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## SYNTHESES OF HETEROCYCLES VIA PALLADIUM-CATALYZED C-H ACTIVATION/CYCLIZATION OF DIAZONIUM SALTS (PART III): PHENANTHRIDIN-6-(5*H*)-ONES

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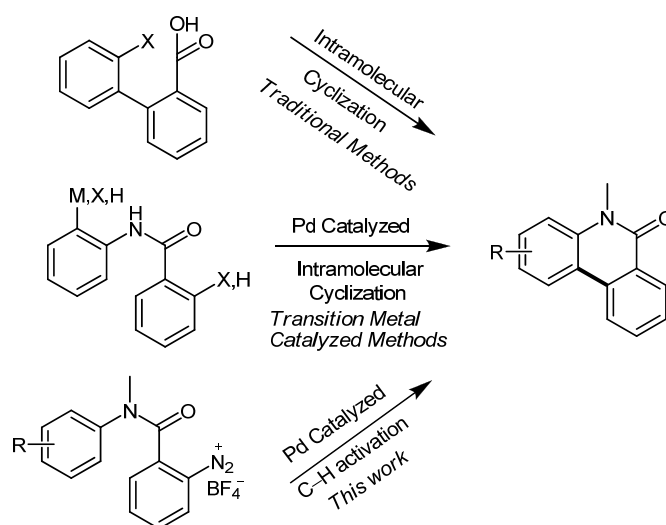
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**Abstract** – A series of phenanthridin-6-(5*H*)-ones were synthesized through a palladium-catalyzed C-H activation/cyclization strategy using diazonium salts in good yields. The best conditions included Pd(OAc)<sub>2</sub> as the catalyst, PPh<sub>3</sub> as the ligand, toluene as the solvent, K<sub>2</sub>CO<sub>3</sub> as the base and 60 °C as the optimal temperature.

Phenanthridin-6-(5*H*)-ones are important moieties in many natural compounds,<sup>1</sup> pharmaceuticals<sup>2</sup> and materials.<sup>3</sup> As a matter of fact, they have been exploited as poly ADP-ribose polymerase (PARP) inhibitors as an anticancer treatment.<sup>4</sup> Some types of reported synthetic methods are metal-catalyzed C-N formation,<sup>5</sup> amide formation,<sup>6</sup> S<sub>N</sub>Ar<sup>7</sup> intramolecular cyclization of biaryl derivatives (Scheme 1, Eq. 1) or Beckmann rearrangement of fluorenones.<sup>8</sup> The major drawbacks of these methods lie in the inconvenience of the preparation of the substrates, the uncertain reaction route and the transition metal catalyzed coupling methods from *N*-phenylbenzamide (Scheme 1, Eq. 2). Since the late 1970s, palladium chemistry has opened new routes to organic synthesis. Therefore, transition metal catalyzed directing group assisted C-H activation has been a hot research topic due to the sustainable and high efficacy of the construction of C-C bonds.<sup>9</sup> Particularly, the one-pot sequential C-H activation/ring closure method has been a popular synthetic approach to nitrogen-containing natural products and heterocycles in drug discovery. In this respect, considerable effort has been put into the synthesis phenanthridin-6-(5*H*)-ones (Scheme 1, Eq. 2). Methods based on halogen-H patterns have been reported by Ding,<sup>10</sup> Aoyama,<sup>11</sup> Harayama,<sup>12</sup> Charette<sup>13</sup> and Kumar.<sup>14</sup> The direct double oxidation of *N*-phenylbenzanilide was disclosed by Ishida.<sup>15</sup> At the same time, double halo *N*-phenylbenzanilides also can be cyclized to

phenanthridin-6-(5*H*)-ones.<sup>16</sup> Although the synthesis of phenanthridin-6(5*H*)-ones via metal-catalyzed cross-coupling based iodo compounds is very versatile, one major weakness associated with these methods is the diseconomy of the starting materials.

In this context, based on our previous work,<sup>17</sup> we envisaged that a palladium catalyzed method using diazonium salts could synthesize this kind of compound. Herein, we wish to report this sequential denitration/C-H activation/cyclization strategy to construct the phenanthridin-6(5*H*)-one skeleton from diazonium salts of *N*-phenylbenzamide.



**Scheme 1.** A = CO<sub>2</sub>H, CN, X = halogen

To commence our study, we utilized 2-(phenylcarbamoyl)benzenediazonium tetrafluoroborate as the substrate; however, the desired reaction did not occur. A literature survey revealed that the lone pair electron of the nitrogen would have a negative effect in this reaction. Next, 2-(methyl(phenyl)carbamoyl)benzenediazonium tetrafluoroborate was adopted as the substrate in model reaction. Initially, the Pd(OAc)<sub>2</sub>/K<sub>2</sub>CO<sub>3</sub>/acetonitrile system (Table 1, entry 1) was tested to achieve a mild and general procedure for the synthesis of phenanthridin-6(5*H*)-ones. However, the desired product was obtained in only 38% yield. Then, a systematic screening of reaction conditions was performed using Pd(OAc)<sub>2</sub> as the catalytic system in a model reaction of 2-(methyl(phenyl)carbamoyl)benzenediazonium tetrafluoroborate; the results are listed in Table 1. The different bases had a slight influence on this reaction (Table 1, entries 1-3), but K<sub>2</sub>CO<sub>3</sub> give the best yield. Without ligands, changes in the solvent (Table 1, entries 4-5) did not give satisfactory results. To our delight, if 0.2 equiv. PPh<sub>3</sub> was added (Table 1, entry 6), the yield was increased remarkably. Our studies subsequently showed that the nature of the reaction solvent seems to be very important for this reaction. In unpolar aromatic solvents (Table 1,

entries 6, 13-14), the cyclized product can generally be given in good yields. To our pleasure, toluene was found to be an excellent solvent in which the cyclization reaction always gave appreciable yields. Subsequently, the palladium catalysts were also screened (Table 1, entries 6, 9-12), and Pd(OAc)<sub>2</sub> was found to be a suitable catalyst of this transformation. The change in the ligand to dppp (Table 1, entry 7) or phen (Table 1, entry 8) did not provide positive results. At last, we set up the optimized reaction conditions, i.e. toluene as the solvent, a 5% molar ratio Pd(OAc)<sub>2</sub> as the catalyst, PPh<sub>3</sub> as the ligand and 1.5 equiv. K<sub>2</sub>CO<sub>3</sub> as the base at 60 °C.

**Table 1.** The optimization of the reaction condition<sup>a</sup>: **1** (R<sup>1</sup> = Me, R<sup>2</sup> = H)

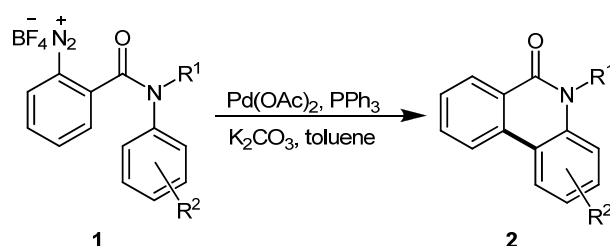
Entry	Catalyst	Ligand	Base	Solvent	Temp(°C)	Yield(%) <sup>b</sup>
1	Pd(OAc) <sub>2</sub>		K <sub>2</sub> CO <sub>3</sub>	MeCN	60	38
2	Pd(OAc) <sub>2</sub>		Na <sub>2</sub> CO <sub>3</sub>	MeCN	60	36
3	Pd(OAc) <sub>2</sub>		Cs <sub>2</sub> CO <sub>3</sub>	MeCN	60	30
4	Pd(PPh <sub>3</sub> ) <sub>4</sub>		K <sub>2</sub> CO <sub>3</sub>	toluene	60	40
5	Pd(OAc) <sub>2</sub>		K <sub>2</sub> CO <sub>3</sub>	toluene	60	18
6	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub> (0.2 equiv.)	K <sub>2</sub> CO <sub>3</sub>	toluene	60	88
7	Pd(OAc) <sub>2</sub>	dppp(0.1 equiv.)	K <sub>2</sub> CO <sub>3</sub>	toluene	60	44
8	Pd(OAc) <sub>2</sub>	phen(0.1 equiv.)	K <sub>2</sub> CO <sub>3</sub>	toluene	60	46
9	Pd(TFA) <sub>2</sub>	PPh <sub>3</sub> (0.2 equiv.)	K <sub>2</sub> CO <sub>3</sub>	toluene	60	37
10	PdCl <sub>2</sub>	PPh <sub>3</sub> (0.2 equiv.)	K <sub>2</sub> CO <sub>3</sub>	toluene	60	21
11	Pd <sub>2</sub> (dba) <sub>3</sub>	PPh <sub>3</sub> (0.2 equiv.)	K <sub>2</sub> CO <sub>3</sub>	toluene	60	5
12	PdCl <sub>2</sub> (MeCN) <sub>2</sub>	PPh <sub>3</sub> (0.2 equiv.)	K <sub>2</sub> CO <sub>3</sub>	toluene	60	18
13	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub> (0.2 equiv.)	K <sub>2</sub> CO <sub>3</sub>	benzene	60	85
14	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub> (0.2 equiv.)	K <sub>2</sub> CO <sub>3</sub>	xylene	60	88
15	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub> (0.2 equiv.)	K <sub>2</sub> CO <sub>3</sub>	cyclohexane	60	37

<sup>a</sup>The catalyst loading 5% molar ratio, base loading 150% molar ratio. <sup>b</sup>Isolated yield.

With the optimized reaction conditions in hand, we next examined the scope of Pd(OAc)<sub>2</sub> catalyzed cyclization of the corresponding diazonium salts for the synthesis of substituted phenanthridin-6(5*H*)-ones. A variety of 2-(alkyl(phenyl)carbamoyl)benzenediazonium tetrafluoroborates with diverse substituents including chloro (Table 2, entries 4, 19), bromo (entries 2-3, 18), acetyl (entries 5, 15), methoxy (entries 10, 14) and ester (entries 6-7, 16-17) groups were subjected to this protocol to give the corresponding phenanthridin-6(5*H*)-ones in good to excellent yields. The bromo and chloro moieties could be functionalized to boric acid or stannane easily, so our method can provide a preparation route for halo substituted phenanthridin-6(5*H*)-ones that other transition metal catalyzed methods including newly published cannot. As for R<sub>1</sub>, the benzyl group can be removed very easily through hydrogenolysis and acidic removal. The electronic nature of R<sub>2</sub>, such as electron-neutral (Table 2, entries

1, 8-9, 12-13), electron-rich (Table 2, entries 10, 14) and electron-deficient (Table 2, entries 6-7, 10, 14), did not have a considerable effect on this transformation. Thus, all the products in our reactions listed in Table 2 were easily characterized on the basis of physical and spectral data and also by comparison with authentic samples. All the substrates used in this paper can be prepared by simple chemical operations with ease.

**Table 2.** Pd(OAc)<sub>2</sub> catalysed the synthesis of substituted phenanthridin-6(5*H*)-ones from corresponding diazonium tetrafluoroborate<sup>a</sup>



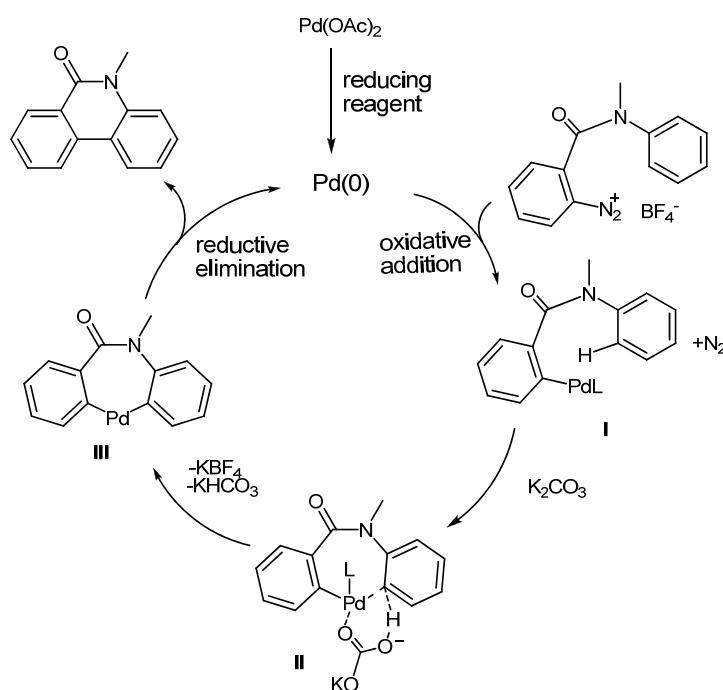
Entry	1	2	Isolated yield(%) <sup>a</sup>
1	R <sup>1</sup> =Me, R <sup>2</sup> =H	R <sup>1</sup> =Me, R <sup>2</sup> =H	88
2	R <sup>1</sup> =Me, R <sup>2</sup> =2-Br	R <sup>1</sup> =Me, R <sup>2</sup> =4-Br	61
3	R <sup>1</sup> =Me, R <sup>2</sup> =4-Br	R <sup>1</sup> =Me, R <sup>2</sup> =2-Br	86
4	R <sup>1</sup> =Me, R <sup>2</sup> =4-Cl	R <sup>1</sup> =Me, R <sup>2</sup> =2-Cl	82
5	R <sup>1</sup> =Me, R <sup>2</sup> =4-Ac	R <sup>1</sup> =Me, R <sup>2</sup> =2-Ac	63
6	R <sup>1</sup> =Me, R <sup>2</sup> =4-CO <sub>2</sub> Me	R <sup>1</sup> =Me, R <sup>2</sup> =2-CO <sub>2</sub> Me	62
7	R <sup>1</sup> =Me, R <sup>2</sup> =2-CO <sub>2</sub> Me	R <sup>1</sup> =Me, R <sup>2</sup> =4-CO <sub>2</sub> Me	54
8	R <sup>1</sup> =Me, R <sup>2</sup> =4-Me	R <sup>1</sup> =Me, R <sup>2</sup> =2-Me	60
9	R <sup>1</sup> =Me, R <sup>2</sup> =2-Me	R <sup>1</sup> =Me, R <sup>2</sup> =4-Me	52
10	R <sup>1</sup> =Me, R <sup>2</sup> =4-OMe	R <sup>1</sup> =Me, R <sup>2</sup> =2-OMe	53
11	R <sup>1</sup> =Me, R <sup>2</sup> =2-F	R <sup>1</sup> =Me, R <sup>2</sup> =4-F	77
12	R <sup>1</sup> =Bn, R <sup>2</sup> =H	R <sup>1</sup> =Bn, R <sup>2</sup> =H	65
13	R <sup>1</sup> =Bn, R <sup>2</sup> =4-Me	R <sup>1</sup> =Bn, R <sup>2</sup> =2-Me	65
14	R <sup>1</sup> =Bn, R <sup>2</sup> =4-OMe	R <sup>1</sup> =Bn, R <sup>2</sup> =2-OMe	51
15	R <sup>1</sup> =Bn, R <sup>2</sup> =4-Ac	R <sup>1</sup> =Bn, R <sup>2</sup> =2-Ac	52
16	R <sup>1</sup> =Bn, R <sup>2</sup> =4-Br	R <sup>1</sup> =Bn, R <sup>2</sup> =2-Br	72
17	R <sup>1</sup> =Bn, R <sup>2</sup> =4-Cl	R <sup>1</sup> =Bn, R <sup>2</sup> =2-Cl	69

<sup>a</sup>Isolated yield.

A plausible mechanism of this intramolecular base assisting C-H activation process is proposed (Scheme 2). Pd (II) was first reduced to Pd (0) by a reducing reagent. Then, oxidative addition to the diazonium salt gave intermediate **I**. Next, the C-H bond was activated at the presence of Pd complex and finally was

broken by potassium carbonate. After the salts was charged out, a palladium metalocycle complex **III** was formed. Finally, reductive elimination of **III** afforded the desired product and regenerated Pd (0) for next circle.

In conclusion, an efficient and practical Pd(OAc)<sub>2</sub> catalytic ring-closure method of the diazonium salts of *N*-phenylbenzamide was developed. This method is bestowed with several unique merits, such as high conversions and yields, simplicity of operation, cost-effectiveness and functional group tolerance. Thus, we believe that this novel methodology will be a practical alternative to the existing procedures to cater to the needs of academia as well as industry. Further work is in progress to broaden the scope of this methodology.



**Scheme 2.** A plausible mechanism of phenanthridin-6(5*H*)-ones formation

## EXPERIMENTAL

General procedure for the preparation of the phenanthridin-6(5*H*)-ones from diazonium salts of *N*-phenylbenzamide: To a stirred suspension of diazonium salts of *N*-phenylbenzamide (1 mmol) in toluene (15 mL), a catalytic Pd(OAc)<sub>2</sub> (11.2 mg, 0.05 mmol), PPh<sub>3</sub> (52.5 mg, 0.2 mmol) and K<sub>2</sub>CO<sub>3</sub> (210 mg, 1.5 mmol) were added. The resulting mixture was maintained to 60 °C 6-12 h. The precipitate of metal was filtered, the filtrate was evaporated under vacuum and the crude product was purified by column chromatography on silica gel eluting with a mixture of petroleum ether and EtOAc to give phenanthridin-6(5*H*)-ones (Table 2). The <sup>1</sup>H-NMR (500 MHz) and <sup>13</sup>C-NMR (125 MHz) data were recorded in CDCl<sub>3</sub> solution with Bruker-NMR DRX 500 spectrometers if not noted otherwise. The chemical shifts are measured relative to TMS (δ = 0) or chloroform (δ = 7.26) and the coupling *J* is

expressed in Hertz. IR spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR and are reported in terms of frequency of absorption ( $\text{cm}^{-1}$ ).

5-Methylphenanthridin-6(5*H*)-one:

Mp 111-112 °C (lit.,<sup>12a</sup> 109-110.5 °C). <sup>1</sup>H NMR:  $\delta$  = 8.49 (d, 1 H,  $J$  = 8.0), 8.13 (d, 2 H,  $J$  = 8.0), 7.67 (t, 1 H,  $J$  = 7.5), 7.52 (t, 1 H,  $J$  = 7.5), 7.45 (t, 1 H,  $J$  = 7.7), 7.28 (d, 1 H,  $J$  = 8.4), 7.22 (t, 1 H,  $J$  = 7.6), 3.7 (s, 3 H). <sup>13</sup>C NMR:  $\delta$  = 161.5, 137.9, 133.4, 132.3, 129.4, 128.7, 127.8, 125.4, 123.1, 122.3, 121.5, 119.1, 114.9, 29.9. IR ( $\text{cm}^{-1}$ ): 3072, 3031, 2996, 2950, 1906, 1659, 1606, 1510, 850, 743, 719.

4-Bromo-5-methylphenanthridin-6(5*H*)-one:

Mp 180-181 °C. <sup>1</sup>H NMR:  $\delta$  = 8.54 (dd, 1 H,  $J_1$  = 1.1,  $J_2$  = 8.0), 8.31 (d, 1 H,  $J$  = 2.3), 8.15 (d, 1 H,  $J$  = 8.2), 7.78 (td, 1 H,  $J_1$  = 1.5,  $J_2$  = 7.7), 7.60 – 7.65 (m, 2 H), 7.26 (d, 1 H,  $J$  = 8.9), 3.78 (s, 3 H). <sup>13</sup>C NMR:  $\delta$  = 161.2, 137.0, 132.6, 132.2, 132.1, 129.0, 128.6, 126.0, 125.7, 121.7, 121.0, 116.7, 115.6, 30.1. IR ( $\text{cm}^{-1}$ ): 3113, 3079, 2995, 2946, 1962, 1646, 1609, 1580, 768, 716.

2-Bromo-5-methylphenanthridin-6(5*H*)-one:

Mp 195-196 °C. <sup>1</sup>H NMR:  $\delta$  = 8.53 (d, 1 H,  $J$  = 8.0), 8.30 (s, 1 H), 8.14 (d, 1 H,  $J$  = 8.2), 7.77 (t, 1 H,  $J$  = 7.2), 7.60 - 7.64 (m, 2 H), 7.25 (d, 1 H,  $J$  = 8.9), 3.77 (s, 3 H). <sup>13</sup>C NMR:  $\delta$  = 161.2, 137.0, 132.6, 132.2, 132.1, 129.0, 128.6, 125.9, 125.7, 121.6, 121.0, 116.7, 115.6, 30.0. IR ( $\text{cm}^{-1}$ ): 3113, 3079, 2995, 2937, 1961, 1645, 1609, 1580, 767, 715.

2-Chloro-5-methylphenanthridin-6(5*H*)-one:

Mp 190-191 °C (lit.,<sup>18</sup> 192 °C). <sup>1</sup>H NMR:  $\delta$  = 8.55 (dd, 1 H,  $J_1$  = 1.2,  $J_2$  = 8.0), 8.16 - 8.18 (m, 2 H), 7.78 (td, 1 H,  $J_1$  = 1.5,  $J_2$  = 7.6), 7.63 (td, 1 H,  $J_1$  = 1.0,  $J_2$  = 8.0), 7.49 (dd, 1 H,  $J_1$  = 2.4,  $J_2$  = 8.8), 7.32 (t, 1 H,  $J$  = 8.0), 3.80 (s, 3 H). <sup>13</sup>C NMR:  $\delta$  = 161.2, 136.6, 132.6, 132.3, 129.3, 129.0, 128.6, 128.2, 125.8, 123.0, 121.7, 120.6, 116.4, 30.1. IR ( $\text{cm}^{-1}$ ): 3083, 2973, 2938, 1610, 1583, 1490, 813, 768.

2-Acetyl-5-methylphenanthridin-6(5*H*)-one:

Mp 192-193 °C. <sup>1</sup>H NMR:  $\delta$  = 8.88 (s, 1 H), 8.55 (d, 1 H,  $J$  = 7.9), 8.36 (d, 1 H,  $J$  = 8.0), 8.12 (d, 1 H,  $J$  = 8.6), 7.82 (t, 1 H,  $J$  = 7.6), 7.65 (t, 1 H,  $J$  = 7.4), 7.45 (d, 1 H,  $J$  = 8.7), 3.84 (s, 3 H), 2.73 (s, 3 H). <sup>13</sup>C NMR:  $\delta$  = 196.7, 161.7, 141.3, 133.1, 132.9, 131.2, 129.5, 129.0, 128.6, 125.6, 123.9, 121.8, 119.0, 115.0, 30.3, 26.6. IR ( $\text{cm}^{-1}$ ): 3079, 2998, 2919, 1926, 1733, 1675, 1650, 1609, 1495, 830, 729, 708.

2-Methoxycarbonyl-5-methylphenanthridin-6(5*H*)-one:

Mp 238-239 °C. <sup>1</sup>H NMR:  $\delta$  = 8.97 (d, 1 H,  $J$  = 1.8), 8.56 (dd, 1 H,  $J_1$  = 1.0,  $J_2$  = 8.0), 8.38 (d, 1 H,  $J$  = 8.2), 8.20 (dd, 1 H,  $J_1$  = 1.9,  $J_2$  = 8.8), 7.83 (t, 1 H,  $J$  = 7.7), 7.65 (t, 1 H,  $J$  = 7.6), 7.45 (t, 1 H,  $J$  = 8.8 Hz), 4.03 (s, 3H), 3.85 (s, 3H) ppm. <sup>13</sup>C NMR:  $\delta$  = 166.6, 161.7, 141.2, 133.1, 132.8, 130.4, 128.9, 128.5, 125.5, 124.1, 121.9, 119.0, 115.0, 52.3, 30.2. IR ( $\text{cm}^{-1}$ ): 3094, 3038, 2999, 2950, 1715, 1650, 1611, 1583, 1493, 1310, 1260, 762, 722.

4-Methoxycarbonylphenanthridin-6(5*H*)-one:

Mp 195.5-196 °C. <sup>1</sup>H NMR: δ = 8.57 (dd, 1 H, *J*<sub>1</sub> = 1.1, *J*<sub>2</sub> = 8.0), 8.41 (dd, 1 H, *J*<sub>1</sub> = 1.3, *J*<sub>2</sub> = 8.0), 8.28 (d, 1 H, *J* = 8.2), 7.81 (td, 1 H, *J*<sub>1</sub> = 1.4, *J*<sub>2</sub> = 7.3), 7.77 (dd, 1 H, *J*<sub>1</sub> = 1.5, *J*<sub>2</sub> = 7.5), 7.65 (t, 1 H, *J* = 7.5), 7.37 (t, 1 H, *J* = 7.8 Hz), 4.02 (s, 3H), 3.67 (s, 3H). <sup>13</sup>C NMR: δ = 169.3, 162.7, 137.6, 133.1, 132.8, 131.0, 128.7, 128.6, 125.8, 125.5, 122.4, 121.9, 121.8, 121.3, 52.8, 36.4. IR (cm<sup>-1</sup>): 3067, 3000, 2950, 2843, 1712, 1653, 1603, 1583, 1501, 1328, 1255, 759, 720.

2-Methyl-5-methylphenanthridin-6(5*H*)-one:

Mp 139-140 °C (lit.,<sup>18</sup> 136-137 °C). <sup>1</sup>H NMR: δ = 8.58 (dd, 1 H, *J*<sub>1</sub> = 1.1, *J*<sub>2</sub> = 8.0), 8.27 (d, 1 H, *J* = 8.0), 8.07 (s, 1 H), 7.74 – 7.78 (m, 1 H), 7.58 – 7.61 (m, 1 H), 7.37 (dd, 1 H, *J*<sub>1</sub> = 1.4, *J*<sub>2</sub> = 8.5), 7.31 (d, 1 H, *J* = 8.5), 3.81 (s, 3 H), 2.51 (s, 3 H). <sup>13</sup>C NMR: δ = 161.5, 136.0, 133.5, 132.2, 131.8, 130.5, 128.9, 127.8, 125.7, 125.7, 123.3, 121.5, 119.1, 114.9, 29.9, 21.0. IR (cm<sup>-1</sup>): 3030, 2970, 2941, 2913, 2892, 2855, 1936, 1634, 1578, 1493, 770, 720.

4-Methyl-5-methylphenanthridin-6(5*H*)-one:

<sup>1</sup>H NMR: δ = 8.54 (dd, 1 H, *J* = *J*<sub>1</sub> = 1.1, *J*<sub>2</sub> = 8.0), 8.25 (d, 1 H, *J* = 8.2), 8.14 (d, 1 H, *J* = 7.8), 7.74 – 7.78 (m, 1 H), 7.59 (t, 1 H, *J* = 7.5), 7.35 (d, 1 H, *J* = 7.1 Hz), 7.25 (t, 1 H, *J* = 7.7 Hz), 3.84 (s, 3H), 2.70 (s, 3H) ppm. <sup>13</sup>C NMR: δ = 164.2, 139.6, 134.0, 133.8, 132.5, 128.5, 127.9, 126.2, 125.5, 122.9, 121.9, 121.4, 121.1, 38.4, 23.6. IR (cm<sup>-1</sup>): 3070, 3029, 2966, 2930, 1646, 1608, 1583, 1500, 797, 754, 693.

2-Methoxy-5-methylphenanthridin-6(5*H*)-one:

Mp 161-162 °C. <sup>1</sup>H NMR: δ = 8.58 (dd, 1 H, *J*<sub>1</sub> = 1.1, *J*<sub>2</sub> = 8.1), 8.21 (d, 1 H, *J* = 8.2), 7.73 – 7.78 (m, 2 H), 7.60 – 7.63 (m, 1 H), 7.34 (d, 1 H, *J* = 9.2), 7.15 (dd, 1 H, *J*<sub>1</sub> = 2.8, *J*<sub>2</sub> = 9.1), 3.96 (s, 3 H), 3.81 (s, 3 H). <sup>13</sup>C NMR: δ = 161.1, 155.1, 133.2, 132.4, 132.2, 129.0, 128.1, 125.9, 121.6, 120.2, 116.5, 116.1, 107.1, 55.7, 30.0. IR (cm<sup>-1</sup>): 3068, 2993, 2960, 2932, 2834, 1960, 1638, 1578, 1494, 1037, 772, 719.

4-Fluoro-5-methylphenanthridin-6(5*H*)-one:

Mp 122-123 °C. <sup>1</sup>H NMR: δ = 8.57 (d, 1 H, *J* = 7.8), 8.25 (d, 1 H, *J* = 8.2), 8.08 (d, 1 H, *J* = 6.7), 7.79 (t, 1 H, *J* = 7.23), 7.64 (t, 1 H, *J* = 7.5), 7.25-7.31 (m, 2 H), 4.01(d, 3H, *J* = 9.4) ppm. <sup>13</sup>C NMR: δ = 162.2, 152.3, 150.3, 133.0, 132.6, 129.0, 128.6, 127.4, 125.7, 122.8, 122.7, 122.4, 122.0, 119.03, 119.00, 117.2, 117.0, 34.4, 34.3. IR (cm<sup>-1</sup>): 3046, 3012, 2955, 1968, 1653, 1611, 1583, 1504, 753, 688.

5-Benzylphenanthridin-6(5*H*)-one:

Mp 100-101 °C. (lit.,<sup>3</sup> 112-113 °C). <sup>1</sup>H NMR: δ = 8.68 (d, 1 H, *J* = 7.8), 8.34 (t, 2 H, *J* = 8.4), 7.84 (t, 1 H, *J* = 7.2), 7.67 (t, 1 H, *J* = 7.4), 7.26 – 7.45 (m, 8 H), 5.7 (s, 2 H). <sup>13</sup>C NMR: δ = 162.0, 137.4, 136.6, 133.9, 132.8, 129.6, 129.2, 128.8, 128.1, 127.2, 126.6, 125.5, 123.3, 122.6, 121.7, 119.6, 116.1, 46.5. IR (cm<sup>-1</sup>): 3065, 3028, 1637, 1604, 1581, 1489, 759, 728, 693.

2-Methyl-5-benzylphenanthridin-6(5*H*)-one:

Mp 166-167 °C. <sup>1</sup>H NMR: δ = 8.67 (dd, 1 H, *J*<sub>1</sub> = 1.0, *J*<sub>2</sub> = 8.0), 8.35 (d, 1 H, *J* = 8.2), 8.12 (s, 1 H), 7.83

(d, 1 H,  $J = 7.7$ ), 7.65 (d, 1 H,  $J = 7.6$ ), 7.24 – 7.35 (m, 7 H), 5.70 (s, 2 H) 2.48 (s, 3H) ppm.  $^{13}\text{C}$  NMR:  $\delta = 161.8, 136.7, 135.2, 133.8, 132.6, 132.0, 130.6, 129.2, 128.8, 127.9, 127.1, 126.6, 125.5, 123.4, 121.7, 119.4, 116.0, 46.4, 21.0$ . IR ( $\text{cm}^{-1}$ ): 3063, 3035, 2952, 2916, 2854, 1970, 1653, 1577, 1499, 770, 749, 709, 689.

2-Methoxy-5-benzylphenanthridin-6(5H)-one:

Mp 169-170 °C.  $^1\text{H}$  NMR:  $\delta = 8.68$  (d, 1 H,  $J = 8.0$ ), 8.28 (d, 1 H,  $J = 8.2$ ), 7.78 – 7.84 (m, 2 H), 7.67 (t, 1 H,  $J = 7.3$ ), 7.26 – 7.35 (m, 6 H), 7.03 (dd, 1 H,  $J_1 = 2.7, J_2 = 9.2$ ), 5.69 (s, 2 H), 3.93 (s, 3 H) ppm.  $^{13}\text{C}$  NMR:  $\delta = 161.5, 155.1, 136.7, 133.5, 132.6, 131.6, 129.3, 128.8, 128.2, 127.2, 126.5, 125.8, 121.8, 120.5, 117.2, 116.5, 107.2, 55.7, 46.6$ . IR ( $\text{cm}^{-1}$ ): 3042, 3002, 2957, 2937, 2834, 1972, 1634, 1578, 1499, 1301, 1241, 757, 712, 689.

2-Acetyl-5-benzylphenanthridin-6(5H)-one:

Mp 231-232 °C.  $^1\text{H}$  NMR:  $\delta = 8.95$  (s, 1 H), 8.66 (d, 1 H,  $J = 7.4$ ), 8.44 (d, 1 H,  $J = 7.7$ ), 7.99 (d, 1 H,  $J = 8.2$ ), 7.89 (t, 1 H,  $J = 6.8$ ), 7.71 (t, 1 H,  $J = 6.8$ ), 7.30 – 7.40 (m, 6 H), 5.72 (s, 2 H), 2.69 (s, 3H).  $^{13}\text{C}$  NMR:  $\delta = 196.6, 162.0, 140.7, 136.0, 133.5, 133.2, 131.3, 129.5, 129.3, 129.0, 128.8, 127.5, 126.5, 125.5, 123.9, 122.0, 119.4, 116.0, 46.7, 26.5$ . IR ( $\text{cm}^{-1}$ ): 3062, 3025, 2997, 2957, 1677, 1650, 1606, 1577, 1498, 757, 712, 690.

2-Bromo-5-benzylphenanthridin-6(5H)-one:

Mp 171-172 °C.  $^1\text{H}$  NMR:  $\delta = 8.66$  (d, 1 H,  $J_1 = 8.0$ ), 8.40 (s, 1 H), 8.25 (s, 1 H,  $J = 8.1$ ), 7.85 (t, 1 H,  $J = 7.3$ ), 7.70 (t, 1 H,  $J = 7.6$ ), 7.49 (d, 1 H,  $J = 8.8$ ), 7.27 – 7.36 (m, 5 H), 7.20 (d, 1 H,  $J = 9.0$ ), 5.67 (s, 2 H).  $^{13}\text{C}$  NMR:  $\delta = 161.6, 136.3, 136.2, 133.0, 132.6, 132.2, 129.3, 128.9, 128.7, 127.4, 126.1, 125.6, 121.8, 121.4, 117.7, 115.8, 46.6$ . IR ( $\text{cm}^{-1}$ ): 3033, 1641, 1577, 1490, 864, 748, 711.

2-Chloro-5-benzylphenanthridin-6(5H)-one:

Mp 171-173 °C (lit.,<sup>19</sup> 167-168 °C).  $^1\text{H}$  NMR:  $\delta = 8.66$  (d, 1 H,  $J = 7.9$ ), 8.25 – 8.26 (m, 2 H), 7.85 (t, 1 H,  $J = 7.7$ ), 7.70 (d, 1 H,  $J = 7.4$ ), 7.25 – 7.37 (m, 7 H), 5.68 (s, 2 H).  $^{13}\text{C}$  NMR:  $\delta = 161.6, 136.2, 135.9, 133.0, 132.7, 129.4, 128.9, 128.8, 128.3, 127.4, 126.5, 125.6, 123.1, 121.8, 120.9, 117.4, 46.6$ . IR ( $\text{cm}^{-1}$ ): 3064, 3037, 2955, 1971, 1640, 1605, 1578, 1492, 768, 747, 711, 692.

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