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

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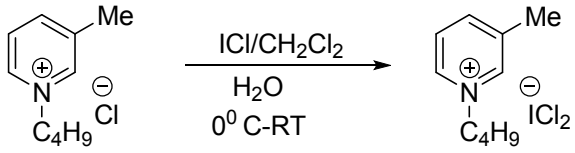
General information: All reagents were purchased from commercial sources (Sigma-Aldrich, Merck and Lancaster) and were used without further purification. Solvents used as reaction media were purchased from local sources and were used after distillation. Reactions were monitored using commercially available, pre-coated thin-layer chromatography (TLC) plates (Merck, silica gel 60 F_{254}, 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. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 200 and 400 instrument operating at 200 MHz (^{1}H), 400 MHz (^{1}H), 500 MHz (^{1}H) and 400 and 500 MHz (^{13}C). Chemical shifts (δ) are quoted in ppm and referenced to internal TMS (δ 0.00 for ^{1}H NMR), DMSO-d_6 (δ 2.50 for ^{1}H NMR & 39.5 for ^{13}C NMR) or $CDCl_3$ (δ 77.0 for ^{13}C 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 ^{0}C and detector temperature was 280 ^{0}C. Sample programmed at 80 ^{0}C for 1 min., hold with ramp of 20 ^{0}C/min. upto 280 ^{0}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:

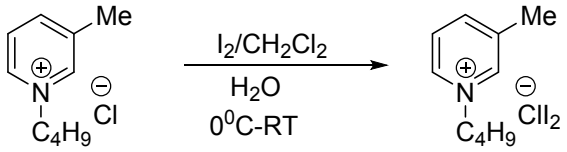
Synthesis of ionic liquid 1-butyl-3-methylpyridinium dichloroiodate (BMPDCI)



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[1] (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 ^{0}C (in refrigerator) for several months without any change in colour, loss of reactivity and degradation (checked by ^{1}H NMR).

^{1}H NMR (200 MHz, DMSO-d_6): δ = 8.87 (s, 1H, Ar-H), 8.80 (d, 1H, *J* = 5.94 Hz, Ar-H), 8.35 (d, 1H, *J* = 7.96 Hz, Ar-H), 7.97 (dd, 1H, *J* = 8.42, 1.37 Hz, Ar-H), 4.43 (t, *J* = 7.3 Hz, 2H, CH_2), 2.40 (s, 3H, Ar-CH_3), 1.87 – 1.72 (m, 2H, -CH_2-CH_2), 1.28 - 1.09 (m, 2H, CH_2-CH_3), 0.81 (t, *J* = 7.3 Hz, 3H, CH_3) ppm; ^{13}C NMR (50 MHz, $CDCl_3$+DMSO-d_6): 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 ^{0}C. (Revolutions per minute (RPM): 550, Full Scale Range (FSR): 12.8%, Shear rate: 3197); HRMS-ESI Positive mode: $[M^+\text{-}ICl_2]^+$ calcd for $C_{10}H_{16}N$ $[M^+\text{-}ICl_2]^+$ 150.1277, found 150.1279. HRMS-ESI negative mode: $[ICl_2^+\text{-}M]^+$ calcd for ICl_2 $[ICl_2^+\text{-}M]^+$ 196.8416, found 196.8423, $[I^+\text{-}MClI]^+$ calcd for I $[I^+\text{-}MClI]^+$ 126.9039, found 126.9041.

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



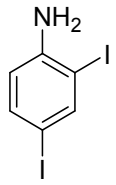
A solution of iodine (0.3 g, 1.18 mmol) in dichloromethane (35 ml) was added drop wise to an ice cold solution of 1-butyl-3-methylpyridinium chloride (0.2 g, 1.0 mmol) in water (16 ml) under stirring and then left at room temperature. After the reaction mixture was stirred for 24 hours at room temperature, 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%).

^{1}H NMR (200 MHz, DMSO-d_6 δ): 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, CH_2), 2.42 (s, 3H, Ar-CH_3), 1.79 (m, 2H, -CH_2-CH_2-), 1.19 (m, 2H, -CH_2-CH_3), 0.79 (t, *J* = 7.1 Hz, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$+DMSO-d_6): 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, 1325, 1251, 1157, 800, 750, 682, 430; HRMS-ESI Positive mode: $[M^+\text{-}ClI_2]^+$ calcd for $C_{10}H_{16}N$ $[M^+\text{-}ClI_2]^+$ 150.1277, found: 150.1277. HRMS-ESI negative mode: $[ClI_2^+\text{-}M]^+$ calcd for ClI_2 $[ClI_2^+\text{-}M]^+$ 288.7772, found 288.7791, $[I^+\text{-}MCl_2]^+$ calcd for I $[I^+\text{-}MCl_2]^+$ 126.9039, found 126.9040.

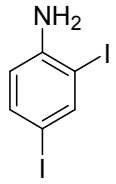
General procedure for the iodination of compounds 1 to 17

A mixture of aromatic/ heteroaromatic amine (1 mmol) and 1-butyl-3-methylpyridinium dichloroiodate (BMPDCI) (1.2 mmol) was heated to 80 ^{0}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 ^{0}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 ^{1}H NMR spectra were matched to literature reports of the identified compounds.

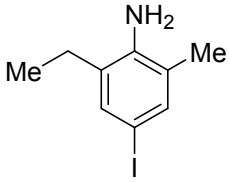
3. Spectral data of the synthesized compounds:



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 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$): 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, NH_2) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ =78.9, 84.8, 116.2, 137.8, 145.8 ppm; All data for this compound matched that of previously reported.[2]

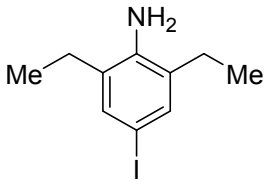


2,4-Diiodoaniline (2): Following the general protocol on 0.456 mmol scale of 2-iodoaniline using BMPDCI, the desired product (0.157 g, 95%) was isolated as white brownish solid by silica gel chromatography using pet ether and ethyl acetate. mp 94-96 ^{0}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, 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, NH_2) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 78.9, 84.8, 116.2, 137.8, 145.8 ppm; All data for this compound matched that of previously reported.[2]

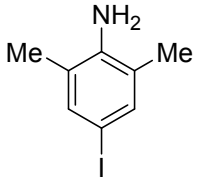


2-Ethyl-4-iodo-6-methylaniline (3): Following the general protocol on 0.74 mmol scale of 2-ethyl-6-methylaniline using BMPDCI, the desired product (0.145 g, 75%) was isolated as brownish liquid by silica gel chromatography using pet ether and

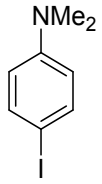
ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (s, 2H, Ar-CH), 3.63 (broad singlet, 2H, NH_2), 2.48 (q, 2H, *J* = 7.6 Hz, CH_2), 2.15 (s, 3H, CH_3), 1.25 (t, *J* = 7.6 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 17.3, 23.9, 79.6, 124.4, 129.8, 134.5, 136.3, 141.9 ppm;



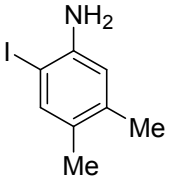
2,6-Diethyl-4-iodoaniline (4): Following the general protocol on 0.67 mmol scale of 2-6-diethylaniline using BMPDCI, the desired product (0.16 g, 90%) was isolated as dark brownish liquid by silica gel chromatography using pet ether and ethyl acetate. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.18 (s, 2H, Ar-CH), 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, $CDCl_3$): δ = 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 ^{0}C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 17.1,79.0, 124.0, 136.3, 142.4 ppm; All data for this compound matched that of previously reported.[4]

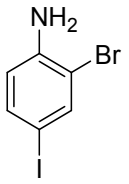


4-Iodo-*N*,*N*-dimethylaniline (6): Following the general protocol on 0.825 mmol scale of *N*,*N*-dimethylaniline using BMPDCI, the desired product (0.176 g, 86%) was isolated as greyish solid by silica gel chromatography using pet ether and ethyl acetate. mp 81-82 ^{0}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 40.4, 77.4, 114.7, 137.5, 149.9 ppm; All data for this compound matched that of previously reported.[5]

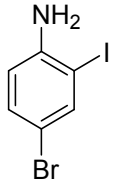


2-Iodo-4,5-dimethylaniline (7): Following the general protocol on 0.825 mmol scale of 3,4-dimethylaniline using BMPDCI, the desired product (0.19 g, 93%) was isolated as white brownish solid by silica gel chromatography using pet ether and ethyl acetate. mp 53-54 ^{0}C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.39 (s, 1H, Ar-CH), 6.58 (s, 1H, Ar-CH), 3.88 (broad singlet, 2H, NH_2),

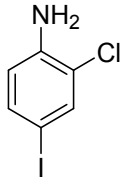
2.14 (d, 6H, Ar-CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9, 19.2, 80.2, 115.9, 128.3, 137.7, 138.8, 144.3 ppm; All data for this compound matched that of previously reported.[6]



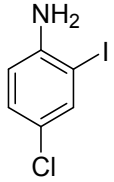
2-Bromo-4-iodoaniline (8): Following the general protocol on 0.57 mmol scale of 2-bromoaniline using BMPDCI, the desired product (0.13 g, 80%) was isolated as light brown crystalline powder by flash chromatography using pet ether and ethyl acetate. mp 75-76 ^{0}C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.61 (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, NH_2) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): 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 ^{0}C. ^{1}H NMR (200 MHz, $CDCl_3$): 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, NH_2) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): 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]

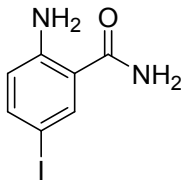


2-Chloro-4-iodoaniline (10): Following the general protocol on 0.78 mmol scale of 2-chloro aniline using BMPDCI, the desired product (0.18 g, 93%) was isolated as grey to light orange crystalline powder by flash chromatography using pet ether and ethyl acetate. mp 70 - 73 ^{0}C. ^{1}H NMR (200 MHz, $CDCl_3$): 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, NH_2) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 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]

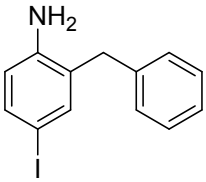


4-Chloro-2-iodoaniline (11): Following the general protocol on 0.78 mmol scale of 4-chloro aniline using BMPDCI, the desired product (0.123 g, 73%) was isolated as pale brown to purple by flash chromatography using pet ether and ethyl acetate. mp 40 ^{0}C.

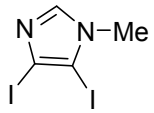
^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.60 (d, 1H, *J* = 2.3 Hz, Ar-CH), 7.12 - 7.07 (dd, 1H, *J* = 8.6, 2.6 Hz, Ar-CH), 6.67 (d, 1H, *J* = 8.3 Hz, Ar-CH), 3.88 (broad singlet, 2H, NH_2) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 83.4. 115.0, 123.1, 129.2, 137.7, 145.5 ppm; All data for this compound matched that of previously reported.[7]



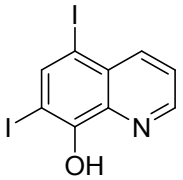
2-Amino-5-iodobenzamide (12): Following the general protocol on 0.73 mmol scale of 2-aminobenzamide using BMPDCI, the desired product (0.138 g, 73%) was isolated as brown solid by flash chromatography using pet ether and ethyl acetate. mp 197–198 ^{0}C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.91 (s, 2H, 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): δ = 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.[8]



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 ^{0}C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.04 - 7.26 (m, 7H, Ar-CH), 6.31 - 6.35 (d, 1H, *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, $CDCl_3$): δ = 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]

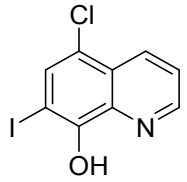


4,5-Diiodo-1-methylimidazole (14): Following the general protocol on 1.218 mmol scale of 1-methylimidazole using BMPDCI, the desired product (0.32 g, 69%) was isolated as brownish solid by silica gel chromatography using pet ether and ethyl acetate. mp 143-145 ^{0}C. ^{1}H NMR (200 MHz, DMSO-d_6): δ = 8.44 (s, 1H, CH), 3.70 (s, 3H, CH_3) ppm; ^{13}C NMR (50 MHz, $CDCl_3$ + DMSO-d_6): δ = 37.5, 87.2, 90.4, 140.7 ppm; All data for this compound matched that of previously reported.[10]

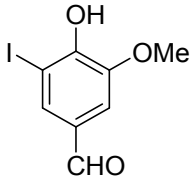


5,7-Diiodo-8-hydroxyquinoline (Iodoquinol) (15): Following the general protocol on 0.689 mmol scale of 8-hydroxyquinoline using BMPDCI, the desired product (0.216 g, 80%) was isolated as brownish solid by silica gel chromatography using pet ether

and ethyl acetate. mp decomposes >210 ^{0}C. ^{1}H NMR (200 MHz, DMSO-d_6): 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; ^{13}C NMR (125 MHz, DMSO-d_6): 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 ^{0}C. ^{1}H NMR (200 MHz, DMSO-d_6): 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; ^{13}C NMR (100 MHz, DMSO-d_6): 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 ^{0}C. ^{1}H NMR (200 MHz, $CDCl_3$): 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, OCH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 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]

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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 nigative mode

Fig. S-7: HRMS-ESI of compound 1-butyl-3-methylpyridinium chlorodiiodide in nigative 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 $CDCl_3$.

Figure S1.

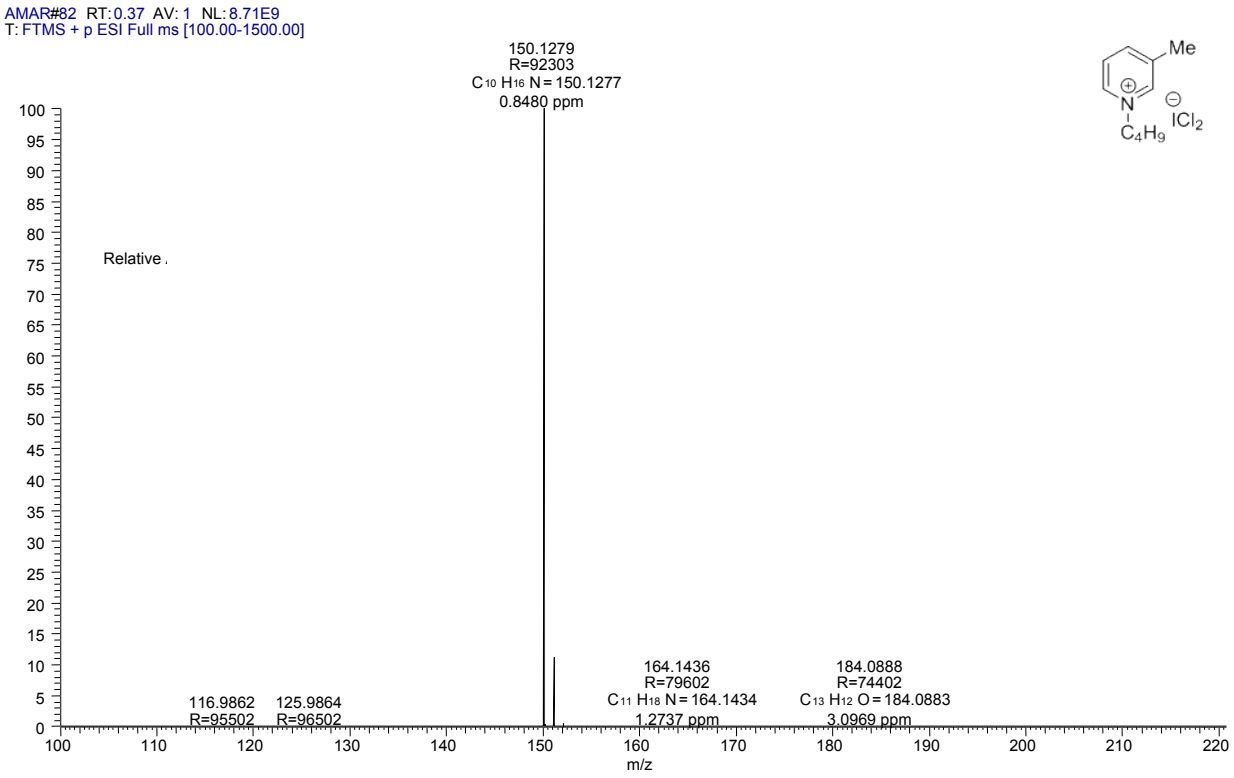

Fig. S-1: HRMS-ESI of compound 1-butyl-3-methylpyridinium dichloroiodate in positive mode $C_{10}H1_6N$ $[M^+\text{-}ICl_2]^+$- Found 150.1279

Figure S2.

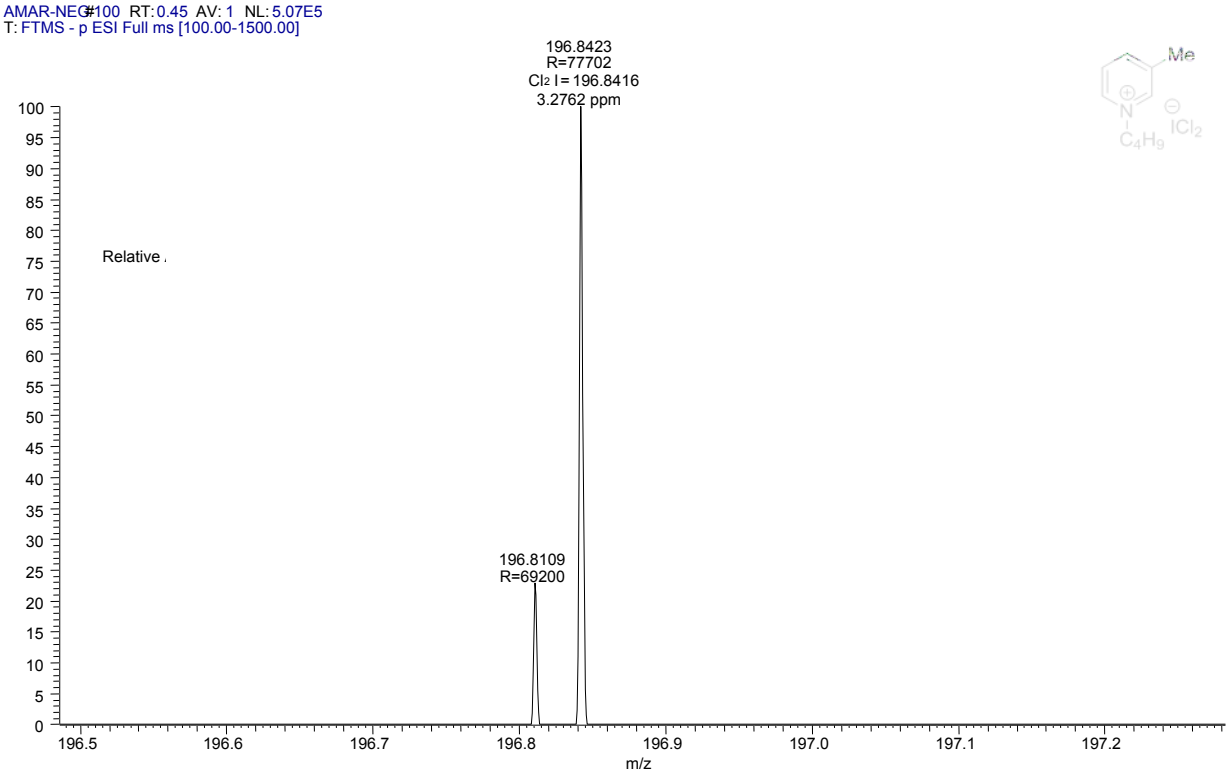

Fig. S-2: HRMS-ESI of compound 1-butyl-3-methylpyridinium dichloroiodate in negative mode ICl_2 $[ICl_2^+\text{-}M]^+$- Found 196.842

Figure S3.

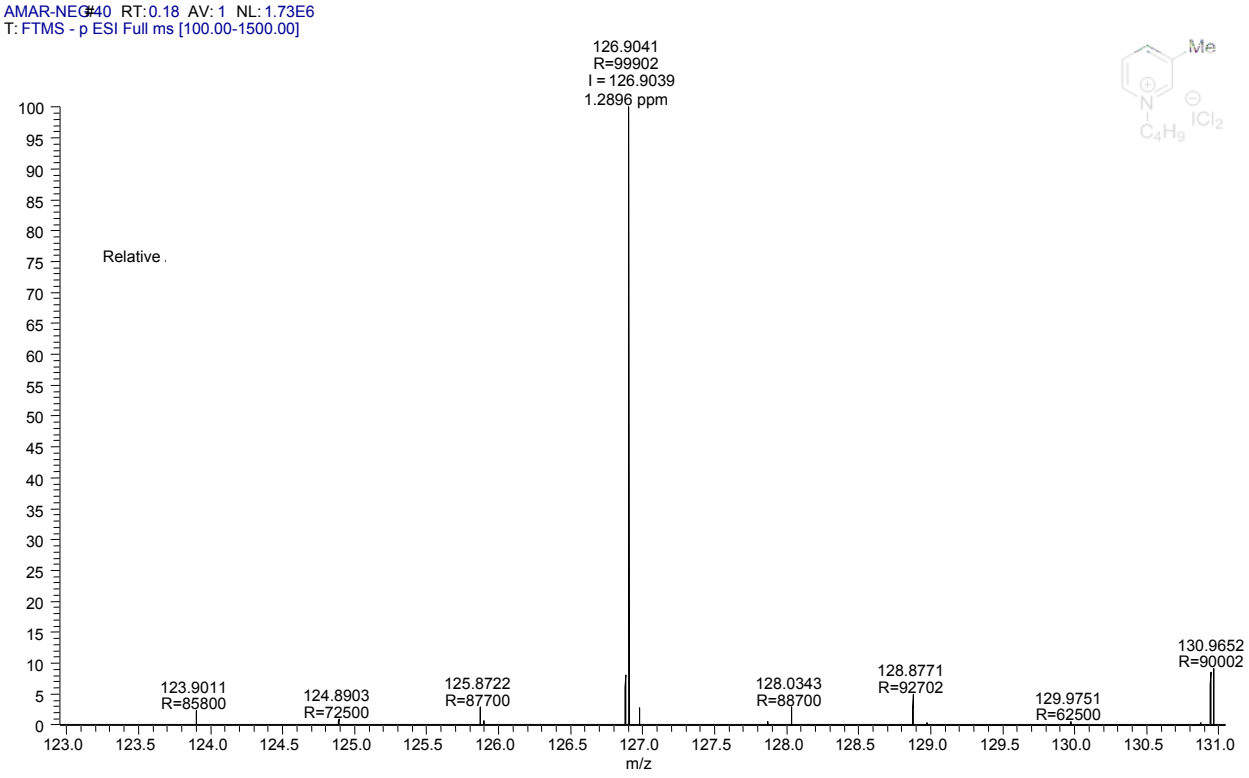

Fig. S-3: HRMS-ESI of compound 1-butyl-3-methylpyridinium dichloroiodate in negative mode I $[I^{+}\text{-}MCl_2]^{+}$- Found 126.9041

Figure S4.

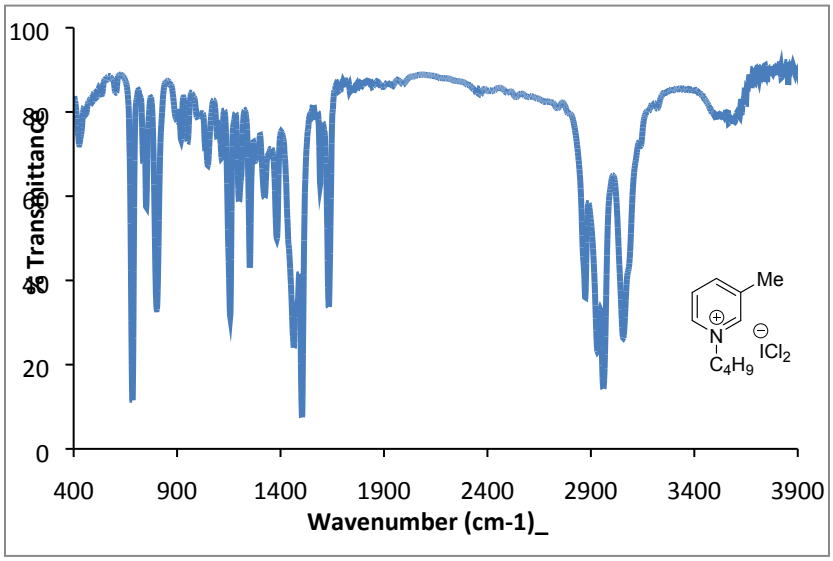

Fig. S-4: IR spectrum of compound 1-butyl-3-methylpyridinium dichloroiodate.

Figure S5.

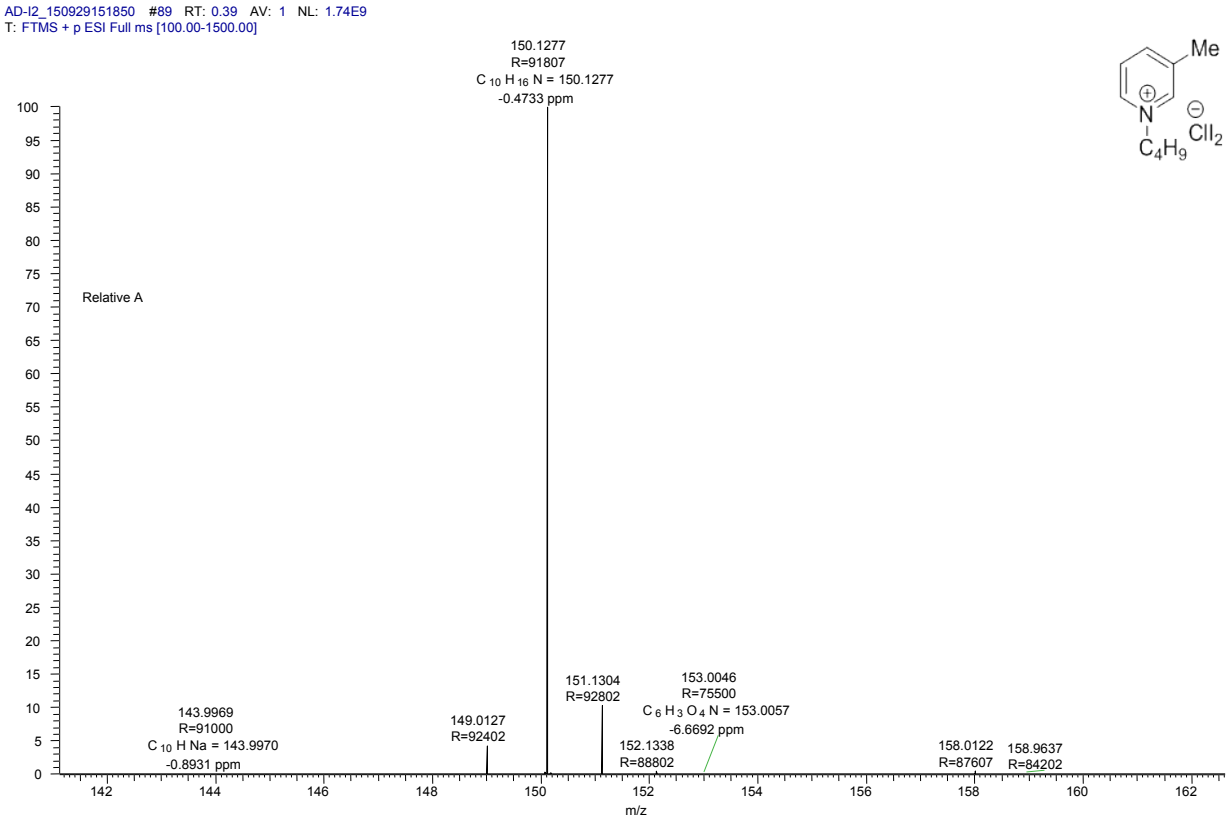

Fig. S-5: HRMS-ESI of compound 1-butyl-3-methylpyridinium chlorodiiodide in positive mode $C_{10}H1_6N$ $[M^+\text{-}ClI_2]^+$- Found 150.1277

Figure S6.

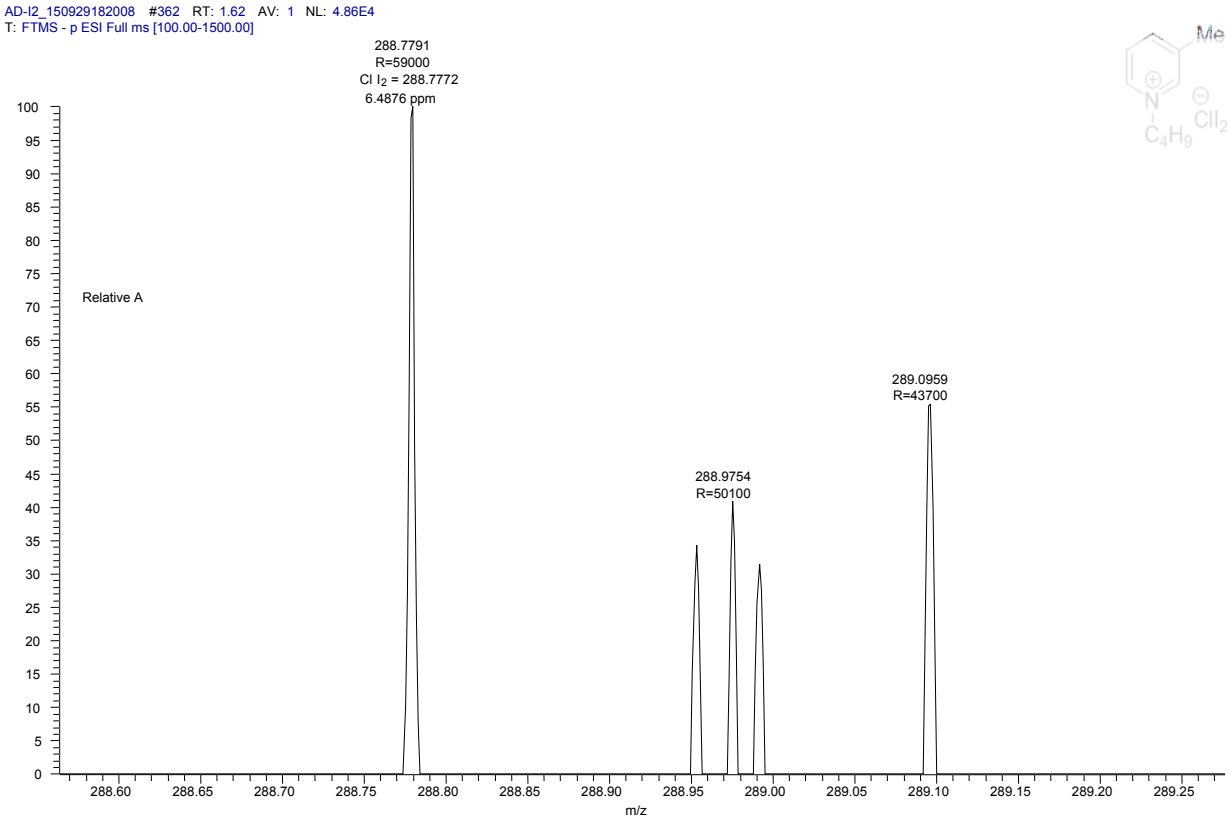

Fig. S-6: HRMS-ESI of compound 1-butyl-3-methylpyridinium chlorodiiodide in nigative mode ClI_2 $[ClI_2^+\text{-}M^+]^+$- Found 288.7791

Figure S7.

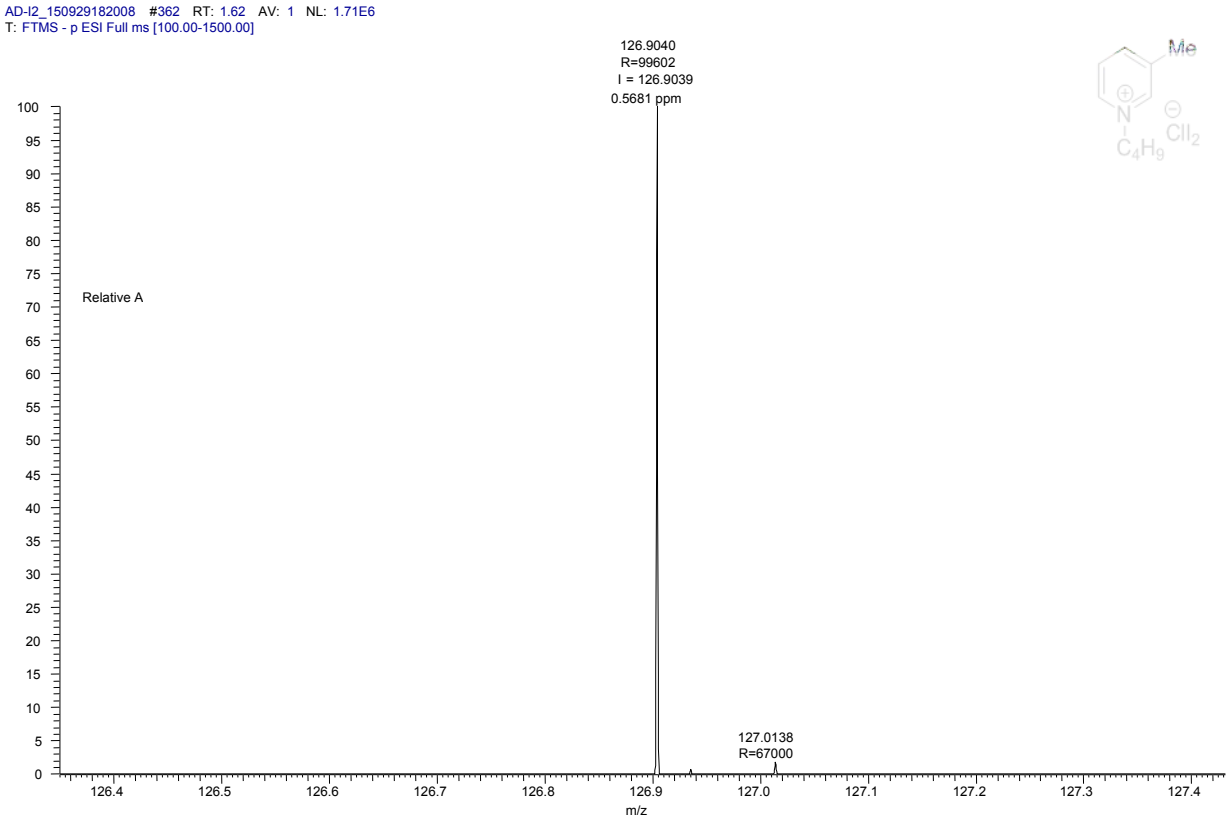

Fig. S-7: HRMS-ESI of compound 1-butyl-3-methylpyridinium chlorodiiodide in nigative mode I $[I^{+}\text{-}MClI^{+}]^{+}$- Found 126.9040

Figure S8.

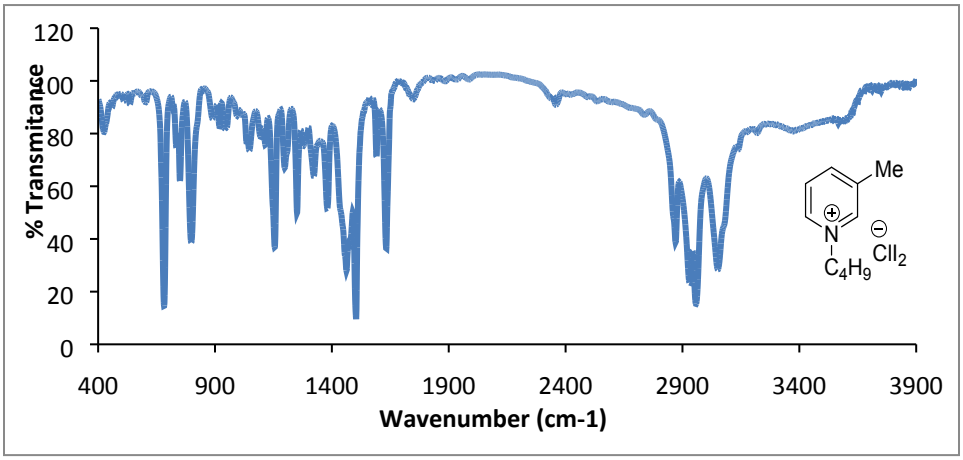

Fig. S-8 : IR spectrum of compound 1-butyl-3-methylpyridinium chlorodiiodide.

Figure S9.

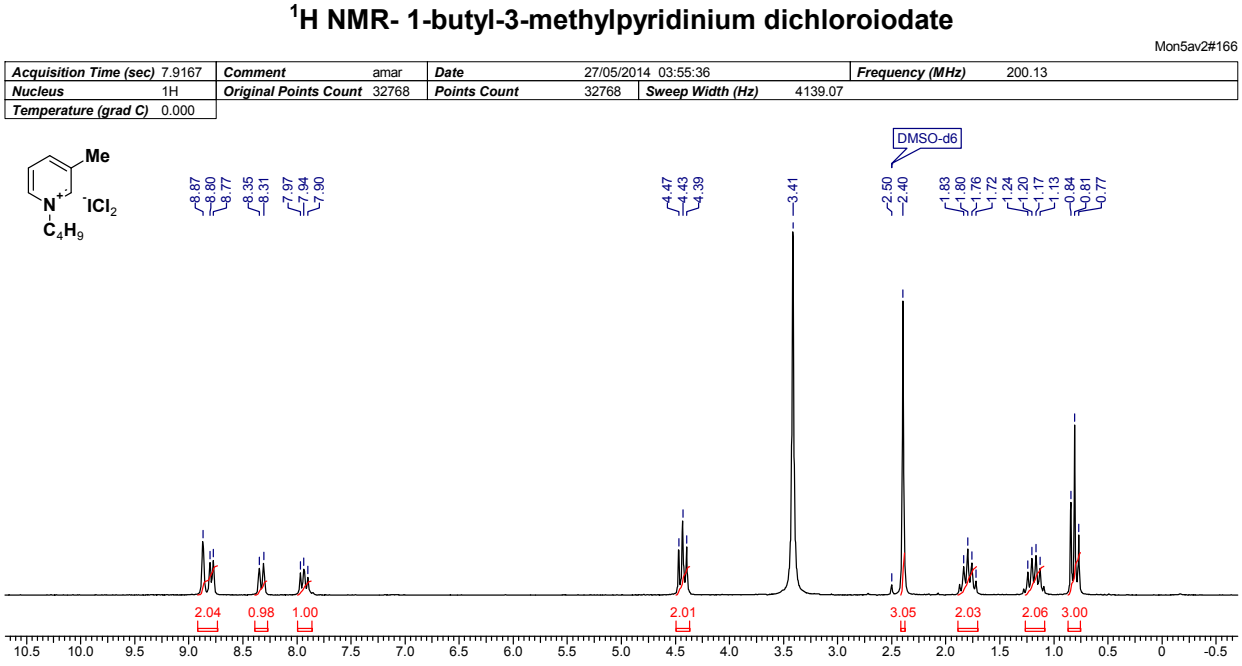

Fig. S-9: ^{1}H-NMR spectrum of compound BMPDCI recorded in DMSO-d_6.

Figure S10.

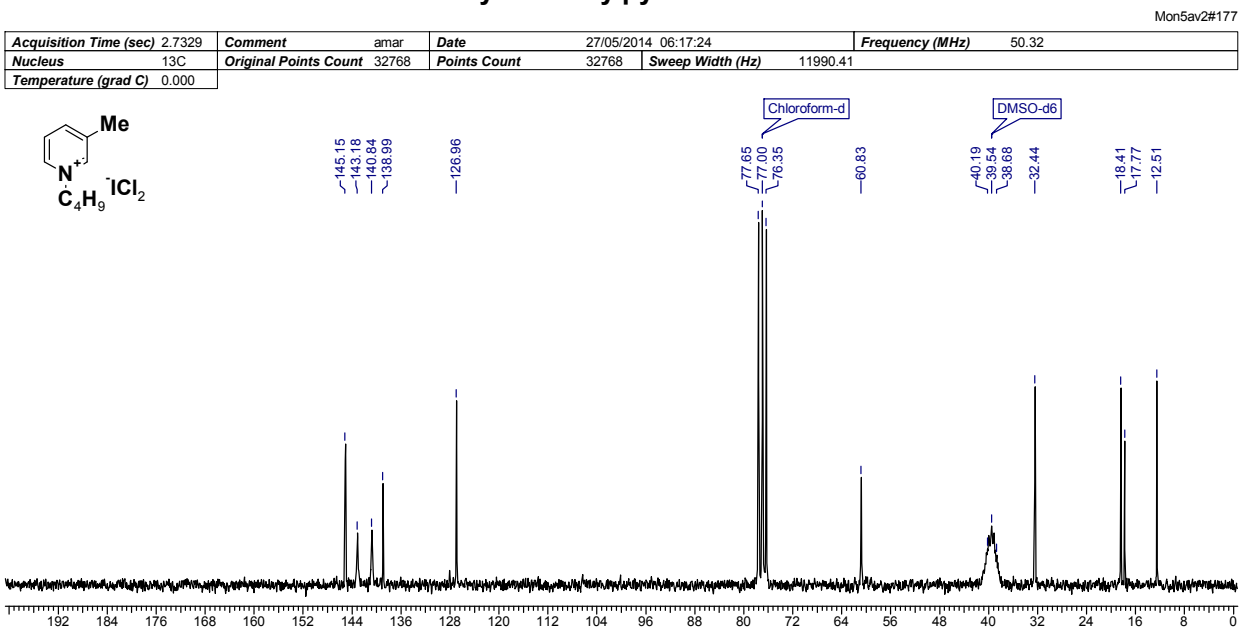

Fig. S-10: ^{13}C-NMR spectrum of compound BMPDCI recorded in $CDCl_3$ and DMSO-d_6.

Figure S11.

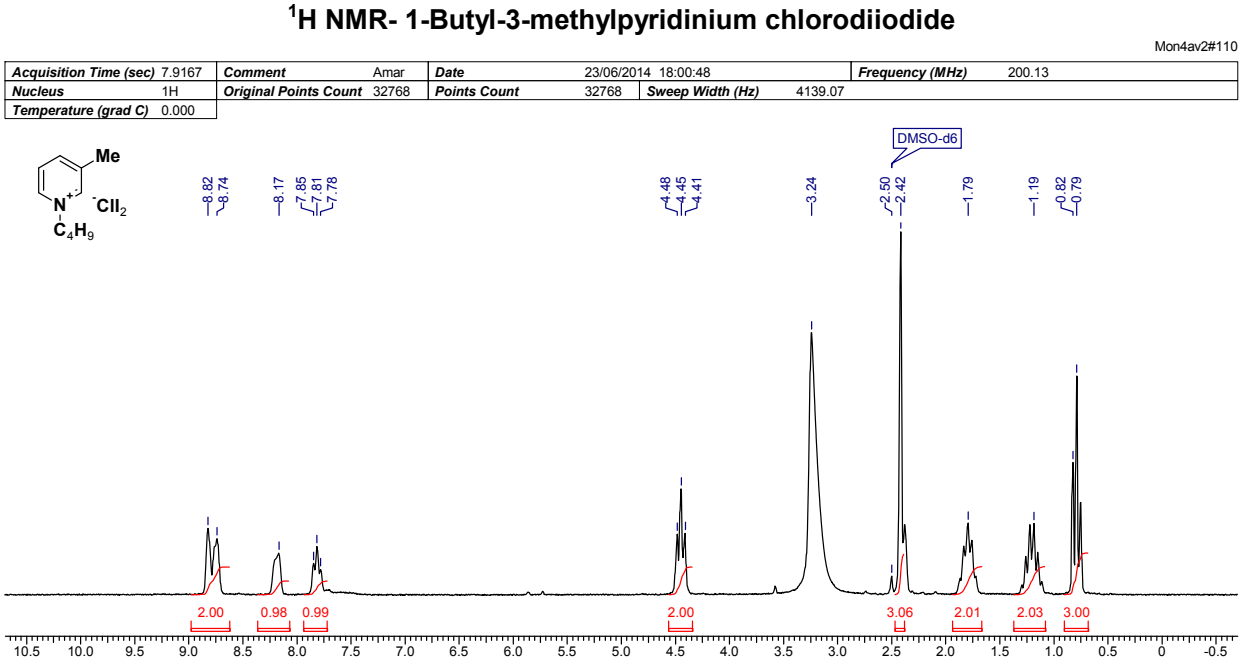

Fig. S-11: ^{1}H-NMR spectrum of compound BMPCDI recorded in DMSO-d_6.

Figure S12.

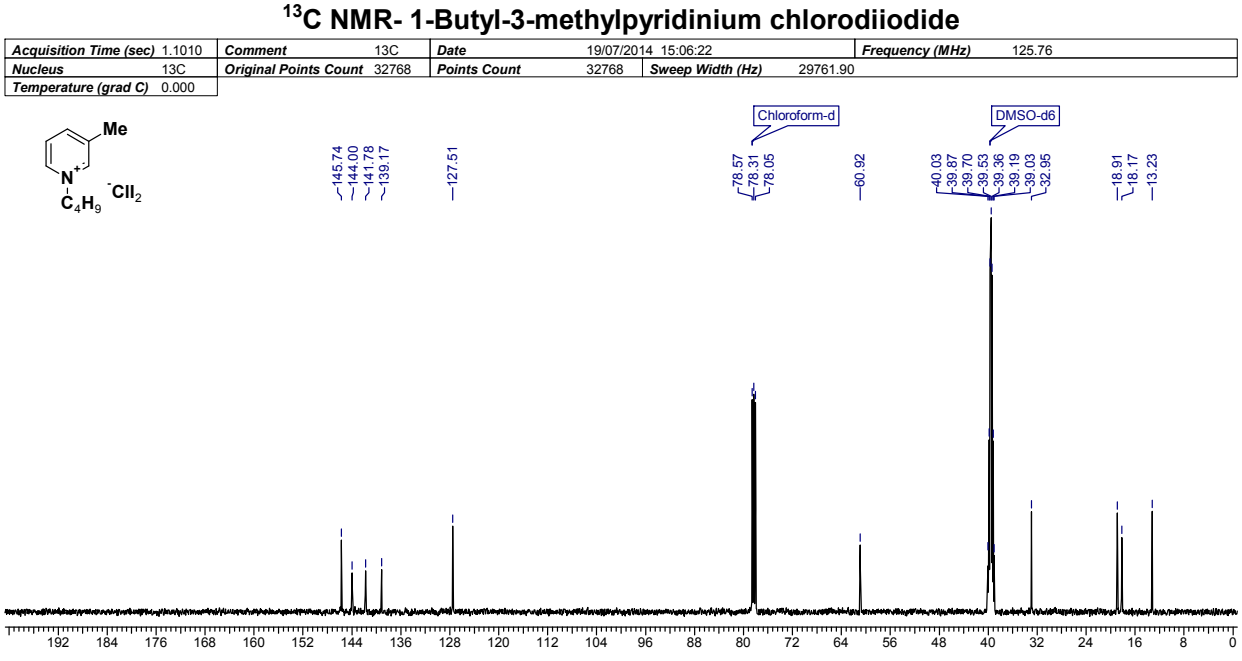

Fig. S-12: ^{13}C-NMR spectrum of compound BMPCDI recorded in $CDCl_3$ and DMSO-d_6.

Figure S13.

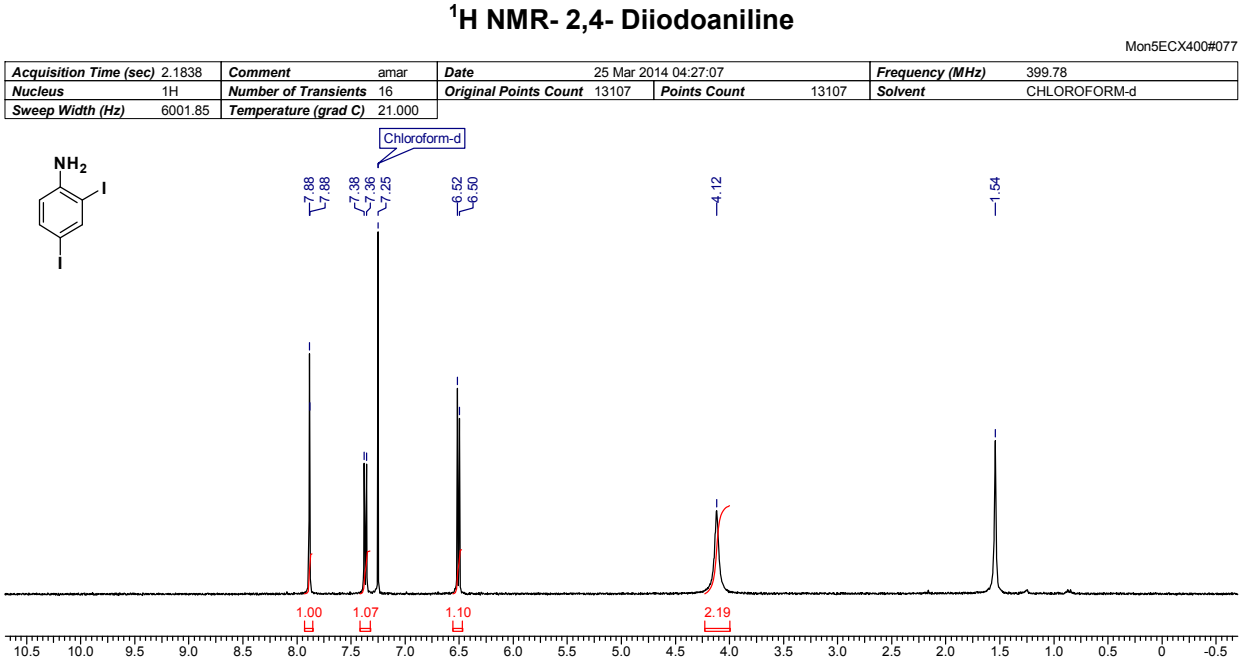

Fig. S-13: ^{1}H-NMR spectrum of compound **1** and **2** recorded in $CDCl_3$.

Figure S14.

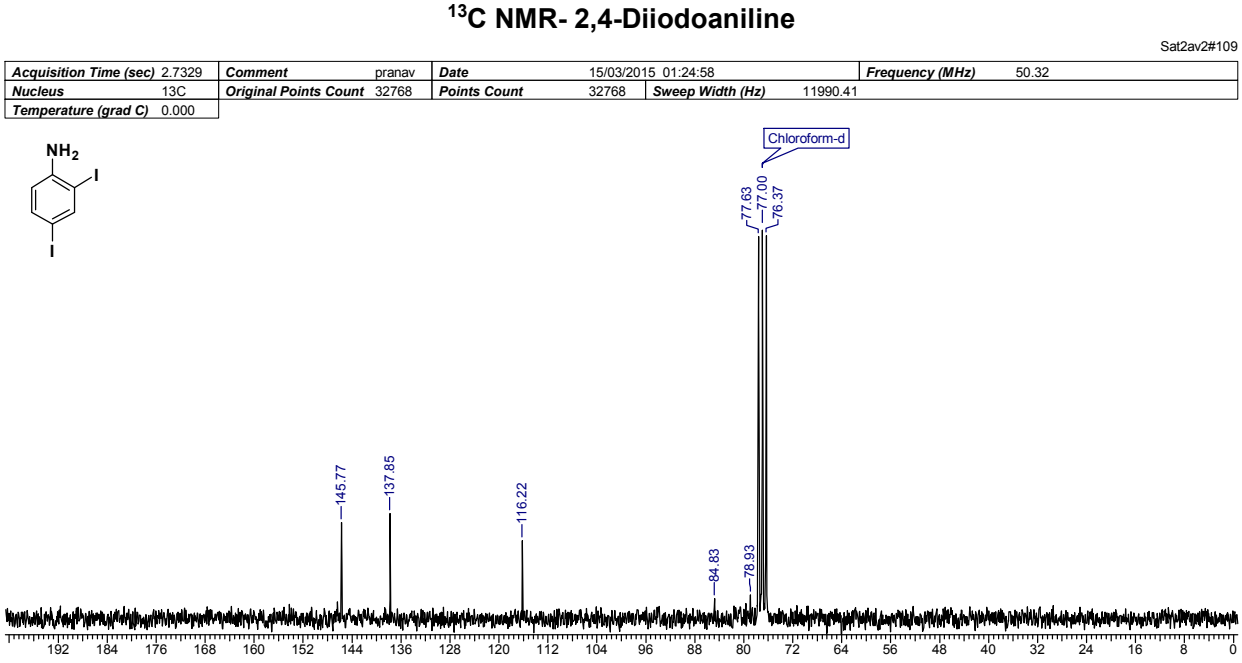

Fig. S-14: ^{13}C-NMR spectrum of compound **1** and **2** recorded in $CDCl_3$.

Figure S15.

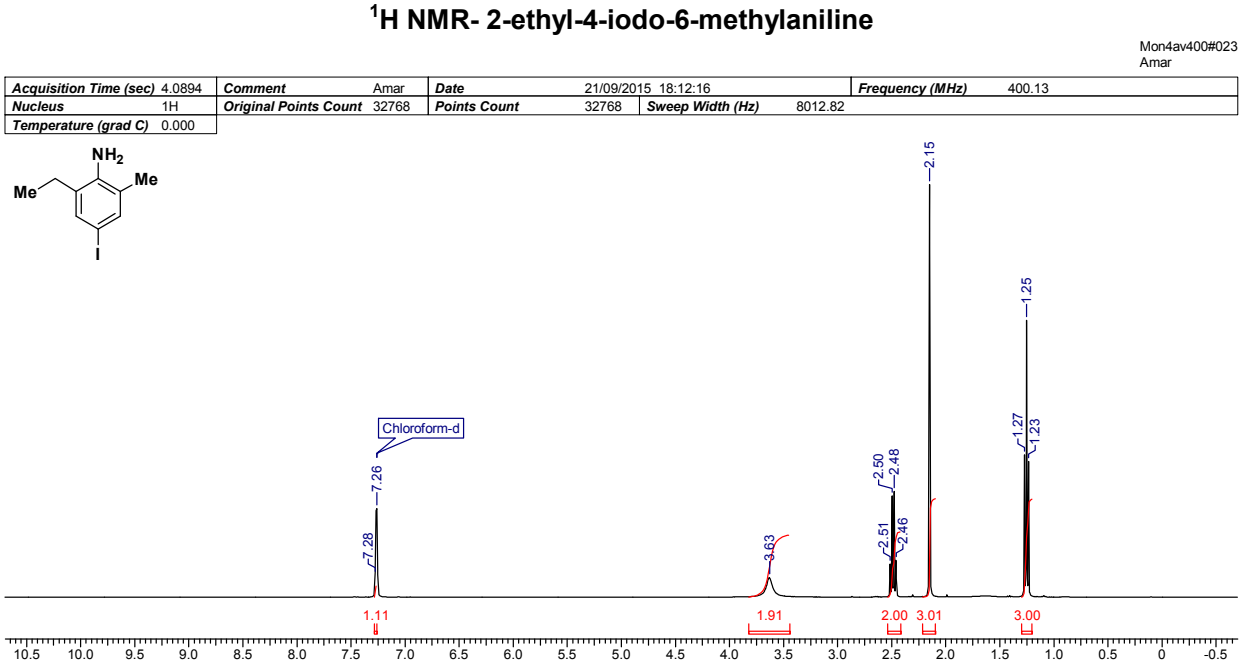

Fig. S-15: ^{1}H-NMR spectrum of compound **3** recorded in $CDCl_3$.

Figure S16.

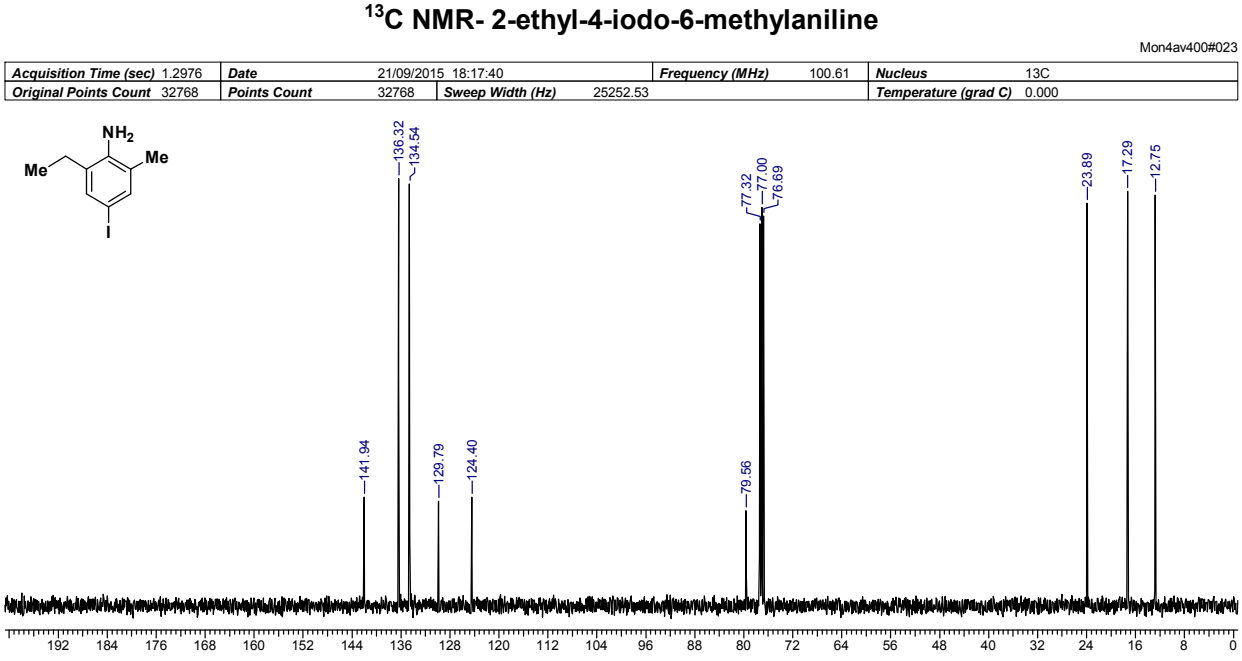

Fig. S-16: ^{13}C-NMR spectrum of compound **3** recorded in $CDCl_3$.

Figure S17.

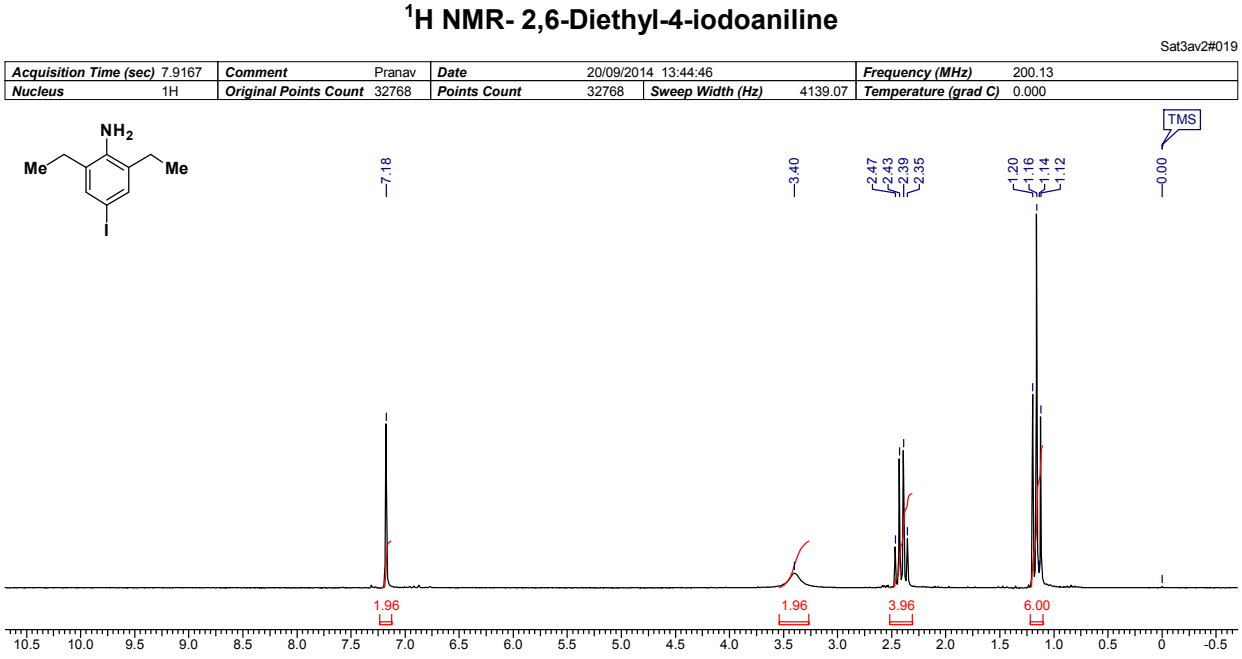

Fig. S-17: ^{1}H-NMR spectrum of compound **4** recorded in $CDCl_3$.

Figure S18.

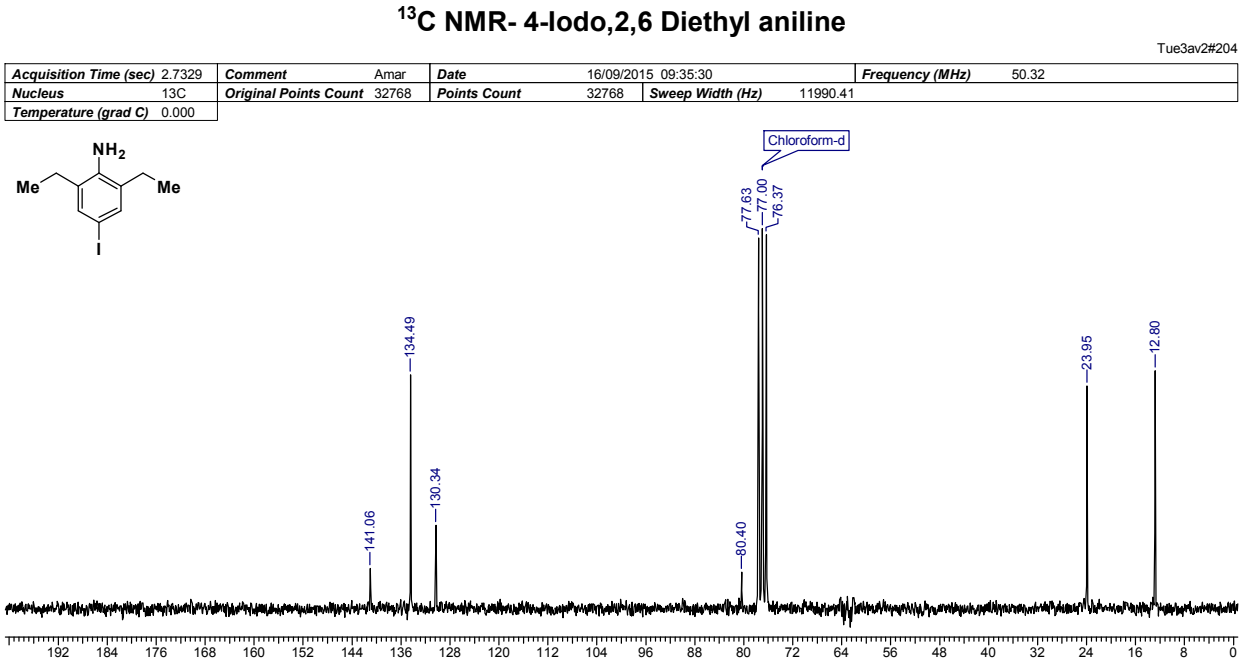

Fig. S-18: ^{13}C-NMR spectrum of compound **4** recorded in $CDCl_3$.

Figure S19.

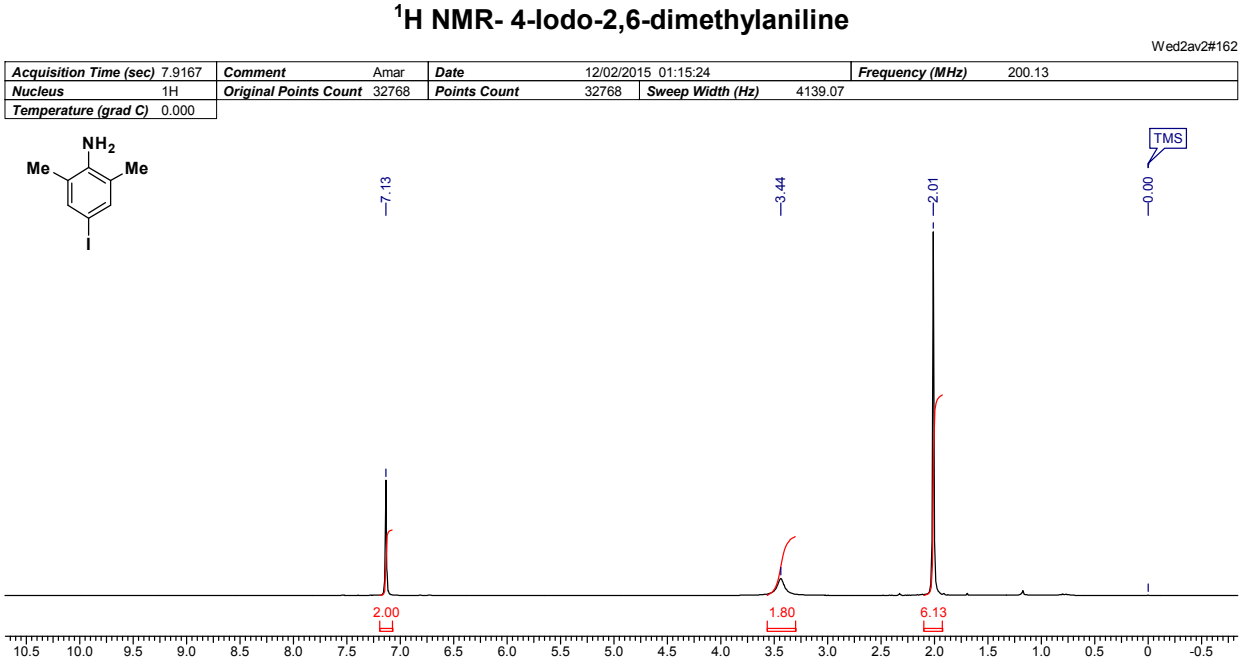

Fig. S-19: ^{1}H-NMR spectrum of compound **5** recorded in $CDCl_3$.

Figure S20.

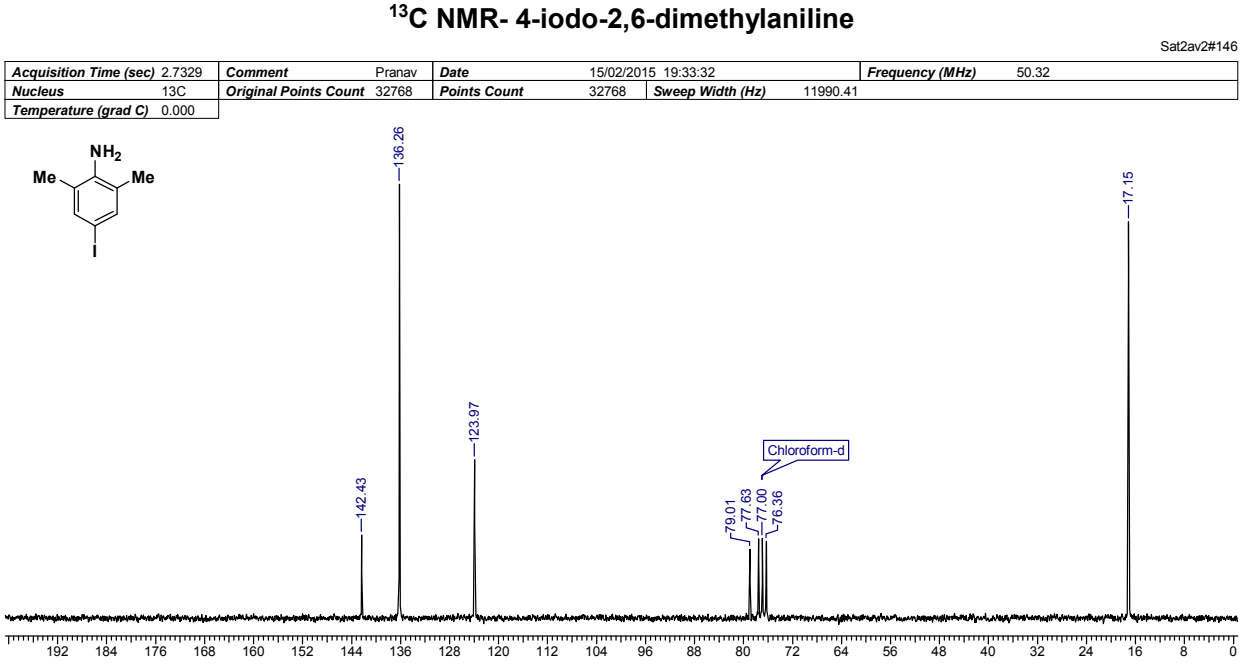

Fig. S-20: ^{13}C-NMR spectrum of compound **5** recorded in $CDCl_3$.

Figure S21.

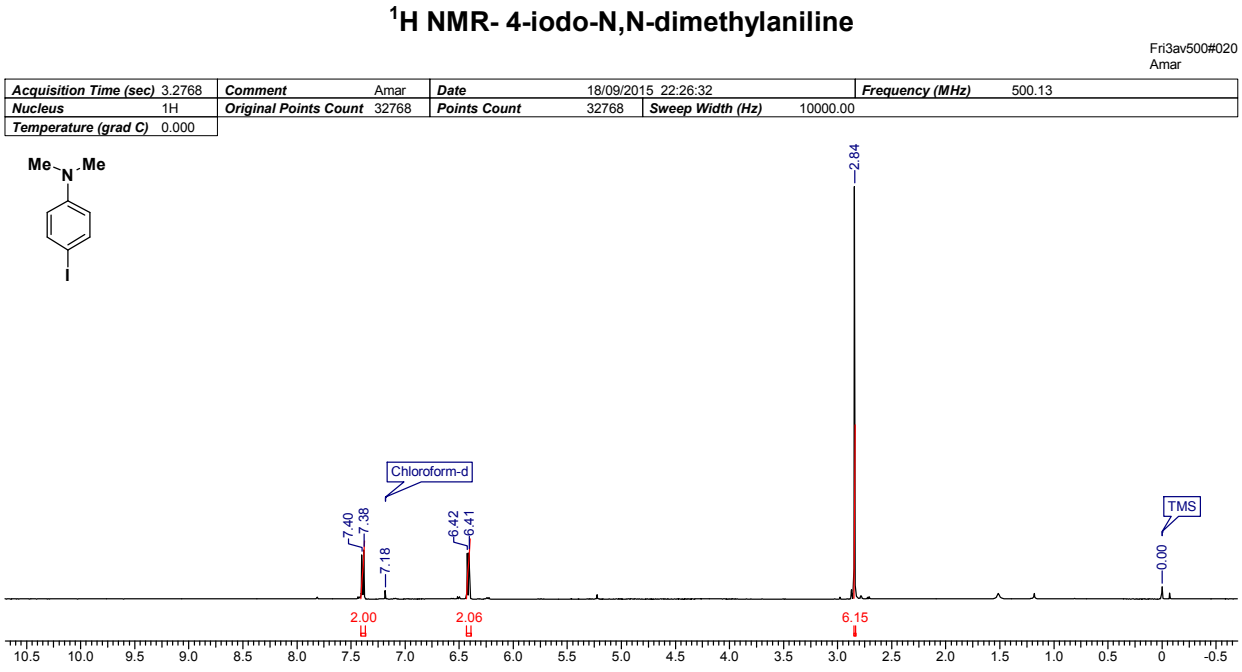

Fig. S-21: ^{1}H-NMR spectrum of compound **6** recorded in $CDCl_3$.

Figure S22.

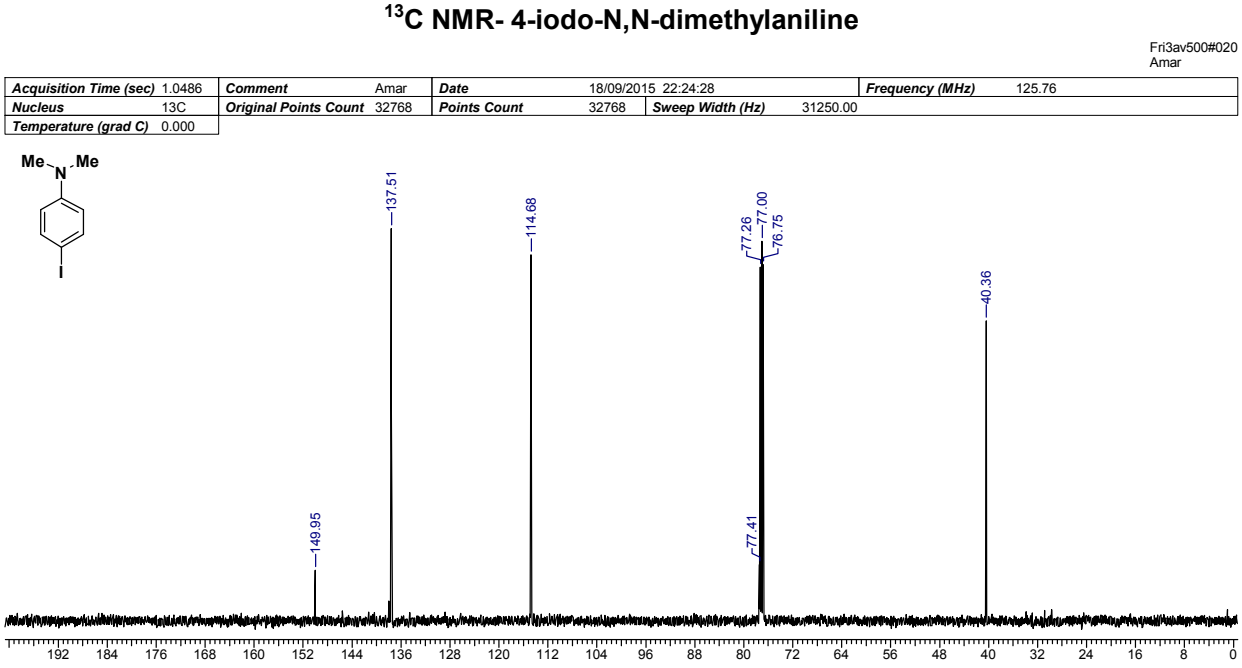

Fig. S-22: ^{13}C-NMR spectrum of compound **6** recorded in $CDCl_3$.

Figure S23.

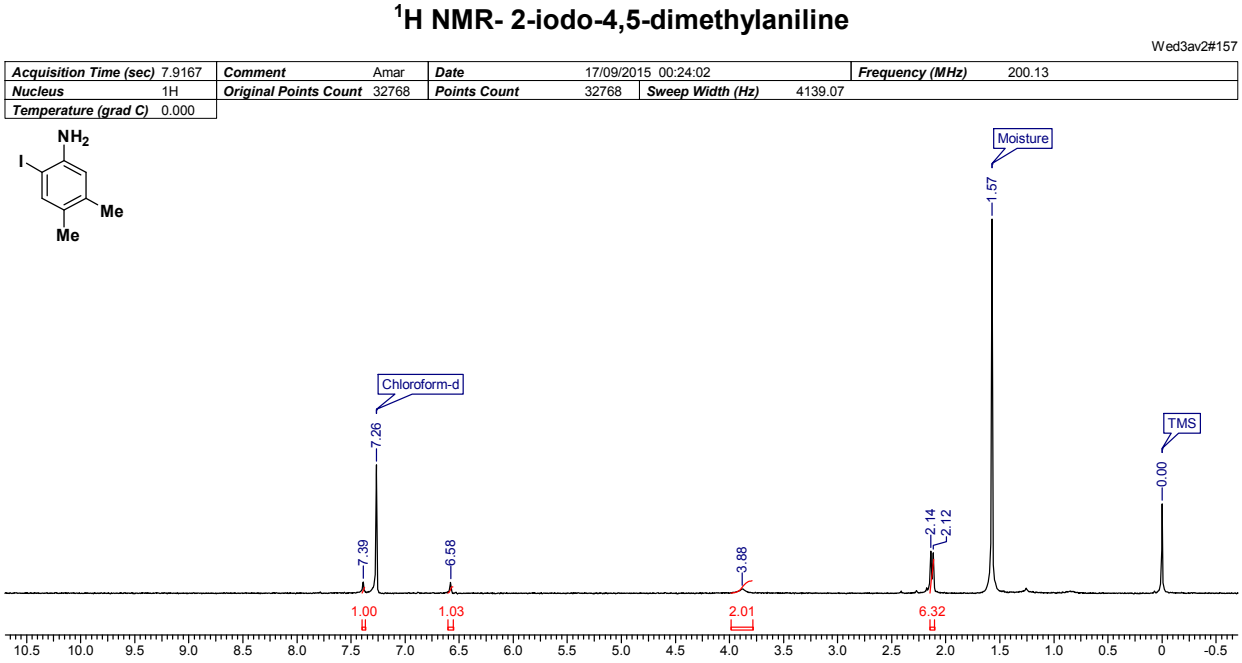

Fig. S-23: ^{1}H-NMR spectrum of compound **7** recorded in $CDCl_3$.

Figure S24.

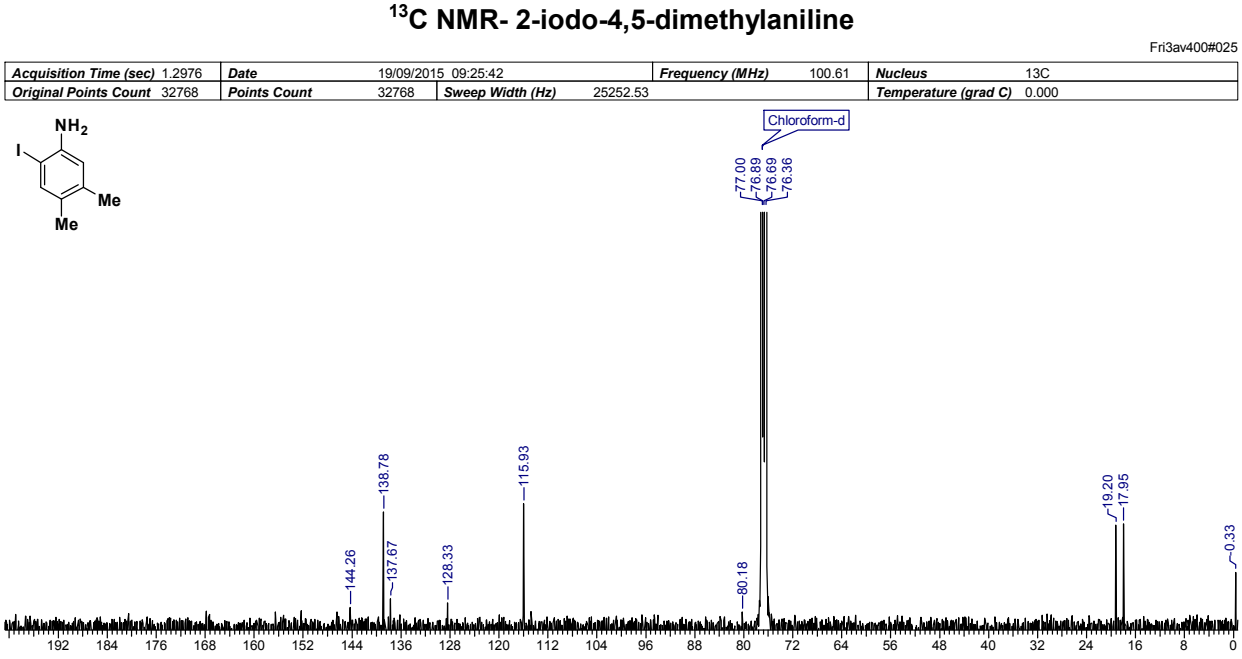

Fig. S-24: ^{13}C-NMR spectrum of compound **7** recorded in $CDCl_3$.

Figure S25.

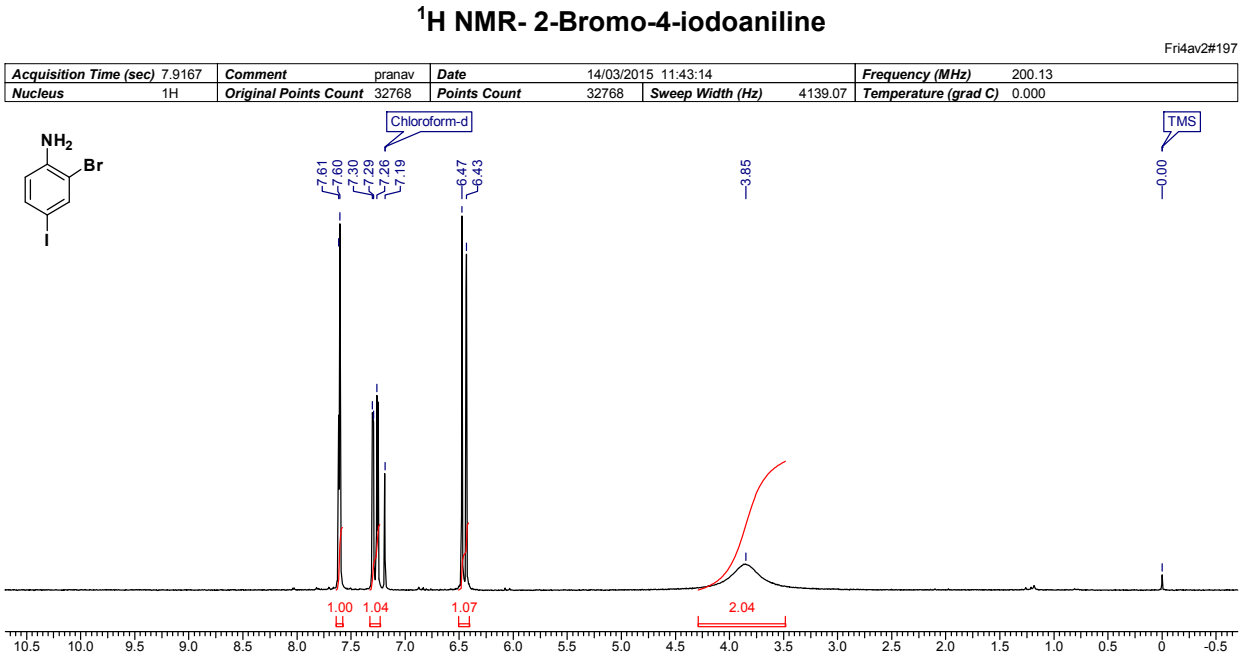

Fig. S-25: ^{1}H-NMR spectrum of compound **8** recorded in $CDCl_3$.

Figure S26.

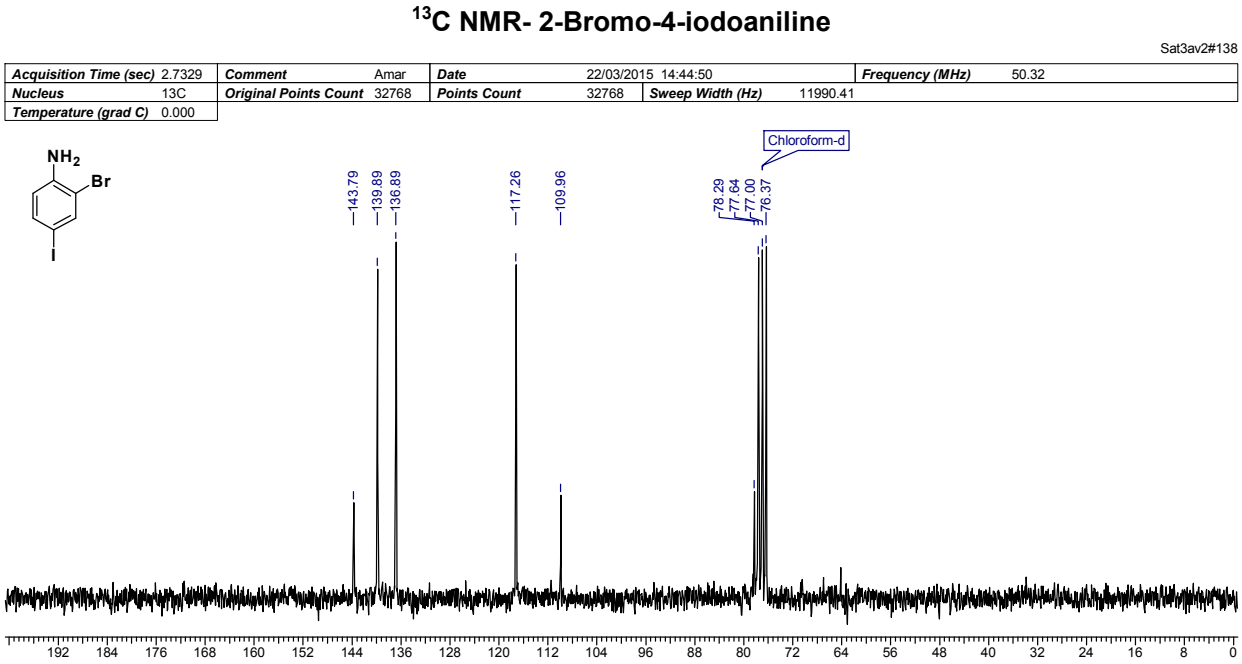

Fig. S-26: ^{13}C-NMR spectrum of compound **8** recorded in $CDCl_3$.

Figure S27.

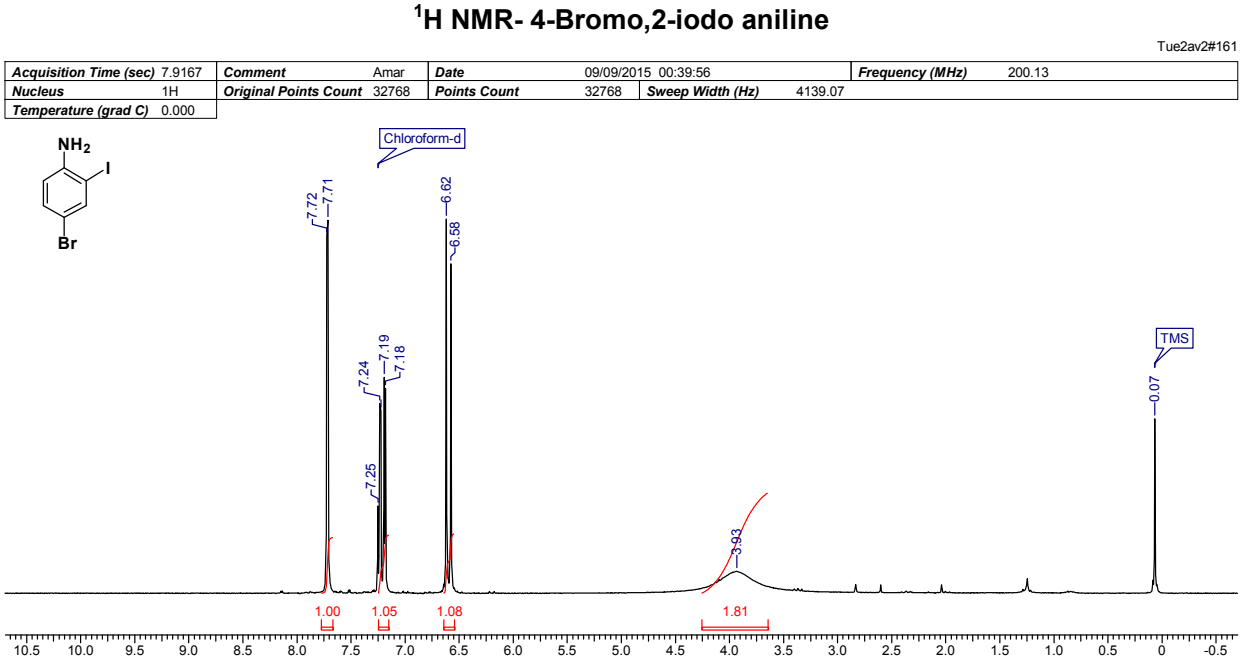

Fig. S-27: ^{1}H-NMR spectrum of compound **9** recorded in $CDCl_3$.

Figure S28.

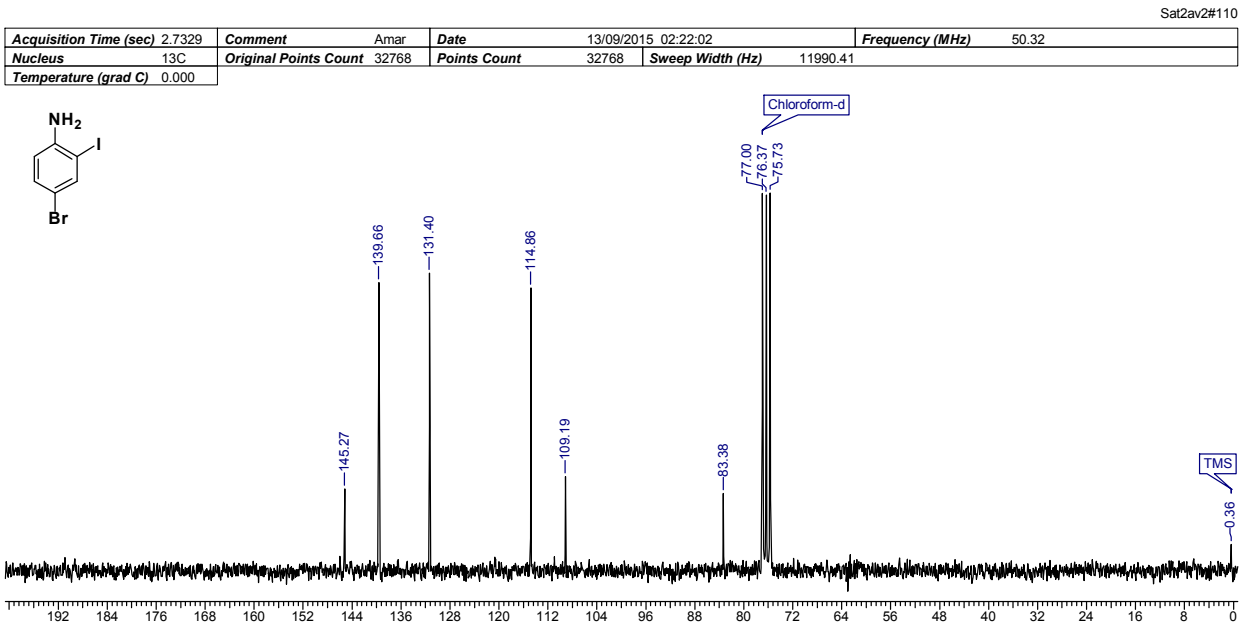

Fig. S-28: ^{13}C-NMR spectrum of compound **9** recorded in $CDCl_3$.

Figure S29.

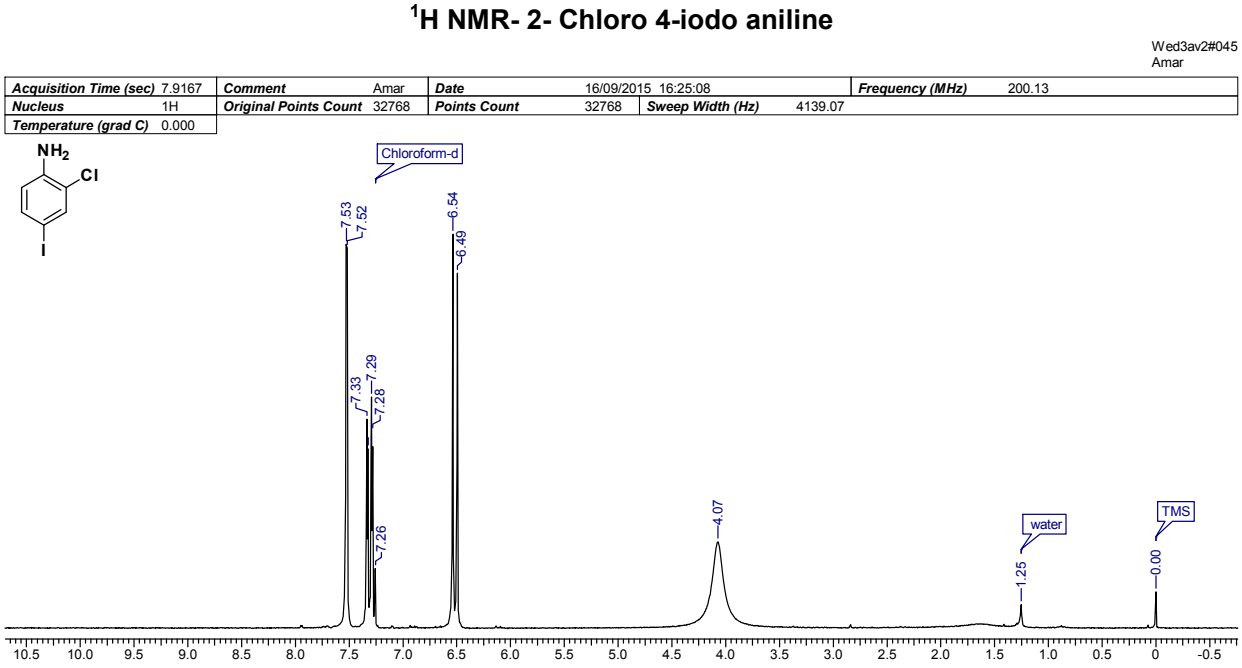

Fig. S-29: ^{1}H-NMR spectrum of compound **10** recorded in $CDCl_3$.

Figure S30.

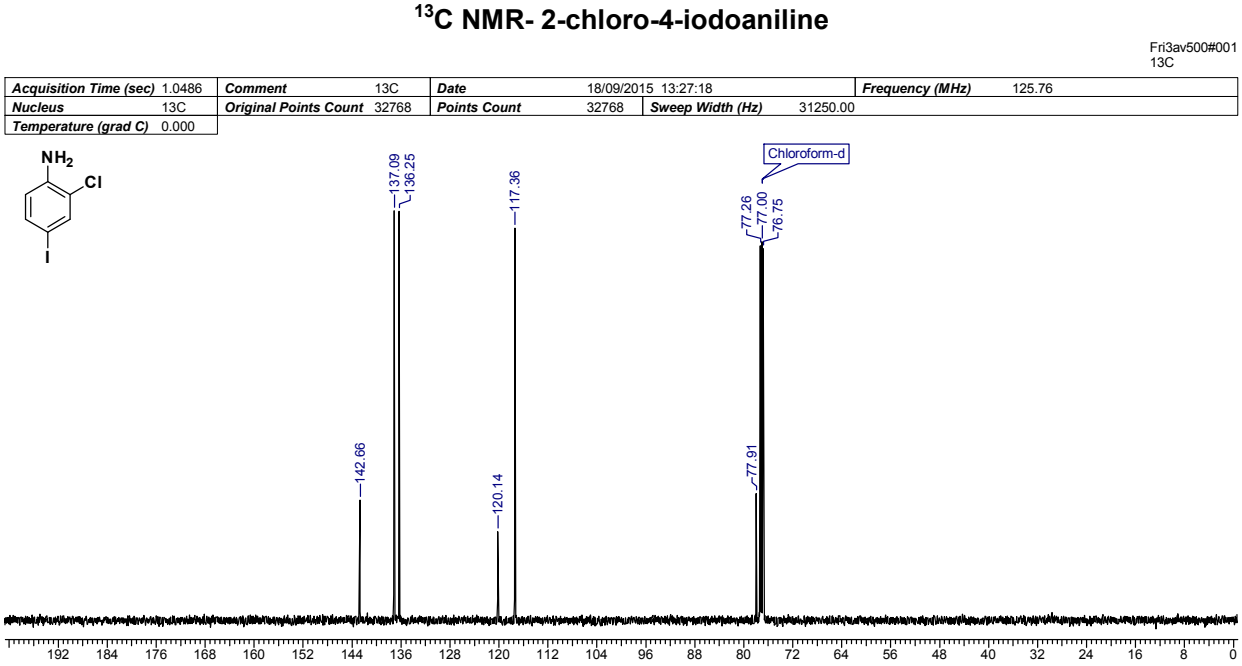

Fig. S-30: ^{13}C-NMR spectrum of compound **10** recorded in $CDCl_3$.

Figure S31.

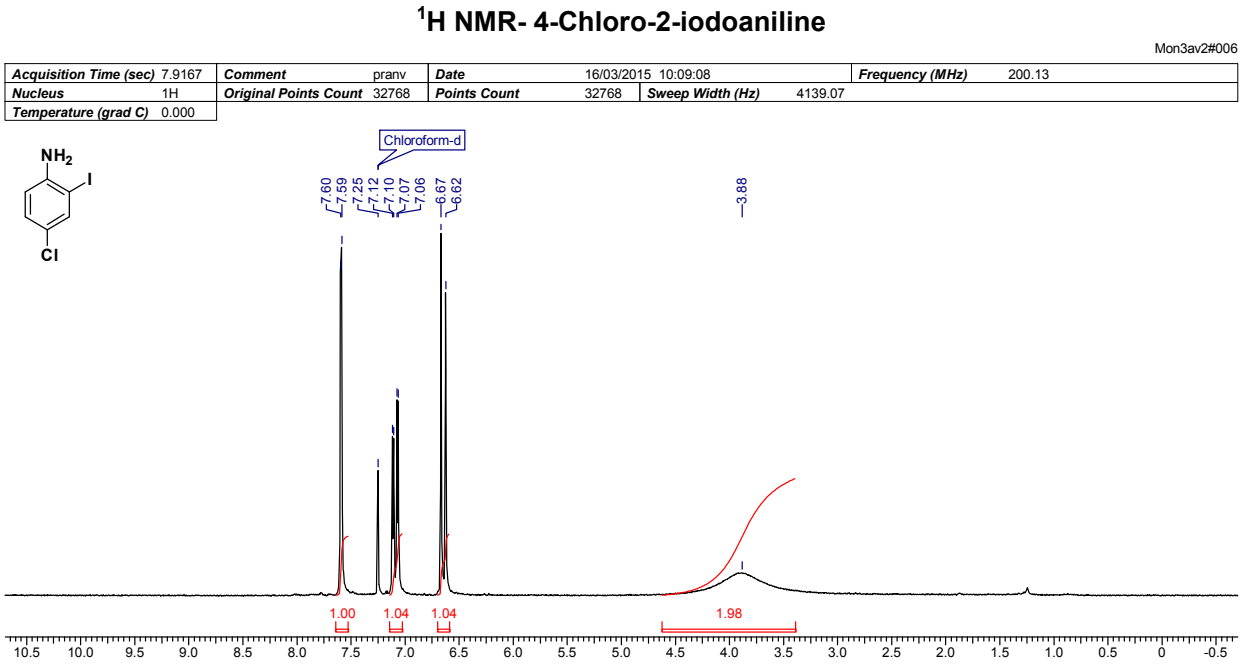

Fig. S-31: ^{1}H-NMR spectrum of compound **11** recorded in $CDCl_3$

Figure S32.

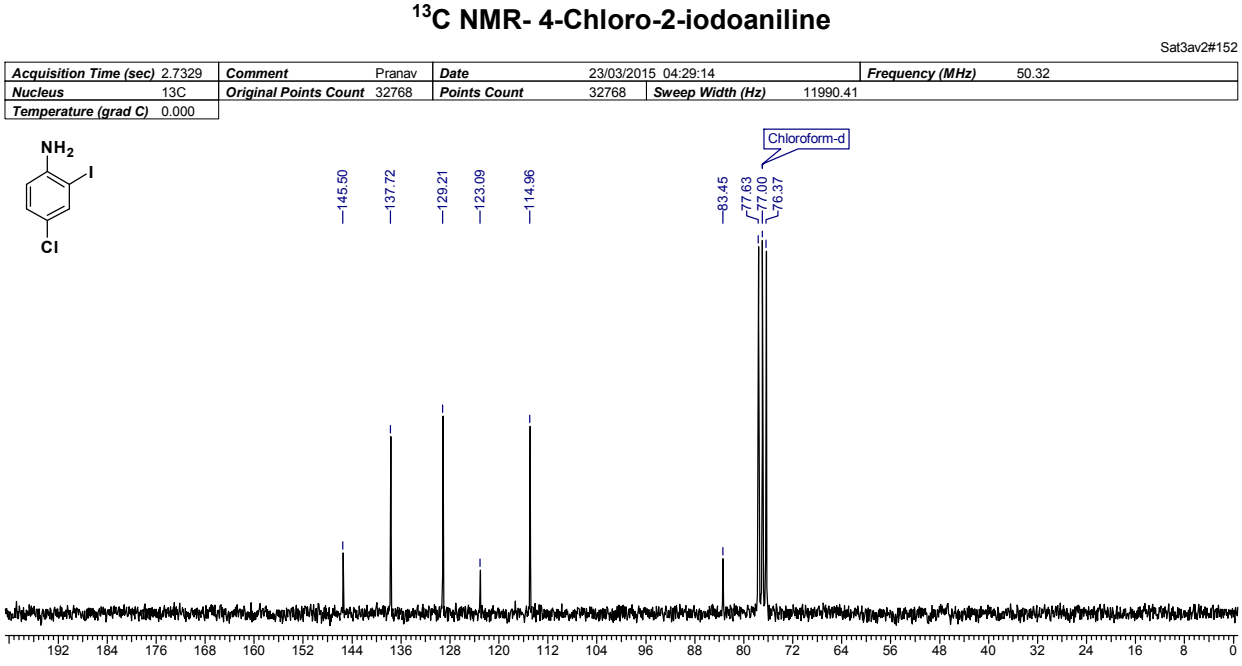

Fig. S-32: ^{13}C-NMR spectrum of compound **11** recorded in $CDCl_3$.

Figure S33.

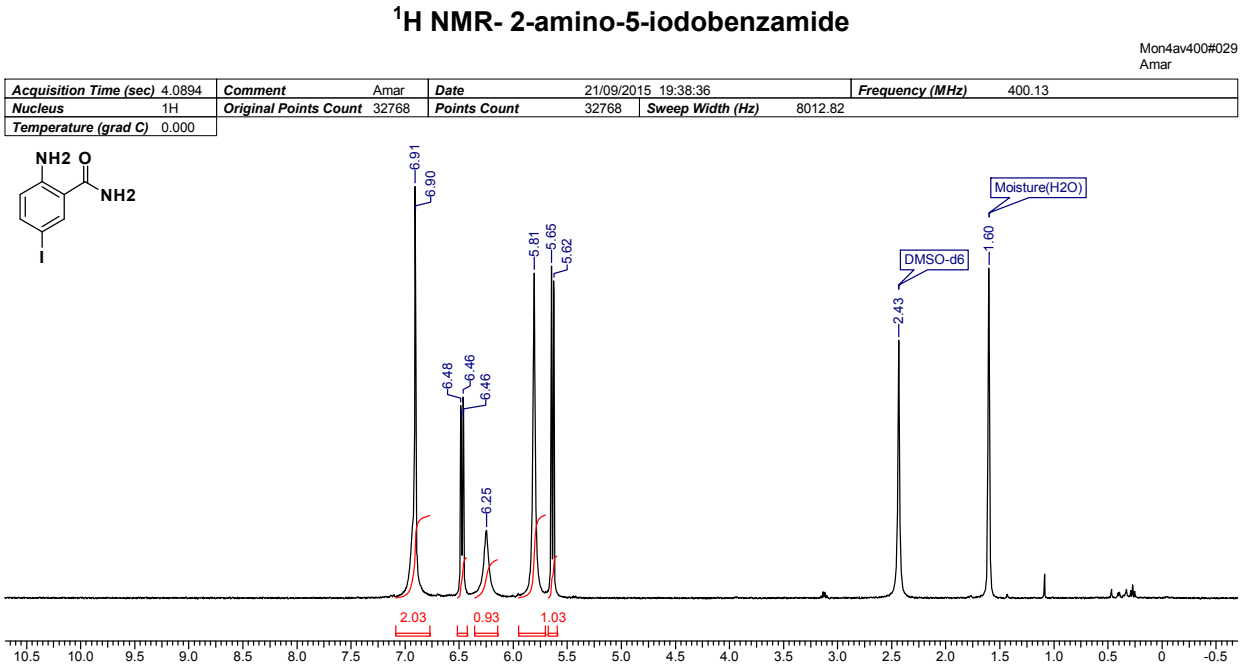

Fig. S-33: ^{1}H-NMR spectrum of compound **12** recorded in DMSO-d_6.

Figure S34.

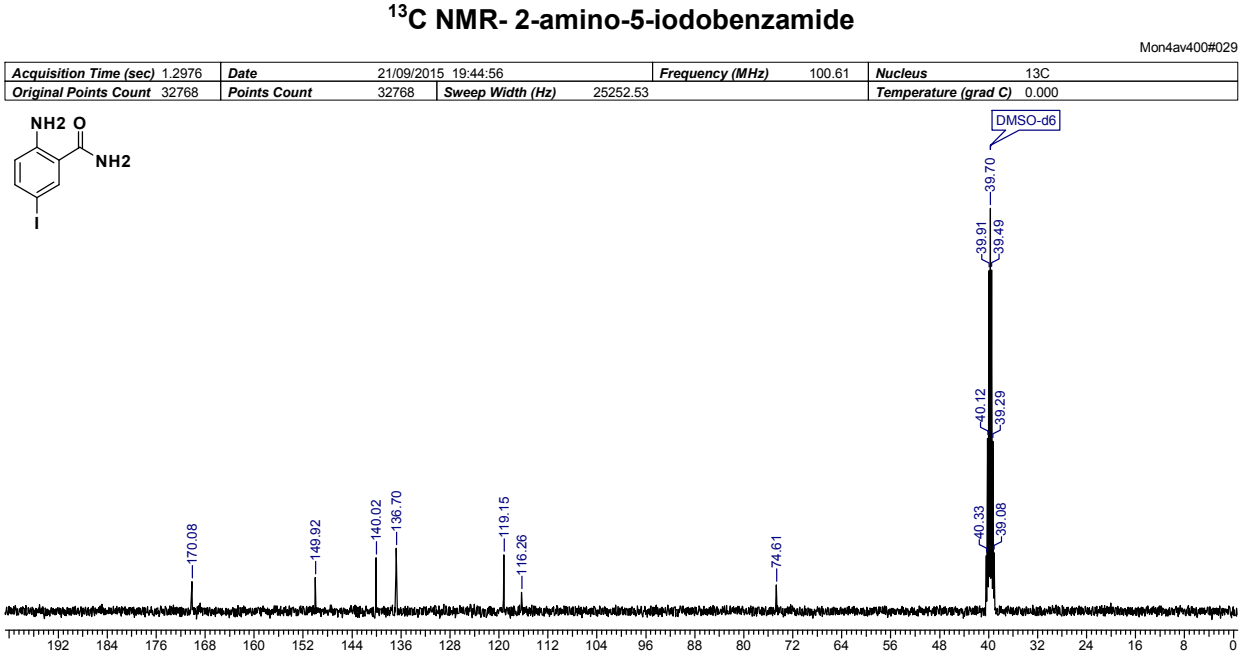

Fig. S-34: ^{13}C-NMR spectrum of compound **12** recorded in DMSO-d_6.

Figure S35.

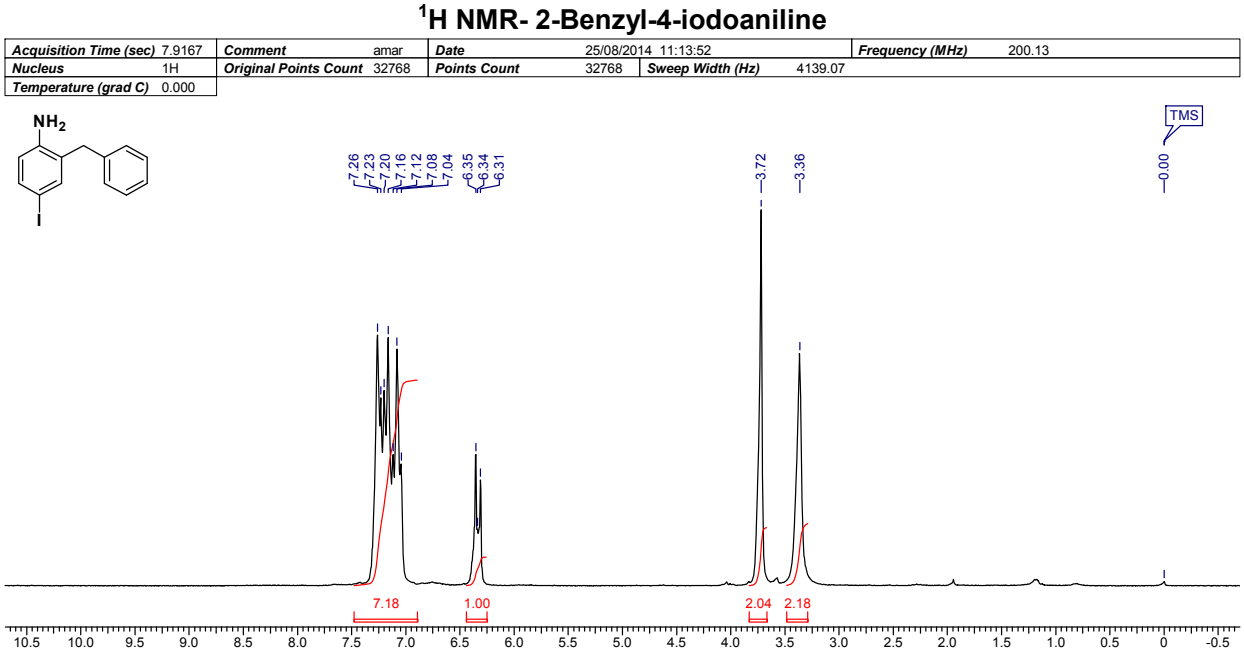

Fig. S-35: ^{1}H-NMR spectrum of compound **13** recorded in $CDCl_3$.

Figure S36.

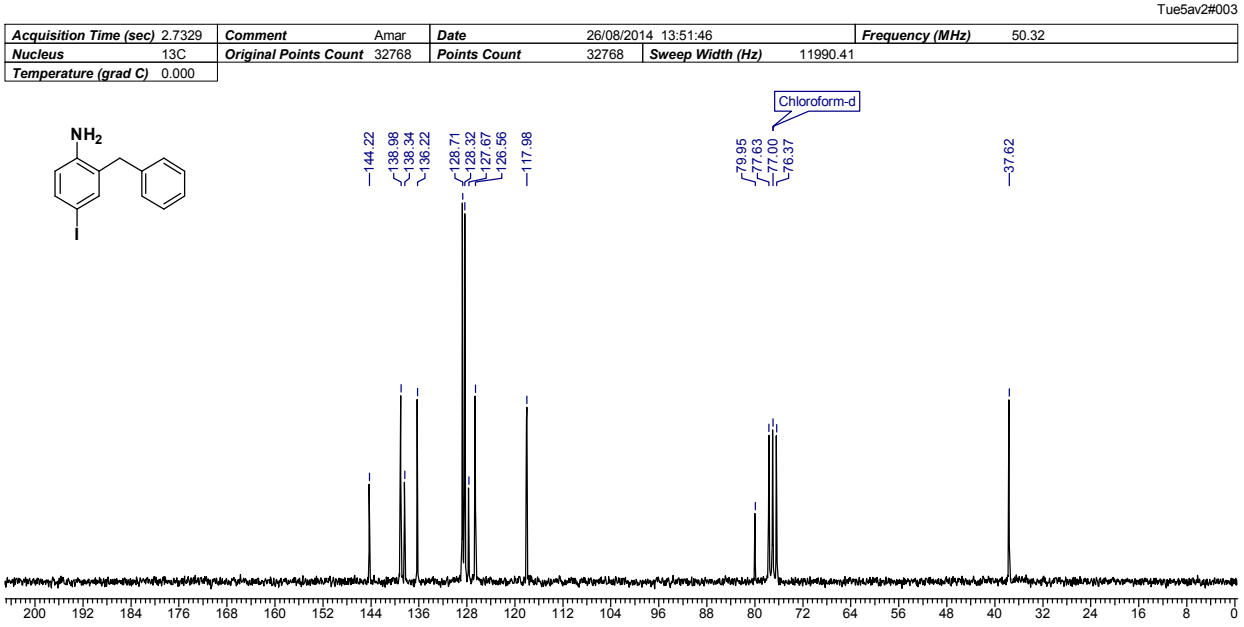

Fig. S-36: ^{13}C-NMR spectrum of compound **13** recorded in $CDCl_3$.

Figure S37.

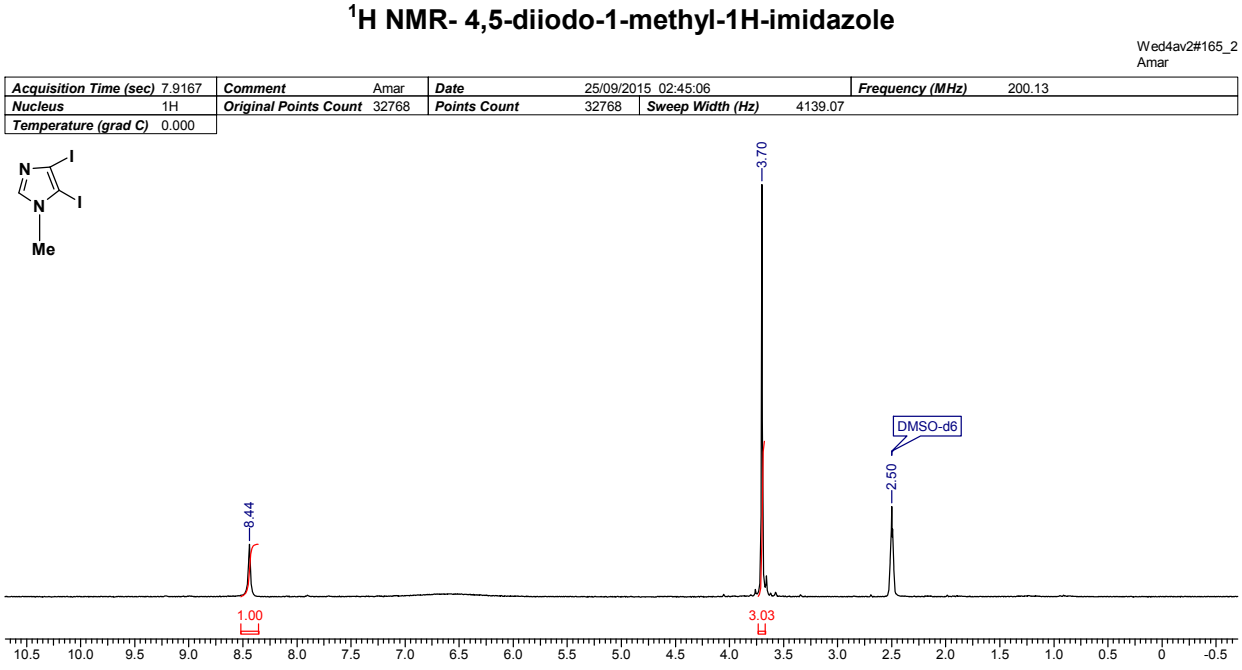

Fig. S-37: ^{1}H-NMR spectrum of compound **14** recorded in DMSO-d_6.

Figure S38.

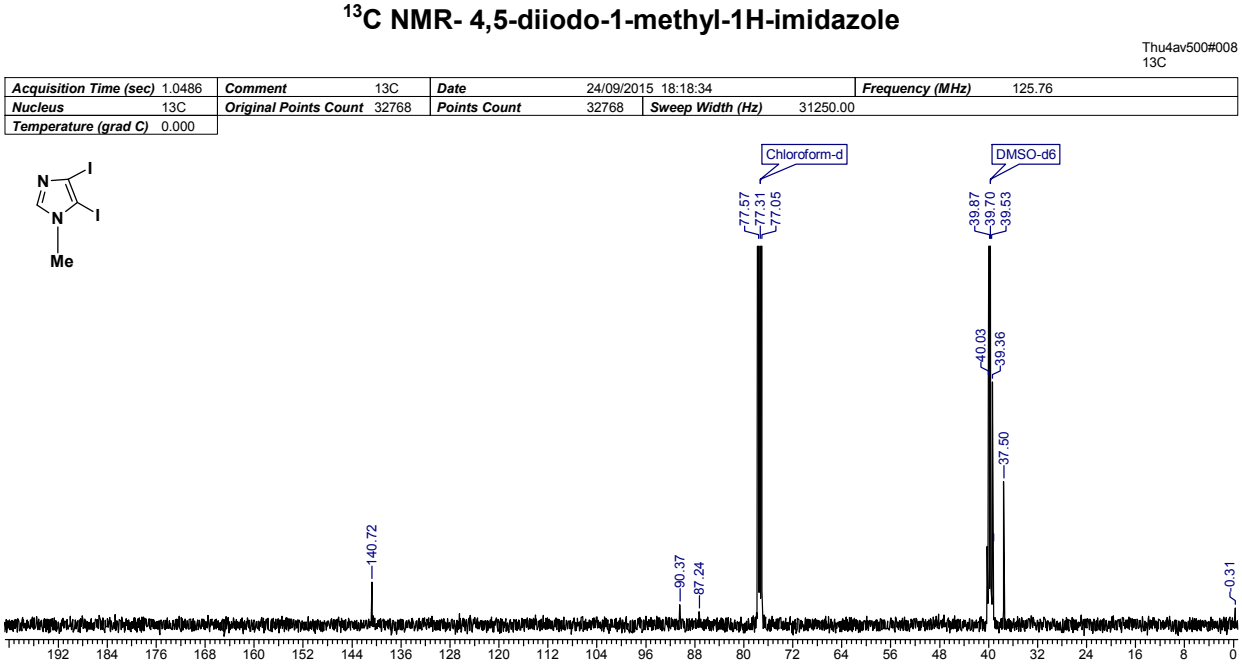

Fig. S-38: ^{1}H-NMR spectrum of compound **14** recorded in $CDCl_3$ and DMSO-d_6.

Figure S39.

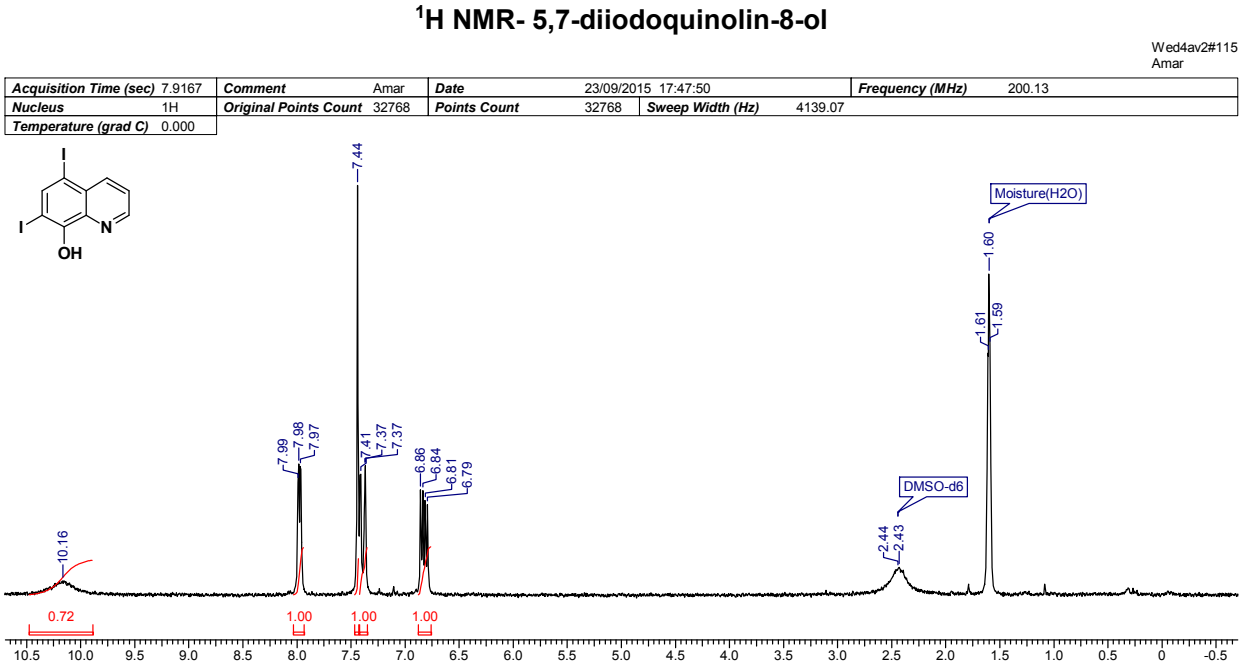

Fig. S-39: ^{1}H-NMR spectrum of compound **15** recorded in DMSO-d_6.

Figure S40.

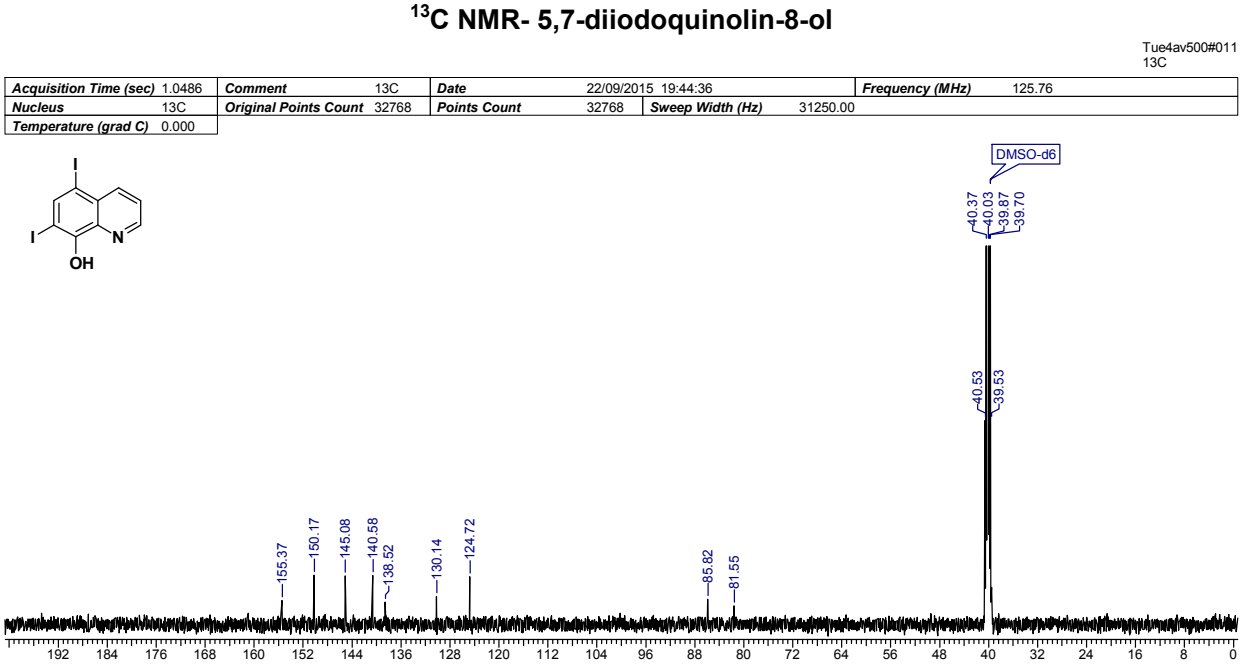

Fig. S-40: ^{13}C-NMR spectrum of compound **15** recorded in DMSO-d_6.

Figure S41.

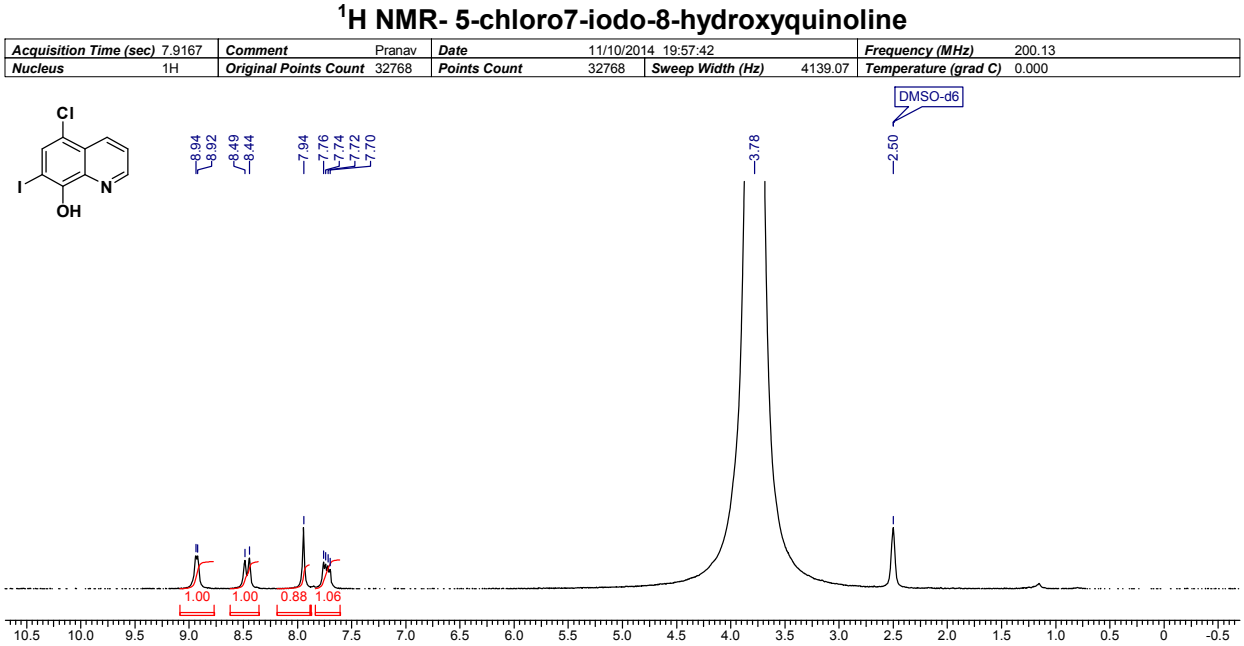

Fig. S-41: ^{1}H-NMR spectrum of compound **16** recorded in DMSO-d_6.

Figure S42.

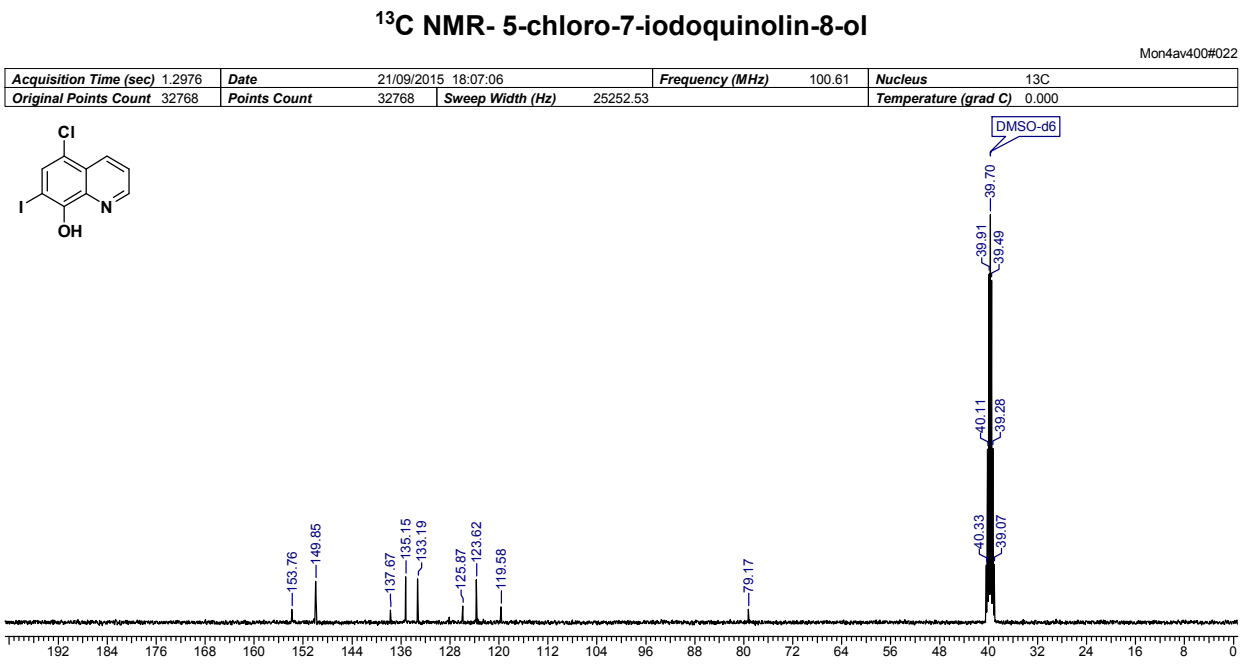

Fig. S-42: ^{13}C-NMR spectrum of compound **16** recorded in DMSO-d_6.

Figure S43.

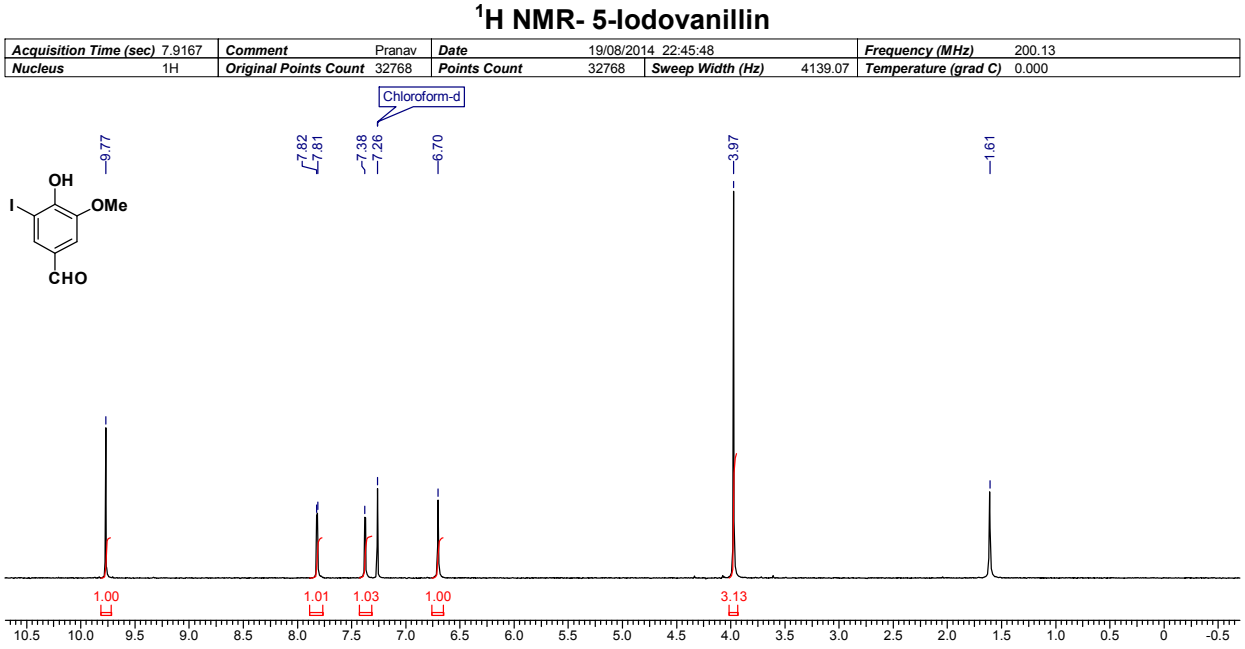

Fig. S-43: ^{1}H-NMR spectrum of compound **17** recorded in $CDCl_3$.

Figure S44.

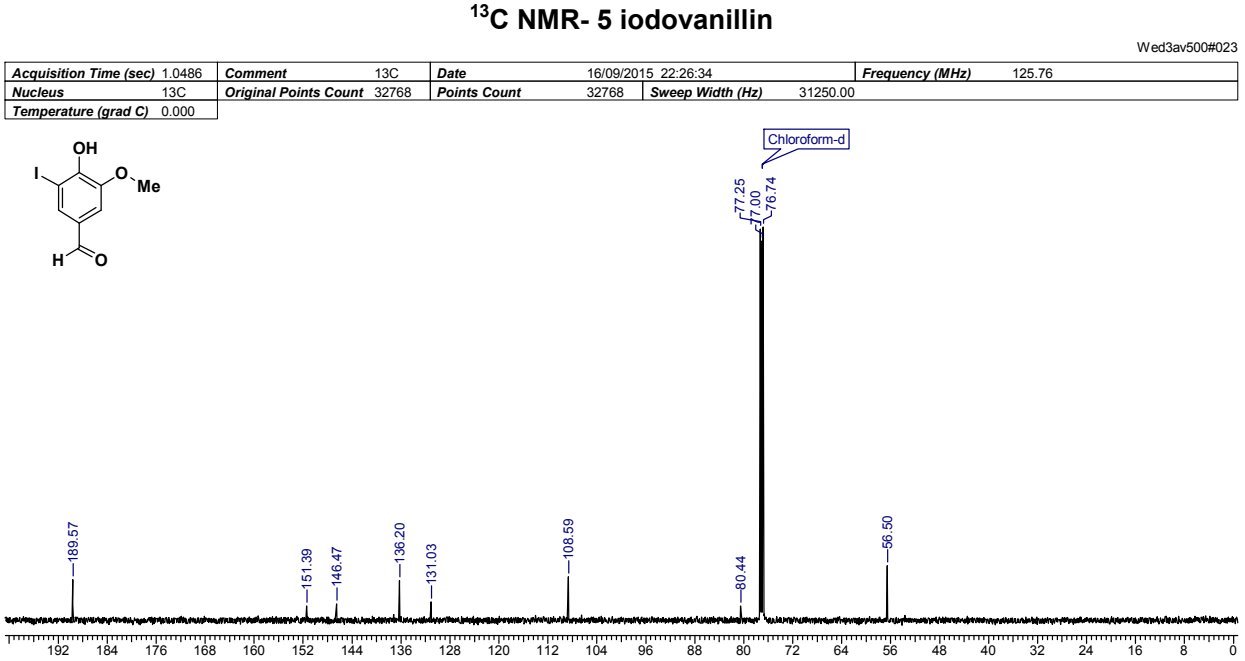

Fig. S-44: ^{13}C-NMR spectrum of compound **17** recorded in $CDCl_3$.