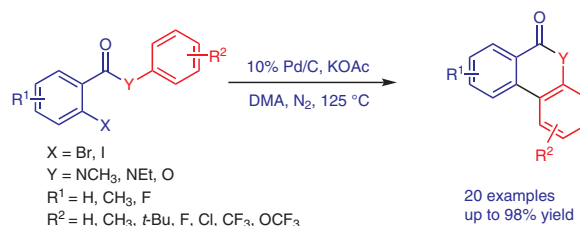


Pd/C-Catalyzed Intramolecular C–H Arylation for the Synthesis of Phenanthridinones and Dibenzo- α -pyrones

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Abstract Pd/C was found to be an efficient and convenient metal catalyst for intramolecular C–H arylation reactions in the synthesis of phenanthridinones and dibenzo- α -pyrones. A variety of phenanthridinones and dibenzo- α -pyrones were synthesized under the highly active catalytic system of Pd/C-KOAc-DMA in moderate to excellent yields. The high catalytic activity, high recyclability, low costs, and ease of removal of Pd/C, combined with its commercial availability, render this protocol attractive for both synthetic and industrial applications.

Key words Pd/C catalysis, intramolecular reactions, C–H arylation, phenanthridinones, dibenzo- α -pyrones, recyclability

Phenanthridinones¹ and dibenzo- α -pyrones² are important classes of molecules in natural products because of their biological and pharmaceutical activities. For example (Figure 1), 5-methyl-8*H*-benzo[*h*]chromeno[2,3-*b*][1,6]naphthyridine-6(5*H*),8-dione (**A**) is a novel derivative of a chromeno[2,3-*b*]pyridine fused quinolinone moiety, which possess significant biological activity.³ The fluorescent dye (**B**) is a polymerizable anthrapyridone dye containing an acryloyl-group, it can copolymerize with methyl methacrylate and 4-chloromethyl styrene, providing fluorescent nanoparticles with reactive chloromethyl groups (Figure 1).⁴ Arnottion I (**C**) and WS-5995A (**D**) are natural products and display important biological activities such as antitumor, antibacterial and antivirus action.⁵

Common synthetic methods used for the construction of phenanthridinones are homolytic aromatic substitution and palladium-catalyzed direct C–H activation. In 2005, Fagnou et al. reported the intramolecular and intermolecular direct arylation reactions of aryl iodides and bromides for the synthesis of 6*H*-benzo[*c*]chromenes and 5-methylphenanthridin-6(5*H*)-one by using Pearlman's catalyst

(Pd(OH)₂/C/KOAc/DMA/130 °C).⁶ In 2008, Itami et al. first reported the *t*-BuOK mediated homolytic aromatic substitution of electron-deficient heteroarenes with aryl halides.⁷ After these reports, several methodologies have emerged that demonstrated different N/O-based ligand promoted biaryl synthesis methods, which proceed through homolytic aromatic substitution mechanisms.⁸ There are also many methodologies for the synthesis of dibenzo- α -pyranones⁹ and the strategies mainly focus on palladium-catalyzed reactions. For example, the Suzuki–Miyaura cross-coupling of *o*-bromoarylcarboxylates and *o*-hydroxyarylboronic acids,¹⁰ the Pd-catalyzed CO insertion into 2-arylphenols¹¹ and 10-hydroxy-10,9-boroxarophenanthrenes,¹² and the new [N,*P*]-pyrrole PdCl₂ complexes catalyzed the formation of dibenzo- α -pyrones via phenyl 2-iodobenzoates.¹³

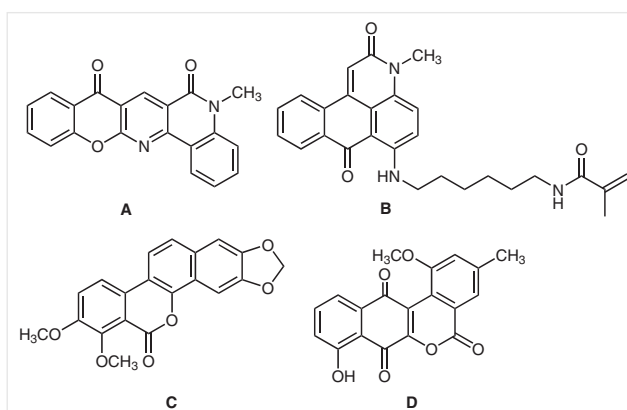


Figure 1 Some useful phenanthridinone and dibenzo- α -pyrone derivatives

In recent years, palladium-catalyzed direct C–H bond activation (sp²-C and sp³-C),¹⁴ particularly the heterogeneous palladium-catalyzed C–H bond activation,¹⁵ has drawn considerable attention because of their convenience and efficiency both on laboratory and industrial scales.

Among palladium catalysts, Pd/C is one of the most commonly used catalysts in organic synthesis because of its large surface area, good pore structure, good load performance and reduction property.¹⁶ It is also attractive for industrial applications because of its high catalytic activity, low costs, ease of removal and commercial availability.¹⁷ In a continuation of our ongoing efforts to assemble these heterocycles,¹⁸ here we report two efficient and convenient Pd/C catalyzed intramolecular C–H arylation reactions for the synthesis of phenanthridinones and dibenzo- α -pyrones, which might be applicable in industrial areas.

Initially, 2-iodo-*N*-methyl-*N*-phenylbenzamide **1a** was selected as the model substrate to identify and optimize the reaction parameters including reaction temperature, base, and solvent. When the reaction was carried out with 10% Pd/C (10% wt% of **1a**, 10 mg), 2-iodo-*N*-methyl-*N*-phenylbenzamide **1a** (0.3 mmol) and KOAc (0.6 mmol) in toluene (2.0 mL) at 130 °C under N₂ atmosphere for 24 h, the desired product 5-methylphenanthridin-6(5*H*)-one **1b** could be isolated in 56% yield (Table 1, entry 1). The reaction was investigated in other solvents (DMSO, DMF, dioxane and DMA) and DMA was found to be the best choice (entries 2–5). The reaction at lower temperature (120 °C) reduced the reaction yields and 125 °C was the optimal temperature (entries 6 and 7). Other economical bases such as K₂CO₃ were also used and the yield was clearly reduced (entry 8). From the experiments we can conclude that both the 10% Pd/C catalyst and the base are important for the reaction (entries 9 and 10). When we reduced the amount of 10% Pd/C, the product was obtained in lower yield (entry 11). We also bought several Pd/C sources from different compa-

nies and the results did not change significantly (see the Supporting Information for experimental data). Table 1, entry 6 summarizes the best reaction conditions.

Table 1 Optimization of the Reaction Conditions^a

Entry	Base	Solvent	T (°C)	Yield (%) ^b
1	KOAc	toluene	130	56
2	KOAc	DMSO	130	75
3	KOAc	DMF	130	82
4	KOAc	dioxane	130	49
5	KOAc	DMA	130	98
6	KOAc	DMA	125	98
7	KOAc	DMA	120	96
8	K ₂ CO ₃	DMA	125	80
9	–	DMA	125	0 ^c
10	KOAc	DMA	125	0 ^d
11	KOAc	DMA	125	89 ^e

^a Reaction conditions: 10% Pd/C (10% wt% of **1a**, 10 mg), 2-iodo-*N*-methyl-*N*-phenylbenzamide **1a** (0.3 mmol), base (0.6 mmol), solvent (2.0 mL) under N₂ atmosphere for 24 h.

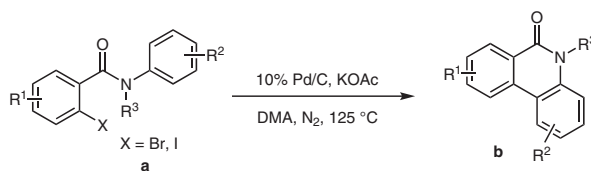
^b Isolated yield after flash chromatography based on **1a**.

^c No base was used.

^d No 10% Pd/C was used.

^e 10% Pd/C (5% wt% of **1a**) was used.

Table 2 Optimization of the Reaction Conditions^a



Entry	A	b	Yield (%) ^b
1			98
2			85

Table 2 (continued)

Entry	A	b	Yield (%) ^b
3	 3a	 3b+3b'	90 ^c
4	 4a	 4b	93
5	 5a	 5b	91
6	 6a	 6b	99
7	 7a	 7b	96
8	 8a	 8b	56
9	 9a	 9b	90

Table 2 (continued)

Entry	A	b	Yield (%) ^b
10			90
11			96
12			97
13		1b	76
14		4b	73
15		1b	0

^a Reaction conditions: 10% Pd/C (10% wt% of **a**), 2-halo-*N*-methyl-*N*-phenylbenzamides **a** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N₂ atmosphere for 24 h.

^b Isolated yield after flash chromatography based on **a**.

^c A mixture of two isomers was obtained, and the isomeric ratio based on ¹H NMR analysis was ca. 1:1.

With the optimized reaction conditions in hand, the scope of the reaction with respect to substrates was further investigated (Table 2). The substrates of 2-halo-*N*-methyl-*N*-phenylbenzamides **a** could generate the desired products **b** in moderate to excellent yields (entries 1–15). When the group R² was a mono-substituted electron-donating group (CH₃ and *t*-Bu) and electron-withdrawing group substituted (F, Cl, and OCF₃), the products were obtained in excellent yield (entries 1–7). When *N*-(2,4-dichlorophenyl)-2-iodo-*N*-methylbenzamide **8a** was used, the desired product **8b** was obtained only in 56% yield (entry 8). The reaction of *N*-ethyl-2-iodo-*N*-phenylbenzamide **9a** was also investigated

and excellent yield was achieved (entry 9). When the group R¹ of 2-halo-*N*-methyl-*N*-phenylbenzamides **a** was an electron-donating group (CH₃) and electron-withdrawing group (F), the corresponding products were also isolated in excellent yields (entries 10–12). 2-Bromo-*N*-methyl-*N*-phenylbenzamide **13a** and 2-bromo-*N*-methyl-*N*-(*p*-tolyl)benzamide **14a** were used to repeat the reaction, but only moderate yields were obtained (entries 13 and 14). When 2-chloro-*N*-methyl-*N*-phenylbenzamide **15a** was used, the reaction did not proceed (entry 15). Then the scope of Pd/C catalyzed cross-coupling reaction for the synthesis of dibenzo- α -pyrones was also investigated. The

substrates of phenyl 2-iodobenzoates **c** could react well under the reaction conditions, and generated the corresponding products **d** in moderate yields (**1d–5d**).

Table 3 Scope of the Pd/C-Catalyzed Cross-Coupling Reaction for the Synthesis of Dibenzo- α -pyrones^a

Entry	c	d	Yield (%) ^b
1			62
2			59
3			60
4			64
5			51

^a Reaction conditions: 10% Pd/C (20% wt% of **c**), phenyl 2-iodobenzoates **c** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N₂ atmosphere for 24 h.

^b Isolated yield after flash chromatography based on **c**.

Table 4 Pd/C Recycling Experiments for the Synthesis of 5-Methylphenanthridin-6(5*H*)-one^a

Cycle	1	2	3	4
Yield (%) ^b	98	98	97	95

^a Reaction conditions: 10% Pd/C (10% wt% of **1a**), 2-halo-*N*-methyl-*N*-phenylbenzamide **1a** (5 mmol), KOAc (10 mmol) in DMA (10 mL) at 125 °C under N₂ atmosphere for 24 h.

^b Isolated yield after flash chromatography based on **1a**.

From an economic and industrial point of view, the recyclability of the Pd/C catalyst was studied. Taking advantage of the insolubility of Pd/C in H₂O and EtOAc, the simple operations of filtration and washing were sufficient to recover the catalyst. The results of the recycling experiment are shown in Table 4. The catalyst could be reused under the same reaction conditions after separation and washing with water. Notably, the Pd/C catalyst remained highly catalytically active after being reused four times. The coupling reaction at the fourth run gave the desired product **1b** in 95% yield.

In summary, we have developed two Pd/C catalyzed intramolecular C–H arylation reactions for the synthesis of phenanthridinones and dibenzo- α -pyrones. The reactions exhibit some functional group tolerance and allows for the preparation of a number of phenanthridinones and dibenzo- α -pyrones in moderate to excellent yields. The high catalytic activity, high recyclability, low costs, ease of removal, and commercial availability of Pd/C render this protocol attractive for both synthetic and industrial applications.

All reagents and solvents were pure analytical grade materials purchased from commercial sources and were used without further purification, if not stated otherwise. All melting points are uncorrected. All starting substrates were prepared according to reported procedures. NMR spectra were recorded in CDCl₃ with an Agilent 400 MHz instrument with TMS as internal standard. High-resolution mass spectra (HRMS) were obtained with a G2-X5 Q-TOF Premier (ESI). TLC was carried out with 0.2 mm thick silica gel plates (GF254). Visualization was accomplished under UV light. Columns for chromatography were hand packed with silica gel (200–300 mesh). All reactions were carried out in an over-dried Schlenk tube equipped with a magnetic stir bar.

Synthesis of Phenanthridinones; General Procedure

An oven-dried Schlenk tube equipped with a Teflon valve was charged with a magnetic stir bar, 10% Pd/C (10 wt% of **a**), 2-halo-*N*-methyl-*N*-phenylbenzamide **a** (0.3 mmol) and KOAc (0.6 mmol). The tube was placed under vacuum for 20 min and backfilled with N₂. Then DMA (2.0 mL) was added through a syringe. The reaction mixture was stirred at 125 °C for 24 h. The reaction was monitored by TLC. When 2-halo-*N*-methyl-*N*-phenylbenzamide **a** was consumed completely, the reaction was stopped and cooled to r.t., EtOAc (40 mL) was added and the mixture was washed with brine (3 × 20 mL). The

organic phase was dried over Na_2SO_4 and concentrated. The residue was purified directly by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 v/v) to give the pure products **b**.

Synthesis of Dibenzo- α -pyrones; General Procedure

An oven-dried Schlenk tube equipped with a Teflon valve was charged with a magnetic stir bar, 10% Pd/C (20 wt% of **c**), phenyl 2-iodobenzoates **c** (0.3 mmol) and KOAc (0.6 mmol). The tube was placed under vacuum for 20 min and backfilled with N_2 . Then DMA (2.0 mL) was added through a syringe. The reaction mixture was stirred at 125 °C for 24 h. The reaction was monitored by TLC. When phenyl 2-iodobenzoates **c** was consumed completely, the reaction was stopped and cooled to r.t., EtOAc (40 mL) was added and the mixture was washed with brine (3×20 mL). The organic phase was dried over Na_2SO_4 and concentrated. The residue was purified directly by column chromatography on silica gel (petroleum ether/Et $_3$ N = 20:1 v/v) to give the pure products **d**.

Synthesis of 5-Methylphenanthridin-6(5H)-one with Pd/C Recycling

A 100 mL oven-dried Schlenk tube equipped with a Teflon valve was charged with a magnetic stir bar, 10% Pd/C (10 wt% of **1a**, 0.169 g), 2-iodo-*N*-methyl-*N*-phenylbenzamide **1a** (5 mmol) and KOAc (10 mmol). The tube was placed under vacuum for 20 min and backfilled with N_2 . Then DMA (20 mL) was added through a syringe. The reaction mixture was stirred at 125 °C for 24 h. The reaction was monitored by TLC. When 2-iodo-*N*-methyl-*N*-phenylbenzamide **1a** was consumed completely, the reaction was stopped and cooled to r.t., H_2O (50 mL) was added and the mixture was filtrated, the black solid residue was washed with EtOAc (3×20 mL), then the black solid residue of Pd/C was collected to repeat the next recycling experiment without purification. The organic phase of the filtrate was separated and the organic phase was washed with brine (3×20 mL). The organic phase was dried over Na_2SO_4 and concentrated. The residue was purified directly by column chromatography on silica gel (petroleum ether/EtOAc = 5:1 v/v) to give the pure product **1b**.

5-Methylphenanthridin-6(5H)-one (1b)

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (10 wt% of **1a**, 10 mg), **1a** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N_2 atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/EtOAc = 5:1 v/v; R_f = 0.45] gave a white solid (61.4 mg, 98% yield); mp 104–106 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.55 (d, J = 8.0 Hz, 1 H), 8.27 (d, J = 7.6 Hz, 1 H), 8.26 (d, J = 8.0 Hz, 1 H), 7.75 (t, J = 7.6 Hz, 1 H), 7.60–7.53 (m, 2 H), 7.41 (d, J = 8.4 Hz, 1 H), 7.32 (t, J = 7.6 Hz, 1 H), 3.81 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 161.76, 138.14, 133.65, 132.50, 129.67, 129.01, 128.06, 125.70, 123.33, 122.58, 121.72, 119.40, 115.16, 30.10.

4,5-Dimethylphenanthridin-6(5H)-one (2b)

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (10 wt% of **2a**, 11 mg), **2a** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N_2 atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/EtOAc = 5:1 v/v; R_f = 0.49] gave a white solid (56.9 mg, 85% yield); mp 57–58 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.48 (d, J = 8.0 Hz, 1 H), 8.17 (d, J = 8.8 Hz, 1 H), 8.06 (d, J = 8.0 Hz, 1 H), 7.69 (t, J = 8.0 Hz, 1 H), 7.53 (t, J = 7.2 Hz, 1 H), 7.27 (d, J = 7.2 Hz, 1 H), 7.18 (t, J = 7.6 Hz, 1 H), 3.77 (s, 3 H), 2.63 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 164.19, 139.52, 133.98, 133.80, 132.49, 128.50, 127.86, 126.21, 125.42, 122.91, 121.89, 121.30, 121.05, 38.42, 23.16.

1,5-Dimethylphenanthridin-6(5H)-one (3b) and 3,5-Dimethylphenanthridin-6(5H)-one (3b')

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (10 wt% of **3a**, 11 mg), **3a** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N_2 atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/EtOAc = 5:1 v/v; R_f = 0.50] gave a mixture of two isomers as a brown oil (60.2 mg, 90% yield, ratio = 1:1).

^1H NMR (400 MHz, CDCl_3): δ = 8.63 (d, J = 8.0 Hz, 1 H), 8.52 (d, J = 8.0 Hz, 1 H), 8.42 (d, J = 8.4 Hz, 1 H), 8.20 (d, J = 8.0 Hz, 1 H), 8.13 (d, J = 8.0 Hz, 1 H), 7.75–7.70 (m, 2 H), 7.60–7.52 (m, 2 H), 7.41 (t, J = 8.0 Hz, 1 H), 7.32 (d, J = 8.4 Hz, 1 H), 7.19–7.11 (m, 3 H), 3.80 (s, 3 H), 3.79 (s, 3 H), 2.93 (s, 3 H), 2.50 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 161.91, 161.74, 139.99, 139.16, 138.08, 136.43, 134.73, 133.74, 132.43, 131.51, 128.97, 128.94, 128.40, 127.55, 127.38, 127.29, 126.73, 125.23, 123.72, 123.19, 121.47, 119.32, 116.92, 115.51, 113.40, 110.11, 30.96, 30.05, 26.61, 22.08.

2,5-Dimethylphenanthridin-6(5H)-one (4b)

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (10 wt% of **4a**, 11 mg), **4a** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N_2 atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/EtOAc = 5:1 v/v; R_f = 0.49] gave a white solid (62.2 mg, 93% yield); mp 130–131 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.51 (d, J = 8.0 Hz, 1 H), 8.18 (d, J = 8.0 Hz, 1 H), 7.97 (s, 1 H), 7.69 (t, J = 8.0 Hz, 1 H), 7.53 (t, J = 7.6 Hz, 1 H), 7.29 (d, J = 8.4 Hz, 1 H), 7.22 (t, J = 8.4 Hz, 1 H), 3.73 (s, 3 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 161.49, 135.88, 133.47, 132.25, 131.87, 130.54, 128.88, 127.79, 125.63, 123.34, 121.58, 119.06, 114.94, 29.98, 21.04.

2-(tert-Butyl)-5-methylphenanthridin-6(5H)-one (5b)

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (10 wt% of **5a**, 12 mg), **5a** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N_2 atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/EtOAc = 5:1 v/v; R_f = 0.47] gave a white solid (72.3 mg, 91% yield); mp 164–167 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.54 (d, J = 8.4 Hz, 1 H), 8.31–8.27 (m, 2 H), 7.45 (t, J = 7.6 Hz, 1 H), 7.60–7.54 (m, 2 H), 7.35 (d, J = 8.4 Hz, 1 H), 3.79 (s, 3 H), 1.43 (s, 9 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 161.64, 145.27, 135.90, 133.85, 132.33, 129.00, 127.81, 127.22, 125.71, 121.56, 119.53, 118.73, 114.93, 34.62, 31.56, 30.01.

HRMS (ESI): m/z calcd for $[\text{C}_{18}\text{H}_{19}\text{NO}+\text{H}^+]$: 266.1545; found: 266.1548.

2-Fluoro-5-methylphenanthridin-6(5H)-one (6b)

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (10 wt% of **6a**, 11 mg), **6a** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N_2 atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/EtOAc = 5:1 v/v; R_f = 0.52] gave a white solid (67.4 mg, 99% yield); mp 168–171 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.51 (d, J = 8.0 Hz, 1 H), 8.09 (d, J = 8.0 Hz, 1 H), 7.85 (dd, J_1 = 2.4 Hz, J_2 = 9.6 Hz, 1 H), 7.74 (t, J = 7.6 Hz, 1 H), 7.59 (t, J = 8.0 Hz, 1 H), 7.34–7.21 (m, 2 H), 3.76 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 161.28, 158.55 (d, J = 240.1 Hz), 134.51, 132.67 (d, J = 2.8 Hz), 132.59, 129.10, 128.71, 125.87, 121.87, 120.69 (d, J = 7.7 Hz), 116.83 (d, J = 23.2 Hz), 116.58 (d, J = 8.1 Hz), 109.28 (d, J = 23.6 Hz), 30.30.

5-Methyl-2-(trifluoromethoxy)phenanthridin-6(5H)-one (7b)

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (10 wt% of **7a**, 13 mg), **7a** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N_2 atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/EtOAc = 5:1 v/v; R_f = 0.45] gave a white solid (84.4 mg, 96% yield); mp 145–147 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.51 (d, J = 8.0 Hz, 1 H), 8.14 (d, J = 8.0 Hz, 1 H), 8.04 (s, 1 H), 7.76 (t, J = 7.6 Hz, 1 H), 7.61 (t, J = 7.6 Hz, 1 H), 7.39 (m, 2 H), 3.78 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 161.38, 144.37 (d, J = 2.2 Hz), 136.66, 132.77, 132.49, 129.13, 128.92, 125.83, 122.42, 121.84, 120.70 (q, J = 255.6 Hz), 120.47, 116.42, 115.95, 30.31.

HRMS (ESI): m/z calcd for $[\text{C}_{15}\text{H}_{10}\text{F}_3\text{NO}_2+\text{H}^+]$: 294.0742; found: 294.0740.

2,4-Dichloro-5-methylphenanthridin-6(5H)-one (8b)

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (10 wt% of **8a**, 12 mg), **8a** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N_2 atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/EtOAc = 5:1 v/v; R_f = 0.50] gave a yellow solid (46.5 mg, 56% yield); mp 156–159 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.50 (d, J = 7.6 Hz, 1 H), 8.15–8.12 (m, 2 H), 7.78 (t, J = 7.6 Hz, 1 H), 7.63 (t, J = 7.6 Hz, 1 H), 7.53 (s, 1 H), 3.92 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 163.47, 135.77, 133.13, 132.06, 131.98, 129.42, 128.97, 128.53, 125.82, 124.13, 122.82, 122.11, 121.91, 38.73.

HRMS (ESI): m/z calcd for $[\text{C}_{14}\text{H}_9\text{Cl}_2\text{NO}+\text{H}^+]$: 278.0139; found: 278.0144.

5-Ethylphenanthridin-6(5H)-one (9b)

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (10 wt% of **9a**, 11 mg), **9a** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N_2 atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/EtOAc = 5:1 v/v; R_f = 0.46] gave a yellow solid (60.2 mg, 90% yield); mp 81–84 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.55 (d, J = 8.0 Hz, 1 H), 8.28 (t, J = 8.8 Hz, 2 H), 7.75 (t, J = 7.6 Hz, 1 H), 7.60–7.53 (m, 2 H), 7.43 (d, J = 8.8 Hz, 1 H), 7.31 (t, J = 7.6 Hz, 1 H), 4.47 (q, J = 7.2 Hz, 2 H), 1.42 (t, J = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 161.25, 136.99, 133.65, 132.48, 129.68, 128.87, 128.02, 125.69, 123.61, 122.38, 121.68, 119.65, 115.08, 37.81, 12.85.

5,9-Dimethylphenanthridin-6(5H)-one (10b)

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (10 wt% of **10a**, 11 mg), **10a** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N_2 atmo-

sphere for 24 h. Flash chromatography [silica gel; petroleum ether/EtOAc = 5:1 v/v; R_f = 0.46] gave a white solid (60.2 mg, 90% yield); mp 127–128 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.33 (s, 1 H), 8.22 (d, J = 7.6 Hz, 1 H), 8.14 (d, J = 8.4 Hz, 1 H), 7.48–7.56 (m, 2 H), 7.38 (d, J = 8.4 Hz, 1 H), 7.27 (t, J = 7.6 Hz, 1 H), 3.80 (s, 3 H), 2.51 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 161.78, 138.18, 137.72, 133.82, 131.13, 129.14, 128.69, 125.47, 123.04, 122.49, 121.71, 119.48, 115.08, 30.09, 21.51.

9-Fluoro-5-methylphenanthridin-6(5H)-one (11b)

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (10 wt% of **11a**, 11 mg), **11a** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N_2 atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/EtOAc = 5:1 v/v; R_f = 0.48] gave a yellow solid (65.4 mg, 96% yield); mp 153–155 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.53 (dd, J_1 = 6.0 Hz, J_2 = 8.8 Hz, 1 H), 8.11 (d, J = 8.0 Hz, 1 H), 7.83 (d, J = 10.0 Hz, 1 H), 7.56 (t, J = 8.0 Hz, 1 H), 7.39 (d, J = 8.4 Hz, 1 H), 7.33–7.23 (m, 2 H), 3.77 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 165.59 (d, J = 250.3 Hz), 160.99, 138.46, 136.15 (d, J = 9.4 Hz), 132.17 (d, J = 9.8 Hz), 130.40, 123.55, 122.67, 122.16, 118.55 (d, J = 3.0 Hz), 116.29 (d, J = 22.7 Hz), 115.31, 107.63 (d, J = 21.3 Hz), 30.04.

HRMS (ESI): m/z calcd for $[\text{C}_{14}\text{H}_{10}\text{FNO}+\text{H}^+]$: 228.0825; found: 228.0826.

8-Fluoro-5-methylphenanthridin-6(5H)-one (12b)

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (10 wt% of **12a**, 11 mg), **12a** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N_2 atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/EtOAc = 5:1 v/v; R_f = 0.50] gave a yellow solid (66.1 mg, 97% yield); mp 172–173 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.24 (dd, J_1 = 4.8 Hz, J_2 = 8.8 Hz, 1 H), 8.20–7.16 (m, 2 H), 7.54 (t, J = 7.2 Hz, 1 H), 7.46 (dt, J_1 = 2.8 Hz, J_2 = 8.8 Hz, 1 H), 7.41 (d, J = 8.4 Hz, 1 H), 7.33 (t, J = 7.6 Hz, 1 H), 3.80 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 162.34 (d, J = 246.9 Hz), 160.80 (d, J = 3.1 Hz), 137.53, 130.07 (d, J = 2.6 Hz), 129.56, 127.48 (d, J = 7.9 Hz), 124.31 (d, J = 7.8 Hz), 123.16, 122.85, 120.90 (d, J = 23.0 Hz), 118.77, 115.28, 114.34 (d, J = 22.8 Hz), 30.27.

HRMS (ESI): m/z calcd for $[\text{C}_{14}\text{H}_{10}\text{FNO}+\text{H}^+]$: 228.0825; found: 228.0822.

6H-Benzo[c]chromen-6-one (1d)

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (20 wt% of **1c**, 19 mg), **1c** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N_2 atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/Et₃N = 20:1 v/v; R_f = 0.40] gave a white solid (36.5 mg, 62% yield); mp 92–94 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.40 (d, J = 8.0 Hz, 1 H), 8.12 (d, J = 8.8 Hz, 1 H), 8.06 (d, J = 7.6 Hz, 1 H), 7.83 (t, J = 8.0 Hz, 1 H), 7.58 (t, J = 8.0 Hz, 1 H), 7.48 (t, J = 8.0 Hz, 1 H), 7.38–7.32 (m, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 161.31, 151.42, 134.97, 134.90, 130.71, 130.57, 129.01, 124.67, 122.89, 121.81, 121.40, 118.17, 117.92.

2-Methyl-6H-benzo[c]chromen-6-one (2d)

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (20 wt% of **2c**, 20 mg), **2c** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N₂ atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/Et₃N = 20:1 v/v; R_f = 0.45] gave a white solid (37.2 mg, 59% yield); mp 118–120 °C.

¹H NMR (400 MHz, CDCl₃): δ = 8.37 (d, J = 8.0 Hz, 1 H), 8.08 (d, J = 8.0 Hz, 1 H), 8.01–7.77 (m, 2 H), 7.55 (t, J = 8.0 Hz, 1 H), 7.27–7.21 (m, 2 H), 2.45 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 161.47, 149.46, 134.92, 134.82, 134.21, 131.44, 130.66, 128.79, 122.84, 121.70, 121.38, 117.72, 117.57, 21.23.

1,3-Dimethyl-6H-benzo[c]chromen-6-one (3d)

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (20 wt% of **3c**, 21 mg), **3c** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N₂ atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/Et₃N = 20:1 v/v; R_f = 0.40] gave a white solid (40.3 mg, 60% yield); mp 133–135 °C.

¹H NMR (400 MHz, CDCl₃): δ = 8.45 (d, J = 7.6 Hz, 1 H), 8.31 (d, J = 7.6 Hz, 1 H), 7.78 (t, J = 7.6 Hz, 1 H), 7.54 (t, J = 7.6 Hz, 1 H), 7.04 (s, 1 H), 6.96 (s, 1 H), 2.82 (s, 3 H), 2.38 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 161.60, 152.30, 140.01, 136.36, 135.95, 134.35, 130.89, 130.11, 127.69, 125.94, 121.80, 116.48, 114.92, 25.56, 21.16.

2,4-Di-tert-butyl-6H-benzo[c]chromen-6-one (4d)

Synthesized according to the general procedure. The procedure was followed starting from 10% Pd/C (20 wt% of **4c**, 26 mg), **4c** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N₂ atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/Et₃N = 20:1 v/v; R_f = 0.44] gave a white solid (59.2 mg, 64% yield); mp 135–137 °C.

¹H NMR (400 MHz, CDCl₃): δ = 8.42 (d, J = 7.6 Hz, 1 H), 8.19 (d, J = 8.8 Hz, 1 H), 7.96 (d, J = 2.0 Hz, 1 H), 7.82 (dt, J₁ = 1.2 Hz, J₂ = 7.6 Hz, 1 H), 7.58–7.55 (m, 2 H), 1.56 (s, 9 H), 1.42 (s, 9 H).

¹³C NMR (100 MHz, CDCl₃): δ = 160.88, 148.20, 146.42, 137.98, 135.90, 134.59, 130.29, 128.39, 125.69, 121.94, 120.94, 115.53, 117.17, 31.62, 30.21.

4-Phenyl-6H-benzo[c]chromen-6-one (5d)

Synthesized according to the general procedure for the dibenzo-α-pyrones. The procedure was followed starting from 10% Pd/C (20 wt% of **5c**, 24 mg), **5c** (0.3 mmol), KOAc (0.6 mmol) in DMA (2.0 mL) at 125 °C under N₂ atmosphere for 24 h. Flash chromatography [silica gel; petroleum ether/Et₃N = 20:1 v/v; R_f = 0.45] gave a yellow solid (41.6 mg, 51% yield); mp 126–128 °C.

¹H NMR (400 MHz, CDCl₃): δ = 8.41 (d, J = 7.6 Hz, 1 H), 8.19 (d, J = 8.8 Hz, 1 H), 8.09 (d, J = 8.0 Hz, 1 H), 7.85 (t, J = 8.0 Hz, 1 H), 7.65–7.58 (m, 3 H), 7.54–7.48 (m, 3 H), 7.43–7.39 (m, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 160.85, 148.28, 136.44, 135.10, 134.95, 132.05, 131.32, 130.65, 129.77, 129.05, 128.54, 127.97, 124.48, 122.13, 122.08, 121.28, 118.57.

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