Synthetic Communications®, 40: 3669–3677, 2010

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910903531615

Taylor & Francis
Taylor & Francis Group

A NOVEL AND EFFICIENT REACTION OF IMIDAZOLIDIN-2-ONE AND *N*-ACYLBENZOTRIAZOLES: A FACILE SYNTHESIS OF 1-ACYLIMIDAZOLIDIN-2-ONE

Jianjun Li, Yan Sun, Zhiwei Chen, and Weike Su
Key Laboratory of Pharmaceutical Engineering of Ministry of Education, College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou, P.R. China

Acylation of imidazolidin-2-one with readily available* N*-acylbenzotriazoles, in the presence of K_2CO_3, produced 1-acylimidazolidin-2-ones and* N,N′*-diacyl-imidazolidin-2-one in moderate to good yields. The utilization of* N*-acylbenzotriazoles which make the reaction simple and mild, may be especially advantageous when the corresponding acid chlorides are not stable or not easily prepared. It's also an example of the reaction of* N*-acylbenzotriazoles and amide.

Keywords: Acylation; *N*-acylbenzotriazoles; 1-acylimidazolidin-2-one; amides

INTRODUCTION

1-Acylimidazolidin-2-ones are important derivates of imidazolidin-2-one and have received considerable attention due to their diverse activities as chemotherapeutic agent for biological process.[1] Moreover, they are also important class of intermediates in the field of drugs and pharmaceuticals.[1c–e] Most derivatives occur widely in the synthesis of biologically active compounds such as penicillin, insecticide and other pesticide.[2]

General procedures of the synthesis of 1-acylimidazolidin-2-one were the interaction of imidazolidin-2-one with the activated derivatives of acids, acyl chloride or acetic anhydride[3] in the presence of base.[4] The use of acyl chloride and acetic anhydride makes the conditions rather acidic. Strong base, such as NaH is needed in some procedure to promote the reaction, which makes the conditions harsh. Direct acylation of imidazolidin-2-one with acid chlorides without base has also been used by our group[5] to form 1-acyl-imidazolidin-2-one. The above methods offer many useful synthetic procedures. However, these methods have certain limitations more or less such as: lower yield, instability, harsh reaction conditions and environment unfriendly.

Received May 16, 2008.
Address correspondence to Weike Su, Key Laboratory of Pharmaceutical Engineering of Ministry of Education, College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou 310014, P.R. China. E-mail: suweike@zjut.edu.cn

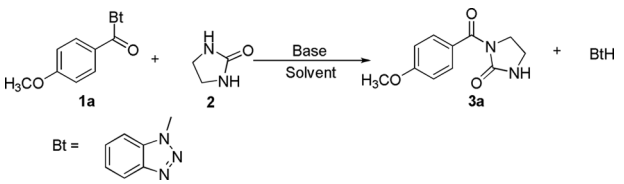
N-acylbenzotriazoles are efficient neutral acylation agents[6] and can be easily prepared from carboxylic acids in one pot.[7] Recently, Katritzky has disclosed efficient acylations using *N*-acylbenzotriazoles, which are used widely in organic synthesis, such as *O*-acylation of aldehydes,[8] alcohols,[9] and steroids,[10] *C*-acylation,[11] *N*-acylation of amines[7a] and sulfamide,[12] and syntheses of some biologically active synthetic compounds.[13] More recently, *N*-aroylation of substituted indoles with *N*-aroylbenzotriazoles under base conditions has been reported.[14] However, few methods have been reported for the acylation of imides from *N*-acylbenzotriazoles to our best knowledge.

Recently much attention has been paid to green chemistry. The sustainable environment needs clean procedures which can avoid using toxic organic reagents. In continuation with our previous study and the acylation of amide with *N*-acylbenzotriazoles, we now present a new method using *N*-acylbenzotriazoles as *N*-acylation agents to prepare 1-acyl-imidazolidin-2-ones. The use of crystalline *N*-acylbenzotriazoles can avoid strong acid and base conditions. This method is especially useful when the corresponding acyl chloride is unstable or unavailable. And the procedures are mild and environment friendly in good yields.

The starting *N*-acylbenzotriazoles (**1**) were prepared according to the literature procedure[7] in good yields. R^1 can be alkyl, aryl and heterocyclic groups, including the case where the corresponding acyl halide is not stable, for instance furyl halide.

Our first attempt was carried out by using 4-methoxybenzoylbenzotriazoles as model substrates. A series of bases were investigated to promote this reaction (Scheme 1) and the results are listed in Table 1. In the study, we undertook the reaction in the presence of base (1 equiv) at room temperature (Table 1, entries 1–5) or at 80 °C (Table 1, entry 1, entries 6–10) for 2 hours. It was found that NaOH, CH_3ONa could not promote the reaction efficiently (Table 1, entries 1–2). In the presence of triethylamine, we obtained low yield of **3a** (Table 1, entry 3). When NaH was used as base, the yield was increased to 83%, but the conditions were harsh. While K_2CO_3 was used, the reaction proceeded smoothly in 82% at the same conditions (Table 1, entry 7). Furthermore, we found that the amount of base could also affect the yield of the product. When the mole ratio of imidazolidin-2-one and K_2CO_3 were 1:0.5, 1:0.75, 1:1, 1:2, the yield were 51%, 76%, 82%, and 78%, respectively (Table 1, entries 7–10).

We also examined some other solvents using K_2CO_3 as base. The results were showed in Table 2. From Table 2 we found that the reaction is affected by solvents. No product appeared when stirred at room temperature for 3 h. Increasing the temperature to 80 °C, trace of **3a** was detected in THF/H_2O, $CHCl_3$ and EtOH (Table 2,



Scheme 1. The *N*-acylation of **1a** and imidazolidin-2-one.

Table 1. Base effect on the reaction of 4-methoxy-benzoylbenzotriazoles and imidazolidin-2-one[a]

Entry	Base	Mole ratio[b]	Solvent	Time (h)	Yield (%)[c]
1	NaOH	1:1	H_2O	2	trace
2	CH_3ONa	1:1	CH_3OH	2	trace
3	$(C_2H_5)_3N$	1:1	THF	2	24
4	NaH	1:1	THF	2	83
5	NaH	1:1	Toluene	2	79
6	K_2CO_3	1:1	THF	2	47
7	K_2CO_3	1:1	Toluene	2	82
8	K_2CO_3	1:0.5	Toluene	5	51
9	K_2CO_3	1:0.75	Toluene	2	76
10	K_2CO_3	1:2	Toluene	2	78

[a]The reactions were all carried out at 80 °C, except that entries 2, 3, 4, and 6 were at reflux temperature.
[b]The mole ratio was **2**: Base.
[c]Isolated yield.

entries 1–3). However, increasing the reaction temperature made the yield improved obviously in other solvents selected (Table 2, entries 4–9). Toluene was found to give maximum yield followed by dioxane.

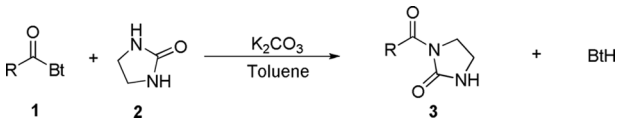
In light of this, subsequent studies were carried out under the optimized conditions: in toluene at 80 °C in the presence of K_2CO_3 as the base.

On the basis of the above results, this process was then extended to other substituted *N*-acylbenzotriazoles to investigate the scope and generality (Scheme 2). The results are summarized in Table 3. Both short chains and long chains alkyl, substitutive aryl containing electron-donating as well as electron-withdrawing groups *N*-acylbenzotriazoles (including the case where the corresponding acyl halide is not stable, for instance furan-2-carbonyl chloride) were applicable to this reaction. The acylation of imidazolidin-2-one using *N*-acylbenzotriazoles as the agents gave the acylation products smoothly in moderate to good yields. Compared with longer train alkyl *N*-acylbenzotriazoles, we obtained better results when the trains is shorter. (Table 3, entries 11–13). This maybe owe to spacial steric effect.

Table 2. Solvent effect on the reaction of 4-methoxy-benzoylbenzotriazoles and imidazolidin-2-one catalyzed by K_2CO_3

Entry	Solvent	Time (h)	Temp (°C)	Yield (%)[a]
1	THF:H_2O = 6:1	2	80	trace
2	$CHCl_3$	2	reflux	trace
3	EtOH	2	reflux	trace
4	Acetone	2	reflux	68
5	THF	2	reflux	47
6	CH_3CN	2	reflux	75
7	CH_2ClCH_2Cl	2	80	73
8	Toluene	2	80	82
9	Dioxane	2	80	78

[a]Isolated yield.



Scheme 2. Reactions for synthesizing 1-acyl-imidazolidin-2-ones.

Furthermore, as showned in Table 3, using aromatic *N*-acylbenzotriazoles as the starting materials, the substituted groups on the aromatic ring have evident influence on the reaction. The aromatic ring bearing electron-donating groups required short time with high yield (Table 3).

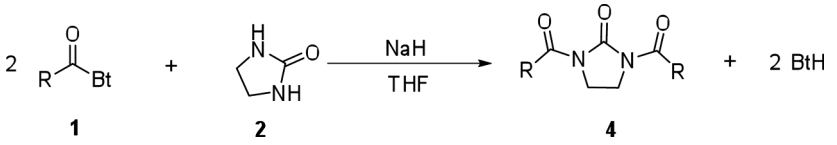
Moreover, the reaction of imidazolidin-2-one with 2 equal *N*-acylbenzotriazoles to provide the *N,N′*-diacylimidazolidin-2-one was studied (Scheme 3). Under the same conditions, we got low yields of **4** in the presence of K_2CO_3. However, when NaH was used as the base, the yield increased to 48%, and 52%, respectively (Table 3, entries 16, 17).

In summery, an efficient and environment friendly method has been found to prepare 1-acylimidazolidin-2-ones using *N*-acylbenzotriazoles as the useful neutral acylation agents. Compared to previous reported methodologies, the procedure offers some advantages including environment friendly procedure, mild and neutral conditions, and simple work up procedure. The method could be advantageous especially when the corresponding acyl chlorides are not stable or not easily prepared. Hence, it is a useful addition to the existing methods.

Table 3. The *N*-acylation of imidazolidin-2-ones with *N*-acylbenzotriazoles in the presence of K_2CO_3[a]

Entry	R	Time (h)	Temp (°C)	Product	Yield (%)[c]
1	*p*-CH_3O-C_6H_4	1	80	3a	82
2	C_6H_5	4	80	3b	73
3	*p*-NO_2-C_6H_4	8	80	3c	65
4	*m*-NO_2-C_6H_4	2	80	3d	70
5	*o*-CH_3O-C_6H_4	2	80	3e	81
6	*o*-Cl-C_6H_4	2	80	3f	76
7	2-Cl-4-NO_2-C_6H_3	10	80	3g	63
8	2-F-6-Cl-C_6H_3	2	80	3h	78
9	3,4-CH_3O-C_6H_3	2	80	3i	86
10	1-cinnamoyl	2	80	3j	69
11	CH_3	2	80	3k	87
12	C_2H_5	2	80	3l	71
13	*n*-$C_{11}H_{23}$	6	80	3m	46
14	2-furyl	2	80	3n	83
15	2-thienyl	2	80	3o	91
16	*o*-Cl-C_6H_4	12	80[c], 25[d]	4a	8[c], 48[d]
17	*p*-CH_3O-C_6H_4	12	80[c], 25[d]	4b	10[c], 52[d]

[a]The reactions were all carried out at 80 °C in toluene except entries 16 and 17.
[b]Isolated yield.
[c]The reactions were carried out at 80 °C in toluene using K_2CO_3 as base.
[d]The reactions were carried out at room temperature in THF using NaH as base.



Scheme 3. The diacylation of imidazolidin-2-one in the presence of NaH.

EXPERIMENTAL

Melting points were obtained with a capillary melting point apparatus and uncorrected. Infrared spectra were recorded on a Thermo Nicolet Avatar 370 spectrophotometer. ^{1}H NMR spectra were performed on a Varian Mercur plus-400 spectrometer (400 MHz) in DMSO using TMS as internal standard. ^{13}C NMR spectra were measured in DMSO and recorded on Varian Mercur plus-100 spectrometer (100 MHz) with TMS as internal standard. Chemical shifts (δ) are expressed in ppm and coupling constants J are given in Hz. Mass spectra were obtained on a Trace DSQ mass spectrometer. Elemental analysis was performed on a VarioEL-3 instrument. The starting materials *N*-acylbenzotriazoles **2** were prepared according to the literature.[7] Organic solvents and imidazolidin-2-one were obtained from commercial sources.

General Procedure for the *N*-Acylimidazolidin-2-ones

A mixture of imidazolidin-2-one (0.086 g, 1 mmol), K_2CO_3 (0.138 g, 1 mmol) and toluene (2 mL) was stirred at room temperature for 0.5 h. Then *N*-acylbenzotriazole was added to the solution. The resulting mixture was heated to 80 °C for indicated time until the disappearance of *N*-acylbenzotriazole (monitored by TLC). The solution was concentrated under reduced pressure. Then the residue was purified by flash chromatography (silica gel: hexane/CH_2Cl_2/EtOAc, 1:1:1) to afford the pure products.

General Procedure for the *N,N'*-Diacylimidazolidin-2-ones

A mixture of imidazolidin-2-one (0.086 g, 1 mmol), NaH (0.080 g, 60%, 2 mmol) and THF (2 mL) was stirred at room temperature for 0.5 h. Then *N*-acylbenzotriazole was added to the solution. The resulting mixture was stirred at r.t. for indicated time until the disappearance of *N*-acylbenzotriazole (monitored by TLC). The solution was concentrated under reduced pressure. Then the residue was purified by flash chromatography (silica gel: hexane/CH_2Cl_2/EtOAc, 1:1:1) to afford the pure products.

Data

1-(4-Methoxybenzoyl)imidazolidin-2-one 3a. White crystal; mp: 167.5–169.7 °C (lit.[15] 167–168 °C); MS (EI): m/z (%) 220 (49), 135 (100), 77 (15); ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.38 (t, $J = 7.2$ Hz, 2H, CH_2), 3.81 (s, 3H, CH_3), 3.88 (t, $J = 7.2$ Hz, 2H, CH_2), 6.92 (d, $J = 8.8$ Hz, 2H, PhH), 7.52 (d, $J = 7.6$ Hz,

2H, PhH), 7.63 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): 36.1, 43.4, 55.3, 112.6, 127.0, 131.0, 155.5, 161.5; IR (KBr) ν_{max}: 3225, 1741, 1655 cm^{-1}.

1-Benzoylimidazolidin-2-one 3b. White crystal; mp: 167.3–169.1 °C (lit.[15] 169–171 °C); MS (EI): m/z (%) 190 (52), 105 (100), 77 (29); ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.39 (t, J = 7.6 Hz, 2H, CH_2), 3.91 (t, J = 7.6 Hz, 2H, CH_2), 7.37 (t, J = 7.2 Hz, 2H, PhH), 7.45–7.52 (m, 3H, PhH), 7.64 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): 36.1, 43.0, 127.3, 128.4, 130.6, 135.3, 155.2, 169.4; IR (KBr) ν_{max}: 3425, 1727, 1665 cm^{-1}.

1-(4-Nitrobenzoyl)imidazolidin-2-one 3c. Yellow crystal; mp: 227.3–229.4 °C; MS (EI): m/z (%) 235 (51), 207 (34), 150 (100); ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.42 (t, J = 8.0 Hz, 2H, CH_2), 3.95 (t, J = 8.0 Hz, 2H, CH_2), 7.72 (d, J = 8.8 Hz, 2H, PhH), 7.80 (s, 1H, NH), 8.22 (d, J = 8.8 Hz, 2H, PhH); ^{13}C NMR (DMSO-d_6, 100 MHz): 36.2, 42.5, 93.9, 122.6, 129.2, 141.8, 154.9, 167.4; IR (KBr) ν_{max}: 3425, 1754, 1660 cm^{-1}.

1-(3-Nitrobenzoyl)imidazolidin-2-one 3d. Yellow crystal; mp: 196.2–197.6 °C; MS (EI): m/z (%) 235 (21), 218 (34), 150 (100), 104 (22); ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.43 (t, J = 7.6 Hz, 2H, CH_2), 3.95 (t, J = 7.6 Hz, 2H, CH_2), 7.69 (t, J = 8.0 Hz, 1H, PhH), 7.79 (s, 1H, NH), 7.93 (d, J = 8.8 Hz, 1H, PhH), 8.31 (s, 1H, PhH), 8.33 (d, J = 8.0 Hz, 1H, PhH); ^{13}C NMR (DMSO-d_6, 100 MHz): 36.1, 42.7, 123.1, 125.0, 129.1, 134.6, 136.9, 146.7, 155.1, 166.9; Anal. Calcd. for $C_{10}H_9N_3O_4$: C, 51.06; H, 3.83; N, 17.87. Found: C, 51.16; H, 3.85; N, 17.92; IR (KBr) ν_{max}: 3425, 1754, 1674 cm^{-1}.

1-(2-Methoxybenzoyl)imidazolidin-2-one 3e. White crystal; mp: 126–128 °C; MS (EI): m/z (%) 220 (21), 189 (40), 135 (100); ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.36 (t, J = 8.0 Hz, 2H, CH_2), 3.71 (s, 3H, CH_3), 3.89 (t, J = 8.0 Hz, 2H, CH_2), 6.90–6.94 (m, 1H, PhH), 6.97–6.99 (m, 1H, PhH), 7.13–7.15 (m, 1H, PhH), 7.32–7.37 (m, 1H, PhH), 7.51 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): 34.9, 42.1, 58.5, 111.0, 119.8, 126.4, 127.6, 130.4, 133.1, 154.6, 166.8; Anal. Calcd. for $C_{11}H_{12}N_2O_3$: C, 60.00; H, 5.45; N, 12.72. Found: C, 59.75; H, 5.46; N, 12.51; IR (KBr) ν_{max}: 3333, 1757, 1670 cm^{-1}.

1-(2-Chlorobenzoyl)imidazolidin-2-one 3f. Yellow crystal; mp: 116.2–118.9 °C; MS (EI): m/z (%) 225 (7), 189 (100), 139 (34), 111 (21); ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.41 (t, J = 8.0 Hz, 2H, CH_2), 3.94 (t, J = 8.0 Hz, 2H, CH_2), 7.33–7.42 (m, 4H, PhH), 7.70 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): 35.9, 41.7, 126.7, 128.0, 128.6, 129.3, 130.2, 136.4, 154.3, 165.8; IR (KBr) ν_{max}: 3299, 1759, 1638 cm^{-1}.

1-(2-Chloro-4-nitrobenzoyl)imidazolidin-2-one 3g. Yellow crystal; mp: 221–223.2 °C; MS (EI): m/z (%) 225 (7), 189 (100), 139 (34), 111 (21); ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.45 (t, J = 8.0 Hz, 2H, CH_2), 3.98 (t, J = 8.0 Hz, 2H, CH_2), 7.68 (d, J = 8.4 Hz, 1H), 7.88 (s, 1H, NH), 8.20–8.23 (m, 1H, PhH), 8.31 (d, J = 2.4 Hz, 1H, PhH); ^{13}C NMR (DMSO-d_6, 100 MHz): 36.2, 41.5, 122.1, 123.7, 129.0, 130.3, 142.6, 147.9, 154.2, 164.1; IR (KBr) ν_{max}: 3424, 1746, 1677 cm^{-1}.

1-(2-Chloro-6-fluorobenzoyl)imidazolidin-2-one 3h. White crystal; mp: 162.4–164.0 °C; MS (EI): m/z (%) 207 (100), 157 (47), 129 (12); ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.43 (t, $J = 7.6$ Hz, 2H, CH_2), 3.98 (t, $J = 7.6$ Hz, 2H, CH_2), 7.25 (t, $J = 8.8$ Hz, 1H, PhH), 7.33 (d, $J = 8.0$ Hz, 1H, PhH), 7.42–7.48 (m, 1H, PhH), 7.87 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): 35.8, 41.5, 114.2, 125.0, 130.1, 131.3, 154.0, 156.9, 159,3, 160.9; Anal. Calcd. for $C_{10}H_8N_2O_2Cl$: C, 49.48; H, 3.30; N, 11.55. Found: C, 49.45; H, 3.30; N, 11.56; IR (KBr) ν_{max}: 3287, 1749, 1636 cm^{-1}.

1-(3,4-Dimethoxybenzoyl)imidazolidin-2-one 3i. White crystal; mp: 180.1–182.9 °C (lit.[15] 182–184 °C); MS (EI): m/z (%) 250 (30), 210 (14), 182 (18), 165 (100); ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.38 (t, $J = 7.6$ Hz, 2H, CH_2), 3.75 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 3.88 (t, $J = 7.6$ Hz, 2H, CH_2), 6.95 (d, $J = 8.4$ Hz, 1H, PhH), 7.13–7.17 (m, 2H, PhH), 7.59 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): 36.1, 43.4, 55.5, 110.1, 112.6, 122.8, 127.0, 147.4, 151.3, 155.5, 169.0; IR (KBr) ν_{max}: 3405, 1737, 1660 cm^{-1}.

1-Cinnamoylimidazolidin-2-one 3j. Yellow crystal; mp: 203.8–205.6 °C (lit.[15] 203–205 °C); MS (EI): m/z (%) 216 (53), 131 (100), 103 (59), 85 (26); ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.36 (t, $J = 7.2$ Hz, 2H, CH_2), 3.87 (t, $J = 7.2$ Hz, 2H, CH_2), 7.42–7.46 (m, 3H, PhH, CH), 7.61–7.67 (m, 3H, PhH), 7.79 (s, 1H, NH), 8.02 (d, $J = 8.0$ Hz, 1H, PhH); ^{13}C NMR (DMSO-d_6, 100 MHz): 35.8, 42.1, 119.1, 127.9, 128.9, 130.0, 134.8, 141.9, 156.0, 164.6; IR (KBr) ν_{max}: 3425, 1737, 1658 cm^{-1}.

1-Acetylimidazolidin-2-one 3k. White crystal; mp: 185.9–187.9 °C (lit.[15] 186–187 °C); MS (EI): m/z (%) 128 (83), 85 (100), 59 (13); ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 2.32 (s, 3H, CH_3), 3.29 (t, $J = 8.0$ Hz, 2H, CH_2), 3.73 (t, $J = 8.0$ Hz, 2H, CH_2), 7.59 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): 22.9, 35.6, 41.7, 156.1, 169.6; IR (KBr) ν_{max}: 3258, 1754, 1652 cm^{-1}.

1-Propionylimidazolidin-2-one 3l. White crystal; mp: 147.5–149.2 °C (lit.[15] 148–149 °C); MS (EI): m/z (%) 142 (100), 85 (94), 57 (47); ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 1.01 (t, $J = 7.2$ Hz, 3H, CH_3), 2.76–2.81 (q, $J = 7.2$ Hz, 2H, CH_2), 3.30 (t, $J = 8.0$ Hz, 2H, CH_2), 3.74 (t, $J = 8.0$ Hz, 2H, CH_2), 7.55 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): 8.9, 27.9, 35.8, 41.9, 156.1, 173.3; IR (KBr) ν_{max}: 3252, 1683, 1623 cm^{-1}.

1-Dodecanoylimidazolidin-2-one 3m. White crystal; mp: 98.4–99.1 °C; MS (EI): m/z (%) 269 (21), 183 (63), 155 (100); ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 0.85 (t, $J = 6.4$ Hz, 3H, CH_3), 1.20–1.30 (m, 16H, CH_2), 1.51 (t, $J = 6.4$ Hz, 2H, CH_2), 2.77–2.80 (m, 2H, CH_2), 3.32 (t, $J = 8.0$ Hz, 2H, CH_2), 3.73 (t, $J = 8.0$ Hz, 2H, CH_2), 7.53 (s, 1H, NH); ^{13}C NMR (DMSO-d_6, 100 MHz): 13.9, 22.1, 24.3, 28.7, 28.8, 28.9, 29.0, 31.3, 34.3, 35.7, 41.8, 156.0, 172.5; IR (KBr) ν_{max}: 3249, 1738, 1677 cm^{-1}.

1-(Furan-5-carbonyl) imidazolidin-2-one 3n. White crystal; mp: 150.5–152.1 °C; MS (EI): m/z (%) 180 (100), 152 (49), 95 (98); ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.38 (t, $J = 7.6$ Hz, 2H, CH_2), 3.88 (t, $J = 7.6$ Hz, 2H, CH_2), 6.63–6.64 (m, 1H, CH), 7.27–7.28 (m, 1H, CH), 7.71 (s, 1H, NH), 7.88 (s, 1H,

CH); ^{13}C NMR (DMSO-d_6, 100 MHz): 36.3, 43.3, 111.5, 118.7, 146.0, 146.1, 155.0, 158.1; IR (KBr) ν_{max}: 3425, 1755, 1626 cm^{-1}.

1-(Thiophene-5-carbonyl)imidazolidin-2-one 3o. Yellow crystal; mp: 243.5–246.8 °C; MS (EI): m/z (%) 196 (36), 168 (34), 111 (100); ^{1}H NMR (DMSO-d_6, 400 MHz): δ_H 3.39 (t, $J = 7.6$ Hz, 2H, CH_2), 3.92 (t, $J = 7.6$ Hz, 2H, CH_2), 7.12–7.14 (m, 1H, CH), 7.73 (s, 1H, NH), 7.84–7.85 (m, 2H, CH); ^{13}C NMR (DMSO-d_6, 100 MHz): 36.2, 43.9, 127.1, 132.4, 134.1, 136.6, 155.3, 162.1; IR (KBr) ν_{max}: 3223, 1748, 1630 cm^{-1}.

(2-Oxoimidazolidine-1,3-diyl)bis((2-chlorophenyl)methanone) 4a. Yellow crystal; mp: 174.4–175.8 °C; MS (EI): m/z (%) 327 (55), 139 (100), 111 (30); ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 4.02 (s, 4H, CH_2), 7.31–7.55 (m, 8H, PhH); ^{13}C NMR ($CDCl_3$, 100 MHz): 36.3, 127.4, 128.7, 129.5, 131.1, 133.0, 135.5, 166.6, 167.2.

(2-Oxoimidazolidine-1,3-diyl)bis((4-methoxyphenylmethanone) 4b. White crystal; mp: 94.1–94.9 °C; MS (EI): m/z (%) 354 (4), 152 (18), 135 (100); ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 3.86 (m, 4H, CH_2), 3.88 (s, 6H, CH_3), 6.95 (d, $J = 8.0$ Hz, 4H, PhH), 8.07 (d, $J = 8.0$ Hz, 4H, PhH);. ^{13}C NMR ($CDCl_3$, 125 MHz): 29.7, 55.5, 113.8, 121.6, 131.8, 132.4, 164.0, 171.0.

ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (No. 20676123) and National Key Technology R&D Program (No. 2007 BAI34B06) for financial support.

REFERENCES

1. (a) Kohn, H. Model Studies on the Mechanism of Biotin Dependent Carboxylations. *J. Am. Chem. Soc.* **1976**, *98*, 3690–3694; (b) Pratt, R. F.; Bruice, T. C. Reactions of S-acylisothioureas.II. Effects of structure and stereochemistry on the rates of hydrolysis, thiol elimination, and S to N acyl migration in acylic systems. *J. Am. Chem. Soc.* **1972**, *94*, 2823–2837; (c) Kohn, H.; Kohn, B. A.; Steenberg, M. L.; Buckley, J. P. Syntheses and pharmacological activity of substituted imidazolidinethiones and thioimidazolines. *J. Med. Chem.* **1977**, *20*, 158–160; (d) Marx, J. L. Cancer immunotherapy: Focus on the drug levamisole. *Science* **1976**, *191*, 57.
2. (a) Euis, C. J. Mezlocillin and azlocillin: An evaluation of two new β-lactam antibiotics. *Antimicrob Chemother.* **1979**, *5*, 517–525; (b) Baker, M. J. *Infection* **1979**, *7*, 67.
3. Gudzenko, V. I.; Salov, B. V. Method for preparing 1-acetyl-2-imidazolidone. Patent, Ru 2237662, **2004**.
4. Kohn, H.; Cravey, M. J. Syntheses and spectral properties of substituted imidazolidones and imidazolines. *J. Org. Chem.* **1977**, *42*, 941–948.
5. Su, W. K.; Yin, X. J.; Lu, Y. J. Synthesis of N-Actyl-Imidazolidone-2. *J. Zhejiang Univ of Technol* (China) **1995**, *23*, 136–140.
6. Katritzky, A. R.; Suzuki, K.; Wang, Z. Acylbenzotriazoles as advantageous *N*-, *C*-, *S*-, and *O*-acylation agents. *Synlett* **2005**, 1656–1665.
7. (a) Katritzky, A. R.; He, H. Y.; Suzuki, K. *N*-Acylbenzotriazoles: Neutral acylating reagents for the preparation of primary, secondary, and tertiary amides. *J. Org. Chem.*

2000, *65*, 8210–8213; (b) Katritzky, A. R.; Zhang, Y.; Singh, S. K. Efficient conversion of carboxylic acids into *N*-acylbenzotriazoles. *Synthesis* **2003**, 2795–2798.
8. Katritzky, A. R.; Pastor, A.; Voronkov, M. V. An efficient general synthesis of 1-(benzotriazol-1-yl)alkyl esters. *J. Heterocycl. Chem.* **1999**, *36*, 777–782.
9. Zou, X.; Wang, X.; Cheng, C.; Kong, L.; Mao, H. Highly regioselective Friedel–Crafts alkylation of indoles with α,β-unsaturated *N*-acylbenzotriazoles. *Tetrahedron Lett.* **2006**, *47*, 3767–3771.
10. Katritzky, A. R.; Suzuki, K.; Singh, S. K.; He, H.-Y. Regiospecific *C*-acylation of pyrroles and indoles using *N*-acylbenzotriazoles. *J. Org. Chem.* **2003**, *68*, 5720–5723.
11. (a) Katritzky, A. R.; Abdel-Fattah, A. A. A.; Wang, M. Expedient acylations of primary and secondary alkyl cyanides to α-substituted β-ketonitriles. *J. Org. Chem.* **2003**, *68*, 4932–4934; (b) Katritzky, A. R.; Pastor, A. Synthesis of β-dicarbonyl compounds using 1-acylbenzotriazoles as regioselective C-acylating reagents. *J. Org. Chem.* **2000**, *65*, 3679–3682; (c) Katritzky, A. R.; Meher, N. K.; Singh, S. K. γ,δ-Unsaturated β-diketones by acylation of ketones. *J. Org. Chem.* **2005**, *70*, 7792–7794; (d) Katritzky, A. R.; Abdel-Fattah, A. A. A.; Gromova, A. V.; Witek, R.; Steel, P. J. α-Nitro ketone synthesis using *N*-acylbenzotriazoles. *J. Org. Chem.* **2005**, *70*, 9211–9214; (e) Katritzky, A. R.; Jiang, R.; Suzuki, K. *N*-Tfa- and *N*-Fmoc-(α-aminoacyl)benzotriazoles as chiral *C*-acylating reagents under Friedel-Crafts reaction conditions. *J. Org. Chem.* **2005**, *70*, 4993–5000; (f) Katritzky, A. R.; Angrish, P.; Hür, D.; Suzuki, K. N-(Cbz- and fmoc-α-aminoacyl)benzotriazoles: Stable derivatives enabling peptide coupling of Tyr, Trp, Cys, Met, and Gln with free amino acids in aqueous media with complete retention of chirality. *Synthesis* **2005**, 397–402.
12. Katritzky, A. R.; Hoffmann, S.; Suzuki, K. *N*-Acylation of sulfonamides using *N*-acylbenzotriazoles. *ARKIVOC* **2004**, *xii*, 14–22.
13. (a) Katritzky, A. R.; Angrish, P.; Suzuki, K. The efficient preparation of Di- and Tripeptides by coupling N-(Cbz- or Fmoc-α -aminoacyl)benzotriazoles with unprotected amino acids. *Synthesis* **2006**, 411–424; (b) Katritzky, A. R.; Tao, H.; Jiang, R.; Suzuki, K.; Kirichenko, K. Novel Syntheses of chiral β- and γ-amino acid derivatives utilizing N-protected(aminoacyl)benzotriazoles from aspartic and glutamic acids. *J. Org. Chem.* **2007**, *72*, 407–414; (c) Katritzky, A. R.; Singh, S. K.; Akhmedova, R.; Cai, C.; Bobrov, S. Efficient synthesis of 1,3-benzodixin-4-one and benzoxazine-2,4-diones. *ARKIVOC* **2007**, *vi*, 6–13; (d) Katritzky, A. R.; Shestopalov, A. A.; Suzuki, K. A new convenient preparation of thiol esters utilizing *N*-acylbenzotriazoles. *Synthesis* **2004**, 1806–1813; (e) Singh, K. N.; Kaur, A. Facile and chemoselective reduction of carboxylic acids into alcohols via sodium borohydride reduction of N-Acylbenzotriazoles. *Synth. Commun.* **2005**, *35*, 2935–2937; (f) Katritzky, A. R.; Angrish, P. Convenient and efficient preparation of N-Protected(a-Aminoacyl)oxy-substituted terpenes and alkanes. *Synthesis* **2006**, 4135–4142; (g) Wang, X.; Zou, X.; Li, J.; Hu, Q. Efficient syntheses of β-amino-*N*-acylbenzotriazoles and cinnamides through regioselective 1,4- or 1,2-addition of amines to N-cinnamoylbenzotriazoles. *Synlett* **2005**, 3042–3046.
14. Katritzky, A. R.; Khelashvili, L.; Mohapatra, P. P.; Steel, P. J. Efficient N-Aroylation of substituted indoles with *N*-Aroylbenzotriazoles. *Synthesis* **2007**, 3673–3677.
15. May, Hans-Joachim; Konig, Horst. Neue 1-acyl-2-imidazoline und Verfahren zu ihrer Herstellung. Patent, Ger Offen DE 2652004 A1, **1978**.