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Stereoselective synthesis of substituted 1,3-dienes from propargylic esters: electrophilic-metal or redox catalysis?

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1,3-Diene architectures are not only widely present in natural products, pharmaceuticals, and functional organic materials but also serve as versatile building blocks to furnish important functionalized molecules in synthetic chemistry due to conjugated repeating C=C units. Accordingly, various strategies to access substituted 1,3-dienes in a stereoselective manner have been developed. However, chemo-, regio- and stereoselective synthesis of highly substituted 1,3-dienes still remains elusive and challenging. Readily available propargylic esters have emerged as an appealing class of synthetic intermediates for accessing functionalized 1,3-dienes, especially challenging tri- or tetrasubstituted variants, *via* transition-metal catalysis, including electrophilic metal and redox neutral catalysis. This review, for the first time, systematically highlights recent advances in transition-metal catalyzed synthesis of substituted 1,3-dienes from propargylic esters, discusses the mechanisms and synthetic utilities, and gives the remaining challenges and potential opportunities in this field.

1, 3-diene, propargylic ester, Lewis acid, redox catalysis, transition metal

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1 Introduction

1,3-Dienes are unique and important backbones, widely present in natural products, bioactive molecules, pharmaceuticals, and functional organic materials (Figure 1) [1]. Due to the different molecular orbital levels, it is not a simple combination of two olefins, and their properties and reactivity are distinct from olefin and non-conjugated dienes. Compared with olefin and non-conjugated diene, 1,3-diene bearing the same substituents has a higher HOMO (highest occupied molecular orbital) and lower LUMO (lowest unoccupied molecular orbital) energies, directly affecting reaction results [2]. Based on the special structure and reactivity, 1,3-dienes have been employed as versatile building blocks in a wide range of transformations (such as cycloaddition [3], transition metal-catalyzed cross-coupling [4], metathesis [5], difunctionalization [6], and ene-reaction [7]), modularly constructing natural products, drugs, and functionalized molecules [8]. Additionally, they are also essential for the development of material science by acting as synthetic intermediates in polymerization processes [9]. Moreover, 1,3-dienes have served as a versatile platform for exploring new transformations, forging structurally novel and valuable compounds [10]. Thus, more and more attention from academic and industrial communities has been paid to synthesizing libraries of 1,3-dienes. As the number and relative position of substituents, as well as the stereochemistry of 1,3-dienes, play vital roles in their synthetic

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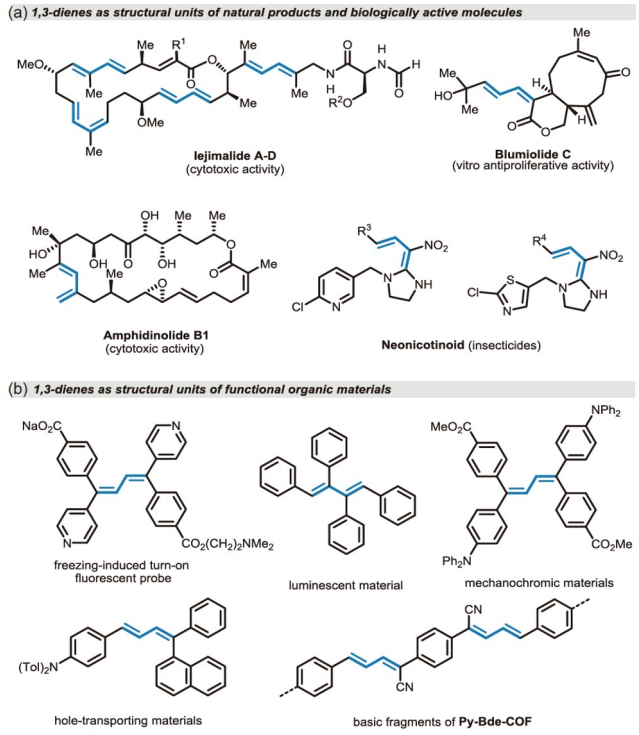


Figure 1 Selected examples of natural products, pharmaceuticals, and functional organic materials containing 1,3-diene architectures (color online).

transformations and bioactivities [11], lots of efforts have been made to develop efficient strategies for the synthesis of highly substituted 1,3-dienes in a chemo-, regio- and stereoselective manner [12,13].

Traditional routes to 1,3-dienes often require multi-step and tedious processes as well as stoichiometric reagents [12c–12e], largely preventing the broad applications of 1,3-dienes. It is essential to develop concise and catalytic methods for synthesizing substituted 1,3-dienes from commercially available starting materials. Over the past decades, an array of elegant catalytic methodologies has been devoted to the synthesis of substituted 1,3-dienes from 1,3-enynes [14], alkenes [15], alkynes [16], and allenes [17]. Despite major advances, they are often restricted to the synthesis of terminal 1,3-dienes and meet with poor generality. Developing highly efficient and general methods is still required.

Propargylic esters are easily accessible compounds, displaying versatile and switchable reactivities under transition-metal catalysis [18–23]. They show great potential for constructing substituted 1,3-dienes, especially tri- and tetra-substituted 1,3-dienes [4a,19]. However, this process is challenging due to multiple competing reactions, such as propargylation [20], allenylation [21], and alkenylation [18,22]. Electrophilic transition metals (such as Au, Cu, Pt, and Zn) have proven to effectively activate propargylic esters towards typical 1,2- and/or 1,3-acyloxy migration (3,3-acyloxy rearrangement), providing a powerful and efficient approach to substituted 1,3-dienes in a chemo-, regio- and stereoselective manner [13a,23]. The selectivity between the competing 1,2- and 1,3-acyloxy migration is primarily influenced by transition metal, temperature, steric hindrance, and electronics of substituents at either end of propargyl moiety [24]. Metal catalyst directly determines the reaction mechanism. Changing the metal type or adjusting the electronic and steric effects of the metal center could switch the reaction activity. It is widely recognized that propargylic esters bearing terminal [25] or electron-poor [26] triple bonds prefer 1,2-acyloxy migration, whereas these with electronically unbiased internal triple bonds undergo 1,3-acyloxy migration [23b,27]. In addition, palladium- or nickel-catalyzed cross-coupling reactions of propargylic esters with carbon, nitrogen, oxygen, or phosphine nucleophiles provide importantly complementary accesses to substituted 1,3-dienes *via* the key metallaocyclobutene intermediate in a redox-neutral, chemo-, regio- and stereoselective manner [18,19]. This review highlights recent advances in the transition-metal catalyzed synthesis of substituted 1,3-dienes from propargylic esters after the year 2005 (Figure 2). For the sake of clarity, we divide this review into the following sections based on the reaction patterns modulated by transition metals: (a) Lewis acid-catalyzed synthesis, (b) transition metal-catalyzed redox-neutral synthesis, and (c) others.

2 Synthesis of substituted 1,3-dienes from propargylic esters

2.1 Lewis acid-catalyzed synthesis

Transition metals such as Au, Cu, Pt and Zn have been employed as Lewis acids to activate propargylic esters, followed by 1,2- or 1,3-acyloxy migration to deliver substituted 1,3-dienes. The regioselective formation of five-membered or six-membered intermediate *via* the attack of oxygen in

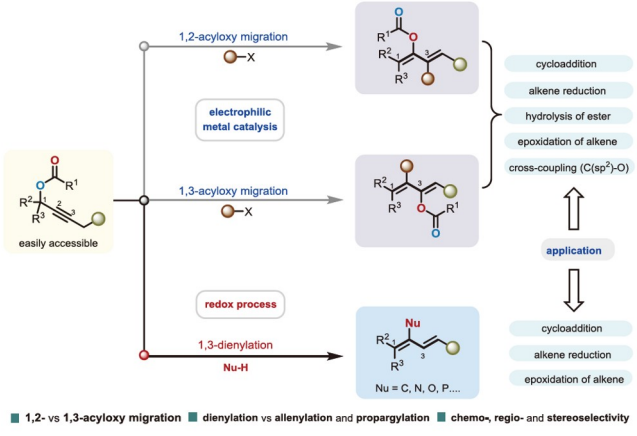
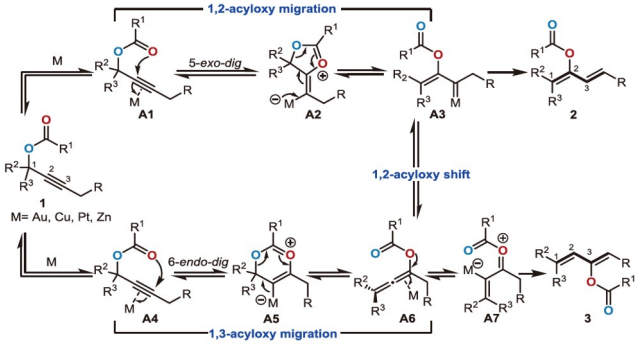


Figure 2 Transition-metal catalyzed synthesis of substituted 1,3-dienes from propargylic esters (color online).

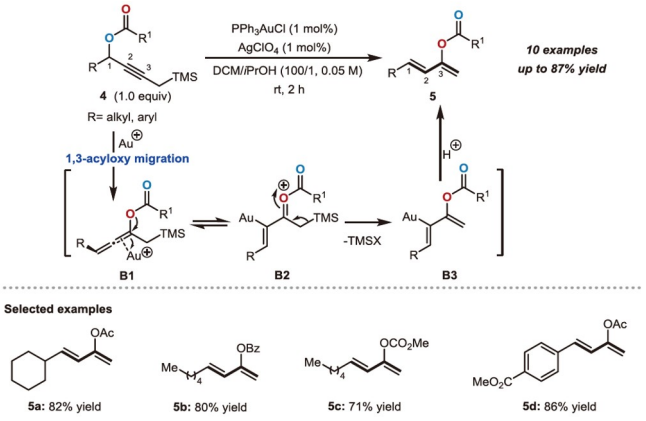
acyl to triple bond is the key step to generate 1,3-dienes bearing different positions of acyloxy groups. Generally, the triple bond in propargylic carboxylates **1** is firstly activated by the coordination with a transition metal, followed by 5-*exo-dig* or 6-*endo-dig* cyclization to give intermediate **A2** or **A5** (Scheme 1) [23a]. Sequential C–O bond cleavage forms carbene **A3** and carboxyallene **A6**. Carbene **A3** undergoes irreversible 1,2-C–H insertion, leading to the generation of 2-acyloxy-1,3-diene **2**. Carboxyallene **A6** is further activated by the metal catalyst to give oxocarbenium **A7**, followed by proton transfer to deliver 3-acyloxy-1,3-diene **3**.

2.1.1 1,3-Acyloxy migration

In 2006, Zhang and co-workers [28] reported a gold(I)-catalyzed reaction of propargylic esters **4** to efficiently synthesize terminal disubstituted 1,3-dienes **5** through tandem Au-catalyzed 1,3-acyloxy migration/desilylation (Scheme 2). For this method, dry DCM had to be used to reduce the formation of side product α,β-unsaturated ketones. Moreover, proton sources such as *i*PrOH were critical for the selective generation of 1,3-dienes. This approach featured mild reaction conditions, high yields, and excellent *E*-selectivity of the nonenolic double bond.



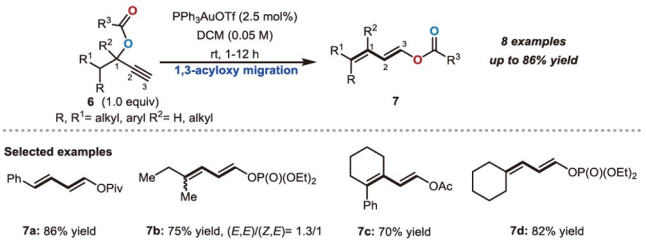
Scheme 1 General pathways to deliver substituted 1,3-dienes through 1,2- or 1,3-acyloxy migration (color online).



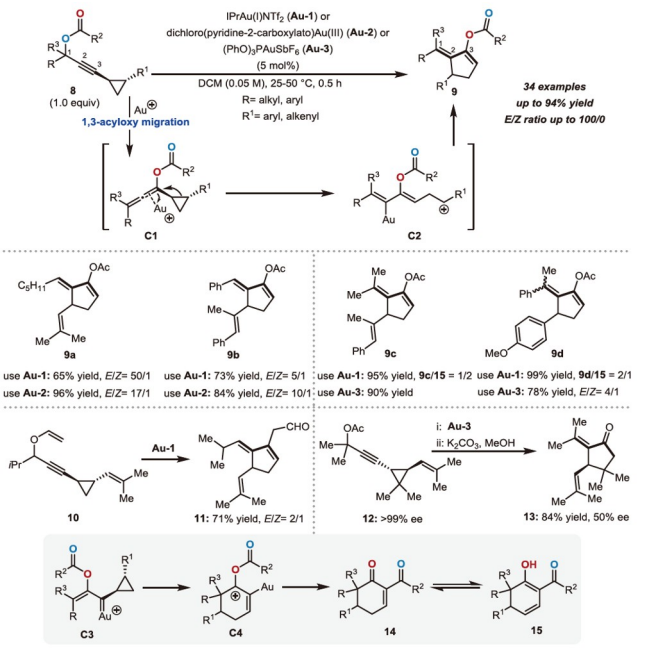
Scheme 2 Synthesis of terminal disubstituted 1,3-dienes through tandem Au-catalyzed 1,3-acyloxy migration/desilylation (color online).

Gevorgyan and co-workers [29] developed a mild and stereoselective gold(I)-catalyzed method of propargylic esters **6** for the construction of internal substituted (1*E*,3*E*)-dienes **7** *via* Au-catalyzed 1,3-acyloxy migration/proton transfer cascade (Scheme 3). This reaction was compatible with propargyl carboxylates and phosphates, giving the sole (1*E*,3*E*)-isomers in high yields. However, for propargyl phosphates bearing unsymmetrical substitutions at the β-position, the isomerization occurred to afford reduced stereoselectivity (**7b**).

In 2010, diverse polysubstituted 1,3-dienes were synthesized by Nevado and co-workers [30]. The selective construction of 5-(*E*)-alkylidenecyclopentenyl acetates **9** was achieved from 3-cyclopropyl propargylic carboxylates **8** (Scheme 4). In the presence of $IPrAuNTf_2$ catalyst, this reaction undergoes tandem 1,3-acyloxy migration and cyclopropyl ring opening, followed by cyclization to deliver the desired dienes. In some cases, dichloro(pyridine-2-carboxylato) gold(III) catalyst gave higher yield and/or better *E*/*Z*



Scheme 3 Synthesis of substituted (1*E*,3*E*)-dienes *via* Au-catalyzed 1,3-acyloxy migration/proton transfer cascade (color online).

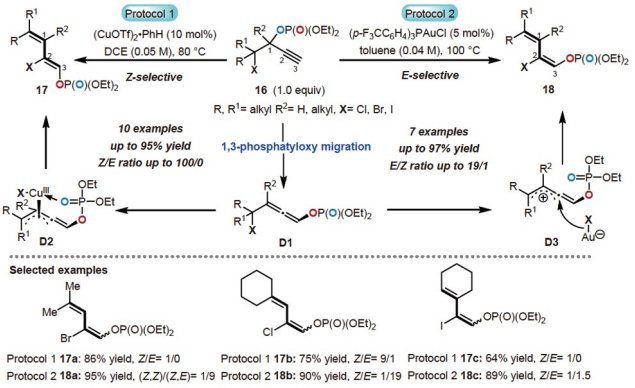


Scheme 4 Synthesis of 5-(*E*)-alkylidenecyclopentenyl acetates from 3-cyclopropyl propargylic carboxylates (color online).

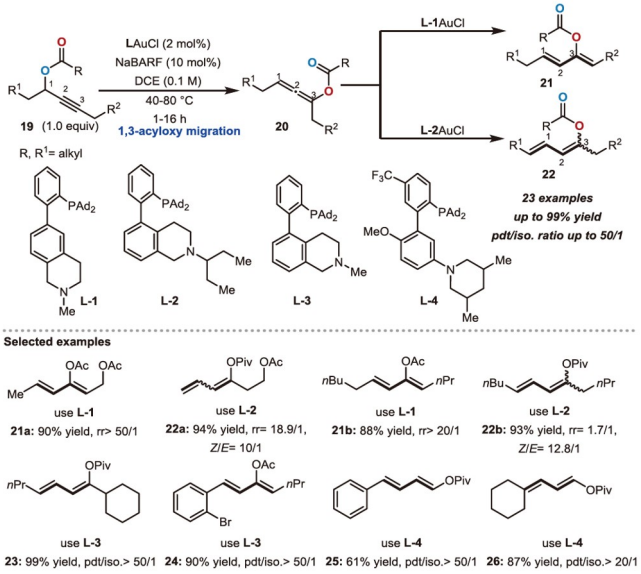
selectivity. Notably, tertiary propargyl acetates were well tolerated to afford the corresponding cyclopentenyl acetates (**9c** and **9d**) under $IPrAuNTf_2$ catalyst, but together with a respectable amount of 1,3-diketones **14**/**15**. The occurrence of 1,3-diketones **14**/**15** was proposed to be attributed to the formation of gold carbene **C3** *via* 1,2-acyloxy migration, followed by sequential cyclopropyl ring opening, cyclization and the fission of the acetate group. Further studies showed that $(PhO)_3PAuSbF_6$ could provide the clean generation of cyclopentenyl acetates in high yields. The distinct results depended on the ligand bound to the gold center. Compared with $IPrAuNTf_2$, $(PhO)_3PAuSbF_6$ is more electrophilic because of the π-acceptor phosphine ligand. The reduced π-donation in gold-to-C probably improves the carbocationic character of reaction intermediates, thus preferring the cyclopentannulation products. Additionally, IPr is a strong σ-donating and weak π-acidic ligand, thus enhancing the carbene-like reactivity. Undeniably, steric hindrance is another important factor. Besides carboxylic groups, propargyl vinyl ether **10** was compatible with this method to form two new C–C bonds. When optically pure propargylic carboxylate **12** was used in this reaction, the chirality transfer was not complete in the cyclopentannulation products. Experimental evidence and DFT calculations suggested that Au-promoted cyclopropyl ring opening/epimerization/ring closure would compete with the desired cyclization, thus eroding the chirality transfer.

Following this line, Gevorgyan and co-workers [31] presented a double migratory transformation of α-halogen-substituted propargylic phosphates **16**, delivering highly functionalized 1,3-dienes **17** and **18** in high yields and stereoselectivities (Scheme 5). The key to the success of this reaction was sequential 1,3-phosphatyloxy migration and 1,3-halogen migration, including chlorine, bromine and even iodine. Under copper catalysis, this reaction exclusively afforded (*Z*)-1,3-dienes **17**, whereas (*E*)-1,3-dienes **18** predominantly formed in the presence of a gold(I) catalyst. As proposed, propargylic phosphate undergoes 1,3-phosphatyloxy migration to give allenyl phosphate **D1**. For copper catalysis, the coordination of copper to phosphate group followed by oxidative addition with halogen affords Cu^{III} complex **D2**. Reductive elimination directed by the phosphate group forms the (*Z*)-1,3-diene **17** in a syn-selective way. Alternatively, for gold catalysis, the halogen abstraction produces π-allyl cation **D3**. Sequential regeneration of carbon-halogen delivers (*E*)-1,3-diene **18** from backside attack.

As we all know, ligands play important roles in transition metal catalysis, such as controlling the chemo-, regio- and stereoselectivity. In 2017, Zhang and co-workers [23b] developed a series of remotely functionalized biphenyl-2-yl-phosphine ligands (**L-1** to **L-4**) to form gold-based frustrated Lewis pairs, that is, basic tertiary amine moieties and the acidic gold center (Scheme 6). Through a rational switch of



Scheme 5 Synthesis of functionalized 1,3-dienes from α-halogen-substituted propargylic phosphates (color online).

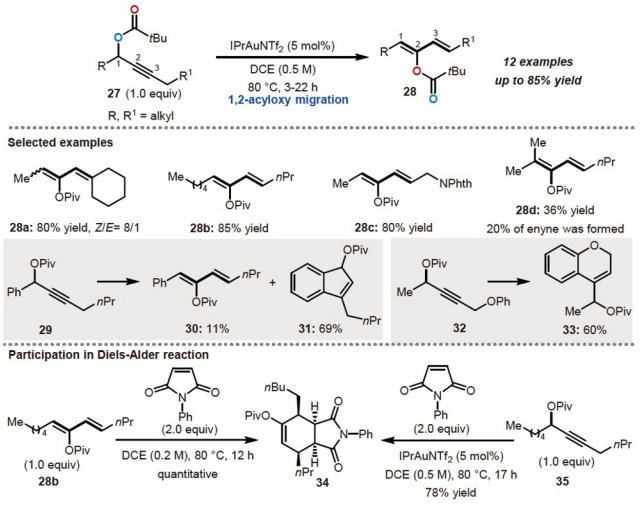


Scheme 6 Isomerization of propargylic esters into dienyl esters using gold-based frustrated Lewis pairs (color online).

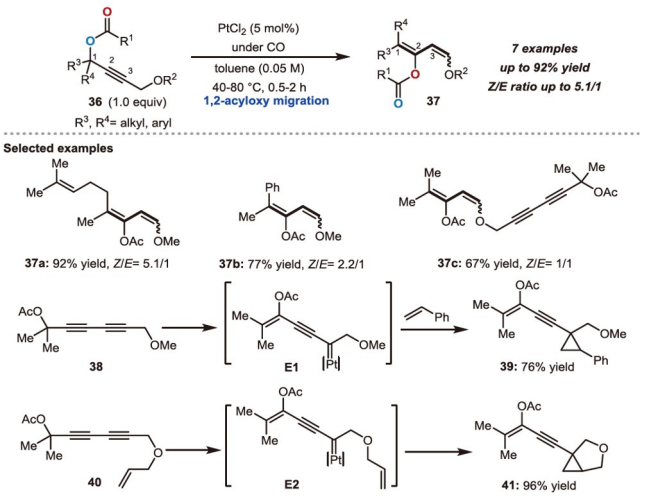
the size and location of a tertiary amine, these Lewis pairs enabled the isomerization of propargylic esters **19** into dienyl esters **21** and **22** under mild conditions in a regiodivergent and stereoselective manner. The worse results of electronically and sterically comparable as well as structurally related JohnPhos indicated that the remote basic tertiary amine moieties in the designed ligands are significantly critical.

2.1.2 1,2-Acyloxy migration

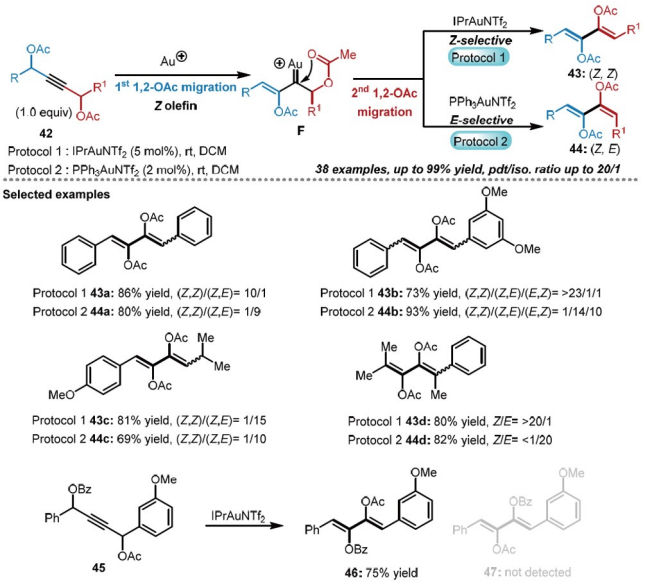
In 2008, Zhang and co-workers [23a] reported a gold(I)-catalyzed 1,2-acyloxy migration of propargylic pivalates **27** bearing electronically unbiased internal alkynes, selectively leading to (1*Z*,3*E*)-2-pivaloxy-1,3-dienes **28** in high yields (Scheme 7). However, propargylic esters derived from ketones (**28d**) did not work well in giving much lower yields (36% yield) due to the major side reaction of the elimination to form enynes. When phenyl-substituted propargylic piva-



Scheme 7 Gold(I)-catalyzed 1,2-acyloxy migration of propargylic pivalates bearing electronically unbiased internal alkynes (color online).



Scheme 8 The role of propargylic oxygen substituent in the preference of 1,2-acyloxy migration by using $PtCl_2$ (color online).



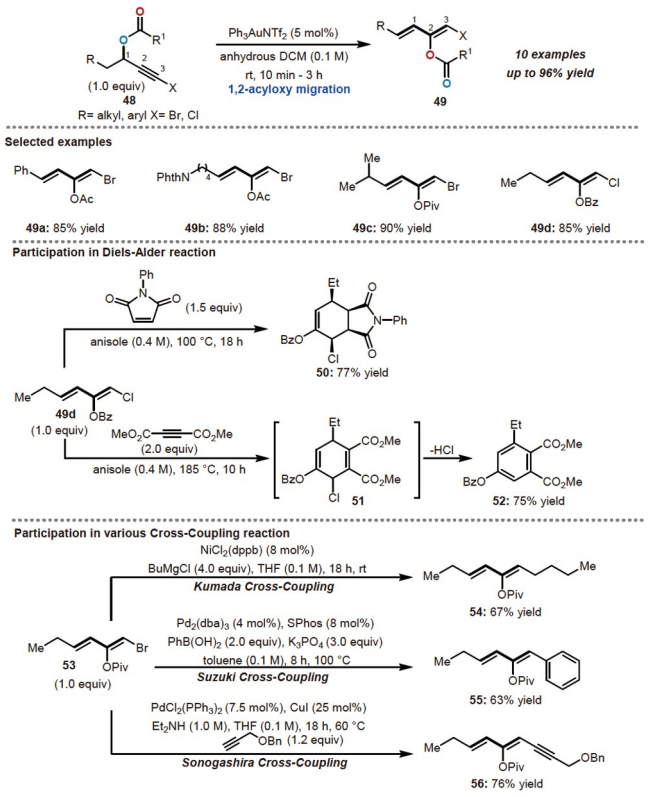
Scheme 9 Gold(I)-catalyzed tandem 1,2-/1,2-bis(acetoxy) migration of 1,4-bis(propargyl acetates) (color online).

lates **29** and **32** were used, electrophilic cyclization of triple bond with phenyl group preferred to mainly give cyclic products (**31** and **33**). The formed dienes were well tolerated in the Diels-Alder reaction to afford cyclic product **34** under thermal conditions. Notably, propargylic pivalate **35** could be employed as the starting materials to deliver the Diels-Alder product **34** in Au(I)-catalyzed one-pot process.

In concurrence with the above report, Lee and Cho [32] described the role of the propargylic oxygen substituent in the preference of 1,2-acyloxy migration by using $PtCl_2$ (Scheme 8). For the sequential carbenoid insertion, vinyl Pt-carbenoids showed a higher tendency to undergo 1,2-H shift, while alkynyl Pt-carbenoids displayed the propensity to undergo addition to π-bonds in an intra- or intermolecular manner. Therefore, substrates containing a propargylic alkoxy substituent underwent 1,2-acyloxy migration and 1,2-H shift cascade to give 1,3-dienes **37**; substrates containing diyne moiety underwent 1,2-acyloxy migration followed by cycloaddition to deliver cyclic products (**39** and **41**). For substrates containing both propargylic alkoxy substituent and diyne moiety preferred to undergo 1,2-acyloxy migration and 1,2-H shift cascade to afford 1,3-dienes (**37c**), indicating that monoyne is more reactive than the corresponding diyne. Further investigations indicated that 1,2- and 1,3-acyloxy migration could be selectively controlled by switching the reaction temperature, the substituents on alkyne, and the catalyst.

In 2009, Nevado and co-workers [13a,13b] reported a gold(I)-catalyzed tandem 1,2-/1,2-bis(acetoxy) migration of 1,4-bis(propargyl acetates) **42** to afford 2,3-bis(acetoxy)-1,3-dienes **43** and **44** in high yields (Scheme 9). By carefully selecting the electronic and steric features of substrates and gold catalysts, (1*Z*,3*Z*)- or (1*Z*,3*E* and 1*E*,3*Z*)-1,3-dienes were selectively generated. In all cases, no allene product was detected. When propargylic ester bearing two different carboxyl groups was used in the presence of $IPrAuNTf_2$, only product **46** involving 1,2-/1,2-bis(acetoxy) migration was observed, ruling out the reaction pathway *via* double 1,3-bis(carboxylate) migration.

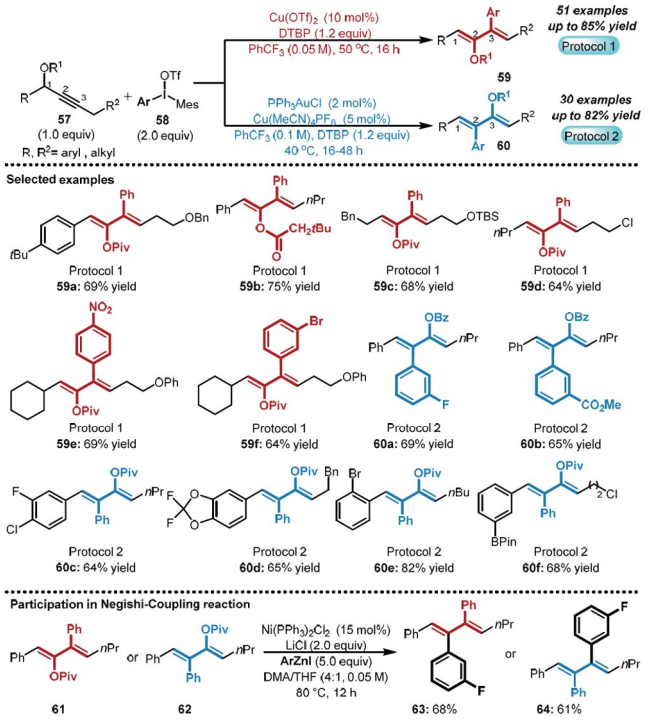
Subsequently, Zhang and co-workers [33] used Br/Cl to improve the regioselective gold(I)-catalyzed 1,2-acyloxy migration of propargylic carboxylates **48**, providing an efficient approach to (1*Z*,3*E*)-1-bromo/chloro-2-carboxy-1,3-dienes **49** in high yields (Scheme 10). This reaction showed excellent stereoselectivity, only giving the (1*Z*,3*E*)-isomers. Notably, the diene products could be employed in the diverse Diels-Alder and transition metal-catalyzed cross-coupling reactions. Compared with bromodienes, chlorodienes (**49d**) rendered cycloadducts more stable and easier to isolate.



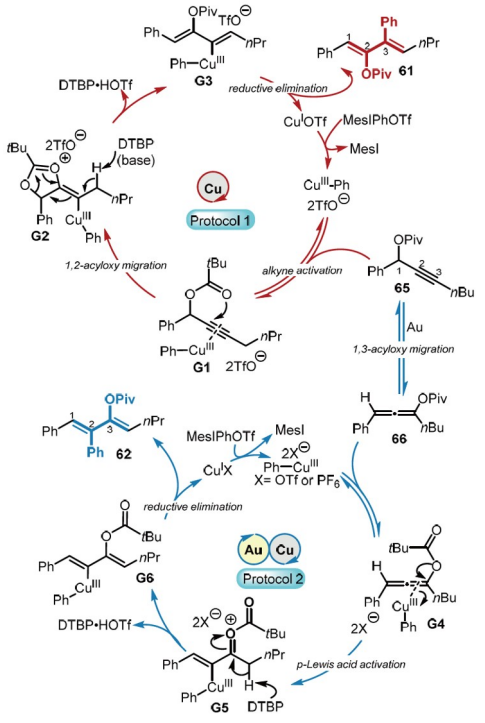
Scheme 10 Gold-catalyzed synthesis of (1*Z*,3*E*)-1-bromo/chloro-2-carboxy-1,3-dienes (color online).

Reacting with dimethyl acetylenedicarboxylate in 185 °C directly afforded highly substituted benzene **52** through *in situ* aromatization of the initial cycloadduct **51**. Reacting with N-phenylmaleimide in lower temperatures delivered enol ester **50** in 77% yield. Besides, the diene products **53** could easily participate in Kumada, Suzuki and Sonogashira cross-coupling reactions to generate various functionalized dienes **54**–**56**.

Very recently, Chen and co-workers [4a] disclosed the first catalyst-controlled regiodivergent synthesis of structurally diverse 1,2,3,4-tetrasubstituted conjugated dienes **59** and **60** with excellent regio- and stereoselectivities from the same propargyl esters **57** and diaryliodonium salts **58** (Scheme 11). By using $Cu(OTf)_2$ as the catalyst, 2-acyloxy-3-aryl dienes **59** were generated in high yields. Through the combination of $Cu(CH_3CN)_4PF_6$ and PPh_3AuCl, 2-aryl-3-acyloxy dienes **60** were produced in high yields with excellent chemo-, regio- and stereoselectivities. The *in situ* formed aryl-Cu^{III} complex not only played the role of alkyne activation/acyloxy migration but also of aryl electrophile equivalent. As proposed, oxidative addition between diaryliodonium triflate and Cu^{I} gives Cu^{III}-Ph intermediate, which activates the triple bond in propargyl ester **65** to form intermediate **G1** (Scheme 12) [4a]. Subsequent 1,2-acyloxy migration *via* 5-*exo*-*dig* cyclization generates the oxocarbenium organocopper **G2**, followed by deprotonation and reductive elimination to deliver 2-acyloxy-3-aryl diene **61** and regenerate Cu^{I}. Alternatively, propargyl ester **65** undergoes 1,3-acyloxy migration by gold(I) catalysis to give carboxyallene **66**,



Scheme 11 Catalyst-controlled regiodivergent synthesis of 1,2,3,4-tetrasubstituted conjugated dienes (color online).



Scheme 12 Mechanism for access to 1,2,3,4-tetrasubstituted 1,3-dienes (color online).

which is activated by Cu^{III}-Ph to form intermediate **G5**. Sequential deprotonation and reductive elimination deliver 2-aryl-3-acyloxy diene **62** and regenerate Cu^{I}.

2.2 Transition metal-catalyzed redox-neutral synthesis

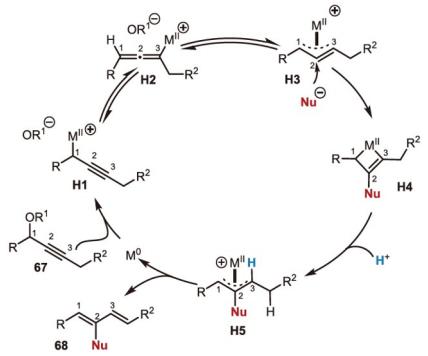
Transition metal-catalyzed cross-coupling reactions of propargyl electrophiles provide a platform for the synthesis of functionally versatile molecules from the same starting materials in a regiodivergent manner. Palladium- or nickel-catalyzed intramolecular or intermolecular cross-coupling reactions of propargylic esters have proven to effectively synthesize substituted 1,3-dienes in a redox-neutral, chemo-, regio- and stereoselective manner. Diverse nucleophiles, such as amides, phenols, indoles, alkanols, silanols, carboxylic acids, diethyl phosphites, phosphine oxides, diarylacetonitriles and 1,3-dicarbonyl compounds, have been explored. Generally, M^0 firstly undergoes oxidative addition with propargylic ester **67** to give three equilibrium intermediates, η^1-σ-propargyl, η^1-σ-allenyl and η^3-π-propargyl metal complexes (**H1**, **H2** and **H3**) (Scheme 13) [18,19]. Subsequently, the nucleophile attacks the central carbon of η^3-π-propargyl-metal complex **H3**, leading to metalacyclobutene intermediate **H4**. Sequential protonation affords π-allyl metal complex **H5**, which undergoes β-H elimination to deliver diene **68** and regenerate M^0 species.

2.2.1 *Intramolecular reaction*

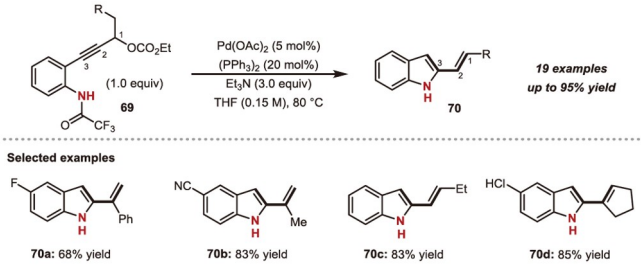
In 2009, Cacchi and co-workers [34] reported a palladium-catalyzed synthesis of 2-vinylic indoles **70** from 3-(*o*-trifluoroacetamidoaryl)-1-propargylic esters **69** bearing an alkyl substituent at the propargylic carbon (Scheme 14). This reaction featured broad scope, high yields and excellent stereoselectivities, only giving *trans* 2-vinylic indoles.

Considering the importance of spirocycles, Hamada and co-workers [35] reported a novel method for the synthesis of spirocycles **73** and **74** from phenols **71** and indoles **72** through palladium-catalyzed intramolecular *ipso*-Friedel-Crafts alkylation (Scheme 15). Spirocyclic adducts **73** and **74** were generated in high yields and excellent selectivities. Control experiments indicated that this reaction undergoes rearomatization-assisted oxidative addition. As proposed, the oxidative addition of Pd^0 into propargylic esters **75** gives η^1-allenylpalladium(II) species, followed by reductive elimination to form intermediate **76**. A rearomatization-assisted oxidative addition of Pd^0 into intermediate **76** generates η^1- and η^3-propargylpalladium(II) complexes (**I1** and **I2**). Intramolecular *ipso*-Friedel-Crafts alkylation produces palladacyclobutene intermediate **I3**. Sequential protonation and β-H elimination deliver spirocyclic adduct **77**.

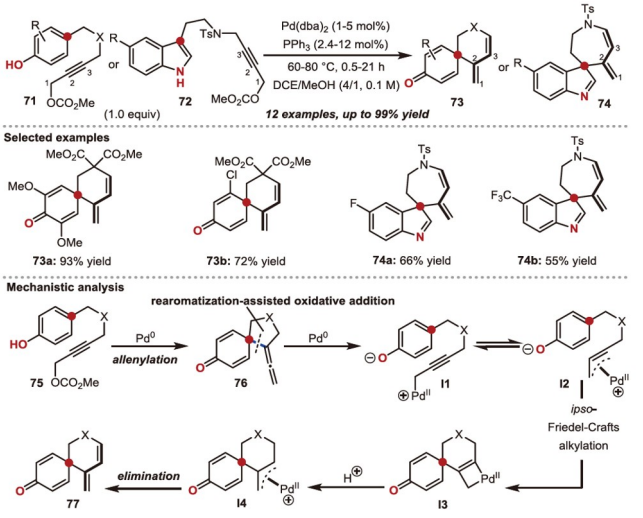
Along the line, Paton and Anderson [36] presented a palladium-catalyzed cyclization of propargylic carbonates **78** for the synthesis of cyclic dienamides **79** and 2-alkynyl azacycles **80** (Scheme 16). The regioselectivity of this reaction profoundly depended on the bite angle of the bidentate phosphine ligand. Ligands bearing small bite angles were beneficial for the attack on the central carbon atom of allenylpalladium intermediate, leading to cyclic dienamides **79**. Ligands with large bite angles mainly resulted in alkynyl azacycles **80**. The regioselectivity was also explained by a computational analysis.



Scheme 13 General pathways to deliver substituted 1,3-dienes through oxidative addition and β-H elimination (color online).



Scheme 14 Palladium-catalyzed synthesis of 2-vinylic indoles from 3-(*o*-trifluoroacetamidoaryl)-1-propargylic esters (color online).



Scheme 15 Palladium-catalyzed intramolecular *ipso*-Friedel-Crafts alkylation of phenols or indoles for the synthesis of spirocycles (color online).

2.2.2 *Intermolecular reaction*

In 2013, Hou and Hu *et al*. [37] reported an efficient method for the synthesis of 1,3-dienylphosphonates **83** from the palladium-catalyzed substitution of terminal propargylic esters **81** with diethyl phosphite **82** (Scheme 17). Alkyl- and aryl-substituted 1,3-dienylphosphonates were obtained in modest to good yields.

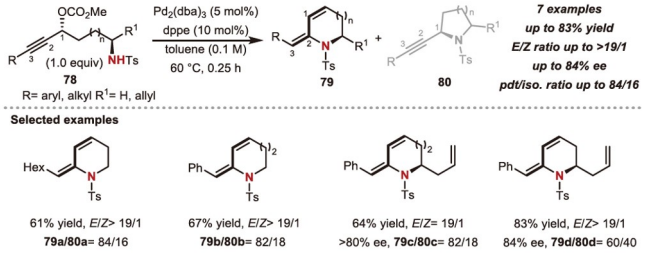
Quaternary carbon centers are widely present in lots of natural products and bioactive molecules. Based on this, Tunge and co-workers [38] reported a palladium-catalyzed addition of diarylacetonitriles **85** to propargylic carbonates **84** in a ligand-controlled and regioselective manner (Scheme 18). By switching the employed phosphine ligand, terminal 1,3-dienyl **86** and propargylated products, **87** could be selectively formed.

In order to extend the scope of nucleophiles, Murakami and co-workers [39] disclosed a nickel-catalyzed stereoselective synthesis of 2-aryoxy-1,3-dienes **90** from propargyl carbonates **88** and phenols **89** (Scheme 19). This reaction featured high yields, excellent functional group tolerance involving iodo, formyl and boryl groups, and broad scope, including substrates derived from natural products. Besides phenols, other oxygen nucleophiles such as alkanols and silanol were also tolerated to give the corresponding 1,3-dienes (**90g** and **90h**) in moderate yields while requiring the employment of nucleophiles (5.0 equiv). Under standard conditions, nitrogen nucleophiles like indazole were not compatible, delivering the corresponding dienes in <5% yields.

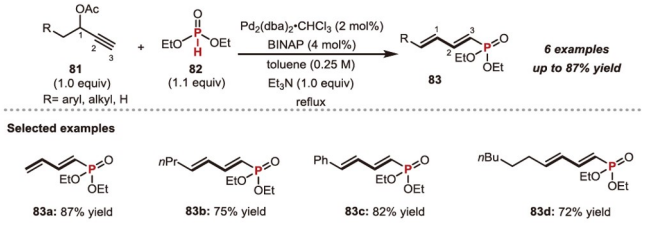
In 2020, Guiry and co-workers [40] reported a palladium-catalyzed C–N cross-coupling reaction from propargyl carbonates **91**, leading to 2-amino-1,3-dienes **93** in excellent yields (Scheme 20). This reaction showed mild neutral conditions and broad substrate scope, such as more than 30 amines involving anilines and indoles.

Following this direction, Ishida and Murakami [41] reported a nickel-catalyzed 1,3-dienylation between 1,3-dicarbonyl compounds **95** and propargylic carbonates **94** (Scheme 21). Diverse quaternary carbon-substituted 1,3-dienes **96** were synthesized in good yields.

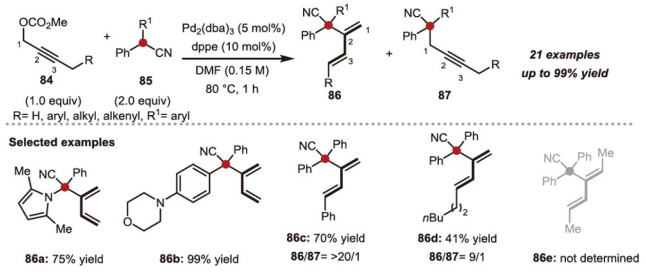
In 2022, Guo and co-workers [42] described a nickel-catalyzed 1,3-dienylation between propargylic carbonates **97** and phosphine oxides **98** (Scheme 22). Using diphenylphosphinic acid as the additive and dcypbz as a ligand delivered functionalized phosphinoyl 1,3-butadienes **99** in up to 93% yield.



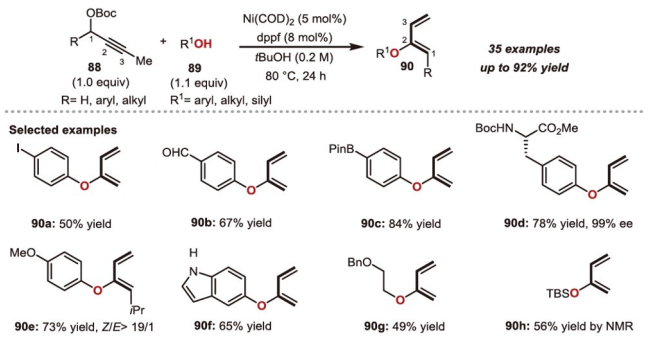
Scheme 16 Palladium-catalyzed cyclization of propargylic carbonates for the synthesis of cyclic dienamides (color online).



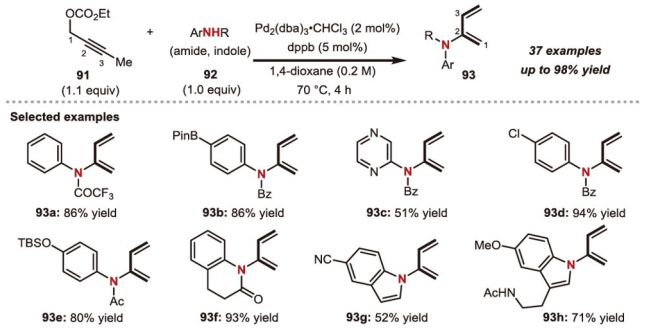
Scheme 17 Synthesis of 1,3-dienylphosphonates from terminal propargylic esters and diethyl phosphite (color online).



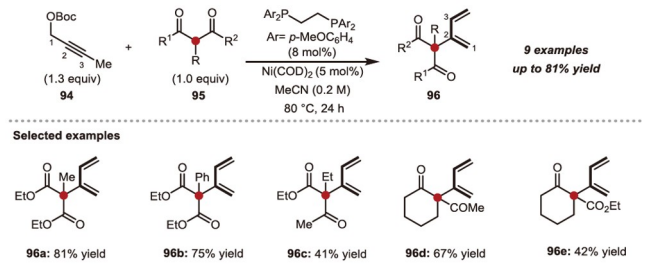
Scheme 18 Palladium-catalyzed addition of diarylacetonitriles to propargylic carbonates (color online).



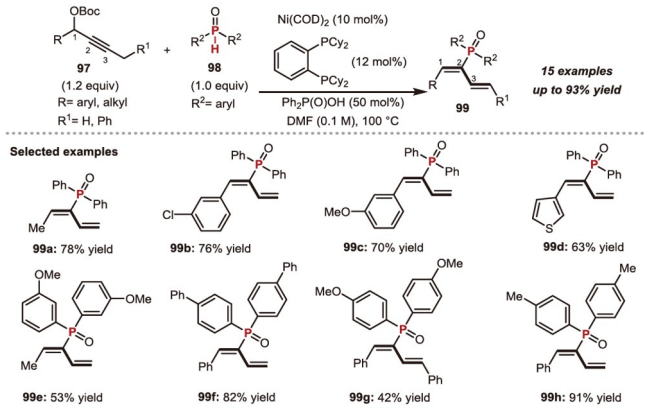
Scheme 19 Nickel-catalyzed stereoselective synthesis of 2-oxy-1,3-dienes from propargyl carbonates and oxygen nucleophiles (color online).



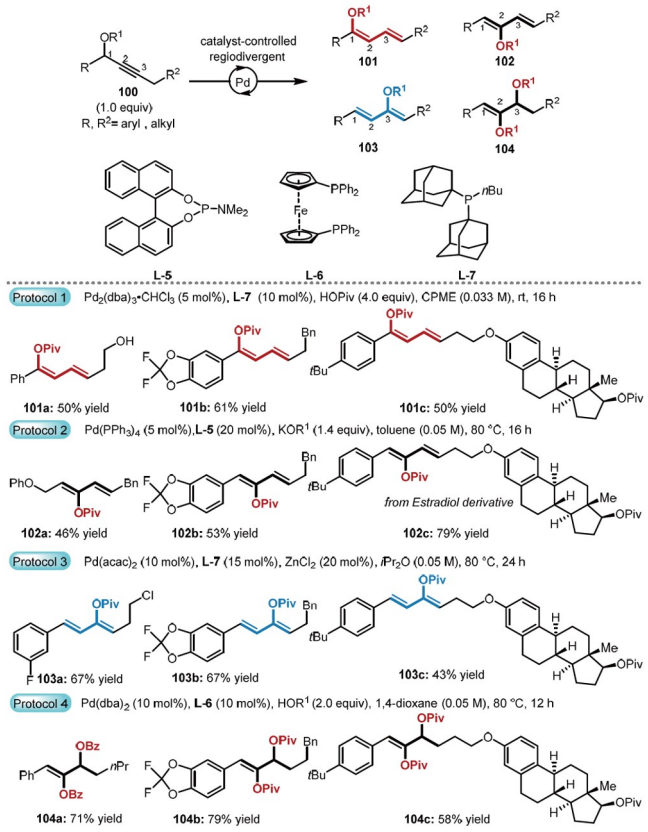
Scheme 20 Palladium-catalyzed C–N cross-coupling reaction from propargyl carbonates and amines (color online).



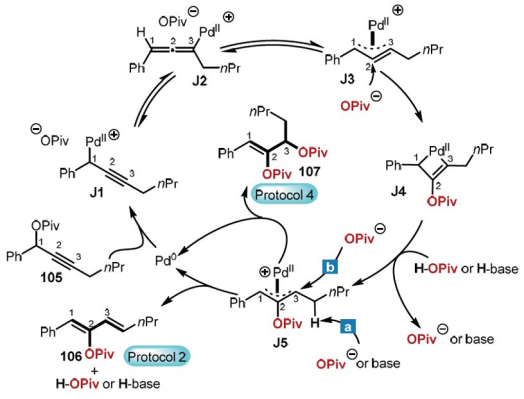
Scheme 21 Nickel-catalyzed α-1,3-dienylation between 1,3-dicarbonyl compounds and propargylic carbonates (color online).



Scheme 22 Nickel-catalyzed 1,3-dienylation between propargylic carbonates and phosphine oxides (color online).



Scheme 23 Palladium-catalyzed regiodivergent synthesis of highly substituted 1,3-dienes and allyl esters from internal aliphatic propargyl esters (color online).



Scheme 24 Mechanism for the formation of 2-acyloxy 1,3-dienes and allyl esters (color online).

Recently, Chen and co-workers [19] developed a palladium-catalyzed regiodivergent synthesis of highly substituted 1,3-dienes **101**–**103** and allyl esters **104** from the internal aliphatic propargyl esters **100** in a catalyst-controlled, tunable and predictable manner (Scheme 23). Considering the used ligands, two pathways were involved in palladium catalysis: electrophilic addition and oxidative addition/reductive elimination. Under $Pd_2(dba)_3{\cdot}CHCl_3$, ligand **L-7** and HOPiv, a range of 1-acyloxy 1,3-dienes **101** were synthesized in good yields. Employing $Pd(PPh_3)_4$, ligand **L-5** and KOR[1], various kinds of 2-acyloxy 1,3-dienes **102** were selectively formed in high yields. With $Pd(acac)_2$, ligand **L-7** and $ZnCl_2$, an array of 3-acyloxy 1,3-dienes **103** were generated in good yields. When $Pd(dba)_2$, ligand **L-6** and HOR[1] were employed, highly substituted allyl esters **104** were obtained in high yields. This method gave facile access to four regioisomers with high regio- and stereoselectivity. The synthetic utility was demonstrated by late-stage diversification of bioactive relevant molecules.

Mechanistically, Pd^0 undergoes oxidative addition with propargyl pivalate **105** to give three possible intermediates (**J1**, **J2** and **J3**) (Scheme 24) [19]. Then, pivalate attacks the cationic η^3-π-propargyl palladium intermediate **J3** to form palladacyclobutene intermediate **J4**, followed by protonation to afford intermediate **J5**. Final β-H elimination delivers 2-acyloxy 1,3-diene **106** and regenerates Pd^0 (path a). Allylic substitution with pivalate provides allyl ester **107** and regenerates Pd^0 (path b). Notably, the regioselectivity is mainly dependent on the coordination nature of the phosphine ligand. The monodentate phosphoramidite ligand (**L-5**) is exceptionally responsible for the regioselective generation of diene **106**, probably because of a vacant coordination site on Pd^{II} favoring β-H elimination. The bidentate ligand (**L-6**) is unlikely to undergo β-H elimination due to the steric hindrance, thus favoring allylic substitution to deliver allyl

product **107**.

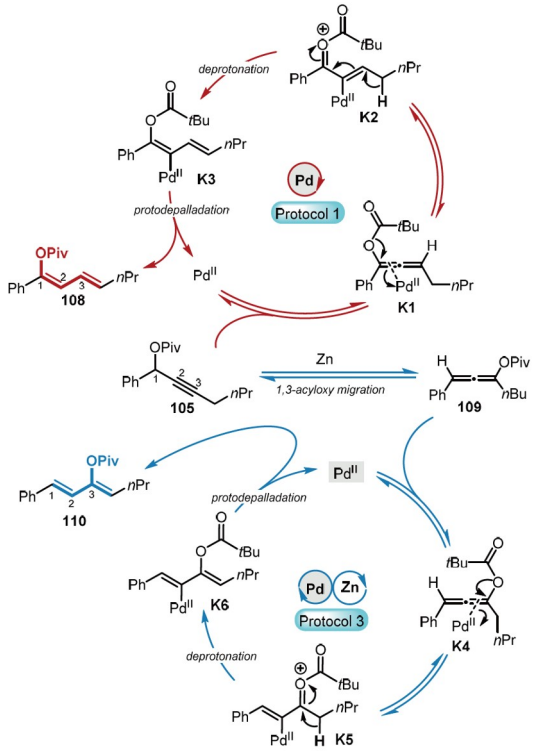
Alternatively, the propargyl pivalate **105** undergoes propargyl-allenyl isomerization, followed by the coordination with Pd^{II} to afford the allenyl pivalate **K1** (Scheme 25) [19]. Further activation gives intermediate **K2**, followed by deprotonation and protodepalladation to afford 1-pivaloxy1,3-diene **108** and release Pd^{II} catalyst. A similar 1,3-acyloxy migration by Zn^{II} catalysis, activation of allene by Pd^{II}, deprotonation and protodepalladation cascade delivers 3-acyloxy 1,3-diene **110** and releases Pd^{II} catalyst.

2.3 Others

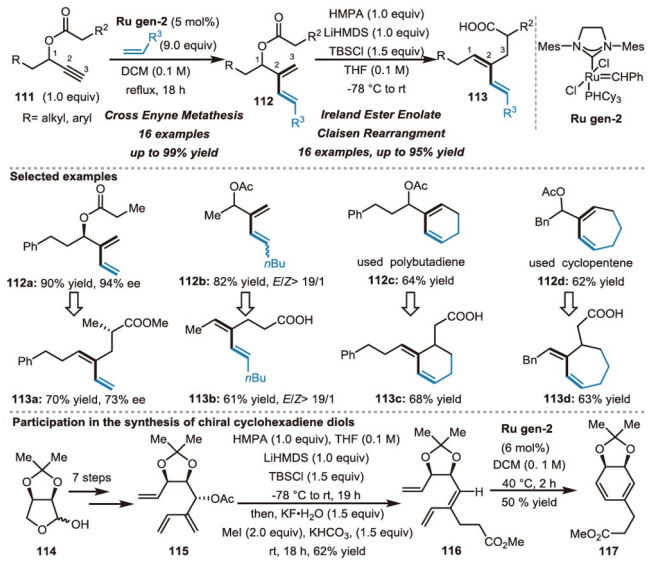
In 2006, Diver and co-workers [43] described a ruthenium carbene-promoted enyne metathesis for the synthesis of conjugated dienes **112** from propargylic esters **111** and alkenes (Scheme 26). Subsequent Ireland-Claisen rearrangement of acyclic or cyclic dienes delivered another kind of conjugated dienes **113**. Interestingly, by using chiral propargylic esters, the Ireland-Claisen rearrangement showed good chirality transfer (**112a** to **113a**). The tandem enyne metathesis/Ireland-Claisen rearrangement could be used as the key step for the synthesis of 4-substituted-3,5-cyclohexadiene diol derivatives (**115** to **117**).

Later on, Hiroi and co-workers [44] reported a novel copper hydride-promoted 1,3-rearrangement of α-cyclopropylpropargylic esters **118** for the synthesis of methylenecyclopentenes **120** (Scheme 27). This reaction featured mild reaction conditions and good yields. According to the mechanism, α-allenylcyclopropane **119** is firstly formed *via* the reaction of α-cyclopropylpropargylic esters **118** and copper hydride. The insertion of copper reagent into cyclopropane ring forms intermediate **M2**, followed by recombination to generate cyclic copper complex **M3**. Reductive elimination delivers the final methylenecyclopentene **120**.

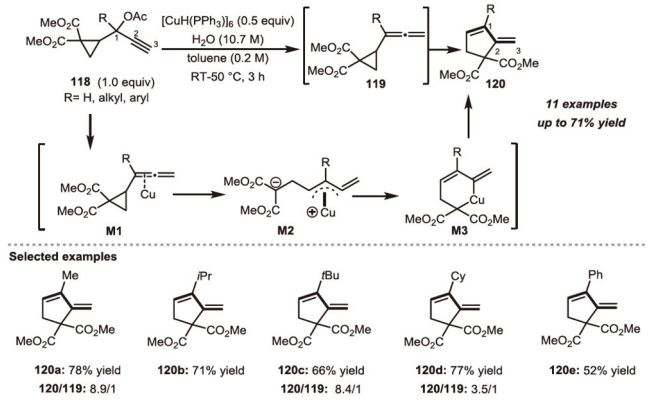
Inspired by the robustness of ruthenium catalysis, Dixneuf and co-workers [45] reported a ruthenium-catalyzed method of propargylic esters **121** for the synthesis of functionalized dienes **123** (Scheme 28). This formal cross-coupling of two carbenes, vinylcarbene from propargylic ester rearrangement and diazoalkane carbene, featured good yields and selectivities. As proposed, ruthenium vinylcarbene **N1** is first formed from propargylic ester **124** through Rautenstrauch rearrangement. Addition with diazoalkane **122** forms intermediate **N2**, subsequently affording diene **126**. Direct reac-



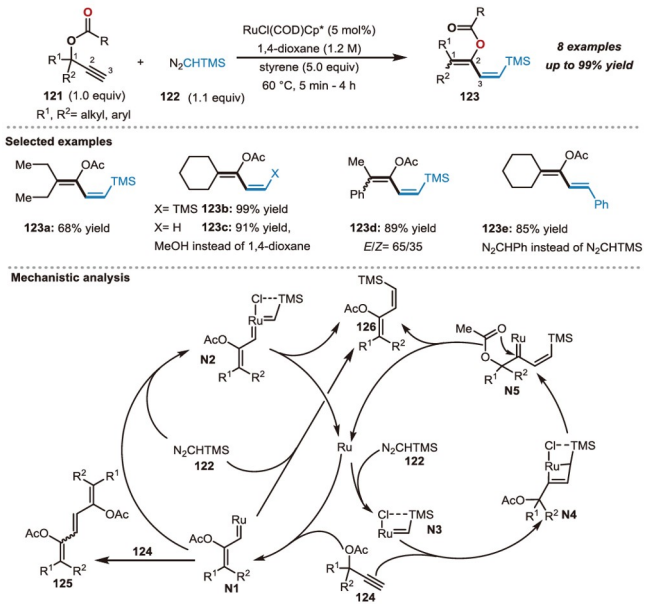
Scheme 25 Mechanism for the formation of 1-acyloxy 1,3-dienes and 3-acyloxy 1,3-dienes (color online).



Scheme 26 Ruthenium carbene-promoted enyne metathesis for the synthesis of conjugated dienes from propargylic esters and alkenes (color online).



Scheme 27 Copper hydride-promoted 1,3-rearrangement of α-cyclopropylpropargylic esters.



Scheme 28 Ruthenium-catalyzed synthesis of functionalized dienes from propargylic esters and diazoalkane carbene (color online).

tion of intermediate **N1** with diazoalkane **122** could also deliver diene **126**. Alternatively, ruthenium catalyst reacts with diazoalkane **122** to give carbene **N3**, followed by [2+2] cycloaddition with triple bond in propargylic ester **124** to afford intermediate **N4**. Sequential isomerization forms vinylcarbene-ruthenium intermediate **N5**, followed by 1,2-shift of acetate to deliver diene **126**.

3 Conclusions and outlook

1,3-Dienes are well-known and important scaffolds that exist in numerous natural products, bioactive compounds, and drugs. They are also versatile synthetic intermediates in different kinds of transformations, affording libraries of valuable molecules and cycles. Considering the number and relative position of substituents as well as the stereochemistry seriously influencing the synthetic transformations and bioactivities, chemo-, regio- and stereoselective synthesis of highly substituted 1,3-dienes is a vital issue. Propargylic esters, easily prepared from commercially available starting materials, possess versatile and tunable reactivities in transition metal catalysis. They have been employed in the efficient construction of substituted 1,3-dienes, especially tri- and tetrasubstituted 1,3-dienes. Through 1,2- or 1,3-acyloxy migration catalyzed by transition metals such as Au, Cu, Pt and Zn, diverse 2-, or 3-, or 4-acyloxy 1,3-dienes are synthesized in high chemo-, regio- and stereoselectivities. By using α-halogen-substituted propargylic phosphates, 3-halogen-4-phosphatyloxy 1,3-dienes are afforded *via* 1,3-phosphatyloxy migration and 1,3-halogen migration. 2-Acyloxy-4-alkoxy 1,3-dienes could be generated from alkoxy-containing propargylic esters *via* 1,2-acyloxy migration. When 1,4-bis(propargyl acetates) are employed, 2,3-bis(acetoxy)-1,3-dienes are formed *via* tandem 1,2-/1,2-bis(acetoxy) migration. By using propargyl esters and diaryliodonium salts, 2-acyloxy-3-aryl and 2-aryl-3-acyloxy tetrasubstituted 1,3-dienes are respectively synthesized *via* 1,2- and 1,3-acyloxy migration in a catalyst-controlled regiodivergent manner. Alternatively, cross-coupling reactions of propargylic esters by transition metals, such as Pd and Ni, provide important complementary access to substituted 1,3-dienes. By using nucleophiles such as amines, alcohols, carboxylic acids, phenols, indoles, phosphine oxides, diarylacetonitriles and 1,3-dicarbonyl compounds, various 2-substituted 1,3-dienes are produced *via* intramolecular or intermolecular cross-coupling. The cross-coupling of terminal propargylic esters and diethyl phosphites gives an approach to 1,3-dienylphosphonates. Moreover, ruthenium carbene chemistry also shows the potential for the synthesis of substituted 1,3-dienes.

Despite major advances in transition metal-catalyzed synthesis of substituted 1,3-dienes from propargylic esters, there are still some limitations that remain. Firstly, the transformations are primarily limited to the preparation of mono-, di- and trisubstituted 1,3-dienes; more complex, challenging and important tetrasubstituted 1,3-dienes are rarely synthesized. Developing general and efficient strategies for constructing tetrasubstituted 1,3-dienes is necessary. Secondly, reaction types and mechanisms are limited, hindering the occurrence of novel substituted 1,3-dienes. It is highly desirable to rationally design propargylic ester substrates, undergoing novel reaction pathways to broaden the scope of 1,3-dienes. Considering the uniqueness of different transition metal catalysts, exploring the synthesis of novel substituted 1,3-dienes by other transition metal catalysts is also demanded. Thirdly, although good chemo-, regio- and stereoselectivities have been obtained, developing controllable and tunable strategies are still required in the achievement of exclusive selectivities. Finally, the utilization of substituted 1,3-diene products is very limited. More attention and efforts should be put into accelerating the applications of 1,3-dienes in chemistry, medicine, and material science. We hope this review will help researchers to better understand the chemistry behind transition metal-catalyzed synthesis of substituted 1,3-dienes from propargylic esters and stimulate future progress in this field.

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Conflict of interest The authors declare no conflict of interest.

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