Organic &
Biomolecular Chemistry

ROYAL SOCIETY OF CHEMISTRY

REVIEW

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2020, **18**, 8597

Received 16th September 2020,
Accepted 2nd October 2020

DOI: 10.1039/d0ob01905d

rsc.li/obc

Catalytic enantioselective synthesis using carbon dioxide as a C1 synthon

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This review summarizes the advances in catalytic enantioselective reactions using CO_2 as a C1 synthon, introduces major synthetic strategies and discusses their advantages and limitations, highlights the application of known protocols, and outlines the synthetic opportunities.

1. Introduction

Since the beginning of the industrial revolution, the concentration of carbon dioxide (CO_2) in the atmosphere has increased dramatically as a result of the combustion of fossil resources, such as natural gas, coal and crude oil, to generate energy.[1] CO_2 is an essential component of greenhouse gases; its rapid increase and the resulting significant impact on the environment, such as global warming, have become an important global issue.[2] During the past few decades, great efforts have been made to control the emission of CO_2 and develop efficient protocols for carbon capture,[3] among which the recycling of CO_2, as a promising alternative carbon-based feedstock to fossil fuel resources, into value-added chemical production has received considerable attention.[4] Although this strategy alone cannot reduce the atmospheric concentration of CO_2 significantly, it can provide access to materials of commercial interest from a non-toxic, renewable, and low-cost resource.[5] In order to compensate for the potential costs of CO_2 capture and recycling, chemical products with a higher market value should be pursued. In this case, the synthesis of high-value-added chiral products from simple starting materials with CO_2 as a C1 feedstock, in particular, based on a catalytic enantioselective manner is highly attractive. Despite the fact that a variety of chemical fixations of CO_2 have been realized, some of which have been applied to industrial production,[6] the catalytic enantioselective fixation of CO_2 remains largely undeveloped,[7] probably owing to the inherent difficulties of catalytic asymmetric synthesis[8] as well as the activation and utilization of CO_2.

As the end product of all carbon-based combustion processes, CO_2 possesses the highest oxidation state of carbon, and it is thermodynamically stable and kinetically inert, all of which make its conversion under mild conditions a huge challenge. In addition, the minuscule steric size of CO_2 makes its enantioselective fixation very difficult.[9] Moreover, the dissociation of the converted species, such as esters or carboxylates, from the catalyst center represents another problem in realizing the catalytic asymmetric transformation of CO_2. In this context, the activation of CO_2 is pivotal to its effective chemical fixation, especially for catalytic asymmetric transformations.

CO_2 is a non-polar linear molecule possessing two polar carbon–oxygen bonds with a C–O bond distance of 1.1600 Å. With the combination of six atomic orbitals from the two oxygens and one carbon, six σ-molecular orbitals (MO) and six π-orbitals are generated in CO_2, with four of each being occupied. Among these MOs, the $1\pi_g$ and $2\pi_u$ orbitals playing the role of HOMOs and LUMOs, respectively, are mainly involved in the chemical reactivity of CO_2 (Scheme 1),[10] while the occupied $1\pi_g$ MOs are mostly localized on the oxygen atoms and the unoccupied $2\pi_u$ MOs are mainly centered on the carbon atom, making CO_2 an amphoteric molecule. The carbon atom of CO_2 plays the role of a Lewis acid center and thus can be attacked by electron-rich species, such as alcohols, amine bases, hydride ion and metals with a low oxidation state. Meanwhile, the oxygen atoms of CO_2 exhibit Lewis base character, enabling the interaction with electron-poor species, such as electron-deficient molecules and metals in a high oxidation state. Since the electrophilicity of the carbon atom is higher than the nucleophilicity of the oxygen atoms, CO_2 is a better electron acceptor than donor.

Based on the above understanding of the structure of CO_2, along with the advances in modern synthetic chemistry, much progress has been made in catalytic enantioselective synthesis

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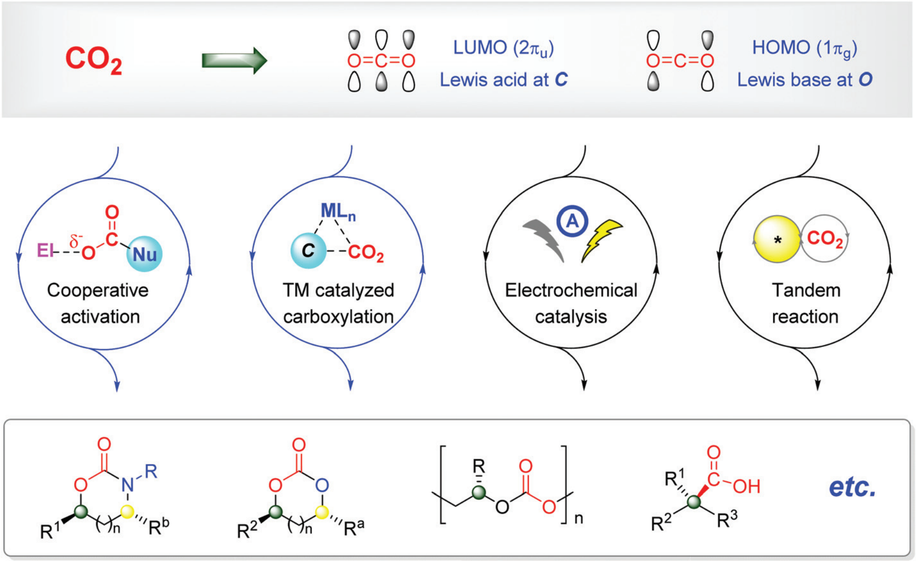


Scheme 1 Catalytic asymmetric fixation of CO_2.

using CO_2 as a C1 synthon on the basis of the four protocols shown in Scheme 1:

(a) Cooperative activation of CO_2. In this tactic, the initial nucleophilic addition of electron-rich species to the carbon atom of CO_2 gives a carboxylate intermediate with an oxygen atom with enhanced nucleophilicity. The reaction of this oxygen atom with prochiral carbon electrophiles induced by chiral catalysts gives the final chiral products *via* the formation of a C–O bond.[11]

(b) Transition metal-catalyzed carboxylation. This is usually used for the construction of chiral carboxylic acid derives from unsaturated compounds *via* an enantioselective C–C bond formation process, in which both the prochiral substrates and CO_2 might be activated by chiral transition metal catalysts.[12]

(c) Electrochemical catalysis. By using chiral catalysts to provide a chiral environment with electrons as redox reagents, this strategy enables the enantioselective reaction of CO_2 with easily available but less reactive compounds.[13]

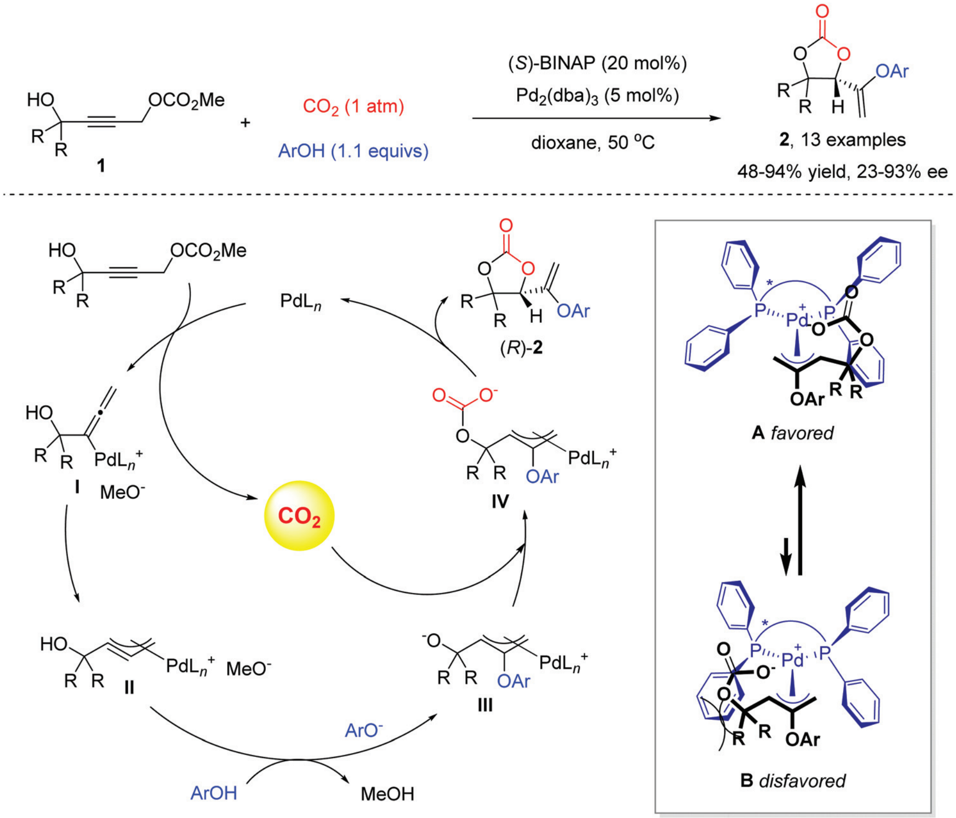
(d) Tandem reaction. The combination of CO_2 chemical fixation with an advanced catalytic asymmetric process in a tandem fashion represents a new type of CO_2-based catalytic enantioselective transformation, in which the CO_2 reacts directly with already generated chiral intermediates, thus enabling the construction of chiral products with high stereoselectivity.[14]

Despite ongoing progress, a comprehensive review summarizing the latest advances in this important and active research field has not been performed yet. General reviews of enantioselective reactions with CO_2 have been given by Kleij,[7a] Lu,[7b] Coates,[7c] Bayer and Hopmann,[7d] Chen and Li and Xia,[7e] and Gui and Yu.[7f] However, most of these reviews have mainly focused on chiral starting material-induced fixation of CO_2. Moreover, the catalytic enantioselective coupling of epoxides and CO_2 to chiral cyclic carbonates, or to polycarbonates, in particular, is not covered or only partly mentioned, so a comprehensive review article is still lacking. In light of these above facts, we feel it necessary to highlight the advances in the catalytic enantioselective fixation of CO_2. Specifically, this review is constructed based on the above-mentioned four protocols for catalytic enantioselective fixation of CO_2, with each part subdivided by the types of substrates, being different from previous reviews, which are mainly divided based on the formation of either C–C or C–O asymmetric bonds with CO_2. Emphasis in this review will be placed on strategies for realizing high enantioselectivity, while the possible mechanisms, applications and remaining challenges for the current transformations will also be discussed. We hope that this concise comprehensive review will inspire researchers and show how competitive these CO_2-based catalytic enantioselective approaches are for the construction of valuable chiral chemicals.

2. Catalytic enantioselective synthesis based on cooperative activation of CO_2

This approach is traditionally employed for the catalytic asymmetric valorization of energy-rich substrates, such as strong nucleophilic alcohols, amines, and epoxides. By incorporating the nucleophilic moiety and electrophilic alkyne or alkene structure unit in one molecule, a variety of optical active cyclic carbonates or carbamate derivates can be constructed based on the enantioselective cooperative activation of CO_2. Both chiral metal catalysis and organo-catalysis have been employed to realize high enantioselectivity.

In 2003, Yoshida, Ihara, and co-workers reported a novel chiral palladium-catalyzed CO_2 recycling reaction. By using (*S*)-



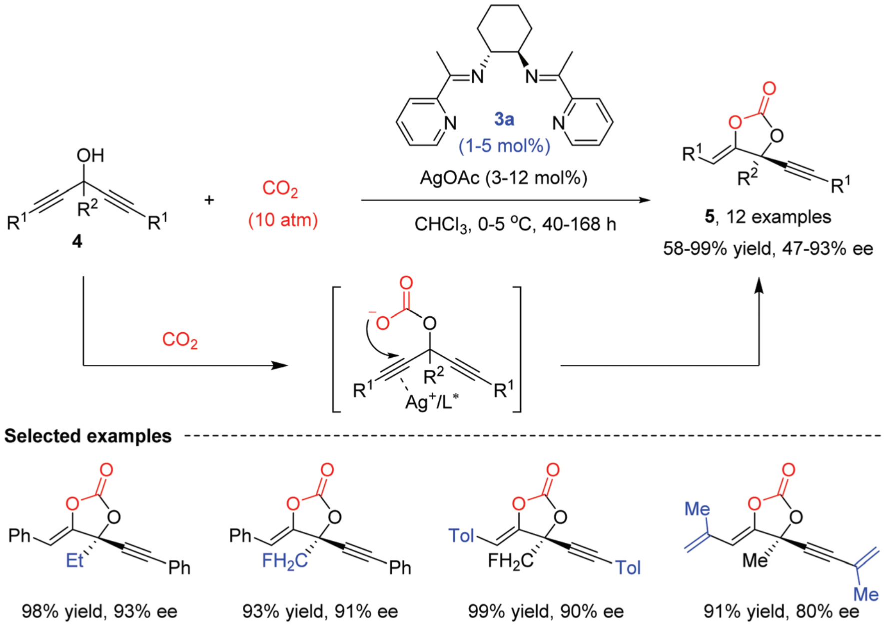
Scheme 2 Chiral palladium-catalyzed CO_2 recycling reaction.

BINAP/$Pd_2(dba)_3$ complex as the catalyst, the reaction of propargylic carbonates **1** with phenols under a CO_2 atmosphere gave the chiral cyclic carbonate **2** in up to 94% yield and 93% ee (Scheme 2).[15] Mechanistic studies revealed that the reaction should be a CO_2 elimination–fixation process. The palladium-catalyzed decarboxylation of propargylic carbonates gave an allenylpalladium methoxide **II**, which reacted with phenoxide to produce a π-allylpalladium intermediate **III**. Then, the incorporation of eliminated CO_2 and cyclization produced the desired product **2** effectively. Two possible transition states, **A** and **B**, were proposed for the enantiodetermining cyclization step. Since there was severe steric repulsion between the *R*-substituent of the substrate and a benzene ring of the BINAP ligand in transition state **B**, the (*R*)-product was preferentially obtained *via* the more stable transition state **A**.

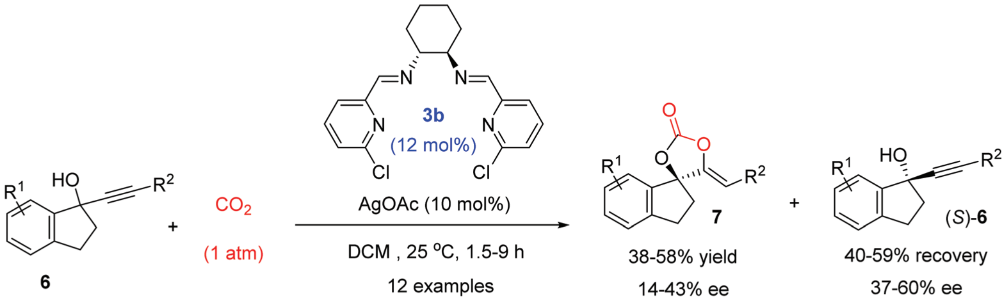
In 2010, the Yamada group developed an elegant catalytic asymmetric carboxylative cyclization of propargyl alcohols with CO_2 based on a desymmetrization strategy. They used the combination of silver acetate and the chiral Schiff-base ligand **3a** to catalyze the asymmetric CO_2 incorporation into prochiral bispropargyl alcohols **4**. The corresponding cyclic carbonates **5** could be obtained with good to excellent enantioselectivity (Scheme 3).[16] It was proposed that the bis-propargylic alcohols could be converted into nucleophilic carbonate anions in the presence of CO_2. One of the carbon–carbon triple bonds was selectively activated by the chiral silver complex, and intramolecular nucleophilic attack of carbonate anion to the activated alkyne moiety delivered the final chiral cyclic carbonates.

Apart from desymmetrization, the kinetic resolution tactic could also be employed for the enantioselective carboxylative cyclization of propargylic alcohols with CO_2, as demonstrated by Shi and our group.[17,18] In 2019, with chiral silver catalysis, we realized the catalytic asymmetric carboxylative cyclization of 1-indanone-derived racemic propargylic alcohols **6** with CO_2. With the combination of the chiral Schiff-base ligand **3b** and AgOAc, chiral cyclic carbonates **7** were synthesized in up to 58% yield and 43% ee. Meanwhile, the optically active propargylic alcohols (*S*)-**6** could be recovered in up to 59% yield and 60% ee (Scheme 4).[17] The kinetic resolution of non-cyclic propargylic alcohol was also attempted but low enantioselectivity was obtained.

At the same time, Shi and co-workers reported the kinetic resolution of oxindole-based racemic propargyl alcohols *via* carboxylative cyclization, based on a novel amino acid-derived bifunctional phosphine catalyst. Under the catalysis of chiral tertiary phosphine **8**, with high nucleophilicity and strong steric hindrance, the carboxylative cyclization of propargyl alcohols **9** with CO_2 proceeded smoothly, delivering the spirocarbonates **10** in 40–52% yield with 79–92% ee, along with the recovery of chiral propargyl alcohols (*R*)-**9** in 65–97% ee (Scheme 5).[18] Mechanistic study revealed that the reaction pro-



Scheme 3 Desymmetric carboxylative cyclization of bispropargyl alcohols.

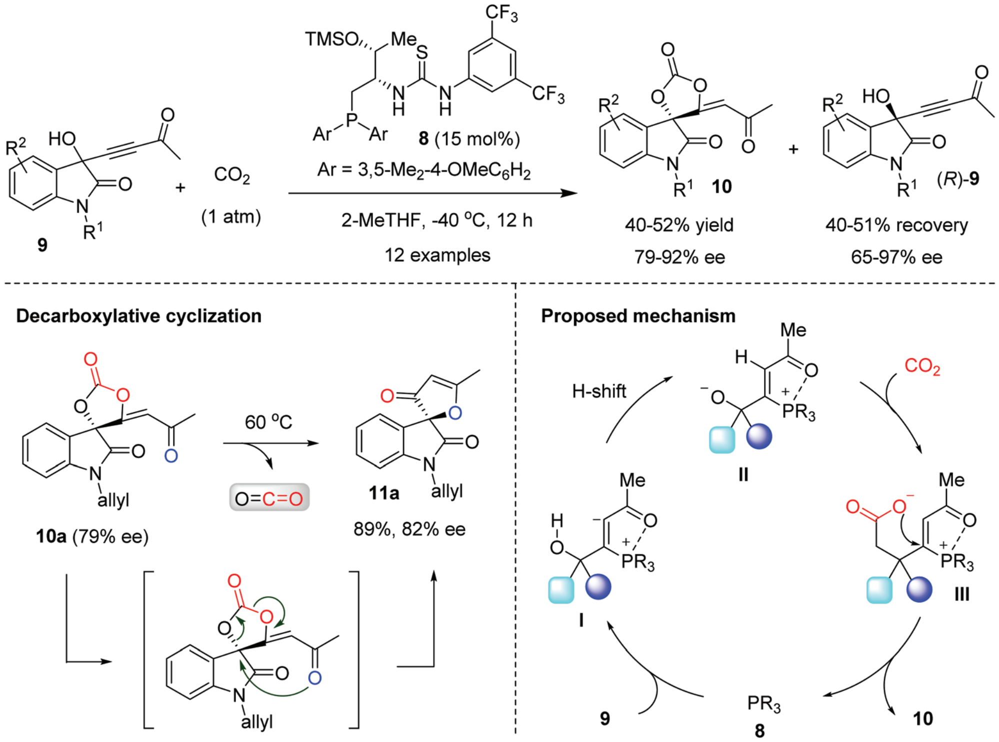


Scheme 4 Kinetic resolution of racemic propargylic alcohol.

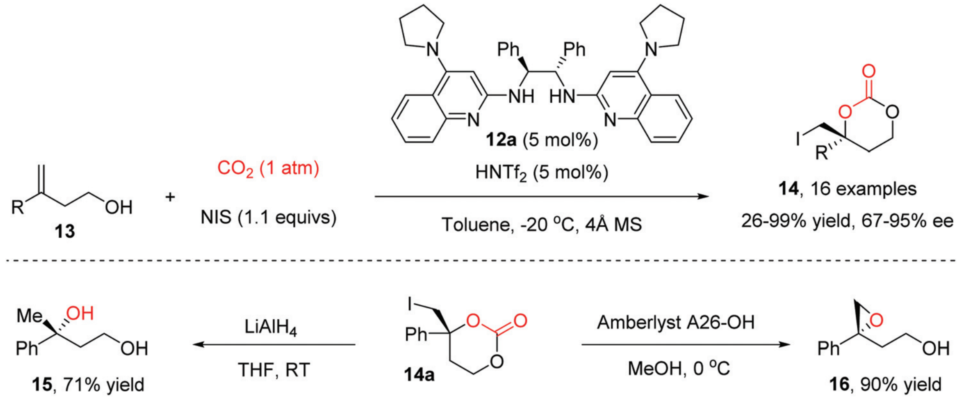
ceeded *via* a nucleophilic catalysis process. The initial nucleophilic addition of chiral tertiary phosphine **8** to the γ-hydroxyl alkynone moiety of **9** afforded a zwitterionic intermediate **I**. Then the intramolecular H-shift and subsequent CO_2 incorporation gave intermediate **III**, which underwent cyclization to furnish product **10** and regenerate the phosphine catalyst. Further investigation revealed that under heating, the thus obtained cyclic carbonates **10** could release CO_2 easily and underwent a decarboxylative cyclization, allowing the effective synthesis of chiral furanones **11** in excellent yields.

Besides the enantioselective carboxylative cyclization of propargyl alcohols, the reaction of homoallylic alcohols with CO_2 represents another effective method of producing optically active carbonate compounds. In 2015, the Johnston group described the first catalytic asymmetric construction of chiral cyclic carbonates from homoallylic alcohols *via* CO_2 capture. By employing chiral pyrrolidine substituted bis(amidine) **12a**·$HNTf_2$ complex as a novel dual Brønsted acid/base catalyst and *N*-iodosuccinimide (NIS) as an electrophilic source of iodine, the carboxylation–alkene iodocarbonation reaction of homoallylic alcohols **13** under a CO_2 atmosphere afforded the six-membered iodocarbonates **14** in up to 99% yield and 95% ee (Scheme 6).[19] This reaction had a broad substrate scope including alkenes bearing aromatic and aliphatic substituents. The resulting cyclic carbonates were valuable synthetic building blocks, as demonstrated by the facile transformation to optically active tertiary alcohol **15** and versatile epoxide **16**, respectively. It was believed that the properly balanced dual Brønsted acid/base catalyst was critical to the reaction, which not only catalyzed the reaction between the relatively weak alcohol nucleophiles and CO_2 to give transient acids but also effectively controlled the stereoselectivity in the subsequent enantioselective C–O bond-forming process.

Encouraged by their success with homoallylic alcohols, Johnston *et al.* further investigated the enantioselective carboxylation–alkene iodocarbonation reaction of homoallylic amines with CO_2 for the construction of optically active cyclic carbamates. Unfortunately, the optimal conditions for homo-



Scheme 5 Chiral tertiary phosphine-catalyzed carboxylative cyclization.

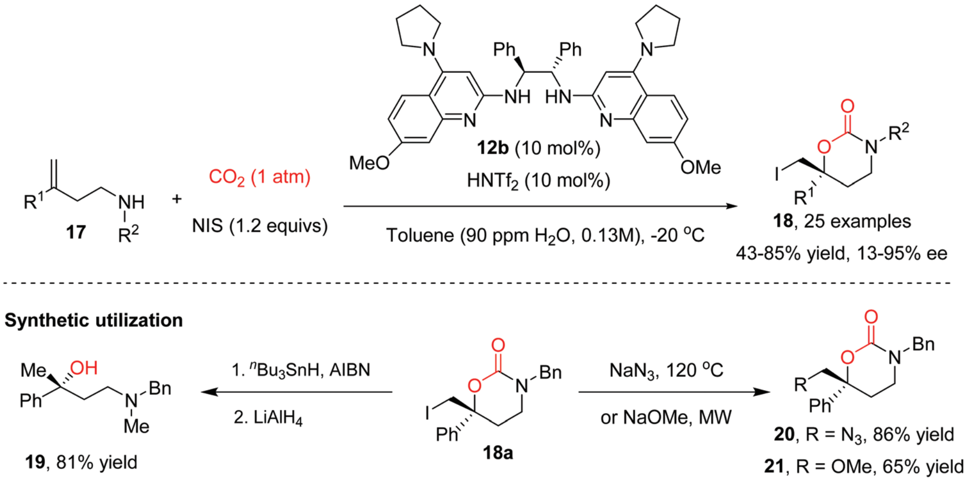


Scheme 6 Brønsted acid/base-catalyzed cyclization of homoallylic alcohols with CO_2.

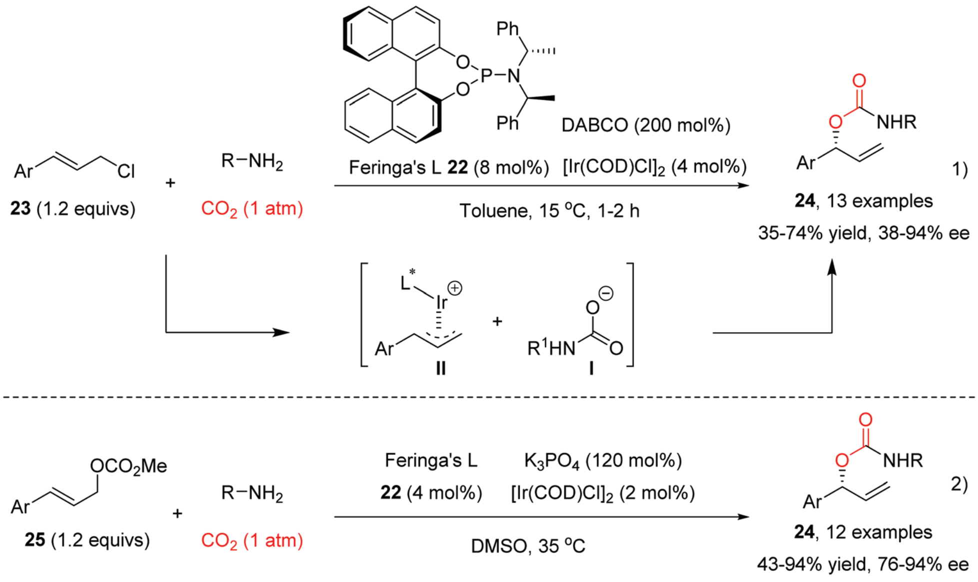
allylic alcohols were powerless for amines, giving low yields and moderate enantioselectivity. Considering that the carbamic acid intermediate might be less acidic than an alkyl carbonic acid, chiral bis(amidine) **12b** with enhanced basicity was recruited to overcome the low reactivity while guiding the subsequent enantioselective C–O bond formation. Finally, its combination with $HNTf_2$ effectively catalyzed the three-component reaction between homoallylic amines **17**, CO_2, and NIS, delivering the chiral cyclic carbamates **18** in good yield with high enantioselectivity.

Notably, a precise amount of water as an additive and the use of a triturating amorphous solid of bis(amidine) **12b** were key to a highly reproducible reaction. The resulting cyclic carbamates are valuable synthons and could be easily elaborated to **19** or **20** and **21** *via* reductive or nucleophilic functionalization, respectively (Scheme 7).[20]

In 2014, an enantioselective domino reaction of CO_2, amines and linear allyl chlorides under iridium catalysis was developed by Zhao *et al.*, which delivered chiral branched carbamates other than cyclic ones effectively. They used primary amines to attack CO_2 to form a carbamate ion **I**, which then reacted with the allyl iridium species **II** generated *in situ via* the reaction of chiral Feringa's ligand **22**/Ir(COD)Cl_2 complex with allyl chloride **23**, enabling the synthesis of chiral allyl carbamates **24** with up to 74% yield and 94% ee (Scheme 8, eqn (1)).[21] In addition to using allyl chloride to generate the allyl



Scheme 7 Brønsted acid/base-catalyzed cyclization of homoallylic amines with CO$_2$.

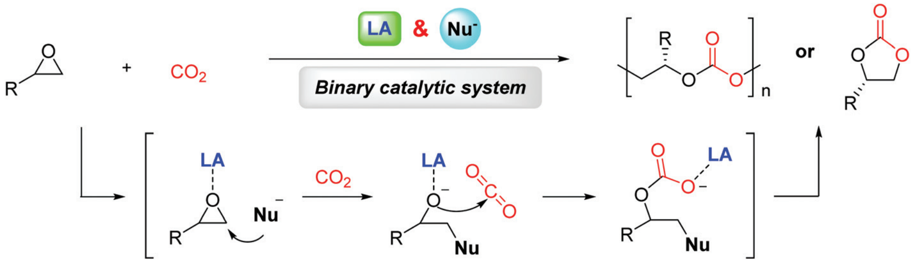


Scheme 8 Chiral Ir-catalyzed three-component reaction of CO$_2$ to branched carbamates.

iridium species, allyl carbonates **25** were also workable. By varying the base to K$_3$PO$_4$ and the solvent to DMSO, the chiral **22**/Ir(COD)Cl$_2$ complex could catalyze the reaction to give up to 94% yield and ee (Scheme 8, eqn (2)). These works provide a simple and efficient route to chiral allyl carbamates with high levels of both enantio- and regio-selectivity.[22]

The enantioselective coupling of epoxides and CO$_2$ has received considerable attention as it features perfect atom economy and can be controlled to give chiral cyclic carbonates or polycarbonates, both of which have a wide range of applications. Based on the type of epoxide, these transformations can be realized *via* the kinetic resolution of racemic epoxides or desymmetrization of *meso*-epoxides. Typically, a binary catalytic system consisting of a chiral Lewis acid for the activation of the epoxide together with a nucleophile as the co-catalyst for the ring-opening are employed. Mechanistically, the *in situ* generated metal alkoxide intermediate reacts with CO$_2$ to afford the desired cyclic carbonates[23] or polycarbonates[24] (Scheme 9). Until now, chiral Schiff-base metal complexes represent the most investigated catalyst system.[25] As early as 2003, Shi and co-workers reported the enantioselective coupling of propylene oxide (PO) and CO$_2$ using chiral binaphthyldiamino (salen)Cu(II) complexes as catalysts. Unfortunately, an ee of only 5% was obtained, which illustrates the difficulty in achieving high enantioselectivity in this synthetically useful transformation.[26]

Inspired by the groundbreaking work of Jacobsen *et al.* with the chiral (salen)Co(III) complex-catalyzed hydrolytic kinetic resolution of racemic epoxides,[27] in 2004 Lu and co-workers reported a highly efficient chiral salenCo(III)/quaternary

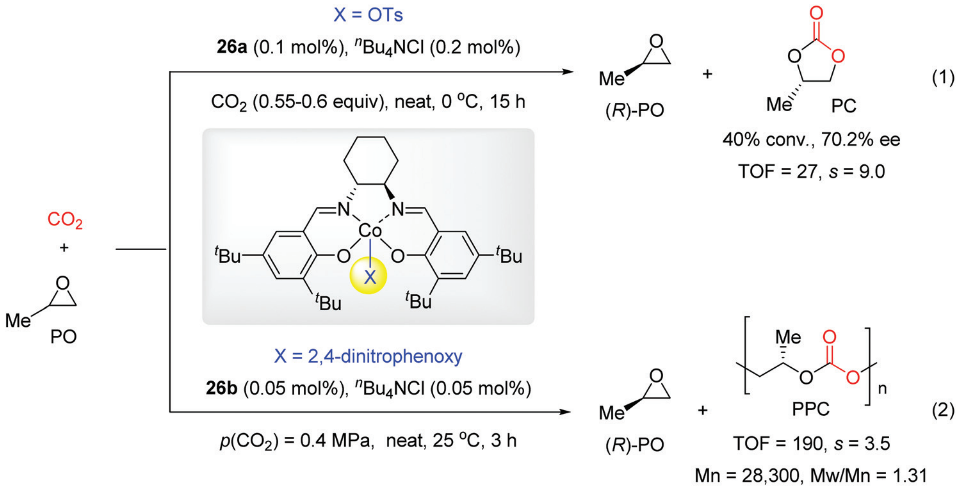


Scheme 9 Coupling of epoxides with CO_2.

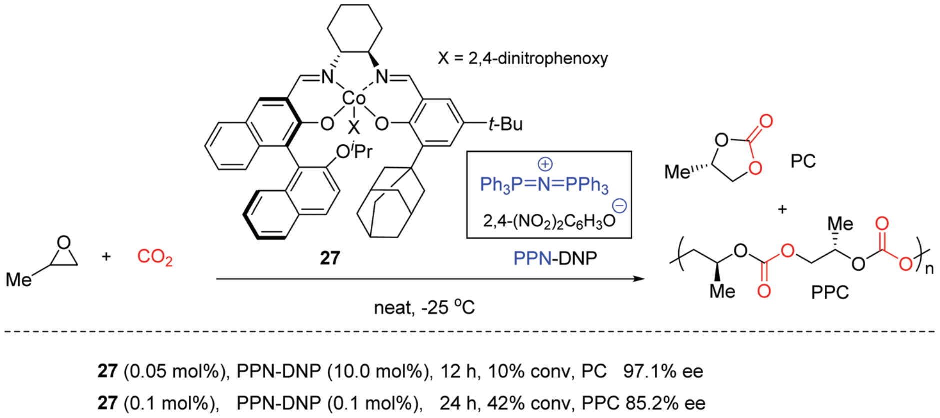
ammonium halide binary catalyst system for the enantioselective coupling of CO_2 and racemic epoxides (Scheme 10). The combination of (salen)Co–OTs **26a** with ^{n}Bu$_4$NCl effectively catalyzed the reaction of PO and CO_2 to give optically active cyclic propylene carbonate (PC) in 70.2% ee with a selectivity factor (*s* factor) of 9.0 (eqn (1)).[28] This work provides an attractive method for synthesizing chiral epoxides and carbonates based on a catalytic kinetic resolution process. Further study revealed that the anion of the (salen)Co(III) complex had a dramatic influence on the poly(propylene carbonate) (PPC)/PC selectivity of the reaction. By changing the axial group X from OTs to 2,4-dinitrophenoxy with poor leaving ability, the alternating copolymerization product PPC was obtained in 99% selectivity with an *s* factor of 3.5 (eqn (2)).[29]

In 2012, they elucidated in detail the effect of the nucleophilic co-catalyst as well as the anion of the (salen)Co(III) complex on the product selectivity and enantioselectivity. In the presence of multi-chiral Co(III) complex **27**, the excess loading of co-catalyst PPN-DNP favored selective production of cyclic carbonate PC, and up to 97.1% ee with an *s* factor of 75.8 were obtained at −25 °C. By contrast, when one equivalent of PPN-DNP was used, the main product was copolymer PPC rather than cyclic carbonate PC (Scheme 11).[30] It was proposed that the weak interaction of the Co(III) ion and the anion X with poor leaving ability is favorable for the coordination of epoxides. In addition, the strong interaction between the cation and the anion of the ammonium salt PPN-DNP was positive for the chiral induction for the coordination of (*S*)-PO and its further ring-opening. Then, the insertion of CO_2 into the Co–O bond delivered the linear carbonate PPC. On the other hand, cyclic carbonate PC was proposed to be generated *via* an intramolecular cyclic elimination, and the presence of excess co-catalyst benefited this process.

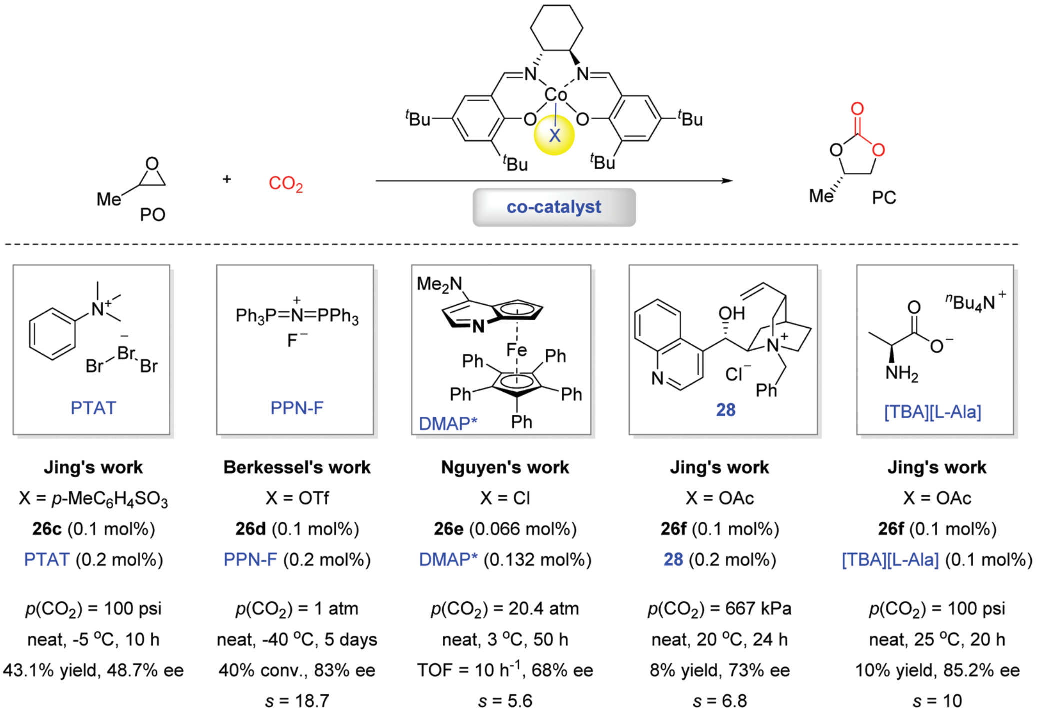
Recognizing that the co-catalysts have an important effect on the reaction outcome, the evaluation of different nucleophiles to improve the enantioselectivity has attracted considerable attention (Scheme 12). Jing *et al.* found that the combination of (salen)Co(III) complex **26c** with PTAT catalyzed the coupling of CO_2 and PO to give PC in 48.7% ee.[31] Berkessel's research using PPN-F as a co-catalyst further improved the enantioselectivity to 83%, with an *s* factor of 18.7.[32] The utilization of chiral complexes as co-catalyst has also been investigated. In 2004, Nguyen found that the combination of (salen) CoCl **26e** with a planar chiral DMAP type co-catalyst was effective, and up to 68% ee with an *s* factor of 5.6 were obtained.[33] Meanwhile, Jing reported the chiral **26f**-catalyzed reaction with cinchona-derived quaternary ammonium salt **28**[34] or chiral ionic liquid TBAL-Ala[35] as co-catalyst, affording optically active PC in 73% and 85.2% ee, respectively.



Scheme 10 Chiral Co(III)-catalyzed coupling of PO with CO_2.



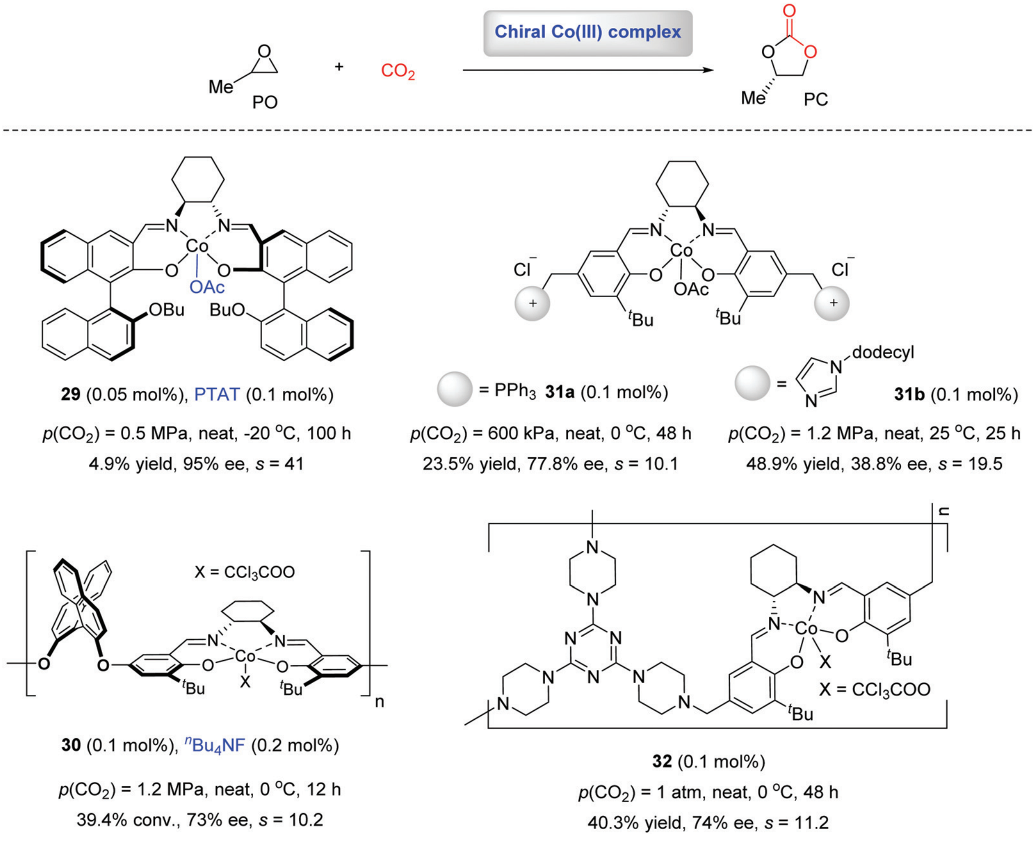
Scheme 11 Multi-chiral Co(III) complex-catalyzed coupling of PO with CO_2.



Scheme 12 Variation of the co-catalyst for the coupling of PO with CO_2.

Modification of the chiral salen-type ligand to improve the efficiency and enantioselectivity for the coupling of PO with CO_2 was also performed (Scheme 13). In 2008, Jing's group developed a multi-chiral BINAD Co(III) complex **29** bearing both axial and central chirality, the combination of which with PTAT gave chiral PC in 95% ee under mild conditions.[36] Based on the fact that polymer catalysts have the unique advantage of being easily separated from the reaction system to recover and reuse, Jing *et al.* designed a novel BINOL-derived polymer (salen)Co(III) complex **30** and applied it to the reaction of PO with CO_2, affording PC in 73% ee with an *s* factor of 10.2, which could be repeatedly used without loss of activity or enantioselectivity.[37] By introducing the quaternary phosphonium or imidazolium group into the salen ligand, Jing and co-workers synthesized novel bifunctional catalysts **31a** and **31b**, which could catalyze the enantioselective coupling of PO and CO_2 effectively to give *s* factors of 10.1 and 19.5, respectively, without the addition of any external co-catalysts.[38] In 2013, by merging the advantages of bifunctional catalysts and polymer catalysts, Kureshy *et al.* developed triazine–piperazine core-based bifunctional chiral polymeric Co(III) salen complexes **32**, which could deliver chiral PC in 40.3% yield and 74% ee, and there was no significant loss in activity after being reused 10 times.[39]

Besides chiral Co(III) catalysts, optically active Co(II) complexes are also applied to the enantioselective coupling of epoxides with CO_2 (Scheme 14). As early as 2004, Yamada reported the combination of chiral ketoiminatocobalt(II)



29 (0.05 mol%), PTAT (0.1 mol%)
$p(CO_2)$ = 0.5 MPa, neat, -20 °C, 100 h
4.9% yield, 95% ee, s = 41

● = PPh_3 **31a** (0.1 mol%)
$p(CO_2)$ = 600 kPa, neat, 0 °C, 48 h
23.5% yield, 77.8% ee, s = 10.1

31b (0.1 mol%)
$p(CO_2)$ = 1.2 MPa, neat, 25 °C, 25 h
48.9% yield, 38.8% ee, s = 19.5

30 (0.1 mol%), ^{n}Bu$_4$NF (0.2 mol%)
$p(CO_2)$ = 1.2 MPa, neat, 0 °C, 12 h
39.4% conv., 73% ee, s = 10.2

32 (0.1 mol%)
$p(CO_2)$ = 1 atm, neat, 0 °C, 48 h
40.3% yield, 74% ee, s = 11.2

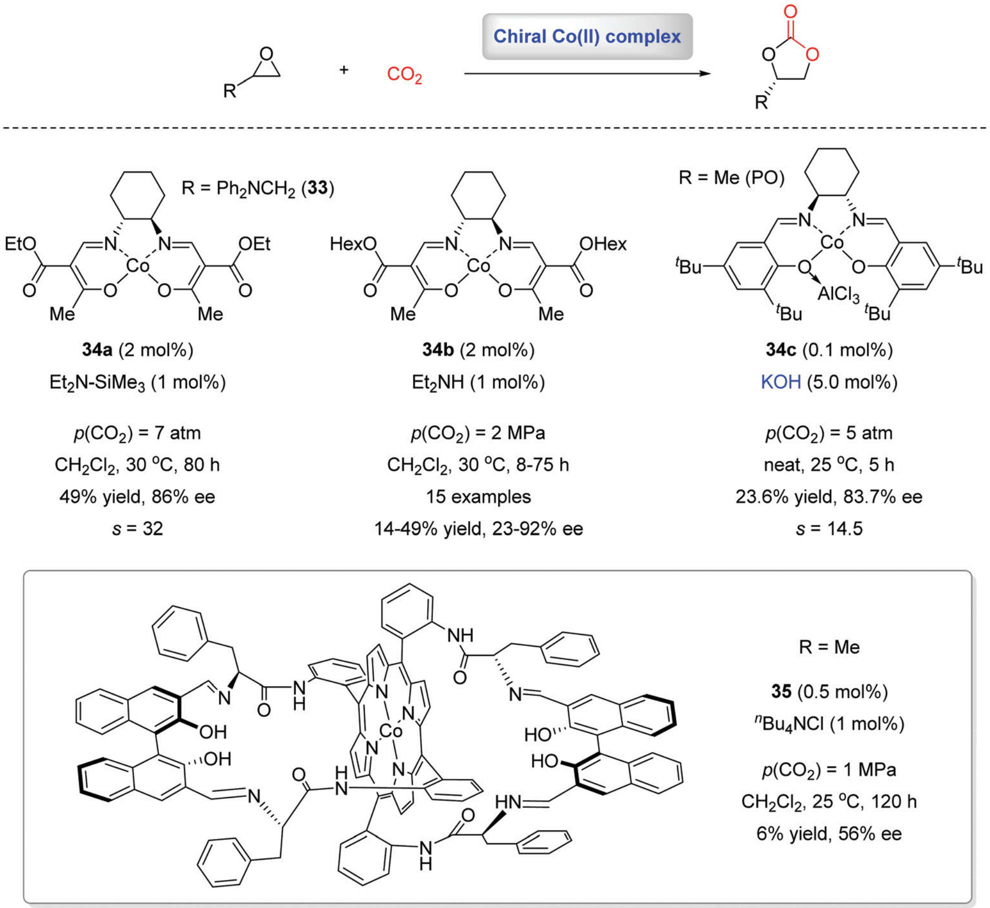
Scheme 13 Chiral Co(III) complex bearing different backbones for the coupling of PO with CO_2.

complex **34a** with $Et_2N–SiMe_3$ for the coupling of terminal epoxide **33** with CO_2 and an s factor of 32 was obtained.[40] By varying the ethyl group on the chiral ligand to hexyl, the resulting complex **34b** could be successfully applied to a variety of epoxides to give the corresponding optically active cyclic carbonates with up to 49% yield and 92% enantioselectivity.[41] Kim and co-workers found that the heterobimetallic (salen)Co(II) complex **34c** could efficiently catalyze the enantioselective coupling of PO with CO_2 in the presence of catalytic amounts of KOH, providing an s factor of 14.5.[42] Recently, Jing's group devised a chiral basket-handle porphyrin–Co(II) complex **35**, the combination of which with ^{n}Bu$_4$NCl yielded chiral PC in 56% ee.[43]

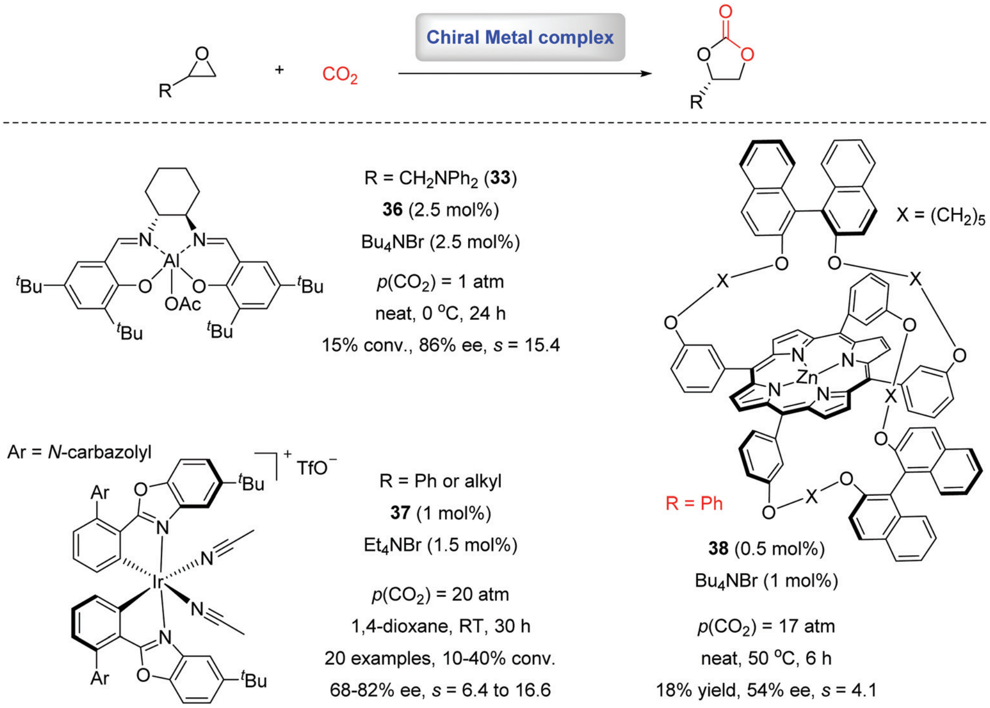
Other metal (Zn, Ir, Ni, Nb, Al, Cr, *etc.*) complexes bearing chiral Schiff-base ligands have also been evaluated for the kinetic resolution of epoxides with CO_2.[44] North used inexpensive and sustainable (salen)Al(III) complexes **36** as catalysts for the kinetic resolution of terminal epoxide **33** with TBAB as the co-catalyst and an s factor of up to 15.4 could be obtained.[45] Meggers and co-workers employed the bis-cyclometalated chiral-at-iridium complex **37** as a catalyst and Et_4NBr as a co-catalyst for the reaction, providing s values of between 6.4 and 16.6 for a total of 20 substrates.[46] Recently, Maeda and Ema developed the chiral Zn(II) porphyrin complex **38**-catalyzed kinetic resolution of styrene oxide with CO_2 and an s value of 4.1 was recorded (Scheme 15).[47]

The kinetic resolution of epoxides with CO_2 can also be realized by organocatalysts (Scheme 16). In 2016, Shirakawa reported the chiral bifunctional quaternary phosphonium salt **39**-catalyzed reaction of epoxide **33** with CO_2, but a low selectivity (s = 1.5) was obtained.[48] In 2017, Ema reported the first example of the kinetic resolution of disubstituted epoxides with CO_2 under the catalysis of chiral macrocyclic organocatalyst **40**, and up to 83% ee could be achieved.[49] Recently, they further utilized hemisquaramide tweezer **41** as a H-bond donor organocatalyst for the coupling of styrene oxide with CO_2 with an s factor of 3.0.[50]

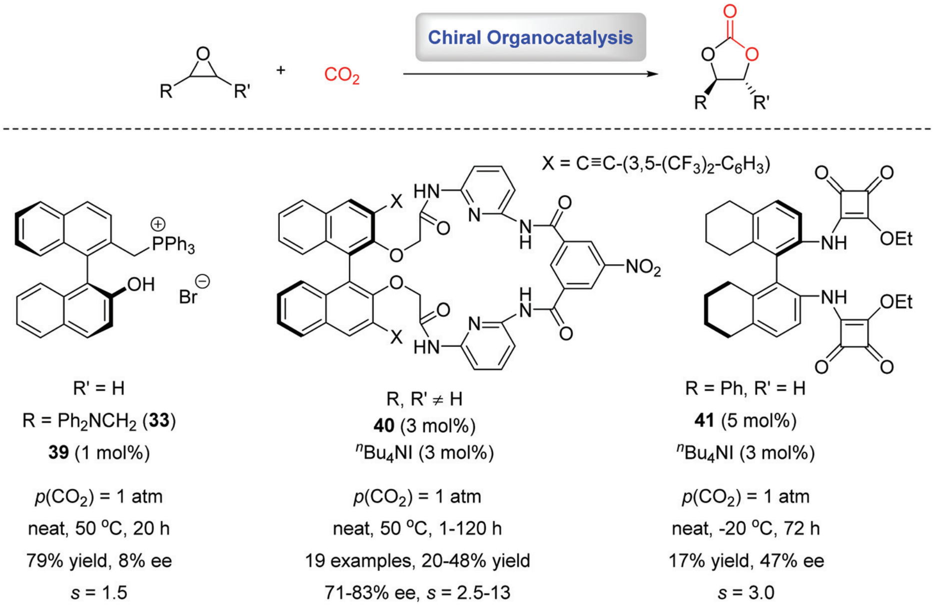
The desymmetrization of *meso*-epoxides with CO_2 is regarded as a valuable strategy for the synthesis of enantiomerically enriched polycarbonates with an (*R*,*R*)- or (*S*,*S*)-*trans*-1,2-diol unit as the ring-opening of a *meso*-epoxide will invert the configuration at one of the two chiral centers. The first example of asymmetric alternating copolymerization of CO_2 with cyclohexene oxide (CHO) was reported by Nozaki in 1999. In the presence of an equimolar mixture of Et_2Zn and chiral amino alcohol **42**, the corresponding optically active poly(cyclohexene carbonate) (PCHC) could be obtained in 70% ee, which was determined after hydrolysis into *trans*-1,2-diol *via* alkali-treatment. This research not only provided a new aspect of asymmetric polymerization but also afforded an unambiguous method to evaluate the degree of asymmetric induction (Scheme 17).[51] Mechanistic study revealed that dimeric zinc



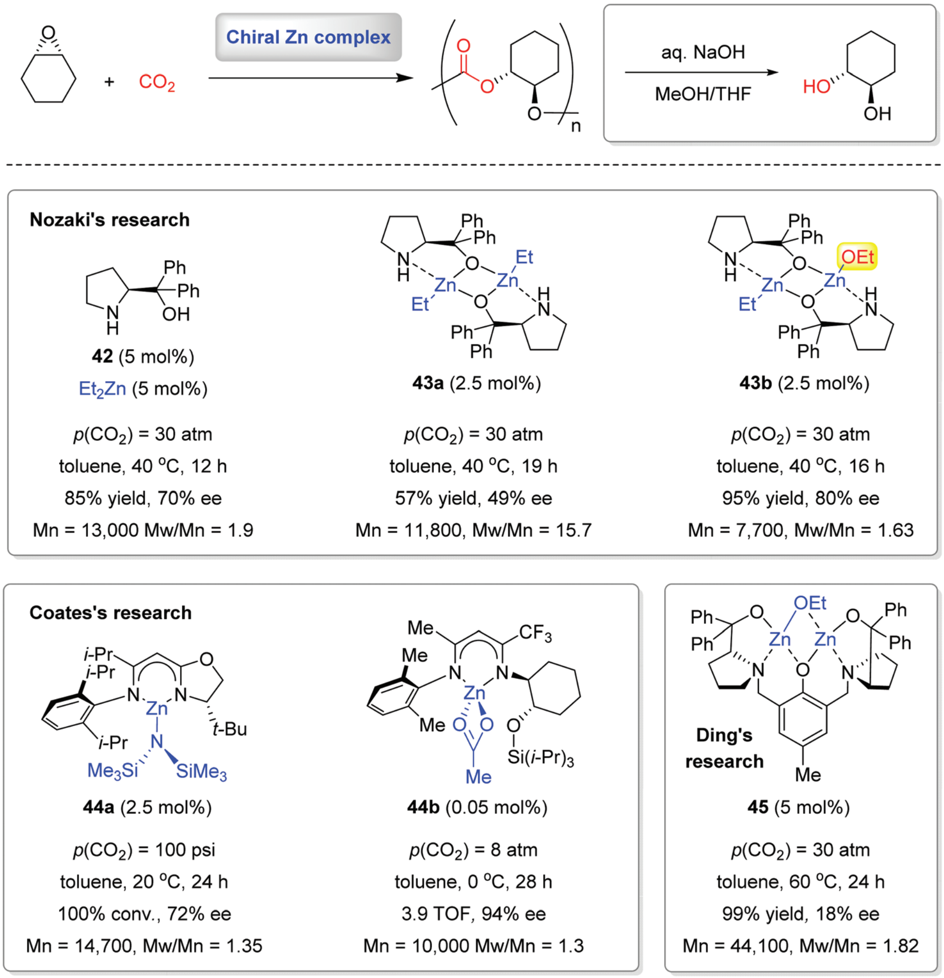
Scheme 14 Chiral Co(II) complex-catalyzed coupling of PO with CO_2.



Scheme 15 Other chiral metal complex-catalyzed couplings of PO with CO_2.



Scheme 16 Enantioselective organo-catalyzed coupling of PO with CO_2.



Scheme 17 Chiral Zn-catalyzed copolymerization of CO_2 with CHO.

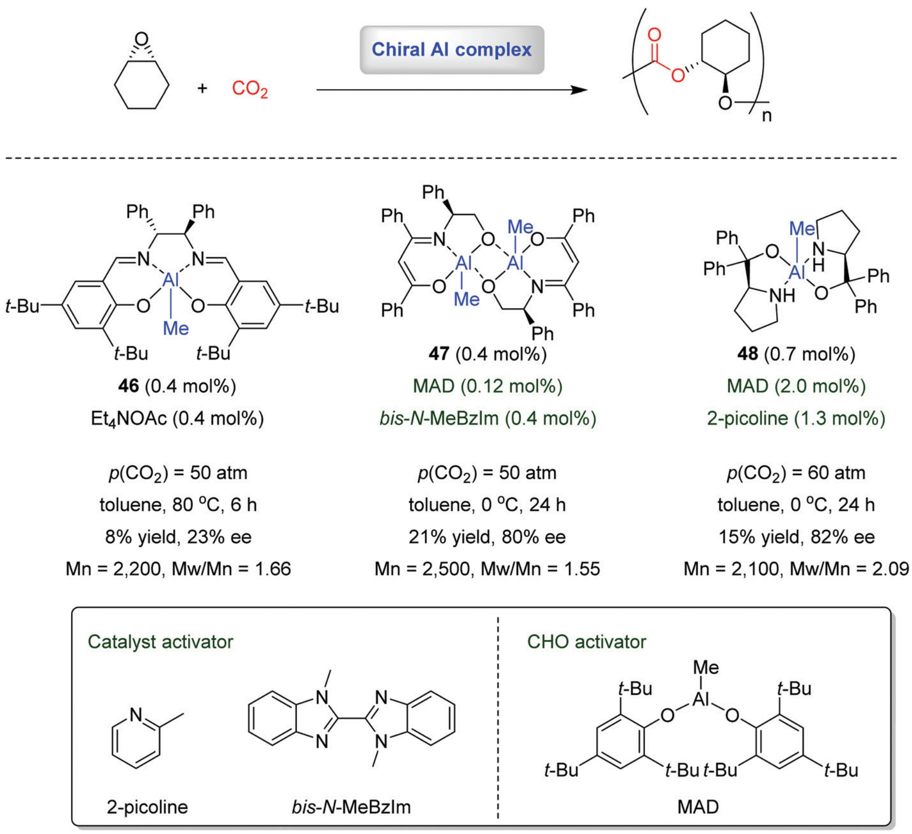
complexes should be the real active species for the copolymerization. However, chiral dimeric zinc complex **43a**, formed by the reaction of equimolar Et_2Zn and chiral amino alcohol **42**, gave only 49% ee. Further investigation revealed that chiral Zn complex **43b**, which was produced from a mixture of (*S*,*S*)-**43a** and ethanol, could catalyze the reaction to give PCHC in 95% yield and 80% ee. It was proposed that the copolymerization might be achieved through CO_2 insertion into the Zn–OEt bond of the dimeric zinc complex.[52] In addition, an asymmetric amplification phenomenon was observed during the course of the reaction, which represents the first example of a nonlinear effect in the enantioselective synthesis of chiral polymers with main-chain chirality.[53]

In 2000, the Coates group designed a novel chiral zinc complex **44a** bearing a hybrid imine-oxazoline ligand, which could catalyze the enantioselective copolymerization of CO_2 and CHO to give a 72% ee.[54] Based on this research, they further designed a C1-symmetric β-diiminate zinc catalyst **44b** for the enantioselective copolymerization in 2014. With only 0.05 mol% catalyst loading, chiral PCHC could be obtained in 94% ee under 8 atm of CO_2 pressure (Scheme 17).[55]

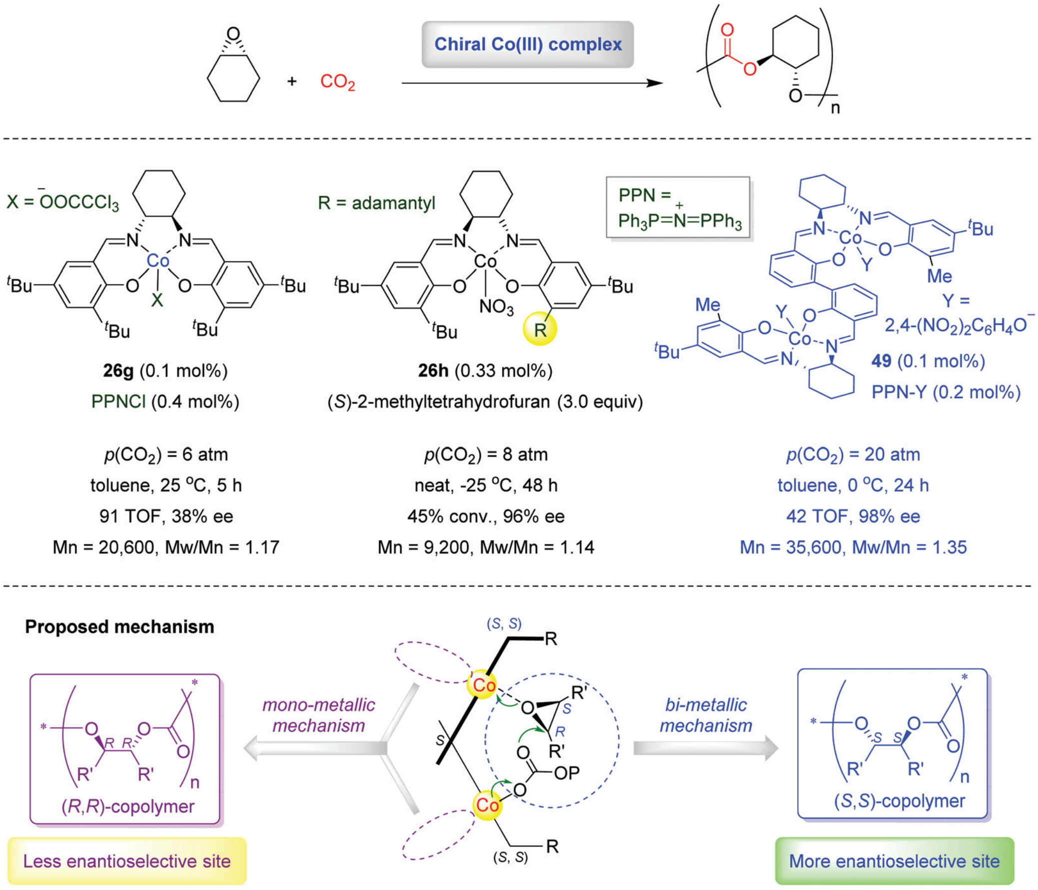
In 2005, Ding and co-workers reported a novel intramolecular dinuclear zinc complex **45**-catalyzed CO_2/CHO copolymerization under mild conditions, which afforded PCHC in an almost quantitative yield with a high M_n value, albeit with low enantioselectivity (Scheme 17).[56] Then, systematic research by Wang and Chang revealed that a dinuclear zinc complex bearing an azetidine rather than a pyrrolidine moiety could catalyze the copolymerization of CO_2 with CHO or cyclopentene oxide (CPO) with excellent enantioselectivity.[57] Du and co-workers developed a series of chiral zinc complexes with C1-symmetric amido-oxazolinate ligands and applied them to the copolymerization of CO_2 and CHO with moderate enantioselectivity obtained.[58]

The chiral aluminum-catalyzed copolymerization reaction of CO_2 and CHO was investigated by the Sugimoto group in 2012 (Scheme 18). Three types of chiral aluminum complexes bearing a salen-type Schiff base, β-ketoiminate, and prolinol ligands were synthesized and investigated. The combination of (salen)AlMe **46** and Et_4NOAc gave only 23% ee. By using MAD as the CHO monomer activator with bis-*N*-MeBzlm or 2-picoline as the catalyst activator, both aluminum β-ketoiminate **47** and aluminum aminoalkoxide **48** could catalyze the copolymerization to give an ee of greater than 80%.[59]

Apart from chiral zinc and aluminum catalysts, chiral cobalt complexes can also be employed for the desymmetric copolymerization of *meso*-epoxides with CO_2, and Lu's group made a great contribution in this area (Scheme 19). As early as 2006, Lu and Peng reported a binary catalyst system for the copolymerization, in which the chiral (salen)CoX complex **26g** in conjunction with bulky ammonium salt PPNCl effectively catalyzed the reaction to give PCHC in 38% ee at room temp-



Scheme 18 Chiral Al-catalyzed copolymerization of CO_2 with CHO.



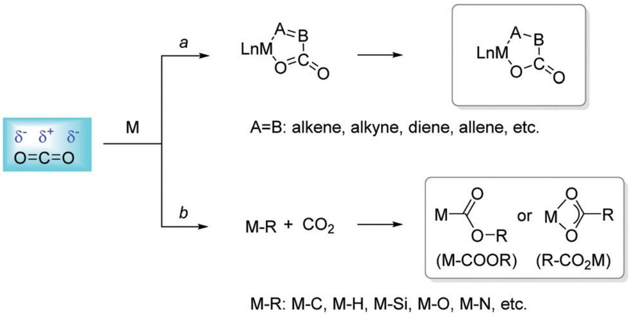
Scheme 19 Chiral Co-catalyzed copolymerization of CO_2 with CHO.

erature and 6 atm CO_2.[60] Considering that the dissymmetry of the ligand structure might be favorable for the induction of enantioselective ring-opening of CHO, they designed a series of asymmetric enantiopure (salen)Co(III) complexes for the enantioselective copolymerization of CHO and CO_2. It was found that the chiral (salen)$CoNO_3$ complex **26h**, bearing an adamantyl group, exhibited higher catalytic reactivity and the addition of stoichiometric quantities of a chiral induction agent could significantly improve the enantioselectivity. In the presence of (*S*)-2-methyltetrahydrofuran (3 equivalents), up to 96% ee could be achieved at −25 °C and 8 atm CO_2.[61]

However, there were disadvantages of rigorous reaction conditions and no activity for the coupling of CO_2 with less reactive CPO. Consequently, they further developed an enantiopure dinuclear cobalt complex **49** with a rigid bridging biphenyl linker for desymmetric copolymerization of *meso*-epoxides (both CPO and CHO) with CO_2. The catalyst system showed higher activity and better enantioselectivity compared to previous mononuclear systems, affording the copolymer product of CHO and CO_2 with 98% ee and also catalyzing the copolymerization of CPO with CO_2 in >99% enantioselectivity.[62] Notably, it could also be utilized for enantioselective copolymerization of 3,4-epoxytetrahydrofuran with CO_2, yielding the corresponding polycarbonate with more than 99% carbonate linkages and up to 99% ee.[63] Moreover, an elegant catalytic enantioselective construction of optically active CO_2-based carbamates from *meso*-epoxide was also realized based on a **49**-catalyzed desymmetric copolymerization and nucleophilic depolymerization tandem reaction.[64] Recently, a terpolymerization of CHO, β-butyrolactone and CO_2 was reported using this catalytic system, with up to 89% ee achieved.[65] Mechanistic study revealed that there are two possible paths for the copolymerization: the less enantioselective site in the outside cleft of the catalyst involving a monometallic mechanism, and the more enantioselective site in the inside cleft involving an intramolecular bimetallic cooperation mechanism, with nucleophilic attack by the growing carboxylate species at one metal center toward the activated epoxide at the other, resulting in alternating chain growth and dissociation taking turns between the two Co(III) ions.[66]

3. Enantioselective transition metal-catalyzed carboxylation

Under the catalysis of chiral transition metal complexes, two major routes for the enantioselective transformation of CO_2 have been developed: oxidative cycloaddition and hydrocarbox-

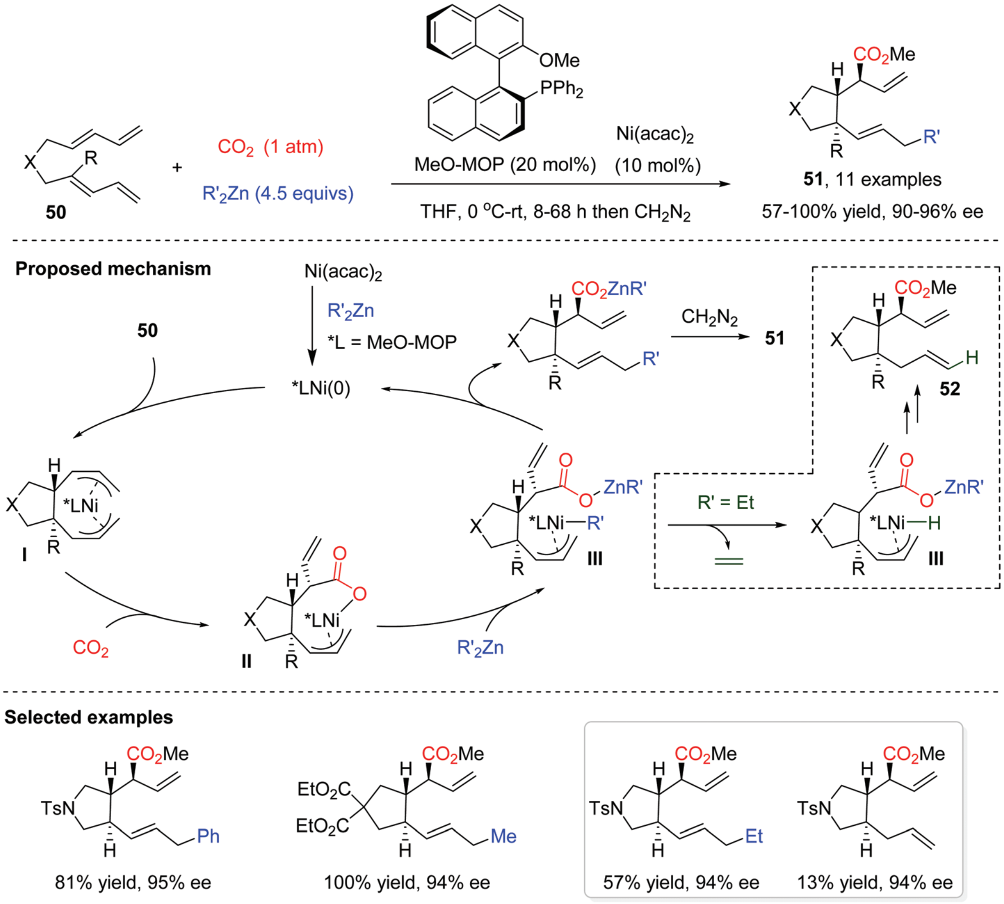


Scheme 20 Chiral transition metal-catalyzed transformation of CO_2.

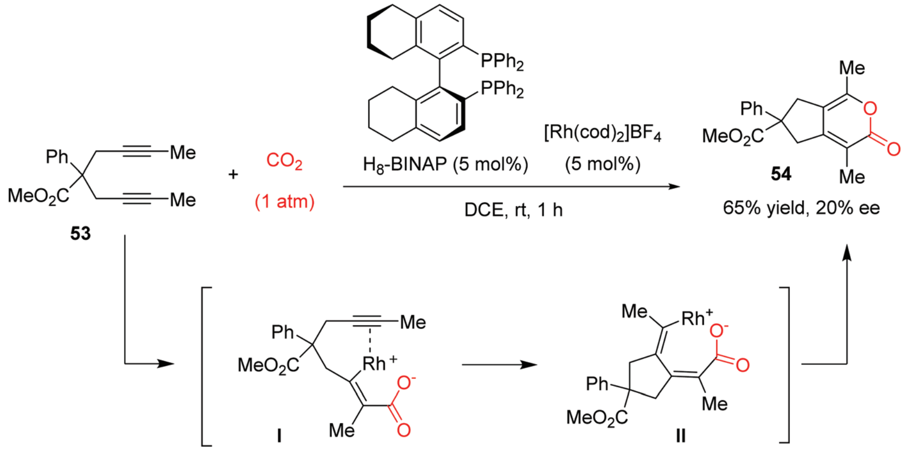
ylation (Scheme 20). The former is often realized through a five-membered metallacycle intermediate, formed *via* the reaction of low valent chiral transition metals, such as Ni(0) or Rh(0), with CO_2 and unsaturated alkenes or alkynes, bearing an extensive π-system (path a), while the latter could effectively combine the hydrometallation of unsaturated compounds with the carboxylation of organometallic nucleophiles formed *in situ*, enabling the effective construction of chiral carboxylic acid derivatives (path b).[67] Among these transformations, the effective dissociation of chiral metal catalysts from the generated products is critical.

In 2004, Mori and co-workers reported the first enantioselective nickel-catalyzed carboxylative cyclization reaction of bis-1,3-dienes. In the presence of chiral phosphine ligand MeO-MOP and $Ni(acac)_2$, the reaction of bis-1,3-dienes **50** with R_2Zn under a CO_2 atmosphere could deliver the chiral carbonate **51** with three new chiral centers in up to 100% yield and 96% ee.[68] As shown in Scheme 21, an intermediate bis-π-allylnickel species **I** was initially formed under the catalysis of the active Ni(0) complex. Then, the enantioselective insertion of CO_2 into the nickel–carbon bond of **I** produced carboxylate intermediate **II**, which subsequently transmetallated with R'_2Zn to afford nickel complex **III**. Reductive elimination followed by treatment with CH_2N_2 gave the desired product **51**. Notably, the addition of excess alkyl zinc was critical to the reaction, which could not only be used as a metal transfer reagent but also as a reducing agent to give the active Ni(0) complex. However, when Et_2Zn was employed, along with the ethylative cyclization, the reductive cyclization product **52** was also obtained owing to the β-hydride elimination of **III**.

In 2014, an enantioselective 2 + 2 + 2 cycloaddition of diynes with CO_2 was realized by Tanaka and co-workers. The cationic (*S*)-H_8-BINAP/Rh(I) complex catalyzed the reaction smoothly to give the chiral cycloaddition adduct **54** in 65% yield, but only 20% enantioselectivity was obtained. It was pro-



Scheme 21 Chiral Ni-catalyzed asymmetric carboxylative cyclization reaction.

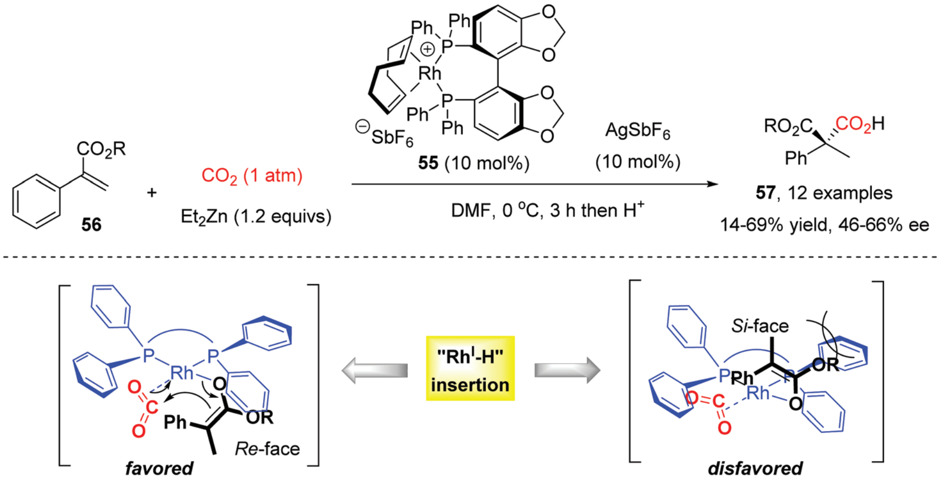


Scheme 22 Chiral Rh-catalyzed asymmetric 2 + 2 + 2 cycloaddition.

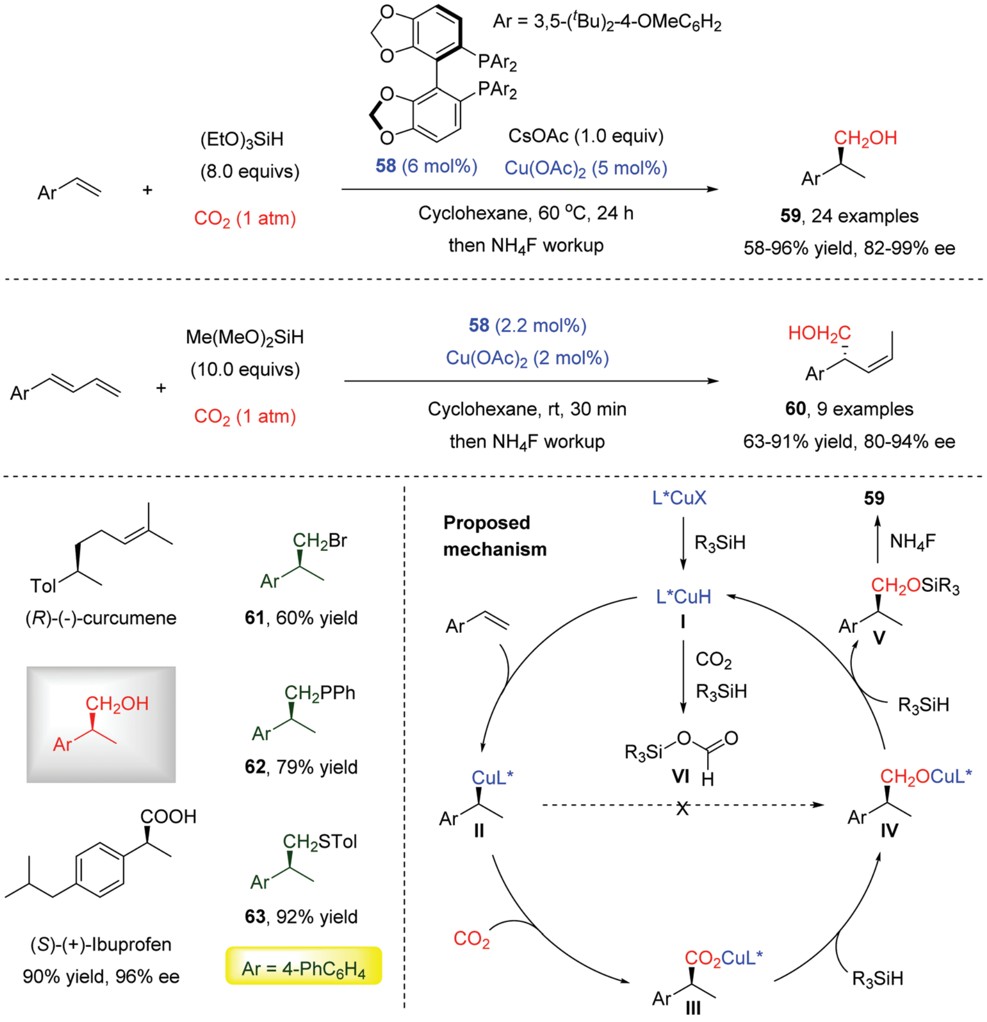
posed that the selective oxidative coupling of one alkyne moiety of **53** with CO_2 afforded heterorhodacyclopentene intermediate **I**, then the insertion of another alkyne moiety and reductive elimination furnished the final cycloadduct (Scheme 22).[69]

In 2016, Mikami's group developed a chiral Rh-catalyzed enantioselective hydrocarboxylation of α,β-unsaturated esters **56** with CO_2 for the construction of chiral carboxylic acids with all-carbon quaternary centers. By using cationic rhodium complex **55** as the catalyst and Et_2Zn as the hydride source, the desired α-aryl carboxylic acids **57** could be obtained in up to 69% yield and 66% ee (Scheme 23).[70] It was found that the addition of a catalytic amount of $AgSbF_6$ gave a higher yield and enantioselectivity, but its effect is currently unclear. During the insertion of CO_2 into chiral rhodium species formed *via* the Rh(I)–H insertion, the attack of the enolate to CO_2 from the *Re*-face of the rhodium side was favorable as a result of the prevention of the equatorial phenyl group on the phosphorus atom on the *Si*-face.

In 2017, the first enantioselective Cu-catalyzed reductive hydroxymethylation of alkenes with CO_2 was reported by Yu's group. The combination of 5.0 mol% $Cu(OAc)_2$ and 6 mol% chiral bisphosphine ligand **58**, along with the utilization of $(EtO)_3SiH$ as a reducing agent, enabled the effective reaction of styrene derivatives to give chiral homobenzylic alcohols **59** in 58–96% yield with 82–99% ee. Further study revealed that 1,3-dienes were also viable substrates. With $Me(MeO)_2SiH$ as the reducing agent, the corresponding allylic alcohols **60** could be obtained in high yields with excellent regio-, enantio- and *Z*-selectivities (Scheme 24).[71] Based on mechanistic studies, it was proposed that a chiral Cu–H species **I** initially formed through the reaction of **58**/$Cu(OAc)_2$ complex with hydrosilane, which subsequently reacted with alkenes in high regio- and enantio-selectivity to produce intermediate **II**. Then the reaction of **II** with CO_2 provided copper carboxylate **III**, which was further reduced by silanes to copper alkoxide **IV**. The following σ-bond metathesis of **IV** with hydrosilane gave the silyl ether product **V**, accompanied by the regeneration of Cu–H species **I**.



Scheme 23 Chiral Rh-catalyzed hydrocarboxylation of α,β-unsaturated esters.

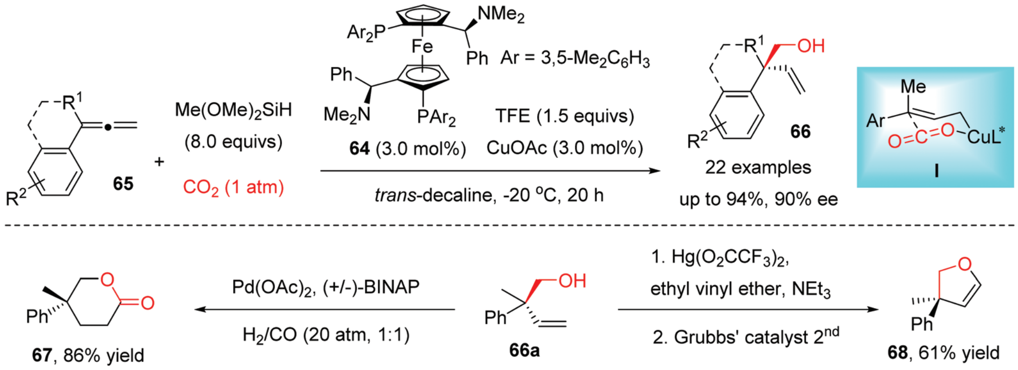


Scheme 24 Chiral Cu-catalyzed reductive hydroxymethylation of alkenes.

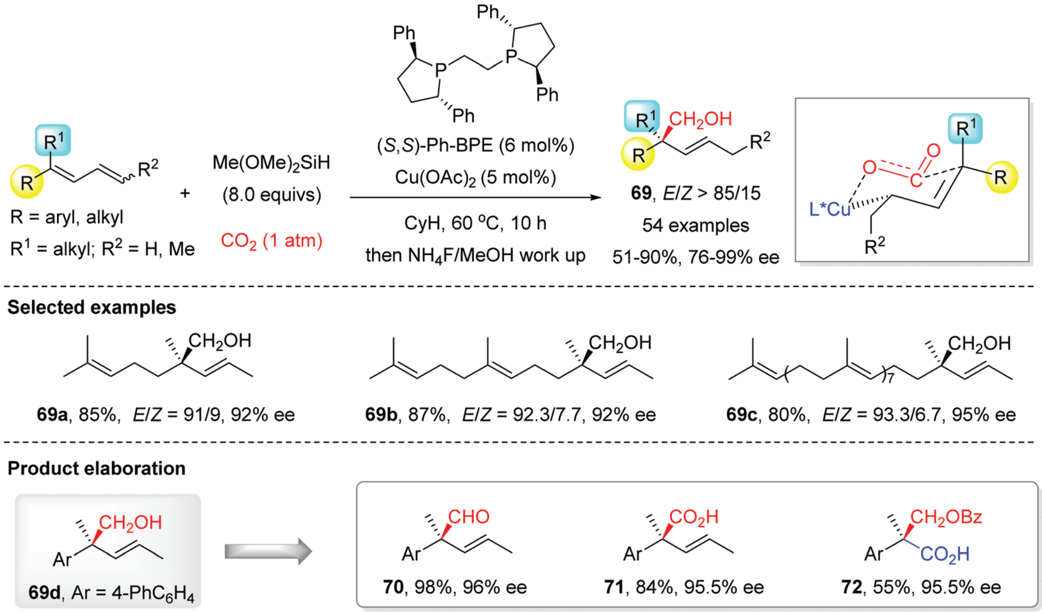
Owing to the competitive copper-catalyzed hydrosilylation of CO_2, a large excess of silane was required, and the silyl formate **VI** was demonstrated not to be the active intermediate. The desired chiral alcohol products were key intermediates in synthetic and medicinal chemistry, as exemplified by the transformation to **61–63** and bioactive compounds such as (*R*)-(−)-curcumene and (*S*)-(+)-ibuprofen.

In 2019, the chiral copper-catalyzed enantioselective reductive hydrocarboxylation of alkenes with CO_2 for the construction of all-carbon quaternary stereocenters was realized by Ding and Wang, and Yu and Lan. Ding and Wang reported that the combination of 3.0 mol% of Mandyphos **64** with CuOAc effectively catalyzed the hydroxymethylation of 1,1-disubstituted allenes with CO_2. With $Me(OMe)_2SiH$ as the reductant and 2,2,2-trifluoroethanol (TFE) as the additive, the chiral homoallylic alcohols **66** bearing all-carbon quaternary centers could be obtained in up to 94% yield and 90% ee (Scheme 25).[72] A six-membered ring transition state **I** between the generated γ,γ-disubstituted allyl metal intermediate with CO_2 was proposed for the construction of sterically congested quaternary carbon centers. The synthetic utility of the resulting homoallylic alcohols was demonstrated by the conversion of **66a** to other interesting chiral compounds, such as the δ-lactone **67** and dihydrofuran derivate **68**.

Yu and Lan established a highly selective copper-catalyzed reductive hydrocarboxylation of 1,1-disubstituted 1,3-dienes with CO_2 for the generation of chiral all-carbon acyclic quaternary stereocenters. By employing 5 mol% $Cu(OAc)_2$ with 6 mol% chiral ligand (*S*,*S*)-Ph-BPE, a wide range of 1-aryl- and 1,1-dialkyl-substituted as well as 1,1,4-trisubstituted 1,3-dienes could be converted to the corresponding chiral homoallylic alcohols **69** in 51–90% yield and 76–99% ee with an *E*/*Z* ratio of more than 85/15 (Scheme 26).[73] Notably, the challenging 1,1-dialkyl-substituted 1,3-dienes derived from terpenoids, possessing up to eight unconjugated double bonds, were also viable substrates to give products such as **69a–c** with high chemo-, regio-, *E*/*Z*- and enantio-selectivities. The potential application of this methodology was illustrated by the scale-up reaction, and the elaboration of chiral product **69d** to quaternary aldehyde **70**, carboxylic acid **71** and β-hydroxy acid **72**.



Scheme 25 Chiral Cu-catalyzed hydrocarboxylation of allenes to quaternary stereocenters.



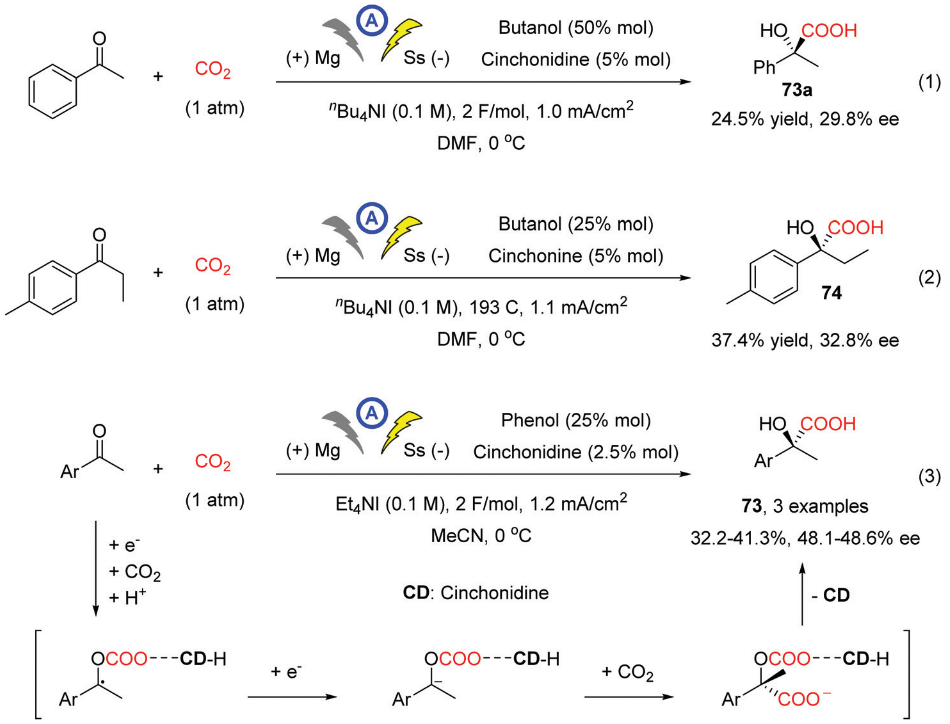
Scheme 26 Chiral Cu-catalyzed hydrocarboxylation of 1,1-disubstituted 1,3-dienes.

Systemic mechanistic investigations using density functional theory calculations revealed that the 1,2-hydrocupration of 1,3-diene proceeded with high π-facial selectivity to give an (*S*)-allylcopper intermediate, the 1,4-addition of which to CO_2 *via* a possible six-membered ring chair-like transition state determined the regio- and stereo-selectivity.

4. Electrochemical catalysis

Electrochemistry represents a useful tool for organic chemists as it affords a very facile and precise way of generating highly energetic intermediates *via* control of the electrode potential, providing good alternatives to traditional chemical methods.[74] Moreover, it could overcome the inherent thermodynamic stability of CO_2 by using electrons as redox reagents. In recent years, enantioselective electro-catalytic CO_2 incorporation, which is convenient, low-cost and eco-friendly, has attracted much attention.

Lu and co-workers pioneered the enantioselective electrochemical carboxylation of prochiral acetophenone with CO_2 catalyzed by chiral alkaloids under mild conditions. With an Mg rod as he sacrificial anode and stainless steel (Ss) as the cathode, the combination of cinchonidine and butanol gave the optical active atrolactic acid in 29.8% ee, which is a crucial intermediate in the production of certain anti-inflammatory drugs (Scheme 27, eqn (1)).[75] Based on cyclic voltammogram (CV) analysis, a possible mechanism was proposed, in which the chiral alkaloid could induce the selective proton transfer to the ketyl radical anion and assist the following CO_2 fixation process. Besides, the addition of butanol as a proton donor gave higher selectivity. Later in 2011, they further realized the asymmetric electrocarboxylation of 4-methylpropiophenone and up to 32.8% ee could be obtained. It was found that both



Scheme 27 Asymmetric electrochemical carboxylation of ketone.

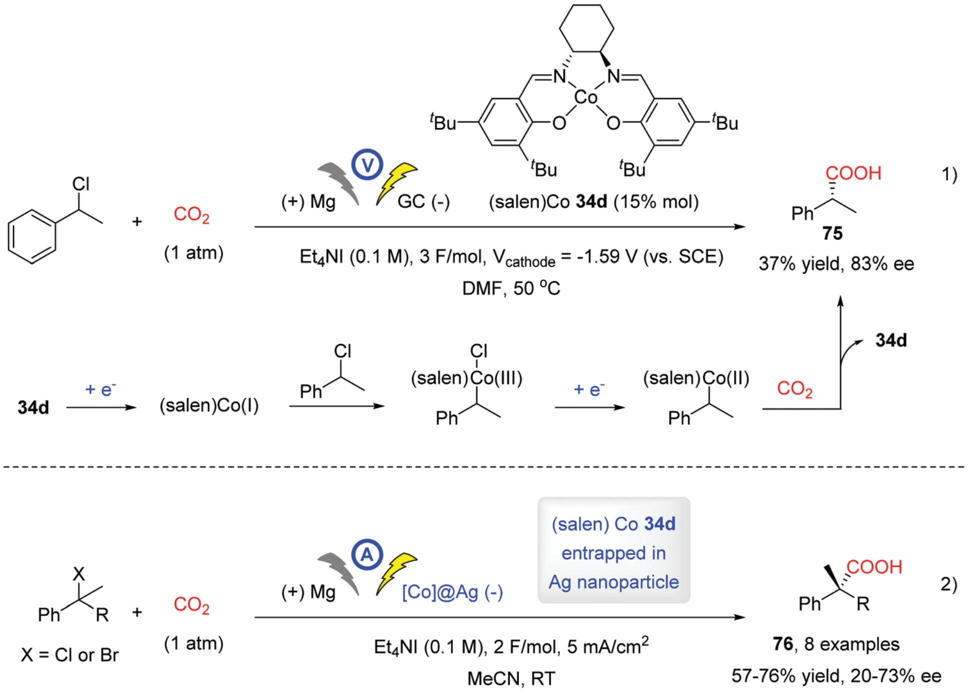
the hydroxyl group and the nucleophilic nitrogen atom on chiral alkaloids were critical for the enantioselective control (Scheme 27, eqn (2)).[76]

In 2014, Lu and Wang further synthetically investigated the enantioselective electrochemical carboxylation of aromatic ketones. By using cinchonidine as a chiral catalyst and phenol as an additive, the enantioselective galvanostatic electrolysis yielded chiral 2-hydroxy-2-arylpropionic acids **73** in up to 48.6% ee (Scheme 27, eqn (3)).[77] Control experiments revealed that the presence of phenol as a proton donor was very necessary to help the alkaloid cinchonidine realize the enantioselective control. According to the electrochemical behavior of ketone substrates in the absence and presence of CO_2, along with the reaction results, a detailed reaction pathway was proposed. It was suggested that the ketyl radical anion could react with CO_2 quickly, then the interaction of *in situ* generated carboxylate radical with protonated alkaloid would induce the subsequent CO_2 capture and deliver the final product.

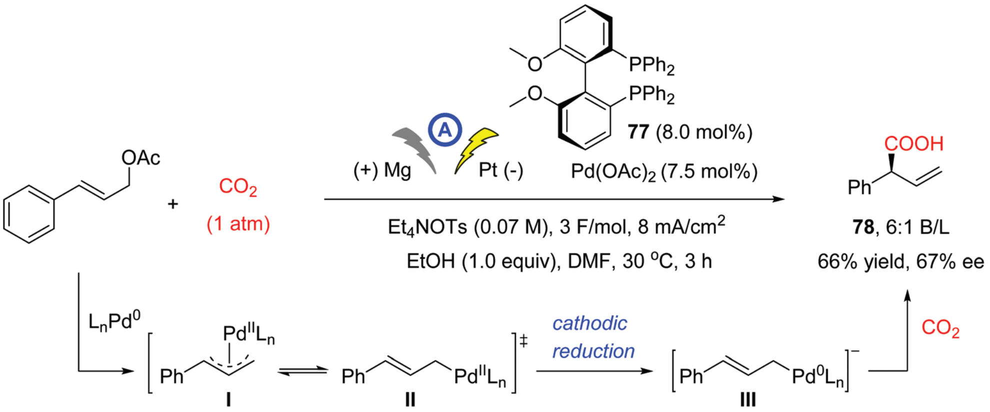
The enantioselective electrocarboxylation of benzyl halide was also realized by Lu and Wang based on chiral cobalt catalysis. In 2014, they developed the first asymmetric electrochemical carboxylation of achiral 1-phenylethyl chloride with CO_2 under potentiostatic electrolysis. The presence of chiral (salen)Co(II) complex **34d** enabled the construction of optically active 2-phenylpropionic acid **75** in 37% yield with 83% ee (Scheme 28, eqn (1)).[78] Study of the electrochemical behavior of (salen)Co(II) complex **34d** indicated that the (salen)Co(I)$^-$ generated from the one-electron transfer should be responsible for inducing the C–Cl bond cleavage, delivering a (salen)Co(III) alkyl complex. Then the subsequent one-electron transfer gave the (salen)Co(II) alkyl complex, which induced the nucleophilic attack to CO_2, thus giving the final chiral product.

Considering that the chiral (salen)Co(II) complex is expensive and hardly recyclable, they further developed a novel Co@Ag composite by entrapping the chiral cobalt complex **34d** within silver nanoparticles, and successfully applied it to the asymmetric carboxylation of benzyl halides with CO_2 in 2015. With this newly developed Co@Ag composite as the cathode as well as the heterogeneous catalyst, the carboxylation of a series of benzyl bromides and chlorides proceeded well to afford the corresponding chiral acids **76** in 57–76% yield and 20–73% ee (Scheme 28, eqn (2)).[79] Remarkably, the Co@Ag composite is highly stable and reusable, and can be recycled at least seven times without a decrease in the catalytic activity.

In 2018, Mei and co-workers described the first catalytic asymmetric electrocarboxylation of cinnamyl acetate with CO_2. Utilizing $Pd(OAc)_2$ as the catalyst and bidentate triarylphosphine **77** as the chiral ligand, the α-aryl carboxylic acid **78** was obtained successfully in 66% yield with moderate enantioselectivity (Scheme 29).[80] A plausible reaction mechanism was proposed based on CV studies, in which the oxidative addition of Pd(0) to cinnamyl acetate generated a cationic π-allylpalladium(II) complex **I**, which is in equilibrium with the terminal η^1-allylpalladium(II) species **II**. Then a two-electron reduction at the cathode formed an anionic η^1-allylpalladium(0) species **III**, the reaction of which with CO_2 gave the final chiral carboxylic acid.



Scheme 28 Asymmetric electrochemical carboxylation of benzyl halide.

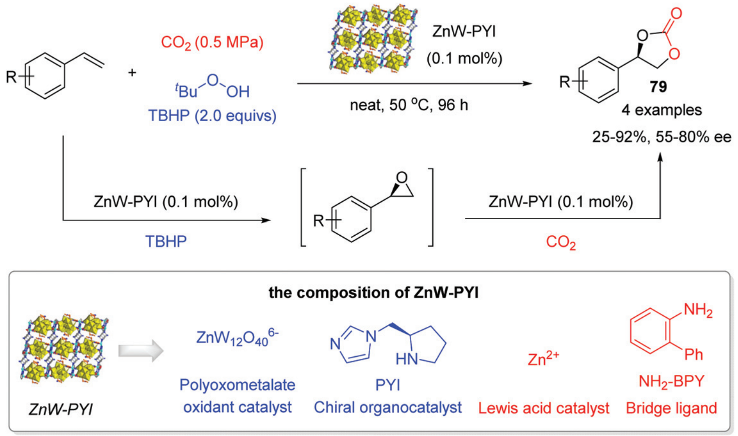


Scheme 29 Asymmetric electrochemical carboxylation of allyl ester.

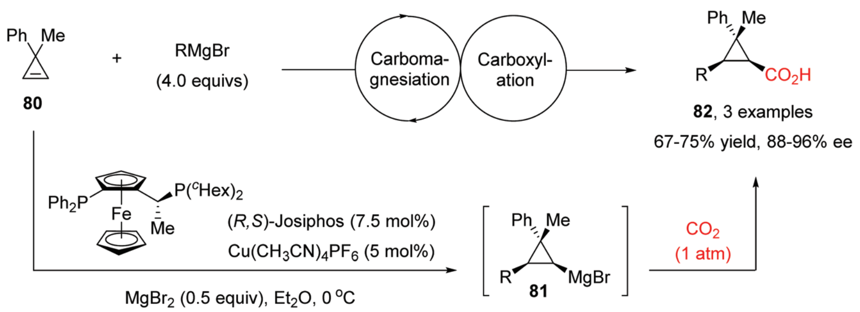
5. Catalytic enantioselective tandem reaction

The modular combination of catalytic asymmetric reactions with CO_2 chemical fixation in a cascade is another powerful strategy for realizing the enantioselective incorporation of CO_2 with value-added enantiomerically pure chemicals, in which CO_2 reacts directly with already formed chiral intermediates. As CO_2 does not participate in the construction of chiral centers, transformations with high enantioselectivity should be anticipated. Although a variety of elegant tandem asymmetric reactions have been reported, research into CO_2-participated cascade reactions is still in its infancy.[14]

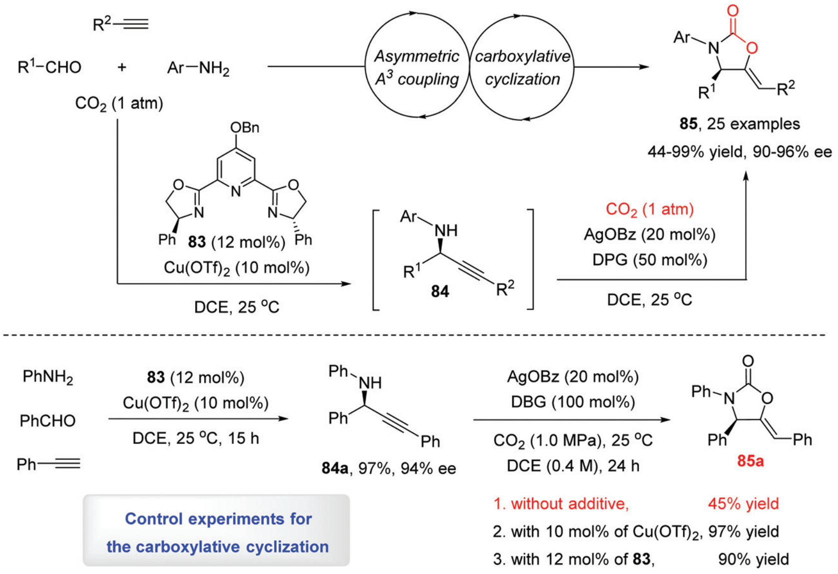
In 2015, Duan developed an attractive auto-tandem epoxidation/cycloaddition reaction by using a structurally novel metal–organic framework (MOF) material ZnW-PYI as the heterogeneous catalyst, in which the chiral organocatalyst PYI, oxidation catalyst polyoxometalate, Lewis acid Zn^{2+} as well as bridge ligand NH_2-BPY were systematically incorporated (Scheme 30).[81] Since the orderly distributed multi-catalytic sites were spatially matched, the chiral cyclic carbonates **79** could be obtained efficiently with high yield and enantioselectivity from simple alkenes, TBHP, and CO_2, without altering any reaction conditions. Mechanistic study revealed that the ZnW-PYI-catalyzed heterogeneous epoxidation possessed higher activity and selectivity than the corresponding homogeneous process. Meanwhile, CO_2 could be effectively trapped and activated by the NH_2 moiety



Scheme 30 Asymmetric auto-tandem epoxidation/coupling of styrene with CO_2.



Scheme 31 Asymmetric carbomagnesiation/carboxylation tandem reaction.



Scheme 32 Asymmetric A^3 coupling/carboxylative cyclization tandem reaction.

of NH_2-BPY in the channels of ZnW-PYI, thus facilitating the cycloaddition process. Notably, this heterogeneous catalyst could also be reused at least three times, albeit with a slight decrease in activity and selectivity.

In 2017, Marek and co-workers reported a highly enantioselective copper-catalyzed carbomagnesiation/carboxylation tandem reaction. Based on catalysis by the (*R*,*S*)-Josiphos/Cu(I) complex, the carbometalation reaction of cyclopropenes with

Grignard reagents delivered the chiral cyclopropylmagnesium halide **81** with high yield and excellent enantioselectivity. It was found that the configuration of the C–Mg bond was stable and could be well maintained when CO_2 was used as an electrophile to give the carboxylic acids **82** in 67–75% yields with 88–96% ee (Scheme 31).[82]

In the same year, we developed a novel tandem asymmetric A^3 coupling–carboxylative cyclization sequence for the highly enantioselective synthesis of chiral *N*-aryl 2-oxazolidinones from simple starting materials and CO_2 under mild conditions (Scheme 32).[83] The combination of $Cu(OTf)_2$ with chiral PyBOX type ligand **83** bearing a bulky C4 shielding group catalyzed the A^3 coupling reaction efficiently to give the chiral propargylic amine with excellent enantioselectivity, then the combination with a silver catalyzed carboxylation afforded the chiral *N*-aryl 2-oxazolidinones **85** with up to 99% yield and 90–96% ee. Notably, the utilization of 1,3-diphenylguanidine (DPG) was critical to the carboxylative cyclization of the *N*-aryl-substituted propargylamine. More importantly, the chiral ligand **83**, the copper species and the remaining aniline from the upstream A^3 reaction could be internally reused to facilitate the downstream Ag-catalyzed carboxylative cyclization, thus making it a rare example of a multicatalyst-promoted asymmetric tandem reaction with CO_2 as the C1 synthon.

6. Conclusion and outlook

Herein, the most recent achievements with catalytic enantioselective reactions with CO_2 as the C1 synthon have been intensively summarized. In particular, both chiral metal catalysis and organic catalysis have been successfully employed for the transformation of CO_2 to value-added chemicals. Based on the cooperative catalysis, a variety of chiral carbonates and carbamates can be effectively synthesized from nucleophilic alcohols and amines bearing an alkyne or alkene moiety. Meanwhile, the enantioselective coupling of CO_2 and epoxides provides an efficient route to optically active cyclic carbonates or polycarbonates with main-chain chirality *via* the controlling of the catalysts or reaction conditions. By using chiral transition metal catalysts, a series of chiral carboxylic acids and their derivatives have been constructed from CO_2 and unsaturated alkynes or alkenes, either through an oxidative cycloaddition or a hydrocarboxylation process. In addition, electrochemical catalysis has also been employed for the enantioselective conversion of CO_2 with ketones or halides, which are easily evaluable but possess low reactivity, based on the fact that electrochemistry can generate highly energetic intermediates in a facile and precise way. Recently, catalytic asymmetric tandem reactions involving CO_2 have emerged as another useful route for the chemical fixation of CO_2 with high enantioselectivity.

Despite these tremendous achievements, there is still ample room for catalytic enantioselective fixation of CO_2 to valuable chiral materials. First of all, the reaction types and the substrate scope need to be expanded, as the reported success most likely focuses on limited substrates. For instance, only three types of catalytic asymmetric tandem reactions involving CO_2 have been reported, two of which involve less than five substrates. Secondary, the efficiency and enantioselectivity should be further improved for some reactions, such as the only enantioselective 2 + 2 + 2 cycloaddition of diynes with CO_2, for which only 20% ee is obtained. Thirdly, a more efficient catalytic system should be developed to realize the reaction under ambient conditions. The relatively harsh conditions not only limit the applications of the reactions, but also make the reactions not so ideal as the heating or cooling may require extra energy and produce more CO_2. In terms of sustainability, the electrochemically catalyzed enantioselective conversion of CO_2 would be more desirable as the electrical energy can be directly generated from renewable sources, such as wind or sunlight. However, the enantioselectivity of the current reactions is still not satisfactory. In addition, the utilization of a sacrificial anode should be avoided in the future. Arguably, the asymmetric photocatalytic transformation of CO_2 using sunlight as energy has not yet been realized. If successful, such technology would be an ideal green method of CO_2 fixation.

Although the catalytic enantioselective fixation of CO_2 has not yet found significant application or commercial success, it is hoped that with the further development of new catalytic systems, new synthetic strategies and new chemical technology, more and more attractive and useful CO_2-based enantioselective transformations will be exploited. Considering the ever-growing number of contributions to this very promising but also challenging research field, a bright future can be forecast.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The financial support from the National Natural Science Foundation of China (21871090 and 81660576), the Fundamental Research Funds for the Central Universities and the projects of Guizhou province (Qian Ke He Zi 20154032 and 20191402) is highly appreciated.

References

1 M. Aresta, *Carbon Dioxide as Chemical Feedstock*, Wiley-VCH, Weinheim, 2010.
2 C. Song, *Catal. Today*, 2006, **115**, 2–32.
3 E. S. Sanz-Perez, C. R. Murdock, S. A. Didas and C. W. Jones, *Chem. Rev.*, 2016, **116**, 11840–11876.
4 N. von der Assen, P. Voll, M. Peters and A. Bardow, *Chem. Soc. Rev.*, 2014, **43**, 7982–7994.

5 A. Otto, T. Grube, S. Schiebahn and D. Stolten, *Energy Environ. Sci.*, 2015, **8**, 3283–3297.

6 (*a*) T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387; (*b*) C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuery, M. Ephritikhine and T. Cantat, *Angew. Chem., Int. Ed.*, 2012, **51**, 187–190; (*c*) M. Börjesson, T. Moragas, D. Gallego and R. Martin, *ACS Catal.*, 2016, **6**, 6739–6749; (*d*) Q.-W. Song, Z.-H. Zhou and L.-N. He, *Green Chem.*, 2017, **19**, 3707–3728; (*e*) A. Tortajada, F. Juliá-Hernández, M. Börjesson, T. Moragas and R. Martin, *Angew. Chem., Int. Ed.*, 2018, **57**, 15948–15982.

7 (*a*) N. Kielland, C. J. Whiteoak and A. W. Kleij, *Adv. Synth. Catal.*, 2013, **355**, 2115–2138; (*b*) X.-B. Lu, *Top. Organomet. Chem.*, 2015, **53**, 171–198; (*c*) M. I. Childers, J. M. Longo, N. J. Van Zee, A. M. LaPointe and G. W. Coates, *Chem. Rev.*, 2014, **114**, 8129–8152; (*d*) J. Vaitla, Y. Guttormsen, J. K. Mannisto, A. Nova, T. Repo, A. Bayer and K. H. Hopmann, *ACS Catal.*, 2017, **7**, 7231–7244; (*e*) X. Guo, Y. Wang, J. Chen, G. Li and J.-B. Xia, *Chin. J. Org. Chem.*, 2020, **40**, 2208–2220; (*f*) C.-K. Ran, X.-W. Chen, Y.-Y. Gui, J. Liu, L. Song, K. Ren and D.-G. Yu, *Sci. China: Chem.*, 2020, **63**, 1336–1351.

8 I. Ojima, *Catalytic Asymmetric Synthesis*, Wiley-VCH, United States, 2001.

9 (*a*) M. D. Burkart, N. Hazari, C. L. Tway and E. L. Zeitler, *ACS Catal.*, 2019, **9**, 7937–7956; (*b*) M. Mikkelsen, M. Jørgensen and F. C. Krebs, *Energy Environ. Sci.*, 2010, **3**, 43–81.

10 M. Aresta, A. Dibenedetto and E. Quaranta, *Reaction Mechanisms in Carbon Dioxide Conversion*, Springer, Berlin, Heidelberg, 2016.

11 Q. Liu, L. Wu, R. Jackstell and M. Beller, *Nat. Commun.*, 2015, **6**, 5933.

12 K. Huang, C.-L. Sun and Z.-J. Shi, *Chem. Soc. Rev.*, 2011, **40**, 2435–2452.

13 (*a*) B. P. Sullivan, K. Krist and H. E. Guard, *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*, Elsevier, Amsterdam, 1993; (*b*) R. Matthessen, J. Fransaer, K. Binnemans and D. E. De Vos, *Beilstein J. Org. Chem.*, 2014, **10**, 2484–2500; (*c*) L. Rossi, *Curr. Green Chem.*, 2015, **2**, 77–89; (*d*) H. Senboku and A. Katayama, *Curr. Opin. Green Sustain. Chem.*, 2017, **3**, 50–54; (*e*) Y. Cao, X. He, N. Wang, H.-R. Li and L.-N. He, *Chin. J. Chem.*, 2018, **36**, 644–659.

14 (*a*) J. Zhou, *Chem. – Asian J.*, 2010, **5**, 422–434; (*b*) Q.-J. Liang, Y.-H. Xu and T.-P. Loh, *Org. Chem. Front.*, 2018, **5**, 2765–2768; (*c*) J. A. Mata, F. E. Hahn and E. Peris, *Chem. Sci.*, 2014, **5**, 1723–1732; (*d*) H. Pellissier, *Adv. Synth. Catal.*, 2020, **362**, 2289–2325.

15 M. Yoshida, M. Fujita, T. Ishii and M. Ihara, *J. Am. Chem. Soc.*, 2003, **125**, 4874–4881.

16 S. Yoshida, K. Fukui, S. Kikuchi and T. Yamada, *J. Am. Chem. Soc.*, 2010, **132**, 4072–4073.

17 S. Xie, X. Gao, F. Zhou, H. Wu and J. Zhou, *Chin. Chem. Lett.*, 2020, **31**, 324–328.

18 Y.-L. Sun, Y. Wei and M. Shi, *Org. Chem. Front.*, 2019, **6**, 2420–2429.

19 B. A. Vara, T. J. Struble, W. Wang, M. C. Dobish and J. N. Johnston, *J. Am. Chem. Soc.*, 2015, **137**, 7302–7305.

20 R. Yousefi, T. J. Struble, J. L. Payne, M. Vishe, N. D. Schley and J. N. Johnston, *J. Am. Chem. Soc.*, 2019, **141**, 618–625.

21 M. Zhang, X. Zhao and S. Zheng, *Chem. Commun.*, 2014, **50**, 4455–4458.

22 S.-C. Zheng, M. Zhang and X.-M. Zhao, *Chem. – Eur. J.*, 2014, **20**, 7216–7221.

23 (*a*) M. North, R. Pasquale and C. Young, *Green Chem.*, 2010, **12**, 1514–1539; (*b*) C. Martín, G. Fiorani and A. W. Kleij, *ACS Catal.*, 2015, **5**, 1353–1370; (*c*) M.-Y. Wang, Q.-W. Song, R. Ma, J.-N. Xie and L.-N. He, *Green Chem.*, 2016, **18**, 282–287; (*d*) R. R. Shaikh, S. Pornpraprom and V. D'Elia, *ACS Catal.*, 2018, **8**, 419–450.

24 X.-B. Lu, W.-M. Ren and G.-P. Wu, *Acc. Chem. Res.*, 2012, **45**, 1721–1735 and ref. 7*c*.

25 (*a*) D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388–2410; (*b*) A. Decortes, A. M. Castilla and A. W. Kleij, *Angew. Chem., Int. Ed.*, 2010, **49**, 9822–9837.

26 Y.-M. Shen, W.-L. Duan and M. Shi, *J. Org. Chem.*, 2003, **68**, 1559–1562.

27 M. Tokunaga, J. F. Larrow, F. Kakiuchi and E. N. Jacobsen, *Science*, 1997, **277**, 936–938.

28 X.-B. Lu, B. Liang, Y.-J. Zhang, Y.-Z. Tian, Y.-M. Wang, C.-X. Bai, H. Wang and R. Zhang, *J. Am. Chem. Soc.*, 2004, **126**, 3732–3733.

29 X.-B. Lu and Y. Wang, *Angew. Chem., Int. Ed.*, 2004, **43**, 3574–3577.

30 W.-M. Ren, G.-P. Wu, F. Lin, J.-Y. Jiang, C. Liu, Y. Luo and X.-B. Lu, *Chem. Sci.*, 2012, **3**, 2094–2102.

31 T. Chang, H.-W. Jing, L.-L. Jin and W.-Y. Qiu, *J. Mol. Catal. A: Chem.*, 2007, **264**, 241–247.

32 A. Berkessel and M. Brandenburg, *Org. Lett.*, 2006, **8**, 4401–4404.

33 R. L. Paddock and S. T. Nguyen, *Chem. Commun.*, 2004, 1622–1623.

34 S. Zhang, Y. Song, H. Jing, P. Yan and Q. Cai, *Chin. J. Catal.*, 2009, **30**, 1255–1260.

35 (*a*) S. Zhang, Y. Huang, H. Jing, W. Yao and P. Yan, *Green Chem.*, 2009, **11**, 935; (*b*) Y. Song, Q. Jin, S. Zhang, H. Jing and Q. Zhu, *Sci. China: Chem.*, 2011, **54**, 1044–1050.

36 L.-L. Jin, Y.-Z. Huang, H.-W. Jing, T. Chang and P. Yan, *Tetrahedron: Asymmetry*, 2008, **19**, 1947–1953.

37 (*a*) P. Yan and H. Jing, *Adv. Synth. Catal.*, 2009, **351**, 1325–1332. For another recent achievement, see: (*b*) Z. Zhu, Y. Zhang, K. Wang, X. Fu, F. Chen and H. Jing, *Catal. Commun.*, 2016, **81**, 50–53.

38 (*a*) T. Chang, L. Jin and H. Jing, *ChemCatChem*, 2009, **1**, 379–383; (*b*) S. Duan, X. Jing, D. Li and H. Jing, *J. Mol. Catal. A: Chem.*, 2016, **411**, 34–39.

39 T. Roy, R. I. Kureshy, N. H. Khan, S. H. R. Abdiab and H. C. Bajaj, *Catal. Sci. Technol.*, 2013, **3**, 2661–2667.

40 H. Tanaka, Y. Kitaichi, M. Sato, T. Ikeno and T. Yamada, *Chem. Lett.*, 2004, **33**, 676–677.

41 W. Yamada, Y. Kitaichi, H. Tanaka, T. Kojima, M. Sato, T. Ikeno and T. Yamada, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 1391–1401.

42 (*a*) R. B. Kawthekar, W. T. Bi and G. J. Kim, *Bull. Korean Chem. Soc.*, 2008, **29**, 313–318; (*b*) D. Y. Jang, H. G. Jang, G. R. Kim and G. J. Kim, *Catal. Today*, 2012, **185**, 306–312; (*c*) S. W. Chen, R. B. Kawthekar and G. J. Kim, *Tetrahedron Lett.*, 2007, **48**, 297–300.

43 X. Fu, X. Jing, L. Jin, L. Zhang, X. Zhang, B. Hu and H. Jing, *Chin. J. Catal.*, 2018, **39**, 997–1003.

44 For chiral Ni catalysis: (*a*) Y. Ren, X. Cheng, S. Yang, C. Qi, H. Jiang and Q. Mao, *Dalton Trans.*, 2013, **42**, 9930–9937. For chiral Ti catalysis: (*b*) M. Brunner, L. Mußmann and D. Vogt, *Synlett*, 1993, 893–894; (*c*) M. Brunner, L. Mußmann and D. Vogt, *Synlett*, 1994, 69–70. For chiral Nb catalysis: (*d*) M. Aresta, A. Dibenedetto, L. Gianfrate and C. Pastore, *Appl. Catal., A*, 2003, **255**, 5–11. For chiral Cr catalysis: (*e*) B. Li, G.-P. Wu, W.-M. Ren, Y.-M. Wang, D.-Y. Rao and X.-B. Lu, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6102–6113.

45 M. North, S. C. Z. Quek, N. E. Pridmore, A. C. Whitwood and X. Wu, *ACS Catal.*, 2015, **5**, 3398–3402.

46 J. Qin, V. A. Larionov, K. Harms and E. Meggers, *ChemSusChem*, 2019, **12**, 320–325.

47 C. Maeda, K. Ogawa, K. Sadanaga, K. Takaishi and T. Ema, *Chem. Commun.*, 2019, **55**, 1064–1067.

48 S. Liu, N. Suematsu, K. Maruok and S. Shirakawa, *Green Chem.*, 2016, **18**, 4611–4615.

49 T. Ema, M. Yokoyama, S. Watanabe, S. Sasaki, H. Ota and K. Takaishi, *Org. Lett.*, 2017, **19**, 4070–4073.

50 K. Takaishi, T. Okuyama, S. Kadosaki, M. Uchiyama and T. Ema, *Org. Lett.*, 2019, **21**, 1397–1401.

51 K. Nozaki, K. Nakano and T. Hiyama, *J. Am. Chem. Soc.*, 1999, **121**, 11008–11009.

52 K. Nakano, K. Nozaki and T. Hiyama, *J. Am. Chem. Soc.*, 2003, **125**, 5501–5510.

53 K. Nakano, T. Hiyamab and K. Nozak, *Chem. Commun.*, 2005, 1871–1873.

54 M. Cheng, N. A. Darling, E. B. Lobkovsky and G. W. Coates, *Chem. Commun.*, 2000, 2007–2008.

55 W. C. Ellis, Y. Jung, M. Mulzer, R. D. Girolamo, E. B. Lobkovsky and G. W. Coates, *Chem. Sci.*, 2014, **5**, 4004–4011.

56 Y. Xiao, Z. Wang and K. Ding, *Chem. – Eur. J.*, 2005, **11**, 3668–3678.

57 (*a*) Y.-Z. Hua, L.-J. Lu, P.-J. Huang, D.-H. Wei, M.-S. Tang, M.-C. Wang and J.-B. Chang, *Chem. – Eur. J.*, 2014, **20**, 12394–12398; (*b*) Y.-Z. Hua, X.-C. Yang, M.-M. Liu, X. Song, M.-C. Wang and J.-B. Chang, *Macromolecules*, 2015, **48**, 1651–1657.

58 S. Abbina and G. Du, *Organometallics*, 2012, **31**, 7394–7403.

59 K. Nishioka, H. Goto and H. Sugimoto, *Macromolecules*, 2012, **45**, 8172–8192.

60 L. Shi, X.-B. Lu, R. Zhang, X.-J. Peng, C.-Q. Zhang, J.-F. Li and X.-M. Peng, *Macromolecules*, 2006, **39**, 5679–5685.

61 (*a*) G.-P. Wu, W.-M. Ren, Y. Luo, B. Li, W.-Z. Zhang and X.-B. Lu, *J. Am. Chem. Soc.*, 2012, **134**, 5682–5688; (*b*) G. P. Wu, S. D. Jiang, X. B. Lu, W. M. Ren and S. K. Yan, *Chin. J. Polym. Sci.*, 2012, **30**, 487–492.

62 Y. Liu, W.-M. Ren, J. Liu and X.-B. Lu, *Angew. Chem., Int. Ed.*, 2013, **52**, 11594–11598.

63 Y. Liu, W.-M. Ren, K.-K. He and X.-B. Lu, *Nat. Commun.*, 2014, **5**, 5687–5693.

64 Y. Liu, W.-M. Ren, K.-K. He, W.-Z. Zhang, W.-B. Li, M. Wang and X.-B. Lu, *J. Org. Chem.*, 2016, **81**, 8959–8966.

65 W.-B. Li, Y. Liu and X.-B. Lu, *Organometallics*, 2020, **39**, 1628–1633.

66 Y. Liu, W.-M. Ren, C. Liu, S. Fu, M. Wang, K.-K. He, R.-R. Li, R. Zhang and X.-B. Lu, *Macromolecules*, 2014, **47**, 7775–7788.

67 (*a*) M. North, *Angew. Chem., Int. Ed.*, 2009, **48**, 4104–4105; (*b*) Y. Zhang and S. N. Riduan, *Angew. Chem., Int. Ed.*, 2011, **50**, 6210–6212.

68 M. Takimoto, Y. Nakamura, K. Kimura and M. Mori, *J. Am. Chem. Soc.*, 2004, **126**, 5956–5957.

69 M. Ishii, F. Mori and K. Tanaka, *Chem. – Eur. J.*, 2014, **20**, 2169–2174.

70 S. Kawashima, K. Aikawa and K. Mikami, *Eur. J. Org. Chem.*, 2016, 3166–3170.

71 Y.-Y. Gui, N. Hu, X.-W. Chen, L.-L. Liao, T. Ju, J.-H. Ye, Z. Zhang, J. Li and D.-G. Yu, *J. Am. Chem. Soc.*, 2017, **139**, 17011–17014.

72 J. Qiu, S. Gao, C. Li, L. Zhang, Z. Wang, X. Wang and K. Ding, *Chem. – Eur. J.*, 2019, **25**, 13874–13878.

73 X.-W. Chen, L. Zhu, Y.-Y. Gui, K. Jing, Y.-X. Jiang, Z.-Y. Bo, Y. Lan, J. Li and D.-G. Yu, *J. Am. Chem. Soc.*, 2019, **141**, 18825–18835.

74 For review, see: (*a*) E. J. Horn, B. R. Rosen and P. S. Baran, *ACS Cent. Sci.*, 2016, **2**, 302–308; (*b*) M. Yan, Y. Kawamata and P. S. Baran, *Chem. Rev.*, 2017, **117**, 13230–13319; (*c*) A. Wiebe, T. Gieshoff, S. Möhle, E. Rodrigo, M. Zirbes and S. R. Waldvogel, *Angew. Chem., Int. Ed.*, 2018, **57**, 5594–5619; (*d*) J. C. Siu, N. Fu and S. Lin, *Acc. Chem. Res.*, 2020, **53**, 547–560. For selected example, see: (*e*) X.-T. Gao, Z. Zhang, X. Wang, J.-S. Tian, S.-L. Xie, F. Zhou and J. Zhou, *Chem. Sci.*, 2020, **11**, 10414–10420.

75 K. Zhang, H. Wang, S.-F. Zhao, D.-F. Niu and J.-X. Lu, *J. Electroanal. Chem.*, 2009, **630**, 35–41.

76 S.-F. Zhao, M.-X. Zhu, K. Zhang, H. Wang and J.-X. Lu, *Tetrahedron Lett.*, 2011, **52**, 2702–2705.

77 B.-L. Chen, Z.-Y. Tu, H.-W. Zhu, W.-W. Sun, H. Wang and J.-X. Lu, *Electrochim. Acta*, 2014, **116**, 475–483.

78 B.-L. Chen, H.-W. Zhu, Y. Xiao, Q.-L. Sun, H. Wang and J.-X. Lu, *Electrochem. Commun.*, 2014, **42**, 55–59.

79 H.-P. Yang, Y.-N. Yue, Q.-L. Sun, Q. Feng, H. Wang and J.-X. Lu, *Chem. Commun.*, 2015, **51**, 12216–12219.

80 K.-J. Jiao, Z.-M. Li, X.-T. Xu, L.-P. Zhang, Y.-Q. Li, K. Zhang and T.-S. Mei, *Org. Chem. Front.*, 2018, **5**, 2244–2248.

81 Q. Han, B. Qi, W. Ren, C. He, J. Niu and C. Duan, *Nat. Commun.*, 2015, **6**, 10007–10014.

82 L. Dian, D. S. Mgller and I. Marek, *Angew. Chem., Int. Ed.*, 2017, **56**, 6783–6787.

83 X.-T. Gao, C.-C. Gan, S.-Y. Liu, F. Zhou, H.-H. Wu and J. Zhou, *ACS Catal.*, 2017, **7**, 8588–8593.