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Enantioselective propargylic substitution reactions via transition metal–allenylidene complexes as key intermediates

Yoshiaki Tanabe, Yoshiaki Nishibayashi*

Department of Applied Chemistry, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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ABSTRACT

Significant progress has been made in recent years in the development of enantioselective propargylic substitution reactions using transition metal complexes as catalysts. In particular, several enantioselective propargylic substitution reactions have been developed with the formation of transition metal–allenylidene complexes as key reactive intermediates. This review focuses on the recent advances in the development of enantioselective propargylic substitution reactions via transition metal–allenylidene complexes as key intermediates.

1. Introduction

Optically active propargylic compounds, where a chiral carbon center is introduced at the propargylic position, are known to furnish versatile pharmacological activity, where the adjacent reactive alkyne moieties provide post-synthetic transformations [1]. It must be noted that similar optically active allylic compounds with a chiral carbon center introduced at the allylic position have been well prepared by transition metal-catalyzed enantioselective allylic substitution reactions of the allylic substrates containing a leaving group (LG) at the allylic position with nucleophiles (Tsuji–Trost reaction), where transition metal–π-allyl complexes work as key reactive intermediates [2,3]. On the other hand, development of catalytic propargylic substitution reactions of the propargylic substrates containing a leaving group at the propargylic position with appropriate nucleophiles faced difficulty to control regioselectivity, because competitive tautomerization between propargylic and allenylic species can lead to the formation of allene compounds as undesired by-products (Fig. 1a) [4]. Propargylic substitution reaction of propargylic alcohols or esters with a nucleophile was first reported in 1977 by Nicholas and a co-worker, who obtained a desired propargylic substituted product by stepwise reactions involving stoichiometric formation of an alkyne-bridged dicobalt complex (**A**) by the reaction of a propargylic alcohol with $Co_2(CO)_8$, where the nucleophilic substitution reaction occurs to afford the propargylic substituted complex (**B**), followed by the oxidative decomplexation of the product on treatment with $Fe(NO_3)_3$ (Fig. 1b) [5].

Catalytic propargylic substitution reaction was later achieved in 1994 independently by three groups of Murahashi, Caporusso, and Godfrey, all using Cu compounds as catalysts to furnish propargylic amination or etherification on treatment of propargylic esters, phosphates, sulphates (Ms = $MeSO_2$), or halides with amines or phenols as *N*- or *O*-centered nucleophiles (Fig. 1c) [6–8]. Since a variety of catalytic propargylic substitution reactions mediated by not only transition metal catalysts, but also main group Lewis acid catalysts and organocatalysts have been developed [9–13]. On the other hand, development of catalytic enantioselective propargylic substitution reactions was left rather unexplored [14,15], whereas the first successful example of catalytic enantioselective propargylic substitution reaction was achieved in 2005 by Nishibayashi and co-workers [16], and several enantioselective propargylic substitution reactions have been developed so far [17–20].

Today, transition metal-catalyzed enantioselective propargylic substitution reactions can be roughly classified into three different types based on the structures of the reactive intermediates: (i) via the formation of allenylidene intermediates [21], well investigated for Ru and Cu-catalyzed propargylic substitution reactions of propargylic compounds bearing a terminal alkyne moiety [11,17–20]; (ii) via the formation of allenyl intermediates [22], well investigated for Pd- and Ni-catalyzed propargylic substitution reactions of propargylic compounds bearing an internal alkyne moiety [12–14,17]; and (iii) via the formation of propargylic radicals [23], first proposed for Ni-catalyzed cross-coupling reactions [24], but now extended to photocatalytic systems (Fig. 1d) [25]. In this review, enantioselective propargylic substitution reactions via transition metal–allenylidene complexes as key reactive intermediates shall be discussed.

2. Enantioselective propargylic substitution reactions via Ru–allenylidene complexes

2.1. Catalytic propargylic substitution reactions via thiolate-bridged diruthenium–allenylidene complexes

Since 2000, Nishibayashi and co-workers have successfully developed catalytic propargylic substitution reactions of propargylic alcohols

* Corresponding author.
E-mail address: ynishiba@g.ecc.u-tokyo.ac.jp (Y. Nishibayashi).

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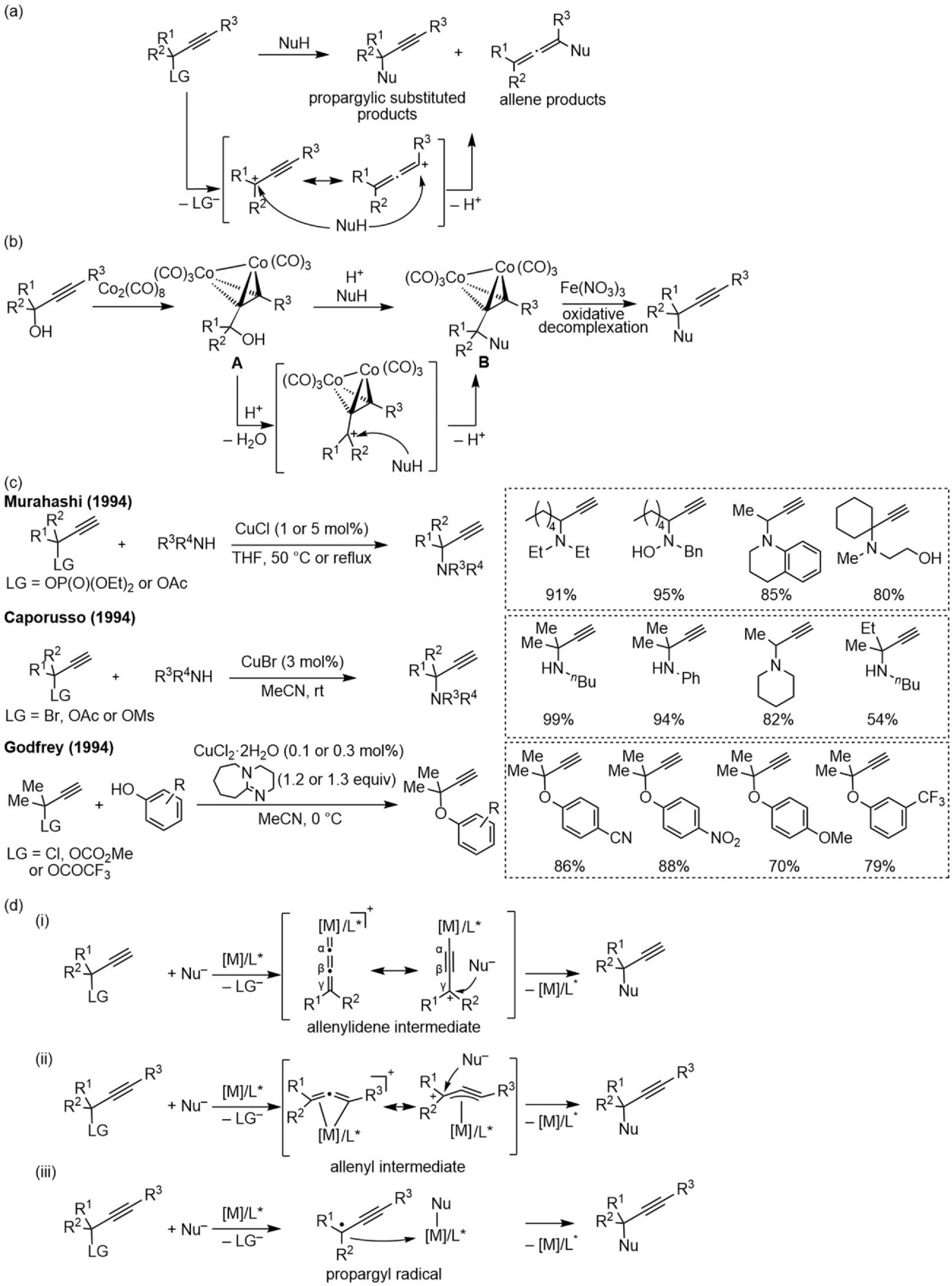

Fig. 1. (a) Formation of allene compounds as side products of propargylic substitution reactions. (b) Nicholas reaction. (c) Early examples of transition metal-catalyzed propargylic substitution reactions. (d) Three types of transition metal-catalyzed enantioselective propargylic substation reactions: (i) via allenylidene intermediates, (ii) via allenyl intermediates, and (iii) via propargylic radicals.

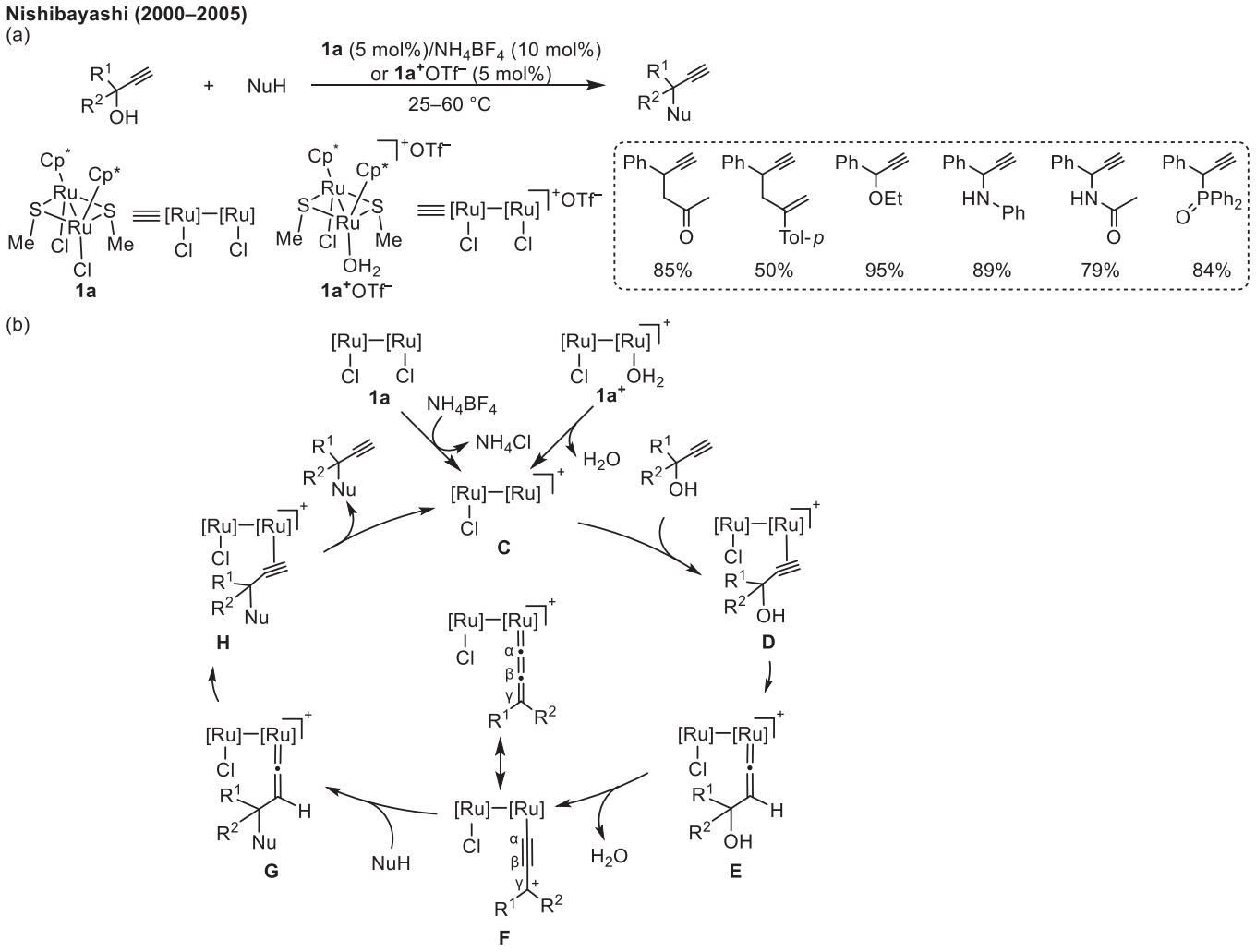

Fig. 2. (a) Ru-catalyzed propargylic substitution reactions of propargylic alcohols with *C*-, *N*-, *S*-, or *P*-centered nucleophiles. (b) Plausible reaction pathway catalyzed by Ru_2 system.

bearing a terminal alkyne moiety with a variety of nucleophiles by using thiolate-bridged diruthenium complexes such as [{Cp*RuCl(μ-SMe)}$_2$] (**1a**, Cp* = η^5-C_5Me_5) and [Cp*RuCl(μ-S^{i}Pr)$_2$Ru(H_2O)Cp*]OTf (**1a**$^+$OTf$^-$, Tf = CF_3SO_2) as catalysts (Fig. 2a) [26–31]. Several *C*-centered nucleophiles such as simple ketones [27,30] or alkenes [28], heteroatom-centered nucleophiles such as amines, amides, alcohols, or phosphine oxides [26,28–31], and *H*-centered nucleophiles [32] have been shown to applicable to this nucleophilic substitution reactions, whereas propargylation of aromatic compounds has been also shown to be applicable [33]. The thiolate-bridged diruthenium complexes, prepared by Hidai and co-workers [34], have been known to afford the corresponding allenylidene complex by the stoichiometric reaction with propargylic alcohols [26,35]. Thus, a plausible catalytic cycle as shown in Fig. 2b has been proposed based on stoichiometric and catalytic reactions, kinetic studies, observation and isolation of several reactive intermediates as well as DFT calculations [31,36]. First, coordinatively unsaturated species (**C**) was formed via the dissociation of Cl^- or H_2O from **1a** or **1a**$^+$, respectively, where coordination of a propargylic alcohol occurs to afford the π-alkyne complex (**D**), followed by the 1,2-shift of the terminal hydrogen atom to afford the vinylidene complex (**E**), and further dehydration to afford the allenylidene complex (**F**). Then a nucleophile attacks at the γ-carbon of the allenylidene ligand in **F** to afford the vinylidene complex (**G**), followed by the rearrangement of hydrogen atom to afford the π-alkyne complex (**H**), where the propargylic substituted product is liberated to recover the starting **C**. Here, DFT calculations have demonstrated the importance of the dimetallic structure of the thiolate-bridged diruthenium core, where one coordinatively saturated ruthenium center works as an electron reservoir for the other ruthenium center in which transformation of substrates occurs [36]. The synergistic effect between two metal centers not only increases the electrophilicity of the γ-carbon atom of the allenylidene ligand in **F**, but also accelerate the ligand exchange of the propargylic substituted product with the propargylic alcohol.

2.2. *Ru-catalyzed enantioselective propargylic C–C bond formation*

The first successful catalytic enantioselective propargylic substitution reaction of propargylic alcohols was achieved by using a thiolate-bridged diruthenium complex bearing a chiral moiety [{Cp*RuCl(μ-SR*)}$_2$] (**1b**, SR* = (*R*)-SCH(Et)$C_6H_2Ph_3$-2,3,5) as a catalyst on treatment with acetone, working as a *C*-centered nucleophile (Fig. 3a) [16]. It must be noted that the Ru–allenylidene complex [Cp*RuCl(μ-SR*)$_2$Ru(CCCHPh)Cp*]BF_4 (**1c'**, SR* = (*R*)-SCH(Et)$C_6H_3Ph_2$-3,5) was isolable by the stoichiometric reaction of similar thiolate-bridged diruthenium complex bearing a chiral moiety [{Cp*RuCl(μ-SR*)}$_2$] (**1c**), also known as a catalyst for the enantioselective propargylic substitution reactions [16], with a propargylic alcohol (Fig. 3b) [37]. Both crystallographic study of **1c'** and DFT calculations have demonstrated the existence of an intramolecular CH/π interaction between the allenylidene moiety and the chiral ligand, which should play a critical role in the asymmetric induction of the enantioselective propargylic substitution reaction with the attack of a nucleophile from *Si* face (Fig. 3b) [37,38]. Consequently,

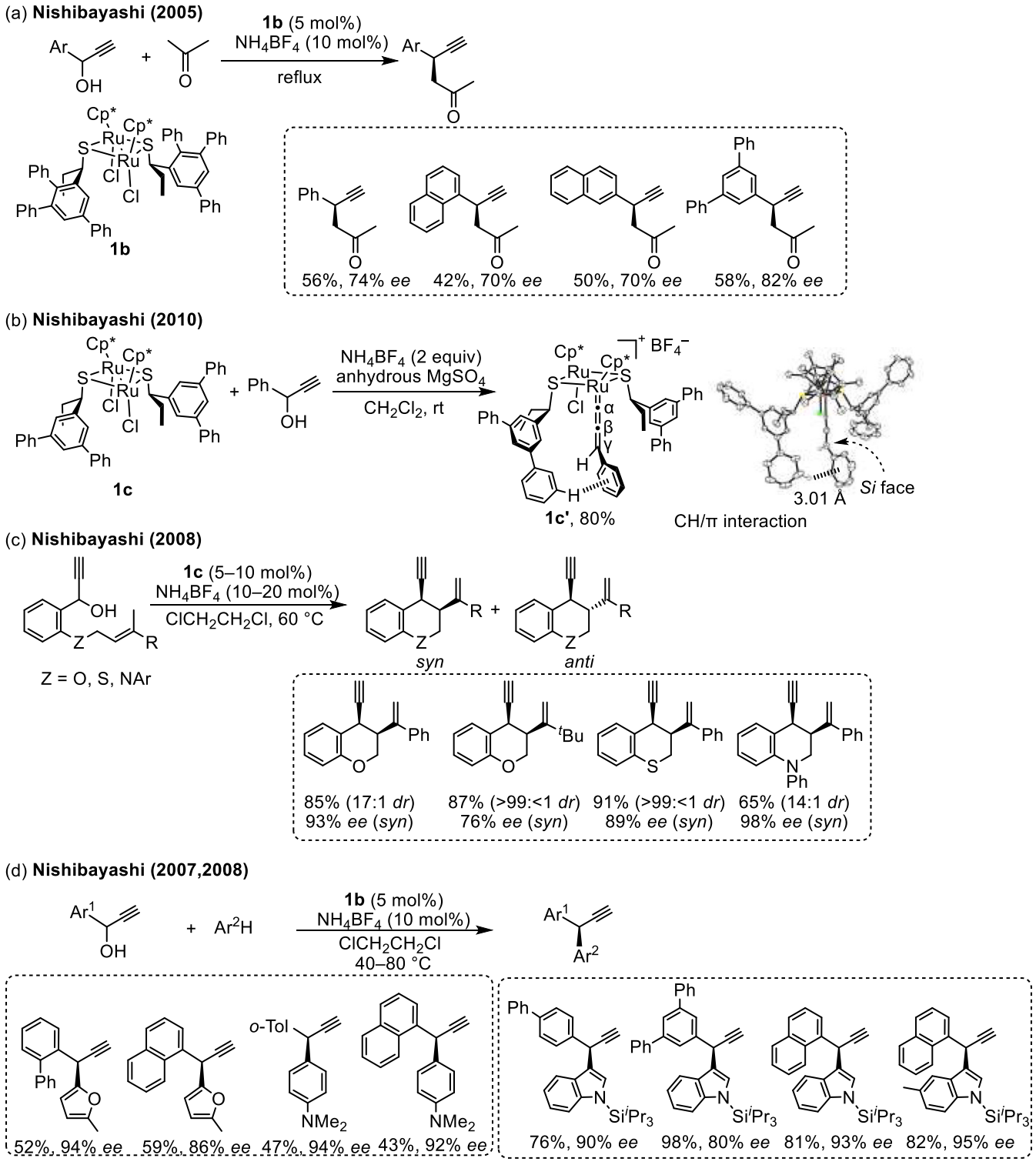

Fig. 3. (a) Ru-catalyzed enantioselective propargylic substitution reaction of propargylic alcohols with acetone. (b) Preparation of a Ru–allenylidene complex bearing a chiral ligand and its structure determined by an X-ray analysis. (c) Ru-catalyzed diastereo- and enantioselective intramolecular propargylic substitution reaction of propargylic alcohols. (d) Ru-catalyzed enantioselective propargylation of aromatic compounds.

a series of thiolate-bridged diruthenium complexes bearing chiral moieties have supplied the first examples of catalytic enantioselective propargylic substitution reactions of propargylic alcohols [15,16].

Not only ketones but also alkenes can be applied as *C*-centered nucleophiles toward the enantioselective propargylic substitution reactions via allenylidene–ene reactions. For example, **1c** was found to catalyze diastereo- and enantioselective intramolecular cyclization of propargylic alcohols bearing alkene moieties to afford a variety of chiral heterocycles such as chromane, thiochromane, and tetrahydroquinoline derivatives in a good to high enantioselectivity (Fig. 3c) [39]. Furthermore, enantioselective propargylation of electron-rich aromatic compounds was also achieved by using **1b** as a catalyst (Fig. 3d) [40,41]).

Until recently, enantioselective propargylic alkylation of propargylic alcohols required alkylation nucleophiles activated by

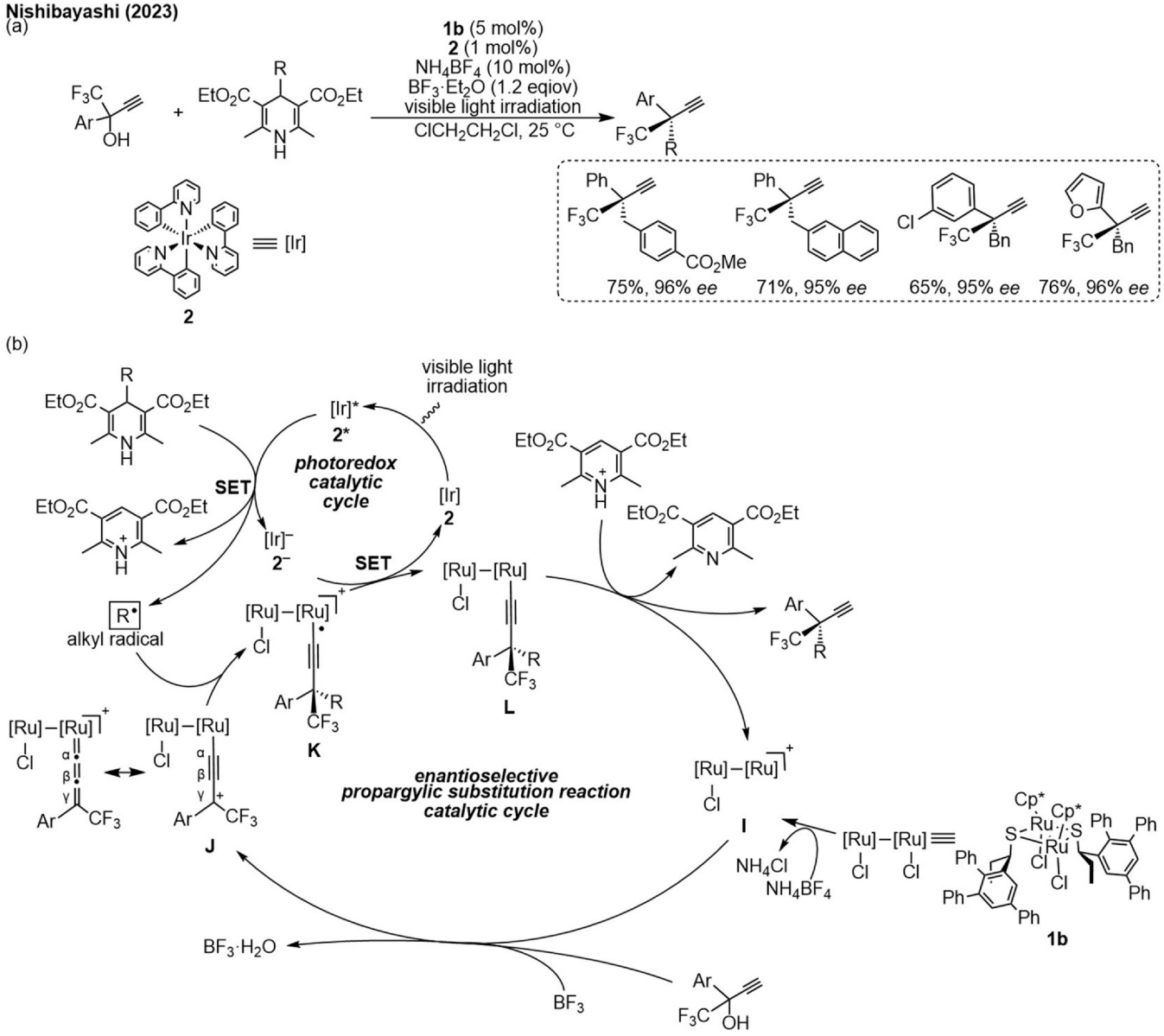

Fig. 4. (a) Ru- and Ir-catalyzed photo-induced enantioselective propargylic alkylation of propargylic alcohols. (b) Plausible reaction pathways consisting of two catalytic cycles.

functional groups such as aldehydes and ketones, while enantioselective propargylic alkylation of propargylic alcohols with non-activated alkylation reagents was found to be difficult due to the requirement of harsh conditions. One of the answers to this problem was to use alkyl radicals generated from 4-alkyl-1,4-dihydropyridines under visible light irradiation [42] instead of ionic alkylation nucleophiles. Indeed, dual photoredox- and Ni- or Pd-catalyzed propargylic alkylation of propargylic esters with 4-alkyl-1,4-dihydropyridines was reported by Liang and co-workers [43], although enantioselective propargylic alkylation was not achieved. Thus, dual photoredox and diruthenium catalytic system, where the photoredox catalyst *fac*-[Ir(ppy)$_3$] (**2**, ppy = 2-(pyridine-2-yl)phenyl) generates alkyl radicals from 4-alkyl-1,4-dihydropyridines under visible light irradiation, and the thiolate-bridged diruthenium catalyst bearing a chiral ligand **1b** traps both propargylic alcohols and alkyl radicals, has been examined by Nishibayashi and co-workers to substantialize the enantioselective propargylic alkylation to afford the propargylic alkylated products bearing a quaternary stereogenic *C* center at the propargylic position in good to high yields with a high enantioselectivity (Fig. 4a) [44]. Based on the mechanistic studies and DFT calculations, a plausible catalytic reaction consisting of two catalytic cycles: photoredox and enantioselective propargylic substitution catalytic cycles can be drawn (Fig. 4b) [45]. In the photoredox catalytic cycle, the iridium catalyst **2** is excited under visible light irradiation to afford a photoexcited iridium catalyst **2***, followed by a single-electron-transfer (SET) process with 4-alkyl-1,4-dihydropyridine to afford the reduced iridium catalyst **2**$^-$, an alkyl radical (R$^\bullet$), and a pyridinium cation via C−C bond scission. On the other hand in the enantioselective propargylic substitution reaction catalytic cycle, the coordinatively unsaturated species (**I**), generated from **1b**, reacts with a propargylic alcohol to afford the allenylidene complex (**J**) via proton transfer and dehydration process accelerated by $BF_3{\cdot}Et_2O$. Then, alkyl radical attacks at the γ-position of the allenylidene ligand of **J** from *Re* face, where the asymmetric induction is brought about by π/π and CF/H interactions [45], to afford the alkynyl radical complex (**K**), followed by SET with **2**$^-$ to afford the alkynyl complex (**L**). Further protonation occurs to afford the coordinatively unsaturated complex **I** and the propargylic alkylated product (Fig. 4b) [44]. Here, the diruthenium core acts as an electron pool to stabilize the

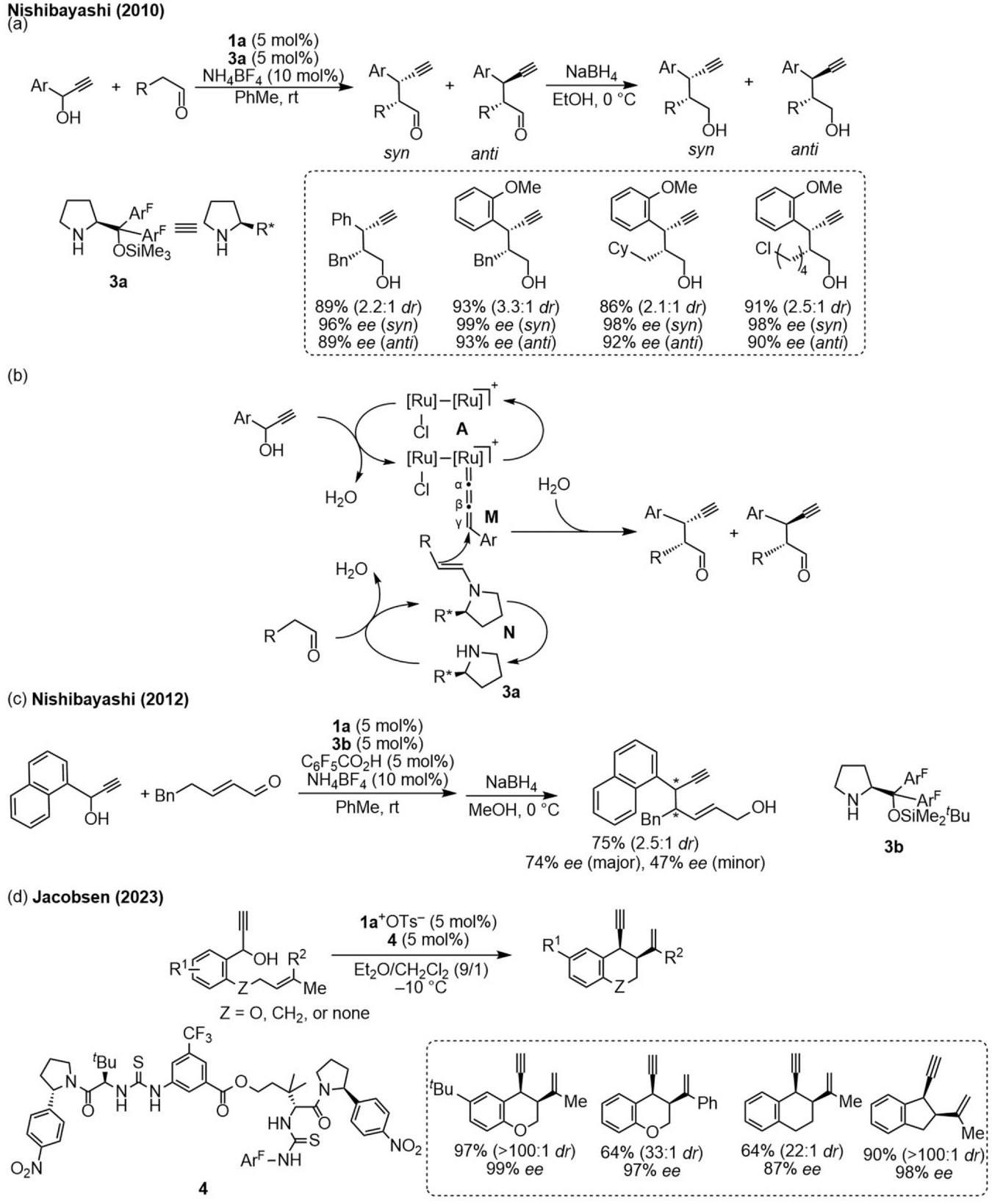

Fig. 5. (a) Ru- and enamine-catalyzed enantioselective propargylic alkylation of propargylic alcohols with aldehydes. (b) Plausible reaction pathways consisting of cooperative catalytic cycles. (c) Ru- and enamine-catalyzed enantioselective propargylic alkylation of propargylic alcohols with an α,β-unsaturated aldehydes. (d) Ru- and thiourea-catalyzed diastereo- and enantioselective intramolecular propargylic alkylation of propargylic alcohols.

catalysis and to furnish the radical redox reaction, providing the first successful example of transition metal-catalyzed enantioselective propargylic substitution reactions with free alkyl radicals.

Nonchiral thiolate-bridged diruthenium complexes were also shown to catalyze enantioselective propargylic substitution reactions, if the reactions were carried out in combination with chiral organocatalysts

[46,47]. For example by using the combination of **1a** and the Hayashi–Jørgensen organocatalyst (*S*)-$Me_3SiOCAr^F_2$-2-C_4H_7N (**3a**, Ar^F = 3,5-$(CF_3)_2C_6H_4$) [48] as a pair of catalysts, enantioselective propargylic alkylation of propargylic alcohols with aldehydes to afford propargylic alkylated products as a mixture of two diastereomers has been achieved (Fig. 5a) [49]. In this reaction system, the ruthenium–allenylidene complex (**M**) is formed by the reaction of the coordinatively unsaturated complex **A** with a propargylic alcohol, whereas an enamine (**N**), generated in situ from an aldehyde and the Hayashi–Jørgensen organocatalyst **3a**, attack at the γ-carbon atom of **M** as a suitable *C*-centered nucleophile to afford the propargylic alkylated product (Fig. 5b) [49]. Similar combination of catalysts (**1a** and (*S*)-^{t}BuMe$_2$SiOCAr$^F_2$-2-C_4H_7N (**3b**)) was applicable for the enantioselective alkylation of propargylic alcohols with an α,β-unsaturated aldehyde (Fig. 5c) [50].

Jacobsen and co-works have also very recently examined the combination of the nonchiral thiolate-bridged diruthenium complexes $\mathbf{1a}^+OTs^-$ (Ts = *p*-$TolSO_2$) and a chiral bis(thiourea)-based hydrogen-bond donor (**4**), which has shown to catalyze the diastereo- and enantioselective intramolecular propargylic substitution reaction of propargylic alcohols containing alkene moieties to afford the corresponding chromanes (Fig. 5d) [51], as have been synthesized by using a thiolate-bridged diruthenium complex bearing a chiral moiety **1c** as a catalyst (Fig. 3c) [39]. Chiral thiourea-based organocatalysts have been known to furnish asymmetric induction via hydrogen bonds [52], and the binding of anions of **4** with the cationic $\mathbf{1a}^+$ has been shown to induce enantioselectivity by DFT calculations [51].

Asymmetric propargylic substitution reactions were also shown to be realized by embedding the organocatalyst moiety onto the thiolate-bridged diruthenium core. Indeed, the hybrid thiolate-bridged diruthenium complex bearing a chiral BINOL–phosphoramide moiety [{Cp*RuCl(μ-SR*)}$_2$] (**1d**, R* = (*R*)-3,3′-Me_2-1,1′-binaphthyl-2,2′-$O_2P(O)NH(CH_2)_3$), with a chiral BINOL-phosphate-derived Brønsted acids [53] connected to the bridging thiolate ligand, was shown to catalyze diastereo- and enantioselective propargylic alkylation of propargylic alcohols with enecarbamates (Fig. 6a) [54].

Nishibayashi and co-workers also developed asymmetric propargylic substitution reactions via Ru–allenylidene complexes by

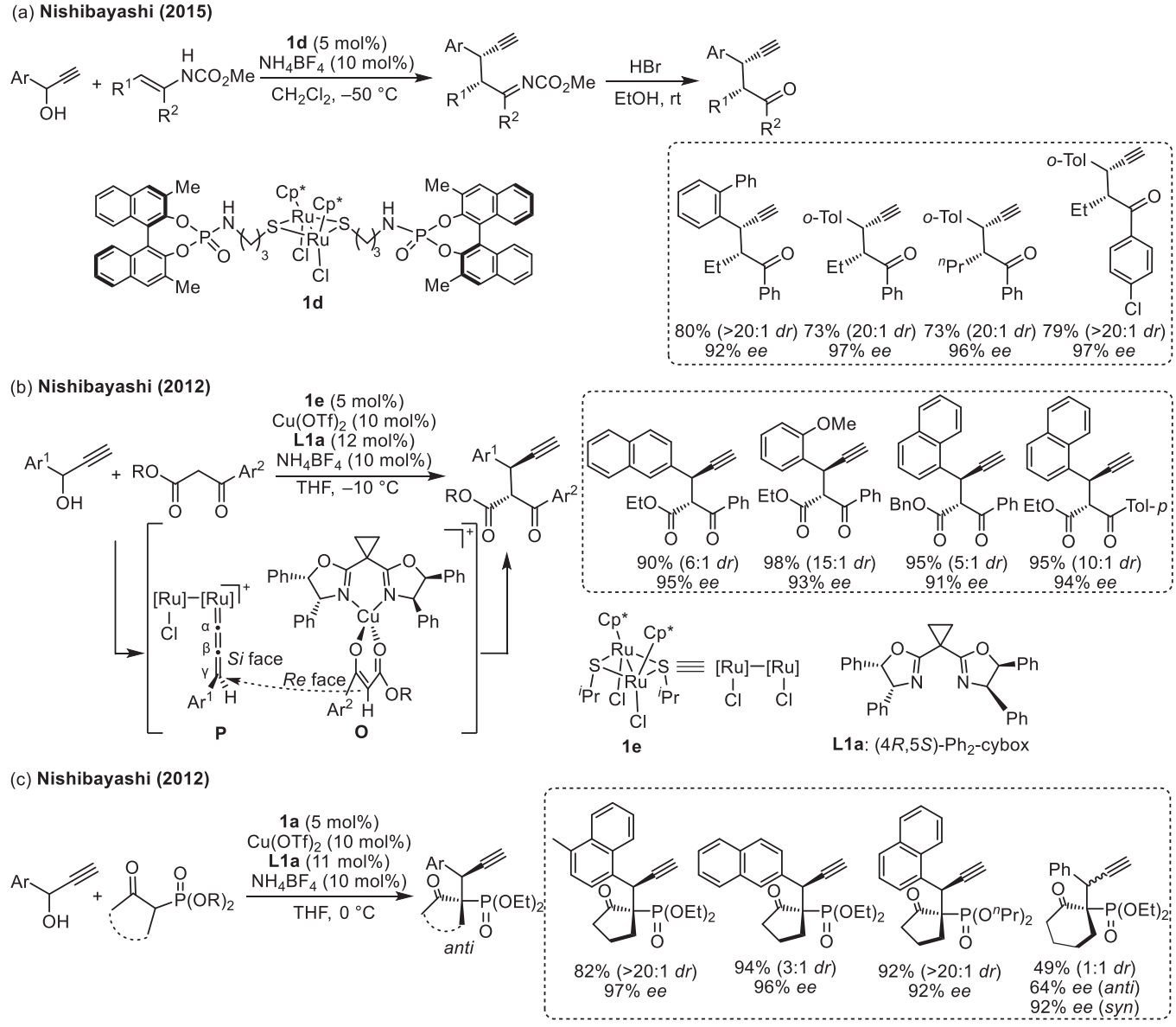

Fig. 6. (a) Ru-catalyzed diastereo- and enantioselective propargylic alkylation of propargylic alcohols with enecarbamates. (b) Ru- and Cu/cybox-catalyzed diastereo- and enantioselective propargylic alkylation of propargylic alcohols with β-keto esters. (c) Ru- and Cu/cybox-catalyzed diastereo- and enantioselective propargylic alkylation of propargylic alcohols with β-keto phosphates.

combing copper catalyst to activate *C*-centered nucleophiles. Indeed, diastereo- and enantioselective propargylic alkylation of propargylic alcohols with β-keto esters was achieved by using the thiolate-bridged diruthenium complex [{Cp*RuCl(μ-S^{i}Pr)}$_2$] (**1e**), Cu(OTf)$_2$, and a C_2-symmetric chiral 2,2′-cyclopropylidene-bis(oxazoline) ligand (4*R*,5*S*)-Ph$_2$-cybox (**L1a**) [55] as a set of catalysts (Fig. 6b) [56]. Here, β-keto ester is proposed to coordinate to the Cu species ligated by **L1a** to form a distorted tetrahedral Cu–enolate complex (**O**), working as a nucleophile to attack at the *Si* face of the Ru–allenylidene complex (**P**) obtained by the reaction of **1e** with a propargylic alcohol from *Re* face of the enolate (Fig. 6b) [56]. Diastereo- and enantioselective alkylation of propargylic alcohols with β-keto phosphonates were also attained to afford the corresponding products (Fig. 6c) [57].

2.3. Ru-catalyzed enantioselective propargylic C–P bond formation

Rather recently, diarylphosphine oxides were also found to be applicable as *P*-centered nucleophiles toward enantioselective propargylic substitution reactions of propargylic alcohols with a high enantioselectivity (Fig. 7a) [58]. In this reaction system, introduction of the CF$_3$ group at the propargylic position of the propargylic alcohols was necessary to operate enantioselective substitution reactions. A stoichiometric reaction of **1c** with a propargylic alcohol bearing a trifluoromethyl group at the propargyl position afforded the corresponding allenylidene complex **1c"**, from which the desired propargylic substituted product was obtained on treatment with a phosphine oxide (Fig. 7b) [58]. DFT calculations for the optimization of the molecular structure of **1c"** have demonstrate that the existence of π/π and CF/H interactions between the allenylidene moiety and the chiral ligands, where the nucleophiles can attack from the *Re* face (Fig. 7b) [45,58], reversing the stereoselectivity opposite to those obtained without the CF$_3$ substituent (Fig. 3b) [37,38].

3. Enantioselective propargylic substitution reactions via Cu–allenylidene complexes

3.1. Cu-catalyzed enantioselective propargylic C–N bond formation

Catalytic propargylic amination of propargylic esters was first achieved in 1994 by using CuCl or CuBr as a catalyst (Fig. 1c) [6,7], although its detailed reaction mechanism was not clarified, and enantioselective propargylic amination was also not achieved [14]. In 2008, groups of Nishibayashi and van Maarseveen independently reported enantioselective propargylic amination almost simultaneously by using the combination of CuOTf·0.5C$_6$H$_6$ and a C_2-symmetric chelating atropisomeric chiral phosphine ligand (*R*)-Cl-MeO-biphep (**L2a**) [59] (Fig. 8a) [60,61] or the combination of CuI and a C_2-symmetric chiral 2,6-pyridine-bis(oxazoline) ligand (4*R*,5*S*)-Ph$_2$-pybox ((*R*,*S*)-**L3a**) [55] as a set of catalysts, respectively (Fig. 8b) [62,63].

A plausible catalytic reaction pathway via the formation of Cu–allenylidene complex was proposed by Nishibayashi and co-workers for the CuOTf/**L2a** case based on DFT calculations (Fig. 8c) [61]. First a π-alkyne complex (**Q**) is formed via the reaction of CuOTf, **L2a**, and a propargylic alcohol, where ^{i}Pr$_2$NEt promotes the deprotonation process to afford the acetylide complex (**R**). Then, protonation occurs at the acetylide moiety to afford the protonated acetylide complex (**S**) by the ^{i}Pr$_2$NHEt$^+$ species, where further deprotonation process takes place to afford the allenylidene complex (**T**) with the removal of acetate by ^{i}Pr$_2$NEt. Then an *N*-centered nucleophile can attack at the γ-position of the allenylidene ligand in **T** from *Re* face to afford the acetylide complex

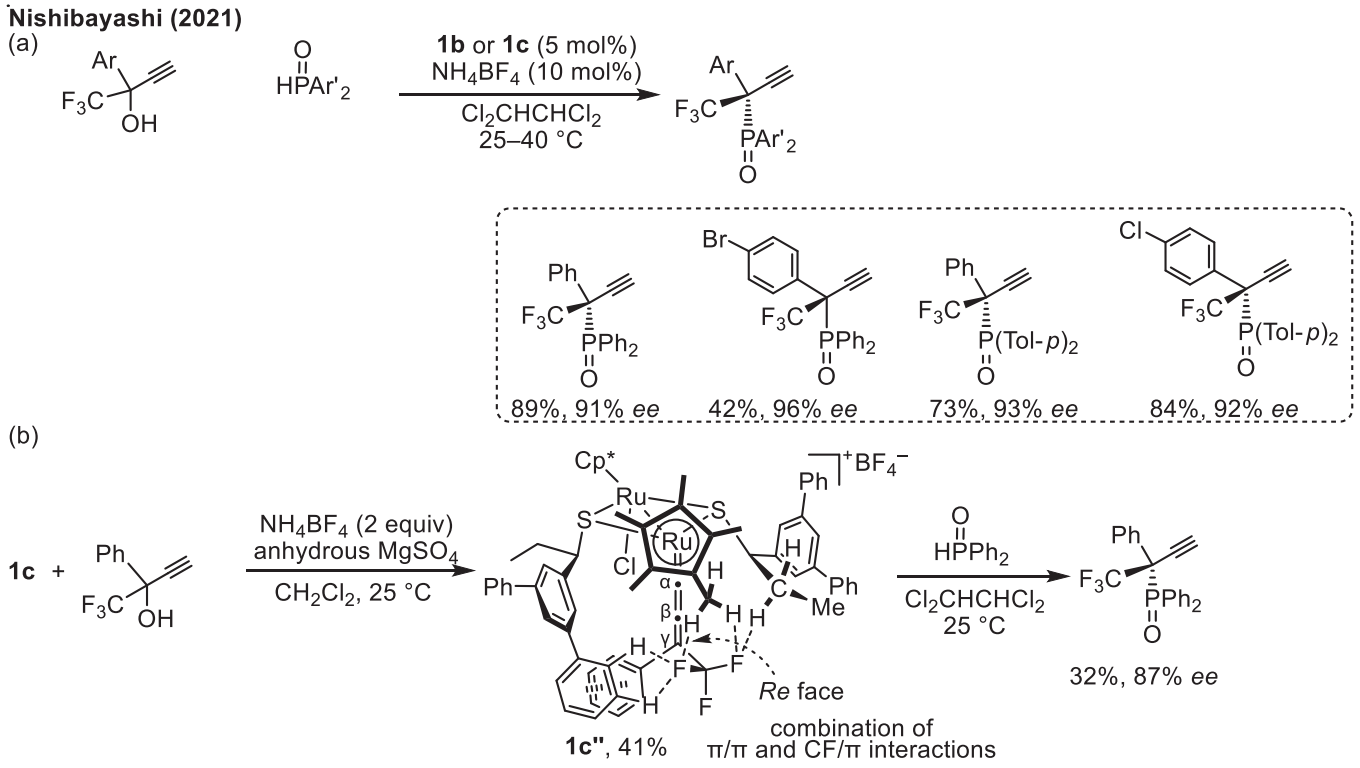

Fig. 7. (a) Ru-catalyzed enantioselective propargylic phosphinylation of propargylic alcohols with phosphine oxides. (b) Preparation of a Ru–allenylidene complex bearing a chiral ligand and its proposed structure based on DFT calculations.

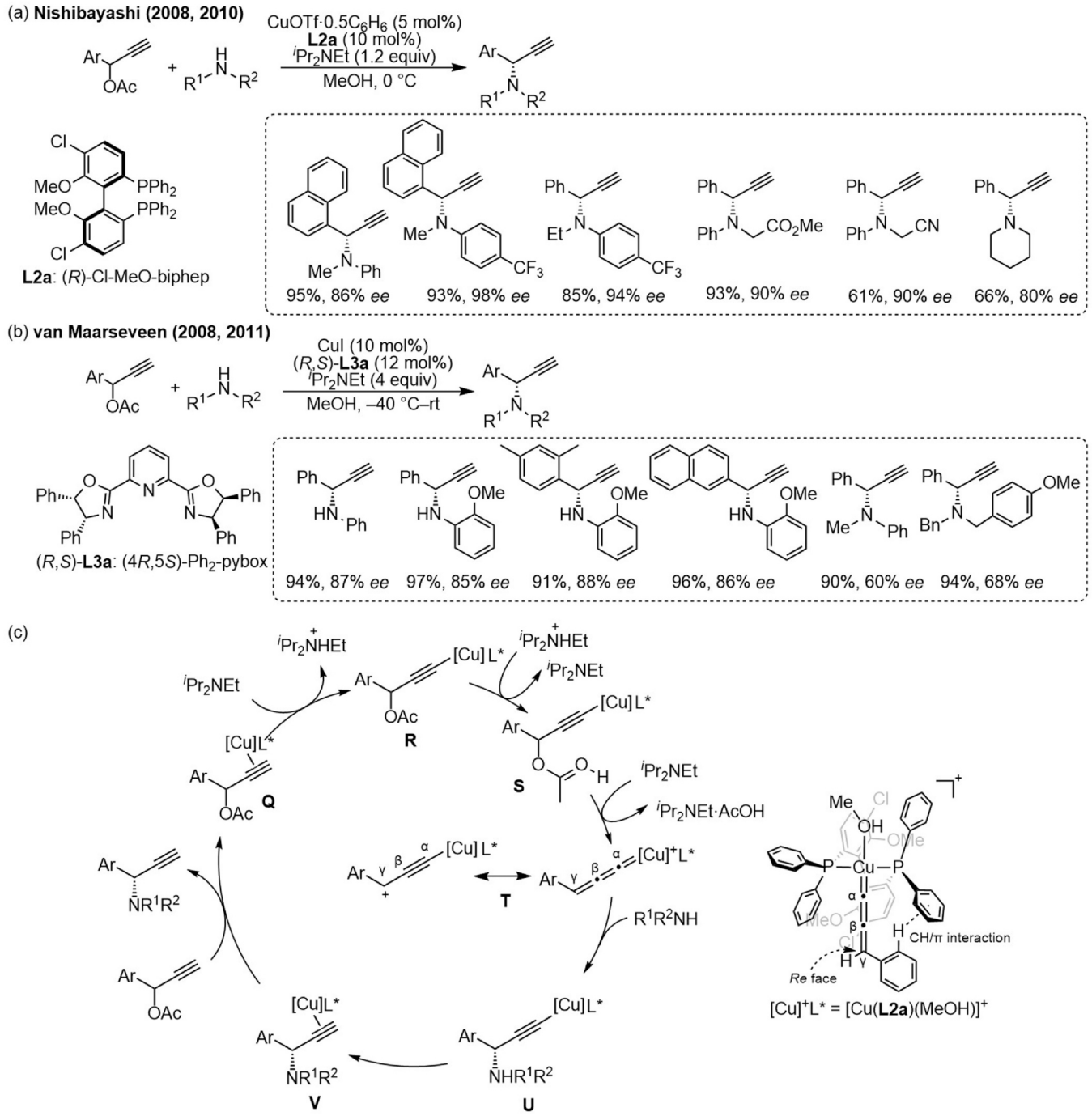

Fig. 8. (a) Cu/biphep-catalyzed enantioselective propargylic amination of propargylic esters with secondary amines. (b) Cu/Ph_2-pybox-catalyzed enantioselective propargylic amination of propargylic esters with primary amines. (c) Plausible reaction pathway catalyzed by Cu/biphep system.

(**U**), where the asymmetric induction is likely brought about by the CH/π interaction between the chiral ligand **L2a** and the allenylidene ligand in **T**. Another π-alkyne complex (**V**) is formed via the proton shift, followed by the ligand exchange with the propargylic alcohol to afford the starting π-alkyne complex **Q** and the propargylic aminated product. Cu–allenylidene complexes have not been yet isolated until now, although several Ag– and Au–allenylidene complexes have been isolated [64,65], whose structures have been analyzed crystallographically.

Since then, considerable amounts of combinations of Cu precursors and chiral ligands have been reported to catalyze propargylic substitution reactions of propargylic compounds, where chiral ligands can be roughly classified into diphosphine [59], bis(oxazoline) [55], bis

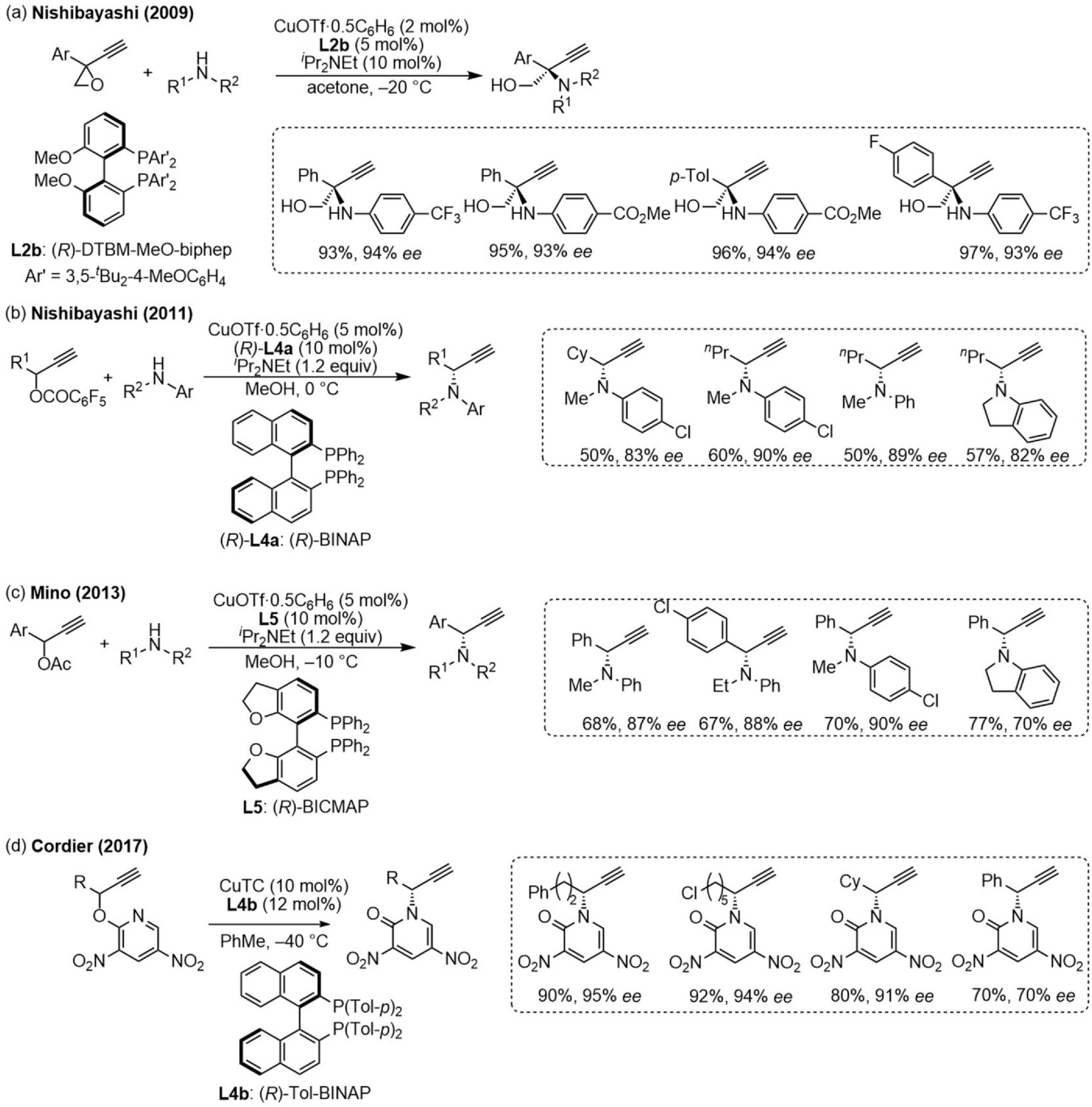

Fig. 9. (a) Cu/biphep-catalyzed enantioselective ring-opening propargylic amination of ethynyl epoxides with amines. (b) Cu/BINAP-catalyzed enantioselective propargylic amination of propargylic esters with anilines. (c) Cu/BICMAP-catalyzed enantioselective propargylic amination of propargylic esters with amines. (d) Cu/Tol-BINAP-catalyzed enantioselective intramolecular propargylic *O*-to-*N* migration of propargylic ethers.

(imidazoline) [66], tridentate ketimine P,N,N-type [67], *N*-Heterocyclic carbene (NHC) [68], and other ligands. From here, catalytic enantioselective propargylic C–N, C–C, C–O, or C–S bond formation under optimized reaction conditions for each article will be summarized according to varieties of chiral ligands.

Similar chiral diphosphine ligand (*R*)-DTBM-MeO-biphep (**L2b**) was also found to catalyze enantioselective ring-opening propargylic amination of ethynyl epoxides with amines to afford β-quaternary β-amino alcohols in combination with CuOTf (Fig. 9a) [69], whereas Cu-catalyzed enantioselective propargylic amination of propargylic esters with anilines was also achieved by using the well-known chiral diphosphine ligand (*R*)-BINAP ((*R*)-**L4a**) (Fig. 9b) [70]. Chiral dihydrobenzofuran-based diphosphine (*R*)-BICMAP (**L5**), prepared by Mino and co-workers [71], also worked efficiently for Cu-catalyzed enantioselective propargylic amination of propargylic esters with amines (Fig. 9c) [72]. Cordier and co-workers found that another chiral diphosphine ligand

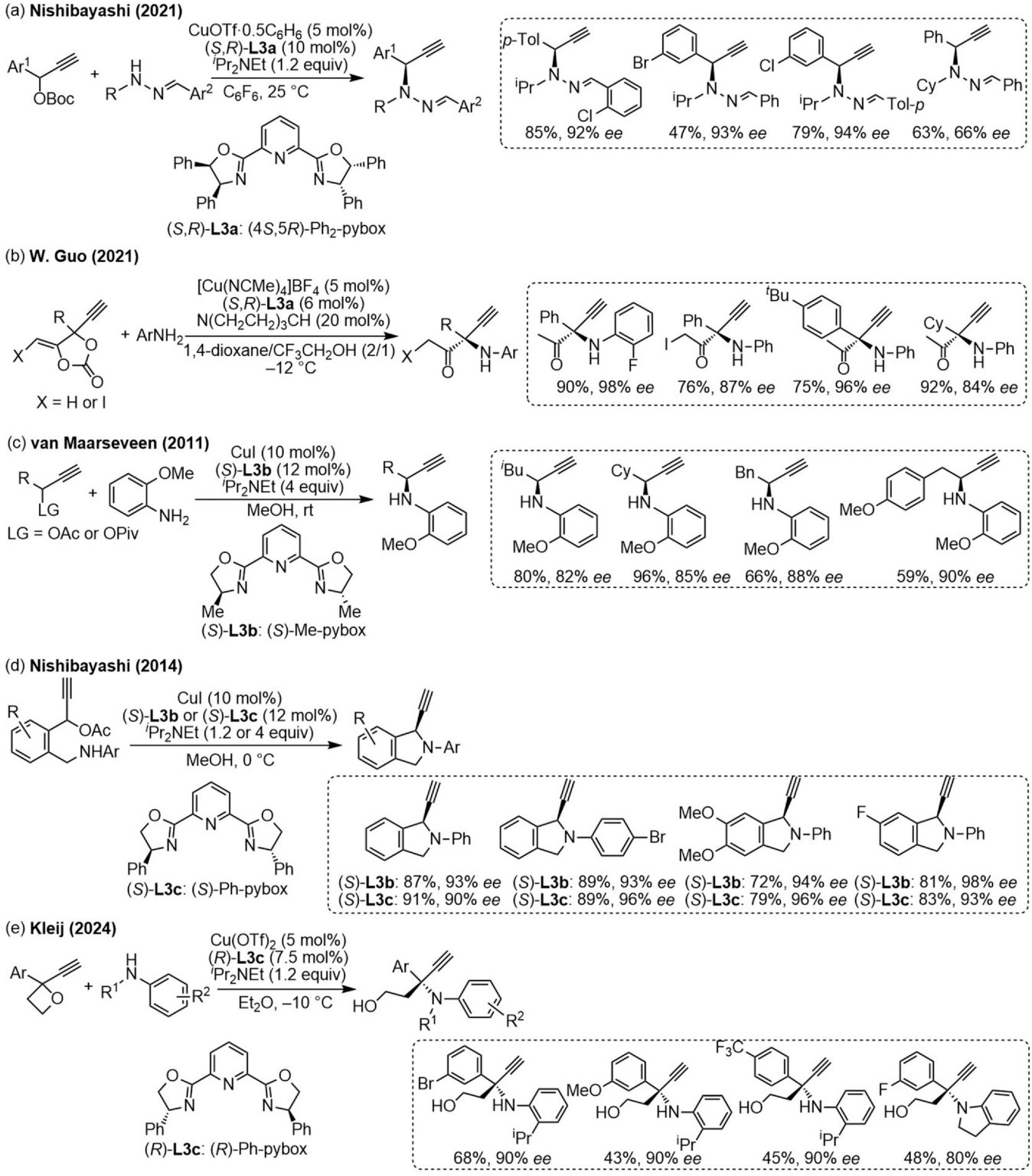

Fig. 10. (a) Cu/Ph_2-pybox-catalyzed enantioselective propargylic substitution reaction of propargylic carbonates with hydrazones. (b) Cu/Ph_2-pybox-catalyzed enantioselective decarboxylative propargylic amination of cyclic propargylic carbonates with anilines. (c) Cu/Me-pybox-catalyzed enantioselective propargylic amination of propargylic esters with *o*-anisidine. (d) Cu/Me-pybox- or Ph-pybox-catalyzed enantioselective intramolecular amination of propargylic esters. (e) Cu/Ph-pybox-catalyzed enantioselective ring-opening propargylic amination of alkynyl oxetanes with anilines.

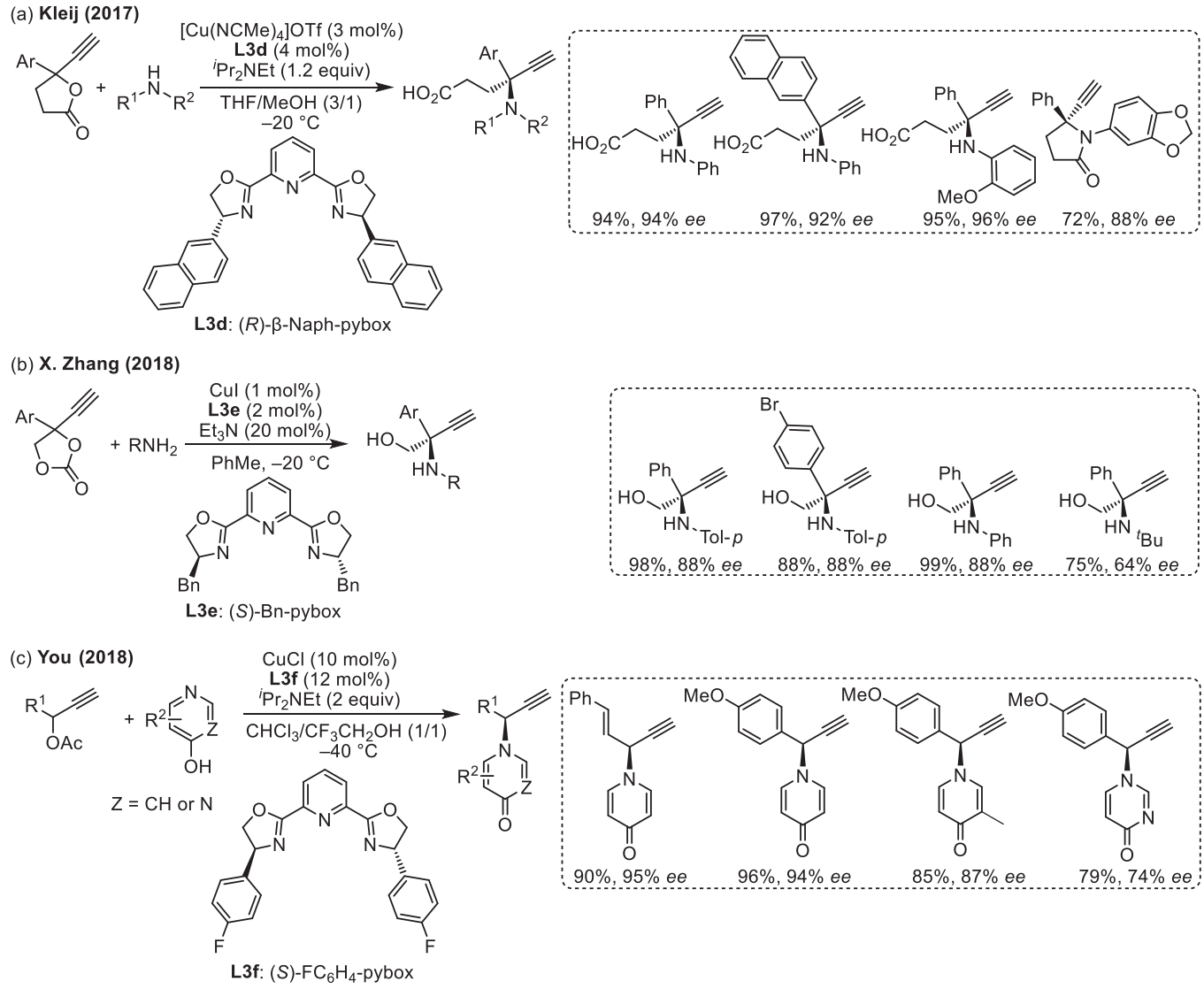

Fig. 11. (a) Cu/β-Naph-pybox-catalyzed enantioselective ring-opening propargylic amination of γ-butyrolactone with amines. (b) Cu/Bn-pybox-catalyzed enantioselective decarboxylative propargylic amination of cyclic propargylic carbonates with amines. (c) Cu/FC_6H_4-pybox-catalyzed enantioselective propargylic amination of propargylic esters with 4-hydroxypyridines or 4-hydroxypyrimidine.

(*R*)-Tol-BINAP (**L4b**) was effective in combination with CuTC (TC = 2-thiophenecarboxylate) for enantioselective intramolecular *O*-to-*N* formal [1,3]-rearrangement of propargylic ethers to afford *N*-propargylic-2-pyridones (Fig. 9d) [73].

A series of pybox-type ligands [55] have been found to furnish several propargylic amination reactions in combination with Cu precursors. As for the Ph_2-pybox ligand already mentioned in Fig. 8b [62], Nishibayashi and co-workers applied the combination of CuOTf and (*S*,*R*)-Ph-pybox ((*S*,*R*)-**L3a**) to enantioselective propargylic substitution reaction of propargylic carbonates with hydrazones to afford the propargylic aminated products (Fig. 10a) [74]. On the other hand, W. Guo and co-workers applied (*S*,*R*)-**L3a** to Cu-catalyzed enantioselective decarboxylative amination of cyclic propargylic carbonates with anilines to afford chiral α-quaternary α-amino ketones (Fig. 10b) [75].

(*S*)-Me-pybox ((*S*)-**L3b**) was introduced as a chiral ligand to coordinate to Cu species by van Maarseveen and co-workers to catalyze enantioselective propargylic amination of propargylic esters or carbonates with *o*-anisidine to afford the propargylic aminated compounds (Fig. 10c, Piv = ^{t}BuCO) [63]. Similar catalytic system of CuI and (*S*)-**L3b** or (*S*)-Ph-pybox ((*S*)-**L3c**) was applied to enantioselective intramolecular propargylic amination of propargylic esters to afford 1-ethynyl-isoindolines by Nishibayashi and co-workers (Fig. 10d) [76]. $Cu(OTf)_2$/(*R*)-Ph-pybox ((*R*)-**L3c**) pair was recently applied by Kleij and co-workers to enantioselective ring-opening propargylic amination of alkynyl oxetanes with anilines to afford γ-quaternary γ-amino alcohols (Fig. 10e) [77].

Kleij and co-workers also reported Cu-catalyzed enantioselective ring-opening propargylic amination of γ-butyrolactone to afford γ-quaternary γ-amino acids by using (*R*)-β-Naph-pybox (**L3d**) as a chiral ligand (Fig. 11a) [78], whereas X. Zhang and co-workers reported Cu-catalyzed enantioselective decarboxylative propargylic substitution reaction of cyclic propargylic carbonates with amines to give β-quaternary β-amino alcohols by using (*S*)-Bn-pybox (**L3e**) as a chiral ligand (Fig. 11b) [79]. You and co-workers utilized (*S*)-FC_6H_4-pybox (**L3f**) as a chiral ligand in combination with CuCl to catalyze propargylic substitution reaction of propargylic esters with 4-hydroxypyridines or 4-hydroxypyrimidin to afford *N*-alkylated 4-pyridones or *N*-alkylated 4-pyrimidone, respectively (Fig. 11c) [80].

On the other hand, Sun and a co-worker developed enantioselective decarboxylative ring-opening [4 + 2] annulation of cyclic propargylic carbamates with hexahydro-1,3–5-triazines to afford tetrahydroquinazolines by using the combination of $[Cu(NCMe)_4]PF_6$ and

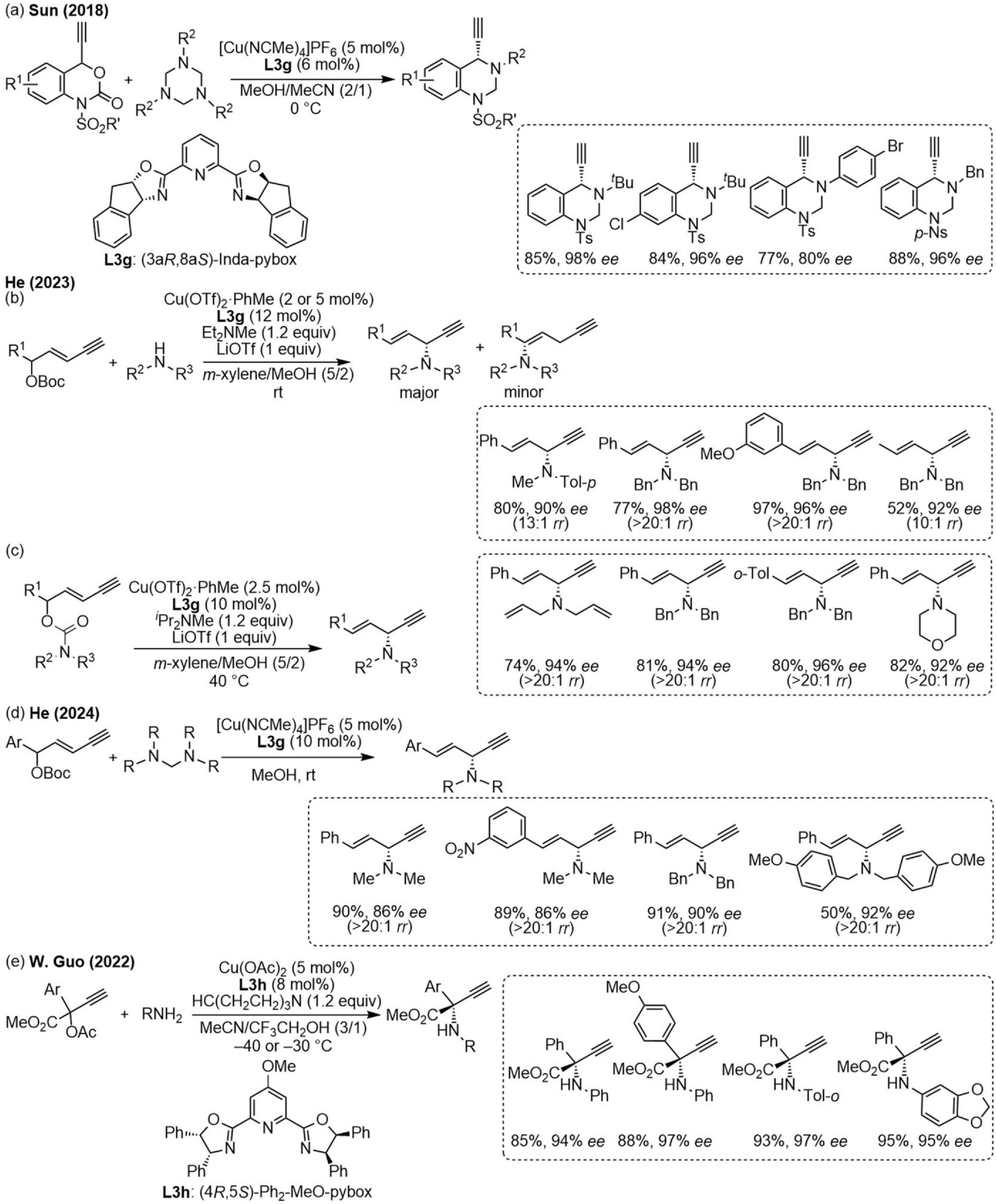

Fig. 12. (a) Cu/Inda-pybox-catalyzed enantioselective decarboxylative ring-opening [4 + 2] annulation of cyclic propargylic carbamates with hexahydro-1,3,5-triazines. (b) Cu/Inda-pybox-catalyzed regio- and enantioselective alkynylallylic amination of 1,3-enynes with amines. (c) Cu/Inda-pybox-catalyzed regio- and enantioselective decarboxylative intramolecular alkynylallylic amination of carbamate-tethered 1,3-enynes. (d) Cu/Inda-pybox-catalyzed regio- and enantioselective alkynylallylic amination of 1,3-enynes with diaminomethanes. (e) Cu/Ph_2-MeO-pybox-catalyzed enantioselective propargylic amination of propargylic esters with amines.

(3a*R*,8a*S*)-Inda-pybox (**L3g**) as a pair of catalysts (Fig. 12a, *p*-Ns = *p*-$NO_2C_6H_4SO_2$) [81]. Similar pair of catalysts have been recently applied by He and co-workers to regio- and enantioselective alkynylallylic substitution reaction of 1,3-enynes bearing *tert*-butylcarbonate as a leaving group remote from the alkyne moiety with amines to afford alkynylallylic aminated 1,4-enynes (Fig. 12b) [82]. Here, alkynylallylic aminated 1,4-enynes have been obtained as the major products, with alkenylic aminated 1,4-enynes obtained rather as minor products. In addition, regio- and enantioselective decarboxylative intramolecular alkynylallylic amination of carbamate-tethered 1,3-enyenes has been found to be catalyzed by the same Cu/ligand pair (Fig. 12c) [82]. More recently, the same chiral ligand has been shown to mediate Cu-catalyzed regio- and enantioselective alkynylallylic amination of 1,3-enynes by using diaminomethanes as *N*-centered nucleophiles (Fig. 12d) [83]).

On the other hand, (4*R*,5*S*)-Ph_2-MeO-pybox (**L3h**) has been utilized by W. Guo and co-workers as a chiral ligand for Cu-catalyzed enantioselective propargylic amination of propargylic esters to construct protected propargylic α-quaternary α-amino acids (Fig. 12e) [84].

More recently, Zhou and co-workers have reported Cu-catalyzed enantioselective propargylic amination of propargylic carbonates with amines to give propargylic aminated products by using (4*R*,5*S*)-Ph_2-3,5-$(MeO)_2C_6H_3CH_2O$-pybox (**L3i**) or (4*R*,5*S*)-Ph_2-Ar^FCH_2O-pybox (**L3j**) as a chiral ligand bearing a bulky shielding group at the C4 position of pyridine (Fig. 13a) [85]. Here, introduction of bulky shielding groups was necessary to achieve high enantioselectivity [86]. DFT calculations have demonstrated that the key reactive intermediate is Cu_2–bridging allenylidene complex (**W**), where nucleophiles can attack from *Re* face (Fig. 13a) [85].

Interestingly, Cu-catalyzed yne-propargylic substitution reaction of diynes has been very recently reported by Fang and co-workers using (*S*)-Cy-pybox (**L3k**) as a chiral ligand, although enantioselectivity is still rather low (Fig. 13b) [87].

Other than chiral diphosphine or oxazoline ligands, Hu and co-workers have introduced several chiral tridentate ketimine P,N,N-type ligands to Cu-catalyzed enantioselective propargylic amination chemistry [67]. Indeed, Cu-catalyzed enantioselective propargylic amination

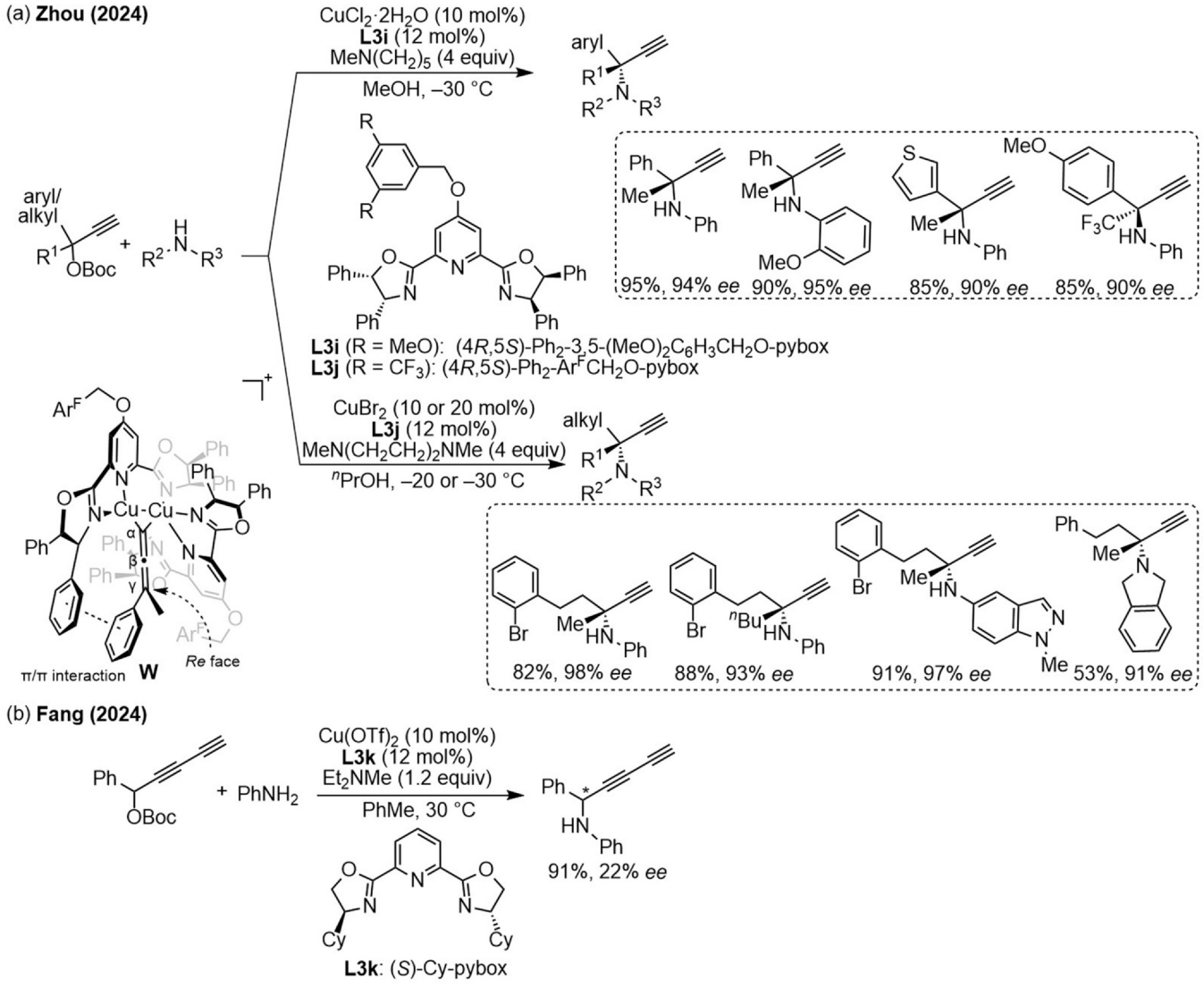

Fig. 13. (a) Cu/Ph_2-3,5-$(MeO)_2C_6H_3CH_2O$-pybox- or Ph_2-Ar^FCH_2O-pybox-catalyzed enantioselective propargylic amination of propargylic carbonates with amines. (b) Cu/Cy-pybox catalyzed enantioselective yne-propargylic amination of diynyl carbonate with aniline.

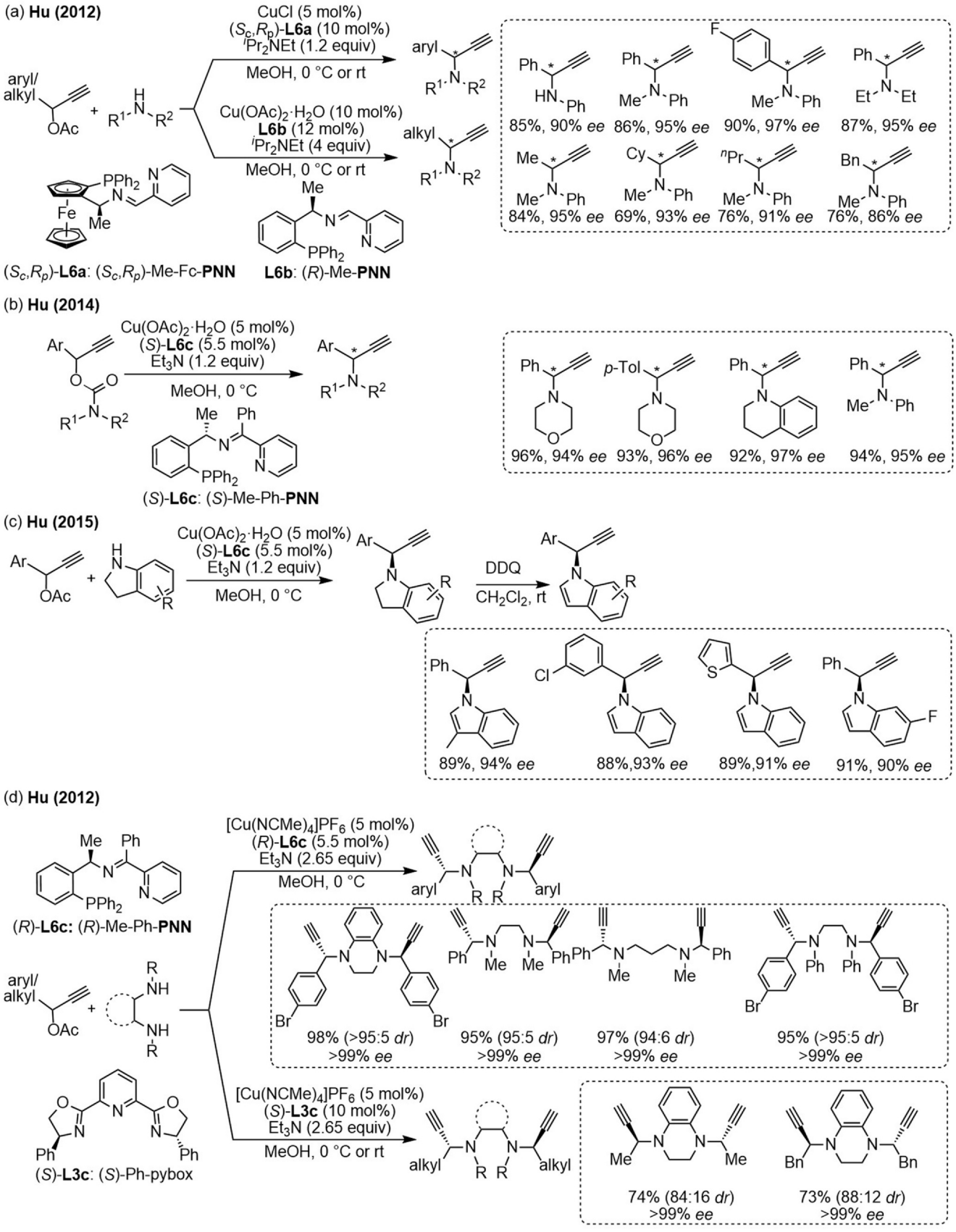

Fig. 14. (a) Cu/Me-Fc-**PNN**- or Me-**PNN**-catalyzed enantioselective propargylic amination of propargylic esters with amines. (b) Cu/Me-Ph-**PNN**-catalyzed enantioselective decarboxylative intramolecular propargylic amination of propargylic esters. (c) Cu/Me-Ph-**PNN**-catalyzed enantioselective *N*-propargylation of indoles. (d) Cu/Me-Ph-**PNN**- and Cu/Ph-pybox-catalyzed diastereo- and enantioselective dipropargylic amination of propargylic esters with 1,2,3,4-tetrahydroquinoxalines.

of aryl or alkyl propargylic esters with amines as *N*-centered nucleophiles was successful by employing (S_c,R_p)-Me-Fc-**PNN** ((S_c,R_p)-**L6a**) or (*R*)-Me-**PNN** (**L6b**) as a chiral ligand, respectively (Fig. 14a) [88], whereas enantioselective decarboxylative intramolecular propargylic amination of propargylic esters was achieved by employing (*S*)-Me-Ph-**PNN** ((*S*)-**L6c**) as a chiral ligand (Fig. 14b) [89]. The same Cu/chiral ligand pair was applicable for enantioselective *N*-propargylation of indolines, followed by dehydrogenation of indolines with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) to afford *N*-propargylindoles (Fig. 14c) [90]. The same Cu/ligand pair has been also applicable to Cu-catalyzed diastereo- and enantioselective dipropargylic amination of aryl propargylic esters to afford bis(propargylic) diamines, whereas similar diastereo- and enantioselective dipropargylic amination of alkyl propargylic esters was rather achieved with the combination with (*S*)-**L3c** (Ph-pybox) (Fig. 14d) [91].

Xu and co-workers also utilized (*S*)-**L6c** as a chiral ligand for Cu-catalyzed enantioselective propargylic amination of propargylic esters or carbonates with amines (Fig. 15a) [92], whereas similar chiral ligand (*S*)-Me-py-**PNN** (**L6d**) was already examined for Cu-catalyzed enantioselective propargylic amination of propargylic esters or carbonates with allylic amines (Fig. 15b) [93].

Precursor of NHC ligands [68] was also found to be effective for Cu-catalyzed enantioselective propargylic C–N bond formation. Jiang and co-workers used the combination of $Cu(OAc)_2$ and an aminoindane-

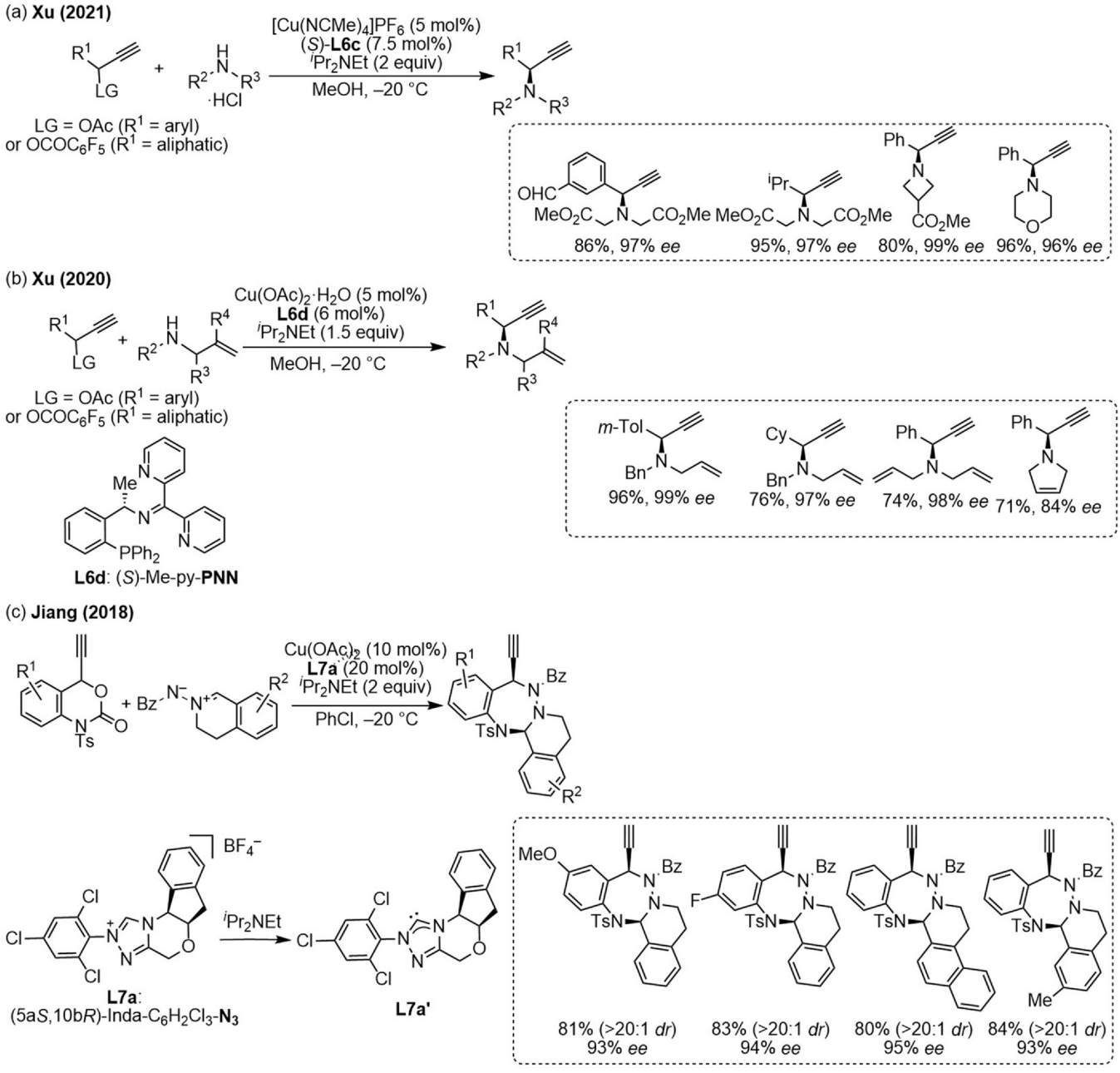

Fig. 15. (a) Cu/Me-Ph-**PNN**-catalyzed enantioselective propargylic amination of propargylic esters with amines. (b) Cu/Me-py-**PNN**-catalyzed enantioselective propargylic amination of propargylic esters with allylic amines. (c) Cu/NHC-catalyzed diastereo- and enantioselective decarboxylative ring-opening [4 + 3] annulation of cyclic propargylic carbamates with *C*,*N*-cyclic azomethine imines.

based triazolium salt (5a*S*,10b*R*)-Inda-$C_6H_2Cl_3$-$\mathbf{N_3}$ (**L7a**), the precursor for an *N*-heterocyclic carbene (NHC) (**L7a'**), as a pair of catalysts for diastereo- and enantioselective decarboxylative ring-opening [4 + 3] annulation of cyclic propargylic carbamates with *C*,*N*-cyclic azomethine imines to afford isoquinoline-fused triazepine derivatives (Fig. 15c) [94].

Very recently, X. Wang and co-workers have reported the isolation of a well-defined dicopper complex [Cu_2I_2(**L8a**)] (**5a**), which is chelated by a tetradentate nitrogen-containing ligand bearing two chiral oxazoline units bridged by a benzo[*c*]cinnoline linker containing ^{t}Bu substituent on oxazoline unit (*S*)-^{t}Bu-bcbox (**L8a**), whose structure has been determined by crystallographic study (Fig. 16a) [95]. **5a** has been shown to work as a catalyst for enantioselective propargylic amination of a propargylic alcohol with aniline to afford the (*R*)-isomer (Fig. 16b) [95], where formation of a dicopper–allenylidene complex (**5a'**) in situ as well as the attack of aniline as an *N*-centerd nucleophile from the *Re* face of the allenylidene unit is suggested by DFT calculations (Fig. 16b) [95]. Similarly, dicopper complex [Cu_2I_2(**L8b**)] (**5b**), chelated by a tetradentate nitrogen-containing ligand bearing two chiral oxazoline units bridged by a benzo[*c*]cinnoline linker containing indane skeleton with cyclohexyl substituent on oxazoline unit (3a*R*,8a*S*)-Cy-Inda-^{t}Bu-bcbox (**L8b**), has been isolated (Fig. 16c) [95], which has been shown to work as a better catalyst for enantioselective propargylic amination of tertiary or quaternary propargylic esters or carbonates with amines to afford propargylic aminated products as (*S*)-isomers (Fig. 16d and e) [95].

3.2. Cu-catalyzed enantioselective propargylic C–C bond formation

Cu-catalyzed enantioselective propargylic substitution reaction with *C*-nucleophiles was first achieved by Hou and a co-worker, who used the combination of [$Cu(NCMe)_4$]ClO_4 and **L2a** ((*R*)-Cl-MeO-biphep) as a pair of catalysts for enantioselective propargylic alkylation of propargylic esters with enamines to afford β-ethynyl-substituted ketones (Fig. 17a) [96].

On the other hand, Nishibayashi and co-workers examined the combination of CuOTf and racemates of BINAP (*rac*-**L4a**) in the presence of a Hayashi–Jørgensen organocatalyst **3a** to catalyze enantioselective propargylic alkylation of propargylic esters with aldehydes to afford the corresponding propargylic alkylated products as a mixture of two diastereomers (Fig. 17b) [97]. Here, asymmetric induction is supposed to brought about by the organocatalyst **3a**, which reacts with an aldehyde to afford a chiral enamine **N**, working as a *C*-centered nucleophile to attack at the *Re* face of the allenylidene ligand

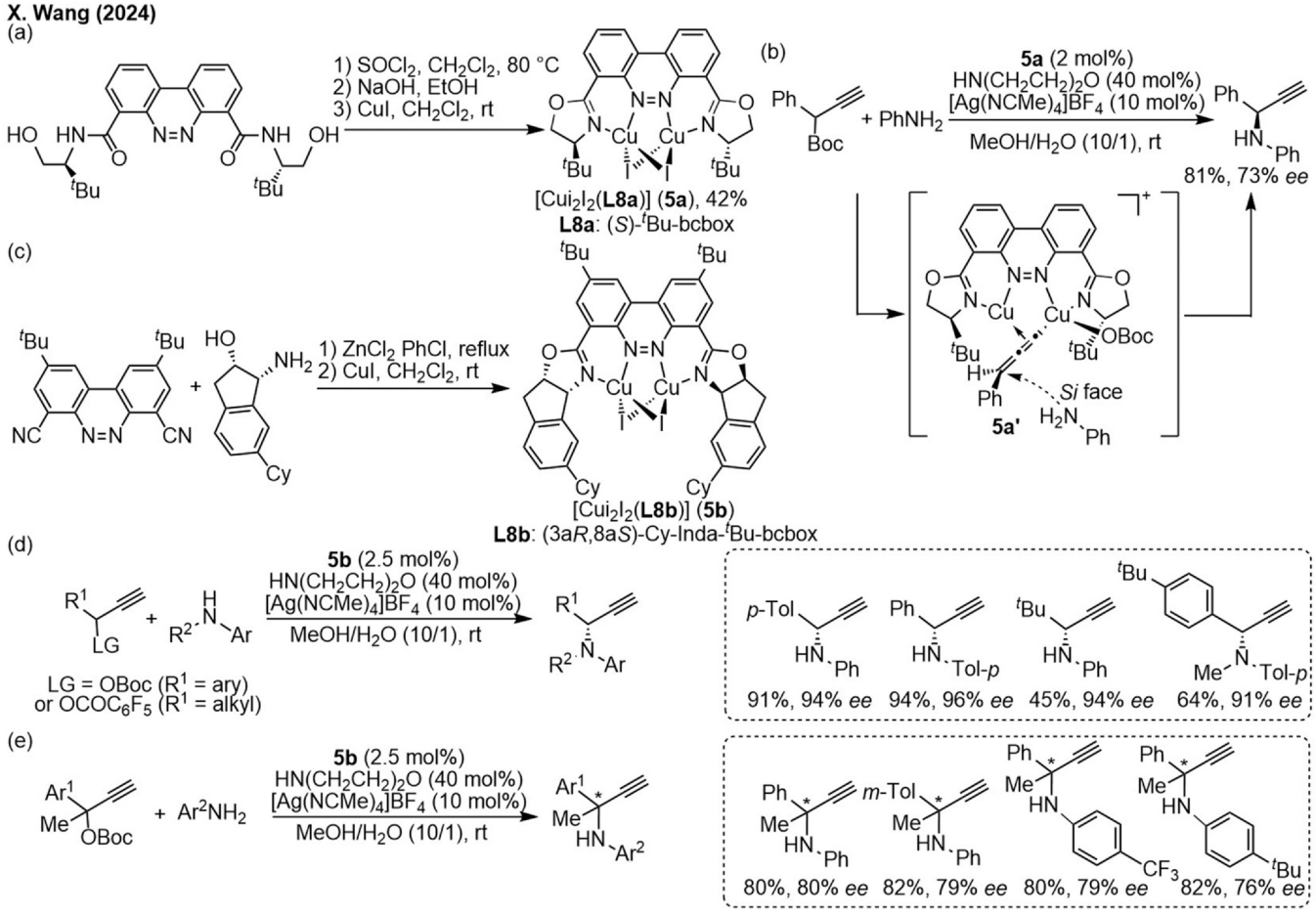

Fig. 16. (a) Preparation of well-defined dicopper complex bearing a benzo[*c*]cinnoline-linked bisoxazoline ligand with ^{t}Bu substituent. (b) Cu-catalyzed enantioselective propargylic amination of a propargylic carbonate with aniline (c) Preparation of well-defined dicopper complex bearing a benzo[*c*]cinnoline-linked bisoxazoline ligand with Cy substituent and indane skeleton. (d) Cu-catalyzed enantioselective propargylic amination of tertiary propargylic esters or carbonates with anilines to construct tertiary stereogenic *C* centers. (e) Cu-catalyzed enantioselective propargylic amination of quaternary propargylic esters with anilines.

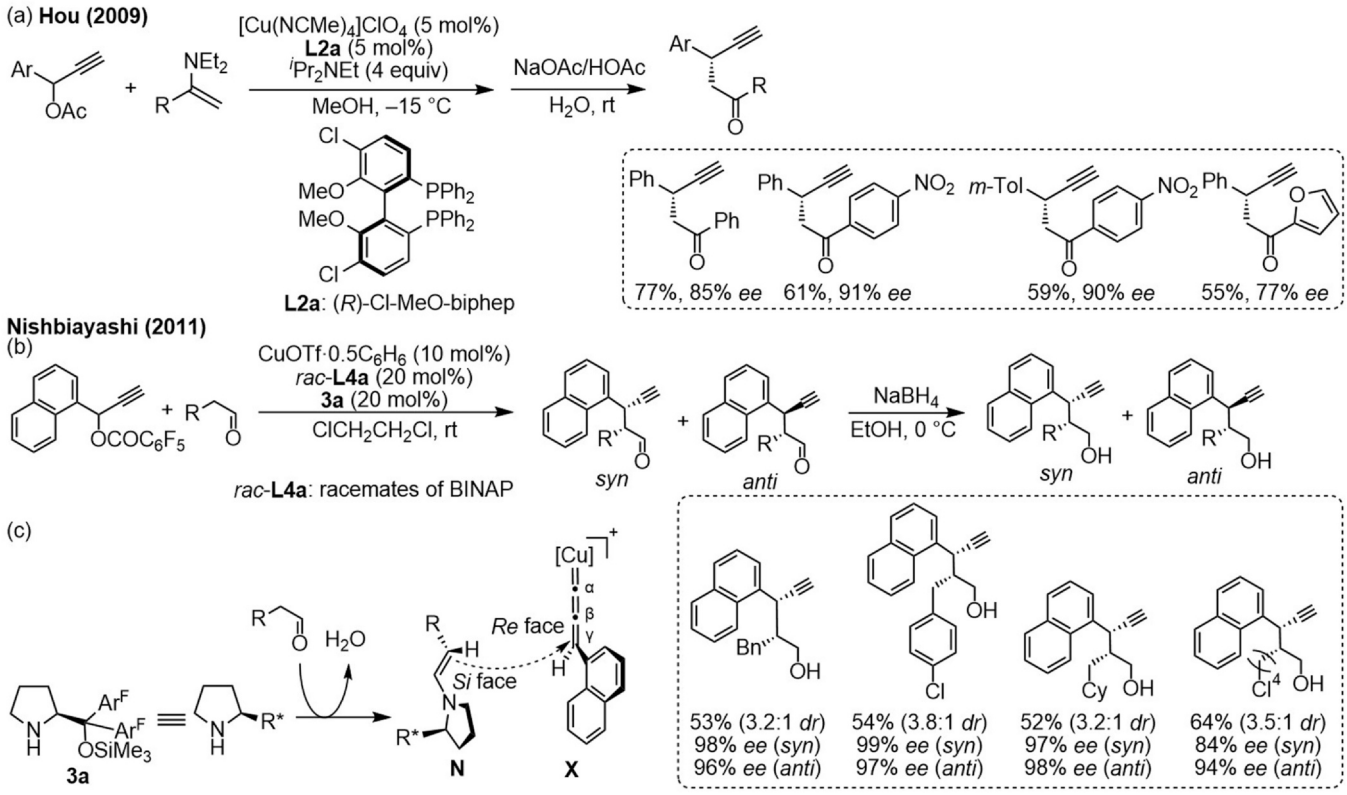

Fig. 17. (a) Cu/biphep-catalyzed enantioselective propargylic alkylation of propargylic esters with enamines. (b) Cu/BINAP- and thiourea-catalyzed enantioselective propargylic alkylation of propargylic esters with aldehydes. (c) Plausible asymmetric induction for Cu/BINAP and thiourea system.

of a Cu–allenylidene complex (**X**) from *Si* face of the enamine, where both Ar^F substituents of the enamine and 1-naphthyl group of the allenylidene ligand do not collide with each other (Fig. 17c) [97].

A variety of pybox ligands have been applied to Cu-catalyzed enantioselective propargylic C–C bond formation. For example, enantioselective propargylation of indoles was achieved by van Maarseveen and co-workers, who used the combination of CuI and (*R*,*S*)-**L3a** (Ph_2-pybox) as a pair of catalysts (Fig. 18a) [63], while diastereo- and enantioselective propargylation of indoles followed by dearomatization to afford furoindolines or pyrroloindolines was reported by You and co-workers using the same pair of catalysts (Fig. 18b) [98]. Using the similar pair of CuOTf·0.5C_6H_6 and (*S*,*R*)-**L3a**, Nishibayashi and co-workers succeeded in the construction of enantioselective propargylation of indoles to afford the desired products bearing a quaternary stereogenic *C* center at the propargylic position (Fig. 18c) [99]. Here, a dicopper complex bearing (*S*,*R*)-**L3a** as an auxiliary ligand [Cu_2(μ-Cl((*S*,*R*)-**L3a**)$_2$][$CuCl_2$] (**6**) was independently prepared (Fig. 18d) [99], which showed similar catalytic activity toward enantioselective propargylation of indoles, demonstrating that the key reactive intermediates may be Cu_2–bridging allenylidene species. Cu-catalyzed enantioselective propargylation of indolizines was also reported by X. Zhang and co-workers (Fig. 18e) [100], who also succeeded in Cu-catalyzed enantioselective difluoroalkylation of secondary propargyl sulfonates (Mes = 2,4,6-$Me_3C_6H_2$) with difluoroenoxysilanes (Fig. 18f) [101].

Combination of [Cu(NCMe)$_4$]PF_6 and (*S*)-**L3b** (Ph-pybox) was examined by Fang and co-workers, who performed enantioselective semipinacol-type rearrangement of cyclic propargylic carbonates containing cyclobutyl ring via decarboxylative ring-opening propargylic alkylation to afford cyclopentanone derivatives bearing a quaternary stereogenic *C* center at the propargylic position (Fig. 19a) [102]. Similar ring expansion of cyclic propargylic carbonates containing azacyclobutane or oxetane units was also found to be catalyzed by the combination of [Cu(NCMe)$_4$]PF_6 and (*S*)-**L3b** or (*S*)-^{i}Pr-pybox (**L3l**) via decarboxylative ring-opening propargylic alkylation to afford pyrrolidin-3-one or tetrahydrofuran-3-one derivatives bearing a quaternary stereogenic *C* center at the propargylic position (Fig. 19b and c) [102].

A series of enantioselective decarboxylative ring-opening annulation of cyclic propargylic carbamates with C-centered nucleophiles have been shown to be catalyzed by the combination of Cu precursors with (*R*)-**L3c** or (*S*)-**L3c** (Ph-pybox). For example, Xiao and co-workers demonstrated diastereo- and enantioselective decarboxylative ring-opening [4 + 1] annulation of cyclic propargylic carbamates with sulfur ylides to afford indolines by using Cu(OTf)$_2$ and (*R*)-**L3c** as a pair of catalysts Fig. 20a) [103]. On the other hand, Wu and co-workers demonstrated diastereo- and enantioselective decarboxylative ring-opening [4 + 2] annulation of cyclic propargylic carbamates with aryl acetic acids to afford quinolines by using the combination of [Cu(NCMe)$_4$]BF_4, (*S*)-**L3c**, and a benzotetramisole (BTM)-type Lewis base organocatalyst (*S*)-Me-BTM (**7a**) [52] as a set of catalysts (Fig. 20b, *o*-Ns

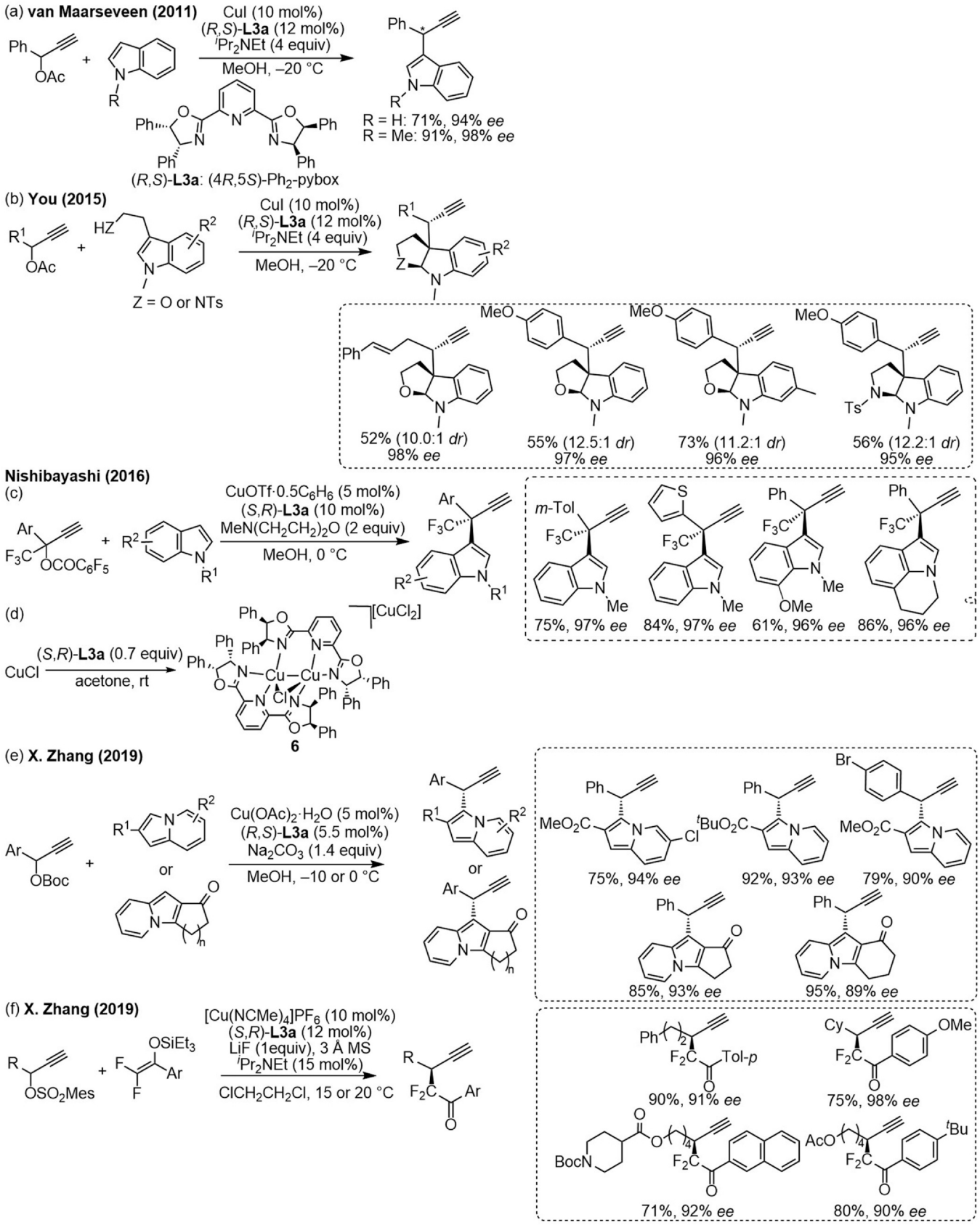

Fig. 18. (a) Cu/Ph_2-pybox-catalyzed enantioselective propargylation of indoles. (b) Cu/Ph_2-pybox-catalyzed diastereo- and enantioselective propargylic dearomatization of indoles. (c) Cu/Ph_2-pybox-catalyzed enantioselective propargylation of indoles to construct quaternary stereogenic *C* centers. (d) Preparation of dicopper complex ligated by Ph_2-pybox. (e) Cu/Ph_2-pybox-catalyzed enantioselective propargylation of indolizines. (f) Cu/Ph_2-pybox-catalyzed enantioselective difluoroalkylation of propargylic sulfonates with difluoroenoxysilanes.

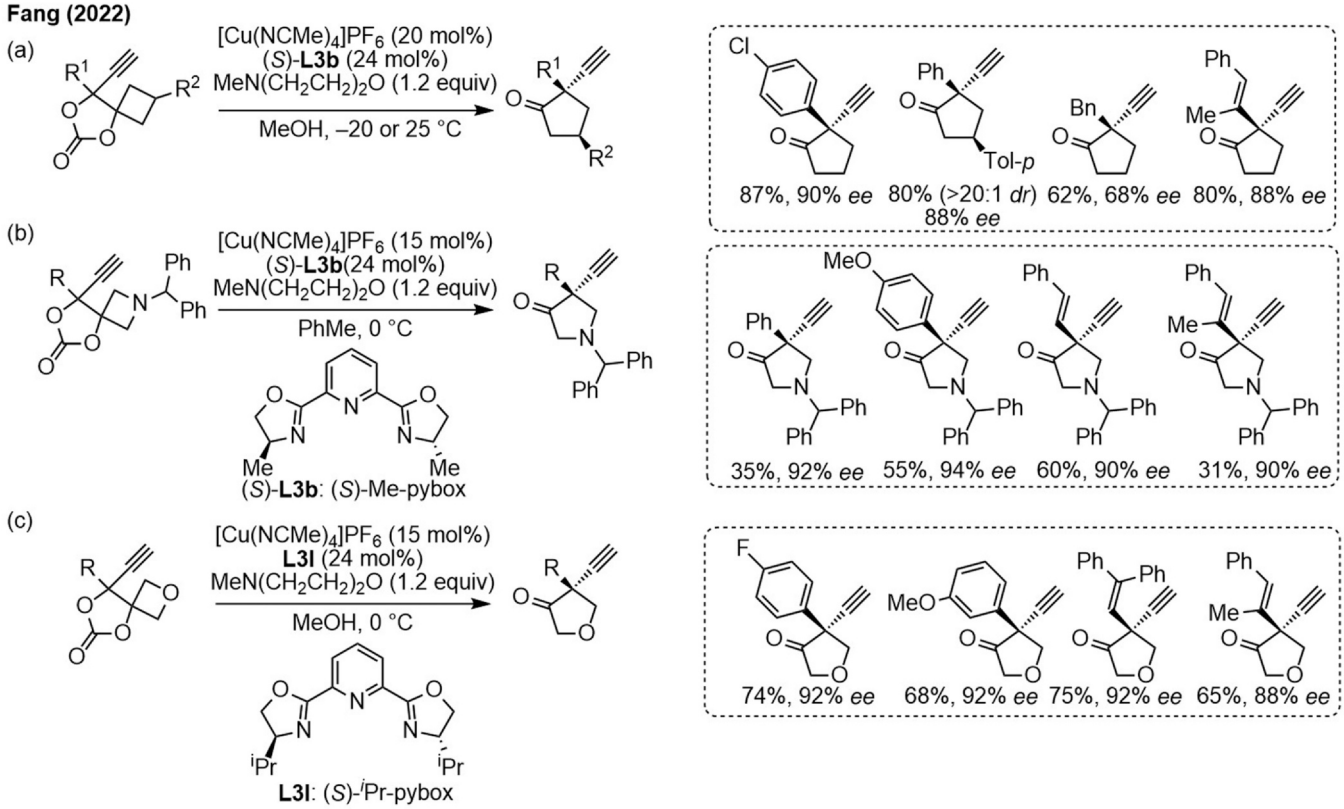

Fig. 19. (a) Cu/Me-pybox-catalyzed enantioselective decarboxylative semipinacol rearrangement of cyclic propargylic carbonates bearing cyclobutane units to afford cyclopentanone derivatives. (b) Cu/Me-pybox-catalyzed enantioselective decarboxylative semipinacol rearrangement of cyclic propargylic carbonates bearing oxetane units to afford five-membered heterocycle derivatives. (c) Cu/^{i}Pr-pybox-catalyzed enantioselective decarboxylative semipinacol rearrangement of cyclic propargylic carbonates bearing azacyclobutane units to afford five-membered heterocycle derivatives.

= *o*-$NO_2C_6H_4SO_2$) [104]. In this reaction system, addition of **7a**, supposed to react with an aryl acetic acid to form a *Z*-enolate (**Y**) with enolate *O* positioned *syn* to *S* of BTM and with its *Re* face sterically hindered by the methyl group, attacks from its *Si* face at the γ-C in the *Re* face of Cu–allenylidene complex (**Z**), generated from CuI, (*S*)-**L3c**, a cyclic propargylic carbamate, and $^{i}Pr_2NEt$ via decarboxylative process, improving both diastereoselectivity and enantioselectivity (Fig. 20c) [104]. Diastereo- and enantioselective decarboxylative ring-opening [4 + 2] annulation of cyclic propargylic carbamates with azalactones to afford 3,4-dihydroquinolin-2-one derivatives was reported by X.-W. Wang and co-workers (Fig. 20d) [105], whereas diastereo- and enantioselective decarboxylative ring-opening [3 + 2] annulation of cyclic propargylic carbamates with γ-butenolides to afford pyrrolidinones bearing a quaternary stereogenic *C* center at the propargylic position was reported by Hu and co-workers (Fig. 20e) [106].

Diastereo- and enantioselective decarboxylative ring-opening [3 + 2] annulation of fused cyclic propargylic carbamates with azalactones to afford pyrrolo[1,2-*a*]indoles via the formation of isolable propargylation intermediates was examined by Deng and co-workers (Fig. 21a) [107]. Yuan and co-workers demonstrated decarboxylative [3 + 2] annulation of cyclic propargylic carbonates with azalactones to afford γ-butyrolactones (Fig. 21b) [108], or diastereo- and enantioselective decarboxylative ring-opening [3 + 2] annulation of cyclic carbamates with azalactones to afford γ-butyrolactams (Fig. 21c) [109], both bearing two vicinal quaternary stereogenic *C* centers.

Recently, Gong and co-workers have developed diastereo- and enantioselective stereodivergent propargylic alkylation of propargylic esters with enals by using the combination of $[Cu(NCMe)_4]PF_6$, (*S*)-**L3c**, and an aminoindane-based triazolium salt (5a*R*,10b*S*)-Inda-Mes-$\mathbf{N_3}$ (**L7b**), the precursor for an *N*-heterocyclic carbene (NHC) (**L7b'**) [68] as a set of catalysts (Fig. 22a) [110]. In this reaction system, coordinatively unsaturated species (**AA**) generated from $[Cu(NCMe)_4]PF_6$ and (*S*)-**L3c** activates a propargylic ester toward the formation of an allenylidene complexes (**AB**), whereas **L7b'** reacts with an enal to form an NHC-bound nucleophile (**AC**), which couples with **AB** to afford the desired product both diastereo- and enantioselectively (Fig. 22b) [110].

Combination of $[Cu(NCMe)_4]PF_6$ and (*S*)-**L3c** has been also shown to catalyze diastereo- and enantioselective propargylic alkylation of propargylic carbonates with 2,2,2-trifluoroethyl-isoxazoles by Wu and co-workers (Fig. 22c) [111]. He and co-workers have also demonstrated regio-, enantio- and (*E*)-selective alkynylallylic monofluoroalkylation of 1,3-enynes on treatment with fluorinated malonates (Fig. 22d) [112].

He and co-workers have also examined the combination of $Cu(OTf)_2{\cdot}0.5PhMe$, **L3g** (Inda-pybox), and dibenzo-1,4-oxaborine-derived borinic acid (**8**) [113] as a set of catalysts for regio- and enantioselective alkynylallylic alkylation of 1,3-enyne bearing a leaving

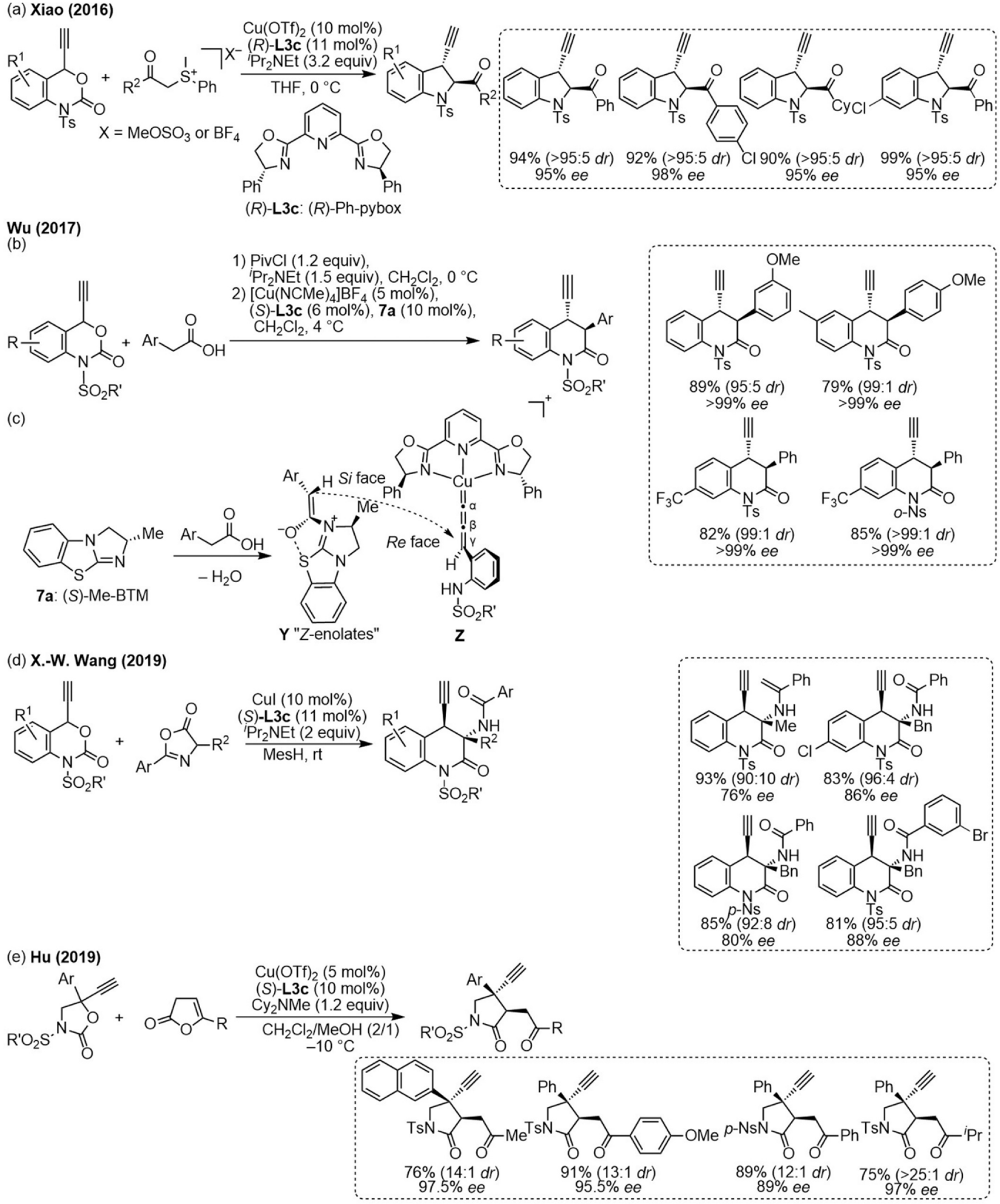

Fig. 20. (a) Cu/Ph-pybox-catalyzed diastereo- and enantioselective decarboxylative ring-opening [4 + 1] annulation of cyclic propargylic carbamates with sulfur ylides. (b) Cu/Ph-pybox- and BTM-catalyzed diastereo- and enantioselective decarboxylative ring-opening [4 + 2] annulation of cyclic propargylic carbamates with aryl acetic acid. (c) Plausible asymmetric induction for Cu/Ph-pybox and BTM system. (d) Cu/Ph-pybox-catalyzed diastereo- and enantioselective decarboxylative ring-opening [4 + 2] annulation of cyclic propargylic carbamates with azalactones. (e) Cu/Ph-pybox-catalyzed diastereo- and enantioselective decarboxylative ring-opening [3 + 2] annulation of cyclic propargylic carbamates with γ-butenolides.

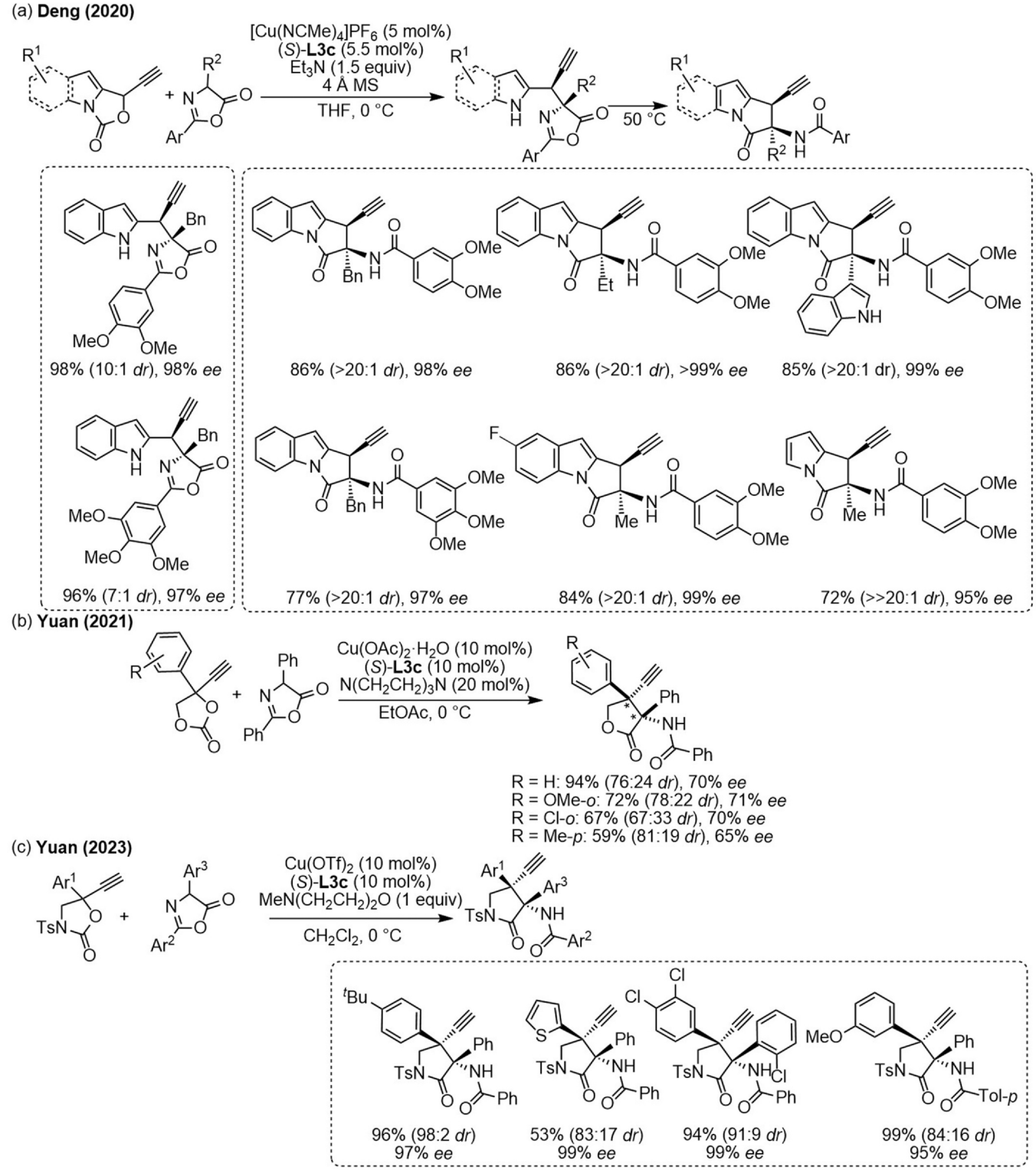

Fig. 21. (a) Cu/Ph-pybox-catalyzed diastereo- and enantioselective decarboxylative ring-opening [3 + 2] annulation of fused cyclic propargylic carbamates with azalactones. (b) Cu/Ph-pybox-catalyzed diastereo- and enantioselective decarboxylative ring-opening [3 + 2] annulation of cyclic propargylic carbonates with azalactones. (c) Cu/Ph-pybox-catalyzed diastereo- and enantioselective decarboxylative ring-opening [3 + 2] annulation of cyclic propargylic carbamates with azalactones.

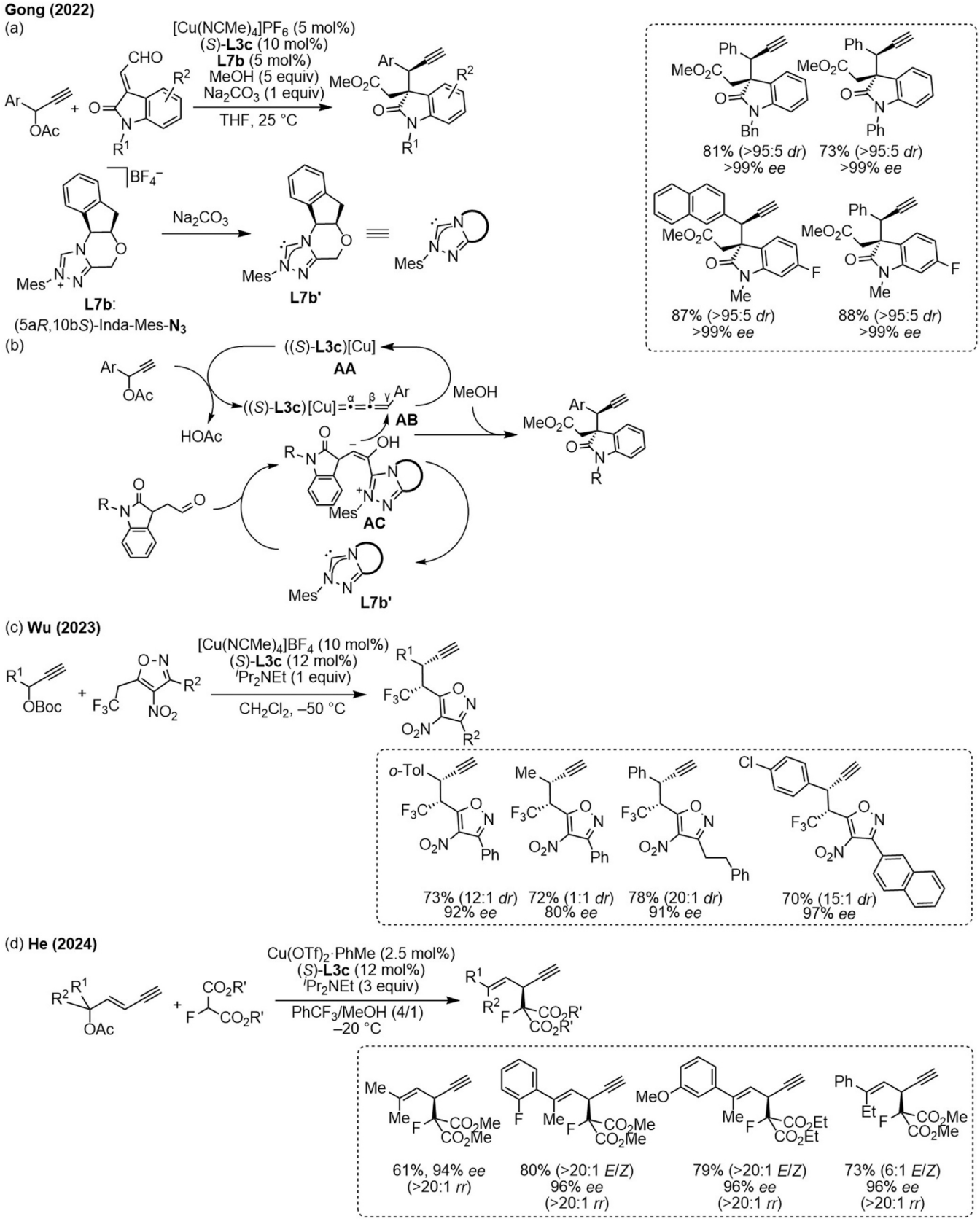

Fig. 22. (a) Cu/Ph-pybox- and NHC-catalyzed diastereo- and enantioselective propargylic alkylation of propargylic esters with enals. (b) Plausible reaction pathways for dual catalytic systems. (c) Cu/Ph-pybox-catalyzed diastereo- and enantioselective alkylation of propargylic carbonates with 2,2,2-trifluoroethyl-isoxazoles. (d) Cu/Ph-pybox-catalyzed regio-, enantio-, and (*E*)-selective monofluoroalkylation of 1,3-enynes with fluorinated malonates.

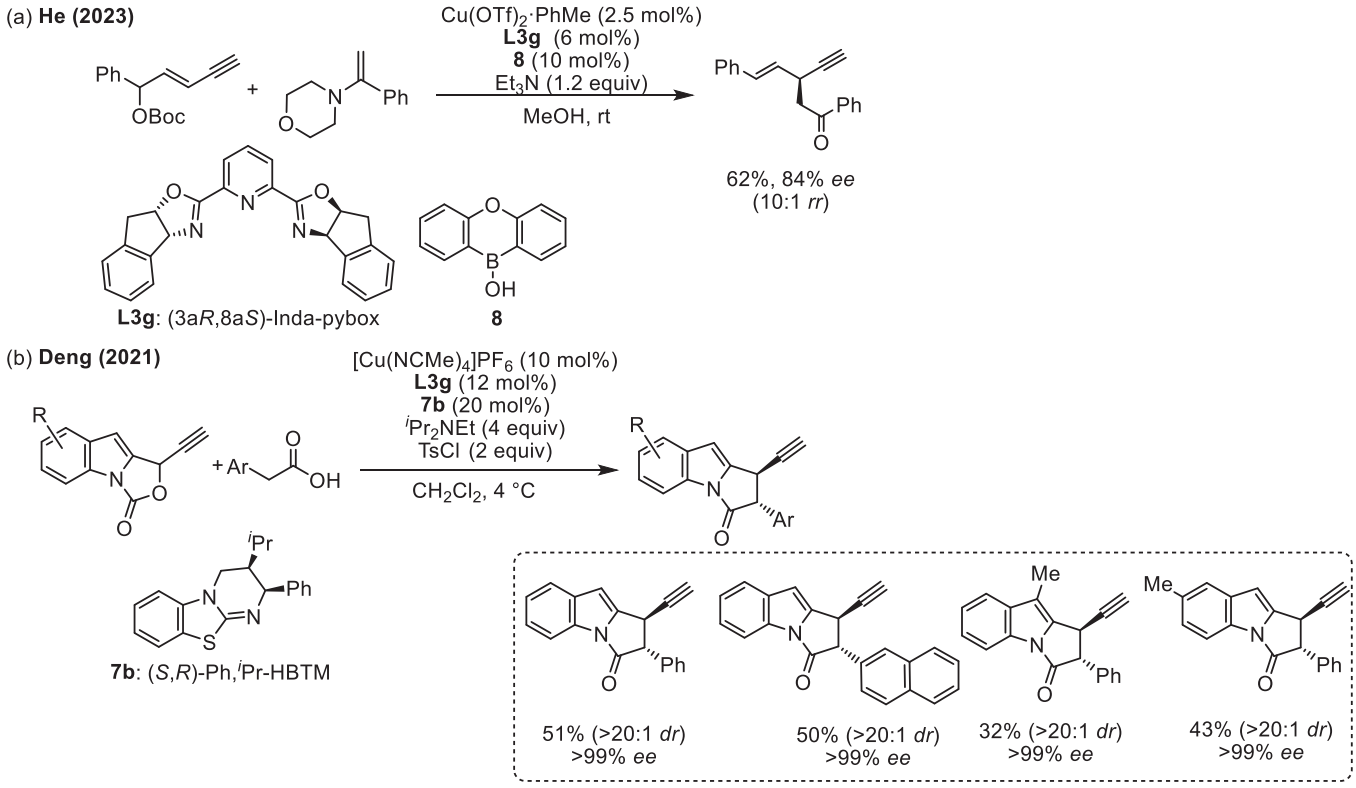

Fig. 23. (a) Cu/Inda-pybox- and borinic acid-catalyzed regio- and enantioselective alkynylallylic alkylation of 1,3-enyne with 4-vinyl morpholine. (b) Cu/Inda-pybox- and BTM-catalyzed diastereo- and enantioselective decarboxylative ring-opening [3 + 2] annulation of 1-ethynyl oxazolo[3,4-a]indol-3-one with aryl acetic acid.

group remote from the alkyne moiety with 4-vinyl morpholine to afford alkynylallylic alkylated product (Fig. 23a) [82]. Here, the borinic acid catalyst **8** traps 4-vinyl morpholine to activate as a *C*-centered nucleophile. Similarly, combination of $[Cu(NCMe)_4]PF_6$, **L3g**, and a BTM-type organocatalyst (*S*,*R*)-Ph,^{i}Pr-HBTM (**7b**) [52] was applied by Deng and co-workers to diastereo- and enantioselective decarboxylative ring-opening [3 + 2] annulation of cyclic propargylic carbamates with aryl acetic acids to afford pyrrolo[1,2,-*a*]indoles (Fig. 23b) [114].

Similarly, Gong an co-workers applied the combination of $[Cu(NCMe)_4]PF_6$, **L3l** (^{i}Pr-pybox), and a BTM-type organocatalyst (*R*)-Ph-BTM (**7c**) as a set of catalysts to diastereo- and enantioselective decarboxylative ring-opening [4 + 2] annulation of cyclic propargylic carbamates with aryl or allylic acetonitriles to afford 3,4-dihydroquinolin-2-one derivatives (Fig. 24a) [115]. On the other hand, Mukherjee and a co-worker demonstrated diastereo- and enantioselective decarboxylative ring-opening [4 + 2] annulation of cyclic propargylic carbamates with vinylogous aza-enamines to afford tetrahydroquinoline derivatives bearing 1,3-stereocenters by using the combination of $[Cu(NCMe)_4]PF_6$ and **L3l** as a pair of catalysts (Fig. 24b) [116].

Combination of CuBr and (*S*,*S*)-*sec*-Bu-pybox (**L3m**) was examined by Wu and co-workers for diastereo- and enantio-selective propargylation of benzofuranones (Fig. 24c) [117] and enantioselective propargylic substitution reactions of propargylic esters with trialkyl methanetricarbonates (Fig. 24d) [118].

You and a co-worker utilized the combination of CuI and (*S*)-Cu/^{t}Bu-Ph_2-pybox (**L3n**) catalyzed as a pair of catalysts toward diastereo- and enantioselective decarboxylative ring-opening [4 + 2] annulation of cyclic propargylic carbamates with indoles to afford tetrahydro-5*H*-Indolo[2,3-*b*]quinolines bearing vicinal quaternary stereogenic *C* centers through propargylic dearomatization process (Fig. 25a) [119].

(*R*)-$HOCH_2$-pybox (**L3o**) was utilized by Xiao and co-workers in combination with CuI for enantioselective propargylic substitution reaction of propargylic esters with stable phosphonium tetrafluoroborates, to afford propargylic phosphine ylides, where further Wittig reaction undergoes to afford α-propargylic acrylates or allenoates on treatment with in situ-generated ketenes derived from formalin or acyl chloride, respectively (Fig. 25b) [120].

Carreira and a co-worker utilized the combination of $[Cu(NCMe)_4]PF_6$ and (*S*)-3,4,5-$(MeO)_3C_6H_2$-pybox (**L3p**) to catalyze enantioselective intramolecular propargylic substitution reaction of a propargylic ester bearing a pyrrole moiety to afford 8-ethynyl-5,6,7,8-tetrahydroindolizine bearing a quaternary stereogenic *C*-center at the propargylic position (Fig. 25c) [121].

Diastereo- and enantioselective decarboxylative ring-opening [4 + 2] annulation of cyclic propargylic carbamates with 2-siloxyfurans was examined by Wu and co-workers by using the combination of $[Cu(NCMe)_4]BF_4$ and (*S*)-Bn-Ph_2-pybox (**L3q**) as a pair of catalysts to afford tetrahydroquinolines fused with γ-lactone moiety (Fig. 26a, Bs = $PhSO_2$) [122].

On the other hand, Niu and co-workers used the combination of $[Cu(NCMe)_4]BF_4$, (*S*)-Me-Cl-pybox (**L3r**), and $ZnEt_2$ or $Ti(O^iPr)_4$ as a set of catalysts for diastereo- and enantioselective propargylation of 5*H*-thiazol-4-ones or 5*H*-oxazol-4-ones to afford the desired products bearing two vicinal quaternary stereogenic *C* centers (Fig. 26b) [123].

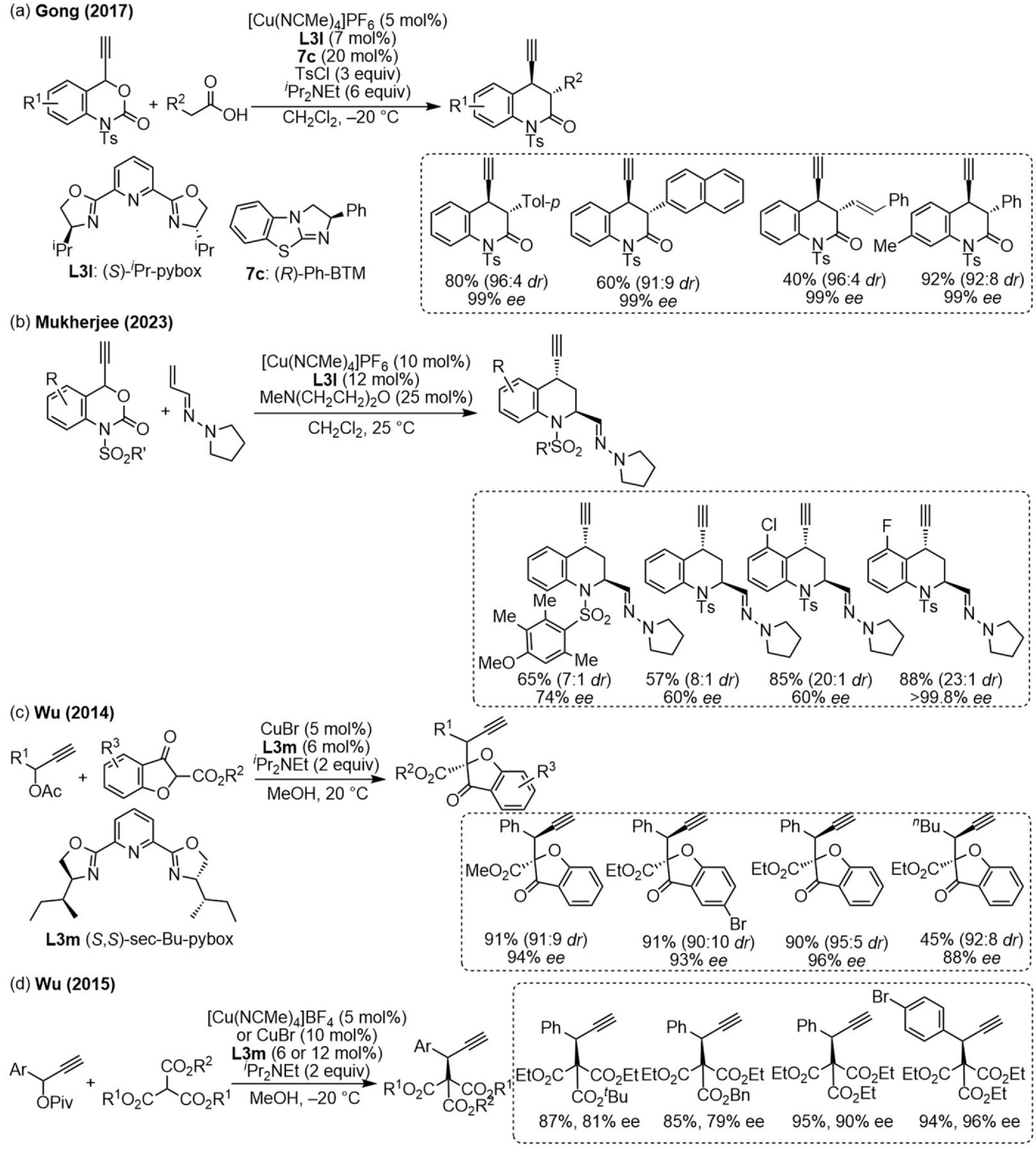

Fig. 24. (a) Cu/^{i}Pr-pybox- and BTM-catalyzed diastereo- and enantioselective decarboxylative ring-opening [4 + 2] annulation of cyclic propargylic carbamates with aryl or allylic acetonitriles. (b) Cu/^{i}Pr-pybox-catalyzed diastereo- and enantioselective decarboxylative ring-opening [4 + 2] annulation of cyclic propargylic carbamates with vinylogous aza-enamines. (c) Cu/*sec*-Bu-pybox-catalyzed diastereo- and enantioselective propargylation of benzofuranones. (d) Cu/*sec*-Bu-pybox-catalyzed enantioselective propargylic substitution reaction of propargylic esters with trialkyl methanetricarboxylates.

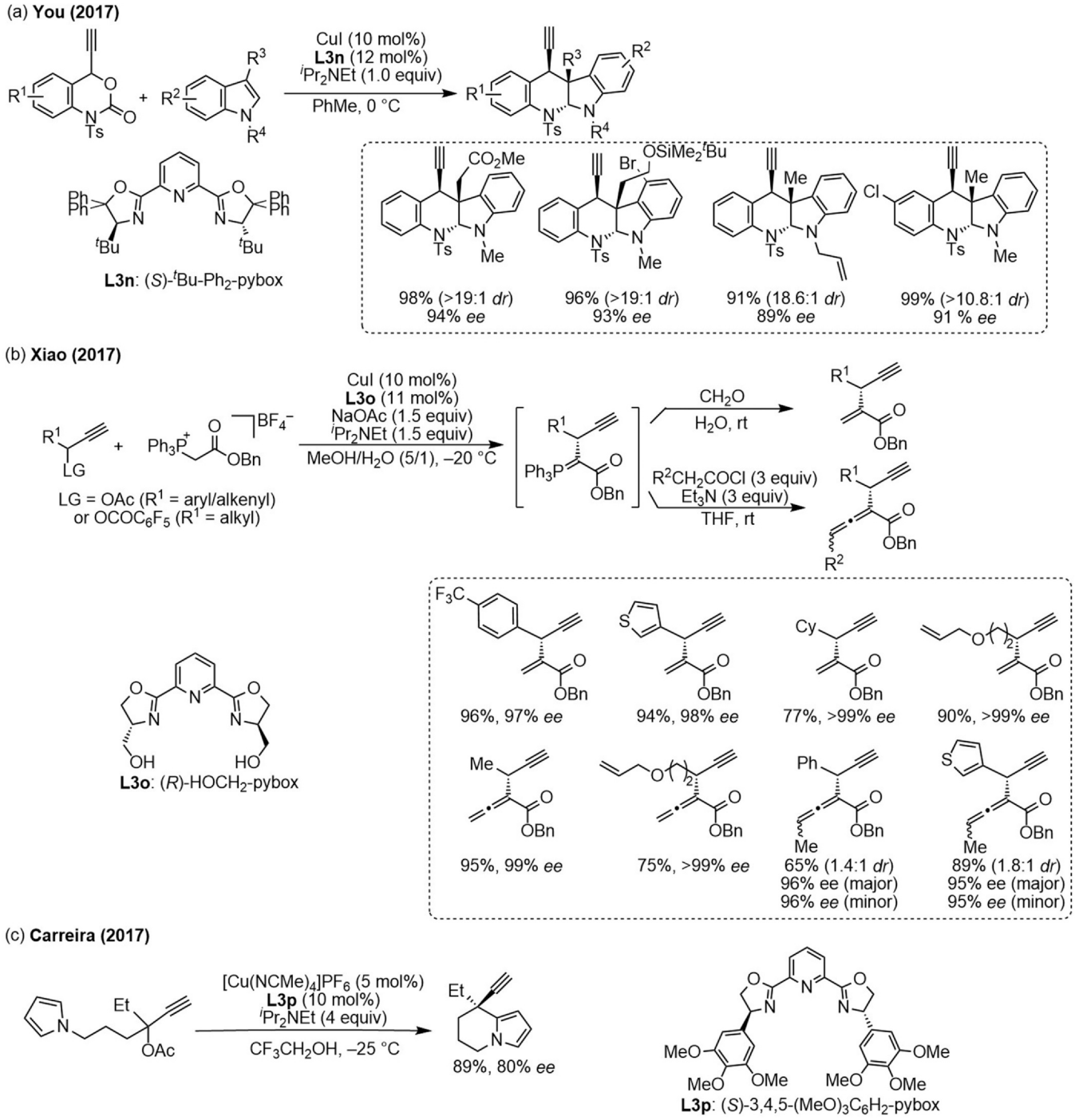

Fig. 25. (a) Cu/^{t}Bu-Ph$_2$-pybox-catalyzed diastereo- and enantioselective decarboxylative ring-opening [4 + 2] annulation of cyclic propargylic carbamates with indoles. (b) Cu/HOCH$_2$-pybox-catalyzed enantioselective propargylic substitution reaction of propargylic esters with stable phosphine ylides, followed by the Wittig reaction with in situ-generated ketenes. (c) Cu/3,4,5-(MeO)$_3$C$_6$H$_2$-pybox-catalyzed enantioselective intramolecular propargylic substitution reaction of a propargylic ester.

Here, $ZnEt_2$ or $Ti(O^iPr)_4$ works as a Lewis acidic oxophilic base likely preferentially binding to 5*H*-thiazol-4-ones or 5*H*-oxazol-4-ones to increase their nucleophilicity. The same combination of catalysts was utilized by C.-J. Wang and co-workers for enantioselective propargylic alkylation of propargylic carbonates with salicylaldehyde-derived imine esters to afford α-amino acid derivatives (Figure 26c) [124].

Combination of $[Cu(NCMe)_4]BF_4$, (*S*)-^{t}Bu-pybox (**L3s**), and (*R*,*R*)-Takemoto urea organocatalyst ((*R*,*R*)-**9a**) [125] as a set of catalysts was applied by Mukherjee and co-workers to diastereo- and enantioselective decarboxylative ring-opening propargylic [4 + 2] annulation of cyclic propargylic carbamates bearing sulfonate substituents with azalactones to afford 3,4-dihydroquinolin-2-one derivatives containing an α-

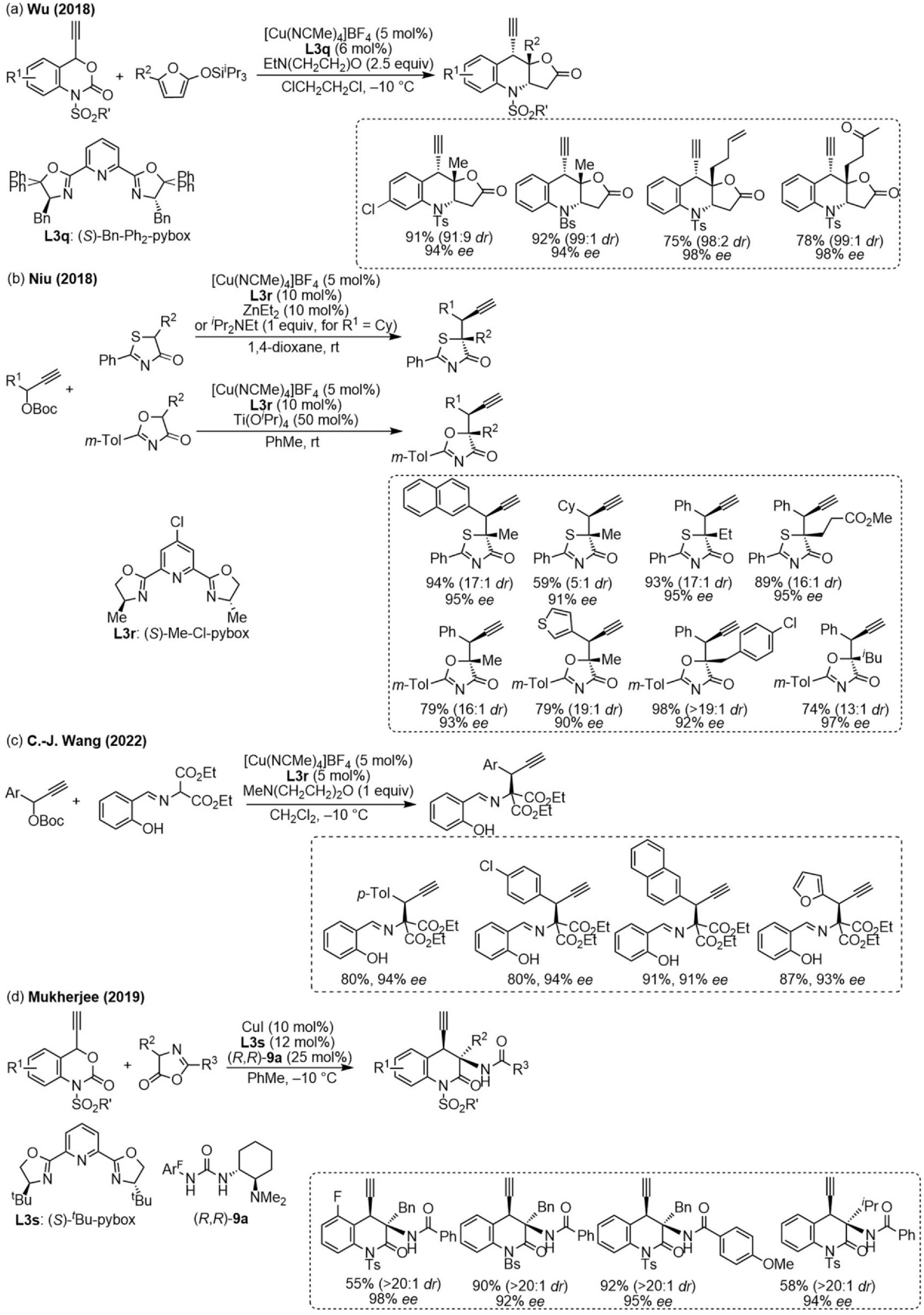

Fig. 26. (a) Cu/Bn-Ph_2-pybox-catalyzed diastereo- and enantioselective decarboxylative ring-opening [4 + 2] annulation of cyclic propargylic carbamates with 2-siloxyfurans. (b) Cu/Me-Cl-pybox- and Zn or Ti-catalyzed diastereo- and enantioselective propargylation of 5*H*-thiazol-4-ones or 5*H*-oxazol-4-ones. (c) Cu/Me-Cl-pybox-catalzyed enantioselective propargylic alkylation of propargylic carbonates with salicylaldehyde-derived imine esters. (d) Cu/^{t}Bu-pybox- and urea-catalyzed diastereo- and enantioselective decarboxylative ring-opening propargylic [4 + 2] annulation of cyclic propargylic carbamates with azalactones.

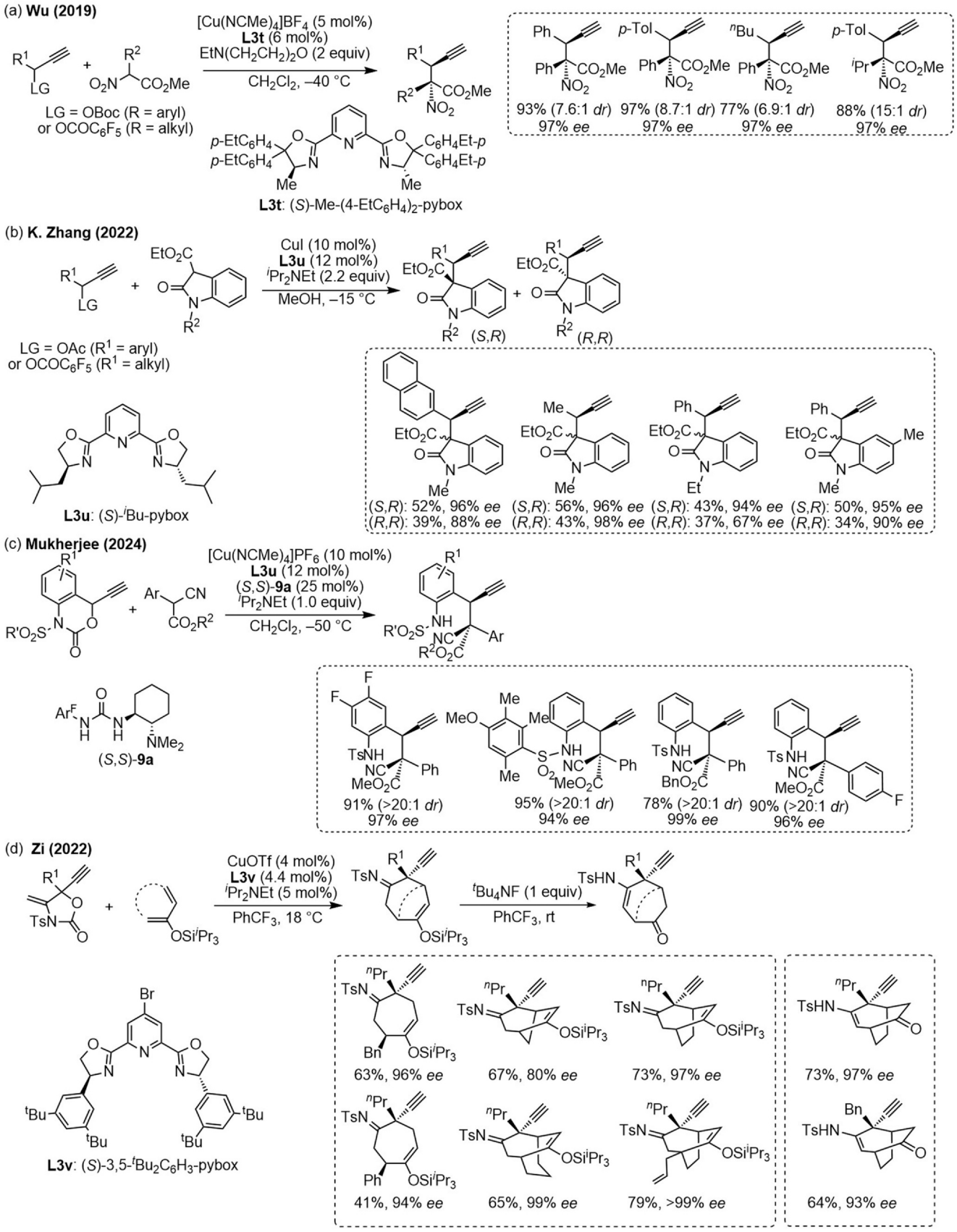

Fig. 27. (a) Cu/Me-(4-EtC$_6$H$_4$)$_2$-pybox-catalyzed diastereo- and enantioselective propargylic alkylation of propargylic esters or carbonates with nitroacetates. (b) Cu/^{i}Bu-pybox-catalyzed enantioselective propargylation of 2-oxindole-3-carboxylate esters. (c) Cu/^{i}Bu-pybox- and urea-catalyzed diastereo- and enantioselective decarboxylative ring-opening propargylic alkylation of cyclic propargylic carbamates with α-cyanoacetates. (d) Cu/3,5-^{t}Bu$_2$C$_6$H$_3$-pybox-catalyzed enantioselective decarboxylative ring-opening propargylic [3 + 2] annulation of cyclic propargylic 4-methylene carbamates with dienol silyl ethers.

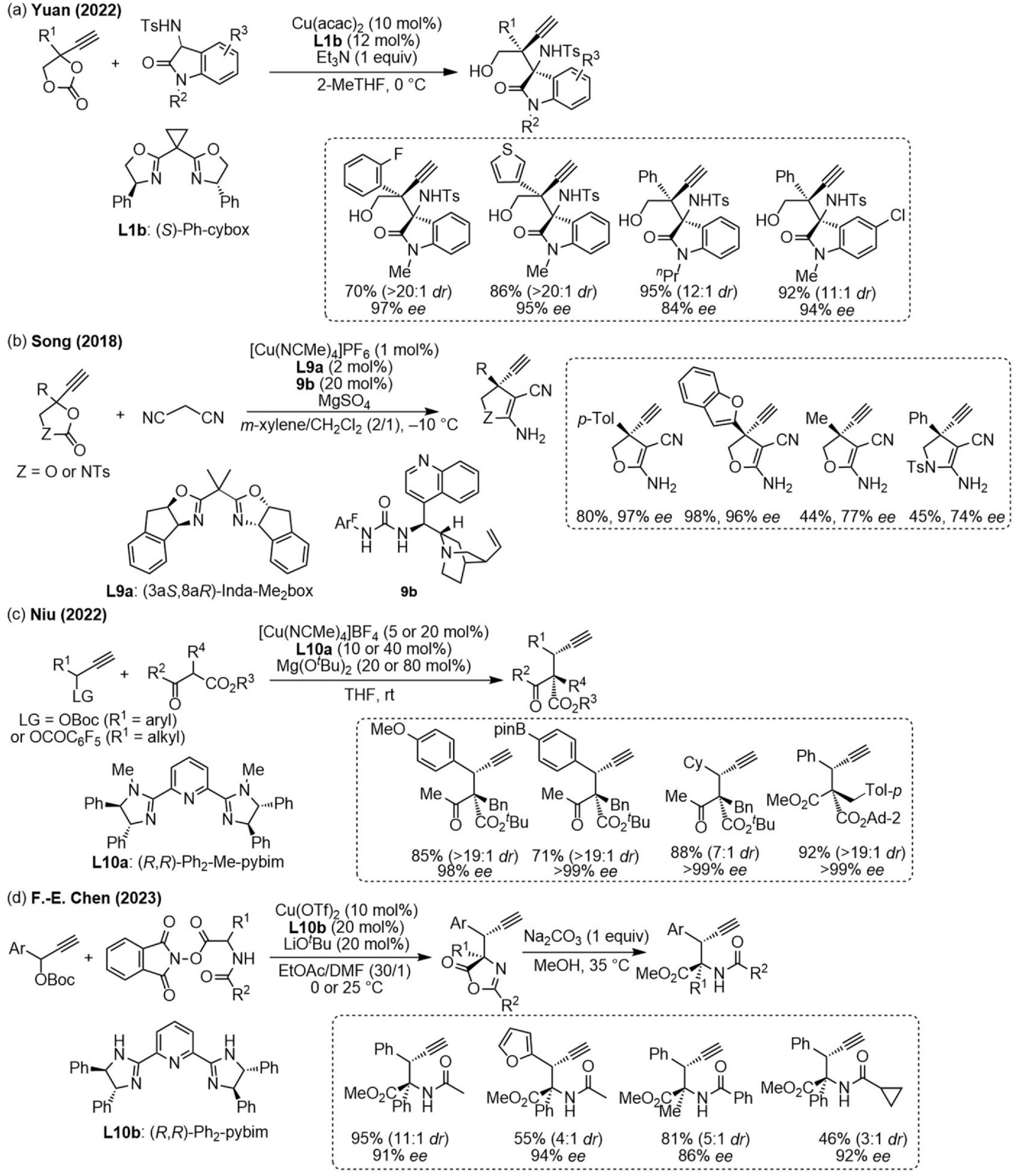

Fig. 28. (a) Cu/Ph-cybox-catalyzed regio- and enantioselective decarboxylative ring-opening propargylation of 3-amino oxindoles. (b) Cu/Inda-Me_2box- and urea-catalyzed enantioselective decarboxylative ring-opening [3 + 2] annulation of cyclic propargylic carbonates or carbamate with malononitrile. (c) Cu/Ph_2-Me-pybim- and Mg-catalyzed regio- and enantioselective propargylic alkylation of propargylic carbonates or esters with β-keto esters. (d) Cu/Ph_2-pybim- and Li-catalyzed regio- and enantioselective propargylic alkylation of propargylic carbonates with *N*-acyl phenylglycine *N*-hydroxyphthalimide esters.

quaternary α-acylaminoamide substituent at the propargylic position (Fig. 26d) [126].

(*S*)-Me-(4-EtC_6H_4)$_2$-pybox (**L3t**) was employed by Wu and co-workers as a chiral ligand in combination with [Cu(NCMe)$_4$]BF_4 to catalyze diastereo- and enantioselective propargylic substitution reaction of propargylic esters or carbonates with nitroacetates to afford propargylic alkylated products containing an α-quaternary α-amino acid substituent at the propargylic position (Fig. 27a) [127].

Combination of CuI and (*S*)-^{i}Bu-pybox (**L3u**) was employed by K. Zhang and co-workers for enantioselective propargylation of 2-oxindole-3-carboxylate esters (Fig. 27b) [128]. On the other hand, combination of [Cu(NCMe)$_4$]PF_6, **L3u**, and (*S*,*S*)-Takemoto urea organocatalyst ((*S*,*S*)-**9a**) [125] as a set of catalysts was applied by Mukherjee and a co-worker to diastereo- and enantioselective decarboxylative ring-opening propargylic alkylation of cyclic propargylic carbamates with α-cyanoacetates to afford acyclic α-propargylic cyanocarbonyls (Figure 27c) [129]. Here, (*S*,*S*)-**9a** activates the nucleophilicity of α-cyanoacetate through the hydrogen bonding interaction, and also controls enantioselectivity to react with the in situ-formed Cu–allenylidene complex. Zi and co-workers demonstrated enantioselective decarboxylative ring-opening propargylic [3 + 2] annulation of cyclic propargylic 4-methylene carbamates with dienol silyl

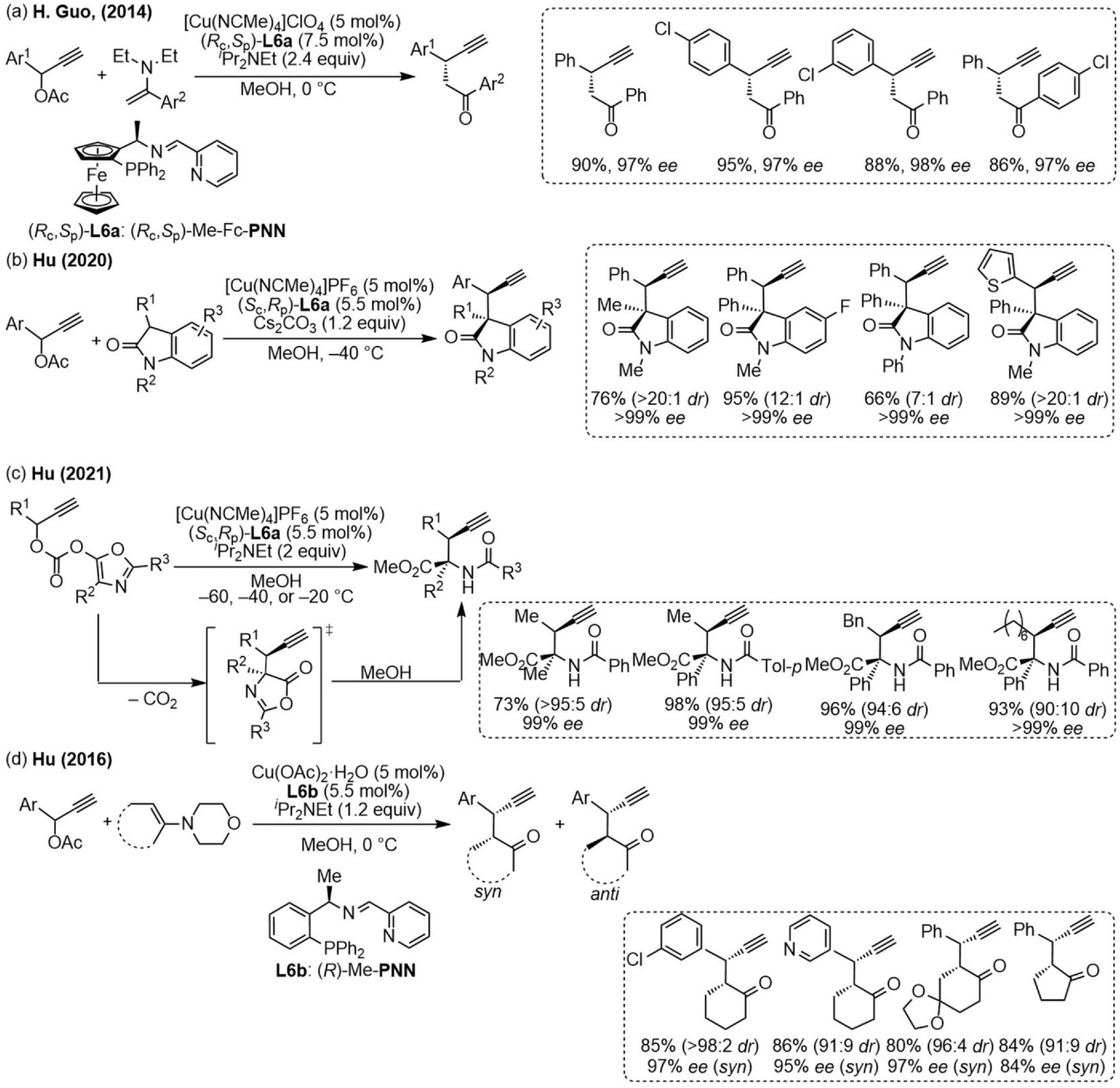

Fig. 29. (a) Cu/Me-Fc-**PNN**-catalyzed enantioselective propargylic alkylation of propargylic esters with enamines, (b) Cu/Me-Fc-**PNN**-catalyzed diastereo- and enantioselective propargylation of oxindoles. (c) Cu/Me-Fc-**PNN**-catalyzed regio- and enantioselective decarboxylative intramolecular propargylic alkylation of enol carbonates. (d) Cu/Me-**PNN**-catalyzed diastereo- and enantioselective propargylic alkylation of propargylic esters with cyclic enamines.

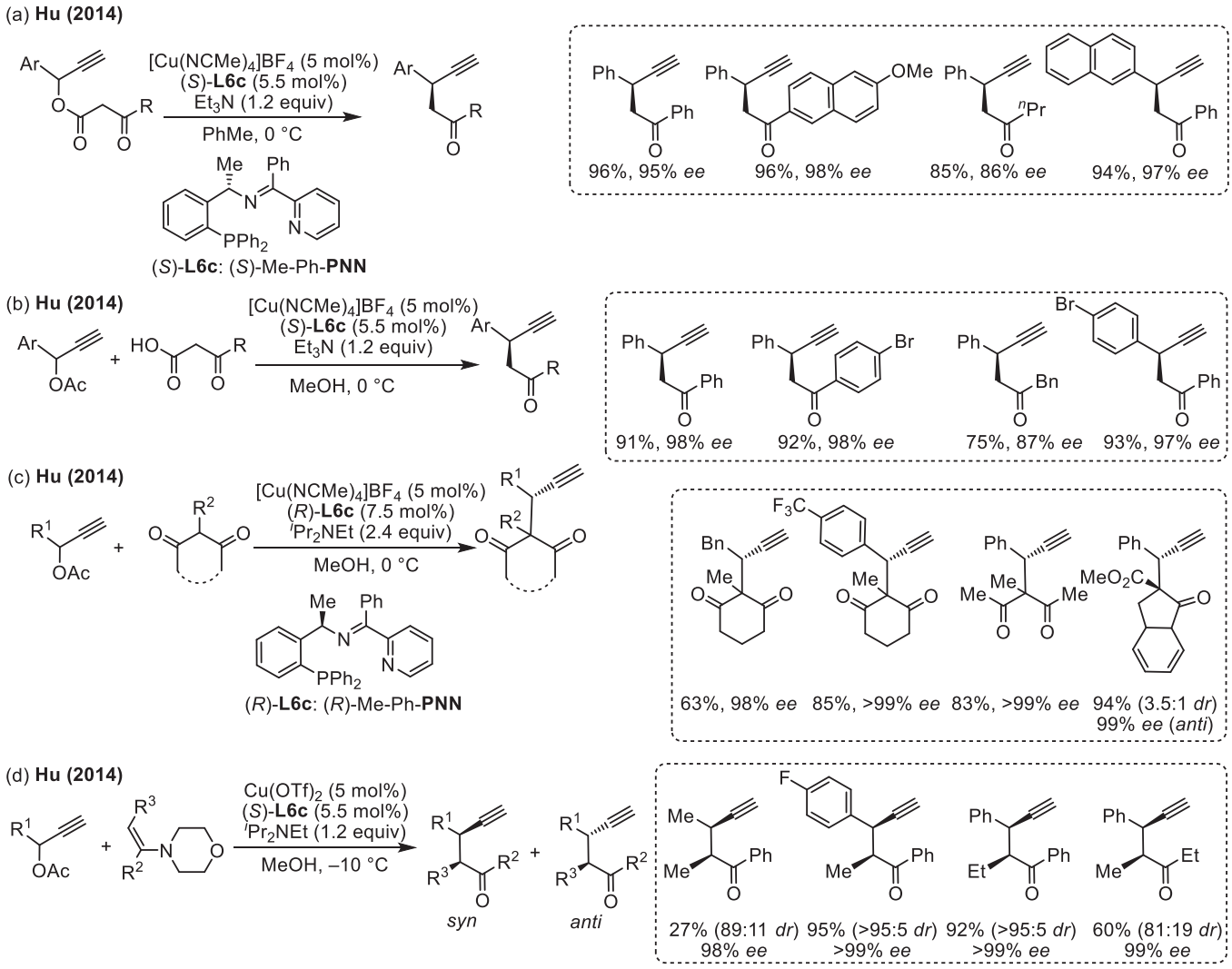

Fig. 30. (a) Cu/Me-Ph-**PNN**-catalyzed enantioselective decarboxylative intramolecular propargylic alkylation of propargyl β-ketoesters. (b) Cu/Me-Ph-**PNN**-catalyzed decarboxylative propargylic alkylation of propargylic esters with β-keto acids. (c) Cu/Me-Ph-**PNN**-catalyzed enantioselective propargylic alkylation of propargylic esters with 1,3-dicarobnyl compounds. (d) Cu/Me-Ph-**PNN**-catalyzed diastereo- and enantioselective propargylic alkylation of propargylic esters with cyclic enamines.

ethers to afford cycloheptanoids by using the combination of CuOTf and (*S*)-3,5-^{t}Bu$_2$C$_6$H$_3$-pybox (**L3v**) as a pair of catalysts (Fig. 27d) [130].

A C_2-symmetric chiral 2,2′-cyclopropylidene-bridged bis(oxazoline) ligand (*S*)-Ph-cybox (**L1b**) [55] has been recently applied as a chiral ligand by Yuan and co-workers together with Cu(acac)$_2$ to regio- and enantioselective decarboxylative ring-opening propargylation of 3-amino oxindoles to afford the desired alkylated products bearing two vicinal quaternary stereogenic *C* centers (Fig. 28a) [131].

Another C_2-symmetric chiral 1,1-dimethylmethylene-bridged bisoxazoline ligand (3a*S*,8a*R*)-Inda-Me$_2$box (**L9a**) [55] was also examined by Song and co-workers in combination with [Cu(NCMe)$_4$]PF$_6$ and a cinchona urea-derived organocatalyst (**9b**) [119] to catalyze enantioselective decarboxylative ring-opening [3 + 2] annulation of cyclic propargylic carbonates (or carbamate) with malononitrile to afford 2-amino-3-cyano-dihydrofurans (or pyrrole) bearing a quaternary stereogenic *C* center at the propargylic position (Fig. 28b) [132]. Here, **9b** reacts with malononitrile to activate as a nucleophile as well as to control enantioselectivity to react with the in situ-formed Cu–allenylidene complex derived from [Cu(NCMe)$_4$]PF$_6$, **L9a**, and a cyclic propargylic carbonate or carbamate via decarboxylative process.

Chiral pyridine-2,6-bis(imidazoline) (pybim) ligands [66] have been also now available for Cu-catalyzed enantioselective propargylic substitution reactions. For example, Niu and co-workers demonstrated regio- and enantioselective propargylic alkylation of propargylic carbonates or esters with β-keto esters to afford the alkylated products bearing two vicinal quaternary stereogenic *C* centers by using the combination of [Cu(NCMe)$_4$]BF$_4$, (*R*,*R*)-Ph$_2$-Me-pybim (**L10a**), and Mg(O^{t}Bu)$_2$ as a set of catalysts (Fig. 28c, 2-Ad = 2-adamantyl) [133]. Here, Mg(O^{t}Bu)$_2$ is bound to β-keto ester moiety to activate its nucleophilicity. Similarly, F.-E. Chen and co-workers demonstrated regio- and enantioselective propargylic alkylation of propargylic carbonates with *N*-acyl phenylglycine *N*-hydroxyphthalimide esters to afford propargylic alkylated products

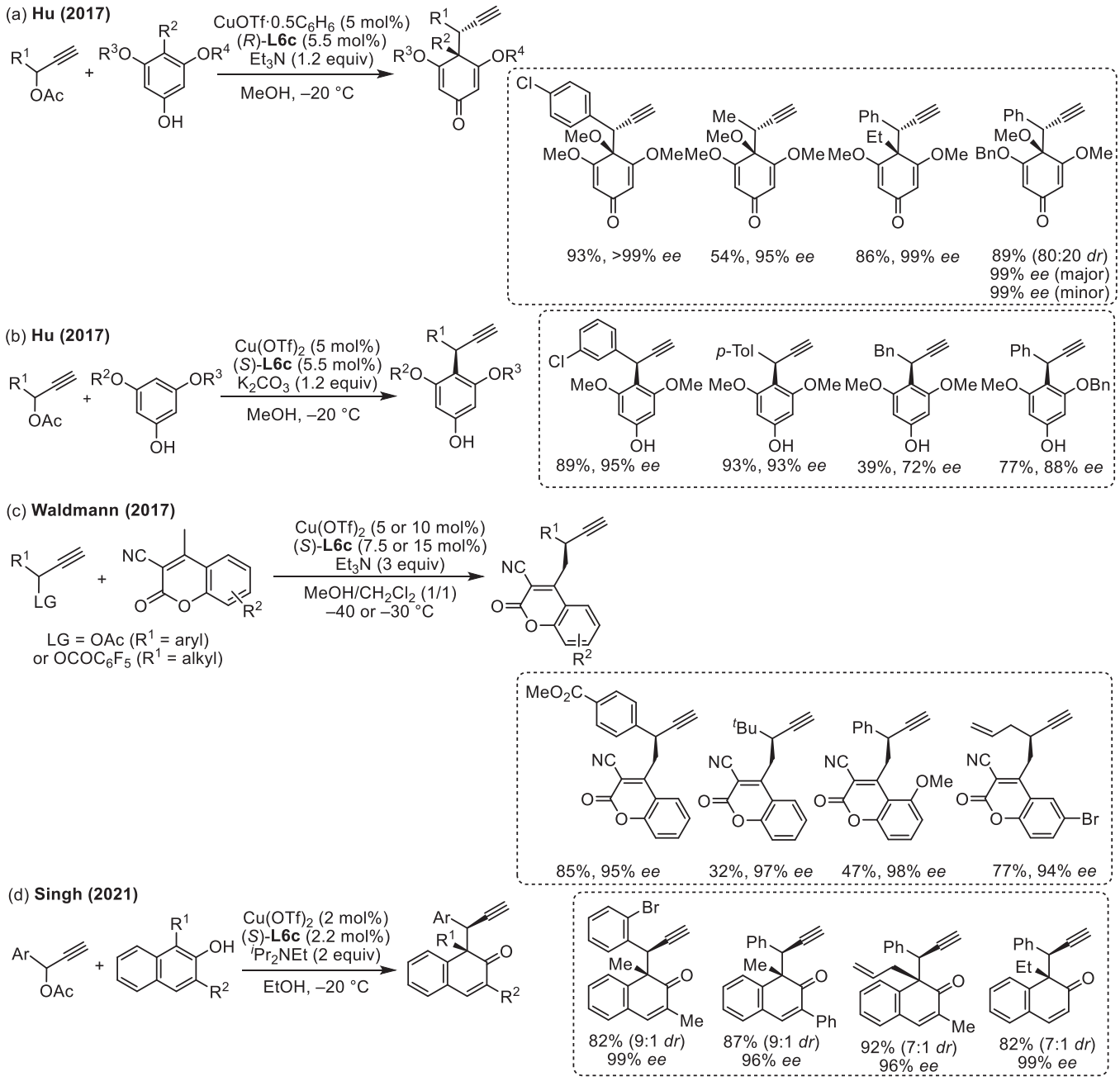

Fig. 31. (a) Cu/Me-Ph-**PNN**-catalyzed diastereo- and enantioselective propargylic dearomatization of phenol derivatives. (b) Cu/Me-Ph-**PNN**-catalyzed enantioselective Friedel-Crafts propargylic alkylation of phenol derivatives. (c) Cu/Me-Ph-**PNN**-catalyzed enantioselective vinylogous propargylation of coumarins. (d) Cu/Me-Ph-**PNN**-catalyzed diastereo- and enantioselective propargylic dearomatization of 2-naphthol derivatives.

containing an α-quaternary α-amino acid substituent at the propargylic position by using the combination of $Cu(OTf)_2$, (*R*,*R*)-Ph_2-pybim (**L10b**), and LiO^tBu as a set of catalysts (Fig. 28d) [134].

Several chiral tridentate ketimine P,N,N-type ligands [67] are also available as chiral catalysts for Cu-catalyzed enantioselective propargylic C–C bond formation. For example, H. Guo and co-workers utilized the combination of (R_c,S_p)-Me-Fc-**PNN** ((R_c,S_p)-**L6a**) as a pair of catalysts for enantioselective propargylic alkylation of propargylic esters with enamines to afford the propargylic alkylated products (Fig. 29a) [135]. Similar catalyst pair was used by Hu and a co-worker for diastereo- and enantioselective propargylation of oxindoles to afford the desired products containing two vicinal quaternary stereogenic *C* centers (Fig. 29b) [136]. Hu and co-workers also demonstrated regio- and enantioselective decarboxylative intramolecular propargylic alkylation of enol carbonates to afford the propargylic alkylated products containing an α-quaternary α-amino acid substituent at the propargylic position via the alcoholysis of intermediary azalactones by using the combination of $[Cu(NCMe)_4]PF_6$ and (S_c,R_p)-**L6a** as a pair of catalysts (Fig. 29c) [137], whereas **L6b** ((*R*)-

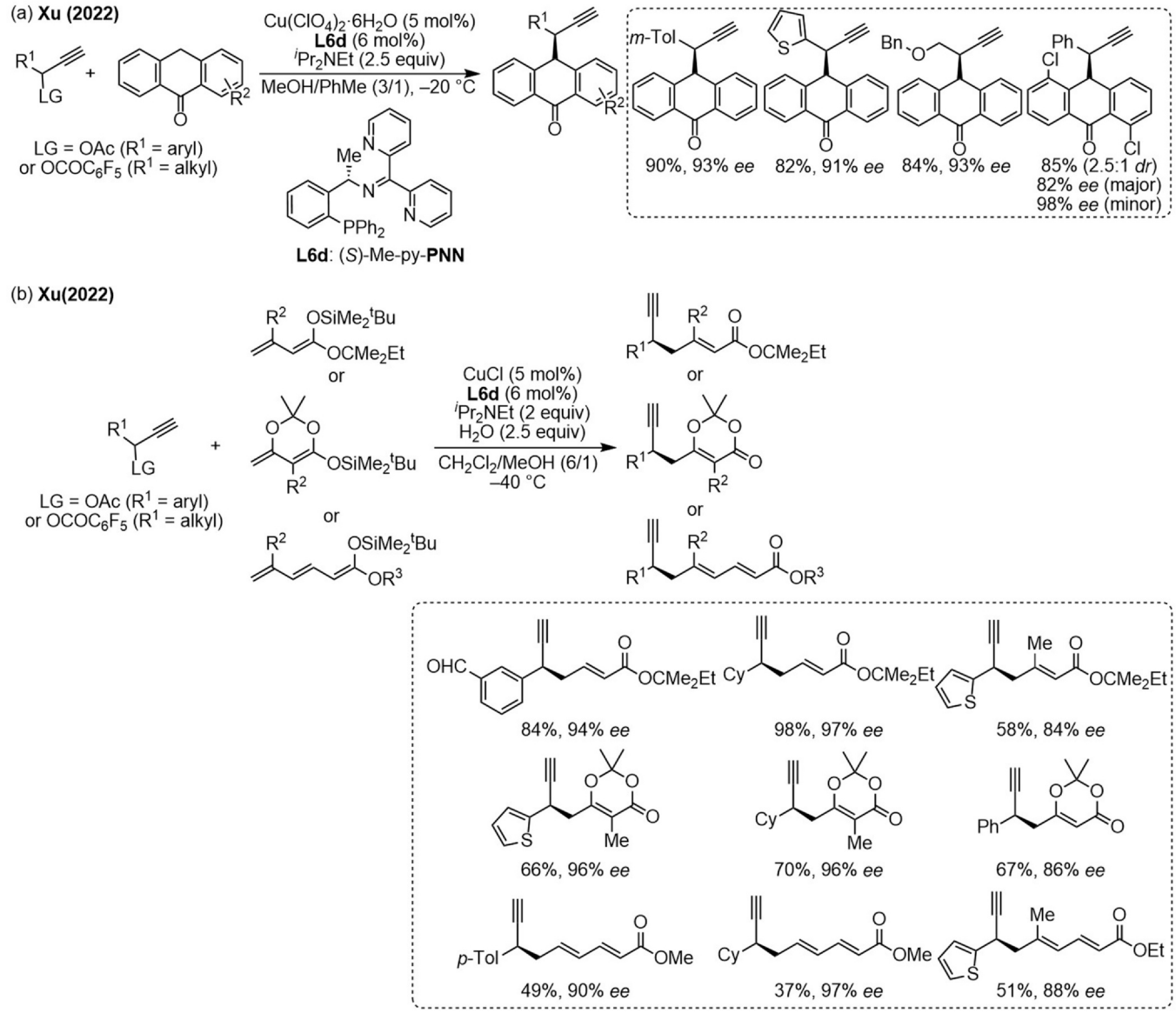

Fig. 32. (a) Cu/Me-py-**PNN**-catalyzed enantioselective propargylic substitution reaction of propargylic esters or carbonates with anthorones. (b) Cu/Me-py-**PNN**-catalyzed regio- and enantioselective vinylogous and bisvinylogous propargylic substitution reaction of propargylic esters or carbonates with silyl ketene acetals.

Me-**PNN**) was utilized in combination with $Cu(OAc)_2{\cdot}H_2O$ for diastereo- and enantioselective propargylic alkylation of propargylic esters with morpholine-derived cyclic enamines (Fig. 29d) [138].

Hu and co-workers have utilized (*R*)-Me-Ph-**PNN** ((*R*)-**L6c**) or (*S*)-**L6c** for several enantioselective propargylic C–C bond formation [139–144]. Enantioselective formation of β-ethynyl ketones was achieved by decarboxylative intramolecular propargylic alkylation of propargyl β-ketoesters (Fig. 30a) [139] or decarboxylative propargylic alkylation of propargylic esters with β-keto acids (Fig. 30b) [140]. Enantioselective propargylic alkylation of propargylic esters with 1,3-dicarobnyl compounds (Fig. 30c) [141] and diastereo- and enantioselective propargylic alkylation of propargylic esters with morpholine-derived cyclic enamines (Fig. 30d) [142] were also achieved.

Hu and a co-worker used the combination $CuOTf{\cdot}0.5C_6H_6$ and (*R*)-**L6c** for diastereo- and enantioselective propargylic dearomatization of phenol derivatives (Fig. 31a) [143], or the combination of $Cu(OTf)_2$ and (*S*)-**L6c** for enantioselective Friedel-Crafts propargylic alkylation of phenol derivatives (Fig. 31b) [144]. The same catalysts pair was utilized by Waldmann and co-workers for enantioselective vinylogous propargylation of coumarins (Fig. 31c) [145], while Singh and co-workers demonstrated diastereo- and enantioselective propargylic dearomatization of 2-naphthol derivatives (Fig. 31d) [146].

Xu and co-workers utilized the combination of $Cu(ClO_4)_2{\cdot}6H_2O$ and **L6d** ((*S*)-Me-py-**PNN**) as a pair of catalysts for enantioselective propargylic substitution reaction of propargylic esters or carbonates with anthorones (Fig. 32a) [147]. Using similar catalyst pairs, regio- and

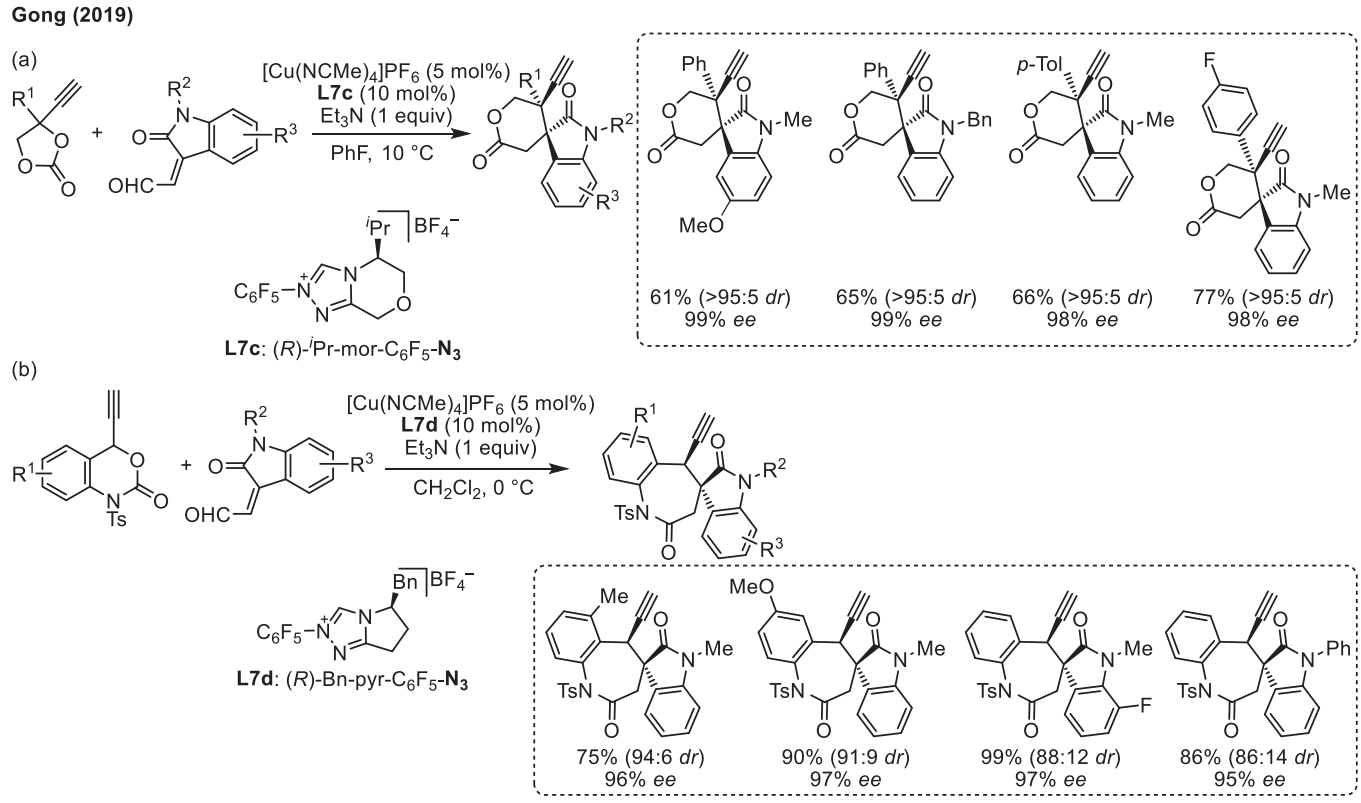

Fig. 33. (a) Cu/NHC-catalyzed diastereo- and enantioselective decarboxylative ring-opening [3 + 3] annulation of cyclic propargylic carbonates with isatin-derived enals. (b) Cu/NHC-catalyzed diastereo- and enantioselective decarboxylative ring-opening [4 + 3] annulation of cyclic propargylic carbamates with isatin-derived enals.

enantioselective vinylogous and bisvinylogous propargylic substitution reaction of propargylic esters or carbonates with silyl ketene acetals has been also achieved (Fig. 32b) [148].

Precursors of NHC ligands [68] was also found to be effective for Cu-catalyzed enantioselective propargylic C–N bond formation by Gong and co-workers, who reported diastereo- and enantioselective decarboxylative ring-opening [3 + 3] or [4 + 3] annulation of cyclic propargylic carbonates or cyclic propargylic carbamates with isatin-derived enals using the combination of $[Cu(NCMe)_4]PF_6$ and morpholine- or pyrrolidine-based triazolium salt, (*R*)-^{i}Pr-C_6F_5-mor-**N_3** (**L7c**) or (*R*)-Bn-pyr-C_6F_5-**N_3** (**L7d**) as a pair of catalysts, respectively, to afford spirooxindoles bearing two vicinal quaternary stereogenic *C* centers (Fig. 33a and b) [149].

Combination of $[Cu(NCMe)_4]BF_4$ and diphenylethylenediamine (dpen) bearing bulky sulfonyl substituent (*S*,*S*)-2,6-(*p*-^{t}BuC_6H_4)$_2C_6H_3SO_2$-dpen (**L11**) was utilized by F.-E. Chen and co-workers for diastereo- and enantioselective decarboxylative ring-opening [3 + 2] annulation of cyclic propargylic carbonates with indanone carboxylates to afford indanone-based spirolactones bearing two vicinal quaternary stereogenic *C* centers (Fig. 34a) [150].

X. Wang and co-workers, who isolated well-defined dicopper complex **5b** (Fig. 16c) [95], also reported Cu-catalysed enantioselective propargylic alkylation of propargylic carbonate with 1,3-diketones, or enantioselective propargylation of indole (Fig. 34b) [95].

3.3. *Cu-catalyzed enantioselective propargylic C–O bond formation*

Catalytic propargylic etherification of propargylic esters was first achieved in 1994 by using $CuCl_2{\cdot}H_2O$ as a catalyst (Fig. 1c) [8], whereas catalytic enantioselective propargylic etherification of propargylic esters with alcohols was first achieved in 2015 by Nishibayashi and co-workers, who used the combination of $CuOTf{\cdot}0.5H_2O$ and (*S*)-**L3b** (Me-pybox)as a pair of catalyst (Fig. 35a) [151].

On the other hand, Niu and co-workers utilized the combination of $[Cu(NCMe)_4]PF_6$, (*S*)-**L3b**, and dibenzo-1,4-oxaborine-derived borinic acid **8** [113] as a set of catalysts for enantioselective propargylic etherification of propargylic carbonates with diols (Fig. 35b) [152]. It must be noteworthy that this set of catalysts can be applied to regioselective *O*-propargylation of carbohydrates (Fig. 35c) [153]. For example, changing the chiral ligand between (*S*)-**L3b** and (*R*)-Me-pybox ((*R*)-**L3b**) can affect the regioselectivity of *O*-propargylation of a mannose derivative toward the formation of 3-*O* and 2-*O* isomers.

Nishibayashi and co-workers also used the combination of $CuOTf{\cdot}0.5H_2O$, (*S*)-**L3c**, (Ph-pybox) and a borinic acid **8** as a set of catalysts for enantioselective propargylic etherification of propargylic carbonates with

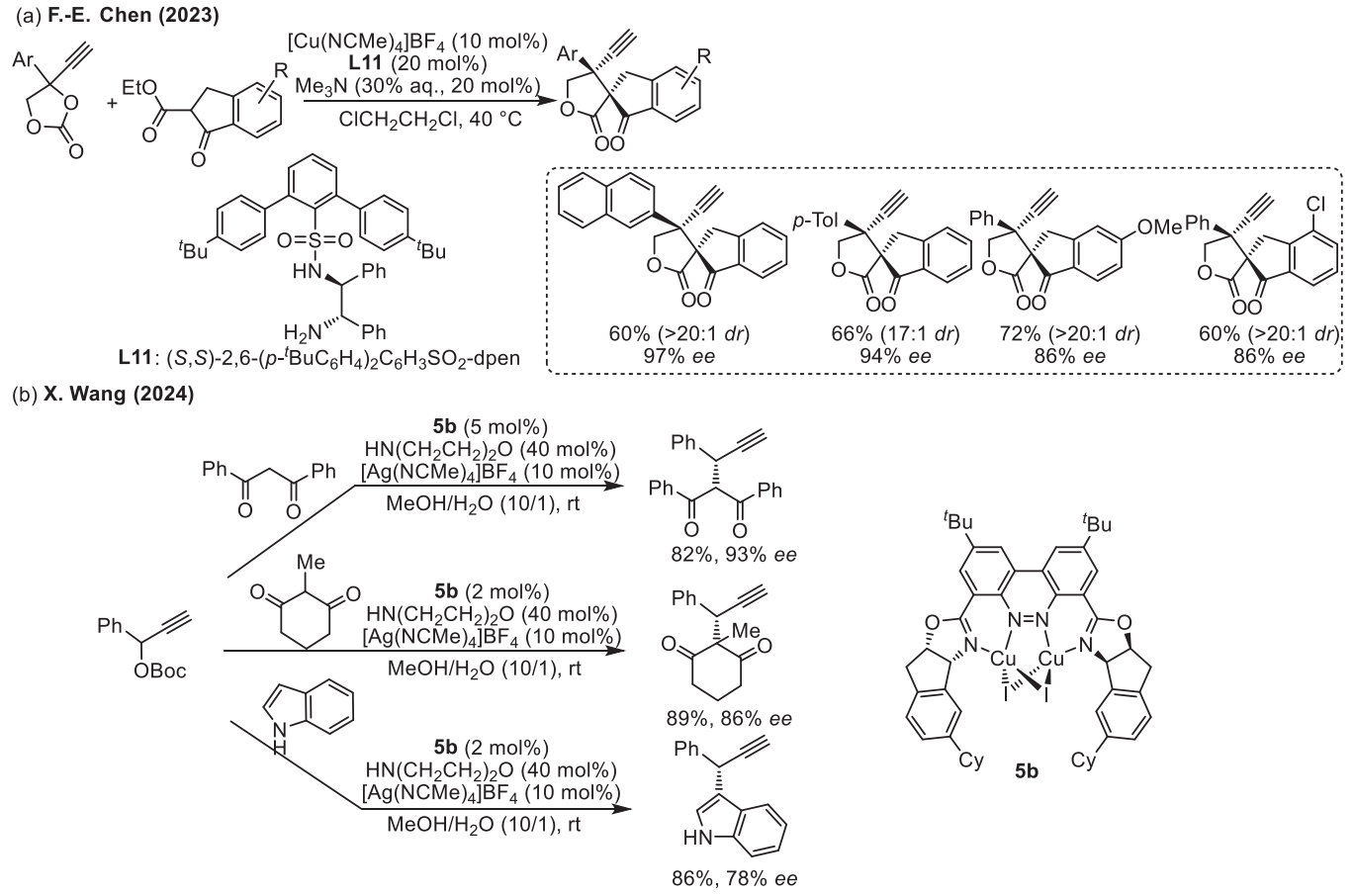

Fig. 34. (a) Cu/dpen-catalyzed diastereo- and enantioselective decarboxylative ring-opening [3 + 2] annulation of cyclic propargylic carbonates with indanone carboxylates. (b) Cu-catalyzed enantioselective propargylic alkylation of propargylic carbonate with 1,3-diketones, or enantioselective propargylation of indole.

benzylic alcohols (Fig. 36a) [154] or enantioselective intramolecular etherification of propargylic esters to afford chiral isochromans (Fig. 36b) [155].

Combination of CuTC and **L3s** (^{t}Bu-pybox) was employed by Tang and co-workers as a pair of catalysts for enantioselective trifluoromethoxylation of propargylic sulfonates with CF_3OTs (Fig. 36c) [156]. He and co-workers have also examined the combination of Cu$(OTf)_2$·0.5PhMe, (*S*)-Ph-Br-pybox (**L3w**), and a borinic acid **8** as a set of catalysts for regio- and enantioselective alkynylallylic etherification of 1,4-enyne bearing a leaving group remote from the alkyne moiety with benzyl alcohol to afford alkynylallylic etherified product (Fig. 36d) [82]. Niu and co-workers utilized the combination of $[Cu(NCMe)_4]BF_4$, (*R*)-$AcOCH_2$-pybox (**L3x**) as a pair of catalysts for enantioselective propargylic etherification of propargylic carbonates with secondary aliphatic alcohols. (Fig. 36e) [157].

(*S*)-**L6c** (Me-Ph-**PNN**) was utilized by Hu and co-workers in combination with CuOTf·0.5C_6H_6 for enantioselective propargylic etherification of propargylic esters with phenols (Fig. 37a) [158], or enantioselective propargylic etherification of propargylic esters with oximes (Fig. 37b) [159]. Similar pair of catalysts was utilized by Singh and co-workers for enantioselective propargylic etherification of propargylic esters with 2-naphthol derivatives (Fig. 37c) [146].

X. Wang and co-workers, who isolated well-defined dicopper complex **5a** (Fig. 16b) [95], also reported **5a**-catalyed enantioselective propargylic etherification of propargylic carbonate with 4-bromophenol (Fig. 37d) [95].

3.4. *Cu-catalyzed enantioselective propargylic C–S bond formation*

Catalytic enantioselective propargylic C–S bond formation was reported by Cordier and co-workers via the intramolecular *O*-to-*S* rearrangement of propargylic carbamothioate to afford propargylic thiocarbamate by using the combination of CuOTf·0.5C_6H_6 and (*R*)-**L4a** (BINAP) as a pair of catalysts, although this reaction was reported as a preliminary result (Fig. 38a) [160].

Enantioselective propargylic C–S bond formation was first reported in 2018 by Kleij and co-workers, who employed the combination of Cu$(OTf)_2$ and a C_2-symmetric chiral 1,1-dimethylmethylene-bridged bisoxazoline ligand (*R*)-Ph-Me_2box (**L9b**) as a pair of catalysts for

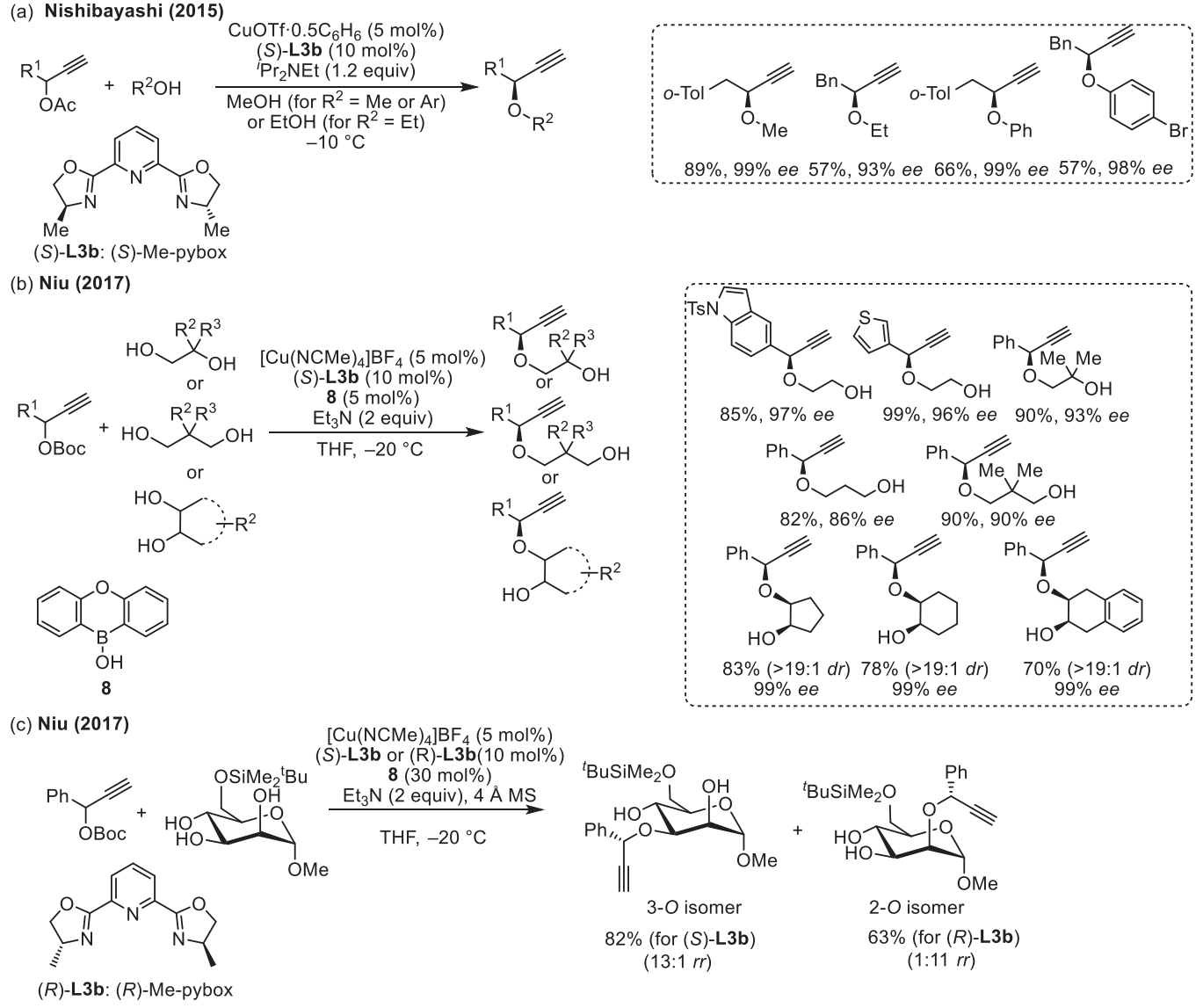

Fig. 35. (a) Cu/Me-pybox-catalyzed enantioselective propargylic etherification of propargylic esters with alcohols. (b) Cu/Me-pybox- and borinic acid-catalyzed (regio- and) enantioselective propargylic etherification of propargylic carbonates with diols (c) Cu/Me-pybox- and borinic acid-catalyzed regio- and enantioselective *O*-propargylation of carbohydrate.

enantioselective decarboxylative propargylic sulfination of cyclic propargylic carbonate with sodium sulfinate to afford propargylic sulfones bearing a quaternary stereogenic *C* center at the propargylic position (Fig. 38b) [161], which was also shown to be obtained by the direct propargylic sulfination of propargylic carbonates with sodium benzenesulfinate (Fig. 38c) [162],

More recently, X. Zhang and co-workers have succeeded in enantioselective propargylic trifluoromethylthiolation of secondary propargyl sulfonates with $AgSCF_3$ by using the combination of Cu $(OTf)_2$ and (*S*)-$PhCH_2CH_2$-pybox (**L3y**) as a pair of catalysts (Fig. 38d) [163].

Enantioselective propargylic *O*-to-*S* rearrangement of propargylic xanthates has been also reported very recently by Cheng and co-workers by using the combination of CuTC and (S_c,S_p)-^{t}Pr-phosferrox (**L12**) as a pair of catalysts (Fig. 38e) [164].

4. Summary and perspectives

Three decades have passed since the first reports of catalytic propargylic substitution reactions of propargylic compounds [6–8], and almost two decades have passed since the first reports of enantioselective propargylic substitution reactions of propargylic compounds [15,16].

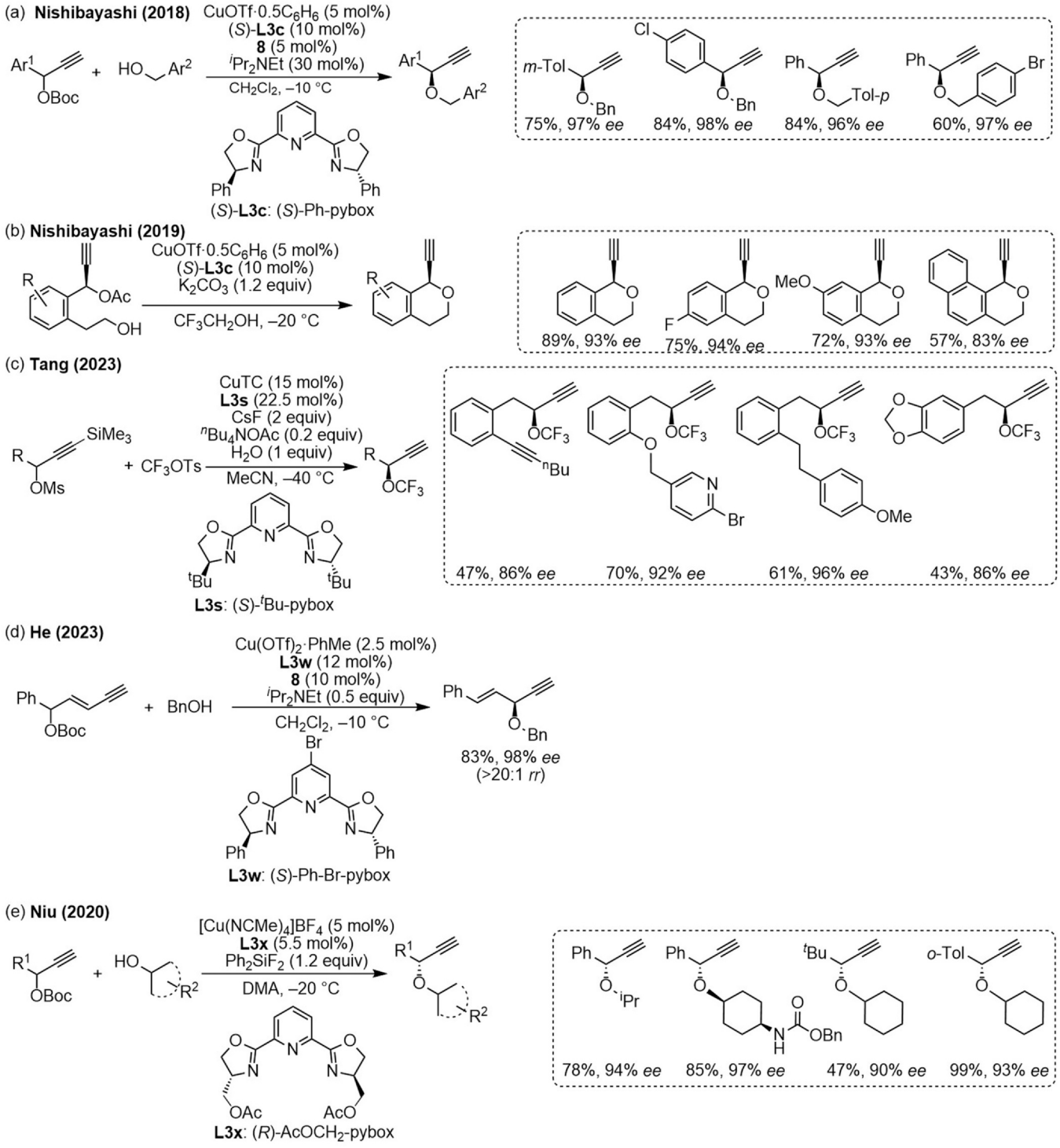

Fig. 36. (a) Cu/Ph-pybox- and borinic acid-catalyzed enantioselective propargylic etherification of propargylic carbonates with benzylic alcohols. (b) Cu/Ph-pybox-catalyzed enantioselective intramolecular etherification of propargylic esters. (c) Cu/^{t}Bu-pybox-catalyzed enantioselective trifluoromethoxylation of propargylic sulfonates with CF_3OTs. (d) Cu/Ph-Br-pybox- and borinic acid-catalyzed regio- and enantioselective alkynylallylic etherification of 1,4-enyne with benzyl alcohol. (e) Cu/$AcOCH_2$-pybox-catalyzed enantioselective propargylic etherification of propargylic carbonates with secondary aliphatic alcohols.

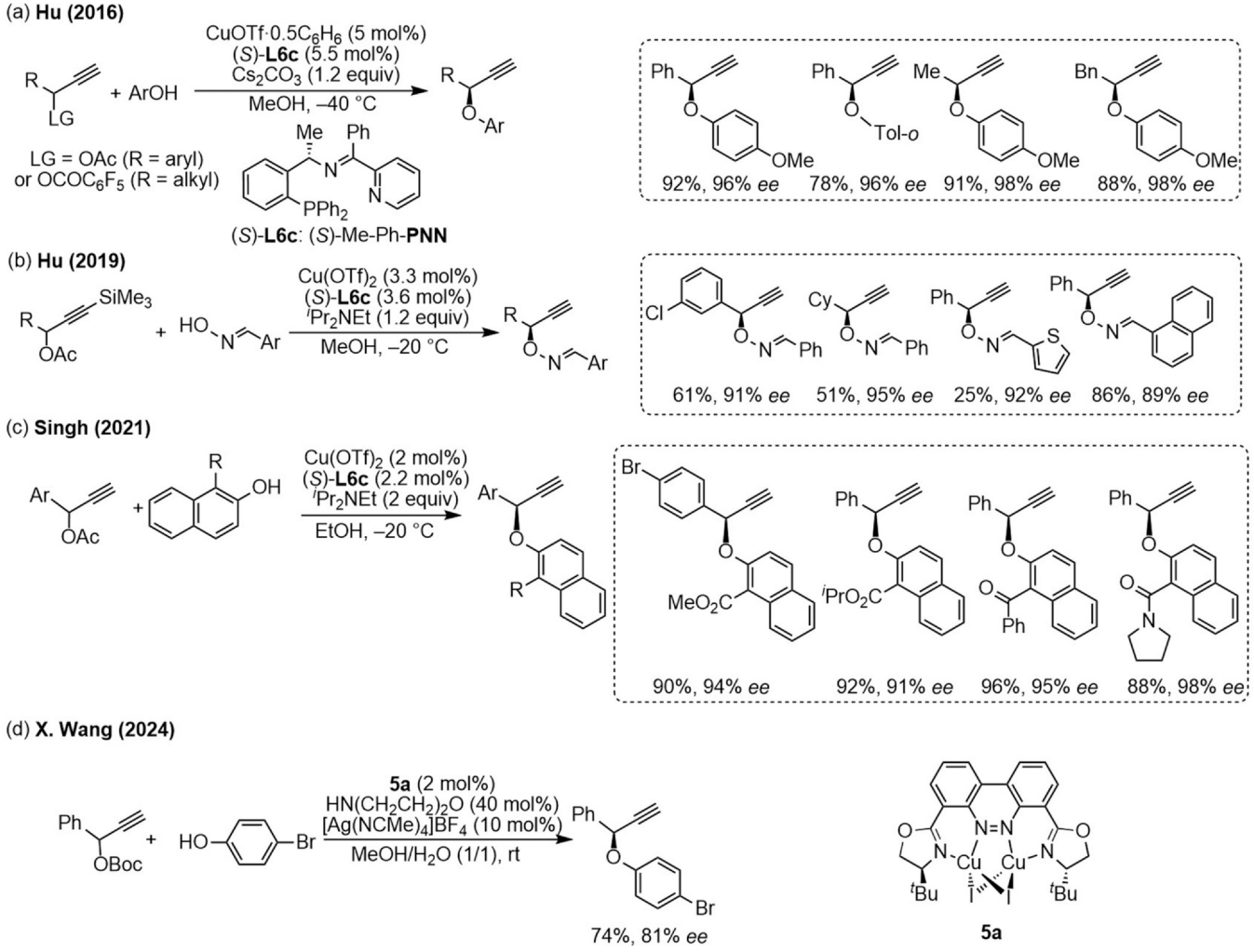

Fig. 37. (a) Cu/Me-Ph-**PNN**-catalyzed enantioselective propargylic etherification of propargylic esters with phenols. (b) Cu/Me-Ph-**PNN**-catalyzed enantioselective propargylic etherification of propargylic esters with oximes. (c) Cu/Me-Ph-**PNN**-catalyzed enantioselective propargylic etherification of propargylic esters with 2-naphthol derivatives. (d) Cu-catalyzed enantioselective propargylic etherification of propargylic carbonate with phenol derivative.

Here, the formation of allenylidene complexes has played key roles not only for accelerating catalyses by increasing electrophilicity at the propargylic position of the propargylic compounds but also for asymmetric induction. Since then, enantioselective propargylic substitution reactions via the formation of allenylidene complexes have been developed [17–20], including enantioselective C–C bond formation [15,16,96], C–N bond formation [60,62], C–O bond formation [151], C–S bond formation [160,161], and C–P bond formation [58] at the propargylic position. In addition, various enantioselective reactions containing functionalization or tandem cyclization of alkyne moiety have been developed [17,18,20], which are not summarized in this review.

On the other hand, transition metals that can furnish enantioselective catalytic propargylic substitution reactions via the formation of allenylidene complexes have been still limited to Ru and Cu [17–20], although many other transition metals and main group catalysts including organocatalysts have been shown to catalyze propargylic substitution reactions [9–13].

However, L. Zhang and co-workers have very recently reported Au-catalyzed propargylic amination of propargylic compounds by using alkynyl benziodoxoles as propargylic substrates. In this reaction, well-defined Au complexes bearing (*R*)-WangPhos (**L13**) as an auxiliary ligand [AuCl(**L13**)] (**10a**) and [Au(NTf_2)(L13)] (**10b**) have been prepared as catalysts (Fig. 39a, Ad = 1-adamantyl) [165,166]. As a preliminary result, enantioselective propargylic amination of alkynyl benziodoxole has been also examined, although its enantioselectivity has been reported to be poor (Fig. 39b) [166]. Anyway, allenylidene

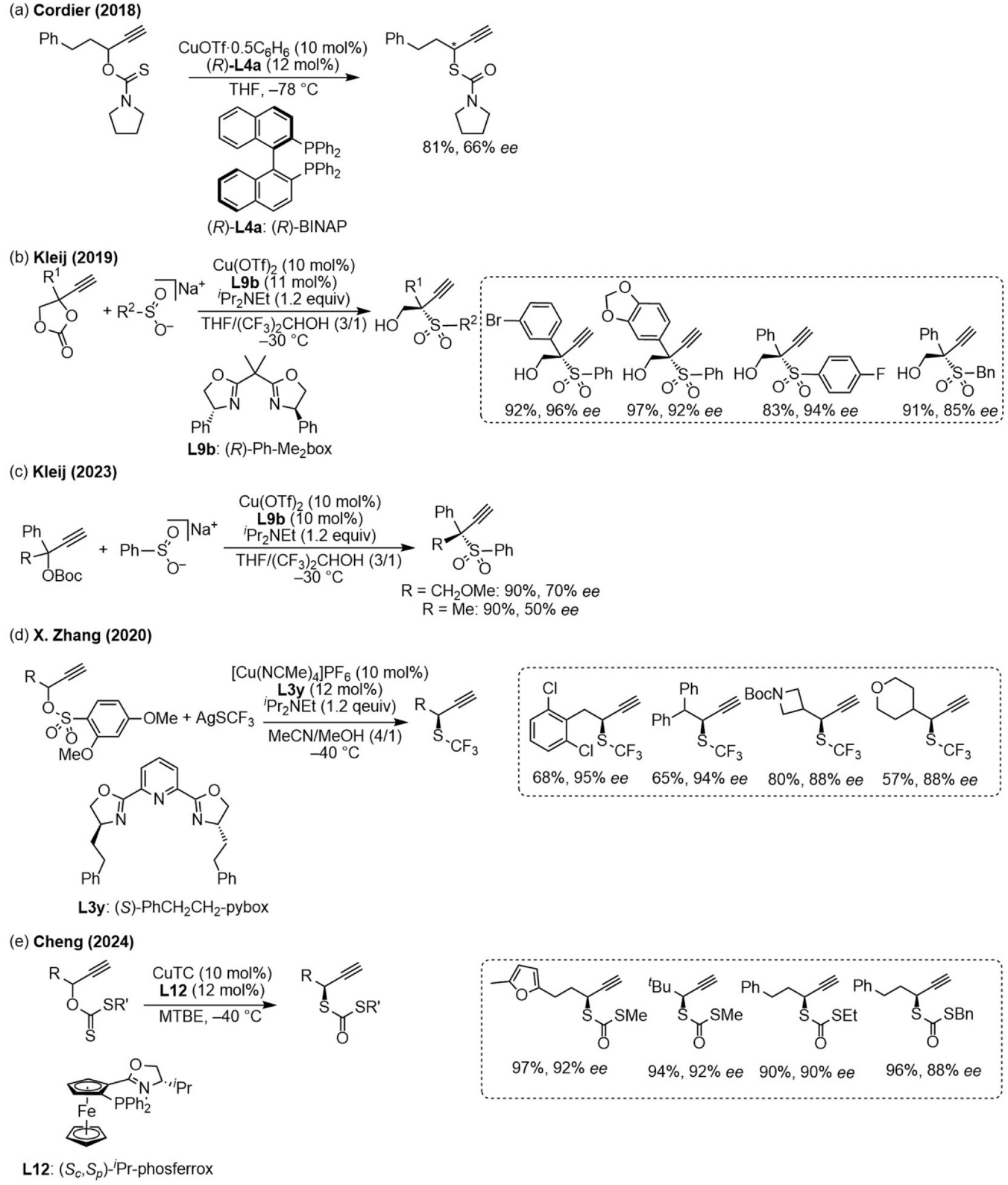

Fig. 38. (a) Preliminary result for Cu/BINAP-catalyzed enantioselective intramolecular *O*-to-*S* rearrangement of propargylic carbamothioate. (b) Cu/Me_2box-catalyzed enantioselective decarboxylative propargylic sulfination of cyclic propargylic carbonate with sodium sulfinate. (c) Cu/Me_2box-catalyzed enantioselective propargylic sulfination of propargylic carbonates with sodium sulfinate. (d) Cu/$PhCH_2CH_2$-pybox-catalyzed enantioselective trifluoromethylthiolation of secondary propargylic sulfonates with $AgSCF_3$. (e) Cu/phosferrox-catalyzed enantioselective intramolecular *O*-to-*S* rearrangement of propargylic xanthates .

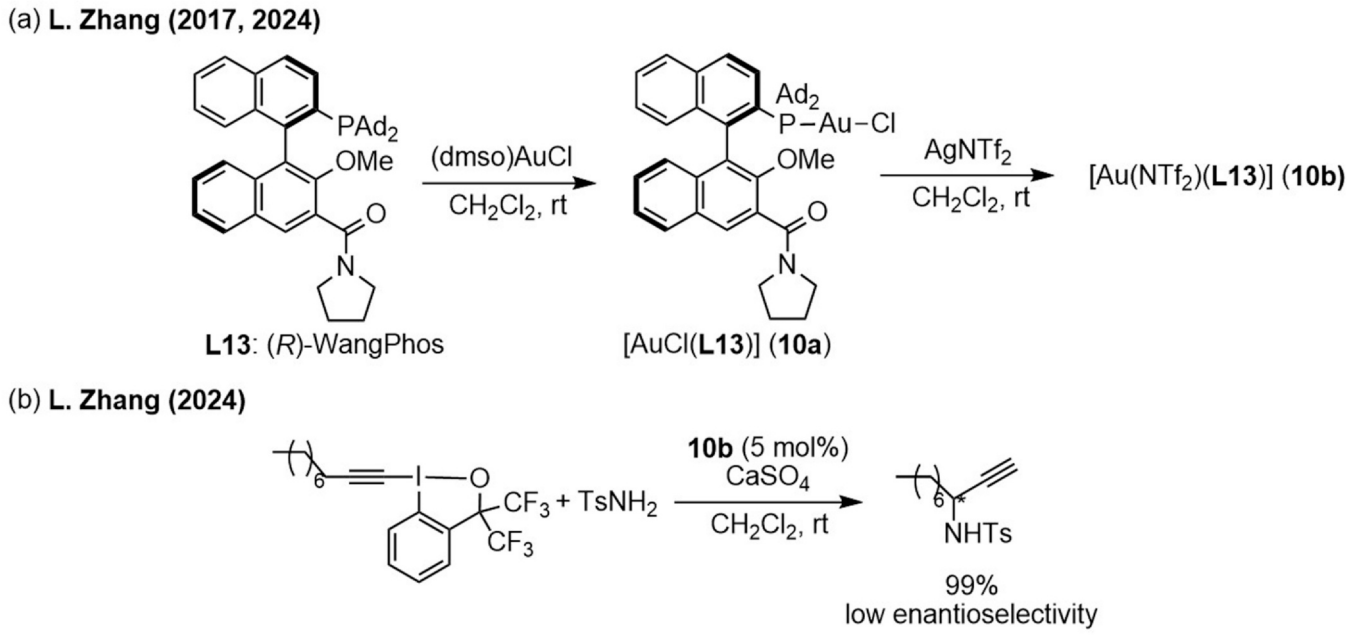

Fig. 39. (a) Preparation of well-defined Au complexes bearing WangPhos as an auxiliary ligand. (b) Au-catalyzed propargylic amination of alkynylbenziodoxole.

complexes have been isolated not only for Au [65] but for many other transition metals other than Ru or Cu [21]. Thus, further expansion of catalytic systems that can furnish enantioselective propargylic substitution reactions is expected.

CRediT authorship contribution statement

Yoshiaki Nishibayashi: Writing – review & editing, Supervision. **Yoshiaki Tanabe:** Writing – original draft.

Data Availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Yoshiaki Nishibayashi reports financial support was provided by Japan Society for the Promotion of Science. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] T.T. Talele, Acetylene group, friend or foe in medicinal chemistry, J. Med. Chem. 63 (2020) 5625–5663, https://doi.org/10.1021/acs.jmedchem.9b01617.
[2] (a) J. Tsuji, J. Kiji, S. Imamura, M. Morikawa, Organic syntheses by means of noble metal compounds. VIII. Catalytic carbonylation of allylic compounds with palladium chloride, J. Am. Chem. Soc. 86 (1964) 4350–4353, https://doi.org/10.1021/ja01074a023;
(b) B.M. Trost, P.E. Strege, Asymmetric induction in catalytic allylic alkylation, J. Am. Chem. Soc. 99 (1977) 1649–1654, https://doi.org/10.1021/ja00447a064.
[3] (a) J. Tsuji, Palladium Reagents and Catalysts: Innovations in Organic Synthesis, Wiley-VCH,, New York, 1995;
(b) B.M. Trost, D.L. Van Vranken, Asymmetric transition metal-catalyzed allylic alkylations, Chem. Rev. 96 (1996) 395–422, https://doi.org/10.1021/cr9409804;
(c) B.M. Trost, C. Lee, Asymmetric carbon–carbon bond-forming reactions: asymmetric allylic alkylation reactions, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, second ed., Wiley-VCH, New York, 2000, pp. 593–649, https://doi.org/10.1002/0471721506.ch19;
(d) B.M. Trost, M.L. Crawley, Asymmetric transition-metal-catalyzed allylic alkylations: applications in total synthesis, Chem. Rev. 103 (2003) 2921–2944, https://doi.org/10.1021/cr020027w;
(e) Y. Nishibayashi, S. Uemura, C–C bond formation (part 2) by substitution reactions: allylic alkylation, in: D.M.P. Mingos, R.H. Crabtree (Eds.), Comprehensive Organometallic Chemistry III, 11 Elsevier, Amsterdam, 2007, pp. 75–122, https://doi.org/10.1016/b0-08-045047-4/00145-x;
(f) Z. Lu, S. Ma, Metal-catalyzed enantioselective allylation in asymmetric synthesis, Angew. Chem. Int. Ed. 47 (2008) 258–297, https://doi.org/10.1002/anie.200605113;
(g) U. Kazmaier (Ed.), Transition Metal Catalyzed Enantioselective Allylic Substitution in Organic Synthesis (Top. Organomet. Chem. 38), Springer, New York, 2012, , https://doi.org/10.1007/978-3-642-22749-3;
(h) B.M. Trost, C.-J. Li (Eds.), Modern Alkyne Chemistry: Catalytic and Atom-Economic Transformations, Wily-VCH, Weinheim, 2015, , https://doi.org/10.1002/9783527677894.
[4] J. Tsuji, T. Mandai, Palladium-catalyzed reactions of propargylic compounds in organic synthesis, Angew. Chem. Int. Ed. Engl. 34 (1995) 2589–2612, https://doi.org/10.1002/anie.199525891.
[5] (a) R.F. Lockwood, K.M. Nicholas, Transition metal-stabilized carbenium ions as synthetic intermediates. I. α-[(alkynyl)dicobalt hexacarbonyl] carbenium ions as propargylating agents, Tetrahedron Lett. 18 (1977) 4163–4165, https://doi.org/10.1016/S0040-4039(01)83455-9;
(b) K.M. Nicholas, Chemistry and synthetic utility of cobalt-complexed propargyl cations, Acc. Chem. Res 20 (20) (1987) 207–214, https://doi.org/10.1021/ar00138a001;
(c) B.J. Teobald, The Nicholas reaction: the use of dicobalt hexacarbonyl-stabilised propargylic cations in synthesis, Tetrahedron 58 (2002) 4133–4170, https://doi.org/10.1016/S0040-4020(02)00315-0.
[6] Y. Imada, M. Yuasa, I. Nakamura, S.-I. Murahashi, Copper(I)-catalyzed amination of propargylic esters. Selective synthesis of propargylamines, 1-alken-3-ylamines, and (Z)-allylamines, J. Org. Chem. 59 (1994) 2282–2284, https://doi.org/10.1021/jo00088a004.
[7] R. Geri, C. Polizzi, L. Lardicci, A.M. Caporusso, Reactions of nitrogen nucleophiles with 1-bromoallenes: regioselective synthesis of propargylamines, Gazz. Chim. Ital. 124 (1994) 241–249, https://doi.org/10.1002/chin.199514071.
[8] J.D. Godfrey Jr., R.H. Mueller, T.C. Sedergran, N. Soundararajan, V.J. Colandrea, Improved synthesis of aryl 1,1-dimethylpropargyl ethers, Tetrahedron Lett. 35 (1994) 6405–6408, https://doi.org/10.1016/S0040-4039(00)78231-1.
[9] (a) Y. Nishibayashi, S. Uemura, C–C bond formation (part 2) by substitution reactions: substitution at propargylic and benzylic positions, in: D.M.P. Mingos, R.H. Crabtree (Eds.), Comprehensive Organometallic Chemistry III, 11 Elsevier, Amsterdam, 2007, pp. 123–150, https://doi.org/10.1016/b0-08-045047-4/00146-1;

(b) N. Ljungdahl, N. Kann, Transition-metal-catalyzed propargylic substitution, Angew. Chem. Int. Ed. 48 (2009) 642–644, https://doi.org/10.1002/anie.200804114;
(c) Y. Miyake, S. Uemura, Y. Nishibayashi, Catalytic propargylic substitution reactions, ChemCatChem 1 (2009) 342–356, https://doi.org/10.1002/cctc.200900214;
(d) R.J. Detz, H. Hiemstra, J.H. van Maarseveen, Catalyzed propargylic substitution, Eur. J. Org. Chem. 2009 (2009) 6263–6276, https://doi.org/10.1002/ejoc.200900877;
(e) R. Roy, S. Saha, Scope and advances in the catalytic propargylic substitution reaction, RSC Adv. 8 (2018) 31129–31193, https://doi.org/10.1039/c8ra04481c;
(f) X.-H. Hu, Z.-T. Liu, L. Shao, X.-P. Hu, Recent advances in catalytic stereocontrolled cycloaddition with terminal propargylic compounds, Synthesis 47 (2015) 913–923, https://doi.org/10.1055/s-0034-1379968;
(g) R. Abonia, D. Insuasty, K.K. Laali, Recent advances in the synthesis of propargyl derivatives, and their application as synthetic intermediates and building blocks, Molecules 28 (2023) 3379, https://doi.org/10.3390/molecules28083379;
(h) F. Doraghi, A.M. Mahdavian, S. Karimian, B. Larijani, M. Mahdavi, Recent progress in application of propargylic alcohols in organic synthesis, Adv. Synth. Catal. 365 (2023) 2991–3019, https://doi.org/10.1002/adsc.202300646.

[10] (a) D.-Y. Zhang, X.-P. Hu, Recent advances in copper-catalyzed propargylic substitution, Tetrahedron Lett. 56 (2015) 283–295, https://doi.org/10.1016/j.tetlet.2014.11.112;
(b) Y. You, Y.-P. Zhang, Z.-H. Wang, J.-Q. Zhao, J.-Q. Yin, W.-C. Yuan, Recent advances in copper-catalyzed decarboxylative reactions of propargylic cyclic carbonates/carbamates, Chem. Commun. 59 (2023) 7483–7505, https://doi.org/10.1039/d3cc01401k.

[11] K. Sakata, Y. Nishibayashi, Mechanism and reactivity of catalytic propargylic substitution reactions via metal–allenylidene intermediates: a theoretical perspective, Catal. Sci. Technol. 8 (2018) 12–25, https://doi.org/10.1039/c7cy01382e.

[12] H. Tsuji, M. Kawatsura, Transition-metal-catalyzed propargylic substitution of propargylic alcohol derivatives bearing an internal alkyne group, Asian J. Org. Chem. 9 (2020) 1924–1941, https://doi.org/10.1002/ajoc.202000422.

[13] F. Tong, D. Hu, C. Zhang, J.-Q. Zhang, H. Ren, Recent advances in nickel-catalyzed propargylic substitution, Org. Chem. Front 11 (2024) 1843–1857, https://doi.org/10.1039/d3qo02129g.

[14] J.A. Marshall, M.A. Wolff, Amination, aminocarbonylation, and alkoxycarbonylation of allenic/propargylic Pd intermediates derived from nonracemic propargylic mesylates: synthesis of nonracemic propargyl amines, allenic amides, and butenolides, J. Org. Chem. 61 (1996) 3238–3239, https://doi.org/10.1021/jo960442m.

[15] Y. Nishibayashi, G. Onodera, Y. Inada, M. Hidai, S. Uemura, Synthesis of diruthenium complexes containing chiral thiolate-bridged ligands and their application to catalytic propargylic alkylation of propargylic alcohols with acetone, Organometallics 22 (2003) 873–876, https://doi.org/10.1021/om020814j.

[16] Y. Inada, Y. Nishibayashi, S. Uemura, Ruthenium-catalyzed asymmetric propargylic substitution reactions of propargylic alcohols with acetone, Angew. Chem. Int. Ed. 44 (2005) 7715–7717, https://doi.org/10.1002/anie.200502981.

[17] (a) C.-H. Ding, X.-L. Hou, Catalytic asymmetric propargylation, Chem. Rev. 111 (2011) 1914–1937, https://doi.org/10.1021/cr100284m;
(b) Y. Nishibayashi, Transition-metal-catalyzed enantioselective propargylic substitution reactions of propargylic alcohol derivatives with nucleophiles, Synthesis 44 (2012) 489–503, https://doi.org/10.1055/s-0031-1290158.

[18] Y. Nishibayashi, Development of asymmetric propargylic substitution reactions using transition metal catalysts, Chem. Lett. 50 (2021) 1282–1288, https://doi.org/10.1246/cl.210126.

[19] Y.-P. Zhang, Y. You, J.-Q. Yin, Z.-H. Wang, J.-Q. Zhao, Q. Li, W.-C. Yuan, Asymmetric propargylic C–C bond formation using metal–allenylidene species, Eur. J. Org. Chem. 26 (2023) e202300728, https://doi.org/10.1002/ejoc.202300728.

[20] M.-D. Li, X.-R. Wang, T.-Y. Lin, Recent advances in copper-catalyzed asymmetric propargylic substitution, Tetrahedron Chem. 11 (2024) 100082, https://doi.org/10.1016/j.tchem.2024.100082.

[21] (a) C. Bruneau, P.H. Dixneuf, Metal vinylidenes and allenylidenes in catalysis: applications in anti-Markovnikov additions to terminal alkynes and alkene metathesis, Angew. Chem. Int. Ed. 45 (2006) 2176–2203, https://doi.org/10.1002/anie.200501391;
(b) C. Bruneau, P.H. Dixneuf (Eds.), Metal Vinylidenes and Allenylidenes in Catalysis: From Reactivity to Applications in Synthesis, Wiley-VCH, Weinheim, 2008, , https://doi.org/10.1002/9783527622870;
(c) V. Cadierno, J. Gimeno, Allenylidene and higher cumulenylidene complexes, Chem. Rev. 109 (2009) 3512–3560, https://doi.org/10.1021/cr8005476;
(d) J.A. Varela, C. González-Rodríguez, C. Saá, Catalytic transformations of alkynes via ruthenium vinylidene and allenylidene intermediates, in: C. Bruneau, P.H. Dixneuf (Eds.), Ruthenium in Catalysis (Top. Organomet. Chem. 48), 48 Springer, Heidelberg, 2014, pp. 237–288, https://doi.org/10.1007/3418_2014_81;
(e) S.W. Roh, K. Choi, C. Lee, Transition metal vinylidene- and allenylidene-mediated catalysis in organic synthesis, Chem. Rev. 119 (2019) 4293–4356, https://doi.org/10.1021/acs.chemrev.8b00568.

[22] Y. Miyazaki, K. Michigami, M. Ohashi, Isolation of cationic η^3-allenylnickel(II) key intermediate complexes: origins of enantioselectivity and regioselectivity in nickel (0)-catalyzed asymmetric propargylic substitutions, J. Am. Chem. Soc. 146 (2024) 8757–8767, https://doi.org/10.1021/jacs.4c01738.

[23] (a) F.-D. Lu, X. Jiang, L.-Q. Lu, W.-J. Xiao, Application of propargylic radicals in organic synthesis, Acta Chim. Sin. (Chin. Ed.) 77 (2019) 803–813, https://doi.org/10.6023/a19060201;
(b) M. Liang, H. Ma, X.-R. Song, Q. Xiao, Recent advances in radical transformations of propargylic alcohols, Adv. Synth. Catal. 366 (2024) 2659–2677, https://doi.org/10.1002/adsc.202400247.

[24] (a) S.W. Smith, G.C. Fu, Nickel-catalyzed Negishi cross-couplings of secondary nucleophiles with secondary propargylic electrophiles at room temperature, Angew. Chem. Int. Ed. 47 (2008) 9334–9336, https://doi.org/10.1002/anie.200802784;
(b) S.W. Smith, G.C. Fu, Nickel-catalyzed asymmetric cross-couplings of racemic propargylic halides with arylzinc reagents, J. Am. Chem. Soc. 130 (2008) 12645–12647, https://doi.org/10.1021/ja805165y;
(c) A.J. Oelke, J. Sun, G.C. Fu, Nickel-catalyzed enantioselective cross-couplings of racemic secondary electrophiles that bear an oxygen leaving group, J. Am. Chem. Soc. 134 (2012) 2966–2969, https://doi.org/10.1021/ja300031w;
(d) N.D. Schley, G.C. Fu, Nickel-catalyzed Negishi arylations of propargylic bromides: a mechanistic investigation, J. Am. Chem. Soc. 136 (2014) 16588–16593, https://doi.org/10.1021/ja508718m.

[25] (a) F.-D. Lu, D. Liu, L. Zhu, L.-Q. Lu, Q. Yang, Q.-Q. Zhou, Y. Wei, Y. Lan, W.-J. Xiao, Asymmetric propargylic radical cyanation enabled by dual organophotoredox and copper catalysis, J. Am. Chem. Soc. 141 (2019) 6167–6172, https://doi.org/10.1021/jacs.9b02338;
(b) Q. Liu, J. Zheng, X. Zhang, S. Ma, Photo and copper dual catalysis for allene syntheses from propargylic derivatives via one-electron process, Nat. Commun. 13 (2022) 3302, https://doi.org/10.1038/s41467-022-30655-3;
(c) L. Wang, C. Lin, Q. Chong, Z. Zhang, F. Meng, Photoredox cobalt-catalyzed regio-, diastereo- and enantioselective propargylation of aldehydes via propargyl radicals, Nat. Commun. 14 (2023) 4825, https://doi.org/10.1038/s41467-023-40488-3.

[26] Y. Nishibayashi, I. Wakiji, M. Hidai, Novel propargylic substitution reactions catalyzed by thiolate-bridged diruthenium complexes via allenylidene intermediates, J. Am. Chem. Soc. 122 (2000) 11019–11020, https://doi.org/10.1021/ja0021161.

[27] (a) Y. Nishibayashi, I. Wakiji, Y. Ishii, S. Uemura, M. Hidai, Ruthenium-catalyzed propargylic alkylation of propargylic alcohols with ketones: straightforward synthesis of γ-keto acetylenes, J. Am. Chem. Soc. 123 (2001) 3393–3394, https://doi.org/10.1021/ja015670z;
(b) Y. Nishibayashi, H. Imajima, G. Onodera, Y. Inada, M. Hidai, S. Uemura, Preparation of alkanechalcogenolate- and benzenechalcogenolate-bridged diruthenium complexes and their catalytic activity toward propargylation of acetone with propargylic alcohol, Organometallics 23 (2004) 5100–5103, https://doi.org/10.1021/om049475f;
(c) Y. Nishibayashi, M. Yoshikawa, Y. Inada, M. Hidai, S. Uemura, Ruthenium-catalyzed cycloaddition between propargylic alcohols and cyclic 1,3-dicarbonyl compounds via an allenylidene intermediate, J. Org. Chem. 69 (2004) 3408–3412, https://doi.org/10.1021/jo0357465.

[28] (a) Y. Nishibayashi, Y. Inada, M. Hidai, S. Uemura, Ruthenium-catalyzed carbon–carbon bond formation between propargylic alcohols and alkenes via the allenylidene-ene reaction, J. Am. Chem. Soc. 125 (2003) 6060–6061, https://doi.org/10.1021/ja035106j;
(b) M. Daini, M. Yoshikawa, Y. Inada, S. Uemura, K. Sakata, K. Kanao, Y. Miyake, Y. Nishibayashi, Ruthenium-catalyzed dienyne formation from propargylic alcohols and 1,3-conjugated dienes, Organometallics 27 (2008) 2046–2051, https://doi.org/10.1021/om800075e.

[29] M.D. Milton, G. Onodera, Y. Nishibayashi, S. Uemura, Double phosphinylation of propargylic alcohols: a novel synthetic route to 1,2-bis(diphenylphosphino)ethane derivatives, Org. Lett. 6 (2004) 3993–3995, https://doi.org/10.1021/ol048347k.

[30] (a) Y. Nishibayashi, H. Imajima, G. Onodera, M. Hidai, S. Uemura, Preparation of a series of chalcogenolate-bridged diruthenium complexes and their catalytic activities toward propargylic substitution reactions, Organometallics 23 (2004) 26–30, https://doi.org/10.1021/om034137k;
(b) Y. Tanabe, K. Kanao, Y. Miyake, Y. Nishibayashi, Remarkable effect of halogens on catalytic activity of thiolato-bridged diruthenium complexes in propargylic substitution reactions, Organometallics 28 (2009) 1138–1142, https://doi.org/10.1021/om8011079.

[31] Y. Nishibayashi, M.D. Milton, Y. Inada, M. Yoshikawa, I. Wakiji, M. Hidai, S. Uemura, Ruthenium-catalyzed propargylic substitution reactions of propargylic alcohols with oxygen-, nitrogen-, and phosphorus-centered nucleophiles, Chem. Eur. J. 11 (2005) 1433–1451, https://doi.org/10.1002/chem.200400833.

[32] (a) M. Yuki, Y. Miyake, Y. Nishibayashi, Preparation of thiolate-bridged dinuclear ruthenium complexes bearing a phosphine ligands and application to propargylic reduction of propargylic alcohols with 2-propanol, Organometallics 29 (2010) 5994–6001, https://doi.org/10.1021/om100852x;
(b) H. Ding, K. Sakata, S. Kuriyama, Y. Nishibayashi, Ruthenium-catalyzed propargylic reduction of propargylic alcohols with Hantzsch ester, Organometallics 39 (2020) 2130–2134, https://doi.org/10.1021/acs.organomet.0c00187.

[33] (a) Y. Nishibayashi, M. Yoshikawa, Y. Inada, M. Hidai, S. Uemura, Ruthenium-catalyzed propargylation of aromatic compounds with propargylic alcohols, J. Am. Chem. Soc. 124 (2002) 11846–11847, https://doi.org/10.1021/ja027023t;
(b) Y. Inada, M. Yoshikawa, M.D. Milton, Y. Nishibayashi, S. Uemura, Ruthenium-catalyzed propargylation of aromatic compounds with propargylic alcohols, Eur. J. Org. Chem. 2006 (2006) 881–890, https://doi.org/10.1002/ejoc.200500858;

(c) K. Kanao, Y. Miyake, Y. Nishibayashi, Ruthenium-catalyzed enantioselective intramolecular propargylation of thiophenes with propargylic alcohols, Organometallics 28 (2009) 2920–2926, https://doi.org/10.1021/om9001186.
[34] (a) S. Dev, K. Imagawa, Y. Mizobe, G. Cheng, Y. Wakatsuki, H. Yamazaki, M. Hidai, Preparation, properties, and some reactions of novel ruthenium thiolate complexes, Organometallics 8 (1989) 1232–1237, https://doi.org/10.1021/om00107a017;
(b) J.-P. Qü, D. Masui, Y. Ishii, M. Hidai, Head-to-head Z dimerization of terminal alkynes catalyzed by thiolate-bridged diruthenium complexes, Chem. Lett. 27 (1998) 1003–1004, https://doi.org/10.1246/cl.1998.1003.
[35] (a) H. Matsuzaka, H. Koizumi, Y. Takagi, M. Nishio, M. Hidai, Coupling of propargyl alcohols via allenylidene–alkynyl or vinylvinylidene–alkynyl combination on a thiolate-bridged diruthenium center. Syntheses and crystal structures of diruthenacyclopentanone and diruthenacyclopentenone complexes, J. Am. Chem. Soc. 115 (1993) 10396–10397, https://doi.org/10.1021/ja00075a080;
(b) H. Matsuzaka, J.-P. Qü, T. Ogino, M. Nishio, Y. Nishibayashi, Y. Ishii, S. Uemura, M. Hidai, Oxidative addition of diferrocenyl dichalcogenides to [{Ru(η^5-C_5Me_5)(μ_3-Cl)}$_4$]. Syntheses, crystal structures and some reactivities of [{Ru(η^5-C_5Me_5)Cl(μ-ER)}$_2$] (E = S, Se or Te; R = ferrocenyl), J. Chem. Soc., Dalton Trans. 25 (1996) 4307–4312, https://doi.org/10.1039/dt9960004307;
(c) M. Hidai, Y. Ishii, S. Kuwata, Novel chemical transformations at diruthenium centres bridged by thiolato ligands, in: G.J. Leigh, N. Winterton (Eds.), Modern Coordination Chemistry: The Legacy of Joseph Chatt, Royal Society of Chemistry, Cambridge, 2002, pp. 208–216, https://doi.org/10.1039/9781847551481-00208.
[36] (a) S.C. Ammal, N. Yoshikai, Y. Inada, Y. Nishibayashi, E. Nakamura, Synergistic dimetallic effects in propargylic substitution reaction catalyzed by thiolate-bridged diruthenium complex, J. Am. Chem. Soc. 127 (2005) 9428–9438, https://doi.org/10.1021/ja050298z;
(b) K. Sakata, Y. Miyake, Y. Nishibayashi, A. DFT, study on the reaction pathways for carbon–carbon bond-forming reactions between propargylic alcohols and alkenes or ketones catalyzed by thiolate-bridged diruthenium complexes, Chem. Asian J. 4 (2009) 81–88, https://doi.org/10.1002/asia.200800236.
[37] K. Kanao, Y. Tanabe, Y. Miyake, Y. Nishibayashi, Intramolecular edge-to-face aromatic π–π interaction in optically active ruthenium–allenylidene complexes for enantioselective propargylic substitution reactions, Organometallics 29 (2010) 2381–2384, https://doi.org/10.1021/om100227n.
[38] K. Sakata, Y. Goto, T. Yoshikawa, Y. Nishibayashi, Enantioselectivity in ruthenium-catalyzed propargylic substitution reactions of propargylic alcohols with acetone: a DFT study, Chem. Asian J. 16 (2021) 3760–3766, https://doi.org/10.1002/asia.202100984.
[39] K. Fukamizu, Y. Miyake, Y. Nishibayashi, Ruthenium-catalyzed enantioselective carbon–carbon bond forming reaction via allenylidene-ene process: synthetic approach to chiral heterocycles such as chromane, thiochromane, and 1,2,3,4-tetrahydroquinoline derivatives, J. Am. Chem. Soc. 130 (2008) 10498–10499, https://doi.org/10.1021/ja8038745.
[40] H. Matsuzawa, Y. Miyake, Y. Nishibayashi, Ruthenium-catalyzed enantioselective propargylation of aromatic compounds with propargylic alcohols via allenylidene intermediates, Angew. Chem. Int. Ed. 46 (2007) 6488–6491, https://doi.org/10.1002/anie.200701261.
[41] (a) H. Matsuzawa, K. Kanao, Y. Miyake, Y. Nishibayashi, Remarkable effect of N-substituent on enantioselective ruthenium-catalyzed propargylation of indoles with propargylic alcohols, Org. Lett. 9 (2007) 5561–5564, https://doi.org/10.1021/ol7025203;
(b) K. Kanao, H. Matsuzawa, Y. Miyake, Y. Nishibayashi, Ruthenium-catalyzed enantioselective propargylation of indoles with propargylic alcohols, Synthesis 40 (2008) 3869–3873, https://doi.org/10.1055/s-0028-1083217.
[42] (a) K. Nakajima, S. Nojima, K. Sakata, Y. Nishibayashi, Visible-light-mediated aromatic substitution reactions of cyanoarenes with 4-alkyl-1,4-dihydropyridines through double carbon–carbon bond cleavage, ChemCatChem 8 (2016) 1028–1032, https://doi.org/10.1002/cctc.201600037;
(b) K. Nakajima, Y. Miyake, Y. Nishibayashi, Synthetic utilization of α-aminoalkyl radicals and related species in visible light photoredox catalysis, Acc. Chem. Res. 49 (2016) 1946–1956, https://doi.org/10.1021/acs.accounts.6b00251;
(c) A.Y. Chan, I.B. Perry, N.B. Bissonnette, B.F. Buksh, G.A. Edwards, L.I. Frye, O. L. Garry, M.N. Lavagnino, B.X. Li, Y. Liang, E. Mao, A. Millet, J.V. Oakley, N.L. Reed, H.A. Sakai, C.P. Seath, D.W.C. MacMillan, Metallaphotoredox: the merger of photoredox and transition metal catalysis, Chem. Rev. 122 (2022) 1485–1542, https://doi.org/10.1021/acs.chemrev.1c00383.
[43] (a) Z.-Z. Zhou, R.-Q. Jiao, K. Yang, X.-M. Chen, Y.-M. Liang, Photoredox/palladium co-catalyzed propargylic benzylation with internal propargylic carbonates, Chem. Commun. 56 (2020) 12957–12960, https://doi.org/10.1039/d0cc04986g;
(b) Z.-Z. Zhou, X.-R. Song, S. Du, K.-J. Xia, W.-F. Tian, Q. Xiao, Y.-M. Liang, Photoredox/nickel dual-catalyzed regioselective alkylation of propargylic carbonates for trisubstituted allene, Chem. Commun. 57 (2021) 9390–9393, https://doi.org/10.1039/d1cc03303d.
[44] Y. Zhang, Y. Tanabe, S. Kuriyama, K. Sakata, Y. Nishibayashi, Interplay of diruthenium catalyst in controlling enantioselective propargylic substitution reactions with visible light-generated alkyl radicals, Nat. Commun. 14 (2023) 859, https://doi.org/10.1038/s41467-023-36453-9.
[45] K. Sakata, Y. Uehara, S. Kohara, T. Yoshikawa, Y. Nishibayashi, Effect of propargylic substituents on enantioselectivity and reactivity in ruthenium-catalyzed propargylic substitution reactions: a DFT study, ACS Omega 7 (2022) 36634–36642, https://doi.org/10.1021/acsomega.2c04645.
[46] (a) D.W.C. MacMillan, The advent and development of organocatalysis, Nature 455 (2008) 304–308, https://doi.org/10.1038/nature07367;
(b) S. Bertelsen, K.A. Jørgensen, Organocatalysis—after the gold rush, Chem. Soc. Rev. 38 (2009) 2178–2189, https://doi.org/10.1039/b903816g;
(c) M.H. Aukland, B. List, Organocatalysts emerging as a technology, Pure Appl. Chem. 93 (2021) 1371–1381, https://doi.org/10.1515/pac-2021-0501.
[47] (a) Z. Du, Z. Shao, Combining transition metal catalysis and organocatalysis - an update, Chem. Soc. Rev. 42 (2013) 1337–1378, https://doi.org/10.1039/c2cs35258c;
(b) D.-F. Chen, L.-Z. Gong, Organo/transition-metal combined catalysis rejuvenates both in asymmetric synthesis, J. Am. Chem. Soc. 144 (2022) 2415–2437, https://doi.org/10.1021/jacs.1c11408;
(c) N. Chakraborty, B. Das, K.K. Rajbongshi, B.K. Patel, Combined power of organo- and transition metal catalysts in organic synthesis, Eur. J. Org. Chem. 2022 (2022) e202200273, https://doi.org/10.1002/ejoc.202200273.
[48] A. Gualandi, L. Mengozzi, C.M. Wilson, P.G. Cozzi, Synergy, compatibility, and innovation: merging Lewis acids with stereoselective enamine catalysis, Chem. Asian J. 9 (2014) 984–995, https://doi.org/10.1002/asia.201301549.
[49] M. Ikeda, Y. Miyake, Y. Nishibayashi, Cooperative catalytic reactions using organocatalysts and transition-metal catalysts: enantioselective propargylic alkylation of propargylic alcohols with aldehydes, Angew. Chem. Int. Ed. 49 (2010) 7289–7293, https://doi.org/10.1002/anie.201002591.
[50] M. Ikeda, Y. Miyake, Y. Nishibayashi, Cooperative catalytic reactions using organocatalysts and transition metal catalysts: propargylic allylation of propargylic alcohols with α,β-unsaturated aldehydes, Organometallics 31 (2012) 3810–3813, https://doi.org/10.1021/om300286b.
[51] J.M. Ovian, P. Vojáčková, E.N. Jacobsen, Enantioselective transition-metal catalysis via an anion-binding approach, Nature 616 (2023) 84–89, https://doi.org/10.1038/s41586-023-05804-3.
[52] (a) J. Merad, J.-M. Pons, O. Chuzel, C. Bressy, Enantioselective catalysis by chiral isothioureas, Eur. J. Org. Chem. 2016 (2016) 5589–5610, https://doi.org/10.1002/ejoc.201600399;
(b) T. Parvin, R. Yadav, L.H. Choudhury, Recent applications of thiourea-based organocatalyst in asymmetric multicomponent reactions (AMCRs), Org. Biomol. Chem. 18 (2020) 5513–5532, https://doi.org/10.1039/d0ob00595a;
(c) L.-M. Entgelmeier, O.G. Mancheño, Activation modes in asymmetric anion-biding catalysis, Synthesis 54 (2022) 3907–3927, https://doi.org/10.1055/a-1846-6139.
[53] (a) D. Parmar, E. Sugiono, S. Raja, M. Rueping, Complete field guide to asymmetric BINOL-phosphate derived Brønsted acid and metal catalysis: history and classification by mode of activation; Brønsted acidity, hydrogen bonding, ion pairing, and metal phosphates, Chem. Rev. 114 (2014) 9047–9153, https://doi.org/10.1021/cr5001496;
(b) Z.-L. Xia, Q.-F. Xu-Xu, C. Zheng, S.-L. You, Chiral phosphoric acid-catalyzed asymmetric dearomatization reactions, Chem. Soc. Rev. 49 (2020) 286–300, https://doi.org/10.1039/c8cs00436f.
[54] Y. Senda, K. Nakajima, Y. Nishibayashi, Cooperative catalysis: enantioselective propargylic alkylation of propargylic alcohols with enecarbamates using ruthenium/phosphoramide hybrid catalysts, Angew. Chem. Int. Ed. 54 (2015) 4060–4064, https://doi.org/10.1002/anie.201411601.
[55] (a) G.C. Hargaden, P.J. Guiry, Recent applications of oxazoline-containing ligands in asymmetric catalysis, Chem. Rev. 109 (2009) 2505–2550, https://doi.org/10.1021/cr800400z;
(b) R. Connon, B. Roche, B.V. Rokade, P.J. Guiry, Further developments and application of oxazoline-containing ligands in asymmetric catalysis, Chem. Rev. 121 (2021) 6373–6521, https://doi.org/10.1021/acs.chemrev.0c00844.
[56] M. Ikeda, Y. Miyake, Y. Nishibayashi, Cooperative catalytic reactions using distinct transition-metal catalysts: ruthenium- and copper-catalyzed enantioselective propargylic alkylation, Chem. Eur. J. 18 (2012) 3321–3328, https://doi.org/10.1002/chem.201103892.
[57] K. Motoyama, M. Ikeda, Y. Miyake, Y. Nishibayashi, Ruthenium- and copper-catalyzed enantioselective propargylic alkylation of propargylic alcohols with β-keto phosphonates, Organometallics 31 (2012) 3426–3430, https://doi.org/10.1021/om300219f.
[58] S. Liu, Y. Tanabe, S. Kuriyama, K. Sakata, Y. Nishibayashi, Ruthenium-catalyzed enantioselective propargylic phosphinylation of propargylic alcohols with phosphine oxides, Angew. Chem. Int. Ed. 60 (2021) 11231–11236, https://doi.org/10.1002/anie.202102779.
[59] P. Rojo, A. Riera, X. Verdaguer, Bulky P-stereogenic ligands. A success story in asymmetric catalysis, Coord. Chem. Rev. 489 (2023) 215192, https://doi.org/10.1016/j.ccr.2023.215192.
[60] G. Hattori, H. Matsuzawa, Y. Miyake, Y. Nishibayashi, Copper-catalyzed asymmetric propargylic substitution reactions of propargylic acetates with amines, Angew. Chem. Int. Ed. 47 (2008) 3781–3783, https://doi.org/10.1002/anie.200800276.
[61] G. Hattori, K. Sakata, H. Matsuzawa, Y. Tanabe, Y. Miyake, Y. Nishibayashi, Copper-catalyzed enantioselective propargylic amination of propargylic esters with amines: copper–allenylidene complexes as key intermediates, J. Am. Chem. Soc. 132 (2010) 10592–10608, https://doi.org/10.1021/ja1047494.
[62] R.J. Detz, M.M.E. Delville, H. Hiemstra, J.H. van Maarseveen, Enantioselective copper-catalyzed propargylic amination, Angew. Chem. Int. Ed. 47 (2008) 3777–3780, https://doi.org/10.1002/anie.200705264.
[63] R. Detz, Z. Abiri, R. le Griel, H. Hiemstra, J.H. van Maarseveen, Enantioselective copper-catalysed propargylic substitution: synthetic scope study and application in formal total synthesis of (+)-anisomycin and (–)-cytoxazone, Chem. Eur. J. 17 (2011) 5921–5930, https://doi.org/10.1002/chem.201003727.
[64] M. Asay, B. Donnadieu, W.W. Schoeller, G. Bertrand, Synthesis of allenylidene lithium and silver complexes, and subsequent transmetalation reactions, Angew. Chem. Int. Ed. 48 (2009) 4796–4799, https://doi.org/10.1002/anie.200901319.
[65] (a) M.M. Hansmann, F. Rominger, A.S.K. Hashmi, Gold–allenylidenes – an experimental and theoretical study, Chem. Sci. 4 (2013) 1552–1559, https://doi.org/10.1039/c3sc22227f;

(b) X.-S. Xiao, W.-L. Kwong, X. Guan, C. Yang, W. Lu, C.-M. Che, Platinum(II) and gold(III) allenylidene complexes: phosphorescence, self-assembled nanostructures and cytotoxicity, Chem. Eur. J. 19 (2013) 9457–9462, https://doi.org/10.1002/chem.201301481;
(c) X.-S. Xiao, C. Zou, X. Guan, C. Yang, W. Lu, C.-M. Che, Homoleptic gold(I) N-heterocyclic allenylidene complexes: excited-state properties and lyotropic chromonics, Chem. Commun. 52 (2016) 4983–4986, https://doi.org/10.1039/c5cc09571a;
(d) L. Jin, M. Melaimi, A. Kostenko, M. Karni, Y. Apeloig, C.E. Moore, A.L. Rheingold, G. Bertrand, Isolation of cationic and neutral (allenylidene)(carbene) and bis(allenylidene)gold complexes, Chem. Sci. 7 (2016) 150–154, https://doi.org/10.1039/c5sc03654b;
(e) N. Kim, R.A. Widenhoefer, Synthesis, characterization, and reactivity of cationic gold diarylallenylidene complexes, Angew. Chem. . Ed. 57 (2018) 4722–4726, https://doi.org/10.1002/anie.201713209.
[66] J. Li, B. Yu, Z. Lu, Chiral imidazoline ligands and their applications in metal-catalyzed asymmetric synthesis, Chin. J. Chem. 39 (2021) 488–514, https://doi.org/10.1002/cjoc.202000486.
[67] D.-H. Liang, C.-J. Hou, Q. Li, H. Qin, L. Li, X.-P. Hu, Chiral P,N,N-ligands for asymmetric hydrogenation, Adv. Synth. Catal. 366 (2024) 2165–2185, https://doi.org/10.1002/adsc.202400092.
[68] (a) M.N. Hopkinson, C. Richter, M. Schedler, F. Glorius, An overview of N-heterocyclic carbenes, Nature 510 (2014) 485–496, https://doi.org/10.1038/nature13384;
(b) D.M. Flanigan, F. Romanov-Michailidis, N.A. White, T. Rovis, Organocatalytic reactions enabled by N-heterocyclic carbenes, Chem. Rev. 115 (2015) 9307–9387, https://doi.org/10.1021/acs.chemrev.5b00060;
(c) D. Sharma, R. Chatterjee, V. Dhayalan, R. Dandela, Recent advances in enantioselective organocatalytic reactions enabled by N-heterocyclic carbenes (NHCs) containing triazolium motifs, Synthesis 54 (2022) 4129–4166, https://doi.org/10.1055/a-1856-5688.
[69] G. Hattori, A. Yoshida, Y. Miyake, Y. Nishibayashi, Enantioselective ring-opening reactions of racemic ethynyl epoxides via copper–allenylidene intermediates: efficient approach to chiral β-amino alcohols, J. Org. Chem. 74 (2009) 7603–7607, https://doi.org/10.1021/jo901064n.
[70] A. Yoshida, G. Hattori, Y. Miyake, Y. Nishibayashi, Copper-catalyzed enantioselective propargylic amination of nonaromatic propargylic esters with amines, Org. Lett. 13 (2011) 2460–2463, https://doi.org/10.1021/ol200703g.
[71] T. Mino, Y. Naruse, S. Kobayashi, S. Oishi, M. Sakamoto, T. Fujita, Synthesis and application of atropisomeric dihydrobenzofuran-based bisphosphine (BICMAP), Tetrahedron Lett. 50 (2009) 2239–2241, https://doi.org/10.1016/j.tetlet.2009.02.182.
[72] T. Mino, H. Taguchi, M. Hashimoto, M. Sakamoto, Copper-catalyzed asymmetric propargylic amination of propargylic acetates with amines using BICMAP, Tetrahedron.: Asymmetry 24 (2013) 1520–1523, https://doi.org/10.1016/j.tetasy.2013.10.007.
[73] L.-J. Cheng, A.P.N. Brown, C.J. Cordier, Enantioselective propargylic [1,3]-rearrangements: copper-catalyzed O-to-N migrations toward C–N bond formation, Chem. Sci. 88 (2017) 4299–4305, https://doi.org/10.1039/c7sc01042g.
[74] S. Liu, Y. Tanabe, S. Kuriyama, K. Sakata, Y. Nishibayashi, Ruthenium- and copper-catalyzed propargylic substitution reactions of propargylic alcohol derivatives with hydrazones, Chem. Eur. J. 27 (2021) 15650–15659, https://doi.org/10.1002/chem.202103287.
[75] W. Guo, L. Zuo, M. Cui, B. Yan, S. Ni, Propargylic amination enabled the access to enantioenriched acyclic α-quaternary α-amino ketones, J. Am. Chem. Soc. 143 (2021) 7629–7634, https://doi.org/10.1021/jacs.1c03182.
[76] M. Shibata, K. Nakajima, Y. Nishibayashi, Enantioselective intramolecular propargylic amination using chiral copper–pybox complexes as catalysts, Chem. Commun. 50 (2014) 7874–7877, https://doi.org/10.1039/c4cc01676a.
[77] A. Delgado, P. Orlando, M. Lanzi, J. Benet-Buchhloz, D. Passarella, A.W. Kleij, Cu-catalyzed asymmetric synthesis of γ-amino alcohols featuring tertiary carbon stereocenters, Org. Lett. 26 (2024) 7596–7600, https://doi.org/10.1021/acs.orglett.4c02682.
[78] J.E. Gómez, W. Guo, S. Gaspa, A.W. Kleij, Copper-catalyzed synthesis of γ-amino acids featuring quaternary stereocenters, Angew. Chem. Int. Ed. 56 (2017) 15035–15038, https://doi.org/10.1002/anie.201709511.
[79] L. Tian, L. Gong, X. Zhang, Copper-catalyzed enantioselective synthesis of β-amino alcohols featuring tetrasubstituted tertiary carbons, Adv. Synth. Catal. 360 (2018) 2055–2059, https://doi.org/10.1002/adsc.201701613.
[80] W. Shao, Y. Wang, Z.-P. Yang, X. Zhang, S.-L. You, Efficient synthesis of N-alkylated 4-pyridones by copper-catalyzed intermolecular asymmetric propargylic amination, Chem. Asian J. 13 (2018) 1103–1107, https://doi.org/10.1002/asia.201800373.
[81] D. Ji, C. Wang, J. Sun, Asymmetric [4 + 2]-cycloaddition of copper–allenylidenes with hexahydro-1,3,5-triazines: access to chiral tetrahydroquinazolines, Org. Lett. 20 (2018) 3710–3713, https://doi.org/10.1021/acs.orglett.8b01584.
[82] J.-S. Ma, H.-Y. Lu, Y.-W. Chen, W.-C. Zhao, Y.-Z. Sun, R.-P. Li, H.-X. Wang, G.-Q. Lin, Z.-T. He, Copper-catalysed convergent regio- and enantioselective alkynylallylic substitution, Nat. Synth. 2 (2023) 37–48, https://doi.org/10.1038/s44160-022-00176-4.
[83] S.-Y. Luo, G.-Q. Lin, Z.-T. He, Asymmetric copper-catalyzed alkynylallylic dimethylamination, Org. Chem. Front. 11 (2024) 690–695, https://doi.org/10.1039/d3qo01749d.
[84] T. Liu, S. Ni, W. Guo, Practical asymmetric amine nucleophilic approach for the modular construction of protected α-quaternary amino acids, Chem. Sci. 13 (2022) 6806–6812, https://doi.org/10.1039/d2sc02318k.
[85] Z. Zhang, Y. Sun, Y. Gong, D.-L. Tang, H. Luo, Z.-P. Zhao, F. Zhou, X. Wang, J. Zhou, Enantioselective propargylic amination and related tandem sequences to α-tertiary ethynylamines and azacycles, Nat. Chem. 16 (2024) 521–532, https://doi.org/10.1038/s41557-024-01479-z.
[86] J.D. Sieber, Copper catalysed asymmetric amination, Nat. Chem. 16 (2024) 483–484, https://doi.org/10.1038/s41557-024-01487-z.
[87] C. Jiang, D. Luo, X. Meng, Q. Cui, L. Zhao, J. Liu, S. Yang, X. Fang, Copper-catalyzed amine-mediated yne-propargylic substitution, Org. Chem. Front. 11 (2024) 3946–3951, https://doi.org/10.1039/d4qo00571f.
[88] C. Zhang, Y.-H. Wang, X.-H. Hu, Z. Zheng, J. Xu, X.-P. Hu, Chiral tridentate P,N,N ligands for highly enantioselective copper-catalyzed propargylic amination with both primary and secondary amines as nucleophiles, Adv. Synth. Catal. 354 (2012) 2854–2858, https://doi.org/10.1002/adsc.201200589.
[89] Y. Zhou, F.-L. Zhu, Z.-C. Duan, Y.-H. Wang, D.-Y. Zhang, Z. Cao, Z. Zheng, X.-P. Hu, Enantioselective Cu-catalyzed decarboxylative propargylic amination of propargyl carbamates, Tetrahedron Lett. 55 (2014) 2033–2036, https://doi.org/10.1016/j.tetlet.2014.02.030.
[90] F. Zhu, X. Hu, Enantioselective N-propargylation of indoles via Cu-catalyzed propargylic alkylation/dehydrogenation of indolines, Chin. J. Catal. 36 (2015) 86–92, https://doi.org/10.1016/S1872-2067(14)60230-8.
[91] J. Ma, X. Wang, Z. Liu, X. Hu, Highly diastereo- and enantioselective copper-catalyzed dipropargylic amination to access bispropargylic diamines, Asian J. Org. Chem. 11 (2022) e202200385, https://doi.org/10.1002/ajoc.202200385.
[92] J. Huang, H.-H. Kong, S.-J. Li, R.-J. Zhang, H.-D. Qian, D.-R. Li, J.-Y. He, Y.-N. Zheng, H. Xu, Asymmetric copper-catalyzed propargylic amination with amine hydrochloride salts, Chem. Commun. 57 (2021) 4674–4677, https://doi.org/10.1039/d1cc00663k.
[93] S.-J. Li, J. Huang, J.-Y. He, R.-J. Zhang, H.-D. Qian, X.-L. Dai, H.-H. Kong, H. Xu, Highly enantioselective copper-catalyzed propargylic amination to access N-tethered 1,6-enynes, RSC Adv. 10 (2020) 38478–38483, https://doi.org/10.1039/d0ra07698h.
[94] Y. Wang, L. Zhu, M. Wang, J. Xiong, N. Chen, X. Feng, Z. Xu, X. Jiang, Catalytic asymmetric [4 + 3] annulation of C,N-cyclic azomethine imines with copper allenylidenes, Org. Lett. 20 (2018) 6506–6510, https://doi.org/10.1021/acs.orglett.8b02828.
[95] Q. Cai, H. Rao, S.-J. Li, Y. Lan, K. Ding, X. Wang, Well-defined chiral dinuclear copper complexes in enantioselective propargylic substitution: for a long-standing supposition on binuclear mechanism, Chem 10 (2024) 265–282, https://doi.org/10.1016/j.chempr.2023.09.006.
[96] P. Fang, X.-L. Hou, Asymmetric copper-catalyzed propargylic substitution reaction of propargylic acetates with enamines, Org. Lett. 11 (2009) 4612–4615, https://doi.org/10.1021/ol901891u.
[97] A. Yoshida, M. Ikeda, G. Hattori, Y. Miyake, Y. Nishibayashi, Cooperative catalytic reactions using organocatalysts and transition metal catalysts: enantioselective propargylic alkylation of propargylic esters with aldehydes, Org. Lett. 13 (2011) 592–595, https://doi.org/10.1021/ol1027865.
[98] W. Shao, H. Li, C. Liu, C.-J. Liu, S.-L. You, Copper-catalyzed intermolecular asymmetric propargylic dearomatization of indoles, Angew. Chem. Int. Ed. 54 (2015) 7684–7687, https://doi.org/10.1002/anie.201503042.
[99] K. Tsuchida, Y. Senda, K. Nakajima, Y. Nishibayashi, Construction of chiral tri-and tetra-arylmethanes bearing quaternary carbon centers: copper-catalyzed enantioselective propargylation of indoles with propargylic esters, Angew. Chem. Int. Ed. 55 (2016) 9728–9732, https://doi.org/10.1002/anie.201604182.
[100] L. Yang, X. Pu, D. Niu, Z. Fu, X. Zhang, Copper-catalyzed asymmetric propargylation of indolizines, Org. Lett. 21 (2019) 8553–8557, https://doi.org/10.1021/acs.orglett.9b03032.
[101] X. Gao, R. Cheng, Y.-L. Xiao, X.-L. Wan, X. Zhang, Copper-catalyzed highly enantioselective difluoroalkylation of secondary propargyl sulfonates with difluoroenoxysilanes, Chem 5 (2019) 2987–2999, https://doi.org/10.1016/j.chempr.2019.09.012.
[102] F. Gong, X. Meng, S. Lan, J. Liu, S. Yang, X. Fang, Asymmetric semipinacol rearrangement enabled by copper-catalyzed propargylic alkylation, ACS Catal. 12 (2022) 12036–12044, https://doi.org/10.1021/acscatal.2c03623.
[103] Q. Wang, T.-R. Li, L.-Q. Lu, M.-M. Li, K. Zhang, W.-J. Xiao, Catalytic asymmetric [4 + 1] annulation of sulfur ylides with copper–allenylidene intermediates, J. Am. Chem. Soc. 138 (2016) 8360–8363, https://doi.org/10.1021/jacs.6b04414.
[104] X. Lu, L. Ge, C. Cheng, J. Chen, W. Cao, X. Wu, Enantioselective cascade reaction for synthesis of quinolinones through synergistic catalysis using Cu-pybox and chiral benzotetramisole as catalysts, Chem. Eur. J. 23 (2017) 7689–7693, https://doi.org/10.1002/chem.201701741.
[105] B.-B. Sun, Q.-X. Hu, J.-M. Hu, J.-Q. Yu, J. Jia, X.-W. Wang, Asymmetric [4 + 2] cycloaddition of azlactones with dipolar copper–allenylidene intermediates for chiral 3,4-dihydroquinolin-2-one derivatives, Tetrahedron Lett. 60 (2019) 1967–1970, https://doi.org/10.1016/j.tetlet.2019.06.041.
[106] Y.-W. Xu, X.-P. Hu, Diastereo- and enantioselective copper-catalyzed decarboxylative ring-opening [3 + 2] annulation of tertiary propargylic carbamates through regioselective α-attack of γ-butenolides, Org. Lett. 21 (2019) 8091–8096, https://doi.org/10.1021/acs.orglett.9b03081.
[107] J. Zhang, T. Ni, W.-L. Yang, W.-P. Deng, Catalytic asymmetric [3 + 2] annulation via indolyl copper–allenylidene intermediates: diastereo- and enantioselective assembly of pyrrolo[1,2-a]indoles, Org. Lett. 22 (2020) 4547–4552, https://doi.org/10.1021/acs.orglett.0c01594.
[108] W.-Y. Lu, Y. Wang, Y. You, Z.-H. Wang, J.-Q. Zhao, M.-Q. Zhou, W.-C. Yuan, Copper-catalyzed decarboxylative [3 + 2] annulation of ethynylethylene carbonates with azlactones: access to γ-butyrolactones bearing two vicinal quaternary carbon centers (https://doi-org.utokyo.idm.oclc.org/), J. Org. Chem. 86 (2021) 1779–1788, https://doi.org/10.1021/acs.joc.0c02621.

[109] T. Wang, Y. You, Z.-H. Wang, J.-Q. Zhao, Y.-P. Zhang, J.-Q. Yin, M.-Q. Zhou, B.-D. Cui, W.-C. Yuan, Copper-catalyzed diastereo- and enantioselective decarboxylative [3 + 2] cyclization of alkyne-substituted cyclic carbamates with azlactones: access to γ-butyrolactams bearing two vicinal tetrasubstituted carbon stereocenters, Org. Lett. 25 (2023) 1274–1279, https://doi.org/10.1021/acs.orglett.3c00075.
[110] Y.-H. Wen, Z.-J. Zhang, S. Li, J. Song, L.-Z. Gong, Stereodivergent propargylic alkylation of enals via cooperative NHC and copper catalysis, Nat. Commun. 13 (2022) 1344, https://doi.org/10.1038/s41467-022-29059-0.
[111] G. Tian, M. Ji, F. Wu, G. Wang, C. Zheng, X. Wu, Copper-catalyzed asymmetric propargylic substitution of 2,2,2-trifluoroethyl-isoxazoles with propargylic alcohol derivatives, Org. Lett. 25 (2023) 4666–4671, https://doi.org/10.1021/acs.orglett.3c01521.
[112] H.-Y. Lu, Z.-H. Li, G.-Q. Lin, Z.-T. He, Asymmetric copper-catalyzed alkynylallylic monofluoroalkylations with fluorinated malonates, Chem. Commun. 60 (2024) 4210–4213, https://doi.org/10.1039/d4cc00371c.
[113] M. Boyet, L. Chabaud, M. Pucheault, Recent advances in the synthesis of borinic acid derivatives, Molecules 28 (2023) 2660, https://doi.org/10.3390/molecules28062660.
[114] J.-H. Shen, F. Tian, W.-L. Yang, W.-P. Deng, Synergistic copper and chiral Lewis base catalysis for the asymmetric synthesis of pyrrolo[1,2-a]indoles, Chin. J. Chem. 39 (2021) 3292–3296, https://doi.org/10.1002/cjoc.202100476.
[115] J. Song, Z.-J. Zhang, L.-Z. Gong, Asymmetric [4+2] annulation of C1 ammonium enolates with copper-allenylidenes, Angew. Chem. Int. Ed. 56 (2017) 5212–5216, https://doi.org/10.1002/anie.201700105.
[116] S. Ghosh, S. Mukherjee, Ligand-controlled diastereodivergency in propargylic alkylation of vinylogous aza-enamines: construction of 1,3-stereocenters, Org. Lett. 25 (2023) 7304–7309, https://doi.org/10.1021/acs.orglett.3c02614.
[117] L. Zhao, G. Huang, B. Guo, L. Xu, J. Chen, W. Cao, G. Zhao, X. Wu, Diastereo- and enantioselective propargylation of benzofuranones catalyzed by pybox-copper complex, Org. Lett. 16 (2014) 5584–5587, https://doi.org/10.1021/ol502615y.
[118] G. Huang, C. Cheng, L. Ge, B. Guo, L. Zhao, X. Wu, Trialkyl methanetricarboxylate as dialkyl malonate surrogate in copper-catalyzed enantioselective propargylic substitution, Org. Lett. 17 (2015) 4894–4897, https://doi.org/10.1021/acs.orglett.5b02463.
[119] W. Shao, S.-L. You, Highly diastereo- and enantioselective synthesis of tetrahydro-5H-indolo[2,3-b]quinolines through copper-catalyzed propargylic dearomatization of indoles, Chem. Eur. J. 23 (2017) 12489–12493, https://doi.org/10.1002/chem.201703443.
[120] K. Zhang, L.-Q. Lu, S. Yao, J.-R. Chen, D.-Q. Shi, W.-J. Xiao, Enantioselective copper catalysis: in situ generation of the chiral phophorus ylide and its Wittig reactions, J. Am. Chem. Soc. 139 (2017) 12847–12854, https://doi.org/10.1021/jacs.7b08207.
[121] A. Shemet, E.M. Carreira, Total synthesis of (–)-rhazinilam and formal synthesis of (+)-eburenine and (+)-aspidospermidine: asymmetric Cu-catalyzed propargylic substitution, Org. Lett. 19 (2017) 5529–5532, https://doi.org/10.1021/acs.orglett.7b02619.
[122] H. Chen, X. Lu, X. Xia, Q. Zhu, Y. Song, J. Chen, W. Cao, X. Wu, Asymmetric catalytic [4 + 2] cycloaddition via Cu–allenylidene intermediate: stereoselective synthesis of tetrahydroquinolines fused with a γ-lactone moiety, Org. Lett. 20 (2018) 1760–1763, https://doi.org/10.1021/acs.orglett.8b00253.
[123] Z. Fu, N. Deng, S.-N. Su, H. Li, R.-Z. Li, X. Zhang, J. Liu, D. Niu, Diastereo- and enantioselective propargylation of 5H-thiazol-4-ones and 5H-oxazol-4-ones as enabled by Cu/Zn and Cu/Ti catalysis, Angew. Chem. Int. Ed. 57 (2018) 15217–15221, https://doi.org/10.1002/anie.201809391.
[124] R.-Q. Wang, C. Shen, X. Cheng, X.-Q. Dong, C.-J. Wang, Copper-catalyzed asymmetric propargylic substitution with salicylaldehyde-derived imine esters, Chem. Commun. 58 (2022) 8552–8555, https://doi.org/10.1039/d2cc01695h.
[125] (a) Y. Takemoto, Recognition and activation by ureas and thioureas: stereoselective reactions using ureas and thioureas as hydrogen-bonding donors, Org. Biomol. Chem. 3 (2005) 4299–4306, https://doi.org/10.1039/b511216h;
(b) B. Atashkar, M.A. Zolfigol, S. Mallakpour, Applications of biological urea-based catalyst in chemical process, Mol. Catal. 452 (2018) 192–246, https://doi.org/10.1016/j.mcat.2018.03.009.
[126] A.K. Simlandy, B. Ghosh, S. Mukherjee, Enantioselective [4 + 2]-annulation of azlactones with copper-allenylidenes under cooperative catalysis: synthesis of α-quaternary α-acylaminoamides, Org. Lett. 21 (2019) 3361–3366, https://doi.org/10.1021/acs.orglett.9b01103.
[127] Q. Zhu, B. Meng, C. Gu, Y. Xu, J. Chen, C. Lei, X. Wu, Diastereo- and enantioselective synthesis of quaternary α-amino acid precursors by copper-catalyzed propargylation, Org. Lett. 21 (2019) 9985–9989, https://doi.org/10.1021/acs.orglett.9b03894.
[128] J.-M. Wang, Y. Zhao, C.-S. Yao, K. Zhang, Stereoselective synthesis of C3-tetra-substituted oxindoles via copper catalyzed asymmetric propargylation, RSC Adv. 12 (2022) 26727–26732, https://doi.org/10.1039/d2ra04603b.
[129] S. Ghosh, S. Mukherjee, Doubly stereoconvergent propargylic alkylation of α-cyanocarbonyls: enantioselective construction of vicinal stereocenters, Org. Lett. 26 (2024) 7733–7738, https://doi.org/10.1021/acs.orglett.4c02880.
[130] L. Shen, Z. Lin, B. Guo, W. Zi, Synthesis of cycloheptanoids through catalytic enantioselective (4 + 3)-cycloadditions of 2-aminoallyl cations with dienol silyl ethers, Nat. Synth. 1 (2022) 883–891, https://doi.org/10.1038/s44160-022-00150-0.
[131] Y. You, T.-T. Li, T.-J. Sun, Y.-P. Zhang, Z.-H. Wang, J.-Q. Zhao, W.-C. Yuan, Enantioselective construction of vicinal quaternary-tetrasubstituted carbon stereocenters by copper-catalyzed decarboxylative propargylic substitution, Org. Lett. 24 (2022) 7671–7676, https://doi.org/10.1021/acs.orglett.2c03244.
[132] Y.-C. Zhang, B.-W. Zhang, R.-L. Geng, J. Song, Enantioselective [3 + 2] cycloaddition reaction of ethynylethylene carbonates with malononitrile enabled by organo/metal cooperative catalysis, Org. Lett. 20 (2018) 7907–7911, https://doi.org/10.1021/acs.orglett.8b03454.
[133] X. Pu, Q.-D. Dang, L. Yang, X. Zhang, D. Niu, Doubly stereoconvergent construction of vicinal all-carbon quaternary and tertiary stereocenters by Cu/Mg-catalyzed propargylic substitution, Nat. Commun. 13 (2022) 2457, https://doi.org/10.1038/s41467-022-29986-y.
[134] C. Gui, Y. Peng, Y. Zhou, Y. Zheng, H. Wang, Q. Yan, H. Zhou, W. Wang, F.-E. Chen, Cu-catalyzed intermolecular asymmetric propargylic substitution of N-hydroxyphthalimide esters with propargyl carbonates, ACS Catal. 13 (2023) 13735–13742, https://doi.org/10.1021/acscatal.3c03814.
[135] B. Wang, C. Liu, H. Guo, Copper-catalyzed enantioselective propargylic substitution of propargylic acetates with enamines, RSC Adv. 4 (2014) 53216–53219, https://doi.org/10.1039/c4ra09431j.
[136] J.-T. Xia, X.-P. Hu, Copper-catalyzed asymmetric propargylic alkylation with oxindoles: diastereo- and enantioselective construction of vicinal tertiary and all-carbon quaternary stereocenters, Org. Lett. 22 (2020) 1102–1107, https://doi.org/10.1021/acs.orglett.9b04621.
[137] J.-T. Xia, L. Li, X.-P. Hu, Copper-catalyzed decarboxylative propargylic alkylation of enol carbonates: Stereoselective synthesis of quaternary α-amino acids, ACS Catal. 11 (2021) 11843–11848, https://doi.org/10.1021/acscatal.1c03421.
[138] C. Zhang, Y.-Z. Hui, D.-Y. Zhang, X.-P. Hu, Highly diastereo-/enantioselective Cu-catalyzed propargylic alkylations of propargyl acetates with cyclic enamines, RSC Adv. 6 (2016) 14763–14767, https://doi.org/10.1039/c5ra25627e.
[139] F.-L. Zhu, Y. Zou, D.-Y. Zhang, Y.-H. Wang, X.-H. Hu, S. Chen, J. Xu, X.-P. Hu, Enantioselective copper-catalyzed decarboxylative propargylic alkylation of propargyl β-ketoesters with a chiral ketimine P,N,N-ligand, Angew. Chem. Int. Ed. 53 (2014) 1410–1414, https://doi.org/10.1002/anie.201309182.
[140] F.-L. Zhu, Y.-H. Wang, D.-Y. Zhang, X.-H. Hu, S. Chen, C.-J. Hou, J. Xu, X.-P. Hu, Enantioselective copper-catalyzed decarboxylative propargylic alkylation of propargylic esters with β-keto acids, Adv. Synth. Catal. 356 (2014) 3231–3236, https://doi.org/10.1002/adsc.201400218.
[141] F.-Z. Han, F.-L. Zhu, Y.-H. Wang, Y. Zou, X.-H. Hu, S. Chen, X.-P. Hu, Highly enantioselective copper-catalyzed propargylic substitution of propargylic acetates with 1,3-dicarbonyl compounds, Org. Lett. 16 (2014) 588–591, https://doi.org/10.1021/ol403469m.
[142] D.-Y. Zhang, F.-L. Zhu, Y.-H. Wang, X.-H. Hu, S. Chen, C.-J. Hou, X.-P. Hu, Highly diastereo- and enantioselective copper-catalyzed propargylic alkylation of acyclic ketone enamines for the construction of two vicinal stereocenters, Chem. Commun. 50 (2014) 14459–14462, https://doi.org/10.1039/c4cc06863g.
[143] L. Shao, X.-P. Hu, Copper-catalyzed intermolecular asymmetric propargylic dearomatization of phenol derivatives, Chem. Commun. 53 (2017) 8192–8195, https://doi.org/10.1039/c7cc03034g.
[144] L. Shao, X.-P. Hu, Cu-catalyzed asymmetric Friedel–Crafts propargylic alkylation of phenol derivatives, Org. Biomol. Chem. 15 (2017) 9837–9844, https://doi.org/10.1039/c7ob02133j.
[145] H. Xu, L. Laraia, L. Schneider, K. Louven, C. Strohmann, A.P. Antonchick, H. Waldmann, Highly enantioselective catalytic vinylogous propargylation of coumarins yields a class of autophagy inhibitors, Angew. Chem. Int. Ed. 56 (2017) 11232–11236, https://doi.org/10.1002/anie.201706005.
[146] B.G. Das, S. Shah, A. Das, V.K. Singh, Cu-catalyzed chemodivergent, stereoselective propargylic dearomatization and etherification of 2-naphthols, Org. Lett. 23 (2021) 6262–6266, https://doi.org/10.1021/acs.orglett.1c02027.
[147] Z. Li, D. Li, H. Xiang, J. Huang, Y. Zheng, C. Zhu, X. Cui, C. Pi, H. Xu, Copper-catalyzed asymmetric propargylic substitution of anthrones and propargylic esters, Chin. Chem. Lett. 33 (2022) 867–870, https://doi.org/10.1016/j.cclet.2021.08.009.
[148] H.-D. Qian, Z.-H. Li, S. Deng, C. Yao, H.-M. Xiang, G. Xu, Z.-Q. Geng, Z. Wang, L. Chen, C. Liu, C. Zhu, X. Qi, H. Xu, Catalytic asymmetric vinylogous and bisvinylogous propargylic substitution, J. Am. Chem. Soc. 144 (2022) 15779–15785, https://doi.org/10.1021/jacs.2c06560.
[149] Z.-J. Zhang, L. Zhang, R.-L. Geng, J. Song, X.-H. Chen, L.-Z. Gong, N-heterocyclic carbene/copper cooperative catalysis for the asymmetric synthesis of spirooxindoles, Angew. Chem. Int. Ed. 58 (2019) 12190–12194, https://doi.org/10.1002/anie.201907188.
[150] S. Zuo, Y. Tao, Z. Liu, K. Zhang, L. Zhang, Y. Ning, F.-E. Chen, Construction of vicinal all-carbon stereogenic centers via copper-catalyzed asymmetric decarboxylative propargylation: enantio- and diastereoselective synthesis of substituted spirolactones, Org. Lett. 25 (2023) 410–415, https://doi.org/10.1021/acs.orglett.2c04113.
[151] K. Nakajima, M. Shibata, Y. Nishibayashi, Copper-catalyzed enantioselective propargylic etherification of propargylic esters with alcohols, J. Am. Chem. Soc. 137 (2015) 2472–2475, https://doi.org/10.1021/jacs.5b00004.
[152] R.-Z. Li, H. Tang, K.R. Yang, L.-Q. Wan, X. Zhang, J. Liu, Z. Fu, D. Niu, Enantioselective propargylation of polyols and desymmetrization of meso 1,2-diols by copper/borinic acid dual catalysis, Angew. Chem. Int. Ed. 56 (2017) 7213–7217, https://doi.org/10.1002/anie.201703029.
[153] R.-Z. Li, H. Tang, L. Wan, X. Zhang, Z. Fu, J. Liu, S. Yang, D. Jia, D. Niu, Site-divergent delivery of terminal propargyls to carbohydrates by synergistic catalysis, Chem 3 (2017) 834–845, https://doi.org/10.1016/j.chempr.2017.09.007.
[154] K. Tsuchida, M. Yuki, K. Nakajima, Y. Nishibayashi, Copper- and borinic acid-catalyzed propargylic etherification of propargylic carbonates with benzyl alcohols, Chem. Lett. 47 (2018) 671–673, https://doi.org/10.1246/cl.180123.
[155] S. Liu, K. Nakajima, Y. Nishibayashi, Copper-catalysed enantioselective intramolecular etherification of propargylic esters: synthetic approach to chiral

isochromans, RSC Adv. 9 (2019) 18918–18922, https://doi.org/10.1039/c9ra03880a.
[156] Y. Hou, Z. Zhang, X. Sun, Z. Yang, Y.-X. Luan, P. Tang, Copper-catalyzed enantioselective trifluoromethoxylation of propargylic sulfonates, Angew. Chem. Int. Ed. 62 (2023) e202218919, https://doi.org/10.1002/anie.202218919.
[157] R.-Z. Li, D.-Q. Liu, D. Niu, Asymmetric O-propargylation of secondary aliphatic alcohols, Nat. Catal. 3 (2020) 672–680, https://doi.org/10.1038/s41929-020-0462-9.
[158] L. Shao, D.-Y. Zhang, Y.-H. Wang, X.-P. Hu, Enantioselective copper-catalyzed propargylic etherification of propargylic esters with phenols promoted by inorganic base additives, Adv. Synth. Catal. 358 (2016) 2558–2563, https://doi.org/10.1002/adsc.201600284.
[159] D.-Q. Wei, Z.-T. Liu, X.-M. Wang, C.-J. Hou, X.-P. Hu, Copper-catalyzed asymmetric propargylic etherification of oximes promoted by chiral tridentate P,N,N-ligand, Tetrahedron Lett. 60 (2019) 151305, https://doi.org/10.1016/j.tetlet.2019.151305.
[160] L.-J. Cheng, A.P.N. Brown, C.J. Cordier, From propargylic fluorination to [1,3]-rearrangements: anion and ligand effects in Cu-acetylide chemistry, Synlett 29 (2018) 1675–1682, https://doi.org/10.1055/s-0036-1591997.
[161] J.E. Gómez, À. Cristòfol, A.W. Kleij, Copper-catalyzed enantioselective construction of tertiary propargylic sulfones, Angew. Chem. Int. Ed. 58 (2019) 3903–3907, https://doi.org/10.1002/anie.201814242.
[162] A. Garcia-Roca, R. Pérez-Soto, G. Stoica, J. Benet-Buchholz, F. Maseras, A.W. Kleij, Comprehensive mechanistic scenario for the Cu-mediated asymmetric propargylic sulfonylation forging tertiary carbon stereocenters, J. Am. Chem. Soc. 145 (2023) 6442–6452, https://doi.org/10.1021/jacs.3c00188.
[163] X. Gao, Y.-L. Xiao, S. Zhang, J. Wu, X. Zhang, Copper-catalyzed enantioselective trifluoromethylthiolation of secondary propargylic sulfonates, CCS Chem. 3 (2020) 1463–1471, https://doi.org/10.31635/ccschem.020.202000353.
[164] C. Wang, M. Xiao, W. Li, L.-J. Cheng, Copper-catalyzed enantioselective O,S-rearrangement of propargylic xanthates: efficient synthesis of chiral propargylic sulfur compounds, ACS Catal. 14 (2024) 13283–13290, https://doi.org/10.1021/acscatal.4c04509.
[165] Z. Wang, C. Nicolini, C. Hervieu, Y.-F. Wong, G. Zanoni, L. Zhang, Remote cooperative group strategy enables ligands for accelerative asymmetric gold catalysis, J. Am. Chem. Soc. 139 (2017) 16064–16067, https://doi.org/10.1021/jacs.7b09136.
[166] Y. Wei, J. Jiang, Y. Jing, Z. Ke, L. Zhang, Bifunctional ligand enables gold-catalyzed propargylic C–H functionalization via reactive gold allenylidene intermediate, Angew. Chem. Int. Ed. 63 (2024) e202402286, https://doi.org/10.1002/anie.202402286.