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Allylation Reactions

Nickel-Catalyzed Unsymmetrical Bis-Allylation of Alkynes

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Abstract: The catalytic bis-allylation of alkynes is an important but challenging protocol to construct all-carbon tetrasubstituted alkenes. Particularly, the catalytic unsymmetrical bis-allylation of alkynes remains as an underexplored task to date. We herein report an unprecedented unsymmetrical bis-allylation by simultaneously utilizing electrophilic trifluoromethyl alkene and nucleophilic allylboronate as the allylic reagents. With the aid of robust Ni^0/NHC catalysis, valuable skipped trienes can be obtained in high regio- and stereo-selectivities under mild conditions. Mechanistic studies indicate that the reaction may proceed through a β-fluorine elimination of a nickelacycle followed by a transmetalation step with allylboronate. The present method exhibits a good tolerance of various functional groups. Besides, the skipped triene products can undergo an array of elaborate transformations, which highlights the potential applications of this strategy.

Introduction

Synthetic methods that can permit the facile synthesis of structurally diverse compounds from easily accessible raw materials are always highly sought-after among the chemical community. As one of the most representative protocols in emulating nature's efficiency, the multicomponent reactions (MCRs) would integrate multiple bond forming processes in a one-pot vessel so as to enable the maximization of molecular libraries.[1] In this context, the multicomponent difunctionalization of alkynes allows the anti- or syn-selective installation of two distinct functional groups across the carbon-carbon triple bonds, providing straightforward access to value-added tri- or tetrasubstituted alkenes.[1b,2] Owing to the versatile reactivity of the allyl unit, developing catalytic reactions for allylic alkylation of alkynes has drawn particular attentions from organic chemists.[3] During the past decades, substantial efforts have been devoted to the mono-allylation of alkynes under catalysis.[2c,e,3b,4] However, the catalytic bis-allylation of alkynes permitting the rapid construction of valuable skipped trienes has still lagged far behind.

In 2006, Hirashita and co-workers reported a symmetrical bis-allylation of internal alkynes with allylindium. To obtain satisfactory yields, a stoichiometric amount of nickel salt was indispensable in this reaction [Figure 1a, Eq. (1)].[5] With the aid of excess $Nb(OEt)_5$ and Grignard reagent, Obora et al. also realized a symmetrical bis-allylation reaction of 4-octyne with allyl bromide [only one example, Figure 1a, Eq. (2)].[6] In 2018, the Osaka group developed a practical method on symmetrical bis-allylation reaction of alkynes with allyl acetates under nickel catalysis using zinc powder as the reductant (Figure 1b).[7] Nevertheless, the catalytic strategies for unsymmetrical bis-allylation of alkynes are rare. Considering that the above-mentioned protocols all employed two electrophiles or two nucleophiles as the bis-allylic precursors, the inherent limitation will complicate the product distribution by their competitive reactivities in unsymmetrical bis-allylation reactions.[8] Moreover, when unsymmetrical alkyne substrates are used to couple with whether two distinct allyl electrophiles or nucleophiles, the regioselectivity control would also impede the success of most developed methods. Therefore, the development of a robust catalysis where multicomponent bis-allylation of alkynes can proceeds with one allyl electrophile and subsequently with another allyl nucleophile should address some of these issues.

The gem-difluoroalkene moiety is a fascinating structure owing to its existence in a variety of biologically active compounds.[9] Consequently, enormous efforts have been made to explore efficient pathways to construct the gem-difluoroalkene motif.[2b,10] The defluorinative coupling reaction of trifluoromethyl alkenes is one of the most applicable approaches to prepare functionalized gem-difluoroalkenes. In recent years, elaborated catalysis has been exploited for this purpose.[11] On our continuous interests for allylation reactions,[12] we envisioned that the trifluoromethyl olefins could be used as the allylic electrophiles in unsymmetrical bis-allylation of alkynes with nucleophilic allylboronates. To realize the above hypothesis, several significant challenges should be expected: 1) the competition of direct allyl-allyl cross-coupling reactions of trifluoromethyl olefins with allylboronates; 2) the regulation of stereo- and regioselectivity in the case of unsymmetrical alkyne substrates; 3) the competitive direct hydroallylation of alkynes with

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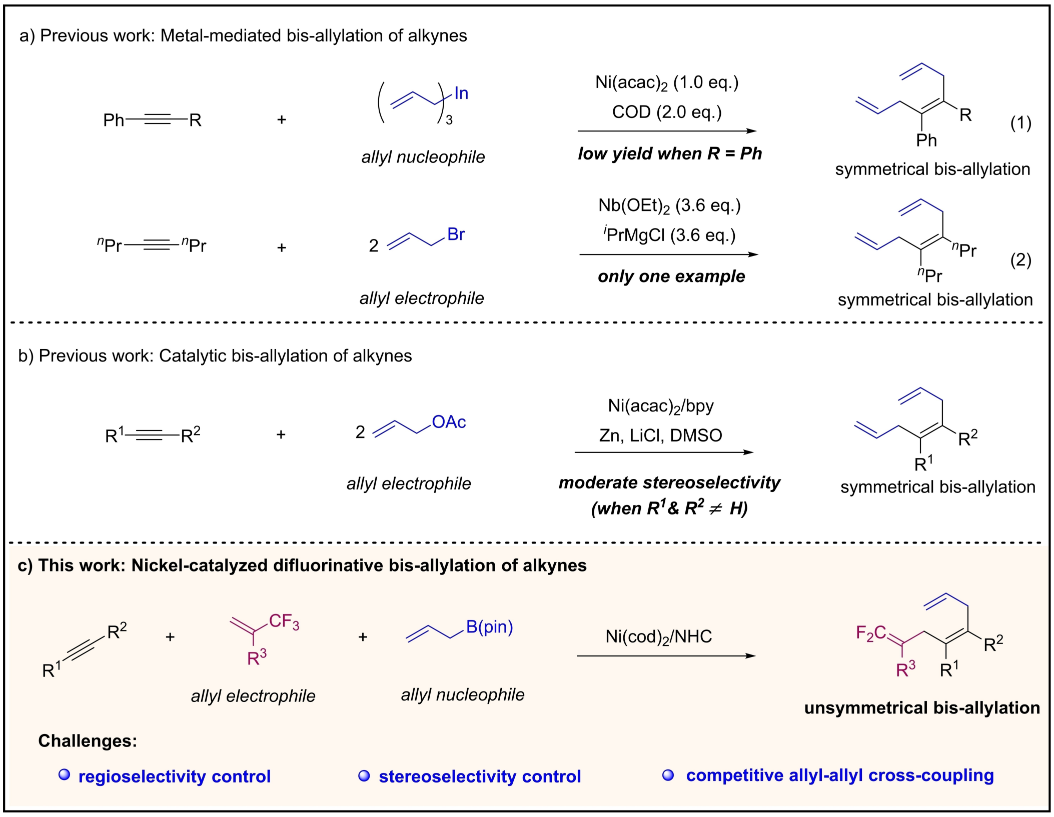


Figure 1. Ni-catalyzed bis-allylation of alkynes.

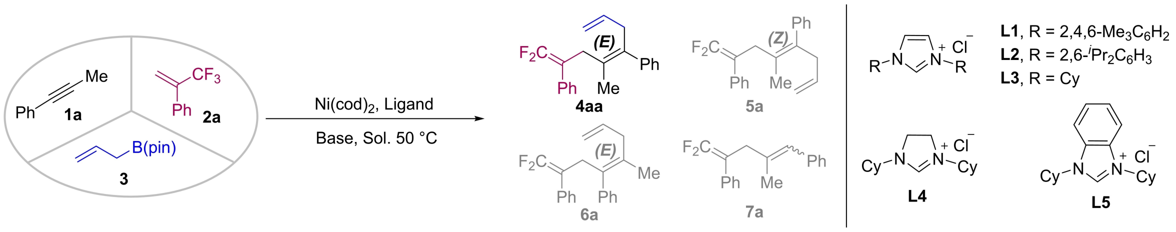
trifluoromethyl olefins. Taking these obstacles in mind, high demands would be called for suitable catalytic systems. Herein, we reported our endeavors for multicomponent unsymmetrical bis-allylation of alkynes with trifluoromethyl alkenes and allylboronate enabled by nickel catalysis (Figure 1c).

Results and Discussion

Initially, 1-phenyl-1-propyne (**1a**), α-trifluoromethyl alkene (**2a**) and allyl pinacol boronate (**3**) were selected as the model substrates to verify our hypothesis (Table 1). When using Ni(cod)$_2$ and PCy$_3$ as catalyst combo in toluene at 50 °C, it was failed to obtain bis-allylic products (entry 1).[11a] With ^{t}BuONa as base, bis-allylic products (**4aa**–**6a**) were produced promisingly but in low regio- and stereo-selectivities along with hydroallylation product **7a** (entry 2). Pleasingly, the selectivity could be slightly improved upon varying to non-polar solvent *n*-hexane (entries 3–5). Evaluation of phosphine ligands suggested that PPh$_2$Cy exhibited better performance in terms of yields (entries 5–8). However, the regio-, stereo- and chemoselectivities all kept in low levels. Therefore, we turned our attentions to NHC ligands (entries 9–13). Although significant erosion of reactivity was observed with bulky ligand **L2**, good yields and selectivities were achieved with Cy-substituted NHC ligands (**L3**–**L5**). With **L5** as the ligand, the effect of base was then investigated (entries 14 and 15). To our delight, the yield of **4aa** was successfully increased to 79 % with maintained selectivity in the presence of ^{t}BuOK. Notably, in the absence of Ni(cod)$_2$ or ligand only, the reactions are completely unproductive (entries 16 and 17).

With the optimized reaction conditions in hand, we then evaluated the substrate scope for current difluorinative bis-allylation of alkynes (Figure 2). For 1-arylpropynes, both the electron-donating (**4aa**–**4da**) and electron-withdrawing substituents (**4ea**–**4ha**) at the *para*-position of the phenyl rings were well tolerated to give desirable products in 26–77 % yields with excellent selectivities (Figure 2A). Substituents at the 3-position of the phenyl group also showed good compatibility (**4ia**, **4ja**). Moreover, naphthyl or heteroaryl-substituted alkynes were feasible substrates as well, delivering the skipped trienes efficiently (**4ka**–**4ma**). Replacing methyl with other alkyl groups, such as *n*-butyl (**4na**) and cyclopropyl (**4oa**), the unsymmetrical alkynes were amenable under the standard condition, giving products in 60 % and 57 % yields, respectively. To our delight, diarylacetylenes were also suitable substrates for current conversions and the corresponding products were effectively afforded in good yields and selectivities (**4pa**–**4sa**). Dialkyl acetylene also could undergo the cross bis-allylation to give desired product (**4ta**). These good results encouraged us to examine more challenging 1,3-enyne substrates (Figure 2B). By employing PCy$_3$ as the ligand, we were pleasing to find that all the 1,3-enynes tested could generate the polyenes in

Table 1: Optimization of the reaction conditions.[a]



Entry	Ligand	Base	Solvent	**4aa** (*E*) [%]	**5a** (*Z*) [%]	**6a** [%]	**7a** [%]
1	PCy$_3$	none	Tol.	N.D.	N.D.	N.D.	N.D.
2	PCy$_3$	^{t}BuONa	Tol.	43	4	1	10
3	PCy$_3$	^{t}BuONa	DCE	1	2	Trace	9
4	PCy$_3$	^{t}BuONa	Dioxane	33	7	2	10
5	PCy$_3$	^{t}BuONa	^{n}Hex	41	2	1	6
6	^{t}Bu$_3$P	^{t}BuONa	^{n}Hex	34	2	2	6
7	PPh$_3$	^{t}BuONa	^{n}Hex	1	N.D.	N.D.	N.D.
8	PPhCy$_2$	^{t}BuONa	^{n}Hex	61	6	4	6
9	**L1**	^{t}BuONa	^{n}Hex	51	5	7	16
10	**L2**	^{t}BuONa	^{n}Hex	N.D.	N.D.	10	N.D.
11	**L3**	^{t}BuONa	^{n}Hex	58	Trace	1	1
12	**L4**	^{t}BuONa	^{n}Hex	52	1	1	2
13	**L5**	^{t}BuONa	^{n}Hex	66	1	1	3
14	**L5**	^{t}BuOLi	^{n}Hex	5	4	N.D.	8
15	**L5**	^{t}BuOK	^{n}Hex	79	Trace	2	N.D.
16[b]	**L5**	^{t}BuOK	^{n}Hex	N.D.	N.D.	N.D.	N.D.
17	–	^{t}BuOK	^{n}Hex	N.D.	N.D.	N.D.	N.D.

[a] Conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), **3** (0.20 mmol), Ni(cod)$_2$ (5 mol %), Mono P (10 mol %) or NHC·HCl (5 mol %), base (1.5 equiv), solvent (0.5 mL), 50 °C, 24 h. Yields and selectivities were determined by GC-FID analysis of crude mixture with mesitylene as the internal standard. [b] Without Ni(cod)$_2$. N.D. = not detected. NHC: *N*-heterocyclic carbene.

decent yields and good selectivities (**4ua**–**4ya**). The internal substituted 1,3-enyne was applicable substrate as well, albeit in a slightly decreased stereoselectivity (**4za**, 7 : 1 *Z*/*E*). The relatively lower yields obtained for products **4ua**–**4za** are mainly attributed to the self-trimerization [2+2+2] of the 1,3-enyne substrates under Ni catalysis. The regioselectivity of reactions with 1,3-enynes was confirmed by NOE (Nuclear Overhauser effect) spectra (see Supporting Information for details). In 2010, Jamison and Houk et al. demonstrated that the π-coordination of the vinyl group with the metal center may reverse regioselectivity during nickel-catalyzed reductive coupling reaction between the 1,3-enyne and an aldehyde.[13] However, we found that the regioselectivity remains unchanged under the current bis-allylation conditions using 1,3-enynes. The steric hindrance of the tertiary C–Ni bond of the nickelacycle potentially renders the η^3-allyl/metal interactions unfavorable.

Subsequently, the scope of trifluoromethyl alkenes was examined under the established conditions. (Figure 3). A wide range of 3- and 4-substituted α-trifluoromethylstyrenes was successfully applied in current protocol, regardless of the electronic factors of the substituents (**4ab**–**4ak**). The substrate having strong electron-withdrawing group (CF$_3$) was a little sluggish, but the selectivity was excellent. Chemically sensitive but useful groups, such as Cl and Br, remained intact in all cases. Notably, *ortho*-substituted styrene was tolerated as well, affording the desired product **4aj** in 39 % yield. Replacing the phenyl group with naphthyl or alkyl group, the substrates were readily transformed into the triene products in acceptable yields (**4al**, **4an**). Of particular interest is the reaction with 3-quinolylalkene (**4am**), where the direct allyl-allyl coupling product **4am′** was also observed in 9 % yield. The stereo configuration of product **4al** was determined by X-ray crystallographic analysis (CCDC: 2222906).[14]

To better understand how side-product **7a** is being formed, control experiments were conducted (Figure 4A). First, in the absence of allylboronate **3**, no hydroallylation product **7a** could be observed with either **L5** or PCy$_3$ as the ligand (Figure 4A, entries 1 and 2). Moreover, the addition of extraneous ^{t}BuOH was also not helpful for the generation of **7a** (Figure 4A, entries 3 and 4). Therefore, we speculated that the hydride source may be attributed to the residue of HB(pin).[11o,15] To verify our hypothesis, the relationship between the amount of HB(pin) and the distribution of products was then evaluated with **L5** or PCy$_3$ as the ligand, respectively (Figure 4B). With the increasing amount of the HB(pin), the hydroallylation product **7a** was indeed promoted and became the major isomer with PCy$_3$ as the ligand. In contrast, the yields and selectivities for bis-allylated products (**4aa**–**6a**) gradually decreased. This observation suggests that HB(pin) may act as the hydride source in the formation of hydroallylated side-product **7a**. It should also be noted that with ligand **L5**, bis-allylated products kept dominance over the mono-allylic product as the addition of HB(pin). This result indicates that NHC **L5** may favor the

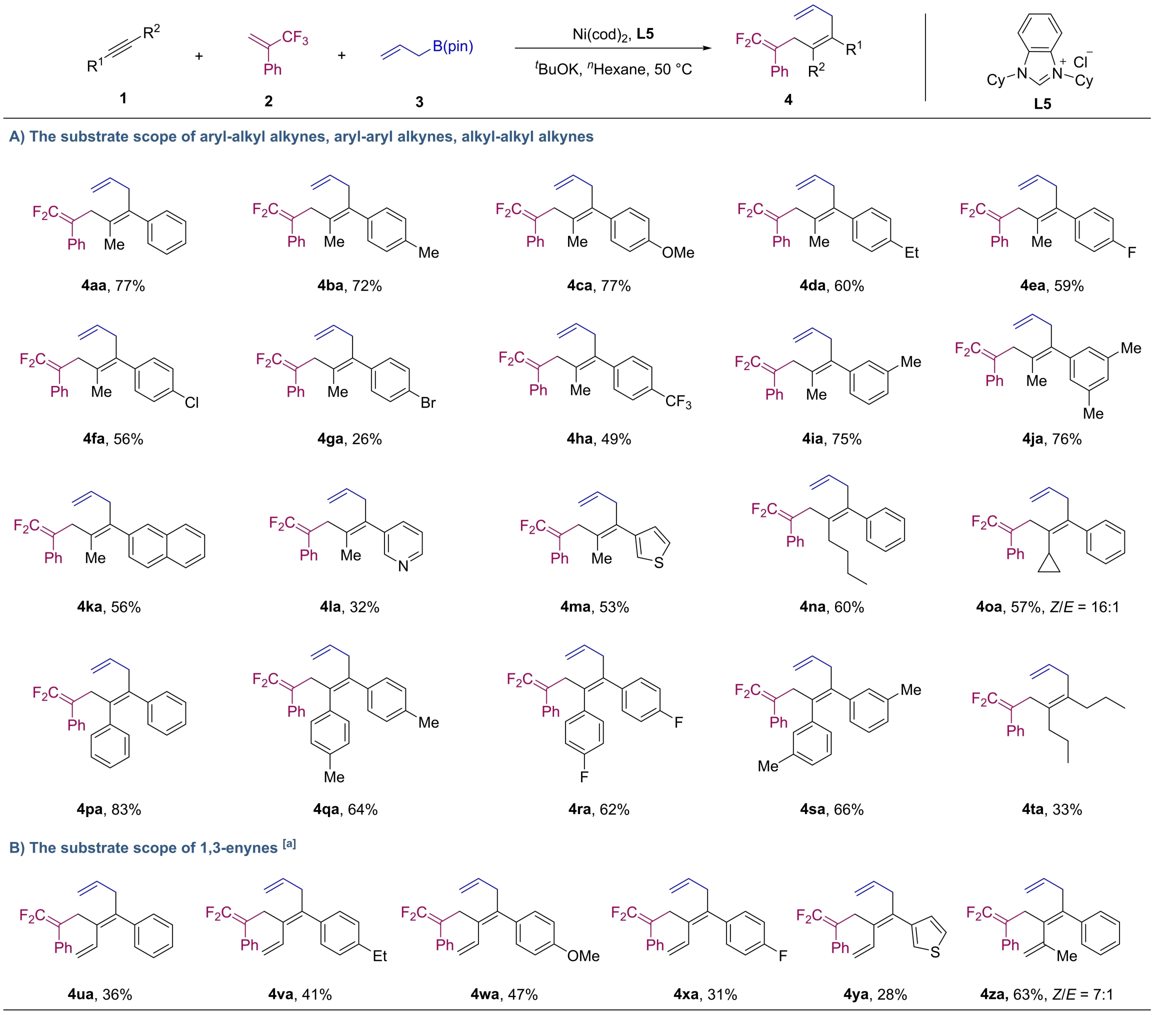


Figure 2. Substrate scope for alkyne substrates. Conditions: **1** (0.24 mmol), **2** (0.20 mmol), **3** (0.40 mmol), Ni(cod)$_2$ (5 mol %), **L5** (5 mol %), ^{t}BuOK (0.30 mmol), ^{n}hexane (1.0 mL), 50 °C, 24 h. Isolated yields were given in all cases. [a] PCy$_3$ (10 mol %) was used as ligand instead of **L5**.

transmetalation step with the allylboronate more than with HB(pin), which can also explain the fact that ligand **L5** exhibited better performance than PCy$_3$ in controlling selectivity.

Based on previous works and the above mechanistic investigation, a plausible mechanism of this unsymmetrical bis-allylation reaction was proposed (Figure 4C).[11o,16] Initially, the oxidative cyclometallation of alkyne **1a** and α-trifluoromethylstyrene **2a** with Ni^0 gives nickelacycle **A**, which favors the syn-addition of alkyne bonds. In addition, based on previous DFT calculation,[17] phenyl group is more electron-deficient and makes its β-carbon relatively electron poorer. Therefore, the nickel metal tends to couple with the Ph-substituted carbon when using aryl-alkyl alkyne substrates. Then, the following *β*-fluorine elimination of intermediate **A** generates alkenylnickel (II) species **B**. Subsequently, promoted by the base, species **B** may proceed through the transmetallation with allylboronate **3** to furnish species **C**. Eventually, the unsymmetrical bis-allylated product **4aa** is obtained after C–C bond reductive elimination of intermediate **C** which also regenerates the Ni^0 catalyst.

To further demonstrate the utility of this method, a scale-up experiment along with derivatizations of triene **4aa** were performed (Figure 5). Under the established conditions, the multicomponent coupling reaction between **1a**, **2a** and **3** could be successfully conducted on 1.0 mmol scale without obvious loss of yield and selectivity. Then, the decoration of tetrasubstituted alkene unit was first evaluated. To our delight, epoxidation reaction of **4aa** by *m*-CPBA occurred exclusively at the internal alkene bond and delivered epoxide product **8** in 82 % yield.[18] Next, we turned our attention to the functionalization of terminal alkene. A Wacker-type oxidation of **4aa** under Pd/Cu catalysis occurred at the terminal C=C bond and produced ketone **9** in 53 % yield.[19] After hydroboration with 9-BBN, the oxidation reaction by NaBO$_3$ could proceed smoothly to furnish alcohol **10** in 65 % yield. On the other hand, a palladium-catalyzed C–C coupling between hydroborated product and methyl 4-bromobenzoate provided skipped diene **11** in 51 % yield.[20] Afterwards, we focused on the transformations of *gem*-difluoroalkene moiety. Treating product **4aa** with 1*H*-imidazole in the presence of K$_3$PO$_4$,

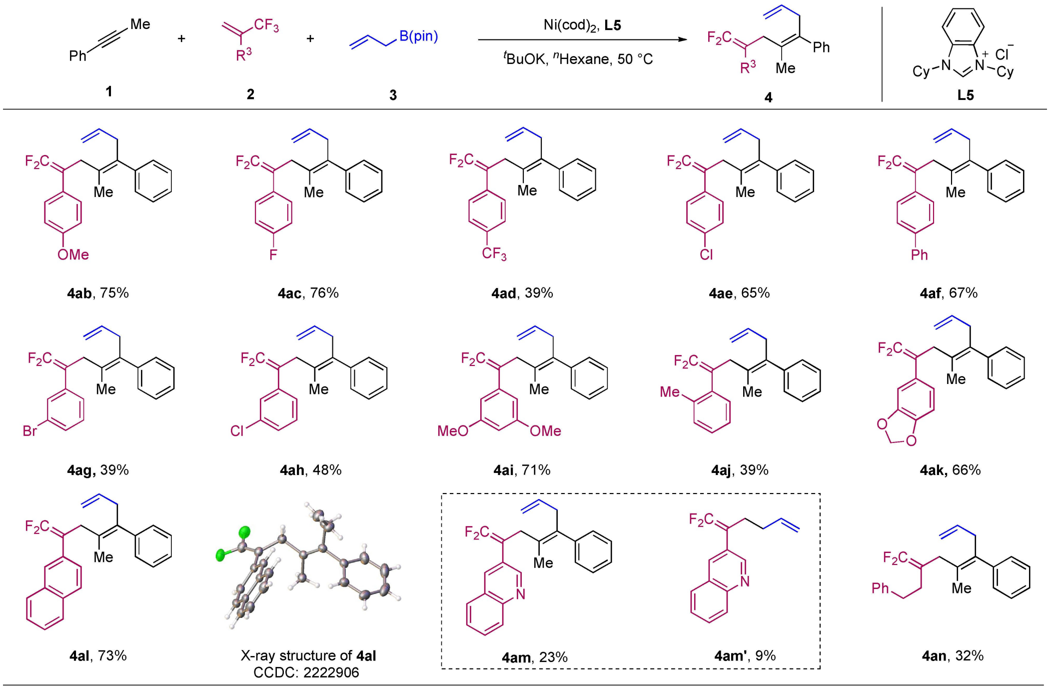
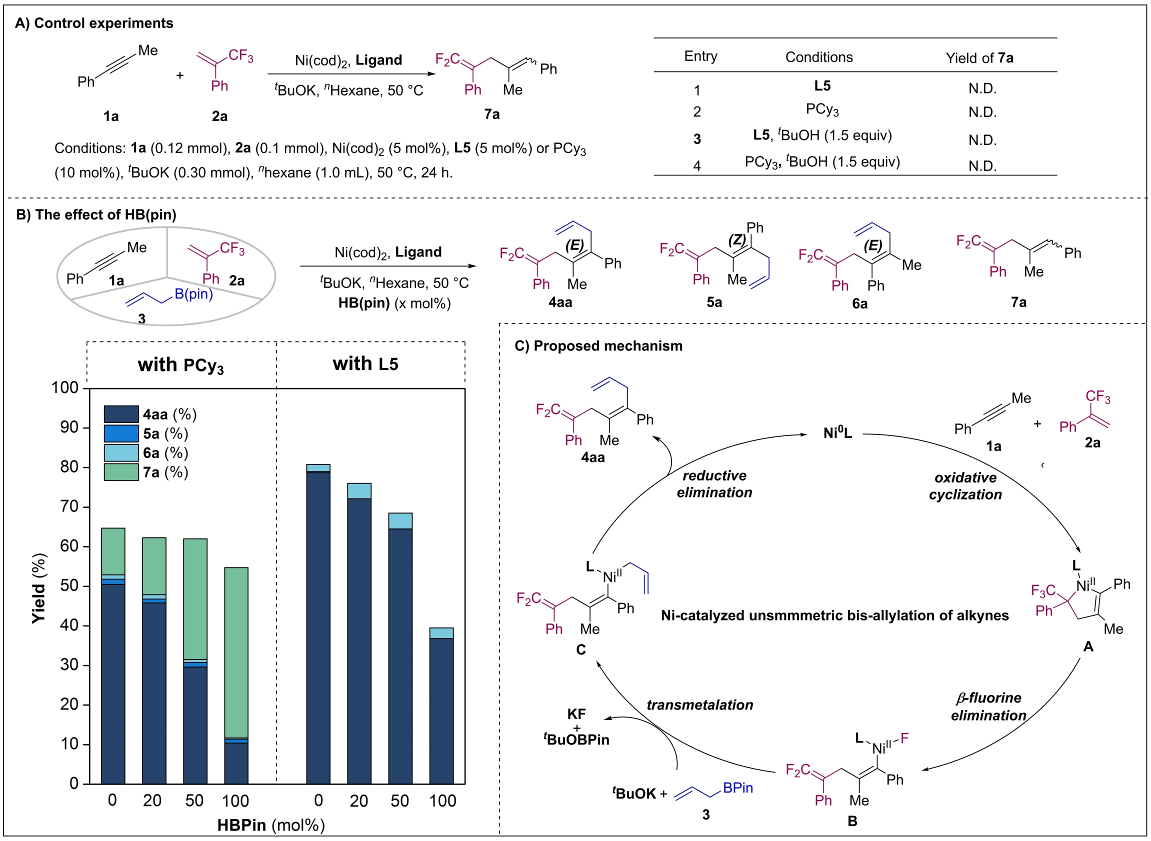


Figure 3. Substrate scope for trifluoromethylalkenes. Conditions: **1** (0.24 mmol), **2** (0.20 mmol), **3** (0.40 mmol), Ni(cod)$_2$ (5 mol%), **L5** (5 mol%), ^{t}BuOK (0.30 mmol), ^{n}hexane (1.0 mL), 50 °C, 24 h. Isolated yields were given in all cases.



Conditions: **1a** (0.12 mmol), **2a** (0.1 mmol), Ni(cod)$_2$ (5 mol%), **L5** (5 mol%) or PCy$_3$ (10 mol%), ^{t}BuOK (0.30 mmol), ^{n}hexane (1.0 mL), 50 °C, 24 h.

Entry	Conditions	Yield of **7a**
1	**L5**	N.D.
2	PCy$_3$	N.D.
3	**L5**, ^{t}BuOH (1.5 equiv)	N.D.
4	PCy$_3$, ^{t}BuOH (1.5 equiv)	N.D.

Figure 4. Mechanistic investigations and plausible mechanism.

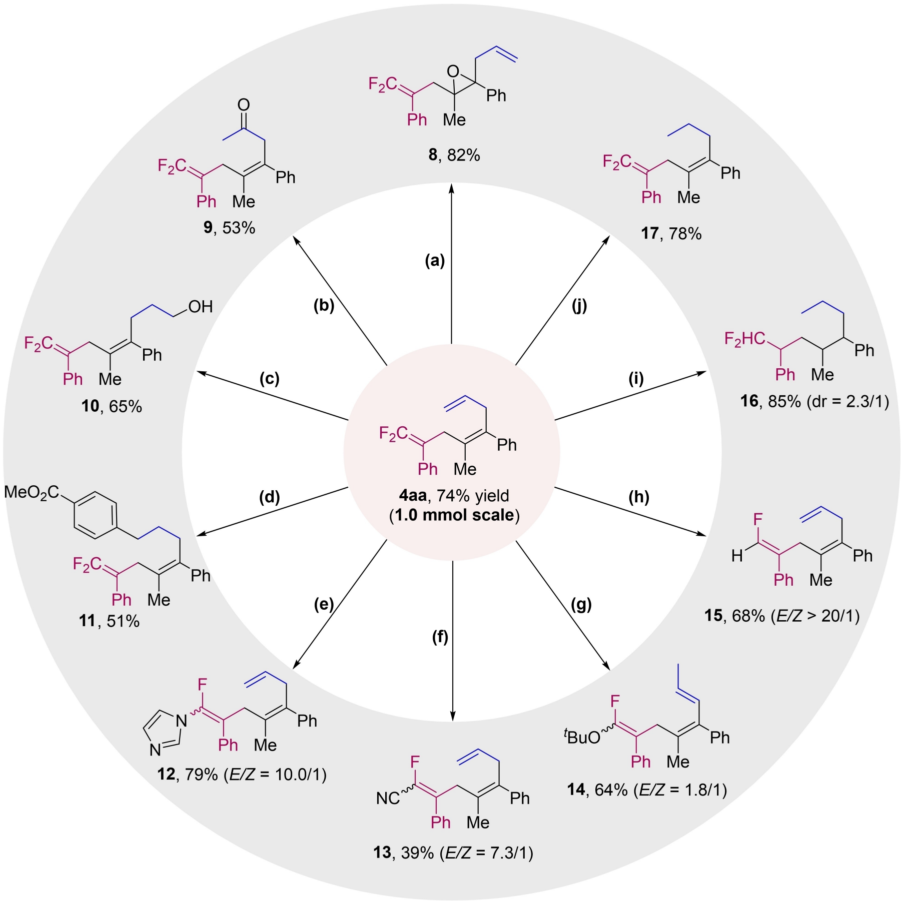


Figure 5. Synthetic transformations. Conditions: a) **4aa** (0.10 mmol), *m*-CPBA (2.0 equiv), DCM, rt; b) **4aa** (0.10 mmol), $PdCl_2$ (15 mol%), CuCl (1.5 equiv), DMF/H_2O, rt; c) step 1: **4aa** (0.10 mmol), 9-BBN dimer (55 mol%), 1,4-dioxane, 100 °C; step 2: $NaBO_3 \cdot 4H_2O$ (3.0 equiv), rt; d) step 1: **4aa** (0.10 mmol), 9-BBN dimer (55 mol%), 1,4-dioxane, 100 °C; step 2: $Pd(OAc)_2$ (5 mol%), PCy_3 (10 mol%), Cs_2CO_3 (3.0 equiv), methyl 4-bromobenzoate (1.1 equiv), 100 °C; e) **4aa** (0.10 mmol), imidazole (1.5 equiv), K_3PO_4 (2.0 equiv), DMF, 25 °C; f) **4aa** (0.10 mmol), TMSCN (3.0 equiv), Cs_2CO_3 (10 mol%), CH_3CN, 50 °C; g) **4aa** (0.10 mmol), ^{t}BuOK (2.0 equiv), THF, 35 °C; h) **4aa** (0.10 mmol), $LiAlH_4$ (2.0 equiv), THF, rt; i) **4aa** (0.10 mmol), Pd/C (10 mol%), H_2 (1.0 MPa), MeOH, rt; j) **4aa** (0.10 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (1 mol%), BINAP (2 mol%), H_2 (3.0 MPa), ^{t}BuOK (2 mol%), MeOH, 50 °C.

functionalized triene product **12** was efficiently afforded in 79 % yield with 10.0:1 *E*/*Z*.[21] Similar substitution of fluoro group could also be conducted with TMSCN, leading to nitrile **13** in 39 % yield.[22] Interestingly, the nucleophilic substitution and alkene isomerization could be operated simultaneously in the presence of ^{t}BuOK to afford product **14** in 64 % yield.[23] In addition, the defluorination of **4aa** with $LiAlH_4$ was observed in excellent stereoselectivity (> 20:1 *E*/*Z*), giving 68 % yield of mono-fluoro substituted alkene **15**.[24] The stereo configuration of product **15** was determined by NOE spectra (see Supporting Information for details). Notably, by choosing proper catalyst, the chemoselective hydrogenation was also a touchable task. For example, with the reactive Pd/C as catalyst, the **4aa** could be hydrogenated completely to deliver product **16** in 85 % yield.[25] In contrast, under ruthenium catalysis, hydrogenation could be precisely regulated at the terminal alkene bond and generated alkylated product **17** in 78 % yield.[26]

Conclusion

In conclusion, we have developed an unsymmetrical bis-allylation of alkynes under nickel catalysis by employing trifluoromethyl alkenes as electrophiles and allylboronate as nucleophiles. Under this robust protocol, various skipped trienes are obtained in good yields and excellent selectivities. Mechanistic studies indicate that the NHC ligand **L5**, which can probably promote the transmetalation process with allyl group, is critical to successfully control the regio-, stereo- and chemoselectivity. The synthetic utility of the skipped triene products is demonstrated in a scale-up reaction and various transformations.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Alkyne · Gem-Difluoroalkene · Nickel Catalysis · Skipped Triene · Unsymmetrical Bis-Allylation

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allyl-Bpin is usually industrially prepared by the reaction with allyl halide and HBpin in the presence of magnesium turnings, the presence of HB(pin) may be attributed to the residual raw material in purchased allyl-Bpin. To testify this possibility, we synthesized allyl-Bpin by a palladium catalyzed cross-coupling between allyl chloride and $B_2(pin)_2$, which can avoid the residue of HBpin. With PCy_3 as the ligand, the formation of hydroallylation product **7a** was indeed suppressed but with slightly decreased regioselectivity using this freshly synthesized allyl-Bpin. In comparison, the reactivity and selectivities all remained intact in the presence of **L5** with whether commercially purchased or home-made allyl-Bpin (for details, see Page S15). Given the economic and scale up issue of palladium catalyzed method for allyl-Bpin and the high performance of nickel/NHC catalysis, we still chose the purchased allyl-Bpin as substrates.

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