Supporting Information

Synthesis of unsymmetrical imidazolium salts by direct quaternization of N-substituted imidazoles using arylboronic acids

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I. General Remarks

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. CuI was washed with THF using a Soxhlet extractor prior to use. Reactions were carried out under ambient atmosphere unless otherwise specified. All the known N-arylimidazole derivatives,\textsuperscript{1-3} N-mesitylimidazole,\textsuperscript{4} N-(2,6-diisopropylphenyl)imidazole,\textsuperscript{5} N\texttext{-}tert\texttext{-}butylimidazole\textsuperscript{5} and (R)-1-(1-phenylethyl)-1\texttext{H}\texttext{-}imidazole\textsuperscript{6} were synthesized according to the literature procedures. NMR spectra were obtained on a Bruker AMX-400. The $^1$H NMR (400 MHz) chemical shifts were reported relative to CDCl$_3$ or DMSO-$d_6$ as the internal reference (CDCl$_3$: $\delta = 7.26$ ppm; DMSO-$d_6$: $\delta = 2.50$ ppm; The $^{13}$C NMR (100 MHz) chemical shifts were given using CDCl$_3$ or DMSO-$d_6$ as the internal standard (CDCl$_3$: $\delta = 77.16$ ppm; DMSO-$d_6$: $\delta = 39.52$ ppm). High-resolution mass spectra (HR-MS) were obtained with a Waters-Q-TOF-Premier (ESI). Melting points were determined with XRC-1 and are uncorrected. The optical rotation was obtained on an Autopol\textsuperscript{®} V instrument and reported as: $[\alpha]^D$ (c g/100 mL, in CH$_2$Cl$_2$).

II. General procedure for the direct quaternization of N-Substituted Imidazoles with arylboronic acids

A Schlenck tube with a magnetic stir bar was charged with a N-substituted imidazole (0.25 mmol, 1.0 equiv), an arylboronic acid (0.375 mmol, 1.5 equiv), Cu(OAc)$_2$-$H_2$O (5 mg, 10 mol%), FeCl$_3$ (4 mg, 10 mol%), HBF$_4$ (40 $\mu$L, 0.25 mmol, 1.0 equiv, 40% wt in aqueous solution), NH$_4$BF$_4$ (66 mg, 2.5 equiv) and DMF (1 mL). The reaction mixture was stirred at 100 °C for 10 h in an oil bath and then cooled down to room temperature. The solvent was removed under reduced pressure, and the residue was passed through a silica gel column eluted with dichloromethane/methanol (v/v, 70/1–20/1) to afford the desired product.
III. Characterization data of the products

1,3-Diphenyl-1H-imidazol-3-ium Tetrafluoroborate (3aa). A white solid (71 mg, 92% yield). $^{1}$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.64$ (t, $J = 7.4$ Hz, 2H), 7.72 (t, $J = 7.8$ Hz, 4H), 7.93 (d, $J = 7.6$ Hz, 4H), 8.58 (d, $J = 1.2$ Hz, 2H), 10.34 (t, $J = 1.6$ Hz, 1H) ppm.

3-Phenyl-1-o-tolyl-1H-imidazol-3-ium Tetrafluoroborate (3ba or 3ab). A gray solid (66 mg, 81% yield; 3ab: 25 mg, 31% yield). $^{1}$H NMR (400 MHz, DMSO-$d_6$): $\delta = 2.33$ (s, 3H), 7.52–7.74 (m, 7H), 7.91 (d, $J = 8.0$ Hz, 2H), 8.35 (t, $J = 1.6$ Hz, 1H), 8.59 (t, $J = 1.8$ Hz, 1H), 10.11 (s, 1H) ppm.

1-(3-Methoxyphenyl)-3-phenyl-1H-imidazol-3-ium Tetrafluoroborate (3ca or 3ac). A gray solid (3ca: 59 mg, 70% yield; 3ac: 55 mg, 65% yield). $^{1}$H NMR (400 MHz, DMSO-$d_6$): $\delta = 3.89$ (s, 3H), 7.21 (dd, $J = 8.4$, 2.4 Hz, 1H), 7.50 (dd, $J = 8.0$, 2.0 Hz, 1H), 7.55 (t, $J = 2.2$ Hz, 1H), 7.61–7.66 (m, 2H), 7.73 (t, $J = 7.6$ Hz, 2H), 7.93 (d, $J = 7.6$ Hz, 2H), 8.59 (t, $J = 1.8$, 1H), 8.61 (t, $J = 1.8$, 1H), 10.34 (t, $J = 1.6$, 1H) ppm.

1-(4-Methoxyphenyl)-3-phenyl-1H-imidazol-3-ium Tetrafluoroborate (3da or 3ad). A gray solid (3da: 60 mg, 71% yield; 3ad: 59 mg, 70% yield). $^{1}$H NMR (400 MHz, DMSO-$d_6$): $\delta = 3.87$ (s, 3H), 7.25 (d, $J = 6.4$ Hz, 2H), 7.63 (br, 1H), 7.71 (br, 2H), 7.84 (d, $J = 6.4$ Hz, 2H), 7.91 (d, $J = 4.8$ Hz, 2H), 8.49 (s, 1H), 8.54 (s, 1H),
1-(4-Chlorophenyl)-3-phenyl-1H-imidazol-3-ium Tetrafluoroborate (3ea). A gray solid (57 mg, 67% yield). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 7.64\) (t, \(J = 7.4\) Hz, 1H), 7.72 (t, \(J = 7.8\) Hz, 2H), 7.83 (d, \(J = 9.2\) Hz, 2H), 7.91 (d, \(J = 7.6\) Hz, 2H), 7.96 (d, \(J = 8.8\) Hz, 2H), 8.58 (s, 2H), 10.36 (s, 1H) ppm.

1-(2-Bromophenyl)-3-phenyl-1H-imidazol-3-ium Tetrafluoroborate (3fa or 3ah). A white solid (3fa: 63 mg, 66% yield; 3ah: 77 mg, 80% yield). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 7.65\) (t, \(J = 7.4\) Hz, 1H), 7.73 (t, \(J = 7.8\) Hz, 2H), 7.89–7.93 (m, 4H), 7.97 (d, \(J = 8.8\) Hz, 2H), 8.58 (s, 1H), 8.59 (s, 1H), 10.36 (s, 1H) ppm.

1-(4-Ethynylphenyl)-3-phenyl-1H-imidazol-3-ium Tetrafluoroborate (3ga). A yellow solid (47 mg, 57% yield). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 4.46\) (s, 1H), 7.64 (t, \(J = 7.4\) Hz, 1H), 7.72 (t, \(J = 7.6\) Hz, 2H), 7.84 (d, \(J = 8.8\) Hz, 2H), 7.92 (d, \(J = 8.0\) Hz, 2H), 7.96 (d, \(J = 8.8\) Hz, 2H), 8.59 (s, 1H), 8.61 (s, 1H), 10.38 (s, 1H) ppm.

1-(4-(Methoxycarbonyl)phenyl)-3-phenyl-1H-imidazol-3-ium Tetrafluoroborate (3ha). A yellow solid (82 mg, 90% yield). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 3.92\) (s, 3H), 7.64 (t, \(J = 7.4\) Hz, 1H), 7.73 (t, \(J = 7.6\) Hz, 2H), 7.92 (d, \(J = 8.0\) Hz, 2H), 8.10 (d, \(J = 8.8\) Hz, 2H), 8.27 (d, \(J = 8.8\) Hz, 2H), 8.61 (t, \(J = 1.8\) Hz, 1H), 8.67 (t, \(J = 1.8\) Hz, 1H), 10.47 (s, 1H) ppm.
1-[4-(Dimethylamino)phenyl]-3-phenyl-1H-imidazol-3-ium Tetrafluoroborate (3ia). A yellow solid (57 mg, 65% yield). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 3.01$ (s, 6H), 6.92 (d, $J = 9.2$ Hz, 2H), 7.60–7.64 (m, 1H), 7.68–7.72 (m, 4H), 7.91 (d, $J = 8.0$ Hz, 2H), 8.44 (t, $J = 2.0$ Hz, 1H), 8.51 (t, $J = 1.8$ Hz, 1H), 10.17 (t, $J = 1.6$ Hz, 1H) ppm.

1-Mesityl-3-phenyl-1H-imidazol-3-ium Tetrafluoroborate (3ja). A gray solid (58 mg, 66% yield). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 2.13$ (s, 6H), 2.35 (s, 3H), 7.19 (s, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.71 (t, $J = 7.6$ Hz, 2H), 7.92 (d, $J = 8.0$ Hz, 2H), 8.20 (t, $J = 1.6$ Hz, 1H), 8.65 (t, $J = 1.8$ Hz, 1H), 10.03 (t, $J = 1.4$ Hz, 1H) ppm.

1-(2,6-Diisopropylphenyl)-3-phenyl-1H-imidazol-3-ium Tetrafluoroborate (3ka). A gray solid (48 mg, 49% yield). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 1.17$ (d, $J = 6.8$ Hz, 6H), 1.19 (d, $J = 6.8$ Hz, 6H), 2.42–2.47 (m, 2H), 7.50 (d, $J = 7.6$ Hz, 2H), 7.62–7.74 (m, 4H), 7.91 (d, $J = 8.0$ Hz, 2H), 8.37 (s, 1H), 8.71 (s, 1H), 10.24 (s, 1H) ppm.

3-Phenyl-1-(pyridin-2-yl)-1H-imidazol-3-ium Tetrafluoroborate (3la). A gray solid (58 mg, 75% yield). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.63–7.66$ (m, 1H), 7.69–7.72 (m, 3H), 7.94 (d, $J = 8.0$ Hz, 2H), 8.16 (d, $J = 8.4$ Hz, 1H), 8.28 (td, $J = 7.8$, 2.0 Hz, 1H), 8.58 (t, $J = 2.0$ Hz, 1H), 8.71–8.72 (m, 1H), 8.76 (t, $J = 2.0$ Hz, 1H), 8.78 (d, $J = 8.4$ Hz, 1H), 8.80 (t, $J = 1.8$ Hz, 1H), 8.83 (d, $J = 8.0$ Hz, 2H), 8.91 (s, 1H), 9.84 (s, 1H) ppm.
10.59 (t, \( J = 1.6 \) Hz, 1H) ppm.

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\text{BF}_4
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1-\textit{tert}-Butyl-3-phenyl-1\textit{H}-imidazol-3-ium Tetrafluoroborate (\textit{3ma}).\textsuperscript{7} A gray solid (65 mg, 91\% yield). \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): \( \delta = 1.66 \) (s, 9H), 7.59 (t, \( J = 7.2 \) Hz, 1H), 7.67 (t, \( J = 7.8 \) Hz, 2H), 7.85 (d, \( J = 8.0 \) Hz, 2H), 8.28 (t, \( J = 2.0 \) Hz, 1H), 8.38 (t, \( J = 1.8 \) Hz, 1H), 9.69 (t, \( J = 1.6 \) Hz, 1H) ppm.

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1,3-Diphenyl-1\textit{H}-benzo[\textit{d}]imidazol-3-ium Tetrafluoroborate (\textit{3na}).\textsuperscript{7} A gray solid (41 mg, 46\% yield). \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): \( \delta = 7.74-7.83 \) (m, 8H), 7.93-7.98 (m, 6H), 10.58 (s, 1H) ppm.

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\textit{(R)}-3-Phenyl-1-(1-phenylethyl)-1\textit{H}-imidazol-3-ium Tetrafluoroborate (\textit{3oa}). A gray semisolid (76 mg, 90\% yield). \([\alpha]_{D}^{12.7} = +36.3 \) (c = 3.01, CH\textsubscript{2}Cl\textsubscript{2}). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta = 1.97 \) (d, \( J = 6.8 \) Hz, 3H), 5.91 (q, \( J = 6.8 \) Hz, 1H), 7.34–7.39 (m, 3H), 7.43–7.48 (m, 6H), 7.60 (d, \( J = 6.8 \) Hz, 2H), 7.66 (s, 1H), 9.33 (s, 1H) ppm. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta = 20.6, 60.6, 121.7, 121.8, 122.1, 127.3, 129.6, 129.7, 130.4, 130.6, 133.5, 134.5, 137.6 \) ppm. HRMS (ESI): calcd for C\textsubscript{15}H\textsubscript{12}N\textsubscript{3}O\textsubscript{2}\textsuperscript{+} ([M–BF\textsubscript{4}\textsuperscript{−}]\textsuperscript{+}) 249.1386, found 249.1395.

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\begin{array}{c}
\text{N} \\
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\end{array}
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3-((1,1'\text{-Biphenyl}-4-yl)-1-phenyl-1\textit{H}-imidazol-3-ium Tetrafluoroborate (\textit{3ae}). A gray solid (62 mg, 65\% yield). M.p.: 169-171 °C. \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): \( \delta = 7.45 \) (t, \( J = 7.4 \) Hz, 1H), 7.54 (t, \( J = 7.4 \) Hz, 2H), 7.65 (t, \( J = 7.4 \) Hz, 1H), 7.74 (t, \( J = 7.4 \) Hz, 2H), 8.28 (t, \( J = 2.0 \) Hz, 1H), 8.38 (t, \( J = 1.8 \) Hz, 1H), 9.69 (t, \( J = 1.6 \) Hz, 1H) ppm.
= 7.8 Hz, 2H), 7.81 (d, J = 7.2 Hz, 2H), 7.95 (d, J = 7.6 Hz, 2H), 8.03 (s, 4H), 8.61 (t, J = 2.0 Hz, 1H), 8.65 (t, J = 1.8 Hz, 1H), 10. 41 (t, J = 1.6 Hz, 1H) ppm. 

$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 121.9, 122.0, 122.1, 122.5, 127.0, 128.3, 128.4, 129.2, 130.1, 130.2, 133.9, 134.5, 134.7, 138.4, 141.7 ppm. HRMS (ESI): calcd for C$_{21}$H$_{17}$N$_2$+ ([M–BF$_4^-$]+) 297.1386, found 297.1380.

3-(3-Nitrophenyl)-1-phenyl-1H-imidazol-3-ium Tetrafluoroborate (3af). A brown solid (63 mg, 72% yield). M.p.: 176-178 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 7.66 (t, J = 7.2 Hz, 1H), 7.74 (t, J = 7.6 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 8.03 (t, J = 8.4 Hz, 1H), 8.39 (dd, J = 8.4, 2.4 Hz, 1H), 8.49 (dd, J = 8.4, 1.6 Hz, 1H), 8.63 (t, J = 1.8 Hz, 1H), 8.72 (t, J = 2.0 Hz, 1H), 8.89 (t, J = 2.2 Hz, 1H), 10. 54 (t, J = 1.6 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ = 117.6, 122.01, 122.02, 122.2, 122.4, 124.7, 128.6, 130.26, 130.30, 131.8, 134.6, 135.5, 135.6, 148.5 ppm. HRMS (ESI): calcd for C$_{15}$H$_{12}$N$_2$O$_2$+ ([M–BF$_4^-$]+) 266.0924, found 266.0926.

3-(4-Acetylphenyl)-1-phenyl-1H-imidazol-3-ium Tetrafluoroborate (3ag). A yellow solid (51 mg, 57% yield). $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 2.68 (s, 3H), 7.65 (t, J = 7.4 Hz, 1H), 7.73 (t, J = 7.8 Hz, 2H), 7.93 (d, J = 7.6 Hz, 2H), 8.09 (d, J = 8.8 Hz, 2H), 8.27 (d, J = 8.8 Hz, 2H), 8.62 (t, J = 2.0 Hz, 1H), 8.69 (t, J = 2.0 Hz, 1H), 10. 47 (t, J = 1.6 Hz, 1H) ppm.

3-(4-Fluorophenyl)-1-phenyl-1H-imidazol-3-ium Tetrafluoroborate (3ah). A white solid (64 mg, 73% yield). $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 7.59–7.64 (m, 3H), 7.73 (t, J = 7.8 Hz, 2H), 7.91 (d, J = 7.6 Hz, 2H), 7.95–7.98 (m, 2H), 8.54 (t, J = 1.8 Hz, 1H), 8.58 (t, J = 1.8 Hz, 1H), 10.32 (t, J = 1.6 Hz, 1H) ppm.
1,3-Bis(4-bromophenyl)-1H-imidazol-3-ium Tetrafluoroborate (3fi). A gray solid (50 mg, 43% yield). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.88$ (d, $J = 8.4$ Hz, 4H), 7.96 (d, $J = 8.8$ Hz, 4H), 8.58 (d, $J = 1.6$ Hz, 2H), 10.41 (d, $J = 1.6$ Hz, 1H) ppm.

1-(4-Bromophenyl)-3-(4-(ethoxycarbonyl)phenyl)-1H-imidazol-3-ium Tetrafluoroborate (3fj). A gray solid (50 mg, 44% yield). M.p.: 198-200 ºC. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 1.37$ (s, 3H), 4.38 (d, $J = 6.4$ Hz, 2H), 7.91 (br, 2H), 7.96 (br, 2H), 8.08 (d, $J = 7.6$ Hz, 2H), 8.26 (d, $J = 7.2$ Hz, 2H), 8.61 (s, 1H), 8.67 (s, 1H), 10.49 (s, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 14.2$, 61.4, 121.8, 122.15, 122.19, 123.2, 124.2, 131.1, 133.1, 133.9, 135.3, 138.0, 138.9, 164.7 ppm. HRMS (ESI): calcd for C$_{15}$H$_{12}$N$_3$O$_2$+ ([M–BF$_4$]$^+$) 371.0390, found 371.0390.

1,3-Diphenyl-1H-imidazol-3-ium chloride (3aa'). 3aa' was prepared by following a modified procedure. A mixture of about 5 g Dowex® 1×4-50 anion exchange resin in the chloride form and 5 mL water was packed in a column. 1,3-Diphenyl-1H-imidazol-3-ium tetrafluoroborate 3aa (77 mg) was dissolved in 5 mL methanol and 2 mL water. The solution was passed through the column and the resin was then washed with methanol/water. The solution obtained was concentrated and run through a short silica gel column (3 cm) with methanol. Vacuum concentration of the collected methanol solution afforded the diphenylimidazolium chloride salt 3aa' as a gray solid (60 mg, 94% yield). $^1$H NMR (400 MHz, DMSO-$d_6$): 7.63 (t, $J = 7.2$ Hz, 2H), 7.71 (t, $J = 7.8$ Hz, 4H), 7.99 (d, $J = 8.0$ Hz, 4H), 8.65 (d, $J = 0.8$ Hz, 2H), 10.54 (s, 1H) ppm.
IV. References

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

$^1$H NMR of 3aa in DMSO

[Image of the NMR spectrum]
$^1$H NMR of 3oa in CDCl$_3$

$^{13}$C NMR of 3oa in CDCl$_3$
$^1$H NMR of 3ae in DMSO

$^{13}$C NMR of 3ae in DMSO
$^{1}$H NMR of 3f in DMSO
$^{13}$C NMR of 3fj in DMSO

$^1$H NMR 3aa' in DMSO