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Z-Selective Semihydrogenation of Alkynes via Ni/Lewis Acid Synergistic Catalyzed System Using DMF as Hydrogen Source and Solvent

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Abstract

A Ni/Lewis acid dual-catalytic system has been developed for the *Z*-selective semihydrogenation of alkynes. Utilizing DMF as both the hydrogen donor and reaction medium, this method affords *Z*-alkenes in high yield with excellent stereoselectivity under mild conditions. The protocol employs cost-effective and readily available catalysts, and demonstrates broad applicability across a wide range of substrates.

Keywords: Z-Selective Semihydrogenation, Alkynes, Ni/Lewis Acid Catalysis, DMF

Introduction

Z-Olefins represent important structural units in natural products, pharmaceuticals, and functional materials, making the stereoselective semihydrogenation of alkynes a fundamental transformation in synthesis[1-3]. Among available methods, transition-metal catalysis has played a dominant role. The classical Lindlar catalyst remains the most widely applied heterogeneous system[4], yet it suffers from several limitations—including batch variability, alkene isomerization, and over-reduction to alkanes, which are particularly problematic for terminal and polar substrates[5-8]. These drawbacks have motivated the search for more efficient and reliable alternatives.

In recent years, homogeneous catalysts based on Ni, Cu, Rh, and Co have shown promise in addressing some of these issues[9-14]. Nickel, in particular, has emerged as an attractive candidate for transfer semihydrogenation, where formic acid or silanes serve as the hydrogen source, often achieving high Z-selectivity through careful ligand design[15-17]. Still, many of these systems depend on expensive ligands, toxic reductants, or relatively forcing conditions, which can limit their practical utility[18-20]. Single-metal catalytic approaches also frequently exhibit modest stereocontrol. While cobalt-based systems have demonstrated some ability to tune Z/E selectivity, they often rely on

ammonia borane as the hydrogen donor, which presents certain atom-economic disadvantages[21-26]. Clearly, new strategies are needed to advance this field.

Synergistic catalysis, which combines two distinct catalytic components, has become a valuable approach for overcoming the limitations of single-catalyst systems[27-29]. Lewis acids are well known for their ability to activate polar functional groups and stabilize reactive intermediates, yet their combination with nickel catalysts has been little explored in alkyne semihydrogenation. We envisioned that merging nickel's competence in alkyne activation and hydrogen transfer with a Lewis acid's capacity to modulate reaction pathways could enhance both selectivity and efficiency.

Dimethylformamide (DMF), a common polar aprotic solvent, has recently attracted interest as a safe and environmentally benign hydrogen donor in catalytic reductions[30-32]. Compared with traditional hydrogen sources such as H_2 or silanes, DMF offers advantages of low toxicity, high stability, and operational simplicity, aligning well with the growing emphasis on sustainable synthesis[16, 33]. Its compatibility with both Lewis acids and nickel catalysts further suggests its potential as a combined solvent and hydrogen donor in a synergistic catalytic manifold[34, 35]. Related amide derivatives, such as formamide, have also been employed as safe cyanide sources or hydrogen-donor precursors, offering useful precedents for their application in reduction chemistry[36, 37].

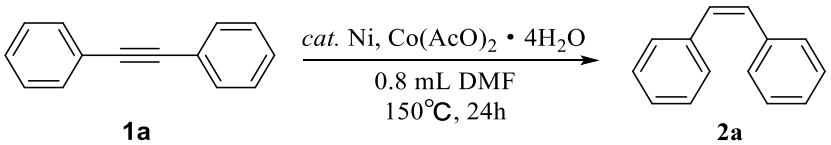
In this work, we describe a new synergistic catalytic system for the cis-selective semihydrogenation of alkynes, utilizing a Lewis acid together with a nickel catalyst and DMF as the hydrogen source. This method achieves excellent Z-selectivity (up to 98:2 Z/E ratio), operates under mild conditions, and avoids noble metals, toxic reductants, and specialized pressure equipment. The synergy between the Lewis acid and the nickel catalyst, coupled with the dual role of DMF, enables efficient conversion of diverse internal and terminal alkynes to the corresponding Z-olefins. Beyond expanding the toolbox for stereocontrolled alkyne semihydrogenation, this study offers fresh perspectives on the design of Lewis acid–metal synergistic catalytic systems.

Results and Discussion

We began by developing a base-metal catalytic system for the semihydrogenation of diphenylacetylene (**1a**), motivated by the practical limitations associated with previous precious-metal Pd catalysts. Capitalizing on DMF's capacity to act as both solvent and hydrogen source, we investigated a Ni/Lewis acid co-catalytic approach. Employing $Co(OAc)_2 \cdot 4H_2O$ as the Lewis acid co-catalyst, we first evaluated the influence of the nickel precursor. As summarized in **Table 1**, the reaction of **1a** was performed in DMF (0.8 mL) at 150 °C for 24 h, using various Ni sources (20 mol%) and $Co(OAc)_2 \cdot 4H_2O$ (50 mol%).

When $NiCl_2$ was used, **2a** (cis-stilbene) was obtained in 68% GC yield (entry 1). In contrast, NiF_2 and $Ni(acac)_2$ proved considerably less effective, yielding only 23% and 6% of **2a**, respectively (entries 2–3). Moderate conversions were observed with $Ni(NO_3)_2 \cdot 6H_2O$, $NiCp_2$, and $(Ph_3P)_2NiBr_2$ (34%, 30%, and 43% yields; entries 4, 5, 7). Notably, phosphine-ligated Ni complexes such as $(dppe)NiCl_2$ showed poor activity (20% yield, entry 6), while $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ and $(dppp)NiCl_2$ afforded **2a** in 45% and 50% yield (entries 9–10). Unsurprisingly, control experiments confirmed that the reaction does not proceed in the absence of a nickel source (entry 11). These findings underscore a strong dependence of catalytic activity on the nature of the Ni precursor, with $NiCl_2$ emerging as the most effective candidate under the conditions screened.

Table 1. Evaluation of Nickel Precursors in the Semihydrogenation of 1,2-Diphenylacetylene (**1a**) Catalyzed by $Ni/Co(OAc)_2 \cdot 4H_2O$.



Entry	[Ni] (20 mol%)	Lewis acid (50 mol%)	Yield [%][a]
1	$NiCl_2$	$Co(AcO)_2 \cdot 4H_2O$	68
2	NiF_2	$Co(AcO)_2 \cdot 4H_2O$	23
3	$Ni(acac)_2$	$Co(AcO)_2 \cdot 4H_2O$	6

4	$Ni(NO_3)_2 \cdot 6H_2O$	$Co(AcO)_2 \cdot 4H_2O$	34
5	$Ni(Cp)_2$	$Co(AcO)_2 \cdot 4H_2O$	30
6	$(dppe)NiCl_2$	$Co(AcO)_2 \cdot 4H_2O$	20
7	$(Ph_3P)_2 \cdot NiCl_2$	$Co(AcO)_2 \cdot 4H_2O$	43
8	$(Ph_3P)_2 \cdot NiBr_2$	$Co(AcO)_2 \cdot 4H_2O$	45
9	$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$	$Co(AcO)_2 \cdot 4H_2O$	2
10	$(dppp)NiCl_2$	$Co(AcO)_2 \cdot 4H_2O$	50
11	--	$Co(AcO)_2 \cdot 4H_2O$	trace

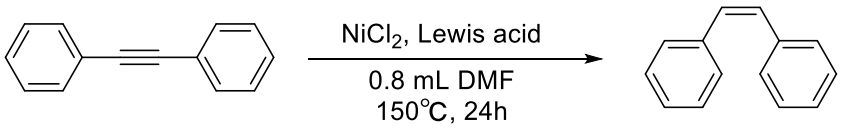
[a]Yields were determined by GC analysis using mesitylene as an internal standard. Value in parentheses is the isolated yield.

Having identified $NiCl_2$ as a suitable nickel source (**Table 1**), we next fixed this component (20 mol%) and proceeded to screen various Lewis acids (50 mol%) for the semihydrogenation of diphenylacetylene (**1a**). Reactions were conducted in DMF at 150 °C for 24 h, and the results are compiled in **Table 2**.

Unsurprisingly, the Lewis acid proved crucial: in its absence, only a 9% GC yield of **2a** was obtained (entry 1). Using $Co(OAc)_2 \cdot 4H_2O$, our initial co-catalyst from the previous screening, gave a 68% yield (entry 2), consistent with earlier data. Screening other Lewis acids, however, revealed considerable variation in performance. $Fe(NO_3)_3 \cdot 9H_2O$ and $BF_3 \cdot Et_2O$, for instance, afforded merely trace product (entries 3 and 7). Other candidates, including $CoCl_2 \cdot 6H_2O$, $Co(acac)_2$, and $SnCl_2 \cdot 2H_2O$, showed low activity, yielding **2a** in 7–17% (entries 5, 6, and 9).

Interestingly, zinc-based Lewis acids stood out. $ZnCl_2$ significantly improved the yield to 96% (entry 4). Most notably, $Zn(OAc)_2 \cdot 2H_2O$ delivered the best performance, achieving a 98% GC yield (95% isolated yield) of **2a** with an excellent *Z*/*E* selectivity of >98:2 (entry 8). These results clearly demonstrate that zinc salts, particularly $Zn(OAc)_2 \cdot 2H_2O$, form a highly effective synergistic pair with $NiCl_2$, dramatically enhancing both the efficiency and stereoselectivity of the transformation.

Table 2. Screening of Lewis Acids for the $NiCl_2$-Cocatalyzed Semihydrogenation of 1,2-Diphenylacetylene (**1a**).



1a **2a**

Entry	[Ni] (20mol%)	Lewis acid (50mol%)	Temp (°C)	Yield [%][a]
1	$NiCl_2$	--	150	9
2	$NiCl_2$	$Co(AcO)_2·4H_2O$	150	68
3	$NiCl_2$	$Fe(NO_3)_3·9H_2O$	150	trace
4	$NiCl_2$	$ZnCl_2$	150	96
5	$NiCl_2$	$CoCl_2·6H_2O$	150	17
6	$NiCl_2$	$Co(acac)_2$	150	7
7	$NiCl_2$	$BF_3·Et_2O$	150	trace
8	$NiCl_2$	$Zn(AcO)_2·2H_2O$	150	98(95;Z/E=98:2) [b]
9	$NiCl_2$	$SnCl_2·2H_2O$	150	11

[a]Yields were determined by GC analysis using mesitylene as an internal standard. Value in parentheses is the isolated yield.

[b]The Z/E ratio of the product was determined via GC of reaction mixture.

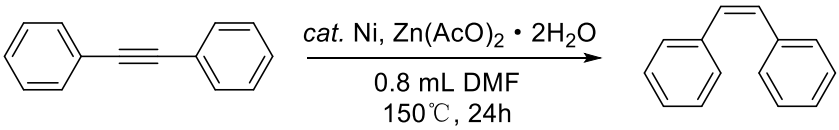
With $Zn(OAc)_2·2H_2O$ established as the optimal Lewis acid (**Table 2**), we proceeded to optimize the remaining reaction parameters, keeping the Lewis acid loading fixed at 50 mol%. The outcomes of this study are summarized in **Table 3**. Consistent with our earlier findings, the nickel catalyst proved indispensable; omitting it resulted in only a trace of product **2a** (entry 1). Screening various nickel precursors confirmed $NiCl_2$ as the most effective, delivering **2a** in 98% GC yield (95% isolated) with excellent *Z*-selectivity (entry 2). Other nickel sources, including $Ni(acac)_2$ and phosphine-ligated complexes such as $(dppe)NiCl_2$, gave notably lower yields (entries 3–12). We then examined the catalyst loading. The combination of 20 mol% $NiCl_2$ and 50 mol% $Zn(OAc)_2·2H_2O$ (entry 2) remained optimal. Reducing either the nickel loading (entry 13) or the Lewis acid amount (entries 14–15) led to a clear decrease in yield. While increasing both loadings slightly improved the yield (entries 16–17), the marginal gain did not justify the higher catalyst use.

The reaction temperature was also critical. The reaction temperature was also critical. A significant drop in yield was observed at 130 °C (entry 18). Although 140 °C provided an 88% yield (entry 19), optimal conversion required 150 °C (entry 2). The reaction time was optimized to 24 hours; shorter (12 h, entry 20) or moderately shorter (18 h, entry 21) durations resulted in incomplete conversion.

Finally, the role of DMF was confirmed. Replacing it with formamide or N-methylformamide led to markedly reduced yields (entries 24–25), further confirming the unique advantages of DMF as both solvent and hydrogen source.

After the above full-parameter condition optimization, the optimized conditions were established as: 20 mol% $NiCl_2$, 50 mol% $Zn(OAc)_2 \cdot 2H_2O$, in DMF at 150 °C for 24 h (entry 2). This protocol afforded **2a** in 98% GC yield (95% isolated) with >98:2 *Z*/*E* selectivity.

Table 3. Optimization of Reaction Conditions for the Semihydrogenation of 1,2-Diphenylacetylene (**1a**) Catalyzed by $NiCl_2/Zn(OAc)_2 \cdot 2H_2O$.



1a **2a**

Entry	[Ni] (20mol%)	Lewis acid (50mol%)	Temp (°C)	Yield [%][a]
1	--	$Zn(AcO)_2 \cdot 2H_2O$	150	trace
2	$NiCl_2$	$Zn(AcO)_2 \cdot 2H_2O$	150	98(95)
3	NiF_2	$Zn(AcO)_2 \cdot 2H_2O$	150	73
4	$Ni(acac)_2$	$Zn(AcO)_2 \cdot 2H_2O$	150	45
5	$Ni(NO_3)_2 \cdot 6H_2O$	$Zn(AcO)_2 \cdot 2H_2O$	150	4
6	$Ni(AcO)_2 \cdot 4H_2O$	$Zn(AcO)_2 \cdot 2H_2O$	150	89
7	(dppe)$NiCl_2$	$Zn(AcO)_2 \cdot 2H_2O$	150	73
8	$(Ph_3P)_2 \cdot NiCl_2$	$Zn(AcO)_2 \cdot 2H_2O$	150	69
9	$(Ph_3P)_2 \cdot NiBr_2$	$Zn(AcO)_2 \cdot 2H_2O$	150	50
10	$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$	$Zn(AcO)_2 \cdot 2H_2O$	150	79
11	(dppp)$NiCl_2$	$Zn(AcO)_2 \cdot 2H_2O$	150	72
12	$NiSO_4 \cdot 6H_2O$	$Zn(AcO)_2 \cdot 2H_2O$	150	78
13	$NiCl_2$ (10%)	$Zn(AcO)_2 \cdot 2H_2O$ (50%)	150	65
14	$NiCl_2$ (20%)	$Zn(AcO)_2 \cdot 2H_2O$ (30%)	150	54

15	$NiCl_2$ (20%)	$Zn(AcO)_2{\cdot}2H_2O$ (40%)	150	85
16	$NiCl_2$ (30%)	$Zn(AcO)_2{\cdot}2H_2O$ (30%)	150	86
17	$NiCl_2$ (30%)	$Zn(AcO)_2{\cdot}2H_2O$ (40%)	150	92
18	$NiCl_2$	$Zn(AcO)_2{\cdot}2H_2O$	130	9
19	$NiCl_2$	$Zn(AcO)_2{\cdot}2H_2O$	140	88
20[b]	$NiCl_2$	$Zn(AcO)_2{\cdot}2H_2O$	150	46
21[c]	$NiCl_2$	$Zn(AcO)_2{\cdot}2H_2O$	150	85
22[d]	$NiCl_2$	$Zn(AcO)_2{\cdot}2H_2O$	150	13
23[e]	$NiCl_2$	$Zn(AcO)_2{\cdot}2H_2O$	150	60

[a] Yields were determined by GC analysis using mesitylene as an internal standard. Value in parentheses is the isolated yield.

[b]Reaction time was 12 h.

[c] Reaction time was 18 h.

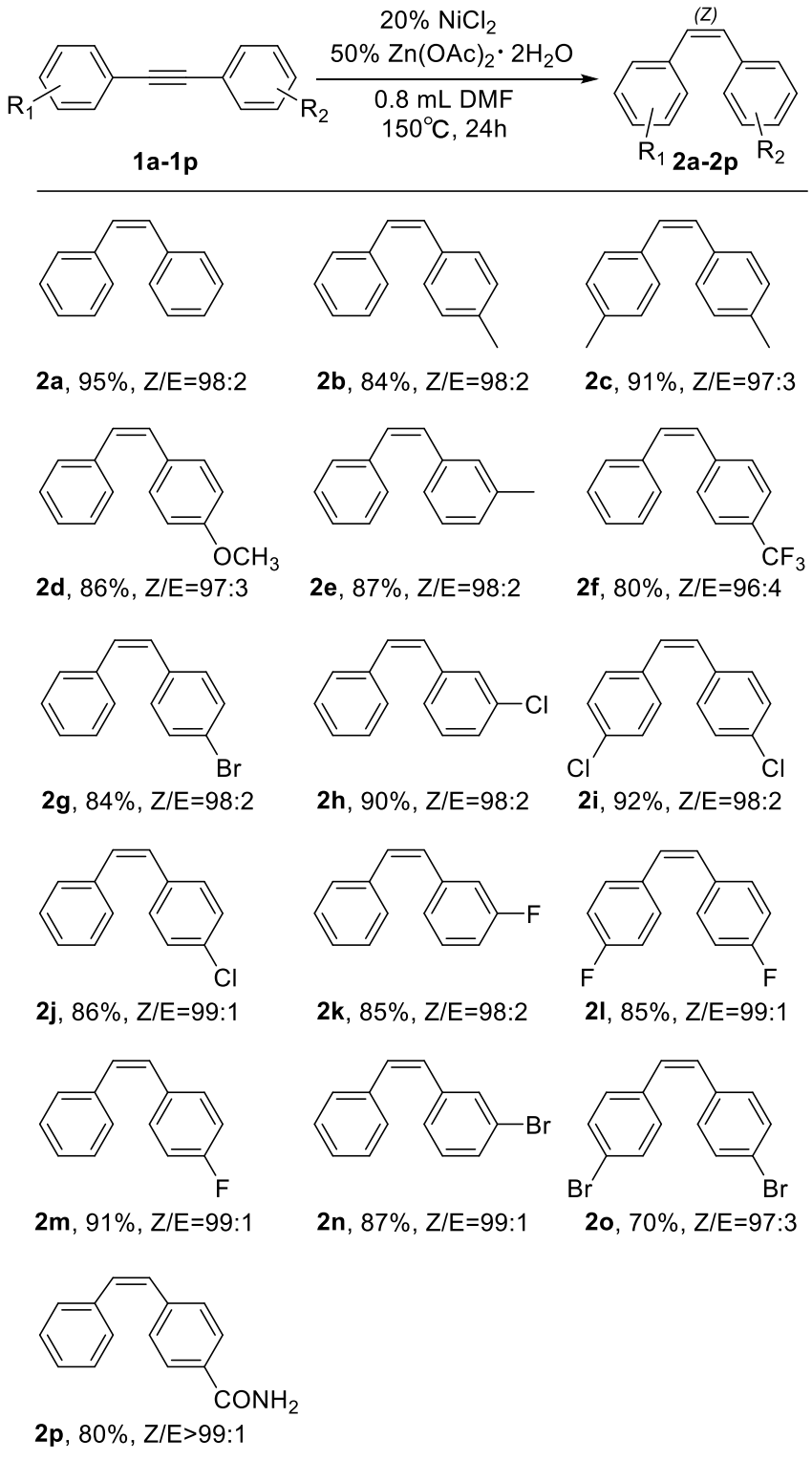
[d]Formamide was used as the solvent/H-donor.

[e]N-Methylformamide was used as the solvent/H-donor.

Under the optimized conditions (20 mol% $NiCl_2$, 50 mol% $Zn(OAc)_2{\cdot}2H_2O$, DMF, 150 °C, 24 h), we evaluated the generality of this *Z*-selective semihydrogenation with various internal alkynes (**Scheme 1**). The system proved broadly effective for both symmetrical and unsymmetrical diarylacetylenes (**1a–1p**). Substrates bearing electron-donating groups (methyl **2b, 2c, 2e**; methoxy **2d**), electron-withdrawing groups (trifluoromethyl **2f**; halogens **2g–2o**), and even an amide moiety (**2p**) were smoothly converted to the corresponding (*Z*)-stilbene derivatives in good to excellent yields (70%–95%), with uniformly high stereoselectivity (*Z*/*E* = 97:3 to >99:1).

The reaction demonstrated excellent functional group tolerance. Ethers, halides (C–Cl, C–Br, C–F), and amides remained intact under the reaction conditions. Notably, substrates with strong electron-withdrawing substituents (e.g., $–CF_3$ in **2f**) or multiple halogen atoms (**2i, 2o**) were also well tolerated, affording the products in good yields and highlighting the robust applicability of this catalytic system.

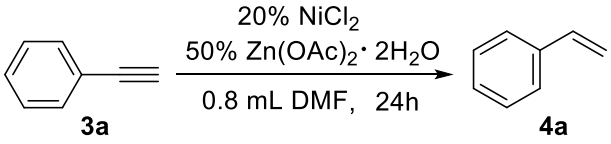
Scheme 1. $NiCl_2/Zn(AcO)_2 \cdot 2H_2O$-Cocatalyzed Z-Selective Semihydrogenation of Internal Alkynes to (Z)-Internal Alkenes.



Having optimized the conditions for internal alkynes such as diphenylacetylene, we next sought to apply this Ni/Zn dual-catalytic system to the semihydrogenation of terminal alkynes. Using phenylacetylene (**3a**) as the model substrate, we focused on screening the reaction temperature while maintaining a fixed reaction time of 24 h. The results are summarized in **Table 4**.

At 130 °C, the GC yield of styrene (**4a**) was only 30% (entry 1). Raising the temperature to 135 °C improved the yield to 58% (entry 2). The optimal performance was observed at 140 °C, providing **4a** in 70% GC yield (64% isolated yield, entry 3). Further increases to 145 °C or 150 °C led to diminished yields of 67% and 51%, respectively (entries 4–5). These results suggest that the reduction of terminal alkynes is more temperature-sensitive than that of internal alkynes, with an optimum at 140 °C compared to 150 °C for diphenylacetylene.

Table 4. Screening of Reaction Temperatures



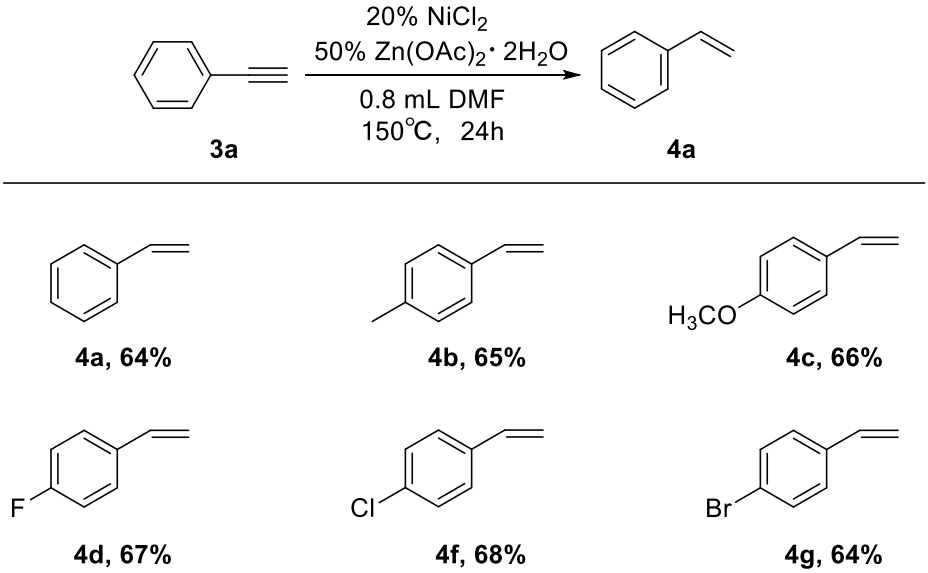
Entry	Temp (°C)	Yield [%][a]
1	130	30
2	135	58
3	140	70(65)
4	145	67
5	150	51

[a] Yields were determined by GC using mesitylene as an internal standard. The value in parentheses is the isolated yield.

With suitable conditions for the terminal alkyne **3a** in hand, we then examined the scope of this Ni/Zn system for various substituted terminal aryl alkynes. Employing the standard protocol (20 mol% $NiCl_2$, 50 mol% $Zn(OAc)_2{\cdot}2H_2O$, DMF, 150 °C, 24 h), substrates bearing methyl (**4b**), methoxy (**4c**), and halogen (F for **4d**, Cl for **4f**, Br for

4g) substituents were smoothly converted to the corresponding styrene derivatives in 64–68% yields. Both electron-donating groups (methyl, methoxy) and halogen functional groups (F, Cl, Br) remained intact under the reaction conditions without side reactions, fully demonstrating the good functional group tolerance and substrate generality of this catalytic system.

Scheme 2. $NiCl_2/Zn(AcO)_2 \cdot 2H_2O$-Cocatalyzed Semihydrogenation of Terminal Alkynes to Terminal Alkenes.



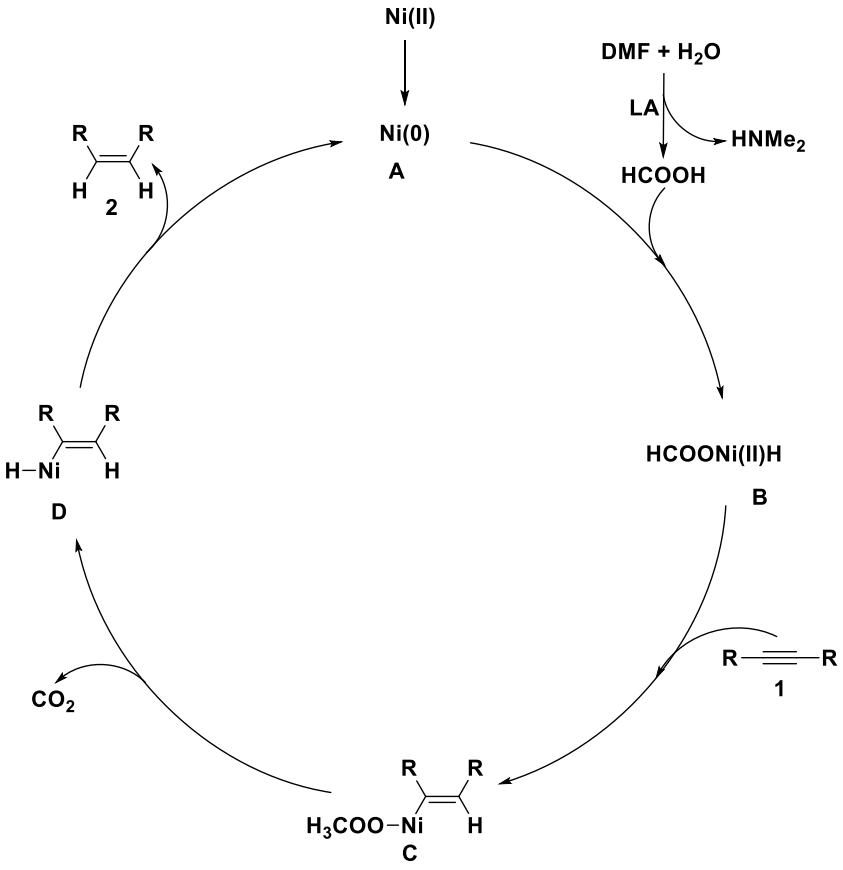
Based on our experimental observations, well-established nickel chemistry[38], and relevant findings from palladium-catalyzed systems[39], we propose a plausible catalytic cycle for the $NiCl_2$-catalyzed semihydrogenation of internal alkynes, as outlined in **Scheme 3**.

The cycle likely begins with the reduction of the Ni(II) precursor to an active Ni(0) species **A**—a common initiation step in nickel-catalyzed transformations. Simultaneously, DMF undergoes Lewis acid-assisted decomposition to generate formic acid (HCOOH) and $HNMe_2$. This *in situ* formation of HCOOH appears critical; while $HCOOH/NEt_3$ can serve as a hydrogen source in related Pd catalysis[39], using stoichiometric HCOOH (or HCOOH/KOH) directly affords only trace alkene, largely

due to competing decomposition into H_2 and CO_2 under the reaction conditions. Maintaining an appropriate concentration of HCOOH via its gradual release from DMF thus seems essential for efficient semihydrogenation, a requirement that parallels findings in Pd systems.

HCOOH then reacts with the Ni species to form a formate nickel hydride intermediate **B** (HCOONi(II)H), a key species documented in nickel-catalyzed hydrogen-transfer reactions. Subsequent selective insertion of the internal alkyne into the Ni–H bond of **B** affords the vinyl-nickel intermediate **C**. Following decarboxylation, the resulting dihydrido vinyl-nickel species **D** undergoes reductive elimination to release the (*Z*)-alkene product and regenerate the Ni(0) catalyst **A**, thereby closing the catalytic cycle.

Scheme 3. Proposed Catalytic Cycle for the Ni/Lewis Acids-Catalyzed Semihydrogenation of Alkynes with DMF.



Conclusions

In summary, we have developed a highly *Z*-selective semihydrogenation of alkynes using a synergistic Ni/Lewis acid dual-catalytic system. The protocol employs DMF as a combined solvent and hydrogen donor, operating under mild conditions without external reductants or pressurized equipment. This method delivers (*Z*)-alkenes in high yields (up to 95%) with excellent stereoselectivity (up to >98:2 *Z*/*E* ratio) and demonstrates broad functional-group compatibility across a range of internal and terminal arylalkynes. Key practical advantages include the use of inexpensive, readily available nickel and zinc salts, as well as the operational simplicity afforded by DMF's dual role. Overall, this work provides a practical and cost-effective alternative to existing semihydrogenation methods and highlights the potential of base-metal synergistic catalysis in stereocontrolled synthetic transformations.

Experimental Section

An oven-dried reaction vessel was charged with diphenylacetylene (0.2 mmol, 35.6 mg), $Zn(OAc)_2 \cdot 2H_2O$ (50 mol%, 22 mg), and $NiCl_2$ (20 mol%, 3.3 mg). DMF (0.8 mL) was then added, the vessel was sealed, and the mixture was stirred and heated at 150 °C (oil bath temperature) for 24 h. The reaction was monitored by GC analysis; upon complete consumption of the starting material, heating was discontinued. After cooling to room temperature, the volatiles were removed under reduced pressure. The resulting crude residue was purified by flash column chromatography on silica gel (eluent: petroleum ether) to afford pure (*Z*)-stilbene (**2a**) as a colorless solid in 95% isolated yield (34.4 mg). The *Z*/*E* ratio (98:2) was determined by GC analysis of the crude mixture.

Acknowledgements

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References

(1) Oger, C.; Balas, L.; Durand, T.; Galano, J.-M. Are Alkyne Reductions Chemo-, Regio-, and Stereoselective Enough To Provide Pure (Z)-Olefins in Polyfunctionalized Bioactive Molecules? *Chem. Rev.* **2013**, *113* (3), 1313-1350. DOI: 10.1021/cr3001753.
(2) Fürstner, A.; Guth, O.; Rumbo, A.; Seidel, G. Ring Closing Alkyne Metathesis. Comparative Investigation of Two Different Catalyst Systems and Application to the Stereoselective Synthesis of Olfactory Lactones, Azamacrolides, and the Macrocyclic Perimeter of the Marine Alkaloid Nakadomarin A. *Journal of the American Chemical Society* **1999**, *121* (48), 11108-11113. DOI: 10.1021/ja992074k.
(3) Liang, S.; Hammond, G. B.; Xu, B. Supported gold nanoparticles catalyzed cis-selective semihydrogenation of alkynes using ammonium formate as the reductant. *Chemical Communications* **2016**, *52* (35), 6013-6016, 10.1039/C6CC01318J. DOI: 10.1039/C6CC01318J.
(4) Lindlar, H. Ein neuer Katalysator für selektive Hydrierungen. *Helvetica Chimica Acta* **1952**, *35* (2), 446-450. DOI: https://doi.org/10.1002/hlca.19520350205 (acccessed 2025/12/20).
(5) Ulan, J. G.; Maier, W. F.; Smith, D. A. Rational design of a heterogeneous palladium catalyst for the selective hydrogenation of alkynes. *The Journal of Organic Chemistry* **1987**, *52* (14), 3132-3142. DOI: 10.1021/jo00390a032.
(6) Kluwer, A. M.; Koblenz, T. S.; Jonischkeit, T.; Woelk, K.; Elsevier, C. J. Kinetic and Spectroscopic Studies of the [Palladium(Ar-bian)]-Catalyzed Semi-Hydrogenation of 4-Octyne. *Journal of the American Chemical Society* **2005**, *127* (44), 15470-15480. DOI: 10.1021/ja052729j.
(7) van Laren, M. W.; Elsevier, C. J. Selective Homogeneous Palladium(0)-Catalyzed Hydrogenation of Alkynes to (Z)-Alkenes. *Angew. Chem. Int. Ed.* **1999**, *38* (24), 3715-3717. DOI: https://doi.org/10.1002/(SICI)1521-3773(19991216)38:24<3715::AID-ANIE3715>3.0.CO;2-O (acccessed 2025/12/20).
(8) Chen, X.-B.; Zhang, J.; Sun, D.-Q.; Chen, K.-Q.; Chen, X.-Y. Phenanthrolines as Energy Transfer Photocatalysts for the E → Z Isomerization of Alkenes. *Synthesis* **2025**, *57* (12), 1928-1935. DOI: 10.1055/a-2502-8374.
(9) Richmond, E.; Moran, J. Ligand Control of E/Z Selectivity in Nickel-Catalyzed Transfer Hydrogenative Alkyne Semireduction. *The Journal of Organic Chemistry* **2015**, *80* (13), 6922-6929. DOI: 10.1021/acs.joc.5b01047.
(10) Han, X.; Hu, J.; Chen, C.; Yuan, Y.; Shi, Z. Copper-catalysed, diboron-mediated cis-dideuterated semihydrogenation of alkynes with heavy water. *Chemical Communications* **2019**, *55* (48), 6922-6925, 10.1039/C9CC03213D. DOI:

10.1039/C9CC03213D.
(11) Fu, S.; Chen, N.-Y.; Liu, X.; Shao, Z.; Luo, S.-P.; Liu, Q. Ligand-Controlled Cobalt-Catalyzed Transfer Hydrogenation of Alkynes: Stereodivergent Synthesis of Z- and E-Alkenes. *Journal of the American Chemical Society* **2016**, *138* (27), 8588-8594. DOI: 10.1021/jacs.6b04271.
(12) Rai, R. K.; Awasthi, M. K.; Singh, V. K.; Barman, S. R.; Behrens, S.; Singh, S. K. Aqueous phase semihydrogenation of alkynes over Ni–Fe bimetallic catalysts. *Catalysis Science & Technology* **2020**, *10* (15), 4968-4980, 10.1039/D0CY01153C. DOI: 10.1039/D0CY01153C.
(13) Sheikh Mohammad, T.; Sakharov, P.; Raje, S.; de Ruiter, G. Z-Selective Semihydrogenation of Alkynes Catalyzed by a Co(I)PCNHCP Pincer Complex: A Simple, Fast, and Practical Methodology. *ACS Catalysis* **2025**, *15* (7), 5370-5377. DOI: 10.1021/acscatal.5c00792.
(14) Xia, S.; Peng, J.; Xie, S.; Xu, T.; Li, L.; Liu, X.; Cao, D.; He, L.-N.; Li, C.-J. Copper-Catalyzed Chemoselective Hydrogenation of Unsaturated Bonds with Formic Acid/Formate as Hydrogen Donor. *Organic Letters* **2025**, *27* (21), 5423-5428. DOI: 10.1021/acs.orglett.5c01372.
(15) Thiel, N. O.; Kaewmee, B.; Tran Ngoc, T.; Teichert, J. F. A Simple Nickel Catalyst Enabling an E-Selective Alkyne Semihydrogenation. *Chemistry – A European Journal* **2020**, *26* (7), 1597-1603. DOI: https://doi.org/10.1002/chem.201903850 (acccessed 2025/12/20).
(16) Pape, F.; Thiel, N. O.; Teichert, J. F. Z-Selective Copper(I)-Catalyzed Alkyne Semihydrogenation with Tethered Cu–Alkoxide Complexes. *Chemistry – A European Journal* **2015**, *21* (45), 15934-15938. DOI: https://doi.org/10.1002/chem.201501739 (acccessed 2025/12/20).
(17) Wu, Y.; Ao, Y.; Li, Z.; Liu, C.; Zhao, J.; Gao, W.; Li, X.; Wang, H.; Liu, Y.; Liu, Y. Modulation of metal species as control point for Ni-catalyzed stereodivergent semihydrogenation of alkynes with water. *Nature Communications* **2023**, *14* (1), 1655. DOI: 10.1038/s41467-023-37022-w.
(18) Wakamatsu, T.; Nagao, K.; Ohmiya, H.; Sawamura, M. Copper-Catalyzed Semihydrogenation of Internal Alkynes with Molecular Hydrogen. *Organometallics* **2016**, *35* (10), 1354-1357. DOI: 10.1021/acs.organomet.6b00126.
(19) Semba, K.; Kameyama, R.; Nakao, Y. Copper-Catalyzed Semihydrogenation of Alkynes to Z-Alkenes. *Synlett* **2015**, *26* (03), 318-322. DOI: 10.1055/s-0034-1379896.
(20) Chugh, V.; Wu, J.; Leutzsch, M.; Randel, H.; Weyhermüller, T.; Auer, A. A.; Farès, C.; Werlé, C. Controlling hydrogen transfer dynamics in adaptive semihydrogenation of alkynes: Unveiling and directing outer- vs. inner-sphere mechanisms. *Chem Catalysis* **2024**, *4* (9). DOI: 10.1016/j.checat.2024.101078 (acccessed 2025/12/20).
(21) Qi, X.; Liu, X.; Qu, L.-B.; Liu, Q.; Lan, Y. Mechanistic insight into cobalt-catalyzed stereodivergent semihydrogenation of alkynes: The story of selectivity control. *Journal of Catalysis* **2018**, *362*, 25-34. DOI: https://doi.org/10.1016/j.jcat.2018.03.016.

(22) Tokmic, K.; Fout, A. R. Alkyne Semihydrogenation with a Well-Defined Nonclassical Co–H2 Catalyst: A H2 Spin on Isomerization and E-Selectivity. *Journal of the American Chemical Society* **2016**, *138* (41), 13700-13705. DOI: 10.1021/jacs.6b08128.
(23) Pandey, D. K.; Khusnutdinova, J. R. Fast Co-Catalyzed Semihydrogenation of Alkynes with Controlled E/Z-Selectivity Using Same Catalyst. *ChemCatChem* **2025**, *17* (8), e202500041. DOI: https://doi.org/10.1002/cctc.202500041 (acccessed 2025/12/20).
(24) Ren, X.; Lu, P.; Zheng, C.; Wang, Y.; Lu, Z. Cobalt-Catalyzed Stereodivergent Semihydrogenation of Alkynes: Synthesis of E- and Z-Alkenes. *Angew. Chem. Int. Ed.* **2025**, *64* (35), e202511269. DOI: https://doi.org/10.1002/anie.202511269 (acccessed 2025/12/20).
(25) Li, K.; Khan, R.; Zhang, X.; Gao, Y.; Zhou, Y.; Tan, H.; Chen, J.; Fan, B. Cobalt catalyzed stereodivergent semi-hydrogenation of alkynes using H2O as the hydrogen source. *Chemical Communications* **2019**, *55* (39), 5663-5666, 10.1039/C9CC01970G. DOI: 10.1039/C9CC01970G.
(26) Feng, W.-J.; Chang, Z.; Lu, X.; Fu, Y. Electrochemical cobalt-catalyzed semi-deuteration of alkynes to access deuterated Z-alkenes. *Nature Communications* **2025**, *16* (1), 2390. DOI: 10.1038/s41467-025-57782-x.
(27) Dong, X.-Q.; Zhao, Q.; Li, P.; Chen, C.; Zhang, X. Metalorganocatalysis: cooperating transition-metal catalysis and organocatalysis through a covalent bond. *Organic Chemistry Frontiers* **2015**, *2* (10), 1425-1431, 10.1039/C5QO00226E. DOI: 10.1039/C5QO00226E.
(28) Deng, Y.; Kumar, S.; Wang, H. Synergistic–cooperative combination of enamine catalysis with transition metal catalysis. *Chemical Communications* **2014**, *50* (33), 4272-4284, 10.1039/C4CC00072B. DOI: 10.1039/C4CC00072B.
(29) Wasilke, J.-C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. Concurrent Tandem Catalysis. *Chem. Rev.* **2005**, *105* (3), 1001-1020. DOI: 10.1021/cr020018n.
(30) Zhao, C.; Wang, Y.; Pham, Q.; Dai, C.; Chatterjee, A.; Wasa, M. Chemical Tagging of Bioactive Amides by Cooperative Catalysis: Applications in the Syntheses of Drug Conjugates. *Journal of the American Chemical Society* **2023**, *145* (26), 14233-14250. DOI: 10.1021/jacs.3c00169.
(31) Lang, Q.; Gu, G.; Cheng, Y.; Yin, Q.; Zhang, X. Highly Enantioselective Synthesis of Chiral γ-Lactams by Rh-Catalyzed Asymmetric Hydrogenation. *ACS Catalysis* **2018**, *8* (6), 4824-4828. DOI: 10.1021/acscatal.8b00827.
(32) Wen, J.; Jiang, J.; Zhang, X. Rhodium-Catalyzed Asymmetric Hydrogenation of α,β-Unsaturated Carbonyl Compounds via Thiourea Hydrogen Bonding. *Organic Letters* **2016**, *18* (18), 4451-4453. DOI: 10.1021/acs.orglett.6b01812.
(33) Gao, Y.; Yang, R.; Wang, C.; Liu, C.; Wu, Y.; Li, H.; Zhang, B. Field-induced reagent concentration and sulfur adsorption enable efficient electrocatalytic semihydrogenation of alkynes. *Science Advances* *8* (8), eabm9477. DOI: 10.1126/sciadv.abm9477 (acccessed 2025/12/20).

(34) Sarkar, S.; Jana, M.; Tadigoppula, N. Transition metal-free domino sequential synthesis of (E)-stilbenes, biaryl methanes and biaryl ethers using Et2AlCl as a Lewis acid. *RSC Advances* **2013**, *3* (41), 18755-18758, 10.1039/C3RA42955E. DOI: 10.1039/C3RA42955E.
(35) Cella, R.; Stefani, H. A. Ultrasound-assisted synthesis of Z and E stilbenes by Suzuki cross-coupling reactions of organotellurides with potassium organotrifluoroborate salts. *Tetrahedron* **2006**, *62* (24), 5656-5662. DOI: https://doi.org/10.1016/j.tet.2006.03.090.
(36) Luo, L.; Dai, H.; Yang, M.-Q.; Yang, L. Nucleophilic Cyanation of Enones and Imines with Formamide as the Cyano Source. *Adv. Synth. Catal.* **2024**, *366* (18), 3920-3924. DOI: https://doi.org/10.1002/adsc.202400482 (acccessed 2025/12/20).
(37) Zhang, J.; Luo, C.-P.; Yang, L. Nickel/Cobalt-Catalyzed Reductive Hydrocyanation of Alkynes with Formamide as the Cyano Source, Dehydrant, Reductant, and Solvent. *Adv. Synth. Catal.* **2021**, *363* (1), 283-288. DOI: https://doi.org/10.1002/adsc.202000935 (acccessed 2025/12/21).
(38) Chen, T.; Xiao, J.; Zhou, Y.; Yin, S.; Han, L.-B. Nickel-catalyzed (E)-selective semihydrogenation of internal alkynes with hypophosphorous acid. *J. Organomet. Chem.* **2014**, *749*, 51-54. DOI: https://doi.org/10.1016/j.jorganchem.2013.09.023.
(39) Li, J.; Hua, R.; Liu, T. Highly Chemo- and Stereoselective Palladium-Catalyzed Transfer Semihydrogenation of Internal Alkynes Affording cis-Alkenes. *The Journal of Organic Chemistry* **2010**, *75* (9), 2966-2970. DOI: 10.1021/jo100247a.