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Photoinduced NiH Catalysis with Trialkylamines for the Stereodivergent Transfer Semi-Hydrogenation of Alkynes

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Abstract: We report a selectivity-switchable nickel hydride-catalyzed methodology that enables the stereocontrolled semi-reduction of internal alkynes to *E*- or *Z*-alkenes under very mild conditions. The proposed transfer semi-hydrogenation process involves the use of a dual nickel/photoredox catalytic system and triethylamine, not only as a sacrificial reductant, but also as a source of hydrogen atoms. Mechanistic studies revealed a pathway involving photo-induced generation of nickel hydride, *syn*-hydronickelation of alkyne, and alkenylnickel isomerization as key steps. Remarkably, mechanistic experiments indicate that the control of the stereoselectivity is not ensuing from a post-reduction alkene photoisomerization under our conditions. Instead, we demonstrate that the stereoselectivity of the reaction is dependent on the rate of a final protonolysis step which can be tuned by adjusting the pKa of an alcohol additive.

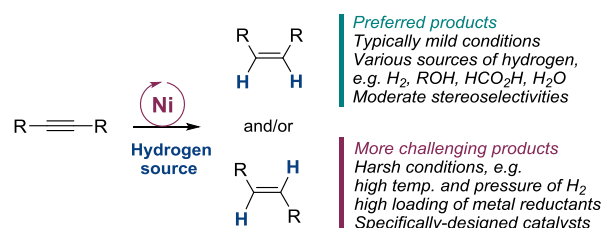
Introduction

The development of reliable and predictable methods that can convert alkynes stereo-selectively to *Z*- or *E*-alkenes, on demand, is of fundamental importance to industries and academia, owing to the prevalence of the alkene functionality in fine chemicals, pharmaceuticals and natural products, which include the high-value stilbenoids.^[1] The privileged systems for selective hydrogenation to *Z*-alkenes are based on palladium heterogeneous catalysts using gaseous hydrogen. These methods often suffer from fast catalyst deactivation, over-reduction, and the presence of toxic lead oxides or excess quinoline. On the other hand, conventional methods to access *E*-alkenes from alkynes rely on unpractical Birch-type reductions featuring harsh conditions and therefore poor functional group tolerance.

Over the recent decades, important research efforts have focused on the development of milder experimental protocols which led to significant advances in applying sustainable organic molecules like alcohols and organic acids, as well as water instead of gaseous hydrogen. New catalysts based on first-row transition-metals (Ni, Co, Cu, Fe, and Mn) have also been extensively developed as viable alternatives to Pd.^[2a] Nevertheless, overcoming issues with chemo- and regio-selectivity has remained a recurrent challenge for the development of catalytic alkyne semi-reduction processes.^[2]

High-efficiency nickel-based catalytic systems have been recently reported for selective reduction of alkynes to *E*- or *Z*-alkenes with limited over-reduction, if any. While *Z*-isomers are often easily formed as the preferred products under mild conditions,^[3] selective methods for *E*-isomers have proved more challenging, often requiring harsh conditions (e.g., high temperature, high pressure of gaseous hydrogen, high loading of metal reductants) or specifically designed catalysts (Figure 1A), and they remain under-developed.^[4]

A. Classical Ni-catalyzed semi-reductions to *Z*- and/or *E*-alkenes:



B. Stereodivergent semi-reductions enabled by Ni/Photoredox catalysis Reaction design:

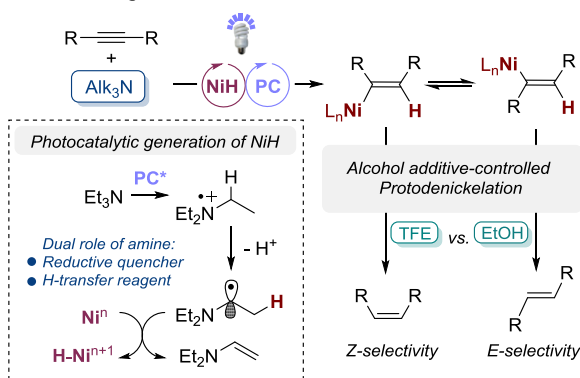


Figure 1. Ni-catalyzed *E*- and *Z*-selective semi-reductions of alkynes. (A) State of the art; (B) Present work.

More interestingly, catalytic methods allowing stereodivergent semi-reduction to *Z* or *E* alkenes are very rare.^[5] These strategies typically rely on the generation of a nickel hydride intermediate from diverse hydride sources,

followed by the formation of a key alkenyl-nickel species and subsequent proto-denickelation that liberates the alkenes. In typical mechanisms, it is proposed that the alkyne is first converted to the *Z*-alkene, which may then be isomerized to the corresponding *E*-alkene by the nickel hydride species.^[6] The isomerization process can be controlled and tuned by changing various reaction parameters, *i.e.* by modifying the nickel catalytic system (nickel source, ligand) or via an additive. However, these methods still require quite harsh conditions and high temperatures that can limit their practical application. Today, the development of mild, operationally simple protocols allowing a stereodivergent production of *Z*- or *E*-alkenes remains a remarkable challenge in this research.

The recent advent of nickel and photoredox dual catalysis has stimulated new conceptual strategies toward the conversion of alkynes to functionalized alkenes under very mild reaction conditions.^[7] However, applications to the simple semi-reduction of alkynes remain elusive in this area. Very rare examples have been recently reported, based on heterogeneous catalytic systems that provide *Z*-alkenes, preferentially, with moderate levels of selectivity.^[8] We envisioned that the development of a nickel/photoredox system, using mild hydrogen donors and allowing selective access to either *E*- or *Z*-alkenes by simple variations of the reaction parameters, would provide a valuable complementary strategy for the stereodivergent semi-reduction of alkynes.

From the outset of our endeavors, we realized that the set-up of a viable catalytic protocol under photocatalytic conditions would raise several challenges to address. Ideally, the stereo-outcome of the semi-reduction should be controlled by the nickel catalyst rather than by the sensitizer. Indeed, visible light photocatalysis has been shown to promote *E/Z* isomerization of alkenes through triplet energy transfer from the excited photocatalyst, which can complicate the design of stereodivergent methodologies.^[9] One possible strategy would be to control the rate of isomerization and protonolysis of the postulated alkenyl-nickel intermediates through careful choice of the species to be involved in the protonolysis step or by ligand electronic tuning. A last but not least challenge would be to find a suitable, mild source of hydrogen atoms capable of promoting the generation of nickel hydride species under photochemical conditions.^[10]

Herein, we report a metallaphotoredox catalytic transfer semihydrogenation methodology that satisfies all these challenges (Figure 1B). Our strategy relies on the use of a simple trialkylamine serving not only as a reductive quencher, but also as hydrogen transfer reagent^[11] capable of providing hydrogen atoms to the catalytic system via its photochemically generated amine radical cation.^[12] An additional remarkable feature of the process is the possibility of inducing a complete selectivity switch by adjusting the pKa of a simple alcohol additive. Mechanistic studies provided some rationale for the origin of stereoselectivity, notably dismissing typical post-reaction alkene isomerization pathways.

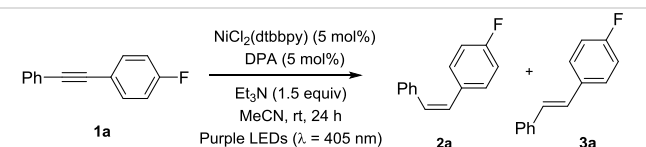
Results and Discussion

The feasibility of the redox process was primarily examined by reacting our model substrate, 1-fluoro-4-(phenylethynyl)-benzene (**1a**), with triethylamine in the presence of a combination of nickel(II) catalyst and photocatalyst under visible light irradiation (Table 1). 9,10-Diphenylanthracene (DPA) was selected as an appropriate photocatalyst for our preliminary experiments. DPA is an inexpensive organic semi-conductor used in OLEDs and blue glow sticks, but remains under-utilized as a photocatalyst.^[13] The oxidation potential of its excited state [$E^* = +1.19$ V vs SCE in DMSO]^[13a] should allow access to amine radical cations via one-electron oxidation of trialkylamines, while the strong reducing power of its ground-state radical anion [$E_{1/2}(\text{DPA}^-/\text{DPA}) = -1.94$ V]^[13b] should be capable of reducing Ni species to sustain the catalytic cycle.

We were pleased to find that nearly full conversion (¹⁹F NMR) of **1a** into the desired semi-reduction products could be achieved by simply using catalytic amounts of Ni(dtbbpy)Cl₂ (5 mol%) (dtbbpy (**L**₁) = 4,4'-di-*tert*-butyl-2,2'-bipyridine) and DPA (5 mol%) as the photocatalyst in the presence of 1.5 equiv of triethylamine. Our benchmark reaction was best conducted in MeCN at room temperature for 24 h under irradiation by a 18 W purple LED lamp (405 nm). Interestingly, under these conditions, the reaction provided a 16:84 mixture of *Z* and *E*-stilbenes **2a/3a**, respectively, with no over-reduction to the corresponding 1,2-diarylethane being observed (Table 1A). This notably confirmed that triethylamine is indeed a potent source of hydrogen atoms in the absence of other H-donors. While the first hydrogen atom is likely to be transferred via the NiH intermediate, we postulated that the second one, which would be introduced *via* protodenickelation, could be provided by the α -amino C–H (pKa = 14.7 in MeCN) of the triethylamine radical cation species.^[12] We thus postulated that the addition of other proton sources may impact the protonolysis step and therefore the stereoselectivity of our benchmark reaction. Nevertheless, the protonolysis reagent should be judiciously chosen to avoid potential protonation of triethylamine and quenching of the photo-oxidation process. In this respect, aliphatic alcohols seemed particularly suitable protonolysis reagents due to their moderate acidities. Interestingly, the addition of alcohol additives (up to 25 equivalents) to the reaction mixture did not affect the formation of the desired stilbenes, and a clear dependence of the reaction stereoselectivity on the acidity of the alcohol could indeed be observed (Table 1B). A slight increase in yield and selectivity towards *E*-isomer **3a** (*E/Z* up to 88:12) was obtained when ethanol or isopropanol were employed. However, a gradual stereoselective enrichment of *Z*-isomer **2a** was observed in the presence of fluorinated alcohols.^[14] While 2-fluoroethanol had only a slight effect on the selectivity, 2,2-difluoroethanol provided nearly equimolar amounts of both stereoisomers. Most remarkably, the more acidic 2,2,2-trifluoroethanol (TFE) induced a switch of the selectivity to afford a 68:32 isomeric ratio in favour of the *Z*-isomer **2a**. Importantly, the presence of triethylamine

remained critical to the success of these experiments. Further increasing the pKa of the alcohol additive was shown to be detrimental to the reaction. Indeed, when the more acidic hexafluoroisopropanol (HFIP) was used, no reaction was observed (entry 13), probably due to the formation of strong hydrogen bond interactions with the amine,^[15] inhibiting the photo-oxidation step. The use of other protic additives, such as carboxylic acids or phenols, also led to increased selectivity in favor of *Z*-isomer **2a**, although in greatly decreased yields (see Table S1).

Table 1. Benchmark semi-reductions of alkyne **1a**: (A) Reaction development; (B) Additive control over *E/Z*-selectivity.^[a]

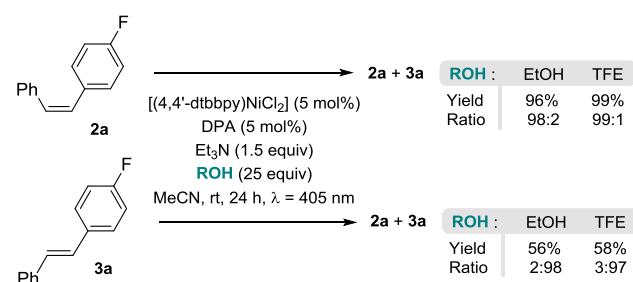


Entry	Deviation from above conditions	Yield (%)	Ratio 2a/3a
A. Reaction development ^[b]			
1	None	92	16:84
2	No photocatalyst	0	-
3	No light (dark)	0	-
4	No Nickel catalyst	0	-
5	NiCl ₂ .glyme as catalyst (no ligand)	44	32:68
6	Ni(COD) ₂ /dtbbpy as catalyst	61	20:80
7	No Et ₃ N	0	-
B. Additive effect over <i>E/Z</i> selectivity ^[c]			
8	Isopropanol	94	12:88
9	Ethanol	98	15:85
10	2-Fluoroethanol	98	18:82
11	2,2-Difluoroethanol	75	55:45
12	2,2,2-Trifluoroethanol (TFE)	93	68:32
13	Hexafluoroopropan-2-ol (HFIP)	0	-

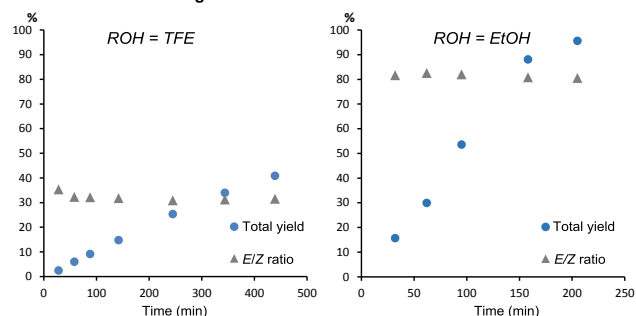
[a] Selected experiments. Reactions were performed on a 0.25 mmol scale using a PhotoRedOx Box device equipped with one 18 W purple LED lamp (405 nm). Yields and ratios are given for crude *E/Z* mixtures, as determined by ¹⁹F NMR spectroscopy using fluorobenzene as an internal standard. [b] 2.5 mL of MeCN were used. [c] 25 equiv of additive were added to the standard reaction mixture (2 mL of MeCN were used).

In order to gain more insights into the origin of the hydrogen atoms and of the stereoselectivity of the reaction, we carried out a series of control experiments (Figure 2).

A. Photoisomerization studies



B. Reaction monitoring



C. Deuteration studies

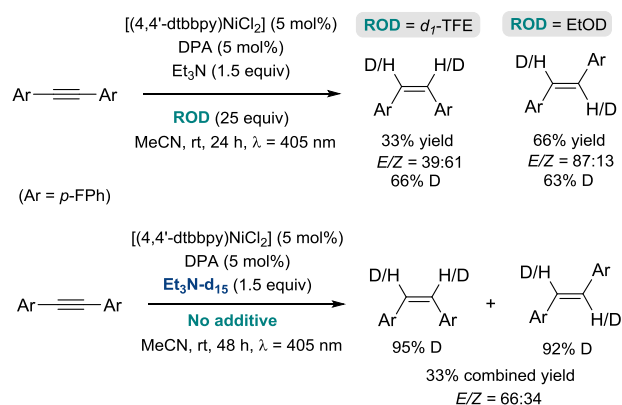


Figure 2. Mechanistic experiments.

We first excluded the possibility of a post-reduction isomerization of the alkene that may involve either nickel hydride catalysis^[6] or photocatalysis.^[9] Indeed, stereoisomerically pure *Z*- or *E*-alkenes, **2a** and **3a**, were engaged in the semi-reduction reaction using EtOH or TFE as additives. In both cases, the configuration of the alkenes was left untouched, which suggests that selectivity is intrinsic to the mechanism of product formation (Figure 2A). This was further confirmed by ¹H NMR spectroscopic monitoring of the semi-reduction reactions, which showed that the *E/Z* ratio was stable through the entire course of the reaction. The monitoring also revealed that the reaction is significantly slower with TFE compared to EtOH (Figure 2B).^[16] Additionally, both reactions seemed to follow an apparent zero order rate law with respect to alkyne, as the rate of both reactions remained constant over most of the reaction course. We thus hypothesized that the slower reaction with TFE may originate from the formation of stronger H-bonding with Et₃N which would result in slower quenching of excited DPA* by

Et₃N.^[17] Having established that stereoselectivity is set during product formation, we sought to determine the source of the two hydrogen atoms incorporated in the product. To do so, the reaction was first carried out with deuterated alcohols. Diminished yields were obtained after 24 h in both cases, thus confirming the involvement of the alcohol in the rate determining step. Interestingly, we observed that in both *E*- and *Z*-selective protocols, the deuterium incorporation is only about 63-66%, which clearly indicates that the alcohol is not delivering the two hydrogen atoms. Remarkably, the ability of Et₃N to act as a potent hydrogen source in the absence of alcohol additives was corroborated by a deuterium labelling experiment using fully deuterated triethylamine (Et₃N-d₁₅). In this condition, almost complete deuterium incorporation at both vinylic positions was observed (Figure 2C). Finally, we also showed that the reaction does not proceed via direct protonation of a Ni(0)-alkyne species.^[16]

Based on these experimental observations, we propose a general pathway for the formation of *E*- or *Z*-alkenes (Figure 3). The reaction starts with the photocatalytic generation of Et₃N^{•+} and Ni(I) species. The next important step involves the formation of a nickel(II) hydride intermediate **C**.^[10] Among the possible pathways that could be envisioned for the photochemical generation of Ni-H species via H-transfer from triethylamine radical cation we postulate the formation of an α -aminoalkyl radical species^[12] that would be subsequently captured by Ni(I) and released as enamine through β -hydride elimination^[10d] (see Supporting Information for mechanistic discussion). The resulting nickel(II) hydride complex **C** would then perform a *syn*-insertion into the alkyne, intermediately leading to alkenylnickel complex **E**. In the presence of a sufficiently acidic proton source, such as TFE, this complex is rapidly protonolysed to give the *Z*-alkene **2**. On the other hand, if the kinetics of the protonolysis are sufficiently slow, alkenylnickel isomerization to the less hindered alkenylnickel isomer **E'** can occur, most likely through the formation of an η^2 -vinylnickel intermediate,^[18,19] ultimately leading to the *E*-alkene **3** after protonolysis.^[20] Noteworthy, such a mechanism differs from recently reported metallaphotoredox semi-reduction processes for which selectivity is generally observed due to post-reduction alkene photo-isomerization.^[21,22]

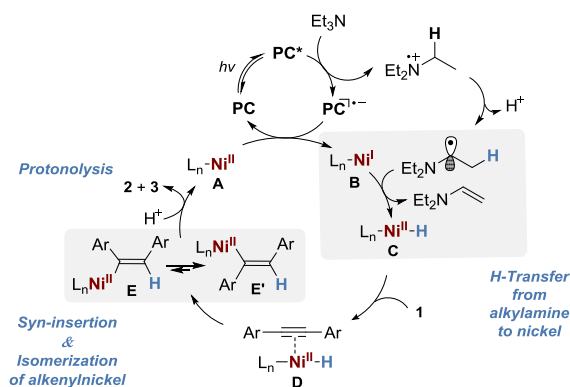


Figure 3. Proposed pathway toward *E*- and *Z*-isomers.

At this stage, we reasoned that the stereoselectivity towards the *Z* isomer could be further improved by adjusting the relative kinetics of the isomerization vs. protonolysis steps. As previously discussed, the use of more acidic protonolysis reagents is detrimental for the reactivity. Another option would be to slow down the isomerization process by tuning the electronic parameter of the nickel catalysts.^[18a] Satisfyingly, using more electron withdrawing 4,4'-dCF₃bpy ligand (**L**₂) instead of 4,4'-d*t*Bubpy (**L**₁) led to an enhancement of the stereoselectivity towards the desired *Z*-isomer (*EZ* ratio, 15:85). Accordingly, the more electron-rich 4,4'-dMeObpy (**L**₃) further increased the amount of the *E*-isomer (*EZ* ratio, 89:11) (Figure 4).

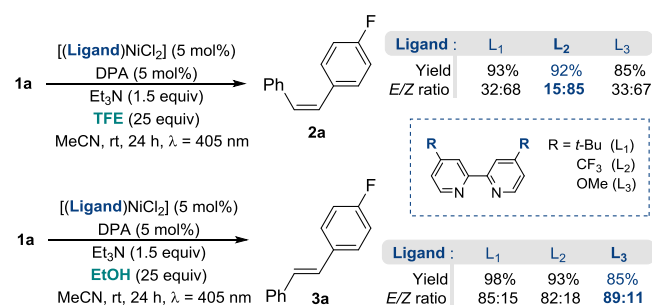
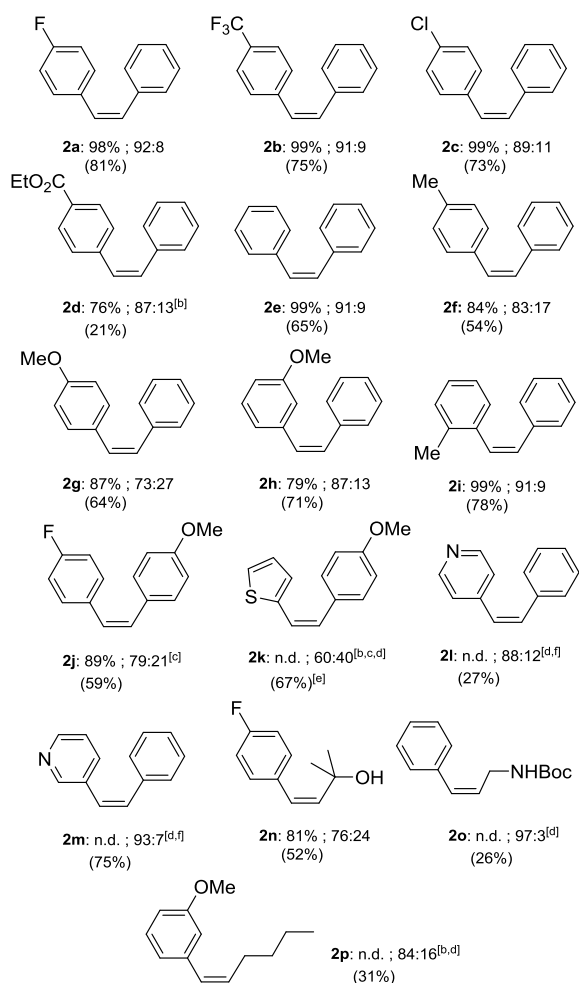
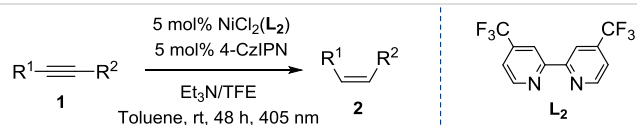


Figure 4. Ligand effect on *EZ* selectivity.

With this information in mind, we then seek to reach optimal conditions toward each stereoisomer. The best protocol for *Z*-isomer **2a** finally consisted in performing the reaction in toluene for 48 h using a combination of **L**₂ as the nickel ligand and 4-CzIPN as an alternative organophotocatalyst. As mentioned earlier, the photo-oxidation of Et₃N in the presence of TFE is more difficult due to the formation of hydrogen bond interactions,^[17] the use of 4-CzIPN exhibiting a higher oxidation potential, afforded higher yields of the stilbenes. Although the use of 4-CzIPN as a photocatalyst featuring higher triplet energy (56.4 kcal.mol⁻¹) with respect to DPA (40.9 kcal.mol⁻¹) can open the possibility for *E* to *Z* photoisomerization to occur in a second process,^[9a] the two photocatalysts afforded similar *EZ* isomer distributions under the *Z*-selective protocol conditions. This protocol covered a wide substrate scope for aromatic alkynes (Table 2) by allowing the preparation of different electron donating or withdrawing group-containing (*Z*)-1,2-bis(hetero)aryl-ethylenes (**2a-m**) with synthetically useful yields and stereoselectivities (*EZ* ratio up to 4:96). Importantly, even monoaryl-substituted internal alkynes reacted well, affording the corresponding conjugated *Z*-alkenes in good yield and selectivity (**2n-p**). This protocol was remarkably insensitive to the stereoelectronic parameters of the substituents, and a variety of functional groups such as ester, chloride, heterocycle, hydroxyl, and NBoc were well tolerated.

Table 2. Scope for *Z*-selective semi-reduction reactions.^[a]

[a] Reaction conditions: Alkyne (0.4 mmol), Ni catalyst (5 mol%), 4-CzIPN (5 mol%), Et_3N (1.5 equiv), TFE (25 equiv), Toluene (3.2 mL), rt, 48 h. Crude yields and *Z/E* ratios are given as determined by 1H or ^{19}F NMR from crude reaction mixtures using CH_2Br_2 or fluorobenzene, respectively, as internal standards. Isolated yields of the pure *Z*-isomers are provided in parentheses. [b] Hardly separable mixture of isomers. [c] 96 h. [d] GC-MS ratio. [e] Isolated yield of the mixture of isomers. [f] 0.2 mmol scale.

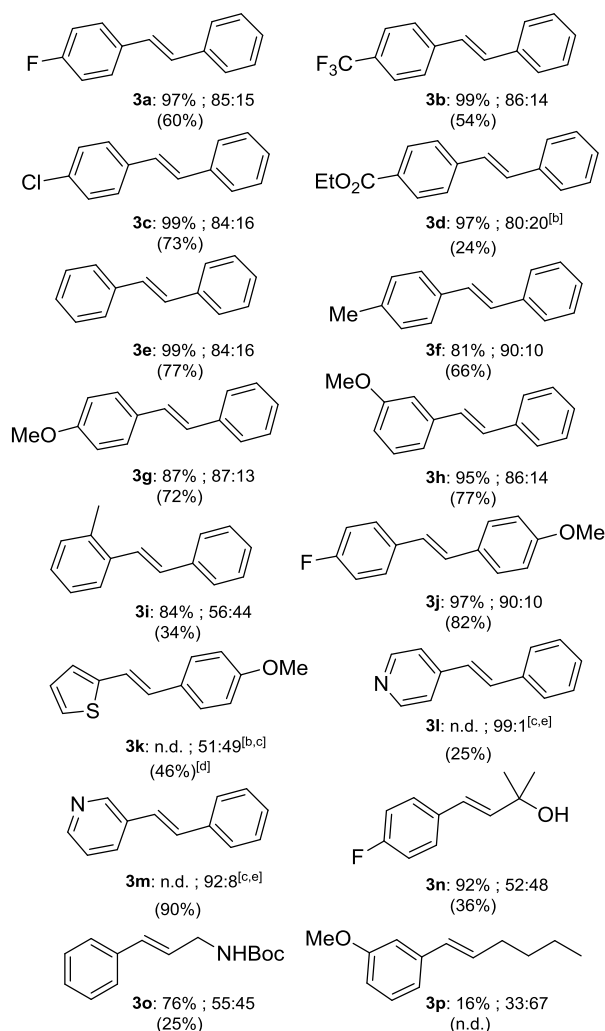
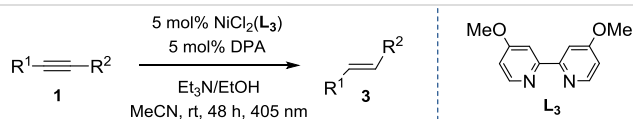
Regarding the selective formation of *E*-alkenes, the best results (95% yield and 89:11 *E/Z* selectivity for **3a**) were obtained by only substituting the dtbbpy ligand by the electron-rich 4,4'-bis(methoxy)-2,2'-bipyridine (**L₃**) under otherwise identical conditions. As shown in Table 3, in most cases the reaction proceeds to completion with high stereoselectivity toward *E*-olefins, except in the case of *ortho*-substituted alkyne (**2i**) and of mono-aryl alkynes (**2n-p**), which both evolved into mixtures of alkenes. This observation is consistent with the proposed mechanism

since the isomerization of alkynylnickel **E** to **E'** should be less favored in these cases (Figure 3). The scope of aromatic alkynes could not be extended to substrates bearing particular functionalities, such as cyano, phenols and alkylamine that did not yield to satisfactory results.^[16]

Remarkably, a 5 mmol preparative-scale synthesis of alkenes **2a** and **3a** could be achieved without further optimization while still maintaining satisfying yields and stereoselectivities, thus demonstrating the robustness of our new protocol.¹⁶

Conclusion

In summary, we have developed an efficient dual nickel/photoredox catalytic system for the stereo-divergent semi-reduction of alkynes to *E*- or *Z*-alkenes under mild photochemical conditions. The methodology is particularly well-suited to produce stilbenes with synthetically useful yields and selectivities. Mechanistic studies provided a set of interesting information: (i) a nickel hydride species is generated via a photoinduced transfer of hydrogen from triethylamine. While the photogeneration of Ni-H species from trialkylamine has been sporadically proposed, it has never been exploited for reduction applications. (ii) The stereoselectivity of the reaction was shown to not result from a post alkene photo-isomerization, which opened the possibility to design stereo-divergent protocols under photocatalytic conditions. (iii) The key parameter to control the stereoselectivity outcome was shown to be the relative kinetic of the isomerization and protonolysis of alkenyl-nickel intermediates. This has been achieved by fine-tuning the pKa of the alcohol additive and the electronic parameters of the ligand. Further applications of photoinduced NiH catalysis from trialkylamines for the functionalization of unsaturated substrates are currently explored in our laboratory.

Table 3. Scope for *E*-selective semi-reduction reactions.^[a]

[a] Reaction conditions: Alkyne (0.4 mmol), Ni catalyst (5 mol%), 4-CzIPN (5 mol%), Et_3N (1.5 equiv), EtOH (25 equiv), Toluene (3.2 mL), rt, 48 h. Crude yields and *E/Z* ratios are given as determined by 1H or ^{19}F NMR from crude reaction mixtures using CH_2Br_2 or fluorobenzene, respectively, as internal standards. Isolated yields of the pure *E*-isomers are provided in parentheses. [b] Hardly separable mixture of isomers. [c] GC-MS ratio. [d] Isolated yield of the mixture of isomers. [e] 0.2 mmol scale.

Experimental Section

General procedure for *Z*-stilbenes. A 8 mL vial equipped with a magnetic stir bar was charged with the alkyne (1 equiv, 0.4 mmol), [(4,4'-dCF₃bpy)NiCl₂] (0.05 equiv, 0.02 mmol, 8.4 mg), and 4-CzIPN (0.05 equiv, 0.02 mmol, 15.8 mg). The vial was flushed under argon for 1 min. Then, toluene (3.2 mL), Et_3N (1.5 equiv, 0.6 mmol, 60.7 mg), and CF₃CH₂OH (25 equiv, 10.4 mmol, 0.75 mL) were added under argon (NB: liquid alkynes were added after the solvent). The vial was capped, and the reaction mixture was stirred at room temperature under irradiation of a 405 nm purple LED lamp for 48 h. The reaction mixture

was then concentrated under vacuum and the crude product was purified by flash chromatography (silica gel, appropriate mixture of cyclohexane/ethyl acetate) to afford the corresponding *Z*-stilbene.

General procedure for *E*-stilbenes. A 8 mL vial equipped with a magnetic stir bar was charged with the alkyne (1 equiv, 0.4 mmol), [(4,4'-dMeObpy)NiCl₂] (0.05 equiv, 0.02 mmol, 7.1 mg), and DPA (0.05 equiv, 0.02 mmol, 6.6 mg). The vial was flushed with argon for 1 min. Then, MeCN (3.2 mL), Et_3N (1.5 equiv, 0.6 mmol, 60.7 mg), and EtOH (25 equiv, 10.4 mmol, 0.6 mL) were added under argon (NB: liquid alkynes were added after the solvent). The vial was capped, and the reaction mixture was stirred at room temperature under irradiation of a 405 nm purple LED lamp for 48 h. The reaction mixture was then concentrated under vacuum and the crude product was purified by flash chromatography on silica gel (appropriate mixture of cyclohexane and ethyl acetate as eluent) or by reversed-phase chromatography (acetonitrile and HPLC grade water with 1% formic acid as eluent) to afford the corresponding *E*-stilbene.

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Keywords: Alkyne semi-reduction • Hydrogen transfer • Nickel catalysis • Photoredox catalysis • Stilbenes

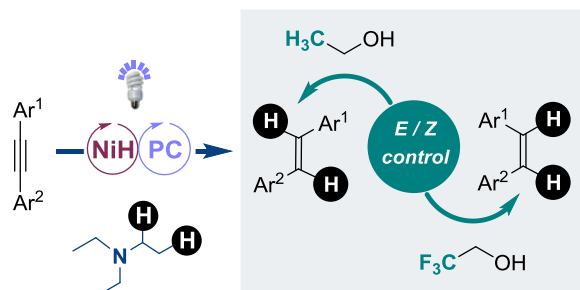
- [1] a) A. M. Kluwer, C. J. Elsevier, in *Handbook for homogeneous hydrogenation*, vol. 1 (Eds: J. G. Vries, C. J. Elsevier), Wiley-VCH, Weinheim, Germany **2007**, p. 375; b) C. Oger, L. Balas, T. Durand, J.-M. Galano, *Chem. Rev.* **2013**, *113*, 1313-1350.
- [2] For reviews of catalytic semi-reductions of alkynes, see: a) B. J. Gregori, M. W. S. Schmotz, A. J. von Wangelin, *ChemCatChem* **2022**, *14*, e202200886; b) D. Decker, H.-J. Drexler, D. Heller, T. Beweries, *Catal. Sci. Technol.* **2020**, *10*, 6449-6463; c) D. M. Sharma, B. Punji, *Chem. Asian J.* **2020**, *15*, 690-708; d) K. C. K. Swamy, A. S. Reddy, K. Sandeep, A. Kalyani, *Tetrahedron Lett.* **2018**, *59*, 419-429; e) M. Crespo-Quesada, F. Cárdenas-Lizana, A.-L. Dessimoz, L. Kiwi-Minsker, *ACS Catal.* **2012**, *2*, 1773-1786.
- [3] a) X. Wen, X. Shi, X. Qiao, Z. Wu, G. Bai, *Chem. Commun.* **2017**, *53*, 5372-5375; For an electrochemical process: b) M.-Y. Lee, C. Kahl, N. Kaeffer, W. Leitner, *JACS Au* **2022**, *2*, 573-578.
- [4] a) D. J. Hale, M. J. Ferguson, L. Turculet, *ACS Catal.* **2022**, *12*, 146-155; b) B. L. Ramirez, C. C. Lu, *J. Am. Chem. Soc.* **2020**, *142*, 5396-5407; c) N. O. Thiel, B. Kaewmee, T. Tran Ngoc, J. F. Teichert, *Chem. Eur. J.* **2020**, *26*, 1597-1603; d) R. Barrios-Francisco, J. J. Garcia, *Inorg. Chem.* **2009**, *48*, 386-393.
- [5] a) K. Li, C. Yang, J. Chen, C. Pan, R. Fan, Y. Zhou, Y. Luo, D. Yang, B. Fan, *Asian J. Org. Chem.* **2021**, *10*, 2143-2146; b) K. Murugesan, C. Beromeo Bheeter, P. R. Linnebank, A. Spannenberg, J. N. H. Reek, R. V. Jagadeesh, M. Beller, *ChemSusChem* **2019**, *12*, 3363-3369; c) E. Richmond, J. Moran, *J. Org. Chem.* **2015**, *80*, 6922-6929.
- [6] Nickel hydride-promoted *Z* to *E* alkene isomerization via the typical protometalation/ β -hydride elimination mechanism has been commonly proposed to account for *E*-selective alkyne semi-reductions. See for instance refs 4a,c and 5b-c. For a review of the chemistry of nickel hydride complexes, see: N. A. Eberhardt, H. Guan, *Chem. Rev.* **2016**, *116*, 8373-8426.

- [7] Reviews: a) S. O. Badir, G. A. Molander, *Chem.* **2020**, *6*, 1327-1339; b) N. Chalotra, J. Kumar, T. Naqvic, B. A. Shah, *Chem. Commun.* **2021**, 57, 11285-11300.
- [8] a) T. Yuan, S. Huan, B. Ge, S. Lin, M. Zheng, X. Wang, *CCS Chem.* **2021**, *3*, 3185-3191; b) T. Jia, D. Meng, R. Duan, H. Ji, H. Sheng, C. Chen, J. Li, W. Song, J. Zhao, *Angew. Chem., Int. Ed.*, **2023**, DOI: 10.1002/anie.202216511.
- [9] a) J. Saltiel, G. S. Hammond, *J. Am. Chem. Soc.* **1963**, *55*, 2516-2517; b) J. Saltiel, G. S. Hammond, *J. Am. Chem. Soc.* **1963**, *55*, 2515-2516; c) K. Singh, S. J. Staig, J. D. Weaver, *J. Am. Chem. Soc.* **2014**, *136*, 5275-5278; d) J. B. Metternich, R. Gilmour, *J. Am. Chem. Soc.* **2015**, *137*, 11254-11257; e) S. E. Chérif, A. Ghosh, S. Chelli, I. M. Dixon, J. Kraiem and S. Lakhdar, *Chem. Sci.* **2022**, *13*, 12065-12070. For reviews of synthetic applications: T. Nevesely, M. Wienhold, J. J. Molloy, R. Gilmour, *Chem. Rev.* **2022**, *122*, 2650-2694; J. Corpas, P. Mauleón, R. Gómez Arrayás, J. C. Carretero, *Adv. Synth. Catal.* **2022**, *364*, 1348-1370.
- [10] For selected papers discussing photochemical generation of Ni-H species, see: a) H.-P. Deng, X.-Z. Fan, Z.-H. Chen, Q.-H. Xu, J. Wu, *J. Am. Chem. Soc.* **2017**, *139*, 13579-13584; b) Q.-Y. Meng, S. Wang, G. S. Huff, B. König, *J. Am. Chem. Soc.* **2018**, *140*, 3198-3201; c) Y.-L. Li, W.-D. Li, Z.-Y. Gu, J. Chen, J.-B. Xia, *ACS Catal.* **2020**, *10*, 1528-1534; d) X. Zhao, S. Zhu, F.-L. Qing, L. Chu, *Chem. Commun.* **2021**, 57, 9414-9417; e) H. Xie, B. Breit, *ACS Catal.* **2022**, *12*, 3249-3255.
- [11] Catalytic transfer hydrogenation processes from trialkylamines to alkynes have been the subject of recent attention: G. J. Roeder, H. R. Kelly, G. Yang, T. J. Bauer, G. L. Haller, V. S. Batista, E. Baráth, *ACS Catal.* **2021**, *11*, 5405-5415 and references cited therein.
- [12] J. W. Beatty, C. R. J. Stephenson, *Acc. Chem. Res.* **2015**, *48*, 1474-1484.
- [13] For physical properties and uses of DPA, see: (a) Y. Chen, X. Wang, X. He, Q. An, Z. Zuo, *J. Am. Chem. Soc.* **2021**, *143*, 4896-4902; b) M. Neumeier, U. Chakraborty, D. Schaarschmidt, V. de la Pena O'Shea, R. Perez-Ruiz, A. Jacobi von Wangelin, *Angew. Chem. Int. Ed.* **2020**, *59*, 13473-13478; c) K. Xu, J. Zhao, X. Cui, J. Ma, *J. Phys. Chem. A* **2015**, *119*, 468-481; d) V. Gray, D. Dzebo, A. Lundin, J. Alborzpour, M. Abrahamsson, B. Albinsson, K. Moth-Poulsen, *J. Mater. Chem. C* **2015**, *3*, 11111-11121; e) S. K. Chattopadhyay, C. V. Kumar, P. K. V. Das, *Chem. Phys. Lett.* **1983**, *98*, 250-254.
- [14] For physical properties and applications of fluorinated alcohols, see: (a) I. A. Shuklov, N. V. Dubrovina, A. Börner, *Synthesis* **2007**, 2925-2943; b) C. Yu, J. Sanjosé-Orduna, F. W. Patureau, M. H. Pérez-Temprano, *Chem. Soc. Rev.* **2020**, *49*, 1643-1652.
- [15] (a) H. F. Motiwala, A. M. Armaly, J. G. Cacioppo, T. C. Coombs, K. R. K. Koehn, V. M. I. V. Norwood and J. Aubé, *Chem. Rev.* **2022**, *122*, 12544-12747; b) V. Pozhydaiev, M. Power, V. Gandon, J. Moran and D. Leboeuf, *Chem. Commun.* **2020**, 56, 11548-11564.
- [16] See Supporting Information for details.
- [17] TFE has been recently shown to enhance the redox stability of aliphatic amines through the formation of H-bonds between the alcohol and the amine, which significantly slow down SET from the amine to the excited photocatalyst: H. Li, Y. He, D. Zhang, L. Yang, J. Zhang, R.-L. Long, J. Lu, J. Wei, L. Yang, S. Wei, D. Yi, Z. Zhang, Q. Fu, *Chem. Commun.* **2022**, 58, 3194-3197.
- [18] The mechanism of isomerization of alkenylnickel species has been recently proposed to proceed through the formation of an η^2 -vinylnickel complex, see: a) D. Zell, C. Kingston, J. Jermaks, S. R. Smith, N. Seeger, J. Wassmer, L. E. Sirois, C. Han, H. Zhang, M. S. Sigman, F. Gosselin, *J. Am. Chem. Soc.* **2021**, *143*, 19078-19090; b) H. Choi, X. Lyu, D. Kim, S. Seo, S. Chang, *J. Am. Chem. Soc.* **2022**, *144*, 10064-10074.
- [19] For reviews of recent applications of alkenylnickel isomerization processes, see: a) W. Liu, W. Kong, *Org. Chem. Front.* **2020**, *7*, 3941-3955; b) S. E. Bottcher, L. E. Hutchinson, D. J. Wilger, *Synthesis* **2020**, 52, 2807-2820.
- [20] For other studies of alkenylnickel isomerization/protodickelation sequences, see: E. R. Barber, H. M. Hynds, C. P. Stephens, H. E. Lemons, E. T. Fredrickson, D. J. Wilger, *J. Org. Chem.* **2019**, *84*, 11612-11622; and ref 18b.
- [21] For rare examples of alkyne semi-reduction processes combining visible light catalysis and amines as H-donors, see: a) W.-F. Tian, Y.-Q. He, X.-R. Song, H.-X. Ding, J. Ye, W.-J. Guo, Q. Xiao, *Adv. Synth. Catal.* **2020**, *362*, 1032-1038; b) J.-J. Zhong, Q. Liu, C.-J. Wu, Q.-Y. Meng, X.-W. Gao, Z.-J. Li, B. Chen, C.-H. Tung, L.-Z. Wu, *Chem. Commun.* **2016**, 52, 1800-1803.
- [22] An alternative yet similar pathway, involving single-electron reduction of complex **E** to a Ni(I)-alkenyl complex prior to isomerization and protonolysis is also possible and cannot be excluded at this stage of our study.

Entry for the Table of Contents

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Trialkylamine as potent H-source



Alcohol additive-induced selectivity switch

Dual nickel and photoredox catalysis enables the semi-reduction of internal aryl alkynes in the presence of a trialkylamine acting both as a reductive quencher and as a transfer hydrogenation reagent. The *E/Z*-stereoselectivity can be controlled with the aid of an alcohol additive.