综述与进展

REVIEW

过渡金属催化的不对称电化学进展

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摘要 总结了近年来过渡金属催化的不对称电化学进展. 过渡金属催化的不对称电化学(AOMCE)分为氧化和还原反应. 在氧化反应方面, 发展了烯烃的不对称官能团化, 二级醇或醛的动力学拆分以及碳氢键的不对称官能团化反应. 在还原反应部分包括二氧化碳的不对称电化学羧化、不对称电化学脱羧反应以及不对称还原偶联反应. 手性配体和过渡金属催化剂与电化学体系的结合构成了一个非常新颖的反应体系, 为解决传统有机电化学合成中立体选择性控制的难题, 提供了一条新途径.

关键词 过渡金属催化的不对称电化学; 有机电化学合成; 不对称催化

Advances in Asymmetric Organotransition Metal-Catalyzed Electrochemistry

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Abstract The recent developments in asymmetric organotransition metal-catalyzed electrochemistry (AOMCE) are summarized. AOMCE processes can be divided into oxidative and reductive variants. In terms of oxidations, asymmetric functionalization of olefins, oxidative kinetic resolution of secondary alcohols or aldehydes, and asymmetric C—H functionalization reactions have been developed. Reductive processes discussed include asymmetric electrochemical carboxylation with carbon dioxide, asymmetric electrochemical decarboxylation, and asymmetric reductive coupling reactions. The combination of chiral ligands, transition-metal catalysts, and electrochemistry provides a novel angle by which to address the longstanding fundamental challenge of stereoinduction in traditional electrochemical organic synthesis.

Keywords asymmetric organotransition metal-catalyzed electrochemistry; electrochemical organic synthesis; asymmetric catalysis

1 Introduction

Kolbe[1] and Baizer[2] successful introduced electricity into organic synthesis by dimerizing carboxylic acids (in 1847) and acrylonitrile (in 1964), respectively. In recent decades, electrochemistry has made tremendous advances as a platform for the discovery of novel synthetic transformations.[3] Through electrochemistry, challenging transformations are made possible by the ability to generate free radical intermediates under mild conditions.[4] At the same time, controlling chemoselectivity, regioselectivity, and stereoselectivity of a given electrochemical transformation can be difficult, particularly converting achiral compounds into chiral ones.

Significant effort has been made to develop efficient enantioselective electrochemical protocols,[5] including via the use of chiral solvents,[6] chiral auxiliaries,[7] chiral supporting electrolytes,[8] chiral mediators,[9] chiral elec-

trodes,[10] or chiral catalysts.[5,11]

Organotransition-metal catalysts provide a particular promising means to realizing high chemoselectivity, regioselectivity, and stereoselectivity within an electrochemical process. Three specific advantages of an organotransition metal-catalyzed approach are: (1) the redox potential of the transition-metal catalyst may be tuned by changing substituents on the ligand, (2) modification of the ligand can dictate the reaction stereoselectivity (and chemoselectivity and regioselectivity), (3) well-established thermochemical organotransition metal-catalyzed methodologies provide a rigorous foundation for the development of electrochemical variants.

In this review, we emphasize the recent advances in asymmetric organotransition metal-catalyzed electrochemistry (AOMCE), which we defined as reactions that require the combination of transition-metal catalyst, chiral ligand, and electricity. AOMCE can be divided into two types: asymmetric electrochemical oxidation and asymmetric electrochemical reduction. In the asymmetric electrochemical oxidation section, olefin functionalization, kinetic resolution of secondary alcohols or aldehydes, and C—H functionalization are discussed. In the reductive section, asymmetric electroreductive carboxylation with carbon dioxide, electrochemical decarboxylation, and reductive couplings are highlighted.

2　Asymmetric organotransition metal-catalyzed electrochemical oxidation

2.1　Asymmetric electrochemical oxidative functionalization of olefins

The osmium tetroxide-catalyzed oxidation of olefins to produce vicinal diols is a well-known and reliable synthetic method in organic chemistry.[12] Due to the high cost and toxicity of osmium, it is employed catalytically for alkene oxidations in the presence of a less expensive and toxic terminal oxidant.[13]

In 1992, Amundsen and co-workers[14] reported the synthesis of a number of chiral diols using a modification of the Sharpless process in an electrolytically regenerated system (Scheme 1a). Osmium tetroxide bearing chiral ligand **L1** (hydroquinidine 4-chlorobenzoate) was employed as catalyst, and a catalytic amount of potassium ferricyanide was used as mediating oxidant. A divided cell was necessary to prevent cathodic reduction of ferricyanide oxidant and electrodeposition of osmium. Enantiomeric selectivity was predicated on having bulky alkene substituents, namely phenyls.[15]

In 1995, Torii and co-workers[16] improved the process of asymmetric electrodihydroxylation of olefins under constant current in an undivided cell using dihydroquinidine phthalazine ligand **L2** and less osmate catalyst and potassium ferricyanide (Scheme 1b). A year later Torii and co-workers[17] developed a variant employing iodine as an oxidizing mediator (Scheme 1c). The desired diols were obtained in high *ee* values and high yields in each of these optimized processes.

Optically active epoxides are versatile intermediates in the synthesis of pharmaceuticals, agrochemicals, and functional materials.[18] Electrochemical asymmetric epoxidation has been investigated as an alternative process avoiding the use of a stoichiometric amount of co-oxidant.[19] In 2001, Tanaka and co-workers[20] reported an efficient enantioselective Mn(salen)-catalyzed electro-epoxidation of olefins in a two-phase CH_2Cl_2/NaCl (aq.) electrolysis system in an undivided cell (Scheme 2a). The electro-epoxidation of indene **3e** gave the corresponding epoxide **4e** in rather low yield and enantioselectivity. Due to the high reactivity of the double bond, which enabled undesired oxidations by an electro-generated chlorine species $[Cl^+]$.

The CH_2Cl_2/water two-phase system played an important role in the reaction. When using water-miscible organic solvents, such as *t*-BuOH and MeCN, a complex mixture of unidentified products was formed in lieu of the desired epoxide, possibly a result of decomposition of Mn(salen) via oxidation at the anode. In the two-phase system, electrochemical oxidation occurs only in the aqueous phase, thereby suppressing direct electrochemical oxidation of Mn(salen) which resides in the organic phase. A plausible mechanism is presented in Scheme 2b.

Recently, Lin and co-workers[21] reported the development of highly enantioselective cyanophosphinoylations or cyanosulfinylations of alkenes using rational ligand design and optimization of the electrolysis conditions (Scheme 3a). Substantial modification of the ligand scaffold was required to break a selectivity ceiling that they encountered. Introduction of an ancillary ligand to the BOX (bisoxazolines) scaffold (specifically an ester group) was used to further stabilize the putative pentacoordinated Cu(III) complex prior to reductive elimination. This modification also served to increase the rigidity of the transition state and improve the stereochemical fidelity of the cyanation process (Scheme 3b). Moreover, Lin and co-workers hypothesized that the multidentate ligand further stabilized the Cu catalyst against cathodic demetallation and present a cationic intermediate (**I**, Scheme 3b) that was more susceptible to reductive elimination.

2.2　Kinetic resolution via electrochemical oxidation

Selective oxidation of hydroxyl groups into carbonyl groups is an important organic transformation. In 2008, Onomura and co-workers[22] reported a copper-catalyzed electrochemical oxidation kinetic resolution of racemic *cis*-cycloalkane-1,2-diols, aminoalcohols, and aminoaldehydes. Their efficient procedure employed copper(II) triflate and (*R*,*R*)-Ph-BOX ligand with tetraethylammonium bromide as the oxidizing mediator (Scheme 4). The method was applicable to the kinetic resolution of some piperidine-3,4-diols (*rac*-**10** and *rac*-**12**, Schemes 4b and 4c respectively). It bears mentioning that these substrates are not efficiently oxidized by NBS (*N*-Bromosuccinimide).[23]

2.3　Asymmetric C—H functionalization

In 1975, Shono and co-workers[25] demonstrated an an-
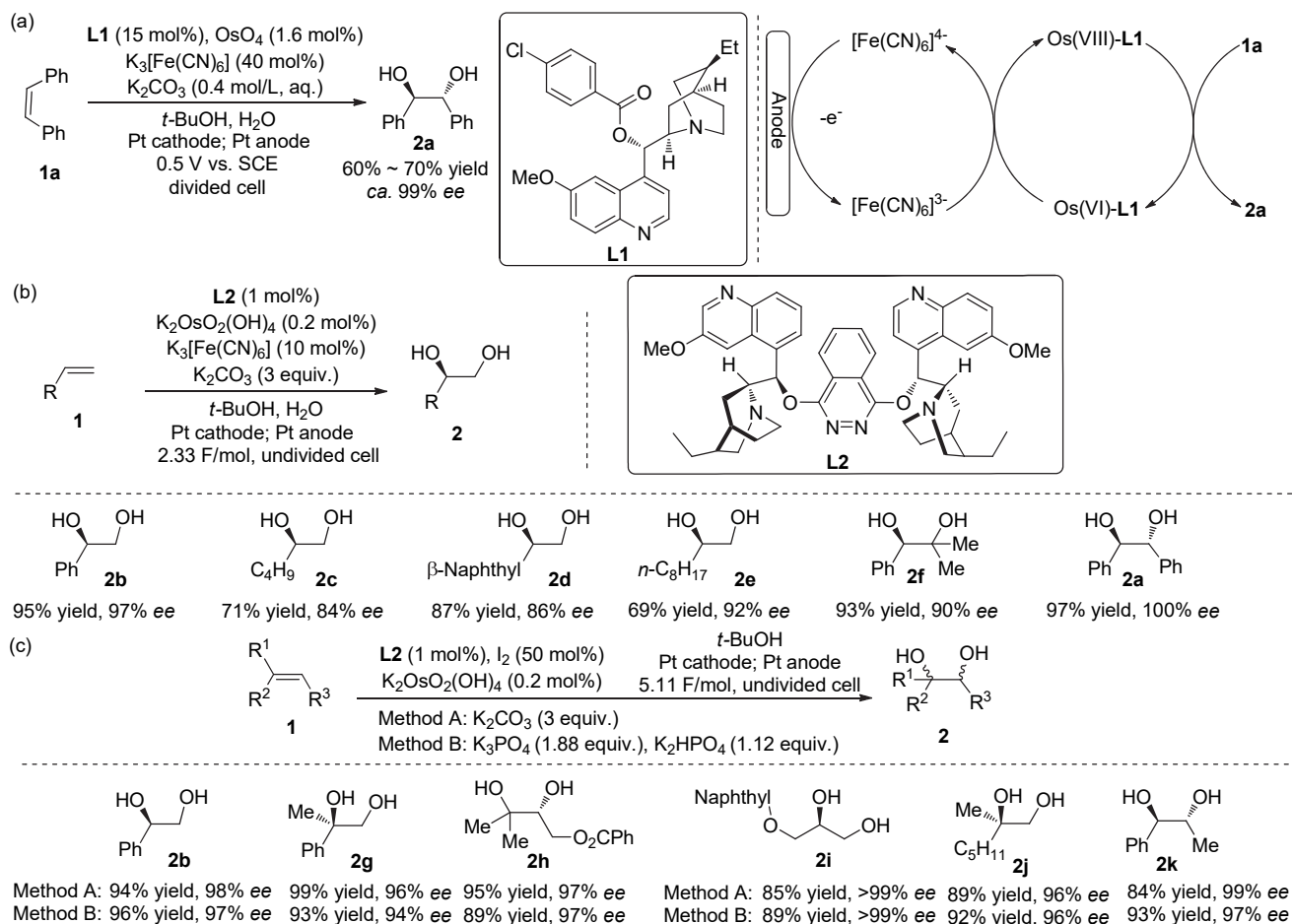
Scheme 1　Os-catalyzed asymmetric electrochemical dihydroxylation of olefins
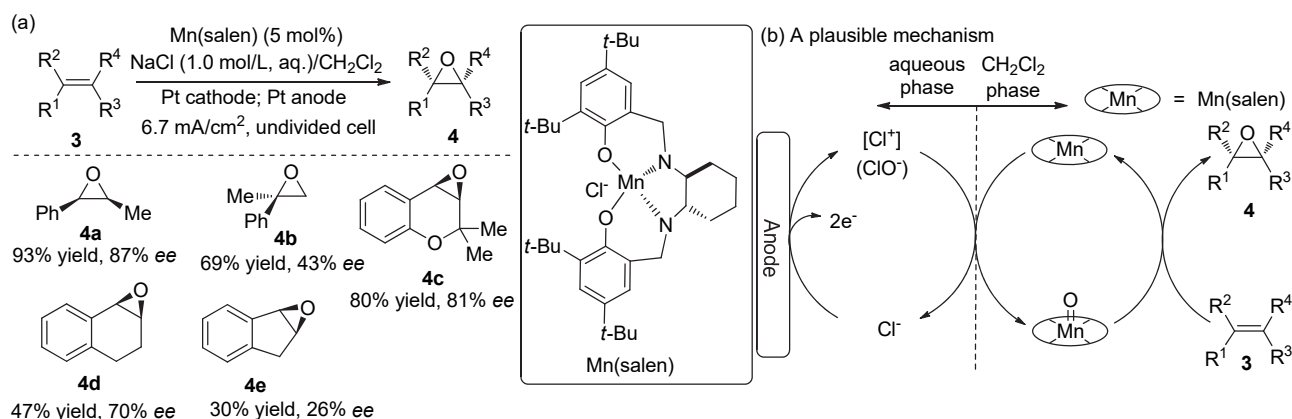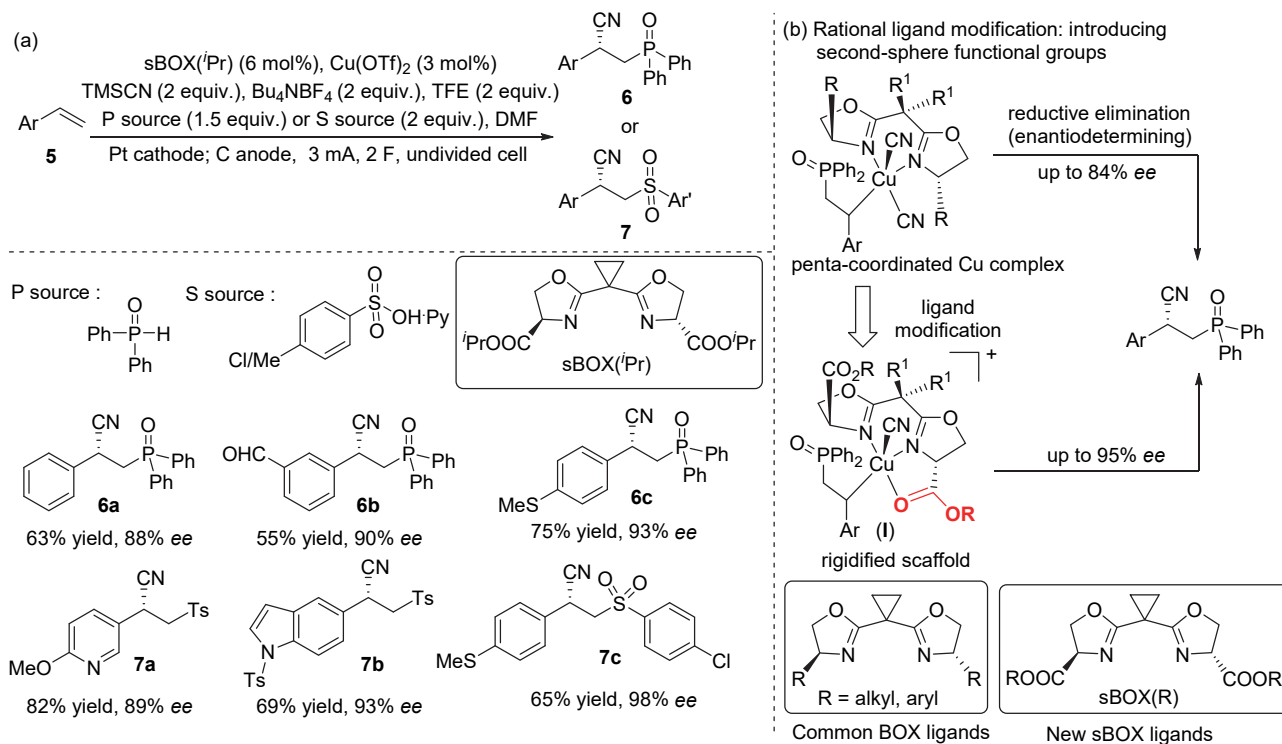

**Scheme 2**　Mn-salen-catalyzed asymmetric electrochemical epoxidation of olefins

odic oxidation of carbamates to *N*-carbamoyl iminium ions.[24] The resulting *N*-carbamoyl iminium ions can be trapped with various nucleophiles, including allyl silanes, cyanide, fluoride, furans, and isocyanides. This provided a powerful tool for the *α*-C—H functionalization of amines.[26] Early attempts at asymmetric Shono-type oxidative cross-couplings relied on chiral auxiliaries and afforded varying levels of stereoselectivity when using alkyl nucleophiles.[27] In 2017, Luo and coworkers[28] developed a protocol using enamine catalysis and

electrochemical C—H oxidation, providing C1-alkylated tetrahydroisoquinolines (THIQs) in good-to-excellent diastereoselectivity and enantioselectivity.

Very recently, Mei and co-workers[29] reported the first example of Cu/TEMPO (2,2,6,6-tetramethylpiperidinyl-*N*-oxyl) co-catalyzed electrochemical enantioselective oxidative cross-coupling between cyclic tertiary amines and terminal alkynes using a novel chiral bisoxazoline ligand in an undivided cell (Scheme 5a). The reaction exhibited high enantioselectivity and broad functional group tolerance.

Scheme 3   Cu-catalyzed asymmetric electro-cyanophosphinoylation or -cyanosulfinylation of alkenes
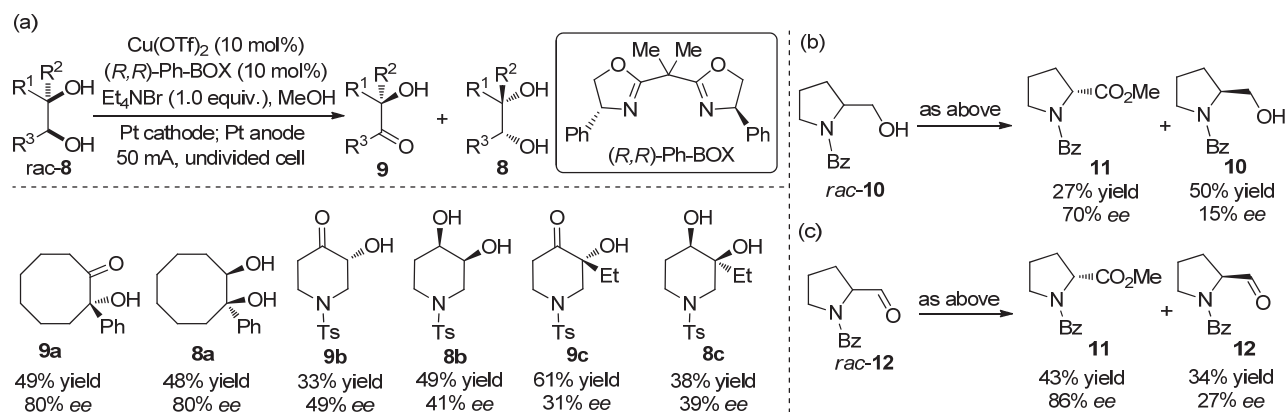

Scheme 4   Kinetic resolution via electro-oxidation

The use of TEMPO as a co-catalytic redox mediator was crucial not only for oxidizing a tetrahydroisoquinoline to an iminium ion species, but also for dimishing the oxidation potential of the reaction. A plausible catalytic cycle is shown in Scheme 5b. First, oxoammonium species (TEMPO$^+$) **17** is formed via anodic oxidation of TEMPO. Upon hydride transfer,[30] iminium intermediate **20** is generated from **13**, with the concomitant formation of TEMPO-H **16**, which can be converted into **17** by anodic oxidation. Addition of the chiral acetylide species **19** (derived from Cu(I) and alkyne **14** in the presence of base) to electrophilic **18** results in the formation of product **15**. Active Cu(I) could be generated by either the reaction of Cu(II) with TEMPO-H, or cathodic reduction of Cu(II).[31] Alternatively, other cooperative modes involving both Cu(II) and TEMPO in the key oxidative iminium-formation step could not be ruled out.[32]

In 2019, Meggers and co-workers[33] reported an electricity-driven asymmetric Δ-Rh-catalyzed oxidative cross-coupling of 2-acyl imidazoles with silyl enol ethers for the generation of enantioenriched 1,4-dicarbonyls in high yield and high enantioselectivity, including access to quaternary stereocenters (Scheme 6a). The reaction exhibited broad functional group tolerance. The chiral Lewis acid catalyst Δ-Rh was shown to be involved in both the electrochemical step and the asymmetric induction. Substrate binding to the catalyst and subsequent deprotonation raised the highest occupied molecular orbital and triggered a mild and selective anodic oxidation to provide a catalyst-bound reactive intermediate that engaged in a stereo-controlled radical C—C bond-forming reaction. A plausible mechanism is shown in (Scheme 6b). Later in 2019, Guo and co-workers[34] reported a Ni-catalyzed asymmetric electrochemical alkylation via benzylic C—H bond functionalization (Scheme 7a).

(a)
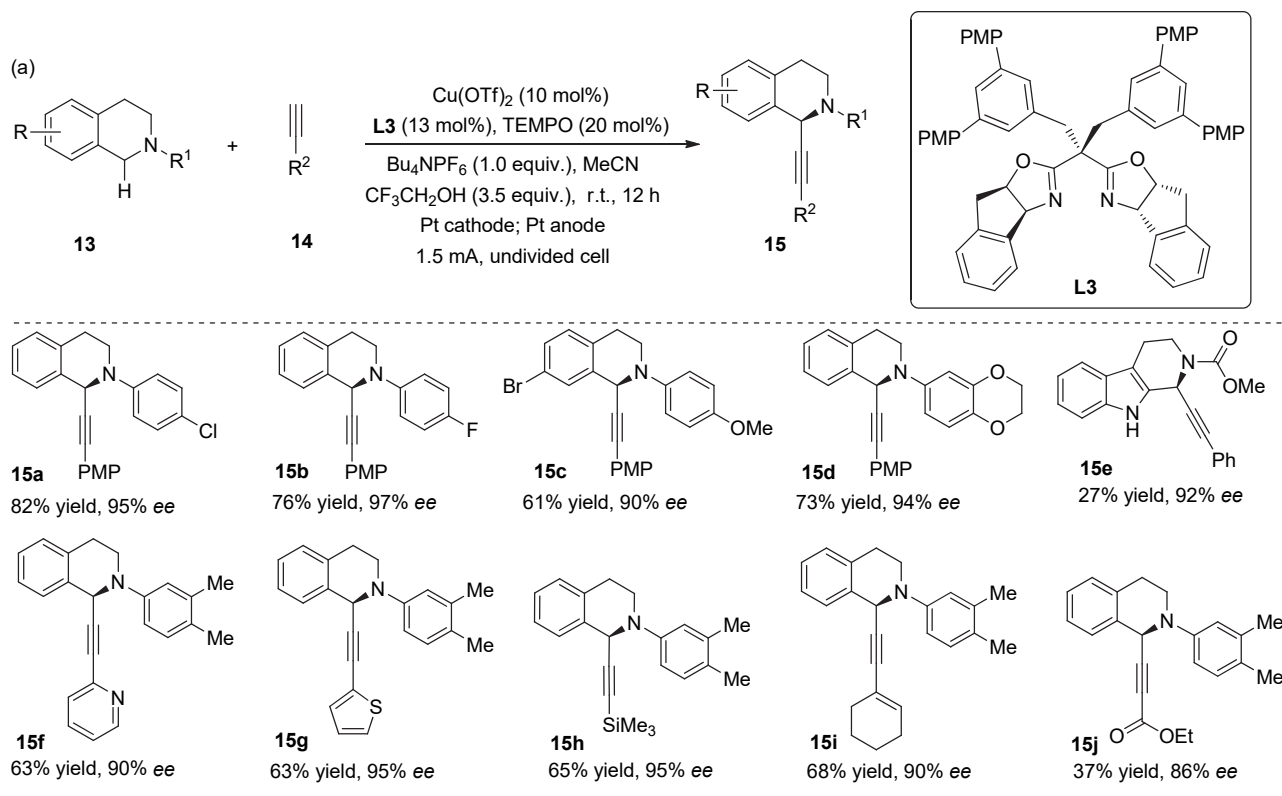
(b) Plausible catalytic cycle
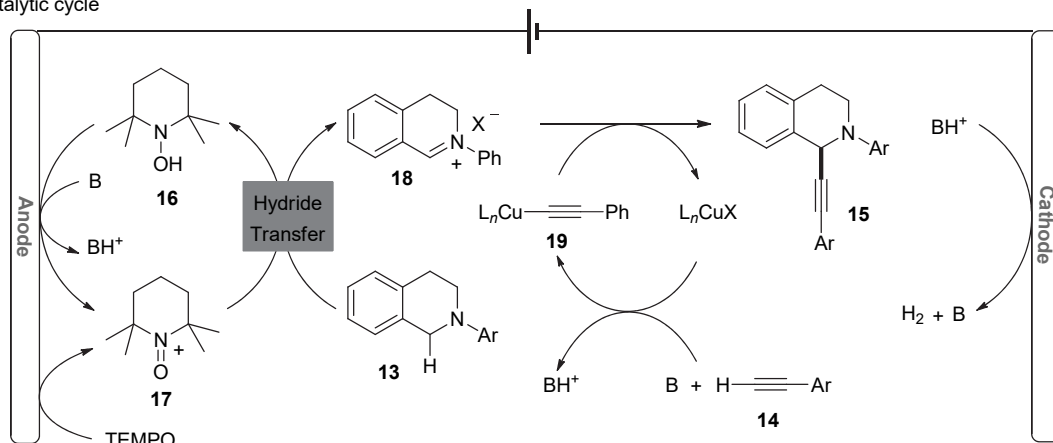
Scheme 5　Cu-catalyzed enantioselective C—H alkynylation via Shono-type oxidation

The imidazole protecting group in substrate **23** proved crucial for the transformation, as there was no alkylation product with other protecting groups. The electrochemical alkylation products were then applied to the synthesis of target compound **26**, which has antibacterial activity (Scheme 7b).[35] The proposed mechanism of the reaction is depicted in Scheme 7c. First, the coordination of Ni-catalyst to substrate **23** affords intermediate **F**, which is deprotonated to afford **G**. Intermediate **G** is then oxidized at the anode to form the radical intermediate **H**, which cross-coupled to electrochemically generated benzylic radical **J** to afford the alkylation product **25**.

Very recently, Ackermann and co-workers published the first electrochemical enantioselective synthesis of axially-chiral biaryls, which used a catalytic amount of transient directing group (TDG) in Pd-catalyzed asymmetric electrochemical C—H olefinations. This protocol afforded highly enantiomerically-enriched biaryls and axially chiral C—N bond scaffolds that the authors showed could be used to expediently access to novel enantio-enriched helicenes, dicarboxylic acids, and 1,1′-Binaphthalene-2,2′-diyl)bis-(diphenylphosphine) (BINOLs) (Scheme 8).[36]

3 Asymmetric organotransition metal-catalyzed electrochemical reduction

3.1 Asymmetric electroreductive carboxylation with carbon dioxide

Catalytic carbon-carbon (C—C) bond-forming reactions that utilize carbon dioxide (CO_2) to directly access carbox-

Scheme 6 Rh-catalyzed electro-oxidative cross-coupling

Scheme 7 Ni-catalyzed asymmetric electrochemical alkylation
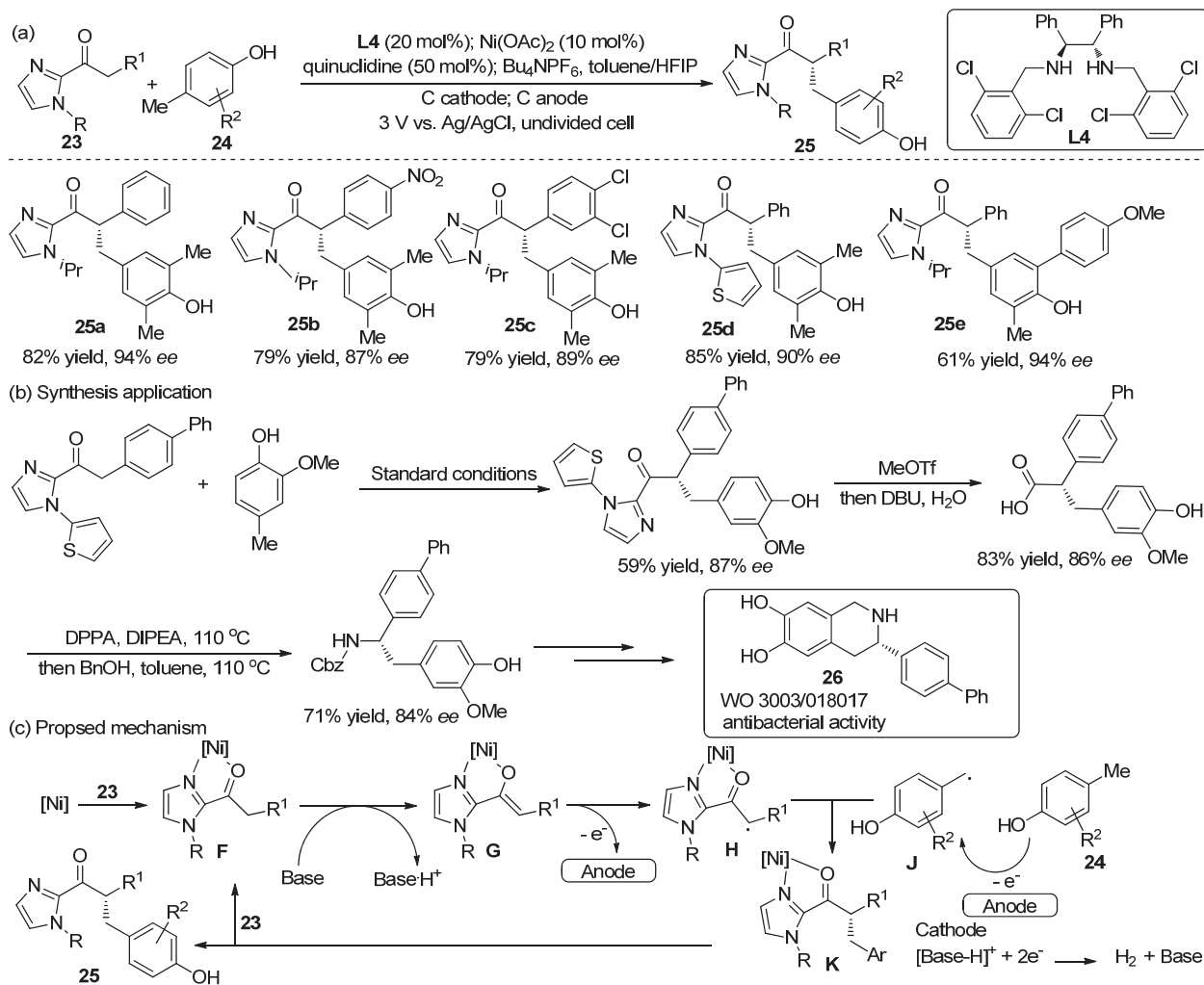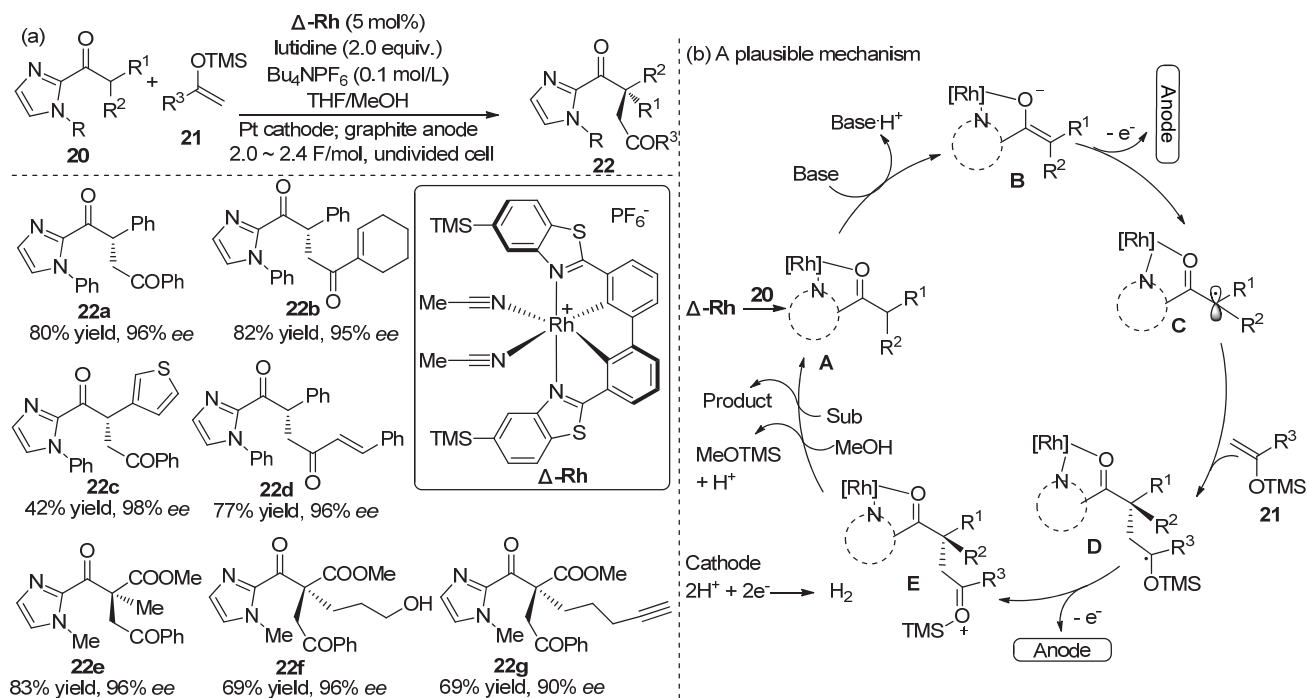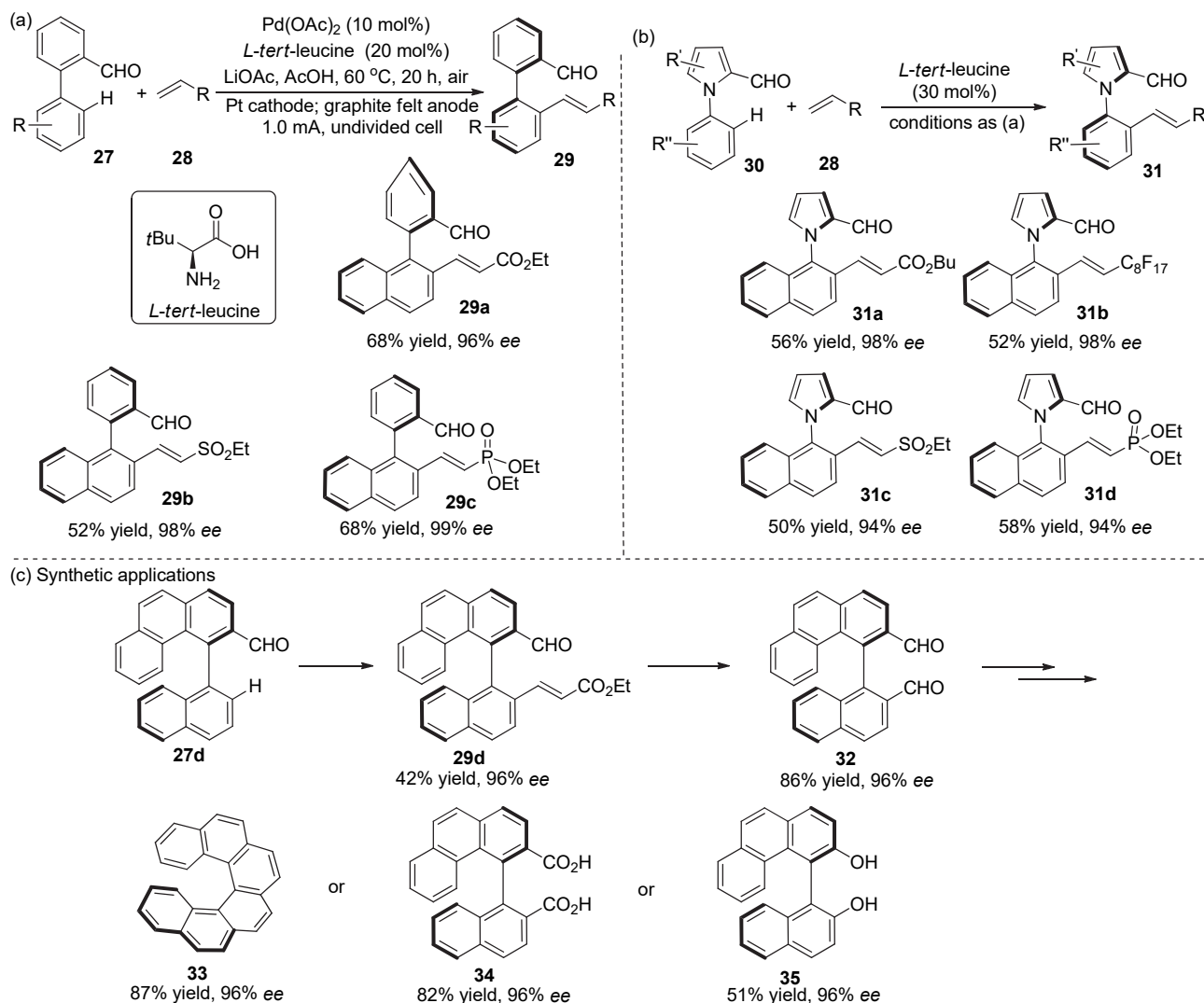
Scheme 8 Pd-catalyzed asymmetric electrochemical C—H olefinations

ylic acids have received extensive attention in recent decades due to the attractiveness of CO_2 as a C1 synthon.

In 2014, Lu and co-workers[37] reported the first investigation of asymmetric electrocarboxylation of 1-phenylethyl chloride catalyzed by an electrogenerated chiral Co(salen) complex. 2-Phenylpropionic acid was afforded in 37% yield and 83% *ee* (Scheme 9a). Although low yielding, this study laid the foundation for further research.

In 2018, Mei and co-workers[38] reported the first Pd-catalyzed regioselective carboxylation of homostyrenyl acetates utilizing electric current as the reductant, and also demonstrated the first catalytic asymmetric carboxylation of cinnamyl acetate, which provided a heretofore unavailable means to construct chiral phenyl acetic acids from homostyrenyl acetates (Scheme 9b). The proposed mechanism for this Pd-catalyzed carboxylation reaction via electrochemical reduction is shown in Scheme 9c.
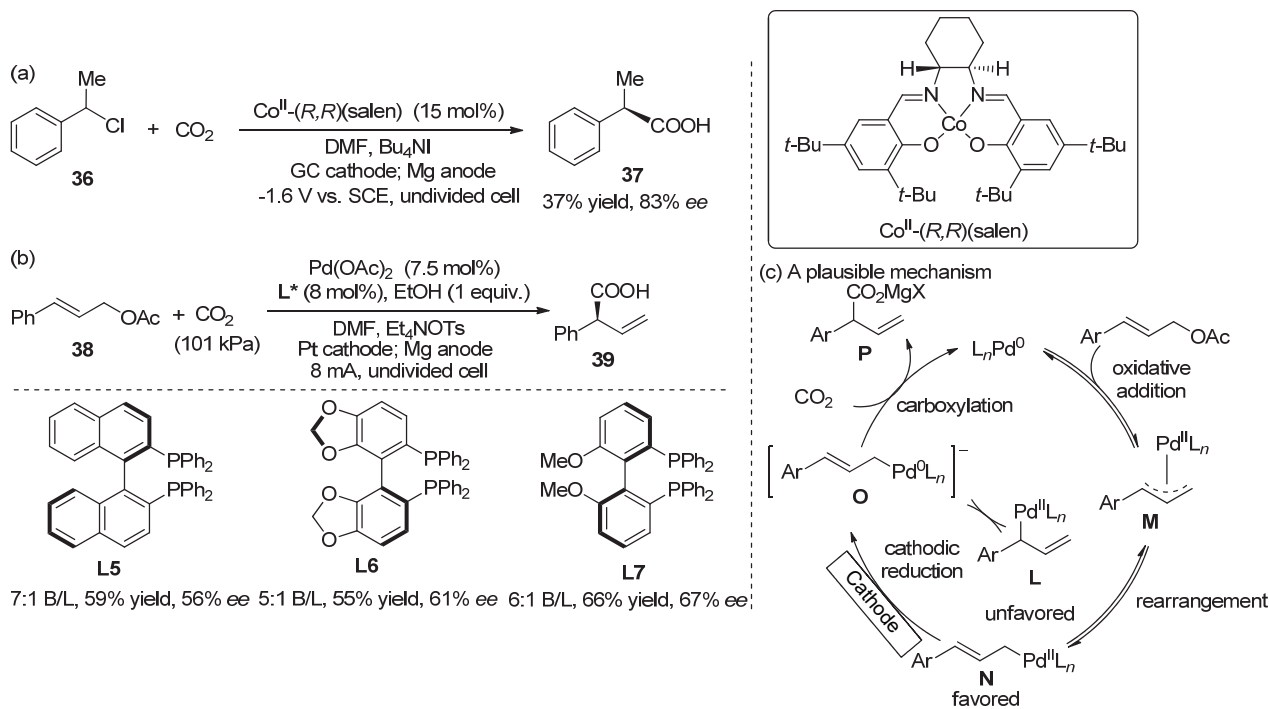
3.2 Reductive asymmetric decarboxylation

In 2002 Duñach and co-workers[39] reported the electroreductive cleavage of the allyl group of allyl 2-methyl-1-tetralone-2-carboxylate which afforded optically active

2-methyl-1-tetralone in low enantioselectivity in the presence of a chiral nickel-complex (Scheme 10). The reaction probably proceeded through the electrochemical generation of Ni(0) complex, which added oxidatively to the C—O bond of the allyl ester group of **40** to form a π-allyl-Ni(II) complex. The formation of **41** and **42** could be the result of deallylation with or without decarboxylation, and **43** was formed from an intramolecular allyl transfer reaction to the carbonyl group.

3.3 Reductive asymmetric couplings

Transition metal-catalyzed reductive cross-coupling is a powerful strategy for the formation of carbon-carbon bonds. However, a superstoichiometric proportion of metal powder is often needed as a reductant for catalyst turnover. In 2019 Reisman and co-workers[40] reported the first asymmetric electrochemical reductive cross-coupling of alkenyl bromides and benzyl chlorides with a nickel catalyst and chiral ligand **L9**. The reaction exhibited high efficiency, high enantioselectivity, and broad functional group tolerance (Scheme 11).

Scheme 9　Asymmetric organotransition metal-catalyzed electrocarboxylation
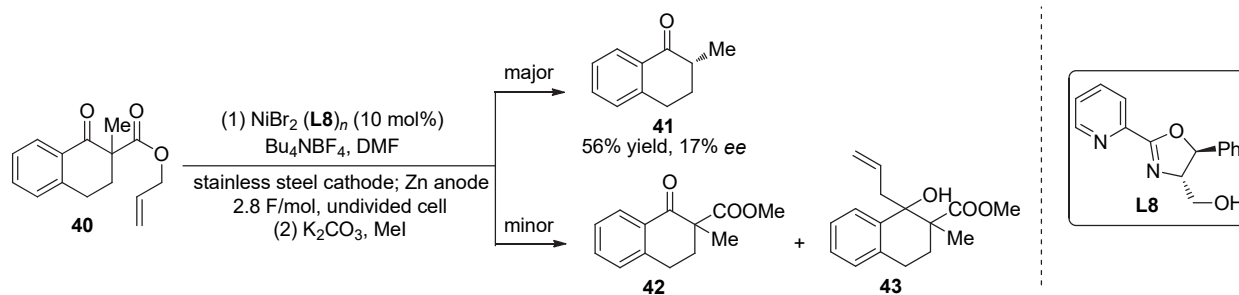
Scheme 10　Ni-catalyzed enantioselective electroreductive C—C bond cleavage
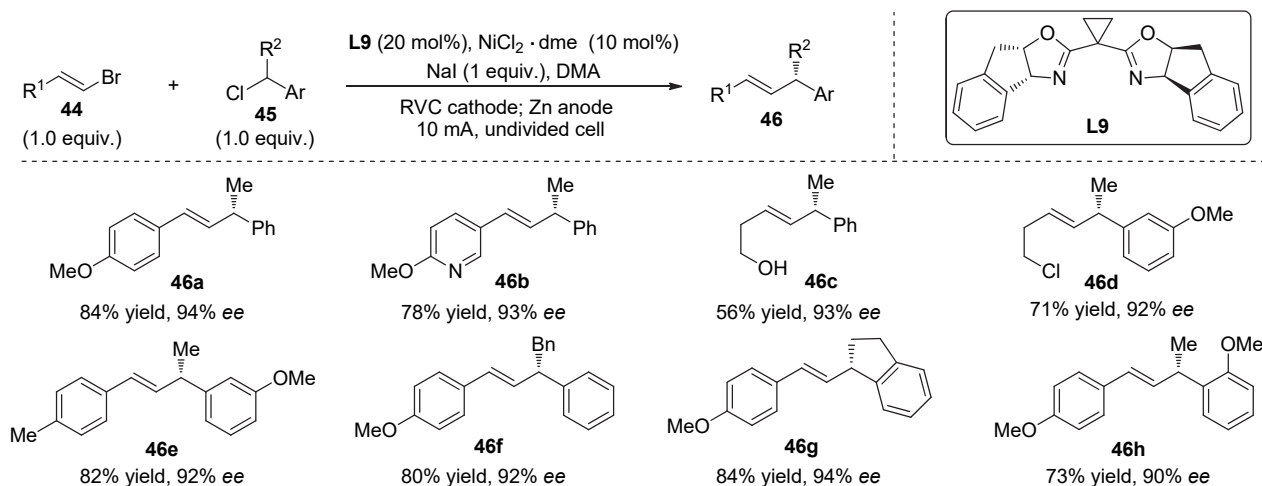
Scheme 11　Ni-catalyzed asymmetric electrochemical reductive cross-coupling

Very recently, Mei and co-workers[41] reported the first example of a Ni-catalyzed enantioselective electrochemical reductive coupling of aryl bromides under very mild con-ditions. This process afforded axially chiral BINOL deriv-atives in good yield and enantiomeric excess (Scheme 12). Common metal reductants such as Mn or Zn powder re-

sulted in significantly lower yields in the absence of electric current under otherwise identical conditions, which underscores the enhanced reactivity enabled by the combination of transition metal catalysis and electrochemistry.

4 Conclusion and outlook

This review summarized recent progress in asymmetric organotransition metal-catalyzed electrochemistry (AOM-CE). Chiral ligands combined with transition metals in the presence of electricity have been established for efficient enantioselective synthesis. Although AOMCE is readily understood, designed, and implemented, examples of AOMCE are rare, some challenges still need to be addressed. For example, AOMCE methods limited to Os, Mn, Cu, Rh, Co, Pd, or Ni catalysis, thus the design of diversified catalysts is highly desired. Furthermore, free metal ions are prone to accept electrons from cathode to yield inert zero-valent metals, which result in poor yields or no reaction at all. We hope that this review provides helpful overview of the current state of AOMCE. We anticipate that the problems mentioned above will be solved in the near future after further investigation, and novel AOMCE methods will also be developed with some regularity.
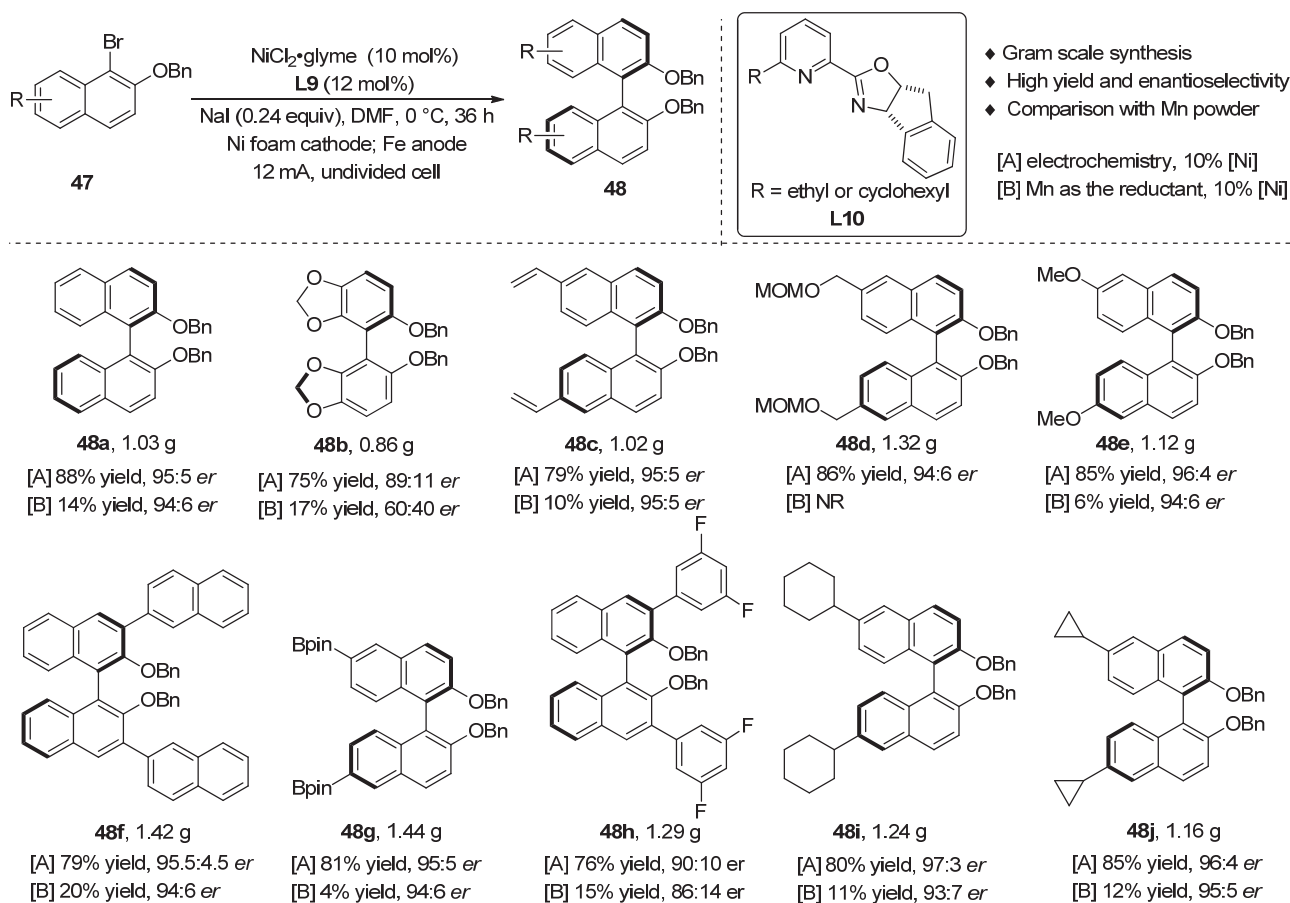
Scheme 12 Ni-catalyzed asymmetric electrochemical reductive cross-coupling

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