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### Recent development of Silver-catalyzed Oxo- and Aza cyclization

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#### Abstract

This article addresses new developments in silver-catalyzed cyclization processes, resulting in the formation of carbocyclic or heterocyclic rings. Some essential techniques in organic chemistry include silver-catalyzed reactions. In addition, silver catalysts have been emerged as a novel catalysis in the last two decades. In these sequences, preparations of oxygen and nitrogen-containing heterocyclic compounds emerge as the most important development of new methodology. Silver catalysts exhibit significant reactivity in mild conditions in contrast to other transition metals such as copper, lead, zinc, ruthenium, gallium, indium, and niobium. These developments have lots of scientific attention due to their potential to synthesise of heterocyclic compounds in medicinal and agrochemical use. This current literature review summarises several silver-catalyzed oxo and aza-cyclization processes using readily available starting materials.

**Keywords:** Aza cyclization, oxo cyclization, silver-catalyzed, pyran, pyrroles.

#### Introduction

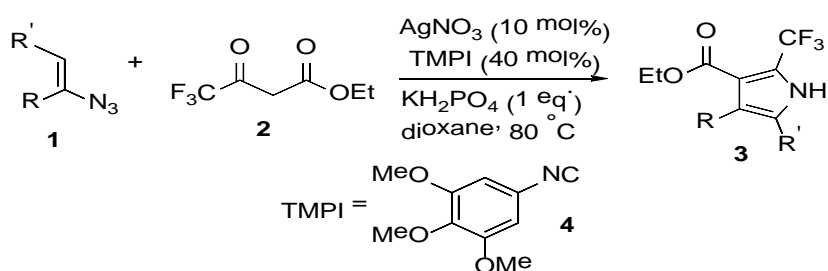
Lewis acids, such as silver catalysts, are widely utilised in organic synthesis and synthesis-related activities. For example, heterocyclic compounds may be synthesised by cyclization processes using alkyne or allene derivatives that are catalysed by silver. This article has examined and summarised the silver-catalyzed or silver-mediated methodologies. Researchers have discovered that silver catalysts may have a unique ability

to react with hetero-atoms such as oxygen and nitrogen during the successive carboxylation and cyclization processes used to create heterocyclic molecules.

Wei et al., (2021) performed one of the most modern, most efficient, and regioselective syntheses known to science. By using a silver-catalyzed cyclization of vinyl azides (1) with ethyl 4,4,4-trifluoro-3-oxobutanoate (2), the synthesis of highly

substituted 2-trifluoromethyl pyrrole derivatives is carried out, resulting in high yields and conditions that are comparatively mild compared to most another recent pyrrole (4) derivative synthetic methodologies (Scheme 1). This conversion may be carried out utilising a variety of aryl,

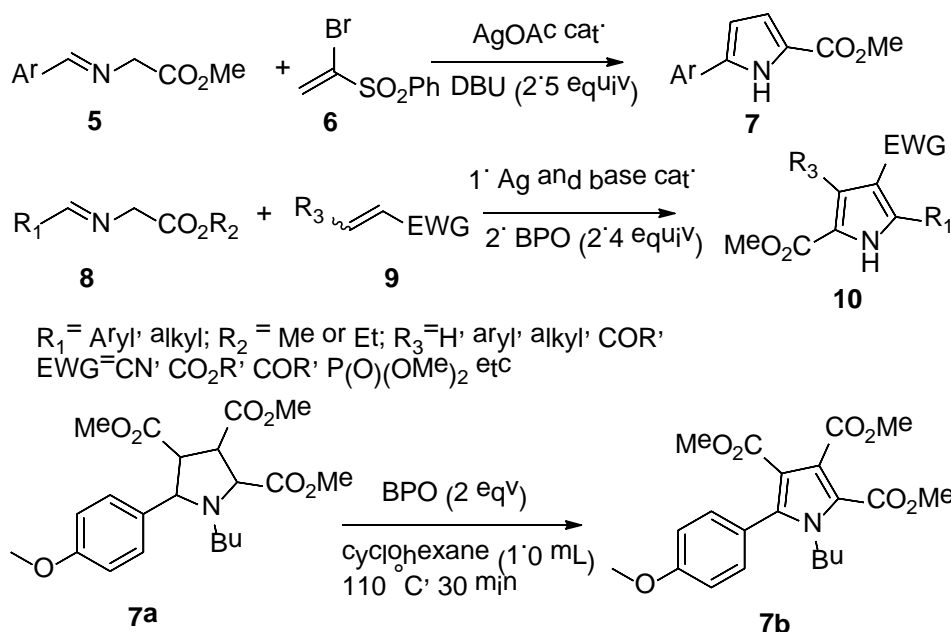
alkyl, and aryl halides, as well as disubstituted vinyl azides and aryl halides. The addition of in situ generated 2H-azirine to the diketone species, followed by intramolecular addition, N-C1 cleavage, and elimination, is most likely the reaction process.



**Scheme 1. Methods for the Synthesis of 2-Trifluoromethylpyrroles Using the Trifluoromethylated Building Block.**

Liu et al., (2017) employed the 1, 3-dipolar cycloaddition procedure to synthesise pyrroles from alkenes, while the tandem 1, 3-dipolar cycloaddition/oxidative dehydrogenative aromatization reaction was used to synthesise indolizines from pyrroles.

According to the researchers, pyrroles may be synthesised via the tandem reaction sequence of oxidative dehydrogenative aromatization reactions of nitrogen-containing heterocycles (Scheme-2).

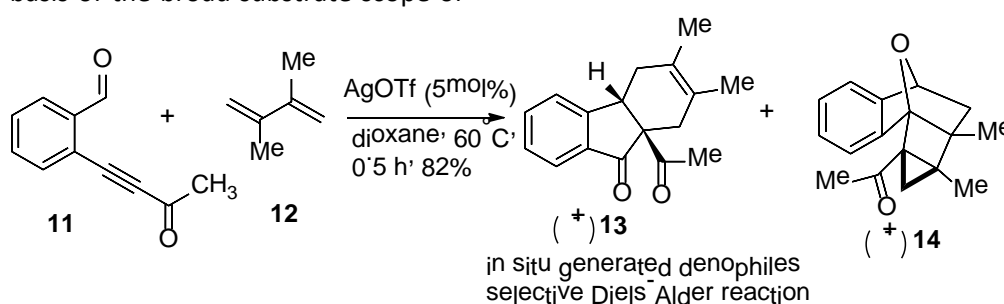


**Scheme 2. One-pot synthetic pathways for the construction of pyrroles from alkenes using a 1,3-dipolar cycloaddition reaction.**

Even with a bulky butyl substituent on the nitrogen of the pyrrolidine ring, these pyrrolidines generated pyrroles in equal yields. The presence of a p-toluenesulfonyl group on the nitrogen atom of pyrrolidine, on the other hand, made the procedure difficult. Despite previous reports that N-p-toluenesulfonyl substituted pyrrolidines were unstable in the absence of BPO, the investigations showed that both 7a and 7b were stable under typical reaction conditions. On the basis of the broad substrate scope of

this transformation and the results of the kinetic and control Scheme-2. Scope of imine component an isolated yield. Yields were determined by  $^1\text{H}$  NMR using DMA internal standard.

Silver-catalyzed domino reactions of orthocarbonylated alkynyl-substituted arylaldehydes with conjugated dienes were used to synthesise pyran derivatives, according to this research by Chao et al., (2016).

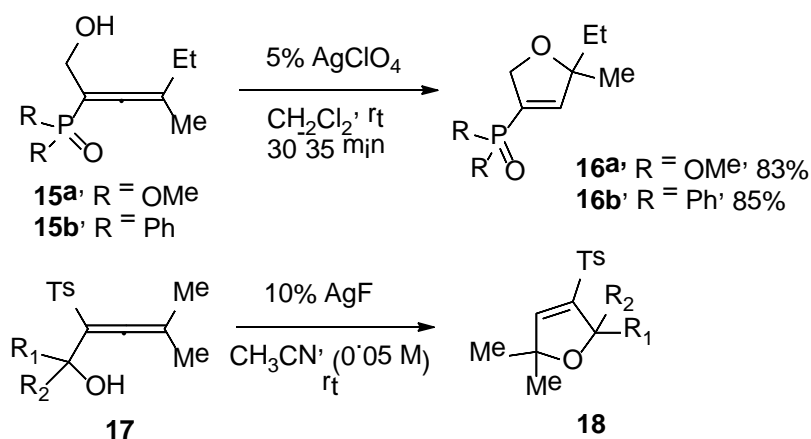


### Scheme 3. The Reactions of Enynals with Conjugated Dienes.

This process can effectively accomplish the synthesis of a wide range of indanone-fused cyclohexene derivatives. According to the authors, these tricyclic compounds may have been synthesised using Diels-Alder processes involving indanone dienophiles and conjugated dienes. This is particularly true for products that are endo/exo selective in nature. To establish reaction conditions, they began by studying the reaction of o-alkynylbenzaldehyde (11) with conjugated diene (12) to determine with different reaction conditions.

The best yield was found that, the use of several Lewis and Brønsted acids ( $\text{AgNTf}_2$  or  $\text{AgOTf}$ ) can promote the generation of tricyclic product (13) with 1,4-dioxane as a solvent at  $60^\circ\text{C}$  in acceptable yields. Whereas the reaction time could be shortened greatly

when the silver salts were selected and the  $\text{AgOTf}$  catalyst gave product (13) in a slightly high yield than  $\text{AgSbF}_6$  and  $\text{AgBF}_4$ . The solvent DSE and  $\text{CHCl}_3$  under same temperature provide the product (14), no (13) has been isolated at all. Although acetonitrile and THF provide (13) but comparatively with low yield. Tata and Michael (2016) used 10% silver fluoride at room temperature to produce 3-tosyl 2,5-dihydrofurans in excellent yield by a 5-endo-trig chain reaction, which they did at room temperature. The hydroxy allenic sulfone starting material was obtained by the process of lithiation and trapping with carbonyl compounds.



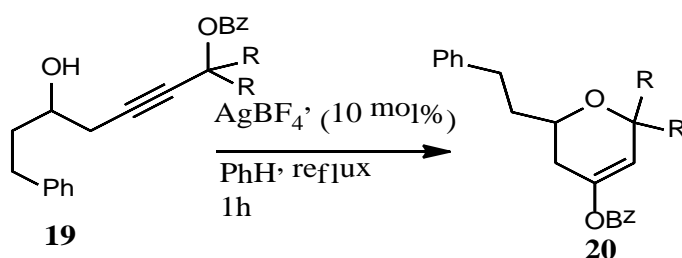
**Scheme 4. Silver-Catalyzed Cyclization of Phosphorus(V)-Substituted Allenes.**

It is worth mentioning that Mukai pioneered the cyclization of allenyl alcohols containing an electron-withdrawing group (such as sulfonyl or phosphonate groups) at the C-1 position to form diverse oxacycles by using potassium tert-butoxide as the catalyst. Silver-catalyzed cyclization of allenyl alcohol gives stable, substituted dihydrofuran compounds by a 5-endo-trig cyclization, which is a distinct conclusion from previous studies.

Aliphatic aldehydes were used to produce allenols, and a high yield was produced. Those made from conjugated aldehydes and benzaldehydes seemed to react more quickly,

with one sample showing a completion time of 30 minutes for those made from these compounds. Allenols derived from ketones exhibited a similar pattern, however, the magnitude of the effect was much reduced, perhaps due to steric effects.

Kazuhiro et al., (2016) aimed to understand the effects of replacement on the propargylic benzoate carbon in the AgCC process in the first instance. It was found that the best circumstances for these cyclizations were found in refluxing benzene.



**Scheme 5. Exploration of Diastereoselective AgCC.**

Higher temperatures (e.g., refluxing toluene or xylenes) resulted in quicker reaction rates; nevertheless, significantly lower yields (about 5-10% lower) were frequently observed. They were thrilled to

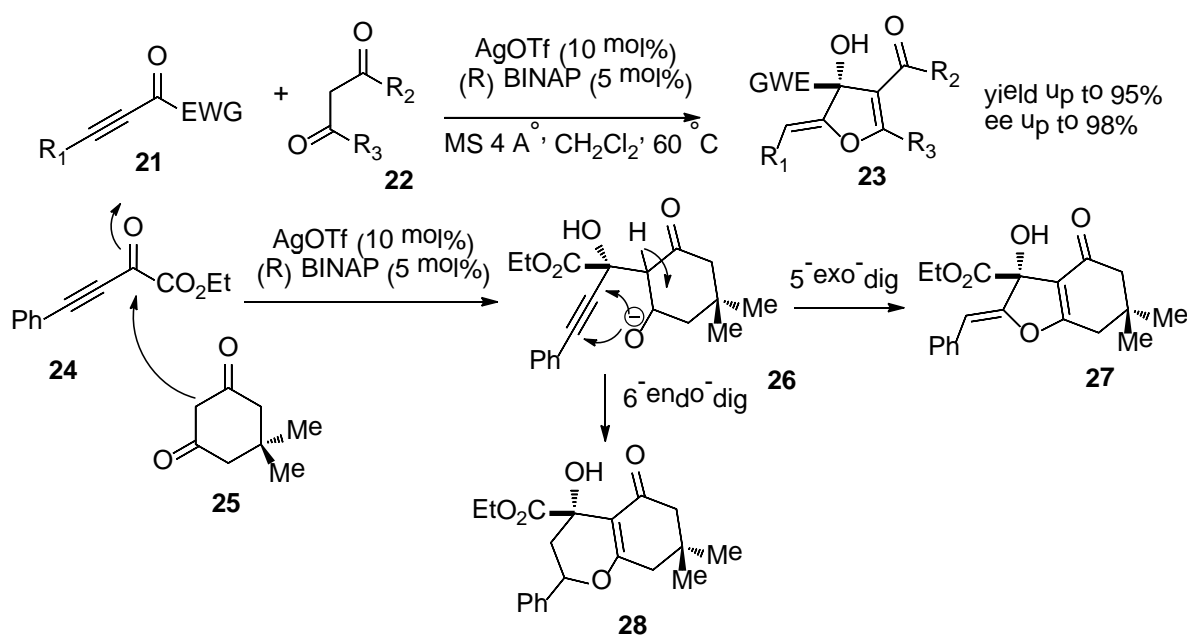
witness clean conversion with the dialkyl benzoate 19 and the expected compounds in 73-76% yield, which was consistent with the expectations.

Interestingly, the diphenyl benzoate

proved to be an issue during the reaction, with breakdown occurring under the circumstances of the reaction. The researchers ascribe this result to the great proclivity of the benzoate moiety to ionize and form the matching 3° carbocation, which would be substantially stabilised by the two phenyl substituents and the alkyne in the molecule in question.

The cyclic systems performed flawlessly, resulting in good to outstanding yields of spirocyclic compounds at the end. In the absence of any replacement at the propargylic benzoate carbon, the primary benzoate 11g failed to react under refluxing benzene conditions and decomposed when heated over 45°Celsius.

According to Sinha et al., (2015) the model ynone and diketone equivalents are Ethyl 4-phenylbut-3-ynoate (21) and dimedone (22) (Table 1). Solution of (R)-BINAP (0.02 mg/mL) and silver trifluoride (0.02 mmol/mL) were slowly added to the dichloromethane solution of ynone (21) and dimedone (22) in dichloromethane at 0°C (0.022 mmol). In only a few short hours, the ynone had evolved into a pair of distinct items. In the reaction, the minor one, identified subsequently as tetrahydro-4H-chromene (28), disintegrated and produced extremely polar unidentified compounds. Only dihydrofuran (23 and 27) was the primary product after column chromatographic purification.



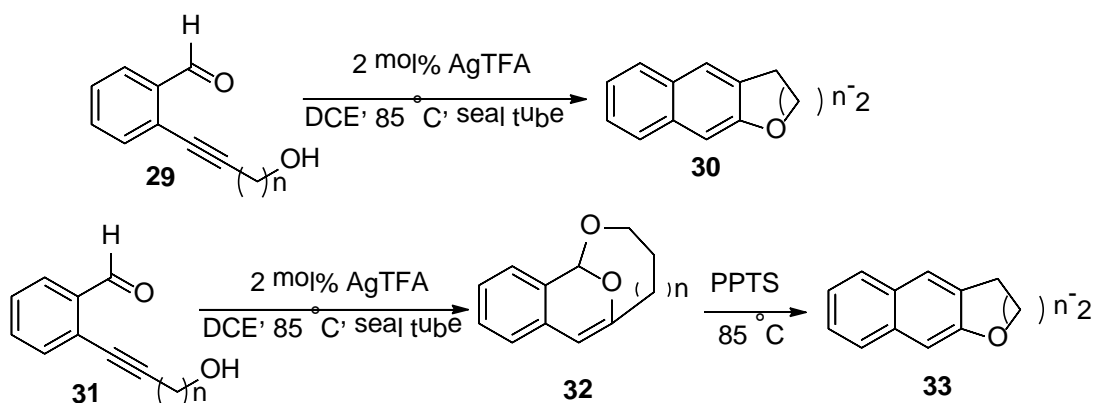
**Scheme 6. Generalized Substrate Scope in Dihydrofuran Synthesis.**

According to Akkachairin et al., (2017) ortho-carbonylarylacetylenols have recently been employed to synthesise dihydronaphthofurans by an AgTFA-catalyzed annulation procedure. It is possible to employ both ortho-keto and ortho-formyl-

arylacetylenes in this transformation, which will result in high yields of the desired products as a consequence. The reaction pathways for these two substrates, are quite different. The reaction of the ketone precursors could be completed in a single

operation, however, the reaction of the aldehyde precursors needed a one-pot two-step procedure, which did not allow for the separation of the bicyclic acetal intermediates, to produce the necessary

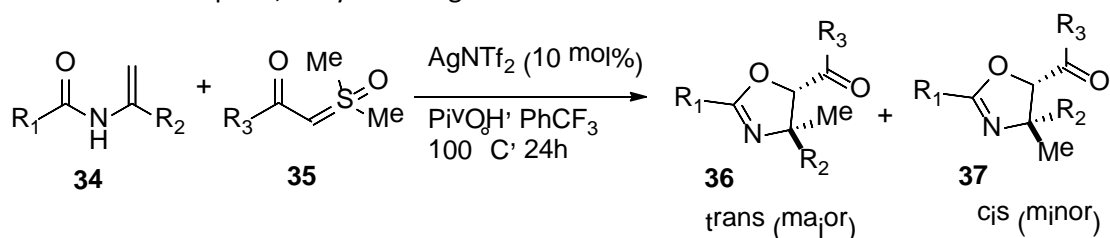
products. Furthermore, this approach was successfully used to synthesise dihydronaphthopyrans, which resulted in very high yields.



**Scheme 7. AgTFA-catalyzed annulation.**

Liu et al., (2021) have evolved sulfoxonium ylides as versatile building blocks in a multitude of annulation reactions depending on their unique ambiphilic tendencies. As a result, sulfoxonium ylides have emerged as flexible building blocks in many annulation reactions (34). This is shown by the fact that numerous privileged carbo- and heterocyclic systems have been built to date by coupling functionalized multiple Cx bonds (where X is any of the elements C, N, O, and so on) effectively and selectively (35). Additionally, since they behave similarly to their stable enamine counterparts, they offer significant

structural motifs with a broad range of potential uses in asymmetric reactions and natural product syntheses (36). Adding electronic properties to olefins by enable them with amide functionalities endows enamides with nucleophilic and electrophilic characteristics, allowing them to engage in various reactions (37). This paper reports that an annulation reaction of secondary enamides with carbonyl sulfoxonium ylides is catalysed by silver. This reaction is useful for the preparation of valuable multi-functionalized oxazoline derivatives.

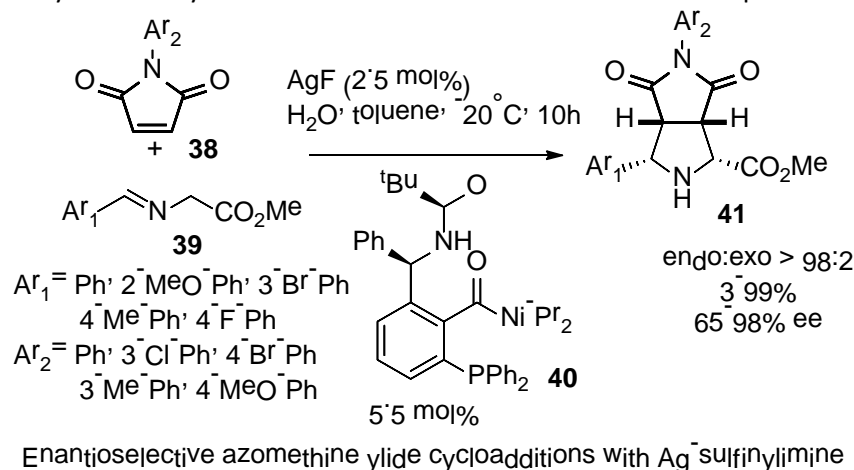


**Scheme 8. Synthesis of tetra-substituted oxazolines.**

A method developed by Bai et al., (2016) included the use of chiral sulfonilimine-

containing nonbiaryl atropisomers of tertiary amide in endo-selective silver catalysed

dipolar cycloaddition of azomethine ylide (Scheme-9) in the cycloaddition of azomethine ylide (39). Highly enantioselective reaction with N-aryl maleimide as dipolarophile was obtained in the presence of the syn-(R,RS)-49 (Xing-Phos) axially chiral ligand syn-(R, RS)-49 (Xing-Phos). The catalytic activity and enantio-



**Scheme 9. Ag(I)-catalyzed [3+2] cycloaddition in presence of aromatic amide-derived non-biaryl atropisomer.**

The researchers of Xu group first ran the reaction at 20°C in THF for 5 hours with 2.5 mol percent AgF and 5.5 mol percent syn-(R, RS)-2h, and they found to be the optimal reaction condition for the cycloaddition of N-benzyl-ideneglycine methyl ester with trans- $\beta$ -nitrostyrene (*exo:endo* 1:4 > 99:1, up to 97% of *ee*). The diastereoselectivity was effectively converted to *endo*-selectivity (*endo:exo* 1/4 > 95:5), although the enantioselectivity was significantly reduced (70 percent *ee*) as compared to that of nitrostyrene. After that, they look at the solvent effect since the solvent might have considerable effects on the 1,3-dipolar cycloaddition process. For example, according to the results reported in the illustration, when DCM was employed as a solvent, the *ee* of *endo*-45 was reduced to 62%. However, because the *endo*-selectivity

selectivity of non-biaryl atropisomers produced from aromatic amides in the silver-catalyzed cycloaddition of azomethine ylides with N-aromatic maleimide were investigated in this study. As a starting point, the cycloaddition of N-benzylideneglycine ethyl ester (39) with N-phenyl maleimide (38) was chosen as the representative reaction.

remained strong, the *endo*-45 was produced in 82 percent of *ee* in toluene, which was a pleasant surprise. On the other hand, the same diastereoselectivity was achieved in xylene, but this solvent was not favourable to enantioselectivity (60% *ee*).

### Conclusion

Recently developed applications of silver catalysis to the synthesis of heterocyclic compounds that include oxygen and nitrogen are discussed in this review; heterocyclic compounds are the most significant precursors for creating current pharmaceutical drugs. Moreover, these transformations can produce a wide range of valuable compounds, such as enantioenriched alkaloid scaffolds, fused carbocycles, pyrrolidines, and a wide range of heterocyclic compounds. These pattern may

be found in a wide variety of compounds with potential bioactivity, and they are of great interest to both synthetic and medicinal chemists. Because of their often wide substrate scope, strong functional group compatibility, high yields, and enantioselectivity, these techniques are considered useful due to their generally high yields. In particular, the cheap cost and low toxicity of silver catalysts, as well as their efficient coordination with a wide range of ligands, make them particularly attractive.

#### Acknowledgement

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