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The unprecedented C-alkylation and tandem C-/O-alkylation of phenanthrolinium salts with cyclic 1,3-dicarbonyl compounds

Hui Li, Chao-Guo Yan *

College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China

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ABSTRACT

N-*p*-Nitrobenzyl- or *N*-phenacylphenanthrolinium bromides reacted with a series of cyclic 1,3-dicarbonyl compounds in acetonitrile in the presence of triethylamine as base catalyst to give the unprecedented *C*-alkylated products and tandem alkylated/intramolecular *O*-alkylated oxazabicyclic compounds according to the structure of cyclic 1,3-dicarbonyl compounds.

1. Introduction

The heterocyclic ammonium salts, especially those bearing an active methylene group have versatile reactivity and were used in a great variety of synthetic reactions for constructing polycyclic systems.[1,2] The most popular used heterocyclic ammonium salt is pyridinium salt. Pyridinium salts with α-halogenocarbonyl compounds are easily deprotonated to give pyridinium ylide, which are prone to be high potential synthons[3] and undergo many types of reactions, such as Michael addition,[4,5] 1,3-dipolar cycloaddition,[6–8] substitution, and others.[2c,9,10] Then the quinolinium and isoquinolinium salts are also attracted much attention because they often showed different reaction modes to the corresponding pyridinium salts.[11,12] In the past few years we have successfully developed several tandem reaction based on the in situ formed reactive pyridinium salts and isoquinolinium salts.[13] In continuation of our efforts to investigate new tandem reactions we want to develop this kind of reactions to other nitrogen-containing heterocyclic systems. Here we wish to report the very interesting reactions of phenanthrolinium bromides with cyclic 1,3-dicarbonyl compounds and the efficient synthesis of pyran-bridged phenanthroline derivatives.

2. Results and discussions

At first we investigated the three-component reaction of *N*-*p*-nitrobenzylphenanthrolinium bromide (**1a**), aromatic benzaldehyde, and dimedone according to our previously established condition for pyridinium and isoquinolinium salts.[13] The mixture of the three components in acetonitrile with triethylamine as base catalyst was carried out at room temperature for several hours. After workup we were surprised to find that the separated product is **3a**, and its structure clearly showed that aromatic aldehyde did not take part in the reaction. Thus no aromatic aldehyde was utilized in the further reactions. The reaction of *N*-*p*-nitrobenzylphenanthrolinium bromide (**1a**) with dimedone (**2a**) in acetonitrile with triethylamine as base catalyst proceeded smoothly to give the product (**3a**) in 66% yields. Then other cyclic 1,3-dicarbonyl compounds were also tested in the reactions (Equation 1). We are pleased to find that 1,3-cyclohexanedione, coumarin also formed the similar oxazabicyclic derivatives **3b** (47%) and **3c** (53%) in moderate yields (Scheme 1). On the other hand the reaction of *N*-*p*-nitrobenzylphenanthrolinium bromide (**1a**) with Meldrum acid, *N*,*N*-dimethylbarbituric acid, thiobarbituric acid, 1,3-cyclopentanedione, and 1,3-thiazolidinedione in acetonitrile in the presence of triethylamine gave completely C-4 alkylated products **4a**–**e** in 43–87% yields. Thus two kinds of products can be obtained from the base catalyzed reaction of cyclic 1,3-dicarbonyl compounds with phenanthrolinium bromide according to the structures of the cyclic 1,3-dicarbonyl compounds.

* Corresponding author. E-mail address: cgyan@yzu.edu.cn (C.-G. Yan).

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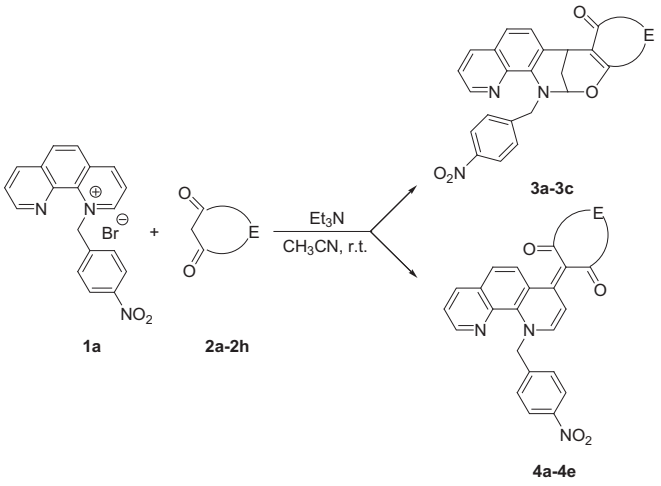


Equation 1. Reactions of *N*-*p*-nitrobenzylphenanthrolinium bromide (**1a**) with cyclic 1,3-diketones.

The structures of the prepared products **3a**–**c** and **4a**–**e** (Scheme 1) were fully characterized by elemental analysis, ^{1}H and ^{13}C NMR, MS, IR spectra, and were further confirmed by single-crystal X-ray diffraction studies performed for three representatives compounds **3a** (Fig. 1), **3c**, and **4a** (Fig. 2). From Fig. 1 we clearly saw that the C-2 and C-4 position of phenanthroline ring were both connected with the C-2 and carbonyl oxygen atom of dimedone, which obviously formed from the tandem C-4 *C*-alkylated and intramolecular C-2 *O*-alkylated of dimedone. Form Fig. 2 we could see that phenanthroline ring was connected with Meldrum acid by C=C double bond. As one of the typical heterocyclic compounds phenanthroline and its derivatives perform interesting chemical activities. 1,10-Phenanthroline and its derivatives have long been known as commonly used ligands in coordination chemistry and catalytic organic synthesis. Sometimes the uses of functionalized phenanthrolines have been limited, which is in part due to the lack of efficient synthetic methods.[14] The efficiency and ease of handling of this reaction should render this reaction applicable to the synthesis of functionalized phenanthrolines. To the best of our knowledge, there are no reports of this kind of oxazabicyclic system based on phenanthroline ring in the literature. A few examples about the oxazabicyclic compounds based on quinoline and isoquinoline have been reported in recently years.[15–18] This year Moghaddam described the addition reactions of 1,3-dicarbonyl compounds to quinolinium salts for the convenient synthesis of the oxazabicyclic systems.[19] Here we have successfully

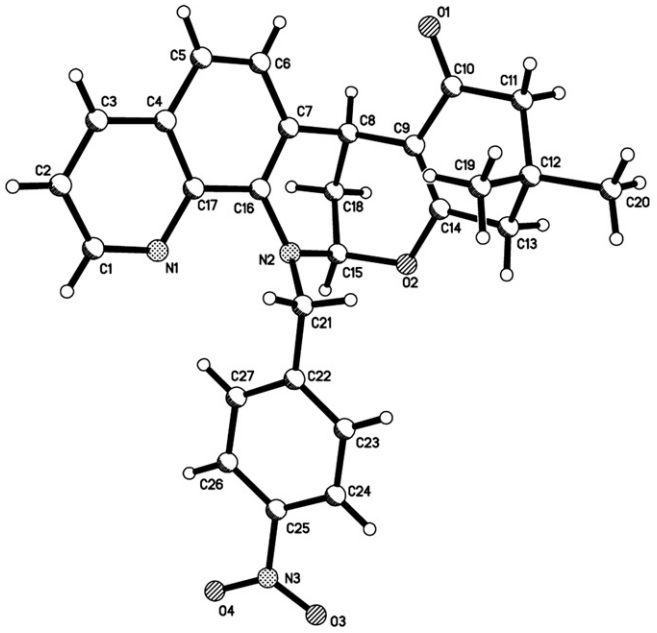
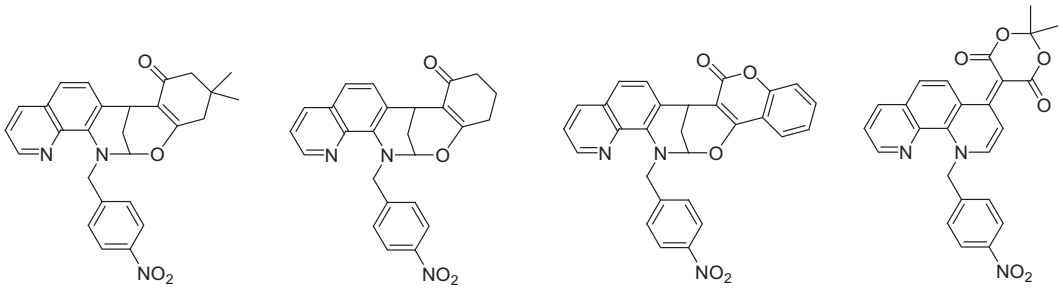
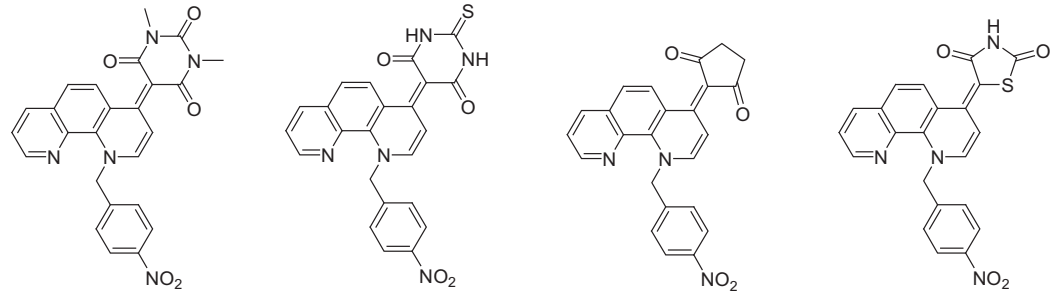


Fig. 1. The molecular structure of compound **3a**.





Scheme 1. The prepared phenanthroline derivatives **3a**–**c** and **4a**–**e**.

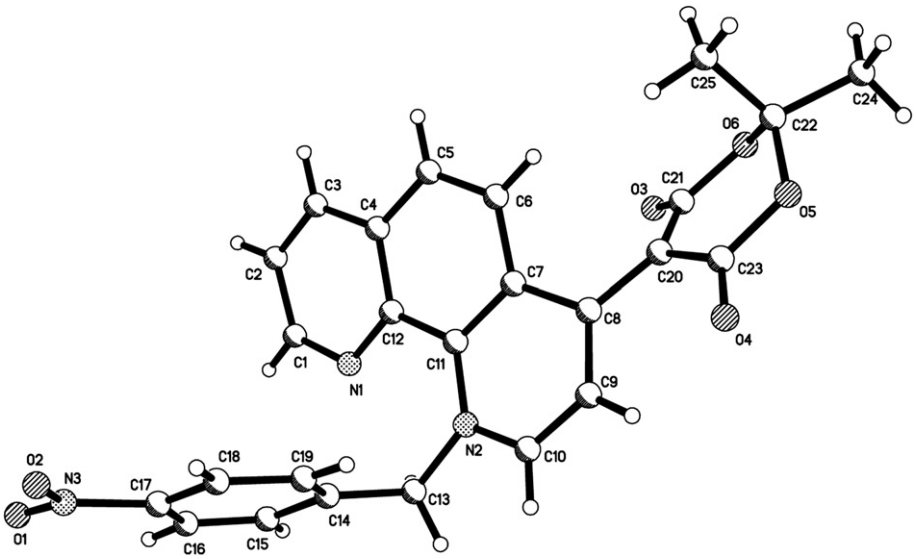
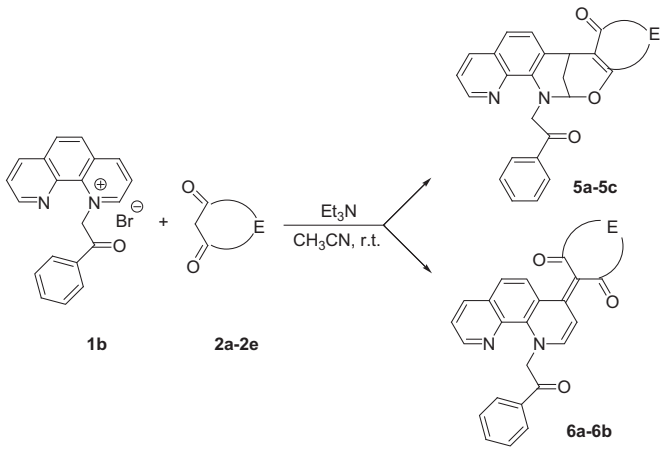


Fig. 2. The molecular structure of compound **4a**.

provided an efficient synthetic method for the functionalized oxazabicyclic phenanthroline derivatives.

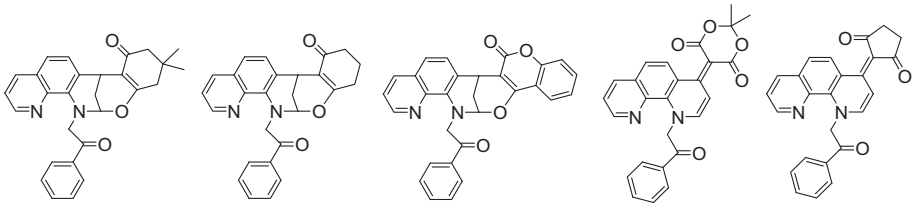
To further demonstrate the superiority of our methodology and to extend the utility of this reaction, the reactions of *N*-phenacylphenanthrolinium bromides **1b** with different kinds of cyclic 1,3-dicarbonyl compounds were also explored (Equation 2). Under similar reaction conditions the *N*-phenacylphenanthrolinium bromides **1b** reacted with dimedone, 1,3-cyclohexanedione, and coumarin gave the oxazabicyclic compounds **5a**–**c** in good yields. The expected C-alkylation products **6a**–**b** were also obtained from the reaction of **1b** with Meldrum acid and 1,3-cyclopentanedione (Scheme 2). The



Equation 2. Reactions of *N*-phenacylphenanthrolinium bromide (**1b**) with cyclic 1,3-diketones.

single-crystal structures of the oxazabicyclic compound **5b** (Fig. 3) and the C-4 alkylated phenanthroline **6b** (Fig. 4) were determined by X-ray diffraction. These results showed that the reaction of phenanthrolinium salts with cyclic 1,3-dicarbonyl compounds is atom efficient and applicable to a wide variety of substrates.

To explain the formation mechanism of the two kinds of products in the reaction, we proposed a plausible reaction mechanism, which is shown in Scheme 3. In phenanthrolinium cation **1** the electrophilic effect of the positive nitrogen makes 2- and 4-position of the aza-cycle relatively electropositive. In other words the positive charge is spread to the C-2 and C-4 carbon atoms (**A**). So C-2 and C-4 carbon atoms become more susceptible to attack by nucleophiles. The cyclic 1,3-dicarbonyl compound is deprotonated by triethylamine to yield the carbanion. The latter in turn attacks the carbon atom of 4-position of phenanthrolinium cation (**A**) to give the intermediate (**B**). Due to the strong electron-withdrawing effect of two carbonyl groups intermediate (**B**) was deprotonated further to give a new carbanion (**C**) in the presence of triethylamine. Then intermediate (**C**) reacts further to two different paths that will yield two different products. On the first reaction path, the carbanium (**C**) transferred to resonance-stabilized enolate ion (**D**) through the keto–enol tautomerization, which in turn attack the relative positive C-2 to give the final oxazabicyclic compound **3** with additional protonation step. On the second path, the carbanium (**C**) was dehydrogenated in air to form a C=C bond between the C-4 of phenanthroline ring and C-2 of Meldrum acid, which resulted in the compound **4** as the final product. We believed that in this proposed reaction mechanism the formation and stability of enolate ion of the cyclic 1,3-dicarbonyl compounds controls the formation of two different products. The stronger acidities of Meldrum acid and related dicarbonyl compounds would be due to its strong



5a (69%) **5b (61%)** **5c (51%)** **6a (74%)** **6b (75%)**

Scheme 2. The synthetic phenanthroline derivatives **5a**–**c** and **6a**–**b**.

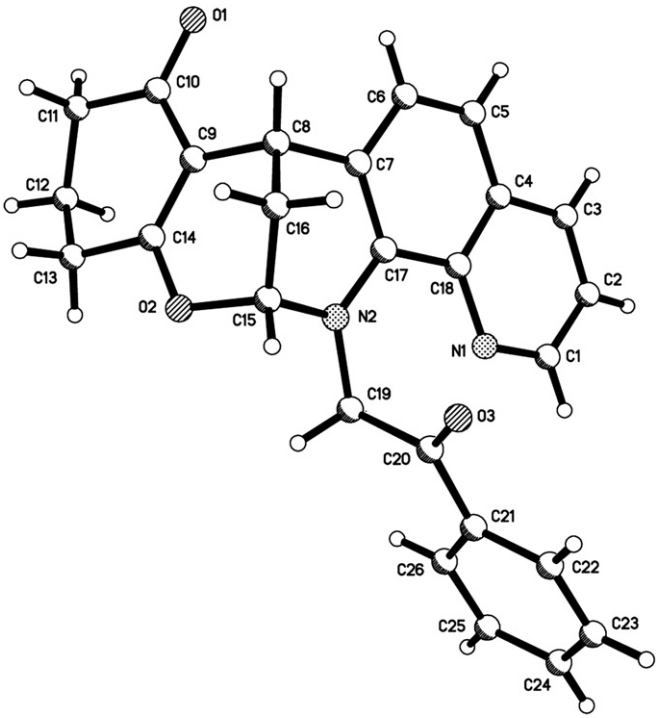


Fig. 3. The molecular structure of compound **5b**.

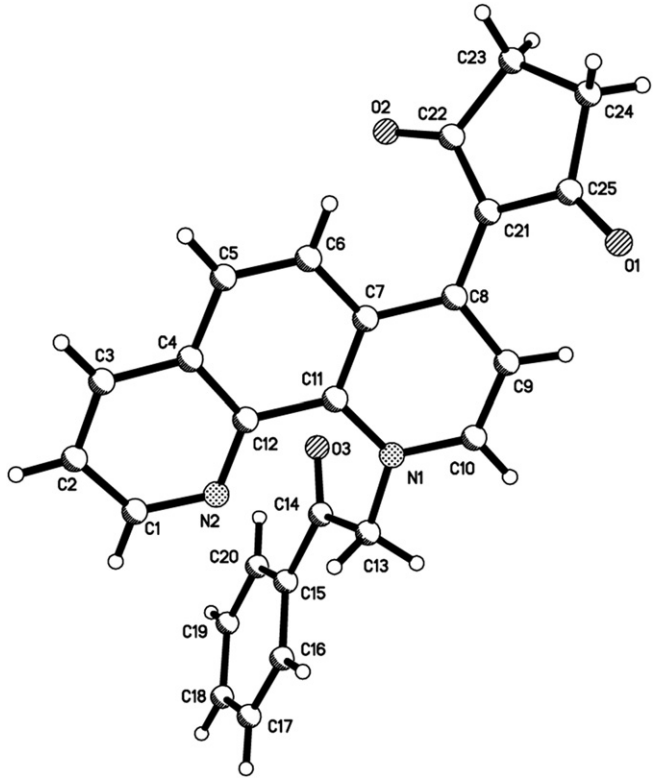


Fig. 4. The molecular structure of compound **6b**.

stabilizing effect of enolate anion, in which the anomeric effect between the oxygen atom (O5) and the vacant antibonding of the O3 (the ether)–C4 bond. Lee and co-workers proposed that deprotonation of Meldrum's acid would lead to increase of electron-delocalization of the nonbonding electrons of the carbanion moiety to the adjacent vacant carbonyl antibonding orbitals and 1,4-attractive electrostatic interaction between C1 and C4.[20] Such strong stabilizing effect is unique to Meldrum acids, in a wider sense, to highly structurally similar substrates like barbituric acid, thiobarbituric acid, and etc., which have additional α-heteroatom to two carbonyl groups in the ring. This stabilizing effect would strongly prevent further O-alkylation because such process requires to disturb such stabilization effect. In contrast, dimedone and 1,3-cyclohexanedione did not possess such unique effect and, as a consequence, would allow the O-alkylation reaction to go to get the oxazabicyclic products. The reactions of *N*-phenacylphenanthrolinium salt gave the corresponding oxazabicyclic derivatives **5** and addition products **6** further demonstrated the reality of the proposed reaction mechanism and generality of this reaction.

In summary an efficient synthetic method for the functionalized oxazabicyclic compounds form the unprecedented reactions of phenanthrolinium salts having active methylene group with cyclic 1.3-dicarbonyl compounds was developed. The structure of cyclic 1,3-dicarbonyl compounds plays a key factor for the formation of *C*-alkylated products and tandem *C*-alkylated/intramolecular *O*-alkylated oxazabicyclic compounds. Furthermore, we established the scope and limitation of this reaction, which enabled further modification that led to molecular diversity. The potential uses of the reaction in synthetic and medicinal chemistry might quite significant.

3. Experimental section

3.1. Preparation of phenanthrolinium bromides (1a–b)

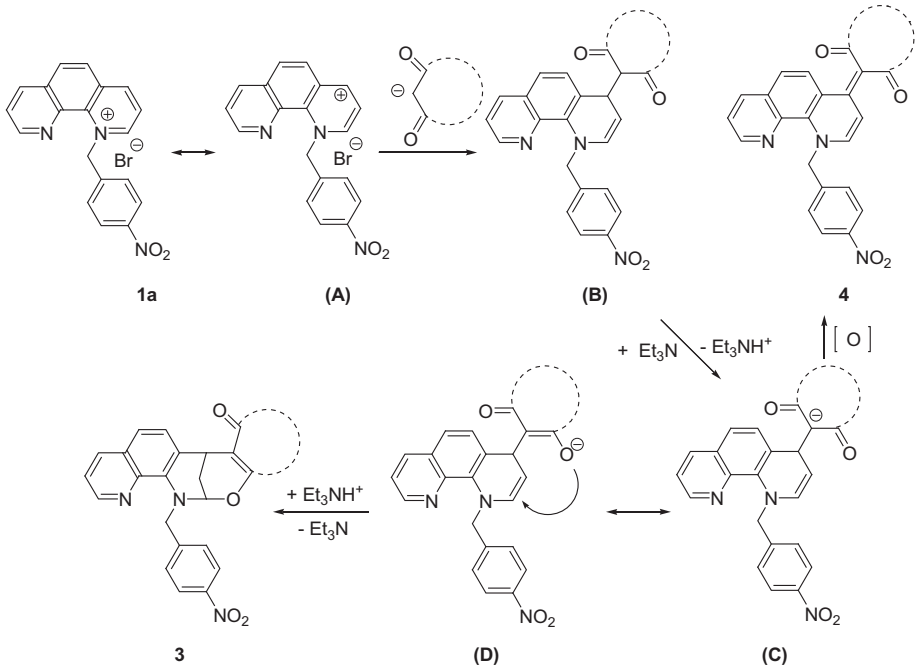
The solution of phenanthroline (2.0 mmol, 0.396 g) and *p*-nitrobenzyl bromide (2.0 mmol, 0.432 g) or α-phenacyl bromide (2.0 mmol, 0.398 g) in 20 mL of acetonitrile was stirred at room temperature for 12 h. The resulting precipitates were collected by filtration and washed with few acetonitrile to give the product.

*3.1.1. N-p-Nitrobenzylphenanthrolinium bromide (**1a**).* White solid, yield: 90%. Mp 212–214 °C. IR (KBr disc) ν: 2984 (m), 1603 (m), 1524 (vs), 1465 (w), 1413 (w), 1347 (s), 1245 (w), 1158 (w), 1109 (w), 854 (w), 804 (w) cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ: 9.85 (d, J=4.8 Hz, 1H, ArH), 9.60 (d, J=7.8 Hz, 1H, ArH), 9.09 (s, 1H, ArH), 8.76 (d, J=7.8 Hz, 1H, ArH), 8.61 (s, 1H, ArH), 8.50–8.46 (m, 2H, ArH), 8.14 (d, J=7.2 Hz, 2H, ArH), 7.98 (d, J=9.6 Hz, 1H, ArH), 7.52 (d, J=7.8 Hz, 2H, ArH), 7.34 (s, 2H, ArH); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 152.2, 149.6, 148.3, 146.8, 144.1, 139.0, 137.8, 136.7, 132.9, 131.7, 130.8, 127.9, 127.1, 125.4, 125.1, 123.6, 65.5. MS (ESI^+): m/z=316.24.

*3.1.2. N-Phenacylphenanthrolinium bromide (**1b**).* Light yellow solid, yield: 85%. Mp 208–210 °C. IR (KBr) ν: 2989 (m), 2916 (w), 1688 (vs), 1630 (w), 1589 (w), 1530 (m), 1442 (m), 1350 (m), 1232 (s), 1171 (w), 995 (w), 857 (w) cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ: 9.74 (d, J=4.2 Hz, 1H, ArH), 9.64 (d, J=7.8 Hz, 1H, ArH), 8.79 (d, J=7.2 Hz, 1H, ArH), 8.65 (s, 1H, ArH), 8.52–8.48 (m, 2H, ArH), 8.46 (s, 1H, ArH), 8.21 (d, J=6.6 Hz, 2H, ArH), 7.92 (t, J=3.6 Hz, 1H, ArH), 7.85 (t, J=7.2 Hz, 1H, ArH), 7.75 (t, J=6.6 Hz, 2H, ArH), 7.36 (s, 2H, ArH); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 190.7, 152.0, 148.6, 148.1, 138.4, 138.0, 136.2, 134.3, 134.1, 132.0, 131.4, 130.6, 129.3, 128.1, 127.0, 125.5, 124.8, 69.5. MS (ESI^+): m/z=299.12.

3.2. The reactions of *N-p*-nitrobenzylphenanthrolinium bromide (1a) with cyclic 1,3-dicarbonyl compounds

N-p-Nitrobenzylphenanthrolinium bromide (1.0 mmol, 0.395 g) and cyclic 1,3-dicarbonyl compound (1.0 mmol) were added to 20 mL of acetonitrile. Then 0.25 mL of triethylamine was added to the mixture. The mixture was stirred at room temperature for 24 h. In most cases the resulting precipitates were collected by filtration, which was recrystallized in ethanol to give the pure products for



Scheme 3. The proposed formation mechanism for the compounds **3** and **4**.

analysis. In few cases the solution was concentrated and the resulting oily solid was titrated with ethanol to give the products.

Compound **3a**: White solid, yield: 66%. Mp 178–180 °C. IR (KBr) ν: 3435 (w), 2935 (m), 2865 (w), 1644 (w), 1615 (vs), 1522 (s), 1458 (m), 1385 (s), 1342 (s), 1306 (w), 1221 (w), 1170 (w), 1107 (m), 1047 (m), 1026 (w), 991 (w), 836 (w) cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ: 8.56 (s, 1H, ArH), 8.18 (d, J=8.4 Hz, 1H, ArH), 8.14 (d, J=8.4 Hz, 2H, ArH), 7.52 (t, J=9.0 Hz, 3H, ArH), 7.34 (d, J=7.8 Hz, 2H, ArH), 5.87 (d, J=16.8 Hz, 1H, CH_2), 5.69 (s, 1H, CH), 5.55 (d, J=16.8 Hz, 1H, CH_2), 4.07 (s, 1H, CH), 2.20 (d, J=17.4 Hz, 1H, CH_2), 2.15–2.08 (m, 2H, CH_2), 2.05 (d, J=13.2 Hz, 1H, CH_2), 1.94 (t, J=13.8 Hz, 2H, CH_2), 0.98 (s, 3H, CH_3), 0.84 (s, 3H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 196.1, 167.6, 148.8, 146.9, 146.5, 139.5, 137.2, 136.5, 129.0, 128.7, 128.6, 127.8, 123.3, 120.1, 119.2, 114.3, 83.8, 54.1, 50.5, 41.7, 32.1, 29.4, 27.4, 26.3, 26.2. MS (ESI^+): m/z=456.65. Anal. Calcd for $C_{27}H_{25}N_3O_4$: C 71.19, H 5.53, N 9.22. Found: C 70.86, H 5.81, N 8.79.

Compound **3b**: White solid, yield: 47%. Mp 136–138 °C. IR (KBr) ν: 2948 (w), 1653 (m), 1621 (vs), 1511 (s), 1459 (m), 1389 (m), 1348 (vs), 1230 (w), 1187 (w), 1168 (w), 1132 (w), 1115 (m), 1063 (w), 1030 (m), 992 (w), 936 (w), 834 (w) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ: 8.56 (d, J=2.4 Hz, 1H, ArH), 8.13 (d, J=8.4 Hz, 2H, ArH), 8.03 (d, J=7.8 Hz, 1H, ArH), 7.72 (d, J=7.8 Hz, 1H, ArH), 7.57 (d, J=8.4 Hz, 2H, ArH), 7.29 (d, J=7.8 Hz, 1H, ArH), 7.25–7.23 (m, 1H, ArH), 5.78 (d, J=16.2 Hz, 1H, NCH), 5.55 (d, J=17.0 Hz, 2H, NCH_2), 4.22 (s, 1H, NCH), 2.43–2.37 (m, 2H, CH_2), 2.28–2.23 (m, 1H, CH_2), 2.14–2.08 (m, 2H, CH_2), 1.98–1.93 (m, 2H, CH_2), 1.88–1.84 (m, 1H, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 196.4, 169.3, 149.0, 146.8, 146.5, 139.5, 137.2, 136.4, 128.9, 128.7, 128.4, 127.9, 123.3, 120.1, 119.2, 115.6, 83.9, 54.3, 36.6, 27.9, 26.4, 26.2, 20.7. MS (ESI^-): m/z=426.33. Anal. Calcd for $C_{25}H_{21}N_3O_4$: C 70.25, H 4.95, N 9.83. Found: C 70.38, H 5.27, N 9.66.

Compound **3c**: Light yellow solid, yield: 53%. Mp 170–172 °C. IR (KBr) ν: 2961 (w), 1705 (vs), 1622 (s), 1519 (m), 1458 (m), 1398 (m), 1342 (s), 1228 (w), 1198 (w), 1139 (w), 1102 (m), 1011 (m), 952 (w), 908 (w), 884 (w) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ: 8.61 (s, 1H, ArH), 8.08 (d, J=7.8 Hz, 1H, ArH), 8.04 (d, J=7.2 Hz, 2H, ArH), 7.83 (d, J=7.2 Hz, 1H, ArH), 7.62 (d, J=7.2 Hz, 1H, ArH), 7.58 (d, J=7.2 Hz, 2H, ArH), 7.47 (t, J=6.6 Hz, 1H, ArH), 7.38 (d, J=7.8 Hz, 1H, ArH), 7.28 (s, 2H, ArH), 7.22 (t, J=7.2 Hz, 1H, ArH), 5.89 (s, 1H, NCH), 5.83 (d, J=16.2 Hz, 1H, NCH_2), 5.67 (d, J=15.6 Hz, 1H, NCH_2), 4.39 (s, 1H, CH), 2.37 (d, J=12.6 Hz, 1H, CH_2), 2.20 (d, J=12.6 Hz, 1H, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 162.0, 158.3, 152.1, 148.6, 146.8, 139.5, 137.4, 136.6, 131.8, 129.1, 128.3, 127.8, 127.6, 123.8, 123.4, 123.3, 120.4, 119.8, 116.6, 115.2, 104.9, 84.7, 77.3, 77.1, 76.9, 54.4, 28.3, 26.2. MS (ESI^-): m/z=476.33. Anal. Calcd for $C_{87}H_{19}N_3O_5$: C 70.43, H 4.01, N 8.80. Found: C 70.54, H 4.42, N 8.59.

Compound **4a**: Light yellow solid, yield: 87%. Mp 219–221 °C. IR (KBr) ν: 3451 (w), 2992 (w), 1634 (vs), 1525 (m), 1421 (m), 1388 (s), 1346 (s), 1271 (w),1230 (w), 1204 (m), 1137 (w), 1106 (w), 1053 (w), 1028 (w), 962 (w), 861 (w), 784 (w) cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ: 9.01 (d, J=7.8 Hz, 1H, ArH), 8.92 (d, J=2.4 Hz, 1H, ArH), 8.69 (d, J=6.6 Hz, 1H, ArH), 8.55 (d, J=7.8 Hz, 1H, ArH), 8.15 (d, J=8.4 Hz, 2H, ArH), 8.01 (d, J=9.0 Hz, 1H, ArH), 7.90 (d, J=9.0 Hz, 1H, ArH), 7.82–7.80 (m, 1H, ArH), 7.44 (d, J=8.4 Hz, 2H, ArH), 6.98 (s, 2H, CH_2), 1.78 (s, 6H, CH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 137.0, 131.8, 121.7, 120.2, 120.1, 119.2, 113.1, 110.3, 109.4, 104.2, 102.0, 101.4, 101.1, 99.0, 98.0, 97.3, 95.2, 74.4, 56.2, 36.9. MS (ESI^+): m/z=458.31. Anal. Calcd for $C_{25}H_{19}N_3O_6$: C 65.64, H 4.19, N 9.19. Found: C 65.28, H 4.33, N 9.30.

Compound **4b**: Yellow solid, yield: 61%. Mp 296–298 °C. IR (KBr) ν: 2926 (w), 1606 (vs), 1521 (s), 1458 (m), 1440 (m), 1424 (m), 1399 (w), 1344 (w), 1276 (w), 1237 (m), 1153 (w), 1103 (w), 840 (w), 800 (w) cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ: 9.07 (d, J=7.2 Hz, 1H, ArH), 8.92 (d, J=3.6 Hz, 1H, ArH), 8.56 (d, J=7.8 Hz, 1H, ArH), 8.50 (d, J=7.2 Hz, 1H, ArH), 8.17 (d, J=8.4 Hz, 2H, ArH), 7.99–7.90 (m, 2H, ArH), 7.83–7.81 (m, 1H, ArH), 7.44 (d, J=8.4 Hz, 2H, ArH), 7.03 (s, 2H, CH_2), 3.22 (s, 6H, NCH_3); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 175.6, 162.3, 161.3, 157.5, 148.1, 146.8, 146.6, 145.3, 139.4, 136.8, 136.1, 131.0, 129.3, 128.3, 127.6, 125.4, 124.5, 124.2, 123.7, 92.9, 63.8, 35.7, 30.7. MS (ESI^+): m/z=470.44. Anal. Calcd for $C_{25}H_{19}N_5O_5$: C 63.96, H 4.08, N 14.92. Found: C 63.83, H 4.37, N 14.56.

Compound **4c**: Yellow solid, yield: 49%. Mp 244–246 °C. IR (KBr) ν: 3403 (w), 3048 (w), 1673 (w), 1663 (m), 1617 (vs), 1524 (s), 1453 (s), 1345 (m), 1276 (w), 1238 (w), 1156 (m), 1100 (w), 851 (w), 801 (w), 775 (w) cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ: 11.38 (s, 2H, NH), 9.14 (d, J=5.4 Hz, 1H, ArH), 8.93 (s, 1H, ArH), 8.58 (d, J=7.2 Hz,

1H, ArH), 8.50 (d, J=6.0 Hz, 1H, ArH), 8.16 (d, J=7.8 Hz, 2H, ArH), 8.00 (s, 2H, ArH), 7.83 (t, J=3.6 Hz, 1H, ArH), 7.46 (d, J=7.2 Hz, 2H, ArH), 7.04 (s, 2H, NCH_2); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 175.6, 162.3, 161.3, 157.5, 148.1, 146.8, 146.6, 145.3, 139.5, 136.8, 136.1, 130.9, 129.3, 128.3, 127.6, 125.4, 124.5, 124.2, 123.7, 92.9, 63.8, 35.7, 30.7. MS (ESI$^+$): m/z=458.62. Anal. Calcd for $C_{23}H_{15}N_5O_4S$: C 60.39, H 3.31, N 15.31. Found: C 60.47, H 3.69, N 15.06.

Compound **4d**: Light yellow solid, yield: 81%. Mp 288–290 °C. IR (KBr) ν: 3024 (w), 2912 (w), 1656 (w), 1573 (vs), 1534 (s), 1520 (s), 1454 (s), 1425 (s), 1398 (m), 1346 (s), 1287 (w), 1241 (m), 1222 (m), 1194 (w), 1133 (w), 1106 (w), 1014 (w), 985 (w), 862 (w) cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.99 (d, J=7.2 Hz, 1H, ArH), 8.90 (d, J=3.0 Hz, 1H, ArH), 8.60–8.56 (m, 2H, ArH), 8.18–8.14 (m, 3H, ArH), 7.96 (d, J=9.0 Hz, 1H ArH), 7.82–7.80 (m, 1H, ArH), 7.42 (d, J=9.0 Hz, 2H, ArH), 6.97 (s, 2H, CH_2), 2.44 (s, 2H, CH_2), 1.05 (t, J=6.6 Hz, 2H, CH_2). MS (ESI$^-$): m/z=410.42. Anal. Calcd for $C_{24}H_{17}N_3O_4$: C 70.07, H 4.16, N 10.21. Found: C 69.72, H 4.50, N 9.87.

Compound **4e**: Yellow solid, yield: 43%. Mp 240–242 °C. IR (KBr) ν: 2927 (w), 2853 (w), 1695 (s), 1641 (vs), 1603 (s), 1513 (m), 1493 (s), 1446 (w), 1424 (w), 1343 (m), 1322 (w), 1250 (w), 1228 (w), 1164 (w), 1132 (w), 967 (w), 861 (w) cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 11.67 (s, 1H, NH), 8.78 (s, 1H, ArH), 8.56 (d, J=6.0 Hz, 1H, ArH), 8.41 (d, J=7.2 Hz, 1H, ArH), 8.12 (d, J=4.8 Hz, 3H, ArH), 7.87 (d, J=6.6 Hz, 1H, ArH), 7.74 (d, J=5.4 Hz, 1H, ArH), 7.64 (t, J=4.2 Hz, 1H, ArH), 7.43 (d, J=6.6 Hz, 2H, ArH), 6.47 (s, 2H, NCH_2); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 168.0, 166.1, 148.0, 147.3, 146.3, 142.0, 140.5, 139.0, 136.6, 136.5, 129.4, 127.3, 123.9, 123.6, 123.4, 123.2, 120.9, 109.6, 95.8, 60.2. MS (ESI$^-$): m/z=429.26. Anal. Calcd for $C_{22}H_{14}N_4O_4S$: C 61.39, H 3.28, N 13.02. Found: C 61.23, H 3.65, N 12.74.

3.3. The reactions of *N*-phenacylphenanthrolinium bromide (1b) with cyclic 1,3-dicarbonyl compounds

N-Phenacylphenanthrolinium bromide (1.0 mmol, 0.378 g) and cyclic 1,3-dicarbonyl compound (1.0 mmol) were added to 20 mL of acetonitrile. Then 0.25 mL of triethylamine was added to the mixture. The mixture was stirred at room temperature for 24 h. In most cases the resulting precipitates were collected by filtration, which was recrystallized in ethanol to give the pure products for analysis. In few cases the solution was concentrated and the resulting oily solid was titrated with ethanol to give the products.

Compound **5a**: White solid, yield: 69%. Mp 164–166 °C. IR (KBr) ν: 3057 (w), 2955 (w), 2886 (w), 1689 (m), 1646 (m), 1614 (vs), 1507 (w), 1465 (s), 1384 (s), 1329 (m), 1305 (m), 1229 (s), 1173 (w), 1147 (s), 1115 (w), 1046 (m), 995 (w), 835 (w) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.04 (d, J=7.2 Hz, 2H, ArH), 7.99 (s, 1H, ArH), 7.93 (d, J=8.4 Hz, 1H, ArH), 7.66 (d, J=7.8 Hz, 1H, ArH), 7.61 (t, J=7.2 Hz, 1H, ArH), 7.53 (t, J=6.6 Hz, 2H, ArH), 7.17 (d, J=7.8 Hz, 1H, ArH), 7.06 (t, J=3.6 Hz, 1H, ArH), 5.87 (s, 1H, NCH), 5.73 (d, J=17.4 Hz, 1H, NCH_2), 7.13 (d, J=17.4 Hz, 1H, NCH_2), 4.25 (s, 1H, CH), 2.27 (s, 2H, CH_2), 2.20 (d, J=9.6 Hz, 2H, CH_2), 2.15 (s, 2H, CH_2), 1.08 (s, 3H, CH_3), 0.99 (s, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 196.3, 168.1, 145.3, 138.6, 137.0, 136.6, 136.2, 132.6, 128.6, 127.9, 127.7, 127.2, 119.7, 117.8, 114.1, 86.3, 57.4, 50.6, 42.0, 32.3, 29.5, 27.4, 26.4, 26.0. MS (ESI$^+$): m/z=439.54. Anal. Calcd for $C_{28}H_{26}N_2O_3$: C 76.69, H 5.98, N 6.39. Found: C 76.41, H 6.30, N 6.11.

Compound **5b**: White solid, yield: 61%. Mp 170–172 °C. IR (KBr) ν: 2947 (w), 1692 (s), 1644 (s), 1609 (vs), 1508 (w), 1468 (s), 1387 (s), 1363 (m), 1330 (w), 1305 (w), 1228 (m), 1190 (w), 1151 (w), 1119 (m), 1028 (m), 974 (m), 834 (w), 793 (w) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.03 (t, J=8.4 Hz, 3H, ArH), 7.93 (d, J=8.4 Hz, 1H, ArH), 7.69 (d, J=7.8 Hz, 1H, ArH), 7.61 (t, J=7.2 Hz, 1H, ArH), 7.53 (t, J=7.2 Hz, 2H, ArH), 7.18 (d, J=7.8 Hz, 1H, ArH), 7.05 (d, J=4.2 Hz, 1H, ArH), 5.86 (s, 1H, NCH), 5.74 (d, J=17.4 Hz, 1H, NCH_2), 5.19 (d, J=17.4 Hz, 1H, NCH_2), 4.24 (s, 1H, CH), 2.46–2.26 (m, 4H, CH_2), 2.15 (t, J=12.6 Hz, 2H, CH_2), 1.95 (t, J=6.0 Hz, 2H, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 196.6, 169.8, 145.4, 136.2, 132.6, 128.6, 127.9, 119.7, 117.8, 115.4, 86.2, 57.5, 36.7, 28.2, 26.5, 26.0, 20.8. MS (ESI$^+$): m/z=411.62. Anal. Calcd for $C_{26}H_{22}N_2O_3$: C 76.08, H 5.40, N 6.82. Found: C 75.94, H 5.75, N 6.36.

Compound **5c**: Light yellow solid, yield: 51%. Mp 168–170 °C. IR (KBr) ν: 2971 (w), 1703 (vs), 1626 (s), 1572 (w), 1500 (w), 1465 (s), 1399 (s), 1361 (w), 1329 (w), 1305 (m), 1229 (m), 1125 (w), 1101 (w), 1042 (w), 1020 (m), 963 (w), 832 (w), 759 (w) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.03 (d, J=6.6 Hz, 2H, ArH), 7.95 (d, J=4.8 Hz, 2H, ArH), 7.80–7.77 (m, 2H, ArH), 7.62 (t, J=6.0 Hz, 1H, ArH), 7.53 (t, J=6.6 Hz, 2H, ArH), 7.48 (t, J=7.2 Hz, 1H, ArH), 7.28 (d, J=7.8 Hz, 1H, ArH), 7.24 (d, J=7.8 Hz, 2H, ArH), 7.07 (d, J=3.6 Hz, 1H, ArH), 6.23 (s, 1H, NCH), 5.88 (d, J=17.4 Hz, 1H, NCH_2), 4.96 (d, J=17.4 Hz, 1H, NCH_2), 4.40 (s, 1H, CH), 2.44–2.36 (m, 2H, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 162.2, 158.7, 152.1, 145.5, 138.5, 137.0, 136.5, 136.2, 132.7, 131.6, 129.0, 128.7, 127.9, 127.5, 125.7, 123.8, 122.6, 120.0, 118.3, 116.6, 115.7, 104.9, 86.9, 57.2, 28.4, 25.9. MS (ESI$^+$): m/z=461.53. Anal. Calcd for $C_{29}H_{20}N_2O_4$: C 75.64, H 4.38, N 6.08. Found: C 75.58, H 4.77, N 5.64.

Compound **6a**: Red solid, yield: 74%. Mp 228–230 °C. IR (KBr) ν: 2994 (w), 1651 (m), 1597 (w), 1542 (m), 1517 (vs), 1314 (s), 1371 (w), 1340 (s), 1273 (s), 1232 (m), 1187 (m), 1156 (m), 1028 (w), 1005 (w), 936 (w), 848 (w) cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.36 (s, 1H, ArH), 8.23 (d, J=8.4 Hz, 1H, ArH), 8.10 (d, J=6.6 Hz, 1H, ArH), 8.06 (d, J=9.0 Hz, 2H, ArH), 8.00 (s, 1H, ArH), 7.96 (d, J=6.6 Hz, 2H, ArH), 7.67 (d, J=8.4 Hz, 2H, ArH), 7.41 (s, 2H, ArH), 7.32 (s, 2H, CH_2), 1.69 (s, 6H, CH_3). MS (ESI$^+$): m/z=441.21. Anal. Calcd for $C_{26}H_{20}N_2O_5$: C 70.90, H 4.58, N 6.36. Found: C 70.59, H 4.81, N 6.17.

Compound **6b**: Yellow solid, yield: 75%. Mp 254–256 °C. IR (KBr) ν: 3668 (w), 3143 (w), 1695 (s), 1641 (vs), 1513 (m), 1445 (s), 1342 (m), 1320 (m), 1227 (w), 1162 (w), 1131 (w), 826 (w), 705 (w) cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.25 (d, J=7.2 Hz, 1H, ArH), 8.14 (d, J=7.2 Hz, 2H, ArH), 7.81 (t, J=7.2 Hz, 1H, ArH), 7.63 (s, 1H, ArH), 7.57–7.52 (m, 2H, ArH), 7.43 (d, J=9.6 Hz, 1H, ArH), 7.34 (s, 3H, ArH), 7.23 (d, J=7.8 Hz, 2H, ArH), 7.05 (s, 1H, NCH_2), 1.22 (s, 2H, CH_2), 0.89 (s, 2H, CH_2); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 175.6, 162.3, 161.3, 157.5, 148.1, 146.6, 145.3, 139.5, 136.8, 136.1, 130.9, 129.3, 128.3, 127.6, 125.4, 124.5, 124.2, 123.7, 92.9, 63.8, 35.7, 30.8. MS (ESI$^-$): m/z=393.40. Anal. Calcd for $C_{25}H_{18}N_2O_3$: C 76.13, H 4.60, N 7.10. Found: C 75.74, H 4.90, N 6.75.

4. Supplementary data

Crystallographic data (**3a**: CCDC 804663; **3c**: CCDC 804662; **4a**: CCDC 804661; **5b**: CCDC 804664; **6b**: CCDC 804660) have been deposited at the Cambridge Crystallographic Database Centre.

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