Review Article

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Gold-catalyzed synthesis of small-sized carbo- and heterocyclic compounds: A review

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Abstract: Research on gold catalysis has flourished over the last 20 years, and gold catalysts are now acknowledged as the "best choice" for a range of organic transformations. Gold complexes have emerged as promising candidates for this use in recent years because of their high reactivity, which enables them to induce a broad range of transformations under mild conditions. Extensive demonstrations have showcased the extraordinary efficiency of synthesizing complex organic compounds from the basic starting components. In addition to its traditional applications in catalysis, gold catalysis has expanded to include the total synthesis of natural compounds, which is a complex and demanding undertaking. The class of molecules known as carbo- and heterocycles, which is arguably the most important, has a significant impact on the synthesis of agrochemicals and pharmaceuticals among the numerous additional products made possible by the novel procedures pioneered. The main topic of this review is how to use Au salts in homogeneous catalysis to create cyclization processes for small heterocyclic and carbocyclic systems. This study gives an overview of most of the books and articles written after 2013 that discuss making three- and four-membered carbo- and heterocyclic rings with gold as a catalyst. We have made every effort to include all outstanding reports on this subject; nonetheless, we apologize for any omissions.

Keywords: gold catalyst, heterocyclic compounds, three-membered rings, four-membered rings, synthesis

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1 Introduction

Gold possesses unique characteristics that set it apart from other elements. The inherent inertness and exceptional resistance to oxidation and chemical attack of bulk metals have historically been considered undesirable qualities for catalytic purposes. Gold, being the metallic element with the highest electronegativity, exhibits a nearly equivalent value to carbon on the Pauling scale, measuring 2.54. The formation of hydrolytically stable and strongly covalent Au–C bonds is seen. In contrast to other noble metals, the delay in conducting investigations into the organometallic chemistry of this particular metal can be attributed to this factor [1]. Significant transformations have occurred at present.

Gold has a unique place in the Periodic Table because it tends to behave like main group elements when it has an oxidation state of +1 and a fully occupied d-shell. It is more likely for the compound to form linear complexes with two-coordinate ligands and much less likely to interact with donor ligands that are positioned in a way that is against the molecular axis [2]. In contrast to compounds of gold in the oxidation state of +I, those in the +III oxidation state possess all the characteristic properties of a transition metal. Furthermore, they primarily adopt the square-planar coordination geometry, which is commonly observed in other heavy metal ions with a d^8 electron configuration. Furthermore, there are significant variations in both the chemical and structural features.

Biologically active natural and synthetic substances, medications, and agrochemicals often contain carbo- and heterocycles as structural architectures. Furthermore, these structural components may play a significant role in organic synthesis as synthons [3–7]. There are a lot of very good ways to make different carbo- and heterocyclic systems, but we are always looking for new ways that use easy-to-find starting materials, require fewer steps for transformation and purification, and are very selective in terms of chemo-, regio-, and stereoselectivity [8]. Gold catalysis has led to the creation of amazing, highly inventive, and ahead of the competition methods that can be used to make a wide

range of chemical changes that are needed to make carbo- and heterocyclic compounds from basic starting materials. Several books and reviews on this field of study have been released in recent years [9–11].

2 Small-sized ring systems

The ubiquitous themes of three- and four-membered rings throughout medicinal chemistry and nature have captivated chemists ever since their discovery. Nevertheless, the construction of small rings often poses significant challenges due to energy considerations. Chemists have since demonstrated a significant level of interest in the characteristics and structural organization of these extensively stretched carbocycles and their derivatives [12–15]. As a result, significant endeavors have been undertaken over the course of time to obtain entry to diverse minor compounds [16] and to examine the distinctive patterns of reactivity exhibited by these molecules.

Due to the inherent strain caused by their 60° C–C bond angles, which deviate from the typical 109.5° Csp3–Csp3 bond angles found in conventional alkanes, three-membered rings often exhibit reactivity that is comparable to alkenes rather than alkanes [17,18]. The techniques used to construct medium- or large-sized rings are very different from those used to assemble severely strained little rings due to uphill thermodynamics.

3 Synthesis of three-membered ring systems

3.1 Gold-catalyzed diazo compound-mediated cyclopropanation

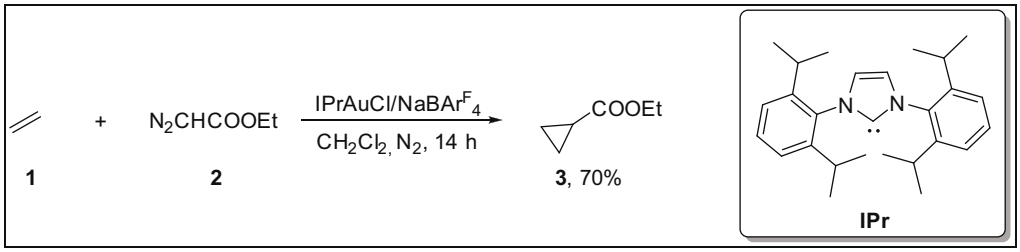
The strategy involving metal-catalyzed carbene transfer from diazo compounds is widely recognized as the most thoroughly investigated approach for the synthesis of acceptor or donor–acceptor cyclopropanes. Metal complexes, such as Au(I) catalysts, can facilitate the transition [19]. Over the past 15 years, several Au(I) complexes have been employed to facilitate carbene transfer processes towards diverse nucleophiles [20].

As of 2019, Pérez et al. revealed that ethylene **1**, which is thought to be the basic alkene, can go through cyclopropanation when it meets ethyl diazoacetate (EDA) **2** and an NHC-Au(I) catalyst [21]. The reaction between **1** and **2** at room temperature is catalyzed by IPrAuCl in the presence of one equivalent of $NaBArF_4$, producing **3** with yields of around 70% (based on EDA) (Scheme 1). This is the first instance of ethylene being directly cyclopropanated using this technology, with notable conversions.

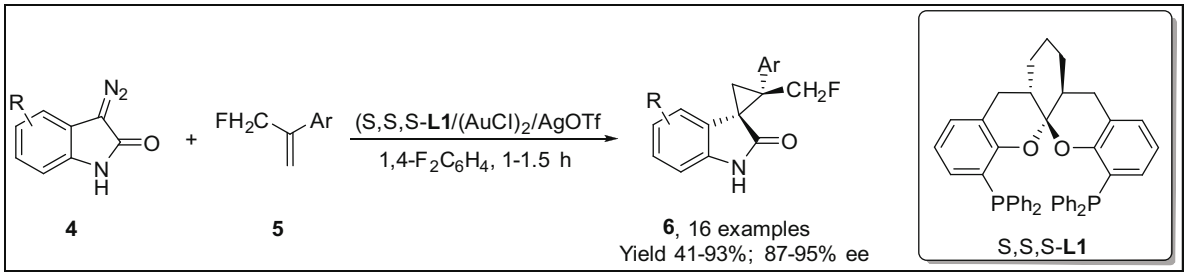
Using diazooxindoles **4** and α-CH_2F and CF_2H styrenes **5**, Cao et al. created a very selective cyclopropanation [22] to obtain 3-spirocyclopropyl oxindoles **6** (Scheme 2) with vicinal all-carbon stereocenters. These are interesting compounds for medical research or could be used to make different kinds of fluorinated spirocyclopropanes [23]. They demonstrate that the formation of C-F···H-X interactions between fluorinated solvents and reactive intermediates may significantly aid the reaction.

This study offers an unparalleled understanding of the role of fluorinated organic solvents in augmenting the reactivity of organic reactions while also presenting supplementary proof for the presence of C-F···H-X interactions.

Liu et al. explained the process of producing spirocyclopropyl oxindoles **9** using a gold(I) catalyst by reacting 1,2,4-substituted dienes **7** with diazooxindoles **8** (Scheme 3) [24]. The authors investigated a unique rearrangement of these spirocyclopropyl oxindoles **9**, resulting in the formation of 3-(cyclopenta-1,3-dien-1-ylmethyl)oxindoles **11** as the product with the same gold catalyst. The reported products **11** of this rearrangement are generated through a thorough cleavage of the cyclopropane ring of spirocyclopropyl oxindoles **9** via a formal methyl C–H insertion at a C(3)–oxindole ring. Based on experimental results, the authors ruled out the possibility of a reversible gold-



Scheme 1: Gold-catalyzed cyclopropanation of ethylene with EDA.



Scheme 2: Gold(I)-mediated enantioselective cyclopropanation using diazooxindoles.

cyclopropanation pathway. In contrast, they proposed the formation of intricate pairs involving gold enolates and 1-methylen-2,3,4-cyclopentadienyl cations, leading to a 1,5-enolate shift.

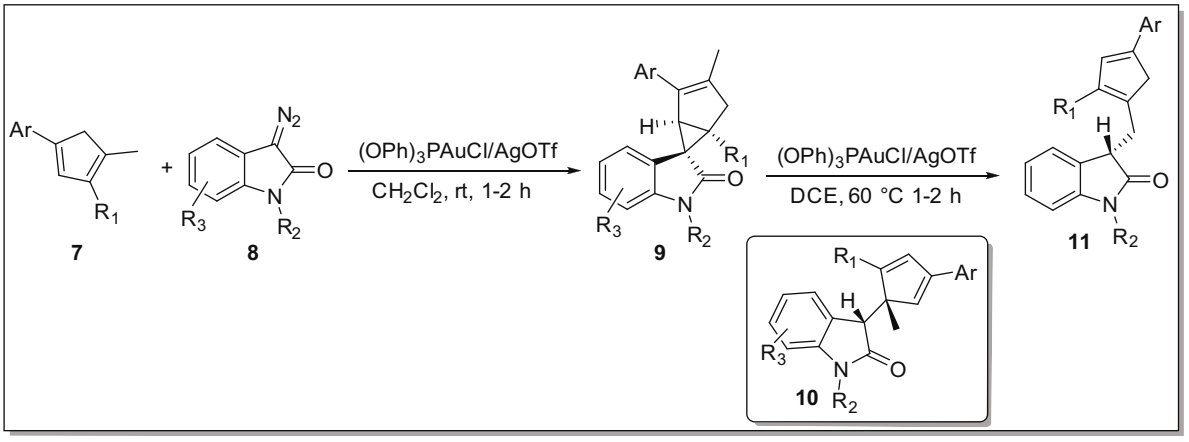
The majority of the time, throughout the cyclopropanation process, small quantities of minor products such as 3-(4-phenylcyclopenta-2,4-dien-1-yl)indolin-2-one derivatives (<10%) were produced, posing challenges in purification using column chromatography.

Zhang et al. [25] reported on the synthesis of densely substituted cyclopropanes **14** (Scheme 4). The authors obtained good yields and great enantioselectivity and diastereoselectivity by using α-diazoarylacetate compounds **13** to help with the enantioselective cyclopropanation of enamides **12**. The reaction exhibited high efficiency when applied to internal or terminal enamides, yielding the desired products in satisfactory quantities with remarkable levels of enantioselectivity (up to 98% ee) and diastereoselectivity, particularly when employing a chiral binol-derived phosphoramidite-gold(I) complex. The present methodology offers a clear and feasible approach for the synthesis of chiral cyclopropylamines possessing consecutive stereogenic centers, a structural feature of utmost importance in the fields of biological investigation and pharmaceutical advancement. The utilization of Carreira ligand **15** [26] in the process led to the synthesis of a broad spectrum of densely substituted donor–acceptor cyclopropanes, exhibiting significant degrees of diastereo- and enantioselectivity.

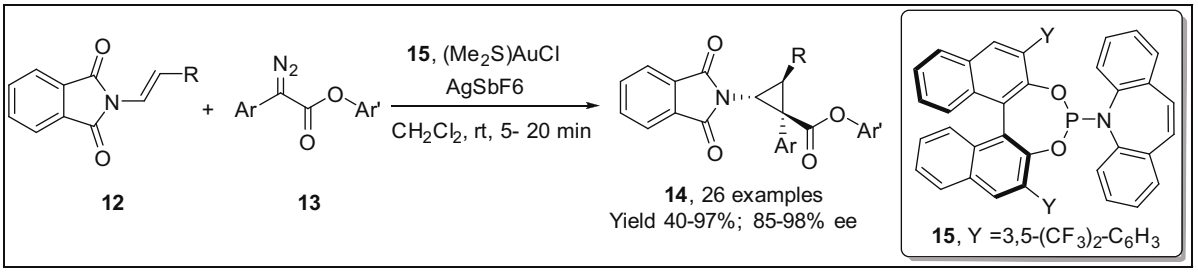
3.2 Gold-catalyzed cyclopropanation by cycloisomerization of unsaturated systems

3.2.1 Cyclopropanation through cycloisomerization of enynes

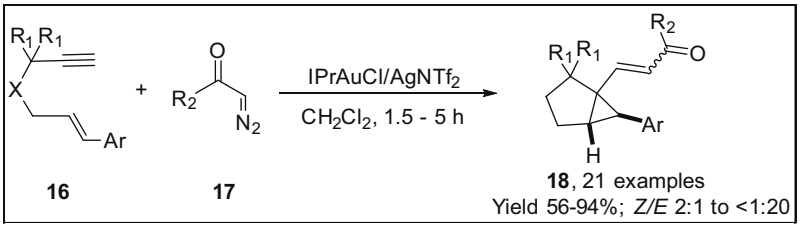
Gold complexes are a kind of carbophilic π acid that have been intentionally designed to have the capability to activate various C–C bonds [27–43]. This includes bonds present in alkynes, alkenes, and allenes. Extensive research has been conducted on the gold-catalyzed cycloisomerizations of enynes within the timeframe of the twenty-first century [44–66]. Au(I) can undergo interaction with an enyne, resulting in the formation of η^2-complexes



Scheme 3: Gold(I)-mediated diastereoselective cyclopropanation using diazooxindoles and dienes.



Scheme 4: Au-catalyzed enantioselective cyclopropanation of enamides using α-diazoarylacetate.



Scheme 5: Gold-catalyzed cycloisomerization of 1,6-enynes using diazo ketone.

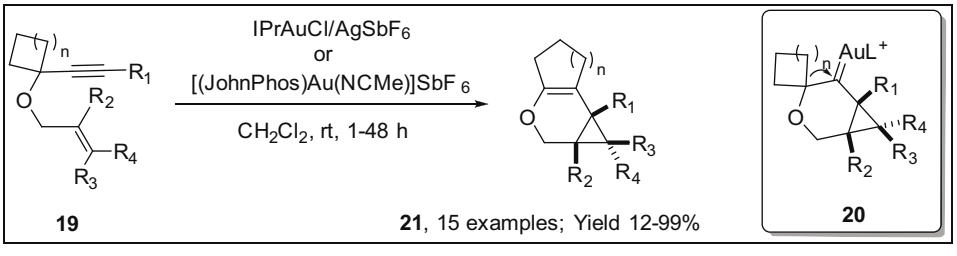
involving either the double bond or the triple bond [67,68]. The η^2-alkyne gold complex has a smaller lowest unoccupied molecular orbital, which makes it more vulnerable to nucleophilic attack. Consequently, this results in a heightened affinity for alkynes over alkenes, a phenomenon commonly referred to as alkynophilicity [69].

3.2.1.1 Cyclopropanation via cycloisomerization of 1,6-enynes

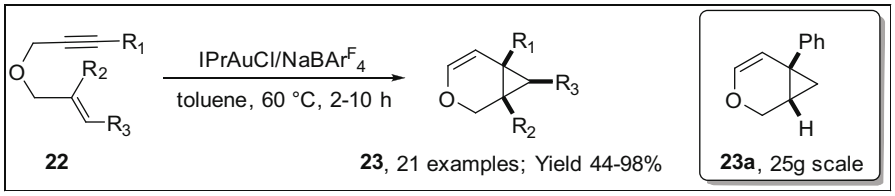
Liu and co-workers reported the cyclization of aryl diazo ketones **17** and 1,6-enynes **16** by gold catalysis, which offers easy access to 3-cyclopropyl-2-en-1-one derivatives **18**. The reaction was initiated through the creation of 5-exo-dig cyclopropyl gold carbenes from 1,6-enynes. As shown in Scheme 5 [70], aryl diazo ketones subsequently trapped these carbenes.

Fensterbank (year) documented the process of cycloisomerization of O-tethered 1,6-enynes **19** using gold catalysis. This reaction resulted in the formation of a four-membered ring [71] inside the molecular structure. An important stage is to expand the Wagner–Meerwein rearrangement onto intermediate carbene center **20**. Good yields of the corresponding cyclopropane-fused tricyclic systems with a dihydropyran moiety **21** were achieved (Scheme 6).

In 2020, Michelet et al. presented a robust method for the rapid synthesis of 3/6-membered moderately volatile enol ethers **23** with distinct olfactive characteristics. In this method, oxygen-tethered enynes **22** were cycloisomerized with the help of gold, as shown in Scheme 7 [72]. The fact that the reaction is feasible and can use a 0.04 mol% catalyst loading on a 25 g scale in mild conditions is proof of its viability. The olfactory characteristics of a library of synthetic bicyclic compounds were investigated. Depending on the substituents, these compounds' odor characteristics can vary greatly. Some of them have aromas that are like some well-known synthetic perfumes, such as rhubafuran, hexalon, and hyacinth body. Various research groups have utilized diverse ligands in their investigations, exploring the gold-catalyzed cycloisomerization of enynes and producing



Scheme 6: Cycloisomerization of O-tethered 1,6-enynes via gold catalysis.

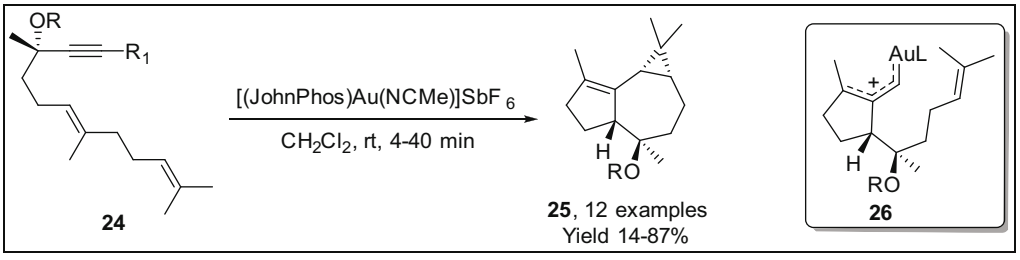


Scheme 7: Gold-catalyzed bicyclic scent synthesis via cycloisomerization of oxygen-tethered enynes.

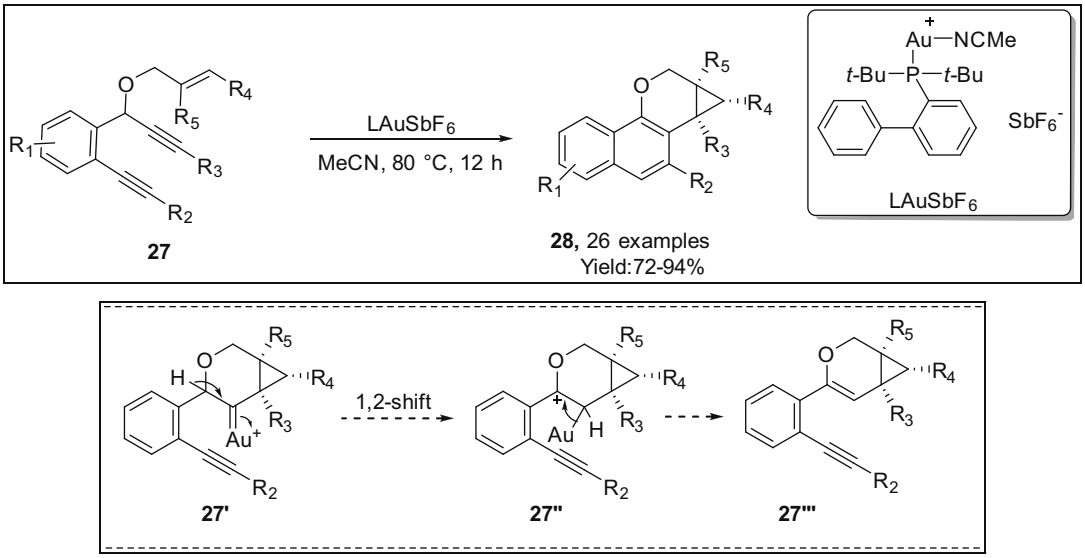
analogous cyclopropane-fused six-membered heterocyclic products [73–76].

According to Calleja et al. (Scheme 8) [77], 1,6-enyne **24** undergoes a cyclization/1,5-OR migration/cyclopropanation reaction under gold catalysis to produce a tricyclic molecule **25**. Given that racemization does not occur in the cascade reaction, it is not possible for propargyl carbocations to form. To synthesize (+)-schisanwilsonene A with better enantiomeric purity, this has been used to prepare important intermediates. Based on density functional theory (DFT) calculations, the 1,5-OR migration seems to move stepwise through a cyclic intermediate **26** after the first cyclization, even though the cleavage occurs through a low barrier.

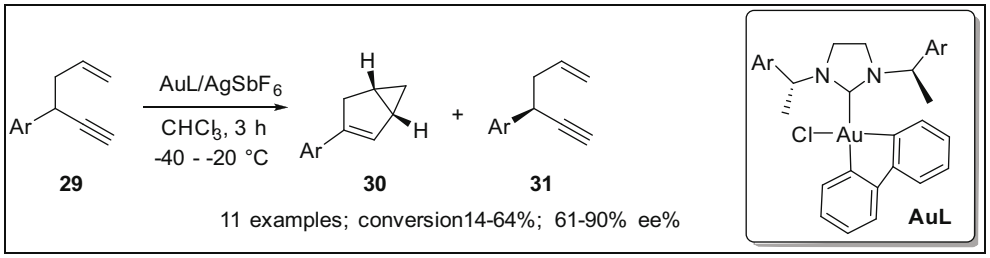
Karunakar et al. have recently devised a method for accessing the tetrahydrobenzo[*h*]cyclopropa[*c*]-chromenes **28** through the cycloisomerization of 1,6-ene-diynes **27** catalyzed by gold (Scheme 9) [78]. Regioselective yields of ≤92% tetrahydrobenzochromenes fused with cyclopropane were achieved. Three new C–C bonds were successively produced in one pot during this atom-economic biological transition. The reaction progresses through cycloisomerization of enyne with gold, producing the gold carbene



Scheme 8: Sequential cyclization, migration, and cyclopropanation in dienynes.



Scheme 9: Au-catalyzed tandem cycloisomerization and 6-endo-dig cyclization of ene-diynes.



Scheme 10: Enantioconvergent cycloisomerization and kinetic resolution of 1,5-enynes catalyzed by Au(III).

intermediate **27′**/1,2-hydride shift/deauration/6-endo-dig cyclization.

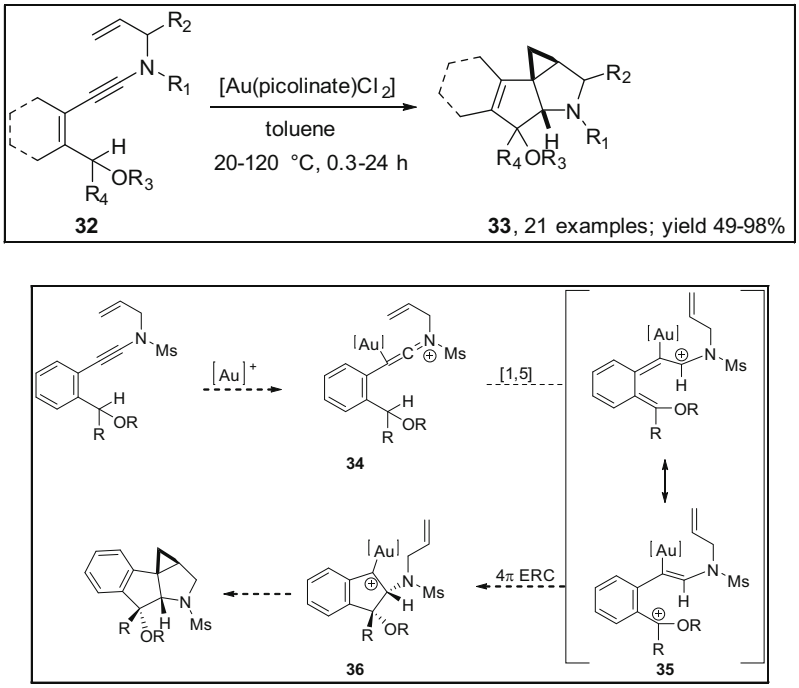
3.2.1.2 Cyclopropanation via cycloisomerization of 1,5-enynes

The enantioconvergent direct 1,5-enyne **29** cycloisomerization and kinetic resolution [79] are part of a new Au(III)-catalyzed process shown in Scheme 10. The reaction also creates 1,5-enynes **31** that are optically more abundant and highly enantioenriched bicyclo[3.1.0]-hexenes **30** at all conversion levels without causing any racemization or symmetrization. Primarily, this finding provides proof for the exceptional capability of Au(III) complexes in enantioselective catalysis. It is also the first time that a very selective enantioselective conversion has been made possible by a carefully studied cationic Au(III) catalyst.

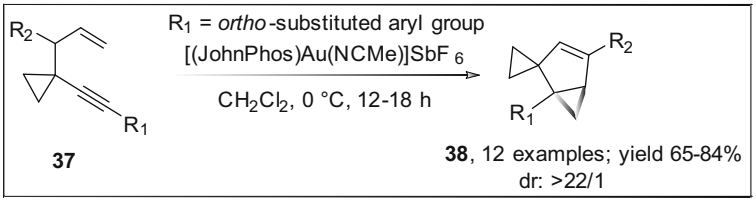
Davies synthesized tetracyclic compounds **33** by a C–H insertion or cyclization cascade of N-homoallyl ynamides **32**, catalyzed by Au(picolinate)Cl_2. The generation of N-homoallyl ynamides **32** resulted in considerable diastereoselectivity in most cases (Scheme 11) [80].

The reaction is likely to occur along the gold keteniminium **34** pathways, which involves [1,5] hydride transfer to create benzylic cation **35**. A 4π electrocyclic ring closure (4π ERC) process can result in the formation of the gold complex **36**, and cyclopropanation can complete the cascade reaction.

Wei et al. have developed a cycloisomerization reaction using Au(I) catalysts to convert easily accessible 1,5-enynes **37** with a cyclopropane ring into biscyclopropane **38**. This reaction has demonstrated moderate to good yields, as reported in Scheme 12 [81]. Through the manipulation of temperature and the choice of gold(I) catalyst, it



Scheme 11: The C–H insertion/cyclization cascade of N-allyl ynamides catalyzed by gold.



Scheme 12: Au(I)-mediated cycloisomerization of cyclopropyl 1,5-enynes.

is possible to selectively synthesize three different products that possess an *ortho* substituent. The required products are made by changing the key intermediate, tricyclic cyclobutene. This is done by first applying a standard enyne cycloisomerization reaction to the 1,5-enyne substrate.

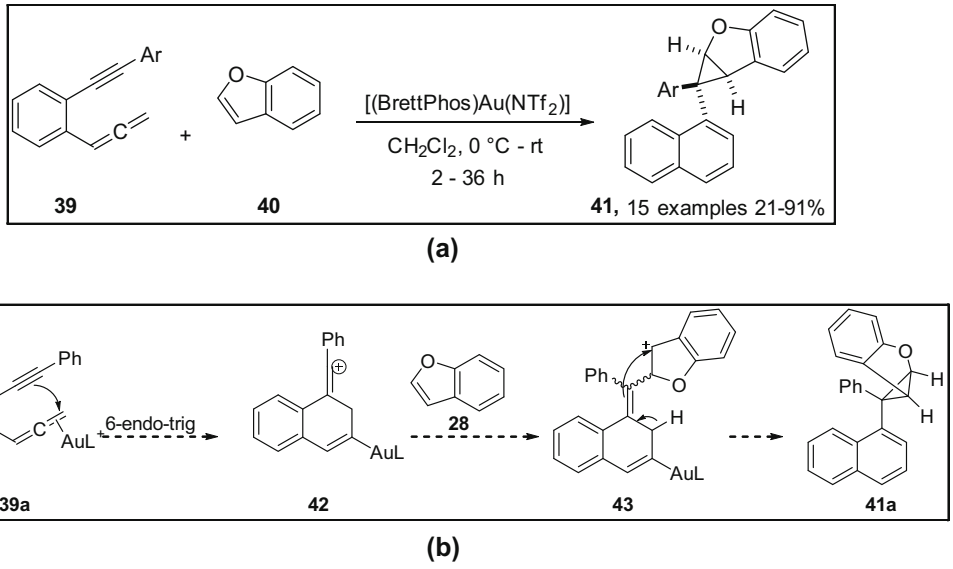
3.2.2 Cyclopropanation through cycloisomerization of allenynes

The production of 1-naphthylcyclopropane-fused benzoheterocycle derivatives **41** was observed by Ohno's group via the reaction of benzoheterocycles **40** with benzene-tethered 5-allenynes **39**, as depicted in Scheme 13a and b [82]. In this transition, benzofuran **40** engages in an attack on the vinyl cation **42** that was formed earlier. The attack takes place at either the 2-position or 3-position of benzofuran **40**. When the ring closes, aromatization and protodeauration occur, and the heterocycle is in the axial position that is least affected by steric hindrance. This yields either (*E*)-**43** or (*Z*)-**43**. This process ultimately leads to the production of the regioselective product **41a**.

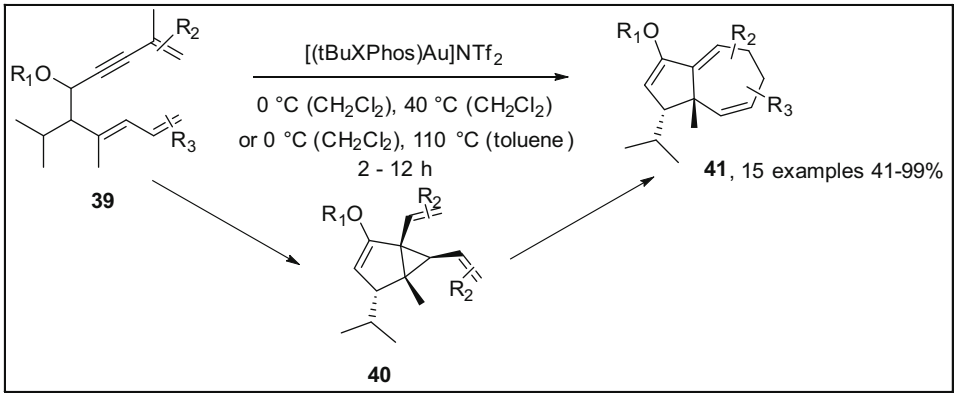
3.2.3 Cycloisomerization of diynes via migration of 1,2- and 1,3-acyloxy groups

The tandem cycloisomerization, or 1,2-OAc shift, of trienynes **44**, which incorporates a propargylic ester, was reported by the Gagosz group. This reaction was catalyzed by Au(I). Because of this, divinyl cyclopropanes **45** were made, and these then went through a thermal Cope rearrangement that created a complex polycyclic structure **46** (Scheme 14) [83].

By reacting styrene **47** with propargyl ester **48** as a model reaction, Reiersølmoen et al. reported employing Bis(pyridine)Au(III) complexes as catalysts for the synthesis of vinyl cyclopropanes **49** (Scheme 15) [84]. They confirmed that the catalytic activity of Au(III) is critically dependent on the electron density of the pyridine ligands. It appears that one pyridine must dissolve to produce the active species because ligands that have electron-withdrawing groups are noticeably more active. The use of ^{15}N NMR (nuclear magnetic resonance) data confirmed the discovery. Furthermore, the application of DFT modeling elucidated that the energy associated with the pivotal transition state was contingent upon the electron density present on the nitrogen atom of the



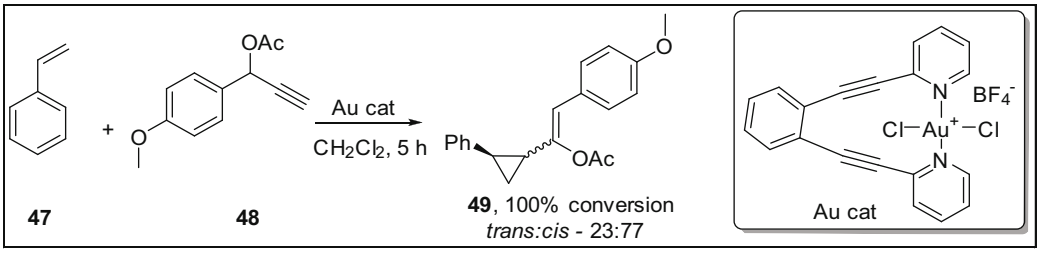
Scheme 13: (a) Gold(I)-catalyzed 5-allenynes cycloisomerization to 1-naphthylcyclopropane systems and (b) possible reaction mechanism.



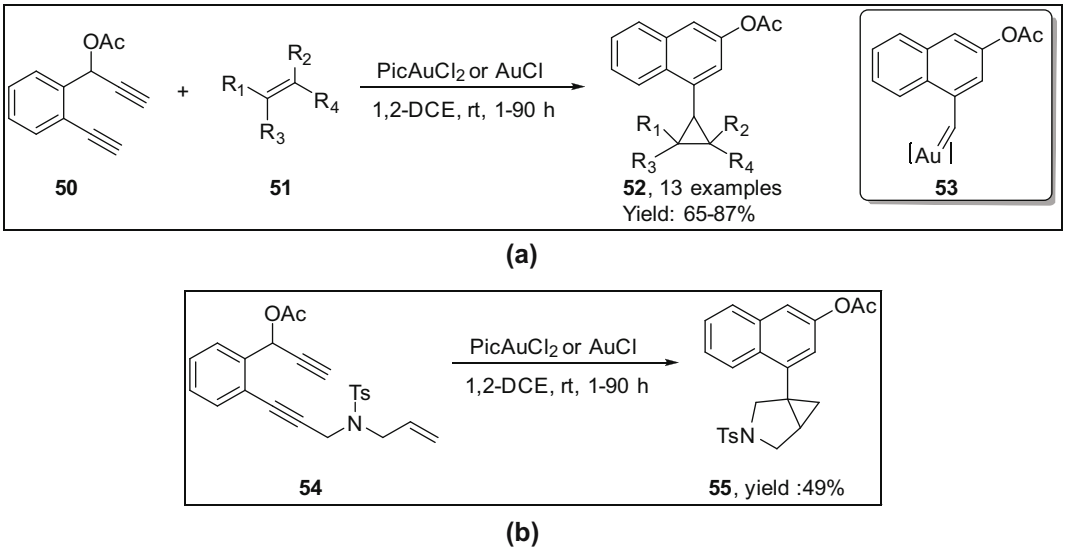
Scheme 14: Tandem Au(I) catalyst cycloisomerization/cope rearrangement.

pyridine ligand. The same research group investigated the impact of various nitrogen ligands coordinated to gold salts in the cyclopropanation reaction involving styrene and propargyl ester [85,86].

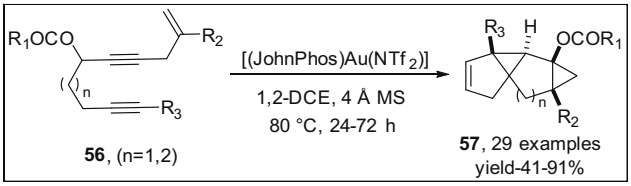
Beginning with simple starting materials, ester-tethered terminal 1,6-diyne **50** and an alkene **51**, the Hashmi group disclosed a unique synthesis method for producing cyclopropylnaphthalene derivatives **52** (Scheme 16a) [87].



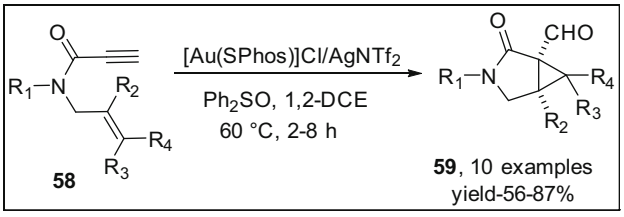
Scheme 15: Au(I)-catalyzed enantioselective styrene cyclopropanation with propargylic esters.



Scheme 16: (a) Intermolecular cyclopropanation of 1,6-diynes using gold catalysis and alkene. (b) Intramolecular cyclopropanation of 1,6-diynes pendant with alkenes.



Scheme 17: Sequential tandem 1,3-migration and dual cyclopropanation in 1-ene-4,*n*-diyne esters.



Scheme 18: Intramolecular cyclization for cyclopropane formation in 1,6-enynes.

A gold-catalyzed process involving the reaction of propargyl esters with a tethered alkynylphenyl group produced key intermediate naphthylcarbene complexes **53**. Following the formation of the unusual carbene complex by a 1,2-carboxylate shift, an alkyne insertion produces a new naphthylcarbene complex. The next step is cyclopropanation with an alkene additive to capture this new complex. A smooth reaction inside the molecule of 1,6-diyne **54** attached to an alkene part also made the required cyclopropylnaphthalene derivatives **55** with a moderate yield (Scheme 16b). Notably, no competing enyne cyclization was seen, suggesting that the naphthyl carbenoid forms quickly. The research teams led by Oh [88] and Hashmi [89] delved into the significant role of gold carbenoids (formed by 1,2-carboxylate shift) in the cycloisomerization reaction of propargylic esters connected to alkyne motifs, aiming to produce naphthylene derivatives.

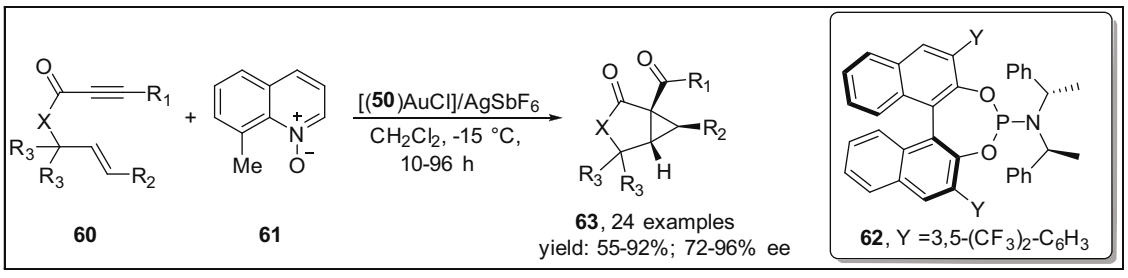
In a study conducted by Rao, Chan, and colleagues, the authors detail the synthesis of tetracyclodecene and tetracycloundecene compounds **57**. We made these chemicals by a series of steps that included an Au(I)-catalyzed tandem 1,3-acyloxy migration and double cyclopropanation of 1-ene-4,9-diyne and 1-ene-4,10-diyne esters **56** (Scheme 17) [90].

3.3 Cyclopropanation by an oxygen-transfer agent via the oxidation of alkynes

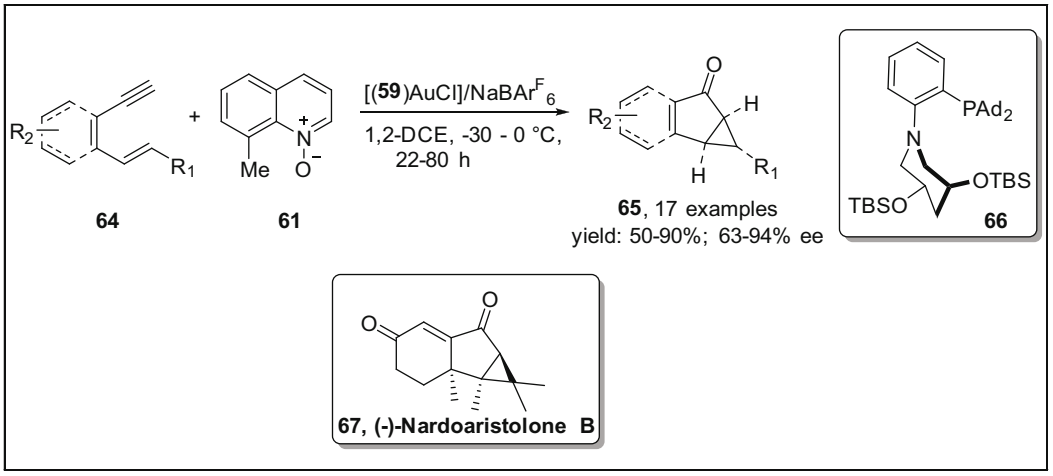
Yeom and Shin showed that oxidative cyclopropanation of 1,6-enynes **58** with a propiolamide moiety attached could occur inside the molecule, creating cyclopropane carboxaldehydes **59** (shown in Scheme 18) [91]. In oxidative cyclopropanation, substrates containing terminal alkynes were initially utilized to produce cyclopropane carboxaldehydes, which possessed unique applications because of their aldehyde functionality. Diphenyl sulfoxide worked well as an oxidant for this kind of substrate, as opposed to pyridine-N-oxides, and this has been shown to have a broad universality about alkenes.

The Zhang group reported a catalytic asymmetric oxidative cyclopropanation of 1,6-enynes **60** in 2014. Because of this reaction, densely functionalized bicyclo[3.1.0]hexanes **63** were made, which had a lot of enantioselectivity (Scheme 19 [92]). A highly effective gold(I) complex with cationic properties was successfully synthesized, utilizing ligand **62**. To facilitate the reaction, 8-methylquinoline N-oxide **61** was selected as the external oxidizing agent.

Ji et al. [93] developed a method for the enantioselective oxidative cyclization of 1,5-enynes **64**, resulting in the formation of cyclopropane fused bicyclic derivatives **65** (Scheme 20). In order to achieve effective enantiocontrol, a hemilabile P,N-ligand [94,95] **66** containing a C2-symmetric piperidine ring was strategically developed. According to the existing literature, it has been suggested that piperidine offers a favorable chiral environment as a result of its capacity to coordinate with the metal center's



Scheme 19: Asymmetric gold-catalyzed oxidative cyclopropanation of 1,6-enyne.



Scheme 20: Asymmetric Au-catalyzed oxidative cyclopropanation in 1,5-enynes.

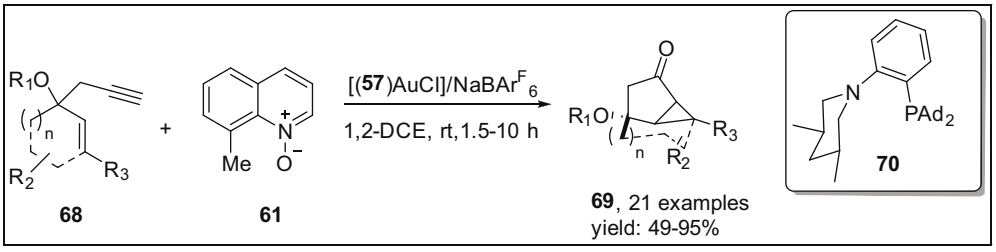
nitrogen atom and provide steric shielding. This helps mitigate the high reactivity of the highly electrophilic α-oxo gold carbene intermediate [96,97]. The approach performed by the Echavarren research team has been previously applied to produce enantioenriched 1,5-enyne **64**, which was then utilized in the overall synthesis of (−)-nardoaristolone B **67** [98].

Employing a conformationally rigid P,N-bidentate ligand **70**, Zhang and colleagues reported a highly efficient three-step intramolecular cyclopropanation of alkyne tethered enals **68** to bicyclic or tricyclic functionalized cyclopropyl ketones **69** (Scheme 21) [99]. The reaction was completed with largely good yields. When considering step economy and operational safety, this reaction exhibits favorable comparisons to similar approaches that rely on the diazo approach.

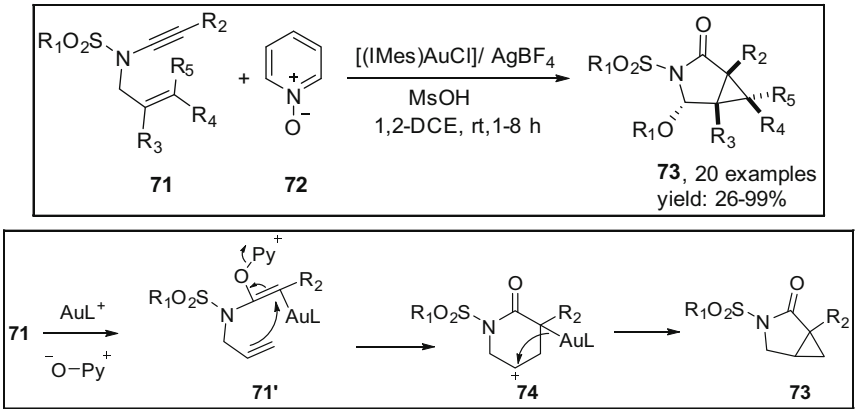
The first-ever gold-catalyzed oxidative cyclopropanation of N-allyl ynamides **71** was reported by Li et al. The catalyst used in this process was [(IMes)AuCl]/AgBF4, and the oxidant employed was pyridine N-oxide **72**. This reaction yielded diverse variants of 3-aza-bicyclo[3.1.0]hexan-2-one **73** (Scheme 22) [100]. Mechanistic studies were conducted to investigate the potential participation of the α-oxo gold carbene as an intermediary. The results of these tests indicated that the α-oxo gold carbene is not involved, hence suggesting that the alkene attacks the electrophilic β-oxypyridinium vinyl gold(I) species **74**.

Because of overoxidation, the oxidative cyclization of ynamides with aromatic substituents rich in electrons at the alkynes terminal was not tolerable. By utilizing various reaction circumstances, Davis and his team were able to solve this concern (Scheme 23) [101]. Diketone **76** was made when N-allylynamides **75** with a tosyl substituent connected to nitrogen went through oxidative cyclization in 1,2-DCE. The cyclopropanation product **77** in nitromethane, on the other hand, was made by oxidative cyclization of N-allylynamides **75**, which had a mesyl substituent connected to nitrogen. An instance of Au(I)-catalyzed yne-ynamide with pendant alkene undergoing cascade reactions involving cyclization, oxidation, and intramolecular cyclopropanation was recently reported by the Hashmi group utilizing diphenyl sulfoxide [102].

This study by Davies and his team showed how N-benzyl ynamides **78** react with oxygen in a Buchner-type way. This reaction creates [5.3.0] azabicycles **79′** (Scheme 24) [101]. The NMR technique effectively demonstrated the presence of a dynamic equilibrium between cyloheptatriene



Scheme 21: Gold-catalyzed synthesis of bi- and tricyclic cyclopropyl ketones through oxidative cyclizations.



Scheme 22: Gold-catalyzed oxidative cyclopropanation of N-allylynamides.

and norcaradiene. The synthesis of Polycycle **80** involved the utilization of a Diels–Alder reaction to capture the norcaradiene tautomer **79b**, resulting in its formation. Conversely, the norcaradiene product **79a** was obtained exclusively. It is easy to obtain benzyl propargyl ethers, which were used successfully by Ji and Zhang in their study to make a gold-catalyzed oxidative cyclization report of a similar nature [103].

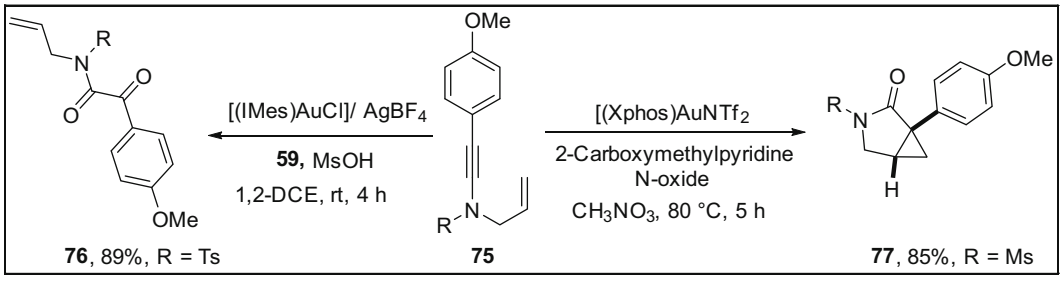
Zhang and others described a method to mix molecules called intermolecular cyclopropanation. They used 2-(*tert*-butyl)-6-chloro pyridine N-oxide as an outside oxidant to make α-oxo gold carbene from sulfonyl alkyne moiety **81** (Scheme 25) [104]. At first, carbene **84** is made when the carbon atom next to the alkyne group undergoes oxidation at the β position. A plausible chemical mechanism and this synthesis support the expected regioselectivity. Episulfone **85** would result from a Friedel–Crafts-style attack on the highly electrophilic carbene center, and it would fragment into α-oxo gold carbene **86** through SO_2 extrusion. It is important to highlight that the oxidation of an internal aryl alkyne is the exclusive approach to generating the resulting carbene as the lesser regioisomer.

The study focused on styrenes that were electronically unbiased, and a surplus of these styrenes, ten times greater than the required amount, was employed. Reactants with a significant electron density, such as 4-methoxystyrene or ethyl vinyl ether, were considered unfavorable. Instead of utilizing cyclopropane, the solvent α-methylstyrene resulted in the formation of a (3 + 2) cycloaddition product.

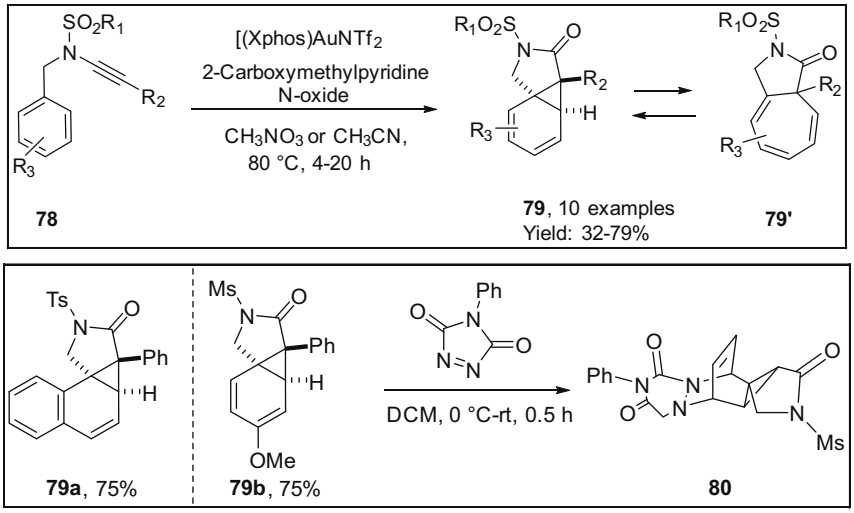
3.4 Oxidative cyclopropanation of alkynes with nitrogen-transfer agents

The first cyclopropanation that made cyclopropane-fused indanimines **90** (Scheme 26) was reported by Liu and colleagues [105]. They used α-imino gold carbene intermediates from earlier research on the oxidative cyclopropanation of 1,5-enynes **87** [106]. The application of iminopyridinium ylides, specifically compound **89**, as nucleophilic nitrenoids is observed. The nitrenoids discussed here are nitrogen-based compounds that share similarities with pyridine N-oxides. Pyridine N-oxides are frequently used as oxidizing agents in the field of α-oxo gold carbenes.

The delivery of cyclopropane-fused indoloquinolines **92** was reported by Ohno et al. through the reaction of (azido)-ynamides 91 with tethered alkenes, as depicted in Scheme 27 [107]. The α-imino gold carbene **93** played a



Scheme 23: Oxidation of electron-rich ynamides by gold catalyst.



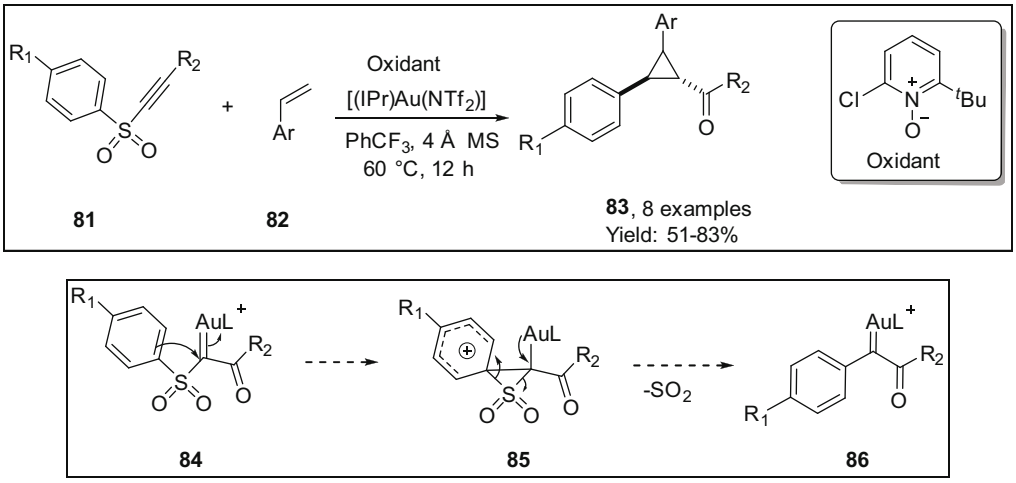
Scheme 24: Intramolecular oxidative cyclopropanation of N-benzyl ynamides.

critical role in the transformation of the ynamide. This was done by the azide attack inside the molecules, which caused the loss of nitrogen and the cyclopropanation of the alkene that was present around.

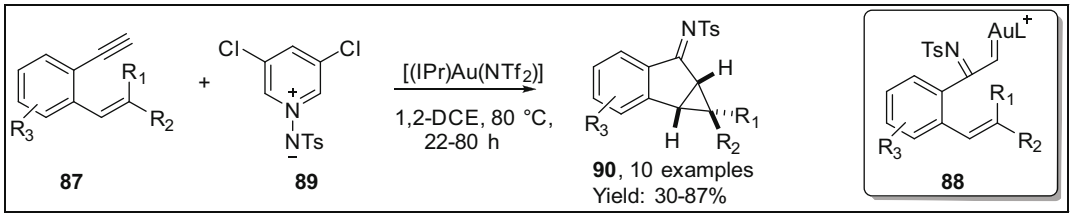
As part of their study, Hashmi et al. showed that adding external nitrene transfer reagents made α-imino gold carbenes more useful for intramolecular cyclopropanations of ynamides **94**. By cutting N–S and attacking gold-activated ynamides across molecules, they made α-imino gold carbenes **97** using N-arylsulfilimines **95** (Scheme 28) [108]. The compound 3-azabicyclo[3.1.0] is of hexan-2-imines **96** and can be synthesized with high yields by employing various methods [109], including the utilization of a tethered alkene as one of the approaches. For the effective progression of the reaction, an electron-withdrawing group is attached to the arene of the sulfilimines, and a temperature of 80°C is necessary. Furthermore, it has been discovered that Au(III) catalysts with Lewis acidity demonstrate superior efficiency in comparison to Au(I) catalysts.

After that, the Hashmi group showed that ynamides **94** could turn into **99** under milder conditions by using different nucleophilic nitrenoids, namely anthranils **98** (Scheme 29) [110].

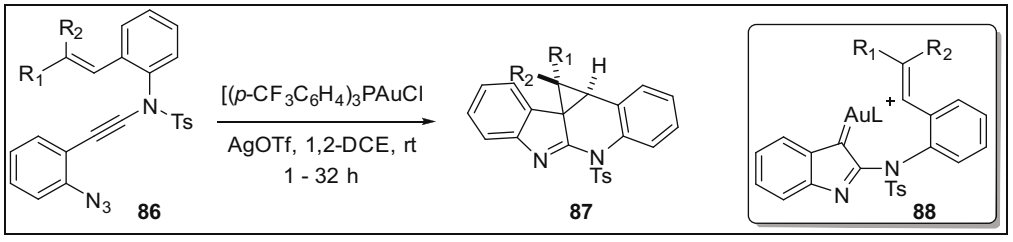
In this instance, the reaction might continue at room temperature with a catalytic quantity of $NaAuCl_4$ dihydrate. A related work with α-imino gold carbenes is worth mentioning, as it allowed the creation of bicyclic compounds fused with cyclopropane in certain situations [111].



Scheme 25: Gold-catalyzed intermolecular oxidative cyclopropanation.



Scheme 26: Gold-catalyzed intramolecular cyclopropanation of 1,5-enynes with iminopyridinium ylides.



Scheme 27: Intramolecular cyclopropanation of azidoynamides.

3.5 Gold-mediated synthesis of cyclopropanes containing heteroatom

Additionally, heterocyclic 3-membered rings such as aziridines and epoxides were produced under gold(I) catalysis in several mechanistic contexts.

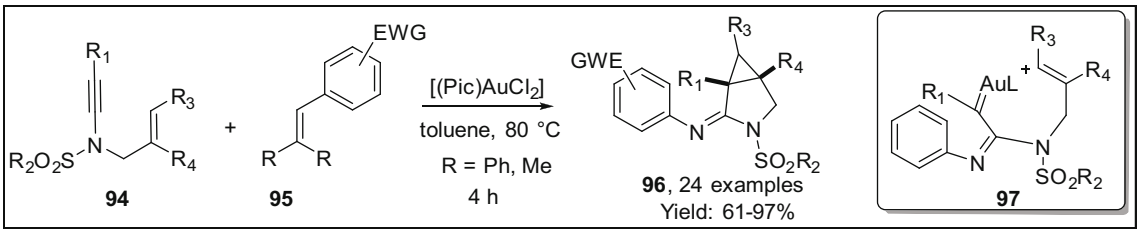
The group demonstrated that reacting 3-hydroxybenzofurans **101** with 2*H*-azirines **102** under gold catalysis generates aziridines **103** (Scheme 30) [112].

In their important work, Sahani and Liu provided a full explanation of the intermolecular (4 + 2) cycloaddition reaction involving benzisoxazoles **105** and electron-poor alkynes **104**, specifically propiolates. The use of gold catalysis in this process led to the formation of tetrahydroquinolines **107**, which possess an epoxide ring. This reaction is illustrated in Scheme 31 [113].

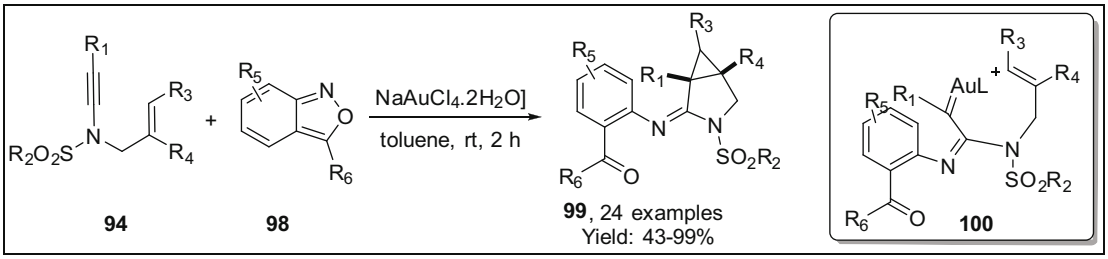
Hashmi's group used electron-rich alkynyl amines in a similar manner [114]. This led to the construction of a novel switchable approach that allowed for the synthesis of quinoline epoxides (containing an Au(III) complex) or 6-acylindoles (containing an Au(I) complex) from the same two substrates by selecting the appropriate gold catalyst.

4 Gold-catalyzed formation of four-membered rings

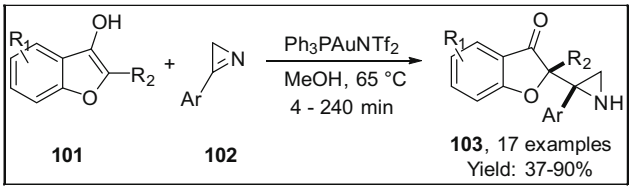
Zhang [115] stated that Au(I) catalysis was used to make the first indoline-fused cyclobutanes. Subsequently, the region has experienced substantial development because of the recognition and implementation of a remarkable array of gold(I)-catalyzed methodologies, the majority of which rely on sequential [2 + 2] cycloadditions and ring expansions [27–34,116–126]. The utilization of these novel methodologies enables the atom-efficient synthesis of a wide range of molecules, encompassing both simple ring structures and complex frameworks seen in natural substances.



Scheme 28: Intermolecular cyclopropanation of ynamides using sulfilimines.



Scheme 29: Anthranil-mediated intramolecular cyclopropanation of ynamides.



Scheme 30: Synthesis of aziridines from 2*H*-azirines via gold catalysis.

4.1 Formation of four-membered rings via cyclopropyl ring expansion

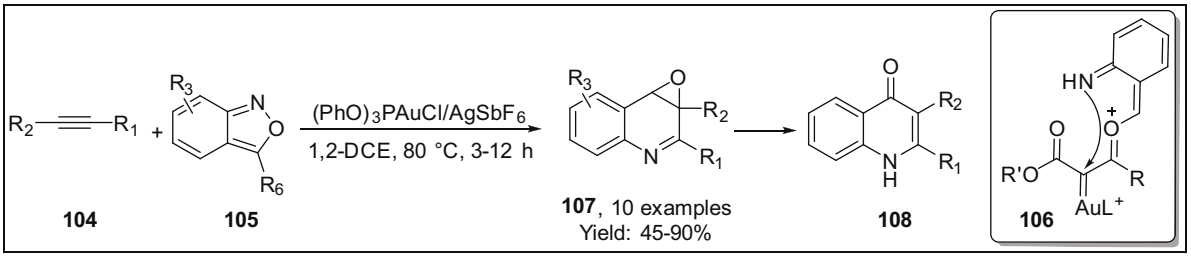
The Echavarren group has reported a diastereoselective Au (I)-catalyzed cascade transformation. In this process, a cyclopropyl group is changed into a cyclobutane through a series of chemical reactions that include ring expansion, enyne cyclization, and Prins cyclization. In particular, the change is made to cyclopropyl 1,6-enynes **109**, which creates tricyclic compounds with a decahydrocyclobuta[a]pentalene skeleton **110**. These compounds exhibit a syn/anti/syn relationship. Following this, the tricyclic compounds are changed into the natural product Repraesentin F **111** in six steps (Scheme 32) [127].

The tricyclic core [128] belonging to the protoilludanes family was successfully obtained by a one-step process utilizing a closely comparable Au(I)-catalyzed allene-vinylcyclopropane cycloisomerization.

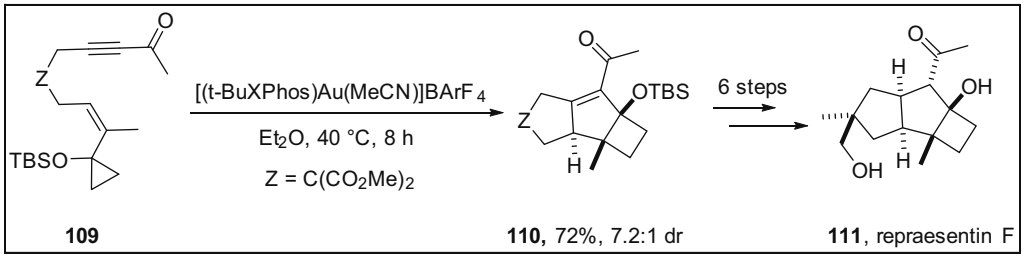
Shi et al. [81] documented the cycloisomerization of 1,5-enynes **112**, which were tethered with a cyclopropyl group, using divergent gold(I) catalysis (Scheme 33). Cyclobutane-fused 1,4-cyclohexadienes **114** were synthesized in cases where the aryl group did not possess *ortho*-substitution, as depicted in Scheme 33a. The *ortho*-substitution of the aryl group facilitated the generation of a switchable protocol. Under controlled temperature conditions, three unique polycyclic scaffolds were synthesized using a suitable gold catalyst. The scaffolds encompass spiro compound **116,** fused-cyclobutane-conjugated cyclohexadiene **115**, and tricyclic cyclobutene **117**. The synthesis was carried out according to Scheme 33b–d, respectively. Both labeling investigations and computational analysis were employed to demonstrate that the *ortho*-substituent effect played a crucial role in determining the transformation of the common biscyclopropane Au(I) carbene intermediate **113** into different products.

The Gagne group reported cyclic 1,5-dienes **118** undergoing Cope rearrangement and cyclopropane ring expansion under gold(I) catalysis to synthesize tricyclic compounds **119** (Scheme 34) [129].

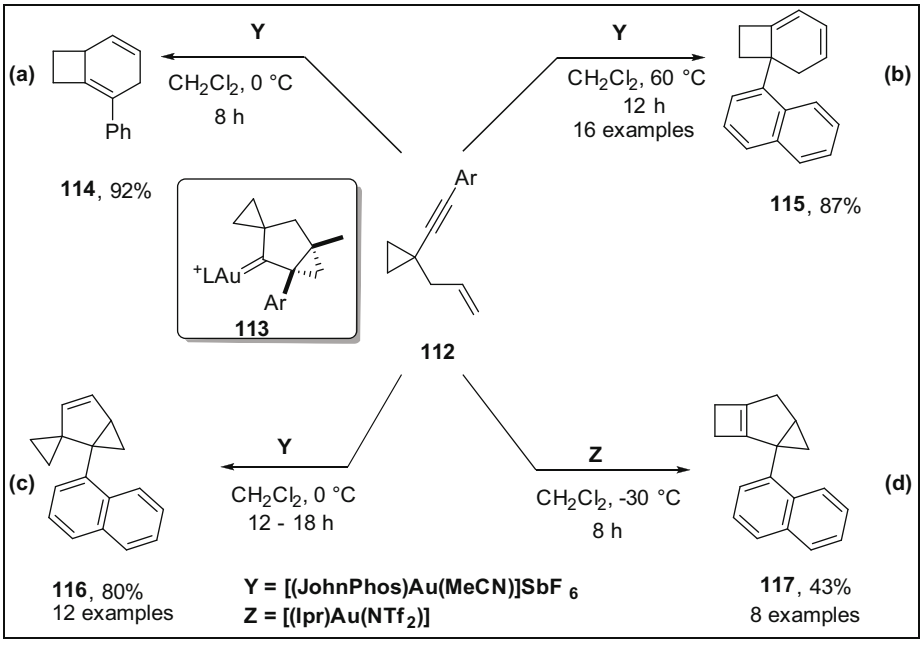
The enantioselective cycloisomerization/ring expansion procedure for cyclopropylidene-containing 1,5-enynes **120** was found by the Gagne research team. This process led to the formation of enantioenriched bicycle [4.2.0] octanes **122** with an enantiomeric excess of up to 70% (Scheme 35, right) [130]. The same group of researchers later found that aldehydes could effectively capture Au(I)-stabilized allyl cation intermediates **121**, which led to the formation of oxo-carbenium cations. The cations we talked about earlier went through Friedel–Crafts annulation, which created polycyclic structures **123** through a cascade reaction with high diastereoselectivity (shown in Scheme 35, left) [131].



Scheme 31: Oxirane synthesis from benzisoxazoles under Au-catalysis.

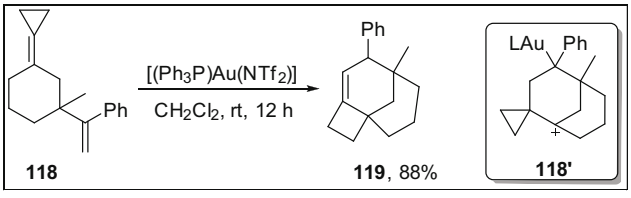


Scheme 32: Synthesis of cyclobutanes via Au-catalyzed expansion of cyclopropanes access to repraesentin-F.



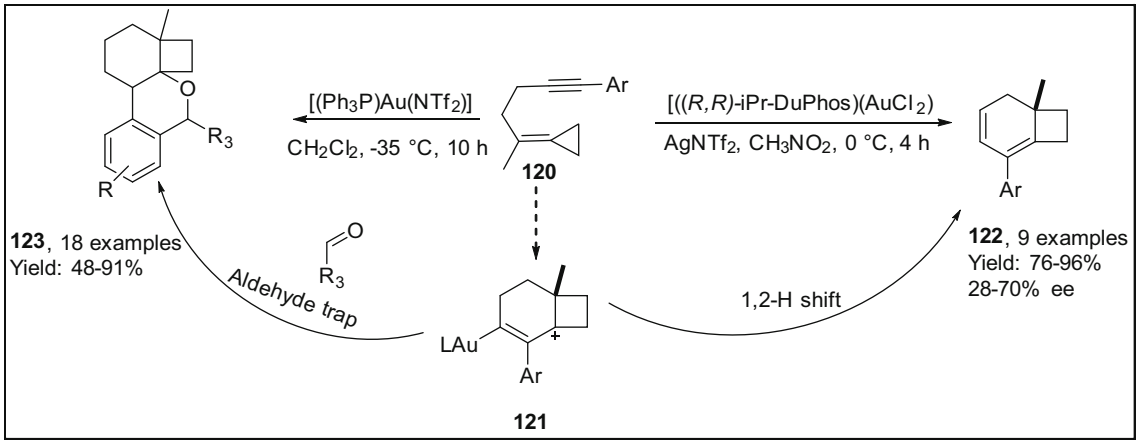
Scheme 33: Gold-catalyzed transformation of 1,5-enynes with cyclopropyl group into (a) cyclobutane-fused 1,4-cyclohexadiene; (b) 1,3-cyclohexadiene; (c) biscyclopropane; (d) tricyclic cyclobutene derivatives.

Carreira has successfully devised a process characterized by a high degree of diastereocontrol that enables the synthesis of cyclobutane derivatives **125** by the employment of Au(I)-catalyzed cyclo-isomerization of cyclic cyclopropylidene 1,5-enynes **124** in conjunction with a terminal alkyne. Harziane diterpenoid **126** (Scheme 36) was obtained through a series of 16 consecutive transformations, starting with the initial cyclobutane precursor [132].

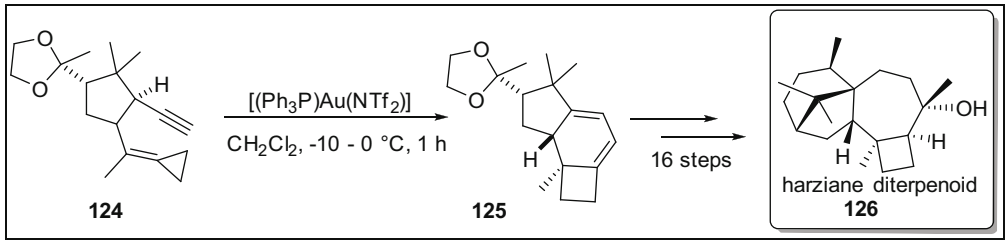


Scheme 34: Cycloisomerization of cyclopropylidene-tethered frameworks.

The Shi group made a big discovery about how *ortho*-substituents affect the phenyl group (R1) in the reaction between (propargyloxy)arenemethylenecyclopropanes **127** and an Au(I) catalyst that attracts electrons, specifically [(p-$CF_3C_6H_4)_3$PAuCl. This reaction exhibited chemodivergent results, as seen in Scheme 37 [133]. There have been observations in chemical reactions that when bulky substituents like t-Bu and t-Am are used, the methylene cyclopropane group moves instead of expanding. This leads to the creation of bicyclic products **129**, as depicted in Scheme 37 on the left. Methoxy (MeO), halogens, or methyl (Me) groups are thought to be non-bulky and can help the ring become bigger and the propargyl group moves around. Au(I) facilitates the catalytic process, which results in the synthesis of 2,3-dihydrobenzofuran cyclobutane fused allene derivatives **131**. The reaction is visually represented in Scheme 37, situated on the right-hand side.

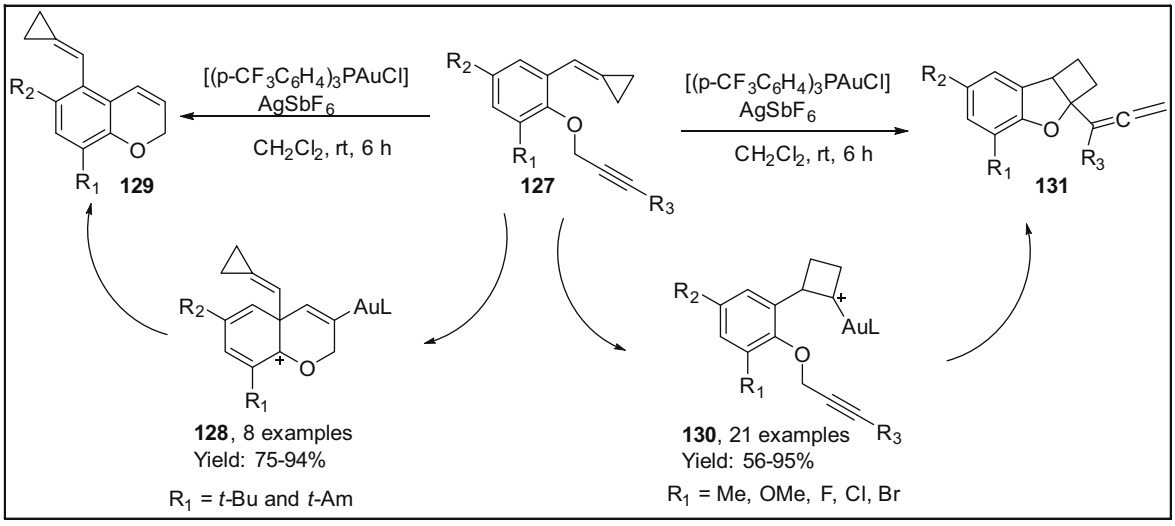


Scheme 35: Au(I)-Catalyzed synthesis of cyclobutane fused systems.

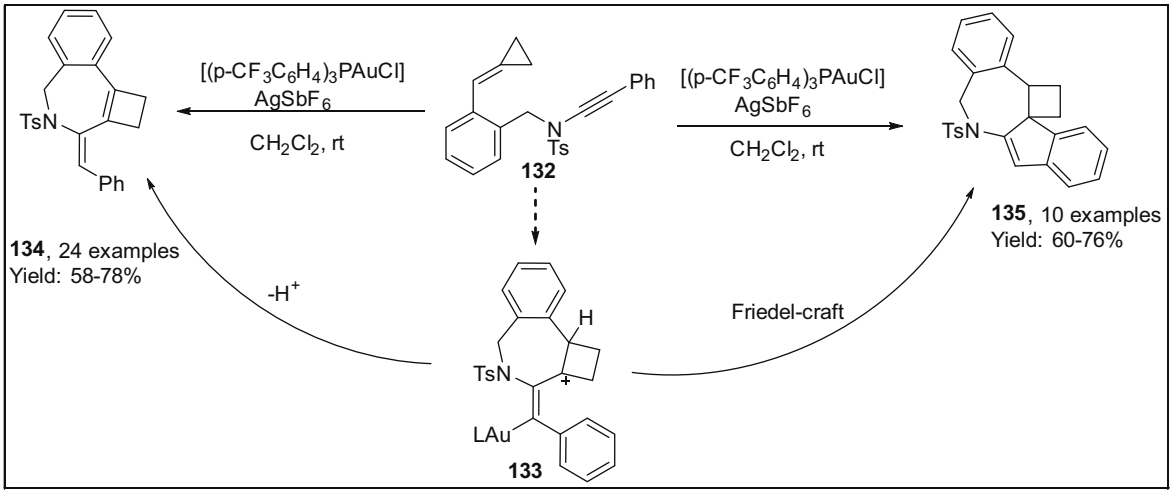


Scheme 36: Cycloisomerization of cyclopropylidene1,5-enynes.

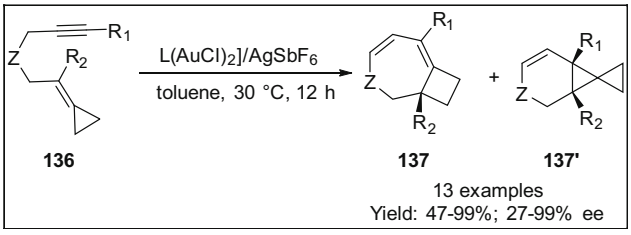
In addition, Shi effectively developed a regiodivergent catalytic cyclization/ring opening sequence (Scheme 38) utilizing alkynylamide-tethered alkylidenecyclopropanes **132** [134]. In this case, the gold(I) catalysts utilized resulted in the formation of two unique types of fused 4-membered rings, namely cyclobutenes **134** and cyclobutanes **135**. The cationic Au(I) catalyst's ligand and counteranion were discovered to be significant factors in the distribution of the product. Cyclobutenes **134** were the only compounds produced when [(Ph3P)AuCl] was employed in conjunction with AgOTf (Scheme 38, left). Cyclobutanes **135** was the lone product, however, because of using JohnPhos as a ligand with



Scheme 37: Regiodivergent cycloisomerization of cyclopropylidene 1,7-enynes catalyzed by Au(I).



Scheme 38: Cycloisomerizations of ynamide-cyclopropylidene 1,7-enyne.



Scheme 39: Enantioselective gold(I)-catalyzed cycloisomerization of cyclopropylidene 1,6-enynes.

the $BArF_4$ counteranion (Scheme 38, right). It is possible for a Friedel–Crafts annulation to create spiropolycyclic cyclobutanes **135** from the Au(I)-stabilized carbocation 133 after the ring has grown. When intermediate **133** is deprotonated, cyclobutene **134** is obtained as an alternative.

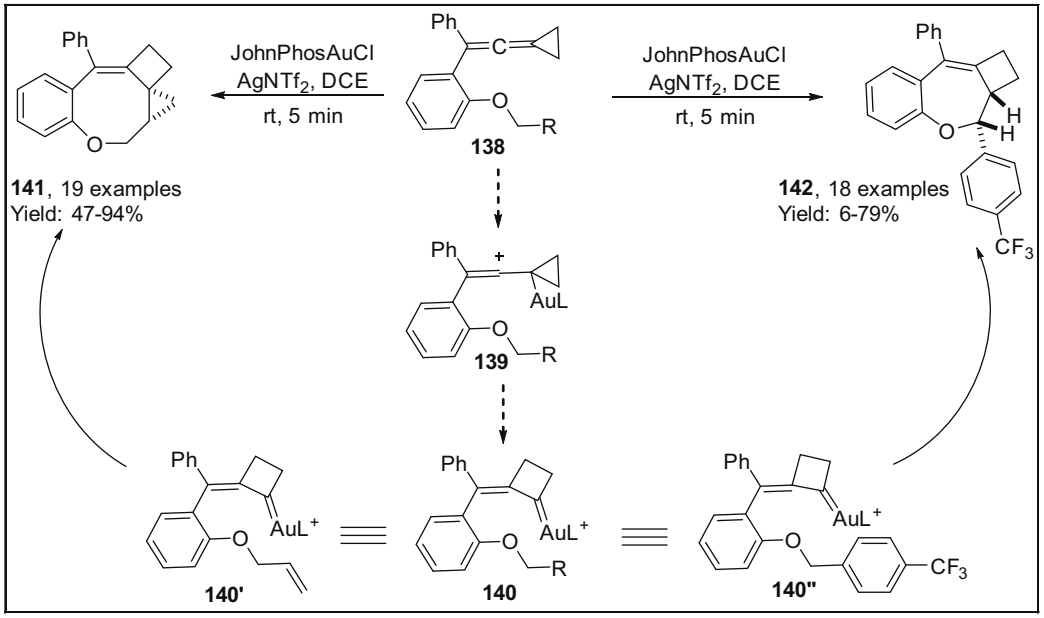
Li and Yu used cyclopropylidene 1,6-enynes **136** as a starting point for the synthesis of azepine-fused cyclobutanes **137**. As shown in Scheme 39 [135], a series of steps involving Au(I)-catalyzed cyclization, C–C cleavage, and Wagner–Meerwein rearrangement were necessary to achieve the result. The authors found that in this instance, the influence of both the counterion and the solvent enhanced enantioinduction. It was shown that $AgSbF_6$, toluene, and [(*R*)-4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP)$(AuCl)_2$] can improve the enantioselectivity of cyclobutane products **137** by as much as 99% ee. Noting the creation of spirocyclic molecule **137′** during the reaction is very important because it shows great chemoselectivity, especially when aryl groups lacking electrons are connected to the cyclopropylidene moiety.

Shi et al. reported a novel method of generating gold(I) carbenes based on vinylidenecyclopropanes' ambiphilic properties. A vinylidene cyclopropane, like **138**, is activated by gold(I) to produce cyclopropyl gold(I) intermediate **139**, which then expands the ring to form Au(I) carbene **140** (Scheme 40) [136].

When this method was used, the pendant alkene part of vinylidenecyclopropane-enes of type 138′ underwent cyclopropanation by temporary Au(I) carbenes **140′**. Therefore, 3-, 4-, and 8-membered fused rings **141** (Scheme 40, left) were constructed in a single step [136]. Vinylidenecyclopropane-enes were the only ones that worked as substrates because they only bound to aromatic rings without *ortho* substitution. The researchers came up with new methods to achieve this. The Au(I) carbene that was made in the reaction mixture was very important in a process called intramolecular C(sp^3)-H insertion. This resulted in the successful synthesis of the required fused cyclobutane products, denoted as **142**. This was achieved by strategically modifying the pendant chain of vinylidene cyclopropanes, as depicted in Scheme 40 (right) [137].

4.2 Gold(I)-catalyzed 1,3-acyloxy migration in propargylic carboxylates

The challenge associated with the 1,3-acyloxy migration of 1,3-diarylpropargyl carboxylates under the influence of a gold(I) catalyst has been ascribed to the formation of uncharacterized amalgamations. In the context of the intermolecular synthesis of cyclobutanes **144b** catalyzed by Au(I), as described by Shi et al., they developed a silver-free process that demonstrates both chemo- and regioselectivity. This methodology was employed to investigate the characteristics of the various products, as depicted in Scheme 41 [138]. Here, the intermolecular [2 + 2] cycloaddition between



Scheme 40: Cycloisomerization of vinylidenecyclopropanes coupled with O-allyl and benzyl moieties.

the *in situ*-produced allenes **143′** is catalyzed by gold(I). Only 1,4-enyne **144a** was produced when silver was present (Scheme 41). On the other hand, depending on the catalyst selected and the carboxylate moiety's substitution pattern, cyclobutane isomer **144b** may be produced as the main product in a silver-free environment.

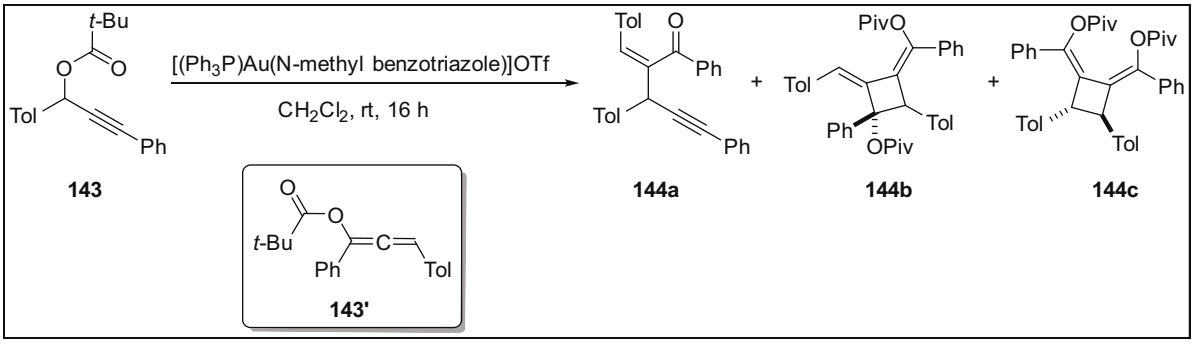
Fiksdahl recently reported an isolated case of this reactivity in the context of [2 + 2 + 2] cyclotrimerizations catalyzed by Au(I) [139].

In the context of a computational modeling investigation on the structural properties of acyclic diaminocarbene ligands, an accompanying enantioselective reaction was performed. The goal of this reaction was to change indolyl substrates **145**, which have a propargyl ester part, into complex tetracyclic scaffolds **146** (shown in Scheme 42) [140].

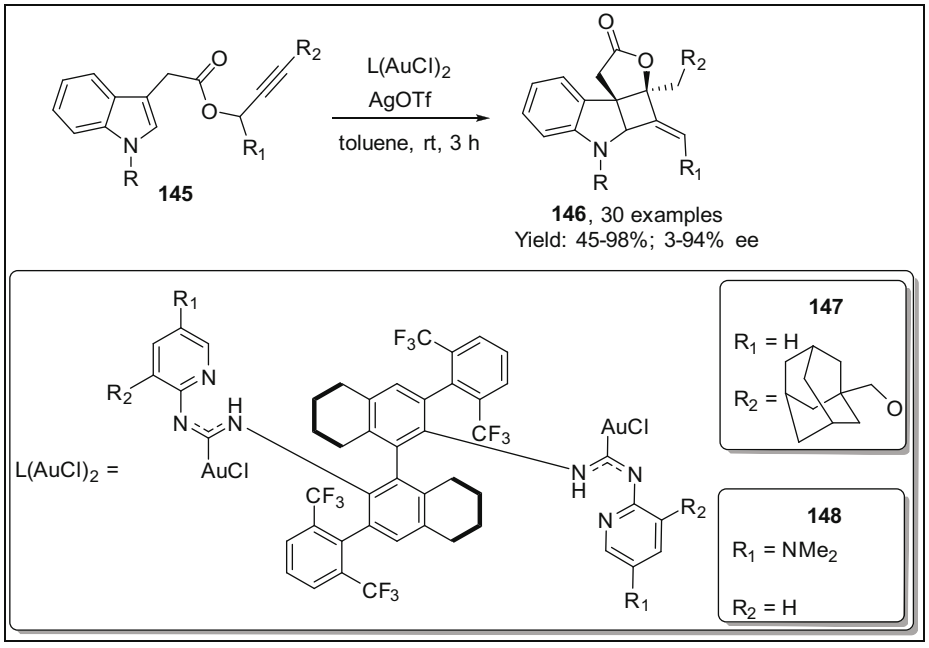
It is easier to tell the difference between enantiomers when gold catalyst **147** is used with bigger alkyl groups on the alkyne moiety. In contrast, complex **148** demonstrates an inverse impact. In general, it can be observed that complex **147** exhibits superior enantioselectivity and yields compared to those of complex **148**.

4.3 Gold(I)-catalyzed [2 + 2]-cycloaddition between allenes and alkenes

The efficacy of 3-(Propa-1,2-dien-1-yl)oxazolidin-2-one **149** as a suitable two-carbon partner in a full regio- and stereocontrolled intramolecular [2 + 2] cycloaddition with alkenes 150 has been established by López et al. As shown in Scheme 43, the presence of gold acts as a catalyst to facilitate this reaction. The formation of *trans* isomer **152** is independent of the alkene 150's structure. The proposed mechanism entails a sequential cationic pathway



Scheme 41: Au(I)-mediated intermolecular 1,3-acyloxy shift followed by [2 + 2] cycloaddition.

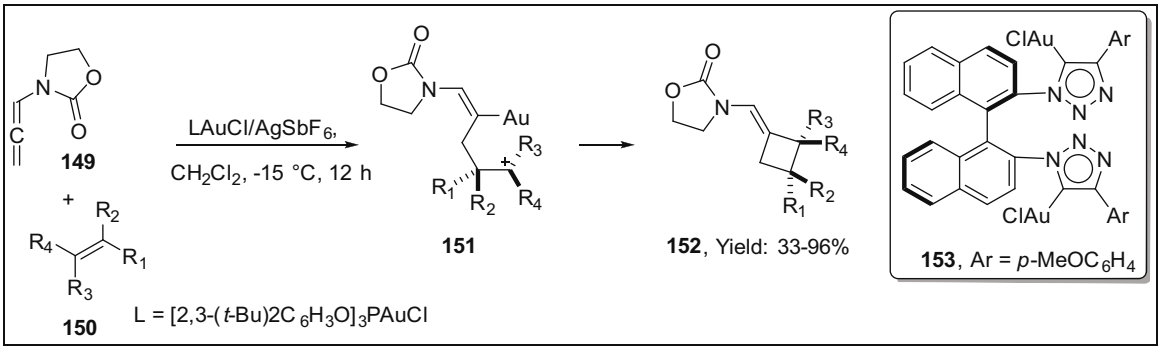


Scheme 42: Enantioselective Au(I)-catalyzed tandem rearrangement and cyclization of indolyl propargylic esters with acyclic diaminocarbene complexes.

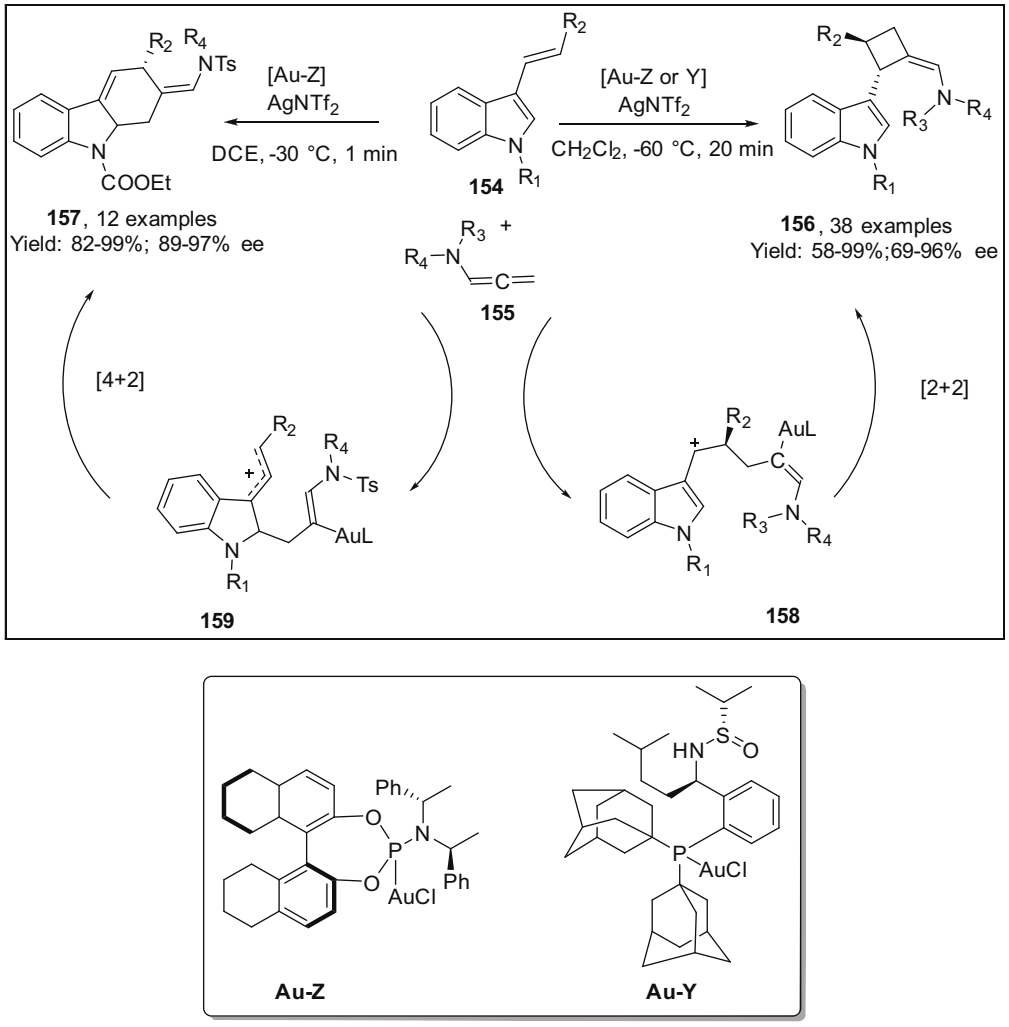
characterized by the formation of cationic intermediates. The regioselectivity of the reaction is determined by the nucleophilic attack of the alkene on a second cationic intermediate **151**. This attack favors the creation of a more stable benzylic or iminium cation [141]. An important discovery was made by Chen et al. about the catalytic properties of the chiral bis-1,2,3-triazol-5-ylidene diAu(I) complex **153** in a recent study. This complex has amazing catalytic properties that the researchers used to show how it can help make cyclobutanes selectively using a [2 + 2] cycloaddition process [142]. This ligand can be used with a wider range of substrates, such as different allenamide and alkene chemical counterparts.

The asymmetric Au(I)-catalyzed cycloadditions of *N*-allenylsulfonamides **155** and 3-styrylindoles **154** were reported by Zhang and colleagues (Scheme 44) [143]. Here, it was discovered that the *N*-substituents' electrical characteristics were responsible for switching the cycloaddition mode. The [4 + 2] cycloaddition reaction leading to the formation of tetrahydrocarbazole scaffolds **157** (Scheme 44, left) was facilitated by substituents with electron deficiency. Conversely, the [2 + 2] cycloaddition reaction resulting in the synthesis of 3-cyclobutylindole **156** (Scheme 44, right) was favored by substituents with electron-donating properties.

Interestingly, it was discovered that employing the identical chiral phosphoramidite gold(I) catalyst allowed



Scheme 43: Gold-catalyzed allenamide-alkene [2 + 2] cycloaddition.

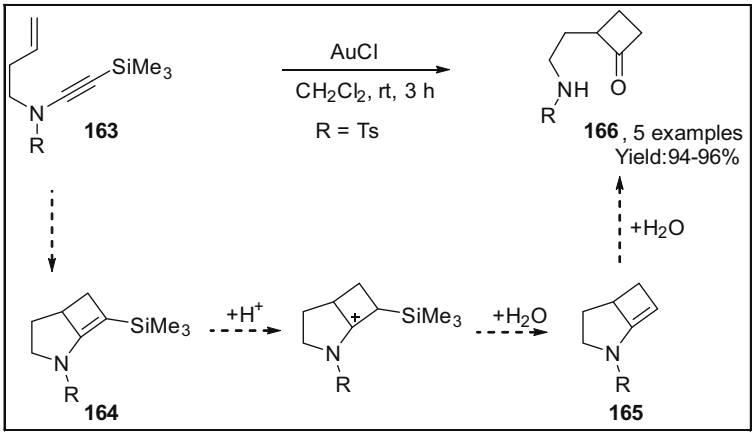


Scheme 44: Enantioselective [2 + 2] and [4 + 2] cycloaddition of 3-styrylindoles with allenamides.

for diastereo- and highlyenantioselectivity in both routes. After that, a new method was created using a chiral Au(I) monophosphine catalyst to make the [2 + 2] cycloaddition process possible with *N*-allenyl oxazolidinone as the electrophilic reactant [144].

The Bandini group devised Scheme 45, an asymmetric technique for the dearomative [2 + 2] cycloaddition of 1,2-substituted indoles **160** and allenamides **161** [145,146]. To obtain very good chemo-, diastereo-, and enantioselectivity in the production of indolincyclobutanes **162**, an electron-rich phosphine-based gold catalyst had to be used. In a previous paper, the same research group showed that indoles could selectively become C3-functionalized when they were exposed to an extremely electrophilic Au(I) catalyst, which is like the scaffolds used in this study [147].

Scheme 45: Enantioselective gold(I)-catalyzed [2 + 2] cycloaddition of indoles with allenes.



Scheme 46: Cycloisomerization of trimethylsilyl-modified 1,6-ene-ynamide.

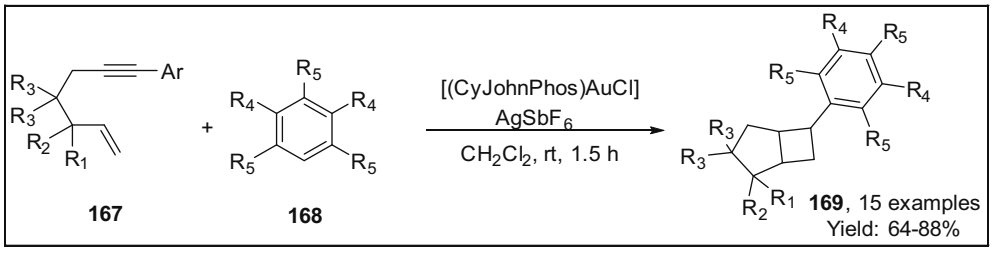
4.4 Gold(I)-catalyzed [2 + 2]-cycloadditions between alkynes and alkenes

Numerous studies have been conducted on the alkene–alkyne system to produce cyclobutanes, cyclobutenes, and cyclobutanones by intra- and intermolecular [2 + 2] cycloaddition [61]. With 1,6- [148–157], 1,7- [158–161], 1,8- [155,162,163], and 1,9-enynes [163] as substrates, many bicycles with four carbon rings have been formed. It was necessary to employ bulky phosphines, primarily biarylphosphines, as ligands for the majority of these unsaturated systems. Additionally, there have been documented instances of multiple situations involving the inclusion of macrocycles with ring sizes ranging from 9 to 15 members [164,165].

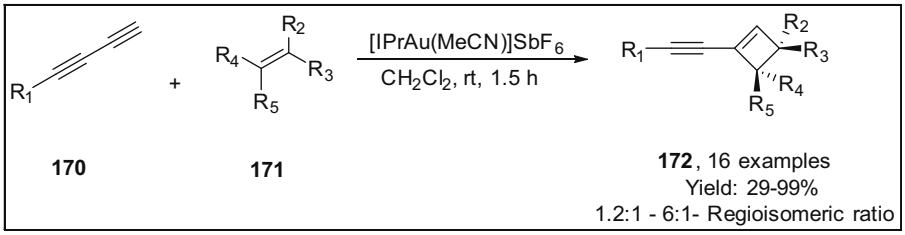
The access to cyclobutanones **166** is facilitated by the gold-catalyzed cycloisomerization of substituted 1,6-ene-ynamides **163**, as described by Cossy [150,153] and Yeh (Scheme 46) [157]. This process involves the hydrolysis of the first formed cyclobutenes to obtain the desired cyclobutanones. The proposed mechanism for the formation of trimethylsilylanol involves the protonation of the double bond in the intermediate compound **164**, which is a cyclobutene replaced with trimethylsilyl groups. This protonation event then triggers the removal of the trimethylsilyl group. The lack of rapid protosilylation in the presence of AuCl can be attributed to the behavior of trimethylsilyl-ynamides. The presence of H_2O leads to the transformation of component **165** into cyclobutanone **166**.

Furthermore, the formation of 6,6-diarylbicyclo[3.2.0] heptanes **169**, which possess a quaternary core, is successfully accomplished by the utilization of a sequential gold-catalyzed cycloaddition/hydroarylation procedure involving 7-aryl-1,6-enynes **167**. By using an arene **168** with a high electron density as the nucleophile, Scheme 47 [156] can perform the reaction. Many mono-, di-, and trisubstituted arenes have gone through this change, which creates diastereoisomer combinations in an endo/exo configuration. The ratios of these combinations vary from 1:7 to 25:1.

It is possible to selectively make substituted cyclobutenes by using Au(I) as an intermolecular catalyst in a [2 + 2] cycloaddition reaction with aromatic or aliphatic alkenes and terminal electron-rich alkynes. Kinetic measurements and DFT calculations support the mechanistic proposal. These results back up the idea that the rate-determining phase involves an associative ligand exchange between the gold-bound alkyne and the alkene. Additionally, the early intermediates are believed to be cyclopropyl Au(I) carbenes. The scope of the reaction includes reactions involving



Scheme 47: Sequential gold-catalyzed [2 + 2] enynes' cycloaddition and hydroarylation.



Scheme 48: Gold-catalyzed regioselective [2 + 2] 1,3-butadiyne cycloaddition with alkenes.

alkenes **171** and 1,3-butadiynes **172**. When the highly substituted carbon of the alkene and the secondary carbon of the alkyne come into contact with each other, a chemoselective [2 + 2] cycloaddition reaction takes place. The only way this reaction can occur is through the terminal alkyne, which makes alkynyl cyclobutenes **172** (shown in Scheme 48) [166].

Similarly, alkenes **173** can combine with the equivalent 1,3-enynes **174** to produce 1-vinyl-3-substituted cyclobutenes **175** (Scheme 49) [167].

Recently, it was reported that the [2 + 2] cycloaddition of unactivated monosubstituted alkenes **177** with chloroethynyls **176** has very good selectivity in certain regions. With 1,2-disubstituted unactivated alkenes, the reaction is essentially stereo-specific (Scheme 50) [168]. The fact that the 1-chlorocyclobutene derivatives **178** worked well as substrates in cross-coupling reactions shows that they are useful for making new things.

They used a gold catalyst with a Josiphos ligand and a $[BAr_4F]^-$ counterion to show enantioselectivity for the first time. This catalyst was applied to di- and trisubstituted alkenes ranging from **180** to limit the formation of digold species, as seen in Scheme 51 [169]. The utilization of this technology in the enantioselective total synthesis of Rumphellaone A, a terpenoid known for its cytotoxicity against human tumor cells, is of particular significance as it involves a sequence of nine steps.

Sparr et al. conducted an experimental investigation on the novel atropisomeric teraryl monophosphine ligand, Joyaphos, employing the same methodology as described in the study of Castrogiovanni et al. [170]. The study's results show that using (Sa)-Ph_2JoyaphosAuCl and Cy_2JoyaphosAuCl with AgSbF6 can help the reaction occur, even though the yields aren't very high and the enantioselectivity isn't very good.

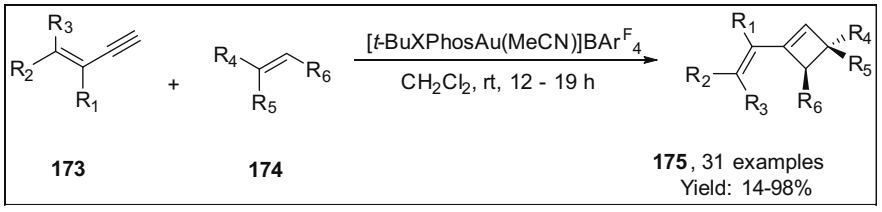
In a recent study, Echavarren et al. conducted research on the enantioselective synthesis of hushinone, a norsesquiterpenoid present in the essential oils obtained from Betula pubescens buds. The synthesis involved a series of 16 steps, resulting in a yield of around 1.1%. Additionally, they also successfully synthesized Rumphellaone A in 12 steps, achieving an approximate yield of 8% [165]. To synthesize the cyclobutene part **183**, the 1,10-enyne **182** needs to be diastereoselectively [2 + 2] macrocyclized with the help of Au(I) catalysis (Scheme 52).

Xu et al. have developed a convergent approach utilizing pinacol rearrangement and Au(I)-catalyzed [2 + 2] enyne **184** cycloaddition. This method enables the formation of the central bridging tricyclic BCD ring system found in norditerpenoid alkaloids, specifically Racemulsonine (Scheme 53) [160].

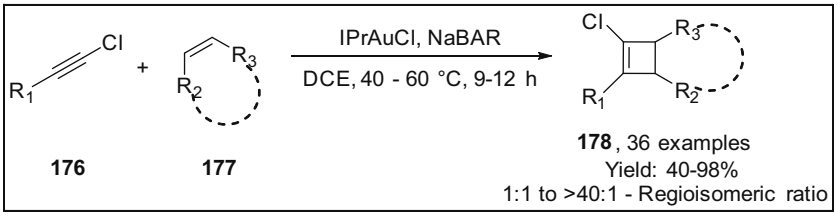
4.5 Gold(I)-mediated alkyne [2 + 2]-cycloadditions

With gold catalysis, 1,*n*-diynes have not been utilized nearly as frequently as 1,*n*-enynes. Every scenario given involves the formal [2 + 2] cycloaddition-mediated evolution of an allene molecule from its initial production.

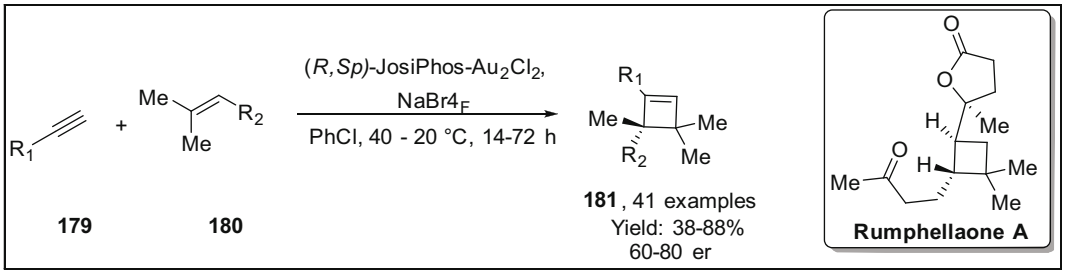
Gold can be used as a catalyst to convert 1,7-diyn-3,6-bis(propargyl) carbonates **187** into functionalized naphtho [*b*]cyclobutenes **188** with great stereoselectivity. The double



Scheme 49: Gold-catalyzed chemoselective alkene-diyne [2 + 2] cycloaddition.



Scheme 50: Gold-catalyzed [2 + 2] cycloaddition of chloroalkynes with unactivated alkenes.



Scheme 51: Enantioselective [2 + 2] cycloaddition between trisubstituted alkenes and terminal alkynes.

3,3-rearrangement that forms bis(allenyl)carbonate **189** in the cascade sequence. The naphthyl derivative 190, which is produced via a 6π-electrocyclic reaction and can be thought of as a highly stabilized biradical **191**, is then followed by cyclobutenyl dicarbonate **192** when it spontaneously cyclizes (Scheme 54) [171]. At last, **188** is obtained through a decarbonylative cyclization (pathway A). On the other hand, approach B suggests that the allenic group attacks the gold-activated allene with a nucleophilic attack inside the molecule, which creates oxocarbenium.

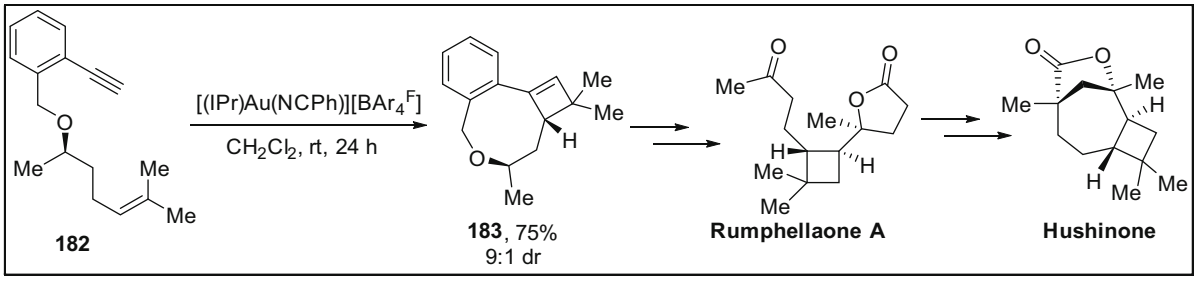
Alternatively, the intramolecular gold-catalyzed cycloisomerization of stable alkylidene tethered diynes **194** can be utilized to facilitate the production of cyclobutene-fused azepines **195**. A viable mechanism, shown in Scheme 55, has been developed based on the findings obtained from the 1H NMR investigation. A single pair of electrons on the nitrogen atom facilitates a 6-endo-dig attack, which is how the reaction starts. This attack results in the nucleophilic addition of an alkene to an activated alkyne.

An allylic cation, **197**, is produced by cleavage of the C–N bond, **196**, and then demetallation to form the allene, **198**. Finally, the activation of the vicinal alkyne [172] causes a [2 + 2] cycloaddition with the former allene.

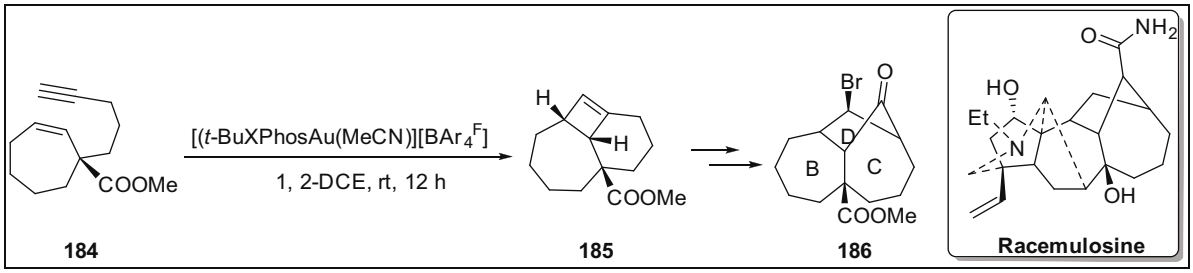
Chan et al. investigated the cycloisomerization of 1,6-diyne esters **199** through 1,3-migration[2 + 2]-cycloaddition. This reaction resulted in the selective formation of bicyclo [3.2.0]hepta-1,5-dienes **200** (Scheme 56) [173].

4.6 Heteroatom-incorporating 4-membered ring synthesis

The approach to creating 4-membered rings, including O and N atoms, was devised by Zhang. This was achieved by



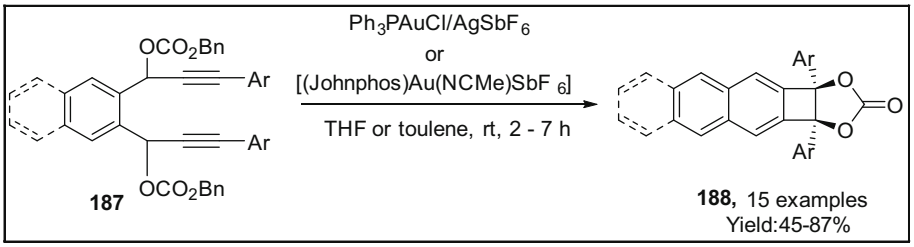
Scheme 52: Crucial step strategy for the total syntheses of hushinone and rumellaone A.

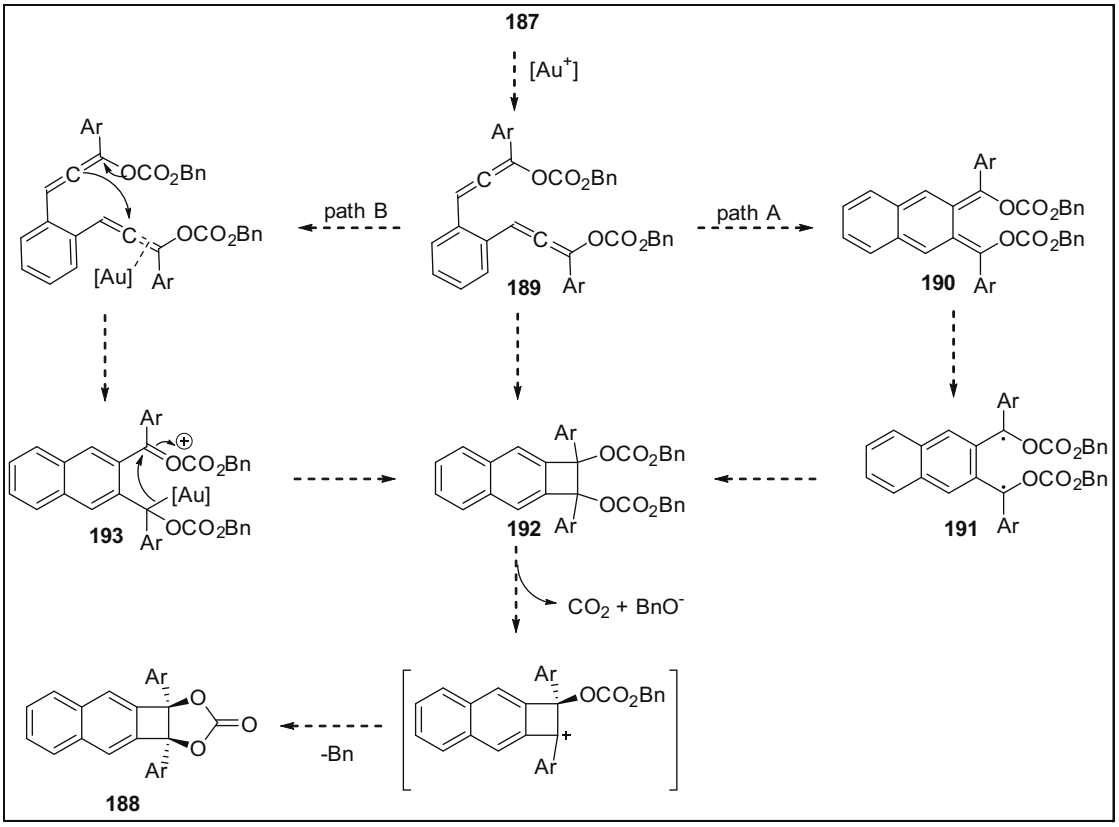


Scheme 53: Synthesis of the bridged tricyclic BCD ring system core.

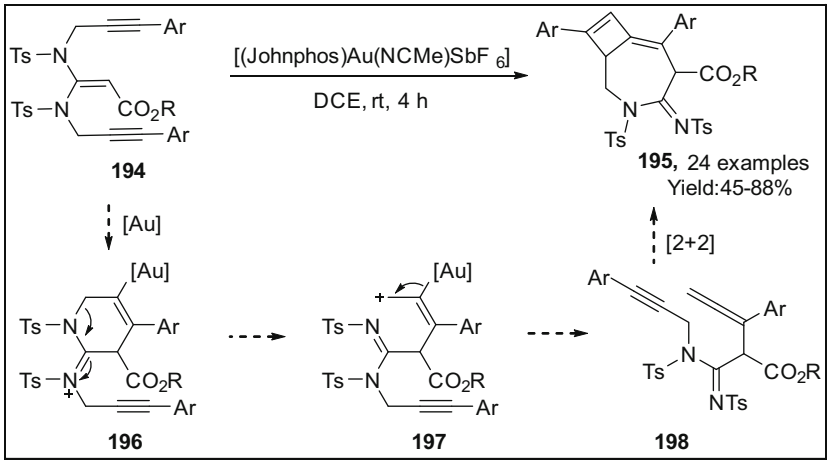
utilizing the intramolecular insertion capacity of α-oxo gold carbenes into N–H and O–H bonds. The carbenes discussed in this study are generated from alkynes via a gold(I)-catalyzed intermolecular oxidation process [174].

A viable approach for the synthesis of oxetan-3-ones [175], **202**, and **204** was devised by utilizing propargylic alcohols **201** [176] that are easily available. The synthesis was conducted under ambient air conditions, employing

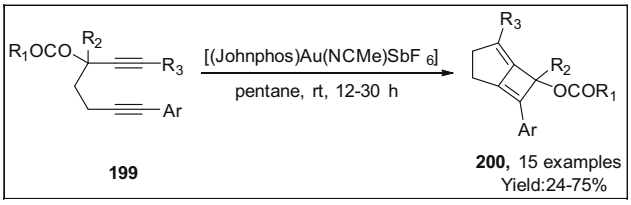




Scheme 54: Gold-catalyzed diyne [2 + 2] cycloaddition for naphtho[*b*]cyclobutene formation.



Scheme 55: [2 + 2] Gold-catalyzed Diyne cycloaddition to cyclobutene-fused azepines.



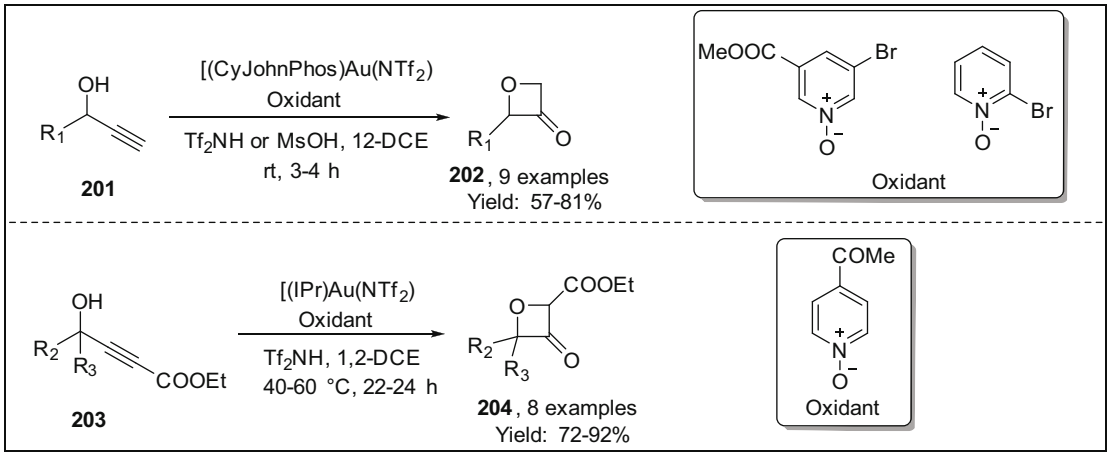
Scheme 56: Synthesis of alkylidencyclobutenes by [2 + 2] Diynes cycloaddition.

pyridine N-oxides as oxidizing agents and catalytic quantities of Au(I) complexes, as illustrated in Scheme 57 [177]. To mitigate potential side reactions arising from the generation of propargylic cations in an acidic environment, it was necessary to include an electron-withdrawing group at the alkyne terminus of tertiary propargylic alcohol substrates **203**.

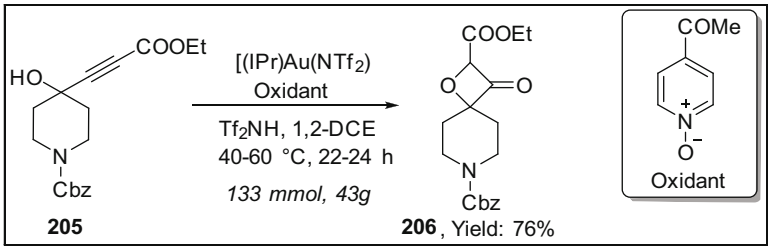
The disclosed technique (Scheme 58) was employed to successfully synthesize a drug discovery library of 419 spirocyclic oxetane-piperidine scaffolds. These scaffolds are considered significant motifs in the field of medicinal chemistry [178–180].

Zhang et al. utilized a similar methodology in order to synthesize **208** from *N-tert*-butylsulfonyl propargylamines [181]. The requirement for acidic additives when working with secondary propargyl amine substrates was eliminated by utilizing a large Buchwald ligand and an electron-deficient, obstructed pyridine N-oxide, hence improving compatibility with functional groups.

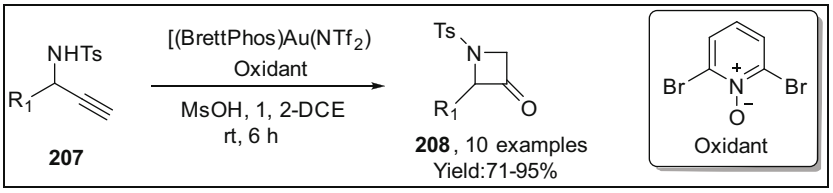
Based on the previous research conducted by Ye et al. [181], a tripartite approach was developed to efficiently synthesize azetidin-3-ones **208** using readily available propargylic alcohols **207** (as shown in Scheme 59) [182]. A convenient and practical method for the synthesis of diverse azetidin-3-ones involves the oxidative cyclization



Scheme 57: Gold(I)-catalyzed formation of oxetan-3-ones via oxidative synthesis.



Scheme 58: Efficient gold(I)-catalyzed production of oxetane–piperidine system at scale.



Scheme 59: Au(I)-catalyzed formation of azetidin-3-ones via oxidative synthesis.

of N-tosyl propargylamines with gold as the catalyst. Several other sulfonyl-protecting groups were found to be suitable for use in this process.

5 Conclusion

Over the past 20 years, Au(I) catalysis has emerged as a highly effective strategy for achieving rapid and efficient synthesis of complex molecules through single-step reactions. The first step in a series of changes that occur when Au(I) π-bonds are activated is the formation of Au(I) carbene intermediates. These intermediate compounds often undergo reactions either within the molecule or between molecules to form carbocycles consisting of three or four carbon atoms. This approach has been extensively utilized to formulate a variety of techniques that effectively enable the precise and streamlined fabrication of diminutive rings. One of the primary obstacles in this domain pertains to the establishment of adaptable procedures that are not dependent on overly complex or specialist beginning materials.

It is imperative to prevent the inclusion of undesirable functional groups in the resultant reaction products. Because these reactions involve a lot of complicated molecules, small changes to the substrate substitution pattern or reaction conditions can often lead to very different results. There are also still problems with making enantioselective versions of some transformations, even though there have been big steps forward in the field of asymmetric Au(I) catalysis in the last 10 years. Utilizing Au(I)-catalyzed intermolecular interactions can result in the synthesis of enantioenriched three- or four-membered rings. However, it is worth noting that these reactions remain infrequent and often exhibit a significant dependence on the specific substrates employed.

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Conflict of interest: Authors state no conflict of interest.

Data availability statement: Data sharing is not applicable to this article as no datasets were generated or analyzed during the current study.

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