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Journal Name

COMMUNICATION

Ni-Catalyzed Chemoselective Alcoholysis of *N*-Acyloxazolidinones

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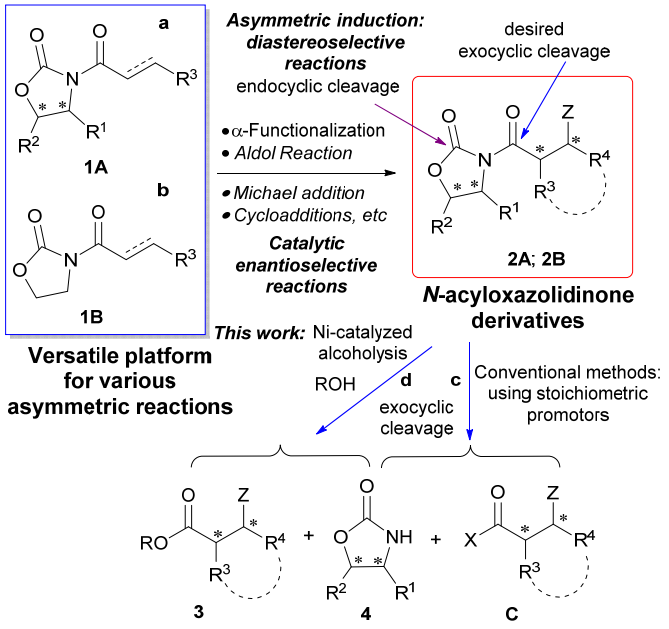
Although *N*-acyloxazolidinone-based (catalytic) asymmetric synthetic methodologies occupies an important position in modern organic synthesis, the catalytic cleavage of the (chiral)auxiliary remains underdeveloped. We report the Ni(cod)$_2$/bipyr.-catalyzed alcoholysis of *N*-acyloxazolidinones to deliver esters. The reaction is broad in scope for both *N*-acyloxazolidinone substrates and alcohol nucleophiles, and displayed good functional group tolerance and excellent chemoselectivity. A gram-scale methanolysis allowed the enantioselective synthesis of the C22-C26 segment of a close analogue of the potent immunosuppressant agent FK506.

25 years ago the concept of Green Chemistry was put forward.[1] In 1991, Trost advanced the concept of atom-economy and indicated that transition metal-catalyzed selective and economical methods represent an important starting point for the long-term goal of atom economy.[2] Today, catalysis is well-recognized as a key strategy for green chemistry.[3] Although tremendous progresses have been made over the past 25 years, and since the 21st century catalytic reactions have been honored three times by the Nobel Prizes for Chemistry,[4,5] current organic synthesis still largely relies on stoichiometric transformations as can be seen from the majority of steps of the reported total syntheses of natural products.[6]

Since the seminal work of Evans started from early 1980s,[7] chiral-non-racemic *N*-acyloxazolidinones **1A** have become a versatile platform for several important asymmetric transformations including α–functionalization of the carbonyl group, aldol addition, Michael addition, Diels-Alder reaction, etc (Scheme 1a).[8] Many of those reactions have been evolved from stoichiometric to catalytic.[9] Later on, many catalytic enantioselective addition reactions of achiral *N*-acyloxazolidinones **1B** have been developed (Scheme 1b).[10] In contrast to the significant progresses made on the catalytic reactions of *N*-acyloxazolidinones, the subsequent transformations of the resulting *N*-acyloxazolidinone derivatives (**2A**/ **2B**) by cleaving the (chiral) auxiliary rely largely on the use of stoichiometric amount of promotors[11-13] (Scheme 1c), catalytic version (Scheme 1d) remains underdeveloped. In this regard, Shi's rhodium/copper-catalyzed annulation of *N*-aroyloxazolidinones with alkynes[14] leading to indenones is a rare example. One of the most demanding transformations of *N*-acyloxazolidinone derivatives (**2A**/ **2B**) is undoubtedly the alcoholysis. The requirements for a synthetically useful alcoholysis reaction reside in good selectivity for the exocyclic



Scheme 1 Generic scheme for the diastereo- and enantio-selective reactions of *N*-acyloxazolidinones and subsequent transformations.

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† Electronic Supplementary Information (ESI) available: screened conditions, experimental procedures, compounds characterization data, ^{1}H and ^{13}C NMR spectra of prepared compounds, HPLC diagrams. See DOI: 10.1039/x0xx00000x

cleavage,[11] versatility for different product classes yielded from different asymmetric reactions, versatility for different alcohol nucleophiles, good functional group tolerance, and mild conditions to avoid racemization at stereogenic center.

Although several protocols for the alcoholysis of *N*-acyloxazolidinone derivatives (**2A/ 2B**) using an excess or stoichiometric quantities of base,[11] acid[12] or $Ti(OR)_4$[13] have been developed, very few examples of the chemoselective catalytic alcoholysis of *N*-acyloxazolidinones have been reported. In the course of the enantioselective total synthesis of altohyrtin C (spongistatin 2), Evans, and Sibi used rare-earth metal triflate $Sm(OTf)_3$ as an efficient catalyst for the methanolysis or aminolysis of an alkylated *N*-acyloxazolidinone.[15]

Subsequently, other Lewis acid-catalyzed alcoholysis methods have been reported by the groups of Fukuzawa (LaI_3),[16] Otera {[*t*-$Bu_2SnCl(OH)]_2$, $MgBr_2$ and $Sc(OTf)_3$},[17] and Collin (SmI_2),[18] respectively. Although some of those methods have found synthetic applications, they suffered from at least one drawback such as the need to use a large excess of alcohol nucleophile (e.g. as a solvent) or stoichiometric amount of Lewis acid,[16] limited scope for substrates (e.g. inapplicable to aldol adducts) or for alcohols (e.g. inapplicable to benzyl alcohol). Crimmins reported that *N*-acyloxazolidinethione auxiliaries are more easily cleaved.[19] Wu and co-workers has developed the DMAP-catalyzed removal of thiazolidinethione auxiliaries with benzyl alcohol.[20] In 2012, Saito reported a conceptually new method consisting of double molecular recognition of β-dicarbonyl derivatives with aminoorganoboron (AOB) complexes followed by *in situ* methanolysis.[21] Using this method, catalytic alcoholysis of *N*-acyloxazolidinones has been achieved regioselectively. However, since only a smaller alcohol can be recognized, the method is restricted to alcoholysis with MeOH. In addition, AOB complexes are not commercially available.

To the best of our knowledge, up to date, transition metal-catalyzed alcoholysis of *N*-acyloxazolidinones has hitherto been unknown.

In the field of organic catalytic transformation, due to the decline of natural resource of precious metals such as palladium and the associated price increases, the development of catalytic reactions based on inexpensive earth abundant first-row transition metals has attracted much attention.[22,23] In this context, the use of nickel in catalysis has emerged as a new frontier.[23] This is due, on one hand, to its cheapness (nickel costs about 0.05% of price of palladium and 0.01% of price of platinum), and on the other hand, to its multiple advantageous characteristics as compare with palladium.[23]

In connection with our interest in developing synthetic methodologies for the direct transformation of amides,[24] we disclosed very recently the first Ni/bis-NHC-catalyzed cross-coupling of *N*-acylpyrrole-type amides with arylboronic esters to deliver diarylketones.[25] As a continuation of those studies, we set to investigate the nickel-catalyzed alcoholysis of *N*-acyloxazolidin-2-ones, and report herein the results.[26]

We opted for **1a** as a model compound to investigate the reaction. A quick survey of catalytic systems showed that no reaction took place in the absence of a catalyst, neither in the presence of several Pd and Ni-catalytic systems (Table ESI-1, entries 1-7). To our delight, $Ni(cod)_2/PCy_3$-catalyzed reaction afforded the desired ester **3a** in 27% yield. Thus, $Ni(cod)_2$ was selected as a catalyst for the methanolysis of **1a**, and its combination with different ligands were examined. While low

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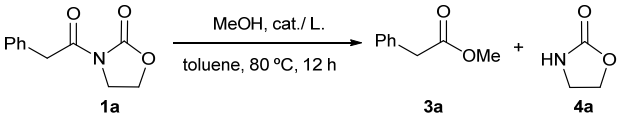
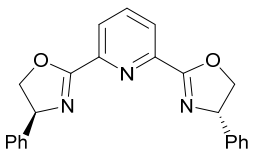
Table 1 Catalyst and ligand screening for the methanolysis of *N*-acyloxazolidinone **1a**[a]

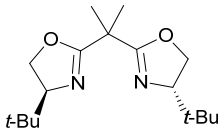


1a **3a** **4a**

Entry	Cat. (10 mol%)	Ligand (10 mol%)	Yield (%)[b]	
			3a	**1a**
1	$Ni(cod)_2$	PCy_3	27	65
2	$Ni(cod)_2$	PPh_3	17	77
3	$Ni(cod)_2$	P^nBu_3	34	56
4	$Ni(cod)_2$	Box**1**	24	75
5	$Ni(cod)_2$	Box**2**	34	62
6	**$Ni(cod)_2$**	**SIPr**	**94**	**trace**
7	$Ni(cod)_2$	IPr	87	10
8	$Ni(cod)_2$	SIMes	86	10
9	**$Ni(cod)_2$**	**IMes**	**95**	**trace**
10	$Ni(cod)_2$	1,10-phenanthroline	54	38
11	**$Ni(cod)_2$**	**2,2'-bipyr.**	**95 (91)[c]**	**trace**
12	**$NiCp_2$**	**2,2'-bipyr.**	**88**	**trace**
13 [d]	**$Ni(cod)_2$**	**2,2'-bipyr.**	**96 (92)[c]**	**trace**
14 [d]	**$Ni(cod)_2$**	**2,2'-bipyr.**	**95 (93)[c,e]**	**trace**
15 [d]	$Ni(cod)_2$	2,2'-bipyr.	94 [f]	trace
16 [d]	**$Ni(cod)_2$**	**2,2'-bipyr.**	**97 (92)[c,g]**	**trace**



Box **1**



Box **2**

[a] Reaction conditions: **1a**, 0.12 mmol; MeOH, 0.144 mmol (1.2 equiv); toluene, 0.25 M; 80 °C ;12 h; [b] Yield determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard; [c] Isolated yield; [d] $Ni(cod)_2$: 5 mol%; 2,2'-bipyr.: 10 mol%; [e] Reaction temperature: 25 °C; [f] Toluene: 0.80 M; [g] MeOH: 1.5 equiv.

yields (17-34%) were obtained with phosphine ligands and BOX [bis(oxazoline)] ligands (Table 1, entries 1-5), NHCs such as SIPr, IPr, SIMes, and IMes turned out to be effective ligands for the $Ni(cod)_2$-catalyzed methanolysis reaction (Table 1, entries 6-9). Despite the effectiveness of the $Ni(cod)_2$-NHC combination, the drawbacks associated with NHC ligands, including low stability, low atom-economy, multi-step preparation, and high price, prompted us to search for a cheaper while equally effective ligand. In this regard, 1,10-phenanthroline appeared to be promising (entry 10). Best result was obtained from the combination of $Ni(cod)_2$ with structurally simple, cheap and easily available 2,2'-bipyridine (2,2'-bipyr.), which afforded the desired ester **3a** in 95% yield (Table 1, entry 11). Interestingly,

the $NiCp_2$/2,2'-bipyr. catalyst system also furnished ester **3a** in 88% yield (Table 1, entry 12). To our satisfaction, reducing equivalents of $Ni(cod)_2$ from 10 mol% to 5 mol%, yield of the methanolysis was unaffected (96%)(Table 1, entry 13). After defining the optimal catalyst system, effects of solvent (see Table ESI-2, entries 10-13), reaction temperature (Table 1, entries 14), concentration (Table 1, 15), amount of catalyst and ligand (Table ESI-3), and equivalents of methanol (Table ESI-4) were examined, and the optimal conditions were established as: in the presence of 5 mol% of $Ni(cod)_2$, 10 mol% of 2,2'-bipyridine, treating *N*-acyloxazolidinone **1a** with 1.5 equiv of MeOH at rt (Table 1, entry 16).

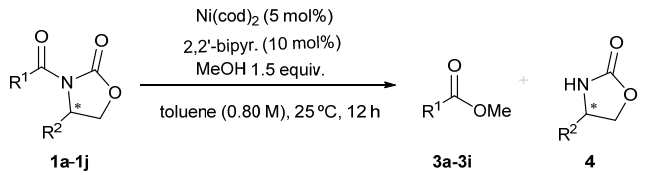
Under the optimized conditions, scope of *N*-acyloxazolidin-2-ones was surveyed (Table 2). An examination of achiral *N*-acyloxazolidinones showed that the reaction worked well with oxazolidinones bearing *N*-aliphatic acyl (**1a**-**1c**), *N*-α,β-unsaturated acyl (**1d**), *N*-aromatic acyl (**1e**, **1f**), electron-rich heteroaromatic acyl (**1g**, **1h**), as well as electron-deficient aromatic acyl groups (**1i**), providing the corresponding methyl esters **3a–3i** in 88–92% yields (Table 2, entries 1-9). Significantly, the catalytic alcoholysis of (*S*)-phenylglycinol-derived *N*-acyloxazolidinone **1j**, a sterically hindered substrate, also proceeded smoothly to afford methyl ester **3a** in 91% yield (Table 2, entry 10), along with recovered chiral auxiliary **4b** in 90% yield. To the best of our knowledge, catalytic alcoholysis of hindered *N*-acyloxazolidinones derived from phenylglycinol have not been reported.

Encouraged by these results, we next focused on the alcoholysis of chiral *N*-acyloxazolidinones (Table 3). For this purpose, *N*-acyloxazolidinone derivatives **2a-2j** were prepared from the corresponding *N*-acyloxazolidinones by alkylation.[7] Catalytic alcoholysis of *N*-acyloxazolidinone **2a** proceeded smoothly to give methyl (*S*)-2-methyl-3-phenylpropanoate (**3j**) in 85% yield. Taking into account that the starting **2a** used being an inseparable diastereomeric mixture in a 98: 2 ratio, racemization is less than 1% during the reaction (assuming that *N*-acyloxazolidinones are enantiopure). Methanolysis of allylic and propargylic derivatives **2b** and **2c** led to methyl esters **3k** and **3l** in 88% and 82% yield, respectively. Catalytic alcoholysis of *cis*-1-amino-2-indanol derived imide **2d** also proceeded smoothly to give ester **3j** in 89% yield. Next, we examined the methanolysis of 2-phenylpropanimides **2e**-**2g**, a sub-class of substrates known to be highly prone to racemization.[13a] The alcoholysis reactions yielded in 82-90% yields. In all cases, racemization were less than 2%. Similarly, methanolysis of **2h** gave **3o** in 83% yield with only 1.1% racemization. The reaction tolerated both electron-withdrawing (**2i**) and electron-donating groups (**2j**), delivering the corresponding methanolysis products **3p** and **3q**. For substrate **2j**, a higher loading of the catalyst $Ni(cod)_2$ enhanced the reaction, giving a better yield. To demonstrate that the chiral auxiliary can be recycled, we recovered chiral auxiliary **4c** in 85% yield from the reaction of **2e** (Table 3, entry 5). Its optical rotation data: $[\alpha]_D^{20}$ + 5.1 (*c* 1.05, EtOH) is comparable with that reported in the literature (ref. 21b): $[\alpha]_D$ + 4.9 (*c* 1.1, EtOH) for >99%*ee*.

After examining the asymmetric alkylation products, we proceeded to investigate the alcoholysis of *N*-acyloxazolidinone derivatives prepared by Diels-Alder reaction (**2k**, Table 4), asymmetric Michael addition (**2l**), tandem asymmetric Michael addition-α-alkylation (**2m**), and asymmetric aldol addition reaction (**2n-2p**)[9] (Table 4). The Diels-Alder adduct **2k** worked well under the established conditions, giving the methyl ester **3r** in 84% yield. Methanolysis of the asymmetric Michael addition product **2l** produced chiral ester **3s** in 83% yield. For sterically more hindered asymmetric Michael addition-α-methylation product **2m**, methanolysis gave methyl ester **3t** in 57% yield, which was slightly improved to 65% when IMes was used as a ligand. Moreover, unprotected asymmetric aldol adduct **2n** underwent smooth catalytic alcoholysis to deliver ester **3u** in excellent yield. The reaction of furan-2-yl derivative afforded methyl ester **3v** in 85% yield. Hindered aldol adduct bearing a naphthalen-1-yl group **2p** also reacted to yield methyl ester **3w** albeit in a modest yield (63%).

To further extend scope of the reaction, we addressed the catalytic alcoholysis using other alcohols than methanol (Table 5). When ethanol was used as an alcoholysis reagent, the reactions of **1b**, **1d**-**1f** proceeded at 80 °C for 12 h to give aromatic (**3x**, **3y**), α,β-unsaturated (**3z**) or aliphatic (**3aa**) ethyl esters in good yields (80-85%) (Table 5, entries 1-4). Benzyl esters, being convertible to the corresponding carboxylic acid by mild catalytic hydrogenolysis,[16,27] are synthetically more useful. However, catalytic benzylolysis of *N*-acyloxazolidinones is scarce and requires the use of either a large excess of (10 – 50 equiv) of benzyl alcohol or 1.0 equiv. of catalyst.[16,18] In our case, under the established conditions, benzyl ester **3ab** was obtained in 76% yield from **1e** (Table 5, entry 5). The Diels-Alder adduct **2k** also reacted smoothly, providing the benzyl ester **3ac**

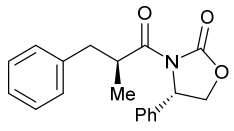
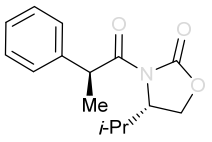
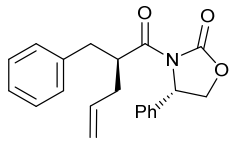
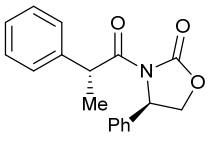
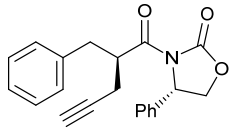
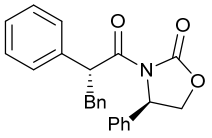
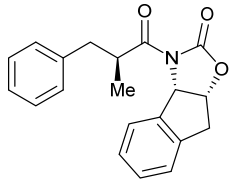
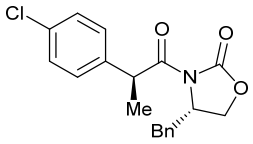
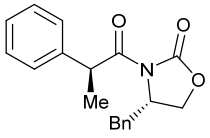
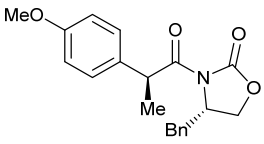
Table 2 Scope of the methanolysis of *N*-acyloxazolidinones[a]



Entry	Substrate	R^1	R^2	Yield (%)[b]
1	**1a**	Bn	H	**3a**: 92
2	**1b**	$Ph(CH_2)_2$	H	**3b**: 88
3	**1c**	*n*-$C_{11}H_{23}$	H	**3c**: 90
4	**1d**	(*E*)-PhCH=CH	H	**3d**: 85
5	**1e**	Ph	H	**3e**: 91
6	**1f**	2-naphthyl	H	**3f**: 90
7	**1g**	2-furyl	H	**3g**: 88
8	**1h**	2-thienyl	H	**3h**: 89
9	**1i**	3,4-Cl-Ph	H	**3i**: 90
10	**1j**	Bn	Ph (*S*)	**3a**: 91[c]

[a] Reaction conditions: **1a-1j**, 0.40 mmol; MeOH, 0.60 mmol (1.5 equiv); toluene, 0.80 M; 25 °C, 12 h ; [b] Isolated yield; [c] Chiral auxiliary **4b** recovered in 90% yield.

Table 3 Scope of the substrate obtained from asymmetric alkylation[a]

Entry	Substrate (*dr*)[b]/ Product (yield,[c] *ee*[d]) (stereoselectivity)[e]	Entry	Substrate (*dr*)[b]/ Product (yield,[c] *ee*[d]) (stereoselectivity)[e]
1	 **2a** (98:2 *dr*) / **3j**, 85%, 94.3% *ee* (99.1%)	6	 **2f** (99:1 *dr*) / **3m**, 88%, 97.4% *ee* (99.0%)
2	 **2b** (99:1*dr*) / **3k**, 88%, 97.9% *ee* (99.4%)	7	 **2g** (95:5 *dr*) / **3n**, 88%, 86.5% *ee* (98.2%)
3	 **2c** (98:2 *dr*) / **3l**, 82%, 95.6% *ee* (99.6%)	8	 **2h** (88:12 *dr*) / **3o**, 83%, 74.4% *ee* (98.9%)
4	 **2d** (98:2 *dr*) / **3j**, 89%, 93.8% *ee* (99.0%)	9	 **2i** (99:1 *dr*) / **3p**, 88%, 99.0% *ee* (>99.0%)
5	 **2e** (97:3 *dr*) / **3m**, 90%, 92.3% *ee* (98.9%) Recovered **4c** [R^3 = (*S*)-Bn], 85%[f]	10	 **2j** (99:1 *dr*) / **3q**, 72%,[g] 95.1% *ee* (99.0%)

[a] Reaction conditions: **2a-2j**, 0.30 mmol; MeOH, 0.45 mmol (1.5 equiv); toluene, 0.80 M; 25 ºC; 12 h; [b] Diastereomeric ratios of **2a-2j** were determined by ^{1}H NMR; [c] Yield of isolated product; [d] Enantiomeric excesses of **3j-3q** were determined by HPLC (see ESI); [e] Stereoselectivity of the reaction calculated by [100 × *er* of **3** / (*dr* of **2**]; [f] Recovered chiral auxiliary **4b**: $[\alpha]_D^{20}$ + 5.1 (*c* 1.05, EtOH), lit $[\alpha]_D$ + 4.9 (*c* 1.1, EtOH) for > 99% *ee*[21b]; [g] Ni(cod)$_2$, 10 mol%.

Table 4 Scope of substrates from diverse asymmetric reactions[a]

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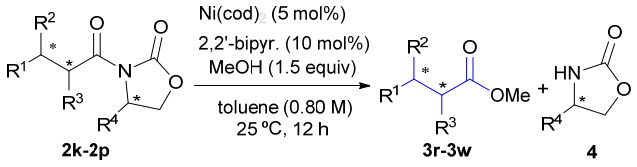
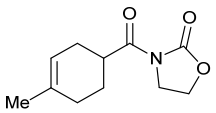
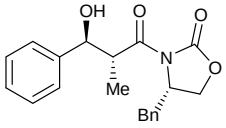
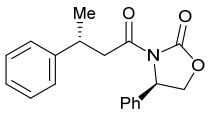
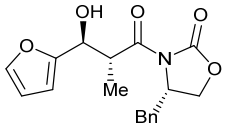
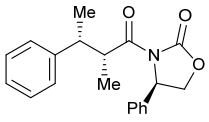
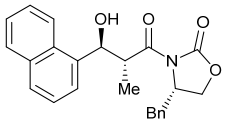


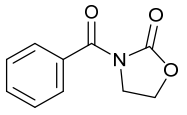
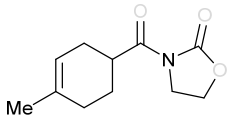
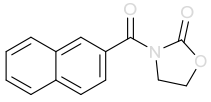
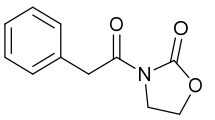
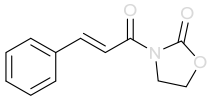
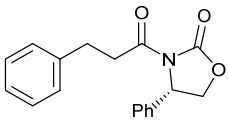
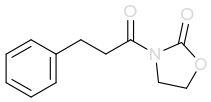
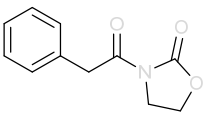
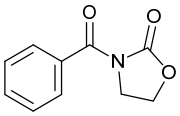
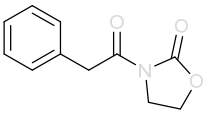
Entry	Substrate/ Product (yield)[b]	Entry	Substrate/ Product (yield)[b]
1	 **2k**/ **3r** (84%)	4	 **2n**/ **3u** (92%)
2	 **2l**/ **3s** (83%)	5	 **2o**/ **3v** (85%)
3	 **2m**/ **3t** (57%[c], 65%[d])	6	 **2p**/ **3w** (63%)

[a] Reaction conditions: **2k-2p**, 0.30 mmol; MeOH, 0.45 mmol (1.5 equiv); toluene, 0.80 M; 25 ºC, 12 h ; [b] Isolated yield; [c] Reaction temperature: 80 ºC; [d] Ligand: IMes (10 mol%), 80 ºC.

in 76% yield (entry 6). Furthermore, the catalytic alcoholysis of chiral *N*-acyloxazolidinone **2e** and **1k** with benzyl alcohol produced the benzyl ester **3af** and **3ae** in good to excellent yields (entries 7 and 8). The alcoholysis of **1a** with secondary alcohols cyclohexanol and isopropanol afforded the corresponding esters in moderate yields (55% and 62%, entries 9 and 10). Attempted alcoholysis of more hindered *tert*-butanol produced the corresponding ester in less than 5% yield with most of the starting material recovered.

To demonstrate the value of our method, the enantioselective synthesis of **9**, the C22-C26 segment (**9**) of a close analogue of the potent immunosuppressant agent FK506[28] was conducted (Scheme 3). Subjecting of **5**[29] to our newly developed Ni-catalyzed methanolysis conditions, run at a gram-scale, afforded methyl ester **6** in 61% yield. Condensation of methyl ester **6** with enolate generated *in situ* from *t*-butyl acetate gave *β*-ketoester **7** in 88% yield. Stereoselective reduction of **7** by Prasad's method[30] produced the all-*cis* diastereomer **8** as a single diastereomer in 90% yield. Treatment of **8** with 2 M NaOH in methanol provided the desired *β*-hydroxy-*δ*-lactone **9** in 80% yield. Lactone **9** has been integrated into an analogue of FK506.[28]

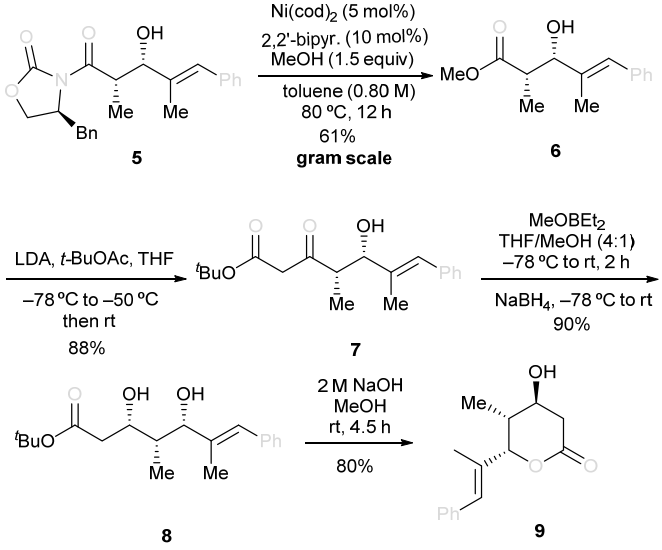
Table 5 Catalytic alcoholysis of *N*-acyloxazolidinones with other alcohols[a]

Entry	Substrate/ Product (yield)[b]	R^3	Entry	Substrate/ Product (yield)[b]	R^3
1	 **1e/ 3x** (85%)	Et	6	 **2k/ 3ac** (76%)	Bn
2	 **1f/ 3y** (82%)	Et	7	 **2e/ 3ad** (75%)	Bn
3	 **1d/ 3z** (80%)	Et	8	 **1k/ 3ae** (93%)	Bn
4	 **1b/ 3aa** (81%)	Et	9	 **1a/ 3af** (55%)	*c*-hex
5	 **1e/ 3ab** (76%)	Bn	10	 **1a/ 3ag** (62%)	*i*-Pr

[a] Reaction conditions: **1b**, **1d-1f**, **2k**, **2e, 1k**, , 0.30 mmol; R^3OH, 0.45 mmol (1.5 equiv); toluene, 0.80 M; 80 °C; 12 h ; [b] Isolated yield.

Conclusions

In summary, we have achieved the first earth-abundant and cheap transition metal-catalyzed alcoholysis of *N*-acyloxazolidinones to deliver esters, a key transformation for the application of the powerful *N*-acyloxazolidinone-based platform for asymmetric synthesis. The combination of cheap Ni
metal with structurally simple, cheap and easy to handle 2,2'-bipyridine as an effective ligand, and only 1.5 equivalents of the alcohol nucleophile used, rend the method expedient, economical and sustainable. Running under exceptionally mild conditions (room temperature for methanolysis, and 80 °C for alcoholysis with other alcohols), the reaction displayed excellent chemoselectivity, good functional group tolerance,



Scheme 2 Asymmetric synthesis of *δ*-lactone **9**.

and the chiral auxiliary can be recycled readily. Less than 1% racemization was observed for substrates bearing epimerizable chiral center, even for racemization-prone substrates, racemization was less than 2%. The method is versatile for *N*-acyloxazolidinones prepared from different asymmetric reactions that cover challenging aldol adducts and hindered *N*-acyloxazolidinones derived from phenylglycinol. Synthetically more useful yet more challenging alcoholysis using benzyl alcohol as a nucleophile can also be achieved. The yields were good to excellent for most substrates, and the reaction could be run at gram-scale. The successful application of the new methodology to the synthesis of the C22–C26 segment of a close analogues of the immunosuppressant agent FK506 will stimulate its application for the synthesis of other natural products and medicinal agents. Further expansion of this methodology is currently ongoing in our laboratory and the results will be reported in due course.

Conflicts of interest

There are no conflicts to declare.

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Ni-Catalyzed Chemoselective Alcoholysis of *N*-Acyloxazolidinones

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We report the first $Ni(cod)_2$/bipyr.-catalyzed alcoholysis of *N*-acyloxazolidinones to deliver esters.