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Copper(0) nanoparticles catalyzed Z-Selective Transfer Semihydrogenation of Internal Alkynes

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Abstract. The use of copper(0) nanoparticles in the transfer semihydrogenation of alkynes has been investigated as a lead-free alternative to Lindlar catalysts. A stereo-selective methodology for the hydrogenation of internal alkynes to the corresponding (*Z*)-alkenes in high isolated yields (86% average) has been developed. This green and sustainable transfer hydrogenation protocol relies on non-noble copper nanoparticles for reduction of both electron-rich and electron-deficient, aliphatic-substituted and aromatic- substituted internal alkynes. Polyols, such as ethylene glycol and glycerol, have been proven to act as hydrogen sources, and excellent stereo- and chemoselectivity have been observed. Enabling technologies, such as microwave and ultrasound irradiation are shown to enhance heat and mass transfer, whether used alone or in combination, resulting in a decrease in reaction time from hours to minutes.

Keywords: Copper; Microwaves; Ultrasound; Transfer hydrogenation; *cis*-alkenes

Introduction

One or more carbon-carbon double bond(s) with well-defined configurations (*E* and/or *Z*) are present in many biologically active compounds, and the search for a new stereochemically controlled approach for their preparation is desirable in applied chemistry.[1] While a number of methods have been developed to address this transformation, the semihydrogenation of internal alkynes is an efficient way to achieve the desired stereochemistry. A wide range of homogeneous and heterogeneous catalysts has been successfully employed to pursue this aim (Pd0, Ru(II), Ni0, Au(I), Cu(I), and Fe(II)).[2] However, this transformation often involves Z/E isomerization, a shift in double-bond position, overhydrogenation to alkanes and poor tolerance of other reducible groups. The Lindlar catalyst is a well-established and effective system for alkyne semihydrogenation, but the presence of lead in its composition makes its replacement desirable in terms of sustainability.[3] Furthermore, the replacement of noble metals, the use of safe hydrogen sources and overhydrogenation are still key issues to address.

Advances in catalytic (de)hydrogenation using 3d transition metals have driven the development of efficient transformations for a variety of functional groups, and, in particular, the C-N and C-O multiple bonds. In this field, first-row transition metals offer a valuable alternative to 4d and 5d metals because they are generally less environmentally harmful and more abundant.[4] Copper-catalysed reductive transformations, coined as copper-hydride-catalysed processes, are, in themselves, a field of great interest.[5] The semihydrogenation of alkynes using molecular hydrogen (H_2) as the reducing agent,[6] has been investigated. However, the flammable nature of this gas means that alternative hydrogen sources have

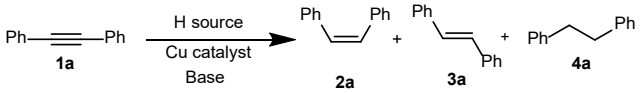
become popular in recent years.[7] The efficient *in-situ* generation of copper(I) hydrides plays a key role in transfer hydrogenation reactions, and hydrosilanes have generally been exploited as stoichiometric hydride sources in Cu-catalysed transfer (semi)hydrogenations [T(s)H].[8] Ammonia borane has also been demonstrated to be highly efficient as a hydrogen source in T(s)H, as catalysed by NHC copper(I) species,[9] as has hypophosphorous acid, although its use is somewhat limited to terminal alkynes.[10] Surprisingly, however, only a few publications have referred to the use of alcohols as sacrificial hydrogen sources in this field. In 2019, J. F. Teichert *et al.* reported that an N-Heterocycle Carbene Cu(I) complex was able to catalyse T(s)H in isopropanol,[11] while the use of ethanol as a hydrogen source in di-boron-assisted Cu-catalysed T(s)H has also been studied.[12]

Efficient heterogeneous catalytic systems are promising solutions to economic and environmental issues because they can be separated and recycled.[13] In fact, the use of solid-supported metal nanoparticles, which are second-generation catalysts, in alkyne semihydrogenation has been studied,[14] but some limitations, specifically unsatisfactory chemoselectivity, have been underlined.[15] The heterogeneity of solid-supported nanocatalysts can lead to lower selectivity than provided by homogeneous catalysis, meaning that bimetallic systems and poisoned catalysts have been designed to improve performance.[16] The applicability of NPs in the transfer semihydrogenation of alkynes is very limited, and noble metals have only been used in a few examples. Palladium NPs have shown good efficiency and regioselectivity in the presence of ammonia borane,[17] and butane 1,4-diol,[18] as hydrogen sources, while gold NPs have been successful with formic acid.[19] Based on our knowledge, cobalt NPs are the only first-row transition-metal NPs that can efficiently act in the transfer semihydrogenation of alkynes in the presence of ammonia-borane,[20] while Nickel NPs do not reduce alkynes in the absence of gaseous H_2.[21] Surprisingly, Copper NPs have never been investigated in this field.

Our previous work on the nano-Cu-catalysed transfer hydrogenation of nitro benzene,[22] has provided the foundations for the application of CuNPs in the transfer semihydrogenation (TsH) of internal alkynes using green and easily-handled ethylene glycol as the hydrogen source, and this reaction is reported herein. The study focuses on proving not only the efficiency, but also the chemoselectivity and regioselectivity of the protocol. Microwave (MW) heating and ultrasound (US) irradiation, which are among the most simple, inexpensive and valuable tools in applied chemistry, have been exploited, in parallel with a conventional procedure, to enhance heat and mass transfer, in order to increase the reaction rate.

Results and Discussion

The efficacy of copper powder to act as a catalyst in transfer hydrogenation has been successfully studied in a nitrobenzene reduction with glycerol, which was used as a sacrificial hydrogen donor.[22] In order to prove its efficacy in alkyne reductions, the reaction was repeated, in this study, with diphenylacetylene (1a) at 150 °C in the presence of 2 equivalents of KOH, as the base, and a set of hydrogen donors (Scheme 1, Table 1). Our previous experience has shown that polyols and amino alcohols have high hydrogen-transferring efficacy, which may be due to their capacity to form five-membered chelating species. [22b, 23] It was therefore decided that several of these species should be compared.



Scheme 1. Cu-catalysed TsH of diphenylacetylene.

Table 1. Cu-Powder-catalysed TsH of alkyne **1a**: Screening of different reducing agents and bases[a]

#	H source	Base	Conv. (%)[b]	Selectivity (%)[b] (**2a/3a/4a**)
1	Ethylenediamine	KOH	6	nd
2	Ethanolamine	KOH	35	nd[e]
3	Serinol	KOH	31	(90/10/-)
4	Isoserinol	KOH	47	(94/6/-)
5	Glycerol	KOH	64	(91/9/-)
6	Ethylene glycol	KOH	73	(93/7/-)
7	Ethylene glycol	KOH[c]	51	(95/5/-)
8	Ethylene glycol	KOH[d]	53	(93/7/-)
9	Ethylene glycol	NaOH	68	(94/6/-)
10	Ethylene glycol	*t*-BuOK	32	(90/10/-)
11	Ethylene glycol	K_2CO_3	69	(92/8/-)
12	Ethylene glycol	Cs_2CO_3	13	(97/3/-)
13	Ethylene glycol	-	2	(>99/-/-)

[a]Reaction conditions: diphenylacetylene (1 mmol), KOH (2 mmol), Cu powder (2 mmol), H source (40 mmol), T: 150ºC, t: 20h. b) Determined by GC-MS; c) 1 eq Cu Powder was added d) 1 eq of the base was added e) the reaction crude was a mixture of compounds.

As reported in Table 1, glycerol and ethylene glycol confirmed their efficacy as hydrogen donors for TH reduction, giving 64 and 73 % alkyne-to-alkene conversion, respectively, in 20 hours (Table 1, entry 5-6). Selectivity to the Z alkene was very high, and 91/7 and 93/7 Z/E ratios were measured by GC/MS. When the reaction was performed in the presence of ethylenediamine as the hydrogen source (Table 1, entry 1), only 6% conversion was detected and the starting material (**1a**) was recovered as the main constituent. Ethanolamine (Table 1, entry 2) showed slightly higher conversion, but the regioselectivity could not be measured because the reaction gave a number of side products. Better results were observed when serinol and isoserinol were used as the solvents (Table 1, entries 3 and 4), with the conversion increasing to 31% and 47%, respectively, while GC MS only revealed stilbene derivatives, with a *Z* selectivity of 90%.

It is known that the role of the base is important in Cu-catalysed reactions, and several inorganic bases (NaOH, KOH, *t*-BuOH, K_2CO_3 and Cs_2CO_3) were therefore tested under the standard conditions, in the presence of Cu powder for 20h at 150ºC (Table 1, entries 6-13). As mentioned above, ethylene glycol was selected as the hydrogen donor. Although the selectivity was comparable in all cases, 2 eq of KOH (Table 1, entry 6) gave the best results, with a 75% yield. When the semihydrogenation was performed in the absence of a base (Table 1, entry 13), only 2% alkene was obtained. The reaction was also carried out with 1 eq of Cu powder (Table 2, entry 8), with the aim of reducing the high amount of catalyst needed, but the yield decreased to 51%.

As shown in Table 1, it is worth noting that no traces of alkane were observed.

The standard reaction was then studied in the presence of different Cu sources, with ethylene glycol being used as the hydrogen donor and KOH as the base.

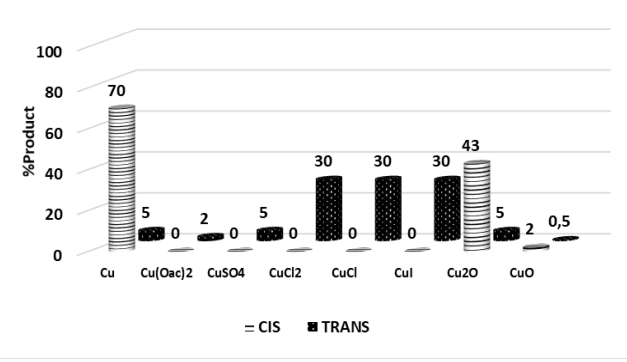
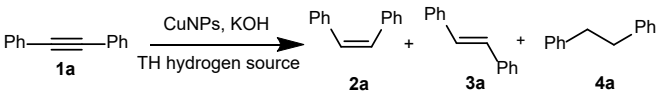


Figure 1. Screening of several copper sources in the Cu-catalysed TsH of **1a**. Reaction conditions: diphenylacetylene (1 mmol), KOH (2 mmol), Cu source (2 mmol), ethylene glycol (40 mmol), T: 150ºC, t: 20h. Product % is determined by GC-MS.

As shown in Figure 1, low conversions were detected when copper salts were used, and the trans-isomer was formed as the main product. Copper oxides (I and II) were then studied, and Cu_2O appeared to be the most reactive, with a conversion of 48%. None of the tested copper salts showed reactivity and stereoselectivity that were comparable with that of copper powder. Nevertheless, no overreduction product was observed.

Mindful of the efficacy of NPs in acting as efficient sources of Cu(0), we decided to prepared copper nanoparticles (NPs) with the aim of reducing catalyst amount.[22b] NPs were prepared via the reduction of $Cu(OH)_2$, which was prepared *in situ* using $NaBH_4$ in water:ethylene glycol (5:1) (see Supporting Info).

Table 2. CuNP-catalysed TsH of the alkyne: Screening of different reducing agents and bases[a]



#.	Hydrogen source	Cu NPs (mol%)	t (h)	Conv (%) Selectivity (**2a/3a/4a**) [b]
1	Ethylene glycol	10	2	>99 (>99/-/-)
2	Ethylene glycol	10	1	68 (>99/-/-)
3	Ethylene glycol	5	2	73 (>99/-/-)
4	Ethylene glycol	5	5	84 (>99/-/-)
5	Ethylene glycol	10[c]	2	52 (>99/-/-)[c]
6	Ethylene glycol	10[d]	2	99 (>99/-/-)[d]
7	Glycerol	10	2	92 (>99/-/-)
8	Glycerol	10	5	>99 (>99/-/-)
9	Ethanolamine	10	2	7 (>99/-/-)
10	Ethanolamine	10	16	>99 (>99/-/-)
11	Diethanolamine	10	2	65 (>99/-/-)
12	Diethanolamine	10	5	>99 (>99/-/-)
13	Serinol	10	2	8 (>99/-/-)
14	Serinol	10	16	15 (>99/-/-)
15	Isoserinol	10	2	23(>99/-/-)
16	Isoserino	10	16	86 (98/2/-)
17	Isopropanol	10[e]	2	-
18	Isopropanol	10[e]	16	-
19	1-Propanol	10[e]	2	-
20	1-Propanol	10[e]	16	-

[a]Reaction conditions: diphenylacetylene (1 mmol), KOH (2 mmol), H source (15 mL), T: 150ºC, [b]Determined by GC-MS; [c] the reaction was performed at 120°C, [d]CuNPs were stored for two months; [e] the reaction was performed at reflux

The standard reaction with diphenylacetylene (**1a**) was performed in the presence of 10 mol% of CuNPs

and 2 eq of KOH (see Table 2). Full conversion was obtained with excellent stereoselectivity in only 2 hours in ethylene glycol (Table 2, entry 1). When the reaction time was decreased to 1hr, the conversion was reduced to 68% (entry 2). 5 mol% of catalyst was also tested for 2 and 5 hours, but, in both cases, some starting material remained (entries 3-4). When the reaction temperature was decreased to 120 ºC, conversion dropped to 52% as well (entry 5). However, excellent stereoselectivity was retained in each case. As already observed with Cu powder, glycerol showed slightly lower reactivity than ethylene glycol, and amino alcohols, such as isoserinol, ethanolamine and diethanolamine, gave excellent results in longer reaction times (Table 2, entries 9-14). Conscious that copper is prone to oxidation and that that nano-sized metal particles are both chemically active and air sensitive, the reaction was also performed in ethylene glycol after the CuNPs had been stored for 2 months. Comparable results were obtained (Table 2, entry 6). When isopropanol and 1-propanol are used as hydrogen source only starting material was recovered.

The reactions with Cu powder and CuNPs were performed in parallel and monitored over time in order to compare conversion and *Z*/*E* selectivity (Figure 2).

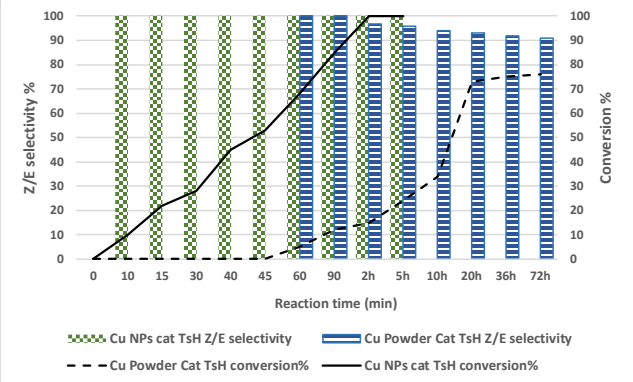
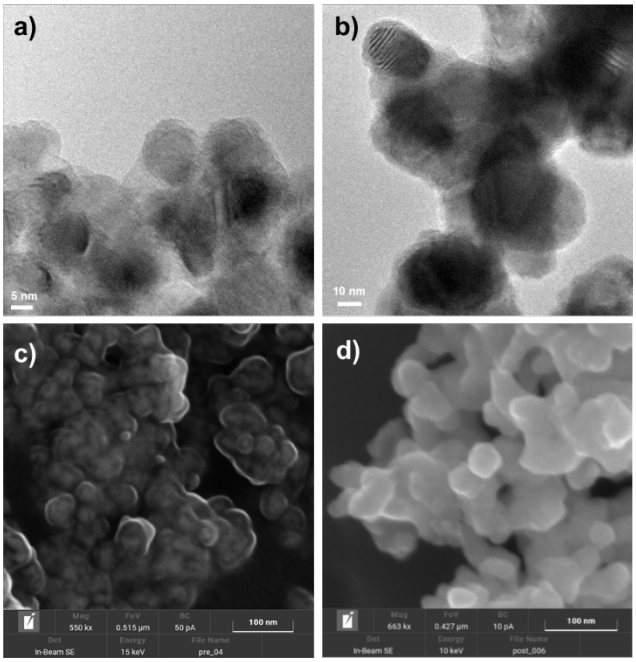


Figure 2. Study of the conversion and selectivity of the TsH of diphenylacetylene in the presence of Cu powder and CuNPs. Reaction conditions: diphenylacetylene (1 mmol), KOH (2 mmol), either Cu powder (2 mmol) or CuNPs (0.1 mmol), ethylene glycol (40 mmol), T: 150 °C.

As depicted in Figure 2, the bulk metal does not permit the full conversion of diphenylacetylene to occur, with 23% starting material being observed after 72 hours. CuNPs, however, not only allowed the catalyst loading to be reduced to 10 mol%, but also gave a significant rate enhancement, with >99% conversion being achieved in only two hours. In addition, faster hydrogenation led to higher selectivity to the Z-product, and isomerization was avoided. As shown in Figure 2, full conversion also meant full selectivity to the Z-alkene in the presence of CuNPs, while, with Cu powder, the E-product increased in amount as the reaction reached maximum conversion at 72 hours. When reaching full conversion of the diphenylacetylene after 2h with CuNPs, the reaction was left for 3 more hours at 150 °C in order to detect the possible formation of the overhydrogenated product. We were delighted to see that after 5 hours of catalytic reaction, full conversion of alkyne was still synonymous of full selectivity to the Z-alkene.

CuNPs were characterized before and after the reaction by electron microscopic techniques. Figure 3 (top panels, a and b) show two representative high resolution TEM images of the samples. Before the reaction (panel a), the crystalline structure of the Cu0 core is hardly detectable, due to the low size and to the presence of an amorphous layer of ethylene glycol embedding the CuNPs. Particle size and crystallinity increase after the reaction, as seen in panel b) of Figure 3. A core shell structure can be clearly observed, with a Cu(0) core (lattice distances compatible with the 220 family of planes of cubic Cu0, JCPDS card 00-004-0836) covered by a 4-5 nm thick shell of ethylene glycol. Due to the difficulty to get more detailed information by TEM, high resolution FESEM was used (bottom panels of Figure 3). These images confirm the dense agglomeration of the particles, embedded in the organic matrix of ethylene glycol which allows to preserve the identity of the primary nanoparticles. Particle size distribution (Figure 3 pannel e) measured on the FESEM images show a relatively narrow range for the sample before the reaction, from 10 to 16 nm and average size of 18.8 ± 3.0 nm. After the reaction the size distribution extends up to 50 nm, with an average size of 29.9 ± 7.0 nm. This estimation includes the amorphous organic shell surrounding the metallic core.



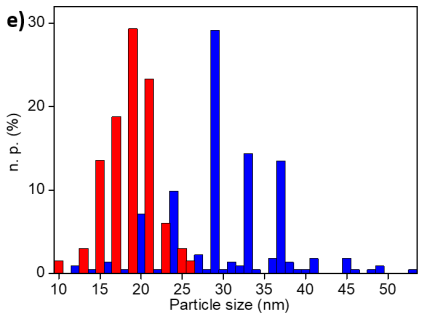


Figure 3 High resolution TEM (a,b) and FESEM images of CuNPs before (a, c) and after (b, d) the catalytic tests.e) Particle size distributions from FESEM images of CuNPs before (red) and after the reaction (blue).

Non-conventional techniques, such as MW and US, have been demonstrated to have a great ability to enhance heterogeneous-catalysed reactions, whether used separately or in combination.[24]

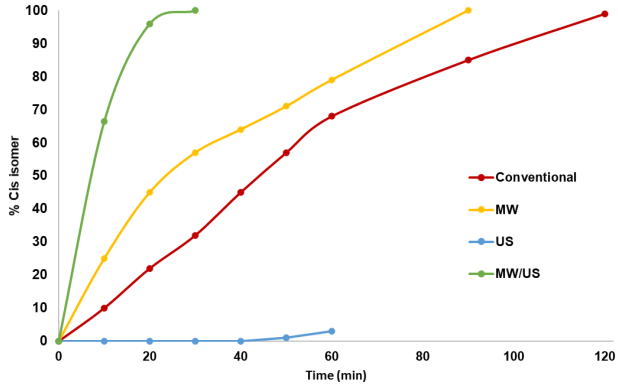
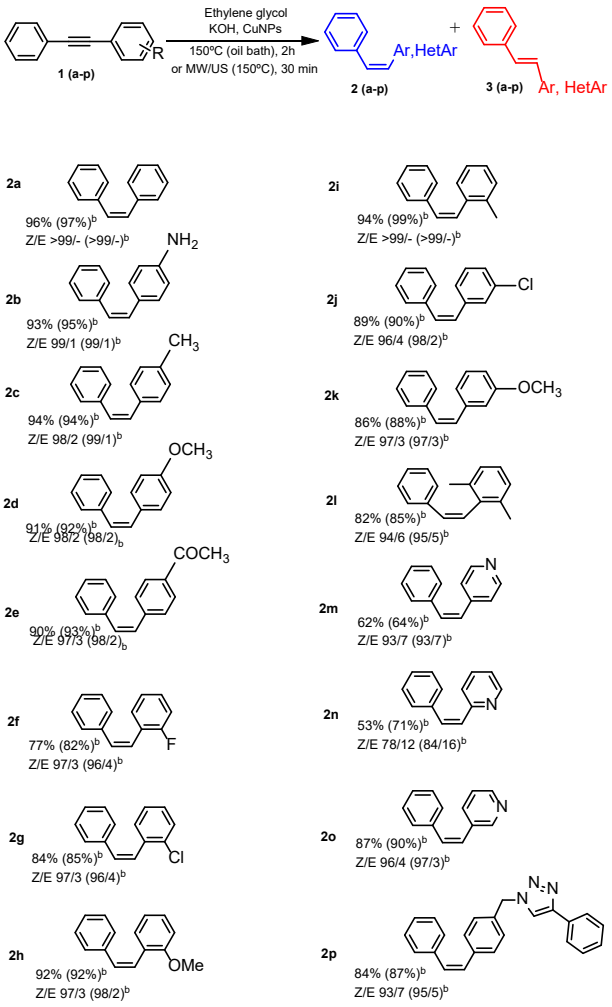


Figure 4. TsH kinetic data using different techniques. Reaction conditions: diphenylacetylene (1 mmol), KOH (2 mmol), CuNPs (10 mol%), ethylene glycol (40 mm0l). T: 150 °C. Determined by GC-MS.

In order to investigate the efficacy of these techniques, the reduction of diphenylacetylene (**1a**), using ethylene glycol as the H donor in the presence of 10 mol% of CuNPs, was performed under conventional heating at 150 °C, MW heating, US irradiation and a combination of MW and US. As shown in Figure 4, full conversion to the *Z*-isomer was obtained after 2 hours of stirring at 150 °C under conventional conditions. The use of MW irradiation (Milestone MicroSynth, constant power: 120W) greatly improved reaction performance, and 90 min were sufficient for reaction completion. As we have already observed in our previous studies, simultaneous irradiation with MW (2.45 GHz, 90 W) and US (20.3 kHz, 40 W) is able to enhance heat and the mass transfer, as well as catalyst deagglomeration, leading to better reaction outcomes in terms of reaction rate and selectivity.[22a] US in fact significantly influenced Cu(0) nanoparticle dimension with a size decreasing providing higher reaction rate. In this case, the combination of the enabling technologies for the selective hydrogenation of diphenylacetylene to *Z*-stilbene gave reaction completion in only 30 minutes, as shown in Figure 4 (green line). US irradiation alone (Pyrex horn, 20.3 kHz, 40 W) was ineffective at promoting the TsH of the alkyne as the thermal energy released under US irradiation increased the reaction-mixture temperature to 70 °C, which is not sufficiently high to successfully convert the starting material (Figure 4, blue line).

Table 3. Scope of the TsH of diaryl alkynes to Z-alkenes catalysed by CuNPs [a]



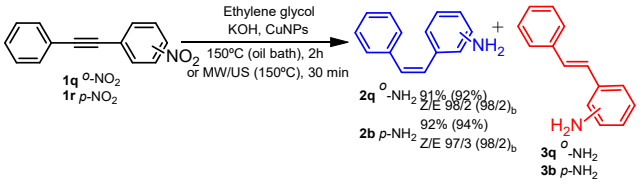
[a] Reaction conditions: alkyne (3 mmol), ethylene glycol (20 mL), KOH (6 mmol), CuNPs (10 mol%), T:150ºC. Reaction performed under conventional stirring in an oil bath at 150 °C for 2 hours. [b] Reaction performed under combined US (20.3 kHz, 30 Wcm^{-2}) and MW (2.45 GHz, 90 W) irradiation, 150 °C, 30 min (see Supporting Info) [c] the Z-stilbene was obtained ad the main product with a yield of 69% when the reaction was performed under MW/US irradiation.

Reaction scope was then explored by reducing a set of internal diphenyl alkyne derivatives that had previously been prepared by means of a Sonogashira coupling reaction. The CuNP-catalysed TsH was

performed under both conventional and non-conventional (MW/US irradiation) conditions (Table 3). The reaction outcomes were comparable and the reduction of the reaction time was reliably maintained. As previously stated, both reactions were performed at 150 °C, and the reaction time was 2 hours under conventional heating and 30 min under MW/US combined irradiation. The filtration, extraction and chromatographic purification of the reduction product of **1a** gave pure *Z*-stilbene **2a** in a 96% isolated yield under conventional conditions, which was slightly improved to 97% by the non-conventional techniques.

Very good results were also obtained with various structurally and electronically diverse diaryl-substituted internal alkynes, which demonstrated the high chemoselectivity of the CuNP-TsH protocol as well as its versatility. The presence of a primary amino group was found to be well tolerated, and the carbonyl moiety remains unaffected at the end of the reaction (Table 3, reduction of **1b** and **1e**). Interestingly, no hydrogenolysis of the C-F and C-Cl bonds took place during the hydrogenation of fluoro-(phenylethynl)benzene and chloro-(phenylethynyl)benzene (Table 3, products **1f**, **1g** and **1j**), while an unsuccessful reaction was observed in the presence of the bromo phenyl substituent and the concomitant reductive dehalogenation gave the *Z*-stilbene as the dominant product instead of the expected (Z)-1-bromo-3-styrylbenzene. It is worth noting that alkynes bearing heterocycles, such as pyridine, were found to be good substrates and the corresponding alkenes were produced with high yields. The influence of heteroatoms was studied and the three different positions were compared (Table 3, products **1m**, **1n** and **1o**). The 4-pyridyl and 2-pyridinyl derivatives were the only substrates over the entire scope of the study to suffer overhydrogenation, and lower chemoselectivity was observed; 10% and 6% of the alkane derivative were observed, starting from **1m** and **1n**, respectively. Interestingly, overhydrogenation was not observed when the heteroatom was situated in the meta-position, and the reaction gave the desired product with high yield and stereoselectivity. The influence of a triazole wing in the p- position (product **1p**) was also investigated and high selectivity to the Z-alkene was retained. When 1-nitro-4-(phenylethynyl)benzene was used as the substrate, complete conversion to 4-styrylaniline was detected (Scheme 2). Evidently, the nitro group is quantitatively reduced to the amino group under these reaction conditions, confirming results observed in our previous work on the TH reduction of aromatic nitro compounds using CuNPs as the catalyst.[22b] The same phenomenon was observed when the $-NO_2$ group was in the ortho- position (**1q**).

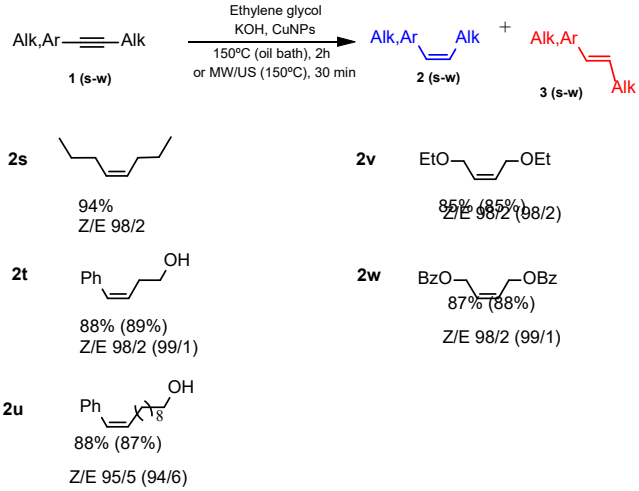
The reduction of a terminal alkyne under similar reaction conditions was also explored, however, a mixture of products was observed. Ethyl benzene and products derived from copper catalysed oxidative Glaser-Hay coupling of terminal alkyne were detected.



Scheme 2. Cu-catalysed TsH of nitro (phenylethynyl)benzene derivatives under conventional conditions and under MW/US irradiation.

The scope of the reaction was afterwards explored in presence of aliphatic internal alkynes. When 4-octyne, was reduced, due to its low boiling point, the reaction was performed at 140ºC in a gas tight glass reactor to prevent evaporation of starting alkyne and desired alkene. Because of the insolubility of 4-octyne in ethylene glycol the reaction happened at the interphase and longer reaction time was necessary to achieve complete conversion. To our delight full conversion and selectivity to the Z oct-4-ene (**2s**) was achieved in 16 hrs and the immiscibility of the final product with the solvent allowed a simplified purification.

Table 4. Scope of the TsH of aryl,alkyl and dialkyl alkynes to Z-alkenes catalysed by CuNPs [a]



[a] Reaction conditions: alkyne (3mmol), ethylene glycol (20 mL), KOH (6 mmol), CuNPs (10 mol%), T:150ºC. Reaction performed under conventional stirring in an oil bath at 150 °C for 2 hours. [b] Reaction performed under combined US (20.3 kHz, 30 Wcm^{-2}) and MW (2.45 GHz, 90 W) irradiation, 150 °C, 30 min. (see Supporting Info).

The scope of the reaction was successfully extended by investigating several aliphatic and mixed alkyl/aryl and dialkyl internal alkynes that bore a range of different functional groups (Table 4). Gratifyingly excellent chemoselectivity was observed in the

presence of the alcohol moiety, and it was confirmed that only poly alcohols can be efficiently oxidized by CuNPs (Table 4, products **1t** and **1u**). When symmetric aliphatic alkyne ethers, such as 1,4-diethoxy-2-propyne (**2v**) and 1,4-bis(benzyloxy)-2-propyne (**2w**), were reduced, full conversion was observed and the (*Z*)-isomers were isolated in good yields, 85% and 88%, respectively. By the same token, the semihydrogenation of aliphatic/aromatic internal alkynes also proceeded with high stereoselectivity, without further reduction to the alkane.

The preponderance of the (*Z)*-isomer drove us to further investigate whether the catalytic activity of the copper involved the NP surfaces. The impact of US irradiation on the reaction rate (see Figure 4 MW versus MW/US irradiation) indicated that the deagglomeration induced by the mechanical waves affected particle size and the catalytic efficiency of the copper nanocatalyst. The reaction was therefore tested by incubating the copper catalyst and base in ethylene glycol under standard reaction conditions overnight. The supernatant was then used as the reaction medium without the addition of copper NPs, and 7% conversion was detected after 20 hours stirring at 150°C. Interestingly, the stereocontrol of the reaction dropped and a 43/57 cis/trans ratio was measured by GC-MS analyses, thus indicating that the reaction cannot occur in the homogeneous phase and Cu(0)NPs are reactive on their surface.

Conclusion

The highly chemo- and stereoselective copper catalysed transfer semihydrogenation of alkynes to *Z*-alkenes has been successfully performed and investigated herein. The advantages of the proposed methodology include the use of eco-friendly and easily available ethylene glycol as the hydrogen source, and the use of copper powder and CuNPs as easily prepared and low-cost catalysts. The reaction has been demonstrated to be highly efficient when using 10 mol % of CuNPs over a set of internal alkynes, and its chemoselectivity versus carbonyl and amino and alcohols has been demonstrated. Despite the oxidability of non-noble metal nanoparticles, this protocol did not display any issues when the CuNPs were used after months of storage. Only polyols and polyamino alcohols can act as hydrogen sources. The use of the enabling technologies, MW and US either alone or in combination, has provided a further reduction in reaction time thanks to enhancements in heat and mass transfer. Ultrasound irradiation facilitates catalyst dispersion and increases the number of catalytically active sites, while microwaves provide fast and selective heating. Ultimately, this method has been shown to be efficient, selective, versatile and able to produce a wide range of internal aromatic and aliphatic (*Z*)-alkenes in short reaction times with high isolated yields.

Experimental Section

General information. All chemicals were purchased from Sigma-Aldrich (Milan, Italy) and used without further purification. Reactions were monitored by TLC on Merck 60 F254 (0.25 mm) plates (Milan, Italy), which were inspected under UV light and/or developed by heating after spraying with 0.5% ninhydrin in either ethanol or phosphomolybdic acid. Reactions were carried out in a conventional oil bath and in a combined microwave/ultrasound (MW/US) system (Figure S1, Supporting Information), which was designed in our laboratory by inserting a sonic horn, made of Pyrex, into a RotoSynth (Milestone) microwave chamber. NMR spectra (300, 400 and 600 MHz, and 75, 101 and 125 MHz for ^{1}H and ^{13}C, respectively) were recorded on a 300 MHz, 400 MHz and 600 MHz JEOL ECZR spectrometer, respectively. Chemical shifts were calibrated to the residual proton and carbon resonances of the solvent; DMSO-d_6 (δ_H = 2.54, δ_C = 39.5), $CDCl_3$ (δ_H = 7.26, δ_C = 77.16). Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. GC-MS analyses were performed in a GC Agilent 6890 (Agilent Technologies, Santa Clara, CA, USA) that was fitted with a mass detector Agilent Network 5973, using a 30 m capillary column, i.d. of 0.25 mm and film thickness 0.25 µm. GC conditions were: injection split 1:10, injector temperature 250 °C, detector temperature 280 °C. Gas carrier: helium (1.2 mL/min). Temperature program: from 50 °C (5 min) to 100 °C (1 min) at 10 °C/min, to 230 °C (1 min) at 20 °C/min, to 300 °C (5 min) at 20 °C/min.

General procedure for the synthesis of CuNPs. Copper (II) sulphate was dissolved in a H_2O: ethylene glycol (5:1) solution (0.01 M), and NaOH (2 M) was added dropwise until pH=11 was reached. After a well-stirred deep-blue solution was achieved, 0.5 M $NaBH_4$ in water was added to the flask. Initially, the solution gradually turned colourless and, afterwards, it became burgundy, confirming the formation of copper colloids. The CuNPs were recovered on a Büchner funnel using a sintered glass disc via washing with water and methanol.

Transmission Electron Microscopy (TEM) images were recorded with a JEOL 3010-UHR microscope (300 kV acceleration potential; LaB6 filament). Specimens were prepared by pouring a few drops of the nanoparticles dispersion onto a carbon-coated copper grid and were imaged after evaporation of the solvent. Field emission scanning electron microscopy (FESEM) images were acquired with a Tescan S9000G microscope. Particle size distribution built from the FESEM images counting 150 – 200 particles (Supporting Information, Figures S2 and S3).

General procedure for the synthesis of internal alkynes. Aryl halide (1 mmol) and phenylacetylene (1.2 mmol) were added to a flask containing 0.02 mol % $Pd(PPh_3)_2Cl_2$ and 0.05 mol % CuI, in 10 mL of anhydrous THF. The mixture was stirred at room temperature overnight under a nitrogen atmosphere. After the reaction was

completed (as monitored by GC), water was added to the reaction mixture and the crude product was extracted with dichloromethane. For further purification, the organic solvent was removed under vacuum and the resulting residue was purified by column chromatography on silica gel, using petroleum ether and ethyl acetate as eluents (8:2). The pure product was analysed using ^{1}H and ^{13}C NMR spectroscopy. (See Supporting Information)

General procedure for the Cu-Powder-catalysed transfer semihydrogenation of internal alkynes to cis-alkenes. The alkyne (3 mmol), KOH (6 mmol) and copper-powder catalyst (6 mmol) were dissolved in 20 mL of ethylene glycol. The reaction was carried out under magnetic stirring in an oil bath at 150 °C for 20-72 hours. The reaction mixture was cooled to room temperature and the catalyst was filtered on a Büchner funnel with a sintered glass disc using CH_2Cl_2 and water. After concentration to half volume under vacuum, 30 mL of water were added and the mixture was extracted with CH_2Cl_2 (3 x 30 mL), and finally dried (Na_2SO_4). After the solvent was removed under reduced pressure, the crude product was analysed by GC-MS and purified by chromatography on silica gel (petroleum ether: ethyl acetate (8:2). Products were analysed using ^{1}H NMR, ^{13}C NMR spectroscopy and GC-MS chromatography.

General procedure for the Cu(0)NP-catalysed transfer semihydrogenation of internal alkynes to cis-alkenes.

Synthesis under conventional heating and stirring. The alkyne (3 mmol), KOH (6 mmol) and CuNP catalyst (10 mol%) were dissolved in 20 mL of ethylene glycol. The reaction was carried out under magnetic stirring in an oil bath at 150 °C for 2 hours. The reaction mixture was cooled to room temperature and the catalyst was filtered on a Büchner funnel with a sintered glass disc using CH_2Cl_2 and water. After concentration under vacuum to half volume, 30 mL of water were added and the mixture extracted with CH_2Cl_2 (3 x 30 mL) and finally dried (Na_2SO_4). After removal of the solvent under reduced pressure, the crude product was analysed by GC-MS and purified by chromatography on silica gel (petroleum ether: ethyl acetate (8:2)). Products were analysed using ^{1}H NMR, ^{13}C NMR spectroscopy and GC-MS chromatography. (See Supporting Information)

Synthesis under MW irradiation. The alkyne (3 mmol), KOH (6 mmol) and CuNP catalyst (10 mol%) were dissolved in 20 mL of ethylene glycol. The reaction was carried out under MW irradiation (Milestone MicroSynth) at 150 °C for 90 min, with a constant power of 120W. The reaction mixture was cooled down to room temperature and the catalyst was filtered on a Büchner funnel with a sintered glass disc using CH_2Cl_2 and water. After concentration under vacuum to half volume, 30 mL of water were added and the mixture was extracted with CH_2Cl_2 (3 x 30 mL) and finally dried (Na_2SO_4). After the solvent was removed under reduced pressure, the crude product was analysed by GC-MS and purified by chromatography on silica gel (petroleum ether: ethyl acetate (8:2)). Products were analysed using ^{1}H NMR, ^{13}C NMR spectroscopy and GC-MS chromatography.

Synthesis under US irradiation. The alkyne (3 mmol), KOH (6 mmol) and CuNP catalyst (10 mol%) were dissolved in 20 mL of ethylene glycol. The reaction mixture was sonicated using a Pyrex horn (20.3 kHz, 40 W) for 60 min. The reaction mixture was cooled to room temperature and the catalyst was filtered on a Büchner funnel with a sintered glass disc using CH_2Cl_2 and water. After concentration under vacuum to half volume, 30 mL of water were added and the mixture was extracted with CH_2Cl_2 (3 x 30 mL) and finally dried (Na_2SO_4). After the solvent was removed under reduced pressure, the crude product was analysed by GC-MS and purified by chromatography on silica gel (petroleum ether: ethyl acetate (8:2)). Products were analysed using ^{1}H NMR, ^{13}C NMR spectroscopy and GC-MS chromatography.

Synthesis under combined MW/US irradiation. Combined US (20.3 kHz, 30 Wcm^{-2}) and MW (2.45 GHz, 90 W) irradiation were used in a reactor (Microsynth-Milestone) equipped with a Pyrex horn inserted from the top. The reaction mixture, which contained the alkyne (3 mmol), KOH (6 mmol), CuNP catalyst (10 mol%) and 20 mL of ethylene glycol, was irradiated in the combined reactor system for 30 min. The reaction mixture was cooled to room temperature and the catalyst was filtered on a Büchner funnel with a sintered glass disc using CH_2Cl_2 and water. After concentration to half volume under vacuum, 30 mL of water were added and the mixture was extracted with CH_2Cl_2 (3 x 30 mL) and finally dried (Na_2SO_4). After the solvent was removed under reduced pressure, the crude product was analysed by GC-MS and purified by chromatography on silica gel (petroleum ether: ethyl acetate (8:2)). Products were analysed using ^{1}H NMR, ^{13}C NMR spectroscopy and GC-MS chromatography. All the following products are known, and spectral data are consistent with previously published literature values: **2a, 2b, 2c, 2d, 2e, 2f, 2g, 2h, 2i, 2j, 2k, 2l, 2m, 2n, 2o, 2p, 2q, 2r, 2s, 2t, 2u, 2v**. Spectral data for some selected compounds are given below:

(Z)-stilbene (**2a**): colourless liquid. Isolated yield under conventional conditions: 96% (518 mg). Isolated yield under MW/US irradiation: 97% (523 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 - 7.19 (m, 10H), 6.60 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.62, 130.63, 129.26, 128.60, 127.47 ppm.

(Z)-4-styrylaniline (**2b**): light yellow oil. Isolated yield when obtained from 1b under conventional conditions: 93% (544 mg). Isolated yield under MW/US irradiation: 95% (556 mg). ^{1}H NMR (600 MHz, CDCl3) δ 7.30 (d, J = 7.5 Hz, 2H), 7.23 (t, J = 7.5 Hz, 2H), 7.18 (d, J = 7.3 Hz, 1H), 7.07 (d, J = 8.5 Hz, 2H), 6.55 (d, J = 8.4 Hz, 2H), 6.46 (d, J = 14.1 Hz, 2H) ppm; ^{13}C NMR (151 MHz, CDCl3) δ 138.03, 130.24, 130.18, 128.89, 128.25, 127.84, 127.74, 127.73, 126.78, 114.85 ppm.

(Z)-1-methyl-4-styrylbenzene (**2c**): colourless oil. Isolated yield under conventional conditions: 94% (550 mg). Isolated yield under MW/US irradiation: 94% (550 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.24 (ddd, *J* = 7.4, 6.2, 1.4 Hz, 2H), 7.20 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.19 – 7.15 (m, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.59 – 6.55 (dd, 2H), 2.32 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.59, 136.97, 134.36, 130.30, 129.65, 129.01, 128.95, 128.89, 128.29, 127.07, 21.35 ppm.

(Z)-1-(4-methoxystyryl)benzene (**2d**): yellow oil. Isolated yield under conventional conditions: 91% (573 mg). Isolated yield under MW/US irradiation: 92% (589 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.20 (m, 7H), 6.77 – 6.79 (m, 2H), 6.54 (d, 2H), 3.80 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.76, 137.71, 130.25, 129.86, 128.91, 128.85, 128.33, 127.00, 113.67, 55.28 ppm.

(Z)-1-(4-styrylphenyl)ethanone (**2e**): yellow oil. Isolated yield under conventional conditions: 90% (600 mg). Isolated yield under MW/US irradiation: 93% (620 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.23 (dd, *J* = 11.8, 6.6 Hz, 5H), 6.72 (d, *J* = 12.2 Hz, 1H), 6.60 (d, *J* = 12.2 Hz, 1H), 2.56 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.61, 142.39, 136.76, 135.70, 132.52, 129.20, 129.14, 128.93, 128.46, 128.41, 127.64, 26.64 ppm.

(Z)-1-fluoro-2-styrylbenzene (**2f**): colourless oil. Isolated yield under conventional conditions: 77% (457 mg). Isolated yield under MW/US irradiation: 82% (487 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.15 (m, 7H), 7.04 (ddd, *J* = 10.0, 8.8, 1.2 Hz, 1H), 6.97 – 6.89 (m, 1H), 6.72 (d, *J* = 12.2 Hz, 1H), 6.62 (d, *J* = 12.2 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.61, 132.24, 132.23, 130.53, 130.50, 128.98, 128.90, 128.75, 128.25, 127.39, 123.64, 123.60, 122.63, 122.60, 115.72 ppm.

(Z)-1-chloro-2-styrylbenzene (**2g**): Colourless oil. Isolated yield under conventional conditions: 84% (539 mg). Isolated yield under MW/US irradiation: 85% (545 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.24 – 7.11 (m, 7H), 7.04 (td, *J* = 7.5, 1.1 Hz, 1H), 6.72 (d, *J* = 12.2 Hz, 1H), 6.67 (d, *J* = 12.2 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.48, 136.07, 133.72, 131.75, 130.78, 129.55, 129.01, 128.53, 128.22, 127.39, 127.28, 126.39 ppm.

(Z)-1-(2-methoxystyryl)benzene (**2h**): colourless liquid. Isolated yield under conventional conditions: 92% (580 mg). Isolated yield under MW/US irradiation: 92% (580 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (dddd, *J* = 13.7, 8.5, 6.0, 4.7 Hz, 7H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 12.3 Hz, 1H), 6.63 (d, *J* = 12.3 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.26, 137.39, 130.33, 130.19, 128.94, 128.69, 128.13, 127.01, 126.27, 125.88, 120.30, 110.72, 55.55 ppm.

(Z)-1-methyl-2-styrylbenzene (**2i**): colourless oil. Isolated yield under conventional conditions: 94% (550 mg). Isolated yield under MW/US irradiation: 95% (555 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.10 (m, 8H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.65 (q, *J* = 12.2 Hz, 2H), 2.29 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.21, 137.12, 136.21, 130.60, 130.17, 129.64, 129.03, 129.01, 128.98, 128.96, 128.95, 128.19, 127.33, 127.14, 125.81, 20.00 ppm.

(Z)-1-chloro-3-styrylbenzene (**2j**): colourless oil. Isolated yield under conventional conditions: 89% (574 mg). Isolated yield under MW/US irradiation: 90% (580 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.22 (m, 6H), 7.16 – 7.11 (m, 3H), 6.65 (d, *J* = 12.2 Hz, 1H), 6.52 (d, *J* = 12.2 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.20, 136.71, 134.15, 131.66, 129.53, 128.93, 128.91, 128.81, 128.42, 127.54, 127.23, 127.10 ppm.

(Z)-1-(3-methoxystyryl)benzene (**2k**): colourless oil. Isolated yield under conventional conditions: 86% (542 mg). Isolated yield under MW/US irradiation: 88% (554 mg). ^{1}H NMR (600 MHz) δ 7.31 – 7.22 (m, 4H), 7.20 (d, *J* = 7.1 Hz, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.82 – 6.78 (m, 1H), 6.78 – 6.73 (m, 1H), 6.60 (q, *J* = 12.2 Hz, 2H), 3.65 (s, 3H) ppm; ^{13}C NMR (151 MHz,) δ 159.44, 138.63, 137.36, 130.58, 130.24, 129.32, 129.01, 128.30, 127.24, 121.61, 113.81, 113.41, 55.09 ppm.

(Z)-1,3-dimethyl-2-styrylbenzene (**2l**): colourless oil. Isolated yield under conventional conditions: 82% (511 mg). Isolated yield under MW/US irradiation: 85% (530 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (dt, *J* = 10.1, 4.6 Hz, 4H), 7.04 (d, *J* = 7.5 Hz, 2H), 7.02 – 6.96 (m, 2H), 6.66 (d, *J* = 12.3 Hz, 1H), 6.54 (d, *J* = 12.3 Hz, 1H), 2.16 (s, 6H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.55, 137.17, 135.70, 131.13, 128.88, 128.31, 128.15, 127.57, 127.24, 126.96, 20.31 ppm.

(Z)-4-styrylpyridine (**2m**): colourless oil. Isolated yield under conventional conditions: 62% (336 mg). Isolated yield under MW/US irradiation: 64% (347 mg). ^{1}H NMR (400 MHz, CDCl3) δ 8.47 (d, *J* = 6.1 Hz, 2H), 7.25 (ddd, *J* = 14.9, 6.2, 2.6 Hz, 5H), 7.12 (d, *J* = 6.0 Hz, 2H), 6.81 (d, *J* = 12.3 Hz, 1H), 6.52 (d, *J* = 12.3 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.86, 144.97, 136.15, 134.04, 128.75, 128.46, 127.85, 127.55, 123.50 ppm.

(Z)-2-styrylpyridine (**2n**): colourless oil. Isolated yield under conventional conditions: 53% (288 mg). Isolated yield under MW/US irradiation: 71% (385 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.51 (m, 1H), 7.42 (td, *J* = 7.7, 1.8 Hz, 1H), 7.28 – 7.21 (m, 5H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.07 (ddd, *J* = 7.4, 4.8, 0.8 Hz, 1H), 6.83 (d, *J* = 12.5 Hz, 1H), 6.69 (d, *J* = 12.4 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.35, 149.55, 136.65, 135.61, 133.24, 130.51, 128.87, 128.29, 127.58, 123.84, 121.74. ppm.

(Z)-3-styrylpyridine (**2o**): light yellow oil. Isolated yield under conventional conditions: 87% (472 mg). Isolated yield under MW/US irradiation: 90% (489 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 1.9 Hz, 1H), 8.42 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.51 (dt, *J* = 7.9, 1.6 Hz, 1H), 7.31 – 7.17 (m, 5H), 7.12 (dd, *J* = 7.9, 4.8 Hz, 1H), 6.75 (d, *J* = 12.2 Hz, 1H), 6.55 (d, *J* = 12.2 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.19, 148.09, 136.52, 135.78, 132.98, 132.68, 128.69, 128.51, 127.58, 126.43, 122.98 ppm.

(Z)-4-phenyl-1-(4-styrylbenzyl)-1H-1,2,3-triazole (**2p**): solid. Isolated yield under conventional conditions: 84% (850 mg). Isolated yield under MW/US irradiation: 87% (880 mg). ^{1}H NMR (600 MHz) δ 7.84 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.70 (s, 1H), 7.47 – 7.41 (m, 2H), 7.38 – 7.33 (m, 1H), 7.31 – 7.25 (m, 6H), 7.26 – 7.21 (m, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.68 (d, *J* = 12.2 Hz, 1H), 6.59 (d, *J* = 12.2 Hz, 1H), 5.56 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.30, 131.30, 129.71, 129.31, 128.91, 128.86, 128.42, 127.98, 125.78, 119.57, 54.05 ppm.

(Z)-2-styrylaniline (**2q**): yellow oil. Isolated yield under conventional conditions: 91% (534 mg). Isolated yield under MW/US irradiation: 92% (540 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 5H), 7.13 – 7.08 (m, 2H), 6.80 – 6.74 (m, 1H), 6.74 – 6.70 (m, 1H), 6.67 (d, *J* = 12.1 Hz, 1H), 6.55 (d, *J* = 12.1 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.78, 136.70, 131.99, 129.72, 128.84, 128.77, 128.51, 128.29, 127.55, 126.64, 126.36, 123.86, 119.16, 116.12 ppm.

(Z)-4-styrylaniline (**2r**): light yellow oil. Isolated yield when obtained from 1r under conventional conditions: 92%. Isolated yield under MW/US irradiation: 94%. ^{1}H NMR and ^{13}C NMR and See **2b**.

(Z)-oct-4-ene (**2s**) colourless liquid. The reaction was performed at 140 °C in a gas tight glass reactor for 16 hrs. Pentane and water were added to the reaction mixture and the aqueous layer was extracted three time with pentane. The organic phase was dried under light vacuum and the pure liquid was collected without any further purification. Isolated yield 94% (316 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.36 (ddd, J = 5.6, 4.5, 1.1 Hz, 2H), 2.00 (td, J = 7.3, 5.7 Hz, 4H), 1.39 – 1.32 (m, 4H), 0.89 (t, J = 7.4 Hz, 6H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 129.92, 29.38, 22.97, 128.39, 13.88 ppm.

(Z)-4-phenylbut-3-en-1-ol (**2t**): colourless oil. Isolated yield under conventional conditions: 88% (390 mg). Isolated yield under MW/US irradiation: 89% (394 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 5H), 6.57 (d, J = 11.7 Hz, 1H), 5.68 (dt, J = 11.7 Hz, 1H), 3.73 (t, J = 6.5 Hz, 2H), 2.68 (t, J = 6.3 Hz, 2H), 2.60 (ddd, J = 13.9, 6.5, 1.8 Hz, 5H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.30, 131.62, 128.82, 128.39, 128.31, 126.91, 62.55, 32.07 ppm.

(Z)-11-phenylundec-10-en-1-ol (**2u**): colourless liquid. Isolated yield under conventional conditions: 88% (650 mg). Isolated yield under MW/US irradiation: 87% (642 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.31 – 7.26 (m, 2H), 7.24 – 7.17 (m, 1H), 6.40 (d, J = 11.7 Hz, 1H), 5.66 (dt, J = 11.7, 7.3 Hz, 1H), 3.74 (s, 1H), 3.63 (t, J = 6.7 Hz, 2H), 2.32 (ddd, J = 15.0, 7.4, 1.8 Hz, 2H), 1.56 (dd, J = 8.2, 6.7 Hz, 2H), 1.44 (dd, J = 15.2, 7.6 Hz, 2H), 1.34 – 1.28 (m, 10H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.89, 133.36, 128.84, 128.75, 128.18, 126.49, 63.17, 32.87, 30.06, 29.63, 29.51, 29.48, 29.41, 28.72, 25.80 ppm.

(Z)-1,4-diethoxybut-2-ene (**2v**): colourless oil. Isolated yield under conventional conditions: 85% (367 mg). Isolated yield under MW/US irradiation: 85% (367 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.73 – 5.68 (m, 2H), 4.03 (d, J = 4.8 Hz, 4H), 3.47 (q, J = 7.0 Hz, 4H), 1.20 (t, J = 7.0 Hz, 6H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 129.48, 66.32, 65.82, 15.30 ppm.

(Z)-1,4-bis(benzyloxy)but-2-ene (**2w**): colourless oil. Isolated yield under conventional conditions: 87% (772 mg). Isolated yield under MW/US irradiation: 88% (777 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (dt, J = 8.6, 6.6 Hz, 10H), 5.79 (t, J = 3.8 Hz, 2H), 4.49 (s, 4H), 4.06 (d, J = 4.7 Hz, 4H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.21, 129.61, 128.51, 127.89, 127.77, 72.35, 65.85 ppm.

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Copper nanoparticles as an efficient catalyst for Z-Selective Transfer Semihydrogenation of Internal Alkynes

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