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Ni-catalyzed direct alcoholysis of *N*-acylpyrrole-type tertiary amides under mild conditions

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N-Acylpyrrole-type amides are a class of versatile building blocks in asymmetric synthesis. We report that by employing $Ni(COD)_2$/2,2′-bipyridine (5 mol%) catalytic system, the direct, catalytic alcoholysis of *N*-acylpyrrole-type aromatic and aliphatic amides with both primary and secondary alcohols can be achieved efficiently under very mild conditions (rt, 1 h) even at gram scale. By increasing the catalyst loading to 10 mol%, prolonging reaction time (18 h), and/or elevating reaction temperature to 50 °C/80 °C, the reaction could be extended to both complex and hindered *N*-acylpyrroles as well as to *N*-acylpyrazoles, *N*-acylindoles, and to other (functionalized) primary and secondary alcohols. In all cases, only 1.5 equiv. of alcohol were used. The value of the method has been demonstrated by the racemization-free, catalytic alcoholysis of chiral amides yielded from other asymmetric methodologies.

amide transformation, C–N bond activation, esterification, catalysis, nickel

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1 Introduction

Amides (*N*-monoacylamines) are a class of highly stable and versatile building blocks in organic synthesis. The transformation of amides into other functional groups is in high demand in both organic chemistry and pharmaceutical industry [1]. However, due to the high stability of amides, synthetically useful methods are either multi-step transformations or required harsh conditions [1]. In recent years, the direct transformation of amides has attracted considerable attention, which resulted in many mild and useful C–C bond forming methods [2,3] including the catalytic ones [4]. As for the transformation of amides into esters, in 1998, Charette *et al.* [5a] and Dossena *et al.* [5b] independently reported a mild method for the one-pot transformation of amides into esters, which features the *in situ* activation of amides with a stoichiometric amount of triflic anhydride. In 2015, Garg and Houk *et al.* [6a] reported the first nickel-catalyzed activation of amide C–N bonds for the direct conversion of tertiary benzanilides to aromatic esters (Scheme 1(a)). Despite the exciting breakthrough [6b–6d], the method is restricted to (hetero)aromatic amides. The efforts to extend the substrate scope to aliphatic amides remained unsuccessful [7]. Subsequently, a two-step protocol to allow the alcoholysis of secondary aliphatic amides was developed [7]. Nevertheless, the catalytic, direct alcoholysis of common tertiary aliphatic amides via C–N activation under mild conditions remains unconquered [8].

N-Acylpyrroles (**A**) [9], *N*-acylpyrazoles (**B**) [10], *N*-acylindoles (**C**) [11,9e], and *N*-acylindolines (**D**) [12,9g] (Scheme 1(b)), a class of heterocyclic tertiary amides, have been proved to be versatile building blocks in organic synthesis in general [9–12], and in asymmetric synthesis [9–12] in particular. It was envisioned that this class of amides

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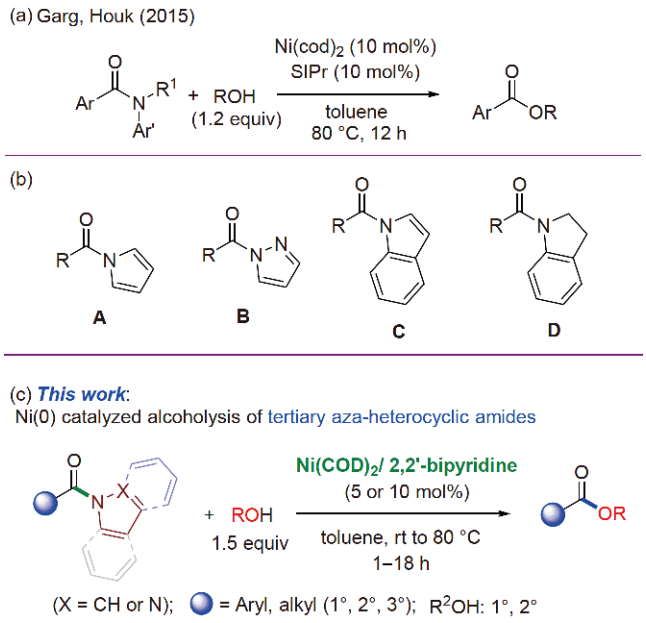


Scheme 1 (a) The first nickel-catalyzed alcoholysis of amides; (b) the useful heterocyclic tertiary amides; c) our plan (color online).

are more reactive than common amides, and the catalytic transformation would be feasible [13]. Indeed, recently we reported a Ni-catalyzed cross-coupling reaction of *N*-acylpyrrole-type amides with organoboron reagents for ketones synthesis [13d]. As regarding the catalytic alcoholysis, three isolated examples have been reported. However, it involved either a *N*-acylpyrrole bearing an electron-withdrawing group at C2 of the pyrrole ring [9e,9f], or a *N*-acylpyrazole derivative [9h], and a large excess of alcohol (benzyl alcohol or methanol) was used for the alcoholysis. The catalytic alcoholysis of common *N*-acylpyrroles remains elusive. Thus, there still remains a need for a versatile method for the alcoholysis of *N*-acylpyrroles to esters that is general for different types of *N*-acylpyrroles, is chemoselective, and without the need for using a large excess of an alcohol. Herein, we report the Ni-catalyzed direct alcoholysis of tertiary heterocyclic amides (**A**–**C**) into esters via C–N bonds activation and cleavage.

2 Experimental

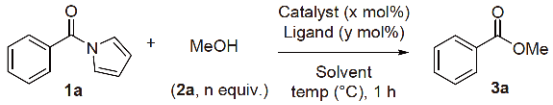
General procedure for the catalytic alcoholysis of N-acylpyrrole type amides. To a vial was added a *N*-acylpyrrole-type amide (0.24 mmol, 1.0 equiv.), 2,2′-bipyridine (1.9 mg, 0.012 mmol, 5 mol%) and a magnetic stir bar. The vial was then taken into a glove box. $Ni(COD)_2$ (3.3 mg, 0.012 mmol, 5 mol%), toluene (0.48 mL, 0.5 mol L^{-1}), and an alcohol (0.36 mmol, 1.5 equiv.) were added successively to the vial. The vial was then sealed with screw cap, removed from the glove box, and stirred vigorously at room temperature for 1 h. The resulting mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography to yield the desired ester.

3 Results and discussion

On the basis of the above mentioned precedents, we opted for the methanolysis of *N*-benzoylpyrrole (**1a**) as a model reaction. In view of developing an economical method, the employment of cheaper and earth abundant metal nickel [14] on one hand, and of cheap and air-stable ligands on the other hand, for C–N bonds activation was envisaged. At the outset of our investigation, nickel (II) salts (NiI_2 and $NiCl_2$)/2,2′-bipyridine solely or in combination with Zn were attempted (Table 1, entries 1–4), but all failed to catalyze the esterification reaction. Interestingly, the $Ni(Cp)_2$/2,2′-bipyridine combination efficiently catalyzed the methanolysis of **1a** to give ester **3a** in 97% yield (Table 1, entry 5). Moreover, Ni $(COD)_2$/1,10-phenanthroline combination (Table 1, entry 6) and $Ni(COD)_2$/2,2′-bipyridine combination (Table 1, entry 7) effectively catalyzed the methanolysis reaction to produce the desired ester **3a** in almost quantitative yield, whereas PPh_3 and PCy_3 (entries 8 and 9) were invalid as ligands. Because 2,2′-bipyridine is much cheaper than 1,10-phenanthroline, the former was selected for further investigation. After screening divers reaction parameters including equivalents of $Ni(COD)_2$ and ligand (2,2′-bipyridine) (entries 10–12), solvent used (entries 13 and 14), equivalents of methanol (entries 15–17), and examining the control experiments (entries 18 and 19), the optimized conditions for the catalytic methanolysis of *N*-acylpyrrole **1a** were defined as those outlined in entry 16, namely, methanolysis in the presence of 5 mol% of $Ni(COD)_2$/2,2′-bipyridine combination with 1.5 equiv. of methanol in toluene at rt for 1 h.

With the optimized reaction conditions in hand, the scope of amide was first investigated and the results are displayed in Table 2. The reaction tolerated both electron-donating (*p*-Me, *p*-Ph, *p*-OMe, 3,4,5-*tri*-OMe, Table 2, entries 2–5) and electron-withdrawing groups (*p*-Cl, *p*-F, *p*-CF_3, *p*-NO_2, *p*-CO_2Me, Table 2, entries 6–10). It is worth mentioning that the high yielding access to esters bearing a F or a CF_3 group is of value because F and CF_3 are two important functional groups for developing pharmaceuticals, agrochemicals, and functional materials [15]. Moreover, the smooth methanolysis or ethanolysis (entry 11) of benzamides bearing functional groups such as nitro and methyl ester groups (entries 9 and 11) to give the corresponding nitro ester **3i** and diester **3jb** in excellent yields (92% and 94%) reflect the good functional group tolerance and chemoselectivity of the reaction. Other aromatic amides such as 2-naphthamide (**1k**) (entry 12) and heteroaromatic amides (**1l** and **1m**, entries 13 and 14) also reacted to give the corresponding esters in 98%,

Table 1 Exploration of reaction conditions



Entry	Catalyst (x mol%)	Ligand (y mol%)	n (equiv.)	Solvent	Temp.	Yield[a)]
1	NiI_2 (10)	2,2′-bipyridine (10)	7.0	toluene	rt	NR
2	$NiCl_2$ (10)	2,2′-bipyridine (10)	7.0	toluene	rt	NR
3	NiI_2/Zn (10)	2,2′-bipyridine (10)	7.0	toluene	rt	NR
4	$NiCl_2$/Zn (10)	2,2′-bipyridine (10)	7.0	toluene	rt	NR
5	$Ni(Cp)_2$ (10)	2,2′-bipyridine (10)	7.0	toluene	rt	97%
6	$Ni(COD)_2$ (10)	1,10-phenanthroline (10)	7.0	toluene	rt	>99%
7	$Ni(COD)_2$ (10)	2,2′-bipyridine (10)	7.0	toluene	rt	>99%
8	$Ni(COD)_2$ (10)	PPh_3 (10)	7.0	toluene	rt	NR
9	$Ni(COD)_2$ (10)	PCy_3 (10)	7.0	toluene	rt	NR
10	$Ni(COD)_2$ (5)	2,2′-bipyridine (10)	7.0	toluene	rt	>99%
11	$Ni(COD)_2$ (5)	2,2′-bipyridine (5)	7.0	toluene	rt	>99%
12	$Ni(COD)_2$ (1)	2,2′-bipyridine (1)	7.0	toluene	rt	71%
13	$Ni(COD)_2$ (5)	2,2′-bipyridine (5)	7.0	THF	66	92%
14	$Ni(COD)_2$ (5)	2,2′-bipyridine (5)	7.0	dichloroethane	84	88%
15	$Ni(COD)_2$ (5)	2,2′-bipyridine (5)	2.0	toluene	rt	>99%
16	$Ni(COD)_2$ (5)	2,2′-bipyridine (5)	1.5	toluene	rt	>99%
17	$Ni(COD)_2$ (5)	2,2′-bipyridine (5)	1.0	toluene	rt	85%
18	–	2,2′-bipyridine (5)	1.5	toluene	rt	NR
19	$Ni(COD)_2$ (5)	–	1.5	toluene	rt	NR
20	$Cu(OTf)_2$ (5)	2,2′-bipyridine (5)	1.5	toluene	rt	NR
21	$Zn(OTf)_2$ (5)	2,2′-bipyridine (5)	1.5	toluene	rt	NR
22	$BF_3{\cdot}Et_2O$ (5)	2,2′-bipyridine (5)	1.5	toluene	rt	NR

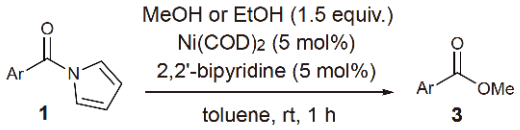
a) Yields determined by ^{1}H NMR analysis of crude mixture using 1,3,5-trimethoxybenzene as an internal standard. NR=No reaction.

87% and 83% yield, respectively.

We next turned our attention to aliphatic amide substrates. Under the standard conditions, the methanolysis of dodecanamide (**1n**) proceeded at rt for 1 h to give methyl ester **3n** in 80% yield (Table 3, entry 1). The reaction of other aliphatic amides **1o**–**1r** produced the corresponding esters **3o**–**3r** in 85%–91% yields (Table 3, entries 2–5). A longer reaction time (18 h) was necessary for the methanolysis of aliphatic amide bearing an ester group (**1s**), which gave the corresponding diester **3s** in 76% yield (entry 6). As illustrated in entries 7 and 8, α-branched aliphatic amide **1t** and even hindered adamantane-1-carboxamide **1u** are viable substrates for the methanolysis when increasing catalyst/ligand loading to 10 mol% and prolonging time (rt, 5 h, **3t**, 93%; or at 50 °C for 3 h, **3u**, 83%). The methanolysis of aliphatic amide bearing a ketone group (**1v**, an amide derivative of the nonsteroidal anti-inflammatory drug loxoprofen, rt, 18 h) proceeded chemoselectively to produce the corresponding keto-ester **3v** in 93% yield (entry 9). Significantly, the methanolysis of complex substrate containing an enone moiety **1w**, (an amide analogue of progesterone) produced chemoselectively the desired ester **3w** in 64% yield (entry 10).

The alcoholysis of pyrrole amide **1a** with other alcohols was next surveyed. As can be seen from Table 4, by employing 10 mol% of the $Ni(COD)_2$/2,2′-bipyridine combination, the reaction can be extended to other primary alcohols (EtOH, *n*-PrOH, BnOH, (adamantan-1-yl)methanol (**2k**), entries 1–3, and 11) and secondary alcohol (cyclohexanol, 80 °C, 18 h, entry 4). Various functionalized alcohols such as geraniol (**2f**), *N*-Boc-L-alaninol (**2g**), tryptophol (**2h**), but-3-yn-1-ol (**2i**), and *N*-Boc (±)-3-hydroxypyrrolidine (**2j**) also reacted smoothly to yield the corresponding esters **3ab**–**3ag** in 75%–98% yields (entries 5a–10). To our surprise, whereas the esterification of cyclohexanol yielded a modest yield (60%, entry 4), that of *N*-Boc 3-hydroxypyrrolidine (**2j**) afforded the desired ester in an excellent yield (98%, entry 10). This may be attributed to the conformational flexibility of five-membered pyrrolidine ring that renders the ring sterically less demanding. Nevertheless, sterically hindered tertiary alcohols 1-adamantanol (**2l**) and

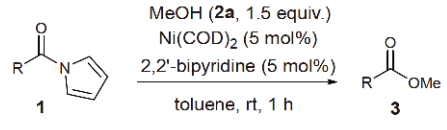
Table 2 Scope of aromatic *N*-acylpyrrole



Entry	Substrate	Product (Yield)[a]
1	**1a** (X = H)	**3a** (X = H, 99%)
2	**1b** (X = *p*-Me)	**3b** (X = *p*-Me, 97%)
3	**1c** (X = *p*-Ph)	**3c** (X = *p*-Ph, 97%)
4	**1d** (X = *p*-OMe)	**3d** (X = *p*-OMe, 95%)
5	**1e** (X = 3,4,5-tri-OMe)	**3e** (X = 3,4,5-tri-OMe, 89%)
6	**1f** (X = *p*-Cl)	**3f** (X = *p*-Cl, 99%)
7	**1g** (X = *p*-F)	**3g** (X = *p*-F, 99%)
8	**1h** (X = *p*-CF_3)	**3h** (X = *p*-CF_3, 99%)
9	**1i** (X = *p*-NO_2)	**3i** (X = *p*-NO_2, 92%)
10	**1j** (X = *p*-CO_2Me)	**3ja** (R = Me, 93%)
11	**1j** (X = *p*-CO_2Me)	**3jb** (R = Et, 94%)[b]
12	**1k**	**3k** (98%)
13	**1l**	**3l** (87%)
14	**1m**	**3m** (83%)

a) Isolated yields; b) Ni $(COD)_2$/2,2′-bipyridine (10 mol%), rt, 18 h.

Table 3 Scope of aliphatic *N*-acylpyrrole



Entry	Substrate	Product (Yield)[a]
1	**1n**	**3n** (80%)
2	**1o** (X = H)	**3o** (X = H, 91%)
3	**1p** (X = Me)	**3p** (X = Me, 88%)
4	**1q** (X = CF_3)	**3q** (X = CF_3, 89%)
5	**1r**	**3r** (85%)
6	**1s**	**3s** (76%)[b]
7	**1t**	**3t** (93%)[c]
8	**1u**	**3u** (83%)[d]
9	**1v**	**3v** (93%)[b]
10	**1w**	**3w** (64%)[b]

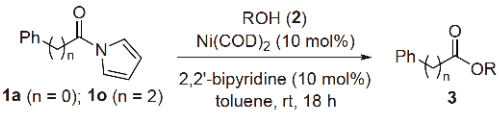
a) Isolated yields; b) Ni $(COD)_2$/2,2′-bipyridine (10 mol%), rt, 18 h; c) Ni $(COD)_2$/2,2'-bipyridine (10 mol%), rt, 5 h; d) Ni $(COD)_2$/2,2′-bipyridine (10 mol%), 50 °C, 3 h.

TBSOH (**2m**), and more acidic phenol **2n** failed to react (entries 12–14) even at a higher temperature (100 °C, entry 12). As demonstrated by the alcoholysis of both aromatic amide **1a** and aliphatic amide **1o** (entries 5b and 7b), the reaction can be run at gram-scale and the yields were basically maintained. By elevating the reaction temperature, the reaction time can be reduced whereas yield retained (Table 4, entry 6b).

To further extend the scope of the catalytic alcoholysis method, the methanolysis reactions of *N*-acylindole **1x**, *N*-acylcarbazole **1y**, *N*-acylpyrazole **1z**, and *N*-acylindazole **1aa** were briefly examined. As can be seen from Table 5, all proceeded smoothly to yield methyl benzoate in excellent yields (90%–96%).

To demonstrate the synthetic value of the method, we turned our attention to the transformation of heteroaromatic amide products of other synthetic methodologies. In 2010, Fu's group [9g] disclosed an asymmetric Suzuki cross-coupling of racemic α-halo-*N*-acylindoles to yield the corresponding α-aryl-*N*-acylindolines in high enantiomeric

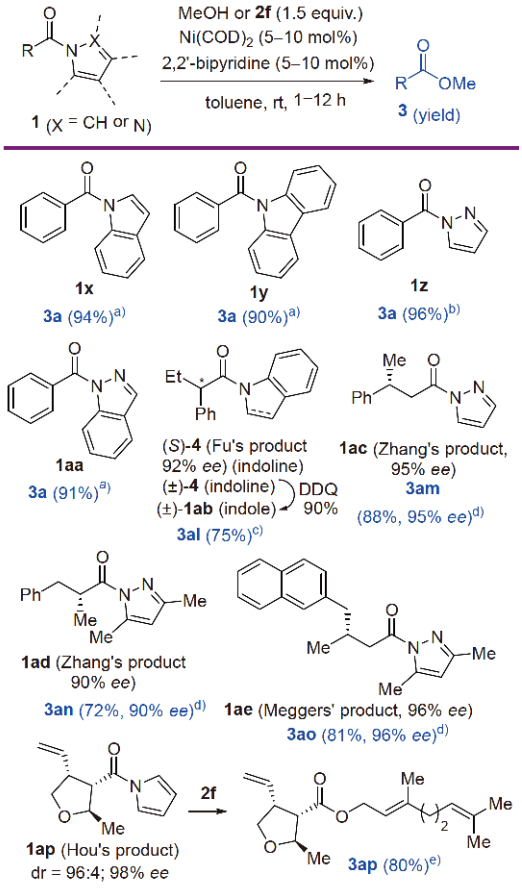
Table 4 Catalytic alcoholysis of *N*-acylpyrroles: scope of alcohol



Entry	Amide	R^2OH	Product (Yield) [a]
1	**1a**	EtOH **2b**	**3x** (90%)
2	**1a**	*n*-PrOH **2c**	**3y** (85%)
3	**1a**	BnOH **2d**	**3z** (84%)
4	**1a**	**2e**	**3aa** (60%)[b]
5a	**1a**	**2f**	**3ab** (87%)
5b	**1a** (1.00 g, 5.84 mmol)		**3ab** (1.28 g, 85%)
6a	**1o**	**2f**	**3ac** (83%)
6b	**1o**		**3ac** (85%)[c]
7a	**1o**	**2g**	**3ad** (92%, 99% *ee*)
7b	**1o** (1.00 g, 5.02 mmol)		**3ad** (1.40 g, 91%)
8	**1o**	**2h**	**3ae** (91%)
9	**1o**	**2i**	**3af** (75%)
10	**1o**	**2j**	**3ag** (98%)[b]
11	**1o**	**2k**	**3ah** (99%)[d]
12	**1o**	**2l**	**3ai** (0%)[d]
13	**1o**	TBS-OH **2m**	**3aj** (0%)
14	**1o**	**2n**	**3ak** (0%)

a) Isolated yields; b) T=80 °C, 18 h; c) T=50 °C, 1 h; d) T=100 °C, 18 h.

Table 5 Ni-Catalyzed alcoholysis of different types of amides and chiral amides produced by other asymmetric methodologies



a) $Ni(COD)_2$/2,2′-bipyridine (10 mol%), rt, 5 h; b) $Ni(COD)_2$/2,2′-bipyridine (5 mol%), rt, 1 h; c) $Ni(COD)_2$/2,2′-bipyridine (10 mol%), 80 °C, 12 h; d) $Ni(COD)_2$/2,2′-bipyridine (10 mol%), rt, 1 h; e) $Ni(COD)_2$/2,2′-bipyridine (10 mol%), rt, 12 h.

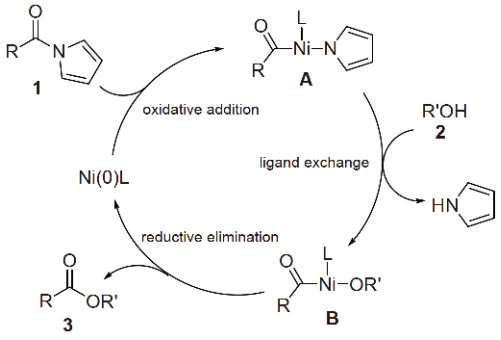
excess. To showcase the feasibility of our method to transform the products obtained by Fu's methodology, we selected one of his product (*S*)-**4** (Table 5) and prepared its racemic form (±)-**4** by another method (cf. Supporting Information online). Exposing the dehydration product (±)-**1ab** (obtained from (±)-**4**) via oxidation with 2,3-dicyano-5,6-dichlorobenzo- quinone (DDQ) to our catalytic methanolysis conditions produced racemic ester (±)-**3al** in 75% yield. Next, we addressed the alcoholysis of chiral *N*-acylpyrazoles **1ac** and **1ad**, synthesized by Zhang's rhodium/bisphosphine-thiourea-catalyzed enantioselective hydrogenation of the corresponding α,β-unsaturated *N*-acylpyrazoles [10b]. Ni-Catalyzed methanolysis of **1ac** and **1ad** under standard conditions proceeded smoothly to yield methyl esters **3am** and **3an** in 88% and 72% yield, respectively. Similarly, the catalytic esterification of chiral *N*-acylpyrazole **1ae**, prepared by Meggers' method [10c] featuring catalytic, enantioselective addition of alkyl radicals to alkenes via visible-light-activated photoredox catalysis with a chiral rhodium complex, produced ester **3ao** in 81% yield. It is worth noting that no racemization was observed in the last three methanolysis reactions, reflecting the mildness of our method. In 2017, Hou's group [9i] developed a highly dia-

stereo- and enantioselective palladium-catalyzed [3+2] cycloaddition of vinyl epoxides and α,β-unsaturated ketones. Subjecting one of his product (amide **1af**) to the alcoholysis with geraniol (**2f**) yielded the corresponding ester **3ap**, a potential substrate for the Ireland-Claisen rearrangement, in 80% yield.

To probe a plausible Lewis acidic effect of $Ni(COD)_2$ on the reaction, Lewis acids $Cu(OTf)_2$, $Zn(OTf)_2$, and BF_3•EtO were employed to replace $Ni(COD)_2$, respectively. In all cases, no expected ester **3a** was detected (Table 1, entries 20–22). Thus in the light of the computational study of Garg and Houk [6a] on the nickel-catalyzed direct conversion of tertiary benzanilides to aromatic esters, a plausible mechanism for the Ni-catalyzed alcoholysis of *N*-acylpyrrole-type tertiary amides is depicted in Scheme 2. The scenario involves an oxidation addition of Ni(0) into amide C–N bond to generate complex **A**. An exchange of ligand with an alcohol forms complex **B**, which then releases ester **3** through reductive elimination.

4 Conclusions

In summary, we have developed a versatile method for the catalytic transformation of *N*-acylpyrrole, *N*-acylpyrazole, *N*-acylindole, and *N*-acylindoline-type tertiary amides into the corresponding esters using only 1.5 equiv. of an alcohol. The method is amenable to both aromatic amides (with an aromatic or heteroaromatic ring attached to the carbonyl) and aliphatic amides on gram-scale. The observed good chemoselectivity and functional group tolerance vis-à-vis sensitive groups such as ketone, enone, and esters, as well as amides bearing a chiral center reflect the mildness of the reaction conditions. The synthetic applicability of this method was demonstrated by the smooth alcoholysis of chiral amides produced by several asymmetric methodologies developed by several groups. The ester formed from geraniol produced a chiral ester that might be used as a substrate for the Ireland-Claisen rearrangement.



Scheme 2 A plausible mechanism for the Ni-catalyzed alcoholysis of *N*-acylpyrrole-type tertiary amides (R=aryl; alkyl).

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Conflict of interest The authors declare that they have no conflict of interest.

Supporting information The supporting information is available online at http://chem.scichina.com and http://link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors

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