CHEMICAL REVIEWS

Review

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Catalytic Asymmetric Synthesis of Butenolides and Butyrolactones

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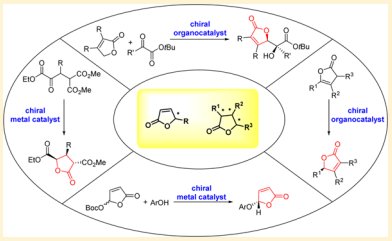
ABSTRACT: γ-Butenolides, γ-butyrolactones, and derivatives, especially in enantiomerically pure form, constitute the structural core of numerous natural products which display an impressive range of biological activities which are important for the development of novel physiological and therapeutic agents. Furthermore, optically active γ-butenolides and γ-butyrolactones serve also as a prominent class of chiral building blocks for the synthesis of diverse biological active compounds and complex molecules. Taking into account the varying biological activity profiles and wide-ranging structural diversity of the optically active γ-butenolide or γ-butyrolactone structure, the development of asymmetric synthetic strategies for assembling such challenging scaffolds has attracted major attention from synthetic chemists in the past decade. This review offers an overview of the different enantioselective synthesis of γ-butenolides and γ-butyrolactones which employ catalytic amounts of metal complexes or organocatalysts, with emphasis focused on the mechanistic issues that account for the observed stereocontrol of the representative reactions, as well as practical applications and synthetic potentials.



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1. INTRODUCTION

The five-membered cyclic ester, the essential framework of γ-butenolide and γ-butyrolactone, constitutes the structural core shared by numerous natural products.[1−14] γ-Butenolides, γ-butyrolactones, and derivatives, especially in enantiomerically pure form, display an impressive range of biological activities which are important for the development of physiological and therapeutic agents.[15] Some representative members of this family are depicted in Figure 1. For example, strigol, featuring the presence of chiral γ-butenolide in addition to γ-butyrolactone, is known to trigger the germination of parasitic plant seeds and inhibit plant shoot branching.[15] Avenolide, a streptomyces hormone bearing a γ-butenolide core, has been shown to control antibiotic production in *Streptomyces avermitilis*.[16,17] Paraconic acids, bearing a carboxylic acid function at the position β to the carbonyl, represent an important group of γ-butyrolactones that display both antitumor and antibiotic activities.[18] Arglabin, a sesquiterpene α-methylene-γ-butyrolactone which is isolated from *Artemisia glabella*, is assumed to prevent protein farnesylation without altering geranylgeranylation.[19,20]

Much controversy exists with respect to the nomenclature of these γ-lactones.[1] In order to avoid any confusion, the term "γ-butenolides" in this review will refer to α,β- as well as β,γ-unsaturated γ-lactones and the term "γ-butyrolactones" will include saturated γ-lactones (I, II, III, Figure 2).[1] The following systematic numbering (α, β, γ) will be used to indicate the position of substitution on the five-membered ring throughout this review.

Optically active γ-butenolides and γ-butyrolactones serve as a prominent class of chiral building blocks for the synthesis of diverse biological active compounds and complex molecules. Numerous transformations could be performed to access a range of chiral products due to the presence of a highly versatile functional group, especially in the furanone structure. For example, the γ-enolizable butenolide offers the possibility to be used as an extended dienolate precursor[21−23] to introduce δ-hydroxy-γ-butenolide through enantioselective vinylogous aldol reaction.[24,25] This transformation enables the stereospecific construction of a vicinal diol functionality, and the resulting products can be further elaborated toward the construction of various important multifunctional building blocks through highly selective substrate-controlled reactions involving the unsaturated ester moiety (Scheme 1).

Taking into account the varying biological activity profiles and wide-ranging structural diversity of the optically active γ-butenolide or γ-butyrolactone structure, the development of asymmetric synthetic strategies for assembling such challenging scaffolds has attracted enormous attention from synthetic chemists. In the past, important reactions such as the homoaldol reaction served as a useful platform for the enantioselective synthesis of butenolides and butyrolactones employing chiral auxiliaries.[26] With the advancement in the field of asymmetric catalysis, an impressive range of catalytic enantioselective transformations[27] have been developed to prepare structurally diverse γ-butenolide and γ-butyrolactone derivatives with exquisite control of the stereoselectivity and synthetic efficiency.

Despite intensive research on this topic in the past decades, few tutorial reviews present the essential information as well as recent advances on catalytic asymmetric approaches to access these privileged furanone structures.[28] In this review, we provide an overview of the different enantioselective synthetic approaches toward γ-butenolides and γ-butyrolactones which employ catalytic amounts of metal complexes or organocatalysts, with emphasis focused on the mechanistic issues that account for the observed stereocontrol of the representative reactions. As

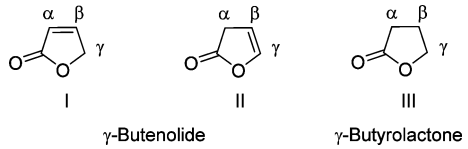

Figure 2. Basic structures of γ-butenolide and γ-butyrolactone.

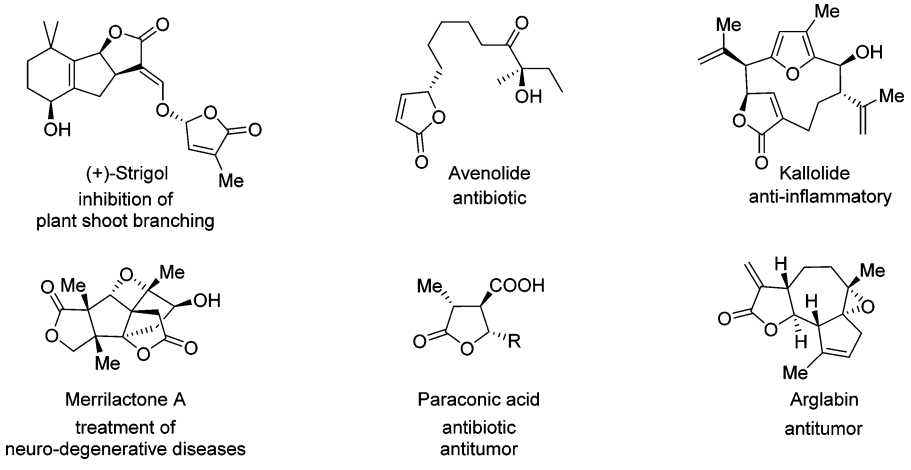

Figure 1. Naturally occurring products which contain chiral γ-butenolide or γ-butyrolactone core.

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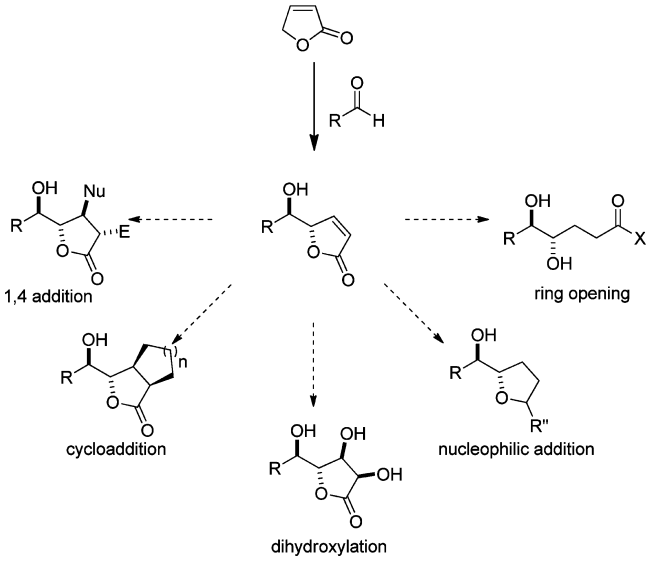
Scheme 1. Illustrative Transformations of γ-Butenolides and γ-Butyrolactones



depicted in Scheme 2, four main sections were classified based on the various assembly modes of the chiral γ-butenolide or γ-butyrolactone core structure in a catalytic asymmetric fashion. Each section is further subdivided according to the different reaction type. Further applications to explore the synthetic utility of the enantiomerically enriched γ-butenolide and γ-butyrolactone derivatives are briefly discussed in the context of synthesis of complex functionalized intermediates and natural products. It is our aim that the review will deliver the critical insights into the overall development in the field along with the opportunity for the innovative approaches of further research.

2. FURANONE-DERIVED ENOLATES AS NUCLEOPHILES

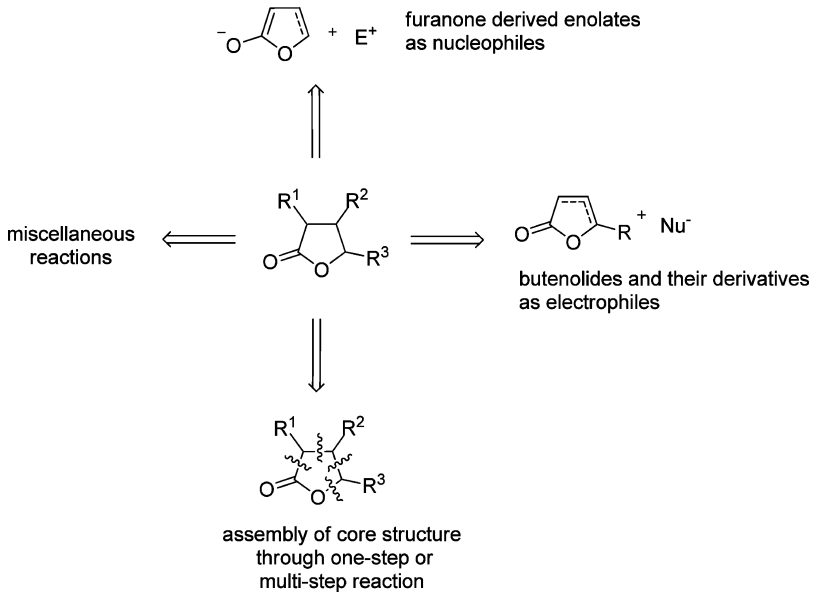
2.1. Asymmetric Aldol Reaction

Catalytic asymmetric aldol reactions have been extensively investigated playing a key role among the most powerful methods for enantioselective C−C bond formation.[29−32] This methodology provides efficient access to functionalized β-hydroxy carbonyl compounds with up to two new vicinal stereocenters. Not unexpectedly, the construction of chiral γ-butenolides involving the vinylogous Mukaiyama aldol reaction (VMAR) of silyloxyfurans[24,25,33−35] as well as the direct vinylogous aldol reaction of 2(5*H*)-furanone derivatives,[28] has been intensively explored. Despite numerous methods dealing with the asymmetric vinylogous aldol reaction (Scheme 3a),[28,33−35] reports on the catalytic enantioselective synthesis of butyrolactones with stereogenic centers at the α position through Mukaiyama aldol type or direct aldol type reactions are relatively rare (Scheme 3b).

2.1.1. Asymmetric Aldol Reaction of Silyloxyfurans. In 1998, Figadère and co-workers reported the first catalytic, enantioselective vinylogous Mukaiyama aldol reaction (VMAR) of 2-(trimethylsilyloxy)furan (TMSOF) **1** with achiral aldehyde **2**, to form the desired γ-butenolide **3** with a high level of enantiomeric excess (96% ee for major *syn* product, Scheme 4).[36] An autoinductive process involving the formation of a multicomponent titanium catalyst **C1** in the presence of (*R*)-1,1′-binaphthol, Ti(O*i*Pr)$_4$, and the newly formed aldol product **3**, was found to be effective in enhancing the stereoselectivity of the reaction.[37] The value of this method has also been demonstrated in a synthetic route to various natural products including (+)-muricatacin[38] and *iso*-cladospolide B.[39]

After the pioneering work of Figadère,[36−39] several catalytic systems involving both metal-based catalysts and organocatalysts have emerged for the effective asymmetric vinylogous aldol reaction (VMAR) between TMSOF **1** and a range of aldehydes (Figure 3).[40−47] The resulting chiral γ-butenolides have been elegantly employed as key building blocks for instance in the total

Scheme 2. Catalytic Asymmetric Synthetic Approaches to γ-Butenolides and γ-Butyrolactone Derivatives



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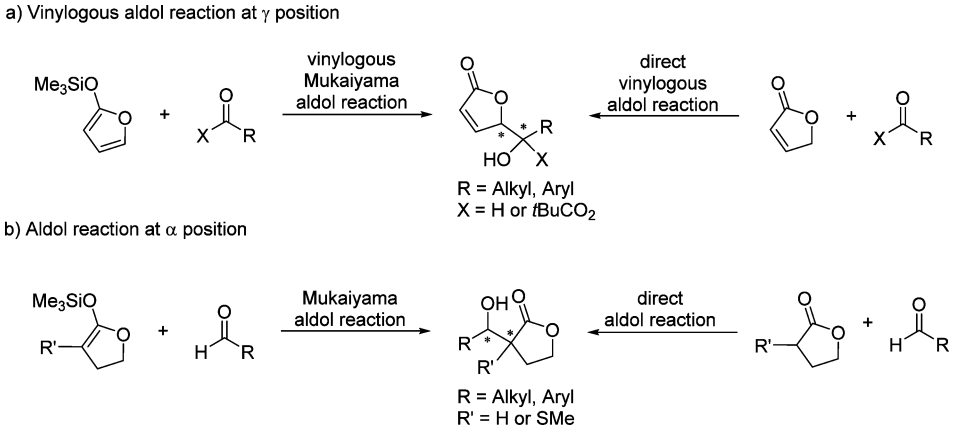
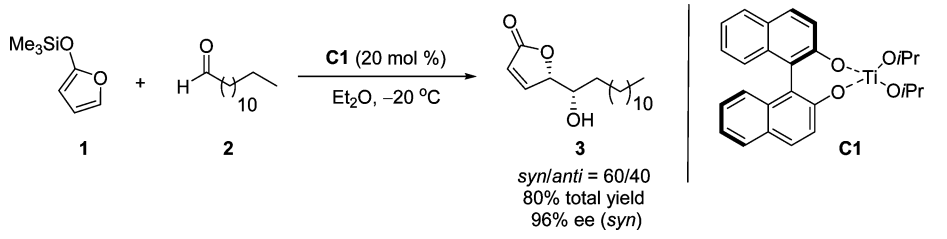
Scheme 3. Catalytic Enantioselective Aldol Reactions for the Construction of γ-Butenolides and γ-Butyrolactone Derivatives



Scheme 4. Vinylogous Aldol Reaction of 2-(Trimethylsilyloxy)furan (TMSOF) Catalyzed by Chiral Titanium−BINOL Complex



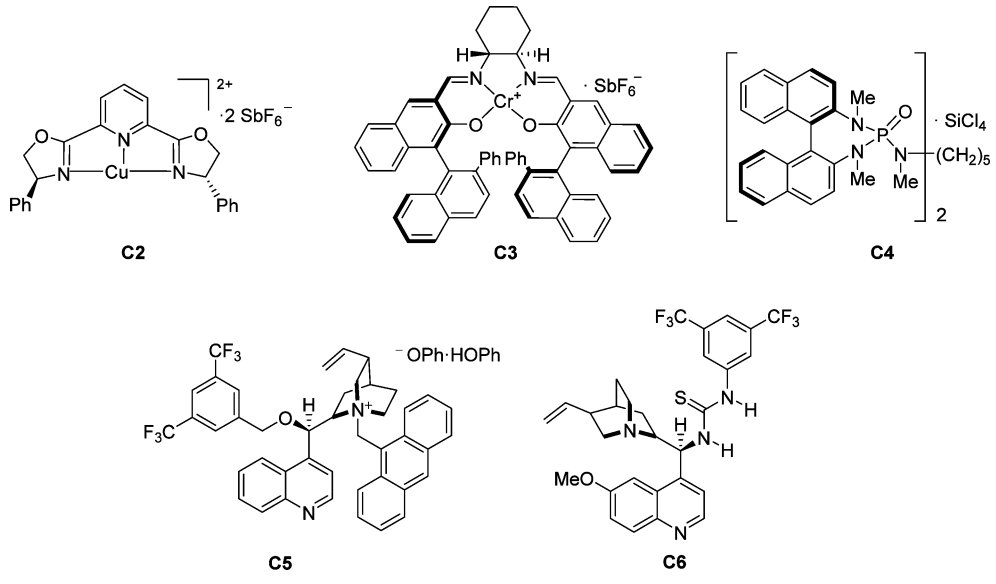


Figure 3. Selected examples of chiral catalysts for the asymmetric vinylogous aldol reaction of TMSOF with aldehydes.

syntheses of (−)-rasfonin[48] (Scheme 5) and (+)-azaspiracid-1[49] (Scheme 6). Since the VMAR of silyl dienolates and aldehydes has been comprehensively documented and reviewed by Denmark,[24] Casiraghi,[33,35] and others,[25,34] the emphasis of this part is based on recent progress in the use of substituted α-ketoesters as electrophiles for the catalytic asymmetric VMAR.

Encouraged by the success of (benzyloxy)acetaldehyde in the Cu(II)-catalyzed aldol reaction in which chelate-controlled association with the Lewis acidic Cu(II) center resulted in excellent facial discrimination at the carbonyl,[40] an investigation on the use of these chiral complexes in aldol reactions of pyruvate esters was undertaken by Evans and co-workers.[50] The first Mukaiyama aldol reaction of TMSOF **1** with methyl pyruvate **11a** was reported to afford predominantly the *anti* aldol product **12** with excellent control with respect to both the yield and stereoselectivity (Scheme 7). Crystallographic structures and semiempirical calculations provided insight into the mode of asymmetric induction, allowing the construction of a model in which chelation of the pyruvate ester **11a** through a square planar Cu(II) complex **C9** accounts for the observed sense of asymmetric induction.[50]

Bolm and co-workers reported the combination of catalytic amount of $Cu(OTf)_2$ and readily available C_1-symmetric aminosulfoximine **L1** as an efficient catalyst to promote the VMAR of TMSOF with ketone electrophiles (Scheme 8).[51,52] Their studies revealed that the use of a weakly coordinating

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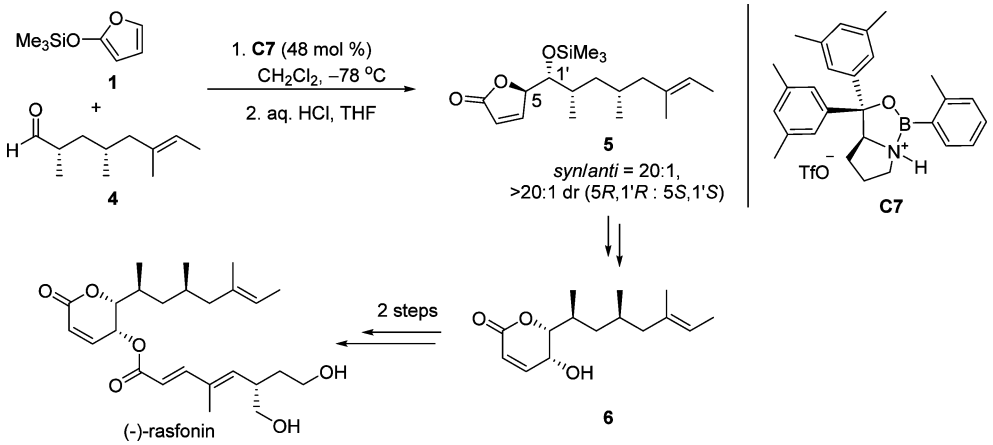
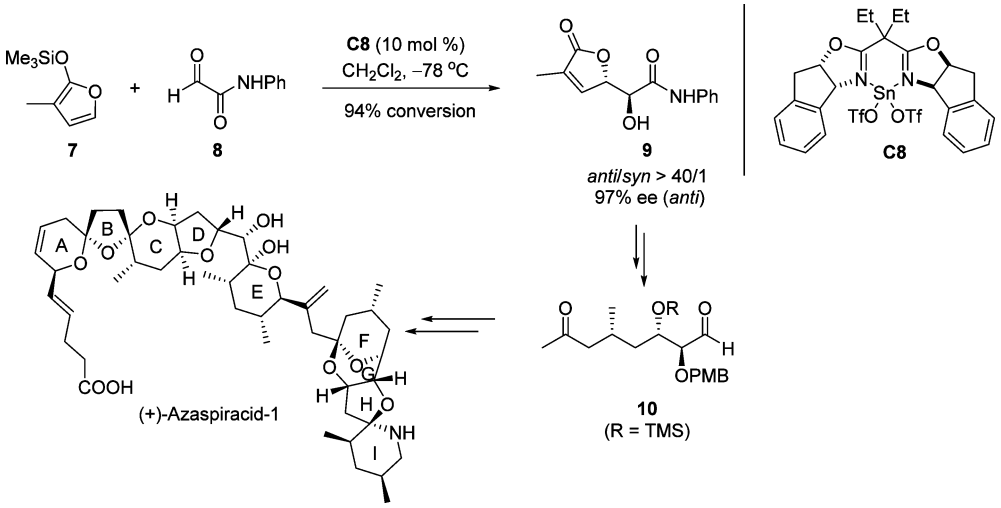
Scheme 5. Use of Protected Chiral γ-Hydroxy Butenolide 5 in the Total Synthesis of (−)-Rasfonin

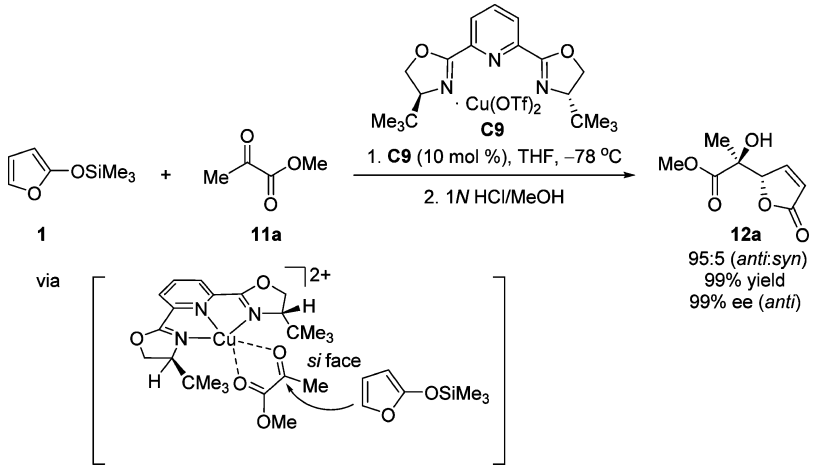


Scheme 6. Application of Chiral γ-Hydroxy Butenolide 9 for the Total Synthesis of (−)-Azaspiracid-1[a]



[a]TMS = trimethylsilyl, PMB = *p*-methoxybenzyl.

Scheme 7. Copper(II)-Catalyzed Mukaiyama Aldol Reaction of 2-(Trimethylsilyloxy)furan (TMSOF) to Methyl Pyruvate 11a



solvent such as diethyl ether is crucial for achieving high enantioselectivities and the presence of 2,2,2-trifluorethanol is associated with a pronounced rate accelerating effect. Recently, the chiral copper sulfoximine complex developed by Bolm and co-workers has been also successfully applied to the VMAR with α-keto phosphonates and various 2-(trimethylsilyloxy)furan, yielding potential biomedical active phosphate butenolides with excellent control of regio-, diastereo-, and enantioselectivities.[53] Apart from facilitating the catalyst turnover and thus giving fast reaction and high yields, the addition of trifluoroethanol (TFE)

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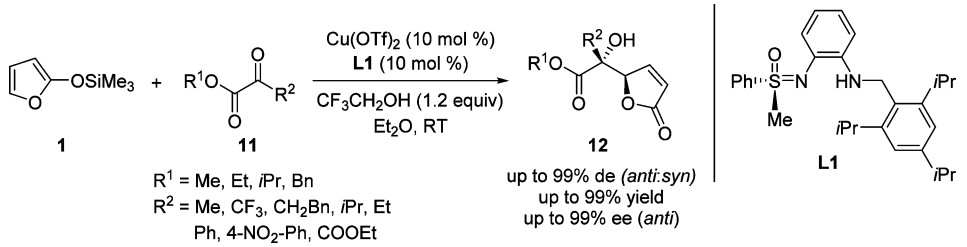
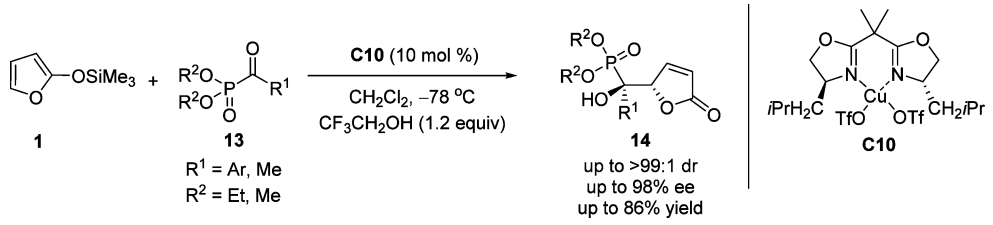
Scheme 8. Copper-Catalyzed VMAR between TMSOF and Electrophiles 11



Scheme 9. VMAR of α-Keto Phosphonates 13 with TMSOF



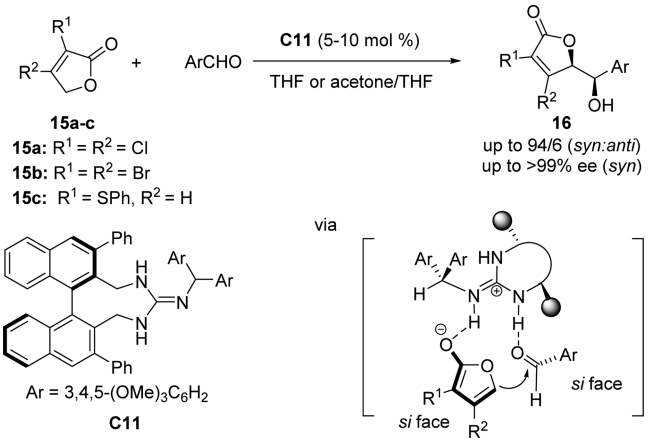
was also observed to affect the asymmetric induction. The authors propose that the possible coordination of TFE with the chiral copper−sulfoximine complex generates a catalytically active species showing enhanced selectivity.

Miao and co-workers developed the VMAR of α-keto phosphonates and TMSOF, using an optimized bis-(oxazoline)−Cu(II) complex **C10** with 2,2,2-trifluoroethanol (TFE) as additive (Scheme 9).[54] This method shows a high tolerance for a broad scope of functionalized α-keto phosphonates **13**, providing the corresponding γ-butenolides **14** in high yields and excellent diastereo- and enantioselectivities.

2.1.2. Direct Vinylogous Aldol Reaction of 2(*5H*)-Furanone Derivatives. To overcome a distinct disadvantage of Mukaiyama aldol chemistry that is the amount of waste generated by employing silyl functionalized pro-nucleophiles, the use of furanone derivatives would provide an atom-economic entry toward the enantioselective synthesis of butenolides and butyrolactones. Due to the low reactivity of furanone derivatives as well as the insufficient regio- and stereocontrol, significant breakthroughs have been made only recently.[25] In light of the racemic synthesis of substituted γ-butenolides, Terada and co-workers reported the first asymmetric vinylogous aldol reaction of dihalofuranones to aldehydes, promoted by chiral guanidine-based catalyst **C11** derived from a binaphthyl scaffold (Scheme 10).[55] Halogenated or α-thio-substituted furanones **15a−15c** instead of unsubstituted furanones were used as nucleophiles to avoid the competition for α-substitution and enhance the reactivity of furanones at the γ position. The proposed mechanism presents the nucleophile undergoing a formal Brønsted acid−base interaction with the guanidine catalyst **C11**, thus activating the dihalofuranone for the addition to the aldehyde. A transition state model was proposed to rationalize the stereochemical outcome, i.e. the configuration of the *syn* product **16** (Scheme 10). In this model the *si* face of the aldehyde is attacked by the *si* face of furanone derived enolate due to the steric repulsion from the phenyl substituents at the 3,3′-position of the binaphthyl backbone and the benzhydryl moiety introduced onto the nitrogen atom of guanidine catalyst.[55]

In 2011, Lu and co-workers disclosed an enantioselective vinylogous aldol reaction of halogenated furanones with α-ketoesters catalyzed by tryptophan-derived bifunctional catalysts **C12** (Scheme 11).[56] High diastereo- and enantioselectivities

Scheme 10. Vinylogous Aldol Reaction of Unactivated γ-Butenolides 15 to Aldehydes Catalyzed by Chiral Guanidine Base Catalyst C11



were observed for a wide range of substituted α-ketoesters including vinylic and alkyl substituents. Unsubstituted 2(5*H*)-furanone **15d** also afforded the corresponding aldol products, albeit a much longer reaction time was required. Moreover, the introduction of 3,4-dibromofuranone **15b** resulted in the formation of a tighter ion pair between the incoming furanone enolate and the thiourea moiety, therefore providing aldol products with improved diastereoselectivity. The utility of this method is exemplified by the facile transformation of chiral γ-butenolides **18** into triol derivatives bearing a tertiary alcohol moiety; for instance, product **19** showing antifungal activity is readily obtained.

As previously mentioned, difficulties often encountered in direct vinylogous aldol reactions of unactivated 2(5*H*)-furanone dealt with competitive regiocontrol as well as decomposition of the resulted product. Cinchona alkaloid derived thiourea **C13** and stilbenediamine derived squaramide **C14** were introduced successively by Feng[57] and by Pansare[58,59] as bifunctional catalysts for the enantioselective vinylogous aldol reactions of 2(5*H*)-furanone **15d** to a variety of aromatic aldehydes (Scheme 12). The formation of the corresponding aldol products via catalysis by squaramide **C14** proceeds with higher diastereose-

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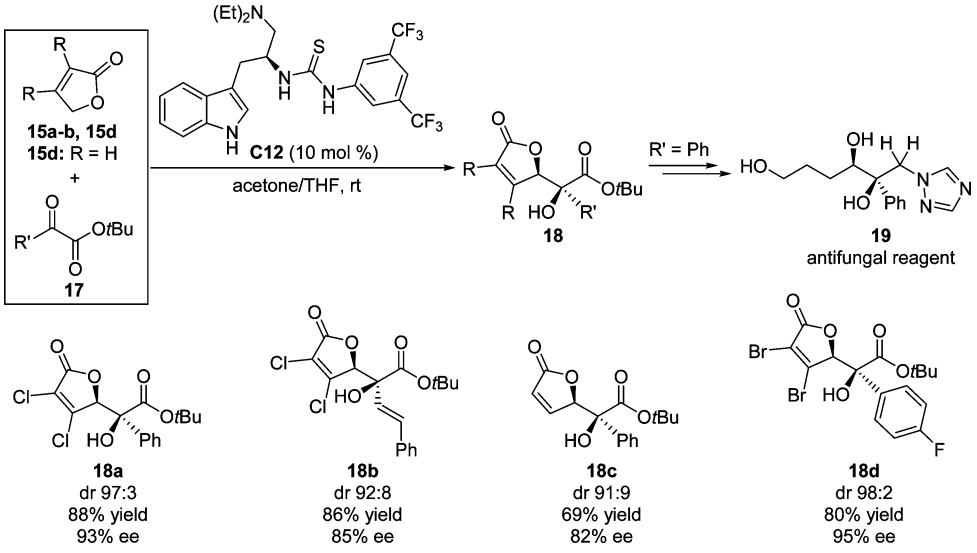
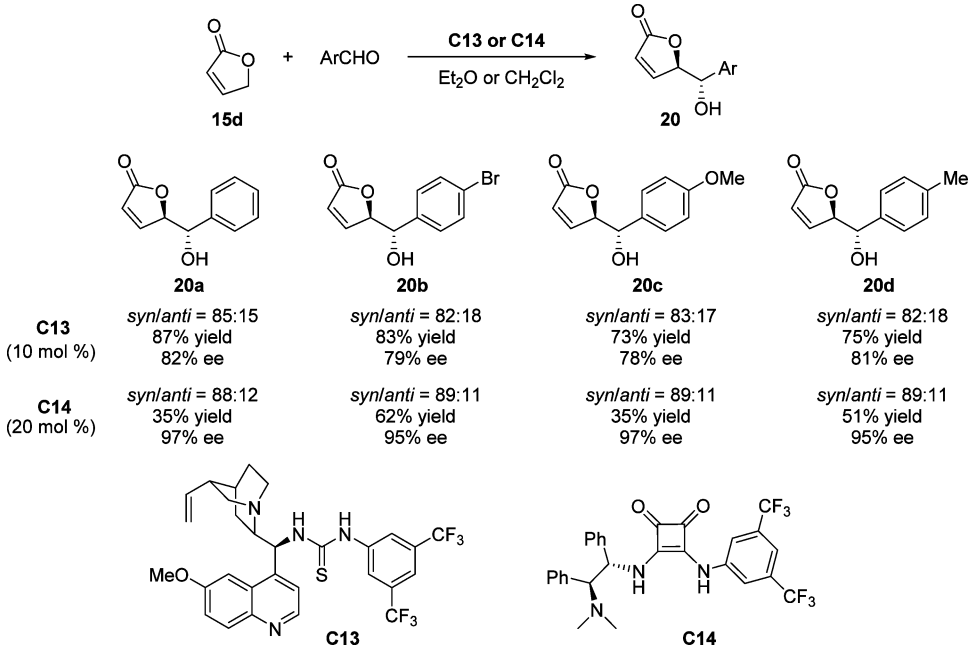
Scheme 11. Vinylogous Aldol Reaction of γ-Butenolides to Aldehydes Catalyzed by Chiral Amine−Thiourea Catalyst C12



Scheme 12. Vinylogous Aldol Reaction between γ-Butenolide 15d and Aromatic Aldehydes



lectivities and enantioselectivities than using thiourea **C13**, albeit lower yields were achieved in the presence of higher catalyst loadings. The major products were the *anti* isomers in both cases, which is in contrast to the *syn* isomers observed in the reactions described above. This could be rationalized by the *Re* face attack from the possible dienolate intermediate to the activated aldehyde through the double hydrogen-bonding interaction that occurs when **C13** and **C14** are applied.

Inspired by the work of Mukaiyama,[45] Levacher and co-workers developed an enantioselective direct vinylogous aldol reaction of 2(5*H*)-furanone derivatives with various aldehydes using the combination of chiral quaternary ammonium aryloxide **C15**/*N*,*O*-bis(trimethylsilyl)acedamide (BSA) as an efficient ion-pairing organocatalytic system (Scheme 13).[60−65] High diastereomeric ratios and excellent enantioselectivities were obtained with both (hetero)aromatic and aliphatic aldehydes. The reaction mechanism was proposed as follows: (a) the in situ generated chiral ammonium aryloxide **A** is activated by the BSA to afford the chiral ammonium amide **B**; (b) the 2(5*H*)-furanone substrate is deprotonated by the ammonium amide **B** to generate the ion pair of ammonium enolate **C**; (c) the vinylogous aldol reaction between ammonium enolate and corresponding aldehyde, followed by the deprotection of the silylated product, gives rise to final product **21**.

2.1.3. Aldol Reaction at the α-Position of Furanone Derivatives. As illustrated above (section 2.1.1), TMSOF **1** has been widely used in Lewis acid catalyzed VMAR reactions in which the nucleophilic reactivity of the silyloxyfuran is typically restricted to the C-5 site. Mlynarski demonstrated that the regioselectivity of this transformation can be switched by using water-containing solvents. Under these conditions the Lewis acid catalyzed Mukaiyama aldol reaction between **1** and a range of aldehydes could be carried out to afford C-3 subsituted α-butenolides in good yields with almost complete control of the

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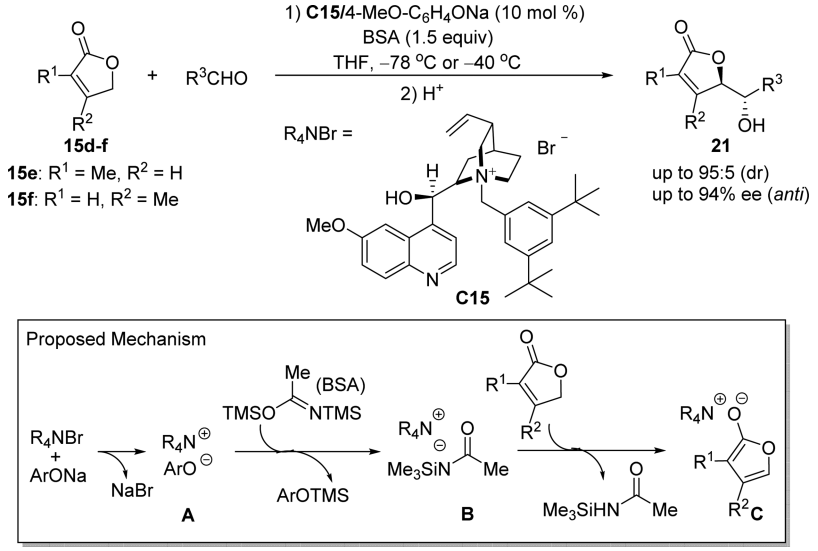
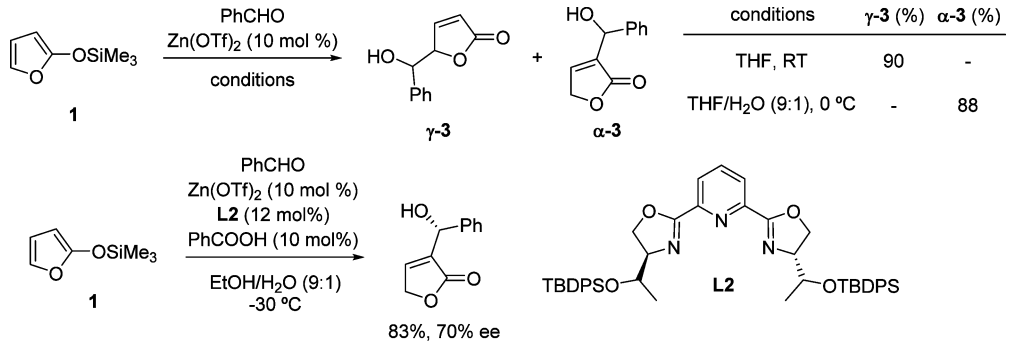
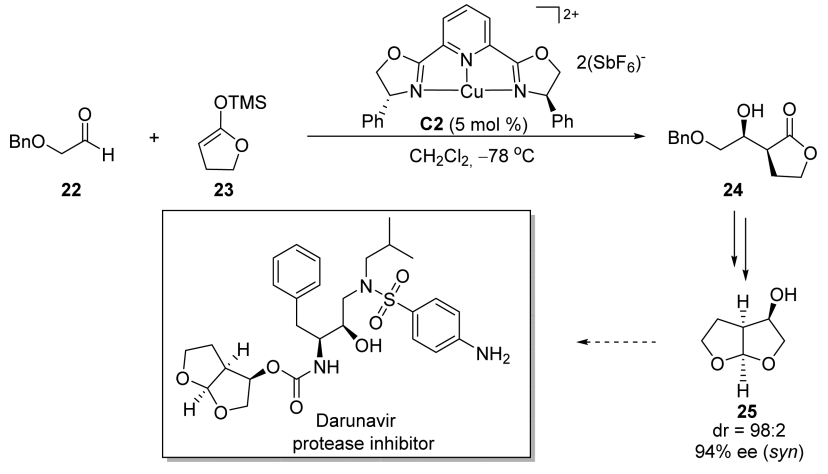
Scheme 13. Enantioselective Direct Vinylogous Aldol Reaction of 2(5*H*)-Furanone Derivatives with Various Aldehydes Using an Ion-Pairing Organocatalytic System



Scheme 14. Switch in Regioselectivity with Aqueous Solvents in the Mukaiyama Aldol Reaction of TMSOF 1 and Aldehydes



Scheme 15. Aldol Reaction of Silylketene Acetal Derived from γ-Butyrolactone and (Benzyloxy)acetaldehyde 22



regioselectivity.[66] The use of a chiral catalyst comprising $Zn(OTf)_2$ and pybox ligand **L2** allowed the reaction to be performed in an enantioselective manner (Scheme 14).

Evans et al. have reported an efficient catalytic asymmetric Mukaiyama aldol reaction of silylketene acetal **23** derived from γ-butyrolactone to (benzyloxy)acetaldehyde **22**, utilizing the C_2-symmetric pyridinebis(oxazolinyl) Cu(II) complex **C2** as catalyst (Scheme 15).[40,67] The *E*-configuration of the silylketene acetal double bond was considered to be the key for the highly selective *syn* aldol reaction with good control at both stereogenic centers.[40] This strategy was applied to the synthesis of bis-tetrahydrofuran alcohol **25** with excellent diastereoselectivity (dr = 98:2) and enantioselectivity (94% ee), which provided an important structural moiety present in several protease inhibitors including darunavir.[68]

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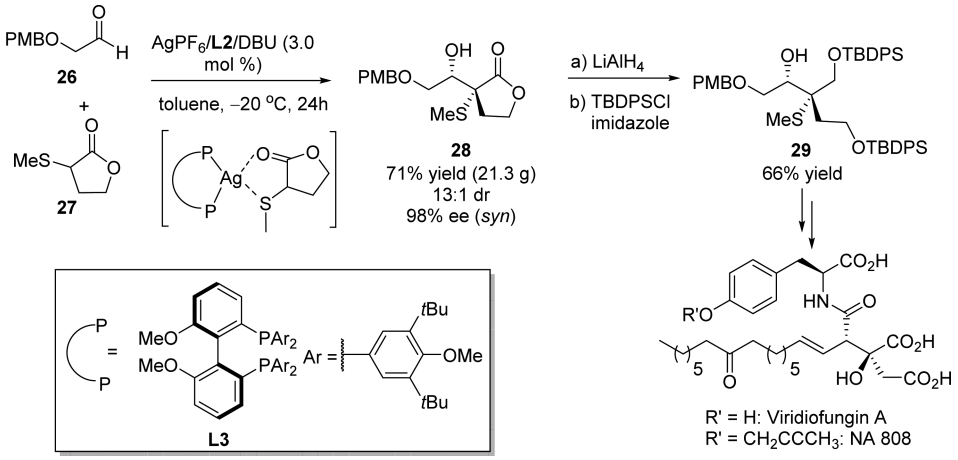
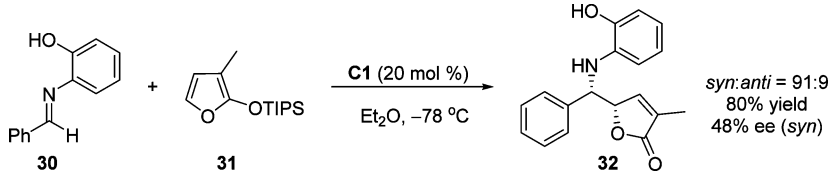
Scheme 16. Direct Aldol Reaction of α-Sulfanyl Lactones and Aldehydes[a]

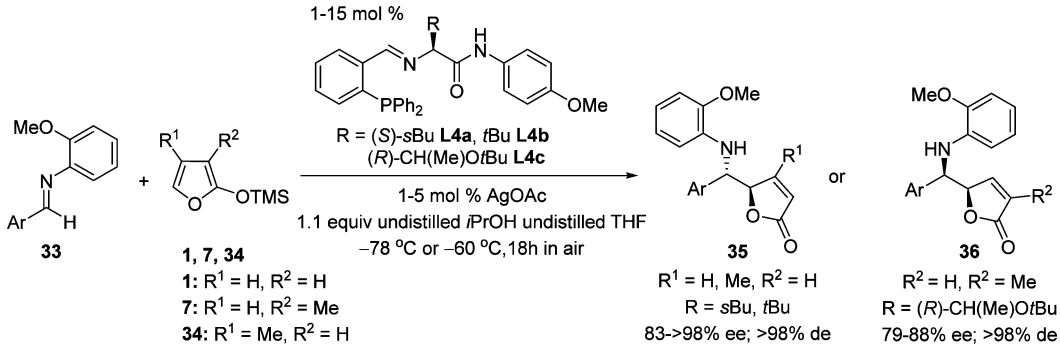


[a]DBU = 1,8-diazabicyclo(5.4.0)undec-7-ene, TBDPS = *tert*-butyldiphenylsilyl.

Scheme 17. Catalytic Asymmetric Vinylogous Mannich Reaction of Triisopropylsilyloxyl Furan and Aldimine



Scheme 18. Ag-Catalyzed Enantioselective Vinylogous Mannich Reaction of Silyloxyfurans



A chemoselective activation strategy developed by Shibasaki and co-workers, using a soft Lewis acid/amine binary catalytic system, has proved to be efficient for the direct asymmetric aldol reaction of α-sulfanyl lactones to aldehydes (Scheme 16).[69] The authors proposed that the selective coordination between the chiral Lewis acid and α-sulfanyl moiety would activate the α position of the butyrolactone **27** for the deprotonation and thereby generate the corresponding Ag enolate in a proper chiral environment. This catalytic reaction could be performed on a 19 g scale, with respect to aldehyde **26**, to afford the desired γ-butyrolactone **28** in 71% yield with high diastereomeric ratio (*syn*/*anti* = 13:1) and excellent enantioselectivity (98% ee). Following reduction and selective protection of the resulting primary alcohol gave rise to compound **29** in 66% yield, which was subsequently used as a key building block to complete the stereoselective synthesis of viridiofungin A and NA 808.[69]

2.2. Asymmetric Mannich Reaction

The asymmetric Mannich reaction of 2(5*H*)-furanone and its derivatives with either an iminium or acyl iminium, provides rapid access to enantiomerically enriched γ-butenolide derivatives bearing an amine functionality, which has been further employed for the synthesis of alkaloids and other nitrogen-containing compounds. In contrast to the well-developed asymmetric aldol reaction, fully catalytic and highly stereoselective procedures for this transformation are scarce.

2.2.1. Vinylogous Mannich (VM) Reaction of Silyloxyfurans. The first catalytic, enantioselective vinylogous Mukaiyama–Mannich reactions of aldimine with 2-silyloxyfuran as nucleophile was reported by the group of Martin in 1999 (Scheme 17).[70] A chiral metal complex formed in situ from Ti(O*i*Pr)$_4$ and (*S*)-1,1′-binaphthol (1:2) in ether was employed as catalyst and provided 5-substituted aminoalkyl γ-butenolide **32** in good yields and moderate enantioselectivities (48% ee for *syn* product). It was assumed that the coordination between the aldimine substrates and the preformed catalyst enforces the specific transition state organization enhancing the enantioselectivity.

In 2006, Hoveyda and co-workers reported a highly diastereo- and enantioselective vinylogous Mannich reaction catalyzed by a silver phosphine complex, in which TMSOF **1** or derivatives **33**

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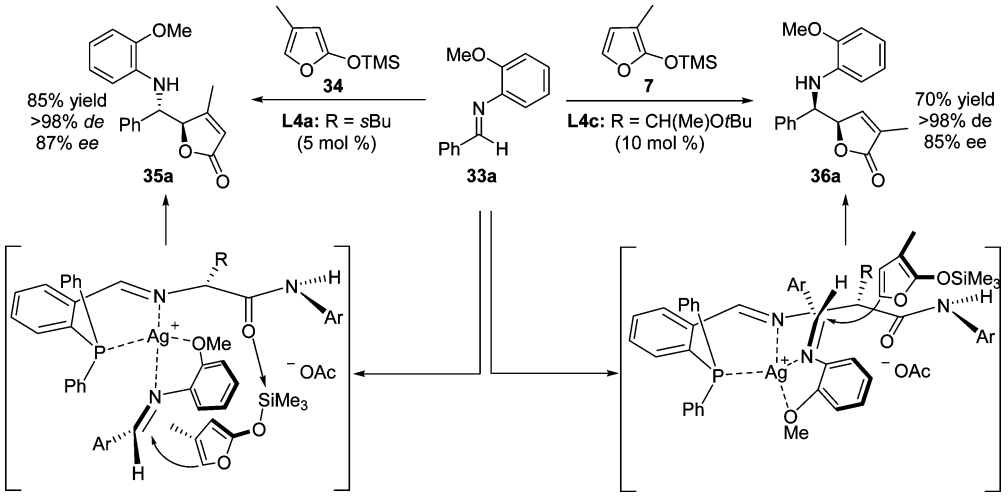
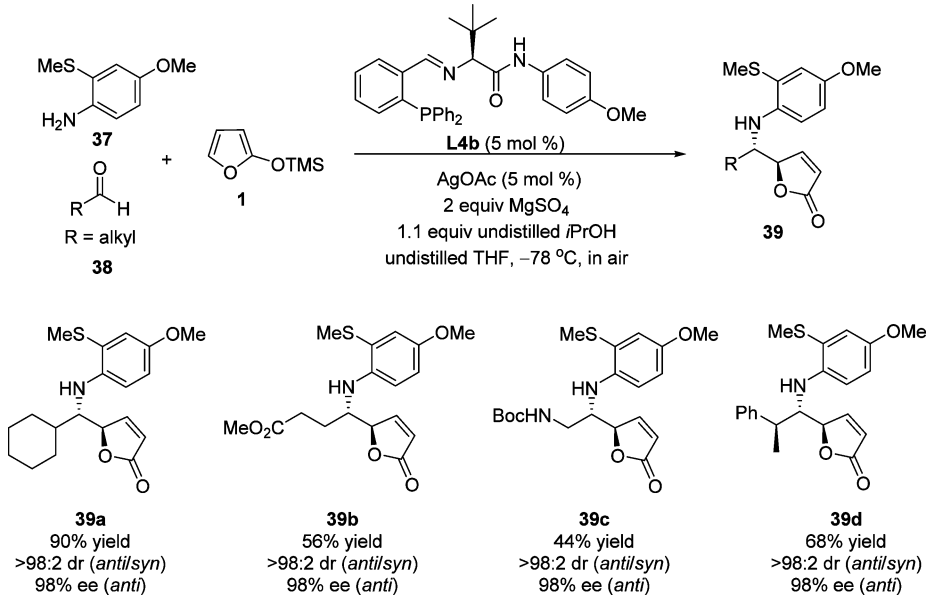
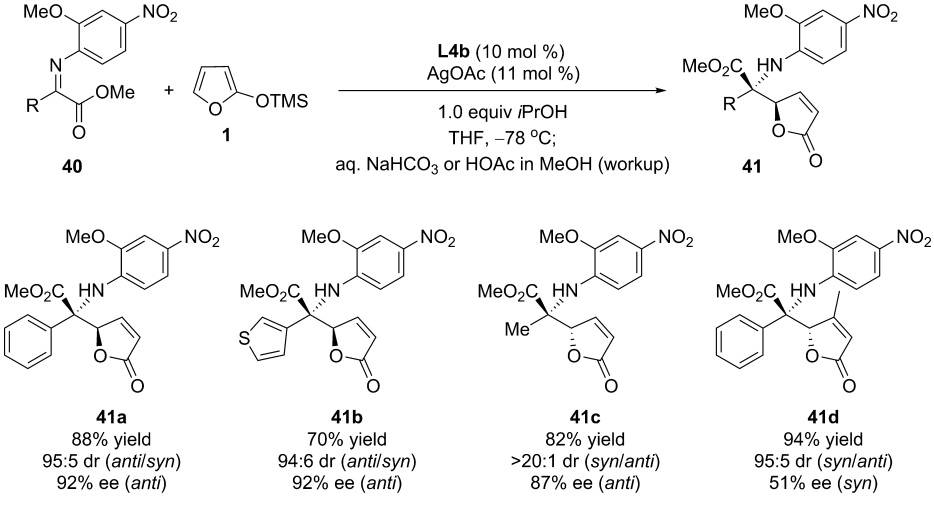
Scheme 19. Ag-Catalyzed Enantioselective Vinylogous Mannich Reaction of Methyl-Substituted Silyloxyfurans



Scheme 20. Ag-Catalyzed Enantioselective Vinylogous Mannich Reaction of 2-Silyloxyfurans



Scheme 21. Silver(I)-Catalyzed Asymmetric VM Reaction of Substituted α-Ketoimine Esters



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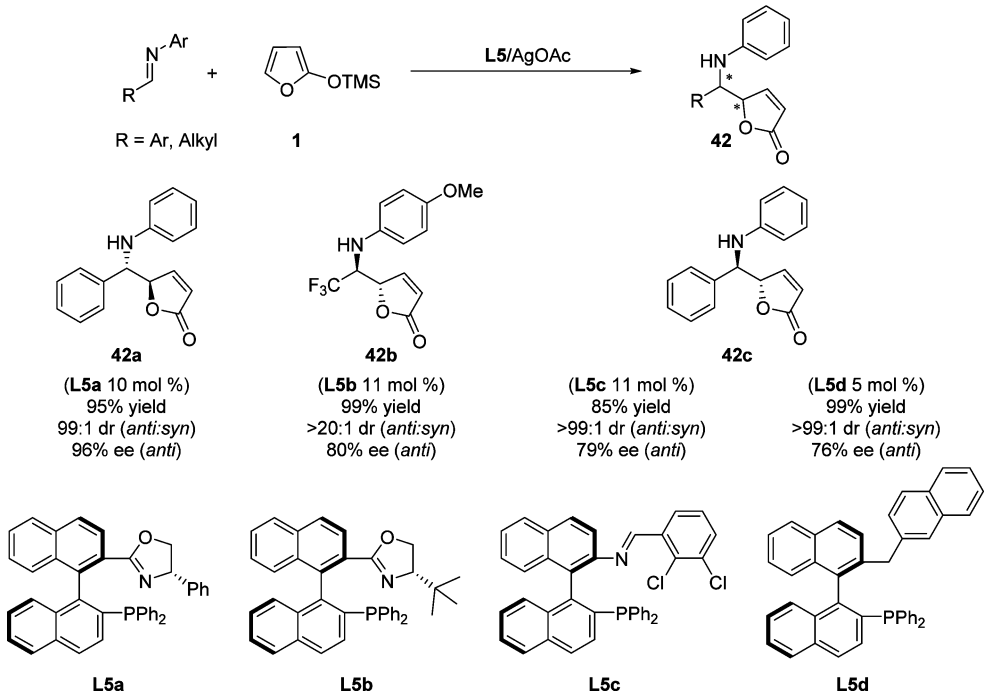
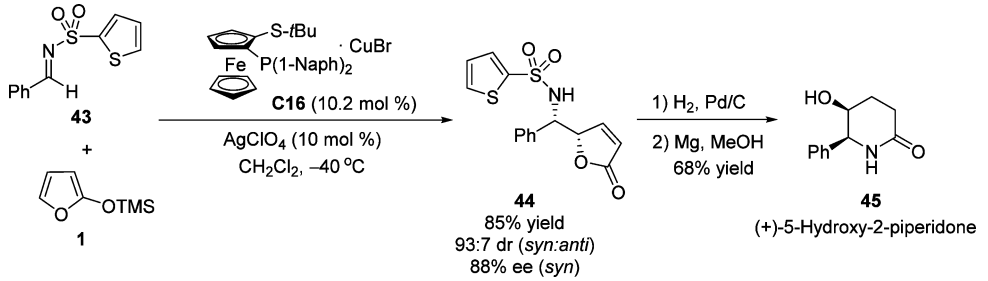
Scheme 22. Other Phosphine Type Ligands in Silver(I)-Catalyzed Asymmetric VM Reaction of Aldimines



Scheme 23. Catalytic Asymmetric Vinylogous Mannich Reaction of *N*-(2-Thienyl)sulfonylimines with Silyloxyfuran



reacted with aromatic aldimines **33** to generate the γ-aminoalkyl-substituted γ-butenolides **35** or **36** (Scheme 18).[71] The process proved to be highly practical as the transformation could be carried out in air with undistilled THF as solvent in the presence of undistilled 2-propanol as additive. The reaction with various methyl-substituted 2-silyloxy furans (**7** and **34**) were also examined to afford the butenolide adducts with excellent diastereo- and enantioselectivities.[72,73]

The use of 2-silyloxyfurans nonsubstituted in the 3-position favored the formation of butenolides with *anti*-configuration. In sharp contrast, 3-Me-substituted 2-silyloxyfuran provided the corresponding adducts with reversed diastereoselectivity in which *endo*-type addition appears to be unfavorable due to the steric repulsion arising from the catalyst-bound imine. A proposed mechanism suggests that the phosphine−silver complex may associate with the aldimine substrate through bidentate chelation and the Lewis basic amide terminus of the chiral ligand conducts the possible intramolecular desilylation, thereby facilitating catalytic turnover (Scheme 19).[72,73] This protocol was amenable to affording the unprotected chiral amine on a multigram scale after simple oxidative removal of the anisidyl group.

Subsequent studies from the same group revealed an extension of this protocol to an efficient three-component Ag-catalyzed enantioselective VM reaction involving commercially available silyloxyfuran (Scheme 20).[72,73] Products **39** were obtained in good yields with excellent diastereo- and enantioselectivities from various aldehydes **38** by the use of in situ formed *o*-thiomethyl-*p*-methoxyaniline-derived aldimines. Futher studies indicated that catalyst control overrides substrate control when aldehydes bearing a stereocenter are used, regardless of the configuration of the starting aldehydes. The stereochemical outcome of the reaction is dictated by the configuration of the chiral ligand **L4b**.

This catalytic asymmetric protocol was then extended to perform the additions of silyloxyfurans to aryl-, heteroaryl-, and methyl-substituted ketoimine esters.[73] Butenolide products **41** bearing an N-substituted quaternary stereogenic center were obtained with high diastereo- and enantioselectivities (Scheme 21). It was found that the chiral monoligated Ag complex (**L**:Ag = 1:1) is the active catalyst in this transformation while a possible competing Ag complex (**L**:Ag = 2:1) might be the cause of diminished stereoselectivity under certain conditions.

The application of other chiral phosphine type ligands in silver(I)-catalyzed asymmetric VM reaction of aldimines with 2-trimethylsiloxyfuran was described by the research groups of Shi[74−77] and Xu[78] (Scheme 22). The combination of phosphine−Schiff base ligand **L5a**,[74] **L5b**,[75,76] **L5c**,[77] or

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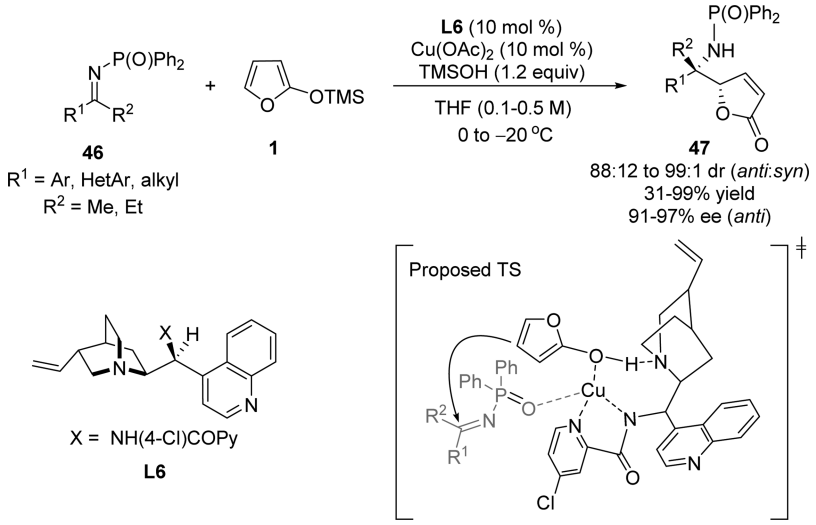
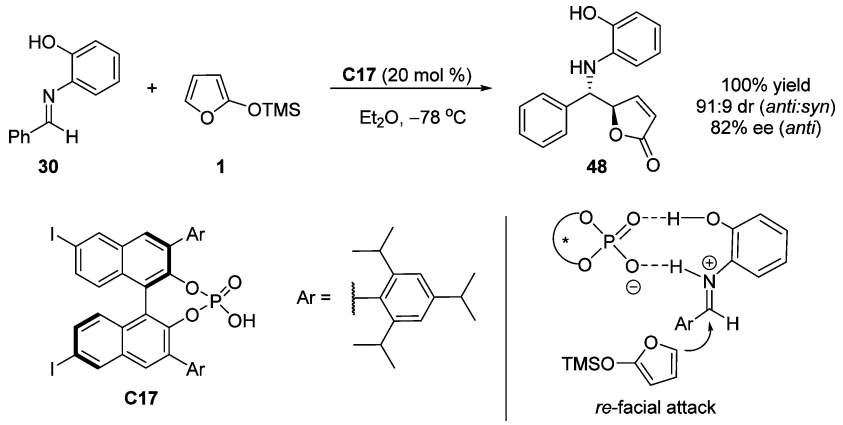
Scheme 24. Vinylogous Mannich Reaction of Phosphinoyl-imines with Silyloxyfurans



Scheme 25. Vinylogous Mannich-Type Reaction Catalyzed by an Iodine-Substituted Chiral Phosphoric Acid



monophosphine ligand **L5d**[78] with silver acetate turned out to be an effective catalytic system similar to those previously reported by Hoveyda[71−73] for the asymmetric VM reaction, affording the resulting butenolide adducts with high to excellent selectivity.

Furthermore, Carretero and co-workers developed an efficient copper-catalyzed asymmetric VM reaction procedure that relies on the use of *N*-(2-thienyl)sulfonylimines as substrates and Cu(I)−Fesulphos complex **C16** and $AgClO_4$ as catalyst (Scheme 23).[79] The 2-(thienyl)sulfonyl group as N-substituent proved to be important for both the reactivity and the selectivity of the reaction involving chelation to copper. The transformation of *syn* γ-butenolide into (+)-5-hydroxy-2-piperidone **45** through a hydrogenation and subsequent deprotection sequence demonstrated the versatility of the Mannich adduct.

Nakamura et al. reported the enantioselective vinylogous Mannich reaction of siloxyfurans with various phosphinoyl-imines **46** derived from unactivated ketones for the first time (Scheme 24).[80] The combination of cinchona alkaloid based ligand **L6** with $Cu(OAc)_2$ as Lewis acid and trimethylsilyl alcohol (TMSOH) as additive afforded the corresponding butenolides **47** with good to excellent diastereoselectivities (*anti*:*syn* = 88:12 to 99:1) and enantioselectivities (91−97% ee). The reaction of methyl-substituted siloxyfurans such as 3-methyl- and 4-methyl-2-silyloxyfurans also afforded the product with excellent selectivities, although 5-methyl-2-silyloxyfuran did not give any product probably due to steric hindrance of this silyloxyfuran. The authors proposed that carbon−carbon bond formation proceeds in the coordination sphere of copper cation where the activated dienolate approaches the *re* face of phosphinoyl-imines to avoid the steric repulsion from the diphenylphosphinoyl group (Scheme 24).[80]

Although several Lewis acids have been developed as catalysts for asymmetric VM reaction of TMSOF, Akiyama et al. reported the first example on the use of a chiral Brønsted acid. 3,3′-Biaryl-BINOL-based phosphoric acid **C17** bearing iodine groups on the 6,6′-positions catalyzes the vinylogous Mannich-type reaction, producing γ-butenolide **48** in good yields with high stereoselectivity (Scheme 25).[81] On the basis of a theoretical study, the authors concluded that the two-point hydrogen bonding interaction makes the biscoordination pathway overwhelmingly favored over the monocoordination pathway. It was proposed that this Mannich-type reaction might proceed through imine protonation followed by the nucleophilic attack involving a zwitterionic nine-membered cyclic transition state (Scheme 25).[82]

2.2.2. Direct Vinylogous Mannich Reaction of Furanone Derivatives. The first example of direct, enantioselective VM reaction between 2-(5*H*)-furanone derivatives and *N*-diphenylphosphinoyl imines **49**, utilizing a chiral lanthanum(III)−pybox catalyst in combination with tetramethylethylenedi-

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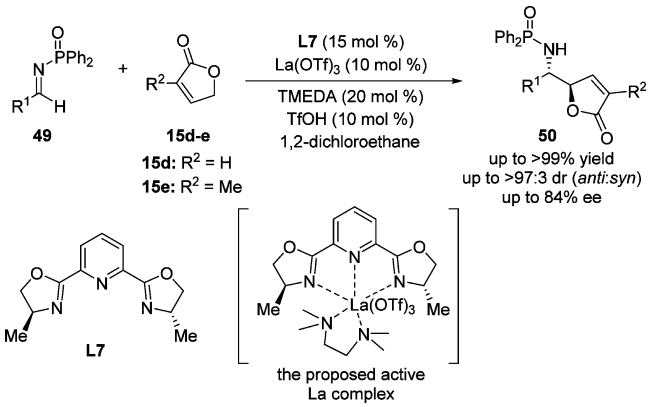
amine (TMEDA) as organic base and triflic acid as Brønsted acid, was reported by the Shibasaki group in 2008 (Scheme 26).[83]

Scheme 26. Direct Catalytic Asymmetric Mannich-Type Reaction of γ-Butenolide and Imines



Under optimized conditions, a highly γ-regioselective vinylogous Mannich reaction occurred affording γ-butenolides **50** with 68−84% ee and up to 97:3 diastereoselectivity. NMR study indicated that the addition of catalytic amount of TfOH was essential to achieve good yield and enantioselectivity for this catalytic asymmetric VM reaction, by supporting the formation of the anticipated chiral lanthanum complex ($La(OTf)_3$/Me-PyBox **L7**/TMEDA = 1:1:1) (Scheme 26). In the absence of TfOH, a competing reaction promoted predominantly by the $(TMEDA)_2La(OTf)_3$ complex resulted in only moderate yield and enantioselectivity.[83]

The Shibasaki group recently developed the direct vinylogous Mannich reaction of γ-butenolides to *N*-thiophosphinoyl ketimines **51**, with the aid of cooperative action of a soft Lewis acid, Cu/Taniaphos **L8** complex, and a hard Brønsted base, i.e. triethylamine (Scheme 27).[84] The reaction of oxygen analogue barely proceeds under the optimized conditions. It indicates that the S···Cu interaction between *N*-thiophosphinoyl ketimines and the copper complex as the soft Lewis acid is key to enhancing the efficiency of the system. The resulting chiral amines **52** were obtained in high yield, high diastereomeric ratios, and excellent enantiomeric excess. Application of this catalytic protocol to the asymmetric synthesis of six-membered lactams was successfully achieved.

An attractive approach for accessing chiral δ-amino γ,γ-disubstituted butenolides was developed by Feng et al.,[85] in which selective activation of γ-butenolide **54** as nucleophile and *N*,*N*′-dioxide−Sc^{III} complex as effective catalyst were required (Scheme 28). A wide range of γ-butenolide products **55** with adjacent quaternary and tertiary stereocenters were obtained via this transformation showing excellent diastereo- and enantioselectivities. The authors suggested the use of **L9** and $Sc(OTf)_3$ in this reaction is likely to generate a hexacoordinate chiral scandium complex in which both oxygens of *N*-oxide and carbonyl oxygens coordinate with scandium in a tetradentate manner. The stereochemical outcome of the reaction was explained by the attack of **54** to the *si* face of the aldimine (Scheme 28).

Recently, Xu and Wang examined the direct vinylogous VM reaction of 3,4-dihalofuran-2(5*H*)-one by applying quinine **C18** as catalyst (Scheme 29).[86] A series of aldimines **56** derived from aromatic aldehydes were employed, affording the δ-amino γ-butenolides in excellent yields (up to 98%) and enantioselectivities (up to 95% ee). The synthetic utility of this method was demonstrated by converting the resulted Mannich products **57** to building blocks such as γ-butyrolactone **58** or amino alcohol **59**.

2.2.3. Mannich Reaction at the α-Position of Furanone Derivatives. Through introduction of ketimine substrates with the intrinsically bound carbamate as nitrogen protecting group, Jørgensen and co-workers employed butyrolactone-derived silylketene acetal **23** in the asymmetric Mannich-type reaction with chiral $Zn(OTf)_2$-((*R*,*R*)-Ph-pybox)$_2$ complex **C19** as catalyst (Scheme 30).[87] Although the reaction afforded Mannich adduct **61** in quantitative yield with 95% ee, only moderate diastereoselectivity was obtained (dr = 1:4.6 (*syn*:*anti*)).

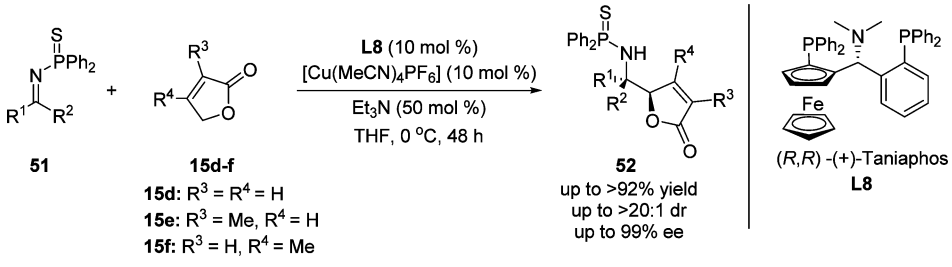
The direct Mannich reaction of 1,3-dicarbonyls, including β-keto lactone **62** to acyl imines **63**, was investigated by Schaus et al., utilizing the cinchonine **C20** as effective catalyst. This reaction allowed access to the construction of cyclic β-amino esters **64** with α-quaternary carbon center in high enantiopurity (Scheme 31).[88] Unfortunately, low levels of diastereoselectivities were observed when β-keto lactone was employed as the heterocyclic nucleophile.

Wang and co-workers have used the rosin-derived bifunctional amine-thiourea **C21** to catalyze the asymmetric Mannich reaction of α-acetyl-γ-butyrolactone **62** with a variety of *N*-Boc-protected aldimines **65**. The formation of adducts **66**, bearing a quaternary stereogenic center, shows high levels of enantio- and diastereoselectivities (up to 99% ee and >20:1 dr).[89] Cooperative catalysis by the urea functionality and the tertiary amino group, with a favorable approach of the resulting enolate at the *si* face of the *N*-Boc-aldimine, was postulated by the authors (Scheme 32).

2.3. Asymmetric Michael Reaction

2.3.1. Asymmetric Mukaiyama−Michael Reaction of Silyloxyfurans. The catalytic asymmetric Mukaiyama−Michael reaction involving 2-silyloxyfurans and α,β-unsaturated carbonyl derivatives has attracted major attention in the organic chemistry community. This method provides highly functionalized

Scheme 27. Direct Catalytic Asymmetric Mannich-Type Reaction of γ-Butenolides and *N*-Thiophosphinoyl Ketimines



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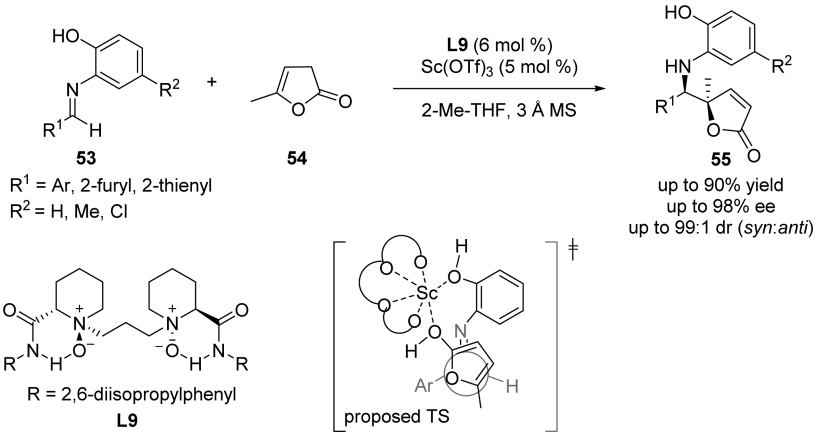
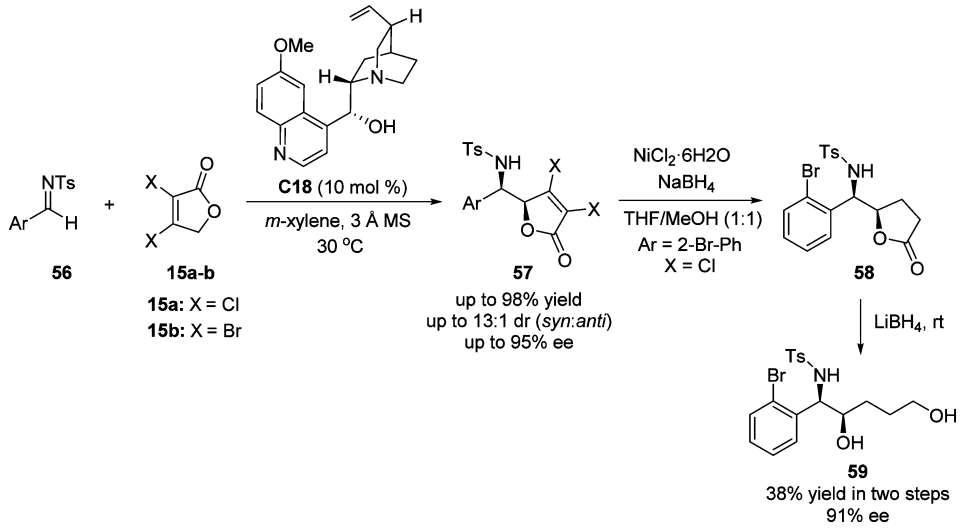
Scheme 28. Catalytic Asymmetric Vinylogous Mannich-Type Reaction of γ-Butenolide 54

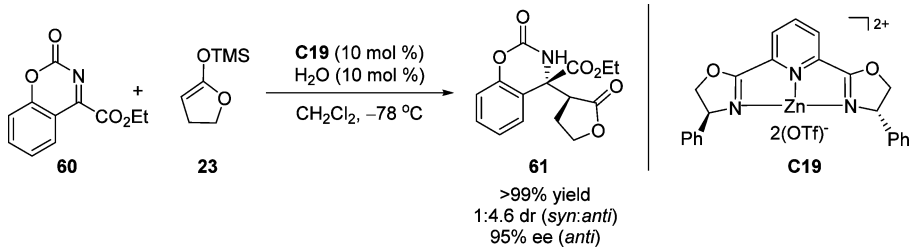


Scheme 29. Direct Asymmetric Vinylogous Mannich Reaction of 3,4-Dihalofuran-2(5*H*)-one 15a and 15b with Aldimines 55 Catalyzed by Quinine[a]



[a]Ts = 4-toluenesulfonyl.

Scheme 30. Vinylogous Mannich Reaction of Butyrolactone-Derived Silylketene Acetal



butenolides which allow many further transformations. Several book chapters[90] and reviews[13,91−95] on this topic have already been published, so this part only covers selected examples and focuses on the synthetic applications of this method.

In 1997, Katsuki et al. described the chiral Lewis acid promoted Mukaiyama−Michael reaction of 2-trimethylsilyloxyfurans and oxazolidinone enoates (Scheme 33).[96,97] An in situ prepared **L11**/Cu(OTf)$_2$ complex exhibited the desired product in excellent *anti*-selectivity and moderate enantioselectvity, while the complex formed from scandium triflate and a 3,3′-diamino methyl substituted (*R*)-BINOL **L10** (1:1 ratio) gave rise to excellent enantiomeric purity and moderate to good *anti*-selectivity. This asymmetric Michael reaction has been used in a short synthesis of (+)-whisky lactone.[98]

Since the pioneering work of Katsuki and co-workers,[96−98] various chiral Lewis acids including nickel,[99] and lanthanide[100] metal complexes have been efficiently used as catalysts for the Mukaiyama−Michael reaction (Figure 4). These early examples typically employed oxazolidinones as Michael acceptors. The use of α′-phenylsulfonyl enones as the Michael acceptors were disclosed by the group of Kim in 2008 (Scheme 34).[101] This catalytic process was highly stereoselective (up to 99% ee) and

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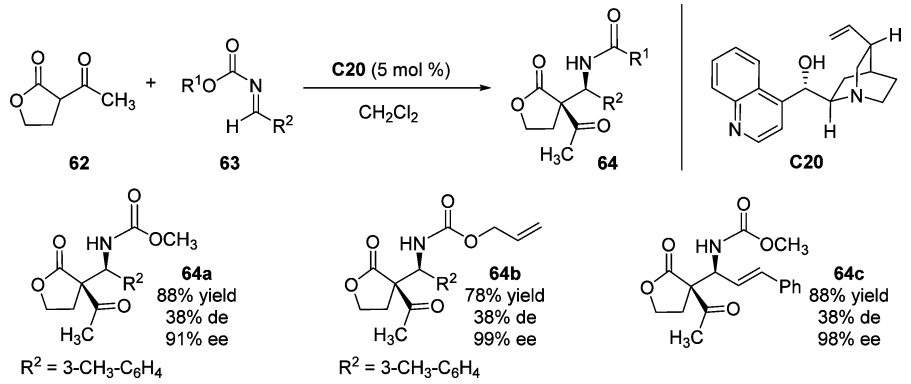
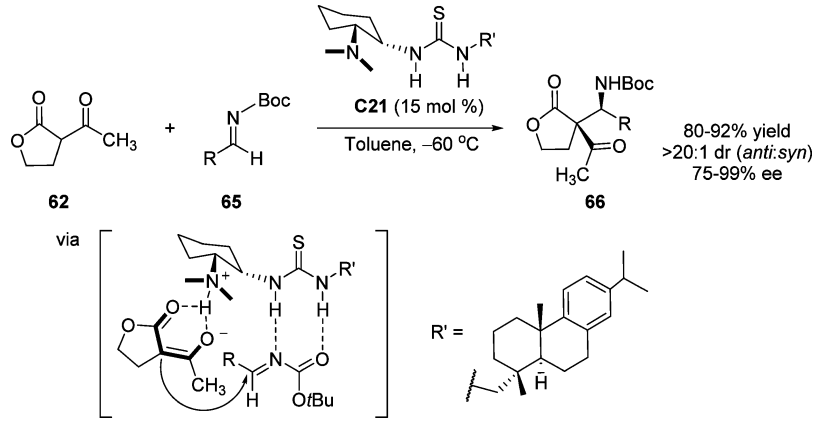
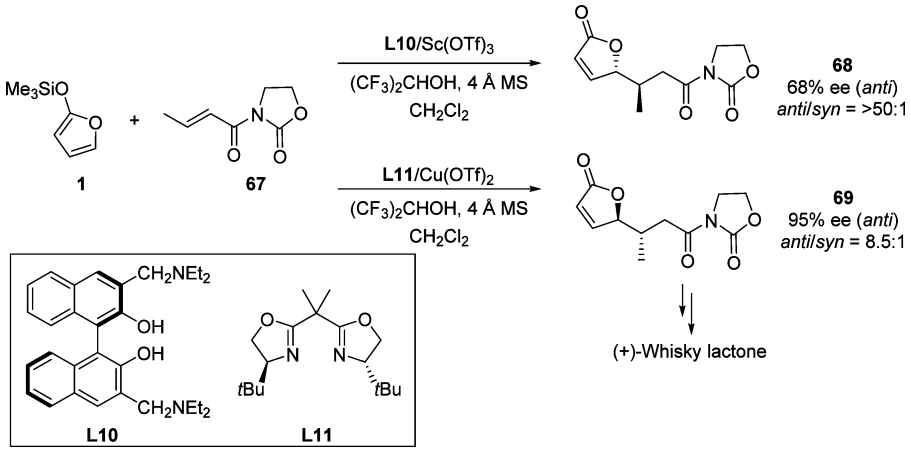
Scheme 31. Direct Asymmetric Vinylogous Mannich Reaction of β-Keto Lactone with Acyl Imines



Scheme 32. Enantioselective Mannich Reaction of β-Keto Lactone with *N*-Boc-Protected Aldimines



Scheme 33. Asymmetric Michael Addition of 2-(Trimethylsilyloxy)furan to Oxazolidinone Enoate



gave almost exclusively the *anti* product with β-methyl substituted enone **71**. The resulting γ-butenolides were converted into a number of building blocks which were applied in the synthesis of natural products.

Feng et al.[102] described the use of chalcones as weak chelating substrates in the asymmetric vinylogous Mukaiyama–Michael reaction of 2-(trimethylsilyloxy)furan using chiral *N*,*N*′-dioxide–scandium(III) complexes as catalysts (Scheme 35). The favored *anti*-diastereoselectivity of the product **73** was rationalized through the *si* face attack of the nucleophile to the chalcone in which the *re* face of chalcone was shielded by the neighboring 2,6-diethylphenyl group of the ligand.[102] A gram-scale synthesis of the chiral γ-substituted butenolide was successfully performed under the optimized conditions, delivering the Michael adducts **73** in excellent yields and diastereoselectivities with only 5 mol % of the catalyst employed.

The asymmetric vinylogous Mukaiyama–Michael reaction of 2-(trimethylsilyloxy)furan and (*E*)-cinnamoyl-pyridine-*N*-oxide **74** was reported by Faita and co-workers.[103] The corresponding butenolide **75** was obtained as a single diastereomer with good enantioselectivity (86% ee) in the presence of chiral bis-(oxazoline)–Cu(II) complex (Scheme 36). A square-pyramidal bis(oxazoline)–Cu(II) complex in which the two oxygen atoms of pyridine-*N*-oxide substrate are coordinated to the copper

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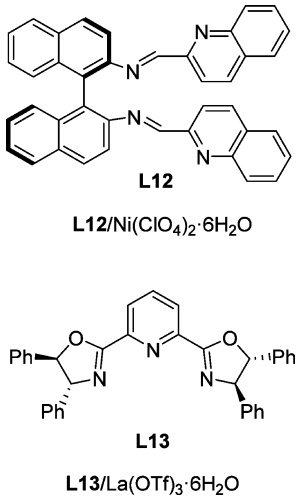


Figure 4. Chiral metal complexes used in the asymmetric vinylogous Mukaiyama–Michael reaction of 2-(trimethylsilyloxy)furans.

cation, as confirmed by X-ray analysis in previous work,[104] was proposed as intermediate for this transformation. Ishihara and Fushimi have reported that the L-DOPA-derived monopeptide **L17**/Cu(II) complex was an efficient catalyst for the enantioselective Mukayama–Michael reaction of TMSOF with α,β-unsaturated 1-acyl-3,5-dimethylpyrazoles.[105] The proposed transition state shows the presence of a π-cation interaction in the copper(II) complex which might explain the observed high enantioselectivity (Scheme 37).

In addition, asymmetric vinylogous Mukaiyama–Michael addition of cyclic dienol silanes to α-keto-β,γ-unsaturated-keto phosphonates **78** was developed by Bolm and co-workers. The system comprising 10 mol % $Cu(ClO_4)_2 \cdot 6H_2O$ and 10 mol % bisoxazoline ligand **L11** proved to be an efficient catalyst for this enantioselective conjugate addition delivering phosphonate-containing γ-butenolides **81** with high stereoselectivity in an *anti* fashion (Scheme 38).[106]

By using a chiral C_2-symmetrical bis(oxazoline)–copper(II) complex, Guillou, Chabaud, and co-workers established a highly enantio- and diastereoselective Mukaiyama–Michael addition of 2-silyloxyfurans to cyclic unsaturated oxo esters **83** (Scheme 39).[107] Two different transition states were proposed by the authors where complex A has relative higher energy compared to complex B due to the nonbonding steric interactions between the ligand and the R^2 substituents.[107] The sense of enantioselectivity and the high level of diastereoselectivity were then rationalized by the attack of silyloxyfuran occurring on the *Si* face of the complex B in which the *Re* face is shielded by the ligand.

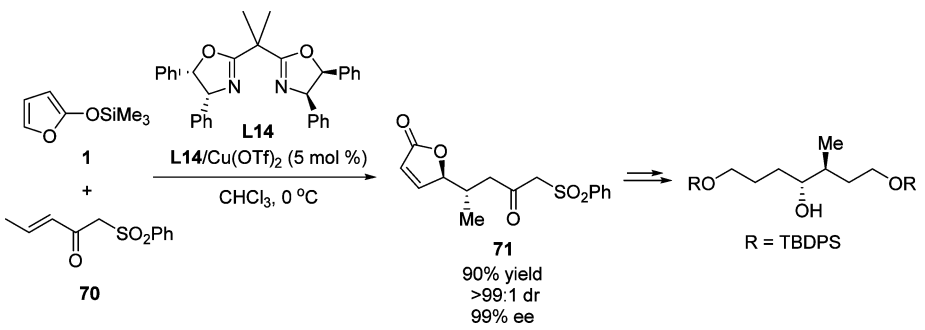
Wang and co-workers described a catalytic asymmetric synthesis of fused butyrolactones via a cascade annulation of 2-silyloxyfurans with azoalkenes catalyzed by a C_2-symmetric bis(oxazoline)–Cu(II) complex. The reaction was proposed to proceed through an initial vinylogous Mukaiyama 1,6-Michael addition followed by an intramolecular Michael addition (Scheme 40). In situ formed metalloazoalkenes acted as the Michael acceptor for the 1,6-addition of 2-silyloxyfurans.[108] The resulting butenolide intermediate undergoes an intramolecular Michael addition promoted by nucleophilic attack of the nitrogen atom and final protonation provided the fused butyrolactone **85** with excellent stereoselectivity control. In this process, the use of a protic additive such as hexafluoroisopropanol (HFIPA) was essential to obtain the reaction products in good yield. This tandem annulation proved to be also compatible with the use of 3- and 5-methyl-substituted 2-silyloxyfurans affording in those cases fused butyrolactones bearing three contiguous stereogenic centers in a highly diastereoselective manner.

The first enantioselective organocatalytic Mukaiyama–Michael reaction of silyloxy furans **88** to α,β-unsaturated aldehydes **89** was accomplished by MacMillan and co-workers (Scheme 41).[109] The use of iminium catalysis involving chiral imidazolidinone **C22** provided a novel strategy toward the synthesis of highly functionalized, enantiomerically enriched butenolide architectures. A demonstration of the utility of resulting butenolide products **90** was presented in the multiple-step synthesis of spiculisporic acid and 5-*epi*-spiculisporic acid.

The usefulness of the organocatalytic enantioselective Mukaiyama–Michael addition was exemplified by the facile construction of (+)-compactin diol bearing four contiguous stereogenic centers (Scheme 42).[110] Moreover, a concise enantioselective synthesis of (*S*)-homocitric acid lactone and its homologue was completed by Pansare et al. in which the key intermediate of chiral butenolide was achieved under the organocatalytic vinylogous Mukaiyama–Michael reaction using MacMillan's catalyst **C22**.[111]

A related organocatalyzed Mukaiyama–Michael addition has been applied to the enantioselective synthesis of the C-5-*epi* ABCDE ring system of rubriflordilactone B (Scheme 43).[112] Proline-derived catalyst **C23** was shown to efficiently catalyze the reaction between silyloxyfuran **94** and (*E*)-α,β-unsaturated aldehyde **95** providing the product **96** in moderate yield with excellent stereoselectivity (68% yield, 97% ee, >20:1 dr).

Scheme 34. Catalytic Enantioselective Mukaiyama–Michael Addition of 2-(Trimethylsilyloxy)furan with α'-Phenylsulfonyl Enone[a]



[a]TBDPS = *tert*-butyldiphenylsilyl.

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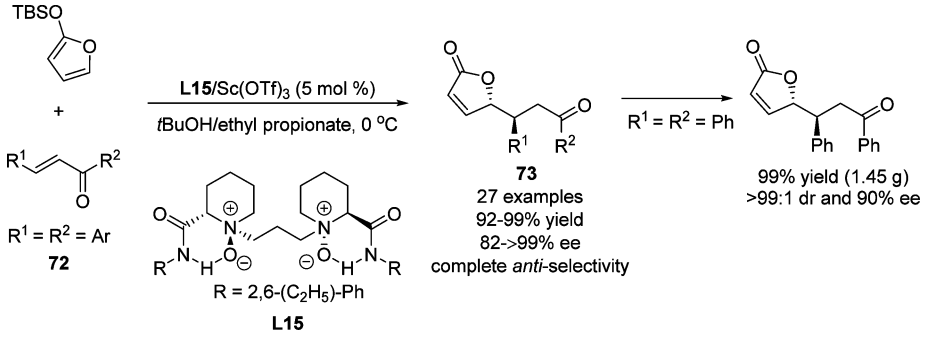
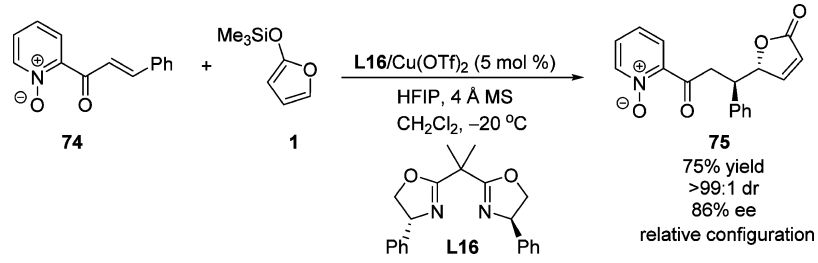
Scheme 35. Catalytic Enantioselective Mukaiyama−Michael Addition of 2-Silyloxyfuran with Chalcones[a]

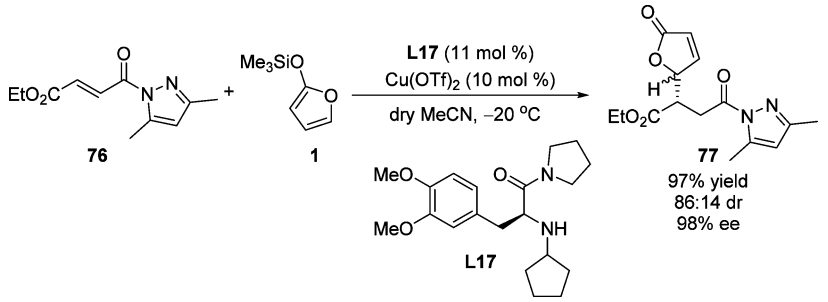


[a]TBS = *tert*-butyldimethylsilyl.

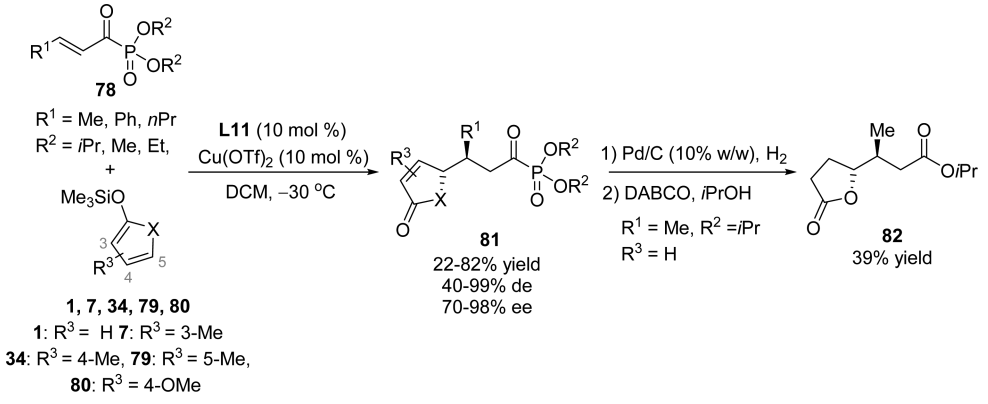
Scheme 36. Catalytic Enantioselective Addition of 2-(Trimethylsilyloxy)furan to (*E*)-Cinnamoyl-pyridine-*N*-oxide 74



Scheme 37. Enantioselective Mukaiyama−Michael Reaction of Silyl Enol Ethers 1 with 76



Scheme 38. Enantioselective Mukaiyama−Michael Reaction of Cyclic Dienol Silanes with α-Keto-β,γ-unsaturated-keto Phosphonates



Surprisingly, the (*Z*)-α,β-unsaturated aldehyde gave rise to the product with same stereoconfiguration. After the introduction of three alkyne functional groups, rhodium-catalyzed intramolecular cycloaddition of triynes was carried out to complete the facile construction of C-5-*epi* ABCDE core **98**.

MacMillan's iminium-catalyzed Mukaiyama−Michael reaction was also tolerant to β-substituted α,β-unsaturated aldehydes such as methacrolein, affording the present γ-butenolide in moderate diastereoselectivity (56:44 dr) and 96% ee. The resulted γ-butenolide **100** was then readily used as a key intermediate for

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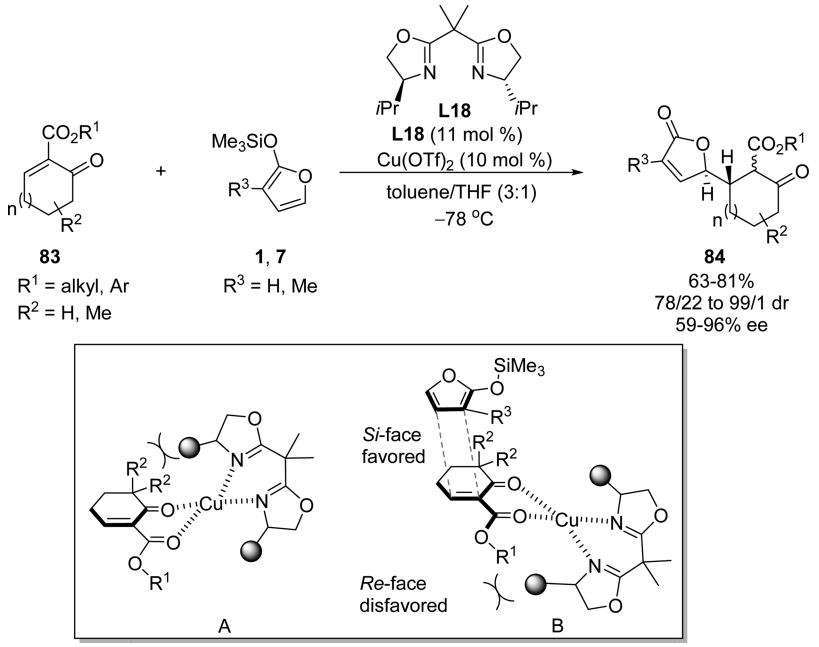
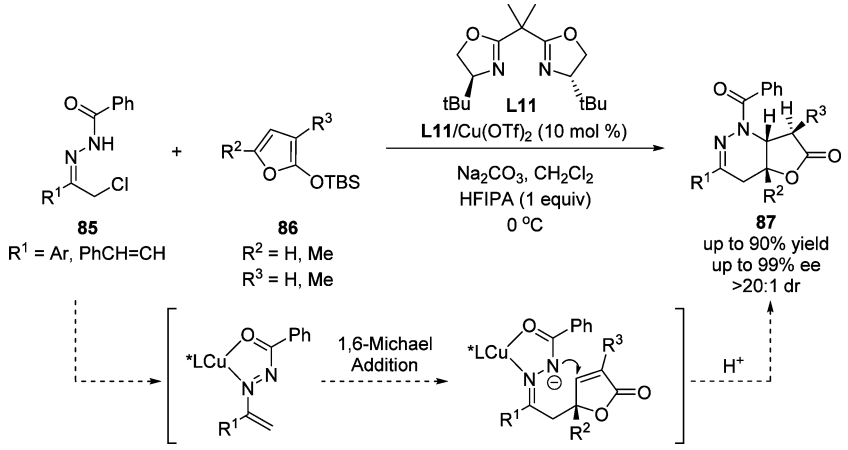
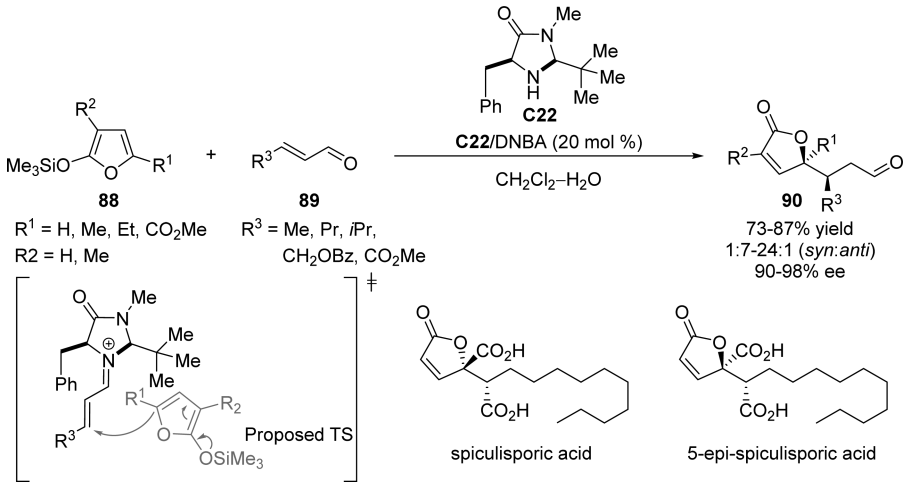
Scheme 39. Catalytic Enantioselective Addition of 2-Silyloxyfurans to Cyclic Unsaturated Oxo Esters 83



Scheme 40. Catalytic Asymmetric Synthesis of Fused Butyrolactones 87



Scheme 41. Organocatalyzed Mukaiyama–Michael Addition of Silyloxy Furans with α,β-Unsaturated Aldehydes[a]



[a]DNBA = 2,4-dinitrobenzoic acid.

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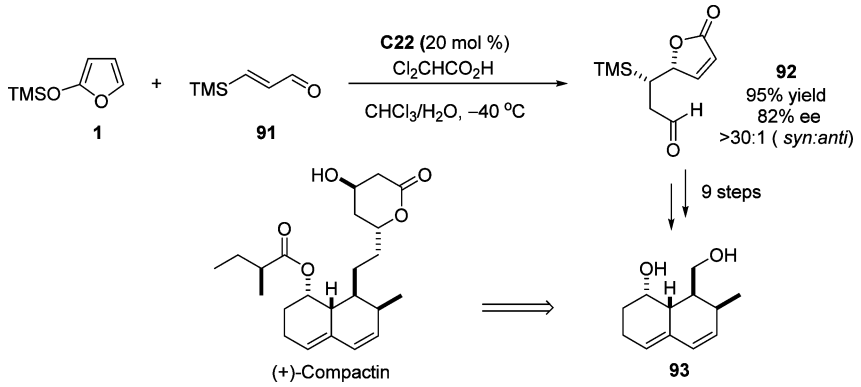
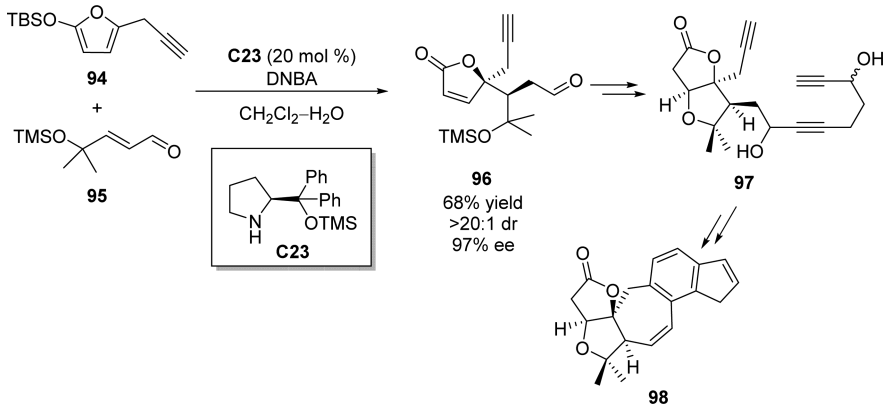
Scheme 42. Formal Synthesis of (+)-Compactin through Organocatalyzed Mukaiyama−Michael Addition

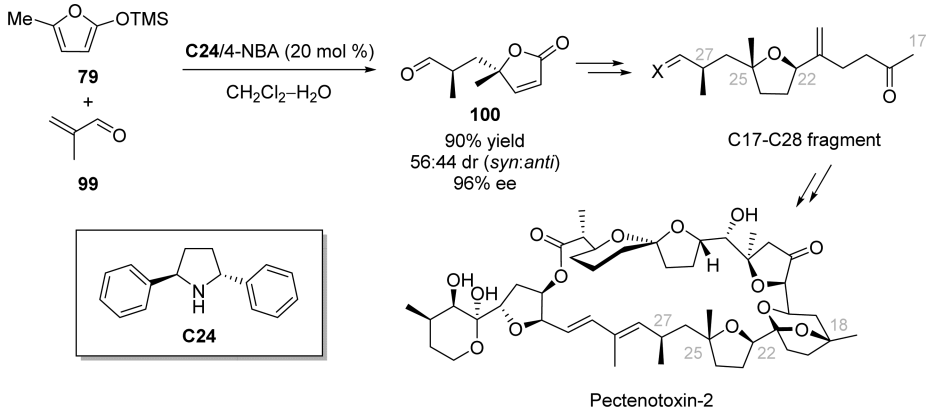


Scheme 43. Enantioselective Synthesis of C-5-*epi* ABCDE Core toward the Construction of Rubriflordilactone B[a]



[a]DNBA = 2,4-dinitrobenzoic acid.

Scheme 44. Catalytic Enantioselective Synthesis of the C17−C28 Fragment of Pectenotoxin-2[a]



[a]4-NBA = 4-nitrobenzoic acid.

the synthesis of C17−C28 fragment of pectenotoxin-2 (Scheme 44).[113]

Upon the exposure of α,β-unsaturated aldehydes to imidazolidinone catalyst **C25**, MacMillan et al. developed an organocascade catalytic strategy merging iminium and enamine catalysis (Scheme 45).[114] The enamine intermediate generated after the attack of TMSOF to the formed iminium cation was then activated and trapped by the chlorinated quinone **101** as the electrophile to afford chloro aldehyde **102** containing three adjacent stereocenters with excellent stereoselective control.

Soon thereafter, the group of MacMillan reported a sequential one-pot synthesis of butenolide **103** which was used as a key intermediate for the enantioselective synthesis of (−)-aromadendranediol (Scheme 46).[115] This bicyclic intermediate was generated through a triple cascade catalysis involving initial cross-metathesis which originated a keto-enal which subsequently underwent iminium-type Mukaiyama−Michael reaction of 5-methyl-2-trimethylsilyloxyfuran followed by enamine-based cycloaldolization. Employing the combination of chiral imdazolidinone and proline as a dual catalyst, the bicyclic butenolide **103** containing four contiguous stereocenters was accessed with 64%

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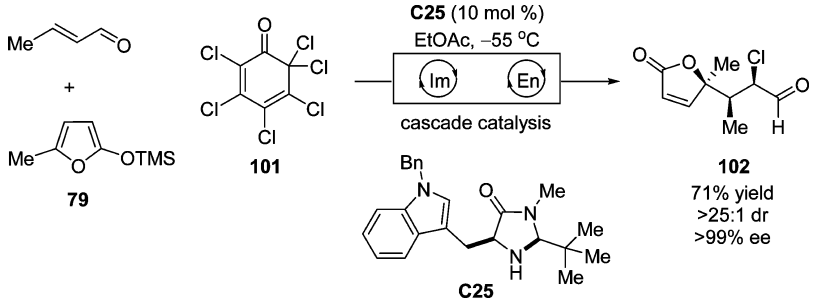
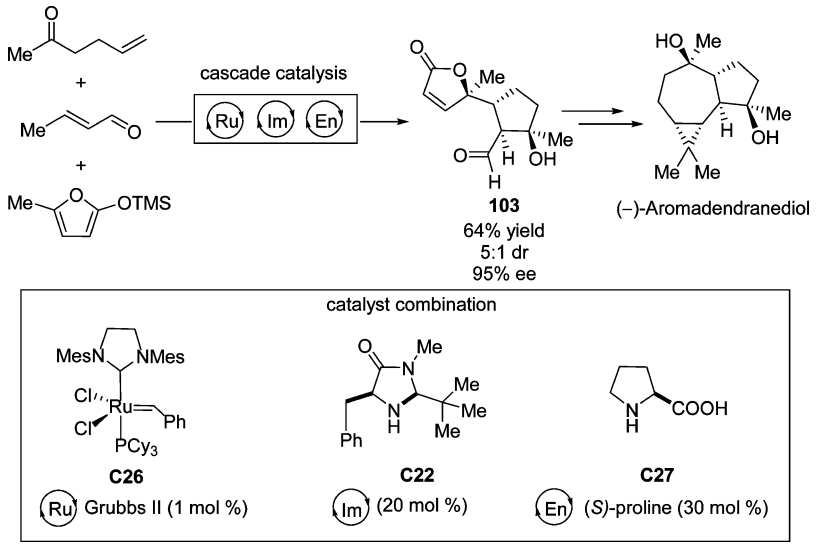
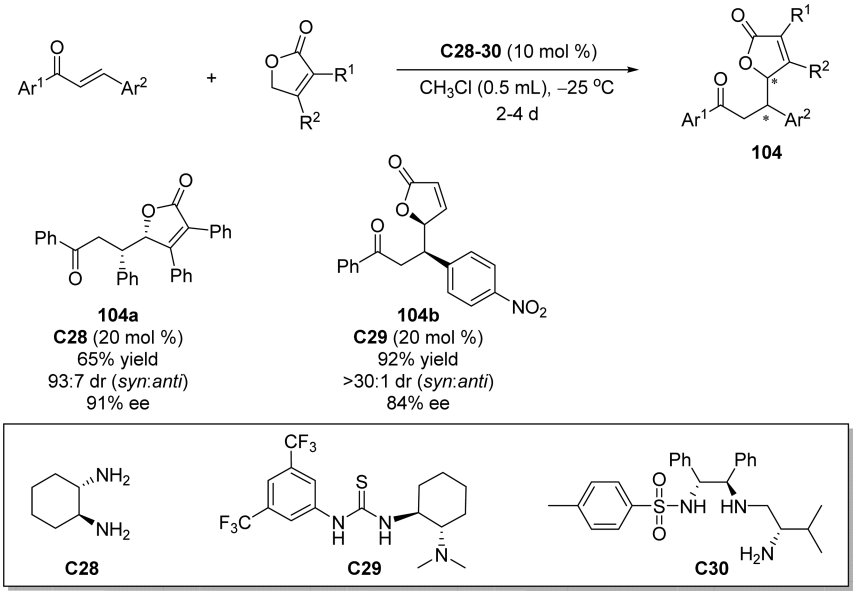
Scheme 45. Diastereo- and Enantioselective Cascade Organocatalysis To Promote the Synthesis of Butenolide Containing Three Adjacent Stereocenters



Scheme 46. Total Synthesis of (−)-Aromadendranediol through Cycle-Specific Organocascade Catalysis



Scheme 47. Typical Chiral Amine Organocatalysts Applied in the Direct Asymmetric Vinylogous Michael Addition of γ-Butenolides



overall yield and excellent stereoinduction. This elegant triple cascade catalysis allows for the synthesis of complex molecular architectures with an exquisite level of simplicity and stereocontrol.

2.3.2. Direct Asymmetric Vinylogous Michael Addition of Unsaturated Butyrolactones. *2.3.2.1. Direct Vinylogous Michael Addition to α,β-Unsaturated Ketones and Derivatives.* In 2010, Li et al.[116] disclosed the first direct organocatalytic

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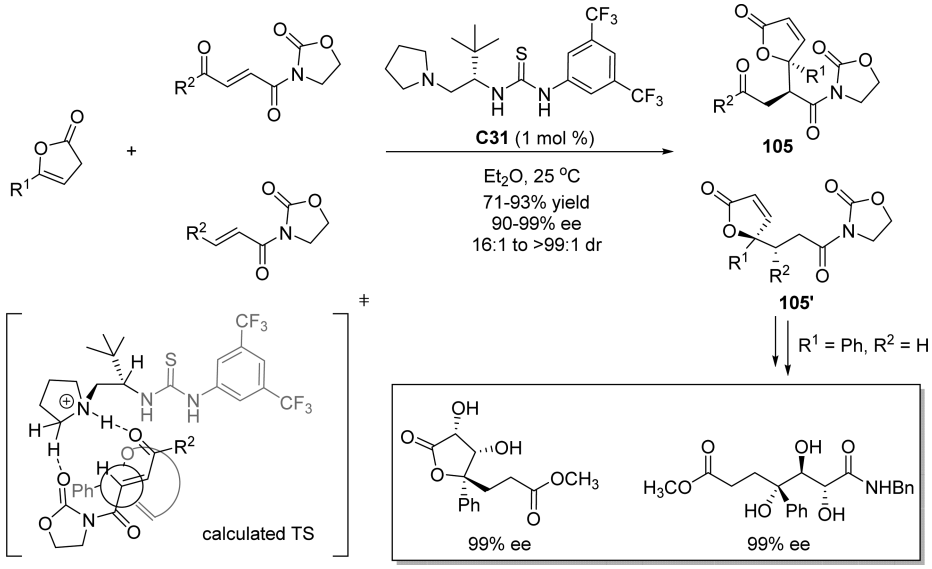
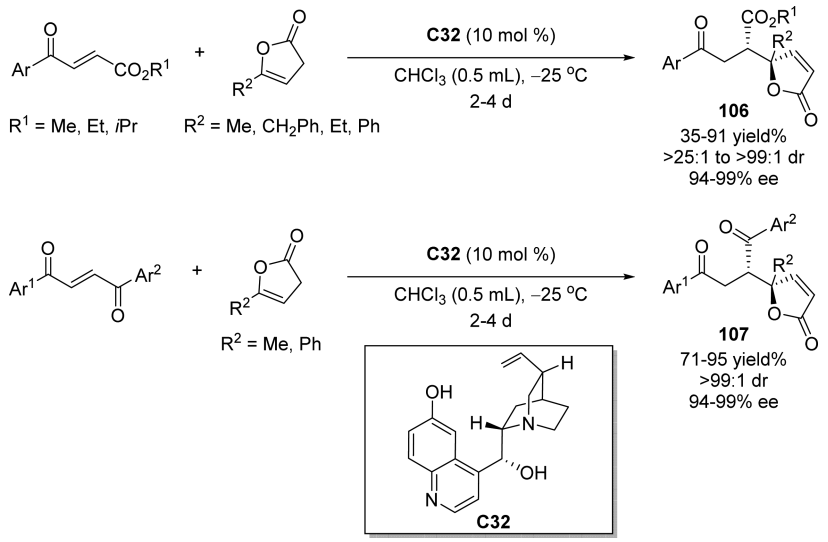
Scheme 48. Catalytic Asymmetric Addition of *β,γ*-Butenolides to *α,β*-Unsaturated Ketones Containing an Oxazolidinone Moiety



Scheme 49. Catalytic Asymmetric Vinylogous Michael Addition of *β,γ*-Butenolides in the Presence of Quinine Catalyst



vinylogous Michael addition of *γ*-butenolides to *α,β*-unsaturated ketones utilizing chiral 1,2-diaminocyclohexane **C28** as novel catalyst. This process which probably involves a diiminium transition state provided *syn*-Michael products with good yieds and high stereoinduction, although substituted *γ*-butenolides as prochiral nucleophiles and chalcones as substrates were required. Soon after, Wang and co-workers reported the studies on the multifunctional amine-thiourea catalyst **C29** promoted direct Michael addition of simple 2(5*H*)-furanone to chalcones (Scheme 47).[117] Based on a combination of experiment (NMR) and theoretical (density functional theory (DFT)) approaches, the dual activation pathway for the direct vinylogous Michael reaction of *α,β*-unsaturated-*γ*-butyrolactam involving bifunctional cinchona alkaloid thiourea organocatalysts was proposed by the same group.[118] A new type of triamine catalyst **C30** was developed almost simultaneously by the group of Ye, in which a variety of enones including benzalacetone, chalcones, and alkyl substituted enones were examined as the suitable substrates to acess the enantiomerically enriched *γ*-substituted butenolides (Scheme 47).[119]

Jiang and co-workers developed the direct asymmetric vinylogous conjugate reaction of *γ*-aryl- and alkyl-substituted butenolides to *α,β*-unsaturated ketones bearing an oxazolidinone motif (Scheme 48).[120] Upon treatment with L-*tert*-leucine-derived amine-thiourea catalyst **C31**, various *γ,γ*-disubstituted butenolides **105** and **105′**, bearing a quaternary stereogenic center, were obtained in 71−93% yields with excellent enantio- and diastereoselectivities. The chirality was controlled through the weak nonbonding interaction of the catalyst with the carbonyl groups of the oxazolidinone-based substrate. The synthetic value of this process was explored by transforming the resulting adducts into biologically important *γ,γ*-disubstituted butenolides or key intermediates such as a glycerol analogue.

Quinine derived catalyst **C32** was successfully employed by the group of Lin for the enantioselective direct Michael addition of *β,γ*-butenolides to a series of 3-aryl acrylates and 1,2-diaroylethylenes (Scheme 49).[121] This method provided *γ,γ*-disubstituted butenolides possessing adjacent tertiary and quaternary stereocenters with excellent enantio- and diastereoselectivities (up to 99% ee and >99:1 dr). A bifunctional

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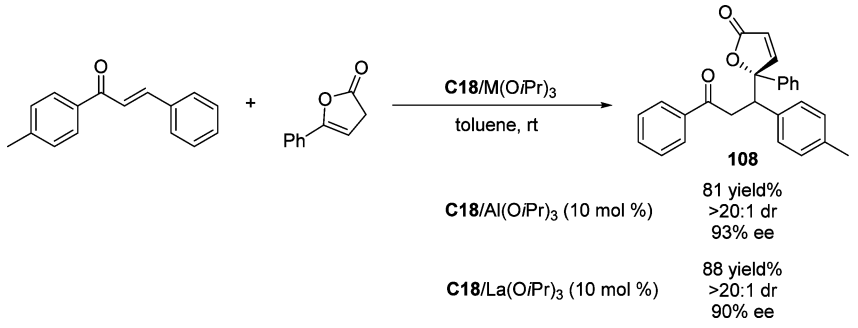
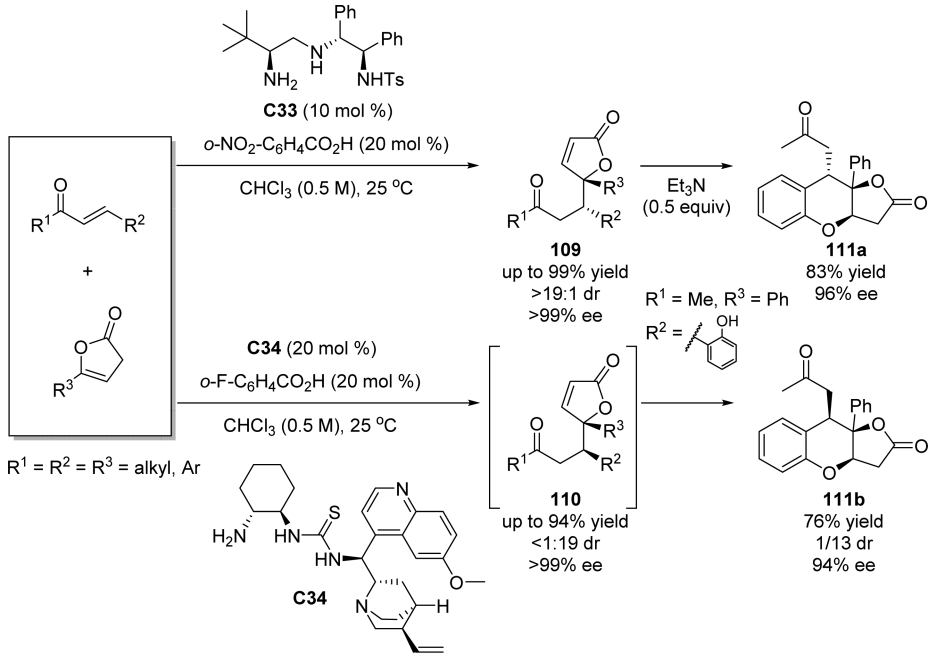
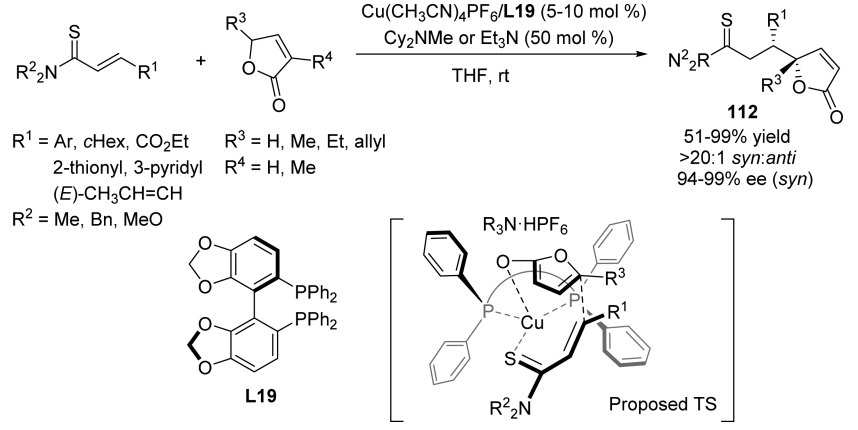
Scheme 50. Direct Vinylogous Michael Addition of β,γ-Unsaturated Butenolide to Chalcone



Scheme 51. Catalyst-Controlled Enantioselective Diastereodivergent Vinylogous Michael Reaction



Scheme 52. Catalytic Asymmetric Vinylogous Conjugated Addition of Butenolides to α,β-Unsaturated Thioamides



activation mechanism in which the phenolic OH group activates the Michael acceptor by forming a possible hydrogen bridge while the tertiary amine abstracts the acidic proton of β,γ-butenolides to generate a dienolate as nucleophile was proposed.

Wang and co-workers have developed a cooperative metal/organo catalytic system composed of quinine **C18** and a metal complex formed from (*R*)-Binol and $Al(OiPr)_3$ or $La(OiPr)_3$ for the efficient direct vinylogous Michael addition of γ-aryl-substituted butenolides to enones (Scheme 50).[122] The cooperative catalyst serves for both activating the butenolide by the Lewis acid assisted Brønsted base to enhance the acidity of α proton and the LUMO activation of the enone by the Lewis acid, providing γ,γ-disubstituted butenolides in good yields and excellent stereoselectivities.

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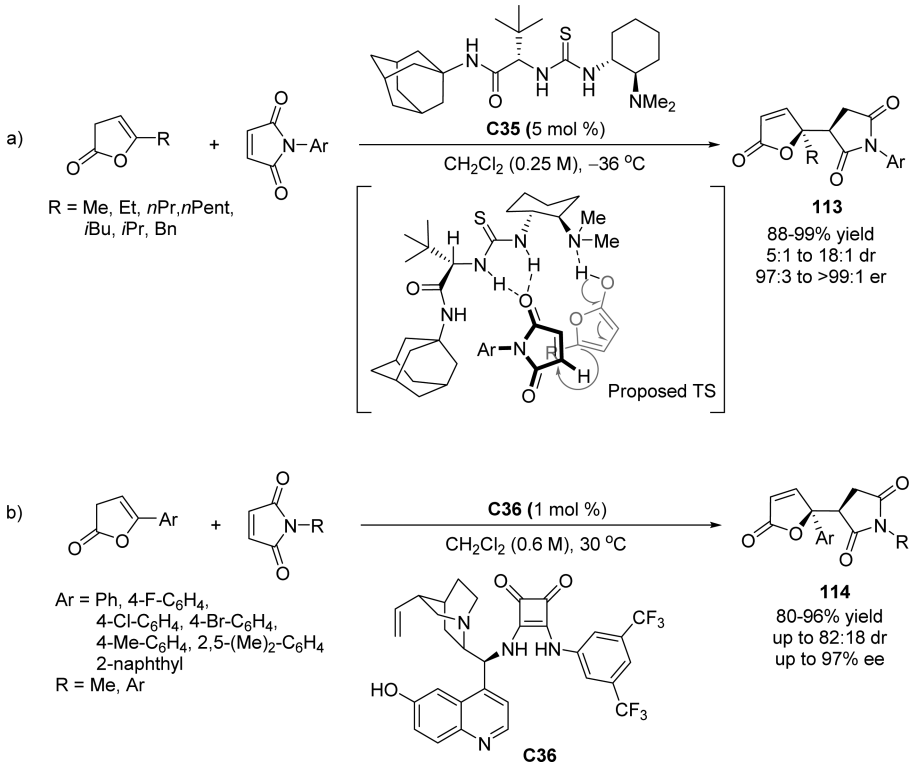
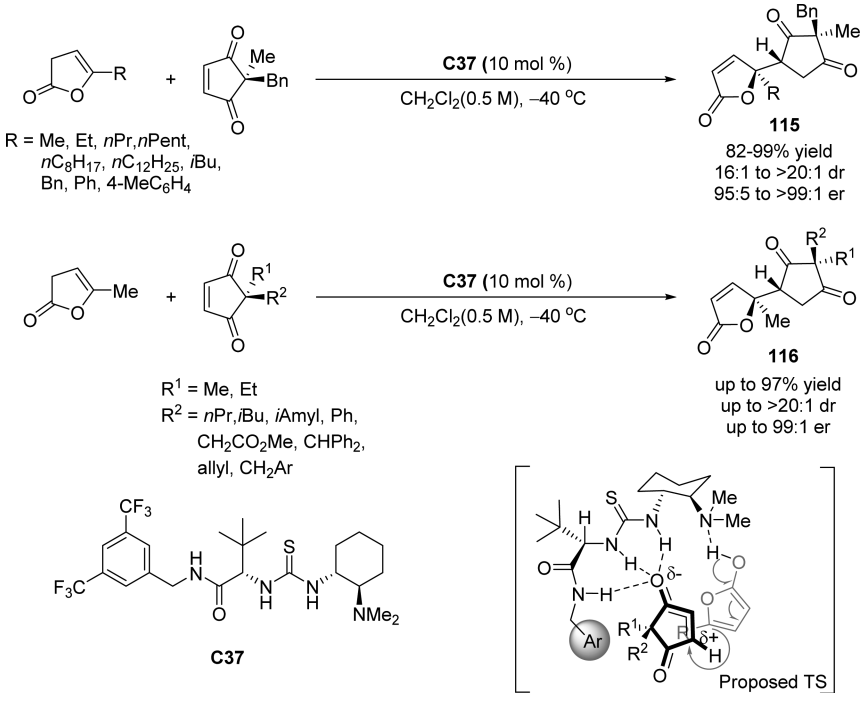
Scheme 53. Asymmetric Vinylogous Michael Addition of γ-Substituted β,γ-Unsaturated Butenolides to Maleimides



Scheme 54. Asymmetric Vinylogous Michael Addition of γ-Substituted β,γ-Unsaturated Butenolides to Cyclopentene-1,3-dione Substrates



Ye and Dixon reported a catalyst-controlled diastereodivergent asymmetric Michael reaction of β,γ-unsaturated butenolides to α,β-unsaturated ketones based on a cooperative use of different organocatalysts and benzoic acids.[123] Organocatalyst **C33** which bears two different amine functionalities was proved to be efficient for providing *anti*-selectivity due to the H-bonding interaction between catalyst, nucleophile, and substrate. Diamine-thiourea catalyst **C34** was described to have a complementary selectivity for this transformation providing *syn*-selective adducts with good yields and excellent enantio- and diastereoselectivities (up to 94% yield, <1:19 dr, >99% ee). The resulting chiral adducts could be further transformed, in a one-pot process, into fused butyrolactones **111a** and **111b** in a totally

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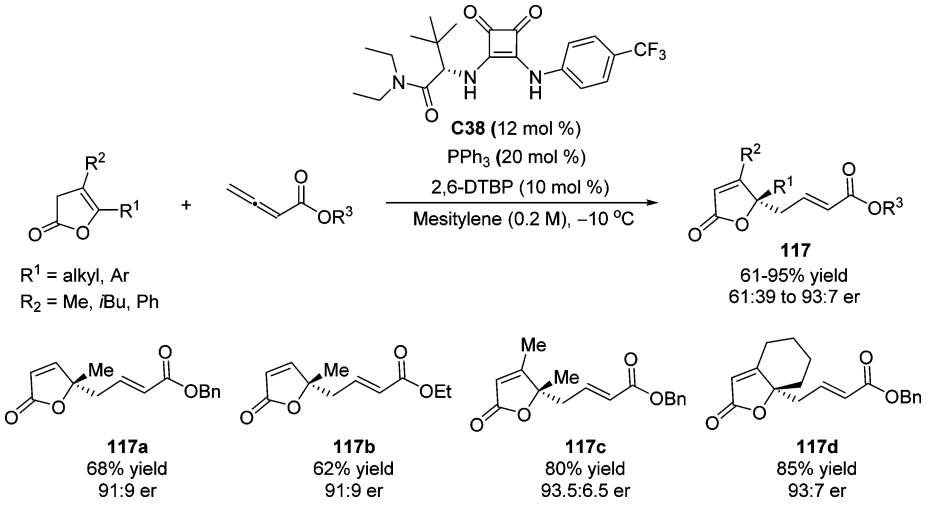
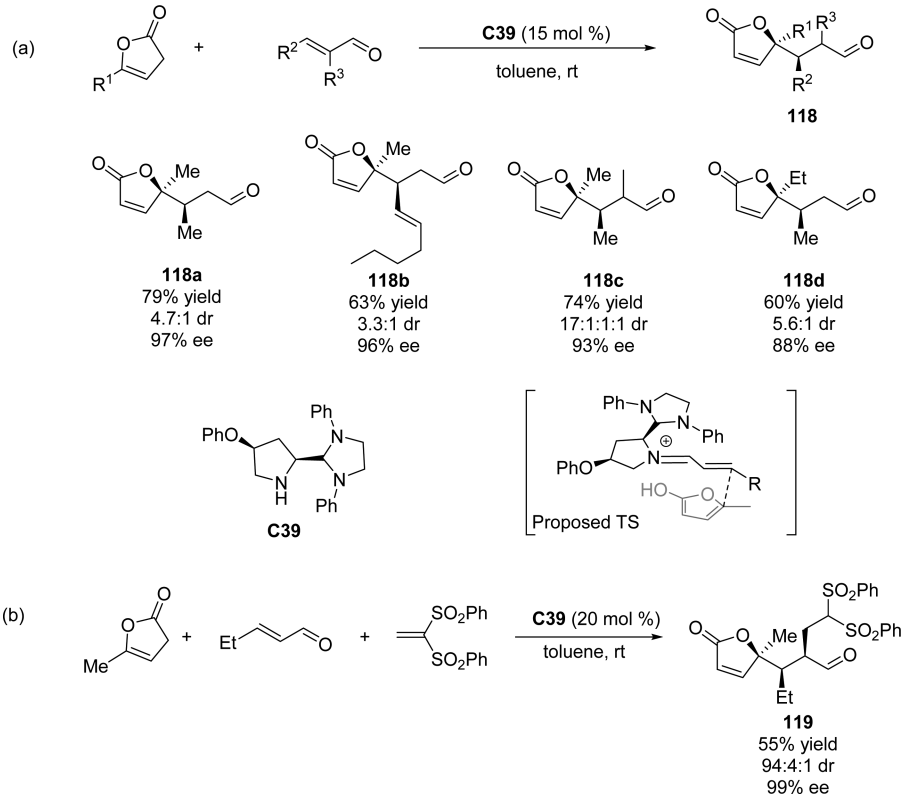
Scheme 55. Enantioselective Direct Vinylogous Addition of γ-Substituted β,γ-Unsaturated Butenolides to Allenoates[a]



[a]2,6-DTBP = 2,6-di-*tert*-butylphenol.

Scheme 56. Organocatalytic Asymmetric Vinylogous Michael Addition of Furanones to Enals



stereoselective way when a substrate bearing an *o*-phenolic group was used (Scheme 51).

Moreover, a soft Lewis acid/Brønsted base cooperative catalyst system was demonstrated by Kumagai and Shibasaki to enable the vinylogous conjugated addition of α,β- and β,γ-unsaturated butyrolactones to α,β-unsaturated thioamides (Scheme 52).[124] The use of the thioamide functionality was essential to achieve high conversion and selectivity. The stereochemical outcome of the reaction arises from a plausible transition state in which a vinylogous Cu(I) enolate, formed with the assistance of tertiary amine, coordinates to the substrate forming a tetracoordinated Cu(I) intermediate in which one side of the substrate is shielded by one phenyl group of the ligand **L19**. The synthetic utility was highlighted by the divergent transformation of the thioamide functionality of the chiral product.

Mukherjee and Manna reported a catalytic asymmetric direct vinylogous Michael addition of γ-alkyl-substituted β,γ-unsaturated butenolides to maleimides, using a chiral thiourea/tertiary-amine bifunctional catalyst **C35** (Scheme 53a).[125] Based on the observed excellent level of product stereoselectivity, a plausible reaction mechanism through hydrogen bonding interaction was proposed. After the preactivation of the butenolide, a face-selective nucleophilic attack takes place between the in situ

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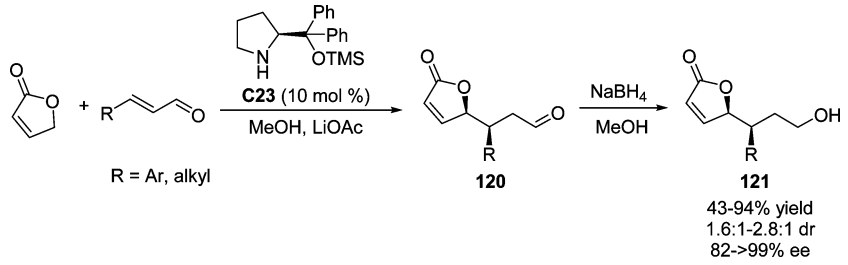
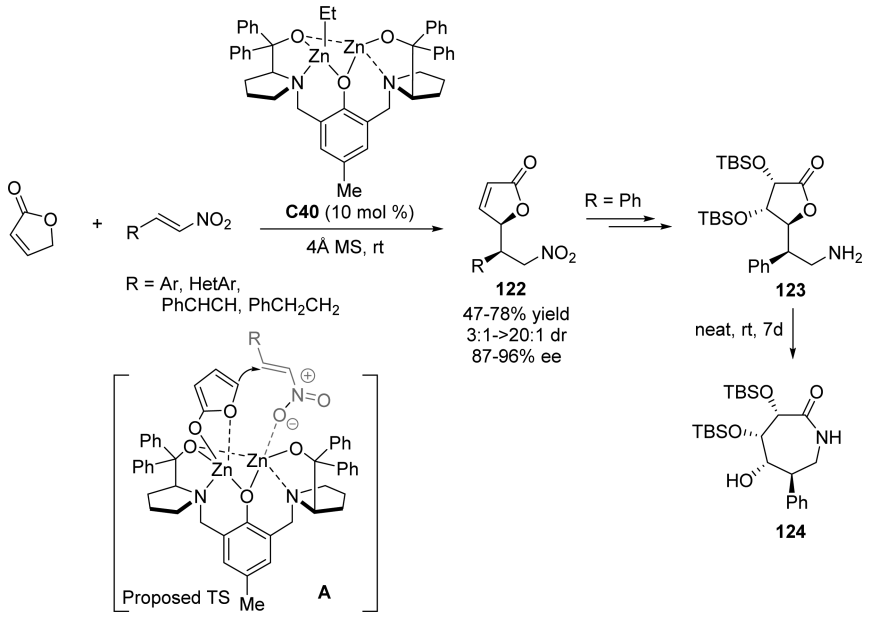
Scheme 57. Vinylogous Michael Reaction of Enals with 2(5*H*)-Furanone Employing Chiral Prolinol-Derived Organocatalyst



Scheme 58. Direct Asymmetric Michael Addition of 2(5*H*)-Furanone to Nitroalkenes



formed dienolate and the maleimide with reduced LUMO energy, providing the product with impressive enantio- and diastereocontrol. Wang and co-workers expanded the γ-alkyl-substituted β,γ-unsaturated butenolides as nucleophiles to the direct VM addition of maleimides, using cinchona alkaloid derived squaramide **C36** as optimized catalyst (Scheme 53b).[126] Low catalyst loading (1 mol %), mild conditions, and high yields and enantioselectivities provide an effective protocol for the construction of optically active γ-butenolides with adjacent stereocenters and functional groups.

Mukherjee and co-workers described a catalytic desymmetrization of 2,2′-disubstituted cyclopentene-1,3-diones through vinylogous Michael addition to a range of deconjugated butenolides, generating quaternary stereocenters with the help of tertiary amine-thiourea based bifunctional catalyst **C37** (Scheme 54).[127] A variety of 2,2-disubstituted cyclopentene-1,3-dione derivatives readily underwent desymmetrization which demonstrated the scope of this protocol. The products containing two quaternary centers and a tertiary stereocenter are obtained with excellent diastereo- and enantioselectivities. Moreover, the authors proposed the secondary amide N−H on the catalyst enhances the catalytic activity by providing an additional H-bonding to the electronic substrate and all three NHs point in the same direction resulting in the shielding of one thiourea face by the aryl ring, which leads to superior diastereofacial discrimination of the cyclopentene-1,3-dione substrates.

The same group also reported an enantioselective vinylogous umpolung addition of various γ-substituted β,γ-unsaturated butenolides to allenoates using an achiral phosphine and a chiral squaramide **C38** as the catalyst combination (Scheme 55).[128] This catalytic asymmetric $C_\gamma-C_\gamma$ bond formation provided a novel protocol to construct the enantioenriched functionalized γ-butenolides **117** bearing a quaternary stereocenter (up to 95% yield and 93:7 er).

2.3.2.2. Vinylogous Michael Addition of Unsaturated Butyrolactones to Enals. In 2011, a direct iminium catalyzed vinylogous addition of deconjugated butenolides to enals was reported by Alexakis and co-workers (Scheme 56a).[129] Substrate screening revealed that various substituents could be tolerated at the 2- and 3-positions of the enal, affording γ-butenolides **118** bearing a tetrasubstituted carbon center with excellent stereoselectivities. A chiral *trans* iminium complex derived from **C39** was postulated to shield the *Re* face attack, while the interaction between the enal group and the entering butenolide favors the formation of the *syn* product. Further study on the organocascade reaction with high-reactive vinyl sulfones led to the corresponding adduct **119** containing three contiguous stereocenters as a single diastereoisomer (Scheme 56b).[130]

Ye and co-workers described the vinylogous Michael reaction of enals with 2(5*H*)-furanone by using the Jørgensen−Hayashi catalyst **C23** and LiOAc as additive (Scheme 57).[119] γ-Butenolide products were obtained in high yields with excellent enantioselectivities, albeit with moderate diastereoselectivities.

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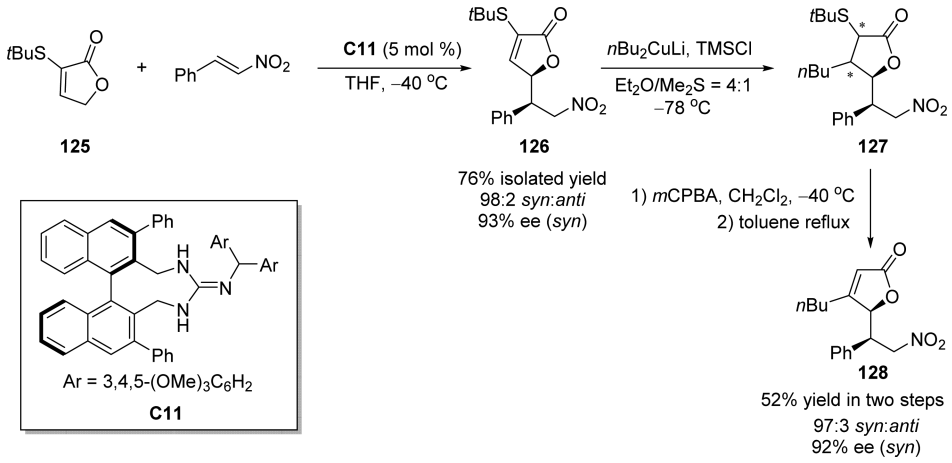
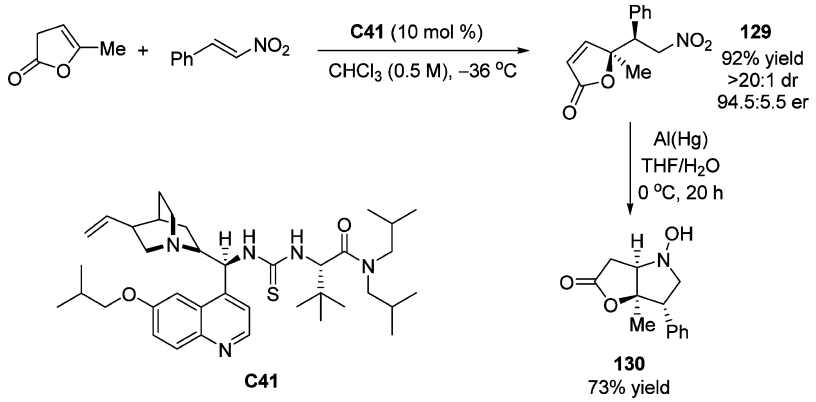
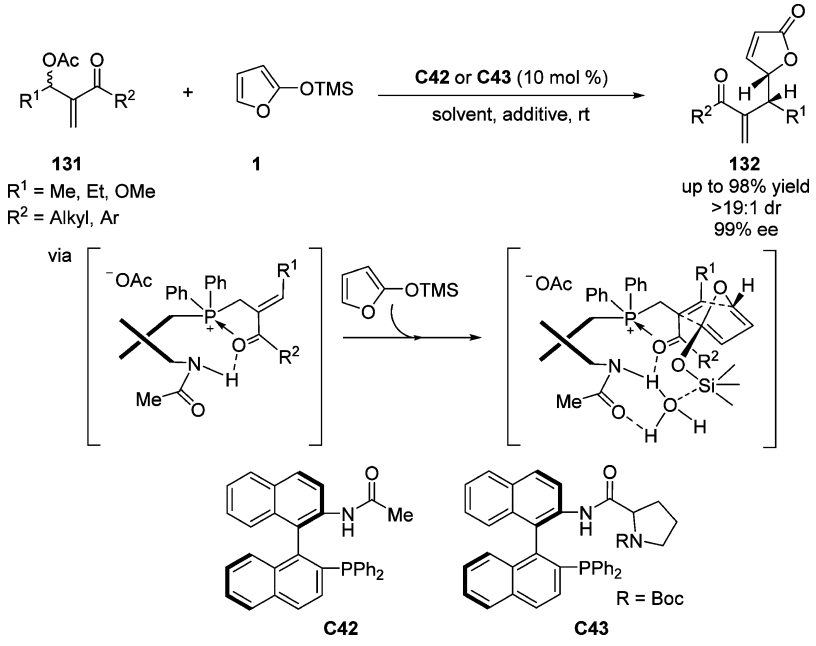
Scheme 59. Direct Asymmetric Michael Addition of α-Substituted Furanone 125 to Nitroalkene Catalyzed by Guanidine C11



Scheme 60. Guanidine-Catalyzed Asymmetric Michael Addition of α-Substituted Deconjugated Butenolide to Nitroalkene



Scheme 61. Asymmetric Substitution of MBH Acetates with 2-Trimethylsilyloxy Furan



2.3.2.3. Vinylogous Michael Addition of Unsaturated Butyrolactones to Nitroalkenes. In 2009, Trost and Hitce showed that a self-assembled dinuclear zinc complex **C40** was able to facilitate the direct asymmetric Michael addition of 2(5*H*)-furanone to nitroalkenes (Scheme 58).[131] This process, in the presence of preformed complex, gave rise to the corresponding Michael adducts **122** in good yields and excellent stereocontrol (up to >20:1 dr and 96% ee). After simple

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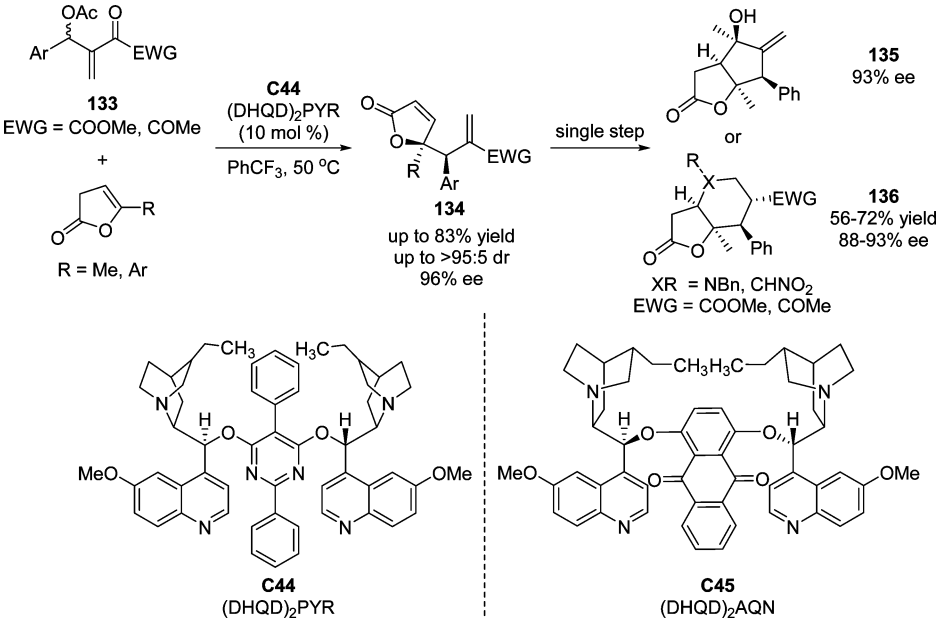
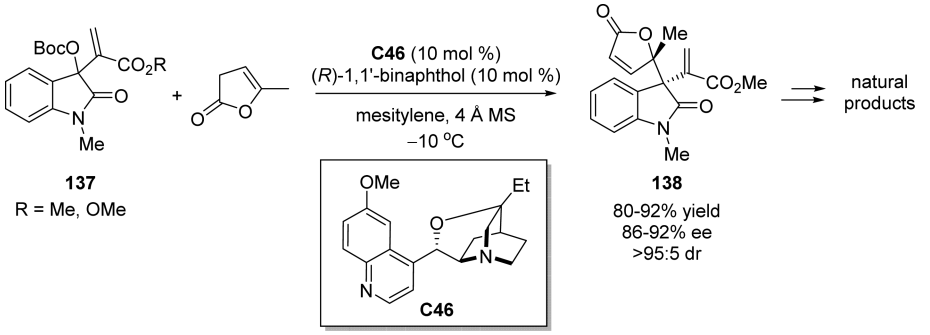
Scheme 62. Direct Substitution of MBH Acetates with β,γ-Unsaturated Butenolides



Scheme 63. Lewis Base Catalyzed Assembly of MBH Carbonates 137 with γ-Methyl-Substituted β,γ-Unsaturated Butenolide



transformation to the densely functionalized primary amine **123**, bioactive lactam **124** was obtained with complete diastereoselectivity. A bidentate bridging aromatic enolate **A** complex was postulated to be involved in the enantioselective C−C bond forming event.

Chiral guanidine base catalyst **C11** developed by Terada and co-workers[55] was also successfully applied in the direct vinylogous Michael addition of α-*tert*-butylthio substituted furanone to conjugate nitroalkenes, affording the adduct **126** in a highly *syn*-diastereo- and enantioselective manner (Scheme 59).[132] Different substituents on the sulfur atom of γ-butenolide were screened in which the sterically demanding *tert*-butyl group exhibited high *syn*-diastereoselectivity. The synthetic potential of this transformation was demonstrated by further elaboration into γ-butenolides **127** and **128** (Scheme 59).

In 2012, Mukherjee and co-workers reported the direct vinylogous Michael reaction of γ-substituted deconjugated butenolides with nitroalkenes catalyzed by quinine derived bifunctional catalyst **C41**. The reaction leads to the desired γ-butenolide **129** with contiguous quaternary and tertiary stereocenters in excellent yield and diastereoselectivity (Scheme 60).[133] Synthesis of bicyclic adduct **130** was achieved in high yield after simple reductive aza-Michael cyclization, thus illustrating the synthetic versatility of this methodology.

2.4. Asymmetric Morita−Baylis−Hillman (MBH) Reaction

As illustrated at the previous sections, the uses of silyloxyfurans or in situ prepared butyrolactone derived enolates as nucleophilic partners in the aldol, Mannich, and Michael type reactions have emerged as effective strategies for the catalytic asymmetric synthesis of butenolides or butyrolactones. Due to the prevalence of these important structures, the development of new electrophilic partners has been one focus of intensive investigation. The Morita−Baylis−Hillman (MBH) reaction represents an example of the use of different electrophilic substrates.[134−140]

Krische and Cho first reported the substitution of Morita−Baylis−Hillman (MBH) acetates with 2-trimethylsilyloxy furan in the presence of substoichiometric amounts of triphenylphosphine.[141] Subsequently, Shi and co-workers developed the asymmetric version of the allylic substitution of acetates **131** resulting from MBH reaction with TMSOF to furnish γ-butenolides **132** employing the chiral phosphine organocatalyst **C42** in toluene and using water as an effective additive (Scheme 61).[142] Further studies revealed that the reaction proceeds smoothly by applying modified catalyst **C43** in the presence of a protic solvent (MeOH) or an aprotic solvent (CH_3CN).[143] A wide range of MBH acetates were explored to generate the substituted products in good to excellent yields with high regio- and diastereoselectivities. A mechanism involving *endo*-selective

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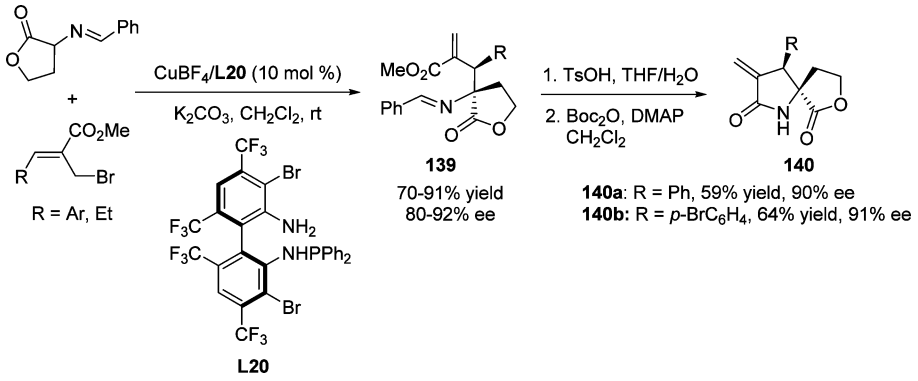
Scheme 64. Cu(I)-Catalyzed Asymmetric Tandem Michael Addition−Elimination Reaction



Diels−Alder cycloaddition of silyloxyfuranate complex with subsequent Grob-type fragmentation was proposed by Shi and co-workers (Scheme 61).[142,143] Computational investigation further supported that Diels−Alder-like transition states could account for the origin of the diastereo- and enantioselectivities, revealing that hydrogen bonding involving the proton of the amide moiety is the critical factor to providing high enantiofacial control.

Employing the modified cinchona alkaloid $(DHQD)_2PYR$ **C44** as catalyst, the direct asymmetric allylic alkylation of β,γ-unsaturated butenolides with MBH carbonates to access γ,γ-disubstituted butenolides was accomplished by Chen and co-workers (Scheme 62).[144] Slightly higher yields and enantioselectivities were obtained by using $(DHQD)_2AQN$ **C45** as catalyst in 1,2-dichloroethane when the substrate scope was expanded to α,β-unsaturated butenolides. This methodology provided the corresponding substitution products **134** with excellent stereoselectivities (86−96% ee, >95:5 dr) and moderate to good yields (50−83%). The synthetic utility was illustrated by the facile construction of bicyclic lactones **135** and **136** bearing up to five stereogenic centers.

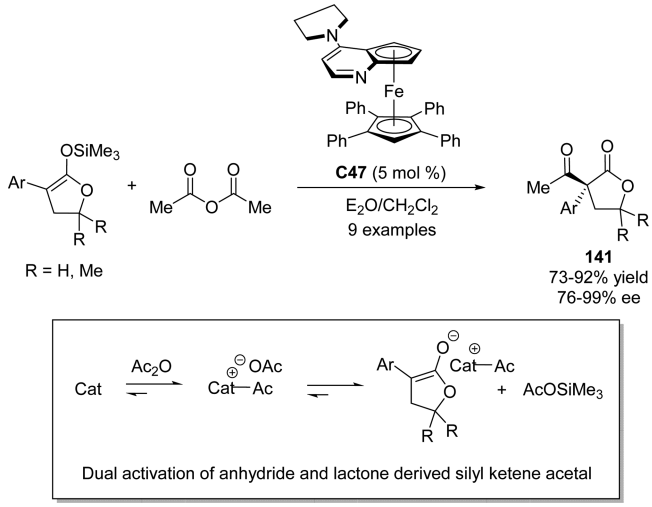
The same group also developed the first organocatalytic asymmetric assembly of 2-oxindole and β,γ-unsaturated butenolides, affording enantioenriched multifunctional products **138** bearing two vicinal quaternary centers in high yields and stereoselectivities (Scheme 63).[145] The presence of molecular sieves and (*R*)-1,1′-binaphthol in combination with isoquinidine catalyst **C46** was observed to slightly enhance the reaction rate in which (*R*)-1,1′-binaphthol might play a role as a Brønsted acid for the activation of MBH carbonates **137**. After simple double Michael addition, reduction, and subsequent intramolecular amidation, natural product-like structures with multiple fused ring systems were obtained maintaining excellent diastereocontrol.

In 2012, Wang and coauthors reported Cu(I)-catalyzed tandem Michael addition−elimination reaction, utilizing MBH bromides as the key nucleophilic acceptors (Scheme 64).[146] Lactone derived cyclic aldimino esters were applied as nucleophiles to provide γ-butenolides **139** bearing adjacent quaternary and tertiary stereogenic centers in a highly regio- and stereoselective manner. This method was successfully applied for the formation of spiro(γ-butyrolactam-γ-butyrolactone) compounds **140**.

2.5. Enantioselective Acylation

With the aid of a "planar-chiral" derivative of 4-(pyrrolidino)-pyridine (PPY),[147−150] Fu and Mermerian reported the first catalytic enantioselective C-acylation of butyrolactone derived silyl ketene acetals. An anhydride served as the electrophilic component to furnish butyrolactones bearing all-carbon quaternary stereocenters with good enantioselectivities and yields (Scheme 65).[151] Mechanistic studies[152] provided strong

Scheme 65. Enantioselective Acylation of Butyrolactone Derived Silyl Ketene Acetals Using a Chiral DMAP Analogue



support for a catalytic pathway that involves activation of both the electrophile (anhydride to acylpyridinium) and the nucleophile (silyl ketene acetal to enolate).[61−65] The authors claimed the rate acceleration is likely due to the transformation of silyl ketene acetal into a free enolate rather than a hypervalent silicate as an intermediate.

By using chiral arylpyrrolidine-based thiourea catalyst **C48** in combination with 4-pyrrolidinopyridine, Jacobsen and co-workers developed a highly enantioselective acylation of silyl ketene acetals to produce α,α-disubstituted butyrolactones **142** (Scheme 66).[153] This transformation was proposed to proceed through anion-binding catalysis, involving the formation of a thiourea-bound acylpyridinium fluoride ion pair, followed by rate-determining desilylation and enantiodetermining acylation promoted by a thiourea-bound acylpyridinium enolate ion pair.[64,153]

On the basis of the pioneering work of Fu,[151] Vedejs and co-workers reported a new class of chiral pyridine catalysts **C49** for the carboxyl migration of furanyl enol carbonates (Scheme 67).[154] Good to excellent yield and enantioselectivity were obtained for the butyrolactone products bearing a quaternary carbon. The authors pointed out that the electronic nature of the

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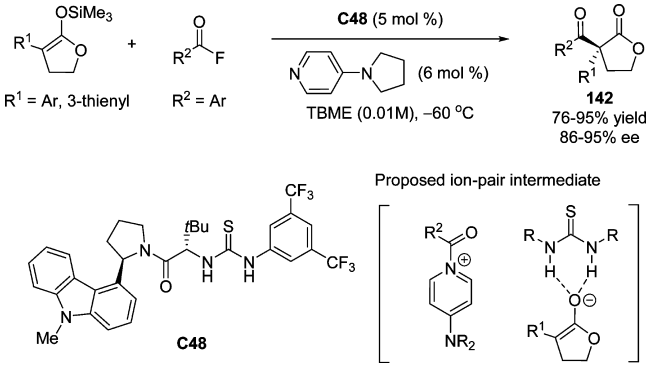
Scheme 66. Enantioselective Acylation through a Thiourea-Bond Acylpyridinium Enolate Ion Pair



C-5 aryl substituent resulted in different regiocontrol in which an electron-deficient substituent favored the γ-carboxyl product **144** while a relatively electron-rich aryl group favored the α-carboxyl product **143**.[155] Further modification to a chiral isothiourea catalyst **C50** was reported by Smith and co-workers,[156,157] promoting the *O*- to *C*-carboxyl transfer of a series of furanyl carbonates with preferential α-regiocontrol.

2.6. Asymmetric Allylic Substitution

The Pd-catalyzed asymmetric allylic substitution (AAS) holds a prominent position among the most versatile methods for carbon−carbon bond formation widely applied in natural product synthesis.[158−164] Although excellent results of allylic alkylation have been reported with preformed or in situ generated enolates, Pd-catalyzed asymmetric allylic alkylation using a nonstabilized silyl enol ether as nucleophile has remained elusive until recently.[165,166] The undesired side reactions as well as insufficient regioselectivity and diastereoselectivity have kept the Pd-catalyzed allylic alkylation of silyl enol ethers and silyl ketenes from being developed further.[165,166]

In 2012, the group of Feringa reported a palladium-catalyzed kinetic resolution of 1,3-disubstituted unsymmetrical allylic acetates and a concomitant allylic alkylation by using 2-trimethylsiloxy furan (TMSOF) as nucleophile, to access the important 3-substituted-γ-butenolides **146** (Scheme 68).[167] The reaction proceeded under mild conditions and provided the desired products in excellent chemo-, regio-, and enantioselectivities. This system exhibited high selectivity factors (up to S > 200), indicating that a near-perfect kinetic resolution could be achieved under the optimized conditions. Mechanistic and DFT studies suggested that hydrogen bonding interactions with the chiral ligand[168] might play a key role in the control of regio- and enantioselectivities.

These findings were soon followed by an iridium-catalyzed asymmetric allylic substitution reaction between TMSOF and a variety of aromatic and aliphatic allylic carbonates or benzoates developed by Hartwig and Chen.[169] This transformation furnished 3-substituted butenolides **147** containing an easily functionalized terminal double bond and various aryl and alkyl groups at the stereogenic center with excellent regio- and enantioselectivities (Scheme 69). Stoichiometric reactions of the Ir−allyl intermediate implied that the reaction proceeds by *anti* attack on the coordinated allyl ligand. The carboxylate leaving group of the substrate was proposed to activate the siloxyfuran.

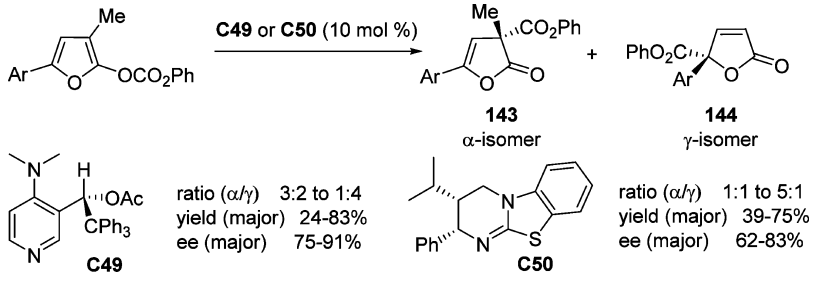
Furanone-derived cyclic dienol carbonates were employed as substrates for the palladium-catalyzed decarboxylative allylic substitution toward the asymmetric synthesis of butyrolactones. Cossy and co-workers employed the chiral Pd/Trost ligand **L21** complex as an efficient catalyst for this reaction to access predominantly the corresponding α-allylated products **148** in a highly enantioselective manner (Scheme 70).[170] The enantioenriched α,α-disubstituted butenolides were then subjected to a microwave-assisted Cope rearrangement, affording the furanones **150** bearing γ-tertiary and γ-quaternary stereogenic centers in quantitative yield with almost no erosion of the optical purity. Another synthetic application of butenolides **148** involves the facile access to β-quaternary butyrolactones **149** through sequential DIBAL−H reduction and PCC-mediated oxidation. The utility of this methodology was demonstrated by transforming the resulted enantioenriched butenolide products into valuable building blocks, as well as natural products including (−)-nephrosteranic acid and (−)-roccellaric acid.

2.7. Enantioselective Arylation and Alkylation

In 2002, Buchwald and Spielvogel disclosed a nickel−BINAP system which could be used for the highly enantioselective α-arylation[171] of α-substituted γ-butyrolactones with aryl chloride and bromides (Scheme 71).[172,173] The addition of 15 mol % $ZnBr_2$ as a THF solution is responsible for a dramatic increase in both the rate of the reaction and the yield of isolated product. A variety of electron-rich and electron-poor aryl halides with *meta* or *para* substituents could be successfully used as electrophiles to generate the desired γ-butyrolactones **152** with excellent enantioselectivities. This protocol was then used to accomplish the asymmetric synthesis of 4,4′-disubstituted azepines.[174]

Zhou and co-workers reported the palladium-catalyzed asymmetric α-arylation of simple silyl enolates derived from γ-butyrolactone with organic triflates. The reaction leads to the corresponding aryl-substituted butyrolatones in excellent yields and stereoselectivities (Scheme 72).[175] β-Substituted lactone derived silyl enolate gave *trans* product with complete diastereoselectivity and with excellent enantioselectivity (up to 99% ee). The diastereoselectivity decreased if a substituent was present at the γ-position (*trans*/*cis* 3:1). DFT calculations indicated that chiral phosphine ligand **L24** participates in arene CH···O hydrogen bonding with palladium enolate while ligand

Scheme 67. Catalytic Asymmetric Synthesis of γ-Butenolides through the Acylation of Furanyl Enol Carbonates



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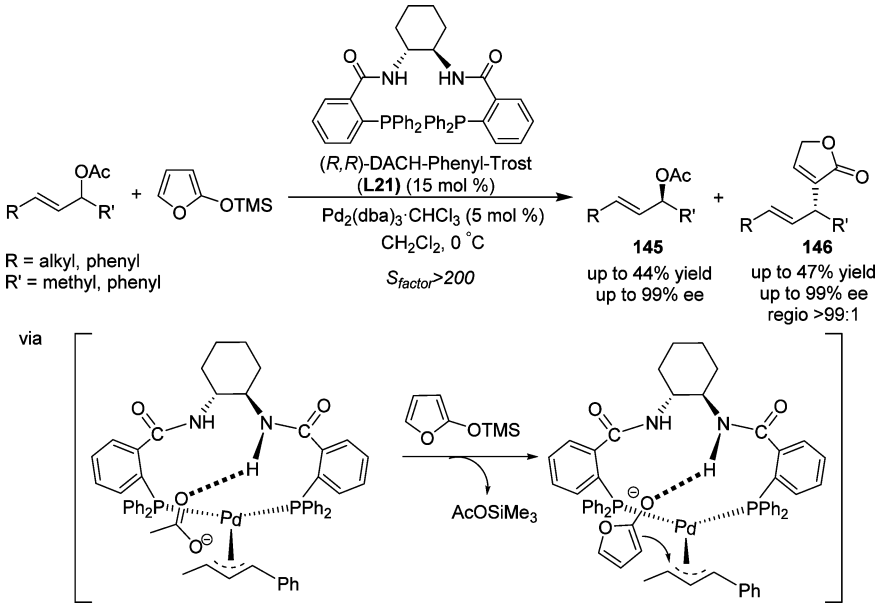
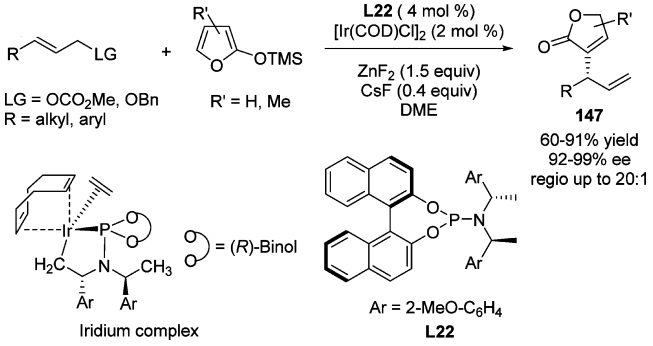
Scheme 68. Palladium-Catalyzed Kinetic Resolution of 1,3-Disubstituted Unsymmetrical Allylic Acetates with Silyloxy Furans[a]

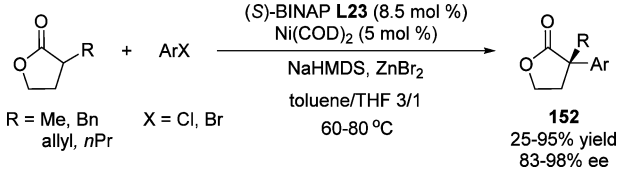


[a]dba = dibenzylideneacetone.

Scheme 69. Iridium-Catalyzed Asymmetric Allylic Substitution Reaction between Silyloxyfurans



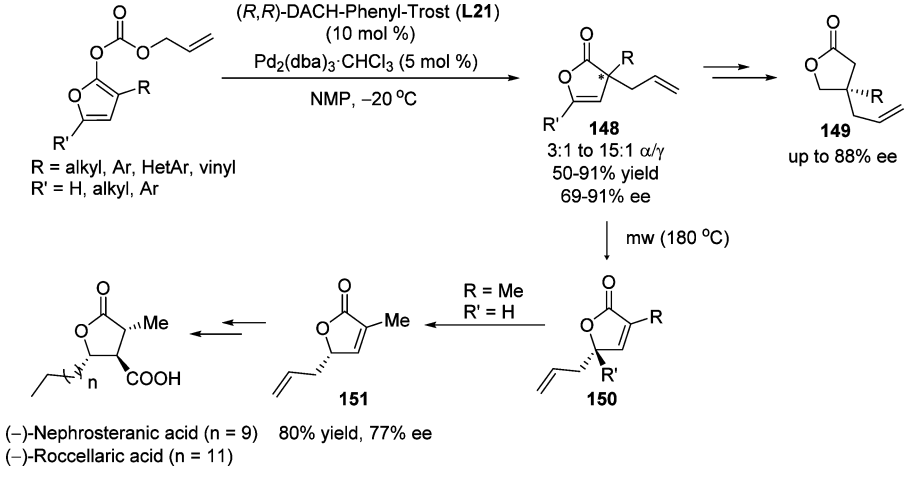
Scheme 71. Nickel–BINAP Catalyzed Asymmetric α-Arylation of α-Substituted γ-Butyrolactones



L25 was capable of forming NH···O (carbonyl) hydrogen bonding. Computational analysis also indicated that the silyl enolate was bound to palladium complex through its β-carbon atom and that the enolate transfer was triggered by external attack of the acetate anion.

An enantioselective alkylation of α-benzoyl-γ-buryrolactones was reported by Maruoka and co-workers. This reaction provided a direct access to enantiomerically enriched α,α-disubstitued buryrolactones bearing an all-carbon quaternary stereocenter (Scheme 73).[176] *N*-Spiro chiral quaternary ammonium bromide **C51** was recognized as the optimized catalyst in terms of both reactivity and selectivity. The use of

Scheme 70. Palladium-Catalyzed Asymmetric Allylic Alkylation of Cyclic Dienol Carbonates



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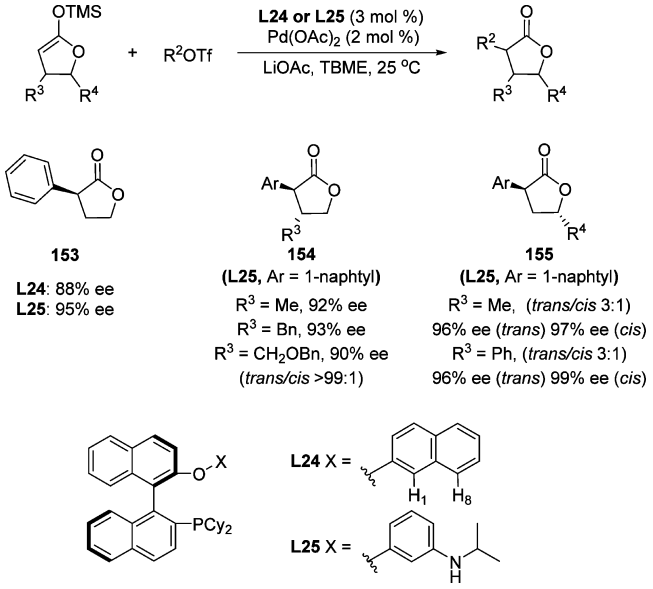
Scheme 72. Palladium Catalyzed Asymmetric α-Arylation of Substituted γ-Butyrolactones



allylic bromides and propargyl bromide as the electronic partner led to an erosion of the stereoselectivity (**156b** and **156c**, Scheme 73). The importance of optically active butyrolactone **156a** as chiral building block was highlighted by the subsequent transformation into α,α-dialkyl-α-amino acid derivative **157**.

An interesting extension of the previous reaction was achieved by Park and co-workers,[177] in which the highly enantioselective α-benzylation and α-allylation of α-*tert*-butoxycarbonyllactone was developed in the presence of the closely related catalyst **C52** (Scheme 74). This asymmetric phase transfer catalytic (PTC) reaction allowed the synthesis of the functionalized α-substituted α-*tert*-butoxycarbonyllactones in high yields (up to 98%) and enantioselectivities (up to 99% ee). It provided excellent starting materials for the facile synthesis of unnatural amino acid derivative **159** and 3-alkyl-3-carboxypyrrolidine **160**.

3. FURANONE DERIVATIVES AS ELECTROPHILES

3.1. Asymmetric 1,4-Addition

Since the first example of rhodium-catalyzed asymmetric 1,4-addition of arylboron reagents to 2(5*H*)-furanone reported by Hayashi and co-workers,[178] 2(5*H*)-furanone has been used as a common Michael acceptor to construct the optically active β-aryl substituted butyrolactone structure. Various chiral rhodium complexes in combination with a range of aryl nucleophiles have been used to afford the corresponding chiral aryl-substituted butyrolactones in good to excellent yields and enantiomeric purities.[179−187] A summary of the most efficient rhodium-based catalytic systems for the 1,4-addition of aryl boron reagents to furanone is depicted Table 1. As this specific transformation has been extensively reviewed,[188−192] this topic is not discussed in detail.

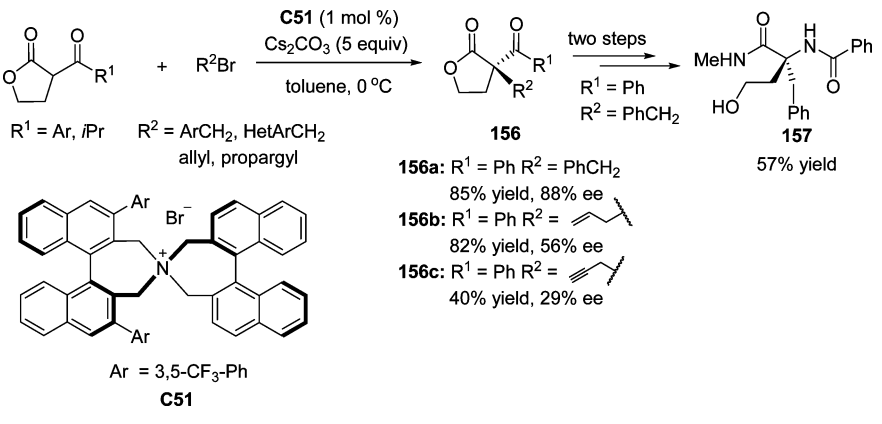
The asymmetric conjugate addition (ACA) of diethylzinc to 2(5*H*)-furanone was achieved for the first time by Chan and co-workers in 2004, using a copper/phosphite complex as the effective catalyst.[193] Hoveyda and co-workers disclosed that the amino acid based phosphine **L34** could be employed to promote the catalytic ACA of dialkylzinc reagents to 2(5*H*)-furanone (Scheme 75).[194] The reaction was carried out in the presence of an aldehyde to trap the enolate intermediate, thus preventing adventitious ketene formation or intermolecular Michael addition. The resulting aldol products could be further oxidized to afford the corresponding diketones **163** in high yields and up to 97% ee.

3.2. Asymmetric Allylic Substitution

Butenolides bearing a good leaving group in the γ-position, such as γ-acyloxybutenolides, are suitable substrates for the allylic substitution reaction. As exemplified by the work of Trost and Toste,[195] Pd(0) complexes can form two different diastereomeric η^2-olefin complexes by the coordination of the γ-butenolide with chiral palladium complex. Ionization of the γ-acyloxybutenolides generates two η^3-π-allyl palladium complexes which could interconvert through the intermediacy of the of the palladium furanoate. If this interconversion is relatively faster than the nucleophilic attack and if one of the diastereomeric η^3-complexes reacts faster than the other, then a palladium-catalyzed dynamic kinetic asymmetric transformation (DYKAT) can operate (Figure 5).[195] However, if the enantiomeric discriminating step is incorporated as one of the other bond forming events, the process would be referred to as a kinetic asymmetric transformation (KAT). Considering its ability to facilitate both the process of kinetic asymmetric transformation (KAT) and dynamic kinetic asymmetric transformation (DYKAT), γ-acyloxybutenolides have proved to be important synthons for the asymmetric synthesis of butenolides and butyrolactones.[195−198]

Using this concept, Trost and Toste reported a highly enantioselective allylic substitution of γ-acyloxybutenolides with

Scheme 73. Enantioselective Phase-Transfer Catalytic α-Alkylation of α-Acyl-γ-butyrolactones



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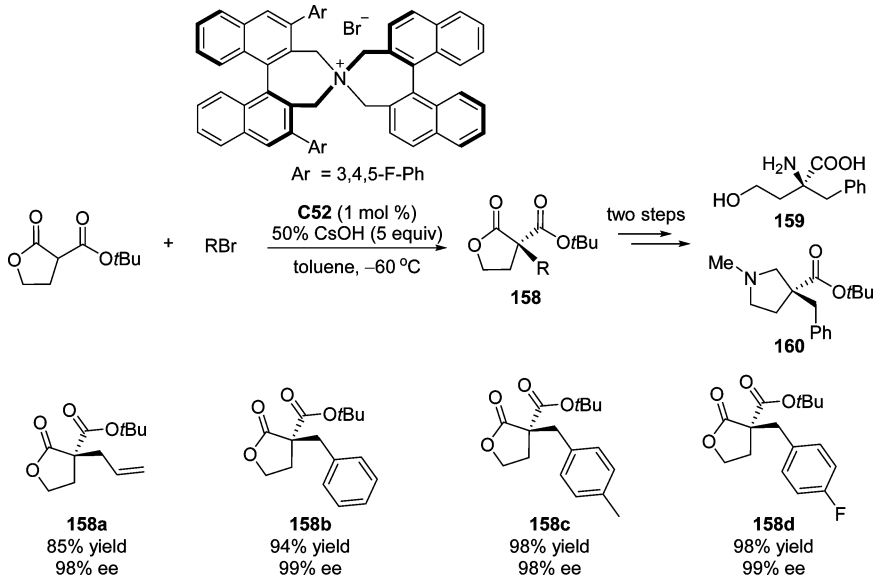
Scheme 74. Enantioselective Phase Transfer Catalytic α-Benzylation and α-Allylation of α-*tert*-Butoxycarbonyl-lactone



phenol nucleophiles in the presence of a Pd(0) complex derived from Trost's chiral biphosphine ligand **L21** (Scheme 76).[195] The authors proposed that the KAT process occurred when the reaction was performed at high concentration (0.5 M) in the presence of a carbonate base. However, when the reaction was performed in the presence of a catalytic amount of Bu_4NCl at the concentration of 0.1 M, the DYKAT process was favored to afford the γ-aryloxybutenolides **164** up to 89% yield and up to 97% ee. The resulted γ-acyloxybutenolide derivatives, utilized as "chiral aldehyde" building blocks, allowed efficient synthesis of (−)-aflatoxin B,[199] BAY 36-7620[200] and (+)-brefeldin A[200] in a highly concise and stereoselective manner.

3.3. Asymmetric Reduction

Asymmetric reduction,[201−203] using molecular hydrogen to convert prochiral olefins, ketones, and imine, has become one of the most efficient and pratical methods for the construction of chiral compounds. The Ru−BINAP system was discovered by Noyori and Takaya in 1980 for the asymmetric hydrogenation of α-(acylamino)acrylic acids,[204] which was also successfully applied for ruthenium-catalyzed asymmetric hydrogenation of γ-butenolides to access optically active β-substituted γ-butyrolactones (Scheme 77).[205] Apart from ruthenium,[205−207] other metals such as rhodium,[202,208,209] iridium,[210] and cobalt[211] have also been used for the catalytic asymmetric hydrogenation of butenolides.

In 2003, Buchwald and co-workers reported the first enantioselective 1,4-reduction of β-substituted γ-butenolides **166**, using in situ generation of a chiral CuH species[212−214] from $CuCl_2·2H_2O$ as copper source, NaO*t*Bu as base, PMHS as hydride source, and *p*-tol-BINAP **L35** as chiral ligand (Scheme 78).[215] The addition of alcoholic additives was crucial to achieve butyrolactone products in high yields.

The rate-accelerating role of the alcohol was also observed in the Cu/DTBM-SEGPHOS-catalyzed 1,4-reduction of α,β-unsaturated lactones reported by Lipshutz and co-workers.[216,217] NMR experiments showed that the rate enhancement arises from a more rapid quenching of the resulting copper enolate by the alcohol than by the silane. The group of Lipshutz also introduced an effective asymmetric hydrosilylation of unsaturated butyrolactones by using a heterogeneous reagent copper in charcoal in the presence of excess poly(methylhydrosiloxane) (PMHS) as the source of hydride along with catalytic amounts of the Takasago 3,5-di-*tert*-butyl-4-methoxydiphenylphosphinyl segphos (DTBM-segphos) ligand and NaOPh, affording butyrolactone products in high yields and with excellent ee values.[218]

Based on this copper-catalyzed conjugate reduction, the same group reported a dynamic kinetic resolution of γ-aryl containing α,β-unsaturated butenolides which resulted in the synthesis of *cis*-β,γ-disubstituted butyrolactone **167** in a short and highly stereoselective manner (93% ee, Scheme 79).[219] The complete conversion of the starting material into the desired product was observed when excess base (NaO*t*Bu) was added at room temperature. This catalytic process was completely diastereoselective; none of the *trans* isomer was detected. The short synthesis of eupomatilone-3 was accomplished by enolization of lactone **167** with NaHMDS followed by diastereoselective alkylation with iodomethane, affording the product **168** in 85% yield.

It was found the commercially available bisphosphine **L37** is the most efficient chiral ligand for the copper-catalyzed conjugate reduction of γ-aryl-containing β-substituted butenolides (except in the case of the natural product **168**, in which **L37** gave the best result), providing the γ-butyrolatones **169** with vicinal stereocenters in high yields (67−87%) and good stereoselectivities (67−87% ee) (Scheme 80).[219] Butenolides with simple alkyl substituents in the γ-position failed to give more than 50% conversion under the same conditions, presumably due to poor racemization of the starting lactone. This reaction provided both diastereomers of the desired product, in which the low enantiomeric purity of *cis* isomer was observed (<25% ee).

3.4. Enantioselective Cycloaddition

The catalytic asymmetric Diels−Alder reaction of butenolide dienophiles was developed by Corey and co-workers.[220] Cationic oxazaborolidine **C55** was employed as an efficient Lewis acid for enantioselective Diels−Alder reaction with cyclopentadiene,

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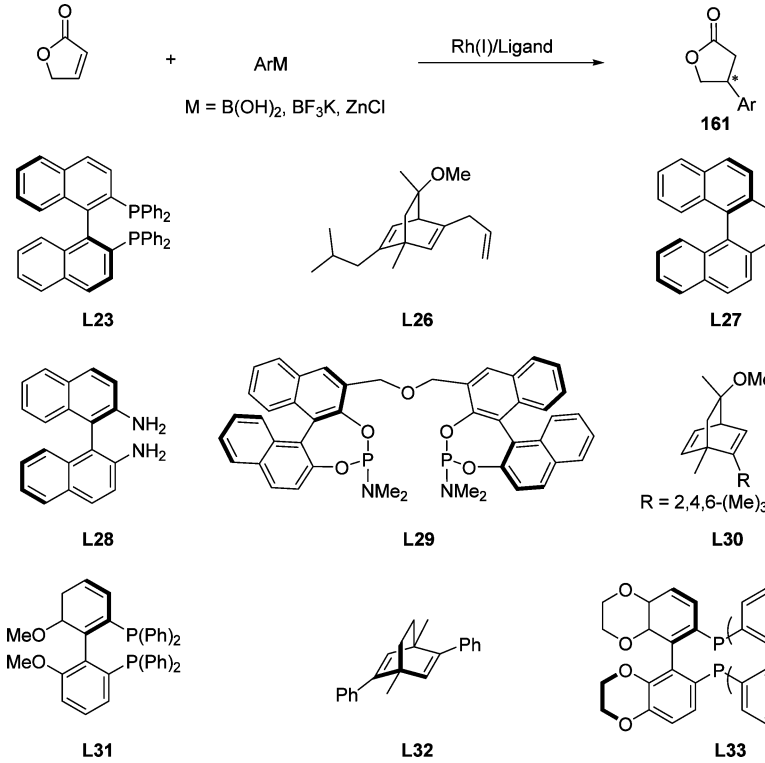
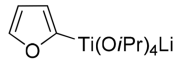
Table 1. Examples of Chiral Ligands Used in Rhodium-Catalyzed Asymmetric 1,4-Addition of Arylboron Reagents to 2(5*H*)-Furanone[a]



Ref.	Ligand	[Rh(I)]	ArMLn	Additive	temp. (°C)	Yield of **161** (%)	Ee (%)
[178]	**L23**	$Rh(acac)(C_2H_4)_2$	$PhB(OH)_2$	none	100	33	98(*S*)
[179]	**L26**	$Rh(acac)(C_2H_4)_2$	$PhB(OH)_2$	KOH	25	80	90(*S*)
[180]	**L27**	$[Rh(cod)_2]PF_6$	$PhBF_3K$	none	110	55	93(*R*)
[181]	**L28**	$[RhCl(Ph\text{-}cod)]_2$	PhZnCl	$AgBF_4$ Me_3SiCl	0	86	96(*R*)
[182]	**L29**	$Rh(nbd)_2BF_4$	$PhB(OH)_2$	Et_3N	25	68	77(*R*)
[183]	**L30**	$[RhCl(C_2H_4)_2]_2$	$PhB(OH)_2$	KOH	rt	56	90(*R*)
[184]	**L31**	$Rh(cod)_2Cl_2$		Me_3SiCl	−78 to rt	60	98(n.d.)
[185]	**L32**	$[RhCl(C_2H_4)_2]_2$	$PhB(OH)_2$	KOH	rt	95	98(*R*)
[186] [187]	**L33**	$[RhCl(C_2H_4)_2]_2$	$PhB(OH)_2$	KOH	20	77	97(*R*)

[a]acac = acetylacetonate, cod = 1,5-cyclooctadiene, nbd = norbornadiene.

affording the *endo* adduct in excellent yield and enantioselectivity (Scheme 81). The face selectivity of this asymmetric cycloaddition was suggested to be the result of the coordination of the Lewis acidic boron atom to the carbonyl oxygen lone pair of butenolide, which facilitates an endo approach.

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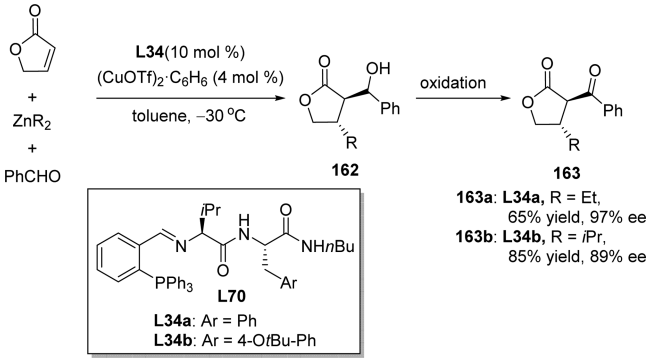
Scheme 75. Enantioselective Cu-Catalyzed Conjugate Additions of Dialkylzinc Reagents to Unsaturated Furanones



4. ASSEMBLY OF THE LACTONE CORE STRUCTURE

4.1. Enantioselective Halolactonization

Taguchi and co-workers reported the first example of the catalytic desymmetrizing enantioselective iodolactonization of malonate derivatives with iodine in the presence of chiral titanium taddolate **C56** to afford the corresponding fused γ-butyrolactone with 96−99% ee (Scheme 82).[221−223] Strong coordination between the chiral titanium taddolate and malonate allows this iodocarbocyclization to proceed in a highly enantiofacial selective manner. Alternative metal-catalyzed enantioselective halolactonization promoted by chiral salen−Co(II) complex **C57**[224] and BINAP−Pd(II) complex **C58**[225] (Figure 6) have been also investigated, allowing facile synthesis of the γ-butyrolactones with good to excellent enantioselectivities.

The first example of organocatalytic asymmetric halolactonization employing chiral quaternary ammonium salts derived from cinchonidine alkaloids was reported by Gao and co-workers.[226] The stereoselective iodolactonization of *trans*-5-aryl-4-pentenoic acids led to a mixture of two isomers in modest to excellent yield (37−98%) and moderate enantioselectivity (*exo* = 42.0% ee, *endo* = 31.0% ee) under mild conditions. Significant progress has been made in this field, and some reviews and perspectives[227−233] have been published. In this review, we only discuss some representive examples.

Using $(DHQD)_2PHAL$ **C59** as an organocatalyst and chlorohydantoin as the chlorine source, Borhan and co-workers reported the first example of a catalytic asymmetric chlorolactonization reaction in a highly stereoselective manner (Scheme 83).[234] A variety of aryl-substituted γ,δ-alkenoic acids were cyclized to afford chlorolactones **172** in high yields and enantioselectivities, albeit there is a strong substituent dependency. The authors propose the formation of intermediate A, resulting from interaction of chlorohydantoin with $(DHQD)_2PHAL$ **C59**. This H-bonded complex A acted as a catalytic chiral chlorine source, and experimental results showed that an increase in the steric demand of the substituents on chlorohydantoin results in a slight increase in enantioselectivity. The putative associated catalyst/chlorine source complex was also demonstrated through a series of matched/mismatched experiments by employing chiral *N*-chlorinated hydantoins.[235]

Based on the anion-binding strategy, Jacobsen and Veitch reported an enantioselective halocyclization reaction using tertiary aminourea **C60** as a chiral promoter (Scheme 84).[236] Reaction with a pentenoic acid derivative in the presence of *N*-iodo-4-fluorophthalimide and a catalytic amount of iodine (0.1 mol %) gave butyrolactone **173** in good yield (82%) and high enantioselectivity (90% ee). The primary function of the iodine additive is believed to be the formation of activated complex with *N*-iodo-4-fluorophthalimide which then binds to the aminourea **C60** to form the complex A. It is plausible that the resulting complex activates the pentenoic acid derivative through a tertiary amino−iodonium ion interaction and the urea-bound phthalimide serves as the base to effect deprotonation of the carboxylic acid.

The first enantioselective bromolactonization of 1,1-disubstituted olefinic acids was developed by Yeung and co-workers, using an amino-thiocarbamate bifunctional catalyst **C61** (Scheme 85a).[237] A similar transformation was carried out using the amino-thiocarbamate catalyst **C62** (Figure 7) in the bromolactonization of the related *cis*-olefinic acid (Scheme 85b).[238] The regioselectivity of the bromolactonization was in favor of the 5-*exo* lactone, affording **175** in 77% yield with 93% ee. Synthetic application was demonstrated by the transformation into δ-azido lactone, which could be used as a synthetic precursor to several biologically active molecules.

L-Proline-derived *O*-alkyl thiocarbamate **C63** containing a 1-naphthyl substituent in combination with *N*-bromophthalimide (NBP) was also developed by the same group for the asymmetric bromolactonization of olefinic acid **179**, which provided γ-

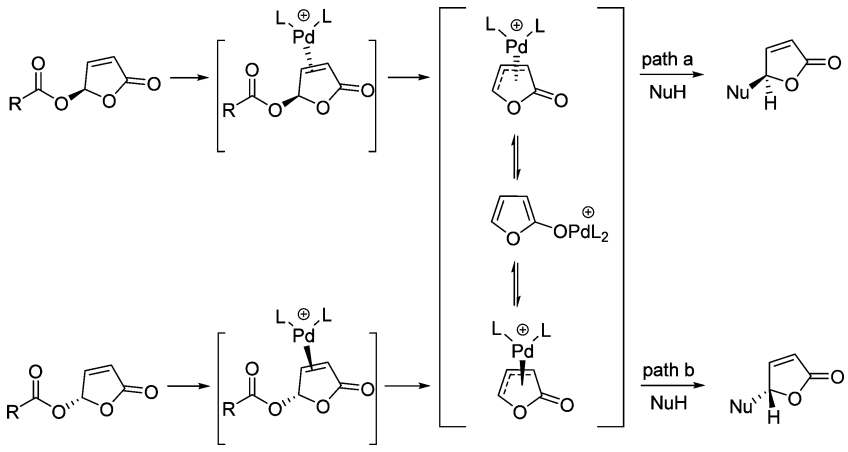


Figure 5. Concept for palladium catalyzed dynamic kinetic asymmetric transformation (DYKAT) of γ-acyloxybutenolides. (Adapted from ref 195. Copyright 1999 American Chemical Society.)

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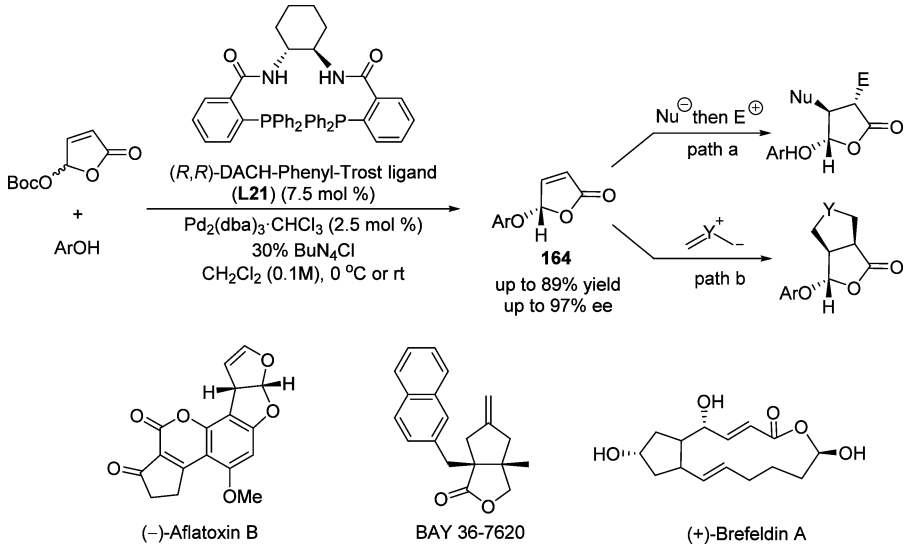
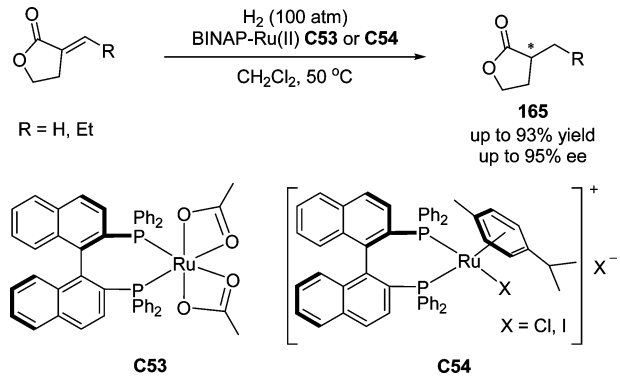
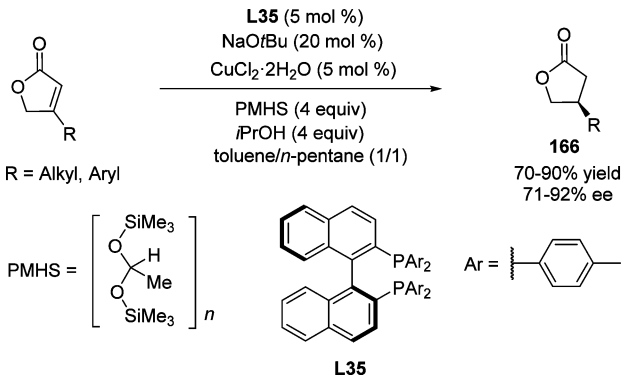
Scheme 76. Highly Enantioselective Allylic Substitution of γ-Acyloxybutenolide with Phenol Nucleophiles



Scheme 77. Chiral Ruthenium Complexes for the Asymmetric Hydrogenation of Butenolides



Scheme 78. Copper-Catalyzed Asymmetric 1,4-Reduction of β-Substituted γ-Butenolides



butyrolactone **180** with moderate enantioselectivity (82% ee) (Scheme 86).[239] This compound could be readily converted into (*R*)-(+)-boivinianin A **181** in 90% yield.

Martin and co-workers reported the novel BINOL-derived bifunctional catalyst **C64** (Figure 8) to promote a highly enantioselective bromolactonization of various substituted unsaturated carboxylic acids.[240] The catalytic enantioselective bromolactonization of alkyl-substituted olefinic acids, proceeding via 5-*exo* cyclization, provided γ-butyrolactones bearing two contiguous stereogenic centers with high diastereo- and enantioselectivities. A tentative working model was proposed suggesting that the hydrogen bonding between the phenolic −OH and the carboxyl group orients the substrate relative to the catalyst while the substituent at the olefin is directed away from the face of the binaphthyl scaffold to minimize torsional strain within the substrate and steric interactions with the catalyst (Scheme 87).[240] The same group also discovered that modified bifunctional catalyst **C65** catalyzed the iodolactonizations of various disubstituted olefinic acids with *N*-iodosuccinimide (NIS) to deliver iodolactones in excellent yields and enantioselectivities.[241]

The synthesis of γ-butyrolactones bearing multiple stereocenters was further exemplified by the enantioselective bromolactonization of cyclohexadiene derivatives promoted by *N*-bromosuccinimide (NBS) (Scheme 88).[242] It is noteworthy that the bicyclic bromolactones **183** were obtained in good to excellent yields (70−90%) with up to 92% ee.

4.2. Enantioselective Oxidative Cyclization

Maruoka et al. reported a selenium-catalyzed enantioselective oxidative cyclization which allowed for the efficient transformation of a range of β,γ-unsaturated carboxylic acids into enantioenriched butenolides (Scheme 89).[243] The rigid catalyst based on an indanol scaffold was designed to enable the highly enantioselective selenofunctionalization at ambient temperature. The *p*-methoxybenzyl selenide was selectively oxidized with *N*-fluorobenzenesulfonimide (NFSI) to generate the electrophilic selenium catalyst directly. Under the optimized conditions, the oxidative cyclization of both aliphatic and aromatic substrates afforded the products **184** in high yields and excellent enantioselectivities. The chiral butenolides could be stereoselectively transformed into products **185** and **186** through tandem 1,4-addition/aldol reaction and DIBAL reduction, respectively.

4.3. Enantioselective Radical Oxyfunctionalization

An efficient and practical approach to highly enantioenriched γ-butyrolactones via a copper-catalyzed radical oxyfunctionalization of alkenes was reported by Buchwald and Zhu.[244,245] The tandem radical addition/enantioselective lactonization was efficiently achieved in the presence of catalytic amount of $Cu(MeCN)_4PF_6$ and (*S,S*)-*t*BuBox ligand **L11**. The scope of this

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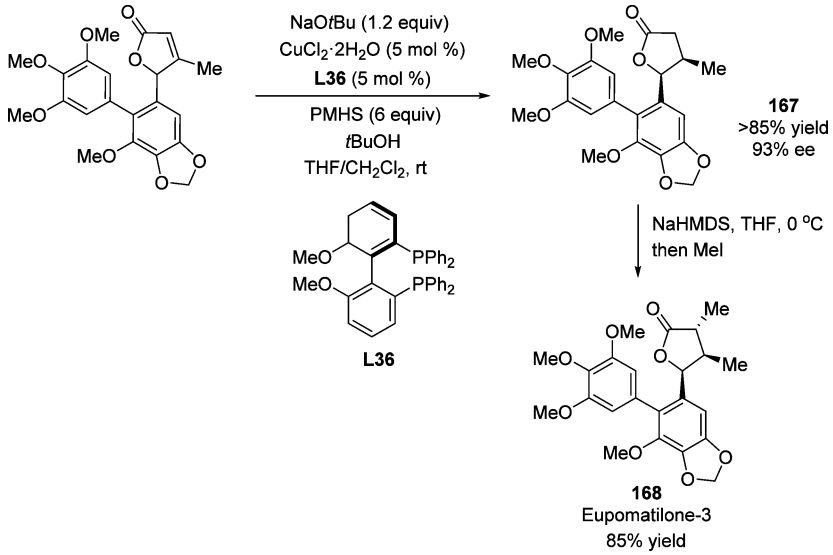
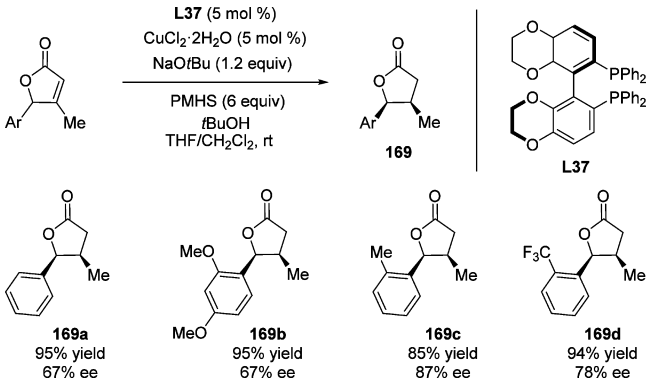
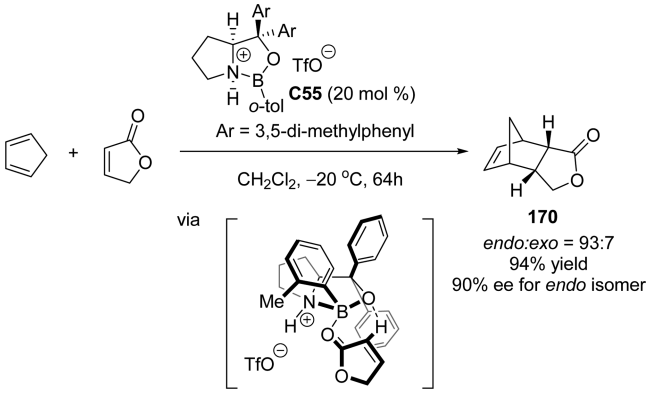
Scheme 79. Catalytic Asymmetric Synthesis of Eupomatilone-3



Scheme 80. Copper-Catalyzed Conjugate Reduction Synthesis of γ-Aryl-Containing β-Substituted Butenolides

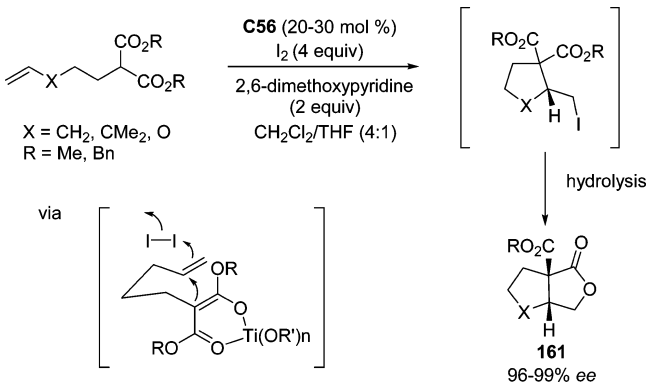


Scheme 81. Cationic Oxazaborolidine Catalyzed Asymmetric Diels–Alder Reaction of Butenolide



transformation was evaluated with a range of unsaturated carboxylic acids bearing (hetero)aryl and alkynyl substituents as well as different radical precursors. Versatile functionalized butenolides **187** containing tetrasubstituted stereogenic centers were readily produced in good yields with excellent enantioselectivities (Scheme 90). Mechanistic studies on the oxytrifluoromethylation of unsaturated carboxylic acids suggested that the enantiodetermining C–O bond formation from

Scheme 82. Asymmetric Synthesis of Fused γ-Butyrolactones through Iodolactonization of Malonate with I_2



tricoordinate Cu(II) carboxylate intermediate proceeds through Cu–C bond formation between Cu(II) center and prochiral alkyl radical and subsequent stereoretentive reductive elimination of the resulting Cu(III) complex.[245]

4.4. Asymmetric Baeyer–Villiger Oxidation

The Baeyer–Villiger (BV) oxidation is one of the most powerful methods employed to convert a cyclobutanone into the corresponding lactone by inserting an oxygen atom into a C–C bond.[246−250] It is generally accepted that the reaction proceeds through a two-step process in which nucleophilic attack of a peroxide to the carbonyl group gives the Criegee adduct, and subsequent carbon-to-oxygen migration to proximal oxygen atom of the peroxide unit produces the corresponding lactone (Figure 9). The asymmetric version of BV oxidation can be achieved by chelation of the Criegee adduct with an appropriate chiral metal complex or an organocatalyst. This section summarizes advances in the catalytic asymmetric synthesis of γ-butyrolactones in the BV oxidation through organocatalysis or metal catalysis.

Pioneering work on the asymmetric Baeyer–Villiger oxidations was reported independently by Bolm[251] and Strukul[252] in 1994. Subsequently, Lopp et al. developed the asymmetric BV oxidation of prochiral cyclobutanones into enantiomerically enriched butyrolactones using stoichiometric amount of chiral

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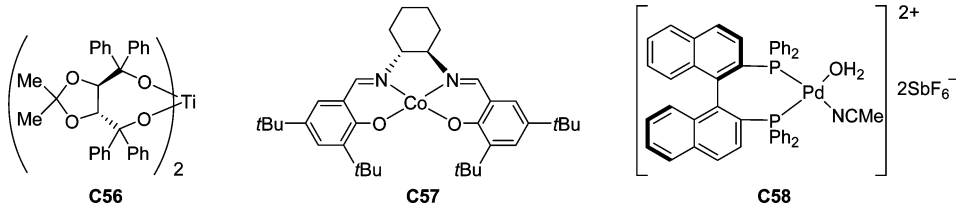
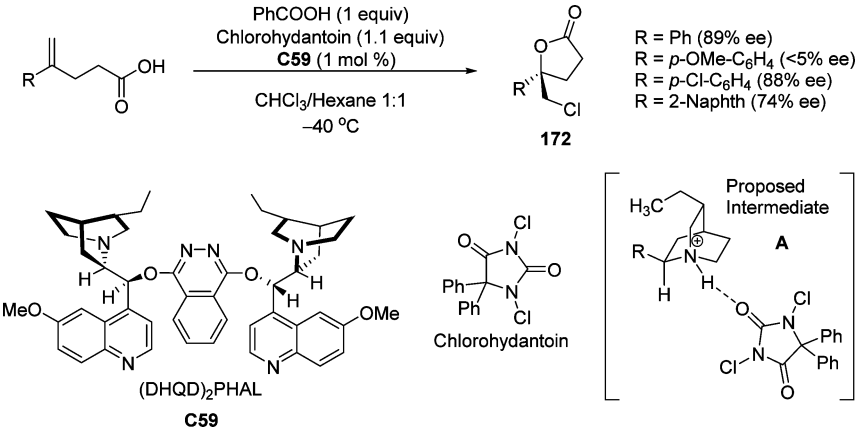
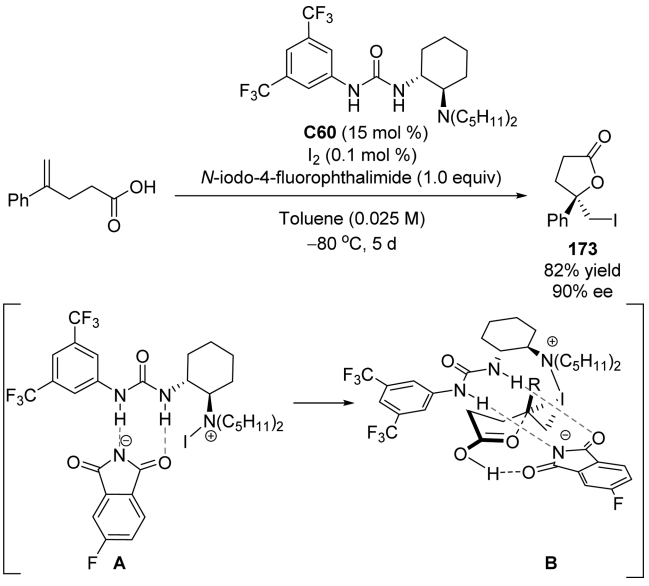


Figure 6. Chiral metal complexes for the enantioselective halolactonization to afford the corresponding γ-butyrolactones.

Scheme 83. Catalytic Asymmetric Chlorolactonization of Alkenoic Acids



Scheme 84. Tertiary Aminourea-Catalyzed Enantioselective Iodolactonization



titanium complex under Sharpless epoxidation conditions.[253,254] On the basis of the aerobic oxidation system, Bolm disclosed a copper-catalyzed BV oxidation comprising the use of copper-oxazoline catalyst **C67** that efficiently promotes this transformation, affording two regioisomeric optically active bicyclic γ-butyrolactones **188** and **189** in a ratio of 3:1 with 67 and 92% ee, respectively (Scheme 91).[255,256]

The stereochemistry of the enantioselective BV oxidation is dictated by two factors: (1) face selectivity in nucleophilic addition of the oxidant and (2) enantiotopic selectivity during migration. As the Criegee adduct formation is a reversible step and the C−C bond migration is an irreversible and rate-determining step, site selection in the migration step is considered to strongly influence the stereoselection of the BV oxidation. Katsuki and co-workers demonstrated that chiral cobalt-salen complex **C68** possessing square planar geometry did not show any enantioselectivity in the BV oxidation of 3-substituted cyclobutanone, while complex **C69** possessing a *cis*-β-structure showed good enantioselectivity (up to 78% ee) in the presence of urea−hydrogen peroxide adduct (UHP) as the oxidant (Scheme 92).[257] A peroxy *cis*-β-zirconium-salen complex **C70** was also an efficient catalyst for the enantioselective Baeyer−Villiger oxidation using UHP as the oxidant (Scheme 92).[258,259] The catalytic performance of **C70** may be explained by the formation of a *cis*-β-Zr(salen) complex chelated by the Criegee adduct intermediate, where topos-selective σ−σ* interaction was regulated by the resulting concave structure of the salen ligand in the enantioselective BV oxidation (Figure 10).

Catalytic asymmetric BV oxidation of butanones to γ-butyrolactones was also achieved in the presence of chiral complexes, based on either transition metals such as Pt[260,261] and Pd[262−264] or nontransition metals such as Mg,[265] Al,[266−269] and Sc.[270] However, depite all these efforts, further improvement, in particular wider substrate scope and/or higher levels of enantioselectivity, in several of these transformations is still needed. Furthermore, there are relatively few examples employing aqueous hydrogen peroxide as an environmentally benign oxidant in the asymmetric BV oxidation.

The first organocatalytic asymmetric BV oxidation of cyclobutanones with hydrogen peroxide was reported by Imada and co-workers in 2002.[271] In the presence of a novel planar-chiral bisflavin catalyst, the corresponding optically active lactones were obtained with up to 74% ee. In 2008, Ding et al. performed the catalytic asymmetric Baeyer−Villiger oxidation using chiral Brønsted acid **C71** with 30% aqueous H_2O_2 as the oxidant to afford the corresponding γ-butyrolactones **190** in excellent yield and up to 93% ee (Scheme 93).[272] Mechanistic studies suggested that chiral phosphoric acid plays the role of a bifunctional catalyst

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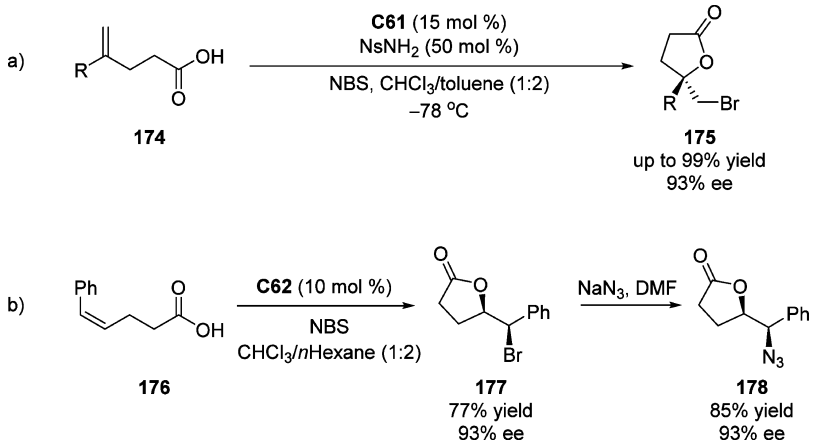
Scheme 85. Enantioselective Bromolactonization of 1,1-Disubstituted Olefinic Acids and *cis*-1,2-Disubstituted Olefinic Acids



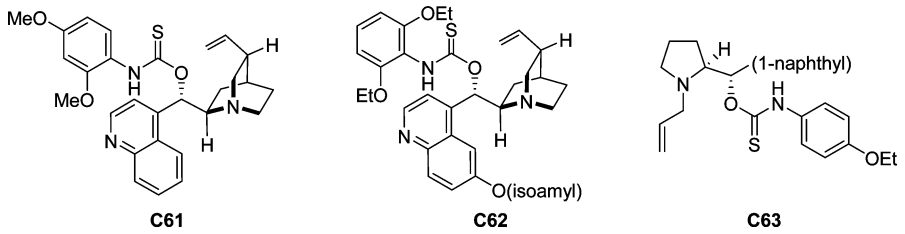
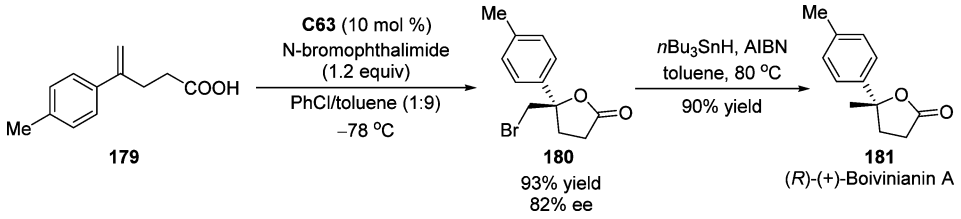


Figure 7. Chiral amino-thiocarbamate catalysts for the enantioselective bromolactonization of 4-pentenoic acid derivatives.

Scheme 86. Enantioselective Synthesis of (*R*)-(+)-Boivinianin A[a]



[a]AIBN = 2,2′-azoisobutyronitrile.

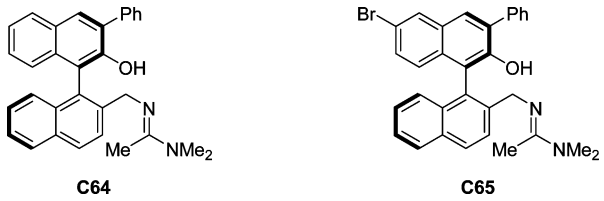


Figure 8. BINOL-derived bifunctional catalysts to promote enantioselective bromolactonizations.

to activate both the reactants and the Criegee intermediate in a synergistic manner.[273,274]

4.5. Asymmetric Hydrogenation

Asymmetric hydrogenation is one of the most powerful tools for the preparation of a wide range of enantiomerically pure or enriched compounds.[201−203] Pioneered by Noyori and co-workers,[204,275] the asymmetric hydrogenation of substituted acrylic acid in the presence of BINAP−Ru(II) dicarboxylate complex followed by cyclization provides a straightforward approach to optically active γ-butyrolactones with excellent results. The utility of this method has been illustrated by Krohn and Riaz with the total synthesis of (+)-xyloketal D.[276] Moreover, Ru-catalyzed hydrogenation of a *meso*-cyclic acid anhydride was successfully established by Kitamura et al. to obtain enantiomerically enriched γ-butyrolactones by using a chiral phosphine ligand.[277]

Catalytic asymmetric hydrogenation of γ-keto esters is another common approach toward the synthesis of γ-butyrolactones.[278−282] A few methods, such as transition metal catalyzed hydrogenation,[283,284] and related hydrosilylation[285] and hydroboration,[286] have been applied to perform this type of reaction. In this context, Vinogradov and co-workers developed a convenient one-step synthesis of various γ-substituted butyrolactones based on the $RuCl_3$-(*R*)-BINAP-HCl catalyzed enantioselective hydrogenation of γ-keto esters (Scheme 94).[281]

Transfer hydrogenation has also been successfully applied in the asymmetric synthesis of γ-butyrolactones. A newly designed (arene)RuCl(monosulfonamide) complex bearing a terphenylsulfonamide with a high affinity for selective β-aryl α-keto ester reduction was introduced by Johnson and co-workers (Scheme 95).[287] A dynamic kinetic resolution of α-keto esters **192** via asymmetric transfer hydrogenation created the α- and β-stereocenters, and the third stereocenter at the γ-position was established through concomitant diastereoselective lactonization, providing direct access to enantioenriched γ-butyrolactones **193** bearing three contiguous stereocenters with complete diastereocontrol (>20:1 dr).

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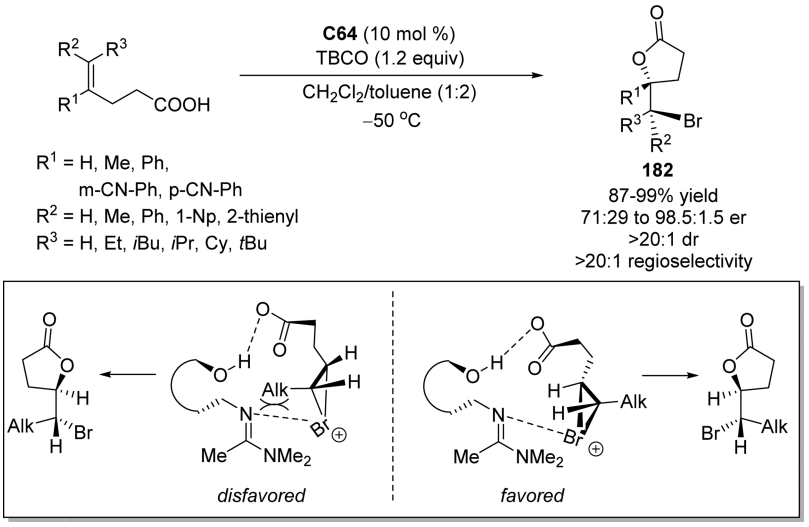
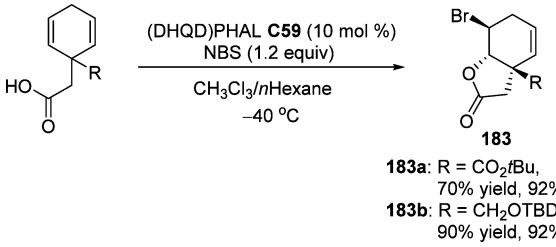
Scheme 87. Enantioselective Bromolactonizations of Substituted Unsaturated Carboxylic Acids[a]



[a]TBCO = 2,4,4,6-tetrabromocyclohexa-2,5-dienone.

Scheme 88. Catalytic Asymmetric Synthesis of Bicyclic Bromolactones with Three Contiguous Stereocenters[a]



[a]TBDPS = *tert*-butyldiphenylsilyl.

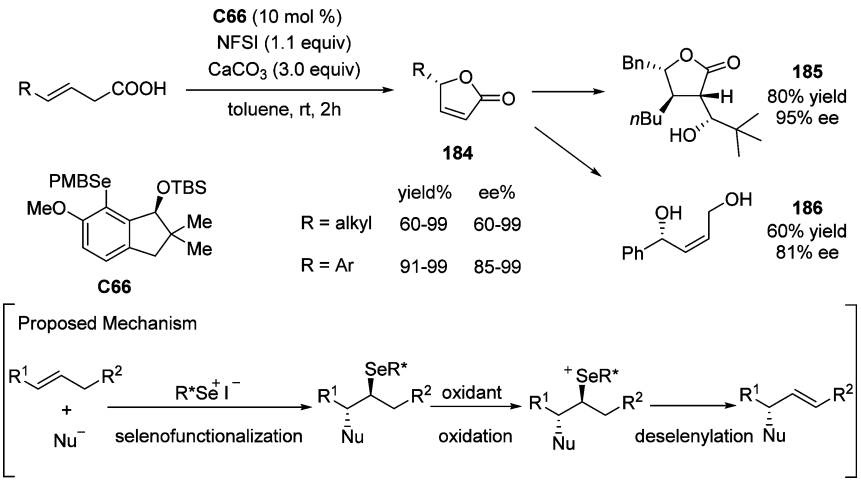
The obtained densely functionalized γ-butyrolactones were deployed in further transformations (Scheme 96).[286,287] Access to α-alkylidene γ-butyrolactone **194** was accomplished upon treatment with K_2CO_3 and CH_2Br_2 followed by dehalodecarboxylation. Krapcho decarboxylation[288] was performed under simple conditions, yielding the α-unsubstituted lactone **195** in high yield. Employing allyl bromide and DBU, a tetrasubstituted γ-butyrolactone **196** bearing an all-carbon quaternary center was obtained in 94% yield with remarkable diastereoselectivity.

More recently, Dong and Murphy directly accessed enantioenriched γ-butyrolactones **197** through enantioselective hydroacylation of keto alcohols in the presence of Noyori's transfer hydrogenation catalyst **C72** (Scheme 97).[289] A range of 1,4-keto alcohol derivatives provided the desired γ-butyrolactones with high enantioselectivity. The addition of isopropyl alcohol (*i*PrOH) was shown to be essential to promote the formation of the ruthenium hydride and accelerate the asymmetric hydrogen transfer (AHT) process, while excess of acetone inhibits the reaction.

4.6. Catalytic Asymmetric Metal Carbene Transformations

The transformation of diazoacetates mediated by the in situ formation of metal carbene has emerged as a powerful tool for the catalytic enantioselective synthesis of butyrolactones. The first examples, reported by Doyle and co-workers,[290] were based on intramolecular carbene C–H insertion as well as cyclopropanation promoted by chiral dirhodium(II) carboxamidate complexes as catalysts. The catalytic asymmetric metal carbene transformation has served as the key step for the synthesis of a

Scheme 89. Selenium-Catalyzed Enantioselective Oxidative Cyclization of β,γ-Unsaturated Carboxylic Acids



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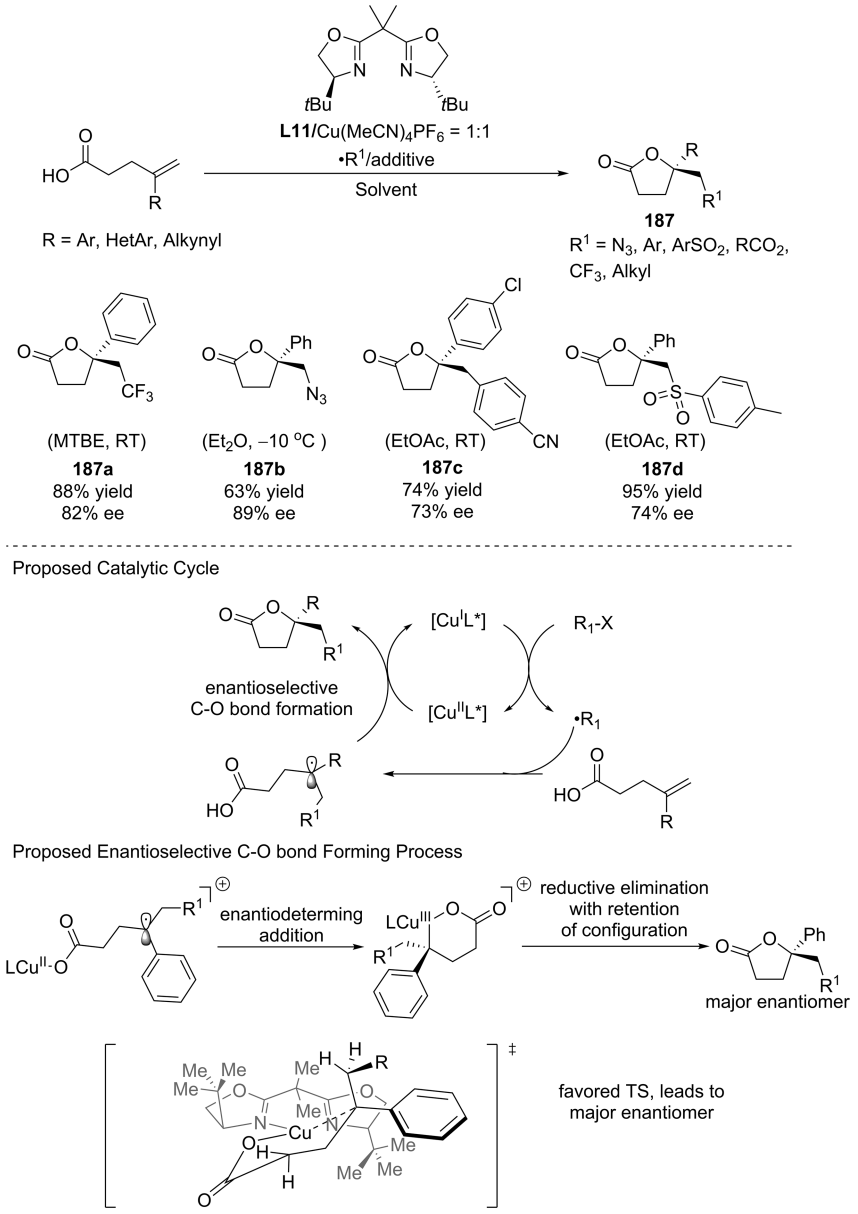
Scheme 90. Enantioselective Synthesis of γ-Butyrolactones via Copper-Catalyzed Radical Oxyfunctionalization of Alkenes[a]



[a]MTBE = methyl *tert*-butyl ether.

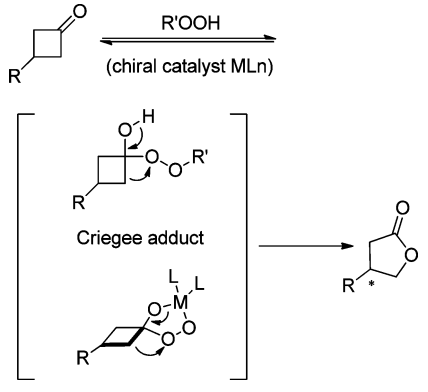
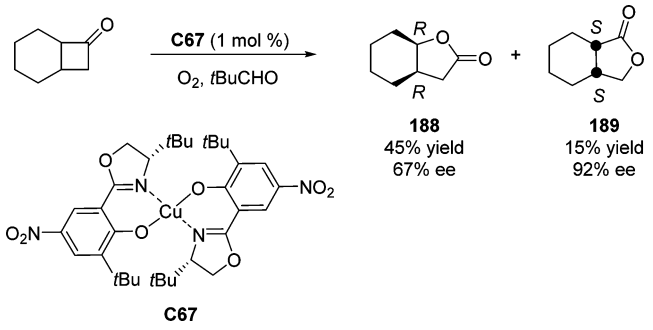


Figure 9. Concept for catalytic asymmetric BV oxidation.

Scheme 91. Synthesis of Bicyclic Butyrolactones by Catalytic Asymmetric BV Oxidation



variety of biological active cyclic[291−295] and bicyclic lactones (Scheme 98).[296−307] Excellent reviews have been published in this field;[308−314] therefore this topic will not be discussed in detail.

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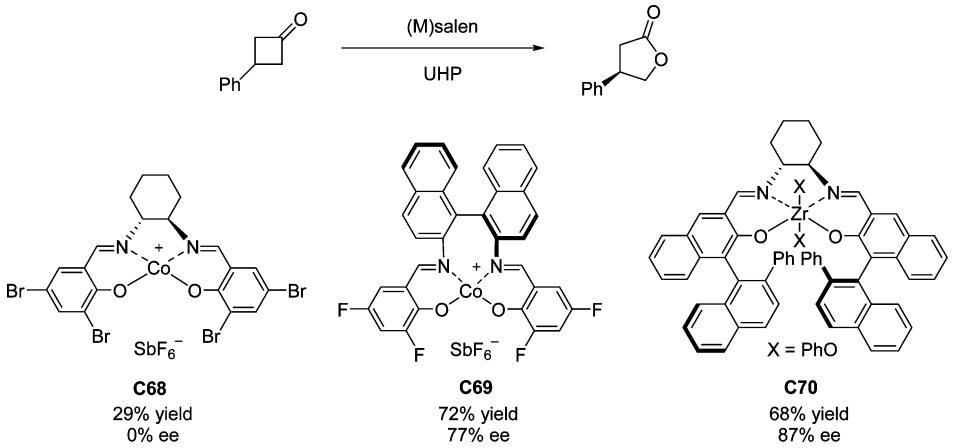
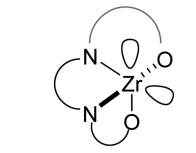
Scheme 92. Chiral Catalysts Employed in the Asymmetric BV Oxidation of 3-Substituted Cyclobutanone



C68
29% yield
0% ee

C69
72% yield
77% ee

C70
68% yield
87% ee



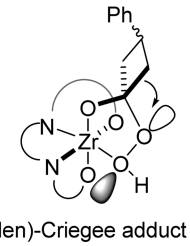
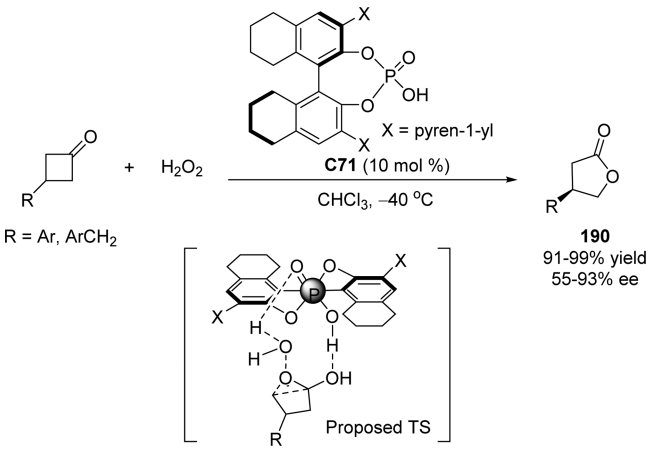


Figure 10. *cis*-β-Zr(salen) complex chelated by the Criegee adduct intermediate.

Scheme 93. Organocatalyzed Asymmetric Baeyer–Villiger Oxidation of Cyclobutanones

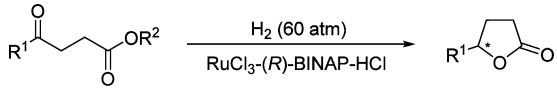


190
91-99% yield
55-93% ee

4.7. Asymmetric Conjugated Umpolung Reaction

Developed independently by Bode[315] and Glorius,[316] N-heterocyclic carbene (NHC) catalyzed umpolung reactions of α,β-unsaturated aldehydes have enabled a powerful method to access the γ-butyrolactone structure.[317−321] This reaction initially proceeds through the formation of a homoenolate intermediate. The resulting homoenolate can react with an aldehyde or a ketone giving rise to a transient alkoxide which evolves by intramolecular trapping by the activated carboxylate, thereby promoting a highly efficient conversion of α,β-unsaturated aldehydes into γ-butyrolactones (Scheme 99). Although the reactivity of the NHC-catalyzed [3 + 2] annulation of enals and carbonyl compounds has been well-established, the control of the stereoselectivity of these reactions turned out to be a major challenge.

Scheme 94. Catalytic Enantioselective Hydrogenation of γ-Keto Esters



R^1 = Me, Et, Pr, *i*Pr, Ph, 4-ClC_6H_4
R^2 = Me or Et

191
57-88% yield
91-99% ee

By employing the chiral imidazolium salt **C76** as catalyst, Glorius and co-workers reported the transformation of cinnamaldehyde into substituted γ-butyrolactones **198** bearing quaternary stereocenters with a diastereomeric ratio of 3:1 and with 12 and 25% ee.[316] You and co-workers have indentified keto esters as valuble electrophiles for the transformation of cinnamaldehyde using chiral carbene ligand **C77**. In this case, 4,5,5-trisubstituted γ-butyrolactones **199** were obtained with low levels of diastereoselectivity (60:40 dr) and 78 and 55% ee, respectively for both diastereosisomers (Scheme 100).[322]

The synthesis of γ-butyrolactone is also feasible by the N-heterocyclic carbene catalyzed reaction between enals and α-hydroxy enones. The use of chiral imidazolium precatalyst **C78** provides the fused γ-butyrolactones in 68−85% yields, with a range of diastereoselectivity from 3:1 to 5:1 and up to 99% ee for the major diastereoisomer **200a** (Scheme 101).[323]

In 2010, Scheidt and Cohen developed a novel cooperative catalysis integrating chiral titanium Lewis acid with N-heterocyclic carbene to explore the catalytic asymmetric synthesis of γ-butyrolactones (Scheme 102).[324] When combining DBU, cinnamaldehyde with TADDOL-based titanium complex **C79**, and achiral imidazolium salt **C80**, only the *cis*-γ-butyrolactone **201** was obtained in 20:1 dr with 60% ee through a dimerization of cinnamaldehyde. The use of a Lewis acid in a cooperative catalysis could expand the substrate scope by activating the conjugate acceptor and provide increased *cis* diastereoselectivity through the preorganization of the sub-

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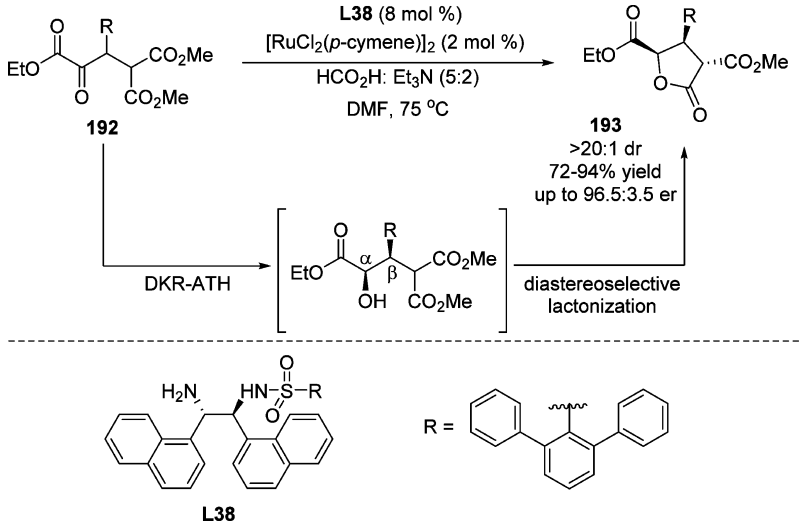
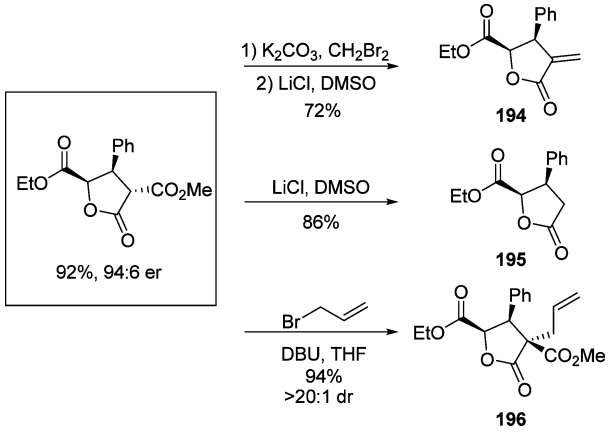
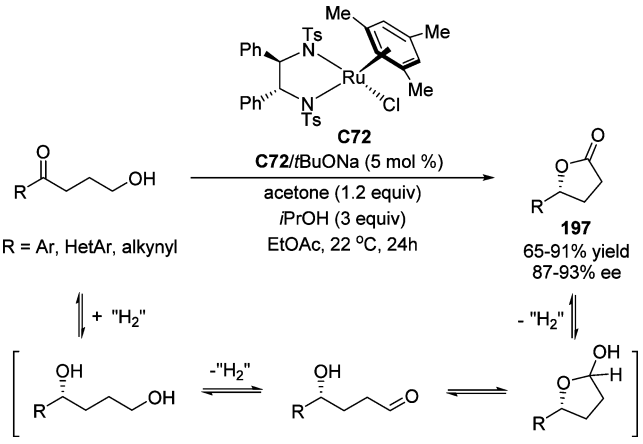
Scheme 95. Dynamic Kinetic Resolution of α-Keto Esters via Asymmetric Transfer Hydrogenation



Scheme 96. Transformations of Densely Functionalized Chiral γ-Butyrolactones



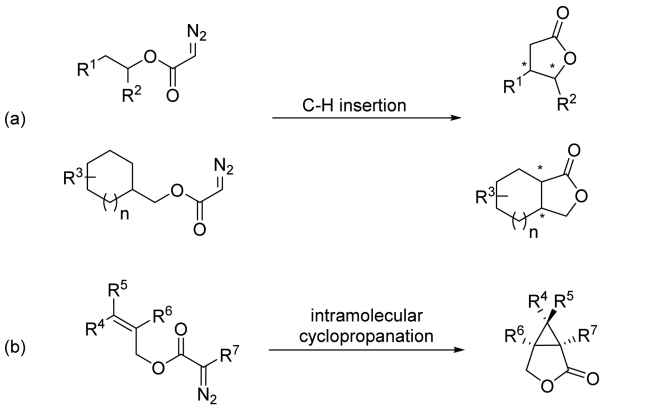
Scheme 97. Synthesis of γ-Butyrolactones via Enantioselective Ketone Hydroacylation

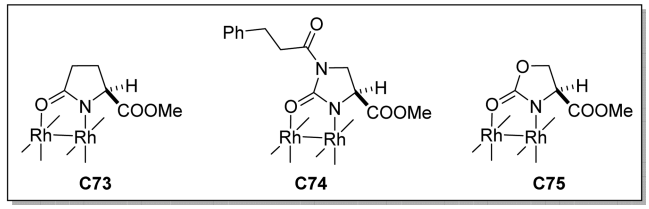


strates.[324] Although the enantioinduction is moderate, this combination of achiral carbenes with chiral Lewis acids offers new opportunities to access the stereoenriched *cis*-γ-butyrolactone **201** (20:1 dr, 60% ee).

Ever since the seminal report on the NHC-catalyzed annulation of enals with isatins by the research group of

Scheme 98. Concept for the Catalytic Asymmetric Synthesis of Cyclic and Bicyclic Lactones through Metal Carbene Transformations





Nair,[325] the enantioselective synthesis of spirocyclic oxindolo-γ-butyrolactone has attracted considerable attention. The study from Ye and co-workers disclosed that the chiral N-heterocyclic carbene **C81** derived from L-pyroglutamic acid bearing a vicinal hydroxy group was an efficient catalyst for the [3 + 2] annulation of enals and isatin, affording the corresponding spirocyclic oxindolo-γ-butyrolactones **202** in good yields with high diastereo- and enantioselectivities (Scheme 103).[326] A possible transition state which involves H-bonding between the enal−catalyst adduct and isatin enhances the reactivity and directs the nuclephilic addition of the resulting homoenolate.

An enantioselective NHC/Lewis acid catalyzed annulation of enals with isatins has been developed by Scheidt and co-workers.[327] The high level of enantioselectivity was proposed to result from lithium cation involved in the transition state through coordination of the enol oxygen atom of NHC-bound

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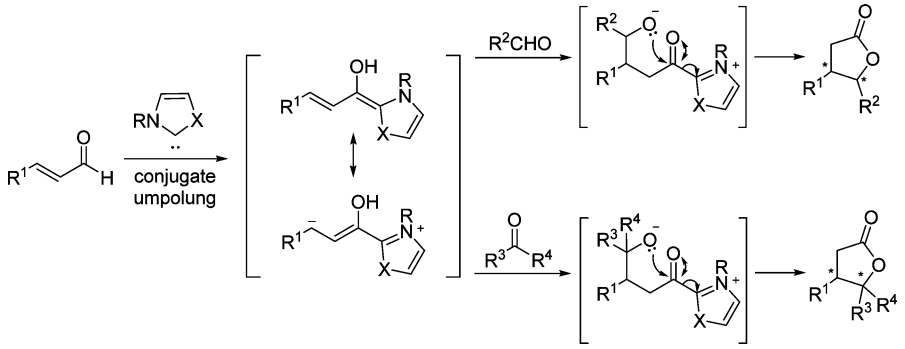
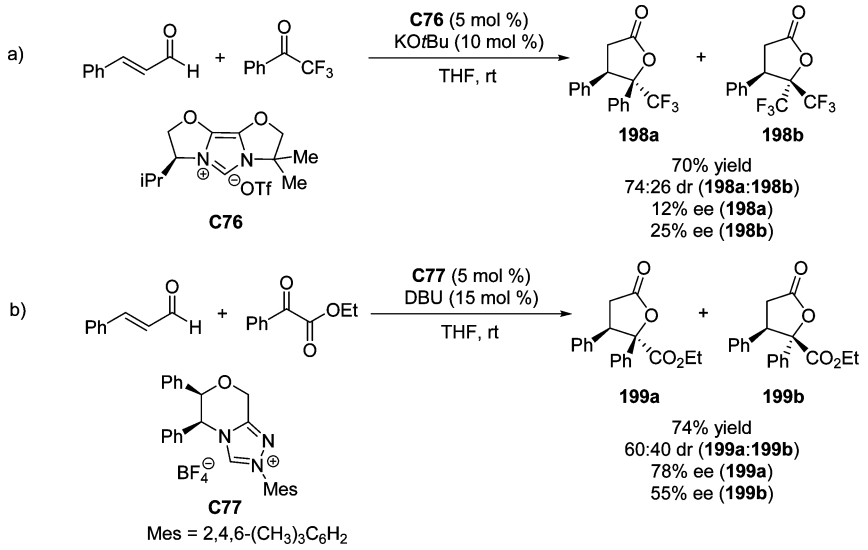
Scheme 99. Concept for the Catalytic Asymmetric Synthesis of Butyrolactones through Conjugated Umpolung Reaction

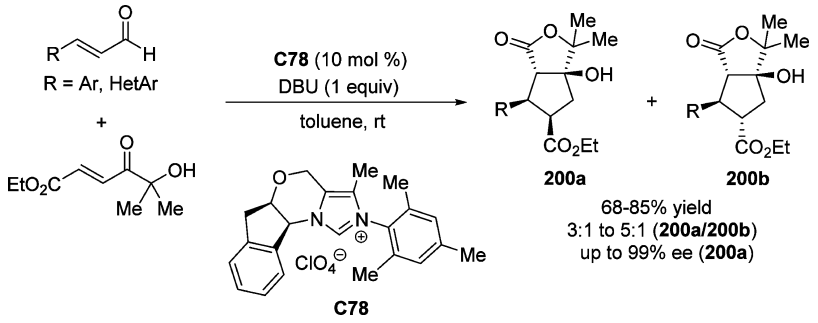


Scheme 100. Stereoselective Synthesis of γ-Butyrolactones via Organocatalytic Annulations of Enals and Keto Esters[a]



[a]DBU = 1,8-diazabicyclo(5.4.0)undec-7-ene.

Scheme 101. Chiral Imidazolium-Derived N-Heterocyclic Carbene Catalysts Applied in the Stereoselective Synthesis of Cyclopentane-Fused Lactones[a]



[a]DBU = 1,8-diazabicyclo(5.4.0)undec-7-ene.

homoenolate and the 1,2-dicarbonyl of the isatin. Although the addition of lithium chloride as a Lewis acid with β-aryl-substituted enals provided the spirolactone products **203a** and **203b** with modest diastereoselectivities and high levels of enantioselectivity in the presence of triazolium catalyst **C82**, lactone **203c** was obtained only in 36% yield and 25% ee. The triazolium precatalyst **C83** was tested with crotonaldehyde to generate the corresponding spiro γ-butyrolactone in 76% yield with 5:1 dr and 78% ee.[327] The enantiopure product was obtained after a single recrystallization and employed as the key intermediate for the first enantioselective total synthesis of maremycin B (Scheme 104).

4.8. Asymmetric Cycloisomerization

Asymmetric cycloisomerization constitutes a powerful and efficient strategy for the enantioselective synthesis of γ-butyrolactones with quantitative atom economy.[328−332] Lu and co-workers developed the asymmetric Pd(II)-catalyzed cycloisomerization of enyne esters for the synthesis of γ-butyrolactones (Scheme 105).[333] The use of chiral bidentate

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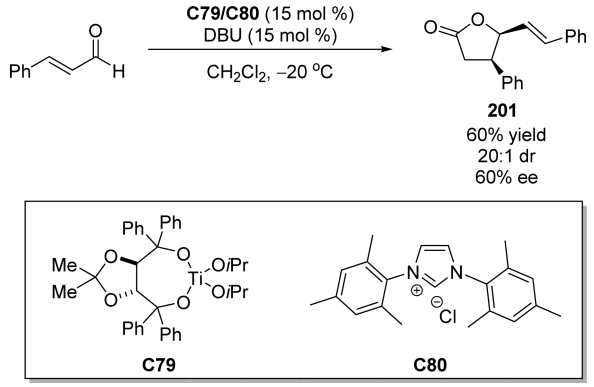
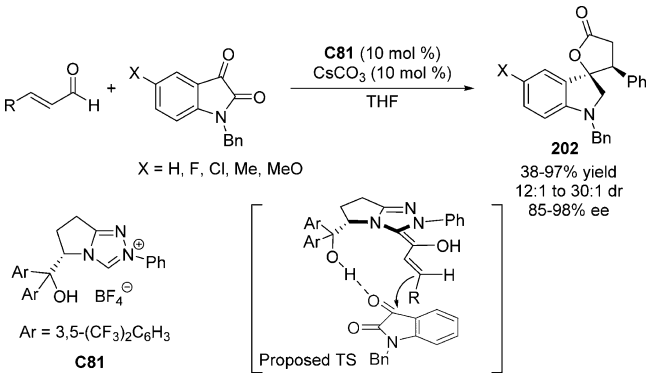
Scheme 102. Enantioselective Synthesis of *cis*-γ-Butyrolactones Promoted by Chiral Titanium Lewis Acid C79 in the Presence of Achiral NHC Catalyst C80



Scheme 103. Enantioselective Synthesis of Spiro γ-Butyrolactones in the Presence of Chiral NHC Catalyst



diamine ligand **L16** or **L39** in the presence of catalytic palladium acetate renders the reaction enantioselective providing a number of optically active γ-butyrolactones **204**. The synthetic utility of this asymmetric transformation was nicely illustrated by the facile synthesis of (3*S*)-(+)-A-factor.

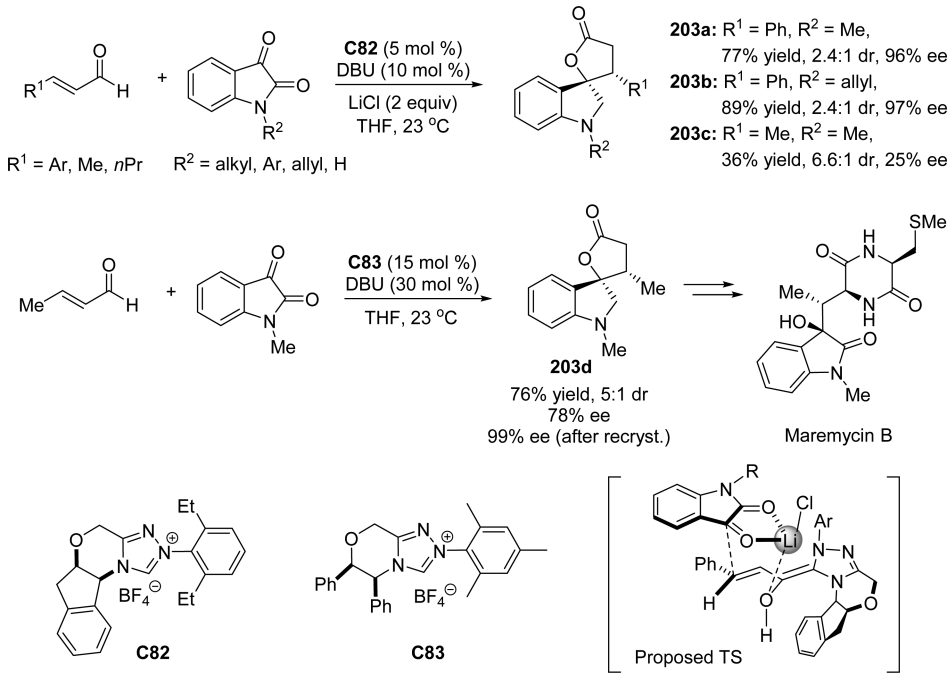
The proposed mechanism for this transformation involves initial *trans*-acetoxypalladation of the triple bond, followed by intramolecular olefinic insertion and deacetoxypalladation to give the desired product and regenerate the catalytic species (Scheme 106).[334] The nitrogen-containing ligand played an important role not only to inhibit the β-hydride elimination but also to facilitate the intramolecular olefinic insertion into the vinyl−palladium bond instead of its protonolysis.

In a seminal contribution, Clark et al. reported the use of Rh(I)-catalyzed cycloisomerization to form the α-methylene-γ-butyrolactone core and its application in the enantioselective synthesis of (+)-anthecotulide, which has attracted interest due to its contact allergen properties and its unusual biosynthesis for a sesquiterpene (Scheme 107).[335] Employing a 1,6-enyne as a substrate, the catalyst [Rh((*R*)-BINAP)]SbF_6 **C84** was found optimal for the synthesis of the desired product, affording α-methylene-γ-butyrolactone **205** in 73% yield and 96:4 er. This process generally involves oxidative cyclization of the substrates to form a metallocycle, followed by β-H elimination and reductive elimination to complete the catalytic cycle. With the highly enantioselective synthesis of aldehyde established, the synthesis of (+)-anthecotulide was completed in 24% overall yield.

4.9. Asymmetric Cyclocarbonylation

The intramolecular cyclocarbonylation of unsaturated alcohols to lactones, as a special class of carbonylation reactions, represents an elegant route to these important heterocycles. Alper et al. reported the first enantioselective palladium-catalyzed cyclocarbonylation of allylic alcohols to γ-buyrolactones (Scheme 108a).[336,337] The reaction proceeds in dichloro-

Scheme 104. Stereoselective Synthesis of Spirooxindole Lactones Using N-Heterocyclic Carbene/Lewis Acid as Cooperative Catalyst System



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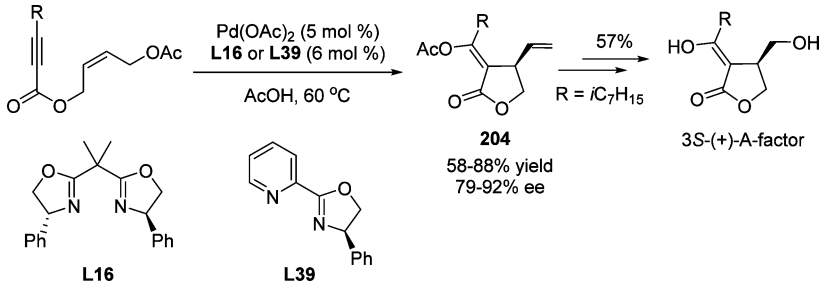
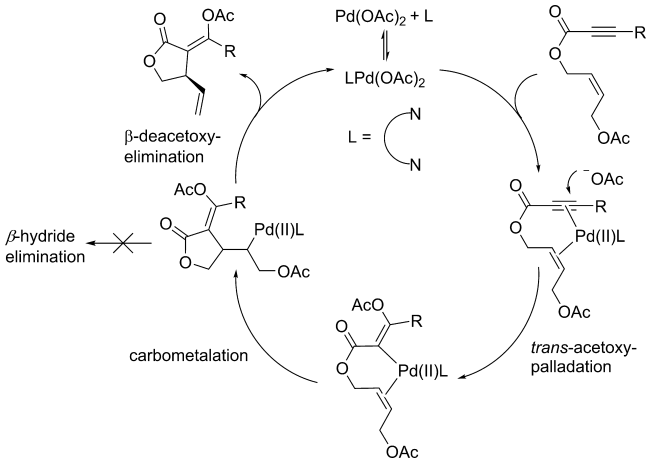
Scheme 105. Synthesis of Optically Active γ-Butyrolactones via Enantioselective Palladium(II)-Catalyzed Cyclization



Scheme 106. Proposed Mechanism in the Enantioselective Palladium(II)-Catalyzed Cyclization of of Enyne Esters (Adapted from ref 334. Copyright 2001 American Chemical Society.)[a]



[a]L = ligand.

methane with a mixture of H_2/CO_2 (1/1) and gives rise to the corresponding butyrolactones **206** with moderate enantioselectivity utilizing chiral bisphosphine ligand **L40**. Soon thereafter, Zhang and Cao demonstrated improved enantioselective cyclocarbonylation for the synthesis of γ-butyrolactones (Scheme 108b).[338] The use of a catalyst prepared from $Pd_2(dba)_3$ and ligand **L41** or **L42** gave, in several cases, high levels of enantioselectivity in the carbonylation of geminally disubstituted allylic alcohols. The combination of $Pd(OAc)_2$ with ligand **L41** or **L42** proved to be an effcient catalyst for the formation of *trans*-α,β-disubstituted chiral lactones **206** with good to excellent enantioselectivities (up to 98% ee).

A possible mechanism of the Pd-catalyzed cyclocarbonylation is depicted in Scheme 109.[338] Coordination of the allylic alcohol to the metal complex followed by *cis* addition of the palladium hydride to the allylic double bond and subsequent CO insertion into Pd−C bond results in an acylpalladium complex. Rotation about the central C−C bond followed by ring closure affords the *trans* substituted lactone with regeneration of the palladium hydride.

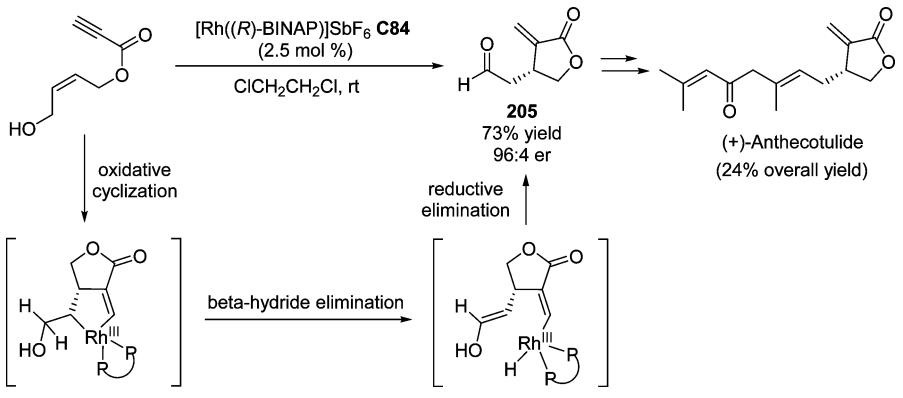
Catalytic asymmetric *hetero* Pauson−Khand reactions where chiral titanocene catalyst **C85** promoted the cyclocarbonylation of enals or enones for the formation of various optically active fused bicyclic γ-butyrolactones **209** were reported by Crowe et al. (Scheme 110).[339] The ansametallocene, (EBTHI)Ti(CO)$_2$, exhibited higher reactivity toward cyclocarbonylation than its unbridged counterpart, CpTi(CO)$_2$. This air-stable chiral titanocene catalyst also allowed for operational simplicity of the procedure.

4.10. Asymmetric Aldol reaction/Cyclization

The synthesis of optically active pantolactone (α,γ-dihydroxy-β,β-dimethylbutyrolactone) has been achieved by enantioselective hydrogenation[340] of 3,3-dimethyl-2-oxobutyrolactone or Sharpless's dihydroxylation[341] of the corresponding cyclic silylketene acetal. In an alternative approach Evans et al. reported an efficient method toward the asymmetric synthesis of substituted and unsubstituted pantolactones combining an enantioselective scandium-catalyzed aldol reaction with a subsequent reduction/cyclization process.[342]

Relying on an organocatalytic cross-aldol reaction with subsequent reduction,[343] Hajra and co-workers developed a concise and efficient method for the synthesis of 4-(hydroxyalkyl)-γ-butyrolactones **210** (Scheme 111).[344] With (*S*)-proline **C86** as the catalyst, a series of enantiomerically enriched γ-

Scheme 107. Enantioselective Synthesis of (+)-Anthecotulide



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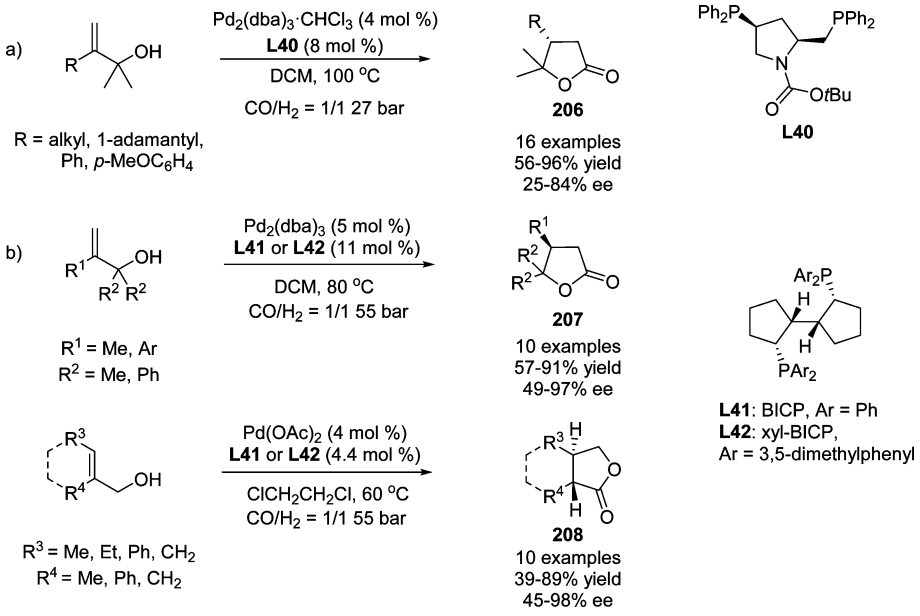
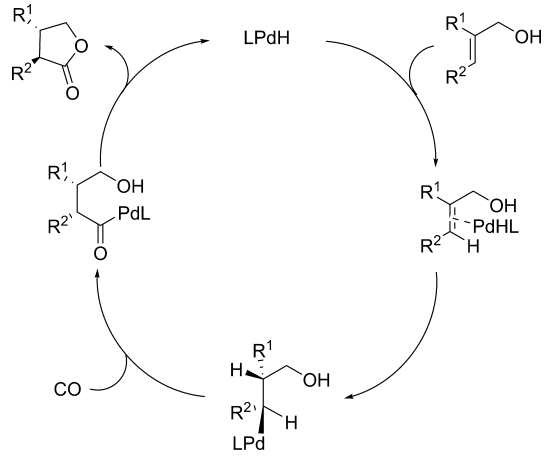
Scheme 108. Synthesis of γ-Butyrolactones via Palladium-Catalyzed Enantioselective Cyclocarbonylation



Scheme 109. Proposed Mechanism for the Palladium Catalyzed Cyclocarbonylation (Adapted from ref 336. Copyright 1997 American Chemical Society.)



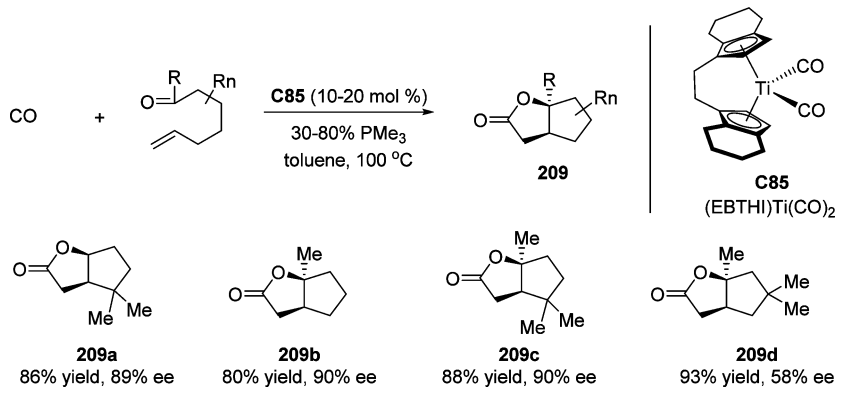
butyrolactone derivatives bearing two contiguous stereogenic centers were obtained in satisfactory yields with moderate to high enantioselectivity up to >99% ee. This transformation served as a key step in the asymmetric synthesis of (−)-enterolactone and (7′*R*)-7′-hydroxyenterolactone.

A novel tandem enantioselective aldol reaction/cyclization of β,γ-dihydro-γ-butyrolactones with aldehydes was studied with the aim of developing the catalytic asymmetric synthesis of optically active γ-butyrolactones (Scheme 112).[345] When the γ-substituted-β,γ-dihydro-γ-butyrolactone was subjected to the catalyst system comprising chiral tin dibromide **C87** and sodium methoxide, the β,γ-disubstituted-γ-butyrolactones **211** were formed with high levels of diastereo- and enantioselectivities.

It is proposed that bromide is replaced by methoxide to form the actual catalyst which promotes the ring opening of the β,γ-dihydro-γ-butyrolactone leading to the formation of the corresponding acyclic chiral tin enolate. Subsequent stereoselective adol reaction followed by cyclization of the resulting tin alkoxide regenerates the tin complex and forms the γ-butyrolactone product (Scheme 113).[345]

An asymmetric organocatalytic formal cycloaddition of aryl succinic anhydrides with aldehydes to lactones was reported by Connon et al. (Scheme 114).[346] Using the cinchona alkaloid derived squaramide **C88** as the catalyst, a series of β,γ-substituted

Scheme 110. Asymmetric *hetero* Pauson−Khand Reaction for the Synthesis of Optically Active Fused Bicyclic γ-Butyrolactones 209



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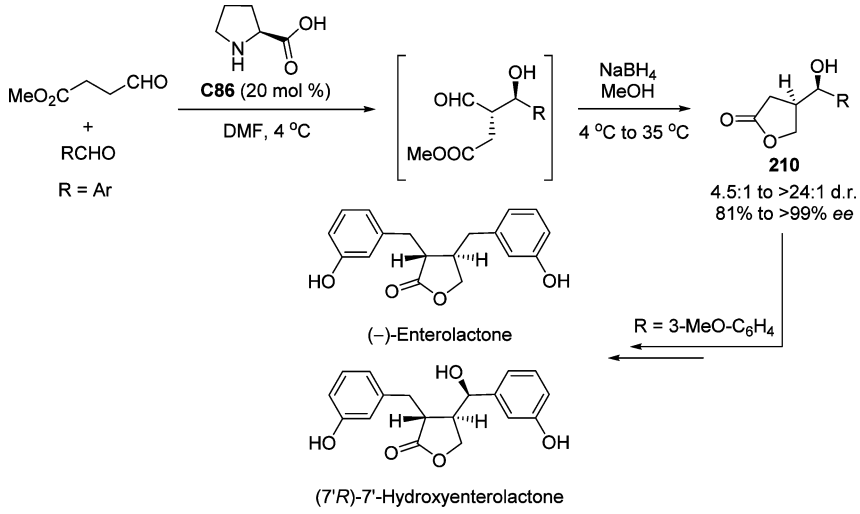
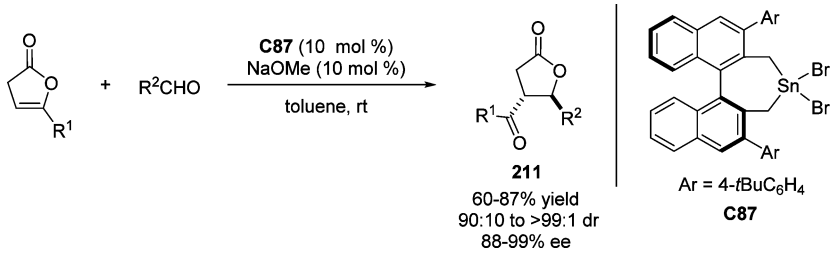
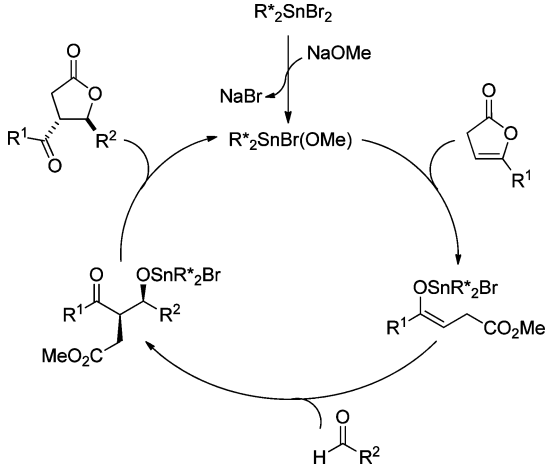
Scheme 111. Organocatalytic Asymmetric Synthesis of 4-(Hydroxyalkyl)-γ-butyrolactones



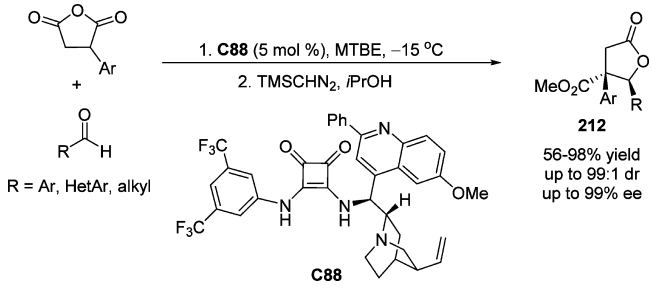
Scheme 112. Synthesis of β,γ-Disubstituted-γ-butyrolactone via a Tandem Enantioselective Aldol Reaction/Cyclization



Scheme 113. Proposed Mechanism for the Tandem Enantioselective Aldol Reaction/Cyclization



Scheme 114. Asymmetric Synthesis of β,γ-Substituted Butyrolactones via Organocatalytic Formal Cycloaddition of Aryl Succinic Anhydrides with Aldehydes



butyrolactone derivatives bearing two contiguous stereogenic centers were obtained with good to excellent stereocontrol under mild conditions. The mechanism possibly involves the enolization of the anhydride, followed by the addition to aldehyde electrophile and fast lactonization. The nature of the aryl substituent on the succinic anhydride turned out to have an important effect on the keto−enol equilibrium, thus affecting the outcome of the reaction. By using an electron-withdrawing α-aryl group, a significant increase in the reactivity was observed leading to lactones with enhanced yield and stereoselectivity.

Catalytic approaches to access optically active isotetronic acids with a butenolide motif have been developed through a related procedure involving an aldol reaction and cyclization. For instance, bisoxazoline/copper(II) and proline have been employed as chiral catalysts to promote the enantioselective homoaldol reaction of pyruvates.[347−349] Landais and co-workers developed an asymmetric organocatalyzed tandem reaction of α-oxocarboxylic acids to aldehydes in the presence of benzoimidazole pyrrolidine **C89**, providing the corresponding isotetronic acids **213** in moderate to good yields and good enantiomeric excess (Scheme 115).[350] The reaction was observed equally efficient in water when liquid and viscous aldehydes were employed, which indicated that chirality amplification might be invoked through a hydrophobic effect.

Recently, Li and co-workers developed a new amphiphilic proline-derived imidazole organocatalyst **C90** using water as the solvent to promote the cacade reaction of α-ketoacids with aldehydes (Scheme 116).[351] High reactivity and stereoselectivity were achieved by the formation of oil/water emulsion system in

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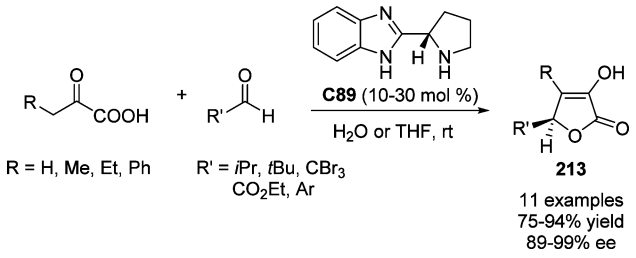
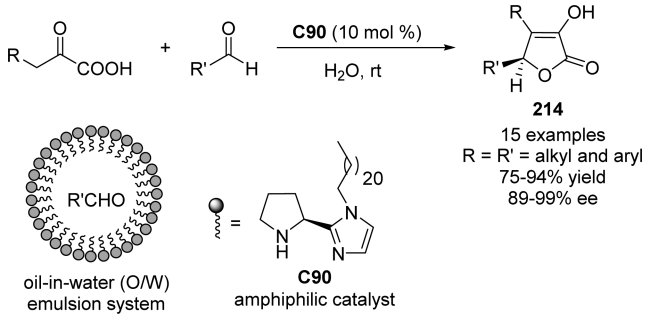
Scheme 115. Synthesis of Chiral Isotetronic Acids 213 with Amphiphilic Imidazole/Pyrrolidine Catalysts Assembled in Oil-in-Water Emulsion Droplets



Scheme 116. Synthesis of Chiral Isotetronic Acids with Amphiphilic Imidazole/Pyrrolidine Catalysts Assembled in Oil-in-Water Emulsion Droplets



the reaction mixture through self-assembly. Fluorescence imaging confirmed that the reaction took place on the surface of emulsion droplets, thus improving both yield and enantioselectivity for the resulted isotetronic acids **214**.

4.11. Asymmetric Dearomatization

In 2008, Kita and co-workers reported the first enantioselective oxidative dearomatization reaction[352] of phenols into spirolactones with a chiral hypervalent iodine(III) reagent bearing a rigid spirobiindane backbone (Scheme 117).[353] The use of catalytic amount of iodine reagent generated in situ from **C91** and *m*CPBA yielded the corresponding spirolactones in moderate yields and enantioselectivities. By applying a modified *ortho*-functionalized spirobiindane catalyst **C92**, the enantioselectivity of the oxidative dearomatizing spirolactonization of naphthols was enhanced.[354] A plausible transition-state model was proposed in which the pendant carboxylic acid would preferentially attack the *ipso* position of the naphthol ring from the unshielded *Re* face of substrate, resulting in formation of the *R* enantiomer of the product (Scheme 118).[354] The group of Ishihara showed a conformationally flexible C_2-symmetric chiral iodoarene **C93** as precatalyst which afforded higher enantioselectivities than previously reported for this oxidative spirolactonization reaction (Scheme 117).[355,356] Experimental observations strongly supported the hypothesis that a chiral iodine(III) species was generated through the oxidation of iodoarene by *m*CPBA.

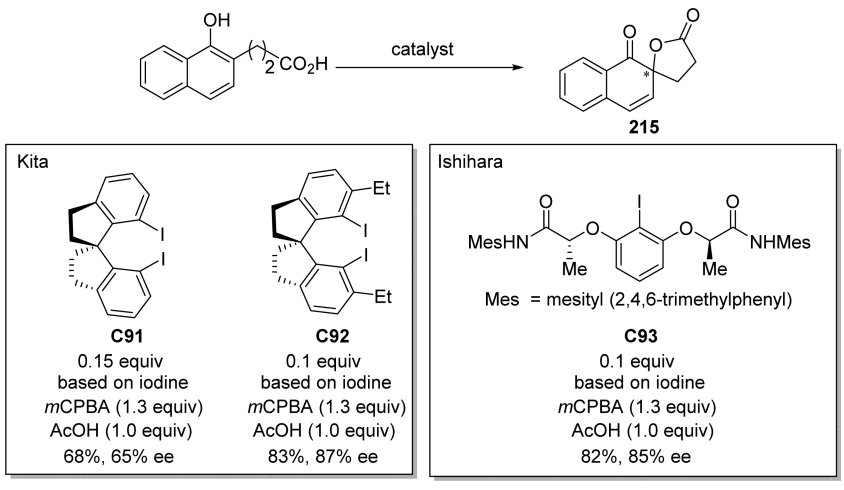
4.12. Asymmetric Desymmetrization

In 2012, Sasai and co-workers reported that a desymmetrization of the prochiral dienones using chiral bifunctional catalyst **C94** promotes highly enantioselective intramolecular Rauhut–Currier reaction which affords a range of α-alkylidene-γ-butyrolactones (Scheme 119).[357] The reaction was proposed to proceed through the Michael addition of an in situ formed phosphonium enolate **217** to the enone function to give intermediate **218** (Scheme 120).[357] Subsequent proton transfer from the α position of the carbonyl group of the lactone to the enolate anion in B facilitated by the tosylamide Brønsted acid moiety leads to the α-alkylidene-γ-butyrolactone and regenerates the catalytically active species.

An efficient synthesis of enantioenriched β-substituted γ-butyrolactone via kinetic resolution was described by Petersen et al., in which simple linear racemic substituted hydroxyl ester was selectively lactonized in the presence of a chiral Brønsted acid **C95**.[358] The desymmetrization of prochiral diesters was also achieved using the same chiral phosphoric acid catalyst to deliver highly enantioenriched lactones (R = Me, 98% ee) (Scheme 121). Treatment of diester substrates containing a different substitution pattern (R group) under optimized conditions provided enantioenriched γ-butyrolactones bearing all-carbon quaternary stereocenters (when R ≠ H) in good to excellent yields and high enantiopurity (90–98% ee).[359] A variety of highly functionalized building blocks was prepare to demonstrate their synthetic versatility.

In 2010, List and co-workers reported the use of chiral phosphoric acid **C96** as organocatalyst for the kinetic resolution of homoaldol acetals through an asymmetric transacetalization reaction (Scheme 122).[360,361] Excellent results were obtained

Scheme 117. Dearomatizing *ortho*-Spirocyclization of Naphthols Using Chiral Hypervalent Iodine Reagents



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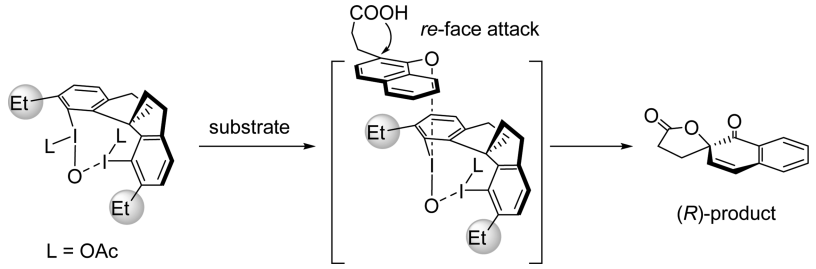
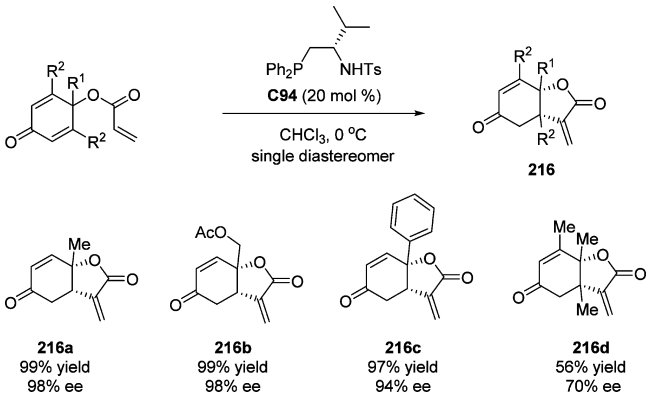
Scheme 118. Proposed Transition-State Model for the Formation of Spirolactone Products (Adapted from ref 354. Copyright 2013 American Chemical Society.)



Scheme 119. Synthesis of α-Alkylidene-γ-butyrolactones through Asymmetric Desymmetrization of the Prochiral Dienones



with various secondary and tertiary substrates in the presence of 1 mol % catalyst, delivering the cyclic acetals **220a** and **220b** with a high level of stereoselectivity. A subsequent Jones oxidation was then applied to convert these acetals into butenolide-containing natural products (*R*)-(+)-boivinianin A and (*S*)-(−)-boivinianin A.

Inspired by the work of Taylor on the enantioselective cobalt-catalyzed desymmetrization of endoperoxides,[362] Kimber and coauthors reported an asymmetric addition of 1,3-dicarbonyl compounds to endoperoxides which affords *trans*-fused γ-butyrolactones **224** with high yields and stereoselectivities (Scheme 123).[363] The enantioselective desymmetrization of the bicyclic endoperoxides to γ-hydroxyenones was achieved through an organocatalyzed Kornblum−DeLaMare rearrangement.[364] The *trans*-fused γ-butyrolactone scaffolds **224** were produced with high levels of diastereoselectivity, resulting from a subsequent intermolecular conjugate addition and intramolecular lactonization (Scheme 123). The significance of this methodology was highlighted by the facile synthesis of *trans*-xanthanolide analogue in three steps.

4.13. Catalytic Enantioselective Allylation

In 2012, Krische and co-workers reported the first examples of catalytic enantioselective carbonyl 2-(alkoxycarbonyl)allylation through iridium-catalyzed transfer hydrogenative C−C coupling of acrylic ester to alcohols. The reaction provides the substituted *α-exo*-methylene γ-butyrolactones with high to excellent levels of enantioselectivity (Scheme 124).[365] To demonstrate the synthetic potential, the resultant butyrolactone products **225** were further converted into disubstituted *α-exo*-methylene γ-butyrolactones **226** via bromination followed by zinc-mediated diastereoselective reductive coupling to aldehydes.

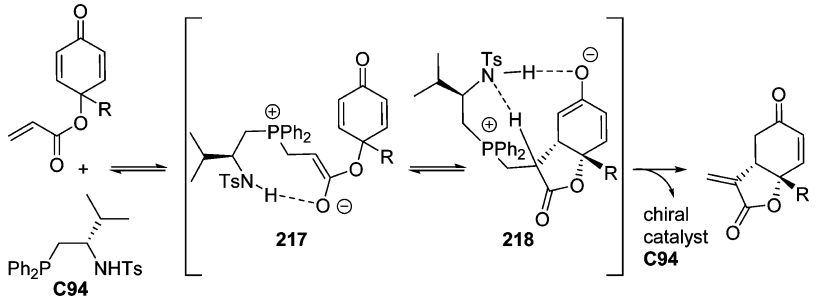
4.14. Catalytic Asymmetric Allylic Alkylation/Ring Closing Metathesis (RCM)

In 2011, Feringa and co-workers reported a catalytic enantioselective synthesis of γ-butenolides bearing γ-stereogenic centers based on a two-step method involving copper-catalyzed *hetero*-allylic asymmetric alkylation (*h*-AAA) followed by an intramolecular ruthenium-catalyzed ring closing metathesis (RCM) (Scheme 125).[366,367] The copper-catalyzed *h*-AAA reaction of cinnamyl substrate **227** with various alkyl substituted Grignard reagents affords the corresponding diolefinic esters **228** in high yields with excellent regioselectivities. The subsequent ring closing metathesis of the diolefinic esters readily proceeds to provide the γ-butenolides **229** in high yields without loss of stereochemical information. The power of this sequential strategy was further demonstrated by the concise stereoselective syntheses of (−)-whisky lactone, (−)-cognac lactone, (−)-nephrosteranic acid, and (−)-roccellaric acid.[367]

4.15. Catalytic Enantioselective Isomerization

Employing a bifunctional chiral aminothiourea catalyst **C100**, Asano and Matsubara described a novel transformation for the asymmetric synthesis of β-mercaptolactones through isomerization of ω-hydroxy-α,β-unsaturated thioesters (Scheme

Scheme 120. Proposed Mechanism for the Formation of Spirolactone Products



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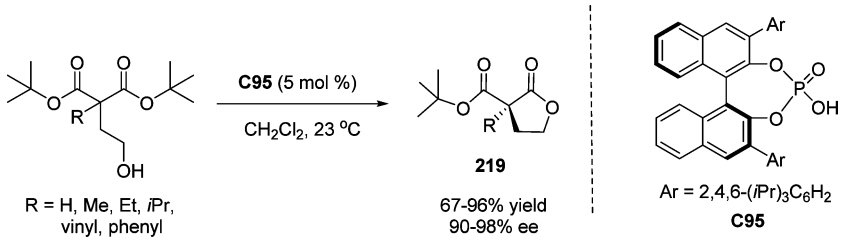
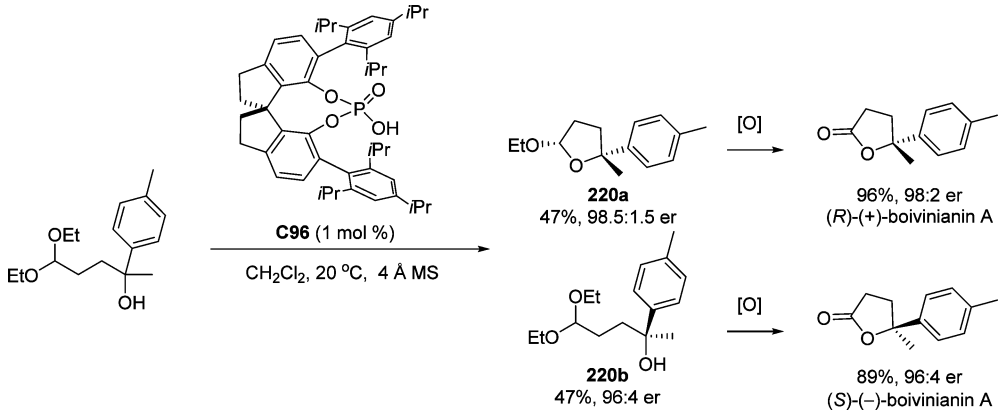
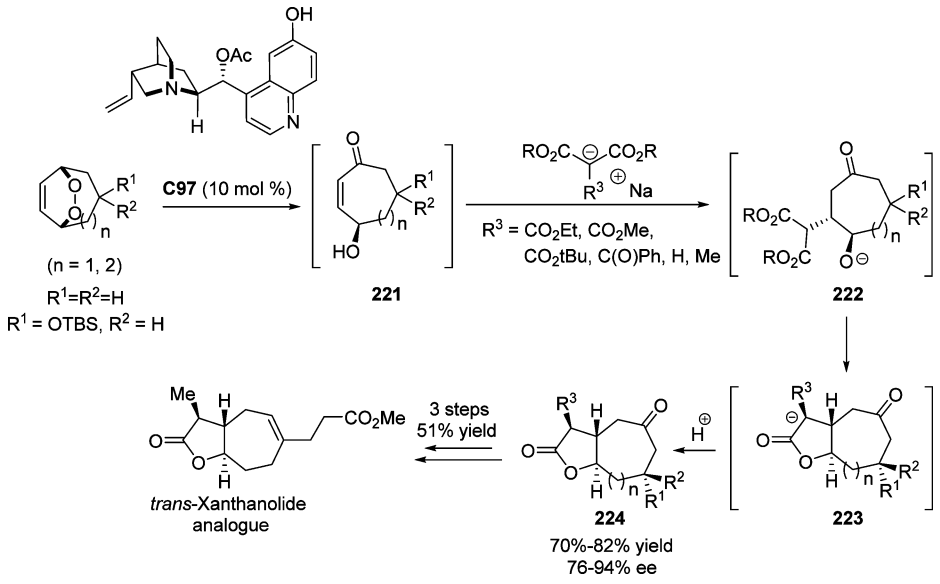
Scheme 121. Synthesis of β-Substituted γ-Butyrolactones through Asymmetric Desymmetrization of Prochiral Diesters



Scheme 122. Asymmetric Synthesis of (*R*)-(+)-Boivinianin A and (*S*)-(−)-Boivinianin A



Scheme 123. Asymmetric Synthesis of *trans*-Fused Butyrolactones 224



126).[368] The authors proposed the formation of ion pair intermediate **230** including a covalent bond between the substrate and the tertiary amine of the catalyst and noncovalent interaction between thiolate anion and thiourea group. This cationic intermediate readily undergoes the stereoselective sulfa-Michael addition, proton transfer, and subsequent cyclization to afford lactone **232** in high yield with excellent enantioselectivity.

4.16. Asymmetric Tandem Michael Addition−Transesterification

Based on the ability of 3-hydroxyoxindoles as an isatinic anion equivalent, Trost and Hirano reported a dinuclear zinc-ProPhenol complex catalyzed asymmetric Michael addition of 3-hydroxyoxindoles to unsaturated esters followed by a subsequent intramolecular transesterification, affording spirocyclic lactones **233** with excellent levels of stereocontrol (up to 99% ee, Scheme 127).[369]

4.17. Asymmetric Sequential Michael Addition and Cyclization

A highly enantioselective synthesis of spirolactones has been achieved by Marini and co-workers (Scheme 128).[370] The key to the success of synthesis is the development of a sequential organocatalyzed Michael addition and cyclization that produce the spirolactones with excellent stereoselective control in the construction of quaternary carbon center (up to 98% ee). The authors proposed the plausible hydrogen bonding interaction between enolic tautomer of cyclic β-ketoesters and vinyl

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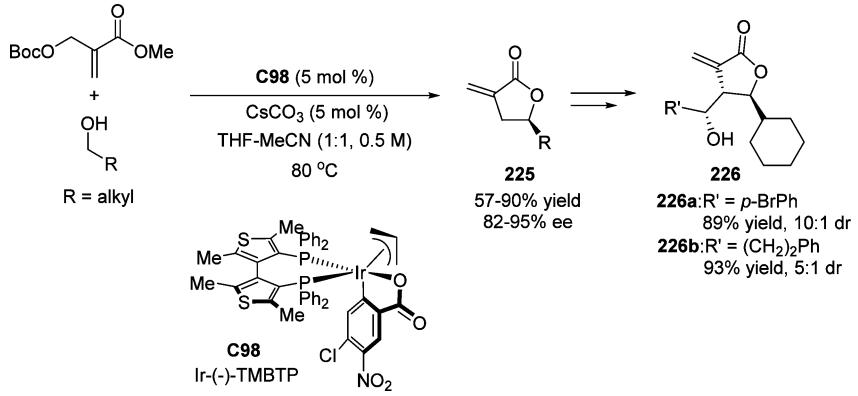
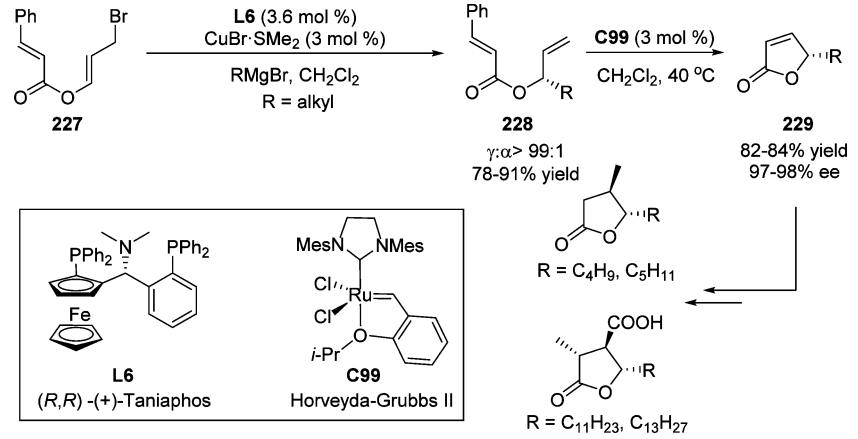
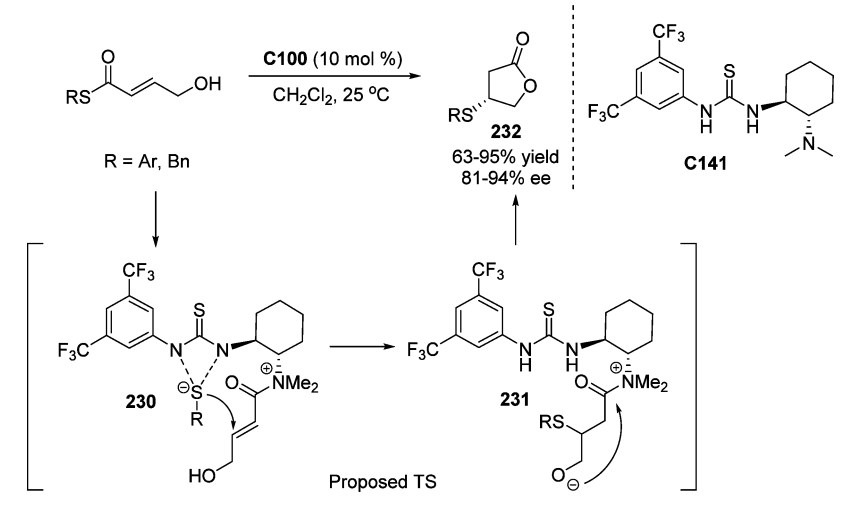
Scheme 124. Synthesis of Substituted *α-exo*-Methylene *γ*-Butyrolactones through Catalytic Enantioselective Carbonyl 2-(Alkoxycarbonyl)allylation



Scheme 125. Catalytic Enantioselective Synthesis of *γ*-Butenolides 229 through Cu-AAA/RCM



Scheme 126. Bifunctional Aminothiourea Catalyzed Asymmetric Isomerization of *ω*-Hydroxy-*α,β*-Unsaturated Thioesters



selenone, which is oriented and activated by quinine-derived catalyst **C101**, is responsible for the observed stereochemical outcome.

4.18. Domino Deracemization and Cyclopropanation

Maulide et al. found that enantioenriched butyrolactones could be obtained through a gold-catalyzed intramolecular cyclopropanation of allylic ester derived olefins with sulfonium ylides (Scheme 129).[371] A dimeric TADDOL-phosphoramidite ligand which forms a bimetallic gold catalyst, in which the two metal centers work synergistically, was essential to enhancing enantioselectivity. A synergistic effect was suggested to accelerate this asymmetric transformation. Domino allylic isomerization and cyclopropanation were both catalyzed by the gold catalyst in high cooperativity under a rare dynamic deracemization process, where both the "linear" and the "branched" allylic esters delivered identical product with the same level of stereoselectivity. The synthetic application of optical active cyclo-

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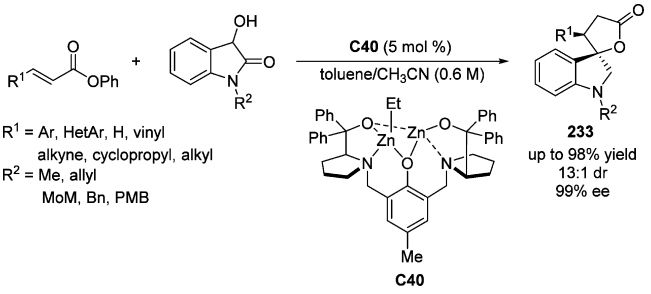
Scheme 127. Dinuclear Zinc Catalyzed Enantioselective Formation of Spirocyclic δ-Lactones



propane products **235** leads to a variety of functionalized lactams and lactones.

5. MISCELLANEOUS REACTIONS

5.1. Asymmetric Isomerization

In 2011, a highly enantioselective olefin isomerization through biomimetic proton transfer catalysis with a chiral cinchona alkaloid catalyst was developed by Deng and coauthors (Scheme 130).[372] This reaction enabled the conversion of a broad range of mono- and disubstituted β,γ-unsaturated butenolides into the corresponding chiral α,β-unsaturated butenolides **236** in high enantioselectivities (81−94% ee) and good to excellent yields (63−95%) with low catalyst loading and simple reaction conditions.

Mechanistic studies have revealed the γ-protonation step as the rate-determining step of the isomerization reaction. The author suggest that the catalytic process was realized through prototropic rearrangement involving the deprotonation of β,γ-unsaturated butenolide followed by γ-protonation (Scheme 131).[372] The regeneration of a conjugated system was believed to be the driving force of this reaction. Further computational studies by Yu and Cheng et al. revealed that the γ-protonation step is rate limiting in olefin isomerization and both the protonated quinuclidine and the 6′-OH group of the catalyst may act as the proton donor in the stereocontrolling step.[373] Multiple C−H···O hydrogen-bonding interactions were proposed to be crucial to inducing the enantioselectivity of the cinchona alkaloid derivative catalyzed asymmetric olefin isomerization. The synthetic utility of this methodology has been illustrated by Hugelshofer and Magauer for the total synthesis of leucosceptroid G, which belongs to the leucosceptroid family of natural products with potent antifeedant activities.[374]

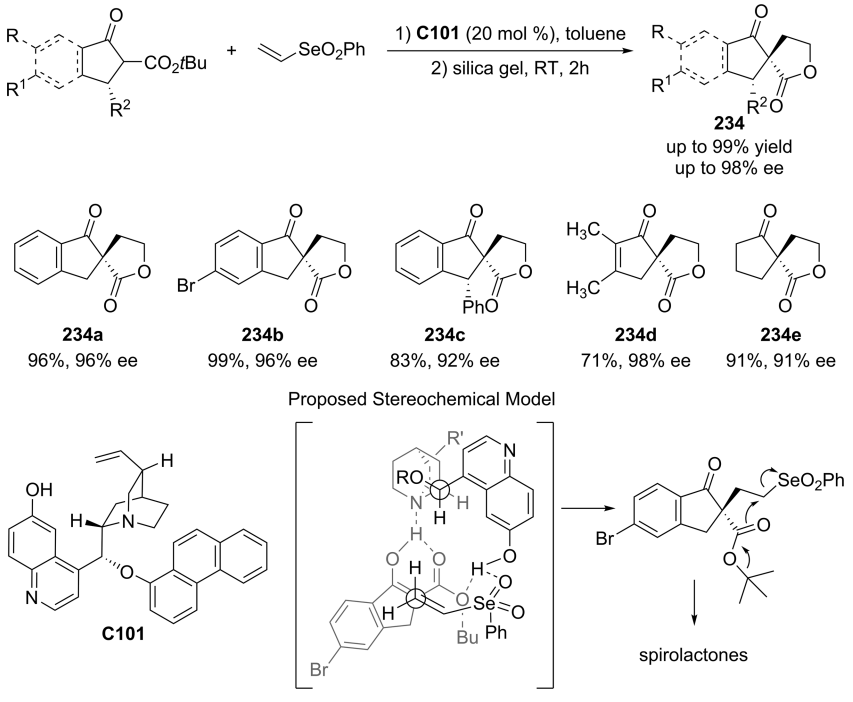
5.2. Catalytic Asymmetric Cycloaddition

In 2006, Shibata and Tsuchikama developed the Rh-catalyzed highly enantioselective cycloaddition between diynes and α-methylene-γ-butyrolactone (Scheme 132).[375] The mechanism of this reaction has been proposed as follows: an oxidative coupling gives a bicyclic metallacyclopentene, in which no asymmetric carbon atom is generated. The subsequent insertion of a 1,1-disubstituted alkene along with reductive elimination affords a chiral quaternary carbon center in the ring.[375] The reaction of nitrogen- and oxygen-tethered dialkynes with α-methylene-γ-butyrolactone gave the desired products **236b** and **236c** with excellent stereoinduction (97% ee, 97% ee). This cycloaddition of an unsymmetrical dialkyne, which possesses a methyl group and a phenyl group on the alkyne termini, provides access to a spirobutyrolactone **237d** bearing a quaternary carbon stereocenter with excellent regio- and enantioselectivities (99% ee).

5.3. Kinetic Resolution by Asymmetric Esterification of α-Hydroxy-γ-butyrolactones

An efficient kinetic resolution of racemic α-hydroxy-γ-butyrolactones involving enantioselective carbamoylation with isocyanates in the presence of chiral Cu(II) bis(oxazoline) catalysts was first studied by the group of Ohkuma.[376] More recently, Shiina and co-workers reported the kinetic resolution of racemic 2-hydroxy-γ-butyrolactones through asymmetric esterification, providing an efficient method to access various optically

Scheme 128. Highly Enantioselective Synthesis of Spirolactones through One-Pot Michael Addition and Cyclization



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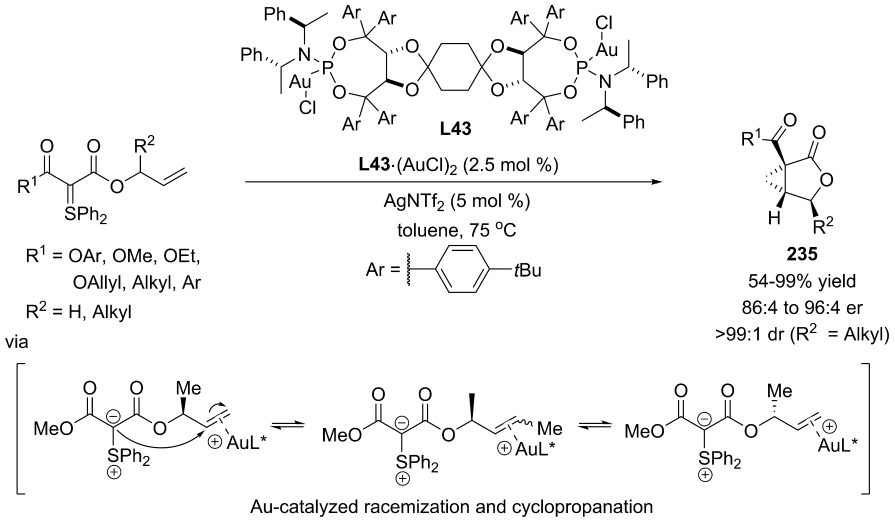
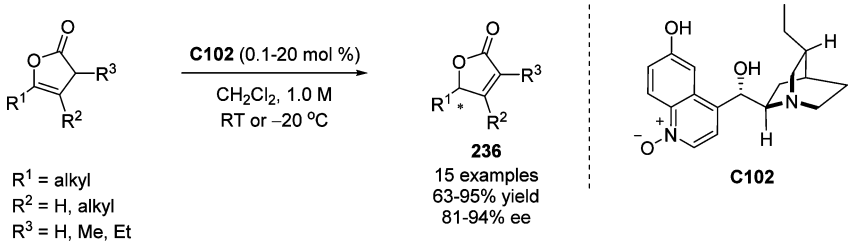
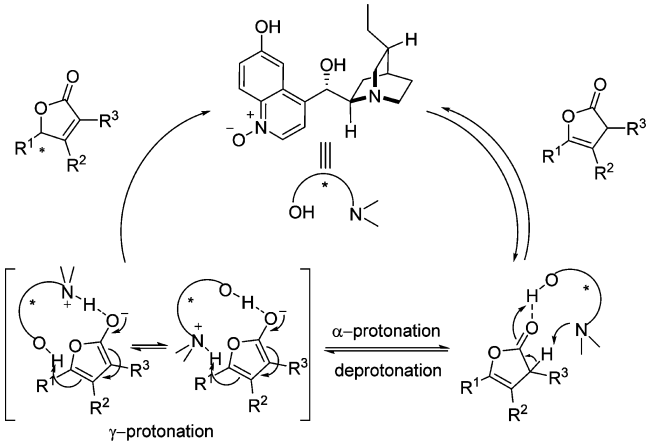
Scheme 129. Enantioselective Synthesis of Butyrolactones 235 via Gold-Catalyzed Domino Deracemization and Cyclopropanation



Scheme 130. Enantioselective Synthesis of γ-Substituted α,β-Unsaturated Butenolides via Olefin Isomerization



Scheme 131. Proposed Mechanism of Asymmetric Olefin Isomerization (Adapted from ref 372. Copyright 2011 American Chemical Society.)



enriched 2-hydroxy-γ-butyrolactone derivatives **238** and **239** (Scheme 133).[377] Promoted by pivalic anhydride and **C103** in the presence of diphenylacetic acid, this kinetic resolution smoothly proceeds to afford the corresponding esters and the recovered alcohols with excellent stereoinduction and high *S*-values up to 1000 (Scheme 133). The calculated transition state shows the complexation of the dihydroimidazolium salt with (*S*)-2-hydroxy-γ-butyrolactone and indicates an unstable structure with higher energy compared to the transition state based on (*R*)-2-hydroxy-γ-butyrolactone. This calculation was supported by the experimental result in which the (*S*)-enantiomer of substrate was consumed while the (*R*)-enantiomer was transformed into 2-acyloxylactone.

5.4. Asymmetric Cyclopropanation

Reiser and co-workers described a synthetic methodology for the synthesis of chiral β,γ-disubstituted γ-butyrolactones based on copper-catalyzed asymmetric cyclopropanation of furan-2-carboxylic esters.[378] It was reported that chiral copper(I) bisoxazoline complexes catalyze the reaction between furans and diazo esters to afford enantio- and diastereoselectively bicyclic structures **240** which arise from a regioselective cyclopropanation of the less substituted double bond. Subsequent ozonolysis and reductive workup give rise to cyclopropanes **241** which can be readily converted into chiral disubstituted γ-butyrolactones **242** by diastereoselective nucleophile addition followed by a retroaldol/lactonization cascade (Scheme 134). This methodology has been applied to the asymmetric synthesis of several natural products including paraconic acids,[378] arglabin,[379] paeonilide,[380] atreludovicinolide,[381] and xanthatin.[382]

6. SUMMARY AND OUTLOOK

In the past decades, the construction of enantioenriched γ-butenolides and γ-butyrolactones has become an important target due to the prevalence of such structural motifs in numerous bioactive natural products and drugs. The challenge of building optically active and highly substituted γ-butenolides and γ-butyrolactones bearing γ-tertiary and quaternary carbon centers has resulted in tremendous progress and extension of known reactivity and the development of novel catalysts and reactions. Moreover, extensive structural and mechanistic studies

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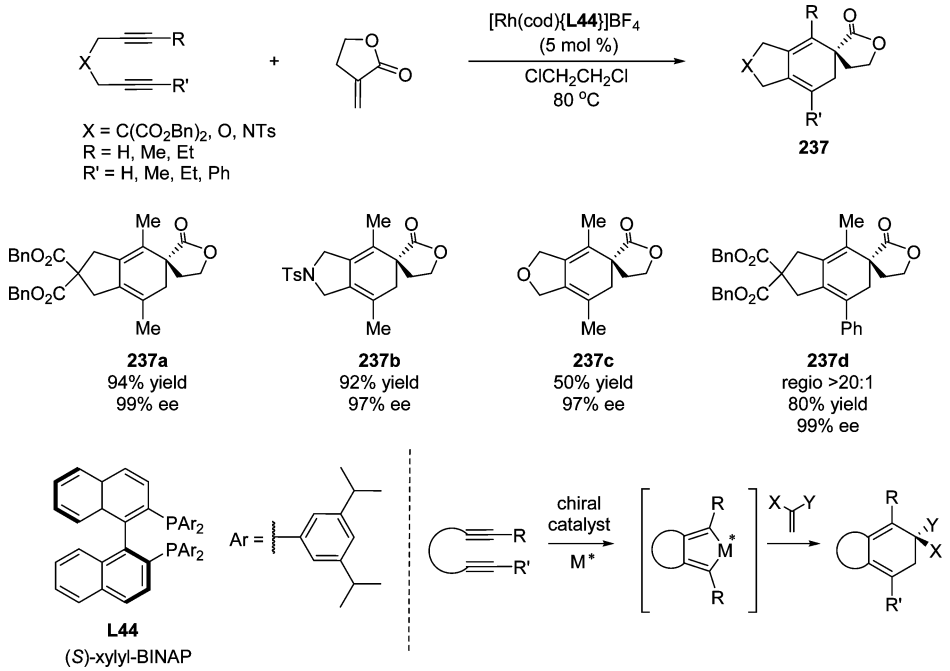
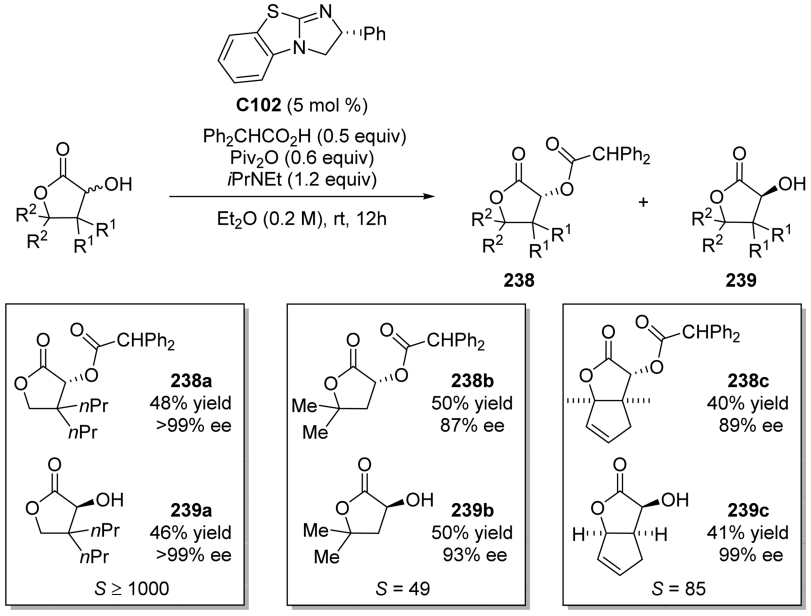
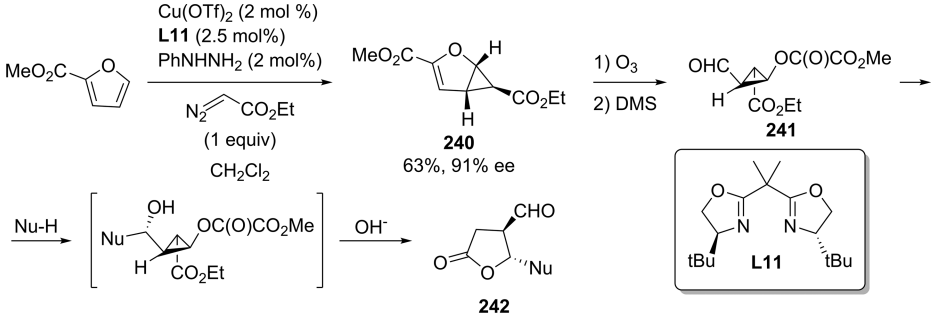
Scheme 132. Rh-Catalyzed Highly Enantioselective Cycloaddition of Diynes with α-Methylene-γ-butyrolactone



Scheme 133. Kinetic Resolution of 2-Hydroxy-γ-butyrolactones by Asymmetric Esterification



Scheme 134. Synthesis of β,γ-Disubstituted γ-Butyrolactones by Copper-Catalyzed Asymmetric Cyclopropanation



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have been devoted to elucidating the reaction mechanisms as well as the origin of stereocontrol during the asymmetric transformation.

As discussed in this review, the use of furanone derived silyl enolates as nucleophiles to access the core structure of γ-butenolides and γ-butyrolactones was investigated due to the intrinsic high reactivity of silyl enol ether and the feasibility of its preparation. In addition, furanone-derived enol ethers were applied as an atom economical source of lactone nucleophile. The use of 2(5*H*)-furanone as Michael acceptor and γ-acyloxybutenolide as allylic substrate also successfully gave rise to the corresponding optically active γ-butenolide or γ-butyrolactone. Continued exploration to assemble the major skeleton of those important structures via one-step or multistep reaction, involving enantioselective halolactonization of disubstituted olefinic acids, asymmetric aldol reaction/cyclization of aldehydes, and catalytic asymmetric hydrogenation of γ-ketoesters, etc., resulted in the discovery of interesting and useful synthetic routes toward the furanone structure.

Despite the enormous success that has been achieved in the catalytic asymmetric synthesis of γ-butenolides and γ-butyrolactones, the development in this field is still in its infancy. Considering the wide range of structural motifs of γ-butenolides and γ-substituted γ-butyrolactones which could be created by employing different methods, the limited literature related to the synthesis of α-butenolides, α- or β-substituted γ-butyrolactones, as well as ring fused or spiro γ-butyrolactones become apparent. γ-Butyrolactones bearing different substitution patterns with excellent enantioselectivity are readily available, although catalytic asymmetric methods which allow the fully diastereoselective installation of stereocenters at the γ-butyrolactone ring are still lacking. γ-Butyrolactones and γ-butenolides continue to offer a marvelous testing ground for new enantioselective catalyst methodology. We are convinced that, by taking advantage of this development, the continued investigation of the synthesis of optically active γ-butenolides and γ-butyrolactones will not only produce a large number of novel and practical reactions but will also lead to a bright future for applying such important motifs in the synthesis of natural products and pharmaceuticals.

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Notes

The authors declare no competing financial interest.

Biographies

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REFERENCES

(1) Rao, Y. S. Chemistry of Butenolides. *Chem. Rev.* **1964**, *64*, 353−388.
(2) Hoffmann, H. M. R.; Rabe, J. Synthesis and Biological Activity of α-Methylene-γ-Butyrolactones. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 94−110.
(3) Negishi, E.; Kotora, M. Regio- and Stereoselective Synthesis of γ-Alkylidenebutenolides and Related Compounds. *Tetrahedron* **1997**, *53*, 6707−6738.
(4) Alali, F. Q.; Liu, X.-X.; McLaughlin, J. L. Annonaceous Acetogenins: Recent Progress. *J. Nat. Prod.* **1999**, *62*, 504−540.
(5) Bruckner, R. The β-Elimination Route to Stereodefined γ-Alkylidenebutenolides. *Chem. Commun.* **2001**, No. 2, 141−152.
(6) Carter, N. B.; Nadany, A. E.; Sweeney, J. B. Recent Developments in the Synthesis of Furan-2(5*H*)-Ones. *J. Chem. Soc., Perkin Trans. 1* **2002**, No. 21, 2324−2342.
(7) Bandichhor, R.; Nosse, B.; Reiser, O. Paraconic Acids - The Natural Products from Lichen Symbiont. *Top. Curr. Chem.* **2005**, *243*, 43−72.
(8) Seitz, M.; Reiser, O. Synthetic Approaches towards Structurally Diverse γ-Butyrolactone Natural-Product-like Compounds. *Curr. Opin. Chem. Biol.* **2005**, *9*, 285−292.
(9) Kitson, R. R. A.; Millemaggi, A.; Taylor, R. J. K. The Renaissance of α-Methylene-γ-Butyrolactones: New Synthetic Approaches. *Angew. Chem., Int. Ed.* **2009**, *48*, 9426−9451.

DOI: 10.1021/acs.chemrev.7b00151
Chem. Rev. 2017, 117, 10502−10566

(10) Montagnon, T.; Tofi, M.; Vassilikogiannakis, G. Using Singlet Oxygen to Synthesize Polyoxygenated Natural Products from Furans. *Acc. Chem. Res.* **2008**, *41*, 1001−1011.
(11) Gil, S.; Parra, M.; Rodriguez, P.; Segura, J. Recent Developments in γ-Lactone Synthesis. *Mini-Rev. Org. Chem.* **2009**, *6*, 345−358.
(12) Kumar, A.; Singh, V.; Ghosh, S. *Butenolide: A Novel Synthesis and Biological Activities*, 1st ed.; LAP LAMBERT Academic Publishing: Saarbrücken, Germany, 2012.
(13) Jusseau, X.; Chabaud, L.; Guillou, C. Synthesis of γ-Butenolides and α,β-Unsaturated γ-Butyrolactams by Addition of Vinylogous Nucleophiles to Michael Acceptors. *Tetrahedron* **2014**, *70*, 2595−2615.
(14) Yanai, H. Chapter 10 - Green and Catalytic Methods for γ-Lactone Synthesis. *Green Synthetic Approaches for Biologically Relevant Heterocycles*; Brahmachari, G., Ed.; Elsevier: Boston, 2015; pp 257−289. DOI: 10.1016/B978-0-12-800070-0.00010-4.
(15) Ottow, E. A.; Brinker, M.; Teichmann, T.; Fritz, E.; Kaiser, W.; Brosche, M.; Kangasjarvi, J.; Jiang, X.; Polle, A. Populus Euphratica Displays Apoplastic Sodium Accumulation, Osmotic Adjustment by Decreases in Calcium and Soluble Carbohydrates, and Develops Leaf Succulence under Salt Stress. *Plant Physiol.* **2005**, *139*, 1762−1772.
(16) Kitani, S.; Miyamoto, K. T.; Takamatsu, S.; Herawati, E.; Iguchi, H.; Nishitomi, K.; Uchida, M.; Nagamitsu, T.; Omura, S.; Ikeda, H.; et al. Avenolide, a Streptomyces Hormone Controlling Antibiotic Production in Streptomyces Avermitilis. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 16410−16415.
(17) Uchida, M.; Takamatsu, S.; Arima, S.; Miyamoto, K. T.; Kitani, S.; Nihira, T.; Ikeda, H.; Nagamitsu, T. Total Synthesis and Absolute Configuration of Avenolide, Extracellular Factor in Streptomyces Avermitilis. *J. Antibiot.* **2011**, *64*, 781−787.
(18) Kumar KC, S.; Müller, K. Lichen Metabolites. 1. Inhibitory Action Against Leukotriene B4 Biosynthesis by a Non-Redox Mechanism. *J. Nat. Prod.* **1999**, *62*, 817−820.
(19) Csuk, R.; Heinold, A.; Siewert, B.; Schwarz, S.; Barthel, A.; Kluge, R.; Ströhl, D. Synthesis and Biological Evaluation of Antitumor-Active Arglabin Derivatives. *Arch. Pharm.* **2012**, *345*, 215−222.
(20) Lone, S. H.; Bhat, K. A.; Khuroo, M. A. Arglabin: From Isolation to Antitumor Evaluation. *Chem.-Biol. Interact.* **2015**, *240*, 180−198.
(21) Casiraghi, G.; Zanardi, F.; Battistini, L.; Rassu, G. Advances in Exploring Heterocyclic Dienoxysilane Nucleophiles in Asymmetric Synthesis. *Synlett* **2009**, *2009*, 1525−1542.
(22) Miao, Z.; Chen, F. Asymmetric Aldol Reactions of Heterocyclic Dienolsilanes and α,β-Unsaturated Carbonyl Derived Dienolsilanes. *Synthesis* **2012**, *44*, 2506−2514.
(23) Bisai, V. Organocatalytic Asymmetric Vinylogous Aldol Reactions. *Synthesis* **2012**, *44*, 1453−1463.
(24) Denmark, S. E.; Heemstra, J. R.; Beutner, G. L. Catalytic, Enantioselective, Vinylogous Aldol Reactions. *Angew. Chem., Int. Ed.* **2005**, *44*, 4682−4698.
(25) Pansare, S. V.; Paul, E. K. The Organocatalytic Vinylogous Aldol Reaction: Recent Advances. *Chem. - Eur. J.* **2011**, *17*, 8770−8779.
(26) Hoppe, D.; Krämer, T.; Schwark, J. R.; Zschage, O. Metallated 2-alkenyl carbamates: chiral homoenolate reagents for asymmetric synthesis. *Pure Appl. Chem.* **1990**, *62*, 1999−2006.
(27) *Catalytic Asymmetric Synthesis*, 3rd ed.; Ojima, I., Ed.; Wiley-VCH: Hoboken, NJ, 2010.
(28) Yan, L.; Wu, X.; Liu, H.; Xie, L.; Jiang, Z. Catalytic Asymmetric Synthesis of γ-Butenolides by Direct Vinylogous Reactions. *Mini-Rev. Med. Chem.* **2013**, *13*, 845−853.
(29) Machajewski, T. D.; Wong, C.-H. The Catalytic Asymmetric Aldol Reaction. *Angew. Chem., Int. Ed.* **2000**, *39*, 1352−1375.
(30) Mlynarski, J.; Paradowska, J. Catalytic Asymmetric Aldol Reactions in Aqueous Media. *Chem. Soc. Rev.* **2008**, *37*, 1502−1511.
(31) Palomo, C.; Oiarbide, M.; Garcia, J. M. Current Progress in the Asymmetric Aldol Addition Reaction. *Chem. Soc. Rev.* **2004**, *33*, 65−75.
(32) Trost, B. M.; Brindle, C. S. The Direct Catalytic Asymmetric Aldol Reaction. *Chem. Soc. Rev.* **2010**, *39*, 1600−1632.
(33) Casiraghi, G.; Zanardi, F.; Appendino, G.; Rassu, G. The Vinylogous Aldol Reaction: A Valuable, Yet Understated Carbon−Carbon Bond-Forming Maneuver. *Chem. Rev.* **2000**, *100*, 1929−1972.
(34) Hosokawa, S.; Tatsuta, K. Asymmetric Vinylogous Mukaiyama Aldol Reactions Using Vinylketene N,O-Acetals in Total Syntheses of Natural Products. *Mini-Rev. Org. Chem.* **2008**, *5*, 1−18.
(35) Casiraghi, G.; Battistini, L.; Curti, C.; Rassu, G.; Zanardi, F. The Vinylogous Aldol and Related Addition Reactions: Ten Years of Progress. *Chem. Rev.* **2011**, *111*, 3076−3154.
(36) Szlosek, M.; Franck, X.; Figadère, B.; Cavé, A. Highly Enantioselective 1,2-Addition of 2-[(Trimethylsilyl)oxy]furan to Aldehydes: Application to Muricatacin Synthesis. *J. Org. Chem.* **1998**, *63*, 5169−5172.
(37) Szlosek, M.; Figadère, B. Highly Enantioselective Aldol Reaction with 2-Trimethylsilyloxyfuran: The First Catalytic Asymmetric Autoinductive Aldol Reaction. *Angew. Chem., Int. Ed.* **2000**, *39*, 1799−1801.
(38) Figadère, B.; Szlosek, M.; Jullian, J.-C.; Hocquemiller, R. Ligand Effects on the Catalytic Asymmetric Autoinductive Aldol Reaction of 2-TMSOF (2-Trimethylsilyloxyfuran) with Aldehydes. *Heterocycles* **2000**, *52*, 1005.
(39) Franck, X.; Vaz Araujo, M. E.; Jullian, J.-C.; Hocquemiller, R.; Figadère, B. Synthesis and Structure Determination of Iso-Cladospolide B. *Tetrahedron Lett.* **2001**, *42*, 2801−2803.
(40) Evans, D. A.; Kozlowski, M. C.; Murry, J. A.; Burgey, C. S.; Campos, K. R.; Connell, B. T.; Staples, R. J. C_2-Symmetric Copper(II) Complexes as Chiral Lewis Acids. Scope and Mechanism of Catalytic Enantioselective Aldol Additions of Enolsilanes to (Benzyloxy)-acetaldehyde. *J. Am. Chem. Soc.* **1999**, *121*, 669−685.
(41) Onitsuka, S.; Matsuoka, Y.; Irie, R.; Katsuki, T. Highly Enantioselective Cr(salen)-Catalyzed Reaction of 2-(Trimethylsilyloxy)furan and Aldehydes. Effect of Alcohol on Enantioselectivity. *Chem. Lett.* **2003**, *32*, 974−975.
(42) Matsuoka, Y.; Irie, R.; Katsuki, T. Enantioselective Addition of 2-(Trimethylsilyloxy)furan to Aldehydes Using Cr(salen) as Catalyst. Effect of Water on Enantioselectivity. *Chem. Lett.* **2003**, *32*, 584−585.
(43) Palombi, L.; Acocella, M. R.; Celenta, N.; Massa, A.; Villano, R.; Scettri, A. Highly Enantioselective Vinylogous Addition of 2-Trimethylsilyloxyfuran to Aldehydes Promoted by the $SiCl_4$/chiral Lewis Base System. *Tetrahedron: Asymmetry* **2006**, *17*, 3300−3303.
(44) Curti, C.; Ranieri, B.; Battistini, L.; Rassu, G.; Zambrano, V.; Pelosi, G.; Casiraghi, G.; Zanardi, F. Catalytic, Asymmetric Vinylogous Mukaiyama Aldol Reactions of Pyrrole- and Furan-Based Dienoxy Silanes: How the Diene Heteroatom Impacts Stereocontrol. *Adv. Synth. Catal.* **2010**, *352*, 2011−2022.
(45) Nagao, H.; Yamane, Y.; Mukaiyama, T. Effective Synthesis of 5-Substituted Butenolide Derivatives by Using Cinchonidine-Derived Quaternary Ammonium Phenoxide Catalyst. *Chem. Lett.* **2007**, *36*, 8−9.
(46) Singh, R. P.; Foxman, B. M.; Deng, L. Asymmetric Vinylogous Aldol Reaction of Silyloxy Furans with a Chiral Organic Salt. *J. Am. Chem. Soc.* **2010**, *132*, 9558−9560.
(47) Zhu, N.; Ma, B.-C.; Zhang, Y.; Wang, W. Organocatalyzed Highly Enantioselective and Anti-Selective Construction of γ-Butenolides through Vinylogous Mukaiyama Aldol Reaction. *Adv. Synth. Catal.* **2010**, *352*, 1291−1295.
(48) Boeckman, R. K., Jr.; Pero, J. E.; Boehmler, D. J. Toward the Development of a General Chiral Auxiliary. Enantioselective Alkylation and a New Catalytic Asymmetric Addition of Silyloxyfurans: Application to a Total Synthesis of (−)-Rasfonin. *J. Am. Chem. Soc.* **2006**, *128*, 11032−11033.
(49) Evans, D. A.; Dunn, T. B.; Kværnø, L.; Beauchemin, A.; Raymer, B.; Olhava, E. J.; Mulder, J. A.; Juhl, M.; Kagechika, K.; Favor, D. A. Total Synthesis of (+)-Azaspiracid-1. Part II: Synthesis of the EFGHI Sulfone and Completion of the Synthesis. *Angew. Chem., Int. Ed.* **2007**, *46*, 4698−4703.
(50) Evans, D. A.; Burgey, C. S.; Kozlowski, M. C.; Tregay, S. W. C_2-Symmetric Copper(II) Complexes as Chiral Lewis Acids. Scope and Mechanism of the Catalytic Enantioselective Aldol Additions of Enolsilanes to Pyruvate Esters. *J. Am. Chem. Soc.* **1999**, *121*, 686−699.
(51) Frings, M.; Atodiresei, I.; Runsink, J.; Raabe, G.; Bolm, C. Catalyzed Vinylogous Mukaiyama Aldol Reactions with Controlled Enantio- and Diastereoselectivities. *Chem. - Eur. J.* **2009**, *15*, 1566−1569.

DOI: 10.1021/acs.chemrev.7b00151
Chem. Rev. 2017, 117, 10502−10566

(52) Frings, M.; Atodiresei, I.; Wang, Y.; Runsink, J.; Raabe, G.; Bolm, C. C1-Symmetric Aminosulfoximines in Copper-Catalyzed Asymmetric Vinylogous Mukaiyama Aldol Reactions. *Chem. - Eur. J.* **2010**, *16*, 4577−4587.
(53) Frings, M.; Thomé, I.; Schiffers, I.; Pan, F.; Bolm, C. Catalytic, Asymmetric Synthesis of Phosphonic γ-(Hydroxyalkyl)butenolides with Contiguous Quaternary and Tertiary Stereogenic Centers. *Chem. - Eur. J.* **2014**, *20*, 1691−1700.
(54) Hou, G.; Yu, J.; Yu, C.; Wu, G.; Miao, Z. Enantio- and Diastereoselective Vinylogous Mukaiyama Aldol Reactions of α-Keto Phosphonates with 2-(Trimethylsilyloxy)- Furan Catalyzed by Bis-(oxazoline)-Copper Complexes. *Adv. Synth. Catal.* **2013**, *355*, 589−593.
(55) Ube, H.; Shimada, N.; Terada, M. Asymmetric Direct Vinylogous Aldol Reaction of Furanone Derivatives Catalyzed by an Axially Chiral Guanidine Base. *Angew. Chem., Int. Ed.* **2010**, *49*, 1858−1861.
(56) Luo, J.; Wang, H.; Han, X.; Xu, L.-W.; Kwiatkowski, J.; Huang, K.-W.; Lu, Y. The Direct Asymmetric Vinylogous Aldol Reaction of Furanones with α-Ketoesters: Access to Chiral γ-Butenolides and Glycerol Derivatives. *Angew. Chem., Int. Ed.* **2011**, *50*, 1861−1864.
(57) Yang, Y.; Zheng, K.; Zhao, J.; Shi, J.; Lin, L.; Liu, X.; Feng, X. Asymmetric Direct Vinylogous Aldol Reaction of Unactivated γ-Butenolide to Aldehydes. *J. Org. Chem.* **2010**, *75*, 5382−5384.
(58) Pansare, S. V.; Paul, E. K. Organocatalytic Asymmetric Direct Vinylogous Aldol Reactions of γ-Crotonolactone with Aromatic Aldehydes. *Chem. Commun.* **2011**, *47*, 1027−1029.
(59) Pansare, S. V.; Paul, E. K. Synthesis of (+)-L-733,060, (+)-CP-99,994 and (2*S*,3*R*)-3-Hydroxypipecolic Acid: Application of an Organocatalytic Direct Vinylogous Aldol Reaction. *Org. Biomol. Chem.* **2012**, *10*, 2119−2125.
(60) Claraz, A.; Oudeyer, S.; Levacher, V. Chiral Quaternary Ammonium Aryloxide/*N*,*O*-Bis(trimethyl- Silyl)acetamide Combination as Efficient Organocatalytic System for the Direct Vinylogous Aldol Reaction of (5*H*)-Furan-2-One Derivatives. *Adv. Synth. Catal.* **2013**, *355*, 841−846.
(61) Beckendorf, S.; Asmus, S.; Mancheño, O. G. H-Donor Anion Acceptor Organocatalysis—The Ionic Electrophile Activation Approach. *ChemCatChem* **2012**, *4*, 926−936.
(62) Phipps, R. J.; Hamilton, G. L.; Toste, F. D. The Progression of Chiral Anions from Concepts to Applications in Asymmetric Catalysis. *Nat. Chem.* **2012**, *4*, 603−614.
(63) Briere, J.-F.; Oudeyer, S.; Dalla, V.; Levacher, V. Recent Advances in Cooperative Ion Pairing in Asymmetric Organocatalysis. *Chem. Soc. Rev.* **2012**, *41*, 1696−1707.
(64) Brak, K.; Jacobsen, E. N. Asymmetric Ion-Pairing Catalysis. *Angew. Chem., Int. Ed.* **2013**, *52*, 534−561.
(65) Mahlau, M.; List, B. Asymmetric Counteranion-Directed Catalysis: Concept, Definition, and Applications. *Angew. Chem., Int. Ed.* **2013**, *52*, 518−533.
(66) Woyciechowska, M.; Forcher, G.; Buda, S.; Mlynarski, J. General switch in regioselectivity in the Mukaiyama aldol reaction of silyloxyfuran with aldehydes in aqueous solvents. *Chem. Commun.* **2012**, *48*, 11029−11031.
(67) Evans, D. A.; Murry, J. A.; Kozlowski, M. C. F_2-Symmetric Copper(II) Complexes as Chiral Lewis Acids. Catalytic Enantioselective Aldol Additions of Silylketene Acetals to (Benzyloxy)acetaldehyde. *J. Am. Chem. Soc.* **1996**, *118*, 5814−5815.
(68) Black, D. M.; Davis, R.; Doan, B. D.; Lovelace, T. C.; Millar, A.; Toczko, J. F.; Xie, S. Highly Diastereo- and Enantioselective Catalytic Synthesis of the Bis-Tetrahydrofuran Alcohol of Brecanavir and Darunavir. *Tetrahedron: Asymmetry* **2008**, *19*, 2015−2019.
(69) Takechi, S.; Yasuda, S.; Kumagai, N.; Shibasaki, M. A Direct Catalytic Asymmetric Aldol Reaction of α-Sulfanyl Lactones: Efficient Synthesis of SPT Inhibitors. *Angew. Chem., Int. Ed.* **2012**, *51*, 4218−4222.
(70) Martin, S. F.; Lopez, O. D. Vinylogous Mannich Reactions. Catalytic, Asymmetric Additions of Triisopropylsilyloxyfurans to Aldimines. *Tetrahedron Lett.* **1999**, *40*, 8949−8953.
(71) Carswell, E. L.; Snapper, M. L.; Hoveyda, A. H. A Highly Efficient and Practical Method for Catalytic Asymmetric Vinylogous Mannich (AVM) Reactions. *Angew. Chem., Int. Ed.* **2006**, *45*, 7230−7233.
(72) Mandai, H.; Mandai, K.; Snapper, M. L.; Hoveyda, A. H. Three-Component Ag-Catalyzed Enantioselective Vinylogous Mannich and Aza-Diels−Alder Reactions with Alkyl-Substituted Aldehydes. *J. Am. Chem. Soc.* **2008**, *130*, 17961−17969.
(73) Wieland, L. C.; Vieira, E. M.; Snapper, M. L.; Hoveyda, A. H. Ag-Catalyzed Diastereo- and Enantioselective Vinylogous Mannich Reactions of α-Ketoimine Esters. Development of a Method and Investigation of Its Mechanism. *J. Am. Chem. Soc.* **2009**, *131*, 570−576.
(74) Deng, H.-P.; Wei, Y.; Shi, M. Axially Chiral Phosphine-Oxazoline Ligands in Silver(I)- Catalyzed Asymmetric Mannich Reaction of Aldimines with Trimethylsiloxyfuran. *Adv. Synth. Catal.* **2009**, *351*, 2897−2902.
(75) Zhao, Q.-Y.; Yuan, Z.-L.; Shi, M. Axially Chiral Phosphine−Oxazoline Ligands in the Silver(I)-Catalyzed Asymmetric Mannich Reaction of Fluorinated Aldimines with Trimethylsiloxyfuran. *Tetrahedron: Asymmetry* **2010**, *21*, 943−951.
(76) Zhao, Q.-Y.; Yuan, Z.-L.; Shi, M. Highly Diastereo- and Enantioselective Vinylogous Mannich Reactions of Fluorinated Aldimines with Siloxyfurans. *Adv. Synth. Catal.* **2011**, *353*, 637−643.
(77) Yuan, Z.-L.; Jiang, J.-J.; Shi, M. The Application of Chiral Phosphine-Schiff Base Type Ligands in Silver(I)-Catalyzed Asymmetric Vinylogous Mannich Reaction of Aldimines with Trimethylsiloxyfuran. *Tetrahedron* **2009**, *65*, 6001−6007.
(78) Zheng, L.-S.; Li, L.; Yang, K.-F.; Zheng, Z.-J.; Xiao, X.-Q.; Xu, L.-W. New Silver(I)−monophosphine Complex Derived from Chiral Ar-BINMOL: Synthesis and Catalytic Activity in Asymmetric Vinylogous Mannich Reaction. *Tetrahedron* **2013**, *69*, 8777−8784.
(79) Salvador González, A.; Gómez Arrayás, R.; Rodríguez Rivero, M.; Carretero, J. C. Catalytic Asymmetric Vinylogous Mannich Reaction of *N*-(2-Thienyl)sulfonylimines. *Org. Lett.* **2008**, *10*, 4335−4337.
(80) Hayashi, M.; Sano, M.; Funahashi, Y.; Nakamura, S. Cinchona Alkaloid Amide/Copper(II) Catalyzed Diastereo- and Enantioselective Vinylogous Mannich Reaction of Ketimines with Siloxyfurans. *Angew. Chem., Int. Ed.* **2013**, *52*, 5557−5560.
(81) Akiyama, T.; Honma, Y.; Itoh, J.; Fuchibe, K. Vinylogous Mannich-Type Reaction Catalyzed by an Iodine-Substituted Chiral Phosphoric Acid. *Adv. Synth. Catal.* **2008**, *350*, 399−402.
(82) Yamanaka, M.; Itoh, J.; Fuchibe, K.; Akiyama, T. Chiral Brønsted Acid Catalyzed Enantioselective Mannich-Type Reaction. *J. Am. Chem. Soc.* **2007**, *129*, 6756−6764.
(83) Yamaguchi, A.; Matsunaga, S.; Shibasaki, M. Direct Catalytic Asymmetric Mannich-Type Reactions of γ-Butenolides: Effectiveness of Brønsted Acid in Chiral Metal Catalysis. *Org. Lett.* **2008**, *10*, 2319−2322.
(84) Yin, L.; Takada, H.; Kumagai, N.; Shibasaki, M. Direct Catalytic Asymmetric Vinylogous Mannich-Type Reaction of γ-Butenolides with Ketimines. *Angew. Chem., Int. Ed.* **2013**, *52*, 7310−7313.
(85) Zhou, L.; Lin, L.; Ji, J.; Xie, M.; Liu, X.; Feng, X. Catalytic Asymmetric Vinylogous Mannich-Type (AVM) Reaction of Non-activated α-Angelica Lactone. *Org. Lett.* **2011**, *13*, 3056−3059.
(86) Guo, Y.-L.; Bai, J.-F.; Peng, L.; Wang, L.-L.; Jia, L.-N.; Luo, X.-Y.; Tian, F.; Xu, X.-Y.; Wang, L.-X. Direct Asymmetric Vinylogous Mannich Reaction of 3,4-Dihalofuran-2(5*H*)-One with Aldimine Catalyzed by Quinine. *J. Org. Chem.* **2012**, *77*, 8338−8343.
(87) Saaby, S.; Nakama, K.; Lie, M. A.; Hazell, R. G.; Jørgensen, K. A. The First Catalytic Highly Enantioselective Alkylation of Ketimines—A Novel Approach to Optically Active Quaternary α-Amino Acids. *Chem. - Eur. J.* **2003**, *9*, 6145−6154.
(88) Ting, A.; Lou, S.; Schaus, S. E. Highly Diastereoselective Asymmetric Mannich Reactions of 1,3-Dicarbonyls with Acyl Imines. *Org. Lett.* **2006**, *8*, 2003−2006.
(89) Jiang, X.; Fu, D.; Zhang, G.; Cao, Y.; Liu, L.; Song, J.; Wang, R. Highly Diastereo- and Enantioselective Mannich Reaction of Lactones with *N*-Boc-Aldimines Catalyzed by Bifunctional Rosin-Derived Amine Thiourea Catalysts. *Chem. Commun.* **2010**, *46*, 4294−4296.
(90) Tomioka, K.; Yamamoto, Y.; Yamada, K. 4.7 C−C Bond Formation (Transition Metal-Catalyzed Michael). *Comprehensive*

DOI: 10.1021/acs.chemrev.7b00151
Chem. Rev. 2017, 117, 10502−10566

Chirality; Elsevier: Amsterdam, 2012; pp 122−131. DOI: 10.1016/B978-0-08-095167-6.00406-7.
(91) Krause, N.; Hoffmann-Röder, A. Recent Advances in Catalytic Enantioselective Michael Additions. *Synthesis* **2001**, *2001*, 0171−0196.
(92) Almaşi, D.; Alonso, D. A.; Nájera, C. Organocatalytic Asymmetric Conjugate Additions. *Tetrahedron: Asymmetry* **2007**, *18*, 299−365.
(93) Tsogoeva, S. B. Recent Advances in Asymmetric Organocatalytic 1,4-Conjugate Additions. *Eur. J. Org. Chem.* **2007**, *2007*, 1701−1716.
(94) Zhang, Y.; Wang, W. Recent Advances in Organocatalytic Asymmetric Michael Reactions. *Catal. Sci. Technol.* **2012**, *2*, 42−53.
(95) Schneider, C.; Abels, F. Catalytic, Enantioselective Vinylogous Michael Reactions. *Org. Biomol. Chem.* **2014**, *12*, 3531−3543.
(96) Kitajima, H.; Katsuki, T. Chiral Lewis Acid Promoted Asymmetric Michael Addition Reaction of 2-(Trimethylsilyloxy)furans. *Synlett* **1997**, *1997*, 568−570.
(97) Kitajima, H.; Ito, K.; Katsuki, T. A New Methodology for the Stereoselective Synthesis of 4-Substituted Butenolides: Asymmetric Michael Addition Reaction of 2-(Trimethylsilyloxy)furans to Oxazolidinone Enoates. *Tetrahedron* **1997**, *53*, 17015−17028.
(98) Nishikori, H.; Ito, K.; Katsuki, T. A Short-Step Synthesis of Trans-Whisky Lactone by an Asymmetric Michael Reaction. *Tetrahedron: Asymmetry* **1998**, *9*, 1165−1170.
(99) Suga, H.; Kitamura, T.; Kakehi, A.; Baba, T. Asymmetric Michael Addition Reactions of 2-Silyloxyfurans Catalyzed by Binaphthyldiimine-Ni(II) Complexes. *Chem. Commun.* **2004**, No. 12, 1414−1415.
(100) Desimoni, G.; Faita, G.; Filippone, S.; Mella, M.; Zampori, M. G.; Zema, M. A New and Highly Efficient Catalyst for the Enantioselective Mukaiyama−Michael Reaction between (*E*)-3-Crotonoyl-1,3-Oxazolidin-2-One and 2-Trimethylsilyloxyfuran. *Tetrahedron* **2001**, *57*, 10203−10212.
(101) Yang, H.; Kim, S. Catalytic Enantioselective Mukaiyama-Michael Reaction of 2-(Trimethylsilyloxy)furan with α′-Phenylsulfonyl Enones. *Synlett* **2008**, *2008*, 555−560.
(102) Zhang, Q.; Xiao, X.; Lin, L.; Liu, X.; Feng, X. Highly Enantioselective Synthesis of γ-Substituted Butenolidesvia the Vinylogous Mukaiyama-Michael Reaction Catalyzed by a Chiral Scandium(III)-*N*,*N*′-Dioxide Complex. *Org. Biomol. Chem.* **2011**, *9*, 5748−5754.
(103) Livieri, A.; Boiocchi, M.; Desimoni, G.; Faita, G. Enantioselective Addition of Cyclic Enol Silyl Ethers to 2-Alkenoyl-Pyridine-*N*-Oxides Catalysed by CuII−Bis(oxazoline) Complexes. *Chem. - Eur. J.* **2012**, *18*, 11662−11668.
(104) Barroso, S.; Blay, G.; Muñoz, M. C.; Pedro, J. R. Highly Enantioselective Nitrone Cycloadditions with 2-Alkenoyl Pyridine *N*-Oxides Catalyzed by Cu(II)−BOX Complexes. *Org. Lett.* **2011**, *13*, 402−405.
(105) Ishihara, K.; Fushimi, M. Design of a Small-Molecule Catalyst Using Intramolecular Cation−π Interactions for Enantioselective Diels−Alder and Mukaiyama−Michael Reactions: $_{L}$-DOPA-Derived Monopeptide·Cu(II) Complex. *Org. Lett.* **2006**, *8*, 1921−1924.
(106) Steinkamp, A.-D.; Frings, M.; Thomé, I.; Schiffers, I.; Bolm, C. Asymmetric Copper-Catalyzed Vinylogous Mukaiyama Michael Addition of Cyclic Dienol Silanes to Unsaturated α-Keto Phosphonates. *Chem. - Eur. J.* **2015**, *21*, 7705−7708.
(107) Jusseau, X.; Retailleau, P.; Chabaud, L.; Guillou, C. Catalytic Enantioselective Vinylogous Mukaiyama−Michael Addition of 2-Silyloxyfurans to Cyclic Unsaturated Oxo Esters. *J. Org. Chem.* **2013**, *78*, 2289−2300.
(108) Li, J.; Huang, R.; Xing, Y.-K.; Qiu, G.; Tao, H.-Y.; Wang, C.-J. Catalytic Asymmetric Cascade Vinylogous Mukaiyama 1,6-Michael/Michael Addition of 2-Silyloxyfurans with Azoalkenes: Direct Approach to Fused Butyrolactones. *J. Am. Chem. Soc.* **2015**, *137*, 10124−10127.
(109) Brown, S. P.; Goodwin, N. C.; MacMillan, D. W. C. The First Enantioselective Organocatalytic Mukaiyama−Michael Reaction: A Direct Method for the Synthesis of Enantioenriched γ-Butenolide Architecture. *J. Am. Chem. Soc.* **2003**, *125*, 1192−1194.
(110) Robichaud, J.; Tremblay, F. Formal Enantioselective Synthesis of (+)-Compactin. *Org. Lett.* **2006**, *8*, 597−600.
(111) Pansare, S. V.; Adsool, S. V.; Dyapa, R. Enantioselective Synthesis of (*S*)-Homocitric Acid Lactone and (*R*)-per-Homocitric Acid Lactone Involving Organocatalysis. *Tetrahedron: Asymmetry* **2010**, *21*, 771−773.
(112) Wang, Y.; Li, Z.; Lv, L.; Xie, Z. Synthetic Study of Rubriflordilactone B: Highly Stereoselective Construction of the C-5-*Epi* ABCDE Ring System. *Org. Lett.* **2016**, *18*, 792−795.
(113) Kemppainen, E. K.; Sahoo, G.; Valkonen, A.; Pihko, P. M. Mukaiyama−Michael Reactions with Acrolein and Methacrolein: A Catalytic Enantioselective Synthesis of the C17−C28 Fragment of Pectenotoxins. *Org. Lett.* **2012**, *14*, 1086−1089.
(114) Huang, Y.; Walji, A. M.; Larsen, C. H.; MacMillan, D. W. C. Enantioselective Organo-Cascade Catalysis. *J. Am. Chem. Soc.* **2005**, *127*, 15051−15053.
(115) Simmons, B.; Walji, A. M.; MacMillan, D. W. C. Cycle-Specific Organocascade Catalysis: Application to Olefin Hydroamination, Hydro-Oxidation, and Amino-Oxidation, and to Natural Product Synthesis. *Angew. Chem., Int. Ed.* **2009**, *48*, 4349−4353.
(116) Wang, J.; Qi, C.; Ge, Z.; Cheng, T.; Li, R. Efficient Direct Asymmetric Vinylogous Michael Addition Reactions of γ-Butenolides to Chalcones Catalyzed by Vicinal Primary-Diamine Salts. *Chem. Commun.* **2010**, *46*, 2124−2126.
(117) Zhang, Y.; Yu, C.; Ji, Y.; Wang, W. Diastereo- and Enantioselective Organocatalytic Direct Conjugate Addition of γ-Butenolide to Chalcones. *Chem. - Asian J.* **2010**, *5*, 1303−1306.
(118) Zhu, J.-L.; Zhang, Y.; Liu, C.; Zheng, A.-M.; Wang, W. Insights into the Dual Activation Mechanism Involving Bifunctional Cinchona Alkaloid Thiourea Organocatalysts: an NMR and DFT Study. *J. Org. Chem.* **2012**, *77*, 9813−9825.
(119) Luo, X.; Zhou, Z.; Yu, F.; Li, X.; Liang, X.; Ye, J. Asymmetric Vinylogous Michael Reaction of α,β-Unsaturated Aldehyde with Buteno-4-Lactone. *Chem. Lett.* **2011**, *40*, 518−520.
(120) Zhang, W.; Tan, D.; Lee, R.; Tong, G.; Chen, W.; Qi, B.; Huang, K.-W.; Tan, C.-H.; Jiang, Z. Highly Enantio- and Diastereoselective Reactions of γ-Substituted Butenolides Through Direct Vinylogous Conjugate Additions. *Angew. Chem., Int. Ed.* **2012**, *51*, 10069−10073.
(121) Das, U.; Chen, Y.-R.; Tsai, Y.-L.; Lin, W. Organocatalytic Enantioselective Direct Vinylogous Michael Addition of γ-Substituted Butenolides to 3-Aroyl Acrylates and 1,2-Diaroylethylenes. *Chem. - Eur. J.* **2013**, *19*, 7713−7717.
(122) Yang, D.; Wang, L.; Zhao, D.; Han, F.; Zhang, B.; Wang, R. Development of Metal/Organo Catalytic Systems for Direct Vinylogous Michael Reactions to Build Chiral γ,γ-Disubstituted Butenolides. *Chem. - Eur. J.* **2013**, *19*, 4691−4694.
(123) Li, X.; Lu, M.; Dong, Y.; Wu, W.; Qian, Q.; Ye, J.; Dixon, D. J. Diastereodivergent Organocatalytic Asymmetric Vinylogous Michael Reactions. *Nat. Commun.* **2014**, *5*, 4479.
(124) Yin, L.; Takada, H.; Lin, S.; Kumagai, N.; Shibasaki, M. Direct Catalytic Asymmetric Vinylogous Conjugate Addition of Unsaturated Butyrolactones to α,β-Unsaturated Thioamides. *Angew. Chem., Int. Ed.* **2014**, *53*, 5327−5331.
(125) Manna, M. S.; Mukherjee, S. Catalytic Asymmetric Direct Vinylogous Michael Addition of Deconjugated Butenolides to Maleimides for the Construction of Quaternary Stereogenic Centers. *Chem. - Eur. J.* **2012**, *18*, 15277−15282.
(126) Guo, Y.-L.; Jia, L.-N.; Peng, L.; Qi, L.-W.; Zhou, J.; Tian, F.; Xu, X.-Y.; Wang, L.-X. Highly Enantioselective Direct Vinylogous Michael Addition of γ-Substituted Deconjugated Butenolides to Maleimides Catalyzed by Chiral Squaramides. *RSC Adv.* **2013**, *3*, 16973−16976.
(127) Manna, M. S.; Mukherjee, S. Remarkable Influence of Secondary Catalyst Site on Enantioselective Desymmetrization of Cyclopentenedione. *Chem. Sci.* **2014**, *5*, 1627−1633.
(128) Kumar, V.; Mukherjee, S. Synergistic Lewis Base and Anion-Binding Catalysis for the Enantioselective Vinylogous Addition of Deconjugated Butenolides to Allenoates. *Chem. Commun.* **2013**, *49*, 11203−11205.
(129) Quintard, A.; Lefranc, A.; Alexakis, A. Highly Enantioselective Direct Vinylogous Michael Addition of γ-Butenolide to Enals. *Org. Lett.* **2011**, *13*, 1540−1543.

DOI: 10.1021/acs.chemrev.7b00151
Chem. Rev. 2017, 117, 10502−10566

(130) Quintard, A.; Alexakis, A. Highly Enantioselective Organocascade Intermolecular Iminium/enamine Michael Addition on Enals. *Chem. Commun.* **2011**, *47*, 7212−7214.
(131) Trost, B. M.; Hitce, J. Direct Asymmetric Michael Addition to Nitroalkenes: Vinylogous Nucleophilicity under Dinuclear Zinc Catalysis. *J. Am. Chem. Soc.* **2009**, *131*, 4572−4573.
(132) Terada, M.; Ando, K. Enantioselective Direct Vinylogous Michael Addition of Functionalized Furanones to Nitroalkenes Catalyzed by an Axially Chiral Guanidine Base. *Org. Lett.* **2011**, *13*, 2026−2029.
(133) Manna, M. S.; Kumar, V.; Mukherjee, S. Catalytic Enantioselective Construction of Quaternary Stereocenters by Direct Vinylogous Michael Addition of Deconjugated Butenolides to Nitroolefins. *Chem. Commun.* **2012**, *48*, 5193−5195.
(134) Langer, P. New Strategies for the Development of an Asymmetric Version of the Baylis−Hillman Reaction. *Angew. Chem., Int. Ed.* **2000**, *39*, 3049−3052.
(135) Basavaiah, D.; Rao, A. J.; Satyanarayana, T. Recent Advances in the Baylis−Hillman Reaction and Applications. *Chem. Rev.* **2003**, *103*, 811−892.
(136) Masson, G.; Housseman, C.; Zhu, J. The Enantioselective Morita−Baylis−Hillman Reaction and Its Aza Counterpart. *Angew. Chem., Int. Ed.* **2007**, *46*, 4614−4628.
(137) Basavaiah, D.; Reddy, B. S.; Badsara, S. S. Recent Contributions from the Baylis−Hillman Reaction to Organic Chemistry. *Chem. Rev.* **2010**, *110*, 5447−5674.
(138) Wei, Y.; Shi, M. Multifunctional Chiral Phosphine Organocatalysts in Catalytic Asymmetric Morita−Baylis−Hillman and Related Reactions. *Acc. Chem. Res.* **2010**, *43*, 1005−1018.
(139) Liu, T.-Y.; Xie, M.; Chen, Y.-C. Organocatalytic Asymmetric Transformations of Modified Morita-Baylis-Hillman Adducts. *Chem. Soc. Rev.* **2012**, *41*, 4101−4112.
(140) Rios, R. Organocatalytic Enantioselective Methodologies Using Morita-Baylis-Hillman Carbonates and Acetates. *Catal. Sci. Technol.* **2012**, *2*, 267−278.
(141) Cho, C.-W.; Krische, M. J. Regio- and Stereoselective Construction of γ-Butenolides through Phosphine-Catalyzed Substitution of Morita−Baylis−Hillman Acetates: An Organocatalytic Allylic Alkylation. *Angew. Chem., Int. Ed.* **2004**, *43*, 6689−6691.
(142) Jiang, Y.-Q.; Shi, Y.-L.; Shi, M. Chiral Phosphine-Catalyzed Enantioselective Construction of γ-Butenolides Through Substitution of Morita−Baylis−Hillman Acetates with 2-Trimethylsilyloxy Furan. *J. Am. Chem. Soc.* **2008**, *130*, 7202−7203.
(143) Wei, Y.; Ma, G.-N.; Shi, M. Diastereo- and Enantioselective Construction of γ-Butenolides through Chiral Phosphane-Catalyzed Allylic Alkylation of Morita−Baylis−Hillman Acetates. *Eur. J. Org. Chem.* **2011**, *2011*, 5146−5155.
(144) Cui, H.-L.; Huang, J.-R.; Lei, J.; Wang, Z.-F.; Chen, S.; Wu, L.; Chen, Y.-C. Direct Asymmetric Allylic Alkylation of Butenolides with Morita−Baylis−Hillman Carbonates. *Org. Lett.* **2010**, *12*, 720−723.
(145) Huang, X.; Peng, J.; Dong, L.; Chen, Y.-C. Asymmetric Assembly of 2-Oxindole and α-Angelica Lactone Units to Construct Vicinal Quaternary Chiral Centers. *Chem. Commun.* **2012**, *48*, 2439−2441.
(146) Teng, H.-L.; Huang, H.; Wang, C.-J. Catalytic Asymmetric Construction of Spiro(γ-Butyrolactam-γ-Butyrolactone) Moieties through Sequential Reactions of Cyclic Imino Esters with Morita−Baylis−Hillman Bromides. *Chem. - Eur. J.* **2012**, *18*, 12614−12618.
(147) Fu, G. C. Enantioselective Nucleophilic Catalysis with "Planar-Chiral" Heterocycles. *Acc. Chem. Res.* **2000**, *33*, 412−420.
(148) France, S.; Guerin, D. J.; Miller, S. J.; Lectka, T. Nucleophilic Chiral Amines as Catalysts in Asymmetric Synthesis. *Chem. Rev.* **2003**, *103*, 2985−3012.
(149) Fu, G. C. Asymmetric Catalysis with "Planar-Chiral" Derivatives of 4-(Dimethylamino)pyridine. *Acc. Chem. Res.* **2004**, *37*, 542−547.
(150) Wurz, R. P. Chiral Dialkylaminopyridine Catalysts in Asymmetric Synthesis. *Chem. Rev.* **2007**, *107*, 5570−5595.
(151) Mermerian, A. H.; Fu, G. C. Catalytic Enantioselective Synthesis of Quaternary Stereocenters via Intermolecular C-Acylation of Silyl Ketene Acetals: Dual Activation of the Electrophile and the Nucleophile. *J. Am. Chem. Soc.* **2003**, *125*, 4050−4051.
(152) Mermerian, A. H.; Fu, G. C. Catalytic Enantioselective Construction of All-Carbon Quaternary Stereocenters: Synthetic and Mechanistic Studies of the *C*-Acylation of Silyl Ketene Acetals. *J. Am. Chem. Soc.* **2005**, *127*, 5604−5607.
(153) Birrell, J. A.; Desrosiers, J.-N.; Jacobsen, E. N. Enantioselective Acylation of Silyl Ketene Acetals through Fluoride Anion-Binding Catalysis. *J. Am. Chem. Soc.* **2011**, *133*, 13872−13875.
(154) Shaw, S. A.; Aleman, P.; Vedejs, E. Development of Chiral Nucleophilic Pyridine Catalysts: Applications in Asymmetric Quaternary Carbon Synthesis. *J. Am. Chem. Soc.* **2003**, *125*, 13368−13369.
(155) Shaw, S. A.; Aleman, P.; Christy, J.; Kampf, J. W.; Va, P.; Vedejs, E. Enantioselective TADMAP-Catalyzed Carboxyl Migration Reactions for the Synthesis of Stereogenic Quaternary Carbon. *J. Am. Chem. Soc.* **2006**, *128*, 925−934.
(156) Woods, P. A.; Morrill, L. C.; Lebl, T.; Slawin, A. M. Z.; Bragg, R. A.; Smith, A. D. Isothiourea-Mediated Stereoselective *C*-Acylation of Silyl Ketene Acetals. *Org. Lett.* **2010**, *12*, 2660−2663.
(157) Joannesse, C.; Morrill, L. C.; Campbell, C. D.; Slawin, A. M. Z.; Smith, A. D. Isothiourea-Catalyzed Asymmetric *O*- to *C*-Carboxyl Transfer of Furanyl Carbonates. *Synthesis* **2011**, *2011*, 1865−1879.
(158) Trost, B. M.; Van Vranken, D. L. Asymmetric Transition Metal-Catalyzed Allylic Alkylations. *Chem. Rev.* **1996**, *96*, 395−422.
(159) Helmchen, G.; Pfaltz, A. PhosphinooxazolinesA New Class of Versatile, Modular *P,N*-Ligands for Asymmetric Catalysis. *Acc. Chem. Res.* **2000**, *33*, 336−345.
(160) Trost, B. M.; Crawley, M. L. Asymmetric Transition-Metal-Catalyzed Allylic Alkylations: Applications in Total Synthesis. *Chem. Rev.* **2003**, *103*, 2921−2944.
(161) Trost, B. M. Asymmetric Allylic Alkylation, an Enabling Methodology. *J. Org. Chem.* **2004**, *69*, 5813−5837.
(162) Pfaltz, A.; Drury, W. J. Design of Chiral Ligands for Asymmetric Catalysis: From C_2-Symmetric *P,P*- and *N,N*-Ligands to Sterically and Electronically Nonsymmetrical *P,N*-Ligands. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 5723−5726.
(163) Trost, B. M.; Machacek, M. R.; Aponick, A. Predicting the Stereochemistry of Diphenylphosphino Benzoic Acid (DPPBA)-Based Palladium-Catalyzed Asymmetric Allylic Alkylation Reactions: A Working Model. *Acc. Chem. Res.* **2006**, *39*, 747−760.
(164) Lu, Z.; Ma, S. Metal-Catalyzed Enantioselective Allylation in Asymmetric Synthesis. *Angew. Chem., Int. Ed.* **2008**, *47*, 258−297.
(165) Braun, M.; Meier, T. Tsuji−Trost Allylic Alkylation with Ketone Enolates. *Angew. Chem., Int. Ed.* **2006**, *45*, 6952−6955.
(166) Braun, M.; Meier, T. New Developments in Stereoselective Palladium-Catalyzed Allylic Alkylations of Preformed Enolates. *Synlett* **2006**, *2006*, 0661−0676.
(167) Mao, B.; Ji, Y.; Fañanás-Mastral, M.; Caroli, G.; Meetsma, A.; Feringa, B. L. Highly Enantioselective Synthesis of 3-Substituted Furanones by Palladium-Catalyzed Kinetic Resolution of Unsymmetrical Allyl Acetates. *Angew. Chem., Int. Ed.* **2012**, *51*, 3168−3173.
(168) Butts, C. P.; Filali, E.; Lloyd-Jones, G. C.; Norrby, P.-O.; Sale, D. A.; Schramm, Y. Structure-Based Rationale for Selectivity in the Asymmetric Allylic Alkylation of Cycloalkenyl Esters Employing the Trost "Standard Ligand" (TSL): Isolation, Analysis and Alkylation of the Monomeric Form of the Cationic η3-Cyclohexenyl Complex [(η3-*c*-C6H9)Pd(TSL)]$^+$. *J. Am. Chem. Soc.* **2009**, *131*, 9945−9957.
(169) Chen, W.; Hartwig, J. F. Iridium-Catalyzed Regioselective and Enantioselective Allylation of Trimethylsiloxyfuran. *J. Am. Chem. Soc.* **2012**, *134*, 15249−15252.
(170) Fournier, J.; Lozano, O.; Menozzi, C.; Arseniyadis, S.; Cossy, J. Palladium-Catalyzed Asymmetric Allylic Alkylation of Cyclic Dienol Carbonates: Efficient Route to Enantioenriched γ-Butenolides Bearing an All-Carbon α-Quaternary Stereogenic Center. *Angew. Chem., Int. Ed.* **2013**, *52*, 1257−1261.
(171) Bellina, F.; Rossi, R. Transition Metal-Catalyzed Direct Arylation of Substrates with Activated sp3-Hybridized C−H Bonds and Some of Their Synthetic Equivalents with Aryl Halides and Pseudohalides. *Chem. Rev.* **2010**, *110*, 1082−1146.

DOI: 10.1021/acs.chemrev.7b00151
Chem. Rev. 2017, 117, 10502−10566

(172) Spielvogel, D. J.; Buchwald, S. L. Nickel-BINAP Catalyzed Enantioselective α-Arylation of α-Substituted γ-Butyrolactones. *J. Am. Chem. Soc.* **2002**, *124*, 3500−3501.
(173) Spielvogel, D. J.; Davis, W. M.; Buchwald, S. L. Preparation, Crystal Structure Analysis, and Catalytic Application of [(*S*)-BINAP]-Ni(COD) and [(*S*)-BINAP]$NiBr_2$. *Organometallics* **2002**, *21*, 3833−3836.
(174) Delhaye, L.; Merschaert, A.; Diker, K.; Houpis, I. N. Synthesis of 4,4′-Disubstituted Azepines via Ring-Closing Metathesis Reaction and Asymmetric Arylation of Lactones. *Synthesis* **2006**, *2006*, 1437−1442.
(175) Huang, Z.; Chen, Z.; Lim, L. H.; Quang, G. C. P.; Hirao, H.; Zhou, J. (Steve). Weak Arene C-H···O Hydrogen Bonding in Palladium-Catalyzed Arylation and Vinylation of Lactones. *Angew. Chem., Int. Ed.* **2013**, *52*, 5807−5812.
(176) Ooi, T.; Miki, T.; Fukumoto, K.; Maruoka, K. Asymmetric Synthesis of α-Acyl-γ-Butyrolactones Possessing All-Carbon Quaternary Stereocenters by Phase-Transfer-Catalyzed Alkylation. *Adv. Synth. Catal.* **2006**, *348*, 1539−1542.
(177) Ha, M. W.; Lee, H.; Yi, H. Y.; Park, Y.; Kim, S.; Hong, S.; Lee, M.; Kim, M.; Kim, T.-S.; Park, H. Enantioselective Phase-Transfer Catalytic α-Benzylation and α-Allylation of α-Tert-Butoxycarbonyllactones. *Adv. Synth. Catal.* **2013**, *355*, 637−642.
(178) Takaya, Y.; Senda, T.; Kurushima, H.; Ogasawara, M.; Hayashi, T. Rhodium-Catalyzed Asymmetric 1,4-Addition of Arylboron Reagents to α,β-Unsaturated Esters. *Tetrahedron: Asymmetry* **1999**, *10*, 4047−4056.
(179) Defieber, C.; Paquin, J.-F.; Serna, S.; Carreira, E. M. Chiral [2.2.2] Dienes as Ligands for Rh(I) in Conjugate Additions of Boronic Acids to a Wide Range of Acceptors. *Org. Lett.* **2004**, *6*, 3873−3876.
(180) Navarre, L.; Pucheault, M.; Darses, S.; Genet, J.-P. Potassium Trifluoro(organo)borates in Rhodium-Catalyzed 1,4-Additions to α,β-Unsaturated Esters. *Tetrahedron Lett.* **2005**, *46*, 4247−4250.
(181) Kina, A.; Ueyama, K.; Hayashi, T. Enantiomerically Pure Rhodium Complexes Bearing 1,5-Diphenyl-1,5-Cyclooctadiene as a Chiral Diene Ligand. Their Use as Catalysts for Asymmetric 1,4-Addition of Phenylzinc Chloride. *Org. Lett.* **2005**, *7*, 5889−5892.
(182) Kurihara, K.; Sugishita, N.; Oshita, K.; Piao, D.; Yamamoto, Y.; Miyaura, N. Enantioselective 1,4-Addition of Arylboronic Acids to α,β-Unsaturated Carbonyl Compounds Catalyzed by rhodium(I)-Chiral Phosphoramidite Complexes. *J. Organomet. Chem.* **2007**, *692*, 428−435.
(183) Gendrineau, T.; Chuzel, O.; Eijsberg, H.; Genet, J.-P.; Darses, S. C_1-Symmetric Monosubstituted Chiral Diene Ligands in Asymmetric Rhodium-Catalyzed 1,4-Addition Reactions. *Angew. Chem., Int. Ed.* **2008**, *47*, 7669−7672.
(184) Smith, A. J.; Abbott, L. K.; Martin, S. F. Enantioselective Conjugate Addition Employing 2-Heteroaryl Titanates and Zinc Reagents. *Org. Lett.* **2009**, *11*, 4200−4203.
(185) Luo, Y.; Carnell, A. J. Chemoenzymatic Synthesis and Application of Bicyclo[2.2.2]octadiene Ligands: Increased Efficiency in Rhodium-Catalyzed Asymmetric Conjugate Additions by Electronic Tuning. *Angew. Chem., Int. Ed.* **2010**, *49*, 2750−2754.
(186) Berhal, F.; Esseiva, O.; Martin, C.-H.; Tone, H.; Genet, J.-P.; Ayad, T.; Ratovelomanana-Vidal, V. (*R*)-3,5-diCF_3-SYNPHOS and (*R*)-*p*-CF_3-SYNPHOS, Electron-Poor Diphosphines for Efficient Room Temperature Rh-Catalyzed Asymmetric Conjugate Addition of Arylboronic Acids. *Org. Lett.* **2011**, *13*, 2806−2809.
(187) Berhal, F.; Wu, Z.; Genet, J.-P.; Ayad, T.; Ratovelomanana-Vidal, V. Rh-Catalyzed Asymmetric 1,4-Addition of Arylboronic Acids to α,β-Unsaturated Ketones with DIFLUORPHOS and SYNPHOS Analogues. *J. Org. Chem.* **2011**, *76*, 6320−6326.
(188) Hayashi, T. Rhodium-Catalyzed Asymmetric 1,4-Addition of Organoboronic Acids and Their Derivatives to Electron Deficient Olefins. *Synlett* **2001**, *2001*, 0879−0887.
(189) Fagnou, K.; Lautens, M. Rhodium-Catalyzed Carbon−Carbon Bond Forming Reactions of Organometallic Compounds. *Chem. Rev.* **2003**, *103*, 169−196.
(190) Hayashi, T.; Yamasaki, K. Rhodium-Catalyzed Asymmetric 1,4-Addition and Its Related Asymmetric Reactions. *Chem. Rev.* **2003**, *103*, 2829−2844.
(191) Darses, S.; Genet, J.-P. Potassium Organotrifluoroborates: New Perspectives in Organic Synthesis. *Chem. Rev.* **2008**, *108*, 288−325.
(192) Edwards, H. J.; Hargrave, J. D.; Penrose, S. D.; Frost, C. G. Synthetic Applications of Rhodium Catalysed Conjugate Addition. *Chem. Soc. Rev.* **2010**, *39*, 2093−2105.
(193) Liang, L.; Yan, M.; Li, Y.-M.; Chan, A. S. C. Highly Enantioselective Copper-Catalyzed 1,4-Conjugate Addition of Diethylzinc to Cyclic Enones and α,β-Unsaturated Lactones. *Tetrahedron: Asymmetry* **2004**, *15*, 2575−2578.
(194) Brown, M. K.; Degrado, S. J.; Hoveyda, A. H. Highly Enantioselective Cu-Catalyzed Conjugate Additions of Dialkylzinc Reagents to Unsaturated Furanones and Pyranones: Preparation of Air-Stable and Catalytically Active Cu−Peptide Complexes. *Angew. Chem., Int. Ed.* **2005**, *44*, 5306−5310.
(195) Trost, B. M.; Toste, F. D. Palladium-Catalyzed Kinetic and Dynamic Kinetic Asymmetric Transformation of 5-Acyloxy-2-(5*H*)-Furanone. Enantioselective Synthesis of (−)-Aflatoxin B Lactone. *J. Am. Chem. Soc.* **1999**, *121*, 3543−3544.
(196) Feringa, B. L.; De Lange, B.; De Jong, J. C. Synthesis of Enantiomerically Pure γ-(Menthyloxy)butenolides and (*R*)- and (*S*)-2-Methyl-1,4-Butanediol. *J. Org. Chem.* **1989**, *54*, 2471−2475.
(197) van der Deen, H.; Cuiper, A. D.; Hof, R. P.; van Oeveren, A.; Feringa, B. L.; Kellogg, R. M. Lipase-Catalyzed Second-Order Asymmetric Transformations as Resolution and Synthesis Strategies for Chiral 5-(Acyloxy)-2(5*H*)-Furanone and Pyrrolinone Synthons. *J. Am. Chem. Soc.* **1996**, *118*, 3801−3803.
(198) van der Deen, H.; van Oeveren, A.; Kellogg, R. M.; Feringa, B. L. Palladium Catalyzed Stereospecific Allylic Substitution of 5-Acetoxy-2(5*H*)-Furanone and 6-Acetoxy-2*H*-Pyran-3(6*H*)-One by Alcohols. *Tetrahedron Lett.* **1999**, *40*, 1755−1758.
(199) Trost, B. M.; Toste, F. D. Palladium Catalyzed Kinetic and Dynamic Kinetic Asymmetric Transformations of γ-Acyloxybutenolides. Enantioselective Total Synthesis of (+)-Aflatoxin B 1 and B 2 a. *J. Am. Chem. Soc.* **2003**, *125*, 3090−3100.
(200) Trost, B. M.; Crawley, M. L. A "Chiral Aldehyde" Equivalent as a Building Block Towards Biologically Active Targets. *Chem. - Eur. J.* **2004**, *10*, 2237−2252.
(201) Tang, W.; Zhang, X. New Chiral Phosphorus Ligands for Enantioselective Hydrogenation. *Chem. Rev.* **2003**, *103*, 3029−3070.
(202) Shimizu, H.; Nagasaki, I.; Saito, T. Recent Advances in Biaryl-Type Bisphosphine Ligands. *Tetrahedron* **2005**, *61*, 5405−5432.
(203) Shimizu, H.; Nagasaki, I.; Matsumura, K.; Sayo, N.; Saito, T. Developments in Asymmetric Hydrogenation from an Industrial Perspective. *Acc. Chem. Res.* **2007**, *40*, 1385−1393.
(204) Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. Synthesis of 2,2′-Bis(diphenylphosphino)-1,1′-Binaphthyl (BINAP), an Atropisomeric Chiral Bis(triaryl)phosphine, and Its Use in the rhodium(I)-Catalyzed Asymmetric Hydrogenation of α-(Acylamino)acrylic Acids. *J. Am. Chem. Soc.* **1980**, *102*, 7932−7934.
(205) Mashima, K.; Kusano, K.; Sato, N.; Matsumura, Y.; Nozaki, K.; Kumobayashi, H.; Sayo, N.; Hori, Y.; Ishizaki, T. Cationic BINAP-Ru(II) Halide Complexes: Highly Efficient Catalysts for Stereoselective Asymmetric Hydrogenation of α- and β-Functionalized Ketones. *J. Org. Chem.* **1994**, *59*, 3064−3076.
(206) Ohta, T.; Miyake, T.; Seido, N.; Kumobayashi, H.; Takaya, H. Asymmetric Hydrogenation of Olefins with Aprotic Oxygen Functionalities Catalyzed by BINAP-Ru(II) Complexes. *J. Org. Chem.* **1995**, *60*, 357−363.
(207) Kamlage, S.; Sefkow, M.; Zimmermann, N.; Peter, M. G. Concise Synthesis of (+)-β-Benzyl γ-Butyrolactones from Butynediol. *Synlett* **2002**, *2002*, 0077−0080.
(208) Donate, P. M.; Frederico, D.; da Silva, R.; Constantino, M. G.; Del Ponte, G.; Bonatto, P. S. Asymmetric Synthesis of γ-Butyrolactones by Enantioselective Hydrogenation of Butenolides. *Tetrahedron: Asymmetry* **2003**, *14*, 3253−3256.
(209) Adam, J.-M.; Foricher, J.; Hanlon, S.; Lohri, B.; Moine, G.; Schmid, R.; Stahr, H.; Weber, M.; Wirz, B.; Zutter, U. Development of a Scalable Synthesis of (*S*)-3-Fluoromethyl-γ-Butyrolactone, Building

DOI: 10.1021/acs.chemrev.7b00151
Chem. Rev. 2017, 117, 10502−10566

Block for Carmegliptin's Lactam Moiety. *Org. Process Res. Dev.* **2011**, *15*, 515−526.
(210) Verendel, J. J.; Li, J.-Q.; Quan, X.; Peters, B.; Zhou, T.; Gautun, O. R.; Govender, T.; Andersson, P. G. Chiral Hetero- and Carbocyclic Compounds from the Asymmetric Hydrogenation of Cyclic Alkenes. *Chem. - Eur. J.* **2012**, *18*, 6507−6513.
(211) Geiger, C.; Kreitmeier, P.; Reiser, O. Cobalt(II)-Azabis(oxazoline)-Catalyzed Conjugate Reduction of α,β-Unsaturated Carbonyl Compounds. *Adv. Synth. Catal.* **2005**, *347*, 249−254.
(212) Deutsch, C.; Krause, N.; Lipshutz, B. H. CuH-Catalyzed Reactions. *Chem. Rev.* **2008**, *108*, 2916−2927.
(213) Rendler, S.; Oestreich, M. Polishing a Diamond in the Rough: "Cu-H" Catalysis with Silanes. *Angew. Chem., Int. Ed.* **2007**, *46*, 498−504.
(214) Lipshutz, B. H. Rediscovering Organocopper Chemistry Through Copper Hydride. It's All About the Ligand. *Synlett* **2009**, *2009*, 509−524.
(215) Hughes, G.; Kimura, M.; Buchwald, S. L. Catalytic Enantioselective Conjugate Reduction of Lactones and Lactams. *J. Am. Chem. Soc.* **2003**, *125*, 11253−11258.
(216) Lipshutz, B. H.; Servesko, J. M.; Taft, B. R. Asymmetric 1,4-Hydrosilylations of α,β-Unsaturated Esters. *J. Am. Chem. Soc.* **2004**, *126*, 8352−8353.
(217) Lipshutz, B. H.; Frieman, B. A.; Unger, J. B.; Nihan, D. M. Thermally Accelerated Asymmetric Hydrosilylations Using Ligated Copper Hydride. *Can. J. Chem.* **2005**, *83*, 606−614.
(218) Lipshutz, B. H.; Frieman, B. A.; Tomaso, A. E. Copper-in-Charcoal (Cu/C): Heterogeneous, Copper-Catalyzed Asymmetric Hydrosilylations. *Angew. Chem., Int. Ed.* **2006**, *45*, 1259−1264.
(219) Rainka, M. P.; Milne, J. E.; Buchwald, S. L. Dynamic Kinetic Resolution of α,β-Unsaturated Lactones through Asymmetric Copper-Catalyzed Conjugate Reduction: Application to the Total Synthesis of Eupomatilone-3. *Angew. Chem., Int. Ed.* **2005**, *44*, 6177−6180.
(220) Ryu, D. H.; Lee, T. W.; Corey, E. J. Broad-Spectrum Enantioselective Diels−Alder Catalysis by Chiral, Cationic Oxazaborolidines. *J. Am. Chem. Soc.* **2002**, *124*, 9992−9993.
(221) Inoue, T.; Kitagawa, O.; Ochiai, O.; Shiro, M.; Taguchi, T. Catalytic Asymmetric Iodocarbocyclization Reaction. *Tetrahedron Lett.* **1995**, *36*, 9333−9336.
(222) Inoue, T.; Kitagawa, O.; Saito, A.; Taguchi, T. Catalytic Asymmetric Iodocarbocyclization Reaction of 4-Alkenylmalonates and Its Application to Enantiotopic Group Selective Reaction. *J. Org. Chem.* **1997**, *62*, 7384−7389.
(223) Kitagawa, O.; Taguchi, T. Iodocarbocyclization and Iodoaminocyclization Reactions Mediated by a Metallic Reagent. *Synlett* **1999**, *1999*, 1191−1199.
(224) Ning, Z.; Jin, R.; Ding, J.; Gao, L. Enantioselective Iodolactonizations of 4-Pentenoic Acid Derivatives Mediated by Chiral Salen-Co(II) Complex. *Synlett* **2009**, *2009*, 2291−2294.
(225) Lee, H. J.; Kim, D. Y. Catalytic Enantioselective Bromolactonization of Alkenoic Acids in the Presence of Palladium Complexes. *Tetrahedron Lett.* **2012**, *53*, 6984−6986.
(226) Wang, M.; Gao, L. X.; Mai, W. P.; Xia, A. X.; Wang, F.; Zhang, S. B. Enantioselective Iodolactonization Catalyzed by Chiral Quaternary Ammonium Salts Derived from Cinchonidine. *J. Org. Chem.* **2004**, *69*, 2874−2876.
(227) French, A. N.; Bissmire, S.; Wirth, T. Iodine Electrophiles in Stereoselective Reactions: Recent Developments and Synthetic Applications. *Chem. Soc. Rev.* **2004**, *33*, 354−362.
(228) Chen, G.; Ma, S. Enantioselective Halocyclization Reactions for the Synthesis of Chiral Cyclic Compounds. *Angew. Chem., Int. Ed.* **2010**, *49*, 8306−8308.
(229) Castellanos, A.; Fletcher, S. P. Current Methods for Asymmetric Halogenation of Olefins. *Chem. - Eur. J.* **2011**, *17*, 5766−5776.
(230) Tan, C. K.; Zhou, L.; Yeung, Y.-Y. Organocatalytic Enantioselective Halolactonizations: Strategies of Halogen Activation. *Synlett* **2011**, *2011*, 1335−1339.
(231) Hennecke, U. New Catalytic Approaches towards the Enantioselective Halogenation of Alkenes. *Chem. - Asian J.* **2012**, *7*, 456−465.
(232) Denmark, S. E.; Kuester, W. E.; Burk, M. T. Catalytic, Asymmetric Halofunctionalization of Alkenes—A Critical Perspective. *Angew. Chem., Int. Ed.* **2012**, *51*, 10938−10953.
(233) Snyder, S. A.; Treitler, D. S.; Brucks, A. P. Halonium-Induced Cyclization Reactions. *Aldrichimica Acta* **2011**, *44*, 27−42.
(234) Whitehead, D. C.; Yousefi, R.; Jaganathan, A.; Borhan, B. An Organocatalytic Asymmetric Chlorolactonization. *J. Am. Chem. Soc.* **2010**, *132*, 3298−3300.
(235) Yousefi, R.; Whitehead, D. C.; Mueller, J. M.; Staples, R. J.; Borhan, B. On the Chlorenium Source in the Asymmetric Chlorolactonization Reaction. *Org. Lett.* **2011**, *13*, 608−611.
(236) Veitch, G. E.; Jacobsen, E. N. Tertiary Aminourea-Catalyzed Enantioselective Iodolactonization. *Angew. Chem., Int. Ed.* **2010**, *49*, 7332−7335.
(237) Zhou, L.; Tan, C. K.; Jiang, X.; Chen, F.; Yeung, Y.-Y. Asymmetric Bromolactonization Using Amino-Thiocarbamate Catalyst. *J. Am. Chem. Soc.* **2010**, *132*, 15474−15476.
(238) Tan, C. K.; Le, C.; Yeung, Y.-Y. Enantioselective Bromolactonization of *cis*-1,2-Disubstituted Olefinic Acids Using an Amino-Thiocarbamate Catalyst. *Chem. Commun.* **2012**, *48*, 5793−5795.
(239) Jiang, X.; Tan, C. K.; Zhou, L.; Yeung, Y.-Y. Enantioselective Bromolactonization Using an S-Alkyl Thiocarbamate Catalyst. *Angew. Chem., Int. Ed.* **2012**, *51*, 7771−7775.
(240) Paull, D. H.; Fang, C.; Donald, J. R.; Pansick, A. D.; Martin, S. F. Bifunctional Catalyst Promotes Highly Enantioselective Bromolactonizations To Generate Stereogenic C−Br Bonds. *J. Am. Chem. Soc.* **2012**, *134*, 11128−11131.
(241) Fang, C.; Paull, D. H.; Hethcox, J. C.; Shugrue, C. R.; Martin, S. F. Enantioselective Iodolactonization of Disubstituted Olefinic Acids Using a Bifunctional Catalyst. *Org. Lett.* **2012**, *14*, 6290−6293.
(242) Ikeuchi, K.; Ido, S.; Yoshimura, S.; Asakawa, T.; Inai, M.; Hamashima, Y.; Kan, T. Catalytic Desymmetrization of Cyclohexadienes by Asymmetric Bromolactonization. *Org. Lett.* **2012**, *14*, 6016−6019.
(243) Kawamata, Y.; Hashimoto, T.; Maruoka, K. A Chiral Electrophilic Selenium Catalyst for Highly Enantioselective Oxidative Cyclization. *J. Am. Chem. Soc.* **2016**, *138*, 5206−5209.
(244) Zhu, R.; Buchwald, S. L. Enantioselective Functionalization of Radical Intermediates in Redox Catalysis: Copper-Catalyzed Asymmetric Oxytrifluoromethylation of Alkenes. *Angew. Chem., Int. Ed.* **2013**, *52*, 12655−12658.
(245) Zhu, R.; Buchwald, S. L. Versatile Enantioselective Synthesis of Functionalized Lactones via Copper-Catalyzed Radical Oxyfunctionalization of Alkenes. *J. Am. Chem. Soc.* **2015**, *137*, 8069−8077.
(246) Haidasz, E. A.; Van Kessel, A. T. M.; Pratt, D. A. A Continuous Visible Light Spectrophotometric Approach To Accurately Determine the Reactivity of Radical-Trapping Antioxidants. *J. Org. Chem.* **2016**, *81*, 737−744.
(247) Strukul, G. Transition Metal Catalysis in the Baeyer−Villiger Oxidation of Ketones. *Angew. Chem., Int. Ed.* **1998**, *37*, 1198−1209.
(248) ten Brink, G.-J.; Arends, I. W. C. E.; Sheldon, R. A. The Baeyer−Villiger Reaction: New Developments toward Greener Procedures. *Chem. Rev.* **2004**, *104*, 4105−4124.
(249) Mihovilovic, M.; Rudroff, F.; Grotzl, B. Enantioselective Baeyer-Villiger Oxidations. *Curr. Org. Chem.* **2004**, *8*, 1057−1069.
(250) Bolm, C. Metal-Catalyzed Asymmetric Oxidations. *Med. Res. Rev.* **1999**, *19*, 348−356.
(251) Bolm, C.; Schlingloff, G.; Weickhardt, K. Optically Active Lactones from a Baeyer−Villiger-Type Metal-Catalyzed Oxidation with Molecular Oxygen. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1848−1849.
(252) Gusso, A.; Baccin, C.; Pinna, F.; Strukul, G. Platinum-Catalyzed Oxidations with Hydrogen Peroxide: Enantiospecific Baeyer-Villiger Oxidation of Cyclic Ketones. *Organometallics* **1994**, *13*, 3442−3451.
(253) Lopp, M.; Paju, A.; Kanger, T.; Pehk, T. Asymmetric Baeyer-Villiger Oxidation of Cyclobutanones. *Tetrahedron Lett.* **1996**, *37*, 7583−7586.

DOI: 10.1021/acs.chemrev.7b00151
Chem. Rev. 2017, 117, 10502−10566

(254) Kanger, T.; Kriis, K.; Paju, A.; Pehk, T.; Lopp, M. Asymmetric Oxidation of Cyclobutanones: Modification of the Sharpless Catalyst. *Tetrahedron: Asymmetry* **1998**, *9*, 4475−4482.
(255) Bolm, C.; Khanh Luong, T. K.; Schlingloff, G. Enantioselective Metal-Catalyzed Baeyer-Villiger Oxidation of Cyclobutanones. *Synlett* **1997**, *1997*, 1151−1152.
(256) Bolm, C.; Schlingloff, G.; Bienewald, F. Copper- and Vanadium-Catalyzed Asymmetric Oxidations. *J. Mol. Catal. A: Chem.* **1997**, *117*, 347−350.
(257) Uchida, T.; Katsuki, T. Cationic Co(III) (salen)-Catalyzed Enantioselective Baeyer−Villiger Oxidation of 3-Arylcyclobutanones Using Hydrogen Peroxide as a Terminal Oxidant. *Tetrahedron Lett.* **2001**, *42*, 6911−6914.
(258) Watanabe, A.; Uchida, T.; Ito, K.; Katsuki, T. Highly Enantioselective Baeyer−Villiger Oxidation Using Zr(salen) Complex as Catalyst. *Tetrahedron Lett.* **2002**, *43*, 4481−4485.
(259) Watanabe, A.; Uchida, T.; Irie, R.; Katsuki, T. Zr[bis-(salicylidene)ethylenediaminato]-Mediated Baeyer−Villiger Oxidation: Stereospecific Synthesis of Abnormal and Normal Lactones. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 5737−5742.
(260) Colladon, M.; Scarso, A.; Strukul, G. Tailoring Pt(II) Chiral Catalyst Design for Asymmetric Baeyer-VilligerOxidation of Cyclic Ketones with Hydrogen Peroxide. *Synlett* **2006**, *2006*, 3515−3520.
(261) Cavarzan, A.; Bianchini, G.; Sgarbossa, P.; Lefort, L.; Gladiali, S.; Scarso, A.; Strukul, G. Catalytic Asymmetric Baeyer−Villiger Oxidation in Water by Using PtII Catalysts and Hydrogen Peroxide: Supramolecular Control of Enantioselectivity. *Chem. - Eur. J.* **2009**, *15*, 7930−7939.
(262) Ito, K.; Ishii, A.; Kuroda, T.; Katsuki, T. Asymmetric Baeyer-Villiger Oxidation of Prochiral Cyclobutanones Using a Chiral Cationic Palladium(II) 2-(Phosphinophenyl)pyridine Complex as Catalyst. *Synlett* **2003**, *2003*, 0643−0646.
(263) Malkov, A. V.; Friscourt, F.; Bell, M.; Swarbrick, M. E.; Kočovský, P. Enantioselective Baeyer−Villiger Oxidation Catalyzed by Palladium(II) Complexes with Chiral *P,N* -Ligands ‖. *J. Org. Chem.* **2008**, *73*, 3996−4003.
(264) Petersen, K. S.; Stoltz, B. M. Palladium-Catalyzed, Asymmetric Baeyer−Villiger Oxidation of Prochiral Cyclobutanones with PHOX Ligands. *Tetrahedron* **2011**, *67*, 4352−4357.
(265) Bolm, C.; Beckmann, O.; Cosp, A.; Palazzi, C. Enantioselective Baeyer-Villiger Oxidations Catalyzed by Chiral Magnesium Complexes. *Synlett* **2001**, *2001*, 1461−1463.
(266) Bolm, C.; Beckmann, O.; Palazzi, C. Chiral Aluminum Complexes as Catalysts in Asymmetric Baeyer-Villiger Reactions of Cyclobutanones. *Can. J. Chem.* **2001**, *79*, 1593−1597.
(267) Bolm, C.; Beckmann, O.; Kühn, T.; Palazzi, C.; Adam, W.; Rao, P. B.; Saha-Möller, C. R. Influence of Hydroperoxides on the Enantioselectivity of Metal-Catalyzed Asymmetric Baeyer−Villiger Oxidation and Epoxidation with Chiral Ligands. *Tetrahedron: Asymmetry* **2001**, *12*, 2441−2446.
(268) Bolm, C.; Frison, J.-C.; Zhang, Y.; Wulff, W. D. Vaulted Biaryls: Efficient Ligands for the Aluminum-Catalyzed Asymmetric Baeyer-Villiger Reaction. *Synlett* **2004**, *2004*, 1619−1621.
(269) Frison, J.-C.; Palazzi, C.; Bolm, C. Ligand Effects in Aluminium-Catalyzed Asymmetric Baeyer−Villiger Reactions. *Tetrahedron* **2006**, *62*, 6700−6706.
(270) Zhou, L.; Liu, X.; Ji, J.; Zhang, Y.; Hu, X.; Lin, L.; Feng, X. Enantioselective Baeyer−Villiger Oxidation: Desymmetrization of Meso Cyclic Ketones and Kinetic Resolution of Racemic 2-Arylcyclohexanones. *J. Am. Chem. Soc.* **2012**, *134*, 17023−17026.
(271) Murahashi, S.-I.; Ono, S.; Imada, Y. Asymmetric Baeyer−Villiger Reaction with Hydrogen Peroxide Catalyzed by a Novel Planar-Chiral Bisflavin. *Angew. Chem., Int. Ed.* **2002**, *41*, 2366−2368.
(272) Xu, S.; Wang, Z.; Zhang, X.; Zhang, X.; Ding, K. Chiral Brønsted Acid Catalyzed Asymmetric Baeyer−Villiger Reaction of 3-Substituted Cyclobutanones by Using Aqueous H_2O_2. *Angew. Chem., Int. Ed.* **2008**, *47*, 2840−2843.
(273) Xu, S.; Wang, Z.; Li, Y.; Zhang, X.; Wang, H.; Ding, K. Mechanistic Investigation of Chiral Phosphoric Acid Catalyzed Asymmetric Baeyer−Villiger Reaction of 3-Substituted Cyclobutanones with H_2O_2 as the Oxidant. *Chem. - Eur. J.* **2010**, *16*, 3021−3035.
(274) Xu, S.; Wang, Z.; Zhang, X.; Ding, K. Asymmetric Baeyer-Villiger Oxidation of 2,3- and 2,3,4-Substituted Cyclobutanones Catalyzed by Chiral Phosphoric Acids with Aqueous H_2O_2 as the Oxidant. *Eur. J. Org. Chem.* **2011**, *2011*, 110−116.
(275) Ohta, T.; Takaya, H.; Kitamura, M.; Nagai, K.; Noyori, R. Asymmetric Hydrogenation of Unsaturated Carboxylic Acids Catalyzed by BINAP-Ruthenium(II) Complexes. *J. Org. Chem.* **1987**, *52*, 3174−3176.
(276) Krohn, K.; Riaz, M. Total Synthesis of (+)-Xyloketal D, a Secondary Metabolite from the Mangrove Fungus Xylaria Sp. *Tetrahedron Lett.* **2004**, *45*, 293−294.
(277) Yoshimura, M.; Tsuda, K.; Nakatsuka, H.; Yamamura, T.; Kitamura, M. Desymmetric Hydrogenation of a Meso-Cyclic Acid Anhydride toward Biotin Synthesis. *Tetrahedron* **2011**, *67*, 10006−10010.
(278) Blandin, V.; Carpentier, J.-F.; Mortreux, A. New One Pot Synthesis of a Chiral α-Hydroxy-γ-Butyrolactone via Sequential Asymmetric Hydrogenation of an α,γ-Diketoester. *Tetrahedron: Asymmetry* **1998**, *9*, 2765−2768.
(279) Blandin, V.; Carpentier, J.-F.; Mortreux, A. Asymmetric Hydrogenation of 2,4-Dioxo Esters: Selective Synthesis of 2-Hydroxy-4-Oxo Esters and Direct Access to Chiral 2-Hydroxy-4-Butyrolactones. *Eur. J. Org. Chem.* **1999**, *1999*, 1787−1793.
(280) Benincori, T.; Rizzo, S.; Pilati, T.; Ponti, A.; Sada, M.; Pagliarini, E.; Ratti, S.; Giuseppe, C.; de Ferra, L.; Sannicolò, F. Process-Scale Preparation of Enantiomerically Pure γ-Lactones by Asymmetric Hydrogenation of γ-Ketoesters and Comparative Tests of the Sensory Properties of Some Antipodes. *Tetrahedron: Asymmetry* **2004**, *15*, 2289−2297.
(281) Starodubtseva, E. V.; Turova, O. V.; Vinogradov, M. G.; Gorshkova, L. S.; Ferapontov, V. A.; Struchkova, M. I. A Convenient Route to Chiral γ-Lactones via Asymmetric Hydrogenation of γ-Ketoesters Using the $RuCl_3$−BINAP−HCl Catalytic System. *Tetrahedron* **2008**, *64*, 11713−11717.
(282) Turova, O. V.; Starodubtseva, E. V.; Vinogradov, M. G.; Ferapontov, V. A.; Struchkova, M. I. A Concise Synthesis of Highly Enantiomerically Enriched 2-Alkylparaconic Acid Esters via Ruthenium-Catalyzed Asymmetric Hydrogenation of Acylsuccinates. *Tetrahedron: Asymmetry* **2009**, *20*, 2121−2124.
(283) Sawamura, M.; Kuwano, R.; Shirai, J.; Ito, Y. Asymmetric Hydrosilylation of Keto Esters Catalyzed by a Rhodium Complex with Trans-Chelating Chiral Diphosphine EtTRAP. *Synlett* **1995**, *1995*, 347−348.
(284) Matsumura, Y.; Ogura, K.; Kouchi, Y.; Iwasaki, F.; Onomura, O. New Efficient Organic Activators for Highly Enantioselective Reduction of Aromatic Ketones by Trichlorosilane. *Org. Lett.* **2006**, *8*, 3789−3792.
(285) Ghosh, A. K.; Swanson, L. Enantioselective Synthesis of (+)-Cryptophycin 52 (LY355703), a Potent Antimitotic Antitumor Agent. *J. Org. Chem.* **2003**, *68*, 9823−9826.
(286) Steward, K. M.; Gentry, E. C.; Johnson, J. S. Dynamic Kinetic Resolution of α-Keto Esters via Asymmetric Transfer Hydrogenation. *J. Am. Chem. Soc.* **2012**, *134*, 7329−7332.
(287) Steward, K. M.; Corbett, M. T.; Goodman, C. G.; Johnson, J. S. Asymmetric Synthesis of Diverse Glycolic Acid Scaffolds via Dynamic Kinetic Resolution of α-Keto Esters. *J. Am. Chem. Soc.* **2012**, *134*, 20197−20206.
(288) Kakisawa, H.; Yanai, M.; Kozima, T.; Nakanishi, K.; Mishima, H. The Stereochemistry of the Grayanotoxins. *Tetrahedron Lett.* **1962**, *3*, 215−219.
(289) Murphy, S. K.; Dong, V. M. Enantioselective Ketone Hydroacylation Using Noyori's Transfer Hydrogenation Catalyst. *J. Am. Chem. Soc.* **2013**, *135*, 5553−5556.
(290) Doyle, M. P.; Van Oeveren, A.; Westrum, L. J.; Protopopova, M. N.; Clayton, T. W. Asymmetric Synthesis of Lactones with High Enantioselectivity by Intramolecular Carbon-Hydrogen Insertion Reactions of Alkyl Diazoacetates Catalyzed by Chiral rhodium(II) Carboxamides. *J. Am. Chem. Soc.* **1991**, *113*, 8982−8984.

DOI: 10.1021/acs.chemrev.7b00151
Chem. Rev. 2017, 117, 10502−10566

(291) Doyle, M. P.; Dyatkin, A. B.; Tedrow, J. S. Synthesis of 2-Deoxyxylolactone from Glycerol Derivatives via Highly Enantioselective Carbon-Hydrogen Insertion Reactions. *Tetrahedron Lett.* **1994**, *35*, 3853−3856.
(292) Bode, J. W.; Doyle, M. P.; Protopopova, M. N.; Zhou, Q.-L. Intramolecular Regioselective Insertion into Unactivated Prochiral Carbon−Hydrogen Bonds with Diazoacetates of Primary Alcohols Catalyzed by Chiral Dirhodium(II) Carboxamidates. Highly Enantioselective Total Synthesis of Natural Lignan Lactones. *J. Org. Chem.* **1996**, *61*, 9146−9155.
(293) Doyle, M. P.; Tedrow, J. S.; Dyatkin, A. B.; Spaans, C. J.; Ene, D. G. Enantioselective Syntheses of 2-Deoxyxylono-1,4-Lactone and 2-Deoxyribono-1,4-Lactone from 1,3-Dioxan-5-yl Diazoacetates. *J. Org. Chem.* **1999**, *64*, 8907−8915.
(294) Doyle, M. P.; Hu, W. Enantioselective Carbon–Hydrogen Insertion Is an Effective and Efficient Methodology for the Synthesis of (*R*)-(−)-Baclofen. *Chirality* **2002**, *14*, 169−172.
(295) Doyle, M. P.; Hu, W.; Valenzuela, M. V. Total Synthesis of (*S*)-(+)-Imperanene. Effective Use of Regio- and Enantioselective Intramolecular Carbon−Hydrogen Insertion Reactions Catalyzed by Chiral Dirhodium(II) Carboxamidates. *J. Org. Chem.* **2002**, *67*, 2954−2959.
(296) Doyle, M. P.; Dyatkin, A. B.; Roos, G. H. P.; Canas, F.; Pierson, D. A.; van Basten, A.; Mueller, P.; Polleux, P. Diastereocontrol for Highly Enantioselective Carbon-Hydrogen Insertion Reactions of Cycloalkyl Diazoacetates. *J. Am. Chem. Soc.* **1994**, *116*, 4507−4508.
(297) Doyle, M. P.; Kalinin, A. V.; Ene, D. G. Chiral Catalyst Controlled Diastereoselection and Regioselection in Intramolecular Carbon−Hydrogen Insertion Reactions of Diazoacetates. *J. Am. Chem. Soc.* **1996**, *118*, 8837−8846.
(298) Doyle, M. P.; Catino, A. J. A Short Stereoselective Synthesis of (+)- and (−)-2-Oxabicyclo[3.3.0]oct-6-En-3-One by Intramolecular Carbon−Hydrogen Insertion Catalyzed by Chiral dirhodium(II) Carboxamidates. *Tetrahedron: Asymmetry* **2003**, *14*, 925−928.
(299) Doyle, M. P.; Dyatkin, A. B.; Kalinin, A. V.; Ruppar, D. A.; Martin, S. F.; Spaller, M. R.; Liras, S. Highly Selective Enantiomer Differentiation in Intramolecular Cyclopropanation Reactions of Racemic Secondary Allylic Diazoacetates. *J. Am. Chem. Soc.* **1995**, *117*, 11021−11022.
(300) Ashfeld, B. L.; Martin, S. F. Enantioselective Syntheses of Tremulenediol A and Tremulenolide A. *Org. Lett.* **2005**, *7*, 4535−4537.
(301) Ashfeld, B. L.; Martin, S. F. Enantioselective Syntheses of Tremulenediol A and Tremulenolide A. *Tetrahedron* **2006**, *62*, 10497−10506.
(302) Doyle, M. P.; Pieters, R. J.; Martin, S. F.; Austin, R. E.; Oalmann, C. J.; Mueller, P. High Enantioselectivity in the Intramolecular Cyclopropanation of Allyl Diazoacetates Using a Novel Rhodium(II) Catalyst. *J. Am. Chem. Soc.* **1991**, *113*, 1423−1424.
(303) Doyle, M. P.; Austin, R. E.; Bailey, A. S.; Dwyer, M. P.; Dyatkin, A. B.; Kalinin, A. V.; Kwan, M. M. Y.; Liras, S.; Oalmann, C. J. Enantioselective Intramolecular Cyclopropanations of Allylic and Homoallylic Diazoacetates and Diazoacetamides Using Chiral Dirhodium(II) Carboxamide Catalysts. *J. Am. Chem. Soc.* **1995**, *117*, 5763−5775.
(304) Doyle, M. P.; Zhou, Q.-L.; Dyatkin, A. B.; Ruppar, D. A. Enhancement of Enantiocontrol/diastereocontrol in Catalytic Intramolecular Cyclopropanation and Carbon-Hydrogen Insertion Reactions of Diazoacetates with Rh_2(4*S*-MPPIM)$_4$. *Tetrahedron Lett.* **1995**, *36*, 7579−7582.
(305) Doyle, M. P.; Protopopova, M. N.; Poulter, C. D.; Rogers, D. H. Macrocyclic Lactones from Dirhodium(II)-Catalyzed Intramolecular Cyclopropanation and Carbon-Hydrogen Insertion. *J. Am. Chem. Soc.* **1995**, *117*, 7281−7282.
(306) Doyle, M. P.; Peterson, C. S.; Zhou, Q.-L.; Nishiyama, H. Comparative Evaluation of Enantiocontrol for Intramolecular Cyclopropanation of Diazoacetates with Chiral CuI, RhII and RuII Catalysts. *Chem. Commun.* **1997**, No. 2, 211−212.
(307) Xu, X.; Lu, H.; Ruppel, J. V.; Cui, X.; Lopez de Mesa, S.; Wojtas, L.; Zhang, X. P. Highly Asymmetric Intramolecular Cyclopropanation of Acceptor-Substituted Diazoacetates by Co(II)-Based Metalloradical Catalysis: Iterative Approach for Development of New-Generation Catalysts. *J. Am. Chem. Soc.* **2011**, *133*, 15292−15295.
(308) Doyle, M. P.; Forbes, D. C. Recent Advances in Asymmetric Catalytic Metal Carbene Transformations. *Chem. Rev.* **1998**, *98*, 911−936.
(309) Giri, R.; Shi, B.-F.; Engle, K. M.; Maugel, N.; Yu, J.-Q. Transition Metal-Catalyzed C-H Activation Reactions: Diastereoselectivity and Enantioselectivity. *Chem. Soc. Rev.* **2009**, *38*, 3242−3272.
(310) Doyle, M. P.; Duffy, R.; Ratnikov, M.; Zhou, L. Catalytic Carbene Insertion into C−H Bonds. *Chem. Rev.* **2010**, *110*, 704−724.
(311) Reissig, H.-U.; Zimmer, R. Donor−Acceptor-Substituted Cyclopropane Derivatives and Their Application in Organic Synthesis. *Chem. Rev.* **2003**, *103*, 1151−1196.
(312) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. Stereoselective Cyclopropanation Reactions. *Chem. Rev.* **2003**, *103*, 977−1050.
(313) Reichelt, A.; Martin, S. F. Synthesis and Properties of Cyclopropane-Derived Peptidomimetics. *Acc. Chem. Res.* **2006**, *39*, 433−442.
(314) Pellissier, H. Recent Developments in Asymmetric Cyclopropanation. *Tetrahedron* **2008**, *64*, 7041−7095.
(315) Sohn, S. S.; Rosen, E. L.; Bode, J. W. N-Heterocyclic Carbene-Catalyzed Generation of Homoenolates: γ-Butyrolactones by Direct Annulations of Enals and Aldehydes. *J. Am. Chem. Soc.* **2004**, *126*, 14370−14371.
(316) Burstein, C.; Glorius, F. Organocatalyzed Conjugate Umpolung of α,β-Unsaturated Aldehydes for the Synthesis of γ-Butyrolactones. *Angew. Chem., Int. Ed.* **2004**, *43*, 6205−6208.
(317) Zeitler, K. Extending Mechanistic Routes in Heterazolium Catalysis−Promising Concepts for Versatile Synthetic Methods. *Angew. Chem., Int. Ed.* **2005**, *44*, 7506−7510.
(318) Cohen, D. T.; Scheidt, K. A. Cooperative Lewis acid/N-Heterocyclic Carbene Catalysis. *Chem. Sci.* **2012**, *3*, 53−57.
(319) Izquierdo, J.; Hutson, G. E.; Cohen, D. T.; Scheidt, K. A. A Continuum of Progress: Applications of *N*-Hetereocyclic Carbene Catalysis in Total Synthesis. *Angew. Chem., Int. Ed.* **2012**, *51*, 11686−11698.
(320) Singh, G. S.; Desta, Z. Y. Isatins As Privileged Molecules in Design and Synthesis of Spiro-Fused Cyclic Frameworks. *Chem. Rev.* **2012**, *112*, 6104−6155.
(321) Vora, H. U.; Wheeler, P.; Rovis, T. Exploiting Acyl and Enol Azolium Intermediates via *N*-Hetero-Cyclic Carbene-Catalyzed Reactions of α-Reducible Aldehydes. *Adv. Synth. Catal.* **2012**, *354*, 1617−1639.
(322) Li, Y.; Zhao, Z.-A.; He, H.; You, S.-L. Stereoselective Synthesis of γ-Butyrolactones via Organocatalytic Annulations of Enals and Keto Esters. *Adv. Synth. Catal.* **2008**, *350*, 1885−1890.
(323) Kaeobamrung, J.; Bode, J. W. Stereodivergency of Triazolium and Imidazolium-Derived NHCs for Catalytic, Enantioselective Cyclopentane Synthesis. *Org. Lett.* **2009**, *11*, 677−680.
(324) Cardinal-David, B.; Raup, D. E. A.; Scheidt, K. A. Cooperative N-Heterocyclic Carbene/Lewis Acid Catalysis for Highly Stereoselective Annulation Reactions with Homoenolates. *J. Am. Chem. Soc.* **2010**, *132*, 5345−5347.
(325) Nair, V.; Vellalath, S.; Poonoth, M.; Mohan, R.; Suresh, E. N-Heterocyclic Carbene Catalyzed Reaction of Enals and 1,2-Dicarbonyl Compounds: Stereoselective Synthesis of Spiro γ-Butyrolactones. *Org. Lett.* **2006**, *8*, 507−509.
(326) Sun, L.-H.; Shen, L.-T.; Ye, S. Highly Diastereo- and Enantioselective NHC-Catalyzed [3 + 2] Annulation of Enals and Isatins. *Chem. Commun.* **2011**, *47*, 10136−10138.
(327) Dugal-Tessier, J.; O'Bryan, E. A.; Schroeder, T. B. H.; Cohen, D. T.; Scheidt, K. A. An N-Heterocyclic Carbene/Lewis Acid Strategy for the Stereoselective Synthesis of Spirooxindole Lactones. *Angew. Chem., Int. Ed.* **2012**, *51*, 4963−4967.
(328) Fairlamb, I. J. S. Asymmetric Cycloisomerization of 1,6- and 1,7-Enynes by Transition-Metal Catalysts. *Angew. Chem., Int. Ed.* **2004**, *43*, 1048−1052.

DOI: 10.1021/acs.chemrev.7b00151
Chem. Rev. 2017, 117, 10502−10566

(329) Nakamura, I.; Yamamoto, Y. Transition-Metal-Catalyzed Reactions in Heterocyclic Synthesis. *Chem. Rev.* **2004**, *104*, 2127−2198.
(330) Michelet, V.; Toullec, P. Y.; Genêt, J.-P. Cycloisomerization of 1,*n*-Enynes: Challenging Metal-Catalyzed Rearrangements and Mechanistic Insights. *Angew. Chem., Int. Ed.* **2008**, *47*, 4268−4315.
(331) Yamamoto, Y. Transition-Metal-Catalyzed Cycloisomerizations of α,ω-Dienes. *Chem. Rev.* **2012**, *112*, 4736−4769.
(332) Watson, I. D. G.; Toste, F. D. Catalytic Enantioselective Carbon-Carbon Bond Formation Using Cycloisomerization Reactions. *Chem. Sci.* **2012**, *3*, 2899−2919.
(333) Zhang, Q.; Lu, X. Highly Enantioselective Palladium(II)-Catalyzed Cyclization of (*Z*)-4′-Acetoxy-2′-Butenyl 2-Alkynoates: An Efficient Synthesis of Optically Active γ-Butyrolactones. *J. Am. Chem. Soc.* **2000**, *122*, 7604−7605.
(334) Zhang, Q.; Lu, X.; Han, X. Palladium(II)-Catalyzed Asymmetric Cyclization of (*Z*)-4′-Acetoxy-2′-Butenyl 2-Alkynoates. Role of Nitrogen-Containing Ligands in Palladium(II)-Mediated Reactions. *J. Org. Chem.* **2001**, *66*, 7676−7684.
(335) Hodgson, D. M.; Talbot, E. P. A.; Clark, B. P. Catalytic Asymmetric Synthesis of (+)-Anthecotulide Using Enyne and Meyer−Schuster Rearrangements. *Org. Lett.* **2011**, *13*, 5751−5753.
(336) Brunner, M.; Alper, H. The First Stereoselective Palladium-Catalyzed Cyclocarbonylation of β,γ-Substituted Allylic Alcohols. *J. Org. Chem.* **1997**, *62*, 7565−7568.
(337) Yu, W.-Y.; Bensimon, C.; Alper, H. A Novel Palladium-Catalyzed Asymmetric Cyclocarbonylation of Allylic Alcohols to γ-Butyrolactones. *Chem. - Eur. J.* **1997**, *3*, 417−423.
(338) Cao, P.; Zhang, X. Highly Enantioselective Cyclocarbonylation of Allylic Alcohols Catalyzed by Novel Pd-1,4-Bisphosphine Complexes. *J. Am. Chem. Soc.* **1999**, *121*, 7708−7709.
(339) Mandal, S. K.; Amin, S. R.; Crowe, W. E. γ-Butyrolactone Synthesis via Catalytic Asymmetric Cyclocarbonylation. *J. Am. Chem. Soc.* **2001**, *123*, 6457−6458.
(340) Upadhya, T. T.; Gurunath, S.; Sudalai, A. A New and Short Enantioselective Synthesis of (*R*)-Pantolactone. *Tetrahedron: Asymmetry* **1999**, *10*, 2899−2904.
(341) Genet, J.-P.; Pinel, C.; Mallart, S.; Juge, S.; Cailhol, N.; Laffitte, J. A. (*R,R*) Dipamp-Ruthenium (II) (2-methylallyl)$_2$: Synthesis and Selected Use in Asymmetric Hydrogenation. *Tetrahedron Lett.* **1992**, *33*, 5343−5346.
(342) Evans, D. A.; Wu, J.; Masse, C. E.; MacMillan, D. W. C. A General Method for the Enantioselective Synthesis of Pantolactone Derivatives. *Org. Lett.* **2002**, *4*, 3379−3382.
(343) Hajra, S.; Giri, A. K. Organocatalytic and Enantioselective Synthesis of β-(Hydroxyalkyl)-γ-Butyrolactones. *J. Org. Chem.* **2008**, *73*, 3935−3937.
(344) Hajra, S.; Giri, A. K.; Hazra, S. Asymmetric Syntheses of (−)-Enterolactone and (7′*R*)-7′-Hydroxyenterolactone via Organocatalyzed Aldol Reaction. *J. Org. Chem.* **2009**, *74*, 7978−7981.
(345) Yanagisawa, A.; Kushihara, N.; Yoshida, K. Catalytic Enantioselective Synthesis of Chiral γ-Butyrolactones. *Org. Lett.* **2011**, *13*, 1576−1578.
(346) Manoni, F.; Cornaggia, C.; Murray, J.; Tallon, S.; Connon, S. J. Catalytic, Enantio- and Diastereoselective Synthesis of γ-Butyrolactones Incorporating Quaternary Stereocentres. *Chem. Commun.* **2012**, *48*, 6502−6504.
(347) Juhl, K.; Gathergood, N.; Jorgensen, K. A. Catalytic Asymmetric Homo-Aldol Reaction of Pyruvate-a Chiral Lewis Acid Catalyst That Mimics Aldolase Enzymes. *Chem. Commun.* **2000**, *22*, 2211−2212.
(348) Burke, E. D.; Lim, N. K.; Gleason, J. L. Catalytic Enantioselective Homoaldol Reactions Using Binol Titanium(IV) Fluoride Catalysts. *Synlett* **2003**, *2003*, 0390−0392.
(349) Gathergood, N.; Juhl, K.; Poulsen, T. B.; Thordrup, K.; Jorgensen, K. A. Direct Catalytic Asymmetric Aldol Reactions of Pyruvates: Scope and Mechanism. *Org. Biomol. Chem.* **2004**, *2*, 1077−1085.
(350) Vincent, J.-M.; Margottin, C.; Berlande, M.; Cavagnat, D.; Buffeteau, T.; Landais, Y. A Concise Organocatalytic and Enantioselective Synthesis of Isotetronic Acids. *Chem. Commun.* **2007**, *45*, 4782−4784.
(351) Zhang, B.; Jiang, Z.; Zhou, X.; Lu, S.; Li, J.; Liu, Y.; Li, C. The Synthesis of Chiral Isotetronic Acids with Amphiphilic Imidazole/Pyrrolidine Catalysts Assembled in Oil-in-Water Emulsion Droplets. *Angew. Chem., Int. Ed.* **2012**, *51*, 13159−13162.
(352) Zhuo, C.-X.; Zhang, W.; You, S.-L. Catalytic Asymmetric Dearomatization Reactions. *Angew. Chem., Int. Ed.* **2012**, *51*, 12662−12686.
(353) Dohi, T.; Maruyama, A.; Takenaga, N.; Senami, K.; Minamitsuji, Y.; Fujioka, H.; Caemmerer, S. B.; Kita, Y. A Chiral Hypervalent Iodine(III) Reagent for Enantioselective Dearomatization of Phenols. *Angew. Chem., Int. Ed.* **2008**, *47*, 3787−3790.
(354) Dohi, T.; Takenaga, N.; Nakae, T.; Toyoda, Y.; Yamasaki, M.; Shiro, M.; Fujioka, H.; Maruyama, A.; Kita, Y. Asymmetric Dearomatizing Spirolactonization of Naphthols Catalyzed by Spirobiindane-Based Chiral Hypervalent Iodine Species. *J. Am. Chem. Soc.* **2013**, *135*, 4558−4566.
(355) Uyanik, M.; Yasui, T.; Ishihara, K. Enantioselective Kita Oxidative Spirolactonization Catalyzed by In Situ Generated Chiral Hypervalent Iodine(III) Species. *Angew. Chem., Int. Ed.* **2010**, *49*, 2175−2177.
(356) Uyanik, M.; Yasui, T.; Ishihara, K. Chiral Hypervalent Iodine-Catalyzed Enantioselective Oxidative Kita Spirolactonization of 1-Naphthol Derivatives and One-Pot Diastereo-Selective Oxidation to Epoxyspirolactones. *Tetrahedron* **2010**, *66*, 5841−5851.
(357) Takizawa, S.; Nguyen, T. M.-N.; Grossmann, A.; Enders, D.; Sasai, H. Enantioselective Synthesis of α-Alkylidene-γ-Butyrolactones: Intramolecular Rauhut−Currier Reaction Promoted by Acid/Base Organocatalysts. *Angew. Chem., Int. Ed.* **2012**, *51*, 5423−5426.
(358) Qabaja, G.; Wilent, J. E.; Benavides, A. R.; Bullard, G. E.; Petersen, K. S. Facile Synthesis of Versatile Enantioenriched α-Substituted Hydroxy Esters through a Brønsted Acid Catalyzed Kinetic Resolution. *Org. Lett.* **2013**, *15*, 1266−1269.
(359) Wilent, J.; Petersen, K. S. Enantioselective Desymmetrization of Diesters. *J. Org. Chem.* **2014**, *79*, 2303−2307.
(360) Čorić, I.; Vellalath, S.; List, B. Catalytic Asymmetric Transacetalization. *J. Am. Chem. Soc.* **2010**, *132*, 8536−8537.
(361) Čorić, I.; Müller, S.; List, B. Kinetic Resolution of Homoaldols via Catalytic Asymmetric Transacetalization. *J. Am. Chem. Soc.* **2010**, *132*, 17370−17373.
(362) Greatrex, B. W.; Kimber, M. C.; Taylor, D. K.; Fallon, G.; Tiekink, E. R. T. 1,2-Dioxines as Masked Cis γ-Hydroxy Enones and Their Versatility in the Synthesis of Highly Substituted γ-Lactones. *J. Org. Chem.* **2002**, *67*, 5307−5314.
(363) Priest, J.; Longland, M. R.; Elsegood, M. R. J.; Kimber, M. C. An Asymmetric Synthesis of Trans-Fused Butyrolactones from Endoperoxides. *J. Org. Chem.* **2013**, *78*, 3476−3481.
(364) Kornblum, N.; DeLaMare, H. E. The Base Catalyzed Decomposition of a Dialkyl Peroxide. *J. Am. Chem. Soc.* **1951**, *73*, 880−881.
(365) Montgomery, T. P.; Hassan, A.; Park, B. Y.; Krische, M. J. Enantioselective Conversion of Primary Alcohols to α-Exo-Methylene γ-Butyrolactones via Iridium-Catalyzed C−C Bond-Forming Transfer Hydrogenation: 2-(Alkoxycarbonyl)allylation. *J. Am. Chem. Soc.* **2012**, *134*, 11100−11103.
(366) Geurts, K.; Fletcher, S. P.; Feringa, B. L. Copper Catalyzed Asymmetric Synthesis of Chiral Allylic Esters. *J. Am. Chem. Soc.* **2006**, *128*, 15572−15573.
(367) Mao, B.; Geurts, K.; Fañanás-Mastral, M.; van Zijl, A. W.; Fletcher, S. P.; Minnaard, A. J.; Feringa, B. L. Catalytic Enantioselective Synthesis of Naturally Occurring Butenolides via *Hetero*-Allylic Alkylation and Ring Closing Metathesis. *Org. Lett.* **2011**, *13*, 948−951.
(368) Fukata, Y.; Okamura, T.; Asano, K.; Matsubara, S. Asymmetric Isomerization of ω-Hydroxy-α,β-Unsaturated Thioesters into β-Mercaptolactones by a Bifunctional Aminothiourea Catalyst. *Org. Lett.* **2014**, *16*, 2184−2187.

DOI: 10.1021/acs.chemrev.7b00151
Chem. Rev. 2017, 117, 10502−10566

(369) Trost, B. M.; Hirano, K. Dinuclear Zinc Catalyzed Asymmetric Spirannulation Reaction: An Umpolung Strategy for Formation of α-Alkylated-α-Hydroxyoxindoles. *Org. Lett.* **2012**, *14*, 2446−2449.
(370) Sternativo, S.; Calandriello, A.; Costantino, F.; Testaferri, L.; Tiecco, M.; Marini, F. A Highly Enantioselective One-Pot Synthesis of Spirolactones by an Organocatalyzed Michael Addition/Cyclization Sequence. *Angew. Chem., Int. Ed.* **2011**, *50*, 9382−9385.
(371) Klimczyk, S.; Misale, A.; Huang, X.; Maulide, N. Dimeric TADDOL Phosphoramidites in Asymmetric Catalysis: Domino Deracemization and Cyclopropanation of Sulfonium Ylides. *Angew. Chem., Int. Ed.* **2015**, *54*, 10365−10369.
(372) Wu, Y.; Singh, R. P.; Deng, L. Asymmetric Olefin Isomerization of Butenolides via Proton Transfer Catalysis by an Organic Molecule. *J. Am. Chem. Soc.* **2011**, *133*, 12458−12461.
(373) Xue, X.-S.; Li, X.; Yu, A.; Yang, C.; Song, C.; Cheng, J.-P. Mechanism and Selectivity of Bioinspired Cinchona Alkaloid Derivatives Catalyzed Asymmetric Olefin Isomerization: A Computational Study. *J. Am. Chem. Soc.* **2013**, *135*, 7462−7473.
(374) Hugelshofer, C. L.; Magauer, T. Total Synthesis of the Leucosceptroid Family of Natural Products. *J. Am. Chem. Soc.* **2015**, *137*, 3807−3810.
(375) Tsuchikama, K.; Kuwata, Y.; Shibata, T. Highly Enantioselective Construction of a Chiral Spirocyclic Structure by the [2 + 2 + 2] Cycloaddition of Diynes and *exo*-Methylene Cyclic Compounds. *J. Am. Chem. Soc.* **2006**, *128*, 13686−13687.
(376) Kurono, N.; Kondo, T.; Wakabayashi, M.; Ooka, H.; Inoue, T.; Tachikawa, H.; Ohkuma, T. Enantiomer-Selective Carbamoylation of Racemic α-Hydroxy γ-Lactones with Chiral CuII Catalysts: an Example of a Highly Active Lewis Acid Catalyzed Reaction. *Chem. - Asian J.* **2008**, *3*, 1289−1297.
(377) Nakata, K.; Gotoh, K.; Ono, K.; Futami, K.; Shiina, I. Kinetic Resolution of Racemic 2-Hydroxy-γ-Butyrolactones by Asymmetric Esterification Using Diphenylacetic Acid with Pivalic Anhydride and a Chiral Acyl-Transfer Catalyst. *Org. Lett.* **2013**, *15*, 1170−1173.
(378) Chhor, R. B.; Nosse, B.; Sörgel, S.; Böhm, C.; Seitz, M.; Reiser, O. Enantioselective Synthesis of Paraconic Acids. *Chem. - Eur. J.* **2003**, *9*, 260−270.
(379) Kalidindi, S.; Jeong, W. B.; Schall, A.; Bandichhor, R.; Nosse, B.; Reiser, O. Enantioselective Synthesis of Arglabin. *Angew. Chem., Int. Ed.* **2007**, *46*, 6361.
(380) Harrar, K.; Reiser, O. Enantioselective synthesis of (−)-paeonilide. *Chem. Commun.* **2012**, *48*, 3457−3459.
(381) Kreuzer, A.; Kerres, S.; Ertl, T.; Rücker, H.; Amslinger, S.; Reiser, O. Asymmetric Synthesis of Both Enantiomers of Arteludovicinolide A. *Org. Lett.* **2013**, *15*, 3420−3423.
(382) Bergmann, A.; Reiser, O. Enantioselective Synthesis of Xanthatin. *Chem. - Eur. J.* **2014**, *20*, 7613−7615.

DOI: 10.1021/acs.chemrev.7b00151
Chem. Rev. 2017, 117, 10502−10566