Carbo- and heterocyclisation of oxygen- and nitrogen-containing electrophiles by platinum, gold, silver and copper species

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In this present perspective, we summarise the recent progress on the use of gold, platinum, silver and copper complexes to activate common oxygen and nitrogen electrophiles.

1. Introduction

Synthetic chemists are constantly challenged to find new synthetic methods that save energy and materials. Gold and platinum catalysis has achieved such goals with activation of alkynes, allenes and alkenes towards nucleophiles.[1,2] The facile C–X bonds occurring on these substrates enable rapid construction of complicated molecules with high efficiencies and effective stereocontrol. Despite many reviews[1,2] on gold and platinum catalysis, none of them is targeted at the activation of oxygen- and nitrogen-containing electrophiles. Although hard Lewis acids are intrinsically more active than soft metals in the initial activations of electrophiles, resulting products from the hard Lewis acids often contain a strong M–O bond that is difficult for regeneration of the catalyst. Soft Lewis acids, with reasonable activity in the activation of electrophiles, are beneficial for new catalyst designs. Herein, we summarise the results of rapidly growing papers in recent years on the use of gold, platinum, silver and copper complexes to activate common oxygen and nitrogen electrophiles. The scope of the reported reactions is strictly limited to the carbo- or heterocyclisation of those substrates bearing common electrophiles, including epoxides, aziridines, aldehydes, ketones, imines, acetals and ketals. Cyclisation reactions of these molecules with external or internal nucleophiles are also included.

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Substrates in reported reactions usually comprise a tethered functionality in addition to an electrophile in order to complete a C–C and C–X (X = O, N) bond in the cyclisation. Scheme 1 summarises four general cascades that are applicable to most instances. Structure **A** represents an initial activation of tether functionality **FG** to induce an attack of the oxygen atom of the electrophile, giving species **C** to complete a cycloisomerisation reaction. A similar cycloisomerisation is also likely to occur with an initial activation of the electrophile, as exemplified by species **B** and **D**. During the coupling of the electrophile with its tethered functionality, the metal may generate a stable carbocation on species **C** and **D**, enabling sufficient trapping of a nucleophile to complete a heterocyclisation. In the final route, the nucleophile first attacks at metal-coordinated electrophile, and the resulting new functionality subsequently attacks at the tethered functionality implemented by metal, completing an alternate nucleophilic cyclisation.

According to these protocols, the tethered functionality **FG** may be a nucleophile like alcohol, amine, silane-, alkene- and arene-based nucleophiles. However, many more examples are focused on the route **A**→**C** with an alkyne as the functionality; this outcome is closely associated with the advent of gold catalysis that starts with alkyne activation. Few examples were reported for the route **E**→**F** in which **FG** was an alkyne. In this review, we report reactions of such pathways according to the nature of cyclisation, *i.e.* "carbocyclisation" and "heterocyclisation", which respectively refer to formation of a new C–C or C–X bond to form a "carbocyclic" or "heterocyclic" ring. We also define

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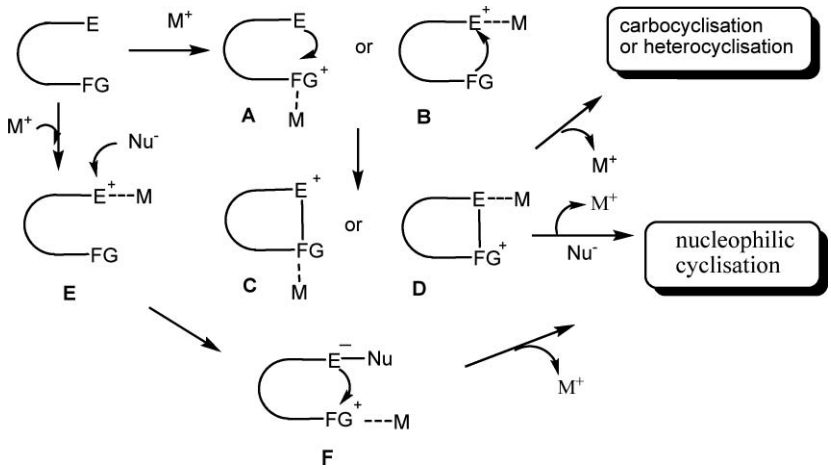

Scheme 1 General mechanistic pathways.

"carbocyclisation" to those examples where both new C–C and C–X bonds are formed simultaneously.

2. Carbocyclisation reactions

2.1 Epoxyalkyne

Hashmi *et al.*[3a] and ourselves have developed[3b] independently a new Au(I)- and Ag(I)-catalysed cycloisomerisation of epoxyalkyne **2-1** to carbocyclic compounds **2-2** and **2-3**. In this carbocyclisation, Au(I) generates a carbenoid species from 1,2-disubstituted epoxides **2a**, whereas Ag(I) gives a carbocation intermediate from trisubstituted epoxides **2g**. PPh_3Au^+ likely complexes with the internal alkyne to induce a 7-*endo*-cyclisation to yield seven-membered oxacyclic species **2b**, of which the gold–enol moiety promotes cleavage of the ether ring to form Au(I)–carbene **2c** that induces an electrocyclisation to generate 1-indanyl cation **2e**, ultimately giving the observed 1-indanone products. Herein, gold α-carbonylcarbenoids are confirmed by trapping with alkene to give cyclopropane products. For silver catalysis, prior rearrangement of epoxide to ketone, we propose that the mechanism likely involves a 1,2-phenyl shift to give oxonium species **2i**, which ultimately gives the desired product through a rearrangement of oxetane intermediate **2j** (Scheme 2).

We extended this gold-catalysed epoxyalkyne cycloisomerisation to nonaromatic epoxides **3-1**, giving corresponding heterocyclic compound **3-2**. The key intermediate is formed by a 6-*exo-dig* attack of the epoxide at the activated alkyne and its structure is best represented by its gold–carbenoid resonance form **3c**, which triggers a Nazarov-type cyclisation to give the observed heterocyclic compound as depicted in Scheme 3. We have applied this new cyclisation for a rapid construction of the central cores of natural products such as pallidol and gibberic acid depicted in Scheme 4.

Sarpong *et al.* revealed[4] an efficient method for the carbocyclisation of epoxy-propargylic acetates **5-1** *via* $PtCl_2$ catalysis as depicted in Scheme 5. This reaction is initiated by π-alkyne activation to cause Rautenstrauch rearrangement to form platinum 2-acetylalkenylcarbenoids **5b**. Such carbenoids are electrophilic and attacked by the tethered epoxide oxygen to give strained intermediate **5c** that undergoes bond isomerisation to yield pyran intermediate **5d**. An electrocyclic ring opening of this species provides dienone **5e** that forms functionalised cyclopentenone **5-2** as depicted in Scheme 5.

2.2 Oxoalkynes

Jin and Yamamoto[5a,b] recently reported an interesting ketone/alkyne metathesis that allowed a transformation of ketone/alkyne substrates **6-1** to conjugated enones **6-2**, catalysed by $AuCl_3/3AgSbF_6$ in hot toluene. They also reported an efficient synthesis of tricyclic enones **6-3** from 1,3-enynl carbonyl substrates, catalysed by $AuCl_3/3AgSbF_6$ (Scheme 6). In the latter, the Au(III) species serves two catalytic tasks: it activates the alkyne moiety for the ketone/alkyne metathesis process and thereafter it activates the carbonyl group of divinyl ketone intermediate **6c** for the ensuing Nazarov cyclisation.

The π-alkyne activation, as depicted in the **A**→**C** route (Scheme 1), is also well manifested by alkynyl enones **7-1** which undergo metal-catalysed carbocyclisation with a wide range of nucleophiles. Pioneering work in this field was developed independently by Yamamoto and Iwasawa. As depicted in Scheme 7, the

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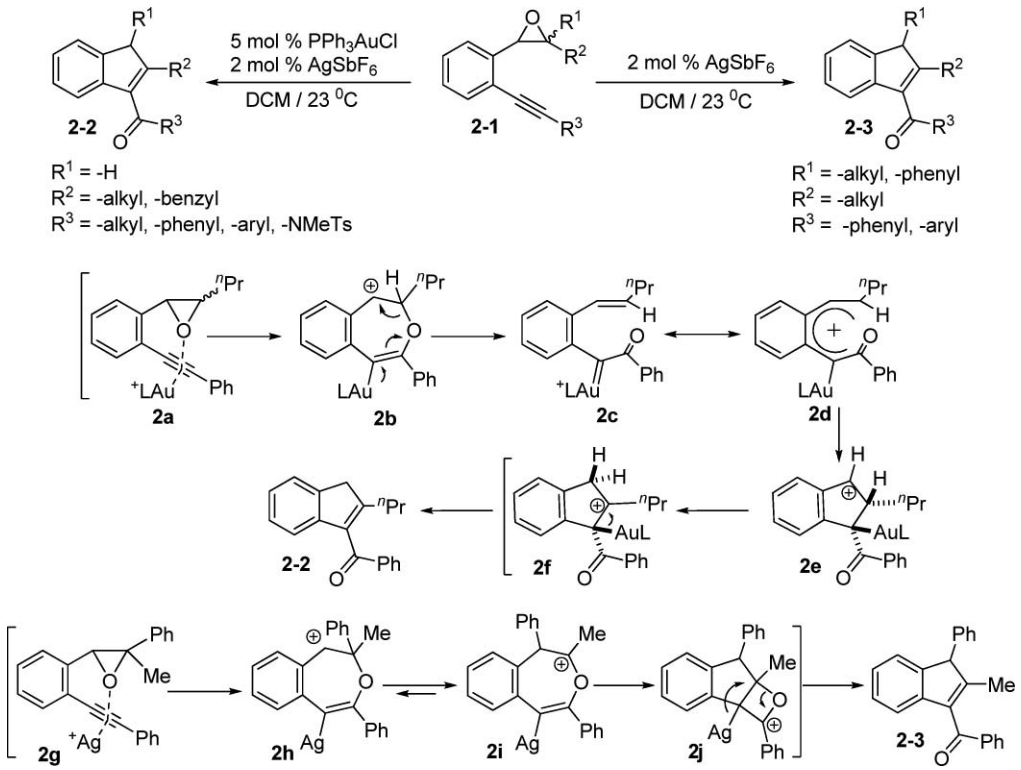
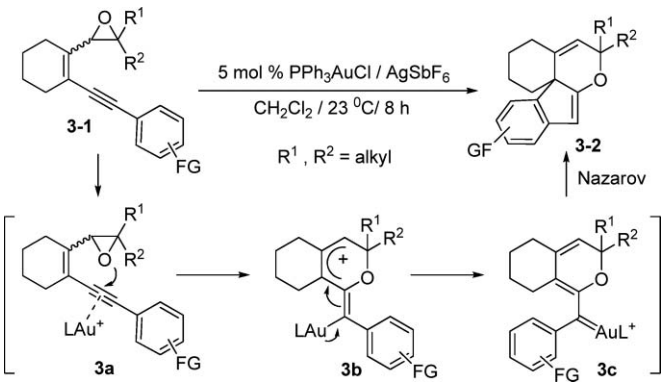


Scheme 2 Diversity in gold- and silver-catalysed cycloisomerisation of epoxiy alkyne.



Scheme 3 Gold-catalysed cycloisomerisation of nonaromatic epoxyalkynes.

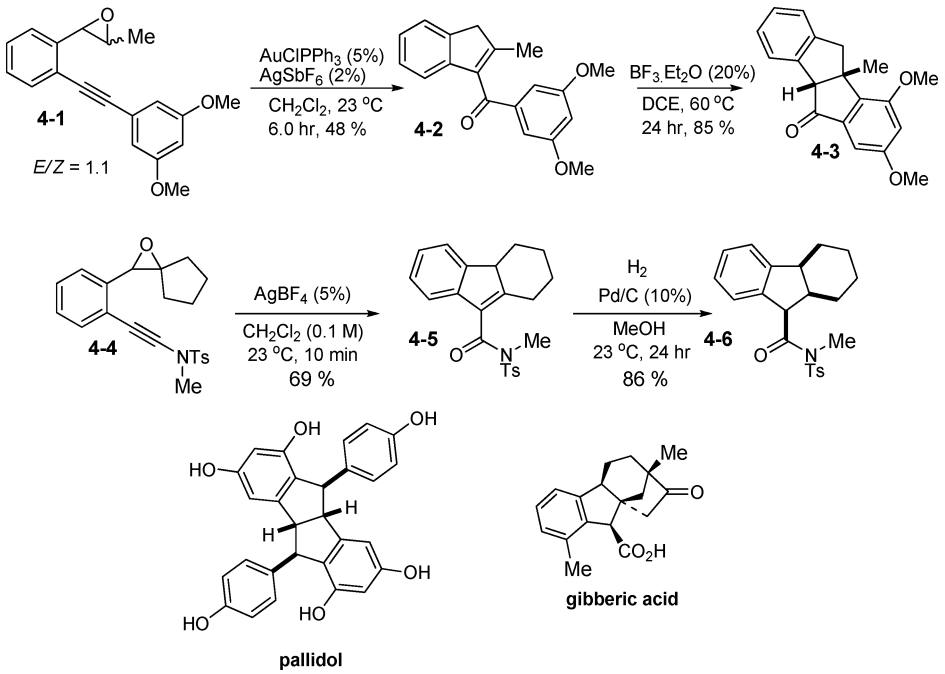
attack of the carbonyl unit onto the tethered π-alkyne generates metal containing benzopyrylium intermediates **7-2** which are active toward cycloadditions with various nucleophiles such as alkynes, alkenes, vinyl ethers and carbonyl compounds, giving diverse products.

In this context, Yamamoto *et al.* published[6] an $AuCl_3$-catalysed [4 + 2] benzannulation between *o*-alkynyl(oxo)benzenes **8-1** and alkynes which gave highly substituted naphthalene derivatives **8-4** and **8-5** in good to high yields. With the use of $Cu(OTf)_2$, they obtained the decarbonylated naphthalenes **8-6** efficiently. This new method is applicable to enynals **8-3** that deliver substituted benzenes **8-7** in good yields (Scheme 8).

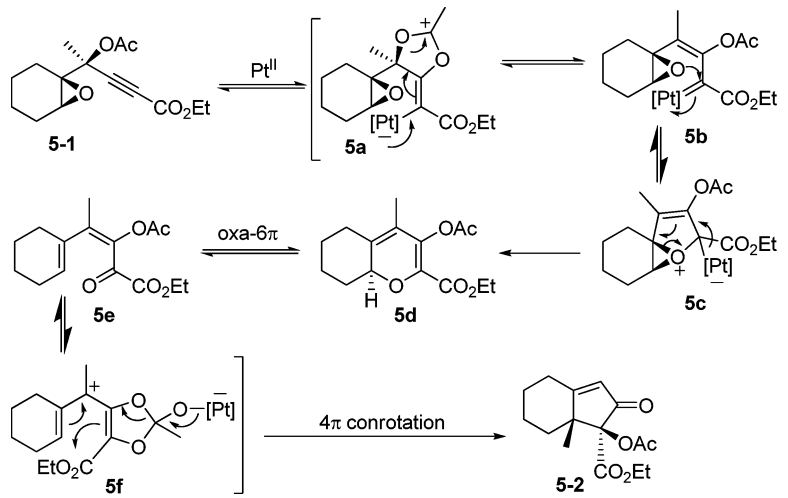
Yamamoto *et al.*[7] elegantly used the $AuCl_3$-catalysed [4 + 2] benzannulation of *o*-alkynylbenzaldehydes **9-1** intramolecularly, as the key step for the synthesis of (+)-rubiginone B_2 (**9-3**) and (+)-ochromycinone (**9-4**), members of the angucyclinone family of natural products (Scheme 9). After the efficient formation of the tetracyclic core **9-2**, oxidation of the dihydrotetraphenones derivative delivers the target natural products.

Common 2-alkynylbenzaldehydes form metal-containing benzopyrilium intermediates that undergo [4 + 2] cycloaddition with alkenes to form cycloadducts; these species suffer from kinetic instability to undergo rapid rearrangement to give 1,2-dihydronaphthalene or naphthalene products. These [4 + 2]-cycloadducts were merely hypothetic intermediates without actual use. In our recent work,[8] we successfully intercept [4 + 2]-cycloadducts using 2-substituted allylic alcohols, as depicted in Scheme 10. Interestingly, we observe two distinct classes of oxacyclic products **10-3** and **10-4** depending on substrates. Tetracyclic ketal **10-3** species are obtained stereoselectively from 2-alkynylbenzaldehydes **10-1** whereas tricyclic oxacyclic compounds **10-4** are produced exclusively from nonaromatic enynals **10-2**. Such distinct pathways stem from separate diastereotopic faces in the cycloaddition of allylic alcohols with benzopyriliums **10a** and pyriliums **10c**.

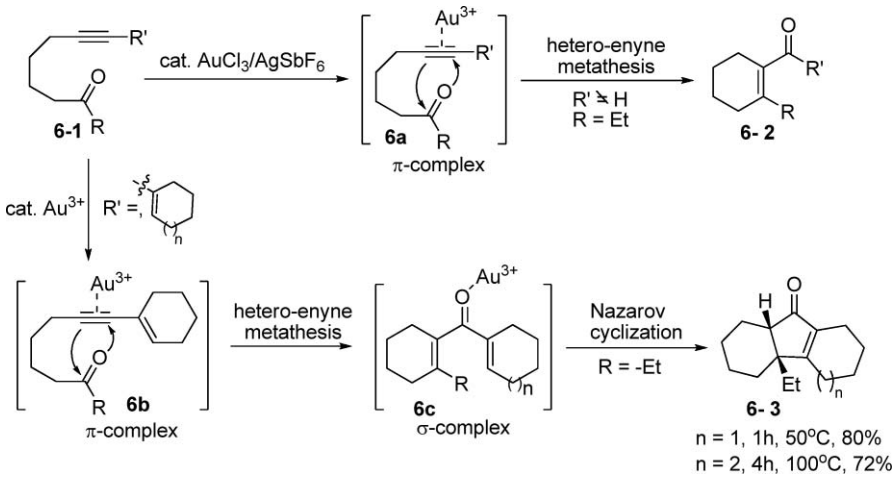
In recent work by Zhang *et al.*,[9] the treatment of 1-(1-alkynyl)cyclopropyl ketone **11-1** with a cationic gold catalyst forms a gold-containing 1,4-dipole intermediate **11b**, generated on cleavage of the cyclopropane ring of carbonyl ylide intermediate **11a**. This all carbon dipole intermediate is reactive toward aldehydes, ketones or indoles through diastereoselective [4 + 2]-cycloadditions (Scheme 11). The same ketone-alkyne substrates show distinct chemoselectivity when enol ethers **12-1** serve as a dipolarophile.[10] In the presence of $IPrAuNTf_2$, a distinct [3 + 2]-annulation occurs through the [3 + 2]-cycloaddition of carbonyl ylide intermediates with enol ethers, giving highly strained



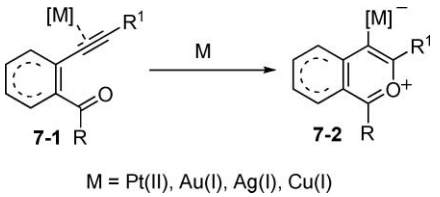
Scheme 4 Synthesis of central core of natural pallidol and gibberic acid.



Scheme 5 Platinum-catalysed cyclopentenone synthesis from epoxy-propargyl acetates.



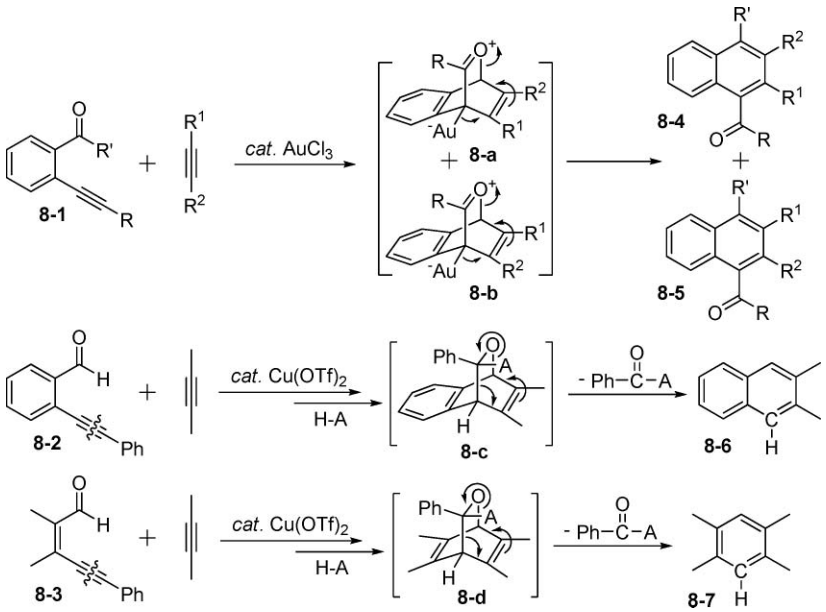
Scheme 6 Au-catalysed tandem heteroenyne metathesis and Nazarov cyclisation.



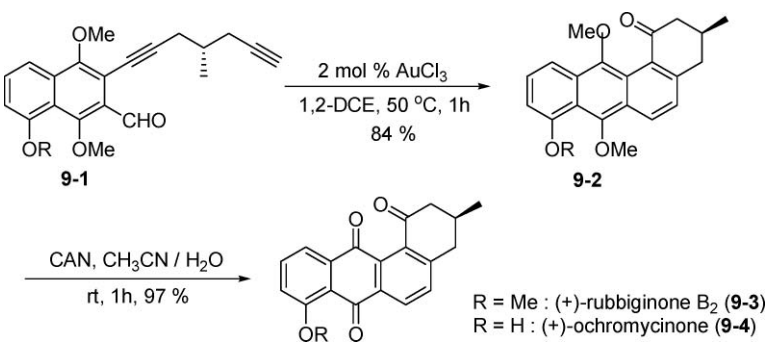
Scheme 7 Formation of metal-containing benzopyrylium-type intermediates.

bicyclo[3.2.0]heptanes **12-2** (Scheme 12). Using a $PtCl_2$ catalyst, Iwasawa *et al.*[11] reported [3 + 2]-cycloaddition reactions of enol ethers with 1-alkynyl-2-oxobenzenes **13-1**. This transformation ultimately renders 4-alkoxy-1-naphthanal **13-2** efficiently through one-pot annulations as shown in Scheme 13.

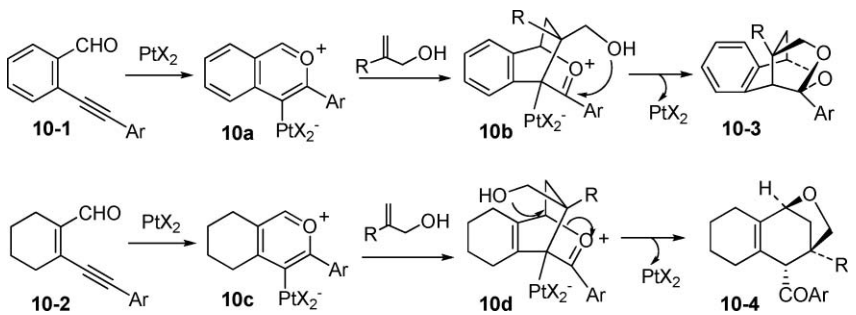
The preceding [3 + 2]-cycloaddition was confirmed by Oh *et al.*, who reported a stereocontrolled synthesis of a complex oxocyclic compound **14-2** *via* a C–H bond insertion of the proximate benzyl ether by a platinum–carbenoid **14a** (Scheme 14).[12]



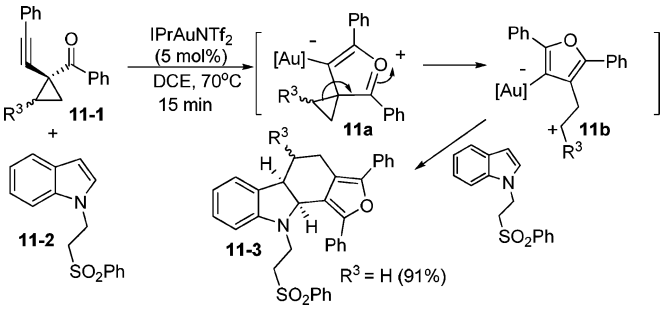
Scheme 8 Benzannulation through a formal intermolecular [4+2] cycloaddition.



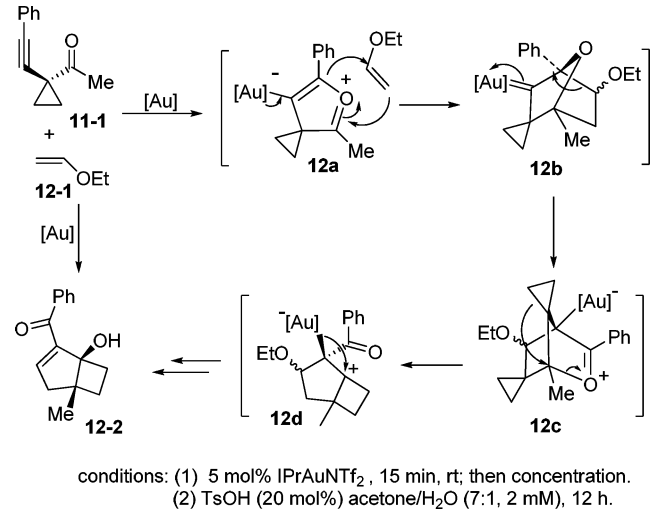
Scheme 9 Synthesis of (+)-rubiginone B_2 and (+)-ochromycinone.



Scheme 10 Platinum-catalysed [4 + 2] cycloadditions and annulations of enynals with allylic alcohols.



Scheme 11 Gold-catalysed annulation of oxoalkyne with indole.



Scheme 12 Gold-catalysed annulation of oxoalkyne with enol ether.

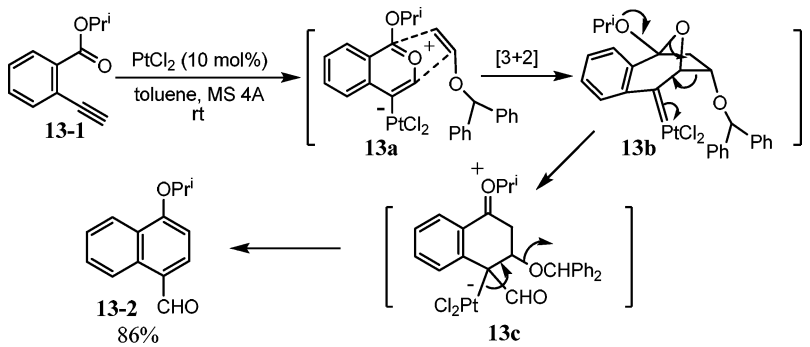
For non-aromatic γ,δ-ynones, Iwasawa *et al.* studied substrate-dependent chemoselectivity in the production of two 8-oxabicyclo[3.2.1]octane isomers **15-2** and **15-3** selectively from acyclic γ,δ-ynones **15-1** and electron-rich alkenes.[13] The R^2-substituent of γ,δ-ynones is crucial for the chemoselectivity as illustrated in Scheme 15. For γ,δ-ynones bearing a propargylic substituent, their $PtCl_2$-catalysed alkyne activation generates Pt-containing carbonyl ylides, which undergo sequential [3 + 2] cycloaddition with vinyl ethers, followed by a 1,2-hydrogen shift, giving 8-oxabicyclo[3.2.1]octene **15-2** in 78% yield. For acyclic γ,δ-ynones lacking a propargylic substituent, the cycloaddition proceeds through a separate pathway involving two successive alkyl migrations to generate another platinum carbenoids **15e**, which go through a 1,2-hydrogen shift to afford isomeric 8-oxabicyclo[3.2.1]octanes **15-3** in 84% yield.

Liang *et al.* employed *o*-alkynyl(oxo)benzenes **16-1** for the regio- and stereoselective synthesis of 8-oxabicyclo[3.2.1]octane derivatives **16-2**.[14] The initially formed benzopyrylium intermediate undergoes [4 + 2] cycloaddition with an external olefin to give cycloadduct intermediate **16a**, which is prone to a 1,2 benzene shift to generate a carbene intermediate **16b**. A final 1,2-H shift renders the product **16-2** (Scheme 16). This synthesis is applicable to cyclooctadiene that provides polycyclic product **16-3** in good yield.

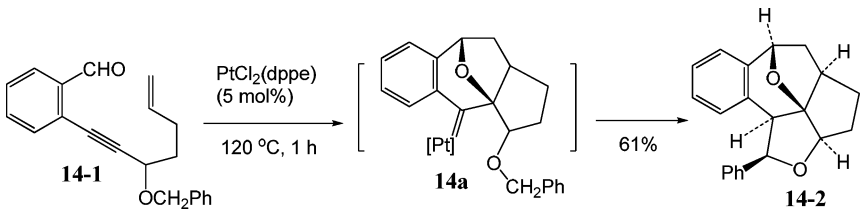
Scheme 17 shows a rare example for a 2-alkynylbenzaldehyde, of which the carbocyclisation does not involve benzopyrilium intermediate. In this process, $PtCl_2$ is responsible for two successive steps: (1) an allylation of an aldehyde and (2) intramolecular hydroalkoxylation of an alkyne, producing 1*H*-isochromene **17b** ultimately. An eventual carbocyclisation relies on Brønsted acid to give 9-oxabicyclo[3.3.1]nona-2,6-dienes **17-2** selectively.[15] A protracted reaction time enables a complete conversion of 2-alkynylbenzaldehyde with allylsilanes to final oxacyclic product in high yield.

2.3 Alkynyl acetals

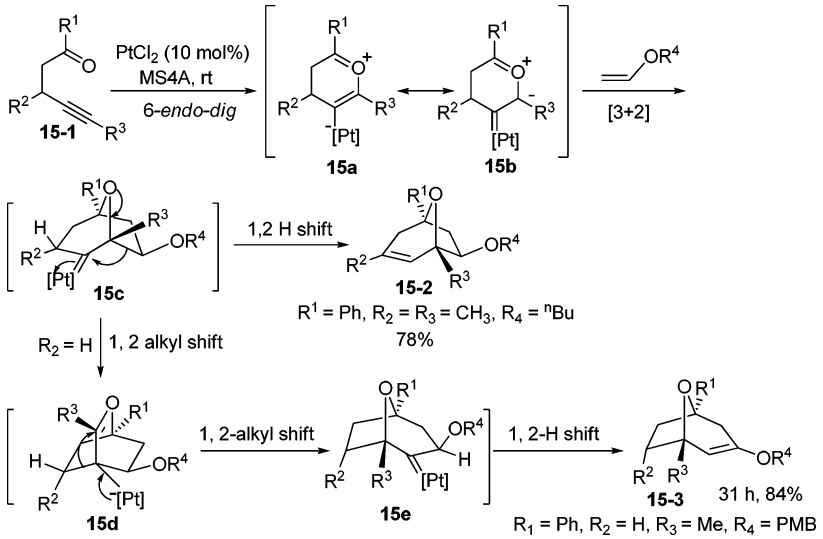
Yamamoto *et al.*[16] studied a platinum-catalysed cycloisomerisation of *o*-alkynylbenzaldehyde acetals and thioacetals **18-1** to give substituted indenes with a 1,2-alkyl shift (**18-2**) or 1,2-heteroatom



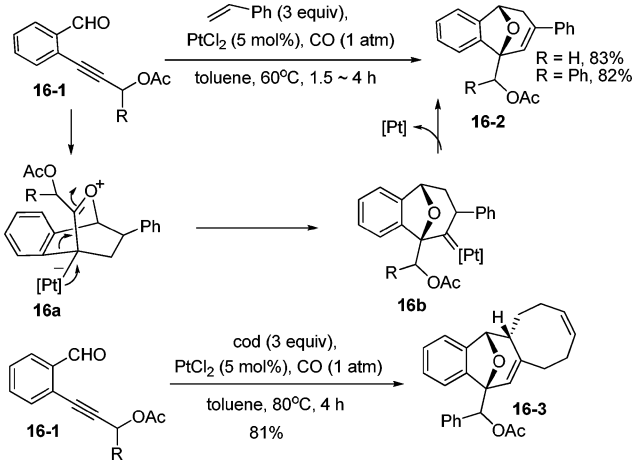
Scheme 13 Platinum-catalysed synthesis of 4-alkoxy-1-naphthanal.



Scheme 14 Platinum-catalysed [3+2] cycloaddition of carbonyl ylides to double bonds.



Scheme 15 Pt-catalysed synthesis of 8-oxabicyclo[3.2.1]octane framework.



Scheme 16 $PtCl_2$-catalysed synthesis of 8-oxabicyclo[3.2.1]octane framework.

shift (**18-3**) as depicted in Scheme 18. Dubé and Toste[17] also revealed a gold-catalysed cyclisation of alkynyl ketals **18-4** which smoothly furnished the 1-indenone adduct **18-5**.

2.4 Allenyl acetals

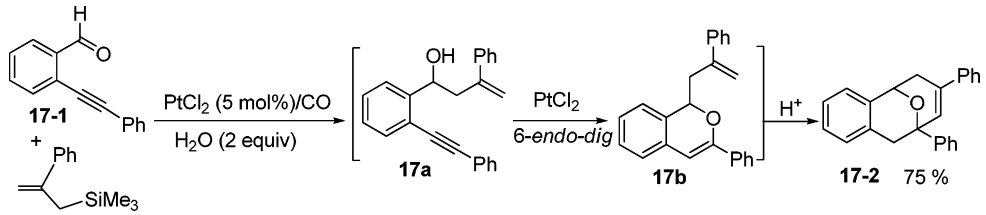
We discovered[18] a stereoselective synthesis of bicyclo[3.2.1]oct-6-en-2-ones **19-2** through Au(I)-catalysed cycloisomerisation of the allenylacetal substrate in **19-1**. Chemoselectivity of the cyclisation is dependent on the catalyst. The use of $PtCl_2$/CO on allenylacetals **19-3** in CH_2Cl_2 follows a Prins-type cyclisation to give cycloisomerisation product **19-4**, whereas a $PPh_3AuCl/AgSbF_6$ catalyst delivers bicyclo[3.2.1]oct-6-en-2-ones **19-2** in high yields. Such a ketone synthesis involves an unprecedented 1,3-addition of a sp^3-hybridised C–H bond to vinylcarbenoid moiety **19a** (Scheme 19). The proposed mechanism is supported by deuterium labeling experiments.

2.5 Oxodienes

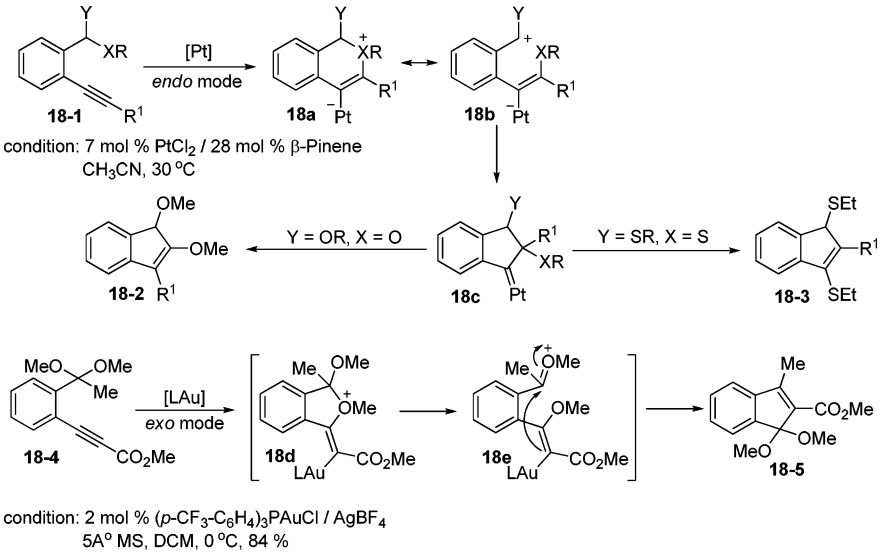
We achieved a Pt(II)-catalysed cycloisomerisation of *cis*-2,4-dien-1-als **20-1** to 3-cyclopentenones **20-2**.[19] A mechanism is depicted in Scheme 20 on the basis of isotope-labeling studies. Activation of the aldehyde-ene functionality by $PtCl_2$ led to the formation of an OPt(IV)–allyl species **20b**, which underwent reductive elimination to form cyclopentadiene epoxide **20c**. Cyclopentadiene epoxide **20c** underwent rearrangement to furnish the final product **20-2**.

We also revealed a gold-catalysed deoxygenated cyclisation of *cis*-2,4-dien-1-als **21-1** with the addition of two nucleophiles in a one-pot operation, giving functionalised cyclopentene derivatives (Scheme 21).[20] Au(I)-initiated 5-*exo* cyclisation of dienal **21-1** gave the allylic cation **21b**, which underwent reaction with pronucleophiles to form gold-alcoholate intermediate **21c**. The electrophilic part (E^+) of the pronucleophile helped to release the active catalyst LAu^+ from species **21c** to generate species **21d**. A second allylic cation **21e** was subjected to a second nucleophilic attack, giving the final products **21-2** or **21-3**.

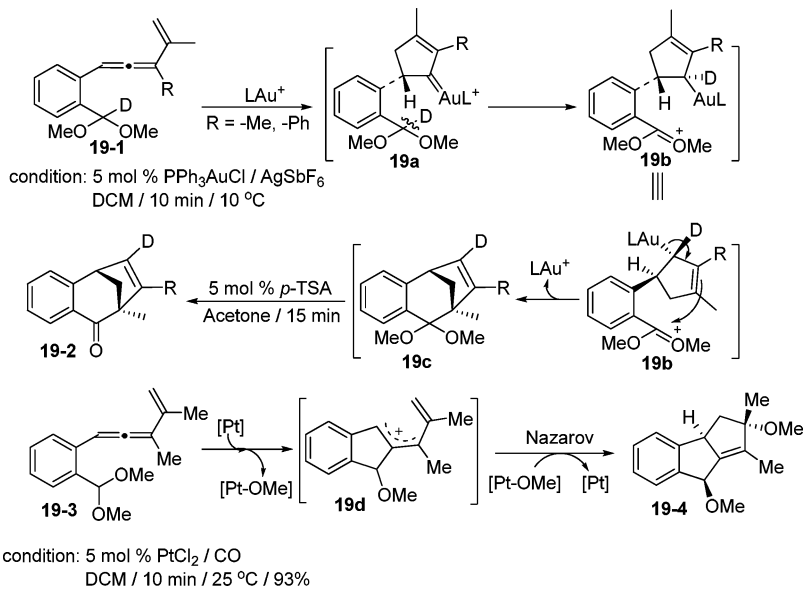
This catalytic protocol was accentuated to realise a new [4 + 3] annulation of *cis*-2,4-dien-1-als **22-1** with allylsilanes for



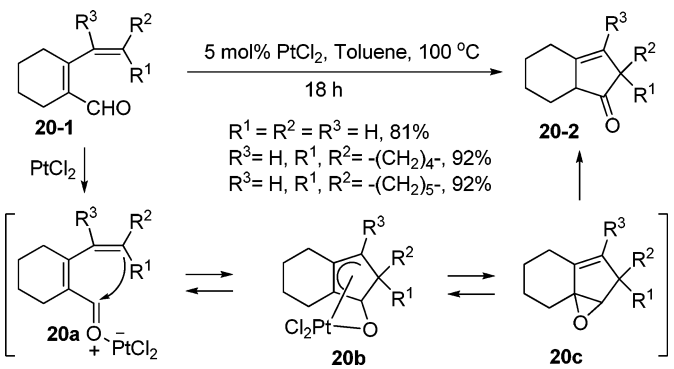
Scheme 17 Pt-catalysed annulation of 2-alkynylbenzaldehydes with allylsilanes.



Scheme 18 Platinum-and gold-catalysed *o*-alkynyl-acetals, thioacetals and ketals.



Scheme 19 Gold- and platinum-catalysed cycloisomerisation of allenene-acetal functionality.

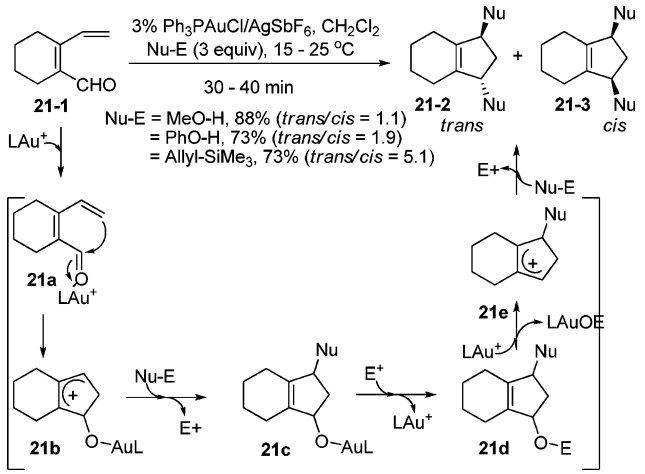


Scheme 20 Pt(II)-catalysed cycloisomerisation of *cis*-2,4-dien-1-als to 3-cyclopentenones.

the stereoselective synthesis of complex molecular frameworks (Scheme 22). As shown in Scheme 22, nucleophilic attack of an allylsilane derivative onto allyl cation species **22a** gave addition product **22b**, which underwent an ionisation/nucleophilic attack to give a new allyl cation **22c**. A carbocyclisation of this species occurred to give the observed annulated product **22-2**. Scheme 23 highlights the synthetic use of this strategy for a short and efficient synthesis of naturally occurring brazilane and synthetic analogues.[21]

2.6 Alkynyl imines

Su and Porco[22a] have developed an efficient synthesis of pyrroloisoquinolines related to the lamellarin[22b] natural products involving domino cycloisomerisation/dipolar cycloaddition of readily available alkynyl *N*-benzylidene glycinates (Scheme 24). Proposed mechanism reveals an initial cycloisomerisation of **24-1** to



Scheme 21 Au(I)-catalysed deoxygenative cyclisation of *cis*-2,4-dien-1-al with the addition of two nucleophiles.

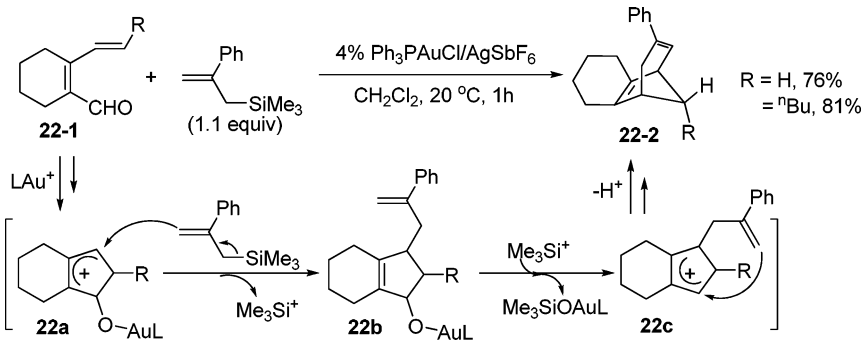
isoquinolinium species **24a**. Subsequent proton transfer and regeneration of Ag(I) affords azomethine ylide **24b**, which is followed by dipolar cycloaddition to dihydropyrrole **24c**. Isomerisation and final oxidation affords pyrrolo-isoquinoline **24-2**.

3. Heterocyclisation

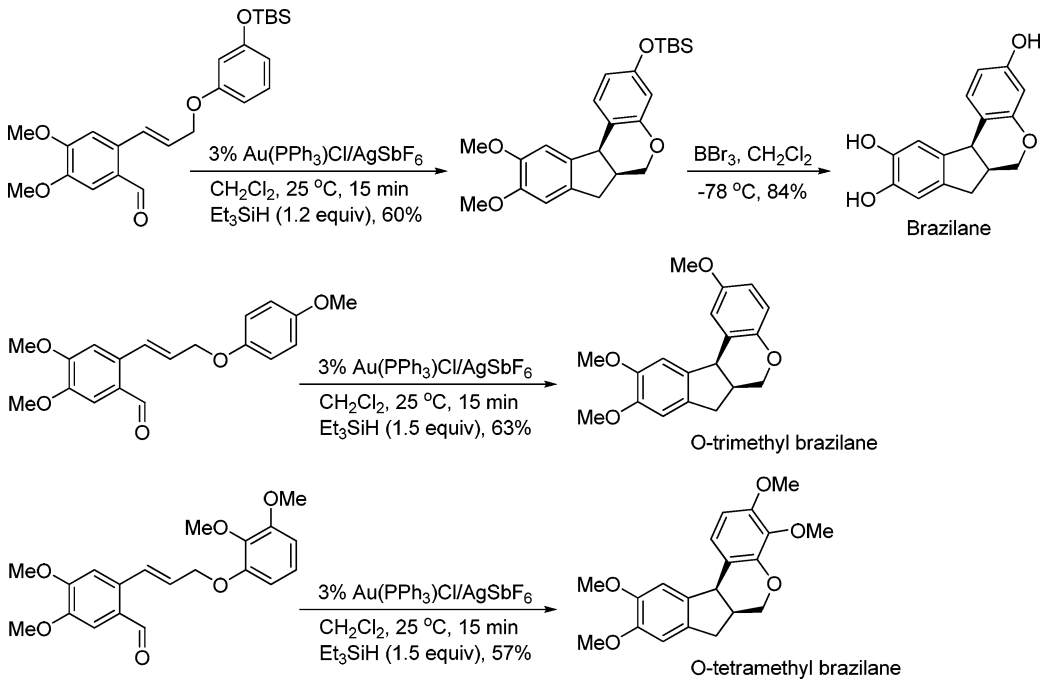
3.1 Epoxyalkynes

Hashmi and Sinha reported[23] a $AuCl_3$-catalysed isomerisation of alkynyl epoxides **25-1** to furan derivatives **25-2** under ambient temperatures. Herein, gold catalysts activate the alkyne to induce attack of the epoxy oxygen at the distal alkynyl carbon, giving oxacyclic cation **25b** that subsequently loses a proton to give the observed furan products **25-2** (Scheme 25). This catalysis is tolerable with various functionalities including aliphatic alcohol or aryl bromides.

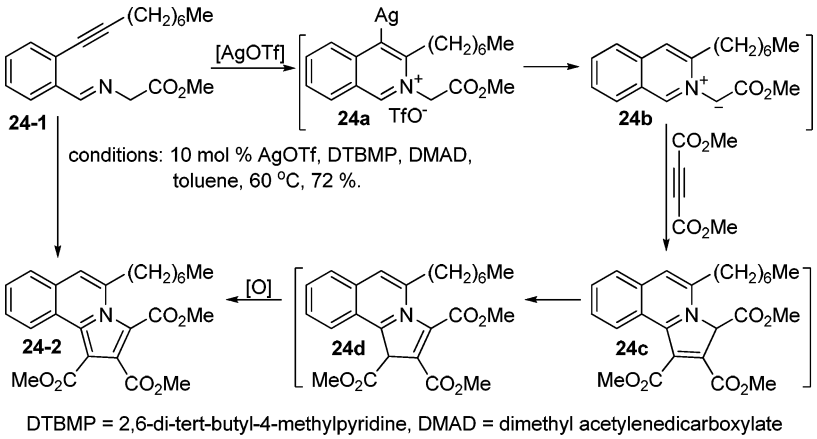
Liang *et al.* reported[24] a gold-catalysed cyclisation of epoxyalkynes **26-1** with alcohols to form 2,5-disubstituted furans **26-2** in moderate to excellent yields. This reaction proceeds efficiently under mild conditions without any additive. Scheme 26 depicts a proposed mechanism involving an initial addition of the epoxy oxygen at π-alkyne intermediates **26a** through



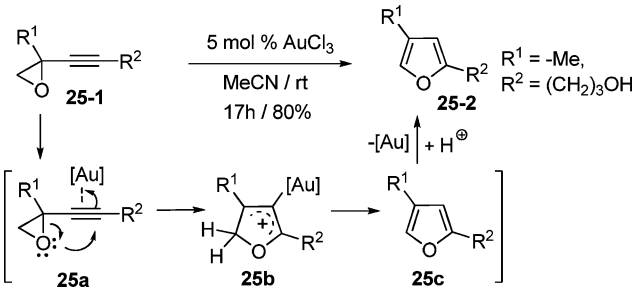
Scheme 22 Metal-catalysed [4 + 3] annulation of *cis*-2,4-dien-1-als with allylsilane derivatives.



Scheme 23 Synthetic application of gold-catalysed cyclisation of *cis*-2,3-diene-1-als in the presence of a hydride donor.



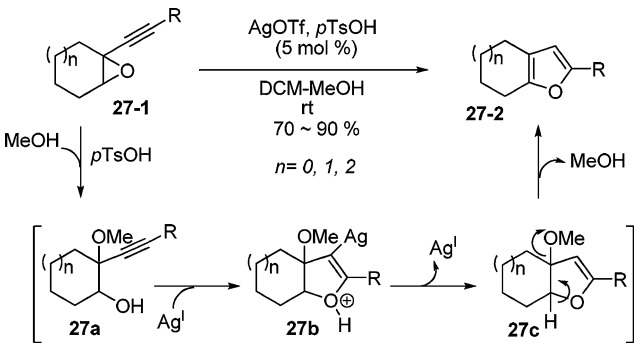
Scheme 24 Silver-catalysed synthesis of pyrrolo-isoquinolines related to lamellarins.



Scheme 25 Gold(III)-catalysed transformation of alkynyl epoxides to furans.

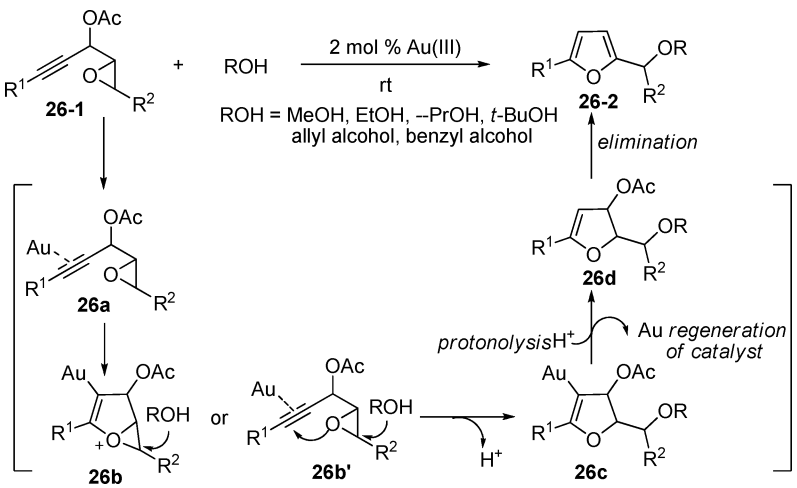
5-*endo-dig* cyclisation; the resulting oxonium species **26b** trap an alcohol to generate 2,3-dihydrofuran intermediates **26c**, ultimately giving furan products **26-2**. An alternative mechanism may involve a prior attack of alcohol at the epoxide **26b′**, to facilitate the addition of epoxy oxygen at its π-alkyne moiety. This pathway will also give the same furan products **26-2** *via* the intermediates **26c** and **26d**.

Pale *et al.*[25] reported a Ag(I)- and Brønsted acid-catalysed rearrangement of epoxy-alkyne **27-1** to furan derivatives **27-2**. The proposed pathway involves a cascade event involving opening of the epoxide with an alcohol catalysed by *p*-toluenesulfonic acid. The resulting α-alkoxy-β-alkynols **27a** react with silver ions, leading to Ag(I)-containing oxacyclic cation **27b**, ultimately giving furan derivatives **27-2** (Scheme 27).

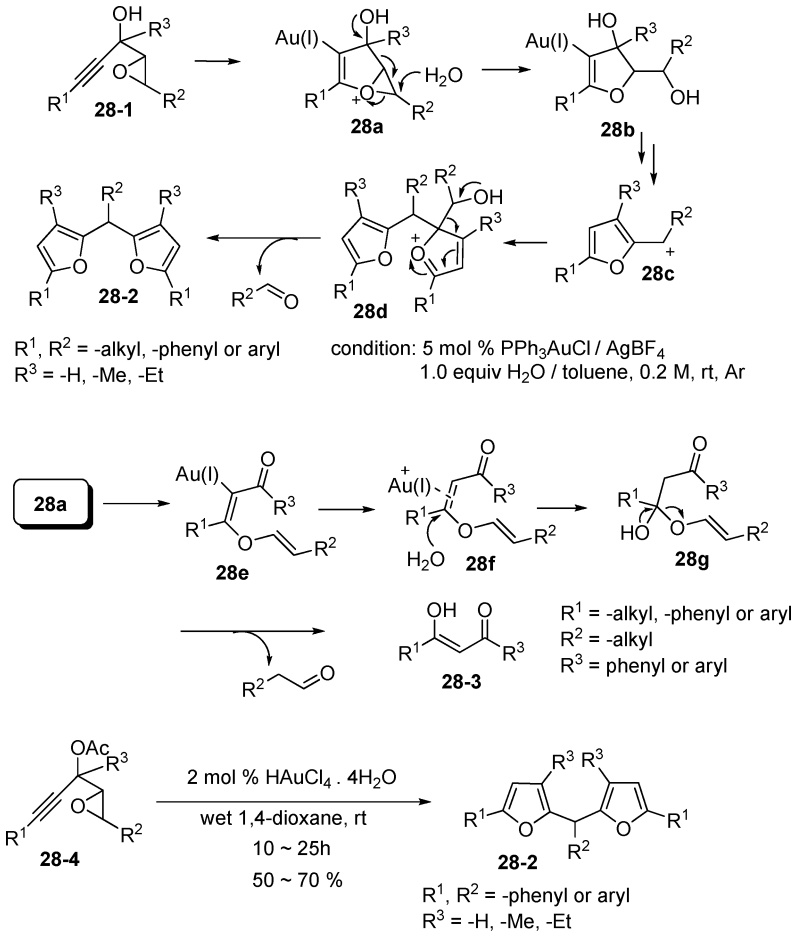


Scheme 27 Ag- and acid-catalysed rearrangement of epoxy-alkynes to furan derivatives.

Difurylmethanes are of interest to the food industry as they are present as natural compounds in foods and beverages, such as licorice.[26a,b] Dai and Shi have discovered a gold-catalysed cyclisation of 1-alkynyl-2,3-epoxy alcohols **28-1** to difurylmethanes **28-2**



Scheme 26 Au(III)-catalysed synthesis of furan compounds.



Scheme 28 Gold-catalysed cyclisation of α-hydroxy-β-epoxyalkynes.

and 1,3-diketones **28-3** depending on whether alcohol is present; a mechanism is proposed in Scheme 28.[26c] In this complicated pathway, formation of difurylmethane species **28-2** is derived from the coupling of cations **28c** and their alcohol derivatives. Liang *et al.* also obtained the same difurylmethane compounds **28-2** from the cyclisation/dimerisation cascade of 1-oxiranyl-2-alkynyl esters **28-4** at room temperature under gold catalysis.[26d]

Many bioactive natural products comprise polyoxacyclic frameworks; notable examples include ionophore antibiotics,[27a] monensin,[27b] okadaic acid,[27c] antiproliferative,[27c] mycalysines,[27d] brevetoxins[27e] and glabrescol.[27f] Oxacyclisation of epoxyalkynes provides rapid access to such complex oxygenated skeletons using electrophilic metal salts. Shi *et al.* developed a new method to obtain ketal skeletons through highly regio- and diastereoselective intermolecular addition of water and alcohols to epoxyalkynes **29-1** catalysed by $Ph_3PAuCl/AgSbF_6$. This procedure involves a domino epoxy opening, 6-*exo*-cycloisomerisation, and subsequent intra- or intermolecular hydroxyl addition to the enol of species **29d** and **29g** as depicted in Scheme 29.[27g] They have further extended this epoxyalkyne cyclisation in an intramolecular fashion to construct spiroketal frameworks **29-5** and **29-6** from epoxy homopropargylic alcohols **29-4** (Scheme 28)[27h]

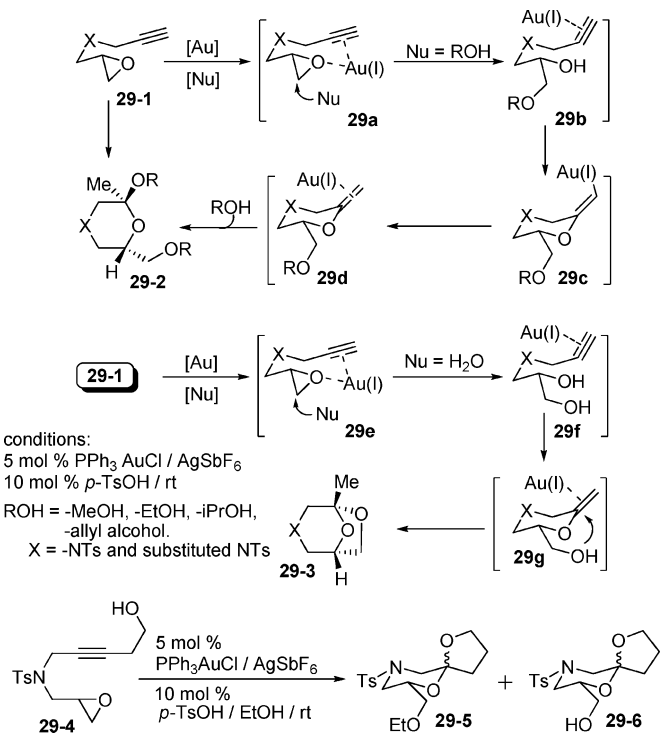
Dai and Shi showed gold(I)-catalysed intramolecular cycloisomerisation of α-epoxyketones **30-1** with their tethered alkynes to form six- or seven-membered heterocyclic compounds.[28] This procedure involves a cascade isomerisation of epoxyketones into 1,3-diketones **30a** that undergo a subsequent gold(I)-catalysed intramolecular addition of an oxygen or a carbon nucleophile to the alkynes (Scheme 30).

3.2 Epoxyallenes

Recently, Gagné *et al.*[29] described gold(I)-catalysed cascade nucleophilic cyclisation of epoxyallenes **31-1** to generate polyether skeletons **31-2** and **31-3** at room temperature in dichloromethane. The catalytic conditions tolerate a range of functional groups including sulfones, esters, ethers and sulfonamides. The chemoselectivity is sensitive to epoxy substituents and the connecting atom **X** of substrate **31-1**. This gold catalysis provides easy entry to fused bicyclic medium-ring ethers **31-2** and **31-3** that are commonly encountered in numerous polyether natural products, as depicted in Scheme 31.

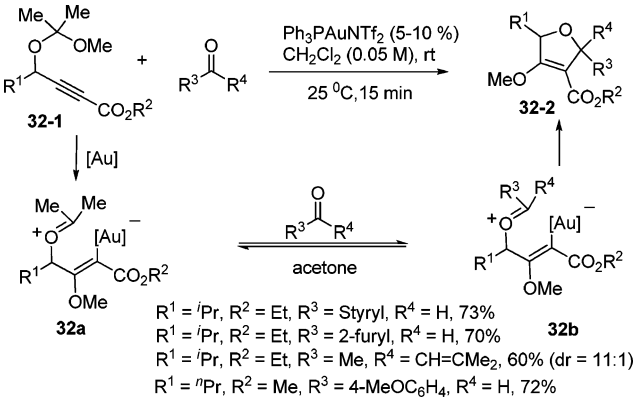
3.3 Alkynylacetals

Zhang published an exquisite synthesis of 2,5-dihydrofuran species **32-2**, produced from the [3 + 2] cycloaddition of Au-containing all-carbon 1,3-dipolar intermediates **32a**.[30] This approach is based on a tandem migration–fragmentation cascade of the alkynylacetal substrate **32-1** to give dipolar intermediates **32a**, which undergo



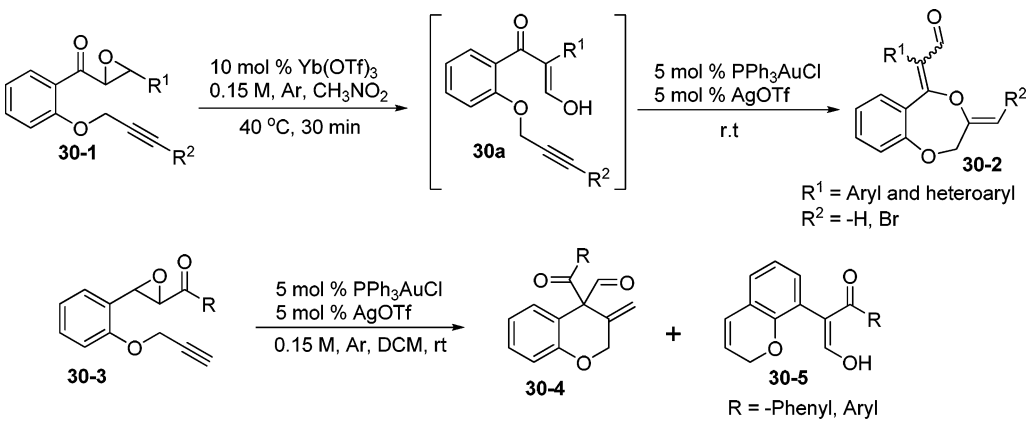
Scheme 29 Gold-catalysed diastereospecific addition of alcohols and water to alkynyl epoxides.

[3 + 2] cycloaddition with aryl aldehydes or enones to afford final products **32-2** (Scheme 32).

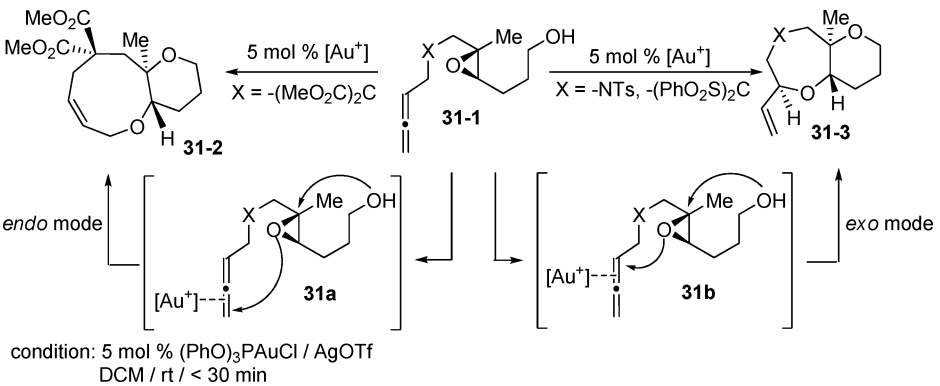


Scheme 32 Au-catalysed all-carbon 1,3-dipoles and their [3 + 2]-cycloaddition.

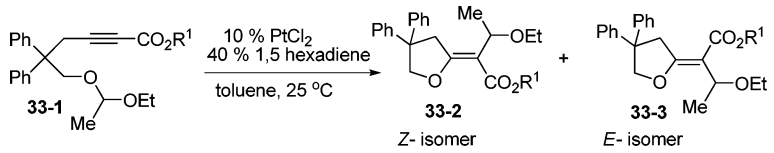
As shown in Scheme 33, cyclisation of 6-(1-alkoxyethyl)hex-2-ynoates **33-1** to 2-dihydrofuran-2(*3H*)-ylidenes **33-2** and **33-3** occurred smoothly in the presence of a Pt(II)–olefin catalyst, reported by Nakamura group (Scheme 33).[31] The stereoselectivity is found to be largely dependent on the electronic nature of the ester functionality; electron-deficient ester moieties give the *Z*-isomers of **33-2** predominantly, while electron-rich esters greatly



Scheme 30 Gold(I)-catalysed selective synthesis of six- or seven-membered oxacyclic species.

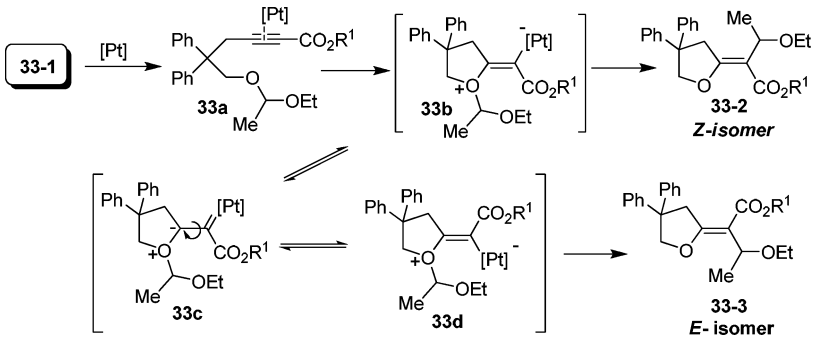


Scheme 31 Gold(I)-catalysed cascade cyclisation of allenyl epoxides.



R^1	time (h)	yield (%)	*Z*/*E*
Cl_3CCH_2	1.5	84	100:0
p-O_2N-C_6H_4	3.5	83	96:4
Me	4.5	54	31:69
p-MeO-C_6H_4	24	32	0:100

Scheme 33 P(II)-catalysed cyclisation of 6-(1-alkoxyethyl)hex-2-ynoates.



Scheme 34 Mechanistic rationale for 2-(dihydrofuran-2(3*H*)-ylidene)acetates.

favor the formation of *E* isomeric product **33-3**. Scheme 34 depicts a proposed mechanism that oxaphilic activation of the alkyne **33a** triggers a 5-*exo*-*dig* attack of the acetal oxygen atom, leading to a vinylplatinum species **33b**, which is also represented by its Pt–carbene resonance form **33c**. The vinyl–platinum intermediate undergoes a [1,3]-α-ethoxyethyl migration to afford the final product.

3.4 Oxoalkynes

Porco *et al.*[32] showed a platinum-catalysed tandem Fiedel–Crafts addition/annulation cascade on 2-alkynylbenzaldehydes **35-1** that reacted with phenols **35-2** to produce bicyclic ketal compound **35-3**. The reaction likely involves an initial Friedel–Crafts reaction of phenol on a benzopyrylium intermediate, followed by nucleophilic attack of phenol at the enol of intermediate **35a**, giving tetracyclic ketal **35-3** that has a similar skeleton to natural product anthrabenzoxocinone.[33] For oxoalkyne substrates **35-4**, Belmont *et al.* reported[34] a silver-catalysed acetalisation–cycloisomerisation reaction to form a broad range of functionalised furoquinolines **35-5** and pyranoquinolines **35-6**, *via* nucleophilic addition of a weak nucleophile and/or hindered alcohol (Scheme 35).

Yamamoto *et al.* reported[35] Ag(I)-catalysed oxacyclisation of alkynones **36-1** with alcohols, providing 1-allenyl isochromenes **36-2**. The reaction proceeds *via* addition of alcohol on the alkynyl C(1)-carbon of benzopyrylium cation **36a**, giving the annulated products as illustrated in Scheme 36.

Hashmi *et al.*[36] demonstrated a gold(III)-catalysed cycloisomerisation of propargyl ketones **37-1** to 2,5-disubstituted furans **37-2** through an initial nucleophilic attack of the carbonyl group to the π-alkyne moiety, followed by heteroaromatisation of arenium intermediate **37a** (Scheme 37). This furan synthesis is implemented by $AuCl_3$ in a very small proportion (0.1 mol%). Kirsch *et al.*[37] also developed a similar furan synthesis with $AuCl_3$ that catalysed efficient conversion of α-hydroxy propargyl ketones **38-1** to 3(2*H*)-furanones **38-2** (Scheme 38). This transformation is accompanied with a 1,2-alkyl migration *via* a pinacol rearrangement.

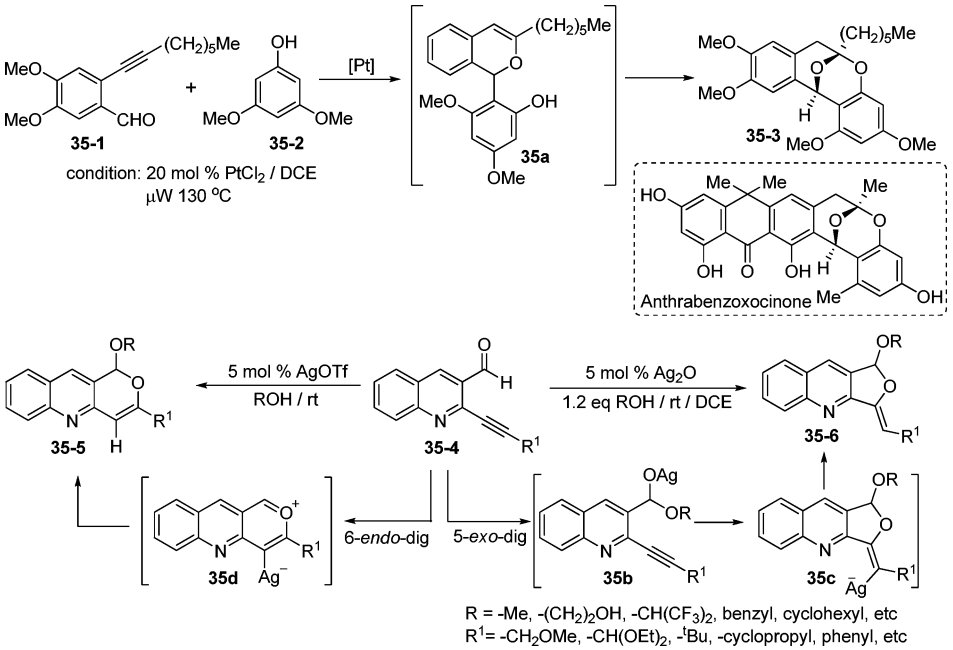
Zhang and Schmalz[38] used 1-carbonyl-1-alkynylpropanes **39-1** for the formation of highly substituted furans **39-2** (Scheme 39). This oxacyclisation is compatible with a wide range of oxygen-based nucleophiles, including ^{i}PrOH, ^{t}BuOH, propargylic alcohols, phenols, 2-pyrrolidone, indole and even acetic acid.

Larock *et al.*[39] and Yamamoto *et al.*[40] independently developed a Au(III)- and Cu(I)-catalysed synthesis of highly substituted furans **40-2** from 2-(1-alkynyl)-2-alkene-1-ones **40-1**. This oxacyclisation likely proceeds *via* two distinct pathways, which involve either an initial attack of nucleophile at the enone, or an alcohol addition to the π-alkyne, as depicted in Scheme 40.

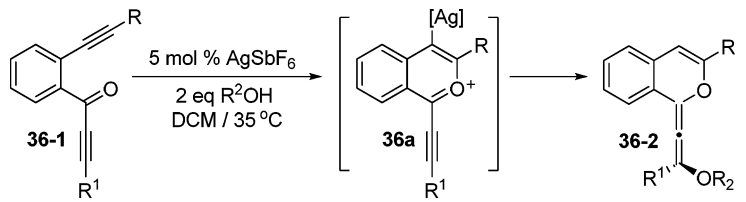
Zhang *et al.*[41] showed a gold-catalysed 1,3-dipolar cycloaddition of 2-(1-alkynyl)-2-alkene-1-ones **41-1** with nitrones, which provides a practical and highly diastereoselective route to heterobicyclic furo[3,4-*d*]-[1,2]-oxazines **41-2**, as depicted in Scheme 41. This cyclisation proceeds *via* attack of the ketone at the π-alkyne moiety to give gold-containing furanyl cation **41a**, which reacts with nitrone to deliver the observed [3 + 2]-cycloadducts

3.5 Oxoallenes

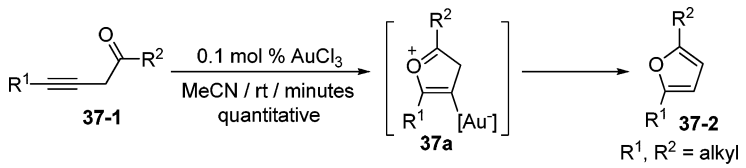
The cycloisomerisation of allenyl ketones **42-1** was reported by Hashmi *et al.*[36] The carbonyl oxygen atom serves as an



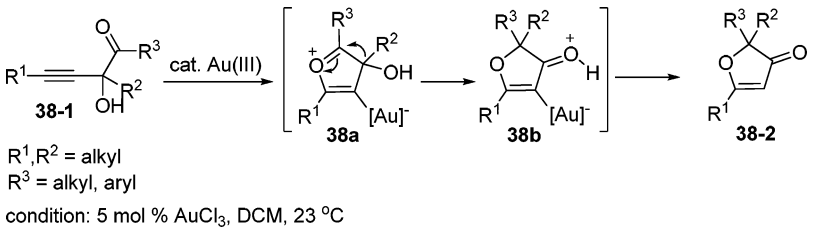
Scheme 35 Heterocyclisation of oxoalkynes in the presence of an external nucleophile.



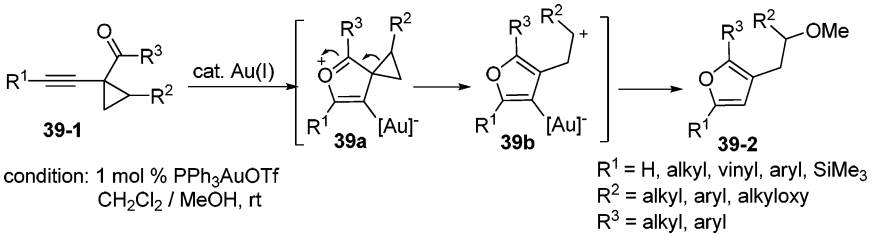
Scheme 36 Ag(I)-catalysed cyclisation of alkynones.



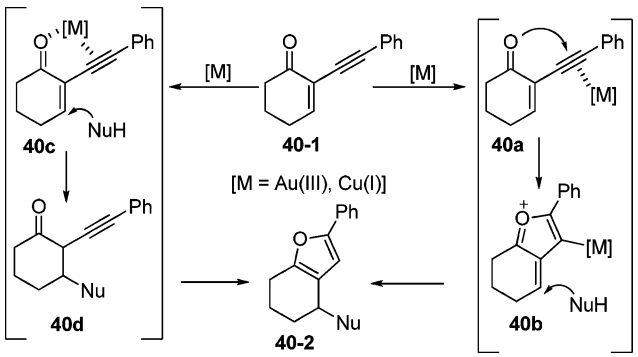
Scheme 37 Gold(III)-catalysed cycloisomerisation of propargyl ketones.



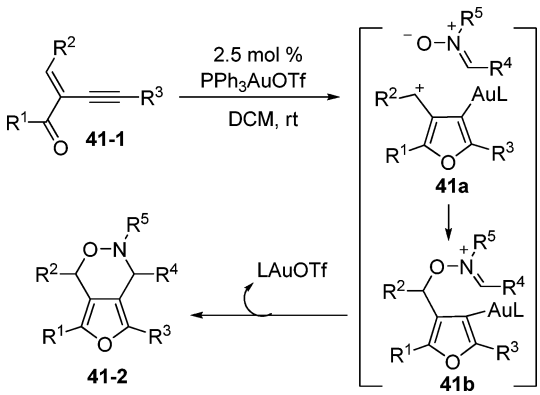
Scheme 38 Gold(III)-catalysed synthesis of 3(2*H*)-furanones from α-hydroxy propargyl ketones.



Scheme 39 Gold(I)-catalysed synthesis of highly substituted furans from alkynyl-cyclopropanes.



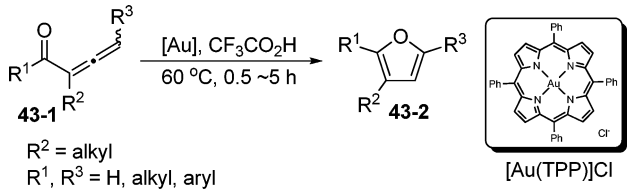
Scheme 40 Au(III)-and Cu(I)-catalysed synthesis of furan.



Scheme 41 Gold-catalysed 1,3-dipolar cycloaddition.

intramolecular nucleophile, producing the Wheland-type intermediate **42a**, which forms product **42-2** by aromatisation and protodeauration (Scheme 42).

Che *et al.*[42] have successfully used gold(III)–porphyrin complexes for the cycloisomerisation of allenyl ketones **43-1** to furans **43-2**. The reactions proceed at 60 °C in the presence of trifluoroacetic acid with an impressive TON of 8300 (Scheme 43).

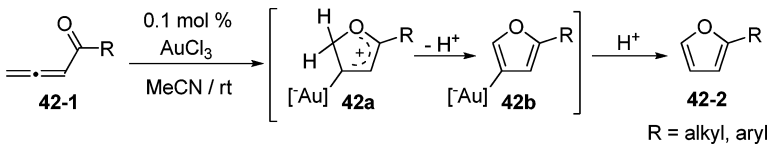


Scheme 43 Gold(III)–porphyrin-catalysed cycloisomerisation of allenones.

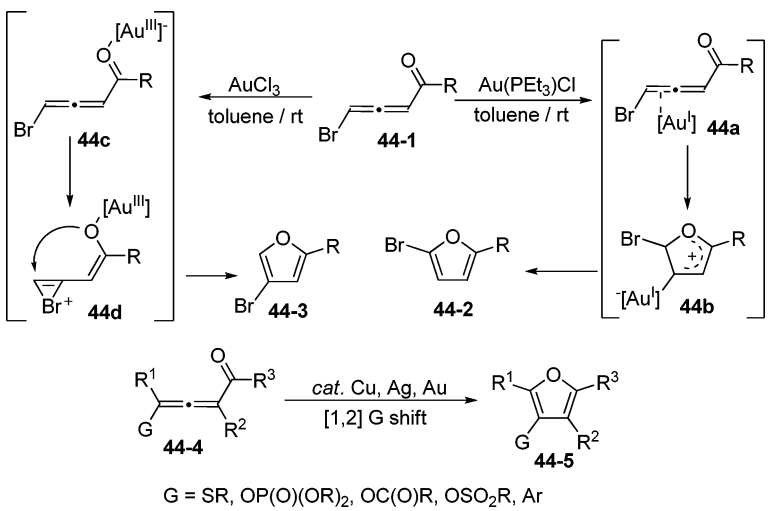
Gevorgyan *et al.*[43] revealed an intriguing observation with bromoallenyl ketone **44-1** that showed catalyst-dependent chemoselectivity in the cycloisomerisation. $AuCl_3$ gives 3-bromofuran **44-3** with a 1,2-bromo shift, whereas $AuPEt_3Cl$ leads to 2-bromofuran **44-2** in a normal process (Scheme 44). This distinction is explained by an enhanced oxophilic behavior of gold(III), as shown by intermediates **44c** and **44d**, while gold(I) is more carbophilic, as depicted in intermediates **44a** and **44b**. Gevorgyan later developed a series of transition metal catalysis (Cu, Ag, Au) to achieve heteroaromatisation of allenyl ketones **44-4** to tetrasubstituted furans **44-5** through a 1,2-migration of various groups (G = SR,[44] $OP(O)(OR)_2$, OC(O)R, OSO_2R,[45] Ar[46]).

3.6 Amino- and hydroxycarbonyl/alkyne compounds

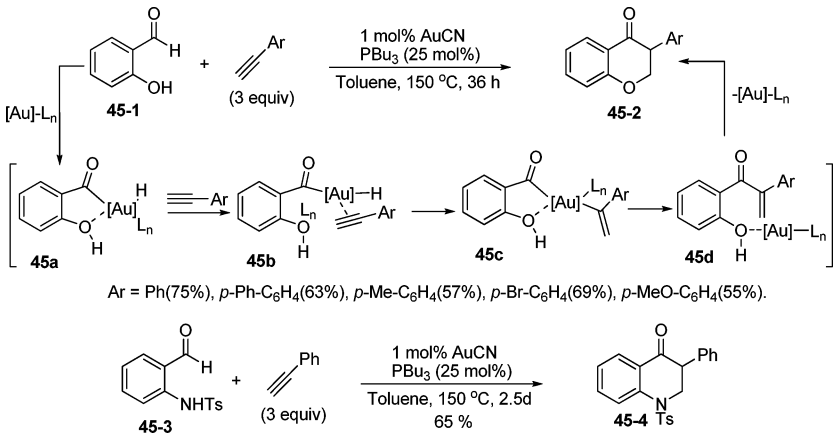
Skouta and Li reported a new annulation of salicylaldehyde with arylalkyne for the synthesis of isoflavanone-type compounds.[47a] This reaction is also mechanistically interesting because a mechanism involving an oxidative addition was proposed around the



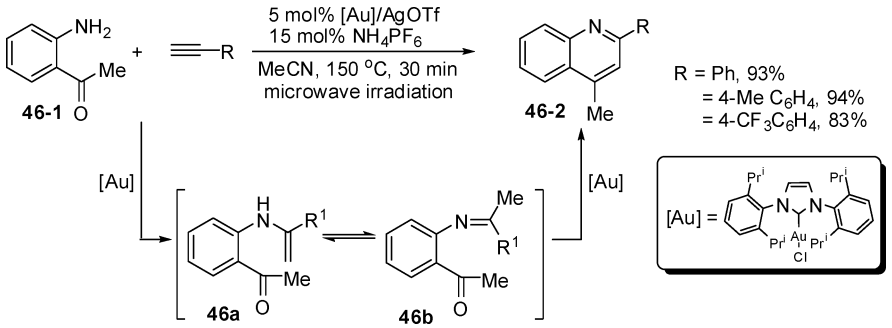
Scheme 42 Gold(III)-catalysed cycloisomerisation of allenyl ketones.



Scheme 44 Metal-catalysed multisubstituted furans synthesis from allenyl ketones *via* a 1,2 shift.



Scheme 45 Gold-catalysed synthesis of flavones by annulation of salicylaldehyde with alkynes.

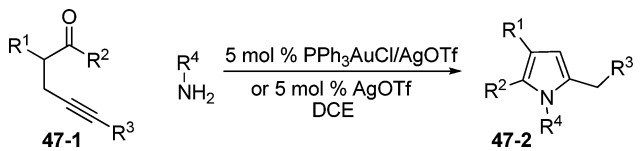


Scheme 46 Gold(I)-catalysed synthesis of quinolines.

gold center to generate an acyl gold(III) hydride intermediate **45a** that undergoes a consecutive alkyne insertion and reductive elimination to give enone, and ultimately the observed compound **45-2** through an intramolecular Michael-type reaction (Scheme 45). They extended this annulation reaction for the synthesis of azaisoflavanones **45-4** from 2-tosylaminobenzaldehydes **45-3** and alkynes.[47b]

Liu and Che showed a microwave-assisted gold catalysed synthesis of quinolines from 2-acylaniline **46-1** and alkynes.[48] As outlined in Scheme 46, gold first catalyses hydroamination of aminoketones to give the enamine intermediates **46a** that undergo condensation/annulation reactions to produce 2,4-disubstituted quinolines **46-2**.

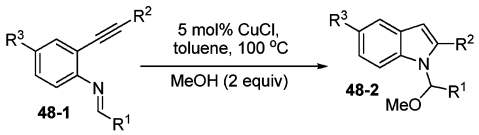
Dake *et al.*[49] have developed an efficient methodology for the synthesis of functionalised pyrrole derivatives **47-2** from the reactions between imines (formed *in situ*) and alkynes using either silver or gold catalysts. One observation in their studies is to confirm the thermal stability of the gold(I) precatalysts at temperatures up to 80 °C, whereas silver salts increase the speed of the reaction and give slightly better yields (Scheme 47).



Scheme 47 Pyrrole synthesis catalysed by Ag(I) or cationic Au(I) complex.

3.7 Iminoalkynes

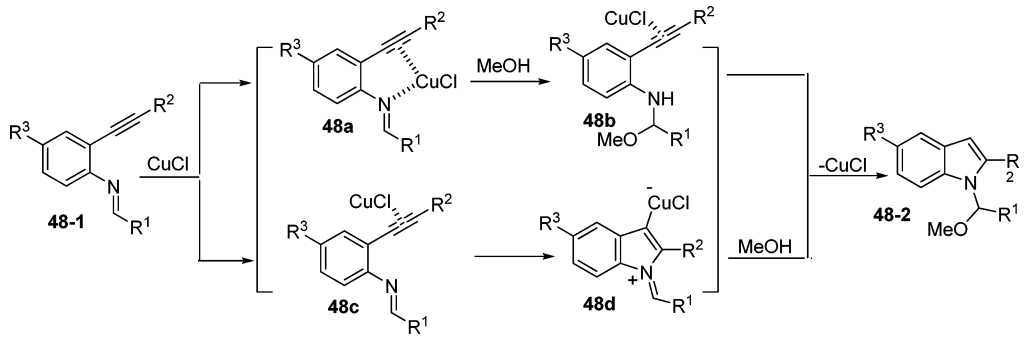
Like carbonyl compounds, imines tethered with an alkyne are amenable to metal-catalysed heterocyclisation to give nitrogen-containing heterocyclic compounds. The first example was reported by Yamamoto *et al.*[50] who showed a convenient synthesis of *N*-(alkyloxybenzyl)indoles **48-2** through treatment of 2-alkynyl-*N*-arylideneanilines **48-1** with alcohols and Cu(II) catalyst (Scheme 48).



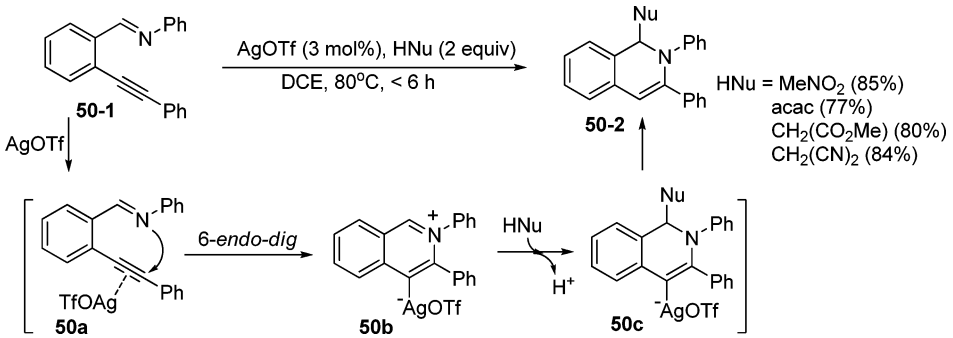
R^1	R^2	R^3	time (h)	yield (%)
p-Me-C_6H_4	Pr	H	2.5	70
m-Me-C_6H_4	Pr	H	4	73
p-Me-C_6H_4	Cyclohexyl	H	6	77
p-Me-C_6H_4	Ph	OMe	3	73

Scheme 48 Copper-catalysed synthesis of indoles.

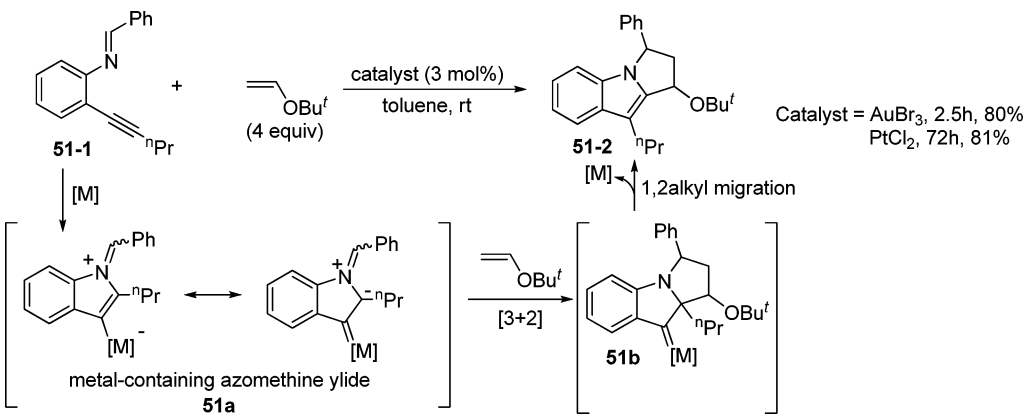
Two alternative mechanisms are likely for this cyclisation, as illustrated in Scheme 49. For iminoalkyne **48-1**, CuCl may coordinate to both the imine and alkyne groups; the imine coordination enhances its electrophilicity to induce an alcohol addition, giving an aniline derivative **48b** that undergoes metal-catalysed hydroamination to furnish the final product **48-2**. Alternatively,



Scheme 49 Proposed mechanism for the Cu-catalysed formation of indoles.



Scheme 50 Silver-catalysed synthesis of 1,2-dihydroisoquinoline derivatives.



Scheme 51 Metal-catalysed [3 + 2] cycloaddition of azomethine ylides.

a metal-catalysed electrophilic activation of the alkyne would result in a nucleophilic attack of the imine group in a 5-*endo-dig* cyclisation mode, giving zwitterionic intermediates **48d** that react with alcohol to afford the same product **48-2**.

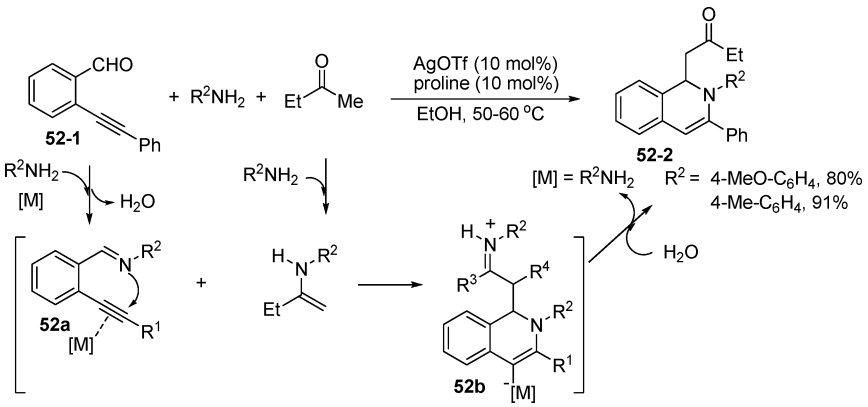
Asao *et al.* reported a convenient synthesis of functionalised 1,2-dihydroisoquinoline derivatives **50-2** from easily prepared *ortho*-alkynylaryl aldimines **50-1** through a direct addition of carbon pronucleophiles.[51] As illustrated in Scheme 50, the initially formed isoquinolinium intermediate **50b** generated from the 6-*endo* cyclisation undergoes a nucleophilic addition–prodemetallation cascade to furnish the final product **50-2**.

Scheme 51 depicts a useful [3 + 2] cycloaddition of metal-containing azomethine ylides **51a** generated from *N*-(*o*-alkynylphenyl)imines **51-1** with enol ethers.[52] The resulting cycloadducts **51b** undergo a 1,2-alkyl migration to provide final product **51-2**.

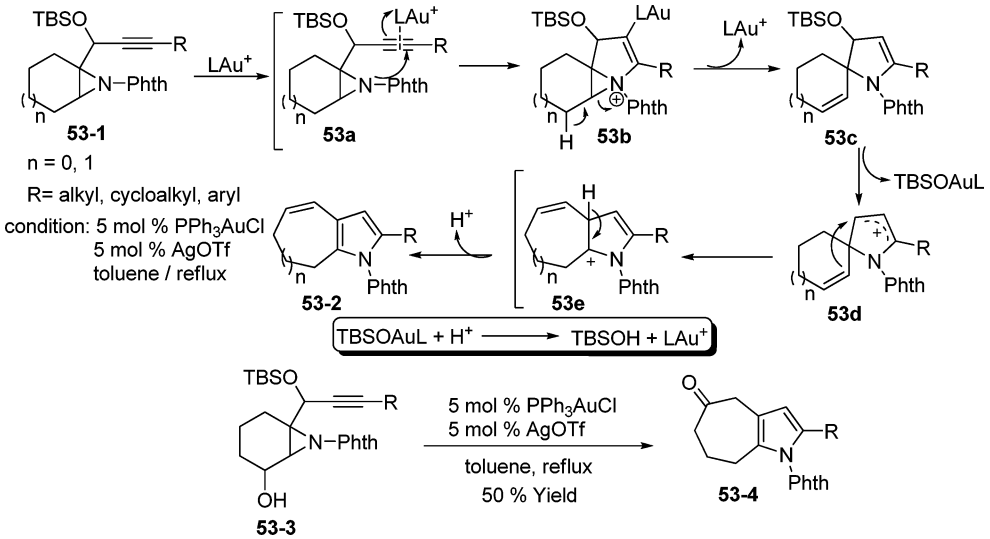
Ding and Wu[53] observed a three component coupling of 2-alkynylbenzaldehydes **52-1**, amines and ketones using a mixture of proline and AgOTf catalysts, producing 1,2-dihydroisoquinolines **52-2**. Scheme 52 shows a plausible mechanism that the initial step involves formation of aldimine **52a** that is attacked by *in situ*-generated enamine to give observed product **52-2**.

3.8 Alkynyl aziridines

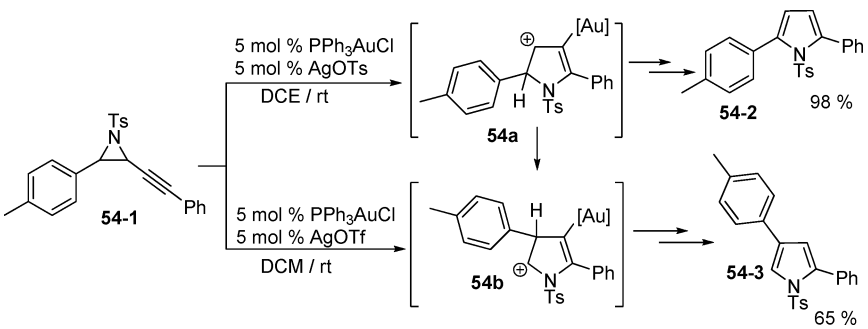
Analogous to epoxides, the electrophilicity of aziridines can be enhanced by Lewis acids to result in ring-opening products in the presence of nucleophiles. Aziridines become versatile building blocks in organic synthesis.[54] In gold catalysis, aziridines bear a close resemblance to epoxides in several instances. For example, Tu *et al.*[55] described a rearrangement of propargylic aziridine **53-1**, giving cycloalkene-fused pyrroles



Scheme 52 Catalytic synthesis using Lewis acid and organocatalysis.



Scheme 53 Au(I)-catalysed rearrangement reaction of propargylic aziridine; synthesis of trisubstituted and cycloalkene-fused pyrroles.



Scheme 54 Counterion effects in a gold-catalysed synthesis of pyrroles from alkynyl aziridines.

53-2 with the use of a $PPh_3AuCl/AgOTf$ catalyst. the formation of such products involves an initial addition of aziridine nitrogen at the alkyne, followed by a ring-opening of aziridine and a final Wagner–Meerwein-type rearrangement, as depicted in Scheme 53.

Davies and Martin[56] described a gold-catalysed cyclisation of alkynyl aziridines **54-1** to give 2,5- or 2,4-substituted pyrroles (**54-2** or **54-3**), depending on the type of counter anion in the gold catalyst. This observation highlights the importance to select a suitable counter anion for gold-catalysed processes as it play an important role in determining the reaction pathway. The use of PPh_3AuOTs leads to formation of 2,5-substituted pyrroles **54-2** with quantitative yields whereas PPh_3AuOTf preferably gives 2,4-substituted pyrroles **54-3** through a 1,2-phenyl shift as exemplified by the **54a**→**54b** conversion (Scheme 54).

4. Conclusion

In this review, we highlight recent progress for carbo- and hetero-cyclisation of common oxygen and nitrogen electrophiles tethered

with a suitable functionality, with the use of platinum, gold, silver and copper catalysts. Such reactions are generally performed more efficiently with these soft metal catalysts than conventional hard acids, reflecting catalyst regeneration is equally important as initial activation. This methodology has emerged as a powerful tool for the efficient and chemoselective synthesis of complex carbo- and heterocyclic molecules. Several instances are targeted at the syntheses of naturally occurring substances to highlight the utility. Notably, large portions of the reported examples are focused on the alkyne substrates bearing a electrophile, owing to their association with recent advent in platinum- and gold-catalysed electrophilic activation of alkynes. Limited examples are reported for other tethered functionalities including allenes, alkenes and dienes. This information reveals large room for future exploration of new substrates. Furthermore, electrophilic activation of alkynes can be also implemented by metal–vinyldene species besides π-alkynes. Design of new cyclization of electrophile-containing substrates *via* metal vinylidene intermediates seems to be an attractive and viable route. A continuation of progressive research is thus anticipated in this area.

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