Modulation of metal species as control point for Ni-catalyzed stereodivergent semihydrogenation of alkynes with water

Divergent catalysis as a particularly appealing strategy from both academic and practical perspectives allows convenient control over selectivity towards different terminal products starting from the same material. Predictably, it would be more beneficial for the distinction of reactivity and selectivity if the two target molecules are achieved in separate mechanistic pathways, which generally requires employment of different catalysts to initiate diverse catalytic cycles. Therefore, it would be mechanistically interesting and also operationally practical to develop novel strategies in which different catalytic species could be generated from the same catalyst precursor by simple adjustment of the reaction factors, leading to different products with high selectivity in two independent catalytic cycles.

Transition metal-catalyzed stereodivergent hydrogen transfer of alkynes to produce both Z- and E-olefins have attracted remarkable interest in recent years. Most pioneering examples actualize this transformation by regulation of catalytic systems to realize a Z to E isomerization process at the late stage. For instance, Moran et al. showed that Ni-catalyzed transfer hydrogenation (TH) of alkynes with CH3OH selectively afforded Z-alkenes, which isomerized to E-alkenes by adding triphos ligand. Another catalyst-modulated system was disclosed by Liu and coworkers in 2016, in which both isomers could be achieved using Co catalysts supported with specified bidentate ligands. The isomerization of Z-alkenes was suppressed by introducing bulky ligand due to the sterically unfavored coordination and insertion processes. Recently Mei et al. reported that Pd-catalyzed semihydrogenation of alkynes with H2O delivered cis-olefins at room temperature in CH3CN, while isomerization of the double bond towards trans-olefins was facilitated at 80 °C in DMF. Mechanistically, E-alkenes in the majority of reported strategies originate from the Z-isomer, requiring subtleness of the reaction conditions and the steric or electronic properties of the substrates. Therefore, mechanistically orthogonal stereodivergent semi-reduction of alkynes to both olefinic isomers, in which E-alkenes are generated directly from alkynes instead of the isomerization from Z-alkenes, is undoubtedly meaningful in both academic and practical perspectives. We envisioned that modulating the catalytic species at an early stage might initiate independent profiles to deliver both isomers in orthogonal manners. Ideally, several issues should be addressed: (a) independent catalytic cycles should be initiated by simple adjustment of the reaction factor(s) to enable high yield and stereoselectivity; (b) nonprecious metals and ligands without toxic additives would be more favorable; (c) water is the first choice of the hydrogen donor for TH process; (d) alkynes with various substituents should be hydrogenated in high yield and stereoselectivity in mild conditions.
over-reduction to saturated alkanes need to be avoided. Pioneered by previous Ni-catalyzed alkyne hydrogenation, we launched a project with nickel catalysts to address the above challenges. After laborious trials, we realize a Ni-catalyzed stereodivergent TH of alkenes with water in an innovative controlling mode, in which the key to the success of modulation is the judicious inclusion of the base. Notably, unlike most existing reports, formation of trans-olefins is unrelated to the isomerization of cis-olefin. Mechanistic investigations suggest that base modulated the valence state of active nickel species derived from the same simple pre-catalyst. Consequently, the isomers are achieved independently in completely disparate catalytic pathways: the in situ formed Ni(II) species delivered Z-alkenes, while the Ni(0) species selectively afforded E-alkenes as final products.

**Results**

**Optimization of the reaction conditions**

We initiated our exploration by evaluating the transfer hydrogenation of the model substrate 1a with simple nickel sources and 2,2'-bipyridine ligands (Table 1). The first obstacle to overcome is the activation of the inert H2O molecule in our nickel catalyst system. Gratifyingly, boron reagents showed unique effect, and the alkenes were obtained in high yield and selectivity using Na2CO3 as base. BPh3 turned out to be more efficient than other diboron compounds such as B2(OH)4, B2C6H4 and B2neo2 (Supplementary Table 1). Although diboron compounds were found to be capable of activating water in Pd-catalyzed systems, including hydrogenation of unsaturated C-C bonds to saturated alkanes, it is, to our knowledge, the first case for such activation effect in Ni catalyst systems. Notably, E-alkene 3a was formed as the major isomer, and over-reduced alkane product was not observed. Solvents turned out to exert a profound influence on the reactivity (Supplementary Table 1), and 72% yield of alkenes were obtained with 11/89 isomeric ratio in DMF (entry 1). The above results inspired us to further proceed with other bases aiming at the optimization for Z-selective transfer semihydrogenation of 1a. As shown in Table 2, CH3CO2K and CH3CO2Cs acted similarly as Na2CO3, indicating that metal ions are not responsible for the selectivity reversal (entries 1 and 2). Only moderate selectivity was achieved when HCO2Na was added (entry 3). To our delight, PhCO2Na gave a promising result, providing the final olefins in 80/20 selectivity (entry 4). Again, dicarboxylate ligand L2 showed dramatically decreased reactivity (entry 5). In contrast, 4,4'-dimethoxy-2,2'-bipyridine L3 improved the selectivity to 93/7 (entry 6). Ligands L4 and L5 bearing methyl groups at 3,3'- or 4,4'-positions both gave slightly reduced selectivity than L3 (entries 7 and 8). When the loading of the catalyst and base were reduced, alkenes were retrieved in slightly improved yield and selectivity (entries 9 and 10). Contrary to E-selective system (Table 1, entry 14), the reaction could still proceed smoothly at a lower temperature of 40 °C, leaving all starting material recovered (entry 15). In contrast, comparable results were observed at higher temperatures (entries 16 and 17).

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**Mechanistic investigations**

Several questions deserve exploration to better understand this unprecedented system: (a) is water in the system indeed the hydrogen donor? (b) are alkenes generated from hydrometallation of in situ formed Ni-H species or hydrolysis of vinyl boron compounds? (c) does isomerization of Z-olefins take effect similarly as most precedents to
afford E-olefins? (d) what are the roles of the bases in modulation of the reaction outcomes? To answer these questions, a series of mechanistic studies were carried out. Firstly, deuterium-labeled experiments were conducted (Fig. 2a). The deuterium was incorporated into both the 1,2-olefinic positions of 2a and 3a with D2O instead of H2O under both standard conditions (equations (1) and (2)). Similar results were also observed for unsymmetric alkynes with 1b, 1c, and 1d, with the former leading to even higher deuterations (equations (3) and (4)). When the reactions of 1a using D2O were placed in hydrogen atmosphere, comparative deuterium isotopic contents as in argon were observed (equations (5) and (6)), proving that releasing of H2 and consequent hydrogenation was not involved in the catalytic pathway. Control experimental studies of vinylboron reagents 4, 5 and diborylated vinyl derivatives 4', 5' were respectively performed under both reaction conditions with 0, 1.0, 2.0, and 3.0 equiv. of B2pin2. Olefin products 2g and 3g were not detected (Fig. 2b, equations (9), (10), (11) and (12)). This, together with the reactions under H2 atmosphere, indicated that Ni-H species were formed between the nickel pre-catalyst and H2O assisted by B2pin2, which would deliver alkenyl nickel intermediates to accomplish the catalytic cycle.

To deeper understand the process of selective semi-reduction, the kinetic behavior of the reaction system was monitored (Fig. 2c). The kinetic profile of Z-selective transfer semihydrogenation system showed that the concentration of 2a increased gradually throughout the reaction period, staying closely aligned with the conversion of 1a. After 5 h, 3a began to show up until the yield reached 6% (Fig. 2c, left). We postulate that the small amount of E-alkene in this system was generated from isomerization of the Z-product, which was suppressed in the initial period due to competitive coordination of alkyne 1a with the metal center. Consumption of most 1a after 5 h left space for the coordination of 2a for the subsequent isomerization process, which still need 1a as auxiliary since the selectivity remained unchanged after disappearance of 1a. The E-selective reaction profile with CF3CO2Na as base clearly indicated the nonexistence of Z/E isomerization (Fig. 2c, right). Approximately 6% of Z-alkene was already formed at the early stage of the reaction, which maintained in this level until 1a was completely converted. The concentration of 3a increased gradually, which was independent with the amount of 2a. The kinetic isotopic effect (kH/kD = 1.68) was observed when H2O was replaced by D2O in the Z-selective reactant stream (Supplementary Figure 1), and a kinetic isotopic effect of 1.08 was also obtained in the Z/E isomerization process, which was promoted by heating 1a to 120°C under the Z-selective condition (Supplementary Fig. 3, equation (3)). Consistently, the reaction of 1a at
Table 2 | Optimization for the Z-selective transfer semihydrogenation of 1a

| Entry | Ligand | Base         | T/°C | Yield/%a | 2a/3a% |
|-------|--------|--------------|------|----------|--------|
| 1     | L1     | CH₃CO₂K     | 80   | 87       | 70/30  |
| 2     | L1     | CH₃CO₂Cs    | 80   | 97       | 72/28  |
| 3     | L1     | HCO₂Na      | 80   | 85       | 56/44  |
| 4     | L1     | PhCO₂Na     | 80   | 93       | 80/20  |
| 5     | L2     | PhCO₂Na     | 80   | 83       |        |
| 6     | L3     | PhCO₂Na     | 80   | 83       | 93/7   |
| 7     | L4     | PhCO₂Na     | 80   | 90       | 90/10  |
| 8     | L5     | PhCO₂Na     | 80   | 93       | 91/9   |
| 9     | L3     | PhCO₂Na     | 80   | 90       | 49/51  |
| 10b   | L3     | PhCO₂Na     | 60   | 90       | 94/6   |
| 11f   | L3     | PhCO₂Na     | 120  | 91       | 90/10  |
| 12    | L3     | PhCO₂Na     | 120  | 91       | 90/10  |
| 13    | L3     | PhCO₂Na     | 120  | 87       | 86/14  |

Reactions were performed with 1a (0.15 mmol), NiBr₂ (10 mol%), L (22 mol%), base (2.0 equiv.), B₂Pin₂ (3.0 equiv.), H₂O (3.0 equiv.), DMF (2 mL), 80 °C, 12 h.

5 mol% of NiBr₂, 11 mol% of L3.
Determined by crude ‘H NMR.
Isolated yield.
1.0 equiv. of PhCO₂Na.
The conversion of 1a was 68% after 15 h.

Fig. 2 | Mechanistic experiments. a Deuterium labeling experiment. b Control experimental studies of vinylboron reagents. c Kinetic profiles of the reaction systems. d Competitive control experiments of the bases.
120 °C under this condition afforded the corresponding olefinic products in 86/14 selectivity (Supplementary Fig. 3, equation (4)), compared with 93/7 at 80 °C.

The color changes between the two reaction systems were significantly different. As shown in Supplementary Fig. 4, the Z-selective system seemed turbid and beige at the very beginning, which turned to light brown after several minutes and got darker later. The color changed to tan-yellow gradually in about one hour and became lighter to milk-white after another one hour, which remained till the end. A completely different visual appearance was observed for the E-selective system, which looked transparent black and got darker quickly at the very early stage. Interestingly, as soon as the reaction was over as monitored of the crude mixture, the color changed to bright yellow immediately, which could be regarded as a simple hint for the completeness of the reaction. We postulate that the dark color ascribes to the coordination of the triple bond to the metal center, which was terminated promptly once alkenes were exhausted. The distinction in colors of the two systems indicates that different nickel species might be involved, leading to the corresponding olefinic products in totally unrelated pathways. The color variation of the control experiments on base was quite similar to the above observation (Supplementary Fig. 4, bottom): the initial pale green color changed to tint of turbidity yellow and clarify black color sequentially after the addition of PhCO$_2$Na and CF$_3$CO$_2$Na, respectively, indicating the formation of different nickel species was modulated with the choice of base.

Control competitive experiments of the bases were conducted to further illustrate their functions (Fig. 2d). After the standard Z-selective mixture using PhCO$_2$Na was stirred for 1 h, another 2.0 equivalent of CF$_3$CO$_2$Na was added, and no apparent influence on the reaction outcomes was observed (equation (15)). By contrary, a worse selectivity was observed after addition of PhCO$_2$Na into the E-selective system (28/72 vs 4/96) (equation (14)).

Further control experiments were carried out to verify the key role of Ni(I) species in the E-selective hydrogenation process. As shown in Fig. 3b, in situ formed Ni(II) species by mixing NiBr$_2$ and Ni(cod)$_2$ resulted in olefin 3a with E-configuration as major product (40% yield, 18/82 Z/E). Noteworthy, the reaction was totally suppressed in this condition without base (Supplementary Table 3, entry 24), which is another evidence for the participation of CF$_3$CO$_2$Na to deliver Ni(II) species. On the other hand, the Z/E ratio dropped appreciably when Mn or Zn was added in the Z-selective condition (Fig. 3c), which might be due to the generation and competitive act of Ni(II) species. Furthermore, the reactivity in condition A was suppressed when Zn or Mn was used instead of B$_2$Pin$_2$ (Fig. 3d), indicating that B$_2$Pin$_2$ not only interacts with bases to deliver active Ni species in this hydrogenation system, but also exists as an activator of water.

Although more experimental supports are awaited to uncover the detailed mechanism (initial NMR studies on the mechanism, see Supplementary Fig. 6), a general scenario could be delineated based on the above results and related literatures. As shown in Fig. 3e, NiBr$_2$ would interact with the bases firstly, delivering carboxylates carrying different counter anions. The difference in electronic properties between the benzene and the trifluoroacetate endows them with distinct reactivities towards B$_2$Pin$_2$. Organic bases such as DABCO and Et$_3$N inclined to give E-olefin 1 (Table 1, entries 11 and 12). Which is in consist of our proposal that counter anion from the base was not equipped to the metal center in the Z-selective catalytic cycle. Consequently, Ni(II) species C is generated directly from the benzene B and B$_2$Pin$_2$ for Z-selective catalytic reaction. Activation of H$_2$O molecule delivers Ni(II)-H species D, which undergo syn-addition to the triple bond to afford alkynyl Ni(II) intermediate E. Participation of another H$_2$O molecule releases the cis-olefin and regenerate C with the assistance of B$_2$Pin$_2$. Based on these kinetic experiments, coordination and insertion of the Z-alkene to the Ni-H species assisted by alkynyl precursor would occur in the late stage of the reaction, followed by isomerization process resulting in slight stereo-impurity. We propose that isomerization of a vinyl Ni(II) species is responsible for the E-selectivity observed in this approach, the specific oxidation state at Ni could provide an opportunity for isomerization. At the beginning of the cycle, Ni(II) species H might be generated firstly from nickel trifluoroacetate G and B$_2$Pin$_2$, which furnishes Ni(II) species I in a reductive elimination step. Comproportionation between H and I occurs instantly, forging Ni(II) species J to initiate the catalytic cycle. Activation of H$_2$O molecule would deliver Ni(II)-H species L, followed by insertion of alkynyl leading to vinyl Ni(II) intermediate M, which may undergo isomerization to E-alkenyl nickel intermediate N. Thermodynamically more stable product 3 is generated by hydrolysis of N, and the acquired nickel hydroxide O could be transformed back to Ni(I) species J in the aid of B$_2$Pin$_2$.

Density functional theory (DFT) calculations were carried out to investigate the remarkably different impact of PhCO$_2$Na and CF$_3$CO$_2$Na on Ni species. The reaction free energy profiles are shown in Fig. 4. The Ni(II) precursor A reacted with PhCO$_2$Na to afford nickel benzoate B, which is exergonic by 44.7 kcal/mol (Fig. 4a). The activation free energy barrier for one-ligand exchange of B towards PhCO$_2$Ni(II)-BPin$_2$ is 25.2 kcal/mol. The activation of H$_2$O molecule would deliver Ni(II)-H species I, followed by insertion of alkynyl leading to vinyl Ni(II) intermediate M, which may undergo isomerization to E-alkenyl nickel intermediate N. Thermodynamically more stable product 3 is generated by hydrolysis of N, and the acquired nickel hydroxide O could be transformed back to Ni(I) species J in the aid of B$_2$Pin$_2$.

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Entry 14). Although we were unable to locate the transition state for further ligand exchange from H to P, the notably higher reaction $\Delta G$ of two-ligand exchange makes it more unlikely. For the one-ligand exchange pathway, subsequent reductive elimination and comproportionation process are exergonic, leading to Ni(I) species J and K to initiate the E-selective catalytic cycle. The activation free energy barrier for the reaction of H with H$_2$O molecule en route to Ni(II)-H species R is nearly 10 kcal/mol higher than that of the reductive elimination. Besides, J + K is lower than R in the potential energy surfaces, basically excluding the participation of R in the catalytic cycle.

**Substrate scope**

The synthetic practicability of this system was sufficiently embodied in the functional group compatibility investigations. In Fig. 5a, the Z-selective semi-reduction of various alkynes 1 using PhCO$_2$Na as base is summarized. This reaction proceeded successfully toward substituted diarylene bearing a diverse set of substituents. Specifically, substrates bearing methyl or tert-butyl groups at $p$- or $o$-positions all worked smoothly under the standard conditions (2a - 2d), as well as hindered isopropyl (2e) or phenyl (2f) groups located in the ortho-position of the aryl terminus, suggesting the insensitivity of the system to steric effect. Electron-donating methoxy substituent was well accommodated, and the diaryl alkenes were generated in high yields and selectivity (2h, 2i and 2j). Amino functional group 2k was no exception, well tolerated in this catalytic transfer semihydrogenation process. Fluoro- and chloro-containing products (2q - 2t) were furnished from the corresponding alkynes, leaving space for further functionalization. Arylalkyne 1u bearing hydroxyl group provided the...
(Values in kcal/mol)

Fig. 4 | DFT calculations for reaction mechanism. a The Free-energy reaction profile of Z-selective catalytic cycle. b The Free-energy reaction profile of E-selective reaction system.
Fig. 5 | The scope of the transfer semihydrogenation system. a Scope of TH of alkynes to 1-alkenes with water. b Exploration of substrate scope in \( \beta \)-selective condition. c Substrate scope with respect to terminal triple bonds, enynes, and diynes.

*Reactions were performed with 1 (0.3 mmol), 1H2O (3.0 equiv), solvent (4 mL), *Reactions were performed at 80 °C. \( \delta \) (5 mmol) of 1H2O. \( \gamma \) (3.0 mmol) of 1H2O. **Condition A: 1 (0.3 mmol), 1H2O (5 mmol), L3 (11 mol%), PhCO2Na (1.0 equiv), Bpy (1.0 equiv), DMF (4 mL), 80 °C, **Condition B: 1 (0.3 mmol), 1H2O (5 mmol), L3 (11 mol%), PhCO2Na (1.0 equiv), Bpy (1.0 equiv), DMF (4 mL), 80 °C, **Condition B: 1 (0.3 mmol), 1H2O (5 mmol), L3 (11 mol%), PhCO2Na (1.0 equiv), Bpy (1.0 equiv), DMF (4 mL), 80 °C, **Condition B: 1 (0.3 mmol), 1H2O (5 mmol), L3 (11 mol%), PhCO2Na (1.0 equiv), Bpy (1.0 equiv), DMF (4 mL), 80 °C,
alkene product with 61/39 Z/E ratio. The relatively lower selectivity might be caused by isomerization of Z-olefin 2u, since the Z/E ratio of the olefins decreased from 86/14 to 53/47 by heating in DMF at 80 °C. The alkylne derivative containing Bpin-substituent was well tolerated, providing alkene 2v in 78% yield and 97/3 Z/E. The generality of the system was further showcased by the tolerance of naphthyl (2w) and heterocycles including thiényl (2x), benzofuranyl (2y) and pyridyl motifs (2z), particularly the latter, considering pyridyl ligands were used in our catalytic system. Moreover, running in a longer reaction time or higher temperature, alkynes carrying both naphthenic and linear alkyl terminuses could be reduced to the corresponding olefinic products efficiently (2bb–2hh). Notably, only Z-alkenes were formed specifically from the alkyl substrates, supporting our previous deduction that the E-alkenes in the Z-selective conditions might derive from the isomerization process, which was sluggish for alkyl alkenes due to their weak coordinating ability to the metallic species. The compatibility of the system was further underlined by successful involvement of unprotected primary OH group (2ff), which was unaffected under the catalytic conditions. Natural product derived alkylne with estrone skeleton proceeded smoothly, and the desired product 2gg was furnished in excellent yield and selectivity. Finally, internal alkyne iii bearing 1,2-dialkyl substituents also gave high yield and perfect stereoselectivity. A survey on the substrate scope was performed next to demonstrate the robustness of the E-selective TH process using CF₃CO₂Na as base (Fig. 5b). Similar as the former system, diatomic internal alkynes with a wide range of functional groups such as methyl (1a–1c), tert-butyldimethyl (1d), isopropyl (1e), methoxyl (1f, 1j), amino (1k), trifluoromethyl (1l), cyano (1m), ester (1o), acyl (1p) and halogen substituents (1q–1t) were all hydrogenated to the desired trans-alkenes uneventfully. Alkyne bearing a hydroxyl on the aromatic ring worked well to furnish the desired product 3u. Bpin group might interact competitively with the active species in this Ni-B hydrogenation system, thus olefin 3v was achieved in inferior selectivity (85/15 Z/E). Heteroaromatic rings including thiényl (1x), benzofuranyl (1y) and pyridyl (1z, 1aa) substituents were compatible again, delivering the alkyne heterocycles selectively. Trans-selective transfer semihydrogenation of alkyl acetylenes turned out to be challenging: monoaryl alkyn 3bh was reduced to 3hh in moderate yield and selectivity, while dialkyl alkyn 3ii delivered 3iin in much more inferior result. Propargyl esters were transformed to E-olefins (3jj–3ll) as single isomers in moderate yields and excellent selectivity. Consistent with the previous observation, for all the E-selective experiments, a mutation of color from black to bright yellow was observed as soon as the reaction finished. Finally, we tested the reactivity of terminal alkynes, which are more inclined to over-reduction. As shown in Fig. 5c, alkene 6 was obtained in high yield in Z-selective conditions from 1mm, and saturated ethyl product was not observed. The condition could also be extended to diynes 1nn and 1oo, with both triple bonds being hydrogenated in high selectivity. Interestingly, the reaction of conjugated enyne 1pp in Z-selective conditions afforded diene 9 with Z-configuration as the major product. On the contrary, Z-enzyme 10 was obtained in high selectivity when 1,3-diyne 1qq was loaded in E-selective conditions.

**Discussion**

In conclusion, we have disclosed an unprecedented Ni-catalyzed stereo- and regio-divergent transfer semihydrogenation of acetylenes with water. The configuration of the olefinic products was controlled by the choice of bases, which were demonstrated to influence the valence states of the catalytic nickel species. Consequently, E-alkenes were achieved independently from the direct reduction of alkyn precursors instead of isomerization of the Z-isomers. The strategy also features use of cheap catalysts and nontoxic reagents, and compatibility with an assortment of alkynyl substrates such as internal and terminal alkynes, 1,3-enynes and diynes. Besides its significance in semihydrogenation of alkynes, we believe that the mechanistic insights would lead to better understanding of the performance of nickel species, and also pave the way to further exploration of the other transition metal catalyst systems. Further pursuit including the development of the catalytic strategy and also detailed mechanistic studies are ongoing in our laboratory.

**Methods**

**General procedure for Z-selective transfer semihydrogenation of alkynes 1**

To a dry sealed tube were added alkyne 1 (0.3 mmol), NiBr₂ (3.3 mg, 0.015 mmol, 5 mol%), L3 (7.1 mg, 0.033 mmol, 11 mol%), PhCO₂Na (43.2 mg, 0.3 mmol, 1.0 equiv.) and B₂pin₂ (228.5 mg, 0.9 mmol, 3.0 equiv.). The flask was evacuated and refilled with argon, followed by the addition of H₂O (16.2 mL, 0.9 mmol, 3.0 equiv.) and DMF (4 mL). The mixture was stirred at 80–100 °C for 5–30 h until the reaction was completed as monitored by TLC. The resultant solution was diluted with ethyl acetate, washed with HCl aqueous solution (1 M) and concentrated in vacuum. The mixture was detected by GC directly or after simple filtration in some cases to determine the Z/E ratio. The crude product was purified by chromatography on silica gel (300–400 mesh), eluted with petroleum ether with 0–20% of ethyl acetate to give alkene product. Careful column chromatography was able to partially deliver the major product in a pure form to provide precise NMR spectra of the major product. The overall isolated yield was calculated based on the combination of all parts.

**General procedure for E-selective transfer semihydrogenation of alkynes 1**

To a sealed tube were added alkyne 1 (0.3 mmol), NiBr₂ (3.3 mg, 0.015 mmol, 5 mol%), L1 (5.2 mg, 0.033 mmol, 11 mol%), CF₃CO₂Na (81.6 mg, 0.6 mmol, 2.0 equiv.) and B₂pin₂ (228.5 mg, 0.9 mmol, 3.0 equiv.). The flask was evacuated and refilled with argon, followed by the addition of H₂O (16.2 mL, 0.9 mmol, 3.0 equiv.) and DMF (4 mL). The mixture was stirred at 80 °C for 10–20 h until the reaction was completed as monitored by TLC. The resultant solution was diluted with ethyl acetate, washed with HCl aqueous solution (1 M) and concentrated in vacuum. The mixture was detected by GC directly or after simple filtration in some cases to determine the Z/E ratio. The crude product was purified by chromatography on silica gel (300–400 mesh), eluted with petroleum ether with 0–20% of ethyl acetate to give alkene product. Careful column chromatography was able to partially deliver the major product in a pure form to provide precise NMR spectra of the major product. The overall isolated yield was calculated based on the combination of all parts. All compounds were characterized (see the Supplementary Information).

**Data availability**

The data that support the findings of this study are available within the article, its Supplementary Information files. All data underlying the findings of this work are available from the corresponding author upon request. Supplementary Data 1 contains the data of the imaginary frequencies, free energies and coordinates of the optimized structures. Supplementary Data 2 contains the 1H, 19F, 13C NMR spectra.

**References**

1. Nájera, C., Beletskaya, I. P. & Yus, M. Metal-catalyzed regiodivergent organic reactions. Chem. Soc. Rev. 48, 4515–4618 (2019).
2. Irimia, P. Beletskaya, I. P., Nájera, C. & Yus, M. Chemodivergent reactions. Chem. Soc. Rev. 49, 7101–7166 (2020).
3. Ping, L., Chung, D. S., Bouffard, J. & Lee, S. Transition metal-catalyzed site- and Regio-divergent C-H bond functionalization. Chem. Soc. Rev. 46, 4299–4328 (2017).
4. Mei, L., Wei, Y., Tang, X. & Shi, M. Catalyst-dependent stereo- and regioselective synthesis of indole-fused
heterocycles through formal cycloadditions of indolyl-allenes. J. Am. Chem. Soc. 137, 8131–8137 (2015).
5. Xu, S. et al. Enantioselective regiodivergent synthesis of chiral pyrrolidines with two quaternary stereocenters via ligand-controlled copper(I)- catalyzed asymmetric 1,3-dipolar cycloadditions. J. Am. Chem. Soc. 140, 2272–2283 (2018).
6. Yuen, O. Y. & So, C. M. Ligand control of palladium-catalyzed site-selective α- and γ-arylation of α,β-unsaturated ketones with (Hetero)aryl halides. Angew. Chem. Int. Ed. 59, 23438–23443 (2020).
7. Wang, J., Wu, P., Wu, J., Mei, G. & Shi, F. Chemodivergent tandem cyclizations of 2-indolylmethanols with tryptophols: C-N versus C-C bond formation. J. Org. Chem. 83, 5931–5946 (2018).
8. Richmond, E. & Moran, J. Ligand control of E/Z selectivity in nickel-catalyzed transfer hydrogenative alkyn semireduction. J. Org. Chem. 80, 6922–6929 (2015).
9. Fu, S. et al. Ligand-controlled cobalt-catalyzed transfer hydrogenation of alkynes: stereodivergent synthesis of Z- and E-alkenes. J. Am. Chem. Soc. 138, 8588–8594 (2016).
10. Zhao, C. Q. et al. Water as a hydrogenating agent: stereodivergent Pd-catalyzed semihydrogenation of alkynes. Org. Lett. 21, 1412–1416 (2019).
11. Shen, R. et al. Facile regio- and stereoselective hydrometallation of alkynes with a combination of carboxylic acids and group 10 transition metal complexes: selective hydrogenation of alkynes with formic acid. J. Am. Chem. Soc. 133, 17037–17044 (2011).
12. Kusy, R. & Grela, K. E- and Z-selective transfer semihydrogenation of alkynes catalyzed by standard ruthenium olefin metathesis catalysts. Org. Lett. 18, 6196–6199 (2016).
13. Yang, J. et al. Ligand-controlled iridium-catalyzed semihydrogenation of alkynes with ethanol: highly stereoselective synthesis of E- and Z-alkynes. Chem. Commun. 55, 1903–1906 (2019).
14. Kusy, R., Lindner, M., Wagner, J. & Grela, K. Ligand-to-metal ratio controls stereoselectivity: highly functional-group tolerant, iridium-based, (E)-selective alkyn transfer semihydrogenation. Chem. Catal. 2, 1346–1361 (2022).
15. Li, J. & Hua, R. Stereodivergent ruthenium-catalyzed transfer semihydrogenation of diaryl alkynes. Chem. Eur. J. 17, 8462–8465 (2011).
16. Chen, T., Xiao, J., Zhou, Y., Yin, S. & Han, L. B. Nickel-catalyzed (E)-selective semihydrogenation of internal alkynes with hypophosphorous acid. J. Organomet. Chem. 749, 51–54 (2014).
17. Li, K. et al. Cobalt catalyzed stereodivergent semi-hydrogenation of alkynes using H2O as the hydrogen source. Chem. Commun. 55, 5663–5666 (2019).
18. Oger, C., Balas, L., Durand, T. & Galano, J. Are alkyn reduction chem-, rego-, and stereoselective enough to provide pure (Z)-olefins in polyfunctionalized bioactive molecules? Chem. Rev. 113, 1313–1350 (2013).
19. Crespo-Quesada, M., Cárdenas-Lizana, F., Dessimoz, A. & Kiwiminsker, L. Modern trends in catalyst and process design for alkyn hydrogenations. ACS Catal. 2, 1773–1786 (2012).
20. Frihde, T. G. & Fürstner, A. Progress in the trans-reduction and trans-hydrometallation of internal alkynes. applications to natural product synthesis. Bull. Chem. Soc. Jpn. 89, 135–160 (2016).
21. Huang, Z., Wang, Y., Leng, X. & Huang, Z. An amine-assisted ionic monohydride mechanism enables selective alkyn cis-semihydrogenation with ethanol: from elementary steps to catalysis. J. Am. Chem. Soc. 143, 4824–4836 (2021).
22. Luo, J. et al. Controlled selectivity through reversible inhibition of the catalyst: stereodivergent semihydrogenation of alkynes. J. Am. Chem. Soc. 144, 13266–13275 (2022).
23. Srimani, D. et al. Iron pincer complex catalyzed, environmentally benign, e-selective semi-hydrogenation of alkynes. Angew. Chem. Int. Ed. 52, 14131–14134 (2013).
24. Cortese, N. A. & Heck, R. F. Palladium-catalyzed reductions of α,β-unsaturated carbonyl compounds, conjugated dienes, and acetylenes with trialkylammonium formamatic acids. J. Org. Chem. 43, 3985–3987 (1978).
25. Semba, K., Fujihara, T., Xu, T. H., Terao, J. & Tsuji, Y. Copper-catalyzed highly selective semihydrogenation of non-polar carbon-carbon multiple bonds using a silane and an alcohol. Adv. Synth. Catal. 354, 1542–1550 (2012).
26. Whittaker, A. M. & Lalic, G. Monophasic catalytic system for the selective semireduction of alkynes. Org. Lett. 15, 1112–1115 (2013).
27. Wang, D. & Astruc, D. The golden age of transfer hydrogenation. Chem. Rev. 115, 6621–6686 (2015).
28. Richards, E. M. & Tebby, J. C. Reactions of phosphines with acetylenes. Part VIII. Synthesis of 1,2-dideuterated olefins. J. Chem. Soc. (C) 1542–1544 (1969).
29. Chou, W., Clark, D. L. & White, J. B. The use of rieke zinc metal in the selective reduction of alkynes. Tetrahedron Lett. 32, 299–302 (1991).
30. Kataoka, Y., Takai, K., Oshima, K. & Utimoto, K. Selective reduction of alkynes to (Z)-alkenes via niobium- or tantalum-alkyne complexes. J. Org. Chem. 57, 1615–1618 (1992).
31. Chen, Z., Luo, M., Wen, Y., Luo, G. & Liu, L. Transition-metal-free semihydrogenation of diarylalkynes: highly stereoselective synthesis of trans-alkenes using Na-S-H2O. Org. Lett. 16, 3020–3023 (2014).
32. van Laren, M. W. & Elsevier, C. J. Selective homogeneous palladium(0)-catalyzed hydrogenation of alkynes to (Z)-alkenes. Angew. Chem. Int. Ed. 38, 3715–3717 (1999).
33. Wang, Y., Huang, Z. & Huang, Z. Catalyst as colour indicator for endpoint detection to enable selective alkyn transfer-hydrogenation with ethanol. Nat. Catal. 2, 529–536 (2019).
34. Thiel, N. O., Kaewmee, B., Ngoc, T. T. & Teichert, J. F. A simple nickel catalyst enabling an E-selective alkyn semihydrogenation. Chem. Eur. J. 26, 1597–1603 (2020).
35. Murugesan, K. et al. Nickel-catalyzed stereodivergent synthesis of E- and Z-alkynes by hydrogenation of alkynes. ChemSusChem 12, 3363–3369 (2019).
36. Li, K. et al. Anion controlled stereodivergent semi-hydrogenation of alkynes using water as hydrogen source. Asian J. Org. Chem. 10, 2143–2146 (2021).
37. Sato, T., Shoji Watanabe, S., Kiuchi, H., Oi, S. & Yoshio Inoue, Y. Hydrogenation of olefins using water and zinc metal catalyzed by a rhodium complex. Tetrahedron Lett. 47, 7703–7705 (2006).
38. Muhammad, O., Sonavane, S. U., Sasson, Y. & Chidambaram, M. Palladium/carbon catalyzed hydrogen transfer reactions using magnesium/water as hydrogen donor. Catal. Lett. 125, 46–51 (2008).
39. Yan, M. et al. Nanoporous gold catalyst for highly selective semi-hydrogenation of alkynes: remarkable effect of amine additives. J. Am. Chem. Soc. 134, 17536–17542 (2012).
40. Cummings, S. P., Le, T. N., Fernandez, G. E., Quiambao, L. G. & Stokes, B. J. Tetrahydroxiboron-mediated palladium-catalyzed transfer hydrogenation and deuteriation of alkynes and alkynes using water as the stoichiometric H or D atom donor. J. Am. Chem. Soc. 138, 6107–6110 (2016).
41. Xuan, Q. & Song, Q. Diboron-assisted palladium-catalyzed transfer hydrogenation of n-heteroaromatics with water as hydrogen donor and solvent. Org. Lett. 18, 4250–4253 (2016).
42. Kong, W., Wang, Q. & Zhu, J. Water as a hydride source in palladium-catalyzed enantioselective reductive Heck reactions. Angew. Chem. Int. Ed. 56, 3987–3991 (2017).
43. Olja, D. P., Gadde, K. & Prabhu, K. R. Generation of hydrogen from water: a Pd-catalyzed reduction of water using diboron reagent at ambient conditions. Org. Lett. 18, 5062–5065 (2016).
44. Flinker, M. et al. Efficient water reduction with sp$^3$-sp$^3$ diboron(4) compounds: application to hydrogenations, H–D exchange reactions, and carbonyl reductions. Angew. Chem. Int. Ed. **56**, 15910–15915 (2017).

45. He, G. et al. Copper(I)-catalyzed highly regio- and stereoselective boron addition–protonolysis of alkynamides. Eur. J. Org. Chem. **2023**, 6979–6987 (2013).

46. Bao, H., Zhou, B., Jin, H. & Liu, Y. Diboron-assisted copper-catalyzed Z-selective semihydrogenation of alkynes using ethanol as a hydrogen donor. J. Org. Chem. **84**, 3579–3589 (2019).

47. Huang, J. et al. Substrate-controlled Cu(OAc)$_2$-catalyzed highly regio- and stereoselective semihydrogenation of alkynes with MeOH as the hydrogen source. ACS Omega **6**, 11740–11749 (2021).

48. King, A. E. et al. GordonNi(bpy)(cod): a convenient entryway into the molecular structure and hard-soft donor sets. Inorg. Chem. **33**, 4869–4877 (1994).

49. James, T. L., Smith, D. M. & Holm, R. H. Stereoelectronic preferences exerted by Zn(II) in the catalytic sp$^2$ C–H activation for light-driven hydrogen production. J. Am. Chem. Soc. **135**, 13246–13249 (2013).