Recyclable ionic liquid iodinating reagent for solvent free, regioselective iodination of activated aromatic and heteroaromatic amines

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General information: All reagents were purchased from commercial sources (Sigma-Aldrich, Merck and Lancaster) and were used without further purification. Solvents used as reaction media were purchased from local sources and were used after distillation. Reactions were monitored using commercially available, pre-coated thin-layer chromatography (TLC) plates (Merck, silica gel 60 F254, 0.25 mm) and compounds were visualized under ultraviolet light (254 nm) and by staining with p-anisaldehyde or iodine. Silica gel (60-120 and 230-400 mesh) was used for column chromatography. ¹H and ¹³C NMR spectra were recorded on a Bruker Advance 200 and 400 instrument operating at 200 MHz (¹H), 400 MHz (¹H), 500 MHz (¹H) and 400 and 500 MHz (¹³C). Chemical shifts (δ) are quoted in ppm and referenced to internal TMS (δ 0.00 for ¹H NMR), DMSO-d₆ (δ 2.50 for ¹H NMR & 39.5 for ¹³C NMR) or CDCl₃ (δ 77.0 for ¹³C NMR); coupling constants (J) are quoted in Hz. Viscosity was determined on Brookfield: CAP 2000+ Viscometer. High-resolution mass spectra (ESI) were obtained with a Q – Exactive (Thermo fisher scientific). Gas chromatography was performed on Agilent 6890 GC, using HP-5 capillary column (30 m × 0.25 mm, 0.25 µm) and flame ionization detector. The injector temperature was 280 °C and detector temperature was 280 °C. Sample programmed at 80 °C for 1 min., hold with ramp of 20 °C/min. upto 280 °C for 10 min.). GC-MS analyses were carried out on an Agilent 5977AMSD, equipped with a single quadrupole mass spectrometer with Agilent 7890B GC system using an electron ionization source (EI). IR spectra were recorded on Shimadzu 8300, on a FT-IR spectrometer and absorption is expressed in cm⁻¹. Melting points were determined on a Buchi instrument and were uncorrected.
Experimental procedures:

Synthesis of ionic liquid 1-butyl-3-methylpyridinium dichloroiodate (BMPDCI)

A black solution of ICl (3.14 g, 19.39 mmol) in dichloromethane (35 ml), was added drop wise to an ice cold solution of 1-butyl-3-methylpyridinium chloride (3.0 g, 16.16 mmol) in water (16 ml) under stirring and then left to attain room temperature. After the reaction mixture was stirred for 1 hour at room temperature, the dichloromethane layer was separated and dried with sodium sulphate and then evaporated under vacuum to afford water soluble dark reddish brown ionic liquid 1-butyl-3-methylpyridinium dichloroiodate (BMPDCI) in quantitative yields (5.5 g, 98%). This ionic liquid was stable and stored in dark at 10 °C (in refrigerator) for several months without any change in colour, loss of reactivity and degradation (checked by 1H NMR).

1H NMR (200 MHz, DMSO-d6):  δ = 8.87 (s, 1H, Ar-H), 8.80 (d, 1H, J = 5.94 Hz, Ar-H), 8.35 (d, 1H, Ar-CH2), 7.97 (dd, 1H, J = 7.3 Hz, 2H, CH2), 2.40 (s, 3H, Ar-CH3), 1.87 – 1.72 (m, 2H, -CH2-CH2-), 1.28 - 1.09 (m, 2H, -CH2-CH3), 0.81 (t, J = 7.3 Hz, 3H, CH3) ppm; 

13C NMR (50 MHz, CDCl3+DMSO-d6):  δ =12.5, 17.8, 18.4, 32.4, 60.8, 127.0, 139.00, 140.8, 143.2, 145.1 ppm; 

IR (thin film, cm⁻¹): 3058, 2962, 2933, 2873, 1633, 1504, 1465, 1382, 1325, 1251, 1201, 1157, 804, 752, 684; Viscosity 43.6 cP at 25 °C. (Revolutions per minute (RPM): 550, Full Scale Range (FSR): 12.8%; Shear rate: 3197); 


Synthesis of ionic liquid 1-butyl-3-methylpyridinium chlorodiiodide (BMPCDI)

A solution of iodine (0.3 g, 1.18 mmol) in dichloromethane (35 ml) was added drop wise to an ice cold solution of 1-butyl-3-methylpyridinium chloride (0.2 g, 1.0 mmol) in water (16 ml) under stirring and then left at room temperature. After the reaction mixture was stirred for 24 hours at room temperature, the dichloromethane layer was separated and dried with sodium sulphate and then evaporated under vacuum to afford water soluble dark reddish brown ionic liquid 1-butyl-3-methylpyridinium chlorodiiodide (BMPCDI) in quantitative yields (0.4 g, 95%).

1H NMR (200 MHz, DMSO-d6):  δ = 8.82 (s, 1H, Ar-H), 8.74 (d, J = 5.12 Hz, 1H, Ar-H), 8.17 (d, 1H, J = 8.12 Hz), 7.81 (t, 1H, Ar-H), 4.45 (t, J = 7.7 Hz, 2H, CH2), 2.42 (s, 3H, Ar-CH3), 1.79 (m, 2H, -CH2-CH2-), 1.19 (m, 2H, -CH2-CH3), 0.79 (t, J = 7.1 Hz, 3H, CH3) ppm; 

13C NMR (125 MHz, CDCl3+DMSO-d6):  δ = 13.2, 18.2, 18.9, 32.9, 60.9, 127.5, 139.2, 141.8, 144.0, 145.7 ppm; IR (thin film, cm⁻¹): 3055, 2960, 2933, 2871, 1633, 1504, 1463, 1382, 1251, 1157, 804, 752, 684; 

General procedure for the iodination of compounds 1 to 17

A mixture of aromatic/ heteroaromatic amine (1 mmol) and 1-butyl-3-methylpyridinium dichloroiodate (BMPDCI) (1.2 mmol) was heated to 80 °C for 1-5 h, in 50 ml single necked round bottomed flask in an inert atmosphere. The reaction was monitored by TLC. After the reaction was completed (TLC), ethyl acetate (20 ml) was added followed by addition of water (30 ml). The entire reaction mixture was extracted with ethyl acetate (3 x 20 ml). The combined ethyl acetate layer was washed with water (3 x 10 ml), brine and dried over anhydrous sodium sulphate. The separated combined organic layers, was evaporated under vacuum, to afford the crude product. This crude product was purified by silica gel column chromatography to afford the pure iodinated product as shown in Table 3. The water layer was evaporated under vacuum at 60-80 °C to recover 1-butyl-3-methylpyridinium chloride (BMPCI). Addition of ICl (1.2 eq.) to BMPCI in water and dichloromethane (as reported in Scheme 1), afforded 1-butyl-3-methylpyridinium dichloroiodate (BMPDCI), which was reused. The ¹H NMR spectra were matched to literature reports of the identified compounds.

3. Spectral data of the synthesized compounds:

**2,4-Diiodoaniline (1):** Following the general protocol on 1.07 mmol scale of aniline using BMPDCI, the desired product (0.15 g, 85%) was isolated as white brownish solid by silica gel chromatography using pet ether and ethyl acetate. mp 94-96 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.88 (d, 1H, J = 1.8 Hz, Ar-H), 7.38 (dd, 1H, J = 8.2, 1.8 Hz, Ar-H), 6.52 (d, 1H, J = 8.2 Hz, Ar-H), 4.12 (broad singlet, 2H, NH₂) ppm; ¹³C NMR (50 MHz, CDCl₃): δ = 78.9, 84.8, 116.2, 137.8, 145.8 ppm; All data for this compound matched that of previously reported².

**2,4-Diiodoaniline (2):** Following the general protocol on 0.456 mmol scale of 2-iodoaniline using BMPDCI, the desired product (0.157 g, 95%) was isolated as white brownish solid by silica gel chromatography using pet ether and ethyl acetate. mp 94-96 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.88 (d, 1H, J = 1.8 Hz, Ar-H), 7.38 (dd, 1H, J = 8.2, 1.8 Hz, Ar-H), 6.52 (d, 1H, J = 8.2 Hz, Ar-H), 4.12 (broad singlet, 2H, NH₂) ppm; ¹³C NMR (50 MHz, CDCl₃): δ = 78.9, 84.8, 116.2, 137.8, 145.8 ppm; All data for this compound matched that of previously reported².

**2-Ethyl-4-iodo-6-methylaniline (3):** Following the general protocol on 0.74 mmol scale of 2-ethyl-6-methylaniline using BMPDCI, the desired product (0.145 g, 75%) was isolated as brownish liquid by silica gel chromatography using pet ether and
ethyl acetate. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.28$ (s, 2H, Ar-CH), 3.63 (broad singlet, 2H, NH$_2$), 2.48 (q, 2H, $J = 7.6$ Hz, CH$_2$), 2.15 (s, 3H, CH$_3$), 1.25 (t, $J = 7.6$ Hz, 3H, CH$_3$) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 12.7$, 17.3, 23.9, 79.6, 124.4, 129.8, 134.5, 136.3, 141.9 ppm; All data for this compound matched that of previously reported.$^3$

2,6-Diethyl-4-iodoaniline (4): Following the general protocol on 0.67 mmol scale of 2,6-diethylaniline using BMPDCI, the desired product (0.16 g, 90%) was isolated as dark brownish liquid by silica gel chromatography using pet ether and ethyl acetate. $^1$H NMR (200 MHz, CDCl$_3$): $\delta = 7.18$ (s, 2H, Ar-CH), 3.40 (broad singlet, 2H, NH$_2$), 2.43 (q, 4H, $J = 7.4$ Hz, CH$_2$), 1.16 (t, $J = 7.6$ Hz, 6H, CH$_3$) ppm; $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta = 12.8$, 23.9, 80.4, 130.3, 134.5, 141.1 ppm; All data for this compound matched that of previously reported.$^3$

2,6-Dimethyl-4-iodoaniline (5): Following the general protocol on 0.825 mmol scale of 2,6-dimethylaniline using BMPDCI, the desired product (0.19 g, 95%) was isolated as brownish solid by silica gel chromatography using pet ether and ethyl acetate. mp 52-54 $^\circ$C. $^1$H NMR (200 MHz, CDCl$_3$): $\delta = 7.13$ (s, 2H, Ar-CH), 3.44 (broad singlet, 2H, NH$_2$), 2.01 (s, 6H, CH$_3$) ppm; $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta = 17.1$, 79.0, 124.0, 136.3, 142.4 ppm; All data for this compound matched that of previously reported.$^4$

4-Iodo-$N,N$-dimethylaniline (6): Following the general protocol on 0.825 mmol scale of $N,N$-dimethylaniline using BMPDCI, the desired product (0.176 g, 86%) was isolated as greyish solid by silica gel chromatography using pet ether and ethyl acetate. mp 81-82 $^\circ$C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.40$ (d, 2H, $J = 9.01$ Hz, Ar-CH), 6.42 (d, 2H, $J = 9.01$ Hz, Ar-CH), 2.84 (s, 6H, CH$_3$) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 40.4$, 77.4, 114.7, 137.5, 149.9 ppm; All data for this compound matched that of previously reported.$^5$

2-Iodo-4,5-dimethylaniline (7): Following the general protocol on 0.825 mmol scale of 3,4-dimethylaniline using BMPDCI, the desired product (0.19 g, 93%) was isolated as white brownish solid by silica gel chromatography using pet ether and ethyl acetate. mp 53-54 $^\circ$C. $^1$H NMR (200 MHz, CDCl$_3$): $\delta = 7.39$ (s, 1H, Ar-CH), 6.58 (s, 1H, Ar-CH), 3.88 (broad singlet, 2H, NH$_2$),
2.14 (d, 6H, Ar-CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 17.9, 19.2, 80.2, 115.9, 128.3, 137.7, 138.8, 144.3 ppm; All data for this compound matched that of previously reported.⁶

**2-Bromo-4-iodoaniline (8):** Following the general protocol on 0.57 mmol scale of 2-bromoaniline using BMPDCI, the desired product (0.13 g, 80%) was isolated as light brown crystalline powder by flash chromatography using pet ether and ethyl acetate. mp 75-76 °C. ¹H NMR (200 MHz, CDCl₃): δ = 7.61 (d, 1H, J = 1.88 Hz, Ar-CH), 7.30 - 7.26 (dd, 1H, J = 8.6, 1.88 Hz, Ar-CH), 6.47 (1H, d, J = 8.4 Hz, Ar-CH), 3.85 (broad singlet 2H, NH₂) ppm; ¹³C NMR (50 MHz, CDCl₃): δ = 78.3, 110.0, 117.3, 136.9, 139.9, 143.8 ppm; All data for this compound matched that of previously reported.⁷

**4-Bromo-2-iodoaniline (9):** Following the general protocol on 0.58 mmol scale of 4-bromo aniline using BMPDCI, the desired product (0.16 g, 98%) was isolated as grey to purple powder by flash chromatography using pet ether and ethyl acetate. mp 69-72 °C. ¹H NMR (200 MHz, CDCl₃): δ = 7.72 (d, 1H, J = 2.12 Hz, Ar-CH), 7.24 - 7.19 (dd, 1H, J = 8.5, 2.3 Hz, Ar-CH), 6.62 (1H, d, J = 8.5 Hz, Ar-CH), 3.93 (broad singlet, 2H, NH₂) ppm; ¹³C NMR (50 MHz, CDCl₃): δ = 83.4, 109.2, 114.9 131.4, 139.9, 145.3 ppm; All data for this compound matched that of previously reported.⁷

**2-Chloro-4-iodoaniline (10):** Following the general protocol on 0.78 mmol scale of 2-chloro aniline using BMPDCI, the desired product (0.18 g, 93%) was isolated as grey to light orange crystalline powder by flash chromatography using pet ether and ethyl acetate. mp 70 - 73 °C. ¹H NMR (200 MHz, CDCl₃): δ = 7.53 (d, 1H, J = 1.91 Hz, Ar-CH), 7.33 - 7.29 (dd, 1H, J = 8.3, 2.7 Hz, Ar-CH), 6.54 (d, 1H, J = 8.4 Hz, Ar-CH), 4.07 (broad singlet, 2H, NH₂) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 77.9, 117.4, 120.1, 136.2, 137.1, 142.7 ppm; All data for this compound matched that of previously reported.⁷

**4-Chloro-2-iodoaniline (11):** Following the general protocol on 0.78 mmol scale of 4-chloro aniline using BMPDCI, the desired product (0.123 g, 73%) was isolated as pale brown to purple by flash chromatography using pet ether and ethyl acetate. mp 40 °C.
2-Amino-5-iodobenzamide (12): Following the general protocol on 0.73 mmol scale of 2-aminobenzamide using BMPDCI, the desired product (0.138 g, 73%) was isolated as brown solid by flash chromatography using pet ether and ethyl acetate. mp 197–198 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 6.91\) (s, 2H, NH\(_2\)), 6.48 (d, 1H, \(J = 8.6\) Hz, Ar-CH), 6.25 (s, 1H, Ar-CH), 5.81 (s, 2H, NH\(_2\)), 5.65 (d, \(J = 8.6\) Hz, 1H, Ar-CH) ppm; \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta = 74.6, 116.3, 119.1, 136.7, 140.0, 149.9, 170.1\) ppm; All data for this compound matched that of previously reported.\(^7\)

2-Benzyl-4-iodoaniline (13): Following the general protocol on 0.54 mmol scale of 2-benzylaniline using BMPDCI, the desired product (0.128 g, 76%) was isolated as light brown liquid by flash chromatography using pet ether and ethyl acetate. mp 166-168 °C. \(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta = 7.04 - 7.26\) (m, 7H, Ar-CH), 6.31 - 6.35 (d, \(J = 8.71\) Hz, Ar-CH), 3.72 (s, 2H, CH\(_2\)), 3.36 (broad singlet, 2H, NH\(_2\)) ppm; \(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \(\delta = 37.6, 79.9, 118.0, 126.6, 127.7, 128.32, 128.7, 136.2, 138.3, 139.0, 144.2\) ppm; All data for this compound matched that of previously reported.\(^8\)

4,5-Diiodo-1-methylimidazole (14): Following the general protocol on 1.218 mmol scale of 1-methylimidazole using BMPDCI, the desired product (0.32 g, 69%) was isolated as brownish solid by silica gel chromatography using pet ether and ethyl acetate. mp 143-145 °C. \(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta = 7.04 - 7.26\) (m, 7H, Ar-CH), 6.31 - 6.35 (d, \(J = 8.71\) Hz, Ar-CH), 3.72 (s, 2H, CH\(_2\)), 3.36 (broad singlet, 2H, NH\(_2\)) ppm; \(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \(\delta = 37.6, 79.9, 118.0, 126.6, 127.7, 128.32, 128.7, 136.2, 138.3, 139.0, 144.2\) ppm; All data for this compound matched that of previously reported.\(^9\)

5,7-Diiodo-8-hydroxyquinoline (Iodoquinol) (15): Following the general protocol on 0.689 mmol scale of 8-hydroxyquinoline using BMPDCI, the desired product (0.216 g, 80%) was isolated as brownish solid by silica gel chromatography using pet ether
and ethyl acetate. mp decomposes >210 °C. 1H NMR (200 MHz, DMSO-d6): δ = 10.16 (s, 1H, OH), 7.99 (d, 1H, J = 4 Hz, Ar-H), 7.44 (s, 1H, Ar-H), 7.41 – 7.37 (dd, 1H, J = 8.6, 1.3 Hz, Ar-H), 6.86 (q, 1H, J = 8.6, 4.4 Hz, Ar-H) ppm; 13C NMR (125 MHz, DMSO-d6): δ = 81.5, 85.8, 124.7, 130.1, 138.5, 140.6, 145.1, 150.2, 155.4 ppm; All data for this compound matched that of previously reported.11

5-Chloro7-iodo-8-hydroxyquinoline (16): Following the general protocol on 0.558 mmol scale of 5-chloro-8-hydroxyquinoline using BMPDCI, the desired product (0.16 g, 94%) was isolated as white solid by silica gel chromatography using pet ether and ethyl acetate. mp 177-178 °C. 1H NMR (200 MHz, DMSO-d6): δ = 8.94 (d, 1H, J = 3.91 Hz, Ar-H), 8.49 (d, 1H, J = 8.66 Hz, Ar-H), 7.94 (s, 1H, Ar-H), 7.74 (dd, 1H, J = 3.92 Hz, J = 8.46 Hz, Ar-H) ppm; 13C NMR (100 MHz, DMSO-d6): δ = 79.2, 119.6, 123.6, 125.9, 133.2, 135.1, 137.7, 149.8, 153.8 ppm; All data for this compound matched that of previously reported.12

5-Iodovanillin (17): Following the general protocol on 0.657 mmol scale of vanillin using BMPDCI, the desired product (0.282 g, 80%) was isolated as brownish solid by silica gel chromatography using pet ether and ethyl acetate. mp 182–183 °C. 1H NMR (200 MHz, CDCl3): δ = 9.77 (s, 1H, CHO), 7.82 (d, 1H, J = 1.91 Hz, Ar-H), 7.38 (d, 1H, J = 1.5 Hz, Ar-H), 6.70 (s, 1H, OH), 3.97 (s, 3H, OCH3) ppm; 13C NMR (125 MHz, CDCl3): δ = 56.5, 80.4, 108.6, 131.0, 136.2, 146.5, 151.4, 189.6 ppm; All data for this compound matched that of previously reported.13

References
Legends for Supplementary figures

Fig. S-1: HRMS-ESI of compound 1-butyl-3-methylpyridinium dichloroiodate in positive mode

Fig. S-2: HRMS-ESI of compound 1-butyl-3-methylpyridinium dichloroiodate in negative mode

Fig. S-3: HRMS-ESI of compound 1-butyl-3-methylpyridinium dichloroiodate in negative mode

Fig. S-4: IR spectrum of compound 1-butyl-3-methylpyridinium dichloroiodate.

Fig. S-5: HRMS-ESI of compound 1-butyl-3-methylpyridinium chlorodiiodide in positive mode

Fig. S-6: HRMS-ESI of compound 1-butyl-3-methylpyridinium chlorodiiodide in negative mode

Fig. S-7: HRMS-ESI of compound 1-butyl-3-methylpyridinium chlorodiiodide in negative mode

Fig. S-8: IR spectrum of compound 1-butyl-3-methylpyridinium chlorodiiodide.

Fig. S-9: $^1$H-NMR spectrum of compound BMPDCI recorded in DMSO-$d_6$.

Fig. S-10: $^{13}$C-NMR spectrum of compound BMPDCI recorded in CDCl$_3$ and DMSO-$d_6$.

Fig. S-11: $^1$H-NMR spectrum of compound BMPCDI recorded in DMSO-$d_6$.

Fig. S-12: $^{13}$C-NMR spectrum of compound BMPCDI recorded in CDCl$_3$ and DMSO-$d_6$.

Fig. S-13: $^1$H-NMR spectrum of compound 1 and 2 recorded in CDCl$_3$.

Fig. S-14: $^{13}$C-NMR spectrum of compound 1 and 2 recorded in CDCl$_3$.

Fig. S-15: $^1$H-NMR spectrum of compound 3 recorded in CDCl$_3$.

Fig. S-16: $^{13}$C-NMR spectrum of compound 3 recorded in CDCl$_3$.

Fig. S-17: $^1$H-NMR spectrum of compound 4 recorded in CDCl$_3$.

Fig. S-18: $^{13}$C-NMR spectrum of compound 4 recorded in CDCl$_3$.

Fig. S-19: $^1$H-NMR spectrum of compound 5 recorded in CDCl$_3$.

Fig. S-20: $^{13}$C-NMR spectrum of compound 5 recorded in CDCl$_3$.

Fig. S-21: $^1$H-NMR spectrum of compound 6 recorded in CDCl$_3$.
Fig. S-22: $^{13}$C-NMR spectrum of compound 6 recorded in CDCl$_3$.

Fig. S-23: $^1$H-NMR spectrum of compound 7 recorded in CDCl$_3$.

Fig. S-24: $^{13}$C-NMR spectrum of compound 7 recorded in CDCl$_3$.

Fig. S-25: $^1$H-NMR spectrum of compound 8 recorded in CDCl$_3$.

Fig. S-26: $^{13}$C-NMR spectrum of compound 8 recorded in CDCl$_3$.

Fig. S-27: $^1$H-NMR spectrum of compound 9 recorded in CDCl$_3$.

Fig. S-28: $^{13}$C-NMR spectrum of compound 9 recorded in CDCl$_3$.

Fig. S-29: $^1$H-NMR spectrum of compound 10 recorded in CDCl$_3$.

Fig. S-30: $^{13}$C-NMR spectrum of compound 10 recorded in CDCl$_3$.

Fig. S-31: $^1$H-NMR spectrum of compound 11 recorded in CDCl$_3$.

Fig. S-32: $^{13}$C-NMR spectrum of compound 11 recorded in CDCl$_3$.

Fig. S-33: $^1$H-NMR spectrum of compound 12 recorded in DMSO-$d_6$.

Fig. S-34: $^{13}$C-NMR spectrum of compound 12 recorded in DMSO-$d_6$.

Fig. S-35: $^1$H-NMR spectrum of compound 13 recorded in CDCl$_3$.

Fig. S-36: $^{13}$C-NMR spectrum of compound 13 recorded in CDCl$_3$.

Fig. S-37: $^1$H-NMR spectrum of compound 14 recorded in DMSO-$d_6$.

Fig. S-38: $^1$H-NMR spectrum of compound 14 recorded in CDCl$_3$ and DMSO-$d_6$.

Fig. S-39: $^1$H-NMR spectrum of compound 15 recorded in DMSO-$d_6$.

Fig. S-40: $^{13}$C-NMR spectrum of compound 15 recorded in DMSO-$d_6$.

Fig. S-41: $^1$H-NMR spectrum of compound 16 recorded in DMSO-$d_6$.

Fig. S-42: $^{13}$C-NMR spectrum of compound 16 recorded in DMSO-$d_6$.

Fig. S-43: $^1$H-NMR spectrum of compound 17 recorded in CDCl$_3$.

Fig. S-44: $^{13}$C-NMR spectrum of compound 17 recorded in CDCl$_3$. 
Fig. S-1: HRMS-ESI of compound 1-butyl-3-methylpyridinium dichloroiodate in positive mode

$\text{C}_{10}\text{H}_{16}\text{N}[\text{M}^-\text{ICl}_2]^-$ - Found 150.1279
Fig. S-2: HRMS-ESI of compound 1-butyl-3-methylpyridinium dichloroiodate in negative mode
ICl₂ [ICl₂⁺M]⁻ - Found 196.842
Fig. S-3: HRMS-ESI of compound 1-butyl-3-methylpyridinium dichloroiodate in negative mode $\text{I} \left[\text{I}^+\text{-MCl}_2\right]^-$ - Found 126.9041

Fig. S-4: IR spectrum of compound 1-butyl-3-methylpyridinium dichloroiodate.
Fig. S-5: HRMS-ESI of compound 1-butyl-3-methylpyridinium chlorodiiodide in positive mode
\[ \text{C}_{10}\text{H}_{16}\text{N} \left[ \text{M}^+\text{-ClI} \right]^+ \] - Found 150.1277
Fig. S-6: HRMS-ESI of compound 1-butyl-3-methylpyridinium chlorodiiodide in negative mode 
\[ \text{CII}_2 [\text{CII}_2^+ - \text{M}^+]^- \] - Found 288.7791
Fig. S-7: HRMS-ESI of compound 1-butyl-3-methylpyridinium chlorodiiodide in negative mode
I [I⁺-MCII⁺]- Found 126.9040

Fig. S-8: IR spectrum of compound 1-butyl-3-methylpyridinium chlorodiiodide.
Figure S9.

1H NMR- 1-butyl-3-methylpyridinium dichloroiodate

Fig. S-9: 1H-NMR spectrum of compound BMPDCI recorded in DMSO-d6.

Figure S10.

13C NMR- 1-Butyl-3-methylpyridinium dichloroiodate

Fig. S-10: 13C-NMR spectrum of compound BMPDCI recorded in CDCl3 and DMSO-d6.
Figure S11.

**1H NMR- 1-Butyl-3-methylpyridinium chlorodiiodide**

![1H NMR spectrum of compound BMPCDI recorded in DMSO-\textit{d}_6.](image)

Fig. S-11: $^1$H-NMR spectrum of compound BMPCDI recorded in DMSO-\textit{d}_6.

Figure S12.

**$^{13}$C NMR- 1-Butyl-3-methylpyridinium chlorodiiodide**

![$^{13}$C NMR spectrum of compound BMPCDI recorded in CDCl\textsubscript{3} and DMSO-\textit{d}_6.](image)

Fig. S-12: $^{13}$C-NMR spectrum of compound BMPCDI recorded in CDCl\textsubscript{3} and DMSO-\textit{d}_6.
Figure S13.

**1H NMR- 2,4- Diidoaniline**

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Sweep Width (Hz) 600.85  Temperature (deg C) 27.000

Fig. S-13: ¹H-NMR spectrum of compound 1 and 2 recorded in CDCl₃.

Figure S14.

**¹³C NMR- 2,4-Diidoaniline**

Acquisition Time (sec) 2.7529  Comment sprrw  Date 15/03/2015 01:24:58  Frequency (MHz) 75.32

Temperature (deg C) 0.000

Fig. S-14: ¹³C-NMR spectrum of compound 1 and 2 recorded in CDCl₃.
**Figure S15.**

\[ ^1H \text{ NMR} - 2\text{-ethyl-4-iodo-6-methylaniline} \]

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Fig. S-15: \(^1H\)-NMR spectrum of compound 3 recorded in CDCl\(_3\).

**Figure S16.**

\[ ^13C \text{ NMR} - 2\text{-ethyl-4-iodo-6-methylaniline} \]

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Fig. S-16: \(^{13}C\)-NMR spectrum of compound 3 recorded in CDCl\(_3\).
Figure S17.

**1H NMR- 2,6-Diethyl-4-idoaniline**

![1H NMR spectrum](image)

**Fig. S-17: 1H-NMR spectrum of compound 4 recorded in CDCl₃.**

Figure S18.

**13C NMR- 4-ido,2,6 Diethyl aniline**

![13C NMR spectrum](image)

**Fig. S-18: 13C-NMR spectrum of compound 4 recorded in CDCl₃.**
Figure S19.

**1H NMR - 4-Iodo-2,6-dimethylaniline**

![1H NMR spectrum of compound 5](image)

Fig. S-19: $^1$H-NMR spectrum of compound 5 recorded in CDCl$_3$.

Figure S20.

**$^{13}$C NMR - 4-Iodo-2,6-dimethylaniline**

![$^{13}$C NMR spectrum of compound 5](image)

Fig. S-20: $^{13}$C-NMR spectrum of compound 5 recorded in CDCl$_3$. 
Figure S21.

**$^1$H NMR - 4-iodo-N,N-dimethylaniline**

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![H-NMR spectrum of compound 6 recorded in CDCl$_3$.](image1)

Fig. S-21: $^1$H-NMR spectrum of compound 6 recorded in CDCl$_3$.

Figure S22.

**$^{13}$C NMR - 4-iodo-N,N-dimethylaniline**

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![C-NMR spectrum of compound 6 recorded in CDCl$_3$.](image2)

Fig. S-22: $^{13}$C-NMR spectrum of compound 6 recorded in CDCl$_3$. 
Figure S23.

**$^1$H NMR- 2-iodo-4,5-dimethylaniline**

Fig. S-23: $^1$H-NMR spectrum of compound 7 recorded in CDCl$_3$.

Figure S24.

**$^{13}$C NMR- 2-iodo-4,5-dimethylaniline**

Fig. S-24: $^{13}$C-NMR spectrum of compound 7 recorded in CDCl$_3$. 
Figure S25.

**1H NMR - 2-Bromo-4-idoaniline**

![1H NMR spectrum of compound 8 recorded in CDCl3.](image)

Fig. S-25: **1H-NMR** spectrum of compound 8 recorded in CDCl3.

Figure S26.

**13C NMR - 2-Bromo-4-idoaniline**

![13C NMR spectrum of compound 8 recorded in CDCl3.](image)

Fig. S-26: **13C-NMR** spectrum of compound 8 recorded in CDCl3.
Figure S27.

**1H NMR- 4-Bromo,2-ido aniline**

![Figure S27](image)

Fig. S-27: ¹H-NMR spectrum of compound 9 recorded in CDCl₃.

Figure S28.

**¹³C NMR- 4-Bromo,2-ido aniline**

![Figure S28](image)

Fig. S-28: ¹³C-NMR spectrum of compound 9 recorded in CDCl₃.
Figure S29.

1H NMR - 2-Chloro 4-iodo aniline

Fig. S-29: 1H-NMR spectrum of compound 10 recorded in CDCl3.

Figure S30.

13C NMR - 2-chloro-4-iodoaniline

Fig. S-30: 13C-NMR spectrum of compound 10 recorded in CDCl3.
Figure S31.

**1H NMR- 4-Chloro-2-iodoaniline**

![1H NMR spectrum of compound 11](image)

**Fig. S-31:** 1H-NMR spectrum of compound 11 recorded in CDCl₃

Figure S32.

**13C NMR- 4-Chloro-2-iodoaniline**

![13C NMR spectrum of compound 11](image)

**Fig. S-32:** 13C-NMR spectrum of compound 11 recorded in CDCl₃.
Figure S33.

**1H NMR- 2-amino-5-iodobenzamide**

![NMR spectrum of 1H](image)

**Fig. S-33**: $^1$H-NMR spectrum of compound 12 recorded in DMSO-$_6$.

Figure S34.

**13C NMR- 2-amino-5-iodobenzamide**

![NMR spectrum of 13C](image)

**Fig. S-34**: $^{13}$C-NMR spectrum of compound 12 recorded in DMSO-$_6$.  

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Source: [SI 28](#)
Figure S35.

\[ ^{1}H\text{ NMR - 2-Benzyl-4-iodoaniline} \]

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Fig. S-35: \(^1\text{H}-\text{NMR} \) spectrum of compound 13 recorded in CDCl\(_3\).

Figure S36.

\[ ^{13}C\text{ NMR - 2-Benzyl-4-iodoaniline} \]

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Fig. S-36: \(^{13}\text{C}-\text{NMR} \) spectrum of compound 13 recorded in CDCl\(_3\).
Figure S37.

\( ^1H \text{NMR-} 4,5\text{-diiodo-1-methyl-1H-imidazole} \)

![H-NMR spectrum of compound 14 recorded in DMSO-\( d_6 \).](image)

Fig. S-37: \(^1H\)-NMR spectrum of compound 14 recorded in DMSO-\( d_6 \).

Figure S38.

\( ^{13}C \text{NMR-} 4,5\text{-diiodo-1-methyl-1H-imidazole} \)

![C-NMR spectrum of compound 14 recorded in CDCl\(_3\) and DMSO-\( d_6 \).](image)

Fig. S-38: \(^1H\)-NMR spectrum of compound 14 recorded in CDCl\(_3\) and DMSO-\( d_6 \).
Figure S39.

1H NMR- 5,7-diiodoquinolin-8-ol

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Fig. S-39: 1H-NMR spectrum of compound 15 recorded in DMSO-d6.

Figure S40.

13C NMR- 5,7-diiodoquinolin-8-ol

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Fig. S-40: 13C-NMR spectrum of compound 15 recorded in DMSO-d6.
Figure S41.

**1H NMR- 5-chloro7-ido-8-hydroxyquinoline**

![NMR spectrum of 5-chloro7-ido-8-hydroxyquinoline](image)

Fig. S-41: $^1$H-NMR spectrum of compound 16 recorded in DMSO-$d_6$.

Figure S42.

**13C NMR- 5-chloro7-idoquinolinol-8-ol**

![NMR spectrum of 5-chloro7-idoquinolinol-8-ol](image)

Fig. S-42: $^{13}$C-NMR spectrum of compound 16 recorded in DMSO-$d_6$. 
Figure S43.

**1H NMR- 5-Iodovanillin**

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Fig. S-43: 1H-NMR spectrum of compound 17 recorded in CDCl3.

Figure S44.

**13C NMR- 5 iodovanillin**

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Fig. S-44: 13C-NMR spectrum of compound 17 recorded in CDCl3.