有机化学 DOI: 10.6023/cjoc202002032 综述与进展
Chinese Journal of Organic Chemistry REVIEW

不对称催化实现的二氧化碳固定直接合成光学活性小分子的最新进展

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摘要 固定二氧化碳(CO_2)的工业过程远远落后于人类活动产生的碳排放量. 由于二氧化碳是一种丰富、无毒且廉价易得的碳资源, 因此开发出将二氧化碳转化为有价值的产品, 以实现可持续发展的化学合成是非常有意义的. 基于过渡金属催化和有机催化活化 CO_2 的机理研究, 近年来已开发出多种有效的 CO_2 的不对称化学固定方法. 讨论了通过 CO_2 的不对称化学固定实现的小分子化合物的手性合成的进展. 通过阐述催化剂、CO_2 和底物之间的相互作用, 旨在激发 CO_2 不对称转化的新型催化系统的设计.

关键词 二氧化碳; 不对称催化; 对映选择性; 羧基化; 环化反应

Recent Advances of CO_2 Fixation via Asymmetric Catalysis for the Direct Synthesis of Optically Active Small Molecules

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Abstract Industrial processes of fixing carbon dioxide (CO_2) lag far behind the carbon emission generated by human activity. Since CO_2 is an abundant, non-toxic, and cost-effective one carbon source, it is highly desirable to develop methodologies on converting CO_2 into valuable products for sustainable purpose. Based on the mechanistic insight of CO_2 activation by transition-metal catalyst and organocatalyst, a variety of efficient asymmetric CO_2 chemical fixation processes have been developed in recent years. This review discusses the advances of enantioselective synthesis of small molecules by asymmetric catalytic reactions with CO_2. The interaction between catalyst, CO_2 and substrate has been elaborated aiming to inspire the design of new catalytic systems for asymmetric CO_2 transformation.

Keywords carbon dioxide; asymmetric catalysis; enantioselectivity; carboxylation; cyclization

The current global economic development has accelerated carbon emission, and the amount of CO_2 generated by human activity is estimated to be 35 billion tons in 2015.[1] The relentless rise of atmospheric CO_2 is thought to be a main cause of global warming and abnormal climate changes. However, CO_2 is an attractive C_1 building block in synthetic chemistry and chemical industry because of its abundance, non-toxicity, and low cost. Therefore, conversion of CO_2 into valuable products will meet the demand of sustainable chemistry, although it earns a small proportion from carbon emission at the present stage. In this respect, a lot of research has been conducted on the development of new transformations using CO_2 as a C_1 source, including transition metal catalysis, photocatalysis, electrocatalysis, ionic liquids catalysis, *etc*.[2-18] Industrial synthetic applications of CO_2 have also been realized in the synthesis of salicylic acid, urea, methanol, and polycarbonates.[18-21]

In general, reactive reagents or harsh conditions are

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Received February 24, 2020; revised May 8, 2020; published online May 15, 2020.
Project supported by the National Natural Science Foundation of China (Nos. 21702212, 21772208) and the Key Research Program of Frontier Sciences of Chinese Academy of Sciences (No. QYZDJSSW-SLH051).
国家自然科学基金(Nos. 21702212, 21772208)和中国科学院前沿科学基金(No. QYZDJSSW-SLH051)资助项目.
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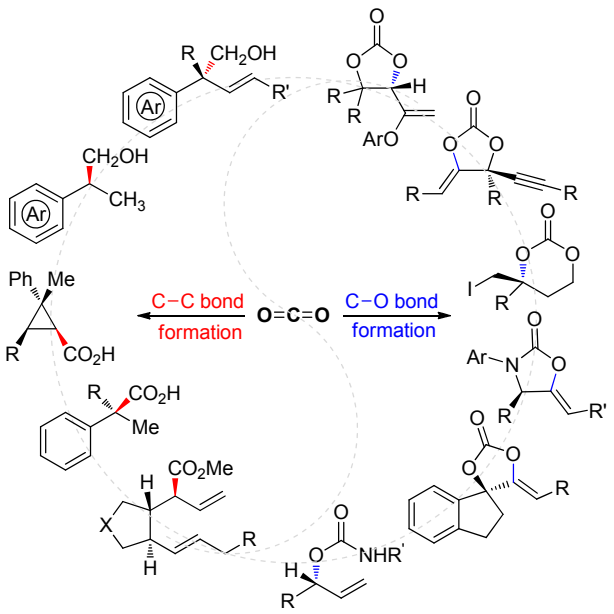
needed in the transformation of CO_2 because of its thermodynamic stability and/or kinetic inertness. First, the thermodynamic stability of CO_2 imposes an input of energy to convert it into fuels or chemicals. The standard reduction potential (E^0_R) is a measure of the spontaneity of a given reaction relative to the hydrogen evolution reaction (HER) as equation $\Delta G° = -nFE^0_{rxn}$. Due to the relative stability of gaseous CO_2 ($\Delta G^0_f = -394.4$ kJ•mol^{-1}), enough energy must be introduced into the reaction to drive its transformation to the products. Second, catalysts are usually required to ensure that the activation barriers remain as low as possible in the presence of chemical transformation processes. Thus, the overall carbon balance for CO_2 utilization is not hampered by thermal loading needed to overcome high energy transition states.[22-23] Traditional methods for the transformation of CO_2 generally need high-energy substrates and reagents, such as strong nucleophilic organometallic reagents (the Grignard reagents or organolithiums), small-ring heterocycles with high ring strain (epoxides or aziridines), and highly reactive reductants, *etc*.[24-26] Physical energy such as light or electricity was also employed to solve the issues brought by thermodynamic stability of CO_2.[27-28] However, these traditional methods usually require multi-steps, resulting in waste or undesirable by-products.

Over the past decades, catalysts have been widely used to activate CO_2 and facilitate its transformations. A variety of transition-metal-catalyzed carboxylations of alkenes, alkynes, dienes, allenes, organic halides, organometallic reagents, or C—H compounds have been reported for the synthesis of carboxylic acids and their derivatives.[29-37] On the other hand, chemists have also utilized organocatalysts, such as *N*-heterocyclic carbenes, phosphines, amines, and frustrated Lewis pairs, to activate CO_2 in its conversion to small molecules.[38-40] The efficiency and applicability of CO_2 transformations were thus improved greatly in organic synthesis. CO_2 fixation and subsequent catalytic conversion to fine chemicals, particularly to chiral molecules, represents a highly value-added process. Enantiopure carbonates, carbamates and carboxylic acid derivatives are versatile synthons and widespread in natural products, drug molecules, and advanced materials. Catalytic enantioselective methods for the synthesis chiral carbonates and carbamates with CO_2 via kinetic resolution of racemic epoxides and aziridines have been well explored. These achievements have been summarized in previous publications [41-43] and will not be discussed here. In 2017, a general review on the enantioselective synthesis of carboxylic acid derivatives and carbamates with CO_2 was reported in broad content, including asymmetric carboxylation, chiral transfer, and ring-opening of epoxides, *etc*.[44] Herein, we would like to focus on the advances of CO_2 fixation by catalytic asymmetric via carbon-carbon (C—C) and carbon–oxygen (C—O) bonds formation (Scheme 1). The interaction between catalyst, CO_2 and substrate will be emphasized in this review to inspire the design of new catalytic systems for asymmetric CO_2 transformations.



Scheme 1 Enantioselective synthesis of small molecules via CO_2 fixation by asymmetric catalysis

1 CO_2 Fixation by asymmetric catalysis via C—C bond formation

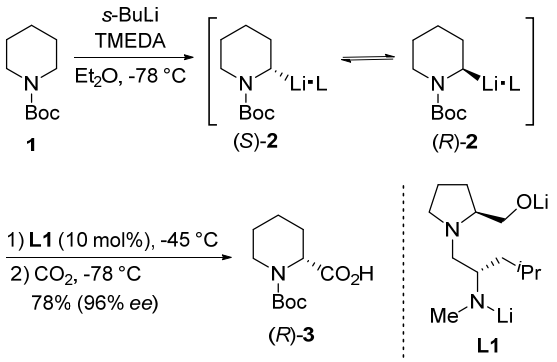
The development of new C—C bond forming reactions using sustainable chemical feedstock is rather attractive in synthetic chemistry. In this respect, conversions of CO_2 into useful chemicals have gained considerable attention in recent years. One of the major challenges to synthesize chemicals with CO_2 as a raw material is to construct C—C bonds with high efficiency and selectivity, including chemo-, regio-, and stereo-selectivity, expecially enantioselectivity. Because of the high thermodynamic and kinetic stability of CO_2, most of the C—C bond-forming reactions with CO_2 were carried out under harsh conditions, such as high pressure of CO_2 and high reaction temperature. It is difficult to control the enantioselectivity in these reactions. Recently, transition-metal-catalyzed CO_2 fixation to form C—C bond has emerged to be a mild and powerful tool to convert CO_2 into useful chemicals. However, highly enantioselective C—C bond-forming reactions with CO_2 as C_1 source by asymmetric catalysis is still challenging and rare.

2 Enantioselective carboxylation

In 1981, an asymmetric CO_2 fixation reaction was reported by Sato and co-workers[45] but with low enantioselectivity control. Asymmetric carboxylation of π-allyltitanium complex tethered with chiral cyclopentadienyl ligand was achieved and 2-methylbut-3-enoic acid was obtained in 70% yield with 19% *ee*.

In 2010, Gawley and co-workers[46] reported a catalytic dynamic resolution of rac-2-lithio-*N*-Boc-piperidine (**2**), which was obtained by deprotonation of *N*-Boc-piperidine (**1**) with *s*-BuLi and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine

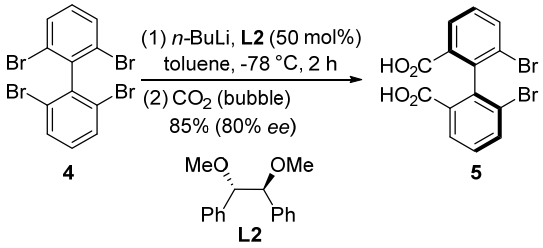
(TMEDA) at a low temperature (Scheme 2). Catalytic dilithiodiaminoalkoxide (**L1**) was found to be an efficient chiral catalyst in this reaction. The authors investigated the plot of ΔG versus temperature for racemization of **2** and dynamic thermodynamic resolution of **2**•**L1** in the presence of TMEDA. The result revealed that the barrier for dynamic thermodynamic resolution of 2•**L1** is lower than racemization of it below −27 ℃. Lithiation of **1** at −78 ℃, followed by ligand exchange at −45 ℃ and quenching with various electrophiles at −78 ℃ afforded 2-substituted *N*-Boc-piperidines with excellent enantioselectivities. When CO_2 was used as an electrophile, (*R*)-*N*-Boc-pipecolic acid (**3**) was obtained in 78% yield with 96% *ee*.



Scheme 2 Asymmetric dynamic resolution of 2-lithio-*N*-Boc-piperidine **2** with CO_2

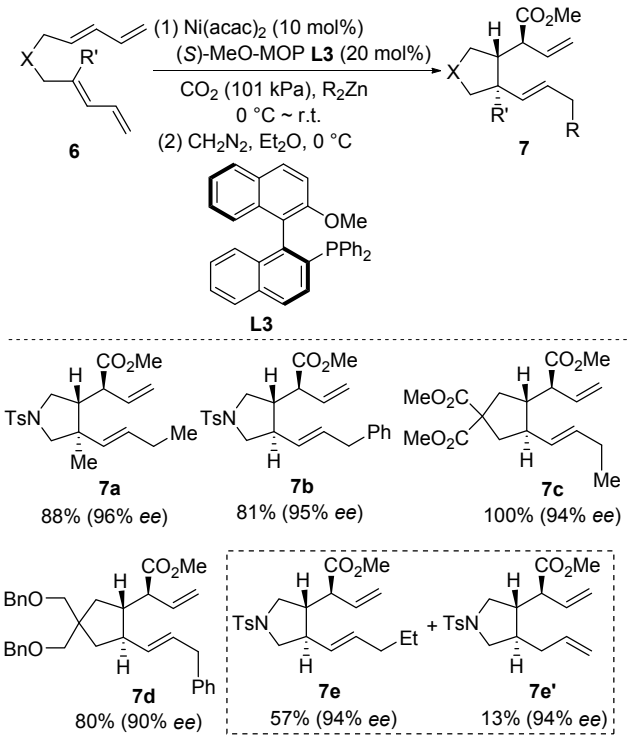
Later, Alexakis and co-workers[47] reported an asymmetric desymmetrization of 2,2'-dibromobiphenyls to synthesize biphenyl molecules with axial chirality via an enantioselective bromine-lithium exchange process. They investigated the influence factors on the backbone of the diether ligand. The increase of enantioselectivity was observed by decreasing the hindrance of the backbone of chiral ligand. With methyl-protected diol derivative **L2** as a chiral ligand, 2,2',6,6'-tetrabromobiphenyl (**4**) was converted to atropoisomeric 1,1'-biphenyl-2,2'-dicarboxylic acid (**5**) in 85% yield with 80% *ee* via bromine-lithium exchange followed by quenching with CO_2 (Scheme 3). This was the first highly selective (up to 82% *ee*) bromine-lithium exchange with a catalytic amount of ligand (0.5 equiv., 25% per BrLi exchange). Recently, Hamashima and co-workers[48] disclosed that (*S*)-1,1'-binaphthyl-2,2'-dicarboxylic acid could be easily accessed by carboxylation of 2,2'-dilithium-1,1'-binaphthalene generated from lithiation of (*S*)-BINOL bis(diethylphosphate) with lithium/naphthalene. Notably, the reaction could be carried out on gram-scale and the corresponding di-acid was obtained with 99% *ee*.

In 2002, a highly regio- and stereo-selective ring-closing carboxylation of bis-1,3-dienes with CO_2 was reported by Mori and co-workers.[49] After that, a breakthrough in asymmetric transition-metal-catalyzed C—C bond-forming reaction with CO_2 was reported by the same group in 2004 (Scheme 4).[50] In the presence of 10 mol% of $Ni(acac)_2$ and 20 mol% of (*S*)-MeO-MOP (**L3**), a highly regio-, diastereo-, and enantio-selective ring-closing carboxylation of bis-1,3-



Scheme 3 Asymmetric bromine-lithium exchange to synthesize axially chiral di-acid with CO_2

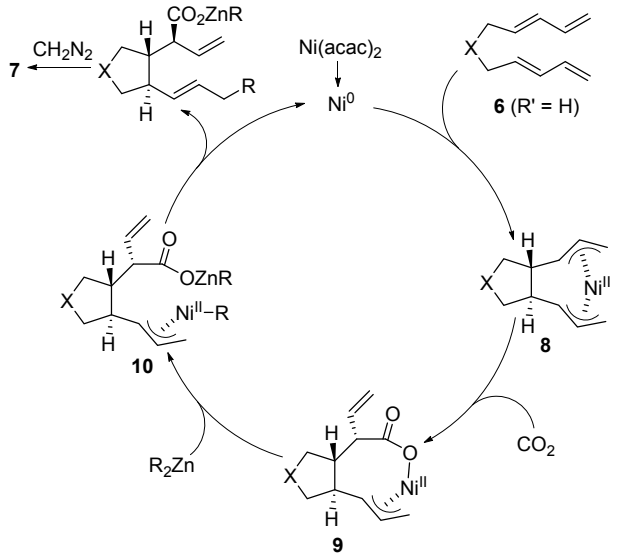
diene (**6**) was realized under atmospheric pressure of CO_2. *Trans*-disubstituted pyrrolidines or cyclopentanes **7** were obtained in high yields with 90%～96% *ee*. Chiral allylic carboxylic acid esters with three continuous stereocenters were synthesized efficiently in one-step. Single diastereoisomer was obtained with dimethylzinc or diphenylzinc as coupling reagents. When diethylzinc was used as a coupling reagent, cyclized products **7e** and **7e'** were obtained simultaneously with the same enantiomeric excess, indicating that they were generated from the same intermediate.



Scheme 4 Ni-catalyzed enantioselective carboxylative cyclization of bis-1,3-dienes with CO_2

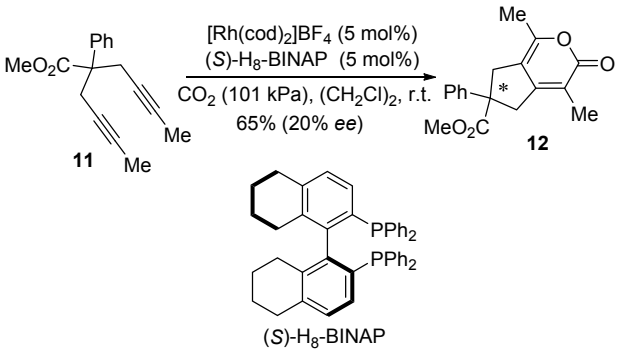
The authors proposed a plausible mechanism in Scheme 5. The reaction is initiated by oxidative cyclometalation of bis-1,3-diene **6** with Ni^0 complex generating cyclized bis-π-allylnickel species **8**. Then insertion of CO_2 into the Ni—C bond produces carboxylates **9**. After transmetallation with an organozinc reagent, π-allylnickel intermediate **10** is generated. Reductive elimination from **10** provides the corresponding carboxylates and regenerates the Ni^0 catalyst. The final product **7** is obtained after quenching with

diazomethane. When diethylzinc is used as coupling reagent, complex **10** can undergo *β*-hydride elimination to afford π-allylnickel hydride complex. Then the byproduct **7e'** is generated after reductive elimination.



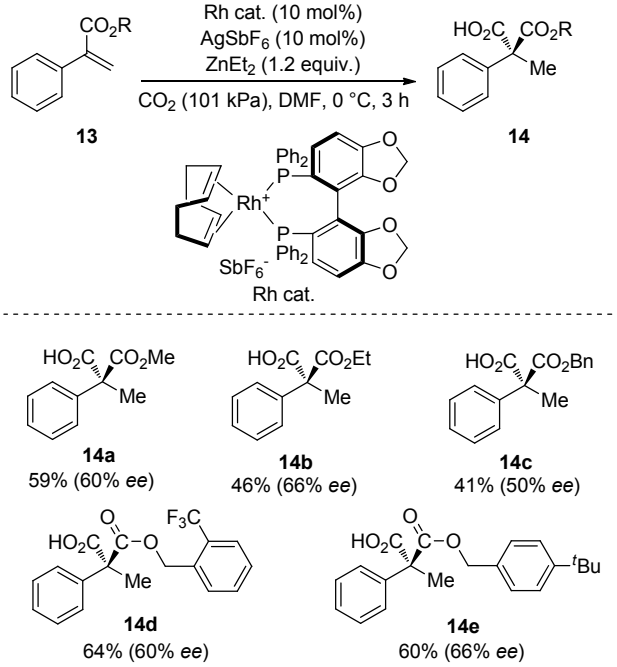
Scheme 5 Mechanism of Ni-catalyzed carboxylative cyclization of bis-1,3-dienes with CO_2

In 2014, Tanaka and co-workers[51] reported an enantioselective cyclization reaction of prochiral 1,6-diyne **11** with CO_2 via desymmetrization (Scheme 6). The [2+2+2] cycloaddition product **12** was obtained in good yield with a promising enantioselectivity (20% *ee*) using catalytic cationic $[Rh(cod)_2]BF_4$ and (*S*)-H_8-BINAP.



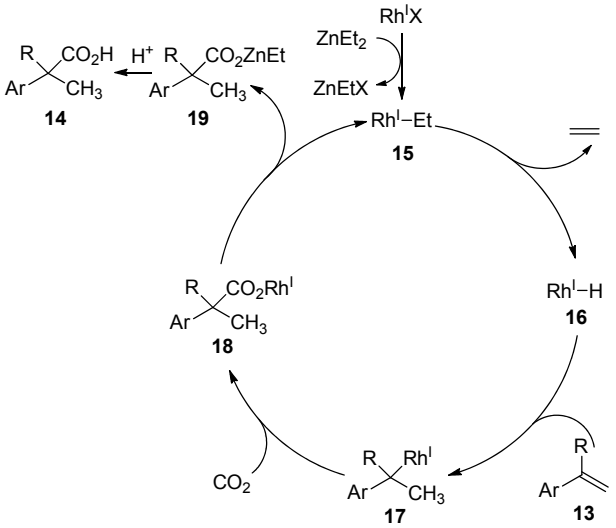
Scheme 6 Rh-catalyzed enantioselective desymmetrization of 1,6-diyne with CO_2

Recently, catalytic hydrocarboxylation of alkenes with CO_2 has been reported using transition-metal-catalyst, such as Ni,[52] Fe,[53] or Co,[54,55] with diethylzinc or ethylmagnesium halides as a hydride source. In 2016, Mikami and co-workers[56] reported a Rh-catalyzed hydrocarboxylation of alkenes with CO_2. Using $[RhCl(cod)]_2$ as catalyst and diethylzinc as hydride source, the corresponding carboxylic acids were obtained in moderate to excellent yields. They also investigated the asymmetric version of this reaction. Enantioselective hydrocarboxylation of *α*-aryl acrylates **13** afforded the corresponding acid **14** bearing a quaternary carbon center with moderate *ee* using cationic (*S*)-Segphos-Rh complex as catalyst and catalytic $AgSbF_6$ as cocatalyst (Scheme 7). In this reaction, the steric and electronic effect on substituent of the ester (R group) has moderate effect on the enantioselectivity of the product. The authors didn't show the influence of aryl group on the enantioselectivity of the product.



Scheme 7 Rh-catalyzed asymmetric hydrocarboxylation of *α*-aryl acrylates

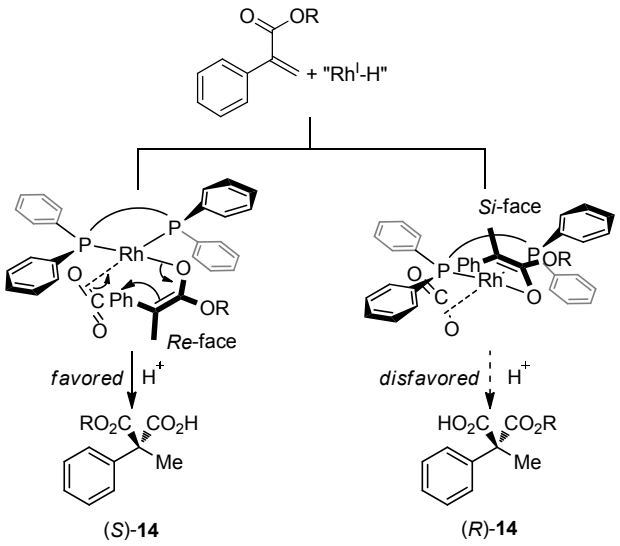
The plausible reaction mechanism is displayed in Scheme 8. First, Rh^I—Et complex **15** is generated by transmetalation of the ethyl group between diethylzinc and Rh^I precursor. Second, *β*-hydride elimination from **15** generates the Rh^I—H species **16** and releases ethylene. Then



Scheme 8 Mechanism of Rh-catalyzed hydrocarboxylation of styrene derivatives with CO_2

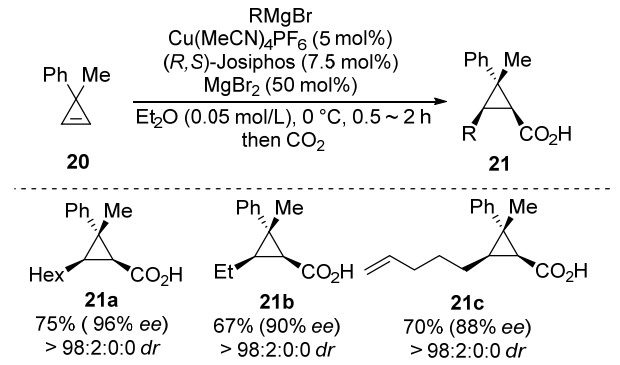
insertion of styrene derivatives into **16** affords benzyl rhodium intermediate **17**, which undergoes insertion of CO_2, followed by transmetalation with diethylzinc producing **19** and regenerates Rh^I—Et complex **15**. Finally, acids **14** are obtained after hydrolysis of **19**.

An enantioselective induction model has been proposed by the authors based on the absolute configuration of product **14** (Scheme 9). The corresponding (*Z*)-Rh^I-enolate is generated by insertion of *α*,*β*-unsaturated esters with Rh^I-H species in an *s*-*trans* fashion. Attack of CO_2 with the enolate by the *Si* face is prevented by the equatorial phenyl group on the phosphorus atom in the chiral ligand. Thus, attack of CO_2 from the *Re* face of the rhodium side would be favored to afford the corresponding product (*S*)-**14**.

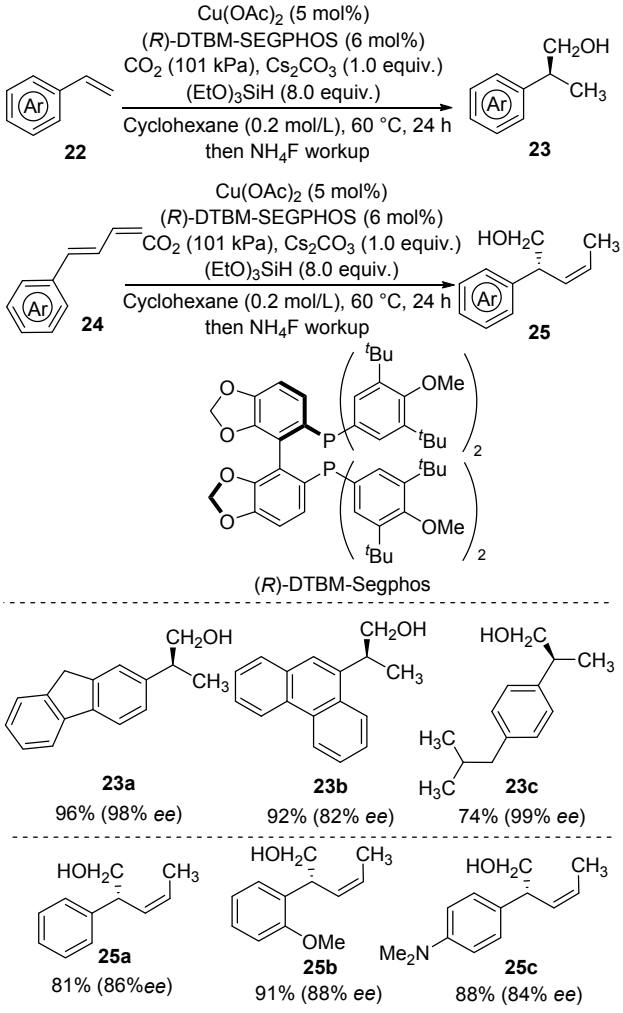


Scheme 9 Plausible reaction model for asymmetric induction of rhodium-catalyzed hydrocarboxylation

In 2017, Marek and co-workers[57] reported a highly diastereo- and enantio-selective Cu-catalyzed carboxylation of poly-substituted cyclopropenes with CO_2 and Grignard reagents. Cyclopropylmetal species was first obtained through a Cu-catalyzed carbomagnesiation reaction, followed by quenching with CO_2 as an electrophile affording the cyclopropyl acid product **21** in good yields with 88%～96% *ee* (Scheme 10). It was shown that the cyclopropylmagnesium species are configurationally stable. The addition of this cyclopropylmagnesium species to electrophile, such as CO_2, leads to the product with clean retention of configuration.



Scheme 10 Cu-catalyzed tandem carboxylation of cyclopropenes with CO_2



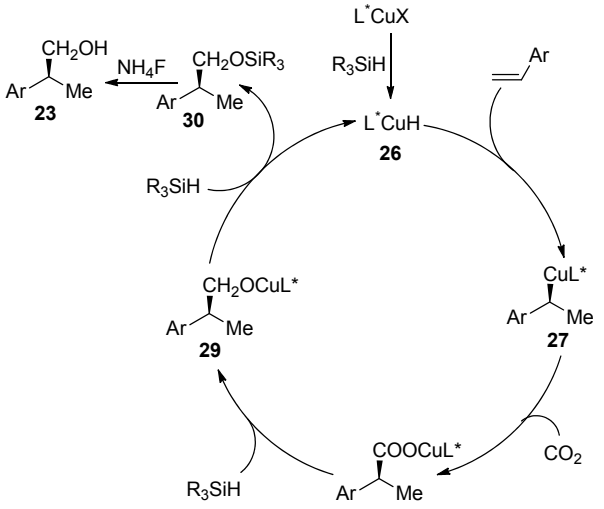
Scheme 11 Cu-catalyzed enantioselective hydroxymethylation of styrenes and 1,3-dienes with CO_2

3 Enantioselective hydroxymethylation

In 2017, Yu and co-workers[58] recently reported the first enantioselective Cu-catalyzed reductive hydroxymethylation of alkenes with CO_2, which provides an efficient method for the synthesis of chiral homobenzylic/allylic alcohols (Scheme 11). Using $Cu(OAc)_2$ as a catalyst, bulky (*R*)-DTBM-Segphos as a chiral ligand, and hydrosilane as a hydride source, styrene derivatives **22** were converted to a variety of chiral homobenzylic alcohols **23** in high yields with excellent enantioselectivities. Moreover, a series of chiral homoallylic alcohols **25** were also generated from aryl substituted 1,3-dienes **24** with high regioselectivity and enantioselectivity under similar conditions. Notably, the homoallylic alcohols were obtained with high *Z*-selectivity for the alkene. The chiral benzylic alcohol **23c** was easily

transformed into the anti-inflammatory drug (*S*)-(+)-ibuprofen.

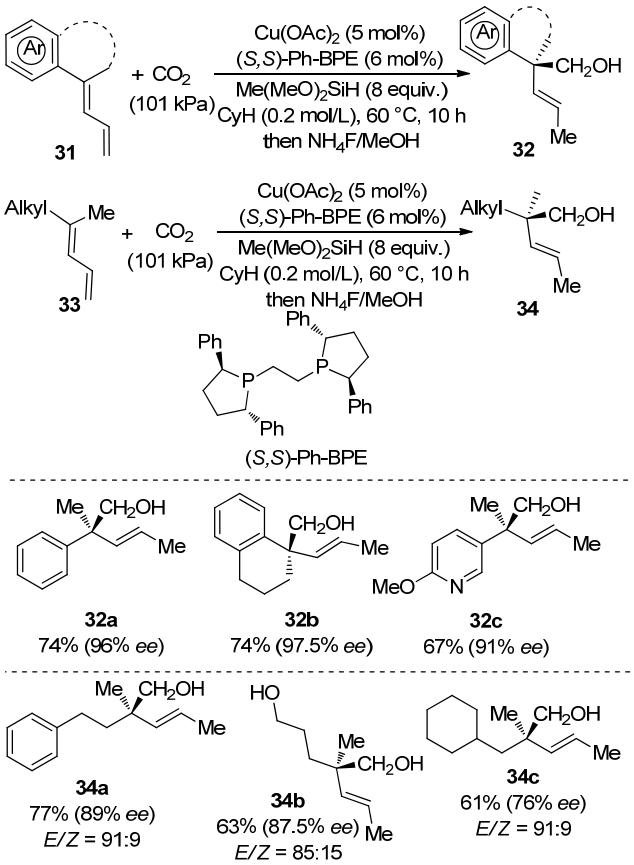
The proposed reaction mechanism is described in Scheme 12. At the beginning, active catalyst L*CuH **26** was generated by reaction of ligand coordinated pre-catalyst with silanes. Then, insertion of alkenes into the Cu—H bond of **26** affords alkyl copper species **27** with excellent regio- and enantio-selectivity. Subsequent carboxylation of **27** with CO_2 generates copper carboxylate **28**. Next, reduction of **28** by hydrosilanes leads to copper alkoxide **29**. Further transmetalation of **29** with hydrosilane generates **30** and releases catalyst **26**. Finally, desilylation of **30** affords the corresponding alcohol **23** by the treatment with NH_4F.



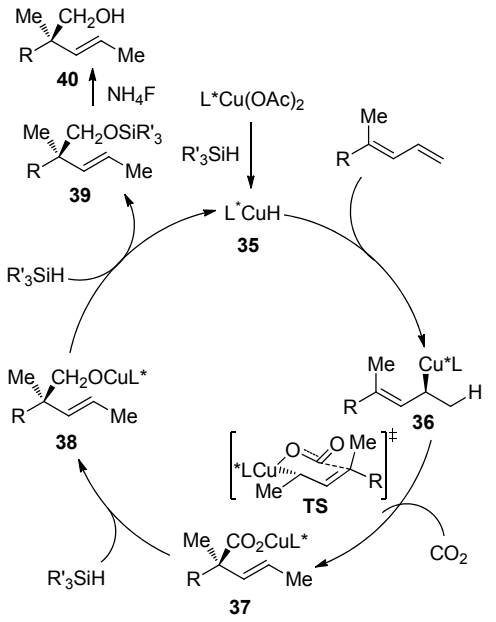
Scheme 12 Mechanism of Cu-catalyzed reductive hydroxymethylation of styrenes

Continuing the previous research, Yu and co-workers[59] recently reported a Cu-catalyzed highly enantioselective hydroxymethylation of 1,3-dienes with CO_2 to construct chiral all-carbon quaternary stereocenter in acyclic molecules. In this studies, homoallylic alcohols **32** or **34** were obtained in moderate to good yields with excellent *ee*s using (*S*,*S*)-Ph-BPE as chiral phosphine ligand and Me-$(MeO)_2SiH$ as hydride source (Scheme 13).

The mechanism of this transformation was shown in Scheme 14. First, a complex between the copper precatalyst and the chiral phosphine ligand reacts with silane generating a catalytically active chiral L*Cu—H species **35**. Then a chiral allylic copper intermediate **36** is formed via a highly regio- and stereo-selective 1,2-*syn*-addition of Cu—H species **35** into 1,3-diene. Steric repulsion might prevent the energy-disfavored 1,3-migration process to generate an isomeric allylcuprate. Through a possible six-membered ring chair like transition state in the nucleophilic addition of **36** to CO_2, the copper carboxylate intermediate **37** is formed. Further reduction of **37** by silane leads to copper alkoxide **38**. Then, σ-bond metathesis of **38** with silane affords silyl ether **39** and regenerates the active catalyst **35**. Finally, the desired alcohol **40** is formed after treatment of **39** with ammonium fluoride.



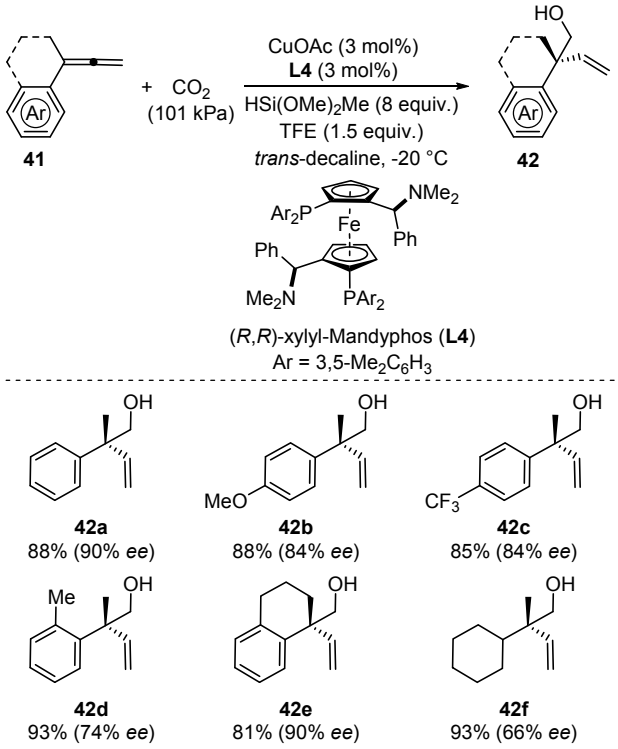
Scheme 13 Cu-catalyzed enantioselective reductive hydroxymethylation of 1,3-dienes to construct all-carbon quaternary stereocenter with CO_2



Scheme 14 Mechanism of Cu-catalyzed enantioselective reductive hydroxymethylation of 1,3-dienes with CO_2

At the same time, Ding and co-workers[60] reported a Cu-catalyzed highly enantioselective hydroxymethylation of 1,1-disubstituted allenes with CO_2 to construct all- carbon chiral quaternary centers. Under the optimized reac-

tion conditions of Cu/Mandyphos (**L4**) catalyst, the corresponding homoallylic alcohol product **42** was obtained in good yields with excellent enantioselectivities from 1,1-disubstituted allenes **41** (Scheme 15).

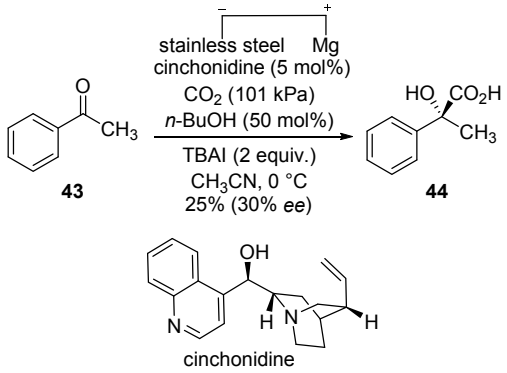


Scheme 15 Cu^{I}-catalyzed enantioselective reductive hydroxymethylation of 1,1-disubstituted allenes with CO_2

4 Enantioselective electrochemical carboxylation

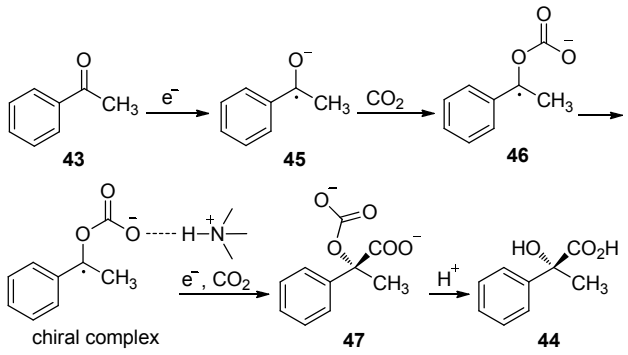
Another noteworthy achievement in CO_2 fixation via asymmetric catalysis is enantioselective electrochemical carboxylation. In 2004, the diastereoselective electrochemical CO_2 fixation using chiral auxiliaries was reported by Feroci, Inesi and co-workers.[61-62] Moderate diastereoselectivity was obtained in electrochemical carboxylation of alkyl halide and cinnamic acid derivatives with CO_2. In 2009, Lu and co-workers[63] reported an inspiring catalytic asymmetric electrochemical reductive carboxylation of acetophenone (**43**) with CO_2 giving 2-hydroxy-2-phenylpropionic acid (**44**) (Scheme 16). The product was obtained in 25% yield with 30% *ee* using cinchonidine as chiral catalyst, butanol as co-catalyst, tetrabutylammonium iodide (TBAI) as supporting electrolyte on stainless steel cathodes. Recently, the efficiency of this reaction was improved by using phenol as co-catalyst and tetrahexyl-ammonium iodide as supporting electrolyte (41% yield, 49% *ee*) under similar conditions.[64]

The authors proposed a possible reaction pathway as shown in Scheme 17. First, a ketyl radical anion **45** is generated from **43** after receiving an electron from the cathode. Next, nucleophilic addition of **45** on CO_2 affords the radical



Scheme 16 Asymmetric electrochemical reductive carboxylation of acetophenone

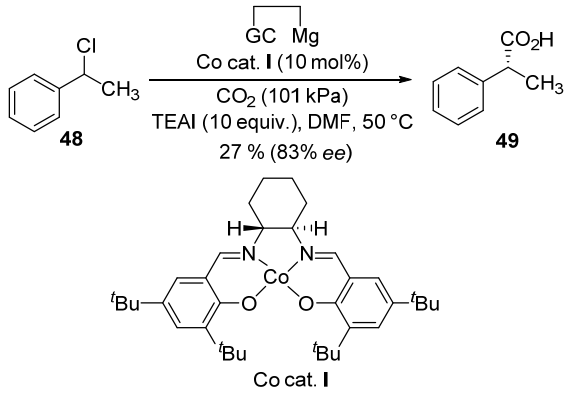
carbonate anion intermediate **46**. A possible chiral proton-donating complex is then generated after **46** bonding to protonated cinchonidine. Further single electron reduction and subsequent carboxylation produces **47**. At last, the final product **44** is formed by decarboxylation and protonation.



Scheme 17 Reaction pathway of electrochemical carboxylation of acetophenone

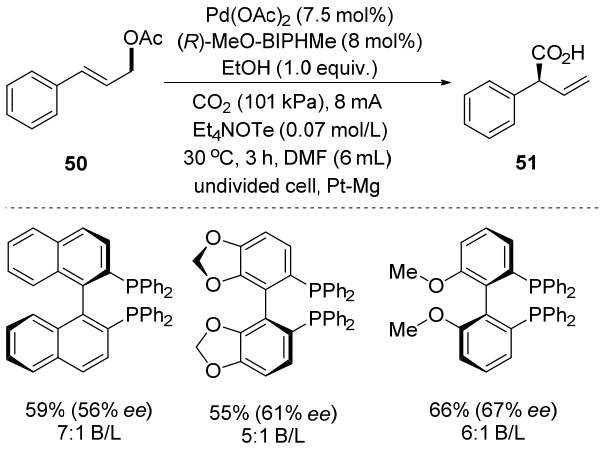
Electrochemical reduction of organic halides has been investigated for several decades. Electrochemical carboxylation of organic halides with CO_2 could produce corresponding carboxylic acids.[65-66] In 2014, Wang, Lu and co-workers[67] reported an asymmetric CO_2 fixation by electrochemical carboxylation of 1-phenylethyl chloride (**48**) (Scheme 18). In the presence of 5 mol% (*R*,*R*)-salen-Co complex (Co cat. **I**) and tetrabutylammonium iodide, racemic 1-phenylethyl chloride **48** was electrocarboxylated affording optically active 2-phenylpropionic acid **49** in 27% yield with 83% *ee* on a glassy carbon (GC) cathode. The electrogenerated [(*R*,*R*)-salen-Co^{I})] species is considered to be the key catalytic species and alkyl Co^{II} complex is thought to be reaction intermediate. Recently, Wang, Lu and co-workers further expanded this reaction into a heterogeneous system.[68] They synthesized a [Co]@Ag composite by entrapment of (*R*,*R*)-salen-Co^{II} complex within silver nanoparticles. Using the chiral [Co]@Ag composite as cathode, electrocarboxylation of racemic 1-phenylethyl bromide with CO_2 afforded **49** in 58% yield with 73% *ee*, without adding additional chiral source. Moreover, the

catalyst [Co]@Ag showed remarkable stability and efficiency. The product could be obtained without significant loss of enantioselecitivity even after recycle the catalyst for 7 times.



Scheme 18 Asymmetric electrocarboxylation of 1-phenylethyl chloride

Recently, Mei and co-worker[69] reported an enantioselective Pd-catalyzed electrochemical carboxylation of allylic acetates with CO_2 (Scheme 19). They found that moderate to good enantioselectivities could be obtained using $Pd(OAc)_2$ as catalyst and chiral bidentate phosphine as ligands. The carboxylation reaction was performed with $Pd(OAc)_2$ as catalyst, Et_4NOTs as electrolyte, EtOH as additive, and DMF as solvent at 30 ℃ under constant current electrolysis conditions of 8.0 mA (J=8.0 mA•cm^{-2}) and 3 F/mol. After screening several chiral bidentate phosphine ligands, carboxylation of **50** with CO_2 gave allylic acid **51** in 66% yield with 67% *ee* using (*R*)-MeO-BIPHMe as ligand.

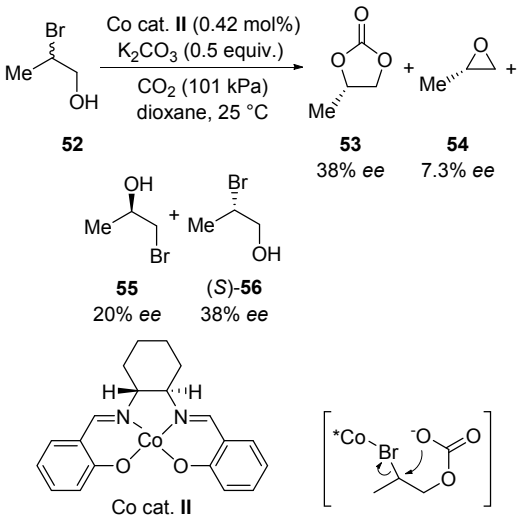


Scheme 19 Pd-catalyzed reductive electrocarboxylation of allyl esters with CO_2

5 CO_2 Fixation by asymmetric catalysis via C—O bond formation

The central carbon atom of CO_2 bears strong electrophilicity and the oxygen atoms act as a Lewis base with weak nucleophilicity. The structure property of CO_2 makes it both an electrophile at carbon atom and a nucleophile at oxygen atom. Accordingly, cyclic carbonates and carbamates have been synthesized by reaction of CO_2 with epoxides and aziridines.[70-72] In the other hand, nucleophiles such as alcohols and amines can attack the central carbon atom of CO_2 generating carbonate and carbamate anion. Subsequent anion trapping with electrophiles affords carbonate and carbamate. By design of proper substrates and choosing of suitable catalysts, chemists have developed several efficient catalytic systems for the enantioselectvie synthesis of carbonate and carbamate with CO_2. This type of asymmetric CO_2 fixation reaction is summarized as below.

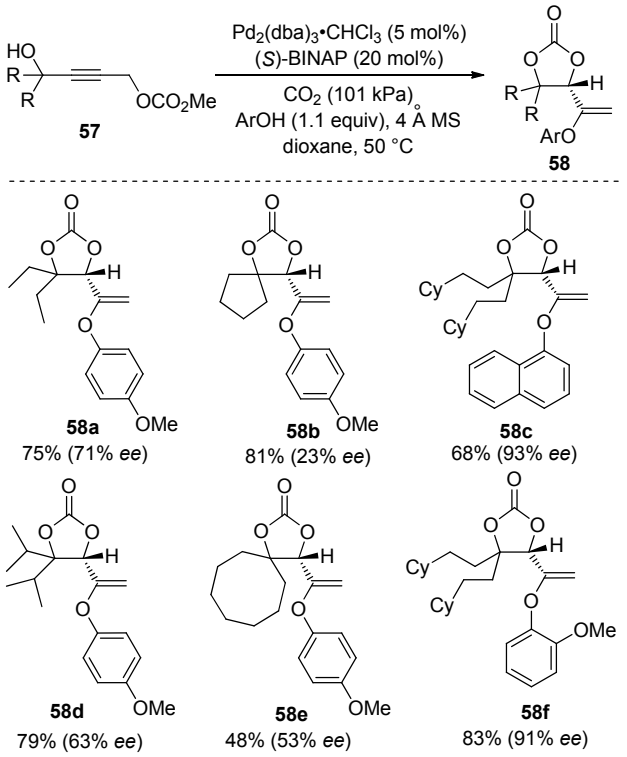
In 1987, Takeichi and co-workers[73] reported a Co-catalyzed kinetic resolution of propylene bromohydrin (Scheme 20). Chiral propylene carbonate **53** was obtained in promising *ee* via cyclization under mild conditions. Based on the configuration of the products, this reaction was considered via an attack of alcoholate anion on CO_2 followed by an intromolecular nucleophilic substitution reaction.



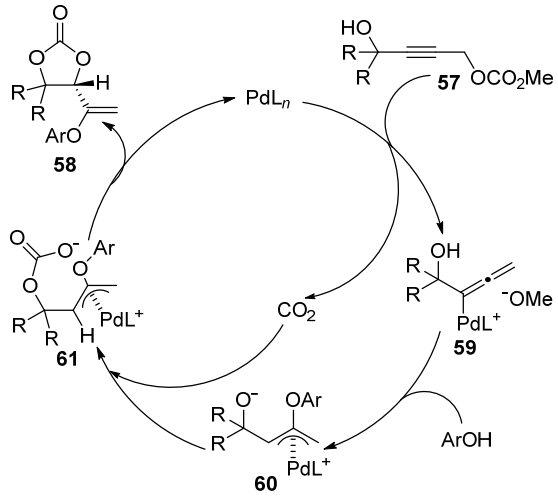
Scheme 20 Co-catalyzed enantioselective cyclization of propylene bromohydrin

In 2003, Yoshida, Ihara and co-workers[74] reported a Pd-catalyzed CO_2 recycling reaction for the preparation of chiral cyclic carbonates based on novel CO_2 elimination-fixation strategy (Scheme 21). With $Pd_2(dba)_3$•$CHCl_3$ as catalyst and (*S*)-BINAP as ligand, the asymmetric CO_2 elimination-fixation reaction of propargylic carbonates **57** with phenols afforded the corresponding cyclic carbonate **58** in 48%～94% yields with 23%～93% *ee*. The authors found that the reactions with longer chain substrates leaded to cyclic carbonates in higher enantiomeric purities. Thus, bulky substituents at the *β*-position of alkyl side chain resulted in increased enantioselectivities.

A plausible mechanism for this CO_2 elimination-fixation is shown in Scheme 22. The key of this transformation is the π-allyl-Pd intermediate **60** generated by nucleophilic attack of allenylpalladium methoxide **59** by phenols. When this reaction is conducted under a CO_2 atmosphere, the released



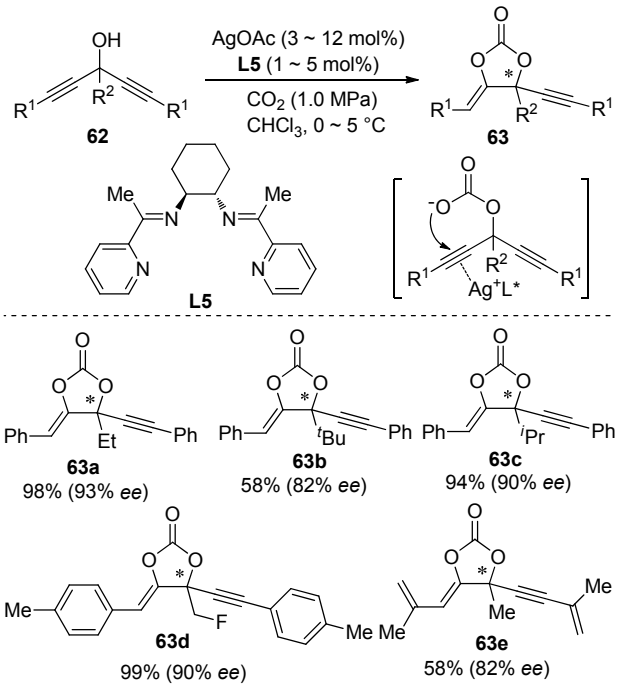
Scheme 21 Pd-catalyzed enantioselective CO_2 elimination-fixation of propargylic carbonates



Scheme 22 Plausible mechanism of Pd-catalyzed elimination-fixation of propargylic carbonates

and external CO_2 promotes the reaction efficiently to generate carbonate. The direct cyclization of **60** leads to the dihydrofuran and epoxide byproducts. A new chiral center is formed by intramolecular nucleophilic attack by the carbonate anion **61** in the presence of (*S*)-BINAP-Pd complex. To examine whether CO_2 dissociates from the substrate in this reaction, the reaction was conducted in both the presence and the absence of added CO_2. While the reaction under argon atmosphere gave cyclic carbonate **58** in 85% yield, the process carried out under 101 kPa of CO_2 leaded to **58** in 96% yield. In addition, when the reaction is run under bubbling argon to remove the resulting CO_2, **58** was formed in only 21% yield together with by-product dihydrofuran (32%) and epoxide (11%). The results suggested that the process proceeded via a pathway involving decarboxylation-followed fixation of the liberated CO_2.

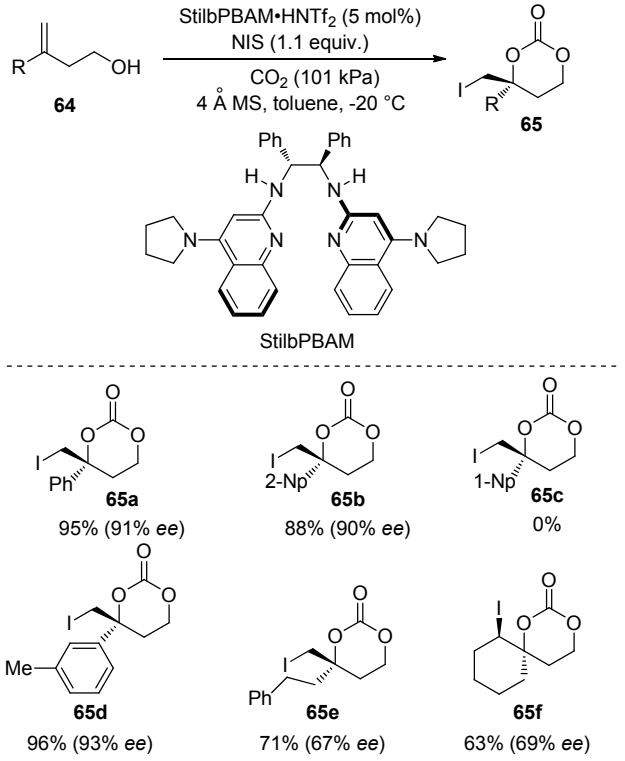
In 2010, another asymmetric CO_2 fixation with propargyl alcohols towards chiral cyclic carbonates is reported by Yamada and co-workers.[75] Asymmetric desymmetrization of bispropargylic alcohols **62** was realized efficiently with chiral silver complex as a catalyst (Scheme 23). The alkyne moiety of bispropargylic alcohols **62** was activated by the π-Lewis acidic Ag-catalyst. Thus, the intramolecular nucleophilic addition of alkyne with the carbonate anion was facilitated from the opposite side of alkyne.[76] By the combination of AgOAc and chiral Schiff base ligand **L5**, a range of *α*-alkylidene cyclic carbonates **63** were obtained in good yield with moderate to high enantioselectivities (47%～93% *ee*). Furthermore, stereospecific hydrolyzation of such products was readily performed to afford the *α*-hydroxyketone bearing a chiral quaternary carbon center without loss of optical purity.



Scheme 23 Ag-catalyzed enantioselectivede symmetrization of bispropargylic alcohols with CO_2

In 2015, Johnston and co-workers[77] described a organocatalytic iodocarbonation of homoallylic alcohols **64** with *N*-iodosuccinimide and CO_2 to produce chiral cyclic carbonates **65** based on dual Brønsted acid/base activation (Scheme 24). They used StilbPBAM•$HNTf_2$ salt as a bifunctional hydrogen-bond donor and acceptor catalyst. The acid/base combination lowered the barrier of CO_2 incorporation and assisted the stabilization of the resulting carbonic acid. A variety of styrene derivatives were tested under the optimal conditions affording the corresponding carbonates

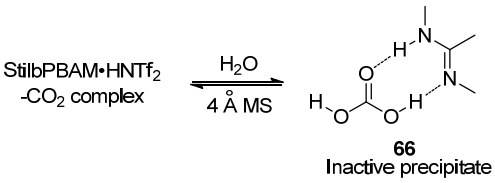
in high yields with good to excellent enantioselectivities. However, no reaction occurred when using styrene derivatives with the bulky aryl group, such as 2-methylphenyl and 1-naphthyl (**65c**). High yield and moderate *ee* were obtained with homoallylic alcohol bearing aliphatic substituents (**65e**). Spirocyclic carbonate could be synthesized with trisubstituted alkene with promising enantioselectivity (**65f**).



Scheme 24 Asymmetric organocatalytic iodo carbonation of homoallylic alcohols

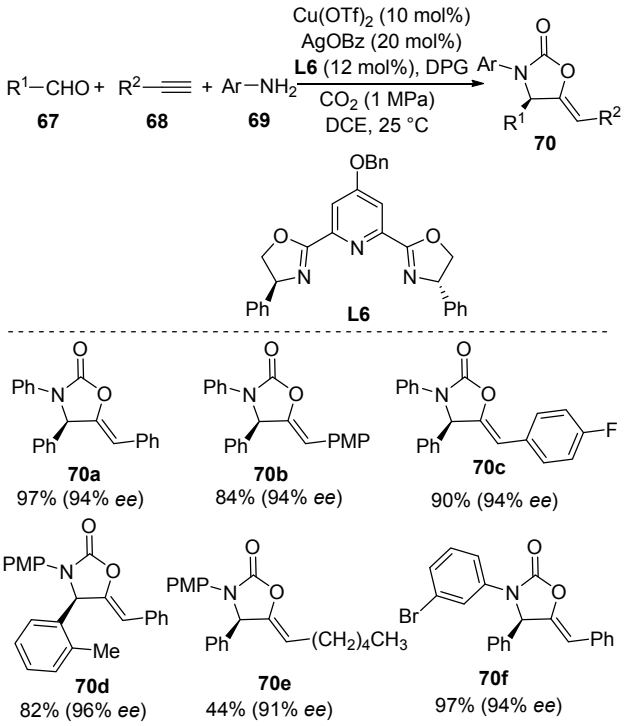
In the course of condition optimization, both efficiency and enantioselectivity were found to be sensitive to a variety of parameters, including concentration, temperature, stirring rate, counterion, and ratio of acid/base. The latter two factors were thought to influence the selectivity-determining hydrogen-bonding network. Moreover, 4Å MS was also crucial to the chemical yield, which attributed to maintaining the active complex formed by catalyst salt and CO_2 (Scheme 25). In the presence of water, carbonic acid salt **66** was formed which consumed the active catalyst. This offers an insight into the interaction between hydrogen-bond donor/acceptor catalyst and CO_2 along with water. Very recently, This group prepared six-membered cyclic carbamates through an high enantioselective amine CO_2-capture/cyclization reaction with MeO-StilbPBAM•$HNTf_2$ salt as catalyst and analogous amine as substrate.[78] And mechanism-guided analysis of the reaction provides insight to various dominant substrate-reagent combinations in the solution.

In 2017, Zhou and co-workers[79] reported a Cu/Ag co-catalyzed tandem asymmetric aldehyde-alkyne-amine coupling-carboxylative cyclization with CO_2 for the highly



Scheme 25 Equilibrium of catalyst poisoning and recovery

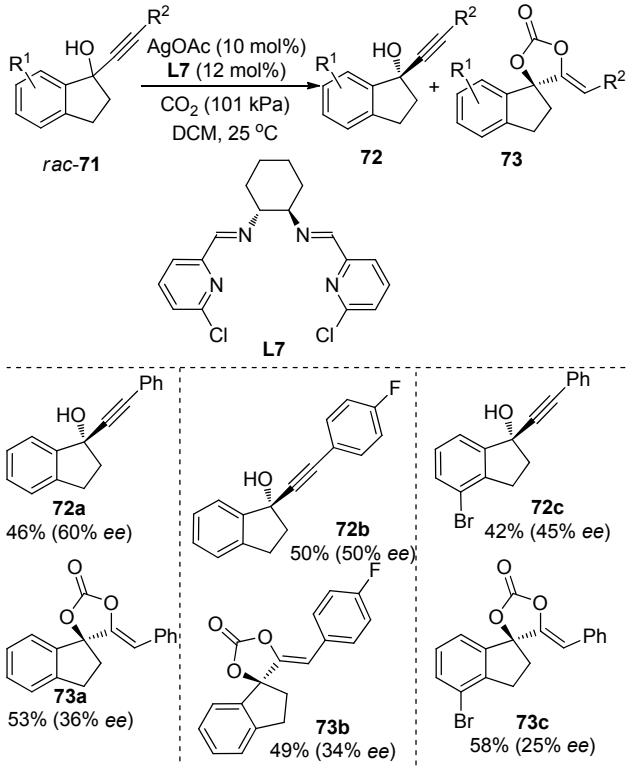
enantioselective synthesis of chiral *N*-aryl 2-oxazolidinones **70** (Scheme 26). In this reaction, the chiral propargylamine was formed first with $Cu(OTf)_2$ as catalyst and PYBOX **L6** as ligand. Then Ag-catalyzed cyclization of propargylamine with CO_2 afforded *N*-aryl 2-oxazolidinones in excellent yields with 90%～96% *ee*.[80] This process is a rare example of multicatalyst-promoted asymmetric tandem reaction using CO_2 as a C_1 synthon.



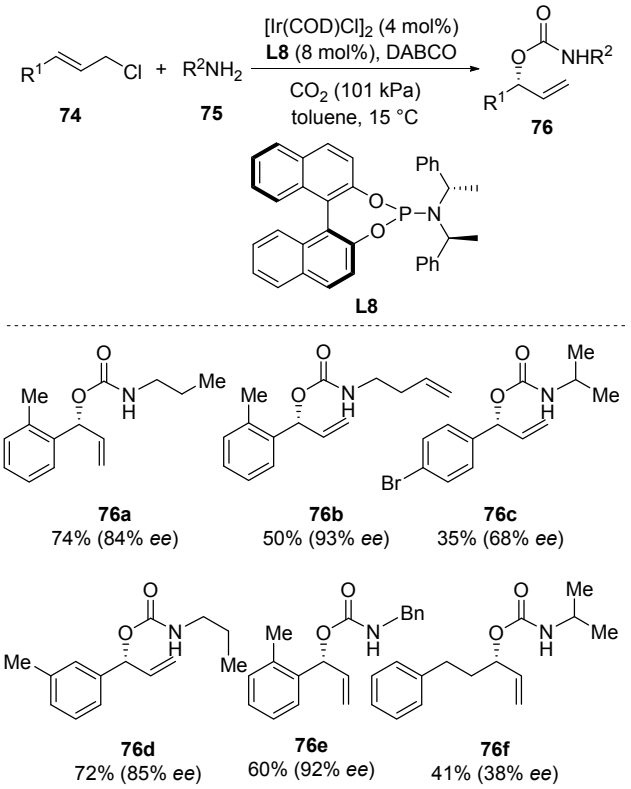
Scheme 26 Cu and Ag cocatalyzed tandem asymmetric coupling-carboxylative cyclization

Very recently, Zhou and co-workers[81] reported an Ag-catalyzed enantioselective carboxylative cyclization of propargylic alcohols and CO_2 via kinetic resolution under mild conditions. The reaction enabled the synthesis of chiral propargylic alcohols **72** and cyclic carbonates **73** with promising yield and enantioselectivity simultaneously (Scheme 27). They found that the substituents on the pyridyl ring had great influence on this reaction when they used the 2-pyridinecarboxyaldehyde derived Schiff base ligand. Chiral ligand **L7** derived from *ortho*-chloro-substituted pyridine was demonstrated to be the best one.

Ir-catalyzed asymmetric allylic amination with alkyl amine has been widely reported for the synthesis of chiral allyl amines.[82-92] Interestingly, Zhao and co-workers[93-94]



Scheme 27 Enantioselective carboxylative cyclization of propargylic alcohol with CO_2 under mild conditions



Scheme 28 Ir-catalyzed asymmetric allylation with CO_2 and amines

reported an Ir-catalyzed asymmetric allylation reaction to synthesize optically active carbamates with CO_2 and amine that involving both C—O and C—N bonds formation (Scheme 28). With linear allylic chlorides **74**, amines **75**, and CO_2 as substrates, Ir-catalyzed three-component domino reaction was developed. By addition of DABCO as base and using slight excess of allyl chlorides, the chiral carbamates were obtained as major products comparing with chiral allyl amines. A variety of alkyl amines and cinnamyl chlorides were employed affording carbamates **76** in moderate yield with high regioseletivity (branched/linear＞9/1) and moderate to good enantioselectivities (48%～94% *ee*). Notably, this reaction featured with excellent *ortho* substituent tolerance of aryl substituent in allylic chlorides, which is difficult in the preparation of branched allyl alcohols.[95] They found that aryl substituted allyl chlorides with the electron-donating groups on the phenyl ring gave the branched allyl carbamates in fair to good yields with a high level of both regio- and enantio-selectivities. Aryl substituted allyl chlorides with the electron-withdrawing groups on the phenyl ring led to a good yields and excellent regioselectivities but with lower enantioselectivities. For substrate bearing an aliphatic group, it provided the corresponding allyl carbamate with lower *ee* value.

6 Conclusions and perspectives

We conclude the recent advances in the CO_2 fixation via asymmetric catalytic reactions for the synthesis of chiral small molecules. Although transformations of CO_2 into valuable chemicals have been widely reported over the last decade, the CO_2 fixation via asymmetric catalysis is still less developed. In general, transition metal catalysis is broadly applied in the CO_2 fixation via asymmetric catalysis. In comparison, there are just several successful examples of organocatalytic asymmetric CO_2 fixation. Notably, electrocatalysis could also be used in the asymmetric CO_2 fixation, albeit with moderate enantioselectivities.

Carboxylic acids and their derivatives with an alpha chirality center are widely found in biological active natural products and medicinal molecules. In order to synthesize these compounds, asymmetric carboxylation of carbon nucleophiles with CO_2 as a building block is an attractive method. Although several efficient methodologies have been developed for the enantioselective synthesis of carboxylic acid derivatives via catalytic C—C bond formation with CO_2, special substrates such as styrenes, 1,3-diene, allenes are needed. Using readily available substrates such as simple alkenes and alkanes will be highly desirable in the asymmetric carboxylation with CO_2 in the future.

Chiral carbonates and carbamates are important chemicals and intermediates in synthetic chemistry. Asymmetric synthesis of these compounds by ring opening of epoxides and aziridines with CO_2 has been well developed. Beyond these achievements, several new asymmetric CO_2 fixation reactions for the synthesis of carbonates and carbamates have been developed with metal-catalysis or organocatalysis. However, the successful reactions are still limited and

new types of asymmetric reactions are needed to be developed in this area.

In summary, significant progress has been made on the asymmetric CO_2 fixation in recent years. Investigation of the mechanism of CO_2 activation is important for the development of CO_2 fixation reaction via asymmetric catalysis. It is anticipated that more researches will emerge in this area. The fixation of CO_2 with high efficiency and excellent stereoselectivities is a longstanding goal under with mild conditions, such as low catalyst loading, room temperature, and atmospheric pressure of CO_2. In this regard, converting CO_2 and H_2O to chiral carbohydrate with light by photosynthesis in nature is a perfect process. Thus, enzyme-catalyzed CO_2 fixation might inspire the development of new catalytic systems on asymmetric catalysis with CO_2 as a sustainable C1 synthon.

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