

Modulation of Metal Species as Early Control Point for Ni-catalyzed Stereodivergent Semihydrogenation of Alkynes with Water

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Abstract

A base-assisted metal species modulation mechanism enables Ni-catalyzed stereodivergent semihydrogenation of alkynes with water, delivering both olefinic isomers smoothly using cheap and nontoxic catalysts and additives. Different from most precedents, in which *E*-alkenes derive from the isomerization of *Z*-alkene products, the isomers were formed in orthogonal catalytic pathways. Mechanistic studies suggest base as a key early element in modulation of the reaction pathways: by adding different bases, nickel species with disparate valence states could be accessed to initiate two catalytic cycles toward different stereoisomers. The practicability of the method was showcased with nearly 70 examples, including internal and terminal triple bonds, enynes and diynes, affording semi-hydrogenated products in high yields and selectivity.

Introduction

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.¹⁻⁷ 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 interests in recent years.⁸⁻¹³ Most pioneering examples actualize this transformation by regulation of catalytic systems to realize a *Z* to *E* isomerization process at the late stage (Scheme 1, above). For instance, Moran, *et al* showed that Ni-catalyzed TH of [alkynes](#) with HCO₂H selectively afforded *Z*-olefins, which isomerized to *E*-isomers by adding triphos ligand.⁸ 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.⁹ 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.¹⁰ 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 point of views. We envisioned that modulating the catalytic species at an early stage might initiate independent profiles to deliver both isomers in orthogonal manners (Scheme 1, bottom). 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;⁸⁻¹⁰ (b) nonprecious metals and ligands without toxic additives would be more favorable;¹⁴⁻¹⁸ (c) water is the first choice of the hydrogen donor for TH process;^{10, 19-22} (d) alkynes with various substituents should be hydrogenated in high yield and stereoselectivity in mild conditions, and over-reduction to saturated alkanes need to be avoided.^{23,24} Based on our interest in Ni-catalyzed reaction and alkyne transformations,²⁵⁻²⁷ We launched a project with nickel catalysts to address the above challenges. After laborious trials, we realized an unprecedented Ni-catalyzed stereodivergent TH of alkynes with water in a novel 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 was unrelated to the isomerization of *cis*-olefin. Mechanistic investigations suggested that base modulated the valence state of active nickel species derived from the same simple pre-catalyst. Consequently, the isomers were achieved independently in completely disparate catalytic pathways: the in situ formed Ni(II) species delivered *Z*-alkenes, while the Ni(I) 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.²⁸⁻³⁰ Gratifyingly, boron reagents showed unique effect, and the alkenes were obtained in high yield and selectivity using Na₂CO₃ as base. B₂pin₂ turned out to be more efficient than other diboron compounds such as B₂(OH)₄, B₂cat₂ and B₂neop₂ (Supplementary Table 1).³¹⁻³³ Although diboron were found to be capable of activating water in Pd-catalyzed systems,³¹⁻³⁵ including hydrogenation of unsaturated C-C bonds to saturated alkanes,³¹ it is, as far as we know, 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), 72% yield of alkenes were obtained with 11/89 isomeric ratio in DMF (entry 1). Decorating the bipyridine ligand with electron-withdrawing ester groups totally suppressed the reactivity (entry 2). Subsequent screening of other bipyridine derivatives as well as phenanthroline ligands **L3-L6** provided comparatively inferior results to 2,2'-bipyridine (entries 3-6). Systematic screening of nickel catalyst, ligand, base, boron and water (Supplementary Table 2 and 3) showed that base exerted an unexpected, yet decisive role in the control of selectivity. As shown in Table 1, the reaction was evidently inclined to *E*-selectivity by K₂CO₃, NaOH and CF₃CO₂Na, with the later showing the best result, affording **3a** in 84% isolated yield and 6/94 *Z/E* ratio (entries 7-9). Interestingly, a slant to *Z*-selectivity was shown with CH₃CO₂Na, providing **2a** with 69/31 *Z/E* ratio (entry 10). Organic bases such as DABCO and Et₃N were also tested, and *E*-alkene **3a** was delivered as the major product (entries 11 and 12). The catalyst loading could be lowered to 5 mol% with no erosion of the yield or selectivity (entry 13). The reactivity was almost totally shut down at a lower temperature of 60 °C (entry 14), which might due to the insufficient energy

for the isomerization of alkenyl nickel intermediate (Figure 1i). In contrast, comparable results were observed at higher temperatures (entries 15 and 16).

The above results inspired us to further proceed with other bases aiming at the optimization for *Z*-selective semihydrogenation of **1a**. As shown in Table 2, CH₃CO₂K and CH₃CO₂Cs acted similarly as CH₃CO₂Na, 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, albeit **1a** was partially recovered (entry 11). Performing the reaction at higher temperatures resulted in poorer selectivities (entries 12 and 13).

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 (Figure 1a). 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 **1z** and **1g**, with the former leading to even higher deuterations (equations (7) and (8)). In contrast, there was no sign of deuteration on the products using DMF-*d*₇ as solvent (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** and **5** were performed under the standard reaction conditions.^{36,37} Olefin products **2a** and **3a** were not detected, excluding the possibility of hydrolysis of vinylboron derivatives (Figure 1b, equations (9) and (10)). 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. 1c). The kinetic profile of *Z*-selective semihydrogenation showed that **2a** was generated by degrees in the initial 5 hours, and the yield stayed closely aligned with the conversion. After this period, **3a** began to show up and gradually increased to 6% yield, alongside with a sharp decline of the yield growth rate of **2a** (Fig. 1c, left). We postulate that the small amount of *E*-alkene in this system

derives from isomerization of the *Z*-isomer, which was suppressed in the initial 5 hours since competitive coordination of alkyne **1a** with the metal center. Consumption of most **1a** after 5 hours 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 $\text{CF}_3\text{CO}_2\text{Na}$ as base clearly indicated the nonexistence of *Z/E* isomerization (Fig. 1c, 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**.

To further verify the above inferences, a series of control experiments were conducted (Fig. 1d). When *Z*-alkene **2a** was put in both standard conditions, only less than 5% of *E*-alkene was detected (equations (11) and (12)), demonstrating the reluctance of the *Z/E* isomerization in these conditions. Elevating the reaction temperature showed a beneficial effect for the isomerization, which was promoted to 13% by heating **2a** at 120 °C under the *Z*-selective condition (equation (13)). Consistently, the reaction of **1a** at 120 °C under this condition afforded the corresponding olefinic products in 86/14 selectivity (equation (14)), compared with 93/7 at 80 °C.

The color changes between the two reaction systems were significantly different. As shown in Figure 1e, 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 mutation 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 complete 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 alkynes were exhausted.²⁴ 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 (Fig. 1e, bottom): the initial pale green color changed to tint of turbidity yellow and clarify black color separately after addition of PhCO_2Na and $\text{CF}_3\text{CO}_2\text{Na}$, respectively, indicating the formation of different nickel species was modulated with the choice of base.

Competitive control experiments of the bases were conducted to further illustrate their functions (Figure 1f). After the standard *Z*-selective mixture using PhCO_2Na was stirred for 1 h, another 2.0 equivalent of $\text{CF}_3\text{CO}_2\text{Na}$ was added, and no apparent influence on the reaction outcomes was observed (equation (15)). By contrary, a worse selectivity was caused by addition of PhCO_2Na into the *E*-selective system (28/72 vs 4/96) (equation (16)).

All the mechanistic insights and the visual phenomenon pointed to distinct catalytic pathways for the two reaction systems, inspiring us to further inquire whether different metal species were taking effect inherently. To detect whether nanoparticles were involved in our Ni-B-H₂O system, general mercury drop experiments were performed^{32,34} (Figure 1g). The yield or selectivity was not affected in either systems (equations (17) and (18)), excluding heterogeneous catalytic pathways. Despite the failure in capture of metallic intermediates, electron paramagnetic resonance (EPR) analyses provided clues on the active nickel species and the base effect. As shown in Figure 1h (2), strong EPR signals were observed in the *E*-selective mixture, indicating the formation of Ni(I) or Ni(III) species.³⁸⁻⁴¹ The signals of such Ni species could not be found at ambient temperature, which is in accordance with our experimental observations that semihydrogenations of **1a** were not permitted at rt (Supplementary Table 3, entry 25). In contrast, EPR active species was not observed in *Z*-selective system (Figure 1h (1)), featuring a Ni(0)/Ni(II) catalytic cycle. In agreement with the competitive experiments of bases (equation (16)), the EPR signals for the reactions using CF₃CO₂Na as base were markedly weakened after the addition of PhCO₂Na (Figure 1h (3)). In line with the fact that use of HCO₂Na as base gave an almost 1:1 ratio of the *Z*- and *E*-alkenes (Table 2, entry 3), the EPR signal of the system with HCO₂Na was less significant than that with CF₃CO₂Na (Figure 1h (4)), but much more significant than that of PhCO₂Na system (Figure 1h (1)).

Although more experimental supports are awaited to uncover the detailed mechanism, a general scenario could be delineated based on the above results and relative literatures^{31,32, 42-50} (Figure 1i): NiBr₂ would interact with the bases firstly, delivering carboxylates carrying different counter anions. The difference in electronic properties between the benzoate and the trifluoroacetate endows them with distinct reactivities towards B₂pin₂. Consequently, Ni(II) species **C** is generated directly from the benzoate **B** and B₂pin₂. Activation of H₂O molecule delivers Ni(II)-H species **D**, which undergo *syn*-addition to the triple bond to afford alkenyl Ni(II) intermediate **E**. Participation of another H₂O molecule release the *cis*-olefin and regenerate **C** with the assistance of B₂pin₂. Based on the kinetic experiments, coordination and insertion of the *Z*-alkene to the Ni-H species assisted by alkyne 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(I) species is responsible for the *E*-selectivity observed in this approach, the specific oxidation state at Ni could provide an opportunity for isomerization^{42,43}. At the beginning of the cycle, Ni(0) species **H** might be generated firstly from nickel trifluoroacetate **G** and B₂pin₂. Oxidative addition of another molecule of B₂pin₂ furnishes Ni(II) species **C**, comproportionation between **C** and **H** occurs instantly, forging Ni(I) species **I** to initiate the catalytic cycle. Activation of H₂O molecule would deliver Ni(I)-H species **J**, followed by insertion of alkyne leading to vinyl Ni(I) intermediate **K**, which may undergo isomerization⁴³ to *E*-alkenyl nickel intermediate **L**. Thermodynamically more stable product **3** is generated by hydrolysis of **L**, and the acquired nickel hydroxide **M** could be transformed back to Ni(I) species **I** in the aid of B₂pin₂.

Substrate scope. The synthetic practicability of this system was sufficiently embodied in the functional group compatibility investigations. In Table 3a, the *Z*-selective semi-reduction of various alkynes **1** using

PhCO₂Na as base is summarized. This reaction proceeded successfully toward substituted diarylethynes bearing a diverse set of substituents. Specifically, substrates bearing methyl or *tert*-butyl groups at *p*- or *m*-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 semihydrogenation process. *Z*-olefins with electron-withdrawing trifluoromethyl (**1l**), cyano (**1m, 1n**), ester (**1o**) and acyl (**1p**) groups could also be achieved uneventfully. Fluoro- and chloro-containing products (**2q-2t**) were furnished from the corresponding alkynes, leaving space for further functionalization. The generality of the system was further showcased by the tolerance of naphthyl (**2u**) and heterocycles including thienyl (**2v**), benzofuryl (**2w**) and pyridyl motifs (**2x**), particularly the latter, considering pyridinyl 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 (**2z-2ff**). 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 (**2dd**), which was unaffected under the catalytic conditions. Natural product derived alkyne with estrone skeleton proceeded smoothly, and the desired product **2ee** was furnished in excellent yield and selectivity. Finally, internal alkyne **1ff** 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 (Table 3b). Similar as the former system, diaromatic internal alkynes with a wide range of functional groups such as methyl (**1a-1c**), *tert*-butyl (**1d**), isopropyl (**1e**), methoxyl (**1i, 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. Heteroaromatic rings including thienyl (**1v**), benzofuryl (**1w**) and pyridyl (**1x, 1y**) substituents were compatible again, delivering the alkenyl heterocycles selectively. The reaction of alkyl acetylene was more challenging, affording alkene **3gg** in moderate yield and inferior selectivity. Propargylic esters were transformed to *E*-olefins (**3hh-3jj**) 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 Table 3c, alkene **6** was obtained in high yield in *Z*-selective conditions from **1kk**, and saturated ethyl product was not observed. The condition could also be extended to diynes **1ll** and **1mm**, with both triple bonds being hydrogenated in high selectivity. Interestingly, the reaction of conjugated enyne **1nn** in *Z*-selective conditions afforded diene **9** with *E*-configuration as the major product. On the contrary, *Z*-enyne **10** was obtained in high selectivity when 1,3-diyne **1oo** was loaded in *E*-selective conditions.

Conclusions

In conclusion, we have disclosed an unprecedented Ni-catalyzed stereodivergent 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 alkyne precursors instead of isomerization of the *Z*-isomers. The strategy also features use of cheap catalysts and nontoxic reagents, and the 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.

Declarations

Competing interests

The authors declare no competing interests.

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Figures

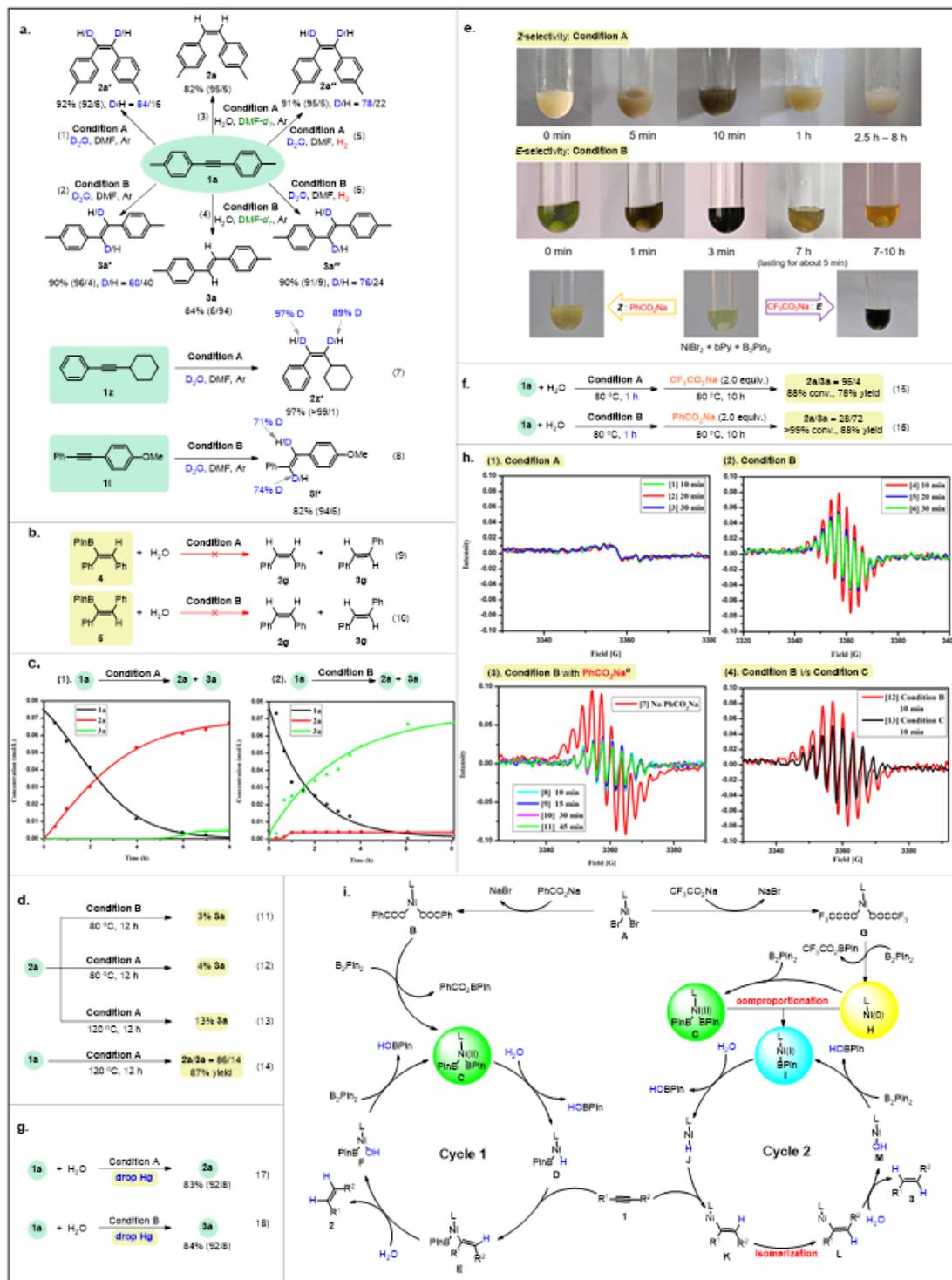


Figure 1

Mechanistic investigations.

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