# **Supporting Information**

# Palladium Catalyzed Direct C3-Cyanation of Indoles Using Acetonitrile as the Cyanide Source

Bifu Liu,<sup>a</sup> Min Liu,<sup>\*a,d</sup> Qiang Li,<sup>b,c</sup> Yuanhua Li,<sup>a</sup> Kejun Feng<sup>a</sup> and Yongbo Zhou<sup>c</sup>

<sup>a</sup> School of Chemistry and Materials Engineering, Huizhou University, Huizhou, 516007, Guangdong, China

<sup>b</sup> College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, Shandong 252059, China

<sup>c</sup> College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China

<sup>d</sup> Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, China

E-mail: minliu1018@163.com;

# Contents

General information	2
Control experiment	2
General Procedure for the preparation of N-benzyl/alkyl indole substrates	3
General Procedure for the preparation of N-phenyl indole substrates	3
General Procedure for the preparation of 1-Benzyl-1H-indole-3-carbonitrile:	4
Characterization and analytical data of products	4
Reference	10
Copies of 1H NMR and 13C NMR spectroscopies1	1-32

## **General information**

All reactions were carried out under O<sub>2</sub> atmosphere (1 atm) using standard Schlenk technique in the parallel synthesizer. All reagent/reactant were commercially available except other noted. The substituted indole substrates were prepared according to the known methods. DMF and CH<sub>3</sub>CN were purified according to the <Purification of Laboratory Chemicals: The Six Edition > before being used. Column chromatography was performed using Silica Gel 60 (particle size 37-54 µm). The pure products were obtained by column chromatography using ethyl acetate/petroleum ether as an eluent and detected by NMR using CDCl<sub>3</sub> as the deuterium reagent. GC analysis was performed on GC 7820A (Shimadzu). GC-MS results were recorded on GC-MS QP2010 (Shimadzu). The <sup>1</sup>H NMR and <sup>13</sup>C NMR data were data were acquired on a Brucker ADVANCE III spectrometer (400 MHz for <sup>1</sup>H NMR spectroscopy and 100 MHz for <sup>13</sup>C NMR spectroscopy). Exact mass was conducted by the College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, 325000, China



# **Control experiment**

#### General Procedure for the preparation of N-benzyl/alkyl indole substrates:

Commercially available substituted indole (10 mmol) was dissolved in a freshly distilled DMF (20 mL) at room temperature under a nitrogen atmosphere. KOH (0.67 g, 12 mmol) was then added into the reaction mixture and kept stirring at room temperature. After all the KOH were dissolved, benzyl bromide/2-bromopropane was added dropwisely. The mixture was then stirred overnight and 25 ml of water was added to the mixture and stirred for 30 min. The mixture was then extracted with dichloromethane (100 ml) and the organic layer was washed with water (100 ml) twice. The solvent was then removed by reduced pressure. The crude product was filtered through a short silica pad ( $3 \times -10$  cm) and washed with DCM/petroleum ether/triethylamine. The solution was evaporated and then dried under vacuum to afford desired products, and the isolated yields of the indole substrates as shown in the image below. All of them are known compounds, the corresponding spectra and compounds data can be found in some articles. <sup>1-4</sup>



## General Procedure for the preparation of N-phenyl indole substrates:

A mixture of indole (0.82 g, 7.0 mmol), iodobenzene (1.02 g, 5.0 mmol), CuI (191 mg, 1.0 mmol),  $Cs_2CO_3$  (3.26 g, 10 mmol), in DMF (10 mL) was vigorously stirred at 120 °C under nitrogen atmosphere for 16 h. After cooling the mixture to ambient temperature, the reaction mixture was diluted with EtOAc (40 mL) and washed with H<sub>2</sub>O (2×30 mL). The aqueous phase was extracted with EtOAc (2×30 mL), and the combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (petroleum ether) to give the corresponding substituted indoles,

and the isolated yields of the indole substrates as shown in the image below. All of them are known compounds, the corresponding spectra and compounds data can be found in some articles. <sup>1-4</sup>



# General Procedure for the preparation of 1-Benzyl-1H-indole-3-carbonitrile:

A mixture of *N*-benzyl indole (0.2 mmol, 41.4 mg), PdCl<sub>2</sub> (0.01 mmol, 1.8 mg), Cu(OAc)<sub>2</sub> (0.3 mmol, 54.3 mg), AgOTf (0.2 mmol, 51.4 mg) and 4-NO<sub>2</sub>-PhCOOH (0.2 mmol, 33.4 mg) was added to a 25 mL Schleck tube with a combined solvent (CH<sub>3</sub>CN/DMF = 3.5 mL/1.5 mL), the solution was then vigorously stirred at 135 °C under O<sub>2</sub> atmosphere (1 atm) for 24 h. After cooling the mixture to ambient temperature, the reaction mixture was filtrated and evaporated to remove the solvent and the crude product was purified by column chromatography on silica gel (DCM/hexane = 1:1, Rf = 0.5) to afforded the desired product **3a** (63%, 29.2 mg) in white solid.

## Characterization and analytical data of products



# **1-Benzyl-1***H***-indole-3-carbonitrile** (3a)<sup>1</sup>

(known compound) Following the general procedure, **3a** was obtained in 63% yield as a brown solid (reacting for 24 h). (DCM/hexane = 1:1, Rf = 0.5); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.80-7.76 (m, 1H), 7.61 (s, 1H), 7.38-7.29 (m, 6H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.34 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  135.6, 135.2, 135.0, 129.2, 128.5, 128.0, 127.1, 124.0, 122.3, 120.0, 115.8, 110.9, 86.3, 50.9.



## 1-Benzyl-5-methoxy-1*H*-indole-3-carbonitrile (3b)<sup>2</sup>

(known compound) Following the general procedure, **3b** was obtained in 59% yield as a white solid (reacting for 36 h). Rf = 0.2 (DCM/hexane = 1:1); <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.55

(s, 1H), 7.37-7.32 (m, 3H), 7.22 (d, J = 8.8 Hz, 1H), 7.18 (d, J = 2.4 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 6.94-6.91 (m, 1H), 5.29 (s, 2H), 3.86 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  156.1, 135.3, 134.9, 130.6, 129.1, 128.9, 128.4, 127.1, 116.1, 114.8, 111.8, 100.9, 85.7, 55.8, 51.1.



#### 1-benzyl-5-fluoro-1H-indole-3-carbonitrile (3c)<sup>1</sup>

(known compound) Following the general procedure, **3c** was obtained in 79% yield as a orange solid (reacting for 36 h). Rf = 0.25 (DCM/hexane = 1:1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.64 (s, 1H), 7.44-7.41 (m, 1H), 7.38-7.34 (m, 3H), 7.29-7.26 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.07-7.02 (m, 1H), 5.33 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  160.5 (d, *J*<sub>F-C</sub> = 240.5 Hz), 136.2, 134.8, 132.1, 129.2, 128.6, 127.1, 115.3, 113.0, 112.7, 112.0 (d, *J*<sub>F-C</sub> = 9.6 Hz), 105.5 (d, *J*<sub>F-C</sub> = 24.8 Hz), 86.4 (d, *J*<sub>F-C</sub> = 4.5 Hz), 51.3.



#### 1-benzyl-5-chloro-1H-indole-3-carbonitrile (3d)<sup>2</sup>

(known compound) Following the general procedure, **3d** was obtained in 88% yield as a yellow solid (reacting for 36 h). (DCM/hexane = 1:1, Rf = 0.4);<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.74 (s, 1H), 7.64 (s, 1H), 7.42-7.38 (m, 3H), 7.32-7.25 (m, 2H), 7.18-7.16 (m, 2H), 5.36 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  136.1, 134.8, 134.0, 129.3, 129.0, 128.7, 128.5, 127.1, 124.6, 119.5, 115.2, 112.1, 86.0, 51.2.



# 1-benzyl-5-formyl-1H-indole-3-carbonitrile (3e)

(new compound) Following the general procedure, **3e** was obtained in 88% yield as a light yellow solid (reacting for 36 h). (DCM/hexane = 2:1, Rf = 0.4); mp 95 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  10.44 (s, 1H), 8.63 (s, 1H), 8.23 (d, *J* = 7.2 Hz, 1H), 8.11 (s, 1H), 7.88-7.65 (m, 4H), 7.56 (s, 2H), 5.78 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  192.0, 139.1, 137.2, 134.9, 131.9, 129.7, 129.2, 128.2, 127.6, 125.1, 124.2, 115.1, 112.1, 88.7, 51.7; HRMS (ESI) calcd for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O [M + H<sup>+</sup>] 261.1022, found 261.1028.



# 1-benzyl-5-nitro-1H-indole-3-carbonitrile (3f)

(new compound) Following the general procedure, **3f** was obtained in 88% yield as a yellow solid (reacting for 36 h). (DCM/hexane = 3:1, Rf = 0.3); mp 103 °C; <sup>1</sup>H NMR (DMSO, 400 MHz, TMS)  $\delta$  8.79 (s, 1H), 8.54 (s, 1H), 8.19 (s, 1H), 7.95 (s, 1H), 7.36 (m, 5H), 5.66 (s, 2H); <sup>13</sup>C NMR (DMSO, 100 MHz, TMS)  $\delta$  143.4, 141.6, 138.5, 136.6, 129.3, 128.6, 127.9, 127.0, 119.3, 116.0, 113.3, 100.0, 87.2, 50.8; HRMS (ESI) calcd for C<sub>16</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub> [M + H<sup>+</sup>] 278.0924, found 278.0928.



## 1-benzyl-3-cyano-1H-indole-6-carboxylate (3h).

(new compound) Following the general procedure, **3h** was obtained in 88% yield as a yellow solid (reacting for 36 h). (DCM/hexane = 2:1, Rf = 0.5); mp 89 °C; <sup>1</sup>H NMR (DMSO, 400 MHz, TMS)  $\delta$  8.66 (s, 1H), 8.25 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.37-7.27 (m, 5H), 5.65 (s, 2H), 3.86 (s, 3H); <sup>13</sup>C NMR (DMSO, 100 MHz, TMS)  $\delta$  166.8, 140.7, 136.9, 135.1, 131.4, 129.3, 128.4, 127.5, 125.4, 123.0, 119.5, 115.7, 114.0, 85.2, 52.6, 50.5; HRMS (ESI) calcd for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> [M + H<sup>+</sup>] 291.1128, found 291.1130.



# 1-benzyl-6-bromo-1H-indole-3-carbonitrile (3i)<sup>1</sup>

(known compound) Following the general procedure, **3i** was obtained in 88% yield as a yellow solid (reacting for 36 h). (DCM/hexane = 1:1, Rf = 0.5); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.68 (d, 3H), 7.39 (m, 4H), 7.2 (m 2H), 5.30 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  136.4, 135.8, 134.9, 129.3, 128.7, 127.3, 126.8, 125.7, 121.2, 117.7, 115.4, 114.0, 86.6, 51.0.



# 1-benzyl-4-bromo-1H-indole-3-carbonitrile (3j)

(new compound) Following the general procedure, **3j** was obtained in 88% yield as a yellow solid (reacting for 36 h). (DCM/hexane = 1:1, Rf = 0.5); mp 69 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS)

δ 7.68 (d, J = 7.2 Hz, 1H), 7.45-7.34 (m, 5H), 7.18-7.14 (m 3H), 5.37 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 137.1, 136.3, 134.7, 129.3, 128.7, 127.2, 126.4, 126.2, 124.9, 115.7, 114.7, 110.3, 87.1, 51.3. HRMS-ESI (m/z): Calcd for C<sub>16</sub>H<sub>11</sub>BrN<sub>2</sub> [M + H<sup>+</sup>], 311.0178; found, 311.0177.



#### 1-benzyl-7-bromo-1H-indole-3-carbonitrile (3k)

(new compound) Following the general procedure, **3k** was obtained in 88% yield as a yellow solid (reacting for 36 h). (DCM/hexane = 1:1, Rf = 0.55); mp 71 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.77-7.75 (m, 1H), 7.60-7.49 (m, 2H), 7.38-7.36 (m 3H), 7.19-7.11 (m, 3H), 5.86 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  137.7, 136.8, 132.2, 130.9, 129.5, 129.1, 128.2, 126.6, 123.5, 119.5, 115.0, 104.8, 87.0, 52.4. HRMS-ESI (m/z) : Calcd for C<sub>16</sub>H<sub>11</sub>BrN<sub>2</sub>[M + H<sup>+</sup>] 311.0178, found, 311.0174.



# 1-(4-methylbenzyl)-1H-indole-3-carbonitrile (3m)<sup>3</sup>

(known compound) Following the general procedure, **3m** was obtained in 68% yield as a yellow solid (reacting for 36 h). (DCM/hexane = 1:1, Rf = 0.7); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.70-7.68 (m, 1H), 7.50 (s, 1H), 7.31-7.28 (m, 1H), 7.24-7.21 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.21 (s, 2H), 2.26 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  138.4, 135.6, 134.9, 132.1, 129.8, 128.0, 127.2, 123.9, 122.3, 120.0, 115.8, 110.8, 86.1, 50.7, 21.1.



#### 1-phenyl-1H-indole-3-carbonitrile (3n)<sup>1</sup>

(known compound) Following the general procedure, **3n** was obtained in 78% yield as a white solid (reacting for 24 h). (DCM/hexane = 1:1, Rf = 0.65); <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.85-7.81 (m, 2H), 7.60-7.56 (m, 2H), 7.53-7.48 (m, 4H), 7.38-7.33 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  137.8, 135.6, 134.7, 130.0, 128.4, 128.0, 124.9, 124.6, 122.8, 120.1, 115.6, 111.5, 88.1.



# 1-(4-methoxyphenyl)-1H-indole-3-carbonitrile (30)<sup>2</sup>.

(known compound) Following the general procedure, **30** was obtained in 76% yield as a white solid (reacting for 36 h).(DCM/hexane = 1:1, Rf = 0.4); <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.83-7.81 (m, 1H), 7.75 (s, 1H), 7.44-7.41 (m, 1H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.34-7.32 (m, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  159.5, 136.1, 135.0, 130.6, 127.8, 126.4, 122.6, 120.0, 115.7, 115.1, 111.5, 87.4, 55.7.



# 1-Methyl-1*H*-indole-3-carbonitrile (3q)<sup>1</sup>

(known compound) Following the general procedure, **3q** was obtained with 30% in as a brown liquid (reacting for 24 h).(DCM/hexane = 1:1, Rf = 0.3); <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.76 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.26-7.41 (m, 3H), 3.86 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  135.9, 135.6, 127.7, 123.8, 122.1, 119.9, 116.0, 110.3, 85.4, 33.7.



# 5-Fluoro-1-methyl-1*H*-indole-3-carbonitrile (3r)<sup>1</sup>

(known compound) Following the general procedure, **3r** was obtained in 43% yield as a yellow liquid (reacting for 24 h). (DCM/hexane = 1:1, Rf = 0.35); <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.57 (s, 1H), 7.41 (dd, J = 2.4, 2.4 Hz, 1H), 7.35-7.31 (m, 1H), 7.13-7.08 (m, 1H), 3.86 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  160.5 (d, J = 238.2 Hz), 136.6, 132.6, 128.5 (d, J = 10.7 Hz), 115.4, 112.8 (d, J = 26.4 Hz), 111.4 (d, J = 3.8 Hz), 105.3 (d, J = 24.8 Hz), 85.6 (d, J = 4.7 Hz), 33.9.



# 1-isopropyl-1H-indole-3-carbonitrile (3t)<sup>2</sup>

(known compound) Following the general procedure, **3t** was obtained in 81% yield as a yellow liquid (reacting for 24 h). (DCM/hexane = 1:1, Rf = 0.4); <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.76 (d, *J* = 7.2 Hz, 1H), 7.71 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.36-7.26 (m, 2H), 4.76-4.66 (m, 1H),

1.56 (d, *J* = 7.2 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 134.9, 131.1, 128.0, 123.6, 122.1, 120.0, 116.2, 110.6, 85.7, 48.3, 22.6.



#### 5-fluoro-1-isopropyl-1H-indole-3-carbonitrile (3u)

(new compound) Following the general procedure, **3u** was obtained in 71% yield as a yellow liquid (reacting for 24 h). (DCM/hexane = 1:1, Rf = 0.45); <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.74 (s, 1H), 7.42-7.36 (m, 2H), 7.11-7.06 (m, 1H), 4.73-4.63 (m, 1H), 1.57 (d, *J* = 7.2 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  160.3 (d, *J*<sub>F-C</sub> = 238.2 Hz), 132.2, 131.5, 128.6 (d, *J*<sub>F-C</sub> = 10.7 Hz), 115.6, 112.5 (d, *J*<sub>F-C</sub> = 26.3 Hz), 111.7 (d, *J*<sub>F-C</sub> = 11.5 Hz), 105.3 (d, *J*<sub>F-C</sub> = 24.6 Hz), 85.8, 48.7, 22.6. HRMS-ESI (m/z) Calcd for C<sub>12</sub>H<sub>11</sub>FN<sub>2</sub>[M + H<sup>+</sup>], 203.0979, found, 203.0976.



# 1-isopropyl-5-methyl-1H-indole-3-carbonitrile (3v)<sup>4</sup>

(known compound) Following the general procedure, **3v** was obtained in 35% yield as a yellow liquid (reacting for 24 h). (DCM/hexane = 1:1, Rf = 0.6); <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.66 (s, 1H), 7.55 (s, 1H), 7.33 (d, J = 8.8 Hz, 1H), 7.15 (d, J = 8.4 Hz, 1H), 4.72-4.61 (m, 1H), 2.48 (s, 3H), 1.55 (d, J = 7.2 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  133.3, 131.8, 131.0, 128.3, 125.2, 119.6, 116.4, 110.3, 85.0, 48.3, 22.6, 21.4.



#### 1-butyl-1H-indole-3-carbonitrile (3w)<sup>4</sup>

(known compound) Following the general procedure, **3w** was obtained in 83% yield as a brown liquid (reacting for 24 h). (DCM/hexane = 1:1, Rf = 0.65); <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.76 (d, J = 7.6 Hz, 1H), 7.59 (s, 1H), 7.35-7.32 (m, 1H), 7.41 (d, J = 8.0 Hz), 7.36-7.26 (m, 2H), 4.15 (t, J = 7.2 Hz, 2H), 1.88-1.81 (m, 2H), 1.39-1.30 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  135.3, 134.7, 128.0, 123.7, 122.0, 120.0, 116.1, 110.5, 85.5, 47.0, 31.9, 20.0, 13.6.



1-Butyl-5-fluoro-1H-indole-3-carbonitrile (3x).

(new compound) Following the general procedure, **3x** was obtained in 75% yield as a brown liquid (reacting for 24 h). (DCM/hexane = 1:1, Rf = 0.55); <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.62 (s, 1H), 7.40 (dd, J = 2.4, 2.4 Hz, 1H), 7.35-7.32 (m, 1H), 7.11-7.06 (m, 1H), 4.14 (t, J = 7.2 Hz, 2H), 1.88-1.80 (m, 2H), 1.39-1.30 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  160.3 (d, J = 231 Hz), 135.7, 131.94, 128.62 (d, J = 10.8 Hz), 115.4, 112.6 (d, J = 26.3 Hz), 111.5 (d, J = 9.6 Hz), 105.4 (d, J = 24.6 Hz), 85.6, 47.3, 31.8, 19.9, 13.5. HRMS-ESI (m/z): Calcd for C<sub>13</sub>H<sub>13</sub>FN<sub>2</sub> [M + H<sup>+</sup>], 217.1136, found, 217.1135.



# 1-butyl-5-methyl-1H-indole-3-carbonitrile (3y)<sup>4</sup>

(known compound) Following the general procedure, **3y** was obtained in 39% yield as a yellow liquid (reacting for 24 h). (DCM/hexane = 1:1, Rf = 0.55); <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.55 (s, 1H), 7.54 (s, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.16-7.14 (m, 1H), 4.12 (t, J = 6.0 Hz, 2H), 2.48 (s, 3H), 1.87-1.79 (m, 2H), 1.38-1.26 (m, 2H), 0.94 (t, J = 6.0 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  134.5, 133.7, 131.8, 128.3, 125.3, 119.6, 116.2, 110.2, 84.8, 47.0, 31.9, 21.4, 20.0, 13.6.



# 1-octyl-1H-indole-3-carbonitrile (3z).

(new compound) Following the general procedure, **3z** was obtained in 56% yield as a brown liquid (reacting for 24 h). (DCM/hexane = 1:1, Rf = 0.65); <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, TMS)  $\delta$  7.76 (d, J = 7.6 Hz, 1H), 7.59 (s, 1H), 7.41 (d, J = 7.2 Hz, 1H), 7.35-3.26 (m, 2H), 4.14 (t, J = 7.2 Hz, 2H), 1.89-1.83 (m, 2H), 1.31-1.25 (m, 10H), 0.87 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, TMS)  $\delta$  135.4, 134.6, 128.0, 123.7, 122.0, 120.0, 116.0, 110.5, 85.5, 47.3, 31.7, 29.8, 29.1, 29.1, 26.8, 22.6, 14.0. HRMS-ESI (m/z) : Calcd for C<sub>17</sub>H<sub>23</sub>N<sub>2</sub>[M + H<sup>+</sup>], 255.1856; found, 255.1858.

## Reference

- 1. M. Zhao, W. Zhang and Z. Shen, J. Org. Chem., 2015, 80, 8868-8873
- O. Y. Yuen, P. Y. Choy, W. K. Chow, W. T. Wong and F. Y. Kwong, J. Org. Chem., 2013, 78, 3374-3378.
- Y. Zhou, Z. Li, J. Dong, S. Yin and L. Han, Faming Zhuanli Shenqing (2015), CN 104788359 A 20150722.
- 4. J. Xiao, Q. Li, T. Chen and L.-B. Han, Tetrahedron Lett., 2015, 56, 5937-5940.
- C. Lai, Z.-F. Tao, K. W. Woods, T. D. Penning, A. J. Souers, M. Anthony, J. M. Miyashiro, Y. Tong, U.S. Pat. Appl. Publ. (2014), US 20140275153 A1 20140918

Copies of 1H NMR and 13C NMR spectroscopies













































