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Recent Applications of α-Carbonyl Sulfoxonium Ylides in Rhodium- and Iridium-Catalyzed C–H Functionalizations

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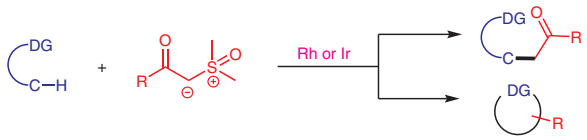

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Abstract Sulfoxonium ylides are a special type of sulfur ylides that serve as new C1 or C2 synthons recently developed for use in C–H functionalization to access acylmethylated or cyclized compounds through the formation of metal carbene species. Many excellent works have reported the syntheses of various useful skeletons from these versatile synthons. These developments have not previously been completely investigated or reviewed. In this review, we summarize recent advances in the use of α-carbonyl sulfoxonium ylides in C–H functionalizations, including *ortho*-C–H acylmethylation reactions and *ortho*-C–H activation/cyclization reactions.

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Key words sulfur ylides, C–H functionalization, acylmethylation, cyclization, metal carbenes

1 Introduction

Sulfur ylides can be classified into four categories according to their chemical structure (Figure 1): sulfur ylides (**I**), sulfoxonium ylides (**II**), sulfonyl ylides (**III**), and sulfenyl ylide (**IV**). Alkylation or acylation of sulfur ylides (**I**) or sulfoxonium ylide (**II**) increases their stability and practicability, permitting them to be widely used in epoxidations, aziridinations, cyclopropanations, rearrangements, and olefinations. A number of elegant reports and reviews by Aggarwal,[1] Tang,[2] Ye,[3] Xiao,[4] and their respective co-workers summarize the impressive successes achieved during different periods.

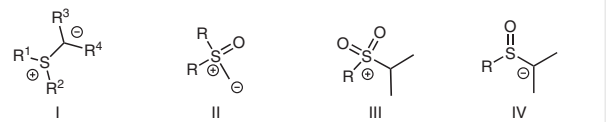
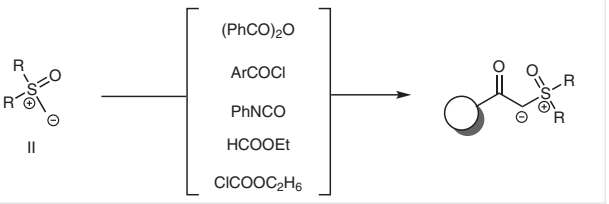


Figure 1 Four types of sulfur ylide

The diversification of sulfoxonium ylides **II** has continually broadened the domain of ylide chemistry. In particular, α-carbonyl sulfoxonium ylides, derived from the reaction of sulfoxonium ylides **II** with acid anhydrides, acyl chlorides, isocyanates, ethyl formate, or methyl chloroformate, has opened new fields in transition-metal-catalyzed C–H functionalization (Scheme 1).



Scheme 1 Synthesis of α-carbonyl sulfoxonium ylides

Recent decades have witnessed great achievements in transition-metal-catalyzed *ortho*-C–H functionalization reactions[5] leading to the efficient and straightforward construction of C–C bonds, a process increasingly viewed as one of the most significant tools available to organic chemists. Meanwhile, numerous synthons have been used in C–H activation reactions; typically, these include benzenes, olefin derivatives, diazo compounds, halides, and boric acid re-

agents, as discussed in reviews by Song and Li[5c] and by Glorius and co-workers.[5d] However, sulfoxonium ylides, which were developed to access carbo- and heterocyclic compounds via metal carbene species, have not been thoroughly investigated and reviewed to date.

Here, we provide an overview of recent achievements in rhodium- and iridium-catalyzed cross-coupling reactions of α-carbonyl sulfoxonium ylides, including *ortho*-C–H acylmethylation reactions and sequential *ortho*-C–H activation/cyclization reactions in one pot.

2 *Ortho*-C–H Acylmethylation Reactions

Since 2017, the chemistry of α-carbonyl sulfoxonium ylides has boomed, following the pioneering work of Aïssa and co-workers on rhodium-catalyzed cross-coupling reactions of sulfoxonium ylides with C(sp^2)–H bonds of arenes or heteroarenes.[6] The $[Cp^*RhCl_2]_2$-catalyzed *ortho*-C–H acylmethylation of 2-phenylpyridine proceeds in moderate to excellent yields. Notably, either 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) or NaOAc can play an essential role in efficient conversion into products.

Biographical Sketches

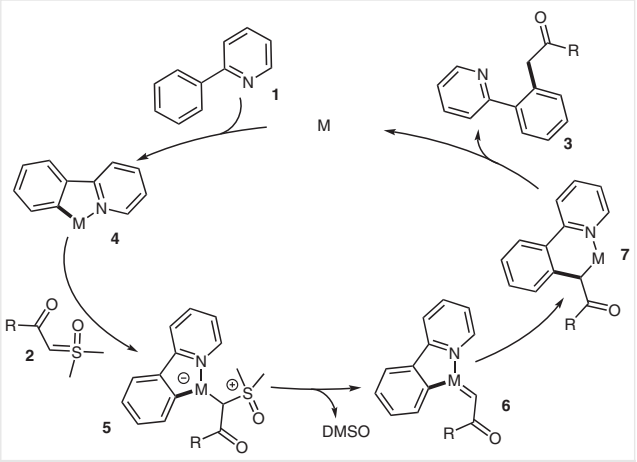
Xiaopeng Wu was born in Jiangsu, P. R. of China, in 1993. He received his B.S. from Changzhou University in 2015. Since then he has been pursuing his master's degree at Changzhou University under the supervision of Professor Cheng. His research focuses mainly on transition-metal-catalyzed C–H functionalization.

Song Sun was born in Jiangsu, P. R. of China in 1985. He received his Ph.D. (2013) from Suzhou University under the supervision of Professor Yingming Yao. In 2013, he joined Changzhou University. His research focuses on carbon dioxide fixation, transition-metal or radical C–H functionalization, and multicomponent reactions.

Jin-Tao Yu was born in Shandong, P. R. of China in 1984. She received her Ph.D. (2012) from the Institute of Chemistry of the Chinese Academy of Sciences under the supervision of Professors Zhi-Tang Huang and Qi-Yu Zheng. In 2012, she joined Professor Jiang Cheng's group at Changzhou University. She was a visiting scientist at Heidelberg University with Professor A. Stephen K. Hashmi from July, 2015 to January 2016. Her current research focuses on cyanation and radical C–H functionalization.

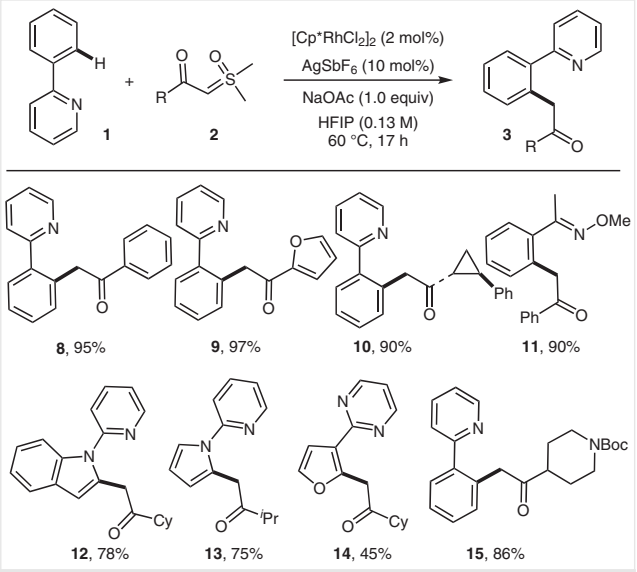
Jiang Cheng was born in Zhejiang, P. R. of China in 1974. He received his B.S. (1994), M.S. (2001), and Ph.D. (2004) from Nanjing University. In 2004, he joined Wenzhou University and was promoted to professor in 2010. In 2011, he moved to Changzhou University. His research focuses on carbon dioxide fixation, cyanation reactions, transition-metal or radical C–H functionalization, and multicomponent reactions.

The mechanism of this reaction has been elucidated by means of deuterium-labelling experiments and X-ray crystallography. The reaction is triggered by insertion of rhodium(III) into 2-phenylpyridine (**1**), leading to the metallized intermediate **4**, which then produces a carbon–metal bond through insertion of the ylide **2** (Scheme 2). After α-elimination of DMSO, intermediate **5** is transformed into a carbene species **6**, which then generates a six-membered-ring intermediate **7** by a 1,1-aryl shift process. Finally, protodemetallation of intermediate **7** delivers the desired cross-coupling product **3**.



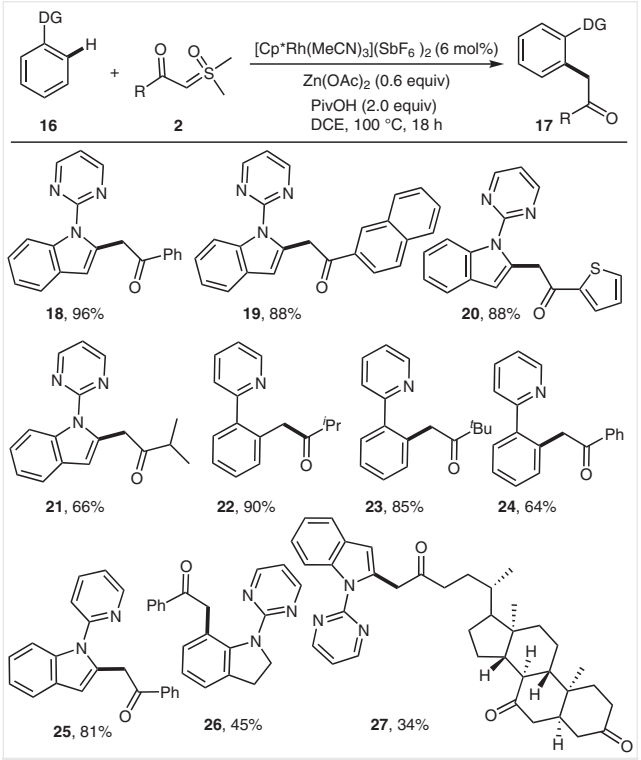
Scheme 2 Tentative mechanism for C–H cross-coupling with α-carbonyl sulfoxonium ylides

The practicability of the reaction was increased by its application to heterocyclic substrates such as indole, furan, or pyrrole with pyridinyl, pyrazolyl, or pyrazinyl directing groups (Scheme 3). Notably, alkyl, aryl, and heterocyclic α-carbonyl sulfoxonium ylides all performed well. Undoubtedly, this provides a new and efficient methodology for *ortho*-C–H acylmethylation.



Scheme 3 Aïssa's *ortho*-C–H acylmethylation

At almost the same time, similar work on C–H activation by sulfoxonium ylide was reported by Li's group.[7] In contrast with Aïssa's work, this reaction was carried out under acidic conditions in which $[Cp^*Rh(MeCN)_3](SbF_6)_2$ exhibited a high reactivity in the presence of 0.6 equivalents of $Zn(OAc)_2$ as an additive in 1,2-dichloroethane (Scheme 4). Gratifyingly, this *ortho*-C-H acylmethylation strategy is not only applicable to the benzene ring, but also to the C(2)–H bond of indole and the C(7)–H bond of indoline. Furthermore, α-carbonyl sulfoxonium ylides containing alkyl, aryl, heterocyclic, or even complex substituent groups, universally worked well in this transformation.



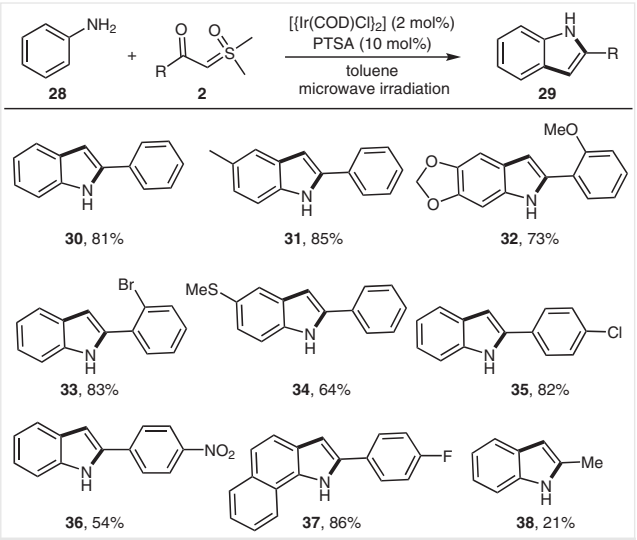
Scheme 4 Li's *ortho*-C–H acylmethylation

3 *Ortho*-C–H Activation/Cyclization Reactions

3.1 *Ortho*-C–H Activation/Cyclization of Anilines and Enamines

Indole derivatives are widely distributed in nature.[8] Moreover, the indole ring is of interest in fragrance chemistry, pesticide chemistry, and dyestuff chemistry.[9] As a result, numerous methods for the construction of indole scaffolds by C–H activation have been developed.[10,11] In 2017, Hopmann[12] reported an Ir(III)-catalyzed regioselectively C–H functionalization of free anilines by sulfoxonium ylides

and subsequent cyclization to access 2-arylindoles **29** in moderate to good yields (Scheme 5). The reaction was carried out by microwave irradiation of the aniline (2.0 equiv) with ylide **2** (1.0 equiv) in the presence of [{Ir(cod)Cl}$_2$] (10 mol%) in toluene at 140 °C. Interestingly, substrates containing halogen atoms or electron-donating groups on the aniline ring afforded only the corresponding N-alkylated anilines instead of indoles.



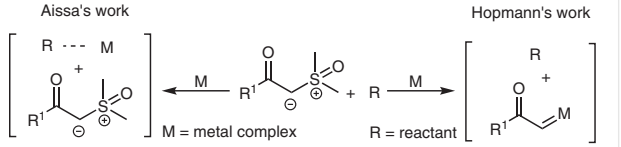
Scheme 5 Reaction of sulfoxonium ylides with free aromatic amines to give indoles

The mechanism of this reaction is unlike that for Aïssa's reaction described above (Scheme 6). The iridium–carbene species **39** is produced by the reaction of iridium with the sulfoxonium ylide (Scheme 7). The acylmethylation intermediate **41** transforms into **42**, which then give **43** through a simple Friedel–Crafts reaction. Intermediate **46** undergoes dehydration in the presence of 4-toluenesulfonic acid to complete the cyclization process.

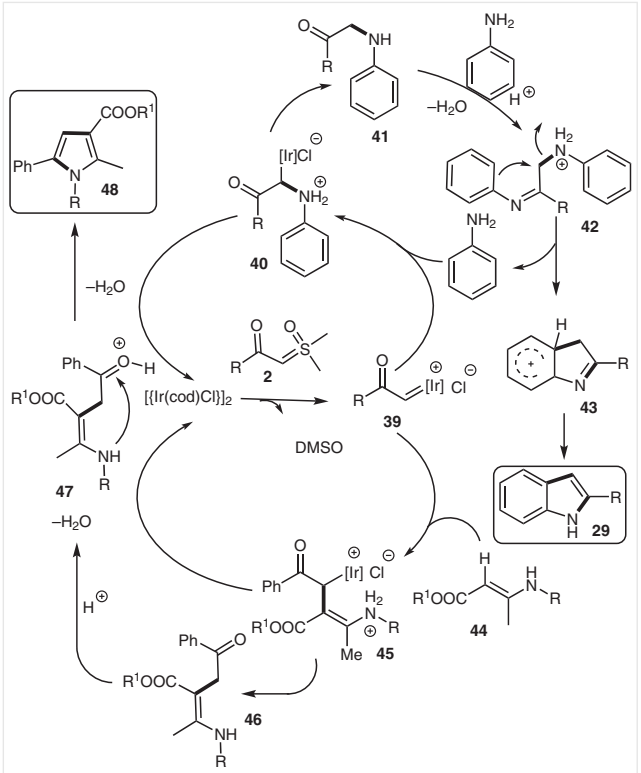
Hopmann's metal carbenoid C–H functionalization strategy has been successfully applied to access pyrroles **50**, including atorvastatin **55**, by the reaction of sulfoxonium ylides **2** with β-enamino esters **49** (Scheme 8).

3.2 *Ortho*-C–H Activation/Cyclization of Azobenzenes

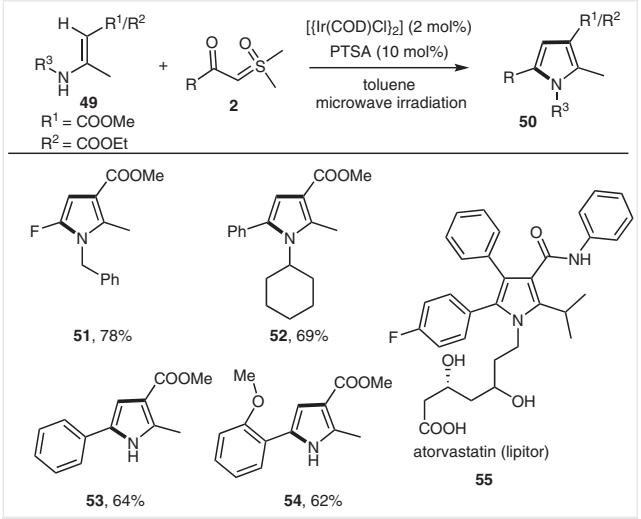
In 2018, Kim[13] and Cheng[14] and their respective coworkers successively developed Rh(III)-catalyzed [4+1] annulation reactions of azobenzenes **56** with sulfoxonium ylides to give 3-acyl-(2*H*)-indazoles **57** (Scheme 9). In these studies, a combination of [Cp*RhCl$_2$]$_2$ with AgSbF$_6$ showed excellent performance in *ortho*-C–H acylmethylations of azobenzenes. Copper salts as oxidants made an important contribution to the cyclization of the intermediate to give the final product. In Kim's work, the substrates were con-



Scheme 6 Carbene routes to α-carbonyl sulfoxonium ylides

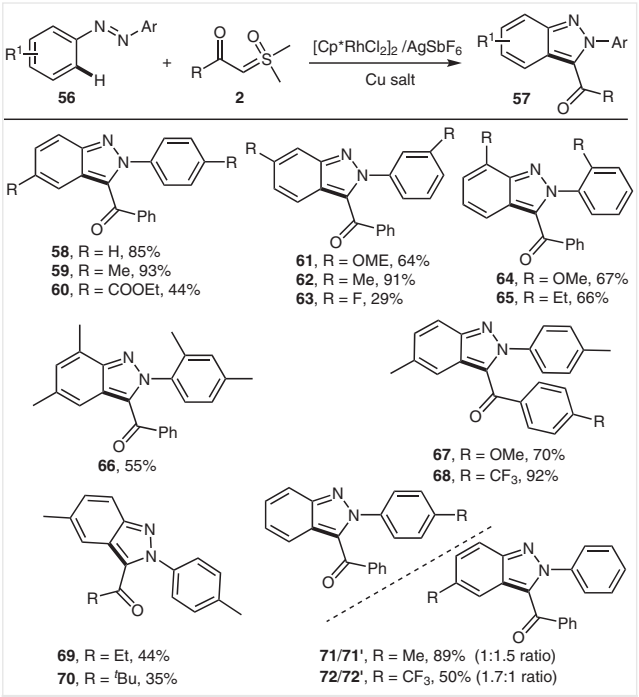


Scheme 7 Proposed mechanism involving an iridium carbene

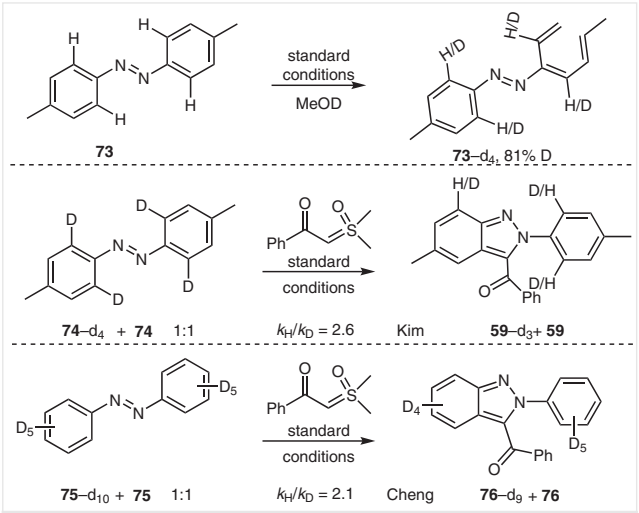


Scheme 8 Reaction of ylides with enamines

fined to symmetrical azobenzenes; in this reaction, substrates with electron-donating groups on the benzene ring showed obvious advantages over those containing electron-withdrawing groups. The reactions of asymmetric azobenzene substrates resulted in mixed products. Moreover, in addition to aryl-substituted sulfoxonium ylides, alkyl-substituted analogues also participated smoothly in the annulation process.



Scheme 9 *Ortho*-C–H activation/cyclization of azobenzenes

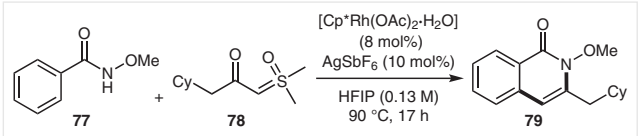


Scheme 10 Deuterium-labeling and KIE experiments with azobenzenes

Deuterium-labeling experiments showed deuterium incorporation (81%) at each of the *ortho*-positions of the azobenzene **73**, and kinetic-isotope-effect (KIE) studies were showed a KIE value of 2.6 for the azobenzene **74** (Scheme 10), indicating that the C–H bond-cleavage process might be the rate-limiting step.

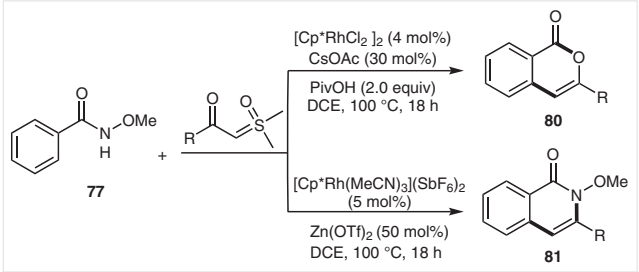
3.3 *Ortho*-C–H Activation/Cyclization of N-Methoxybenzamide

N-Methoxybenzamide, a common synthetic fragment, has been widely applied in syntheses of heterocyclic compounds through C–H functionalization.[15] In 2017, Aïssa and co-workers reported a convenient synthesis of valuable heterocycles, such as the 3-substituted 2-methoxyisoquinolin-1(2*H*)-one **79** (Scheme 11), in their remarkable work on Rh(III)-catalyzed C–H acylmethylation of arenes.[6]



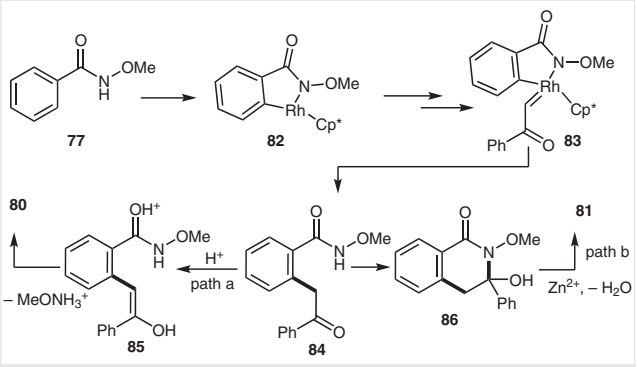
Scheme 11 *Ortho*-C–H activation/cyclization of *N*-methoxybenzamide by Aïssa

In 2018, Li[16] reported Rh(III)-catalyzed chemodivergent annulations of *N*-methoxybenzamide (**77**) with sulfoxonium ylides to give the isocoumarins **80** or the isoquinolinones **81** under acidic conditions (Scheme 12).



Scheme 12 *Ortho*-C–H activation/cyclization of *N*-methoxybenzamide by Li

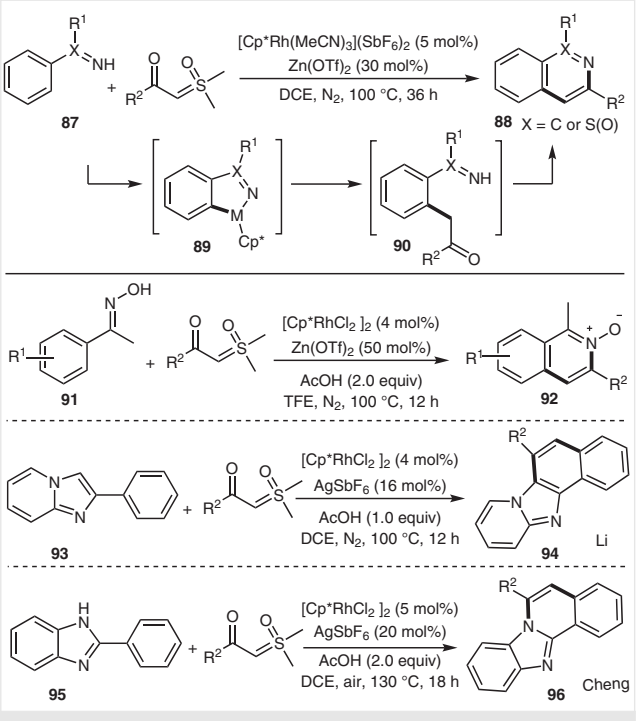
Both reactions involve the coordination of Rh(III) with *N*-methoxybenzamide (**77**) to form a carbene species **83**, which is then converted into a rhodacycle, which releases the rhodium catalyst to form an *ortho*-acylmethyl intermediate **84** (Scheme 13). The additives promote a further transformation that is the key step in this process. In fact, PivOH activates the amide carbonyl group toward attack by oxygen, leading to the isocoumarin **80** with the elimination of $MeONH_3^+$. With the Lewis acid $Zn(OTf)_2$ as additive and $[RhCp^*(MeCN)_3](SbF_6)_2$ as the catalyst, the isoquinolin-1(2*H*)-ones **81** become the major products.



Scheme 13 Acid-controlled *ortho*-C–H acylmethyl/cyclization process

3.4 *Ortho*-C–H Activation/Cyclization of Imines

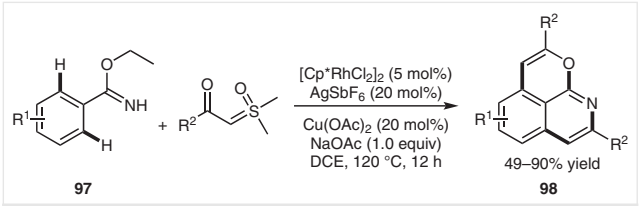
The imide group, a well-known directing group due to its strong ability to coordinate with transition metals, participates in many [4+1] and [4+2] C–H activation/cyclization reactions in the presence of common C2 synthons, such as alkynes,[17] diazo compounds,[18] 1,4,2-dioxazol-5-one,[19] or alkenes.[20] Sulfoxonium ylide have the potential to act as versatile and general-purpose C2 synthons in C–H functionalization and cyclization reactions to give heterocycles. Such a reaction was reported in 2018 by Li and co-workers,[21] who obtained a range of six-membered nitrogen heterocycles through the Rh(III)-catalyzed C–H activation of sulfoximines, *N*-aryl- or *N*-alkylbenzamidines, or benzophenone NH imines (Scheme 14).



Scheme 14 *Ortho*-C–H activation/cyclization of imines

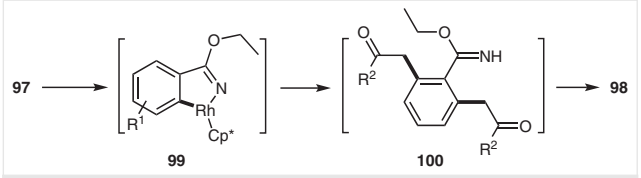
This strategy has been applied in syntheses of benzothiazines, isoquinolines, and isoquinoline *N*-oxides. Moreover, sulfoxonium ylides showed high reactivity with 2-arylimidazo[1,2-*a*]pyridines to deliver fused heterocyclic products. Coincidentally, we recently reported a $[Cp^*RhCl_2]_2$-catalyzed reaction of 2-phenylbenzimidazole with sulfoxonium ylides to generate isoquinolines.[22]

We later reported a rhodium(III)-catalyzed C–H activation of ethyl benzimidates **97** with sulfoxonium ylides (Scheme 15).[23] The dual *ortho*-C–H functionalization and cyclization of ethyl benzimidates with sulfoxonium ylides in one pot led to pyrano[4,3,2-*ij*]isoquinoline derivatives **98** with interesting optoelectronic properties.



Scheme 15 Dual *ortho*-C–H activation/cyclization of ethyl benzimides

The reaction mechanism was elucidated by means of a series of control experiments. Initially, coordination of Rh(III) to the ethyl benzimide **97** after dedimerization of $[Cp^*RhCl_2]_2$ produces a rhodacyclic intermediate **99** (Scheme 16). Migratory insertion of the carbene species and protonolysis then affords the acylmethylated intermediate **100**. Unlike other reported reactions, the intermediate does not dehydrate immediately and, instead, is dehydrated after completion of a secondary catalytic cycle.



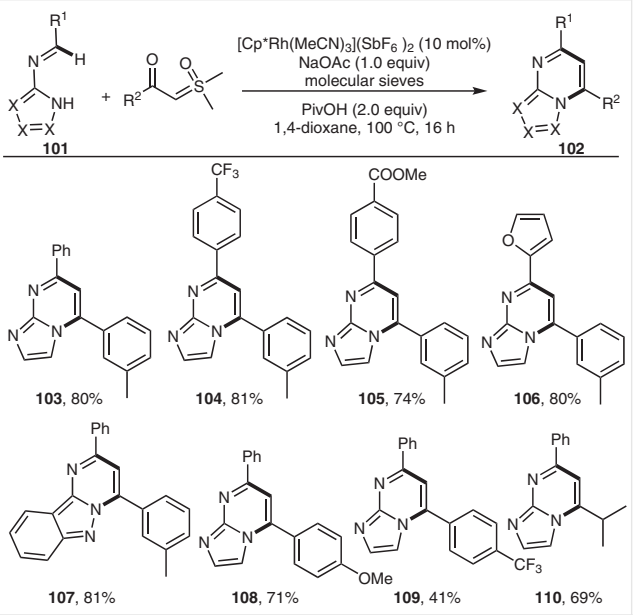
Scheme 16 Proposed mechanism for the dual *ortho*-C–H functionalization/annulation of ethyl benzimidates

3.5 *Ortho*-C–H Activation/Cyclization of N-Azoloimines

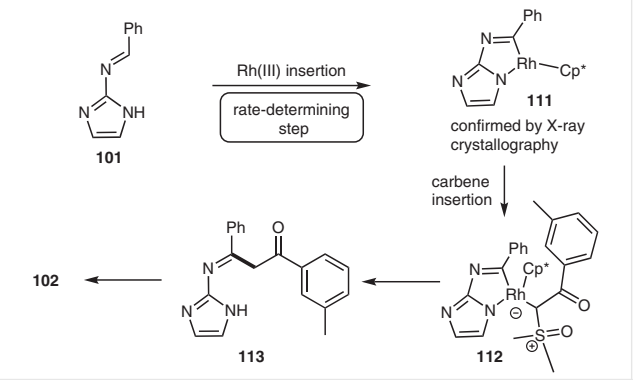
Ellman and co-workers reported the rhodium(III)-catalyzed C–H functionalization of alkenyl azoles with 1,4,2-dioxazolones, acetylenes, or diazones to give the corresponding [5,6]-bicyclic heterocycles.[24] A year later, this [4+2] reaction strategy was applied to annulations of *N*-azoloimines under redox-neutral conditions (Scheme 17). Notably, the group of reaction partners contained not only acetylenes and diazo ketones, but also sulfoxonium ylides. This significant work pioneered the application of Rh(III) catalysts in direct imidoyl C–H activation, providing a range of polysubstituted imidazopyrimidines with good functional-

group tolerance and high stereoselectivity (Scheme 17). Both electron-rich and electron-deficient imines **101** reacted readily with phenyl sulfoxonium ylides to give the corresponding imidazopyrimidines **102**, generally in high yields. A furfural-derived imine and an aminopyrazole-derived imine showed the high reactivities, giving the corresponding products **106** and **107** in high yields. With regard to the ylide, the effects of various substituents on the reaction were investigated, and it was found that ylides containing electron-rich aryl groups showed greater efficiency than their electron-deficient analogues in the cross-coupling reaction.

The mechanism was elucidate after the identification of the C–H activation intermediate rhodacycle **111** through X-ray analysis (Scheme 18). C–H activation of the imine **101** produces the rhodacyclic intermediate **111**, which is then transformed into **112** through insertion of the sulfoxonium



Scheme 17 *Ortho*-C–H activation/cyclization of *N*-azoloimines

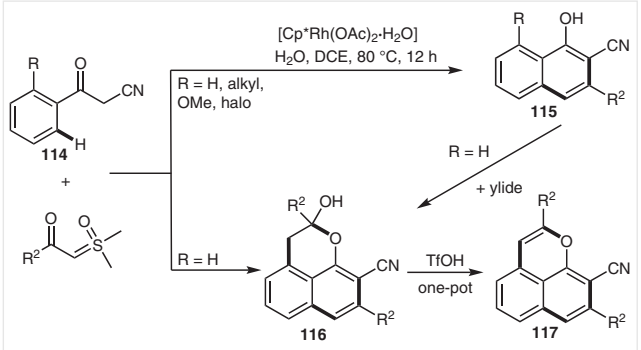


Scheme 18 Mechanism of *ortho*-C–H functionalization/annulation of *N*-azoloimines

ylide. After sequential α-elimination of DMSO, migration, protonolysis, and dehydration, rhodacycle **102** is formed. Deuterium and kinetic-isotope experiments suggested that the formation of rhodacycle **111** through concerted metalation/deprotonation of imine **101** controls the reaction rate. Therefore, breaking of the C–H bond is the rate-determining step.

3.6 *Ortho*-C–H Activation/Cyclization of Benzoylacetonitriles

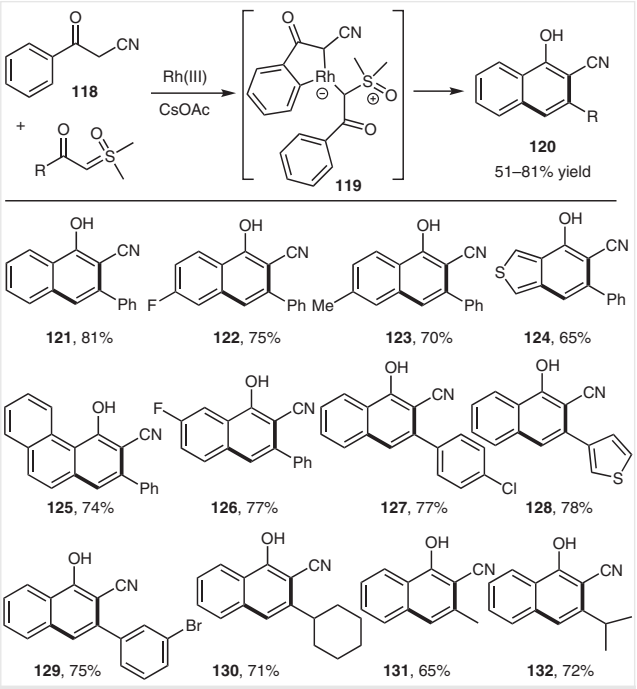
In the reactions discussed above, the nitrogen atom of the directing group plays a key role in metal coordination and C–H activation. However, as a result of Wang's pioneering work on Rh(III)-catalyzed oxidative annulation of benzoylacetonitriles to give naphthols and naphtho[1,8-*bc*]pyrans,[25] interest was aroused in the use of benzoylacetonitrile derivatives in transition-metal-catalyzed C–H activations in which there are no NH directing groups.[26] Li and co-workers developed several syntheses of 1-naphthols, especially an excellent recent synthesis involving sulfoxonium ylides.[27] In that work, sulfoxonium ylides served as C2 synthons in reactions with benzoylacetonitriles to give 1-naphthols 115 or naphtho[1,8-*bc*]pyrans 117 (Scheme 19). This alternative transformation was catalyzed by $Cp^*Rh(OAc)_2{\cdot}H_2O$ under mild conditions in DCE and gave polysubstituted cyclization products. Notably, because of the high reaction efficiency of sulfoxonium ylides, the desired naphthols 115 could be generated only when the *ortho*-positions of the benzoylacetonitriles were blocked. Otherwise, dihydronaphtho[1,8-*bc*]pyrans 116 were obtained, and these could undergo further dehydration to 117 in the presence of trifluoromethanesulfonic acid in a one-pot process.



Scheme 19 *Ortho*-C–H activation/cyclization of benzoylacetonitriles by Wang

Recently, Zhou et al. successfully developed a procedure for accessing 3-substituted naphthols through a Rh(III)-catalyzed relay functionalization with benzoylacetonitriles and sulfoxonium ylides (Scheme 20).[28] The significant steps were concerted metalation/deprotonation of the benzoyl-

acetonitrile and the formation of intermediate **119**. Unlike Li's work, this transformation of benzoylacetonitrile can be controlled by replacing water with CsOAc and reducing the temperature of the reaction system to 50 °C, with catalysis by $[Cp^*Rh(Cl)_2]_2$, to give the 1-naphthol **120** as the sole product.

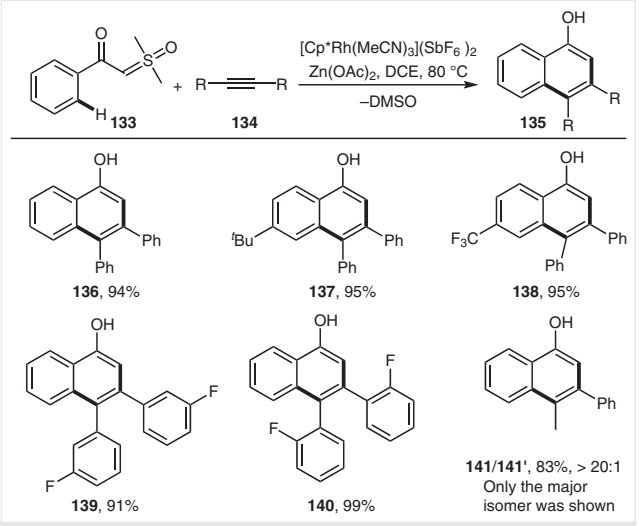


Scheme 20 *Ortho*-C–H activation/cyclization of benzoylacetonitriles by Zhou

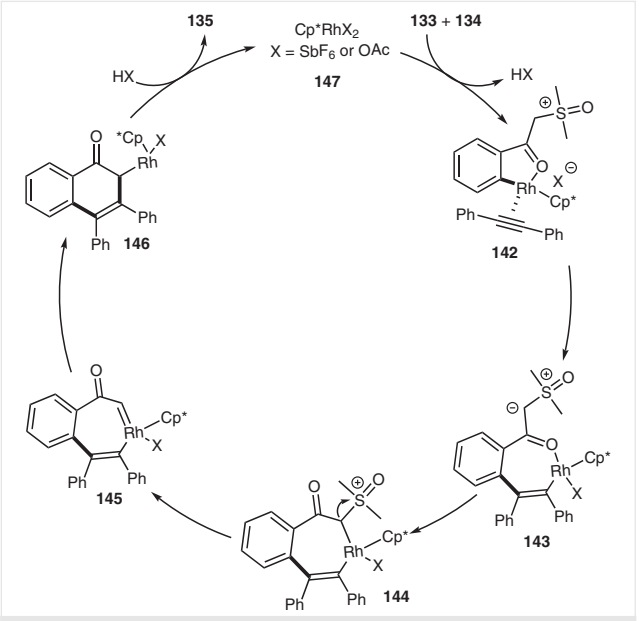
3.7 *Ortho*-C–H Activation/Cyclization of Benzoyl Sulfoxonium Ylides

Sulfoxonium ylide can serve not only as C2 carbene synthons, but also as traceless bifunctional directing groups. Li and co-workers were the first to apply benzoyl sulfoxonium ylides **133** in C–H activation reactions with symmetrical alkynes **134** to give a range of 3,4-disubstituted naphthalen-1-ols **135** in moderate to excellent yields (Scheme 21).[29]

The following mechanism was proposed by the authors (Scheme 22). Coordination of the oxygen atom in the benzoyl sulfoxonium ylide **133** to the rhodium catalyst gives a five-membered rhodacyclic intermediate **142**, which then transforms into the seven-membered rhodacyclic intermediate **143** through the coordination of the alkyne and migratory insertion of the aryl group. The key rhodium carbene species **145** is formed after release of DMSO. Subsequent protonolysis completes the rhodium catalytic cycle and releases the final product, the 1-naphthol **135**.



Scheme 21 *Ortho*-C–H activation/cyclization of benzoyl sulfoxonium ylides



Scheme 22 Proposed mechanism for the C–H activation of benzoyl sulfoxonium ylides

4 Conclusion

In this review, we have described how a variety of important chemical skeletons, such as indoles, pyrroles, isoquinolones, isocoumarins, pyrimidines, 1-naphthols, pyrano[4,3,2-*ij*]isoquinolines, and other fused heterocycles, have been obtained by routes involving metal carbenes, thereby markedly promoting the progress of sulfur ylide chemistry in transition-metal-catalyzed C–H functionalizations.

Although remarkable achievements have been made over the past few years, the scope of substrates is mainly focused on the activation of sp^2 C–H bonds. Therefore, great challenges still exist, especially in terms of innovation in substrates. More improvements need to be carried out to achieve activation of sp^3 C–H bonds. In addition, new catalytic systems beyond rhodium and iridium urgently need to be developed to provide milder reaction conditions. Finally, a diversity of sulfur ylides needs to be exploited to increase the practicability of the methods discussed above. Therefore, the core of future work will involve improvements in substrates, the optimization of catalytic systems, and the search for new applications of sulfur ylide reagents in chemical synthesis.

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