Palladium-Catalyzed Coupling of Ammonia with Aryl Chlorides, Bromides, Iodides and Sulfonates: A General Method for the Preparation of Primary Arylamines

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SUPPORTING INFORMATION

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GENERAL EXPERIMENTAL INFORMATION

General Procedures. Unless otherwise noted, all manipulations were conducted under an inert nitrogen atmosphere, using flame-dried glassware. A N_2-filled glovebox was used as indicated and had O_2 level below 10 ppm. Rotary evaporation was done at 25-30 ^oC. Flash column chromatography was performed as described by Still et al[1] on silica gel (Silicycle, 60 A pore size, 40-64 mm particle size, pH suspension 10%: 6.5-7.5). Analytical thin-layer chromatography was performed on glass plates coated with silica gel (Silicycle, 60 A pore size, 40-64 mm particle size) and visualized with both ultraviolet light and ninhydrin stain.

Materials. 1,4-Dioxane (anhydrous, 99.9%) was purchased from Aldrich and used without further purification. Ammonia in 1,4-dioxane solution (0.5 M) was either purchased from Aldrich and used without further purification or prepared according the procedure described below.[2] Ammonia (anhydrous, 99.99%) was purchased from Matheson Tri-Gas and used without further purification. Palladium bis(tri-*o*-tolylphosphine), $Pd[P(o\text{-}tol)_3]_2$, was prepared according to procedures reported by Tokutaro and Hartwig,[3] or was obtained as a gift from Johnson-Matthey. This complex is now commercially available from Johnson-Matthey and Aldrich. (*R*)-(-)-1-[(*S*)-2-(Dicyclohexylphosphino)ferrocenyl]ethyl-di-*tert*-butylphosphine (CyPF-*t*-Bu) was obtained as a gift from Solvias or can be purchased from Strem Chemicals. Sodium *tert*-butoxide was purchased from Sigma-Aldrich and used without further purification. All aryl halides and acyl chlorides were purchased from Aldrich and used without further purification. Analytically pure aryl tosylates were prepared by the procedure reported by Kubota and Nakada.[4] Solvents for filtration and chromatography were certified ACS grade.

Instruments. ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on Varian Unity-400 or 500 MHz (126 MHz, ^{13}C) spectrometers. Spectra are referenced either to residual chloroform (d = 7.26 ppm, ^1H; 77.0 ppm, ^{13}C), residual benzene (d = 7.15 ppm, ^1H; 128.62 ppm, ^{13}C), external standard reference $CFCl_3$ (d = 0 ppm, ^{19}F), or H_3PO_4 (d = 0 ppm, ^{31}P). Chemical shifts are reported in ppm. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and b (broad). Coupling constants, *J*, are reported in hertz, and integration is provided and assignments are indicated. Chemical shifts downfield of the standard are reported as positive values. Analytical gas chromatography (GC) was performed using a Hewlett-Packard 5890 Gas Chromatograph fitted with a flame ionization detector and a Hewlett-Packard HP5 (30m x 0.32 mm) capillary column. The injector temperature was 250 ^oC, and the detector temperature was 300 ^oC with a helium carrier gas flow of 16 mL/min. The column temperature program was as follows: 120 ^oC to 250 ^oC at 40 ^oC/min, then hold for 3 min for a total run time of 6.25 min. Retention times (t_R) were obtained using Agilent Chemstation software. Response factors were generated by triplicate runs of three molar ratios of the analyte to dodecane standard dissolved in ethyl acetate.

EXPERIMENTAL PROCEDURES

Procedure for the Preparation of 0.5 M Ammonia Solution in 1,4-Dioxane. Into an oven-dried 100-mL, Kjeldahl-shaped Schlenk flask (14/20, glass stopcock), contained a magnetic stir bar and fitted with a vacuum valve adapter (14/20 joints), was added 1,4-dioxane (50 mL). The entire assembly was sealed and fitted onto one end of a 250-mL gas bulb, and the other end of the gas bulb was connected to a vacuum manifold. 1,4-Dioxane was frozen, and the entire assembly was evacuated to a reduced pressure, ca. 50 mTorr. Ammonia (250 mL at 37.2 cmHg) was condensed into the flask 5 times. The solution was warmed to room temperature before use.

Preparation of 2.5 x 10^{-3} M M Stock Solution of Catalysts. $Pd[P(o\text{-}tol)_3]_2$ (0.0018 g, 0.0025 mmol) and CyPF-*t*-Bu (0.0014 g, 0.0025 mmol) were dissolved in 1,4-dioxane (1.0 mL). The resulting orange solution was stirred at room temperature for 5 minutes before immediate use.

General Procedure A: The Coupling of Ammonia with *o*-Substituted Aryl Bromides at 0.1 mol % Catalytic Loading (Table 2). Inside a N_2-filled glovebox, the 2.5 x 10^{-3} M stock solution of the catalyst (0.20 mL) containing $Pd[P(o\text{-}tol)_3]_2$ (0.00050 mmol) and CyPF-*t*-Bu (0.00050 mmol) was added to a mixture of NaO-*t*-Bu (1.4 equiv) and aryl halide (0.50 mmol) in a 20-mL scintillation vial. Ammonia

(5 mL of a 0.5 M solution in dioxane) was added via a gas-tight syringe. The vial was sealed with a Teflon-lined cap and removed from the glovebox and placed in an oil bath at 100 ^{o}C for 12 h. After GC analysis indicated full conversion of the aryl halide, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered through a plug of Celite. The product was purified by flash column chromatography.

General Procedure B: The Coupling of Ammonia with Aryl Halides Lacking Base-sensitive Functional Groups (Table 4 and 6). Into an oven-dried 25-mL round-bottomed flask containing a magnetic stir bar, Pd[P(*o*-tol)$_3$]$_2$ (0.5-2.0 mol %), CyPF-*t*-Bu (0.5-2 mol %), NaO-*t*-Bu (1.4 equiv) and the aryl halide (0.50 mmol) (if solid) were added. The flask was sealed with a rubber septum, evacuated and refilled with nitrogen three times. 1,4-Dioxane (5 - 8 mL) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane) were added via a gas-tight syringe. The aryl halide (0.50 mmol), if liquid, was added via a gas-tight syringe. The flask was then placed in an oil bath at 80-100 ^{o}C for 4-12 h. After GC analysis indicated full conversion of the aryl halide, the reaction mixture was then diluted with ethyl acetate (10 mL) and filtered through a plug of Celite. The product was purified by flash column chromatography.

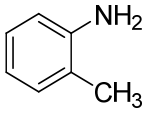
General Procedure C: The Coupling of Ammonia with Aryl Tosylates (Table 7). Into an oven-dried 25-mL round-bottomed flask containing a magnetic stir bar, Pd[P(*o*-tol)$_3$]$_2$ (2.0 mol %), CyPF-*t*-Bu (2.0 mol %) and NaO-*t*-Bu (1.4 equiv) and the aryl tosylate (0.50 mmol) were added. The flask was sealed with a rubber septum, evacuated, and refilled with nitrogen three times. 1,4-Dioxane (0-5 mL) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane) were added by gas-tight syringe. The flask was then placed in an oil bath at 50 ^{o}C for 12-24 h. After GC analysis indicated full conversion of the aryl halide, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered through a plug of Celite. The product was purified by flash column chromatography.

General Procedure D: The Coupling of Ammonia with Aryl Halides and Tosylates Bearing Base-sensitive Functional Groups (Table 8). Inside a glovebox, Pd[P(*o*-tol)$_3$]$_2$ (0.50 mol %), CyPF-*t*-Bu (0.50 mol %), K_3PO_4 (1.4 equiv), aryl halide or tosylate (0.50 mmol), and 1,4-dioxane (5 mL) were added to a 50 mL Parr bomb that contains a magnetic stir bar. The Parr bomb was sealed, brought out of the glovebox, and connected to an ammonia cylinder. The bomb was pressurized to 80 psi, and the mixture was stirred at room temperature for 30 min. The bomb was then sealed and disconnected from the ammonia cylinder and placed in an oil bath at 70 ^{o}C for 12 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and filtered through a plug of Celite. The product was purified by flash column chromatography.

General Procedure E: One-pot Synthesis of Amides and Imides (Table 9). Inside a glovebox, Pd[P(*o*-tol)$_3$]$_2$ (0.10-1.0 mol %) and CyPF-*t*-Bu (0.10-1.0 mol %) were added to a mixture of NaO-*t*-Bu (1.4 equiv) and the aryl halide (1-2 mmol) contained in a 20-mL scintillation vial equipped with a magnetic stir bar. 1,4-Dioxane (0-5 mL) and ammonia (5-20 mL of a 0.5 M solution in dioxane) were added via a gas-tight syringe. The vial was sealed with a Teflon-lined cap and removed from the glovebox and placed in an oil bath at 90-100 ^{o}C for 12 h. Then the excess ammonia was removed under reduced pressure for 5 min. The reaction mixture was then divided into equal portions using a syringe. The anhydride alone or the combination of triethylamine (1 equiv), followed by the acid chloride, were then added. After GC analysis showed complete conversion of the aniline, the reaction mixtures were diluted with ethyl acetate and filtered through a plug of Celite. The products were purified by flash column chromatography.

General Procedure F: The One-pot Synthesis of N-Boc Protected Anilines (Table 9). The general procedure E was followed except for the work up procedure. After filtration of the reaction mixture through Celite, the solvent was removed under reduced pressure. Ethanol (ACS reagent, >99.5%, 2 mL) was added, followed by imidazole (0.5 equiv) (ACS reagent, >99%).[5] The resulting solution was stirred at room temperature for 1 h. The solvent was then removed under reduced pressure. The product was purified by flash column chromatography.

EXPERIMENTAL DETAILS AND COMPOUND CHARACTERIZATION



***o*-Toluidine[6] (Table 3, entry 1).** The general procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol) and CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-bromotoluene (0.086 g, 0.50 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography (silica gel, 3:1 hexanes:ethyl acetate) to give *o*-toluidine as a pale yellow liquid (0.044 g, 83%). R_f = 0.27 (3:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (t, *J* = 7.9 Hz, 2H, Ar**H**), 6.77 (t, *J* = 7.4Hz, 1H, Ar**H**), 6.72 (d, *J* = 7.7 Hz, 1H, Ar**H**), 3.62 (s, br, 2H, N**H**$_2$), 2.22 (s, 3H, C**H**$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 130.3, 126.8, 122.2, 118.5, 114.8, 17.3.

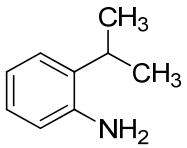
***o*-Toluidine (Table 3, entry 2).** General procedure A was followed with a 2.5 x 10^{-3} M stock solution of catalysts (0.20 mL, 0.00050 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-bromotoluene (0.086 g, 0.50 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography to give *o*-toluidine as a pale yellow liquid (0.038 g, 71%).

***o*-Toluidine (Table 6, entry 1).** General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol) and CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-chlorotoluene (0.063 g, 0.50 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography to give *o*-toluidine as a pale yellow liquid (0.034 g, 64%).

***o*-Toluidine (Table 6, entry 2).** General procedure A was followed with a 2.5 x 10^{-3} M stock solution of catalysts (0.20 mL, 0.00050 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-chlorotoluene (0.063 g, 0.50 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography to give *o*-toluidine as a pale yellow liquid (0.033 g, 63%).

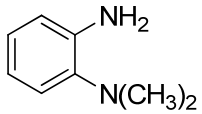
***o*-Toluidine (Table 7, entry 1).** General procedure C was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0072 g, 0.010 mmol), CyPF-*t*-Bu (0.0055 g, 0.010 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-methylphenyl *p*-toluenesulfonate (0.131 g, 0.50 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The crude product was purified by flash-column chromatography to give *o*-toluidine as a pale yellow liquid (0.035 g, 65%).

***o*-Toluidine (Table 6, entry 12).** General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol) and CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-iodotoluene (0.109 g, 0.50 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane) at 90 ^{o}C. The product was purified by flash-column chromatography to give *o*-toluidine as a pale yellow liquid (0.078 g, 73%).



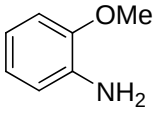
2-Isopropylaniline[6] (Table 3, entry 3). General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-isopropylbromobenzene (0.100 g, 0.50 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography (silica gel, 7:1 hexanes:ethyl acetate) to give 2-isopropylaniline as a pale yellow liquid (0.063 g, 93%). R_f = 0.30 (7:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 1.1, 7.7 Hz, 1H, Ar**H**), 7.10 (td, *J* = 1.5, 7.7 Hz, 1H, Ar**H**), 6.87 (t, *J* = 7.5 Hz, 1H, Ar**H**), 6.74 (dd, *J* = 0.9, 7.9 Hz, 1H, Ar**H**), 3.70 (s, br, 2H, N**H**$_2$), 2.97 (m, 1H, C**H**$(CH_3)_2$), 1.34 (d, *J* = 6.8 Hz, 6H, CH(C**H**$_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 132.5, 126.4, 125.3, 118.9, 115.7, 27.5, 22.2.

2-Isopropylaniline (Table 3, entry 4). General procedure A was followed with the 2.5 x 10^{-3} M stock solution of the catalyst (0.20 mL, 0.00050 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-isopropylbromobenzene (0.100 g, 0.500 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography to give 2-isopropylaniline as a pale yellow liquid (0.057 g, 84%).



***N*,*N*-Dimethyl-1,2-benzenediamine[7] (Table 3, entry 5).** General procedure A was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-bromo-*N*,*N*-dimethylaniline (0.100 g, 0.50 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography (silica gel, 6:1 hexanes:ethyl acetate) to give *N*,*N*-dimethyl-1,2-benzenediamine as a pale yellow liquid (0.061 g, 89%). R_f = 0.30 (6:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 1.27, 7.82 Hz, 1H, Ar**H**), 6.98 (td, *J* = 1.37, 7.61 Hz, 1H, Ar**H**), 6.80 (m, 2H, Ar**H**), 4.03 (s, br, 2H, N**H**$_2$), 2.73 (s, 6H, N(C**H**$_3$)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.3, 140.5, 124.0, 119.2, 118.3, 115.0, 43.5.

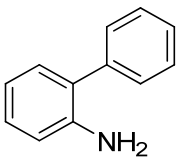
***N*,*N*-Dimethyl-1,2-benzenediamine (Table 3, entry 6).** General procedure B was followed with the 2.5 x 10^{-3} M stock solution of the catalyst (0.20 mL, 0.00050 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-bromo-*N*,*N*-dimethylaniline (0.100 g, 0.50 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography to give *N*,*N*-dimethyl-1,2-benzenediamine as a pale yellow liquid (0.056 g, 82%).



***o*-Anisidine[8] (Table 3, entry 7).** General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-bromoanisole (0.094 g, 0.50 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography (silica gel, 6:1 hexanes:ethyl acetate) to give *o*-anisidine as a pale yellow liquid (0.052 g, 85%). R_f = 0.19 (6:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (m, 2H, Ar**H**), 6.78 (m, 2H, Ar**H**), 3.88 (s, 3H, OC**H**$_3$), 3.81 (s, br, N**H**$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 136.0, 120.9, 118.3, 114.8, 110.3, 55.2.

***o*-Anisidine (Table 3, entry 8).** General procedure B was followed with the 2.5 x 10^{-3}M stock solution of the catalyst (0.20 mL, 0.00050 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-bromoanisole (0.094g, 0.50 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography to give *o*-anisidine as a pale yellow liquid (0.059 g, 95%).

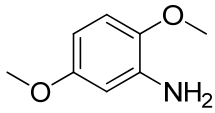
***o*-Anisidine (Table 6, entry 5).** General procedure B was followed with the 2.5 x 10^{-3} M stock solution of the catalyst (0.20 mL, 0.00050 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-chloroanisole (0.071 g, 0.50 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography to give *o*-anisidine as a pale yellow liquid (0.051 g, 84%).



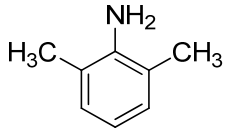
2-Aminobiphenyl[6] (Table 3, entry 9). General procedure A was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.50 mmol), CyPF-*t*-Bu (0.0014 g, 0.50 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-bromobiphenyl (0.117 g, 0.500 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by

flash-column chromatography (silica gel, 9:1 hexanes:ethyl acetate) to give 2-aminobiphenyl as a pale yellow liquid (0.081 g, 96%). R_f = 0.25 (9:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.44 (m, 4H, Ar**H**), 7.36-7.37 (m, 1H, Ar**H**), 7.19-7.14 (m, 2H, Ar**H**), 6.84 (m, 1H, Ar**H**), 6.78 (m, 1H, Ar**H**), 3.77 (s, 1H, N**H**$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 139.5, 130.4, 129.1, 128.8, 128.5, 127.6, 127.1, 118.6, 115.6.

2-Aminobiphenyl (Table 3, entry 10). General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-bromobiphenyl (0.117 g, 0.500 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography (silica gel, 9:1 hexanes:ethyl acetate) to give 2-aminobiphenyl as a pale yellow liquid (0.081 g, 99%).

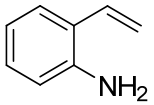


2,5-Dimethoxyaniline[9] (Table 3, entry 11). General procedure B was followed with the 2.5 x 10^{-3} M stock solution of the catalyst (0.20 mL, 0.00050 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 1-bromo-2,5-dimethoxybenzene (0.109 g, 0.500 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography (silica gel, 3:1 hexanes:ethyl acetate) to give 2,5-dimethoxyaniline as a white, crystalline solid (0.073 g, 95%). R_f = 0.20 (3:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.70 (d, *J* = 8.7 Hz, 1H, Ar**H**), 6.34 (d, *J* = 2.8 Hz, 1H, Ar**H**), 6.25 (dd, *J* = 2.8, 8.7 Hz, 1H, Ar**H**), 3.82 (s, br, 2H, N**H**$_2$), 3.81 (s, 3H, *o*-OC**H**$_3$), 3.73 (s, 3H, *m*-OC**H**$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 141.7, 137.1, 111.2, 101.9, 101.7, 56.0, 55.4.



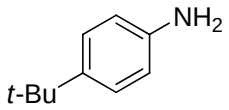
2,6-Dimethylaniline[10] (Table 3, entry 12). General procedure A was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-bromo-*m*-xylene (0.093 g, 0.50 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography (silica gel, 6:1 hexanes:ethyl acetate) to give 2,6-dimethylaniline as a pale yellow liquid (0.053 g, 88%). R_f = 0.34 (5:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.4 Hz, 2H, Ar**H**), 6.75 (t, *J* = 7.4, 7.4 Hz, 1H, Ar**H**), 3.64 (s, br, 2H, N**H**$_2$), 2.27 (s, 6H, C**H**$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 128.1, 121.5, 17.8, 17.5.

2,6-Dimethylaniline (Table 6, entry 6). General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-chloro-*m*-xylene (0.070 g, 0.50 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography to give 2,6-dimethylaniline as a pale yellow liquid (0.054 g, 89%).

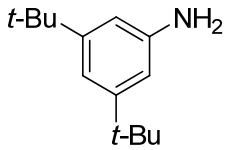


2-Aminostyrene[11] (Table 3, entry 13). General procedure A was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-bromostyrene (0.093 g, 1.0 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography (silica gel, 9:1 hexanes:ethyl acetate) to give 2-aminostyrene as colorless oil (0.0391 g, 66%). R_f = 0.25 (9:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.6 Hz, 1H, Ar**H**), 7.12 (m, 1H, Ar**H**), 6.80 (m, 2H, Ar**H**), 6.70 (d, *J* = 7.9 Hz, 1H,

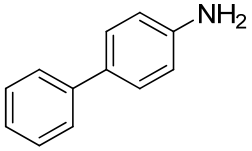
ArC**H**CH_2), 5.66 (dd, *J* = 1.2, 17.4 Hz, 1H, ArCHC**H(trans)**H(cis)), 5.35 (dd, *J* = 1.3, 11.1 Hz, 1H, ArCHCH(trans)**H(cis)**), 3.8 (s, br, N**H**$_2$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 132.6, 128.7, 127.2, 124.0, 118.8, 116.0, 115.6.



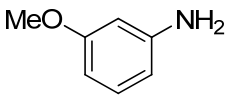
4-*t*-Butylaniline[6] (Table 4, entry 1). General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 1-bromo-4-*t*-butylbenzene (0.107 g, 0.500 mmol), ammonia (5 mL of a 0.5 M solution in 1,4-dioxane) and 1,4-dioxane (8 mL). The product was purified by flash-column chromatography (silica gel, 6:1 hexanes:ethyl acetate) to give 4-*t*-butylaniline as a clear, pale yellow liquid (0.0659 g, 88%). R_f = 0.30 (6:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.6 Hz, 2H, Ar**H**), 6.68 (d, *J* = 8.6 Hz, 2H, Ar**H**), 3.52 (s, br, 2H, N**H**$_2$), 1.33 (s, 9H, C**H**$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 141.3, 126.0, 114.9, 33.8, 31.4.



3,5-Di-*t*-butylaniline[12] (Table 4, entry 2). General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 1-bromo-3,5-di-*t*-butylbenzene (0.134 g, 0.500 mmol), ammonia (5 mL of a 0.5 M solution in 1,4-dioxane) and and 1,4-dioxane (8 mL). The product was purified by flash-column chromatography (silica gel, 9:1 hexanes:ethyl acetate) to give 3,5-di-*t*-butylaniline as a white solid (0.080 g, 78%). R_f = 0.25 (9:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (d, *J* = 6.9 Hz, 1H, Ar**H**), 6.57 (d, *J* = 6.6 Hz, 2H, Ar**H**), 3.59 (s, br, 2H, N**H**$_2$), 1.30 (s, 18H, C**H**$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 145.5, 113.1, 109.8, 34.7, 31.4.



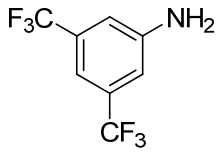
4-Aminobiphenyl[13] (Table 4, entry 3). General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 4-bromobiphenyl (0.117 g, 0.500 mmol), ammonia (5 mL of a 0.5 M solution in 1,4-dioxane) and 1,4-dioxane (8 mL). The product was purified by flash-column chromatography (silica gel, 3:1 hexanes:ethyl acetate) to give 4-aminobiphenyl as a white solid (0.083 g, 98%). R_f = 0.27 (3:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.2 Hz, 2H, Ar**H**), 7.42 (m, 4H, Ar**H**), 7.28 (m, 1H, Ar**H**), 6.77 (m, 2H, Ar**H**), 3.73 (s, br, N**H**$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.8, 141.1, 131.5, 128.6, 128.0, 126.4, 126.2, 115.3.



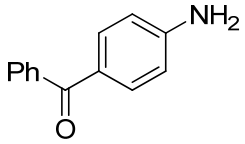
***m*-Anisidine[13] (Table 4, entry 4).** General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 3-bromoanisole (0.094 g, 0.50 mmol), ammonia (5 mL of a 0.5 M solution in 1,4-dioxane), and 1,4-dioxane (8 mL). The

product was purified by flash-column chromatography (silica gel, 3:1 hexanes:ethyl acetate) to give *m*-anisidine as a pale yellow liquid (0.061 g, 99%). R_f = 0.23 (3:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (t, *J* = 8.0, 8.0 Hz, 1H, Ar**H**), 6.36 (dd, *J* = 2.4, 8.2 Hz, 1H, Ar**H**), 6.31 (dd, *J* = 1.4, 7.9 Hz, 1H, Ar**H**), 6.26 (t, *J* = 2.2, 2.2 Hz, 1H, Ar**H**), 3.78 (s, 3H, OC**H**$_3$), 3.71 (s, br, N**H**$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 147.7, 130.0, 107.8, 103.7, 100.9, 54.9.

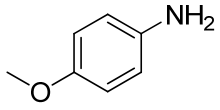
***m*-Anisidine (Table 6, entry 9).** General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 3-chloroanisole (0.071 g, 0.50 mmol), ammonia (5 mL of a 0.5 M solution in 1,4-dioxane) and 1,4-dioxane (8 mL). The product was purified by flash-column chromatography to give *m*-anisidine as a pale yellow liquid (0.061 g, 99%).



3,5-Bis(trifluoromethyl)aniline[9] (Table 4, entry 5). General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 3,5-bis(trifluoromethyl)bromobenzene (0.146 g, 0.50 mmol), ammonia (5 mL of a 0.5 M solution in 1,4-dioxane) and 1,4-dioxane (8 mL). The product was purified by flash-column chromatography (silica gel, 6:1 hexanes:ethyl acetate) to give 3,5-bis(trifluoromethyl)aniline as a pale yellow oil (0.0897 g, 61%). R_f = 0.27 (6:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (s, 1H, Ar**H**), 7.03 (s, 2H, Ar**H**), 4.07 (s, br, N**H**$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.3 (s), 132.5 (q, *J* = 32.9 Hz), 123.4 (q, *J* = 272.6 Hz), 114.1 (d, *J* = 2.95 Hz), 111.5 (dt, *J* = 3.9Hz). ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$ standard) δ -66.2.

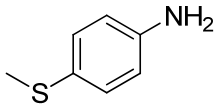


4-Aminobenzophenone[13] (Table 4, entry 6). General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 4-bromobenzophenone (0.131 g, 0.50 mmol), ammonia (5 mL of a 0.5 M solution in 1,4-dioxane) and 1,4-dioxane (8 mL). The product was purified by flash-column chromatography (silica gel, 2:1 hexanes:ethyl acetate) to give 4-aminobenzophenone as an orange solid (0.076 g, 77%). R_f = 0.27 (2:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73-7.71 (m, 4H, Ar**H**), 7.53 (t, *J* = 7.4 Hz, 1H, Ar**H**), 7.45 (t, *J* = 7.4 Hz, 2H, Ar**H**), 6.67 (m, 2H, Ar**H**), 4.17 (s, br, N**H**$_2$) ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.3, 150.9, 138.8, 132.9, 131.4, 129.5, 128.0, 127.3, 113.6.

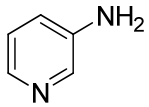


***p*-Anisidine[13] (Table 4, entry 7).** General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0036 g, 0.0050 mmol), CyPF-*t*-Bu (0.0028 g, 0.0050 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 4-bromoanisole (0.094 g, 0.50 mmol), ammonia (5 mL of a 0.5 M solution in 1,4-dioxane), and 1,4-dioxane (5 mL) at 100 ^{o}C. The product was purified by flash-column chromatography (silica gel, 1:1 hexanes:ethyl acetate) to give *p*-anisidine as dark brown needles (0.033 g, 53%). R_f = 0.27 (1:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (d, *J* = 8.8 Hz, 2H, Ar**H**), 6.65 (d, *J* = 8.8 Hz, 2H, Ar**H**), 3.75 (s, 3H, OC**H**$_3$), 3.43 (s, br, N**H**$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 139.9, 116.3, 114.7, 55.6.

***p*-Anisidine (Table 6, entry 10).** General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0036 g, 0.0050 mmol), CyPF-*t*-Bu (0.0028 g, 0.0050 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 4-chloroanisole (0.071 g, 0.50 mmol), ammonia (5 mL of a 0.5 M solution in 1,4-dioxane), and 1,4-dioxane (5 mL) at 100 ^{o}C. The product was purified by flash-column chromatography (silica gel, 1:1 hexanes:ethyl acetate) to give *p*-anisidine as a pale yellow liquid (0.085 g, 69%).

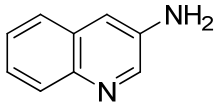


4-Aminothioanisole[14] (Table 4, entry 8). General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 4-bromothioanisole (0.102 g, 0.500 mmol), ammonia (5 mL of a 0.5 M solution in 1,4-dioxane) and 1,4-dioxane (5 mL) 90 ^{o}C. The product was purified by flash-column chromatography (silica gel, 2:1 hexanes:ethyl acetate) to give 4-aminothioanisole as a dark orange liquid (0.064 g, 91%). R_f = 0.27 (2:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.6 Hz, 2H, Ar**H**), 6.62 (d, *J* = 8.6 Hz, 2H, Ar**H**), 3.66 (s, br, N**H**$_2$), 2.42 (s, 3H, SC**H**$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 130.9, 125.5, 115.6, 18.6.

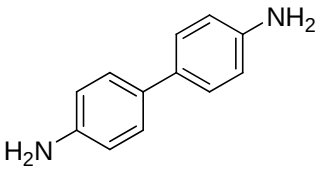


3-Aminopyridine[15] (Table 4, entry 9). General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), and 3-bromopyridine (0.0790 g, 0.500 mmol). The product was purified by flash-column chromatography (silica gel, ethyl acetate) to give 3-aminopyridine as a colorless solid (0.0281 g, 60%). R_f = 0.20 (ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 2.7 Hz, 1H, Ar**H**), 7.96 (d, *J* = 4.6 Hz, 1H, Ar**H**), 7.02 (dd, *J* = 4.7, 8.1 Hz, 1H, Ar**H**), 6.92 (m, 1H, Ar**H**), 3.80 (s, br, 2H, N**H**$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 139.7, 137.3, 123.6, 121.3.

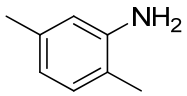
3-Aminopyridine (Table 6, entry 11). General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), and 3-chloropyridine (0.057 g, 0.50 mmol). The product was purified by flash-column chromatography to give 3-aminopyridine as a colorless solid (0.030 g, 64%).



3-Aminoquinoline[9] (Table 4, entry 10). General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 3-bromoquinoline (0.104 g, 0.50 mmol). The product was purified by flash-column chromatography (silica gel, ethyl acetate) to give 3-aminopyridine as a colorless solid (0.046 g, 64%). R_f = 0.26 (ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 2.7 Hz, 1H, Ar**H**), 7.96 (m, 1H, Ar**H**), 7.55 (m, 1H, Ar**H**), 7.48-7.35 (m, 2H, Ar**H**), 7.16 (d, *J* = 2.7 Hz, 1H, Ar**H**), 4.05 (s, br, 2H, N**H**$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 142.5, 139.8, 129.0, 128.8, 126.8, 125.7, 125.4, 114.7.

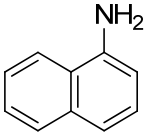


4,4'-Diaminobiphenyl[9] (Table 4, entry 11). The procedure for the preparation of 4,4'-diaminobiphenyl is modified from general procedure B, Pd[P(*o*-tol)$_3$]$_2$ (0.0072 g, 0.010 mmol), CyPF-*t*-Bu (0.0055 g, 0.0010 mmol), NaO-*t*-Bu (0.135 g, 1.40 mmol), and 4,4'-dibromobiphenyl (0.156 g, 0.500 mmol). The product was purified by flash-column chromatography (silica gel, 1:1 hexanes:ethyl acetate) to give 4,4'-diaminobiphenyl as a colorless solid (0.072 g, 79%). R_f = 0.26 (silica gel, 1:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.9 Hz, 4H, Ar**H**), 6.68 (d, *J* = 7.9 Hz, 4H, Ar**H**), 3.68 (s, br, 4H, N**H**$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 131.6, 127.2, 115.3.



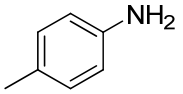
2,5-Dimethylaniline[9] (Table 6, entry 3). General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), and 2,5-dimethylchlorobenzene (0.070 g, 0.50 mmol). The product was purified by flash-column chromatography (silica gel, 6:1 hexanes:ethyl acetate) to give 2,5-dimethylaniline as a pale yellow liquid (0.051 g, 85%). R_f = 0.27 (6:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (d, *J* = 7.5 Hz, 1H, Ar**H**), 6.59 (d, *J* = 7.5 Hz, 1H, Ar**H**), 6.55 (s, 1H, Ar**H**), 3.56 (s, 2H, N**H**$_2$), 2.31 (s, 3H, *m*-C**H**$_3$), 2.28 (s, 3H, *o*-C**H**$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.3, 136.5, 130.2, 119.3, 119.2, 115.6, 21.0, 16.8.

2,5-Dimethylaniline (Table 6, entry 4). General procedure A was followed with the 2.5 x 10^{-3} M stock solution of the catalyst (0.25 mL, 0.00050 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2,5-dimethylchlorobenzene (0.070 g, 0.50 mmol). The product was purified by flash-column chromatography to give 2,5-dimethylaniline as a pale yellow liquid (0.038 g, 63%).

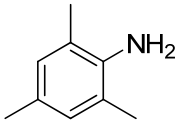


1-Aminonaphthalene[6] (Table 6, entry 7). General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 1-chloronaphthalene (0.081 g, 0.50 mmol), ammonia (5 mL of a 0.5 M solution in 1,4-dioxane) and 1,4-dioxane (8 mL) . The product was purified by flash-column chromatography (silica gel, 3:1 hexanes:ethyl acetate) to give the title compound as a colorless solid (0.064 g, 89%). R_f = 0.23 (3:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88-7.83 (m, 2H, Ar**H**), 7.51-7.48 (m, 2H, Ar**H**), 7.40-7.34 (m, 2H, Ar**H**), 6.81 (dd, *J* = 1.3, 7.1 Hz, 1H Ar**H**), 4.15 (s, br, 2H, N**H**$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.0, 134.3, 128.5, 126.3, 125.8, 124.8, 123.6, 120.7, 118.9, 109.6.

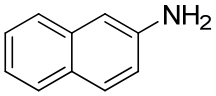
1-Aminonaphthalene (Table 7, entry 3). General procedure C was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0072 g, 0.010 mmol), CyPF-*t*-Bu (0.0055 g, 0.010 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 1-naphthyl *p*-toluenesulfonate (0.149 g, 0.500 mmol), ammonia (5 mL of a 0.5 M solution in 1,4-dioxane) and 1,4-dioxane (5 mL). The product was purified by flash-column chromatography to give 1-aminonaphthalene as a colorless solid (0.048 g, 67%).



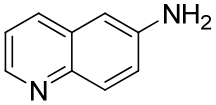
***p*-Toluidine[9] (Table 6, entry 8).** General procedure B was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0036 g, 0. 0.0050 mmol), CyPF-*t*-Bu (0.0028 g, 0.0050 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), and 4-chlorotoluene (0.063 g, 0.50 mmol). The product was purified by flash-column chromatography (silica gel, 6:1 hexanes:ethyl acetate) to give 4-methylaniline as a clear colorless liquid (0.054 g, 55%). R_f = 0.25 (6:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.0 Hz, 2H, Ar**H**), 6.64 (d, *J* = 8.3 Hz, 2H, Ar**H**), 3.65 (s, br, 2H, N**H**$_2$), 2.28 (s, 3H, ArC**H**$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 129.7, 127.7, 115.2, 20.4.



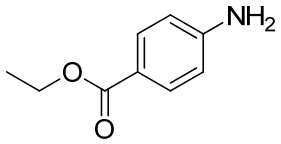
2,4,6-Trimethylaniline[9] (Table 7, entry 2). General procedure C was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0072 g, 0.010 mmol), CyPF-*t*-Bu (0.0055 g, 0.010 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2,4,6-trimethylphenyl *p*-toluenesulfonate (0.145 g, 0.50 mmol) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane). The product was purified by flash-column chromatography (silica gel, 6:1 hexanes:ethyl acetate) to give the title compound as a clear colorless liquid (0.058 g, 86%). R_f = 0.27 (6:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (s, 2H, Ar**H**), 3.50 (s, br, 2H, N**H**$_2$), 2.29 (s, 3H, *p*-C**H**$_3$), 2.24 (s, 6H, *o*-(C**H**$_3$)$_2$**).** ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 128.7, 127.0, 121.7, 20.3, 17.5.



2-Aminonaphthalene[9] (Table 7, entry 4). General procedure C was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0072 g, 0.010 mmol), CyPF-*t*-Bu (0.0055 g, 0.010 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 2-naphthyl *p*-toluenesulfonate (0.149 g, 0.500 mmol), ammonia (5 mL of a 0.5 M solution in 1,4-dioxane) and 1,4-dioxane (5 mL). The product was purified by flash-column chromatography (silica gel, 6:1 hexanes:ethyl acetate) to give the title compound as a colorless solid (0.048 g, 67%). R_f = 0.23 (3:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H, Ar**H**), 7.70 (d, *J* = 8.6 Hz, 1H, Ar**H**), 7.63 (d, *J* = 8.3 Hz, 1H, Ar**H**), 7.42 (t, *J* = 7.4 Hz, 1H, Ar**H**), 7.20 (t, *J* = 7.4 Hz, 1H, Ar**H**), 7.00 (s, 1H, Ar**H**), 6.96 (d, *J* = 8.6 Hz, 1H, Ar**H**), 3.81 (s, br, 2H, N**H**$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 134.8, 129.1, 127.9, 127.7, 126.3, 125.7, 122.4, 118.2, 108.5.

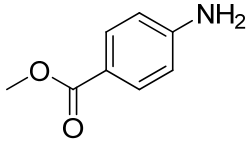


6-Aminoquinoline[9] (Table 7, entry 5). General procedure C was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0072 g, 0.010 mmol), CyPF-*t*-Bu (0.0055 g, 0.010 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 6-quinolinyl *p*-toluenesulfonate (0.150 g, 0.50 mmol), ammonia (5 mL of a 0.5 M solution in 1,4-dioxane) and 1,4-dioxane (5 mL). The product was purified flash-column chromatography (silica gel, ethyl acetate) to give the title compound as a gray solid (0.040 g, 55%). R_f = 0.27 (ethyl acetate; UV, ninhydrin). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 1.6, 4.2 Hz, 1H, Ar**H**), 7.88 (d, *J* = 8.9 Hz, 1H, Ar**H**), 7.83 (dd, *J* = 0.5, 8.3 Hz, 1H, Ar**H**), 7.21 (dd, *J* = 4.2, 7.2 Hz, 1H, Ar**H**), 7.11 (dd, *J* = 2.6, 8.9 Hz, 1H, Ar**H**), 6.83 (d, *J* = 2.5 Hz,1H, Ar**H**), 4.03 (s, br, 2H, N**H**$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6, 144.6, 143.26, 133.6, 130.3, 129.7, 121.5, 121.2, 107.2.



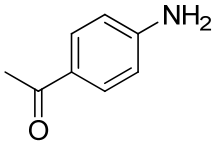
Ethyl 4-aminobenzoate[9] (Table 8, entry 1). General procedure D was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), K_3PO_4 (0.530 g, 2.50 mmol), and ethyl 4-bromobenzoate (0.115 g, 0.500 mmol). The product was purified by flash-column chromatography (silica gel, gradient elution 5%, 10%, 15%, 20% and then 25% ethyl acetate in hexanes) to give ethyl 4-aminobenzoate as a colorless solid (0.070 g, 84%). R_f = 0.30 (3:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 2H, Ar**H**), 6.63 (d, *J* = 8.8 Hz, 2H, Ar**H**), 4.31 (q, *J* = 7.0 Hz, 2H, $CH_3C\mathbf{H}_2$), 4.05 (br, 2H, N$\mathbf{H}_2$), 1.35 (t, *J* = 7.0 Hz, 3H, C$\mathbf{H}_3CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 151.1, 131.8, 120.1, 114.0, 60.6, 14.7.

Ethyl 4-aminobenzoate (Table 8, entry 2). General procedure D was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0036 g, 0.0050 mmol), CyPF-*t*-Bu (0.0028 g, 0.0050 mmol), K_3PO_4 (0.530 g, 2.50 mmol), and ethyl 4-{[(4-methylphenyl)sulfonyl]oxy}benzoate (0.160 g, 0.50 mmol). The product was purified by flash-column chromatography to give ethyl 4-aminobenzoate as a colorless solid (0.053 g, 65%).



Methyl 4-aminobenzoate[13] (Table 8, entry 3). General procedure D was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), K_3PO_4 (0.530 g, 2.50 mmol), and methyl 4-bromobenzoate (0.108 g, 0.500 mmol). The product was purified by flash-column chromatography (silica gel, 3:1 hexanes:ethyl acetate) to give methyl 4-aminobenzoate as a colorless solid (0.063 g, 83%). R_f = 0.22 (3:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.8 Hz, 2H, Ar**H**), 6.63 (d, *J* = 8.8 Hz, 2H, Ar**H**), 4.08 (br, 2H, N$\mathbf{H}_2$), 3.84 (s, 3H, OC$\mathbf{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 151.1, 131.8, 119.9, 114.0, 51.9.

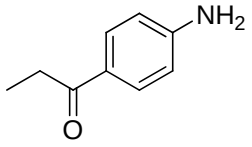
Methyl 4-aminobenzoate (Table 8, entry 4). General procedure D was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), K_3PO_4 (0.530 g, 2.50 mmol), and methyl 4-chlorobenzoate (0.085 g, 0.50 mmol). The product was purified by flash-column chromatography to give methyl 4-aminobenzoate as a colorless solid (0.060 g, 79%).



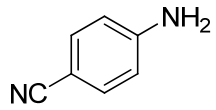
4'-Aminoacetophenone[14] (Table 8, entry 5). General procedure D was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), K_3PO_4 (0.530 g, 0.700 mmol), and 4'-bromoacetophenone (0.100 g, 0.500 mmol). The product was purified by flash-column chromatography (silica gel, 2:1 hexanes:ethyl acetate) to give methyl 4'-aminoacetophenone as a colorless solid (0.051 g, 76%). R_f = 0.22 (3:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 2H, Ar**H**), 6.64 (d, *J* = 8.5 Hz, 2H, Ar**H**), 4.19 (s, br, 2H, N$\mathbf{H}_2$), 2.50 (s, 3H, C$\mathbf{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 151.2, 130.7, 127.6, 113.6, 26.0.

4'-Aminoacetophenone (Table 8, entry 6). General procedure D was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0036 g, 0.0050mmol), CyPF-*t*-Bu (0.0028 g, 0.0050 mmol), K_3PO_4 (0.530 g, 2.50 mmol), and 4'-iodoacetophenone (0.123 g, 0.500 mmol). The product was purified by flash-column chromatography

(silica gel, 2:1 hexanes:ethyl acetate) to give methyl 4'-aminoacetophenone as a colorless solid (0.052 g, 78%).



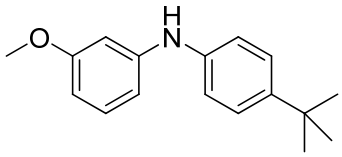
4'-Aminopropiophenone[16] (Table 8, entry 7). General procedure D was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), K_3PO_4 (0.530 g, 2.50 mmol), and 4'-bromopropiophenone (0.107 g, 0.500 mmol). The product was purified by flash-column chromatography (silica gel, gradient elution 5%, 10%, 20% and 25% ethyl acetate in hexanes) to give 4'aminopropiophenone as a colorless solid (0.063 g, 85%). R_f = 0.30 (3:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.8 Hz, 2H, Ar**H**), 6.64 (d, *J* = 8.8 Hz, 2H, Ar**H**), 4.15 (s, br, 2H, N**H**$_2$), 2.89 (q, *J* = 7.2, 7.2, 7.2 Hz, 2H, $CH_3C\mathbf{H}_2$), 1.18 (t, *J* = 7.2, 7.2 Hz, 3H, $CH_3C\mathbf{H}_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 151.2, 130.6, 127.7, 114.0, 31.3, 8.9.



4-Aminobenzonitrile[14] (Table 8, entry 8). General procedure D was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), K_3PO_4 (0.530 g, 2.50 mmol), and 4-bromobenzonitrile (0.091 g, 0.50 mmol). The product was purified by flash-column chromatography (silica gel, gradient elution 5%, 10%, 20% and 25% ethyl acetate in hexanes) to give 4-aminobenzonitrile as a colorless solid (0.042 g, 71%). R_f = 0.26 (2:1 hexanes:ethyl acetate; UV, ninhydrin). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 2H, Ar**H**), 6.62 (d, *J* = 8.7 Hz, 2H, Ar**H**), 4.32 (s, br, 2H, N**H**$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 133.7, 120.2, 114.4, 100.0.

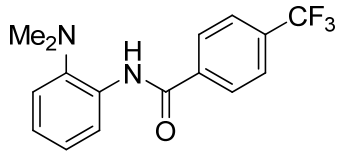
4-Aminopropiophenone (Table 8, entry 9). General procedure D was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), K_3PO_4 (0.530 g, 2.50 mmol), and 4-chlorobenzonitrile (0.069 g, 0.50 mmol). The product was purified by flash-column chromatography to give 4-aminobenzonitrile as a colorless solid (0.025 g, 44%).

4-Aminopropiophenone (Table 8, entry 10). General procedure D was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0036 g, 0.0050mmol), CyPF-*t*-Bu (0.0028 g, 0.0050 mmol), K_3PO_4 (0.530 g, 2.50 mmol), and 4-cyanophenyl *p*-toluenesulfonate (0.137 g, 0.500 mmol). The product was purified by flash-column chromatography to give 4-aminobenzonitrile as a colorless solid (0.045 g, 77%).

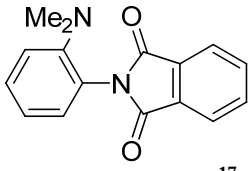


3-Methoxy-*N*-(4-*tert*-Butylphenyl)aniline (Equation 2). Inside a drybox, Pd[P(*o*-tol)$_3$]$_2$ (0.0018 g, 0.0025 mmol), CyPF-*t*-Bu (0.0014 g, 0.0025 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol) and 4-*tert*-butylbromobenzene (0.106 g, 0.500 mmol) were added to a 20-mL scintillation vial. The vial was placed in an 80 °C oil bath for 5 hours. Then the solvent was evaporated under reduced pressure. Into this vial were added 3-methoxyphenyl *p*-toluenesulfonate (0.139 g, 0.500 mmol) and NaO-*t*-Bu (0.067 g, 0.70 mmol). The vial was then placed in a 80 °C oil bath for 8 h. The reaction mixture was filtered through a plug of Celite, concentrated, and purified by flash-column chromatography (silica gel, 4:1 hexanes:ethyl acetate) to give the title compound as a slightly yellow oil (0.112 g, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.6 Hz, 2H, Ar**H**), 7.21 (m, 1H, Ar**H**), 7.11 (d, *J* = 8.6 Hz, 2H, Ar**H**), 6.69 (d, *J* = 2.2 Hz, 2H, Ar**H**), 6.52 (d, *J* = 8.2 Hz, 1H, Ar**H**), 5.73 (s, 1H, N**H**), 3.82 (s, 3H, OC**H**$_3$), 1.40 (s, 9H, C(C**H**$_3$)$_3$. ^{13}C

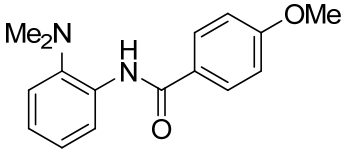
NMR (126 MHz, $CDCl_3$) δ 160.6, 145.1, 144.3, 139.9, 130.0, 126.0, 118.5, 109.5, 105.4, 102.5, 55.0, 34.1, 31.4. Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 80.05; H, 8.57; N, 5.32.



***N*-(2-Dimethylaminophenyl)-4-trifluoromethylbenzamide (Table 9, entry 1).** General procedure E was followed with $Pd[P(o\text{-tol})_3]_2$ (0.0014 g, 0.0025 mmol), CyPF-*t*-Bu (0.0011 g, 0.0025 mmol), NaO-*t*-Bu (0.269 g, 2.80 mmol), 2-bromo-*N*,*N*-dimethylaniline (0.400 g, 2.00 mmol) and ammonia (15 mL of a 0.5 M solution in 1,4-dioxane) in a 20-mL scintillation vial. After the excess ammonia was removed, the reaction mixture was then divided into 4 equal portions. 4-(Trifluoromethyl)benzoyl chloride (0.104 g, 0.500 mmol) and Et_3N (0.050 g, 0.50 mmol) was added to one of the four portions. The resulting mixture was stirred at room temperature. The product was purified by flash-column chromatography (silica gel, 9:1 hexanes:ethyl acetate) to give *N*-(2-dimethylaminophenyl)-4-trifluoromethylbenzamide as a colorless solid (0.134 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.48 (s, br, 1H, N**H**), 8.54 (d, *J* = 8.0 Hz, 1H, Ar**H**), 8.05 (d, *J* = 8.1 Hz, 2H, Ar**H**), 7.79 (d, *J* = 8.1 Hz, 2H, Ar**H**), 7.27 (d, *J* = 7.6 Hz, 1H, Ar**H**), 7.22 (t, *J* = 7.7 Hz, 1H, Ar**H**), 7.14 (t, *J* = 7.6 Hz, 1H, Ar**H**), 2.72 (s, 6H, $N(C\mathbf{H}_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.5, 143.1, 138.5, 133.2 (q, *J* = 32.7 Hz), 133.1. 127.4, 125.8 (q, *J* = 3.7 Hz), 125.3, 124.3, 123.6 (q, J = 273.5 Hz), 120.1, 119.4, 44.9. Anal. Calcd for $C_{16}H_{15}F_3N_2O$: C, 62.33; H, 4.90; N, 9.09. Found: C, 62.43; H, 5.00; N, 8.83.

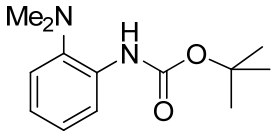


2-[2-(Dimethylamino)phenyl]-1H-isoindole-1,3(2H)-dione[17] (Table 9, entry 2). Following general procedure E and the procedure described for Table 9, entry 1, phthalic anhydride (0.074 g, 0.50 mmol) was added to one of the four portions of the solution from the crude amination process. The resulting mixture was stirred at room temperature. The product was purified by flash-column chromatography (silica gel, 3:1 hexanes:ethyl acetate) to give the title compound as a colorless solid (0.068 g, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 3.1, 5.4 Hz, 2H, Ar**H**), 7.78 (dd, *J* = 3.0, 5.5 Hz, 2H, Ar**H**), 7.40 (m, 1H, Ar**H**), 7.19 (ddd, *J* = 1.4, 7.9, 14.3 Hz, 2H, Ar**H**), 7.10 (td, *J* = 1.3, 7.6 Hz, 1H, Ar**H**), 2.64 (s, 6H, $N(C\mathbf{H}_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 151.6, 134.1, 132.1, 130.2, 130.1, 124.7, 123.6, 122.5, 120.2, 43.7.

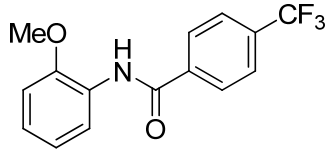


***N*-(2-Dimethylaminophenyl)-4-methoxybenzamide (Table 9, entry 3).** Following general procedure E and the procedure described for Table 9, entry 1, 4-anisolyl chloride (0.085 g, 0.50 mmol) and Et_3N (0.050 g, 0.50 mmol) were added to one of the four portions of the solution from the crude amination process. The resulting mixture was stirred at room temperature 12 h. The product was purified by flash-column chromatography (silica gel, 9:1 hexanes to ethyl acetate) to give the title compound as a colorless solid (0.100 g, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.31 (s, br, 1H, N**H**), 8.52 (d, *J* = 8.1 Hz, 1H, Ar**H**), 7.90 (d, *J* = 8.7 Hz, 2H, Ar**H**), 7.21 (d, *J* = 7.9 Hz, 1H, Ar**H**), 7.17 (t, *J* = 7.7 Hz, 1H, Ar**H**), 7.07 (t, *J* =

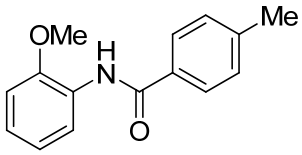
7.6, 1H, Ar**H**), 6.99 (d, *J* = 8.7 Hz, 2H, Ar**H**), 3.86 (s, 6H, N(C**H**$_3$)$_2$), 2.70 (s, 6H, OC**H**$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 162.3, 142.9, 133.6, 128.7, 127.5, 125.1, 123.5, 119.8, 119.3, 113.9, 55.3, 44.8. Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.37; H, 6.59; N, 10.19.



***N*-(2-*N*,*N*-Dimethylaminophenyl)-1,1-dimethylethyl ester carbamic acid[7] (Table 9, entry 4).** Following general procedure F and the procedure described for Table 9, entry 1, di-*tert*-butyl dicarbonate (0.109 g, 0.50 mmol) was added to one of the four portions of the solution from the crude amination process. The resulting mixture was stirred at 80 °C for 12 h. After evaporation of the solvent, a solution of imidazole (0.017 g, 0.025 mmol) in ethanol (2 mL) was added. The product was purified by flash-column chromatography (silica gel, 4% ethyl acetate in hexanes) to give the title compound as a colorless solid (0.089 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 6.3 Hz, 1H, N**H**), 7.71 (s, 1H, Ar**H**), 7.14 (d, *J* = 7.9 Hz, 1H, Ar**H**), 7.09 (t, *J* = 7.8 Hz, 1H, Ar**H**), 6.97 (t, *J* = 7.0 Hz, 1H, Ar**H**), 2.63 (s, 6H, N(C**H**$_3$)$_2$), 1.55 (s, 9H, C(C**H**$_3$)$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 142.1, 133.9, 125.0, 122.3, 120.0, 117.7, 80.1, 44.7, 28.4.

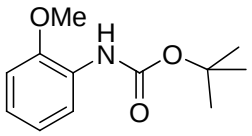


***N*-(2-Methoxyphenyl)-4-trifluoromethylbenzamide (Table 9, entry 5).** General procedure E was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0014 g, 0.0025 mmol), CyPF-*t*-Bu (0.0011 g, 0.0025 mmol), NaO-*t*-Bu (0.269 g, 2.8 mmol), 2-chloroanisole (0.285 g, 2.0 mmol) and ammonia (15 mL of a 0.5 M solution in 1,4-dioxane) in a 20-mL scintillation vial. After the excess ammonia was removed, the reaction mixture was divided into 4 equal portions. 4-(Trifluoromethyl)benzoyl chloride (0.104 g, 0.500 mmol) and Et_3N (0.050 g, 0.50 mmol) were added to one of the portions. The resulting mixture was stirred at room temperature for 12 h. The product was purified by flash-column chromatography (silica gel, 9:1 hexanes:ethyl acetate) to give the title compound as a colorless solid (0.121 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (s, br, 1H, N**H**), 8.51 (d, *J* = 7.9 Hz, 1H, Ar**H**), 8.00 (d, *J* = 8.0 Hz, 2H, Ar**H**), 7.76 (d, *J* = 8.0 Hz, 2H, Ar**H**), 7.12 (t, *J* = 7.8, 7.8 Hz, 1H, Ar**H**), 7.04 (t, *J* = 7.7, 7.7 Hz, 1H, Ar**H**), 6.94 (d, *J* = 8.1 Hz, 1H, Ar**H**), 3.93 (s, 3H, OC**H**$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 148.1, 138.6, 133.3 (q, *J* = 38.9, 38.9, 38.9 Hz), 133.1. 127.5, 125.8 (q, *J* = 3.6, 3.6, 3.6 Hz), 125.7, 124.3, 123.6 (q, J = 273.4, 273.4, 273.4 Hz), 121.2, 119.9, 55.8. Anal. Calcd for $C_{15}H_{12}F_3NO_2$: C, 61.02; H, 4.10; N, 4.74. Found: C, 61.02; H, 3.97; N, 4.71.

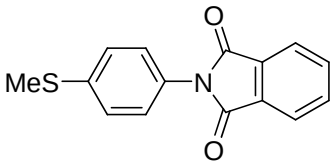


***N*-(2-Methoxyphenyl)-4-methyl-benzamide (Table 9, entry 6).** Following general procedure E and the procedure described for Table 9, entry 5, *p*-toluoyl chloride (0.077 g, 0.50 mmol) and Et_3N (0.050 g, 0.50 mmol) were added to one of the four portions of the solution from the crude amination process. The resulting mixture was stirred at room temperature. The product was purified by flash-column chromatography (silica gel, 4% ethyl acetate in hexanes) to give the title compound as a colorless solid (0.113 g, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, br, 1H, N**H**), 8.53 (s, 1H, Ar**H**), 7.80 (d, *J* = 8.0 Hz, 2H, Ar**H**), 7.30 (d, *J* = 7.9 Hz, 2H, Ar**H**), 7.08 (t, *J* = 7.7 Hz, 1H, Ar**H**), 7.02 (t, *J* = 7.6 Hz, 1H, Ar**H**),

6.92 (d, *J* = 8.0 Hz, 1H, Ar**H**), 3.93 (s, 3H, OC**H**$_3$), 2.43 (s, 3H, ArC**H**$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 148.0, 142.0, 132.3, 129.2, 127.8, 126.9, 123.6, 121.0, 119.6, 109.8, 55.6, 21.3. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.29; H, 6.31; N, 5.71.



***N*-(2-Methoxyphenyl)-1,1-dimethylethyl ester carbamic acid[18] (Table 9, entry 7).** Following general procedure F and the procedure described for Table 9, entry 5, di-*tert*-butyl dicarbonate (0.109 g, 0.500 mmol) was added to one of the four portions of the solution from the crude amination process. The resulting mixture was stirred at 80 °C for 12 h. After evaporation of the solvent, a solution of imidazole (0.017 g, 0.025 mmol) in ethanol (2 mL) was added. The product was purified by flash-column chromatography (silica gel, 4% ethyl acetate in hexanes) to give the title compound as a colorless solid (0.076 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H, N**H**), 7.12 (s, 1H, Ar**H**), 6.96 (m, 2H, Ar**H**), 6.89 (d, *J* = 9.1 Hz, 1H, Ar**H**), 3.85 (s, 3H, OC**H**$_3$), 1.54 (s, 9H, C(C**H**$_3$)$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 147.4, 128.0, 122.2, 121.0, 118.0, 109.8, 80.1, 55.5, 28.3.



2-[4-Thioanisylphenyl]-1H-isoindole-1,3(2H)-dione (Table 9, entry 8). General procedure E was followed with Pd[P(*o*-tol)$_3$]$_2$ (0.0036 g, 0.0050 mmol), CyPF-*t*-Bu (0.0028 g, 0.0050 mmol), NaO-*t*-Bu (0.067 g, 0.70 mmol), 4-bromothioanisole (0.102 g, 0.500 mmol), 1,4-dioxane (5 mL) and ammonia (5 mL of a 0.5 M solution in 1,4-dioxane) in a 20-mL scintillation vial. After the excess ammonia was removed, phthalic anhydride (0.074 g, 0.50 mmol) was added. The resulting mixture was stirred at room temperature for 12 h. The product was purified by flash-column chromatography (silica gel, 6:1 hexanes:ethyl acetate) to give the title compound as a colorless solid (0.100 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 3.1, 5.3 Hz, 2H, Ar**H**), 7.79 (dd, *J* = 3.1, 5.3 Hz, 2H, Ar**H**), 7.37 (s, 4H, Ar**H**), 2.51 (s, 3H, SC**H**$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 138.9, 134.4, 131.7, 128.6, 126.9, 126.8, 123.7, 15.8. Anal. Calcd for $C_{15}H_{11}NO_2S$: C, 66.89; H, 4.12; N, 5.20. Found: C, 66.89; H, 4.41; N, 4.86.

References

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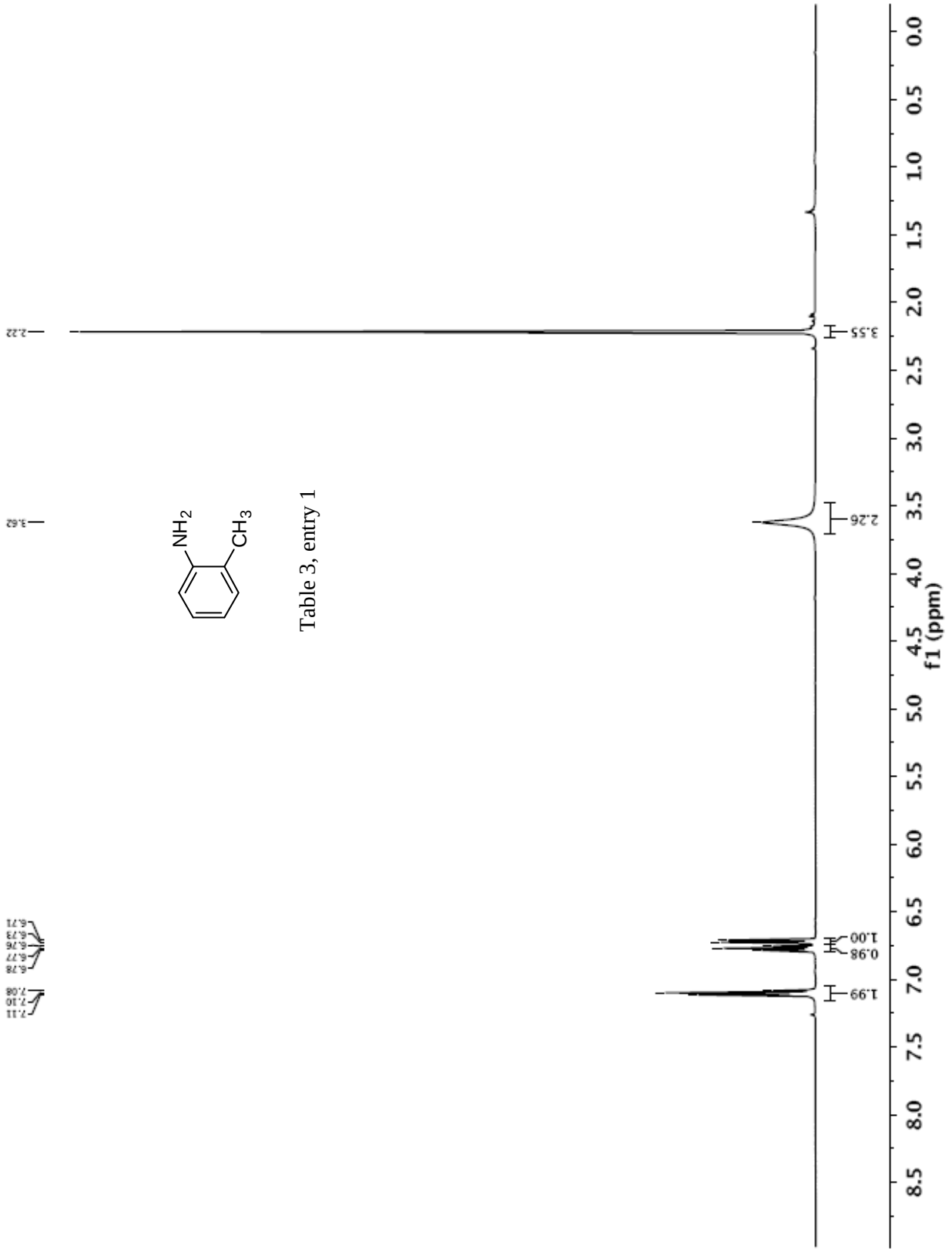

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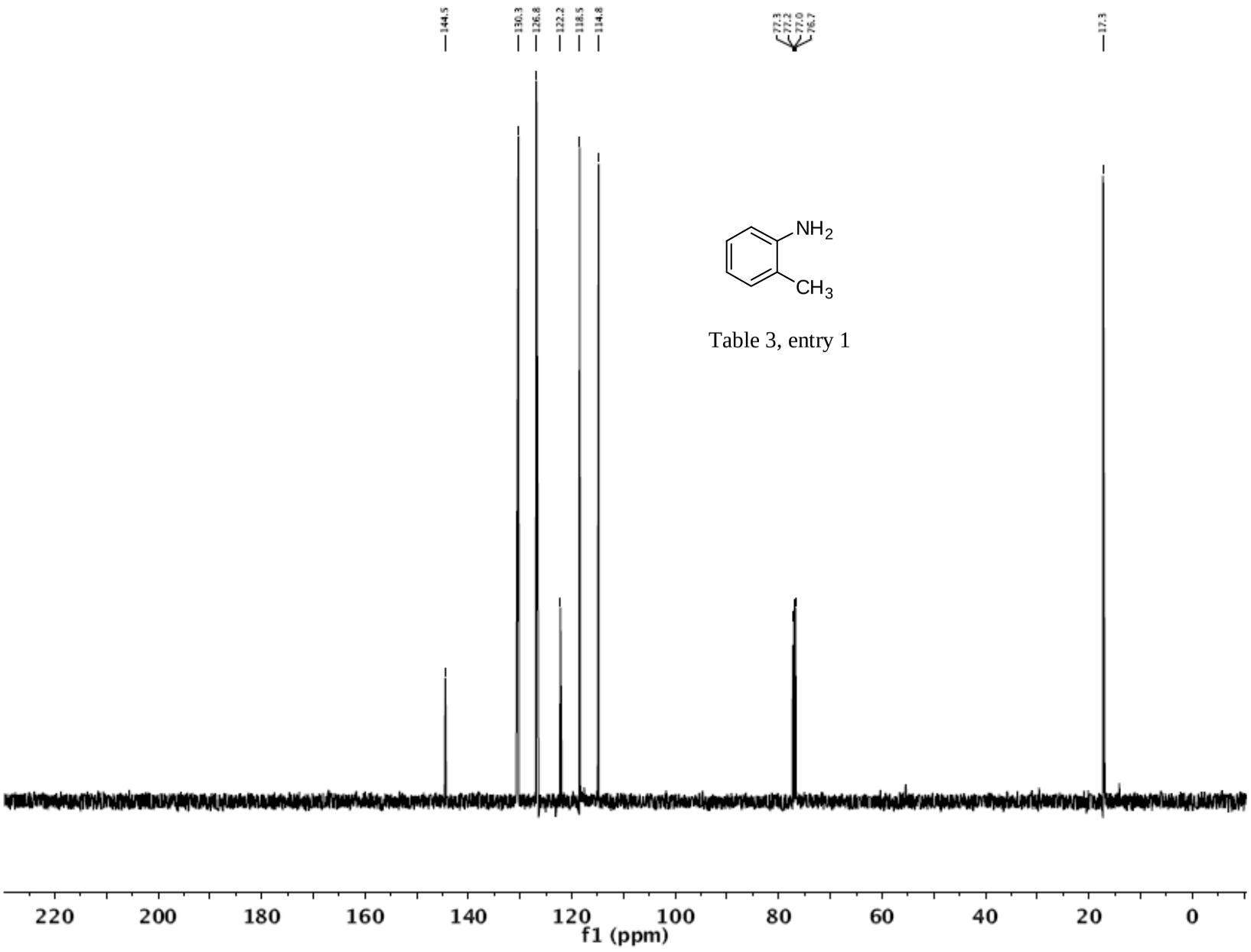

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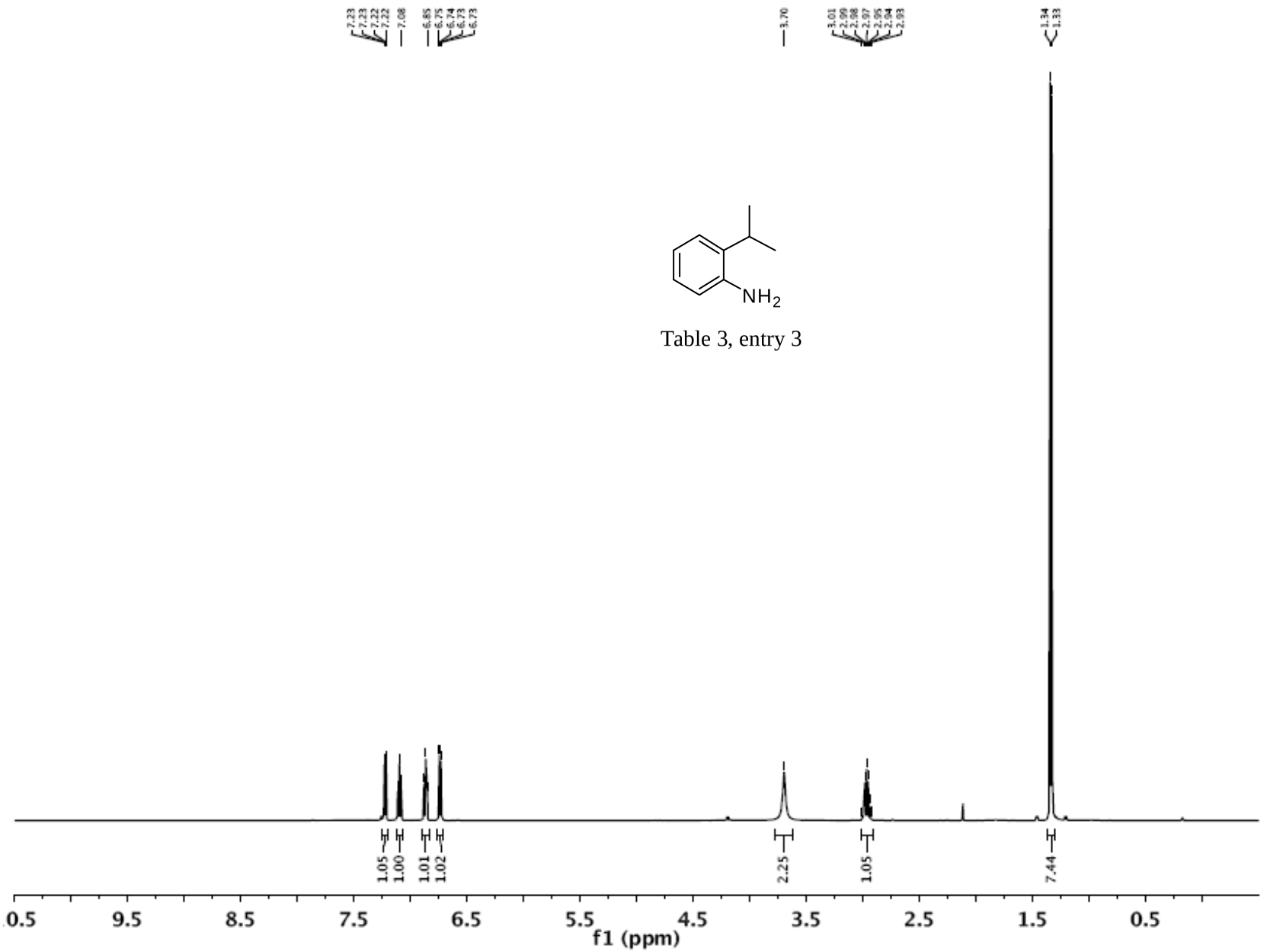
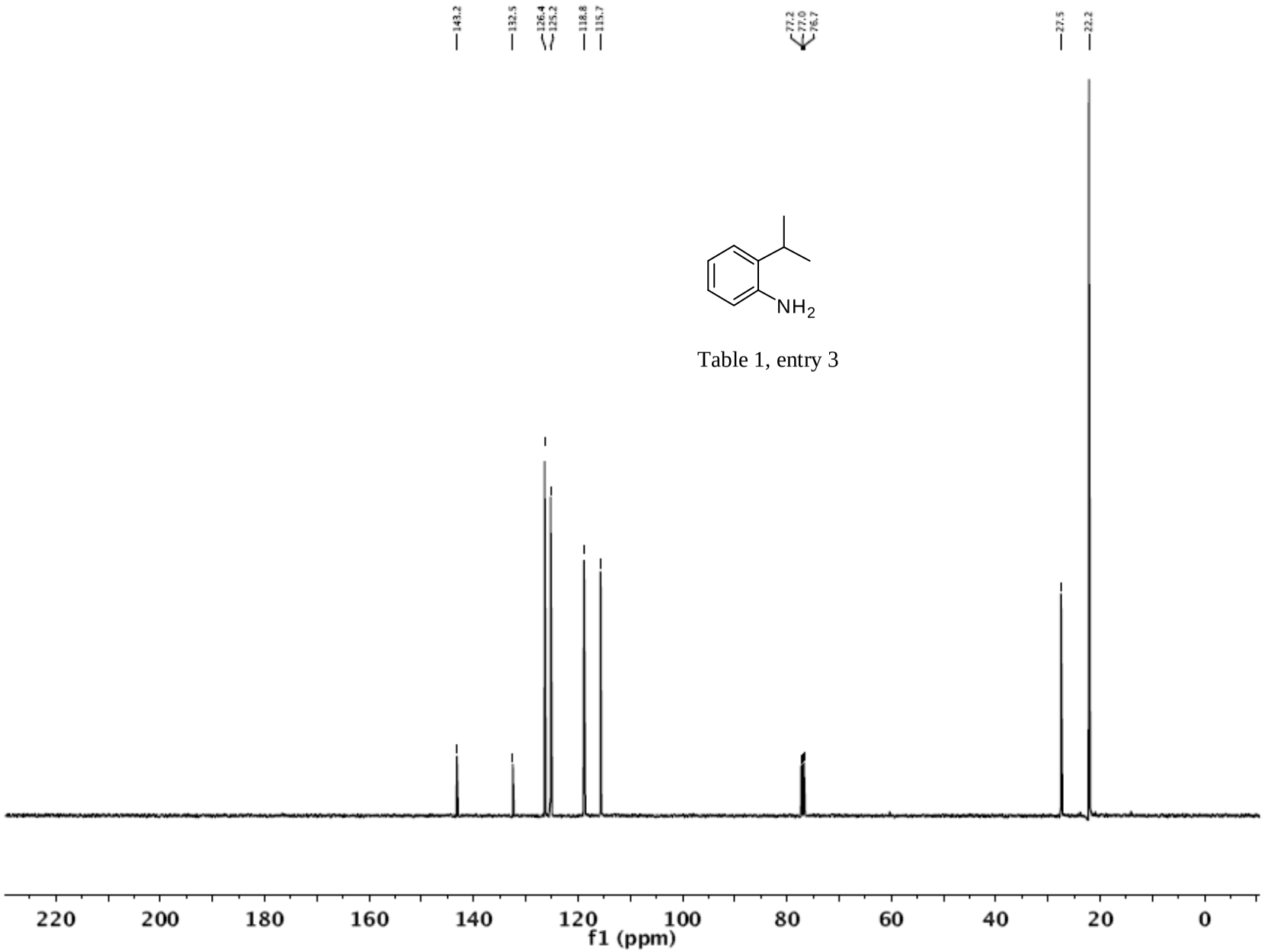


Table 3, entry 3



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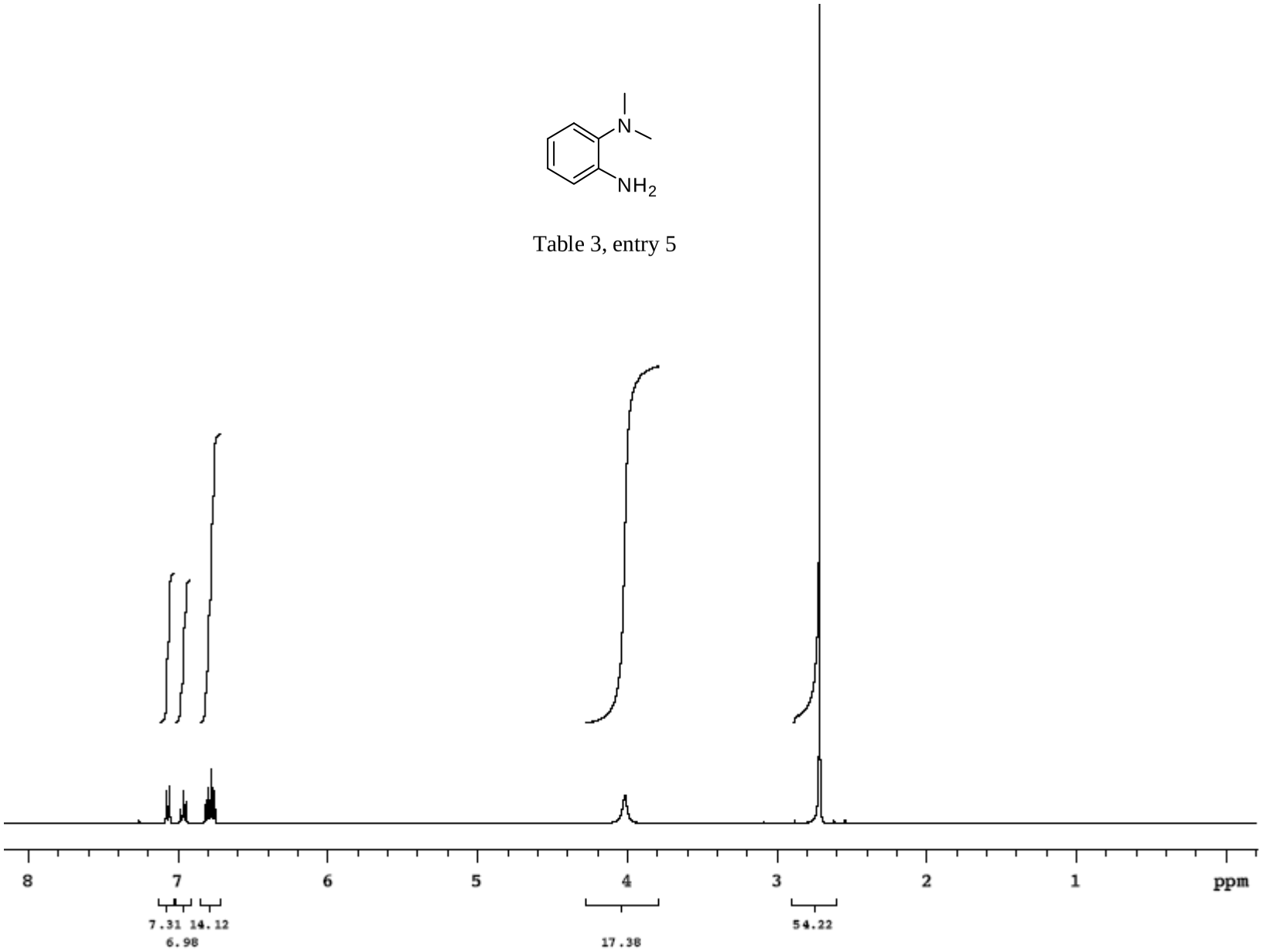

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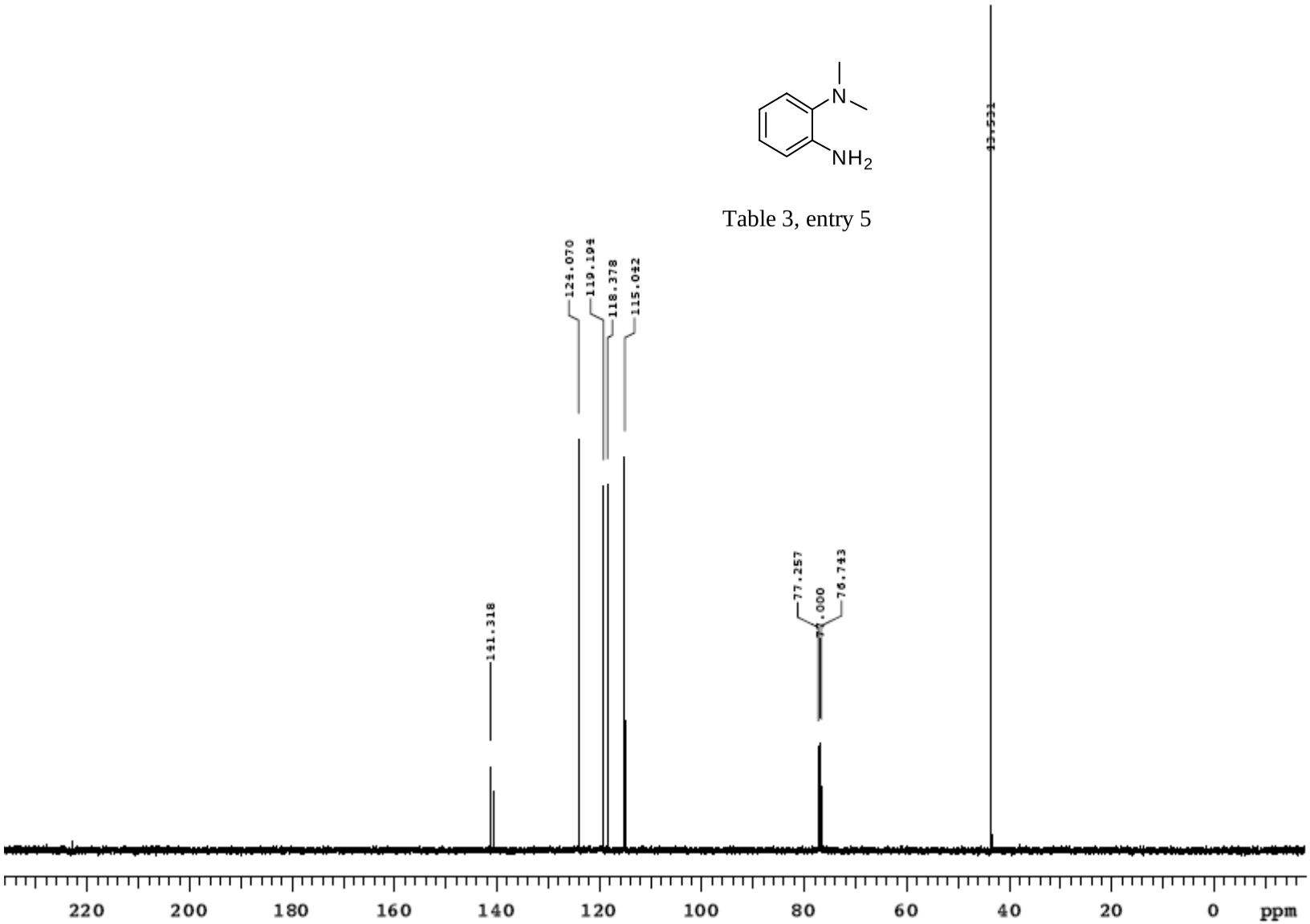
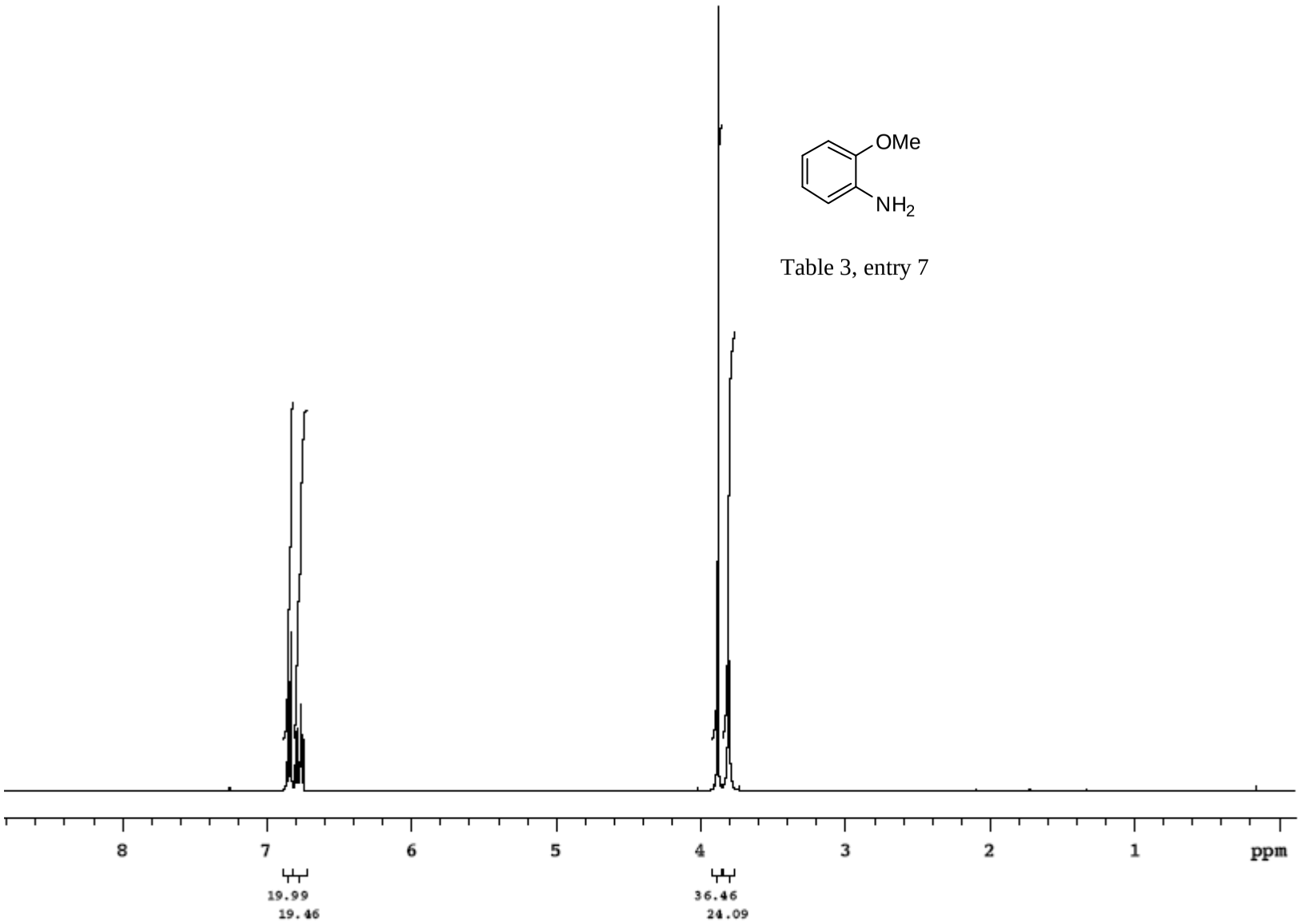


Table 3, entry 5



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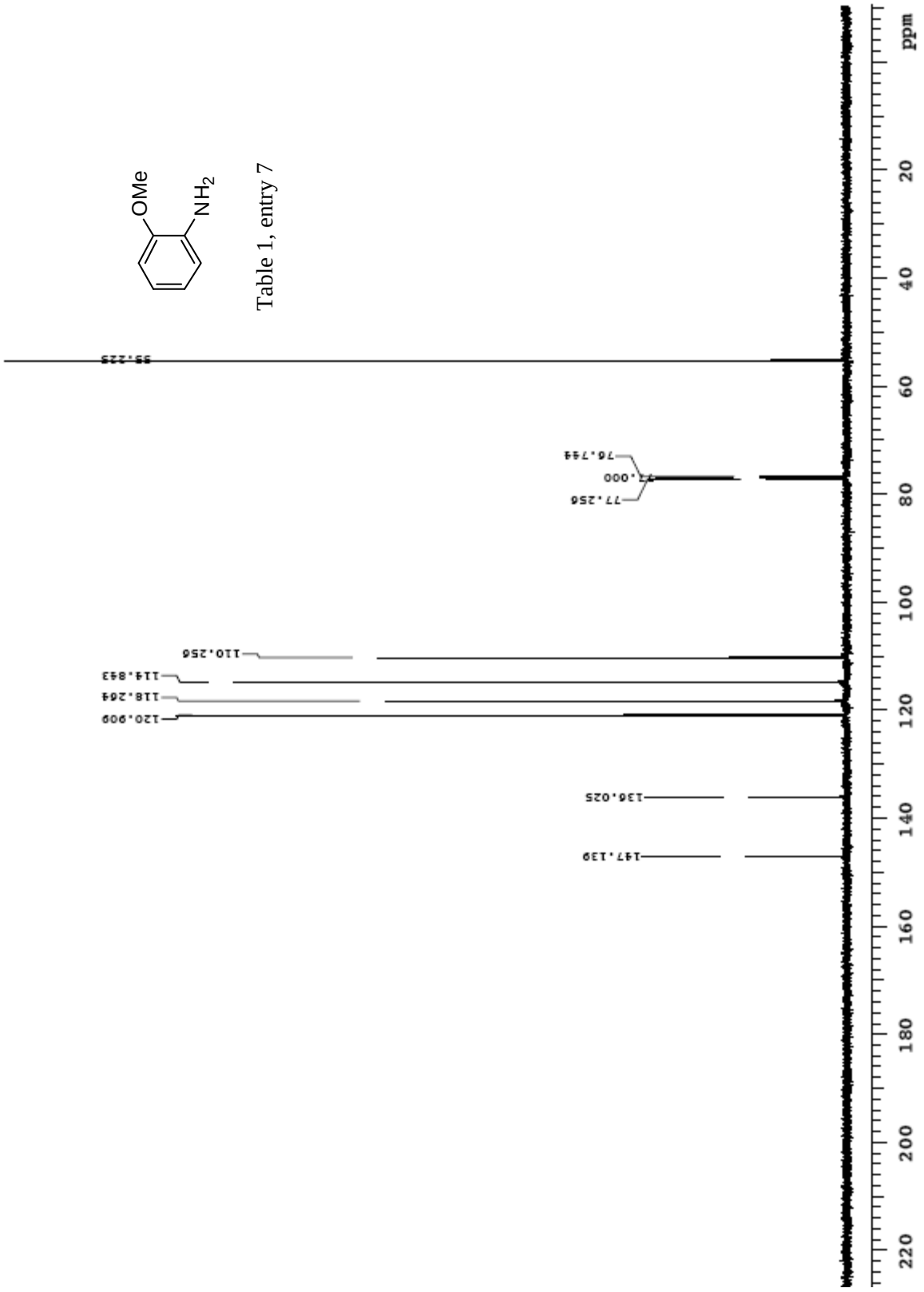
OMe
NH2
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77.000
77.256
110.256
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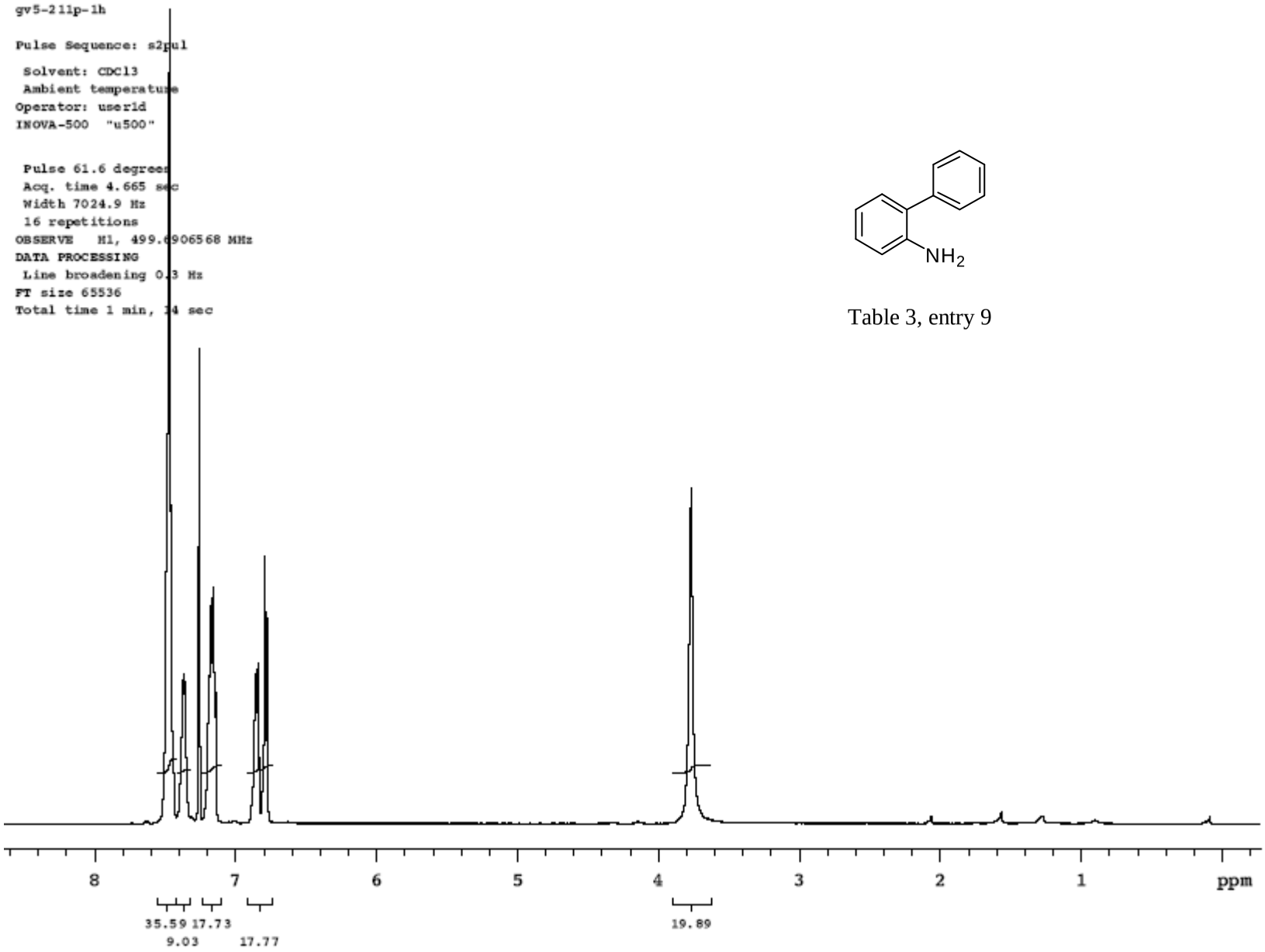
118.264
120.909
136.025
147.139
ppm
20
40
60
80
100
120
140
160
180
200
220



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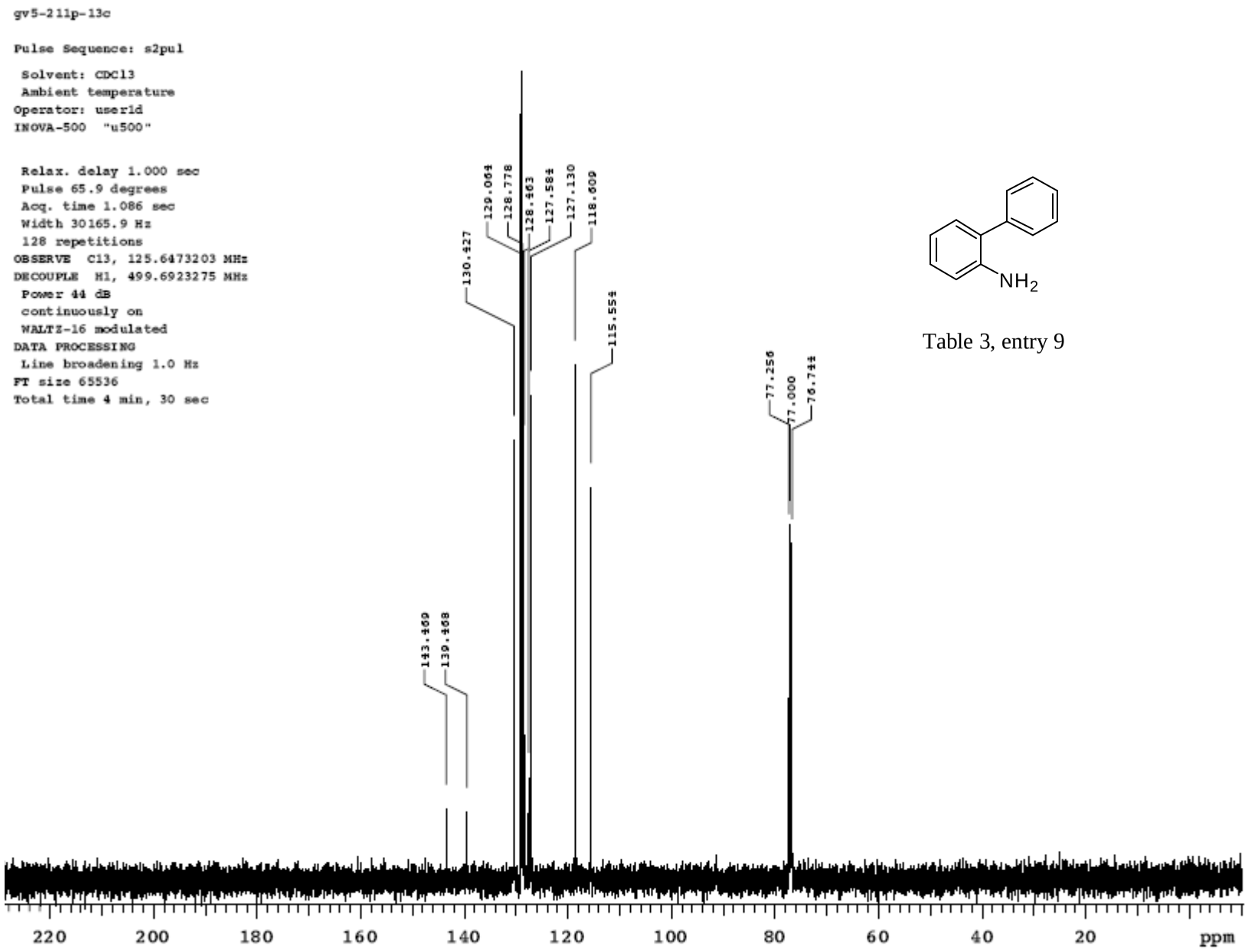

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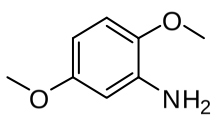

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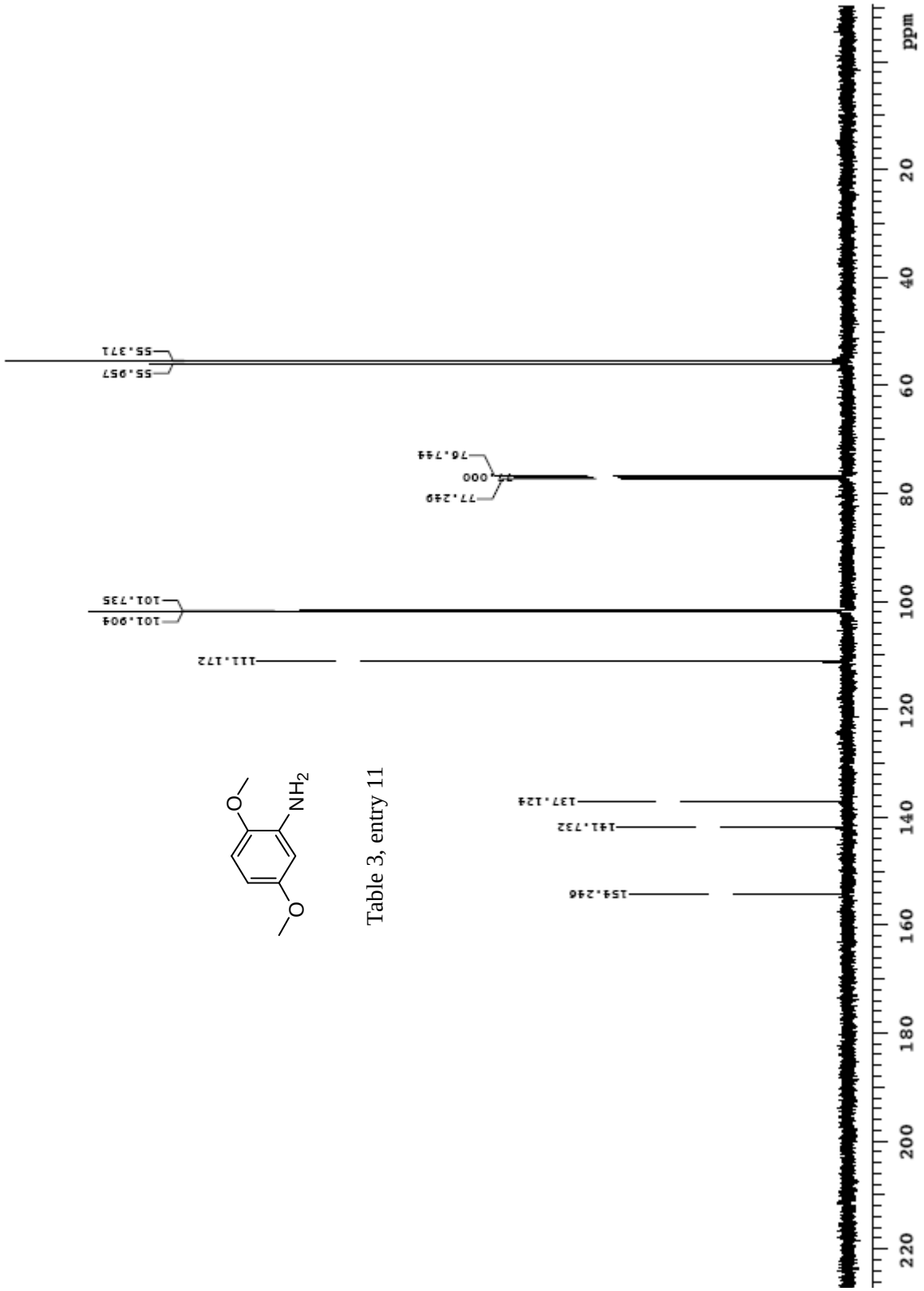

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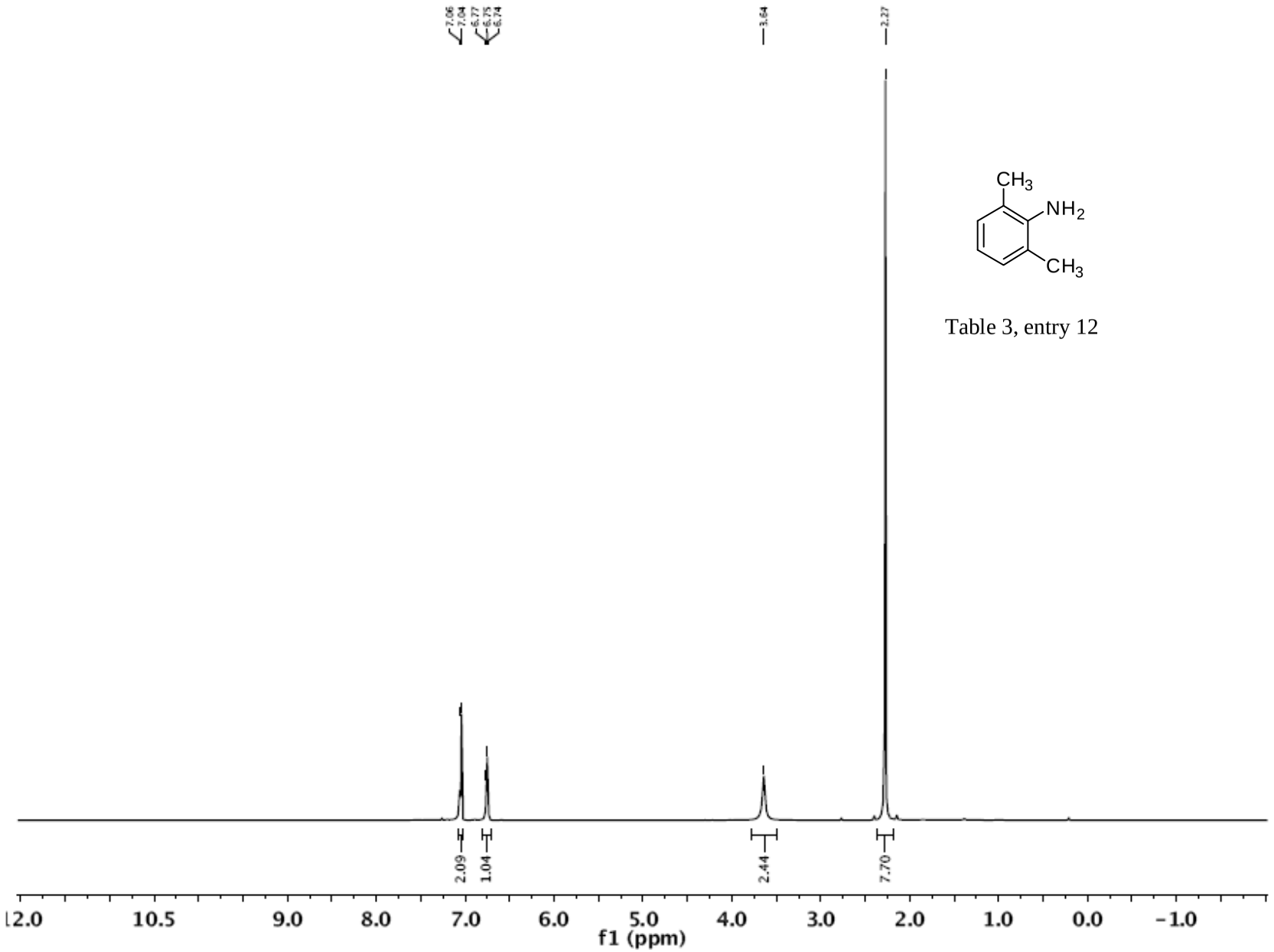

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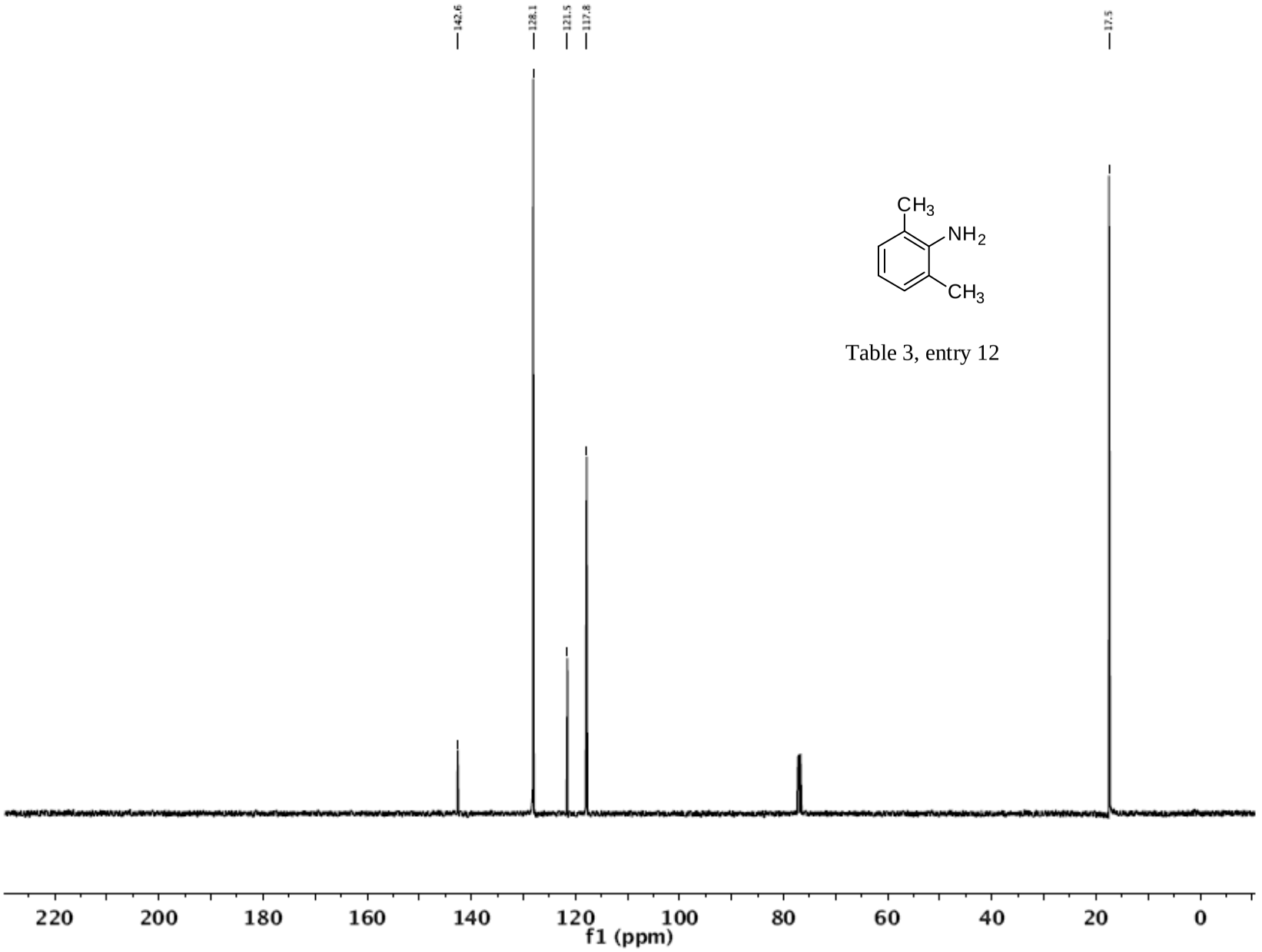

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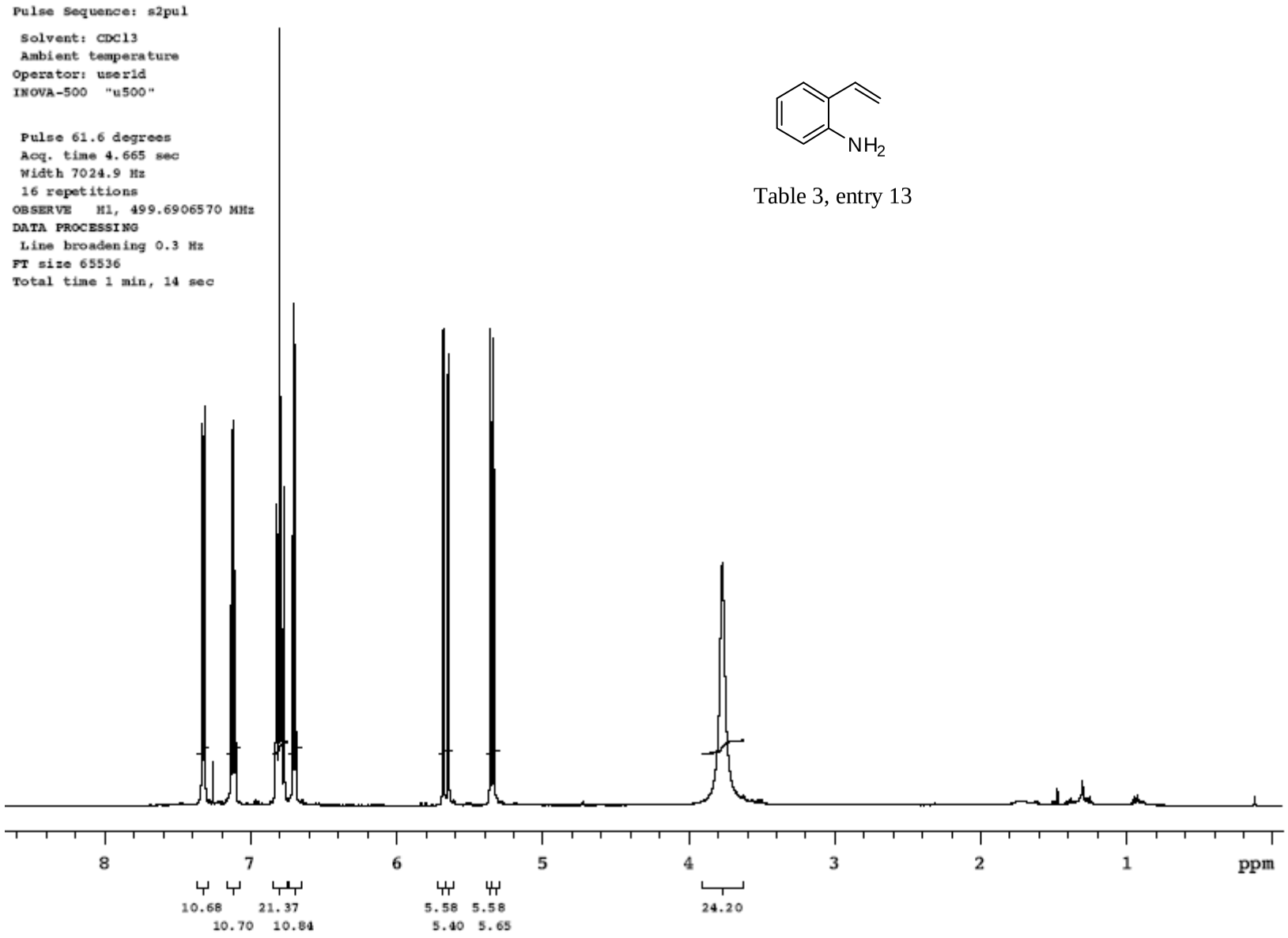

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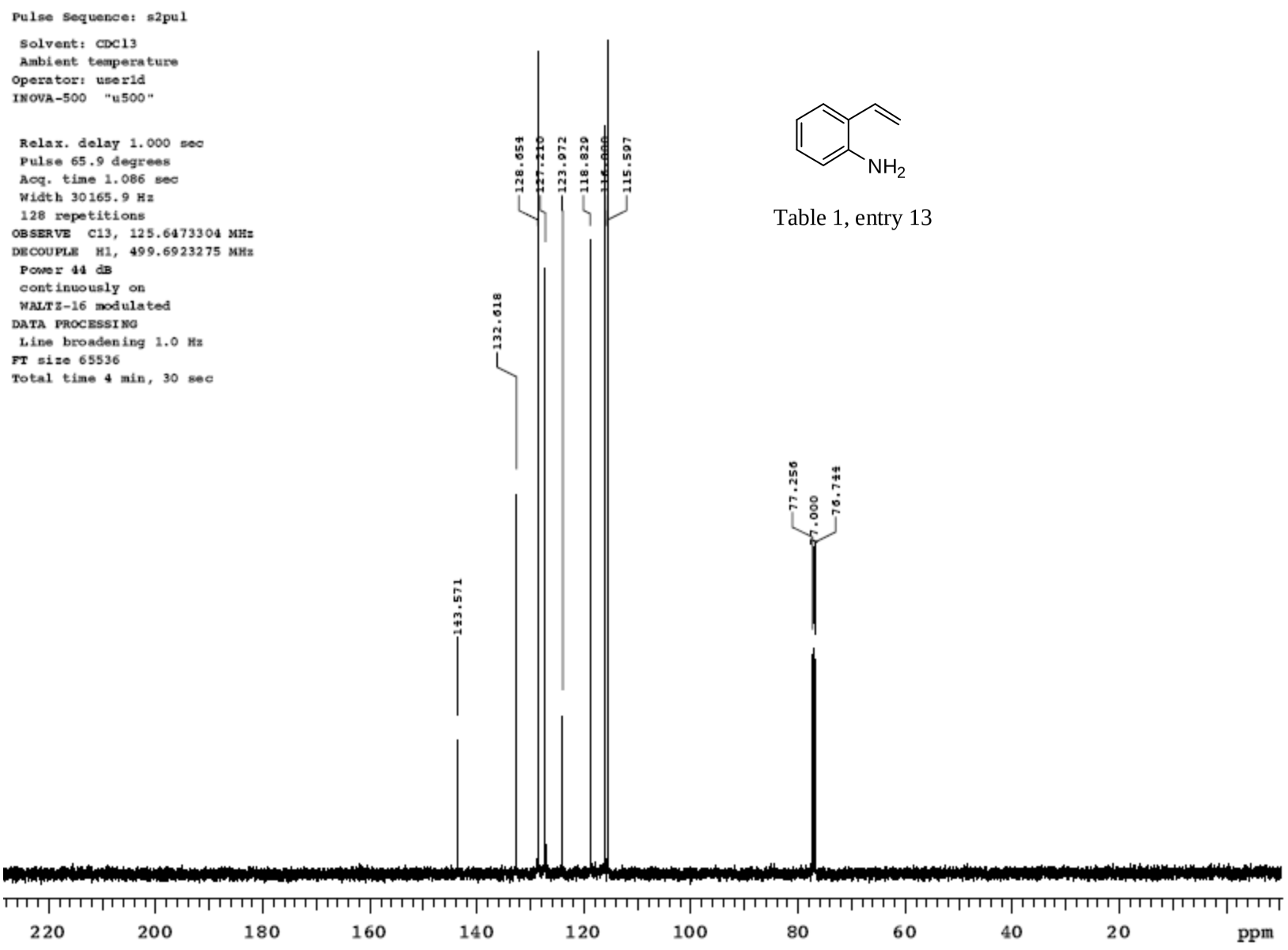

Table 1, entry 13

gv5-232p-1h

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Solvent: CDCl3
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Pulse 45.0 degrees
Acq. time 4.096 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 399.9486787 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 2 min, 11 sec

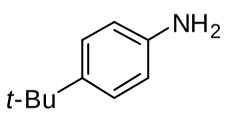
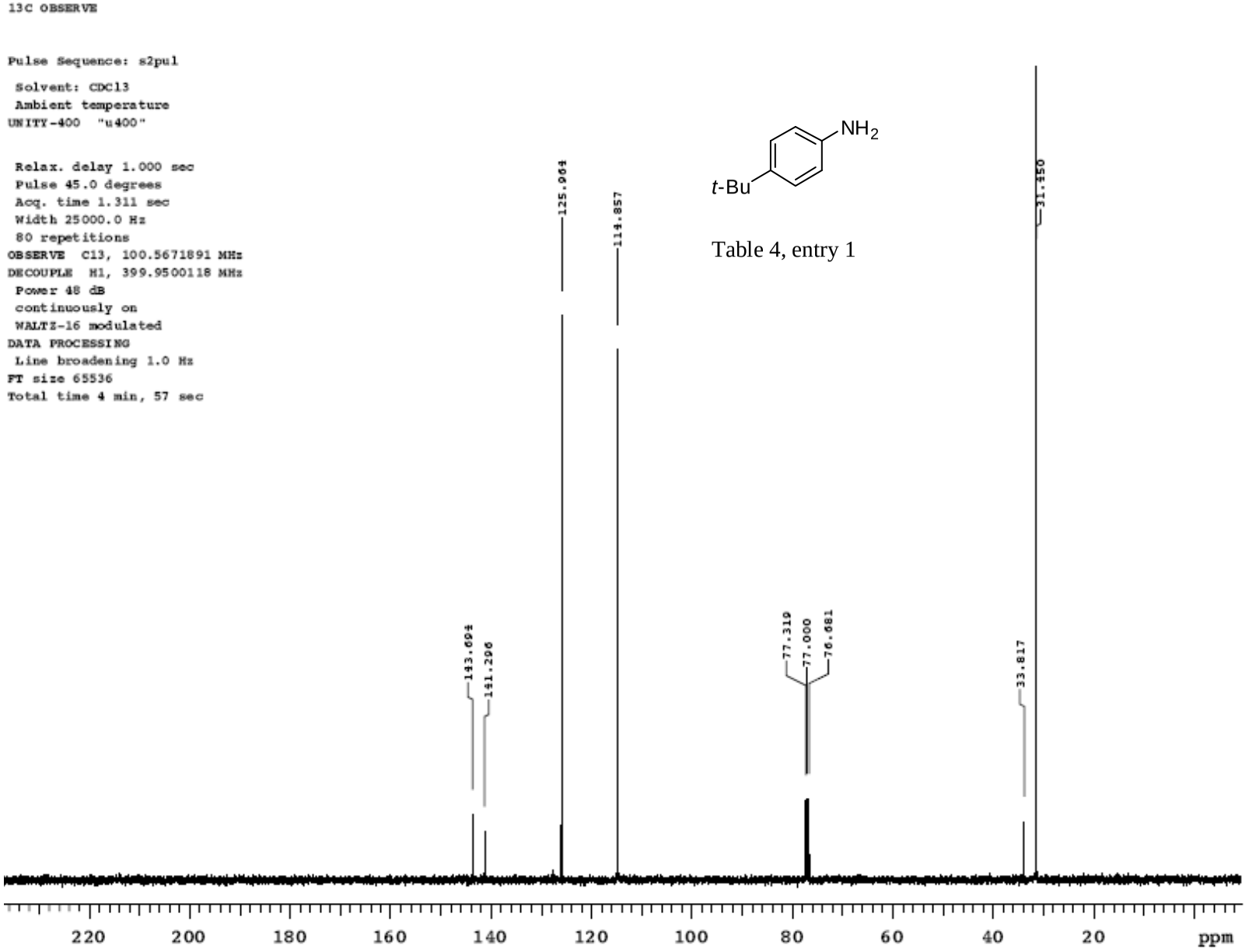


Table 4, entry 1


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
UNITY-400 "u400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
80 repetitions
OBSERVE C13, 100.5671891 MHz
DECOUPLE H1, 399.9500118 MHz
Power 48 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 4 min, 57 sec
NH2
t-Bu
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31.450
143.694
141.296
77.319
77.000
76.681
33.817
220
200
180
160
140
120
100
80
60
40
20
ppm

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Operator: userid
INOVA-500 "u500"

Pulse 61.6 degrees
Acq. time 4.665 sec
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Line broadening 0.3 Hz
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Total time 1 min, 14 sec

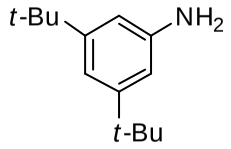

Table 4, entry 2

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 Solvent: CDCl3
 Ambient temperature
Operator: userid
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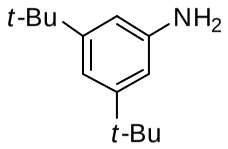
 Pulse 65.9 degrees
 Acq. time 1.086 sec
 Width 30165.9 Hz
 128 repetitions
OBSERVE  C13, 125.6473203 MHz
DECOUPLE  H1, 499.6923275 MHz
 Power 44 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 4 min, 30 sec
```



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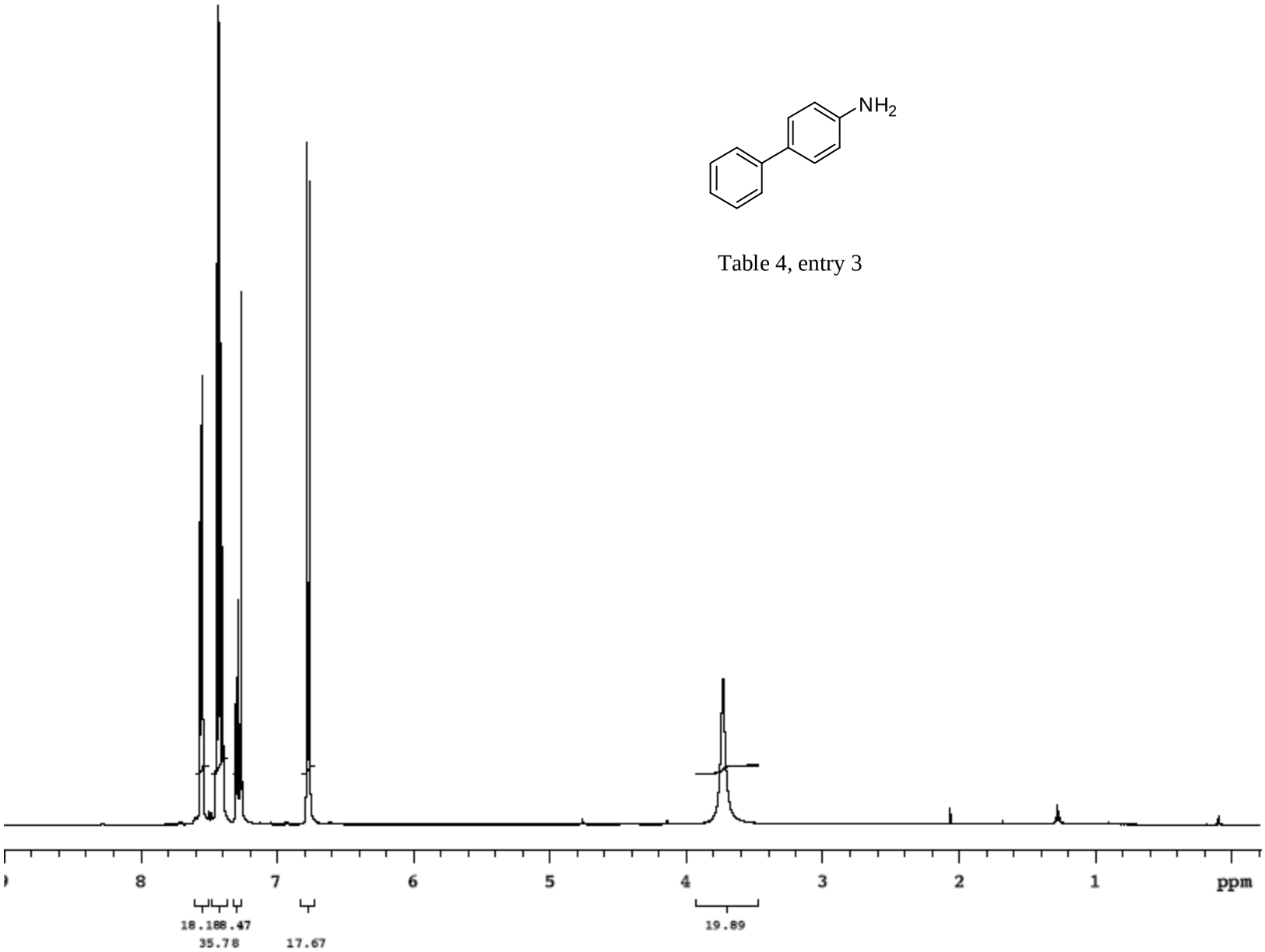

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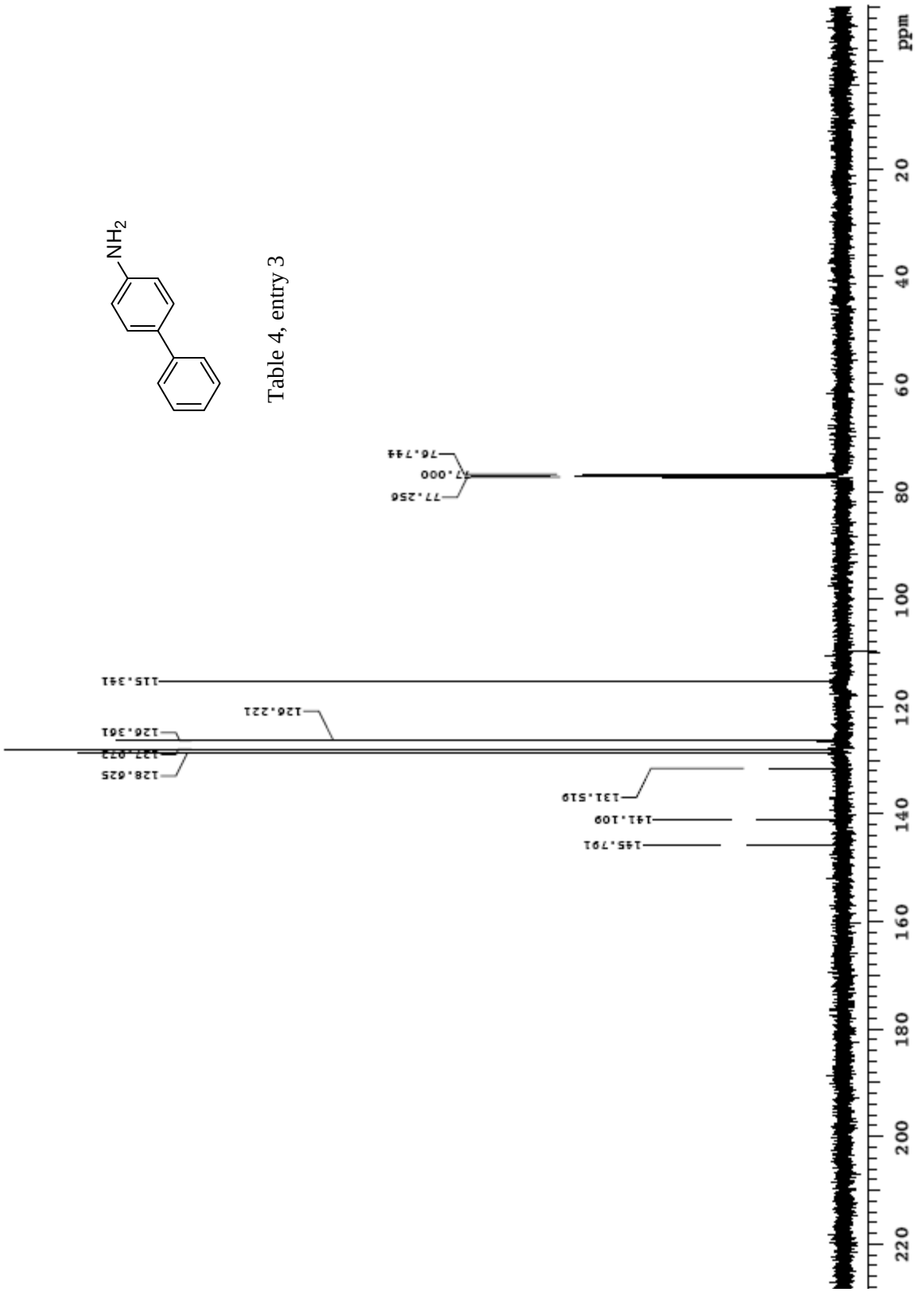
NH2
Table 4, entry 3
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60
80
100
120
140
160
180
200
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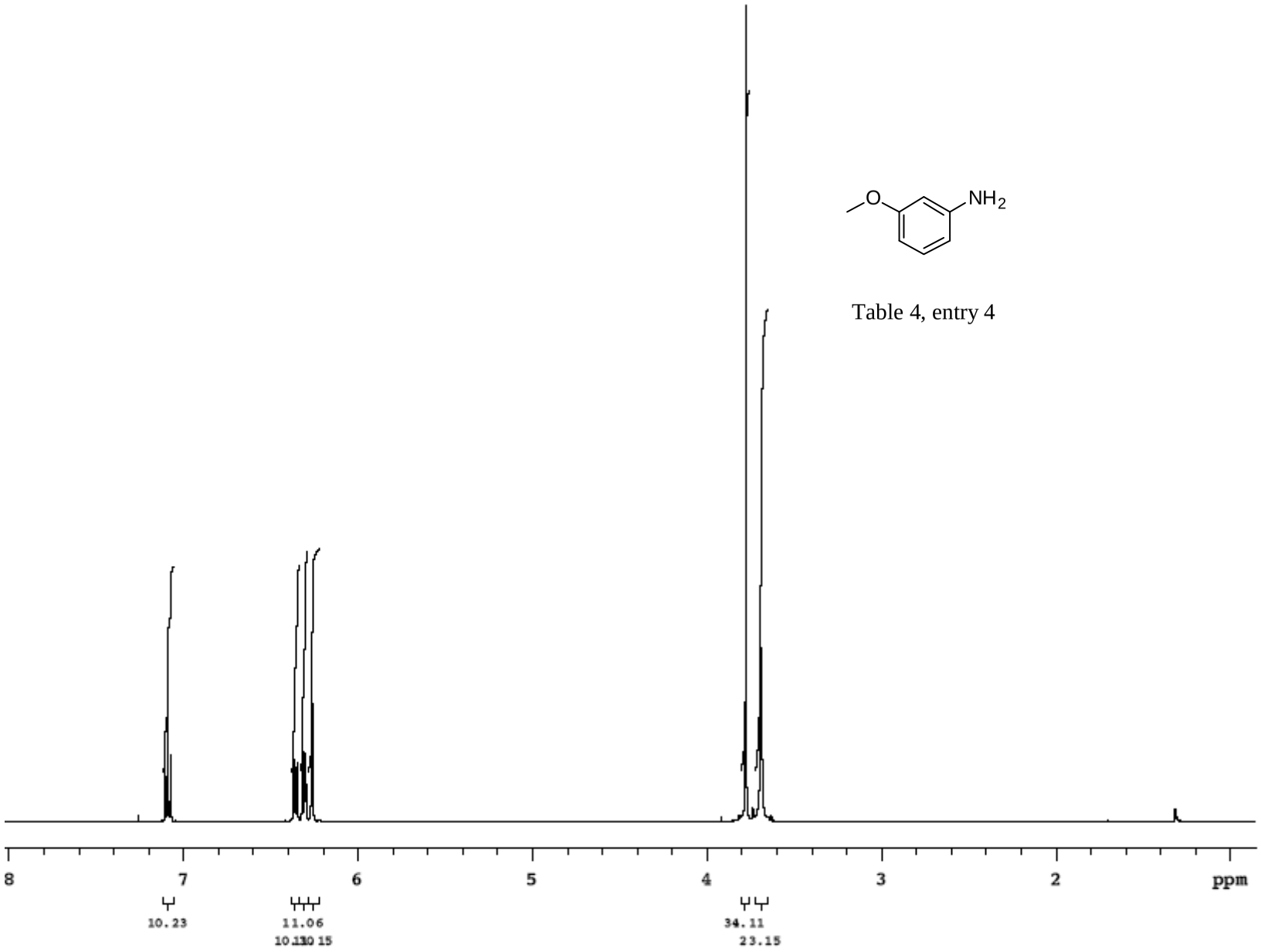
145.701



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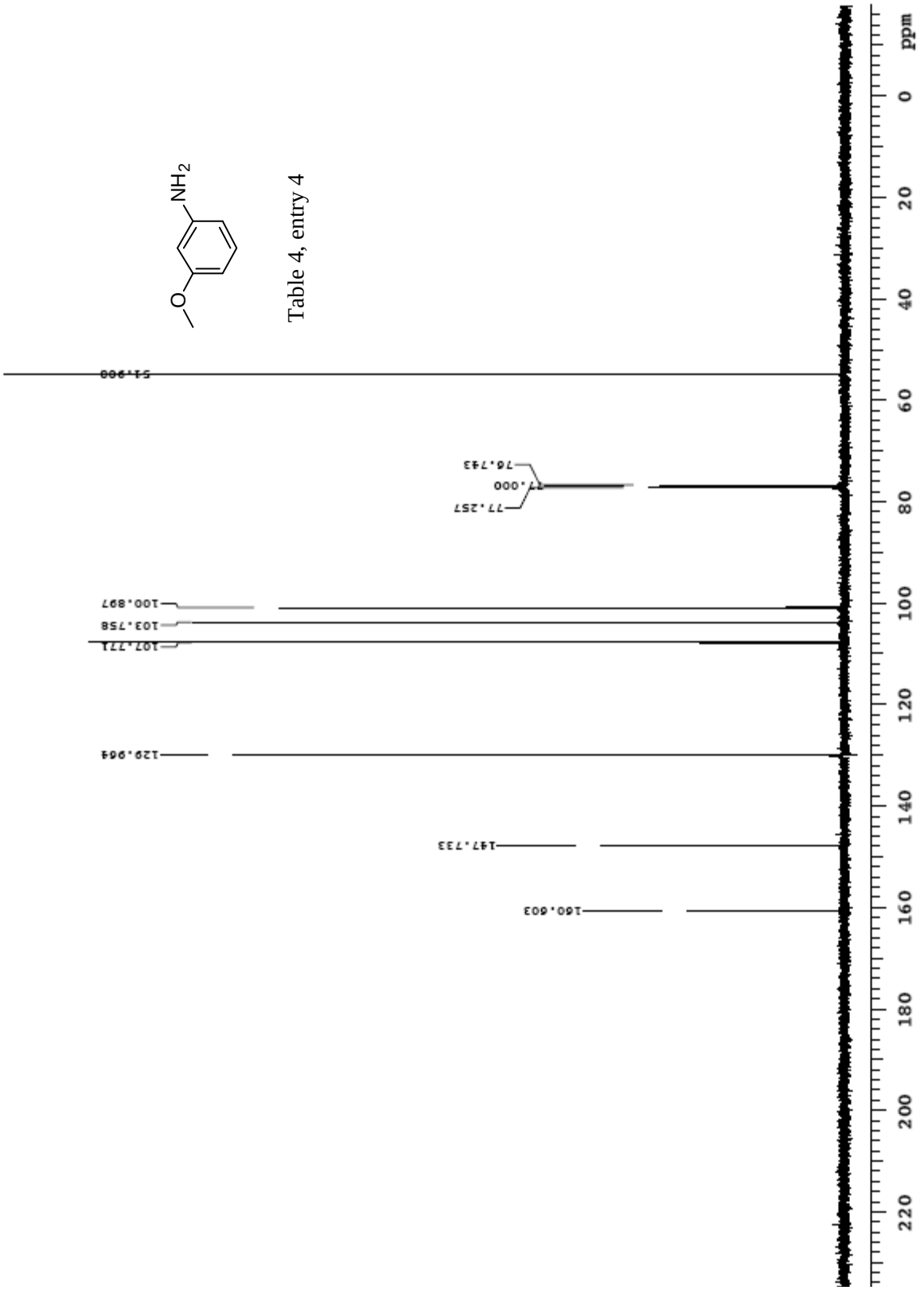
Table 4, entry 4
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ppm

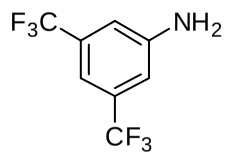
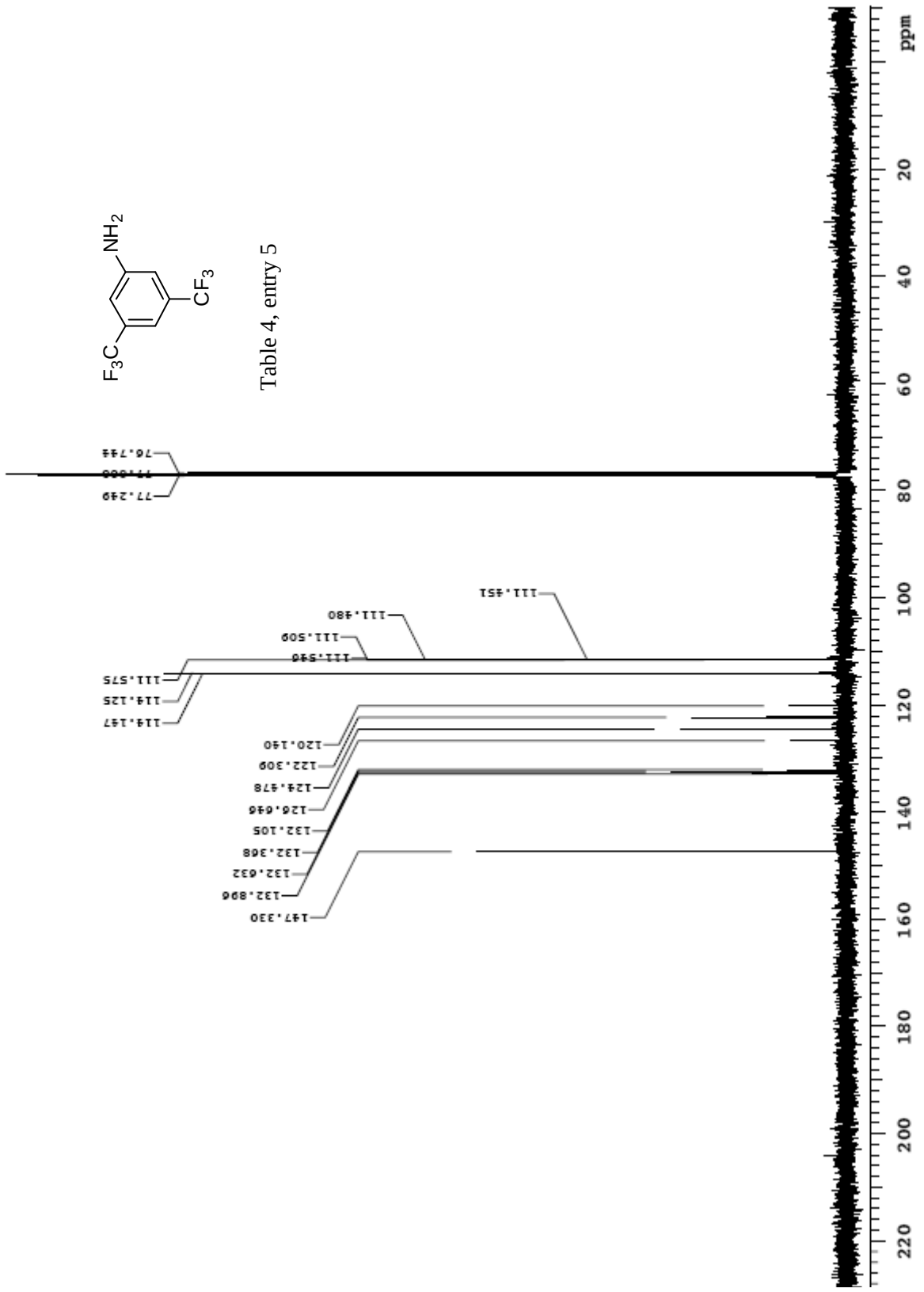


Table 4, entry 5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F3C
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60
80
100
120
140
160
180
200
220
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77.249
111.451
111.480
111.509
111.540
111.575
114.125
114.147
120.150
122.309
124.478
126.646
132.105
132.368
132.632
132.896
147.330

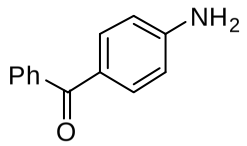
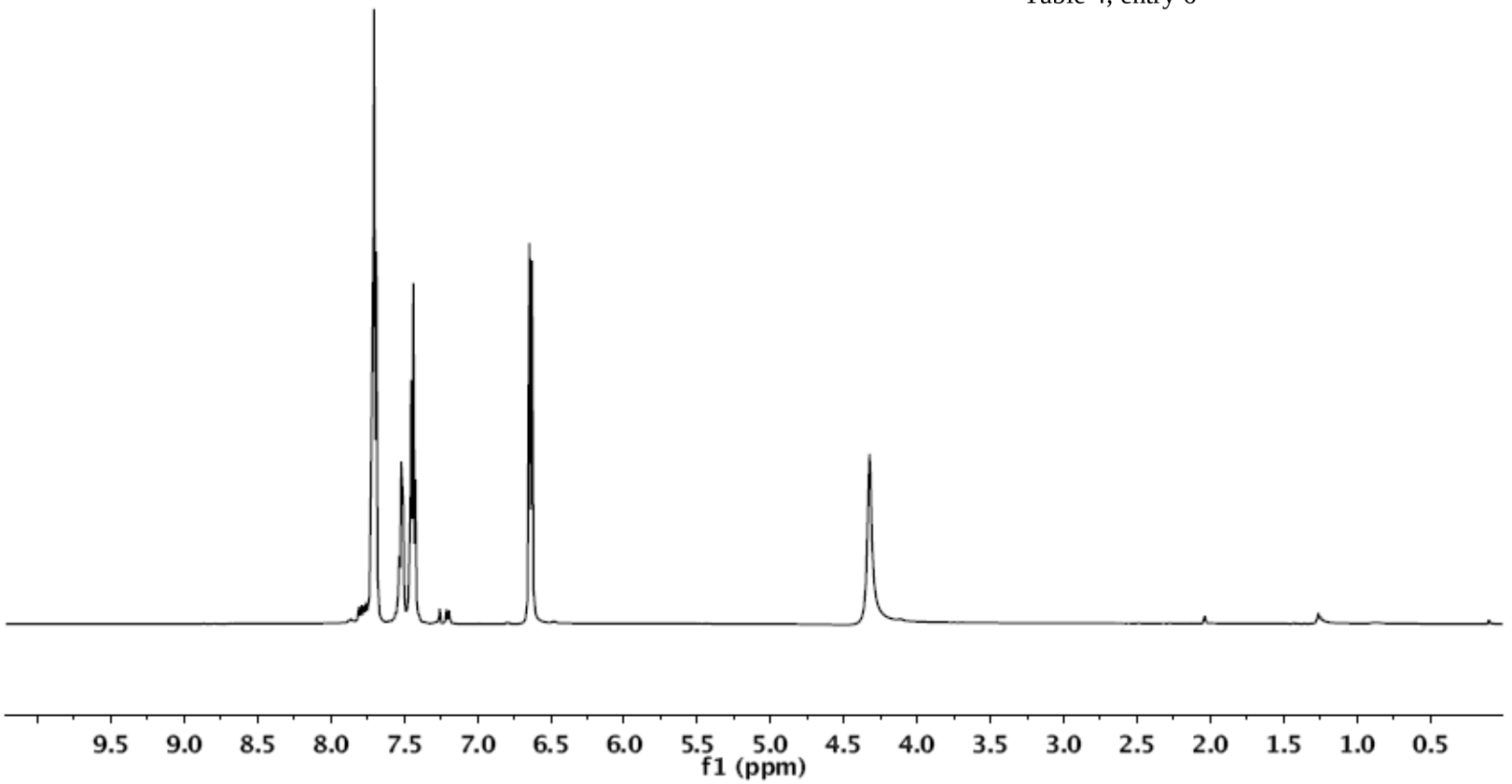


Table 4, entry 6



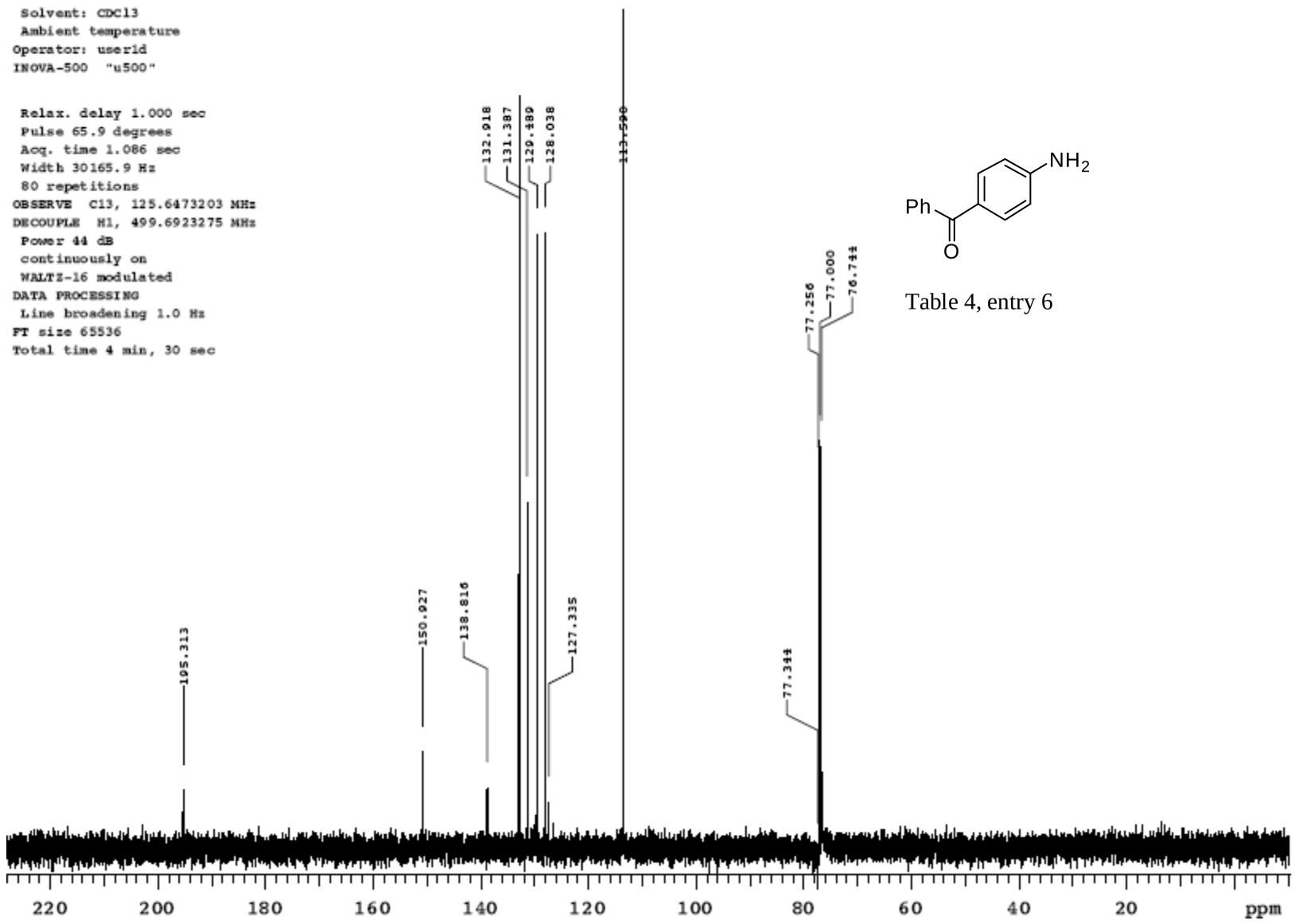


Table 4, entry 6

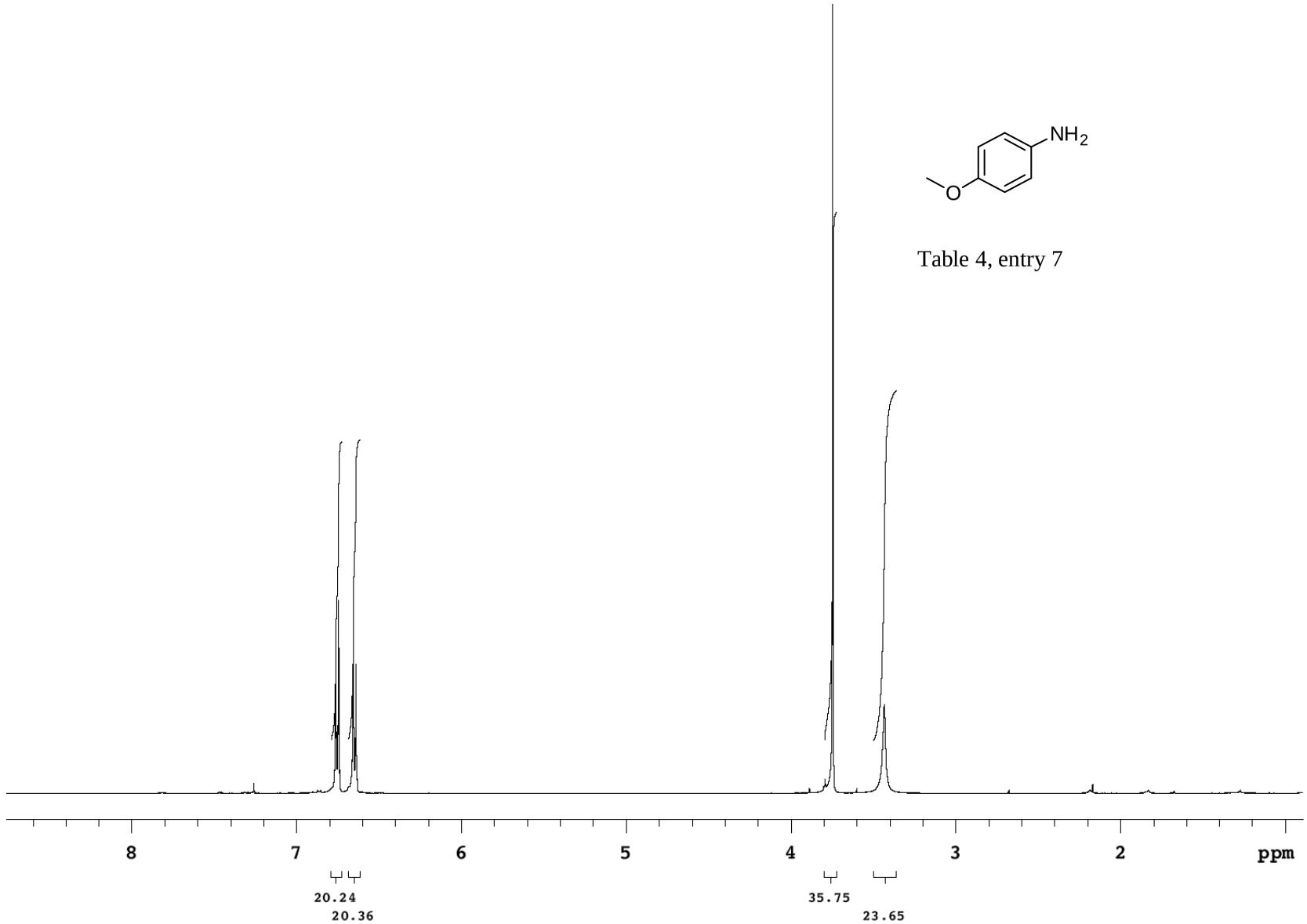


Table 4, entry 7

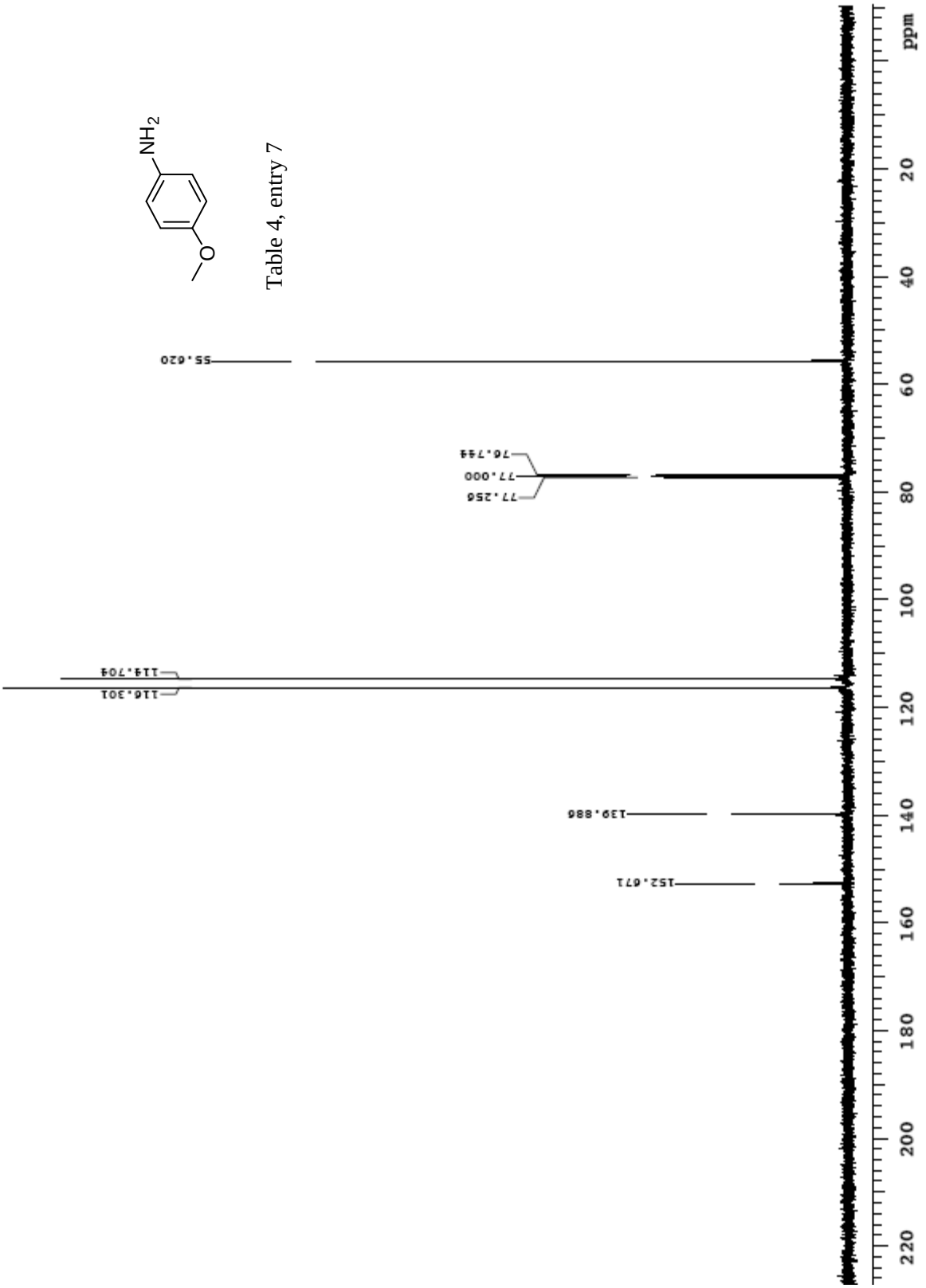


Table 4, entry 7
NH2
O
55.620
76.744
77.000
77.256
116.301
119.709
139.886
152.671
ppm
20
40
60
80
100
120
140
160
180
200
220

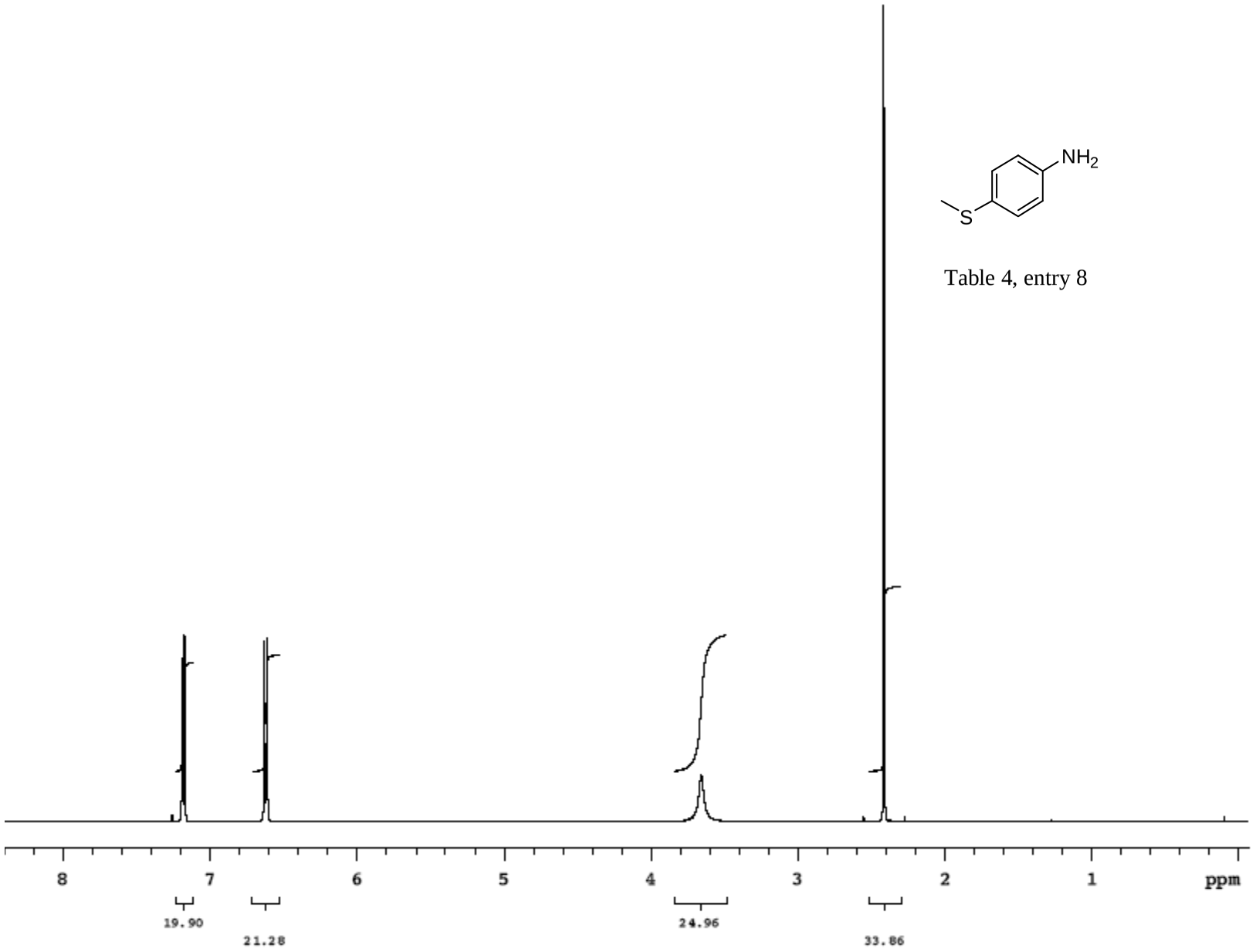
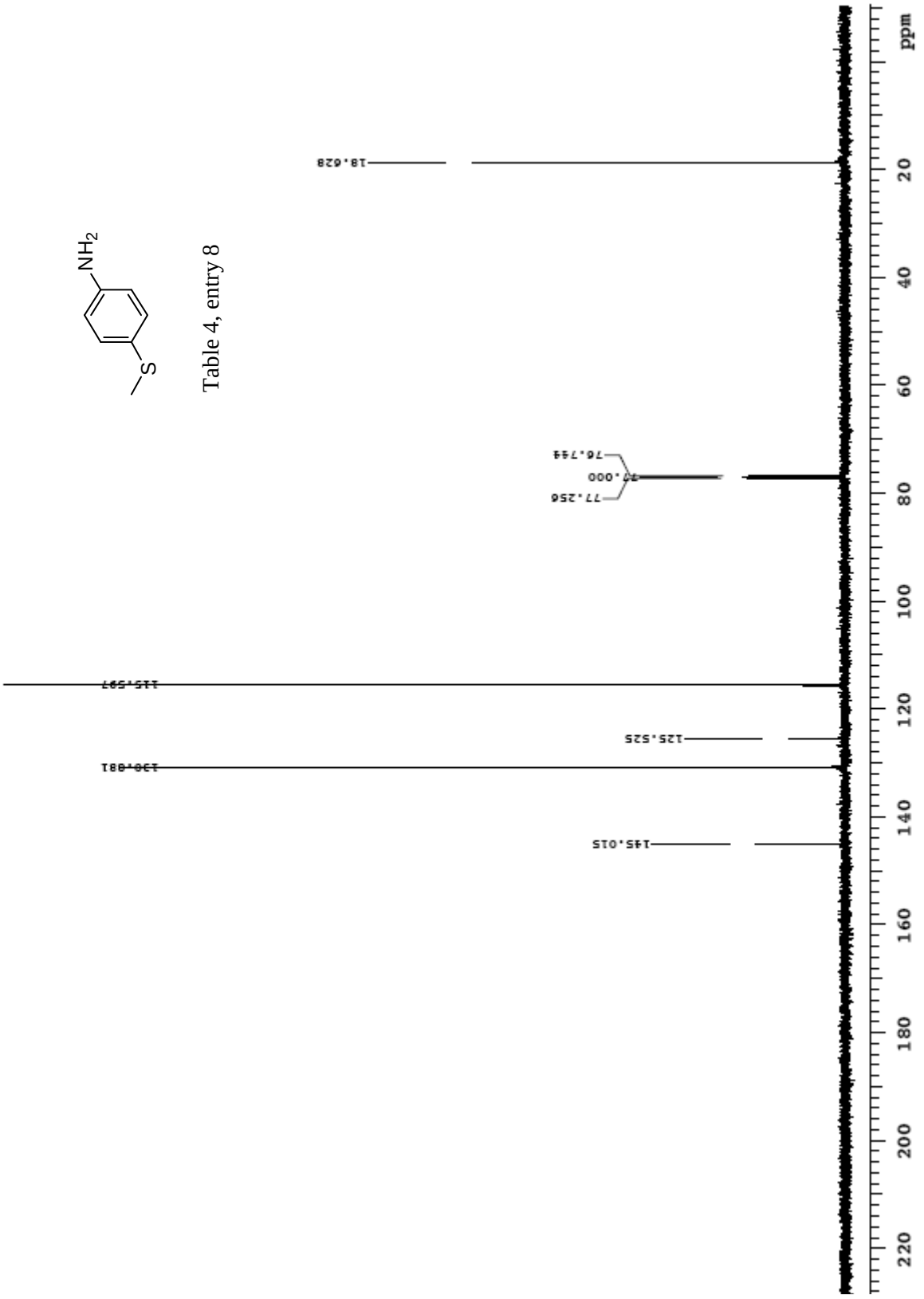


Table 4, entry 8


NH2
S
Table 4, entry 8
18.628
76.744
77.000
77.256
115.597
125.525
130.081
145.015
ppm
20
40
60
80
100
120
140
160
180
200
220

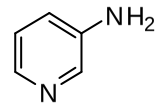
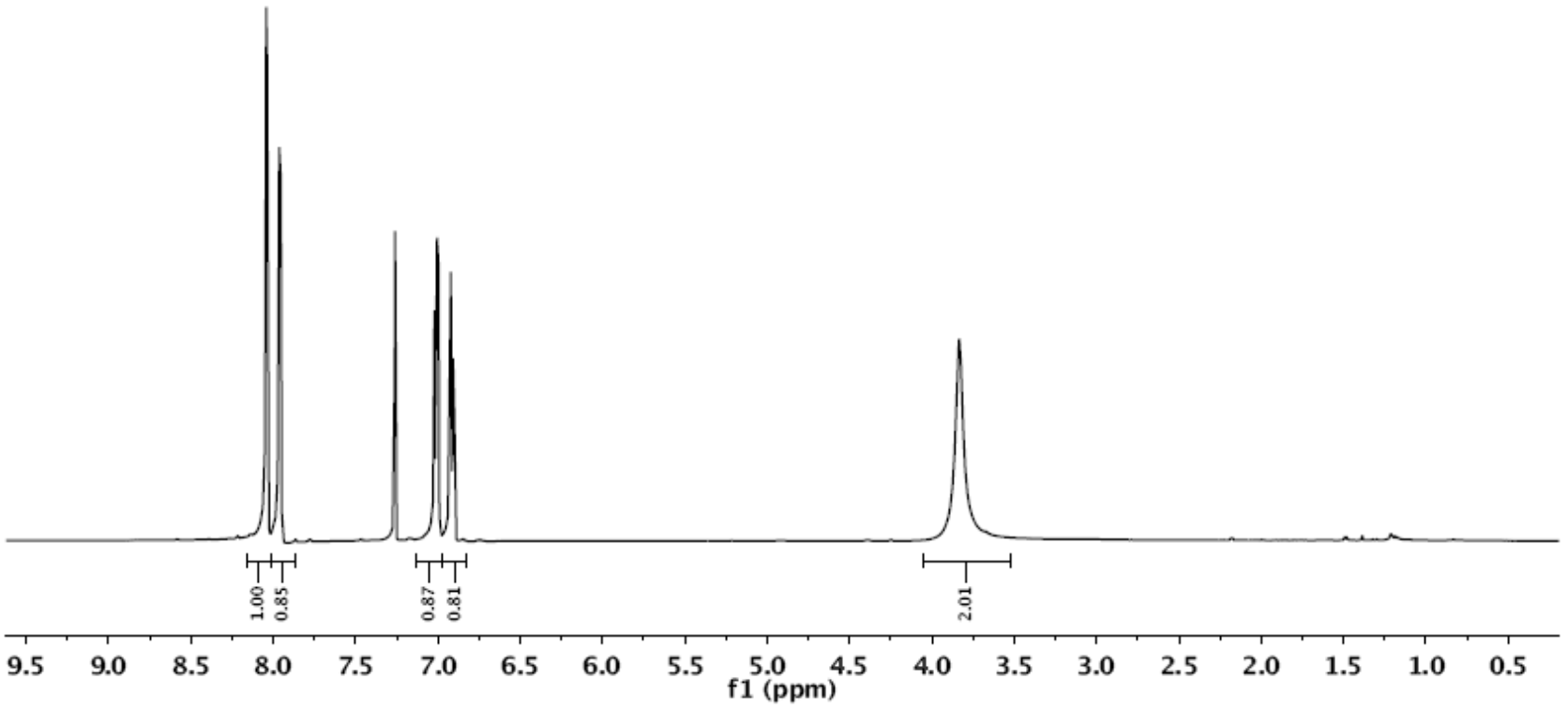


Table 4, entry 9



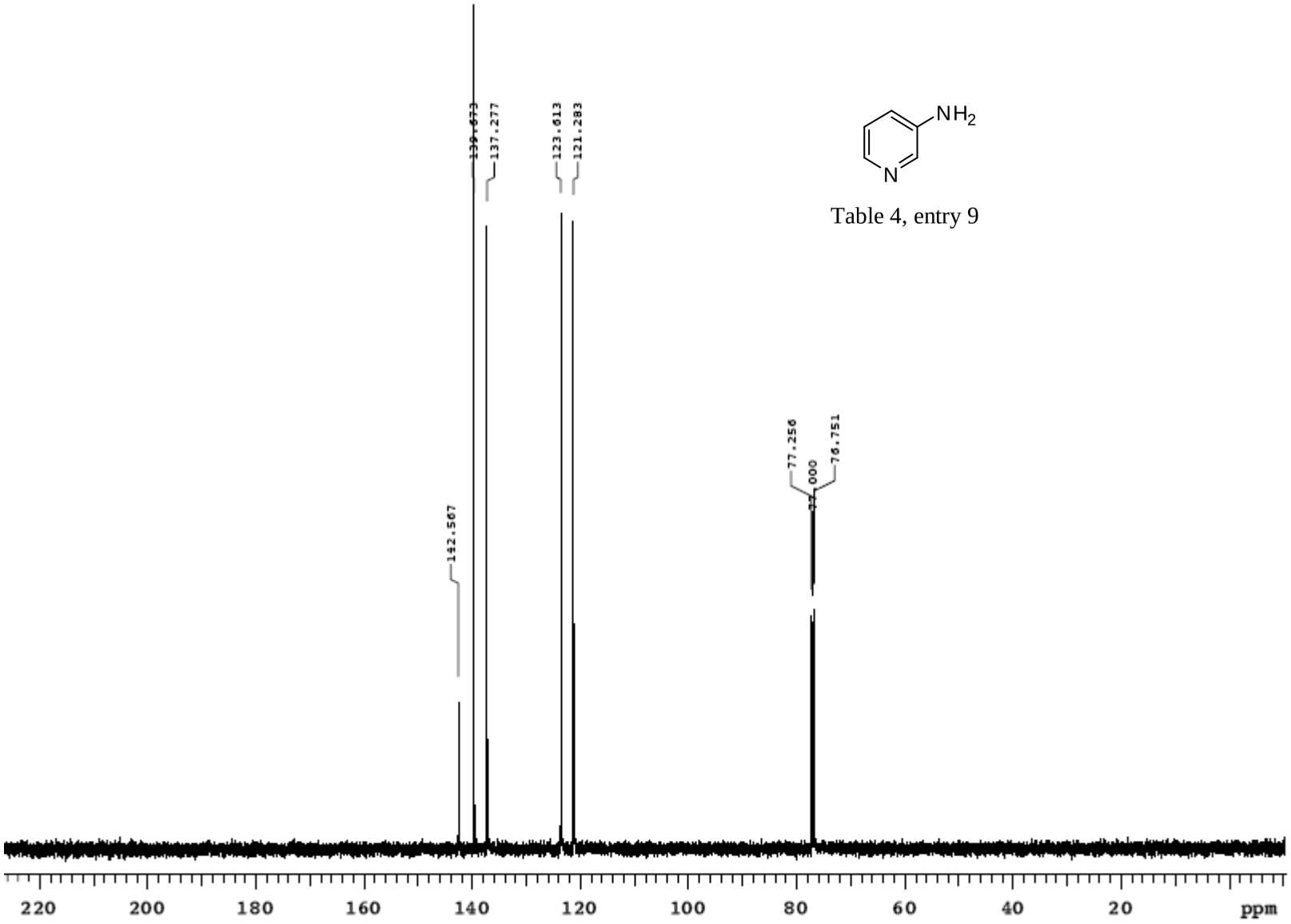


Table 4, entry 9

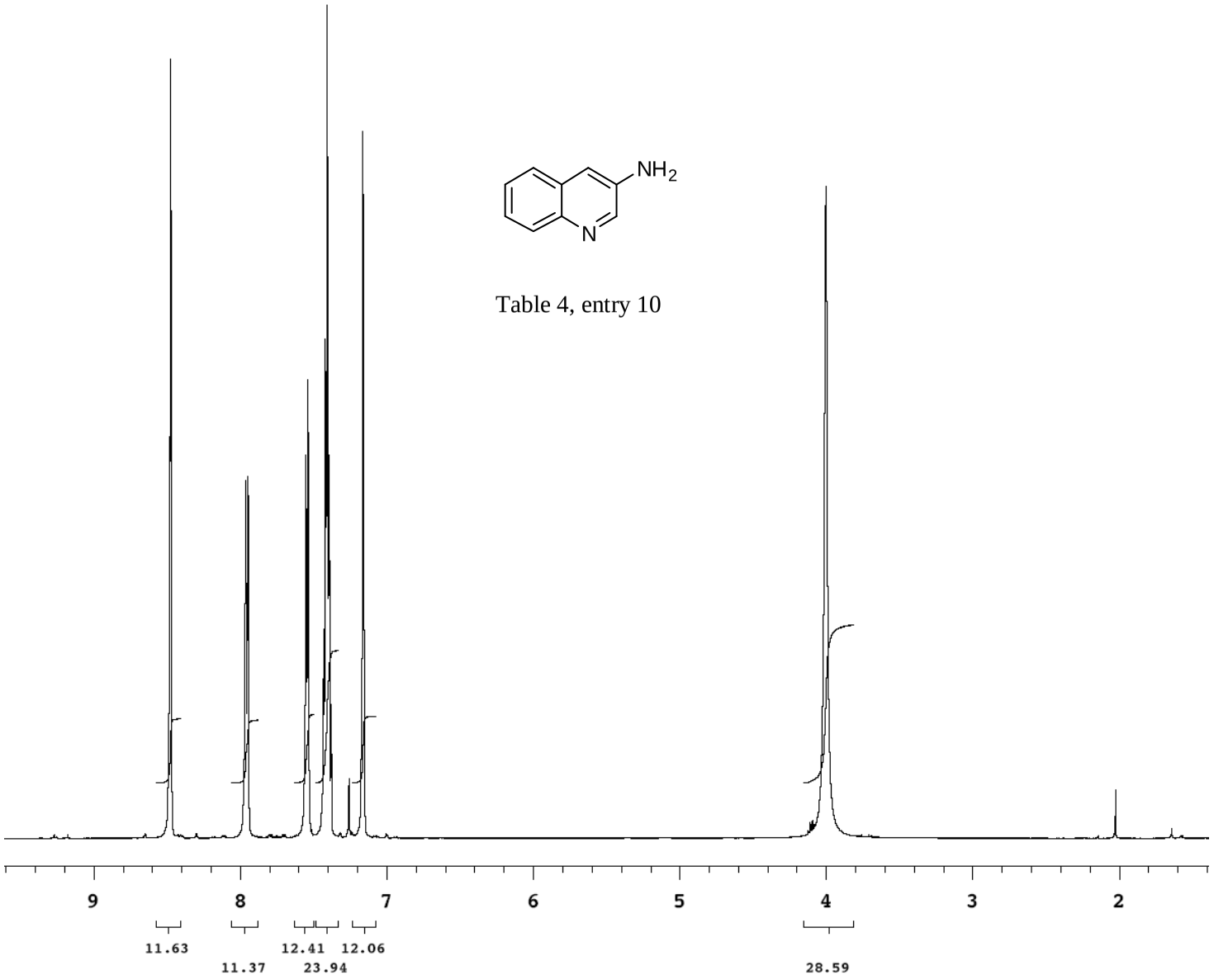
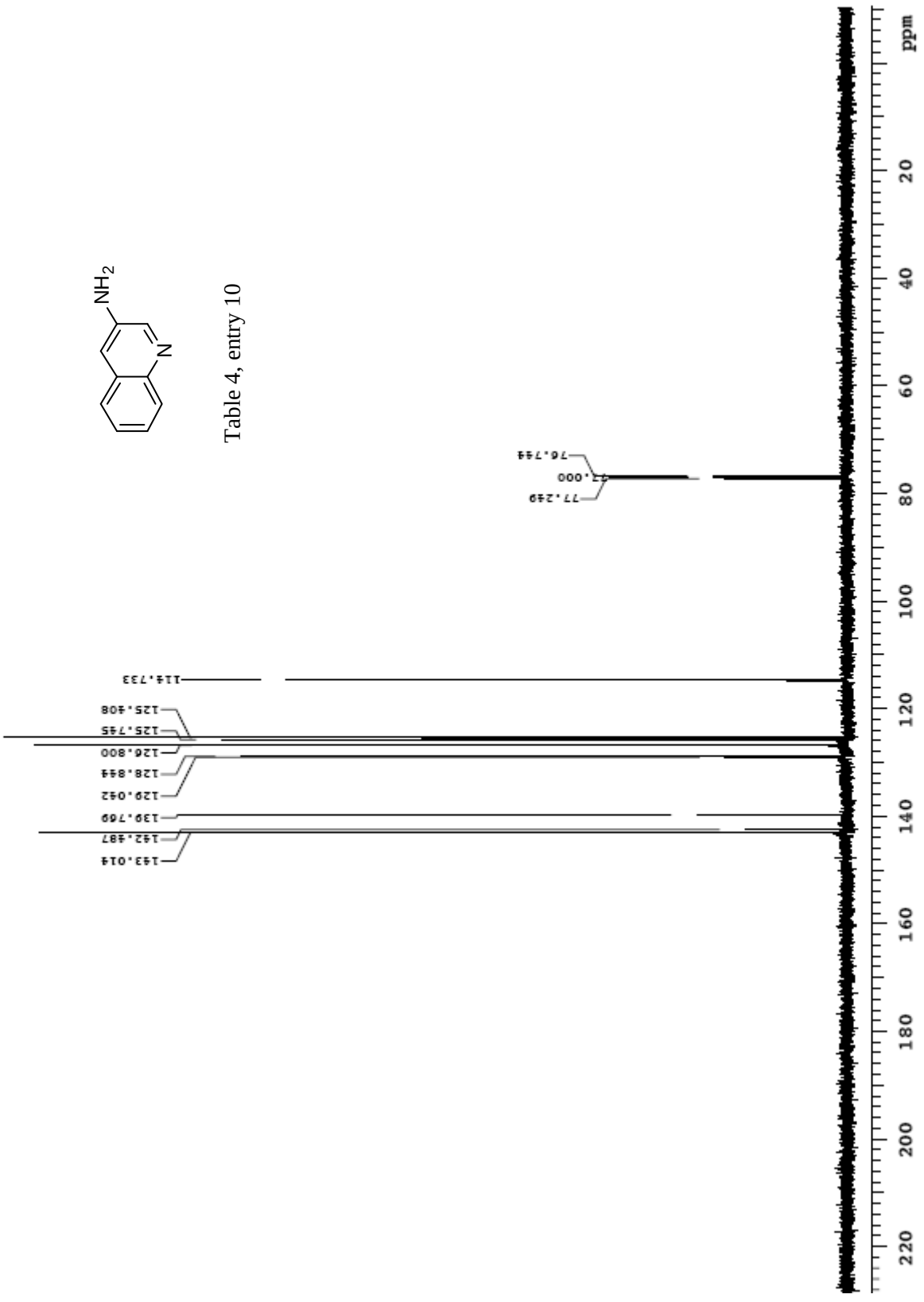


Table 4, entry 10


NH2
N
Table 4, entry 10
143.014
142.387
139.769
129.042
128.844
126.800
125.745
125.408
114.733
77.249
77.000
76.744
ppm
220
200
180
160
140
120
100
80
60
40
20

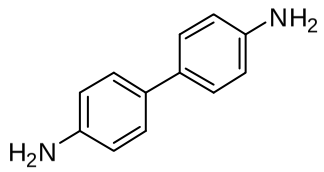


Table 4, entry 11

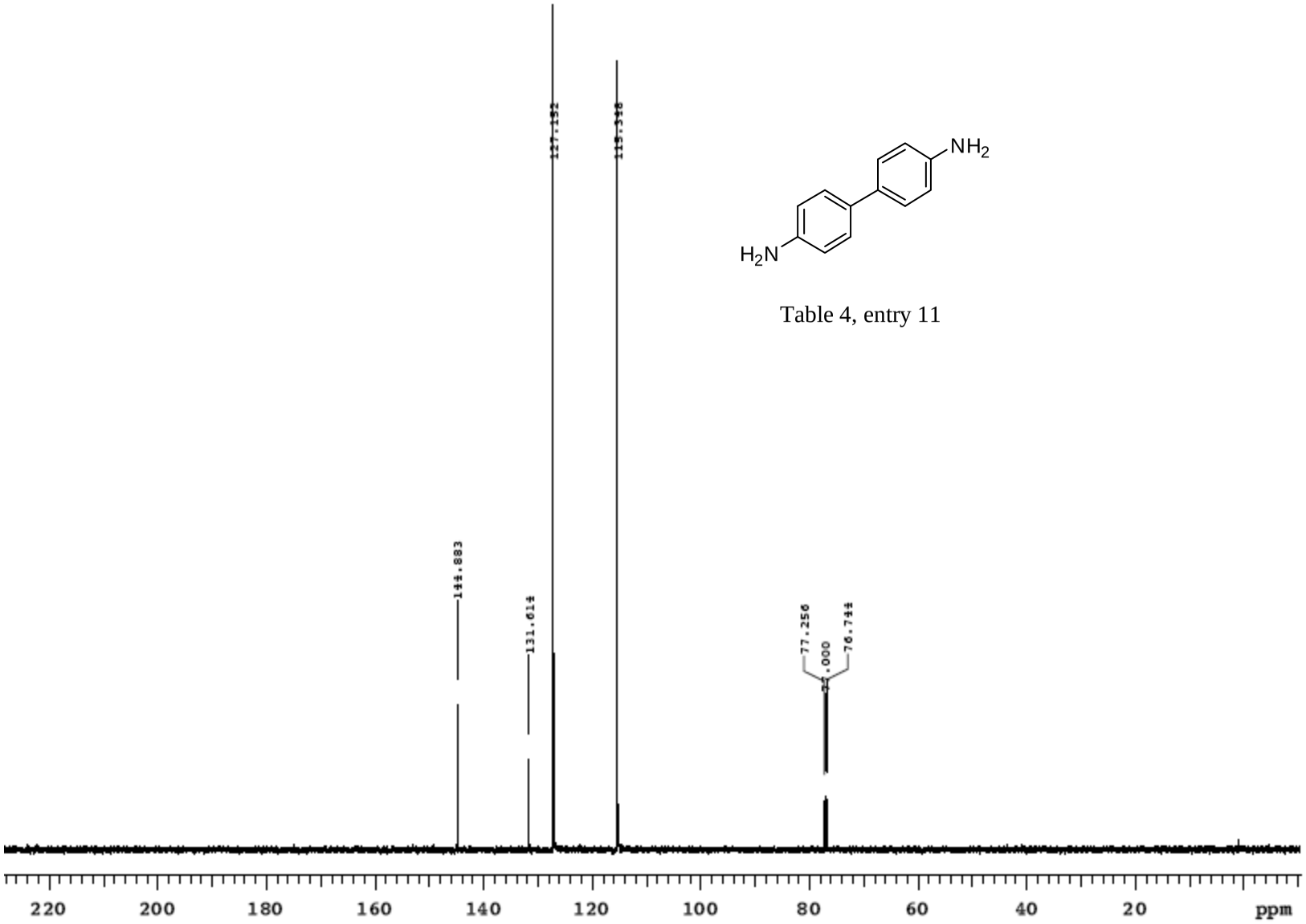


Table 4, entry 11

gv5-158p-1h

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Operator: user1d
INOVA-500 "u500"

Pulse 61.6 degrees
Acq. time 4.665 sec
Width 7024.9 Hz
16 repetitions
OBSERVE H1, 499.6906566 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min, 14 sec

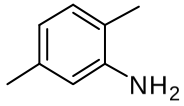


Table 6, entry 3

gv5-158p-13c

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Operator: user1d
INOVA-500 "u500"

Relax. delay 1.000 sec
Pulse 65.9 degrees
Acq. time 1.086 sec
Width 30165.9 Hz
112 repetitions
OBSERVE C13, 125.6473331 MHz
DECOUPLE H1, 499.6923275 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 4 min, 30 sec

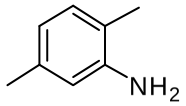


Table 6, entry 3

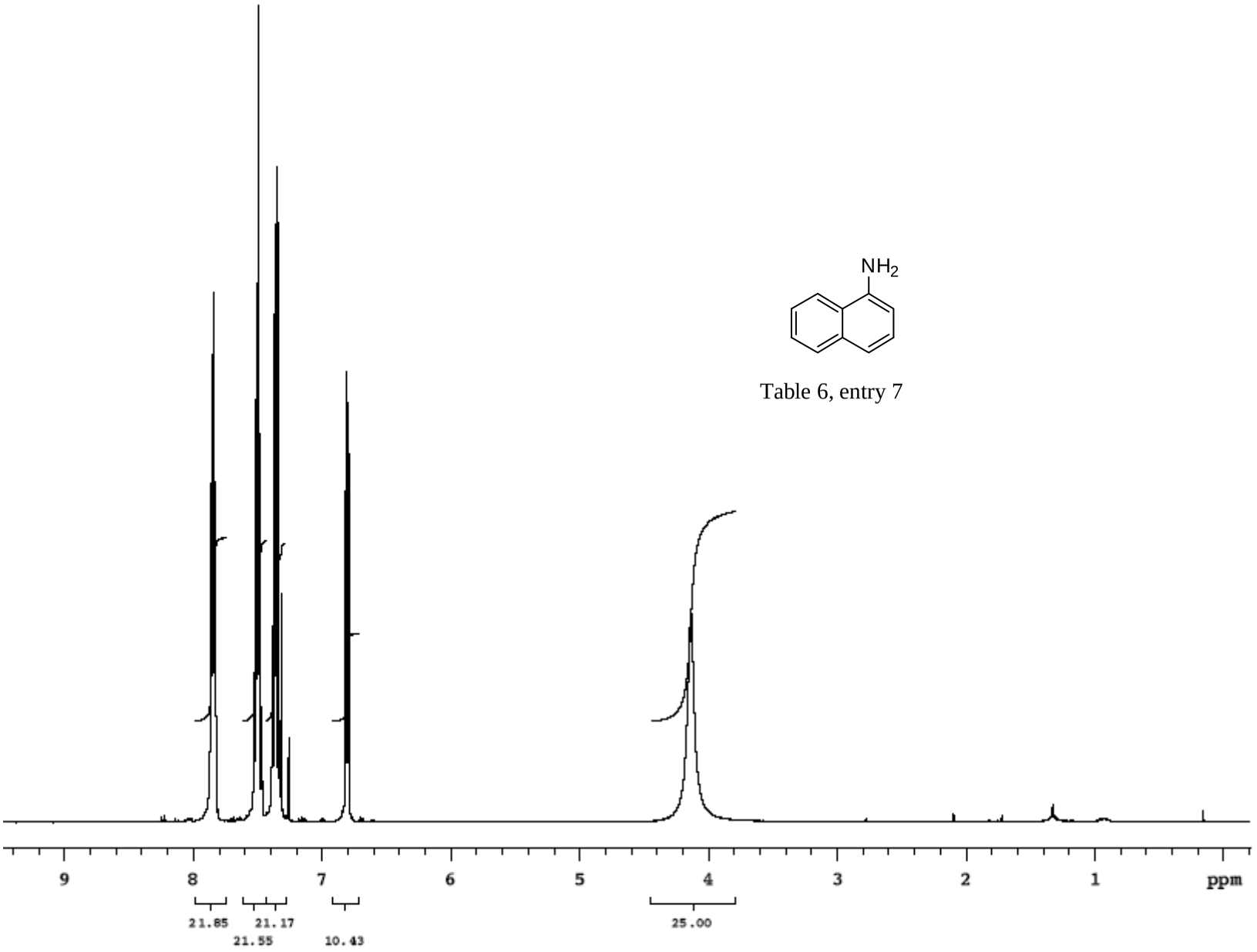
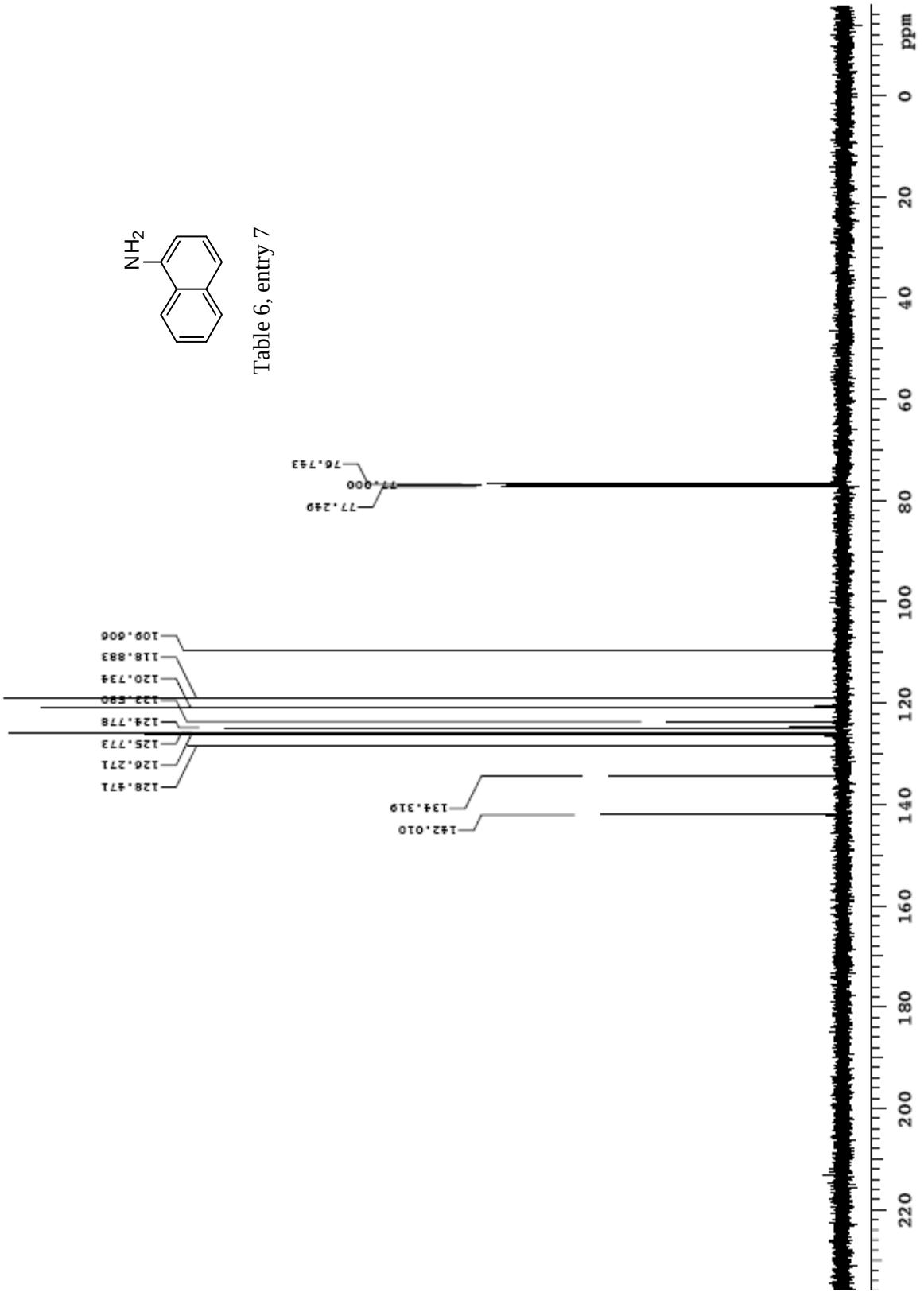


Table 6, entry 7


NH2
Table 6, entry 7
76.743
77.000
77.249
109.606
118.883
120.734
123.690
124.778
125.773
126.271
128.471
134.319
142.010
ppm
0
20
40
60
80
100
120
140
160
180
200
220

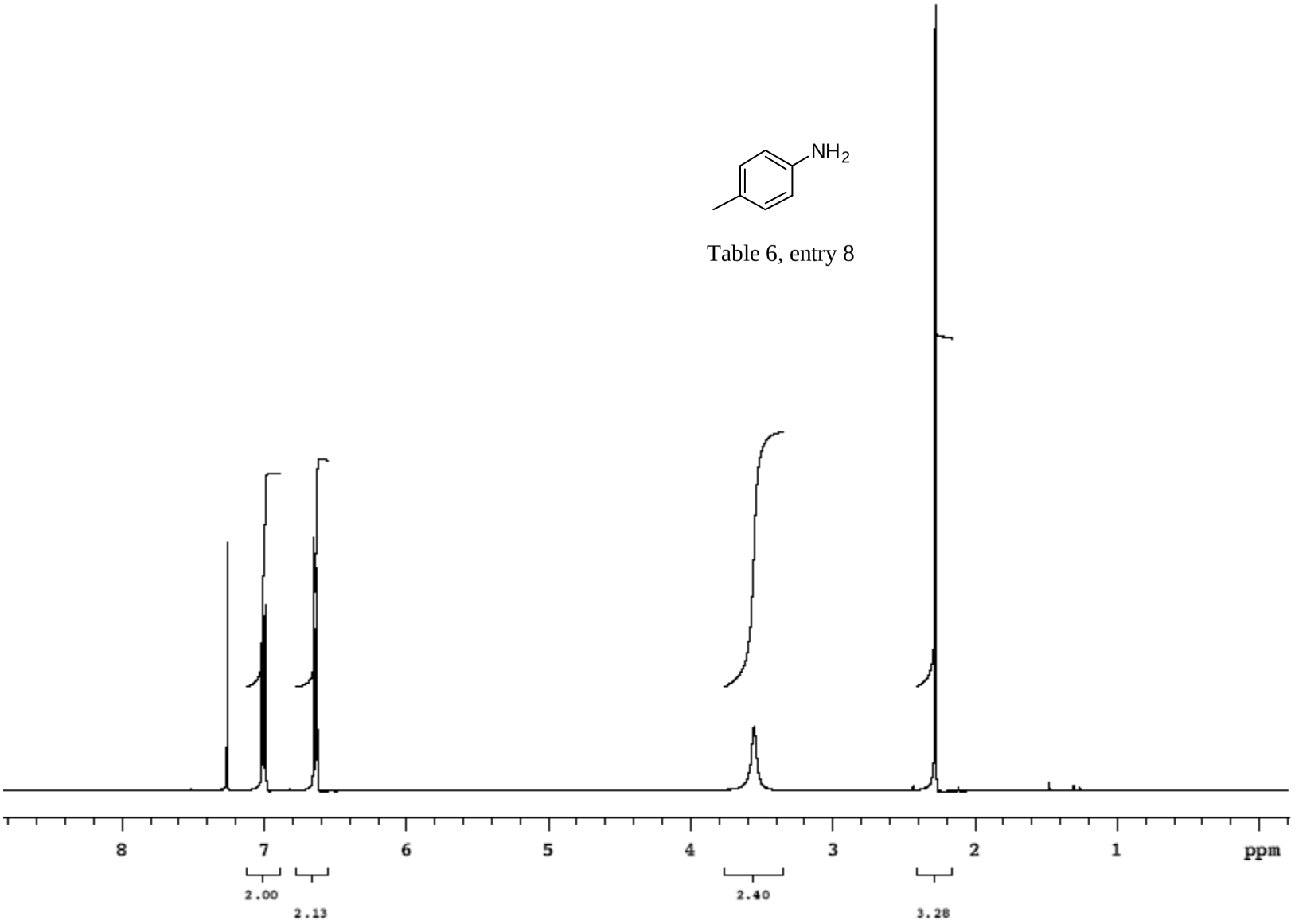


Table 6, entry 8

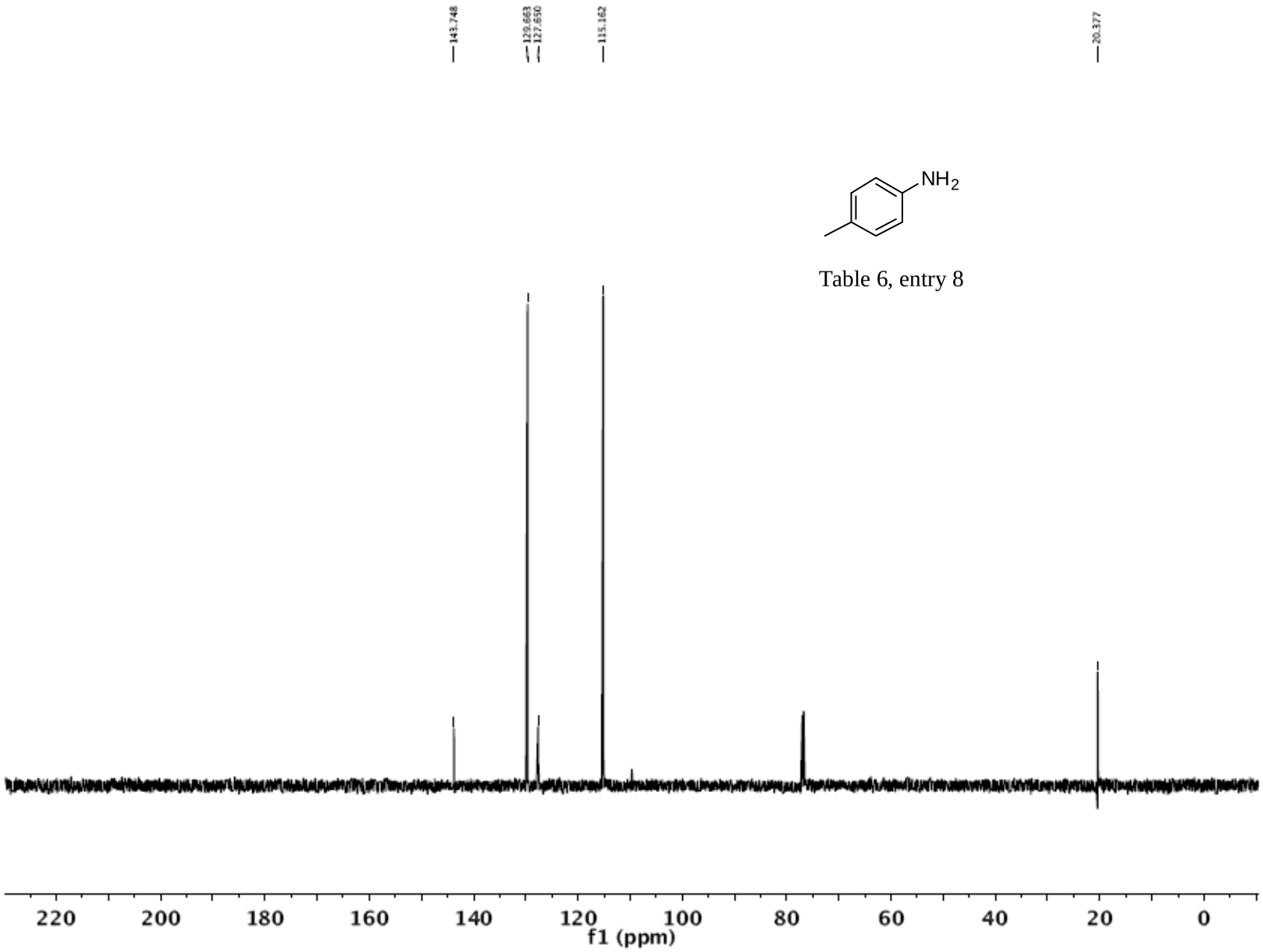


Table 6, entry 8

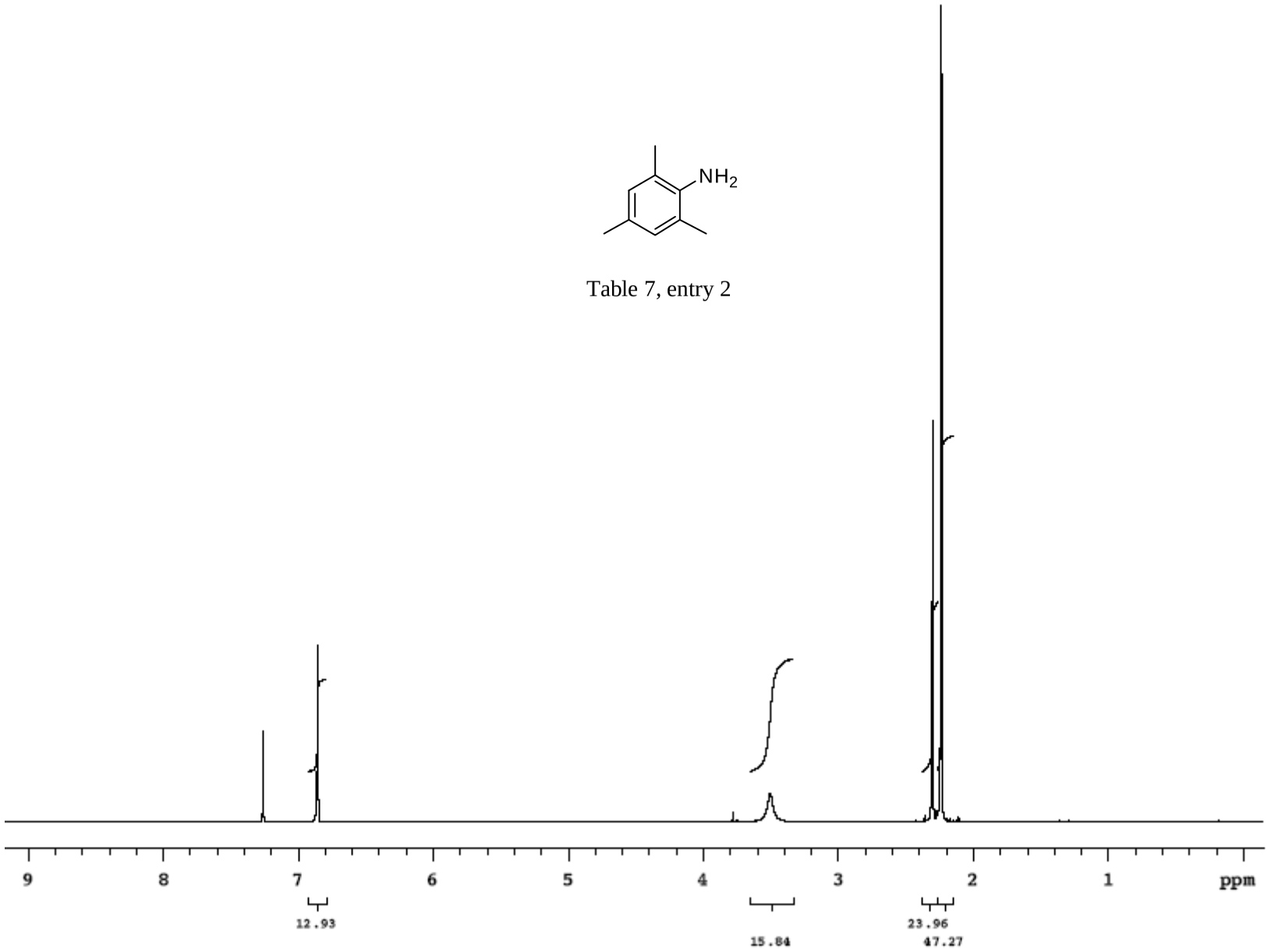
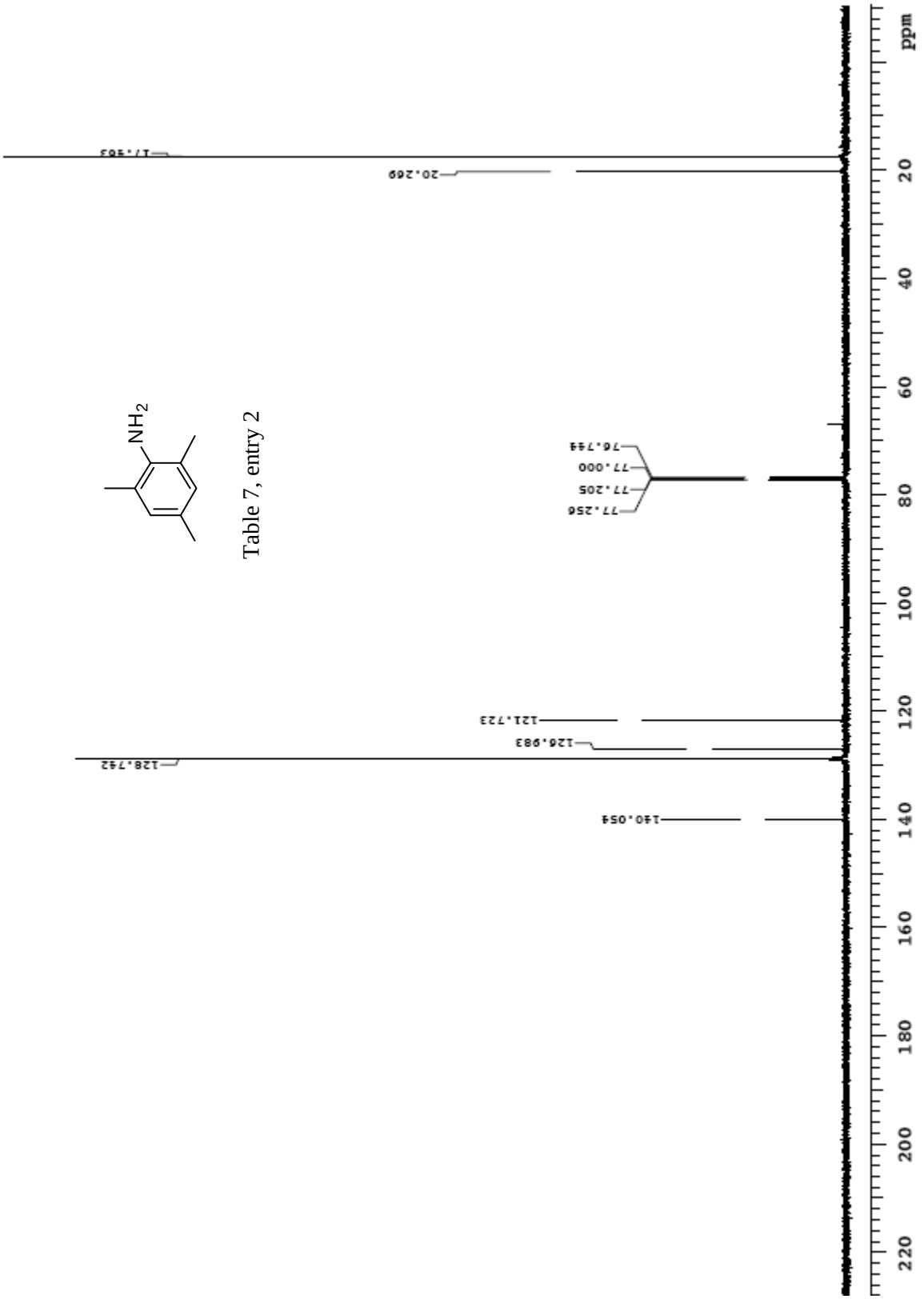


Table 7, entry 2


NH2
Table 7, entry 2
17.363
20.269
76.744
77.000
77.205
77.256
121.723
126.983
128.742
140.054
ppm
220
200
180
160
140
120
100
80
60
40
20

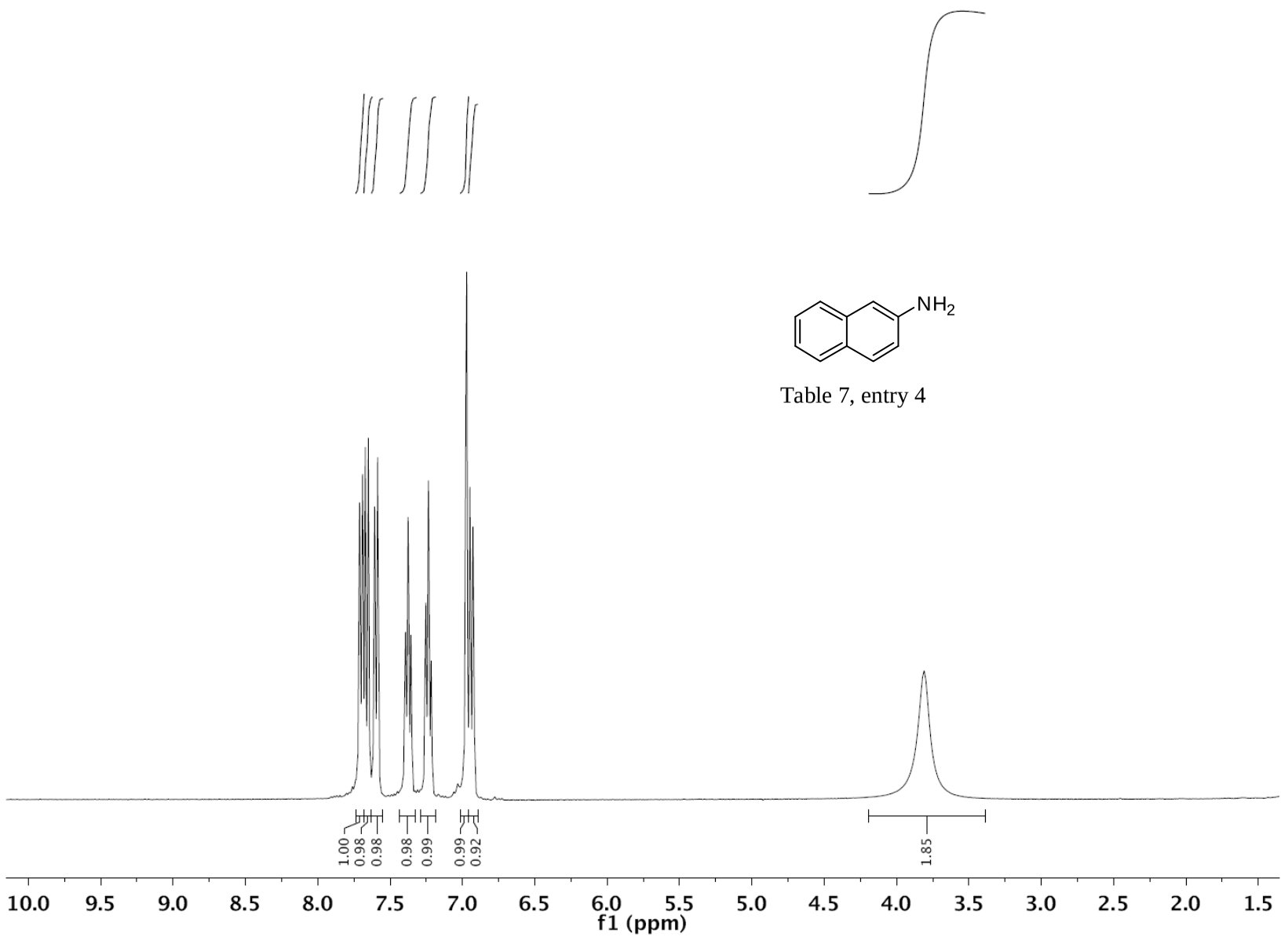


Table 7, entry 4

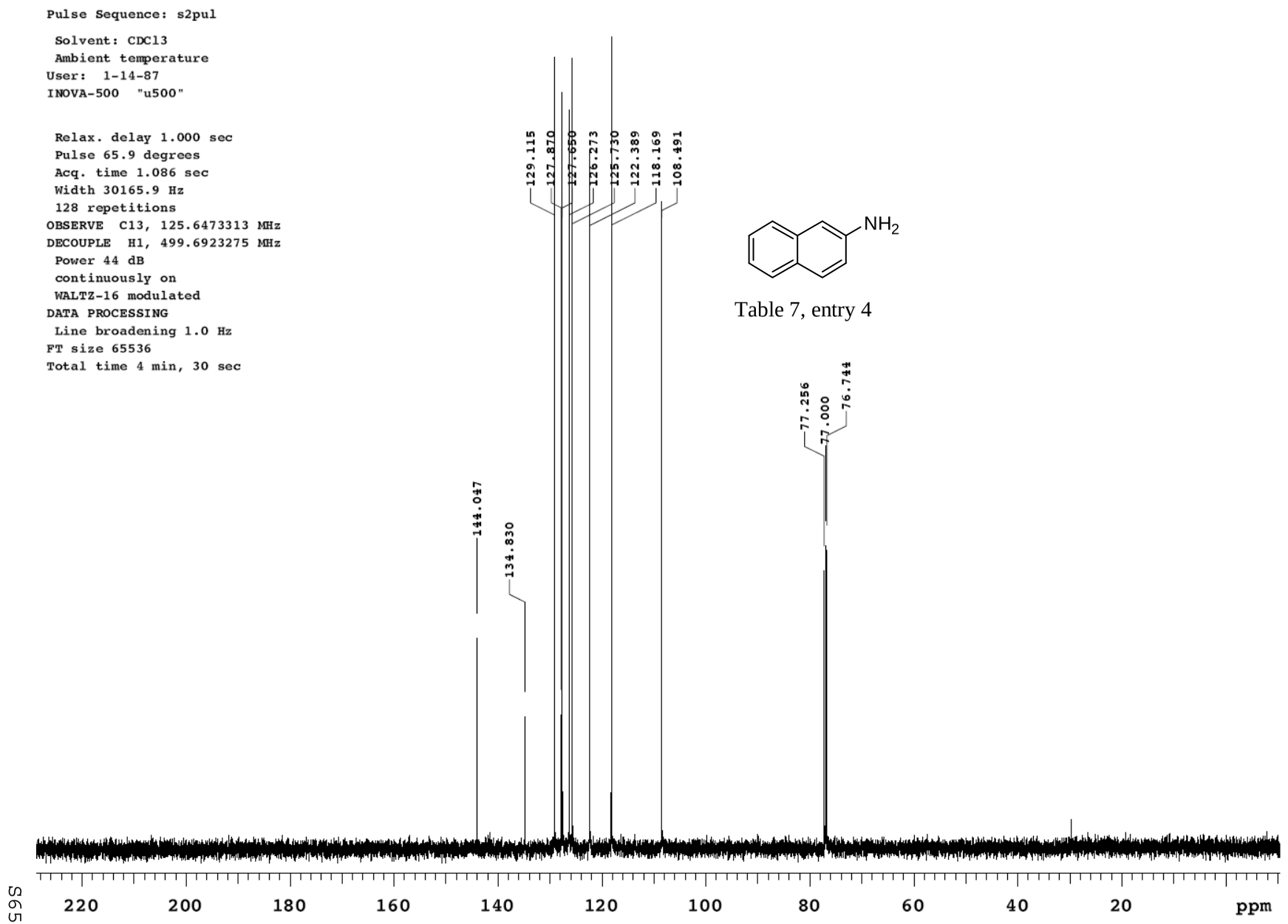


Table 7, entry 4

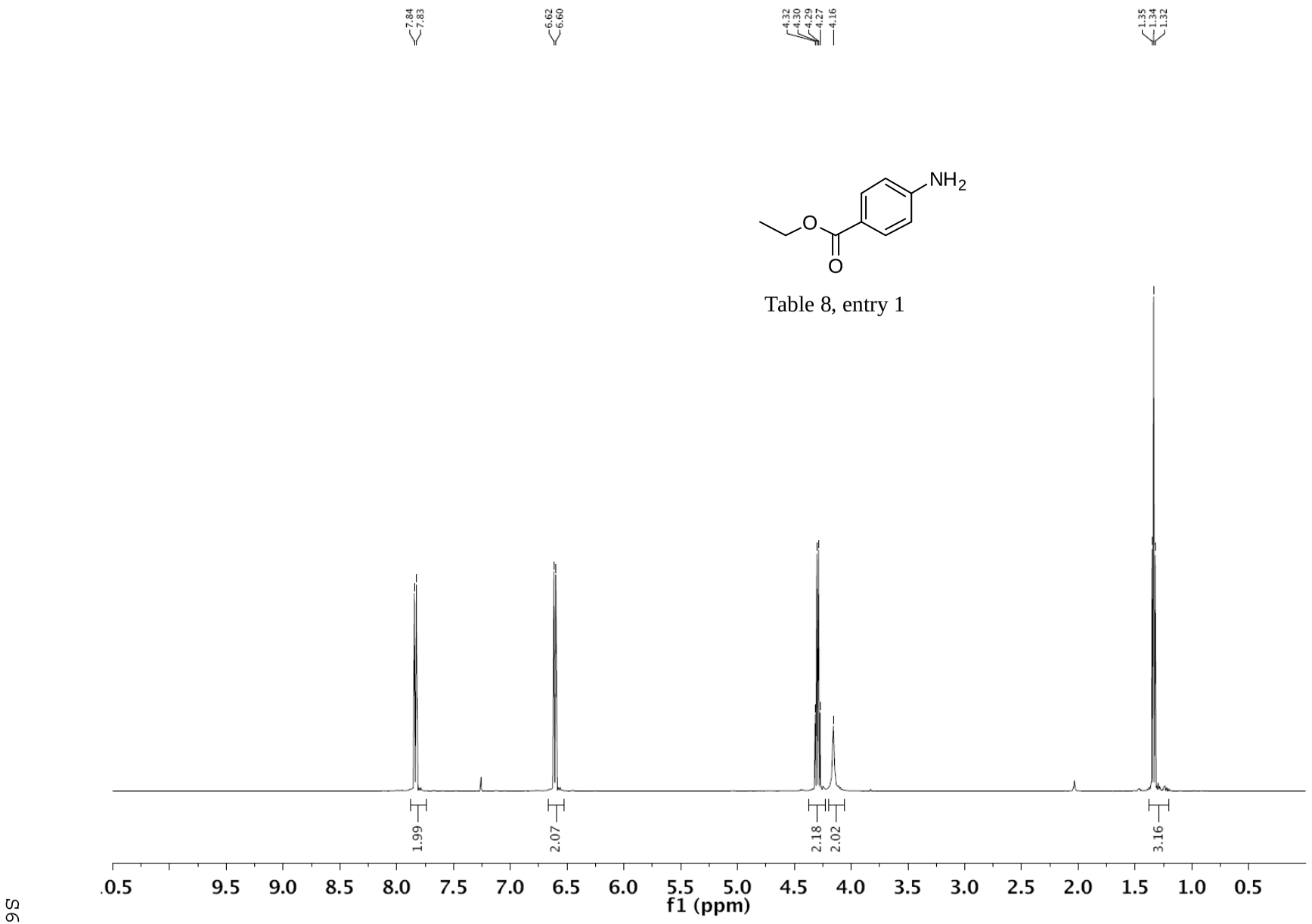


Table 8, entry 1

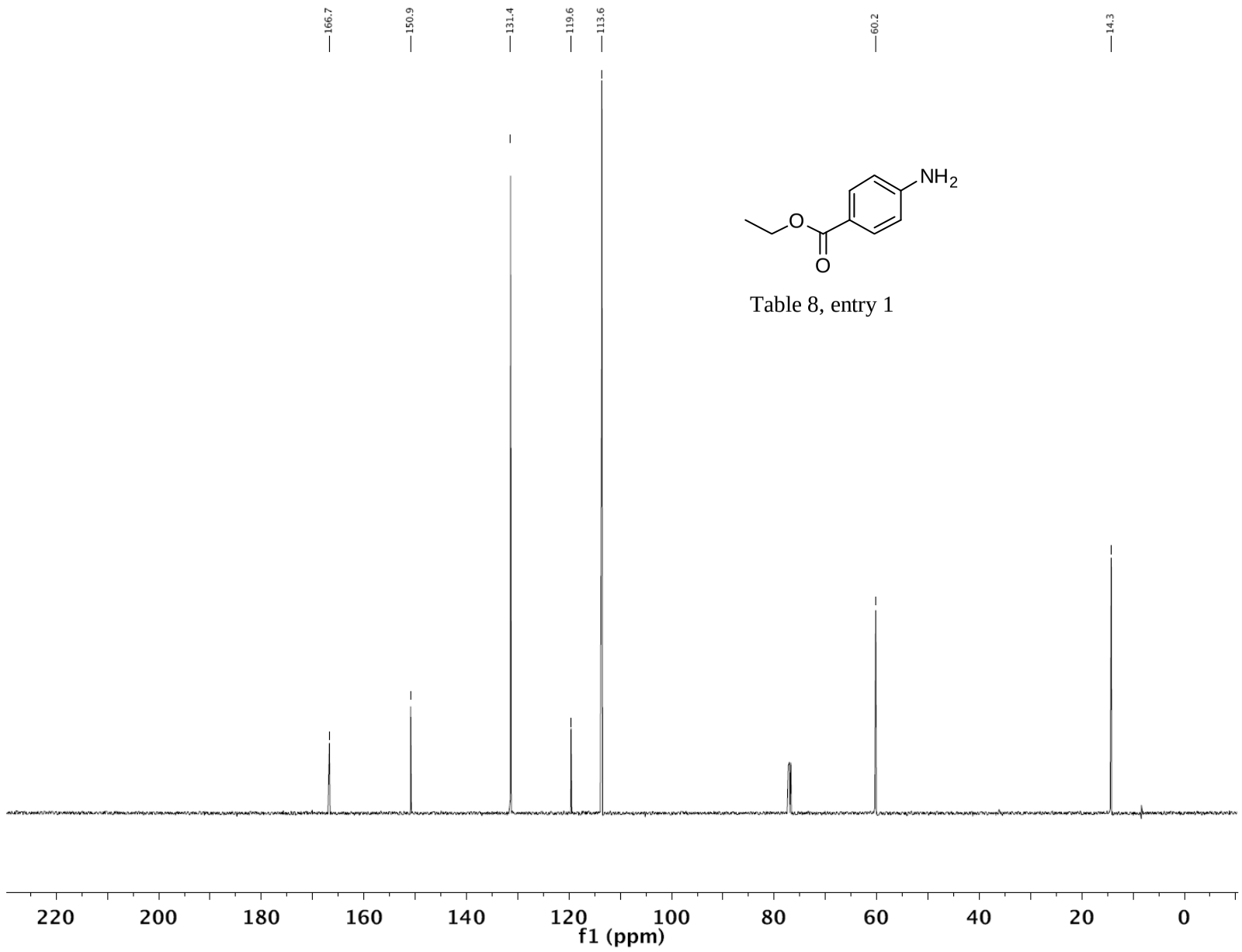


Table 8, entry 1

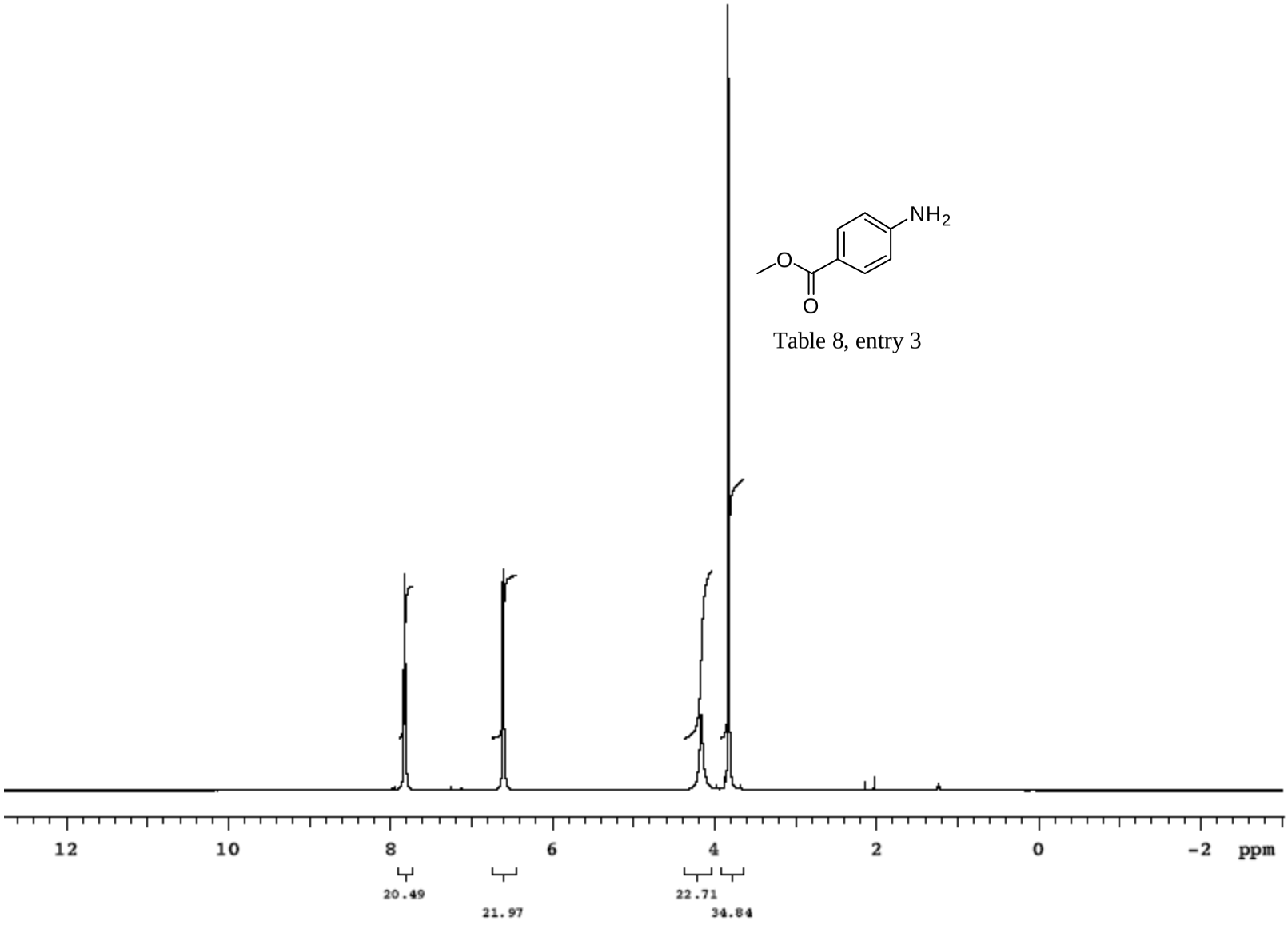


Table 8, entry 3

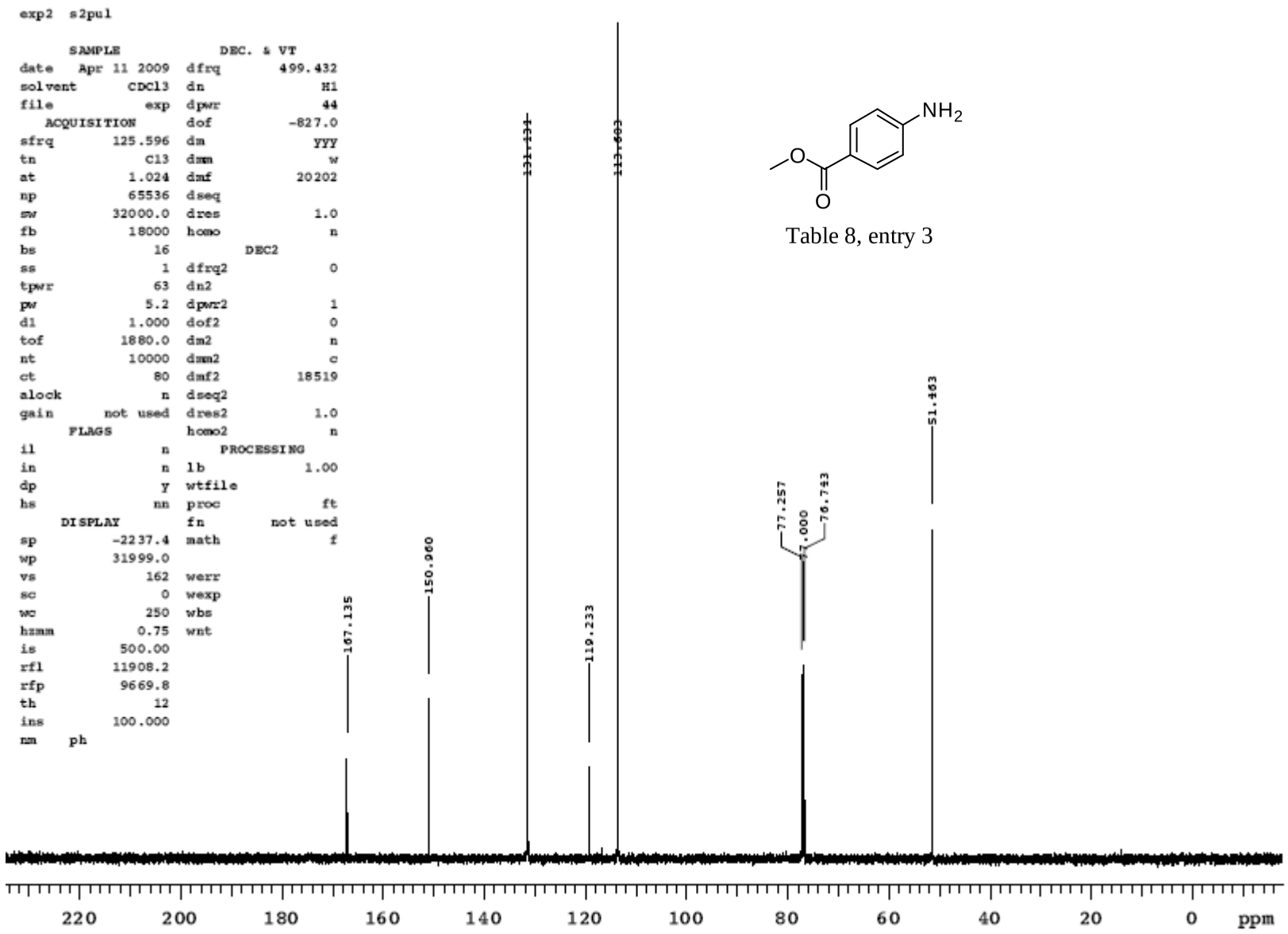


Table 8, entry 3

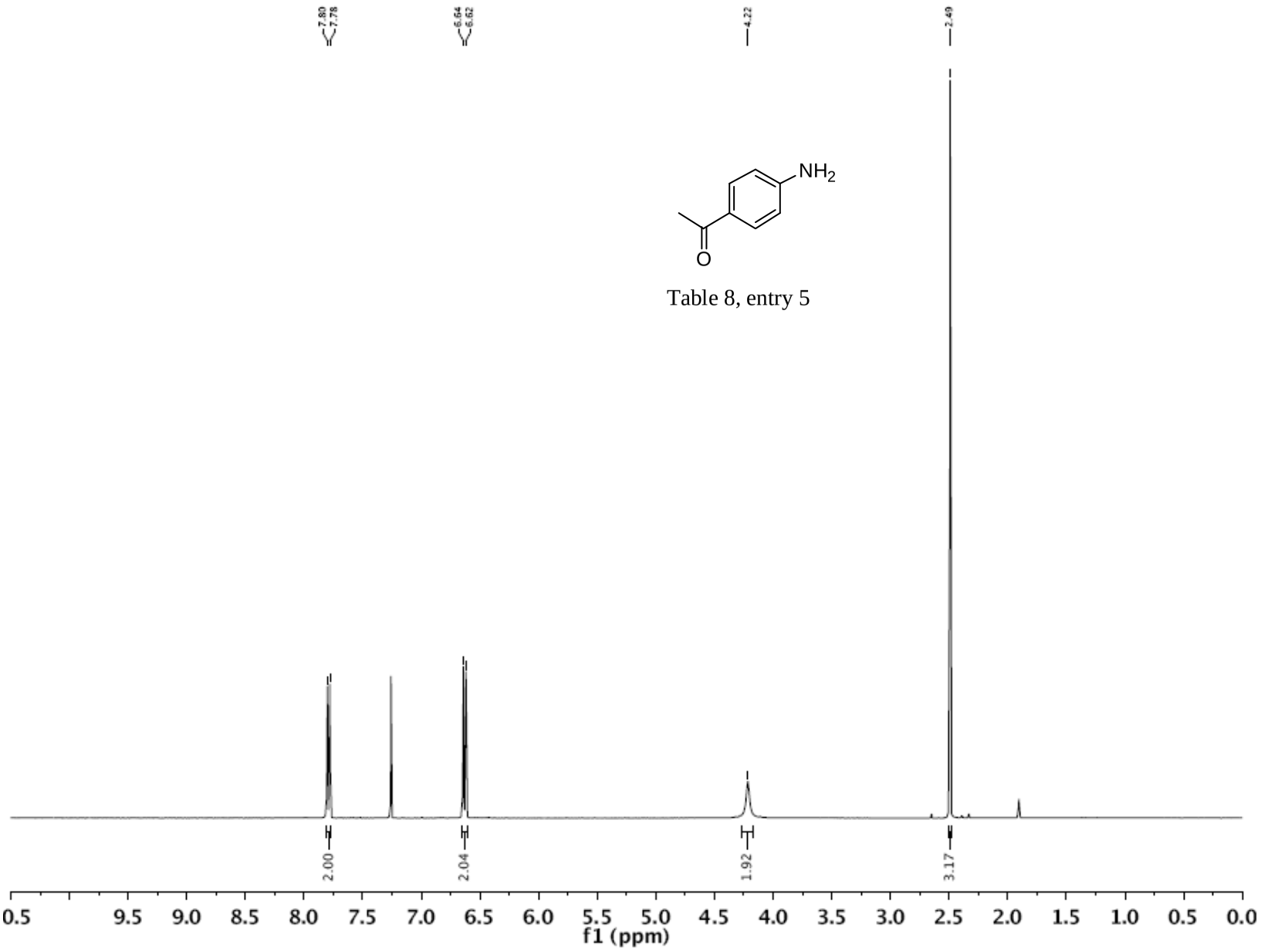


Table 8, entry 5

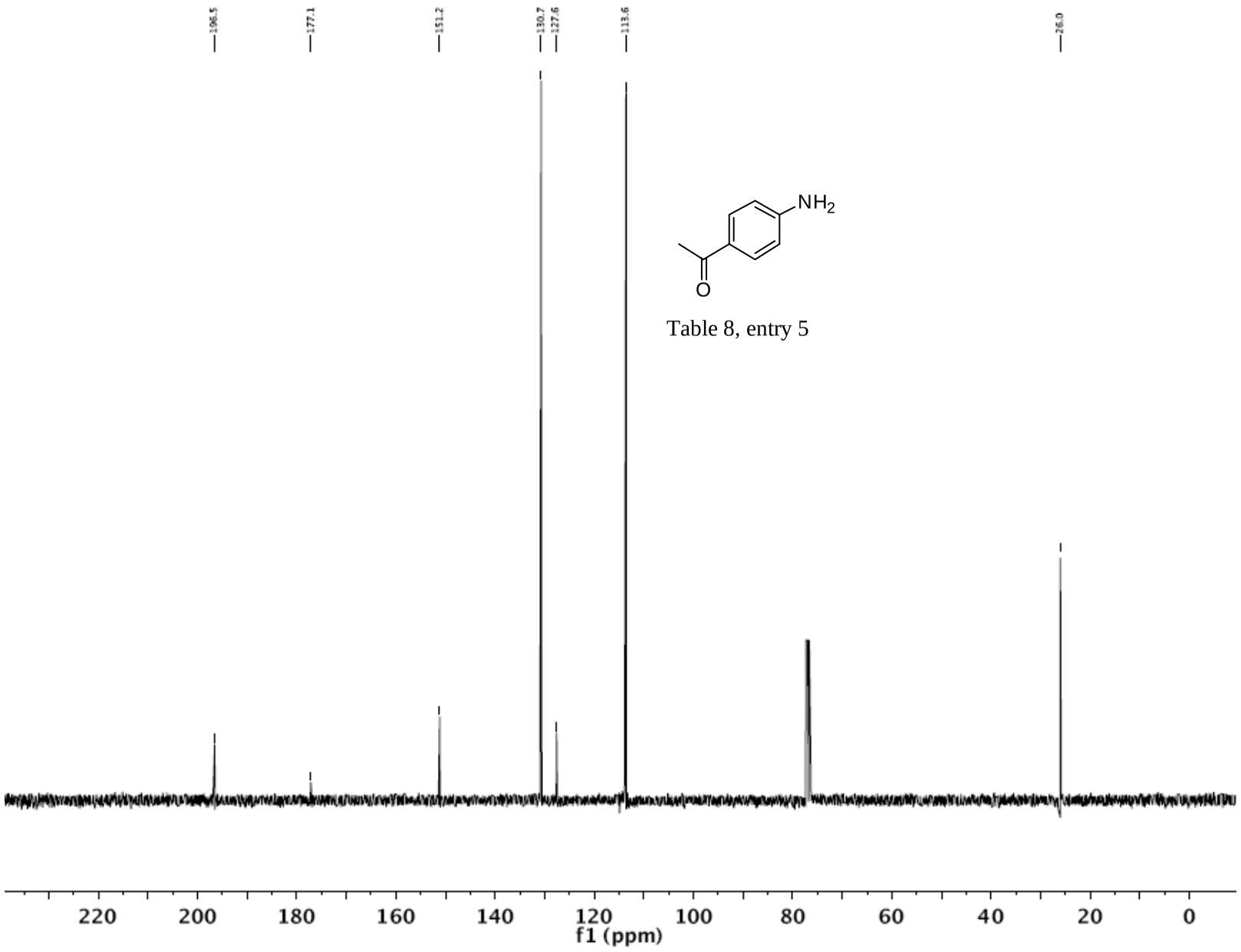


Table 8, entry 5

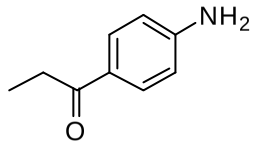
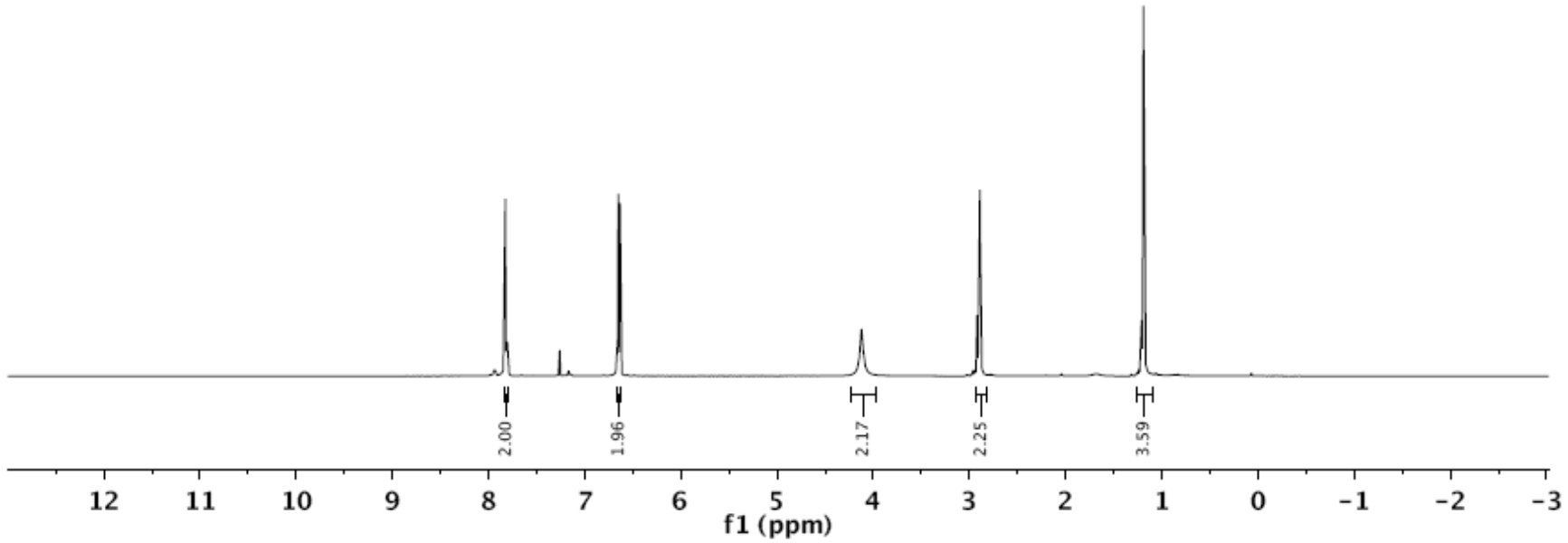


Table 8, entry 7



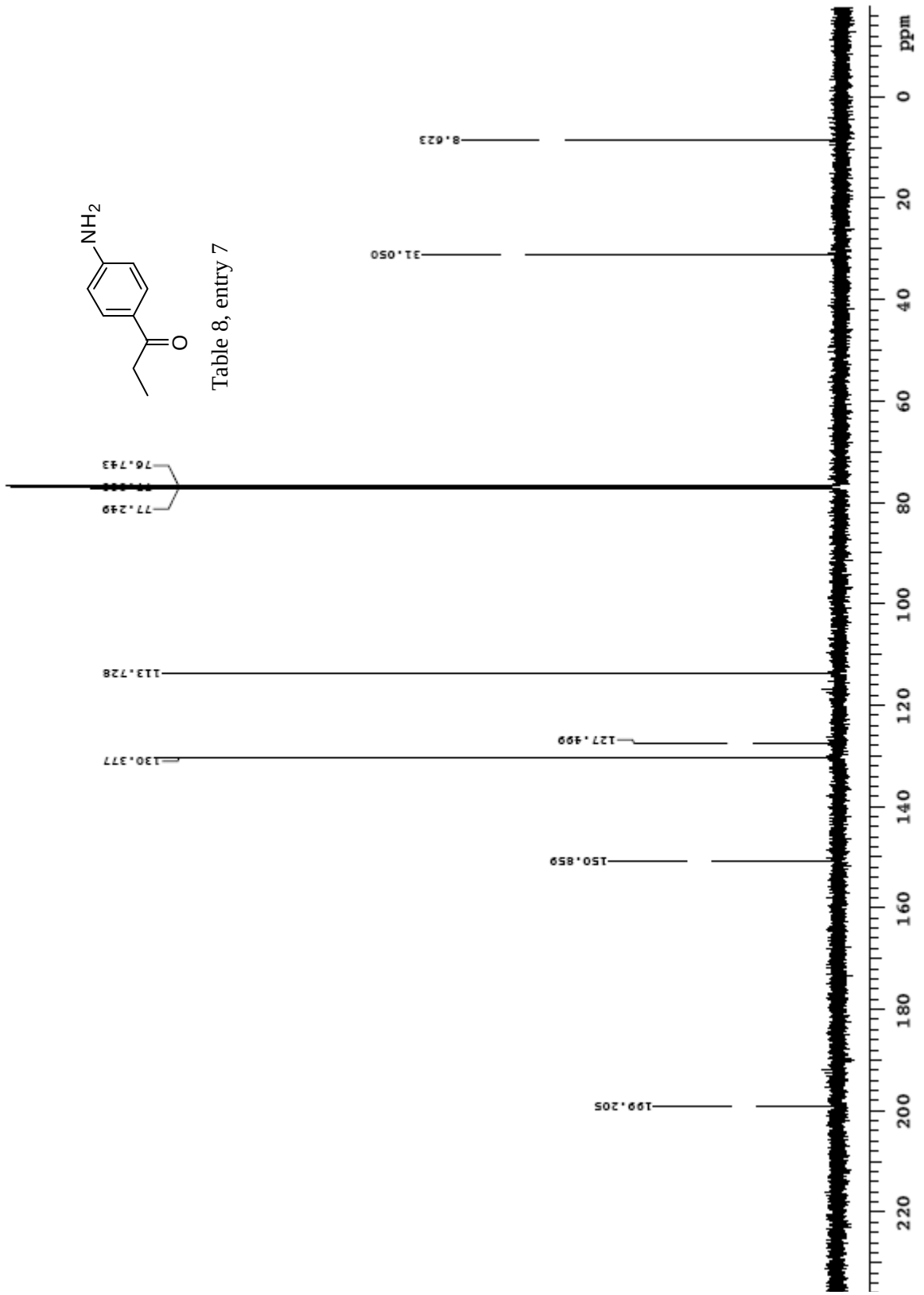
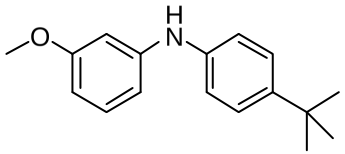
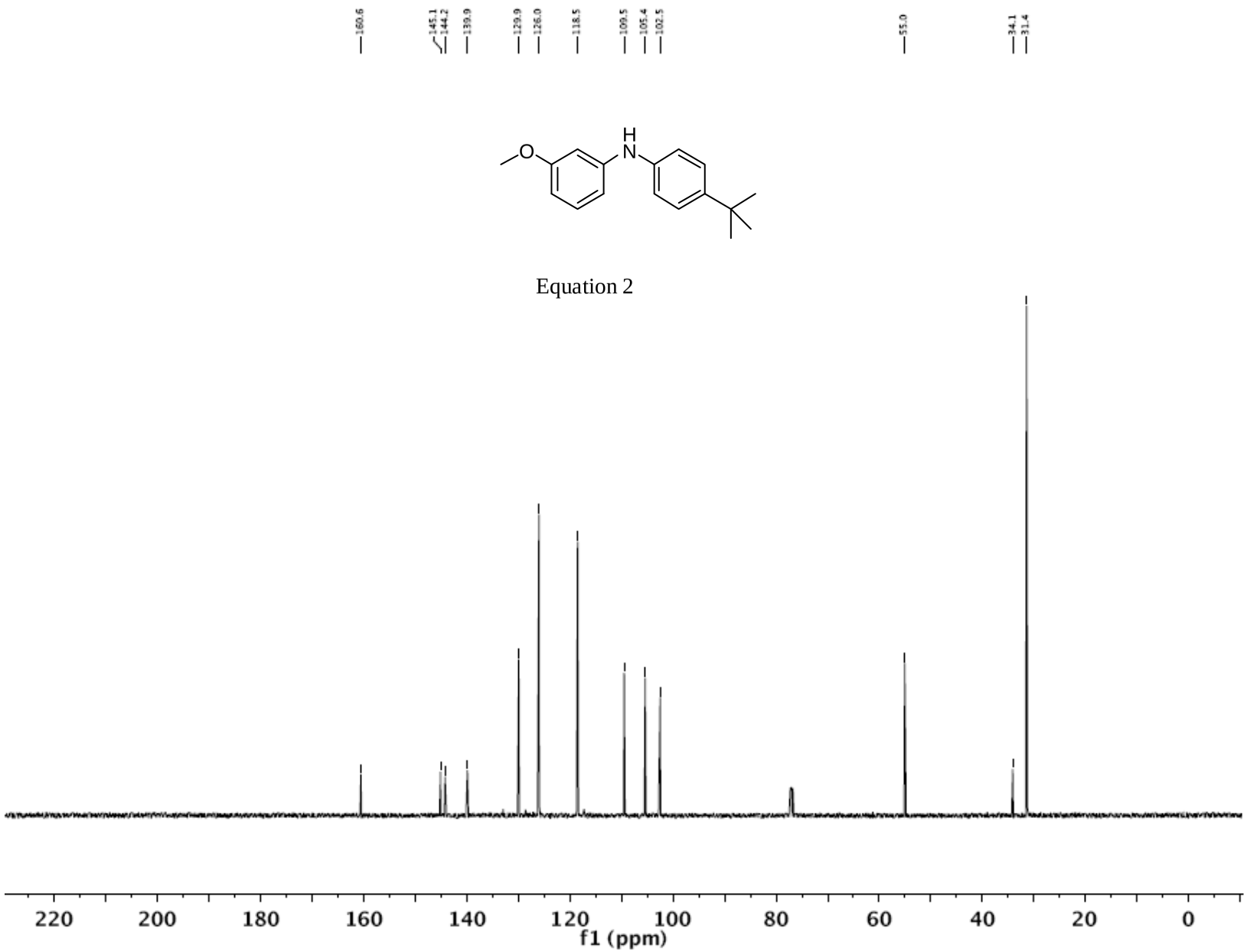


Table 8, entry 7
NH2
O
8.623
31.050
76.743
77.249
113.728
127.499
130.377
150.859
199.205
ppm
0
20
40
60
80
100
120
140
160
180
200
220



Equation 2


160.6
145.1
144.2
139.9
129.9
126.0
118.5
109.5
105.4
102.5
55.0
34.1
31.4
O
H
N
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

Equation 2

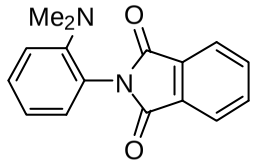


Table 9, entry 2

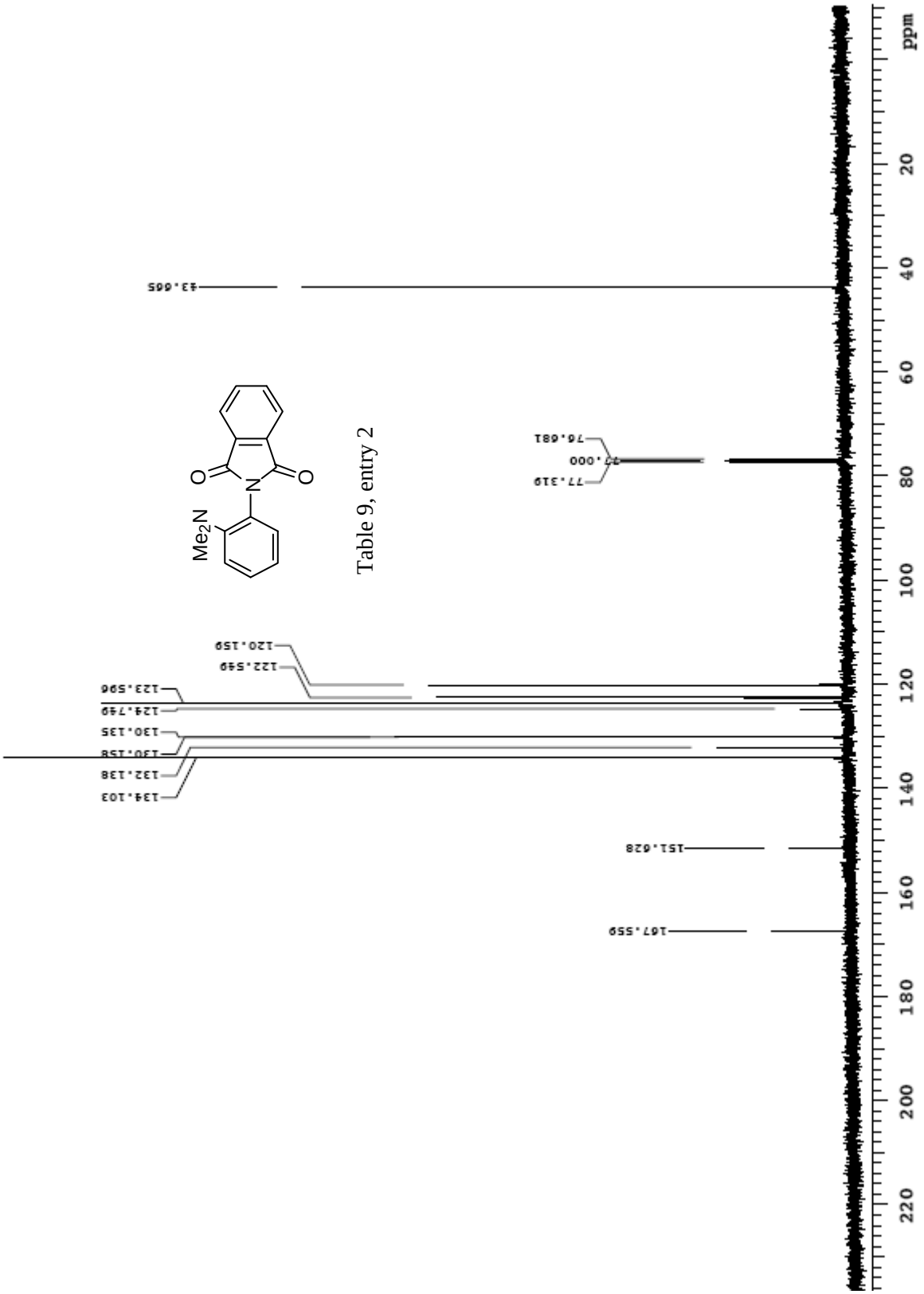


Table 9, entry 2

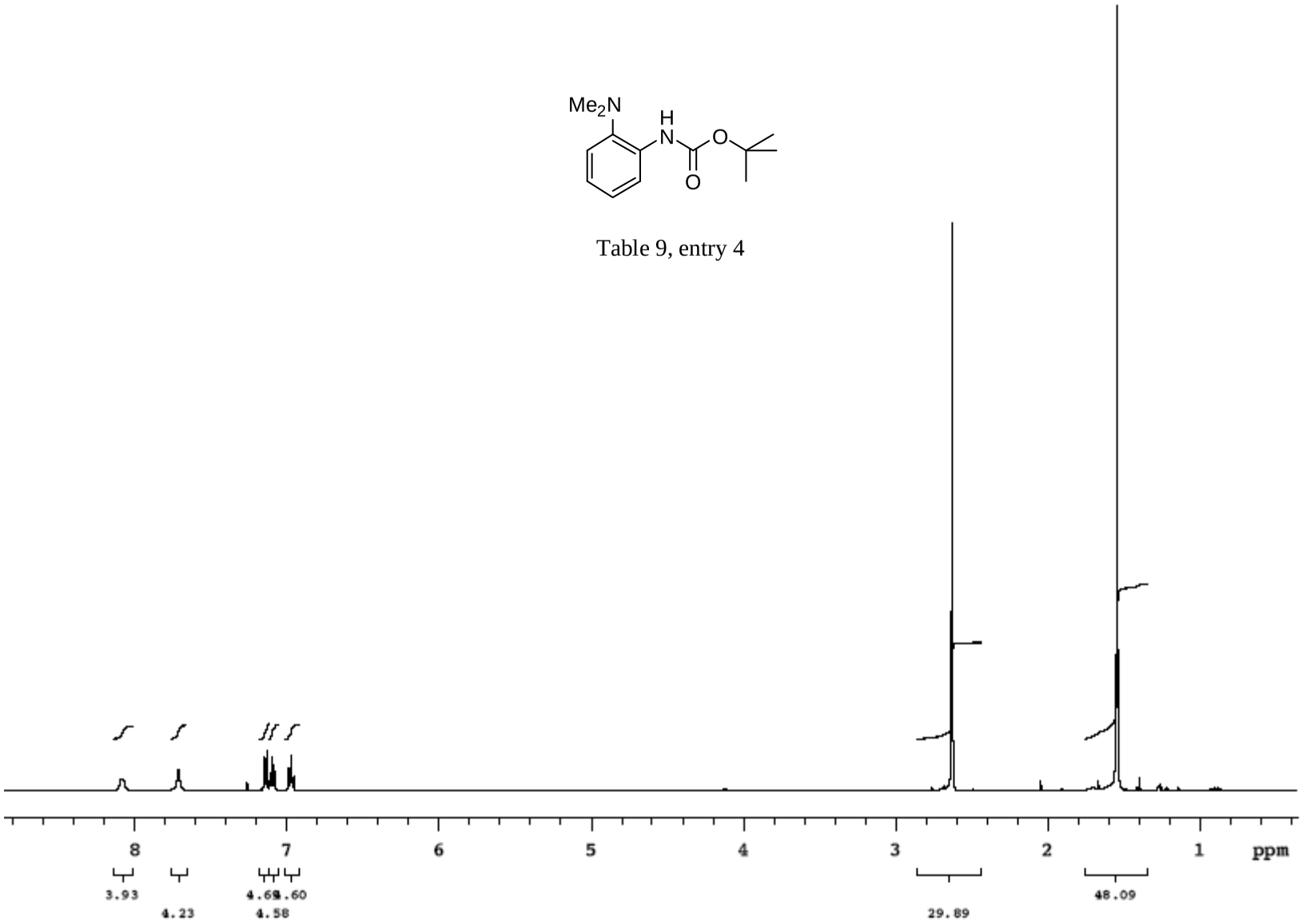


Table 9, entry 4

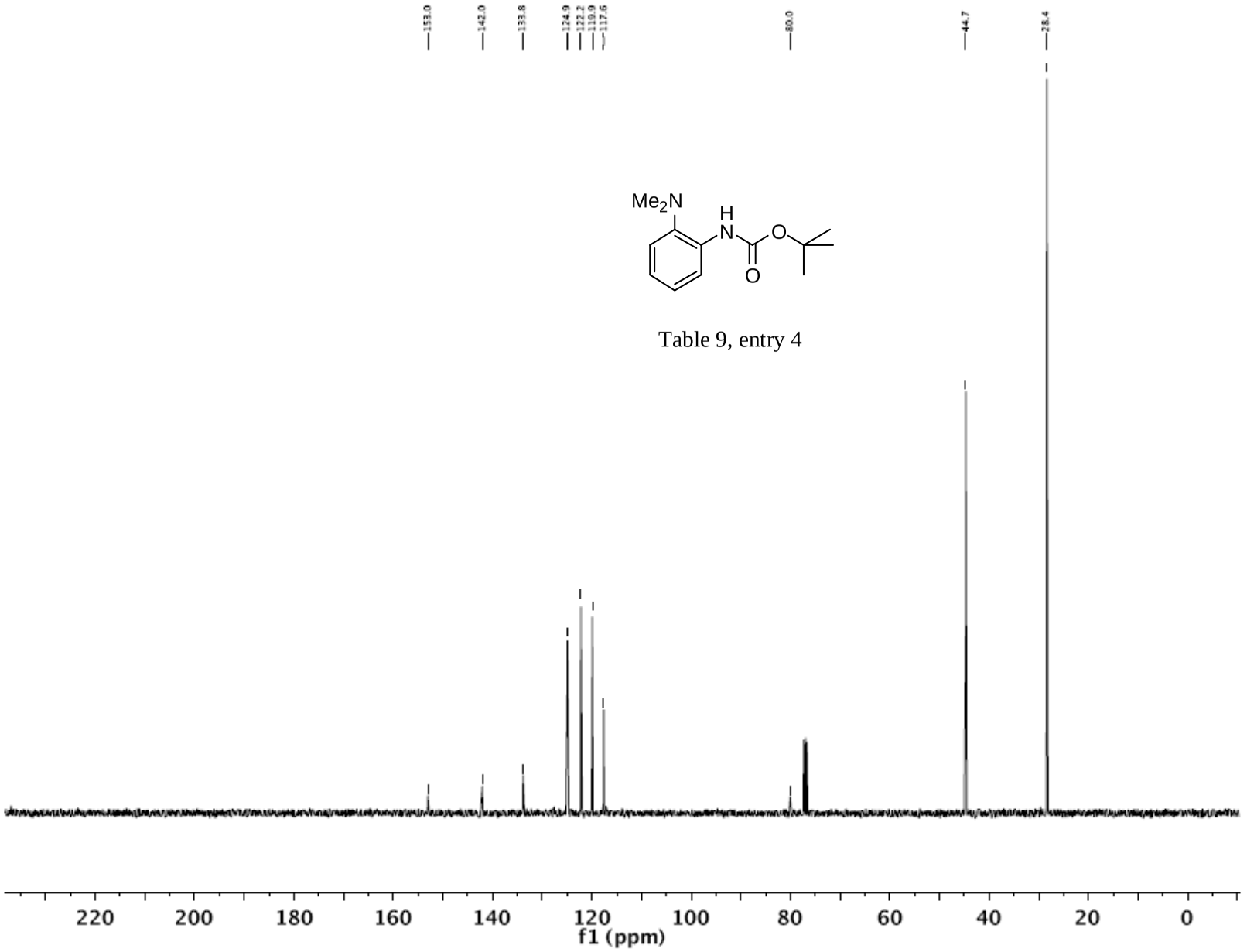


Table 9, entry 4