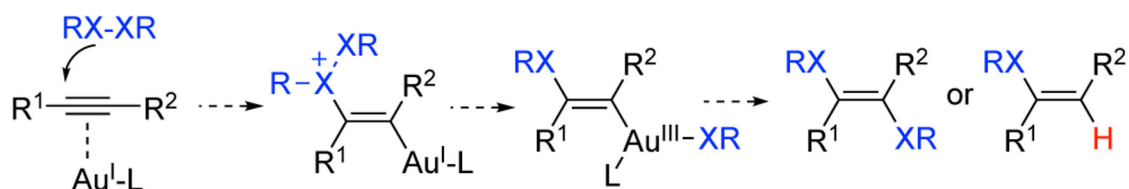
$R^1\equiv R^2$

Au^I-L

$\begin{array}{c} R-X^+\diagup XR \\ R^1 \diagdown R^2 \\ Au^I\text{-L} \end{array}$

$\begin{array}{c} RX \quad R^2 \\ R^1 \quad Au^{III}\text{-}XR \\ L' \end{array}$

$\begin{array}{c} RX \quad R^2 \\ R^1 \quad XR \end{array}$ or $\begin{array}{c} RX \quad R^2 \\ R^1 \quad H \end{array}$
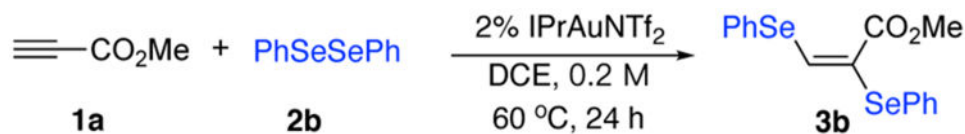
Tasks: 1) developing new alkyne/allene difunctionalization under mild conditions;
2) evaluating choice of RXXR (X=O,N,S etc.); 3) confirming gold redox process.

Scheme 1.
Recent development on gold redox catalysis.

Table 1.

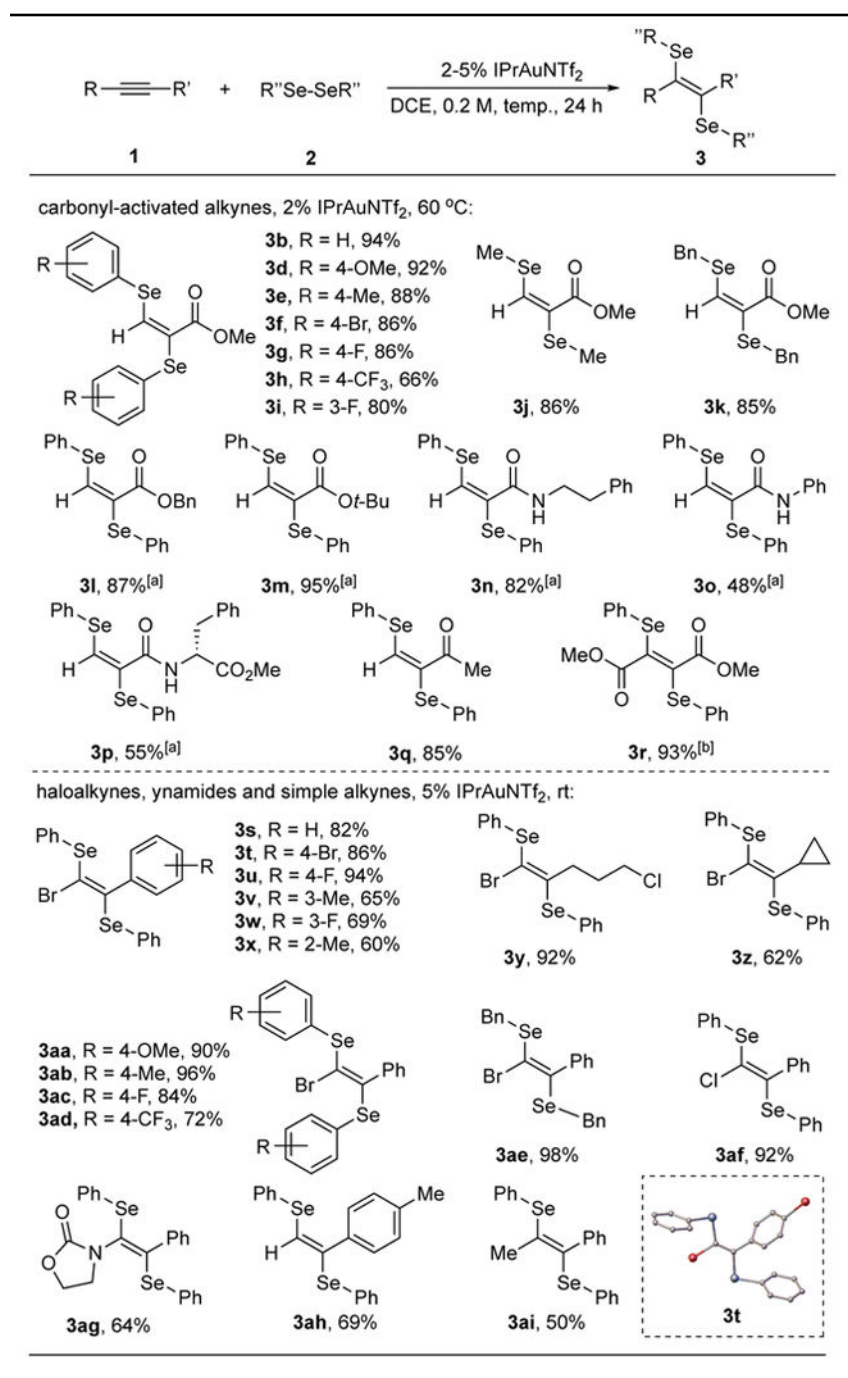Gold-catalyzed alkyne diselenation: condition screening

entry	Variation from standard conditions	conv.	3b (*E/Z*)	3b'
1	none	100%	92% (>100:1)	5%
2	5% $Ph_3PAuNTf_2$	60%	46%	-
3	5% $(PhO)_3PAuNTf_2$	60%	31%	-
4	5% $XPhosAuNTf_2$	100%	72% (40:1)	14%
5	2% $IPrAuNTf_2$ (0.5 M)	100%	85% (32:1)	7%
6	1% $IPrAuNTf_2$ (0.5 M)	100%	85% (20:1)	8%
7	Other [Au] catalyst	-	-	-
8	10% $PtCl_2$	80%	67%	-
9	other metal catalysts (Ag, Cu, Fe, etc)		<60%	
10	other solvents		<80%	
11	10% HOTf	<5%	nd	-
12	no catalyst	<5%	nd	-

Reaction conditions: the catalyst (2%) was added into a DCE solution of alkyne (0.3 mmol) and diselenide (0.2 mmol), and reacted at 60 °C for 24 h. Conversion and yield were determined by ^{1}H NMR spectroscopy with dimethyl sulfone as the internal standard.

Table 2

Substrate scope for diselenation of alkynes

carbonyl-activated alkynes, 2% IPrAuNTf$_2$, 60 °C:

3b, R = H, 94%
3d, R = 4-OMe, 92%
3e, R = 4-Me, 88%
3f, R = 4-Br, 86%
3g, R = 4-F, 86%
3h, R = 4-CF$_3$, 66%
3i, R = 3-F, 80%

3j, 86%

3k, 85%

3l, 87%[a]

3m, 95%[a]

3n, 82%[a]

3o, 48%[a]

3p, 55%[a]

3q, 85%

3r, 93%[b]

haloalkynes, ynamides and simple alkynes, 5% IPrAuNTf$_2$, rt:

3s, R = H, 82%
3t, R = 4-Br, 86%
3u, R = 4-F, 94%
3v, R = 3-Me, 65%
3w, R = 3-F, 69%
3x, R = 2-Me, 60%

3y, 92%

3z, 62%

3aa, R = 4-OMe, 90%
3ab, R = 4-Me, 96%
3ac, R = 4-F, 84%
3ad, R = 4-CF$_3$, 72%

3ae, 98%

3af, 92%

3ag, 64%

3ah, 69%

3ai, 50%

3t

Reaction conditions: the catalyst was added into a DCE solution of alkyne (0.3 mmol) and diselenide (0.2 mmol), and reacted at given temperature for 24 h. Isolated yield. [a] 0.2 mmol alkyne and 0.3 mmol diselenide were used for the ease of purification. [b] React at 80 °C.

Table 3.

Substrate scope for diselenation of allenes
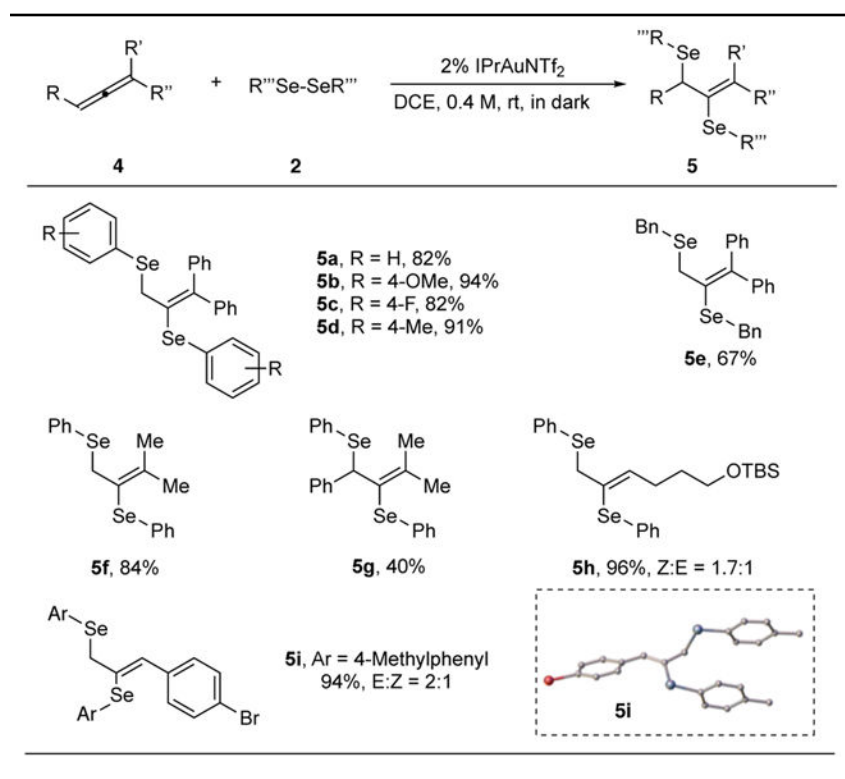
Reaction conditions: the catalyst (2%) was added into a DCE solution of allene (0.6 mmol) and diselenide (0.2 mmol) and reacted at rt for 24 h. Isolated yield.