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Selective Reductive Removal of Ester and Amide Groups from Arenes and Heteroarenes via Nickel Catalyzed C-O and C-N Bond Activation

Huifeng Yue, Lin Guo, Shao-Chi Lee, Xiangqian Liu, and Magnus Rueping*

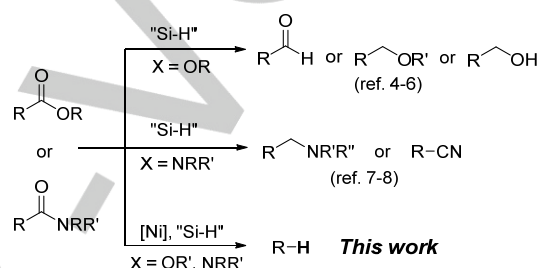
Abstract: An efficient metal-catalyzed reductive defunctionalization of aryl and heteroaryl esters with hydrosilane via a decarbonylative pathway has been achieved for the first time. This new reduction protocol is based on the use of an inexpensive nickel(II) catalyst providing a versatile method for the removal of ester and amide functional groups from various organic molecules. Moreover, a scale-up experiment and a synthetic application which uses as a removable carbonyl directing group proves the usefulness of this reaction.

The reduction of readily available carboxylic acid derivatives such as esters and amides is one of the most fundamental and important transformations in synthetic organic chemistry.^[1] Organometallic hydrides such as sodium borohydride and lithium aluminum hydride are used to accomplish such transformations.^[2] However, these reactive reducing agents may suffer from cumbersome work-up procedures and poor functional group tolerance. Recently highly chemoselective catalytic hydrosilylation of carboxylic acid derivatives by using easy to handle and practical hydrosilanes has been developed.^[3] In general, alcohols,^[4] ethers,^[5] or aldehydes^[6] are obtained after hydrosilylation of esters, while amines^[7] or nitriles^[8] are achieved upon hydrosilylation of amides (Scheme 1). However, to date, despite the great importance of replacing functionalities in organic synthesis, very little is known about the removal of ester and amides from aromatic and heteroaromatic rings^[9] via a catalytic reductive pathway.

Regarding the activation/functionalization of C-O and C-N bonds of esters and amides,^[10-11] progress has been achieved in recent years.^[10-16] With regard to decarbonylative transformations, the Ni-catalyzed C-C bond formation of aryl esters was achieved.^[12] Additionally, Heck and Suzuki type cross-couplings of twisted amides via a decarbonylative pathway were reported^[13] as well as decarbonylative borylations, aminations and silylations of esters and amides were realized.^[14-15]

As part of our continuing efforts in developing viable protocols

for the activation of inert bonds by nickel catalysis,^[16] we herein describe the first Ni-catalyzed reductive defunctionalization of aryl and heteroaryl esters via a decarbonylative pathway, providing a versatile method for the late stage removal of ester as well as amide groups from organic molecules.



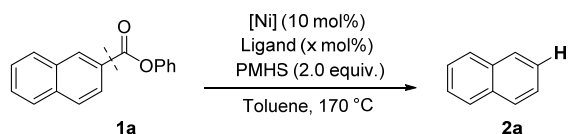
Scheme 1. Transition-metal-catalyzed reduction of esters and amides using hydrosilanes.

We initiated our studies by evaluating the reductive defunctionalization of phenyl naphthalene-2-carboxylate (**1a**) using inexpensive, non-toxic and air stable polymethylhydrosiloxane (PMHS) as a reducing agent and Ni(cod)₂ as catalyst. Since ligands typically play an important role in Ni-catalyzed transformations, we firstly tested several phosphine ligands (entries 1-3) and identified the bidentate phosphine ligand 1,2-bis(dicyclohexylphosphino)ethane (dcype) as the optimal one, providing the desired product in 69% yield. The addition of potassium fluoride as base had no beneficial effect on the reaction yield (entry 4). However, the yield was significantly improved to 88% just by extending the reaction time (entry 5). A series of nickel catalysts were subsequently examined and the inexpensive and air stable Ni(OAc)₂·4H₂O was found to give a slightly better result (90%, entry 6) compared to the Ni(0) species, whereas other Ni(II) catalysts, such as NiCl₂, NiBr₂, NiI₂, all gave no desired product (entries 7-9). The yield of the product decreased to 68% when 10 mol% of dcype ligand was used (entry 10). The utilization of other solvents such as 1,4-dioxane and the decrease of temperature proved to be less productive (entries 11 and 12). Control experiments demonstrated that no desired product is generated in the absence of the nickel catalyst (entry 13).

With the optimized reaction conditions in hand, the scope of ester substrates was firstly evaluated (Table 2). Notably, a wide variety of aryl esters bearing electron-rich and electron-poor functional groups provided the corresponding products in good to excellent yields. For example, naphthalen-2-yl esters **1a-c** underwent the reaction smoothly and gave products in high yields (71-99%).

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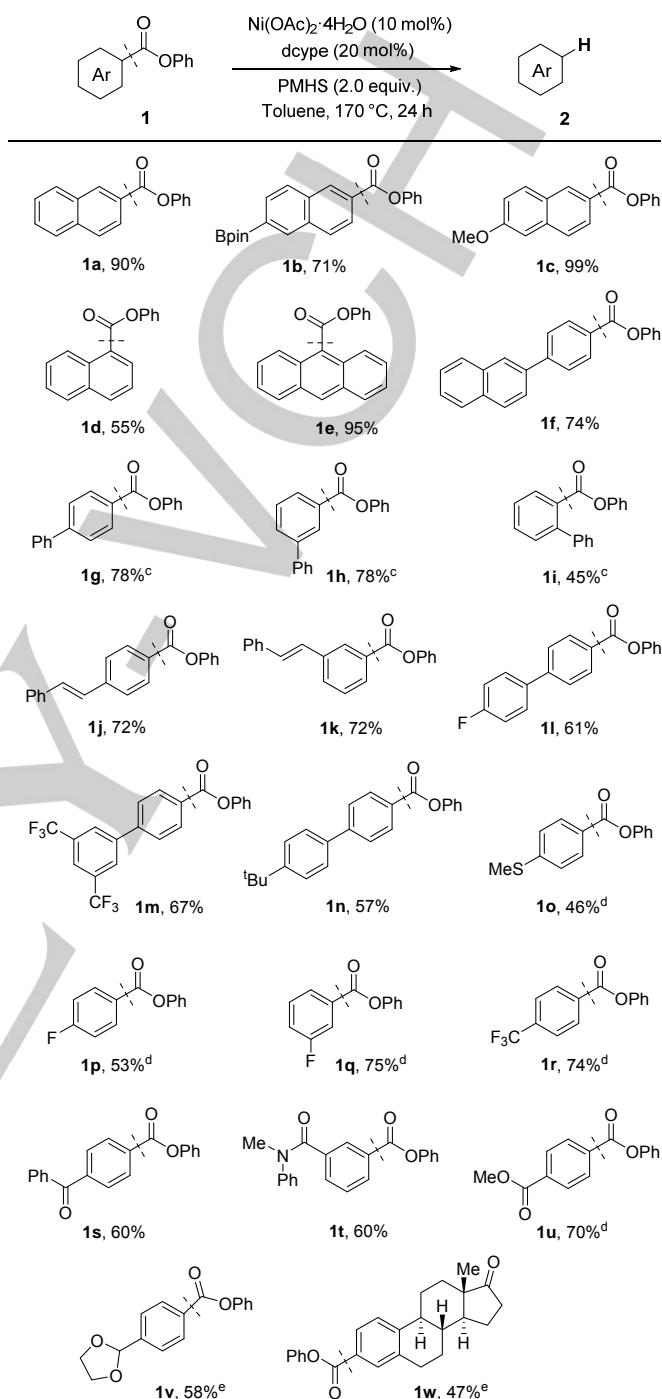
Table 1. Optimization of the reaction conditions^[a].

Entry	[Ni]	Ligand (x mol%)	Time (h)	Yield (%) ^[b]
1	Ni(cod) ₂	dcype (20)	12	69
2	Ni(cod) ₂	PCy ₃ (40)	12	trace
3	Ni(cod) ₂	P ⁿ Bu ₃ (40)	12	43
4 ^[c]	Ni(cod) ₂	dcype (20)	12	57
5	Ni(cod) ₂	dcype (20)	24	88
6	Ni(OAc)₂·4H₂O	dcype (20)	24	90
7	NiCl ₂	dcype (20)	24	0
8	NiBr ₂	dcype (20)	24	0
9	NiI ₂	dcype (20)	24	0
10	Ni(OAc) ₂ ·4H ₂ O	dcype (10)	24	68
11 ^[d]	Ni(OAc) ₂ ·4H ₂ O	dcype (20)	24	51
12 ^[e]	Ni(OAc) ₂ ·4H ₂ O	dcype (20)	24	30
13	-	dcype (20)	24	0

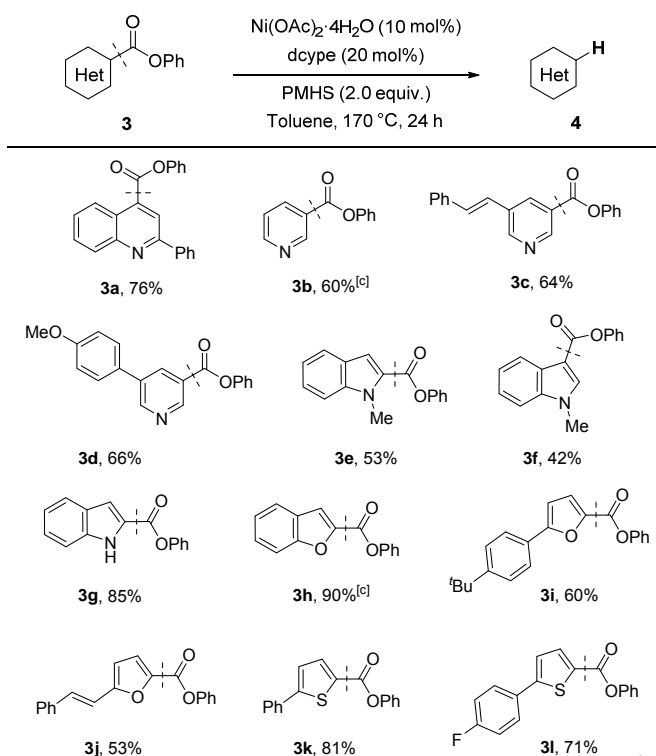
[a] Reaction conditions: phenyl naphthalene-2-carboxylate **1a** (0.2 mmol), PMHS (0.4 mmol), [Ni] (0.02 mmol), ligand (0.04 mmol) in toluene (1.0 ml) at 170 °C. [b] Yield after purification. [c] KF (2 equiv.) was added. [d] Dioxane was used as solvent. [e] 150 °C.

Also, the decarbonylative reduction of polycyclic substrate **1e** and π -extended ester **1f** proceeded in good to excellent yields. Although the *para* and *meta* biphenyl esters (**1g** and **1h**) could undergo this transformation with high yields, *ortho* biphenyl ester **1i** gave the product in a moderate yield only, indicating that the reaction is slightly hampered by the increased steric hindrance. Furthermore, other functional groups including double bonds (**1j** and **1k**), fluoro (**1l**, **1p** and **1q**), trifluoromethyl (**1m** and **1r**), *t*-butyl (**1n**), methylthio (**1o**), ketone (**1s**), amide (**1t**), and acetal (**1v**) were perfectly tolerated under our reaction conditions, which highlights the advantages of our newly developed reductive decarbonylation. Moreover, this protocol could selectively reduce the phenyl ester group and keep the methyl ester group untouched (**1u**). It is noteworthy that estrone derived phenyl ester did also undergo the defunctionalization (**1w**).

It is important to note that in contrast to previous reports, substrates with a methoxy (**1c**), thiomethyl (**1o**) or fluoro group (**1l**, **1p** and **1q**), as well as methylester or amides are well tolerated highlighting the chemoselectivity of this new catalytic reductive decarbonylation. The generality of the present Ni-catalyzed reductive defunctionalization protocol was further demonstrated by using a series of heteroaryl esters, which play an important role in medicinal chemistry (Table 3). As shown, reduction of quinoline derived ester **3a** under the optimal conditions afforded the corresponding product in good yield. Similar success was obtained for the pyridine derived esters **3b-d**. In addition to indole and benzofuran derived esters **3e-h**, furan and thiophene derived esters **3i-l** were also suitable substrates for this transformation, giving the desired products in moderate to excellent yields.

Table 2. Scope of the aryl esters.^[a, b]

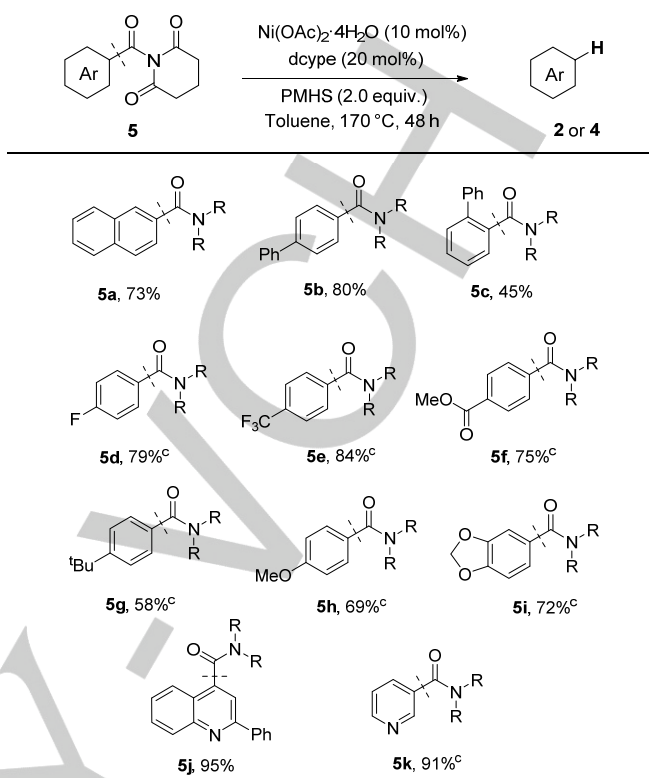
[a] Reaction conditions: Aryl ester **1** (0.2 mmol), PMHS (0.4 mmol, 2 equiv.), Ni(OAc)₂·4H₂O (0.02 mmol, 10 mol%), dcype (0.04 mmol, 20 mol%) in toluene (1 ml) at 170 °C for 24 h. [b] Yield after purification. [c] Ni(cod)₂ (0.02 mmol, 20 mol%), 48 h. [d] Yield was determined by GC due to the volatility of the product. [e] 72 h

Table 3. Scope of the heteroaryl esters.^[a, b]

[a] Reaction conditions: Heteroaryl ester **3** (0.2 mmol), PMHS (0.4 mmol, 2 equiv.), Ni(OAc)₂·4H₂O (0.02 mmol, 10 mol%), dcype (0.04 mmol, 20 mol%) in toluene (1 ml) at 170 °C for 24 h. [b] Yield after purification. [c] Yield was determined by GC due to the volatility of the product.

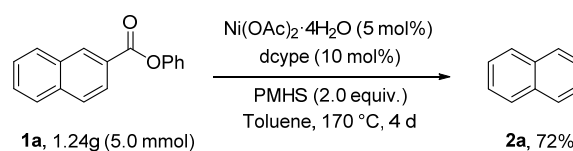
Furthermore, our reductive defunctionalization protocol could also be readily extended to aryl and heteroaryl amides. As shown in Table 4, the reaction of naphthyl amide **5a** proceeded in good yield. Likewise, *para* biphenyl amide **5b** could be reduced in high yield, whereas *ortho* biphenyl amide **5c** gave the desired product in moderate yield. Moreover, a wide range of phenyl amides possessing fluoro (**5d**), trifluoromethyl (**5e**), methyl ester (**5f**), *t*-butyl (**5g**), methoxy (**5h**), and acetal (**5i**) functionalities were all suitable substrates, giving the corresponding products in good to high yields. In addition, quinoline and pyridine derived amides (**5j**) and **5k**) both underwent this reaction in excellent yields.

In order to demonstrate the practicability of this newly developed decarbonylative reduction methodology, a gram-scale experiment with phenyl naphthalene-2-carboxylate **1a** was conducted, and the desired product **2a** was isolated in 72% yield in the presence of 5 mol% nickel(II) catalyst only (Scheme 2a). Furthermore, based on the property of carbonyl groups as directing group in aromatic C–H functionalization and subsequently be removal *via* reductive defunctionalization of the corresponding ester, we also achieved an orthogonal synthesis, showing the advantages of our developed protocol (Scheme 2b). Thus ester and amide groups often used in organic synthesis as directing group in aromatic substitutions or *ortho* directing groups in CH-functionalizations can be readily replaced.

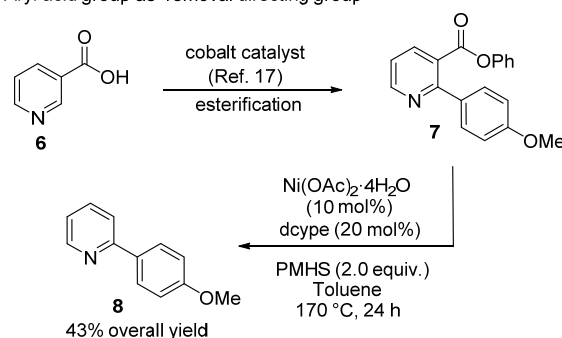
Table 4. Scope of the aryl and heteroaryl amides^[a, b]

[a] Reaction conditions: Aryl or heteroaryl amide **5** (0.2 mmol), PMHS (0.4 mmol, 2 equiv.), Ni(OAc)₂·4H₂O (0.02 mmol, 10 mol%), dcype (0.04 mmol, 20 mol%) in toluene (1 ml) at 170 °C for 48 h. [b] Yield after purification. [c] Yield was determined by GC due to the volatility of the product.

a) Gram-scale reductive defunctionalization

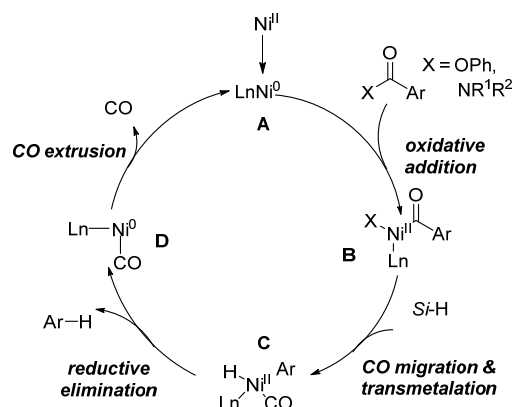


b) Aryl acid group as removal directing group

**Scheme 2.** Gram-scale reaction and synthetic application.

Based on our results^[14] and previous studies,^[18] a mechanism for this Ni-catalyzed reductive defunctionalization protocol is proposed (Scheme 3).

Oxidative addition of C(acyl)–X bond of aryl ester and amide to the LnNi^0 complex **A** gives an acyl nickel(II) intermediate **B**, which subsequently undergoes CO migration and transmetalation with hydrosilane, affording an aryl-hydride nickel(II) intermediate **C**. Reductive elimination of **C** produces $\text{Ln}_n\text{Ni}^0\text{CO}$ specie **D** and delivers the reductive product. Finally, extrusion of CO from **D** regenerates the active LnNi^0 catalyst **A**.



Scheme 3. Proposed mechanism for the nickel catalyzed reductive deesterification and deamidation.

In summary, we have developed an efficient decarbonylative reductive protocol of a wide range of readily available aryl and heteroaryl esters and amides. This method relies on the use of an inexpensive and air stable $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ catalyst and commercially available hydrosilane, providing a versatile method for the removal of ester and amide functional groups from organic molecules. In contrast to previously reported hydrosilylations which result in the formation of alcohols, aldehydes, ethers or amines the new protocol allows the full removal of an ester or amide group which can be useful for late stage modifications or reaction sequences in which carbonyl groups are initially used as directing groups for ortho-lithiations or CH-functionalizations. It is also important to note that various functional groups, often used as electrophiles in nickel catalyzed cross coupling reactions or reductions are compatible with the employed reaction conditions. Furthermore, the new protocol can be easily scaled-up and applied as key step in synthetic transformations which use a carbonyl group as a removable directing group. Efforts to expand the scope of this transformation to other types of esters and amides are currently ongoing in our laboratories.

Acknowledgements

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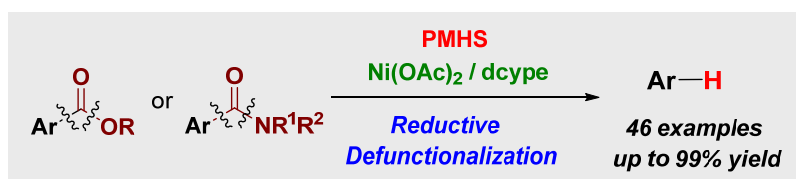
Keywords: Nickel • reductive defunctionalization • Ester • Amide

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Layout 2:

COMMUNICATION



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Selective Reductive Removal of Ester and
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An efficient nickel-catalyzed reductive defunctionalization of aryl and heteroaryl esters and amides with hydrosilane via a decarbonylative pathway has been achieved. This new reduction protocol is based on the use of an inexpensive nickel(II) catalyst providing a versatile method for the removal of ester and amide functional groups from various organic molecules.