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Divergent 1,2-carboallylation of terminal alkynes enabled by metallaphotoredox catalysis with switchable triplet energy transfer†

Jian Qin, Zhuzhu Zhang, Yi Lu, Shengqing Zhu and Lingling Chu *

We report a metallaphotoredox strategy for stereodivergent three-component carboallylation of terminal alkynes with allylic carbonates and alkyl trifluoroborates. This redox-neutral dual catalytic protocol utilizes commercially available organic photocatalyst 4CzIPN and nickel catalysts to trigger a radical addition/alkenyl–allyl coupling sequence, enabling straightforward access to functionalized 1,4-dienes in a highly chemo-, regio-selective, and stereodivergent fashion. This reaction features a broad substrate generality and a tunable triplet energy transfer control with pyrene as a simple triplet energy modulator, offering a facile synthesis of complex *trans*- and *cis*-selective skipped dienes with the same set of readily available substrates.

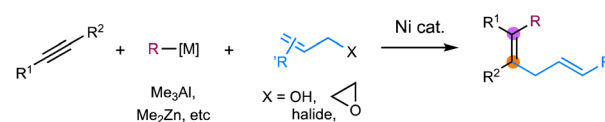
Introduction

The 1,4-diene motifs, also known as skipped dienes, are widely present in different classes of natural products and biologically active compounds and serve as valuable synthetic synthons in chemical synthesis due to their versatile reactivity.¹ Therefore, the development of efficient methods for constructing these skipped dienes has received increasing attention. Among various synthetic methods developed,^{2–5} transition metal-catalyzed hydroallylation of alkynes represents one of the most straightforward and reliable approaches to accessing skipped dienes.⁵ Since the seminal report by Trost in 1998,^{5a} a number of elegant examples of catalytic hydroallylation of alkynes, enabled by stoichiometric reductants or hydrides in the presence of nickel, copper, or cobalt catalysts, have later been developed by several other groups, providing efficient and regioselective methods for the synthesis of skipped alkenes.⁵ Despite these advancements, selective assembly of highly substituted 1,4-dienes remains challenging.

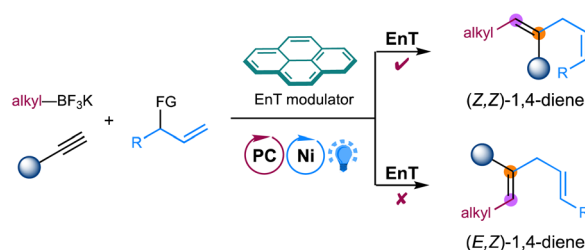
Transition metal-catalyzed 1,2-carboallylation of alkynes, in which an allyl moiety and another carbon-centered functionality are spontaneously incorporated in one pot, represents a practical tactic for synthesizing substituted 1,4-dienes.^{6,7} Despite attractive, only a few examples of 1,2-carboallylation of alkynes, which generally proceed through a two-electron redox

process, *i.e.*, carbo-metalation of alkynes followed by cross-couplings, have been successfully developed *via* nickel catalysis (Fig. 1a). Typically, highly active organometallic agents such as Me₃Al, Me₂Zn, or alkynyltins are employed for requisite couplings.⁶ To our knowledge, catalytic three-component carboallylation of alkynes enabled by transition metal-catalyzed photoinduced electron transfer strategies,⁸ an emerging area that has attracted increasing attention in chemical synthesis, remains unknown. Recently, elegant progress has been made in geometric isomerization of alkenes facilitated by triplet–triplet energy transfer (EnT) catalysis, providing a facile

a) Nickel-catalyzed 1,2-carboallylation of alkynes



b) This work: metallaphotoredox divergent 1,2-carboallylation of alkynes



■ Synergistic catalysis with pyrene as EnT modulator

■ Selective & stereo-divergent ■ Tunable SET & E_nT process

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Chemistry and Chemical Engineering, Center for Advanced Low-Dimension Materials, Donghua University, Shanghai 201620, China. E-mail: lingling.chu1@dhu.edu.cn

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Fig. 1 Divergent three-component carboallylation of alkynes *via* metallaphotoredox catalysis.



approach to access thermodynamically less stable yet synthetically challenging Z-alkenes.^{9–11} More importantly, a metallaphotoredox system combining EnT process with single-electron transfer (SET) events allows for the stereo-selective and even -divergent construction of structurally diverse alkenes from simple starting materials.¹¹ Inspired by these elegant examples, we envisage that metallaphotoredox-enabled carboallylation of alkynes would not only enable a precise assembly of substituted 1,4-dienes but also allow for a stereo-selective modulation for the resulting dienes. Herein, we describe a redox-neutral, stereo-divergent 1,2-carboallylation of alkynes with alkyl trifluoroborates and allylic electrophiles *via* dual photoredox and nickel catalysis (Fig. 1b). This reaction takes advantage of the versatile reactivity of open-shell alkenyl radicals,¹² *in situ* generated *via* radical addition to alkynes, to ensure the facile assembly of substituted skipped dienes with complementary reactivity and selectivity. More importantly, this synergistic protocol allows for a divergent regulation of the stereochemistry of 1,4-diene products with pyrene as a simple EnT modulator, providing a complementary strategy to the previously developed photoinduced divergent synthesis of substituted alkenes that rely on using different photocatalysts or metal complexes.^{11d–g,11i–k}

Results and discussion

We began our investigations by employing terminal alkyne **1a** as the template substrate, allylic carbonate **2a** as the electrophilic coupling partner, and *tert*-butyl trifluoroborate **3a** as the alkyl radical precursor. As shown in Table 1, the optimal results were obtained with a catalytic combination of Ni(phen)Cl₂ as a pre-catalyst, 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbbpy) as a ligand, 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) as a photocatalyst,¹³ and pyrene as an additive. The reaction is performed in a DMAc/MeCN solvent with an irradiation of blue LED ($\lambda_{\max} = 467$ nm) at 35 °C, delivering the desired (*E,Z*)-1,4-diene product **4a** in 84% yield and high stereoselectivity (*E/Z* = 92 : 8) (entry 1). The use of Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ ($E_{1/2}^{*III/II} = +1.21$ V vs. SCE),¹⁴ a commonly employed photocatalyst in synergistic nickel catalysis, results in a significant decrease in the yield of product **4a/5a** with an inversed *E/Z* selectivity of double bond 1, probably due to its higher triplet energy ($E_T = 60.1$ kcal mol⁻¹)^{9c} (entry 2). Switching it to Ir(ppy)₃, a more reducing photocatalyst, leads to a trace amount of product (entry 3). Control experiments indicate that both nickel catalysts and visible light are essential to the success of this transformation, and the addition of exogenous nitrogen ligands is beneficial to

Table 1 Optimization of reaction conditions^a

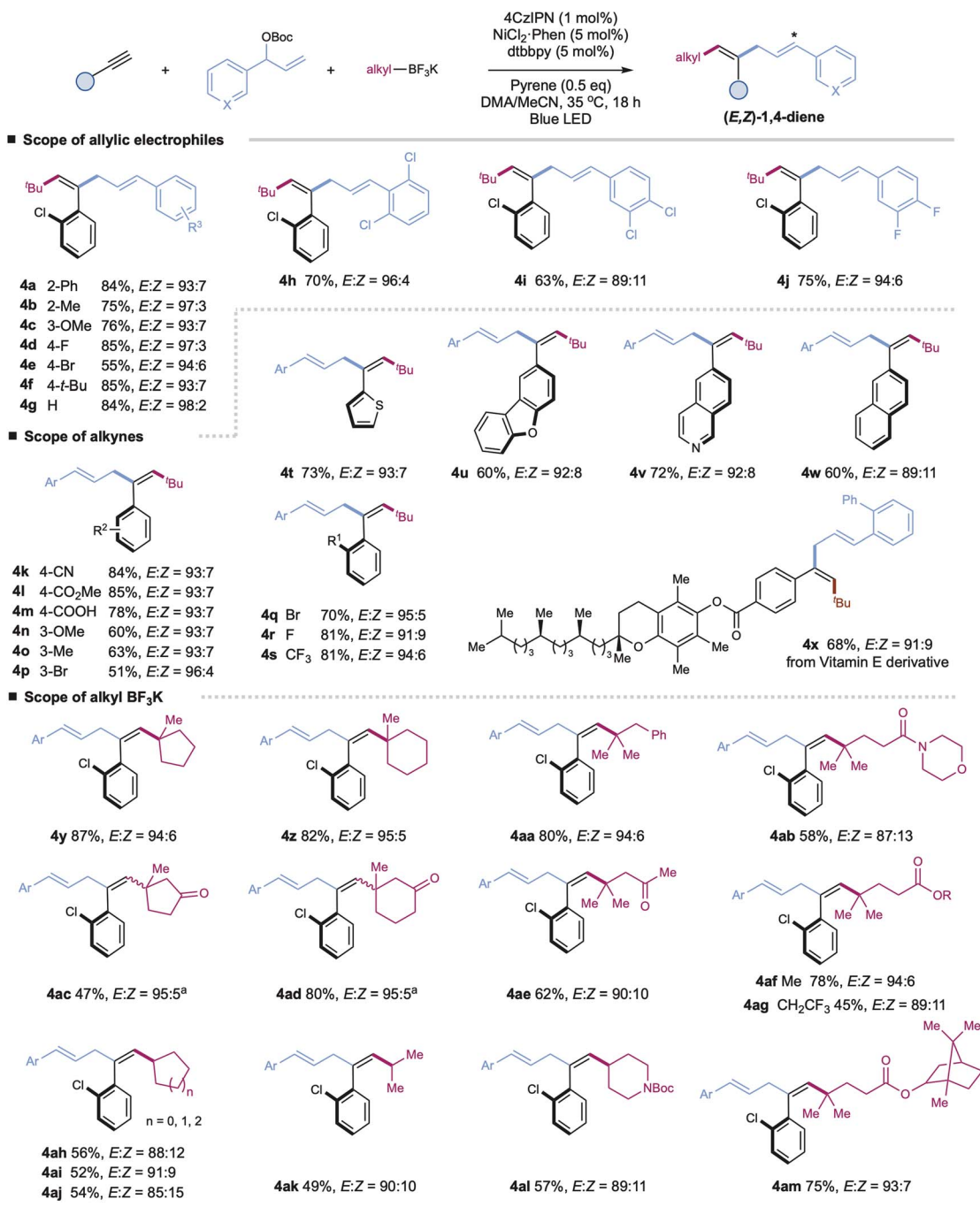
Entry	Variations from “standard” condition	Yield of 4a/5a	<i>E/Z</i>
1	None	87% (84%)	92/8
2	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆ , instead of 4CzIPN	37%	17/83
3	Ir(ppy) ₃ , instead of 4CzIPN	8%	63 : 37
4	No 4CzIPN	23%	97/3
5	No pyrene & 4CzIPN	8%	—
6	No Ni catalyst	0	—
7	No ligand	64%	87/13
8	No light	0	—
9	No pyrene	79%	16/84
10 ^b	No pyrene	75% (71%)	6/94

^a Reaction conditions: alkyne **1a** (0.1 mmol), allylic ester **2a** (1.5 equiv.), *tert*-Bu trifluoroborates **3a** (1.5 equiv.), 4CzIPN (1 mol%), Ni(phen)Cl₂ (5 mol%), dtbbpy (5 mol%), pyrene (0.5 equiv.), DMAc/CH₃CN [0.05 M] (v/v 3 : 1), blue LED (90 W, $\lambda_{\max} = 467$ nm), ~35 °C, 18 h. Yields and *E/Z* ratios were determined by GC analysis of the reaction mixture with dodecane as an internal standard. Isolated yields are given in parentheses.

^b With DME as solvent.

improving the coupling efficiency (entries 6–8). Interestingly, product **4a** (*E*/*Z*/*Z* = 97 : 3) was still observed in 23% yield in the absence of 4CzIPN, while only a trace amount of products **4a/5a** was detected in the absence of 4CzIPN and pyrene (entries 4 and 5). These results suggest that pyrene might also function as a photocatalyst to gear the nickel cycle yet cannot promote the *E* to *Z* isomerization of double bond 1. Intriguingly, performing the reaction in the absence of pyrene, the stereoisomer (*Z,Z*)-1,4-diene

5a was obtained in 79% yield with opposite stereoselectivity (*E*/*Z* = 16 : 84) (entry 9). Switching the solvent to DME improved the *Z*-selectivity of **5a** to 94 : 6 with comparable yields (entry 10). This protocol represents an operationally simple approach to accessing both *Z/E*-alkenes by adding or removing pyrene additive. It should be noted that no stereoisomers regarding double bond 4 of 1,4-dienes were observed in these cases, probably due to the augmented $A_{1,3}$ -strains in the 4*Z* isomers (Table 1).^{9b,c}



Scheme 1 Substrate scope for (1*E*,4*Z*)-1,4-dienes. Reaction conditions: alkyne (0.2 mmol), allylic carbonate (1.5 equiv.), alkyl trifluoroborate (1.5 equiv.), 4CzIPN (1 mol%), Ni(phen)Cl₂ (5 mol%), dtbbpy (5 mol%), pyrene (0.5 equiv.), DMAc/CH₃CN [0.05 M] (v/v 3 : 1), blue LED (90 W, λ_{max} = 467 nm), ~35 °C, 18 h. Isolated yields. *E*/*Z* ratios were determined by ¹H NMR. ^a *E*/*Z* ratio of double bond 4 is around 1 : 1.

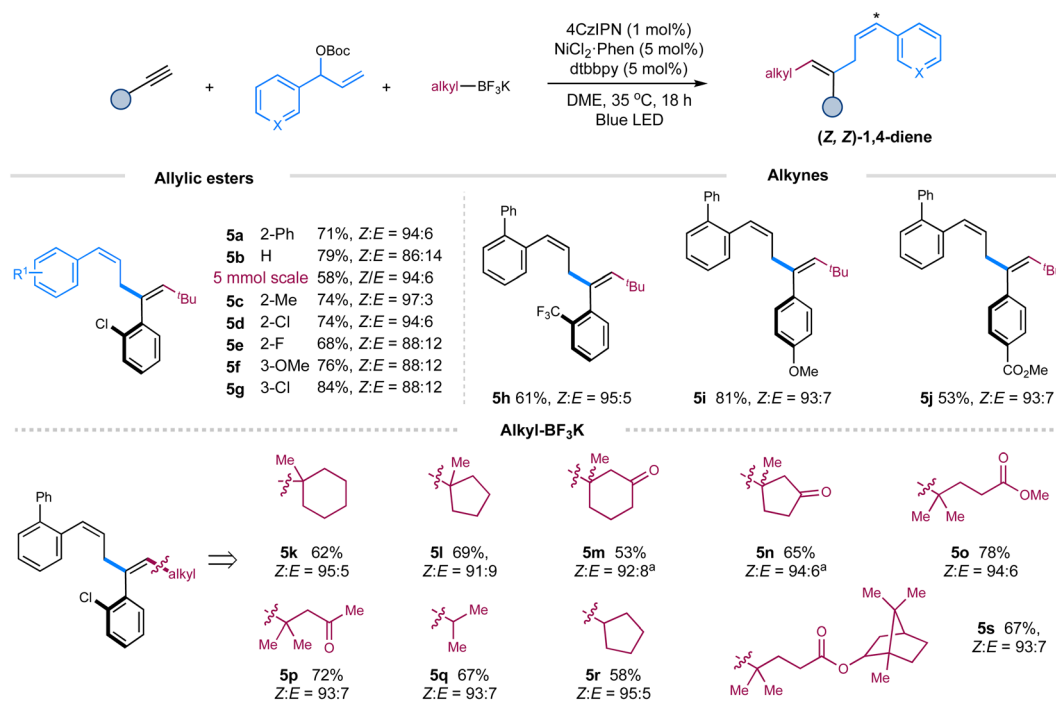
With the optimal conditions in hand, we turned our attention to investigating the generality of this protocol. As shown in Scheme 1, a wide range of aryl-substituted branched allylic carbonates couple efficiently with aryl alkynes and ^tBuBF₃K under the standard *E,Z*-selective conditions (with pyrene) (Table 1, entry 1), affording the corresponding tri-substituted 1,4-dienes with high yield and excellent stereoselectivity (**4a–4j**, *E/Z* up to 98 : 2). Installation of electron-donating or electron-poor substituents at the *para*-, *meta*-, or *ortho*-positions of the aromatic rings has no significant effect on the reaction efficiency or stereoselectivity (**4a–4j**). Alkyl-substituted allylic carbonates are applicable coupling partners, affording the desired products in moderate yields, yet as mixtures of *trans/cis* isomers (*E/Z* = 3 : 1 for product **54an** in ESI†).

A wide range of terminal aryl alkynes with various electron-donating or withdrawing functional groups are applicable with high efficiency and excellent stereoselectivity in this catalytic system (**4k–4x**, *E/Z* up to 96 : 4). The electronic property or steric hindrance of the aromatic rings of alkynes has no significant effect on the stereoselectivity of resulting 1,4-dienes. The mild conditions are tolerated with many important functional groups, including cyanides, esters, carboxylic acids, and halides (**4k–4m**, **4p**, **4q–4r**). Moreover, heteroaryl-, such as thiophenyl-, dibenzo[*b,d*]furan-yl-, quinolinyl-, and naphthalenyl-substituted alkynes, are suitable substrates with good yields and stereoselectivity under the optimal conditions (**4t–4w**). The reactions with complex terminal alkynes, exemplified by the one derived from vitamin E, proceed smoothly to afford corresponding functionalized 1,4-dienes under mild conditions (**4x**).

Nevertheless, internal alkynes are unsuitable coupling partners due to the competitive cross-couplings between allyl carbonates and alkyl trifluoroborates and self-couplings of allyl carbonates.

Next, we further evaluate the generality regarding alkyl precursors (**4y–4am**, *E/Z* up to 95 : 5). Both linear and cyclic tertiary alkyl trifluoroborates, including those derived from biologically active molecules, show high reactivity, allowing for the facile installation of alkyl units at the end of 1,4-dienes (**4y–4ag**, **4am**). Besides tertiary alkyl precursors, cyclic and acyclic secondary alkyl trifluoroborates are applicable with excellent chemo- and regioselectivity, albeit with slightly decreased yields and stereoselectivity (**4ah–4al**). The tethered ketones, amides, and esters are well-compatible (**4ac–4ae**, **4ab**, **4al**, **4af–4ag**, and **4am**). Generally, this chemistry affords excellent control for the configuration of double bond 4 of 1,4-dienes, probably due to the less sterically hindered *E*-alkenyl radicals combining faster with nickel complexes to form *trans*-adduct alkenylnickel species.¹⁵ Nevertheless, in the cases of cyclic ketone-derived alkyl trifluoroborates, we observed a significant loss in the stereoselectivity of double bond 4 (**4ac** and **4ad**). We reason that the potential chelation between the cyclic ketone and nickel species¹⁶ could affect the stereoselective radical capture process, leading to the formation of *trans/cis* mixtures of alkenylnickel species and, finally, the *Z/E* isomers of double bond 4 (see Table S8†).

Then, we turned our attention to exploring the scope of these components under the *Z*-selective conditions (without pyrene) (Table 1, entry 10). As shown in Scheme 2, this protocol is applicable to a wide array of terminal aryl alkynes, allylic carbonates, tertiary and secondary alkyl trifluoroborates,

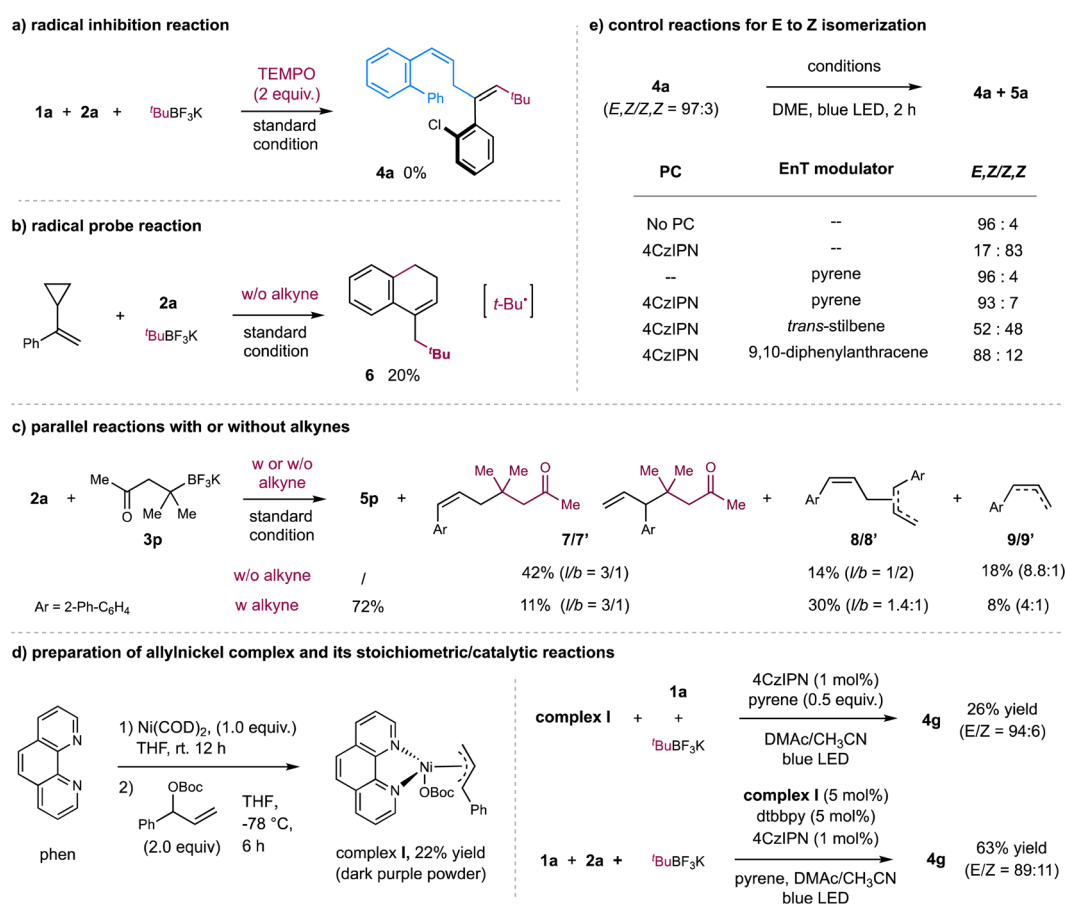


Scheme 2 Substrate scope of (*Z,Z*)-1,4-dienes. Reaction conditions: alkynes (0.2 mmol), allylic esters (1.5 equiv.), alkyl trifluoroborates (1.5 equiv.), 4CzIPN (1 mol%), Ni(phen)Cl₂ (5 mol%), dtbbpy (5 mol%), DME [0.05 M] (v/v 3 : 1), blue LED (90 W, λ_{max} = 467 nm), ~35 °C, 18 h. Isolated yields. *E/Z* ratios were determined by ¹H NMR. ^a *E/Z* ratio of double bond 4 is around 1 : 1.

affording the corresponding *Z,Z*-skipped dienes with moderate to good yields and high selectivity (5a–5s). Pleasingly, performing the reaction on a gram scale still led to the formation of product 5a with excellent selectivity, albeit in a decreased yield. The presence of an *ortho*-substituent on the aromatic ring of allylic carbonates is vital to maintain the excellent *Z*-selectivity of double bond 4 of 1,4-dienes due to the augmented $A_{1,3}$ -strain.^{9b,c}

We further performed several preliminary experiments to gain insight into the mechanism (Scheme 3). Light-on/off experiments demonstrated that continuous light irradiation is required for product formation and stereoselectivity in these reactions (see Fig. S12–S15 in ESI†). Moreover, Stern–Volmer fluorescence quenching experiments revealed that the photo-excited state of 4CzIPN was quenched by alkyl trifluoroborates instead of alkynes and allylic esters (see Fig. S7–S10 in ESI†). Furthermore, the radical inhibition experiment with 2.0 equivalents of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) led to no formation of the coupling product 4a (Scheme 3a). To probe the nature of radical species, (1-cyclopropylvinyl) benzene was used as a radical probe to react with allylic ester 2a and *t*-BuBF₃K under the standard condition (Scheme 3b). 20% yield of product 6, probably generated *via* a radical addition/radical ring-opening/cyclization sequence, was observed, suggesting

the involvement of *t*-Bu• radical. On the other hand, the reaction of allylic ester 2a with alkyl trifluoroborate 3p in the absence of alkyne 1a gave 42% of allyl-alkyl coupling product 7/7' (branch & linear),¹⁷ together with 14% of allyl-allyl homo-coupling product 8/8' (branch & linear) and 18% of reductive product 9/9' (Scheme 3c). In contrast, the standard 3-component reaction of 2a afforded the desired product 5p in 72% yield, with only an 11% yield of by-product 7/7'. These results imply that the addition rate of *t*-Bu• to alkyne might be faster than its coupling rate with allylic carbonate, thus leading to the desired 3-component carboallylation reaction.¹⁸ The observation of the allyl-derived side products also implies the potential involvement of allylnickel species. To verify this hypothesis, we prepared π -allyl nickel complex I. The reaction of Ni(COD)₂, 1,10-phen, and allylic carbonate in THF gave a 22% yield of nickel complex I as a dark purple powder (Scheme 3d).¹⁹ The stoichiometric reaction of allylnickel complex I with alkyne 1a and ^tBuBF₃K in the presence of catalytic 4CzIPN and pyrene with blue LED irradiation gave 26% yield of 1,4-diene product 4g (*E/Z* = 94 : 6); and the reaction of 1a, allylic carbonate, and ^tBuBF₃K with catalytic complex I under otherwise same condition gave product 4g in 63% yield (*E/Z* = 89 : 11). These results suggest that allylnickel species could be involved in this carboallylation reaction.



Scheme 3 Mechanistic studies. (a) Radical inhibition reaction; (b) radical probe reaction; (c) parallel reactions with or without alkyne; (d) stoichiometric reaction with allylnickel complex; (e) control reactions regarding *E* to *Z* isomerization.

Next, we carried out several control reactions to investigate the stereoselectivity. As shown in Scheme 3e, (*E,Z*)-1,4-diene **4a** (*E/Z* = 97 : 3) was efficiently converted to corresponding (*Z,Z*)-isomer **5a** (*E/Z* = 17 : 83) in the presence of catalytic 4CzIPN and blue LED, while with no significant isomerization in the presence of catalytic pyrene (*E/Z* = 96 : 4). Based on these results, we reason that (*E,Z*)-1,4-dienes could undergo a selective EnT process with photoexcited [4CzIPN]^{*} ($E_T = 56.4 \text{ kcal mol}^{-1}$),^{9c,20} to afford (*Z,Z*)-1,4-dienes; while the addition of pyrene, likely acting as a triplet energy modulator ($E_T = 2.10 \text{ eV}$),²¹ suppresses the EnT process to leave (*E,Z*)-1,4-dienes as they are. This assumption is also consistent with the fluorescence quenching experimental results, as pyrene showed a slightly more significant quenching to photoexcited [4CzIPN]^{*} than (*E,Z*)-1,4-diene **4a**, which could proceed *via* a selective EnT²¹ or triplet-triplet annihilation²² process (Fig. S11 and S18–S21†).²³ We also tested several potential triplet energy modulators, such as *trans*-stilbene²⁴ and 9,10-diphenylanthracene (Scheme 3e). 9,10-Diphenylanthracene, the structure of which is similar to pyrene, gave a comparable effect to pyrene (Scheme 3e); at the same time, the addition of *trans*-stilbene led to the formation of *cis/trans*-isomers (Scheme 3e), echoed with its no quenching effect to [4CzIPN]^{*} (Fig. S11†).

We propose a potential catalytic cycle for this metallaphotoredox-catalyzed carboallylation of alkynes, as depicted in Fig. 2. A single-electron oxidation of alkyl trifluoroborate ($E_{1/2}^{\text{red}} = +1.26 \text{ V vs. SCE}$)²⁵ by the photoexcited [4CzIPN]^{*} ($E_{1/2} = +1.35 \text{ V vs. SCE}$)¹³ generates alkyl radical **I**, which then adds to an alkyne to form alkenyl radical **II**. The nickel cycle starts from Ni(0) species. Oxidative addition of allylic ester **IV** to Ni(0) **III** affords allylnickel intermediate **V**,^{19,26} which then capture alkenyl radical **II** to form *trans*-(alkenyl)(allyl)Ni(III) **VI**. Subsequent reductive elimination of Ni(III) **VI** would deliver the (*E,Z*)-skipped diene product and Ni(I) **VII**. The final SET event between the reducing photocatalyst and Ni(I) **VII**

will regenerate the ground-state photocatalyst and Ni(0) to close the two catalytic cycles. While we are unable to rigorously rule out the possibility of alkenylnickel intermediate, generated *via* direct radical capture of alkenyl radical by Ni(0). Concerning the *E/Z* selectivity of products, we assume that (*E,Z*)-skipped diene remains intact in the presence of pyrene, while undergoing a photoinduced *4CzIPN-enabled *E* to *Z* isomerization in the absence of pyrene, thus securing divergent and modular access to both *trans*- and *cis*-1,4-dienes.

Conclusions

In summary, we report a metallaphotoredox-catalyzed stereo-divergent carboallylation strategy for the straightforward synthesis of highly functionalized skipped dienes with readily available terminal alkynes, allylic carbonates, and alkyl trifluoroborates. Utilizing 4CzIPN as an organic photocatalyst and Ni(phen)Cl₂ as a nickel catalyst, this dual protocol enables stereoselective access to a wide range of *E,Z*-1,4-dienes with pyrene as a triplet energy modulator. Furthermore, this protocol allows for modular synthesis of corresponding *Z,Z*-isomers with the same substrates and catalysts by removing pyrene additive. These transformations show a broad substrate scope with excellent chemo-, regio-, and stereo-selective controls. Mechanistic investigations shed some light on the reaction pathways and stereoselectivity.

Author contributions

J. Q., Z. Z., Y. L. conducted the investigation under L. C.'s supervision. L. C. wrote the manuscript and J. Q., S. Z. prepared the ESI.† All authors contributed to the conceptualization of the project and the editing of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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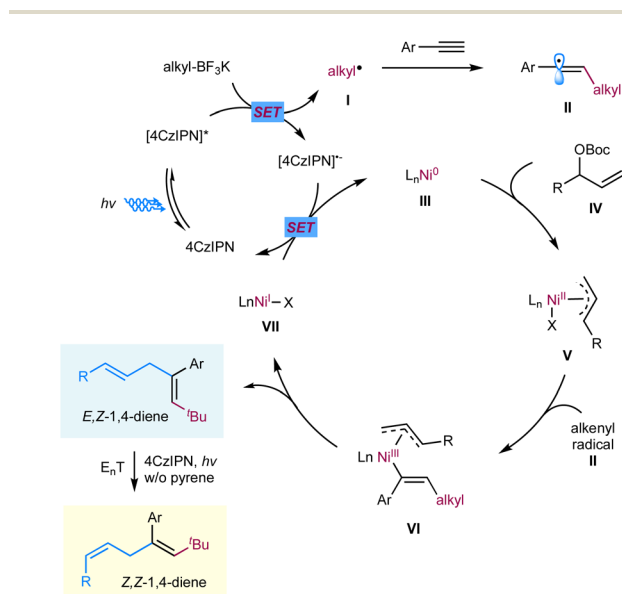


Fig. 2 Proposed mechanism.

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