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Selective deprotection and amidation of 2-pyridyl esters via N-methylation

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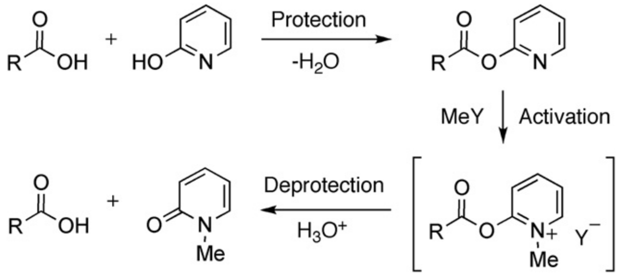
ABSTRACT

The 2-pyridyl residue serves as a protecting group for various carboxylic acids. The protecting group is selectively cleaved under mild conditions via N-methylation of the pyridyl group. During the deprotection process, the various functional groups as well as the other ester moieties remain intact. The *N*-methylated active esters can be subsequently transformed into amides.

1. Introduction

The protection of carboxylic acids is quite often required in the various stages of organic synthesis. The transformation of carboxylic acids into esters is a common method of protection[1] due to the widespread availability of the esterification methods and the stability of esters under a wide variety of reaction and workup conditions.[1] Despite the great advantages associated with the protection of carboxylic acids through esterification, acidic or basic conditions are necessary to cleave the ester bonds. Therefore, various substituted esters that can be deprotected under mild conditions using photolysis,[2] electrolysis,[3] hydrogenolysis,[4] reduction with metals,[5] and nucleophilic deprotections[6] have been developed.

We focused on a 2-pyridyl residue as a protecting group, as N-methylation of the pyridyl moiety proceeds easily to produce an active ester, which is subject to hydrolysis to give parent carboxylic acids (Scheme 1). The utility of the *N*-methylpyridinium moiety as a leaving group has been established and applied to the cyclopropanation of olefins,[7] benzylation of alcohols,[8] esterification,[9,10] and amidation[10] of carboxylic acids, and as a photolabile protecting group for carboxylic acids.[11] In this paper, we report the usefulness of 2-pyridyl esters for protection of carboxylic acids, which can be readily removed via N-methylation of the pyridyl group while leaving the remaining functional groups intact (Scheme 1). In addition, its application to the transformation of the pyridyl esters into carboxyamides through the same *N*-methylated active esters is described.



Scheme 1. A new protective group for carboxylic acids.

2. Results and discussion

As model substrates we employed benzoic acid derivatives **1a–d**,[12] 4-methoxycinnamic acid (**1e**), and adipinic acid monoallyl ester (**1f**).[13] Protection of these carboxylic acids with 2-hydroxypyridine was performed in the presence of WSC or DCC according to general procedures to give the corresponding 2-pyridyl esters **2a–f**[14,15] in up to 97% isolated yields. No decomposition was detected during the purification of these esters by silica gel column chromatography.

To remove the protecting group under neutral conditions, the pyridyl group was activated by methylation with methyl iodide. When the ester **2a** and methyl iodide in CH_3CN were heated under reflux for 47 h, no methylation occurred (Table 1, entry 1). The ester and an excess of MeI were heated in a sealed tube at 50 °C for 6 h followed by hydrolysis with H_2O/THF at room temperature to give deprotected carboxylic acid **1a** in 40% yield (entry 2). When the reaction was conducted at 100 °C, the yield was much improved

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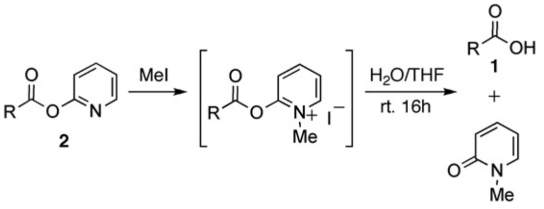
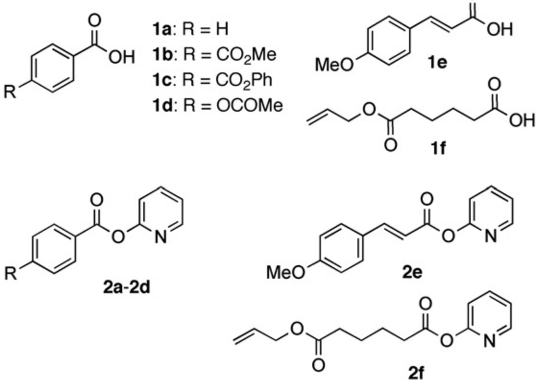
Table 1
Cleavage of 2-pyridyl esters with MeI



Entry	Substrate	Methylation conditions	Yield of **1** (%)
1	**2a**	MeI(3 equiv)/CH$_3$CN/reflux/47h	0[a]
2	**2a**	MeI(10 equiv)/50 °C/6 h[b]	40[a]
3	**2a**	MeI(10 equiv)/100 °C/6 h[b]	88[a] (78)[c]
4	**2b**	MeI(10 equiv)/100 °C/6 h[b]	94[a] (85)[c]

[a] Determined by ^{1}H NMR spectra using nitromethane as an internal standard.
[b] The reaction was carried out in a sealed tube.
[c] Isolated yield.

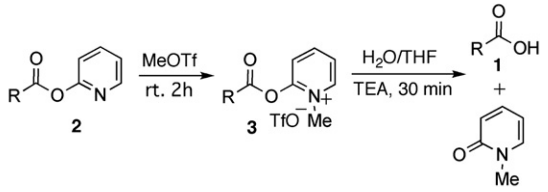
(entry 3). In the case of **2b**, which has another ester moiety in the same molecule, a selective deprotection of the pyridyl ester proceeded in high yield (entry 4).



Although activation by N-methylation with methyl iodide has been used for the deprotection of 2-(2-pyridyl)ethyl ester[16] and 2-(2-pyridyl)ethoxy carbamate,[17] a nucleophile, such as dimethylamine was required to cleave the ester bonds, suggesting that the *N*-methylpyridinium intermediate using in the present method has a much higher reactivity.

Next, MeOTf was employed as a N-methylation reagent. The treatment of **2a** with 1.1 equiv of MeOTf in toluene at room temperature gave the pyridinium salt **3a** as a white precipitate in 98% yield, the stirring of which in H$_2$O/THF in the presence of Et$_3$N for 0.5 h gave **1a** quantitatively together with *N*-methylpyridone (Table 2, entry 1). Methylation of the pyridyl esters **2b** and **2d**, possessing a methyl ester and an acetoxy moiety yielded **3b** and **3d**, respectively, the hydrolysis of which gave **1b** and **1d** in high yields (entries 2 and 4). These results indicate that the electronic properties of the substituent gave little effect on this reaction. The intermediary pyridinium salts **3a**, **3b**, and **3d**, the structures of which were fully identified by ^{1}H NMR and MS spectra, were stable in a refrigerator for a few days. The methylation of **2c** was carried out in CHCl$_3$ due to its lower solubility in toluene. As the methylation of **2c**, **2e**, and **2f** produced no precipitation, the reaction mixtures were hydrolyzed without isolation of the pyridinium salts (entries 3, 5, and 6). A key feature in this deprotection is that the other functional groups in the same molecules, such as methyl, phenyl, and allyl ester groups, and acetoxy, methoxy, and double bond moieties remain intact during these deprotection processes.

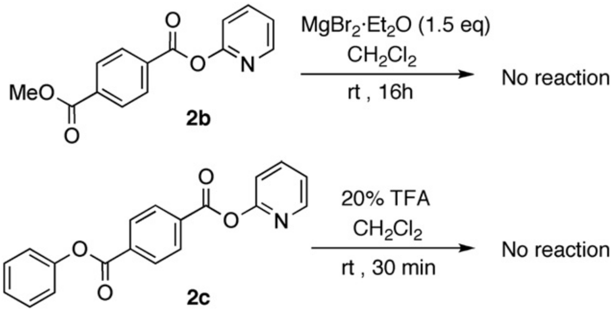
Table 2
Cleavage of 2-pyridyl esters with MeOTf



Entry	Ester	Solvent	Product	Yield of **3**[a] (%)	Yield of **1**[b] (%)
1	**2a**	Toluene	**3a**	98	96 (88)[a]
2	**2b**	Toluene	**3b**	94	85 (75)[a]
3	**2c**	CHCl$_3$	**3c**	ND	80 (72)[a]
4	**2d**	Toluene	**3d**	95	88 (76)[a]
5	**2e**	Toluene	**3e**	ND	97 (90)[a]
6	**2f**	Toluene	**3f**	ND	91 (74)[a]

[a] Isolated yields.
[b] Determined by ^{1}H NMR spectra using nitromethane as an internal standard.

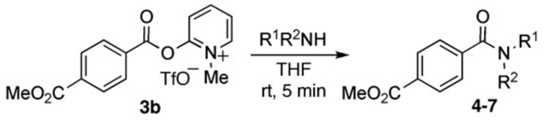
The stability of the pyridyl esters was examined under acidic conditions. The stirring of a solution of pyridyl ester **2b** in the presence of MgBr$_2$·OEt$_2$ (1.5 equiv) overnight resulted in the recovery of **2b**. Treatment of 20% TFA in CH$_2$Cl$_2$ for 0.5 h at room temperature resulted in no reaction with the recovery **2c** (Scheme 2). Also during the workup with 5% NaHCO$_3$ solution, no hydrolysis was observed. Although the 2-pyridyl esters of amino acids have been suggested to have higher reactivities toward hydrolysis than do general esters,[18] the present results show the utility of the pyridyl esters in organic synthesis.

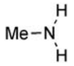
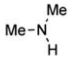
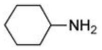
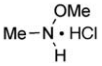


Scheme 2. Stability of esters under acidic conditions.

The isolated pyridinium salts **3a**, **3b**, and **3d** shown in Table 2 have a similar structure to the active esters reported by Mukaiyama et al[10] for the synthesis of carboxyamides, which prompted us to examine the conversion of **3b** into amides **4**-**7**[19] (Table 3). The reaction of the pyridinium salt **3b** with methylamine and dimethylamine for 5 min at room temperature gave the corresponding amides **4** and **5** in quantitative yields. Sterically hindered cyclohexylamine also served as a nucleophile to give amide **6**. In the reaction with electron deficient *N*,*O*-dimethylhydroxyamine hydrochloride, the Weinreb amide **7** was produced. These results demonstrate that the 2-pyridyl esters can be converted into various amides via activation of the protecting group. It has been reported that pyridyl esters produced from amino acids can be employed as active esters for peptide synthesis.[18] In addition, the pyridyl esters are postulated as intermediates in the acylation and amidation of carboxylic acids by di-2-pyridyl carbonate or *O*,*O*′-di(2-pyridyl) thiocarbonate.[20] It should be noted that the direct amidation of the pyridyl ester **2b** with *N*,*O*-dimethylhydroxyamine hydrochloride is much slower than that of **3b**; under the same reaction condition, amide **7** was obtained in 41% yield after stirring for 1 h. Therefore, the present method using

Table 3
Application to the synthesis of amides



Entry	Amine	Product	Yield (%)
1		**4**	>99[a] (94)[b]
2		**5**	>99[a] (95)[b]
3		**6**	99[a] (80)[b]
4		**7**	>99[a] (84)[b]

[a] Determined by ^{1}H NMR spectra using nitromethane as an internal standard.
[b] Isolated yield.

N-methylated pyridyl esters would be more effective for the formation of a wide variety of amides.

The significant effect of N-methylation on the activation of esters can be explained by DFT calculations of molecules **A** and **B**, which are models of the pyridyl ester and corresponding *N*-methylpyridinium, respectively (Fig. 1). A comparison of the optimized geometries for **A** and **B** calculated at the B3LYP/6-31G* level[21] clearly shows significant geometrical differences between them. The acetyl moiety of molecule **A** is situated perpendicular to the pyridine plane, whereas the acetyl moiety and the pyridinium ring in **B** are coplanar. The C(O)–O bond length of **B** (1.442 Å) is much longer than that of **A** (1.391 Å), whereas the C–O bond length of **B** (1.342 Å) is much shorter than that of **A** (1.374 Å). These geometrical features suggest that the resonance structures of **A2** and **B2** have significant contribution in molecules **A** and **B**, respectively. The resonance mode in **A** is the same as that observed in general esters, whereas the resonance mode in **B** is significantly different from that of **A** and suggests that the *N*-methylpyridyl moiety has good leaving properties. This characteristic resonance mode in **B** is thought to be responsible for its higher reactivity.

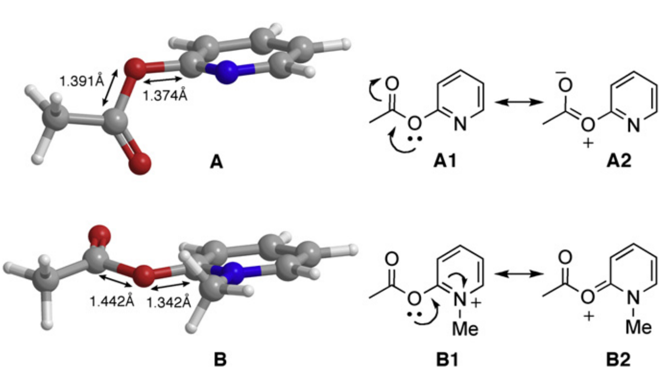


Fig. 1. Optimized geometries for the model compounds **A** and **B** with resonance structures.

3. Conclusion

We demonstrated that the 2-pyridyl residue serves as a new protective group for various carboxylic acids and can be readily removed via N-methylation of the pyridyl group without affecting the other functional groups. This method enables the selective deprotection of polyester compounds under mild conditions. In addition, the pyridyl esters can be converted into their corresponding amides via *N*-methylated pyridinium intermediates.

4. Experimental

4.1. General

Melting points were determined with a Yanaco model MP microscope. Column chromatography was carried out using Merck silica gel 60 N or Florisil (100–200 mesh). TLC was carried out on a Merck silica gel 60 PF_{254}. IR spectra were taken on PERKIN–ELMER SPECTRUM 2000 and SHIMADZU FTIR-8700 spectrometer as KBr pellets. NMR spectra were recorded on JEOL EX-400 spectrometer. ^{1}H NMR spectra were obtained at 400 MHz as dilute solution in $CDCl_3$, and the chemical shifts were reported relative to internal TMS. The yields were determined by ^{1}H NMR spectra using nitromethane as an internal standard. High- and Low-resolution mass spectra were recorded on AccuTOF GCv (JEOL) equipped with FD probe or AccuTOF TLC (JEOL) with DART ionization mode. DFT calculations were performed by using Spartan 06'.

4.2. General procedure for the preparation of 2-pyridyl esters 2a–f

To a solution of **1** (0.47 mmol), 2-hydroxypyridine (0.47 mmol), and 4-dimethylaminopyridine (0.05 mmol) in dry dichloromethane (2.3 mL) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (0.51 mmol). The mixture was stirred at room temperature for 4 h under nitrogen atmosphere. The reaction mixture was concentrated, and the residue was purified by silica gel column chromatography (hexane/ethyl acetate=3/1) to give **2** as a white solid.

4.2.1. Pyridin-2-yl benzoate ***2a****.* White crystal: 91% yield. The spectral data were in agreement with those reported.[14a,b]

4.2.2. 1-Methyl 4-pyridin-2-yl benzene-1,4-dicarboate ***2b****.* White crystal: 81% yield. The spectral data were in agreement with those reported.[14c]

4.2.3. 1-Phenyl 4-pyridin-2-yl benzene-1,4-dicarboate ***2c****.* White crystal (98.8 mg, 66%); mp 176–178 °C; IR (KBr) 3077, 1739, 1590, 1435, 1266, 1204, 1069, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (dd, J=1.2, 4.8 Hz, 1H), 8.37 (d, J=8.8 Hz, 2H), 8.34 (d, J=8.8 Hz, 2H), 7.88 (ddd, J=1.2, 7.2, 9.2 Hz, 1H), 7.46 (t, J=7.2 Hz, 2H), 7.33–7.29 (m, 2H), 7.27–7.24 (m, 3H). MS m/z 320 ((M+H)$^+$, 100%), HRMS calcd for $C_{19}H_{14}NO_4$ 320.09228 (M+H)$^+$, found 320.09209.

4.2.4. Preparation of 4-acetoxy-benzoic acid pyridine-2-yl ester ***2d****.* To a solution of **1d** (155 mg, 0.86 mmol) and 2-hydroxypyridine (90.6 mg, 0.94 mmol) in dry dichloromethane (2.8 mL) were added *N*,*N*-diisopropylethylamine (161 mL, 0.94 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (181 mg, 0.94 mmol). The solution was stirred at room temperature overnight under nitrogen atmosphere and concentrated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate=2/1) to give **2d** as white solid (86.9 mg, 34%); mp 77–78 °C; IR (KBr) 3062, 1743, 1733, 1602, 1591, 1432, 1212, 1200, 1163 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, J=1.6, 4.8 Hz, 1H), 8.26 (d, J=8.8 Hz, 2H), 7.84 (dt, J=1.6, 8.0 Hz, 1H), 7.29–7.26 (m, 1H), 7.26 (d, J=8.8 Hz, 2H), 7.21 (d, J=8.0 Hz, 1H), 2.34 (s, 3H). MS m/z 258 ((M+H)$^+$, 57%), HRMS calcd for $C_{14}H_{12}NO_4$ 258.07663 (M+H)$^+$, found 258.07584.

4.2.5. (E)-Pyridin-2-yl 3-(4-methoxyphenyl)prop-2-enoate ***2e****.* White crystal: 69% yield. The spectral data were in agreement with those reported.[14d]

4.2.6. Preparation of 1-allyl 6-pyridin-2-yl hexanedioate ***2f****.* To a solution of **1f** (102 mg, 0.54 mmol), 2-hydroxypyridine (50.0 mg, 0.54 mmol), and 4-dimethylaminopyridine (6.5 mg, 0.054 mmol) in dry dichloromethane (1.8 mL) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (113 mg, 0.59 mmol). The solution was stirred for 3 h at room temperature under nitrogen atmosphere. The reaction mixture was washed with 0.5 N hydrochloric acid and saturated sodium hydrogen carbonate successively. The organic layer was dried over magnesium sulfate and filtered. The filtrate was concentrated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate=2/1) to give **2f** as an oil (77.5 mg, 55%); IR (neat) 2945, 2875, 1732, 1649, 1610, 1601, 1592, 1469, 1433, 1375, 1123, 994, 926 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, J=1.2, 4.8 Hz, 1H), 7.79 (dt, J=1.2, 8.0 Hz, 1H), 7.23 (ddd, J=1.2, 4.8, 8.0 Hz, 1H), 7.07 (d, J=8.0 Hz, 1H), 5.89–5.93 (m, 1H), 5.32 (dt, J=1.2, 17.6 Hz, 1H), 5.24 (dd, J=1.2, 10.4, 1H), 4.59 (d, J=7.2 Hz, 2H), 2.65 (t, J=7.2 Hz, 2H), 2.38–2.43 (m, 2H), 1.77–1.82 (m, 4H). MS m/z 264 ((M+H)$^+$, 100%), 191 (64), HRMS calcd for $C_{14}H_{18}NO_4$ 264.12358 (M+H)$^+$, found 264.11909.

4.3. General procedure for the deprotection with MeI

A mixture of pyridyl ester and methyl iodide (4.3 mL for 1 mmol) was heated in a sealed tube at 100 °C for 6 h. After cooling to room temperature, excess methyl iodide was evaporated. Tetrahydrofuran (4.3 mL for 1 mmol) and water (1.4 mL for 1 mmol) were added to the residue, and the solution was stirred at room temperature for 16 h. Evaporation of the solvent and purification by general method gave carboxylic acid.

4.4. General procedure for the synthesis of pyridinium salt 3a–f with MeOTf and their hydrolysis

To an ice-cooled solution of **2a**–**f** in dry toluene (1.4 mL for 1 mmol) was added methyl trifluoromethanesulfonate (1.1 equiv). The mixture was stirred at room temperature. Pyridinium salts **3a**, **3b**, and **3d** were precipitated as white solids within a few minutes, which were corrected by filtration. The solid was dissolved in a 2.5:1 mixture of THF/H_2O in the presence of Et_3N (2 equiv) and the solution was stirred for 5 min at room temperature. After the solvent was removed, 10% citric acid solution was added to the residue, which was extracted with chloroform three times. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated to give a crude product. This was purified by preparative TLC using a 1:1 mixture of ethyl acetate and dichloromethane as an eluent solvent to give a pure carboxylic acid. On the other hand, **3c**, **3e**, and **3f** were hydrolyzed without isolation to give corresponding carboxylic acids, which were purified as described above. The isolated yields and NMR yields are listed in Table 2.

4.4.1. 2-Benzoyloxy-1-methylpyridinium triflate ***3a****.* White solid; 98% yield; mp 84–85 °C; IR (KBr) 3107, 3073, 1778, 192, 1262, 1227, 1159, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, J=6.4 Hz, 1H), 8.55 (t, J=7.6 Hz, 1H), 8.25 (d, J=7.2 Hz, 2H), 7.99 (d, J=8.4 Hz, 1H), 7.92 (t, J=6.8 Hz, 1H), 7.80 (t, J=7.2 Hz, 1H), 7.62 (t, J=7.8 Hz, 2H), 4.41 (s, 3H). MS m/z 214 ((M−TfO$^-$)$^+$, 100%), HRMS calcd for $C_{13}H_{12}NO_2$ 214.08680 (M−TfO$^-$)$^+$, found 214.09302.

4.4.2. 2-(4-Methoxycarbonyl-benzoyloxy)-1-methylpyridinium triflate ***3b****.* White solid; 94% yield; mp 132–133 °C; IR (KBr) 3100, 3068, 2959, 1775, 1722, 1711, 1305, 1262 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (dd, J=6.4, 2.0 Hz, 1H), 8.55 (dt, J=8.6, 2.0 Hz, 1H), 8.34 (d, J=8.8 Hz, 2H), 8.28 (d, J=8.8 Hz, 2H), 8.02 (d, J=7.6 Hz, 1H), 7.92 (t, J=7.2, 1H), 4.47 (s, 3H), 4.01 (s, 3H). MS m/z 272 ((M−TfO$^-$)$^+$, 100%), HRMS calcd for $C_{15}H_{14}NO_4$ 272.09228 (M−TfO$^-$)$^+$, found 272.09633.

4.4.3. 2-(4-Acetoxy-benzoyloxy)-1-methylpyridinium triflate ***3d****.* White solid; 95% yield; mp 108–109 °C; IR (KBr) 3098, 3080, 1784, 1760, 1277, 1158, 1000 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, J=6.0 Hz, 1H), 8.53 (t, J=7.6 Hz, 1H), 8.30 (d, J=8.8 Hz, 2H), 7.98 (d, J=8.8 Hz, 1H), 7.91 (t, J=6.8 Hz, 1H), 7.38 (d, J=8.8 Hz, 2H), 4.43 (s, 3H), 2.36 (s, 3H). MS m/z 272 ((M−TfO$^-$)$^+$, 100%), HRMS calcd for $C_{15}H_{14}NO_4$ 272.09228 (M−TfO$^-$)$^+$, found 272.08481.

4.5. Examination of the stability of pyridyl ester 2b under acidic conditions

To a solution of **2b** (19.3 mg, 0.07 mmol) in dry dichloromethane, magnesium bromide etherate (30.2 mg, 0.12 mmol) was added at 0 °C. The solution was stirred at room temperature for 22 h under nitrogen atmosphere. A saturated sodium hydrogen carbonate solution was added to the mixture and the product was extracted with dichloromethane. The organic layer was dried over magnesium sulfate and filtered. Concentration of the filtrate afforded recovered **2b** (18.6 mg).

4.6. Examination of the stability of pyridyl ester 2c under acidic conditions

Trifluoroacetic acid (40 μl, 0.53 mmol) was added to a solution of **2c** (6.8 mg, 0.02 mmol) in dry dichloromethane (160 μl). After stirring for 30 min at room temperature under nitrogen atmosphere, the reaction mixture was quenched by triethylamine. The solution was extracted with dichloromethane and washed with saturated sodium hydrogen carbonate and brine successively. Evaporation of the solvent afforded recovered **2c** (6.4 mg).

4.7. General procedure for conversion of pyridinium salt 3b into amides 4–7

To a solution of **3b** in dry tetrahydrofuran was added amine at room temperature. The solution was stirred for 5 min, and the solvent was evaporated to give a crude product, which was purified by preparative TLC to give a pure amide. The isolated yields and NMR yields are listed in Table 3.

4.7.1. Conversion of pyridinium salt ***3b*** *into amides* ***4****.* To a solution of **3b** (14.4 mg, 0.035 mmol) in dry tetrahydrofuran (0.35 mL) was introduced gaseous methylamine, which was generated from 40% $MeNH_2$ solution by heating at 60 °C, by bubbling at room temperature. The solution was stirred for 5 min and the solvent was evaporated to give a crude product, which was purified by preparative TLC using a 1:1 mixture of ethyl acetate and dichloromethane as an eluent solvent to give pure amide **4** (6.3 mg, 94%).

4.7.2. Conversion of pyridinium salt ***3b*** *into amide* ***5****.* To a solution of **3b** (14.3 mg, 0.034 mmol) in dry tetrahydrofuran (0.35 mL) was introduced gaseous dimethylamine, which was generated from Me_2NH solution by heating at 60 °C, by bubbling at room temperature. The solution was stirred for 5 min and the solvent was evaporated to give a crude product, which was purified by preparative TLC using a 1:1 mixture of ethyl acetate and dichloromethane as an eluent solvent to give pure amide **5** (6.7 mg, 95%).

*4.7.3. Conversion of pyridinium salt **3b** into amide **6**.* To a solution of **3b** (10.0 mg, 0.024 mmol) in dry tetrahydrofuran (0.1 mL) was added cyclohexylamine (11.0 μl, 0.095 mmol) at room temperature. The solution was stirred for 5 min, and the solvent was evaporated to give a crude product, which was purified by preparative TLC using a 1:1 mixture of ethyl acetate and dichloromethane as an eluent solvent to give pure amide **6** (5.0 mg, 80%).

*4.7.4. Conversion of pyridinium salt **3b** into amide* **7**. To a solution of **3b** (24.3 mg, 0.058 mmol) in dry tetrahydrofuran (0.16 mL), *N*,*O*-dimethylhydroxyamine hydrochloride (22.5 mg, 0.23 mmol) was added at room temperature. The solution was stirred under nitrogen atmosphere for 5 min, and the solvent was evaporated to give a crude product, which was purified by preparative TLC using a 1:1 mixture of hexane and ethyl acetate as an eluent solvent to give pure amide **7** (10.8 mg, 84%).

Acknowledgements

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Supplementary data

Supplementary data (^{1}H NMR spectra and details of structural optimization) associated with this article can be found, in the online version, at doi:10.1016/j.tet.2010.09.016. These data include MOL files and InChIKeys of the most important compounds described in this article.

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