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Nickel/photoredox dual-catalyzed reductive cross-coupling of aryl halides and aldehydes†

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A straightforward reductive cross-coupling of aryl halides and aldehydes to afford silyl-protected secondary alcohols is reported. The catalytic system features the use of nickel/photoredox dual catalysis and α-silylamine as a mild, easily accessible organic reductant, thus enabling the coupling process to occur smoothly under mild conditions without the necessity of pre-preparing highly reactive organometallic reagents and using stoichiometric amounts of metal-based reductants (such as Mn and Zn). The key to the success of this reductive coupling is to identify α-silylamine as a bifunctional organic reductant that simultaneously serves as a reducing agent and a transmetallic reagent to restore the nickel catalyst. The reaction shows a broad substrate scope and tolerates various functional groups, and a variety of (hetero) aryl and aliphatic aldehydes are compatible, thus providing a complementary approach towards Zn/Mn-mediated reductive coupling systems.

Introduction

Diaryl carbinols are ubiquitous structural units in natural products and drug molecules.[1] Traditional approaches towards diaryl carbinols were based on the addition of organometallic reagents to aldehydes,[2] such as the Grignard reaction[3] or a related one-pot Barbier-type reaction.[4] Nevertheless, the need to pre-prepare organometallic reagents from the corresponding organic halides results in low atom- and step-economy, and more particularly, the stoichiometric use of highly reactive organometallic reagents generally leads to limited functional group compatibility. Therefore, it has been highly desirable to develop mild and convenient methods to fulfil the arylation of aldehydes that bypass the use of organometallic intermediates.

In the past decades, the development of a reductive coupling strategy[5] that directly uses aryl halides instead of organometallic reagents has been considered an attractive approach for carbon–carbon bond formation events due to its mild conditions, economical steps, and good functional group tolerance.[6] Inspired by an early study on nickel-catalyzed, Zn-mediated reductive arylation of aryl aldehydes from the Cheng group,[7] Weix and co-workers recently demonstrated significant progress in the reductive coupling of diverse aryl bromides with aromatic and aliphatic aldehydes, allowing for the synthesis of hindered benzyl alcohols with the Ni/Zn system.[8] Moreover, the Montgomery group further extended the reaction to unactivated alkyl halides and aliphatic aldehydes utilizing Mn as a stoichiometric reductant and silyl chloride as a transmetallic reagent.[9] Very recently, the intermolecular asymmetric reductive coupling of aryl halides with aldehydes to provide optically active secondary alcohols has also been demonstrated by Ohmiya,[10] Li,[11] Shi,[12] and Xiao[13] groups. In spite of the impressive advancements, however, in most cases, a (super)stoichiometric amount of metal reductants such as Mn or Zn dust was needed to facilitate the reaction (Scheme 1a), which hinders the practical application in large-scale synthesis due to issues of safety and the disposal of a large amount of metal waste. Thus, exploring stable, user-friendly, and inexpensive homogeneous organic reductants to replace metallic reductants is highly desirable. In this regard, the Krische group demonstrated the first example of reductive carbonyl arylation that exploited a mild organic reductant, sodium formate, *via* rhodium-catalyzed transfer hydrogenation under forcing conditions (130 °C).[14] Later on, Newman and co-workers described a reductive coupling of aryl iodides and aldehydes enabled by a Ni catalyst and a unique 1,5-diaza-3,7-diphosphacyclooctane ligand, in which secondary benzyl alcohol was used as a mild stoichiometric reducing agent.[15] Xiao and Lu and co-workers reported a photoredox-assisted cobalt-catalyzed reductive arylation of aldehydes with aryl iodides with a Hantzsch ester (HE) as a reductant

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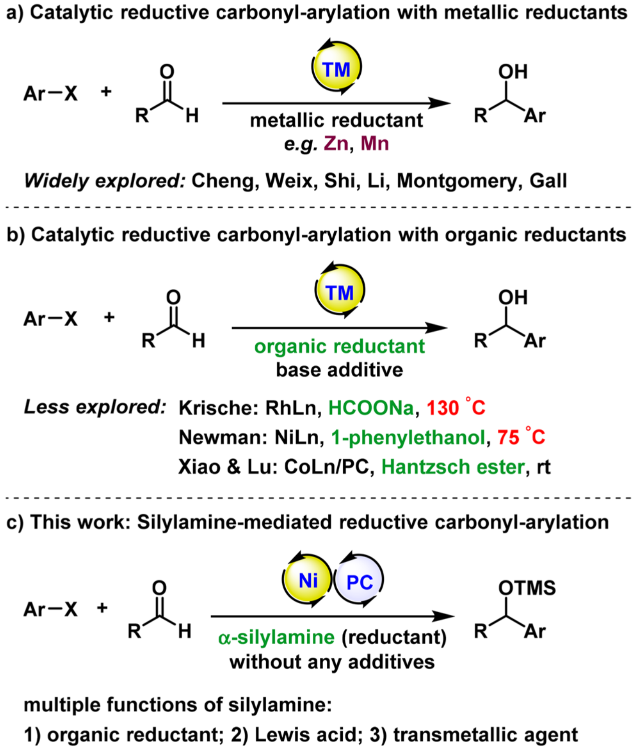


Scheme 1 Catalytic reductive coupling of aryl halides and aldehydes.

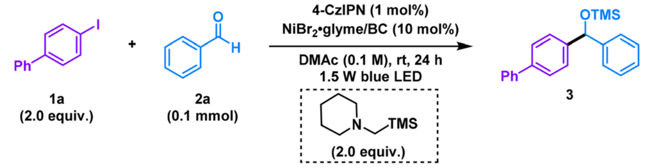
(Scheme 1b).[13] Recently, our lab has demonstrated a conjugate reductive coupling of aryl halides, aldehydes, and alkenes *via* a nickel/photoredox dual catalysis.[16] In this process, α-silylamine was identified as a uniquely efficient organic reductant. Based on our ongoing interest in photoredox-assisted reductive cross-coupling,[16,17] we herein reported a photoredox/nickel-catalyzed reductive coupling of aryl halides with aldehydes to prepare silyl-protected secondary alcohols using α-silylamines as very mild, stable, and readily available reductants (ease to prepare: a one-step S_N2 reaction from secondary amines and $TMSCH_2X$) (Scheme 1c). This organic reductant-mediated carbonyl-reductive cross-coupling features extremely mild conditions with no need for any additives[9,11–13] (*e.g.* silyl chlorides, Lewis acid activators, bases, or inorganic salts). We proposed that α-silylamine has the following functions: (1) used as an organic reductant to restore the nickel catalyst, (2) *in situ* releases a silylium ion species as a Lewis acid to activate aldehydes, and (3) serves as a transmetallic reagent to cleave the Ni–O bond of an alkoxynickel intermediate. This work expands the emerging paradigm of α-silylamine as an alternative organic reductant to metallic reductants in carbonyl addition.

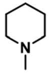
Results and discussion

Optimization studies

We selected 4-iodo-1,1′-biphenyl (**1a**) and benzaldehyde (**2a**) as model substrates to test the feasibility of this nickel/photoredox dual-catalyzed reductive coupling of aryl halides and aldehydes. After extensive condition optimization (see the ESI† for details), TMS-protected diaryl carbinol **3** could be afforded in 89% GC yield when the reaction was performed in DMAc with 1 mol% of 4-CzIPN, 10 mol% of $NiBr_2$·glyme, and 10 mol% BC ligand using 2.0 equiv. of 1-((trimethylsilyl)methyl)piperidine as an organic reductant (Table 1, entry 1). $Ni(cod)_2$ could also catalyze the reaction and give a good yield (entry 2). Replacing DMAc with other solvents such as NMP or DMF resulted in a decreased yield (entries 3 and 4). Of particular note, α-silyl-substituted tertiary amines turned out to be highly efficient organic reductants for facilitating this reductive carbonyl-aryl coupling. As illustrated, native tertiary amines including Et_3N, DIPEA, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), as well as other commonly used organic reductants such as HE and $B_2(pin)_2$, were invalid reducing agents in this system, and no desired product could be detected in all cases (entries 5–9). The unique effect of α-silylamine was further demonstrated in comparison with the structurally analogous 1-methylpiperidine with or without extra TMSCl, which failed to deliver any desired product (entry 10). Other silyl groups such as $SiMe_2Ph$ were examined but with a lower reactivity (46% yield). Controlled experiments showed that the nickel catalyst, photocatalyst, and visible light irradiation were indispensable (entry 11). Interestingly, without the ligand, the reaction could still proceed but with a low yield, indicating that the ligand largely enhanced the catalytic reactivity (entry 12).

Table 1 Optimization of the reaction conditions[a]



Entry	Deviation from the standard conditions	Yield of **3** [b] (%)
1	None	89 (93[c])
2	$Ni(cod)_2$	70
3	NMP instead of DMAc	78
4	DMF instead of DMAc	41
5	Et_3N was used as a reductant	0
6	DIPEA was used as a reductant	0
7	TMEDA was used as a reductant	0
8	HE was used as a reductant	0
9	$B_2(pin)_2$ was used as a reductant	0
10		0
11	No Ni, or no PC, or no light	0
12	No ligand	32

[a] All reactions were conducted with **1a** (0.20 mmol, 2.0 equiv.), **2a** (0.10 mmol, 1.0 equiv.), and a reductant (0.2 mmol, 2.0 equiv.). [b] Yields were determined by GC with *n*-tridecane as an internal standard. BC = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline. [c] Isolated yield.

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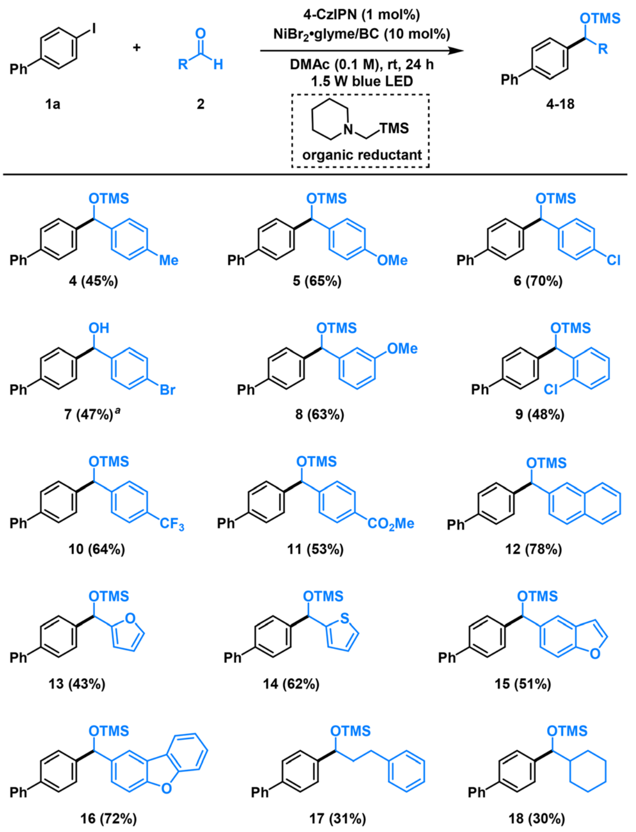
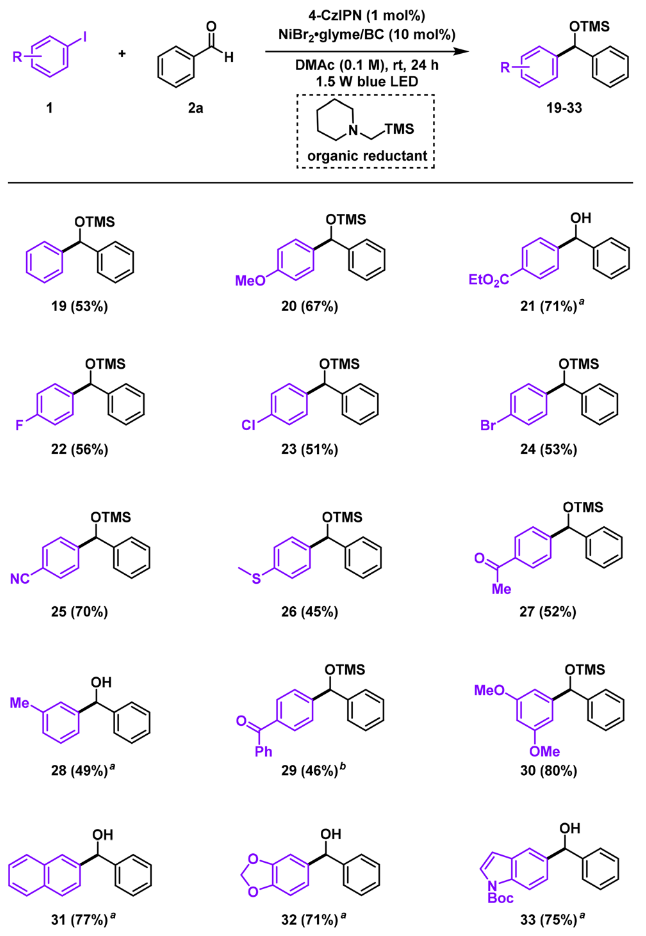
With the optimized conditions in hand, the substrate scope with respect to aldehydes for the nickel/photoredox dual-catalyzed reductive arylation of aldehydes was first investigated (Scheme 2). Aromatic aldehydes containing various substituents irrespective of having electron-donating and -withdrawing properties at *para*, *meta*, and *ortho* positions were coupled smoothly to afford the corresponding silyl-protected secondary benzyl alcohols in moderate to good yields (**4**, **5**, **6**, **7**, **8**, **9**, **10**, and **11**). Naphthalen-2-yl aldehyde reacted with a high efficiency (**12**). In addition, a variety of heteroaryl aldehydes such as furan-2-carbaldehyde, thiophene-2-carbaldehyde, benzofuran-5-carbaldehyde, and dibenzo[*b*,*d*]furan-2-carbaldehyde were successfully incorporated (**13**, **14**, **15**, and **16**). Of note, aliphatic aldehydes participated as well but showed largely decreased efficiency and reacted with 4-iodo-1,1′-biphenyl to afford the desired products in lower yields (**17** and **18**).



Scheme 2 Substrate scope of aldehydes. Reactions were conducted on a 0.2 mmol scale with **1a** (0.4 mmol, 2.0 equiv.), **2** (0.2 mmol), and α-silylamine (0.4 mmol, 2.0 equiv.). Yields are isolated yields after chromatography on silica gel. [a] The corresponding secondary alcohol was obtained after chromatography on silica gel and the isolated yield of the secondary alcohol was given. BC = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline.



Scheme 3 Substrate scope of aryl iodides. Reactions were conducted on a 0.2 mmol scale with **1** (0.4 mmol, 2.0 equiv.), **2a** (0.2 mmol), and α-silylamine (0.4 mmol, 2.0 equiv.). Yields are isolated yields after chromatography on silica gel. [a] The corresponding secondary alcohol was obtained after chromatography on silica gel and the isolated yield of the secondary alcohol was given. BC = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline. [b] Aryl bromide was used.

We next turned our attention to the scope generality of aryl iodides (Scheme 3). Aryl iodides with various *para*-substituted functional groups including OMe (**20**), ester (**21**), F (**22**), Cl (**23**), Br (**24**), CN (**25**), SMe (**26**), ketone (**27**) and aryl bromide (**29**) were well tolerated, delivering the corresponding products in moderate to good yields. *meta*-Substituted and 3,5-disubstituted benzyl iodides worked as well (**28** and **30**). Heteroaryl iodides including 1,3-benzodioxole and *N*-Boc-protected iodol yielded the desired secondary alcohols in good yields *via* the reductive coupling strategy (**32** and **33**). It should be noted that in some cases, desilylation was observed to afford free alcohols directly during the purification stage.

In order to gain insight into the reaction mechanism, the Stern–Volmer quenching experiments were performed. The results revealed that the oxidative quenching of the excited state of the photocatalyst by α-silylamine is much more efficient than other components (Scheme 4a). The coupling reaction was completely suppressed when adding the radical scavenger [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] (TEMPO), and the 1,1′-biphenyl radical-trapped adduct was detected by HRMS (Scheme 4b). This result suggests the formation of an aryl radical in the catalytic cycle. Besides, silyl-protected 1,2-diols generated from the pinacol homocoupling of an

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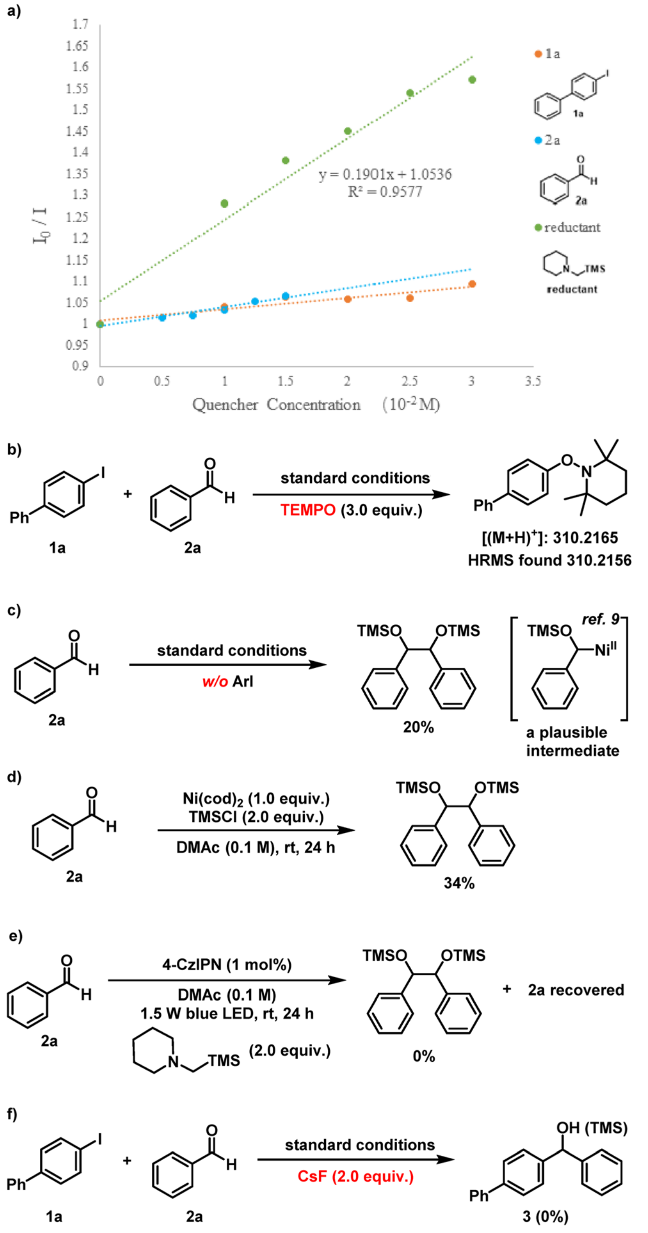
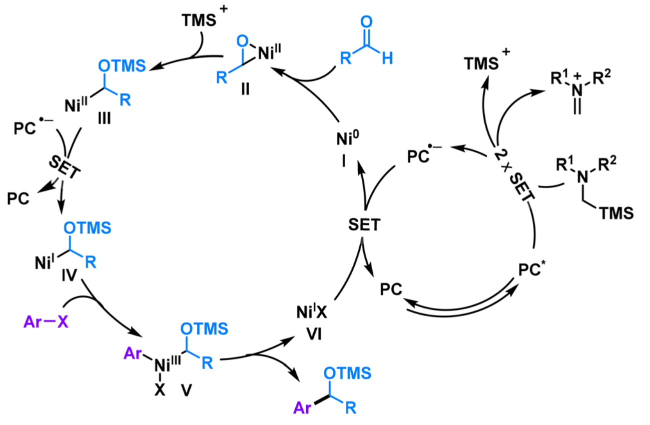


Scheme 4 Mechanistic studies. (a) The Stern-Volmer quenching experiment. (b) Radical-trapping experiment. (c) Control experiment without aryl iodide. (d) Control experiment with adding Ni(cod)$_2$ and TMSCl under dark condition. (e) Control experiment without nickel catalyst and aryl iodide. (f) Control experiment with adding CsF.

α-silyloxy benzyl radical were obtained under standard conditions without aryl iodide, indicating a plausible intermediate α-silyloxy(alkyl)nickel generated in the catalytic system[9,18] (Scheme 4c). Furthermore, performing the reaction of aldehyde **2a** with a stoichiometric amount of Ni(cod)$_2$ and TMSCl under dark conditions can afford the same product (Scheme 4d). Taking both results together provides evidence for the formation of an α-silyloxy(alkyl)nickel species. Upon omitting both the nickel catalyst and aryl iodide, only aldehyde **2a** cannot undergo single-electron reduction in the presence of a photocatalyst and α-silylamine, thus excluding the possibility of photocatalytic single-electron reduction of aldehydes to afford ketyl radicals (Scheme 4e). Adding 2.0 equivalents of CsF as a TMS trapping reagent into the reaction system resulted in no reaction (Scheme 4f), indicating the indispensable role of the silyl group in this photoredox-assisted reductive carbonyl-aryl coupling.

Based on the above experimental results and literature reports,[7–9,11–13,15] a proposed mechanism was depicted (Scheme 5). Double single-electron-transfer (SET) between PC* ($E_{1/2}$PC*/PC$^{•-}$ = +1.35 V *vs.* SCE)[19] and α-silylamine ($E^{\text{ox}}_{1/2}$ = +0.71 V *vs.* SCE)[20] generates PC$^{•-}$ and iminium ion species by losing a silylium ion. PC$^{•-}$ possessing a strong reducing ability ($E_{1/2}$PC/PC$^{•-}$ = −1.21 V *vs.* SCE)[19] can reduce Ni$^{\text{II}}$ to Ni^{0} [$E_{1/2}$(Ni$^{\text{II}}$/Ni^{0}) = −1.2 V *vs.* SCE].[21] Oxidative addition of Ni^{0} to the C═O of an aldehyde *via* η^2 coordination affords an oxa-nickelacycle intermediate,[22] which undergoes transmetallation with the silylium ion species to generate an α-silyloxy(alkyl) nickel(II) intermediate. Then, a single-electron reduction by the reduced state of the photocatalyst forms a Ni$^{\text{I}}$ intermediate, which reacts with aryl halides *via* halogen atom transfer (XAT) to afford Ni$^{\text{II}}$ and an aryl radical. Radical rebounding forms Ni$^{\text{III}}$. The resulting Ni$^{\text{III}}$ intermediate can then undergo reductive elimination to furnish the coupled product and Ni$^{\text{I}}$. The final SET between Ni$^{\text{I}}$ [$E_{1/2}$(Ni$^{\text{I}}$/Ni^{0}) = −1.17 V *vs.* SCE][23] and PC$^{•-}$ ($E_{1/2}$PC/PC$^{•-}$ = −1.21 V *vs.* SCE)[19] concurrently restores both the nickel catalyst and the photocatalyst. According to the results of the Stern–Volmer quenching study and control experiments shown in Scheme 4e, single-electron reduction of aldehydes by the photocatalyst to afford free ketyl radicals as a possible intermediate in the catalytic cycle can be excluded.[24] Moreover, the observation of the pinacol homocoupling product suggests that an alternative reaction pathway proposed in the literature involving a sequential oxidative addition of aryl halides and 1,2-migratory insertion of aryl-nickel into the aldehyde is rather unlikely, but the Ni^{0}/Ni$^{\text{II}}$/Ni^{0} catalytic cycle cannot be firmly excluded.



Scheme 5 Proposed mechanism.

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Conclusions

In conclusion, we developed a photoredox-assisted nickel-catalyzed reductive cross-coupling of aryl halides and aldehydes to afford silyl-protected secondary alcohols. Tertiary amines modified with an α-silyl group were identified as solely efficient organic reductants to facilitate the carbonyl-aryl reductive coupling reaction. Mechanistic studies suggest that the coupling reaction is preferentially initiated by an oxidative addition of Ni^0 to an aldehyde to afford an α-silyloxy(alkyl) nickel intermediate and a putative $Ni^0/Ni^{II}/Ni^I/Ni^{III}/Ni^I$ catalytic cycle is proposed. This dual catalytic platform features mild conditions, a good substrate scope, and complements previously dominated reductive carbonyl-coupling systems with a stoichiometric amount of Zn or Mn as a reductant.

Author contributions

J. L., Y. C., and H. Z. performed the experiments and prepared the ESI.† W. Y. directed the project. All authors discussed the results and prepared the manuscript.

Conflicts of interest

The authors declare that there are no conflicts to declare.

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