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Review

Organocatalytic Transformations from Sulfur Ylides

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Abstract: Sulfur ylides are an important class of organic compounds due to their ability to perform many different transformations that can give diverse and interesting products with a high degree of complexity. Although metal-catalyzed transformations are frequent in this class of compounds, organocatalyzed transformations remain scarce. From initial works, this review aims to show organocatalyzed transformations from sulfur ylides, involving cyclopropanation and formal N–H, S–H, and C–H insertion reactions, including enantioselective versions. The proposed mechanisms and the modes of activation of these organocatalysts will be covered. Furthermore, advances in this area and potential challenges to be circumvented in the near future will also be discussed.

Keywords: sulfur ylide; sulfoxonium; sulfonium; organocatalysis

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1. Introduction

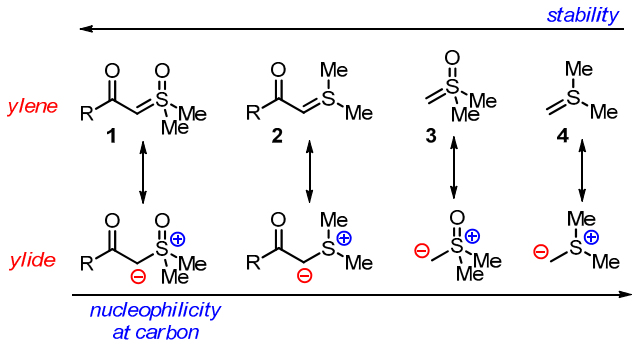
Organocatalysis, a term coined in 2003, by List and MacMillan independently, emerged as a powerful strategy to achieve complex compounds using small molecules as catalysts, with recognition for both researchers in the 2021 Nobel Prize in Chemistry [1]. From the synthesis of complex small molecules to total synthesis, the exponential rise of organocatalysis in organic synthesis showcases its importance [2–7]. The main advantage of organocatalysis, compared to metal catalysis and biocatalysis, is generally the use of small, stable molecules as catalysts. Using chiral pool strategies, for instance, can be accomplished in a few steps. Moreover, the stability of such molecules enables a desired reaction to be run under moisture and air [8].

Sulfur ylides, introduced by Ingold and Jessop in 1930 [9] and initially applied in organic synthesis by Johnson, in 1961 [10], and Corey and Chaykovsky, in 1965 [11–13], are versatile compounds with several possible applications since they can be synthesized through small rings, Stevens rearrangement, and metal carbene formation [14,15]. This versatility makes them surrogates of diazo compounds, especially considering their higher stability and similar reactivity. Electron-withdrawing groups in the α position to a sulfur ylide enhance their thermal stability, to a point where these compounds can be handled at larger-scale reactions [16].

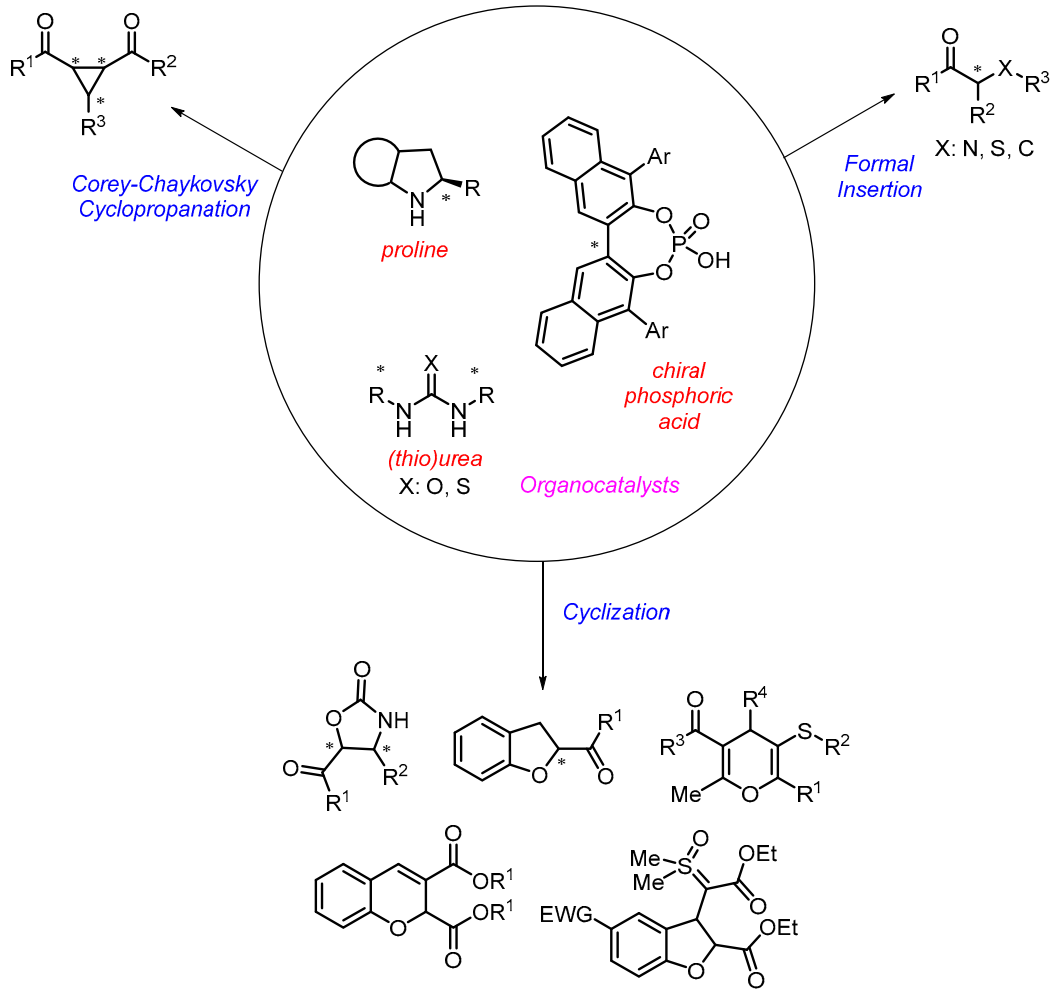
Sulfonium and sulfoxonium ylides have an interesting reactivity: the ylidic carbon is nucleophilic but becomes electrophilic after the reaction with an electrophile. In this latter case releasing a sulfide and a sulfoxide, respectively. The difference in the nucleophilicity of these ylides resides in the oxidation state of the sulfur atom, where sulfonium ylides are more nucleophilic at the carbon atom than sulfoxonium ylides [17,18]. This difference in oxidation state results in divergent preferences in reactions, which will be discussed further (Scheme 1).

Even though sulfur ylide has been utilized for a long time in metal catalysis due to its ability to produce metal carbenes, it has not been utilized much in organocatalysis despite its ability to produce complex molecules in one step [14,19]. This review will discuss the advances in the organocatalyzed reactions from sulfur ylides, such as Corey–Chaykovsky cyclopropanations, formal C–H, C–X, and X–H insertion reactions, and cycloadditions

(Scheme 2). Asymmetric transformations involving chiral and enantioenriched sulfur ylides as reactants will not be covered in this review [20–22].



Scheme 1. Sulfur ylides and their stability and nucleophilicity at carbon.



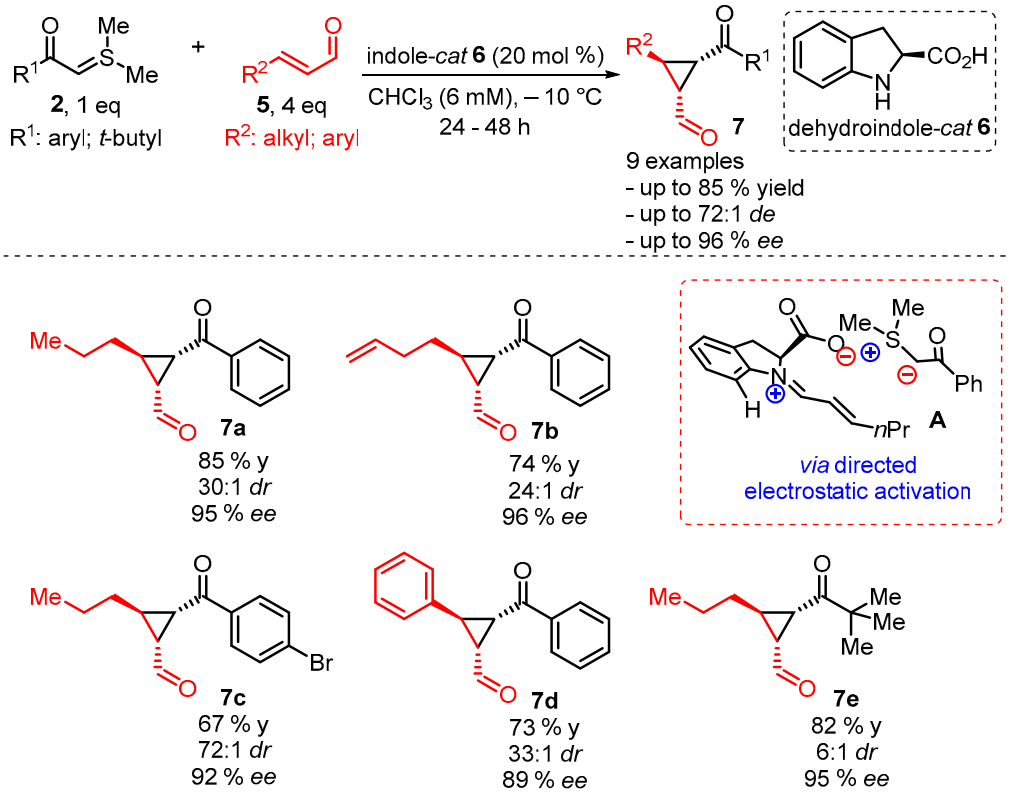
Scheme 2. Organocatalyzed reactions from sulfur ylides.

2. Organocatalytic Corey–Chaykovsky Reaction

Cyclopropanes are a class of molecules that are widely present in nature, with their corresponding natural products containing this structure [23]. Because of its potential as a bioisostere of double bonds, the efficient synthesis of natural and pharmaceutical products containing a cyclopropane moiety is being explored by several research groups and industries [24,25]. Some cyclopropanation reactions, such as the Simmons–Smith reaction, employ metal catalysis with the intermediacy of carbenes [26]. On the other hand, Corey

and Chaykovsky published a metal-free cyclopropanation reaction involving electron-poor olefins and sulfonium ylides in 1965 [13]. Since then, enantioselective cyclopropanation has remained exclusive to metal catalysis in the Simmons–Smith reaction (use of chiral auxiliary and metal carbenes) [20–22,27].

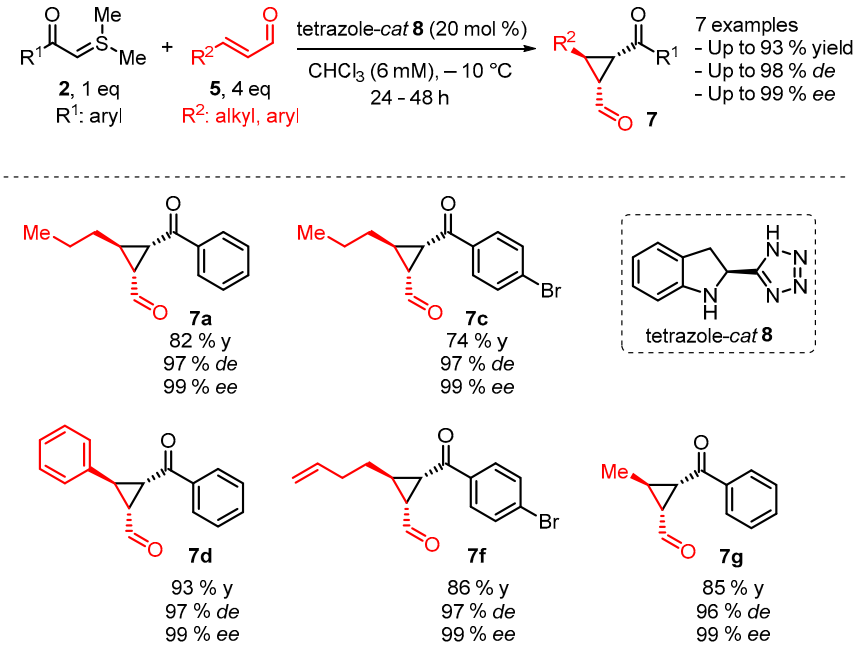
The first contribution of an organocatalytic Corey–Chaykovsky cyclopropanation came from MacMillan and coworkers in 2005, where they used sulfonium ylides **2**, *α*,*β*-unsaturated aldehydes **5,** and a chiral dehydroindole organocatalyst (indole-*cat* **6**). Cyclopropanes **7** (9 examples) were achieved in good yields (up to 85%) with excellent diastereoselectivities (up to 72:1) and enantioselectivities (up to 96% *ee*). The authors proposed a mode of activation that involved a directed electrostatic activation from the carboxylate and sulfonium functions, via intermediate **A**. The iminium *Z* isomer was suggested considering the minimization of the Van der Walls interaction between the aryl hydrogen and olefin (Scheme 3) [28].



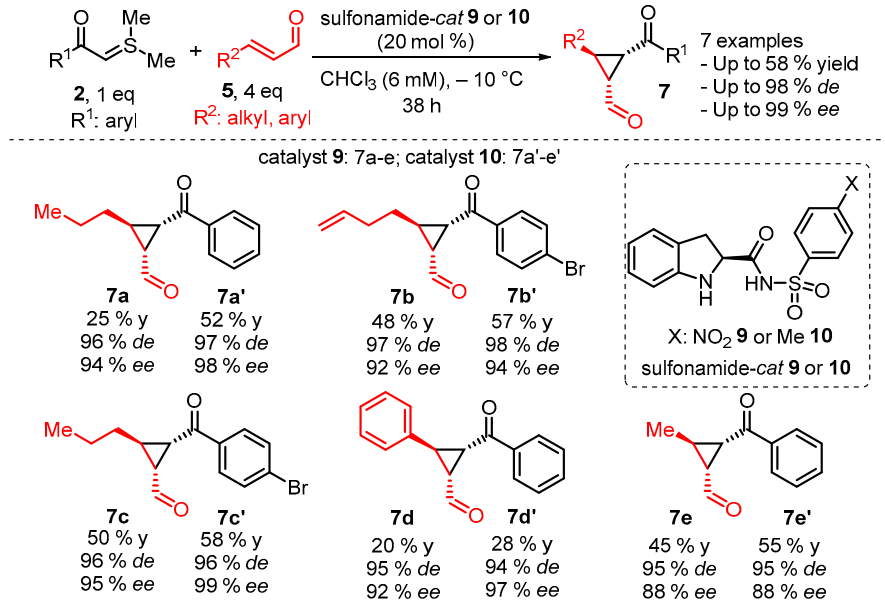
Scheme 3. Indole-organocatalyst catalyzed cyclopropanation, with selected examples.

In 2007, Arvidsson and colleagues improved the enantioselective Corey–Chaykovsky cyclopropanation protocol, modifying the organocatalyst indole-*cat* **6**, using tetrazolic acid as a substitute for carboxylic acid. Compared to Macmillan's work, Arvidsson showed that the designed organocatalyst **8** improved the yields (up to 93%), diastereoselectivities (up to 98% *de*), and enantioselectivities (up to 99% *ee*) of cyclopropanes **7** (7 examples). The tetrazolic acid, which has a larger group than carboxylic acid, imposed a steric hindrance on the nucleophilic attack step of the sulfonium ylide. This improves the enantioselectivity (Scheme 4) [29].

In the same year, Arvidsson and coworkers reported more modifications of organocatalysts using a sulfonamide group, which shared the same dehydroindole core with **6** and **8**. A comparison with their and MacMillan's work showed that the new organocatalysts **9** and **10** furnish the cyclopropanes **7a**–**7e**, **7a′**–**e′**, with high selectivity (up to 98% *de* and 99% *ee*), although at lower yields (up to 58%) (Scheme 5) [30].

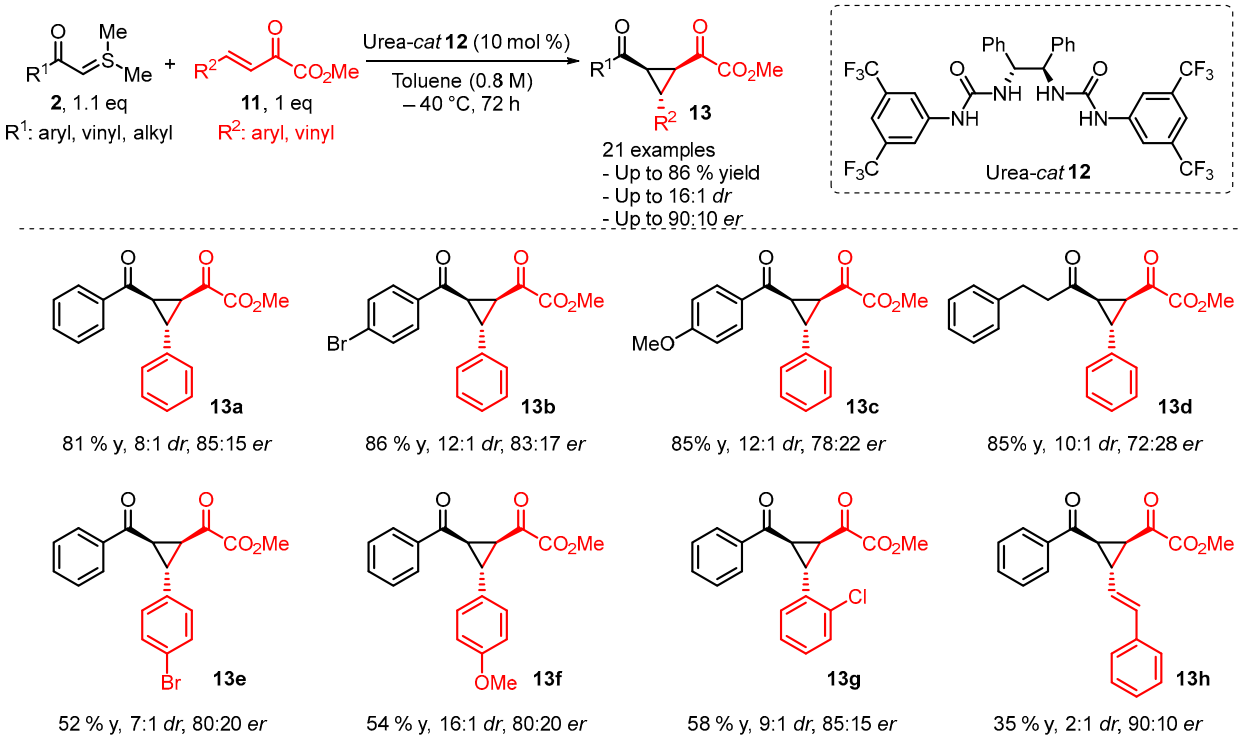


Scheme 4. Tetrazole-organocatalyst catalyzed cyclopropanation, with selected examples.

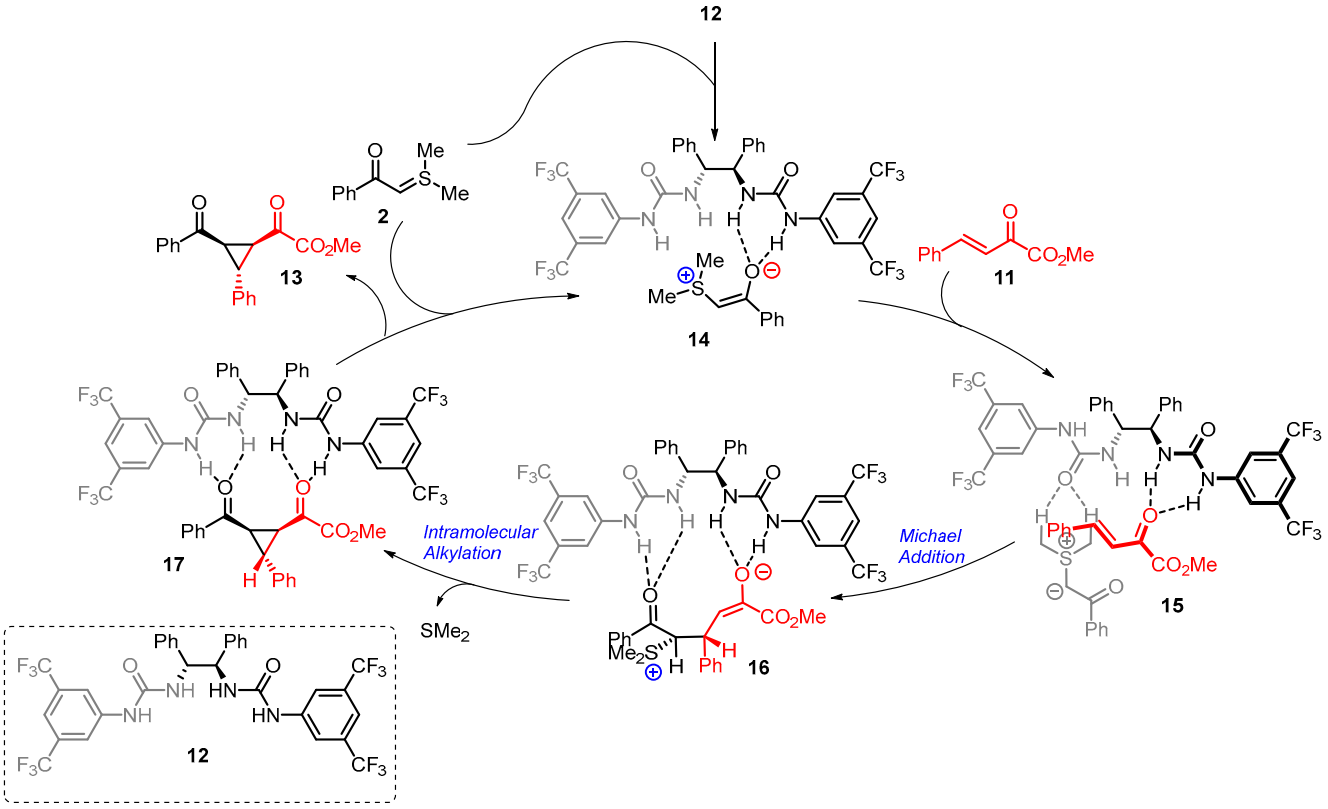


Scheme 5. Sulfonamide-organocatalyst catalyzed cyclopropanation, with selected examples.

In 2011, Chen, Xiao, and coworkers reported asymmetric cyclopropanation of β,γ-unsaturated-α-keto-esters **11** with sulfoxonium ylides **2**, catalyzed by chiral urea (urea-*cat* **12**), which afforded 1,2,3-trisubstituted cyclopropanes **13** (21 examples) in good yields (up to 86%) and moderate to good selectivities (up to 16:1 *dr* and up to 90:10 *er*). The use of toluene as solvent at a low temperature (−40 °C) for 72 h provided the optimal condition (Scheme 6) [31]. The authors proposed a catalytic cycle starting with the coordination of urea-cat **12** with sulfonium ylide **2**, followed by the coordination of β,γ-unsaturated-α-keto-ester **11**. The chiral environment in intermediate **15** leads to an enantioselective Michael addition, followed by alkylation, giving complex **17**. This regenerates the organocatalyst, furnishing the cyclopropane **13** (Scheme 7) [31,32].



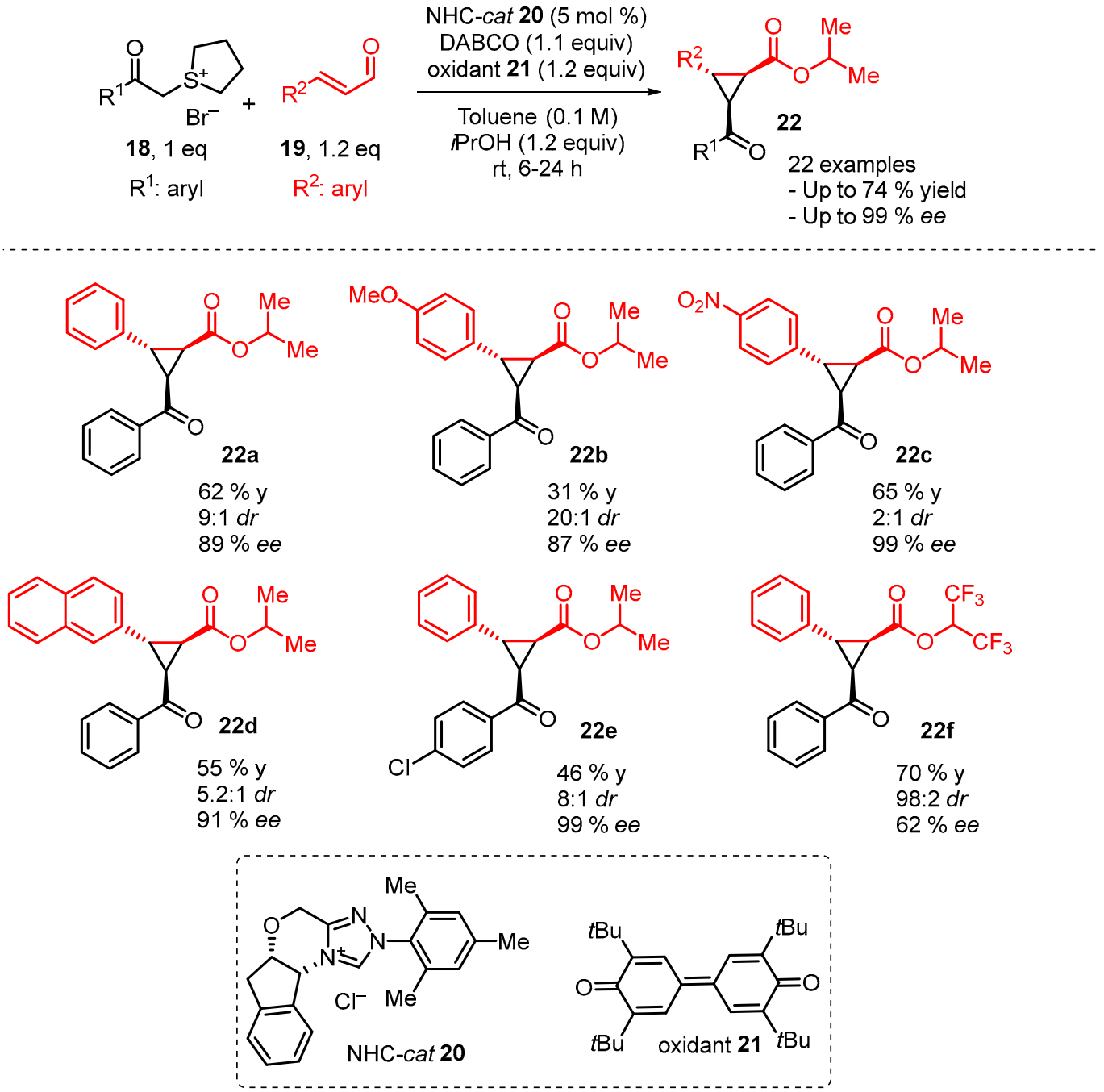
Scheme 6. Urea-organocatalyst catalyzed cyclopropanation, with selected examples.



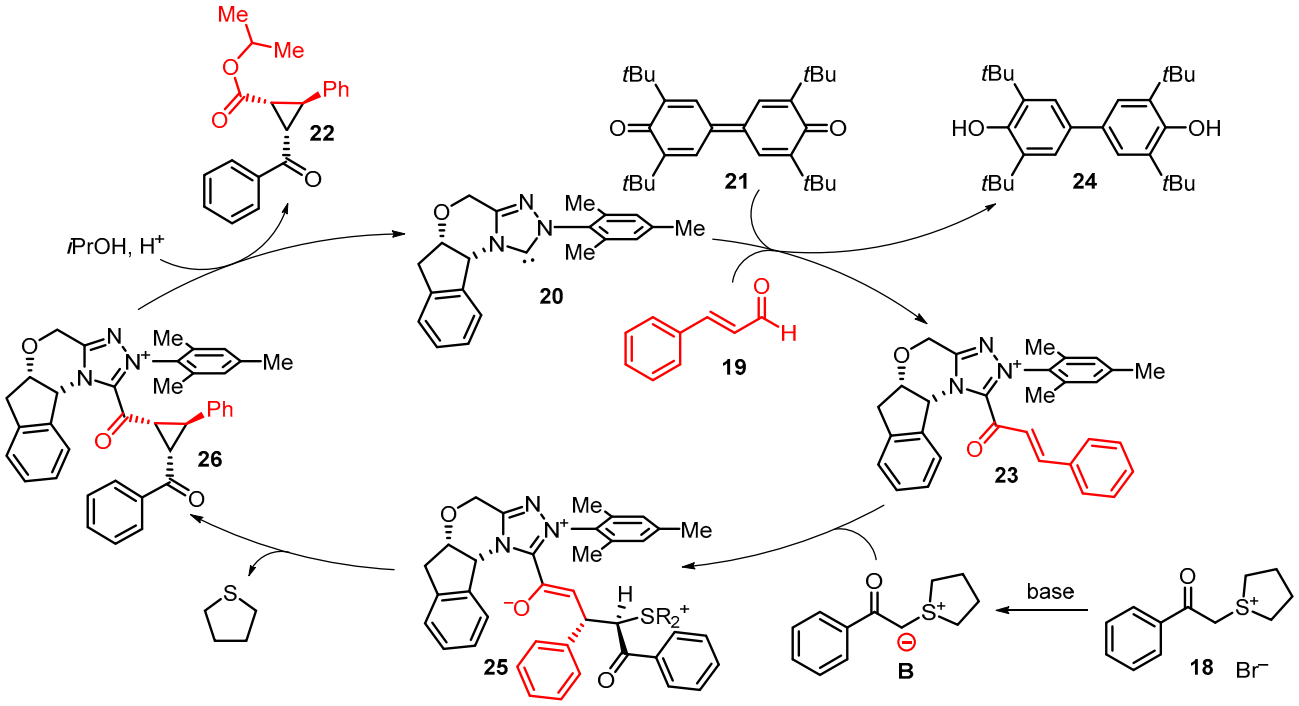
Scheme 7. Proposed catalytic cycle of urea-catalyzed cyclopropanation of β,γ-unsaturated-α-keto-ester.

In 2012, Studer and coworkers reported an oxidative NHC-catalyzed Corey–Chaykovsky cyclopropanation of α,β-unsaturated aldehydes **19** with sulfonium ylides **18**. Chiral NHC-catalyst (NHC-*cat* **20**), DABCO, benzoquinone-derivative **21,** and *i*PrOH were used in

toluene at rt to afford cyclopropanes **22** (22 examples) in good yields (up to 74%) and excellent *ee* (up to 99%) (Scheme 8) [33]. The authors proposed a catalytic cycle involving the addition of NHC-*cat* **20** to aldehyde **19** to form a Breslow intermediate, which is oxidized by quinone to form intermediate **23**. 1,4-addition of sulfonium ylide **B**, which was formed in situ from sulfonium salt **18**, to intermediate **23** gives enolate **25**, followed by cyclopropanation to furnish intermediate **26**. Next, alcoholysis releases product **22**, regenerating the NHC-*cat* (Scheme 9) [33–35].



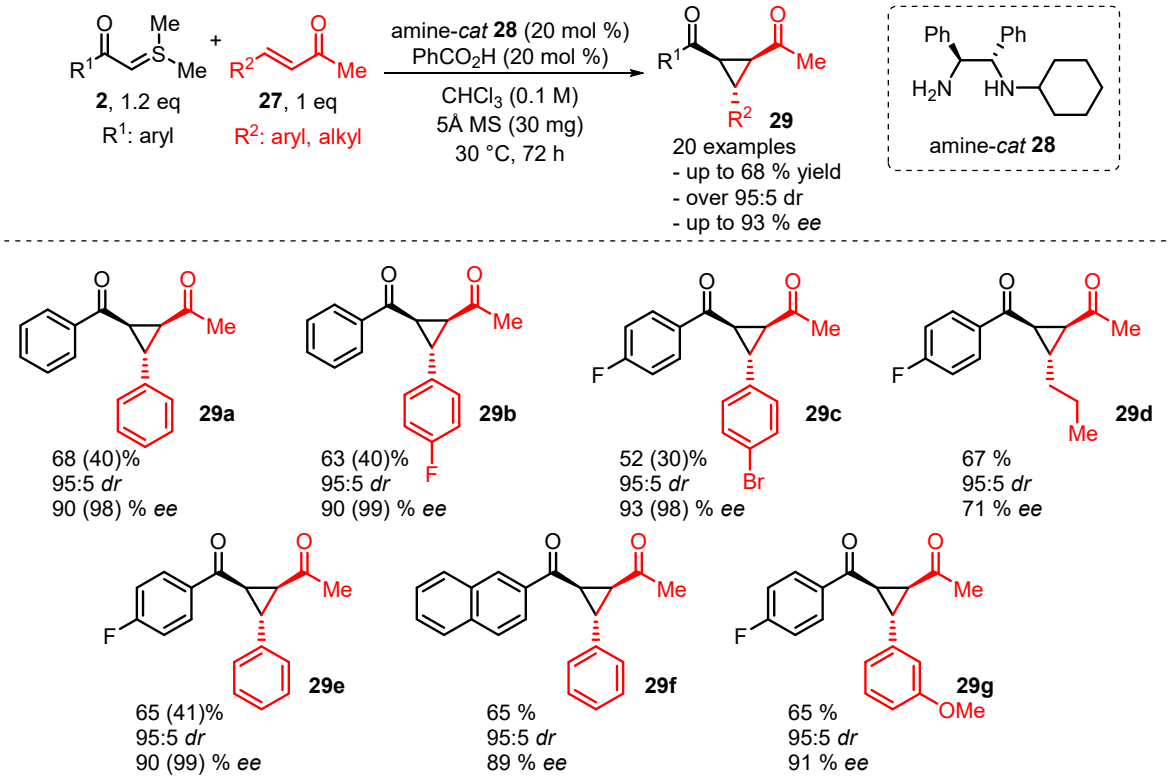
Scheme 8. Oxidative NHC-catalyzed cyclopropanation of unsaturated aldehydes with selected examples.



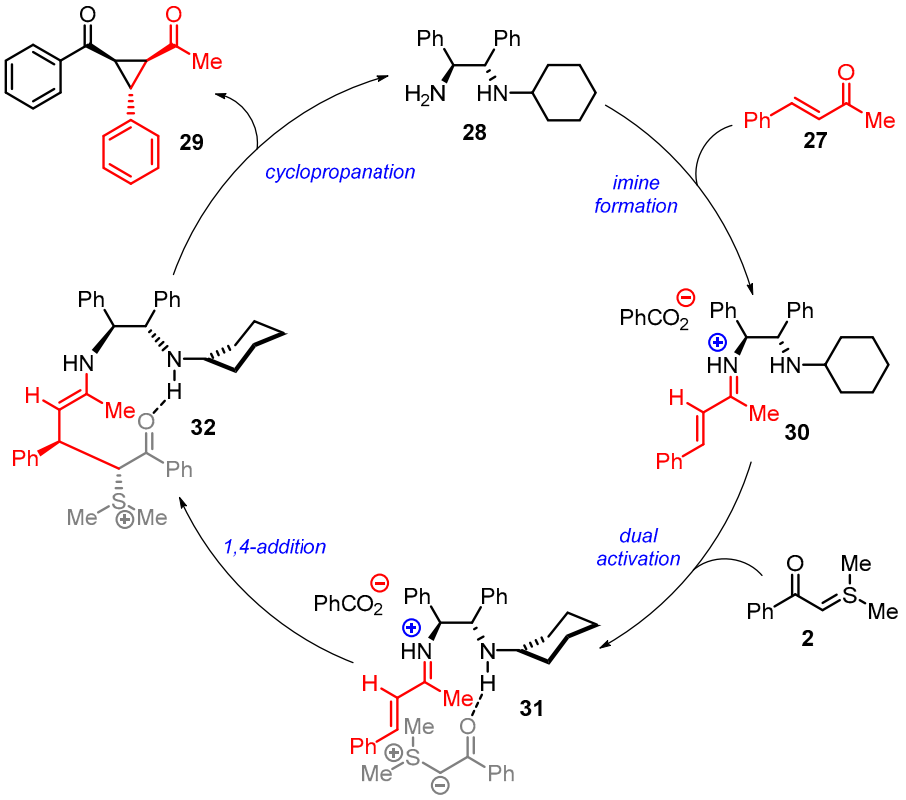
Scheme 9. Proposed catalytic cycle of NHC-catalyzed cyclopropanation of *α*,*β*-unsaturated aldehyde.

In 2013, Liu, Feng, and coworkers reported an asymmetric Corey–Chaykovsky cyclopropanation of *α*,*β*-unsaturated ketones **27** with sulfonium ylides **2**, catalyzed by chiral amine **28**. Furthermore, benzoic acid, $CHCl_3$, and 5 Å MS were used at 30 °C to furnish cyclopropanes **29** (20 examples) in good yields (up to 68%) and excellent *ee* and *dr* (up to 93% *ee* and >95:5 *dr*), with an improvement in *ee* after a single recrystallization (up to 99% *ee*) (Scheme 10). The authors have proposed that the mechanism starts with the formation of iminium **30** from the reaction of amine-cat **28** and unsaturated ketone **27**, mediated by benzoic acid. Next, the secondary amine group from intermediate **30** coordinates with sulfonium ylide **2** via hydrogen bonding. This was followed by 1,4-addition and cyclopropanation by enamine attack to furnish the desired product **29** (after hydrolysis) and the amine-cat **28** (Scheme 11) [36].

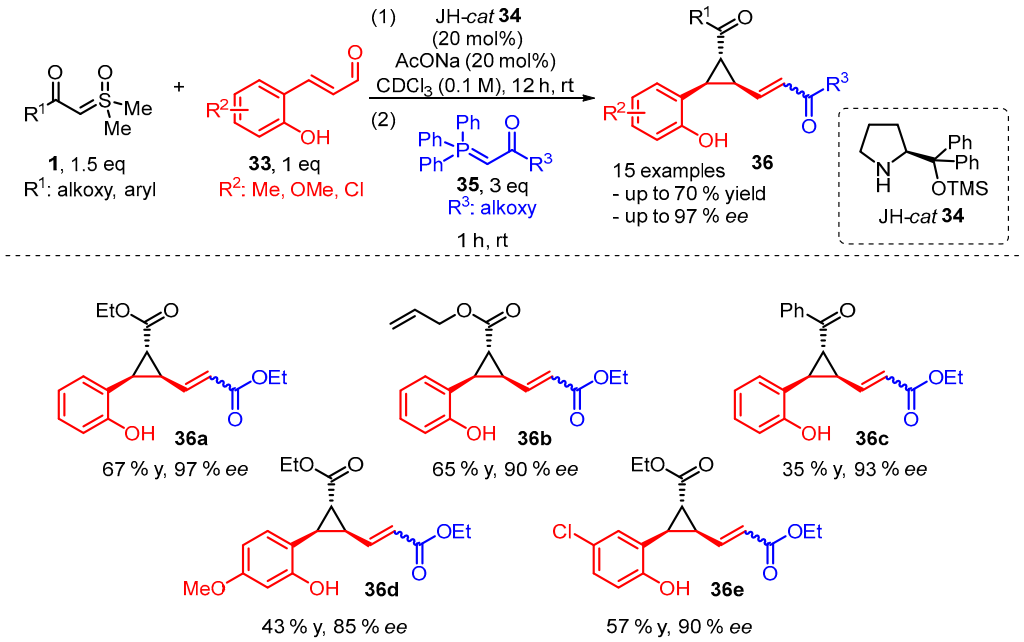
In 2022, Fochi, Bernardi, and coworkers reported a Corey–Chaykoyvsky-type cyclopropanation using sulfoxonium ylides **1**, 2-hydroxy-cinnamaldehydes **33**, NaOAc, and Jørgensen–Hayashi proline **34** as an organocatalyst (JH-*cat*). Subsequently, the Wittig reaction was employed via a one-pot procedure to afford substituted cyclopropanes **36** (15 examples) in moderate to good yields (up to 70%) and excellent *ee* (up to 97%) (Scheme 12). Their initial proposed catalytic cycle starts with the formation of iminium **37** from JH-cat **34** and 2-hydroxy-cinnamaldehyde **33**, which is in equilibrium with the hemiaminal **37′** form, the latter being unreactive and more stable. The sulfoxonium ylide **1** selectively attacks the olefin, followed by the enamine **38** attack to displace DMSO, yielding the cyclopropane **39**. The iminium is then hydrolyzed to recover the catalyst, furnishing the aldehyde **40** (which epimerizes to **41** and cyclizes to the more stable hemiacetal **41a′**) (Scheme 13). After optimization, the authors found that the basic condition (NaOAc) provided the best results. This shows that the phenol moiety is sufficiently acidic to form the iminium intermediate for the next step. In this case, the base is necessary to remove any acidic species that could be harmful to the sulfoxonium ylide [37].



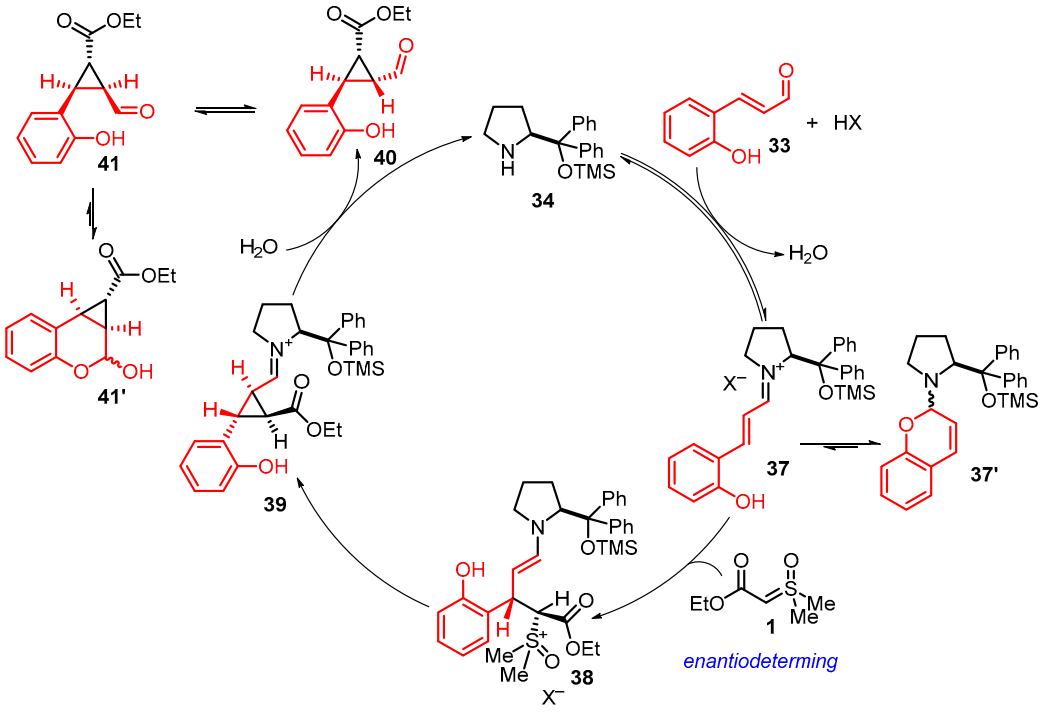
Scheme 10. Amine-catalyzed cyclopropanation of unsaturated ketones with selected examples (in parentheses yield and *ee* after recrystallization).



Scheme 11. Proposed catalytic cycle of amine-catalyzed cyclopropanation of α,β-unsaturated ketone by dual activation.



Scheme 12. (1) Proline-derivative catalyzed cyclopropanation of aldehydes and sulfoxonium ylides, followed by (2) Wittig reaction, with selected examples.

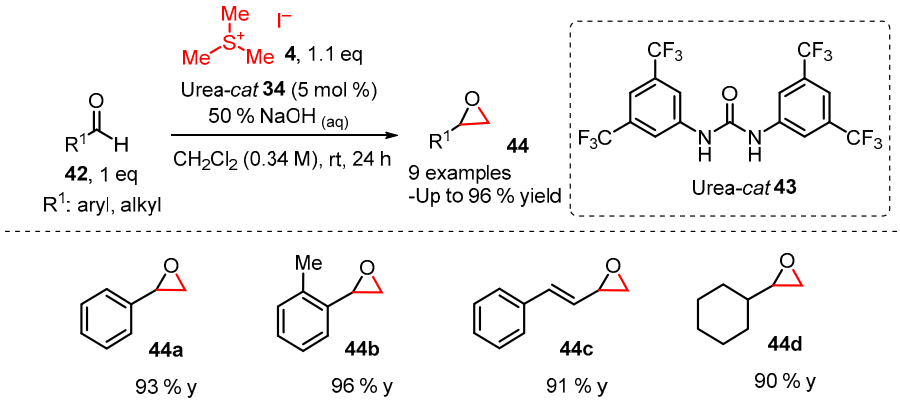


Scheme 13. Proposed catalytic cycle of cyclopropanation via iminium/enamine sequence.

Epoxides are a versatile class of compounds in organic synthesis, with extensive applications in the total synthesis of natural products and pharmaceuticals. In this scenario, the Corey–Chaykovsky epoxidation reaction is an interesting strategy for the synthesis of epoxides due to the use of aldehydes and trimethylsulfonium iodide as starting materials in mild conditions [38].

In 2008, Connon and coworkers reported urea-organocatalyzed Corey–Chaykovsky epoxidation using aldehydes **42**, trimethylsulfonium iodide **4**, and aqueous NaOH in CH_2Cl_2 at rt to furnish epoxides **44** (9 examples) in excellent yields (up to 96%). The

purpose of the urea-*cat* **43** was to accelerate the attack of the sulfonium methylide on the carbonyl group of **42**, which is the rate-determining step in this reaction (Scheme 14) [39].



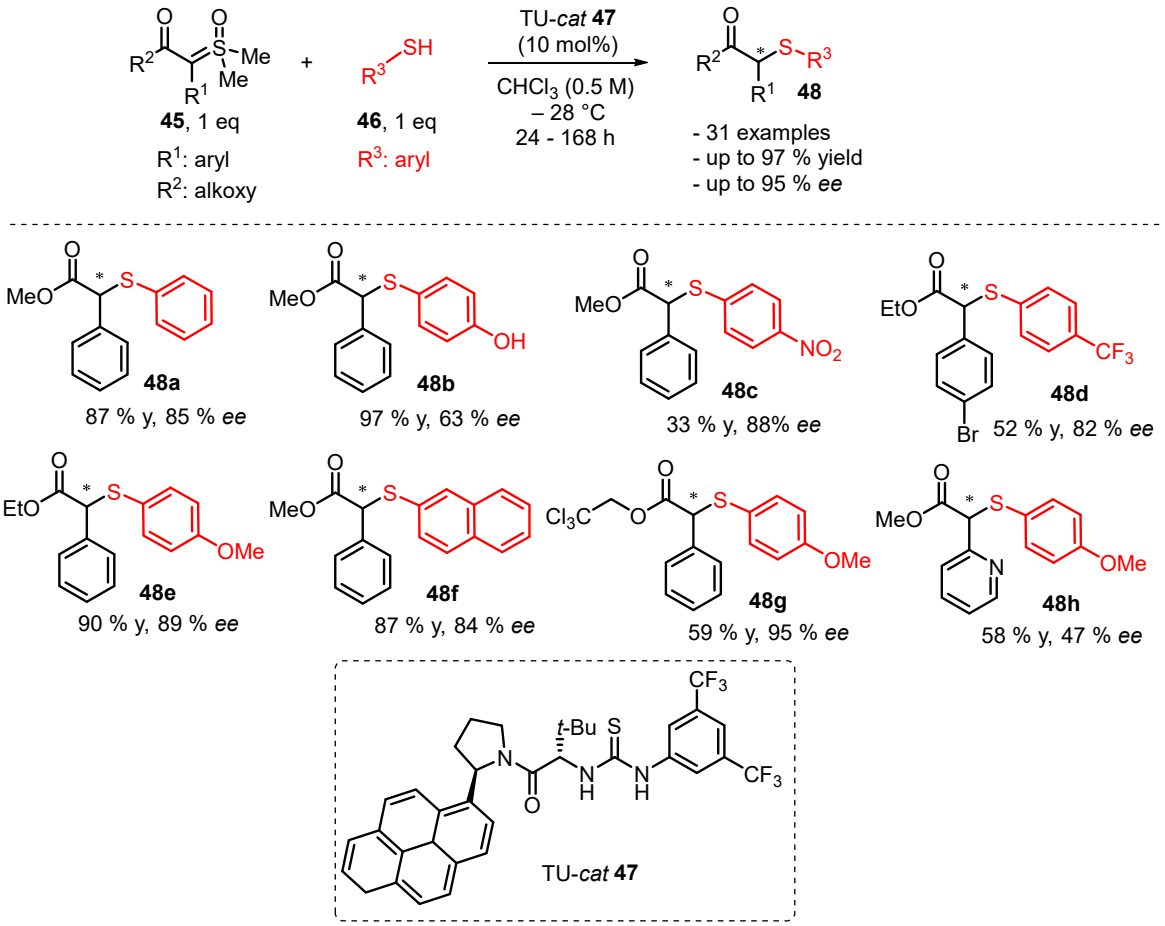
Scheme 14. Urea-catalyzed epoxidation of aldehydes with selected examples.

3. Organocatalytic Formal C–H, N–H, and S–H Insertion

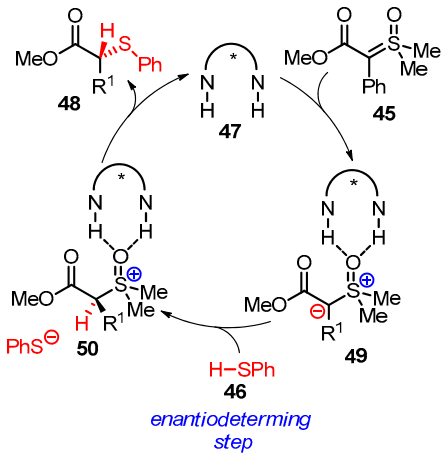
The chemistry of sulfur ylides has recently gained more attention due to their ability to provide a formal insertion bond leading to α-substituted carbonyl compounds [17,18]. One of the seminal works comes from Baldwin and coworkers in 1993, where they treated β-lactams with trimethylsulfoxonium iodide, and upon exposure to diverse reagents and catalysts, several products of N–H, O–H, Cl–H, and Br–H insertion reactions were obtained [40,41]. Specifically in the N–H insertion reaction, the discovery of the carbene pathway has made sulfur ylides surrogates of diazo compounds [41]. Additionally, one of the most important applications comes from the N–H insertion reaction of key intermediates in the pharmaceutical industry. In 2011, Mangion and coworkers at Merck developed the synthesis of MK-7655, a β-lactamase inhibitor, via iridium-catalyzed N–H insertion. In 2012, Molinaro and colleagues at Merck reported the three different synthetic routes to MK-7246, a selective CRTH2 antagonist for the treatment of respiratory diseases. The final route, or manufacturing route, used the intramolecular N–H insertion of sulfoxonium ylide, catalyzed by iridium. In 2022, Ruck and coworkers at Merck reported the synthesis of MK-1029, a CRTH2 antagonist, via intramolecular N–H insertion of sulfoxonium ylide with indole, catalyzed by iridium [42–44].

As an alternative to metal-catalyzed X–H insertions from carbonyl sulfur ylides, capable of generating a stereogenic center at the α-carbonyl position, the use of organocatalyzed reactions is another way to obtain such compounds in mild conditions. In this case, a prerequisite to achieving enantioselectivity is the use of "pro-chiral" sulfoxonium ylides. Two methods to prepare these more complex sulfur ylides (without passing through diazo compounds as intermediates) have been described independently by the research groups of Burtoloso and Aïssa. The former developed an aryne approach to coupling with sulfoxonium ylides, while the latter reported a palladium-catalyzed coupling of aryl halides with sulfoxonium ylides [45–47].

In 2020, Mattson, Burtoloso, and coworkers reported the first enantioselective formal S–H insertion reaction of pro-chiral sulfoxonium ylides **45**. Besides the ylide, an aromatic thiol **46** and thiourea organocatalyst (TU-*cat* **47**) in $CHCl_3$ were used. The reaction was carried out at a lower temperature (–28 °C) and afforded α-thiol ester **48** (31 examples) in excellent yields (up to 97%) and with excellent enantioselectivity (up to 95% *ee*) (Scheme 15). The proposed mechanism, supported by ^{1}H NMR and DFT calculations, indicates that the first step is the formation of a hydrogen bond between the TU-*cat* and the S=O bond of the sulfoxonium ylide to yield the intermediate **49**. The next step is the protonation of **49** with H–SPh, which is both a rate-determing and enantiodetermining step, leading to **50**. The S_N2 reaction of thiolate with **50** then furnishes the desired product **48** and regenerates the organocatalyst **47** (Scheme 16) [48,49].



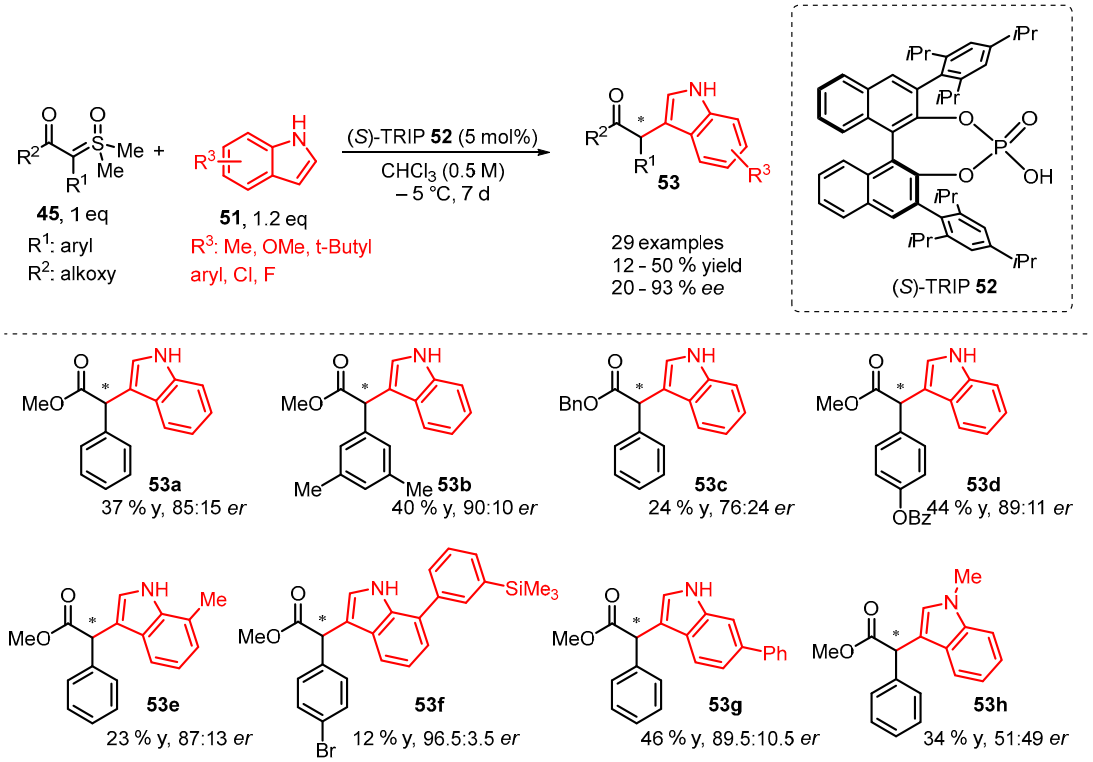
Scheme 15. Thiourea-catalyzed S–H insertion of sulfoxonium ylides by aryl thiol with selected examples.



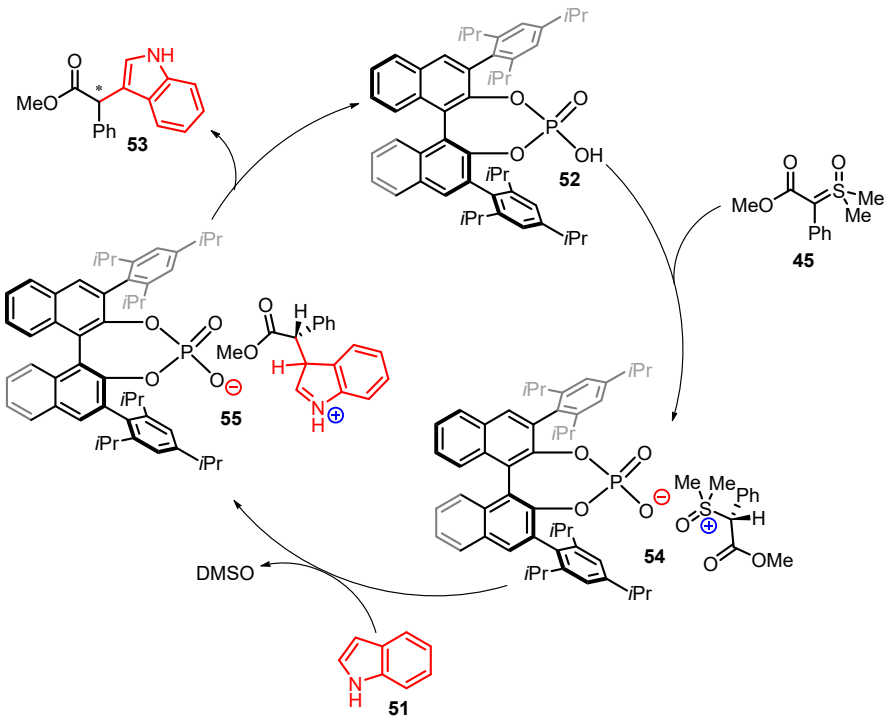
Scheme 16. Proposed catalytic cycle of enantioselective S–H insertion.

In 2021, Mattson, Burtoloso, and coworkers developed a formal C–H insertion reaction of indoles **51** into sulfoxonium ylide esters **45**, using a chiral phosphoric acid (*S*)-TRIP **52** in $CHCl_3$ at low temperature (−5 °C), providing the C–C bond adducts **53** (29 examples) in moderate yields (up to 50%) and good to excellent enantioselectivity (up to 93% *ee*). It is noteworthy that no indole protection is required (Scheme 17). The mechanism proposed by the authors involves the protonation of sulfoxonium ylide with (*S*)-TRIP, forming complex **54**, with charged species in protonated ylide and organocatalyst. Subsequently, indole performs an electrophilic aromatic substitution reaction, leading to the intermediate **55**,

which undergoes a rearomatization of the indole ring via proton abstraction from (*S*)-TRIP, yielding the product **53**, and regenerating the organocatalyst **52** (Scheme 18) [50].



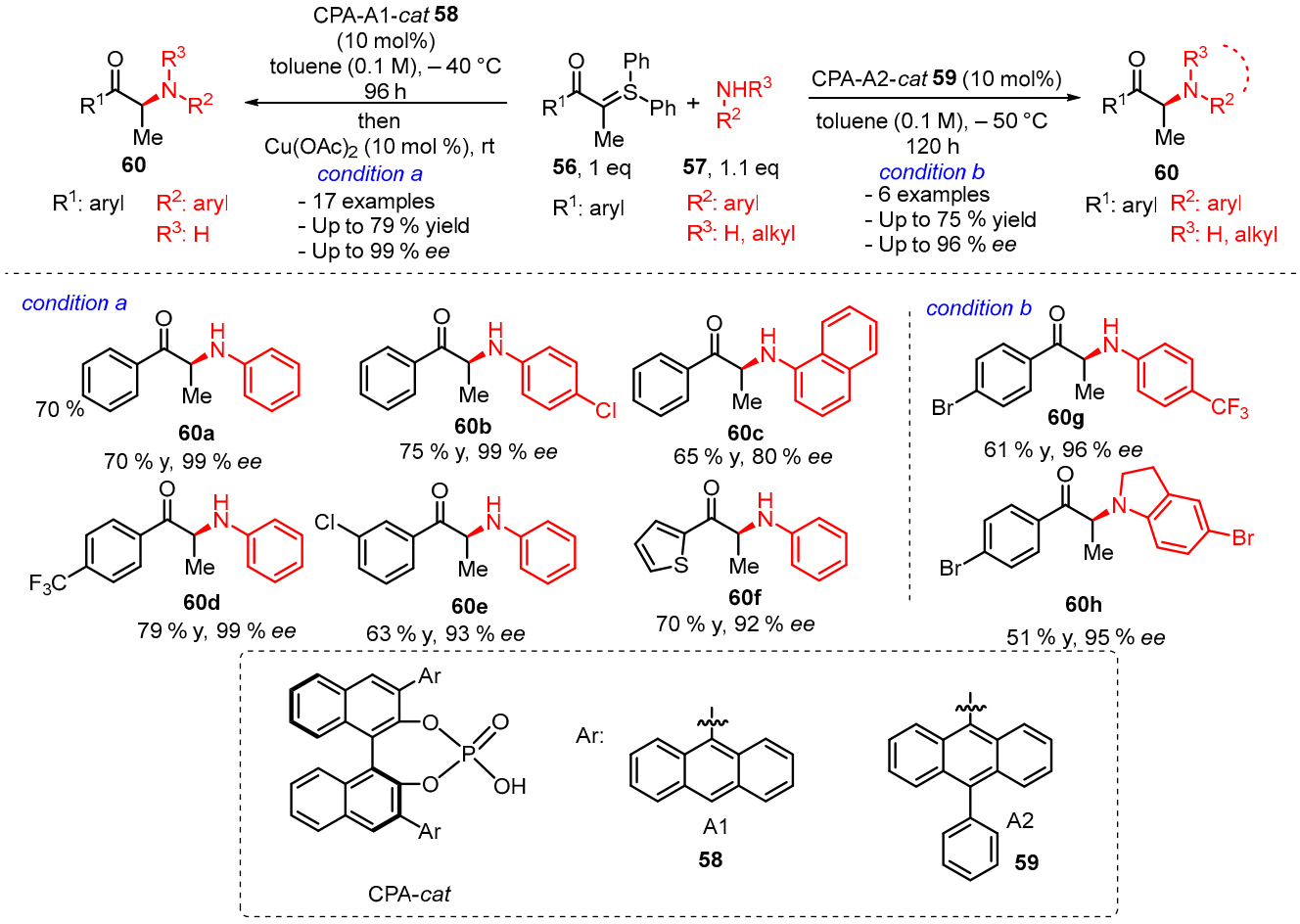
Scheme 17. (*S*)-TRIP-catalyzed C–H insertion of sulfoxonium ylides by indoles with selected examples.



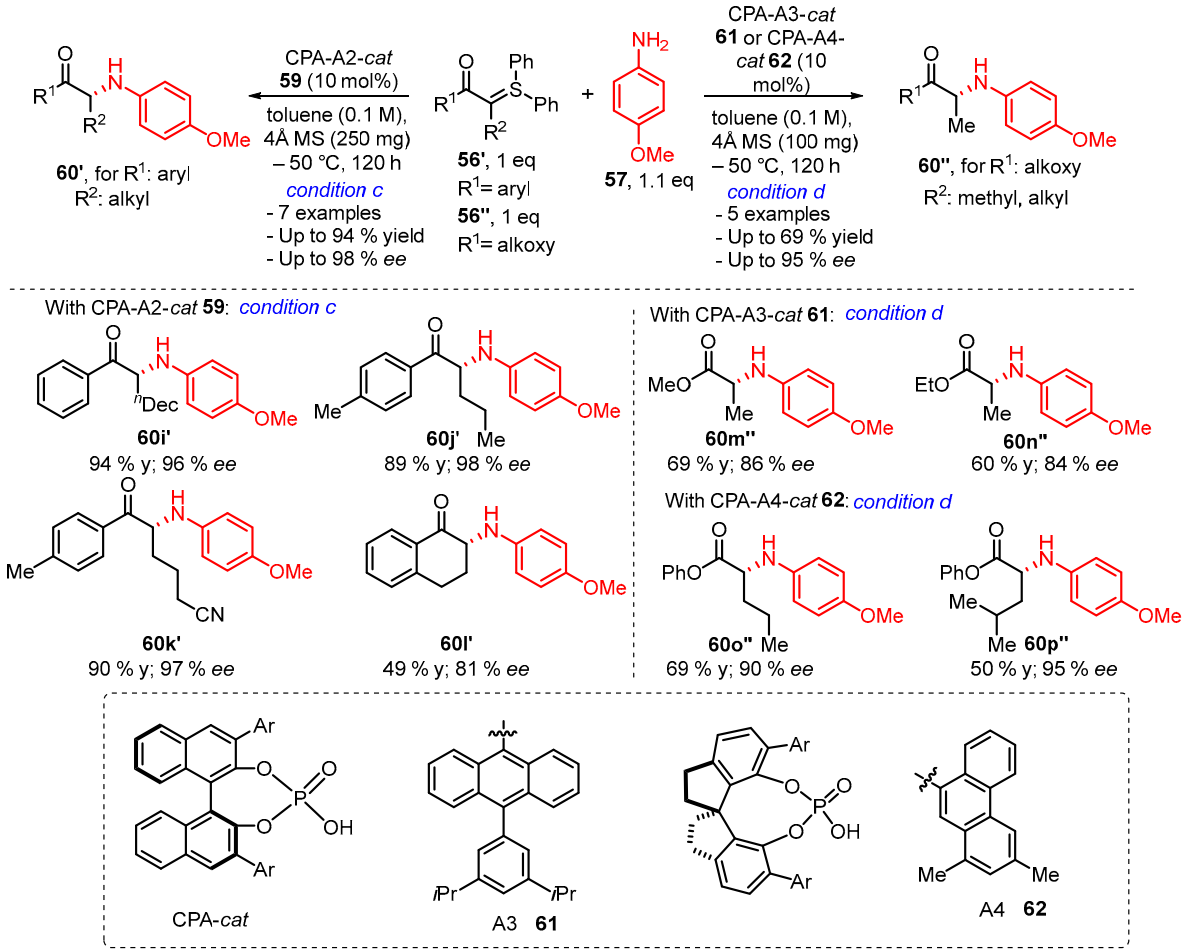
Scheme 18. Proposed catalytic cycle of enantioselective C–H insertion.

In 2020, Li, Sun, and coworkers reported an organocatalytic formal N–H insertion reaction using sulfonium ylides **56** and anilines **57**, catalyzed by chiral phosphoric acid

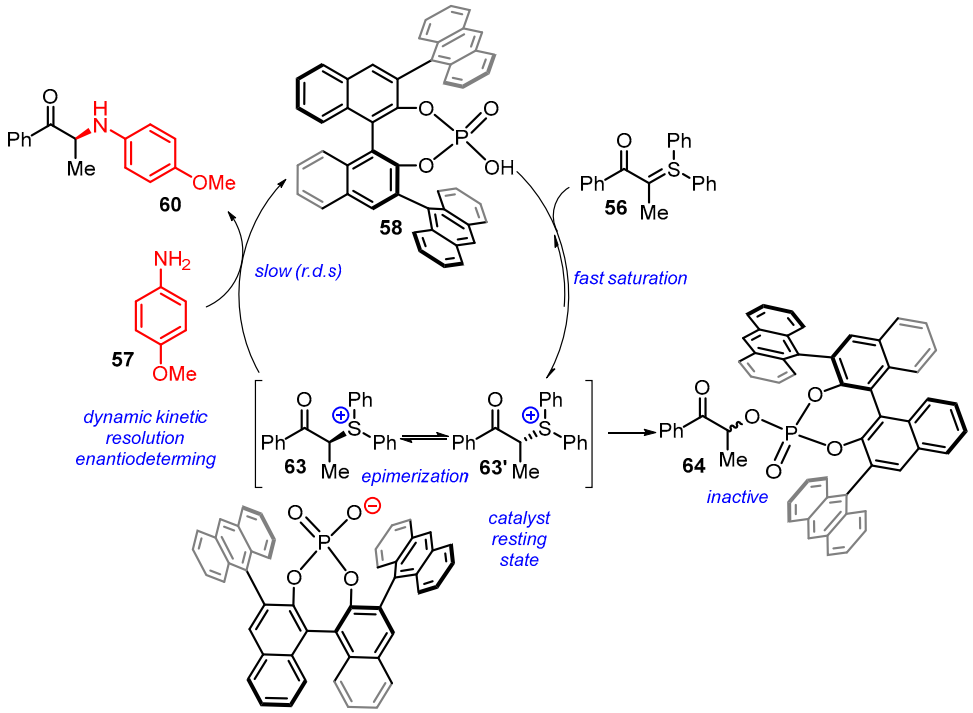
(CPA-*cat*). In the majority of examples (EDG and slightly EWG), a two-step procedure involving the formal N–H insertion reaction catalyzed by CPA-A1-*cat* **58**, followed by a $Cu(OAc)_2$-mediated oxidation, was employed. α-amino ketones **60** (17 examples) were obtained with excellent enantioselectivities (up to 99%). For secondary amines and alkyl groups (R^2) in sulfonium ylides, CPA-A2-*cat* **59** allowed the products **60** (6 examples) and **60′** (7 examples), respectively, in excellent selectivities (up to 96% *ee* and 98% *ee*, respectively), without any additional operation (Schemes 19 and 20). In the case of α-amino esters **60″**, with the Me group at R^2, CPA-A3-*cat* **61** was employed, leading to products with very good selectivities (up to 86% *ee*). However, with longer alkyl groups, the SPINOL catalyst (CPA-A4-*cat* **62**) provided the α-amino esters **60″** in excellent *ee* (up to 95%; Scheme 20). The authors proposed a mechanism starting with the protonation of the sulfonium ylide by CPA-*cat*, leading to the intermediate **63**, which was epimerized to **63′** in equilibrium. The attack of aniline in preferred face furnished product **60**, via dynamic kinetic resolution, with extrusion of Ph_2S and regeneration of the organocatalyst. If the applied aniline is not reactive, the deprotonated CPA-*cat* will dispose of the Ph_2S, leading to an inactive subproduct **64** (Scheme 21) [51].



Scheme 19. Chiral Phosphoric Acid-catalyzed N–H insertion of sulfonium ylides by anilines, with selected examples.

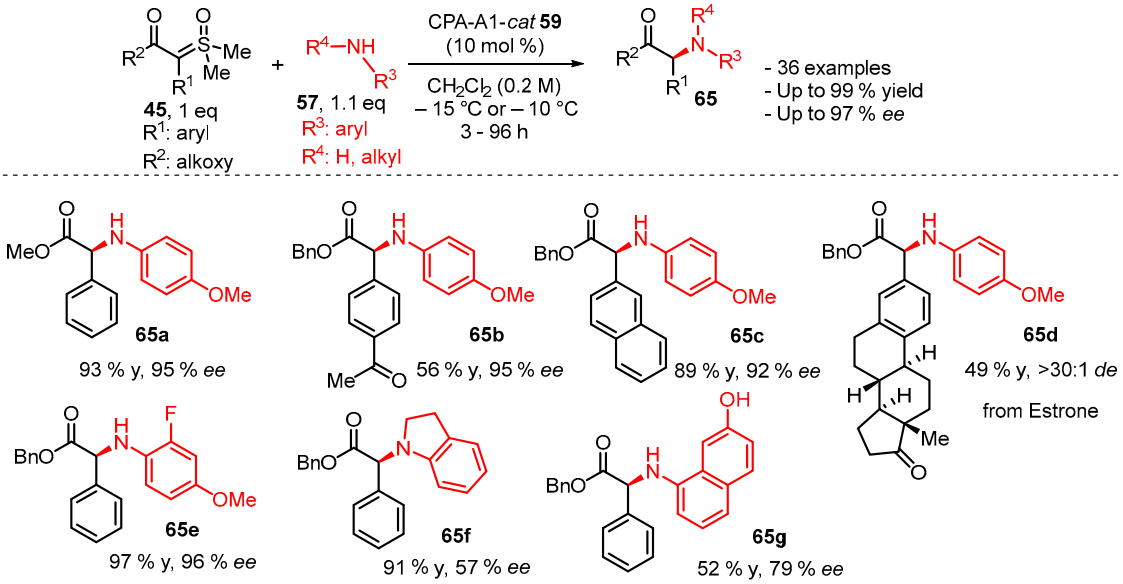


Scheme 20. Chiral phosphoric acid-catalyzed N–H insertion of sulfonium ylides by anilines, with selected examples and catalysts.

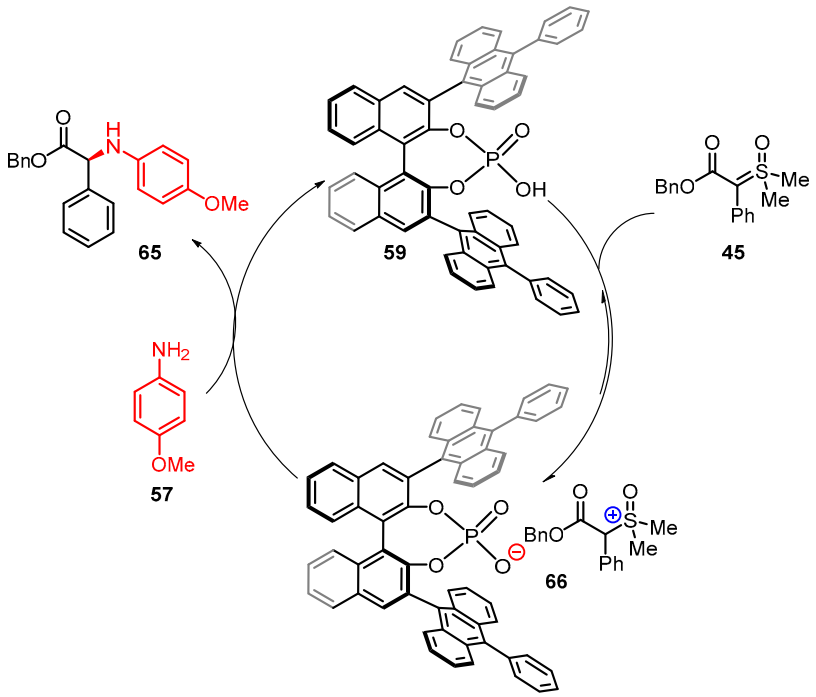


Scheme 21. Proposed catalytic cycle of enantioselective N–H insertion of sulfonium ylide.

In 2021, Sun, Huang, and coworkers reported an organocatalytic N–H insertion using esters of sulfoxonium ylides **45**, unprotected amines **57**, and chiral phosphoric acid catalyst (CPA-A1-*cat* **59**) in CH_2Cl_2 at low temperature to enable enantioenriched *α*-aryl glycines **65** (36 examples) with excellent yields (up to 99%) and enantioselectivities (up to 97% *ee*; Scheme 22). Compared to Burtoloso's N–H insertion work, which used a copper/squaramide co-catalyzed system, this report used a metal-free approach [52,53]. The mechanism proposed by the authors involves protonation of the sulfoxonium ylide with CPA-A1-*cat* **59** in an equilibrium favoring intermediate **66**. The nucleophilic attack of the amine **57** is rate the determing step, providing the product **65** and regenerating the organocatalyst **59** (Scheme 23) [54].

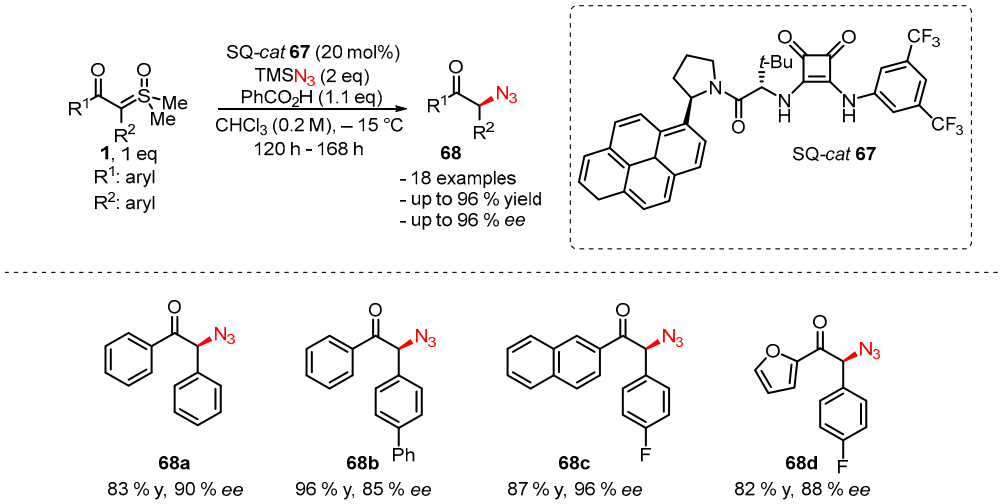


Scheme 22. Chiral phosphoric acid-catalyzed N–H insertion of sulfoxonium ylides by anilines, with selected examples.

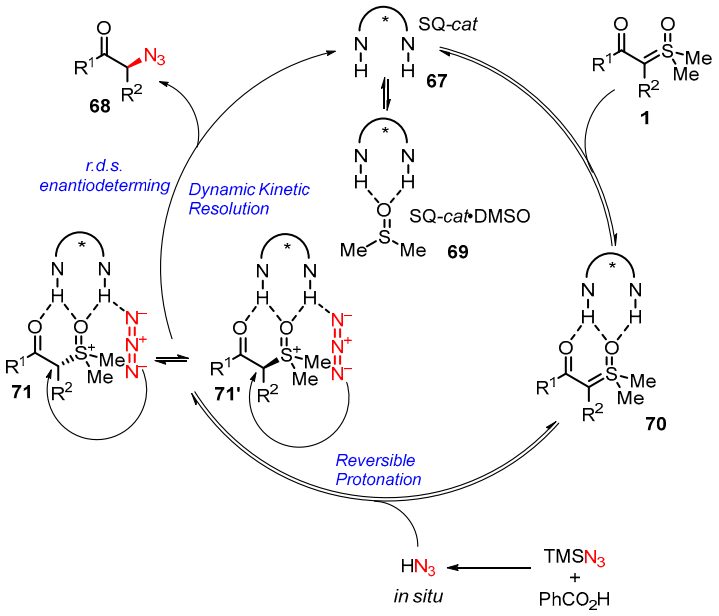


Scheme 23. Proposed catalytic cycle of enantioselective N–H insertion of sulfoxonium ylide.

In 2022, Guo, Sun, and collaborators reported an organocatalyzed azidation of sulfoxonium ylides **1** to afford chiral tertiary azides **68** (18 examples) in excellent yields (up to 96%) and enantioselectivities (up to 96% *ee*). In this reaction, pro-chiral sulfoxonium ylides were employed, and a squaramide organocatalyst (SQ-*cat* **67**), $TMSN_3$, and $PhCO_2H$ were used as reactants to obtain HN_3 in situ. Although acid was involved in the reaction, mechanistic studies showed that no epimerization occurred. The choice of $CHCl_3$ as the solvent and the lower temperature proved to be crucial in obtaining higher enantioselectivity (Scheme 24). The authors proposed a mechanism involving the first hydrogen bonding of SQ-*cat* **67** to sulfoxonium ylide **1**, yielding intermediate **70**, followed by protonation with HN_3. In this case, the step provides two epimerizable intermediates **71** and **71′**, in reversible protonation. The next step, rate determing and enantiodetermining, involves the S_N2 reaction of azide with intermediate **71**, via dynamic kinetic resolution, providing the product **68** and the SQ-*cat* **67**, capable of coordinating with DMSO (SQ-*cat*•DMSO **69**) (Scheme 25) [55].



Scheme 24. Squaramide-catalyzed N–H insertion of sulfoxonium ylides by azides, with selected examples.

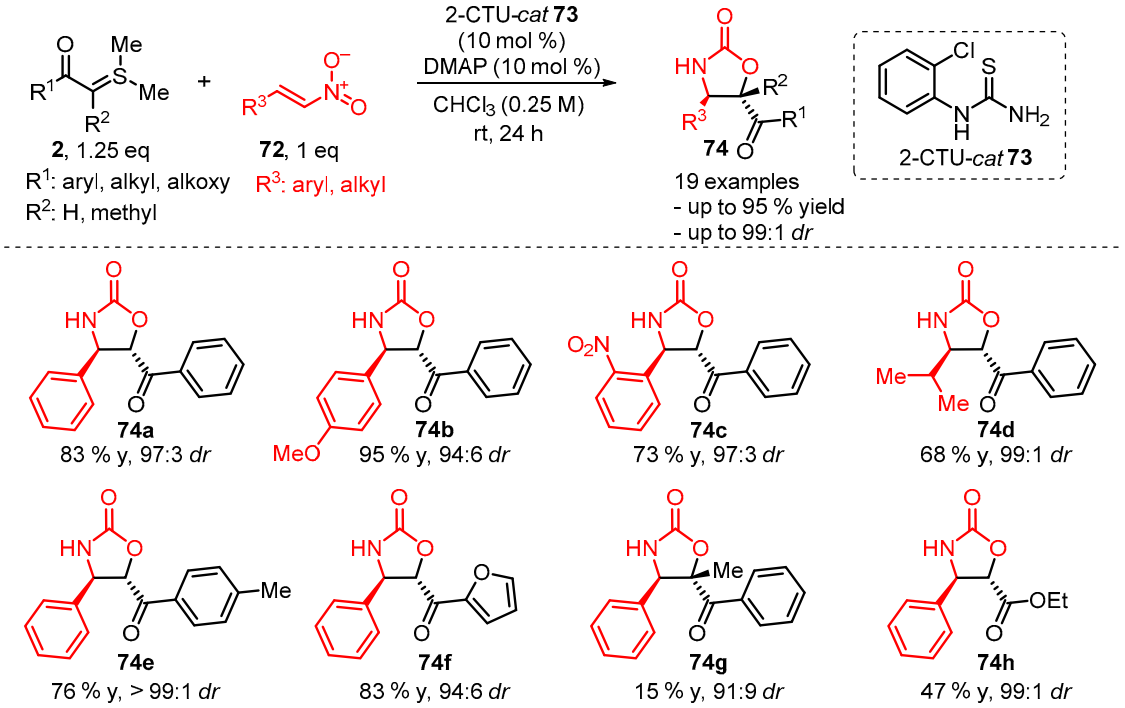


Scheme 25. Proposed catalytic cycle of enantioselective N–H azidation of sulfoxonium ylide.

4. Cyclization

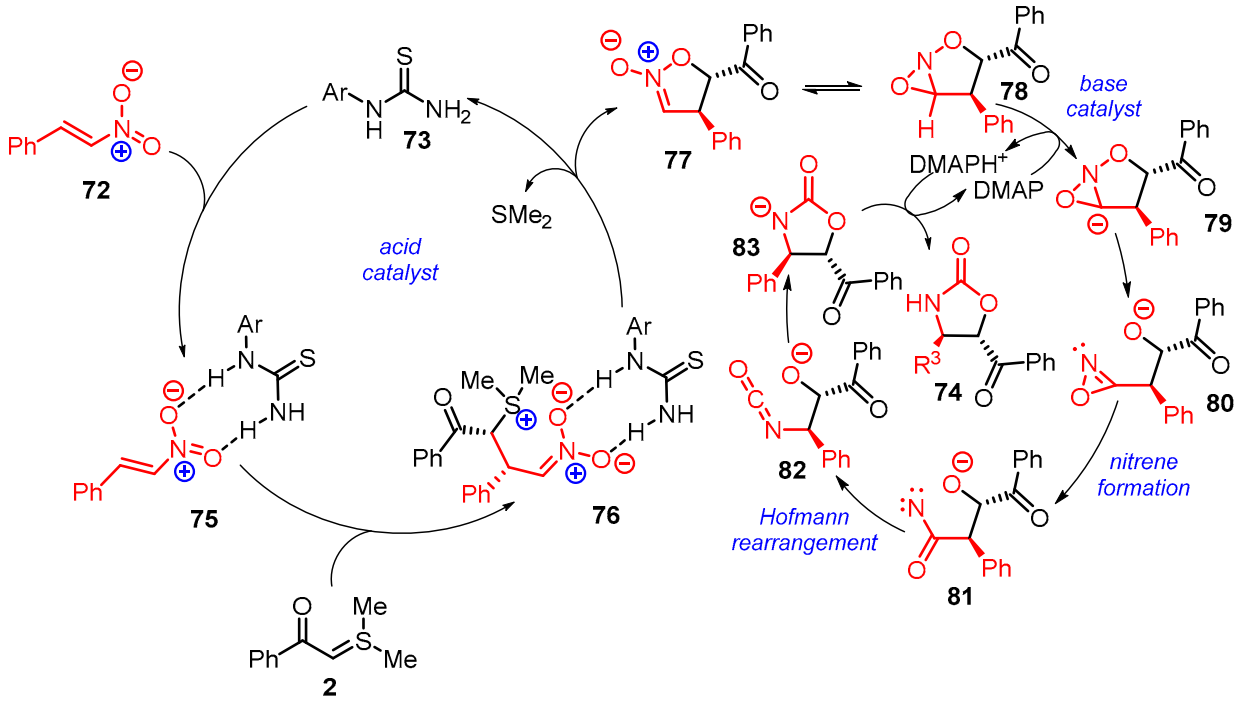
In addition to the Corey–Chaykoysky reaction, formal cyclizations have emerged as powerful methods for obtaining enantioenriched 5- to 6-membered cyclic products using organocatalytic cascade transformations of sulfur ylides [14].

In 2008, Xiao and coworkers reported a urea catalyzed (4 + 1)/rearrangement cascade reaction of sulfonium ylides **2** with nitroolefins **72** that furnished 4,5-disubstituted oxazolidinones **74** (19 examples) in excellent yields (up to 96%) and with excellent diastereoselectivity (up to >99:1 *dr*). It was important to use 2-CTU **73** and DMAP as additives because both promoted the complex formation and rearrangement steps, respectively. This method proved to be tolerant to a wide range of nitroolefins and sulfonium ylides, although substitution at the *α*-carbonyl position of the sulfonium ylide resulted in lower yields (Scheme 26). Their proposed catalytic cycle, supported by NMR and labeling studies, starts with the coordination of 2-CTU-*cat* **73** with nitroolefin to obtain the intermediate **75**. Michael's addition of sulfonium ylide led to Michael adduct **76**, and subsequent intramolecular O-alkylation afforded intermediate **77**, in equilibrium with bicycle **78**. The deprotonation of **78** by DMAP, followed by ring opening, furnishes intermediate **79** and oxazirene **80**, respectively. Ring opening by strain release of the three-membered ring leads to the formation of nitrene **81**, followed by Hofmann rearrangement, yielding isocyanate **82**. The ring-closing reaction and protonation give intermediate **83** and oxazolidinone **74**, respectively (Scheme 27) [56].

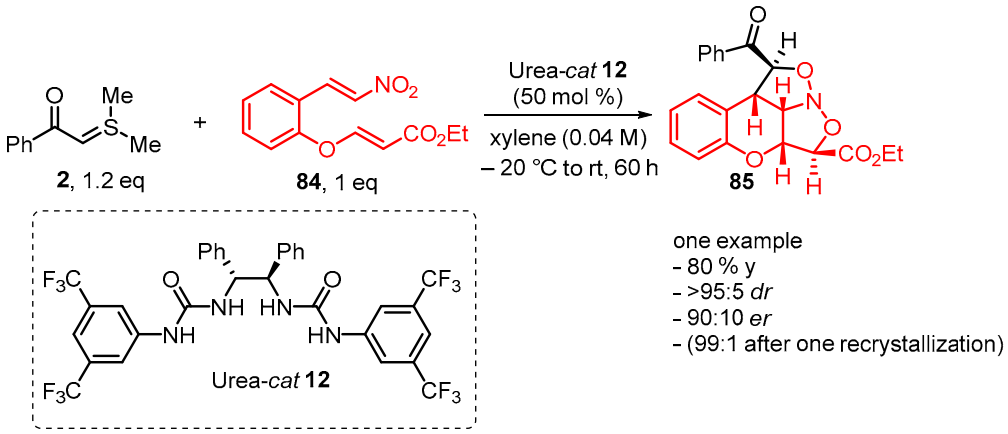


Scheme 26. Thiourea-catalyzed (4 + 1) cyclization/rearrangement cascade reaction with selected examples.

In 2009, as an application of the formal (4 + 1)/(3 + 2) cycloaddition cascade of sulfonium ylide **2** and nitroolefin **84**, Xiao and coworkers employed chiral urea organocatalyst (Urea-*cat*-**12**) in xylene at low temperature to deliver the desired product **85** in 80% yield, 95:5 *dr* and 90:10 *er* (with an increase to 99:1 after one recrystallization). In this reaction, five stereocenters were obtained in one step, and at the time it represented the first successful example of a chiral Brønsted acid catalyzed reaction involving sulfur ylides (Scheme 28) [57].

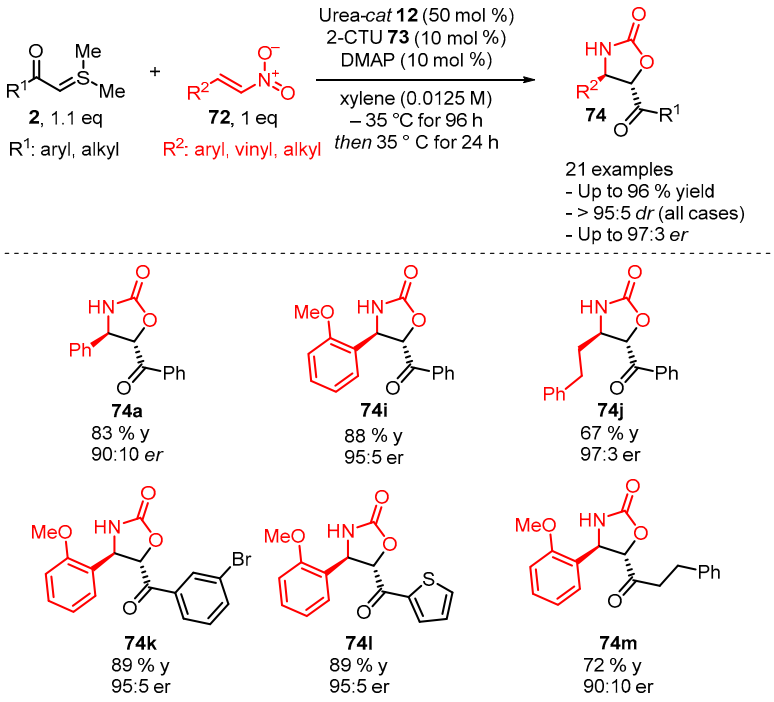


Scheme 27. Proposed mechanism of (4 + 1) cyclization/rearrangement cascade reaction.

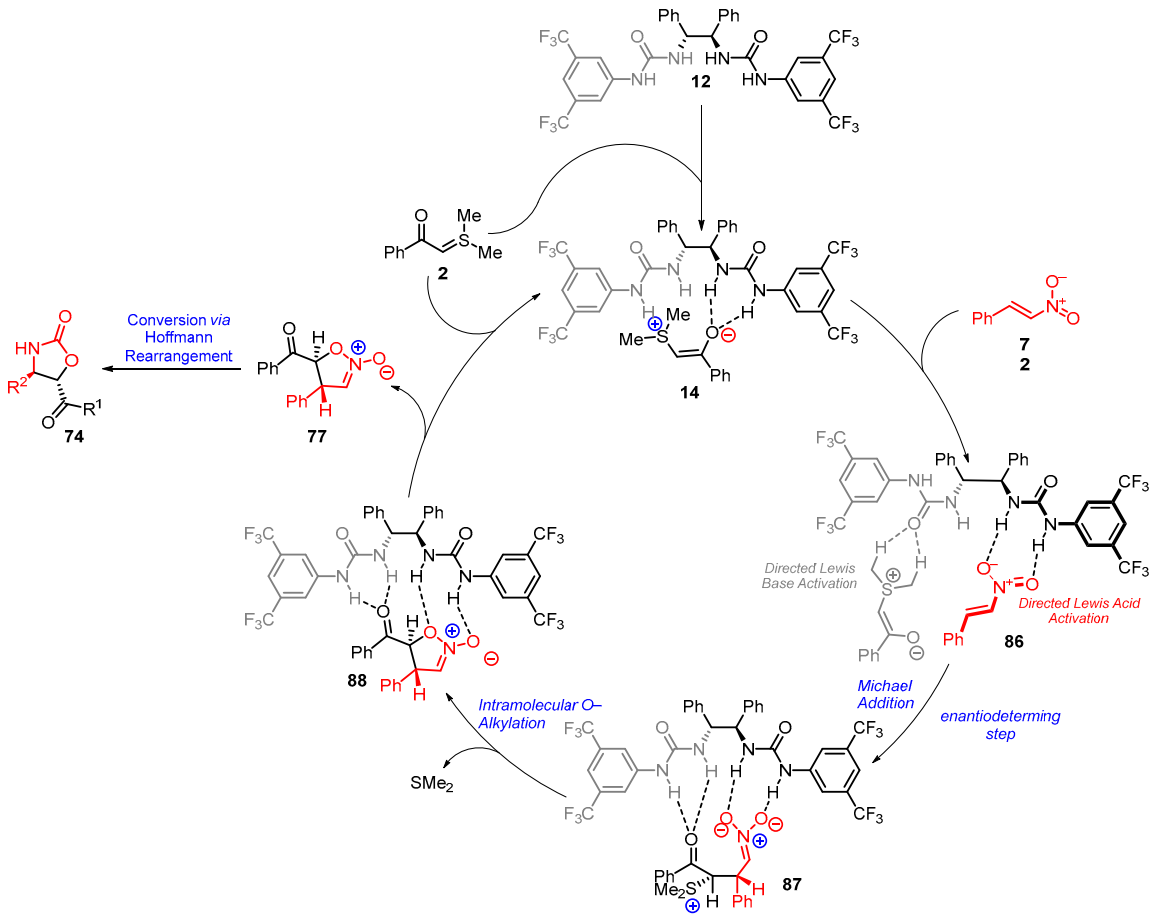


Scheme 28. Enantioselective (4 + 1)/(3 + 2) cycloaddition cascade of sulfonium ylide and nitroolefin.

In 2012, the same group reported a chiral urea-catalyzed (4 + 1)/rearrangement cascade reaction of sulfonium ylide **2** with nitro olefin **72**, affording 4,5-disubstituted oxazolidinones **74** (21 examples) in excellent yields and enantiomeric/diastereomeric ratios. In all cases, 95:5 of the *anti* diastereoisomer was obtained. Temperature control was crucial (Scheme 29). Based on their mechanistic studies, the proposed catalytic cycle involves the formation of a complex between the organocatalyst and sulfonium ylide **14** through strong hydrogen bonding, followed by coordination with nitroolefin **72**. This intermediate **86** undergoes a dual activation by a direct Lewis acid activation of the urea catalyst with nitroolefin and a direct Lewis base activation by sulfur ylide. The next step involves a Michael addition of sulfur ylide to the nitro olefin, leading to the Michael adduct **87** in an enantiodeterming step (followed by intramolecular O-alkylation to give complex **88**). The release of the nitronate intermediate with coordination of the unreacted sulfur ylide **2** regenerates the organocatalyst. Increasing the temperature favors the Hoffmann rearrangement, providing the desired product **74** (Scheme 30) [58].

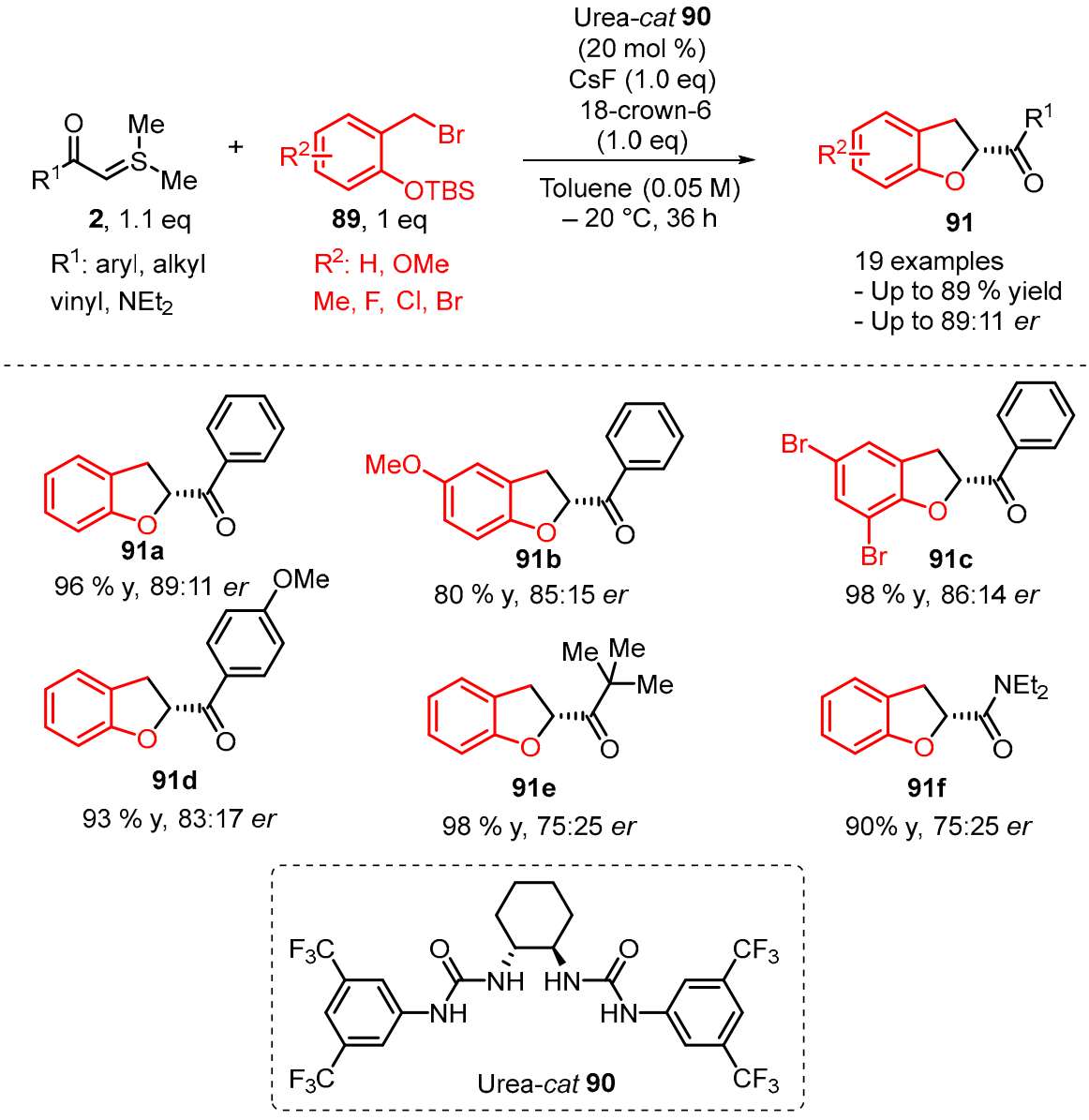


Scheme 29. Urea-catalyzed enantioselective (4 + 1) cyclization/rearrangement cascade reaction with selected examples.



Scheme 30. Proposed mechanism of enantioselective (4 + 1) cyclization/rearrangement cascade reaction.

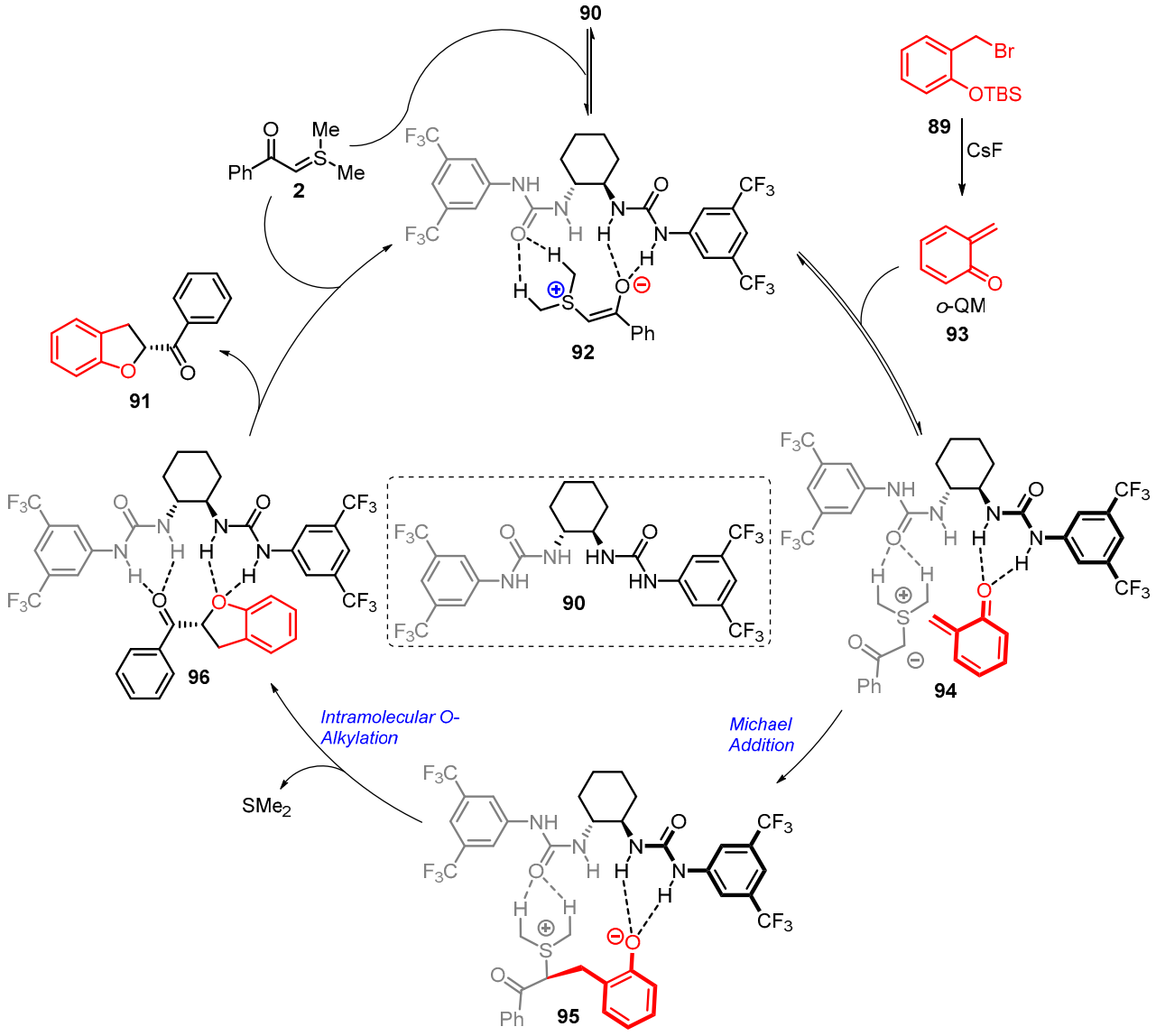
In 2017, Yang and coworkers reported an asymmetric dihydrobenzofuran synthesis from sulfonium ylides **2** and ortho-quinone methide (*o*-QM) generated in situ from halides **89**. A chiral urea organocatalyst (Urea-*cat* **90**) was used to induce stereoselectivity, CsF was used to promote the *o*-QM formation, and 18-crown-6 to enhance fluorine reactivity in toluene at low temperatures. The desired product **91** (19 examples) was obtained with excellent yields (up to 98%) and good selectivity (up to 89:11 *er*; Scheme 31). The authors have proposed a catalytic cycle involving the coordination of urea-*cat* with sulfonium ylide, leading to intermediate **92**, followed by the coordination of *o*-QM **93**, which is formed in situ by treating **89** with CsF, to form complex **94**. The Michael addition, which is the stereoselective step, furnishes intermediate **95**, with subsequent intramolecular O-alkylation and SMe_2 extrusion. This leads to the dihydrobenzofuran product **91** and regenerates the urea-*cat* (Scheme 32) [59].



Scheme 31. Urea-catalyzed enantioselective (4 + 1) formal cyclization of sulfonium ylides and in situ generated *o*-QM.

In 2012, Tong and coworkers developed an amine-catalyzed formal (3 + 3) cycloaddition of 2-(acetoxymethyl)buta-2,3-dienoate **97** with sulfonium ylides **2** to provide 4H-pyrans **98** in yields up to 96%. The allene moiety proved to be critical in this reaction, as cyclization

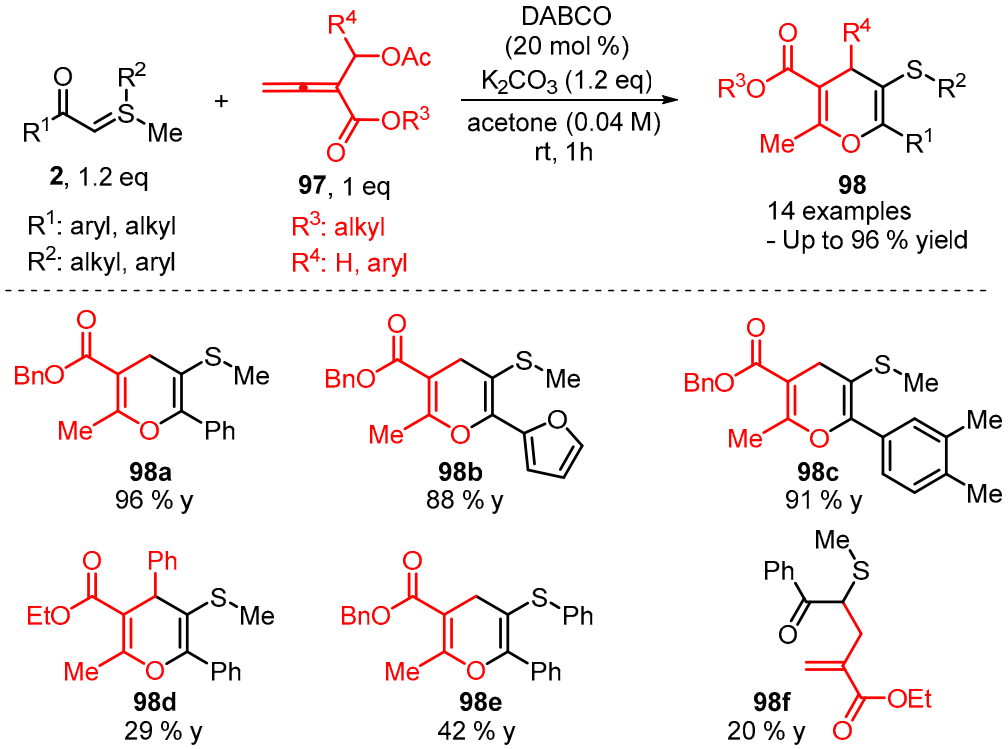
did not occur when olefin **98f** was used instead of allene **97** (Scheme 33). The authors have proposed a mechanism involving an attack of DABCO on allene **97** via S_N2', followed by 1,4-addition with sulfonium ylide **2**, leading to intermediates **99** and **100**, respectively. Instead of the Corey–Chaykovsky cyclopropanation, an 1,2-elimination regenerates the DABCO, and the allene intermediate **101** is obtained. Nucleophilic attack (Br^- or AcO^-) on sulfonium **101** provided sulfide **102** via the S–Me cleavage. Subsequent *oxa*-Michael addition leads to 4H-pyran **98** (Scheme 34) [60].



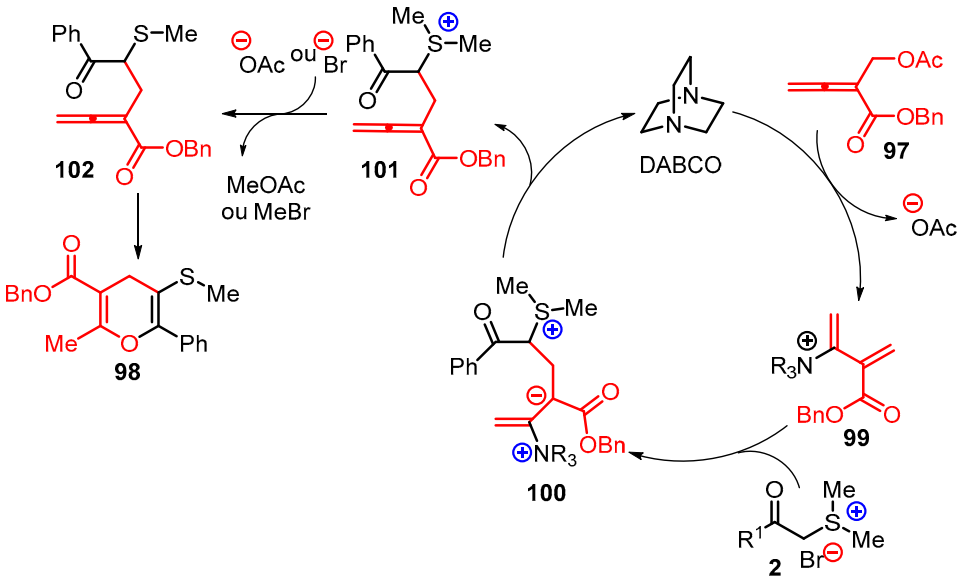
Scheme 32. Proposed mechanism of enantioselective (4 + 1) cyclization reaction.

In 2021, Bernardi and coworkers reported a catalyst- and substrate-dependent chemodivergent reaction between sulfoxonium ylides **1** and salicylaldehydes **103**, yielding 2H-chromenes **105** (for EDG and H in 16 examples) and dihydrobenzofurans **106** (for EWG in 3 examples). In the former case, Brønsted-acid organocatalyst (PA-*cat* **104**) led to 2H-chromenes **105** with good yields (up to 81%). In the latter case, without the use of a catalyst, dihydrobenzofurans **106** were obtained in good yields (up to 85%) (Scheme 35). In these two cases, the proposed mechanism was explained after some control experiments. For EDG and H substituents, the catalytic cycle involves the coordination of PA-*cat* **104** with salicylaldehyde via intermediate **107**, followed by an attack of sulfoxonium ylide **1**, leading

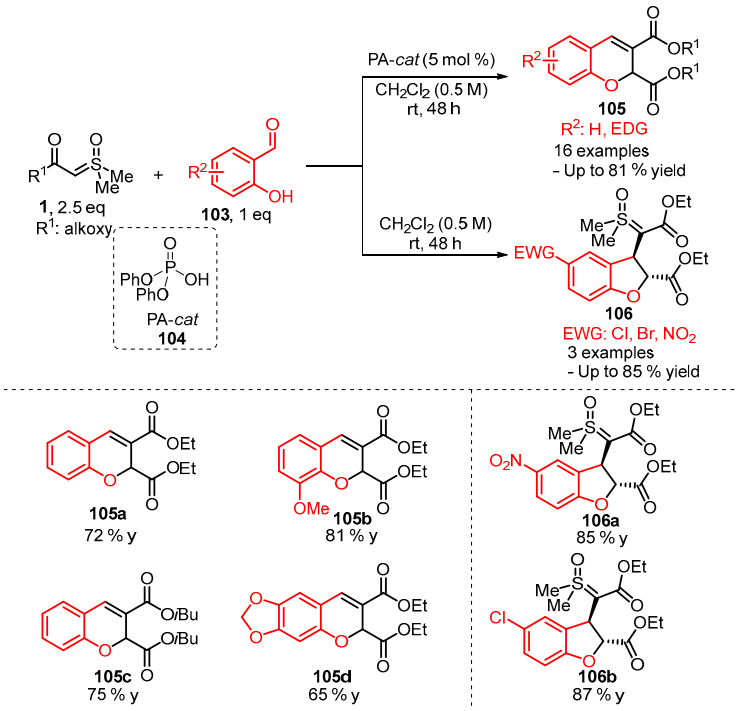
to intermediate **108**. The attack of the second ylide **1** yields the second intermediate **109** with the extrusion of DMSO. The nucleophilic attack of phenol **110** leads to the formation of chromane **111**, which is dehydrated to furnish 2H-chromene **105** (Scheme 36; Pathway a). For EWG, sulfoxonium ylide **1** directly attacks salicylaldehyde **103**. Proton transfer to intermediate **113**, followed by dehydration, yields *o*-QM **114** in situ. A formal (4 + 1) of the *o*-QM intermediate **114** with another equivalent of sulfoxonium ylide **1** led to the formation of dihydrobenzofuran **106** (Scheme 36; Pathway b) [61].



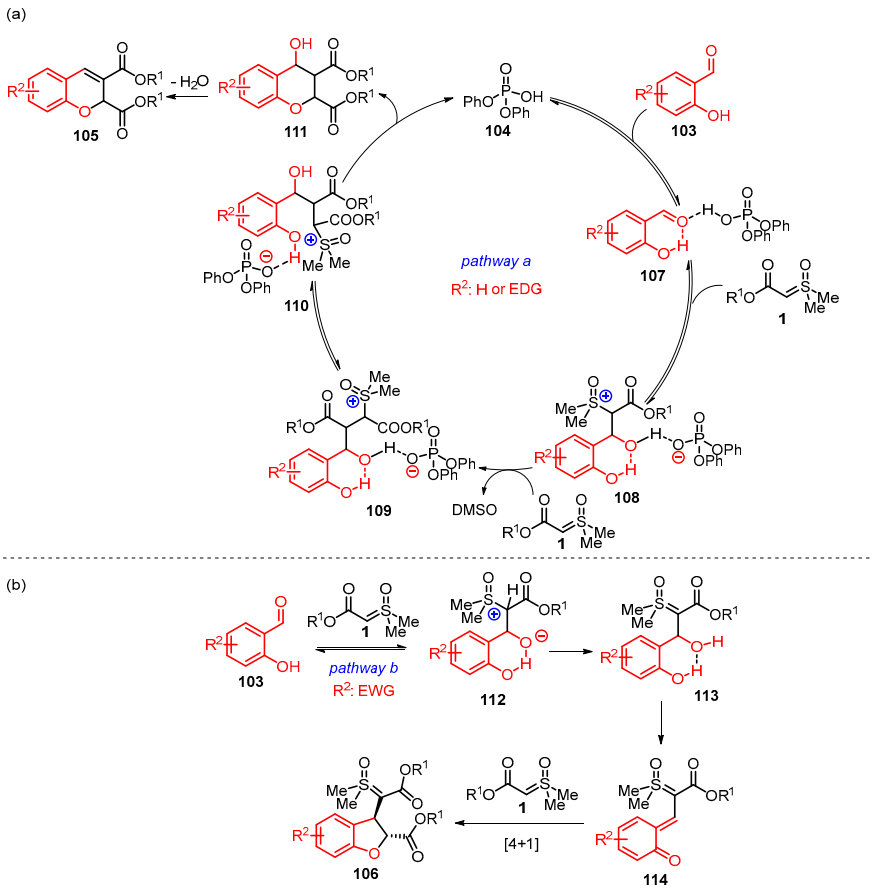
Scheme 33. DABCO-catalyzed formal (3 + 3) cycloaddition with selected examples.



Scheme 34. Proposed mechanism of formal (3 + 3) cycloaddition.



Scheme 35. Phosphoric acid-catalyzed chemodivergent annulations between sulfoxonium ylides and salicylaldehydes.



Scheme 36. Proposed mechanisms of (**a**) 2H-chromene synthesis catalyzed by PA-*cat*; (**b**) dihydrobenzofuran synthesis.

5. Conclusions

Organocatalytic transformations from sulfur ylides have proven to be an essential strategy to obtain enantioenriched products, for example, cyclopropanes, 5- or 6-membered cycles, or even *gem*-disubstituted carbonyl compounds. However, there are potential challenges to be faced. For instance, sulfonium ylides were predominant in cyclization reactions, and sulfoxonium ylides were the best substrates for formal bond insertion reactions. To distinguish the reactivity of sulfur ylides and to expand the scope of methodologies, studies of sulfonium ylides in formal insertion reactions and sulfoxonium ylides in cyclization are required.

Although examples of enantioselective formal X–H insertion reactions were described, asymmetric insertions in X–Y bonds (dihalogenation or fluoration-azidation, for example) are desired. By using different sources of nucleophiles and electrophiles, this type of difunctionalization can increase the degree of functionalization and provide interesting *gem*-difunctionalized carbonyl compounds in a single step [62].

This review [63] has covered organocatalytic transformations of sulfur ylides, indicating the mechanism and the corresponding modes of activation. We intend to inspire the reader to explore this exciting area by developing novel methodologies in organic synthesis with this fascinating class of organic compounds, either by developing new sulfur ylides or organocatalysts with divergent modes of activation.

Author Contributions: Conceptualization, A.C.B.B. and M.H.; writing—original draft preparation, M.H.; writing—review and editing, A.C.B.B.; visualization, A.C.B.B.; supervision, A.C.B.B.; project administration, A.C.B.B.; funding acquisition, A.C.B.B. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane
AcO	acetyl
Å	Angstrom
aq	aqueous
Ar	aryl
Bn	benzyl
Bu	butyl
cat	catalyst
DABCO	1,4-diazabicyclo[2.2.2]octane
Dec	decanyl
DMAP	N,N-4-dimethylaminopyridine
DMSO	dimethylsulfoxide
de	diastereomeric excess
dr	diastereomeric ratio
EDG	electron directing group
ee	enantiomeric excess
eq	equivalent
er	enatiomeric ratio
Et	ethyl
EWG	electron withdrawing group

i	iso
m	mili
M	molar (mol·L^{-1})
Me	methyl
MS	molecular sieves
n	normal
NHC	N-heterocyclic carbene
o	ortho
Ph	phenyl
Pr	propyl
QM	quinone methide
rt	room temperature
t	tert
TBS	tert-butyldimethylsilyl
TMS	trimethylsilyl
y	yield

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