Supporting Information for

Cu-Catalyzed Controllable C–H Mono-/Di-/Triarylations of Imidazolium Salts for Ionic Functional Materials

Shiqing Li, Junbin Tang, Ruyong Jiang, Yinsong Zhao, Tianbao wang, Ge Gao* and Jingsong You*

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, Sichuan University, 29 Wangjiang Road, Chengdu 610064, P. R. China
E-mail: gg2b@scu.edu.cn; jsyou@scu.edu.cn

Table of contents

I. General remarks .................................................................1
II. General procedure for the C–H functionalization of imidazolium salts .........................1
III. General procedure for the sequential C–H arylation of imidazolium salts .................2
IV. Synthesis of 7 and 8 ..............................................................................................................3
V. Electrochromism of 7 ............................................................................................................4
VI. Photochromism of 8 ............................................................................................................5
VII. Characterization of the products .....................................................................................5
VIII. References .........................................................................................................................20
IX. Copies of $^1$H and $^{13}$C NMR spectra ........................................................................21
I. General remarks

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Cu₂O (97% purity) was directly used as purchased from Energy Chemical (China) Co., Ltd. All syntheses and manipulations were carried out under a N₂ atmosphere using standard Schlenk or vacuum line techniques. DMF was dried by refluxing over CaH₂. Analytical thin layer chromatography was performed on HG/T2354-92 GF254 plates (Qingdao Haiyang Chemical Co., Ltd.). The (benz)imidazolium substrates are prepared by N-quaternizing of aryl alkyl or alkyl alkyl substituted (benz)imidazoles with iodomethane, iodoethane, and 1-iodobutane, 1,3-diphenylimidazolium tetrafluoroborate 2-ethylimidazo[1,5-a]pyridin-2-ium iodide, 1,3-dibutyl-4,5-diphenyl-1H-imidazol-3-ium iodide, (E)-(2-iodovinyl)benzene, (iodoethynyl)benzene, were prepared according to the literature procedures.

NMR spectra were obtained on a Bruker AV II-400 MHz. The ¹H NMR (400 MHz) chemical shifts were measured relative to CDCl₃ or DMSO-d₆ as the internal reference (CDCl₃: δ = 7.26 ppm; DMSO-d₆: δ = 2.50 ppm). The ¹³C NMR (100 MHz) chemical shifts were obtained using CDCl₃ or DMSO-d₆ as the internal standard (CDCl₃: δ = 77.16 ppm; DMSO-d₆: δ = 39.52 ppm). High-resolution mass spectra (HR-MS) were obtained on a Waters-Q-TOF-Premier (ESI). Melting points were determined with XRC-1 and are uncorrected.

II. General procedure for the C–H functionalization of imidazolium salts

A Schlenk tube with a magnetic stir bar was charged with an imidazolium salt 1 (0.2 mmol, 1.0 equiv), an iodide 2 (2.0-5.0 equiv), Cu₂O (5.7 mg, 20 mol%), NaOAc (16 mg, 1.0 equiv) or K₂CO₃ (2.0-5.0 equiv) and DMF (1 mL). The reaction mixture was stirred at 120 °C for 24 h or 36 h in an oil bath under a N₂ atmosphere and then cooled down to room temperature. DMF was removed under reduced pressure, and the residue was passed through a silica gel column eluted with dichloromethane/methanol (v/v, 100/1–20/1) to afford the desired product.
Table S1. Screening of the catalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat./mol%</th>
<th>Base/1 equiv</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt;</th>
<th>3aa:4aa:5aa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu&lt;sub&gt;2&lt;/sub&gt;O/10</td>
<td>NaOAc</td>
<td>87:0:0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cu&lt;sub&gt;2&lt;/sub&gt;O/5</td>
<td>NaOAc</td>
<td>65:0:0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Cu&lt;sub&gt;2&lt;/sub&gt;O/2</td>
<td>NaOAc</td>
<td>47:0:0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>CuI/20</td>
<td>NaOAc</td>
<td>75:0:0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>CuI/40</td>
<td>NaOAc</td>
<td>88:0:0</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 1a (0.2 mmol), 2a (2 equiv), catalyst (x mol%) and NaOAc (1 equiv) in DMF (1 mL) at 120 °C for 24 h under a N<sub>2</sub> atmosphere. <sup>b</sup> Isolated yield.

General procedure for the C2-arylation of 1a with arylbromides

\[
\begin{align*}
\text{N} & \quad \text{Br} \\
\text{1a} & \quad \text{R} \\
1) \ & \text{Cu}_2\text{O, NaOAc} \\
2) \ & \text{NaBF}_4
\end{align*}
\]

A Schlenk tube with a magnetic stir bar was charged with 1a (0.2 mmol, 1.0 equiv), an aryl bromide (0.4 mmol, 2.0 equiv), Cu<sub>2</sub>O (5.7 mg, 20 mol%), NaOAc (16 mg, 1.0 equiv) and DMF (1 mL). The reaction mixture was stirred at 120 °C for 24 h in an oil bath under a N<sub>2</sub> atmosphere. After the mixture was cooled down to room temperature, NaBF<sub>4</sub> (1 mol, 5 equiv) was added to stir for another 2 h. DMF was then removed under reduced pressure, and the residue was passed through a silica gel column eluted with dichloromethane/methanol (v/v, 50/1–20/1) to afford the desired product.

III. General procedure for the sequential C–H arylation of imidazolium salts

A Schlenk tube with a magnetic stir bar was charged with imidazolium salt 1a (0.2 mmol, 1.0 equiv), an Ar<sup>1</sup>I (0.2 mmol, 1.0 equiv), Cu<sub>2</sub>O (5.7 mg, 20 mol%), NaOAc (0.2 mmol, 1.0 equiv) and DMF (1 mL). The reaction mixture was stirred at 120 °C for 24 h in an oil bath under a N<sub>2</sub> atmosphere. After the reaction was cooled down to room temperature, Cu<sub>2</sub>O (2.9 mg, 10 mol%), an Ar<sup>2</sup>I (0.2 mmol, 1.0 equiv) and KCO<sub>3</sub> (0.2 mmol, 1.0 equiv) were added under the protection of N<sub>2</sub>. The reaction was stirred at 120 °C for another 24 h. After the reaction was cooled down to room temperature, Cu<sub>2</sub>O (2.9 mg, 10 mol%), an Ar<sup>3</sup>I (0.6 mmol, 3.0 equiv) and KCO<sub>3</sub> (0.6 mmol, 3.0 equiv) were added again under the protection of N<sub>2</sub>. The
mixture was reacted at 120 °C for further 24 h. Finally, DMF was removed under reduced pressure after the mixture was cooled down to room temperature. The residue was passed through a silica gel column eluted with dichloromethane/methanol (v/v, 100/1−50/1) to afford the desired product.

IV. Synthesis of 7 and 8

**2,2′-(1,4-Phenylene)bis(3-ethyl-1-phenyl-1H-benzo[d]imidazol-3-ium) diiodide (7).** A Schlenk tube with a magnetic stir bar was charged with imidazolium salt 1i (0.1 mmol), 1,4-diiodobenzene (0.1 mmol), Cu₂O (5.7 mg, 40 mol%), NaOAc (16 mg, 2.0 equiv) and DMF (1 mL). The reaction mixture was stirred at 120 °C for 30 h in an oil bath. After the volatiles were removed under reduced pressure, the residue was passed through a silica gel column eluted with dichloromethane/methanol (v/v, 50/1−10/1) to afford 7 as a light yellow solid (65 mg, 84% yield). M.p.: > 250 ºC. ¹H NMR (400 MHz, DMSO-d₆): δ = 1.45 (t, J = 7.2 Hz, 6H), 4.49 (q, J = 7.2 Hz, 4H), 7.46–7.52 (m, 8H), 7.58–7.63 (m, 4H), 7.76 (t, J = 8.0 Hz, 2H), 7.85 (t, J = 8.0 Hz, 2H), 7.95 (s, 4H), 8.35 (d, J = 8.4 Hz, 2H) ppm. ¹³C NMR (100 MHz, DMSO-d₆): δ = 14.4, 41.8, 113.3, 114.0, 125.4, 127.2, 127.3, 127.7, 130.0, 130.6, 130.7, 131.4, 132.1, 132.6, 148.9 ppm. HRMS (ESI): calcd for C₃₆H₃₂IN₄⁺ ([M−I]⁺) 647.1666, found 647.1669.

**2-(4-Cyanophenyl)-4,5-bis(2,5-dimethylthiophen-3-yl)-1,3-dimethyl-1H-imidazol-3-ium iodide (8).** A Schlenk tube with a magnetic stir bar was charged with imidazolium salt 1a (0.2 mmol, 1 equiv), 4-iodobenzonitrile (0.2 mmol, 1 equiv), Cu₂O (5.7 mg, 20 mol%), NaOAc (16 mg, 1 equiv) and DMF (1 mL). The reaction mixture was stirred at 120 °C for 24 h in an oil bath. The reaction was cooled down to room temperature, and 3-iodo-2,5-dimethylthiophene (0.6 mmol, 3 equiv), Cu₂O (2.9 mg, 10 mol%), K₂CO₃ (83 mg, 3 equiv) were added under the protection of N₂. Then the mixture was reacted at 120 °C for another 24 h. The volatiles were then removed under reduced pressure after the mixture was cooled down to room temperature. The residue was passed through a silica gel column eluted with
dichloromethane/methanol (v/v, 100/1–50/1) to afford 8 as a white solid (51 mg, 47% yield). M.p.: 245–247 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 1.97$ (s, 4H), 2.21 (s, 2H), 2.42 (s, 6H), 3.49 (s, 6H), 6.62 (s, 0.8H), 6.89 (s, 1.2H), 8.12 (d, $J = 6.8$ Hz, 2H), 8.28 (d, $J = 7.2$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 13.5, 14.9, 34.2, 114.9, 118.0, 121.6, 126.5, 127.7, 132.0, 133.3, 137.5$ ppm. HRMS (ESI): calcd for C$_{24}$H$_{24}$N$_3$S$_2^+$ ([M−I$^-$]+) 418.1406, found 418.1401.

V. Electrochromism of 7

**Fabrication of an electrochromic device:** Two pieces of FTO coated glasses using as the electrodes were spaced with two pieces of parafilm (thickness of about 50 µm). The two closed glasses were pressed to stick together with parafilm for several minutes by two spring clips. After removal of the spring clips, the device was used as described. The acetonitrile solutions of 7 without any supporting electrolyte were injected into the space of the two pieces of FTO glasses by a syringe, respectively. The adding potential was output from an alkaline battery and the voltage was measured by a multimeter.

![Diagram of the assembly of electrochromic device.](image)

*Figure S1.* Diagram of the assembly of electrochromic device.

![Cyclic voltammogram of 7 at different scan rates in DMF solution with [NBu$_4$N][PF$_6$] as supporting electrolyte (0.1 M), referenced to Fe/Fe$^+$.](image)

*Figure S2.* Cyclic voltammogram of 7 at different scan rates in DMF solution with [NBu$_4$N][PF$_6$] as supporting electrolyte (0.1 M), referenced to Fe/Fe$^+$. 

S4
VI. Photochromism of 8

![Absorption Spectra](image)

*Figure S3.* Absorption spectra of 8 in acetonitrile (10 μM) irradiated with an UV light (365 nm, 4 W).

VII. Characterization of the products

1,3-Dimethyl-2-phenyl-1H-imidazol-3-ium iodide (3aa). A white solid (57 mg, 95% yield). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 3.70 (s, 6H), 7.69–7.78 (m, 5H), 7.88 (s, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 35.7, 121.2, 123.2, 129.4, 130.6, 132.3, 144.1 ppm.

1,3-Dimethyl-2-phenyl-1H-imidazol-3-ium tetrafluoroborate (3aa-BF$_4$). A white solid (35 mg, 67% yield). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 3.70 (s, 6H), 7.69–7.78 (m, 5H), 7.88 (s, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 35.7, 121.2, 123.2, 129.4, 130.6, 132.3, 144.1 ppm. $^{19}$F NMR (DMSO-$d_6$, 376 MHz): $\delta$ = -148.35 (s), -148.29 (s) ppm.

2-(4-Methoxyphenyl)-1,3-dimethyl-1H-imidazol-3-ium iodide (3ab). A light yellow solid (63 mg, 95%
yield). M.p.: 55–57 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.84$ (s, 6H), 3.89 (s, 3H), 7.13 (d, $J = 8.4$ Hz, 2H), 7.67 (d, $J = 8.8$ Hz, 2H), 7.76 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 37.1$, 55.9, 112.2, 115.5, 123.8, 132.8, 145.0, 162.8 ppm. HRMS (ESI): calcd for C$_{12}$H$_{15}$N$_2$O$^+$ ([M–I$^-$$]$$^+$) 203.1179, found 203.1180.

![](image)

2-(4-(Dimethylamino)phenyl)-1,3-dimethyl-1$H$-imidazol-3-ium iodide (3ac). A white solid (50 mg, 72% yield). M.p.: 181–183 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.07$ (s, 6H), 3.85 (s, 6H), 6.82 (d, $J = 8.8$ Hz, 2H), 7.44 (d, $J = 8.8$ Hz, 2H), 7.71 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 36.9$, 40.2, 105.7, 112.2, 123.3, 131.7, 143.3, 152.7 ppm. HRMS (ESI): calcd for C$_{13}$H$_{18}$N$_3$$^+$ ([M–I$^-$$]$$^+$) 216.1495, found 216.1494.

![](image)

1,3-Dimethyl-2-(4-nitrophenyl)-1$H$-imidazol-3-ium iodide (3ad). A yellow solid (61 mg, 88% yield). M.p.: 148–150 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 3.72$ (s, 6H), 7.94 (s, 2H), 8.11 (d, $J = 8.4$ Hz, 2H), 8.52 (d, $J = 8.4$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 35.8$, 123.8, 124.2, 127.3, 132.7, 142.2, 149.6 ppm. HRMS (ESI): calcd for C$_{11}$H$_{12}$N$_3$O$_2$$^+$ ([M–I$^-$$]$$^+$) 218.0924, found 218.0926.

![](image)

2-(4-Cyanophenyl)-1,3-dimethyl-1$H$-imidazol-3-ium iodide (3ae). A yellow solid (60 mg, 92% yield). M.p.: 156–160 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 3.71$ (s, 6H), 7.92 (s, 2H), 8.01 (d, $J = 8.4$ Hz, 2H), 8.21 (d, $J = 8.0$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 35.8$, 114.9, 117.9, 123.7, 125.7, 131.9, 133.2, 142.5 ppm. HRMS (ESI): calcd for C$_{12}$H$_{12}$N$_3$$^+$ ([M–I$^-$$]$$^+$) 198.1026, found 198.1028.
2-(4-Cyanophenyl)-1,3-dimethyl-1H-imidazol-3-ium tetrafluoroborate (3ae-BF₄). A light yellow solid (47 mg, 82% yield). ¹H NMR (400 MHz, DMSO-$_d$₆): δ = 3.70 (s, 6H), 7.91 (s, 2H), 8.00 (d, J = 8.4 Hz, 2H), 8.20 (d, J = 8.0 Hz, 2H) ppm. ¹³C NMR (100 MHz, DMSO-$_d$₆): δ = 35.8, 114.9, 117.9, 123.7, 125.7, 131.8, 133.2, 142.5 ppm. ¹⁹F NMR (DMSO-$_d$₆, 376 MHz): δ = -148.43 (s), -148.38 (s) ppm.

1,3-Dimethyl-2-(4-(trifluoromethyl)phenyl)-1H-imidazol-3-ium iodide (3af). A light yellow solid (66 mg, 89% yield). M.p.: 56–58 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.87 (s, 6H), 7.86 (s, 2H), 7.91 (d, J = 8.0 Hz, 2H), 8.09 (d, J = 8.0 Hz, 2H) ppm. ¹³C NMR (100 MHz, DMSO-$_d$₆): δ = 37.4, 110.1, 123.3 (q, $J_{C-F} = 271.6$ Hz), 124.5, 126.9 (q, $J_{C-F} = 3.7$ Hz), 132.4, 134.6 (d, $J_{C-F} = 33.0$ Hz), 143.3 ppm. HRMS (ESI): calcd for C$_{12}$H$_{12}$F$_3$N$_2$I$^+$ ([M−I$^-$]$^+$) 241.0947, found 241.0947.

2-(4-Acetylphenyl)-1,3-dimethyl-1H-imidazol-3-ium iodide (3ag). A yellow solid (61 mg, 90% yield). M.p.: 148–150 °C. ¹H NMR (400 MHz, DMSO-$_d$₆): δ = 2.69 (s, 3H), 3.71 (s, 6H), 7.91 (s, 2H), 7.95 (d, J = 8.4 Hz, 2H), 8.22 (d, J = 8.4 Hz, 2H) ppm. ¹³C NMR (100 MHz, DMSO-$_d$₆): δ = 27.1, 35.8, 123.5, 125.2, 128.8, 131.2, 139.3, 143.2, 197.6 ppm. HRMS (ESI): calcd for C$_{13}$H$_{15}$N$_2$O$^+$ ([M−I$^-$]$^+$) 215.1179, found 215.1179.

2-(4-Bromophenyl)-1,3-dimethyl-1H-imidazol-3-ium iodide (3ah). A white solid (63 mg, 83% yield). M.p.: 144–146 °C. ¹H NMR (400 MHz, DMSO-$_d$₆): δ = 3.69 (s, 6H), 7.74 (d, J = 8.4 Hz, 2H), 7.88 (s,
2H), 7.94 (d, J = 8.4 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 35.7, 120.4, 123.4, 126.5, 132.5, 132.8, 143.2 ppm. HRMS (ESI): calcd for C$_{11}$H$_{12}$BrN$_2^+$ ([M−I$^-$]$^+$) 251.0178, found 251.0151.

### 2-(4-Chlorophenyl)-1,3-dimethyl-1$H$-imidazol-3-ium (3ai)
A white solid (60 mg, 90% yield). M.p.: 166–168 ºC. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 3.69 (s, 6H), 7.79–7.84 (m, 4H), 7.89 (s, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 35.8, 120.0, 123.4, 129.6, 132.7, 137.4, 143.1 ppm. HRMS (ESI): calcd for C$_{11}$H$_{12}$ClN$_2^+$ ([M−I$^-$]$^+$) 207.0684, found 207.0680.

### 2-(2-Methoxyphenyl)-1,3-dimethyl-1$H$-imidazol-3-ium iodide (3aj)
A light yellow solid (54 mg, 82% yield). M.p.: 196–198 ºC. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 3.63 (s, 6H), 3.86 (s, 3H), 7.25 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 6.8 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.90 (s, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 35.4, 56.2, 109.1, 112.6, 121.2, 123.3, 132.0, 134.7, 142.1, 157.6 ppm. HRMS (ESI): calcd for C$_{12}$H$_{15}$N$_2$O$^+$ ([M−I$^-$]$^+$) 203.1179, found 203.1180.

### 2-(3-Acetylphenyl)-1,3-dimethyl-1$H$-imidazol-3-ium iodide (3ak)
A light yellow solid (55 mg, 81% yield). M.p.: 195–197 ºC. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 2.66 (s, 3H), 3.70 (s, 6H), 7.86 (t, J = 7.6 Hz, 1H), 7.90 (s, 2H), 8.03 (d, J = 7.6 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.34 (s, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 27.0, 35.7, 121.8, 123.3, 130.0, 130.6, 131.6, 135.0, 137.5, 143.3, 197.2 ppm. HRMS (ESI): calcd for C$_{13}$H$_{15}$N$_2$O$^+$ ([M−I$^-$]$^+$) 215.1179, found 215.1175.
2-Mesityl-1,3-dimethyl-1\textit{H}-imidazol-3-ium iodide (3al). A light yellow solid (42 mg, 62% yield). M.p.: 102–104 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.03 (s, 6H), 2.38 (s, 3H), 3.75 (s, 6H), 7.07 (s, 2H), 8.15 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 20.0, 21.5, 36.1, 110.1, 116.9, 124.3, 129.7, 138.9, 143.9 ppm. HRMS (ESI): calcd for C$_{14}$H$_{19}$N$_2$ $^{+}$ ([M–I$^{−}$]$^{+}$) 215.1543, found 215.1537.

\[
\begin{array}{c}
\text{N} \\
\text{N} \\
/ \text{S} \\
\end{array}
\]

1,3-Dimethyl-2-(thiophen-2-yl)-1\textit{H}-imidazol-3-ium iodide (3am). A yellow solid (55 mg, 90% yield). M.p.: 104–106 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.92 (s, 6H), 7.34 (dd, $J$ = 5.2 Hz, 3.6 Hz, 1H), 7.83 (dd, $J$ = 5.2 Hz, 1.2 Hz, 1H), 7.88–7.90 (m, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 37.4, 118.5, 124.7, 129.0, 133.1, 136.3, 139.5 ppm. HRMS (ESI): calcd for C$_9$H$_{11}$N$_2$S $^{+}$ ([M–I$^{−}$]$^{+}$) 179.0637, found 179.0638.

\[
\begin{array}{c}
\text{N} \\
\text{N} \\
/ \text{S} \\
\end{array}
\]

(E)-1,3-Dimethyl-2-styryl-1\textit{H}-imidazol-3-ium iodide (3an). A gray solid (40 mg, 62% yield). M.p.: 182–184 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 3.95 (s, 6H), 7.29 (d, $J$ = 16.8 Hz, 1H), 7.49–7.52 (m, 3H), 7.58 (d, $J$ = 16.8 Hz, 1H), 7.76 (s, 2H), 7.83 (d, $J$ = 6.4 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 36.1, 108.1, 123.4, 128.0, 129.0, 130.4, 134.6, 142.0, 142.4 ppm. HRMS (ESI): calcd for C$_{13}$H$_{15}$N$_2$ $^{+}$ ([M–I$^{−}$]$^{+}$) 199.1230, found 199.1225.

\[
\begin{array}{c}
\text{N} \\
\text{N} \\
/ \text{S} \\
\end{array}
\]

1,3-Dimethyl-2-(phenylethynyl)-1\textit{H}-imidazol-3-ium iodide (3ao). A light brown solid (21 mg, 32% yield). M.p.: 156–158 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 3.96 (s, 6H), 7.58 (t, $J$ = 7.6 Hz, 2H), 7.64 (t, $J$ = 7.6 Hz, 1H), 7.84 (d, $J$ = 7.2 Hz, 2H), 7.87 (s, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 36.0,
70.2, 105.0, 118.3, 124.2, 129.2, 131.7, 132.4 ppm. HRMS (ESI): calcd for C$_{13}$H$_{13}$N$_2^+$ ([M–I$^-$$]^{+}$) 197.1073, found 197.1069.

1-Butyl-3-methyl-2-phenyl-1$H$-imidazol-3-ium iodide (3ba). Light yellow oil (62 mg, 91% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.83 (t, $J$ = 7.6 Hz, 3H), 1.22–1.31 (m, 2H), 1.73–1.80 (m, 2H), 3.85 (s, 3H), 4.08 (t, $J$ = 7.6 Hz, 2H), 7.64–7.74 (m, 6H), 7.90 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 13.5, 19.6, 32.1, 37.1, 49.3, 121.0, 122.3, 124.5, 130.1, 131.0, 132.9, 144.5 ppm. HRMS (ESI): calcd for C$_{14}$H$_{19}$N$_2^+$ ([M–I$^-$$]^{+}$) 215.1543, found 215.1541.

1,3-Dibutyl-2-phenyl-1$H$-imidazol-3-ium iodide iodide (3ca). Yellow oil (69 mg, 90% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.81 (t, $J$ = 7.6 Hz, 6H), 1.20–1.29 (m, 4H), 1.71–1.77 (m, 4H), 4.07 (t, $J$ = 7.6 Hz, 4H), 7.66–7.73 (m, 5H), 7.85 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 13.5, 19.6, 32.1, 49.2, 121.0, 122.7, 130.2, 130.8, 133.0, 144.2 ppm. HRMS (ESI): calcd for C$_{17}$H$_{25}$N$_2^+$ ([M–I$^-$$]^{+}$) 257.2012, found 257.2016.

3-Methyl-1,2-diphenyl-1$H$-imidazol-3-ium iodide (3da). A light yellow solid (69 mg, 96% yield). M.p.: 170–172 ºC. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 3.79 (s, 3H), 7.40–7.60 (m, 10H), 8.13 (s, 1H), 8.18 (s, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 35.9, 121.4, 123.5, 123.7, 126.2, 129.0, 129.6, 130.1, 130.9, 132.0, 135.0, 144.3 ppm. HRMS (ESI): calcd for C$_{16}$H$_{16}$N$_2^+$ ([M–I$^-$$]^{+}$) 235.1230, found 235.1227.
2-(4-Methoxyphenyl)-3-methyl-1-phenyl-1H-imidazol-3-ium iodide (3db). A yellow semisolid (74 mg, 95% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.80$ (s, 3H), 4.01 (s, 3H), 6.93 (d, $J = 8.8$ Hz, 2H), 7.39–7.43 (m, 5H), 7.55 (d, $J = 8.8$ Hz, 2H), 7.57 (t, $J = 0.8$ Hz, 1H), 8.03 (t, $J = 2.0$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 37.7, 55.7, 112.5, 115.1, 123.4, 124.8, 126.4, 130.1, 130.4, 133.2, 135.2, 144.9, 162.5$ ppm. HRMS (ESI): calcd for C$_{17}$H$_{17}$N$_2$O$^+$ ([M−I$^-$]$^+$) 265.1335, found 265.1334.

2-(4-Cyanophenyl)-3-methyl-1-phenyl-1H-imidazol-3-ium iodide (3de). A yellow solid (71 mg, 92% yield). M.p.: 96–98 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 4.04$ (s, 3H), 7.36–7.47 (m, 3H), 7.50 (d, $J = 7.6$ Hz, 2H), 7.67 (s, 1H), 7.74 (d, $J = 8.0$ Hz, 2H), 8.01 (d, $J = 8.4$ Hz, 2H), 8.11 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 38.0, 116.2, 117.4, 124.2, 125.5, 126.5, 128.6, 128.9, 130.3, 131.0, 133.0, 134.6, 142.7$ ppm. HRMS (ESI): calcd for C$_{17}$H$_{14}$N$_3$+ ([M−I$^-$]$^+$) 260.1182, found 260.1181.

2-(2-Methoxyphenyl)-3-methyl-1-phenyl-1H-imidazol-3-ium iodide (3dj). A brown solid (63 mg, 81% yield). M.p.: 92–94 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.71$ (s, 3H), 3.92 (s, 3H), 6.95 (d, $J = 8.4$ Hz, 1H), 7.03 (t, $J = 7.6$ Hz, 1H), 7.32–7.41 (m, 5H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.65 (s, 1H), 7.71 (d, $J = 7.2$ Hz, 1H), 8.20 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 37.2, 56.0, 109.6, 111.6, 121.8, 123.5, 125.1, 125.5, 129.9, 130.4, 133.5, 134.8, 135.2, 142.5, 157.7$ ppm. HRMS (ESI): calcd for C$_{17}$H$_{17}$N$_2$O$^+$ ([M−I$^-$]$^+$) 265.1335, found 265.1333.
1,2,3-Triphenyl-1\textit{H}-imidazol-3-ium tetrafluoroborate (3ea). A white solid (68 mg, 88\% yield). M.p.: 236–238 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.33$ (t, $J = 7.6$ Hz, 2H), 7.40–7.43 (m, 3H), 7.48–7.54 (m, 10H), 8.42 (s, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 121.6, 124.0, 126.4, 128.6, 129.7, 130.3, 131.2, 131.8, 135.0, 144.5$ ppm. $^{19}$F NMR (DMSO-$d_6$, 376 MHz): $\delta = -148.32$ (s), -148.27 (s) ppm. HRMS (ESI): calcd for C$_{21}$H$_{17}$N$_2$ [(M−BF$_4$)$^+$] 297.1386, found 297.1382.

![1,2,3-Triphenyl-1H-imidazol-3-ium tetrafluoroborate (3ea)](image)

1,3-Dimethyl-2-phenyl-1\textit{H}-benzo[\textit{d}]imidazol-3-ium iodide (3fa). A white solid (61 mg, 87\% yield). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 3.90$ (s, 6H), 7.78–7.87 (m, 5H), 7.91 (d, $J = 6.8$ Hz, 2H), 8.14 (t, $J = 3.2$ Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 32.8, 113.4, 121.0, 126.6, 129.4, 130.7, 131.7, 132.9, 150.3$ ppm.

![1,3-Dimethyl-2-phenyl-1H-benzo[d]imidazol-3-ium iodide (3fa)](image)

1-Butyl-3-methyl-2-phenyl-1\textit{H}-benzo[\textit{d}]imidazol-3-ium iodide (3ga). A semisolid (88 mg, 98\% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.83$ (t, $J = 7.2$ Hz, 3H), 1.16–1.23 (m, 10H), 1.79–1.87 (m, 2H), 3.99 (s, 3H), 4.34 (t, $J = 7.6$ Hz, 2H), 7.67–7.69 (m, 2H), 7.72–7.80 (m, 4H), 7.88 (t, $J = 5.6$ Hz, 1H), 7.93 (d, $J = 7.6$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 14.2, 22.6, 26.6, 28.8, 29.0, 29.4, 31.7, 34.4, 47.3, 113.5, 114.1, 120.7, 127.71, 127.74, 130.2, 131.0, 131.1, 132.3, 133.5, 150.1$ ppm. HRMS (ESI): calcd for C$_{22}$H$_{29}$N$_2^+$ [(M−I)$^+$] 321.2325, found 321.2321.

![1-Butyl-3-methyl-2-phenyl-1H-benzo[d]imidazol-3-ium iodide (3ga)](image)

3-Butyl-1-octyl-2-phenyl-1\textit{H}-benzo[\textit{d}]imidazol-3-ium iodide (3ha). A semisolid (95 mg, 97\% yield).

![3-Butyl-1-octyl-2-phenyl-1H-benzo[d]imidazol-3-ium iodide (3ha)](image)
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.79‒0.84$ (m, 6H), 1.15‒1.31 (m, 12H), 1.79‒1.84 (m, 4H), 4.32‒4.38 (m, 4H), 7.67‒7.71 (m, 2H), 7.73‒7.81 (m, 3H), 7.84‒7.90 (m, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 13.5, 14.2, 20.0, 22.6, 26.6, 28.8, 29.0, 29.4, 31.4, 31.7, 47.3, 47.5, 113.9, 114.0, 120.9, 127.7, 130.3, 130.6, 131.3, 133.5, 149.8 ppm. HRMS (ESI): calcd for C$_{25}$H$_{35}$N$_2^+$ ([M–I$^-$$]^+)$ 363.2795, found 363.2772.

3-Ethyl-1,2-diphenyl-$1$H-benzo[$d$]imidazol-3-ium iodide (3ia). A gray solid (83 mg, 98% yield). M.p.: 188‒190 °C. $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta = 1.45$ (t, $J = 7.2$ Hz, 3H), 4.45 (q, $J = 7.2$ Hz, 2H), 7.53‒7.67 (m, 9H), 7.71‒7.85 (m, 4H), 8.33 (d, $J = 8.0$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$_d_6$): $\delta = 14.3, 41.6, 113.2, 113.8, 121.4, 126.9, 127.4, 127.6, 129.1, 130.0, 130.5, 130.6, 132.5, 132.7, 150.3 ppm. HRMS (ESI): calcd for C$_{21}$H$_{19}$N$_2^+$ ([M–I$^-$$]^+)$ 299.1543, found 299.1540.

1,3-Dibutyl-2,4,5-triphenyl-$1$H-imidazol-3-ium iodide (3ja). A yellow solid (100 mg, 93% yield). M.p.: 128‒130 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.54$ (t, $J = 7.6$ Hz, 6H), 0.92‒1.01 (m, 4H), 1.37‒1.44 (m, 4H), 3.96 (t, $J = 8.0$ Hz, 4H), 7.37‒7.38 (m, 6H), 7.63‒7.65 (m, 4H), 7.70‒7.72 (m, 3H), 8.10 (d, $J = 7.6$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 13.0, 19.4, 31.6, 46.9, 122.0, 125.4, 129.0, 130.0, 130.1, 131.2, 131.3, 132.0, 132.6, 143.6 ppm. HRMS (ESI): calcd for C$_{29}$H$_{33}$N$_2^+$ ([M–I$^-$$]^+)$ 409.2638, found 409.2648.

1,3-Dibutyl-4,5-diphenyl-2-(4-(prop-1-en-2-yl)phenyl)-$1$H-imidazol-3-ium iodide (3jp). A white solid (112 mg, 97% yield). M.p.: 131‒133 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.56$ (t, $J = 7.6$ Hz, 6H), 0.94‒1.03 (m, 4H), 1.38‒1.46 (m, 4H), 2.21 (s, 3H), 3.96 (t, $J = 7.6$ Hz, 4H), 5.27 (s, 1H), 5.56 (s, 1H), 5.82 (s, 1H), 7.16 (d, $J = 7.6$ Hz, 2H), 7.38 (m, 6H), 7.69 (m, 3H) ppm. HRMS (ESI): calcd for C$_{37}$H$_{43}$N$_2^+$ ([M–I$^-$$]^+)$ 515.3185, found 515.3180.
7.37–7.39 (m, 6H), 7.63–7.65 (m, 4H), 7.77 (d, \(J = 8.0\) Hz, 2H), 8.07 (d, \(J = 8.0\) Hz, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 12.1, 18.6, 20.7, 30.8, 46.1, 114.6, 119.8, 124.7, 125.9, 128.1, 129.3, 130.3, 130.5, 131.2, 140.9, 142.7, 144.3\) ppm. HRMS (ESI): calcd for C\(_{32}\)H\(_{37}\)N\(_2\)\(^+\) ([M–I\(^–\)]\(^+\)) 449.2957, found 449.2946.

\[\text{2-Ethyl-3-phenylimidazo[1,5-a]pyridin-2-ium iodide (3ka).} \]
A gray solid (54 mg, 77% yield). M.p.: 102–104 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.59\) (t, \(J = 7.2\) Hz, 3H), 4.57 (q, \(J = 7.2\) Hz, 2H), 7.04 (t, \(J = 6.8\) Hz, 1H), 7.22 (t, \(J = 7.2\) Hz, 1H), 8.07–8.18 (m, 6H), 8.28 (d, \(J = 9.2\) Hz, 1H), 8.65 (s, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 16.3, 45.9, 114.6, 118.9, 119.8, 120.5, 121.5, 124.9, 129.8, 130.7, 131.1, 133.2\) ppm. HRMS (ESI): calcd for C\(_{15}\)H\(_{15}\)N\(_2\)\(^+\) ([M–I\(^–\)]\(^+\)) 223.1230, found 223.1220.

\[\text{1,3-Dimethyl-2,5-diphenyl-1H-imidazol-3-ium iodide (4aa).} \]
A light yellow solid (65 mg, 87% yield). M.p.: 75–77 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.61\) (s, 3H), 3.83 (s, 3H), 7.47 (br, 3H), 7.65–7.66 (m, 4H), 7.71 (d, \(J = 6.4\) Hz, 2H), 7.93 (d, \(J = 6.8\) Hz, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 35.1, 37.0, 121.3, 121.4, 125.3, 129.3, 130.0, 130.5, 130.6, 131.4, 132.8, 135.3, 145.1\) ppm. HRMS (ESI): calcd for C\(_{17}\)H\(_{17}\)N\(_2\)\(^+\) ([M–I\(^–\)]\(^+\)) 249.1386, found 249.1375.
2,5-Bis(4-methoxyphenyl)-1,3-dimethyl-1H-imidazol-3-ium iodide (4ab). A light green solid (67 mg, 77% yield). M.p.: 176–178 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ = 3.60 (s, 3H), 3.80 (s, 3H), 3.82 (s, 3H), 3.88 (s, 3H), 6.97 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 7.55 (s, 1H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.85 (d, $J = 8.4$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 34.9, 36.7, 55.6, 55.8, 112.9, 114.7, 115.4, 117.4, 120.6, 131.8, 133.0, 135.2, 145.1, 161.3, 162.8 ppm. HRMS (ESI): calcd for C$_{19}$H$_{21}$N$_2$O$_2$+ ([M−I$^-$_]+) 309.1598, found 309.1584.

2,5-Bis(4-cyanophenyl)-1,3-dimethyl-1H-imidazol-3-ium iodide (4ae). A yellow solid (35 mg, 41% yield). M.p.: 100–102 °C. $^1$H NMR (400 MHz, DMSO-$d$_6): δ = 3.63 (s, 3H), 3.78 (s, 3H), 7.86 (d, $J = 7.6$ Hz, 2H), 8.06 (d, $J = 7.2$ Hz, 2H), 8.13 (d, $J = 7.2$ Hz, 2H), 8.26–8.29 (m, 3H), ppm. $^{13}$C NMR (100 MHz, DMSO-$d$_6): δ = 35.0, 36.1, 112.7, 115.1, 117.9, 118.2, 122.8, 125.7, 130.0, 130.2, 131.9, 132.9, 133.2, 133.3, 143.9 ppm. HRMS (ESI): calcd for C$_{19}$H$_{15}$N$_4$+ ([M−I$^-$_]+) 299.1291, found 299.1293.
1,3-Dimethyl-2,5-bis(4-(prop-1-en-2-yl)phenyl)-1H-imidazol-3-ium iodide (4ap). A white solid (55 mg, 60% yield). M.p.: 191–193 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.14$ (s, 3H), 2.19 (s, 3H), 3.65 (s, 3H), 3.87 (s, 1H), 5.16 (s, 1H), 5.26 (s, 1H), 5.42 (s, 1H), 5.52 (s, 1H), 7.57 (d, $J = 6.8$ Hz, 2H), 7.65 (s, 1H), 7.68 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.87 (d, $J = 7.2$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.7$, 21.8, 35.2, 37.1, 114.4, 115.8, 119.8, 121.4, 124.1, 126.4, 127.0, 130.3, 131.3, 135.3, 141.9, 142.3, 143.3, 145.2, 145.6 ppm. HRMS (ESI): calcd for C$_{23}$H$_{25}$N$_2$+ ([M–I]$^+$) 329.2012, found 329.2011.

3-butyl-1-methyl-2,4-diphenyl-1H-imidazol-3-ium iodide (4ba) and 3-Butyl-1-methyl-2,5-diphenyl-1H-imidazol-3-ium iodide (4ba’). An inseparable mixture with an ratio of 1:2 as determined by $^1$H NMR spectrum. Light yellow semisolid (55 mg, 65% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.54$ (t, $J = 7.2$ Hz, 1.5H), 0.83 (t, $J = 7.2$ Hz, 3H), 0.92–0.99 (m, 1H), 1.29–1.32 (m, 3H), 1.76–1.84 (m, 2H), 7.49–7.50 (m, 4H), 7.58 (s, 1H), 7.62 (s, 0.5H), 7.67–7.74 (m, 8H), 7.89–7.94 (m, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 13.1$, 13.5, 19.4, 19.7, 31.6, 32.0, 35.0, 37.1, 46.9, 49.3, 119.7, 121.5, 122.1, 125.3, 125.6, 129.4, 130.1, 130.48, 130.54, 130.6, 130.7, 131.2, 131.3, 132.9, 135.7, 144.9 ppm. HRMS (ESI): calcd for C$_{20}$H$_{23}$N$_2$+ ([M–I]$^+$) 291.1856, found 291.1849.
3-Methyl-1,2,5-triphenyl-1H-imidazol-3-ium iodide (4da). A white solid (31 mg, 35% yield). M.p.: 108–110 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 3.70 (s, 3H), 7.48–7.59 (m, 8H), 7.62–7.66 (m, 5H), 7.76 (d, $J = 6.8$ Hz, 2H), 8.45 (s, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 35.9, 121.6, 125.7, 128.3, 128.87, 128.91, 129.6, 129.7, 130.5, 130.9, 132.0, 133.4, 145.5 ppm. HRMS (ESI): calcd for C$_{22}$H$_{19}$N$_2^+$ ([M−I$^-$]+) 311.1543, found 311.1537.

1,3-Dimethyl-2,4,5-triphenyl-1H-imidazol-3-ium iodide (5aa). A light yellow solid (80 mg, 89% yield). M.p.: 186–188 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ = 3.58 (s, 6H), 7.32–7.39 (m, 6H), 7.59 (d, $J = 7.2$ Hz, 4H), 7.65 (br, 3H), 8.12 (br, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 35.0, 122.0, 125.5, 129.1, 129.9, 130.2, 131.4, 131.7, 132.5, 132.7, 144.5 ppm. HRMS (ESI): calcd for C$_{23}$H$_{21}$N$_2^+$ ([M−I$^-$]+) 325.1699, found 325.1691.

2,4,5-Tris(4-cyanophenyl)-1,3-dimethyl-1H-imidazol-3-ium iodide (5ae). A light yellow solid (78 mg, 74% yield). M.p.: 185–187 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ = 3.58 (s, 6H), 7.66 (d, $J = 7.2$ Hz, 4H),
8.03 (d, \(J = 7.2\) Hz, 4H), 8.13 (d, \(J = 6.4\) Hz, 2H), 8.31 (d, \(J = 7.2\) Hz, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 34.9, 113.1, 115.2, 117.9, 118.0, 125.9, 129.6, 130.9, 131.7, 132.1, 133.2, 133.5, 143.7\) ppm. HRMS (ESI): calcd for C\(_{26}\)H\(_{18}\)N\(_5^+\) ([M−I−]−) 400.1557, found 400.1558.

![Structure of 2,4,5-Tris(4-chlorophenyl)-1,3-dimethyl-1H-imidazol-3-ium iodide (5ai).](image)

2,4,5-Tris(4-chlorophenyl)-1,3-dimethyl-1H-imidazol-3-ium iodide (5ai). A white solid (72 mg, 65% yield). M.p.: 140–142. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.56\) (s, 6H), 7.35 (d, \(J = 7.2\) Hz, 4H), 7.59 (d, \(J = 8.0\) Hz, 4H), 7.63 (d, \(J = 7.2\) Hz, 2H), 8.14 (d, \(J = 8.0\) Hz, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 35.1, 120.1, 123.6, 129.6, 130.4, 131.9, 132.9, 133.3, 137.0, 139.6, 143.9\) ppm. HRMS (ESI): calcd for C\(_{23}\)H\(_{18}\)Cl\(_3\)N\(_2^+\) ([M−I−]−) 427.0530, found 427.0522.

![Structure of 1,3-Dimethyl-2,4,5-tri(pyridin-4-yl)-1H-imidazol-3-ium iodide (5aq).](image)

1,3-Dimethyl-2,4,5-tri(pyridin-4-yl)-1H-imidazol-3-ium iodide (5aq). A yellow solid (44 mg, 48% yield). M.p.: > 250 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 3.61\) (s, 6H), 7.47 (d, \(J = 4.0\) Hz, 4H), 7.94 (d, \(J = 4.0\) Hz, 2H), 8.70 (br, 4H), 8.99 (d, \(J = 4.4\) Hz, 2H) ppm. \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta = 35.0, 125.0, 129.5, 130.3, 132.9, 143.2, 150.6, 151.0\) ppm. HRMS (ESI): calcd for C\(_{20}\)H\(_{18}\)N\(_5^+\) ([M−I−]−) 328.1557, found 328.1560.
1-Butyl-3-methyl-2,4,5-triphenyl-1\textit{H}-imidazol-3-ium iodide (5ba). A light yellow solid (70 mg, 71\% yield). M.p.: 79–81 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.53$ (t, $J = 7.2$ Hz, 3H), 0.94–0.99 (m, 2H), 1.39–1.43 (m, 2H), 3.56 (s, 3H), 7.35–7.39 (m, 6H), 7.61 (d, $J = 5.2$ Hz, 4H), 7.68 (br, 3H), 8.11 (d, $J = 4.4$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 12.9, 19.4, 31.6, 34.9, 46.9, 122.0, 125.2, 125.6, 128.9, 129.0, 129.96, 130.04, 130.2, 131.30, 131.33, 131.4, 131.7, 132.6, 132.7, 144.0 ppm. HRMS (ESI): calcd for C$_{26}$H$_{27}$N$_2$+ ([M–I$^-\text{+}$]) 367.2169, found 367.2162.

3-Methyl-1,2,4,5-tetraphenyl-1\textit{H}-imidazol-3-ium iodide (5da). A white solid (45 mg, 44\% yield). M.p.: 95–97 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 3.63$ (s, 3H), 7.20–7.25 (m, 5H), 7.31 (br, 3H), 7.40 (br, 2H), 7.52 (br, 8H), 7.67 (d, $J = 6.8$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 34.5, 122.1, 125.4, 125.5, 128.4, 128.5, 129.06, 129.14, 129.3, 129.7, 130.3, 130.8, 130.9, 131.0, 131.3, 131.9, 132.1, 133.4, 144.5 ppm. HRMS (ESI): calcd for C$_{26}$H$_{27}$N$_2$+ ([M–I$^-\text{+}$]) 367.2169, found 367.2176.

5-(4-Cyanophenyl)-4-(4-methoxyphenyl)-1,3-dimethyl-2-phenyl-1\textit{H}-imidazol-3-ium iodide (6a). A yellow solid (58 mg, 57\% yield). M.p.: 110–112 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.55$ (s, 3H), 3.62 (s, 3H), 3.79 (s, 3H), 6.89 (d, $J = 8.0$ Hz, 2H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.64–7.67 (m, 5H), 7.83 (d, $J =$
7.6 Hz, 2H), 8.11 (d, \(J = 6.0\) Hz, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 34.9, 35.4, 55.5, 114.0, 114.9, 116.6, 118.1, 121.8, 130.0, 130.5, 130.6, 131.7, 132.4, 132.8, 132.86, 132.90, 133.4, 145.2, 161.3\) ppm. HRMS (ESI): calcd for C\(_{25}\)H\(_{22}\)N\(_3\)O\(^+\) ([M–I\(^–\)]\(^+\)) 380.1757, found 380.1752.

**5-(4-Cyanophenyl)-2-(4-methoxyphenyl)-1,3-dimethyl-4-phenyl-1H-imidazol-3-ium iodide (6b).** A yellow solid (63 mg, 62% yield). M.p.: 126–128 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.62\) (s, 3H), 3.83 (s, 6H), 6.97 (t, \(J = 7.6\) Hz, 1H), 7.13 (d, \(J = 8.4\) Hz, 2H), 7.49–7.68 (m, 8H), 7.87 (d, \(J = 8.8\) Hz, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 35.0, 36.8, 55.8, 112.8, 114.1, 114.8, 115.4, 121.0, 125.5, 129.3, 130.0, 130.4, 130.6, 131.4, 133.0, 145.5, 162.9\) ppm. HRMS (ESI): calcd for C\(_{25}\)H\(_{22}\)N\(_3\)O\(^+\) ([M–I\(^–\)]\(^+\)) 380.1757, found 380.1752.

**2-(4-Cyanophenyl)-4-(4-methoxyphenyl)-1,3-dimethyl-5-phenyl-1H-imidazol-3-ium iodide (6c).** A yellow solid (53 mg, 52% yield). M.p.: 113–115 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.60\) (s, 6H), 3.77 (s, 3H), 6.87 (d, \(J = 7.6\) Hz, 2H), 7.36–7.40 (m, 3H), 7.51 (d, \(J = 8.4\) Hz, 2H), 7.59 (d, \(J = 6.8\) Hz, 2H), 7.97 (d, \(J = 8.0\) Hz, 2H), 8.40 (d, \(J = 8.0\) Hz, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 35.1, 35.2, 55.5, 114.7, 116.6, 116.9, 117.5, 125.3, 126.5, 129.2, 130.5, 131.0, 131.5, 132.9, 133.0, 133.4, 133.6, 142.1, 161.2\) ppm. HRMS (ESI): calcd for C\(_{25}\)H\(_{22}\)N\(_3\)O\(^+\) ([M–I\(^–\)]\(^+\)) 380.1757, found 380.1763.

**VIII. References**


IX. Copies of $^1$H and $^{13}$C NMR spectra