# One-Pot Synthesis of Pyrrolo[1,2-*a*]quinolin-1-ones by the Cyclocondensation of 5-Hydroxy-1-arylpyrrolidin-2-ones with Dicarbonyls



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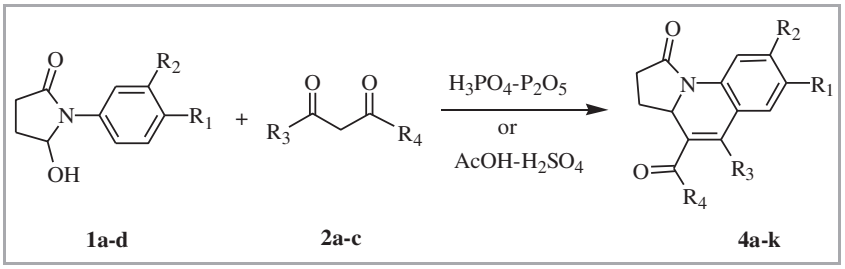


A one-pot synthesis of pyrrolo[1,2-*a*]quinolin-1-ones has been developed from the reactions of 5-hydroxy-1-arylpyrrolidin-2-ones with 1,3-dicarbonyl compounds under the promotion of $H_3PO_4/P_2O_5$ or $HOAc/H_2SO_4$. The pyrrolo[1,2-*a*]quinolin-1-ones are formed by two-step reactions, that is, the coupling of *N*-acyliminium ion intermediates produced from 5-hydroxy-1-arylpyrrolidin-2-ones with 1,3-dicarbonyls and subsequent Friedel–Crafts reactions of the resulting ketone with the aryl ring.

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## INTRODUCTION

*N*-acyliminium ions are important, reactive species in organic synthesis for the construction of carbon–carbon and carbon-heteroatom bonds [1,2]. The high electrophilicity of *N*-acyliminium ions made these species much suitable for electrophilic addition to multiple bonds and aromatic electrophilic substitution reactions. The intramolecular reaction of *N*-acyliminium ions has been widely used in the synthesis of polycyclic compounds, such as natural alkaloid products [1,3], and the intermolecular addition or coupling reactions of *N*-acyliminium ions with nucleophiles lead to various polyfunctional compounds [2]. We recently reported the synthesis of isoindolo[2,1-*a*]quinolin-11-ones by the [4 + 2] reactions of *N*-aryl-*N*-acyliminium ions with olefins or by coupling and cyclocondensation with 1,3-dicarbonyls [4]. As part of our continuing interest in the chemistry of *N*-acyliminium ions, we report here an efficient one-pot synthesis of pyrrolo[1,2-*a*]quinolin-1-ones by reactions of *N*-acyliminium cations, generated from 5-hydroxy-1-arylpyrrolidin-2-one, with dicarbonyls (Scheme 1).

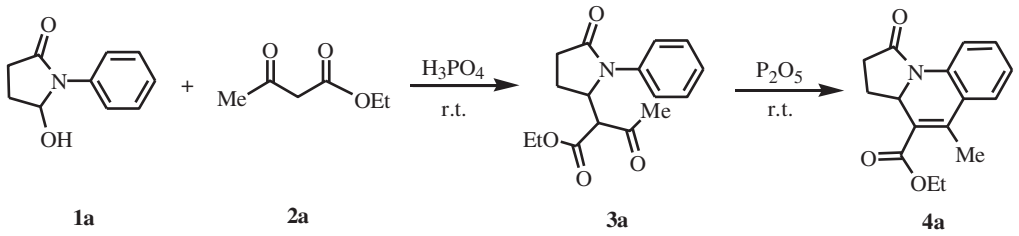
Pyrrolo[1,2-*a*]quinolinone derivatives are a class of molecules that possess a wide range of biological activities [5], such as antileukemic, antiallergic, and antibacterial activities. Pyrrolo[1,2-*a*]quinolinones are also used as versatile key intermediates in the synthesis of alkaloid gephyrotoxins [6]. Therefore, a variety of methodologies for the synthesis of pyrrolo[1,2-*a*]quinolinone derivatives have been developed [7], for example, stereoselective intramolecular addition of *N*-acyliminium ions to alkene and ring contraction [7a], gold-catalyzed one-pot cascade construction of highly functionalized pyrrolo[1,2-*a*]quinolin-1-ones [7b], Lewis acid-catalyzed ring-opening and rearrangement of aryl epoxyazides [7c], Reformatsky reaction between diethyl bromomalonate and *N*-arylpyrrolidine-2-thiones and cyclization of the resulting enaminone intermediates in polyphosphoric acid [3a], and the intramolecular Friedel–Crafts reactions of pyrrolidin-2-one-5-acetyl chlorides [3g]. Despite these great achievements, the development of more efficient and practical strategy for the synthesis of pyrrolo[1,2-*a*]quinolinone derivatives is still highly desirable.

## RESULTS AND DISCUSSION

The reaction of 5-hydroxy-1-phenylpyrrolidin-2-one (**1a**) with ethyl acetoacetate (**2a)** was chosen as a representative for the investigation of the reaction conditions (Scheme 1). It was found that the reaction of **1a** with **2a** proceeded quickly to give the coupling product **3a** under the $H_3PO_4$ catalysis at room temperature (RT), but the subsequent intramolecular Friedel–Crafts reaction of **3a** to produce **4a** was difficult. Only by the addition of strong dehydration agents, such as $P_2O_5$ or $H_2SO_4$, could the intramolecular Friedel–Crafts reaction in **3a** proceed smoothly to yield the product pyrrolo[1,2-*a*]quinolinone **4a**.

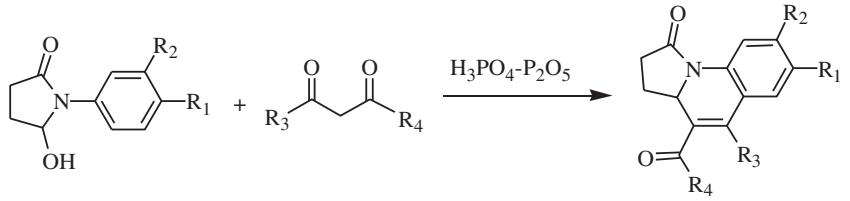
We surveyed the effects of different catalysts to the reaction of **1a** with **2a** (Table 1) and found that the combination

**Scheme 1.** Reactions of 5-hydroxy-1-phenylpyrrolidin-2-one (**1a**) with ethyl acetoacetate (**2a**).




**1a** **2a** **3a** **4a**

**Scheme 2.** Reactions of 5-hydroxy-1-arylpyrrolidin-2-one (**1a–d**) with **2a–c** under selected conditions.




**1a-d** **2a-c** **4a-k**

of $H_3PO_4$ and $P_2O_5$ or AcOH and $H_3PO_4$ was more effective than other single catalyst. Comparatively, a better result could be obtained from catalysis of $H_3PO_4/P_2O_5$ (Method A). Thus, $H_3PO_4/P_2O_5$ was selected as the reagent system for the reactions of all other substrates.

A range of 5-hydroxy-2-arylpyrrolidin-2-ones (**1a–d**) and 1,3-dicarbonyls (**2a–d**) was examined to explore the generality of this one-pot synthesis of pyrrolo[1,2-*a*]quinolinones (Scheme 2 and Table 2). It could be observed from Table 2 that all 5-hydroxy-1-aryl-pyrrolidin-2-ones (**1a–d**) could react with 1,3-dicarbonyls (**2a–c**) smoothly under selected conditions to afford the cyclization products **3a–k** in moderate to highly yields. But for reaction of **1a** with ethyl benzoylacetate (**2d**), the coupling reaction proceeded quickly under the catalysis of $H_3PO_4/P_2O_5$ to afford ethyl 2-(5-oxo-1-phenylpyrrolidin-2-yl)-2-benzoylacetate **3d**; no further intramolecular Friedel–Crafts reaction took place even at a heating temperature of 70°C (Scheme 3). This result indicated that the intramolecular Friedel–Crafts reaction for the benzoyl group was difficult under these conditions, and this selectivity could also be observed from the reaction of **1a** with **2c** in which only the acetyl group took part in the intramolecular Friedel–Crafts reaction. These results may be derived from both the lower reactivity of the protonated carbonyl group in benzoyl group and the larger steric hindrance of benzoyl group than those of acetyl group. All products were fully identified by $^1$H NMR, $^{13}$C NMR, MS, and HRMS.

**Table 1**

Reaction of **1a** with **2a** under different conditions.

| Entry | Method | | T (°C) | t (h) | Product | Yield[a] (%) |
|---|---|---|---|---|---|---|
| 1 | $H_3PO_4/P_2O_5$ | A | RT | 10 | **4a** | 60 |
| 2 | $H_3PO_4/P_2O_5$ | B | 70 | 5 | **4a** | 48 |
| 3 | $CH_3CO_2H/H_2SO_4$ | C | RT | 10 | **4a** | 55 |
| 4 | $CF_3SO_3H/CH_2Cl_2$ | D | RT. | 20 | **4a** | 33 |
| 5 | $CF_3CO_2H/CH_2Cl_2$ | E | RT | 20 | **4a** | 15 |

[a]Isolated yields.

Although the reactions of **1a–d** and **2a–c** all afforded the cyclization products **4a–k**, great differences for the reactivity of the substrates could be observed in Table 2. For 1,3-dicarbonyls **2a–c**, acetylacetone (**2b)** was the most reactive, and the yields of the corresponding products **4b**, **4e**, **4h**, and **4j** were relatively higher, probably because two acetyl groups were present in them. The substituents on phenyl ring in **1a–d** also have great influence to the reaction rate. The electron-donating groups such as methyl in **1b** and methoxy group in **1c** promoted the reactions and increased yields of the product **4d–h**, but the electron-attracting groups such as the chlorine atom in **1d** retarded the process, and the reactions of **1d** with **2a–c** needed to be carried out at higher temperature. Meanwhile, the yields of the product **4i–k** were decreased. These results could be ascribed to the activating effect of methyl and methoxy group and the deactivating effect of chlorine atom. It could be inferred that the electronic effects of these substituents affected mainly to the intramolecular Friedel–Crafts

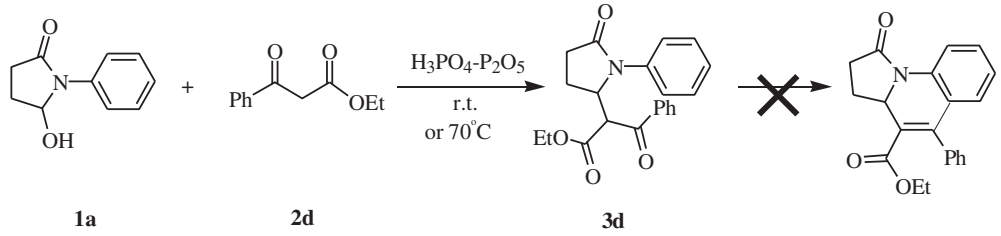
**Table 2**

Reactions of 5-hydroxy-2-arylpyrrolidin-2-one (**1a–d**) with 1,3-dicarbonyls (**2a–d**).

| | Reactants | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Entry | | $R^1$ | $R^2$ | | $R^3$ | $R^4$ | Method[a] | Time (h) | Product | Yield[b] (%) |
| 1 | **1a** | H | H | **2a** | $CH_3$ | OEt | A | 10 | **4a** | 60 |
| 2 | **1a** | H | H | **2b** | $CH_3$ | $CH_3$ | A | 1.5 | **4b** | 62 |
| 3 | **1a** | H | H | **2c** | $CH_3$ | Ph | A | 20 | **4c** | 51 |
| 4 | **1a** | H | H | **2d** | Ph | OEt | A or B | 24 | **3d** | 85 |
| 5 | **1b** | $CH_3$ | H | **2a** | $CH_3$ | OEt | A | 6 | **4d** | 65 |
| 6 | **1b** | $CH_3$ | H | **2b** | $CH_3$ | $CH_3$ | A | 1 | **4e** | 68 |
| 7 | **1b** | $CH_3$ | H | **2c** | $CH_3$ | Ph | A | 16 | **4f** | 50 |
| 8 | **1c** | $OCH_3$ | $OCH_3$ | **2a** | $CH_3$ | OEt | A | 4 | **4g** | 80 |
| 9 | **1c** | $OCH_3$ | $OCH_3$ | **2b** | $CH_3$ | $CH_3$ | A | 0.5 | **4h** | 83 |
| 10 | **1d** | Cl | H | **2a** | $CH_3$ | OEt | B | 12 | **4i** | 38 |
| 11 | **1d** | Cl | H | **2b** | $CH_3$ | $CH_3$ | B | 2 | **4j** | 40 |
| 12 | **1d** | Cl | H | **2c** | $CH_3$ | Ph | B | 24 | **4k** | 32 |

[a]See Table 1 for reaction conditions.
[b]Isolation yields based on **1a–d**.

**Scheme 3.** Reactions of 5-hydroxy-1-phenylpyrrolidin-2-one (**1a**) with ethyl benzoylacetate (**2d**).




**1a** **2d** **3d**

reaction because the first coupling reactions of **1a–d** with **2a–c** were usually very quick.

A mechanism is proposed to explain the formation of **4a** as depicted in Scheme 4. The reaction is initiated by the formation of the *N*-acyliminium ion (**1aa**) by acid-catalyzed dehydroxylation, and the coupling of the *N*-acyliminium ion with **2a** gives the adduct **3a;** the intramolecular Friedel–Crafts reaction of **3a** takes place with the acid promotion to give the product **4a**.

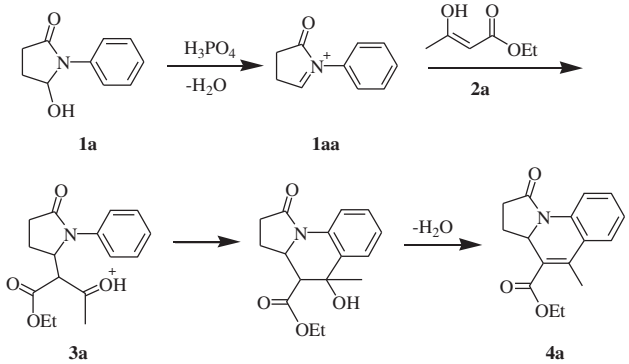
## CONCLUSION

An efficient method for the synthesis of pyrrolo[1,2-*a*] quinolin-1-ones has been achieved by the one-pot reactions of 5-hydroxy-1-arylpyrrolidin-2-ones with 1,3-dicarbonyls under the catalysis of $H_3PO_4/P_2O_5$ or $HOAc/H_2SO_4$. The products pyrrolo[1,2-*a*]quinolin-1-ones are formed by two-step reactions. Generally, only the coupling products from the *N*-acyliminium ions, produced by dehydroxylation of 5-hydroxy-1-phenylpyrrolidin-2-ones, with 1,3-dicarbonyls are formed under the catalysis of $H_3PO_4$ or HOAc at RT, but the coupling products can be transformed to the cyclization products pyrrolo[1,2-*a*]quinolin-1-ones by the addition of small amount of $P_2O_5$ or $H_2SO_4$.

## EXPERIMENTAL

All reagents were purchased from commercial suppliers and used without further purification. Flash chromatography was carried out with silica gel (200–300 mesh). Analytical TLC was

**Scheme 4.** Proposed mechanism for the formation of **4a**.



performed with silica gel GF254 plates (Merct Co., USA), and the products were visualized by UV detection. $^1$H NMR and $^{13}$C NMR (400 and 100 MHz, respectively) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm using TMS as internal standard and spin–spin coupling contants (*J*) are given in Hz. The high resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEXII47e spectrometer (Bruker Co., Germany) by ESI.

**General procedure for the preparation of 5-hydroxy-1-phenylpyrrolidin-2-one (1a-d).** *N*-aryllmaleimide (1.0 mmol) and $CeCl_3.7H_2O$ (1.0 mmol) were dissolved in anhydrous MeOH (10 mL), and the mixture was stirred for 10 min at 0°C; then, $NaBH_4$ (1.1 mmol) was added portion-wise over 5–10 min; $NiCl_2.6H_2O$ (1 mmol) was added immediately, and additional $NaBH_4$ (1.0 mmol) was added. After the mixture was stirred for 5 min at 0°C, the reaction was quenched by addition of water, and the mixture extracted with ethyl acetate (3 × 20 mL). The combined organic layer was dried with anhydrous $Na_2SO_4$ and concentrated in vacuum. The residue was isolated by silica gel column chromatography to obtain the corresponding products **1a–d** (70–85%).

**General procedure for the reaction of 1a–d with 2a–d**.

***Method A.*** To a stirred mixture of 5-hydroxy-1-phenylpyrrolidin-2-one (**1a**, 89 mg, 0.5 mmol) and ethyl acetoacetate (**2a**, 71 mg, 0.55 mmol) was added $H_3PO_4$ (2 mL). After the mixture became homogenous, $P_2O_5$ (1 g, 7 mmol) was added at one portion at RT, and stirring was continued at RT for 10 h. The reaction was quenched with crushed ice, and the solution was extracted with $CH_2Cl_2$ (3 × 15 mL). The organic phase was washed with sat. aq $NaHCO_3$ solution (10 mL) and $H_2O$, respectively, and then dried ($Na_2SO_4$). Concentration at reduced pressure furnished the crude product that was purified by silica gel column chromatography to give 162 mg 1,2,3,3a-tetrahydropyrrolo[1,2-*a*]quinolin-1-one (**4a**) (60%) and recrystalized from ethanol.

***Method C.*** Similarly to Method A, only the $H_3PO_4/P_2O_5$ was replaced by $CH_3CO_2H/H_2SO_4$ (conc.).

***Ethyl 5-methyl-1-oxo-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline-4-carboxylate*** (***4a***). Yellow syrup. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.35 (t, 3H, *J* = 7.2 Hz), 1.93–2.00 (m, 1H), 2.33 (s, 3H), 2.46–2.61 (m, 3H), 4.25–4.36 (m, 2H), 4.89 (t, 1H, *J* = 6.8 Hz), 7.14 (t, 1H, *J* = 8.0 Hz), 7.34 (t, 1H, *J* = 8.0 Hz), 7.44 (d, 1H, *J* = 7.6 Hz), 8.20 (d, 1H, *J* = 8.4 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 14.2, 15.0, 26.0, 31.1, 56.7, 60.6, 120.1, 124.5, 125.3, 127.7, 128.0, 129.8, 135.0, 136.5, 165.9, 174.1. MS *m/z* (relative intensity, %): 270 (46.3), 242 (83.8), 214 (40.9), 198 (100.0), 170 (43.6), 129 (32.2), 115 (22.4), 57 (21.7). ESI–HRMS: *m/z* Calcd for $C_{16}H_{17}NO_3 + H^+$: 272.1281, found 272.1289.

***4-Acetyl-5-methyl-3,3a-dihydro-2H-pyrrolo[1,2-a]quinolin-1-ones*** (***4b***). Yellow syrup. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.88–1.98 (m, 1H), 2.16 (d, 3H, *J* = 2.0 Hz), 2.40 (s, 3H), 2.42–2.65 (m, 3H), 4.95–4.99 (m, 1H), 7.14 (dt, 1H, *J* = 7.6 Hz, 1.2 Hz), 7.35 (dt, 1H, *J* = 7.8 Hz, 1.2 Hz), 7.41 (dd, 1H, *J* = 8.0 Hz, 1.2 Hz), 8.20 (dd, 1H, *J* = 8.0 Hz, 0.8 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 15.1, 25.3, 31.1, 31.5, 56.9, 120.1, 124.5, 125.0, 126.9, 129.6, 130.8, 134.9, 136.9, 173.7, 201.7. MS *m/z* (relative intensity, %): 241 (27.5), 226 (77.2), 198 (100.0), 170 (48.1), 115 (20.8). ESI–HRMS: *m/z* Calcd for $C_{15}H_{15}NO_2 + H^+$: 242.1176, found 242.1281.

***4-Benzoyl-5-methyl-3,3a-dihydropyrrolo[1,2-a]quinolin-1-one*** (***4c***). White solid, mp 120–122°C. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.90 (s, 3H), 1.88–2.01 (m, 1H), 2.15–2.23 (m, 1H), 2.41–2.60 (m, 3H), 5.06 (t, 1H, *J* = 7.6 Hz), 7.16 (t, 1H, *J* = 7.6 Hz), 7.36 (q, 2H, *J* = 7.6 Hz), 7.51 (t, 2H, *J* = 7.4 Hz), 7.63 (t, 1H, *J* = 7.0 Hz), 7.97 (d, 2H, *J* = 8.0 Hz), 8.30 (d, 1H, *J* = 8.0 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 16.2, 24.6, 31.3, 57.5, 119.9, 124.4, 124.7, 126.7, 129.0 (2C), 129.2 (2C), 129.5, 131.1, 133.6, 133.9, 135.0, 137.4, 173.5, 196.2. MS *m/z* (relative intensity, %): 303 (1.5), 288 (2.4), 161 (5.5), 84 (30.5), 70 (19.8), 40 (100.0). ESI–HRMS: *m/z* Calcd for $C_{20}H_{17}NO_2 + H^+$: 304.1332, found 304.1328.

***Ethyl 5,7-Dimethyl-1-oxo-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline-4-carboxylate*** (***4d***). White solid, mp 147–149°C. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.35 (t, 3H, *J* = 7.0 Hz), 1.91–2.02 (m, 1H), 2.31 (d, 3H, *J* = 2.0 Hz), 2.33 (s, 3H), 2.43–2.67 (m, 3H), 4.24–4.36 (m, 2H), 4.83–4.87 (m, 1H), 7.14 (dd, 1H, *J* = 8.0 Hz, 1.2 Hz), 7.24 (d, 1H, *J* = 1.2 Hz), 8.08 (d, 1H, *J* = 8.4 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 14.2, 14.9, 21.0, 25.9, 31.0, 56.7, 60.4, 119.9, 125.7, 126.9, 127.9, 130.2, 132.6, 133.8, 136.5, 165.6, 173.7. MS *m/z* (relative intensity, %): 285 (41.8), 256 (86.2), 228 (46.3), 212 (100.0), 120 (71.3). ESI–HRMS: *m/z* Calcd for $C_{17}H_{19}NO_3 + H^+$: 286.1438, found 286.1429.

***4-Acetyl-5,7-dimethyl-3,3a-dihydropyrrolo[1,2-a]quinolin-1-one*** (***4e***). White solid, mp 125–127°C. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.86–1.93 (m, 1H), 2.15 (s, 3H), 2.32 (s, 3H), 2.38 (s, 3H), 2.38–2.60 (m, 3H), 4.89–4.94 (m, 1H), 7.14 (d, 1H, *J* = 8.4 Hz), 7.20 (s, 1H), 8.07 (d, 1H, *J* = 8.0 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 15.0, 21.0, 25.2, 31.0, 31.4, 56.6, 119.8, 125.4, 126.6, 130.0, 130.7, 132.3, 133.9, 136.7, 173.3, 201.6. MS *m/z* (relative intensity, %): 255 (6.8), 240 (21.2), 212 (20.5), 173 (100.0), 144 (46.0), 40 (48.0). ESI–HRMS: *m/z* Calcd for $C_{16}H_{17}NO_2 + H^+$: 256.1332, found 256.1325.

***4-Benzoyl-5,7-dimethyl-3,3a-dihydropyrrolo[1,2-a]quinolin-1-one*** (***4f***). Pale yellow solid, mp 137–139°C. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.88–1.99 (m, 1H), 1.93 (s, 1H), 2.14–2.22 (m, 1H), 2.35 (s, 1H), 2.40–2.60 (m, 2H), 5.04 (t, 1H, *J* = 1.6 Hz), 7.17 (d, 1H, *J* = 8.0 Hz), 7.19 (s, 1H), 7.50 (t, 2H, *J* = 7.6 Hz), 7.63 (t, 1H, *J* = 7.6 Hz), 7.97 (d, 2H, *J* = 7.6 Hz), 8.17 (d, 1H, *J* = 8.0 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 16.3, 21.1, 24.6, 31.3, 57.5, 119.7, 125.2, 126.5, 129.0 (2C), 129.2 (2C), 129.8, 131.2, 132.5, 133.5, 133.8, 133.9, 137.4, 173.6, 196.3. MS *m/z* (relative intensity, %): 317 (4.1), 302 (5.5), 149 (18.7), 84 (25.2), 70 (26.0), 43 (100.0). ESI–HRMS: *m/z* Calcd for $C_{21}H_{19}NO_2 + H^+$: 318.1489, found 318.1494.

***Ethyl 7,8-dimethoxy-5-methyl-1-oxo-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline-4-carboxylate*** (***4g***). Pale yellow solid, mp 148–150°C. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.35 (t, 3H, *J* = 7.2 Hz), 1.95–2.02 (m, 1H), 2.34 (s, 3H), 2.34–2.65 (m, 3H), 3.89 (s, 3H), 3.94 (s, 3H), 4.24–4.35 (m, 2H), 4.85–4.88 (m, 1H), 6.94 (s, 1H), 7.94 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 14.2, 15.1, 26.0, 31.1, 56.0, 56.3, 57.1, 60.4, 104.0, 108.5, 119.8, 125.4, 129.7, 137.2, 145.4, 149.8, 166.0, 173.9. MS *m/z* (relative intensity, %): 331 (14.2), 302 (14.1), 261 (70.7), 246 (100.0), 40 (85.8). ESI–HRMS: *m/z* Calcd for $C_{18}H_{21}NO_5 + H^+$: 332.1493, found 332.1486.

***4-Acetyl-7,8-dimethoxy-5-methyl-3,3a-dihydropyrrolo[1,2-a]quinolin-1-one*** (***4h***). Pale yellow solid, mp 168–170°C. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.85–1.96 (m, 1H), 2.18 (d, 3H, *J* = 2.0 Hz), 2.37 (s, 3H), 2.43–2.60 (m, 3H), 3.89 (s, 3H), 3.93 (s, 3H), 4.92–4.96 (m, 1H), 6.90 (s, 1H), 7.94 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 15.2, 25.2, 31.1, 31.4, 56.2, 56.2, 57.3, 103.9, 108.2, 118.9, 129.5, 131.6, 134.5, 145.4, 149.7, 173.4, 201.2. MS *m/z* (relative intensity, %): 301 (5.5), 235 (100.0), 220 (35.6), 138 (37.4), 40 (77.7). ESI–HRMS: *m/z* Calcd for $C_{17}H_{19}NO_4 + H^+$: 302.1387, found 302.1393.

***Ethyl 7-chloro-5-methyl-1-oxo-1,2,3,3a-tetrahydropyrrolo[1,2-a]quinoline-4-carboxylate*** (***4i***). White solid, mp 160–162°C. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.33 (t, 3H, *J* = 7.2 Hz), 1.97–2.04

(m, 1H), 2.90 (d, 3H, $J = 2.0$ Hz), 4.25–4.37 (m, 2H), 4.85–4.90 (m, 1H), 7.29 (dd, 1H, $J = 8.8$ Hz, 2.4 Hz), 7.39 (d, 1H, $J = 2.4$ Hz), 8.17 (d, 1H, $J = 8.8$ Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 14.2, 14.9, 26.0, 31.0, 56.6, 60.7, 121.2, 125.3, 128.7, 129.0, 129.4, 129.7, 133.5, 135.1, 165.6, 173.9. MS *m/z* (relative intensity, %): 305 (16.7), 276 (46.9), 248 (46.9), 232 (100.0), 204 (50.9). ESI–HRMS: *m/z* Calcd for $C_{16}H_{16}ClNO_3 + H^+$: 306.0892, found 306.0887.

***4-Acetyl-7-chloro-5-methyl-3,3a-dihydropyrrolo[1,2-a]quinolin-1-one*** (***4j***). Pale yellow solid, mp 134–136°C. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.91–1.99 (m, 1H), 2.12 (d, 3H, $J = 1.6$ Hz), 2.38 (s, 3H), 2.48–2.63 (m, 3H), 4.92–4.97 (m, 1H), 7.28 (dd, 1H, $J = 8.4$ Hz, 2.4 Hz), 7.35 (d, 1H, $J = 2.4$ Hz), 8.17 (d, 1H, $J = 8.8$ Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 15.0, 25.3, 31.0, 31.5, 56.6, 121.2, 125.0, 128.5, 129.2, 129.4, 129.7, 133.3, 137.7, 173.6, 201.4. MS *m/z* (relative intensity, %): 275 (22.1), 260 (78.2), 193 (100.0), 138 (50.9), 111 (38.3). ESI–HRMS: *m/z* Calcd for $C_{15}H_{14}ClNO_2 + H^+$: 276.0786, found 276.0787.

***4-Benzoyl-7-chloro-5-methyl-3,3a-dihydropyrrolo[1,2-a]quinolin-1-one*** (***4k***). Yellow solid, mp 145–147°C. $^1$H NMR (400 MHz, $CDCl_3$): δ 1.91 (d, 3H, $J = 2.0$ Hz), 1.94–2.01 (m, 1H), 2.16–2.23 (m, 1H), 2.43–2.55 (m, 3H), 5.06 (t, 1H, $J = 7.2$ Hz), 7.32 (d, 1H, $J = 8.8$ Hz), 7.33 (s, 1H), 7.52 (t, 2H, $J = 7.6$ Hz), 7.65 (t, 1H, $J = 7.6$ Hz), 7.96 (d, 2H, $J = 7.2$ Hz), 8.26 (d, 1H, $J = 8.8$ Hz). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 16.2, 24.7, 31.4, 57.4, 121.1, 124.8, 129.1, 129.20, 129.24 (2C), 129.7 (2C), 129.9, 130.0, 133.4, 134.2, 134.6, 137.0, 173.9, 195.9. ESI–HRMS: *m/z* Calcd for $C_{20}H_{16}ClNO_2 + H^+$: 338.0876, found 338.0880.

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