Supporting Information For:

A Novel Iodide-catalyzed Reduction of Nitroarenes and Aryl Ketones with H_3PO_2 or H_3PO_3: its Application to the Synthesis of a Potential Anticancer Agent

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General. All reactions were carried out under a positive pressure of nitrogen. Thin Layer chromatography was performed on Merck precoated silica gel F-254 plates.

All isolated products were characterized against to their purchased authentic samples where available by GC-MS or LC-MS and NMR (Bruker, 400 Hz). All of the authentic samples were purchased from Aldrich or Acros.

General procedure A for the reduction of nitroarenes in the presence of halogen substituents. A mixture of one equivalent of nitro substrate, two equivalents of sodium iodide and four equivalents of phosphorous acid or hypophosphorous acid in hydrobromic acid (48% w/w) (1.5 mL/mmole of substrate) and acetic acid (glacial) (1.5 mL/mmole of substrate) is heated to gentle reflux at 115 °C until reaction is completed. The reaction mixture is cooled to ambient temperature and neutralized with sodium hydroxide to pH 7. The product is then extracted with ethyl acetate and washed with saturated $NaHCO_3$ and brine. The solvent is then removed *in vacuo* to give the product.

General procedure B for the reduction of nitro arylketones. A mixture of substrate (10 mmol) and sodium iodide (1 to 20 mmol), phosphorous acid (H_3PO_3, 40 mmol) in hydrobromic acid (48%, 10 to 50 ml) and water (2.5 to 10 ml, hydrobromic acid : water = 4:1) is heated to 110 °C and stirred for 4 hours. After cooled to 60 °C, hypophosphorous acid (H_3PO_2, 20 mmol) is added. The reaction mixture is heated to 110 °C and stirred for another 6 hours. The reaction is cooled to ambient temperature. The reaction mixture is slowly transferred into ammonium hydroxide solution. The solid is filtrated, washed with water.

3-bromo-8-chloro-7/9-nitro-6,11-dihydro-5H-benzo[5,6]-cyclohepta[1,2-b]pyridin-11-one (Compounds **1a** and **1b**). To a solution of 3-bromo -8-chloro -6,11-dihydro-5H-benzo[5,6]-cyclohepta [1,2-b]pyridin-11-one hydrogen bromide (**3**) (84 g, 260 mmol) in concentrated sulfuric acid (98%, 355.3 g, 411 mmol) was added slowly concentrated nitric acid (70%, 25.2 ml, 603 mmol) while maintaining the temperature at about 35 °C.

After 2 hours at 35 °C, the reaction mixture is cooled to 25 °C and slowly added into water while maintaining the temperature below 40 °C. The resulting slurry is neutralized with ammonium hydroxide (25 Baume) and filtered at a temperature between 10 and 20 °C. The wet cake is washed with water and dried in a draft oven at a temperature between 50 and 60 °C to give 94 g solid (98% yield) as a mixture of **1a** and **1b** (70:30). A small analytical sample was purified by silica gel column, eluting with EtOAc and hexanes to give compound **1a** and **1b**. **1a** (9-nitro isomer): Mp: 173-175 °C. ^{1}H NMR ($CDCl_3$) δ 8.75 (d, *J* = 2.0 Hz, 1H), 8.62 (s, 1H), 7.85 (d, *J* = 2.0 Hz, 1H), 7.49 (s, 1H), 3.32-3.30 (m, 2H), 3.28-3.19 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 189.4, 151.2, 150.3, 146.4, 140.1, 138.4, 136.1, 133.3, 131.2, 128.9, 124.3, 34.0, 31.9. **1b** (7-nitro isomer): Mp: 201-203 °C. ^{1}H NMR ($CDCl_3$) δ 8.74 (d, *J* = 2.0 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 3.24-3.21 (m, 2H), 3.16-3.13 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 191.2, 151.3, 150.3, 140.1, 137.7, 137.6, 133.4, 132.9, 129.4, 129.2, 124.2, 31.3, 28.4. Anal. Calcd for $C_{14}H_8BrClN_2O_3$ (**1a** + **1b**): C, 45.91; H, 2.20; N, 7.65; Found: C, 45.55; H, 2.33; N, 7.59.

7/9-Amino-8-chloro-3-bromo-5,6-dihydro-11H-benzo[5,6]cycloheptal[1,2-b]pyridine (**2a** and **2b**): To a 1L three-neck flask equipped with a mechanical stirrer, a thermometer and a condenser were added, under nitrogen, 50.0 g (0.14 mol) compound **1**, 2.0 g of sodium iodide (13.3 mmol) , 45.0 g of phosphorous acid (H_3PO_3, 0.55 mol). To the mixture were added 250 ml of hydrobromic acid (48%) and 50 ml of water. The resulting suspension was heated to 107-110 °C and stirred at this temperature for 4 hrs. The reaction mixture was then cooled to 60 °C and 40 ml (0.30 mol) of hypophosphorous acid (H_3PO_2, 50% w/w) was added. The reaction mixture was heated to 100 to 110 °C and stirred at this temperature for 6 hours. The reaction mixture was cooled to 20 °C and was slowly transferred into a solution of 200 ml of ammonium hydroxide and 100 ml of methanol while maintaining the temperature under 30 °C. The pH was adjusted to 5.0 with ammonium hydroxide and the suspension was stirred for 1 hour at room temperature. The solid was filtered and washed with 50 ml of water. Drying the solid in a vacuum oven at 60 °C for 20 hours gave 46.9 g of compound **2** as a mixture of a pair of isomers in about 70:30 (9-:7-isomer) ratio with 94% HPLC purity and 99% yield. **2a (**9-Amino isomer): Mp: 191-192 °C. ^{1}H NMR (DMSO-D_6) δ 8.32 (d, *J* = 2.3 Hz, 1H), 7.75 (d, *J* = 2.3 Hz, 1H), 6.98 (s, 1H), 6.65 (s, 1H), 5.14 (br. s, 2H), 4.08 (s, 2H), 3.03-3.00 (m, 2H), 2.97-2.90 (m, 2H). ^{13}C NMR (DMSO-D_6) δ 156.1, 146.3, 142.6, 139.7, 136.5, 136.4, 129.2, 127.2, 117.9, 115.8, 115.2, 42.0, 30.9, 29.2. Anal. Calcd for $C_{14}H_{12}BrClN_2$: C, 51.96; H, 3.74; N, 8.65; Found: C, 51.96; H, 3.76; N, 8.44. **2b** (7-Amino isomer): Mp: 188-189 °C. ^{1}H NMR (DMSO-d_6) δ 8.33 (d, *J* = 2.3 Hz, 1H), 7.86 (d, *J* = 2.3 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.46 (d, *J* = 8.1Hz, 1H), 5.06 (br. s, 2H), 4.16 (s, 2H), 3.12-3.11 (m, 2H), 2.88-2.85 (m, 2H). ^{13}C NMR (DMSO-D_6) δ 157.4, 146.9, 142.5, 139.0, 137.0, 135.9, 126.6, 123.3, 118.9, 118.4, 116.7, 42.4, 29.0, 26.3. Anal. Calcd for $C_{14}H_{12}BrClN_2$: C, 51.96; H, 3.74; N, 8.65; Found: C, 51.85; H, 3.70; N, 8.42.

Preparation of 4a and 4b: To a suspension of 30.0 g of compound **2** (as a mixture of **2a** and **2b**) from above in 90 mL of methanol and 30 mL of acetic acid was added 15 mL of a solution of hydrobromic acid (48%) while maintaining the temperature between 10 to 20 °C. 4.5 mL of bromine (87.1 mmol) was added to the solution portion wise at a

temperature between 15 to 20 °C. The reaction mixture was stirred at ambient temperature for 1h and was then poured into a solution of 6.0 g of sodium thiosulfate pentahydrate in 150 mL of water and 60 mL of ammonium hydroxide at a temperature between 10 and 20 °C. The resulting suspension was heated to 40 °C and the mixture was stirred for 1h while the temperature was allowed to warm to 20 °C. The precipitate was filtered, washed with 30 mL of water and dried in a vacuum oven at 60 °C to give 33.3 g of compound IV (as a mixture of isomers **4a** and **4b**) with a HPLC purity of 94% and 89.0% yield). Major product (9-amino-isomer, **4a**): Mp: 183-185 °C. ^{1}H NMR ($CDCl_3$): δ 8.39 (d, *J* = 2.1 Hz, 1 H), 7.47 (d, *J* = 2.1 Hz, 1 H), 7.09 (s, 1 H), 4.50 (s, 2 H), 4.49 (bs, 2 H), 3.10-3.05 (m, 4 H). ^{13}C NMR ($CDCl_3$): 153.8, 147.6, 140.9, 140.0, 137.3, 135.3, 130.4, 127.8, 118.8, 117.2, 111.6, 41.7, 32.4, 30.9. Anal. Calcd for $C_{14}H_{11}Br_2ClN_2$: C, 41.78; H, 2.75; N, 6.96; Found: C, 41.83; H, 2.65; N, 6.88. Minor product (7-amino-isomer, **4b**): Mp: 187-189 °C. ^{1}H NMR ($CDCl_3$): δ 8.40 (d, *J* = 1.8 Hz, 1 H), 7.51 (d, *J* = 1.8 Hz, 1 H), 7.39 (s, 1 H), 4.53 (s, 2 H), 4.07 (bs, 2 H), 3.14-3.10 (m, 2 H). 3.05-3.01 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 154.9, 147.8, 139.8, 139.7, 135.9, 135.1, 130.5, 125.3, 119.1, 118.8, 112.1, 40.8, 30.0, 26.4. Anal. Calcd for $C_{14}H_{11}Br_2ClN_2$: C, 41.78; H, 2.75; N, 6.96; Found: C, 41.91; H, 2.64; N, 6.84.

One-pot procedure to compound 4a and 4b from 1: A mixture of compound **1** (as a mixture of isomers **1a** and **1b**) (10g, 27.2 mmol), phosphorous acid, H_3PO_3, (9 g, 109.8 mmol), sodium iodide (0.4g, 2.7mmol), hydrobromic acid (48%) (50 mL) and water (10 mL) was heated with agitation at 105 °C for 6 hours and cooled to about 100 °C. Hypophosphorous acid, H_3PO_2, (50%) (8 mL, 60.6 mmol) was added to the solution, which was then heated at 110 °C for about 6hrs until the reaction is judged complete by HPLC. The solution was cooled to about 90 °C and acetic acid (20 mL) and ethanol (50 mL) were added and the solution continued to cool to 15 °C. Bromine (3.3 mL, 63.9 mmol) was dropped into the mixture at a temperature between 15 to 20 °C and the mixture was stirred for another one hour. Ammonium hydroxide (25%) (60 mL) was slowly added to the mixture at a rate to keep the temperature below 50 °C. After the ammonium hydroxide was added, the mixture was held at 50 °C for one hour. After cooled to 25 °C, the mixture was filtered. The solid was collected and slurried with water (150 mL) at 50 °C and collected again by filtration. The yield of **IV** is 10.3 g (93% yield). The analytical data is identical to the sample prepared from the two-pot procedure described above.

Preparation of 5 from 4. To a vigorously stirred suspension of 100.0 g mixture (94.0% purity, 0.231 mol) of compound **4** as a mixture of isomers **4a** and **4b** from above in 200 mL of water at between 5 and 10 °C under sweeping nitrogen was added 300 mL of 98% sulfuric acid solution while allowing the internal temperature to rise to between 60 and 65 °C. The resulting brown thick solution was cooled to between 5 and 10 °C. Hypophosphorous acid (400 mL, 50% H_3PO_2 in water, 3.85 mol) was added followed by a solution of sodium nitrite (20.3 g, 0.286 mol) in 100 mL of water while maintaining the temperature between 10 and 20 °C. After addition of sodium nitrite, 1.25 mL of Antifoam B silicone emulsion (J. T. Baker) was added. The reaction mixture was warmed to between 20 and 25 °C, held for 2 hours, further heated to between 40 and 45 °C over a period of 2 hours and held for 4 hours. Upon the reaction completion, the

resulting slurry was cooled to between –5 and 5 °C, held for 6 hrs and filtered. The cake was washed with 200 mL of 30% aqueous sulfuric acid solution and dissolved into 1.5 L of a deoxygenated methanol solution containing 1% water, 1% sulfuric acid and 1.3% hypophosphorous acid between 50 and 60 °C. To the resulting brown solution was added 10 g of activated carbon (Nuchar SN). After 30 minutes, the mixture was filtered through a half-inch pad of Celite between 50 and 60 °C. The filtrate was heated to between 50 and 60 °C and slowly neutralized with 300 mL of a 2:1 solution of triethylamine (1.42 mole) and methanol until the solution pH value higher than 9 (on a water wet pH paper). The resulting slurry was cooled to between 0 and 5 °C in a period of 1 hour, held for 2 hours and filtered. The cake was washed with methanol, dried at 60 and 65 °C under vacuum to give 73 g of compound **5**, 8-chloro-3,10-dibromo-5,6-dihydro-11H-benzo[5,6]cycloheptal[1,2-b]pyridine, as a light yellow solid in 82% yield. Mp 163-164 ^{o} C. ^{1}H NMR ($CDCl_3$): δ 8.40 (d, *J* = 2.1 Hz, 1H), 7.48 (d, *J* = 2.1 Hz, 1H), 7.46 (d, *J* = 2.1 Hz, 1H), 7.15 (d, *J* = 2.1 Hz, 1H), 4.55 (s, 2H), 3.22-3.17 (m, 2H), 3.13-3.08 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 153.5, 147.8, 143.1, 140.1, 136.5, 134.9, 133.1, 130.8, 127.9, 124.6, 118.9, 40.7, 31.8, 31.7. Anal. Calcd for $C_{14}H_{10}Br_2ClN$: C, 43.38; H, 2.58; N, 3.62; Br, 41.31; Cl, 9.17; Found: C, 43.33; H, 2.66; N, 3.69; Br, 41.06; Cl, 9.11.

2-Chloroaniline (9)

General procedure A was followed in the synthesis of this compound. A mixture of 0.957 g (6.1 mmol) of 2-chloroaniline, 1.801 g (12.0 mmol) of sodium iodide, and 2.6 mL (12.0 mmol) of hypophosphorous acid (50% w/w) in 7 mL of hydrobromic acid (48%) and 7.0 mL of acetic acid (glacial) was heated to a gentle reflux at 115 °C for 8 hrs. After workup, the solvent was removed under vacuum to give 0.697 g product as a brown oil (90% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.09 (td, *J* = 7.5, 1.6 Hz, 1H), 6.78 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.70 (td, *J* = 7.5, 1.6 Hz, 1H), 4.06 (br. s, 2H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 143.0, 129.5, 127.7, 119.2, 116.0. GC-MS *m*/*z* (relative intensity) 127 (M^+, 100), 95 (M^+-Cl, 29).

Aniline (11) from 1-bromo-2-nitrobenzene

A mixture of 1.21 g (6.0 mmol) of 1-bromo-2-nitrobenzene, 0.089 g (0.6 mmol) of sodium iodide, and 2.4 mL (22.0 mmol) of hypophosphorous acid (50% w/w) in 9.0 mL of hydrobromic acid (48%) was heated to a gentle reflux at 115 °C for 2 hrs. After workup, the solvent was removed to give 0.535 g the product as a dark red/brown oil. (96% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.19 (dt, *J* = 7.4, 0.9 Hz, 2H), 6.80 (td, *J* = 7.4, 0.9 Hz, 1H), 6.71 (dd, *J* = 7.4, 0.9 Hz, 2H), 3.69 (brs, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ 146.4, 129.3, 118.6, 115.2. GC-MS *m*/*z* (relative intensity) 93 (M^+, 100).

Aniline (11) from 1-bromo-4-nitrobenzene

General procedure A was followed in the synthesis of this compound. A mixture of 3.06 g (15.1 mmol) of 1-bromo-4-nitrobenzene, 4.50 g (30.0 mmol) of sodium iodide, and 6.6 mL (60.3 mmol) of hypophosphorous acid (50% w/w) in 23 mL of hydrobromic acid (48%) and 24 mL of acetic acid (glacial) was heated to a gentle reflux at 115 °C for 10 hours. After workup, the solvent was removed under vacuum to give 1.16 g of product as a brown oil. (84% yield). The ^{1}H and ^{13}C NMR spectra of the product were identical to that of both aniline produced above as well as the purchased standard.

Aniline (11) from 1-iodo-2-nitrobenzene
General procedure A was followed in the synthesis of this compound. A mixture of 1.51 g (6.0 mmol) of 1-iodo-2-nitrobenzene, 1.807g (12.1 mmol) of sodium iodide, and 2.6 mL (24.0 mmol) of hypophosphorous acid (50% w/w) in 7.0 mL of hydrobromic acid (48%) and 7.0 mL of acetic acid (glacial) was heated to gentle reflux at 115 °C for 8 hours. After workup, the solvent was removed under vacuum to give 0.52 g of product as a brown oil. (92% yield). The ^{1}H and ^{13}C NMR spectra of the product were identical to that of both aniline produced from 1-bromo-2-nitrobenzene as well as the purchased standard.

2,6-Diamino-toluene (15)
General procedure A was followed in the synthesis of this compound. A mixture of 3.32 g (18.2 mmol) of 2,6-dinitrotoulene, 5.41 g (36.1 mmol) of sodium iodide, and 7.8 mL (71.3 mmol) of hypophosphorous acid (50% w/w) in 27 mL of hydrobromic acid (48%) and 27 mL of acetic acid (glacial) was heated to a gentle reflux at 115 °C for 8 hours. After workup, the solvent was removed under vacuum to give 1.86 g of product as a amber oil. (84% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.84 (t, *J* = 8.0 Hz, 1H), 6.20 (d, *J* = 8.0 Hz, 2H), 3.56 (bs, 4H), 1.98 (s, 3H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ 145.3, 126.9, 107.4, 106.8, 10.3. GC-MS *m*/*z* (relative intensity) 122 (M^+, 100).

1-Amino-naphthalene (17)
General procedure A was followed in the synthesis of this compound. A mixture of 3.34 g (19.3 mmol) 1-nitronaphthalene, 5.74 g (38.3 mmol) of sodium iodide, and 8.4 mL (76.2 mmol) of hypophosphorous acid (50% w/w) in 28 mL of hydrobromic acid (48%) and 28 mL of acetic acid (glacial) was heated to a gentle reflux at 115 °C for 8 hours. After workup, the solvent was removed under vacuum to give 2.70 g of product as a dark purple solid. (98% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84-7.80 (m, 2H), 7.48-7.44 (m, 2H), 7.34-7.21 (m, 2H), 6.80 (dd, *J* = 6.8, 1.7 Hz, 1H), 4.13 (bs, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ 142.2, 134.6, 128.7, 126.5, 125.9, 125.0, 123.8, 120.9, 119.1, 109.8. GC-MS *m*/*z* (relative intensity) 143 (M^+, 100).

2-Amino-6-bromo toluene (19): General procedure A was followed in the synthesis of this compound. To a mixture of 2-Bromo-6-nitrotoluene (**18**, 4.0 g, 18.5 mmol), sodium iodide (5.5 g, 36.7 mmol) and phosphorous acid (6.07 g, 74.0 mmol), were added 48% of hydrobromic acid (20 ml) and acetic acid (20 ml). The slurry was heated to a gentle reflux at 115 °C for 8 hours. The reaction was cooled to 20 °C and 50 ml of Ethyl Acetate was added. Adjust pH of the mixture to 4 – 5 by adding 45% potassium hydroxide solution and potassium phosphate tribasic solution. The layers were separated and aqueous layer was extracted with 50 ml Ethyl Acetate. The combined organic later was dried with Na_2SO_4 and concentrated to give 3.3 g of **19** as a dark oil. (96% yield). All Analytical data are identical to that of the authentic sample. ^{1}H NMR (DMSO-d_6, 400 MHz) (Conform to known compound) δ 6.79 (t, *J* = 8.0 Hz, 1H), 6.74 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.60 (dd, *J* = 8.0, 1.0 Hz, 1H), 5.20 (bs, 1H), 2.14 (s, 3H).

2-Amino-4-bromo benzoic acid (21): To a mixture of 4-Bromo-2-nitrobenzoic acid (**20**, 4.0 g, 16.3 mmol), sodium iodide (4.87 g, 32.5 mmol) and phosphorous acid (5.33 g, 65 mmol), were added 48% of hydrobromic acid (20 ml) and acetic acid (20 ml). The slurry was heated to a gentle reflux at 115 °C for 8 hrs. The reaction mixture was cooled to 20 °C. The pH of the mixture was adjusted to 4 – 5 by using 45% potassium hydroxide solution and potassium phosphate tribasic solution. After cooling the mixture to 10 °C, the solid was filtered to obtain 2.9 g of **21**. (83% yield). All Analytical data are identical to that of the authentic sample. ^{1}H NMR (DMSO-d_6, 400 MHz) (Conform to known compound) δ 7.59 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.65 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.35 (s, 2H).

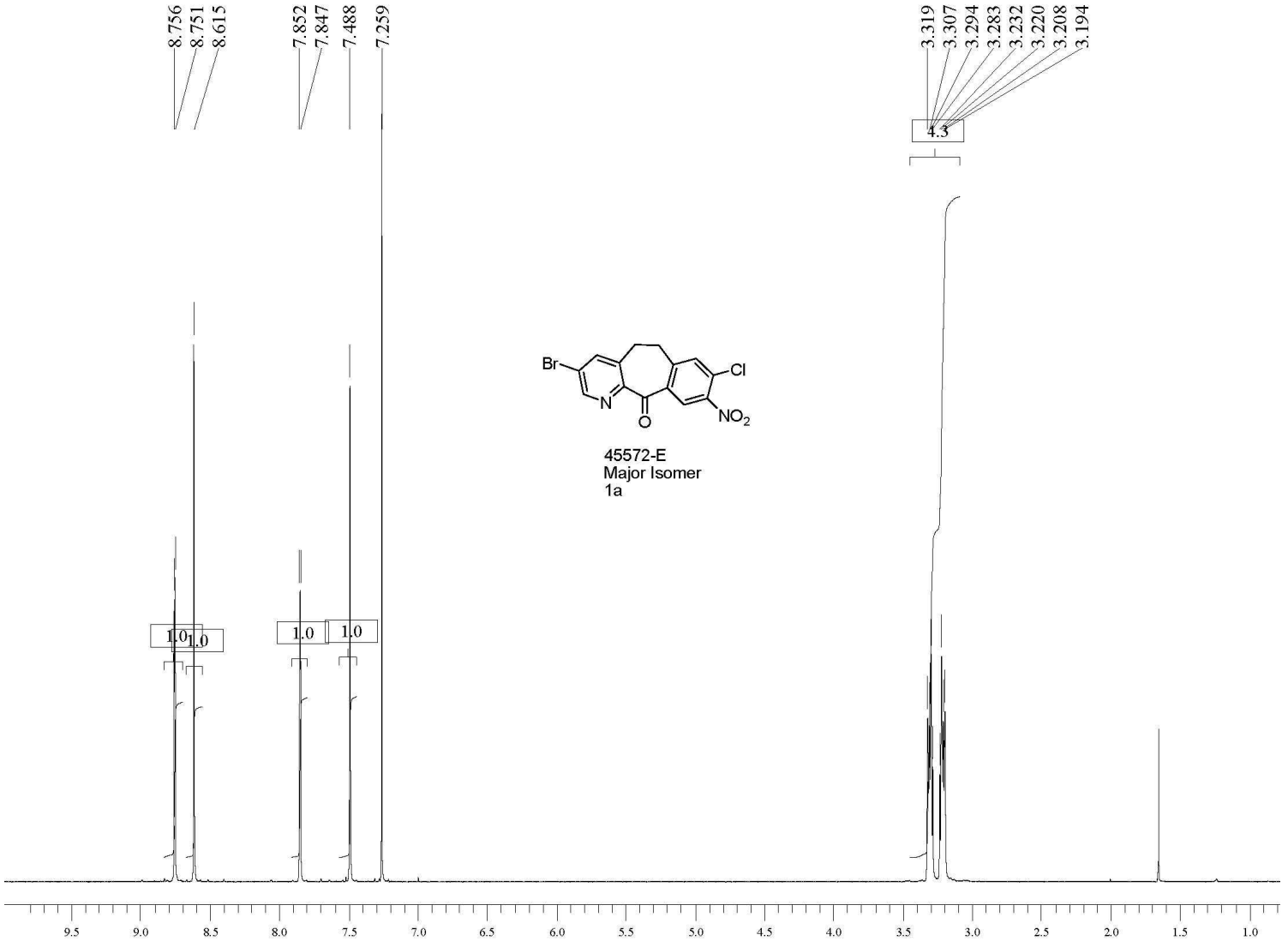
2-Benzylpridine (**23**)**:** A mixture of 2-benzoylpyridine (**22**, 2.0 g, 11 mmol), sodium iodide (3.3 g, 22 mmol) in hydrobromic acid (12 ml) and acetic acid (8 ml) was heated to a gentle reflux at 115 °C. Hypophosphorous acid (3.4 ml, 50%, 33 mmol) was slowly added to the reaction through syringe pump in 30 minutes. The reaction was heated for a total of 5 hours. After workup, the solvent was removed under vacuum to give 1.66 g of product as a bright red liquid. (90% yield). The NMR of the crude product was identical to that of the authentic sample. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.54 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.56 (td, *J* = 7.8, 2.0 Hz, 1H), 7.32-7.21 (m, 5H), 7.08 (td, *J* = 7.8, 1.1Hz, 2H), 4.16 (s, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ 161.1, 149.5, 139.6, 136.6, 129.2, 128.7, 126.5, 123.2, 121.3, 44.8. GC-MS *m/z* (relative intensity) 169 (M^+, 73) 168 (M^+-H, 100), 91 (M^+-$C_5N_1H_4$, 15)**.**

4-Benzylpridine (**25**): A mixture of 4-benzoylpyridine (**24**, 2.0 g, 11 mmol), sodium iodide (3.3 g, 22 mmol) in hydrobromic acid (12 ml) and acetic acid (8 ml) was heated to a gentle reflux at 115 °C. Hypophosphorous acid (3.4 ml, 50%, 33 mmol) was slowly added to the reaction through a syringe pump in 30 minutes. The reaction was monitored by TLC and completed in 5 hours. Workup and removal of solvent afforded 1.7 g of dark red oil. (92% yield). The NMR of the crude reaction product was identical to that of the authentic sample. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.53(d, *J* = 5.9 Hz, 2H), 7.35 (td, *J* = 6.4, 1.2 Hz, 2H), 7.28 (td, *J* = 7.0, 1.4 Hz, 1H), 7.21 (d, *J* = 7.0 Hz, 2H), 7.13 (d, *J* = 5.9 Hz, 2H), 4.00 (s, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ 149.9, 138.9, 129.1, 128.8, 126.8, 124.3, 41.3. GC-MS *m/z* (relative intensity) 169 (M^+, 100) 168 (M^+-H, 94), 91 (M^+-$C_5N_1H_4$, 36).

4-Benzoyl aniline (**27**): A mixture of 4-benzoylnitrobenzene (**26**, 5.0 g, 22 mmol), sodium iodide (6.6 g, 44 mmol) in hydrobromic acid (25 ml, 48%) and acetic acid (25 ml) was heated to a gentle reflux at 115 °C. The reaction mixture became a clear solution. Hypophosphorous acid (50% aqueous solution, 11.4 ml) was slowly added to the reaction over a period of 2 hour through a syringe pump. The reaction was monitored by TLC and completed in one hour. There was no further reaction after addition of hypophosphorous acid. HPLC showed about 99% solution yield of nitro reduced product. The reaction mixture was cooled to ambient temperature and quenched with a solution of NaOH (80 ml, 25%). Extra 50 ml of water was added and the suspension mixture was filtered, followed by water washes. After drying, 4.1 g of product (**27**) was obtained. (95% yield)

as a solid. The NMR showed a clean product and identical to its authentic sample. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (dd, *J* = 8.2, 1.4 Hz, 4H), 7.52 (tt, *J* = 6.4, 1.4 Hz, 1H), 7.45 (td, *J* = 6.4, 1.2 Hz, 2H), 6.68 (td, *J* = 6.8, 2.0 Hz, 2H), 4.12(bs, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ 195.4, 151.0, 139.0, 133.1, 131.5, 129.7, 128.2, 127.6, 113.8. GC-MS *m*/*z* (relative intensity) 197 (M^+, 80) 120 (M^+-C_6H_5, 100), 92 (M^+-C_5H_5CO, 23) 77 (C_6H_5, 19).

3-Aminoacetophenone (**29**): A mixture of 3-nitroacetophenone (**28**, 5.0 g, 30 mmol), sodium iodide (9.0 g, 60 mmol) in hydrobromic acid (34 ml, 48%) was heated to a gentle reflux at 115 °C. Hypophosphorous acid (50% aqueous solution, 6.2 ml, 60 mmol) was slowly added into the reaction in 1 hour through a syringe pump. Reaction was monitored by TLC and nitro reduction was completed in one hour. There was no further reaction after addition of hypophosphorous acid. Solution yield was ca. 85% as deterimined by HPLC. Reaction mixture was cooled to ambient temperature and slowly poured into a solution of NaOH (40 ml, 25%) and water (100 ml). Solid was filtered. The aqueous was extracted with EtOAc (3 X 100 ml). After concentration, total solid was 2.4 g. Purification by column chromatography obtained 2.0 g of product. Final crystallization with EtOAc/Hexane gave 1.54 g of product as 3-aminoacetophenone. (38% yield). The NMR the product was identical to its authentic sample. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 (ddd, *J* = 8.6, 1.5, 0.6 Hz, 1H), 7.31 (td, *J* = 6.9, 2.1 Hz, 1H), 7.28 (t, *J* = 7.9 Hz, 1H), 6.91 (ddd, *J* = 7.9, 2.4, 1.1 Hz, 1H), 3.84 (bs, 2H), 2.60 (s, 3H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ 198.5, 146.8, 138.4, 129.6, 119.8, 119.0, 114.1. GC-MS *m*/*z* (relative intensity) 135 (M^+,100) 120 (M^+-CH_3, 99), 92 (M^+-$COCH_3$, 93).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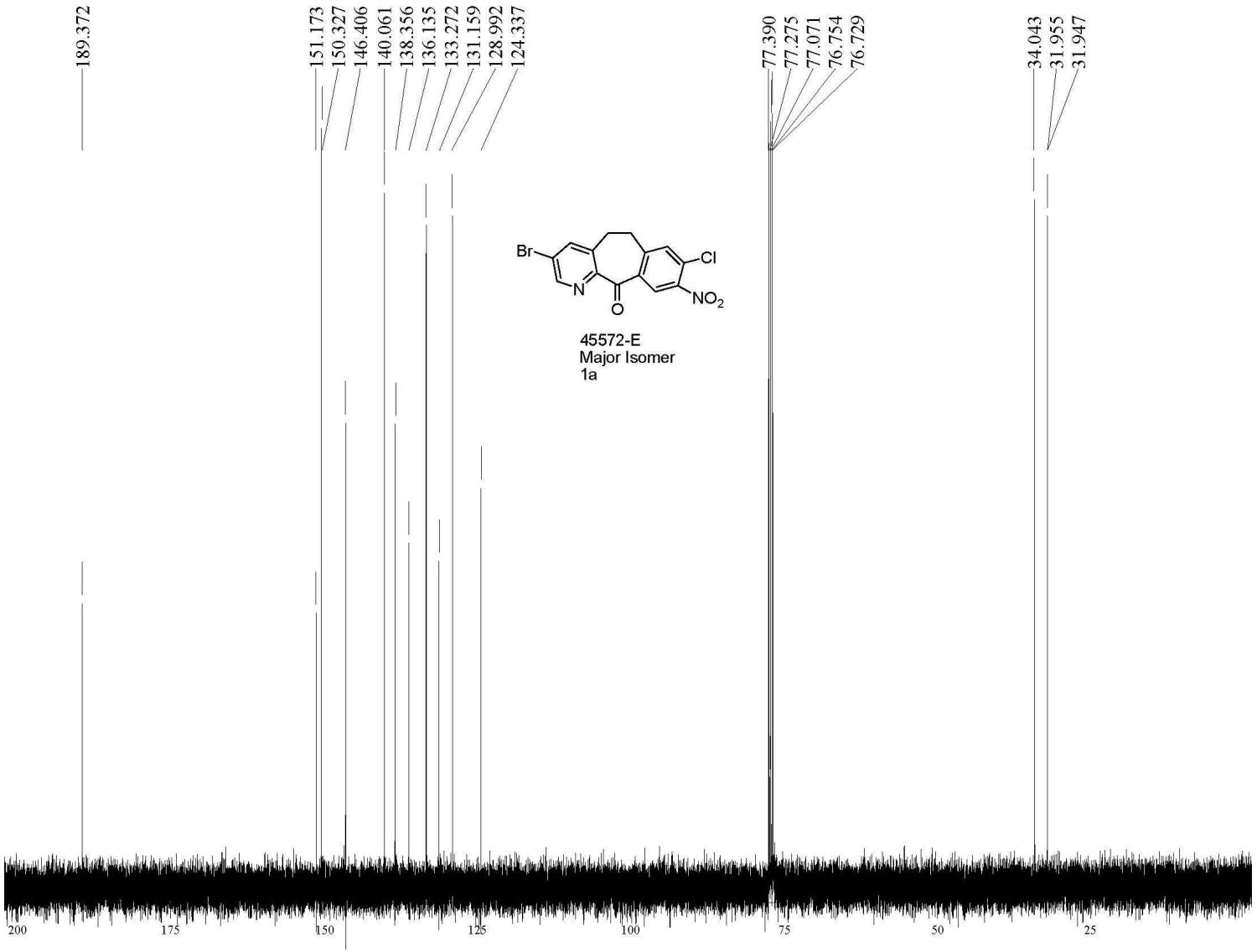
3.220
3.208
3.194
4.3
1.0
1.0
1.0
1.0
Br
Cl
N
O
NO2
45572-E
Major Isomer
1a
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0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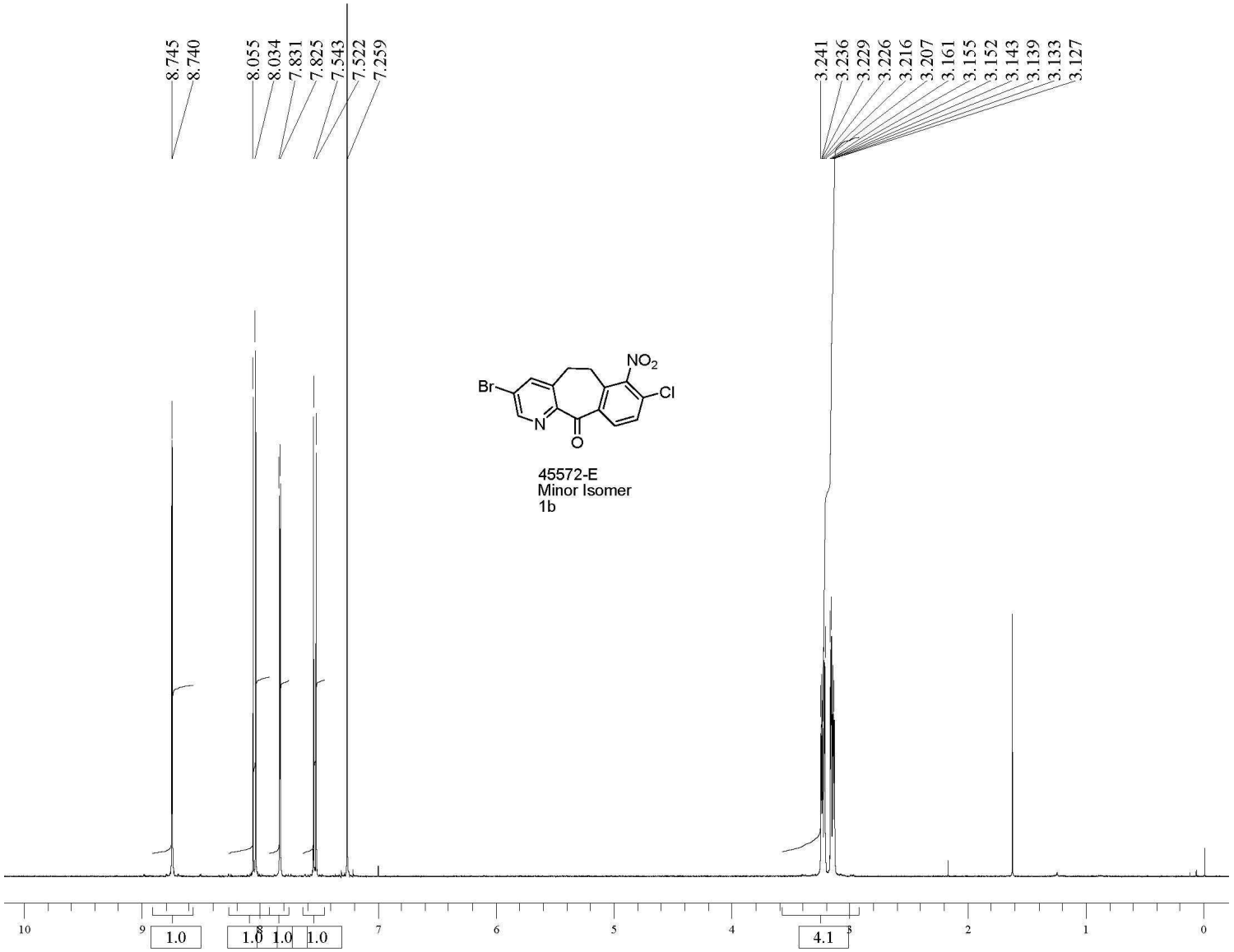
151.173
150.327
146.406
140.061
138.356
136.135
133.272
131.159
128.992
124.337
77.390
77.275
77.071
76.754
76.729
34.043
31.955
31.947
Br
Cl
N
O
NO2
45572-E
Major Isomer
1a
200
175
150
125
100
75
50
25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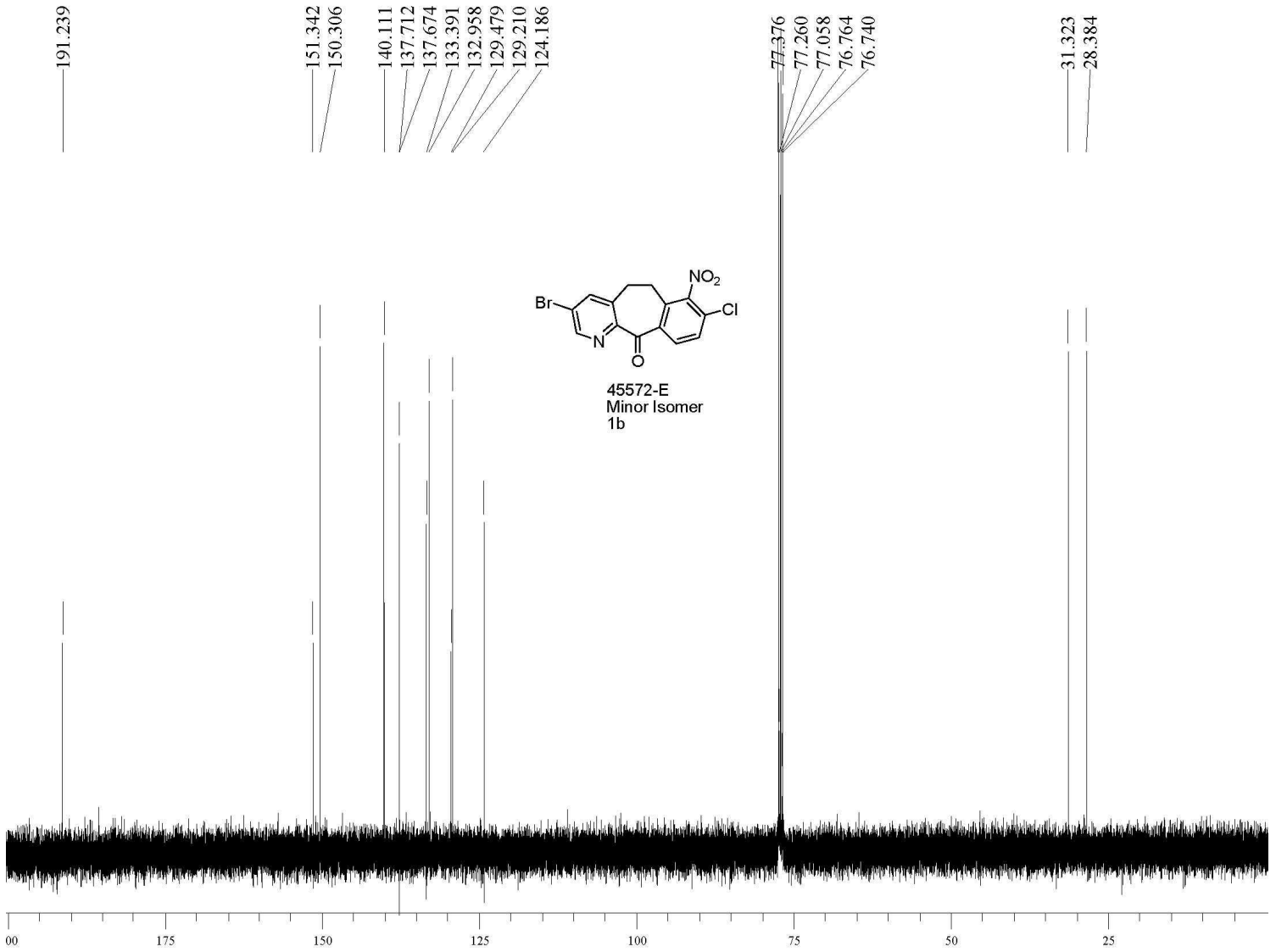
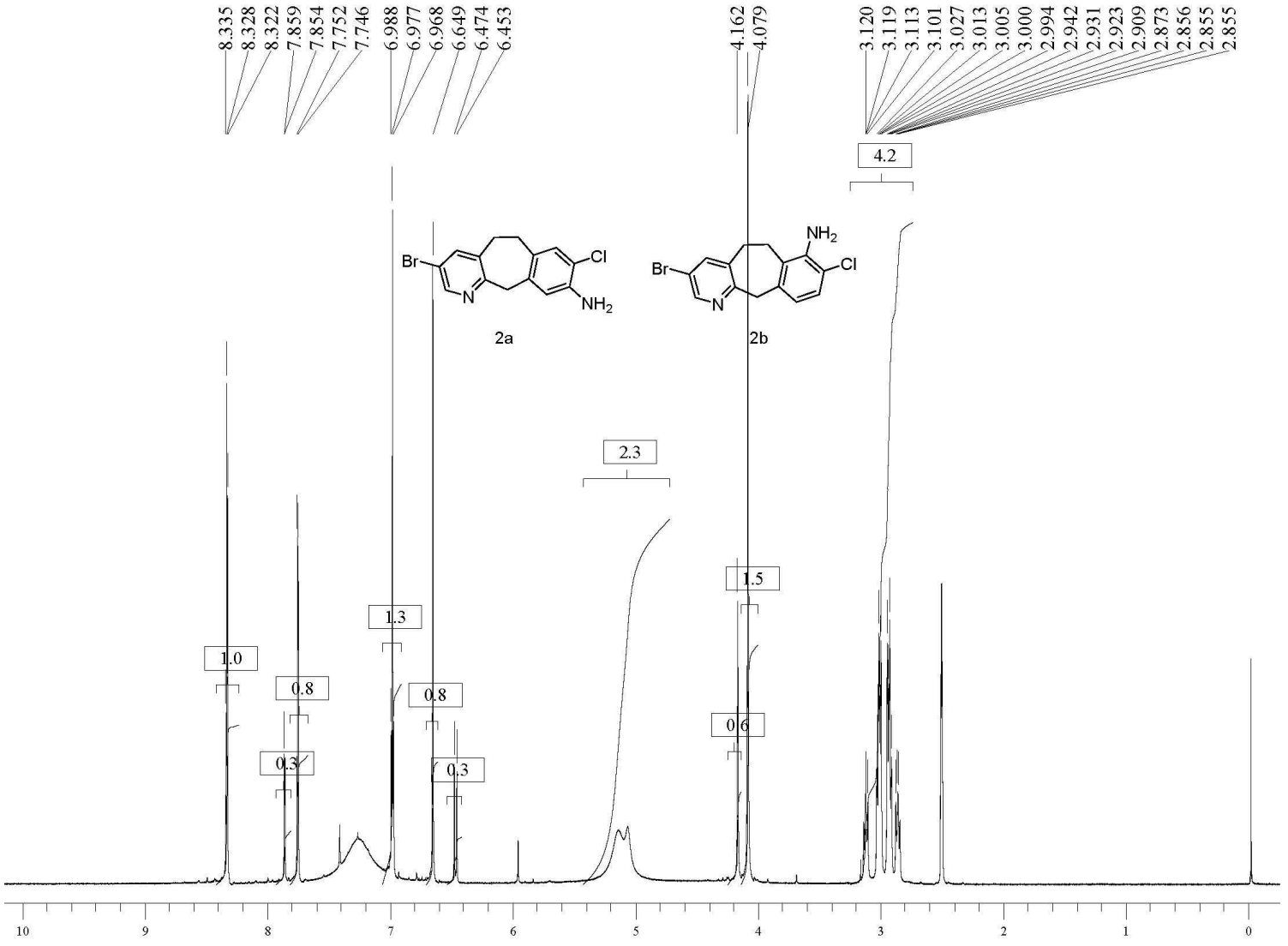
8.740
8.055
8.034
7.831
7.825
7.543
7.522
7.259
3.241
3.236
3.229
3.226
3.216
3.207
3.161
3.155
3.152
3.143
3.139
3.133
3.127
NO2
Br
Cl
N
O
45572-E
Minor Isomer
1b
1.0
1.0
1.0
1.0
4.1


191.239
151.342
150.306
140.111
137.712
137.674
133.391
132.958
129.479
129.210
124.186
77.376
77.260
77.058
76.764
76.740
31.323
28.384
NO2
Br
Cl
N
O
45572-E
Minor Isomer
1b
00
175
150
125
100
75
50
25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7.746
6.988
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6.968
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6.474
6.453
4.162
4.079
3.120
3.119
3.113
3.101
3.027
3.013
3.005
3.000
2.994
2.942
2.931
2.923
2.909
2.873
2.856
2.855
2.855
Br
Cl
NH2
N
2a
Br
NH2
Cl
N
2b
4.2
2.3
1.5
1.3
1.0
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0.6
0.3
0.3
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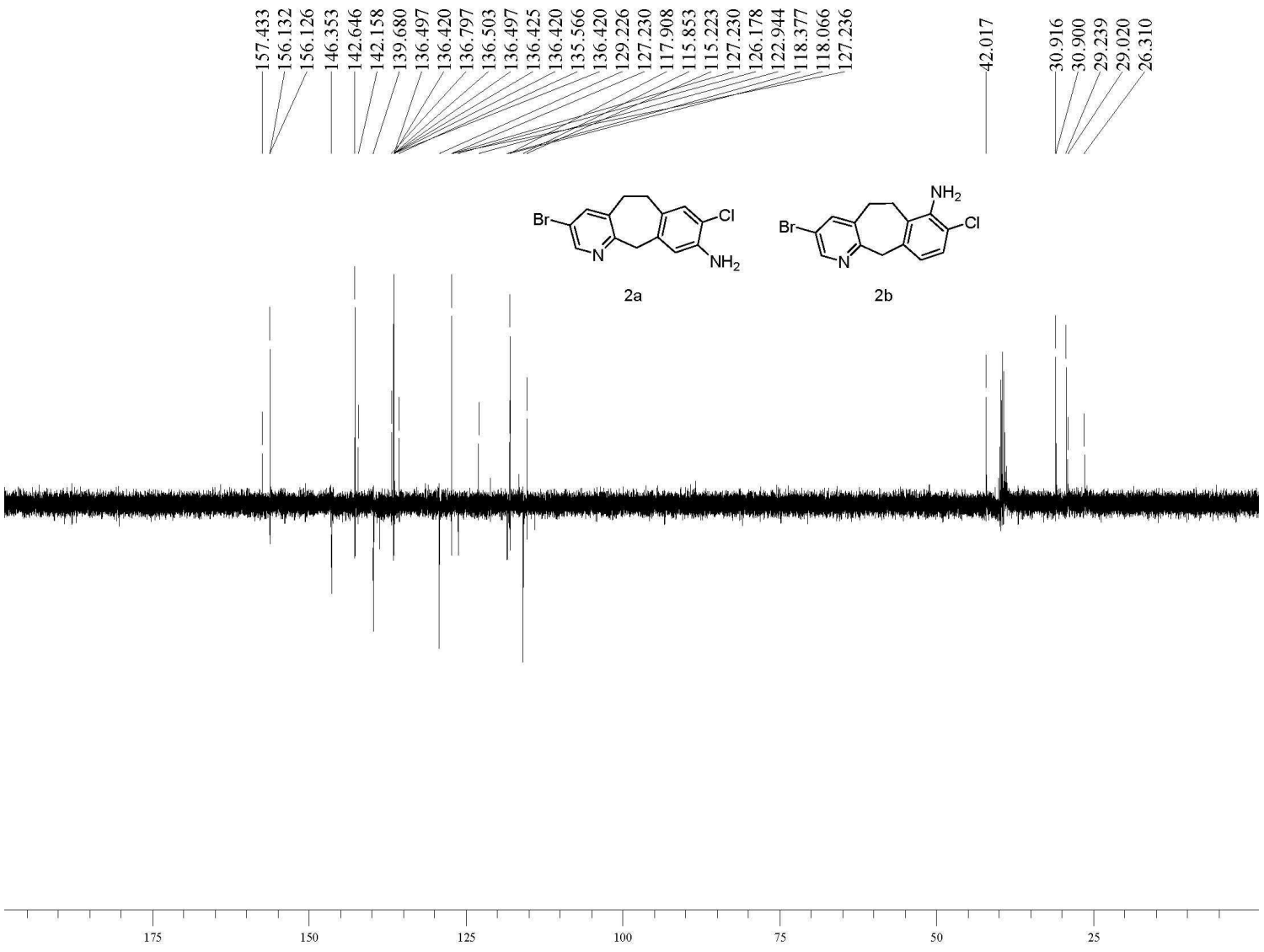
9
8
7
6
5
4
3
2
1
0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156.126
146.353
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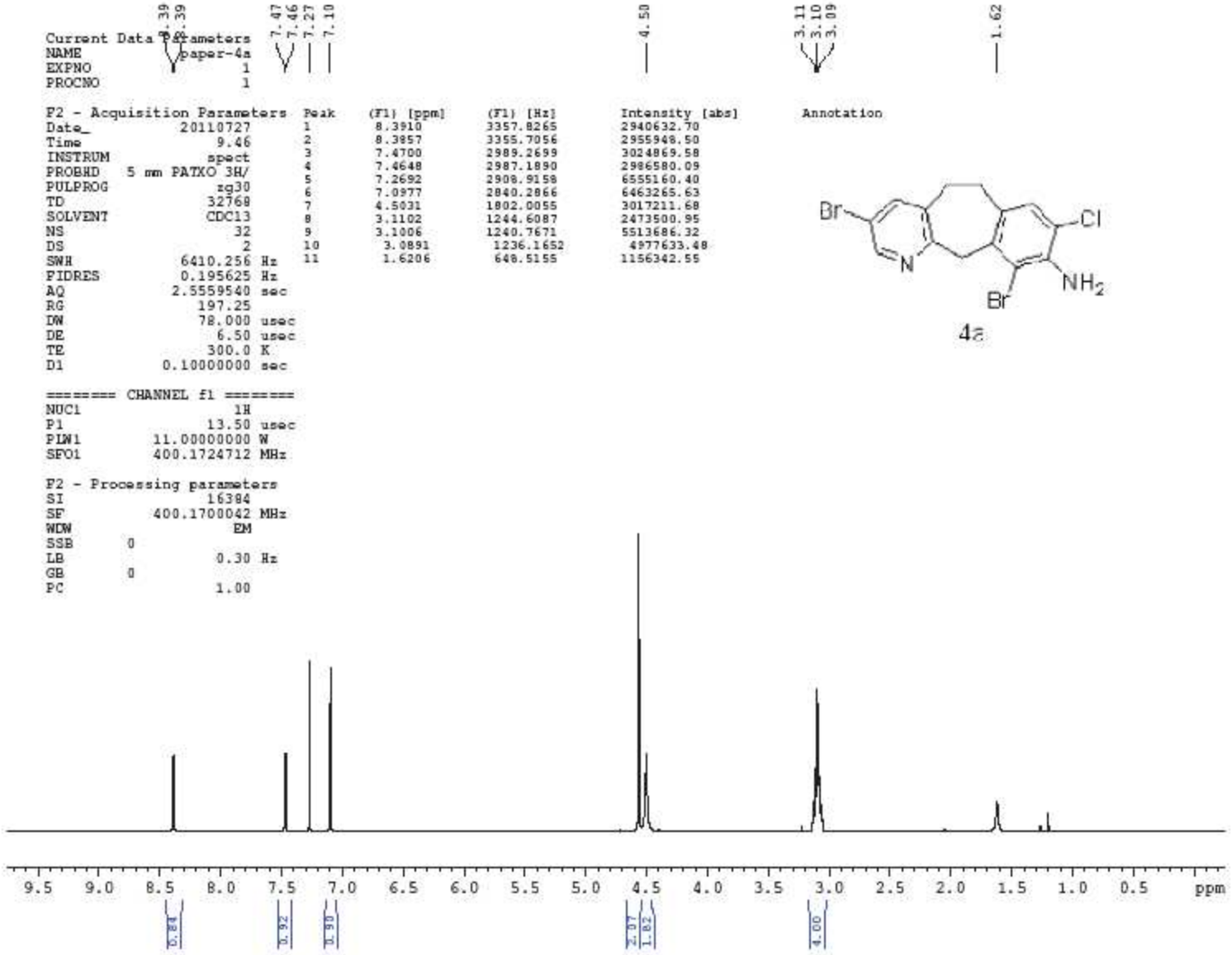
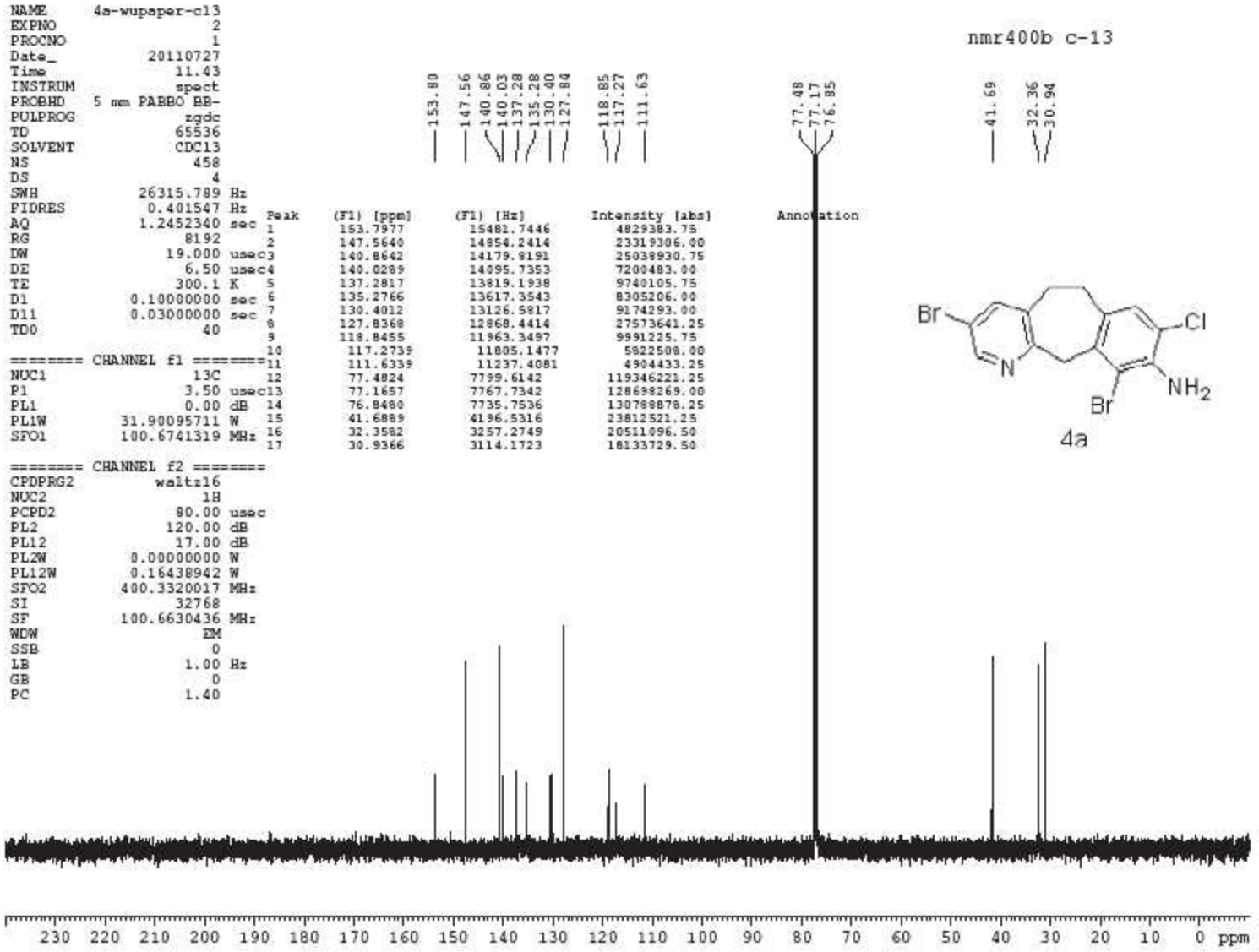
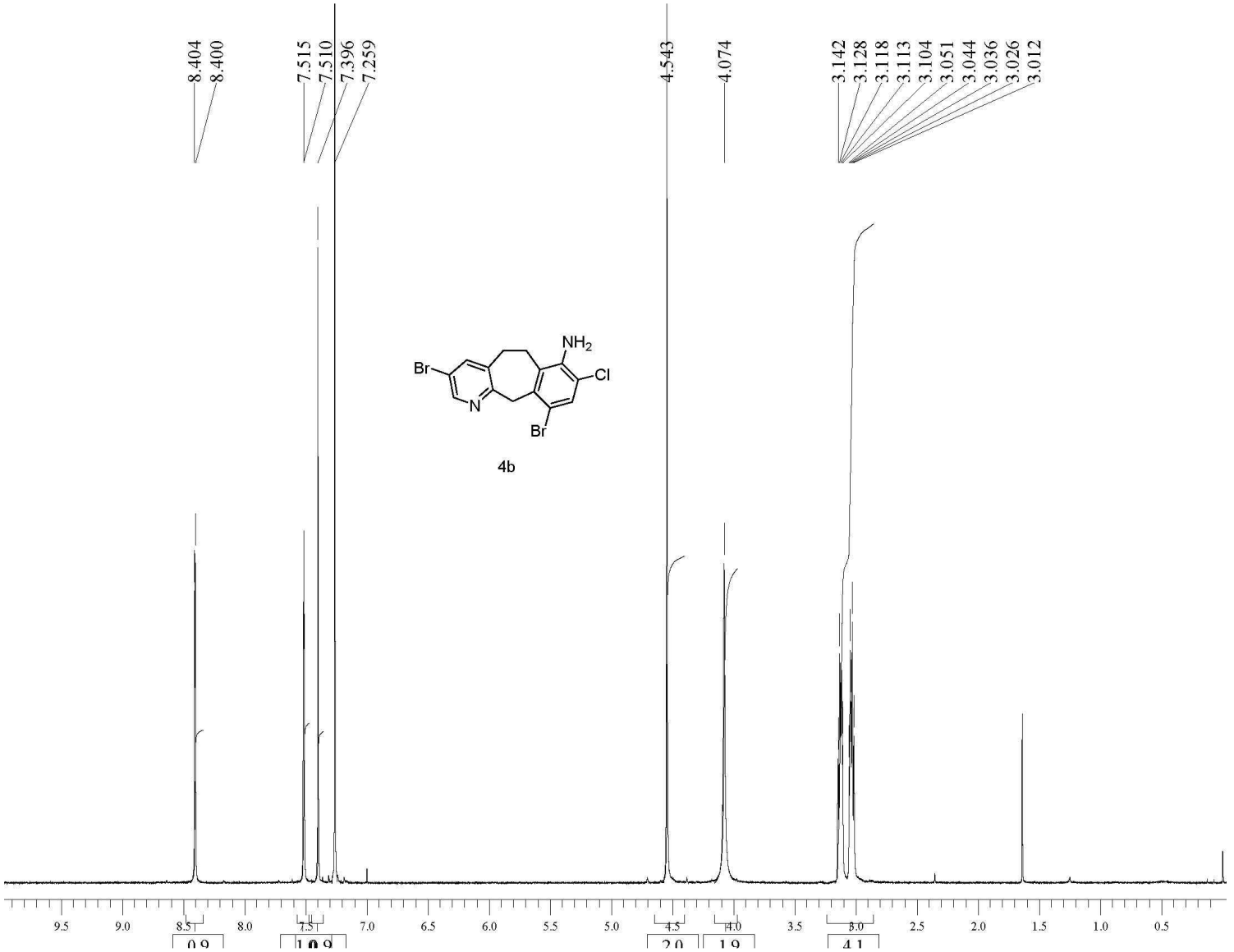
136.497
136.420
136.797
136.503
136.497
136.425
136.420
135.566
136.420
129.226
127.230
117.908
115.853
115.223
127.230
126.178
122.944
118.377
118.066
127.236
42.017
30.916
30.900
29.239
29.020
26.310
Br
Cl
NH2
N
2a
Br
NH2
Cl
N
2b
175
150
125
100
75
50
25


8.39
8.39
7.47
7.46
7.27
7.10
4.50
3.11
3.10
3.09
1.62
Current Data Parameters
NAME paper-4a
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110727
Time 9.46
INSTRUM spect
PROBHD 5 mm PATXO 3H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 197.25
DW 78.000 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PLW1 11.00000000 W
SFO1 400.1724712 MHz
F2 - Processing parameters
SI 16384
SF 400.1700042 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Peak (F1) [ppm] (F1) [Hz] Intensity [abs] Annotation
1 8.3910 3357.8265 2940632.70
2 8.3857 3355.7056 2955948.50
3 7.4700 2989.2699 3024869.58
4 7.4648 2987.1890 2986580.09
5 7.2692 2908.9158 6555160.40
6 7.0977 2840.2866 6463265.63
7 4.5031 1802.0055 3017211.68
8 3.1102 1244.6087 2473500.95
9 3.1006 1240.7671 5513686.32
10 3.0891 1236.1652 4977633.48
11 1.6206 648.5155 1156342.55
Br
Cl
N
NH2
Br
4a
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.84
0.92
0.90
2.07
1.82
4.00


NAME 4a-wupaper-c13
EXPNO 2
PROCNO 1
Date_ 20110727
Time 11.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgdc
TD 65536
SOLVENT CDC13
NS 458
DS 4
SWH 26315.789 Hz
FIDRES 0.401547 Hz
AQ 1.2452340 sec
RG 8192
DW 19.000 usec
DE 6.50 usec
TE 300.1 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 40
======== CHANNEL f1 ========
NUC1 13C
P1 3.50 usec
PL1 0.00 dB
PL1W 31.90095711 W
SFO1 100.6741319 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 17.00 dB
PL2W 0.00000000 W
PL12W 0.16438942 W
SFO2 400.3320017 MHz
SI 32768
SF 100.6630436 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
153.80
147.56
140.86
140.03
137.28
135.28
130.40
127.84
118.85
117.27
111.63
77.48
77.17
76.85
41.69
32.36
30.94
Peak (F1) [ppm] (F1) [Hz] Intensity [abs] Annotation
1 153.7977 15481.7446 4829383.75
2 147.5640 14854.2414 23319306.00
3 140.8642 14179.8191 25038930.75
4 140.0289 14095.7353 7200483.00
5 137.2817 13819.1938 9740105.75
6 135.2766 13617.3543 8305206.00
7 130.4012 13126.5817 9174293.00
8 127.8368 12868.4414 27573641.25
9 118.8455 11963.3497 9991225.75
10 117.2739 11805.1477 5822508.00
11 111.6339 11237.4081 4904433.25
12 77.4824 7799.6142 119346221.25
13 77.1657 7767.7342 128698269.00
14 76.8480 7735.7536 130788878.25
15 41.6889 4196.5316 23812521.25
16 32.3582 3257.2749 20511096.50
17 30.9366 3114.1723 18133729.50
nmr400b c-13
Br
Cl
N
NH2
Br
4a
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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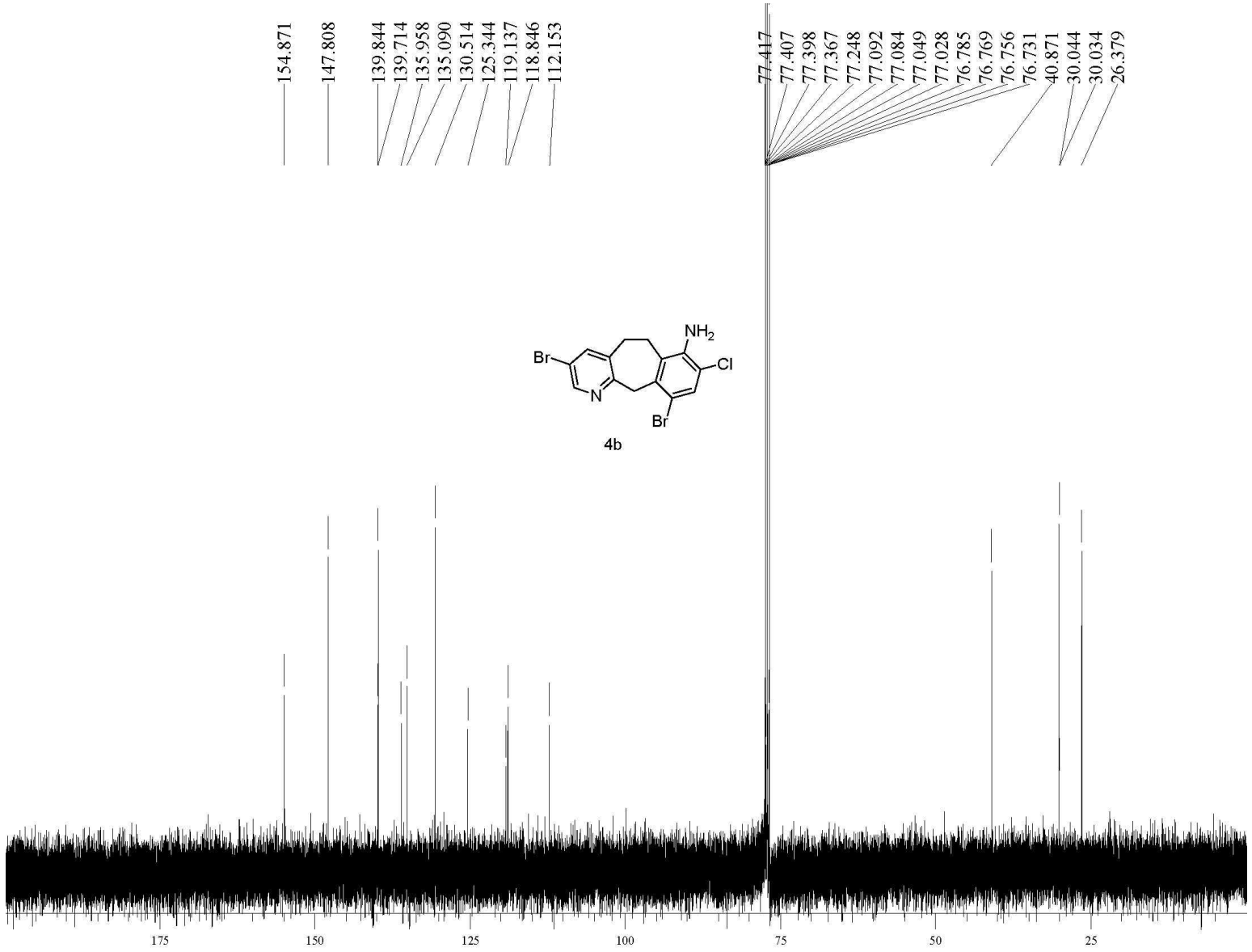
7.515
7.510
7.396
7.259
4.543
4.074
3.142
3.128
3.118
3.113
3.104
3.051
3.044
3.036
3.026
3.012
NH2
Br
Cl
N
Br
4b
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.9
1.0
2.0
1.9
4.1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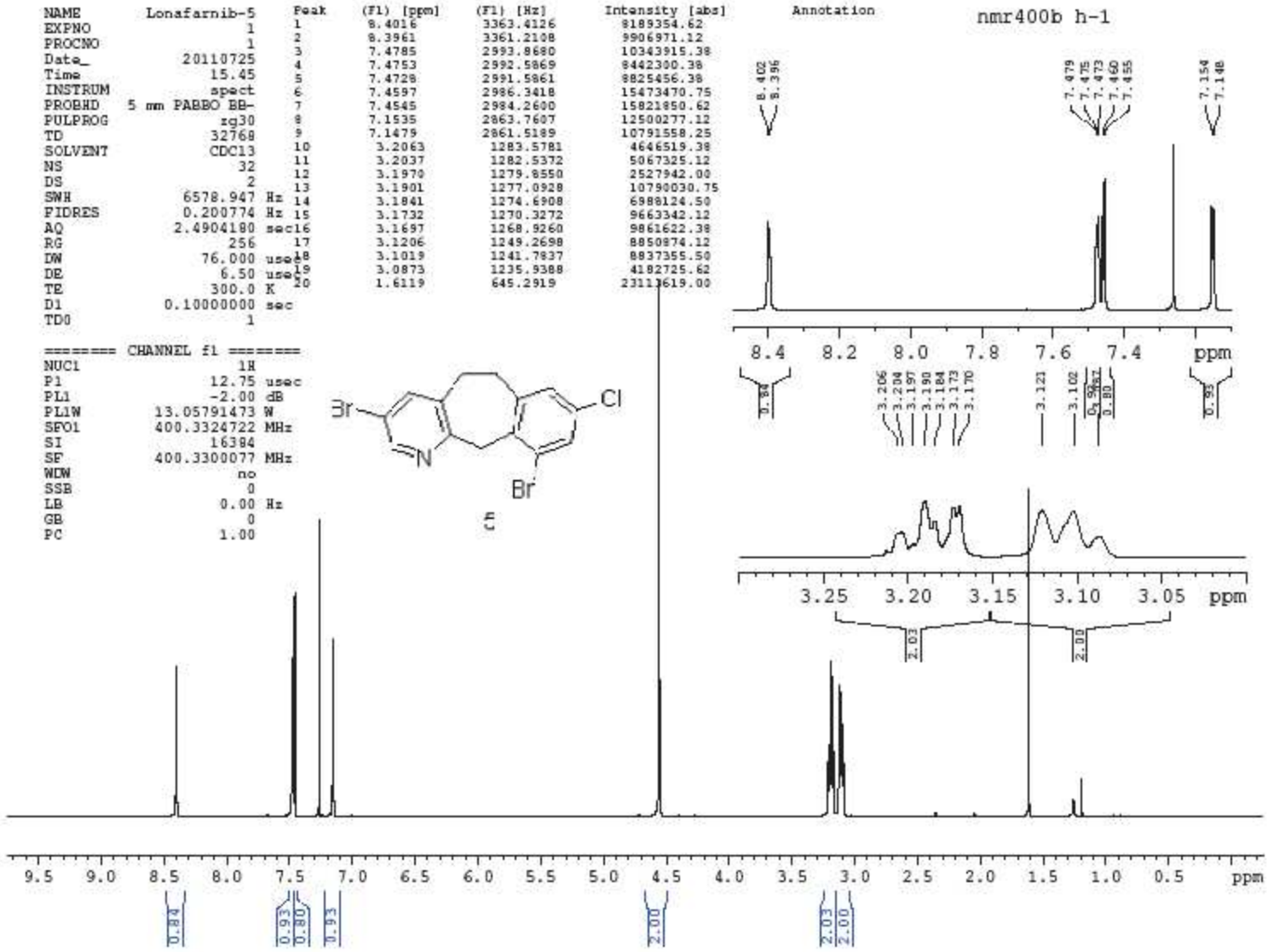
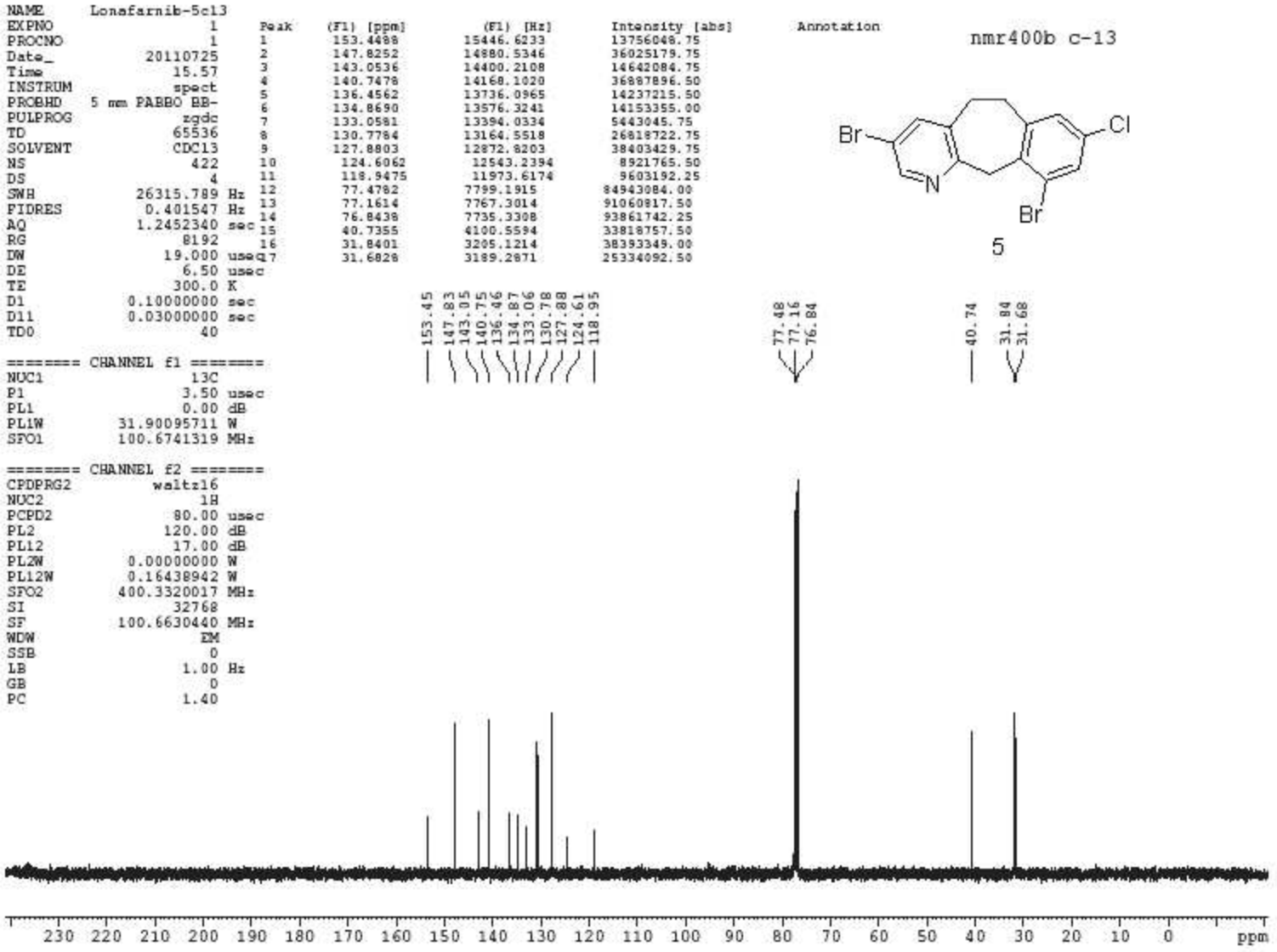
139.844
139.714
135.958
135.090
130.514
125.344
119.137
118.846
112.153
77.417
77.407
77.398
77.367
77.248
77.092
77.084
77.049
77.028
76.785
76.769
76.756
76.731
40.871
30.044
30.034
26.379
NH2
Br
Cl
N
Br
4b
175
150
125
100
75
50
25

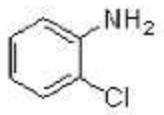

NAME Lonafarnib-5
EXPNO 1
PROCNO 1
Date_ 20110725
Time 15.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6578.947 Hz
FIDRES 0.200774 Hz
AQ 2.4904180 sec
RG 256
DW 76.000 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.75 usec
PL1 -2.00 dB
PL1W 13.05791473 W
SFO1 400.3324722 MHz
SI 16384
SF 400.3300077 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
Peak (F1) [ppm] (F1) [Hz] Intensity [abs]
1 8.4016 3363.4126 8189354.62
2 8.3961 3361.2108 9906971.12
3 7.4785 2993.8680 10343915.38
4 7.4753 2992.5869 8442300.38
5 7.4728 2991.5861 8825456.38
6 7.4597 2986.3418 15473470.75
7 7.4545 2984.2600 15821850.62
8 7.1535 2863.7607 12500277.12
9 7.1479 2861.5189 10791558.25
10 3.2063 1283.5781 4646519.38
11 3.2037 1282.5372 5067325.12
12 3.1970 1279.8550 2527942.00
13 3.1901 1277.0928 10790030.75
14 3.1841 1274.6908 6988124.50
15 3.1732 1270.3272 9663342.12
16 3.1697 1268.9260 9861622.38
17 3.1206 1249.2698 8850874.12
18 3.1019 1241.7837 8837355.50
19 3.0873 1235.9388 4182725.62
20 1.6119 645.2919 23113619.00
Annotation
nmr400b h-1
Br
Cl
N
Br
ch
8.402
8.396
7.479
7.475
7.473
7.460
7.455
7.154
7.148
8.4
8.2
8.0
7.8
7.6
7.4
ppm
0.84
3.206
3.204
3.197
3.190
3.184
3.173
3.170
3.121
3.102
0.96
0.80
0.95
3.25
3.20
3.15
3.10
3.05
ppm
2.03
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.84
0.93
0.80
0.93
2.00
2.03
2.00


NAME Lonafarnib-5c13
EXPNO 1
PROCNO 1
Date_ 20110725
Time 15.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgdc
TD 65536
SOLVENT CDC13
NS 422
DS 4
SWH 26315.789 Hz
FIDRES 0.401547 Hz
AQ 1.2452340 sec
RG 8192
DW 19.000 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 40
======== CHANNEL f1 ========
NUC1 13C
P1 3.50 usec
PL1 0.00 dB
PL1W 31.90095711 W
SFO1 100.6741319 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 17.00 dB
PL2W 0.00000000 W
PL12W 0.16438942 W
SFO2 400.3320017 MHz
SI 32768
SF 100.6630440 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Peak (F1) [ppm] (F1) [Hz] Intensity [abs] Annotation
1 153.4488 15446.6233 13756048.75
2 147.8252 14880.5346 36025179.75
3 143.0536 14400.2108 14642084.75
4 140.7478 14168.1020 36887896.50
5 136.4562 13736.0965 14237215.50
6 134.8690 13576.3241 14153355.00
7 133.0581 13394.0334 5443045.75
8 130.7784 13164.5518 26818722.75
9 127.8803 12872.8203 38403429.75
10 124.6062 12543.2394 8921765.50
11 118.9475 11973.6174 9603192.25
12 77.4782 7799.1915 84943084.00
13 77.1614 7767.3014 91060817.50
14 76.8438 7735.3308 93861742.25
15 40.7355 4100.5594 33818757.50
16 31.8401 3205.1214 38393349.00
17 31.6828 3189.2871 25334092.50
nmr400b c-13
Br
Cl
N
Br
5
153.45
147.83
143.05
140.75
136.46
134.87
133.06
130.78
127.88
124.61
118.95
77.48
77.16
76.84
40.74
31.84
31.68
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

NAME	95051-0011-h1final		Peak	(F1) [ppm]	(F1) [Hz]	Intensity [abs]	Annotation
EXPNO	1		1	7.2796	2914.2423	19235209.44	
PROCNO	1		2	7.2764	2912.9612	14419191.19	
Date_	20110706		3	7.2598	2906.3157	16017842.19	
Time	15.53		4	7.2564	2904.9546	14807854.81	
INSTRUM	spect		5	7.1090	2845.9460	7046063.62	
PROBHD	5 mm PABBO BB-		6	7.1050	2844.3446	6710665.25	
PULPROG	zg30		7	7.0894	2838.0995	15184469.31	
TD	32768		8	7.0870	2837.1387	13947276.38	
SOLVENT	CDCl3		9	7.0709	2830.6934	8608520.94	
NS	32		10	7.0670	2829.1321	8902633.69	
DS	2		11	6.7957	2720.5226	16200148.50	
SWH	6578.947	Hz	12	6.7923	2719.1615	16807377.75	
FIDRES	0.200774	Hz	13	6.7757	2712.5160	14378812.75	
AQ	2.4904180	sec	14	6.7724	2711.1949	14594737.81	
RG	128		15	6.7358	2696.5428	8635900.94	
DW	76.000	usec	16	6.7320	2695.0216	7646846.94	
DE	6.50	usec	17	6.7172	2689.0967	14226921.62	
TE	300.0	K	18	6.7157	2688.4962	13547161.50	
D1	0.10000000	sec	19	6.7137	2687.6955	12564019.25	
TD0	1		20	6.6977	2681.2902	7397216.38	
			21	6.6938	2679.7290	6560028.06	
			22	4.0649	1627.3014	3424272.81	

======== CHANNEL f1 ========		
NUC1	1H	
P1	12.75	usec
PL1	-2.00	dB
PL1W	13.05791473	W
SFO1	400.3324722	MHz
SI	16384	
SF	400.3300000	MHz
WDW	no	
SSB	0	
LB	0.00	Hz
GB	0	
PC	1.00	

nmr400b h-1



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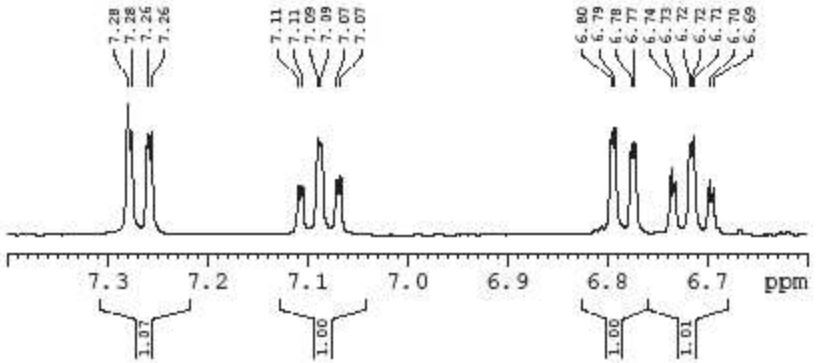
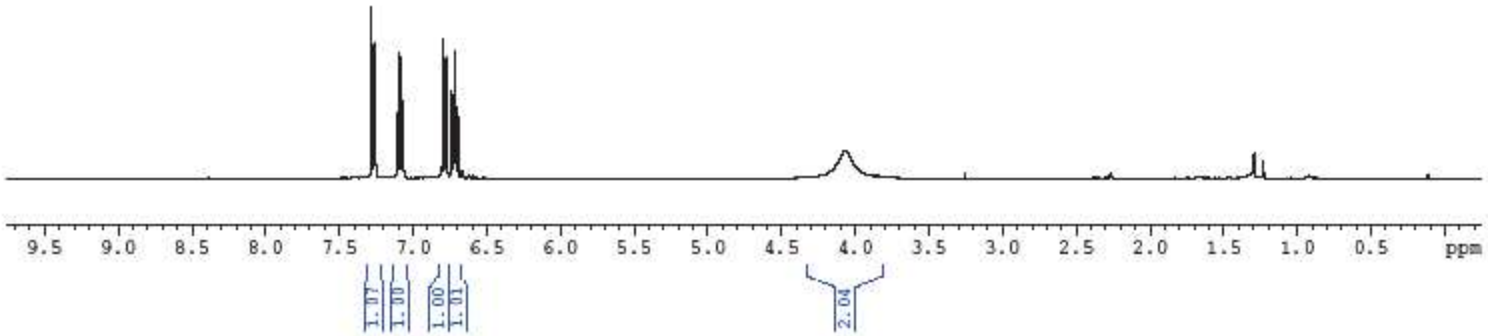




NAME	95851-0011-3
EXPNO	1
PROCNO	1
Date_	20110617
Time	15.05
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc
TD	65536
SOLVENT	CDC13
NS	57
DS	4
SWH	26315.789 Hz
FIDRES	0.401547 Hz
AQ	1.2452340 sec
RG	8192
DW	19.000 usec
DE	6.50 usec
TE	300.0 K
D1	0.10000000 sec
D11	0.03000000 sec
TD0	40

======== CHANNEL f1 ========

NUC1	13C
P1	3.50 usec
PL1	0.00 dB
PL1W	31.90095711 W
SFO1	100.6741319 MHz

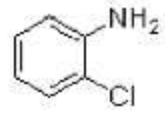
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	120.00 dB
PL12	17.00 dB
PL2W	0.00000000 W
PL12W	0.16438942 W
SFO2	400.3320017 MHz
SI	32768
SF	100.6630852 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Peak	(F1) [ppm]	(F1) [Hz]	Intensity [abs]	Annotation
1	143.0102	14395.8479	3972806.81	
2	129.5300	13038.8894	8896226.12	
3	127.7397	12858.6723	15740405.00	
4	119.1590	11994.9126	10924872.81	
5	116.0062	11677.5420	17918896.19	

nmr400b c-13

143.01
129.53
127.74
119.16
116.01



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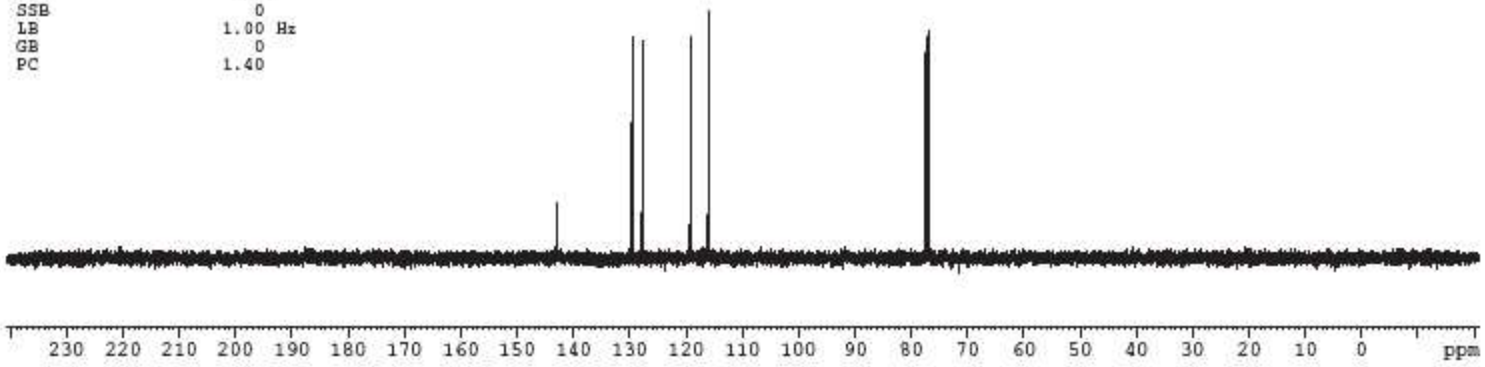
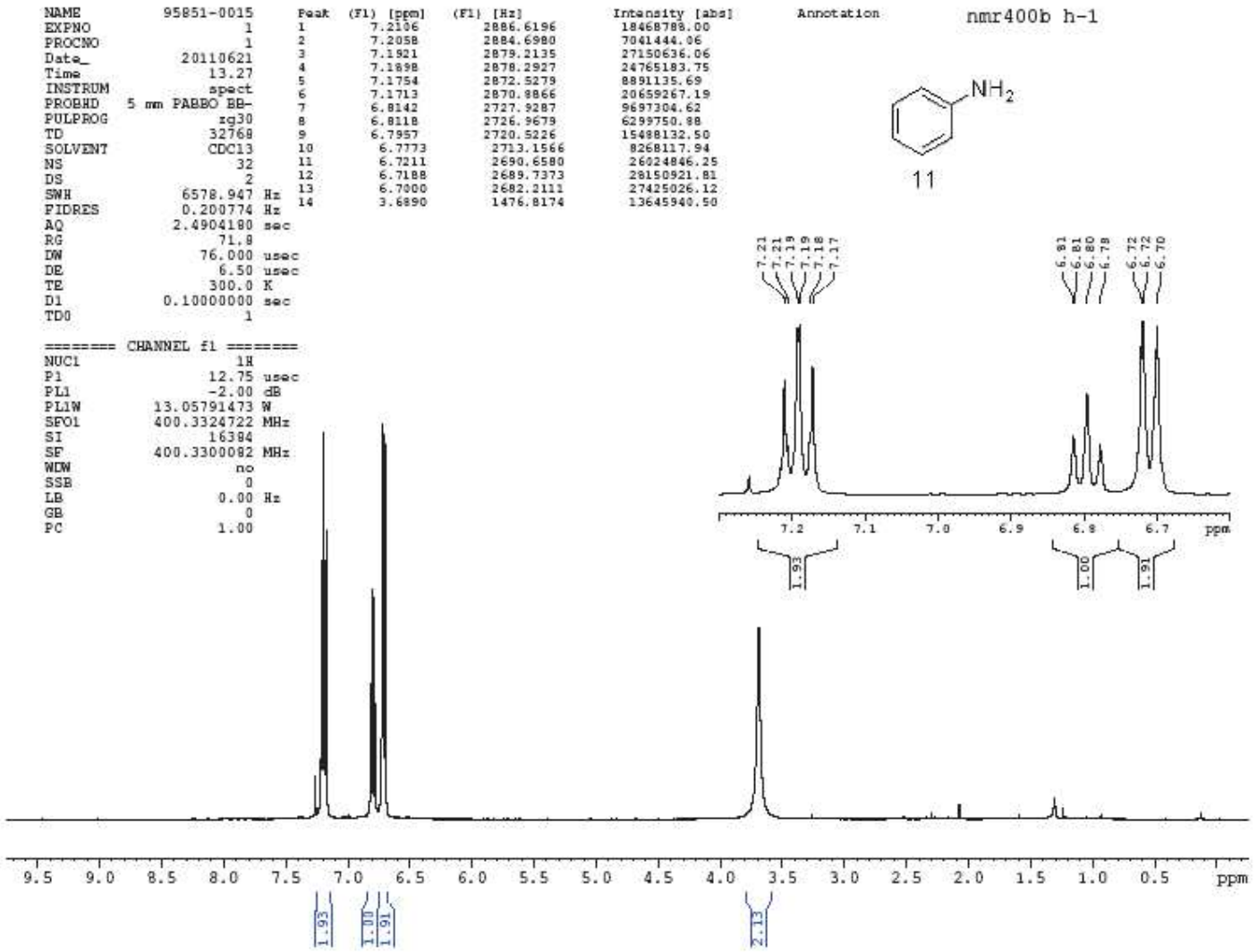



NAME 95851-0015
EXPNO 1
PROCNO 1
Date_ 20110621
Time 13.27
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6578.947 Hz
FIDRES 0.200774 Hz
AQ 2.4904180 sec
RG 71.8
DW 76.000 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.75 usec
PL1 -2.00 dB
PL1W 13.05791473 W
SFO1 400.3324722 MHz
SI 16384
SF 400.3300082 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
Peak (F1) [ppm] (F1) [Hz] Intensity [abs] Annotation
1 7.2106 2886.6196 18468788.00
2 7.2058 2884.6980 7041444.06
3 7.1921 2879.2135 27150636.06
4 7.1898 2878.2927 24765183.75
5 7.1754 2872.5279 8891135.69
6 7.1713 2870.8866 20659267.19
7 6.8142 2727.9287 9697304.62
8 6.8118 2726.9679 6299750.88
9 6.7957 2720.5226 15488132.50
10 6.7773 2713.1566 8268117.94
11 6.7211 2690.6580 26024846.25
12 6.7188 2689.7373 28150921.81
13 6.7000 2682.2111 27425026.12
14 3.6890 1476.8174 13645940.50
nmr400b h-1
NH2
11
7.21
7.21
7.19
7.19
7.18
7.17
6.81
6.81
6.80
6.78
6.72
6.72
6.70
7.2
7.1
7.0
6.9
6.8
6.7
ppm
1.93
1.00
1.91
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.93
1.00
1.91
2.13

NAME	95851-0015-1
EXPNO	1
PROCNO	1
Date_	20110621
Time	13.35
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc
TD	65536
SOLVENT	CDCl3
NS	81
DS	4
SWH	26315.789 Hz
FIDRES	0.401547 Hz
AQ	1.2452340 sec
RG	8192
DW	19.000 usec
DE	6.50 usec
TE	300.0 K
D1	0.10000000 sec
D11	0.03000000 sec
TD0	40

======== CHANNEL f1 ========

NUC1	13C
P1	3.50 usec
PL1	0.00 dB
PL1W	31.90095711 W
SFO1	100.6741319 MHz

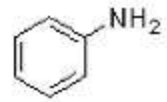
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	120.00 dB
PL12	17.00 dB
PL2W	0.00000000 W
PL12W	0.16438942 W
SFO2	400.3320017 MHz
SI	32768
SF	100.6630590 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

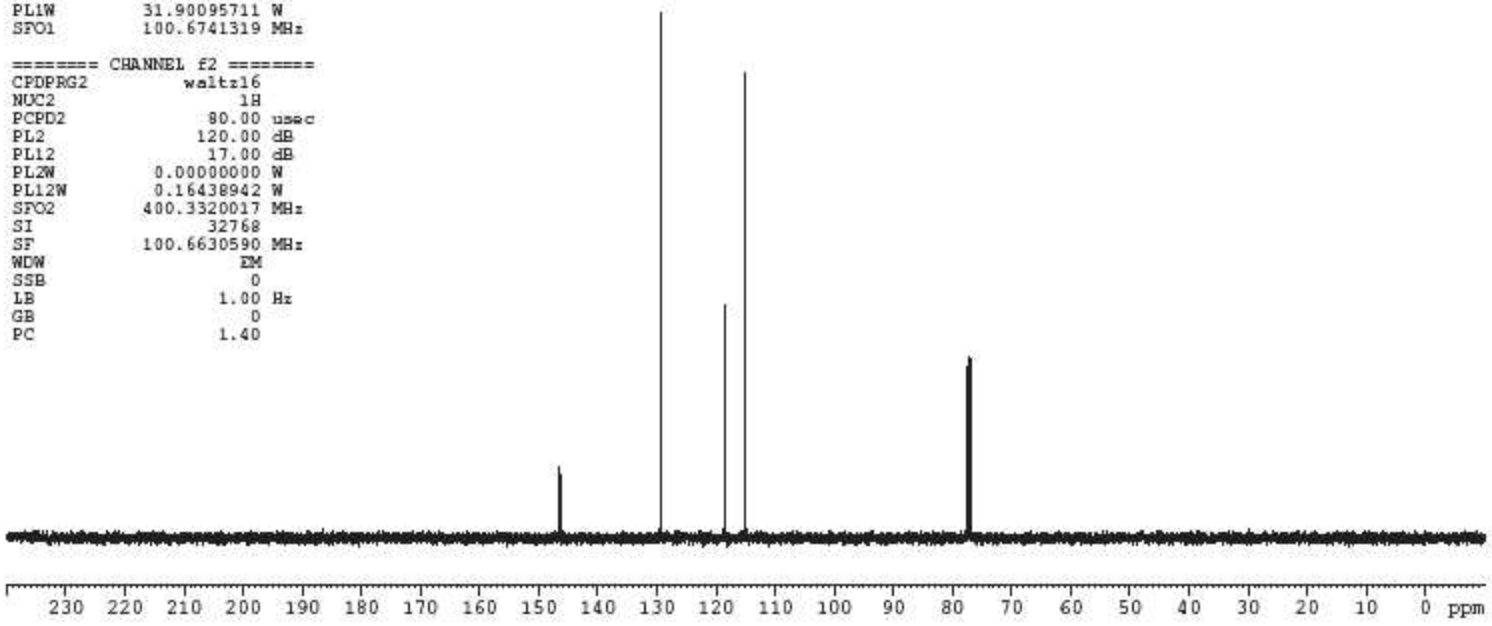
Peak	(F1) [ppm]	(F1) [Hz]	Intensity [abs]	Annotation
1	146.4153	14738.6120	8117957.50	
2	129.3275	13018.5018	35633936.75	
3	118.5987	11938.5079	22903399.75	
4	115.1673	11593.0927	38541407.12	

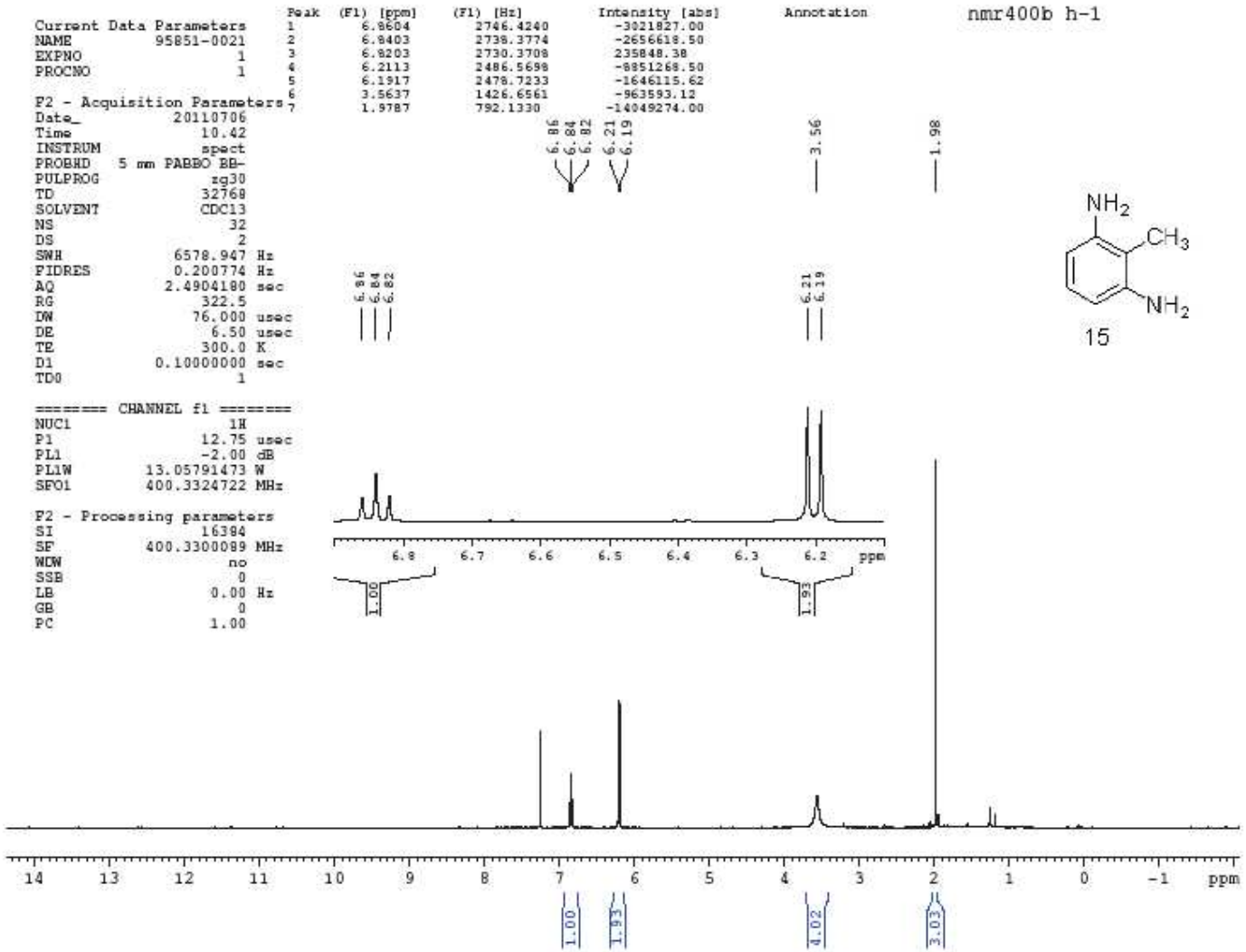
nmr400b c-13

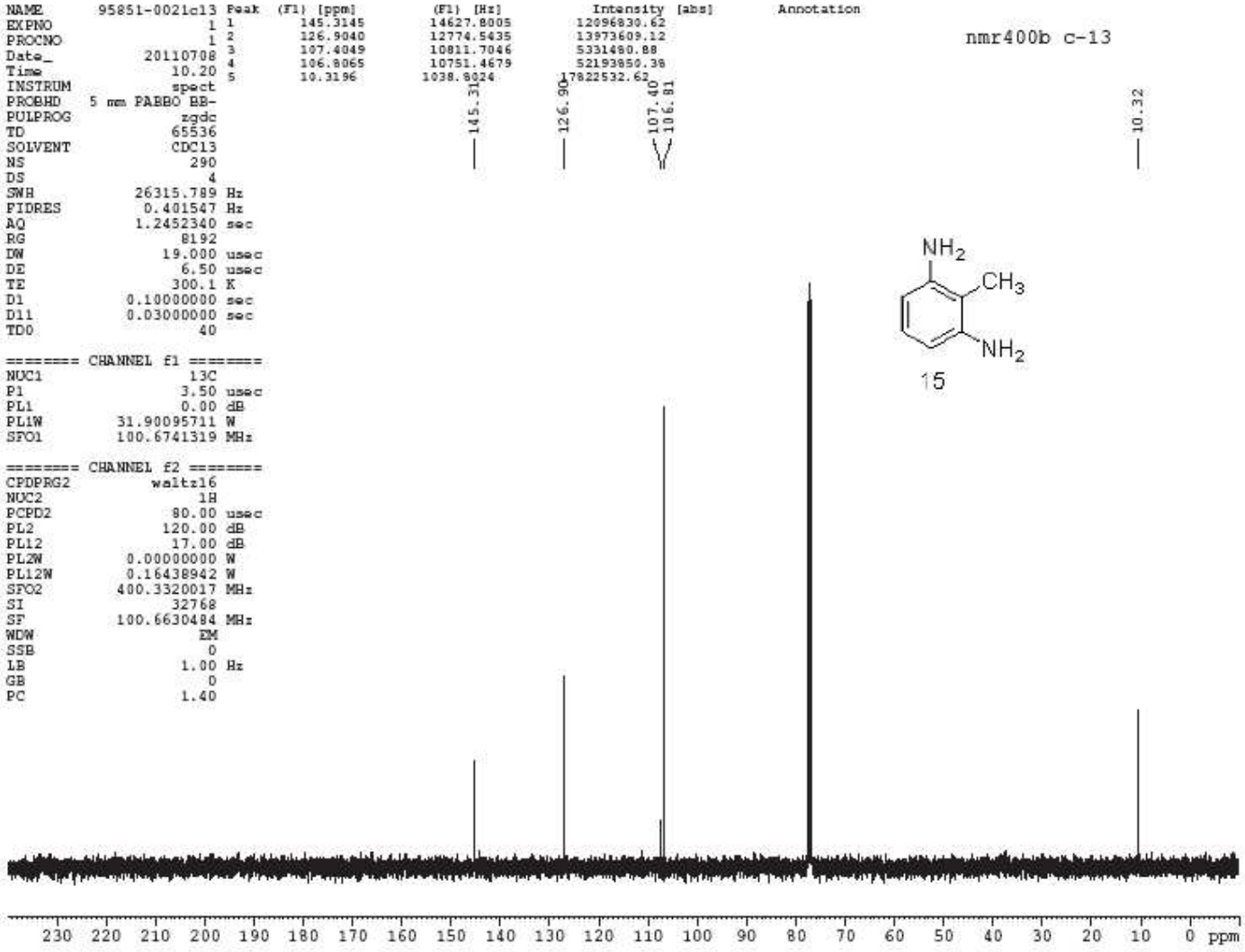
146.42
129.33
118.60
115.17

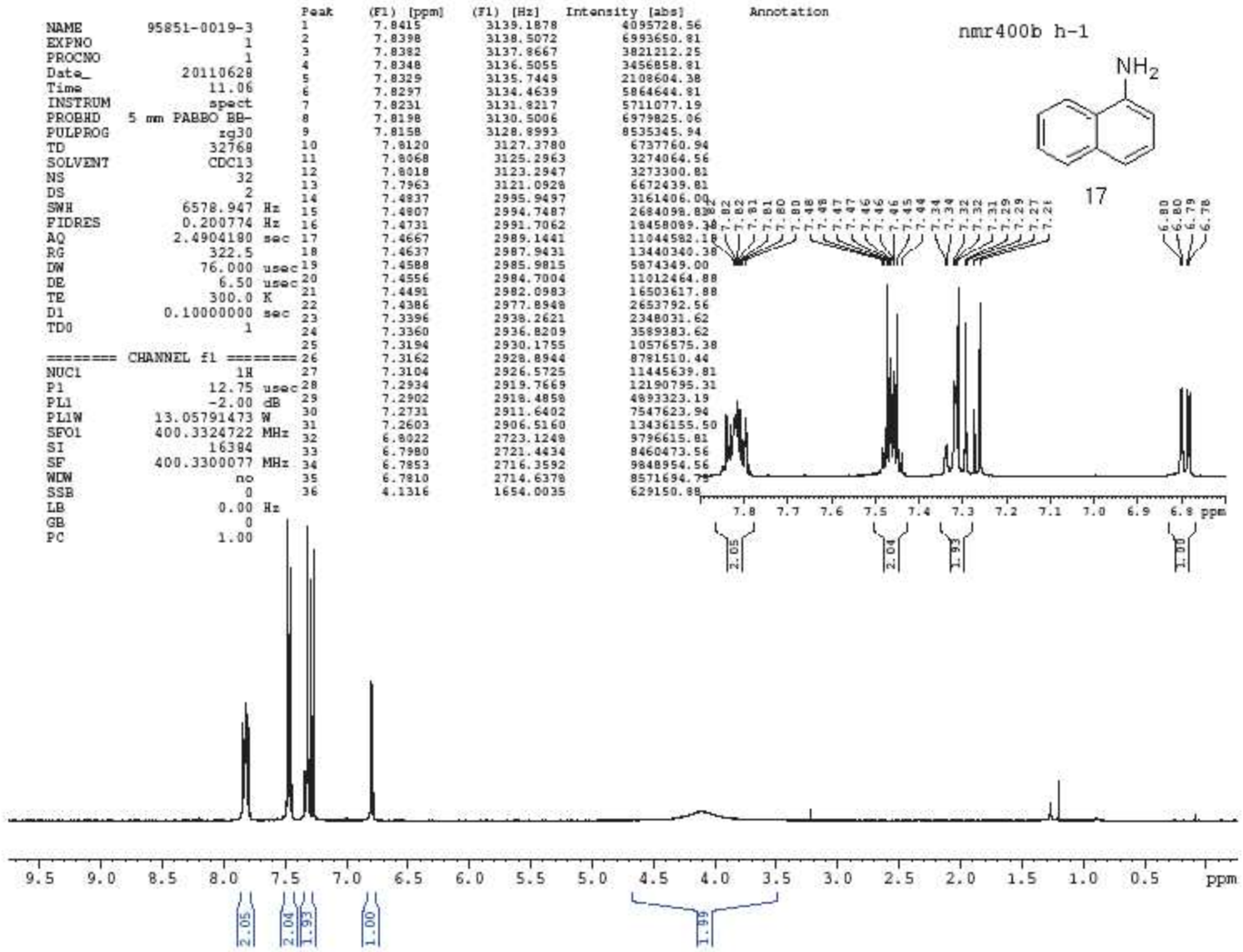


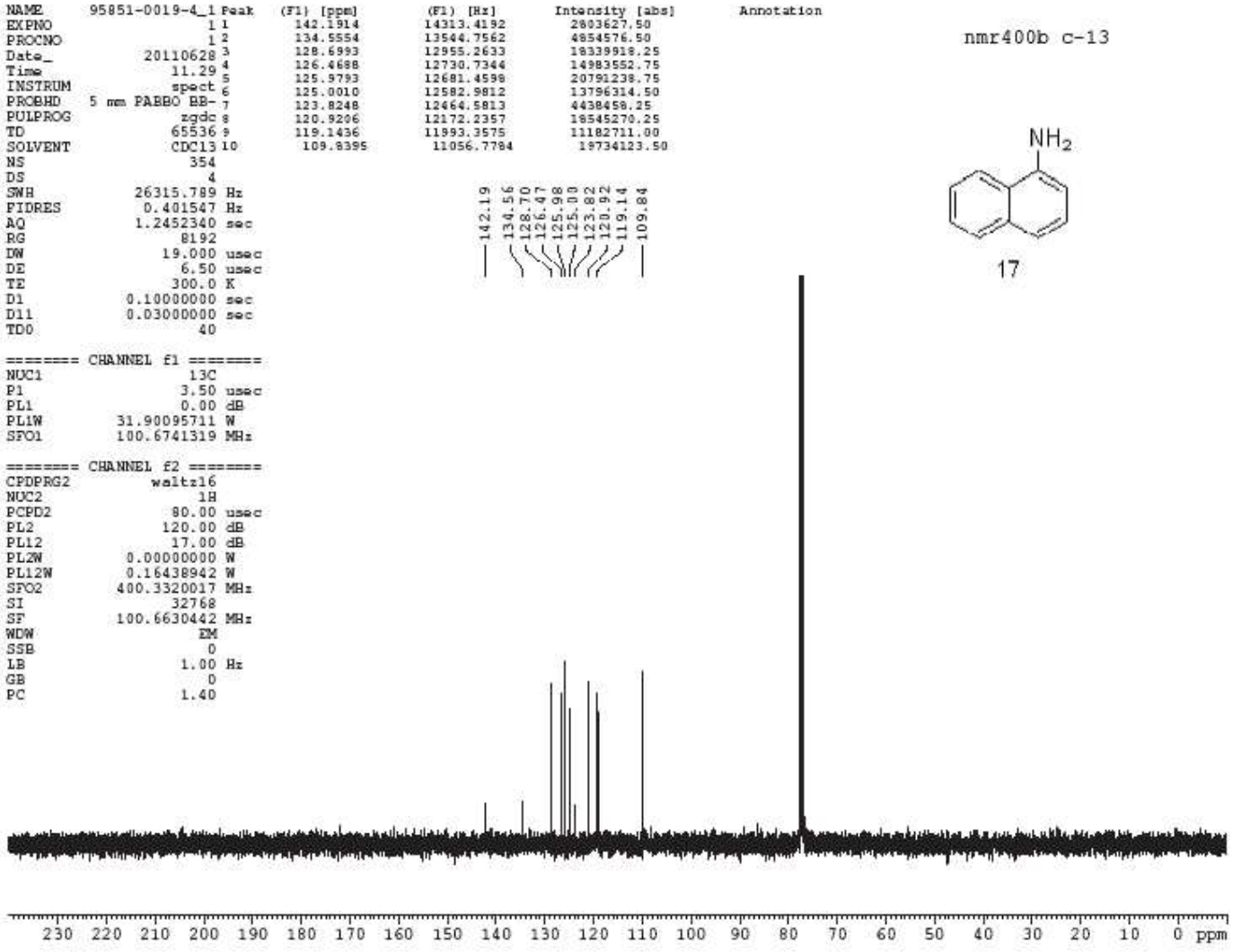
11

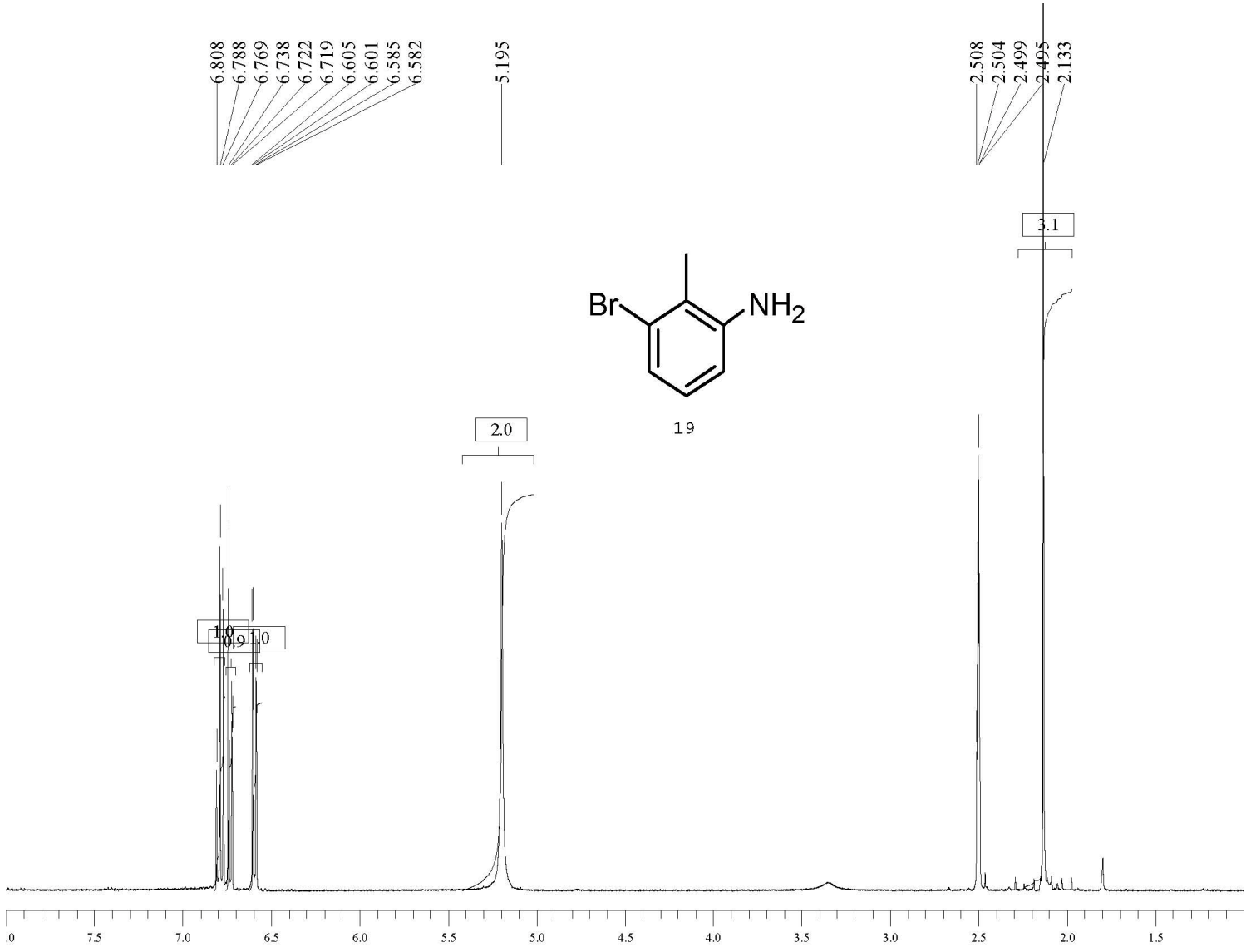


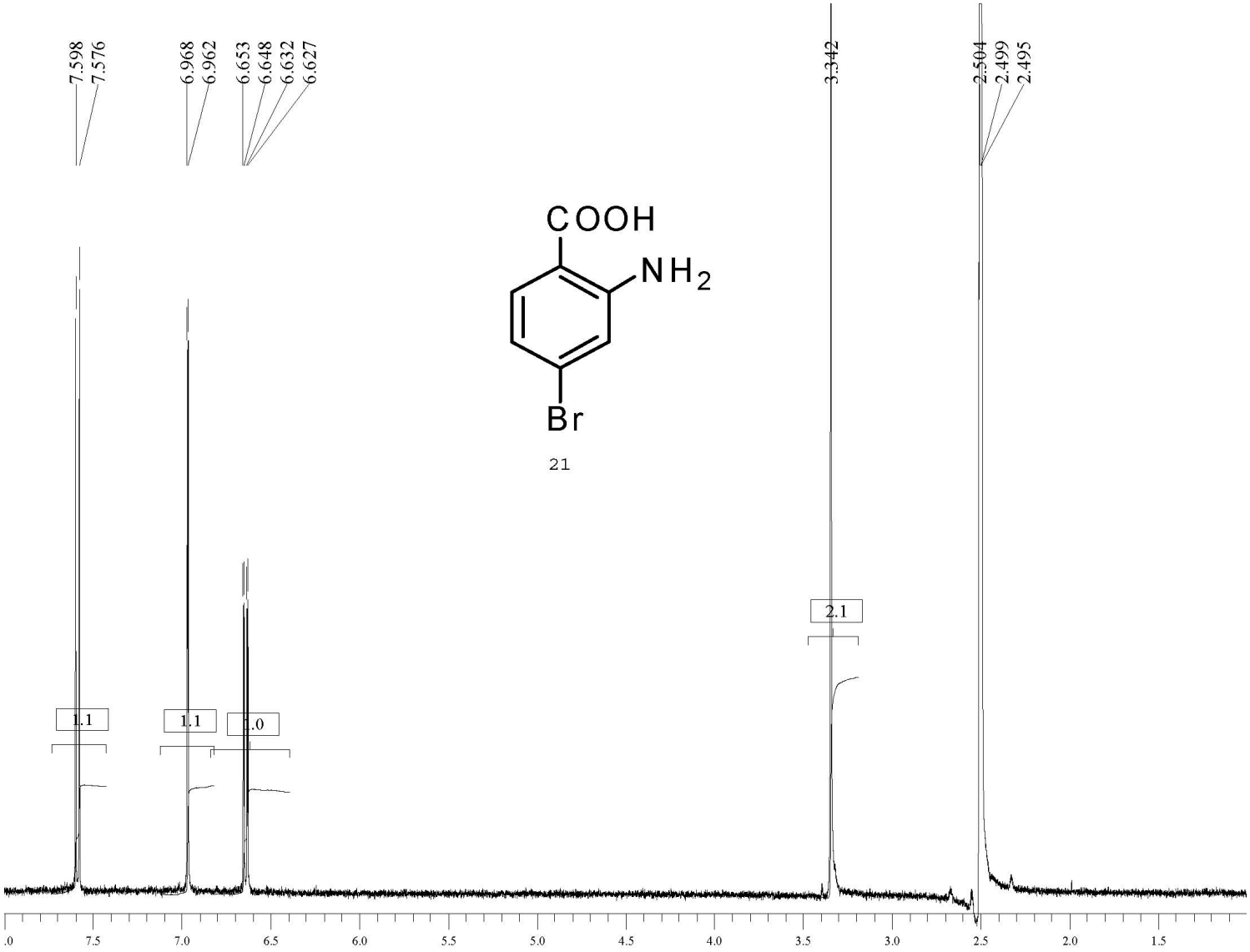

nmr400b h-1
Current Data Parameters
NAME 95851-0021
EXPNO 1
PROCNO 1
P2 - Acquisition Parameters
Date_ 20110706
Time 10.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDC13
NS 32
DS 2
SWH 6578.947 Hz
FIDRES 0.200774 Hz
AQ 2.4904180 sec
RG 322.5
DW 76.000 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.75 usec
PL1 -2.00 dB
PL1W 13.05791473 W
SFO1 400.3324722 MHz
P2 - Processing parameters
SI 16384
SF 400.3300089 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
Peak (F1) [ppm] (F1) [Hz] Intensity [abs] Annotation
1 6.8604 2746.4240 -3021827.00
2 6.8403 2738.3774 -2656618.50
3 6.8203 2730.3708 235848.38
4 6.2113 2486.5698 -8851268.50
5 6.1917 2478.7233 -1646115.62
6 3.5637 1426.6561 -963593.12
7 1.9787 792.1330 -14049274.00
6.86
6.84
6.82
6.21
6.19
3.56
1.98
NH2
CH3
NH2
15
1.00
1.93
ppm
1.00
1.93
4.02
3.03
ppm

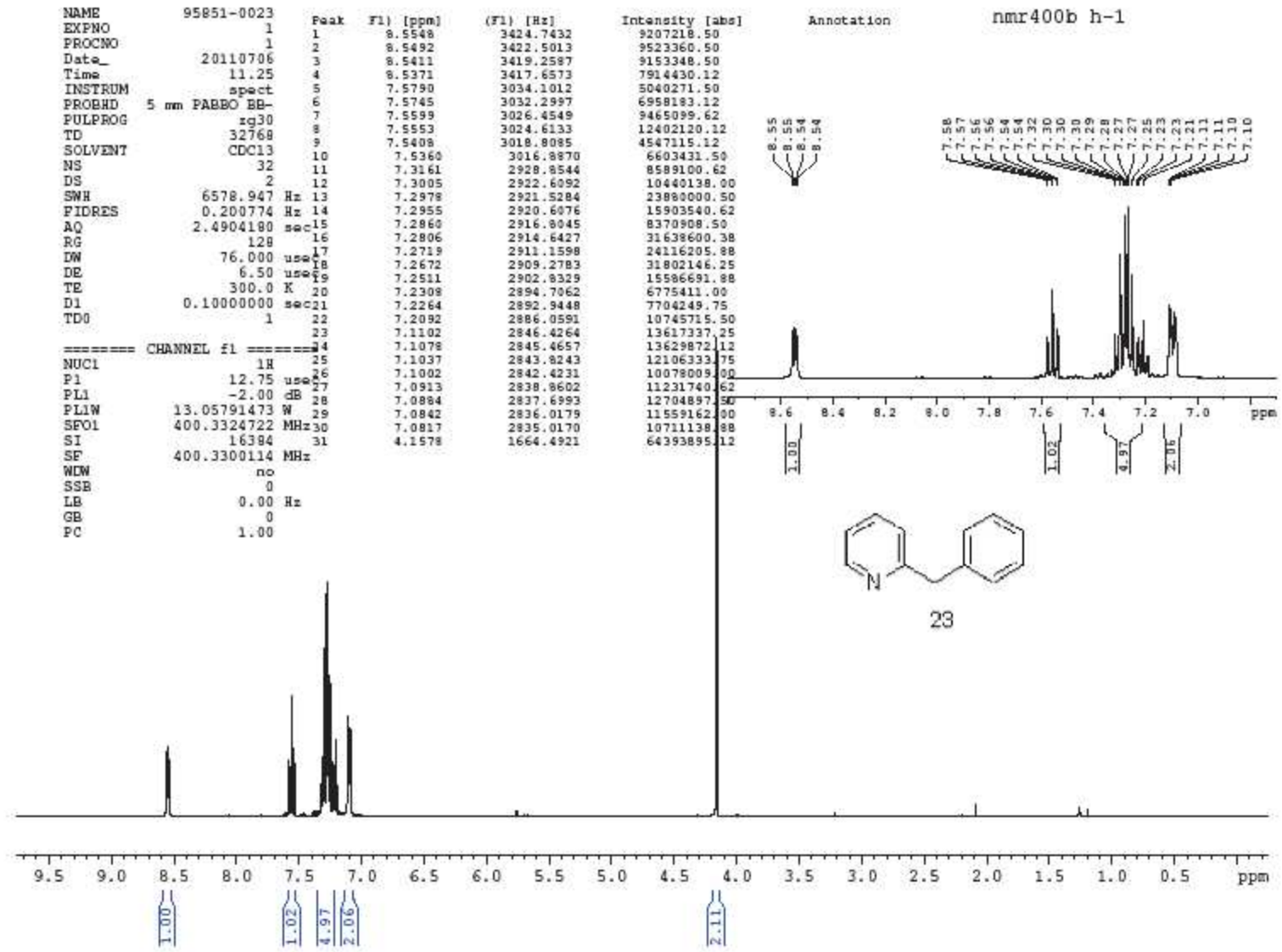

NAME 95851-0021c13
EXPNO 1
PROCNO 1
Date_ 20110708
Time 10.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgdc
TD 65536
SOLVENT CDCl3
NS 290
DS 4
SWH 26315.789 Hz
FIDRES 0.401547 Hz
AQ 1.2452340 sec
RG 8192
DW 19.000 usec
DE 6.50 usec
TE 300.1 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 40
======== CHANNEL f1 ========
NUC1 13C
P1 3.50 usec
PL1 0.00 dB
PL1W 31.90095711 W
SFO1 100.6741319 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 17.00 dB
PL2W 0.00000000 W
PL12W 0.16438942 W
SFO2 400.3320017 MHz
SI 32768
SF 100.6630484 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Peak (F1) [ppm] (F1) [Hz] Intensity [abs] Annotation
1 145.3145 14627.8005 12096830.62
2 126.9040 12774.5435 13973609.12
3 107.4049 10811.7046 5331480.88
4 106.8065 10751.4679 52193850.38
5 10.3196 1038.8024 17822532.62
145.31
126.90
107.40
106.81
10.32
nmr400b c-13
NH2
CH3
NH2
15
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

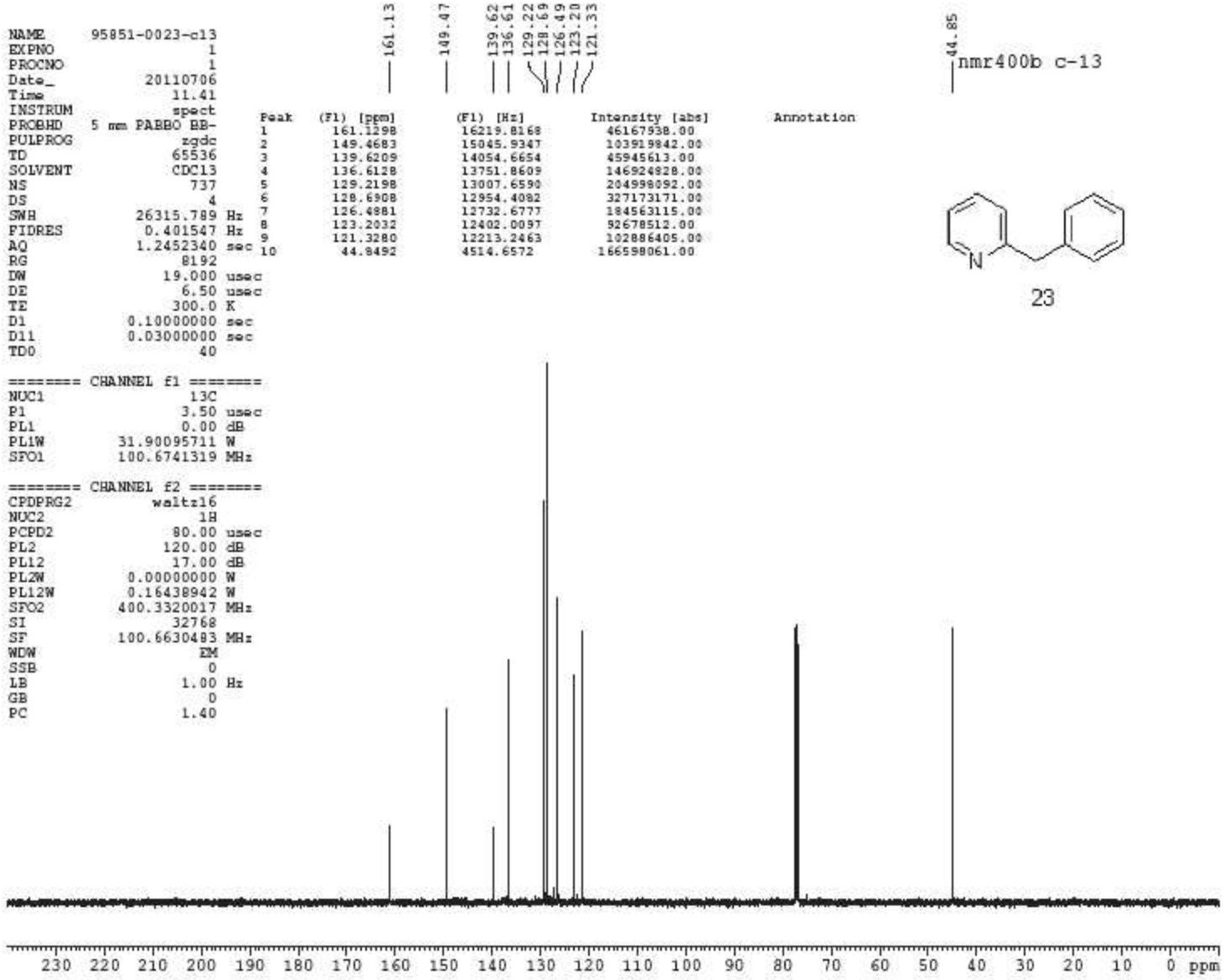

NAME 95851-0019-3
EXPNO 1
PROCNO 1
Date_ 20110628
Time 11.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6578.947 Hz
FIDRES 0.200774 Hz
AQ 2.4904180 sec
RG 322.5
DW 76.000 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.75 usec
PL1 -2.00 dB
PL1W 13.05791473 W
SFO1 400.3324722 MHz
SI 16384
SF 400.3300077 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
Peak (F1) [ppm] (F1) [Hz] Intensity [abs] Annotation
1 7.8415 3139.1878 4095728.56
2 7.8398 3138.5072 6993650.81
3 7.8382 3137.8667 3821212.25
4 7.8348 3136.5055 3456858.81
5 7.8329 3135.7449 2108604.38
6 7.8297 3134.4639 5864644.81
7 7.8231 3131.8217 5711077.19
8 7.8198 3130.5006 6979825.06
9 7.8158 3128.8993 8535345.94
10 7.8120 3127.3780 6737760.94
11 7.8068 3125.2963 3274064.56
12 7.8018 3123.2947 3273300.81
13 7.7963 3121.0928 6672439.81
14 7.4837 2995.9497 3161406.00
15 7.4807 2994.7487 2684098.88
16 7.4731 2991.7062 18458089.38
17 7.4667 2989.1441 11044582.18
18 7.4637 2987.9431 13440340.38
19 7.4588 2985.9815 5874349.00
20 7.4556 2984.7004 11012464.88
21 7.4491 2982.0983 16503617.88
22 7.4386 2977.8948 2653792.56
23 7.3396 2938.2621 2348031.62
24 7.3360 2936.8209 3589383.62
25 7.3194 2930.1755 10576575.38
26 7.3162 2928.8944 8781510.44
27 7.3104 2926.5725 11445639.81
28 7.2934 2919.7669 12190795.31
29 7.2902 2918.4858 4893323.19
30 7.2731 2911.6402 7547623.94
31 7.2603 2906.5160 13436155.50
32 6.8022 2723.1248 9796615.81
33 6.7980 2721.4434 8460473.56
34 6.7853 2716.3592 9848954.56
35 6.7810 2714.6378 8571694.75
36 4.1316 1654.0035 629150.88
nmr400b h-1
NH2
17
7.82 7.82 7.81 7.81 7.80 7.80 7.48 7.47 7.47 7.46 7.46 7.45 7.44 7.34 7.32 7.32 7.31 7.29 7.29 7.27 7.21
6.80 6.80 6.79 6.78
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 ppm
2.05 2.04 1.93 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.05 2.04 1.93 1.00 1.99


NAME 95851-0019-4_1
EXPNO 1
PROCNO 1
Date_ 20110628
Time 11.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgdc
TD 65536
SOLVENT CDC13
NS 354
DS 4
SWH 26315.789 Hz
FIDRES 0.401547 Hz
AQ 1.2452340 sec
RG 8192
DW 19.000 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 40
======== CHANNEL f1 ========
NUC1 13C
P1 3.50 usec
PL1 0.00 dB
PL1W 31.90095711 W
SFO1 100.6741319 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 17.00 dB
PL2W 0.00000000 W
PL12W 0.16438942 W
SFO2 400.3320017 MHz
SI 32768
SF 100.6630442 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Peak (F1) [ppm] (F1) [Hz] Intensity [abs] Annotation
1 142.1914 14313.4192 2803627.50
2 134.5554 13544.7562 4854576.50
3 128.6993 12955.2633 18339918.25
4 126.4688 12730.7344 14983552.75
5 125.9793 12681.4598 20791238.75
6 125.0010 12582.9812 13796314.50
7 123.8248 12464.5813 4438458.25
8 120.9206 12172.2357 18545270.25
9 119.1436 11993.3575 11182711.00
10 109.8395 11056.7784 19734123.50
142.19
134.56
128.70
126.47
125.98
125.00
123.82
120.92
119.14
109.84
nmr400b c-13
NH2
17
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


6.808
6.788
6.769
6.738
6.722
6.719
6.605
6.601
6.585
6.582
5.195
2.508
2.504
2.499
2.495
2.133
3.1
Br
NH2
19
2.0
1.0
0.9
1.0
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

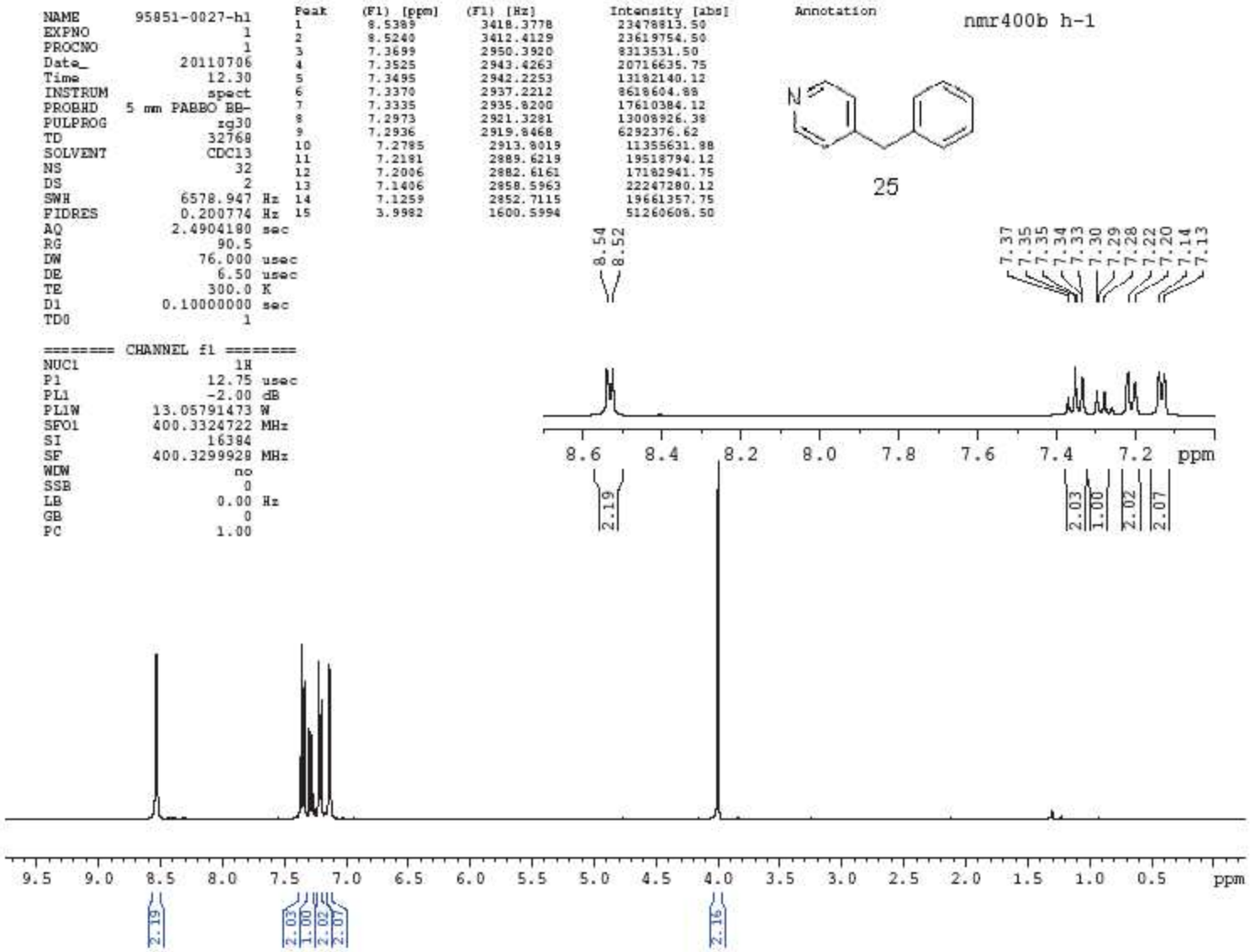

7.598
7.576
6.968
6.962
6.653
6.648
6.632
6.627
3.342
2.504
2.499
2.495
COOH
NH2
Br
21
1.1
1.1
2.0
2.1
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


NAME 95851-0023
EXPNO 1
PROCNO 1
Date_ 20110706
Time 11.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6578.947 Hz
FIDRES 0.200774 Hz
AQ 2.4904180 sec
RG 128
DW 76.000 use
DE 6.50 use
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.75 use
PL1 -2.00 dB
PL1W 13.05791473 W
SFO1 400.3324722 MHz
SI 16384
SF 400.3300114 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
Peak f1) [ppm] (f1) [Hz] Intensity [abs] Annotation
1 8.5548 3424.7432 9207218.50
2 8.5492 3422.5013 9523360.50
3 8.5411 3419.2587 9153348.50
4 8.5371 3417.6573 7914430.12
5 7.5790 3034.1012 5040271.50
6 7.5745 3032.2997 6958183.12
7 7.5599 3026.4549 9465099.62
8 7.5553 3024.6133 12402120.12
9 7.5408 3018.8085 4547115.12
10 7.5360 3016.8870 6603431.50
11 7.3161 2928.8544 8589100.62
12 7.3005 2922.6092 10440138.00
13 7.2978 2921.5284 23880000.50
14 7.2955 2920.6076 15903540.62
15 7.2860 2916.8045 8370908.50
16 7.2806 2914.6427 31638600.38
17 7.2719 2911.1598 24116205.88
18 7.2672 2909.2783 31802146.25
19 7.2511 2902.8329 15586691.88
20 7.2308 2894.7062 6775411.00
21 7.2264 2892.9448 7704249.75
22 7.2092 2886.0591 10745715.50
23 7.1102 2846.4264 13617337.25
24 7.1078 2845.4657 13629872.12
25 7.1037 2843.8243 12106333.75
26 7.1002 2842.4231 10078009.00
27 7.0913 2838.8602 11231740.62
28 7.0884 2837.6993 12704897.50
29 7.0842 2836.0179 11559162.00
30 7.0817 2835.0170 10711138.88
31 4.1578 1664.4921 6439389.12
nmr400b h-1
8.55 8.55 8.54 8.54
7.58 7.57 7.56 7.56 7.54 7.54 7.32 7.30 7.30 7.30 7.29 7.28 7.27 7.27 7.25 7.23 7.23 7.21 7.11 7.11 7.10 7.10
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 ppm
1.00 1.02 4.97 2.06
N
23
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.02 4.97 2.06 2.11



NAME	95851-0023-c13
EXPNO	1
PROCNO	1
Date_	20110706
Time	11.41
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc
TD	65536
SOLVENT	CDCl3
NS	737
DS	4
SWH	26315.789 Hz
FIDRES	0.401547 Hz
AQ	1.2452340 sec
RG	8192
DW	19.000 usec
DE	6.50 usec
TE	300.0 K
D1	0.10000000 sec
D11	0.03000000 sec
TD0	40
======== CHANNEL f1 ========	
NUC1	13C
P1	3.50 usec
PL1	0.00 dB
PL1W	31.90095711 W
SFO1	100.6741319 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	120.00 dB
PL12	17.00 dB
PL2W	0.00000000 W
PL12W	0.16438942 W
SFO2	400.3320017 MHz
SI	32768
SF	100.6630483 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Peak	(F1) [ppm]	(F1) [Hz]	Intensity [abs]	Annotation
1	161.1298	16219.8168	46167938.00	
2	149.4683	15045.9347	103919842.00	
3	139.6209	14054.6654	45945613.00	
4	136.6128	13751.8609	146924828.00	
5	129.2198	13007.6590	204998092.00	
6	128.6908	12954.4082	327173171.00	
7	126.4881	12732.6777	184563115.00	
8	123.2032	12402.0097	92678512.00	
9	121.3280	12213.2463	102886405.00	
10	44.8492	4514.6572	166598061.00	

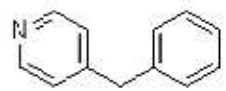

NAME 95851-0027-h1
EXPNO 1
PROCNO 1
Date_ 20110706
Time 12.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6578.947 Hz
FIDRES 0.200774 Hz
AQ 2.4904180 sec
RG 90.5
DW 76.000 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.75 usec
PL1 -2.00 dB
PL1W 13.05791473 W
SFO1 400.3324722 MHz
SI 16384
SF 400.3299928 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
Peak (F1) [ppm] (F1) [Hz] Intensity [abs]
1 8.5389 3418.3778 23478813.50
2 8.5240 3412.4129 23619754.50
3 7.3699 2950.3920 8313531.50
4 7.3525 2943.4263 20716635.75
5 7.3495 2942.2253 13182140.12
6 7.3370 2937.2212 8618604.88
7 7.3335 2935.8200 17610384.12
8 7.2973 2921.3281 13008926.38
9 7.2936 2919.8468 6292376.62
10 7.2785 2913.8019 11355631.88
11 7.2181 2889.6219 19518794.12
12 7.2006 2882.6161 17182941.75
13 7.1406 2858.5963 22247280.12
14 7.1259 2852.7115 19661357.75
15 3.9982 1600.5994 51260608.50
Annotation
nmr400b h-1
N
25
8.54
8.52
7.37
7.35
7.35
7.34
7.33
7.30
7.29
7.28
7.22
7.20
7.14
7.13
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
2.19
2.03
1.00
2.02
2.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.19
2.03
1.00
2.02
2.07
2.16

NAME	95851-0027-c13
EXPNO	1
PROCNO	1
Date_	20110706
Time	12.45
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc
TD	65536
SOLVENT	CDCl3
NS	222
DS	4
SWH	26315.789 Hz
FIDRES	0.401547 Hz
AQ	1.2452340 sec
RG	8192
DW	19.000 usec
DE	6.50 usec
TE	300.0 K
D1	0.10000000 sec
D11	0.03000000 sec
TD0	40
======= CHANNEL f1 =======	
NUC1	13C
P1	3.50 usec
PL1	0.00 dB
PL1W	31.90095711 W
SFO1	100.6741319 MHz
======= CHANNEL f2 =======	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	120.00 dB
PL12	17.00 dB
PL2W	0.00000000 W
PL12W	0.16438942 W
SFO2	400.3320017 MHz
SI	32768
SF	100.6630519 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Peak	(F1) [ppm]	(F1) [Hz]	Intensity [abs]	Annotation
1	149.9198	15091.3846	76543608.50	
2	138.9397	13986.0942	20083338.00	
3	129.1107	12996.6771	136658617.50	
4	128.8069	12966.0957	132380718.00	
5	126.7562	12759.6659	77555248.50	
6	124.2513	12507.5151	99006754.00	
7	41.3138	4158.7732	51452585.00	

nmr400b c-13

149.92 138.94 129.11 128.81 126.76 124.25 41.31



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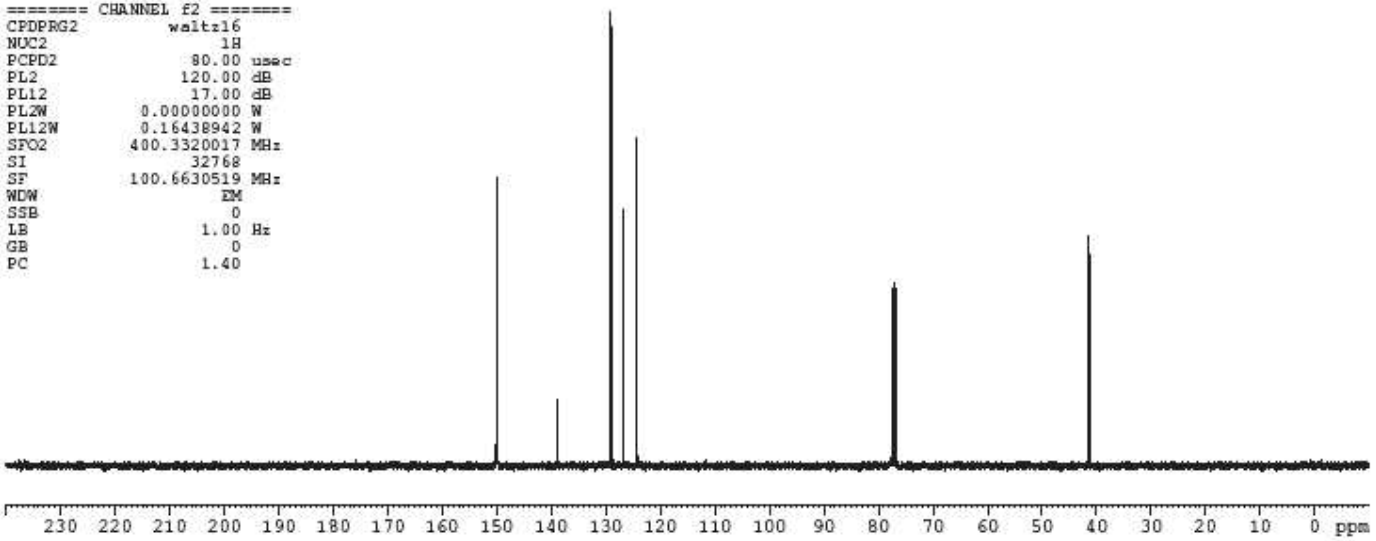
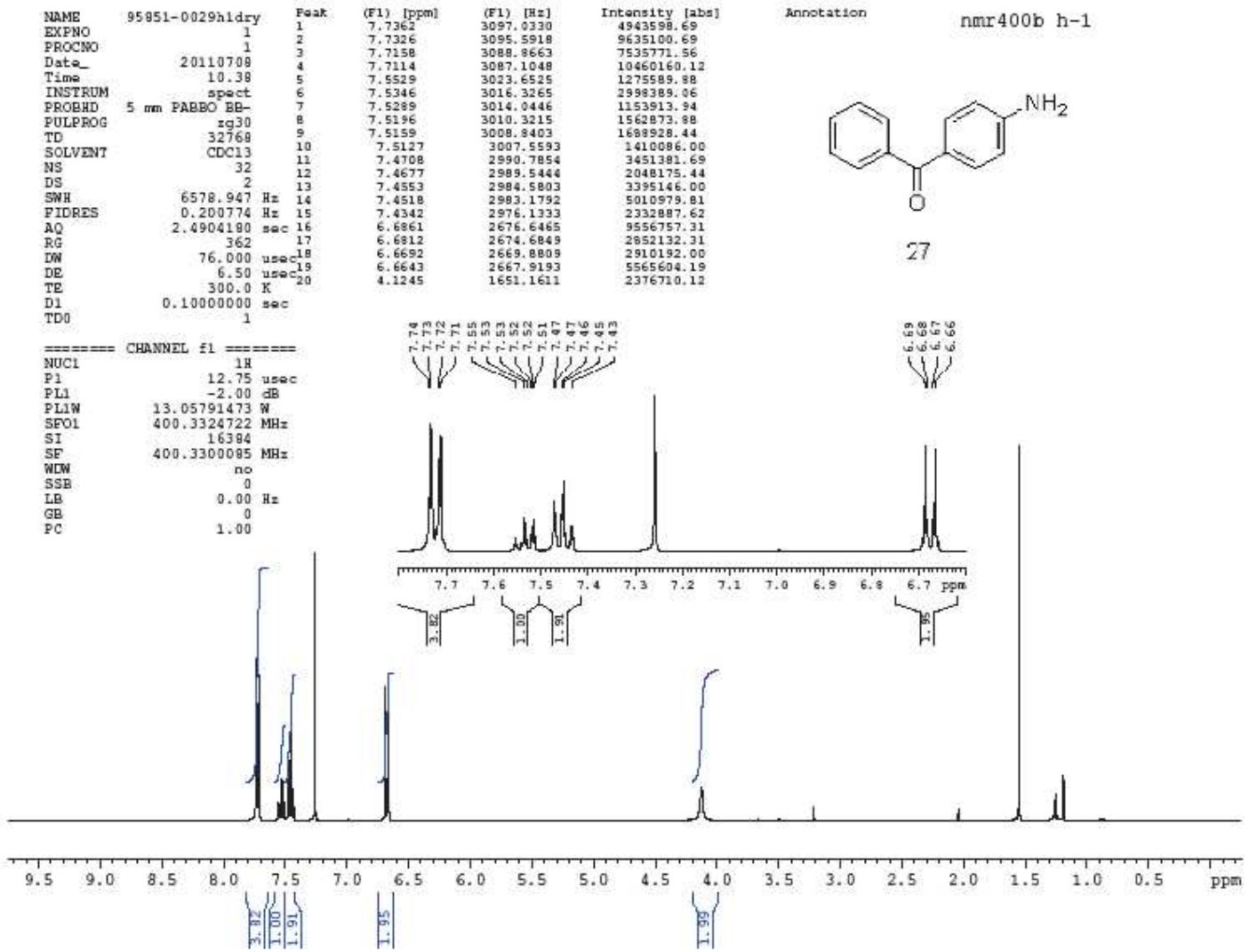



NAME 95951-0029h1dry
EXPNO 1
PROCNO 1
Date_ 20110708
Time 10.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6578.947 Hz
FIDRES 0.200774 Hz
AQ 2.4904180 sec
RG 362
DW 76.000 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.75 usec
PL1 -2.00 dB
PL1W 13.05791473 W
SFO1 400.3324722 MHz
SI 16384
SF 400.3300085 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
Peak (F1) [ppm] (F1) [Hz] Intensity [abs] Annotation
1 7.7362 3097.0330 4943598.69
2 7.7326 3095.5918 9635100.69
3 7.7158 3088.8663 7535771.56
4 7.7114 3087.1048 10460160.12
5 7.5529 3023.6525 1275589.88
6 7.5346 3016.3265 2998389.06
7 7.5289 3014.0446 1153913.94
8 7.5196 3010.3215 1562873.88
9 7.5159 3008.8403 1688928.44
10 7.5127 3007.5593 1410086.00
11 7.4708 2990.7854 3451381.69
12 7.4677 2989.5444 2048175.44
13 7.4553 2984.5803 3395146.00
14 7.4518 2983.1792 5010979.81
15 7.4342 2976.1333 2332887.62
16 6.6861 2676.6465 9556757.31
17 6.6812 2674.6849 2852132.31
18 6.6692 2669.8809 2910192.00
19 6.6643 2667.9193 5565604.19
20 4.1245 1651.1611 2376710.12
nmr400b h-1
NH2
O
27
7.74 7.73 7.72 7.71 7.55 7.53 7.53 7.52 7.52 7.51 7.47 7.47 7.46 7.45 7.43
6.69 6.68 6.67 6.66
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 ppm
3.82 1.00 1.91 1.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.82 1.00 1.91 1.95 1.99

NAME	95851-0029c13concent
EXPNO	1
PROCNO	1
Date_	20110708
Time	14.04
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc
TD	65536
SOLVENT	CDCl3
NS	460
DS	4
SWH	26315.789 Hz
FIDRES	0.401547 Hz
AQ	1.2452340 sec
RG	8192
DW	19.000 usec
DE	6.50 usec
TE	300.0 K
D1	0.10000000 sec
D11	0.03000000 sec
TD0	40

======== CHANNEL f1 ========

NUC1	13C
P1	3.50 usec
PL1	0.00 dB
PL1W	31.90095711 W
SFO1	100.6741319 MHz

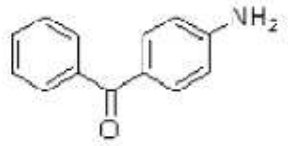
======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	120.00 dB
PL12	17.00 dB
PL2W	0.00000000 W
PL12W	0.16438942 W
SFO2	400.3320017 MHz
SI	32768
SF	100.6630445 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Peak	(F1) [ppm]	(F1) [Hz]	Intensity [abs]	Annotation
1	195.4182	19671.3910	3793209.00	
2	151.0441	15204.5590	6007874.50	
3	139.0365	13995.8374	8304534.25	
4	133.0701	13395.2414	36492441.50	
5	131.5306	13240.2706	18375673.00	
6	129.6617	13052.1415	57440292.75	
7	128.2095	12905.9586	55269514.25	
8	127.6362	12848.2485	8365140.00	
9	113.7838	11453.8237	49266583.50	

195.42 151.04 139.04 133.07 131.53 129.66 128.21 127.64 113.78

nmr400b c-13



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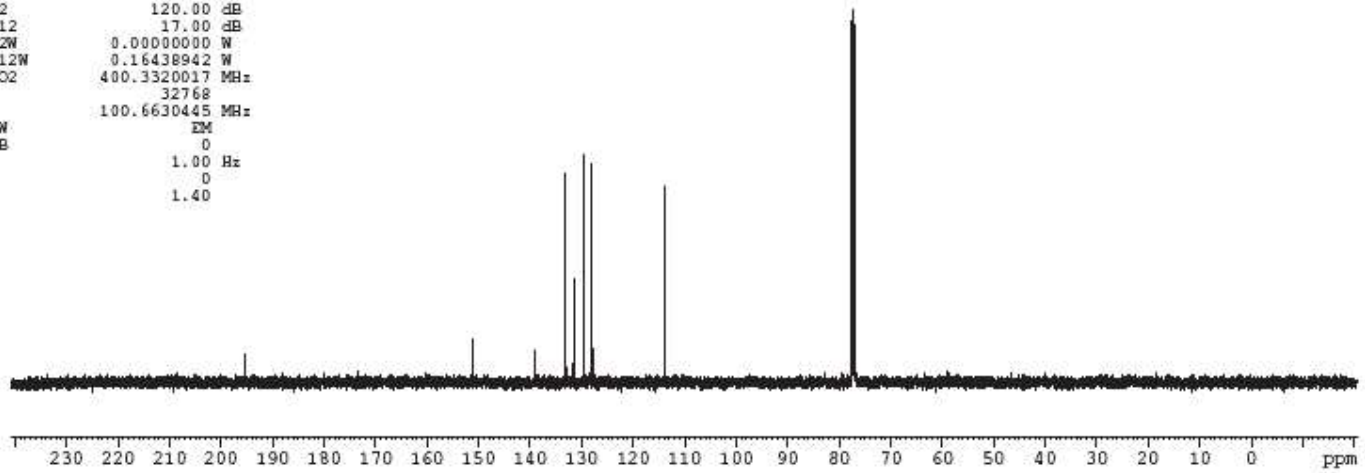
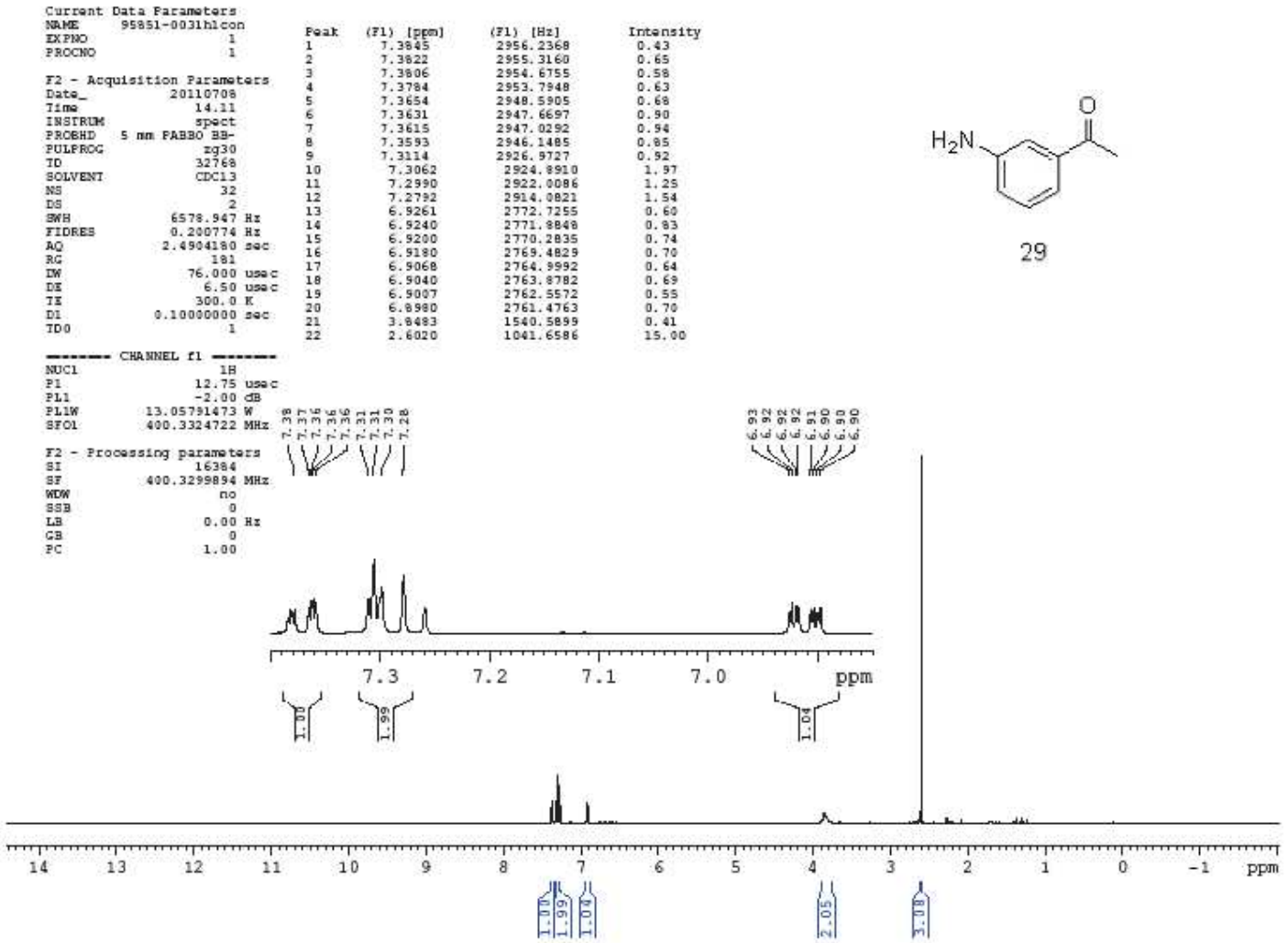
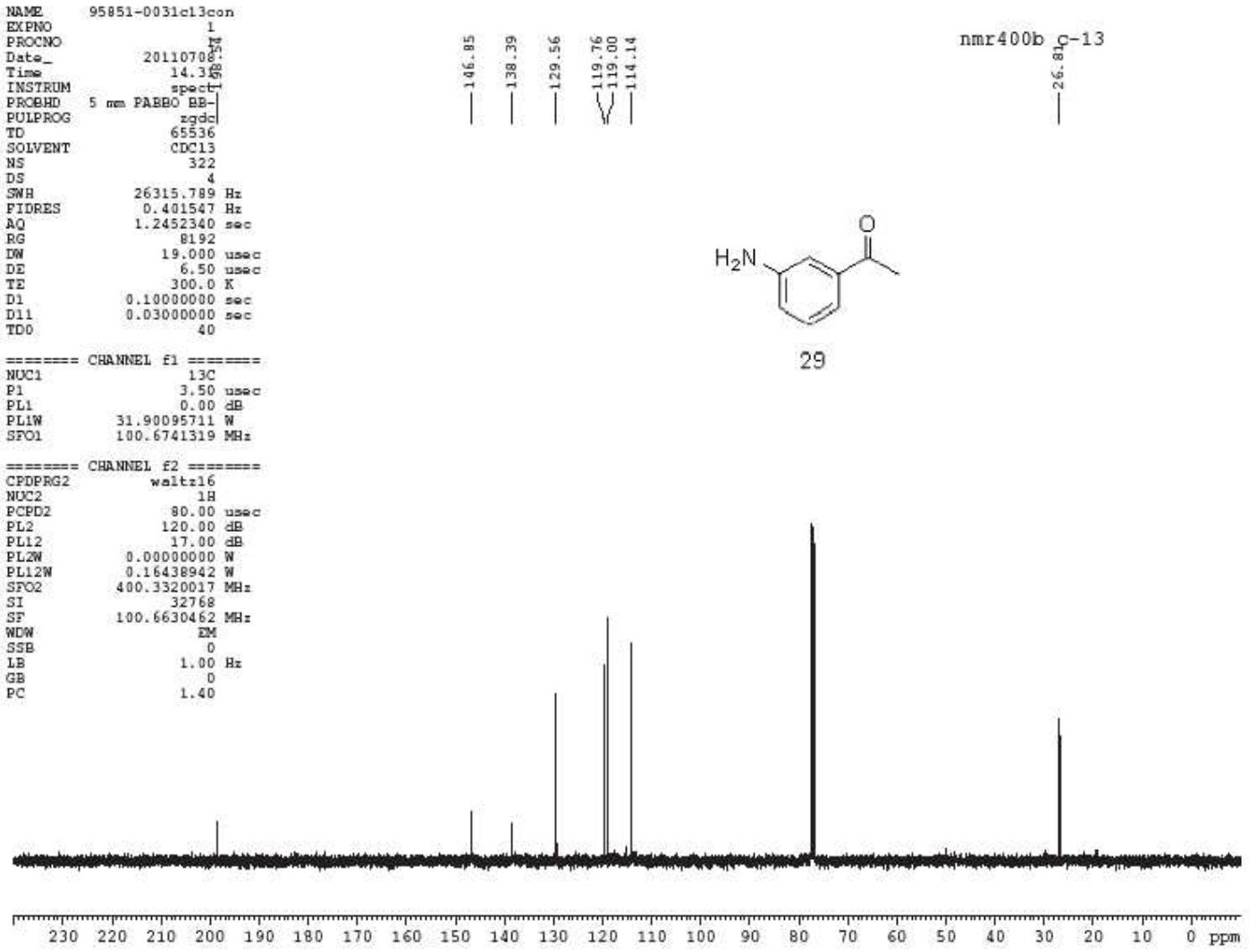



Current Data Parameters
NAME 95851-0031hlcon
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110708
Time 14.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 6578.947 Hz
FIDRES 0.200774 Hz
AQ 2.4904180 sec
RG 181
DW 76.000 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 12.75 usec
PL1 -2.00 dB
PL1W 13.05791473 W
SFO1 400.3324722 MHz
F2 - Processing parameters
SI 16384
SF 400.3299894 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
Peak (F1) [ppm] (F1) [Hz] Intensity
1 7.3845 2956.2368 0.43
2 7.3822 2955.3160 0.65
3 7.3806 2954.6755 0.58
4 7.3784 2953.7948 0.63
5 7.3654 2948.5905 0.68
6 7.3631 2947.6697 0.90
7 7.3615 2947.0292 0.94
8 7.3593 2946.1485 0.85
9 7.3114 2926.9727 0.92
10 7.3062 2924.8910 1.97
11 7.2990 2922.0086 1.25
12 7.2792 2914.0821 1.54
13 6.9261 2772.7255 0.60
14 6.9240 2771.8848 0.83
15 6.9200 2770.2835 0.74
16 6.9180 2769.4829 0.70
17 6.9068 2764.9992 0.64
18 6.9040 2763.8782 0.69
19 6.9007 2762.5572 0.55
20 6.8980 2761.4763 0.70
21 3.8483 1540.5899 0.41
22 2.6020 1041.6586 15.00
H2N
O
29
7.38 7.37 7.36 7.36 7.36 7.31 7.31 7.30 7.28
6.93 6.92 6.92 6.92 6.92 6.91 6.90 6.90 6.90 6.90
7.3 7.2 7.1 7.0 ppm
1.00 1.99 1.04
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
1.00 1.99 1.04 2.05 3.08


NAME 95851-0031c13con
EXPNO 1
PROCNO 1
Date_ 20110708
Time 14.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgdc
TD 65536
SOLVENT CDC13
NS 322
DS 4
SWH 26315.789 Hz
FIDRES 0.401547 Hz
AQ 1.2452340 sec
RG 8192
DW 19.000 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 40
======== CHANNEL f1 ========
NUC1 13C
P1 3.50 usec
PL1 0.00 dB
PL1W 31.90095711 W
SFO1 100.6741319 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 17.00 dB
PL2W 0.00000000 W
PL12W 0.16438942 W
SFO2 400.3320017 MHz
SI 32768
SF 100.6630462 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
146.85
138.39
129.56
119.76
119.00
114.14
77.54
77.18
76.81
26.81
nmr400b c-13
H2N
O
29
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm