

## Supporting Information

### Ruthenium-Catalyzed Synthesis of Indole Derivatives From N-Aryl-2-aminopyridines and *alpha*-Carbonyl Sulfoxonium Ylides

*State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, Department of Chemistry, Lanzhou University, Lanzhou 730000, China. E-mail: hgs@lzu.edu.cn*

Xin-Feng Cui,<sup>[a]</sup> Zi-Hui Ban,<sup>[a]</sup> Wa-Fa Tian,<sup>[b]</sup> Fang-Peng Hu,<sup>[a]</sup> Xiao-Qiang Zhou,<sup>[a,c]</sup> Hao-Jie Ma,<sup>[a]</sup> Zhen-Zhen Zhan<sup>[a]</sup> and Guo-Sheng Huang\*<sup>[a]</sup>

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- [a] State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, Department of Chemistry, Lanzhou University, Lanzhou 730000, China. E-mail: hgs@lzu.edu.cn  
[b] Institute of Organic Chemistry, Jiangxi Science & Technology Normal University, Key Laboratory of Organic Chemistry, Jiangxi Province, Nanchang 330013. China. E-mail: [tianwf12@lzu.edu.cn](mailto:tianwf12@lzu.edu.cn)  
[c] College of Chemistry and Material, Weinan Normal University, Shanxi Province, Weinan 714099. China. E-mail: zhouxq2017@163.com.

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## General methods

Commercially available reagents were used without additional purification, unless otherwise stated. Nuclear magnetic resonance spectra ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) were recorded on a Bruker Unity 300 MHz spectrometer for  $\text{CDCl}_3$  solutions and chemical shifts are reported as parts per million (ppm) relative to, respectively, residual  $\text{CHCl}_3$   $\delta\text{H}$  (7.24 ppm) and  $\text{CDCl}_3$   $\delta\text{C}$  (77.23 ppm) as internal standards. Resonance patterns are reported with the notations s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). In addition, the notation br is used to indicate a broad signal. Coupling constants (J) are reported in hertz (Hz).

### General procedure for the synthesis of pyrimidyl arylamines:<sup>1-3</sup>

To an oven-dried flask charged with aniline (977.8 mg, 10.5 mmol, 150 mol %), 2-chloropyrimidine (801.7 mg, 7.0 mmol, 100 mol %) and acetic acid (7 mL) in 1,4-dioxane (19 mL) was added. The reaction mixture was stirred at 110 °C for 24 h and monitored by TLC. Upon completion, the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 20$  mL) and washed with brine. The organic layer was dried over  $\text{Mg}_2\text{SO}_4$  and concentrated in vacuo. The residue was purified by flash column chromatography (n-hexanes/EtOAc) to give N-phenylpyrimidin-2-amine **1a** (990.6 mg) in 82% yield.

### General procedure for the synthesis of pyridinyl arylamines:<sup>1-3</sup>

To an oven-dried flask charged with aniline (1.4 g, 15 mmol, 100 mol %), 2-bromopyridine (2.4 g, 15 mmol, 100 mol %) was added. The reaction mixture was stirred at 160 °C for 7 h and monitored by TLC. Upon completion, saturated  $\text{NaHCO}_3$  was added and the mixture was extracted with EtOAc ( $3 \times 15$  mL). The combined organic phase was washed with brine and dried over  $\text{Mg}_2\text{SO}_4$ . The solid was filtered off and the filtrate was evaporated in vacuum. The crude product was purified by flash column chromatography (n-hexanes/EtOAc) to give N-phenylpyridin-2-amine **1a** (2.44 g) in 95% yield.

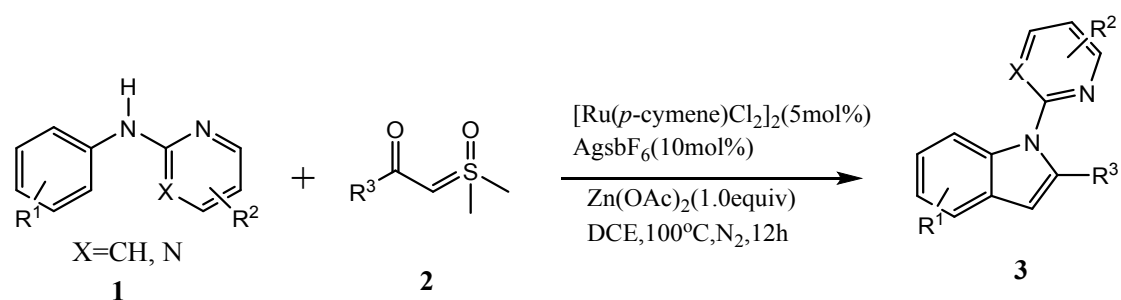
### General procedure for the synthesis of sulfoxonium ylides<sup>4</sup>

In a 250 mL flame-dried round bottom flask attached to a reflux condenser, under argon atmosphere, 6.0 g of potassium tert-butanolate (54.4 mmol, 4.0 equiv) and 60.0 mL of anhydrous THF was added. Then, 8.9 g of trimethylsulfoxonium iodide (40.8 mmol, 3.0 equiv) was added in one portion. The suspension was heated at reflux and maintained for 2 hours. After this time, the mixture was cooled to 0 °C, followed by slow addition of a 1.0 M solution of the benzoyl chlorides (13.6 mmol, 1.0 equiv) in anhydrous THF. The reaction mixture was allowed to warm to room temperature and stirred for additional 3 hours. Next, the solvent was removed on a rotary evaporator, 15.0 mL of water was added and the product extracted with EtOAc ( $3 \times 50$  mL). The organic phase was washed with saturated NaCl solution ( $2 \times 10$  mL) and dried over with  $\text{Na}_2\text{SO}_4$ . The crude product was purified by recrystallization with EtOAc.

## References:

- [1] X. Huang, S. Xu, Q. Tan, M. Gao, M. Lia and B. Xu, *Chem. Commun.*, 2014, **50**, 1465.
- [2] L. Ackermann and A. V. Lygin, *Org. Lett.*, 2012, **14**, 764.
- [3] G. Qian, B. Liu, Q. Tan, S. Zhang and B. Xu, *Eur. J. Org. Chem.*, 2014, 4837.
- [4] Barday, M.; Janot, C.; Halcovitch, N. R.; Muir, J.; Aïssa, C. *Angew. Chem., Int. Ed.* 2017, **56**, 13117.

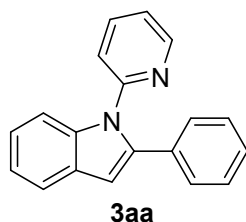
**Typical procedure for the for the Ru-Catalyzed Cyclization between Pyridin-2-amine and sulfoxonium ylides**



A pressure tube was charged with [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (8mg, 5mol%), AgSbF<sub>6</sub> (7mg, 10mol%), Zn(OAc)<sub>2</sub> (38mg, 1equiv) additive, pyridin-2-amine (**1**, 0.2 mmol), and dimethyloxosulfonium benzoylmethylide (**2**, 0.3mmol), DCE (2 mL) was then added and the mixture was stirred at 100 °C for 12h. Then the solvent was evaporated and the crude product was purified by column chromatography to afford the desired compound **3**.

## Characterization Data for the all Products

### 2-phenyl-1-(pyridin-2-yl)-1H-indole(3aa)

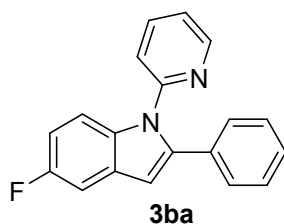


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3aa** as a white solid. M.p. 132-134 °C.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.63 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.67 (m, 2H), 7.60 (m, 1H), 7.29 – 7.18 (m, 8H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.80 (s, 1H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 152.06, 149.16, 139.94, 138.48, 137.72, 132.67, 128.72, 128.29, 127.40, 122.99, 121.99, 121.45, 120.54, 111.49, 105.59.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>H<sup>+</sup>, Calcd: 271.1230, Found: 271.1231.

### 5-fluoro-2-phenyl-1-(pyridin-2-yl)-1H-indole(3ba)

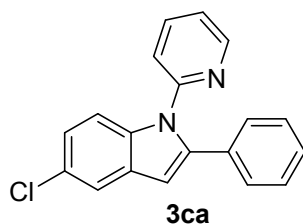


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ba** as a colorless liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.65 (m, 1H), 7.67 – 7.58 (m, 2H), 7.31 – 7.27 (m, 5H), 7.26 – 7.20 (m, 1H), 7.13 (dd, *J* = 10.4, 5.7 Hz, 1H), 6.97 (m, 1H), 6.84 (m, 1H), 6.76 (d, *J* = 0.7 Hz, 1H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 160.18, 157.05, 151.74, 149.05, 141.32, 137.69, 134.86, 132.21, 128.62, 128.25, 127.59, 121.71 (d, *J* = 12.6 Hz), 112.37 (d, *J* = 9.4 Hz), 111.11, 110.77, 105.25 (dd, *J* = 14.0, 9.6 Hz).

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>13</sub>FN<sub>2</sub>H<sup>+</sup>, Calcd: 289.1136, Found: 289.1137.

### 5-chloro-2-phenyl-1-(pyridin-2-yl)-1H-indole(3ca)

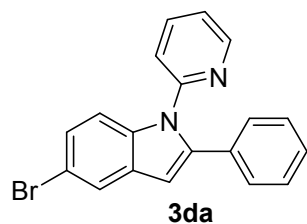


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ca** as a yellowish liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.63 (m, 1H), 7.63 – 7.56 (m, 3H), 7.27 – 7.19 (m, 6H), 7.15 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.83 (m, 1H), 6.72 (d, *J* = 0.7 Hz, 1H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 151.93, 149.48, 141.47, 138.13, 137.07, 132.42, 129.98, 129.02, 128.65, 128.05, 127.07, 123.38, 122.17, 120.14, 112.98, 105.13.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>13</sub>ClN<sub>2</sub>H<sup>+</sup>, Calcd: 305.0840, Found: 305.0842.

### 5-bromo-2-phenyl-1-(pyridin-2-yl)-1H-indole(3da)

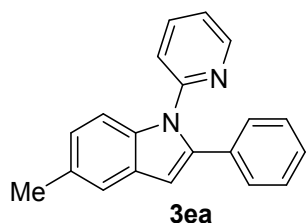


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3da** as a yellowish liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.64 (m, 1H), 7.81 – 7.77 (m, 1H), 7.64 – 7.55 (m, 2H), 7.32 – 7.21 (m, 7H), 6.85 (m, 1H), 6.73 (d, *J* = 0.5 Hz, 1H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 151.88, 149.49, 141.34, 138.16, 137.38, 132.36, 130.62, 129.04, 128.67, 128.08, 125.96, 123.24, 122.20, 114.70, 113.42, 105.00.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>13</sub>BrN<sub>2</sub>H<sup>+</sup>, Calcd: 349.0335, Found: 349.0336.

### 5-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole(3ea)

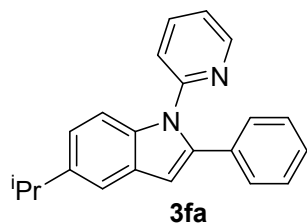


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ea** as a colorless liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.68 – 8.62 (m, 1H), 7.62 (m, 2H), 7.47 (s, 1H), 7.31 – 7.19 (m, 6H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.76 (s, 1H), 2.49 (s, 3H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 152.19 (s), 149.07 (s), 139.91, 137.62, 136.91, 132.79, 130.59, 128.91, 128.62, 128.23, 127.26, 124.52, 121.79, 121.35, 120.21, 111.18, 105.33, 21.38.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>H<sup>+</sup>, Calcd: 285.1386, Found: 285.1387.

### 5-isopropyl-2-phenyl-1-(pyridin-2-yl)-1H-indole(3fa)

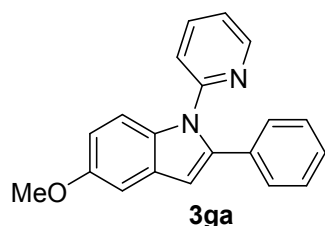


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3fa** as a yellowish liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.62 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.65 – 7.54 (m, 2H), 7.52 (d, *J* = 1.3 Hz, 1H), 7.29 – 7.11 (m, 7H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.76 (s, 1H), 3.03 (m, 1H), 1.33 (d, *J* = 6.9 Hz, 6H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 152.11, 149.02, 142.02, 139.90, 137.51, 137.00, 132.78, 128.63, 128.16, 127.19, 122.16, 121.68, 121.26, 117.34, 111.23, 105.47, 34.05, 24.47.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>H<sup>+</sup>, Calcd: 313.1699, Found: 313.1697.

### 5-methoxy-2-phenyl-1-(pyridin-2-yl)-1H-indole(3ga)

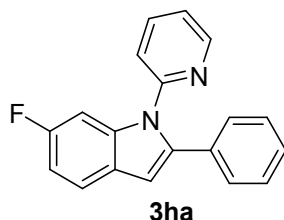


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ga** as a white solid. M.p. 91-92 °C.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ= 8.61 (m, 1H), 7.65 – 7.53 (m, 2H), 7.29 – 7.22 (m, 5H), 7.18 (m, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 6.90 – 6.79 (m, 2H), 6.73 (d, *J* = 0.7 Hz, 1H), 3.87 (s, 3H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ= 155.44, 152.40, 149.36, 140.64, 137.95, 133.94, 132.98, 129.46, 128.93, 128.58, 127.67, 122.04, 121.67, 113.13, 112.76, 105.79, 102.48, 56.05.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>OH<sup>+</sup>, Calcd: 301.1336, Found: 301.1337.

**6-fluoro-2-phenyl-1-(pyridin-2-yl)-1H-indole(3ha)**

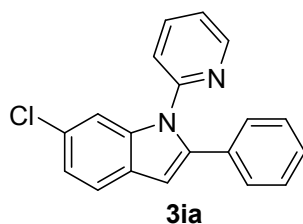


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ha** as a colorless liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ= 8.65 (m, 1H), 7.67 – 7.60 (m, 1H), 7.48 – 7.43 (m, 1H), 7.29 – 7.22 (m, 6H), 7.18 – 7.10 (m, 1H), 6.92 – 6.85 (m, 3H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ= 157.98, 154.71, 152.03, 149.53, 141.02 (d, *J* = 10.6 Hz), 140.27, 138.17, 132.41, 129.05, 128.65, 128.00, 123.65 (d, *J* = 7.6 Hz), 122.30 (d, *J* = 1.8 Hz), 118.22, 117.92, 107.89 (d, *J* = 3.7 Hz), 106.38 (d, *J* = 18.7 Hz), 101.26.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>13</sub>FN<sub>2</sub>H<sup>+</sup>, Calcd: 289.1136, Found: 289.1139.

**6-chloro-2-phenyl-1-(pyridin-2-yl)-1H-indole(3ia)**

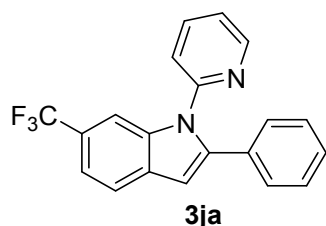


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ia** as a yellowish liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ=8.65 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.70 (d, *J* = 1.3 Hz, 1H), 7.61 (m, 2H), 7.29 – 7.21 (m, 6H), 7.16 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.76 (s, 1H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ =151.51, 149.24, 140.58, 138.68, 137.86, 132.14, 128.64, 128.33, 127.64, 127.15, 122.17, 121.67, 121.28, 111.66, 105.30.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>13</sub>ClN<sub>2</sub>H<sup>+</sup>, Calcd: 305.0840, Found: 305.0843.

**2-phenyl-1-(pyridin-2-yl)-6-(trifluoromethyl)-1H-indole(3ja)**

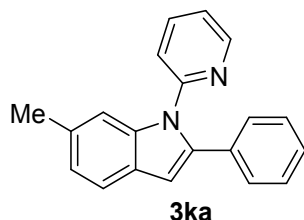


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ja** as a yellowish liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ= 8.67 (d, *J* = 4.8 Hz, 1H), 7.96 (s, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.63 (m, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.28 (s, 6H), 6.88 – 6.80 (m, 2H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ= 151.24, 149.34, 142.48, 137.98, 137.24, 131.82, 130.93, 128.78, 128.38, 127.98, 122.04 (d, *J* = 14.6 Hz), 120.77, 117.90 (d, *J* = 3.4 Hz), 109.20 (d, *J* = 4.5 Hz), 105.14.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>20</sub>H<sub>13</sub>F<sub>3</sub>N<sub>2</sub>H<sup>+</sup>, Calcd: 339.1104, Found: 339.1106.

**6-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole(3ka)**

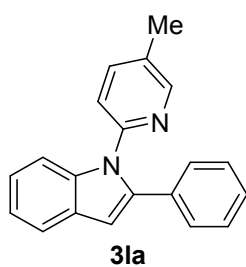


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ka** as a white solid. M.p. 147-149 °C.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ=8.66 (m, 1H), 7.65 – 7.47 (m, 3H), 7.29 – 7.20 (m, 6H), 7.07 – 7.00 (m, 1H), 6.90 – 6.84 (m, 1H), 6.76 (d, *J* = 0.8 Hz, 1H), 2.46 (s, 3H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ=152.46, 149.39, 139.61, 139.18, 137.96, 133.16, 128.86, 128.51, 127.46, 126.77, 123.28, 122.32, 121.73, 120.43, 111.63, 105.79, 22.19.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>H<sup>+</sup>, Calcd: 285.1386, Found: 285.1388.

**1-(5-methylpyridin-2-yl)-2-phenyl-1H-indole(3la)**

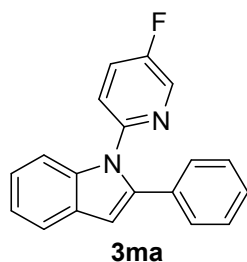


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3la** as a yellowish liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ= 8.44 (d, *J* = 2.2 Hz, 1H), 7.63 (m, 2H), 7.41 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.30 – 7.16 (m, 7H), 6.79 (t, *J* = 4.0 Hz, 2H), 2.35 (s, 3H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ =149.66, 149.29, 139.95, 138.45, 132.68, 131.29, 128.60, 128.20, 127.26, 122.77, 121.42, 121.07, 120.43, 111.35, 105.04, 17.93.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>H<sup>+</sup>, Calcd: 285.1386, Found: 285.1385.

**1-(5-fluoropyridin-2-yl)-2-phenyl-1H-indole(3ma)**

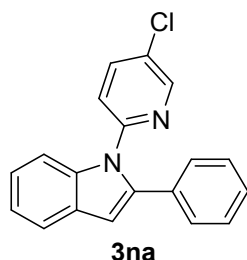


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ma** as a yellowish liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ= 8.48 (d, *J* = 3.0 Hz, 1H), 7.67 (m, 1H), 7.62 – 7.57 (m, 1H), 7.38 – 7.20 (m, 8H), 6.87 (m, 1H), 6.80 (t, *J* = 1.0 Hz, 1H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ= 159.68, 156.29, 148.36, 140.25, 138.79, 137.42, 137.08, 132.69, 129.22 – 128.55 (m), 127.84, 125.15 (d, *J* = 20.0 Hz), 123.59 – 122.99 (m), 121.72, 120.91, 111.50, 105.80.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>13</sub>FN<sub>2</sub>H<sup>+</sup>, Calcd: 289.1136, Found: 289.1138.

#### 1-(5-chloropyridin-2-yl)-2-phenyl-1H-indole(**3na**)

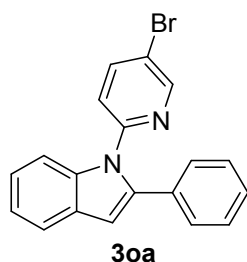


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3na** as a colorless liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.57 (dd, *J* = 2.6, 0.6 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.54 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.30 – 7.20 (m, 7H), 6.81 – 6.75 (m, 2H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 150.57, 148.12, 140.05, 138.58, 137.73, 132.66, 129.72, 129.53, 128.62, 127.92, 123.53, 122.73, 121.92, 120.95, 111.77, 106.45.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>13</sub>ClN<sub>2</sub>H<sup>+</sup>, Calcd: 305.0840, Found: 305.0843.

#### 1-(5-bromopyridin-2-yl)-2-phenyl-1H-indole(**3oa**)



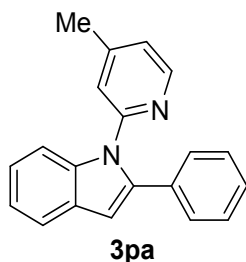
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3oa** as a yellowish liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.68 – 8.64 (m, 1H), 7.72 – 7.62 (m, 3H), 7.32 – 7.19 (m, 8H), 6.79 (d, *J* = 0.8 Hz, 1H), 6.73 – 6.68 (m, 1H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 151.00, 150.36, 140.53, 140.00, 138.53, 132.66, 128.93, 127.94, 123.57, 123.22, 121.96, 120.96, 118.05, 111.83, 106.58.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>13</sub>BrN<sub>2</sub>H<sup>+</sup>, Calcd: 349.0335, Found: 349.0334.

#### 1-(4-methylpyridin-2-yl)-2-phenyl-1H-indole(**3pa**)



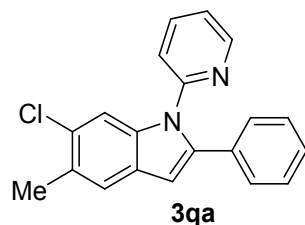


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3pa** as a yellowish liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.45 (d, *J* = 5.1 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.22 (m, 7H), 7.03 (d, *J* = 5.1 Hz, 1H), 6.83 – 6.72 (m, 2H), 2.21 (s, 3H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 152.03, 149.28, 148.80, 140.07, 138.59, 132.74, 128.73, 128.22, 127.32, 123.11, 122.53, 121.17, 120.52, 111.42, 105.25, 20.91.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>H<sup>+</sup>, Calcd: 285.1386, Found: 285.1389.

**6-chloro-5-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole(3qa)**

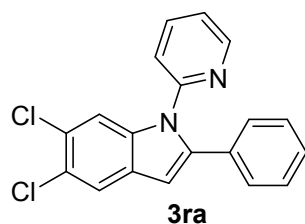


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3qa** as a yellowish liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.63 (d, *J* = 3.8 Hz, 1H), 7.74 (s, 1H), 7.58 (m, 1H), 7.47 (s, 1H), 7.29 – 7.18 (m, 6H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.69 (s, 1H), 2.46 (s, 3H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 151.72, 149.19, 140.42, 137.79, 137.40, 132.31, 129.58, 128.66, 128.33, 127.58, 121.62, 111.96, 105.06, 20.33.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>20</sub>H<sub>15</sub>ClN<sub>2</sub>H<sup>+</sup>, Calcd: 319.0997, Found: 319.0999.

**5,6-dichloro-2-phenyl-1-(pyridin-2-yl)-1H-indole(3ra)**

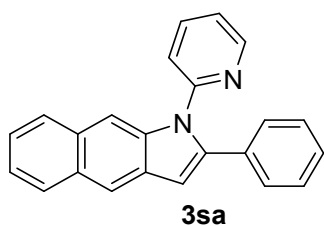


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ra** as a yellowish liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.67 – 8.62 (m, 1H), 7.83 (s, 1H), 7.71 (s, 1H), 7.61 (m, 1H), 7.31 – 7.21 (m, 6H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.69 (s, 1H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 151.27, 149.30, 141.77, 137.98, 137.10, 131.75, 128.72, 128.59, 127.87, 126.61, 125.14, 122.10, 121.76, 121.30, 113.37, 104.61.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>2</sub>H<sup>+</sup>, Calcd: 339.0451, Found: 339.0450.

**2-phenyl-1-(pyridin-2-yl)-1H-benzo[f]indole(3sa)**

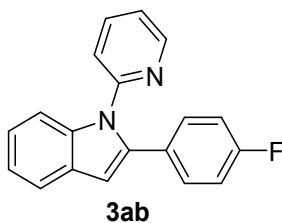


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3sa** as a yellow solid. M.p. 167-169 °C.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ= 8.68 (d, *J* = 3.5 Hz, 1H), 8.15 (d, *J* = 17.5 Hz, 2H), 7.90 (m, 2H), 7.61 (m, 1H), 7.39 – 7.16 (m, 8H), 6.96 – 6.82 (m, 2H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ= 152.38, 149.20, 143.56, 138.93, 137.75, 132.41, 130.96, 130.01, 129.75, 128.67, 128.38, 127.87, 123.89, 123.17, 121.75, 121.33, 117.97, 107.22, 105.45.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>23</sub>H<sub>16</sub>N<sub>2</sub>H<sup>+</sup>, Calcd: 321.1386, Found: 321.1387.

**2-(4-fluorophenyl)-1-(pyridin-2-yl)-1H-indole(3ab)**

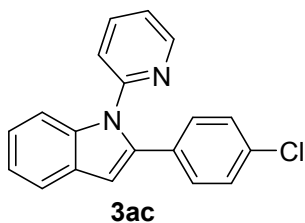


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ab** as a white solid. M.p. 143-145 °C.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ= 8.62 (dd, *J* = 4.9, 1.9 Hz, 1H), 7.69 – 7.60 (m, 3H), 7.27 – 7.18 (m, 5H), 7.00 – 6.87 (m, 3H), 6.76 (s, 1H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ= 163.67, 160.39, 151.71, 149.14, 138.76, 138.25, 137.70, 130.21, 128.56, 122.92, 121.68, 121.26, 120.40, 115.37, 115.08, 111.26, 105.32.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>13</sub>FN<sub>2</sub>H<sup>+</sup>, Calcd: 289.1136, Found: 289.1134.

**2-(4-chlorophenyl)-1-(pyridin-2-yl)-1H-indole(3ac)**

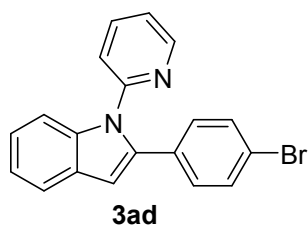


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ac** as a white solid. M.p. 111-1113 °C.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ= 8.63 – 8.57 (m, 1H), 7.63 (m, 3H), 7.25 – 7.15 (m, 7H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.79 (s, 1H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ= 151.78, 149.34, 138.64, 137.96, 133.39, 131.19, 129.82, 128.56, 123.27, 121.86, 121.49, 120.68, 111.43, 105.89.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>13</sub>ClN<sub>2</sub>H<sup>+</sup>, Calcd: 305.0840, Found: 305.0841.

**2-(4-bromophenyl)-1-(pyridin-2-yl)-1H-indole(3ad)**

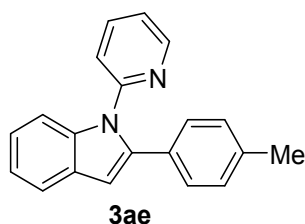


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ad** as a white solid. M.p. 123-126 °C.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.65 – 8.58 (m, 1H), 7.70 – 7.60 (m, 3H), 7.42 – 7.34 (m, 2H), 7.27 – 7.18 (m, 3H), 7.15 – 7.08 (m, 2H), 6.96 – 6.89 (m, 1H), 6.80 (s, 1H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 151.83, 149.42, 138.72, 138.05, 131.63, 130.16, 128.62, 123.37, 121.78, 120.75, 111.50, 105.99.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>13</sub>BrN<sub>2</sub>H<sup>+</sup>, Calcd: 349.0335, Found: 349.0334.

**1-(pyridin-2-yl)-2-(p-tolyl)-1H-indole(3ae)**

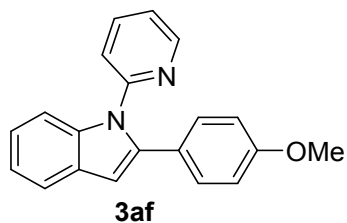


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ae** as a yellowish liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.62 (m, 1H), 7.69 – 7.54 (m, 3H), 7.23 – 7.13 (m, 5H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.90 – 6.84 (m, 1H), 6.78 – 6.74 (m, 1H), 2.31 (s, 3H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 152.43, 149.40, 140.35, 138.71, 138.00, 137.57, 130.04, 129.33, 128.97, 125.42, 123.10, 122.33, 121.83, 121.56, 120.71, 111.76, 105.43, 21.48.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>H<sup>+</sup>, Calcd: 285.1386, Found: 285.1388.

**2-(4-methoxyphenyl)-1-(pyridin-2-yl)-1H-indole(3af)**

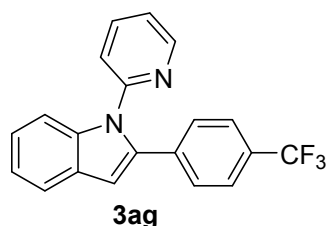


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3af** as a white solid. M.p. 125-127 °C.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.65 – 8.60 (m, 1H), 7.68 – 7.56 (m, 3H), 7.23 – 7.15 (m, 5H), 6.90 – 6.84 (m, 1H), 6.84 – 6.76 (m, 2H), 6.75 – 6.71 (m, 1H), 3.77 (s, 3H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 159.32, 152.43, 149.39, 140.11, 138.57, 137.99, 130.25, 129.06, 125.45, 122.94, 122.32, 121.80, 121.53, 120.57, 114.08, 111.69, 104.93, 55.48.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>20</sub>H<sub>16</sub>ON<sub>2</sub>H<sup>+</sup>, Calcd: 301.1336, Found: 301.1338.

**1-(pyridin-2-yl)-2-(4-(trifluoromethyl)phenyl)-1H-indole(3ag)**

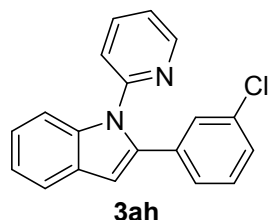


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ag** as a white solid. M.p. 138-140 °C.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.66 – 8.59 (m, 1H), 7.73 – 7.62 (m, 3H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.17 (m, 3H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.88 (s, 1H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 151.67, 149.49, 138.86, 138.24 (d, *J* = 16.7 Hz), 136.26, 128.58 (d, *J* = 12.9 Hz), 125.29 (d, *J* = 3.7 Hz), 123.70, 122.15, 121.38, 120.96, 111.47, 106.92.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>20</sub>H<sub>13</sub>F<sub>3</sub>N<sub>2</sub>H<sup>+</sup>, Calcd: 339.1104, Found: 339.1105.

**2-(3-chlorophenyl)-1-(pyridin-2-yl)-1H-indole(3ah)**

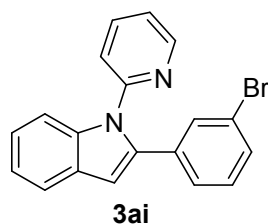


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ah** as a white solid. M.p. 133-136 °C.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.62 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.66 (m, 3H), 7.33 (d, *J* = 1.6 Hz, 1H), 7.29 – 7.12 (m, 5H), 7.08 – 7.02 (m, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.83 (s, 1H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 151.89, 149.56, 138.70, 138.15, 134.69, 134.40, 129.65, 128.69, 127.59, 126.97, 123.61, 122.07, 121.70, 120.98, 111.64, 106.48.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>13</sub>ClN<sub>2</sub>H<sup>+</sup>, Calcd: 305.0840, Found: 305.0842.

**2-(3-bromophenyl)-1-(pyridin-2-yl)-1H-indole(3ai)**

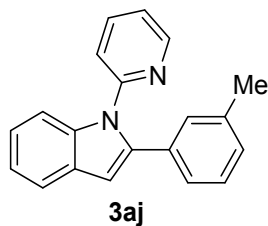


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3ai** as a gray solid. M.p. 129-132 °C.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.62 (m, 1H), 7.70 – 7.62 (m, 3H), 7.49 (m, 1H), 7.35 (m, 1H), 7.26 – 7.16 (m, 3H), 7.10 – 7.05 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 0.5 Hz, 1H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 151.94, 149.63, 138.90, 138.53, 138.23, 135.02, 131.65, 130.56, 129.97, 128.75, 127.48, 123.70, 122.63, 122.16, 121.78, 121.07, 111.71, 106.59.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>13</sub>BrN<sub>2</sub>H<sup>+</sup>, Calcd: 349.0335, Found: 349.0333.

**1-(pyridin-2-yl)-2-(m-tolyl)-1H-indole(3aj)**

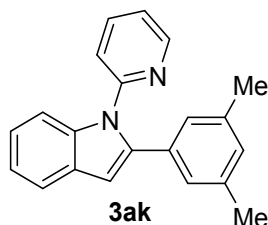


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3aa** as a white solid. M.p. 103-105 °C.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.63 (m, 1H), 7.71 – 7.57 (m, 3H), 7.24 – 7.14 (m, 4H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.89 (dd, *J* = 8.1, 0.8 Hz, 1H), 6.79 (d, *J* = 0.6 Hz, 1H), 2.28 (s, 3H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 152.14, 149.11, 140.14, 138.48, 137.98, 137.68, 132.56, 129.41, 128.73, 128.15, 125.88, 122.91, 122.03, 121.41, 120.51, 111.50, 105.46, 21.40.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>H<sup>+</sup>, Calcd: 285.1386, Found: 285.1387.

### 2-(3,5-dimethylphenyl)-1-(pyridin-2-yl)-1H-indole(**3ak**)

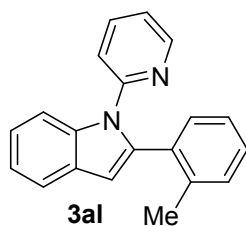


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3aa** as a yellowish liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.65 – 8.60 (m, 1H), 7.70 – 7.56 (m, 3H), 7.25 – 7.15 (m, 3H), 6.89 (dd, *J* = 7.0, 0.7 Hz, 4H), 6.79 – 6.76 (m, 1H), 2.21 (d, *J* = 0.5 Hz, 6H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 152.25, 149.08, 140.32, 138.48, 137.71, 132.49, 129.18, 128.78, 126.63, 122.85, 122.09, 121.39, 120.50, 111.53, 105.37, 21.29.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>H<sup>+</sup>, Calcd: 299.1543, Found: 299.1545.

### 1-(pyridin-2-yl)-2-(o-tolyl)-1H-indole(**3al**)

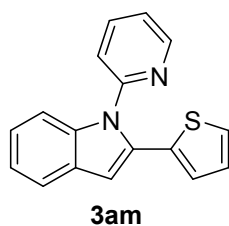


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3aa** as a white solid. M.p. 151-154 °C.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.57 (m, 1H), 7.88 – 7.82 (m, 1H), 7.69 – 7.64 (m, 1H), 7.48 (m, 1H), 7.33 – 7.27 (m, 1H), 7.26 – 7.20 (m, 3H), 7.19 – 7.09 (m, 3H), 6.69 (m, 2H), 2.06 (s, 3H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 152.16, 149.11, 139.23, 137.93, 137.00, 132.99, 131.33, 130.42, 128.89, 128.52, 125.84, 123.10, 121.39, 120.69, 112.23, 106.43, 20.42.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>H<sup>+</sup>, Calcd: 285.1386, Found: 285.1387.

### 1-(pyridin-2-yl)-2-(thiophen-2-yl)-1H-indole(**3am**)

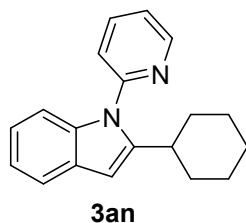


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3aa** as a yellow solid. M.p. 154-157 °C.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ= 8.69 (m, 1H), 7.74 (m, 1H), 7.66 (m, 1H), 7.52 – 7.47 (m, 1H), 7.32 (m, 1H), 7.27 – 7.17 (m, 3H), 7.14 (m, 1H), 6.94 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.88 (d, *J* = 0.7 Hz, 1H), 6.77 (dd, *J* = 3.6, 1.1 Hz, 1H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ= 151.80, 149.65, 138.85, 138.28, 134.56, 133.49, 128.61, 127.56, 126.82, 126.02, 123.44, 122.70, 121.62, 120.79, 111.40, 105.81.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>SH<sup>+</sup>, Calcd: 277.0794, Found: 277.0795.

**2-cyclohexyl-1-(pyridin-2-yl)-1H-indole(3an)**



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) give **3aa** as a colorless liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ = 8.66 (m, 1H), 7.87 (m, 1H), 7.61 – 7.54 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.22 (m, 2H), 7.14 – 7.06 (m, 2H), 6.44 (s, 1H), 2.99 (m, 1H), 1.90 (d, *J* = 12.9 Hz, 2H), 1.70 (m, 3H), 1.46 – 1.33 (m, 2H), 1.28 – 1.18 (m, 3H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ = 151.99, 149.90, 147.45, 138.53, 137.54, 128.82, 122.39, 121.72, 120.72, 120.22, 110.18, 100.08, 35.86, 33.44, 26.72, 26.44.

**HRMS [ESI, (M+H)<sup>+</sup>]:** C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>H<sup>+</sup>, Calcd: 277.1699, Found: 277.1698.

