

## **Supporting information**

# **2-IODOIMIDAZOLINIUM SALT-CATALYZED FRIEDEL–CRAFTS REACTION: SYNTHESIS OF BIS(INDOLYL)METHANE ALKALOIDS**

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## General

Dry solvents were purchased from commercial suppliers and used without further purification. Analytical thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230-400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). Silica gel column chromatography was performed on Kanto silica gel 60 (spherical, 63-210  $\mu\text{m}$ ). IR spectra were recorded on JASCO FT/IR-4100 using ATR.  $^1\text{H}$  NMR spectra were recorded on JEOL ECS-400 (400MHz), ECA-500 (500MHz) spectrometers. Chemical shifts of  $^1\text{H}$  NMR spectra were reported relative to tetramethylsilane ( $\delta$  0).  $^{13}\text{C}$  NMR spectra were recorded on JEOL ECS400 (100MHz), ECA-500 (125MHz) spectrometers. Chemical shifts of  $^{13}\text{C}$  NMR spectra were reported relative to  $\text{CDCl}_3$  ( $\delta$  77.0). Splitting patterns were reported as s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.

## General procedure for halogen-bond donor catalyzed Friedel-Crafts reaction

2-Iodoimidazolium triflate **1d** (0.01 mmol, 0.1 eq) was added to a test tube containing a mixture of indole **2** (0.21 mmol, 2.1eq), aldehyde **3** (0.1 mmol, 1 eq) and  $\text{CHCl}_3$  (0.5 ml) under Ar. After being stirred for appropriate time, the reaction mixture was directly purified by silica gel column chromatography (hexane/ethyl acetate = 10/1-3/1) to afford the product.

## Analytical data for product 4

### 3,3'-(Phenylmethylene)bis(1-methyl-1H-indole): **4a**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.39-7.33 (m, 4H), 7.30-7.26 (m, 4H), 7.23-7.18 (m, 3H), 7.01-6.98 (m, 2H), 6.52 (d,  $J$  = 0.7 Hz, 2H), 5.88 (s, 1H), 3.68 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 144.4, 137.3, 128.6, 128.2, 128.1, 127.4, 126.0, 121.4, 120.0, 118.6, 118.2, 109.0, 40.0, 32.6; HRMS calcd for  $\text{C}_{25}\text{H}_{21}\text{N}_2$  (M-H) $^+$ : 349.1699, found:  $m/z$  349.1690.

### 3,3'-((4-Bromophenyl)methylene)bis(1-methyl-1H-indole): **4b**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.39 (d,  $J$  = 8.4 Hz, 2H), 7.35 (d,  $J$  = 7.9 Hz, 2H), 7.30 (d,  $J$  = 8.2 Hz, 2H), 7.19-7.23 (m, 4H), 7.01 (t,  $J$  = 7.5 Hz, 2H), 6.51 (s, 2H), 5.83 (s, 1H), 3.69 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 143.5, 137.4, 131.2, 130.4, 128.2, 127.2, 121.5, 119.9, 119.8, 118.7, 117.6, 109.1, 39.5, 32.7; HRMS calcd for  $\text{C}_{25}\text{H}_{20}\text{BrN}_2$  (M-H) $^+$ : 427.0804, found:  $m/z$  427.0809.

### 3,3'-((4-Methoxyphenyl)methylene)bis(1-methyl-1H-indole): **4c**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.38 (d,  $J$  = 8.1 Hz, 2H), 7.30-7.23 (m, 4H), 7.22-7.18 (m, 2H), 7.01-6.97 (m, 2H), 6.83-6.80 (m, 2H), 6.51 (s, 2H), 5.83 (s, 1H), 3.78 (s, 3H), 3.68 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 157.8, 137.4, 136.6, 129.5, 128.2, 127.4, 121.3, 120.0, 118.5, 113.5, 109.0, 55.1, 39.2, 32.6; HRMS calcd for  $\text{C}_{26}\text{H}_{23}\text{N}_2\text{O}$  (M-H) $^+$ : 379.1805, found:  $m/z$  379.1810.

### 3,3'-(*p*-Tolylmethylene)bis(1-methyl-1H-indole): **4d**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.41-7.36 (m, 2H), 7.28 (d,  $J$  = 8.3 Hz, 2H), 7.23-7.17 (m, 4H), 7.09-7.05 (m, 2H), 6.99 (t,  $J$  = 7.5 Hz, 2H), 6.53 (s, 2H), 5.84 (s, 1H), 3.67 (s, 6H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR

(100 MHz, CDCl<sub>3</sub>)  $\delta$  = 141.4, 137.4, 135.3, 128.9, 128.5, 128.2, 127.4, 121.3, 120.0, 118.5, 118.4, 109.0, 39.6, 32.6, 21.1; HRMS calcd for C<sub>26</sub>H<sub>23</sub>N<sub>2</sub> (M-H)<sup>+</sup>: 363.1856, found:  $m/z$  363.1853.

**3,3'-(*m*-Tolylmethylene)bis(1-methyl-1*H*-indole): 4e**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.39 (d,  $J$  = 7.9 Hz, 2H), 7.30-7.11 (m, 7H), 7.03-6.97 (m, 3H), 6.52 (s, 2H), 5.83 (s, 1H), 3.68 (s, 6H), 2.29 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 144.3, 137.6, 137.3, 129.4, 128.2, 128.0, 127.4, 126.8, 125.7, 121.3, 120.0, 118.6, 118.3, 109.0, 40.0, 32.7, 21.5; HRMS calcd for C<sub>26</sub>H<sub>23</sub>N<sub>2</sub> (M-H)<sup>+</sup>: 363.1856, found:  $m/z$  363.1859.

**3,3'-(*o*-Tolylmethylene)bis(1-methyl-1*H*-indole): 4f**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.35 (d,  $J$  = 7.9 Hz, 2H), 7.30 (d,  $J$  = 8.1 Hz, 2H), 7.22-7.18 (m, 3H), 7.15-7.10 (m, 2H), 7.06-6.97 (m, 3H), 6.44 (d,  $J$  = 0.7 Hz, 2H), 6.02 (s, 1H), 3.67 (s, 6H), 2.38 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 142.5, 137.4, 135.9, 130.1, 128.5, 128.3, 127.5, 125.9, 125.7, 121.3, 119.8, 118.5, 117.6, 109.0, 35.9, 32.6, 19.6; HRMS calcd for C<sub>26</sub>H<sub>23</sub>N<sub>2</sub> (M-H)<sup>+</sup>: 363.1856, found:  $m/z$  363.1859.

**3,3'-(Phenylmethylene)bis(1*H*-indole): 4g**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.91 (s, 2H), 7.42-7.34 (m, 6H), 7.30-7.26 (m, 2H), 7.23-7.10 (m, 3H), 7.02-6.98 (m, 2H), 6.66 (t,  $J$  = 1.2 Hz, 2H), 5.89 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 143.9, 136.6, 128.7, 128.2, 127.0, 126.1, 123.6, 121.9, 119.9, 119.6, 119.2, 111.0, 40.1; HRMS calcd for C<sub>23</sub>H<sub>17</sub>N<sub>2</sub> (M-H)<sup>+</sup>: 321.1386, found:  $m/z$  321.1383.

**3,3'-(Phenylmethylene)bis(5-methyl-1*H*-indole): 4h**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.82 (s, 2H), 7.35-7.19 (m, 9H), 7.00 (dd,  $J$  = 8.4, 1.6 Hz, 2H), 6.60 (d,  $J$  = 2.3 Hz, 2H), 5.83 (s, 1H), 2.35 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 144.1, 135.0, 128.7, 128.4, 128.2, 127.3, 126.0, 123.9, 123.5, 119.4, 119.2, 110.7, 40.0, 21.4; HRMS calcd for C<sub>25</sub>H<sub>21</sub>N<sub>2</sub> (M-H)<sup>+</sup>: 349.1699, found:  $m/z$  349.1697.

**3,3'-(Phenylmethylene)bis(5-methoxy-1*H*-indole): 4i**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.82 (s, 2H), 7.36-7.19 (m, 7H), 6.84-6.79 (m, 4H), 6.67 (d,  $J$  = 1.8 Hz, 2H), 5.77 (s, 1H), 3.69 (s, 6H); <sup>13</sup>C NMR (100 MHz, Acetone-d<sub>6</sub>)  $\delta$  = 154.3, 145.9, 133.2, 129.5, 128.8, 128.4, 126.6, 125.2, 119.4, 112.7, 111.9, 102.4, 55.6, 41.1; HRMS calcd for C<sub>25</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub> (M-H)<sup>+</sup>: 381.1598, found:  $m/z$  381.1599.

**3,3'-(Phenylmethylene)bis(5-bromo-1*H*-indole): 4j**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.99 (s, 2H), 7.47 (d,  $J$  = 0.7 Hz, 2H), 7.31-7.24 (m, 9H), 6.65 (q,  $J$  = 1.1 Hz, 2H), 5.76 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 143.0, 135.3, 128.6, 128.5, 128.4, 126.5,

124.9, 124.7, 122.2, 119.0, 112.6, 112.6, 39.8; HRMS calcd for C<sub>23</sub>H<sub>15</sub>Br<sub>2</sub>N<sub>2</sub> (M-H)<sup>-</sup>: 476.9607, found: *m/z* 476.9616.

**3,3'-(Ethane-1,1-diyl)bis(1*H*-indole): 4k**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.90 (s, 2H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.18-7.14 (m, 2H), 7.04 (t, *J* = 7.5 Hz, 2H), 6.94 (d, *J* = 2.2 Hz, 2H), 4.68 (q, *J* = 7.1 Hz, 1H), 1.81 (d, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 136.6, 126.8, 121.7, 121.6, 121.2, 119.7, 119.0, 111.0, 28.1, 21.7; HRMS calcd for C<sub>18</sub>H<sub>15</sub>N<sub>2</sub> (M-H)<sup>-</sup>: 259.1241, found: *m/z* 259.1245.

**Di(1*H*-indol-3-yl)methane: 4l**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.92 (s, 2H), 7.63 (d, *J* = 7.0 Hz, 2H), 7.38-7.36 (m, 2H), 7.21-7.17 (m, 2H), 7.11-7.07 (m, 2H), 6.96 (t, *J* = 1.2 Hz, 2H), 4.25 (t, *J* = 0.9 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 136.4, 127.5, 122.2, 121.8, 119.2, 119.2, 115.6, 111.0, 21.2; HRMS calcd for C<sub>17</sub>H<sub>15</sub>N<sub>2</sub> (M+H)<sup>+</sup>: 247.1230, found: *m/z* 247.1228.

**1-(3-(Di(1*H*-indol-3-yl)methyl)-1*H*-indol-1-yl)ethan-1-one: 4m**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.46 (s, 1H), 7.96 (s, 2H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.40 (dd, *J* = 14.0, 8.0 Hz, 3H), 7.34-7.30 (m, 1H), 7.22-7.13 (m, 3H), 7.06-7.02 (m, 2H), 6.98 (s, 1H), 6.79 (dd, *J* = 2.4, 0.8 Hz, 2H), 6.10 (d, *J* = 1.1 Hz, 1H), 2.42 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 168.7, 136.7, 136.4, 130.2, 126.8, 125.6, 125.0, 123.7, 123.4, 123.3, 122.0, 120.1, 119.7, 119.3, 117.7, 116.6, 111.1, 31.0, 24.0; HRMS calcd for C<sub>27</sub>H<sub>20</sub>N<sub>3</sub>O (M-H)<sup>+</sup>: 402.1612 found: *m/z* 402.1618.