

Supporting Information
for
A practical route to 2-iodoanilines via transition-metal-free and base-free decarboxylative iodination of anthranilic acids under oxygen

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1. General Information

The Reagents used for experiments were commercially available and were used as received unless otherwise noted. The high-pressure stainless-steel reactor, temperature controller and IKA magnetic stirring apparatus was supplied by Kemi company. ^1H , ^{13}C and ^{19}F NMR spectra were recorded on Bruker AVANCE NEO 400 spectrometer. Chemical shifts are reported parts per million (ppm) referenced to CDCl_3 (δ 7.26 ppm), $\text{DMSO-}d_6$ (δ 2.50 ppm) for ^1H NMR; CDCl_3 (δ 77.16 ppm), $\text{DMSO-}d_6$ (δ 39.52 ppm) for ^{13}C NMR. The following abbreviations are used to describe peak patterns where appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet, td = triple doublet. Coupling constants (J) are reported in Hertz (Hz). HRMS were performed on Triple TOF 5600 LC/MS/MS(AB Sciex). Melting points were measured with micro melting point apparatus.

2. General Procedure for 2a Synthesis

2-Amino-4-bromobenzoic acid (216.0 mg, 1.0 mmol), I_2 (126.5 mg, 0.5 equiv), KI (99.6 mg, 0.6 equiv) and 10 mL of CH_3CN were added to an autoclave with a 50 mL glass liner. The autoclave was purged by three cycles of pressurization/venting with O_2 before pressurization with O_2 (10 bar). The reaction mixture was stirring at 180 °C for 4 h in the heating mantle. After completion of the reaction, the reactor was cooled with a water bath. Then the solution was diluted with ethyl acetate and transferred

to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel.

3. The Radical Trapping Experiment

2-amino-6-fluorobenzoic acid **1k** (155.0 mg, 1.0 mmol), I₂ (126.5 mg, 0.5 equiv), KI (99.6 mg, 0.6 equiv), 1,1-Diphenylethylene (360.0 mg, 2.0 equiv) and 10 mL of CH₃CN were added to an autoclave with a 50 mL glass liner. The autoclave was purged by three cycles of pressurization/venting with O₂ before pressurization with O₂ (10 bar). The reaction mixture was stirring at 160 °C for 2 h in the heating mantle. After completion of the reaction, the reactor was cooled with a water bath. the products were detected by HRMS techniques. Figure S1 showed that 1,1-diphenylethylene, the most common trapping agent, captured 3-fluoroaniline radical with 1,1-diphenylethylene-trapped compound **5** observed. HRMS (ESI): compound **5**, HRMS (ESI) calcd for [C₂₀H₁₆FN+H⁺]: 290.1345, found: 290.1355.

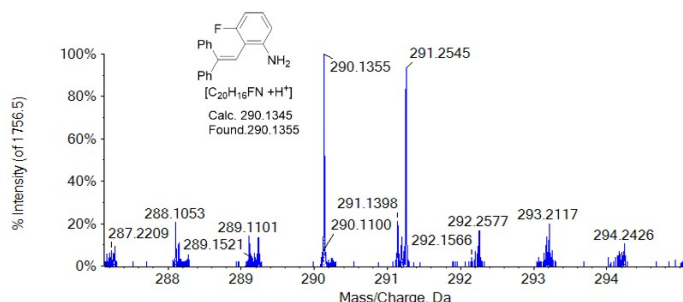


Figure S1. Radical trapping experiment for **1k** under standard conditions with ethene-1,1-diylidibenzene (2.0 equiv)

4. KI Oxidation Reaction by Oxygen

4.1 In the presence of **1a**

2-Amino-4-bromobenzoic acid **1a** (216.0 mg, 1.0 mmol), KI (199.2 mg, 1.2 equiv), 10 mL of CH₃CN were added to an autoclave with a 50 mL glass liner. The autoclave was purged by three cycles of pressurization/venting with O₂ before pressurization with O₂ (10 bar). The reaction mixture was stirring at 180 °C for 0 h in the heating mantle. After completion of the reaction, the reactor was cooled with a water bath. Figure S2 showed that the color of fresh starch solution changed to blue when the reaction system was dropwise into the solution. It indicated that the iodine was formed at beginning of the reaction.

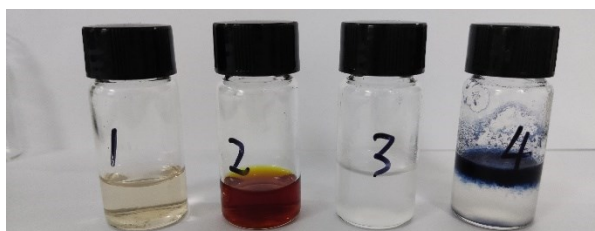


Figure S2 In the presence of **1a**. 1. Before reaction. 2. After completion of the reaction. 3. Fresh starch solution. 4. Fresh starch solution and 2.

4.2 In the absence of **1a**

Except for the absence of **1a**, the reaction conditions were the same as in 4.1. The reaction mixture was stirring at 180 °C for 0 h in the heating mantle. After completion of the reaction, the reactor was cooled with a water bath. In Figure S3, the color did not change before and after the reaction, as well as fresh starch solution. It indicated that although KI

reaction with O₂ is kind of slow, with the addition of the substrate **1a**, it promoted this oxidation reaction.

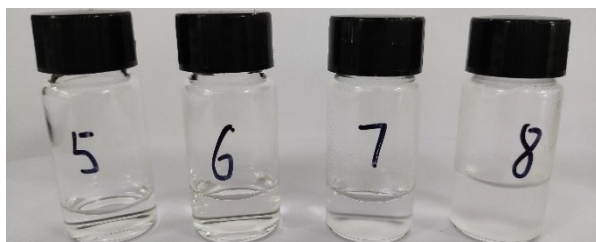


Figure S3 In the absence of **1a**. 5.

Before reaction. 6. After completion of the reaction. 7. Fresh starch solution. 8. Fresh starch solution and 6.

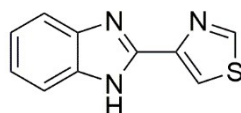
5. Gram-scale Synthesis of **2a** and the Functionalization of **2w**

Gram-scale synthesis of **2a**

An autoclave with a 50 mL glass liner was charged with 2-Amino-4-bromobenzoic acid (5.0 mmol), I₂ (2.5 mmol, 0.5 equiv), KI (3.0 mmol, 0.6 equiv) and 20 mL of CH₃CN. The reaction mixture was stirring at 180 °C for 4 h. After completion of the reaction, the reactor was cooled with a water bath, the crude product was concentrated under vacuum. The residue was purified by column chromatography on silica gel to afford 1.04 g of **2a** in 70% yield.

The functionalization of 2-iodoaniline **2w**

tiabendazole **3**

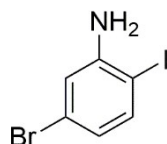


In an oven-dried Schlenk tube 25 mL, CuCl (5.0 mg, 0.05 mmol), 2-iodoaniline (219 mg, 1.0 mmol), NaN₃ (130.0 mg, 2.0 mmol), N,N,N',N'-tetramethylethylenediamine (TMEDA) (6.0 mg, 0.05 mmol), and thiazole-

4-carboxaldehyde (136.0 mg, 1.2 mmol) were reacted in 5.0 mL of DMSO. The reaction mixture was heated to 120°C for 12 h. After cooling, the mixture was poured into the EtOAc (50.0 mL), washed with brine (25.0 mL) and water (2 × 25.0 mL), dried over MgSO₄ and then concentrated under vacuum. The residue was purified by column chromatography on silica gel and eluted with petroleum ether/ethylacetate(v/v=1:1) to afford the **3** in 80% yield.

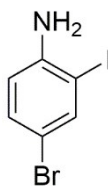
6. Analytical data for products

5-Bromo-2-iodoaniline (**2a**)¹



Yellow solid (229 mg, 77% yield), m.p. 58 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.46 (d, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.60 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 1H), 4.14 (s, 2H); ¹³C NMR (400 MHz, CDCl₃): 148.1, 140.1, 123.2, 123.0, 117.2, 82.0. HRMS (ESI): calculated for [C₆H₅BrIN+H⁺] 297.8728, found 297.8713 Flash chromatographic condition: ethyl acetate/petroleum ether = 1/20 (v/v).

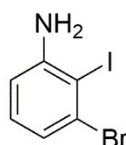
4-Bromo-2-iodoaniline (**2b**)²



Grey solid (220 mg, 74% yield), m.p. 72°C; ¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, *J* = 2.4 Hz, 1H), 7.22 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.0 Hz, 1H), 6.92 (d,

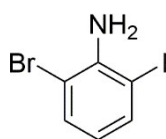
$J = 8.8$ Hz, 1H), 4.10 (s, 2H); ^{13}C NMR (400 MHz, CDCl_3): 146.1, 140.5, 132.2, 115.7, 110.0, 84.2. HRMS (ESI): calculated for $[\text{C}_6\text{H}_5\text{BrIN}+\text{H}^+]$ 297.8728, found 297.8712. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/20 (v/v).

3-Bromo-2-iodoaniline (2c)³



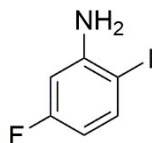
Yellow solid (169 mg, 57% yield), m.p. 48 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.03-6.96 (m, 2H), 6.63 (dd, $J_1 = 7.6$ Hz, $J_2 = 2.0$ Hz, 1H), 4.34 (s, 2H); ^{13}C NMR (400 MHz, CDCl_3): 149.4, 130.7, 130.1, 122.3, 112.6, 91.3. HRMS (ESI): calculated for $[\text{C}_6\text{H}_5\text{BrIN}+\text{H}^+]$ 297.8728, found 297.8720. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/20 (v/v).

2-Bromo-6-iodoaniline (2d)²



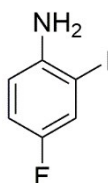
Yellow liquid (74 mg, 25% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.58 (dd, $J_1 = 7.6$ Hz, $J_2 = 0.9$ Hz, 1H), 7.39 (dd, $J_1 = 8.0$ Hz, $J_2 = 0.9$ Hz, 1H), 6.33 (t, $J = 8.0$ Hz, 1H), 4.58 (s, 2H); ^{13}C NMR (400 MHz, CDCl_3): 144.3, 138.4, 133.0, 120.1, 107.5, 83.2. HRMS (ESI): calculated for $[\text{C}_6\text{H}_5\text{BrIN}+\text{H}^+]$ 297.8728, found 297.8717. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/20 (v/v).

5-Fluoro-2-iodoaniline (2e)⁴



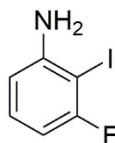
Grey solid (161 mg, 68% yield), m.p. 43°C; ¹H NMR (400 MHz, CDCl₃): δ 7.54 (t, *J* = 7.6 Hz, 1H), 6.47 (d, *J* = 10.8 Hz, 1H), 6.27 (t, *J* = 8.8 Hz, 1H), 4.19 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): 164.1 (d, *J* = 243.0 Hz), 148.2 (d, *J* = 6.0 Hz), 139.8 (d, *J* = 10.0 Hz), 107.3 (d, *J* = 22.0 Hz), 101.7 (d, *J* = 25.0 Hz), 77.1 (d, *J* = 3.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -113.4 (s, 1F). HRMS (ESI): calculated for [C₆H₅FIN+H⁺] 237.9528, found 237.9519. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/50 (v/v).

4-Fluoro-2-iodoaniline (2f)⁵



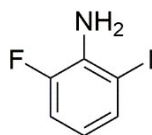
Brown oil (159 mg, 67% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.37 (dd, *J*₁ = 8.0 Hz, *J*₂ = 2.8 Hz, 1H), 6.92-6.87 (m, 1H), 6.68 (dd, *J*₁ = 8.8 Hz, *J*₂ = 5.2 Hz, 1H), 3.77 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): 155.4 (d, *J* = 249.0 Hz), 143.4 (d, *J* = 2.0 Hz), 125.2 (d, *J* = 25.0 Hz), 116.3 (d, *J* = 22.0 Hz), 114.8 (d, *J* = 8.0 Hz), 82.8 (d, *J* = 9.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -125.4 (s, 1F). HRMS (ESI): calculated for [C₆H₅FIN+H⁺] 237.9528, found 237.9525. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/50 (v/v).

3-Fluoro-2-iodoaniline (2g)⁶



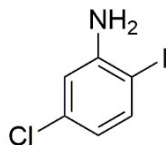
White solid (213 mg, 90% yield), m.p. 54 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.10-7.04 (m, 1H), 6.51 (dt, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H), 6.44 (td, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H), 4.27 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): 162.5 (d, *J* = 241.0 Hz), 148.9 (d, *J* = 5.0 Hz), 130.2 (d, *J* = 10.0 Hz), 109.9 (d, *J* = 3.0 Hz), 104.8 (d, *J* = 24.0 Hz), 71.9 (d, *J* = 28.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -91.3 (s, 1F). HRMS (ESI): calculated for [C₆H₅FIN+H⁺] 237.9528, found 237.9533. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/50 (v/v).

2-Fluoro-6-iodoaniline (2h)



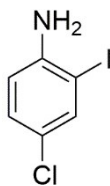
Brown oil (116 mg, 49% yield), m.p. 54 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.40 (dt, *J*₁ = 8.0 Hz, *J*₂ = 1.6 Hz, 1H), 6.99-6.94 (m, 1H), 6.45 (td, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H), 3.70 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): 150.1 (d, *J* = 242.0 Hz), 136.3 (d, *J* = 14.0 Hz), 134.0 (d, *J* = 4.0 Hz), 119.5 (d, *J* = 8.0 Hz), 115.2 (d, *J* = 19.0 Hz), 84.2 (d, *J* = 2.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -129.0 (s, 1F). HRMS (ESI): calculated for [C₆H₅FIN+H⁺] 237.9528, found 237.9520. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/50 (v/v).

5-Chloro-2-iodoaniline (2i)⁵



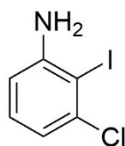
Brown solid (149 mg, 59% yield), m.p. 43 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.52 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 6.47 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 1H), 4.15 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): 147.9, 139.8, 135.3, 120.1, 114.4, 81.2. HRMS (ESI): calculated for [C₆H₅ClIN+H⁺] 253.9233, found 253.9218. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/50 (v/v).

4-Chloro-2-iodoaniline (2j)²



White solid (172 mg, 68% yield), m.p. 42 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, *J* = 2.4 Hz, 1H), 7.10 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.4 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 1H), 4.09 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): 145.7, 137.9, 129.4, 123.3, 115.1, 83.6. HRMS (ESI): calculated for [C₆H₅ClIN+H⁺] 253.9233, found 253.9219. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/50 (v/v).

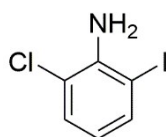
3-Chloro-2-iodoaniline (2k)⁷



Yellow oil (213 mg, 84% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.04 (t, *J*

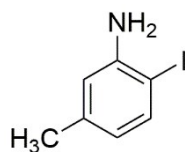
= 7.6 Hz, 1H), 6.84 (dd, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz, 1H), 6.60 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 4.32 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): 149.2, 139.3, 129.7, 118.9, 112.2, 88.4. HRMS (ESI): calculated for $[\text{C}_6\text{H}_5\text{ClIN}+\text{H}^+]$ 253.9233, found 253.9228. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/50 (v/v).

2-Chloro-6-iodoaniline (2l)⁸



Yellow solid (116 mg, 46% yield), m.p. 68 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.54 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 7.23 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 6.41 (t, $J = 8.4$ Hz, 1H), 4.53 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): 143.5, 137.6, 129.7, 120.0, 118.0, 83.6. HRMS (ESI): calculated for $[\text{C}_6\text{H}_5\text{ClIN}+\text{H}^+]$ 253.9233, found 253.9220. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/50 (v/v).

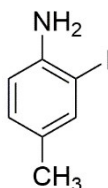
2-Iodo-5-methylaniline (2m)⁵



Brown solid (117 mg, 50% yield), m.p. 40 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.50 (d, $J = 8.0$ Hz, 1H), 6.59 (d, $J = 2.0$ Hz, 1H), 6.33 (d, $J = 8.0$ Hz, 1H), 3.93 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): 146.6, 139.6, 138.7, 121.3, 115.7, 80.4, 21.2. HRMS (ESI): calculated for $[\text{C}_7\text{H}_8\text{IN}+\text{H}^+]$ 233.9780, found 233.9772. Flash chromatographic

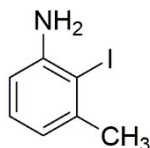
condition: ethyl acetate/petroleum ether = 1/10 (v/v).

2-Iodo-4-methylaniline (2n)²



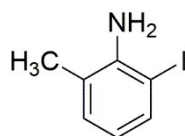
Brown solid (124 mg, 53% yield), m.p. 39 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.47 (d, *J* = 1.6 Hz, 1H), 6.95 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.6 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 2H), 2.21 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 144.4, 139.2, 130.2, 129.7, 114.8, 84.5, 20.0. HRMS (ESI): calculated for [C₇H₈IN+H⁺] 233.9780, found 233.9760. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/10 (v/v).

2-Iodo-3-methylaniline (2o)²



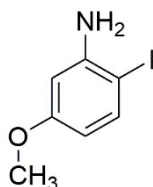
Yellow solid (182 mg, 78% yield), m.p. 43 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.01 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 147.2, 142.6, 128.6, 119.7, 112.0, 91.7, 29.4. HRMS (ESI): calculated for [C₇H₈IN+H⁺] 233.9780, found 233.9765. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/10 (v/v).

2-Iodo-6-methylaniline (2p)²



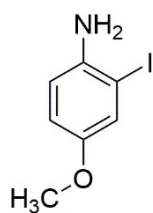
Yellow solid (121 mg, 52% yield), m.p. 41 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.52 (dd, *J*₁ = 8.0 Hz, *J*₂ = 0.8 Hz, 1H), 7.01 (dd, *J*₁ = 7.2 Hz, *J*₂ = 0.4 Hz, 1H), 6.42 (t, *J* = 8.0 Hz, 1H), 4.07 (s, 2H), 2.23 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 144.9, 137.0, 130.6, 122.7, 119.9, 84.8, 19.0. HRMS (ESI): calculated for [C₇H₈IN+H⁺] 233.9780, found 233.9778. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/10 (v/v).

2-Iodo-5-methoxyaniline (2q)⁵



Yellow solid (130 mg, 52% yield), m.p. 40 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.48 (d, *J* = 8.8 Hz, 1H), 6.32 (d, *J* = 2.8 Hz, 1H), 6.42 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.8 Hz, 1H), 4.07 (s, 2H), 3.74 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): 161.2, 147.7, 139.3, 106.7, 100.6, 73.6, 55.4. HRMS (ESI): calculated for [C₇H₈INO+H⁺] 249.9729, found 249.9720. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/10 (v/v).

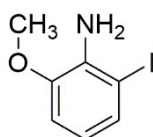
2-Iodo-4-methoxyaniline (2r)²



Orange oil (57 mg, 23% yield); ¹H NMR (400 MHz, CDCl₃): δ 7.21 (d, *J*

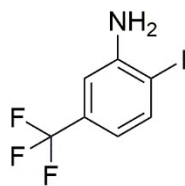
= 2.8 Hz, 1H), 6.77 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.8$ Hz, 1H), 6.70 (d, $J = 8.8$ Hz, 1H), 3.73 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): 152.8, 140.9, 123.6, 116.2, 115.5, 84.4, 56.1. HRMS (ESI): calculated for $[\text{C}_7\text{H}_8\text{INO}+\text{H}^+]$ 249.9729, found 249.9713. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/10 (v/v).

2-Iodo-6-methoxyaniline (2s)



Orange oil (154 mg, 62% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.24 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz, 1H), 6.74 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 6.47 (t, $J = 8.0$ Hz, 1H), 4.23 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): 146.7, 137.6, 130.6, 119.4, 110.1, 83.4, 55.9. HRMS (ESI): calculated for $[\text{C}_7\text{H}_8\text{INO}+\text{H}^+]$ 249.9729, found 249.9727. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/10 (v/v)

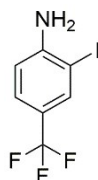
2-Iodo-5-(trifluoromethyl)aniline (2t)⁵



Brown oil (60 mg, 21% yield); ^1H NMR (400 MHz, CDCl_3): δ 7.74 (d, $J = 8.4$ Hz, 1H), 6.94 (d, $J = 2.0$ Hz, 1H), 6.70 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.0$ Hz, 1H), 4.30 (s, 2H); ^{13}C NMR (400 MHz, CDCl_3): 147.3, 139.7, 132.0 (q, $J = 32.0$ Hz), 122.7 (q, $J = 271.0$ Hz), 116.1 (q, $J = 4.0$ Hz), 110.8 (q, $J = 4.0$ Hz), 87.6; ^{19}F NMR (376 MHz, CDCl_3) δ -63.2 (s, 3F). HRMS (ESI):

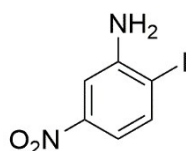
calculated for $[C_7H_5F_3IN+H^+]$ 287.9497, found 287.8479. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/6 (v/v).

2-Iodo-4-(trifluoromethyl)aniline (**2u**)⁹



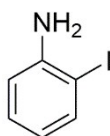
White solid (101 mg, 35% yield), m.p. 50 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.87 (d, *J* = 2.0 Hz, 1H), 7.37 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.0 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 4.41 (s, 2H); ¹³C NMR (400 MHz, CDCl₃): 149.7, 136.3 (q, *J* = 4.0 Hz), 126.9 (q, *J* = 4.0 Hz), 123.7 (q, *J* = 270.0 Hz), 121.6 (q, *J* = 3.0 Hz), 113.6, 82.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -61.4 (s, 3F). HRMS (ESI): calculated for $[C_7H_5F_3IN+H^+]$ 287.9497, found 287.9481. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/5 (v/v).

2-Iodo-5-nitroaniline (**2v**)⁶



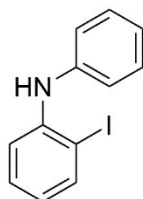
Yellow solid (53 mg, 20% yield), m.p. 105 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.55 (d, *J* = 2.8 Hz, 1H), 8.04 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.4 Hz, 1H), 6.70 (d, *J* = 9.2 Hz, 1H), 4.84 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): 152.5, 139.3, 135.63, 125.9, 112.4, 80.7. HRMS (ESI): calculated for $[C_6H_5IN_2O_2+H^+]$ 264.9474, found 264.9468. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/6 (v/v).

2-Iodoaniline (**2w**)¹⁰



Brown solid (114 mg, 52% yield), m.p. 58 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.64 (dd, *J*₁ = 7.6 Hz, *J*₂ = 1.2 Hz, 1H), 7.14 (td, *J*₁ = 7.2 Hz, *J*₂ = 1.6 Hz, 1H), 6.75 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H), 6.48 (td, *J*₁ = 7.6 Hz, *J*₂ = 1.2 Hz, 1H), 4.08 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): 146.9, 139.1, 129.5, 120.1, 114.9, 84.3. HRMS (ESI): calculated for [C₆H₆IN+H⁺] 219.9623, found 219.9607. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/50 (v/v).

2-Iodo-N-phenylaniline (2x)¹¹



Yellow solid (171 mg, 58% yield), m.p. 58 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.32-7.30 (m, 2H), 7.21-7.20 (m, 2H), 7.15-7.13 (m, 2H), 7.04 (td, *J*₁ = 7.2 Hz, *J*₂ = 1.2 Hz, 1H), 6.65-6.61 (m, 1H), 5.92 (s, 1H); ¹³C NMR (400 MHz, CDCl₃): 144.1, 142.1, 139.7, 129.6, 129.2, 122.7, 122.1, 120.1, 116.0, 88.9. HRMS (ESI): calculated for [C₁₂H₁₀IN+H⁺] 295.9936, found 295.9927. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/50 (v/v).

tiabendazole 3¹²



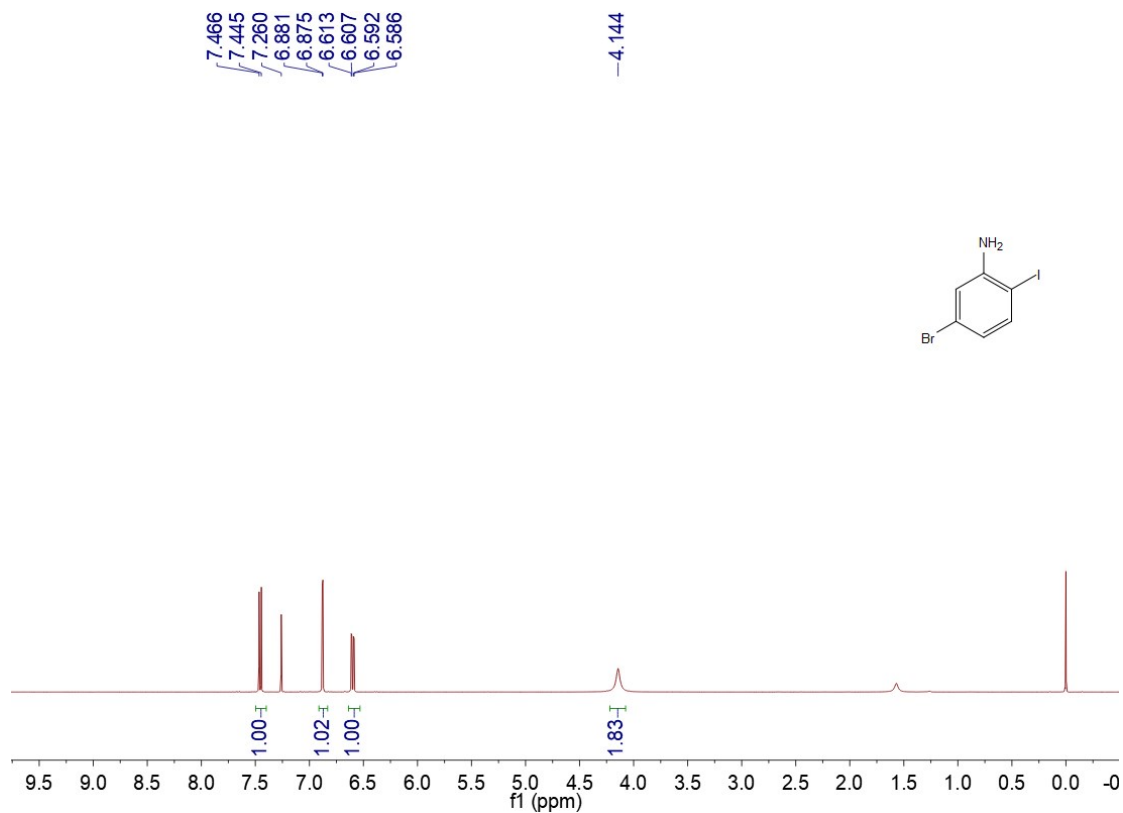
White solid (161 mg, 80% yield), m.p. 295 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ 12.96 (s, 1H), 9.32 (d, *J* = 2.0 Hz, 1H), 7.21-7.20 (m, 2H), 8.45 (t, *J* = 2.4 Hz, 1H), 7.59 (s, 2H), 7.23-7.18 (m, 2H); ¹³C NMR (400 MHz, DMSO-*d*₆): 155.6, 147.1, 147.0, 122.2, 119.4. HRMS (ESI): calculated for [C₁₀H₇N₃S+H⁺] 202.0439, found 202.0416. Flash chromatographic condition: ethyl acetate/petroleum ether = 1/1 (v/v).

7. Reference

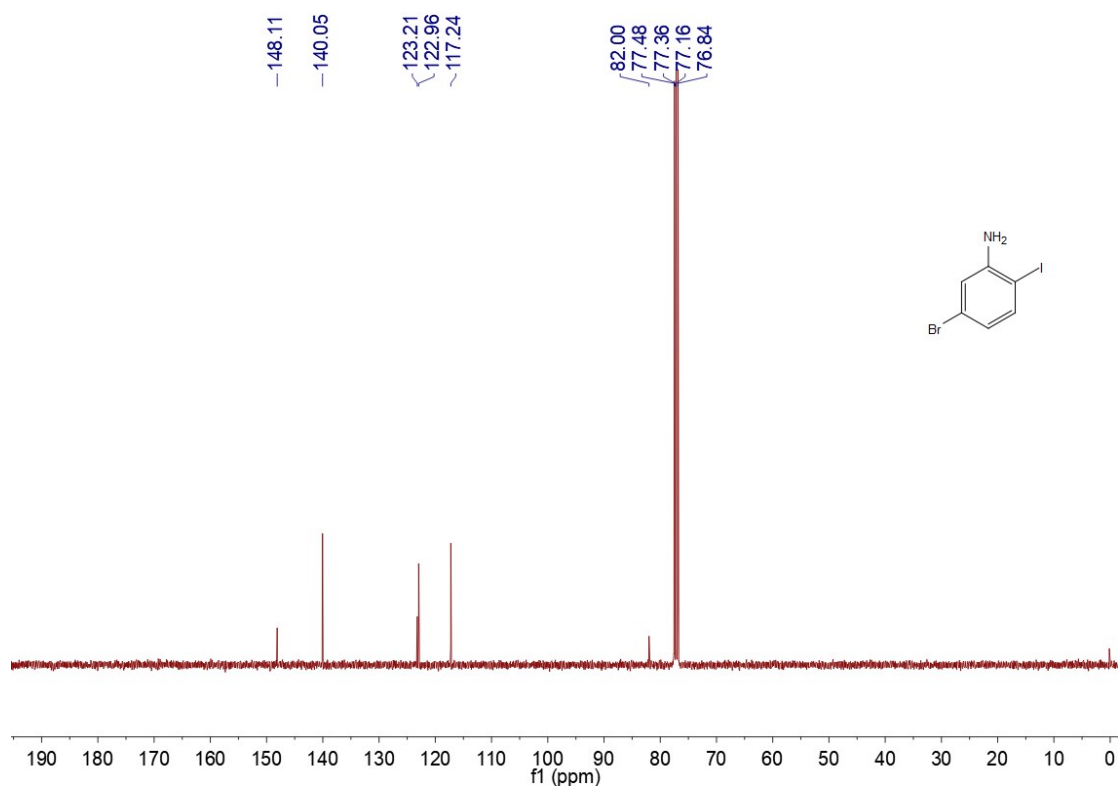
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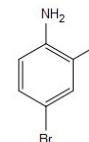
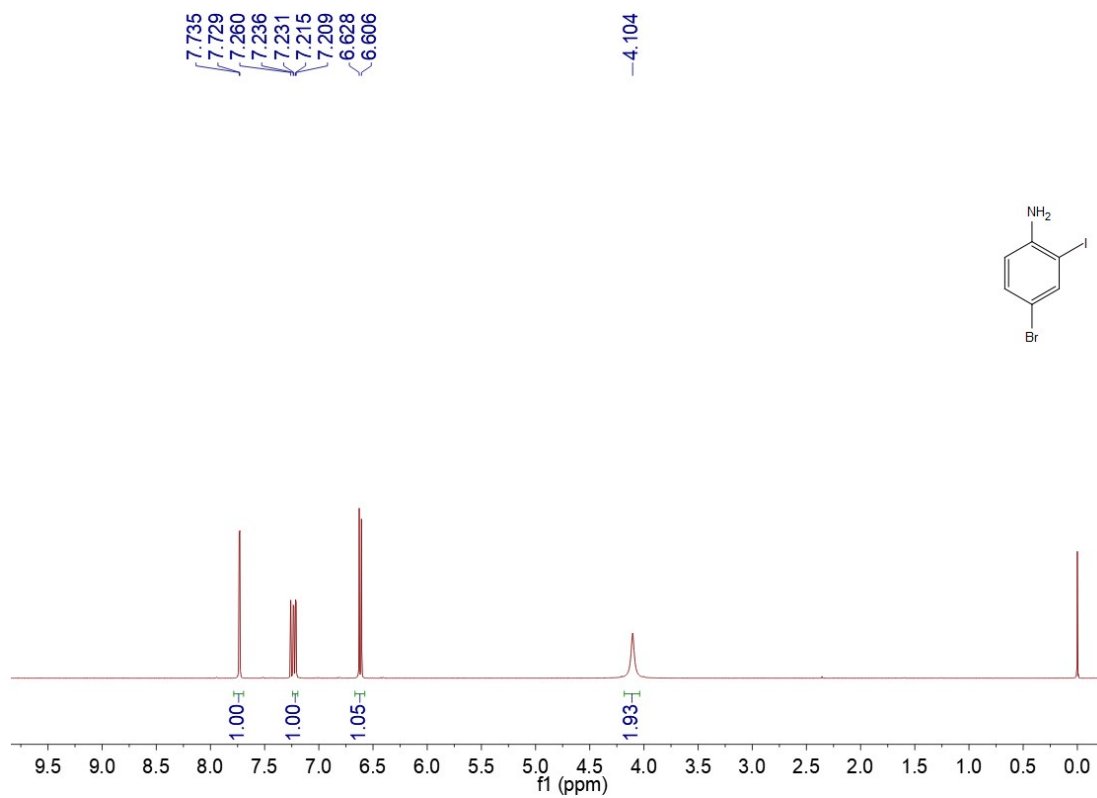
8. NMR spectra for all substrates



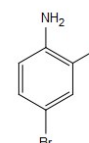
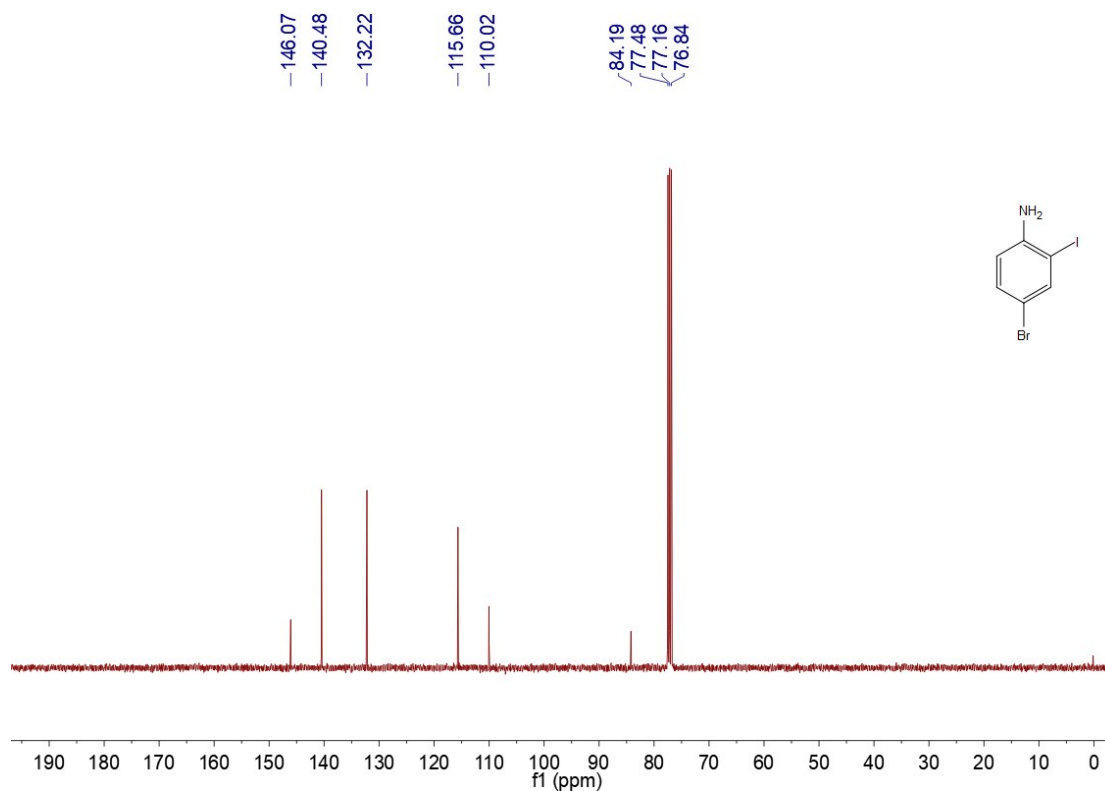
2a (¹H NMR, 400 MHz, CDCl₃)



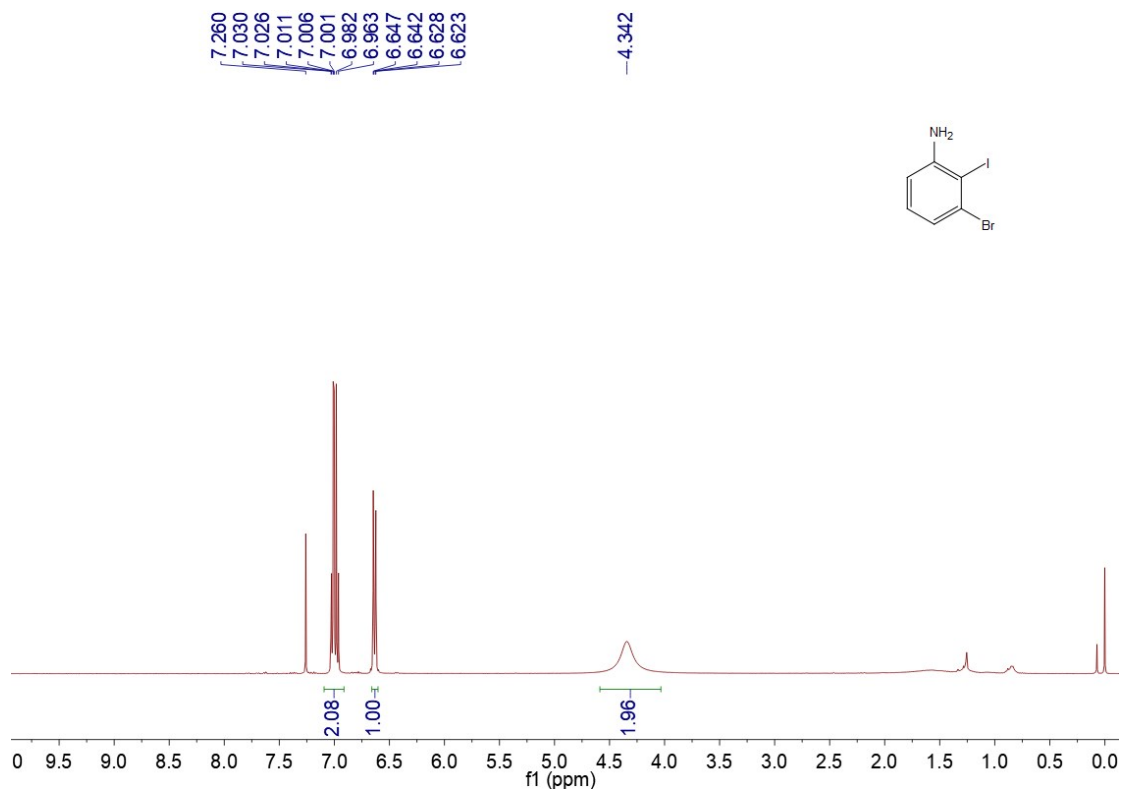
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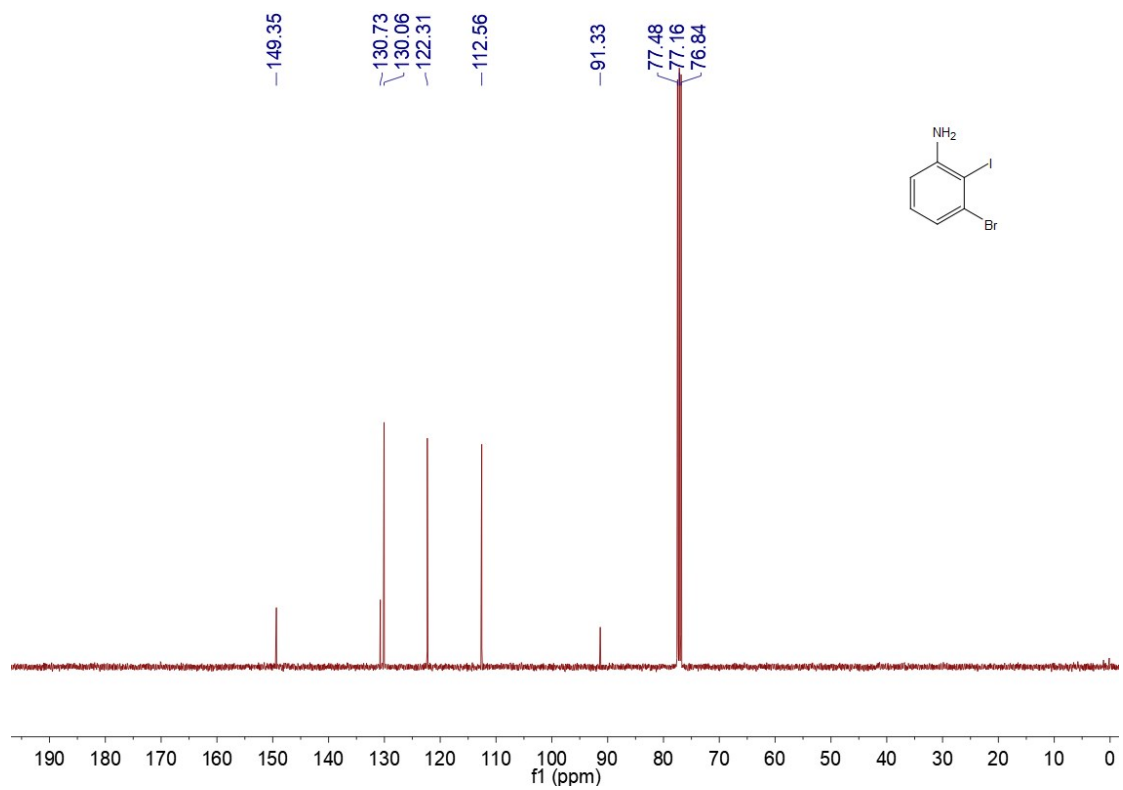
2b (^1H NMR, 400 MHz, CDCl_3)



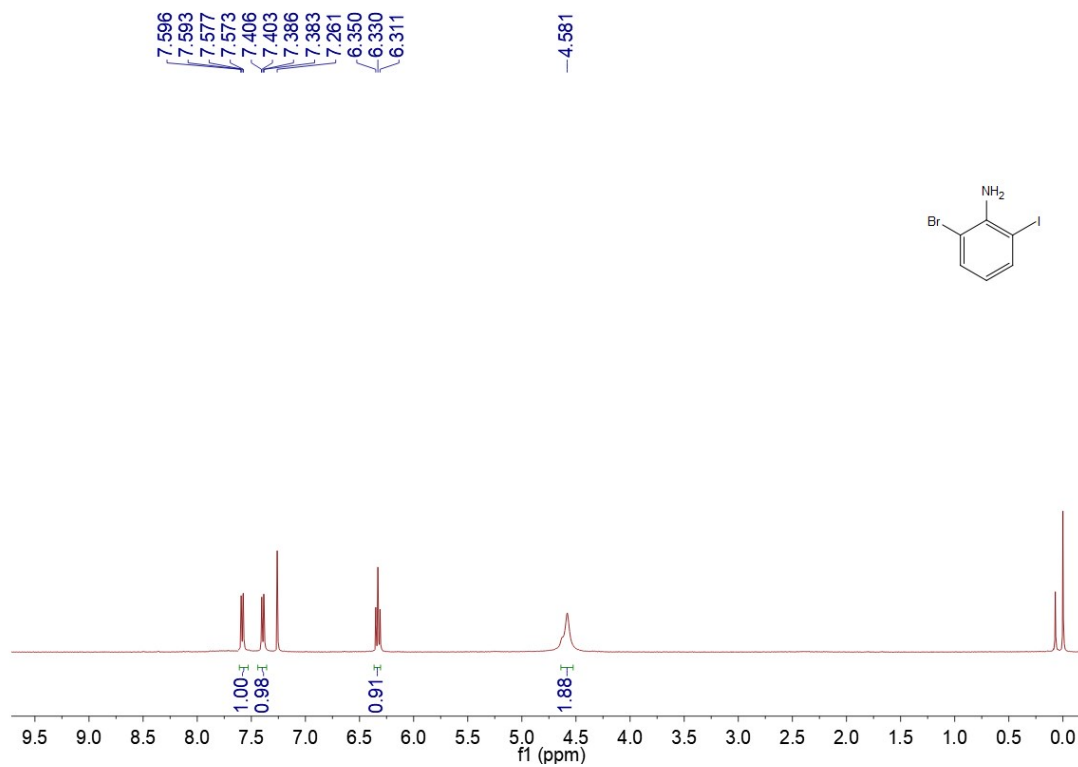
2b (^{13}C NMR, 100 MHz, CDCl_3)



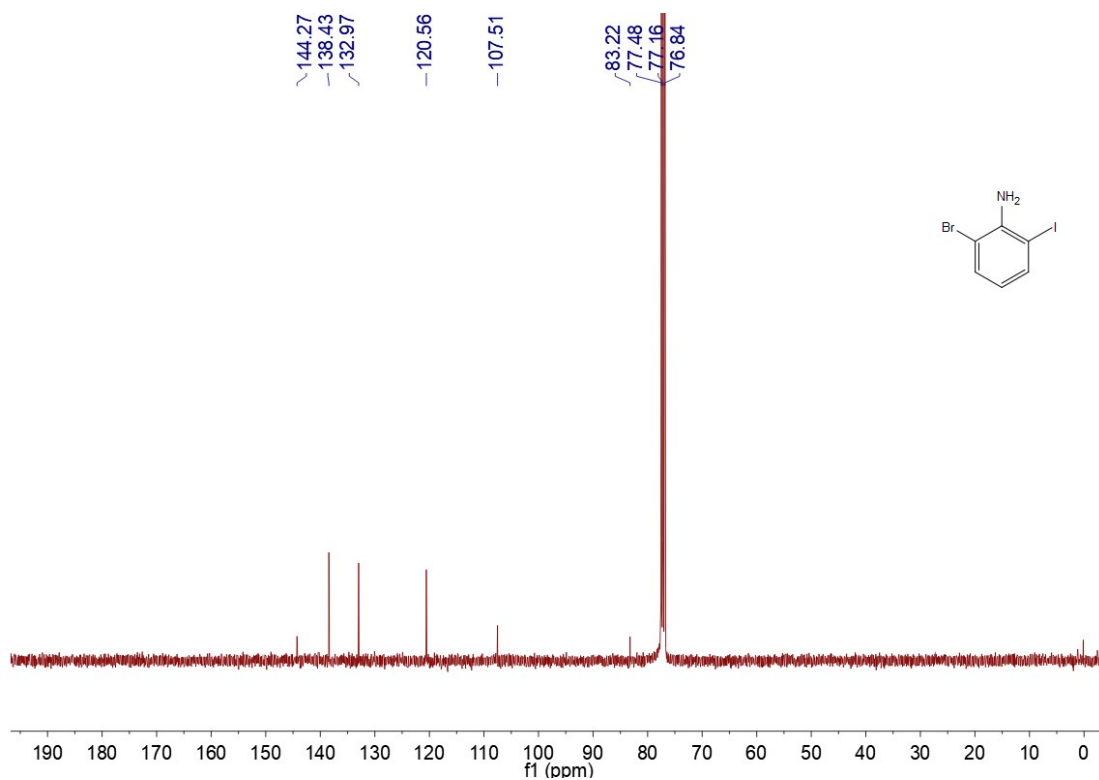
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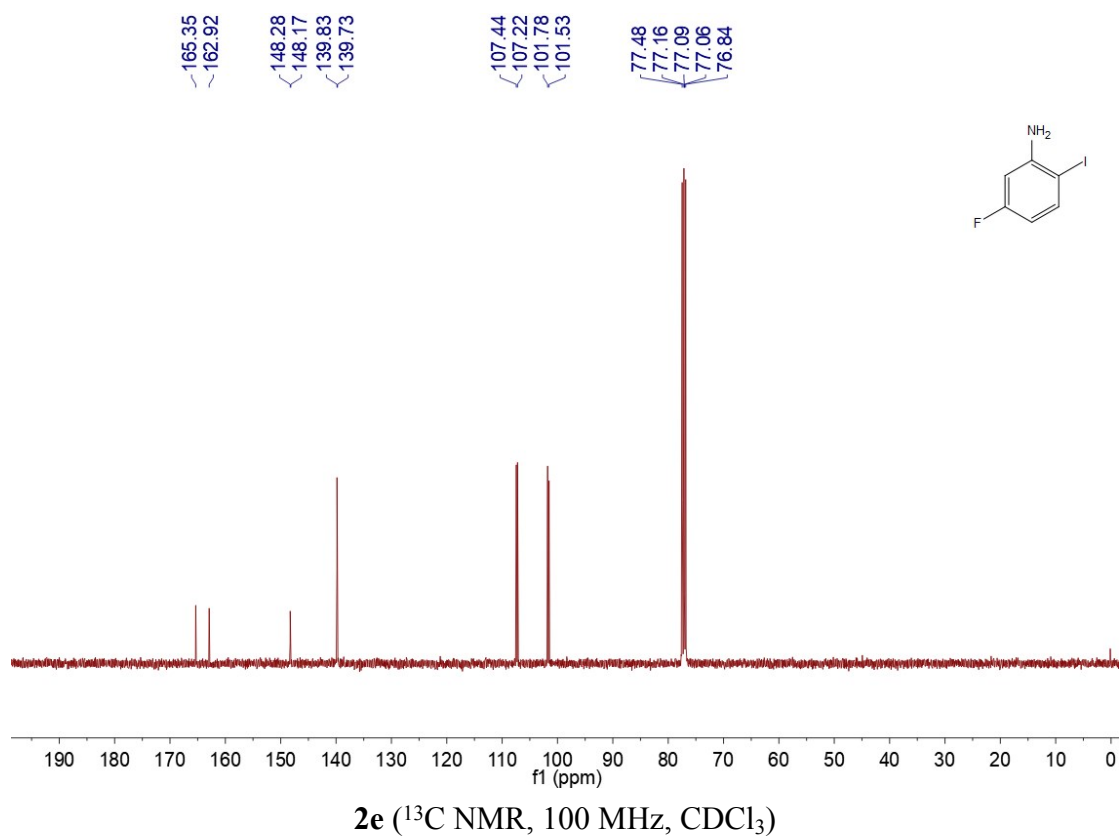
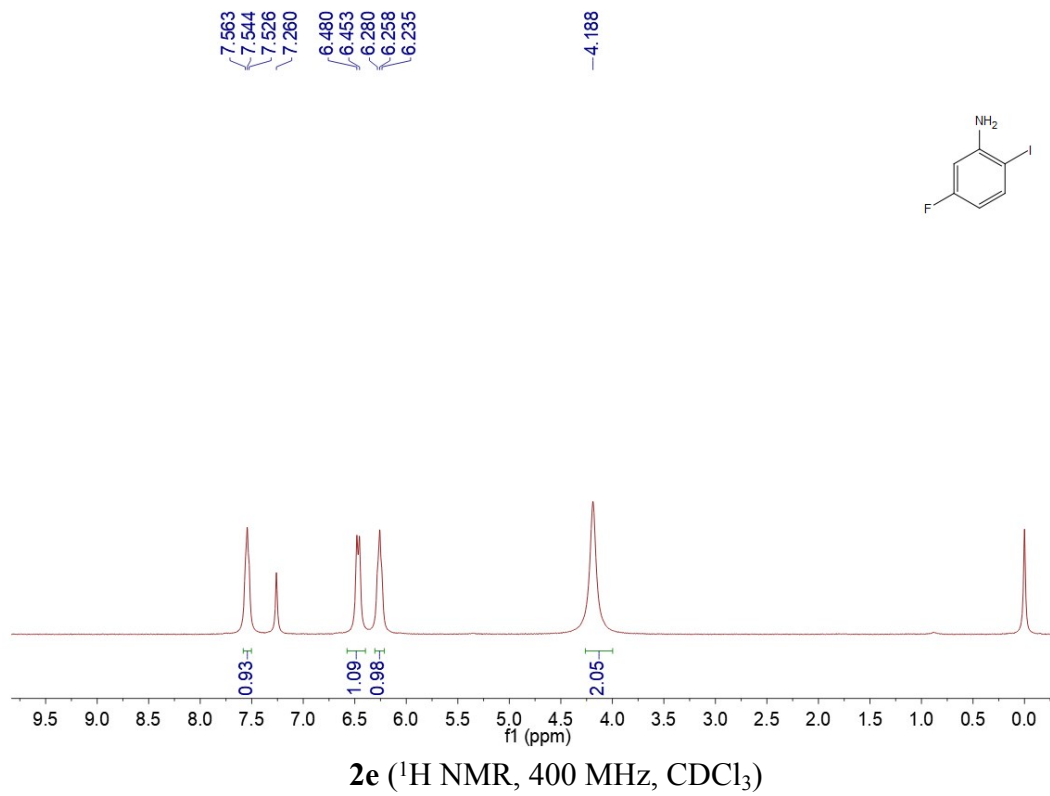
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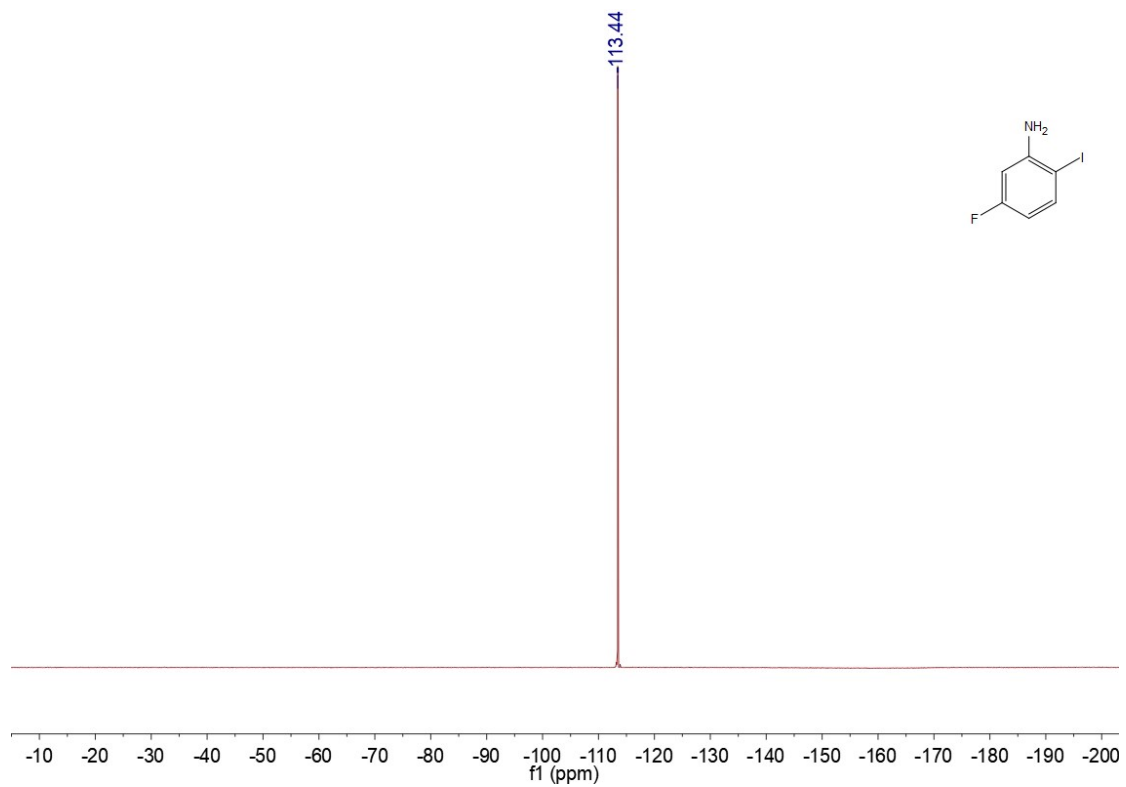


2d (^1H NMR, 400 MHz, CDCl_3)

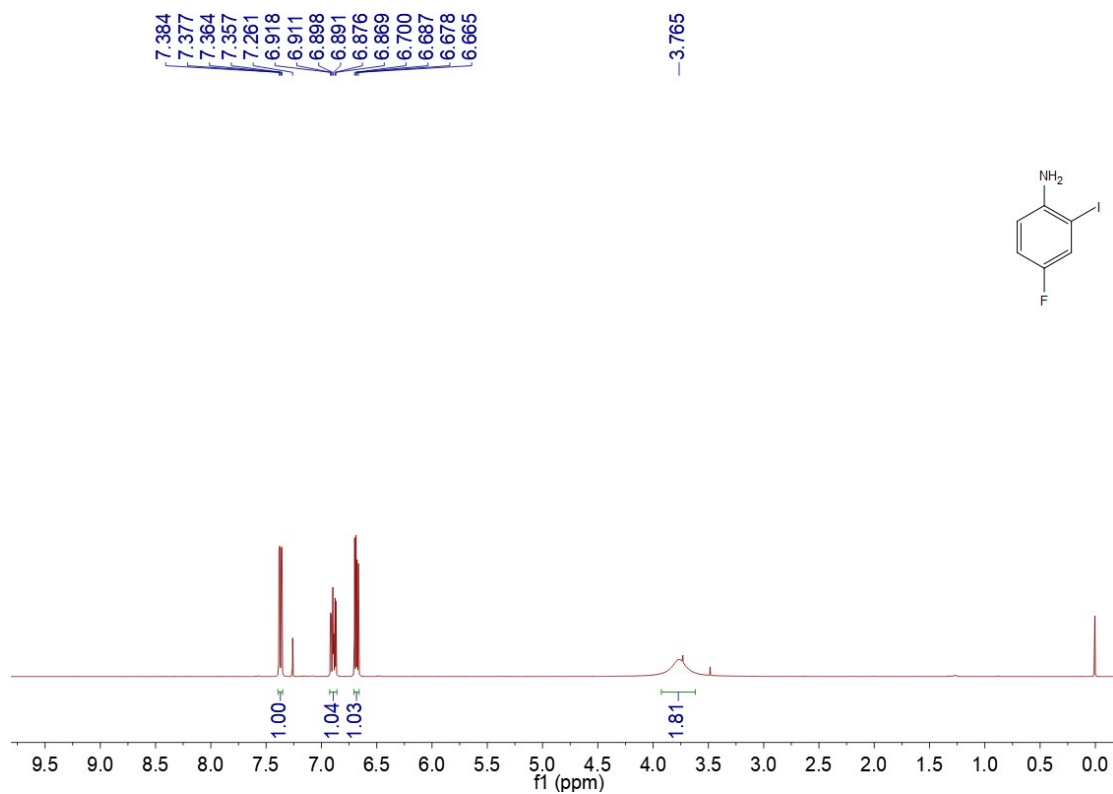


2d (^{13}C NMR, 100 MHz, CDCl_3)

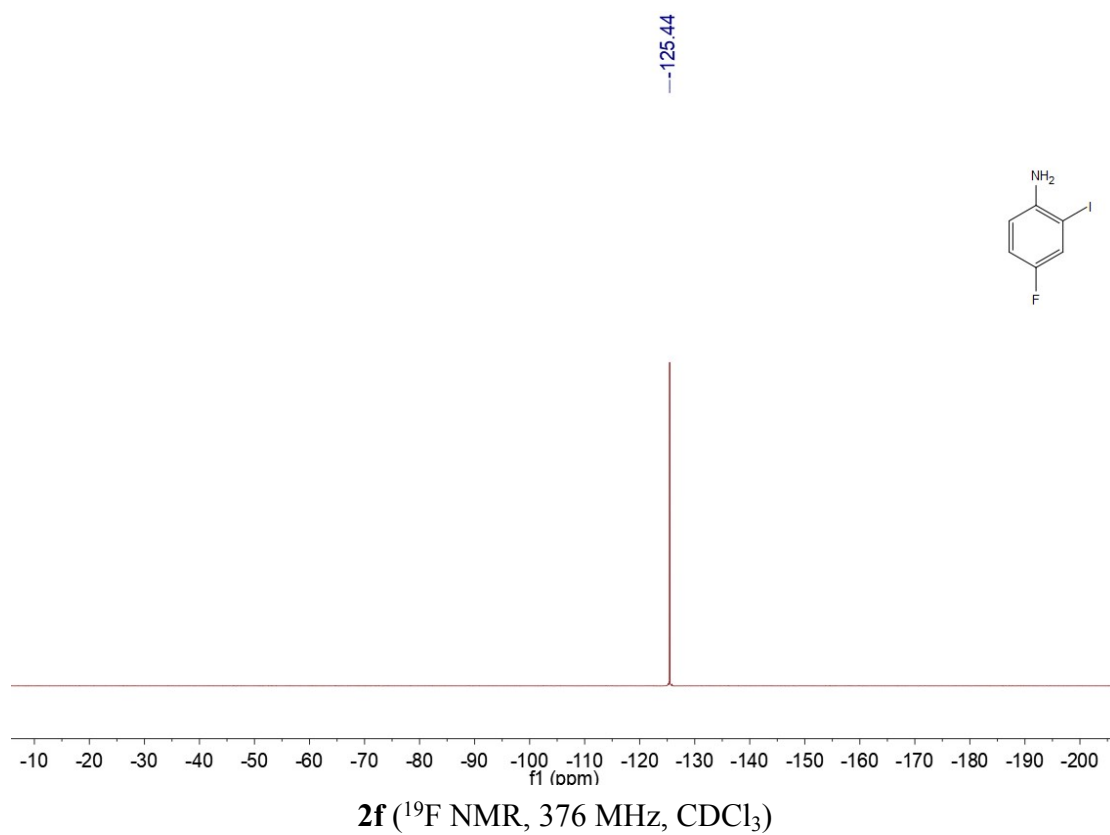
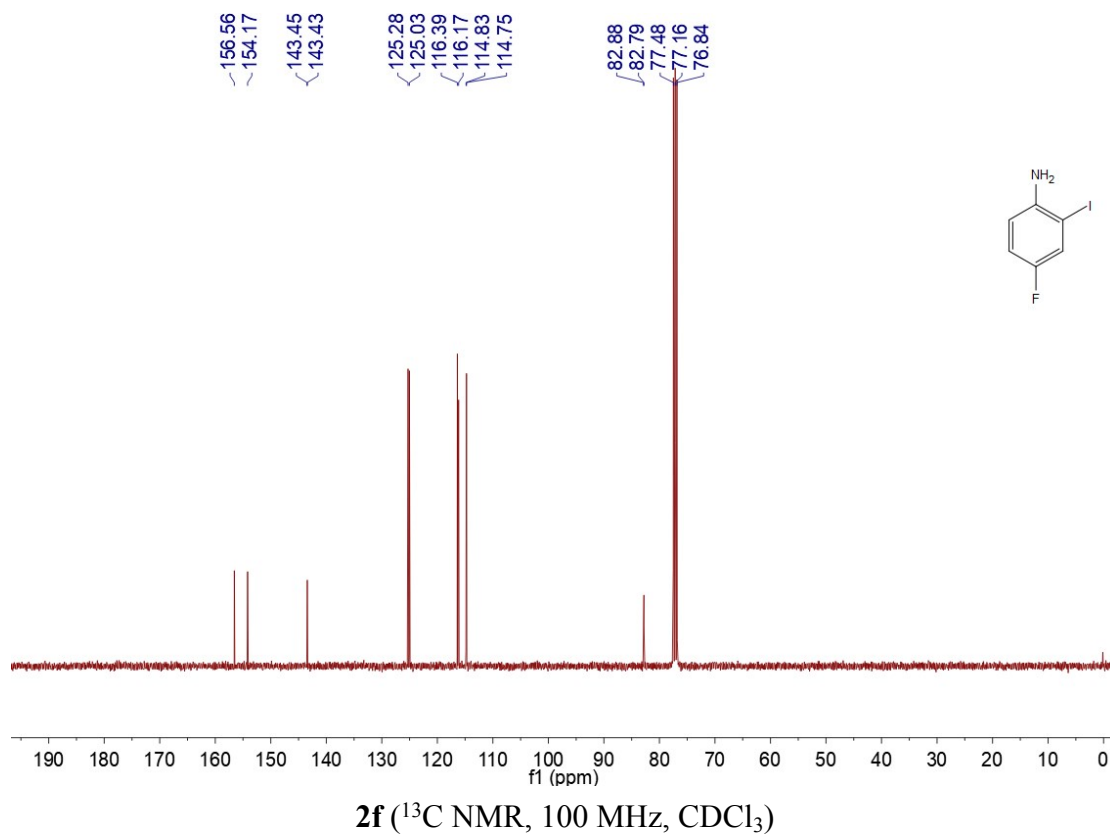


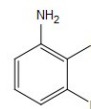
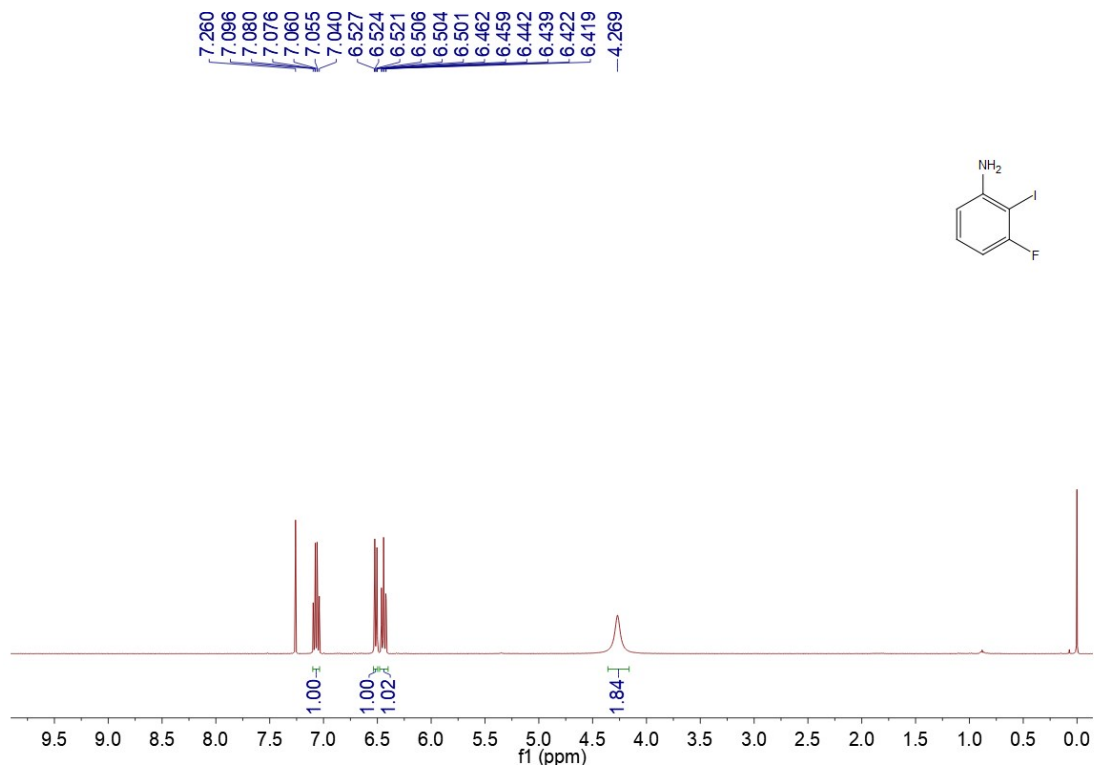


2e (^{19}F NMR, 376 MHz, CDCl_3)

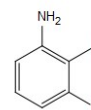
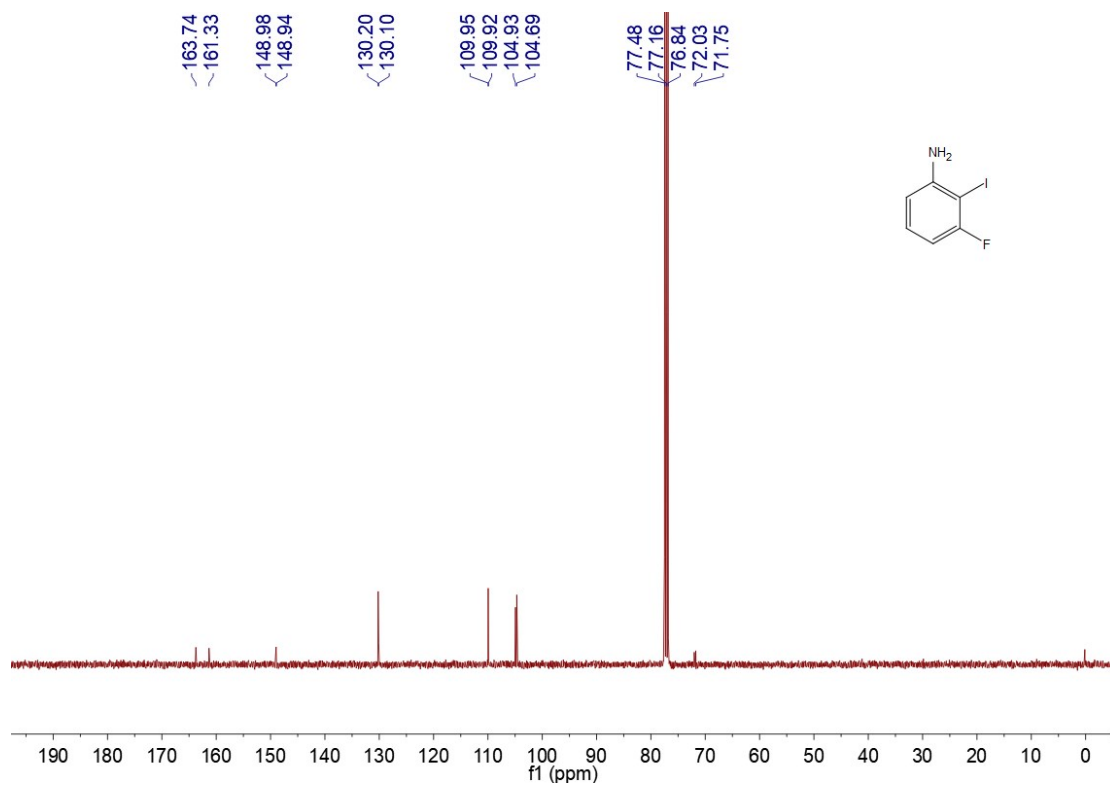


2f (^1H NMR, 400 MHz, CDCl_3)

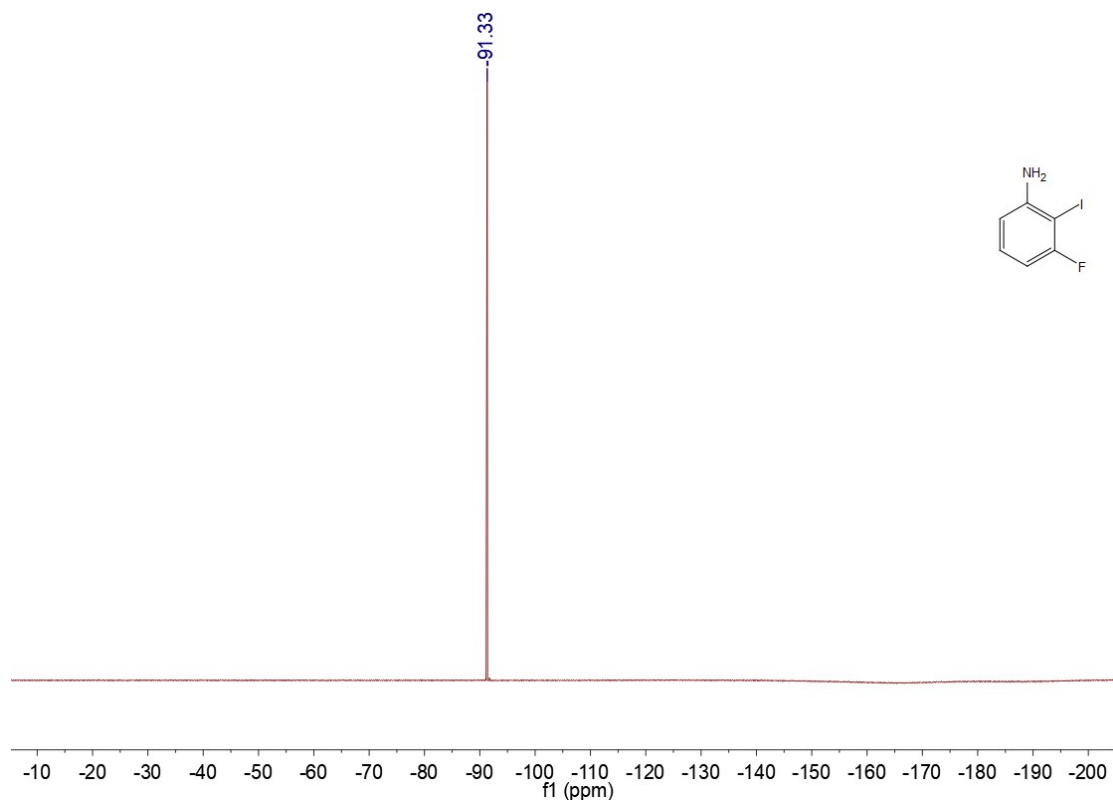




2g (^1H NMR, 400 MHz, CDCl_3)



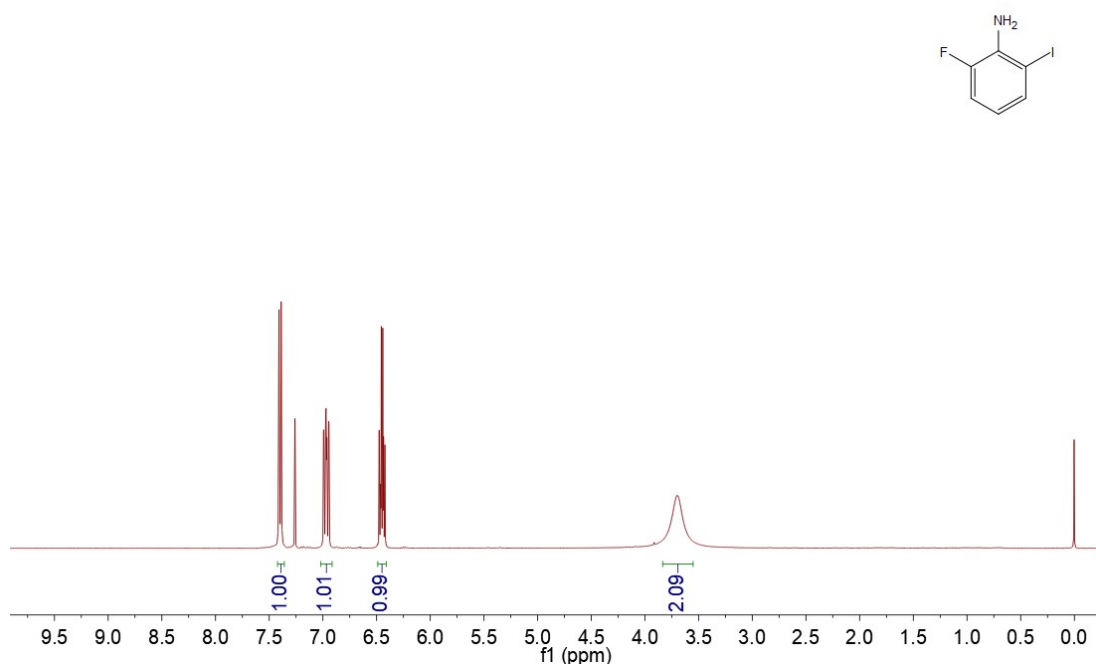
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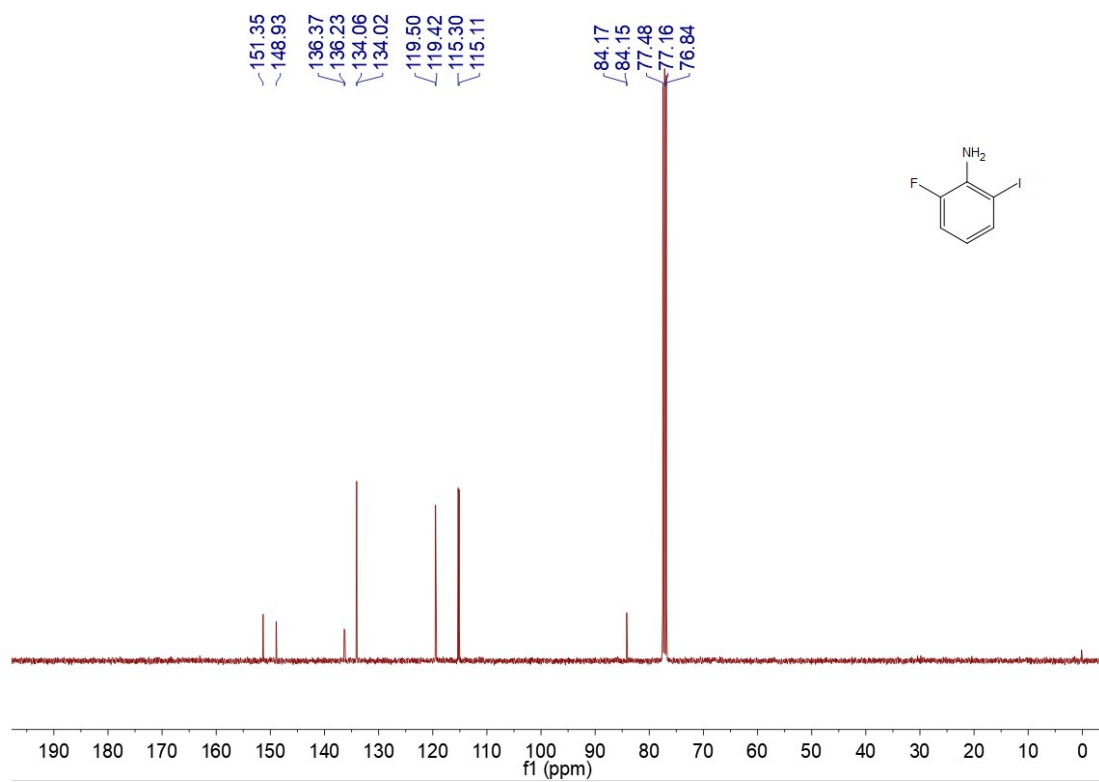
2g (^{19}F NMR, 376 MHz, CDCl_3)

7.412
7.408
7.405
7.392
7.388
7.385
7.260
6.994
6.990
6.973
6.970
6.967
6.963
6.946
6.943
6.475
6.462
6.455
6.442
6.435
6.421

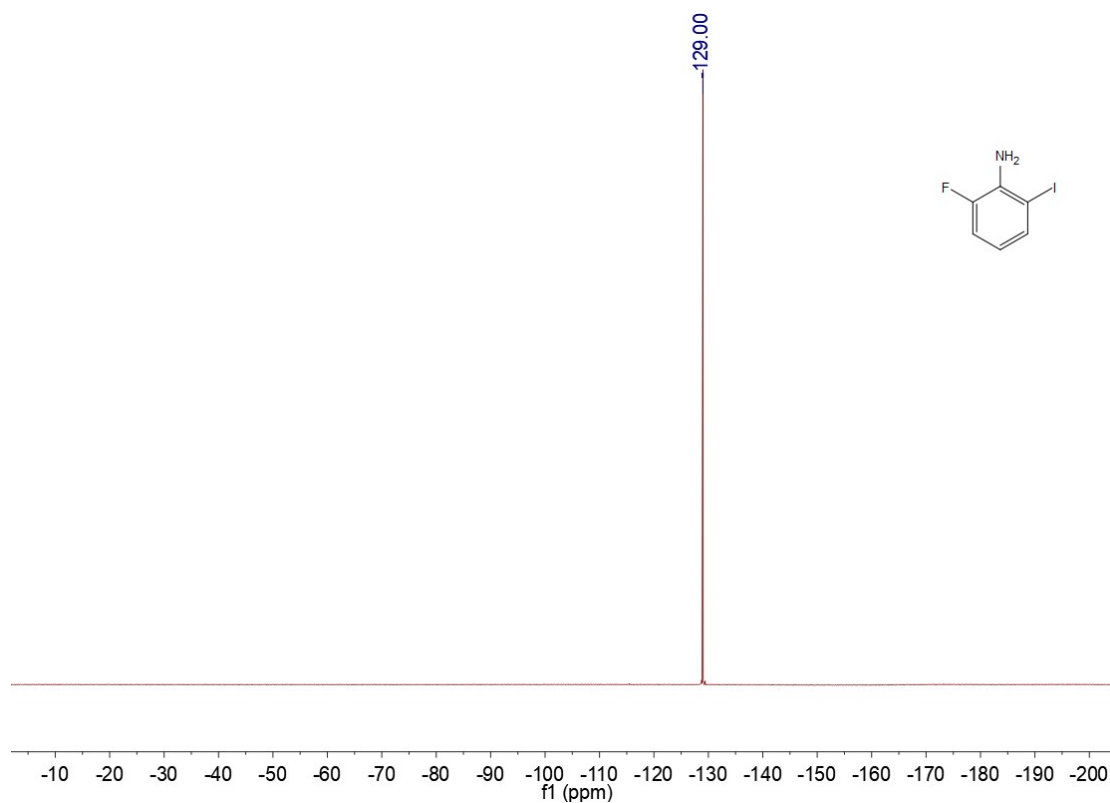
-3.699



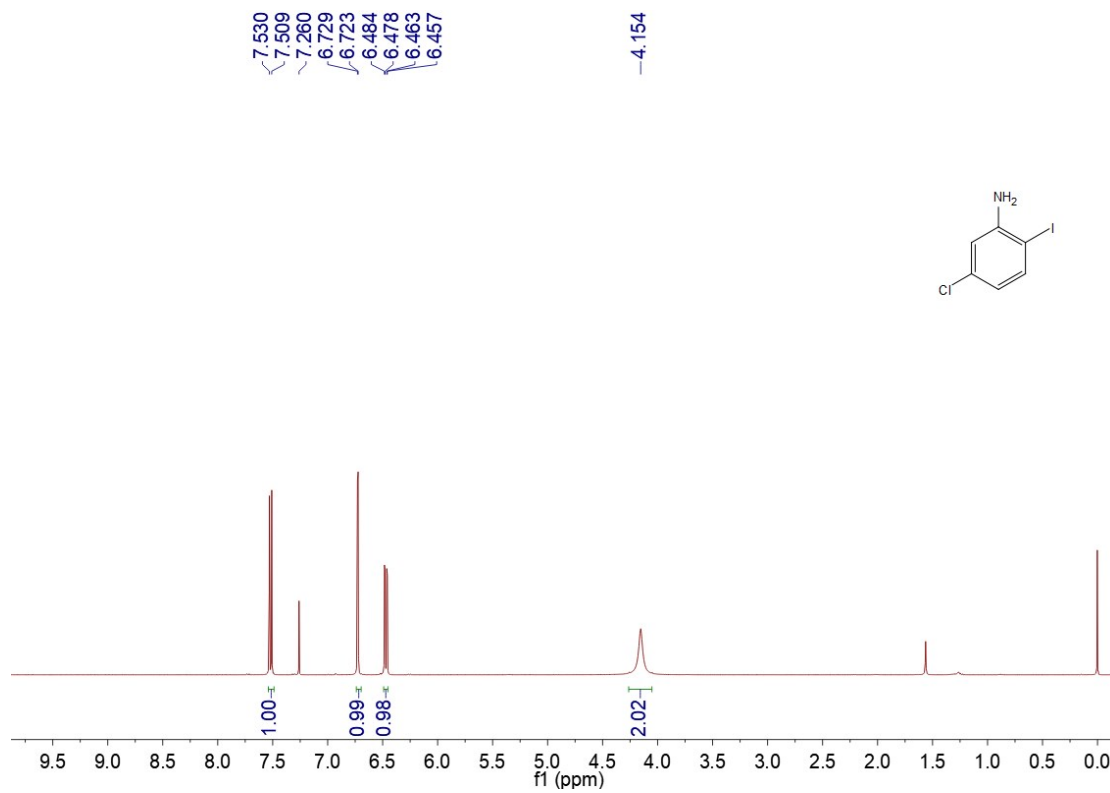
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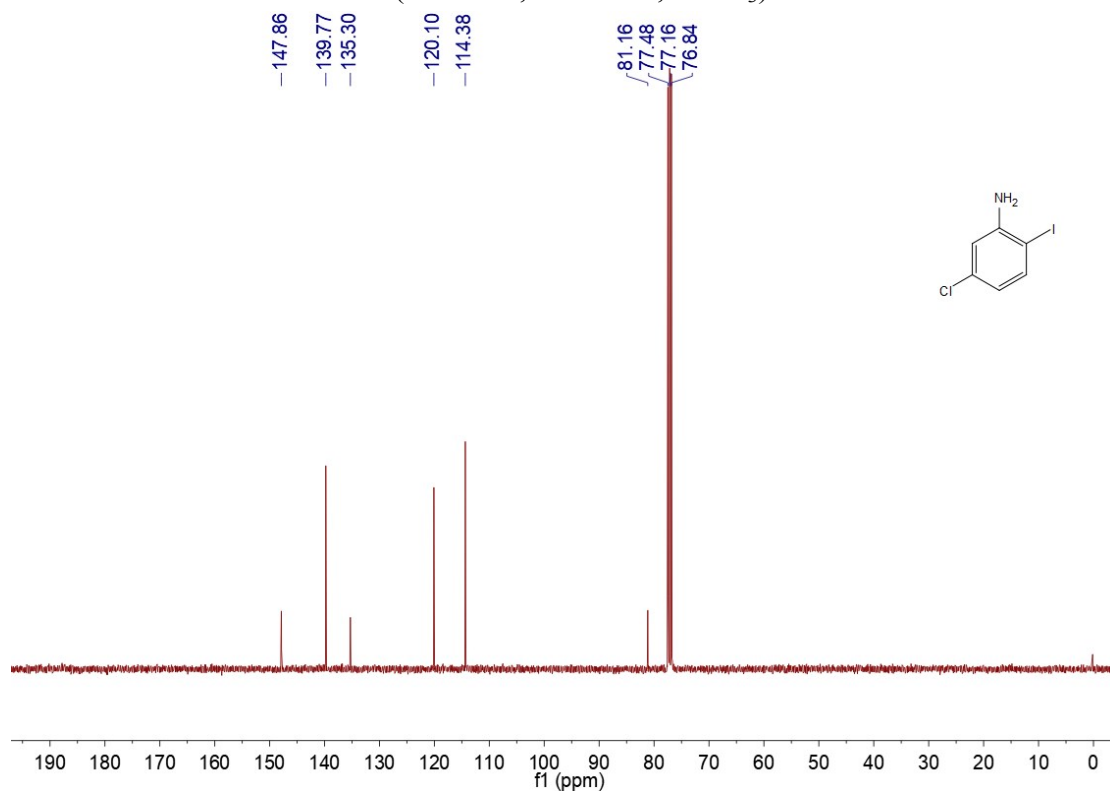
2h (¹³C NMR, 100 MHz, CDCl₃)



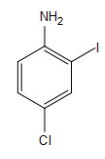
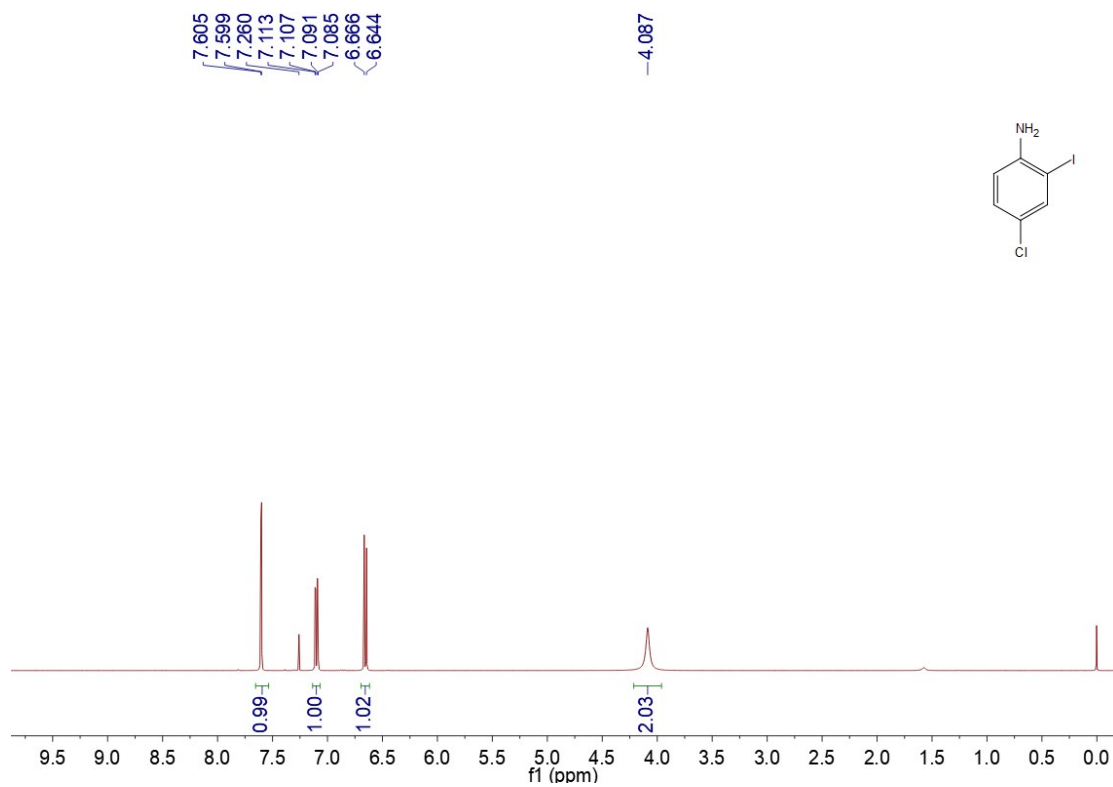
2h (¹⁹F NMR, 376 MHz, CDCl₃)



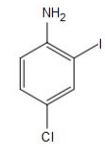
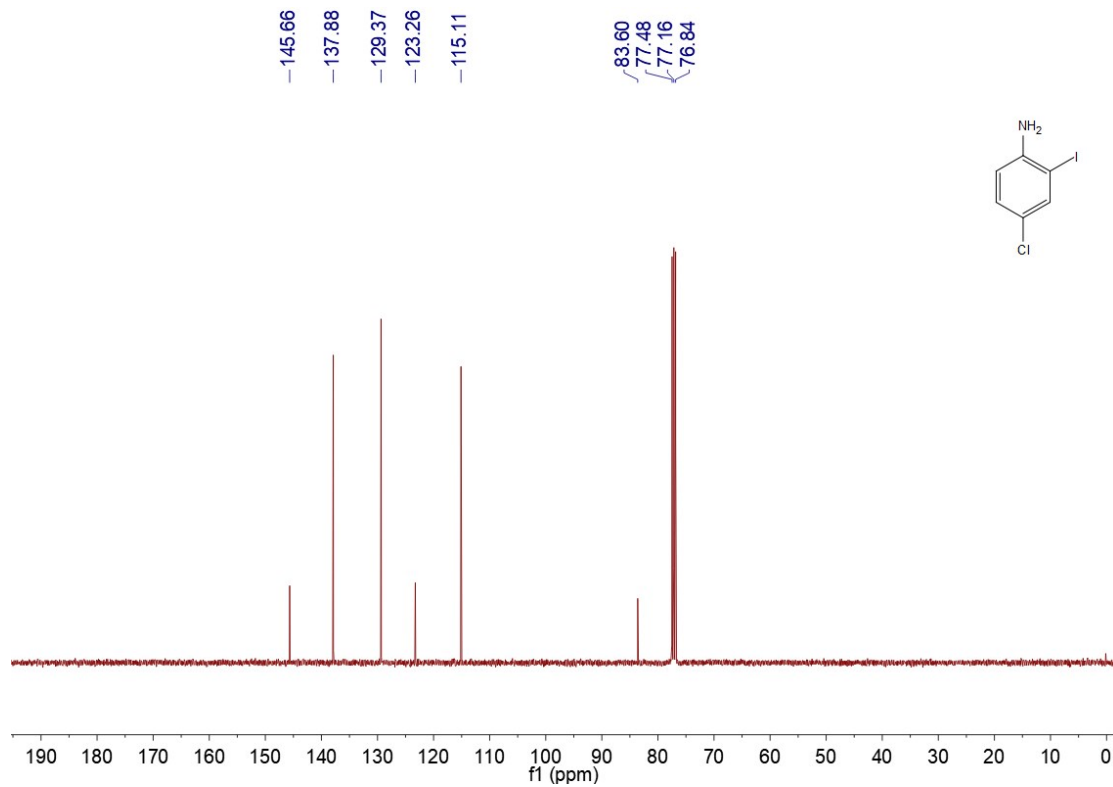
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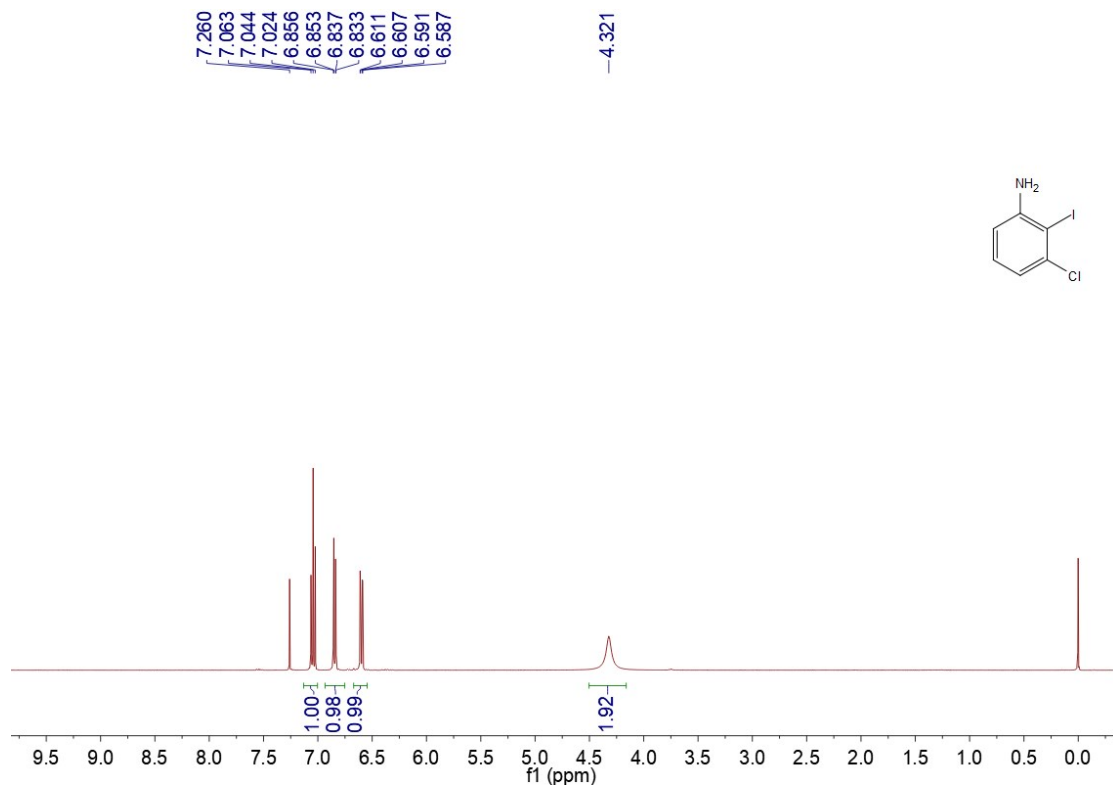
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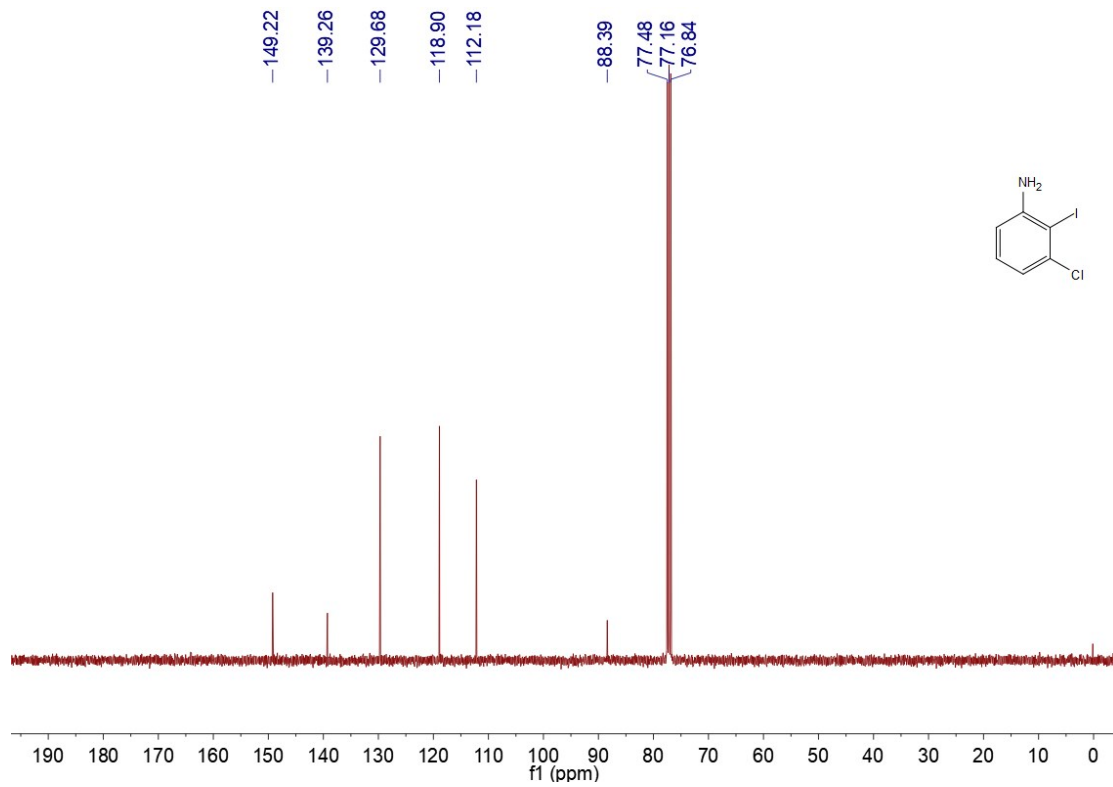
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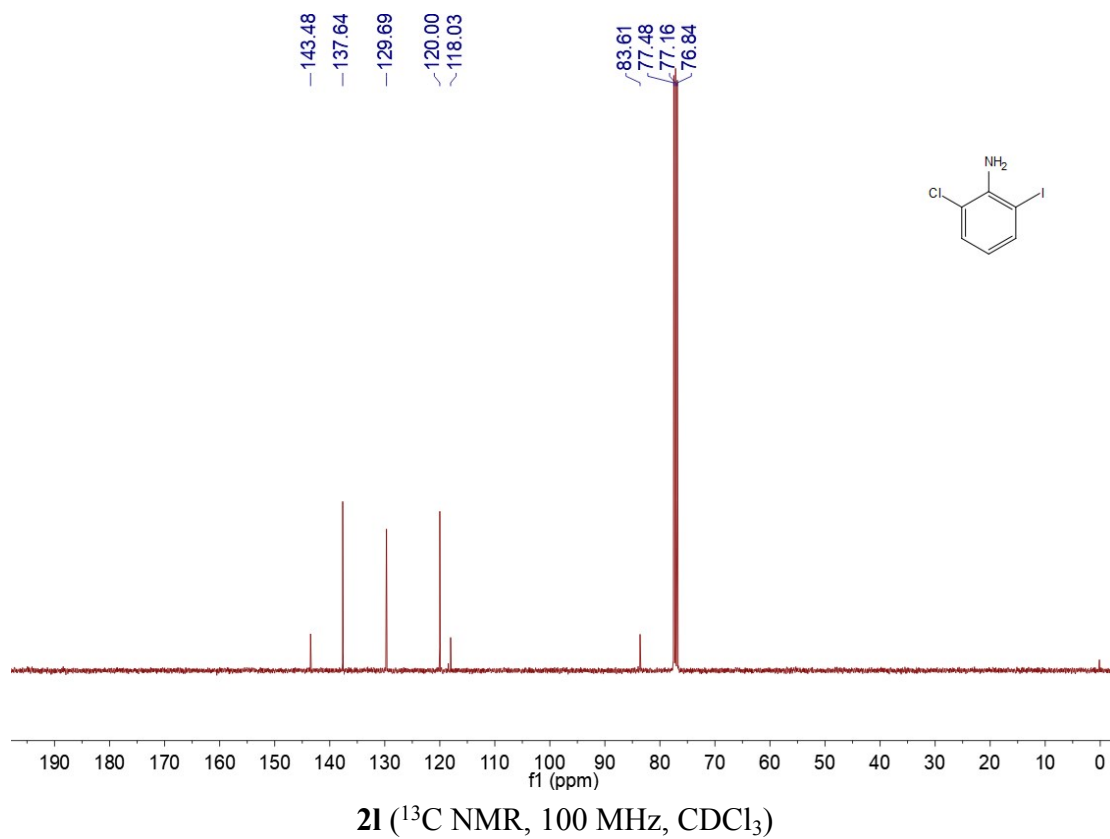
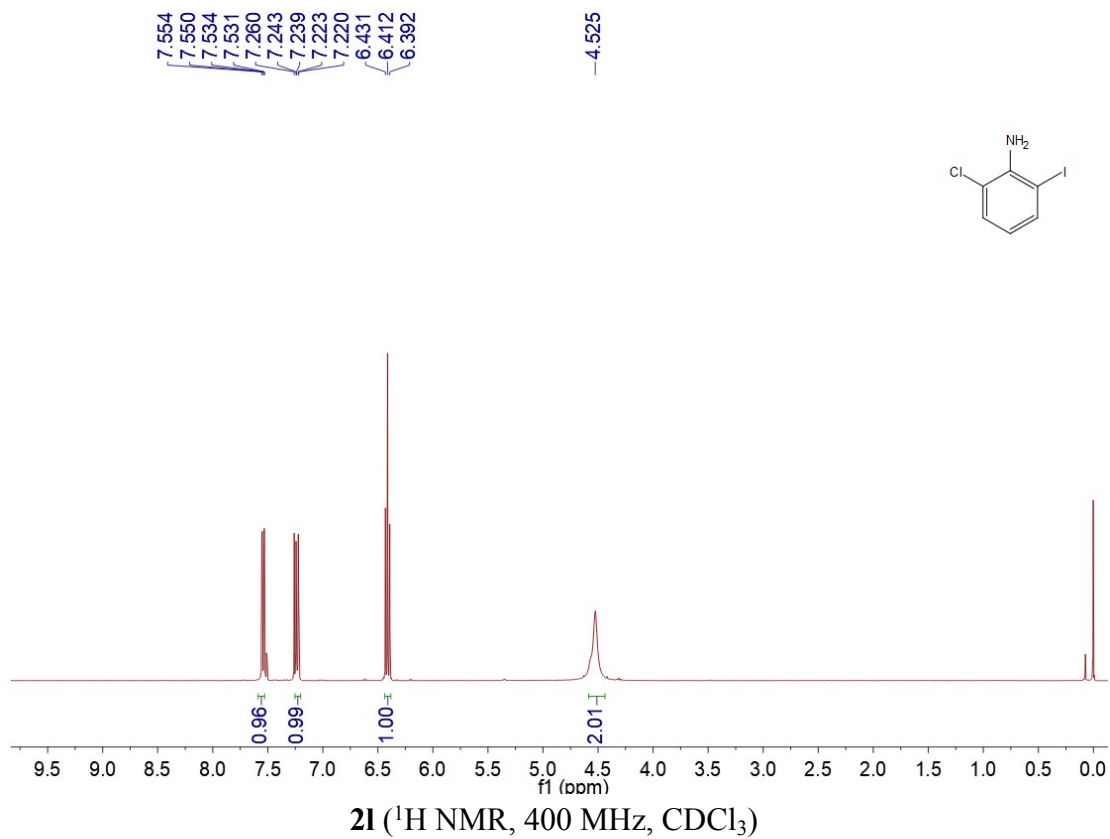
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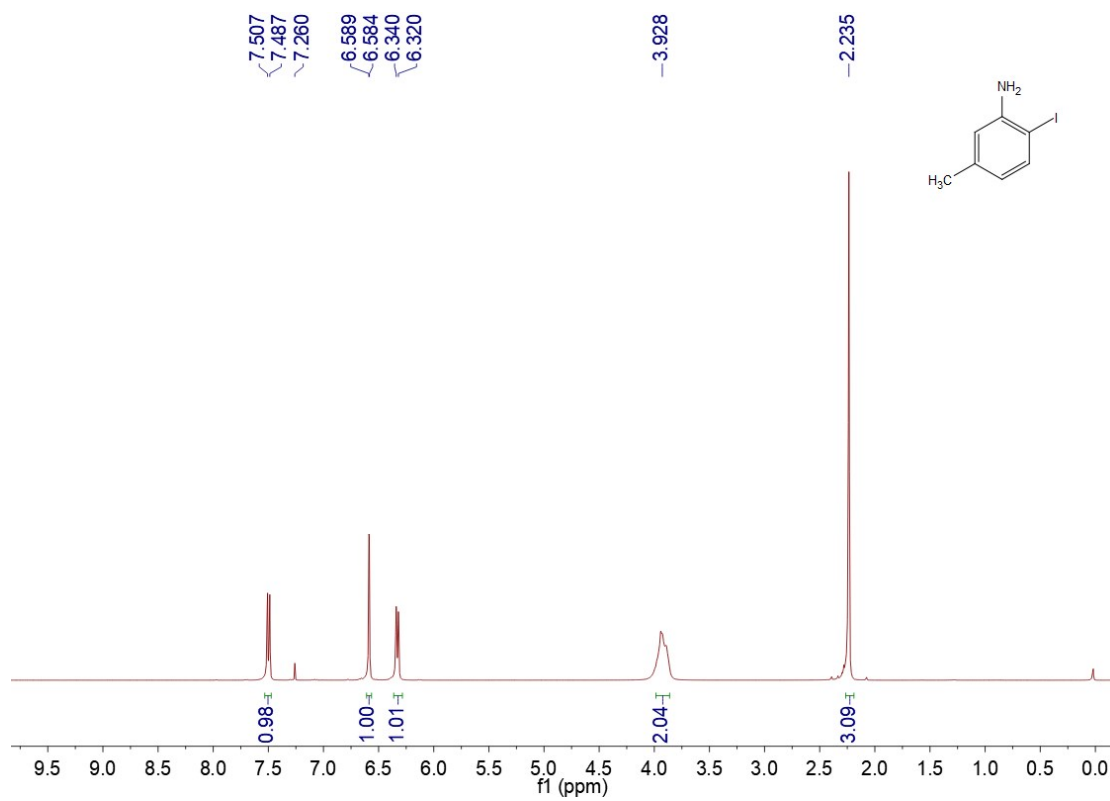


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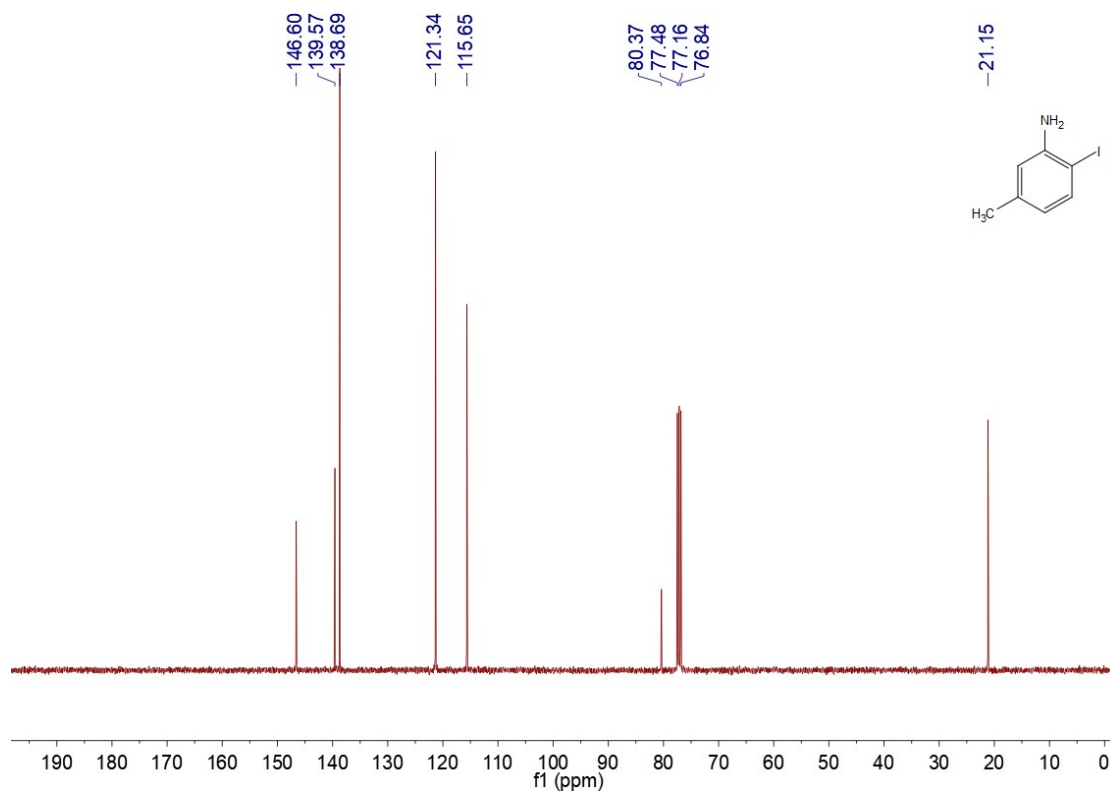


2k (^{13}C NMR, 100 MHz, CDCl_3)

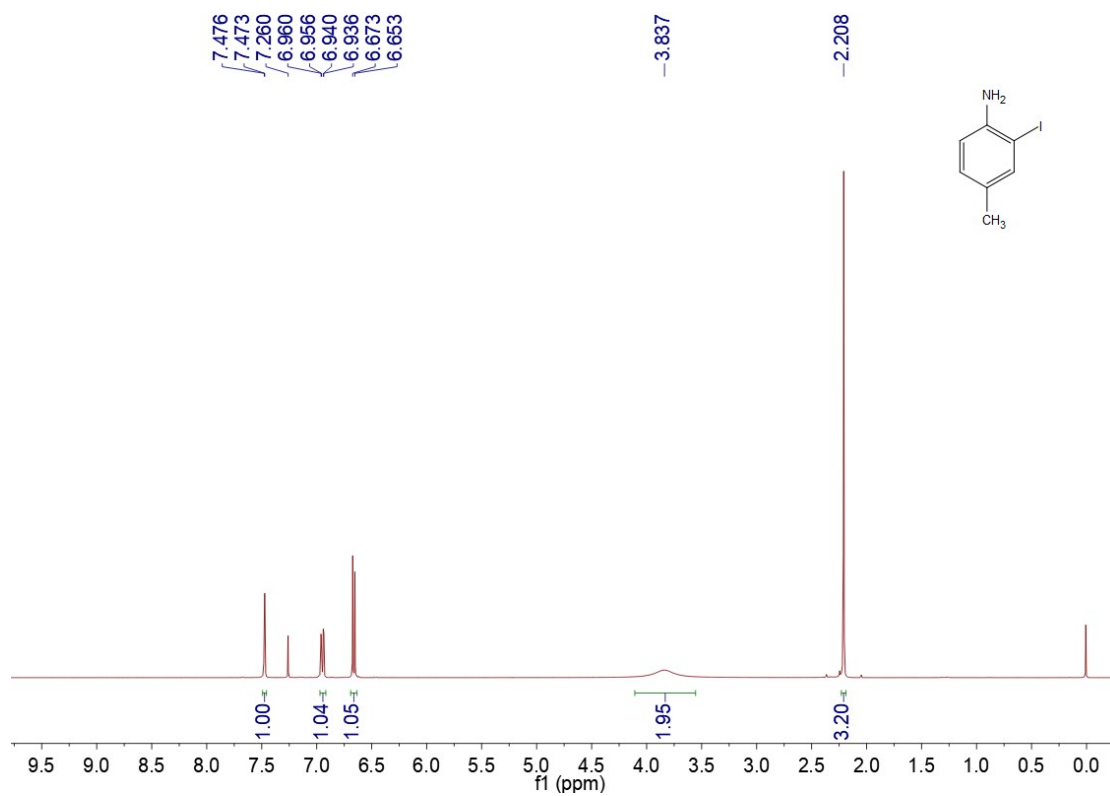




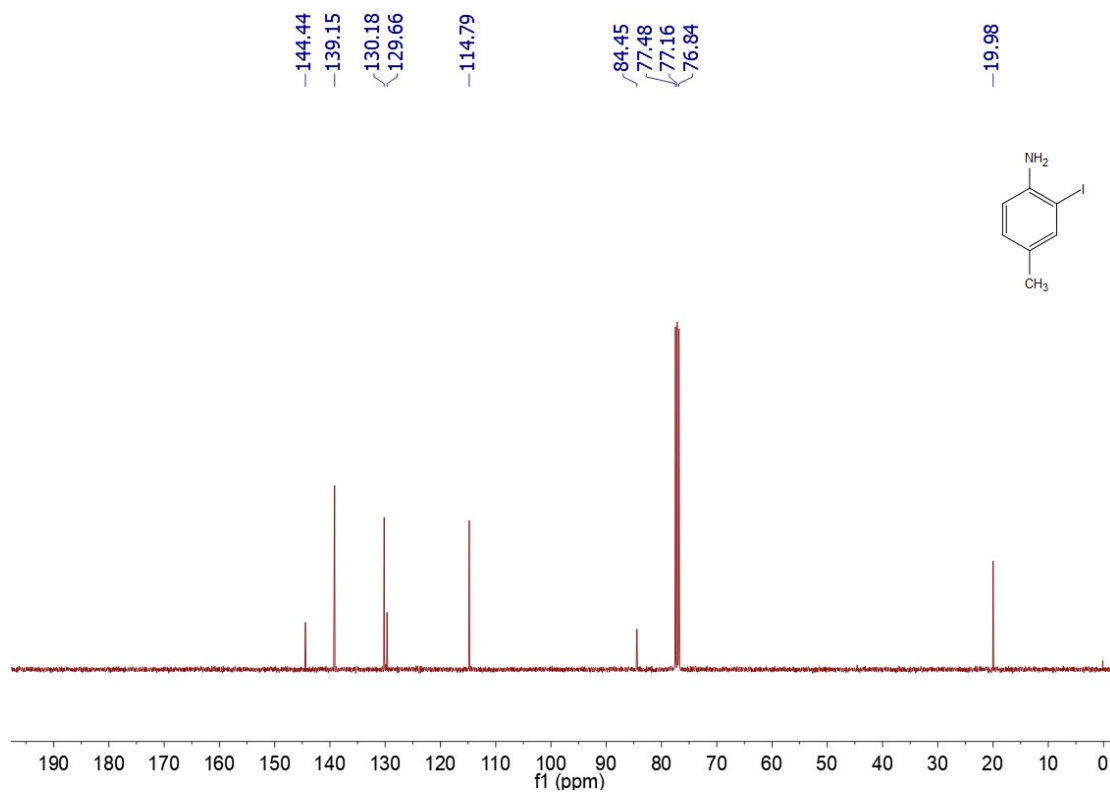
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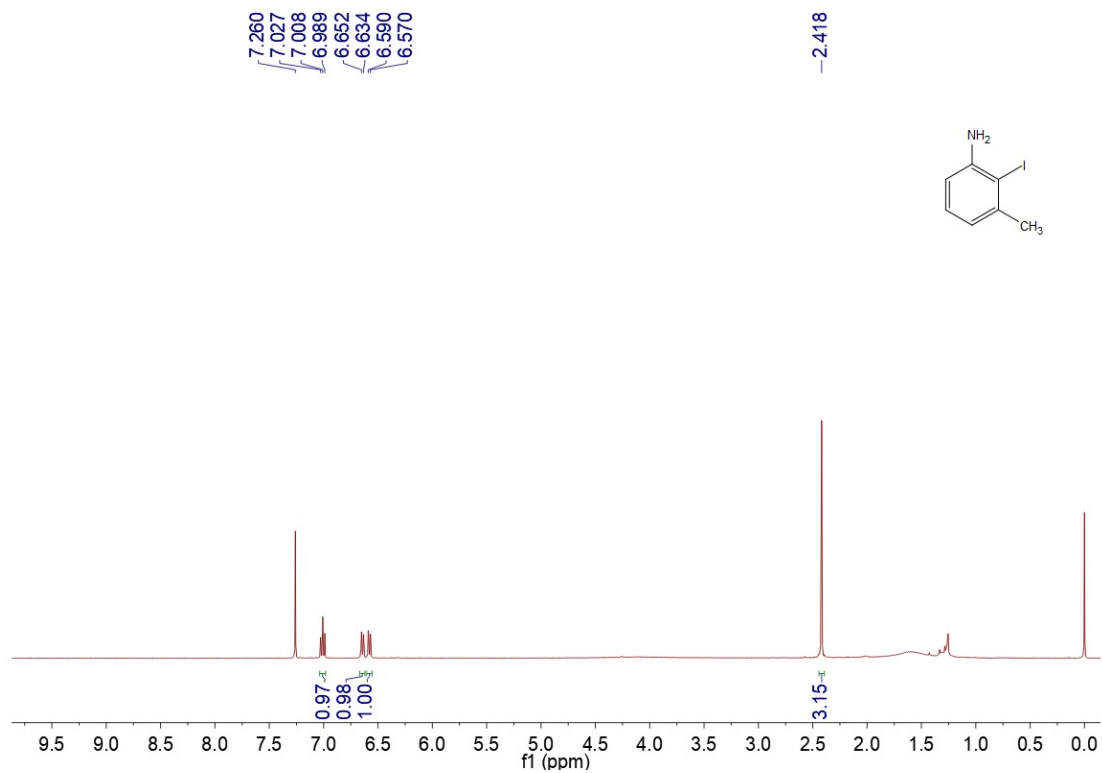
2m (^{13}C NMR, 100 MHz, CDCl_3)



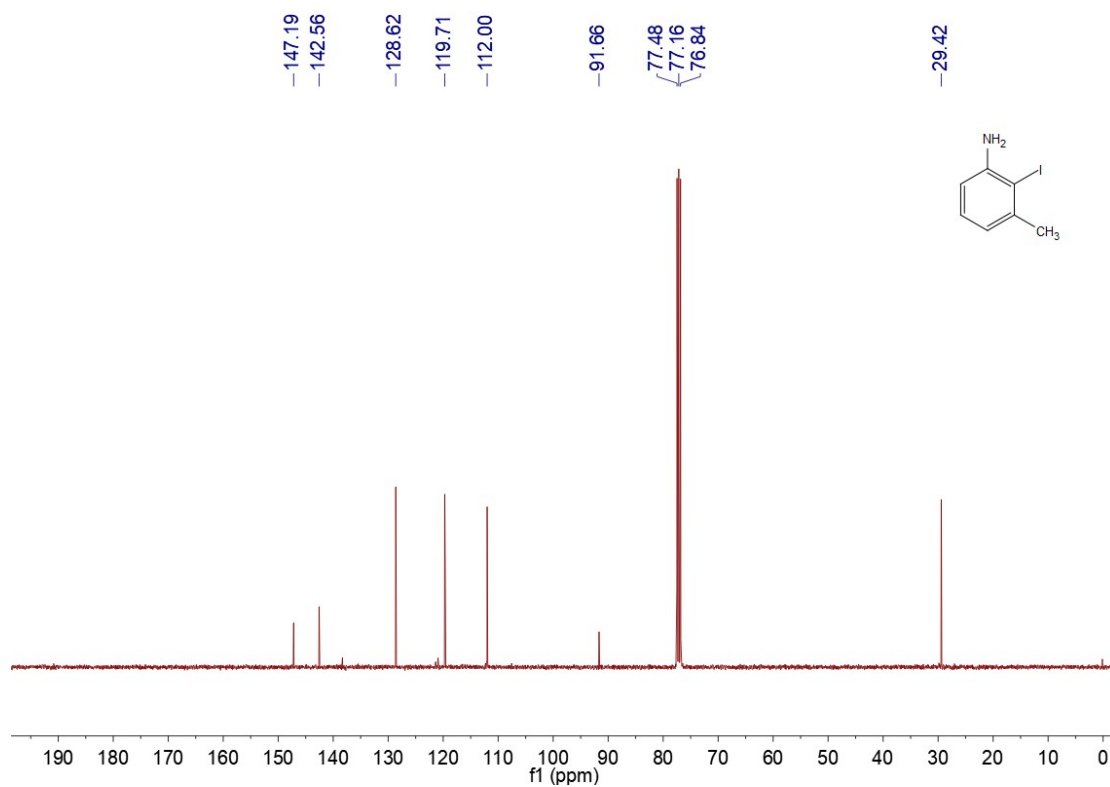
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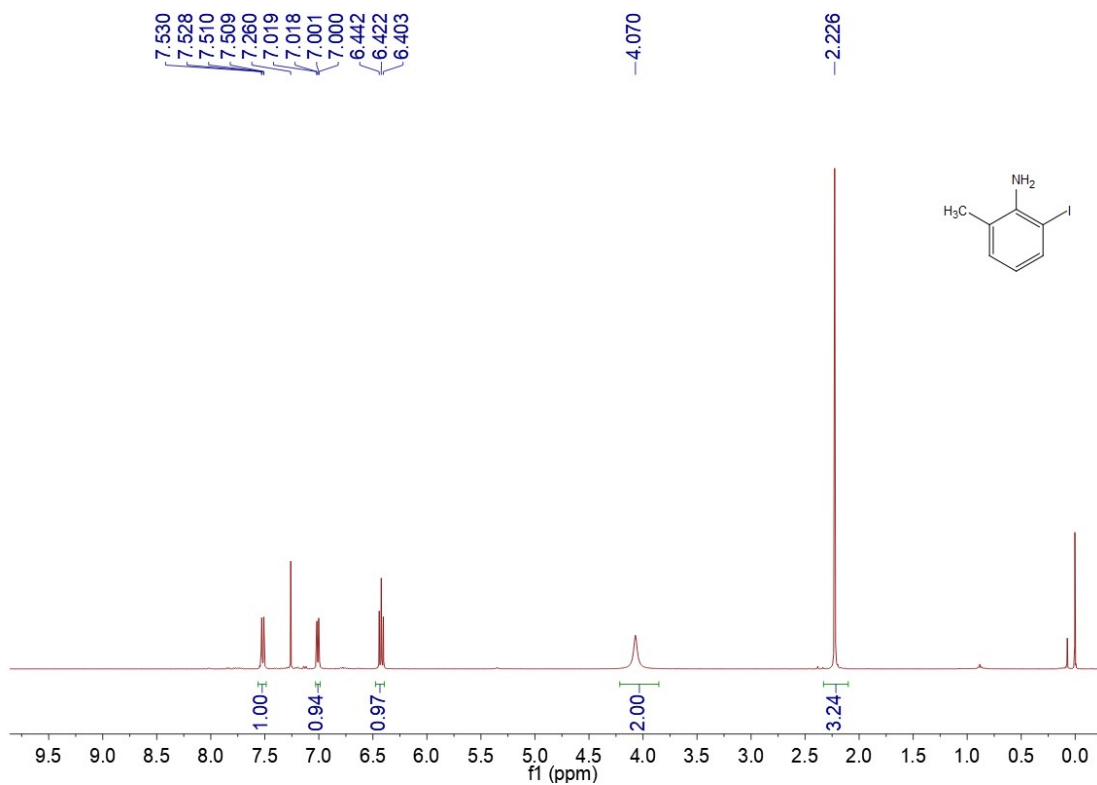
2n (^{13}C NMR, 100 MHz, CDCl_3)



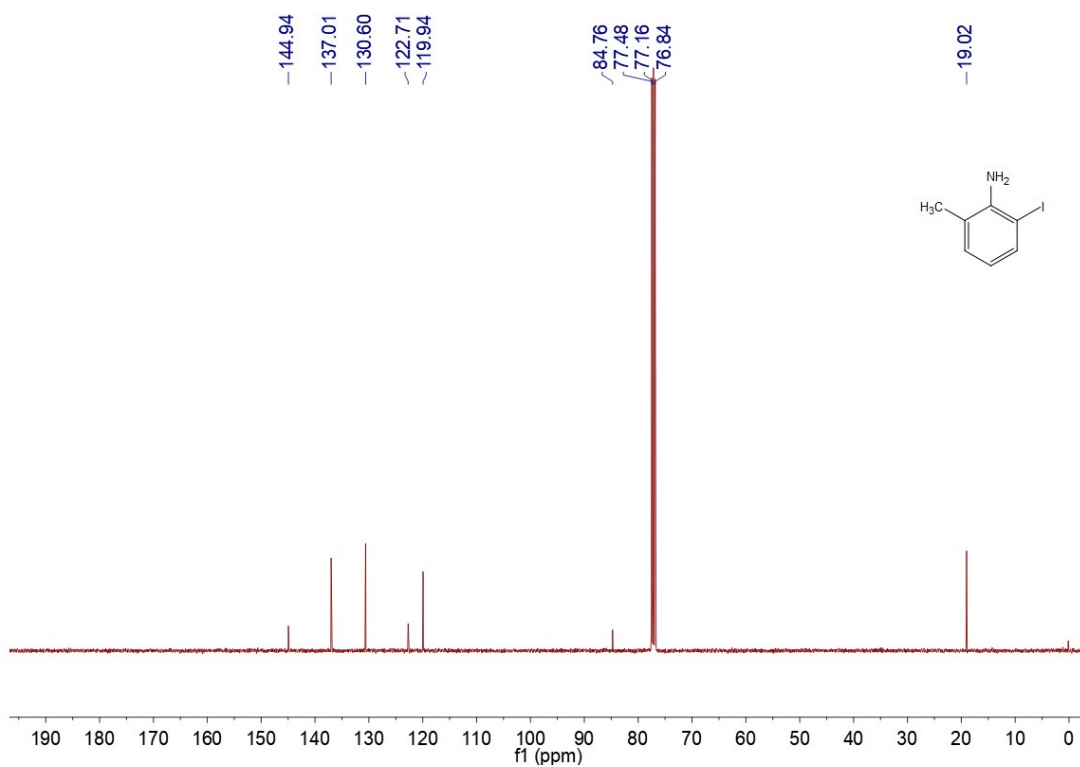
2o (¹H NMR, 400 MHz, CDCl₃)



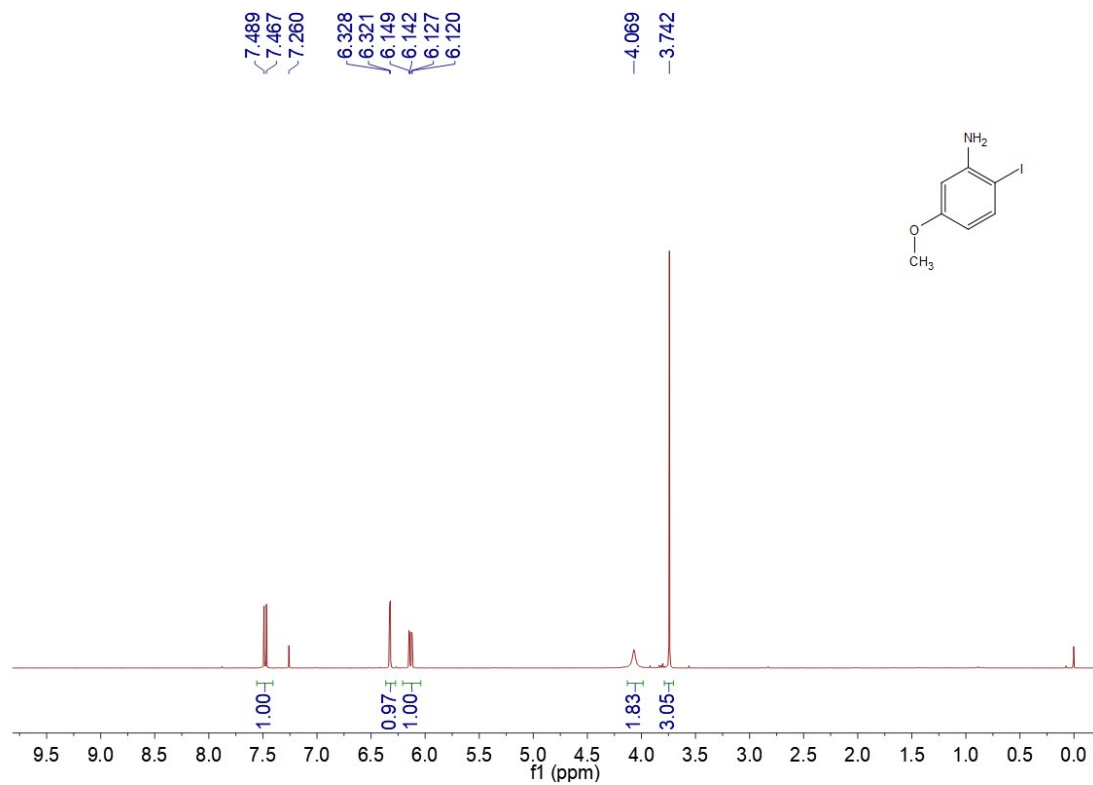
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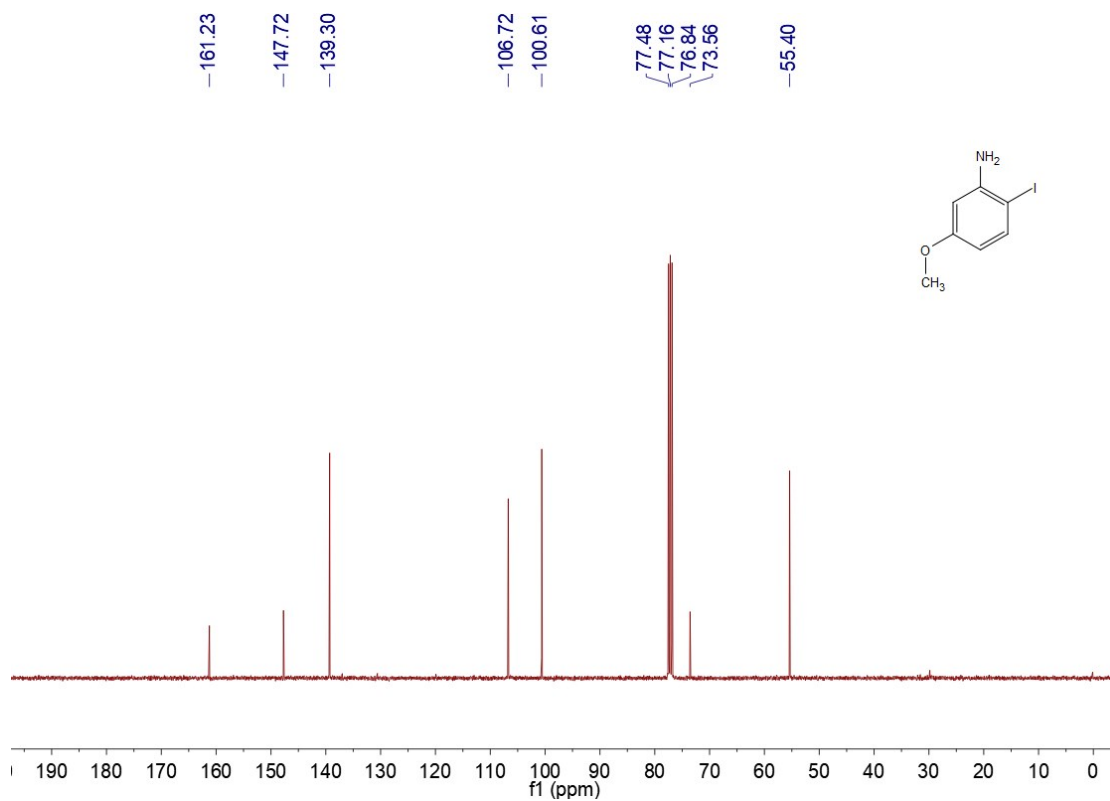
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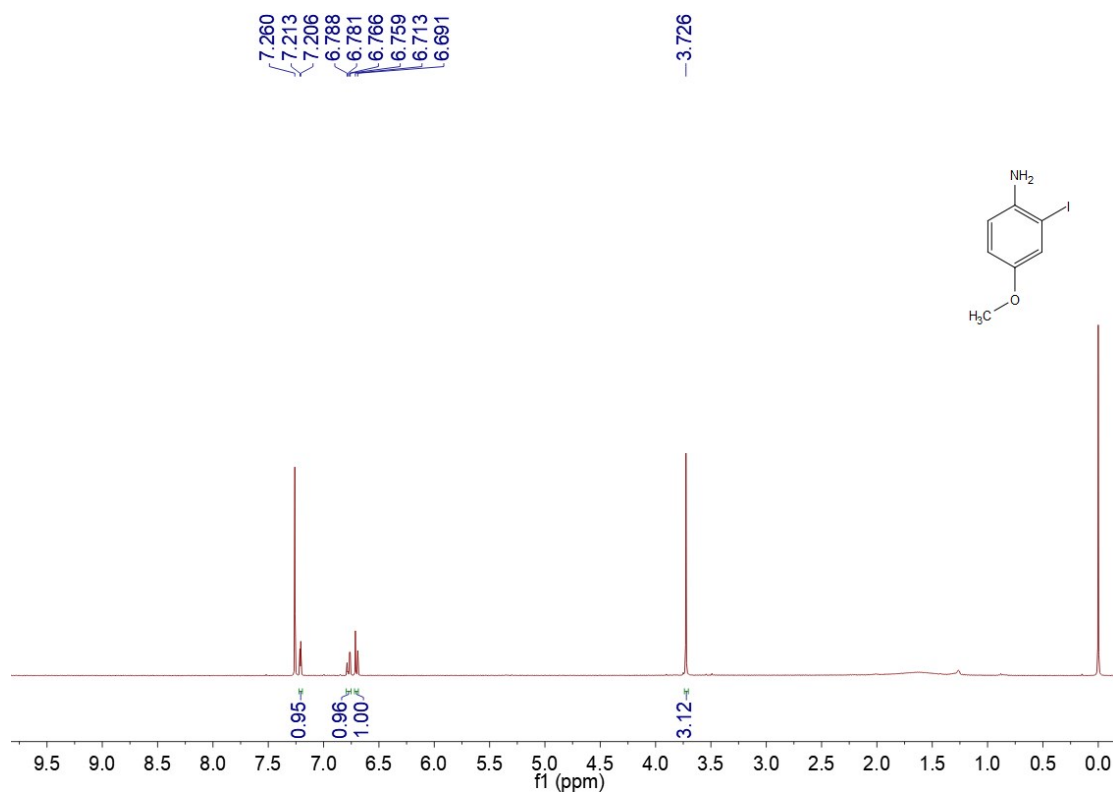
2p (^{13}C NMR, 100 MHz, CDCl_3)



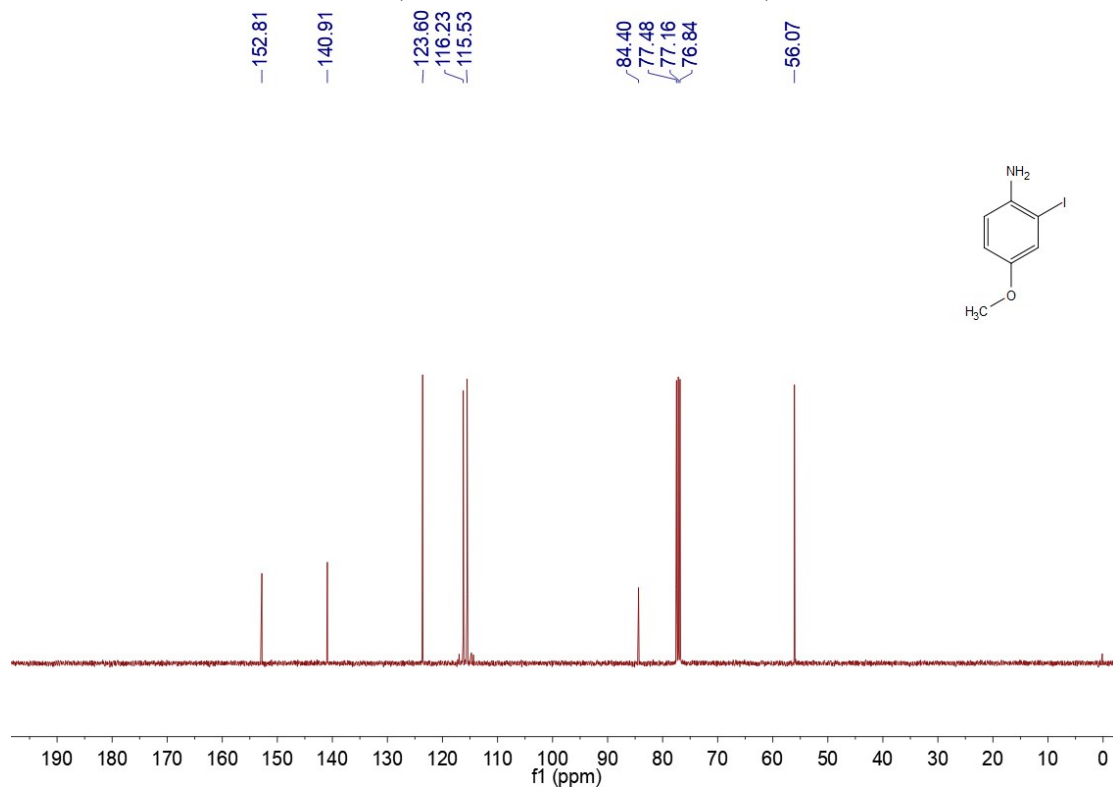
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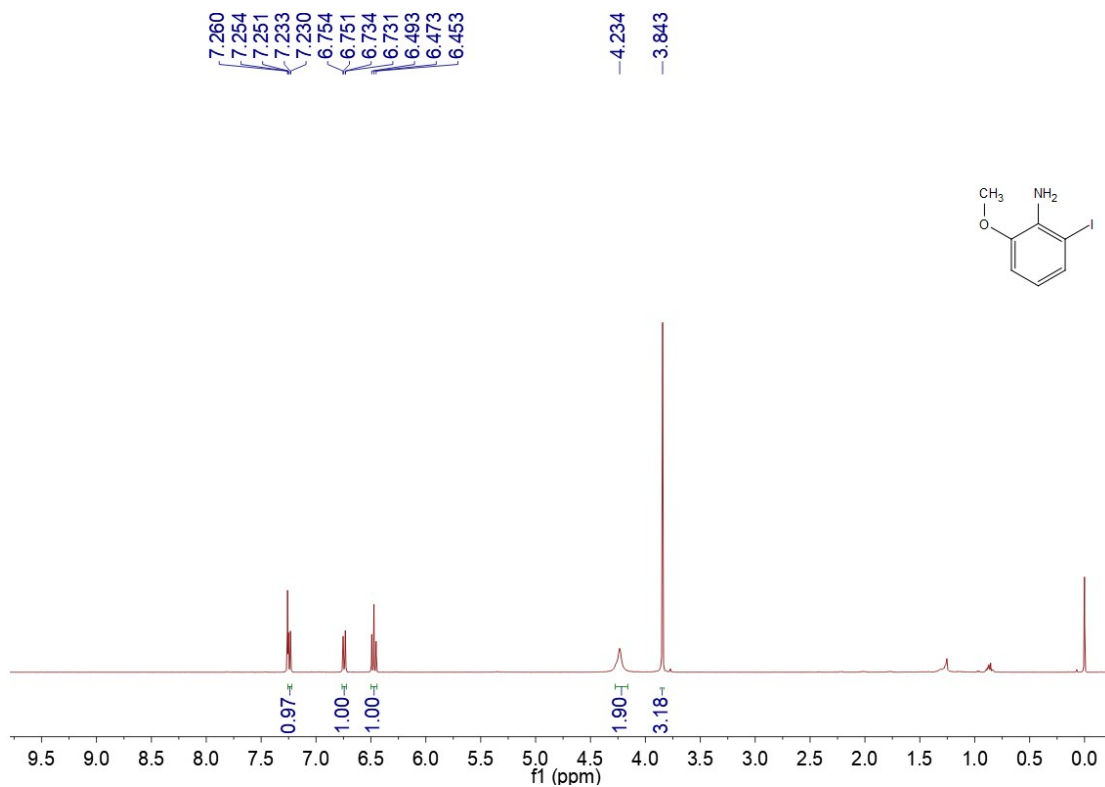
2q (^{13}C NMR, 100 MHz, CDCl_3)



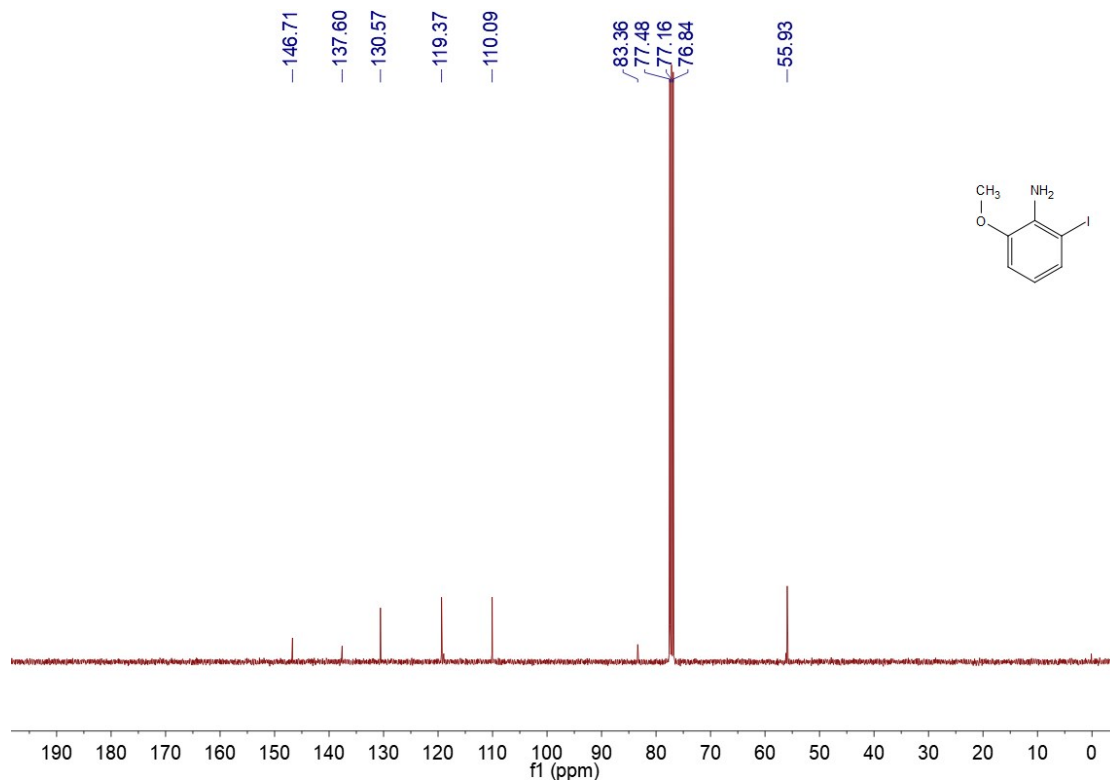
2r (^1H NMR, 400 MHz, CDCl_3)



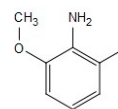
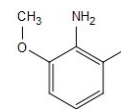
2r (^{13}C NMR, 100 MHz, CDCl_3)

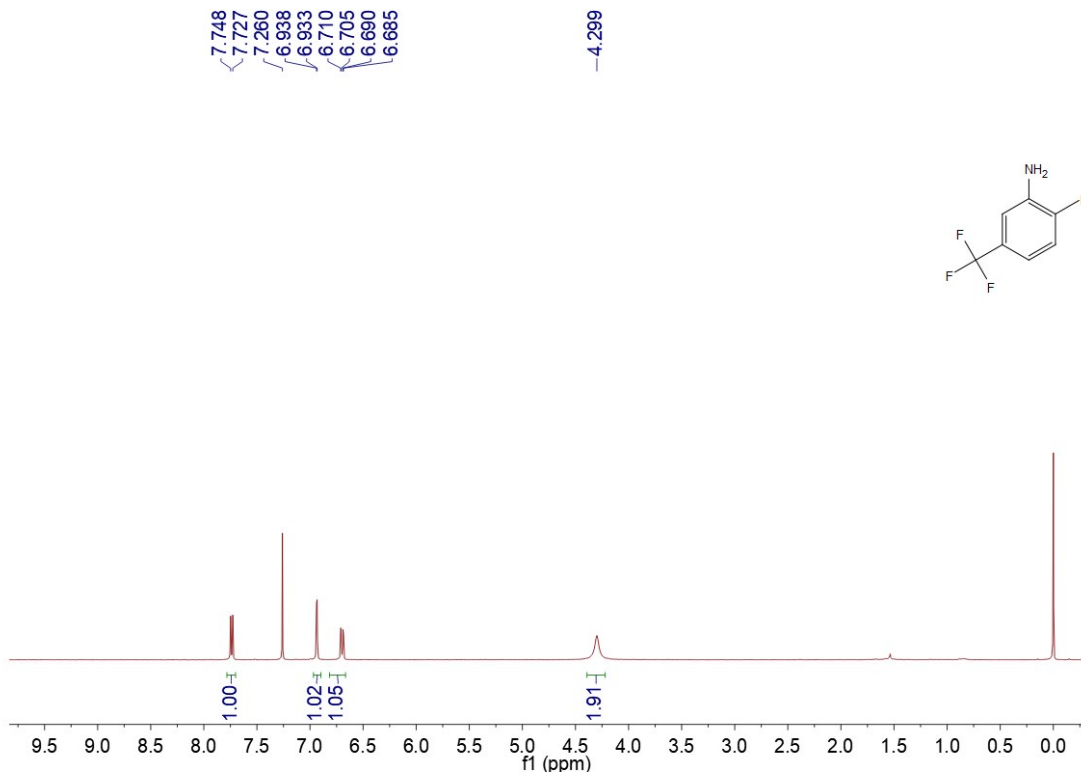


2s (^1H NMR, 400 MHz, CDCl_3)

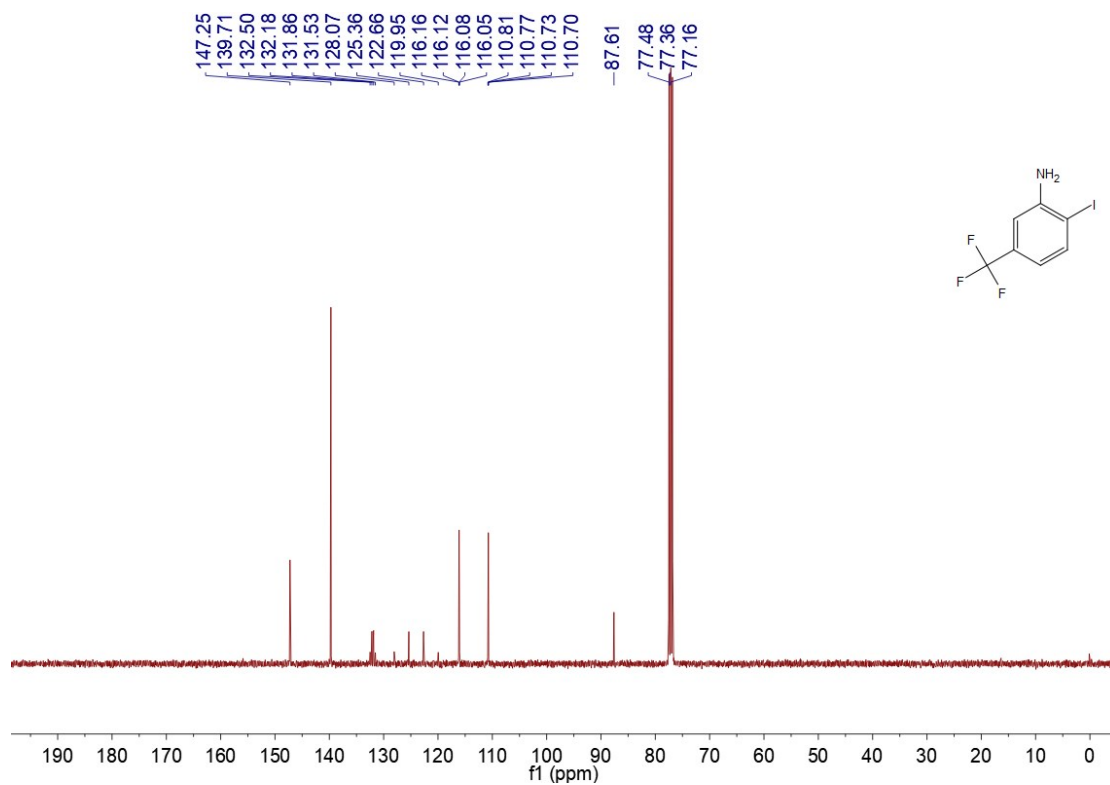


2s (^{13}C NMR, 100 MHz, CDCl_3)

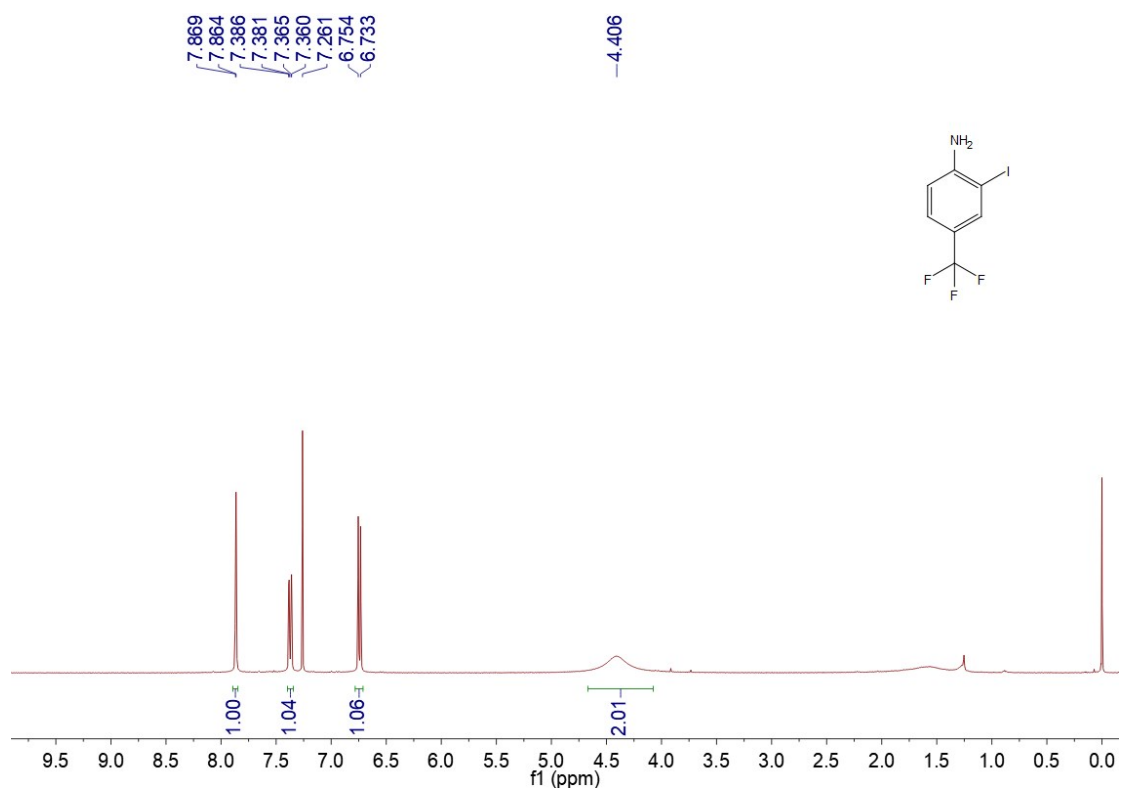
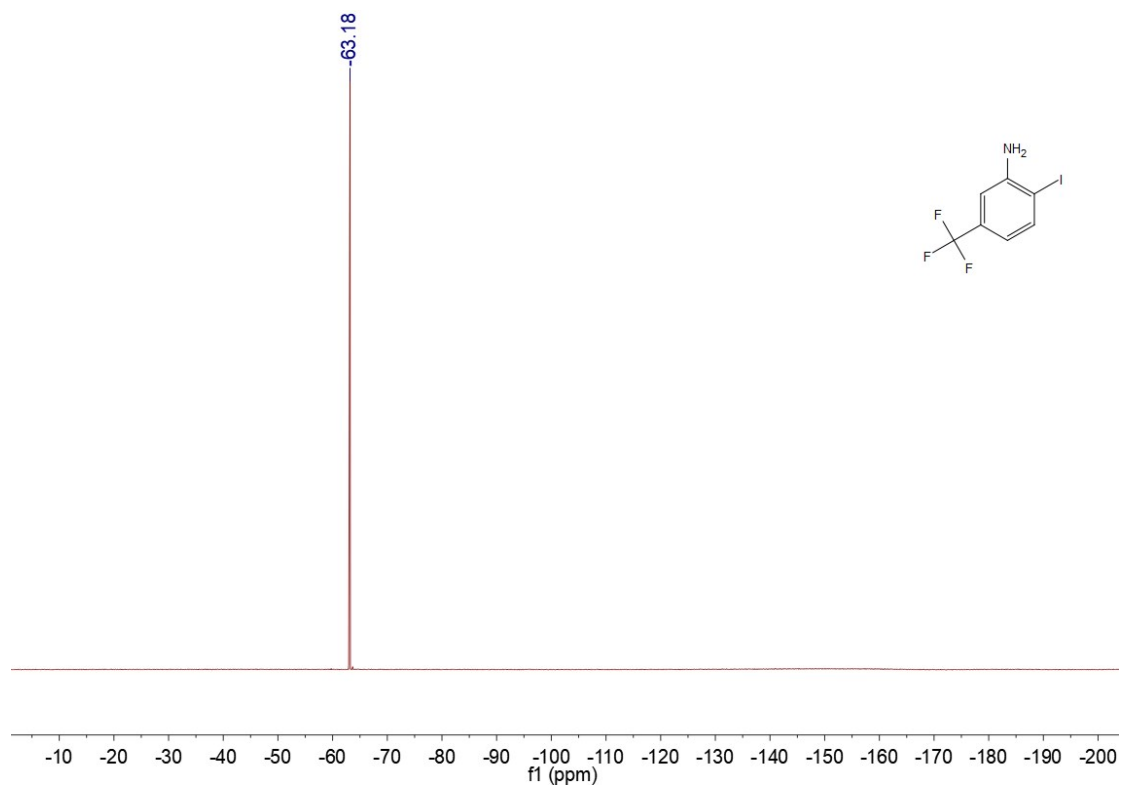


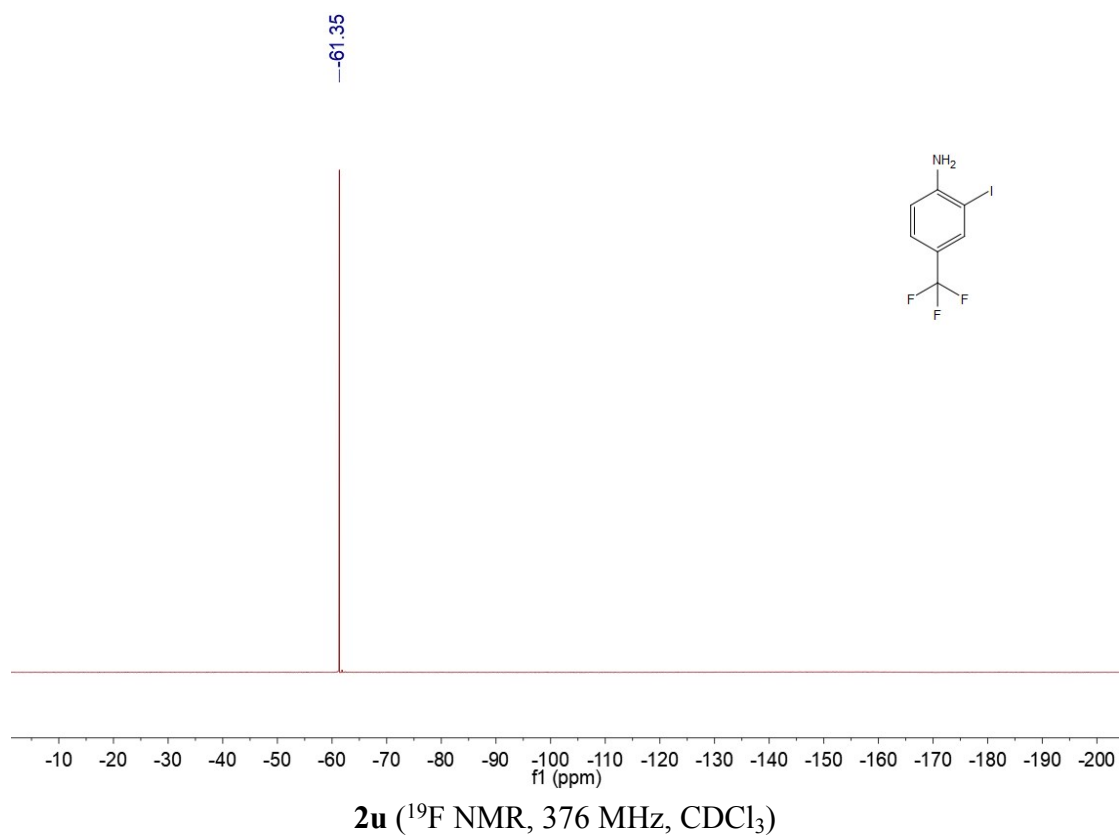
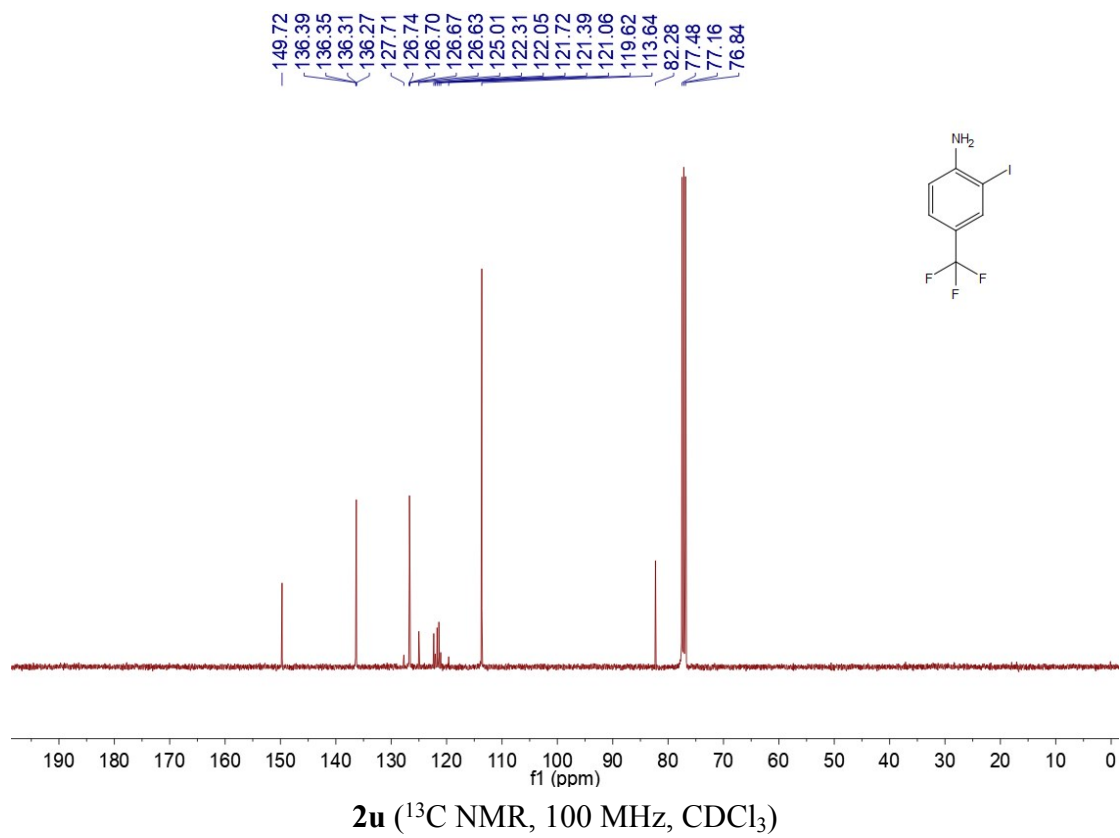


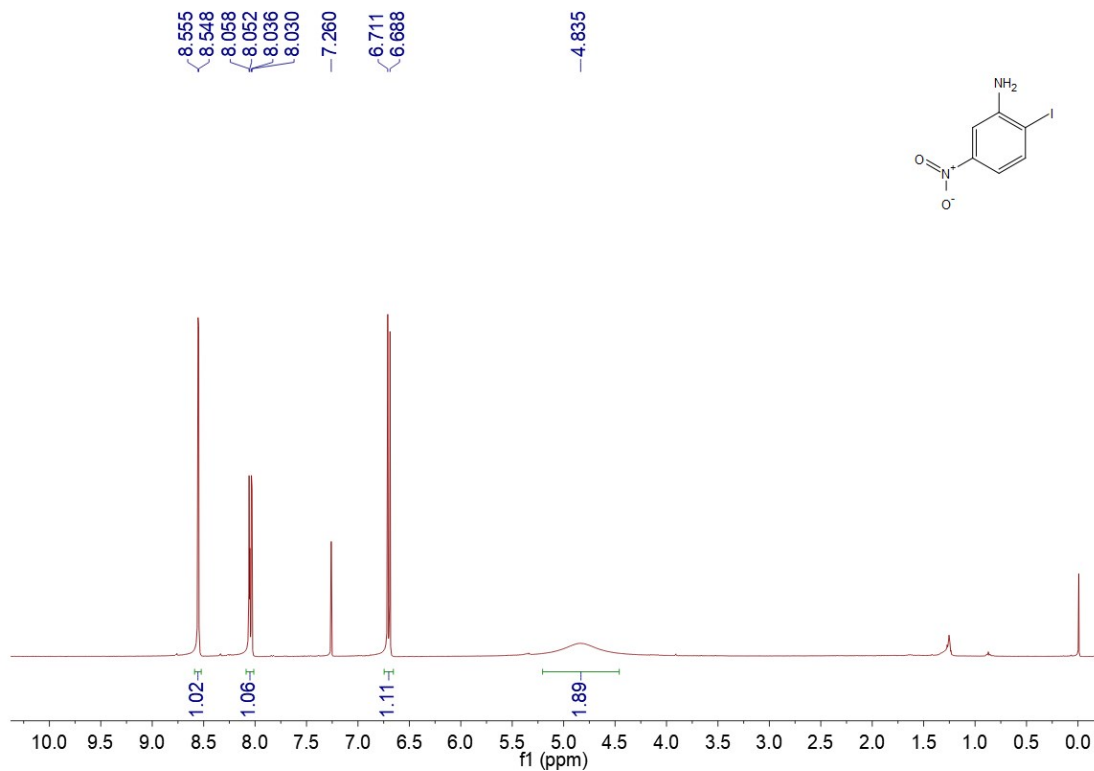
2t (^1H NMR, 400 MHz, CDCl_3)



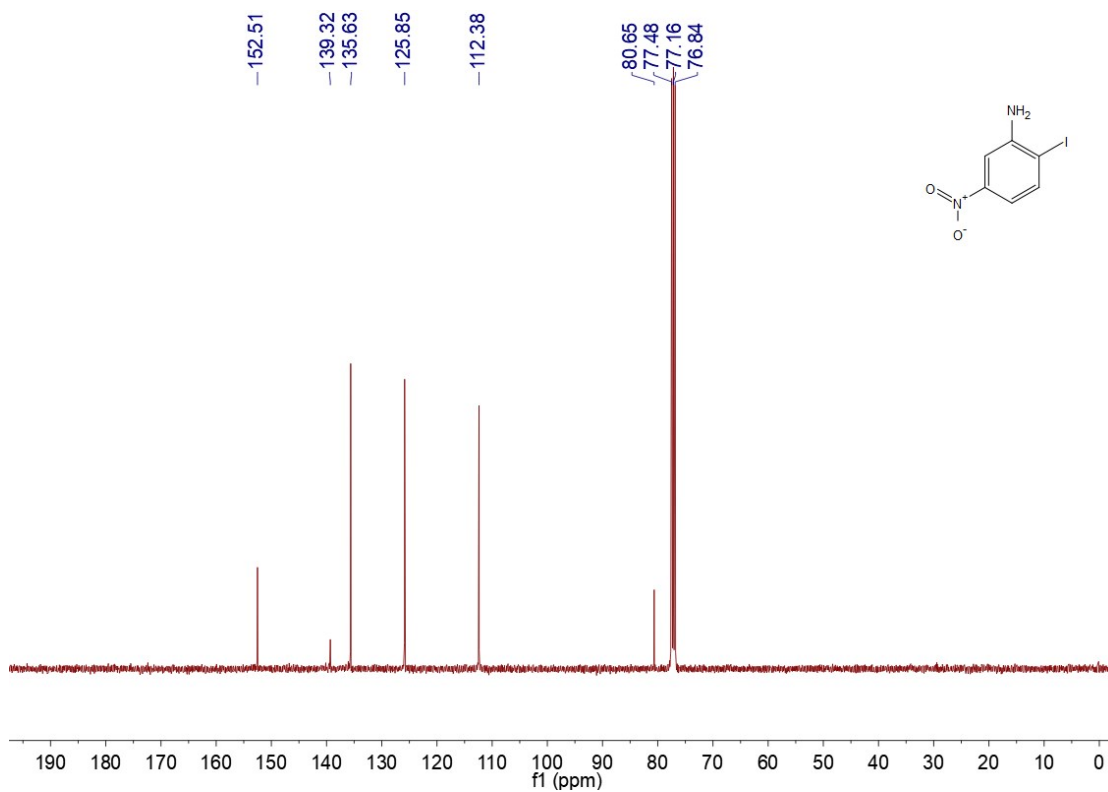
2t (^{13}C NMR, 100 MHz, CDCl_3)



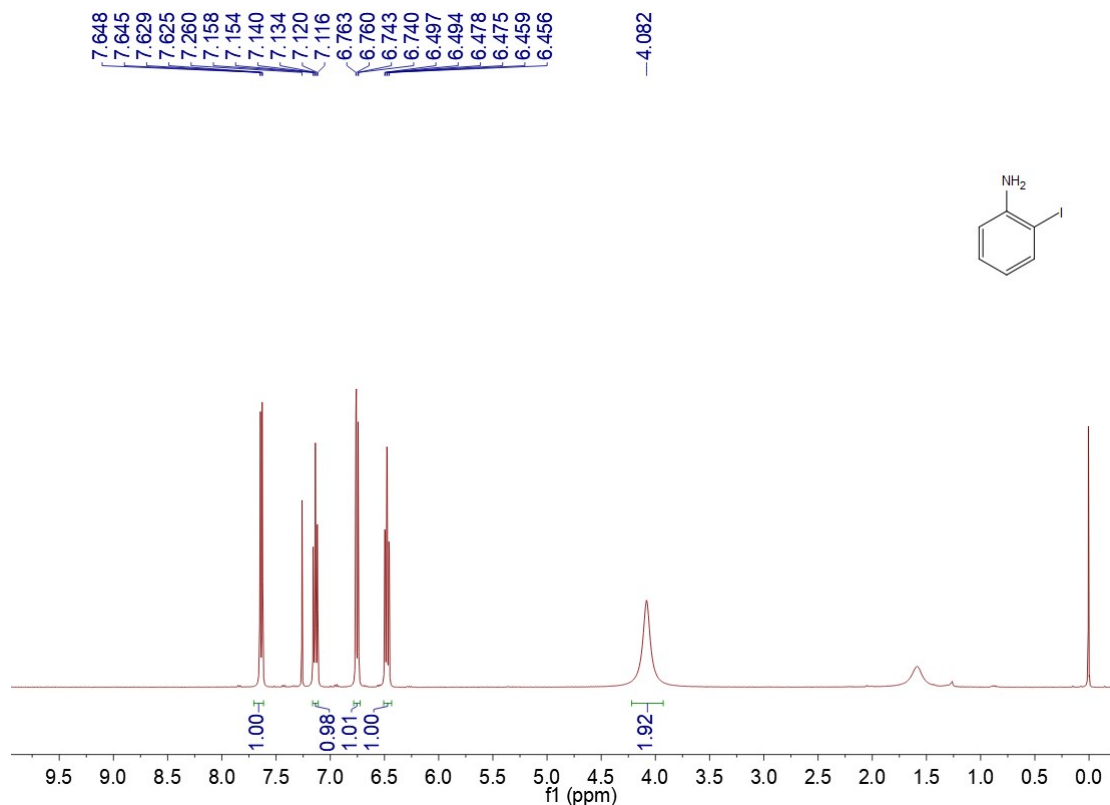




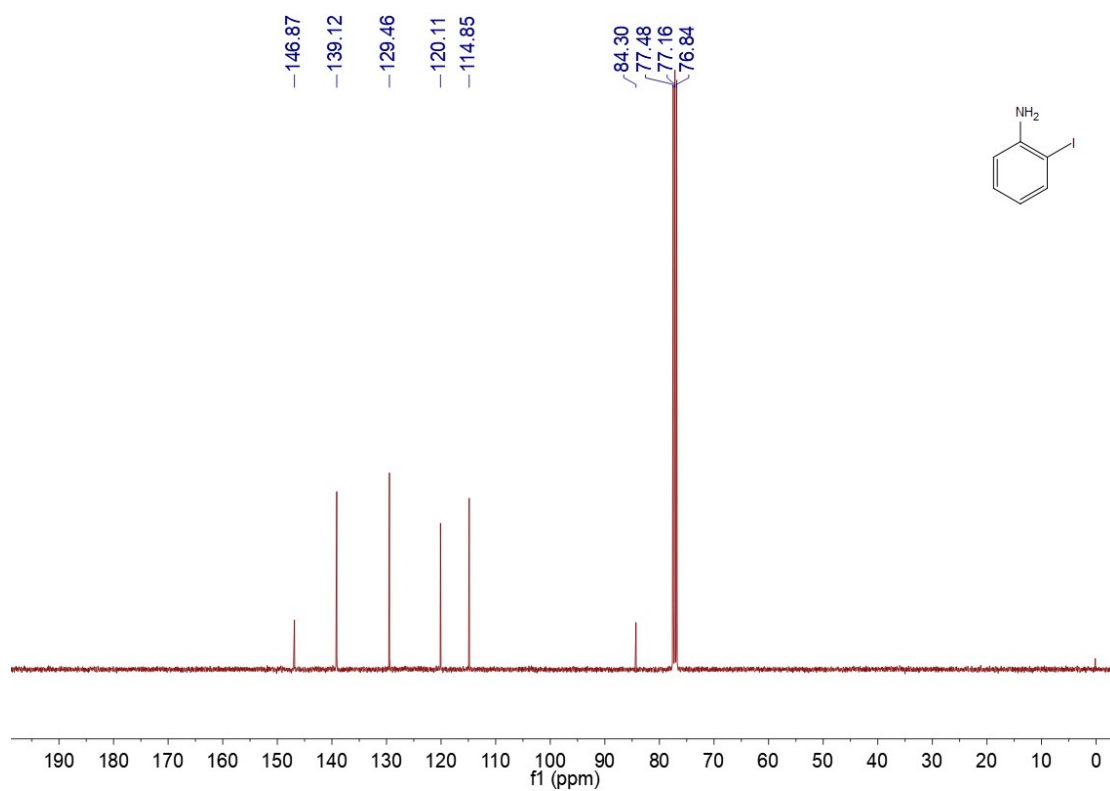
2v ($^1\text{H NMR}$, 400 MHz, CDCl_3)



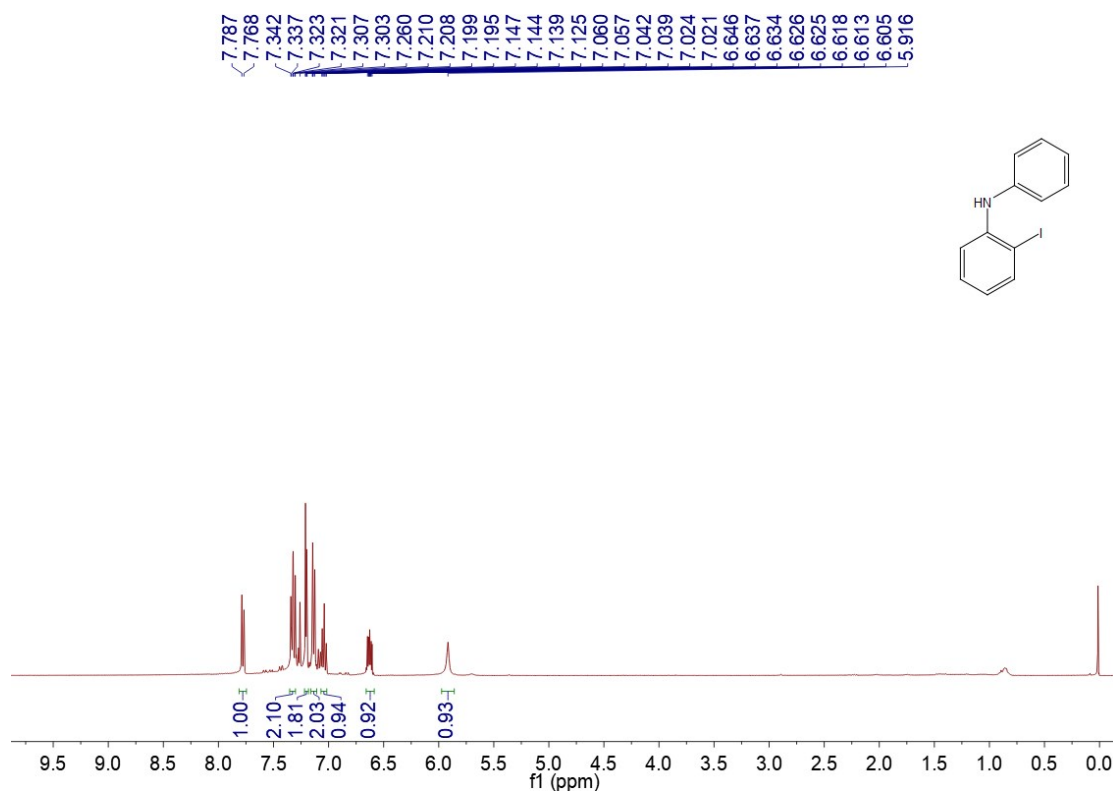
2v ($^{13}\text{C NMR}$, 100 MHz, CDCl_3)



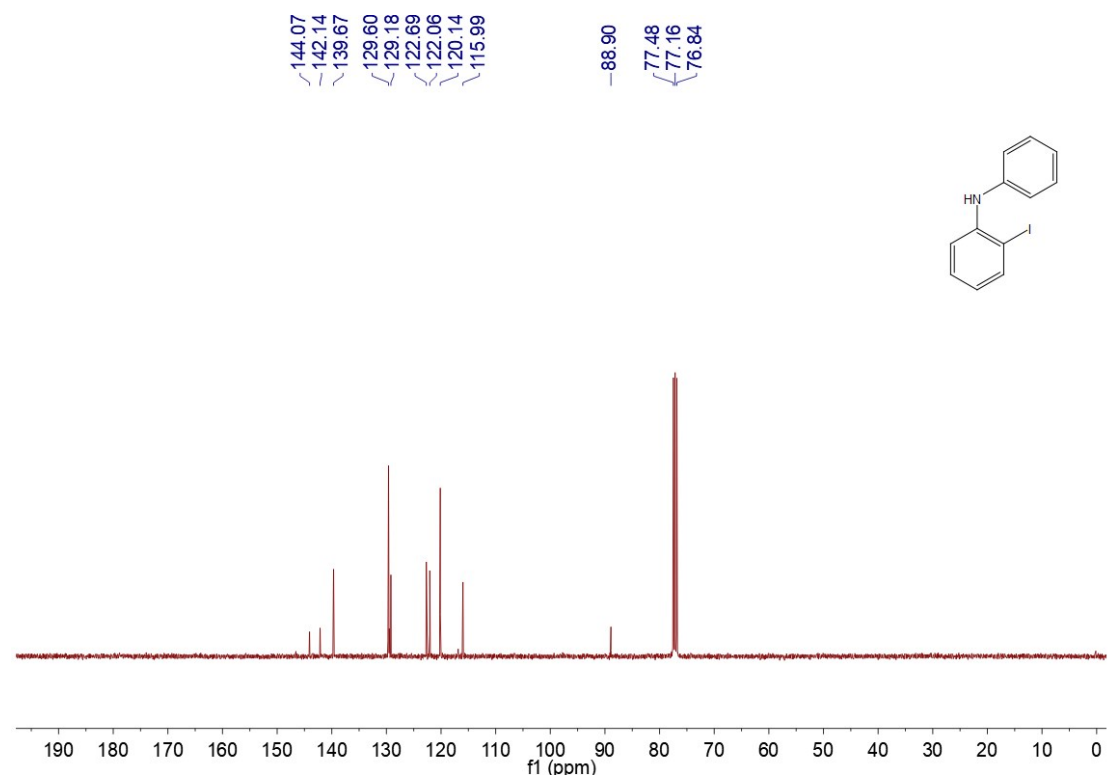
2w (^1H NMR, 400 MHz, CDCl_3)



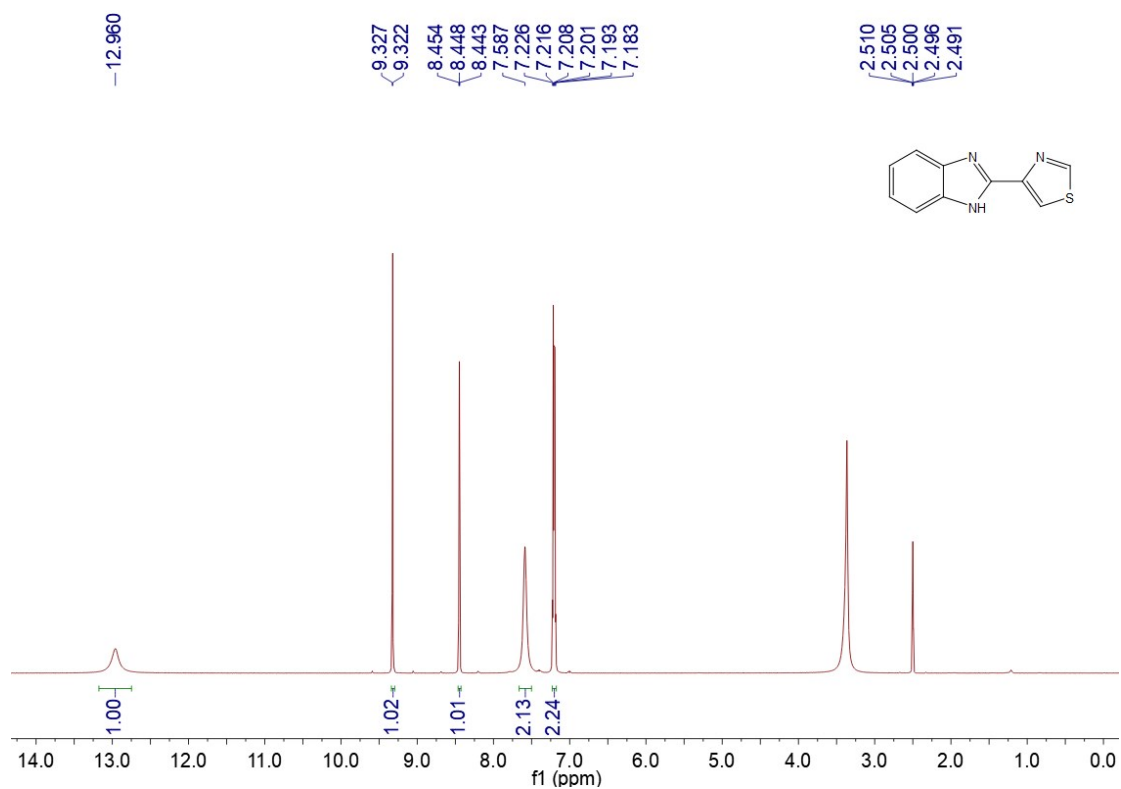
2w (^{13}C NMR, 100 MHz, CDCl_3)



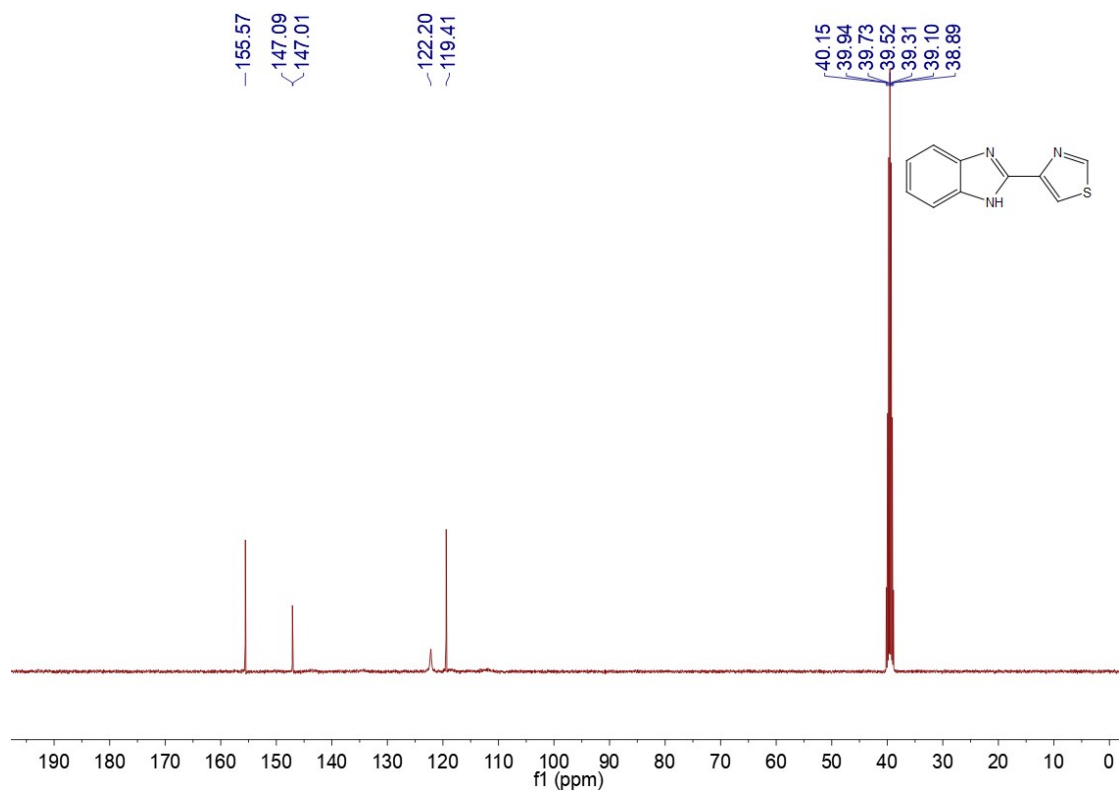
2x ($^1\text{H NMR}$, 400 MHz, CDCl_3)



2x ($^{13}\text{C NMR}$, 100 MHz, CDCl_3)



3 (^1H NMR, 400 MHz, $\text{DMSO-}d_6$)



3 (^{13}C NMR, 100 MHz, $\text{DMSO-}d_6$)