DOI: 10.1002/cjoc.201100238

Efficient Synthesis of Pyrrolo[2,1-*a*]isoquinoline and Pyrrolo[1,2-*a*]quinoline Derivatives via One-pot Two-step Metal-catalyzed Three-component Reactions

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A sequential one-pot two-step reaction for efficient synthesis of pyrrolo[2,1-*a*]isoquinoline and pyrrolo[1,2-*a*]-quinoline derivatives in good yields has been successfully developed. The reaction included firstly Cu-catalyzed three-component reaction of isoquinoline (quinoline), acetylenedicarboxylate and alkynylbenzene and then Pd-catalyzed intramolecular C(sp)-C(sp^2) coupling reaction of initially formed 1-alkenyl-2-alkynyl-1,2-dihydroiso-quinoline (1,2-dihydroquinoline).

Keywords indolizine, pyrrolo[2,1-*a*]isoquinoline, isoquinoline, C-C coupling reaction, three-component reaction

Introduction

Indolizines constitutes the core structure of many naturally occurring alkaloids and have displayed important biological activities which can find a variety of applications in pharmaceutical use.[1,2] Consequently, the syntheses of indolizines have attracted much attention in the past years.[3-5] Among various synthetic approaches for indolizines, 1,3-dipolar cycloaddition reaction of pyridinium *N*-ylide generated *in situ* from a pyridinium salt in the presence of a base with an electron-deficient alkene/alkyne is the most typical methodology, which has been proved to be versatile in terms of efficiency and to have a wide scope of applications.[6-10] Recently the metal-catalyzed C—N bond-forming procedures have proved to be efficient methods for versatile indolizine derivatives.[11,12] These include CuX-mediated cycloisomerization of alkynyl pyridines,[13] and Pd/Cu catalyzed one-pot synthesis of 3-aminoindolizines through the cascade coupling/cycloisomerization reactions of propargyl amines or amides with heteroaryl bromides.[14] However, the starting materials were not easy to synthesize in some cases. Thus developing practical synthetic routes for the efficient synthesis of indolizine derivatives is still highly desirable. As part of our continuing effort into the design of new multicomponent reactions for the preparation of *N*,*O*-containing heterocycles,[15] herein we report the efficient synthesis of the functionalized pyrrolo[2,1-*a*]isoquinolines and pyrrolo[1,2-*a*]quinolines via one-pot two-step metal-catalyzed three-component coupling reaction.

Results and Discussion

As shown in Scheme 1, we anticipated smooth intramolecular cyclization of 1-alkenyl-2-alkynyl-1,2-dihydroisoquinoline **1** by the Pd-catalyzed C(sp)-C(sp^2) coupling reactions, which is inspired by the several successful examples of preparation of indenes by Pd-catalyzed carbocylization reaction of 1-alkenyl-2-alkynylbenzene.[16] To test this idea, the cyclization precursor **1a** was first prepared by the three-component reaction of isoquinoline, dimethyl acetylenedicarboxylate and phenylacetylene according to the reported procedure.[17] Then the Pd-catalyzed cyclization reaction was performed by employing **1a** in the presence of 5 mol% of $Pd(OAc)_2$ and 20 mol% $CuCl_2$ in DMAc as solvent, which was used in the Pd-catalyzed synthesis of indene.[16a] After stirring the reaction mixture at 80 ℃ for about 10 h, we are pleased to isolate the expected cyclization product **2a** in 63% yield. In order to increase the yield of product, the reaction conditions are screened with choice of the solvent, temperature and catalyst. The reaction gave low yields of **2a** in 45% yield in DMF and less than 30% of **2a** in solvent such as THF, toluene, CH_3CN and dioxane. $PdCl_2$ showed much less activity for this reaction (33% of **2a**) and more than 20 mol% of $CuCl_2$ could not increase the yield further. The optimized reaction condition is similar to the that of the reported Pd-catalyzed tandem reaction for indene.[16a] Then the similar cyclizations of 1,2-dihydroisoquinolines **1b** and **1c** were also carried out in this optimized condition and the corresponding pyrrolo[2,1-*a*] isoquinolines

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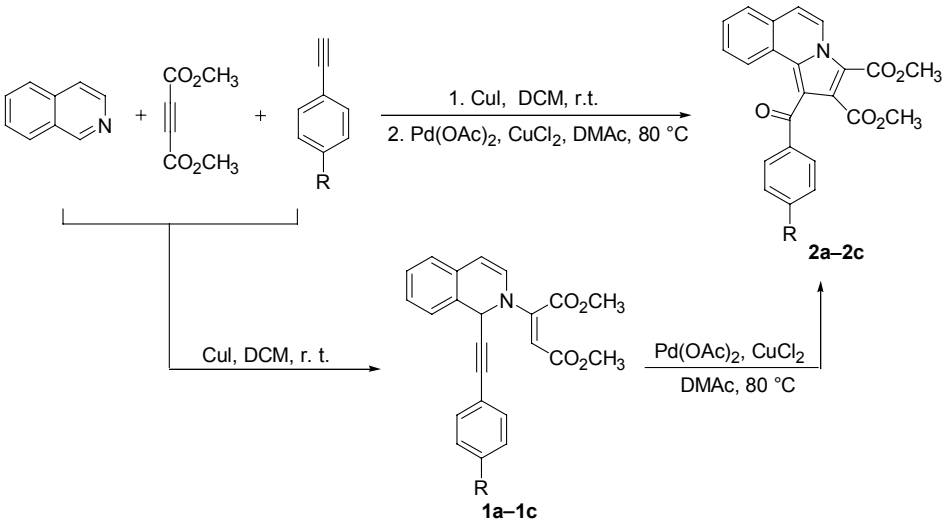
Received August 15, 2011; accepted September 24, 2011; published online February 29, 2012.

CHINESE JOURNAL OF CHEMISTRY

Scheme 1 Preparation routes of pyrrolo[2,1-*a*]isoquinolines

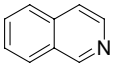
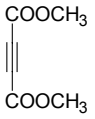
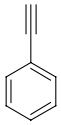
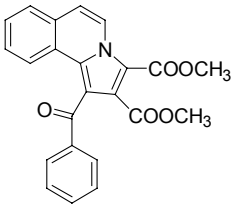
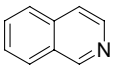
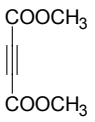
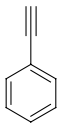
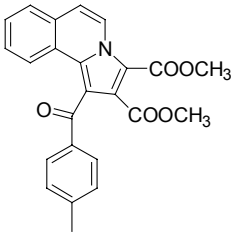


2b and **2c** were produced in 55% and 60% yields.

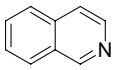
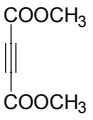
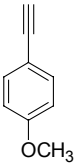
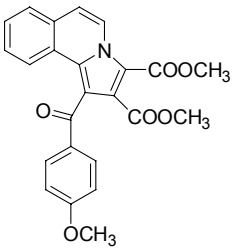
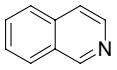
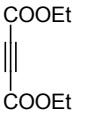
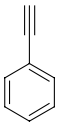
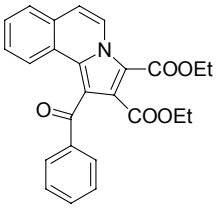
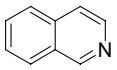
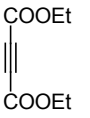
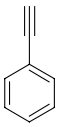
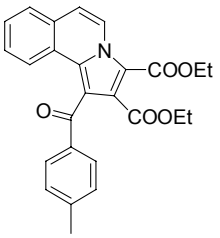
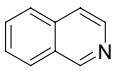
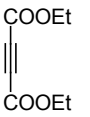
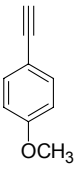
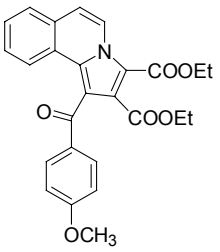
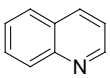
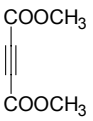
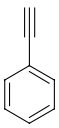
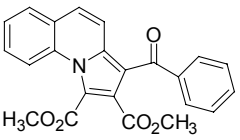
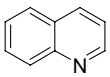
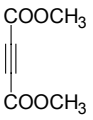
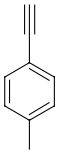
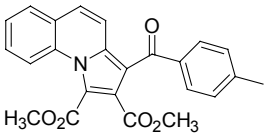
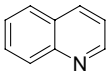
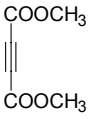
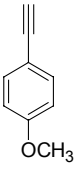
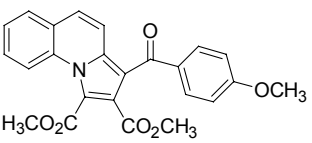
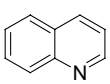
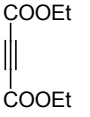
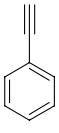
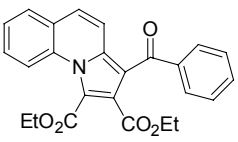
This initially successful preparation of pyrrolo-[2,1-*a*]isoquinolines **2a**—**2c** encouraged us to combine the two separated metal-catalyzed reactions into a one-pot two-step procedure without separating the cyclization precursor **1**. Hence after completion of first Cu-catalyzed three-component reaction of isoquinoline, acetylenedicarboxylate and phenylacetylene in DCM, the catalyst $Pd(OAc)_2$ and $CuCl_2$ as well as the solvent DMAc were added and the mixture was heated to 80 ℃ for 10 h. Under this sequential reaction procedure the pyrrolo[2,1-*a*]isoquinolines **2a** was also prepared in nearly same yield (60%). Thus a one-pot two-step three-component reaction is successfully established. Under similar reaction conditions isoquinoline, *p*-methyl and *p*-methoxyphenylacetylenes and diethyl acetylenedicarboxylates were utilized to give the corresponding pyrrolo[2,1-*a*]isoquinoline derivatives **2b**—**2f** in moderate to good yields (Table 1). In an attempt of extend this protocol to other nitrogen-containing heterocycles, quinoline was also used to react with arylacetylenes and acetylenedicarboxylates in the one-pot two-step Pd-catalyzed reaction. All reactions proceeded smoothly to result in the required pyrrolo[1,2-*a*]quinolines **2g**—**2l** in moderate yields (Table 1, Entries 7—12), which indicates that this one-pot two-step three-component reaction has a broad variety of substrates.

The structures of the prepared pyrrolo[2,1-*a*]isoquinolines and pyrrolo[1,2-*a*]quinoline **2a**—**2l** were established by IR, MS, ^1H and ^{13}C NMR spectroscopy and confirmed by the X-ray determination of single crystal structures of **2a** and **2k** (Figure 1). It should be pointed out that these compounds have been prepared by 1,3-dipolar addition reaction of isoquinolinium or quinolinium bromides with electron-deficient alkynes.[18,19] Recently Yavari reported the preparation of these compounds from the three-component reaction of activated acetylenes, benzoylnitromethanes, and

Table 1 Ppreparation of benzoindolizines **2a**—**2l** via one-pot two-step reactions

Entry	Compd.	Isoquinoline/quinoline	Acetylene-dicarboxylate	Aryl acetylene	Product	Yield/%
1	**2a**					60
2	**2b**					54

Continued

Entry	Compd.	Isoquinoline/quinoline	Acetylene-dicarboxylate	Aryl acetylene	Product	Yield/%
3	**2c**					57
4	**2d**					62
5	**2e**					48
6	**2f**					51
7	**2g**					58
8	**2h**					54
9	**2i**					52
10	**2j**					63

CHINESE JOURNAL OF CHEMISTRY

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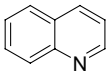
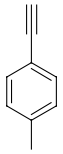
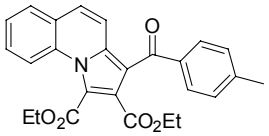
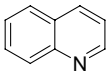
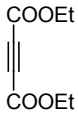
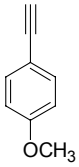
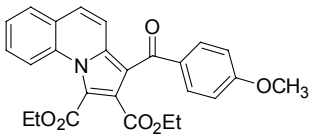
Entry	Compd.	Isoquinoline/quinoline	Acetylene-dicarboxylate	Aryl acetylene	Product	Yield/%
11	**2k**					55
12	**2l**					45

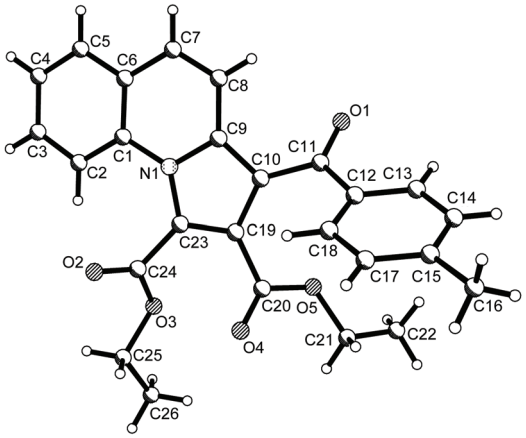


Figure 1 Molecular structure of **2k**.

isoquinoline.[20]

Although we have not investigated the reaction mechanism in an experimental manner, a reasonable reaction paths was proposed in Scheme 2 based on previously reported formation of the cyclization precursor[17] and sequential Pd-catalyzed carbocylization reaction.[16a] At first isoquinoline reacts with acetylenedicarboxylate to form a zwitterionic intermediate (**A**), which in turn reacts with phenylacetylene activated by CuI to furnish the desired 1-alkenyl-2-alkynyl-1,2-dihydroisoquinoline **1**. Secondly the $Pd(Ac)_2$ activated C-C triple band was attacked by nucleophilic carbanion to result in a five-membered ring intermediate (**B**) with an exocyclic double band. Hydration of the carbanion (**B**) gives an enol intermediate (**C**). Then intermediate (**C**) was tautomerized to the ketone form, which at last was dehydrogenated to give the final product **2** under the catalysis of $CuCl_2$.

Conclusions

In summary we have described an efficient synthetic procedure for pyrrolo[2,1-*a*]isoquinolines and pyrrolo[1,2-*a*]quinolines in good yields by the one-pot two-step metal-catalyzed three-component reactions of isoquinoline (quinoline), acetylenedicarboxylates and arylacetylenes. Prominent among the advantages of this new method are novelty, operational simplicity, and good yields. Applications to other metal-catalyzed multicomponent reactions are in progress in our laboratory.

Experimental

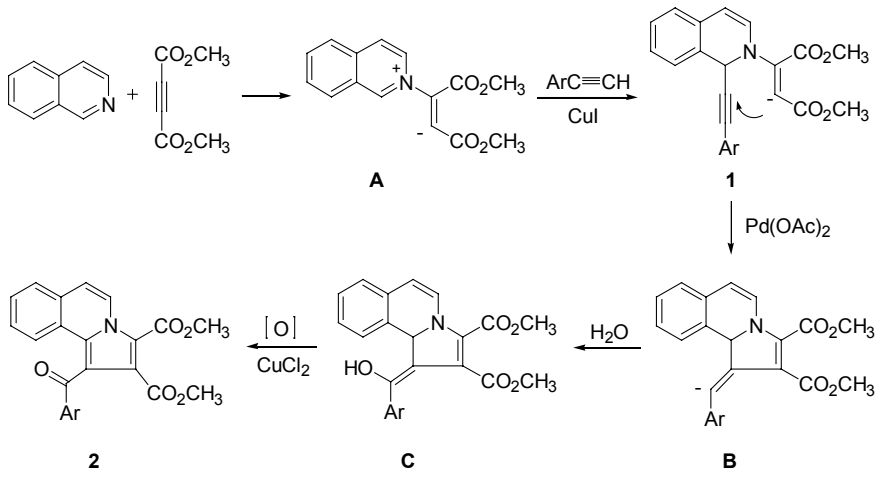
General procedure for the preparation of pyrrolo-[2,1-*a*]isoquinolines and pyrrolo[1,2-*a*]quinolines (2a—2l) from one-pot two-step three-component reactions

Acetylenedicarboxylate (1.2 mmol) was added to a stirred solution of CuI (0.05 mmol), isoquinoline (1.0 mmol), arylacetylene (1.0 mmol) in dichloromethane (5.0 mL). The resulting reaction mixture was stirred at room temp. for 2 h. Then $Pd(OAc)_2$ (0.05 mmol, 5 mol%), $CuCl_2$ (0.2 mmol, 20 mol%) and DMA (6.0 mL) were added. The mixture was stirred at 80 ℃ for an additional 10 h. Then the reaction was quenched with water, extracted with EtOAc (10 mL×2), dried by anhydrate Na_2SO_4. The solvent was evaporated and the residue was subjected to silica gel column chromatography (100—200 mesh) using light petroleum/ethyl acetate (4∶1) as eluent, affording the pure product for analysis.

2a: Dimethyl 1-benzoylpyrrolo[2,1-*a*] isoquinoline-2,3-dicarboxylate, yellow solid, m.p. 146—148 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.21 (brs, 1H, CH), 8.07—8.06 (m, 1H, CH), 7.90 (brs, 2H, ArH), 7.68 (brs, 1H, ArH), 7.56 (brs, 1H, ArH), 7.50 (brs, 1H, ArH), 7.43 (brs, 2H, ArH), 7.36 (brs, 1H, ArH), 7.19—7.18 (m, 1H, ArH), 3.92 (s, 3H, OCH_3), 3.50 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 193.5, 166.5, 165.0, 164.3, 160.8, 138.4, 133.4, 129.8, 129.3, 128.7, 128.6, 128.1, 127.2, 127.0, 125.3, 123.9, 117.0, 116.0, 115.7, 52.7,52.2, 52.2, 52.1; IR (KBr) v: 3670 (w), 2950 (w), 1742 (s), 1699 (s), 1650 (s), 1511 (m), 1438 (m), 1375 (m), 1211 (s), 1095 (m), 886 (w), 790 (w), 742 (w) cm^{-1}; MS (ESI^+) m/z (%): 410.23 ($[M+Na]^+$, 100).

2b: Dimethyl 1-*p*-methylbenzoylpyrrolo[2,1-*a*]-isoquinoline-2,3-dicarboxylate, yellow solid, m.p .160—162 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.21 (d, J= 7.2 Hz, 1H, CH), 8.04 (d, J=7.2 Hz, 1H, CH), 7.81 (d,

Scheme 2 Plausible reaction mechanism



J=8.4 Hz, 2H, ArH), 7.68 (d, J=7.8 Hz, 1H, ArH), 7.50 (t, J=7.5 Hz, 1H, ArH), 7.36 (t, J=7.8 Hz, 1H, ArH), 7.23 (d, J=7.8 Hz, 2H, ArH), 7.18 (d, J=7.8 Hz, 1H, ArH), 3.92 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 2.41 (s, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 193.2, 165.0, 160.9, 157.2, 144.5, 135.8, 131.8, 130.0, 129.3, 129.1, 128.6, 128.1, 127.2, 126.8, 125.2, 124.2, 124.0, 117.2, 115.6, 114.1, 52.3, 52.1, 21.8; IR (KBr) v: 3672 (w), 2951 (w), 1737 (s), 1703 (s), 1649 (s), 1509 (m), 1457 (m), 1376 (m), 1215 (vs), 1099 (m), 892 (w), 792 (m) cm^{-1}; MS (ESI$^+$) m/z (%): 424.30 ([M+Na]$^+$, 100).

2c: Dimethyl 1-*p*-methoxybenzoylpyrrolo[2,1-*a*]-isoquinoline-2,3-dicarboxylate, yellow solid, m.p. 124—126 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.22 (d, J=7.8 Hz, 1H, CH), 8.03 (d, J=7.8 Hz, 1H, CH), 7.90 (d, J=8.4 Hz, 2H, ArH), 7.69 (d, J=7.2 Hz, 1H, ArH), 7.50 (t, J=7.2 Hz, 1H, ArH), 7.37 (t, J=7.2 Hz, 1H, ArH), 7.19 (d, J=7.2 Hz, 1H, ArH), 6.91 (d, J=8.4 Hz, 2H, ArH), 3.93 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.58 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 192.1, 165.1, 164.0, 160.9, 132.2, 131.5, 131.2, 129.0, 128.6, 128.5, 128.1, 127.2, 126.7, 125.2, 124.2, 124.0, 117.2, 115.5, 114.1, 113.8, 55.5, 52.3, 52.2, 52.1; IR (KBr) v: 3671 (w), 2954 (w), 1714 (s), 1647 (s), 1595 (m), 1509 (m), 1456 (m), 1371 (m), 1311 (w), 1221 (vs), 1169 (s), 1097 (m), 934 (w), 797 (m) cm^{-1}; MS (ESI$^+$) m/z (%): 440.24 ([M+Na]$^+$, 100).

2d: Diethyl 1-benzoylpyrrolo[2,1-*a*]isoquinoline-2,3-dicarboxylate, white solid, m.p. 114 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.26 (d, J=6.0 Hz, 1H, CH), 8.07 (d, J=7.2 Hz, 1H, ArH), 7.93 (d, J=6.6 Hz, 2H, ArH), 7.70 (d, J=7.2 Hz, 1H, ArH), 7.58 (brs, 1H, ArH), 7.50 (d, J=6.6 Hz, 1H, ArH), 7.45 (d, J=7.2 Hz, 2H, ArH), 7.37 (d, J=6.6 Hz, 1H, ArH), 7.20 (d, J=6.0 Hz, 1H, CH), 4.40 (q, J=6.0 Hz, 2H, CH_2), 3.93 (q, J=6.0 Hz, 2H, CH_2), 1.35 (t, J=5.6 Hz, 3H, CH_3), 1.08 (t, J=5.6 Hz, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 193.5, 164.6, 160.5, 138.4, 133.5, 132.0, 129.1, 128.6, 128.5, 128.1, 127.3, 127.2, 125.2, 124.2, 124.0, 116.8, 115.5, 114.3, 61.5, 61.2, 14.0, 13.7; IR (KBr) v: 3675 (w), 2981 (w), 1740 (s), 1696 (s), 1651 (s), 1509 (m), 1388 (m), 1211 (vs), 1098 (s), 791 (m), 738 (w) cm^{-1}; MS (ESI$^+$) m/z (%): 438.25 ([M+Na]$^+$, 100).

2e: Diethyl 1-*p*-methxylbenzoylpyrrolo[2,1-*a*]-isoquinoline-2,3-dicarboxylate, yellow solid, m.p. 116 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.25 (d, J=7.8 Hz, 1H, CH), 8.05 (d, J=8.4 Hz, 1H, ArH), 7.83 (d, J=7.8 Hz, 2H, ArH), 7.69 (d, J=7.8 Hz, 1H, ArH), 7.50 (d, J=7.5 Hz, 1H, ArH), 7.36 (d, J=7.5 Hz, 1H, ArH), 7.23 (d, J=7.8 Hz, 2H, ArH), 7.18 (d, J=7.8 Hz, 1H, CH), 4.40 (q, J=7.2 Hz, 2H, CH_2), 3.96 (q, J=7.2 Hz, 2H, CH_2), 2.41 (s, 3H, CH_3), 1.36 (t, J=7.2 Hz, 3H, CH_3), 1.10 (t, J=7.2 Hz, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 193.2, 164.6, 160.5, 144.4, 135.9, 131.7, 130.1, 129.2, 129.0, 128.5, 128.0, 127.2, 127.1, 125.2, 124.2, 124.0, 117.0, 115.4, 114.2, 61.5, 61.1, 21.8, 14.0, 13.7; IR (KBr) v: 3670 (w), 2982 (w), 1704 (s), 1651 (s), 1517 (m), 1470 (m), 1377 (m), 1223 (vs), 1099 (m), 1052 (w), 797 (w) cm^{-1}; MS (ESI$^+$) m/z (%): 452.35 ([M+Na]$^+$, 100).

2f: Diethyl 1-*p*-methoxybenzoylpyrrolo[2,1-*a*]-isoquinoline-2,3-dicarboxylate, white solid, m.p. 118 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.24 (d, J=7.8 Hz, 1H, CH), 8.03 (d, J=8.4 Hz, 1H, ArH), 7.92 (d, J=8.4 Hz, 2H, ArH), 7.69 (d, J=7.8 Hz, 1H, ArH), 7.50 (d, J=7.5 Hz, 1H, ArH), 7.37 (d, J=7.5 Hz, 1H, ArH), 7.17 (d, J=7.8 Hz, 1H, CH), 6.91 (d, J=8.4 Hz, 2H, ArH), 4.40 (q, J=7.2 Hz, 2H, CH_2), 4.02 (q, J=7.2 Hz, 2H, CH_2), 3.86 (s, 3H, OCH_3), 1.37 (t, J=7.2 Hz, 3H, CH_3), 1.11 (t, J=7.2 Hz, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 192.1, 164.7, 164.0, 160.5, 132.4, 131.5, 131.3, 129.0, 128.4, 128.1, 127.2, 126.9, 125.1, 124.3, 124.0, 117.0, 115.3, 114.1, 113.8, 61.5, 61.1, 55.5, 14.1, 13.8; IR (KBr) v: 3671 (w), 2982 (w), 1704 (s), 1648 (s), 1597 (m), 1511 (m), 1465 (m), 1220 (vs), 1169 (m), 1098 (m), 1031 (m), 855 (w), 799 (m), 613 (w) cm^{-1}; MS (ESI$^+$) m/z (%): 468.31 ([M+Na]$^+$, 100).

2g: Dimethyl 3-benzoylpyrrolo[1,2-*a*]quinoline-1,2-dicarboxylate, yellow solid, m.p. 140—142 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.94 (d, J=9.0 Hz, 1H, CH), 7.76—7.79 (m, 3H, ArH), 7.72 (d, J=9.0 Hz, 1H, CH), 7.59 (t, J=7.8 Hz, 1H, ArH), 7.54 (t, J=7.2 Hz, 1H, ArH), 7.50 (t, J=7.2 Hz, 1H, ArH), 7.44 (q, J=7.5 Hz, 3H, ArH), 4.06 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 191.3, 164.3, 163.5, 140.0, 135.3, 132.5, 132.3, 129.2, 129.0, 128.9, 128.4, 126.6, 126.0, 125.5, 124.0, 121.0, 117.7, 117.5, 114.9, 53.3, 51.9; IR (KBr) v: 3677 (w), 2953 (w), 1723 (vs), 1638 (s), 1512 (s), 1435 (m), 1378 (w), 1220 (vs), 1108 (m), 959 (w), 812 (w), 757 (w) cm^{-1}; MS (ESI$^+$) m/z (%): 410.21 ([M+Na]$^+$, 100).

2h: Dimethyl 3-*p*-methylbenzoylpyrrolo[1,2-*a*]-quinoline-1,2-dicarboxylate, yellow solid, m.p. 114—116 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.93 (d, J=8.4 Hz, 1H, CH), 7.76 (d, J=8.4 Hz, 1H, CH), 7.70 (d, J=7.8 Hz, 2H, ArH), 7.65 (d, J=9.0 Hz, 1H, ArH), 7.59 (t, J=8.1 Hz, 1H, ArH), 7.50 (t, J=7.2 Hz, 1H, ArH), 7.40 (d, J=9.0 Hz, 1H, ArH), 7.25 (d, J=7.8 Hz, 2H, ArH), 4.06 (s, 3H, OCH_3), 3.45 (s, 3H, OCH_3), 2.42 (s, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 191.0, 164.3, 163.5, 143.2, 137.2, 135.0, 132.6, 129.2, 129.1, 129.0, 128.9, 126.2, 125.9, 125.4, 123.9, 120.9, 117.7, 117.5, 115.3, 58.4, 53.3, 52.0, 21.7, 18.4; IR (KBr) v: 3665 (w), 2950 (w), 1727 (s), 1634 (s), 1514 (m), 1436 (m), 1380 (w), 1222 (vs), 1110 (m), 1054 (w), 936 (w), 809 (m), 758 (m) cm^{-1}; MS (ESI$^+$) m/z (%): 424.24 ([M+Na]$^+$, 100).

2i: Dimethyl 3-*p*-methoxybenzoylpyrrolo[1,2-*a*]-quinoline-1,2-dicarboxylate, yellow solid, m.p. 122—124 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.92 (d, J=9.0 Hz, 1H, CH), 7.80 (d, J=9.0 Hz, 2H, ArH), 7.75 (d, J=7.2 Hz, 1H, ArH), 7.59 (d, J=8.4 Hz, 2H, ArH), 7.49 (t, J=7.5 Hz, 1H, ArH), 7.37 (d, J=9.0 Hz, 1H, CH), 6.93 (d, J=9.0 Hz, 2H, ArH), 4.07 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.51 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 190.0, 164.3, 163.6, 163.2, 134.6, 132.5, 131.4, 130.9, 129.2, 128.8, 125.9, 125.4, 123.5, 121.0, 117.7, 117.4, 113.6, 58.4, 55.5, 53.3, 52.1, 18.4; IR (KBr) v: 3666 (w), 2952 (w), 1724 (vs), 1606 (s), 1497 (m), 1440 (m), 1385 (w), 1223 (vs), 1173 (m), 1032 (m), 925 (w), 806 (w), 614 (w) cm^{-1}; MS (ESI$^+$) m/z (%): 440.22 ([M+Na]$^+$, 100).

2j: Diethyl 3-benzoylpyrrolo[1,2-*a*]quinoline-1,2-dicarboxylate, white solid, m.p.102—104 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.98 (d, J=8.4 Hz, 1H, CH), 7.82 (d, J=7.8 Hz, 2H, ArH), 7.77 (d, J=7.8 Hz, 1H, ArH), 7.72 (d, J=8.4 Hz, 1H, CH), 7.59 (t, J=7.8 Hz, 1H, ArH), 7.55 (t, J=7.8 Hz, 1H, ArH), 7.50 (t, J=7.5 Hz, 1H, ArH),7.46—7.41 (m, 3H, ArH), 4.55 (q, J=7.2 Hz, 2H, CH_2), 3.86 (q, J=7.2 Hz, 2H, CH_2), 1.44 (t, J=6.9 Hz, 3H, CH_3), 0.95 (t, J=6.9 Hz, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 191.3, 163.8, 163.1, 140.0, 135.1, 132.7, 132.4, 129.2, 129.1, 128.8, 128.4, 126.3, 125.9, 125.5, 123.8, 121.6, 117.8, 117.6, 114.8, 62.6, 61.3, 13.9, 13.5; IR (KBr) v: 3673 (w), 2984 (w), 1725 (s), 1637 (s), 1507 (m), 1436 (m), 1384 (w), 1221 (vs), 1113 (m), 1020 (m), 962 (w), 859 (w), 802 (m), 753 (m) cm^{-1}; MS (ESI$^+$) m/z (%): 438.26 ([M+Na]$^+$, 100).

2k: Diethyl 3-*p*-methylbenzoylpyrrolo[1,2-*a*]-quinoline-1,2-dicarboxylate, white solid, m.p 118—120 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.97 (d, J=9.0 Hz, 1H, CH), 7.75 (d, J=7.8 Hz, 1H, ArH), 7.73 (d, J=8.4 Hz, 2H, ArH), 7.65 (d, J=9.6 Hz, 1H, ArH), 7.58 (t, J=8.2 Hz, 1H, ArH), 7.49 (d, J=7.5 Hz, 1H, ArH), 7.39 (d, J=9.0 Hz, 1H, CH), 7.24 (d, J=7.8 Hz, 2H, ArH), 4.55 (q, J=7.2 Hz, 2H, CH_2), 3.92 (q, J=7.2 Hz, 2H, CH_2), 2.42 (s, 3H, CH_3), 1.44 (t, J=7.2 Hz, 3H, CH_3), 0.98 (t, J=7.2 Hz, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 191.0, 163.9, 163.2, 143.2, 137.3, 134.8, 132.6, 129.4, 129.2, 129.0, 128.7, 126.0, 125.8, 125.6, 123.7, 121.4, 117.8, 117.6, 115.2, 62.6, 61.2, 58.5, 21.6, 18.5, 13.9, 13.6; IR (KBr) v: 3672 (w), 2983 (w), 1724 (vs), 1638 (s), 1505 (m), 1436 (m), 1384 (m), 1221 (vs), 1110 (m), 1022 (m), 960 (w), 857 (w), 801 (m), 754 (w), 684 (w), 610 (w) cm^{-1}; MS (ESI$^+$) m/z (%): 452.22 ([M+Na]$^+$, 100).

2l: Diethyl 3-*p*-methoxbenzoylpyrrolo[1,2-*a*]-quinoline-1,2-dicarboxylate, white solid, 50%, m.p. 100—102 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.97 (d, J=9.0 Hz, 1H, CH), 7.82 (d, J=8.4 Hz, 2H, ArH), 7.75 (d, J=7.8 Hz, 1H, ArH), 7.61 (d, J=9.6 Hz, 1H, ArH), 7.57 (t, J=7.8 Hz, 1H, ArH), 7.49 (t, J=7.2 Hz, 1H, ArH), 7.37 (d, J=9.0 Hz, 1H, CH), 6.93 (d, J=8.4 Hz, 2H, ArH), 4.55 (q, J=7.1 Hz, 2H, CH_2), 3.97 (d, J=7.1Hz, 2H, CH_2), 3.87 (s, 3H, OCH_3), 1.45 (t, J=7.2 Hz, 3H, CH_3), 1.00 (t, J=7.2 Hz, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 190.0, 163.9, 163.3, 163.2, 134.4, 132.6, 131.6, 129.2, 128.7, 125.8, 125.7, 125.4, 123.2, 121.5, 117.7, 117.4, 115.4, 113.6, 62.6, 61.2, 58.4, 55.5, 18.4, 13.9, 13.6; IR (KBr) v: 3673 (w), 2981 (w), 1722 (vs), 1646 (s), 1600 (m), 1508 (m), 1435 (m), 1386 (m), 1232 (vs), 1183 (vs), 1109 (w), 1020 (m), 959 (w), 855 (m), 805 (m), 753 (w), 609 (w) cm^{-1}; MS (ESI$^+$) m/z (%): 468.34 ([M+Na]$^+$, 100).

Acknowledgement

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

Supporting Information Available

Crystallographic data of **2a** (CCDC 830600) and **2k** (CCDC 830601) have been deposited at the Cambridge Crystallographic Database Centre.

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