RESEARCH ARTICLE

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Ligandless nickel-catalyzed transfer hydrogenation of alkenes and alkynes using water as the hydrogen donor†

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The first general route for nickel-catalyzed transfer hydrogenation reaction of alkenes and alkynes using water as the hydrogen source has been developed. The method features the use of inexpensive and air-stable nickel(ɪɪ) salt as the pre-catalyst and zinc powder as a reducing agent, allowing the TH reaction to occur under mild reaction conditions with a wide substrate scope and functional group tolerance. No ligand was required for this reaction. The reaction has also been applied successfully to the reduction of nitrogen-containing heterocycles.

Introduction

Transition-metal-catalyzed hydrogenation of unsaturated π-systems is one of the most fundamental and important reactions in organic chemistry.[1] These reactions usually proceed with hydrogen, a highly flammable and explosive gas. Recently, catalytic transfer hydrogenation (TH) has emerged as a promising and powerful strategy because it is operationally simple and much safer than direct hydrogenation using hydrogen gas, as no gas containment or pressure vessel is necessary.[2] Compared with the TH reactions of polarized substrates such as aldehydes,[2] ketones,[2] imines[2] and α,β-unsaturated carbonyl compounds,[3] the TH reactions of non-polarized unsaturated compounds such as normal alkenes or alkynes have been less developed. A variety of reagents including formic acid,[4] ethanol,[5] isopropanol,[6] 1,4-cyclohexadiene,[7] amine–borane adducts[8] *etc.* have been used as possible *in situ* hydrogen sources in the TH reactions of alkenes or alkynes. However, there are a few examples using water as the hydrogen donor. The use of water as the hydrogen donor is highly attractive since it is cheap, non-toxic, and environmentally friendly, and allows the easy isotopic labeling of the products by D₂O.

It may also offer the opportunity to disclose new reaction patterns or selectivity. However, formidable challenges remain in water-mediated reactions catalyzed by a transition metal since the resulting organometallic intermediates are generally considered to be incompatible with water. It was known that in the presence of a reductant such as zinc, nickel salts could promote the reduction of unsaturated compounds in water; however, most of these reports were restricted to α,β-unsaturated carbonyls. In addition, a high catalyst loading (>30% to excess amounts of nickel salts) was required.[9] It was also reported that a combination of a stoichiometric amount of NiCl₂·2H₂O with a large excess of lithium powder (8 equiv.) in the presence of an arene as an electron carrier was effective for the conversion of alkenes or alkynes into alkanes or alkenes.[10] The hydrogen source came from the water content in the nickel salt in these cases.[10] In these reactions, a high catalyst loading and a large excess of the reductant were employed. Therefore, a general and catalytic version of the Ni-catalyzed reduction of common alkenes and alkynes using water has not been reported to date. Recently, Pd/Ni or Pd-catalyzed transfer hydrogenation of alkenes or alkynes using water[11] in the presence of magnesium,[11a] Cp₂TiCl,[11b] Me₃SiSiMe₃,[11c] B₂(OH)₄,[11d] or B₂Pin₂,[11e] or Rh-catalyzed reaction in the presence of zinc[12] has been reported. During our manuscript preparation, a Pd/Mn-catalyzed transfer hydrogenation of alkynes using water was reported.[13] Nevertheless, the catalytic TH reactions by utilization of the inexpensive and earth-abundant metal catalysts are quite rare and will be highly desirable in organic chemistry. Recently, we focused our efforts on the Ni-catalyzed hydrocyanation reactions of alkynes[14] and alkenes[15] using Zn(CN)₂ as the cyanide source and water as the hydrogen source. During the course of the

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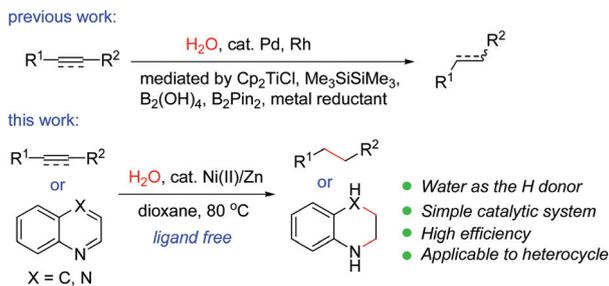
Scheme 1 Transition-metal-catalyzed transfer hydrogenation reactions.

mechanistic study, we occasionally found that alkynes could be reduced by nickel-catalyzed transfer hydrogenation in the presence of water.[14] Inspired by our work, we decided to conduct an in-depth study on this topic. We now discovered that the simple combination of an air-stable nickel(II) pre-catalyst with a reducing metal under ligandless conditions is highly effective for transfer hydrogenation of alkenes and alkynes with water as the hydrogen donor (Scheme 1). The method proceeds with high generality, a wide substrate scope and good functional group tolerance. Remarkably, the reaction is also applicable to the reduction of nitrogen-containing heterocycles, which has not been achieved in nickel-catalyzed TH reactions using water.[16]

Results and discussion

We initially investigated the nickel-catalyzed transfer hydrogenation of 2-vinylnaphthalene **1a** with H_2O. After a thorough screening of the nickel catalysts, ligands, reductants, solvents, additives *etc.*, a highly efficient catalyst system featuring $NiCl_2 \cdot 6H_2O$ (5 mol%) and zinc powder (2.0 equiv.) in dioxane/H_2O (5 : 1, 56 equiv. H_2O) at 80 °C was established. To our surprise, the reaction proceeded without the need for a ligand. Under these reaction conditions, **1a** was reduced smoothly to afford 2-ethylnaphthalene **2a** in 88% yield (Table 1, entry 1). The use of other nickel salts such as $NiCl_2$, $NiBr_2$ or NiI_2 as the catalyst was also effective for this reaction (entries 2–4). However, the use of NiF_2 or $Ni(acac)_2$ led to either a trace amount of **2a** or no conversion (entries 5 and 6). Inferior results were found when other reducing agents such as Al, Mn, and Mg were employed (entries 7–9). The reaction proceeded smoothly in DMF/H_2O and THF/H_2O, with the formation of **2a** in 90% and 95% yields, respectively (entries 10 and 11). Unexpectedly, the use of MeCN/H_2O significantly lowered the conversion, and only a trace amount of **2a** was observed (entry 12). The amount of H_2O also played an important role in this reaction, since decreasing the amount of H_2O (dioxane/H_2O = 25 : 1, 11 equiv. H_2O) afforded **2a** in only 33% yield (entry 13). The best result was achieved by using dioxane/H_2O = 3 : 1 (entry 14, 93 equiv. H_2O). The results indicated that a sufficient amount of water was required for this reaction. A
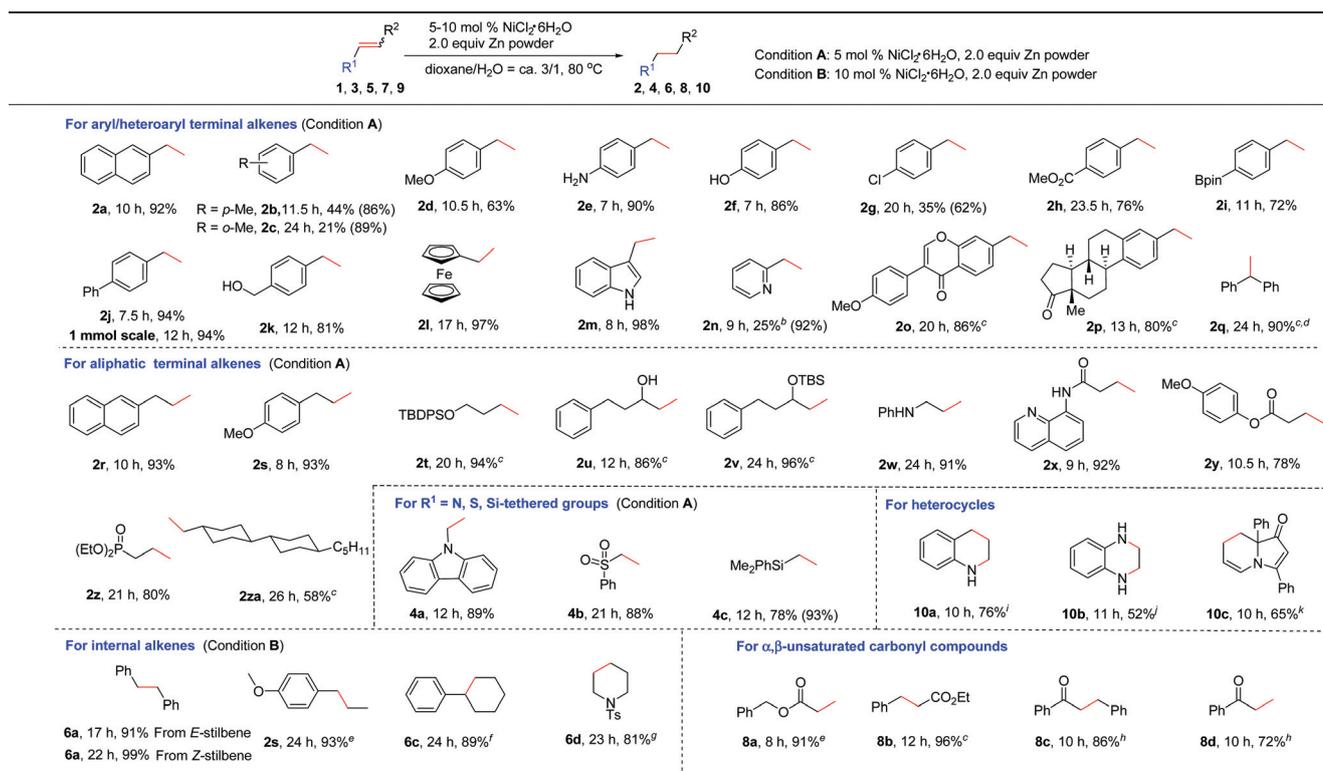
Table 1 Optimization of reaction conditions

Entry	Catalyst	Reductant	Solvent	Time (h)	Yield[a] (%)
1	$NiCl_2 \cdot 6H_2O$	Zn	Dioxane/H_2O (5/1)	10	88
2	$NiCl_2$	Zn	Dioxane/H_2O (5/1)	10	89
3	$NiBr_2$	Zn	Dioxane/H_2O (5/1)	10	89
4	NiI_2	Zn	Dioxane/H_2O (5/1)	10	79 (7)
5	NiF_2	Zn	Dioxane/H_2O (5/1)	10	2 (85)
6	$Ni(acac)_2$	Zn	Dioxane/H_2O (5/1)	10	— (89)
7	$NiCl_2 \cdot 6H_2O$	Al	Dioxane/H_2O (5/1)	10	24 (68)
8	$NiCl_2 \cdot 6H_2O$	Mn	Dioxane/H_2O (5/1)	10	13 (81)
9	$NiCl_2 \cdot 6H_2O$	Mg	Dioxane/H_2O (5/1)	10	— (96)
10	$NiCl_2 \cdot 6H_2O$	Zn	DMF/H_2O (5/1)	10	90 (1)
11	$NiCl_2 \cdot 6H_2O$	Zn	THF/H_2O (5/1)	10	95
12	$NiCl_2 \cdot 6H_2O$	Zn	CH_3CN/H_2O (5/1)	10	1 (58)
13	$NiCl_2 \cdot 6H_2O$	Zn	Dioxane/H_2O (25/1)	10	33 (59)
14	**$NiCl_2 \cdot 6H_2O$**	**Zn**	**Dioxane/H_2O (3/1)**	**10**	**96**
15	$NiCl_2 \cdot 6H_2O$	Zn	Dioxane/H_2O (3/1)	5	95
16[b]	$NiCl_2 \cdot 6H_2O$	Zn	Dioxane/H_2O (3/1)	5	48 (48)
17[c]	$NiCl_2 \cdot 6H_2O$	Zn	Dioxane/H_2O (3/1)	5	32 (63)
18	—	Zn	Dioxane/H_2O (3/1)	5	— (94)
19	$NiCl_2 \cdot 6H_2O$	—	Dioxane/H_2O (3/1)	5	— (94)

[a] Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. The yields of the unreacted **1a** are shown in parentheses. [b] 1.0 equiv. of Zn was used. [c] 50 °C.

high yield of **2a** could also be observed when reducing the reaction time to 5 h (entry 15). Decreasing the amount of Zn or lowering the reaction temperature resulted in lower yields of **2a** (entries 16 and 17). Control experiments indicated that both the nickel catalyst and Zn were essential for the reaction (entries 18 and 19).

Next, the generality of this nickel-catalyzed transfer hydrogenation protocol was investigated. The scope of aryl alkenes was first studied under the conditions shown in Table 1, entry 14. A wide range of aryl/heteroaryl alkenes were compatible for this reaction (Table 2). Aryl alkenes bearing a methyl group at the *para*- or *ortho*-position afforded high yields of **2b** and **2c** (86–89%); however, a longer reaction time was needed for **2c**. The results indicated that steric hindrance has a certain influence on this reaction. Electron-donating groups such as *p*-MeO, free amino and OH groups as well as electron-withdrawing groups such as *p*-Cl, *p*-CO_2Me on the aryl rings were well tolerated, and the corresponding products of **2d–2h** were obtained in 62–90% yields. Notably, a chlorine substituent was well suited in this reaction (**2g**). Special alkenes such as *p*-boron-, *p*-phenyl-, *p*-CH_2OH-aryl alkenes and ferrocenyl-alkenes turned out to be efficient substrates (**2i–2l**). Heteroaryl alkenes such as indolyl and pyridyl alkenes reacted with water very well to form **2m** and **2n** in excellent yields. The reaction could be readily applied to natural product derivatives, for example estrone or formononetin derived alkenes transformed to **2o** and **2p** in high efficiency, while the ketone moiety in these substrates remained intact. In these cases, increasing the catalyst loading to 10 mol% was required to consume the

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Table 2 Scope of the Ni-catalyzed transfer hydrogenation reactions of alkenes with H_2O^a

Reaction scheme: 5–10 mol % NiCl₂·6H₂O, 2.0 equiv Zn powder, dioxane/H₂O = ca. 3/1, 80 °C. Condition A: 5 mol % NiCl₂·6H₂O, 2.0 equiv Zn powder. Condition B: 10 mol % NiCl₂·6H₂O, 2.0 equiv Zn powder.

For aryl/heteroaryl terminal alkenes (Condition **A**)

2a, 10 h, 92% — R = *p*-Me, 2b, 11.5 h, 44% (86%); R = *o*-Me, 2c, 24 h, 21% (89%) — 2d, 10.5 h, 63% — 2e, 7 h, 90% — 2f, 7 h, 86% — 2g, 20 h, 35% (62%) — 2h, 23.5 h, 76% — 2i, 11 h, 72%

2j, 7.5 h, 94% / 1 mmol scale, 12 h, 94% — 2k, 12 h, 81% — 2l, 17 h, 97% — 2m, 8 h, 98% — 2n, 9 h, 25%[b] (92%) — 2o, 20 h, 86%[c] — 2p, 13 h, 80%[c] — 2q, 24 h, 90%[c,d]

For aliphatic terminal alkenes (Condition **A**)

2r, 10 h, 93% — 2s, 8 h, 93% — 2t, 20 h, 94%[c] — 2u, 12 h, 86%[c] — 2v, 24 h, 96%[c] — 2w, 24 h, 91% — 2x, 9 h, 92% — 2y, 10.5 h, 78%

2z, 21 h, 80% — 2za, 26 h, 58%[c]

For R¹ = N, S, Si-tethered groups (Condition **A**)

4a, 12 h, 89% — 4b, 21 h, 88% — 4c, 12 h, 78% (93%)

For heterocycles

10a, 10 h, 76%[i] — 10b, 11 h, 52%[j] — 10c, 10 h, 65%[k]

For internal alkenes (Condition **B**)

6a, 17 h, 91% From *E*-stilbene / 6a, 22 h, 99% From *Z*-stilbene — 2s, 24 h, 93%[e] — 6c, 24 h, 89%[f] — 6d, 23 h, 81%[g]

For α,β-unsaturated carbonyl compounds

8a, 8 h, 91%[e] — 8b, 12 h, 96%[c] — 8c, 10 h, 86%[h] — 8d, 10 h, 72%[h]

[a] Isolated yields. The ^1H NMR yields of the volatile products are shown in parentheses. [b] Containing a small amount of stabilizer and solvent. [c] Condition **B**. [d] 2.0 equiv. of Zn flakes (325 mesh) were used. [e] Condition **A**. [f] 3.0 equiv. of Zn flakes (325 mesh) were used. [g] 3.0 equiv. of Zn powder were used. [h] 20 mol% NiCl₂·6H₂O and 4.0 equiv. of Al powder (200 mesh) in dioxane/H₂O (5 : 1). [i] 10 mol% NiCl₂·6H₂O, 3.0 equiv. of Zn powder and 1.0 equiv. of Et₃N at 100 °C in dioxane/H₂O (5 : 1). [j] 10 mol% NiCl₂·6H₂O and 3.0 equiv. of Zn powder at 100 °C in dioxane/H₂O (3 : 1). [k] 10 mol% NiCl₂·6H₂O, 2.0 equiv. of Zn powder and 1.0 equiv. of Et₃N at 100 °C in dioxane/H₂O (5 : 1).

substrates completely. When sterically hindered 1,1-diphenyl-ethylene **1q** was employed as the substrate, a high yield of the desired **2q** (*ca.* 94%) was also observed; however, a small amount of the starting material (5%) remained, which could not be separated from **2q** by column chromatography. **1q** was reduced completely and cleanly by replacing zinc powder by zinc flakes in the presence of 10 mol% NiCl₂·6H₂O. Possibly, zinc flakes may reduce Ni(II)-salt or related nickel intermediates more efficiently than zinc powder.

Aliphatic alkenes were also easily reduced to give the corresponding alkanes in good to excellent yields. As expected, allylic-naphthalene (**1r**) and -benzene (**1s**) gave **2r** and **2s** in high yields. An alkyl side chain bearing an OTBDPS group was also suitable (**2t**). Non-protected or protected allylic alcohols transformed to **2u** and **2v** efficiently. In the case of **2u**, the isomerization to the corresponding ketone product was not observed.[17] Allylic amine **1w** was also confirmed to be valuable substrate for this reaction to afford the desired alkane **2w** in 91% yield. The possible deallylation product was not observed although it was known that Ni could catalyze the C–N bond cleavage reaction in allylic amines.[18] In addition, a series of allylic substrates bearing various functional groups such as amide, ester or phosphate groups were converted to desired **2x–2z** successfully. Alkene **1za** without any functional group was reduced smoothly

(**2za**). The reactivity of various activated alkenes was also examined, and alkenes tethered with carbazolyl, sulfonyl, and silyl groups were all compatible with this system (**4a–4c**).

As for internal alkenes, high conversions were achieved from both *cis*-(*Z*-**5a**) and *trans*-stilbene (*E*-**5a**), indicating that the reaction was not sensitive to the geometry of the double bond. A common naturally occurring *trans*-anethole worked well (**2s**). The reaction with tri-substituted alkenes such as 2,3,4,5-tetrahydro-1,1′-biphenyl required the use of 3.0 equiv. of zinc flakes as the reductant (**6c**). In the case of cyclic alkene **5d**, double bond migration (chain walking) to the closer position of the NTs group was observed during the reaction. A high yield of the alkane **6d** was achieved by increasing the amount of Zn to 3.0 equiv. The use of an α,β-unsaturated ester revealed a faster and clean reduction (**8a** and **8b**). When the reaction was applied to an α,β-unsaturated ketone such as chalcone, only a low yield (23%) of the double bond reduction product **8c** was obtained due to the competing side reactions such as over-reduction or alkene oligomerization. To our delight, highly chemoselective reduction of the C=C bond over the C=O bond could be achieved by switching the reductant of Zn to Al and using 20 mol% NiCl₂·6H₂O as the catalyst (**8c**).[19] Under this condition, a terminal unsaturated ketone was also reduced selectively (**8d**).

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Reduction of heteroaromatic compounds is generally more difficult than alkenes and alkynes due to the resonance stabilization and the possible deactivation of the catalyst by either the substrate or the product. The transfer hydrogenation of heterocycles has been much less developed.[20] When the reaction of quinoline was carried out in the presence of 10 mol% NiCl$_2$·6H$_2$O/3.0 equiv. Zn, only a little product was observed, along with various byproducts. After many efforts, we found that the addition of 1.0 equiv. of Et$_3$N significantly improved the efficiency of this reaction to provide the desired **10a** in 76% yield. The role of Et$_3$N is not clear yet. It might help to stabilize the catalytically active species by a weak coordination.[21] Quinoxaline was reduced to **10b** in 52% yield, and in this case, the addition of Et$_3$N resulted in a complex mixture. Notably, selective reduction of one of the C=C bonds was observed with indolizinone (**10c**).

The reactivity of alkynes was also evaluated (Table 3). In these cases, 3.0 equiv. of Zn were required in order to reduce alkynes completely to alkanes. Terminal arylacetylenes bearing electron-withdrawing groups or electron-rich groups were well compatible (**2d–2e** and **12c**). Alkynes with a biphenyl (**2j**) or 2-naphthyl group (**2a**) were also smoothly reduced. Aliphatic terminal alkynes bearing various functional groups such as ether, amide, OH, or phenyl groups and silyl alkyne worked well to afford the corresponding **12f–12j** in moderate to good yields. Particularly, propargyl amide (**12g**) and tertiary propargyl alcohol (**12h**) were tolerable. Bis(aryl)alkynes such as diphenyl-acetylene were cleanly reduced (**6a**). Reduction of phenyl, alkyl-acetylene and dialkyl acetylene also proceeded smoothly (**12l** and **12m**). In alkyne reductions, we could observe the formation of alkenes at the early stage of the reaction in some cases. Thus, the reaction proceeds *via* generation of an alkene intermediate which undergoes further reduction to deliver the alkane product.

In order to understand the mechanism, various control experiments were performed. Reduction of diphenylacetylene with D$_2$O using NiCl$_2$ as the catalyst afforded the deuterated
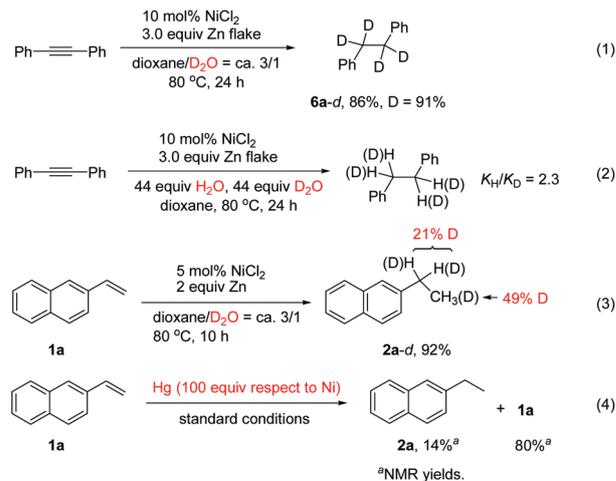

Scheme 2 Control experiments.

product **6a**-*d* in 86% yield with high deuterium incorporation (Scheme 2, eqn (1)), indicating that water acts as the hydrogen source for this reaction. A kinetic isotope effect was examined by employing an equimolar mixture of H$_2$O and D$_2$O as the H and D donor, which revealed a primary kinetic isotope effect ($k_H/k_D = 2.3$). Parallel experiments indicated that $k_H/k_D = 3$.[22] The results imply that the O–H bond cleavage of H$_2$O is likely involved in the rate-determining step (Scheme 2, eqn (2)).[11d] In the reaction of alkene **1a** with D$_2$O, deuterium was found in both the benzylic position and methyl group (Scheme 2, eqn (3)). The results indicated that a Ni–H species might be generated, and addition of Ni–H to the alkene is reversible under the reaction conditions. The yield of the product **2a** was decreased significantly upon addition of mercury (Scheme 2, eqn (4)), indicating that a heterogeneous system might be involved in this transfer hydrogenation reaction. We also noted that hydrogen gas evolution could be detected at 80 °C regardless of the presence or absence of a substrate.[9d] The detailed reaction mechanism was not clear yet at the moment. Possibly, a Ni(0) species is first generated through reduction of the Ni(II) salt by Zn. This is followed by a catalytic hydrogenation process involving reduction of the substrate on the nickel surface with the absorbed H$_2$ gas.[9d,23]

Conclusions

In summary, we have developed the first general and operationally simple protocol for nickel-catalyzed transfer hydrogenation reaction of alkenes and alkynes using water as the hydrogen source. The method features the use of inexpensive and air-stable nickel(II) salt as the pre-catalyst and zinc as a reducing agent, allowing the TH reaction to occur under mild reaction conditions with a wide substrate scope and functional group tolerance. The method does not require the use of a ligand. The reaction has also been applied successfully to the

Table 3 Scope of alkynes[a]
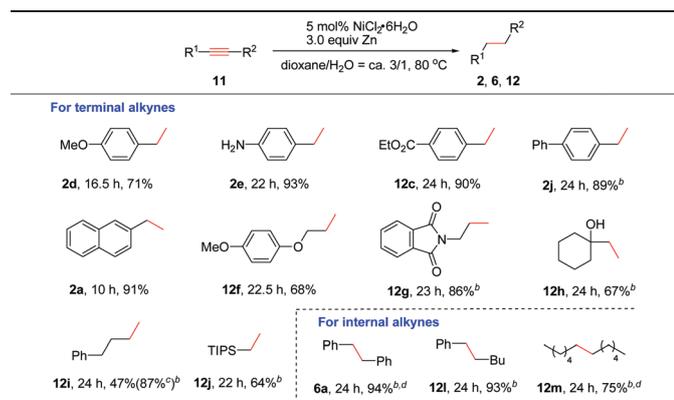
[a] Isolated yields. [b] 10 mol% NiCl$_2$·6H$_2$O was used. [c] ^{1}H NMR yield using 1,3,5-trimethoxybenzene as an internal standard. [d] Zn flakes (325 mesh) were used.

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reduction of nitrogen-containing heterocycles. Further investigations on the detailed reaction mechanism and application of this chemistry are in progress.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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19 An $Al/NiCl_2 \cdot 6H_2O$ system with high loading (10 equiv.) for both metals has been used to reduce α,β-unsaturated compounds, see ref. 9e.

20 For other metal-catalyzed TH reactions using water or alcohol as the hydrogen source, see: (a) V. H. Mai and G. I. Nikonov, *Organometallics*, 2016, **35**, 943; (b) Ref. 16b and c (c) Ref. 5.

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22 See the ESI.†

23 We found that in several cases, the yields of the desired products were influenced by the volume of the reaction vessel. The yield of the product was decreased by using a larger tube. The results indicated that the H_2 gas concentration may have an important impact on the reaction.

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