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REVIEW PAPER

Recent advances of organocatalytic enantioselective Michael-addition to chalcone

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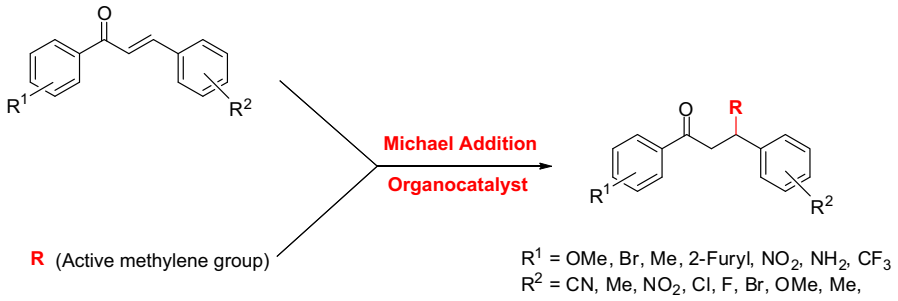
Abstracts This review summarizes wonderful achievements in the field of the organocatalytic enantioselective Michael addition reaction involving nucleophilic attack of nitro alkane, malonates, cyanoacetates, hydroxyamines, malononitrile, thiols, cyanomethylphosphate, butenolide, coumarin, and 1-fluoro-1-nitro (phenylsulfonyl) methane to chalcones. A large number of efficient organocatalytic systems have been used to generate chiral Michael adducts with high enatioselectivity with excellent yield.

Graphical Abstract



Keywords Michael addition · Chalcones · Catalysis · Chiral ligands · Conjugate addition · Enantioselectivity · Distereoselectivity

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Introduction

The Michael addition [1] is the 1,4-addition of a resonance stabilized carbanion to an activated olefins. This is the one of the most powerful methods in organic synthesis for C–C and C–X (X=O, N,S) bond formation. In the case of obtaining a Michael adduct enantioselectively, organocatalytic asymmetric synthesis has been recognized as an important candidate, as a result of the explosive growth of organocatalysis in the past decades [2–5]. Asymmetric Michael addition of chalcones by various nucleophiles using organocatalysts has been well reported in recent years and the Michael adducts obtained were used as valuable intermediates for further reactions. Here, in this review article we have discussed Michael-addition of various nucleophiles such as nitro alkane, malonate, cyanoacetate, hydroxyamine, malononitrile, thiol, cyanomethylphosphate, butenolide, coumarin, 1-fluoro-1-nitro(phenylsulfonyl)methane to chalcones using a variety of catalysts such as cinchona-based, and bifunctional organocatalysts covering from the year 2011–2014 (Fig. 1).

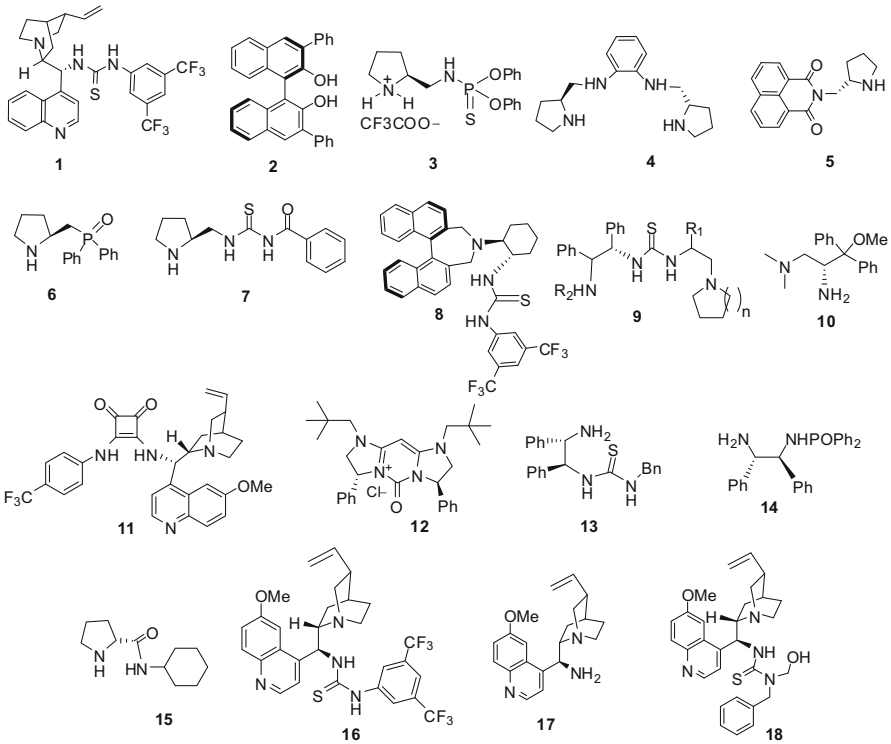


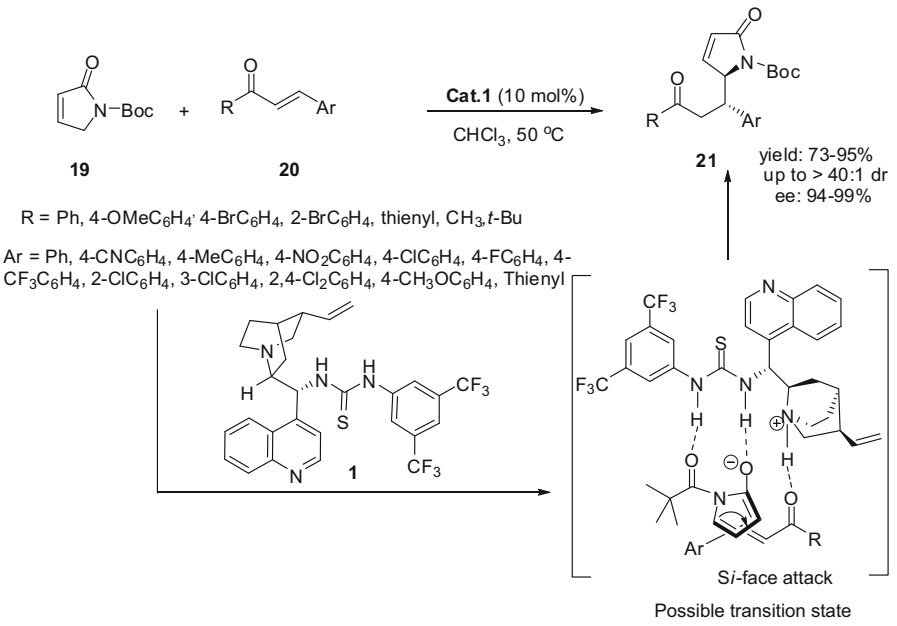
Fig. 1 Organocatalyst **1–18** used for various Michael addition to chalcones

Organocatalytic Michael addition

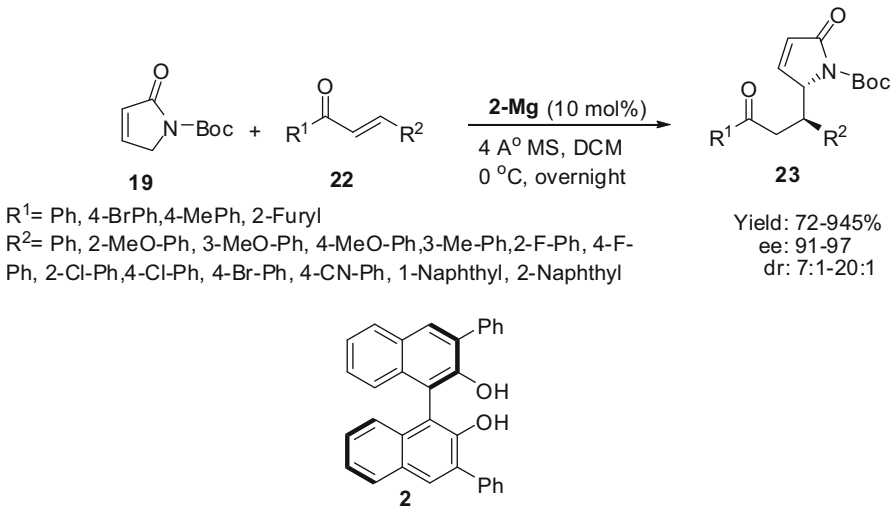
Michael addition of γ-butyrolactam to chalcone

In 2011 Wang et al. [6] disclosed the enantioselective vinylogous Michael addition of α,β-unsaturated γ-butyrolactam **19** to α,β-unsaturated carbonyl **20** catalysed by bifunctional thiourea-tertiary amine catalyst **1** affording the γ-substituted butyrolactam **21** with high diastereo- and enantioselectivity. Interestingly, no acidic co-catalyst was required in this reaction, and excellent results in terms of yield and selectivity were obtained. However, when R was an aliphatic moiety, the reaction did not occur due to low reactivity of the enone substrate. The proposed transition state is more favorable for the stereoselective outcome of **21**. The carbonyl group of the chalcone **20** was activated by the N–H proton of ammonium through a hydrogen bond and the thiourea coordinated to **19**. The *Si*-face attack provided the desired product (5*R*, 6*R*)-**21** (Scheme 1).

Chen et al. [7] and Ye et al. [8] reported previously organocatalytic asymmetric vinylogous Michael addition of α,β-unsaturated γ-butyrolactams to α,β-unsaturated aldehydes as well as enones. Since the alkaline earth metal has been well recognized for its vast abundance and being inexpensive as well as relatively nontoxic compared to transition metals, Wang and co-workers [9] reported the asymmetric vinylogous Michael additions of α,β-unsaturated γ-butyrolactam **19** to chalcones **22** in combination with a chiral bifunctional 3,3′-Ph_2-BINOL-Mg catalyst, which furnished the products **23** with exceptional diastereo- and enantioselectivity (Scheme 2).



Scheme 1 Enantioselective direct vinylogous Michael addition of α,β-Unsaturated γ-Butyrolactam **19** to Chalcones **20** catalysed by **1**

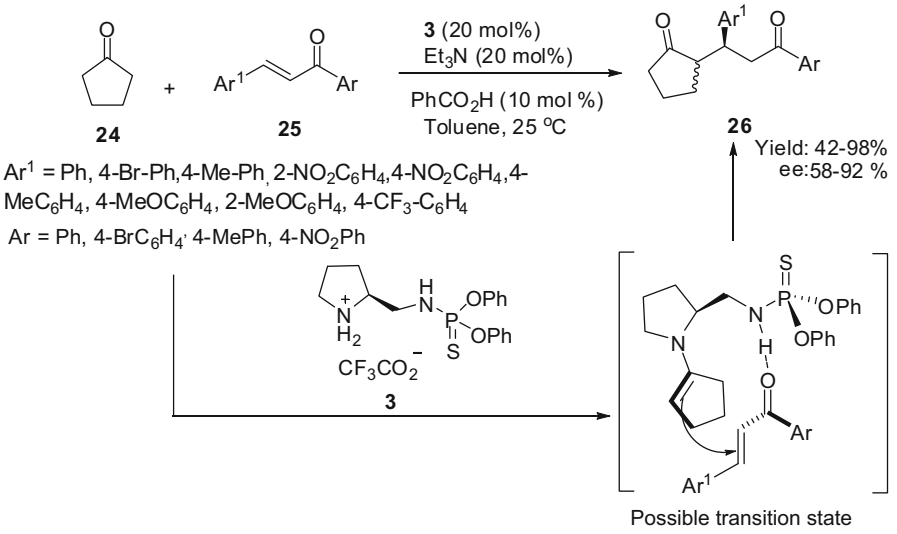


Scheme 2 Enantioselective direct vinylogous Michael addition of α,β-Unsaturated γ-Butyrolactam **19** to α,β- unsaturated carbonyl **22** catalysed by **2**

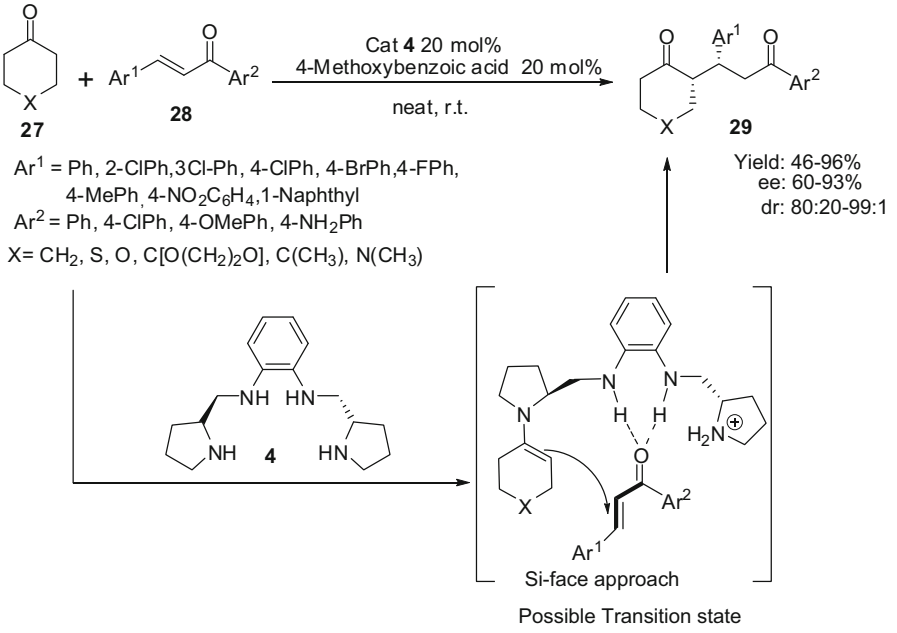
Michael addition of cyclic ketone to chalcone

Wang and Zhou [10] established the conjugate addition of cyclopentanone **24** to chalcone **25** catalysed by a chiral bifunctional thiophosphoramide catalyst **3** (Scheme 3). Using 20 mol % of catalyst, the reaction of different chalcones proceeded smoothly to afford the corresponding adducts **26** with moderate to excellent diastereo- and enantioselectivities. Unsubstituted chalcone gave the conjugate addition product with a high level of enantioselectivity (92 % *ee*). The introduction of a substituent on either Ar or Ar^1 led to the decrease in enantioselectivity, affording the desired product with only moderate *ee* values (ranging from 58 to 71 % *ee* for the major diastereomer). Although the electronic nature of the substituents on Ar^1 in the chalcones did not influence the enantioselectivity, the diastereoselectivity of the reaction was significantly influenced by the nature of the substituent on Ar^1. Generally an electron donating group is favourable for anti-selectivity of the reaction, while the introduction of an electron withdrawing group on Ar^1 resulted in a marked decrease in diastereoselectivity (Scheme 3). In the transition state **3** behaves as a bifunctional catalyst. The pyrrolidine ring of **3** first reacts with cyclopentanone to form an enamine with the aid of benzoic acid. Subsequently, the acidic hydrogen activated and orientated the carbonyl group of chalcones **25** through a hydrogen-bonding interaction so that the enamine will undertake preferentially a nucleophilic attack from its *Re*-face onto the *Re*-face of the chalcones to give the (*S*,*S*)-product as the major stereoisomer.

Wang et al. reported [11] that the asymmetric Michael addition of cyclic ketones **27** to chalcones **28** using a C2-Symmetric proline derived tetraamine **4** catalyst provided Michael adduct **29** in good yields with high levels of diastereo- and enantioselectivities under mild conditions (Scheme 4). The stereochemical outcome



Scheme 3 Asymmetric Michael addition of cyclopentanone **24** to chalcones **25**

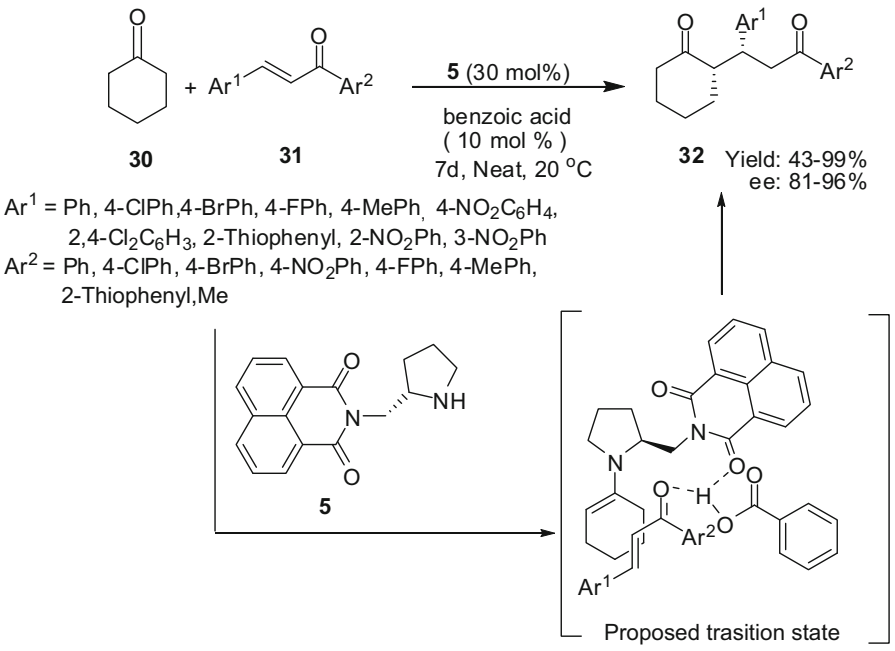


Scheme 4 Michael addition of cyclic ketones **27** to chalcones **28**

was explained from the transition state of Scheme 4. Protonated catalyst **4** first forms a chiral enamine with ketones **27**, and then a Michael reaction between the activated enamine and the chalcones **28** in the *Si*-face approach leads to the formation of the corresponding products **29**.

To induce the potential catalytic activity, Li et al. [12] introduced pyrrolidine-based 1,8-Naphthalimide catalyst **5** for asymmetric Michael addition reaction of cyclic ketones **30** to chalcones **31**. Moderate to excellent diastereoselectivities and enatioselectivities were obtained for this catalyst system **5**. The presence of a Bronsted acid with proper acidity, such as benzoic acid was shown to be critical for the excellent performance of this catalyst system. Reactions with six-membered ring ketones gave the Michael adducts with excellent enantioselectivities (92–94 % *ee*). But when cyclopentanone, cycloheptanone, and acetone were used as substrate, only reasonable enatioselectivity was obtained. The stereochemical outcome was well determined from the transition state (Scheme 5). The catalyst **5** first forms enamine by reaction with **30** in the presence of Bronsted acid (benzoic acid), in which the imide carbonyl oxygen atom plays an important role in shielding the *Si*-face of the enamine double bond and activating the chalcones **31**.

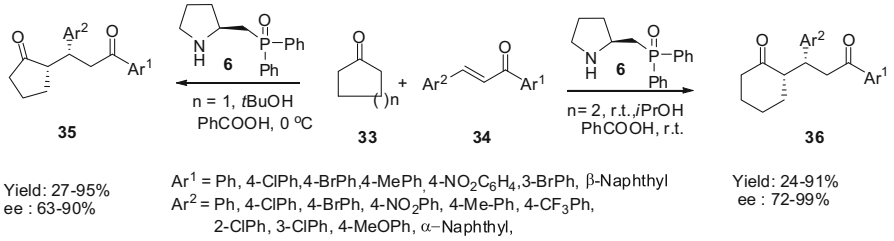
In 2013, Li et al. [13] disclosed the organophosphane catalysed direct Michael addition of cyclicketones to various weakly active chalcone acceptors. The reaction was catalysed by **6**, giving rise to corresponding adducts with good yields and high diastereo- and enantio-selectivities. In marked contrast, insertion of an electron-withdrawing group on Ar^2 of chalcones favored an increased yield whereas an electron-donating group resulted in a significant decrease in yield. Both cyclohexanone and cyclopentanone reacted efficiently with various chalcones in the presence of this catalyst. The diastereoselectivities of Michael addition between cyclopentanone and chalcones are lower than the Michael addition of the cyclohexanone with chalcones. This is due to the ring strain in the five membered ring.



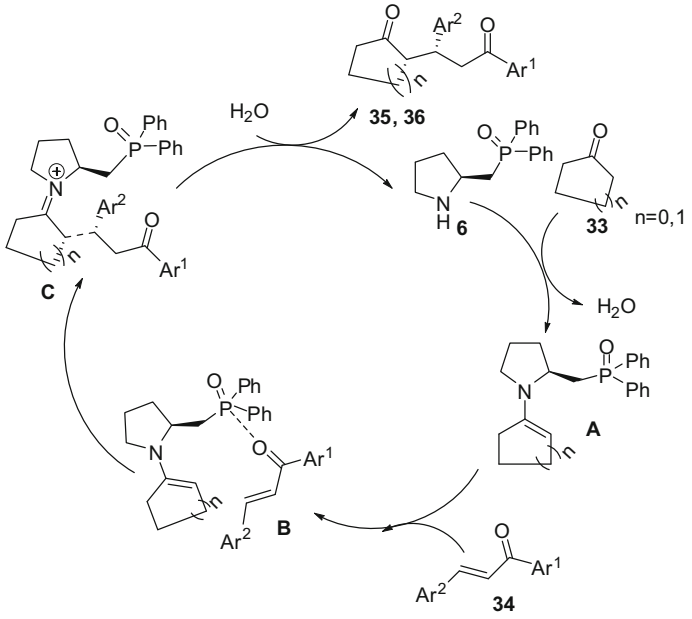
Scheme 5 Catalytic asymmetric Michael addition of cyclohexanone **30** to chalcones **31**

Mechanistically the cyclic ketones **33** would be activated and form the enamine intermediates **A** with organocatalyst **6**. Simultaneously, the chalcones **34** would associate with the organocatalyst to form the intermediates **B** through electrostatic interaction between the polarized P=O bond and the chalcone carbonyl oxygen atoms. The enamines would further attack the activated chalcone carbon–carbon double bonds via an intermediate **C** to give the final products **35** and **36**, simultaneously releasing the organocatalyst **6** (Schemes 6, 7).

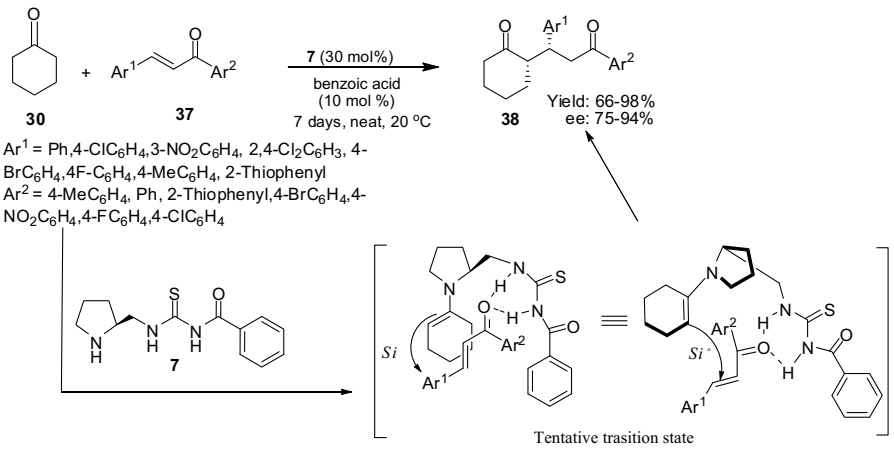
The asymmetric addition of simple cyclic ketones with chalcones catalyzed by organocatalysts remains a synthetic challenge probably due to the low reactivity and high steric hindrance of the substrates. To overcome this synthetic challenge, Li and his co-workers [12] in 2012 utilised a pyrrolidine-based imides catalysis mode to establish the asymmetric Michael addition reaction of cyclic ketones to chalcones. The same group [14] in 2014 discovered a related process using benzoylthiourea–



Scheme 6 Asymmetric Michael addition of cyclic ketones **33** to chalcones **34** catalyzed by an organophosphane based on proline **6**



Scheme 7 Catalytic cycle and the proposed mechanism for Michael addition catalyzed by organocatalyst **6**



Scheme 8 Catalytic asymmetric Michael addition of cyclohexanone **30** to chalcones **37** by using organocatalyst **7**

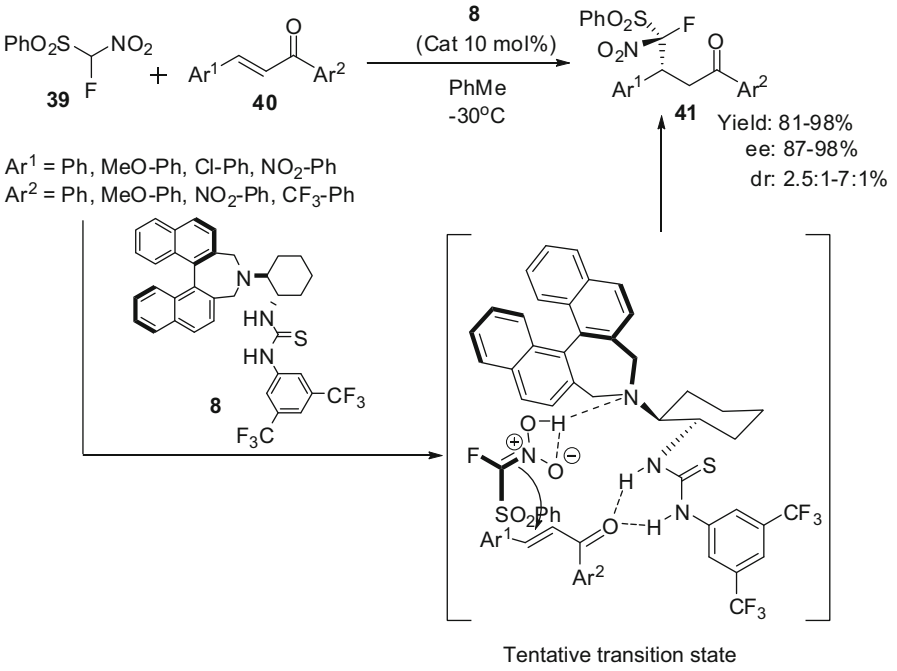
pyrrolidine catalyst **7**, with benzoic acid as the additive, affording the desired products **38** with excellent yields and high diastereo- and good enantioselectivities. The nature of the substituent on the benzene ring exhibited a slight influence on the reaction rate and yield, when an electron donating substituent was present in the benzene ring, low yield was obtained. The stereochemical outcome was explained by the tentative transition state of Scheme 8. In the transition state, catalyst **7** act as a bifunctional catalyst. The pyrrolidine reacted with carbonyl compounds **30** to form an enamine and the benzoylthiourea activated to the chalcones **37** via N–H hydrogen bonds. The enamine attacked the chalcones from the *Si*-face to afford the product **38** (Scheme 8).

Michael addition of 1-fluoro-1-nitro (phenylsulfonyl)methane to chalcones

Kim et al. [15] in 2012 developed a highly enantioselective catalytic conjugate addition reaction of 1-fluoro-1-nitro (phenylsulfonyl) methane FNSM **39** to chalcones **40** derivatives using a binaphthyl-derived tertiary amine-thiourea organocatalyst **8** (Scheme 9). Maximum yield and enantioselectivities (94 % yield, 98 % *ee*) were obtained (Ar^1 = Ph, Ar^2 = 4-CF_3Ph) when toluene was used as solvent, and the reaction was carried out at −30 °C. The stereochemical outcome and reaction rate were proposed from the tentative transition state of Scheme 9. The carbonyl group of the chalcone **40** is activated by the thiourea moiety of catalyst **8** through hydrogen bonding, and the FNSM (**39**) is activated by the basic nitrogen atom in tertiary amine resulting in the stereochemical outcome of **41**.

Michael addition of 5H-oxazol-4-ones to chalcone

Ye et al. [16] reported the successful effective diastereoselective and enantioselective Michael addition of 5*H*-oxazol-4-ones **42** to α,β-unsaturated ketones **43**



Scheme 9 Catalytic asymmetric Michael addition of 1-fluoro-1-nitro(phenylsulfonyl)methane **39** to chalcones **40** catalyzed by binaphthyl-derived organocatalyst **8**

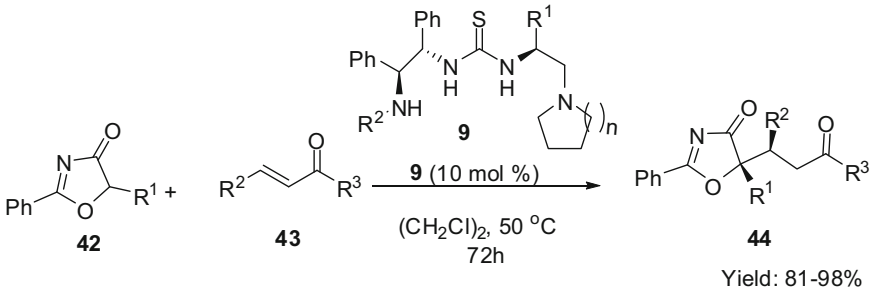
catalyzed by a *L*-tertleucine derived chiral thiourea–tertiary amine organocatalyst **9**. With a catalyst loading of 10 mol%, the Michael adduct **44** obtained high yields with good diastereoselectivities and enantioselectivities (Scheme 10). In the case of chalcones, the reaction proceeded very well with perfect stereoselectivity and only a single isomer (>30:1 *dr* and >99 % *ee*) was obtained whereas the reactions of aliphatic α,β-unsaturated ketone showed a slightly low reaction rate.

Michael addition of rhodanine to chalcone

The same group also extended this approach by introducing chiral primary amine catalyst and applied in the direct diastereo and enantioselective Michael addition of substituted rhodanines to α,β-unsaturated ketones. In the presence of catalyst **10**, chalcone underwent this reaction smoothly, affording the desired products **47** in good yields and high enantioselectivities with excellent diastereoselectivities (Scheme 11) [17].

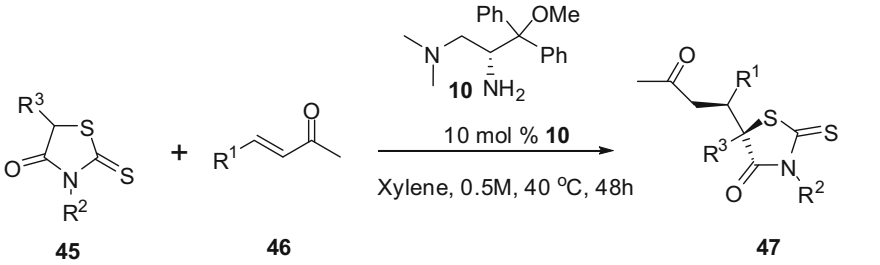
Michael addition of malononitrile to chalcone

In the pioneering investigation done by Du et al. [18] in 2012, there was reported a highly enantioselective Michael addition of malononitrile **48** to chalcones **49** by a chiral quinine-derived squaramide **11** (0.5 mol%) catalyst under mild reaction



R^1= Me,Et, *n*-Pr, *i*-Pr
R^2 = Ph, Me, -$(CH_2)_3$-, 2-$MeOC_6H_4$,3-$MeOC_6H_4$,3-MeC_6H_4, 4-FC_6H_4, Styryl, Hexyl, 2,3-$(MeO)_2C_6H_3$, 3-BrC_6H_4, 4-BrC_6H_4, 2-ClC_6H_4,4-ClC_6H_4, 2-Naphthyl, 2-furanyl, 4-ClC_6H_4,3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 2-Thiophenyl,
R^3 = Ph,Me, *i*-Pr,Bu

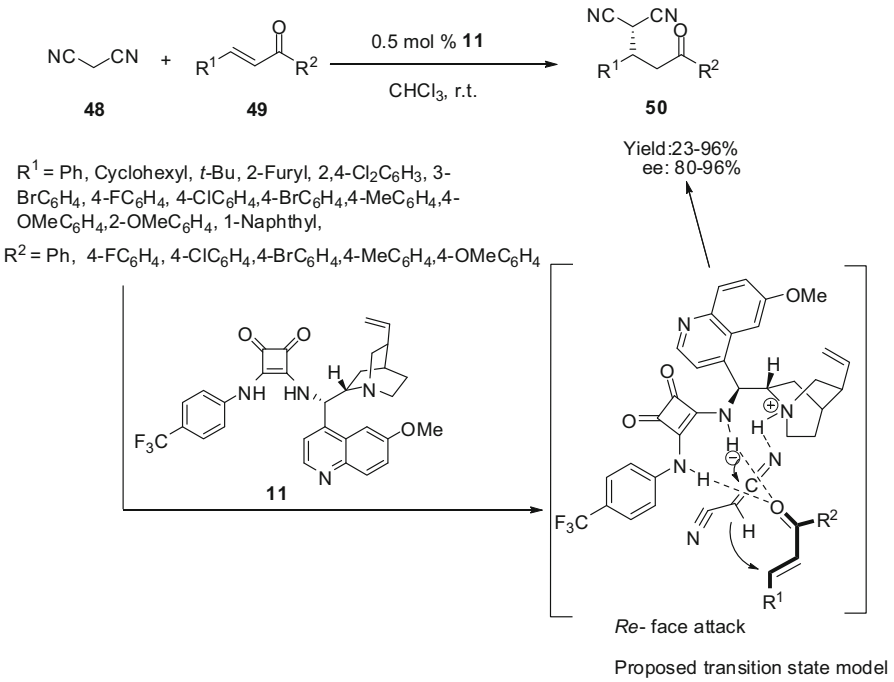
Scheme 10 Direct Michael addition of various 5H-oxazol-4-ones **42** and α,β-unsaturated ketones **43** using organocatalyst **9**



R^1 = Ph, *p*-MePh, *m*-CH_3OPh, *m*-Br Ph, *p*-Cl Ph, *o*-NO_2Ph, Nap, 2-thiophenyl, 2-furanyl,CH_3, $PhCH_2CH_2$, *E*-Ph CH=CH, *p*-BrPh, *p*-NO_2Ph
R^2 = Ph, *p*-CH_3OPh, Bn, *i*-Pr
R^3 =CH_3, C_2H_5, *i*-Pr

Scheme 11 Direct Michael reaction of rhodanine **45** to α,β unsaturated ketones **46**

conditions resulting in the synthesis of **50** in high yield and good enantiomeric excesses. A possible transition-state model for the catalytic reaction of chalcone **49** and malononitrile **48** is hypothesized and shown in Scheme 12. The chiral squaramide **11** may act as a bifunctional catalyst. Malononitrile **48** is deprotonated by the basic nitrogen atom of the tertiary amine. Meanwhile, the squaramide moiety as a Bronsted acid activates chalcone **49** through double hydrogen bonding. The deprotonated malononitrile attacks the activated chalcone from the *Re*-face to afford the *S*-configured product **50**.



Scheme 12 Asymmetric Michael addition of malononitrile **48** to chalcones **49**

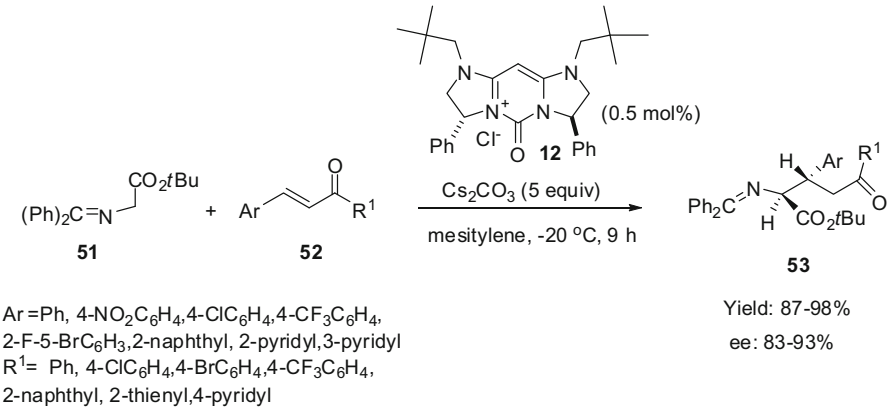
Michael addition of glycine imine ester to chalcones

Hii et al. [19] in 2013 independently reported an efficient asymmetric Michael addition of glycine imine ester **51** to chalcones **52** by utilizing 2-oxopyrimidinium salt **12** as catalyst. The reaction proceeded in high yields with high enantioselectivity (Scheme 13). Although the catalyst contains only planar nitrogen moieties, they are entirely devoid of Bronsted basicity. This reaction has a greater scope for base labile moieties.

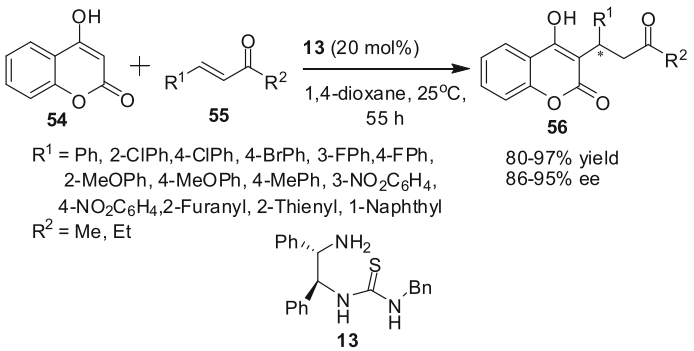
Michael addition of coumarin to chalcones

In 2011 Wang et al. [20] reported the highly asymmetric Michael addition of α,β-unsaturated ketones **55** to 4-hydroxycoumarin **54** catalysed by chiral primary amine thiourea bifunctional catalyst **13** affording **56** in high yields with excellent enantioselectivities (Scheme 14).

In 2012, Du et al. [21] demonstrated that employing 4-hydroxycoumarin **54** to α,β-unsaturated ketone **57** catalyzed by primary amine–phosphinamide bifunctional catalysts **14** led to the formation of corresponding Warfarin analogues **58** with moderate to excellent yields and good to excellent enantioselectivities under mild conditions. According to the absolute configuration of Warfarin analogues **58**, a



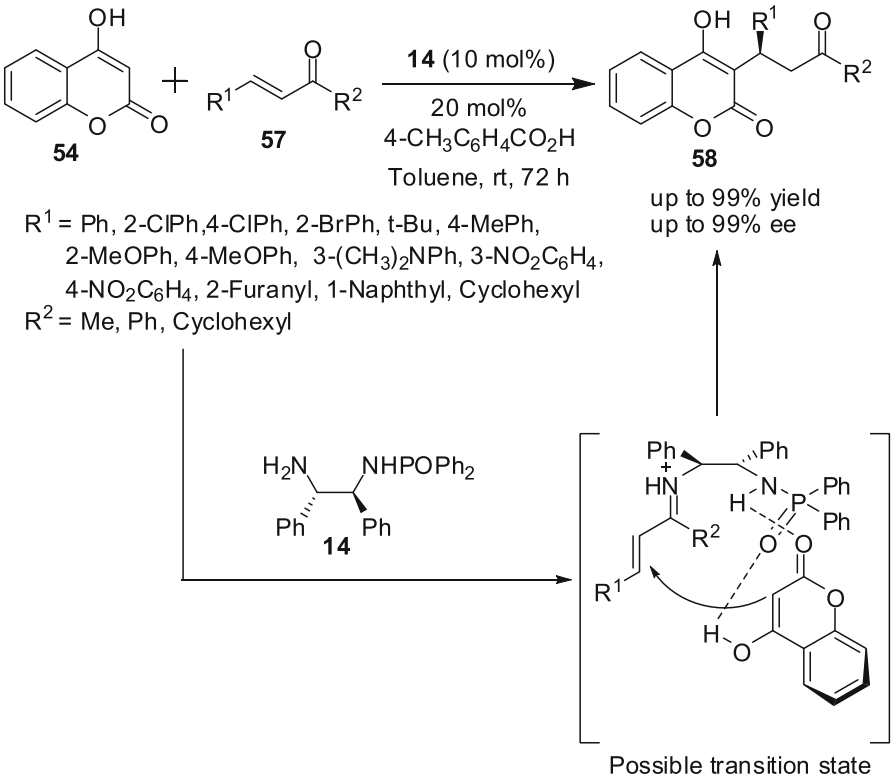
Scheme 13 Conjugate addition of **51** to a chalcone derivatives **52**



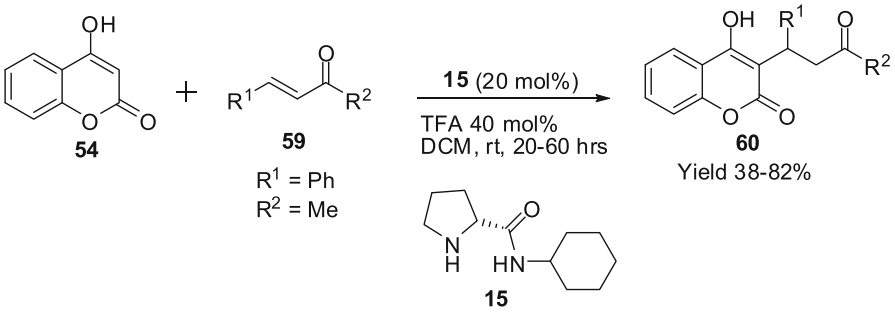
Scheme 14 Asymmetric Michael addition of α,β-unsaturated ketone **55** to 4-hydroxycoumarin **54**

possible transition state model was proposed (Scheme 15). An iminium ion intermediate was formed by reaction with the primary amine of the catalyst **14** and the unsaturated enone. The 4-hydroxycoumarin was activated through hydrogen bonding interaction with the P=O group. The P=O group was also working as a Lewis base for deprotonation of acidic hydrogen, and enhancing the nucleophilic ability of 4-hydroxycoumarin **54**. (R)-Warfarin analogue **58** was obtained through the attack of 4-hydroxycoumarin to the *Re*-face of the iminium ion.

Sabir et al. [22] in 2013 reported a Michael addition reaction between substituted α,β-unsaturated ketones **59** and 4-hydroxy coumarin **54** by proline derived organocatalyt **15**. The yield of the Michael adduct **60** was improved by the variation of mol% of catalysts and solvents. The maximum yield was obtained for 20 mol% **15** in DCM while TFA was used as a co-catalyst. Maximum yield of products were obtained when methyl and phenyl groups were selected as the substituents on α, β-unsaturated ketones (Scheme 16).



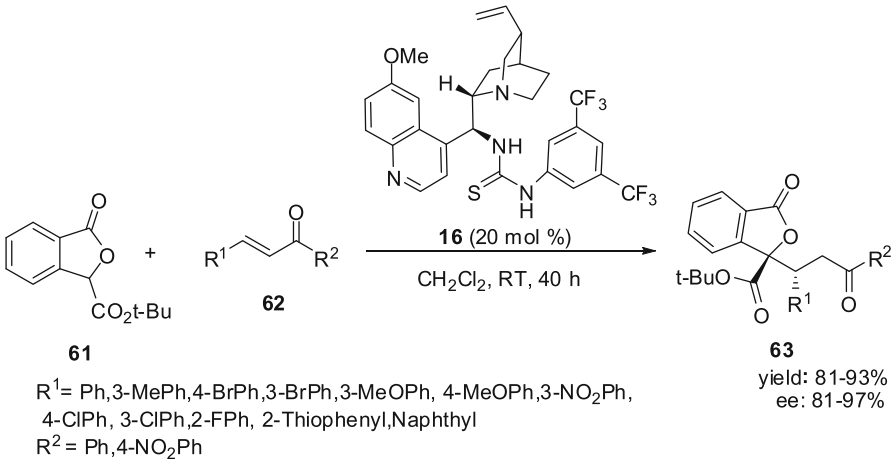
Scheme 15 Conjugate addition of 4-hydroxycoumarin **54** to α,β-unsaturated ketone **57** using organocatalyst **14**



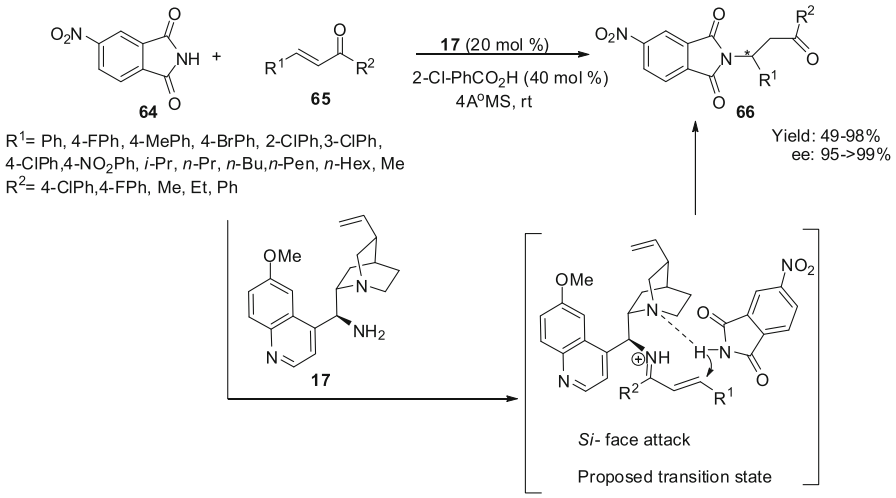
Scheme 16 Conjugate addition of Coumarin **54** to the chalcone derivatives **59**

Michael addition of phthalides to chalcones

Lu and co-workers [23] established the asymmetric conjugate addition of phthalides **61** to chalcones **62** catalysed by a chiral bifunctional amine-thiourea catalyst **16**.



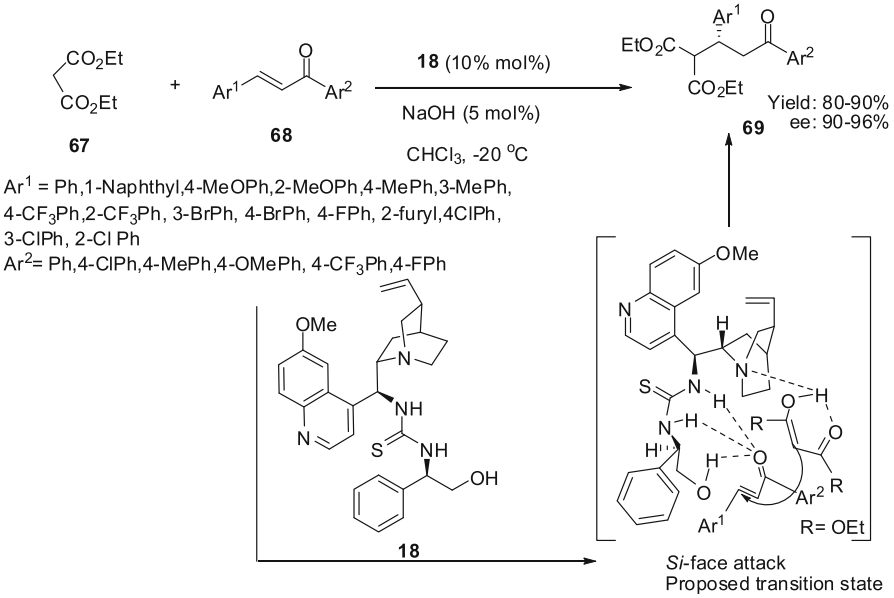
Scheme 17 Direct asymmetric Michael addition of phthalide derivatives **61** to chalcones **62**



Scheme 18 Asymmetric organocatalytic aza-Michael addition reactions of 4-nitrophthalimide **64** to α,β-unsaturated ketones **65**

The reaction resulted in a single diastereomeric Michael adduct **63** and with excellent yield and enantioselectivities (Scheme 17).

In 2013, Huang and Wang et al. [24] reported the aza-Michael addition reactions of nitrophthalimide **64** to α,β-unsaturated ketones **65** using catalyst 9-epi-9-amino-9-deoxyquinine **17**. The reaction provided the corresponding adducts **66** with moderate to high yields and up to high enantioselectivities. In the proposed transition state (Scheme 18), **64** bind to the basic group of the catalyst **17** through hydrogen-bonding interactions (N–H–N) more easily, activating the nitrogen



Scheme 19 The asymmetric Michael reaction of diethyl malonate **67** to chalcones **68** catalyzed by catalyst **18**

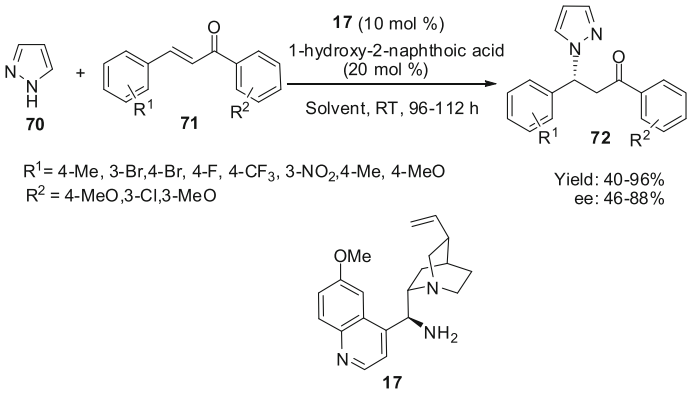
nucleophile for nucleophilic attack in the *Si*-face of the activated α,β-unsaturated ketone, resulting in high enantioselectivity of the reaction.

Michael addition of diethyl malonate to chalcones

Various alkaloids based on cinchona have been used for the enantioselective Michael addition. In 2014, He and co-workers [25] reported the enantioselective Michael addition of diethyl malonate **67** to chalcones **68** utilising a bifunctional tertiary amine-thioureas catalyst **18** bearing multiple hydrogen-bonding donors. A variety of substituted chalcones were used to provide the addition products *R* (-) **69** in high yields and with high to excellent enantioselectivities. The stereochemical outcome was explained by the plausible transition state (TS) models for the Michael reactions of chalcones **68** and diethyl malonate **67** catalyzed by **18** (Scheme 19). In the transition state, the carbonyl group of chalcone is activated by the multiple hydrogen bonding interactions between the oxygen atom of the carbonyl with the thiourea moiety and the extra hydroxyl group of **18**. Meanwhile, diethyl malonate **67** is deprotonated by the basic nitrogen atom of the quinuclidine in cinchona alkaloid moiety.

Michael addition of pyrazole to chalcones

In 2014, Li and Wang et al. [26] demonstrated that employing pyrazole **70** as nitrogen nucleophiles for additions to chalcones **71** catalyzed by **17** led to the formation of 1,4-adducts **72** in moderate to good yields and excellent asymmetry induction. Variation of the solvents had a pronounced effect on the yields and



Scheme 20 Aza-Michael addition of pyrazole **70** to chalcones **71** using catalyst **17**

enantioselectivities. The reaction was studied with Et_2O and 1,4-dioxane (Scheme 20).

Conclusion

In this review, we have summarized significant works regarding Michael addition reactions of various nucleophiles to chalcones using different organocatalysts. The Michael addition involves a wide range of nucleophiles as Michael donors and chalcones act as Michael acceptors. Future work would be the utilization of these powerful strategies for the efficient assembly of biologically interesting molecules including natural and unnatural products. Finally, creative combination of new catalysts and new reaction sequences will further broaden the scope and applicability of chalcones as Michael acceptors in Michael addition reactions for the efficient synthesis of biologically interesting molecules.

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