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Gold as a catalyst. Part II. Alkynes in the reactions of carbon – carbon bond formation

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This publication continues the series of reviews devoted to the current state of gold catalysis in organic chemistry. The second review addresses Au-catalyzed reactions of alkynes, giving rise to carbon – carbon bonds. Most of the described reactions are addition reactions involving the triple bond of alkynes. The review covers both intramolecular reactions, including cyclization of various substrates (enynes, diynes, enediynes, *etc.*) and enyne isomerization without ring formation, and intermolecular reactions, including alkyne reactions with alkenes, other alkynes, heteroaromatic compounds, *etc.*, in particular, tandem reactions. A special part is devoted to dual gold catalysis involving the intermediate formation of binuclear complexes with σ- and π-coordinated metal atoms. The last part of the review deals with the carbon – carbon bond formation reactions in which the alkyne triple bond is retained.
The bibliography includes 369 references.

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1. Introduction

Currently, an enormous number of publications have been devoted to the use of various gold derivatives in catalysis, and the number of these studies is steadily growing. The following issues have been addressed: application of AuCl, $AuCl_3$ and $NaAuCl_4$ and their complexes and also gold nanoparticles in a variety of reactions including oxidation; reduction; formation of carbon – carbon and carbon – heteroatom bonds; cyclizations and cycloisomerizations resulting in the formation of carbo- and heterocycles; and tandem reactions giving rise to complex polycyclic systems.

It is of interest that in many reactions, gold catalysis proves to be more efficient than catalysis by complexes of other metals. Moreover, some transformations are particularly specific to gold. Although many aspects of application of ligands and mechanisms of gold-catalyzed reactions are still to be comprehended, it is quite obvious that the soft Lewis acidity of gold salts makes them indispensable catalysts for reactions involving unsaturated compounds, especially those containing multiple carbon – carbon bonds.

The chemical and biological activities and the physical properties of an organic compound are largely determined by the presence of particular functional groups in its molecules. The introduction of various functional groups into organic molecules has been considered in the first review of this series in relation to gold-catalyzed nucleophilic addition to alkynes.[1] Since the backbone of an organic molecule is the carbon skeleton, we considered it necessary to write a separate review addressing gold-catalyzed reactions of alkynes giving carbon – carbon bonds. Metal-catalyzed reactions of carbon – carbon bond formation are highly important in modern organic synthesis. The C – C bond formation in the reactions of alkynes is the subject of several

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published reviews (see, for example, Ref. 2). The present review covers both the fundamental studies reported earlier and also papers tht appeared after publication of the previous reviews; in addition, studies that have not been cited previously are analyzed. Since the carbon – carbon bond formation is only a part of our series of reviews devoted to gold-catalyzed reactions, a different concept was used to present the material.

The following abbreviations are used:

Boc — *tert*-butoxycarbonyl;
Cbz — benzyloxycarbonyl;
Cp* — η^5-pentamethylcyclopentadienyl;
m-CPBA — *m*-chloroperbenzoic acid;
Cy — cyclohexyl;
dba — dibenzylideneacetone;
DCE — 1,2-dichloroethane;
DCM — dichloromethane;
DDQ — 2,3-dichloro-5,6-dicyano-1,4-benzoquinone;
DFT — density functional theory;
DMB — 2,4-dimethoxybenzyl;
dppe — 1,2-bis(diphenylphosphino)ethane;
dr — diastereomer ratio;
er — enantiomer ratio;
EWG — electron-withdrawing group;
Fc — ferrocenyl;
Fu — furyl;
Hex — n-hexyl;
IAd — 1,3-di(1-adamantyl)imidazol-2-ylidene;
IMes — 1,3-dimesitylimidazol-2-ylidene;
IPr — 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene;
ITM — tetramethylimidazol-2-ylidene;
JohnPhos — (2-biphenyl)di-*tert*-butylphosphine;
Mes — 2,4,6-trimethylphenyl (mesityl);
MS — molecular sieves;
MW — microwave radiation;
Naph — naphthyl;
NHC — N-heterocyclic carbene;
NMP — *N*-methyl-2-pyrrolidone;
NP — nanoparticles;
Pent^t — *tert*-pentyl;
phen — phenanthroline;
PhthN — phthalimido;
Piv — pivaloyl;
PMB — *p*-methoxybenzyl;
PMP — *p*-methoxyphenyl;
PNB — *p*-nitrobenzoyl;
Py — pyridyl;
rt — room temperature;
SIMes — 1,3-dimesityldihydroimidazol-2-ylidene;
SIPr — 1,3-bis(2,6-diisopropylphenyl)dihydroimidazol-2-ylidene;
Solv — solvent;
TA — benzotriazole;
TBS — *tert*-butyldimethylsilyl;
TES — triethylsilyl;
Tf — trifluoromethanesulfonyl (triflyl);
TFA — trifluoroacetic acid;
Th — thienyl;
THP — tetrahydropyran-2-yl;
TIPS — triisopropylsilyl;
TMS — trimethylsilyl;
Ts — *p*-toluenesulfonyl (tosyl);
TS — transition state;
XPhos — 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl.

2. Reactions of C – C bond formation in which the alkyne triple bond is not retained

2.1. Intramolecular reactions

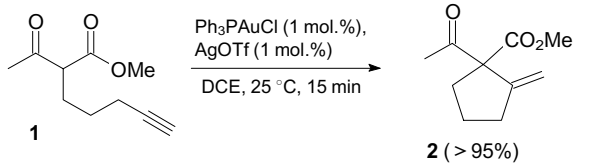
2.1.1. Cyclizations

Cyclization of alkynes is addressed in a review of Gilmore and Alabugin,[3] who give detailed consideration of the mechanisms and stereochemistry of these reactions conducted under various conditions, in particular, with gold catalysts. A volume of *Organic Reactions*[4] published in 2017 is devoted to gold-catalyzed cyclizations of alkynes with alkenes and arenes; this volume includes a large body of theoretical and experimental data obtained by 2014. This Section of the review covers publications up to 2018.

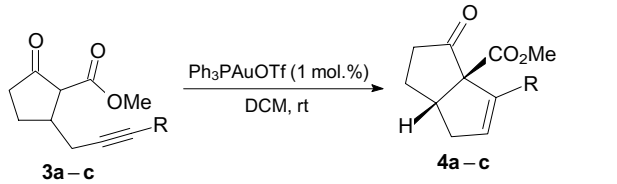
2.1.1.1. Cyclizations involving compounds with a triple bond and an activated methylene group

The addition of enolate to a gold-activated triple bond was described back in 2004.[5] This so-called Conia-ene reaction is, perhaps, the most vivid example of addition of a carbon nucleophile to a triple bond. The corresponding cyclic products were obtained in high yields, for example, as shown for product **2** in Scheme 1. The

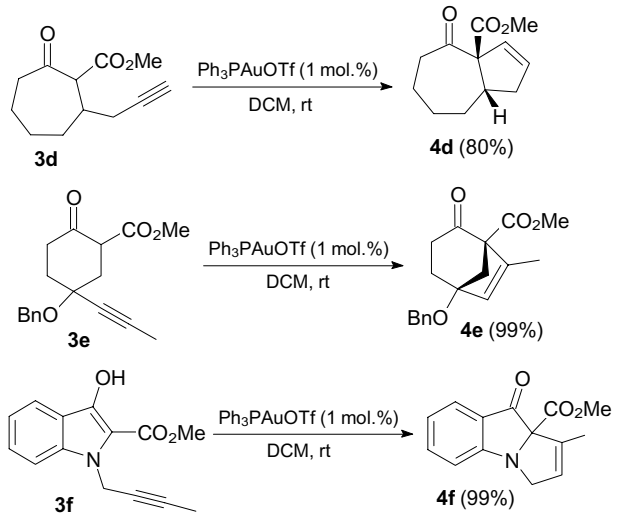
Scheme 1



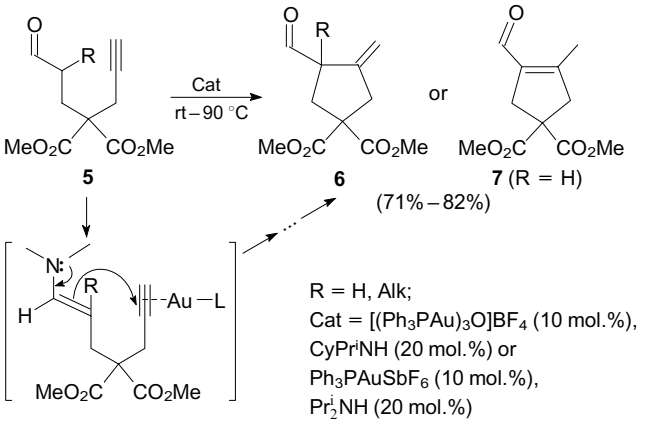
Scheme 2



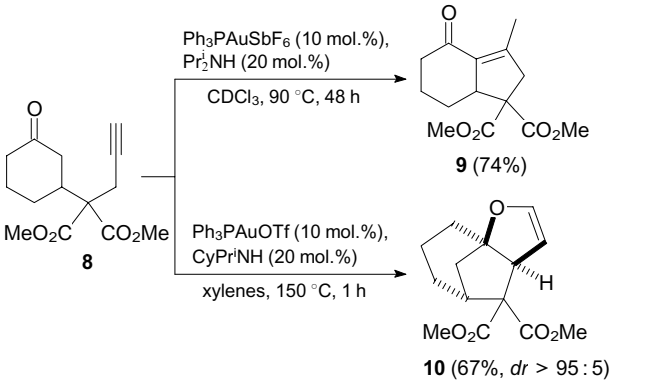
R = H (**a**, 87% yield), Me (**b**, 74%), Ph (**c**, 94%)



Scheme 3



Scheme 4



reaction proceeds *via* the enol form of compound **1**, as demonstrated using deuterium-labelled reactants; thus, this reaction actually involves the substrate double bond [5–7] that has formed during this reaction.

The same method was employed to convert a number of β-keto esters **3** to bi- and tricyclic compounds **4** (Scheme 2).[6]

In 2008, Kirsch and co-workers [8] demonstrated an efficient combination of amine and Au^I cationic complex catalysts for successful intramolecular cyclization of terminal alkynes **5** (Scheme 3).

The reaction proceeds as the 5-*exo*-*dig*-cyclization. In the case of unbranched aldehydes **5** (R = H), the cyclization is followed by double bond migration and, instead of cyclopentanes **6**, cyclopentene **7** is formed. In the case of cyclization of α-substituted aldehydes **5** (R = Alk), no double bond migration takes place. This reaction can also proceed for ketones, for instance, cyclohexanone **8**, to give good yields of the product, in this particular case, bicyclic compound **9**. A slight change in the reaction conditions enables the formal [3 + 2]-cycloaddition to proceed, giving rise to tricyclic product **10** in a moderate yield and with high diastereoselectivity (Scheme 4).

2.1.1.2. Cyclizations involving triple and double bonds. Cycloisomerization of enynes

Enyne cycloisomerization is one of the most popular routes to C – C bond formation catalyzed by electrophilic metal complexes. This transformation is widely applied in synthetic chemistry, because it can serve for the synthesis of complex structures under mild conditions from readily accessible starting compounds. This reaction can follow an intricate mechanism; it can include interactions with external nucleophiles (which often function as solvents) and can be catalyzed by a variety of transition metals, in particular, Pd,[9] Pt,[10] Hg [11] or Ru [12] and protic acids.[13] In 2004, it was shown by several research teams [13–15] that Au^I complexes possess high activity and selectivity as catalysts of enyne cycloisomerization. Gold(III) compounds are also applicable as catalysts for this reaction.[16] The key advantages of using gold compounds for reactions of this type are milder reaction conditions (room temperature) and potential possibility of asymmetric synthesis.

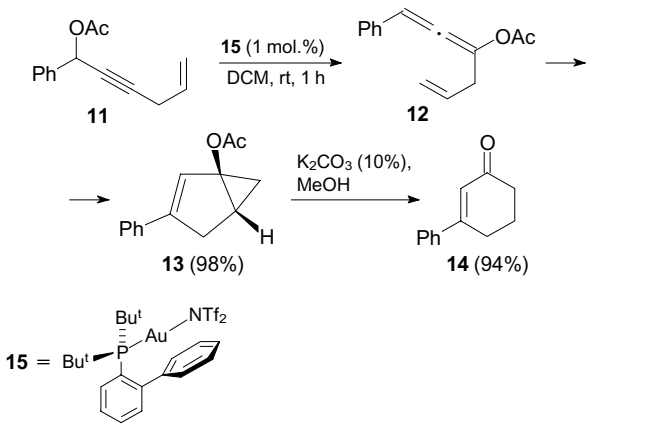
Gold(I) activates alkynes in the presence of other unsaturated functional groups *via* the formation of the (η^2-alkyne) – gold(I) complex.[17] This complex reacts with nucleophiles, in particular, with electron-rich alkenes.[18, 19] In the latter case, gold(I) cyclopropyl carbenoids are formed as intermediates. In the absence of external nucleophiles, 1,*n*-enynes can be converted *via* intramolecular skeletal rearrangement, which markedly differs from the metathesis initiated by the [2 + 2]-cycloaddition of the Grubbs carbene or other metal carbenes.

In general, gold(I) selectively activates alkynes in the presence of alkenes and some functional groups.[18] High alkynophilicity of gold(I) is not related to the thermodynamics of coordination to alkynes (in comparison with other functional groups). It is caused, first of all, by high reactivity of the (η^2-alkyne) – gold(I) complex towards nucleophilic attack.[20]

2.1.1.2.1. Cycloisomerization of 1,4-enynes

Cycloisomerization of 1,4-enyne acetate **11** in the presence of catalyst **15** affords bicyclo[3.1.0]hexenes **13**.[21] The reaction involves the intermediate formation of triene **12** as a result of 1,3-migration of the acetoxy group (Scheme 5); cyclization of intermediate **12** occurs according to the 1,5-enyne cycloisomerization pathway.

Scheme 5

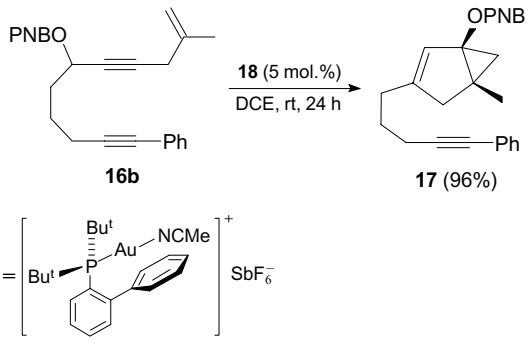


On treatment with a base (10% K_2CO_3 in methanol), bicyclic product **13** is converted to 3-phenylcyclohex-2-enone (**14**). The product yields are high in both steps; substrate **11** can have some substituents (*e.g.*, in the benzene ring or at the double bond; an alkyl group can

be present instead of phenyl), with high yields being maintained.

Chen *et al.*[22] reported a study of cycloisomerization of 1-ene-4,9-diyne and 1-ene-4,10-diyne **16a**,**b** with a 1,4-enynecarboxylate moiety in the molecule. In particular, it was found that 1-ene-4,10-diyne **16b** is converted to bicyclohexene derivative **17** at room temperature in the presence of Au^{I} complex **18** as the catalyst (Scheme 6).

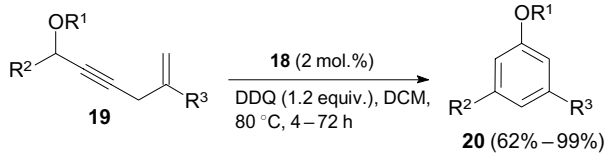
Scheme 6



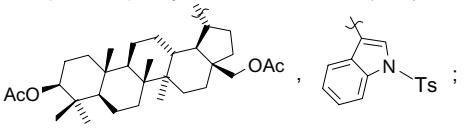
The reaction is accompanied by 1,3-migration of the 4-nitrobenzoate moiety with subsequent cyclization. Conduction of the reaction at 80 °C in the presence of molecular sieves induces the second tandem cyclization to give a tetracyclic derivative (see below, Section 2.1.1.7, Scheme 130).

The cyclization of acyloxy-substituted 1,4-enynes **19** in the presence of 1.2 – 2 equiv. of an oxidant (*e.g.*, DDQ) results in the formation of 3,5-disubstituted acyloxy phenol derivatives **20** in a good yield (Scheme 7).[23]

Scheme 7



R^1 = 4-$O_2NC_6H_4C(O)$, Ac; R^2 = Ph, 4-MeC_6H_4, 4-BrC_6H_4, 4-PhC_6H_4, 2-BrC_6H_4, 2-IC_6H_4, 2-Br-4,5-$(MeO)_2C_6H_2$, 1-Naph, 2-Naph, cyclo-C_3H_5, Et_2CH, $Ph(CH_2)_3$,



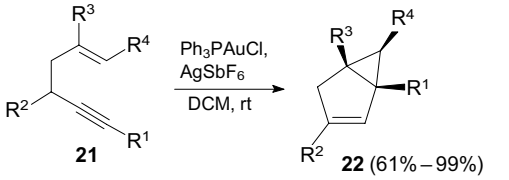
R^3 = Me, $PhOCH_2$, $CMe(CO_2Et)_2CH_2$, $N(Ts)PhCH_2$

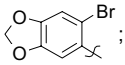
The phenol moiety is an important part of molecules of valuable biologically active compounds, including natural products, pharmaceuticals and polymers.[24 – 27] Development of new efficient methods for the preparation of these compounds is highly important in modern synthetic chemistry. This goal faces quite a number of challenges with no easy solution. In particular, the regioselective preparation of 3,5-disubstituted phenols by the traditional electrophilic aromatic substitution of phenols proves to be inefficient because of the strong *ortho*,*para*-directing effect of the hydroxy group. Although several methods for solving this problem have been proposed in recent years,[28 – 33] including gold-catalyzed annulation of non-aromatic precursors,[34] the preparation of 3,5-disubstituted phenols from available substrates under mild, easily implementable conditions reported by Chen *et al.*[23] is an efficient synthetic method considerably extending the scope of organic synthesis and demonstrating the unique character of gold-catalyzed reactions.

2.1.1.2.2. Cycloisomerization of 1,5-enynes

The cycloisomerization of 1,5-enynes[15, 35, 36] can be catalyzed by both Au^{I} and Au^{III} salts. For example, Toste and co-workers[15] have shown that cycloisomerization of 1,5-enynes **21** under mild conditions affords bicyclo[3.1.0]hexenes **22** (Scheme 8), which are present in the molecules of some natural products.[37 – 40]

Scheme 8



R^1 = H, Ph; R^2 = H, Ph, Bn, 2,3-$(MeO)_2C_6H_3$, 

; R^3 = H, $AcOCH_2$; R^4 = H, Et, Pr^n, $TIPSOCH_2$

Analogous results were obtained by Gagosz[41] for 1,5-enynes **23a** – **d**, although in this case, apart from bicyclic products **24**, skeletal rearrangement products **25** were obtained (Scheme 9).

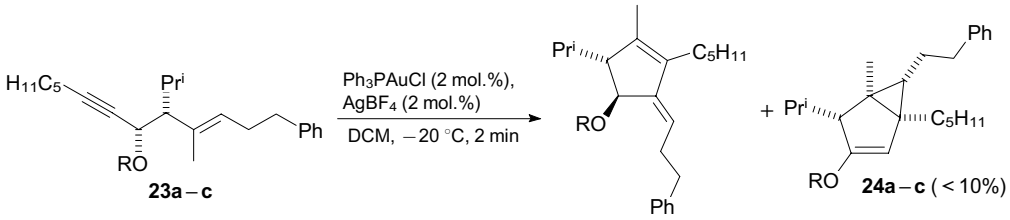
Intramolecular cyclopropanation of 1,5-enynes involves the formation of *endo*-carbene.[42] The mechanism proposed for these reactions[43] is shown in Scheme 10. Gold carbenoid **26** can react with an external nucleophile to give cyclohexene **27**.[15] The loss of stereospecificity observed in some of these reactions attests for intermediate formation of five-membered cyclic carbocation **28**.[41, 44, 45]

Kozmin and co-workers[46, 47] have shown that on treatment with an Au^{I} catalyst, silyloxy-1,5-enynes **29** are converted to cyclohexadienes **30**. When the silyloxy group, which is able to stabilize the cationic intermediate, is present in the substrate, the reaction pathway shown in Scheme 8 changes.[47] In this case, the reaction seems to occur *via* double skeletal rearrangement (two 1,2-shifts of the alkyl group) followed by fragmentation of zwitter-ionic intermediate **A** and formation of six-membered gold carbene complex **B** (Scheme 11). The formation of either non-conjugated or conjugated hexadiene is determined by the nature of the substituent R^5 ($R^5 = H$ or $R^5 \neq H$). Similar transformations were observed for other 1,5-enynes.[41, 46]

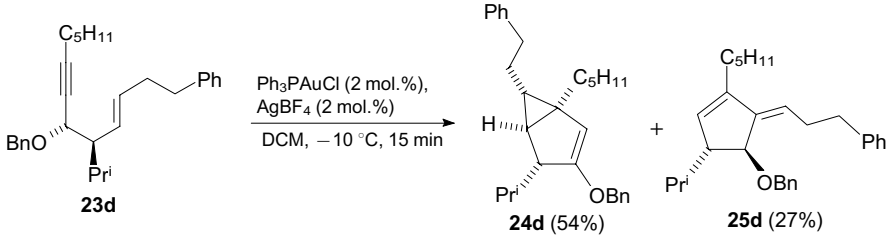
Cyclization reactions of 2-alkenyl-1-alkynylbenzenes resulting in the formation of naphthalenes have been reported.[48, 49] For example, enol ethers **31** or enamines **33** undergo 6-*endo*-*dig*-cyclization to form a fused benzene ring in products **32** or **34** (Scheme 12).[48]

The cyclization of propargyl vinyl ethers **35** in the presence of water or alcohols affords dihydropyrans **36** as mixtures of anomers (in 1 : 1 to 1.3 : 1 ratio) in good

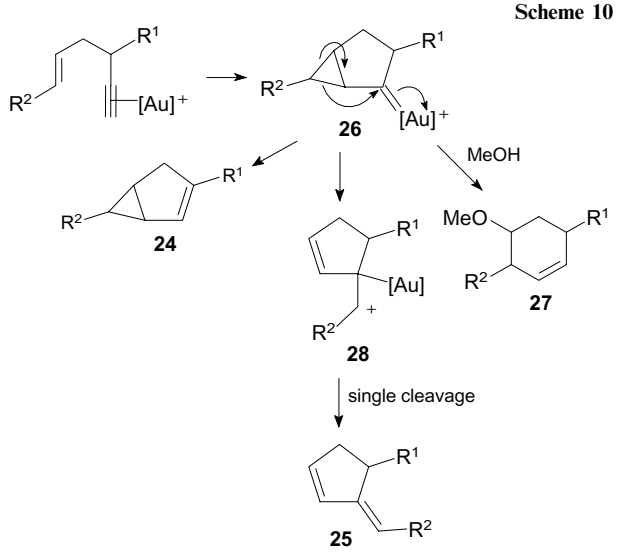
Scheme 9



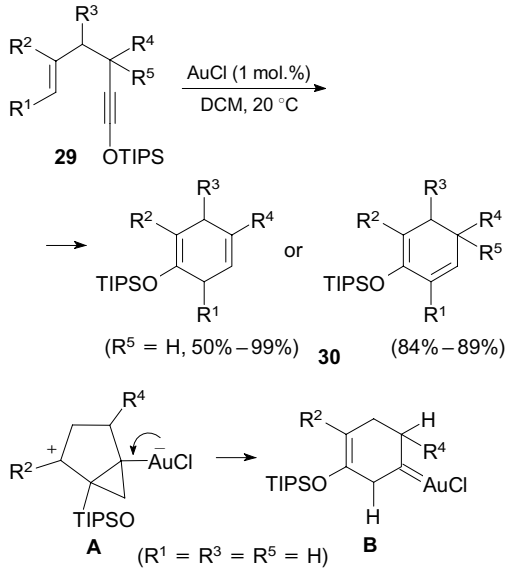
R = H, Bn, Ac



Scheme 10

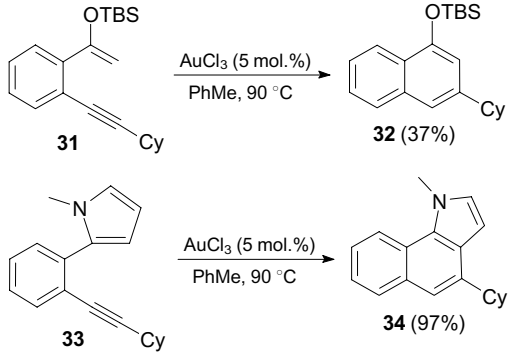


Scheme 11

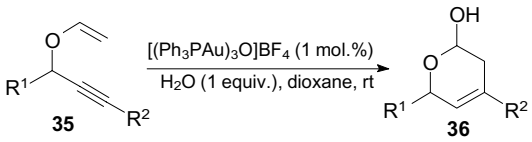


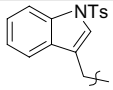
R1 = H, Me; R2 = Me, Ph, CH_2TMS; R3 = H, Me;
R4 = Me, Prn, n-C_5H_{11}, $(CH_2)_3CH{=}CH_2$, Ph; R5 = H, Me

Scheme 12



Scheme 13

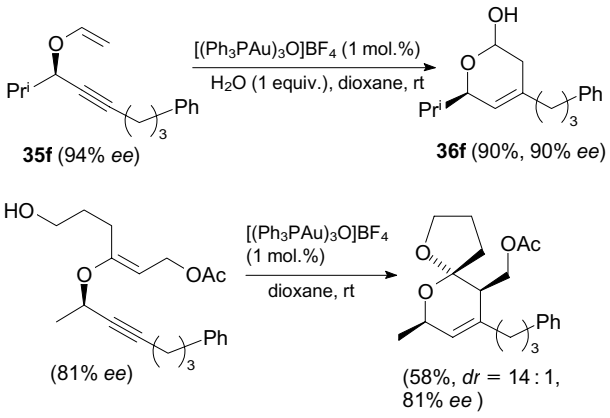


Compounds **35**, **36**	R^1	R^2	Yield of **36** (%)
a	$Ph(CH_2)_2$	$TsO(CH_2)_4$	89
b	$Ph(CH_2)_2$	$NC(CH_2)_4$	88
c	$Ph(CH_2)_2$	cyclo-C_3H_5	92
d	$Ph(CH_2)_2$	Cy	80
e	$Ph(CH_2)_2$	Bu^t	60
f	Pr^i	$Ph(CH_2)_3$	90
g	Bn	Bu^n	95
h	$TBSOCH_2$	Bu^n	77
i	$Me_2C{=}CH(CH_2)_2$	Bu^n	92
j		Bu^n	83

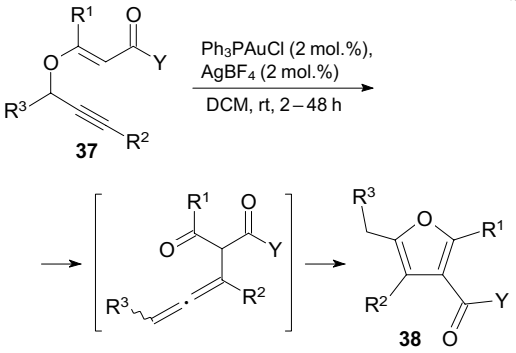
yields (Scheme 13).[50] The cycloisomerization in the presence of an external nucleophile is considered in more detail below (see Section 2.1.1.6).

The reaction follows the 6-*endo*-*dig*-cyclization mechanism and is highly stereoselective (Scheme 14).

Scheme 14

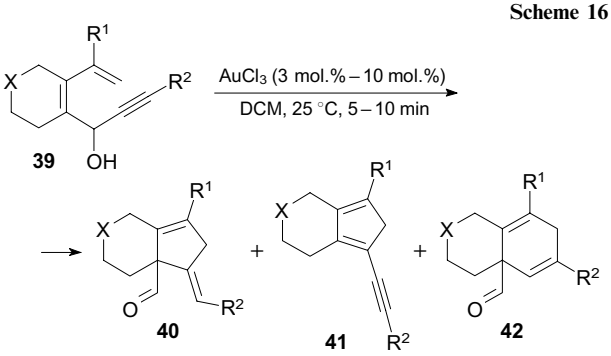


Scheme 15



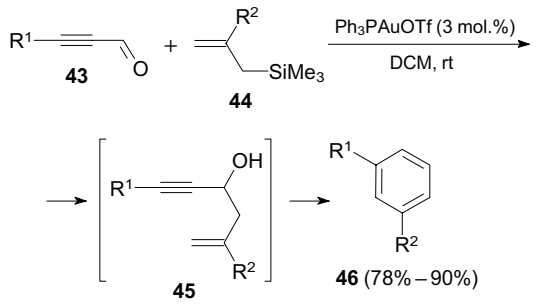
R^1 = H, Me, n-C_5H_{11}, Ph; R^2 = H, Me, Ph, TBS, 2-$MeOC_6H_4$, 3-Th, 2-Py, $CyCH_2$, $TBSOCH_2CH_2$; R^3 = H, Me; Y = Ph, MeO, EtO; for R^3 = H the yield is 72% – 99%; for R^1 = Ph, R^2 = R^3 = Me, Y = EtO the yield is 45%

Scheme 16



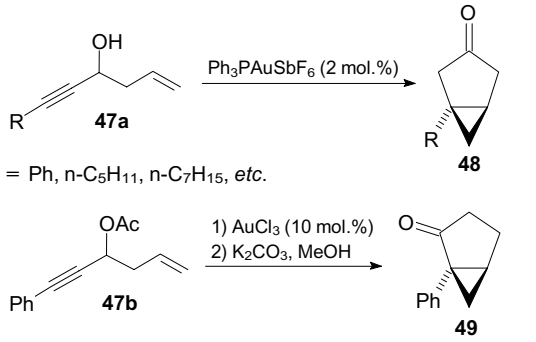
Substituents	Products (yield)
X = CH_2 R^1 = Ph: R^2 = H, Me; R^1 = Et, R^2 = H X = O R^1 = Ph: R^2 = H, Bu^n, Ph; R^1 = Me, R^2 = H	**40** (65% – 98%)
X = CH_2, R^1 = Ph: R^2 = Pr^n, Ph	**40** (68% – 70%) + + **41** (6% – 10%)
X = O, R^2 = TMS: R^1 = Me, Ph	**40** (50% – 70%) + **42** (11%)

Scheme 17



R^1 = Hex, Ph, 4-$MeOC_6H_4$, 3-$MeOC_6H_4$, 4-$O_2NC_6H_4$, 4-$F_3CC_6H_4$; R^2 = Me, Ph

Scheme 18



If an electron-withdrawing group is present at the substrate double bond, like, for example, in compound **37**, the reaction gives furan derivatives **38**, formed *via* the Claisen rearrangement – cyclization sequence (Scheme 15).[51]

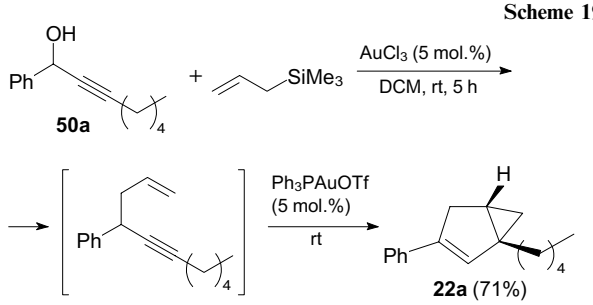
The use of *cis*-4,6-dien-1-yn-3-ols **39** resulted in the preparation of bicyclic compounds **40** – **42** (Scheme 16).[52] Bicyclic aldehyde **40** was the major product in all cases.

1,5-Enynes **45** with the propargyl alcoholic group, which are generated *in situ* from substrates **43** and **44**, can be converted to benzene derivatives **46** *via* the tandem allylation – cyclization sequence (Scheme 17).[53]

The use of hydroxy- and acetoxyenyne derivatives **47a**,**b** in the $AuCl_3$- or $Ph_3PAuSbF_6$-catalyzed reaction affords regioisomeric bicyclic ketones **48** and **49**, respectively (Scheme 18).[14, 40, 54, 55]

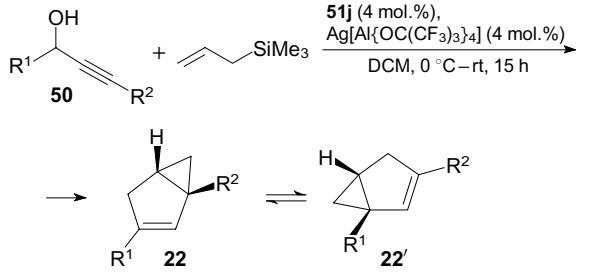
Dual catalytic systems are known, comprising a Lewis or Brønsted acid and an Au^I compound. The acid component catalyzes the nucleophilic substitution of propargyl alcohols on treatment with allylsilane, while an Au^I compound catalyzes the subsequent cycloisomerization of 1,5-enyne. In particular, a combination of Re and Au compounds catalyzed the nucleophilic substitution – cycloisomerization reactions of 1,3-diphenylprop-2-yn-1-ol with allyltrimethylsilane.[15] The combination of nucleophilic substitution catalyzed by *p*-toluenesulfonic acid and subsequent cycloisomerization catalyzed by $PPh_3AuCl – AgSbF_6$ has also been studied.[56] The reaction of 1-phenyloct-2-yn-1-ol (**50a**) and allyltrimethylsilane aimed at the preparation of bicyclo[3.1.0]hexene **22a** *via* intermediate 1,5-enyne was carried out using the $AuCl_3 – Ph_3PAuOTf$ system as the catalyst (Scheme 19).[57]

Scheme 19



It was found[58] that complex **51j** (see below Scheme 21) can catalyze the tandem nucleophilic substitution – cycloisomerization reaction of 1,5-enyne (Scheme 20). In this process, substrates **50** react with allyltrimethylsilane to give a mixture of isomers **22** and **22′** owing to thermal 1,3 carbon shift.

Scheme 20



R^1	R^2	Yield of **22** + **22′** (%)	**22** : **22′**
Ph	Bu^n	76	94 : 6
Ph	TMS	75[a]	–
Ph	Ph	91	–
2-Naph	Ph	68	56 : 44
Mes	Ph	72	35 : 65
4-ClC_6H_4	Ph	90	59 : 41

[a] A mixture of silylated and desilylated (R^2 = H) products.

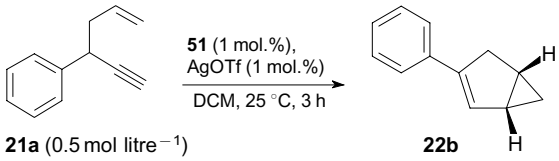
It was found that Au^{III} complexes **51a** – **r** possess high catalytic activity towards cycloisomerization of 4-phenylhex-1-en-5-yne (**21a**) ($R^1 = R^3 = R^4 = H$; R^2 = Ph) to give bicyclic product **22b**.[59] The presence of more electronegative imidates as a part of catalyst **51** leads to increasing conversion (Scheme 21).

1,5-Enynes **52** containing a cyclopropene moiety can be converted, at room temperature, to benzene derivatives **53** and **54** in high yields (Scheme 22).[60]

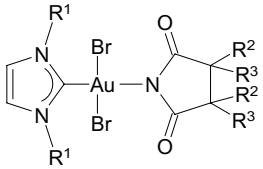
The cycloisomerization of 1,5-enynes containing a heteroatom makes it possible to prepare a wide range of heterocyclic compounds, for example, pyridinones **55** (Scheme 23).[61]

This method was employed to synthesize a number of polysubstituted acridines **57** from 2-alkynyl-3-(silyloxyalkenyl)quinoline derivatives **56** by means of benzannulation.[62] The reaction was catalyzed either by the silver-activated gold salt Ph_3 $PAuSbF_6$ or by a silver salt ($AgSbF_6$, $AgPF_6$, AgOTf, $AgNO_3$ or $AgCO_2CF_3$) (Scheme 24).

Scheme 21

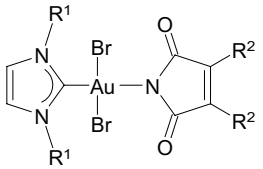


21a (0.5 mol litre^{-1}) **22b**



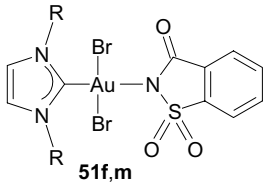
51a – **c**,**h** – **j**,**o**

R^1 = Bu^t: $R^2 = R^3$ = H (**a**), F (**c**);
R^2 = H, R^3 = Br (**b**); R^1 = $Pent^t$:
$R^2 = R^3$ = H (**h**), F(**j**); R^2 = H,
R^3 = Br (**i**); R^1 = Mes,
$R^2 = R^3$ = H (**o**);



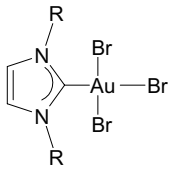
51d,**e**,**k**,**l**,**p**,**q**

R^1 = Bu^t: R^2 = H (**d**),
$R^2 – R^2$ is benzo (**e**); R^1 = $Pent^t$:
R^2 = H (**k**), $R^2 – R^2$ is benzo (**l**);
R^1 = Mes: R^2 = H (**p**),
$R^2 – R^2$ is benzo (**q**);



51f,**m**

R = Bu^t (**f**), $Pent^t$ (**m**);

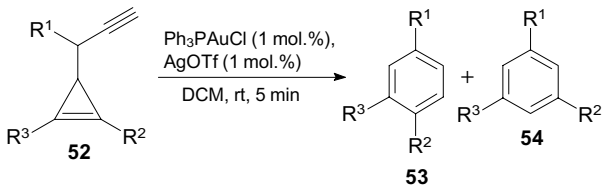


51g,**n**,**r**

R = Bu^t (**g**), $Pent^t$ (**n**), Mes (**r**)

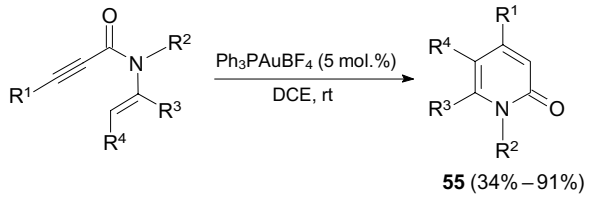
Catalyst	Conversion (%)	Catalyst	Conversion (%)
51a	32	**51j**	89
51b	87	**51k**	99
51c	81	**51l**	18
51d	94	**51m**	95
51e	53	**51n**	32
51f	83	**51o**	51
51g	34	**51p**	18
51h	35	**51q**	51
51i	95	**51r**	3

Scheme 22



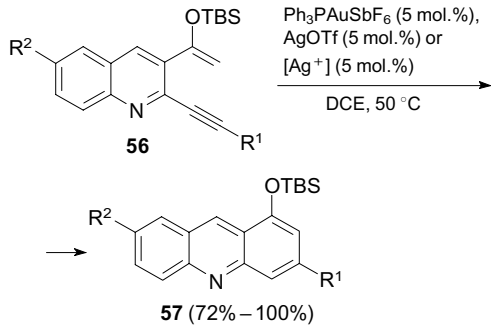
R^1	R^2	R^3	Yield of **53** + **54** (%)	**53** : **54**
OH	Ph	Ph	99	1 : 1
H	Ph	Ph	97	1 : 0
OH	Bu^n	Bu^n	87	0 : 1
OH	Bu^n	TMS	84	0 : 1

Scheme 23



R^1 = Me, Ph, 4-$MeOC_6H_4$, 4-$F_3CC_6H_4$, TMS; R^2 = Bn, Bu^tCH_2; R^3 = H, Me; R^4 = H; $R^3 - R^4$ = $(CH_2)_3$, $(CH_2)_4$

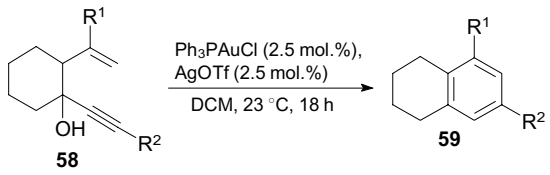
Scheme 24



R^1 = CH_2OMe, Ph, Fc, Bu^n, Bu^t, TMS, cyclo-C_3H_5, CH_2OTHP, $CH_2N(Me)Bn$, 4-Py, $C_6H_4CO_2Me$-2; R_2 = H, OMe

Gold-catalyzed benzannulation of 4-hydroxy-1,5-enynes **58** carried out under mild conditions gives rise to substituted tetrahydronaphthalenes **59** in high yields (Scheme 25).[63, 64] This reaction can also be performed for substituted cycloheptanes and cyclopentanes in which one methylene group can be replaced by a heteroatom (O or NTs).

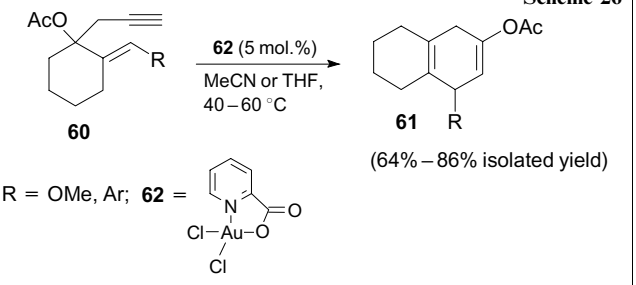
Scheme 25



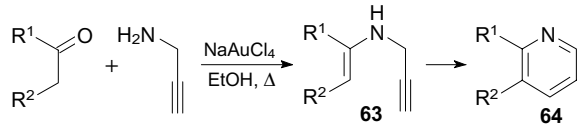
R^1 = H, Me, Ph; R^2 = H, Me, Ph, 4-$O_2NC_6H_4$, 4-$Ac(H)NC_6H_4$, 4-methylpyridin-2-yl; for R^1 = R^2 = H the yield is 10%, in other cases 66% – 86%

Wang and Zhang[65] converted homopropargyl esters **60** to products **61** with the 1-acetoxycyclohexa-1,4-diene skeleton. Gold(III) dichloro(pyridine-2-carboxylate) complex **62**, in some cases, with addition of $KAuCl_4$, was used as the reaction catalyst (Scheme 26). The catalyst was prepared by mixing gold(III) chloride with 2-picolinic acid. The reaction is accompanied by 1,3-migration of the acetyl group. The reaction conditions depend on the substrate nature; for example, in the case of R = Ph, the reaction takes place in THF at 40 °C within 1 h, while at R = 4-$F_3CC_6H_4$, the reaction proceeds in acetonitrile at 60 °C in the presence of 2 equiv. of CaO and a catalytic amount of $KAuCl_4$.

Scheme 26



Scheme 27



Arcadi's research team[66] employed $NaAuCl_4$-catalyzed cyclization of 1,5-enynes **63** to obtain substituted pyridines **64**. Enamines **63** were formed *in situ* from propargylamine and the corresponding carbonyl compound (Scheme 27, Table 1).

The cycloisomerization of 3-aza-1,5-enynes **65** with a carbonyl-containing group at the N atom catalyzed by Au^I complex **18** may give rise to highly substituted 1,2-dihydropyridine derivatives **66** (Scheme 28).[67] 6-*endo-dig*-Cyclization occurs with a high yield, with nucleophilic attack by the double bond on the gold-activated alkynyl moiety being the key step of the reaction.

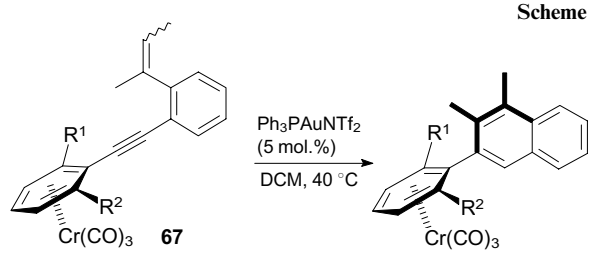
Scheme 28



R^2 = H: R^1 = Cy, Ph, 2-Naph, 2-Fu, 4-$MeOC_6H_4$, 4-FC_6H_4, 4-BrC_6H_4, 4-PhC_6H_4; $R^1 - R^2$ = $(CH_2)_4$; R^3 = H, Me, Me_3Si, Ph, 4-$MeOC_6H_4$, 3-MeC_6H_4, 2-NCC_6H_4; R^4 = H, Me; R^5 = Me, Ph, BnO

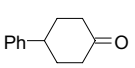
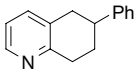
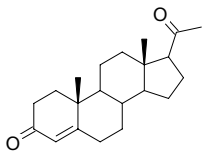
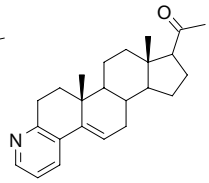
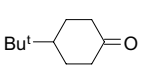
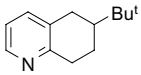
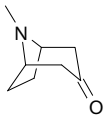
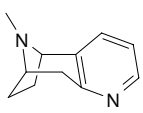
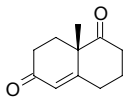
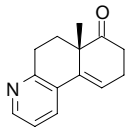
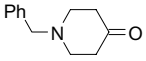
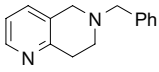
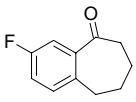
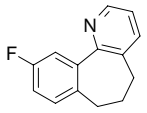
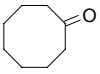
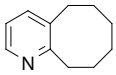
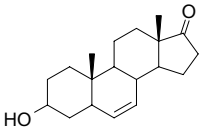
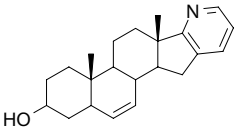
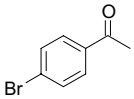
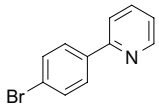
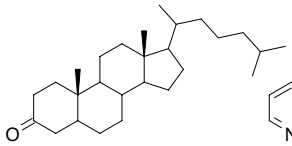
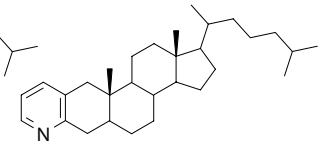
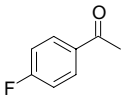
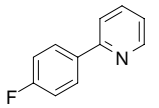
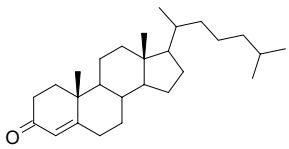
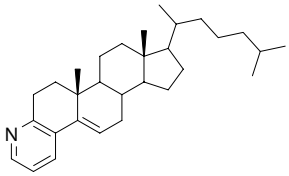
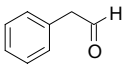
The cycloisomerization of arene chromium complexes **67** catalyzed by an Au^I complex affords biaryls **68**, which possess axial chirality (Scheme 29).[68, 69]

Scheme 29

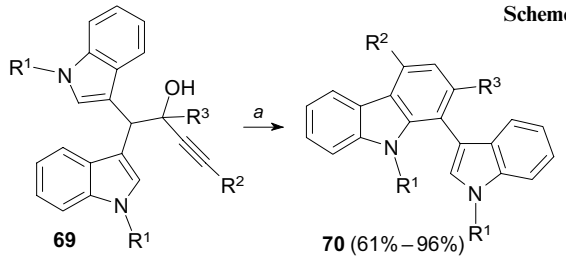


R^1 = H, OMe; R^2 = H, Me, CH_2OH, CH_2OMe

Table 1. Initial ketones, reaction conditions and yields of products **64** (see Scheme 27).[66]

Carbonyl compound	Pyridine **64**	*T* /°C	Time /h	Yield of **64** (%)	Carbonyl compound	Pyridine **64**	*T* /°C	Time /h	Yield of **64** (%)
		78	5	74			78	24	64
		78	5	69					
		100	7	66			78	24	68
		78	7	57					
		78	7	77			100	6	65
		78	12	67					
		100	24	56			100	12	68
		100	24	56			100	12	66
							100	12	78
		78	24	60			78	12	96

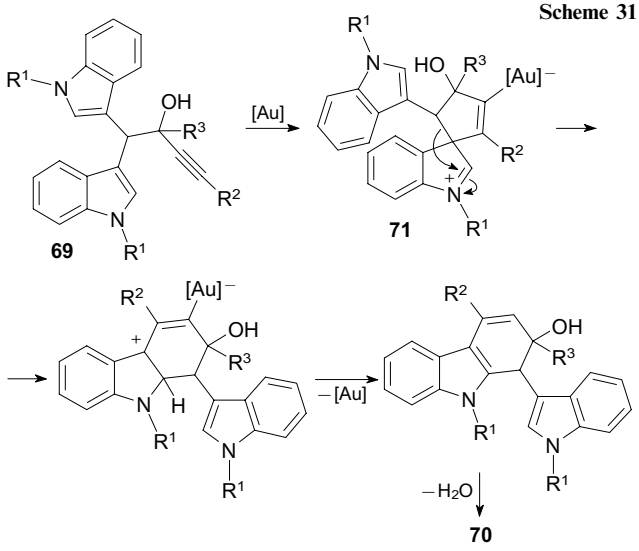
Scheme 30



(*a*) $NaAuCl_4 \cdot 2H_2O$ (5 mol.%), DCM, rt, 2 – 3 h;
R^1 = H, Me; R^2 = H, Bu^n, cyclo-C_3H_5, cyclohexen-1-yl, 3-Th, Ph, $Ph(CH_2)_2$, 4-$MeOC_6H_4$, 4-MeC_6H_4, 3-$MeOC_6H_4$;
R^3 = H, Me, Bu^t, Ph, 4-$MeOC_6H_4$, 2-$F_3CC_6H_4$;
for $R^1 = R^2 = R^3$ = H the yield is 40%

Gold(III)-catalyzed cycloisomerization of α-bis(indol-3-yl)methylalkynols **69** allows selective synthesis of 1-(indol-3-yl)carbazoles **70** (Scheme 30).[70]

Scheme 31



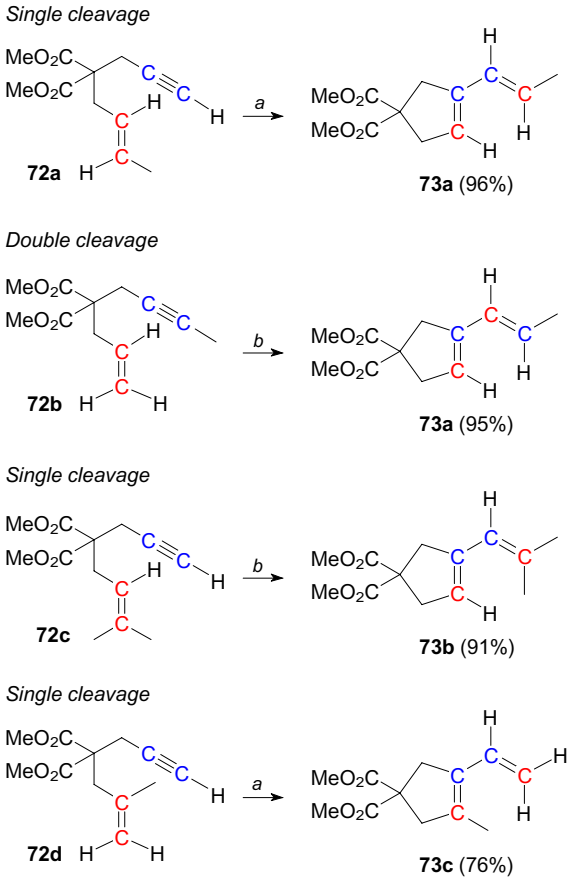
The reaction proceeds *via* selective 1,2-migration of the alkyl group in spiro intermediate **71** and proves to be efficient also for tertiary alcohols and for internal alkynes (Scheme 31). The mechanism proposed by the authors[70] was confirmed by quantum chemical calculations (M06/def2-tzvpp(PCM, CH_2Cl_2)//B3LYP/6-31G*, LANL2DZ(PCM, CH_2Cl_2).

2.1.1.2.3. Cycloisomerization of 1,6-enynes

By analogy with platinum(II)-catalyzed cyclization,[71 – 74] gold(I) activation of alkynes results in the formation of the (η^2-alkyne)–metal complex (**A**, Scheme 32). The further transformation pathway is determined by the length of the hydrocarbon chain and the nature of substituents;[43] the substituents in alkene have a considerable effect on the regioselectivity of the nucleophilic attack.[18] In the case of 1,6-enynes, the gold-activated alkyne moiety of complex **A** reacts with the alkene group as an electrophile to give intermediate gold(I) cyclopropylcarbene complexes **B** or **C** *via* *anti*-5-*exo*-*dig*- or 6-*endo*-*dig*-cyclization, respectively (see Scheme 32).[13, 75 – 78]

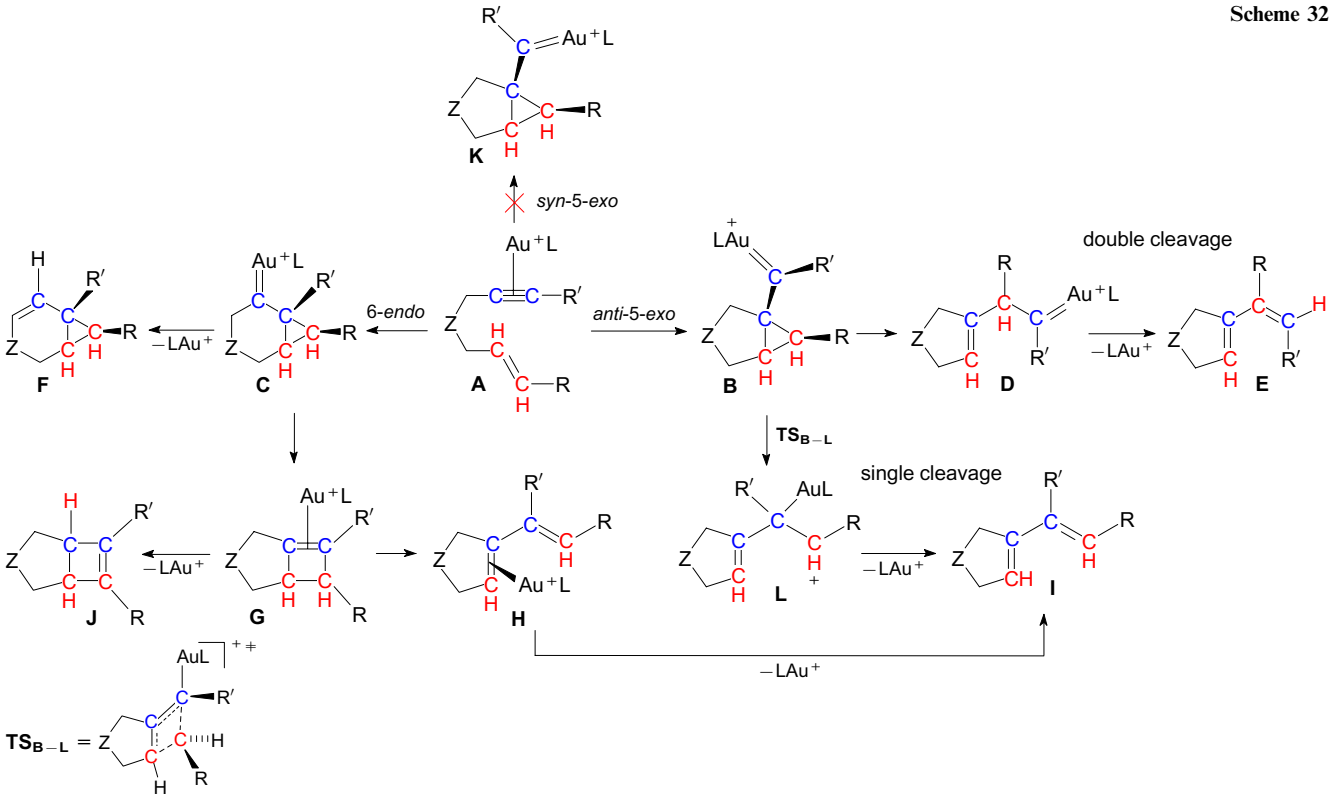
Intermediate **B** can be converted to carbenoid **D**, which eliminates the α-proton to give 1,3-diene **E** resulting from the cleavage of two C–C bonds (double cleavage). In this process, both alkyne and alkene are cleaved *via* intramolecular transformation (double cleavage). Although both configurations have been observed in the products, (*Z*)-**E** products (R = H) are formed most often.[79, 80] However, in intermediate **B**, only one bond can be cleaved in the alkene moiety (single cleavage) to give rearrangement product **I** formed *via* transition state $\mathbf{TS_{B-L}}$ and intermediate **L** (see Scheme 32). According to density functional theory (DTF) calculations, *syn*-5-*exo*-

Scheme 33

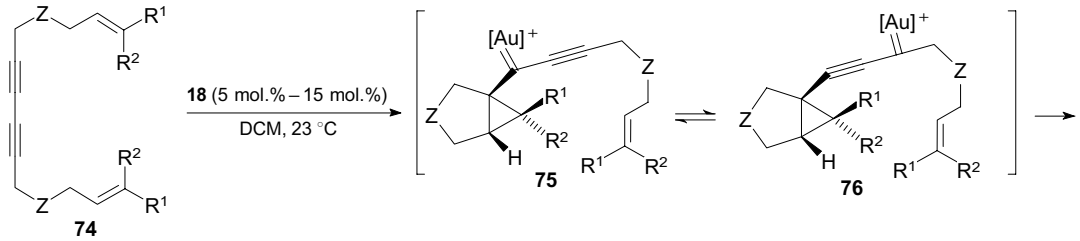


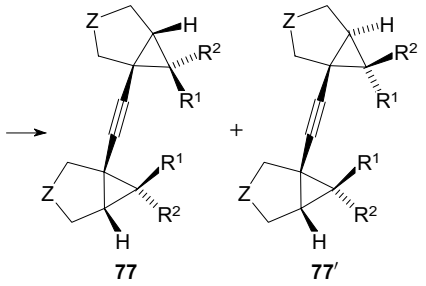
(*a*) Ph_3PAuCl (2 mol.%), $AgBF_4$ (2 mol.%), DCM, rt;
(*b*) Ph_3PAuCl (2 mol.%), $AgSbF_6$ (2 mol.%), DCM, rt

Scheme 32



Scheme 34





R^1	R^2	Yield of **77** + **77′** (%)	**77** : **77′**
H	H	91	1 : 1
Me	H	87	3 : 1
Me	Me	90	1.5 : 1

Z = $C(CO_2Me)_2$

dig-cyclization *via* intermediate **K** does not compete with the other two pathways.[75, 76]

1,6-Enyne **72a**, which is a terminal alkyne and disubstituted alkene, reacts in the presence of the cationic catalyst, which is formed *in situ* from Ph_3PAuCl and $AgBF_4$, to give exclusively diene **73a** upon a single cleavage process.[75] An identical product **73a** was obtained from 1,6-enyne **72b** with a methyl substituent in the alkyne moiety *via* highly selective double-cleavage rearrangement.[81] The transformations of 1,6-enynes **72c**,**d** to products **73b**,**c** involve a single bond cleavage (Scheme 33).[81, 82]

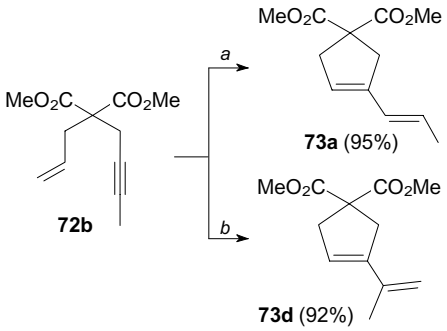
Intermediate **C** formed *via* 6-*endo*-*dig*-cyclization (see Scheme 32) can yield bicyclo[4.1.0]hept-2-ene derivative **F** upon α-proton elimination.[81, 83–85] Alternatively, isomerization of this intermediate with cyclopropane ring expansion gives (η^2-cyclobutene) – gold(I) complex **G**. The opening of this complex in a reaction with only alkene bond cleavage affords complex **H**, the precursor of 1,3-diene **I**. Intermediate **G** can also isomerize giving rise to bicyclo[3.2.0]hept-2-ene **J**.[81, 83] Similarly, 1,5- (Refs 46, 47) and 1,7-enynes undergo rearrangement under the action of an Au^I-based catalyst by a similar mechanism.[86]

More evidence for the participation of gold carbenoids in these ractions was derived from studying the cyclization of dimeric substrates **74**, resulting in the formation of disubstituted alkynes **77** and **77′** (Scheme 34).[87]

In this reaction, gold cyclopropyl carbenoid **75** formed initially isomerizes *via* [1,3]-metallotropic shift to give intermediate **76**; this is followed by intramolecular interaction of gold carbenoid with the double bond. Other examples of [1,3]-metallotropic shifts in the chemistry of gold have also been reported.[88, 89]

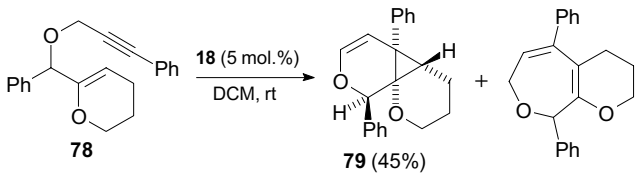
The catalyst nature has a considerable effect on the cycloisomerization pathway. Indeed, cycloisomerization of 1,6-enyne **72b** with a homogeneous Au^I catalyst leads to selective formation of product **73a** upon a double cleavage process (Scheme 35).[75]

Scheme 35



(*a*) Ph_3PAuCl (2 mol.%), $AgSbF_6$ (2 mol.%), DCM, 23 °C, 5 min (double cleavage); (*b*) Au/TiO_2 (1.2 mol.%), DCE, 70°C, 4 days (single cleavage)

Scheme 36



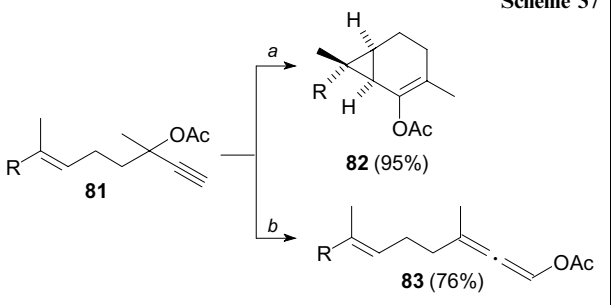
The use of TiO_2-supported Au nanoparticles leads to selective formation of cyclopentene **73d** upon a single bond cleavage.[90]

An example of *6-endo*-cyclization of 1,6-enynes has been reported:[43] enyne **78** is converted to a mixture of tri- and bicyclic products **79** and **80** (Scheme 36).

The cyclopropanation of 1,6-enynes containing a styrene moiety has been reported.[91, 92]

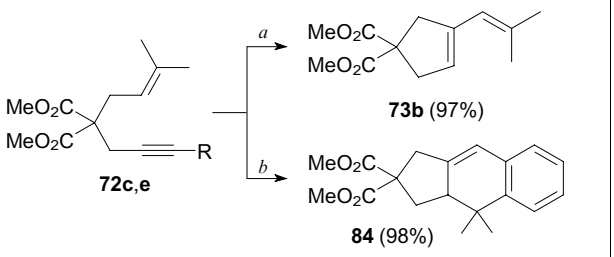
It is of interest that in the case of substrate **81**, $AuCl_3$ catalysis results in the formation of bicyclic structure **82**, whereas in the presence of $AgBF_4$, the reaction gives allene **83** (Scheme 37).[40]

Scheme 37



(*a*) $AuCl_3$ (5 mol.%), DCE, rt; (*b*) $AgBF_4$, DME;
R = $Me_2C{=}CHCH_2$

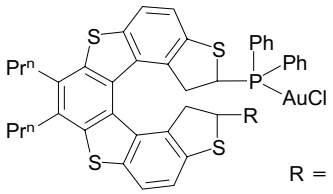
Scheme 38



(*a*) $Ph_3PAuNTf_2$ (0.01 mol.%), 30 min (for R = H);
(*b*) $Ph_3PAuNTf_2$ (2 mol.%), 1 h (for R = Ph); **72**: R = H (**c**), Ph (**e**)

The pathway of cycloisomerization of 1,6-enynes is considerably affected by the nature of substituents[44] at the triple bond (first of all, whether the bond is terminal or internal). Depending on the nature of the substituent R in 1,6-enynes **72c**,**e**, structurally different products **73b** and **84** can be obtained (Scheme 38).

Structures 85



R = H (**a**), PPh_2AuCl (**b**)

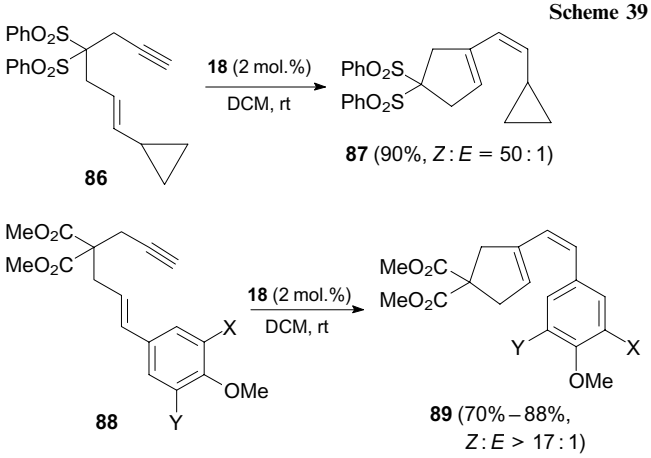
85a,**b**

The Au^I-catalyzed single-cleavage rearrangement is usually a stereospecific reaction in which the alkene configuration is retained.[19] This reaction was conducted in the presence of mono- and binuclear complexes **85a**,**b**,[93] which were obtained from the corresponding phosphine ligands.[94]

However, in the case of (*E*)-1,6-enynes **86** and **88** with strong electron-donating substituents at the alkene terminal atom, the reaction followed an abnormal pathway, resulting in the selective formation of *Z*-configured dienes **87** and **89**, respectively (Scheme 39).[95–97]

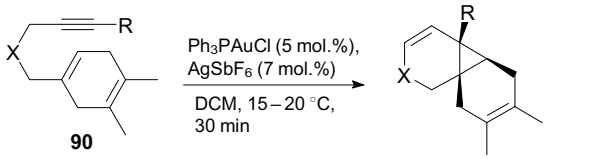
It is noteworthy that, unlike Pd^{II} (Ref. 98) or Pt^{II} (Refs 9, 99), Au^I does not activate the Alder-ene cycloisomerization. This cycloisomerization would require simultaneous coordination of the gold atom to alkyne and alkene, which is impossible for a metal with a linear dicoordination geometry. The Au^I to Au^{III} oxidation,

Scheme 39



X = H, OMe; Y = H, OMe

Scheme 40

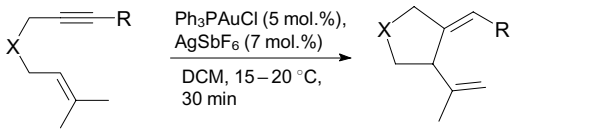


X = TsN, $(MeO_2C)_2C$;
R = Me, Et, cyclo-C_3H_5, Ph,
4-MeC_6H_4, PMP, 2-BrC_6H_4,
3,5-$Me_2C_6H_3$, 2-Naph

which is an obligatory step in the Alder-ene cycloisomerization, also seems unlikely.[100]

Korean researchers[101] reported cycloisomerization of 1,6-enynes **90** (Scheme 40), giving rise to polycyclic derivatives **91** as a result of attack on the gold-activated triple bond by the terminal carbon atom of the double bond. A mixture of Ph_3PAuCl (5 mol.%) and $AgSbF_6$ (7 mol.%) was used as the catalyst.

Scheme 41

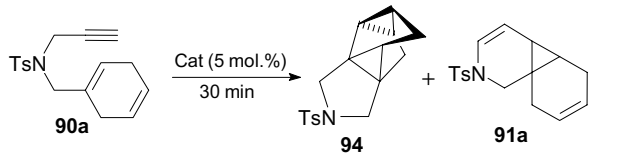


X = NTs, O; R = Me, cyclo-C_3H_5, Ph, Ar

If the 1,6-enyne double bond is disubstituted at the terminal side, as, for example, in substrate **92**, 5-*exo*-*dig*-cyclization takes place to give five-membered ring **93** upon the attack by the monosubstuted double bond carbon (Scheme 41).[102]

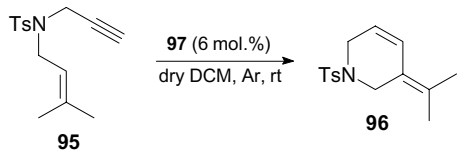
The cycloisomerization of dienyne **90a**, containing a terminal triple bond and a double bond monosubstituted at the terminal side, furnishes tetracyclo[3.3.0.$0^{2,8}$.$0^{4,6}$]octane **94** as the major reaction product.[103] In this case, gold carbene complexes prove to be more efficient catalysts (Scheme 42).

Scheme 42



Catalyst, conditions	Yield of **94** (%)	Yield of **91a** (%)
(IPr)AuSbF$_6$, DCM, rt	70	30
(IMes)AuSbF$_6$, DCM, rt	66	34
Ph$_3$PAuSbF$_6$, DCM, rt	37	7
PtCl$_2$, PhMe, 80 °C	45	55
GaCl$_3$, PhMe, 60 °C	0	0

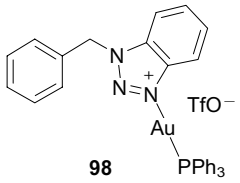
Scheme 43



Cycle	Time /min	Yield of **96** (%)
1	30	93
2	60	93
3	90	90
4	180	81
5	420	75
6	1440	70

The cyclization of 1,6-enyne **95** to tetrahydropyridine **96** was catalyzed by Au^{I} complex **97** immobilized on polystyrene (PS) (Scheme 43),[104] which is an analogue of catalyst **98**. The preparation of the immobilized catalyst is depicted in Scheme 44.

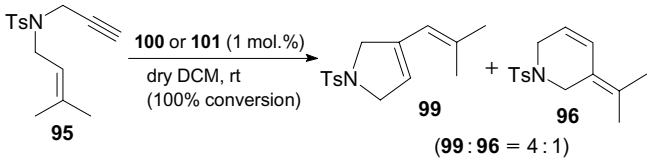
Structure 98



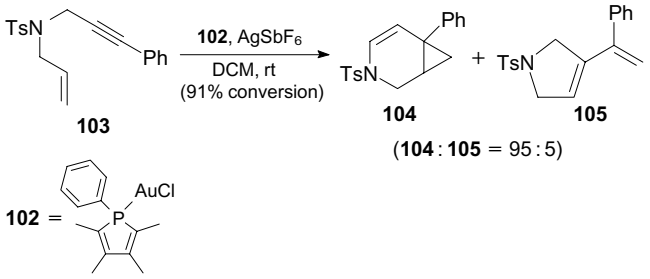
As distinct from the 5-*exo*-*dig*-cyclization described above (see Scheme 41), this reaction proceeds as a 6-*endo*-*dig*-cyclization, giving product **96** in a high yield. Catalyst **97** can be used repeatedly (see Scheme 43).

Catalyst **97** demonstrated also high activity towards the conversion of enynyl acetates to cyclopentanones (tandem 3,3-rearrangement and Nazarov reaction) and towards the rearrangement of alkynylfuran to phenol (Hashmi phenol synthesis).[104]

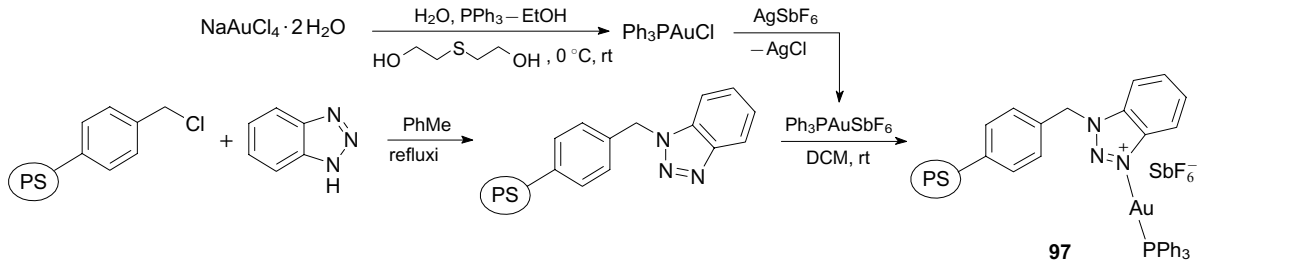
Scheme 45



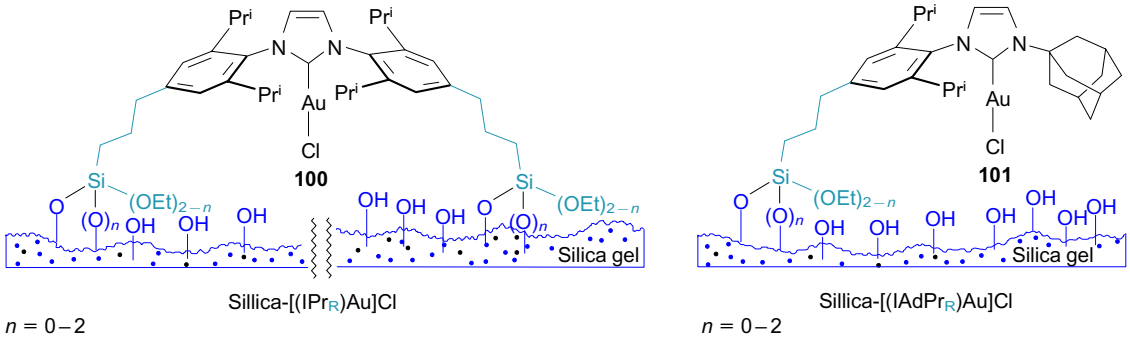
Scheme 46



Scheme 44



Structures 100, 101



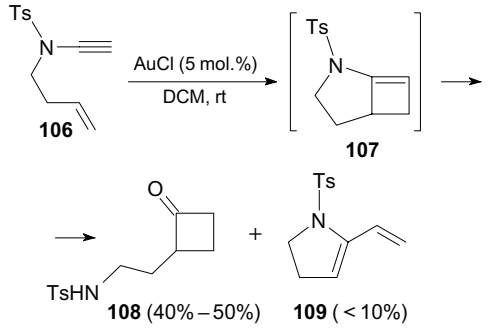
Immobilized NHC-Au-complexes **100** and **101** were used for the cyclization of 1,6-enyne **95**.[105] In this case, diene **99** was formed as the major product (Scheme 45).

In the presence of an Au^{I} complex with 1-phenyl-2,3,4,5-tetramethylphosphole (TMP) **102** as the catalyst, the reaction of enyne **103** gives bicyclic compound **104** as the major product (Scheme 46).[106]

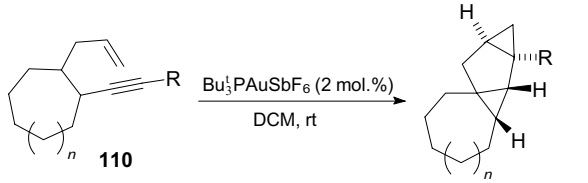
The Hashmi phenol synthesis[107] is also a reaction of new carbon – carbon bond formation involving an alkyne; this reaction occurs as cycloisomerization of 1,6-enyne. However, since an oxygen atom participates in the cycloisomerization and, furthermore, its participation determines the product structure, this aspect is considered below in a separate part of the review.

The gold-catalyzed reaction of 1,6-enyne amide **106** affords mainly cyclobutanone **108**, apparently, *via* unstable bicyclic enamine **107**,[108] which is hydrolyzed in air (Scheme 47).

Scheme 47



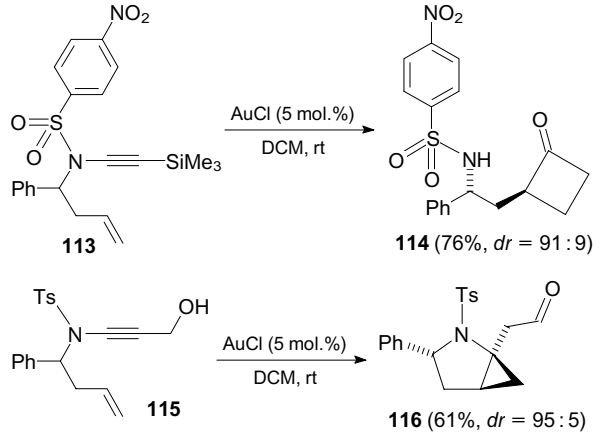
Scheme 48



The cycloisomerization of 1,6-enyne **110** in the presence of $Bu^t_3PAuSbF_6$ (2 mol.%) affords bis(cyclopropane)carbocycle **111** *via* a C,H-insertion reaction (Scheme 48).[109]

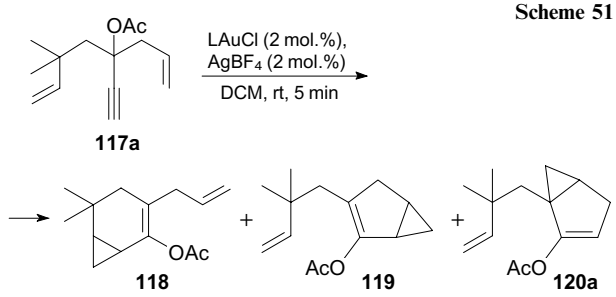
The 1,6-enyne cyclization proceeds equally efficiently with either $Ph_3PAuNTf_2$[45] or catalyst **18**.[75] The choice of the optimal catalyst considerably shortens the reaction time (Scheme 49).

Scheme 50



Under the action of AuCl, 1,6-enyne amides, for example, compound **113** are converted to cyclobutanones (*e.g.*, **114**) with high diastereoselectivity (Scheme 50).[108, 110] Under the same conditions, enyne amide **115** containing a propargyl alcohol group is converted to carbonyl derivative **116** with the 2-azabicyclo[3.1.0]hexane moiety.

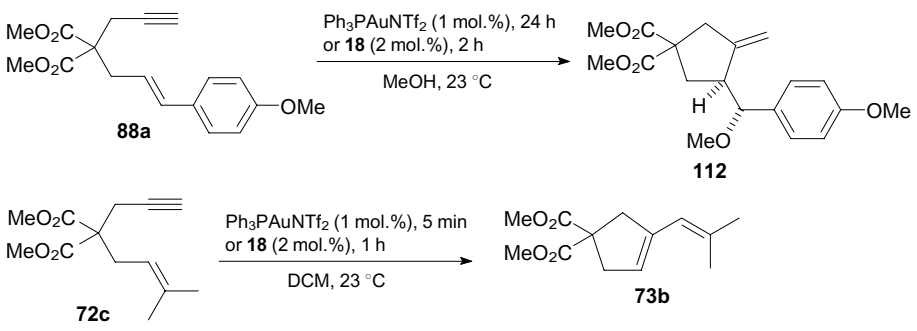
Scheme 51



L	Yield of **118** (%) (see [a])	Yield of **119** (%) (see [a])	Yield of **120a** (%) (see [a])
IMes	26	12	40
SIMes	23	9	40
IPr	30	12	42
SIPr	41	13	36
IAd	54	6	35
ITM	52	8	12
PPh_3	50	2	12

[a] NMR yields averaged over two experiments.

Scheme 49

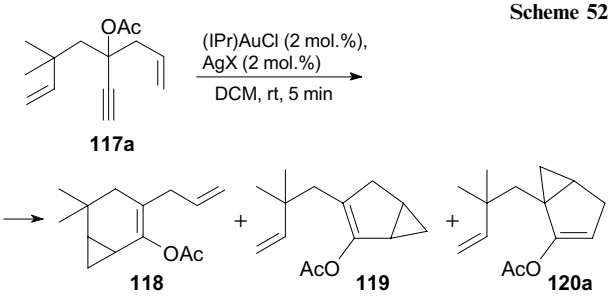


Catalyst	Yield, of **112** (%)	Yield, of **73b** (%)
$Ph_3PAuNTf_2$	96	96
18	94	97

2.1.1.2.4. Cycloisomerization of 1,5;1,6-dienynes

An interesting situation occurs in the cycloisomerization of dienyne **117a**. This 1,6-enyne system, which contains both a propargyl substituent and an acetate group, can be used for the preparation [37] of bicyclo[3.1.0]hexenes **119**, **120a** and bicyclo[4.1.0]heptene **118**, with gold complexes containing N-heterocyclic carbene ligands being used as catalysts (Scheme 51). The reaction is accompanied by acetoxy group migration.

Scheme 52



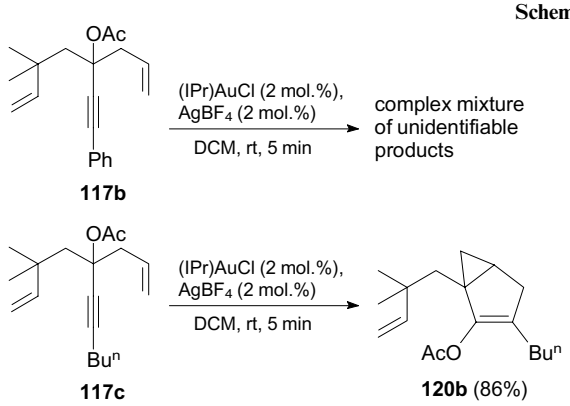
AgX	Yield of **118** (%) (see [a])	Yield of **119** (%) (see [a])	Yield of **120a** (%) (see [a])
$AgBF_4$	30	12	42
$AgPF_6$	32	19	39
$AgSbF_6$	40	18	27
AgOTf	63	13	–
AgOAc	The starting **117a** only		

[a] NMR yields averaged over two experiments.

As can be seen from Scheme 51, the reaction gives a mixture of three products, the ratio of which is determined by the nature of the ligand. Also, the reaction pathway depends substantially on the nature of the counter-ion (silver salt) (Scheme 52).

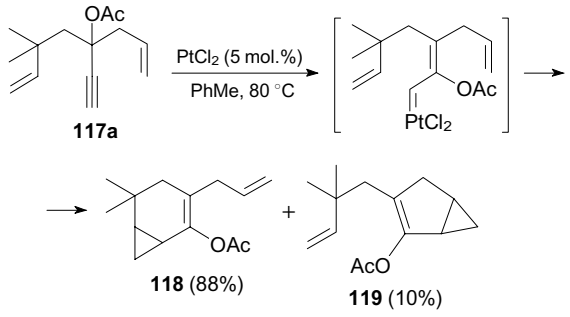
Finally, as was to be expected, the nature of substituents has a pronounced effect on the reaction pathway. Indeed, the cycloisomerization of the internal phenyl-substituted alkyne **117b** affords a complex mixture of unidentifiable products (Scheme 53), while the cycloisomerization of butyl-substituted internal alkyne **117c** results in the selective formation of bicyclo[3.1.0]hexene **120b** (analogue of **120a**) in a high yield (see Scheme 53). The researchers [37] failed to explain this selectivity, but they proposed a reaction mechanism, which enables the formation of all three products (Scheme 54).

Scheme 53

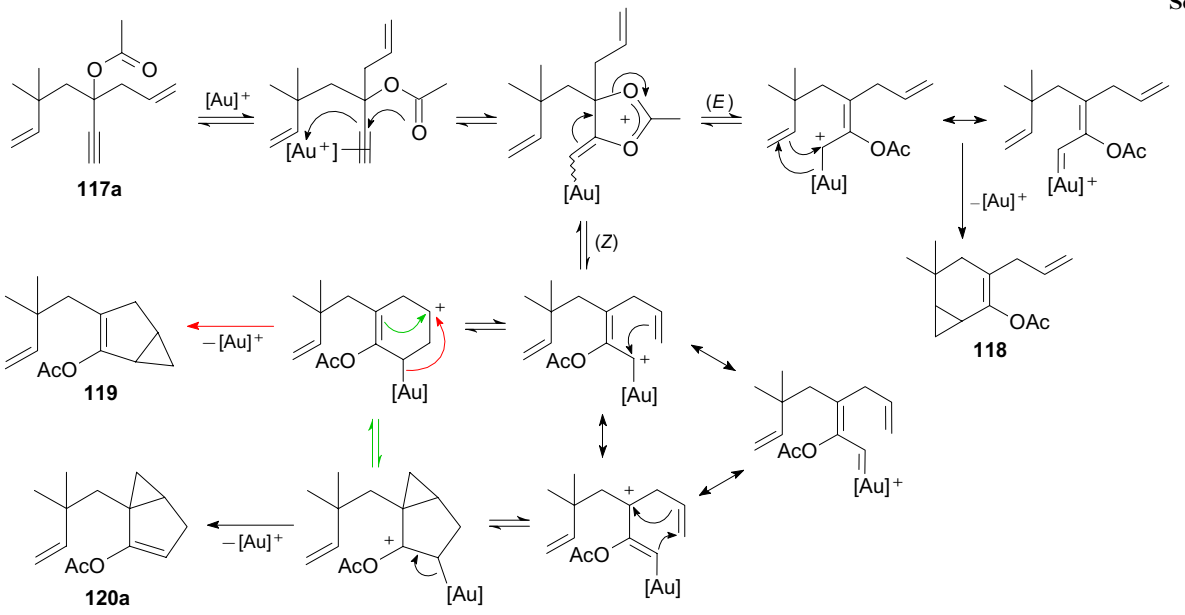


The cycloisomerization of substrate **117a** can also be catalyzed by platinum chloride.[111] The reaction proceeds

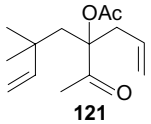
Scheme 55



Scheme 54



Structure 121



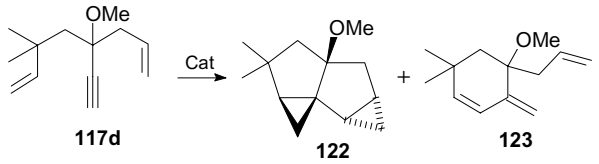
121

at higher temperature and furnishes a mixture of products **118** and **119** (Scheme 55).

The cycloisomerization of dienyne **117a** in ionic liquids ([BMIM]X, BMIM is 1-n-butyl-3-methylimidazolium, X = PF_6, NTf_2, BF_4) at room temperature with gold salts (either AuCl or $AuCl_3$) and complexes ($Ph_3PAuCl-AgPF_6$) can provide the preparation of products **118**, **119** and **120a**;[112] however, in this case, product **121** has also been detected. It is formed upon hydration of the triple bond of substrate **117a** without cycloisomerization or acetoxy group migration.

The replacement of the acetoxy group in **117a** by the methoxy group, which cannot migrate under the reaction conditions, changes crucially the reaction pathway and the structure of products.[112] Indeed, in the reactions catalyzed by Pt^{II} or Pt^{IV} salts, $AuBr_3$ or AuCl, dienyne **117d** is converted to only one isolated product **122** in a good yield *via* double cyclization. However, when a cationic gold complex is used, the reaction gives a product mixture; compounds **122** and **123** have been isolated from the mixture, the latter being the major product (Scheme 56).

Scheme 56



117d → **122** + **123**

Cat (amount)	Conditions	Yield of **122** (%)	Yield of **123** (%)
$PtCl_2$ (5 mol.%)	PhMe, 80 °C, 2 h	73	–
$PtCl_4$ (5 mol.%)	PhMe, 80 °C, 2 h	77	–
$AuBr_3$ (2 mol.%)	DCM, rt, 20 min	69	–
AuCl (2 mol.%)	DCM, rt, 20 min	72	–
Ph_3PAuCl (5 mol.%) + $AgSbF_6$ (5 mol.%)	DCM, rt, 20 min	22	58

The reaction of substrate **117d** in ionic liquids catalyzed by gold salts also yields a product mixture, in which cyclohexene **123** predominates.[112]

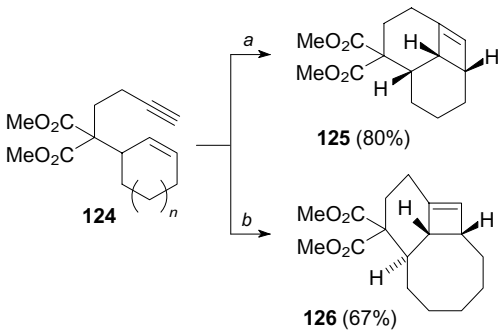
2.1.1.2.5. Cycloisomerization of 1,7-enynes

Several gold-catalyzed skeletal rearrangements of 1,7-enynes with a single bond cleavage have been reported.[86] Thus Au^{I}-catalyzed cyclization of 1,7-enynes **124** affords cyclobutenes **125** and **126** as a result of *syn*-attack on the alkene by the (η^2-alkyne)–gold(I) complex (Scheme 57).[75]

2.1.1.2.6. Cycloisomerization of 1,8-enynes

Gold(I)-catalyzed intramolecular regioselective 7-*exo*-*dig*-cyclization producing 3-methylene-3,4-dihydrobenzo[*b*]-oxepinones, with a large scope of potential applications

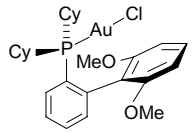
Scheme 57



124 → (*a*) **125** (80%); (*b*) **126** (67%)

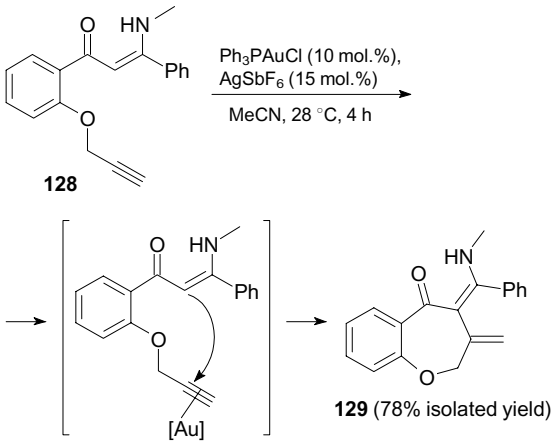
(*a*) **18** (2 mol.%), DCM, rt, 14 h (for *n* = 1);
(*b*) **127** (2 mol.%), $AgSbF_6$ (2 mol.%), DCM, rt, 45 min (for *n* = 3)

127 =



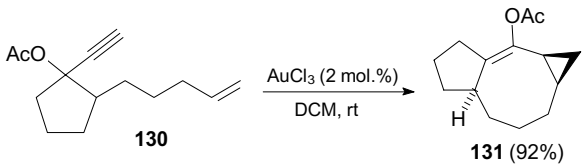
(see, for example, Refs 113 and 114), in up to 95% yield has been reported.[115] The authors studied a broad range of gold-containing catalytic systems and solvents; the best results for the model substrate were obtained by using the Ph_3PAuCl (10 mol.%)–$AgSbF_6$ (15 mol.%) system in acetonitrile at room (28 °C in India) temperature. The reaction was carried out in a nitrogen atmosphere. When other silver salts ($AgBF_4$, AgOTf, $AgNTf_2$) and other solvents tested by the authors (THF, dichloroethane, 1,4-dioxane, toluene) were used, the product was formed in a lower yield. In DMF, a complex mixture of products was obtained; the same was observed with $AuCl_3$ or $AuBr_3$ as the catalyst. The reaction tolerated a broad range of substituents in the aromatic ring, at the

Scheme 58



128 → **129** (78% isolated yield)

Scheme 59



130 → **131** (92%)

triple bond and in the amine moiety of the substrate; the yields of target products were 72% – 95%. As an example of this reaction, the conversion of substrate **128** to benzoxepinone **129** is shown in Scheme 58.

Moreau *et al.*[116] described the cyclization of 1,8-enyne **130** accompanied by the 1,2 acetoxy shift, resulting in the formation of tricyclic product **131** (Scheme 59). When $PtCl_2$ is used as the catalyst, the reaction gives a mixture of products.

2.1.1.2.7. Cycloisomerization of 1,*n*-enynes ($n \geqslant 9$)

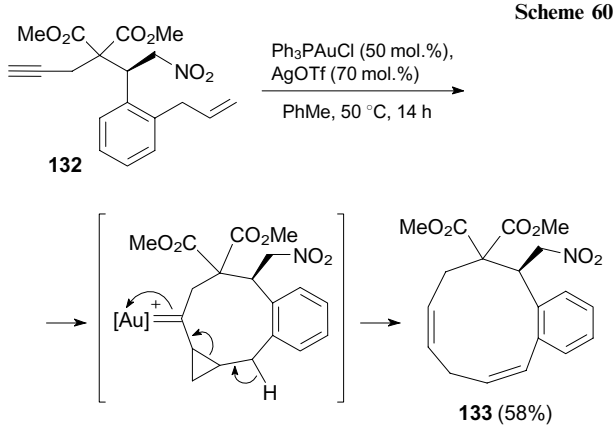
As has already been noted above, one of the benefits of gold-based catalysts is the possibility to obtain medium rings and macrocycles. Macrocycles are encountered in many important natural products and show a broad spectrum of biological activity.[117] Unlike the cyclization of 1,*n*-enynes with small n ($n = 5-8$), in which the entropy factor is favourable for the reaction, cyclization of 1,*n*-enynes for $n > 9$ is hampered.

The gold-catalyzed cyclization of 1,9-enyne **132** can serve for the synthesis of 10-membered ring **133** (Scheme 60).[118] The cyclization requires a large amount of the catalyst (50 mol.%) and affords the target product **133** in a moderate yield.

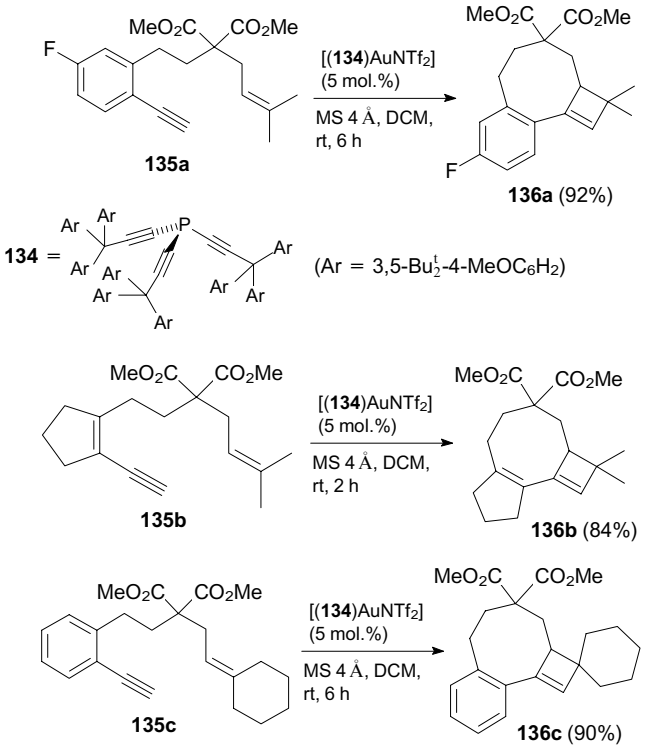
Cationic gold(I) complex with a hollow-shaped triethynylphosphine ligand **134** catalyzes highly efficient cycloisomerization of 1,9-enynes **135a – c** under mild conditions giving good yields of products (Scheme 61).[119] The reaction requires 5 mol.% of the catalyst. The resulting eight-membered carbocycles **136a – c** annulated to a cyclobutene moiety are difficult to prepare with other catalytic systems. The reaction formally proceeds as an intramolecular [2 + 2]-cycloaddition.

Obradors *et al.*[120] presented examples of Au^I-catalyzed macrocyclization of 1,*n*-enynes ($n = 10-16$). For enynes with large n values, the double and triple bonds should preferably be proximate to each other in the stable conformation of the molecule, which allows efficient conduction of the reaction under mild conditions. If this requirement is not met, the reaction does not occur, which is the case, for example, for substrate **137** (Scheme 62).

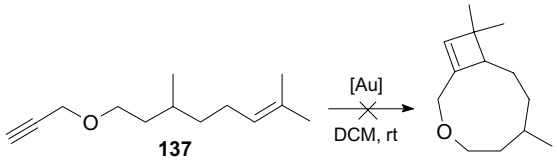
Scheme 60



Scheme 61

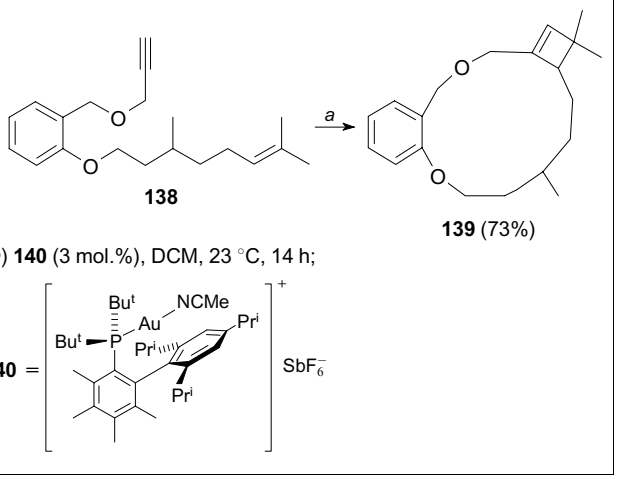


Scheme 62

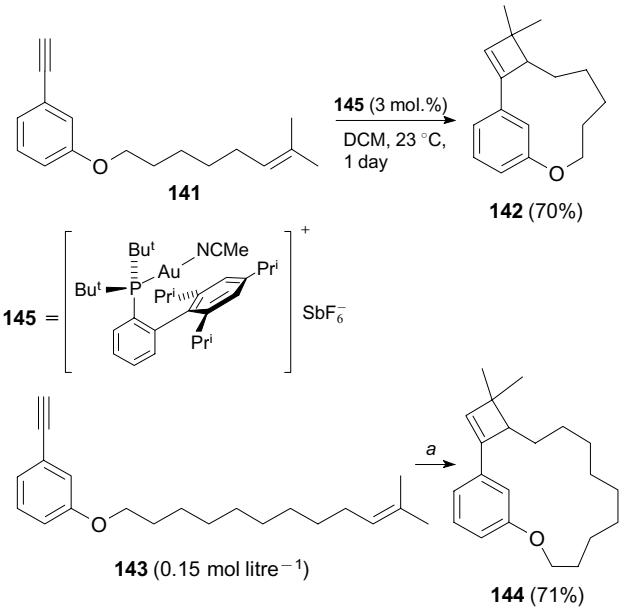


As can be seen in Schemes 60 – 62, the above-described successful cyclizations proceed for substrates in which the reactive groups are arranged in space in a definite way as a result of *ortho*-addition to the ring present in the molecule (cyclopentene or benzene). The use of this approach allowed Obradors *et al.*[120] to prepare a number of macrocyclic derivatives in moderate to high yields from large 1,*n*-enynes ($n > 9$) as a result of the Au^I-catalyzed [2 + 2]-cycloaddition reaction under mild conditions. An example of such reaction is depicted

Scheme 63



Scheme 64



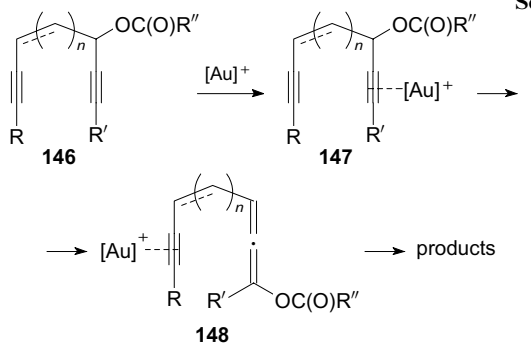
in Scheme 63. The yield of product **139** is inversely proportional to the concentration of substrate **138**, which is attributable to prevention of intermolecular interactions upon dilution.

Macrocycles **142** and **144** were obtained from 1,*n*-enynes **141** and **143**, the alkyne and alkene moieties of which are connected to the *meta*-substituted benzene linker (Scheme 64).[120] The double bond of cyclobutene **142** (**144**) can be selectively reduced with hydrogen using palladium supported on carbon in methanol in the presence of pyridine.

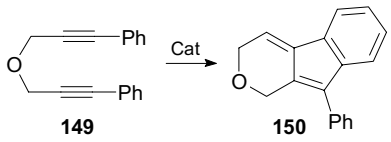
2.1.1.3. Cyclization of diynes

The cycloisomerization of 1,*n*-diynes catalyzed by Au^{I} or Au^{II} complexes is currently one of the most efficient and economic strategies for one-step synthesis of complex molecules.[121 – 123] A series of cyclic compounds have been prepared from 1,*n*-diyne carbonates and esters **146**.[124 – 126] The reaction usually occurs *via* allenyl intermediate **148**, which is formed upon 1,3-migration of the acyloxy group in gold-activated substrate **147** (Scheme 65).

Scheme 65



Scheme 66



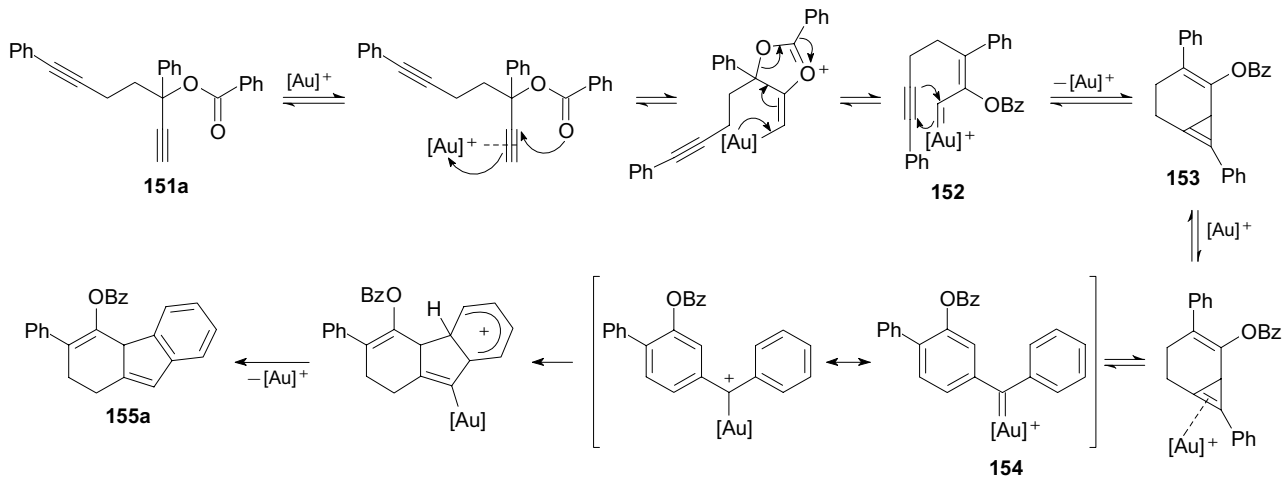
Cat	Reaction conditions	Yield of **150** (%)
$PtCl_2$	PhMe, 100 °C, 12 h	51
$Ph_3PAuCl - AgSbF_6$	DCM, 23 °C, 0.5 h	93

2.1.1.3.1. Cycloisomerization of 1,6-diynes

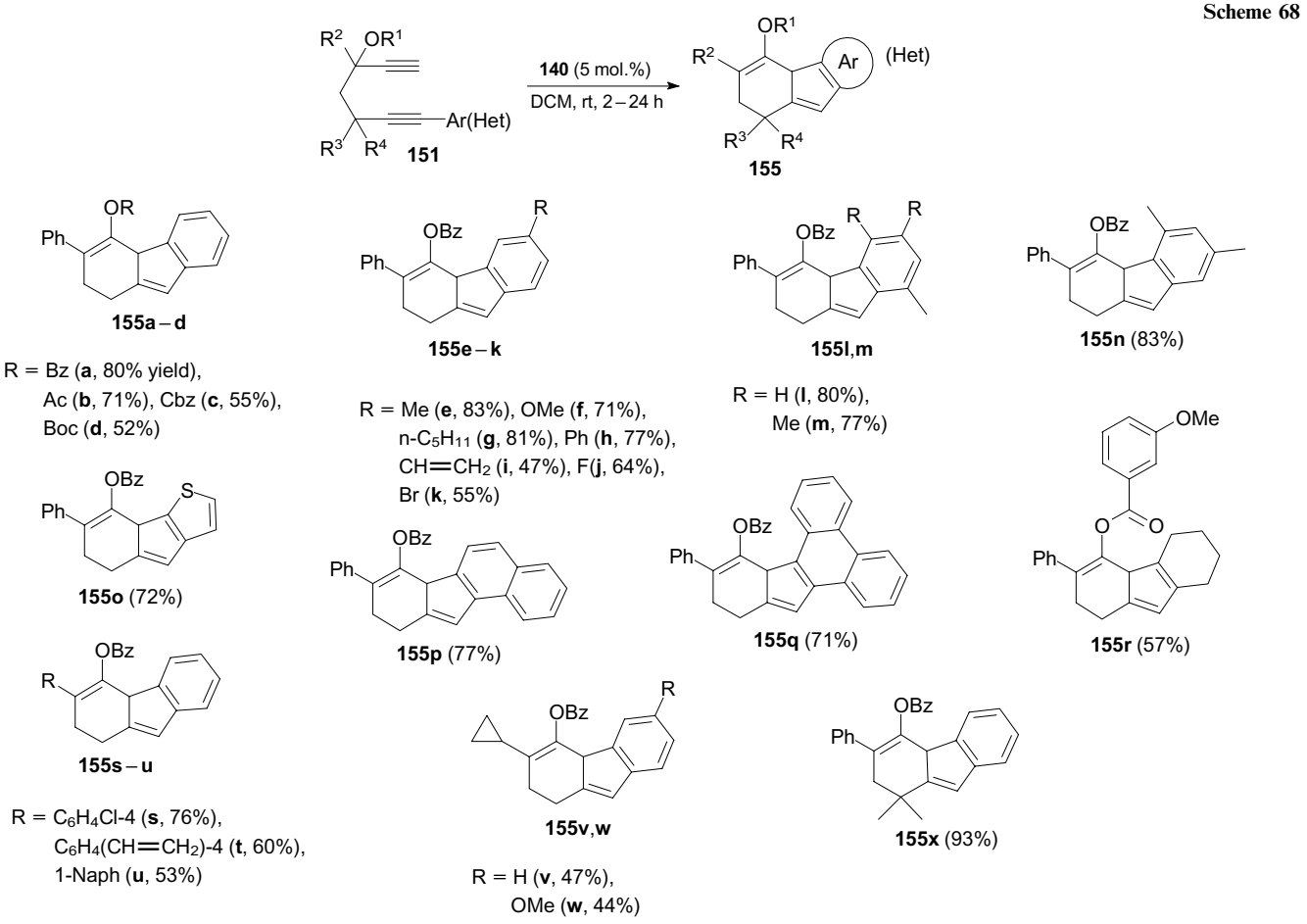
Lian *et al.*[127] reported a gold-catalyzed cycloisomerization of 1,6-diyne **149**. The reaction can also proceed with a platinum catalyst, but in this case, more drastic conditions and longer times are required, and product **150** is formed in a lower yield (Scheme 66).

The gold-catalyzed cycloisomerization of 1,6-diyne carbonates or esters containing a terminal alkyne group in the α-position to the carbonate or ester function (for example, compound **151a**) involves carbenoid intermediate **152**, which is formed *via* 1,2-migration of the acyloxy group.[128] The intermediate **152** is converted to cyclopropene intermediate **153**, which undergoes cyclorever-

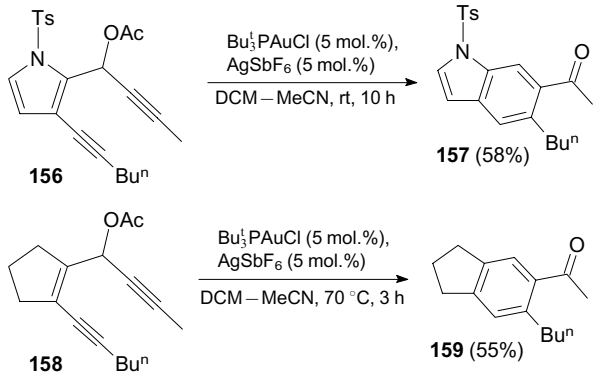
Scheme 67



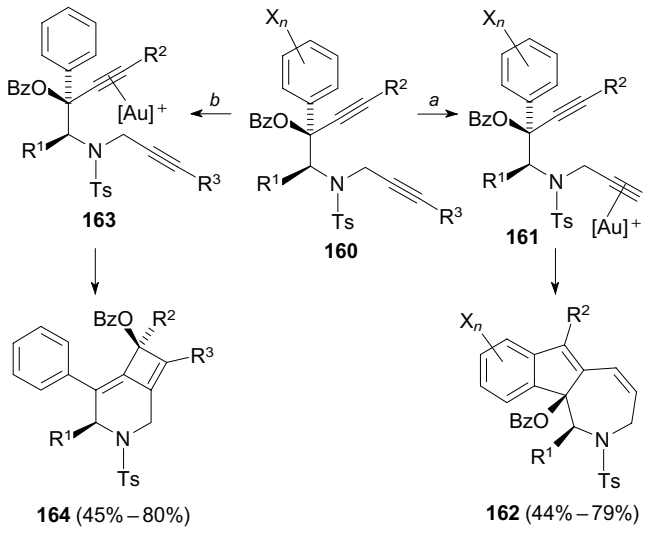
Scheme 68



Scheme 69



Scheme 70



sion to give gold carbenoid **154**. The Nazarov cyclization of the latter yields 2,4a-dihydro-1*H*-fluorene derivative **155a** (Scheme 67).

The set of possible substrates for this reaction and the yields of products are presented in Scheme 68.[128]

Gold-catalyzed cycloisomerization of 1,6-diynes **156** and **158** leads to bicyclic aromatic ketones **157** and **159**, respectively (Scheme 69).[129] The reaction is accompanied by acetyl group migration giving a diene moiety, which attacks the gold-activated second triple bond. Note that in the case of dialkynyl-substituted benzene, silver catalysis is more efficient.

(*a*) **18** (5 mol.%), MS 4 Å, PhMe, 80 °C, 24 h (for R^3 = H);
(*b*) **18** (5 mol.%), PhMe, rt, 15 h (for R^3 = Ph, 3-Th; X_n = H);
162: X_n = H, 4-Me, 4-Cl, 4-CH_2=CH, 3,5-Me_2; R^1 = Me, Et, Pr^n, Pr^i, Bu^i, Ph, Bn, $TBSOCH_2$, $MeSO_2CH_2CH_2$; R^2 = Ph, 4-MeC_6H_4, 4-BrC_6H_4, 3-Th, Bu^n, cyclo-C_5H_9, cyclohexen-1-yl;
164: R^1 = Me, Et, Pr^n, Bu^i, Ph, Bn, $TBSOCH_2$; R^2, R^3 = Ph, 3-Th

2.1.1.3.2. Cycloisomerization of 1,7-diynes

1,7-Diyne benzoates **160** undergo tandem 5-*endo-dig*-7-*endo-dig*-cyclization to give indeno[1,2-*c*]azepines **162** *via* adduct **161**, or azabicyclo[4.2.0]octa-1(8),5-dienes **164** *via* adduct **163** (Scheme 70).[124]

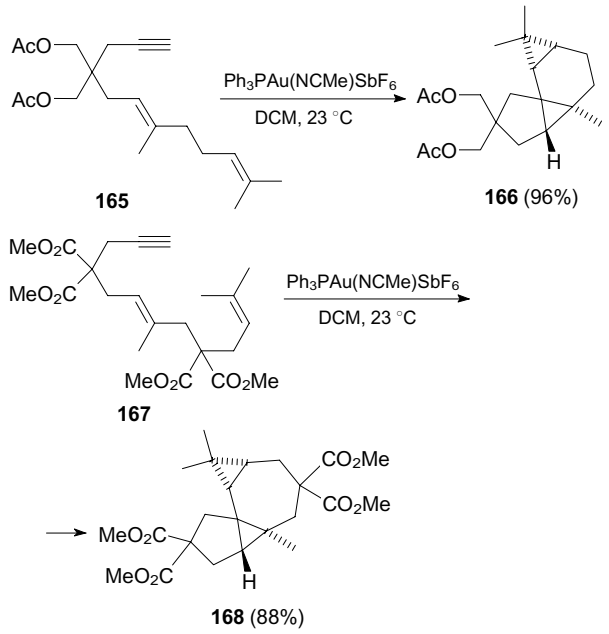
The gold-catalyzed tandem cyclizations of compounds containing a triple bond are considered in more detail below.

2.1.1.4. Cyclization of dienynes

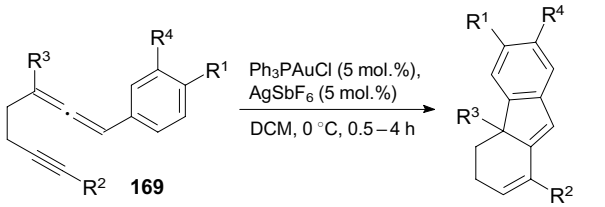
The carbene-like nature of intermediates arising in a metal-catalyzed cycloisomerization is explicitly manifested in the intra- and intermolecular cyclopropanation reactions of dienynes.[130] Thus, with Au^I participation, dienynes **165** and **167** are stereoselectively converted to tetracyclic compounds **166** and **168** (Scheme 71).[87, 92]

Allenynes are well-known precursors of bicyclic compounds.[131] Since recently, enyne cycloisomerization has become a significant trend in the efficient use of homogeneous gold catalysts.[13, 132]

Scheme 71

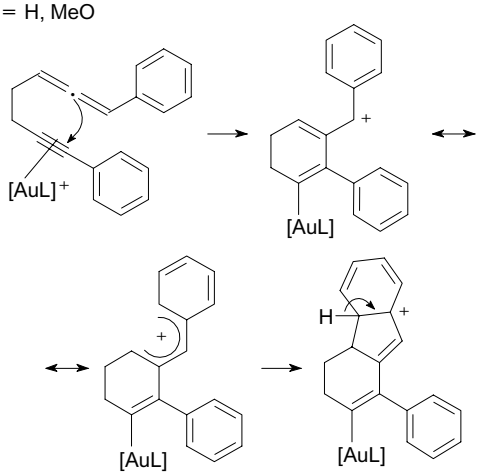


Scheme 72



R^1 = H, F, Me, MeO; R^2 = Ph, 4-FC_6H_4, 4-$MeOC_6H_4$, 4-MeC_6H_4, 1-Naph; R^3 = H, Alk; R^4 = H, MeO

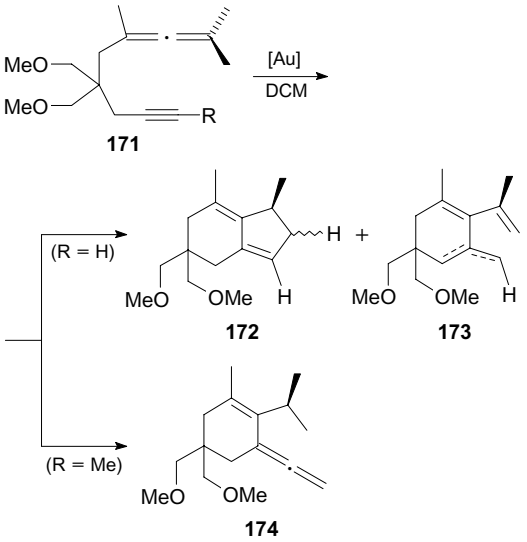
170 (26% – 81%, yield after column chromatography)



The cyclization of 1,6-allenynes **169** catalyzed by $Ph_3PAuSbF_6$ (5 mol.%) conducted in cold dichloromethane (0 °C) affords bicyclo[4.3.0]nonadienes (dihydrofluorenes) **170** (Scheme 72).[133] The reaction is carried out at a low concentration of the substrate (0.2 mol litre^{-1}) to prevent its polymerization. The mechanism of this reaction proposed by the authors includes 6-*endo-dig*-cyclization of the Au^I alkyne complex and the subsequent Nazarov cyclization.

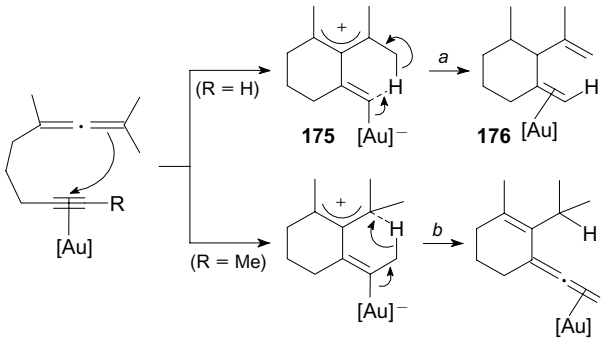
The cyclization of allenynes **171** occurs with gold compounds as catalysts. The structure of reaction prod-

Scheme 73



Catalyst	Conditions	Yield of **172** (%)	Yield of **173** (%)	**173** *exo*: *endo*	Yield of **174** (%)
		R = H			
$AuCl_3$ (1 mol.%)	DCM, 0 °C, 0.5 h	80	Traces	–	
$NaAuCl_4$ (1 mol.%)	DCM, 0 °C, 1 h	75	Traces	–	
AuCl (1 mol.%)	DCM, 0 °C, 0.5 h	79	Traces	–	
$Ph_3PAuSbF_6$ (1 mol.%)	DCM, 0 °C, 0.25 h	0	70	1 : 1	
$Ph_3PAuNTf_2$ (1 mol.%)	DCM, 0 °C, 6 h	5	68	2 : 1	
		R = Me			
$AuCl_3$ (1 mol.%)	DCM, rt, < 5 min				92
AuCl (1 mol.%)	DCM, rt, < 5 min				89
$Ph_3PAuSbF_6$ (1 mol.%)	DCM, rt, < 5 min				79

Scheme 74

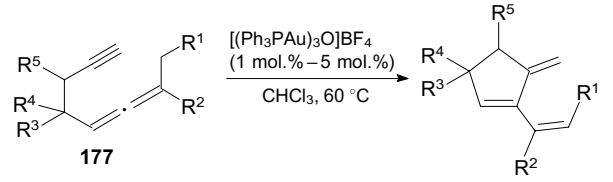


(*a*) 1,5-proton shift; (*b*) 1,5-hydride shift

ucts **172** – **174** is determined by the natures of the catalyst and substituent R (Scheme 73).[134] In the case of R = H, the reaction proceeds *via* intermediate **175**, involves a 1,5-proton shift, and gives the Alder-ene reaction product **176**. In the case of internal alkyne **171** (R = Me), exocyclic allene **174** is obtained, the reaction being accompanied by the 1,5-hydride shift (Scheme 74). The Au^{I} and Au^{III} chlorides and the Au^{I} triphenylphosphine complex with different weakly coordinating anions were used as catalysts. Similar results were obtained with Pt^{II} and Pt^{IV} chlorides and complexes; however, in this case, the products were formed in lower yields and the reaction time was as long as two days.

In 2008, Houk, Toste and co-workers[135] proposed a new reaction mechanism for cycloisomerization of 1,6-allenynes **177**. With the $[(Ph_3PAu)_3O]BF_4$ catalyst, cross-conjugated triene **178** was obtained (Scheme 75).

Scheme 75



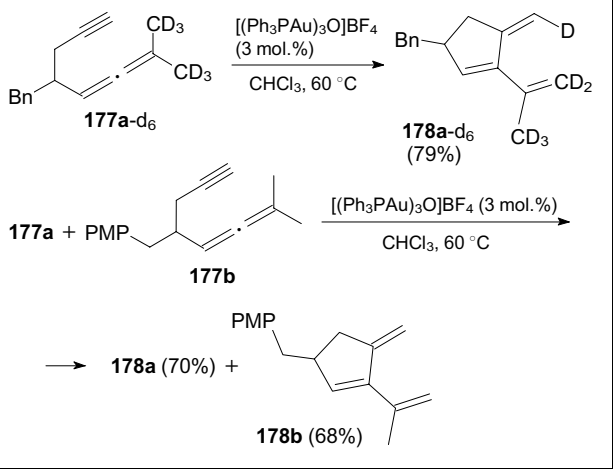
R^1 = H, Ph; R^2 = Me; $R^1 - R^2 = (CH_2)_3$;
R^3 = H, Bn, CH_2PMB, CO_2Me; R^4 = H, Ph, CO_2Me;
R^5 = H; $R^4 - R^5 = (CH_2)_4$

Only terminal alkynes participated in the reaction. Deuterium-labelled compound **177a** showed diastereoselectivity of hydrogen transfer (Scheme 76). The crossover experiment involving substrates **177a** and **177b** demonstrated that this process is intramolecular.

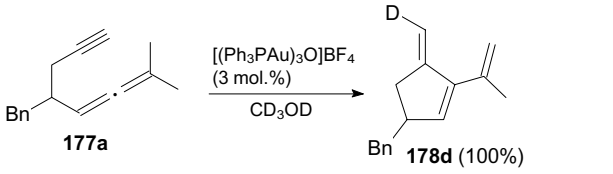
When the reaction was carried out in CD_3OD, hydrogen – deuterium exchange was detected for the terminal alkyne (the deuterium content reached 93%), indicating the formation of gold acetylenide (Scheme 77).

The primary kinetic isotope effect for this 1,5-H-shift proved to be much lower (1.8 – 1.9) than for other 1,5-sigmatropic shifts. Additional experiments included the preparation of gold(I) acetylenide **179**, which was a stable compound and was converted to product **178a** in the presence of a catalytic amount of Au^{I} cations, or Zn^{II} type Lewis acid, or even trifluoromethanesulfonic acid

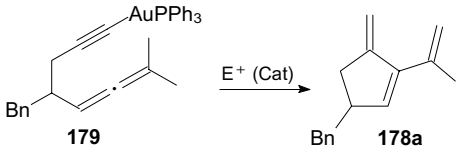
Scheme 76



Scheme 77



Scheme 78



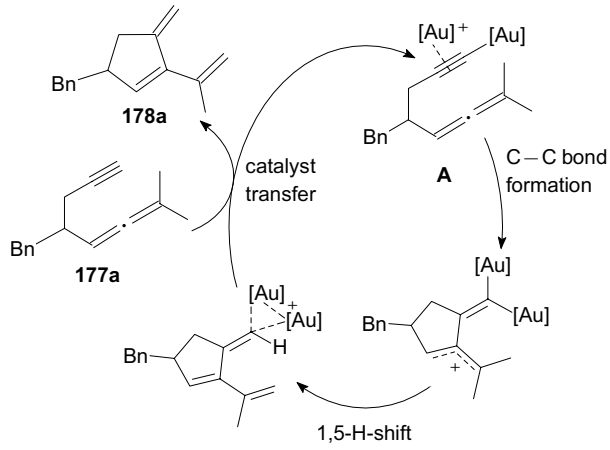
$E^+ = Ph_3PAu^+$, $ZnCl_2$, HOTf

(Scheme 78). The silver acetylenide counterpart does not undergo this reaction.

The proposed reaction mechanism is depicted in Scheme 79. It implies the formation of complex **A** with two gold ions, one forming a σ-complex and the other forming a π-complex.

This transformation is classified as a so-called dual gold-activated reaction, which is considered below in a separate part of the review.

Scheme 79

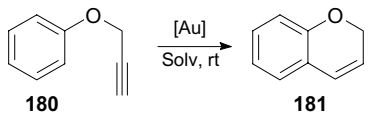


2.1.1.5. Intramolecular triple bond hydroarylation reactions

2.1.1.5.1. Cycloisomerization of carboaromatic alkynes

The first example of such reaction was reported for compound **180** by Pastine *et al.*[136] The yield of the target product **181** did not exceed 6% (Scheme 80). The use of complex **18** increased the yield of product **181** to 62%.[137]

Scheme 80

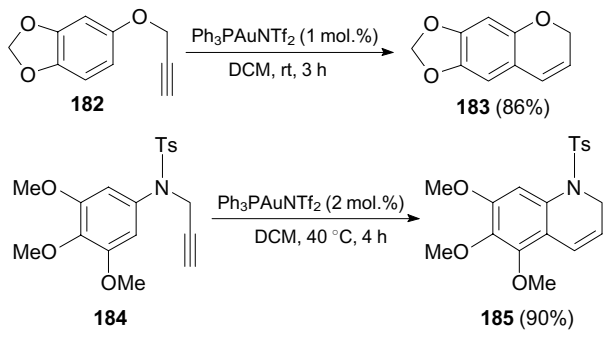


180 **181**

[Au]	[Au] amount (mol.%)	Solv	Yield of **181** (%)
$AuCl_3$	5	PhMe	6
18	1	DCM	62

Further development of this line of research can be found in the literature.[138–146] For example, hydroarylation of alkynes **182** and **184** catalyzed by $Ph_3PAuNTf_2$ resulted in the synthesis of 2*H*-chromene **183** and dihydroquinoline **185** in good yields (Scheme 81).[142] It can be seen that the benzene ring is activated in both cases by electron-donating groups.

Scheme 81



182 **183** (86%)

184 **185** (90%)

Analogous transformations, for example, as shown in Scheme 82 for substrates **186** and catalyst **18**, were reported by Menon *et al.*[137] The reaction was conducted in dichloromethane at room temperature.

Scheme 82

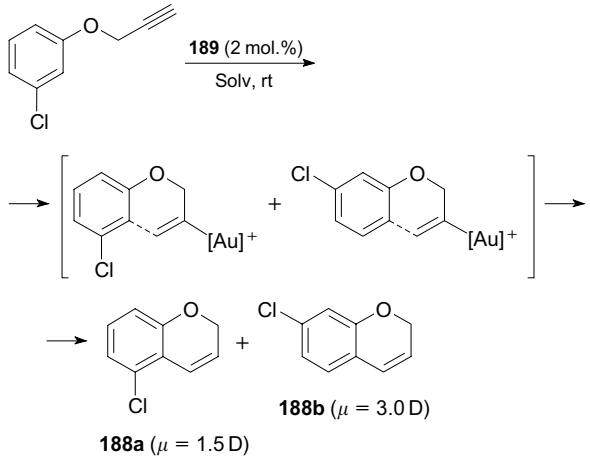


186 **187**

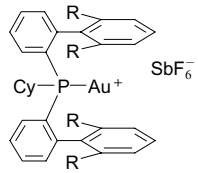
R^1	R^2	X	Yield of **187** (%)
Me	H	O	66
OMe	H	O	73
H	Cl	O	90
H	H	NTs	81
OMe	H	NTs	79
Cl	H	NTs	52

The regioselectivity issues for Au^I-catalyzed hydroarylation were described in detail by Lau *et al.*,[147] who studied the effects of the ligand, the solvent, substituents in the substrate and the counter-ion. In particular, in the reaction shown in Scheme 83, the **188a** : **188b** ratio of products regularly decreased with increasing dielectric constant of the solvent (ε).

Scheme 83



188a (μ = 1.5 D) **188b** (μ = 3.0 D)

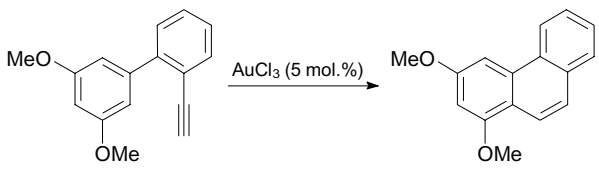
189 =  (R = OPr^i)

Solvent	ε	**188a** : **188b**	Yield of **188a** + **188b** (%)
PhMe	2.4	5.0 : 1	67
PhMe – $CHCl_3$ (4 : 1)	3.0	4.3 : 1	78
PhMe – $CHCl_3$ (1 : 1)	3.8	3.6 : 1	83
PhMe – DCM (4 : 1)	4.3	2.7 : 1	50
$CHCl_3$	4.8	1.9 : 1	80
$CHCl_3$ – DCM (4 : 1)	5.8	1.5 : 1	50
PhMe – DCM (1 : 1)	6.4	1.5 : 1	74
$CHCl_3$ – DCM (1 : 1)	7.1	1.0 : 1	71
PhMe – DCM (1 : 4)	8.1	0.9 : 1	78
DCM	8.9	0.8 : 1	66
DCE	10.4	0.8 : 1	80

One more example of participation of a benzene double bond activated by electron-donating groups in the cycloisomerization reaction with an alkyne can be found in a paper by Mamane *et al.*[148] (Scheme 84).

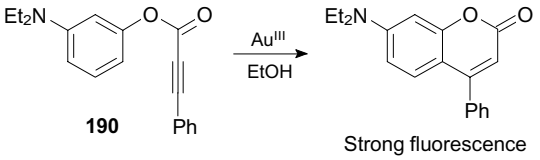
The intramolecular hydroarylation of alkyne **190** was proposed[149] for detection of Au^{III} cations. The reaction

Scheme 84



(95%)

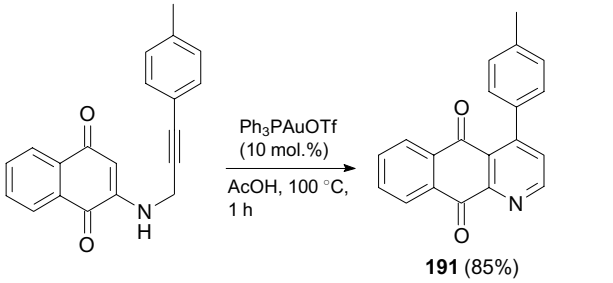
Scheme 85



is highly selective and highly sensitive (Scheme 85) and can be accomplished even in protic solvents.

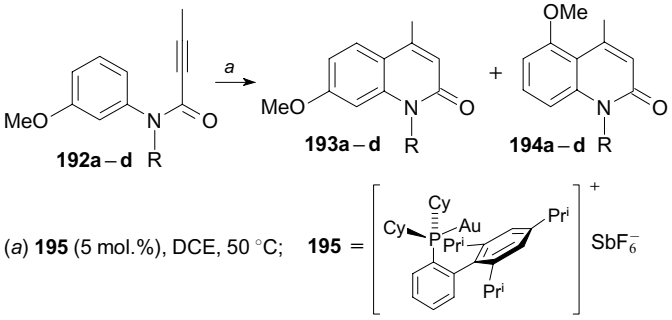
The $Ph_3PAuOTf$-catalyzed 6-*endo*-*dig*-cycloisomerization of *N*-propargylaminoquinones results in the synthesis of azaanthraquinones in moderate and high yields, for example, azaanthraquinone **191** (Scheme 86).[150] The reaction is carried out in air, which probably acts as the oxidant in the aromatization step.

Scheme 86



The gold-catalyzed hydroarylation of *N*-arylalkynylamides **192** results in 2-quinolinones **193** and **194**.[151] Compound **192** may have substituents at the triple bond, at the amide nitrogen atom and in the aromatic ring. The benzene ring may be incorporated in a fused

Scheme 87

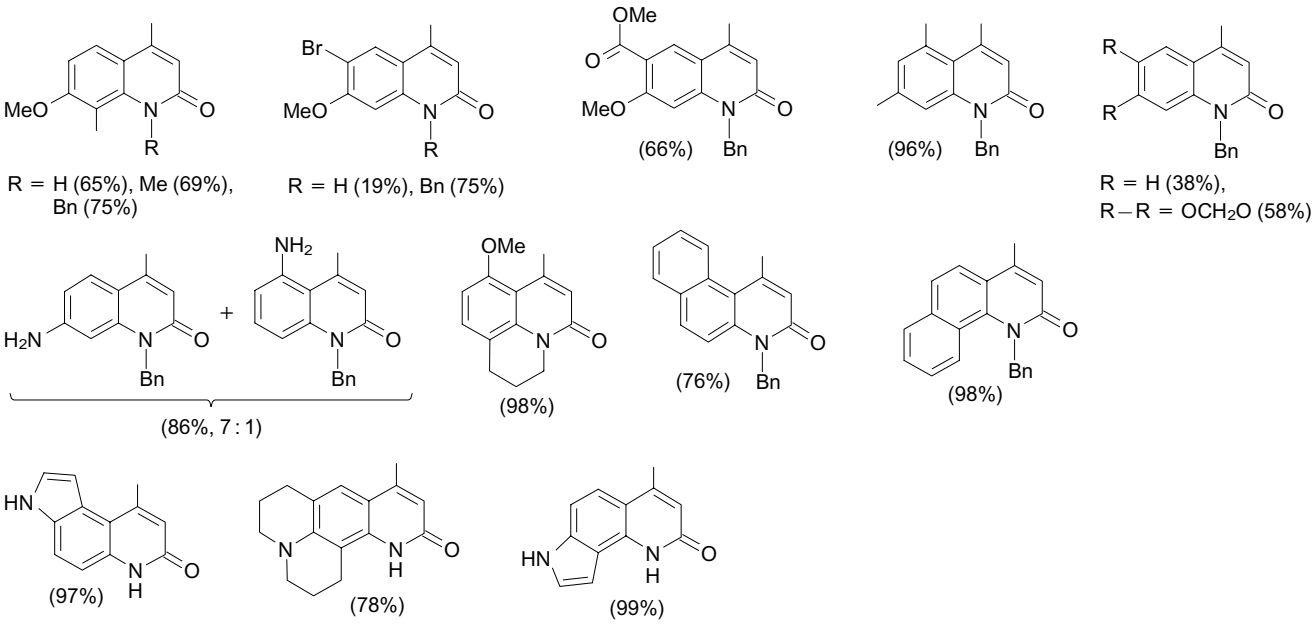


Compounds **192** – **194**	R	Yield of **193** + **194** (%)	**193** : **194**
a	Me	80	2 : 1
b	Bn	87	1.7 : 1
c	Ph	75	1.4 : 1
d	PhCH=CHCH$_2$	72	1.8 : 1



Compounds **192**, **193**	R	Yield of **193** (%)
e	H	68
f	Br	70
g	Et	83
h	cyclo-C_3H_5	73
i	Ph	71

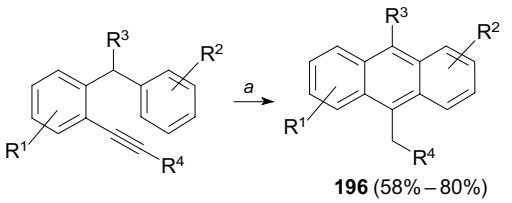
Other possible products



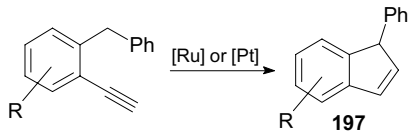
system. In all cases, the reaction occurs under mild conditions to give moderate and good yields of products (Scheme 87). The presence of electron-donating groups in the aromatic ring is favourable for the reaction. Such a group can activate both the *ortho*-position and the *para*-position of the ring.

o-Alkynyldiarylmethanes were converted under mild conditions [152] to anthracenes **196** in moderate and good yields (Scheme 88). Reaction product **196** differs from the one obtained previously (bicyclic compound **197**) with ruthenium and platinum complexes used as catalysts.[153, 154]

Scheme 88

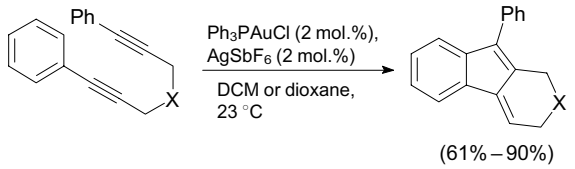


(*a*) $Et_3NAuNTf_2$ (5 mol.%), $HNTf_2$ (0.5 mol.%), DCE, 80 °C, 5 h;
R^1 = H, F, Br, Me; R^2 = H, F, Me, OMe, OAc; R^3 = H, Alk, Ar;
R^4 = H, Alk, OAlk, Ar



Benzene ring participation in the cascade cycloisomerization can be exemplified by the reaction shown in Scheme 89.[155] This reaction can also be catalyzed by $PtCl_2$, but gold proved to be a more active catalyst, which allows one to conduct this process at low temperature.

Scheme 89

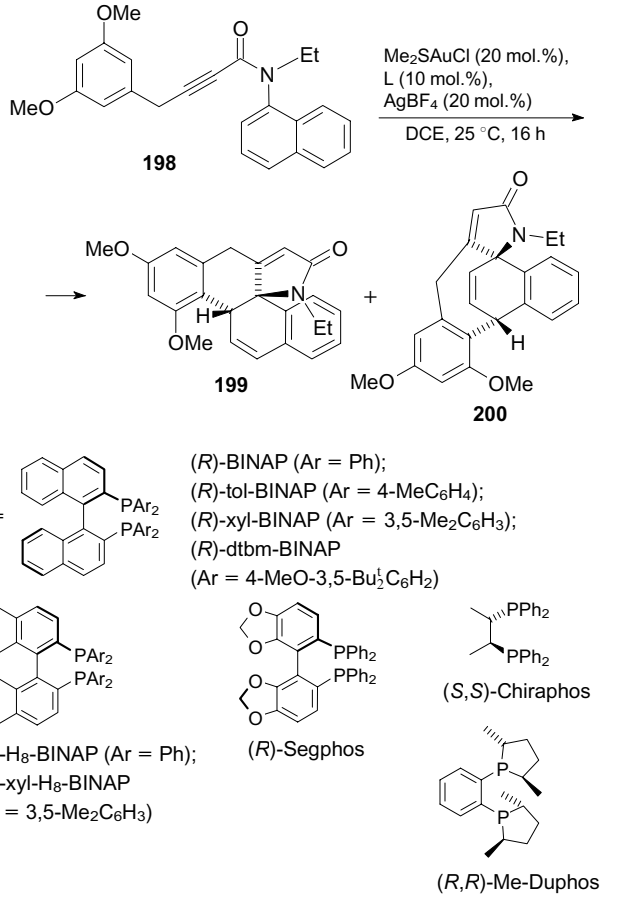


X = CH_2, NTs, $C(CO_2Me)_2$, $C(SO_2Ph)_2$

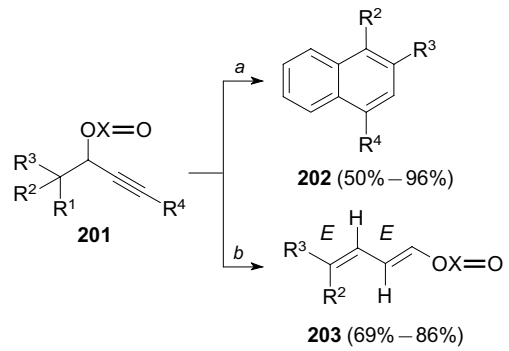
The catalytic asymmetric dearomatization of arenes upon C – C bond formation is a relevant method for the synthesis of chiral cyclic systems.[156, 157] Oka *et al.*[158] reported the first example of catalytic asymmetric dearomatization of arene **198** using a cationic Au^I complex with chiral biphosphine ligands as a catalyst. The reaction proceeds at low temperature and affords products **199** and **200** containing two *cis*-C – C bonds (Scheme 90). Compound **199** was the major product in all cases. The highest yield of this product (74%; 76% *ee*) was attained by using the ligand (*R*)-xyl-BINAP, with product **200** being also formed in 26% yield (40% *ee*).

Dudnik *et al.*[159, 160] described cycloisomerization of propargyl esters **201** yielding unsymmetrically substituted naphthalenes **202**. The cascade reaction includes a previously unknown tandem sequence of 1,3- and 1,2-migrations of two different groups. The authors suggested that the reaction involves a 1,3-diene intermediate or its precursor, the cyclization and subsequent aromatization of which leads to substituted naphthalene **202** (Scheme 91). If the substituents R^1 and R^4 in ester **201** are hydrogen atoms, product **203** is formed, either selectively or predominantly, as the *E*,*E*-isomer.

Scheme 90



Scheme 91



(*a*) $Ph_3PAuOTf$ (10 mol.%) or $(F_5C_6)_3PAuSbF_6$ (10 mol.%), 0.05 M in DCE, rt (for R^1 = Ph); (*b*) $Ph_3PAuOTf$ (2.5 mol.%), 0.05 M in DCE, rt (for R^1, R^4 = H);
X = $P(OEt)_2$, CMe; R^1 = H, Ph; R^2 = H, Me, Et, Cy, Ph;
R^3 = Me, Ph; $R^2 – R^3$ = $(CH_2)_4$, $(CH_2)_5$; R^4 = H, Bu^n, Hex, Ph, 4-$MeOC_6H_4$, 4-$F_3CC_6H_4$, 2-Fu

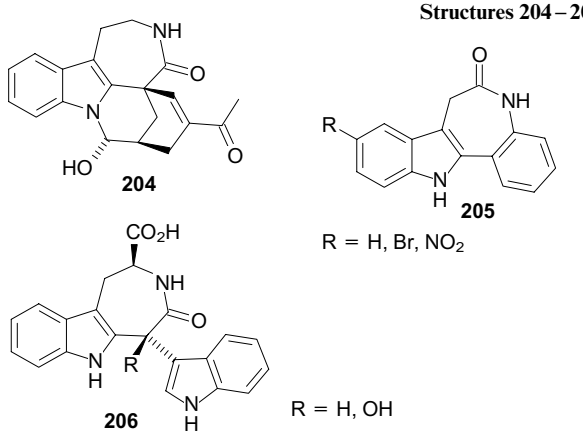
A review[161] devoted to gold-catalyzed benzannulations has been published

2.1.1.5.2. Cycloisomerization of heteroaromatic alkynes

Gold-catalyzed cyclization of aromatic and heteroaromatic compounds with alkynes can serve for the synthesis of a variety of natural products and structurally complex heterocyclic derivatives.[2,162–165] A considerable part of existing publications are devoted to gold-catalyzed highly regioselective intramolecular hydroarylation of alkynes (or alkynylation of arenes) involving the carbon atoms in positions 2 and 3 of the pyrrole (indole) ring.

The indoloazepinone moiety is the core of quite a few natural products such as the indole alkaloids tronocarpine **204**,[166] paullones **205** (Ref. 167) and malassezindoles **206**.[168] In addition, some azepinoindoles show anticancer activity[169] and can be used for the therapy of some diseases of the central nervous system.[170]

Structures 204 – 206

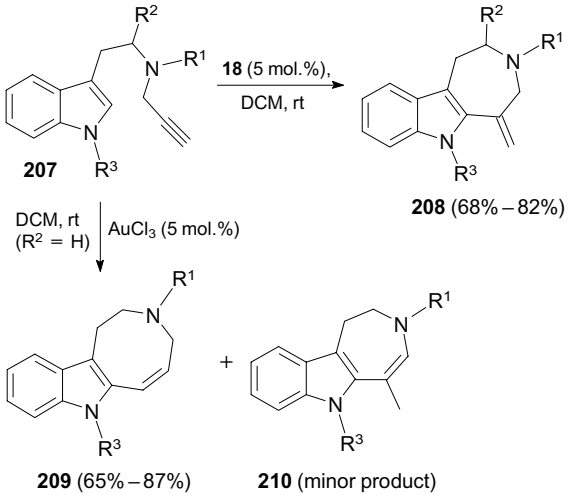


Ferrer and Echavarren[146] were the first to use gold catalysis for the synthesis of azepino[4,5-*b*]indoles **208** and azocino[5,4-*b*]indoles **209**. The reaction pathway is determined by the nature of the gold catalyst. For example, the cyclization of substrate **207** by a cationic Au^{I} complex yields azepino[4,5-*b*]indoles **208**, while more electrophilic $AuCl_3$ provides the synthesis of azocino[5,4-*b*]indoles **209** *via* an 8-*endo*-*dig*-reaction (Scheme 92). In the latter case, azepino[4,5-*b*]indoles **210** are also formed in a minor quantity. The reaction was conducted in dichloromethane at room temperature.

Donets *et al.*[171] made a successful attempt to replace toxic mercury(II)-based catalysts by gold catalysts for the synthesis of substituted azocino[5,4-*b*]indoles **212**. The use of AuCl or $AuCl_3$ as catalysts (as well as the use of Ag^{I}, Pd^{II} or Pt^{II} salts) did not lead to the desired outcome. However, in the presence of the $Ph_3PAuCl-AgOTf$ system (5 mol.% each), 100% conversion of substrate **211** took place to give *endo*-cyclization product **212** (Scheme 93).[172]

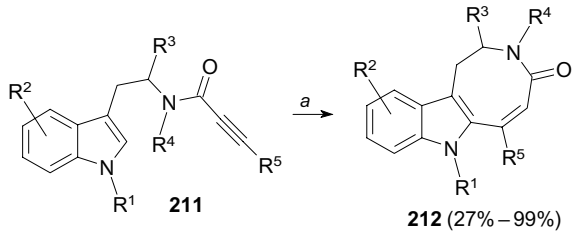
The subsequent studies of Van der Eycken's team[173] were meant to extend the scope of applicability of this transformation and to elucidate the reaction mechanism. The synthetic approach to indoloazocines they used combined the multicomponent Ugi reaction (Ugi MCR) with transition metal (gold) catalysis. Using this approach, it is possible to reduce the number of steps and increase the efficiency. For example, in the case

Scheme 92



$R^1 = SO_2Ph$, DNBS; R^2 = H, CO_2Me; R^3 = H, All;
DNBS = $2,4\text{-}(O_2N)_2C_6H_3SO_2$

Scheme 93



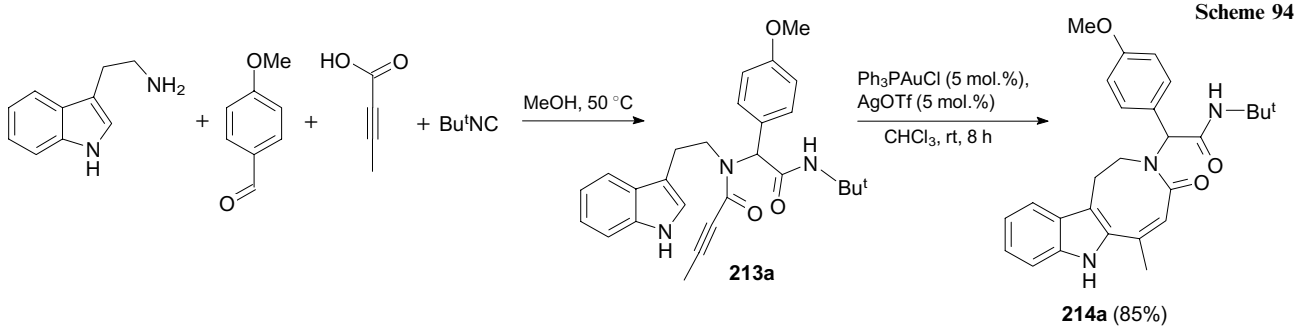
(*a*) $Hg(OTf)_2$ (5 mol.% – 25 mol.%), DCM, MW or $Ph_3PAuOTf$ (5 mol.%), $CHCl_3$, rt or 50 °C; R^1 = H, Me; R^2 = H, OMe; R^3 = H, CO_2Me, CH_2OTIPS; R^4 = Me, Bn; R^5 = Me, Pr^i, Ph

of substrate **213a**, the reaction catalyzed by the $Ph_3PAuCl-AgOTf$ system (5 mol.% each) proceeds at room temperature in chloroform within 8 h, the conversion reaches 100%, and the isolated yield of product **214a** can be as high as 85% (Scheme 94). The authors proposed the cyclization mechanism shown in Scheme 95. The reaction comprises a nucleophilic attack on the gold-activated triple bond by the indole C(3) atom to give spiro intermediate **215a**, which then undergoes 1,2-shift to be converted to azocino[5,4-*b*]indole **214a**.

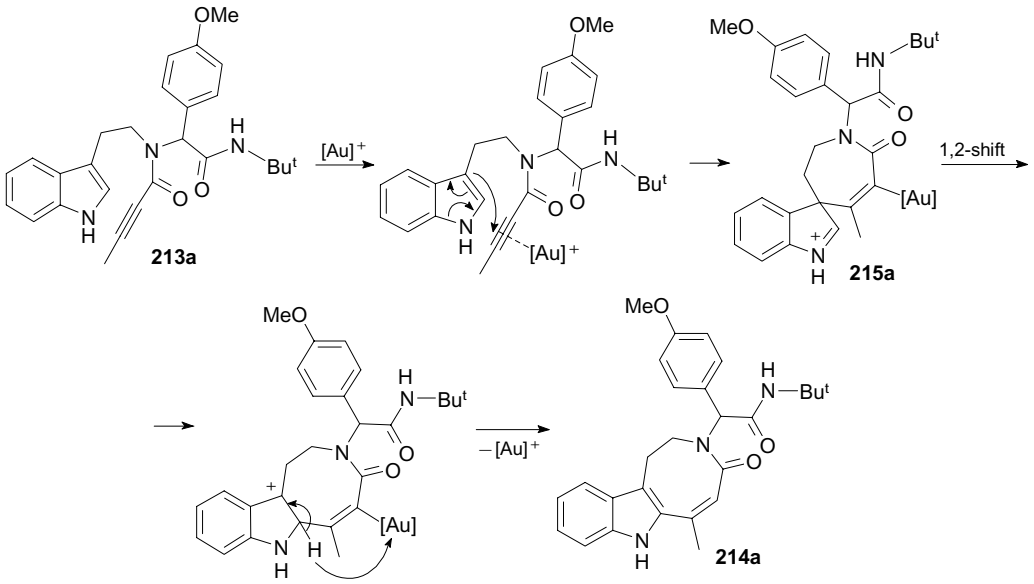
A later study of Van der Eycken's team[174] is concerned with the influence of the structure of substrate **213** on the cyclization pathway and on the nature of the resulting product. It was shown that cyclization of substrate **213** with $n = 1$ gives product **216** with a seven-membered ring (indoloazepinones); cyclization of **213** with $n = 2$ affords product **214** with an eight-membered ring (indoloazocinones). In the case of **213** containing a terminal alkyne moiety, the formal *exo*-cyclization product **217** is formed. In all cases, the gold-activated triple bond is attacked by the C(3) atom and this is followed by the 1,2-shift (Scheme 96).

One more example of attachment of the indole C(3) atom to the gold-activated triple bond has been

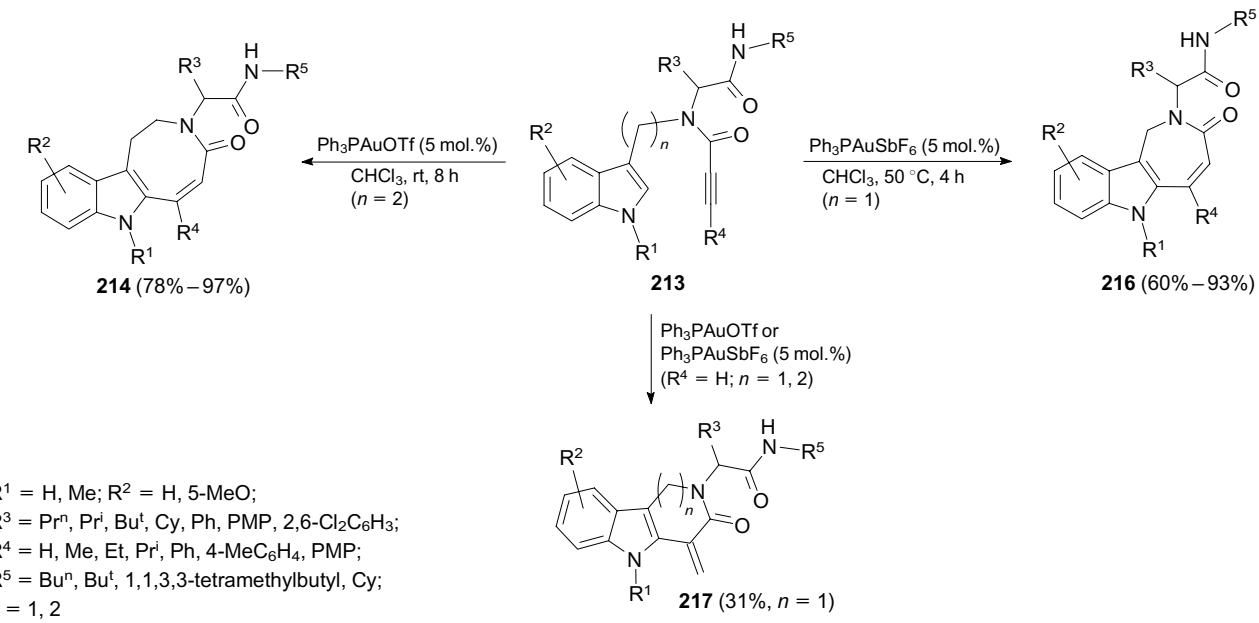
Scheme 94



Scheme 95

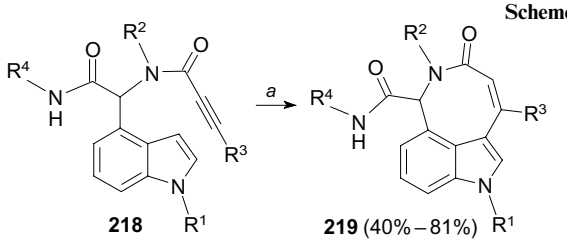


Scheme 96



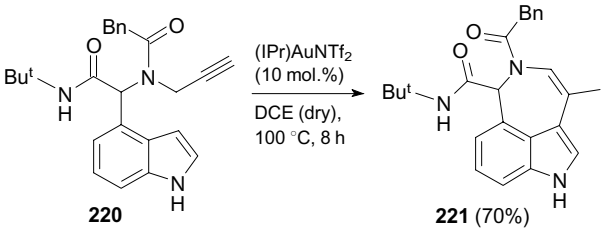
reported.[175] The 8-*endo*-*dig*-cyclization of 4-substituted indoles **218** affords azocino[*c*,*d*]indolones **219** (Scheme 97). An eight-membered ring is formed in the case of both terminal and internal alkynes. When In^{III} is used as the catalyst, the reaction is *exo*-selective and gives azepino[*c*,*d*]indolones.

Scheme 97



(*a*) (IPr)AuNTf$_2$ (10 mol.%), DCE, 100 °C, 8 h;
R^1 = H, Me, Ts; R^2 = PMB, Bu^n; R^3 = H, Me, Et, Ph;
R^4 = Bu^t, Cy

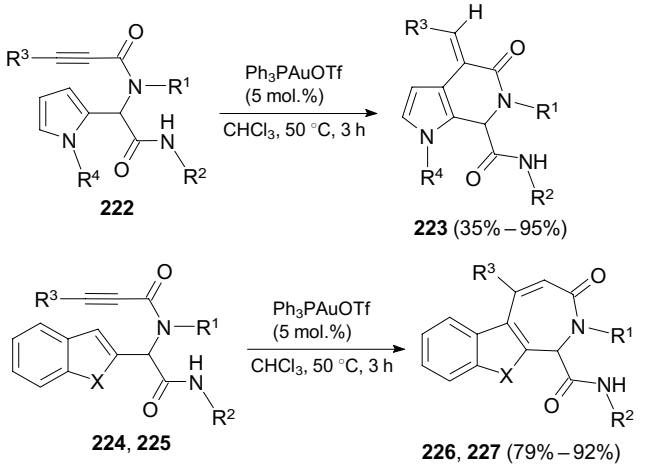
Scheme 98



Propargylamine derivative **220** participates in the (IPr)AuNTf$_2$-catalyzed intramolecular 7-*exo-dig*-hydroarylation to be selectively converted to azepinoindole **221** (Scheme 98).[175]

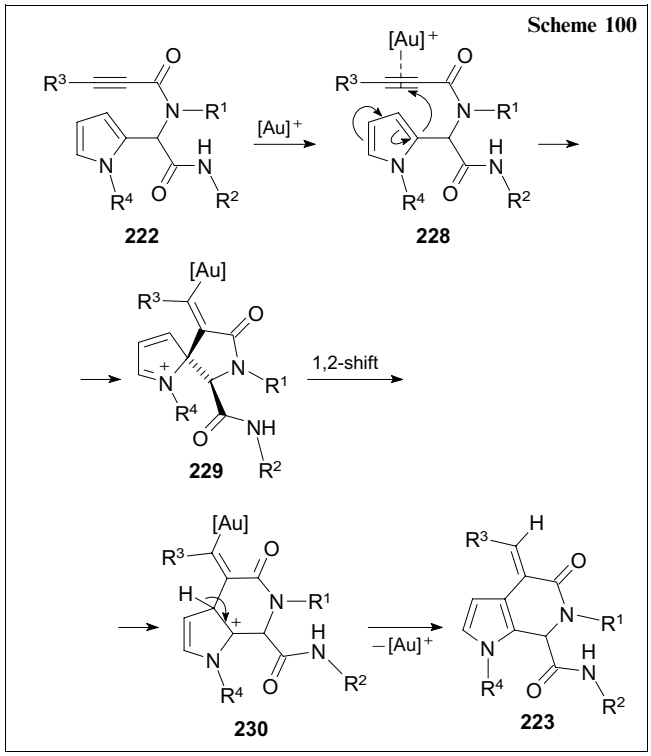
In order to compare the reactivities of pyrroles and indoles in the intramolecular hydroarylation of alkynes, a series of alkyne substrates **222**, **224** and **225** have been prepared.[176, 177] The reaction was carried out in chloroform at 50 °C using the cationic gold complex $Ph_3PAuOTf$ as the catalyst (Scheme 99). For pyrroles **222**, a six-membered ring was selectively formed as a result of 5-*exo-dig*-attack by the heteroaromatic ring on the gold-activated triple bond, which gave rise to pyrrolopyridinones **223**. In the case of indoles **224**, the alkynamide substrate underwent the selective 7-*endo-dig*-cyclization, resulting in the formation of azepinoindoles

Scheme 99



X = NR^4 (**224**, **226**), S (**225**, **227**); R^1 = Bu^n, n-C_5H_{11}, Cy, Bn, PMP, cyclo-C_3H_5; R^2 = Bu^t, Cy; R^3 = Me, Et, Ph, PMP; R^4 = H, Me, Bn, 4-MeC_6H_4, Ts

Scheme 100

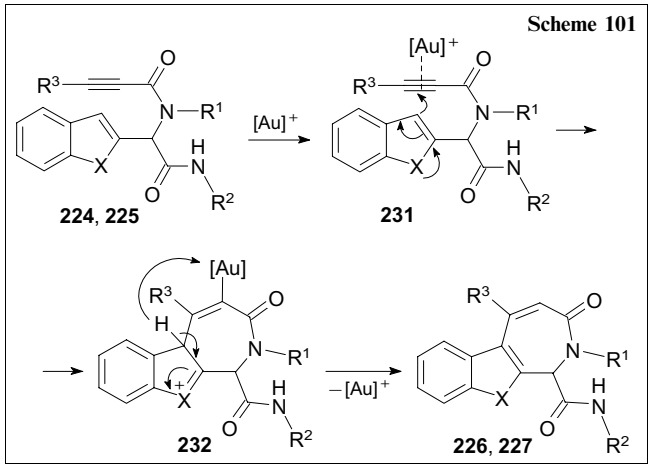


226. A similar situation was also observed for benzothiophenes **225**, which underwent 7-*endo-dig*-cyclization, being converted to azepinobenzothiophenes **227**.

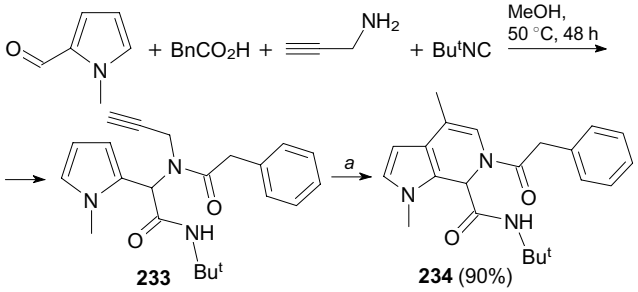
The mechanism of this reaction for pyrrole derivatives **222** is shown in Scheme 100. It is known[177–180] that nucleophilic attack of pyrroles occurs with their C(2) atom (α-carbon). Gold(I) activates the triple bond. In the case of pyrroles **222**, the nucleophilic *exo-dig*-attack of the activated alkyne **228** takes place to give spiro intermediate **229**, which is converted to intermediate **230** *via* 1,2-shift; the latter is deprotonated and protodeaurated, thus being converted to pyrrolopyridinone **223**. It is of interest that the direction of the attack is substantially affected by the nature of the catalyst used. Thus in the presence of Au^{III}, a nucleophilic *endo-dig*-attack takes place to give a seven-membered ring (see below Scheme 105).

In the case of indoles **224** and benzothiophene **225**, nucleophilic attack by the C(3) atom (β-carbon, Scheme 101), which does not give a spiro intermediate,

Scheme 101

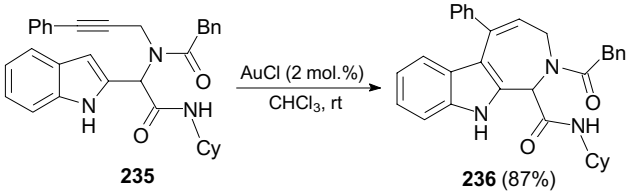


Scheme 102

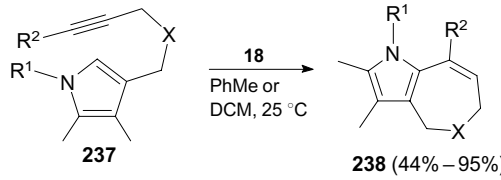


(*a*) AuCl (2 mol.%), $CHCl_3$, rt

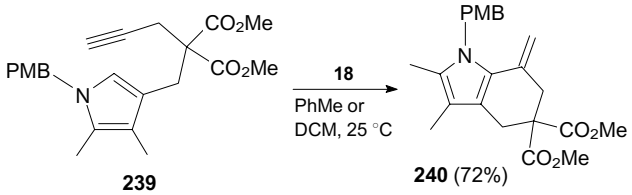
Scheme 103



Scheme 104

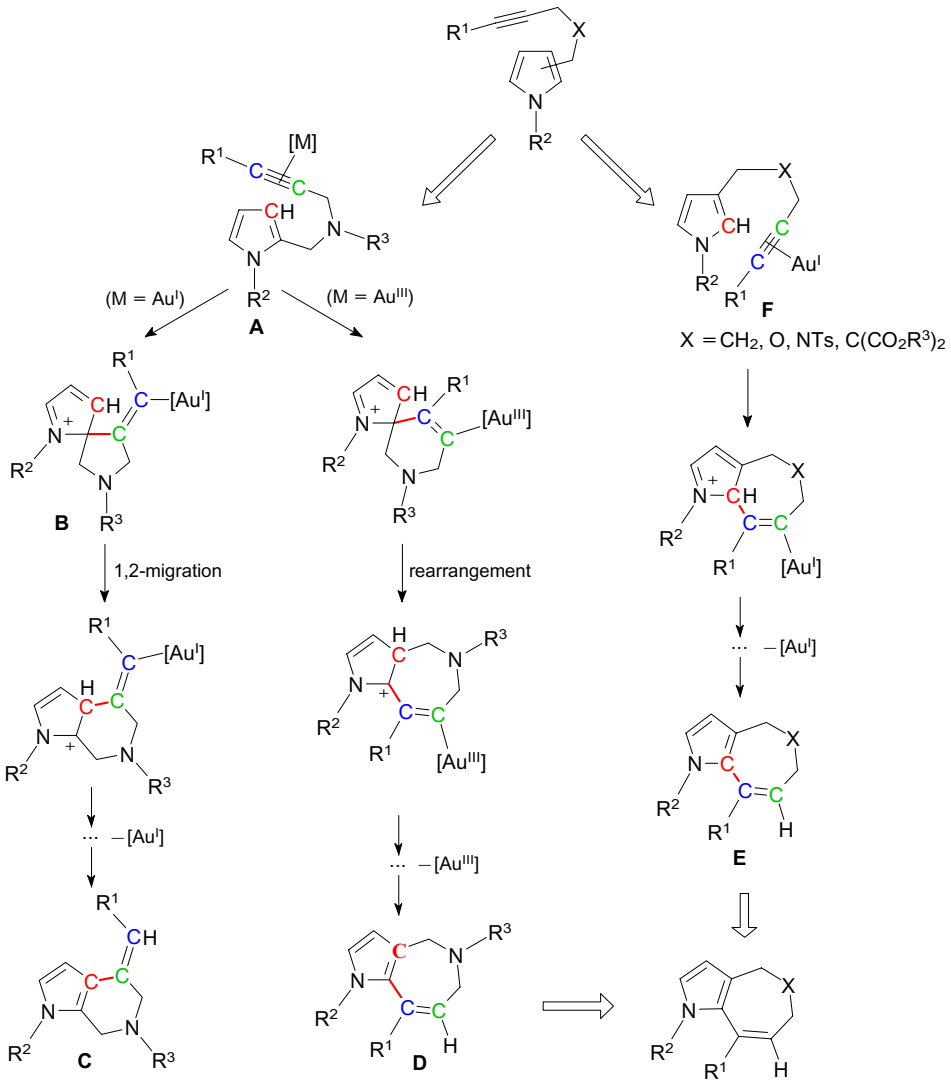


R^1 = Bn, 2-$MeOC_6H_4CH_2$, 3-$MeOC_6H_4CH_2$, 4-$MeOC_6H_4CH_2$, PhCH(Me), Cy, $(MeO)_2CHCH_2$; R^2 = Me, Ph; X = $C(CO_2Me)_2$, CH_2, NTs, O



is more usual. The direct attack by the C(3) atom of the heterocycle on the gold-activated triple bond in intermediate **231** occurs in the *endo-dig* mode to give inter-

Scheme 105



mediate **232**. The subsequent deprotonation and protodeauration lead to azepinones **226** and **227**.

Derivative **233** obtained by the Ugi reaction was also used for this type of cyclization.[181] A combination of four-component Ugi reaction and gold(I)-catalyzed hydroarylation under mild conditions can be used to obtain complex polycyclic compounds, for example, product **234** (Scheme 102).

The reaction is carried out in the presence of 2 mol.% AuCl in chloroform at room temperature. The key stage is 5-*exo*-*dig*-cyclization in which the pyrrole C(2) atom acts as the nucleophile that attacks the gold-activated triple bond. If the product of the Ugi reaction contains an indole moiety (substrate **235**), the reaction proceeds as 7-*endo*-*dig*-cyclization to give tricyclic compound **236** (Scheme 103).

Pan *et al.*[182] described an efficient approach to alkenylation of β-alkynylpyrroles **237** in which the double bond of the heterocycle acted as the alkene component. The intramolecular *endo*-selective reaction afforded a number of pyrrole derivatives **238** with a fused seven-membered ring (Scheme 104).

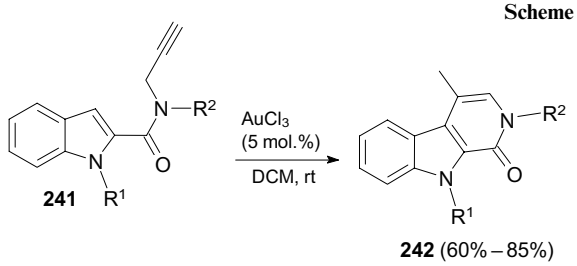
For substrate **239** in which R^2 = H, selective 6-*exo*-*dig*-cyclization takes place to give product **240** in 72% yield (see Scheme 104). In the case of R^2 = TMS, the reaction product is not formed.

As noted above (see Scheme 100), in the case of α-alkynylpyrroles **A**, the gold-activated triple bond is also attacked initially by a more nucleophilic α-carbon atom to give spiro intermediate **B**, which then rearranges (Scheme 105).[180] The structure of the reaction product depends on the nature of the catalyst: in the case of Au^I, the *exo*-product **C** with an annulated six-membered ring is formed selectively, whereas the use of the Au^{III} catalyst affords annulated seven-membered ring **D**. The structure of product **D** is, in this case, identical to the structure of product **E** derived from β-substituted substrate **F**, which is caused by the rearrangement.

The cycloisomerization of 1,6-enyne indole derivatives **241** can lead to the synthesis of tricyclic heterocycles **242** (Scheme 106).[183]

Liu and co-workers[184] employed the Au^I-catalyzed cycloisomerization of 3-acylindolines **243** to prepare

Scheme 106

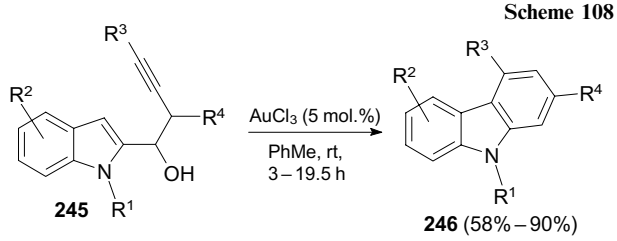


R^1 = Me, Bn; R^2 = Me, Ac, Ts, Boc, Cbz

carbazole derivatives **244** (Scheme 107), which are important intermediates in the synthesis of natural products.[185] The 6-*endo*-*dig*-cyclization proceeds at room temperature in the presence of $(4\text{-}F_3CC_6H_4)_3PAuOTf$ (5 mol.%) and 5 equiv. of H_2O. The yield of 2-hydroxycarbazole **244**, which is formed as the only product, reaches 80%. Water participates in the reaction; when no water is added, the yield of product **244** drastically decreases. The mechanism of this reaction proposed by the authors is depicted in Scheme 107.

Gold(III) catalyzes the benzannulation of alk-3-ynyl-1-ol-substituted indole **245**, resulting in the formation of substituted carbazoles **246** (Scheme 108).[186, 187]

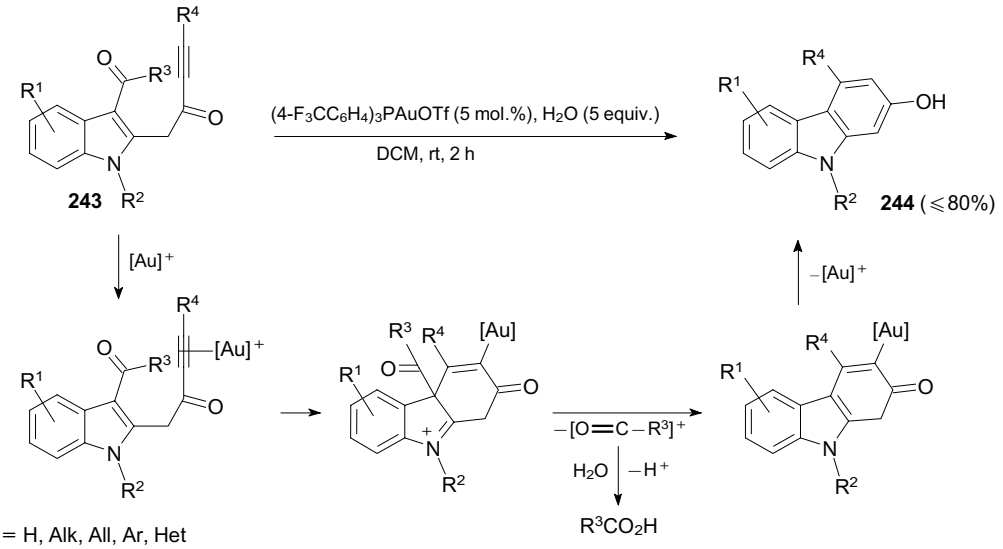
Scheme 108



R^1 = Et, Bn, PMB; R^2 = H, 5-Me, 5-OMe, 5-Br, 4-Me, 7-Me; R^3 = Me, Et, Ph; R^4 = Et, Bu^n, Ph

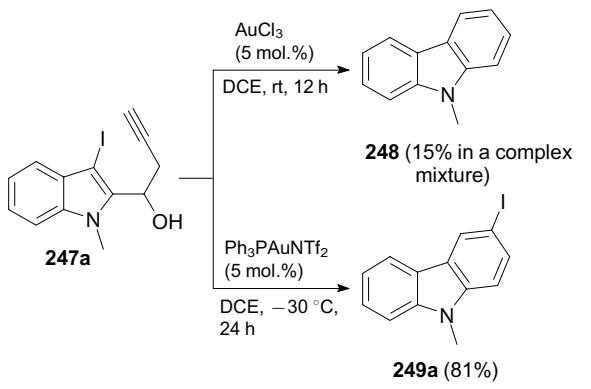
In the case of substrate **247a**, the $AuCl_3$-catalyzed reaction at room temperature affords a complex mixture containing 15% of product **248**.[188] However, in the

Scheme 107

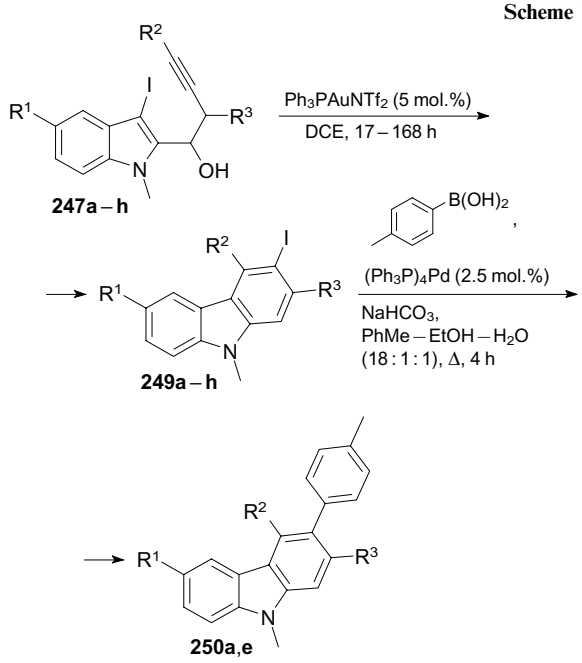


R^1, R^2, R^3, R^4 = H, Alk, All, Ar, Het

Scheme 109



Scheme 110

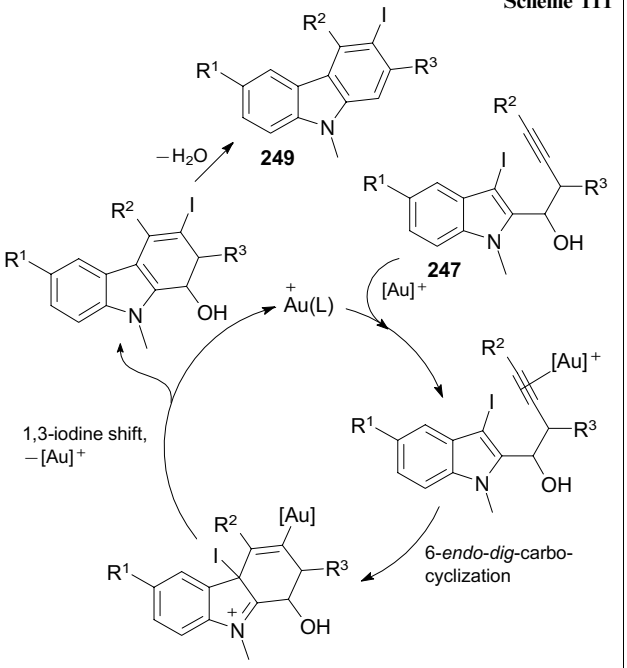


Compounds **247**, **249**, **250**	R^1	R^2	R^3	Yield of **249** (%)	Yield of **250** (%)
a	H	H	H	81	83
b	H	Ph	Me	71	–
c	H	Et	Me	70	–
d	MeO	H	H	9	–
e	MeO	Ph	Me	58	83
f	MeO	Et	Me	51	–
g	Cl	H	H	40	–
h	Cl	Ph	Me	not isolated	–

presence of $Ph_3PAuNTf_2$ at −30 °C, compound **249a** is formed in 81% yield (Scheme 109).

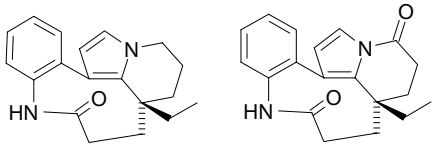
This reaction can be carried out for substrates with different substituents (Scheme 110). The first step is 6-*endo*-*dig*-carbocyclization of the alkyne upon the chemo- and regiospecific attack on the indole C(3) atom by the outer carbon atom of the alkyne followed by stepwise 1,3-migration of the iodine atom and dehydration. Products **249** can be used in subsequent transformations, *e.g.*, in the Suzuki reaction (see Scheme 110, compounds **249a**,**e**). The mechanism proposed[188] for the cyclization of alkynes **247** is shown in Scheme 111.

Scheme 111



Heterocyclic compounds with medium rings are widely encountered among natural biologically active products and are considered, more and more often, as potential pharmaceuticals.[189–191] For example, (−)-rhazinilam (**251**) and (−)-rhazinicine (**252**) — alkaloids containing a nine-membered heterocycle — exhibit anticancer activity.[192]

Structures 251, 252

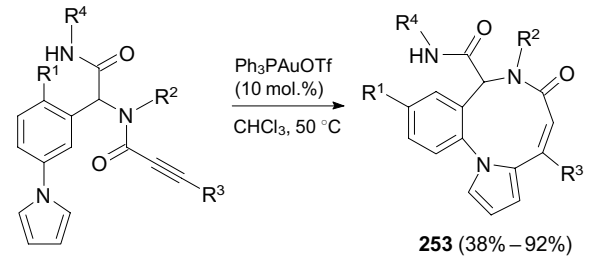


251 **252**

The difficulty of laboratory synthesis of compounds of this type are due to both enthalpy and entropy factors, and, as a result of certain conformational restrictions in acyclic precursors, direct methods for their cyclization are often inefficient.[193] A possible strategy to tackle this synthetic challenge is to use ring expansion reactions. Both in this case and in the case of thermodynamically feasible direct cyclization, considerable advances in this synthetic area have been made owing to transition metal catalysis,[194] in particular, catalysis by gold cations.[195]

The approach used rather widely by Van der Eycken's group, comprising a combination of the multicomponent Ugi reaction and gold catalysis, allowed the efficient synthesis of benzo[*b*]pyrrolo[2,1-*i*][1,5]diazonin-7(6*H*)-ones **253** containing a nine-membered heterocycle (Scheme 112).[195]

Scheme 112



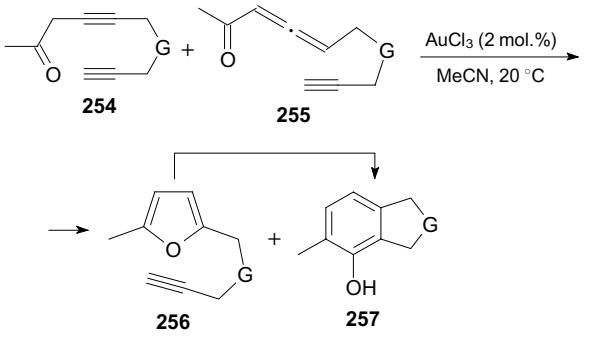
253 (38% – 92%)

R^1 = H, Cl; R^2 = PMB, 3,4-DMB; R^3 = H, Me, Et, Ph; R^4 = Bu^n, Bu^t, 4-MeC_6H_4

In his pioneering studies of the gold-catalyzed organic reactions, A.Stephen K.Hashmi addressed the formation processes of new C – C and C – O bonds.[107, 132, 196] In particular, he intended to convert a mixture of substrates **254** and **255** to alkynyl-substituted furan **256** *via* an $AuCl_3$-catalyzed reaction. This product was actually obtained,[136] but as a mixture with phenol **257** (Scheme 113).

Hashmi *et al.*[132] suggested and demonstrated that product **256** is formed from substrates **254** and/or **255** *via* the nucleophilic addition of the oxygen atom to gold-activated triple bond. In turn, product **256** can undergo the subsequent gold-catalyzed cycloisomerization to afford phenol **257**. Thus, in this case, gold catalyzes two separate successive reactions, resulting in a mixture of products **256** and **257**. It was shown[136] that compound **256** is completely converted to phenol **257** under the action of a gold catalyst. Since the phenol-containing reaction proceeds in good yield, which allows its practical use, this reaction was named as the Hashmi phenol synthesis. Examples of Hashmi syntheses of phenols are depicted in Scheme 114.[197 – 201]

Scheme 113



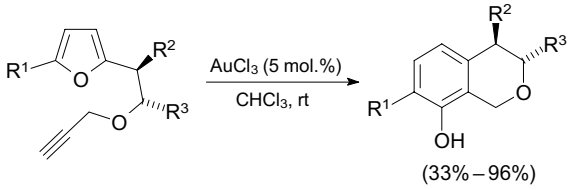
254 **255** **256** **257**

G	Yield of **256** (%)	Yield of **257** (%)
CH_2	24	35
O	5	52
NTs	55	36

A reasonable mechanism for the gold-catalyzed synthesis of phenols was proposed by a Chinese research team[202] on the basis of analysis of known experimental data and quantum chemical modelling (DFT TPSSh/def2-TZVP method). This mechanism is shown in Scheme 115.

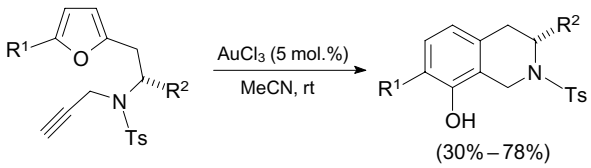
The mechanism implies cycloisomerization of 1,6-enyne **256** to afford carbenoid intermediate **259**, which undergoes double cleavage to be finally converted to oxirane **259′**, which then rearranges to phenol **257**.

Scheme 114



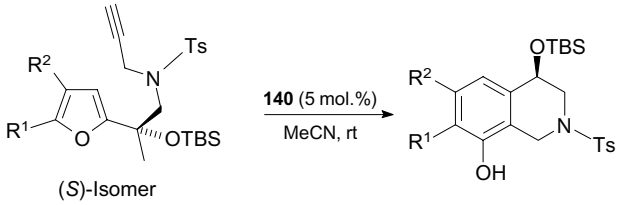
(33% – 96%)

R^2 = H: R^1 = H, Me, n-C_5H_{11}; R^3 = H, Bu^n, Ph, $CH_2OCH_2CH{=}CH_2$; $R^2 – R^3$ = $(CH_2)_3$, $(CH_2)_4$ (Ref. 197)



(30% – 78%)

R^1 = Me, n-C_5H_{11}; R^2 = H, Me (Ref. 198)



(*S*)-Isomer

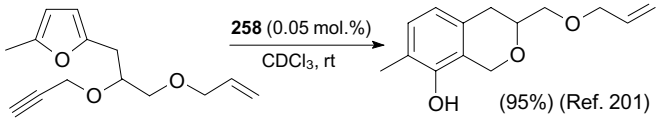
(*R*)-Isomer (45% – 99%, *ee* ⩽99%)

R^1 = H, Me, Et, Ph;
R^2 = H, Me (Ref. 199)

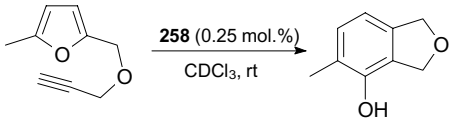


(51% – 99%)

R^1 = H, Me, 3-$F_3CC_6H_4$; R^2 = H, Me; R^3 = Bu^t, 4-MeC_6H_4;
R^4 = Et, Ph, $HC{\equiv}CCH_2$, cyclo-C_3H_5 (Ref. 200)



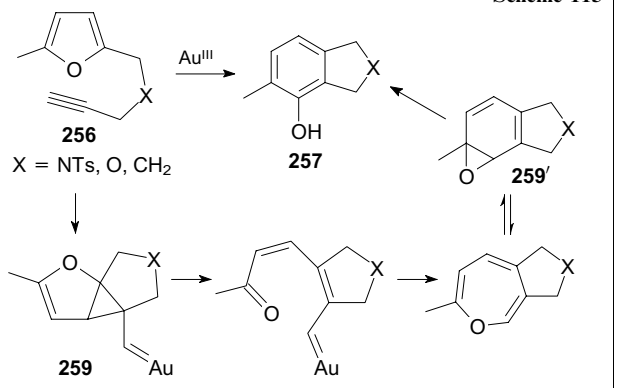
(95%) (Ref. 201)



(70%) (Ref. 201)

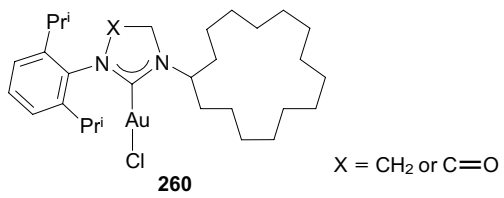
258 =

Scheme 115



Zargaran *et al.*[203] reported a study of new unsymmetrical substituted five-membered saturated N-heterocyclic carbene (NHC) and N-heterocyclic oxocarbene (NHOC) Au^{I} complexes, which proved to be efficient, in particular, in the Hashmi synthesis of phenols, for example, complexes **260**.

Structure 260

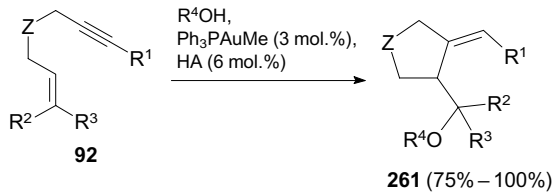


2.1.1.6. Cyclization of alkynes in the presence of a nucleophile

In the presence of a nucleophile representing either a nucleophilic group in the molecule or another molecule, the behaviour of the gold cyclopropyl carbenoid changes, and its electrophilic activity is delocalized. The nucleophilic attack can be directed to either the cyclopropane moiety or the carbenoid carbon atom. Examples of such reactions have been considered above in the discussion of enyne cycloisomerization; here we will dwell on this aspect in more detail.

Under conditions used for O-nucleophile addition to alkyne by Tanaka and co-workers[204] and considered in the previous review,[1] 1,6-enynes **92** are converted to methoxycyclization products **261** (Scheme 116).[81]

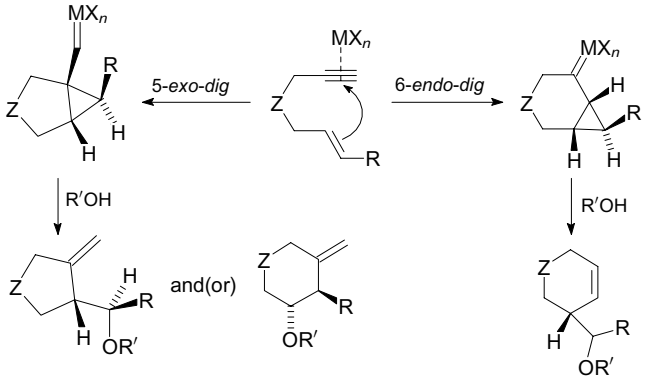
Scheme 116



Z = $C(CO_2Me)_2$, $C(SO_2Ph)_2$, NTs; R^1 = H, Ph; R^2 = H, Me; R^3 = Me, OMe; R^4 = H, Me, Et; HA is protic acid

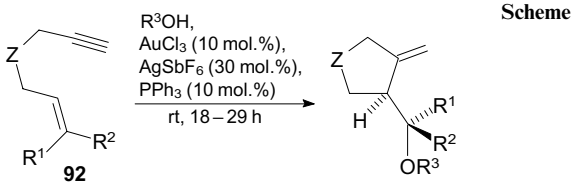
The mechanism of this reaction is presented in Scheme 117. Gold(I) was found to be the most active catalyst for the cycloisomerization of enynes accompanied by nucleophile addition. Gold compounds are more efficient than Pt^{II}-based catalysts.[205] In addition, being alkynophilic, gold activates the reaction by beeing selectively coordinated (as a complex) to the enyne triple bond. The reaction follows a mechanism differing from those described for Pd^{II}-, Hg^{II}- or Rh^{I}-based catalysts.

Scheme 117

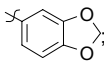


A similar cyclization of 1,6-enynes **92** in the presence of an external nucleophile has been reported by Genin *et al.*[16] (Scheme 118).The researchers used $AuCl_3$ mixed with a silver salt and triphenylphosphine as the catalyst, while primary, secondary and allylic alcohols or a water – dioxane mixture served as external nucleophiles (and solvents). The reaction was carried out at room temperature. The cyclization afforded cyclopentane, tetrahydrofuran and pyrrolidine derivatives **261**. In the case of cyclization of 1,7-enynes under similar conditions, the corresponding six-membered cyclic compounds were formed, but in lower yields, because of the competing triple bond hydration.

Scheme 118



Z = $C(CO_2Me)_2$, $C(SO_2Ph)_2$, NTs, O;

R^1 = Me, geranyl, ; R^2 = H, Me; R^3 = H, Me, Et, All

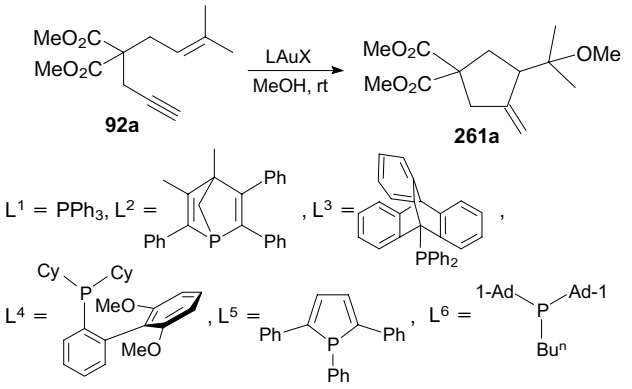
A similar result was also reported by other authors,[44,83] who used various phosphine ligands for methoxycyclization (Scheme 119).

Jiménez-Núñez *et al.*[97] considered the stereoselectivity of alkoxycyclization of *E*-1,6-enynes **92b – g**, which depended on the enyne and solvent natures (Scheme 120). The reactions showed *anti*-selectivity or predominant formation of the *anti*-isomer.

Leyva-Pérez and Corma[206] reported Au-, Pt- and Hg-catalyzed alkoxy(hydroxy)carbocyclizations of 1,6-enyne **92a** (Scheme 121).

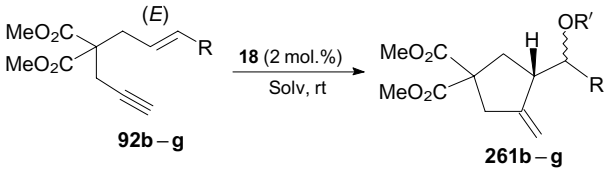
In the presence of the chiral Au^{I} complex, cycloisomerization of enynes with addition of an external

Scheme 119



Cat (mol.%)	Time	Yield of **261a** (%)
L^1AuNTf_2 (1)	2 h	94
L^1AuNTf_2 (0.1)	24 h	77
L^1AuSbF_6 (2)	3 h	84
L^2AuNTf_2 (1)	2 h	94
L^3AuNTf_2 (1)	75 min	97
L^4AuSbF_6 (2)	15 min	89
L^5AuNTf_2 (1)	75 min	96
L^6AuNTf_2 (1)	20 min	97

Scheme 120



Compounds **92**, **261**	R	Solv	R′	Time /min	Yield of **261** (%)	*anti* : *syn*
b	cyclo-C_3H_5	MeOH	Me	5	86	100 : 0
c	4-$MeOC_6H_4$	MeOH	Me	60	100	100 : 0
d	4-$MeOC_6H_4$	DCM – MeOH (5 equiv.)	Me	60	95	60 : 40
e	*N*-Boc-indol-3-yl	EtOH	Et	5	98	100 : 0
f	*N*-Boc-indol-3-yl	DCM – EtOH (5 equiv.)	Et	5	82	52 : 48
g	Ph	DCM – MeOH (5 equiv.)	Me	60	84	100 : 0

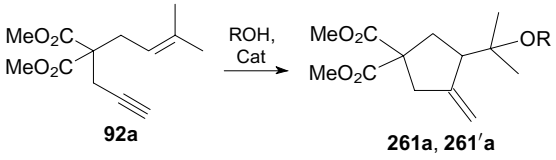
nucleophile proceeds with a high enantioselectivity (Scheme 122).[205]

If the nucleophilic group is a part of the enyne, an intramolecular reaction takes place, as, for example, for substrate **262**, which is converted to product **263** in a quantitative yield (Scheme 123).

The intramolecular version of this reaction including an attack by the hydroxy group, which is initially present in enynes **264** and **266**, results in the formation of tetrahydrofuran derivatives **265** and **267** in good yields (Scheme 124).[81]

Under the action of Au^I in the presence of alcohols, allylsilylalkynes **268** are converted to cyclic (**269**) or

Scheme 121

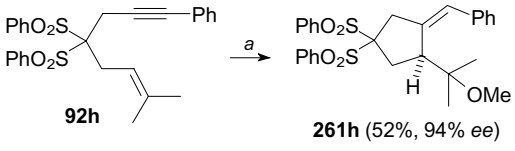


R = Me (**261b**), H (**261′b**)

Cat	Conditions	R [a]	Yield of **261a**, **261′a** (%)	Ref.
$PtCl_2$ (5 mol.%)	MeOH, 60 °C, 14 – 17 h	Me	63	207
$AuCl_3$ (5 mol.%)	MeOH, 60 °C, 14 – 17 h	Me	98	207
$[Pt(MeCN)_2Cl_2]$ – $AgSbF_6$ (5 mol.%)	MeOH, 60 °C, 14 – 17 h	Me	69	207
Ph_3PAuCl – $AgSbF_6$ (2 mol.%)	MeOH, rt, 3 h	Me	84	83
$PtCl_2$ (10 mol.%)	Me_2CO, 40 °C, 17 h	H	57	74
$Hg(OTf)_2$ (10 mol.%)	$MeNO_2$ – MeCN (9 : 1), rt, 20 h	H	90	208

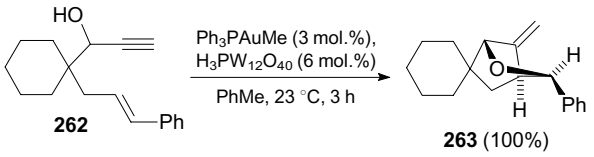
[a] In the product.

Scheme 122

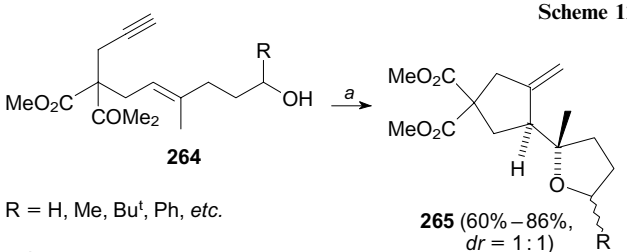


(*a*) [(*R*)-tol-BINAP-$(AuCl)_2$], $AgSbF_6$, MeOH, rt

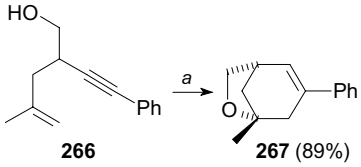
Scheme 123



Scheme 124

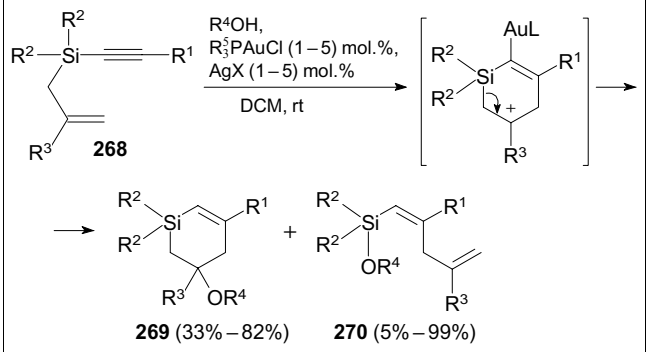


R = H, Me, Bu^t, Ph, *etc.*



(*a*) Ph_3PAuCl (3 mol.%), $AgSbF_6$ (3 mol.%), DCM, 23 °C

Scheme 125



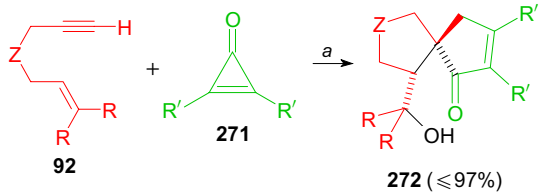
R^1 = H, Bu^n, Hex, CH_2OBn, Cy, CH(OH)Ph, CO_2Me, $(CH_2)_3Ph$; R^2 = Me, Ph; R^3 = H, Me; R^4 = Me, Pr^i, Bu^t, Bn, Ph; R^5 = Bu^t, Ph; X^- = SbF_6^-, BF_4^-

linear (**270**) alkenylsilanes (Scheme 125).[209,210] Both types of products result from the endocyclic cleavage of gold carbenoid induced by the attack of the nucleophile on the silicon or carbon atom.

The reaction pathway is considerably affected by the nature of alcohol used. Thus methanol provides predominant (or even selective) formation of cyclic product **269**; phenol leads to acyclic derivative **270**, which is formed either selectively or with a minor content of the cyclic product.

Gold(I)-catalyzed spiro-annulation of cyclopropenones **271** with 1,6-enynes **92** accompanied by ring expansion has been described by Matsuda and Sakurai[211] (Scheme 126). The reaction comprises initial 5-*exo*-*dig*-cyclization to give carbenoid **273** (Scheme 127) and the subsequent nucleophilic cyclopropane ring opening to give intermediate **274**. Cyclopropenone **271** acts as the nucleophile. A series of subsequent transformations afford intermediate **275**, which is also attacked by an external nucleophile, this time a water molecule, being converted to spirocyclic product **272**.

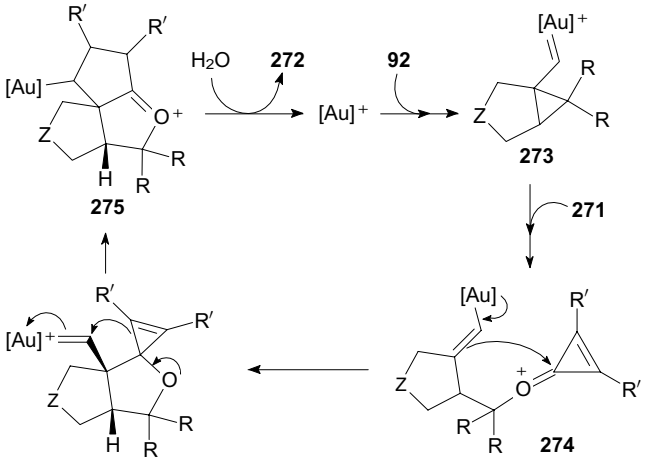
Scheme 126



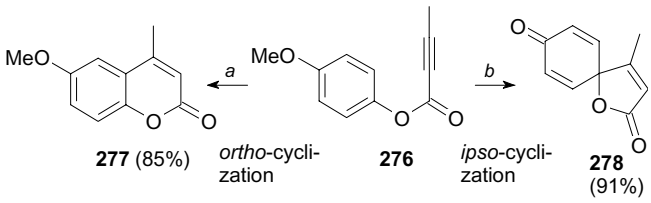
(*a*) $(IPr)AuNTf_2$ (2 mol.%), DCM (H_2O traces), rt;
Z = TsN, MsN, PhN, O, $(MeO_2C)_2C$; R = Me, Ph; R – R = $(CH_2)_5$;
R′ = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, Me, Pr^n

An example of how the reaction pathway changes in the presence of an external nucleophile has been reported by Aparece and Vadola[212] (Scheme 128). If substrate **276** reacts in anhydrous dichloroethane, coumarin **277** is formed in 85% yield. In the presence of 1 equiv. of water, *ipso*-cyclization takes place to give spirolactone **278** in 91% yield.

Scheme 127



Scheme 128

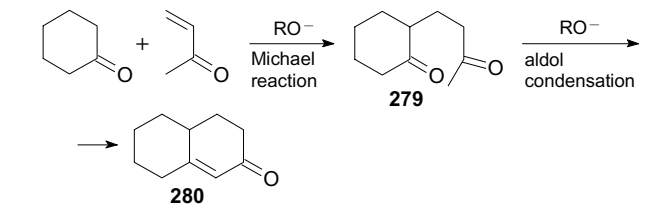


(*a*) Ph_3PAuCl (5 mol.%), AgOTf (5 mol.%), DCE (anhydr.), rt;
(*b*) Ph_3PAuCl (5 mol.%), AgOTf (5 mol.%), DCE , H_2O (1 equiv.), rt

2.1.1.7. Tandem cyclization

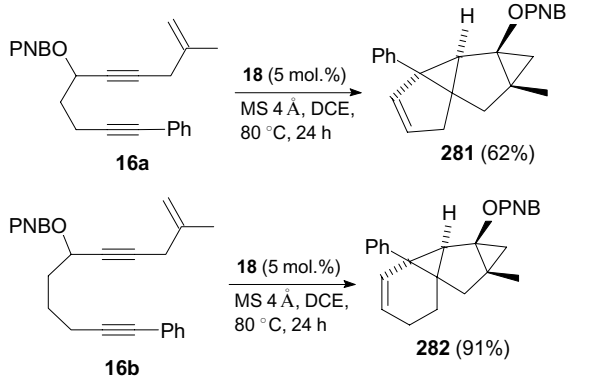
Tandem reactions are those in which structural features of primary products promote further transformations under the reaction conditions. An example of tandem reaction is the Robinson annulation.[213] For example, the reaction of cyclohexanone and methyl vinyl ketone gives diketone **279** in the first step and cyclic ketone **280** in the second step (Scheme 129).

Scheme 129



A particular case of a tandem process is the domino reaction. In this case, in the first step, a functional group is formed in the substrate; in the second step, this group reacts to give a new functional group, which reacts in the third step, *etc*. In recent years, reactions of this type have been receiving much attention,[214–217] because they allow the synthesis of complex organic compounds in one synthetic process with high efficiency. The scope of application of reactions of this type is constantly extending as new catalytic systems and reagents appear. Several reviews have been published (see, for example, Refs 215 and 218) on tandem (cascade) reactions of alkynes catalyzed by gold compounds and providing substantial complication of the molecular structure.

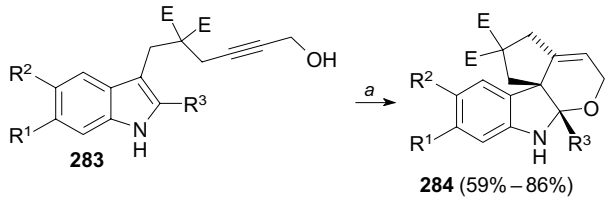
Scheme 130



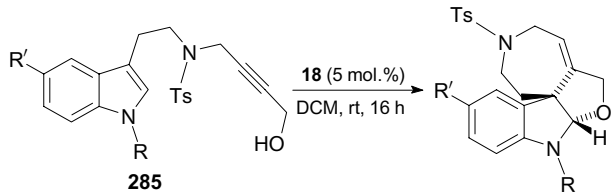
Chen *et al.*[22] reported data on the cycloisomerization of 1-ene-4,9-diyne **16a** and 1-ene-4,10-diyne **16b**, resulting in tetracarbocyclic compounds: tetracyclodecene **281** and tetracycloundecene **282**, respectively (Scheme 130). The reaction represents a tandem sequence of 1,3-migration of 4-nitrobenzoate (OPNB) and double cyclopropanation.

Indoline alkaloids with a definite stereochemical configuration have long been synthesized using multistage sequences of reactions.[219, 220] The situation has started to change in recent years, among other reasons, owing to the use of gold catalysts. Gold-catalyzed tandem reactions furnish complex heterocyclic compounds under very mild conditions.[221] For example, Italian chemists[222] used accessible N-unprotected indolylpropargyl alcohols **283** and **285** to prepare fused tetracyclic pyranoindolines **284** and furoindolines **286** *via* a gold-catalyzed tandem reaction (Scheme 131).

Scheme 131



(*a*) **18** (5 mol.%), DCM, rt, 16 h; R^1 = H, Cl; R^2 = H, Me, OMe, Cl, Br; R^3 = H, Me; E = CO_2Me, CO_2Et, CO_2Bu^t

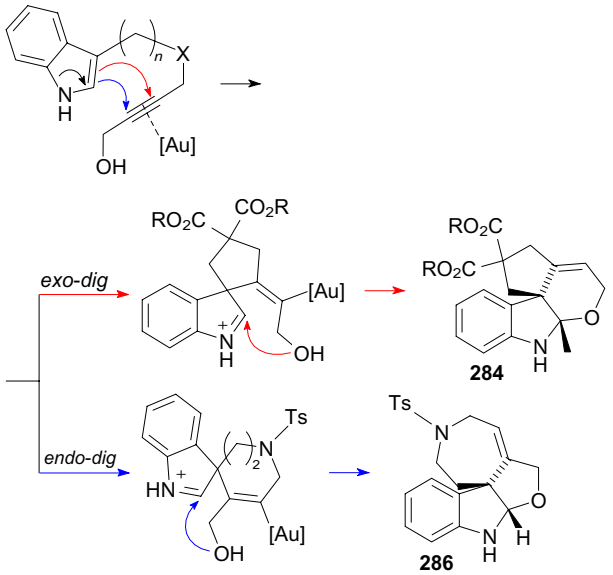


R = H, Me; R′ = H, Cl, OMe

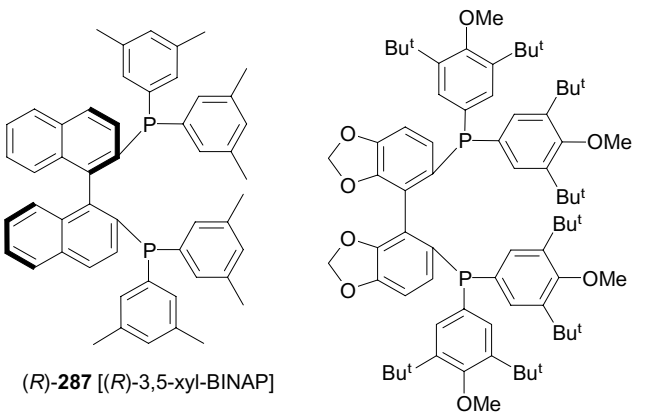
The presumptive mechanism of this reaction is presented in Scheme 132.[222] The reaction starts from the electrophilic activation of the triple bond by Au^I. This is followed by formation of spirocyclic intermediates.

Later, these tetracyclic compounds were obtained with high enantioselectivity owing to the use of gold complexes with chiral ligands: [{(*R*)-**287**}$(AuBF_4)_2$] for product **284** and [{(*S*)-**288**}$(AuOTf)_2$] for product **286**.[223]

Scheme 132

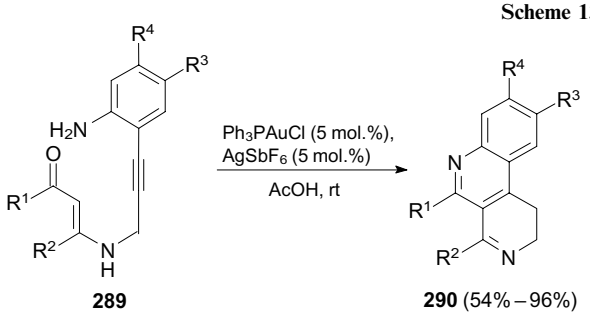


Structures 287, 288



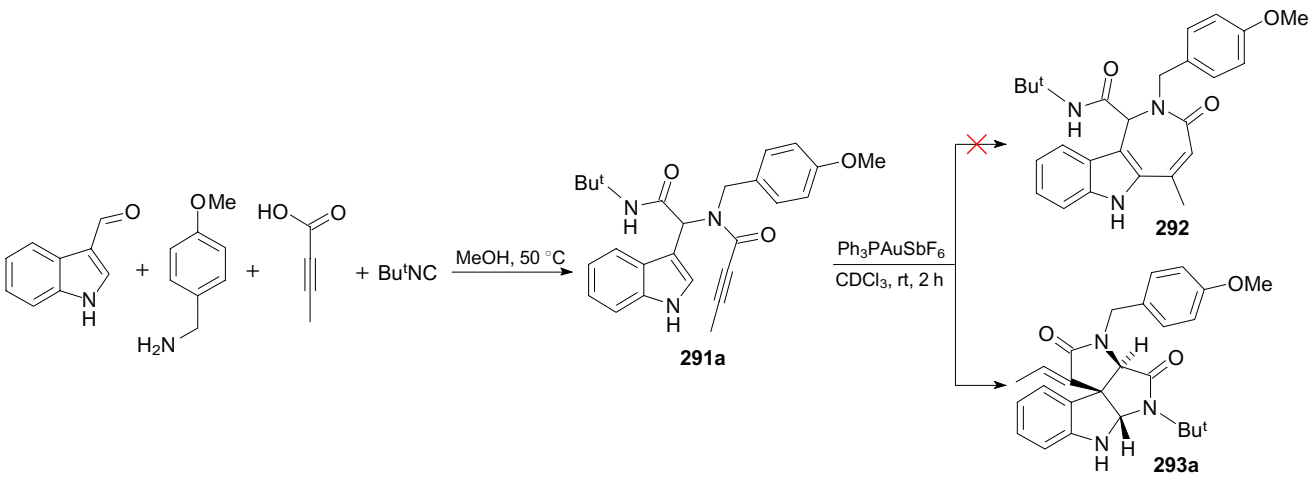
The gold-catalyzed tandem intramolecular cyclization – condensation of 2-alkynylanilines **289** can serve to obtain 1,2-dihydrobenzo[*c*][2,7]naphthyridines **290** in high yields under mild conditions (Scheme 133).[224] The reaction is accompanied by successive formation of new

Scheme 133

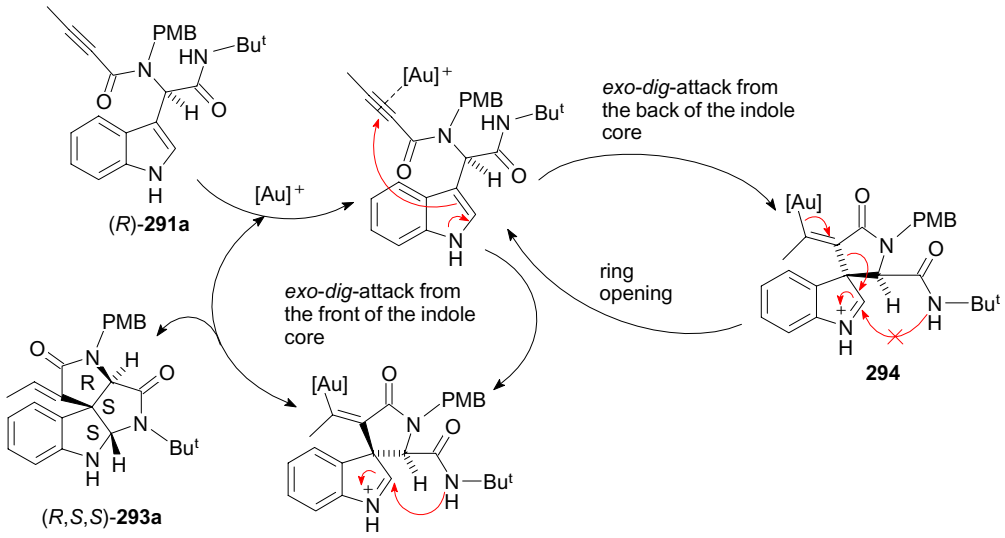


R^1 = Ph, 4-BrC_6H_4, 4-ClC_6H_4, 4-NCC_6H_4, 4-$F_3CC_6H_4$, 4-FC_6H_4, 4-$MeOC_6H_4$, 4-$Bu^tC_6H_4$, 4-EtC_6H_4, 2-Naph, 2-Th, Cy;
R^2 = Ph, 4-MeC_6H_4, n-C_5H_{11}; R^3 = H, Me, Cl; R^4 = H, Cl

Scheme 134



Scheme 135



C – C and C – N bonds as a result of 6-*endo-dig*-cyclization and condensation, respectively.

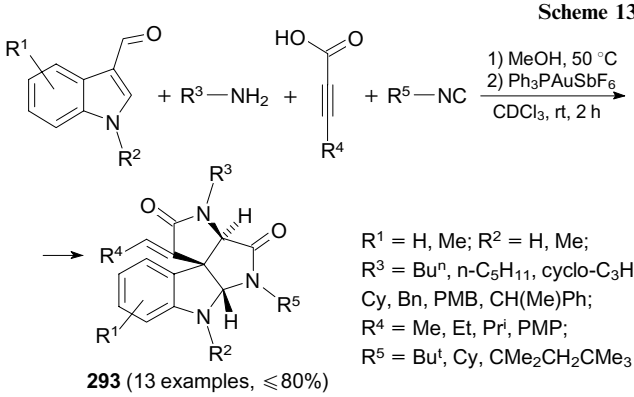
Van der Eycken's research team with a great experience in gold-catalyzed transformations of Ugi reaction products [165, 174] prepared the corresponding adduct **291a** in 71% yield (Scheme 134).

Modha *et al.*[225] intended to convert compound **291a** to indoloazepinone **292** *via* gold-catalyzed 7-*endo-dig*-cyclization [with the attack by the indole C(2) atom on the gold-activated triple bond] followed by rearrangement. However, it was found that the reaction follows the *exo-dig*-cyclization pathway with subsequent intramolecular formation of the spiro intermediate, which finally leads to diastereoselective preparation of the tetracyclic spiroindoline **293a** in 61% yield (see Scheme 134). This result was unexpected, because the α-nucleophilic attack on an alkyne conjugated to an amide is a rare case, as also the formation of a spiro intermediate by the sterically hindered *tert*-butylamide.

Scheme 135 presents the mechanism of this reaction proposed by the authors,[225] which accounts, in particular, for the diastereoselectivity of the reaction. Thus, the nucleophilic attack by the amide nitrogen atom on the indole C(2) atom in intermediate **294**, which has formed upon *exo-dig*-attack from the back side of the indole core, is impossible. Hence, the chiral centre that is already present in substrate **291** dictates the diastereoselectivity of the domino cyclization.

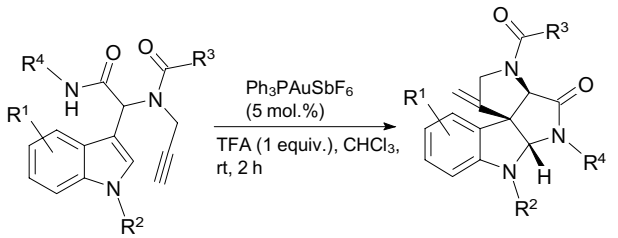
A sequence comprising the multicomponent Ugi reaction and the tandem cycloisomerization reaction allowed the authors to considerably complicate the structure of the initial indole-3-carbaldehydes in only two steps [225] with diastereoselective formation of tetracyclic spiroindolines **293** (Scheme 136). However, if R^2 = Ts or R^5 = Bu^n, no cycloisomerization takes place.

Scheme 136



R^1 = H, Me; R^2 = H, Me;
R^3 = Bu^n, n-C_5H_{11}, cyclo-C_3H_5, Cy, Bn, PMB, CH(Me)Ph;
R^4 = Me, Et, Pr^i, PMP;
R^5 = Bu^t, Cy, $CMe_2CH_2CMe_3$

Scheme 137



(±)-**295** (60% – 81%)

R^1, R^2 = H, Me; R^3 = Bn, PMB, Bu^t, $(CH_2)_2Ph$; R^4 = Bu^n, Bu^t, Cy

A similar protocol was used to prepare tetracyclic indoline derivatives **295**.[226] In this case, propargylamines (see Scheme 102) rather than but-2-ynoic acids (see Schemes 94, 134) served as the source of the triple bond. This reaction also proceeds with absolute diastereoselectivity (Scheme 137).

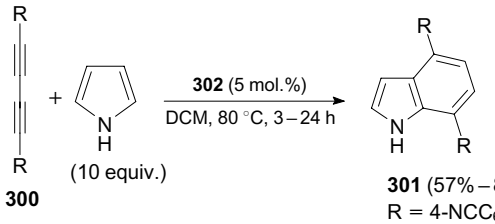
A tandem reaction including successive 5-*endo-dig*- and 7-*endo-dig*-cyclizations, both catalyzed by Au^I, has been reported by Naoe *et al.*[227] The reaction is carried out for aniline derivative **296** containing a conjugated diyne moiety (Scheme 138). The first step includes intramolecular hydroamination of one triple bond to give indole **297**, which undergoes one more cycloisomerization to give indole fused to a seven-membered ring of indole **298**. Indoles **299** with a six-membered fused heterocycle were detected as minor products.

The cascade reactions of symmetrically substituted 1,3-diynes **300** (Ref. 228) and 1,4-diynes **303** (Ref. 229) with pyrrole catalyzed by gold phosphine complexes **302** and **18** produce indoles **301** and 1,6-dihydrocyclohepta[*b*]pyrroles **304**, respectively, in good yields (Scheme 139).

In the case of unsymmetrically substituted alkynes and for substituted pyrrole, the product yields in the above reactions markedly decrease.

A tandem conversion of propargyl vinyl ethers **37** to furans **38** comprising the Claisen rearrangement and cyclization is shown in Scheme 15 (see Section 2.1.1.2.2). The synthetic route to highly substituted pyrroles **305** based on the tandem rearrangement – condensation – cyclization reaction catalyzed by silver and gold (Scheme 140) proposed by Kirsch's research team[230] can be considered as a version of this approach. The one-pot reaction proceeds *via* the Ag^I-catalyzed Claisen rear-

Scheme 139

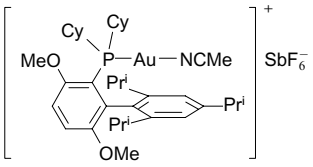


300

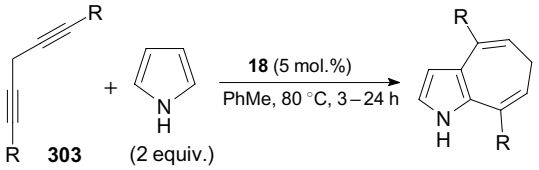
301 (57% – 85%;
R = 4-NCC_6H_4: < 18%,
4-$MeO_2CC_6H_4$: < 26%,
Cy: 35%)

R = Bu^n, Cy, Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-NCC_6H_4, 4-$MeO_2CC_6H_4$, 4-MeC_6H_4, 3-MeC_6H_4, 2-MeC_6H_4, 2-Th, 3-Th

302 =



[BrettPhosAu(MeCN)SbF_6]

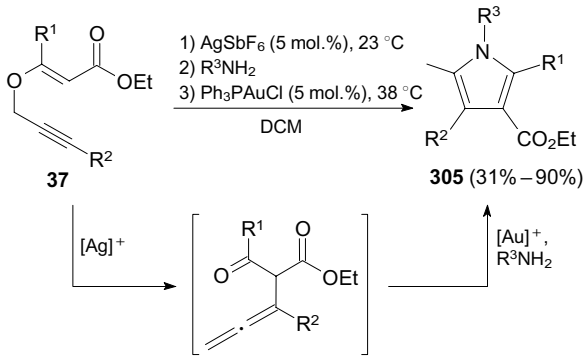


303

R = Bu^n, Ph, 4-$MeOC_6H_4$, 4-BrC_6H_4, 4-NCC_6H_4, 4-MeC_6H_4, 3-MeC_6H_4, 2-MeC_6H_4

304 (64% – 80%;
R = Bu^n: < 24%,
4-NCC_6H_4: 32%)

Scheme 140

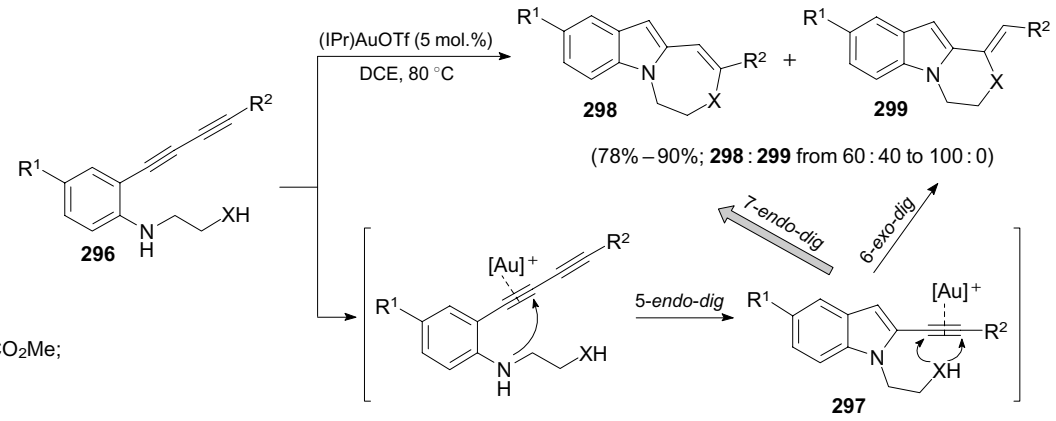


37

305 (31% – 90%)

R^1 = Me, n-C_5H_{11}, Ph; R^2 = H, Me, Ph, TBS, 2-$MeOC_6H_4$, 3-Th;
R^3 = Ph, PMP, 4-$Pr^iC_6H_4$, 3-ClC_6H_4, 4-BrC_6H_4, 1-Naph

Scheme 138



296

298 **299**

(78% – 90%; **298** : **299** from 60 : 40 to 100 : 0)

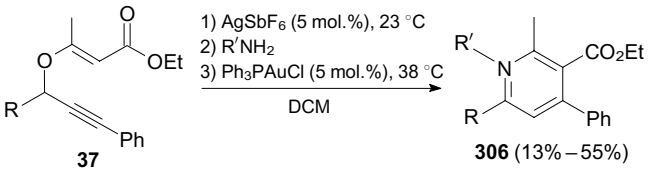
297

X = O, NBoc;
R^1 = H, OCF_3, CO_2Me;
R^2 = Alk, Ar

rangement, condensation with the amine and Au^I-catalyzed 5-*exo*-*dig*-heterocyclization. 2-Iodoxybenzoic acid (IBX) can selectively oxidize the obtained products **305** to the corresponding 5-formylpyrroles, which bear a high synthetic potential and can be used for further transformations.

If the propargyl moiety of substrate **37** contains R ≠ H, the yield of pyrrole **305** decreases (R = Me) or the whole reaction pathway changes. In the case of R = Et or Ph, six-membered heterocycle **306** is formed (Scheme 141).

Scheme 141

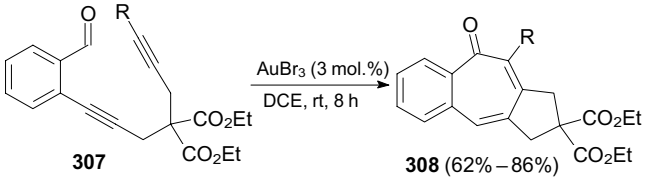


R = Et, Ph; R′ = Ph, 4-Pr^{i}C$_6$H$_4$, 3-ClC$_6$H$_4$

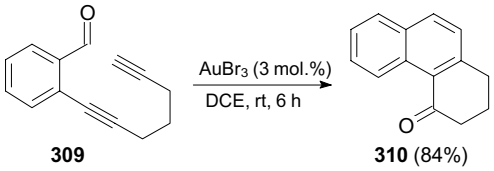
The cycloisomerization of *o*-alkynylbenzaldehydes **307** yields tricyclic compounds **308** *via* [3 + 2]-cycloaddition (Scheme 142).[231] It is of interest that in the case of substrate **309**, which is devoid of the *gem*-diester group between the alkyne moieties, the reaction affords dihydrophenanthrenone **310** as a result of [4 + 2]-benzannulation (see Scheme 142).

The tandem alkynylation – cyclization sequence starting from terminal alkynes with *o*-alkynylarylaldehydes **311** leads to 1-alkynyl-1*H*-isochromenes **312** (Scheme 143).[232]

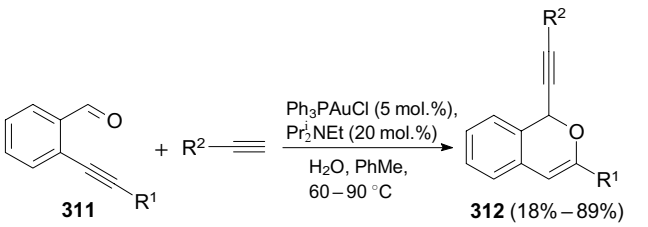
Scheme 142



R = H, Me, Bu^n, SiMe$_3$, Ph



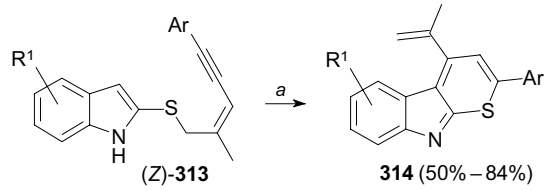
Scheme 143



R^1 = Bu^n, Bu^t, cyclohexen-1-yl; R^2 = Hex, cyclohexen-1-yl, Ph, 4-MeC$_6$H$_4$, 4-BrC$_6$H$_4$, 4-MeOC$_6$H$_4$

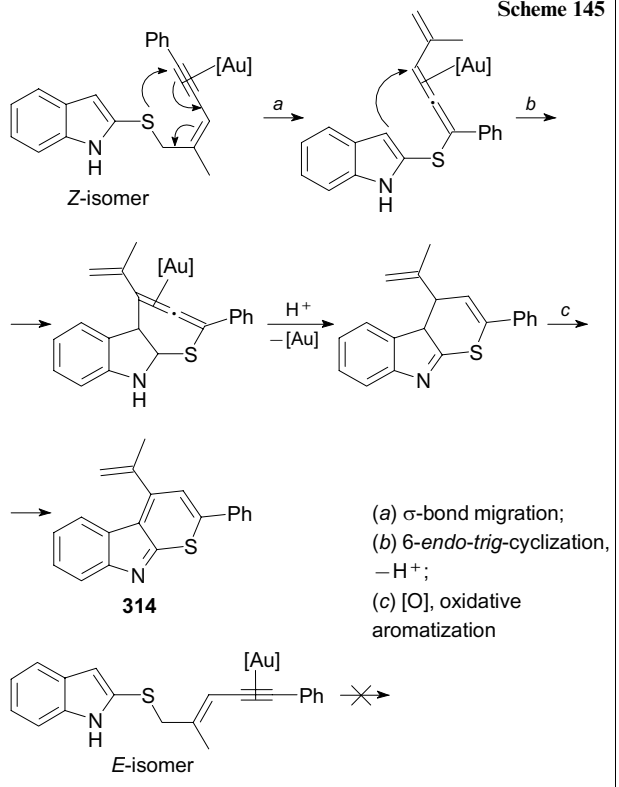
Jha *et al.*[233] described the synthesis of thiopyrano[2,3-*b*]indoles **314** by the Au-catalyzed tandem rearrangement – hydroarylation reaction (Scheme 144; here and in Scheme 146, the locants are shown for the substrate). The transformation mechanism proposed by the authors is shown in Scheme 145. As can be seen, only the *Z*-isomer of indole derivative **313** reacts.

Scheme 144



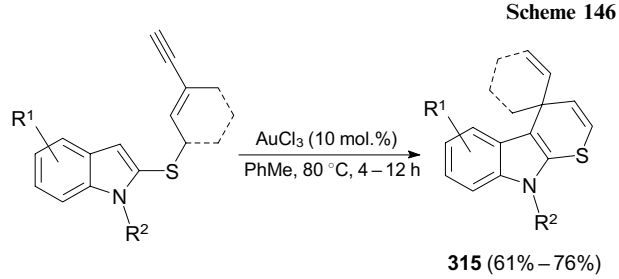
(*a*) AuCl$_3$ (5 mol.%), PhMe, 80 °C, 5 – 7 h;
R^1 = H, 5-F, 5-Br, 5-OMe, 6-Cl, 6-CO$_2$Me, 7-Cl;
Ar = Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$

Scheme 145



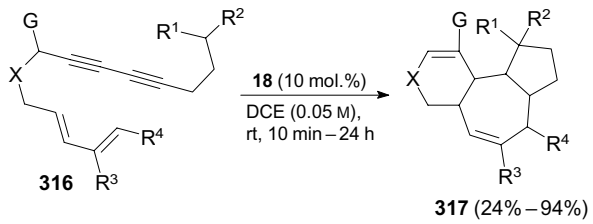
A similar mechanism was proposed[234] for the reaction giving thiopyrano[2,3-*b*]indoles **315**, which is shown in Scheme 146.

Scheme 146



R^1 = H, 5-F, 5-Cl, 5-Br, 6-Cl; R^2 = H, Me, Ph

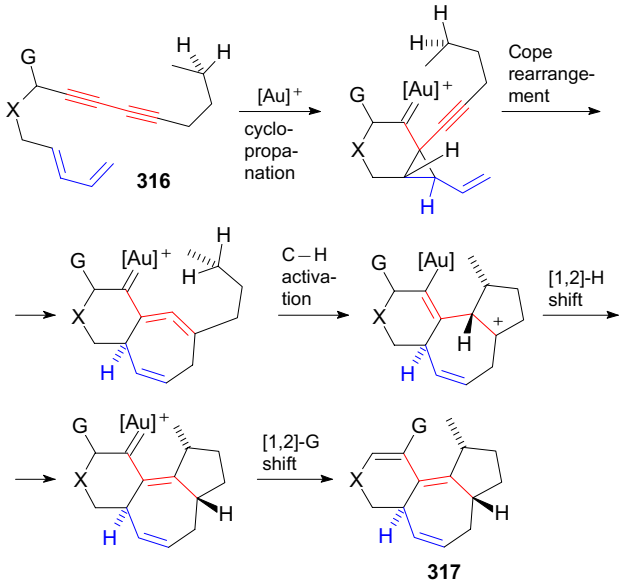
Scheme 147



X = NTs, O, CH_2; G = H, OAc; R^1 = H, Me, Et, n-C_5H_{11}, CH_2OTBS, Ph; R^2 = H, Me; R^3 = H, Me, Pr^i, Bn; R^4 = H, Me

Tandem polycyclization of linear dienediynes **316** to give polycyclic compounds **317** containing a six-membered ring has been reported by Cai *et al.*[235] (Scheme 147). The reaction proceeds as the formal [4 + 3]-addition followed by C – H activation, but actually it is a tandem cyclopropanation followed by the Cope rearrangement and C – H activation. The mechanism of the reaction is shown in Scheme 148.

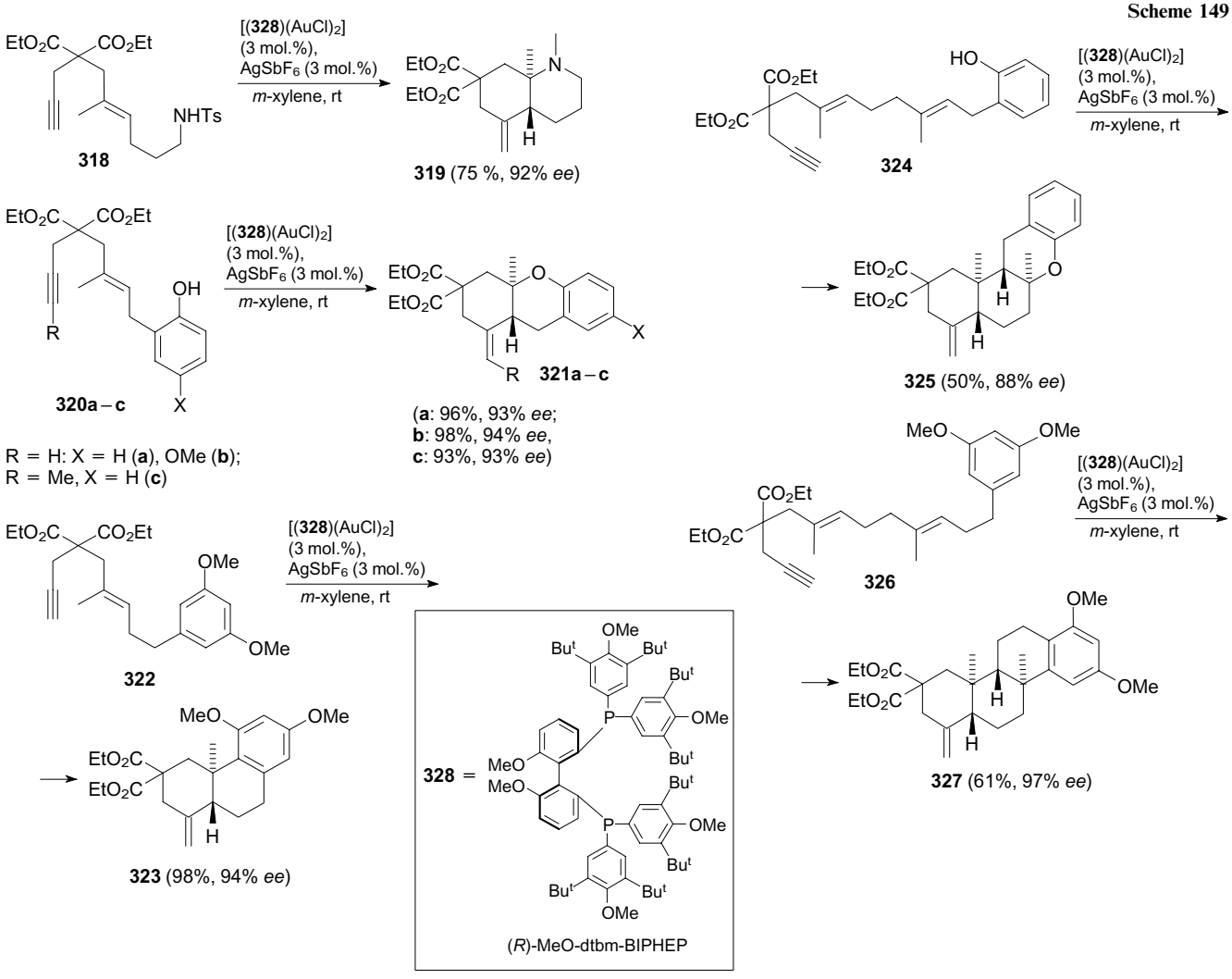
Scheme 148



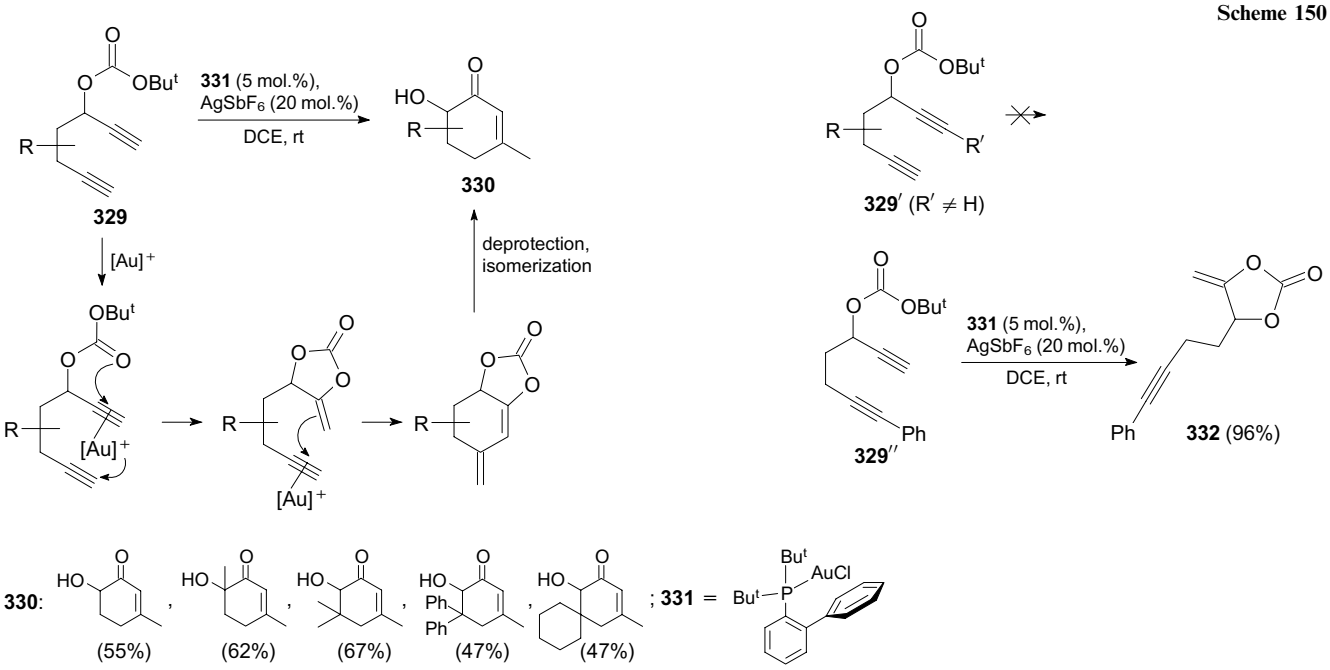
Sethofer *et al.*[236] described a number of tandem polycyclizations of enynes **318**, **320a – c** and **322** and dienynes **324** and **326** , which are highly enantioselective and result in the formation of polycyclic structures **319**, **321a – c**, **323**, **325** and **327** (Scheme 149). The gold(I) complex with the (*R*)-MeO-dtbm-BIPHEP ligand (**328**) served as the catalyst.

1,6-Diynes **329** with the *tert*-butyl carbonate group in the propargyl position undergo Au^I-catalyzed domino cyclization yielding α-hydroxycyclohexanones **330**

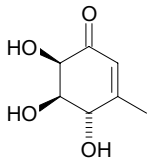
Scheme 149



Scheme 150



Structure 333



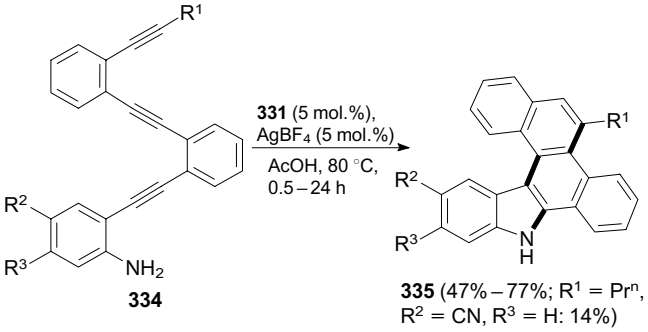
333

(Scheme 150).[237] Scheme 150 shows the thus obtained products **330** and their yields. The reaction is possible for terminal alkynes. When a substituent is present at the triple bond of the propargyl ester moiety ($R' \neq H$ in substrate **329′**), the reaction does not proceed. If the substituent $R'' \neq H$ is bound to the second triple bond of the molecule (substrate **329″**), product **332** is formed upon a single cyclization.

This reaction was used as the first step in the synthesis of (−)-6-*epi*-Gabosine H (**333**) in an overall yield of 61% and its epimer.[237]

The Au^I-catalyzed tandem hydroamination – double hydroarylation reaction of aniline derivatives **334** gives benzo[*a*]naphtho[2,1-*c*]carbazoles **335** in good yields (Scheme 151; the forming bonds in the product are highlighted).[238]

Scheme 151

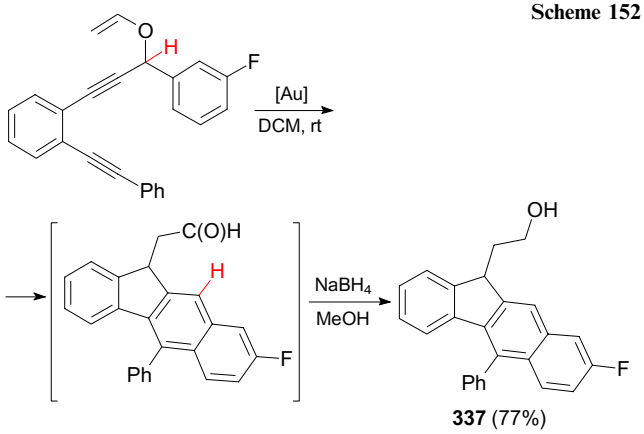


R^1 = Pr^n, Cy, Ph, 4-NCC_6H_4, 4-ClC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$; R^2 = H, Me, Cl, CN; R^3 = H, Cl

Gold(I) benzotriazole complex **336** was successfully used to carry out the Schmittel cyclization under mild conditions.[239] In this case, there was no need to use bulky groups (such as *tert*-butyl) in the propargyl position. In the presence of other gold catalysts, complex mixtures of products were formed (Scheme 152).

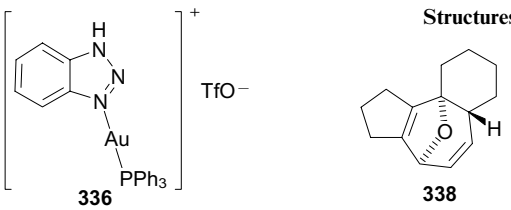
A gold(I)-catalyzed cascade reaction can be used to generate the tetracyclic carbon skeleton of diterpenoid **338**.[240]

Scheme 152

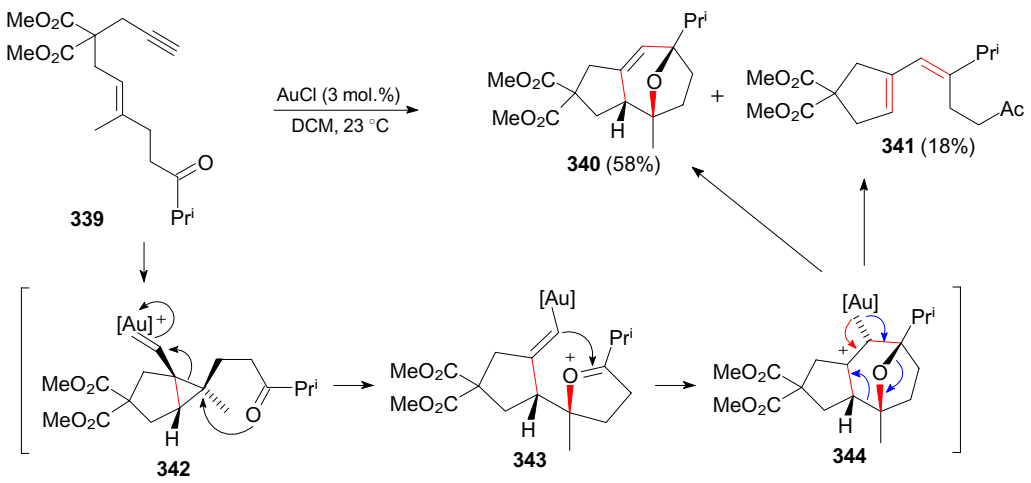


[Au] (mol.%)	Product
$Ph_3PAuOTf$ (5)	Complex mixture
(IPr)$AuSbF_6$ (5)	The same
(XPhos)$AuBF_4$ (5)	»
336 (3)	**337** (77% yield)

Structures 336, 338



Scheme 153



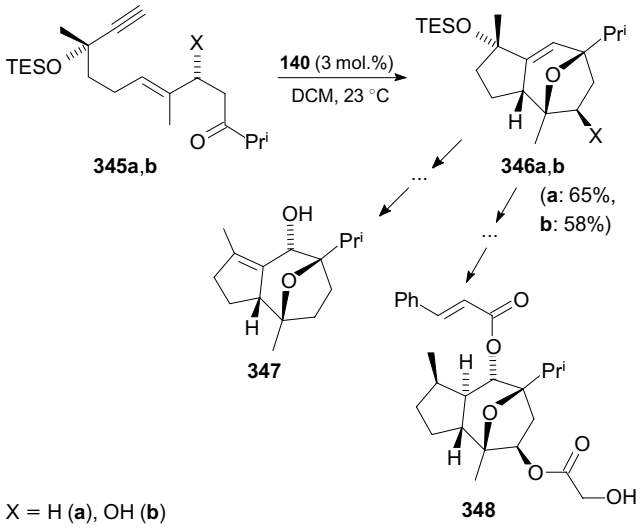
Of considerable interest for synthetic organic chemistry are cascade reactions of oxoenynes. For example, 1,6-enyne **339** with a carbonyl group in the alkenyl part of the chain is converted to oxatricyclic derivative **340** *via* the Au^I-catalyzed cascade [2 + 2 + 2]-cycloaddition (alkyne – alkene – carbonyl), in which two C – C bonds and one C – O bond are formed.[241] Diene **341** is formed as a minor product (Scheme 153).

The reaction is likely to involve nucleophilic cyclopropane ring opening in intermediate **342** induced by the attack by the carbonyl oxygen atom, giving rise to oxonium cation **343**, which is converted to intermediate **344** upon intramolecular seven-membered ring closure reaction (similar to the Prins reaction). Intermediate **344** is then transformed into oxatricyclic derivative **340** upon metal elimination or into diene **341** upon fragmentation.

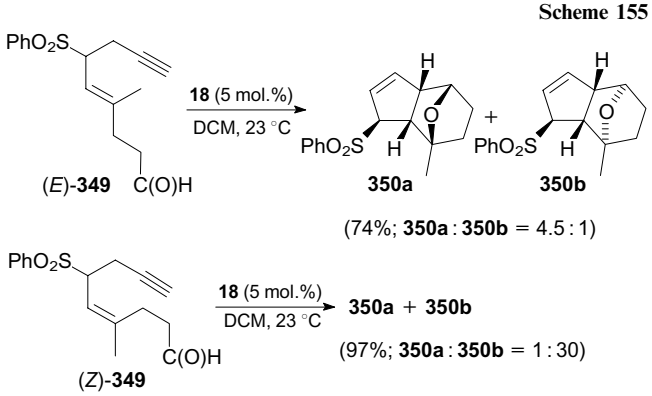
The [2 + 2 + 2]-cycloaddition of substrates **345a**,**b** gives rise to functionalized tricyclic products **346a**,**b** (Scheme 154), which have been converted to natural products, (+)-orientalol F (**347**)[242] and (–)-englerin A (**348**).[243]

Oxo-1,5-enynes **349** also undergo cyclization induced by Au^I to give tricyclic derivatives **350** (Scheme 155).[244]

Scheme 154



Scheme 155



2.1.1.8. Oxidative cyclization

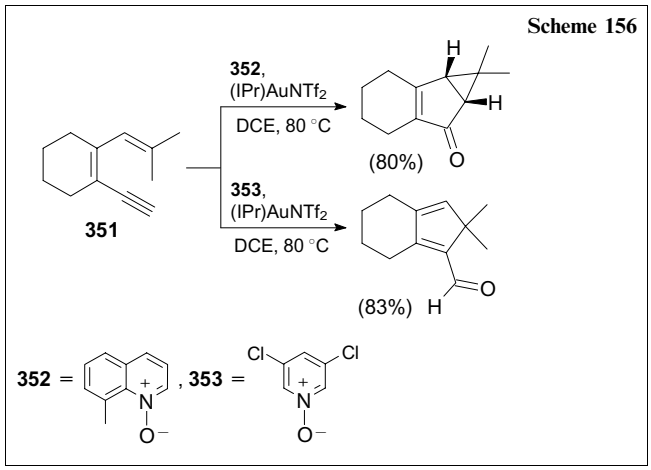
2.1.1.8.1. Oxidative cyclization of dienynes

The pathway of gold-catalyzed oxidative cyclization of 3,4,6,6-tetrasubstituted 3,5-dien-1-yne **351** depends on the nature of the oxidant used (Scheme 156).[245,246] The formation of different products was attributed to different nucleophilic activities of N-oxides, which interact during the reaction with the gold-activated triple bond of the substrate.

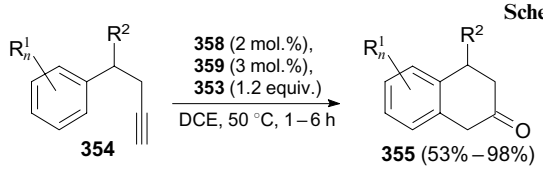
2.1.1.8.2. Oxidative cyclization of terminal alkynes with a carboaromatic moiety

Ling *et al.*[247] described an efficient method for oxidative cyclization of terminal alkynes **354** and **356** with the carboaromatic moiety of the same molecule, resulting in the formation of dihydronaphthalen-2(1*H*)-ones **355** and

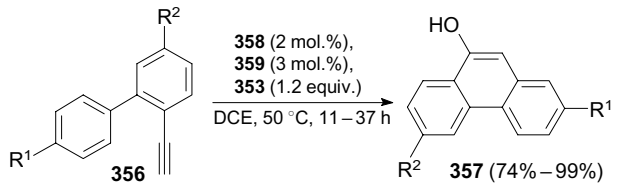
Scheme 156



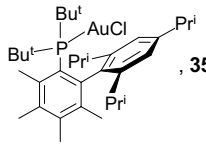
Scheme 157



R^1_n = H, 4-MeO, 4-BnO, 4-CH_2=$CHCH_2O$, 3,4-$(MeO)_2$, 3,4,5-$(MeO)_3$, 4-AcO; R^2 = H, Me



R^1 = H, MeO, F, Cl; R^2 = H, F;



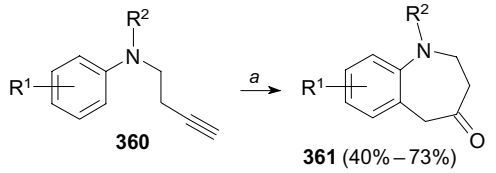
358 = , **359** = $[\{3,5\text{-}(F_3C)_2C_6H_3\}_4B]^-Na^+$

phenanthrenols **357** in good yields (Scheme 157). The reaction proceeds with a relatively low amount of a gold catalyst (2 mol.%).

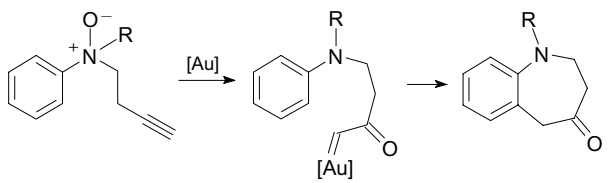
The nucleophilic addition of arenes with simultaneous oxidation of the triple bond has been reported by Cui *et al.*[248] Tertiary anilines **360** were converted to tetrahydrobenzo[*b*]azepin-4-ones **361** (Scheme 158). This structural moiety is a part of molecules of a variety of biologically active compounds, including natural products.[248 – 252] The authors established that the aniline nitrogen atom transfers oxygen from the peroxy acid to the triple bond, which is usually inert to oxidants under the reaction conditions. In the case of 3-substituted aniline derivative **360**, the reaction gives a mixture of *para*- and *ortho*-products **361** in ~1 : 1 ratio. The reaction mechanism proposed by Cui *et al.*[248] is shown in Scheme 159.

In the case of internal alkynes with strong electron-withdrawing groups, the reaction can proceed without the gold complex (see Scheme 159). Cyclization of substrate **362** with EWG = 4-$O_2NC_6H_4$ requires the presence

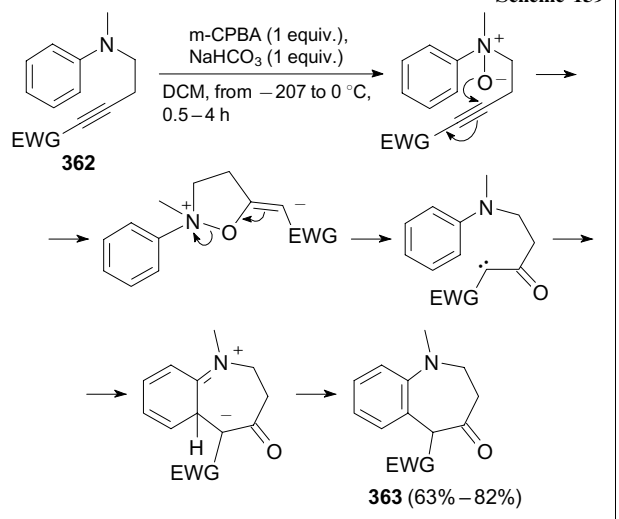
Scheme 158



(*a*) 1) m-CPBA (1 equiv.), $NaHCO_3$ (1 equiv.), DCM or DCE, 0 °C, 15 min – 2 h; 2) $Ph_3PAuNTf_2$, (5 mol.%), – 20 °C, 30 min;
R^1 = H, 4-Br, 4-I, 4-Me, 4-OMe, 3-NO_2, 3-Me, 4-CO_2Et; R^2 = Me, Bn



Scheme 159



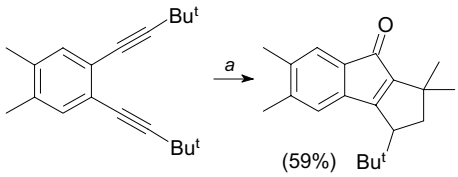
EWG = CO_2Me, Ac, Bz, SO_2Me

of a gold complex catalyst (the yield of product **363** in this case is 44%).

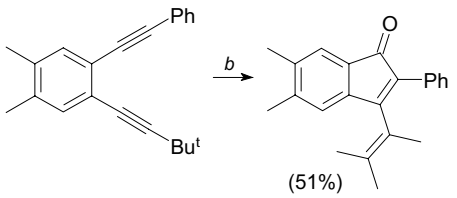
2.1.1.8.3. Oxidative cyclization of diynes

The formation of highly reactive carbene (vinylidene) intermediates enables quite a few highly efficient transformations,[121, 123, 253 – 256] examples of which are presented in Scheme 160.

Scheme 160



(*a*) $(IPr)AuNTf_2$ (5 mol.%), **364** (1.3 equiv.), PhH, 80 °C, overnight



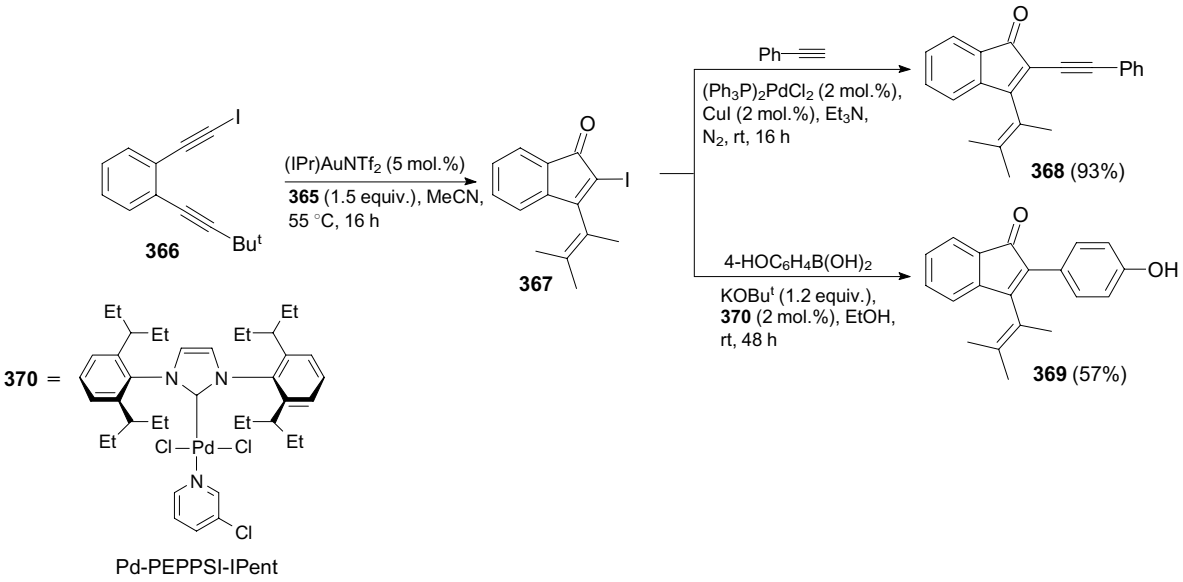
(*b*) $(IPr)AuNTf_2$ (5 mol.%), **365** (1.3 equiv.), PhH, rt, overnight;

364 = , **365** =

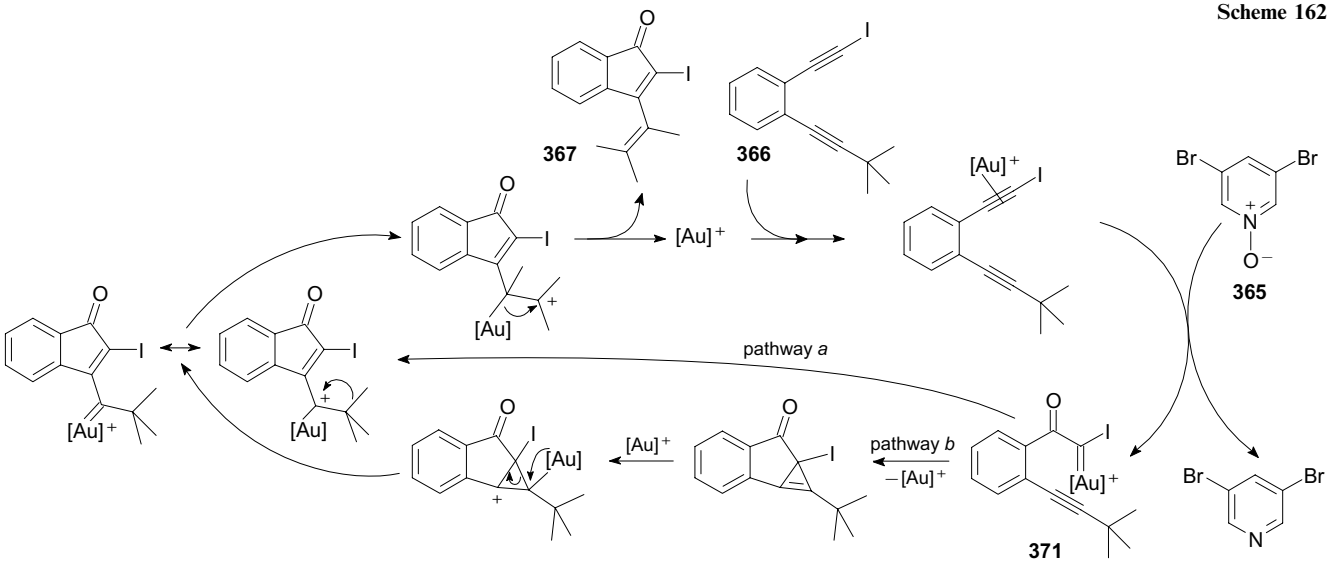
Iodoalkynes are also suitable as the starting compounds.[257] For example, the reaction of diacetylene **366** in the presence of N-oxide **365** and the $(IPr)AuCl – AgNTf_2$ catalytic system affords product **367**, which can then undergo a number of transformations to give substituted cyclic structures **368** and **369** (Scheme 161).[258]

The key step of the reaction is the formation of gold carbenoid **371** by oxygen transfer from N-oxide to the gold-activated substrate (Scheme 162).

Scheme 161



Scheme 162



2.1.2. Enyne isomerization without ring formation

2.1.2.1. Claisen rearrangement

The [3,3]-sigmatropic rearrangements of allyl vinyl ethers represent an efficient tool of modern organic synthesis.[259] The search for optimal catalysts for this reaction has been, and still is, a significant task.[260, 261] The Lewis acids used to catalyze the Claisen rearrangement can be divided into two groups: (1) hard Lewis acids, which catalyze the reaction by being coordinated to the oxygen atom[262] and (2) soft Lewis acids, which catalyze the reaction by being coordinated to π-bonds.[263] Owing to the use of gold, which is known for its alkynophilic properties, this reaction could be carried out for propargyl vinyl ethers.[264]

Propargyl vinyl ethers (1,5-enynes) **35** undergo Au^I-catalyzed Claisen rearrangement, resulting in the formation of allenes. Since the formed aldehydes are unstable, Sherry and Toste[264] reduced them *in situ* to obtain stable alcohols **372**, which were isolated (Scheme 163).

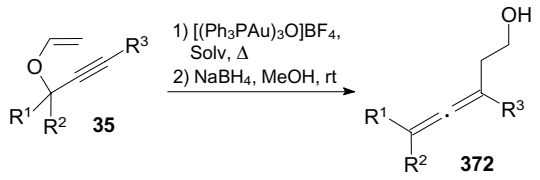
When the reaction is carried out in the presence of water or alcohol, dihydropyrans **36** are formed in good yields (see Scheme 13 in Section 2.1.1.2.2).[50]

Cases of gold-catalyzed Claisen rearrangement of propargyl allyl ethers (1,6-enynes) have been reported.[77, 265] For example, allene **375** is formed upon the AuCl-catalyzed isomerization of 1,6-enyne **373** to 1,5-enyne **374** followed by the Claisen rearrangement, which is apparently also catalyzed by gold (Scheme 164);[81] $AuCl_3$ is also suitable as a catalyst for this reaction.[265]

2.1.2.2. Rearrangement of allylsilylalkynes

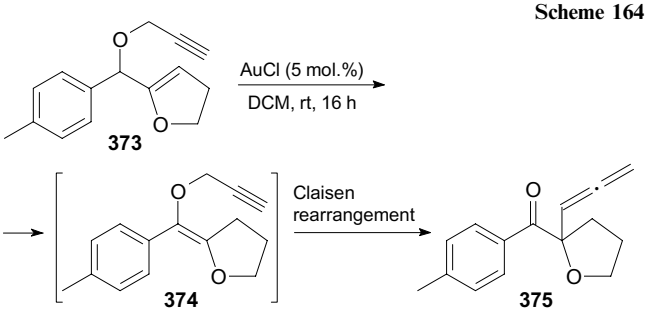
Park and Lee[209] (Scheme 165) and Toste and co-workers[210] (Scheme 166) demonstrated that allylsilylalkynes **268** are converted to cyclic (**269**, see above, Scheme 125) and acyclic (**270**) alkenylsilanes in the presence of an Au^I catalyst and an alcohol. The product structure is deter-

Scheme 163

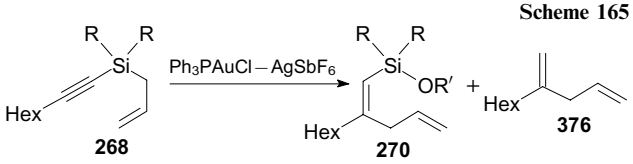


R^1	R^2	R^3	Solv, amount of the catalyst (mol.%)	Temperature /°C, time /h	Yield of **372** (mol.%)
Ph	H	H	DCM, 1.0	25, 5	78
Ph	H	$TBSO(CH_2)_3$	DCM, 1.0	25, 0.5	89
Ph	H	$PivOCH_2$	DCM, 1.0	25, 25	81
PMP	H	Bu^n	DCM, 1.0	25, 12	89
4-$CF_3C_6H_4$	H	Me	DCM, 1.0	25, 19	86
2-BrC_6H_4	H	Bu^n	DCM, 0.1	25, 6.5	96
n-C_5H_{11}	H	Ph	DCM, 0.1	25, 5	93
Pr^i	H	Ph	DCM, 0.1	25, 6	87
$TBSOCH_2$	H	Bu^n	DCM, 1.0	25, 23	76
Me	H	$Ph(CH_2)_3$	DCM, 1.0	25, 12	84
n-C_5H_{11}	H	cyclo-C_3H_5	DCM, 0.1	25, 6	90
$BnCH_2$	Me	Me	DCE, 1.0	75, 1	91
$(CH_2)_5$		$Ph(CH_2)_3$	DCE, 1.0	75, 1	61

Scheme 164



Scheme 165



R	Conditions	R′	Yield of **270** + **376** (%)	**270** : **376**
Me	'moist' DCM, rt	H	93	1 : 20
Ph	DCM, Pr^iOH, rt	Pr^i	75	9 : 1

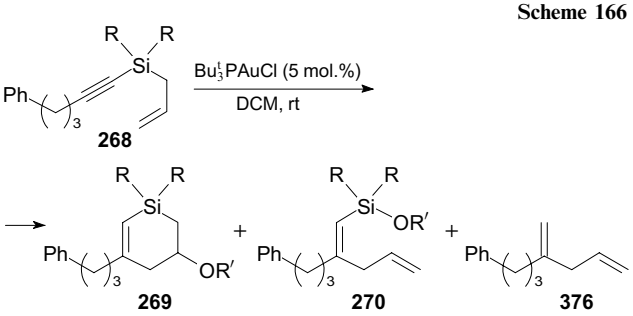
mined by the natures of substituents and alcohol. In some cases, desilylated products **376** are formed.

2.2. Dual gold activation

Hashmi's [256] and Zhang'd [253] research teams found interesting details for gold catalysis of alkyne reactions.

In most cases of homogeneous gold catalysis, the intermediate formation of a mononuclear gold-containing active complex is assumed, that is, only one gold

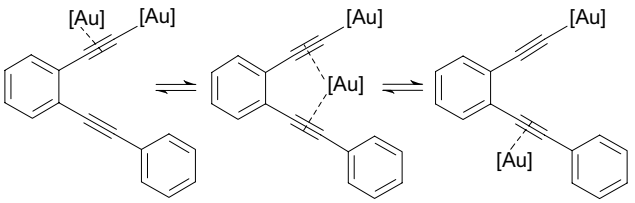
Scheme 166



R	Cocatalyst	Conditions	R′	Yield of **269** (%)	Yield of **270** (%)	Yield of **376** (%)
Me	$AgSbF_6$ (5 mol.%)	MeOH (3 equiv.), 1 h	Me	0	0	78
Ph	$AgSbF_6$ (5 mol.%)	MeOH (3 equiv.), 2 h	Me	0	0	78
Ph	$AgBF_4$ (5 mol.%)	Pr^iOH (3 equiv.), 12 h	Pr^i	84	Traces	0
Ph	$AgBF_4$ (5 mol.%)	PhOH (3 equiv.), 12 h	Ph	Traces	77	0

atom participates in the activation. However, several cases have been reported [266] in which substrate is activated by a binuclear gold complex, with the two gold ions activating the substrate in different ways: one complex is formed *via* the σ-bond with the terminal alkynyl group of the substrate and the other one is formed through π-coordination (Scheme 167).

Scheme 167



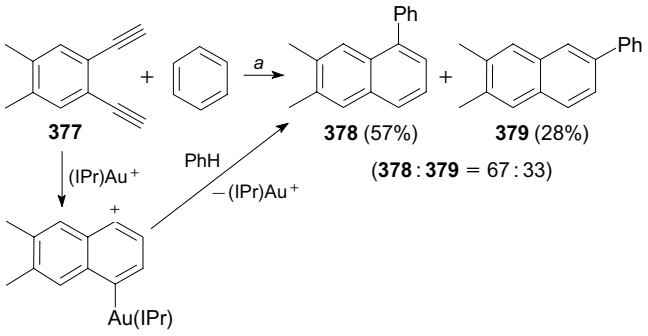
Only in several cases, was a combination of σ-coordination and π-coordination observed for reactions with one alkynyl group. Most often, the reaction proceeds *via* an intermediate in which one triple bond forms the σ-bond with the metal and the other triple bond forms the π-complex.

As follows from the review of Schmidbaur and Schier,[267] acetylenides σ,π-coordinated by two gold ions are not a rare case in organometallic chemistry. It was reported that acetylene can be coordinated to four gold ions.[268] The maximum number of triple bonds that can be π-coordinated to one gold ion is three.[269] Blanco *et al.*[270] described a σ,π-coordinated digold acetylenide bearing two phosphine ligands on the π-coordinated gold ion and having unusual unsymmetrical alkyne coordination with gold – gold interaction.

It remained unclear how gold acetylenides are formed. In 2011, this problem was studied in detail.[271,272] Brown and Widenhoefer[272] showed that $NHCAu^+$ generated *in situ* at low temperature forms the π-complex with phenylacetylene. This π-complex is converted to digold σ,π-acetylenide at temperatures above −20 °C. A number of digold σ,π-acetylenide complexes with bulky phosphine ligands have also been synthesized.[271,273] These complexes possess high catalytic activity in the intermolecular [2 + 2]-cycloaddition of alkenes to alkynes.[274] For an intramolecular enyne cycloisomerization, the formation of a binuclear gold complex was detected by electrospray ionization technique;[275] however, it was not proved that these species are involved in cycloisomerization.

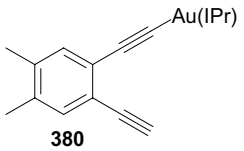
In 2012, in the reaction of diyne **377** with benzene, two products, naphthalenes **378** and **379**, were unexpectedly obtained (Scheme 168).[254] No isomerization of pure product **378** to naphthalene **379** takes place in the presence of a catalyst. According to investigation, product **378** is formed initially at a high rate, but when the conversion of reactant **377** is < 50%, the reaction rate decreases and, simultaneously, the formation of product **379** starts. It was assumed that the reaction mechanism and the nature of gold active species change, in particular, acetylenide complex **380** is slowly formed. This complex was prepared and isolated. Compound **380** proved to be stable under the reaction conditions at 80 °C. However, in the presence of a catalytic amount of the Au^I complex, compound **380** is converted to **379**, whereas no isomer **378** is detected in this case. These facts attest to competition of two catalytic cycles. Initially, classical electrophilic activation of substrate **377** takes place, and product **378** is formed with high selectivity. Simultaneously, the gold complex, which drives the formation of naphthalene **379**, is accumulated. In the presence of bases, such as triethylamine or even Al_2O_3, which promote the formation of acetylenide **380**, isomer **379** is formed as the major product (**379** : **378** = 98 : 2). With a substoichiometric amount of the catalyst, intermediate **381** was isolated upon mere addition of Et_3N (Scheme 169).[276]

Scheme 168

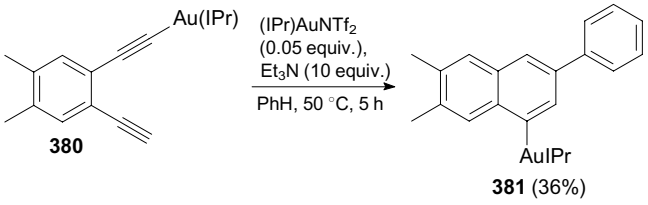


(*a*) (IPr)AuNTf$_2$ (5 mol.%), PhH, 80 °C, 24 h

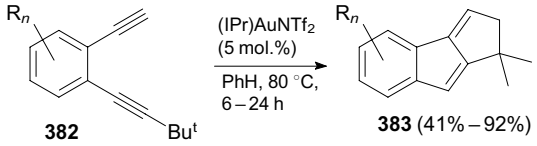
Structure 380



Scheme 169



Scheme 170



R_n = H, 4-MeO, 4,5-$(MeO)_2$, 3,4-(OCH_2O), 5-Me, 4-F, 4,6-Cl_2

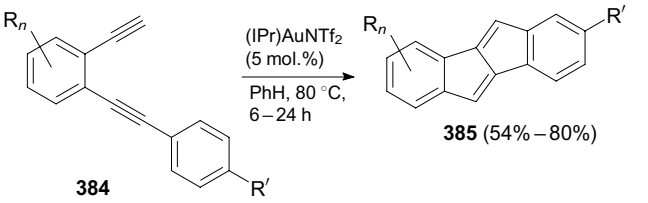
Cyclization of substrate **382** with a *tert*-butyl group at one triple bond affords benzofulvenes **383** instead of naphthalenes (Scheme 170).[256]

This result implies the initial formation of a five-membered ring followed by C—H activation of the methyl group of the *tert*-butyl substituent, resulting in the formation of the second five-membered ring. A similar reaction was reported Ye *et al.*,[253] who used Au^I with the BrettPhos ligand [2-(dicyclohexylphosphino)-3,6-dimethoxy-2′,4′,6′-triisopropylbiphenyl] in the presence of N-oxide as the catalyst. Detailed calculations for the possible mechanism revealed a bifurcation point in which the reaction can proceed to give either vinylidene species *via* 5-*exo*-*dig*-cyclization or a gold-containing aryl cation as a reactive species *via* initial 6-*endo*-*dig*-cyclization. The hypothesis of the initial formation of a five-membered ring was confirmed in the reaction of substrate **384** containing an aryl group instead of the *tert*-butyl group. In this case, two five-membered rings are also formed, the reaction yielding dibenzopentalene **385** (Scheme 171).[255]

Parallel studies[253,256] that included quantum chemical calculations and experiments with deuterated compounds made it possible to propose[266] a mechanism for this reaction, which is shown in Scheme 172.

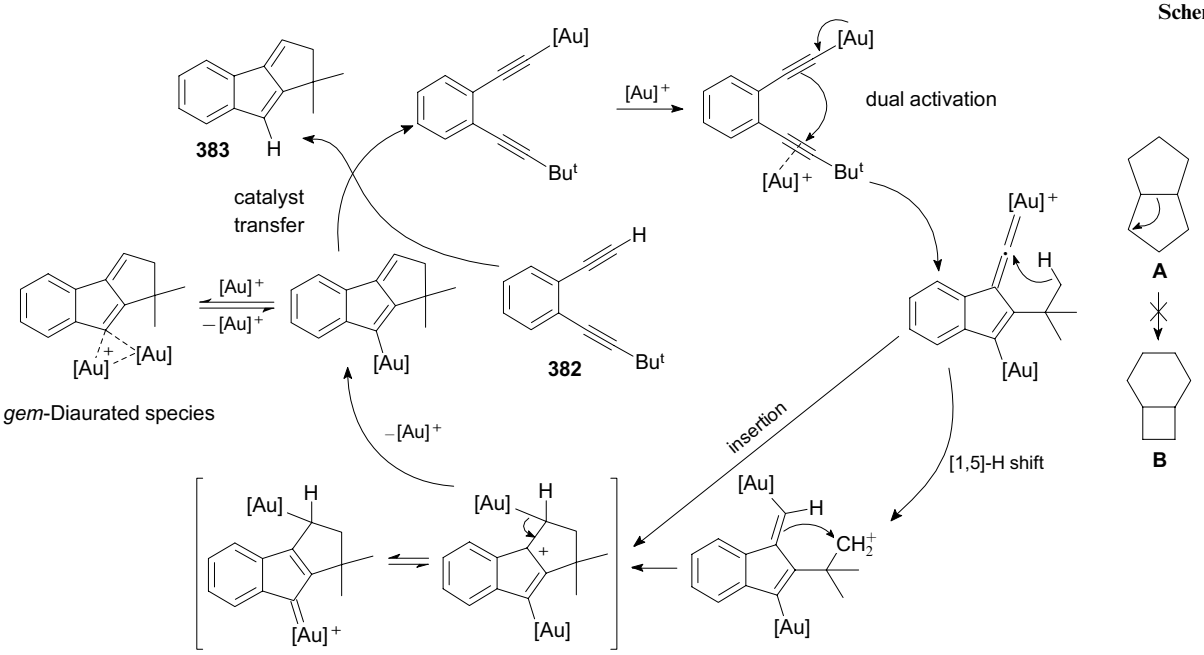
The formation of six-membered ring **B** is impossible in this case, because this would require the formation of the second four-membered ring, which is thermodynamically unfavourable.

Scheme 171



R_n = H, 3,4-$(MeO)_2$, 3,4-(OCH_2O); R′ = H, Bu^n, MeO

Scheme 172



Naphthalene **379** is formed in an intermolecular reaction (Scheme 173). This is accompanied by intramolecular hydrogen shift in the step of conversion of intermediate **386** to carbenoid **387**; the latter undergoes 1,2-shift with ring expansion, being converted to intermediate **388**. The catalytic cycle presented in the Scheme is specific to the preparation of β-substituted naphthalene **379**.

The use of dual activation in gold catalysis enabled the four-component Ugi reaction (4CR Ugi) for the synthesis of compound **389** (Scheme 174).[277]

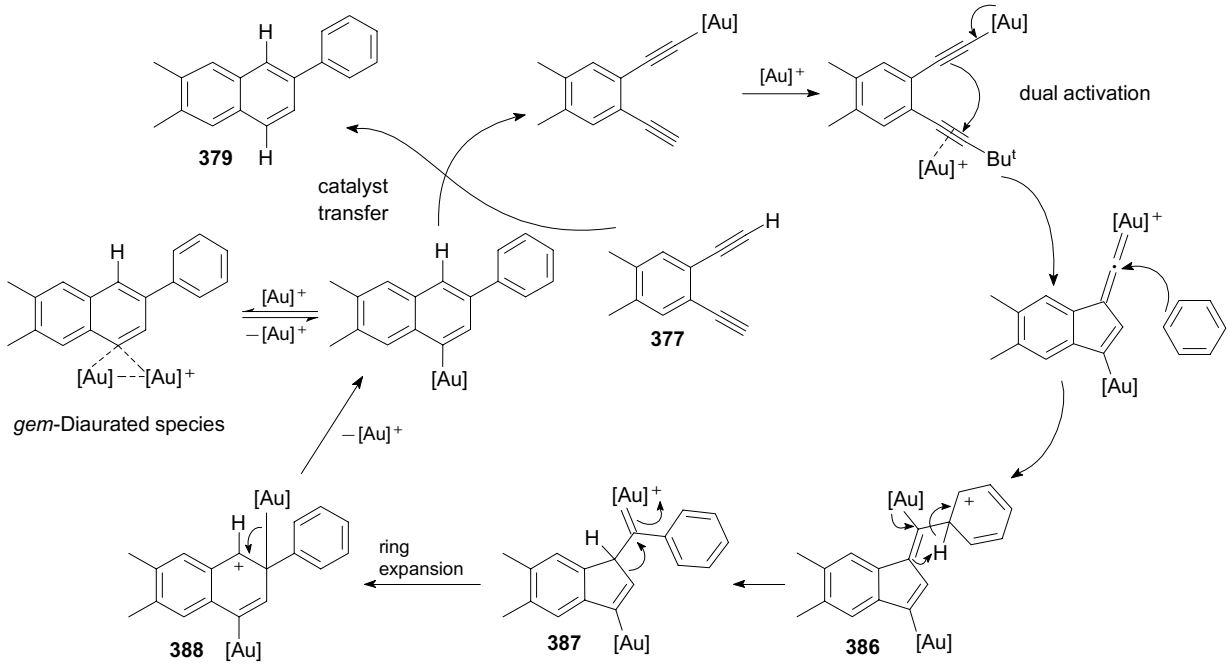
A combination of the C,H-activation with halogenation was accomplished to prepare iodinated benzofulvene **383′** (Scheme 175).[257]

An interesting reaction took place upon the activation of substrate **390** with gold acetylenide **391**. In this reaction, tosylate **390** was converted to five-membered ring **392** (Scheme 176).[278]

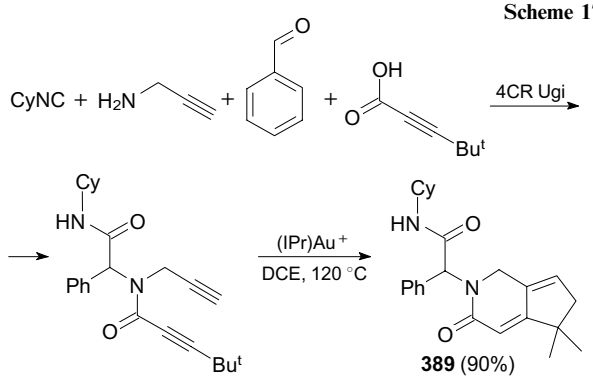
Dual activation was detected in the gold-catalyzed synthesis of bicyclic and tricyclic pyrroles **394** from *N*-propargyl ynamides, for example, compounds **393**;[279] high efficiency was found for catalyst **395** (Scheme 177).

Ynamides are more electrophilic than simple alkynes; therefore, nucleophilic addition is, most often, regiose-

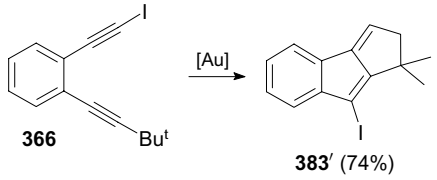
Scheme 173



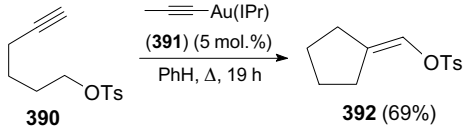
Scheme 174



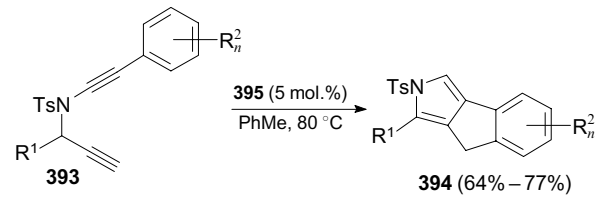
Scheme 175



Scheme 176



Scheme 177



R^1 = H, Et, Pr^n, Bn; R^2_n = H, 4-F, 4-Cl, 4-Br, 4-Me, 4-MeO, 3,5-Me_2

395 = [Au(IPr)–Au(IPr)]$^+$ PF_6^-

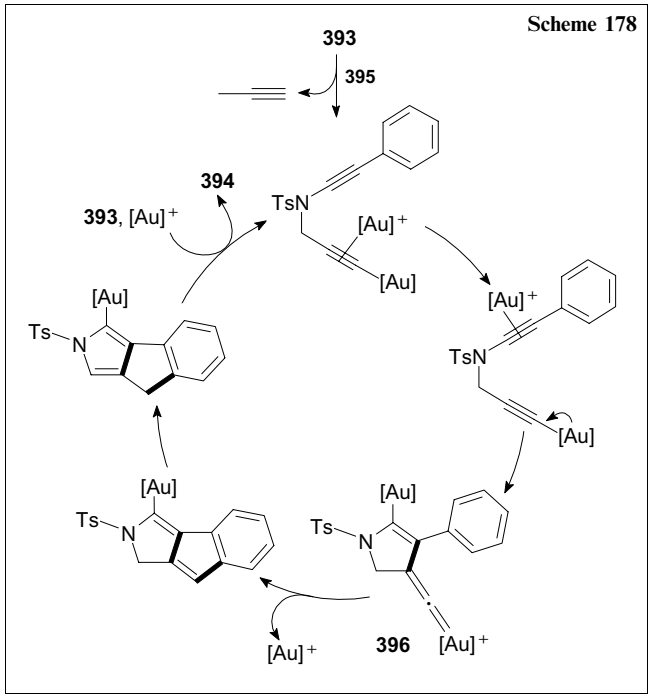
DAC-PF_6

lective and involves the triple bond located in the α-position to nitrogen. This regioselectivity is attributable to the effect of the electron-withdrawing amide group on the ynamide triple bond. The mechanism proposed by the authors is presented in Scheme 178 (the forming bonds are highlighted).

The reaction starts with nucleophilic addition of gold acetylenide to the ynamide α-triple bond into the β-position relative to the nitrogen atom. This gives vinylidene gold complex **396**, which participates in the next cyclization.

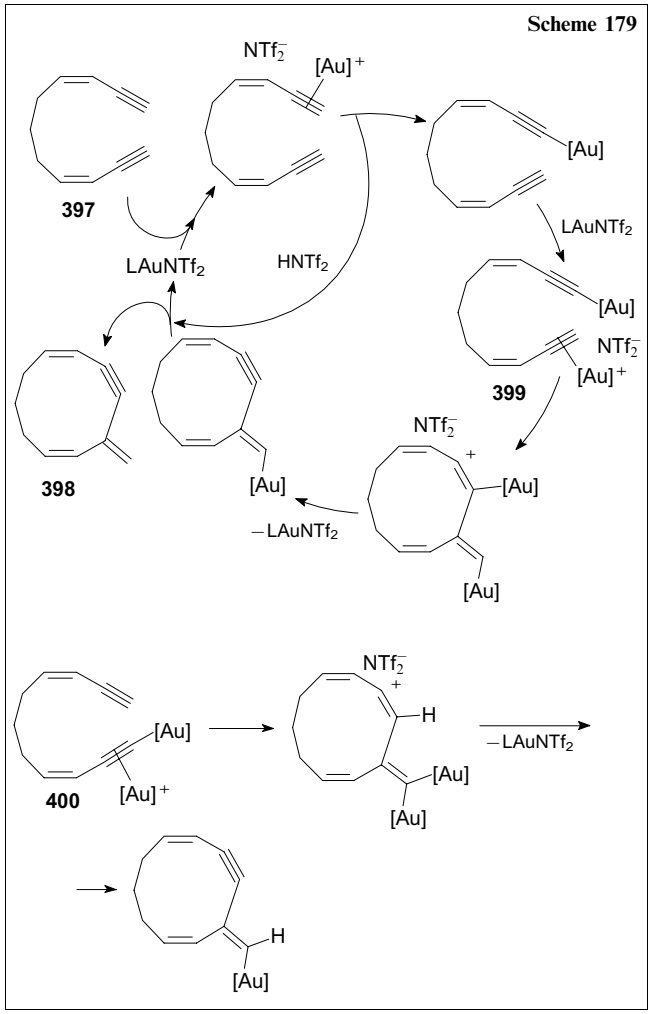
The preparation of ten-membered cycloalkyne **398** from 1,10-diyne **397** also involves the formation of a gold σ,π-complex.[280] Two possible mechanisms were proposed for this transformation (Scheme 179), but the use of deuterium-labelled reactants did not allow the authors to choose either of them. One of the mechanisms

Scheme 178



implies the activation of two triple bonds to give intermediate **399**; according to the other mechanism, two gold ions participate in activation of one triple bond (inter-

Scheme 179



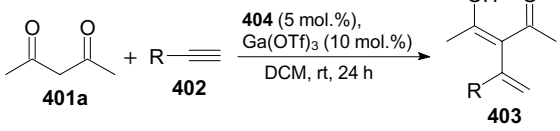
mediate **400**). A mechanism without dual activation has also been considered. The issues of dual activation by gold catalysts are discussed in a review.[281]

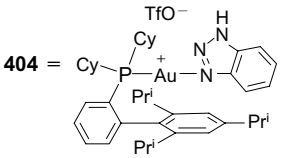
2.3. Intermolecular reactions

2.3.1. Alkyne reactions with methylene active compounds

The intermolecular addition of 1,3-dicarbonyl compounds **401** to non-activated terminal alkynes **402** (Nakamura reaction) can be accomplished at room temperature by using synergistic catalysis by gold and gallium compounds.[282] This is exemplified in Scheme 180, which depicts the reaction of pentane-2,4-dione (**401a**) with terminal alkynes **402**, resulting in the formation of 3-substituted 2,4-diones **403**.

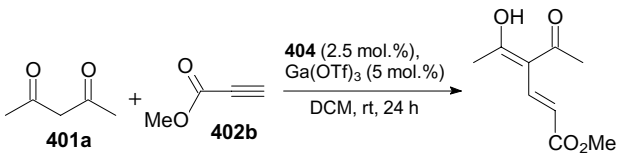
Scheme 180





R	Yield of **403** (%)	R	Yield of **403** (%)
Ph (**402a**)	92	3-ClC_6H_4	90
4-$MeOC_6H_4$	84	2-MeC_6H_4	80
4-$F_3CC_6H_4$	90	3-Th	85
4-$Bu^tC_6H_4$	94	Cy	40
4-FC_6H_4	89	Cyclohexen-1-yl	48
3-MeC_6H_4	94		

Scheme 181



If the substituent R in alkyne **402** is an electron-withdrawing group (CO_2Me), product **403′** is formed (Scheme 181).

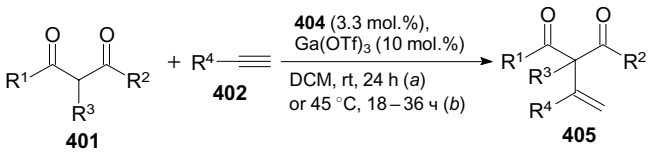
If the starting 2,4-dione **401** contains a substituent at C(3), the reaction gives dicarbonyl derivatives **405** with a quaternary carbon atom (Scheme 182).

The mechanism proposed by Wang *et al.*[282] comprises two catalytic cycles (Scheme 183; exemplified for substrate **401b**). However, the nature of species that actually catalyze the reaction is not entirely clear.

2.3.2. Reactions of alkynes with alkenes

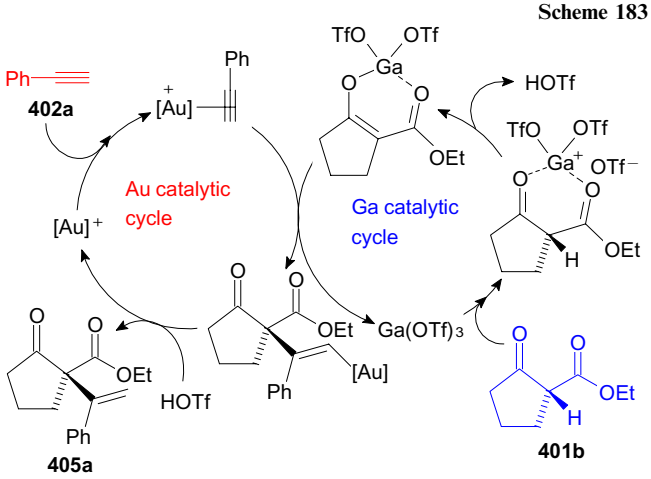
The intermolecular reaction of alkynes with alkenes catalyzed by gold(I) complexes is rather problematic by

Scheme 182



R^1	R^3	R^2	R^4	Conditions	Yield of **405** (%)
$(CH_2)_3$		OEt	Ph	*a*	96
$(CH_2)_3$		OEt	4-$Bu^tC_6H_4$	*a*	95
$(CH_2)_3$		OEt	4-FC_6H_4	*a*	92
$(CH_2)_3$		OEt	Fc	*a*	52
OCH_2CH_2		Me	Ph	*a*	92
$(CH_2)_3$		Me	Ph	*a*	93
$(CH_2)_4$		OEt	Ph	*b*	87
$(CH_2)_4$		Me	Ph	*b*	66
$(CH_2)_6$		OEt	Ph	*b*	86
Me	Me	OEt	Ph	*b*	93
Me	Me	Me	Ph	*b*	79

Scheme 183

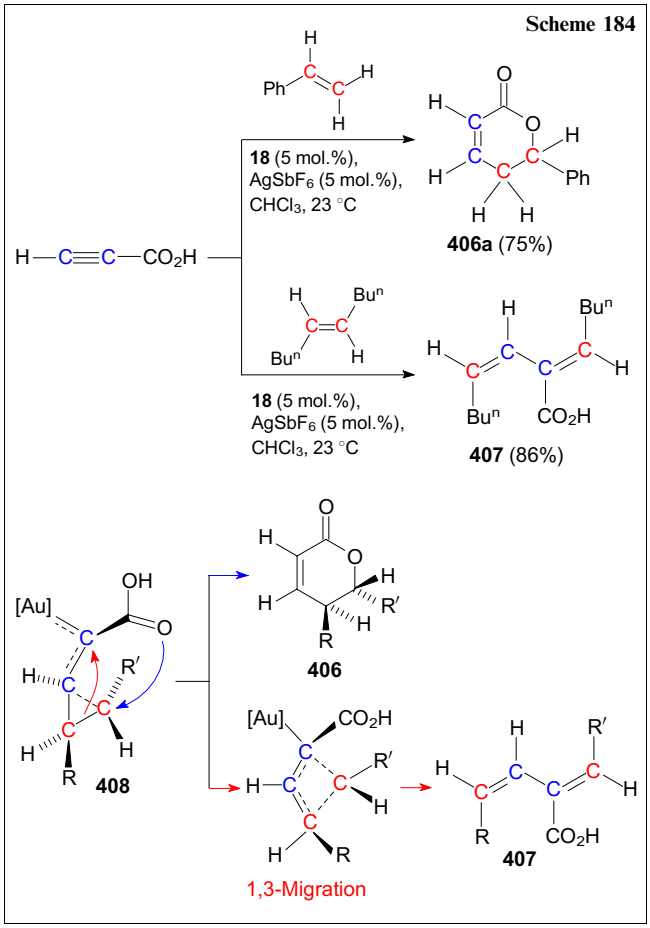


itself, because products of this reaction are substituted alkenes, which can compete with the initial alkenes and generate oligomerization products. In addition, electron-rich alkenes, which are best suited for this reaction, would be coordinated to Au^I, thus decreasing the concentration of the active (η^2-alkyne)–Au^I complex.

It is of interest that the intermolecular reaction of propiolic acid with alkenes proceeds *via* regioisomeric Au^I cyclopropyl carbene intermediate **408**, in which the gold atom is linked to the internal carbon atom of the alkyne.[283] An unsymmetrically substituted alkene, for example, styrene leads to the formation of lactone **406a** upon the attack by the carboxyl group on the most substituted carbon atom of the alkene. Meanwhile, alkenes with two identical or closely similar substituents, for example, dec-5-ene, undergo 1,3-migration with stereospecific formation of 1,3-dienes **407** (Scheme 184).

The first intermolecular gold-catalyzed coupling reaction between alkynoates and allyl ethers was described by Korean researchers.[284] The reaction results in selective formation of (*Z*)-β-alkoxyacrylates; for example, methyl

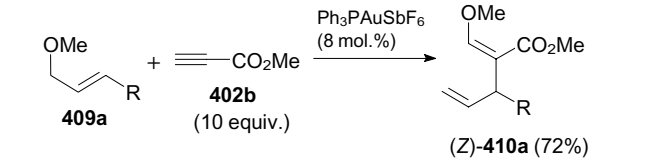
Scheme 184



propynoate (**402b**) and ether **409a** form product (*Z*)-**410a** (Scheme 185).

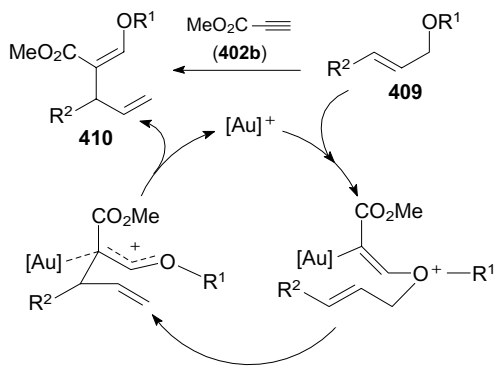
The reaction is accompanied by addition of O-nucleophile to the gold-activated triple bond with subsequent [3,3]-sigmatropic rearrangement (Scheme 186).

Scheme 185



R = $(CH_2)_3CO_2Bu^n$

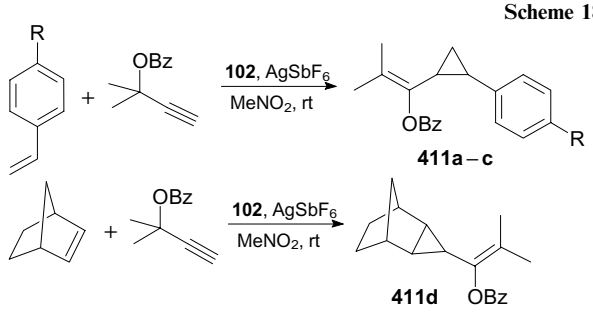
Scheme 186



2.3.2.1. Intermolecular cyclopropanation

Catalysis by Au^I complex **102** leads to the products of intermolecular cyclopropanation of alkenes with alkynes (**411**) in moderate yields (for alkyne conversion of 99%) (Scheme 187).[106]

Scheme 187



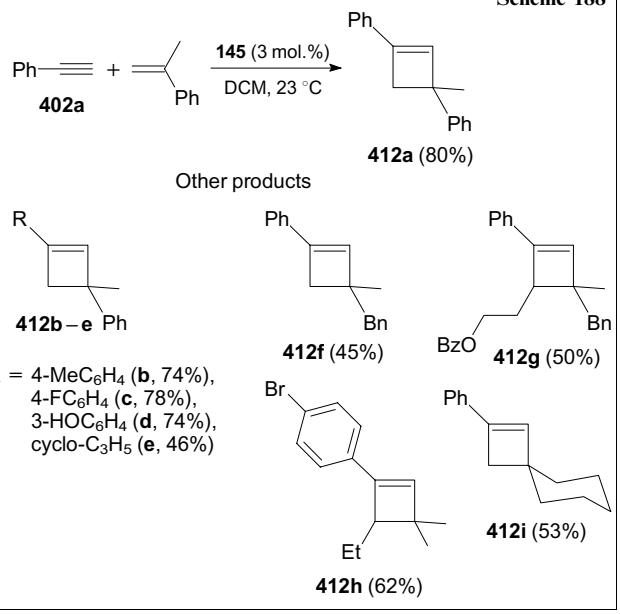
Compounds **411**	Yield of **411** (%)	*cis* : *trans*
a (R = OMe)	57	80 : 20
b (R = H)	71	> 99 : 1
c (R = OBu^t)	72	70 : 30
d	71	85 : 15

2.3.2.2. Formation of four-membered carbocycles. [2 + 2]-Cycloaddition

After numerous experiments with various Au^I complexes, cyclobutenes **412** were obtained in this intermolecular reaction in the presence of cationic gold(I) complex **145** with a bulky phosphine ligand (Scheme 188).[278]

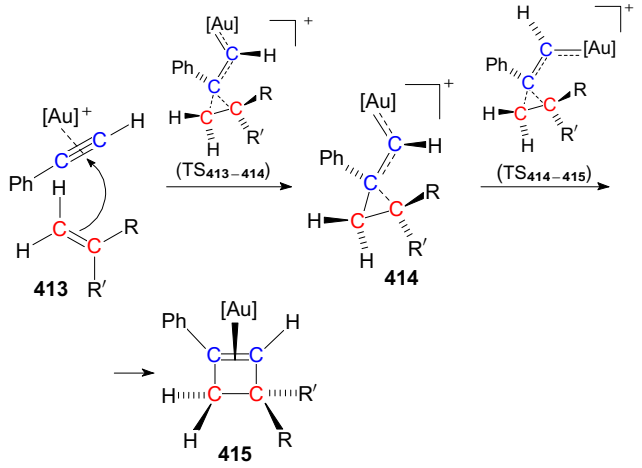
The regiochemistry of this [2 + 2]-cycloaddition is consistent with the mechanism of electrophilic addition to the alkene *via* transition state $TS_{413-414}$ to give highly distorted cyclopropyl Au^I carbene **414**, which undergoes ring expansion *via* transition state $TS_{414-415}$ to give (η^2-cyclobutene) – Au^I complex **415** (Scheme 189). Intermediate **414** can be involved in an intramolecular reaction giving cyclopropane.[274]

Scheme 188



R = 4-MeC_6H_4 (**b**, 74%), 4-FC_6H_4 (**c**, 78%), 3-HOC_6H_4 (**d**, 74%), cyclo-C_3H_5 (**e**, 46%)

Scheme 189



Despite the great success of the use of homogeneous gold catalysts in organic synthesis, the range of highly enantioselective reactions of alkynes is still not very broad,[285–287] especially as regards intermolecular reactions.[288–291] This is due, first of all, to the linear geometry of a two-coordinate gold complex. In this complex, a chiral ligand is too remote from the reaction centre, as shown in Fig. 1.

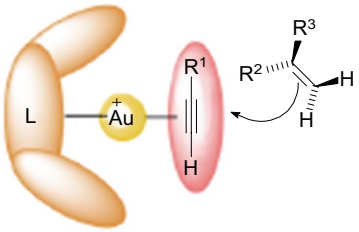


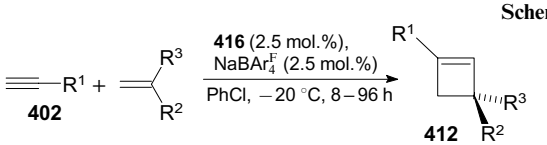
Figure 1. Schematic view of an alkyne activated by the gold(I) complex with a chiral ligand towards the reaction with alkene.[292]

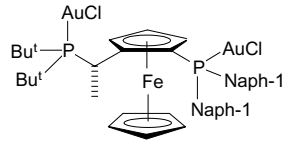
Chiral complexes **416** and **417** containing two gold(I) ions and Josiphos type ligands effected the intermolecular [2 + 2]-cycloaddition of alkene to alkyne with a high yield and high enantioselectivity.[292] It was shown that one Au^I centre is involved in the triple bond activation, while the other Au^I centre induces the enantioselectivity. Examples of reactions yielding cyclobutenes **412** and bis(cyclobutenes) **418** are depicted in Schemes 190 and 191.

2.3.3. Intermolecular reaction of alkynes

The intermolecular version of alkyne addition reaction to give enynes **419** was reported in 2012 by Zhang and coworkers [293] (Scheme 192). Gold(I) complex **420** served as the catalyst in this reaction. The authors proposed a reaction mechanism that included the intermolecular interaction of gold acetylenide formed from substrate **419** with a second alkyne molecule to give the π-complex with a gold ion.

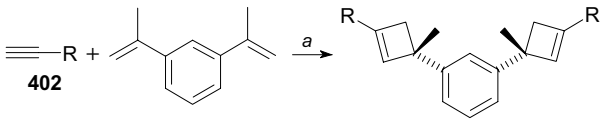
Scheme 190



(*S*,R_p)-**416** = 

; Ar^F = 3,5-$(F_3C)_2C_6H_3$

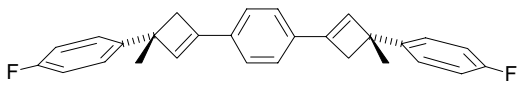
R^1	R^2	R^3	Yield of **412** (%)	*er*
Ph	Me	Ph	70	90 : 10
4-PhC_6H_4	Me	Ph	57	91 : 9
4-MeC_6H_4	Me	Ph	82	82 : 18
4-$Bu^tC_6H_4$	Me	Ph	80	87 : 13
4-ClC_6H_4	Me	Ph	47	93 : 7
4-BrC_6H_4	Me	Ph	45	93 : 7
3-MeC_6H_4	Me	Ph	74	90 : 10
3-$MeOC_6H_4$	Me	Ph	60	91 : 9
3-Th	Me	Ph	78	84 : 16
4-$Bu^tC_6H_4$	Me	4-FC_6H_4	85	87 : 13
4-ClC_6H_4	Me	4-FC_6H_4	37	91 : 9
4-BrC_6H_4	Me	4-FC_6H_4	84	88 : 12
3-$MeOC_6H_4$	Me	4-FC_6H_4	40	89 : 11
3-Th	Me	4-FC_6H_4	85	86 : 14
Ph	Me	4-FC_6H_4	72	91 : 9
Ph	Me	4-ClC_6H_4	57	86 : 14
Ph	Me	4-BrC_6H_4	66	87 : 13
Ph	Me	4-MeC_6H_4	57	89 : 11
Ph	Me	4-$Pr^iC_6H_4$	52	88 : 12
Ph	Me	4-$Bu^tC_6H_4$	89	88 : 12
4-$Bu^tC_6H_4$	Me	4-$Bu^tC_6H_4$	63	89 : 11
3-Th	Me	4-$Bu^tC_6H_4$	56	94 : 6
Ph	Cy	Me	67	64 : 36
Ph	H	Ph	53	66 : 34
Ph	Et	Ph	83	83 : 17
4-ClC_6H_4	Et	Ph	92	88 : 12
4-BrC_6H_4	Et	Ph	81	85 : 15
3-$MeOC_6H_4$	Et	Ph	88	89 : 11
3-Th	Et	Ph	87	83 : 17



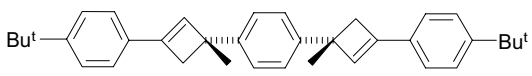
418a–c

(*a*) **416** (2.5 mol.%), $NaBAr^F_4$ (2.5 mol.%), PhCl, –20 °C, 8–96 h

Compounds **418**	R	Yield of **418** (%)	*er*
a	3-MeC_6H_4	45	98 : 2
b	4-$Bu^tC_6H_4$	67	96 : 4
c	3-Th	70	96 : 4

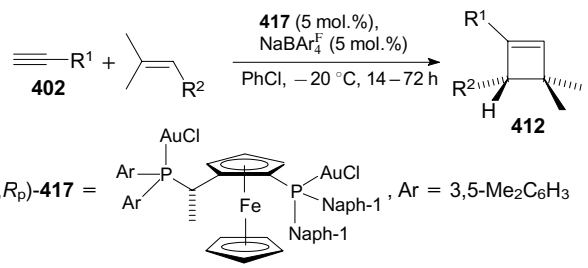


418d (41%, *er* = 97 : 3)



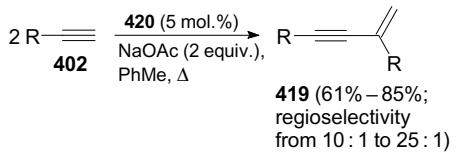
418e (60%, *er* = 95 : 5)

Scheme 191

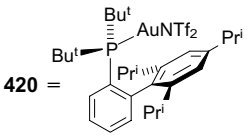


R^1	R^2	Yield of **412** (%)	*er*
Ph	$Ph(CH_2)_2$	51	90 : 10
4-BrC_6H_4	$Ph(CH_2)_2$	50	85 : 15
4-$Bu^tC_6H_4$	Me	85	89 : 11
4-ClC_6H_4	Me	38	83 : 17
4-BrC_6H_4	Me	78	83 : 17
4-$Bu^tC_6H_4$	Et	78	89 : 11
4-ClC_6H_4	Et	88	86 : 14
4-BrC_6H_4	Et	78	83 : 17

Scheme 192



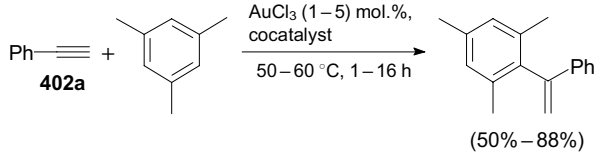
R = Ph, $Ph(CH_2)_2$, $PhS(CH_2)_3$, $AcO(CH_2)_3$, $PhthN(CH_2)_3$, n-$C_{10}H_{21}$, Cy, cyclo-C_5H_9;



2.3.4. Intermolecular hydroarylation

The nucleophilic addition of arenes can also be intermolecular, which is exemplified in Scheme 193.[138]

Scheme 193

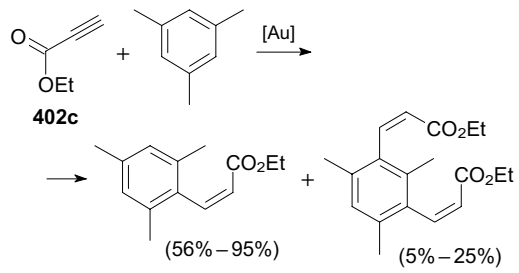


Cocatalyst: $AgOTf$, $AgBF_4$, $AgSbF_6$

The reaction is carried out in nitromethane and is catalyzed by $AuCl_3$ with various silver salts. The best results were attained when $AgSbF_6$ was present as the cocatalyst. Without a silver salt, the yield of the product did not exceed 20% and with the $AgClO_4$ cocatalyst, the yield was only 5%. This reaction can be carried out for both terminal and internal alkynes; in the case of aryl-alkyl-substituted alkynes, the addition products were obtained in good yields (up to 94%).

Reetz and Sommer[138] also studied the reaction of an arene with electron-deficient alkynes, for example, with ester **402c** , which is shown in Scheme 194. In this case, alkyne adds to the mesitylene aromatic ring through the triple bond β-atom, which is due to the electron-withdrawing properties of the ester group. The reaction does not occur for internal alkynes containing electron-withdrawing groups.

Scheme 194



[Au] = $AuCl_3 - AgBF_4$, $Ph_3PAuCl - AgBF_4$, $AuCl - BF_3 \cdot OEt_2$, $Et_3PAuCl - BF_3 \cdot OEt_2$, $Ph_3PAuCl - BF_3 \cdot OEt_2$;
reaction conditions: $MeNO_2$, rt – 60 °C, 4 – 16 h

Both above reactions (see Schemes 193 and 194) proceed as nucleophilic addition of arene to the gold-activated triple bond.

The reaction of phenylacetylene with mesitylene (see Scheme 193) was studied by Alcarazo and co-workers,[294] who ascertained that gold catalysts with cationic phosphine ligands are highly active in this reaction. Figure 2 presents a number of ligands arranged in the order of increasing catalyst activity in this reaction. The catalysts and silver salts were taken in amounts of 5 mol.% in all

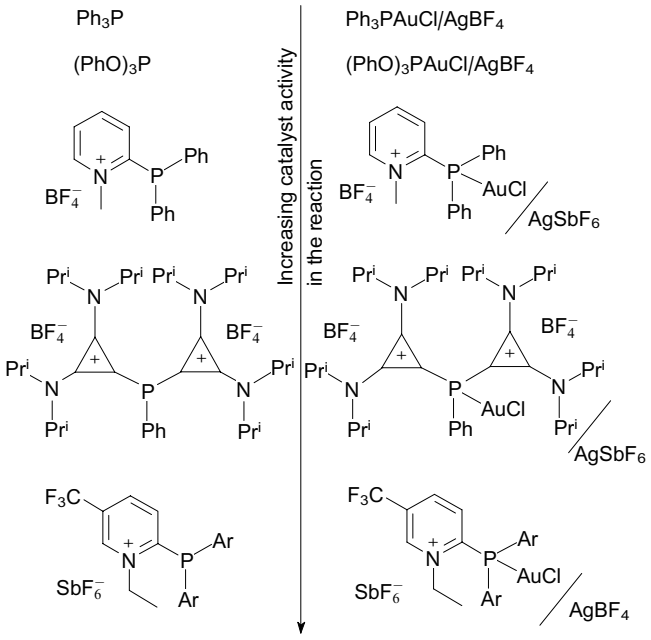


Figure 2. Catalyst activity towards the reaction of phenylacetylene with mesitylene.[294]

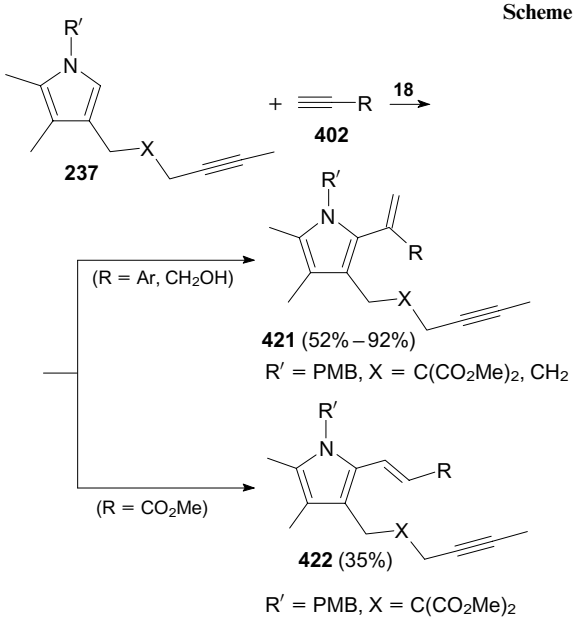
cases; the reaction was carried out in dichloroethane at 60 °C.

Ligands are known [295–297] to play an important role in the catalytic activity and even selectivity (ranging from regio- or chemoselectivity to enantioselectivity) of transition metals. It was established that α-cationic phosphine ligands (see Fig. 2) substantially boost the activity of catalysts that behave as π-acids.[298] The effect of an α-cationic substituent linked to the PPh_2 moiety was investigated for the first time in relation to the phenylacetylene reaction with mesitylene. The reaction mechanism corresponds to the nucleophilic addition of mesitylene to the triple bond activated by the cationic gold complex. This is the rate-limiting step.[299] A quantum chemical modelling (B2LYP) of this reaction catalyzed by gold complexes with various α-cationic ligands was reported.[298]

2.3.5. Reactions of alkynes with heteroaromatic compounds

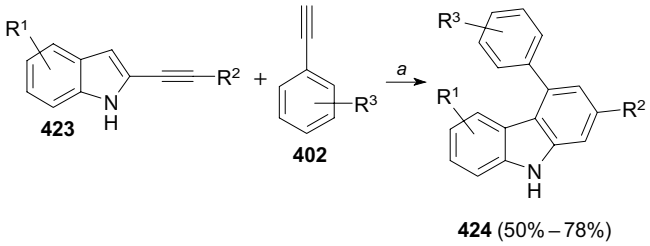
An interesting version of intermolecular reaction of an alkyne with a heterocyclic system was reported by Pan *et al.*[182] The intramolecular cyclization of compound **237** has been considered above (see Scheme 104 in Section 2.1.1.5.2); in the presence of alkyne, this substrate can also undergo intermolecular reaction to give products **421** and **422** in moderate to high yields (Scheme 195). It is worth noting that the nature of substituent R in the alkyne has a crucial effect on the reaction pathway and regioselectivity: thus the electron-withdrawing CO_2Me group changes the reaction pathway towards the formation of product **422** as the *E*-isomer. Meanwhile, if R = Cy or Bu^t, the intermolecular reaction does not take place, and the intramolecular cyclization product **238** is formed.

Scheme 195



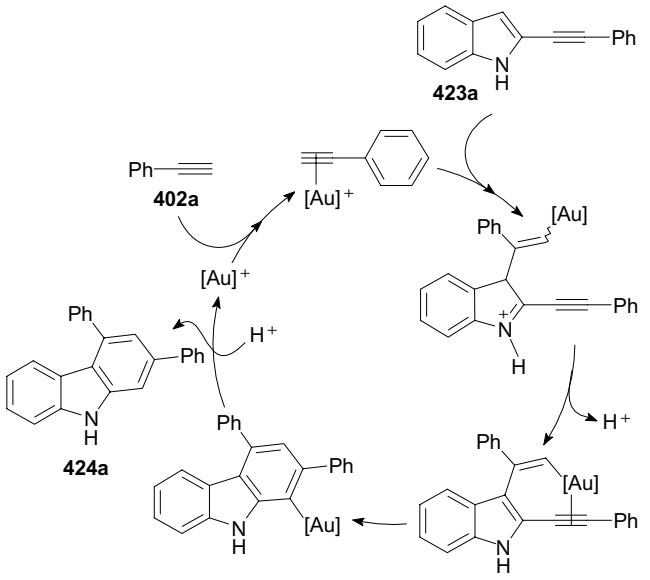
The synthesis of NH-carbazoles **424** by one-pot-hydroarylation of alkynes **423** followed by 6-*endo*-*dig*-carbocyclization was reported by Samala *et al.*[300] (Scheme 196). The mechanism of this reaction is shown in Scheme 197 in relation to substrates **423a** and **402a**. The first step is the nucleophilic attack by indole **423** on the gold-activated triple bond of alkyne **402**.

Scheme 196



(*a*) Ph_3PAuCl (15 mol.%), $AgSbF_6$ (15 mol.%), PhMe, 110 °C, 6 – 24 h; R^1 = H, 5-Cl; R^2 = H, Me, Bu^n, Bu^t, cyclohexen-1-yl, Ph; R^3 = H, 4-OMe, 4-Me, 4-Bu^t, 4-F, 4-CN

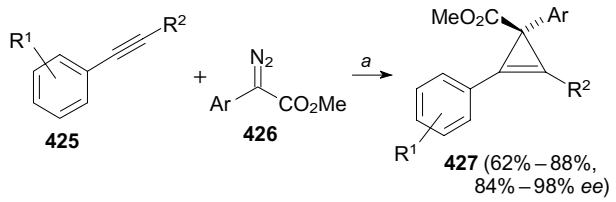
Scheme 197



2.3.6. Cyclopropenation

Cyclopropenes are extensively used in modern organic synthesis.[301] They can be stereoselectively prepared by the reaction of diazo compounds with alkynes catalyzed by transition metal complexes, *e.g.*, rhodium,[302, 303] cobalt or iridium complexes.[304, 305] However, asymmetric cyclopropention of internal alkynes was a challenge, and the product *ee* for this reaction did not exceed 20%.[306] The use of the binuclear gold(I) complex (*S*)-3,5-xyl-BINAP(AuCl)$_2$ [(*S*)-**287**] in the presence of $AgSbF_6$ effected the cyclopropenation of internal alkynes **425**

Scheme 198



(*a*) (*S*)-**287** (12 mol.%), $AgSbF_6$ (10 mol.%), DCM, 0 °C; R^1 = H, 2-Me, 4-Br; R^2 = Me, Et, Bu^n, Bu^i, Cy, $CyCH_2$, $TBSOCH_2$; Ar = Ph, 2-MeC_6H_4, 3-MeC_6H_4, 3-ClC_6H_4, 3-BrC_6H_4, 3-PhC_6H_4, 4-BrC_6H_4, 4-$TfOC_6H_4$, 4-Bu^tC_6H_4, 3,4-$Cl_2C_6H_3$

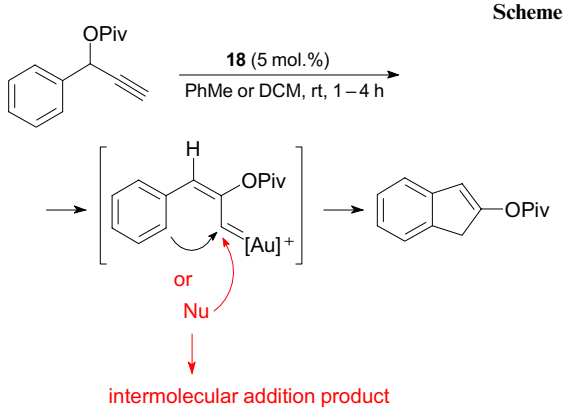
with aryl diazoacetates **426** with high enantioselectivity and good yields of cyclopropenes **427** (Scheme 198).[307] The reaction involves the formation of gold carbenoid.

2.3.7. Reactions of propargyl esters

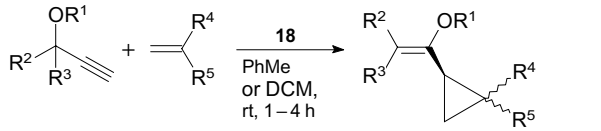
Gold activation of propargyl esters underlies quite a few cycloaddition reactions comprehensively described in the literature. Several recent publications can be cited as examples.[120, 308, 309] Equally numerous are papers devoted to cyclization of the corresponding propargyl acetals (see, for example, Refs 310–312).

Propargyl esters react with vinyl derivatives to give vinyl-substituted cyclopropanes.[313] The reaction is accompanied by the 1,2-shift of the acyl group giving rise to gold carbenoid, which is attacked by an external nucleophile. If no external nucleophile is present, the reaction follows the intramolecular mechanism, with the benzene ring acting as the nucleophile (Scheme 199).

Scheme 199



Scheme 200



(48%–82%; for R^1 = Piv, R^2 = R^3 = Me, R^4 = Ph, R^5 = N(Me)Ts: 19%)

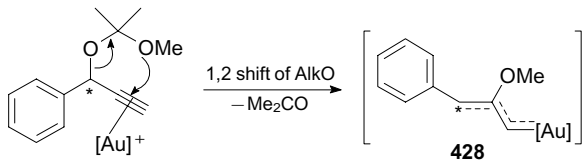
R^1 = Ac, Piv; R^2 = Me, Ph; R^3 = H, Me; R^4 = H, Me, Ph, *etc.*, R^5 = OAc, N(Me)Ts

Scheme 200 shows the reaction of propargyl esters with vinyl derivatives as external nucleophiles.

The cycloaddition of propargyl acetals is accompanied by 1,4-shift of the alkoxy group and elimination of the ketone to give highly reactive gold carbenoid **428** (Scheme 201; the asterisk marks the C atom that is initially bound to the ketal group).

The subsequent attack of gold carbenoid **428** by various nucleophiles affords the products of cycloaddition. The reactions described to date are summarized in Table 2 as particular examples with indication of nucleophilic reagent, type of the reaction and the reaction product.

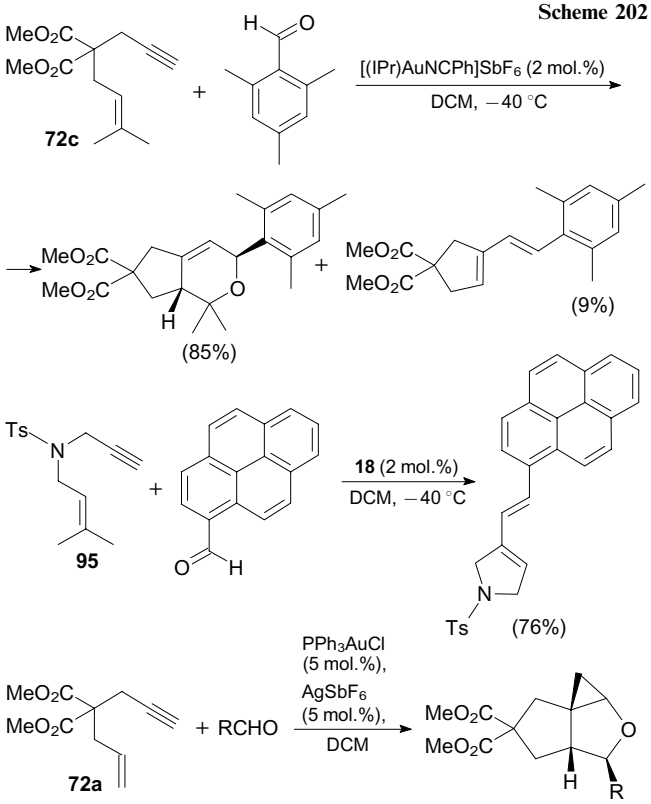
Scheme 201



2.3.8. Intermolecular tandem reactions. Cascade reactions of oxoenynes

The intermolecular reactions of 1,6-enynes with carbonyl compounds in the presence of Au^I catalysts can give different products depending on the nature of substituents in the alkene moiety (Scheme 202). In particular, they can be used for the synthesis of 1-substituted 1,3-dienes, which are difficult to obtain by other methods. These reactions are formally classified as [2 + 2 + 2]-cycloaddition.[320–322]

Scheme 202



R = 2-$O_2NC_6H_4$, Pr^i

The intermolecular Au^I-catalyzed reaction of terminal alkynes with oxoalkenes affords 8-oxabicyclo[3.2.1]oct-3-enes *via* a reaction similar to [2 + 2 + 2]-cycloaddition. An example is presented in Scheme 203; the reaction involves the formation of intermediate **429**, in which two C–C bonds and one C–O bond are formed.[323]

Scheme 203

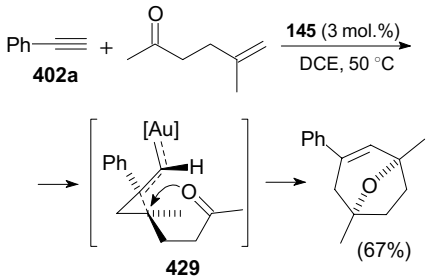
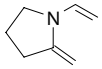
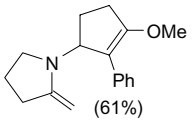
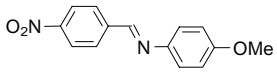
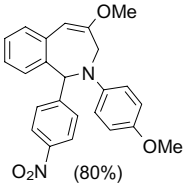
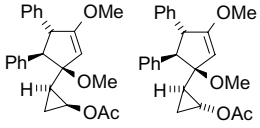
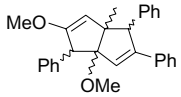
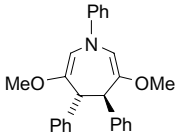
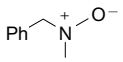
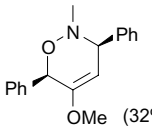


Table 2. Reaction of the acetal (HC≡C)CH(Ph)OCMe$_2$OMe with nucleophiles.

Nucleophile, reaction conditions	Reaction type	Product (yield)	Ref.
 **18**, DCM, rt, 15 min	[2 + 3]-Cycloaddition	 (61%)	314
 **18**, DCM, rt, 15 min	[2 + 5]-Cycloaddition	 (80%)	315
 **18**, DCM, −78 °C, N_2, 15 min	Tandem cyclization	 *cis* *trans* (69%, *cis* : *trans* = 50 : 50)	316
18, DCM, rt, 15 min	Tandem cyclization	 (60%)	317
PhN_3 **18**, DCM, 0°C, 30 min	[3 + 4]-Cycloaddition	 (84%)	318
 **18**, DCM, rt, 2 h	[3 + 3]-Cycloaddition	 (32%)	319

The one-pot synthesis of tetracyclic indole derivatives **431** *via* gold-catalyzed tandem annulation of 1,2-dialkynyl-2-en-1-ones **430** to indole has been proposed.[324] The reaction includes successive carbonyl-yne cyclization, Friedel – Crafts reaction and indole-yne cyclization. Scheme 204 shows examples of products **431** formed in the reaction and the presumptive reaction mechanism.

3. Formation of the C – C bond with retention of the alkyne triple bond

3.1. Acetylenide as the nucleophile

The AuCl – AgOTf system catalyzes the reaction of terminal alkynes **402** with aryl trichloroacetamidates **432**, which yields arylmethylated products **433** in moderate and good yields (Scheme 205).[325]

3.2. Sonogashira reaction

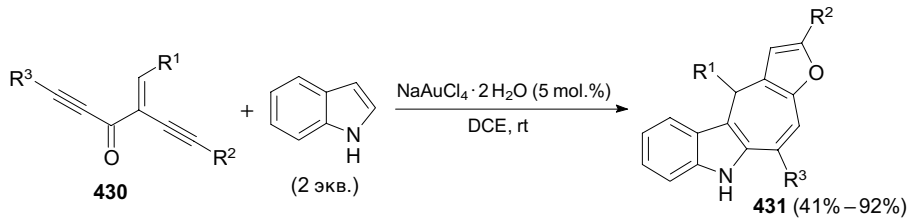
The Sonogashira reaction is not induced by the AuI – dppe catalytic system. However, the addition of 0.12 mol.% [$Pd_2(dba)_3 \cdot CHCl_3$] leads to a 100% conversion of substrate **402d** to afford coupling product **434** in 82% yield (Scheme 206). A possible reaction mechanism was proposed by Lauerbach *et al.*[100]

Corma and co-workers[326] found that the simultaneous use of gold clusters and nanoparticles in a Sonogashira type reaction dramatically increases the catalyst activity; in this case, aromatic and aliphatic alkynes can react not only with aryl iodides or bromides, but also with activated aryl chlorides. Subnanometre-size gold clusters in combination with supported gold nanoparticles (Au-NP) were used to catalyze the Sonogashira coupling (Scheme 207).[326] Figure 3 shows schematic illustration of the disassembling of commercially available gold nanocrystals into nanoclusters and nanoparticles.

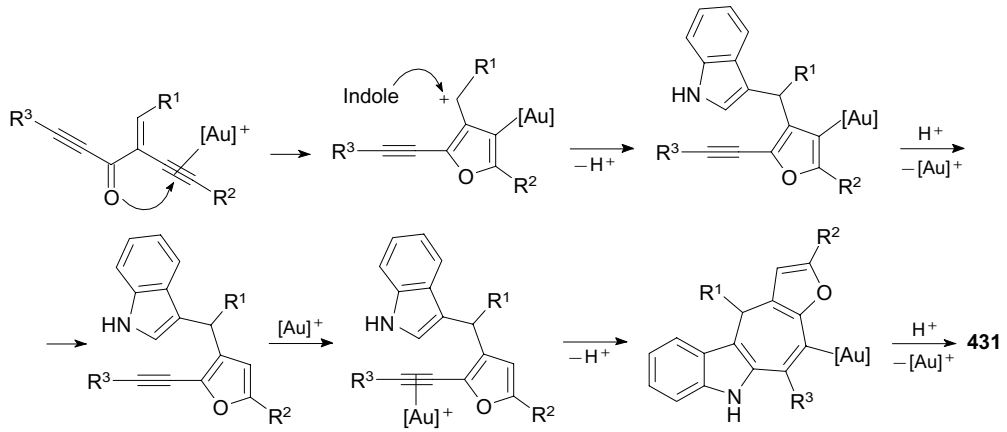
3.3. Synthesis of diacetylenes. Gold redox cycle

It was repeatedly indicated above that the area of chemistry related to gold catalysis for any state of gold is being rapidly developed. Interestingly, this success is, to some extent, due to the fact that gold usually does not change its oxidative state during a catalyzed reaction,[206, 327] which is attributable, first of all, to high redox potential of the Au^I/Au^{III} pair. However, the use of an external oxidant such as Selectfluor™ or peroxy acids triggers the redox cycle of gold, which additionally extends its scope of application.[328 – 332]

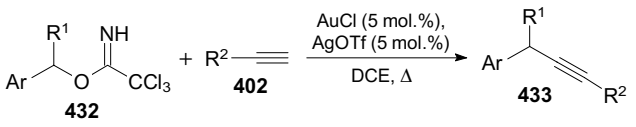
Scheme 204



R^1 = Me, Ph; R^2 = Bu^n, cyclohexen-1-yl, Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4; R^3 = Bu^n, Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-$F_3CC_6H_4$

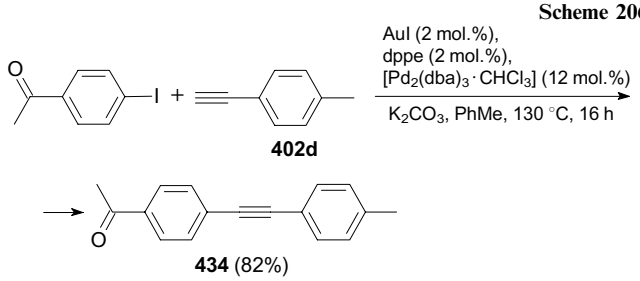


Scheme 205

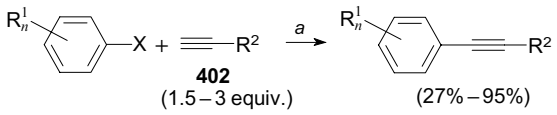


Ar	R^1	R^2	Time /h	Yield of **433** (%)
Ph	H	Ph	3	65
2-ClC_6H_4	H	Ph	4	54
2-BrC_6H_4	H	Ph	4	62
2-IC_6H_4	H	Ph	3.5	63
3-ClC_6H_4	H	Ph	10	79
3-BrC_6H_4	H	Ph	10	85
4-FC_6H_4	H	Ph	4	55
4-ClC_6H_4	H	Ph	4	69
4-BrC_6H_4	H	Ph	4	63
3-Me-4-BrC_6H_3	H	Ph	3	84
2-MeC_6H_4	H	Ph	4	66
4-PhC_6H_4	H	Ph	5	48
4-$Bu^tC_6H_4$	H	Ph	3	66
Ph	Ph	Ph	4	55
Ph	H	4-BrC_6H_4	4	57
Ph	H	Bu^n	4	30
4-$O_2NC_6H_4$	H	Ph	5	0
6-Methylpyridyl	H	Ph	5	0

Scheme 206



Scheme 207



(*a*) Au-NP (0.2 – 3) mol.%, Au clusters (0.005 – 0.06) mol.%, NMP (0.25 M), KOAc (4 equiv.), 135 – 160 °C, 24 h; X = Cl, Br, I; R^1_n = H, 4-C(O)H, 4-Bu^t, 4-CN, 2,4-F_2, 3-Cl-4-F, 3,4,5-$(OMe)_3$, 4-F, 4-OMe, 4-Me, 2-C(O)H, 4-C(O)Me, 4-CF_3-2-C(O)Me, 2-CN; R^2 = Ph, 2-ClC_6H_4, 4-BrC_6H_4, 3-$[(MeO)_2CH]C_6H_4$, PhCH=CH, 4-ClC_6H_4, $Me_2C(OH)$, 4-$H_2NC_6H_4$, n-C_8H_{17}, $HO(CH_2)_9$, 2-$MeOC_6H_4$, 4-MeC_6H_4, 3-MeC_6H_4

In recent years, rapid progress has been made in the chemistry of 1,3-diynes.[333 – 335] This is largely due to increasing application of these compounds as intermediates for the synthesis of biologically active products and pharmaceuticals,[336] optoelectronic materials[337] and polymers.[338] Compounds of this type were usually prepared by the Glaser oxidative coupling of alkynes, for example,

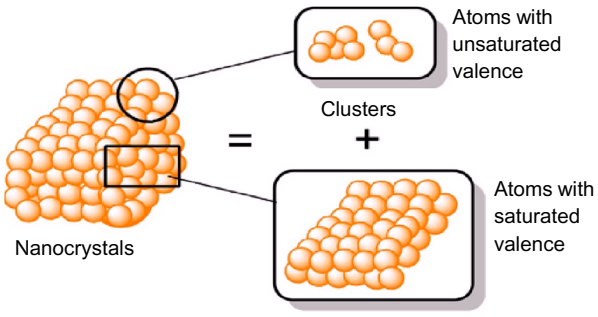
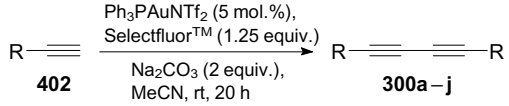


Figure 3. Schematic illustration of artificial disassembling of gold nanocrystals into nanoclusters and low-faceted nanoparticles.[326]

the Glaser – Eglinton coupling [339] using $Cu(OAc)_2$ or the Glaser-Hay coupling [340] catalyzed by CuI in the presence of a ligand and oxygen.

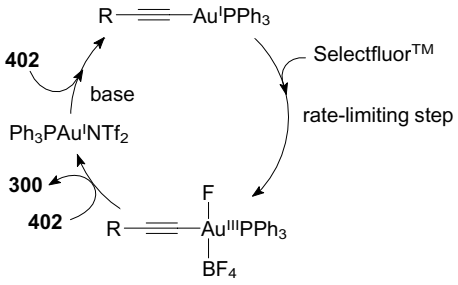
Leyva-Pérez *et al.*[341] described the homocoupling of terminal alkynes **402** catalyzed by gold(I) in the presence of an oxidant (Scheme 208). The mechanism of formation of diynes **300** proposed by the authors is depicted in Scheme 209.

Scheme 208



Compounds **300**	R	Yield of **300** (%)
a	Ph	80
b	2-$MeOC_6H_4$	> 99
c	3-$MeOC_6H_4$	> 99
d	4-$MeOC_6H_4$	> 99
e	2-MeC_6H_4	76
f	3-MeC_6H_4	47
g	2-ClC_6H_4	78
h	2-BrC_6H_4	75
i	Bu^n	> 99
j	Hex	> 99

Scheme 209

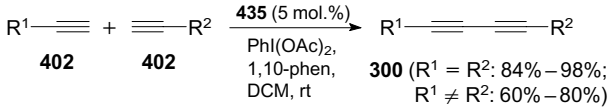


Heterogeneous catalysis has some advantages over homogeneous catalysis. The key advantage is that the catalyst is more easily isolated from the reaction mixture and, hence, can be reused. Homocoupling of alkynes has been carried out with copper-, palladium- and nickel-based catalysts.[342 – 344] The drawbacks of these catalysts include the complexity and/or high cost of their synthesis, large amounts needed to conduct the reaction, the necessity of a large amount of a base and high temperatures. Only some of these catalysts are suitable for coupling of two different alkynes (heterocoupling).[345, 346]

In 2016, Beloqui Redondo proposed [347] a new material representing exceptionally small gold nanoparticles (0.8 ± 0.2 nm in diameter) supported on 3-aminopropyl-functionalized silicate SBA-15 (catalyst **435**). This material exhibited high catalytic activity in quite a few reactions,[347] in particular, in the oxidative coupling of alkynes, including both homocoupling and heterocoupling.[348] The range of substrates and products of these reactions is presented in Scheme 210.[349]

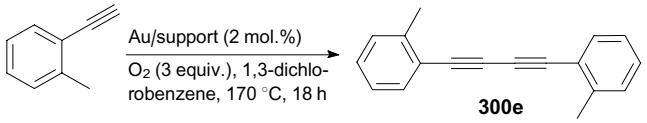
Homocoupling of alkynes **402** under aerobic conditions was catalyzed by gold nanoparticles supported on different materials (Scheme 211).[350] Quantum chemical calculations (DFT) and kinetic measurements indicated

Scheme 210



$R^1 = R^2$ = Ph, 4-MeC_6H_4, 4-PhC_6H_4, pyren-1-yl, 4-$MeOC_6H_4$, $PhOCH_2$, 4-FC_6H_4, 3,5-$(F_3C)_2C_6H_3$, 4-$(F_3CO)C_6H_4$, 4-$H(O)CC_6H_4$; R^1 = 4-$MeOC_6H_4$: R^2 = 4-FC_6H_4, 4-$(F_3CO)C_6H_4$, 3,5-$(F_3C)_2C_6H_3$

Scheme 211

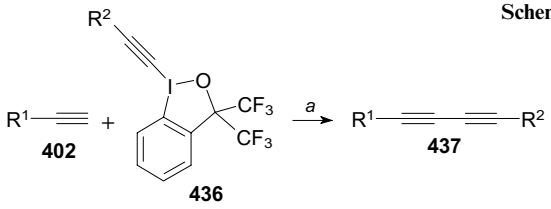


Au/support	Yield of **300e** (%)	Au/support	Yield of **300e** (%)
Au/CeO_2	50	Au/ZnO	85
Au/C	88	Au/TiO_2	73
Au/Fe_2O_3	43		

that oxygen dissociation on gold nanoparticles is the rate-limiting step of the reaction.

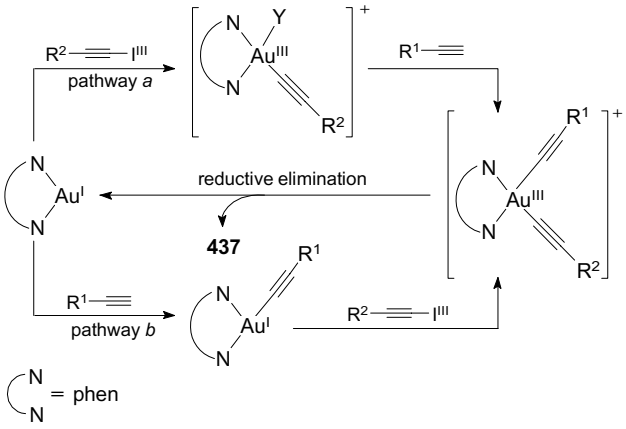
A new efficient synthetic route to unsymmetrical buta-1,3-diynes **437** *via* gold-catalyzed C(sp) – C(sp) coupling of terminal alkynes **402** with the alkynyl trivalent

Scheme 212



(*a*) **336** (5 mol.%), AgOTs (5 mol.%), phen (0.5 equiv.), MeCN, rt, 15 min – 6 h; R^1 = 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 4-$EtO_2CC_6H_4$, 4-$F_3CC_6H_4$, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-CbzHNC_6H_4, 2-MeC_6H_4, 2-$F_3CC_6H_4$, 3,4,5-$(MeO)_3C_6H_2$, 2,4,6-$Me_3C_6H_2$, 1-Naph, 2-Th, 2-Py, cyclohexen-1-yl, Bu^n, n-$C_{10}H_{21}$, cyclo-C_3H_5, Ph, Bn, $Ph(CH_2)_2$, $NC(CH_2)_3$, $BnO(CH_2)_2$, $MeOCH_2$, PhN(Ts)CH_2, $Me_2(OH)C$, EtO_2C, TMS, TIPS, $Cl(CH_2)_3$; R^2 = Ph, 4-MeC_6H_4, 4-NCC_6H_4, 4-$EtO_2CC_6H_4$, 4-$O_2NC_6H_4$, Bu^n

Scheme 213



iodine reagent **436** has been reported[351] (Scheme 212). The reaction proceeds in the presence of phenanthroline, which is complexed with gold. The reaction mechanism proposed by the authors is shown in Scheme 213 and implies a change in the gold oxidation state in the transition complex.

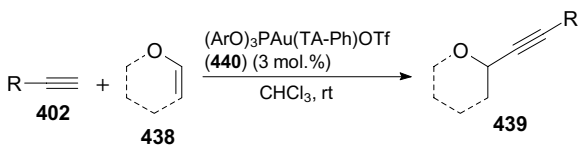
3.4. Intermolecular reaction of alkynes and alkenes

It is known that the Au^I cation exhibits a higher π-acidity with respect to alkynes than to alkenes. For example, this is manifested in the cycloisomerization of enynes considered above or in the [2 + 2]-cycloaddition. The reaction includes nucleophilic addition of the alkene to gold-activated alkyne. However, an attempt to use vinyl ethers as the alkene component in the reaction with terminal alkynes had an unexpected outcome:[352] vinyl ethers **438** reacted with terminal alkynes **402** with selective formation of propargyl ethers **439** (Scheme 214). Meanwhile, no [2 + 2]-addition products (cyclobutenes) were detected. Screening of catalysts allowed researchers[352] to identify complex **440**, which was most stable under reaction conditions and did not decompose.

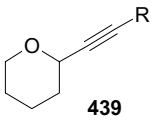
Although vinyl ethers **438** have a higher π-electron density due to the effect of the oxygen atom conjugated with the double bond, gold acetylenide acts as a nucleophile in this case, while vinyl ether is an electrophile. It was found[352] that a minor amount of the acid that remained, for example, after catalyst preparation, activates the reaction.

Notably, this reaction is suitable for efficient stereoselective glycosylation (Scheme 215).

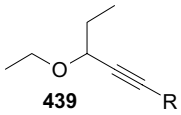
Scheme 214



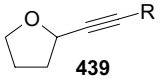
Ar = 2,4-$Bu^t_2C_6H_3$, TA-Ph is 1-phenylbenzotriazole;



R = Ph (78% yield), 3-ClC_6H_4 (76%), 3-FC_6H_4 (75%), 4-$Bu^tC_6H_4$ (82%), 4-$MeOC_6H_4$ (73%), cyclo-C_3H_5 (70%), cyclo-C_5H_9 (68%), cyclohexen-1-yl (66%), 3-(HC≡C)C_6H_4 (58%), 3-Th (73%)

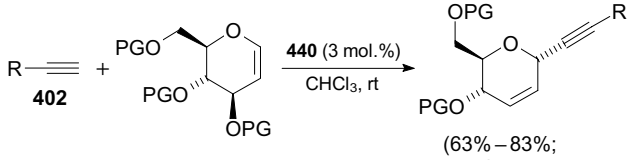


R = Ph (83%), 3-ClC_6H_4 (80%), 4-$Bu^tC_6H_4$ (85%)



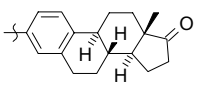
R = Ph (73%), 3-FC_6H_4 (72%)

Scheme 215



(63% – 83%; α : β from 95 : 5 to 99 : 1)

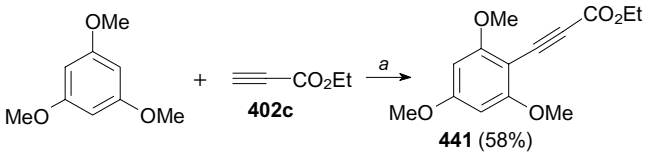
PG = Ac, Bn, Bz, TBS; R = Ph, 4-$Bu^tC_6H_4$, 3-ClC_6H_4, 4-FC_6H_4, 4-BrC_6H_4, 4-H(O)CC_6H_4,



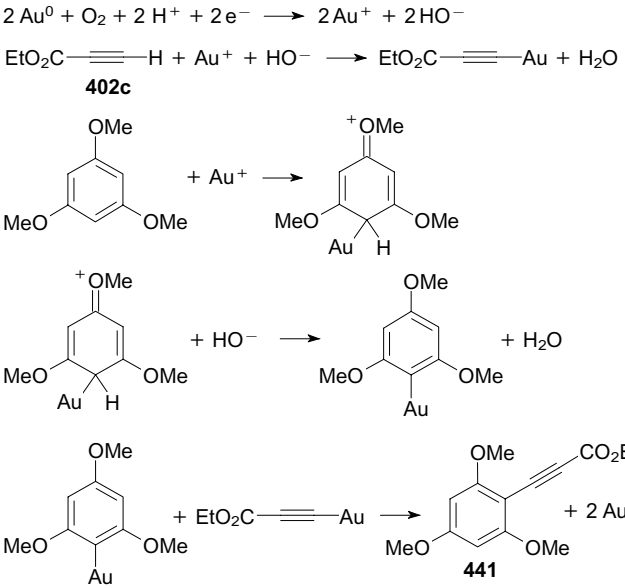
3.5. C – H-Alkynylation of aromatic compounds

Electron-rich arenes, for example, 1,3,5-trimethoxybenzene, can react with propiolates, for example, ester **402c**, with gold nanoparticles as catalysts to give a new C – C bond.[353] The reaction involves oxygen as the oxidant and gives alkynylated arenes (for example, product **441**). The mechanism proposed for this reaction[353] is shown in Scheme 216.

Scheme 216



(*a*) Au/C (5 mol.%), O_2, 1,2-dichlorobenzene, 140 °C, 40 h; $-H_2O$



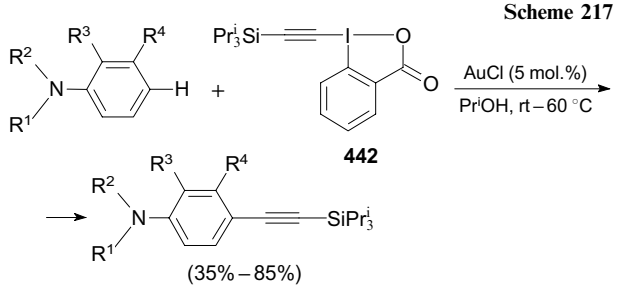
Brand and Waser[354] described a process for *para*-selective alkynylation of anilines catalyzed by AuCl. (Triisopropylsilyl)ethynyl-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX, **442**) was used as an electrophilic alkyne equivalent. The reaction equation and the scope of possible substrates are given in Scheme 217. It is worth noting that alkynylation of anilines in the presence of a Pd catalyst [$Pd(OAc)_2$ – AgOTf] results in the selective formation of *ortho*-substituted anilines.[355]

The above-described method was utilized for the selective direct alkynylation of azulenes **443** (Scheme 218).[356]

3.6. C – H-Alkynylation of heterocyclic compounds

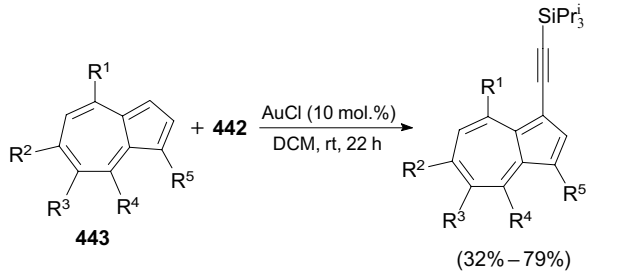
Throughout the last decades, C – H functionalization of heterocyclic compounds in reactions catalyzed by tran-

Scheme 217



R^1 = H, Me, Et, Bu^n, Bn; R^2 = Me, Et, Bu^n, Bn, PhCH(Me);
R^3 = H, Me, MeO, Ph; R^4 = H, Me, MeO, Cl, Br;
$R^3 - R^4$ = CH=CH–CH=CH

Scheme 218



R^1 = H, Me; R^2 = H, Me, Bu^t, Ph; R^3 = H, Pr^i; R^4 = H, Me;
R^5 = H, I, Me, C(O)H, $C(O)CH_2Cl$

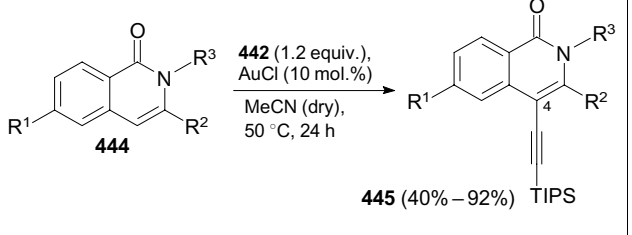
sition metals has been a topical issue for organic synthesis, because it is efficient, economical and simple in comparison with classical methods of synthesis. There are a lot of examples, and we will cite only some publications.[357 – 360]

It is noteworthy that the nature of transition metal often affects considerably the reaction pathway. For example, when the alkynylation of isoquinolones **444** on treatment with (triisopropylsilyl)ethynyl-1,2-benziodoxol-3(1*H*)-one (**442**) is catalyzed by AuCl, selective C(4)-alkynylation takes place to give products **445** (Scheme 219; when R^3 = Ph, no reaction occurs).

Meanwhile, in the presence of the complex $[RhCp^*Cl_2]_2$, the reaction results in the selective formation of C(8)-alkynylation products **446** (Scheme 220).[361]

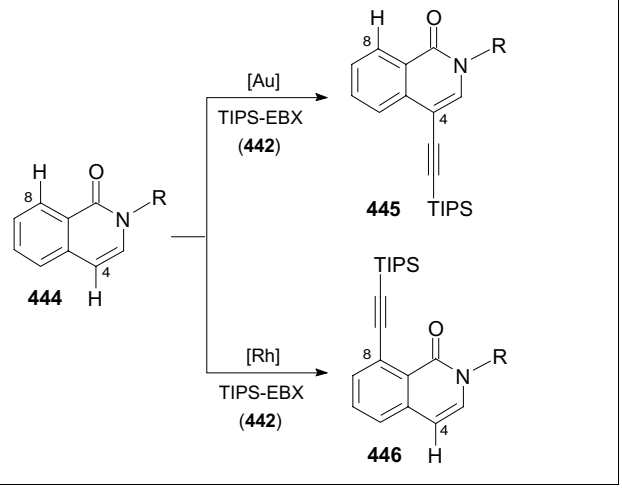
Apparently, the reason is that gold is a softer Lewis acid and an alkynophile, which activates the alkyne moiety of reactant **442**, thus increasing its electrophilicity; this results in the attack on the most nucleophilic

Scheme 219



R^1 = H, Me, OMe, F, Cl, Br, CF_3; R^2 = H, Bu^n, cyclo-C_3H_5, Ph;
R^3 = Me, Et, Pr^i, Bu^n, cyclo-C_5H_9, Bn

Scheme 220



position of the substrate. The Rh complex, which is more oxophilic, is coordinated to the oxygen atom of substrate **444**, thus activating the nearest C – H bond.

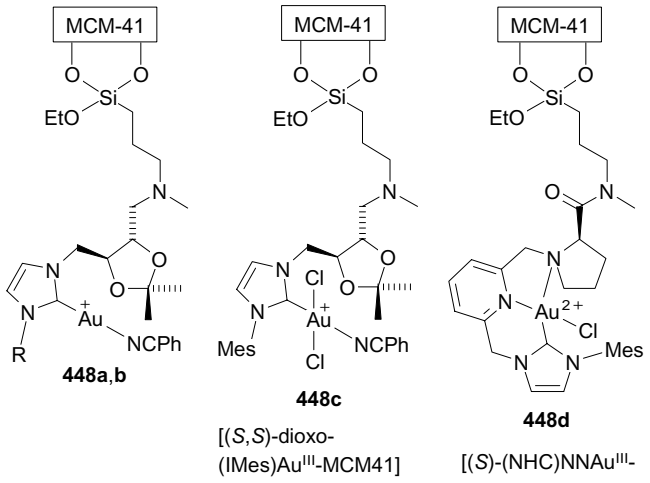
3.7. Preparation of propargylamines. Immobilized catalysts

Villaaverde *et al.*[362] described the synthesis of propargylamines **447** *via* a multicomponent (three-component) chemical reaction on a heterogenized gold carbene complex, which is a green chemistry process. The heterogenized complex can be reused at least six times without the loss of activity. Propargylamines are important building blocks in organic synthesis;[363] their structural moiety has been found in a number of natural compounds[364] and is present in some potential pharmaceutical agents.[365, 366]

MCM-41, a mesoporous silicate with hierarchical structure developed by Mobil Oil researchers in the 1990s and often used as a catalyst or catalyst support, was employed as the support in the case.[367] Immobilized gold(I) complex **448a**,**b** and gold(III) complex **448c**,**d** were also used as catalysts.[362]

Scheme 221 presents the reaction equation. Note that reasonable yields of product **447** were attained only for cyclic amines — piperidine and pyrrolidine. The yield of

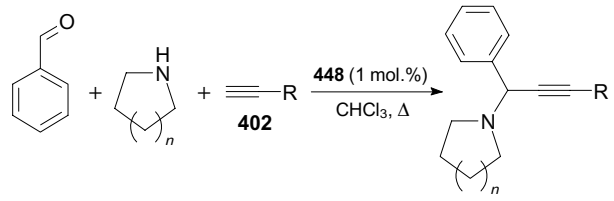
Structures 448



R = Mes [**a**, (*S*,*S*)-dioxo(IMes)Au^I-MCM41],
2,6-$Pr^i_2C_6H_3$ [**b**, (*S*,*S*)-dioxo(IPr)Au^I-MCM41]

product **447** depends on the nature of catalyst **448**. The best results were obtained for piperidine and dec-1-yne with catalyst **448a** (97%).

Scheme 221



R = n-C_8H_{17}, Ph, 4-MeC_6H_4; *n* = 1, 2 **447** (40% – 97%)

This three-component reaction was also catalyzed by mixed Fe_3O_4@Au nanoparticles (Au-coated Fe_3O_4 nanoparticles),[368] which can be magnetically separated from the reaction mixture and reused without the loss of activity.

4. Conclusion

The use of gold as a catalyst allows various modifications of alkynes (often, rather complex modifications in one step) containing a broad range of substituents under mild conditions to obtain target products in high yields. Until now, extensive application of gold in organic synthesis has been restricted, among other factors, by high cost of the catalysts. The implementation of immobilized gold-containing ionic catalysts and gold nanoparticles made it possible to conduct cyclic reactions that, furthermore, comply with the green chemistry requirements. This, in turn, stimulates further intensive development of this field of catalysis.

In conclusion, we would like to note that, with the best will in the world, we cannot fully cover the diversity of gold-catalyzed transformations. Many new reactions were accomplished as this review was under preparation; a number of new reviews appeared (see, for example, Ref. 369). In particular, neither of our two reviews considers the reactions of alkynes with organosilicon compounds, halogens or hydrogen halides, or triple bond oxidation and reduction reactions, which we plan to describe in the next review of this series.

Figure 3 is a courtesy of John Wiley and Sons.

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