DOI: 10.1002/ejoc.201100008

Molecular Diversity of Three-Component Reactions of Aromatic Aldehydes, Arylamines, and Acetylenedicarboxylates

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Keywords: Multicomponent reactions / Domino reactions / Nitrogen heterocycles / Aldehydes / Amines / Acetylenedicarboxylates

The three-component reactions of aromatic aldehydes, arylamines, and acetylenedicarboxylates show very interesting molecular diversity. In an aqueous ethanol solution the three-component reaction gave polysubstituted 2-hydroxyhydropyridines. In absolute ethanol 1,4-dihydropyridines were produced in satisfactory yields. Finally, under acid catalysis, this three-component reaction afforded polysubstituted 2-pyrrolidinones. The reaction mechanism for the formation of the three products is briefly explained.

Introduction

Enaminones and enamino esters combine the nucleophilic enamine and the electrophilic enone (ester) moieties into one molecule. They are readily obtainable and versatile reagents, and their chemistry has received considerable attention in recent years.[1,2] Besides their use as bidentate ligands in metal-complex synthesis, β-enaminones and enamino esters have been extensively employed as synthons for the synthesis of a wide variety of heterocycles and pharmaceutical compounds.[3,4] The most well-known synthetic route to β-enaminones and enamino esters is the direct condensation of β-dicarbonyl compounds with primary and secondary amines in the appropriate solvent. For this purpose, various improved procedures have been developed.[5] The Huisgen addition is the addition of nitrogen-containing heterocycles such as pyridine and isoquinoline to electron-deficient alkynes giving a very potent intermediate, which can then be trapped by various reagents.[3c,6] In fact, the Huisgen addition is also a convenient method for the preparation of β-enaminones and esters by adding aliphatic and aromatic amines to activated alkynes with carbonyl groups.[7,8] The domino reactions of a primary amine, an acetylenedicarboxylate, and a third component have provided elegant procedures for the synthesis of various N- and N,O-heterocycles.[9–11] Recently, we have found that the four-component reactions of arylamines, acetylenedicarboxylate, aromatic aldehydes, and acetonitrile derivatives provide an efficient and practical method for the synthesis of 1,4-dihydropyridines.[12] In this paper we report the new molecular diversity that can be achieved by the three-component reactions of aromatic aldehydes, arylamines, and acetylenedicarboxylates, as well as an efficient synthesis for hydroxy-substituted hydropyridine and pyrrolidinone derivatives.

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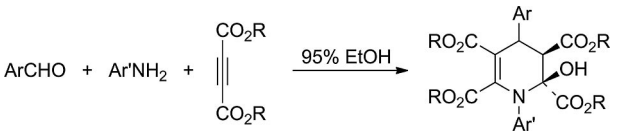
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201100008.

Results and Discussion

It is known that the conjugate addition of aniline to acetylenedicarboxylate rapidly gives 2-(phenylamino)but-2-enedioate.[8,13] We believe that a double conjugate adduct could be achieved if a second molecule of acetylenedicarboxylate was added to the reaction system, and that this adduct might be useful as a potential synthon for tandem reactions. Recently, the $AgBF_4$-catalyzed addition and oxidative cyclization of two molecules of alkynoates with benzylamine to give polysubstituted pyrroles[14] and the one-pot sequential reaction of benzoylacetylene with 2-furylmethylamine to give 1,4-dihydropyridines[15] have been reported as two successful examples of this synthetic methodology. With this concept in mind, we began to investigate the reaction with dimethyl acetylenedicarboxylate. An ethanol solution of 1 M aniline and 2 M dimethyl acetylenedicarboxylate was stirred at room temperature for 10 min. A 1 M solution of *p*-methylbenzaldehyde was then added, and the whole mixture was stirred at room temperature for an additional 48 h. After workup, we were very pleased to find that the polysubstituted 2-hydroxyhydropyridine **1a** was produced in satisfactory yield (71%). In fact, it was constructed from the corresponding units of one molecule of aniline, one molecule of *p*-methylbenzaldehyde, and two molecules of dimethyl acetylenedicarboxylate. The existence of one hydroxy group at the C-2 position was totally unexpected, which clearly resulted from a hydration step in the reaction process. Next, the reaction conditions of the three-component reaction were examined with regard to base cat-

alyst, solvent, temperature, and sequence of the addition of substrates. The reaction was much slower in solvents such as acetonitrile, tetrahydrofuran, dichloromethane, or chloroform. If the reaction was carried out at an elevated temperature or with the addition of a base catalyst, a complicated mixture was formed. Although the reaction time was a little longer, it was best to conduct this three-component reaction in alcohol at room temperature over 2 d. Under identical conditions, reactions between similar aromatic aldehydes and arylamines gave the corresponding polysubstituted 2-hydroxyhydropyridines **1b**–**1n** in high yields (Table 1). Aromatic aldehydes and amines with either electron-donating or -withdrawing substituents showed similar reactivity and efficiently afforded the desired products. Both α-naphthylamine and benzylamine were used in the reaction and resulted in good yields of products (Table 1, Entries 12 and 13), and diethyl acetylenedicarboxylate also showed very high reactivity (Table 1, Entry 14). These results indicate that this three-component reaction is general and has a very broad substrate scope. The structures of 2-hydroxyhydropyridines **1a**–**1n** were supported by elemental analysis, ^{1}H and ^{13}C NMR and IR spectroscopy as well as mass spectrometry. Further confirmation of the structure with single-crystal X-ray diffraction was used for compounds **1b** and **1d** (Figure 1). From Figure 1 it is clear that the hydroxy group is connected to the C-2 atom of the pyridyl ring. The tetrahydropyridine ring exists in a boat conformation, and the two ester groups at C-2 and C-3 are in the *trans* position. The other two ester groups are attached to the C=C bond.

Table 1. Synthesis of polysubstituted 2-hydroxytetrahydropyridines.



Entry	Product	Ar	Ar′	R	Yield [%]
1	**1a**	*p*-$CH_3C_6H_4$	C_6H_5	Me	71
2	**1b**	*m*-$O_2NC_6H_4$	C_6H_5	Me	81
3	**1c**	C_6H_5	*p*-$CH_3C_6H_4$	Me	73
4	**1d**	*p*-ClC_6H_4	*p*-$CH_3C_6H_4$	Me	79
5	**1e**	*p*-BrC_6H_4	*p*-$CH_3C_6H_4$	Me	72
6	**1f**	*m*-$O_2NC_6H_4$	*p*-$CH_3C_6H_4$	Me	84
7	**1g**	C_6H_5	*p*-$CH_3OC_6H_4$	Me	78
8	**1h**	*p*-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	Me	78
9	**1i**	*m*-$O_2NC_6H_4$	*p*-$CH_3OC_6H_4$	Me	86
10	**1j**	C_6H_5	*p*-ClC_6H_4	Me	74
11	**1k**	*m*-$O_2NC_6H_4$	*p*-ClC_6H_4	Me	87
12	**1l**	*m*-$O_2NC_6H_4$	α-naphthyl	Me	68
13	**1m**	*p*-$CH_3OC_6H_4$	$C_6H_5CH_2$	Me	70
14	**1n**	*m*-$O_2NC_6H_4$	*p*-$CH_3OC_6H_4$	Et	74

The formation of 2-hydroxytetrahydropyridine from the three-component reaction of an aldehyde, an amine, and an acetylenedicarboxylate indicated that water in the alcohol participated in the reaction. It was very interesting to investigate this three-component reaction in a strictly nonaqueous system. Thus, we carried out the three-component reactions of aromatic aldehydes and arylamines in absolute ethanol under nitrogen using a Schlenk line. Under these absolutely dry conditions, we successfully obtained the expected polysubstituted 1,4-dihydropyridines **2a**–**2f** in 68–81% yields (Table 2).

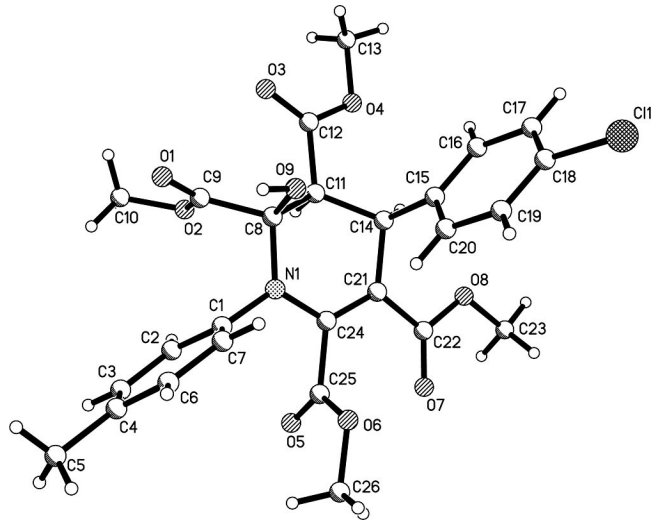
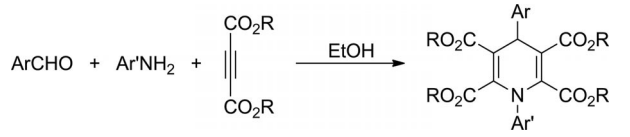


Figure 1. Molecular structure of 2-hydroxyhydropyridine **1d**.

Table 2. Synthesis of polysubstituted 1,4-dihydropyridines.

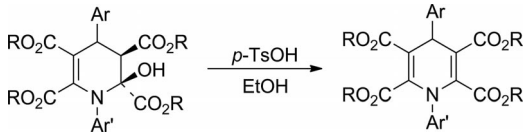


Entry	Product	Ar	Ar′	R	Yield [%]
1	**2a**	*p*-$CH_3OC_6H_4$	*p*-$CH_3C_6H_4$	Me	69
2	**2b**	*m*-$O_2NC_6H_4$	*p*-$CH_3C_6H_4$	Me	77
3	**2c**	*p*-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	Me	75
4	**2d**	*m*-$O_2NC_6H_4$	*p*-ClC_6H_4	Me	81
5	**2e**	*m*-$O_2NC_6H_4$	C_6H_5	Et	68
6	**2f**	*m*-$O_2NC_6H_4$	*p*-ClC_6H_4	Et	71

To examine the reaction mechanism of this three-component reaction, we tested the reactivity of the prepared 2-hydroxytetrahydropyridines in a dehydration reaction. In the presence of the catalyst *p*-toluenesulfonic acid (TsOH), a solution of the 2-hydroxyhydropyridines in ethanol was heated to reflux for approximately 1 h. The 2-hydroxypyridines were successfully dehydrated to give the corresponding 1,4-dihydropyridines in nearly quantitative yields (Table 3). It should be pointed out that 1,4-dihydropyridines **2b** and **2c** (Table 3, Entries 1 and 2) were also prepared directly by a three-component reaction in absolute ethanol (Table 2, Entries 2 and 3). The other 1,4-dihydropyridines **2g**–**2j** (Table 3, Entries 3–6) were new products, prepared by this acid-catalyzed dehydration reaction. The crystal structure of 1,4-dihydropyridine **2i** was determined by X-ray diffraction (Figure 2). It is noteworthy that 1,4-dihydropyridines in an aqueous ethanol solution at either room temperature or at an elevated temperature did not convert

to 2-hydroxypyridines, which indicates that 1,4-dihydropyridines might not result from the hydration of 2-hydroxypyridines.

Table 3. Synthesis of polysubstituted 1,4-dihydropyridines.



Entry	Product	Ar	Ar′	R	Yield [%]
1	**2b**	*m*-$O_2NC_6H_4$	*p*-$CH_3C_6H_4$	Me	97
2	**2c**	*p*-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	Me	97
3	**2g**	*m*-$O_2NC_6H_4$	C_6H_5	Me	95
4	**2h**	C_6H_5	*p*-$CH_3C_6H_4$	Me	98
5	**2i**	*m*-$O_2NC_6H_4$	*p*-$CH_3OC_6H_4$	Me	95
6	**2j**	*m*-$O_2NC_6H_4$	*p*-$CH_3OC_6H_4$	Et	95

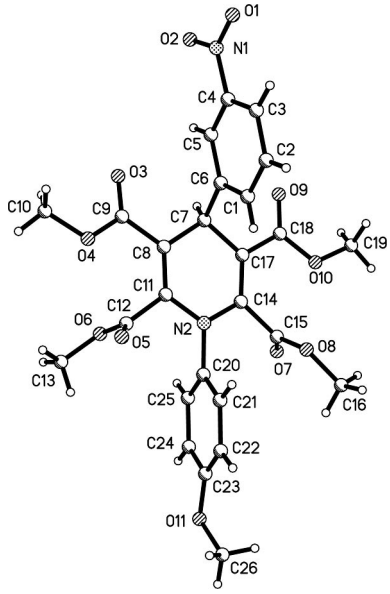
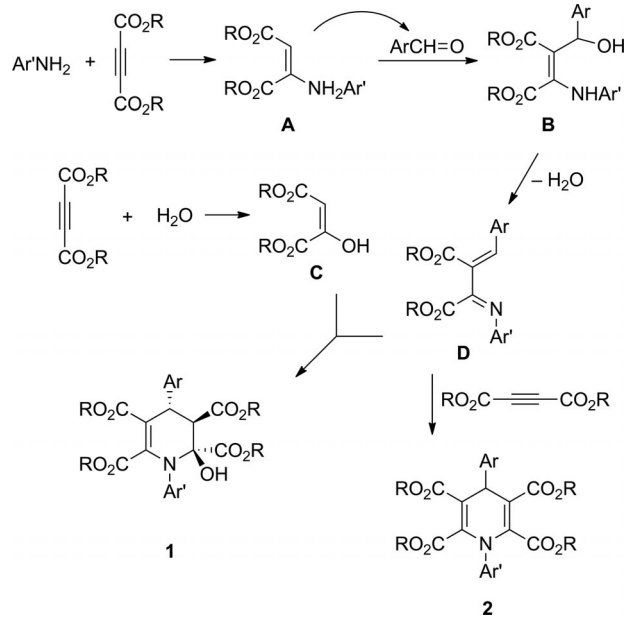


Figure 2. Molecular structure of 1,4-dihydropyridine **2i**.

On the basis of the results from the three-component and acid dehydration reactions, a possible mechanism is proposed in Scheme 1. First, arylamine adds to the acetylenedicarboxylate to give 1,3-dipolar intermediate **A**. Secondly, the nucleophilic addition of 1,3-dipolar intermediate **A** to the aromatic aldehyde produces intermediate **B**. Thirdly, intermediate **B** is dehydrated to yield 1-aza-1,3-diene intermediate **D**. Finally, the hetero-Diels–Alder reaction of 1-aza-1,3-diene **D** with a second molecule of acetylenedicarboxylate results in 1,4-dihydropyridine **2**. In an aqueous ethanol solution, the nucleophilic addition of water to the second molecule of acetylenedicarboxylate gives the 2-hydroxy-but-2-enedioate **C**. A similar hetero-Diels–Alder reaction of 1-aza-1,3-diene **D** with 2-hydroxy-but-2-enedioate **C** yields 2-hydroxyhydropyridine **1** as the final product. It should be noted that at present this mechanism including the hetero-Diels–Alder reaction is only theoretical. The exact reaction mechanism requires more experimental support. There are many examples in the literature of hetero-Diels–Alder reactions of 1-azabutadienes in the preparation of pyridines and dihydropyridines[16] which might support the present mechanism.

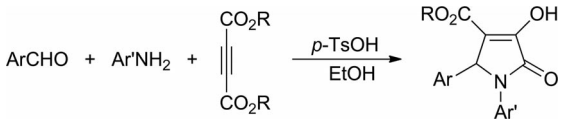


Scheme 1. Proposed mechanism for the three-component reaction.

Encouraged by the above results, we turned our attention to combine the three-component reaction and acid-catalyzed dehydration reaction into a more convenient one-step process. The reaction of benzaldehyde, aniline, dimethyl acetylenedicarboxylate, and a catalytic amount of *p*-toluensulfonic acid in ethanol did not give the expected 1,4-dihydroxypyridine, but resulted in 2-hydroxytetrahydroxypyridine and a new pyrrolidinone derivative as the main products. This result is very interesting, because there have been no reports for the preparation of pyrrolidinones from an addition reaction to electron-deficient alkynes. To obtain pyrrolidinone as the main product, reaction conditions for this acid-catalyzed three-component reaction were carefully examined. It was best to combine benzaldehyde, aniline, and 20 mol-% of *p*-toluensulfonic acid as the catalyst in ethanol, and stir the mixture at room temperature for 30 min. The acetylenedicarboxylate was then introduced, and the entire reaction was terminated after 24 h to give polysubstituted pyrrolidinone **3a** in 62% yield (Table 4). With the optimized conditions in hand, we turned our attention to examine the scope of the reaction. Other aromatic aldehydes and arylamines were treated with dimethyl or diethyl acetylenedicarboxylate to give the corresponding pyrrolidinone derivatives **3b**–**3j** in good yields (Table 4, Entries 2–10). Benzylamine was also successfully used in the reactions to give *N*-benzylpyrrolidinone derivatives **3k**–**3n** in 56–62% yields (Table 4, Entries 11–14). These results demonstrate that a domino reaction for the efficient synthesis of versatile and functionalized *N*-arylpyrrolidinones has been successfully established. The structures of the prepared polysubstituted pyrrolidinones **3a**–**3n** were supported by elemental analysis, ^1H and ^{13}C NMR and IR spectroscopy as well as

mass spectrometry. In addition, the structures of compounds **3c** and **3h** were confirmed by single-crystal X-ray diffraction (Figure 3).

Table 4. Synthesis of polysubstituted pyrrolidinones.



Entry	Product	Ar	Ar′	R	Yield [%]
1	**3a**	C_6H_5	C_6H_5	Me	62
2	**3b**	*m*-$O_2NC_6H_4$	C_6H_5	Me	76
3	**3c**	C_6H_5	C_6H_5	Et	61
4	**3d**	*p*-$CH_3OC_6H_4$	C_6H_5	Et	52
5	**3e**	*m*-$O_2NC_6H_4$	C_6H_5	Et	72
6	**3f**	C_6H_5	*p*-$CH_3C_6H_4$	Me	54
7	**3g**	C_6H_5	*p*-$CH_3OC_6H_4$	Me	59
8	**3h**	C_6H_5	*p*-ClC_6H_4	Me	60
9	**3i**	*p*-ClC_6H_4	*p*-ClC_6H_4	Me	61
10	**3j**	*m*-$O_2NC_6H_4$	*p*-ClC_6H_4	Me	65
11	**3k**	*p*-FC_6H_4	$C_6H_5CH_2$	Me	60
12	**3l**	*p*-ClC_6H_4	$C_6H_5CH_2$	Me	56
13	**3m**	*m*-$O_2NC_6H_4$	$C_6H_5CH_2$	Me	62
14	**3n**	*m*-$O_2NC_6H_4$	$C_6H_5CH_2$	Et	60

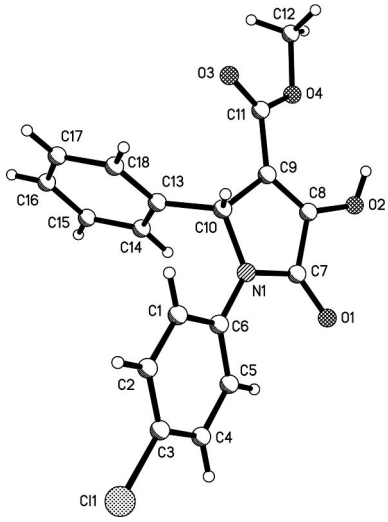
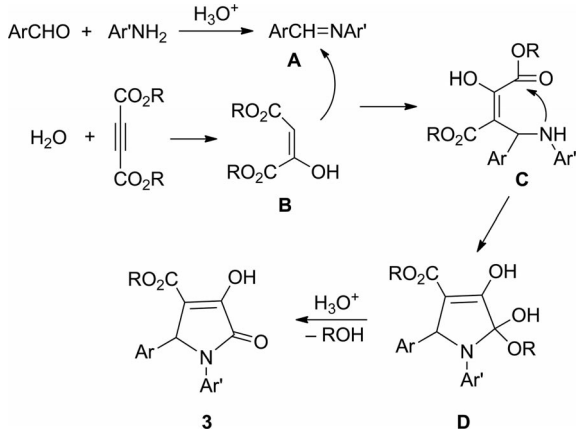


Figure 3. Molecular structure of pyrrolidinone **3h**.

The ^{1}H NMR spectra of pyrrolidinones **3a**–**3n** typically had one broad peak at $\delta \approx 9.00$ ppm assigned to the 3-hydroxy group, which suggests that the product is predominately in the enol form. The crystal structures of **3c** and **3h** clearly indicate the existence of a carbonyl group at C-2 and a hydroxy group at C-3 of the pyrrolidine ring.

The formation of pyrrolidinones suggests that the acid-catalyzed three-component reaction of the aldehyde, amine, and acetylenedicarboxylate proceeded according to an alternative reaction path, which is tentatively proposed in Scheme 2. First, the acid-catalyzed condensation of the aromatic aldehyde with the arylamine in ethanol produces imine **A**. When acetylenedicarboxylate is added to the mixture, water undergoes a nucleophilic addition to the dicarboxylate giving 1,3-dipolar intermediate **B**. Addition of 1,3-dipolar intermediate **B** to imine **A** gives intermediate **C**. The intramolecular attack of the amino group on one of the esters results in the formation of the nitrogen-containing five-membered ring. Finally, the protonated alcohol is eliminated to yield the final pyrrolidinone product. In this reaction pathway, the key step is the acid-catalyzed reaction of the imine with the hydroxylated acetylenedicarboxylate. Reactions of an imine with an activated alkyne or the multicomponent reactions of an aldehyde, an amine, and an electron-deficient alkyne have been extensively investigated by several groups, and versatile N- and N,O-containing heterocyclic systems have been prepared from these reactions.[17–21] Jiang and co-workers have described a similar one-pot multicomponent reaction with acetylenedicarboxylates, amines, and aldehydes in the presence of acetic acid to give 3-arylamino-2-pyrrolidinone derivatives in good yields.[22] Here our result provides an unprecedented synthetic method for the preparation of 3-hydroxy-2-pyrrolidinone derivatives.



Scheme 2. Mechanism of the acid-catalyzed three-component reaction.

Conclusions

We investigated the three-component reaction of an aromatic aldehyde, an arylamine, and an acetylenedicarboxylate under different reaction conditions and found very interesting molecular diversity for this multicomponent reaction based on the easy formation and versatile reactivity of β-enamino esters. This reaction provides a convenient and selective procedure for the preparation of functionalized 2-hydroxyhydropyridines, 1,4-dihydropyridines, and 2-pyrrolidinones in satisfactory yields. Furthermore, we have proposed rational reaction mechanisms and have established the scope and limitation for this reaction, which enabled further modification and led to molecular diversity. The potential uses for the reaction in synthetic and medicinal chemistry might be quite significant.

Experimental Section

General Procedure for the Synthesis of Polysubstituted 2-Hydroxyhydropyridines: In a round-bottomed flask a solution of arylamine

(2.0 mmol) and dimethyl acetylenedicarboxylate (0.284 g, 2.0 mmol) in ethanol (5 mL) was stirred at room temperature for 10 min. The aromatic aldehyde (2.0 mmol) was then added, and the mixture was stirred at room temperature for 48 h. The resulting precipitates were collected and washed with cold ethanol to give pure white solid **1a** (71%). M.p. 160–162 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62 (s, 1 H, Ar), 7.34–7.32 (m, 2 H, Ar), 7.29 (d, J = 7.8 Hz, 3 H, Ar), 7.09 (br., 1 H, Ar), 7.06 (d, J = 7.8 Hz, 2 H, Ar), 4.62 (d, J = 6.6 Hz, 1 H, CH), 4.26 (s, 1 H, OH), 3.98 (d, J = 6.0 Hz, 1 H, CH), 3.74 (s, 3 H, OCH_3), 3.52 (s, 3 H, OCH_3), 3.45 (s, 3 H, OCH_3), 3.43 (s, 3 H, OCH_3), 2.31 (s, 3 H, CH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 171.2, 170.1, 166.4, 164.7, 147.7, 138.3, 136.4, 135.2, 129.4, 129.1, 128.4, 99.8, 85.4, 53.3, 52.3, 52.1, 51.6, 50.4, 37.6, 21.1 ppm. IR (KBr): $\tilde{\nu}$ = 3472, 2955, 1756, 1696, 1596, 1498, 1441, 1337, 1236, 1159, 1116, 1059, 975, 892, 854, 809 cm^{-1}. MS: m/z (%) = 496.71 (100) $[M - 1]^+$. $C_{26}H_{27}NO_9$ (497.49): calcd. C 62.77, H 5.47, N 2.82; found C 62.46, H 5.71, N 2.57.

General Procedure for the Synthesis of Polysubstituted Dihydropyridines: Under nitrogen a solution of arylamine (2.0 mmol) and dimethyl acetylenedicarboxylate (0.284 g, 2.0 mmol) in absolute ethanol (5 mL, distilled before use from Mg) was stirred at room temperature for 10 min. The aromatic aldehyde (2.0 mmol) in absolute ethanol (2 mL) was then added by syringe, and the mixture was stirred at room temperature for 48 h. The resulting precipitates were collected and washed with cold ethanol to give pure yellow solid **2a** (69%). M.p. 169–170 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36 (br. s, 2 H, Ar), 7.20 (br. s, 2 H, Ar), 7.16 (br. s, 2 H, Ar), 6.88 (br. s, 2 H, Ar), 4.99 (s, 1 H, CH), 3.80 (s, 3 H, OCH_3), 3.65 (s, 6 H, OCH_3), 3.46 (s, 6 H, OCH_3), 2.36 (s, 3 H, CH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.9, 163.6, 158.7, 141.8, 140.0, 137.2, 134.4, 130.0, 129.5, 129.0, 114.0, 106.1, 55.2, 52.5, 52.0, 36.3, 21.3 ppm. IR (KBr): $\tilde{\nu}$ = 3008, 2951, 1748, 1706, 1643, 1595, 1508, 1439, 1328, 1218, 1115, 1079, 1030, 975, 851 cm^{-1}. MS: m/z (%) = 508.36 (100) $[M - 1]^+$. $C_{27}H_{27}NO_9$ (509.5): calcd. C 63.65, H 5.34, N 2.75; found C 63.41, H 5.63, N 2.69.

General Procedure for the Synthesis of Polysubstituted Dihydropyridines from the Acid-Catalyzed Dehydration of 2-Hydroxyhydropyridines: A solution of the 2-hydroxyhydropyridines (1.0 mmol) and *p*-toluenesulfonic acid (0.5 mmol) in ethanol (10 mL) was refluxed for about 1 h. The solution was then concentrated to half the volume. The resulting precipitates were collected and washed with cold ethanol to give pure light-yellow solid **2g** (95%). M.p. 185–186 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.40 (s, 1 H, Ar), 8.14 (d, J = 7.8 Hz, 1 H, Ar), 7.80 (d, J = 6.6 Hz, 1 H, Ar), 7.54 (t, J = 7.2 Hz, 1 H, Ar), 7.44–7.41 (m, 5 H, Ar), 5.20 (s, 1 H, CH), 3.67 (s, 6 H, OCH_3), 3.45 (s, 6 H, OCH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.2, 163.0, 148.7, 146.7, 142.6, 136.6, 134.0, 130.3, 130.2, 129.5, 129.1, 123.0, 122.3, 105.1, 52.7, 52.2, 37.2 ppm. IR (KBr): $\tilde{\nu}$ = 3003, 2952, 1747, 1709, 1648, 1594, 1526, 1489, 1437, 1318, 1223, 1117, 1078, 978, 946, 901, 856, 814, 770 cm^{-1}. MS: m/z (%) = 509.48 (100) $[M - 1]^+$. $C_{25}H_{22}N_2O_{10}$ (510.45): calcd. C 58.82, H 4.34, N 5.49; found C 58.74, H 4.49, N 5.23.

General Procedure for the Synthesis of Polysubstituted Pyrrolidinones: In a 50 mL flask, a solution of an aromatic aldehyde (2.0 mmol), an arylamine (2.0 mmol), and *p*-toluenesulfonic acid (0.4 mmol) in ethanol (5 mL) was stirred at room temperature for approximately 30 min. Acetylenedicarboxylate (2.0 mmol) was then added, and the mixture was stirred at room temperature for 48 h. The resulting precipitates were collected and washed with cold ethanol to give pure light yellow solid **3a** (62%). M.p. 180–182 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.97 (s, 1 H, OH), 7.47 (d, J = 7.8 Hz, 2 H, Ar), 7.29–7.26 (m, 4 H, Ar), 7.24 (d, J = 6.6 Hz, 3 H, Ar), 7.11 (t, J = 7.8 Hz, 1 H, Ar), 5.75 (s, 1 H, CH), 3.76 (s, 3 H, OCH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 165.2, 162.9, 156.1, 136.2, 135.0, 129.0, 128.7, 128.6, 127.5, 125.9, 122.4, 112.9, 61.7, 52.1 ppm. IR (KBr): $\tilde{\nu}$ = 3209, 2956, 1681, 1596, 1498, 1458, 1382, 1303, 1234, 1196, 1131, 996, 928, 833, 759 cm^{-1}. MS: m/z (%) = 308.77 (100) $[M - 1]^+$. $C_{18}H_{15}NO_4$ (309.32): calcd. C 69.89, H 4.89, N 4.53; found C 69.64, H 5.27, N 4.16.

CCDC-804511 (**1b**), -804512 (**1d**), -805708 (**2i**), -805782 (**3c**), -805709 (**3h**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Molecular structures of **1b** to **3c**; experimental procedures and spectroscopic data for all new compounds.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Grant No. 20972132).

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Received: January 5, 2011
Published Online: April 26, 2011

