

## *Supporting Information*

# **A highly efficient Pd-catalyzed decarboxylative *ortho*-arylation of amides with aryl acylperoxides**

Dengke Li,<sup>a</sup> Ning Xu,<sup>a</sup> Yicheng Zhang,<sup>a</sup> and Lei Wang<sup>\*a,b</sup>

<sup>a</sup> *Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, China* Tel: +86-561-3802-069

Fax: +86-561-3090-518 E-mail: [leiwang@chnu.edu.cn](mailto:leiwang@chnu.edu.cn).

<sup>b</sup> *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

### ***Table of Contents for Supporting Information***

1. General information.....	2
2. Preparation of the starting materials.....	2
3. General procedure for the reactions.....	6
4. Mechanistic studies .....	12
5. Characterization data for the products.....	13
6. References .....	20
7. <sup>1</sup> H and <sup>13</sup> C NMR spectra of the products.....	21

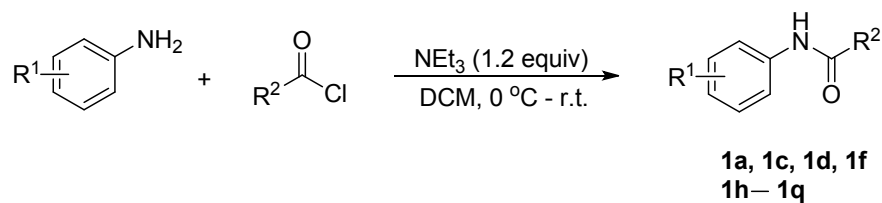
## 1. General information

All the solvents and commercially available reagents were purchased from commercial suppliers. Solvents (CH<sub>3</sub>CN, DMF, DCE, DME, DMSO, 1,4-dioxane or toluene) were dried. Molecular sieves were activated before use. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz or 100 MHz, respectively). All chemical shifts are given as  $\delta$  value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). The infrared spectra were obtained using a Thermo Nicolet 6700 Spectrometer. High Resolution Mass (MS) analysis was obtained using Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS system with Electrospray Ionization (ESI). Melting points were measured on a Mel-Temp apparatus and are uncorrected.

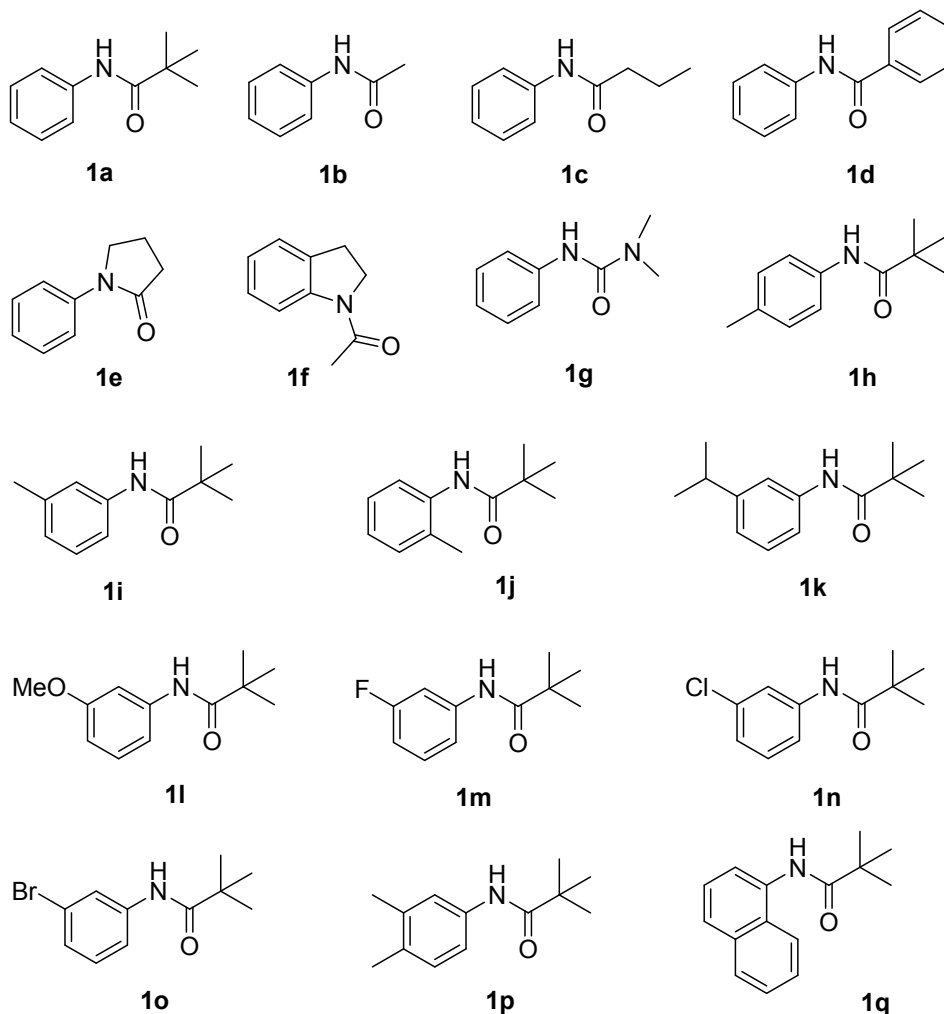
## 2. Preparation of the starting materials

Anilides **1b** and **1e** were purchased from Alfa Aesar. Benzoyl peroxide (**2a**) was purchased from Aldrich. Other starting materials used in the reaction, including **1a**, **1c**, **1d**, **1f–1q**, **2b–2j**, and **5a–5k** were prepared according to the reported literatures.<sup>1-4</sup>

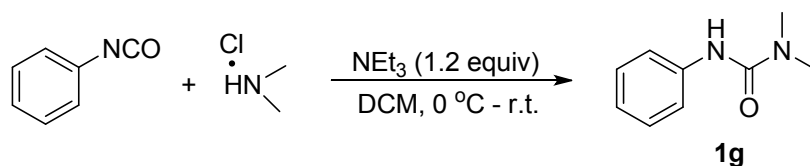
## 2.1 General procedure for the preparation of 1a, 1c, 1d, 1f, and 1h–1q<sup>1</sup>



A round-bottom flask was charged with acyl chloride (10 mmol) in dichloromethane (DCM, 10 mL), and the solution was cooled to 0 °C in an ice-bath. Then triethylamine (12 mmol) and aniline (10 mmol) were added slowly. The mixture was stirred for 12 h at room temperature (monitored by TLC). After the reaction was completed, it was quenched with a solution of HCl (aq. 1.0 mol/L). The resulting mixture was then extracted with DCM. The combined organic layers were dried by Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuum to afford the crude product, which was further purified by recrystallizing from DCM/hexane to give the desired product.

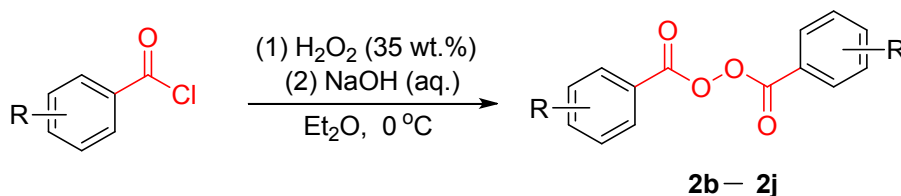


## 2.2 General procedure for the preparation of **1g**<sup>2</sup>

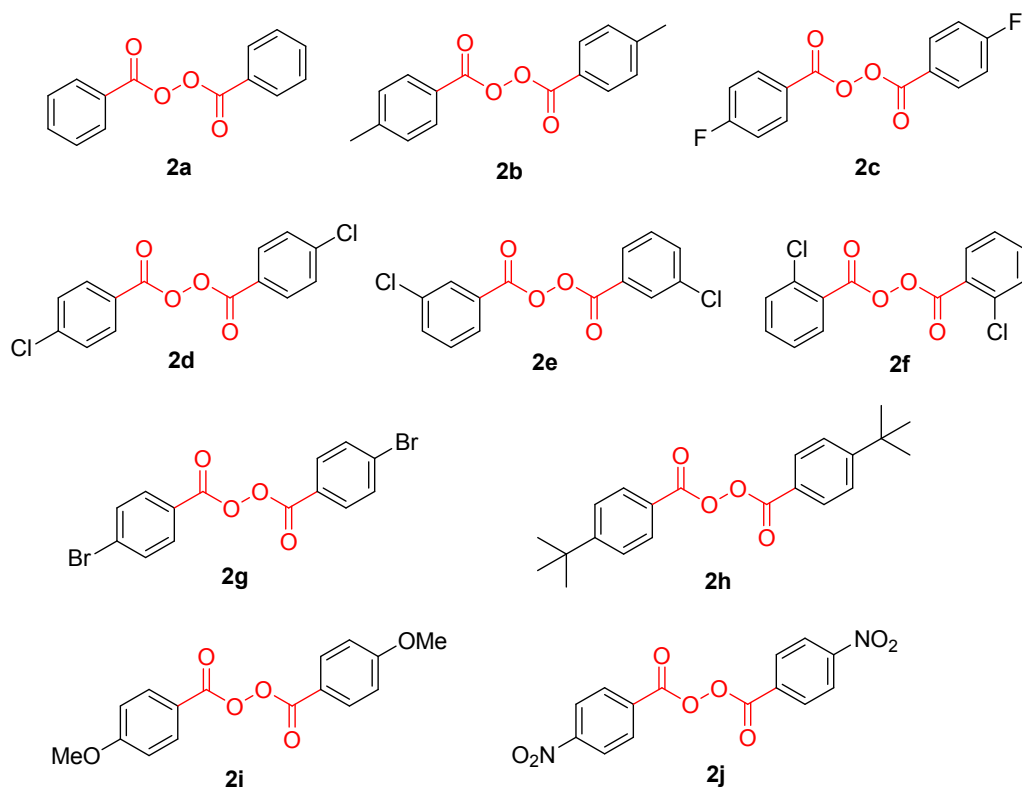


In a round-bottom flask charged with a solution of dimethylamine hydrochloride (12 mmol) in dry dichloromethane (DCM, 20 mL) at 0 °C, triethylamine (12 mmol) was added and then the solution was stirred for 10 minutes. To this solution, phenyl isocyanate (10 mmol) was added and the mixture was allowed to stir at room temperature for 16 h (monitored by TLC). After the reaction was completed, the solution was washed with HCl (aq. 2.0 mol/L, 3×10 mL) and extracted with DCM (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated in vacuum to afford the crude product. The resulting white solid was recrystallised from toluene to yield pure urea **1g**.

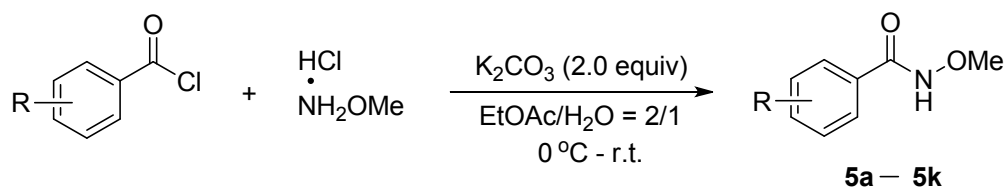
## 2.3 General procedure for the preparation of aryl acylperoxides **2b–2j**<sup>3</sup>



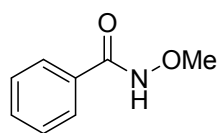
In a round-bottomed flask, the solution of acid chloride (10 mmol) in diethyl ether (5 mL) was cooled to 0 °C in an ice-bath. Then, hydrogen peroxide (0.556 g, 35 wt.% in H<sub>2</sub>O, 5.73 mmol) was added dropwise over 10 minutes to the cold solution. This was followed by the dropwise addition of an aqueous solution of NaOH (0.506g, 12.64 mmol, 4 mL) over 20 minutes. The resulting white precipitate was collected by filtration. After washing with water (3×5 mL) and diethyl ether (3×5 mL), the solid was crystallized from a cold acetone/water mixture (v/v = 1/3) to give the pure aryl acylperoxide.



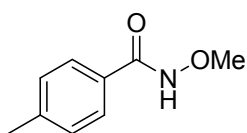
#### 2.4 General procedure for the preparation of 5a–5k<sup>4</sup>



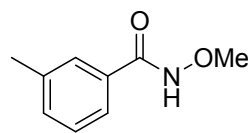
In a round-bottomed flask, *O*-methylhydroxylamine hydrochloride (10 mmol) and  $\text{K}_2\text{CO}_3$  (20 mmol) were dissolved in water (15 mL) and EtOAc (30 mL). The solution was cooled to 0 °C in an ice-bath and then acyl chloride (10 mmol) was added. After the solution was stirred at room temperature overnight, the aqueous layer was separated and the organic layer was washed with water and brine. After it was dried by  $\text{Na}_2\text{SO}_4$ , evaporation of the solvent gave the crude product. Recrystallization of crude product from petroleum ether/ethyl acetate gave the pure desired product.



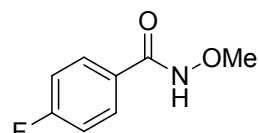
5a



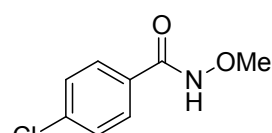
5b



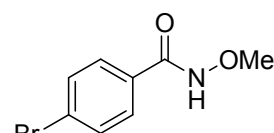
5c



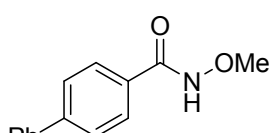
5d



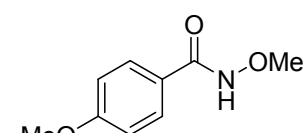
5e



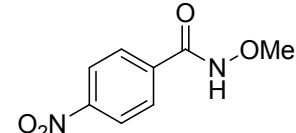
5f



5g



5h



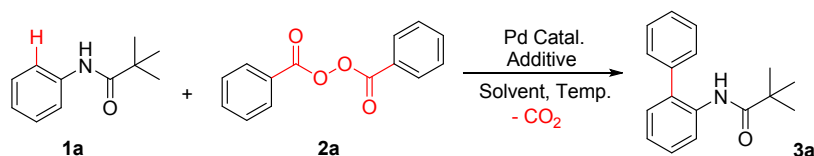
5k

### 3. General procedure for the reactions

#### 3.1 Optimization of the reaction conditions in decarboxylative *ortho*-arylation of anilides with aryl acylperoxides

Under air atmosphere, a 25 mL sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with *N*-phenylpivalamide (**1a**, 0.25 mmol), benzoyl peroxide (**2a**, 0.40 mmol, 1.6 equiv), Pd(OAc)<sub>2</sub> (7.5 mol%), additive (0.50 mmol, 2.0 equiv), activated 3Å molecular sieves (70 mg) and solvent (2.0 mL). Then the reaction vessel was placed in an oil bath at 80 °C for 32 h (monitored by TLC). After the reaction was completed, it was cooled to room temperature and quenched with K<sub>2</sub>CO<sub>3</sub> (aq.), then extracted with ethyl acetate and dried with Na<sub>2</sub>SO<sub>4</sub>. The resulting solution was directly filtered through a pad of silica gel using a sintered glass funnel, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant: petroleum ether/ethyl acetate = 15/1) to give the desired product (**3a**).

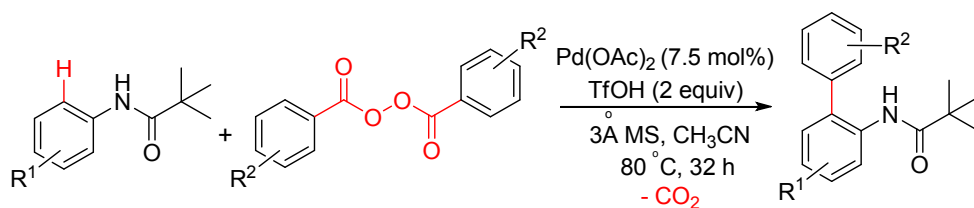
**Table S1** Optimization of the decarboxylative *ortho*-arylation of *N*-phenylpivalamide (**1a**) with benzoyl peroxide (**2a**)<sup>a</sup>



Entry	Catalyst	Additive	Solvent	Temp. (°C)	Yield (%) <sup>b</sup>
1	Pd(OAc) <sub>2</sub>	TfOH/-	CH <sub>3</sub> CN	80	53
2	<i>Pd(OAc)<sub>2</sub></i>	<i>TfOH/3Å MS</i>	<i>CH<sub>3</sub>CN</i>	<i>80</i>	<i>77</i>
3	Pd(OAc) <sub>2</sub>	TfOH/4Å MS	CH <sub>3</sub> CN	80	61
4	Pd(OAc) <sub>2</sub>	-/3Å MS	CH <sub>3</sub> CN	80	N.R.
5	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub> /3Å MS	CH <sub>3</sub> CN	80	N.R.
6	Pd(OAc) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub> /3Å MS	CH <sub>3</sub> CN	80	N.R.
7	Pd(OAc) <sub>2</sub>	NEt <sub>3</sub> /3Å MS	CH <sub>3</sub> CN	80	N.R.
8	Pd(OAc) <sub>2</sub>	TFA/3Å MS	CH <sub>3</sub> CN	80	N.R.
9	Pd(OAc) <sub>2</sub>	HOAc/3Å MS	CH <sub>3</sub> CN	80	N.R.
10	Pd(OAc) <sub>2</sub>	PivOH/3Å MS	CH <sub>3</sub> CN	80	N.R.
11	Pd(OAc) <sub>2</sub>	<i>p</i> -TsOH/3Å MS	CH <sub>3</sub> CN	80	31
12	Pd(OAc) <sub>2</sub>	CH <sub>3</sub> SO <sub>3</sub> H/3Å MS	CH <sub>3</sub> CN	80	35
13	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	CH <sub>3</sub> CN	80	38 <sup>c</sup>
14	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	CH <sub>3</sub> CN	80	57 <sup>d</sup>
15	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	CH <sub>3</sub> CN	80	58 <sup>e</sup>
16	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	CH <sub>3</sub> CN	60	18
17	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	CH <sub>3</sub> CN	100	65
18	-	TfOH	CH <sub>3</sub> CN	80	N.R.
19	-	-	CH <sub>3</sub> CN	80	N.R.
20	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	CH <sub>3</sub> CN	80	61 <sup>f</sup>
21	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	CH <sub>3</sub> CN	80	78 <sup>g</sup>
22	Pd(TFA) <sub>2</sub>	TfOH/3Å MS	CH <sub>3</sub> CN	80	51
23	PdCl <sub>2</sub>	TfOH/3Å MS	CH <sub>3</sub> CN	80	43
24	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl	TfOH/3Å MS	CH <sub>3</sub> CN	80	29
25	Pd(PPh <sub>3</sub> ) <sub>4</sub>	TfOH/3Å MS	CH <sub>3</sub> CN	80	38
26	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	toluene	80	<5
27	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	DCE	80	trace
28	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	1,4-dioxane	80	trace
29	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	DMF	80	N.R.
30	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	DMSO	80	N.R.
31	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	DME	80	10
32	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	CH <sub>3</sub> CN/HOAc=1/1	80	13
33	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	CH <sub>3</sub> CN	80	50 <sup>h</sup>
34	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	CH <sub>3</sub> CN	80	55 <sup>i</sup>

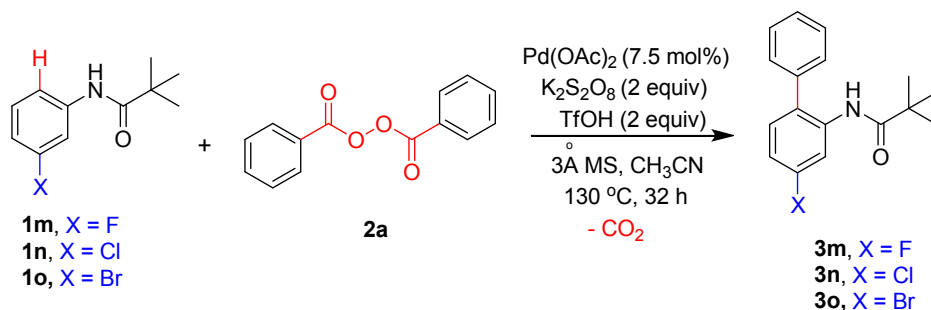
<sup>a</sup> Reaction conditions: **1a** (0.25 mmol), **2a** (1.6 equiv, 0.4 mmol), Pd(OAc)<sub>2</sub> (7.5 mol%), additive (2.0 equiv, 0.5 mmol), activated 3Å MS (70 mg), solvent (2.0 mL), air atmosphere, 80 °C, 32 h. <sup>b</sup> Isolated yields. <sup>c</sup> TfOH (1.0 equiv) was used. <sup>d</sup> TfOH (4.0 equiv) was used. <sup>e</sup> for 24 h. <sup>f</sup> Pd(OAc)<sub>2</sub> (5.0 mol%) was used. <sup>g</sup> Pd(OAc)<sub>2</sub> (10 mol%) was used. <sup>h</sup> **2a** (1.2 equiv) was used. <sup>i</sup> **2a** (2.0 equiv) was used.

### 3.2 General procedure for the decarboxylative *ortho*-arylation reactions of anilides with aryl acylperoxides



Under air atmosphere, a 25 mL sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with anilide (0.25 mmol), aryl acylperoxide (0.40 mmol, 1.6 equiv),  $Pd(OAc)_2$  (7.5 mol%),  $TfOH$  (0.50 mmol, 2.0 equiv), activated 3Å molecular sieves (70 mg) and  $CH_3CN$  (2.0 mL). Then the reaction vessel was placed in an oil bath at  $80^\circ C$  for 32 h (monitored by TLC). After the reaction was completed, it was cooled to room temperature and quenched with  $K_2CO_3$  (aq.), then extracted with ethyl acetate and dried with  $Na_2SO_4$ . The resulting solution was directly filtered through a pad of silica gel using a sintered glass funnel, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant: petroleum ether/ethyl acetate) to give the desired product.

### 3.3 General procedure for the decarboxylative *ortho*-arylation reactions of anilides **1m**, **1n**, **1o** with benzoyl peroxide (**2a**)



Under air atmosphere, a 25 mL sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with **1m**, **1n** or **1o** (0.25 mmol), benzoyl peroxide (**2a**, 0.40 mmol, 1.6 equiv),  $Pd(OAc)_2$  (7.5 mol%),  $K_2S_2O_8$  (2.0



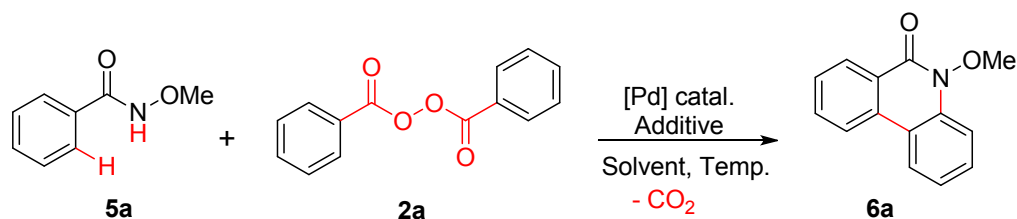
equiv) was added as co-oxidant, TfOH (2.0 equiv), activated 3Å molecular sieves (70 mg) and CH<sub>3</sub>CN (2.0 mL), at 130 °C for 32 h (monitored by TLC). After the reaction was completed, it was cooled to room temperature and quenched with K<sub>2</sub>CO<sub>3</sub> (aq.), then extracted with ethyl acetate and dried with Na<sub>2</sub>SO<sub>4</sub>. The resulting solution was directly filtered through a pad of silica gel using a sintered glass funnel, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant: petroleum ether/ethyl acetate =15/1) to give the desired product (**3m**, **3n**, or **3o**).

### **3.4 Optimization of the decarboxylative arylation and cyclization of *N*-methoxybenzamide with benzoyl peroxide for the synthesis of phenanthridinone**

Under air atmosphere, a 25 mL sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with *N*-methoxybenzamide (**5a**, 0.25 mmol), benzoyl peroxide (**2a**, 0.40 mmol, 1.6 equiv), Pd(OAc)<sub>2</sub> (7.5 mol%), additive (0.50 mmol, 2.0 equiv), activated 4Å molecular sieves (70 mg) and solvent (2.0 mL). Then the reaction vessel placed in an oil bath at 80 °C for 24 h (monitored by TLC). After the reaction was completed, it was cooled to room temperature and quenched with K<sub>2</sub>CO<sub>3</sub> (aq.), then extracted with ethyl acetate and dried with Na<sub>2</sub>SO<sub>4</sub>. The resulting solution was directly filtered through a pad of silica gel using a sintered glass funnel, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant: petroleum ether/ethyl acetate = 4/1) to give the desired product (**6a**).

**Table S2** Optimization of the decarboxylative arylation and cyclization of

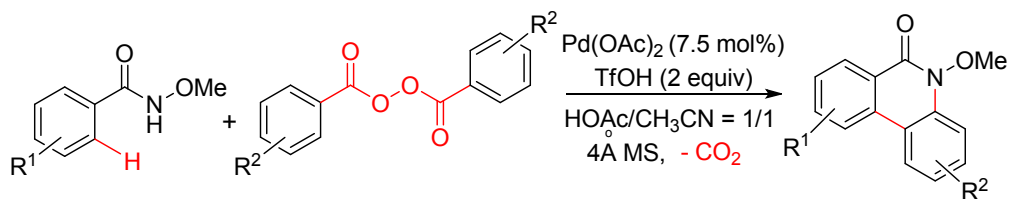
benzamides with benzoyl peroxide for the synthesis of phenanthridinone <sup>a</sup>



Entry	Catalyst	Additive	Solvent	Temp. (°C)	Yield (%) <sup>b</sup>
1	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	CH <sub>3</sub> CN	80	21 <sup>c</sup>
2	Pd(OAc) <sub>2</sub>	TfOH/3Å MS	HOAc/CH <sub>3</sub> CN=1/1	80	47
3	<i>Pd(OAc)<sub>2</sub></i>	<i>TfOH/4Å MS</i>	<i>HOAc/CH<sub>3</sub>CN=1/1</i>	<i>80</i>	<i>60</i>
4	Pd(OAc) <sub>2</sub>	TfOH/4Å MS	HOAc/CH <sub>3</sub> CN=2/1	80	41
5	Pd(OAc) <sub>2</sub>	TfOH/4Å MS	HOAc/CH <sub>3</sub> CN=1/2	80	52
6	Pd(OAc) <sub>2</sub>	TfOH/4Å MS	HOAc/CH <sub>3</sub> CN=1/3	80	44
7	Pd(OAc) <sub>2</sub>	TfOH/-	HOAc/CH <sub>3</sub> CN=1/1	80	25
8	Pd(OAc) <sub>2</sub>	-/4Å MS	HOAc/CH <sub>3</sub> CN=1/1	80	<10
9	Pd(OAc) <sub>2</sub>	TfOH/4Å MS	HOAc/CH <sub>3</sub> CN=1/1	80	47 <sup>d</sup>
10	Pd(OAc) <sub>2</sub>	TfOH/4Å MS	HOAc/CH <sub>3</sub> CN=1/1	80	40 <sup>e</sup>
11	Pd(OAc) <sub>2</sub>	TFA/4Å MS	HOAc/CH <sub>3</sub> CN=1/1	80	13
12	Pd(OAc) <sub>2</sub>	PivOH/4Å MS	HOAc/CH <sub>3</sub> CN=1/1	80	10
13	Pd(OAc) <sub>2</sub>	<i>p</i> -TsOH/4ÅMS	HOAc/CH <sub>3</sub> CN=1/1	80	15
14	-	TfOH/4Å MS	HOAc/CH <sub>3</sub> CN=1/1	80	N.R.
15	Pd(OAc) <sub>2</sub>	TfOH/4Å MS	HOAc/CH <sub>3</sub> CN=1/1	80	62 <sup>f</sup>
16	Pd(TFA) <sub>2</sub>	TfOH/4Å MS	HOAc/CH <sub>3</sub> CN=1/1	80	47
17	PdCl <sub>2</sub>	TfOH/4Å MS	HOAc/CH <sub>3</sub> CN=1/1	80	<10
18	Pd(OAc) <sub>2</sub>	TfOH/4Å MS	HOAc/CH <sub>3</sub> CN=1/1	80	50 <sup>g</sup>
19	Pd(OAc) <sub>2</sub>	TfOH/4Å MS	HOAc/CH <sub>3</sub> CN=1/1	80	48 <sup>h</sup>
20	Pd(OAc) <sub>2</sub>	TfOH/4Å MS	HOAc/CH <sub>3</sub> CN=1/1	60	36
21	Pd(OAc) <sub>2</sub>	TfOH/4Å MS	HOAc/CH <sub>3</sub> CN=1/1	100	41

<sup>a</sup> Reaction conditions: **5a** (0.25 mmol), **2a** (0.4 mmol, 1.6 equiv), Pd(OAc)<sub>2</sub> (7.5 mol%), additive (2.0 equiv, 0.5 mmol), activated MS (70 mg), solvent (2.0 mL), air atmosphere, at 80 °C for 24 h. <sup>b</sup> Isolated yields. <sup>c</sup> 32h. <sup>d</sup> TfOH (1.0 equiv) was used. <sup>e</sup> TfOH (4.0 equiv) was used. <sup>f</sup> Pd(OAc)<sub>2</sub> (10 mol%) was used. <sup>g</sup> **2a** (1.2 equiv) was used. <sup>h</sup> **2a** (2.0 equiv) was used.

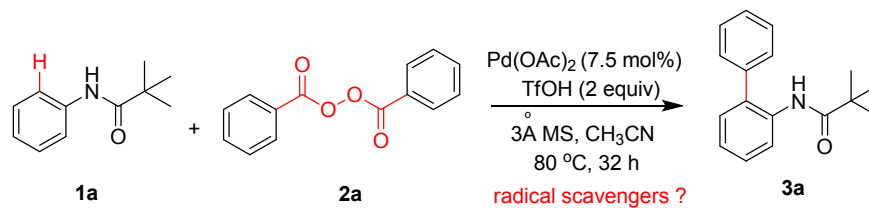
### 3.5 General procedure for the decarboxylative arylation and cyclization of *N*-methoxyarylamides with aryl acylperoxides to phenanthridinones



Under air atmosphere, a 25 mL sealable reaction tube with a Teflon-coated screw cap equipped with a magnetic stir bar was charged with *N*-methoxyarylamide (0.25 mmol), aryl acylperoxide (0.40 mmol, 1.6 equiv), Pd(OAc)<sub>2</sub> (7.5 mol%), TfOH (0.50 mmol, 2.0 equiv), activated 4Å molecular sieves (70 mg) and HOAc/CH<sub>3</sub>CN (V/V = 1/1, 2.0 mL). Then the reaction vessel was placed in an oil bath at 80 °C for 24 h (monitored by TLC). After the reaction was completed, it was cooled to room temperature and quenched with K<sub>2</sub>CO<sub>3</sub> (aq.), then extracted with ethyl acetate and dried with Na<sub>2</sub>SO<sub>4</sub>. The resulting solution was directly filtered through a pad of silica gel using a sintered glass funnel, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluant: petroleum ether/ethyl acetate) to give the desired product phenanthridinone.

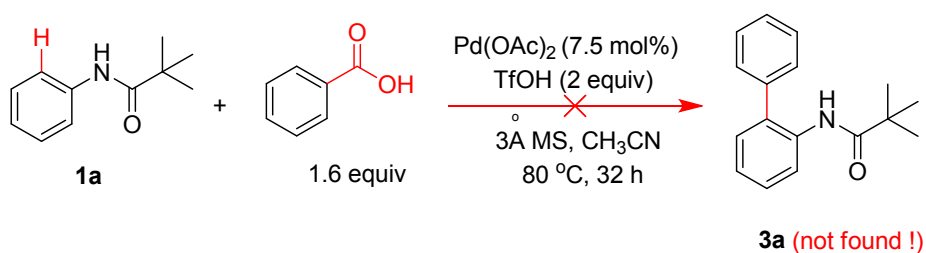
## 4. Mechanistic studies

### 4.1 Table S3 the effect of radical scavengers on the model reaction

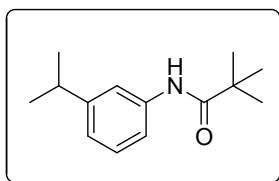


radical scavenger	amount (mol%)	yield of <b>3a</b> (%)	yield of <b>1a</b> (%)
no	0	77	12
TEMPO	50	17	74
	100	trace	90
ascorbic acid	50	18	75
	100	trace	94

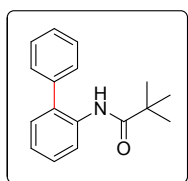
### 4.2 The control experiment



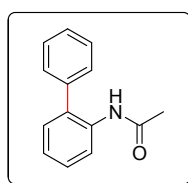
## 5. Characterization data for the products



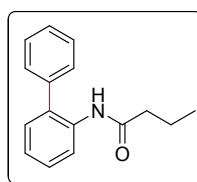
**1k, N-(3-iso-Propylphenyl)pivalamide.** White solid. mp 89 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.48 (s, 2H), 7.35–7.33 (m, 1H), 7.24–7.20 (m, 1H), 6.98–6.96 (m, 1H), 2.91–2.83 (m, 1H), 1.32 (s, 9H), 1.24 (d, *J* = 8.0 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 176.52, 149.75, 138.00, 128.65, 122.19, 118.14, 117.47, 39.46, 34.05, 27.52, 23.79. HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>14</sub>H<sub>22</sub>NO: 220.1701 Found: 220.1698. IR (KBr, v/cm<sup>-1</sup>) 3287, 1655.



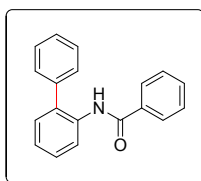
**3a, N-([1,1'-Biphenyl]-2-yl)pivalamide.** Yellow solid. mp 65–67 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.37 (d, *J* = 8.0 Hz, 1H), 7.52–7.37 (m, 7H), 7.26–7.24 (m, 1H), 7.19–7.15 (m, 1H), 1.10 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 176.14, 138.03, 135.07, 132.11, 129.57, 129.22, 128.91, 128.35, 127.92, 123.76, 120.83, 39.65, 27.24. HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>17</sub>H<sub>20</sub>NO: 254.1545 Found: 254.1544. IR (KBr, v/cm<sup>-1</sup>) 3263, 1646.



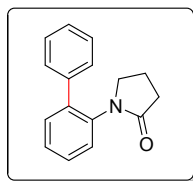
**3b, N-([1,1'-Biphenyl]-2-yl)acetamide.**<sup>5</sup> Yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.24 (d, *J* = 8.0 Hz, 1H), 7.51–7.47 (m, 2H), 7.44–7.42 (m, 1H), 7.39–7.35 (m, 3H), 7.26–7.17 (m, 3H), 2.01 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 168.20, 138.12, 134.60, 132.30, 129.95, 129.10, 128.94, 128.27, 127.83, 124.32, 121.79, 24.36. HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>14</sub>H<sub>14</sub>NO: 212.1075 Found: 212.1073.



**3c, N-([1,1'-Biphenyl]-2-yl)butyramide.** White solid. mp 86 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.31 (d, *J* = 8.0 Hz, 1H), 7.52–7.48 (m, 2H), 7.45–7.43 (m, 1H), 7.41–7.36 (m, 3H), 7.27–7.25 (m, 1H), 7.20–7.16 (m, 2H), 2.18 (t, *J* = 8.0 Hz, 2H), 1.67–1.58 (m, 2H), 0.93 (t, *J* = 8.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 170.97, 138.10, 134.68, 132.08, 129.88, 129.16, 128.94, 128.30, 127.86, 124.09, 121.49, 39.60, 18.76, 13.53. HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>16</sub>H<sub>18</sub>NO: 240.1388 Found: 240.1392. IR (KBr, v/cm<sup>-1</sup>) 3249, 1648.

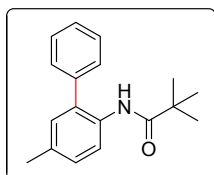


**3d, N-([1,1'-Biphenyl]-2-yl)benzamide.** Yellow solid. mp 77–79 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.56 (d, *J* = 8.0 Hz, 1H), 8.03 (br, s, 1H), 7.63–7.61 (m, 2H), 7.55–7.52 (m, 2H), 7.49–7.43 (m, 5H), 7.42–7.38 (m, 2H), 7.33–7.31 (m, 1H), 7.26–7.22 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 164.86, 138.00, 134.84, 134.71, 132.30, 131.59, 129.87, 129.25, 129.11, 128.62, 128.49, 128.07, 126.70, 124.26, 121.10. HRMS (ESI) [M+H]<sup>+</sup> Calcd. for C<sub>19</sub>H<sub>16</sub>NO: 274.1232 Found: 274.1228. IR (KBr, v/cm<sup>-1</sup>) 3264, 1664.



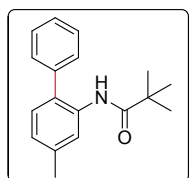
**3e, 1-([1,1'-Biphenyl]-2-yl)pyrrolidin-2-one.**<sup>6</sup> Yellow oil.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.42–7.31 (m, 9H), 3.20 (t,  $J$  = 8.0 Hz, 2H), 2.42 (t,  $J$  = 8.0 Hz, 2H), 1.89–1.82 (m, 2H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 175.51, 139.55, 139.03, 136.25, 130.73, 128.45, 128.31, 128.29, 128.25, 127.92, 127.48, 50.07, 31.09, 18.87. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>16</sub>H<sub>16</sub>NO: 238.1232 Found: 238.1230.



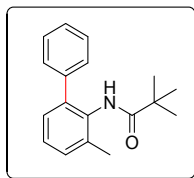
**3h, N-(5-Methyl-[1,1'-biphenyl]-2-yl)pivalamide.** Yellow solid.

mp 91–92 °C. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.21 (d,  $J$  = 8.0 Hz, 1H), 7.50–7.47 (m, 2H), 7.43–7.35 (m, 4H), 7.19 (d,  $J$  = 8.0 Hz, 1H), 7.07 (s, 1H), 2.36 (s, 3H), 1.11 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 176.06, 138.23, 133.40, 132.49, 132.30, 130.16, 129.18, 128.82, 127.79, 121.11, 39.55, 27.27, 20.69. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>18</sub>H<sub>22</sub>NO: 268.1701 Found: 268.1701. **IR (KBr, v/cm<sup>-1</sup>)** 3294, 1645.



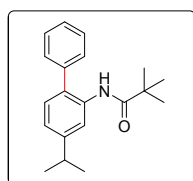
**3i, N-(4-Methyl-[1,1'-biphenyl]-2-yl)pivalamide.**<sup>6</sup> Yellow solid.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.25 (s, 1H), 7.51–7.35 (m, 6H), 7.16–7.14 (m, 1H), 7.00–6.98 (m, 1H), 2.41 (s, 3H), 1.11 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 176.20, 138.39, 138.07, 134.81, 129.40, 129.33, 128.88, 127.75, 124.56, 121.34, 39.67, 27.25, 21.36. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>18</sub>H<sub>22</sub>NO: 268.1701 Found: 268.1700.



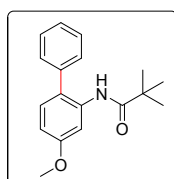
**3j, N-(3-Methyl-[1,1'-biphenyl]-2-yl)pivalamide.**<sup>7</sup> Yellow solid.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.42–7.35 (m, 3H), 7.31–7.29 (m, 2H), 7.26–7.25 (m, 2H), 7.18–7.16 (m, 1H), 6.82 (br, s, 1H), 2.27 (s, 3H), 1.12 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 176.59, 139.51, 139.44, 136.49, 132.72, 129.95, 128.87, 128.12, 127.50, 127.24, 126.87, 38.97, 27.37, 18.37. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>18</sub>H<sub>22</sub>NO: 268.1701 Found: 268.1702.



**3k, N-(4-iso-Propyl-[1,1'-biphenyl]-2-yl)pivalamide.** Yellow solid.

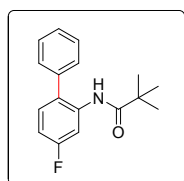
mp 99–100 °C. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.34 (s, 1H), 7.51–7.47 (m, 3H), 7.43–7.37 (m, 3H), 7.20–7.18 (m, 1H), 7.06–7.04 (m, 1H), 3.04–2.93 (m, 1H), 1.33 (d,  $J$  = 8.0 Hz, 6H), 1.12 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 176.16, 149.43, 138.11, 134.96, 129.57, 129.48, 129.33, 128.89, 127.75, 121.82, 118.89, 39.70, 34.11, 27.28, 23.83. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>20</sub>H<sub>26</sub>NO: 296.2014 Found: 296.2010. **IR (KBr, v/cm<sup>-1</sup>)** 3286, 1643.



**3l, N-(4-Methoxy-[1,1'-biphenyl]-2-yl)pivalamide.**<sup>8</sup> Yellow solid.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 8.15 (d,  $J$  = 2.4 Hz, 1H), 7.55 (br, s, 1H), 7.51–7.47 (m, 2H), 7.43–7.39 (m, 1H), 7.36–7.34 (m, 2H), 7.15 (d,  $J$  = 8.0 Hz, 1H), 6.73 (dd,  $J$  = 8.0 Hz, 2.4 Hz, 1H), 3.88 (s, 3H), 1.11 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 176.29, 159.62, 137.83, 136.09,

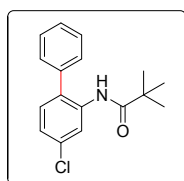
130.23, 129.49, 128.95, 127.67, 124.13, 110.51, 105.05, 55.33, 39.80, 27.23. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>18</sub>H<sub>22</sub>NO<sub>2</sub>: 284.1651 Found: 284.1649.



**3m, N-(4-Fluoro-[1,1'-biphenyl]-2-yl)pivalamide.**<sup>7</sup> Yellow solid.

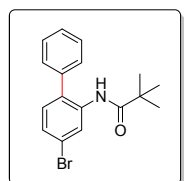
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.28 (dd, *J* = 12.0 Hz, 2.4 Hz, 1H), 7.56–7.49 (m, 3H), 7.46–7.42 (m, 1H), 7.34–7.32 (m, 2H), 7.19–7.16 (m, 1H), 6.86–6.82 (m, 1H), 1.09 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 176.25, 162.34 (d, *J* = 243.0 Hz), 137.09 (d, *J* = 1.0 Hz), 136.46 (d, *J* = 11.8 Hz), 130.47 (d, *J* = 9.3 Hz), 129.32, 129.12, 128.19, 127.48 (d, *J* = 3.2 Hz), 110.20 (d, *J* = 21.6 Hz), 107.70 (d, *J* = 27.7 Hz), 39.76, 27.14.

**HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>17</sub>H<sub>19</sub>FNO: 272.1451 Found: 272.1451.



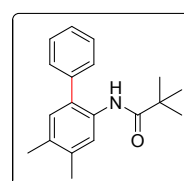
**3n, N-(4-Chloro-[1,1'-biphenyl]-2-yl)pivalamide.** Yellow solid. mp 96–97 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.52 (d, *J* = 1.6 Hz, 1H), 7.53–7.43 (m, 4H), 7.35–7.33 (m, 2H), 7.18–7.12 (m, 2H), 1.10 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 176.26, 136.92, 136.05, 134.09, 130.39, 130.08, 129.14, 128.30, 123.68, 120.52, 39.75, 27.16. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>17</sub>H<sub>19</sub>ClNO: 288.1155 Found: 288.1154. **IR (KBr, v/cm<sup>-1</sup>)** 3229, 1648.



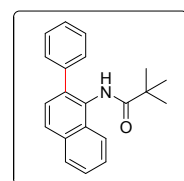
**3o, N-(4-Bromo-[1,1'-biphenyl]-2-yl)pivalamide.** Yellow solid. mp 110 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.67 (d, *J* = 2.0 Hz, 1H), 7.53–7.43 (m, 4H), 7.34–7.33 (m, 2H), 7.30–7.27 (m, 1H), 7.11–7.09 (m, 1H), 1.09 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 176.23, 136.92, 136.22, 130.69, 130.59, 129.14, 129.06, 128.33, 126.65, 123.37, 122.08, 39.74, 27.16. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>17</sub>H<sub>19</sub>BrNO: 332.0650 Found: 332.0642. **IR (KBr, v/cm<sup>-1</sup>)** 3240, 1647.



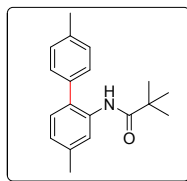
**3p, N-(4,5-Dimethyl-[1,1'-biphenyl]-2-yl)pivalamide.**<sup>6</sup> Yellow solid.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.15 (s, 1H), 7.50–7.46 (m, 2H), 7.42–7.35 (m, 4H), 7.04 (s, 1H), 2.33 (s, 3H), 2.27 (s, 3H), 1.12 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 176.13, 138.16, 136.70, 132.54, 132.15, 130.65, 129.91, 129.28, 128.80, 127.63, 122.31, 39.57, 27.28, 19.65, 19.06. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>19</sub>H<sub>24</sub>NO: 282.1858 Found: 282.1857.



**3q, N-(2-Phenyl-naphthalen-1-yl)pivalamide.** Yellow solid. mp 171–172 °C.

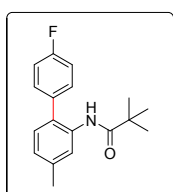
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 7.90–7.82 (m, 3H), 7.57–7.39 (m, 8H), 7.20 (br, s, 1H), 1.20 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 177.63, 139.63, 136.96, 133.53, 130.68, 129.89, 129.02, 128.18, 128.04, 127.55, 127.51, 127.35, 126.73, 125.95, 123.50, 39.14, 27.47. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>21</sub>H<sub>22</sub>NO: 304.1701 Found: 304.1699. **IR (KBr, v/cm<sup>-1</sup>)** 3262, 1649.



**3r**, *N*-(4,4'-Dimethyl-[1,1'-biphenyl]-2-yl)pivalamide.<sup>7</sup> Yellow oil.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.27 (s, 1H), 7.53 (br, s, 1H), 7.31–7.25 (m, 4H), 7.14–7.12 (m, 1H), 6.99–6.97 (m, 1H), 2.44 (s, 3H), 2.42 (s, 3H), 1.14 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 176.18, 138.11, 137.51, 135.03, 134.91, 129.58, 129.53, 129.25, 129.18, 124.52, 121.26, 39.69, 27.31, 21.36, 21.09. **HRMS (ESI) [M+H]<sup>+</sup>**

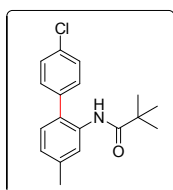
Calcd. for C<sub>19</sub>H<sub>24</sub>NO: 282.1858 Found: 282.1856.



**3s**, *N*-(4'-Fluoro-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide. White solid.

mp 103–104 °C. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.18 (s, 1H), 7.35–7.31 (m, 3H), 7.20–7.16 (m, 2H), 7.12–7.10 (m, 1H), 6.99–6.98 (m, 1H), 2.40 (s, 3H), 1.12 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 176.22, 162.29 (d, *J* = 246.1 Hz), 138.61, 134.78, 134.04 (d, *J* = 3.4 Hz), 131.05 (d, *J* = 8.0 Hz), 129.53, 128.50, 124.76, 121.78, 115.83 (d, *J* = 21.3 Hz), 39.65, 27.27, 21.32. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>18</sub>H<sub>21</sub>FNO:

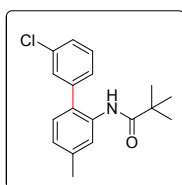
286.1607 Found: 286.1606. **IR (KBr, v/cm<sup>-1</sup>)** 3276, 1644.



**3t**, *N*-(4'-Chloro-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide. White solid.

mp 132–133 °C. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.16 (s, 1H), 7.47–7.45 (m, 2H), 7.33–7.29 (m, 3H), 7.11–7.09 (m, 1H), 7.00–6.98 (m, 1H), 2.40 (s, 3H), 1.14 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 176.27, 138.81, 136.58, 134.59, 133.83, 130.67, 129.47, 129.04, 128.37, 124.93, 122.02, 39.68, 27.31, 21.34. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>18</sub>H<sub>21</sub>ClNO:

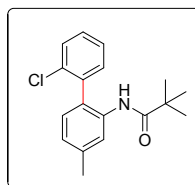
302.1312 Found: 302.1308. **IR (KBr, v/cm<sup>-1</sup>)** 3273, 1647.



**3u**, *N*-(3'-Chloro-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide. Yellow solid.

mp 100–101 °C. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.14 (s, 1H), 7.43–7.37 (m, 4H), 7.26–7.24 (m, 1H), 7.13–7.11 (m, 1H), 7.01–6.99 (m, 1H), 2.40 (s, 3H), 1.15 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 176.26, 139.98, 138.95, 134.70, 134.54, 130.11, 129.46, 129.35, 128.30, 127.79, 127.46, 125.01, 122.25, 39.67, 27.28, 21.34. **HRMS (ESI)**

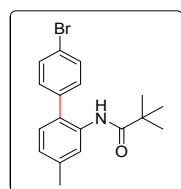
**[M+H]<sup>+</sup>** Calcd. for C<sub>18</sub>H<sub>21</sub>ClNO: 302.1312 Found: 302.1306. **IR (KBr, v/cm<sup>-1</sup>)** 3320, 1644.



**3v**, *N*-(2'-Chloro-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide. Yellow oil.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.13 (s, 1H), 7.55–7.53 (m, 1H), 7.39–7.37 (m, 2H), 7.33–7.29 (m, 1H), 7.13 (br, s, 1H), 7.10–7.08 (m, 1H), 7.03–7.01 (m, 1H), 2.42 (s, 3H), 1.07 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 176.21, 139.07, 136.78, 135.08, 133.74, 132.01, 129.64, 129.51, 129.26, 127.28, 127.25, 124.75, 121.93, 39.49, 27.11,

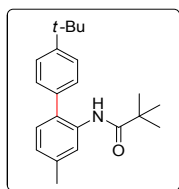
21.43. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>18</sub>H<sub>21</sub>ClNO: 302.1312 Found: 302.1314. **IR (KBr, v/cm<sup>-1</sup>)** 3441, 1692.



**3w**, *N*-(4'-Bromo-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide. White



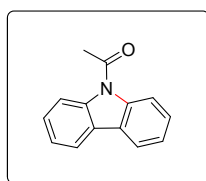
solid. mp 139 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.15 (s, 1H), 7.62–7.60 (m, 2H), 7.32 (br, s, 1H), 7.25–7.23 (m, 2H), 7.11–7.09 (m, 1H), 7.00–6.98 (m, 1H), 2.40 (s, 3H), 1.14 (s, 9H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 176.26, 138.83, 137.09, 134.54, 131.99, 130.97, 129.41, 128.40, 124.95, 122.10, 121.94, 39.67, 27.31, 21.33. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for  $\text{C}_{18}\text{H}_{21}\text{BrNO}$ : 346.0807 Found: 346.0809. **IR** (KBr,  $\text{v}/\text{cm}^{-1}$ ) 3266, 1646.



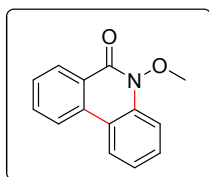
**3x**, *N*-(4'-(*tert*-Butyl)-4-methyl-[1,1'-biphenyl]-2-yl)pivalamide.

White solid. mp 109–110 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.24 (s, 1H), 7.52–7.47 (m, 3H), 7.30–7.28 (m, 2H), 7.16–7.14 (m, 1H), 6.99–6.97 (m, 1H), 2.41 (s, 3H), 1.38 (s, 9H), 1.10 (s, 9H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 176.17, 150.87, 138.16, 134.97, 129.34, 129.26, 129.00, 125.74, 124.48, 121.20, 39.65, 34.53, 31.19, 27.19, 21.35.

**HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for  $\text{C}_{22}\text{H}_{30}\text{NO}$ : 324.2327 Found: 324.2325. **IR** (KBr,  $\text{v}/\text{cm}^{-1}$ ) 3277, 1647.



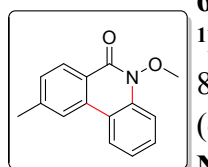
**4b**, 1-(9*H*-Carbazol-9-yl)ethanone.<sup>5</sup> White solid.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.22 (d,  $J$  = 8.0 Hz, 2H), 8.00 (d,  $J$  = 8.0 Hz, 2H), 7.51–7.47 (m, 2H), 7.42–7.38 (m, 2H), 2.89 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 169.91, 138.55, 127.21, 126.31, 123.54, 119.70, 116.13, 27.56. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for  $\text{C}_{14}\text{H}_{12}\text{NO}$ : 210.0919 Found: 210.0906.



**6a**, 5-Methoxyphenanthridin-6(5*H*)-one.<sup>9,10</sup> White solid.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.53 (d,  $J$  = 8.0 Hz, 1H), 8.23–8.20 (m, 2H), 7.75–7.72 (m, 1H), 7.65–7.63 (m, 1H), 7.58–7.53 (m, 2H), 7.33–7.29 (m, 1H), 4.13 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 157.12, 135.68, 132.83, 132.45, 129.79, 128.34, 127.88, 126.19, 123.05, 123.04, 121.78, 118.40, 112.45, 62.56. **HRMS (ESI)**

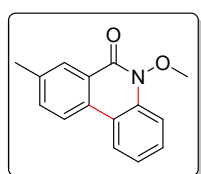
**[M+H]<sup>+</sup>** Calcd. for  $\text{C}_{14}\text{H}_{12}\text{NO}_2$ : 226.0868 Found: 226.0864.



**6b**, 5-Methoxy-9-methylphenanthridin-6(5*H*)-one.<sup>10</sup> White solid.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.45 (d,  $J$  = 8.0 Hz, 1H), 8.26 (d,  $J$  = 8.0 Hz, 1H), 8.06 (s, 1H), 7.68–7.66 (m, 1H), 7.60–7.56 (m, 1H), 7.42 (d,  $J$  = 8.0 Hz, 1H), 7.36–7.32 (m, 1H), 4.14 (s, 3H), 2.57 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 157.21, 143.07, 135.87, 132.85, 129.67, 129.35, 128.40, 123.95, 123.02, 122.90, 121.85, 118.41, 112.48, 62.55,

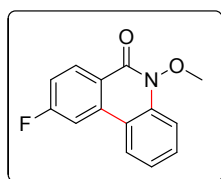
22.00. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for  $\text{C}_{15}\text{H}_{14}\text{NO}_2$ : 240.1025 Found: 240.1029.



**6c**, 5-Methoxy-8-methylphenanthridin-6(5*H*)-one.<sup>10</sup> White solid.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.37 (s, 1H), 8.24 (d,  $J$  = 8.0 Hz, 1H), 8.17 (d,  $J$  = 8.0 Hz, 1H), 7.69–7.67 (m, 1H), 7.61–7.55 (m, 2H), 7.36–7.33 (m, 1H), 4.15 (s, 3H), 2.54 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 157.24, 138.23, 135.38, 133.83, 130.41, 129.31, 128.15,

126.11, 123.00, 122.83, 121.81, 118.60, 112.46, 62.53, 21.18. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>15</sub>H<sub>14</sub>NO<sub>2</sub>: 240.1025 Found: 240.1022.

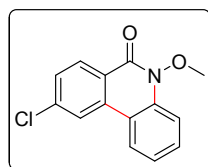


**6d, 9-Fluoro-5-methoxyphenanthridin-6(5H)-one.**<sup>10</sup> White solid.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.55 (dd, *J* = 8.0 Hz, 6.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.83 (dd, *J* = 12.0 Hz, 2.0 Hz, 1H), 7.66–7.58 (m, 2H), 7.35–7.31 (m, 1H), 7.29–7.24 (m, 1H), 4.13 (s, 3H);

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 165.52 (d, *J* = 251.0 Hz), 156.46, 136.12, 135.45 (d, *J* = 10.0 Hz), 131.51 (d, *J* = 10.0 Hz), 130.56,

123.28, 123.14, 122.71 (d, *J* = 2.0 Hz), 117.57 (d, *J* = 3.0 Hz), 116.17 (d, *J* = 23.0 Hz), 112.64, 107.82 (d, *J* = 24.0 Hz), 62.64. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>14</sub>H<sub>11</sub>FNO<sub>2</sub>: 244.0774 Found: 244.0769.

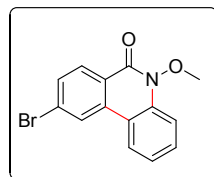


**6e, 9-Chloro-5-methoxyphenanthridin-6(5H)-one.**<sup>10</sup> White solid.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.47 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 1.6 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.67–7.59 (m, 2H), 7.53 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.37–7.33 (m, 1H), 4.14 (s, 3H); **<sup>13</sup>C**

**NMR (100 MHz, CDCl<sub>3</sub>):** δ = 156.51, 139.33, 136.13, 134.30, 130.57, 130.14, 128.32, 124.57, 123.26, 123.19, 121.76, 117.29,

112.65, 62.66. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>14</sub>H<sub>11</sub>ClNO<sub>2</sub>: 260.0478 Found: 260.0474.

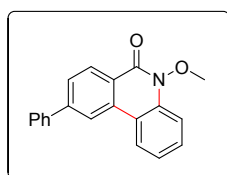


**6f, 9-Bromo-5-methoxyphenanthridin-6(5H)-one.**<sup>10</sup> Yellow solid.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.36 (d, *J* = 8.0 Hz, 1H), 8.33 (d, *J* = 1.2 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.67–7.56 (m, 3H), 7.34–7.30 (m, 1H), 4.12 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ =

156.59, 136.06, 134.39, 131.12, 130.56, 130.11, 127.94, 124.89, 124.84, 123.27, 123.16, 117.14, 112.62, 62.65. **HRMS (ESI)**

**[M+H]<sup>+</sup>** Calcd. for C<sub>14</sub>H<sub>11</sub>BrNO<sub>2</sub>: 303.9973 Found: 303.9971.

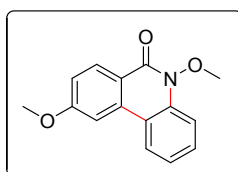


**6g, 5-Methoxy-9-phenylphenanthridin-6(5H)-one.**<sup>10</sup> White solid.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.63 (d, *J* = 8.0 Hz, 1H), 8.46 (s, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 7.83 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.75–7.70 (m, 3H), 7.63–7.60 (m, 1H), 7.56–7.52 (m, 2H), 7.48–7.44 (m, 1H), 7.40–7.36 (m, 1H), 4.17 (s, 3H); **<sup>13</sup>C NMR (100 MHz,**

**CDCl<sub>3</sub>):** δ = 157.10, 145.44, 140.10, 136.00, 133.23, 129.96, 129.03,

128.94, 128.27, 127.44, 127.12, 125.08, 123.11, 123.07, 120.32, 118.50, 112.61, 62.62. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>20</sub>H<sub>16</sub>NO<sub>2</sub>: 302.1181 Found: 302.1177.

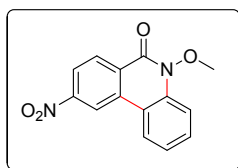


**6h, 5,9-Dimethoxyphenanthridin-6(5H)-one.**<sup>10</sup> White solid. **<sup>1</sup>H**

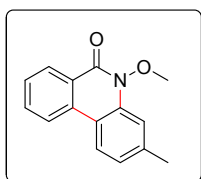
**NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.48 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.66–7.62 (m, 2H), 7.60–7.56 (m, 1H), 7.35–7.31 (m, 1H), 7.16 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 4.13 (s, 3H), 3.99 (s,

3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 163.03, 157.03, 136.12, 134.80, 130.52, 129.95, 123.08, 122.79, 119.77, 118.17, 115.76,

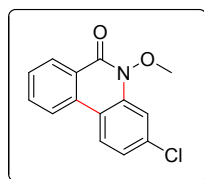
112.54, 104.82, 62.58, 55.47. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>15</sub>H<sub>14</sub>NO<sub>3</sub>: 256.0974  
Found: 256.0970.



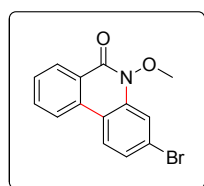
**6i, 5-Methoxy-9-nitrophenanthridin-6(5H)-one.**<sup>10</sup> Yellow solid. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 9.13 (d, *J* = 1.6 Hz, 1H), 8.75–8.72 (m, 1H), 8.38–8.33 (m, 2H), 7.75–7.68 (m, 2H), 7.48–7.44 (m, 1H), 4.18 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 155.71, 150.42, 136.32, 134.04, 131.43, 130.49, 130.18, 123.84, 123.57, 121.60, 117.65, 117.24, 112.93, 62.82. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>14</sub>H<sub>11</sub>N<sub>2</sub>O<sub>4</sub>: 271.0719 Found: 271.0714.



**6j, 5-Methoxy-3-methylphenanthridin-6(5H)-one.**<sup>9,10</sup> White solid. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.53 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.76–7.72 (m, 1H), 7.58–7.54 (m, 1H), 7.47 (s, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 4.14 (s, 3H), 2.52 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 157.31, 140.42, 135.67, 133.00, 132.41, 128.35, 127.41, 125.79, 124.27, 122.99, 121.56, 116.05, 112.55, 62.54, 21.73. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>15</sub>H<sub>14</sub>NO<sub>2</sub>: 240.1025 Found: 240.1023.



**6k, 3-Chloro-5-methoxyphenanthridin-6(5H)-one.**<sup>9</sup> White solid. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.54 (d, *J* = 8.0 Hz, 1H), 8.22–8.16 (m, 2H), 7.81–7.77 (m, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.64–7.60 (m, 1H), 7.31 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 4.15 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 157.13, 136.58, 135.96, 132.77, 132.21, 128.54, 128.24, 126.00, 124.42, 123.35, 121.78, 116.94, 112.50, 62.81. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>14</sub>H<sub>11</sub>ClNO<sub>2</sub>: 260.0478 Found: 260.0479.



**6l, 3-Bromo-5-methoxyphenanthridin-6(5H)-one.**<sup>10</sup> White solid. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ = 8.54 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.84–7.83 (m, 1H), 7.81–7.77 (m, 1H), 7.65–7.61 (m, 1H), 7.46 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 4.15 (s, 3H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ = 157.04, 136.64, 132.76, 132.24, 128.56, 128.32, 126.18, 126.10, 124.51, 123.95, 121.75, 117.34, 115.40, 62.82. **HRMS (ESI) [M+H]<sup>+</sup>** Calcd. for C<sub>14</sub>H<sub>11</sub>BrNO<sub>2</sub>: 303.9973 Found: 303.9969.

## 6. References

- (1) X. Yang, G. Shan and Y. Rao, *Org. Lett.*, 2013, **15**, 2334.
- (2) C. E. Houlden, C. D. Bailey, J. G. Ford, M. R. Gagné, G. C. Lloyd-Jones and K. I. Booker-Milburn, *J. Am. Chem. Soc.*, 2008, **130**, 10066.

- (3) W.-Y. Yu, W. N. Sit, Z. Zhou and A. S.-C. Chan, *Org. Lett.*, 2009, **11**, 3174.
- (4) G.-W. Wang, T.-T. Yuan and D.-D. Li, *Angew. Chem. Int. Ed.*, 2011, **50**, 1380.
- (5) R. K. Chinnagolla and M. Jeganmohan, *Chem. Commun.*, 2014, **50**, 2442.
- (6) C. S. Yeung, X. Zhao, N. Borduas and V. M. Dong, *Chem. Sci.*, 2010, **1**, 331.
- (7) G. Brasche, J. García-Fortanet and S. L. Buchwald, *Org. Lett.*, 2008, **10**, 2207.
- (8) C.-L. Ciana, R. J. Phipps, J. R. Brandt, F.-M. Meyer and M. J. Gaunt, *Angew. Chem. Int. Ed.*, 2011, **50**, 458.
- (9) J. Karthikeyan and C.-H. Cheng, *Angew. Chem. Int. Ed.*, 2011, **50**, 9880.
- (10) J. Karthikeyan, R. Haridharan and C.-H. Cheng, *Angew. Chem. Int. Ed.*, 2012, **51**, 12343.

## 7. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the products

