Advanced Synthesis & Catalysis

DOI: 10.1002/adsc.201400970

Nickel-Catalyzed Reductive Benzylation of Aldehydes with Benzyl Halides and Pseudohalides

Farhad Panahi,[a] Marzieh Bahmani,[a] and Nasser Iranpoor[a,*]

[a] Department of Chemistry, College of Sciences, Shiraz University, Shiraz, 71454, Iran
E-mail: iranpoor@chem.susc.ac.ir

Received: October 9, 2014; Revised: February 5, 2015; Published online: ■■ ▮▮, 0000

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201400970.

Abstract: The reductive benzylation of aromatic and aliphatic aldehydes with benzylic halides is reported using a nickel/zinc catalyst system. In addition to benzylic halides, the first report on the addition of benzylic triflates, acetates, tosylates and tritylates to aldehydes is also presented. By this new method a range of alcohols was synthesized efficiently from aldehydes and benzylic substrates at room temperature in moderate to high yields. The mild reaction conditions and good functional group tolerance make this nickel-catalyzed process synthetically useful for the synthesis of diverse benzylic alcohols.

Keywords: alcohols; aldehydes; benzylation; nickel-catalyzed reaction; reductive coupling

Introduction

The addition of organometallic reagents to aldehydes toward the synthesis of alcohols has become a useful and efficient strategy in organic chemistry.[1] The most important organometallic reagents that have been used so far are lithium,[2] magnesium,[3] aluminum,[4] zinc,[5] tin,[6] silicium,[7] gallium,[8] indium[9] and boranes.[10] Also, in recent years some other methods have been developed based on aryl C–H addition to aldehydes to give the corresponding alcohols (Figure 1).[11]

Despite considerable advances in the addition of organometallic reagents to aldehydes, most of these methods suffer from some disadvantages including sensitivity to air and moisture, toxicity of the organometallic reagent, less functional group compatibility, limited commercial availability, and the use of harsh reaction conditions.[2–10] In view of the importance of addition reactions to aldehydes for the synthesis of alcohols, a great challenge still remains regarding the use of new catalysts, reagents and methods. Among all of the used reagents, organoboron species have significant practical advantages over other organometallics.[12] Nevertheless, the main practical limitations of organoborons for addition to aldehydes are substrate limitation, and use of expensive reagents and additives for their preparation.[10] Another problem associated with some of the aforementioned organometallic reagents is their instability which cause undesired side reactions. To avoid these limitations, one of the best applicable methods is the direct addition of the *in situ* generated organometallic reagents to aldehydes.[13]

On the other hand, transition metal-catalyzed reductive coupling reactions are among the most proficient approaches for carbon-carbon bond formation reactions in modern organic chemistry.[14] The reductive cross-coupling reactions permit us to connect two electrophilic reagents without the formation of a stoichiometric organometallic species.[15] Ni-catalyzed re-

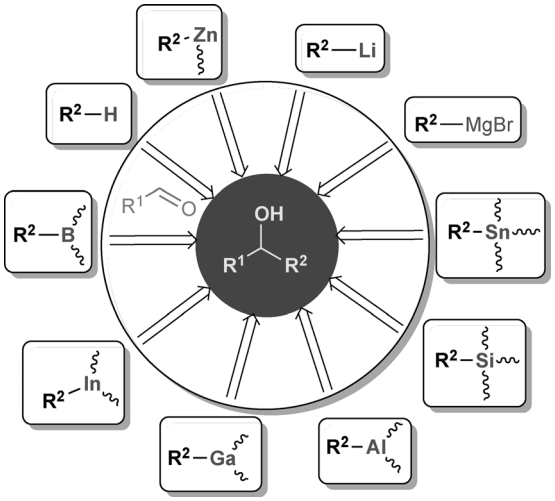
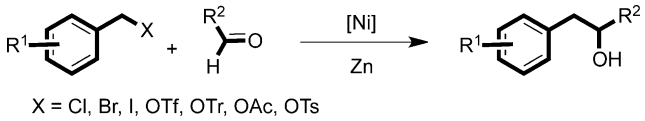


Figure 1. Addition of the most widely used organometallic reagents to aldehydes.



Scheme 1. Nickel-catalyzed addition of benzylic reagents to aldehydes.

ductive coupling reactions have thus opened up a new direction for the direct coupling of aryl/alkyl halides and carbonyl compounds.[17] This strategy has considerable attractive features, both from an experimental simplicity and also step-economical points of view. In reductive cross-coupling processes the differentiation between electrophilic natures of the two used electrophiles is an important factor in order to prevent the homo-coupling of either component.[18] Since the electrophilic activity differences of halides and carbonyl compounds are remarkable, this strategy is highly efficient for the addition of halides to aldehydes.[19] Previously, Majumdar and Cheng reported an efficient method for the arylation of aromatic aldehydes using an Ni(II)/Zn catalyst system.[13b] Recently, Tan et al. reported a nickel-catalyzed asymmetric reductive allylation of aldehydes with allylic carbonates and the procedure was efficient for 2-arylallylic carbonates in order to generate the corresponding homoallylic compounds in good to excellent yields and *ee*s.[19] However, as far as we know, there is no general report in the literature on the nickel-catalyzed reductive benzylation of aldehydes with benzylic substrates.

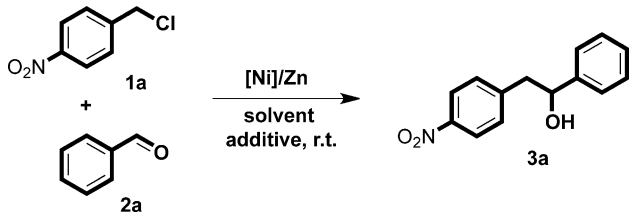
In the current study we would like to introduce a nickel-catalyzed addition of benzylic halides as well as protected benzylic alcohols to aldehydes at room temperature without the use of pre-prepared organometallic reagents (Scheme 1).

Results and Discussion

At first, we focused on the addition of 4-nitrobenzyl chloride (**1a**) to benzaldehyde (**2a**) as a model reaction and screened different reaction conditions in order to optimize the reaction yield. The obtained results are depicted in Table 1.

Under the first set of conditions tested ($NiCl_2$, DMF, $MgCl_2$ and Zn), the desired product was obtained in 48% yield (Table 1, entry 1). In the absence of Ni catalyst, no product was observed, illustrating the important role of the Ni catalyst for this process (Table 1, entry 2). Regarding the important role of ligands in metal-catalyzed reactions,[20] we changed the type of ligand in the Ni catalyst and the obtained results showed that under similar conditions, $NiCl_2$(dppf) was superior to the other ones (Table 1, entries 3–7). The role of metal ions in this reaction is important. When $MgCl_2$ was not added to the reaction mixture, the yield decreased significantly, demonstrating that the presence of this salt is necessary for the reaction to progress (Table 1, entry 8).[21] When other metal halides such as $ZnCl_2$, LiCl, and $MgBr_2$ were employed as the additive instead of $MgCl_2$, a sharp decrease in the reaction yield was observed (Table 1, entries 9–11). In the absence of reducing agent the reaction did not proceed, demonstrating that the presence of Zn is also essential (Table 1, entry 12). Also, on change of Zn with Mn no improvement in the reaction yield was observed, which shows that Zn is more efficient than Mn for this process (Table 1, entry 13).[22] Attempts to improve the yield by changing the solvent to NMP, acetonitrile and toluene were found to be fruitless (Table 1, entries 14–16). Also, efforts to increase the yield by conducting the reaction at higher temperatures resulted in a decrease in the yield of the reaction (Table 1,

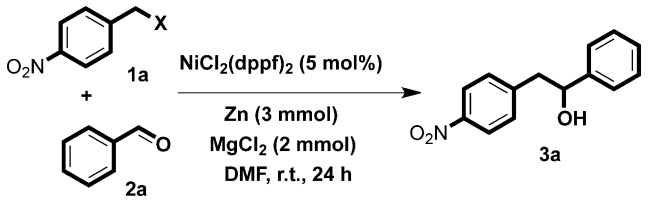
Table 1. Optimization of the reaction conditions.[a]



Entry	[Ni]	Solvent	Additive	Yield [%][b]
1	$NiCl_2 \cdot 5H_2O$	DMF	$MgCl_2$	48
2	–	DMF	$MgCl_2$	0
3	$NiCl_2(PPh_3)_2$	DMF	$MgCl_2$	60
4	$NiCl_2(PCy_3)_2$	DMF	$MgCl_2$	70
5	$NiCl_2$(dppe)	DMF	$MgCl_2$	71
6	$NiCl_2$(dppp)	DMF	$MgCl_2$	75
7	$NiCl_2$(dppf)	DMF	$MgCl_2$	80
8	$NiCl_2$(dppf)	DMF	–	30
9	$NiCl_2$(dppf)	DMF	$ZnCl_2$	55
10	$NiCl_2$(dppf)	DMF	LiCl	38
11	$NiCl_2$(dppf)	DMF	$MgBr_2$	73
12	$NiCl_2$(dppf)	DMF	$MgCl_2$	0[c]
13	$NiCl_2$(dppf)	DMF	$MgCl_2$	70[d]
14	$NiCl_2$(dppf)	NMP	$MgCl_2$	76
15	$NiCl_2$(dppf)	CH_3CN	$MgCl_2$	35
16	$NiCl_2$(dppf)	toluene	$MgCl_2$	26
17	$NiCl_2$(dppf)	DMF	$MgCl_2$	77[e]
18	$NiCl_2$(dppf)	DMF	$MgCl_2$	83[f]
19	$NiCl_2$(dppf)	DMF	$MgCl_2$	64 [g]

[a] *Reaction conditions:* 4-nitrobenzyl chloride (1 mmol), benzaldehyde (1 mmol), [Ni] (5 mol%), Zn (3 mmol), $MgCl_2$ (2 mmol), DMF (5 mL) at room temperature for 24 h.
[b] Isolated yield.
[c] Zn was not used.
[d] Mn was used instead of Zn.
[e] Reaction was performed at 50 °C.
[f] 7.5 mol% of the catalyst was used.
[g] 2.5 mol % of the catalyst was used.

Table 2. Direct Ni-catalyzed addition of benzylic substrates to benzaldehyde.[a]



Entry	X	Time [h]	Yield [%][b]
1	Cl	24	80
2	Br	20	83
3	I	12	85
4	OH	48	0
5	OTf	24	87
6	OTs	24	78
7	OTr	24	62
8	OAc	24	82

[a] *Reaction conditions:* 4-nitrobenzylic substrate (1 mmol), benzaldehyde (1 mmol), $NiCl_2$(dppf) (5 mol%), Zn (3 mmol), $MgCl_2$ (2 mmol), DMF (5 mL) at room temperature for 24 h.

[b] Isolated yield.

entry 17). Increasing the amount of the catalyst to 7.5 mol% did not increase the obtained yield of **3a** (Table 1, entry 18). As a result of reducing the amount of catalyst, a decrease in the yield of product was observed (Table 1, entry 19). In the light of these results, we established that the reaction conditions shown in entry 7 (Table 1) are the optimal to offer the highest yield of the product in our designed protocol.

Since there is no report in the literature on the addition of protected benzylic alcohols to aldehydes, we decided to explore the possibility of using other benzylic sustrates such as benzylic triflates, acetates, tosylates and tritylates instead of benzylic halides in this reductive benzylation of aldehydes (Table 2).

As shown in Table 2, in addition to benzylic halides, a range of benzylic substrates including triflate, acetate tosylate, and tritylate were used successfully in this protocol. It is known that alcohols are not suitable substrates to be used for the reductive addition to aldehydes, however, our finding makes it possible to use protected benzylic alcohols for this transformation. The order of yields for benzylic substrates was found to be OTf > I > Br > OAc > Cl > OTs > OTr in the model reaction.

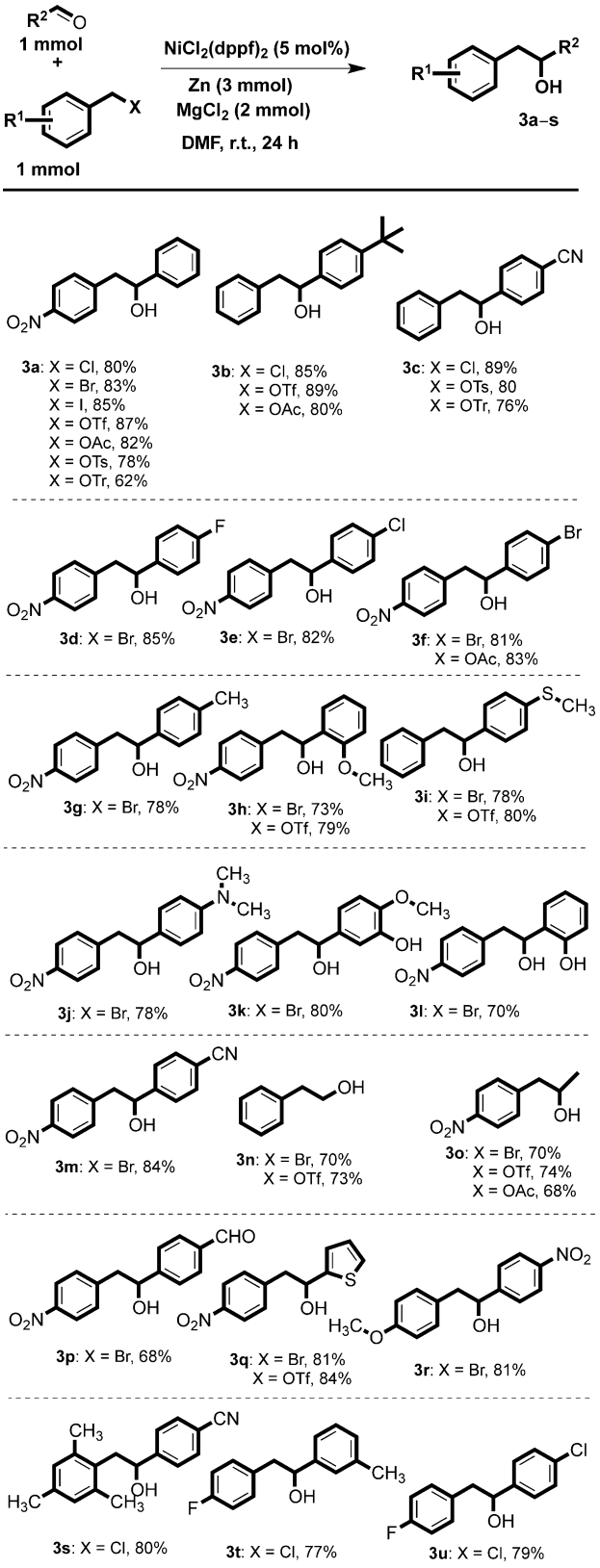
From this point of view our method is highlighted because it permits us to use diverse benzylic substrates for the benzylation of aldehydes. This is despite the fact that in reductive benzylation methods, only benzyl halides have so far been used as benzylating agent.[23]

With the optimal conditions in hand, the reaction of various aldehydes with different benzylic substrates was examined to explore the scope of the reaction (Scheme 2).

Under the optimized conditions, the reactivity of different benzylic substrates was investigated. Simple benzyl substrates were added to different aldehydes and good yields of the products were obtained. For example, with a *tert*-butyl group (**3b**) and a cyano group (**3c**), the reactions showed good reactivity. Then, 4-nitrobenzylchloride was used as an easy to handle substrate (some of the benzylic halides are quite volatile at room temperature) in order to synthesize a range of target compounds under our optimized conditions. Various electron-donating and electron-withdrawing groups on the aldehyde source were tested. Since it has been reported that the presence of halogen atoms on the aldehyde substrate is a limitation in many of the previous methods,[2,3] initially, 4-fluoro-, 4-chloro- and 4-bromobenzaldehydes were examined which offered good yields of the corresponding products (**3d–f**). It was found that the donating groups such as Me, OMe, NMe_2 and SMe also give a remarkable yield of their resultant product (**3g–j**). Significantly, the unprotected hydroxy group was also compatible under the optimized conditions (**3k** and **3l**). It is known that the presence of free a hydroxy group is a limitation in organometallic reagents especially with Mg and Li.

This transformation showed good compatibility with electron-withdrawing groups, such as CN (**3m**). For substrates containing nitro, formyl and cyano functionalities no reduced products were observed. It is worthy to note that the benzylic substrates could react with an aliphatic aldehyde, affording the corresponding alcohols in good yields (**3n** and **3o**). For example, reactions of benzyl bromide and triflate with formalin resulted in the production of compound **3n** in 70% and 73% yields, respectively. Also, good yields of the corresponding alcohols were produced on using acetaldehyde (**3o**).

When terephthalaldehyde was used for the mono-addition reaction, compound **3p** which has the potential chance for further functionalization was obtained in 68% yield. In this study a heterocyclic substrate (thiophene-2-carbaldehyde) was also examined and compound **3q** was obtained in 84% isolated yield. Compound **3r** was synthesized from the reaction of 4-methoxybenzyl bromide carrying an electron-donating group and 4-nitrobenzaldehyde in 81% isolated yield. In order to show the applicability of other benzylic substrates in this protocol, 2,4,6-trimethylbenzyl chloride was used and compound **3s** was obtained in 80% isolated yield. 4-Flourobenzyl chloride as a halogen-substituted benzyl halide was also used in the reaction with 3-methylbenzaldehyde and 4-chlorobenzaldehyde and compounds **3t** and **3u** were produced in 77 and 79% isolated yields, respectively.



Scheme 2. The products from the nickel-catalyzed addition of benzylic substrates to aldehydes. *Reaction conditions:* benzylic substrate (1 mmol), aldehyde (1 mmol), $NiCl_2(dppf)$ (5 mol%), Zn (3 mmol), $MgCl_2$ (2 mmol), DMF (5 mL) at room temperature for 24 h. All yields are of isolated products.

In order to show further the functional group compatibility of this method, two aldehydes (**2v** and **2w**) were synthesized and used in the reaction with 4-nitrobenzyl chloride. Under the optimized conditions compounds **3v** and **3w** were obtained in 65 and 71% yields, respectively (Scheme 3). This experiment revealed that the amide and ester groups are inert in the presence of aldehyde group in our strategy.

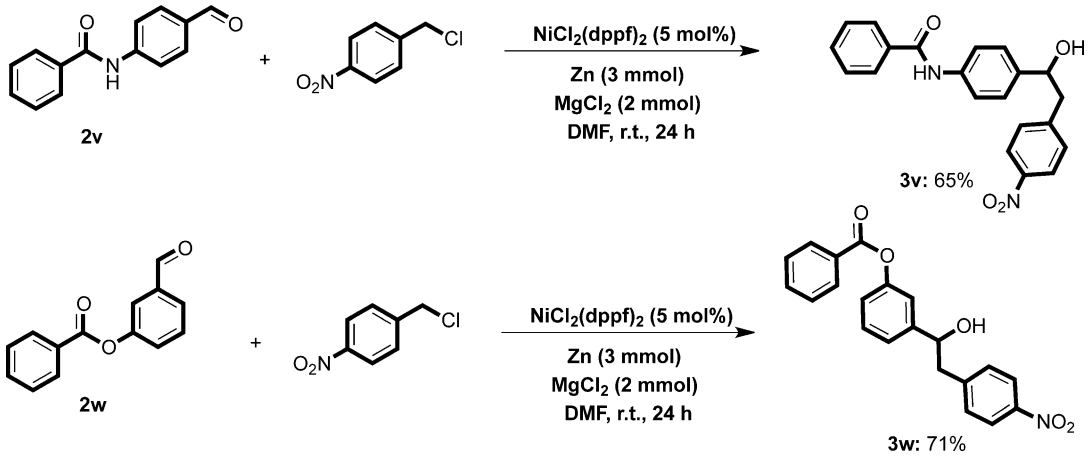
Acetophenone and benzophenone failed to react under these conditions demonstrating that ketones are also inactive under our optimized conditions. To further explore this chemoselectivity, we ran a competition experiment involving both ketones and aldehydes. As a simple test, one equiv. of 4-nitrobenzyl chloride was reacted with one equiv. of each of benzaldehyde and acetophenone and only compound **3a** was produced. This result also confirms that ketones are inactive under the optimized conditions (Scheme 4).

The protocol could also be extended to secondary or tertiary benzylic substrates to afford the desired products. With the optimized conditions, some examples with secondary or tertiary benzylic substrates were investigated and the corresponding products were obtained in moderate yields. Trityl chloride was reacted with 4-formylbenzonitrile and **3x** was produced in 65% isolated yield. Additions of benzhydryl triflate and acetate to 4-nitrobenzaldehyde resulted in the production of **3y** in 64 and 60% isolated yields, respectively. Compound **3z** also was synthesized in 67% yield. Also compound **3aa** was synthesized by using the reaction of (1-bromoethyl)benzene or 1-phenylethyl tosylate as a secondary benzylic substrates with 4-nitrobenzaldehyde (Scheme 5). Thus, this strategy is applicable for secondary or tertiary benzylic substrates.

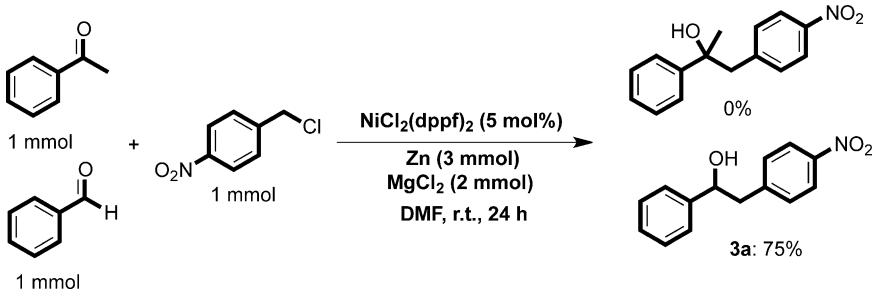
It was interesting to use 4-nitrotoluene instead of 4-nitrobenzyl chloride in this study. When this experiment was performed under our optimized conditions, no product was obtained and 4-nitrotoluene remained intact even in the presence of different bases. However, when 4-nitrotoluene was reacted with benzaldehyde in the presence of K_2CO_3 as base in a mixture of water and PEG-200 as solvent at 80 °C, 4-nitrostilbene was obtained. This finding is in agreement with the work of Ruby (Scheme 6).[24]

This study clarifies that our simple procedure is effective for the synthesis of the desired alcohols without the formation of eliminated products *via* a dehydration reaction.

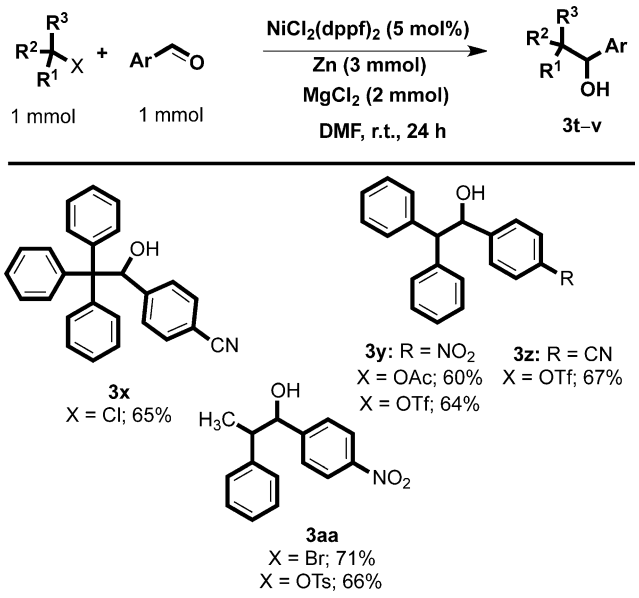
Some experiments were conducted to obtain deeper insights into the reaction mechanism. Interestingly, the reaction could also be performed in the presence of $Ni(PPh_3)_2(CO)_2$ as a Ni(0) catalyst system (Scheme 7). This experiment reveals that this is a Ni(0)-catalyzed process, since in the presence of Ni(0) this reaction occurs, while no progress was ob-



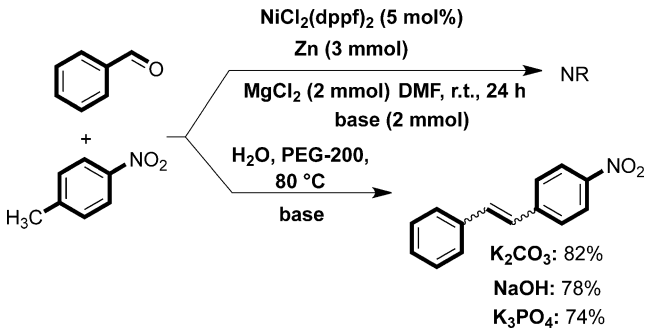
Scheme 3. Nickel-catalyzed addition of benzylic reagents to aldehydes in the presence of amide and ester groups.



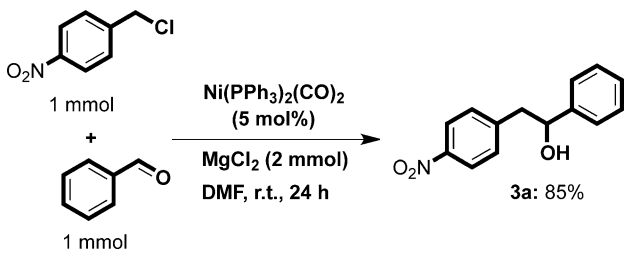
Scheme 4. Competition experiment between ketones and aldehydes.



Scheme 5. The products of the nickel-catalyzed addition of secondary or tertiary benzylic substrates to aldehydes. All yields are of isolated products.



Scheme 6. Reaction of 4-nitrotoluene and benzalaldehyde under different conditions.



Scheme 7. Ni(0)-catalyzed addition of 4-nitrobenzyl chloride to benzaldehyde.

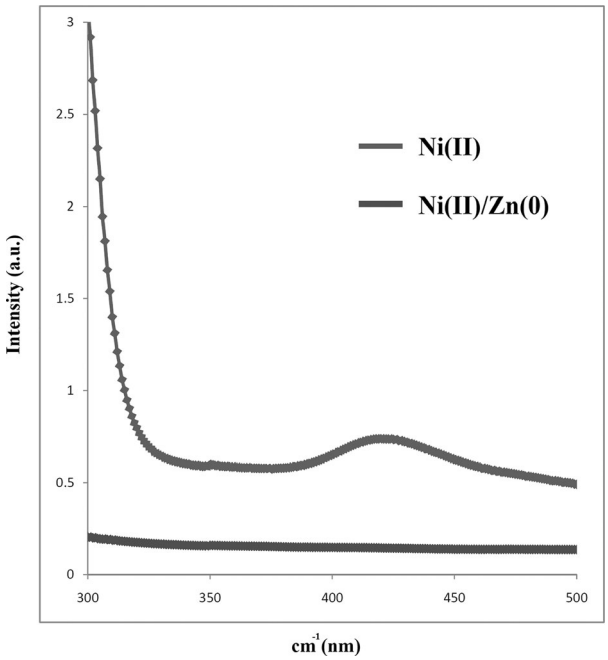
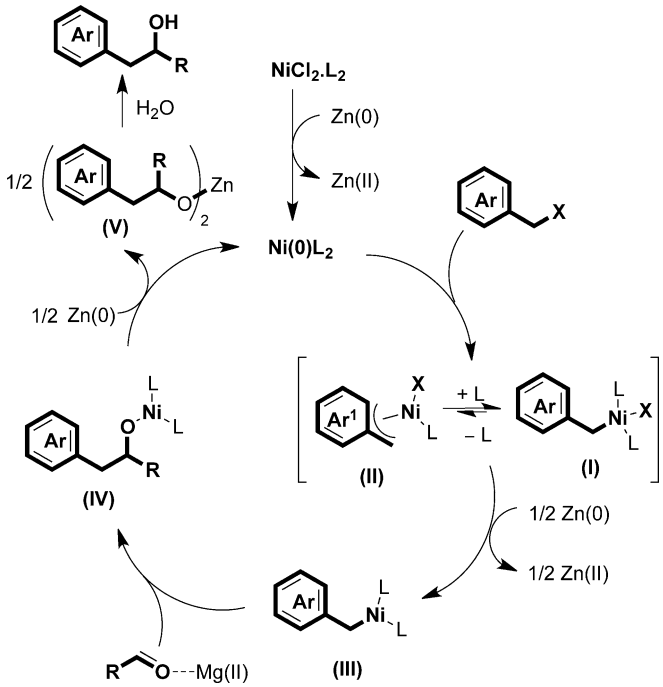


Figure 2. UV spectra of $NiCl_2$ and $NiCl_2$ in the presence of Zn(0).



Scheme 8. Proposed reaction mechanism.

served for the reaction in the presence of an Ni(II) catalyst (Table 1, entry 2).

It seems that the role of Zn in this process is the reduction of Ni(II). In order to find evidence in support of this reduction, the reduction of Ni(II) to Ni(0) with Zn was studied by UV spectroscopy under our optimized conditions (Figure 2). Disappearance of the band around 420 nm is indicative of the reduction of Ni(II) to Ni(0) under these conditions.

On the basis of the literature reports, and experiments done, a plausible reaction mechanism as outlined in Scheme 8 is proposed. First, reduction of $NiCl_2{\cdot}L_2$ with Zn affords $Ni(0){\cdot}L_2$.[25] Subsequently, oxidative addition of $Ni(0){\cdot}L_2$ to the alkyl halide readily occurs to afford the intermediate **I** as a η^1-bound nickel complex. The intermediate **I** can be in equilibrium with **II** (η^3-bound nickel complex).[26] The reduction of these intermediate (**I** and **II**) with Zn generates the intermediate **III** as a Ni(I) complex.[16a] Reaction of **III** with the activated C=O bond promoted by $MgCl_2$ takes place to give intermediate **IV**. It should be mentioned that Metzger et al. have also shown that the sluggish reactivity of organozinc reagents towards aldehydes, can be dramatically improved by the addition of $MgCl_2$.[27]

The ultimate action of **IV** with Zn would regenerate the active $Ni(0){\cdot}L_2$ species and gives zinc alkoxy complex **V**. The complex **V** then undergoes hydrolysis with water to yield the target product.[16,22]

Conclusions

In conclusion, we have illustrated the first examples of the 1,2-addition of aldehydes with benzylic substrates using a Ni(0) catalytic system. This strategy represents a constructive and practical synthetic approach for the assembly of a wide range of alcohols. Also a wide range of benzylic substrates (Cl, Br, I, OTf, OAc, OTs and OTr) was used for addition to aldehydes, demonstrating the wide scope of this method. The reaction provides a simple option to the other existing methodologies that need the preparation of sensitive organometallic reagents.

Experimental Section

General

Chemicals were purchased from Fluka and Aldrich chemical companies and used without further purification. The known products were characterized by comparison of their spectral and physical data with those reported in the literature. ^1H (250 MHz) and ^{13}C NMR (62.9 MHz) spectra were recorded on a Bruker Avance spectrometer in $CDCl_3$ solutions with tetramethylsilane (TMS) as the internal standard. FT-IR spectroscopy (Shimadzu FT-IR 8300 spectrophotometer) was employed for characterization of the products. Melting points were determined in open capillary tubes in a Barnstead electro-thermal 9100 BZ circulating oil melting point apparatus. The reaction monitoring was accomplished by TLC on silica gel PolyGram SILG/UV254 plates.

Column chromatography was carried out on columns of silica gel 60 (70–230 mesh).

General Procedure for Ni-Catalyzed Reductive Benzylation of Aldehydes

Into a canonical flask (50 mL), a mixture of aldehyde (1 mmol), benzyl halide (1 mmol), Zn (3 mmol), $MgCl_2$ (2 mmol) and $NiCl_2$(dppf) (5 mol%) was stirred in dry DMF (5 mL) for 24 h at room temperature. After completion of the reaction as confirmed by TLC, 50 mL of ethyl acetate and 50 mL of water were added to the reaction mixture. After separation of the organic layer from water, the aqueous phases were extracted with ethyl acetate (2×25 mL) again. The combined organic layers were then dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to yield the crude product. The crude product was purified by column chromatography (*n*-hexane/ethyl acetate) to obtain the desired purity.

2-(4-Nitrophenyl)-1-phenylethanol (3a): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.24 (s, 1H), 3.07 s, 2H), 4.94 (m, 1H), 7.25–7.29 (m, 5H), 7.46 (d, J = 7.5 Hz, 2H), 8.13 (d, J = 7.5 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 45.3, 74.6, 123.8, 125.9, 128.3, 129.3, 129.9, 143.3, 146.6, 148.0; anal. calcd. for $C_{14}H_{13}NO_3$ (243.26): C 69.12, H 5.39, N 5.76; found: C 69.23, H 5.31, N 5.84.

1-[4-(*tert*-Butyl)phenyl]-2-phenylethanol (3b): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.59 (s, 9H), 3.19 (s, 2H), 3.29 (s, 1H), 5.10–5.16 (m, 1H), 7.44–7.63 (m, 9H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 31.8, 38.3, 46.2, 75.6, 125.7, 126.1, 126.3, 128.8, 129.9, 138.7, 141.1, 151.0; anal. calcd. for $C_{18}H_{22}O$ (254.37): C 84.99, H 8.72; found: C 84.81, H 8.65.

4-(1-Hydroxy-2-phenylethyl) benzonitrile (3c): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 2.27 (s, 1H), 2.89–3.07 (m, 2H), 4.92–4.97 (m, 1H), 7.22–7.35 (m, 3H), 7.43 (d, J = 7.5 Hz, 2H), 7.61 (d, J = 10.0 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 46.0, 74.5, 111.2, 118.9, 126.6, 127.0, 128.7, 129.5, 132.2, 136.9, 149.0; anal. calcd. for $C_{15}H_{13}NO$ (223.27): C 80.69, H 5.87, N 6.27; found: C 80.61, H 5.82, N 6.20.

1-(4-Fluorophenyl)-2-(4-nitrophenyl)ethanol (3d): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.17 (s, 1H), 2.96 (s, 2H), 4.78–4.83 (m, 1H), 7.04–7.22 (m, 4H), 7.55–8.38 (m, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 45.4, 74.4, 115.7, 123.7, 127.6, 129.3, 133.3, 145.9, 146.5, 165.7; anal. calcd. for $C_{14}H_{12}FNO_3$ (261.08): C 64.36, H 4.63, N 5.36; found: C 64.43, H 4.67, N 5.46.

1-(4-Chlorophenyl)-2-(4-nitrophenyl)ethanol (3e): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.56 (s, 1H), 3.08 (s, 2H), 5.03 (m, 1H), 7.25–7.30 (m, 4H), 7.45 (d, J = 10.0 Hz, 2H), 8.15 (d, J = 10.0 Hz, 2H); ^{13}CNMR (62.5 MHz, $CDCl_3$/TMS): δ = 36.9, 73.7, 123.8, 127.7, 128.1, 129.27, 136.1, 141.6, 146.9, 148.6; anal. calcd. for $C_{14}H_{12}ClNO_3$ (277.70): C 60.55, H 4.36, N 5.04; found: C 60.62, H 4.32, N 5.11.

1-(4-Bromophenyl)-2-(4-nitrophenyl)ethanol (3f): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.18 (s, 1H), 2.98–3.08 (m, 2H), 4.81–4.86 (m, 1H), 7.06–7.10 (m, 2H), 7.18–7.23 (m, 2H), 7.33–7.40 (m, 2H), 8.02–8.07 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 45.4, 74.2, 123.8, 127.5, 129.3, 130.5, 131.6, 137.5, 146.7, 148.1; anal. calcd. for $C_{14}H_{12}BrNO_3$ (322.15): C 52.20, H 3.75, N 4.35; found: C 52.14, H 3.70, N 4.28.

2-(4-Nitrophenyl)-1-(*para*-tolyl)ethanol (3g): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.29 (s, 1H), 2.41 (s, 3H), 3.02–3.05 (m, 2H), 4.75–4.80 (m, 1H), 7.47 (d, J = 7.5 Hz, 2H), 8.13 (d, J = 5.0 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 23.6, 45.4, 74.4, 123.7, 127.5, 129.2, 129.3, 137.2, 142.7, 146.5, 148.6; anal. calcd. for $C_{15}H_{15}NO_3$ (257.28): C 70.02, H 5.88, N 5.44; found: C 70.08, H 5.82, N 5.49.

1-(2-Methoxyphenyl)-2-(4-nitrophenyl)ethanol (3h): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.18 (s, 1H), 2.99 (s, 2H), 3.82 (s, 3H), 5.05–5.09 (m, 1H), 6.84 (q, J = 7.5 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.15–7.27 (m, 4H), 8.05 (d, J = 7.5 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 43.7, 55.3, 71.3, 110.5, 120.8, 123.8, 129.1, 129.3, 130.3, 132.5, 146.7, 148.1, 155.9; anal. calcd. for $C_{15}H_{15}NO_4$ (273.28): C 65.92, H 5.53, N 5.13; found: C 65.97, H 5.58, N 5.19.

1-[4-(Methylthio)phenyl]-2-phenylethanol (3i): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.97 (s, 1H), 2.40 (s, 3H), 2.89–2.92 (m, 2H), 4.74–4.79 (m, 1H), 7.08–7.22 (m, 9H). ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 38.5, 46.1, 75.6, 128.4, 128.6, 132.0, 132.1, 136.2, 137.0, 137.1; anal. calcd. for $C_{15}H_{16}OS$ (244.35): C 73.73, H 6.60; found: C 73.65, H, 6.54.

1-[4-(Dimethylamino)phenyl]-2-(4-nitrophenyl)ethanol (3j): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.18 (s, 1H), 2.88–3.01 (m, 8H), 4.74–4.79 (m, 2H), 6.61–6.68 (m, 2H), 7.04–7.11 (m, 2H), 7.65–7.72 (m, 2H), 8.04–8.08 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 40.1, 40.2, 72.9, 111.6, 120.9, 123.6, 129.1, 130.5, 145.6, 148.0, 150.2; anal. calcd. for $C_{16}H_{18}N_2O_3$ (286.33): C 67.12, H 6.34, N 9.78; found: C 67.20, H 6.39, N 9.86.

5-[1-Hydroxy-2-(4-nitrophenyl)ethyl]-2-methoxyphenol (3k): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.18 (s, 1H), 2.32 (s, 2H), 2.88 (s, 1H), 3.83 (s, 3H), 4.62–4.63 (m, 1H), 6.82 (d, J = 7.5 Hz, 1H), 7.18 (d, J = 5.0 Hz, 2H), 7.43 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 8.02 (d, J = 7.5 Hz, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 45.1, 55.8, 66.6, 110.6, 115.4, 121.5, 123.5, 129.8, 135.8, 146.2, 146.3, 150.0, 165.0; anal. calcd. for $C_{15}H_{15}NO_5$ (289.28): C 62.28, H 5.23, N 4.84; found: C 62.19, H 5.18, N 4.75.

2-[1-Hydroxy-2-(4-nitrophenyl)ethyl]phenol (3l): ^{1}HNMR (250 MHz, $CDCl_3$/TMS): δ = 1.25 (s, 1H), 2.91–3.07 (m, 3H), 5.56 (m, 1H), 6.78–6.88 (m, 2H), 7.19–7.30 (m, 4H), 8.14 (d, J = 10.0 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 45.3, 67.1, 115.4, 121.1, 123.8, 127.4, 128.8, 129.3, 129.4, 146.1, 148.0, 155.0; anal. calcd. for $C_{14}H_{13}NO_4$ (259.26): C 64.86, H 5.05, N 5.40; found: C 64.79, H 5.00, N 5.31.

4-[1-Hydroxy-2-(4-nitrophenyl)ethyl]benzonitrile (3m): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.58 (s, 1H), 3.06–3.11 (m, 2H), 5.00–5.04 (m, 1H), 7.25–7.29 (m, 4H), 7.63 (d, J = 7.5 Hz, 2H), 8.12 (d, J = 7.5 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 45.3, 74.1, 109.6, 118.6, 123.8, 126.5, 129.3, 130.4, 146.3, 147.6, 148.0; anal. calcd. for $C_{15}H_{12}N_2O_3$ (268.27): C 67.16, H 4.51, N 10.44; found: C 67.08, H 4.46, N 10.37.

2-Phenylethanol (3n): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 2.89–2.94 (m, 2H), 3.45 (s, 1H), 3.82–3.88 (m, 2H), 7.30–7.44 (m, 5H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 39.3, 63.5, 126.4, 128.6, 129.2, 138.9.

1-(4-Nitrophenyl)propan-2-ol (3o): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.18 (s, 1H), 1.40 (d, J = 7.5 Hz, 3H), 3.01 (s, 2H), 4.29–4.33 (m, 1H), 7.21 (d, J = 10.0 Hz, 2H), 8.06 (d, J = 7.5 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ =

23.5, 48.5, 61.5, 123.8, 129.3, 148.1, 148.7; anal. calcd. for $C_9H_{11}NO_3$ (181.19): C 59.66, H 6.12, N 7.73; found: C 59.58, H 6.07, N 7.65.

4-(1-Hydroxy-2-phenylethyl)benzaldehyde (3p): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 2.08 (s, 1H), 2.93–3.11 (m, 2H), 4.97–5.02 (m, 1H), 7.17–7.20 (m, 2H), 7.26–7.35 (m, 3H), 7.52 (d, J = 10.0 Hz, 2H), 7.86 (d, J = 7.5 Hz, 2H), 10.01 (s, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 46.1, 74.8, 126.4, 127.0, 128.7, 129.5, 129.9, 137.1, 137.5, 150.5, 192.0; anal. calcd. for $C_{15}H_{14}O_2$ (226.27); C 79.62, H 6.24; found: C 79.55, H 6.20.

2-(4-Nitrophenyl)-1-(thiophen-2-yl)ethanol (3q): ^{1}HNMR (250 MHz, $CDCl_3$/TMS): δ = 1.18 (s, 1H), 3.00 (s, 2H), 5.11–5.15 (m, 1H), 7.15–7.23 (m, 3H), 7.28 (d, J = 5.0 Hz, 1H), 7.46 (d, J = 10.0 Hz, 1H), 8.06 (d, J = 7.5 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 40.2, 69.1, 120.9, 123.6, 125.5, 127.2, 129.1, 143.3, 145.6, 148.0; anal. calcd. for $C_{12}H_{11}NO_3S$ (249.29): C 57.82, H 4.45, N 5.62; found: C 57.75, H 4.41, N 5.54.

2-(4-Methoxyphenyl)-1-(4-nitrophenyl)ethanol (3r): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.18 (s, 1H), 2.82 (s, 1H), 2.89 (s, 1H), 3.72 (s, 3H), 4.87 (s, 1H), 6.76–6.89 (m, 4H), 7.34 (d, J = 7.5 Hz, 2H), 7.99 (d, J = 10.0 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 47.3, 55.5, 75.6, 113.7, 123.5, 127.5, 128.5, 130.8, 147.3, 150.1, 159.2; anal. calcd. for $C_{15}H_{15}NO_4$ (273.28): C 65.92, H 5.53, N 5.13; found: C 65.83, H 5.44, N 5.01.

4-(1-Hydroxy-2-mesitylethyl)benzonitrile (3s): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.98 (s, 1H), 2.23–2.26 (m, 9H), 2.82 (s, 1H), 2.90 (s, 1H), 4.93 (s, 1H), 6.81 (s, 2H), 7.13 (d, J = 7.5 Hz, 2H), 7.48 (d, J = 7.5 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 20.9, 21.3, 40.9, 74.0, 108.6, 119.4, 125.5, 128.1, 130.1, 132.1, 139.0, 147.9, 159.8; anal. calcd. for $C_{18}H_{19}NO$ (265.35): C 81.47, H 7.22, N 5.28; found: C 81.40, H 7.14, N 5.20.

2-(4-Fluorophenyl)-1-(*meta*-tolyl)ethanol (3t): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 2.13–2.22 (m, 4H), 2.70–2.76 (m, 2H), 4.48 (s, 1H), 6.95–7.12 (m, 8H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 21.4, 36.6, 65.1, 115.4, 124.0, 124.3, 127.7, 128.2, 132.2, 133.6, 138.1, 141.0, 161.8; anal. calcd. for $C_{15}H_{15}FO$ (230.28): C 78.24, H 6.57; found: C 78.17, H 6.51.

1-(4-Chlorophenyl)-2-(4-fluorophenyl)ethanol (3u): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.94 (s, 1H), 2.75 (s, 1H), 2.83 (s, 1H), 4.52 (s, 1H), 6.88–6.98 (m, 2H), 7.15–7.24 (m, 6H). ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 36.6, 64.2, 115.4, 128.1, 128.5, 129.8, 133.1, 134.5, 139.5, 161.8; anal. calcd. for $C_{14}H_{12}ClFO$ (250.70): C 67.07, H 4.82; found: C 66.95, H 4.74.

***N*-(4-Formylphenyl)benzamide (2v):** ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 7.42–7.61 (m, 3H), 7.82–7.91 (m, 4H), 8.08 (d, J = 7.5 Hz, 2H), 8.61 (s, 1H), 9.90 (s, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 119.1, 127.3, 128.8, 131.1, 133.6, 134.3, 143.8, 166.3, 191.2; anal. calcd. for $C_{14}H_{11}NO_2$ (225.24): C 74.65, H 4.92, N 6.22; found: C 74.56, H 4.87, N 6.14.

***N*-{4-[1-Hydroxy-2-(4-nitrophenyl)ethyl]phenyl}benzamide (3v):** ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.60 (s, 1H), 2.81–3.09 (m, 2H), 4.70–4.88 (m, 1H), 7.42–7.60 (m, 5H), 7.77–7.86 (m, 4H), 7.94–8.07 (m, 4H), 8.34 (s, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 34.7, 73.3, 121.5, 121.8, 127.0, 129.6, 131.9, 133.9, 134.3, 136.1, 144.9, 162.7; anal. calcd. for $C_{21}H_{18}N_2O_4$ (362.38): C 69.60, H 5.01, N 7.73; found: C 69.51, H 4.92, N 7.66.

4-Formylphenyl benzoate (2w): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 7.53–7.56 (m, 3H), 7.64 (t, J = 7.5 Hz, 2H), 7.80 (t, J = 7.5 Hz, 1H), 7.98 (s, 1H), 8.04 (d, J = 7.5 Hz, 2H), 10.04 (s, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 122.5, 123.6, 127.4, 127.7, 128.0, 128.6, 128.7, 130.2, 133.7, 151.0, 171.1, 191.3: anal. calcd. for $C_{14}H_{10}O_3$ (226.23): C 74.33, H 4.46; found: C 74.27, H 4.39.

3-[1-Hydroxy-2-(4-nitrophenyl)ethyl]phenyl benzoate (3w): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.18 (s, 1H), 2.83–2.91 (m, 2H), 4.97–5.05 (m, 1H), 7.36–7.58 (m, 8H), 7.89 (s, 1H), 8.04 (d, J = 7.5 Hz, 2H), 8.13 (d, J = 7.5 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 45.2, 74.3, 118.0, 119.8, 122.5, 123.5, 128.7, 129.6, 130.2, 133.9, 141.7, 146.1, 151.0, 165.0; anal. calcd. for $C_{21}H_{17}NO_5$ (363.36): C 69.41, H 4.72, N 3.85; found: C 69.35, H 4.66, N 3.78.

4-(1-Hydroxy-2,2,2-triphenylethyl)benzonitrile (3x): ^{1}H NMR (250 MHz,$CDCl_3$/TMS): δ = 2.00 (s, 1H), 4.70 (s, 1H), 7.15 (s, 3H), 7.26–7.34 (m, 6H), 7.48–7.54 (m, 6H), 8.21 (d, J = 7.5 Hz, 2H), 8.44 (d, J = 7.5 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 63.7, 84.8, 110.6, 118.9, 127.0, 128.5, 131.6, 131.7, 132.1, 146.9, 148.6; anal. calcd. for $C_{27}H_{21}NO$ (375.46): C 86.37, H 5.64, N 3.73; found: C 86.30, H 5.58, N 3.65.

1-(4-Nitrophenyl)-2,2-diphenylethanol (3y): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.18 (s, 1H), 2.81 (s, 1H), 7.23–7.33 (m, 4H), 7.94–8.03 (m, 6H), 8.21 (d, J = 7.5 Hz, 2H), 8.50 (d, J = 7.5 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 62.3, 75.4, 115.9, 125.9, 127.8, 131.5, 131.7, 138.6, 148.7, 155.2; anal. calcd. for $C_{20}H_{17}NO_3$ (319.35): C 75.22, H 5.37, N 4.39; found: C 75.15, H 5.30, N 4.31.

4-(1-Hydroxy-2,2-diphenylethyl)benzonitrile (3z): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 1.18 (s, 1H), 4.66 (s, 1H), 4.94 (s, 1H), 7.13–7.18 (m, 6H), 7.24 (s, 4H), 7.44 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 7.5 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/TMS): δ = 63.0, 81.4, 11.5, 118.6, 125.9, 127.7, 127.8, 131.5, 131.7, 138.6, 145.2; anal. calcd. for $C_{21}H_{17}NO$ (299.37): C 84.25, H 5.72, N, 4.68; found: C 84.19, H 5.68, N 4.61.

1-(4-nitrophenyl)-2-phenylpropan-1-ol (3aa): ^{1}H NMR (250 MHz, $CDCl_3$/TMS): δ = 0.75–0.80 (m, 3H), 1.30 (s, 1H), 2.63–3.02 (m, 1H), 5.05 (m, 1H), 7.22–7.39 (m, 5H), 7.69 (d, J = 7.5 Hz, 2H), 7.65 (d, J = 7.5 Hz, 2H); ^{13}CNMR (62.5 MHz, $CDCl_3$/TMS): δ = 16.5, 47.0, 84.6, 123.1, 127.8, 127.9, 129.2, 129.6, 144.6, 149.2, 150.1; anal. calcd. for $C_{15}H_{15}NO_3$ (257.28): C 70.02, H 5.88, N 5.44; found: C 69.94, H 5.81, N 5.38.

Acknowledgements

The financial support of the Research Council of Shiraz University and the grant from the Iran National Elite Foundation is gratefully acknowledged.

References

[1] a) L. Pu, H.-B. Yu, *Chem. Rev.* **2001**, *101*, 757–824; b) A. Fürstner, *Chem. Rev.* **1999**, *99*, 991–1045; c) D.

Guijarro, M. Yus, *Tetrahedron* **2000**, *56*, 1135–1138; d) J.-S. Lee, R. Velarde-Ortiz, A. Guijarro, J. R. Wurst, R. D. Rieke, *J. Org. Chem.* **2000**, *65*, 5428–5430; e) R. Noyori, M. Kitamura, *Angew. Chem.* **1991**, *103*, 34–55; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 49–69; f) Y. Ogawa, M. Mori, A. Saiga, K. Takagi, *Chem. Lett.* **1996**, 1069–1083.

[2] a) M. R. Luderer, W. F. Bailey, M. R. Luderer, J. D. Fair, R. J. Dancer, M. B. Sommer, *Tetrahedron: Asymmetry* **2009**, *20*, 981–1094; b) E. Fernández-Mateos, B. Maciá, M. Yus, *Eur. J. Org. Chem.* **2012**, 3732–3736.

[3] a) C.-S. Da, J.-R. Wang, X.-G. Yin, X.-Y. Fan, Y. Liu, S.-L. Yu, *Org. Lett.* **2009**, *11*, 5578–5581; b) E. Fernández-Mateos, B. Maci, M. Yus, *Adv. Synth. Catal.* **2013**, *355*, 1249–1254; c) S. M. Manolikakes, M. Jaric, K. Karaghiosoff, P. Knochel, *Chem. Commun.* **2013**, *49*, 2124–2126.

[4] a) H. Schumann, J. Kaufmann, S. Dechert, H.-G. Schmalz, *Tetrahedron Lett.* **2002**, *43*, 3507–3511; b) K. Biswas, O. Prieto, P. J. Goldsmith, S. Woodward, *Angew. Chem.* **2005**, *117*, 2272–2274; *Angew. Chem. Int. Ed.* **2005**, *44*, 2232–2234; c) S. Alegre, M. Diéguez, O. Pàmies, *Tetrahedron: Asymmetry* **2011**, *22*, 834–839.

[5] a) L. Pu, *Tetrahedron* **2003**, *59*, 9873–9886; b) A. M. DeBerardinis, M. Turlington, L. Pu, *Org. Lett.* **2008**, *10*, 2709–2712; c) W. A. Nugent, *Org. Lett.* **2002**, *4*, 2133–2136; d) B. D. Dangel, R. Polt, *Org. Lett.* **2000**, *2*, 3003–3006; e) A. D. Wouters, D. S. Ludtke, *Org. Lett.* **2012**, *14*, 3962–3965; f) P. G. Cozzi, P. Kotrusz, *J. Am. Chem. Soc.* **2006**, *128*, 4940–4941; g) D.-X. Liu, L.-C. Zhang, Q. Wang, C.-S. Da, Z.-Q. Xin, R. Wang, M. C. K. Choi, A. S. C. Chan, *Org. Lett.* **2001**, *3*, 2733–2735; h) A. M. DeBerardinis, M. Turlington, L. Pu, *Angew. Chem.* **2011**, *123*, 2416–2418; *Angew. Chem. Int. Ed.* **2011**, *50*, 2368–2370; i) M.-J. Jin, Y.-M. Kim, K.-S. Lee, *Tetrahedron Lett.* **2005**, *46*, 2695–2696; j) M. L. Richmond, C. M. Sprout, C. T. Seto, *J. Org. Chem.* **2005**, *70*, 8835–8840; k) M. P. Sibi, L. M. Stanley, *Tetrahedron: Asymmetry* **2004**, *15*, 3353–3356; l) Y.-C. Qin, L. Pu, *Angew. Chem.* **2006**, *118*, 279–283; *Angew. Chem. Int. Ed.* **2006**, *45*, 273–277; m) S.-L. Tseng, T.-K. Yang, *Tetrahedron: Asymmetry* **2005**, *16*, 773–782; n) Z. Huang, H. Lai, Y. Qin, *J. Org. Chem.* **2007**, *72*, 1373–1378; o) A. L. Braga, R. M. Rubim, H. S. Schrekker, L. A. Wessjohann, M. W. G. de Bolster, G. Zenia, J. A. Sehnema, *Tetrahedron: Asymmetry* **2003**, *14*, 3291–3295.

[6] H. Nakamura, H. Iwama, Y. Yamamoto, *J. Am. Chem. Soc.* **1996**, *118*, 6641–6647.

[7] a) S. Oi, M. Moro, Y. Inoue, *Organometallics* **2001**, *20*, 1036–1037; b) S. Chakraborty, J. A. Krause, H. Guan, *Organometallics* **2009**, *28*, 582–586.

[8] Z. Dai, C. Zhu, M. Yang, Y. Zheng, Y. Pan, *Tetrahedron: Asymmetry* **2005**, *16*, 605–608.

[9] a) J. Bouffard, K. Itami, *Org. Lett.* **2009**, *11*, 4410–4413; b) H. Zheng, Q. Zhang, J. Chen, M. Liu, S. Cheng, J. Ding, H. Wu, W. Su, *J. Org. Chem.* **2009**, *74*, 943–945; c) H.-F. Duan, J.-H. Xie, W.-J. Shi, Q. Zhang, Q.-L. Zhou, *Org. Lett.* **2006**, *8*, 1479–1481; d) T. Zou, S.-S. Pi, J.-H. Li, *Org. Lett.* **2009**, *11*, 453–456; e) M. Kuriyama, R. Shimazawa, T. Enomoto, R. Shirai, *J. Org. Chem.* **2008**, *73*, 6939–6942; f) T. Yamamoto, T. Ohta, Y. Ito, *Org. Lett.* **2005**, *7*, 4153–4155; g) R. A. Batey, A. N. Thadani, D. V. Smil, *Org. Lett.* **1999**, *1*, 1683–1686; h) C. Qin, H. Wu, J. Cheng, X. Chen, X. Liu, W. Zhang, W. Su, J. Ding, *J. Org. Chem.* **2007**, *72*, 4102–4107; i) Y. He, C. Cai, *Chem. Commun.* **2011**, *47*, 12319–12321; j) G. Takahashi, E. Shirakawa, T. Tsuchimotoa, Y. Kawakami, *Chem. Commun.* **2005**, 1459–1461; k) L. Zhou, X. Du, R. He, Z. Ci, Z. Bao, *Tetrahedron Lett.* **2009**, *50*, 406–408; l) J. Chen, X. Zhang, Q. Feng, M. Luo, *J. Organomet. Chem.* **2006**, *691*, 470–474; m) N. Miyaura, *Synlett* **2009**, 2039–2050.

[10] F. Zhang, Y. Liu, L. Xie, X. Xu, *RSC Adv.* **2014**, *4*, 17218–17221.

[11] a) Y. Li, X.-S. Zhang, K. Chen, K.-H. He, F. Pan, B.-J. Li, Z.-J. Shi, *Org. Lett.* **2012**, *14*, 636–639; b) F.-F. Wang, C.-P. Luo, Y. Wang, G. Deng, L. Yang, *Org. Biomol. Chem.* **2012**, *10*, 8605–8608; c) B.-J. Lia, Z.-J. Shi, *Chem. Sci.* **2011**, *2*, 488–493.

[12] a) E. P. Gillis, M. D. Burke, *J. Am. Chem. Soc.* **2008**, *130*, 14084–14085; b) H. Ihara, M. Suginome, *J. Am. Chem. Soc.* **2009**, *131*, 7502–7503.

[13] a) A. Fürstner, N. Shi, *J. Am. Chem. Soc.* **1996**, *118*, 12349–12357; b) K. K. Majumdar, C.-H. Cheng, *Org. Lett.* **2000**, *2*, 2295–2298.

[14] a) S. Venkatraman, C.-J. Li, *Org. Lett.* **1999**, *1*, 1133–1135; b) A. Krasovskiy, C. Duplais, B. H. Lipshutz, *J. Am. Chem. Soc.* **2009**, *131*, 15592–15593; c) M. Kimura, D. Nojiri, M. Fukushima, S. Oi, Y. Sonoda, Y. Inoue, *Org. Lett.* **2009**, *11*, 3794–3797; d) B. Sam, T. P. Montgomery, M. J. Krische, *Org. Lett.* **2013**, *15*, 3790–3793; e) W. M. Czaplik, M. Mayer, A. Jacobi von Wangelin, *ChemCatChem* **2011**, *3*, 135–138.

[15] a) D. A. Everson, R. Shrestha, D. J. Weix, *J. Am. Chem. Soc.* **2010**, *132*, 920–921; b) D. A. Everson, B. A. Jones, D. J. Weix, *J. Am. Chem. Soc.* **2012**, *134*, 6146–6159; c) S. Biswas, D. J. Weix, *J. Am. Chem. Soc.* **2013**, *135*, 16192–16197; d) A. H. Cherney, S. E. Reisman, *J. Am. Chem. Soc.* **2014**, *136*, 14365–14368; e) C. E. I. Knappke, S. Grupe, D. Gärtner, M. Corpet, C. Gosmini, A. Jacobi von Wangelin, *Chem. Eur. J.* **2014**, *20*, 6828–6842.

[16] a) T. León, A. Correa, R. Martin, *J. Am. Chem. Soc.* **2013**, *135*, 1221–1224; b) A. Correa, R. Martin, *J. Am. Chem. Soc.* **2014**, *136*, 7253–7256; c) T. Fujihara, K. Nogi, T. Xu, J. Terao, Y. Tsuji, *J. Am. Chem. Soc.* **2012**, *134*, 9106–9109; d) D. A. Everson, D. J. Weix, *J. Org. Chem.* **2014**, *79*, 4793–4798.

[17] S. Z. Tasker, E. A. Standley, T. F. Jamison, *Nature* **2014**, *509*, 299–309.

[18] T. Moragas, A. Correa, R. Martin, *Chem. Eur. J.* **2014**, *20*, 8242–8258.

[19] Z. Tan, X. Wan, Z. Zang, Q. Qian, W. Deng, H. Gong, *Chem. Commun.* **2014**, *50*, 3827–3830.

[20] a) A. A. C. Braga, N. H. Morgon, G. Ujaque, A. Liedos, F. Maseras, *J. Organomet. Chem.* **2006**, *691*, 4459–4466; b) A. A. C. Braga, N. H. Morgon, G. Ujaque, F. Maseras, *J. Am. Chem. Soc.* **2005**, *127*, 9298–9307.

[21] Y. Dai, F. Wu, Z. Zang, H. You, H. Gong, *Chem. Eur. J.* **2012**, *18*, 808–812.

[22] A. Correa, T. León, R. Martin, *J. Am. Chem. Soc.* **2014**, *136*, 1062–1069.

[23] H.-W. Shih, M. N. V. Wal, R. L. Grange, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2010**, *132*, 13600–13603.
[24] W. R. Ruby, *Preparation of 4-nitrostilbenes. U.S. Patent* 3,514,495 A, **1970**.
[25] a) S. Wang, Q. Qian, H. Gong, *Org. Lett.* **2012**, *14*, 3352–3355; b) F. Wu, W. Lu, Q. Qian, Q. Ren, H. Gong, *Org. Lett.* **2012**, *14*, 3044–3047.
[26] E. Carmona, J. M. Marin, M. Paneque, M. L. Poveda, *Organometallics* **1987**, *6*, 1757–1765.
[27] A. Metzger, S. Bernhardt, G. Manolikakes, P. Knochel, *Angew. Chem.* **2010**, *122*, 4769–4773; *Angew. Chem. Int. Ed.* **2010**, *49*, 4665–4668.

Nickel-Catalyzed Reductive Benzylation of Aldehydes with Benzyl Halides and Pseudohalides

Adv. Synth. Catal. **2015**, *357*, 1 – 11

Farhad Panahi, Marzieh Bahmani, Nasser Iranpoor*

11