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Review

Recent Organic Transformations with Silver Carbonate as a Key External Base and Oxidant

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Abstract: Silver carbonate (Ag_2CO_3), a common transition metal-based inorganic carbonate, is widely utilized in palladium-catalyzed C–H activations as an oxidant in the redox cycle. Silver carbonate can also act as an external base in the reaction medium, especially in organic solvents with acidic protons. Its superior alkynophilicity and basicity make silver carbonate an ideal catalyst for organic reactions with alkynes, carboxylic acids, and related compounds. This review describes recent reports of silver carbonate-catalyzed and silver carbonate-mediated organic transformations, including cyclizations, cross-couplings, and decarboxylations.

Keywords: silver; silver carbonate; Lewis acid; basicity; alkynophilicity

1. Introduction

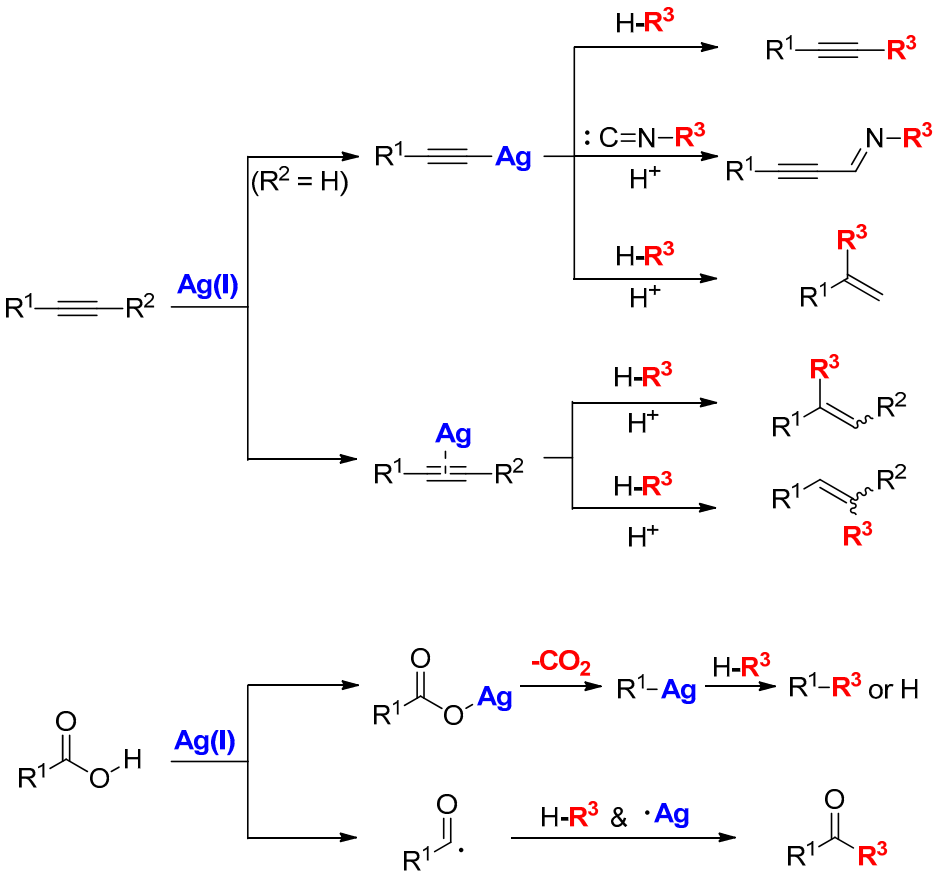
Organic transformations using transition metal catalysts are essential synthetic techniques in total synthesis, medicinal chemistry, industrial chemistry, and chemical engineering [1]. A variety of transition metal catalysts have been developed and studied for various organic reactions, and they are generally used for selective bond formation and the interconversion of specific organic functional groups. Transition metal-catalyzed reactions can generally be classified into three types based on the role of the metal catalyst. The first class includes those in which the catalytic reaction is based on the oxidation/reduction cycle of the transition metal. As many transition metals can have more than two relatively stable oxidation states, the interconversion between oxidation states of a metal can be utilized to oxidize or reduce target molecules or functionalities. The second class of catalytic reactions are those in which the transition metal serves as a Lewis acid. The final group of organic transformations are those catalyzed by coinage metals [2]. As both Cu(I) and Cu(II) are generally stable states for copper, copper-catalyzed organic transformations have been widely studied. However, silver- and gold-promoted organic reactions are relatively rare.

Silver catalysts are generally less reactive than other transition metal catalysts; therefore, in organic reactions, silver compounds are generally used as cocatalysts or bond activators due to their Lewis acidity [3,4]. In addition, Ag(I) is one of the softest Lewis-acidic metal cations; thus, Ag(I) forms organometallic complexes with π-donor functionalities, such as alkenes, alkynes, allenes, and aromatic

rings. Concurrently, Ag(I) generates relatively stable organometallic complexes with n-donor type molecules, for example, ethers, amines, and phosphines.

In the last decade, various silver-catalyzed organic transformations, such as carboxylations, halogenations, C–H bond functionalizations, cycloadditions, and oxidative couplings, have been reported [5–8]. The reported silver-catalyzed reactions were performed under relatively milder reaction conditions than the reactions by other methodologies, and silver complexes are less expensive than other rare transition metals, such as palladium, rhodium, ruthenium, and platinum.

Among the various silver species, silver carbonate (Ag_2CO_3) is not typically used as a catalyst or mediator of organic reactions, but it is known as a good oxidant (for example in the Fetizon oxidation) and inorganic base (for example in the Wittig reaction) [9,10]. Scheme 1 describes the general reactions involving Ag_2CO_3. Ag_2CO_3 enables the use of Lewis acids with internal alkynes, and readily activates alkynes to nucleophilic attack, providing the corresponding addition products. With terminal alkynes, Ag_2CO_3 generates silver acetylide intermediates through C–H functionalization, and then various reactions (for example, cross-couplings, and cycloadditions) can be used to convert these intermediates into useful organic frameworks, such as furans [11], pyrroles [12], and nitriles [13]. Additionally, Ag_2CO_3 is used as an oxidant for single-electron transfer (SET) processes to generate reactive radical species for various organic transformations, for example, the generation of acyl radicals from carboxylic acids. In addition, the basicity of the carbonate moiety can help prepare reactive partners from acidic organic molecules such as carboxylic acids, terminal alkynes, and 1,3-dicarbonyl compounds.



Scheme 1. The role of Ag(I) in transformations of alkynes and carboxylic acids.

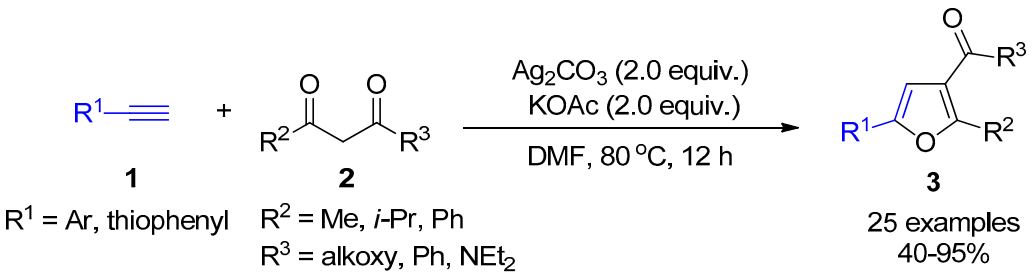
In this review, we summarize the recently reported Ag_2CO_3-catalyzed and Ag_2CO_3-mediated organic transformations and small molecule syntheses from 2005 to 2019 based on the reactivity of Ag(I) and the basicity of Ag_2CO_3. The focus will be on their synthesis and substrate scope as well

as the principle reactivity of silver carbonate, and the substrates will also be discussed based on mechanistic clues.

2. Activation of Alkynes Using Silver Carbonate

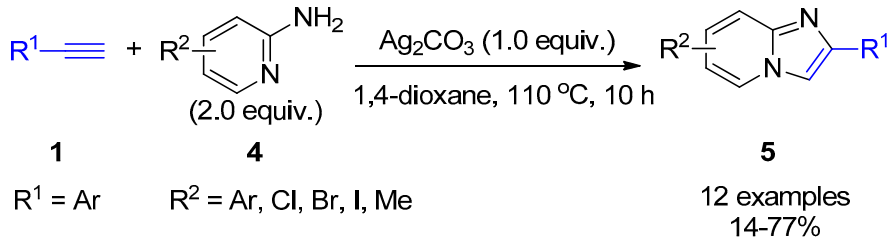
2.1. Terminal Alkynes: Cross-Coupling Reactions

Oxidative double C–H functionalization/cross-coupling reactions are considered an attractive strategy for the synthesis of various heterocycles. The Ag_2CO_3-mediated activation of terminal alkynes is a good starting point for this heteroaromatic cyclization. In 2012, Lei and co-workers reported the direct C–H functionalization and oxidative coupling of two C–H bonds as an ideal synthetic strategy for accessing highly substituted furans (Scheme 2) [14]. Although synthetic methods for preparing substituted furans have been reported previously [15], new synthetic strategies are required to achieve selective cross coupling of two more hydrocarbons. The homocoupling of terminal alkynes occurs easily under most oxidative conditions [16]. This report shows that Ag_2CO_3 can be used as a mediator to induce C–H/C–H functionalization of terminal alkynes and 1,3-dicarbonyl compounds. This reaction affords furans with several functional groups in a facile, one-step manner. Terminal alkyne **1** can be converted to the corresponding silver acetylide intermediate by Ag_2CO_3, and furan **3** is synthesized by alkylation with 1,3-dicarbonyl compound **2** followed by oxidative radical cyclization.



Scheme 2. Silver-mediated oxidative C–H/C–H functionalization process to afford highly substituted furans.

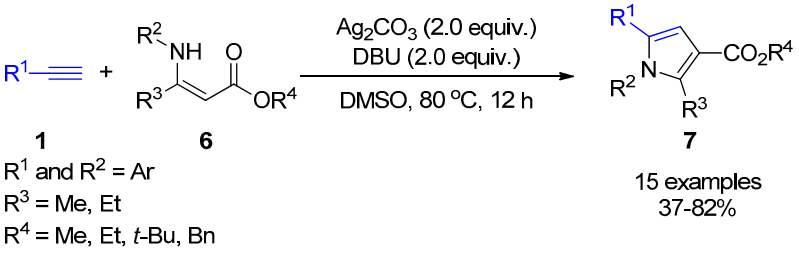
In the same year, the Lei group reported a Ag-mediated, highly selective C–C/N–H oxidative cross-coupling/cyclization to construct imidazo[1,2-*a*]pyridines **5** from 2-aminopyridines **4** and terminal alkynes **1** (Scheme 3) [17]. This reaction is also initiated by the generation of a silver acetylide intermediate from the Ag salt and phenylacetylene; then, subsequent Ag-promoted nucleophilic attack and oxidative cyclization form imidazo[1,2-*a*]pyridine **5** as the product. After the reaction, the spent silver species can be recycled by filtration and treatment with nitric acid and Na_2CO_3.



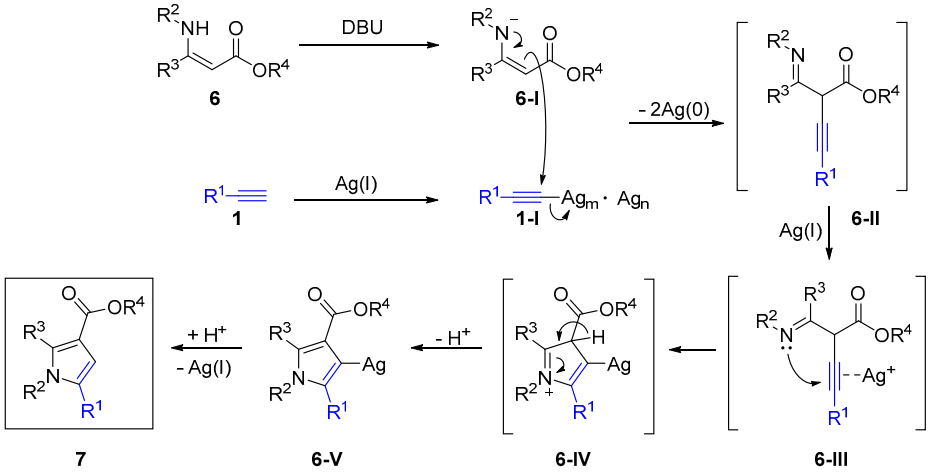
Scheme 3. Ag-mediated C–H/N–H oxidative cross-coupling/cyclization.

As described above, oxidative C–H functionalization/cross-coupling reactions are considered an attractive strategy for the synthesis of various heterocycles. Pyrroles, as 5-membered heterocycles, are also a basic building block of numerous biologically and pharmaceutically important natural compounds [12], and the regiospecific synthesis of pyrroles is an attractive synthetic tool. The Lei group reported that pyrroles **7** containing various functional groups can be effectively synthesized

by the C–H/C–H oxidative cross coupling/cyclization of terminal alkynes **1** and β-enamino esters **6** using Ag_2CO_3 as a mediator (Scheme 4) [18]. The proposed mechanism is shown in Scheme 5. Due to the effects of Ag_2CO_3, terminal alkyne **1** is primarily converted to silver acetylide **1-I**; then, the nucleophilic addition of deprotonated β-enamino ester intermediate **6-I** to silver acetylide **1-I** delivers oxidative cross-coupling intermediate **6-II** via two single-electron oxidations. The coordination of Ag(I) generated internal alkyne **6-III**, which is cyclized by an intramolecular nucleophilic addition to provide cyclic intermediate **6-IV**, and subsequent aromatization and protodemetallation give highly substituted pyrrole **7** as the product.

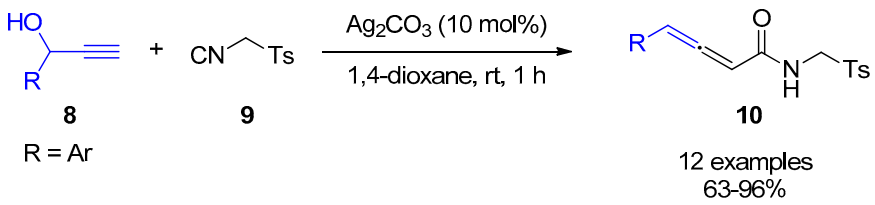


Scheme 4. Synthesis of polysubstituted pyrroles via Ag-mediated oxidative cyclization.



Scheme 5. Proposed mechanism for Ag-mediated pyrrole synthesis. Chem. Commun. 2013, 49, 7549–7551, doi:10.1039/c3cc43682a—Reproduced by permission of The Royal Society of Chemistry.

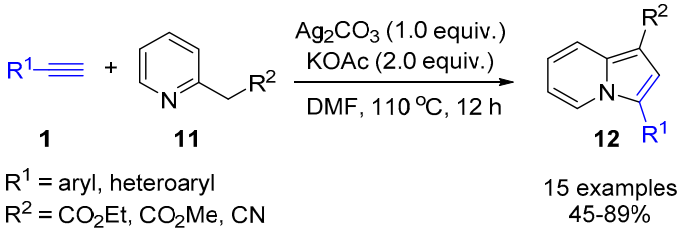
In 2014, Bi and co-workers reported an Ag_2CO_3-catalyzed cross-coupling reaction of propargylic alcohols **8** with isocyanides **9** to give 2,3-allenamides **10** (Scheme 6) [19]. Although the reaction mechanism is not clear, this reaction involves a unique β-C–C coupling and oxygen transposition of propargylic alcohols.



Scheme 6. Ag-catalyzed cross coupling of propargylic alcohols with isocyanides.

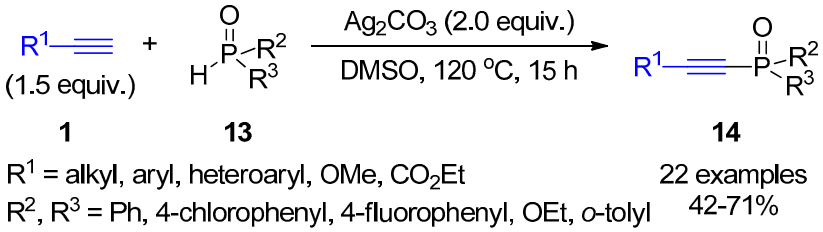
The Agrawal group reported the synthesis of indolizines **12** via a Ag-mediated oxidative C–H functionalization and cyclization of terminal alkynes **1** with pyridine derivatives **11** (Scheme 7) [20]. Indolizine is a basic organic building block for many alkaloids and bioactive molecules, so the development of regioselective synthetic pathways is an attractive topic in organic synthesis [21].

This reaction allows the highly selective synthesis of indolizines from readily available starting materials via a 5-*endo-dig* cyclization between the silver phenylacetylide generated from alkyne **1** and a chelated intermediate from the deprotonation of 2-pyridine derivative **11**. After the reaction, Ag_2CO_3 can be recycled and reused.



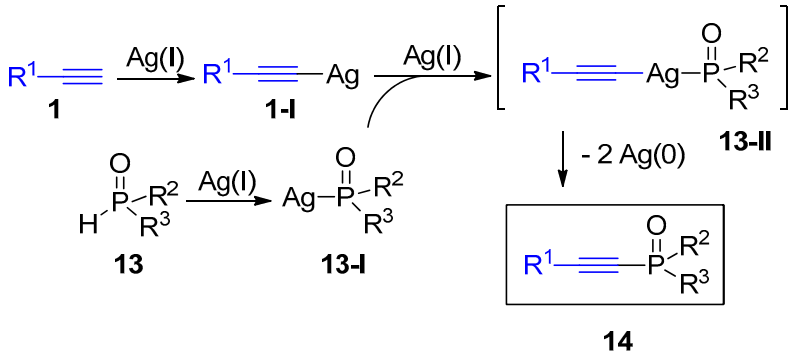
Scheme 7. Ag-mediated oxidative C–H functionalization to synthesize indolizines.

In 2015, Lei and co-workers developed a Ag(I)-mediated selective oxidative cross coupling between C–H and P–H bonds to afford alkynyl (diaryl) phosphine oxides **14** (Scheme 8) [22]. To determine the mechanism of this reaction, the authors performed experiments with silver complexes as the starting materials. Phenylacetylide was mixed with $Ph_2P(O)H$ and prepared silver; the reaction only provided only 17% of the desired product, but 60% of the desired product was obtained when an additional 1.0 equiv. of Ag_2CO_3 was added. When the reaction used $Ph_2P(O)Ag$ instead of $Ph_2P(O)H$, only a trace amount of the product was obtained with phenylacetylene. In the presence of an additional 1.0 equiv. of Ag_2CO_3 in the same reaction, 37% of the product was obtained. With both silver phenylacetylide and $Ph_2P(O)Ag$, the reaction provided 30% of the desired product, and 71% of the product was produced when an additional 1.0 equiv. of Ag_2CO_3 was added.



Scheme 8. Ag-mediated selective oxidative cross coupling between C–H and P–H. Adapted with permission from Org. Lett. 2015, 17, 118–121, doi:10.1021/ol503341t. Copyright (2019) American Chemical Society.

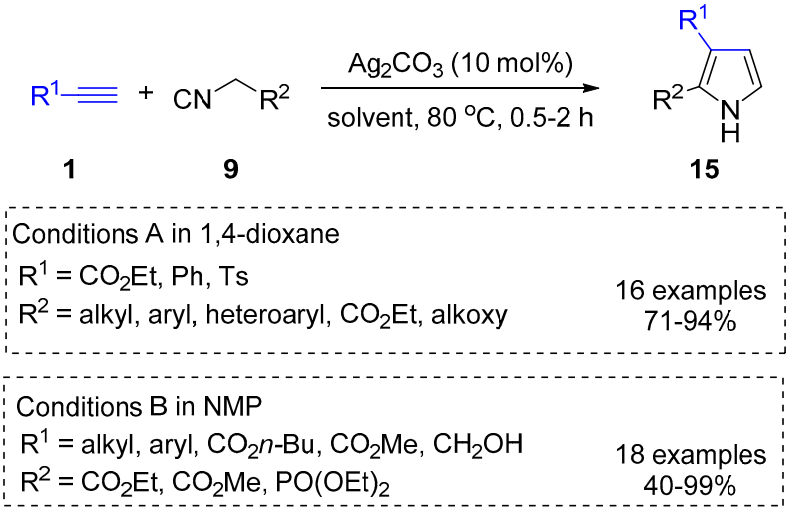
Based on the experimental results, a mechanism was proposed as shown in Scheme 9. Silver acetylide **1-I** and disubstituted phosphoryl silver species **13-I** are formed from silver carbonate, and a cascade involving coordination and cross-coupling reactions via two single-electron oxidations provided alkynyl(diaryl)phosphine oxides **14**.



Scheme 9. Proposed mechanism of the Ag-mediated oxidative cross coupling between C–H and P–H.

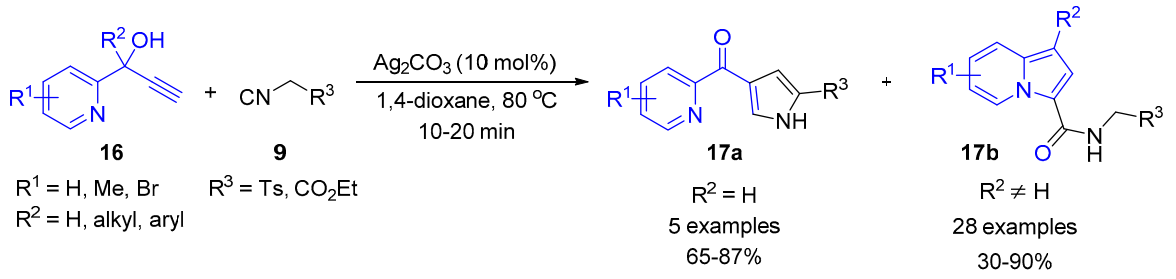
2.2. Terminal Alkynes: Cycloaddition Reactions

The ideal method for the synthesis of substituted pyrroles is the cycloaddition of an alkyne and an isocyanide. Isocyanide-alkyne cycloaddition reactions are usually limited to use electron-deficient alkynes, and the yields are low. In 2013, two interesting papers were published on the synthesis of pyrroles via Ag_2CO_3-catalyzed cycloadditions of isocyanides and terminal alkynes. One is from the Bi group (Scheme 10, Conditions A) [23], and the other is from the Lei group (Scheme 10, Conditions B) [24]. The reaction mechanism is unclear, so these two groups explained the reaction mechanism in different ways. Based on the results of a deuterium-labeling experiment, Bi suggests that the reaction is initiated by the formation of a silver acetylide from terminal alkyne **1** and the Ag(I) catalyst, and this is followed by the 1,1-insertion of isocyanide **9** into the Ag–C bond. Protonolysis and intramolecular cyclization provide a pyrrolenine intermediate, and a 1,5-hydrogen shift gives the pyrrole. On the other hand, Lei suggests that the mechanism involves a click reaction like a Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) [25], because they observed the coordination of the silver to the isocyano group by in situ IR spectroscopy of the stoichiometric reaction between ethyl 2-isocyanoacetate and Ag_2CO_3. Therefore, the Ag_2CO_3 catalyst generates both a silver acetylide and a silver isocyanide complex, and click cyclization provides substituted pyrroles **15**.

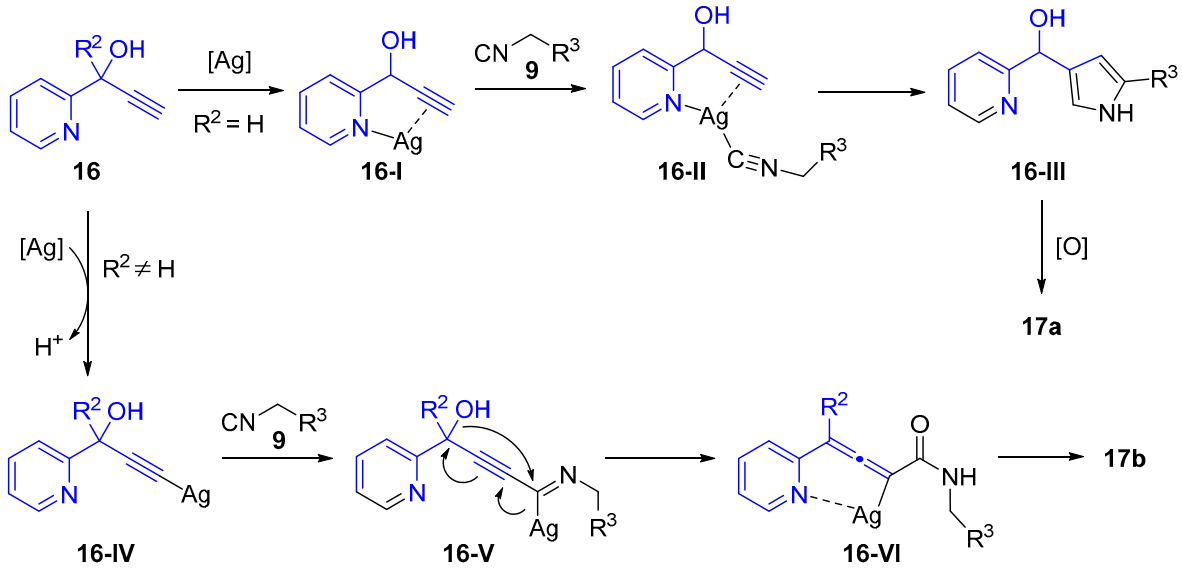


Scheme 10. Ag-catalyzed cycloaddition of alkynes and isocyanides.

In 2014, Bi and co-workers reported the synthesis of pyrroles and indolizines from the cyclization of 2-pyridyl alkynyl carbinols with isocyanides (Scheme 11) [26]. The divergent pathways are described in Scheme 12. 2,4-Disubstituted pyrroles **17a** were synthesized from secondary 2-pyridyl alkynyl carbinols **16** by a regioselective [3+2] cycloaddition. Coordination of the pyridine moiety affords coordinated silver acetylide **16-I**, and an additional coordination occurs with isocyanide **9** to form intermediate **16-II**. [3+2] Cycloaddition affords 2,4-disubstituted pyrrole **16-III**, and subsequent oxidation gives pyrrole **17a** as the product. The indolizines are generated from tertiary propargyl alcohols **16**. The Ag(I) catalyst reacts with terminal alkyne **16** to provide silver acetylide **16-IV**, and then a 1,1-insertion of isocyanide **9** into the Ag–C bond affords acetylenic imido intermediate **16-V**. Intramolecular rearrangement converts **16-V** to 2,3-allenamide **16-VI**, and subsequent intramolecular cycloisomerization gives indolizine **17b**.



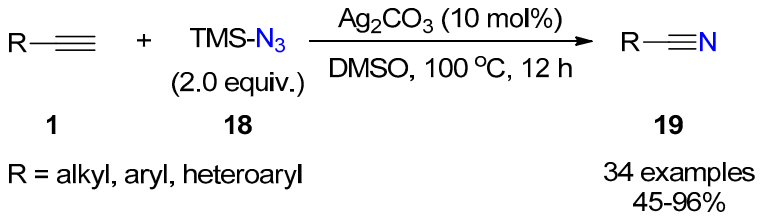
Scheme 11. Ag-catalyzed cyclization of 2-pyridyl alkynyl carbinols with isocyanides.



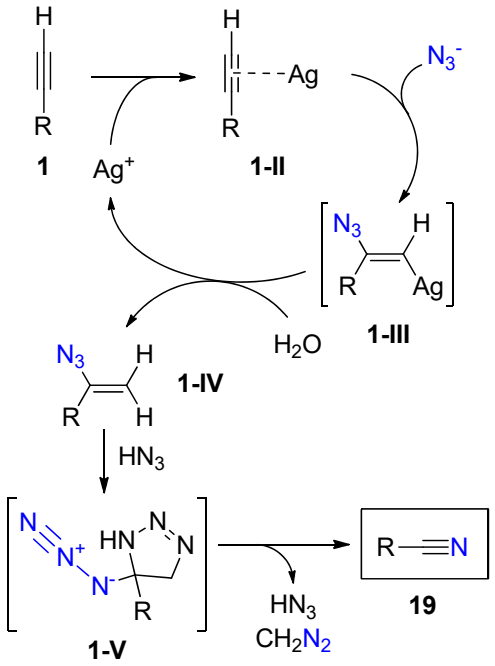
Scheme 12. Proposed mechanism for Ag-catalyzed cyclization of 2-pyridyl alkynyl carbinols with isocyanides. Chem. Commun. 2014, 50, 11837–11839, doi:10.1039/c4cc04905e—Reproduced by permission of The Royal Society of Chemistry.

2.3. Terminal Alkynes: Reactions with Azide

In 2013, the Jiao group reported an Ag-catalyzed nitrogenation of alkynes, representing the first direct conversion of alkynes to nitriles via C≡C bond cleavage (Scheme 13) [27]. The reaction was performed with various alkynes as the starting material, including aryl-, heteroaryl-, alkyl- and alkenyl-substituted alkynes. In the proposed reaction mechanism (Scheme 14), Ag(I) simply coordinates to the alkyne, and no silver acetylide is generated. Then, the azide nucleophile adds to the activated alkyne (**1-II**) to form alkenyl metal complex **1-III**. The protodemetallation of **1-III** provides vinyl azide **1-IV**, and unstable intermediate **1-V** is formed by the click reaction of vinyl azide **1-IV**. Upon the release of HN_3 and CH_2N_2, intermediate **1-V** provides nitrile product **19**.

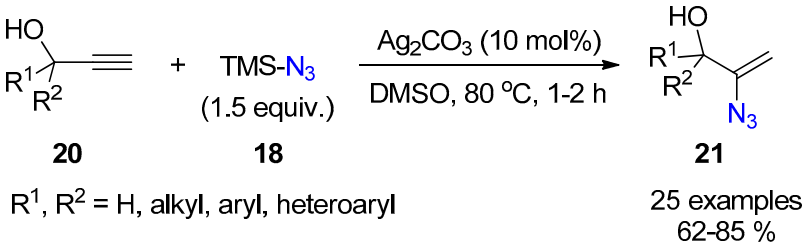


Scheme 13. Ag-catalyzed nitrogenation of alkynes.

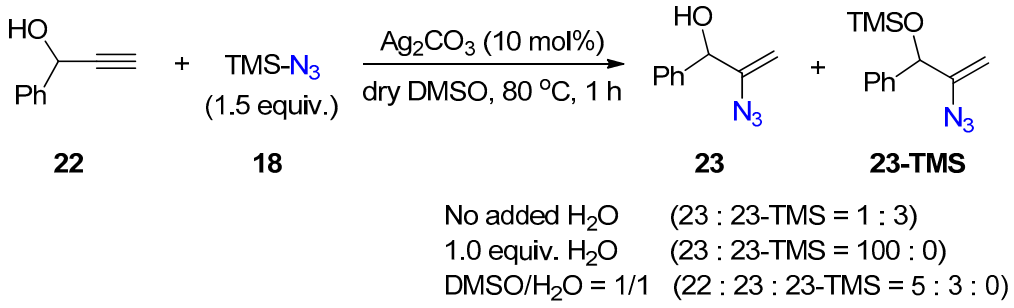


Scheme 14. Proposed mechanism of the Ag-catalyzed nitrogenation.

In 2014, the Bi group reported a Ag(I)-catalyzed hydroazidation to provide 2-azidoallyl alcohols **21** from ethynyl carbinols **20** (Scheme 15) [28]. Hydroazidation is one of the most attractive routes for synthesizing vinyl azides [29]. In a study of the effects of residual water in DMSO as the solvent (Scheme 16), dry DMSO provided a mixture of product **23** and TMS-protected product **23-TMS** in a 1:3 ratio. When 1.0 equivalents of H_2O was added, only the TMS-free product was obtained. When a large amount of water was added, a substantial amount of unreacted starting material **22** remained in the reaction. Based on the results of these reactions, water must play an important role in the reaction.



Scheme 15. Ag-catalyzed hydroazidation of ethynyl carbinols.

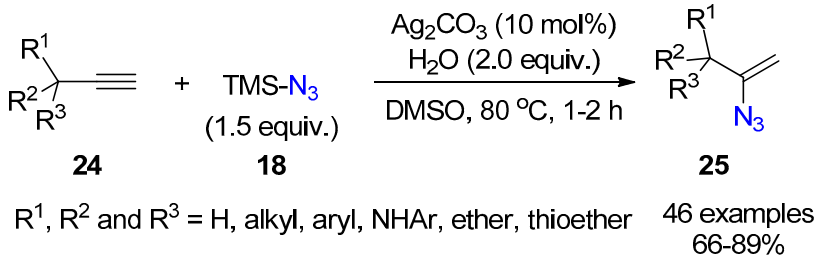


Scheme 16. Effect of water as an additive in the Ag-catalyzed hydroazidation.

Based on a deuterium-labeling experiment, the Ag catalyst generates a silver acetylide from ethylnyl carbinol **20** and HN_3 by the Ag(I)-catalyzed hydrolysis of TMS-N_3 **18**. HN_3 adds to the silver

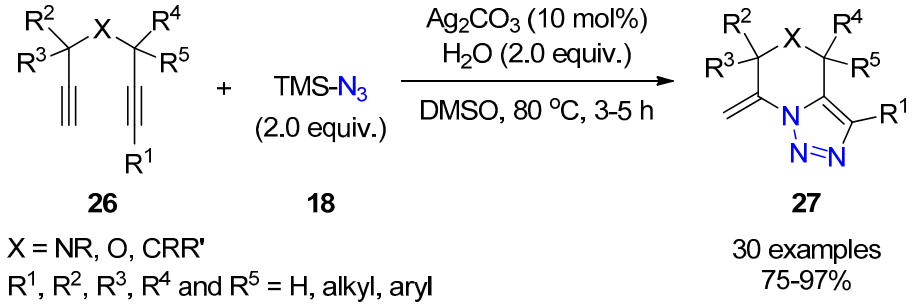
acetylide to give a vinyl silver intermediate, and subsequent protodemetallation gives 2-azidoallyl alcohol **21** as the product.

Unactivated terminal alkynes also provide vinyl azides via a Ag-catalyzed hydroazidation with TMS-N_3 (Scheme 17) [30]. Thus, various terminal alkynes with or without hydroxyl groups at the propargyl position can be successfully converted into vinyl azides in the presence of water.



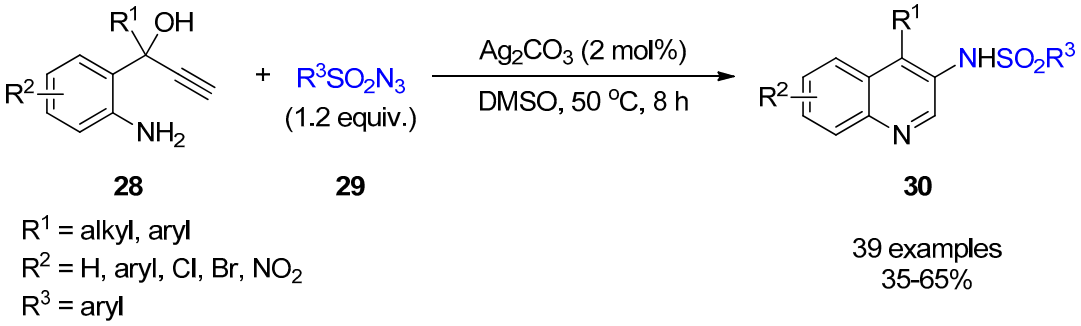
Scheme 17. Ag-catalyzed hydroazidation of propargyl compounds. Adapted with permission from Org. Lett. 2014, 16, 3668–3671, doi:10.1021/ol501661k. Copyright (2019) American Chemical Society.

With diynes, the generated vinyl azides can go on to react with the second alkyne moiety via an intramolecular pathway. The Bi group reported a Ag(I)-catalyzed tandem hydroazidation and alkyne-azide cycloaddition of diynes **26** to give 1,5-fused 1,2,3-triazole frameworks (Scheme 18) [31]. As discussed above, terminal alkynes readily provide vinyl azides via Ag-catalyzed hydroazidation. The remaining unreacted alkyne undergoes an intramolecular alkyne-azide 1,3-dipolar cycloaddition to give bicyclic 1,2,3-triazoles **27**.



Scheme 18. Ag-catalyzed tandem hydroazidation/alkyne-azide cycloaddition of diynes with TMS-N_3. Adapted with permission from Org. Lett. 2015, 17, 2198–2201, doi:10.1021/acs.orglett.5b00784. Copyright (2019) American Chemical Society.

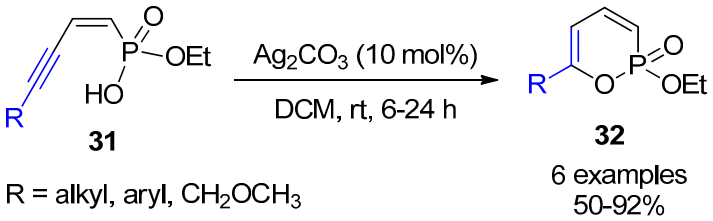
In 2015, Reddy and co-workers developed an efficient pathway for accessing 3-amino quinoline derivatives **30** from readily available 1-(2-aminophenyl) propargyl alcohols **28** (Scheme 19) [32]. The Ag(I) catalyst activates the terminal alkynes to promote the 5-*exo-dig* cyclization with the amine group. [2+3] Cycloaddition with azide **29** and a C–N bond migration with N_2 expulsion results in ring expansion and 6-*endo* cyclization. Subsequent tautomerization and dehydration afford 4-substituted 3-tosylaminoquinolines **30**. This is a rare example of a 6-*endo-dig* reaction of a terminal alkyne, which tend to undergo 5-*exo-dig* cyclizations.



Scheme 19. Ag-catalyzed hydroamination, [2+3] cycloaddition and ring expansion.

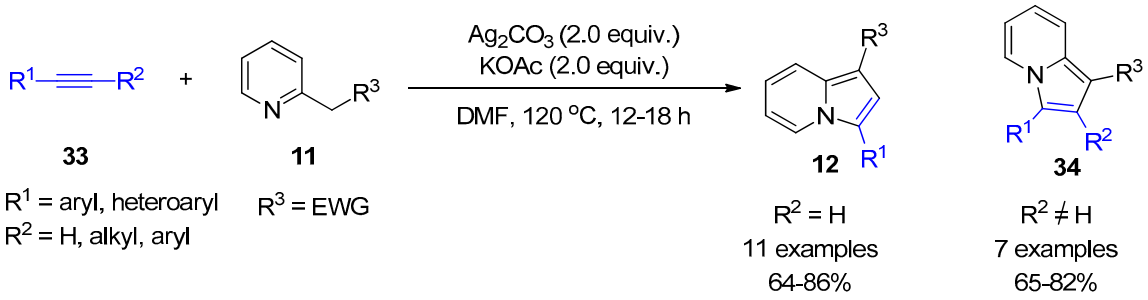
2.4. Internal Alkynes: Synthesis of Heterocyclic Compounds

Although internal alkynes cannot form reactive silver acetylides with Ag(I), where terminal alkynes easily can, internal alkynes can be activated by coordination. In 2005, the Ding group used internal alkynes, (*Z*)-2-alken-4-ynylphosphonic monoesters **31**, as the starting material to access 2*H*-1,2-oxaphosphorin 2-oxides **32** by a Ag(I)-catalyzed cyclization (Scheme 20) [33]. Compared with using (*Z*)-2-en-4-ynoic acid to prepare the five- or six-membered ring products [34], this reaction provides high 6-*endo-dig* regioselectivity. The phosphonyl oxygen regioselectively attacks the Ag(I)-activated C≡C bond in an *endo* manner to give a vinyl silver intermediate, and subsequent proton transfer and protodemetallation provided 2-ethoxy-2*H*-1,2-oxaphosphorin 2-oxides under mild conditions. The cyclization of P–OH onto an internal alkyne is a unique reaction, and this platform provides an effective synthetic route for accessing potentially bioactive phosphorus-containing heterocycles.

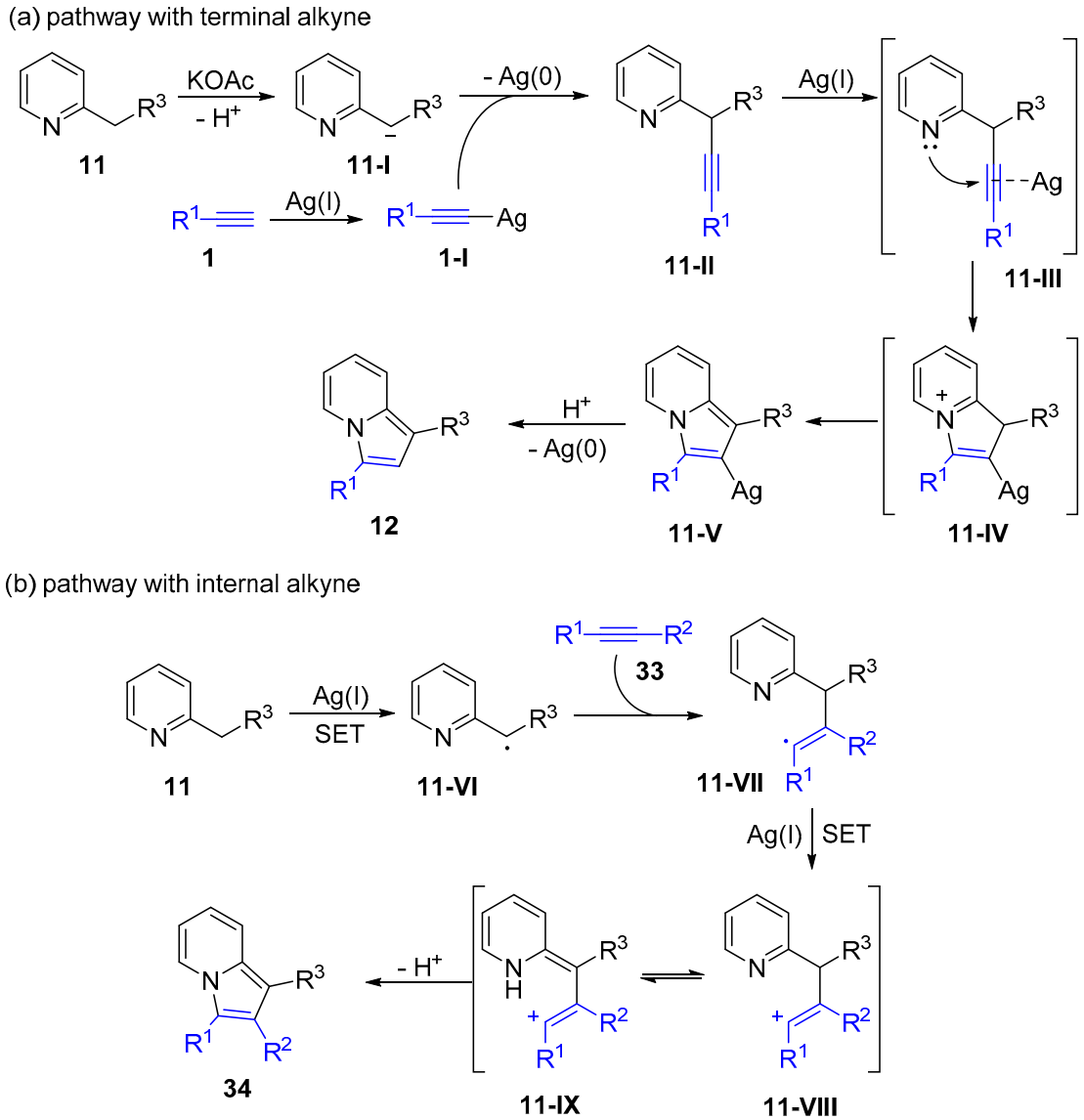


Scheme 20. Ag-catalyzed cyclization of (*Z*)-2-alken-4-ynyl-phosphonic monoesters. Adapted with permission from Org. Lett. 2005, 7, 3299–3301, doi:10.1021/OL051126+. Copyright (2019) American Chemical Society.

In 2014, Pan and co-workers reported the construction of substituted indolizines via a Ag(I)-mediated C–H bond functionalization of 2-alkylazaarenes with alkynes (Scheme 21) [35]. We already discussed a Ag(I)-mediated synthesis of indolizines **12** from terminal alkynes **1** and pyridine derivatives **11** (Scheme 7), and the reaction was proposed to involve a 5-*endo-dig* cyclization between silver phenylacetylide and a chelated intermediate. Here, the authors suggested a reaction mechanism based on the results of a deuterium-labeling experiment. In the case of a terminal alkyne (Scheme 22a), silver acetylide **1-I** was initially generated from alkyne **1** and Ag(I), and 2-alkylazaarene **11** was separately deprotonated by KOAc. The nucleophilic attack of anion **11-I** by silver acetylide **1-I** provides oxidative cross-coupled intermediate **11-II**. Subsequent Ag(I)-assisted cycloisomerization and protodemetallation give indolizine product **12**. In cases with internal alkynes (Scheme 22b), no silver acetylide intermediate is formed. 2-Alkylazaarene **11** undergoes single-electron oxidation to give radical intermediate **11-VI**. Then, single-electron insertion into internal alkyne **33** provides intermediate **11-VII**. Further oxidation of intermediate **11-VII** by Ag(I) generates carbocation **11-VIII**, and indolizine **34** is produced by intramolecular condensation.



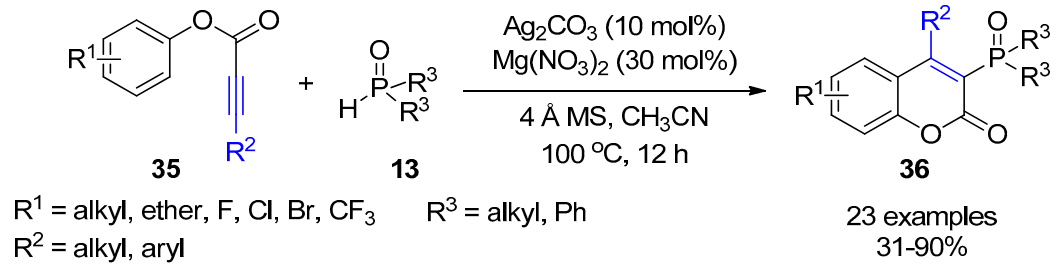
Scheme 21. Ag-mediated one-pot synthesis of indolizines from alkynes and 2-alkylazaarenes.



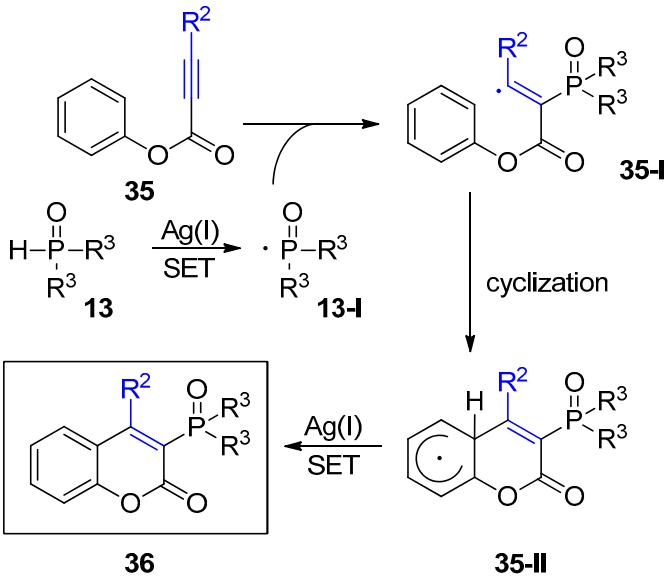
Scheme 22. Proposed mechanisms for Ag-mediated indolizine synthesis with terminal and internal alkynes.

A Ag(I)-mediated synthesis of alkynyl (diaryl) phosphine oxides from terminal alkyne with $Ph_2P(O)H$ was previously described in Scheme 8. The reaction involves the generation of silver acetylide and an oxidative cross coupling. The Wu group developed a version of this reaction with an internal alkyne, namely, a Ag(I)-catalyzed synthesis of 3-phosphorated coumarins **36** via the radical cyclization of alkynoates **35** and dialkyl *H*-phosphonates **13** in a highly regioselective

manner (Scheme 23) [36]. The reaction was completely suppressed by the presence of stoichiometric TEMPO ((2,2,6,6,-tetramethylpiperidin-1-yl)oxyl), which implies that the reaction proceeds through a radical pathway. With this experimental result in hand, a reaction mechanism was proposed, as shown in Scheme 24. Phosphorus radical **13-I** is generated from diethyl *H*-phosphonate **13** by Ag(I), and subsequent selective addition of the P-radical to the α-position of the C=O bond in the alkynoate gives vinyl radical **35-I**. Cyclization of intermediate **35-I** generates intermediate **35-II**, and subsequent SET from **35-II** to Ag(I) releases 3-phosphorated coumarin **36**.

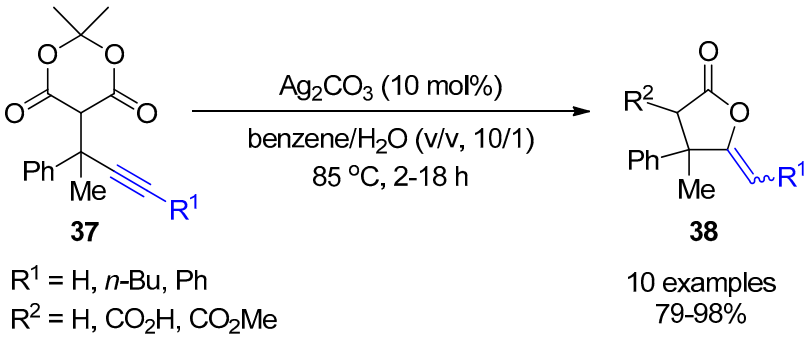


Scheme 23. Ag-catalyzed phosphorus carbocyclization of alkynoates. Adapted with permission from Org. Lett. 2014, 16, 3356–3359, doi:10.1021/ol5013839. Copyright (2019) American Chemical Society.



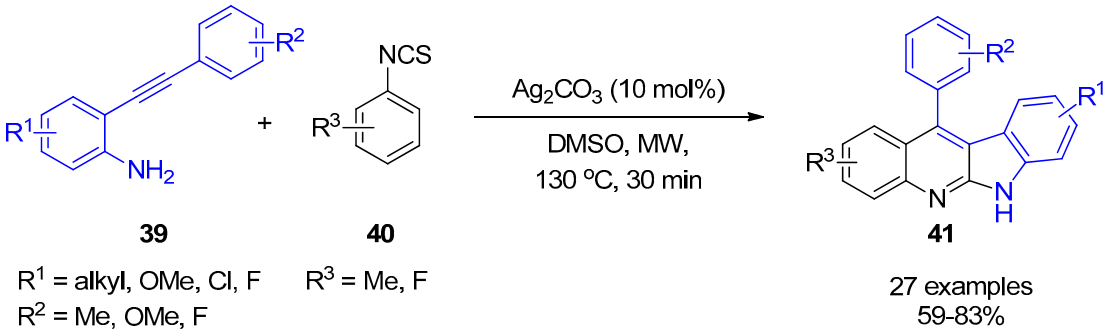
Scheme 24. Proposed mechanism for the Ag-catalyzed phosphorus carbocyclization.

In 2014, the Fillion group reported a Ag(I)-catalyzed 5-*exo-dig* cyclization of propargylic Meldrum's acid derivatives **37** to give γ-alkylidene butyrolactones **38** (Scheme 25) [37]. The formation of the *E*/*Z*-isomers of the product is controlled by the coordination of Ag(I). The alkyne-Ag(I) complex determines the form of an *E*- or *Z*-isomer based on the 5-*exo-dig* cyclization through the attack of the carbonyl-*O*. Syn-attack of the carbonyl-*O* and Ag(I)-activated alkyne provides the *E*-intermediate; on the other hand, anti-attack of the carbonyl-*O* onto the Ag(I)-coordinated alkyne gives the *Z*-intermediate. Both intermediates undergo thermally induced cycloreversion to provide the corresponding acylketene intermediates; then, γ-alkylidene butyrolactones **38** are obtained by nucleophilic attack of the solvent.



Scheme 25. Ag-catalyzed formation of alkylidene γ-butyrolactones.

Indoloquinolines are among the most important skeletons in the design, development, and synthesis of drugs currently on the market [38]. Most synthetic approaches rely on the use of indole or its derivatives as a coupling partner, and a new synthetic pathway for indolo[2,3-*b*]quinolone has been developed via a cascade radical annulation of *o*-alkynylthiourea [39]. In 2017, the Patel group reported a microwave-assisted Ag(I)-catalyzed cascade reaction toward indolo[2,3-*b*]quinolines **41** via the in situ generation of *o*-alkynylthioureas from 2-(phenylethynyl)anilines **39** with phenyl isothiocyanate **40** (Scheme 26) [40]. The reaction of 2-(phenylethynyl)anilines **39** and phenyl isothiocyanate **40** provides thiourea, followed by desulfurization in the presence of Ag_2CO_3, to give a carbodiimide intermediate. An intramolecular thermal cyclization drives the carbodiimide intermediate to a carbene-type intermediate; then, indoloquinoline **41** is produced by carbene C−H insertion followed by aromatization.



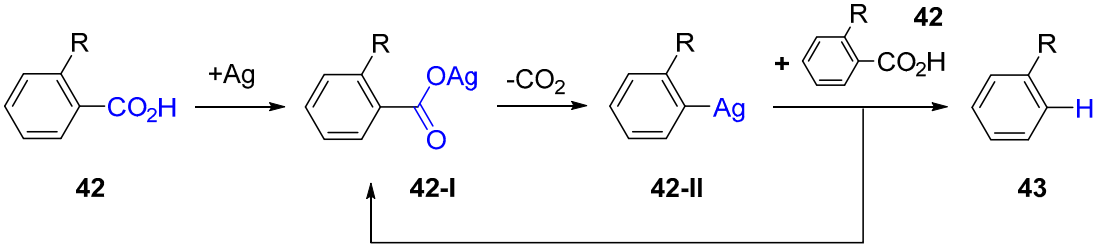
Scheme 26. Ag-catalyzed cascade cyclization by the reaction of 2-(phenylethynyl)aniline and isothiocyanate. Adapted with permission from J. Org. Chem. 2017, 82, 2089–2096, doi:10.1021/acs.joc.6b02912. Copyright (2019) American Chemical Society.

3. Functionalization of Carboxylic Acid Using Ag_2CO_3

3.1. Decarboxylation of Carboxylic Acids

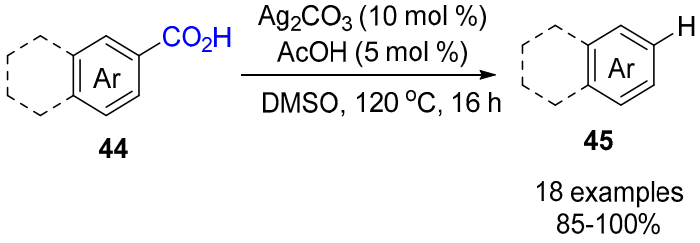
In 2009, the Larrosa group reported a Ag(I)-catalyzed protodecarboxylation of *ortho*-substituted benzoic acids **42** (Scheme 27) [41]. This reaction only proceeds with *ortho*-substituted benzoic acids although they can have a range of functionalities, such as halogens, NO_2, alkoxides, and even unprotected phenols and amines, regardless of the presence of any functional group at positions other than the *ortho*-position of the benzoic acid. A proposed mechanism for the reaction involves conversion of the Ag(I) species to the silver carboxylate with benzoic acid **42**. After decarboxylation of the silver carboxylate, the silver arene intermediate gives corresponding arene **43** by protodemetallation with concomitant generation of a new silver carboxylate to turn over the catalytic cycle (Scheme 28).

Scheme 27. Ag-catalyzed decarboxylation of *ortho*-substituted benzoic acids.



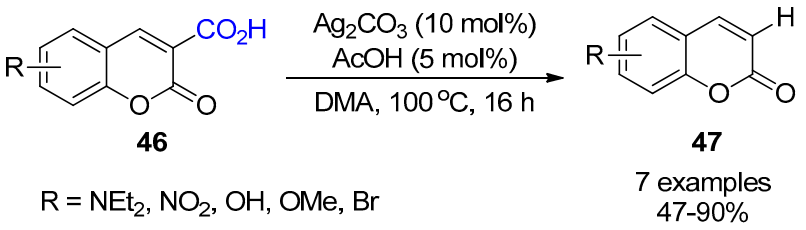
Scheme 28. Proposed mechanism for decarboxylation of *ortho*-substituted benzoic acids.

In the same year, the Larrosa group reported another Ag(I)-catalyzed protodecarboxylation of various heteroaromatic carboxylic acids **44** (Scheme 29) [42]. This reaction uses acetic acid as an additive. Not only α-heteroaromatic carboxylic acids but also *ortho*-substituted benzoic acids are converted to silver carboxylates by Ag(I), and the silver carboxylates then undergo decarboxylation. The details of the role of the heteroatoms in the decarboxylation are difficult to predict, but heteroatoms are expected to serve as activators in this reaction. Diacids were also subjected to these conditions, and they provided the corresponding monoacids with complete regioselectivity. In the case of heteroaromatic compounds, the reactivity of the carboxylic acid at the α-position is still controlled by the heteroatoms. In addition to the effect of the α-heteroatom, the conversion to the monoacid proceeds well even if an electron-withdrawing group is located at the *ortho*-position. Since both acids, 1,2-diacid and 1,4-diacid, underwent decarboxylation with high yields, the number of adjacent carboxylic acids seems to have no effect on the decarboxylation.



Scheme 29. Protodecarboxylation of heteroaromatic carboxylic acids.

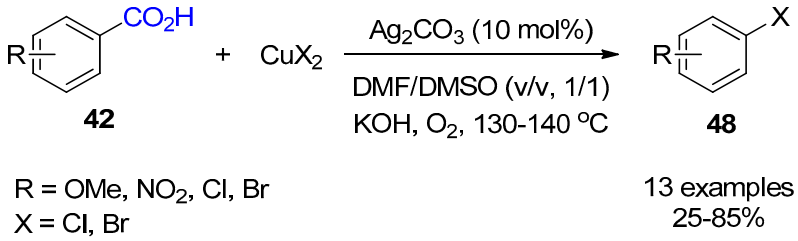
The Jafapour group reported a Ag(I)-catalyzed decarboxylation of heteroaromatic compounds (Scheme 30) [43]. In the case of coumarins, the decarboxylation is restricted to carboxylic acids containing α-heteroatoms. After tuning the solvent, even unactivated coumarin-3-carboxylic acids **46** produced corresponding decarboxylated products **47** under mild conditions with wide substrate compatibility.



Scheme 30. Ag-catalyzed protodecarboxylation of coumarin-3-carboxylic acid.

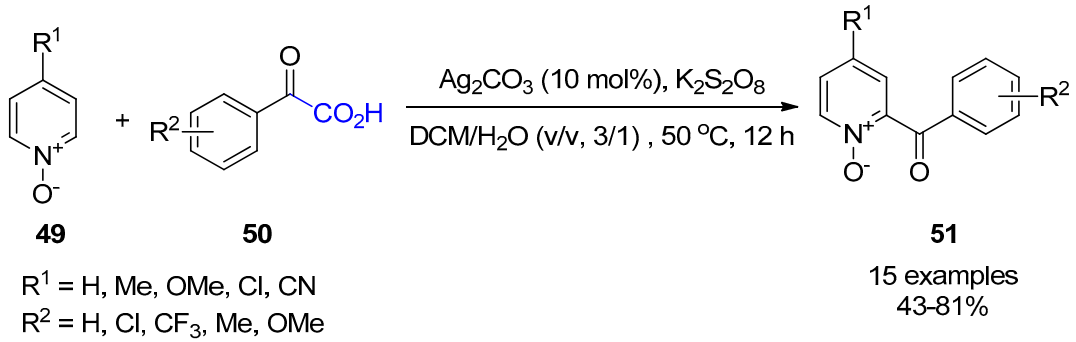
3.2. Decarboxylative Functionalization and Carboxylations

Aryl halides are useful synthetic intermediates and can be used for a variety of reactions [44]. In general, boron–halogen exchange reactions have attracted attention as a synthetic pathway for accessing aryl halides. Previous common decarboxylative halogenation reactions use very insoluble NaCl and LiCl as chloride sources. In 2010, the Wu group reported a Ag(I)-catalyzed decarboxylative halogenation of benzoic acids in the presence of Cu(II) halides to provide the corresponding aryl halides (Scheme 31) [45]. Cu(II) halides are inexpensive organometallic reagents and readily available halide sources with superior solubility in organic solvents.



Scheme 31. Ag-catalyzed decarboxylative halogenation of carboxylic acids.

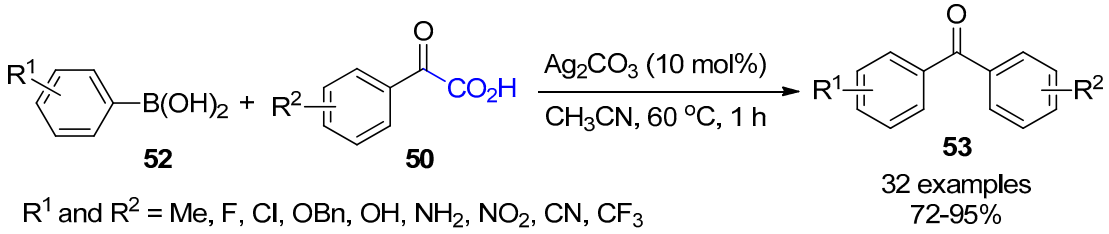
Decarboxylation can lead to changes in the functional groups on the starting material as well as the formation of new C−C bonds. Muthusubramanian and co-workers reported a Ag-catalyzed acylation of pyridine *N*-oxides **49** by α-oxocarboxylic acids **50** in 2014 (Scheme 32) [46]. Through this reaction, various aryl ketones can be synthesized by effectively promoting the acylation at the C-2 position of the pyridine. When this reaction was conducted in the presence of TEMPO, the acylated TEMPO adduct was formed, indicating that the reaction proceeds through an acyl radical intermediate. Based on this result, the reaction may start by generating a silver dicarboxylate intermediate, and then the acyl radical intermediate is generated by the release of CO_2 and a Ag(I) carboxylate. A new C−C bond between the acyl radical and pyridine *N*-oxide **49** was generated by a radical addition reaction, affording acylated pyridine *N*-oxide **51** as the product.



Scheme 32. Ag-catalyzed decarboxylative acylation of pyridine *N*-oxides.

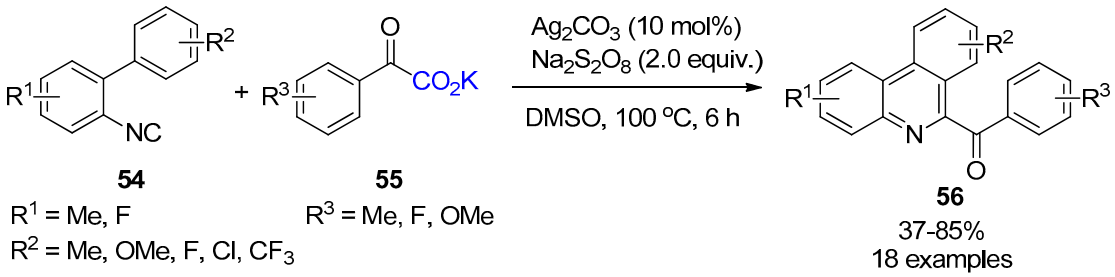
In 2014, Qi and co-workers reported Ag-catalyzed decarboxylative acylation of arylglyoxylic acids **50** with arylboronic acids **52** (Scheme 33) [47]. This Ag_2CO_3-catlayzed decarboxylation enables

the synthesis of ketones **53** with aromatic rings bearing various functional groups. The most useful feature of this reaction is not only the fact that the arylglyoxylic acid bears a carboxylic acid but also the decarboxylative acylation that occurs when a phenylboronic acid has a carboxylic acid. The reaction pathway may be initiated by a free radical because no product was generated in the presence of TEMPO. Acyl radicals can be prepared by decarboxylation of silver carboxylate, and subsequent radical transformation can provide cross-coupled diaryl ketone **53**.



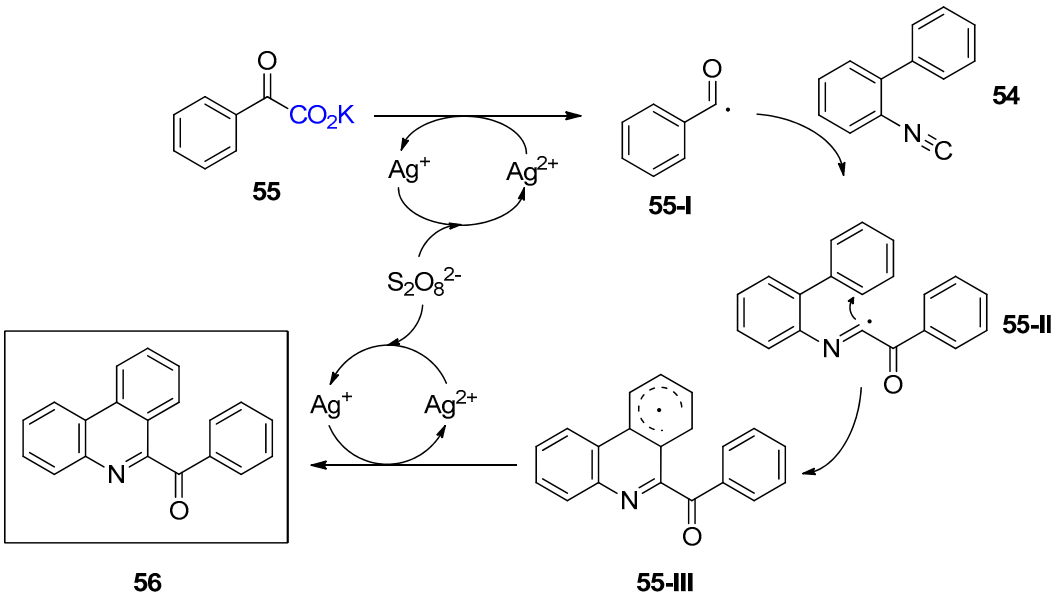
Scheme 33. Ag-catalyzed cross coupling of arylboronic acids with arylglyoxylic acids.

Among the various C1 insertion reactions, CO is the most common acceptor for generating new acyl radicals through carbonylation. Isocyanide is also a radical acceptor for imidoyl radical formation. In recent years, decarboxylations of carboxylic acids using transition metals have contributed significantly to the formation of various C–C bonds and C–heteroatom bonds [48]. The Lei group reported an Ag-mediated oxidative radical decarboxylation-cyclization of α-oxocarboxylates **55** and isocyanides **54** to give 6-acyl phenanthridines **56** (Scheme 34) [49]. In the proposed mechanism (Scheme 35), acyl radical **55-I** is formed by oxidative radical decarboxylation in the presence of Ag_2CO_3 as a catalyst. Then, radical addition to isocyanide **54** provided imidoyl radical **55-II**. The intramolecular cyclization of imidoyl radical **55-II** then gave cyclohexadienyl radical **55-III**, and SET from Ag(I) provides 6-acyl phenanthridine **56** as the product.

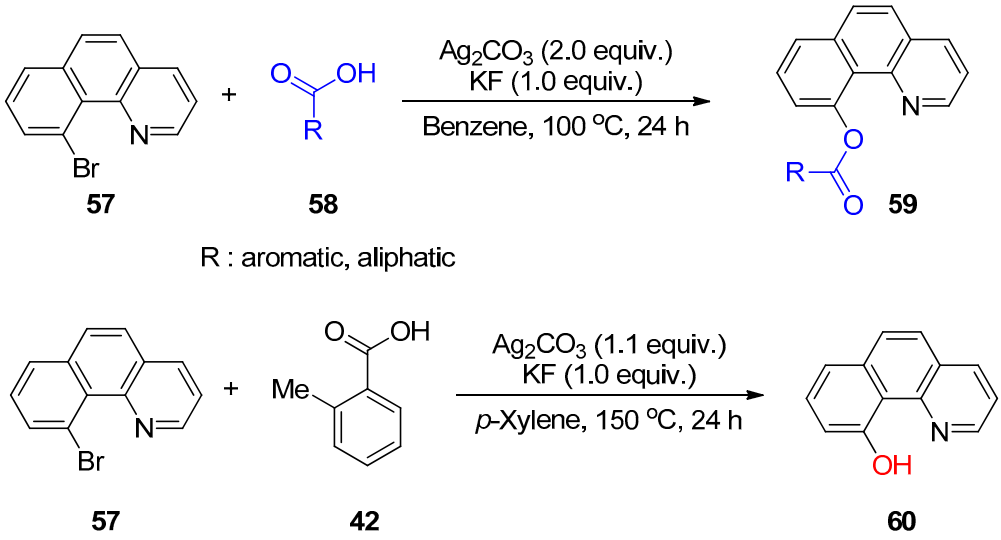


Scheme 34. Oxidative radical decarboxylation/cyclization of α-oxocarboxylates and isocyanides. Chem. Commun. 2014, 50, 2145–2147, doi:10.1039/c3cc49026b—Reproduced by permission of The Royal Society of Chemistry.

In 2016, the Kim group developed an Ag-mediated temperature-controlled acyloxylations and subsequent hydrolysis for hydroxylation (Scheme 36) [50]. At lower temperature (100 °C), various esters **59** were synthesized from 10-bromobenzo[h]quinoline **57**. Interestingly, at higher temperature (150 °C), ester products **59** were hydrolyzed to 10-hydroxybenzo[h]quinoline **60**. 2-Methylbenzoic acid showed the best conversion in this hydroxylation. The silver species activated the carboxylic acid through silver benzoate formation, and the two-step acyloxylation and hydrolysis were confirmed by NMR spectroscopy.



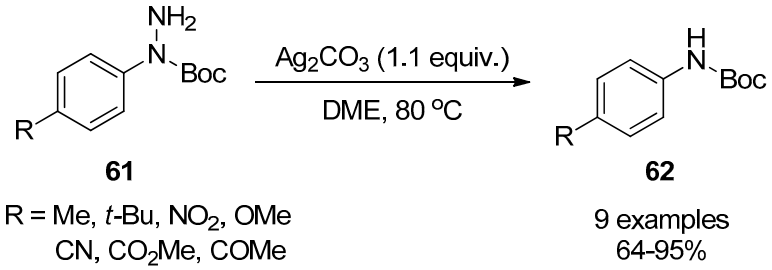
Scheme 35. Proposed mechanism of the Ag-catalyzed oxidative radical decarboxylation/cyclization. Chem. Commun. 2014, 50, 2145–2147, doi:10.1039/c3cc49026b—Reproduced by permission of The Royal Society of Chemistry.



Scheme 36. Temperature-controlled acyloxylation and hydroxylation of bromoarene.

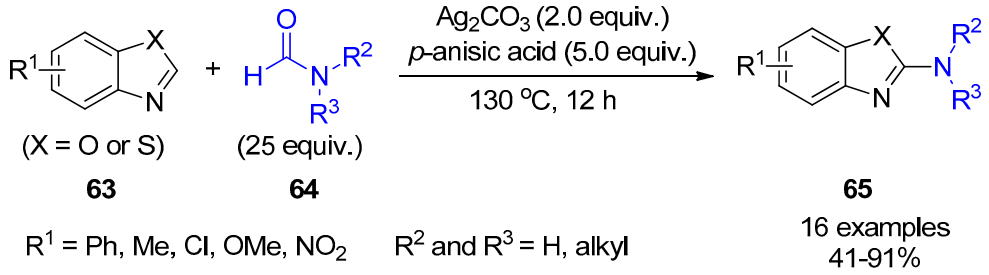
4. Miscellaneous

Leblanc's deamination of hydrazides is a useful reaction using Zn and acetic acid [51]. In general, hydrazides are converted into hydrazines instead of generating the corresponding amines from transition metal-catalyzed hydrogenolytic N–N bond cleavage [52]. In 2002, the Cho group reported a Ag(I)-mediated deamination of *N*-Boc aryl hydrazines **61** to afford *N*-Boc aryl amines **62** (Scheme 37) [53]. When an electron-donating group was present on the substrate, the corresponding products were obtained in high yields within relatively short reaction time (2 h). When an electron-withdrawing group was present on the substrate, the required reaction time increased to over 48 h (NO_2) or 72 h (CO_2Me) and the yields were relatively low.



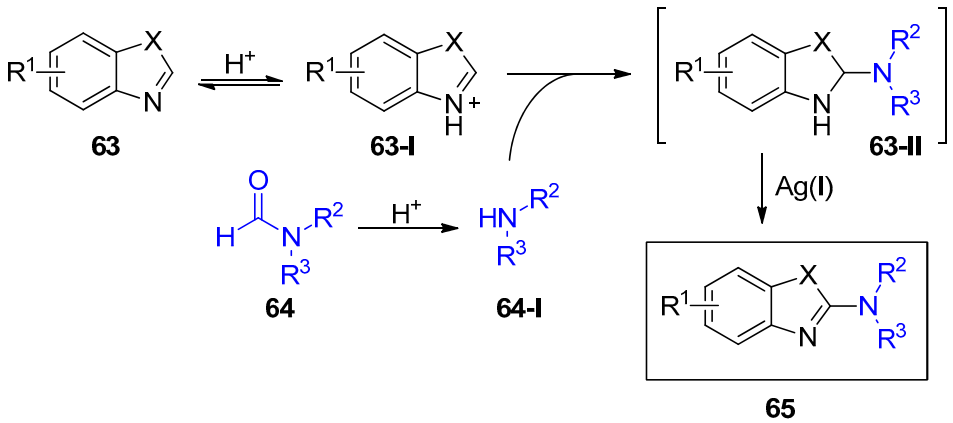
Scheme 37. Ag-mediated deamination of *N*-Boc aryl hydrazines.

The construction of C–N bonds in heteroaromatic compounds is important in the fields of biological, pharmaceutical, and materials science [54]. Although hydroamination [55] and oxidative amination [56], for the formation of C–N bonds, have been studied in great detail in recent decades, the direct installation of amino groups or their surrogates into aryl or alkyl C–H bonds is still challenging. In 2009, the Chang group reported a Ag-mediated amination of benzoxazoles **63** using formamides **64** or their parent amines (Scheme 38) [57]. The reaction gives 2-aminobenzoxazoles **65** with various functional groups by the regioselective formation of C–N bonds through the direct C(sp^2)–H functionalization of heteroarenes.



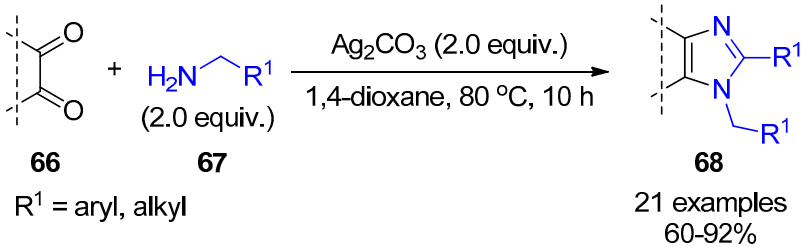
Scheme 38. Ag-mediated direct amination of benzoxazoles.

A possible reaction mechanism is shown in Scheme 39. First, the acid promotes the decarbonylation of formamide **64** to give corresponding secondary amine **64-I**. Secondary amine **64-I** reacts with protonated benzoxazole **63-I** to form 2-amino benzoxazoline intermediate **63-II**. Finally, Ag_2CO_3 facilitates rearomatization to provide 2-aminated benzoxazole **65**.



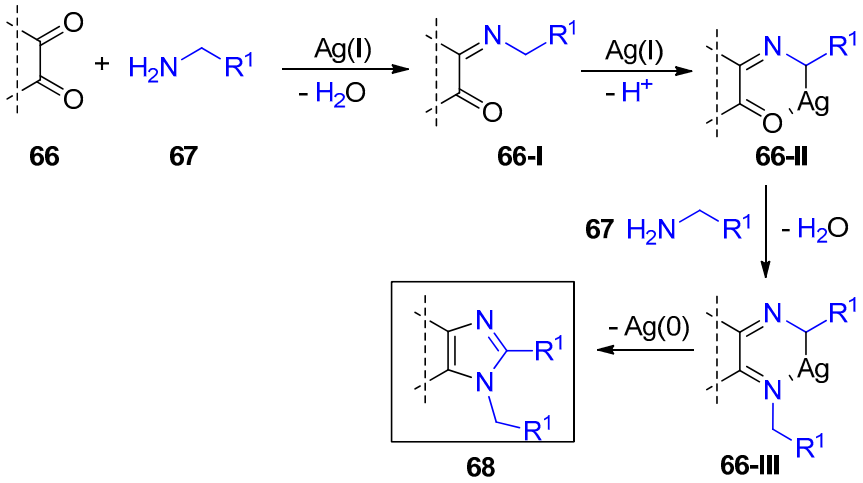
Scheme 39. Proposed mechanism for the Ag-mediated direct amination of benzoxazoles.

Mukhopadhyay reported a Ag(I)-mediated synthesis of diverse 1,2,4,5-tetrasubstituted imidazoles **68** via the tandem C_α(sp^3)–H bond functionalization of primary amines **67** and oxidative C–N cross-coupling reaction (Scheme 40) [58]. Although the reaction required stoichiometric Ag_2CO_3, the recycled silver reagent provided the product in good yield without any loss of activity.



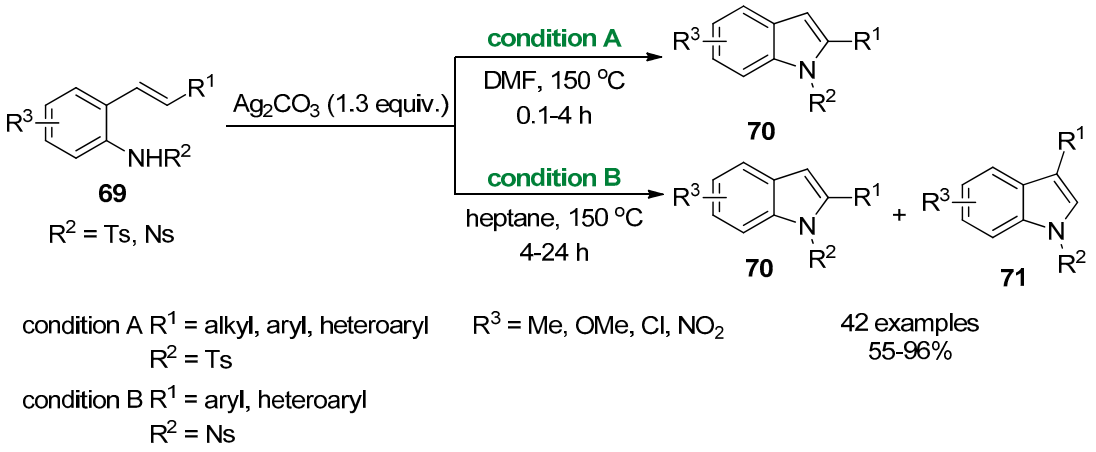
Scheme 40. Ag-mediated C–N coupling for the synthesis of imidazoles.

According to the proposed mechanism (Scheme 41), the reaction is initiated by the generation of imino ketone **66-I** from diketone **66** and primary amine **67**. Ag(I)-mediated C–H functionalization then gives intermediate **66-II**, and the subsequent addition of another equivalent of amine **67** provides diamine intermediate **66-III**. Finally, the silver-mediated oxidative cyclization of **66-III** gives imidazole product **68**.



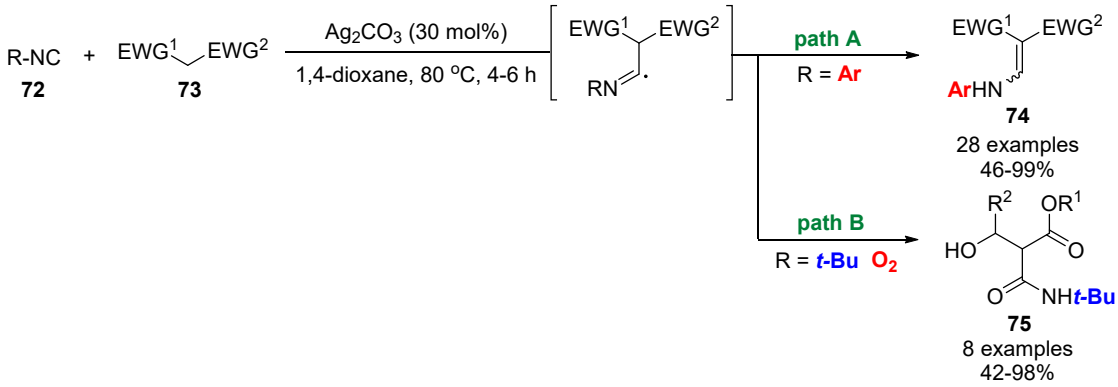
Scheme 41. Proposed mechanism for the Ag-mediated C-N coupling to afford imidazoles.

In 2015, the Youn group reported the silver(I)-mediated synthesis of diverse substituted indoles via the C–H amination of 2-alkenylanilines **69** (Scheme 42) [59]. Interestingly, the products are dependent on the reaction solvents. In DMF, indoles **70** with R^1 at the 2-position are selectively obtained; however, mixtures of 2- and 3-substituted indoles are observed when heptane is used as the solvent. To elucidate the reaction mechanism, the reaction was performed in the presence of TEMPO and BHT (butylated hydroxytoluene). In the absence of radical scavengers, the reaction was completed in 30 min, but it took 3 h for the reaction to reach completion with 1.0 equiv. of TEMPO. With 1.0 equivalent of BHT, 80% of the starting material remained unreacted after 24 h. Based on the results of the reactions with radical scavengers, the reaction should proceed through a radical pathway. According to the proposed mechanism, a nitrogen radical cation is generated from substrate **69** with Ag(I) salt by a SET; then, the nitrogen radical undergoes an intramolecular electrophilic addition to the alkene to provide a benzylic radical with the loss of a proton. A benzylic carbocation is generated by a SET from the benzylic radical to Ag(I), and subsequent deprotonation affords desired indole product **70**.



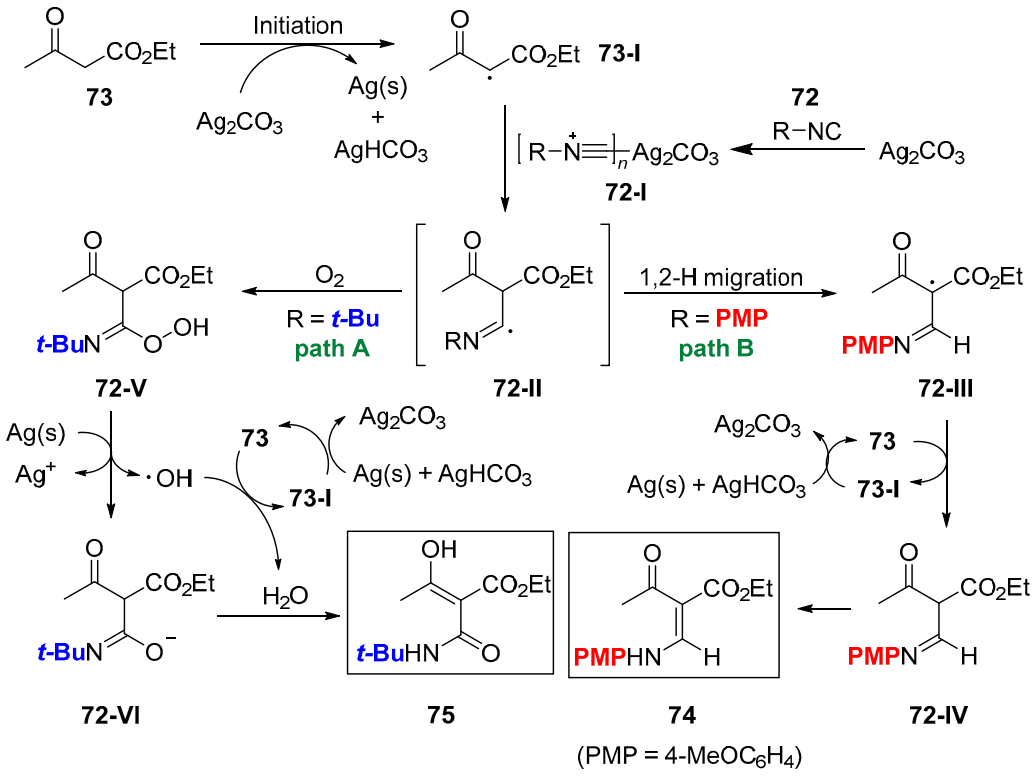
Scheme 42. Ag-mediated oxidative C–H amination of 2-alkenylanilines.

The isocyanide group has the similar reactivity as carbenes, making them useful reagents for generating new C–C bonds, and they are used as building blocks in organic synthesis [60]. In addition, isocyanides have reactivities similar to multicomponent reactions, and they are often used for C–H functionalization reactions. In 2015, the Bi group reported a silver-catalyzed cross coupling of isocyanides **72** and active methylene compounds **73** to access various β-aminoenones **74** and tricarbonylmethanes **75** by a radical process (Scheme 43) [61].



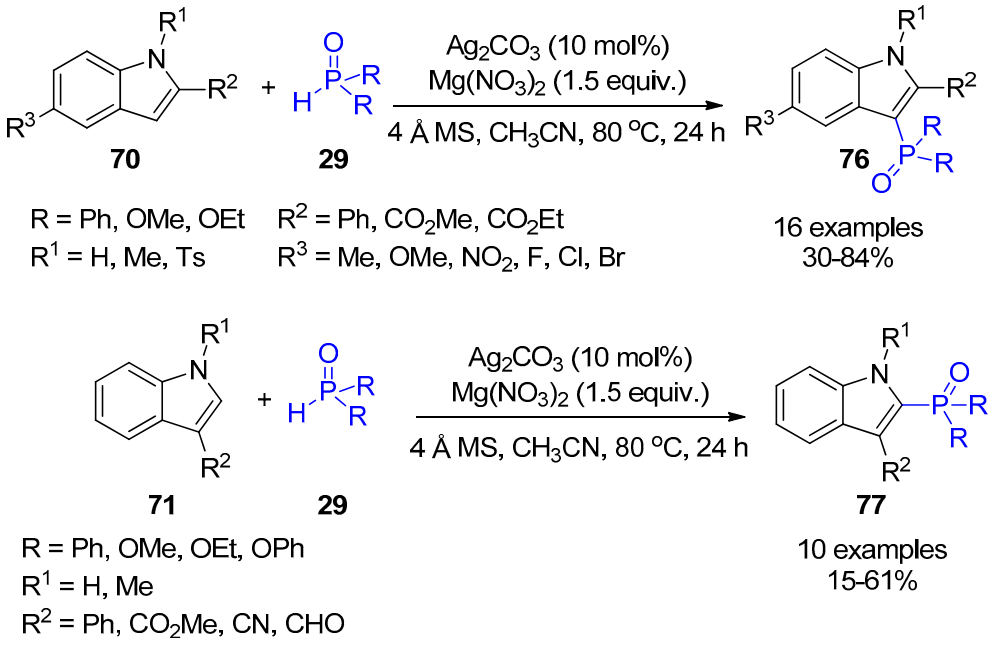
Scheme 43. Ag-catalyzed cross coupling of isocyanides and activated methylene compounds.

To determine the reaction mechanism, both isotope-labeling studies and control experiments with radical scavengers were performed, and the reaction did not proceed in the presence of radical scavengers. Based on the deuterium-labeling experiments, hydrogen atom transfer occurred from the α-hydrogen of methylene compound **72** to the hydrogen on the olefin of product **74**. In the ^{18}O-labeling experiments, $^{18}O_2$ provided a high degree of ^{18}O-incorporated product **75**, but $H_2{}^{18}O$ did not produce any ^{18}O-incorporated **75**. Based on these experimental results, a plausible mechanism was proposed as described in Scheme 44. Ag_2CO_3 abstracts a proton from **73** due to its basicity, and subsequent oxidation by Ag(I) generates radical intermediate **73-I**. Ag_2CO_3 has a dual role as a base and a one-electron oxidant. At the same time, Ag_2CO_3 coordinates to isocyanide **72** to form **72-I**. The coupling reaction between radical **73-I** and silver complex **72-I** produces imidoyl radical **72-II**. With an aromatic isocyanide, imidoyl radical **72-II** can provide imine intermediate **72-IV** by abstracting a H atom from the generated $AgHCO_3$ during the one-electron oxidation or by a 1,2-H migration to form stable tricarbonylmethenyl radical **72-III** followed by abstraction of an H atom from $AgHCO_3$. Imine **72-IV** gives β-aminoenone **74** by tautomerization. With *tert*-butyl isocyanide, radical **72-II** is converted to hydroperoxide **72-V** by oxygenation. Hydroperoxide **72-V** is reduced by Ag(s) to form oxyanion intermediate **72-VI**, and the protonation gives tricarbonylmethane **75** as the product.



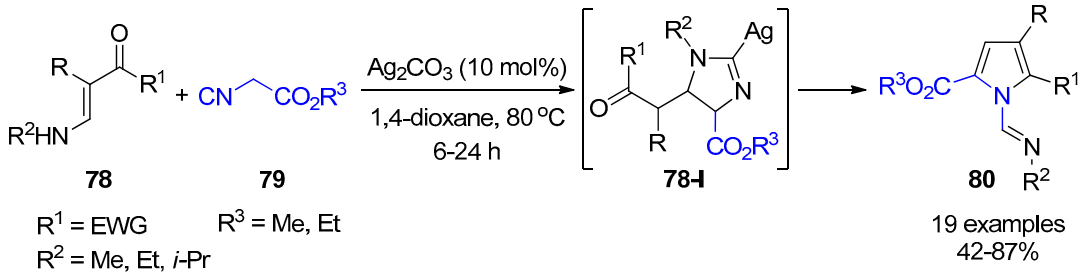
Scheme 44. Proposed mechanism for Ag-catalyzed cross-couplings with isocyanide.

Zou and co-workers reported a silver-catalyzed direct C(sp^2)–H phosphorylation of indoles in the presence of $Mg(NO_3)_2$ leading to phosphoindoles (Scheme 45) [62]. Ag_2CO_3 is used as an oxidant and $Mg(NO_3)_2$ is used as an additive to form a new C–P bond. The reaction occurs by the addition of the electrophilic phosphorous radical to the available C(sp^2)–H position of the indole, followed by a SET by Ag(I) and aromatization by deprotonation to give the phosphoindole product.



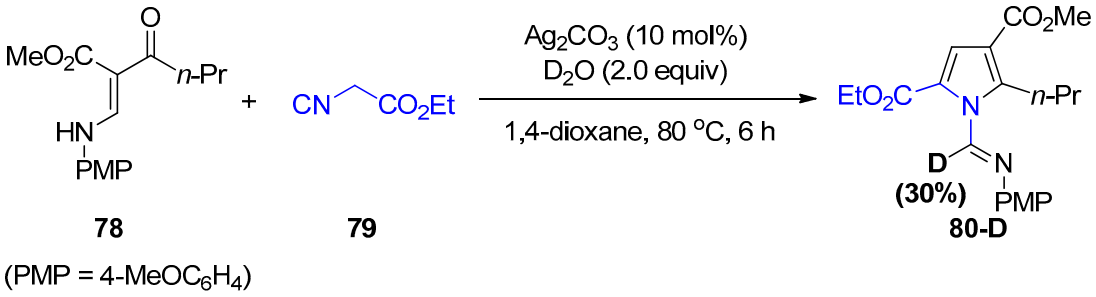
Scheme 45. Ag-catalyzed direct Csp_2–H phosphorylation of 2- and 3-substituted indoles.

Recently, the Bi group reported the Ag(I)-catalyzed synthesis of 1,2,4,5-tetrasubstituted pyrroles **80** via the cascade reaction of β-enaminones **78** and isocyanoacetates **79** (Scheme 46) [63]. β-Enaminones are used as building blocks in a variety of reactions and are easily obtained. One of the key features of β-enaminones is their tautomeric equilibrium with β-ketoimines. As β-ketoimines are a minor product, imines are present in this equilibrium system.



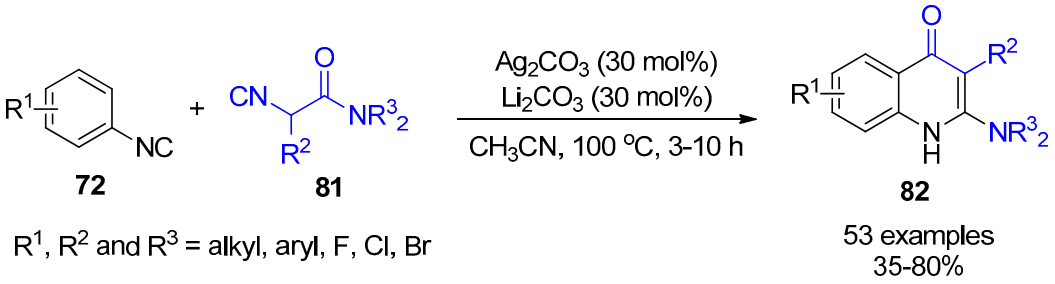
Scheme 46. Construction of pyrroles via the cascade reaction of β-enaminones and isocyanoacetates.

To investigate the reaction pathway, a deuterium-labeling experiment was performed using 2.0 equiv. of D_2O. As shown in Scheme 47, deuterium-labeled pyrrole **80-D** was obtained, and the reaction should involve a proton transfer between the imine-metal complex and D_2O. Based on this experimental result, the reaction may be initiated by the deprotonation of isocyanoacetate **79** by basic Ag_2CO_3 to form an α-metalated isocyanoacetate. Then, [3+2] dipolar cycloaddition with β-ketoimine follows, and the β-ketoimine was derived from β-enaminone **78**. The retro-hetero-Michael addition ring-opens the 2-imidazoline (**78-I**) to give the imidamide intermediate, and then a cascade involving nucleophilic addition, proton transfer, and dehydration provides highly substituted pyrrole **80** as the product.



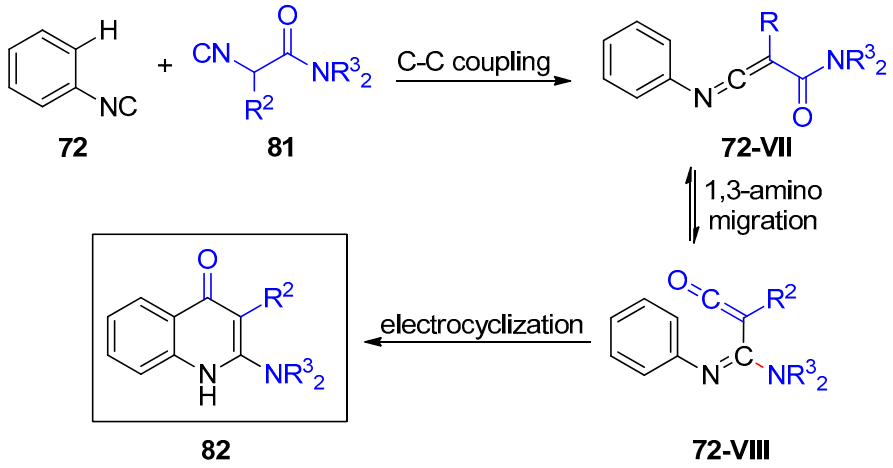
Scheme 47. Mechanistic investigation of the Ag-mediated pyrrole synthesis. Adapted with permission from Org. Lett. 2017, 19, 1346–1349, doi:10.1021/acs.orglett.7b00201. Copyright (2019) American Chemical Society.

In 2017, Xu and co-workers developed a silver-catalyzed chemoselective [4+2] annulation of aryl and heteroaryl isocyanides **72** with α-substituted isocyanoacetamides **81** to afford pyridone-fused carbo- and heterocycles **82** (Scheme 48) [64]. To determine the reaction mechanism, the reaction was performed with a ^{13}C labeled isocyanide group in **72**, and the NMR spectrum showed the benzo[*h*]quinolone product **82** with ^{13}C at the 2-position. This result indicated that an α-amidoketenimine is a likely reaction intermediate.



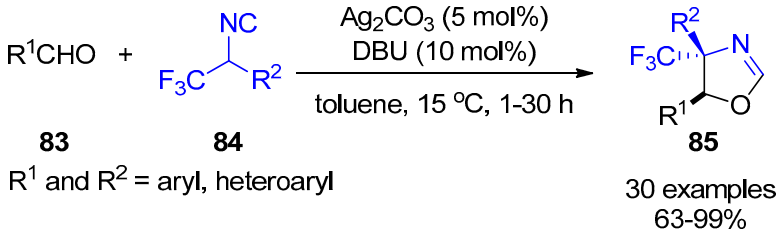
Scheme 48. Ag-catalyzed cycloaddition reactions of isocyanoacetamides.

Based on the ^{13}C-labeling experiments, a mechanism was proposed as described in Scheme 49. Ag_2CO_3 abstracts a proton from isocyanoactamide **81** and coordinates to the isocyanide moiety. Another equivalent of Ag_2CO_3 coordinates to isocyanide **72**, and the subsequent C–C coupling occurs via a nucleophilic attack and elimination to generate amidoketenimine **72-VII**. The rearrangement of α-amidoketenimine **72-VII** to α-imidoylketene **72-VIII** occurs via a 1,3-amino migration. Subsequent 6π electrocyclization and 1,3-proton shift convert **72-VIII** to quinolone **82**. In this reaction, a catalytic amount of Li_2CO_3 was used as an additive to promote the regeneration of the Ag_2CO_3 catalyst.



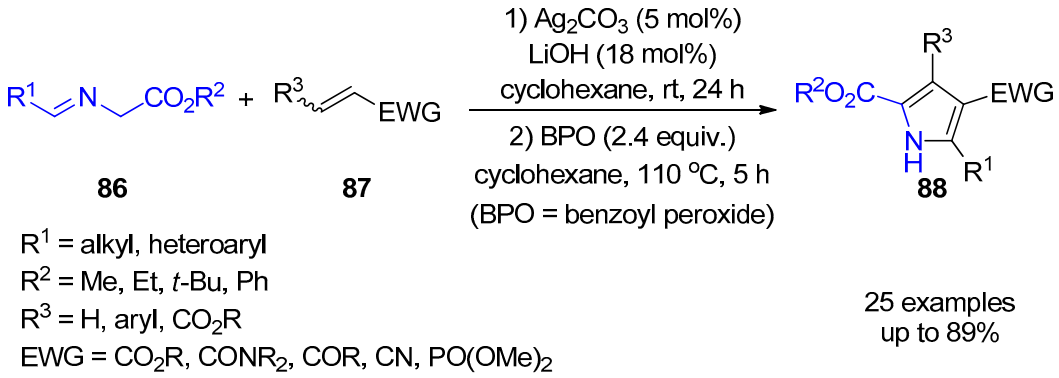
Scheme 49. Proposed mechanism for the cycloaddition of isocyanoacetamide.

In 2017, the Xu group developed a formal [3+2] cycloaddition of α-trifluoromethylated methyl isocyanides **84** and aldehydes **83** for the silver-catalyzed divergent synthesis of trifluoromethylated heterocycles (Scheme 50) [65]. With imines or acrylonitriles instead of aldehyde **83**, the reaction produces the corresponding imidazoles or pyrrolines as the major products. Ag(I) coordinates to isocyanide **84**, then DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) abstracts a proton to form the carbanion nucleophile. A formal [3+2] cycloaddition, which consists of the nucleophilic addition of the carbanion from the isocyanide to aldehyde **83** and cyclization, affords an oxazoline silver complex; then, protodemetallation gives oxazoline **85**.



Scheme 50. Ag-catalyzed cycloaddition of α-trifluoromethylated methyl isocyanides.

In 2017, Wang and co-workers reported the synthesis of pyrroles via a tandem Ag-catalyzed 1,3-dipolar cycloaddition and BPO (benzoyl peroxide)-mediated oxidative dehydrogenative aromatization (Scheme 51) [66]. Ag_2CO_3 facilitates the [3+2] cycloaddition of the 1,3-dipolar intermediate generated from compound **86** by deprotonation of the α-position with alkene **87** to form a tetrasubstituted pyrrolidine. Peroxide abstracts a H atom from the α-position of the pyrrolidine, then two oxidations, which each consists of a SET and tautomerization, provide highly substituted pyrrole **88**.



Scheme 51. Synthesis of pyrrole via a Ag-catalyzed tandem 1,3-dipolar cycloaddition/oxidative dehydrogenative aromatization reaction. Adapted with permission from J. Org. Chem. 2017, 82, 4194-4202, doi:10.1021/acs.joc.7b00180. Copyright (2019) American Chemical Society.

5. Conclusions

In this review, we summarized the recent studies and developments in Ag_2CO_3-catalyzed/mediated organic transformations. Silver carbonates were employed as either external bases for activating acidic molecules or an external oxidant for turning over catalytic cycles. Notably, heteroaromatic compounds can be elegantly synthesized using silver carbonate to combine heteroatom-containing fragments and more than two carbon skeletons through alkyne activation. At the same time, silver carboxylate can be generated from the simple reaction between silver carbonates and various carboxylic acids. The following cross-couplings and decarboxylative reactions were investigated.

Despite the substantial progress and important advances described in these reports, there is still significant room for improvement at the present level. For example, alkene-related substrates cannot be efficiently activated by silver carbonate. The utilization of an alkene could expand the possible synthetic targets of these silver carbonate-catalyzed reactions. Further detailed studies on the transmetallation from silver to other transition/main group metals should be conducted. In addition, detailed mechanism studies, including the structural determination of various intermediates should be performed. We hope that this review will inspire the development of various silver carbonate-catalyzed organic reactions and other related methodologies.

Author Contributions: K.Y., D.G.J., and H.-E.L. contributed equally to this work. K.Y., D.G.J. and M.K. designed and conceptualized the original project. K.Y., D.G.J., and H.J.K. categorized target reactions. H.-E.L. and C.K. built the mechanism discussion. All authors wrote the manuscript together.

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