# **Supporting Information**

## The benzoyl peroxide-promoted functionalization of simple

## alkane with 2-aryl phenyl isonitrile

Wanxing Sha,<sup>†</sup> Jin-Tao Yu,<sup>†</sup> Haitao Yang,<sup>†</sup> Yan Jiang,<sup>†</sup> and Jiang Cheng<sup>\*†‡</sup>

<sup>†</sup> School of Petrochemical Engineering, Jiangsu Key Laboratory of Advanced Catalytic Materials & Technology, Jiangsu Province Key Laboratory of Fine Petrochemical Engineering, Changzhou University, Changzhou 213164, P. R. China

<sup>‡</sup> State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China

Email: jiangcheng@cczu.edu.cn

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#### **1** General experimental details

Chemicals were used as received without special purification unless stated otherwise. <sup>1</sup>H and <sup>13</sup>C NMR were recorded at ambient temperature on a 400 MHz NMR spectrometer (100 MHz for <sup>13</sup>C NMR). NMR experiments are reported in  $\delta$  units, parts per million (ppm), and were referenced to CDCl<sub>3</sub> ( $\delta$  7.26 or 77.0 ppm) as the internal standard. The coupling constants *J* are given in Hz.

#### **General synthetic procedures**

A sealed tube was charged with isocyanide (0.2 mmol), benzoyl peroxide (ca. 0.44 mmol) (The purity of BPO was 99%, containing 40% of water) and cyclohexane (2.0 mL). The mixture was kept stirring under air at 100 °C for 4 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product.

#### **2** Intermolecular KIE experiments

#### 2.1 KIE experiment of 1a and d<sub>5</sub>-la

In a sealed tube, the mixture of **1a** (0.1 mmol) and **d**<sub>5</sub>-**1a** (0.1 mmol) was treated under standard procedures and heated for **3** min.. After that, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether- ethyl acetate as eluent to give **3aa** and **d**<sub>4</sub>-**3aa**. The mixture of **3aa** and **d**<sub>4</sub>-**3aa** was analyzed using <sup>1</sup>H NMR spectrometer. As shown in **Figure S1-1**, the ratio of **3aa** and **d**<sub>4</sub>-**3aa** is nearly 1: 1.





Figure S1-1 The <sup>1</sup>H NMR spectrum of the KIE results with 3aa and d<sub>4</sub>-3aa

In a sealed tube, the mixture of 1a (0.1 mmol) and  $d_5-1a$  (0.1 mmol) was treated

under standard procedures and heated for 1 h. After that, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether- ethyl acetate as eluent to give **3aa** and **d**<sub>4</sub>-**3aa**. The mixture of **3aa** and **d**<sub>4</sub>-**3aa** was analyzed using <sup>1</sup>H NMR spectrometer. As shown in Figure S1-2, the ratio of **3aa** and **d**<sub>4</sub>-**3aa** is nearly 1.2: 1.



Scheme S1-2 KIE experiment of 1a and d<sub>5</sub>-la





Figure S1-2 The <sup>1</sup>H NMR spectrum of the KIE results with 3aa and d<sub>4</sub>-3aa

In a sealed tube, the mixture of **1a** (0.1 mmol) and **d**<sub>5</sub>-**1a** (0.1 mmol) was treated under standard procedures and heated for **2** h.. After that, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether- ethyl acetate as eluent to give **3aa** and **d**<sub>4</sub>-**3aa**. The mixture of **3aa** and **d**<sub>4</sub>-**3aa** was analyzed using <sup>1</sup>H NMR spectrometer. As shown in





Scheme S1-3 KIE experiment of 1a and d5-la



Figure S1-3 The <sup>1</sup>H NMR spectrum of the KIE results with 3aa and d<sub>4</sub>-3aa

#### 2.2 KIE experiment of d<sub>1</sub>-1a

In a sealed tube,  $d_1$ -1a (0.2 mmol) was treated by standard procedures. After completion of the reaction, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give product 3aa and  $d_1$ -3aa. The mixture was analyzed using <sup>1</sup>H NMR spectrometer. As shown in Figure S2, the ratio of 3aa and  $d_1$ -3aa is nearly 1: 1.



Scheme S2 KIE experiment of d<sub>1</sub>-1a



Figure S2 The <sup>1</sup>H NMR spectrum of the KIE results

#### **3** The KIE studies on cyclohexane

In a sealed tube, the mixture of **1a** (0.2 mmol), **cyclohexane/d<sub>12</sub>-cyclohexane** (1: 1, 2.0 mL) was treated under standard conditions for **3** min.. After that, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give product **3aa** and **d<sub>11</sub>-3aa**. The mixture was analyzed using <sup>1</sup>H NMR spectrometer. As shown in **Figure S3-1**, the ratio of **3aa** and **d<sub>11</sub>-3aa** is nearly 8.1: 1.



Scheme S3-1 KIE experiment of cyclohexane and d<sub>12</sub>-cyclohexane



Figure S3-1 The <sup>1</sup>H NMR spectrum of the KIE results

In a sealed tube, the mixture of **1a** (0.1 mmol), **cyclohexane/d<sub>12</sub>-cyclohexane** (1: 1, 1.0 mL) was treated under standard conditions for **1** h.. After that, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give product **3aa** and **d<sub>11</sub>-3aa**. The mixture was analyzed using <sup>1</sup>H NMR spectrometer. As shown in **Figure S3-2**, the ratio of **3aa** and **d<sub>11</sub>-3aa** is nearly 7.3: 1.



Scheme S3-2 KIE experiment of cyclohexane and  $d_{12}$ -cyclohexane



Figure S3-2 The <sup>1</sup>H NMR spectrum of the KIE results

In a sealed tube, the mixture of **1a** (0.1 mmol), **cyclohexane/d<sub>12</sub>-cyclohexane** (1: 1, 1.0 mL) was treated under standard conditions for **2** h.. After that, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give product **3aa** and **d<sub>11</sub>-3aa**. The mixture was analyzed using <sup>1</sup>H NMR spectrometer. As shown in **Figure S3-3**, the ratio of **3aa** and **d<sub>11</sub>-3aa** is nearly 6.1: 1.



Scheme S3-3 KIE experiment of cyclohexane and d<sub>12</sub>-cyclohexane



Figure S3-3 The <sup>1</sup>H NMR spectrum of the KIE results

## 4 Free radical capture experiments

### 4.1 Standard procedure





Residual time of 3aa: 13.217 min



4.2 Add 1.0 eq. of TEMPO to the reaction mixture







Figure S4 GC-MS spectra of free radical capture results

### 5 Characterization data for the products

6-cyclohexylphenanthridine (3aa)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 200) give **3aa** (39.2 mg, 75% yield) as yellowish oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.64 (d, J = 8.2 Hz, 1H), 8.54 (d, J = 8.1 Hz, 1H), 8.32 (d, J = 8.2 Hz, 1H), 8.16 (d, J = 8.1 Hz, 1H), 7.80 (t, J = 7.5 Hz, 1H), 7.73-7.67 (m, 2H), 7.61 (t, J = 7.7 Hz, 1H), 3.66-3.60 (m, 1H), 2.12-2.09 (m, 2H), 2.01-1.96 (m, 4H), 1.88-1.83 (m, 1H), 1.64-1.58 (m, 2H), 1.50-1.44 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 165.2, 143.8, 132.9, 129.9, 129.8, 128.3, 127.0, 126.1, 125.5, 124.7, 123.3, 122.5, 121.8, 41.9, 32.2, 26.8, 26.3.

MS (EI): 261 (M<sup>+</sup>); HRMS (APCI): Calcd. for  $C_{19}H_{20}N$  (M+H)<sup>+</sup> 262.1590, found 262.1593.

6-cyclohexyl-8-methylphenanthridine (3ba)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 200) give **3ba** (38.5 mg, 70% yield) as white solid. Mp: 128-131 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.54-8.48 (m, 2H), 8.12 (d, J = 8.0 Hz, 1H), 8.07 (s, 1H), 7.69-7.62 (m, 2H), 7.58 (t, J = 7.6 Hz, 1H), 3.63-3.57 (m, 1H), 2.62 (s, 3H), 2.08-1.84 (m, 7H), 1.64-1.55 (m, 2H), 1.49-1.43 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 165.0, 143.5, 136.8, 131.6, 130.8, 129.8, 127.9, 126.0, 125.0, 124.8, 123.4, 122.4, 121.6, 41.8, 32.2, 26.8, 26.3, 22.0.

MS (EI): 275 (M<sup>+</sup>); HRMS (APCI): Calcd. for  $C_{20}H_{22}N$  (M+H)<sup>+</sup> 276.1747, found 276.1749.

#### 6-cyclohexyl-3-methylphenanthridine (3ca)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 200) give **3ca** (37.4 mg, 68% yield) as yellowish solid. Mp: 91-94 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.61 (d, J = 8.2, 1H), 8.41 (d, J = 8.3 Hz, 1H), 8.29 (d,

J = 8.3 Hz, 1H), 7.95 (s, 1H), 7.79 (t, J = 7.2 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.43 (d, J = 8.2 Hz, 1H), 3.63-3.58 (m, 1H), 2.58 (s, 3H), 2.09-1.83 (m, 7H), 1.66-1.53 (m, 2H), 1.48-1.42 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  165.3, 143.9, 138.5, 133.0, 129.8, 129.5, 127.8, 126.6, 125.6, 124.4, 122.4, 121.6, 121.0, 41.9, 32.3, 26.8, 26.3, 21.4.

MS (EI): 275 (M<sup>+</sup>); HRMS (APCI): Calcd. for  $C_{20}H_{22}N$  (M+H)<sup>+</sup> 276.1747, found 276.1747.

#### 6-cyclohexyl-8-fluorophenanthridine (3da)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 200) give **3da** (42.4 mg, 76% yield) as yellowish solid. Mp: 96-99 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.59 (t, *J* = 7.6 Hz, 1H), 8.44 (d, *J* = 8.1 Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 10.3 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 3.50-3.43 (m, 1H), 2.08-2.05 (m, 2H), 2.00-1.84 (m, 5H), 1.63-1.53 (m, 2H), 1.49-1.41 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  164.3, 161.4 (d *J*<sub>C-F</sub> = 245.6 Hz), 143.5, 130.0, 129.7 (d, *J*<sub>C-F</sub> = 1.4 Hz), 128.2, 126.4, 126.0 (d, *J*<sub>C-F</sub> = 7.4 Hz), 125.0 (d, *J*<sub>C-F</sub> = 8.3 Hz), 122.8, 121.5, 118.9 (d, *J*<sub>C-F</sub> = 23.7 Hz), 110.2 (d, *J*<sub>C-F</sub> = 21.3 Hz), 42.1, 32.1, 26.7, 26.2.

MS (EI): 279 (M<sup>+</sup>); HRMS (APCI): Calcd. for  $C_{19}H_{19}FN$  (M+H)<sup>+</sup> 280.1496, found 280.1500.

#### 8-chloro-6-cyclohexylphenanthridine (3ea)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 200) give **3ea** (44.3 mg, 75% yield) as white solid. Mp: 145-146  $^{\circ}$ C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.57 (d, J = 8.8 Hz, 1H), 8.47 (d, J = 8.2 Hz, 1H), 8.24 (s, 1H), 8.13 (d, J = 8.1 Hz, 1H), 7.76-7.69 (m, 2H), 7.61 (t, J = 7.5 Hz, 1H), 3.53-3.48 (m, 1H), 2.06-1.84 (m, 7H), 1.60-1.53 (m, 2H), 1.47-1.41 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 164.2, 143.8, 133.0, 131.4, 130.4, 130.0, 128.7, 126.5, 125.7, 125.0, 124.4, 122.7, 121.7, 41.9, 32.2, 26.7, 26.2.

MS (EI): 295 (M<sup>+</sup>); HRMS (APCI): Calcd. for  $C_{19}H_{19}ClN (M+H)^+$  296.1201, found 296.1204.

#### 6-cyclohexyl-8-(trifluoromethyl)phenanthridine (3fa)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 200) give **3fa** (48.0 mg, 73% yield) as white solid. Mp: 122-125 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.72 (d, *J* = 8.6 Hz, 1H), 8.55 (s, 1H), 8.51 (d, *J* = 8.1 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 3.61-3.57 (m, 1H), 2.08-1.86 (m, 7H), 1.63-1.59 (m, 2H), 1.49-1.42 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  165.0, 144.5, 135.2, 130.1, 129.5, 128.8 (q, *J*<sub>C-F</sub> = 32.4 Hz), 126.7, 125.7 (q, *J*<sub>C-F</sub> = 3.1 Hz), 124.2 (q, *J*<sub>C-F</sub> = 270.7 Hz), 124.0, 123.6, 122.9 (q, *J*<sub>C-F</sub> = 4.2 Hz), 122.3, 122.1, 41.9, 32.3, 26.7, 26.2.

MS (EI): 329 (M<sup>+</sup>); HRMS (APCI): Calcd. for  $C_{20}H_{19}F_3N$  (M+H)<sup>+</sup> 330.1464, found 330.1465.

#### 6-cyclohexylphenanthridine-8-carbonitrile (3ga)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 100) give **3ga** (30.3 mg, 53% yield) as yellowish solid. Mp: 202-204 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.67 (d, J = 8.6 Hz, 1H), 8.61 (s, 1H), 8.48 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.78 (t, J = 7.4 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 3.54-3.48 (m, 1H), 2.04-1.85 (m, 7H), 1.63-1.54 (m, 2H), 1.46-1.40 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  164.4, 144.7, 135.6, 131.1, 131.0, 130.2, 130.1, 126.9, 124.0, 123.8, 122.2, 121.9, 118.8, 110.4, 41.9, 32.3, 26.6, 26.1. MS (EI): 286 (M<sup>+</sup>); HRMS (APCI): Calcd. for C<sub>20</sub>H<sub>19</sub>N<sub>2</sub> (M+H)<sup>+</sup> 287.1543, found 287.1543.

#### 1-(6-cyclohexylphenanthridin-8-yl)ethanone (3ha)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 40) give **3ha** (30.9 mg, 51% yield) as white solid. Mp: 120-123  $^{\circ}$ C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.90 (s, 1H), 8.66 (d, J = 8.6 Hz, 1H), 8.52 (d, J = 8.2 Hz, 1H), 8.31 (d, J = 8.6 Hz, 1H), 8.14 (d, J = 8.2 Hz, 1H), 7.75 (t, J = 7.7 Hz, 1H), 7.62 (t, J = 7.9 Hz, 1H), 3.67-3.65 (m, 1H), 2.78 (s, 3H), 2.08-2.05 (m, 2H), 1.99-1.85

(m, 5H), 1.66-1.56 (m, 2H), 1.48-1.42 (m, 1H);  $^{13}$ C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  197.4, 165.8, 144.7, 136.1, 135.2, 130.0, 129.6, 128.5, 126.5, 126.5, 124.1, 123.1, 122.5, 122.4, 41.9, 32.4, 26.8, 26.7, 26.2.

MS (EI): 303 (M<sup>+</sup>); HRMS (ESI): Calcd. for  $C_{21}H_{22}NO (M+H)^+$  304.1696, found 304.1687.

methyl 6-cyclohexylphenanthridine-8-carboxylate (3ia)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 100) give **3ia** (28.7 mg, 45% yield) as white solid. Mp: 148-151  $^{\circ}$ C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 9.01 (s, 1H), 8.65 (d, J = 8.6 Hz, 1H), 8.52 (d, J = 8.2 Hz, 1H), 8.38 (d, J = 8.6 Hz, 1H), 8.14 (d, J = 8.2 Hz, 1H), 7.74 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 4.04 (s, 3H), 3.71-3.66 (m, 1H), 2.08-2.05 (m, 2H), 1.99-1.93 (m, 4H), 1.89-1.85 (m, 1H), 1.67-1.57 (m, 2H), 1.48-1.39 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 166.8, 165.7, 144.6, 136.1, 130.0, 129.6, 129.5, 128.4, 127.9, 126.4, 124.1, 122.8, 122.6, 122.4, 52.4, 41.7, 32.4, 26.7, 26.2.

MS (EI): 319 (M<sup>+</sup>); HRMS (APCI): Calcd. for  $C_{21}H_{22}NO_2$  (M+H)<sup>+</sup> 320.1645, found 320.1646.

#### 6-cyclohexyl-3-fluorophenanthridine (3ja)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 200) give **3ja** (37.9 mg, 68% yield) as white solid. Mp: 103-105 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.53 (d, J = 8.2 Hz, 1H), 8.46 (dd,  $J_I$  = 9.0 Hz,  $J_2$  = 5.9 Hz, 1H), 8.30 (d, J = 8.3 Hz, 1H), 7.81-7.77 (m, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 8.6 Hz, 1H), 3.64-3.57 (m, 1H), 2.08-1.80 (m, 7H), 1.63-1.53 (m, 2H), 1.49-1.38 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  166.7, 162.5 (d,  $J_{C-F}$  = 245.7 Hz), 145.2 (d,  $J_{C-F}$  = 11.7 Hz), 132.7, 130.2, 126.8, 125.7, 124.2, 123.6 (d,  $J_{C-F}$  = 9.5 Hz), 122.3, 120.0 (d,  $J_{C-F}$  = 2.1 Hz), 115.0 (d,  $J_{C-F}$  = 23.5 Hz), 114.3 (d,  $J_{C-F}$  = 20 Hz), 42.0, 32.2, 26.8, 26.2.

MS (EI): 279 (M<sup>+</sup>); HRMS (APCI): Calcd. for  $C_{19}H_{19}FN$  (M+H)<sup>+</sup> 280.1496, found 280.1490.

6-cyclohexyl-2-fluorophenanthridine (3ka)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 200) give **3ka** (40.7 mg, 73% yield) as white solid. Mp: 123-125  $^{\circ}$ C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.50 (d, J = 8.2 Hz, 1H), 8.31 (d, J = 8.2 Hz, 1H), 8.13-8.09 (m, 2H), 7.81 (t, J = 7.6 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 8.3 Hz, 1H), 3.63-3.56 (m, 1H), 2.08-2.05 (m, 2H), 2.00-1.83 (m, 5H), 1.63-1.52 (m, 2H), 1.48-1.40 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  164.5, 160.8 (d  $J_{C-F}$  = 243.8 Hz), 140.7, 132.4 (d,  $J_{C-F}$  = 4.0 Hz), 132.0 (d,  $J_{C-F}$  = 9.0 Hz), 129.9, 127.7, 125.7, 124.7, 124.5 (d,  $J_{C-F}$  = 9.3 Hz), 122.7, 117.1 (d,  $J_{C-F}$  = 24.0 Hz), 106.7 (d,  $J_{C-F}$  = 22.9 Hz), 41.9, 32.3, 26.8, 26.3.

MS (EI): 279 (M<sup>+</sup>); HRMS (APCI): Calcd. for  $C_{19}H_{19}FN$  (M+H)<sup>+</sup> 280.1496, found 280.1490.

6-cyclohexyl-9-methylphenanthridine and 6-cyclohexyl-7-methylphenanthridine (3:2) (3la)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 200) give **3la** (40.2 mg, 73% yield) as yellowish oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.56-8.49 (m, 3.5H), 8.43 (s, 1.5H), 8.20 (d, J = 8.4 Hz, 1.5H), 8.14 (d, J = 8.1 Hz, 1.5H), 8.09 (d, J = 8.1 Hz, 1H), 7.71-7.66 (m, 2.5H), 7.64-7.55 (m, 3.5H), 7.51-7.47 (m, 2.5H), 3.83-3.76 (m, 1H), 3.62-3.56 (m, 1.5H), 3.02 (s, 3H), 2.64 (s, 4.5H), 2.04-1.85 (m, 17H), 1.60-1.45 (m, 8H);

MS (EI): 275 (M<sup>+</sup>); HRMS (APCI): Calcd. for  $C_{20}H_{22}N$  (M+H)<sup>+</sup> 276.1747, found 276.1753.

#### 6-cyclohexyl-2,4-difluorophenanthridine (3ma)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 200) give **3ma** (42.2 mg, 71% yield) as yellowish solid. Mp: 146-148 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.44 (d, J = 8.2 Hz, 1H), 8.32 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 9.8 Hz, 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.21-7.16 (m, 1H), 3.62-3.55 (m, 1H), 2.09-1.82 (m, 7H), 1.62-1.51 (m, 2H), 1.48-1.41 (m, 1H); <sup>13</sup>C

NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  164.8, 160.7 (dd  $J_I$ = 12.0 Hz  $J_2$ = 79.4 Hz), 158.2(dd  $J_I$ = 12.1 Hz  $J_2$  = 90.4 Hz), 131.8 (dd  $J_I$  = 3.2 Hz  $J_2$  = 4.1 Hz), 130.6 (dd  $J_I$ = 2.0 Hz  $J_2$  = 9.8 Hz), 130.3, 128.2, 125.8, 125.7 (dd  $J_I$  = 2.9 Hz  $J_2$  = 10.2 Hz), 125.1, 122.9, 103.7 (dd  $J_I$  = 23.5 Hz  $J_2$  = 27.9 Hz), 102.4 (dd  $J_I$  = 4.5 Hz  $J_2$  = 22.6 Hz), 42.2, 32.3, 26.8, 26.2.

MS (EI): 297 (M<sup>+</sup>); HRMS (APCI): Calcd. for  $C_{19}H_{18}F_2N$  (M+H)<sup>+</sup> 298.1402, found 298.1404.

6-cyclopentylphenanthridi (3ab)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 200) give **3ab** (33.1 mg, 67% yield) as yellowish oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.64 (d, J = 8.2 Hz, 1H), 8.53 (d, J = 8.1 Hz, 1H), 8.34 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 8.1 Hz, 1H), 7.81 (t, J = 8.1 Hz, 1H), 7.73-7.67 (m, 2H), 7.61 (t, J = 8.1 Hz, 1H), 4.12-4.04 (m, 1H), 2.31-2.16 (m, 4H), 2.00-1.92 (m, 2H), 1.86-1.80 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  164.1, 143.7, 132.9, 129.9, 129.8, 128.3, 127.0, 126.2, 126.0, 125.6, 123.4, 122.3, 121.8, 43.5, 32.1, 26.0. MS (EI): 247 (M<sup>+</sup>); HRMS (ESI): Calcd. for C<sub>18</sub>H<sub>18</sub>N (M+H)<sup>+</sup> 248.1434, found 248.1414.

#### 6-cycloheptylphenanthridine (3ac)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 200) give **3ac** (44.0 mg, 80% yield) as yellowish oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.64 (d, J = 8.2 Hz, 1H), 8.53 (d, J = 8.1 Hz, 1H), 8.30 (d, J = 8.3 Hz, 1H), 8.15 (d, J = 8.1 Hz, 1H), 7.80 (t, J = 7.6 Hz, 1H), 7.78-7.67 (m, 2H), 7.60 (t, J = 7.8 Hz, 1H), 3.83-3.76 (m, 1H), 2.18-2.12 (m, 4H), 1.99-1.95 (m, 2H), 1.84-1.07 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  166.5, 143.7, 133.0, 129.8, 129.8, 128.3, 127.0, 126.0, 125.7, 124.5, 123.2, 122.5, 121.7, 34.1, 28.1, 27.5 (possibly overlapped);

MS (EI): 275 (M<sup>+</sup>); HRMS (APCI): Calcd. for  $C_{20}H_{22}N$  (M+H)<sup>+</sup> 276.1747, found 276.1748.

#### 6-cyclooctylphenanthridine (3ad)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 200) give **3ad** (46.8 mg, 81% yield) as yellowish oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.65 (d, J = 8.2 Hz, 1H), 8.53 (d, J = 8.1 Hz, 1H), 8.31 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 8.1 Hz, 1H), 7.81 (t, J = 7.9 Hz, 1H), 7.73-7.68 (m, 2H), 7.60 (t, J = 8.1 Hz, 1H), 3.94-3.87 (m, 1H), 2.25-2.07 (m, 4H), 1.95-1.88 (m, 2H), 1.83-1.66 (m, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  167.1, 143.7, 133.1, 129.8, 129.8, 128.3, 127.0, 126.0, 125.7, 124.5, 123.2, 122.6, 121.7, 32.5, 26.8, 26.2 (possibly overlapped);

MS (EI): 289 (M<sup>+</sup>); HRMS (APCI): Calcd. for  $C_{21}H_{24}N$  (M+H)<sup>+</sup> 290.1903, found 290.1900.

#### 6-(hexan-2-yl)phenanthridine and 6-(hexan-3-yl)phenanthridine (1:1) (3ae)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 200) give **3ae** (32.6 mg, 62% yield) as yellowish oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.67 (d, J = 8.2 Hz, 2H), 8.57-8.54 (m, 2H), 8.37 (d, J = 8.3 Hz, 1H), 8.34 (d, J = 8.3 Hz, 1H), 8.17 (d, J = 8.1 Hz, 2H), 7.82 (t, J = 7.2 Hz, 2H), 7.74-7.68 (m, 4H), 7.62 (t, J = 7.4 Hz, 2H), 3.90-3.81 (m, 1H), 3.74-3.67 (m, 1H), 2.20-2.07 (m, 3H), 1.92-1.75 (m, 3H), 1.51 (d, J = 6.8 Hz, 3H), 1.47-1.21 (m, 8H), 0.92-0.88 (m, 7H);

MS (EI): 263 (M<sup>+</sup>); HRMS (APCI): Calcd. for  $C_{19}H_{22}N$  (M+H)<sup>+</sup> 264.1747, found 264.1748.

#### (R)-6-(3,3-dimethylbutan-2-yl)phenanthridine (3af)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 200) give **3af** (16.0 mg, 30% yield) as yellowish oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  8.67 (d, J = 8.2 Hz, 1H), 8.56 (d, J = 8.3 Hz, 1H), 8.42 (d, J = 8.3 Hz, 1H), 8.15 (d, J = 9.0 Hz, 1H), 7.81 (t, J = 7.0 Hz, 1H), 7.73-7.66 (m, 2H), 7.61 (t, J = 7.5 Hz, 1H), 3.86-3.81 (m, 1H), 1.49 (d, J = 6.9 Hz, 3H), 1.06 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  165.0, 143.5, 132.8, 130.1, 129.7, 128.2, 126.8, 126.3,

126.2, 126.0, 123.0, 122.4, 121.7, 43.4, 35.2, 28.3, 15.9. MS (EI): 263 (M<sup>+</sup>); HRMS (APCI): Calcd. for  $C_{19}H_{22}N$  (M+H)<sup>+</sup> 264.1747, found 264.1748.

## 6 Copies of <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra









































