Res Chem Intermed
DOI 10.1007/s11164-012-0829-x

An efficient synthesis of 2-amino-4-aryl-3, 5-dicarbonitrile-6-ethoxypyridine derivatives by the solvent taking part in the reaction

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Received: 6 July 2012 / Accepted: 20 September 2012

Abstract An efficient and facile synthesis of 2-amino-4-aryl-3,5-dicarbonitrile-6-ethoxypyridine via reaction of aromatic aldehydes, malononitrile, and ethanol in the presence of NaOH has been developed, without using the classic reagents amines and 1,3-dicarbonyl compounds. It is interesting that weak nucleophilic reagent ethanol could take part in the reaction without using strong base catalyst sodium ethylate. Compared with existing methods, the reported process has the advantages of excellent yields, easily obtainable raw materials, and mild reaction conditions.

Keywords Pyridine · Malononitrile · Ethanol · Synthesis · Solvent effect

Introduction

The pyridine substructure is one of the most prevalent heterocycles found in natural products, pharmaceuticals, and functional materials [1–3]. The Hantzsch reaction is the classical method for synthesis of pyridine from 1,3-dicarbonyl compounds, aldehyde, and ammonia [4, 5]. Many other powerful methodologies for synthesis of these heterocycles rely on condensation of amines and carbonyl compounds or cycloaddition reactions [6–13]. Cross-coupling chemistry also allows introduction of substituents to activated heterocycles [14]. In reported methods, amines and 1,3-dicarbonyl compounds are the most commonly used substrates. Herein, we report a different method for preparation of pyridine derivatives without using amines and 1,3-dicarbonyl compounds.

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Published online: 02 October 2012

Results and discussion

We previously reported some 2-amino-1,3-dicarbonitrile compounds [acceptor–donor–acceptor (A–D–A)] by the reaction of aromatic aldehydes, malononitrile, and different ketones [15–17]. In our recent research, we wanted to use aromatic aldehyde, malononitrile, and 2-methylcyclopentane-1,3-dione in ethanol (95 %) to synthesize some new 2-amino-1,3-dicarbonitrile compounds. 4-Fluorobenzaldehyde, malononitrile, and 2-methylcyclopentane-1,3-dione were chosen to carry out this reaction using Et_3N as catalyst. Unfortunately, we did not get the anticipated 1,3-dicarbonitrile compound; however, a different product was obtained. In its ^1H nuclear magnetic resonance (NMR), two obvious signals could be found. One is a triplet signal at $\delta = 1.43$ (3H), and the other is a quartet signal at $\delta = 4.47$ (2H). The coupling constants of both are $J = 7.2$ Hz, clearly indicating mutual coupling between them. Taking into account the reaction reagents and solvent, we believed that the solvent, viz. ethanol, must take part in the reaction, and we could conclude the structure is 2-amino-3,5-dicarbonitrile-6-ethoxy-4-(4-fluorophenyl)pyridine **4a**.

Since the structure of the product has been identified, we wanted to know whether other methods have been reported for the synthesis of these compounds. Investigating the literature, we found that few methods to prepare these compounds have been reported. Only in 1970, Álvarez-Insúa reported synthesis of similar structures under rigorous conditions using strong base sodium alkoxide and absolute alcohol, but with very low yields (3–49 %). In our research, we found Et_3N could also catalyze this reaction, so we reasoned that this method may offer better conditions for synthesis of these compounds.

To identify other efficient conditions for this reaction, 4-fluorobenzaldehyde and malononitrile were chosen also as starting substrates, and different catalysts were used in 95 % ethanol. After the reactions were completed, different results were obtained as listed in Table 1. Table 1 shows that, when strong organic base, such as NaOEt and $KOBu^t$, was used in reaction, the yields were below average. The catalytic effect of benzylamine, DBU, and piperidine is similar to that of Et_3N, with 21, 19, and 18 % yield, respectively. However, when inorganic base NaOH was used in the reaction, the reaction could proceed smoothly with the best yield. We also tested the reaction time, the loading amount of NaOH, and the reaction temperature for the model reaction. The results showed that NaOH is the preferred catalyst for this synthesis (Scheme 1).

Under this optimized condition, different aromatic aldehydes were chosen to react with malononitrile and 95 % ethanol, and corresponding 2-amino-4-aryl-3,5-dicarbonitrile-6-ethoxypyridine products could be obtained in good yield (Scheme 2). In these reactions, we found that aromatic aldehydes bearing electron-donating substituents, such as methyl, methoxy, were more efficient reagents for synthesis of target products compared with electron-withdrawing counterparts. The results of the reactions are summarized in Table 2.

According to the product, a possible mechanism is presented in Scheme 3. Firstly, the aromatic aldehyde and malononitrile react together to give condensation compound cinnamonitrile **5**, then Michael addition occurs between **5** and malononitrile. Ethanol as a nucleophilic reagent reacts with **6** to give **7**. Finally,

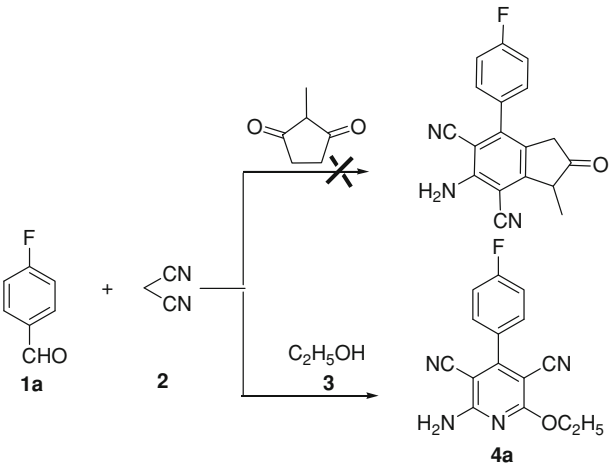
Table 1 Effect of catalyst and temperature on the model reaction[a]

Entry	Catalyst (mmol)	Temperature (°C)	Time (h)	Yield[b] (%)
1	$PhCH_2NH_2$ (1)	80	20	21
2	NaOEt (1)	80	6	28
3	$KOBu^t$ (1)	80	6	25
4	DBU (1)	80	20	19
5	Piperidine (1)	80	20	18
6	Et_3N (1)	80	20	20
7	NaOH (1)	80	6	54
8	NaOH (0.8)	80	6	53
9	NaOH (0.5)	80	6	54
10	NaOH (0.2)	80	6	25
11	NaOH (0.1)	80	6	20
12	NaOH (0.5)	80	5	52
13	**NaOH (0.5)**	**80**	**4**	**53**
14	NaOH (0.5)	70	6	35
15	NaOH (0.5)	70	6	30
16	NaOH (0.5)	60	6	25

[a] Reagents and conditions: 4-fluorobenzaldehyde **1a** (2 mmol), malononitrile **2** (4 mmol), EtOH (10 mL)

[b] Isolated yields

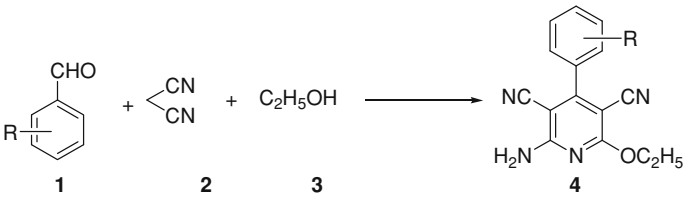
Bold indicates the optimized reaction condition



Scheme 1 Reaction of 4-fluorobenzaldehyde and malononitrile

cyclization reaction, tautomerism, and oxidation reaction are carried out to give products **4**.

The structures of all the products were confirmed on the basis of spectroscopic data, particularly ^1H NMR and ^{13}C NMR analysis, and high-resolution mass

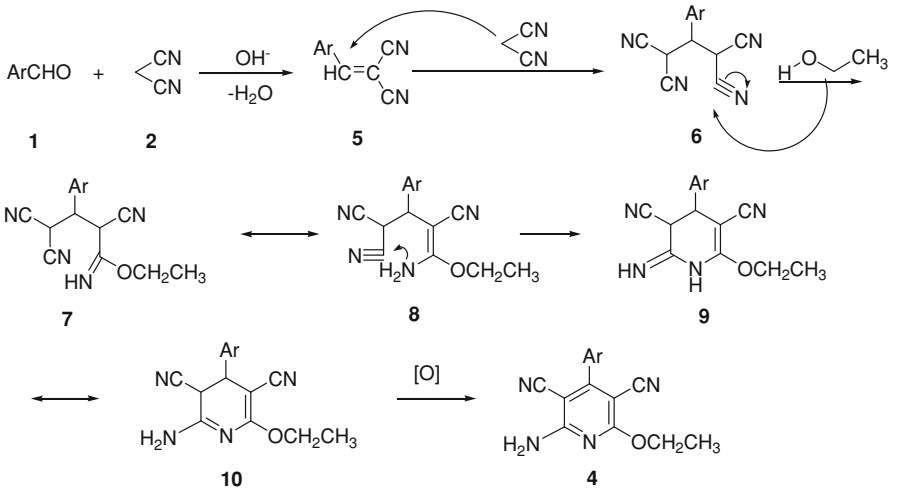


Scheme 2 Synthesis of 2-amino-6-ethoxy-4-arylpyridine-3,5-dicarbonitrile

Table 2 Synthetic results of compounds **4**

Entry	Ar	Product	Yield[a] (%)
1	4-FC_6H_4	**4a**	53
2	2-FC_6H_4	**4b**	58
3	4-$CH_3C_6H_4$	**4c**	60
4	2-$CH_3OC_6H_4$	**4d**	63
5	3-$CH_3OC_6H_4$	**4e**	61
6	4-$CH_3OC_6H_4$	**4f**	63
7	3,4-$(CH_3)_2C_6H_3$	**4g**	65
8	3,4-$(CH_3O)_2C_6H_3$	**4h**	71
9	3,4-$OCH_2OC_6H_3$	**4i**	68
10	3,4,5-$(CH_3O)_3C_6H_2$	**4j**	62

[a] Isolated yields



Scheme 3 Possible reaction mechanism

spectroscopy (HRMS). We take **4a** as an example for structural analysis. The ^1H NMR spectrum of **4a** revealed a triplet signal at $\delta = 1.43$ ppm (3H, $\delta = 7.2$ Hz), and a quartet signal at $\delta = 4.47$ ppm (2H, $\delta = 7.2$ Hz) due to CH_3– and –CH_2– of

ethoxy (CH_3CH_2O–). A singlet signal at 5.65 ppm is due to the two protons of NH_2. The triplet signal at $\delta = 7.22$ (2H, $J = 9.6$ Hz) and doublet signals at 7.53 (2H, $J = 5.4$ Hz, $J = 6.6$ Hz) are due to four phenyl protons. The ^{13}C NMR spectrum of **4a** revealed signals at 14.49, 64.64, 84.07, 114.73, 115.78, 116.37, 116.66, 116.90, 130.86, 130.98, 159.89, 161.04, 165.99, and 166.60, respectively. In the HRMS spectrum, the calculated *m/z* ($C_{15}H_{11}FN_4O$ $[M + Na]^+$) of **4a** is 305.0815, and the found *m/z* is 305.0820.

Conclusions

We have successfully developed an efficient and facile method to prepare pyridine derivatives via reaction of different aromatic aldehydes, malononitrile, and solvent ethanol (95 %), without using the classic reagents amines and 1,3-dicarbonyl compounds. It is interesting that the weak nucleophilic reagent ethanol could take part in the reaction in the presence of NaOH, without using strong base catalyst such as sodium ethylate. This protocol has the advantages of mild conditions, easily obtainable raw materials, and good yields.

Experimental

Melting points were determined on XT-5 microscopic melting-point apparatus and were uncorrected. Infrared (IR) spectra were recorded on a FT Bruker Tensor 27 spectrometer. ^1H and ^{13}C NMR spectra were obtained from solution in dimethyl sulfoxide (DMSO)-d_6 with Me_4Si as internal standard using a Bruker-400 and Bruker-300 spectrometer. HRMS spectra were obtained with a Bruker microTOF-Q 134 instrument.

General procedure for the synthesis of 2-amino-4-aryl-3,5-dicarbonitrile-6-ethoxypyridine

A mixture of aromatic aldehydes **1** (2 mmol), malononitrile **2** (2 mmol), CH_3CH_2OH (10 mL), and NaOH (0.5 mmol) was put in a reaction flask at 80 °C for about 4 h. After completion, the reaction mixture was poured into water, filtered, and then washed with water thoroughly. The products were dried and recrystallized from 95 % ethanol.

*2-Amino-3,5-dicarbonitrile-6-ethoxy-4-(4-fluorophenyl)pyridine (**4a**)*

M.p. 163–164 °C; IR (KBr, *v*, cm^{-1}): 3,482, 3,337, 3,221, 2,225, 1,624, 1,559, 1,508, 1,387, 1,341, 1,303, 1,185, 1,162, 1,020, 857, 784 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) (δ, ppm): 1.43 (3H, t, $J = 7.2$ Hz, CH_3), 4.47 (2H, q, $J = 7.2$ Hz, CH_2), 5.65 (2H, s, NH_2), 7.22 (2H, t, $J = 9.6$ Hz, ArH), 7.53 (2H, dd, $J = 5.4$ Hz, $J = 6.6$ Hz, ArH). ^{13}C NMR (300 MHz, $CDCl_3$) (δ, ppm): 14.49, 64.64, 84.07, 114.73, 115.78, 116.37, 116.66, 116.90, 130.86, 130.98, 159.89,

161.04, 165.99, 166.60. HRMS *m/z* calculated for $C_{15}H_{11}FN_4O$ $[M + Na]^+$: 305.0815, found: 305.0820.

*2-Amino-3,5-dicarbonitrile-6-ethoxy-4-(2-fluorophenyl)pyridine (**4b**)*

M.p. 203–204 °C; IR (KBr, *v*, cm^{-1}): 3,471, 3,329, 3,327, 2,227, 1,627, 1,589, 1,555, 1,498, 1,457, 1,384, 1,347, 1,301, 1,270, 1,230, 1,189, 1,105, 1,019, 769 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) (δ, ppm): 1.43 (3H, t, $J = 7.5$ Hz, CH_3), 4.47 (2H, q, $J = 7.2$ Hz, CH_2), 5.68 (2H, s, NH_2), 7.27 (2H, dt, $J = 9.9$ Hz, $J = 7.5$ Hz, ArH), 7.40 (1H, t, $J = 7.5$ Hz), 7.53 (1H, q, $J = 6.6$ Hz, ArH). ^{13}C NMR (300 MHz, $CDCl_3$) (δ, ppm): 14.48, 64.63, 85.08, 114.31, 115.27, 116.71, 124.96, 130.44, 130.47, 133.00, 133.11, 155.58, 157.33, 160.80, 166.29. HRMS *m/z* calculated for $C_{15}H_{11}FN_4O$ $[M + Na]^+$: 305.0815, found: 305.0817.

*2-Amino-3,5-dicarbonitrile-4-(4-methylphenyl)-6-ethoxypyridine (**4c**)*

M.p. 184–185 °C; IR (KBr, *v*, cm^{-1}): 3,330, 2,227, 1,622, 1,583, 1,556, 1,516, 1,472, 1,435, 1,418, 1,382, 1,339, 669 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.35 (3H, t, $J = 6.8$ Hz, CH_3), 2.40 (3H, s, CH_3), 4.44 (2H, q, $J = 6.8$ Hz, CH_2), 7.39 (4H, q, $J = 8.0$ Hz, ArH), 7.96 (2H, s, NH_2). ^{13}C NMR (300 MHz, $CDCl_3$) (δ, ppm): 14.52, 20.07, 64.41, 114.62, 115.67, 116.25, 116.29, 125.76, 131.44, 131.57, 160.68, 162.13, 163.18, 166.72. HRMS *m/z* calculated for $C_{16}H_{14}N_4O$ $[M + Na]^+$: 301.1065, found: 301.1071.

*2-Amino-3,5-dicarbonitrile-6-ethoxy-4-(2-methoxyphenyl)pyridine (**4d**)*

M.p. 185–186 °C; IR (KBr, *v*, cm^{-1}): 3,438, 3,338, 3,226, 3,012, 2,221, 1,635, 1,550, 1,496, 1,429, 1,382, 1,346, 1,298, 1,279, 1,254, 1,177, 1,113, 1,014, 916, 784, 759 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) (δ, ppm): 1.43 (3H, t, $J = 6.9$ Hz, CH_3), 3.87 (3H, s, OCH_3), 4.46 (2H, q, $J = 6.9$ Hz, CH_2), 5.56 (2H, s, NH_2), 7.07 (2H, dd, $J = 7.5$ Hz, $J = 14.1$ Hz, ArH), 7.27 (1H, d, $J = 7.2$ Hz, ArH), 7.47 (1H, t, $J = 7.2$ Hz, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) (δ, ppm): 14.54, 55.85, 64.34, 85.47, 111.92, 114.85, 115.85, 121.14, 122.72, 130.12, 132.43, 156.28, 158.79, 160.72, 166.27. HRMS *m/z* calculated for $C_{16}H_{14}N_4O_2$ $[M + Na]^+$: 317.1014, found: 317.1028.

*2-Amino-3,5-dicarbonitrile-6-ethoxy-4-(3-methoxyphenyl)pyridine (**4e**)*

M.p. >280 °C; IR (KBr, *v*, cm^{-1}): 3,430, 3,340, 3,238, 2,985, 2,216, 1,648, 1,570, 1,436, 1,381, 1,340, 1,300, 1,260, 1,180, 1,033, 883, 807 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) (δ, ppm): 1.43 (3H, t, $J = 7.2$ Hz, CH_3), 3.86 (3H, s, OCH_3), 4.48 (2H, q, $J = 7.2$ Hz, CH_2), 5.62 (2H, s, NH_2), 7.03–7.11 (3H, m, ArH), 7.44 (1H, t, $J = 7.8$ Hz, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) (δ, ppm): 14.51, 55.67, 64.55, 84.95, 104.32, 113.94, 116.93, 120.87, 120.92, 130.34, 130.37, 130.42, 134.78, 143.18, 160.95, 161.40, 164.51. HRMS *m/z* calculated for $C_{16}H_{14}N_4O_2$ $[M + H]^+$: 295.1195, found: 295.1198.

*2-Amino-3,5-dicarbonitrile-6-ethoxy-4-(4-methoxyphenyl)pyridine (**4f**)*

M.p. >280 °C; IR (KBr, *v*, cm^{-1}): 3,415, 3,342, 3,241, 2,967, 2,936, 2,842, 2,214, 1,652, 1,608, 1,543, 1,517, 1,381, 1,340, 1,299, 1,244, 1,180, 1,021, 924, 840, 786, 663, 611 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) (δ, ppm): 1.43 (3H, t, $J = 7.2$ Hz, CH_3), 3.86 (3H, s, OCH_3), 4.46 (2H, q, $J = 7.2$ Hz, CH_2), 5.64 (2H, s, NH_2), 7.03 (2H, d, $J = 8.7$ Hz, ArH), 7.51 (2H, d, $J = 8.7$ Hz, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) (δ, ppm): 14.53, 55.64, 64.45, 83.90, 114.60, 114.65, 115.23, 116.28, 125.75, 130.42, 130.47, 160.66, 161.16, 161.78, 166.70. HRMS *m/z* calculated for $C_{16}H_{14}N_4O_2$ $[M + Na]^+$: 317.1014, found: 317.1016.

*2-Amino-3,5-dicarbonitrile-4-(3,4-dimethylphenyl)-6-ethoxypyridine (**4g**)*

M.p. 198–200 °C; IR (KBr, *v*, cm^{-1}): 3,472, 3,324, 3,219, 2,980, 2,922, 2,226, 1,623, 1,581, 1,552, 1,436, 1,378, 1,343, 1,301, 1,252, 1,178, 1,029, 833, 784 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm): 1.43 (3H, t, $J = 7.2$ Hz, CH_3), 2.32 (3H, s,CH_3), 2.33 (3H, s,CH_3), 4.47 (2H, q, $J = 7.2$ Hz, CH_2), 5.60 (2H, s, NH_2), 7.28 (3H, s, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) (δ, ppm): 14.53, 20.08, 64.43, 84.11, 115.05, 126.08, 129.60, 130.36, 130.49, 131.16, 137.55, 140.09, 161.03, 161.28. HRMS *m/z* calculated for $C_{17}H_{16}N_4O$ $[M + Na]^+$: 315.1222, found: 315.1228.

*2-Amino-3,5-dicarbonitrile-4-(3,4-dimethoxyphenyl)-6-ethoxypyridine (**4h**)*

M.p. 213–215 °C; IR (KBr, *v*, cm^{-1}): 3,443, 3,334, 3,231, 2,222, 1,634, 1,567, 1,519, 1,435, 1,384, 1,342, 1,325, 1,265, 1,177, 1,144, 1,021 cm^{-1}; ^{1}H NMR 300 MHz, $CDCl_3$) (δ, ppm): 1.43 (3H, t, $J = 6.9$ Hz, CH_3), 3.94 (3H, s, OCH_3), 3.94 (3H, s, OCH_3), 4.47 (2H, q, $J = 6.9$ Hz, CH_2), 5.61 (2H, s, NH_2), 7.00 (1H, d, $J = 8.4$ Hz, ArH), 7.07 (1H, s, ArH), 7.17–7.20 (1H, m, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) (δ, ppm): 14.56, 56.20, 56.32, 64.47, 83.92, 111.32, 111.85, 115.23, 116.30, 122.09, 125.78, 149.12, 151.33, 160.57, 161.14, 161.16. HRMS *m/z* calculated for $C_{17}H_{16}N_4O_3$ $[M + Na]^+$: 347.1120, found: 347.1132.

*2-Amino-3,5-dicarbonitrile-4-(benzo[d][1,3]dioxol-4-yl)-6-ethoxypyridine (**4i**)*

M.p. 189–191 °C; IR (KBr, *v*, cm^{-1}): 3,456, 3,356, 3,237, 2,908, 2,210, 1,648, 1,637, 1,573, 1,544, 1,504, 1,449, 1,429, 1,384, 1,384, 1,345, 1,252, 1,187, 1,101, 1,036, 932, 876, 821, 781 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm): 1.43 (3H, t, $J = 7.2$ Hz, CH_3), 4.46 (2H, q, $J = 7.2$ Hz, CH_2), 5.63 (2H, s, NH_2), 6.06 (2H, s, CH_2), 6.94 (1H, d, $J = 7.8$ Hz, ArH), 6.99 (1H, s, ArH), 7.03 (1H, dd, $J = 1.2$ Hz, J = 7.8 Hz, ArH); 14.51, 64.52, 84.08, 102.05, 104.32, 109.04, 109.09, 114.96, 116.02, 123.40, 123.45, 127.14, 148.28, 150.05, 160.55, 161.07, 166.63. HRMS *m/z* calculated for $C_{16}H_{12}N_4O_3$ $[M + Na]^+$: 331.0807, found: 331.0810.

*2-Amino-3,5-dicarbonitrile-6-ethoxy-4-(3,4,5-trimethoxyphenyl)pyridine (**4j**)*

M.p. 207–209 °C; IR (KBr, v, cm^{-1}): 3,330, 2,940, 2,208, 1,633, 1,568, 1,512, 1,384, 1,318, 1,252, 1,175, 1,127, 895, 669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) (δ, ppm): 1.44 (3H, t, $J = 7.2$ Hz, CH_3), 3.91 (9H, s, $3XOCH_3$), 4.48 (2H, q, $J = 7.2$ Hz, CH_2), 5.66 (2H, s, NH_2), 6.77 (2H, s, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) (δ, ppm): 14.52, 56.54, 61.23, 64.55, 83.94, 106.27, 115.04, 116.12, 128.55, 140.17, 140.18, 153.52, 160.63, 161.12, 166.70. HRMS *m/z* calculated for $C_{18}H_{18}N_4O_4$ $[M + H]^+$: 355.1406, found: 355.1420.

Acknowledgments We are grateful to the National Natural Science Foundation of China (NSFC) (21172188), the Foundation of Xuzhou Normal University (10XLS02), and the Priority Academic Program Development of Jiangsu Higher Education Institutions for financial support.

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