Communication

Photoredox-Catalyzed Acylation/Cyclization of 2-Isocyanobiaryls with Oxime Esters for the Synthesis of 6-Acyl Phenanthridines

Boxiao Tang 1, Chuan Ding 2, Min Ou 1, Yu Liu 2,*, Junwei Liu 1 and Yilin Liu 1,* 1

Hunan Engineering Laboratory for Preparation Technology of Polyvinyl Alcohol (PVA) Fiber Material, Institute of Organic Synthesis, Huaihua University, Huaihua 418000, China
2 Department of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang 414006, China
* Correspondence: 12015015@hnist.edu.cn (Y.L.); lyl@hhtc.edu.cn (Y.L.)

Abstract: An efficient acylation/cyclization reaction of 6-acyl phenanthridines with oxime esters using photoredox catalysis has been developed. This radical acyl transfer strategy enables a facile access to acyl-substituted phenanthridines with good yield and excellent selectivity. The developed method is redox neutral and has broad substrate scope and excellent functional group tolerance.

Keywords: photocatalysis; domino reactions; 2-isocyanobiaryls; oxime esters; phenanthridines

1. Introduction

Nitrogen heterocycles are ubiquitous and significant structure frameworks, widely embedded in natural products and pharmaceuticals [1]. Phenanthridines, common nitrogen-containing aromatic fused heterocycles, have been received much attention for their existence in many drug candidates with outstanding medicinal properties, such as cytotoxic, antifungal, antibacterial, and antitumor activities [2–4]. Therefore, the development of efficient methodologies to synthesize phenanthridines and their derivatives is highly important. Different synthetic strategies for the synthesis of phenanthridines have been documented to date, such as the Pictet–Hubert reaction [5], Morgan–Walls reaction [6], Bischler–Napieralski reaction [7], cycloaddition [8–11], transition metal-mediated reaction [12–16], and so forth [17,18]. Despite efficiency, these reactions often suffer harsh reaction conditions, which lead to the restriction of their application in organic synthesis. Consequently, it is highly desirable to exploit mild and effective approaches for the preparation of phenanthridines.

Owing to their unique reactive properties of isonitrile functionality, isocyanides have become ponderable building blocks in synthetic chemistry. In general, isocyanides are regarded as isoelectronic with carbon monoxide, and could undergo typical insertion reactions [19–21]. The common insertion mode is that a radical attacks an isocyanide moiety to afford imidoyl radicals, which could be further coupled with the second radical or radical acceptors such as arenes [22–24]. Based on this concept, a variety of radical transformations between 2-isocyanobiphenyls with diverse radicals, such as alkyl [25–31], aryl [32–35], fluoroalkyl [36–40], trifluoromethyl [41–44], phosphoryl sources [45–47], and so on [48–50], to generate 6-substituted phenanthridines, have been reported. However, most of them have been focused on the generation of 6-alkyl, aryl, and trifluoromethyl substituted phenanthridines, and only a few studies have been developed to the introduction of acyl functionality to the phenanthridine framework at the sixth position [51–54]. The pioneering work was conducted by the Studer group [51], in which aroyl radicals were generated from aromatic aldehydes in the presence of an iron catalyst and tert-ButOOH as an oxidant (Scheme 1a). Subsequently, Lei and co-workers [52] disclosed an alternative route towards the synthesis of 6-acyl phenanthridines via a silver-catalyzed oxidative radical decarboxylation–cyclization strategy (Scheme 1a). Later on, Ding and co-workers [53]...
reported Fe-catalyzed oxidative acyl radical cyclization to prepare 6-acyl phenanthridines using benzylic alcohols or toluene as an aroyl source (Scheme 1a). Recently, Xuan et al. [54] reported an elegant strategy to construct phenanthridines via the direct photoreduction of benzothiazolines to induce a tandem radical cyclization with isonitriles (Scheme 1b). In spite of these achievements, challenges are still faced in this field. Stoichiometric oxidants such as tBuOOH and Na$_2$S$_2$O$_8$ are necessary to generate aroyl radicals [51–53], and these methods are not applicable to generate alkyl-substituted acyl radicals [51–54]. Thus, the exploration of a new approach to afford both aroyl and alkyl acylated phenanthridines under neutral reaction conditions is still desirable. Herein, we report the photoredox-catalyzed [55,56] radical acylation/cyclization of 2-isocyanobiphenyl for the synthesis of 6-acyl phenanthridines using oxime esters [57–61] as the acyl source (Scheme 1c).

Scheme 1. Synthesis of 6-acyl phenanthridines.

2. Results and Discussion

We commenced our study with the optimization of reaction conditions using 2-isocynano-4'-methyl-1,1'-biphenyl (1a) and O-4-CF$_3$C$_6$H$_4$CO acyl oxime (2a) as model substrates (Table 1). To our delight, under 5 W blue LED light irradiation, the acylation/cyclization product 3aa was obtained in 94% isolated yield in the presence of Ir(ppy)$_3$ (1 mol%), DMF as solvent, and heated to 100 °C for 12 h (entry 1). The photocatalyst was essential to this transformation, and no target molecule was observed without Ir(ppy)$_3$ (entry 2). Replacing Ir(ppy)$_3$ with other photosensitizers, such as Ru(bpy)$_3$Cl$_2$, Eosin Y, and Na$_2$-Eosin Y, led to unsatisfactory results (entries 3–5).

When the catalyst loading was increased to 2 mol%, the yield of 3aa was little changed (entry 6). The tandem acyl transfer and cyclization reaction could even occur to afford 3aa in 49% yield without irradiation (entry 7). Variation of light sources revealed that 5 W blue LED light was the best choice among them (entries 8–10). Then, O-acylated acyl oximes including C$_6$H$_5$CO, C$_6$F$_5$CO, p-FC$_6$H$_4$CO, p-NO$_2$C$_6$H$_4$CO, p-OMeC$_6$H$_4$CO, and CH$_3$CO were investigated, which indicated that the O-p-CF$_3$C$_6$H$_4$CO acyl oxime was the most effective acyl precursor (entries 11–16). The screening of other solvents, such as CH$_3$CN, THF, DCE, tBuOAc, toluene, and DMSO, showed that DMF was the optimal solvent for the photoinduced acyl transfer reaction (entries 17–22). In addition, the acylation/cyclization reactions could occur at 80 °C or 120 °C, albeit with a low yield of 3aa (entries 23–24). Prolonging the reaction time to 24 h has no positive effect on the isocyanide insertion transformation (entry 25). When replacing N$_2$ with argon, the transformation occurred smoothly (entry 26). However, the reaction could not even take place in the presence of air (entry 27). Pleasingly, a 1 mmol scale synthesis of 3aa was achieved with 70% yield, indicating that this robust method could be extended to further applications (entry 28).
Table 1. Screening Optimal Conditions 1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Variation from the Standard Conditions</th>
<th>Yield (%) 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>Without Ir(ppy)3</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Ru(bpy)3Cl2 instead of Ir(ppy)3</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>Eosin Y instead of Ir(ppy)3</td>
<td>36</td>
</tr>
<tr>
<td>5</td>
<td>Na2-Eosin Y instead of Ir(ppy)3</td>
<td>16</td>
</tr>
<tr>
<td>6</td>
<td>Ir(ppy)3 (2 mol%)</td>
<td>95</td>
</tr>
<tr>
<td>7</td>
<td>Without additional light</td>
<td>49</td>
</tr>
<tr>
<td>8</td>
<td>3 W blue LED light instead of 5 W blue LED light</td>
<td>63</td>
</tr>
<tr>
<td>9</td>
<td>7 W blue LED light instead of 5 W blue LED light</td>
<td>84</td>
</tr>
<tr>
<td>10</td>
<td>36 W compact fluorescent light instead of 5 W blue LED light</td>
<td>52</td>
</tr>
<tr>
<td>11</td>
<td>2a-1 instead of 2a</td>
<td>31</td>
</tr>
<tr>
<td>12</td>
<td>2a-2 instead of 2a</td>
<td>46</td>
</tr>
<tr>
<td>13</td>
<td>2a-3 instead of 2a</td>
<td>40</td>
</tr>
<tr>
<td>14</td>
<td>2a-4 instead of 2a</td>
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<tr>
<td>15</td>
<td>2a-5 instead of 2a</td>
<td>52</td>
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<tr>
<td>16</td>
<td>2a-6 instead of 2a</td>
<td>13</td>
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<tr>
<td>17</td>
<td>CH3CN instead of DMF</td>
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<tr>
<td>18</td>
<td>THF instead of DMF</td>
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<tr>
<td>19</td>
<td>DCE instead of DMF</td>
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<tr>
<td>20</td>
<td>nBuOAc instead of DMF</td>
<td>21</td>
</tr>
<tr>
<td>21</td>
<td>toluene instead of DMF</td>
<td>48</td>
</tr>
<tr>
<td>22</td>
<td>DMSO instead of DMF</td>
<td>52</td>
</tr>
<tr>
<td>23</td>
<td>at 80 °C</td>
<td>74</td>
</tr>
<tr>
<td>24</td>
<td>at 120 °C</td>
<td>88</td>
</tr>
<tr>
<td>25</td>
<td>for 24 h</td>
<td>94</td>
</tr>
<tr>
<td>26</td>
<td>Argon instead of nitrogen</td>
<td>93</td>
</tr>
<tr>
<td>27</td>
<td>Air instead of nitrogen</td>
<td>0</td>
</tr>
<tr>
<td>28</td>
<td>None</td>
<td>70</td>
</tr>
</tbody>
</table>

1 Reaction conditions: 1a (0.2 mmol), 2a (0.3 mmol, 1.5 equiv), Ir(ppy)3 (1 mol%) and DMF (2 mL) at 100 °C in the presence of N2 under 5 W blue light for 12 h. 2 Isolated yield. 3 1 mmol scale reaction.

With the optimal conditions established, a series of biaryl isocyanides were first examined for the scope of this photoredox-catalyzed acylation/cyclization reaction in the presence of 2a (Table 2). Initially, 2-isocyanobiaryl compounds 1b-h embedding a variety of substituents with electron-donating (1b-h) or withdrawing groups (1c-h) at the para-position of the phenyl that does not contain the isonitrile motif reacted smoothly with 2a to furnish the corresponding phenanthridine derivatives 3ba-ha in good yields, ranging from 70% to 89%. The transformation of acyl oxime ester 2a with 3-substituted isocyanides 1i and 1j delivered two regioisomers, respectively. Isocyanides 1k-m bearing substituents at the ortho position of the arene that bears the isonitrile moiety could undergo the acylation/cyclization reaction to provide phenanthridines with good results. Interestingly, a satisfactory 79% yield and specific regioselectivity were obtained with isocyanide 1n containing a naphthyl moiety, while 1o bearing benzodioxole was applied as substrate and resulted in two regioisomers with a 90% total yield. In addition, the desired product, 3pa, bearing a fused benzoquinone, could also be obtained using the present synthetic method. Then, 2-isocyanobiaryl 1q-v carrying different substituents at the arenene that bears the isonitrile moiety were explored under the optimized conditions. Obviously, the substituents with different electronic properties at the different positions of the arenes did not affect the reaction efficiency, demonstrating the broad substrate scope of this reaction.
Table 2. Scope of 2-isocyanobiaryls (1)\(^1,2\).

\[
\begin{array}{c|c|c|c}
\hline
R^1 & R^2 & R^3 & R^4 \\
\hline
& & & \\
\hline
\end{array}
\]

\(^1\) Reaction conditions: 1 (0.2 mmol), 2a (0.3 mmol, 1.5 equiv), Ir(ppy)_3 (1 mol%) and DMF (2 mL) at 100 °C in the presence of N\(_2\) under 5 W blue light for 12 h. \(^2\) Cited yields are of isolated material following chromatography.

Then, the reactions of biphenyl isocyanide (1a) with a variety of acyl oxime esters under the optimized condition were exploited (Table 3). For R^4 = Me, pleasingly, both aliphatic acyl and aroyl oxime esters were suitable for the acylation/cyclization transformations to provide 6-acyl phenanthridines, which differed from the previous reports [51–54] that overwhelmingly produced aliphatic acyl 6-substituted phenanthridines. The acyl oxime esters 2b-f with different chain lengths could be smoothly converted to the corresponding acyl radical in the presence of the photocatalyst, followed by isocyanide insertion to produce 3ab-f in good yields. In addition, aroyl oxime esters 2g-n containing a variety of groups on the phenyl rings were investigated. To our delight, the expected radical addition/cyclization products 3ag-n were isolated in 71–82% yields. Notably, 2-thienylacyl substituted phenanthridine 3ao could be obtained from the corresponding acyl oxime ester 2o in a yield of 76%. This conversion was successfully amenable to oxime esters 2o and 2p with variation in the iminyl group (R^4), and both of them afforded 6-acyl substituted nitrogen heterocycles 3ab and 3ac in 77% and 81% yields, respectively.
Table 3. Scope of acyl oxime esters (2) 1,2.

![Diagram of reaction](image)

1 Reaction conditions: 1a (0.2 mmol), 2 (0.3 mmol, 1.5 equiv), Ir(ppy)$_3$ (1 mol%) and DMF (2 mL) at 100 $^\circ$C in the presence of N$_2$ under 5 W blue light for 12 h. 2 Cited yields are of isolated material following chromatography.

To investigate the reaction mechanism, control experiments were performed (Scheme 2). The common radical scavengers, such as TEMPO, BHT, and 1,1-diphenylethene, were applied to detect the reactive species. As a result, the reactions were almost completely inhibited, and benzoic radicals were captured by the scavengers, which suggested that this reaction involved the radical mechanism.

![Scheme 2. Control Experiments](image)

According to the above control experimental results and previous reports [25–54], a possible mechanism was proposed (Scheme 3). At first, upon visible-light irradiation, the photocatalyst Ir$^{3+}$ was converted to its excited state Ir$^{3+}$* (E$_{1/2}$Ir$^{4+}$/Ir$^{3+}$* = −1.73 V versus SCE) [58], which underwent single-electron transfer (SET) with oxime ester 2a (E$_{\text{red}}$ of approximately −1.45 V versus SCE) [62,63] to produce iminyl radical A via the removal of the ester group and the generation of the oxidation state Ir$^{3+}$ complex at the same time. The β-fragmentation of iminyl radical A occurred to afford acetonitrile and acyl radical B, which underwent isonitrile radical insertion with isocyanobiaryl 1a to produce imidoyl radical C. Next, the intramolecular cyclization occurred to furnish intermediate D, which was further oxidized by Ir$^{4+}$ to produce cation E and the regeneration of photocatalyst. Finally, the product 3aa was obtained from E via the release of a proton.
3. Materials and Methods

3.1. General Information

Commercially available reagents were used throughout without purification unless otherwise stated. The starting biaryl isocyanide (1) [64] and acyl oxime esters (2) [65] were prepared by methods reported in the literature. ¹H and ¹³C NMR spectra were recorded on a Bruker AC-400 instrument (400 MHz for ¹H and 100 MHz for ¹³C) at 20 °C. Chemical shifts (d) are given in ppm downfield from Me₄Si and are referenced as internal standard to the residual solvent (unless indicated) CDCl₃ (d = 7.26 for ¹H and d = 77.00 for ¹³C). Coupling constants, J, are reported in hertz (Hz). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet, and br = broad. Melting points were determined in a capillary tube and are uncorrected. TLC was carried out on SiO₂ (silica gel 60 F254), and the spots were located with UV light. Flash chromatography was carried out on SiO₂ (silica gel 60, 230–400 mesh ASTM). Drying of organic extracts during work-up of reactions was performed over anhydrous Na₂SO₄. Evaporation of solvents was accomplished with a Büchi rotatory evaporator. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

3.2. General Procedure for the Synthesis of 3

To a Schlenk tube were added 1 (0.2 mmol), 2 (0.4 mmol, 2 equiv.), DMF (2 mL), and Ir(ppy)₃ (1 mol%). Then, the mixture was stirred at 100 °C (oil bath temperature) in an N₂ atmosphere for 12 h until the complete consumption of the starting material was monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (petroleum ether/ethyl acetate = 80:1 to 40:1) to afford the desired products 3.

3.3. Characterization Data for 6-Acyl Phenanthridines

For 1-(8-Methylphenanthridin-6-yl)ethan-1-one (3aa) (see Supplementary Materials for NMR spectra copies of the compounds), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (80:1) to afford a white solid in 94% yield (50.2 mg); mp: 183.0–183.5 °C (uncorrected). ¹H NMR (400 MHz, CDCl₃) δ: 8.64 (d, J = 1.8 Hz, 1H), 8.59–8.49 (m, 2H), 8.24–8.15 (m, 1H), 7.78–7.65 (m, 3H), 2.94 (s, 3H), 2.59 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 203.12, 151.37, 140.84, 138.97, 138.00, 132.28, 131.80, 129.02, 128.53, 127.00, 125.47, 123.00, 122.08, 119.66, 28.59, 21.89; HRMS (ESI-TOF) m/z: C₁₆H₁₄NO (M + H)⁺ calculated for 236.1072, found 236.1065.

For 1-(8-(tert-butyl)phenanthridin-6-yl)ethan-1-one (3ba), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (60:1) to afford a white solid.
in 87% yield (48.2 mg); mp: 183.0–183.5 °C (uncorrected). 1H NMR (400 MHz, CDCl3) δ: 8.90 (d, J = 1.6 Hz, 1H), 8.59–8.54 (m, 2H), 8.22–8.19 (m, 1H), 7.96–7.93 (m, 1H), 7.75–7.24 (m, 2H), 2.96 (s, 3H), 1.46 (s, 9H); 13C NMR (100 MHz, CDCl3) δ: 203.0, 153.9, 151.1, 142.2, 131.4, 130.8, 129.1, 128.6, 128.4, 125.3, 123.3, 123.0, 121.9, 121.7, 35.2, 31.2, 28.7; HRMS (ESI-TOF) m/z: C19H23NO (M + H)+ calculated for 278.1467, found 278.1461.

For 1-(8-Fluorophenanthridin-6-yl)ethan-1-one (3ca), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethanol acetate (50:1) to afford a yellow solid in 86% yield (41.1 mg); mp: 183.1–183.6 °C (uncorrected). 1H NMR (400 MHz, CDCl3) δ: 8.74–8.72 (m, 1H), 8.62–8.60 (m, 1H), 8.52–8.49 (m, 1H), 8.24–8.21 (m, 1H), 7.79–7.74 (m, 2H), 7.62–7.57 (m, 1H), 2.94 (s, 3H); 13C NMR (100 MHz, CDCl3) δ: 202.3, 161.9 (d, J = 246.8 Hz, 1C), 152.5 (d, J = 5 Hz, 1C), 142.0, 131.2 (2C), 130.2 (d, J = 1 Hz, 1C), 129.3, 128.7, 125.1, 124.3 (q, J = 11 Hz, 1C), 121.8, 120.0 (d, J = 24 Hz, 1C), 112.7 (d, J = 23 Hz, 1C), 28.2; 19F NMR (376 MHz, CDCl3) δ: −110.6 (s, 1F); HRMS (ESI-TOF) m/z: C15H11FNO (M + H)+ calculated for 240.0746, found 240.0749.

For 1-(8-Chlorophenanthridin-6-yl)ethan-1-one (3da), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethanol acetate (50:1) to afford a yellow solid in 89% yield (45.1 mg); mp: 142.0–142.5 °C (uncorrected). 1H NMR (400 MHz, CDCl3) δ: 8.99 (d, J = 2.0 Hz, 1H), 8.53–8.47 (m, 2H), 8.22–8.20 (m, 1H), 7.81–7.73 (m, 3H), 2.93 (s, 3H); 13C NMR (100 MHz, CDCl3) δ: 202.2, 151.9, 142.2, 134.2, 131.8, 131.2, 131.1, 129.3, 129.1, 127.1, 124.8, 123.8, 123.5, 121.9, 28.3; HRMS (ESI-TOF) m/z: C15H11ClNO (M + H)+ calculated for 255.0451, found 255.0459.

For 1-(8-Bromophenanthridin-6-yl)ethan-1-one (3ea), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethanol acetate (50:1) to afford a yellow solid in 80% yield (47.6 mg); mp: 136.3–136.8 °C (uncorrected). 1H NMR (400 MHz, CDCl3) δ: 9.09 (d, J = 2.0 Hz, 1H), 8.43–8.40 (m, 1H), 8.36 (d, J = 8.8 Hz, 1H), 8.17–8.15 (m, 1H), 7.85–7.82 (m, 1H), 7.78–7.69 (m, 2H), 2.91 (s, 3H); 13C NMR (100 MHz, CDCl3) δ: 202.2, 151.9, 142.2, 133.9, 132.0, 131.2, 130.3, 129.3, 129.2, 124.8, 121.4, 121.3, 121.5, 28.3; HRMS (ESI-TOF) m/z: C15H11BrNO (M + H)+ calculated for 299.9949, found 299.9949.

For 1-(6-(Trifluoromethyl)phenanthridin-6-yl)ethan-1-one (3fa), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethanol acetate (60:1) to afford a white solid in 77% yield (44.5 mg); mp: 126.0–126.5 °C (uncorrected). 1H NMR (400 MHz, CDCl3) δ: 9.30 (s, 1H), 8.68 (d, J = 8.8 Hz, 1H), 8.55–8.52 (m, 1H), 8.25–8.23 (m, 1H), 8.01–7.99 (m, 1H), 7.86–7.77 (m, 2H), 2.95 (s, 3H); 13C NMR (100 MHz, CDCl3) δ: 202.1, 152.7, 142.9, 135.4, 131.2, 130.0, 129.8 (q, J = 32.7 Hz, 1C), 129.5, 126.5 (q, J = 3.2 Hz, 1C), 125.7 (q, J = 4.4 Hz, 1C), 124.4 (2C), 122.9, 123.9 (q, J = 270.9 Hz, 1C), 122.3, 28.2; 19F NMR (376 MHz, CDCl3) δ: −62.3 (s, 3H); HRMS (ESI-TOF) m/z: C15H13F3NO (M + H)+ calculated for 290.0714, found 290.0719.

For 6-Acetylphenanthidine-8-carbonitrile (3ga), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethanol acetate (30:1) to afford a yellow solid in 75% yield (36.9 mg); mp: 156.3–156.8 °C (uncorrected). 1H NMR (400 MHz, CDCl3) δ: 9.48–9.47 (m, 1H), 8.75 (d, J = 8.4 Hz, 1H), 8.61–8.59 (m, 1H), 8.31–8.29 (m, 1H), 8.03–8.01 (m, 1H), 7.93–7.83 (m, 2H), 2.97 (s, 3H); 13C NMR (100 MHz, CDCl3) δ: 202.0, 151.9, 143.3, 135.8, 133.8, 131.9, 131.5, 130.6, 129.8, 124.2, 123.2, 122.6, 118.4, 111.8, 28.2; HRMS (ESI-TOF) m/z: C16H13N2O (M + H)+ calculated for 247.0793, found 247.0799.

For 1,1′-Phenanthridine-6,8-diylbis(ethan-1-one) (3ha), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethanol acetate (40:1) to afford a white solid in 70% yield (36.8 mg); mp: 130.1–130.6 °C (uncorrected). 1H NMR (400 MHz, CDCl3) δ: 9.57 (d, J = 2.0 Hz, 1H), 8.66 (d, J = 8.8 Hz, 1H), 8.58–8.56 (m, 1H), 8.40–8.38 (m, 1H), 8.26–8.24 (m, 1H), 7.87–7.77 (m, 2H), 2.98 (s, 3H), 2.78 (s, 3H); 13C NMR (100 MHz, CDCl3) δ: 202.6,
197.7, 153.2, 143.2, 136.3, 136.0, 131.2, 130.1, 129.6, 129.3, 128.7, 124.6, 122.6, 122.5, 28.4, 26.6; HRMS (ESI-TOF) m/z: C_{17}H_{14}NO (M + H)^+ calculated for 264.0946, found 264.0949.

For (9-Methylphenanthridin-6-yl)ethan-1-one (3ia), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a yellow solid in 42% yield (20.3 mg); mp: 172.0–172.5 °C (uncorrected). 1H NMR (400 MHz, CDCl3): δ: 8.78 (d, J = 8.4 Hz, 1H), 8.59–8.56 (m, 1H), 8.44 (s, 1H), 8.22–8.20 (m, 1H), 7.78–7.71 (m, 2H), 7.56–7.53 (m, 1H), 2.94 (s, 3H), 2.65 (s, 3H); 13C NMR (100 MHz, CDCl3): δ: 202.9, 153.7, 142.6, 141.2, 133.7, 130.9, 129.8, 128.7, 128.5, 125.2, 122.0, 121.1, 128.5, 22.3; HRMS (ESI-TOF) m/z: C_{16}H_{14}NO (M + H)^+ calculated for 236.0997, found 236.0995.

For 1-(7-Methylphenanthridin-6-yl)ethan-1-one (3ka), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50:1) to afford a white solid in 66% yield (25.9 mg). 1H NMR (400 MHz, CDCl3): δ: 8.56–8.51 (m, 2H), 8.15–8.12 (m, 1H), 7.75–7.65 (m, 3H), 7.50–7.48 (m, 1H), 2.97 (s, 3H), 2.60 (s, 3H); 13C NMR (100 MHz, CDCl3): δ: 203.77, 158.70, 141.94, 135.74, 134.51, 130.81, 130.64, 130.06, 128.81, 127.94, 124.79, 122.33, 122.01, 120.33, 77.32, 77.00, 76.68, 29.16, 24.01; HRMS (ESI-TOF) m/z: C_{15}H_{13}NO (M + H)^+ calculated for 236.0945, found 236.0959.

For 1-(9-Chlorophenanthridin-6-yl)ethan-1-one (3ja), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50:1) to afford a white solid in 42% yield (24.4 mg). 1H NMR (400 MHz, CDCl3): δ: 8.58 (d, J = 8.2 Hz, 1H), 8.50–8.47 (m, 1H), 8.24–8.21 (m, 1H), 7.78–7.75 (m, 2H), 7.66–7.64 (m, 1H), 2.94 (s, 3H); 13C NMR (100 MHz, CDCl3): δ: 202.4, 152.8, 147.2, 137.3, 134.8, 131.1, 129.6, 129.5, 129.1, 128.7, 124.2, 122.0, 121.6, 121.3, 28.3; HRMS (ESI-TOF) m/z: C_{16}H_{13}ClNO (M + H)^+ calculated for 252.0945, found 252.0941.

For 1-(7-Chlorophenanthridin-6-yl)ethan-1-one (3ka), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50:1) to afford a white solid in 88% yield (21.9 mg); mp: 120.3–120.6 °C (uncorrected). 1H NMR (400 MHz, CDCl3): δ: 8.51 (d, J = 8.1 Hz, 1H), 8.15–8.12 (m, 1H), 7.85–7.65 (m, 4H), 2.91 (s, 3H); 13C NMR (100 MHz, CDCl3): δ: 202.9, 153.7, 142.7, 137.3, 134.8, 131.1, 129.6, 129.5, 129.1, 128.7, 124.2, 122.0, 121.6, 121.3, 28.3; HRMS (ESI-TOF) m/z: C_{15}H_{13}ClNO (M + H)^+ calculated for 256.0959, found 256.0955.
δ: 9.83–9.81 (m, 1H), 8.79–8.76 (m, 1H), 8.26–8.24 (m, 1H), 7.95–7.94 (m, 1H), 7.85–7.75 (m, 2H), 7.62 (t, J = 8.0 Hz, 1H), 2.94 (s, 3H); 13C NMR (100 MHz, CDCl3): δ: 202.4, 154.3, 143.5, 134.6, 131.1, 130.4, 129.2, 128.2, 127.7, 127.0, 126.4, 125.3, 123.4, 28.8; HRMS (ESI-TOF) m/z: C13H14ClNO (M + H)+ calculated for 256.0451, found 256.0458.

For 1-(Benzo[i]phenanthridin-5-yl)ethan-1-one-1 (3na), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (60:1) to afford a yellow solid in 79% yield (42.8 mg); mp: 92.1–92.6 ºC; 1H NMR (400 MHz, CDCl3): δ: 9.02 (d, J = 8.0 Hz, 1H), 8.71 (d, J = 8.8 Hz, 1H), 8.35–8.33 (m, 1H), 8.06–8.04 (m, 1H), 7.99 (d, J = 8.8 Hz, 1H), 7.85–7.71 (m, 4H), 2.99 (s, 3H); 13C NMR (100 MHz, CDCl3): δ: 203.1, 153.3, 144.3, 134.6, 132.9, 130.6, 128.9, 128.7, 128.5, 128.4, 128.2, 128.1, 127.1, 126.7, 125.4, 123.2, 122.0, 28.9; HRMS (ESI-TOF) m/z: C13H14ClNO (M + H)+ calculated for 272.0997, found 272.0994.

For 1-(1,3-Dioxolo[4,5-j]phenanthridin-6-yl)ethan-1-one (3oa), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50:1) to afford a yellow solid in 44% yield (22.3 mg); mp: 190.1–190.6 ºC (uncorrected). 1H NMR (400 MHz, CDCl3): δ: 8.18 (d, J = 7.2 Hz, 1H), 7.73 (s, 1H), 7.73–7.67 (m, 2H), 6.16 (s, 2H), 2.93 (s, 3H); 13C NMR (100 MHz, CDCl3): δ: 203.14, 151.90, 148.82, 142.20, 131.71, 130.92, 128.42, 128.21, 125.47, 121.85, 119.74, 105.01, 101.98, 99.72, 77.32, 77.00, 76.68, 28.55; HRMS (ESI-TOF) m/z: C26H12NO3 (M + H)+ calculated for 366.0739, found 366.0742.

For 1-(3,8-Dimethylphenanthridin-6-yl)ethan-1-one (3pa), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (60:1) to afford a yellow solid in 42% yield (20.7 mg). 1H NMR (400 MHz, CDCl3): δ: 8.36 (d, J = 5.6 Hz, 2H), 8.17 (d, J = 7.7 Hz, 1H), 7.90 (s, 1H), 7.71 (s, J = 6.8 Hz, 2H), 6.15 (s, 2H), 2.93 (s, 3H); 13C NMR (100 MHz, CDCl3): δ: 203.1, 151.90, 150.95, 148.82, 142.20, 131.71, 130.92, 128.42, 128.21, 125.47, 121.85, 119.74, 105.01, 101.98, 99.72, 77.32, 77.00, 76.68, 28.55; HRMS (ESI-TOF) m/z: C19H16NO (M + H)+ calculated for 250.1157, found 250.1158.

For 1-(1,3-Dioxolo[4,5-j]phenanthridin-6-yl)ethan-1-one (3oa′), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50:1) to afford a yellow solid in 42% yield (20.7 mg). 1H NMR (400 MHz, CDCl3): δ: 8.36 (d, J = 5.6 Hz, 2H), 8.17 (d, J = 7.7 Hz, 1H), 7.90 (s, 1H), 7.71 (s, J = 6.8 Hz, 2H), 6.15 (s, 2H), 2.93 (s, 3H); 13C NMR (100 MHz, CDCl3): δ: 203.14, 151.90, 150.95, 148.82, 142.20, 131.71, 130.92, 128.42, 128.21, 125.47, 121.85, 119.74, 105.01, 101.98, 99.72, 77.32, 77.00, 76.68, 28.55; HRMS (ESI-TOF) m/z: C19H16NO (M + H)+ calculated for 250.1154, found 250.1157.

For 1-(8,4-Dimethylphenanthridin-6-yl)ethan-1-one (3qa), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (60:1) to afford a yellow solid in 85% yield (42.3 mg); mp: 136.0–136.5 ºC (uncorrected). 1H NMR (400 MHz, CDCl3): δ: 8.85 (s, 1H), 8.44 (d, J = 8.4 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 7.97 (s, 1H), 7.63–7.61 (m, 1H), 7.53–7.51 (m, 1H), 2.92 (s, 3H), 2.57 (t, J = 8.4 Hz, 2H); 13C NMR (100 MHz, CDCl3): δ: 202.9, 153.6, 142.2, 138.5, 137.5, 132.4, 131.4, 130.4, 130.2, 126.9, 123.0, 122.7, 121.6, 121.6, 28.6, 21.8, 21.3; HRMS (ESI-TOF) m/z: C17H16NO (M + H)+ calculated for 250.1154, found 250.1158.
For 1-(3-Fluoro-8-methylphenanthridin-6-yl)ethan-1-one (3sa), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50:1) to afford a yellow solid in 83% yield (41.9 mg); mp: 139.2–139.7 °C (uncorrected). $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.59 (s, 1H), 8.48 (t, $J = 3.6$ Hz, 1H), 8.43 (d, $J = 8.4$ Hz, 1H), 7.83–7.81 (m, 1H), 7.68–7.66 (m, 1H), 7.49–7.44 (m, 1H), 2.91 (s, 3H), 2.58 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 202.6, 162.3 (d, $J = 24.6$ Hz, 1C), 154.8, 143.2 (d, $J = 12$ Hz, 1C), 137.9, 132.9, 131.3, 127.1, 123.7 (d, $J = 9$ Hz, 1C), 122.6, 122.1, 121.6, 117.7 (d, $J = 24$ Hz, 1C), 115.0 (d, $J = 20$ Hz, 1C), 28.6, 21.8; $^{19}$F NMR (376 MHz, CDCl$_3$) δ: −112.3 (s, 1F); HRMS (ESI-TOF) m/z: C$_{16}$H$_{14}$FNO (M + H)$^+$ calculated for 254.0903, found 254.0908.

For 1-(2,8-Dimethylphenanthridin-6-yl)ethan-1-one (3ta), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a white solid in 85% yield (42.3 mg); mp: 134.3–134.9 °C (uncorrected). $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.66 (s, 1H), 8.48 (d, $J = 8.4$ Hz, 1H), 8.29 (s, 1H), 8.07 (d, $J = 8.4$ Hz, 1H), 7.64–7.62 (m, 1H), 7.56–7.54 (m, 1H), 2.92 (s, 3H), 2.62 (s, 3H), 2.57 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 202.9, 152.6, 140.4, 138.9, 137.9, 132.2, 131.1, 130.6, 130.2, 127.0, 125.2, 123.2, 121.7, 121.4, 28.6, 22.1, 21.8; HRMS (ESI-TOF) m/z: C$_{25}$H$_{24}$NO (M + H)$^+$ calculated for 250.1154, found 250.1162.

For 5-Acetyl-8-methylphenanthridine-2-carbonitride (3ua), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a yellow solid in 80% yield (41.6 mg); mp: 191.4–194.8 °C (uncorrected). $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.78 (d, $J = 2.0$ Hz, 1H), 8.57 (s, 1H), 8.42 (d, $J = 8.4$ Hz, 1H), 8.21 (d, $J = 8.4$ Hz, 1H), 7.88–7.85 (m, 1H), 7.73 (d, $J = 1.6$ Hz, 1H), 2.91 (s, 3H), 2.60 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 202.1, 156.2, 143.5, 139.6, 133.5, 131.8, 130.3, 129.7, 127.5, 127.4, 125.2, 123.1, 121.7, 118.7, 111.7, 28.5, 21.8; HRMS (ESI-TOF) m/z: C$_{25}$H$_{18}$N$_2$O (M + H)$^+$ calculated for 261.0950, found 261.0953.

For 1-(1,8-Dimethylphenanthridin-6-yl)ethan-1-one (3va), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (70:1) to afford a yellow solid in 83% yield (41.3 mg); mp: 125.3–125.8 °C (uncorrected). $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.73 (d, $J = 8.8$ Hz, 1H), 8.61 (s, 1H), 8.09 (d, $J = 7.6$ Hz, 1H), 7.65–7.53 (m, 2H), 7.54 (d, $J = 7.2$ Hz, 1H), 3.06 (s, 3H), 2.93 (s, 3H), 2.57 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 202.9, 153.7, 143.6, 137.1, 134.6, 132.7, 132.5, 131.5, 129.6, 127.5, 126.9, 126.2, 125.1, 123.9, 28.7, 26.5, 21.6; HRMS (ESI-TOF) m/z: C$_{25}$H$_{20}$NO (M + H)$^+$ calculated for 250.1154, found 250.1159.

For 1-(8-Methylphenanthridin-6-yl)propan-1-one (3ab), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (60:1) to afford a white solid in 78% yield (38.9 mg); mp: 92.1–92.6 °C (uncorrected). $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.56–8.51 (m, 3H), 8.20–8.17 (m, 1H), 7.74–7.67 (m, 3H), 3.46–3.40 (m, 2H), 2.58 (s, 3H), 1.32 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 205.6, 154.5, 142.1, 138.0, 132.5, 131.3, 130.7, 128.4, 128.4, 126.9, 125.2, 123.1, 121.8, 121.9, 33.8, 21.8, 7.9; HRMS (ESI-TOF) m/z: C$_{25}$H$_{19}$NO (M + H)$^+$ calculated for 250.1154, found 250.1159.

For 1-(8-Methylphenanthridin-6-yl)butan-1-one (3ac), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (60:1) to afford a yellow solid in 81% yield (42.6 mg); mp: 67.2–67.6 °C (uncorrected). $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.66–8.44 (m, 3H), 8.29–8.14 (m, 1H), 7.80–7.70 (m, 2H), 3.38 (t, $J = 7.7$ Hz, 2H), 2.59 (s, 3H), 1.91–1.82 (m, 2H), 1.08 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 205.2, 154.6, 142.1, 138.0, 132.5, 131.4, 130.7, 128.4, 128.4, 126.9, 125.2, 123.1, 121.9, 121.8, 42.4, 21.8, 17.5, 13.9; HRMS (ESI-TOF) m/z: C$_{27}$H$_{21}$NO (M + H)$^+$ calculated for 264.1310, found 264.1315.

For 1-(8-Methylphenanthridin-6-yl)pentan-1-one (3ad), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (60:1) to afford a yellow solid in 82% yield (45.4 mg); mp: 63.4–63.9 °C (uncorrected). $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.56–8.50 (m, 3H),
For 1-(8-Methylphenanthridin-6-yl)hexan-1-one (3ae), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (60:1) to afford a yellow solid in 80% yield (46.5 mg); mp: 72.1–72.6 °C (uncorrected). 1H NMR (400 MHz, CDCl₃) δ: 8.54–8.50 (m, 3H), 8.20–8.18 (m, 1H), 7.52–7.65 (m, 3H), 3.43–3.36 (m, 2H), 2.58 (s, 3H), 1.87–1.79 (m, 2H), 1.49–1.30 (m, 4H), 0.93 (t, J = 6.8 Hz, 3H); 13C NMR (100 MHz, CDCl₃) δ: 205.3, 154.6, 142.1, 138.0, 132.5, 131.3, 130.7, 128.4, 128.3, 126.9, 125.2, 123.1, 121.8, 121.8, 40.5, 31.5, 23.7, 22.5, 21.8, 13.9; HRMS (ESI-TOF) m/z: C₁₉H₂₂NO (M + H)⁺ calculated for 278.1467, found 278.1469.

For 4-Methyl-1-(8-methylphenanthridin-6-yl)pentan-1-one (3af), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50:1) to afford a brown liquid in 84% yield (48.9 mg). 1H NMR (400 MHz, CDCl₃) δ: 8.55–8.52 (m, 3H), 8.21–8.19 (m, 1H), 7.76–7.66 (m, 3H), 3.45–3.40 (m, 1H), 3.21–3.15 (m, 1H), 2.58 (s, 3H), 2.22–2.14 (m, 1H), 1.39–1.28 (m, 2H), 1.05 (d, J = 6.8 Hz, 3H), 0.96 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl₃) δ: 205.2, 154.6, 142.1, 138.0, 132.5, 131.4, 130.8, 128.5, 126.8, 125.2, 123.1, 121.9, 121.8, 47.3, 31.2, 29.7, 21.8, 19.7, 11.4; HRMS (ESI-TOF) m/z: C₂₀H₂₂NO (M + H)⁺ calculated for 292.1623, found 292.1628.

For (4-Methoxyphenyl)(8-methylphenanthridin-6-yl)methanone (3ag), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40:1) to afford a white solid in 88% yield (57.4 mg); mp: 154.3–154.9 °C (uncorrected). 1H NMR (400 MHz, CDCl₃) δ: 8.61–8.58 (m, 2H), 8.20–8.16 (m, 1H), 7.72–7.70 (m, 3H), 7.26 (t, J = 8 Hz, 2H), 2.51 (s, 3H), 2.43 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ: 193.5, 164.3, 157.6, 142.2, 137.8, 133.1, 133.1, 131.1, 130.3, 129.2, 128.5, 127.9, 126.6, 124.5, 123.9, 122.1, 121.9, 113.9, 55.5, 21.6; HRMS (ESI-TOF) m/z: C₂₂H₂₂NO₂ (M + H)⁺ calculated for 328.1259, found 328.1361.

For (8-Methylphenanthridin-6-yl)methanone(8-methylphenanthridin-6-yl)(p-tolyl)methanone (3ah), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (60:1) to afford a white solid in 87% yield (54.1 mg); mp: 177.2–177.6 °C (uncorrected). 1H NMR (400 MHz, CDCl₃) δ: 8.61–8.58 (m, 2H), 8.20–8.16 (m, 1H), 7.92 (t, J = 8.4 Hz, 2H), 7.75–7.70 (m, 3H), 7.26 (t, J = 8 Hz, 2H), 2.51 (s, 3H), 2.43 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ: 194.6, 157.5, 145.0, 142.3, 137.8, 133.6, 133.0, 131.0, 130.4, 129.3, 128.5, 127.9, 126.5, 124.4, 124.3, 122.1, 121.9, 21.8, 21.6; HRMS (ESI-TOF) m/z: C₂₂H₂₂NO₂ (M + H)⁺ calculated for 312.1310, found 312.1314.

For (8-Methylphenanthridin-6-yl)(phenyl)methanone (3ai), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (60:1) to afford a yellow solid in 82% yield (48.3 mg); mp: 162.1–162.8 °C (uncorrected). 1H NMR (400 MHz, CDCl₃) δ: 8.55–8.52 (m, 3H), 8.21–8.19 (m, 1H), 7.75–7.70 (m, 3H), 7.26 (t, J = 8 Hz, 2H), 2.51 (s, 3H), 2.43 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ: 194.6, 157.5, 145.0, 142.3, 137.8, 133.6, 133.0, 131.0, 130.4, 129.3, 128.5, 127.9, 126.5, 124.4, 124.3, 122.1, 121.9, 21.8, 21.6; HRMS (ESI-TOF) m/z: C₂₂H₂₂NO₂ (M + H)⁺ calculated for 298.1154, found 298.1151.
For (4-Chlorophenyl)(8-methylphenanthridin-6-yl)methanone (3ak), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50:1) to afford a brown solid in 77% yield (50.9 mg); mp: 173.3–173.8 °C (uncorrected). ^1H NMR (400 MHz, CDCl₃) δ: 8.62–8.60 (m, 2H), 8.19–8.16 (m, 1H), 8.01–7.93 (m, 2H), 7.93 (s, 1H), 7.77–7.72 (m, 3H), 7.47–7.45 (m, 2H), 2.54 (s, 3H); ^13C NMR (100 MHz, CDCl₃) δ: 193.5, 156.3, 142.2, 140.4, 138.1, 134.6, 133.2, 132.2, 131.3, 130.6, 128.9, 128.7, 128.3, 126.4, 126.4, 123.9, 122.2, 121.9, 21.7; HRMS (ESI-TOF) m/z: C₂₁H₁₅FNO (M + H)^+ calculated for 316.1059, found 316.1153.

For (4-Bromophenyl)(8-methylphenanthridin-6-yl)methanone (3al), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (50:1) to afford a yellow solid in 78% yield (58.5 mg); mp: 187.1–187.6 °C (uncorrected). ^1H NMR (400 MHz, CDCl₃) δ: 8.63–8.60 (m, 2H), 8.18–8.16 (m, 1H), 7.92 (d, J = 8.4 Hz, 3H), 7.77–7.72 (m, 3H), 7.63 (d, J = 8.4 Hz, 2H), 2.54 (s, 3H); ^13C NMR (100 MHz, CDCl₃) δ: 193.7, 156.3, 142.1, 138.1, 134.9, 133.2, 132.2, 131.8, 131.2, 130.5, 129.3, 128.6, 128.3, 126.4, 124.6, 123.8, 122.2, 121.9, 21.7; HRMS (ESI-TOF) m/z: C₂₁H₁₅BrNO (M + H)^+ calculated for 332.0764, found 332.0768.

For (8-Methylphenanthridin-6-yl)(m-tolyl)methanone (3am), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (60:1) to afford a white solid in 76% yield (46.5 mg); mp: 181.7–181.6 °C (uncorrected). ^1H NMR (400 MHz, CDCl₃) δ: 8.60–8.57 (m, 2H), 8.19 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 5.6 Hz, 2H), 7.80 (d, J = 7.6 Hz, 1H), 7.74–7.68 (m, 3H), 7.43 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 2.50 (s, 3H), 2.37 (s, 3H); ^13C NMR (100 MHz, CDCl₃) δ: 195.1, 157.4, 142.3, 138.4, 137.8, 136.1, 136.1, 134.8, 133.0, 131.0, 130.5, 128.5, 128.4, 128.2, 127.9, 126.5, 124.5, 123.9, 122.1, 121.9, 21.6, 21.3; HRMS (ESI-TOF) m/z: C₂₁H₁₅NO (M + H)^+ calculated for 312.1310, found 312.1314.

For (9-Fluorophenanthridin-6-yl)(thiophen-2-yl)methanone (3an), the title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (30:1) to afford a white solid in 76% yield (47.2 mg); mp: 207.0–207.5 °C (uncorrected). ^1H NMR (400 MHz, CDCl₃) δ: 8.71–8.68 (m, 1H), 8.59–8.57 (m, 1H), 8.36–8.29 (m, 2H), 8.04–8.02 (m, 1H), 7.82–7.78 (m, 3H), 7.67–7.62 (m, 1H), 7.20–7.18 (m, 1H); ^13C NMR (100 MHz, CDCl₃) δ: 185.4, 161.7 (d, J = 247.7 Hz, 1C), 153.7 (d, J = 4.2 Hz, 1C) 141.9, 136.8, 136.6, 130.8, 130.2 (d, J = 1.8 Hz, 1C), 129.1, 128.9, 128.0, 124.7, 124.6, 121.9, 120.7, 120.4, 112.4, 112.2; ^19F NMR (376 MHz, CDCl₃) δ: −110.6 (s, 1F); HRMS (ESI-TOF) m/z: C₁₈H₁₃FNOS (M + H)^+ calculated for 308.0467, found 308.0469.

4. Conclusions

In conclusion, a novel and efficient strategy for the photoredox-catalyzed radical acylation/cyclization of isocyanobiaryls to produce 6-acyl phenanthridines was developed. This method has broad substrate applicability and functional group tolerance. Notably, a variety of acyl radical species could be efficiently generated under neutral conditions without the aid of an external stoichiometric oxidant, which provides an alternative environmentally friendly synthetic route to access phenanthridine derivatives. Further studies on this topic are underway in our laboratory and will be reported in due course.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12111446/s1, copies of NMR spectra.

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