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Supporting Information

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A General Intermolecular Palladium-Catalyzed α-Arylation of Aldehydes

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GENERAL EXPERIMENTAL INFORMATION

General Procedures. Unless otherwise noted, all manipulations were conducted under an inert nitrogen or argon atmosphere, using flame-dried glassware. Rotary evaporation was done at 25-30 °C. Flash column chromatography was performed as described by Still et al on silica gel (Silicycle, 60 A pore size, 40-64 μm particle size, pH Suspension 10%: 6.5-7.5).[1] Analytical thin-layer chromatography was performed on glass plates coated with silica gel (Silicycle, 60 A pore size, 40-64 μm particle size) and visualized with both ultraviolet light and dinitrophenylhydrazine (DNP) solution.

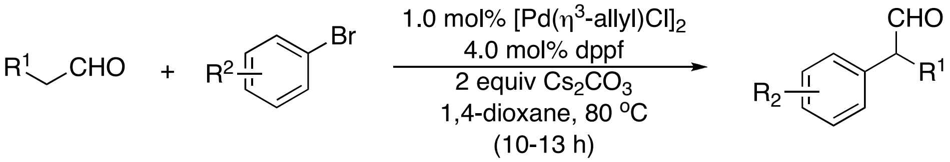
Materials. 1,1'-Bis(diphenylphosphino)ferrocene (DPPF) was purchased from Strem Chemicals and used without further purification. 1,2,3,4,5-Pentaphenyl-1'-(di-tert-butylphosphino)ferrocene (Q-phos) was obtained as a gift from Johnson-Matthey or synthesized as described by Hartwig and coworkers.[2] Allylpalladiumchloride dimer was purchased from Strem Chemicals or synthesis as described by Auburn et al.[3] $Pd(OAc)_2$ was obtained as a gift from Johnson-Matthey. Cesium carbonate (99.9%) was purchased from Aldrich and used without further purification. All aldehydes were fractionally distilled, followed by sparging with nitrogen gas before use. All aryl halides were purchased from Aldrich and used without further purification. 1,4-Dioxane was either purchased from Aldrich (ACS Reagent grade) and dried over a sodium-benzophenone ketyl, followed by vacuum transferred before use or purchased from Aldrich (99.8%, anhydrous grade) and used without further purification. Tetrahydrofuran were degassed by purging with argon for 20-30 minutes and dried with a solvent purification system containing a 1 m column of activated alumina. Solvents for filtration and chromatography were certified ACS grade.

Instruments. ^{1}H and ^{13}C NMR spectra were recorded on Varian Unity-400 or 500 MHz (126 MHz, ^{13}C) spectrometers. Spectra are referenced to residual chloroform (d = 7.26 ppm, ^{1}H; 77.0 ppm, ^{13}C) or residual benzene (d = 7.15 ppm, ^{1}H; 128.62 ppm, ^{13}C). 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. The GC method used involved injections onto a Hewlett-Packard HP5

(30m x 0.32 mm) capillary column. The injector temperature was 250 °C and the detector temperature was 300 °C with a H_2 carrier gas flow of 16 mL/min. The column temperature program was as follows: 120 °C to 250 °C at 40 °C/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. Infrared (IR) spectra were measured as thin films (neat) in NaCl cells by a Perkin Elmer Spectrum BX spectrophotometer, and peaks are reported in cm^{-1} along with relative signal intensities: s (strong); m (medium); w (weak). Microanalysis (CHN) was performed on an Exeter CE440 analyzer at the University of Illinois Microanalysis Laboratory or at Robertson Microlit Laboratories, Edison, New Jersey.

EXPERIMENTAL PROCEDURES

General Procedures for the α-Arylation of Linear Aldehydes (Table 2)



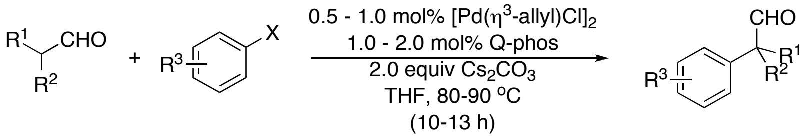
Without use of a drybox:

Allylpalladiumchloride dimer ([Pd(η^3-allyl)Cl]$_2$ (3.7 mg, 0.010 mmol), DPPF (0.0222 mg, 0.0400 mmol), cesium carbonate (0.652 g, 2.00 mmol) and an aryl halide (if it is a solid) (1.00 mmol) were added in the described order to a 25-mL Schlenk flask that contained a magnetic stirbar. The flask was evacuated and back-filled with nitrogen three times. A solution of a linear aldehyde (1.10 mmol) and an aryl halide (if it is a liquid (1.00 mmol) in 1,4-dioxane (4 mL) was then added via a gas-tight syringe. The flask was placed in an 80 °C oilbath for 10-13 h. After complete conversion of the aryl halide was determined by GC analysis, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered through a pad of Celite. The filtrate was concentrated *in vacuo* and the crude product was purified using flash column chromatography on silical gel (hexanes/diethyl ether) to give the α-aryl aldehyde.

With use of a drybox:

Inside a nitrogen-filled drybox, allylpalladium chloride dimer ([Pd(η^3-allyl)Cl]$_2$ (3.7 mg, 0.010 mmol), DPPF (0.0222 mg, 0.0400 mmol), cesium carbonate (0.652 g, 2.00 mmol), a linear aldehyde (1.20 mmol) and an aryl halide (1.00 mmol) were added in the described order to a 5-dram scintillation vial containing a magnetic stirbar. 1,4-Dioxane (4 mL) was then added via a gas-tight syringe. The vial was sealed with a Teflon-lined screwcap, removed from the drybox, and placed in a 80 °C oilbath for 10-13 h. After complete conversion of the aryl halide was observed by GC analysis, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered through a pad of Celite. The filtrate was concentrated *in vacuo* and the crude product was purified by flash column chromatography on silical gel using (hexanes/diethyl ether) to give the α-aryl aldehyde.

General Procedures for the α-Arylation of Branched Aldehydes (Table 3).

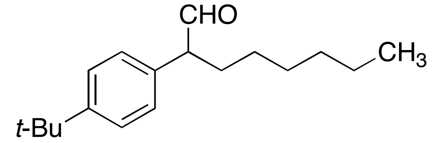


General Procedures for the α-Arylation of Branched Aldehydes with Aryl Bromides.

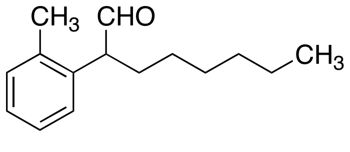
Inside a nitrogen-filled drybox, [Pd(η^3-allyl)Cl]$_2$ (0.0018 g, 0.005 mmol), Q-phos (0.0071 g, 0.010 mmol), and THF (2 mL) were added to a 1-dram scintillation vial containing a magnetic stirbar. The mixture was stirred for 5 mins at room temperature. Cesium carbonate (0.652 g, 2.00 mmol), a branched aldehyde (1.20 mmol) and an aryl bromide (1.00 mmol) were then added. THF (2 mL) was then added via a gas-tight syringe. The vial was sealed with a Teflon-lined screwcap, removed from the drybox, and placed in a 80 °C oilbath for 10-13 h. After complete conversion of the aryl halide was observed by GC/MS analysis, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered through a pad of Celite. The filtrate was concentrated *in vacuo* and the crude product was purified by flash column chromatography on silical gel using (hexanes/diethyl ether) to give the α-aryl aldehyde.

General Procedures for the α-Arylation of Branched Aldehydes with Aryl Chlorides. The general procedure for α-arylation of branched aldehydes with aryl bromides was followed with the following modifications: reactions were conducted with [Pd(η^3-allyl)Cl]$_2$ (0.0037 g, 0.01 mmol), Q-phos (14.2 mg, 0.020 mmol) and THF (4 mL) at 90 °C.

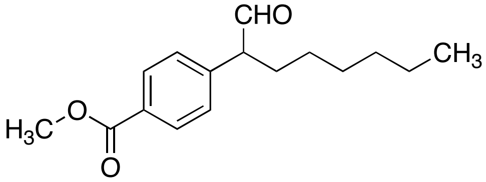
EXPERIMENTAL AND COMPOUND CHARACTERIZATION DATA



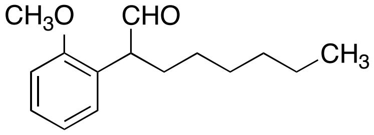
2-(4-*t*-Butylphenyl)octanal (Table 2, entry 1). Following the general procedure for α-arylation of linear aldehydes, [Pd(η^3-allyl)Cl]$_2$ (0.0037 g, 0.010 mmol), DPPF (0.0222 g, 0.0400 mmol), cesium carbonate (0.652 g, 2.00 mmol), octyl aldehyde (0.141 g, 1.10 mmol), 1-bromo-4-*t*-butylbenzene (0.213 g, 1.00 mmol) were combined in 1,4-dioxane (4.0 mL) and stirred at 80 °C for 12 h. Following the general procedure for work up, the filtrate was purified using flash-column chromatography (silica gel, 2% ether-hexanes) to give the title compound as a clear, colorless oil (0.216 g, 83%). R_f = 0.41 (4% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.65 (d, *J* = 2.2 Hz, 1H, C**H**O), 7.39 (d, *J* = 8.4 Hz, 2H, Ar**H**), 7.13 (d, *J* = 8.3 Hz, 2H, Ar**H**), 3.47 (dt, *J* = 8.0, 8.0, 2.2 Hz, 1H, C**H**CHO), 2.06 (m, 1H, C**H**$_2$CH(Ar)CHO), 1.73 (m, 1H, C**H**$_2$CH(Ar)CHO), 1.33 (s, 9H, C(C**H**$_3$)$_3$). 1.34-1.21 (m, 8H, CH$_3$(C**H**$_2$)$_4$CH$_2$CH(Ar)CHO), 0.87 (t, *J* = 6.9, 6.9 Hz, 3H, C**H**$_3$CH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 201.2, 150.3, 133.3, 128.4, 125.9, 58.7, 34.5, 31.6, 31.3, 29.6, 29.1, 27.1, 22.6, 14.0. IR (NaCl, thin film, neat) 2958 (s), 2929 (s), 2858 (s), 2708 (w), 1725 (s), 1687 (s), 1508 (m), 1466 (m), 1364 (m), 1269 (m), 1109 (m), 829 (m).



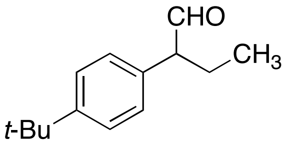
2-(2-Methylphenyl)octanal (Table 2, entry 2). Following the general procedure for α-arylation of linear aldehydes, [Pd(η^3-allyl)Cl]$_2$ (0.0037 g, 0.010 mmol), DPPF (0.0222 g, 0.0400 mmol), cesium carbonate (0.652 g, 2.00 mmol), octyl aldehyde (0.141 g, 1.10 mmol), 1-bromo-2-methylbenzene (0.171 g, 1.00 mmol) were combined in 1,4-dioxane (4.0 mL) and stirred at 80 °C for 12 h. Following the general procedure for work up, the filtrate was purified using flash-column chromatography (silica gel, 4% ether-hexanes) to give the title compound as a clear, colorless oil (0.205 g, 94%). R_f = 0.25 (4% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, *J* = 2.0 Hz, 1H, C**H**O), 7.25-7.17 (m, 3H, Ar**H**), 7.11-7.08 (m, 1H, Ar**H**), 3.75 (dt, *J* = 7.2, 7.2, 2.0 Hz, 1H, C**H**CHO), 2.36 (s, 3H, ArC**H**$_3$), 2.10 (m, 1H, C**H**$_2$CH(Ar)CHO), 1.71 (m, 1H, C**H**$_2$CH(Ar)CHO), 1.35-1.20 (m, 8H, CH_3(C**H**$_2$)$_4$$CH_2$CH(Ar)CHO), 0.87 (t, *J* = 6.8, 6.8 Hz, 3H, C**H**$_3$$CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 137.1, 134.9, 130.8, 127.8, 127.3, 126.5, 55.0, 31.6, 29.5, 29.3, 27.1, 22.5, 19.9, 14.0. IR (NaCl, thin film, neat) 3065 (w), 3020 (w), 2955 (s), 2928 (s), 2857 (s), 2811 (m), 2711 (w), 1723 (s), 1685 (m), 1685 (m), 1490 (m), 1462 (s), 1379 (m), 756 (m), 726 (m).



Methyl 4-(2-oxo-1-*n*-hexylethyl)benzoate (Table 2, entry 3). Following the general procedure for α-arylation of linear aldehydes, [Pd(η^3-allyl)Cl]$_2$ (0.0037 g, 0.010 mmol), DPPF (0.0222 g, 0.0400 mmol), cesium carbonate (0.652 g, 2.00 mmol), octyl aldehyde (0.141 g, 1.10 mmol), methyl 4-bromobenzoate (0.215 g, 1.00 mmol) were combined in 1,4-dioxane (4.0 mL) and stirred at 80 °C for 12 h. Following the general procedure for work up, the filtrate was purified using flash-column chromatography (silica gel, gradient elution 4%, 8%, 12% and 16% diethyl ether-hexanes) to give the title compound as a clear, colorless oil (0.1674 g, 64%). R_f = 0.27 (16% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (d, *J* = 2.0 Hz, 1H, C**H**O), 8.03 (d, *J* = 8.4 Hz, 2H, Ar**H**), 7.26 (d, *J* = 8.3 Hz, 2H, Ar**H**), 3.90 (s, 3H, C**H**$_3$O), 3.56 (ddd, *J* = 8.4, 6.5, 1.9 Hz, 1H, C**H**CHO), 2.08 (m, 1H, C**H**$_2$CH(Ar)CHO), 1.74 (m, 1H, C**H**$_2$CH(Ar)CHO), 1.33-1.16 (m, 8H, CH_3(C**H**$_2$)$_4$$CH_2$CH(Ar)CHO), 0.84 (t, *J* = 6.9, 6.9 Hz, 3H, C**H**$_3$$CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 166.7, 141.7, 130.2, 129.3, 128.7, 59.1, 52.1, 31.5, 29.7, 29.0, 26.9, 22.5, 14.0. IR (NaCl, thin film, neat) 2928 (s), 2857 (s), 1727 (s), 1611 (m), 1576 (w), 1435 (s), 1417 (m), 1279 (b), 1181 (m), 1113 (s), 1019 (m). Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 72.99; H, 8.73.

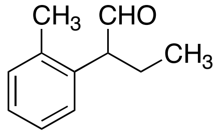


2-(2-Methoxyphenyl)octanal (Table 2, entry 4). Following the general procedure for α-arylation of linear aldehydes, Pd(η^3-allyl)Cl]$_2$ (0.0037 g, 0.010 mmol), DPPF (0.0222 g, 0.0400 mmol), cesium carbonate (0.652 g, 2.00 mmol), octyl aldehyde (0.141 g, 1.20 mmol), 2-bromoanisole (0.187 g, 1.00 mmol) were combined in 1,4-dioxane (4.0 mL) and stirred at 80 ºC for 12 h. Following the general procedure for work up, the filtrate was purified using flash-column chromatography (silica gel, gradient elution 1%, 2%, 3% and 4% ether-hexanes) to give the title compound as a clear, colorless oil (0.180 g, 77%). R_f = 0.28 (4% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (d, *J* = 1.0 Hz, 1H, C**HO**), 7.29 (dd, *J* = 7.9, 1.4 Hz, 1H, Ar**H**), 7.10 (dd, *J* = 7.5, 1.7 Hz, 1H, Ar**H**), 6.96 (td, *J* = 7.5, 7.5, 1.0 Hz, 1H, **ArH**), 6.91 (d, *J* = 8.2 Hz, 1H, Ar**H**), 3.81 (s, 3H, OC**H**$_3$), 3.76 (dd, *J* = 7.9, 6.5 Hz, 1H, C**H**CHO), 2.08 (m, 1H, C**H**$_2$CH(Ar)CHO), 1.70 (m, 1H, C**H**$_2$CH(Ar)CHO), 1.33-1.18 (m, 8H, CH_3(C**H**$_2$)$_4$$CH_2$CH(Ar)CHO), 0.85 (t, *J* = 6.9, 6.9 Hz, 3H, C**H**$_3$$CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 157.4, 129.8, 128.6, 125.7, 120.8, 110.8, 55.4, 53.1, 31.6, 29.2, 28.3, 27.2, 22.6, 14.1. IR (NaCl, thin film, neat) 3002 (w), 2928 (s), 2856 (s), 2709 (m), 1725 (s), 1599 (m), 1586 (m), 1493 (s), 1465 (s), 1438 (m), 1289 (m), 1246 (s), 1051 (m), 1030 (m), 754 (s).

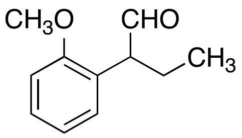


2-(4-*tert*-Butylphenyl)butyraldehyde (Table 2, entry 5). Following the general procedure for α-arylation of linear aldehydes, [Pd(η^3-allyl)Cl]$_2$ (0.0037 g, 0.010 mmol), DPPF (0.0222 g, 0.0400 mmol), cesium carbonate (0.652 g, 2.00 mmol), butyraldehyde (0.0865 g, 1.20 mmol), 1-bromo-4-*tert*-butylbenzene (0.213 g, 1.00 mmol) were combined in 1,4-dioxane

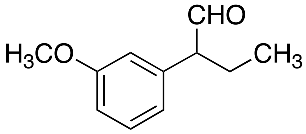
(4.0 mL) and stirred at 80 °C for 12 h. The crude product was purified using flash-column chromatography (silica gel, gradient elution: 1% ether-hexanes, 2% ether-hexanes, 3% ether-hexanes, then 4% ether-hexanes) to give the title compound as a clear, colorless oil (0.137 g, 67%). $R_f = 0.25$ (4% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (d, $J = 2.2$ Hz, 1H, C**H**O), 7.39 (d, $J = 8.4$ Hz, 2H, Ar**H**), 7.13 (d, $J = 8.2$ Hz, 2H, Ar**H**), 3.39 (m, 1H, C**H**CHO), 2.10 (m, 1H, C**H**$_2$CH(Ar)CHO), 1.75 (m, 1H, C**H**$_2$CH(Ar)CHO), 1.32 (s, 9H, ArC(C**H**$_3$)$_3$), 0.91 (t, $J = 7.4$, 7.4 Hz, 3H, C**H**$_3$CH$_2$CH(Ar)CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 150.4, 133.1, 128.4, 125.9, 60.3, 34.5, 31.3, 22.8, 11.8. IR (NaCl, thin film, neat) 2963 (s), 2904 (m), 2873 (m), 2811 (w), 2710 (w), 1726 (s), 1685 (w), 1507 (m), 1463 (m), 1364 (m), 1269 (m), 1109 (m), 1017 (w), 829 (m). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.44; H, 10.04.



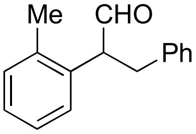
2-(2-Methylphenyl)butyraldehyde (Table 2, entry 6). Following the general procedure for α-arylation of linear aldehydes, $[Pd(\eta^3\text{-allyl})Cl]_2$ (0.0037 g, 0.010 mmol), DPPF (0.0222 g, 0.0400 mmol), cesium carbonate (0.652 g, 2.00 mmol), butyraldehyde (0.0865 g, 1.20 mmol), 1-bromo-2-methylbenzene (0.171 g, 1.00 mmol) were combined in 1,4-dioxane (4.0 mL) and stirred at 80 °C for 12.5 h. Following the general procedure for work up, the filtrate was purified using flash-column chromatography (silica gel, gradient elution: 1% ether-hexanes, 2% ether-hexanes, 3% ether-hexanes, then 4% ether-hexanes) to give the title compound as a clear, colorless oil (0.122 g, 75%). $R_f = 0.23$ (4% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (d, $J = 2.0$ Hz, 1H, C**H**O), 7.25-7.18 (m, 3H, Ar**H**), 7.08 (m, 1H, Ar**H**), 3.69 (dt, $J = 7.2$, 7.2, 1.9 Hz, 1H, C**H**CHO), 2.36 (s, 3H, ArC**H**$_3$), 2.14 (m, 1H, CH$_3$C**H**$_2$CH(Ar)CHO), 1.75 (m, 1H, CH$_3$C**H**$_2$CH(Ar)CHO), 0.93 (t, $J = 7.6$, 7.2 Hz, 3H, C**H**$_3$CH$_2$CH(Ar)CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 137.2, 134.7, 130.8, 127.8, 127.3, 126.5, 56.5, 22.7, 19.9, 11.8. IR (NaCl, thin film, neat) 3065 (w), 3020 (w), 2965 (s), 1934 (m), 2875 (m), 2813 (w), 2711 (w), 1718 (s), 1490 (m), 1462 (m), 1381 (m), 757 (s), 726 (m). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.29; H, 9.00.



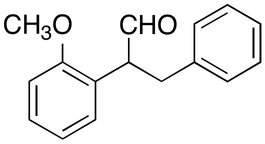
2-(2-Methoxyphenyl)butyraldehyde (Table 2, entry 7). Following the general procedure for α-arylation of linear aldehydes, [Pd(η^3-allyl)Cl]$_2$ (0.0037 g, 0.010 mmol), DPPF (0.0222 g, 0.0400 mmol), cesium carbonate (0.652 g, 2.00 mmol), butyraldehyde (0.0865 g, 1.20 mmol), 1-bromo-2-methoxybenzene (0.187 g, 1.00 mmol) were combined in THF (4.0 mL) and stirred at 80 °C for 12 h. Following the general procedure for work up, the filtrate was purified using flash-column chromatography (silica gel, gradient elution: 2% ether-hexanes, 4% ether-hexanes, 6% ether-hexanes, then 8% ether-hexanes) to give the title compound as a clear, colorless oil (0.128 g, 71%). R$_f$ = 0.28 (8% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.67 (d, *J* = 0.8 Hz, 1H, C**H**O), 7.31-7.30 (m, 1H, Ar**H**), 7.09 (dd, *J* = 8.0, 1.7 Hz, 1H, Ar**H**), 6.99-6.91 (m, 2H, Ar**H**), 3.81 (s, 3H, OC**H**$_3$), 3.69 (dt, *J* = 7.2, 7.2, 7.2, 7.2, 0.8 Hz, 1H, C**H**CHO), 2.18-2.08 (m, 1H, CH$_3$C**H**$_2$CH(Ar)CHO), 1.78-1.67 (m, 1H, CH$_3$C**H**$_2$CH(Ar)CHO), 0.89 (t, *J* = 7.4, 7.4 Hz, 3H, C**H**$_3$CH$_2$CH(Ar)CHO). ^{13}C NMR (100 MHz, CDCl$_3$) δ 201.8, 157.4, 129.9, 128.6, 125.4, 120.8, 110.7, 55.3, 54.7, 21.5, 11.8. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.21; H, 8.15.



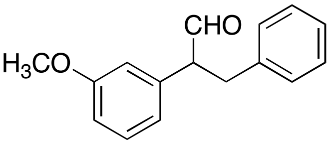
2-(3-Methoxyphenyl)butyraldehyde (Table 2, entry 8). Following the general procedure for α-arylation of linear aldehydes, [Pd(η^3-allyl)Cl]$_2$ (3.7 mg, 0.010 mmol), DPPF (0.0222 mg, 0.0400 mmol), cesium carbonate (0.652 g, 2.00 mmol), butyraldehyde (0.0865 g, 1.20 mmol), 1-bromo-3-methoxybenzene (0.187 g, 1.00 mmol) were combined in 1,4-dioxane (4.0 mL) and stirred at 80 °C for 12 h. Following the general procedure for work up, the filtrate was purified using flash-column chromatography (silica gel, gradient elution: 2% ether-hexanes, 4% ether-hexanes, 6% ether-hexanes, then 8% ether-hexanes) to give the title compound as a clear, colorless oil (0.125 g, 70%). R$_f$ = 0.26 (8% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.66 (d, *J* = 2.0 Hz, 1H, C**H**O), 7.29 (t, *J* = 7.9, 7.9 Hz, 1H, Ar**H**), 6.84 (m, 1H, Ar**H**), 6.79 (d, *J* = 7.6 Hz, 1H, Ar**H**), 6.73 (m, 1H, Ar**H**), 3.81 (s, 3H, OCH_3), 3.38 (dt, *J* = 8.4, 6.7, 2.0 Hz, C**H**CHO), 2.09 (m, 1H, $CH_3C\mathbf{H}_2$CH(Ar)CHO), 1.75 (m, 1H, $CH_3C\mathbf{H}_2$CH(Ar)CHO), 0.90 (t, *J* = 7.4, 7.4 Hz, 3H, $C\mathbf{H}_3CH_2$CH(Ar)CHO). ^{13}C (100 MHz, $CDCl_3$) δ 200.9, 160.0, 137.7, 130.0, 121.1, 114.5, 112.7, 60.8, 55.2, 22.8, 11.7. IR (NaCl, thin film, neat) 2964 (s), 2936 (s), 2876 (m), 2836 (m), 2715 (w), 1722 (s), 1600 (s), 1584 (s), 1492 (s), 1464 (s), 1436 (s), 1380 (w), 1319 (m), 1293 (s), 1261 (s), 1157 (m), 1126 (w), 1048 (s), 996 (w), 876 (w), 780 (s), 700 (s). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.18; H, 8.01.



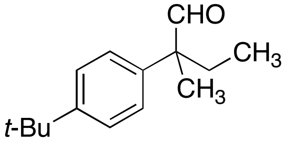
2-(2-Methylphenyl)-3-phenylpropionaldehyde (Table 2, entry 9). Following the general procedure for α-arylation of linear aldehydes, [Pd(η^3-allyl)Cl]$_2$ (0.0037 g, 0.010 mmol), DPPF (0.0222 g, 0.0400 mmol), cesium carbonate (0.652 g, 2.00 mmol), hydrocinnamaldehyde (0.134 g, 1.00 mmol), 1-bromo-2-methylbenzene (0.171 g, 1.00 mmol) were combined in 1,4-dioxane (4.0 mL) and stirred at 80 °C for 12 h. Following the general procedure for work up, the filtrate was purified using flash-column chromatography (silica gel, gradient eluction: 1%, 2%, 3%, and then 4% diethyl ether in hexanes) to give the title compound as a clear, colorless oil (0.149 g, 67%). R_f = 0.26 (12% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, *J* = 1.2 Hz, 1H, C**H**O), 7.27-7.04 (m, 9H, Ar**H**), 4.09 (ddd, *J* = 1.2, 6.4, 7.7 Hz, 1H, C**H**CHO), 3.51 (dd, *J* = 6.4, 13.6 Hz, 1H, PhC$\mathbf{H}_2$CH(Ar)CHO), 2.90 (dd, *J* = 7.7, 13.6 Hz, 1H, PhC$\mathbf{H}_2$CH(Ar)CHO), 2.12 (s, 3H, ArC$\mathbf{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 139.3, 137.6, 134.6, 131.2, 129.3, 128.6, 128.5, 127.8, 126.9, 126.5, 57.2, 36.5, 19.9. IR (NaCl, thin film, neat) 3062 (m), 3026 (m), 2948 (m), 2927 (m), 2860 (w), 2816 (m), 2719 (m), 1722 (s), 1602 (m), 1495 (s), 1453 (s), 1383 (w), 1146 (m), 1078 (w), 1048 (w), 1030 (m), 862 (w), 757 (s), 726 (s), 670 (s).



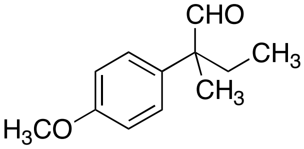
2-(2-Methoxyphenyl)-3-phenylpropionaldehyde (Table 2, entry 10). Following the general procedure for α-arylation of linear aldehydes, $[Pd(\eta^3\text{-allyl})Cl]_2$ (0.0037 g, 0.010 mmol), DPPF (0.0222 g, 0.0400 mmol), cesium carbonate (0.652 g, 2.00 mmol), hydrocinnamaldehyde (0.134 g, 1.00 mmol), 1-bromo-2-methoxybenzene (0.187 g, 1.00 mmol) were combined in 1,4-dioxane (4.0 mL) and stirred in a 5-dram scintillation vial at 80 °C for 12 h. Following the general procedure for work up, the filtrate was purified using flash-column chromatography (silica gel, gradient eluction: 2.5%, 5%, 7.5% and then 10% diethyl ether-hexanes) to give the title compound as a clear, colorless oil (0.182 g, 76%). R_f= 0.23 (12% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H, C**H**O), 7.30-7.13 (m, 4H, Ar**H**), 7.07-7.05 (m, 2H, Ar**H**), 6.97-6.88 (m, 3H, Ar**H**), 4.06 (dd, *J* = 6.4, 8.0 Hz, 1H, C**H**CHO), 3.76 (s, 3H, OC**H**$_3$), 3.50 (dd, *J* = 6.4, 13.8 Hz, 1H, PhC**H**$_2$CH(Ar)CHO), 2.95 (dd, *J* = 8.0, 13.8 Hz, 1H, PhC**H**$_2$CH(Ar)CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 157.2, 139.5, 130.3, 129.1, 128.9, 128.1, 126.0, 124.9, 120.8, 110.8, 55.4, 55.3, 34.6. IR (NaCl, thin film, neat) 3062 (m), 3027 (m), 3003 (m), 2937 (m), 2836 (m), 2724 (m), 1724 (s), 1600 (s), 1586 (s), 1494 (s), 1464 (s), 1454 (s), 1438 (s), 1387 (w), 1324 (m), 1290 (m), 1247 (s), 1179 (m), 1163 (m), 1119 (m), 1080 (m), 1051 (s), 1029 (s), 864 (w), 754 (s), 700 (s). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.11; H, 6.90.



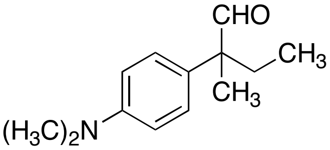
3-Phenyl-2-(3-methoxyphenyl)propionaldehyde (Table 10, entry 11). Following the general procedure for α-arylation of linear aldehydes, $[Pd(\eta^3\text{-allyl})Cl]_2$ (0.0037 g, 0.010 mmol), DPPF (0.0222 g, 0.0400 mmol), cesium carbonate (0.652 g, 2.00 mmol), hydrocinnamaldehyde (0.134 g, 1.00 mmol), 1-bromo-3-methoxybenzene (0.187 g, 1.00 mmol) were combined in 1,4-dioxane (4.0 mL) and stirred in a 5-dram scintillation vial at 80 °C for 12 h. The crude product was purified using flash-column chromatography (silica gel, gradient elution: 2.5%, 5%, 7.5% and then 10% diethyl ether in hexanes) to give the title compound as a clear, colorless oil (0.182 g, 61%). R_f= 0.23 (12% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (d, *J* = 1.5 Hz, 1H, C**H**O), 7.29-7.07 (m, 6H, ArH), 6.83 (dd, *J* = 2.5, 8.3 Hz, 1H, Ar**H**), 6.74 (d, *J* = 7.6 Hz, 1H, Ar**H**), 6.67 (m, 1H, Ar**H**), 3.81 (m, 1H, C**H**CHO), 3.77 (s, 3H, OC**H**$_3$), 3.46 (dd, *J* = 6.8, 14.0 Hz, 1H, PhC**H**$_2$CH(Ar)CHO), 2.97 (dd, *J* = 7.8, 14.0 Hz, 1H, PhC**H**$_2$CH(Ar)CHO). ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.7, 159.9, 138.7, 137.1, 129.0, 130.0, 128.3, 126.3, 121.2, 114.6, 113.0, 60.9, 55.2, 35.9. IR (NaCl, thin film, neat) 3085 (w), 3061 (m), 3027 (m), 3003 (w), 2938 (m), 2835 (m), 2719 (m), 1728 (s), 1683 (m), 1600 (s), 1584 (s), 1495 (s), 1464 (s), 1435 (s), 1387 (w), 1320 (m), 1287 (s), 1260 (s), 1151 (s), 1076 (w), 1048 (s), 873 (m), 781 (m), 752 (m), 600 (s).



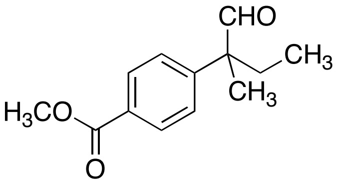
2-(4-*t*-Butylphenyl)-2-methyl-butyraldehyde (Table 3, entry 1). Following the general procedure for α-arylation of branched aldehydes, [Pd(η^3-allyl)Cl]$_2$ (0.0018 g, 0.005 mmol), Q-phos (0.0071 g, 0.010 mmol), cesium carbonate (0.652 g, 2.00 mmol), 2-methylbutyraldehyde (0.103 g, 1.20 mmol), 1-bromo-4-*tert*-butylbenzene (0.213 g, 1.00 mmol) were combined in THF (2.0 mL) and stirred at 80 °C for 13 h. The crude product was purified using flash-column chromatography (silica gel, 2% diethyl ether-hexanes) to give the title compound as a clear, colorless oil (0.200 g, 91%). R$_f$ = 0.26 (2% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.49 (s, 1H, C**H**O), 7.39 (d, *J* = 8.4 Hz, 2H, Ar**H**), 7.18 (d, *J* = 8.4 Hz, 2H, Ar**H**), 2.02-1.86 (m, 2H, CH$_3$C**H**$_2$), 1.42 (s, 3H, CH$_3$CH$_2$C(C**H**$_3$)(Ar)CHO), 1.32 (s, 9H, ArC(C**H**$_3$)$_3$), 0.81 (t, *J* **=** 7.6, 7.6 Hz, 3H, C**H**$_3$CH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 202.91, 149.96, 136.75, 126.84, 125.67, 53.85, 34.40, 31.26, 28.36, 18.19, 8.45. IR (NaCl, thin film, neat) 3031 (w), 2964 (s), 2871 (m), 2802 (w), 2706 (w), 1725 (s), 1509 (m), 1462 (m), 1394 (m), 1363 (m), 1271 (m), 1119 (m), 1015 (m), 907 (w), 827 (m).



2-(4-Methoxyphenyl)-2-methylbutyraldehyde (Table 3, entry 2). Following the general procedure for α-arylation of branched aldehydes, [Pd(η^3-allyl)Cl]$_2$ (0.0018 g, 0.005 mmol), Q-phos (0.0071 g, 0.010 mmol), cesium carbonate (0.652 g, 2.00 mmol), 2-methylbutyraldehyde (0.103 g, 1.20 mmol), 4-bromoanisole (0.187 g, 1.00 mmol) were combined in THF (2.0 mL) and stirred at 80 °C for 13 h. The crude product was purified using flash-column chromatography (silica gel, 4% diethyl ether-hexanes) to give the title compound as a clear, colorless oil (0.156 g, 81%). R_f = 0.21 (4% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H, C**H**O), 7.16 (d, *J* = 8.8 Hz, 2H, Ar**H**), 6.91 (d, *J* = 8.8 Hz, 2H, Ar**H**), 3.79 (s, 3H, OC**H**$_3$), 2.02-1.82 (m, 2H, CH_3C**H**$_2$), 1.40 (s, 3H, CH_3CH_2C(C**H**$_3$)(Ar)CHO), 0.78 (t, *J* = 7.6, 7.2 Hz, 3H, C**H**$_3$$CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9, 158.8, 131.8, 128.6, 114.4, 55.5, 53.8, 28.7, 18.5, 8.6. IR (NaCl, thin film, neat) 2968 (s), 2936 (s), 2879 (m), 2836 (m), 2707 (m), 2706 (m), 1718 (s), 1609 (s), 1580 (m), 1513 (s), 1458 (s), 1443 (m), 1388 (w), 1370 (w), 1299 (m), 1253 (s), 1116 (w), 1035 (s), 1010 (w), 907 (m), 828 (s), 791 (m), 776 (m). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.85; H, 8.25.

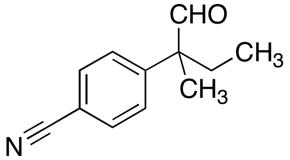


2-(4-*N,N*-dimethylaminophenyl)-2-methylbutyraldehyde (Table 3, entry 3). Following the general procedure for α-arylation of branched aldehydes, [Pd(η^3-allyl)Cl]$_2$ (0.0018 g, 0.005 mmol), Q-phos (0.0071 g, 0.010 mmol), cesium carbonate (0.652 g, 2.00 mmol), 2-methylbutyraldehyde (0.103 g, 1.20 mmol), 4-bromo-*N,N*-dimethylaniline (0.200 g, 1.00 mmol) were combined in THF (2.0 mL) and stirred at 80 °C for 13 h. The crude product was purified using flash-column chromatography (silica gel, gradient elution: 4%, 5%, 6%, then 8% ether-hexanes) to give the title compound as a clear, colorless oil (0.176 g, 86%). R_f = 0.26 (8% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H, C**H**O), 7.14 (d, *J* = 8.4 Hz, 2H, Ar**H**), 6.76 (d, *J* = 8.8 Hz, 2H, Ar**H**), 2.96 (s, 6H, N(C**H**$_3$)$_2$), 1.97-1.84 (m, 2H, CH_3C**H**$_2$), 1.41 (s, 3H, CH_3CH_2C(C**H**$_3$)(Ar)CHO), 0.82 (t, *J* = 7.6, 7.6 Hz, 3H, C**H**$_3$$CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 149.4, 127.9, 126.7, 112.6, 53.2, 40.4, 28.1, 17.9, 8.3. Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 75.88; H, 9.56; N, 6.80.



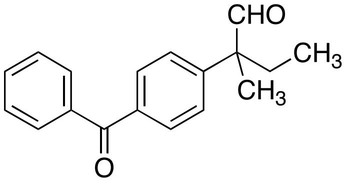
Methyl 4-(2-oxo-1-ethyl-1-methylethyl)benzoate (Table 3, entry 4). Following the general procedure for α-arylation of branched aldehydes, $[Pd(\eta^3\text{-allyl})Cl]_2$ (0.0018 g, 0.005 mmol), Q-phos (0.0071 g, 0.010 mmol), cesium carbonate (0.652 g, 2.00 mmol), 2-methylbutyraldehyde (0.103 g, 1.20 mmol), methyl 4-bromobenzoate (0.200 g, 1.00 mmol) were combined in THF (2.0 mL) and stirred at 80 °C for 13 h. The crude product was purified using flash-column chromatography (silica gel, 8% diethyl ether-hexanes) to give the title compound as a clear, colorless oil (0.179 g, 81%). R_f = 0.21 (8% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H, C**H**O), 8.00 (d, *J* = 8.8 Hz, 2H, Ar**H**), 7.30 (d, *J* = 8.8 Hz, 2H, Ar**H**), 3.88 (s, 3H, $CO_2C\mathbf{H}_3$), 2.02-1.82 (m, 2H, $CH_3C\mathbf{H}_2$), 1.42 (s, 3H, $CH_3CH_2C(C\mathbf{H}_3)(Ar)CHO$), 0.75 (t, *J* = 7.2, 7.6 Hz, 3H, $C\mathbf{H}_3CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 166.6, 145.1, 129.8, 128.9, 127.1, 54.4, 52.0, 28.6, 18.1, 8.2. IR (NaCl, thin film, neat) 2971 (s), 2880 (m), 2843 (m), 2809 (m), 2710 (w), 1736 (s), 1731 (s), 1716 (s), 1609 (s), 1572 (w), 1508 (w), 1460 (m), 1435 (s), 1410 (m), 1383 (w), 1372 (w), 1316 (s), 1278 (br), 1191 (s), 1117 (s), 1018 (s), 966 (w), 909 (w), 856 (w), 822 (w), 771 (s), 707 (s). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.58; H, 7.29.

Methyl 4-(2-oxo-1-ethyl-1-methylethyl)benzoate (Table 3, entry 5). Following the general procedure for α-arylation of branched aldehydes with bromoarenes, $[Pd(\eta^3\text{-allyl})Cl]_2$ (0.0037 g, 0.010 mmol), Q-phos (0.0142 g, 0.0200 mmol), cesium carbonate (0.652 g, 2.00 mmol), 2-methylbutyraldehyde (0.103 g, 1.20 mmol), methyl 4-chlorobenzoate (0.171 g, 1.00 mmol) were combined in THF (4.0 mL) and stirred at 90 °C for 15 h. The crude product was purified to give the title compound as a clear, colorless oil (0.170 g, 77%).



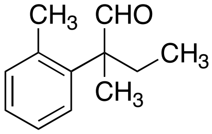
2-(4-Cyanophenyl)-2-methylbutyraldehyde (Table 3, entry 6). Following the general procedure for α-arylation of branched aldehydes, [Pd(η^3-allyl)Cl]$_2$ (0.0018 g, 0.005 mmol), Q-phos (0.0071 g, 0.010 mmol), cesium carbonate (0.652 g, 2.00 mmol), 2-methylbutyraldehyde (0.103 g, 1.20 mmol), 4-bromobenzonitrile (0.182 g, 1.00 mmol) were combined in THF (2.0 mL) and stirred at 80 °C for 13 h. The crude product was purified using flash-column chromatography (silica gel, 16% diethyl ether-hexanes) to give the title compound as a clear, colorless oil (0.150 g, 80%). R_f = 0.20 (8% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.51 (s, 1H, C**H**O), 7.65 (d, *J* = 8.4 Hz, 2H, Ar**H**), 7.36 (d, *J* = 7.7 Hz, 2H, Ar**H**), 1.99-1.85 (m, 2H, CH$_3$C**H**$_2$), 1.45 (s, 3H, CH$_3$CH$_2$C(C**H**$_3$)(Ar)CHO), 0.77 (t, *J* = 7.2, 7.6 Hz, 3H, C**H**$_3$CH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 201.4, 145.5, 132.4, 128.0, 118.5, 111.1, 54.6, 28.7, 18.2, 8.2. IR (NaCl, thin film, neat) 2972 (s), 2939 (m), 2881 (m), 2813 (w), 2714 (w), 2229 (s), 1725 (s), 1607 (s), 1505 (m), 1460 (m), 1403 (m), 1018 (m), 1005 (w), 908 (m), 833 (m), 785 (w), 734 (w). Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00. Found: C, 76.90; H, 7.60.

2-(4-Cyanophenyl)-2-methylbutyraldehyde (Table 11, entry 7). Following the general procedure for α-arylation of branched aldehydes with bromoarenes, [Pd(η^3-allyl)Cl]$_2$ (0.0037 g, 0.010 mmol), Q-phos (0.0142 g, 0.0200 mmol), cesium carbonate (0.652 g, 2.00 mmol), 2-methylbutyraldehyde (0.103 g, 1.20 mmol), 4-chlorobenzonitrile (0.138 g, 1.00 mmol) were combined in THF (4.0 mL) and stirred at 90 °C for 15 h. The crude product was purified to give the title compound as a clear, colorless oil (0.126 g, 67%).

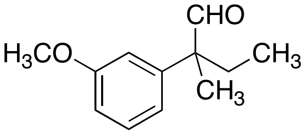


2-(4-Benzoylphenyl)-2-methylbutyraldehyde (Table 3, entry 8). Following the general procedure for α-arylation of branched aldehydes, [Pd(η^3-allyl)Cl]$_2$ (0.0018 g, 0.005 mmol), Q-phos (0.0071 g, 0.010 mmol), cesium carbonate (0.652 g, 2.00 mmol), 2-

methylbutyraldehyde (0.103 g, 1.20 mmol), 4-bromobenzophenone (0.261 g, 1.00 mmol) were combined in THF (2.0 mL) and stirred at 80 °C for 12 h. The crude product was purified using flash-column chromatography (silica gel, 16% diethyl ether-hexanes) to give the title compound as a clear, colorless oil (0.194 g, 73%). R_f = 0.23 (16% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 1H, C**H**O), 7.84-7.79 (m, 4H, Ar**H**), 7.59 (m, 1H, Ar**H**), 7.48 (m, 2H, Ar**H**), 7.38 (m, 2H, Ar**H**), 1.99 (m, 2H, $CH_3C\mathbf{H}_2$), 1.48 (s, 3H, $CH_3CH_2C(C\mathbf{H}_3)(Ar)CHO$), 0.82 (t, *J* = 7.5, 7.5 Hz, 3H, $C\mathbf{H}_3CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 196.1, 144.7, 137.3, 136.3, 132.5, 130.4, 130.0, 128.3, 127.1, 54.6, 28.7, 18.3, 8.3. IR (NaCl, thin film, neat) 3059 (w), 2970 (s), 2879 (m), 2808 (w), 2710 (w), 1724 (s), 1659 (s), 1605 (s), 1579 (s), 1565 (w), 1447 (m), 1406 (m), 1317 (s), 1278 (s), 1196 (w), 1179 (m), 1152 (w), 1090 (w), 1027 (w), 1017 (w), 1001 (w), 939 (s), 926 (s), 849 (m), 794 (m), 751 (m), 702 (s), 647 (m). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.89; H, 6.49.

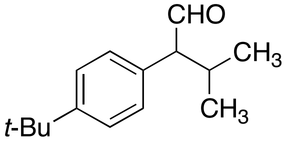


2-(2-methylphenyl)-2-methylbutyraldehyde (Table 3, entry 9). Following the general procedure for α-arylation of branched aldehydes, $[Pd(\eta^3\text{-allyl})Cl]_2$ (0.0018 g, 0.005 mmol), Q-phos (0.0071 g, 0.010 mmol), cesium carbonate (0.652 g, 2.00 mmol), 2-methylbutyraldehyde (0.103 g, 1.20 mmol), 2-bromotoluene (0.171 g, 1.00 mmol) were combined in THF (2.0 mL) and stirred at 80 °C for 12 h. The crude product was purified using flash-column chromatography (silica gel, 2% diethyl ether-hexanes) to give the title compound as a clear, colorless oil (0.125 g, 71%). R_f = 0.21 (2% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H, C**H**O), 7.34-7.16 (m, 4H, Ar**H**), 2.23 (s, 3H, $ArC\mathbf{H}_3$), 2.10-1.91 (m, 2H, $CH_3C\mathbf{H}_2$), 1.41 (s, 3H, $CH_3CH_2C(C\mathbf{H}_3)(Ar)CHO$), 0.76 (t, *J* = 7.6, 7.6 Hz, 3H, $C\mathbf{H}_3CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 138.4, 136.6, 132.2, 127.6, 127.4, 126.1, 54.7, 26.8, 21.1, 19.7, 8.3. IR (NaCl, thin film, neat) 3060 (w), 3017 (w), 2969 (s), 2938 (m), 2879 (m), 2798 (m), 2701 (m), 1724 (s), 1488 (m), 1459 (m), 1386 (m), 905 (m), 758 (s), 726 (s). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.58; H, 9.43.

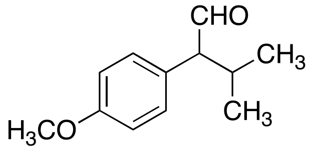


2-(3-Methoxyphenyl)-2-methylbutyraldehyde (Table 3, entry 10). Following the general procedure for α-arylation of branched aldehydes, [Pd(η^3-allyl)Cl]$_2$ (0.0018 g, 0.005 mmol), Q-phos (0.0071 g, 0.010 mmol), cesium carbonate (0.652 g, 2.00 mmol), 2-methylbutyraldehyde (0.103 g, 1.20 mmol), 3-bromoanisole (0.187 g, 1.00 mmol) were combined in THF (2.0 mL) and stirred at 80 °C for 12 h. The crude product was purified using flash-column chromatography (silica gel, 2% diethyl ether-hexanes) to give the title compound as a clear, colorless oil (0.160 g, 83%). $R_f = 0.22$ (2% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H, C**H**O), 7.29 (t, *J* = 8.0, 8.0 Hz, 1H, Ar**H**), 6.84-6.78 (m, 3H, Ar**H**), 3.80 (s, 3H, OC**H**$_3$), 2.02-1.83 (m, 2H, CH_3C**H**$_2$), 1.41 (s, 3H, CH_3CH_2C(C**H**$_3$)(Ar)CHO), 0.79 (t, *J* = 7.6, 7.6 Hz, 3H, C**H**$_3$$CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 159.8, 141.5, 129.7, 119.5, 113.5, 111.8, 55.1, 54.2, 28.4, 18.1, 8.3. IR (NaCl, thin film, neat) 2969 (s), 2938 (s), 2879 (m), 2835 (m), 2805 (w), 2707 (w), 1725 (s) 1600 (s), 1582 (s), 1492 (s), 1463 (s), 1433 (s), 1388 (w), 1371 (w), 1317 (m), 1292 (s), 1256 (s), 1206 (m), 1174 (m), 1045 (s), 1004 (w), 911 (m), 778 (s), 701 (s). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.21; H, 8.61.

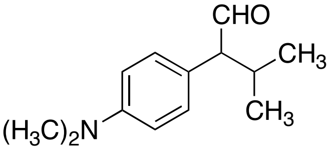
2-(3-Methoxyphenyl)-2-methylbutyraldehyde (Table 3, entry 11). Following the general procedure for α-arylation of branched aldehydes with bromoarenes, [Pd(η^3-allyl)Cl]$_2$ (0.0037 g, 0.010 mmol), Q-phos (0.0142 g, 0.0200 mmol), cesium carbonate (0.652 g, 2.00 mmol), 2-methylbutyraldehyde (0.103 g, 1.20 mmol), 3-chloroanisole (0.138 g, 1.00 mmol) were combined in THF (4.0 mL) and stirred at 90 °C for 15 h. The crude product was purified to give the title compound as a clear, colorless oil (0.146 g, 76%).



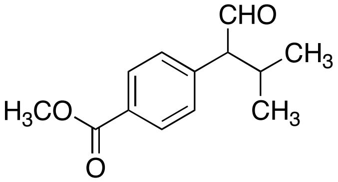
2-(4-*t*-Butylphenyl)-3-methylbutyraldehyde (Table 3, entry 12). Following the general procedure for α-arylation of branched aldehydes, [Pd(η^3-allyl)Cl]$_2$ (0.0018 g, 0.005 mmol), Q-phos (0.0071 g, 0.010 mmol), cesium carbonate (0.652 g, 2.00 mmol), 3-methylbutyraldehyde (0.103 g, 1.20 mmol), 1-bromo-4-*t*-butylbenzene (0.213 g, 1.00 mmol) were combined in THF (2.0 mL) and stirred at 80 ºC for 12 h. The crude product was purified using flash-column chromatography (silica gel, 2% diethyl ether-hexanes) to give the title compound as a clear, colorless oil (0.174 g, 80%). R_f = 0.25 (2% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (d, *J* = 3.2 Hz, 1H, C**H**O), 7.37 (d, *J* = 8.4 Hz, 2H, Ar**H**), 7.11 (d, *J* = 8.4 Hz, 2H, Ar**H**), 3.15 (dd, *J* = 3.2 Hz, 9.4 Hz, 1H, C**H**CHO), 2.40 (m, 1H, $(CH_3)_2$C**H**), 1.31 (s, 9H, C(C**H**$_3$)$_3$), 1.03 (d, *J* = 6.4 Hz, 3H, (C**H**$_3$)$_2$CHCH(Ar)CHO), 0.77 (d, *J* = 6.8 Hz, 3H, (C**H**$_3$)$_2$CHCH(Ar)CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 150.3, 132.2, 128.9, 125.8, 66.3, 34.5, 31.3, 28.6, 21.2, 20.1. Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.19; H, 10.01.



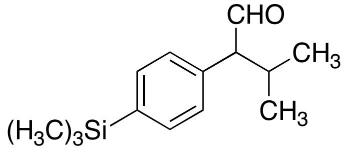
2-(4-Methoxyphenyl)-3-methylbutyraldehyde (Table 3, entry 13). Following the general procedure for α-arylation of branched aldehydes, [Pd(η^3-allyl)Cl]$_2$ (0.0018 g, 0.005 mmol), Q-phos (0.0071 g, 0.010 mmol), cesium carbonate (0.652 g, 2.00 mmol), 3-methylbutyraldehyde (0.103 g, 1.20 mmol), 1-bromo-4-methoxybenzene (0.187 g, 1.00 mmol) were combined in THF (2.0 mL) and stirred in a 1-dram scintillation vial at 80 ºC for 12 h. The crude product was purified using flash-column chromatography (silica gel, 8% diethyl ether-hexanes) to give the title compound as a clear, colorless oil (0.140 g, 73%). R_f= 0.28 (8% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (d, *J* = 3.2 Hz, 1H, C**H**O), 7.09 (d, *J* = 8.8 Hz, 2H, Ar**H**), 6.89 (d, *J* = 8.8 Hz, 2H, Ar**H**), 3.79 (s, 3H, OC**H**$_3$), 3.12 (dd, *J* = 9.6, 3.2 Hz, 1H, C**H**CHO), 2.37 (m, 1H, $(CH_3)_2$C**H**CH(Ar)CHO), 1.02 (d, *J* = 6.4 Hz, 3H, (C**H**$_3$)$_2$CH), 0.75 (d, *J* = 6.4 Hz, 3H, (C**H**$_3$)$_2$CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 158.9, 130.2, 127.2, 114.2, 65.9, 55.1, 28.5, 21.1, 19.9. IR (NaCl, thin film, neat) 2959 (s), 2909 (m), 2871 (m), 2836 (m), 2709 (w), 1723 (s), 1610 (s), 1582 (w), 1511 (s), 1466 (m), 1442 (w), 1387 (w), 1368 (w), 1319 (w), 1303 (m), 1251 (s), 1180 (s), 1140 (w), 1121 (w), 1035 (s), 829 (m). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.67; H, 8.49.



2-(4-*N,N'*-Dimethylaminophenyl)-3-methylbutyraldehyde (Table 3, entry 14). Following the general procedure for α-arylation of branched aldehydes, $[Pd(\eta^3\text{-allyl})Cl]_2$ (0.0018 g, 0.005 mmol), Q-phos (0.0071 g, 0.010 mmol), cesium carbonate (0.652 g, 2.00 mmol), 3-methylbutyraldehyde (0.103 g, 1.20 mmol), 4-bromo-*N,N*-dimethylaniline (0.200 g, 1.00 mmol) were combined in THF (2.0 mL) and stirred at 80 °C for 12 h. The crude product was purified using flash-column chromatography (silica gel, 10% diethyl ether-hexanes) to give the title compound as a clear, colorless oil (0.138 g, 67%). R_f = 0.26 (10% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (d, *J* = 3.2 Hz, 1H, C**H**O), 7.04 (d, *J* = 8.8 Hz, 2H, Ar**H**), 6.72 (d, *J* = 8.8 Hz, 2H, Ar**H**), 3.07 (dd, *J* = 9.4, 3.2 Hz, 1H, C**H**CHO), 2.95 (s, 6H, N(C**H**$_3$)$_2$), 2.36 (m, 1H, $(CH_3)_2$C**H**CH(Ar)CHO), 1.02 (d, *J* = 6.4 Hz, 3H, (C**H**$_3$)$_2$CH), 0.78 (d, *J* = 6.4 Hz, 3H, (C**H**$_3$)$_2$CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 149.8, 130.0, 122.5, 112.8, 65.9, 40.5, 28.3, 21.2, 20.0. IR (NaCl, thin film, neat) 3075 (w), 2957 (s), 2928 (s), 2908 (s), 2869 (s), 2805 (s), 2707 (m), 1721 (s), 1613 (s), 1564 (w), 1519 (s), 1481 (m), 1467 (m), 1445 (m), 1387 (m), 1352 (s), 1223 (m), 1205 (m), 1189 (w), 1165 (m), 1142 (m), 1128 (m), 1061 (m), 947 (m), 815 (s). Anal. Calcd for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 76.21; H, 9.51; N, 6.84.



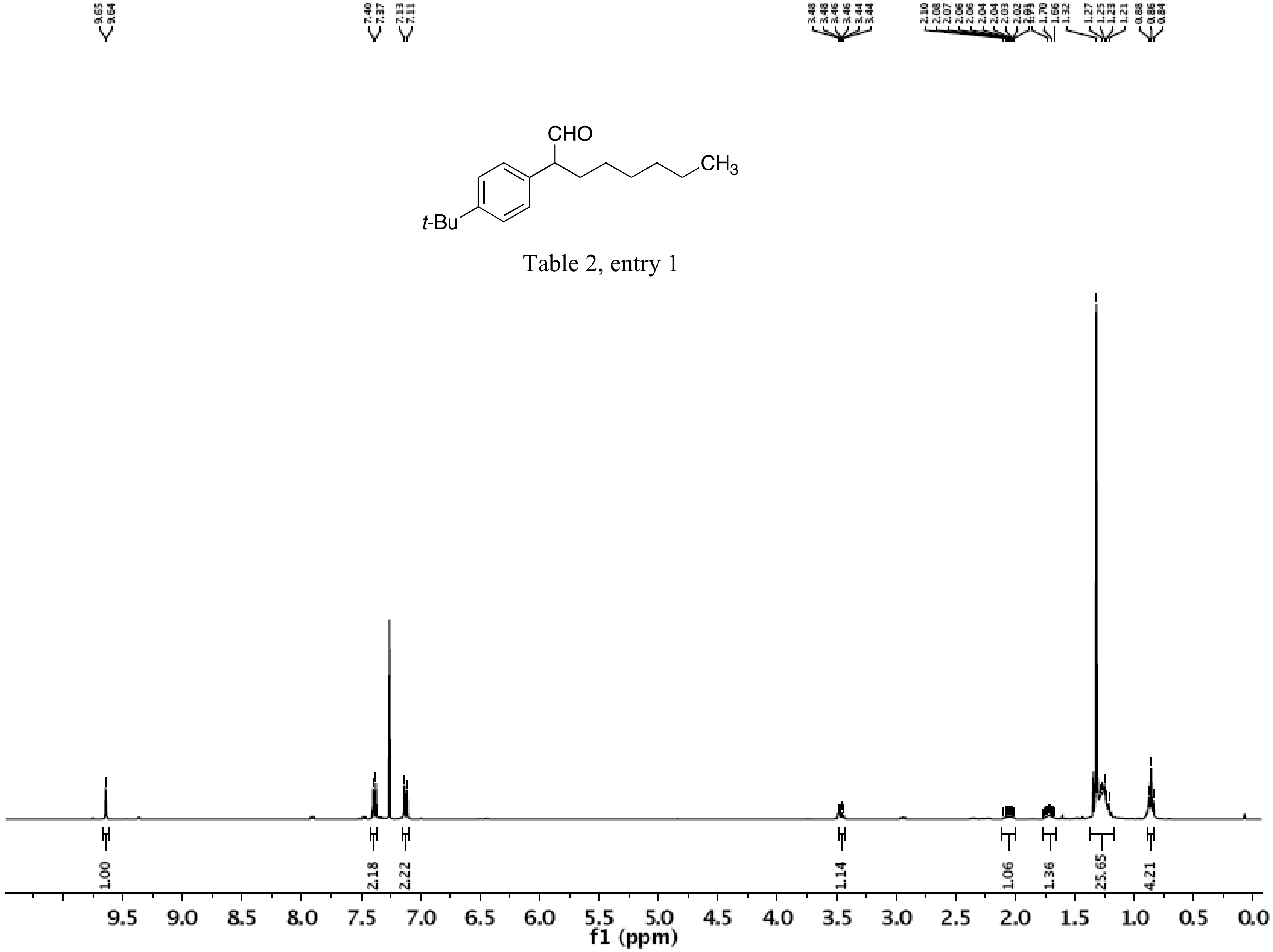
Methyl 4-(2-oxy-1-isopropylethyl)benzoate (Table 3, entry 15). Following the general procedure for α-arylation of branched aldehydes, $[Pd(\eta^3\text{-allyl})Cl]_2$ (0.0018 g, 0.005 mmol), Q-phos (0.0071 g, 0.010 mmol), cesium carbonate (0.652 g, 2.00 mmol), 3-methylbutyraldehyde (0.103 g, 1.20 mmol), methyl 4-bromobenzoate (0.215 g, 1.00 mmol) were combined in THF (2.0 mL) and stirred at 80 °C for 12 h. The crude product was purified using flash-column chromatography (silica gel, 12% diethyl ether-hexanes) to give the title compound as a clear, colorless oil (0.148 g, 67%). R_f = 0.21 (10% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, *J* = 3.2 Hz, 1H, C**H**O), 8.02 (d, *J* = 8.1 Hz, 2H, Ar**H**), 7.26 (d, *J* = 8.1 Hz, 2H, Ar**H**), 3.90 (s, 3H, $ArCO_2C\mathbf{H}_3$), 3.26 (dd, *J* = 3.2, 9.5 Hz, 1H, C**H**CHO), 2.44 (m, 1H, $(CH_3)_2C\mathbf{H}CH(Ar)CHO$), 1.04 (d, *J* = 6.6 Hz, 3H, $(C\mathbf{H}_3)_2CH$), 0.75 (d, *J* = 6.7 Hz, 3H, $(C\mathbf{H}_3)_2CH$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 166.7, 140.7, 130.0, 129.3 (overlap of two peaks), 66.6, 52.1, 29.1, 21.1, 20.0. IR (NaCl, thin film, neat) 2960 (s), 2873 (m), 2843 (m), 2715 (w), 1722 (s), 1609 (s), 1574 (w), 1467 (m), 1436 (s), 1418 (m), 1389 (w), 1370 (w), 1282 (br), 1182 (s), 1140 (w), 1113 (s), 1045 (w), 1020 (m), 966 (w), 857 (w), 770 (s), 708 (s). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.96; H, 7.59.



2-(4-Trimethylsilylphenyl)-3-methylbutyraldehyde (Table 3, entry 16). Following the general procedure for α-arylation of linear aldehydes, $[Pd(\eta^3\text{-allyl})Cl]_2$ (0.0037 g, 0.010 mmol), DPPF (0.0222 g, 0.0400 mmol), cesium carbonate (0.652 g, 2.00 mmol), isovaleraldehyde (0.103 g, 1.20 mmol), 1-bromo-4-(trimethylsilyl)benzene (0.229 g, 1.00 mmol) were combined in 1,4-dioxane (4.0 mL) and stirred at 80 °C for 12 h. The crude product was purified using flash-column chromatography (silica gel, 2% diethyl ether in hexanes) to give the title compound as a clear, colorless oil (0.199 g, 85%). R_f = 0.28 (2% diethyl ether-hexanes; UV, DNP). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (d, *J* = 3.3 Hz, 2H, Ar**H**), 7.51 (d, *J* = 8.1 Hz, 2H, Ar**H**), 7.18 (d, *J* = 7.9 Hz, 2H, Ar**H**), 3.17 (dd, *J* = 3.3 Hz, 9.5 Hz, 1H, C**H**CHO), 2.43 (m, 1H, $(CH_3)_2C\mathbf{H}$), 1.04 (d, *J* = 6.6 Hz, 3H, $(C\mathbf{H}_3)_2CH$), 0.78 (d, *J* = 6.7 Hz, 3H, $(C\mathbf{H}_3)_2CH$), 0.27 (s, 9H, $ArSi(C\mathbf{H}_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 139.6, 135.9, 133.9, 128.7, 66.8, 28.7, 21.2, 20.1, -1.2. Anal. Calcd. for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46. Found: C, 71.74; H, 9.74.

References

[1] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923-2925.
[2] N. Kataoka, Q. Shelby, J. P. Stambuli, J. F. Hartwig, *J. Org. Chem.* **2002**, *67*, 5553-5566.
[3] P. R. Auburn, P. B. Mackenzie, B. Bosnich, *J. Am. Chem. Soc.* **1985**, *107*, 2033-2046.



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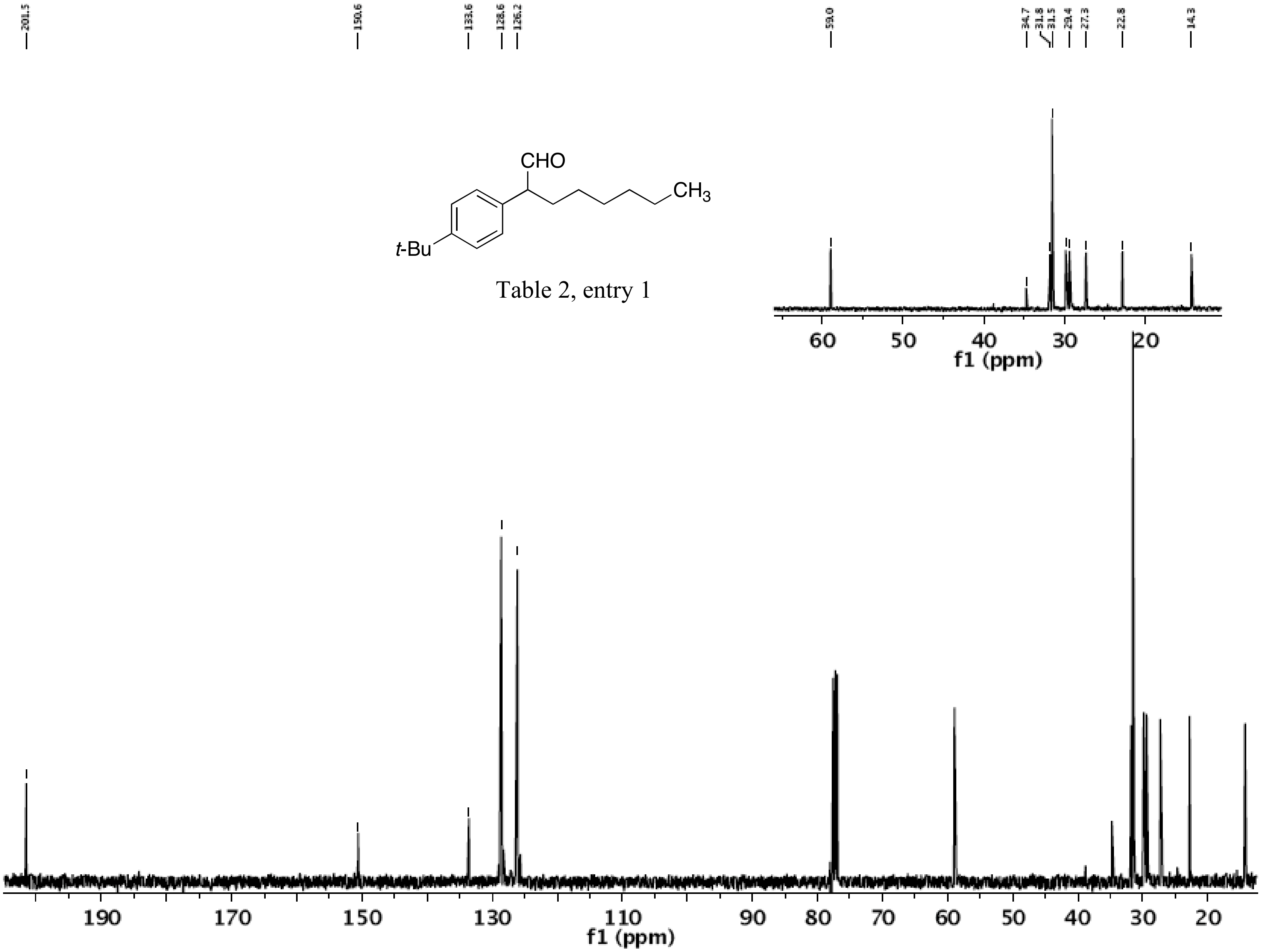

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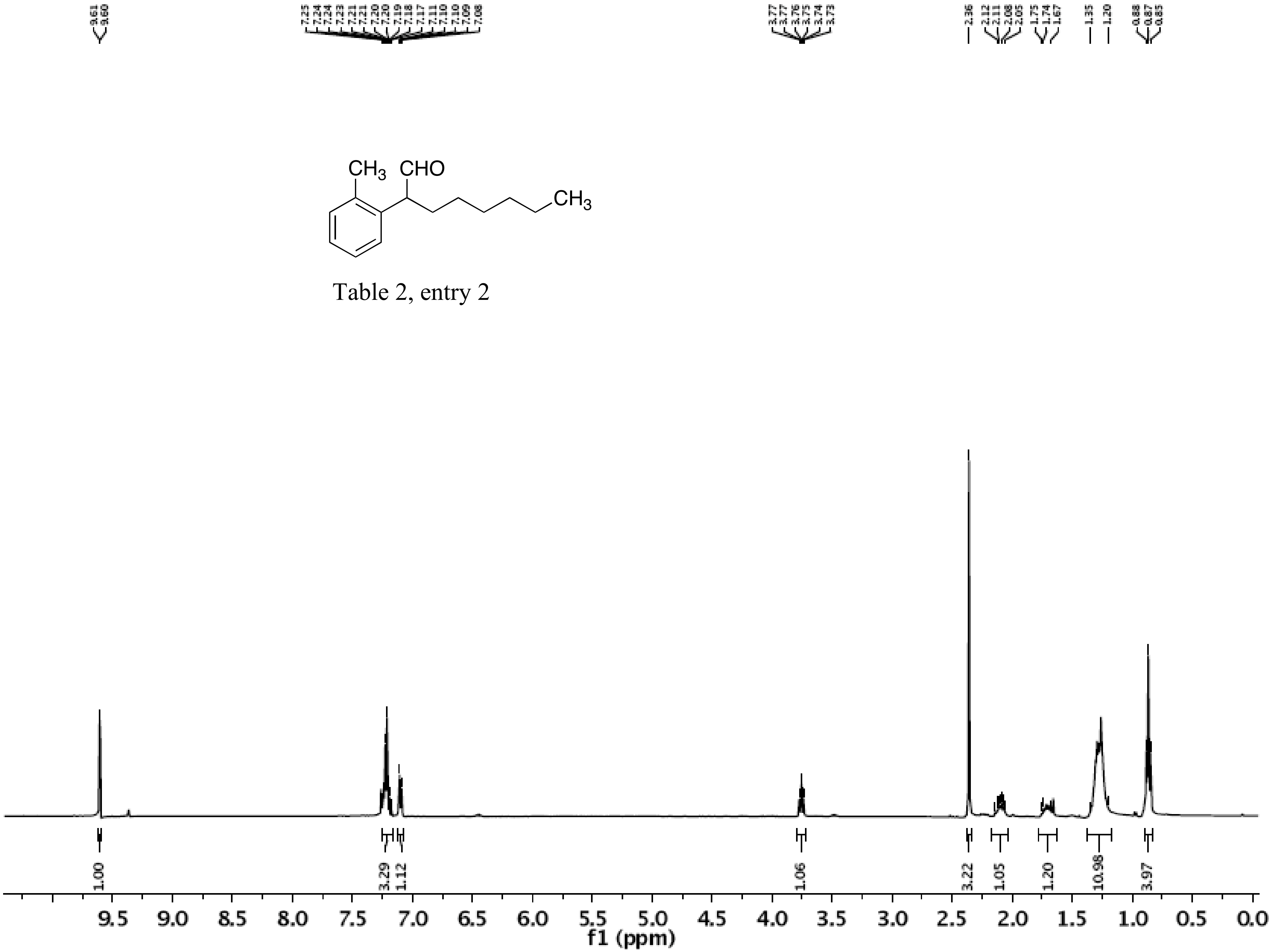

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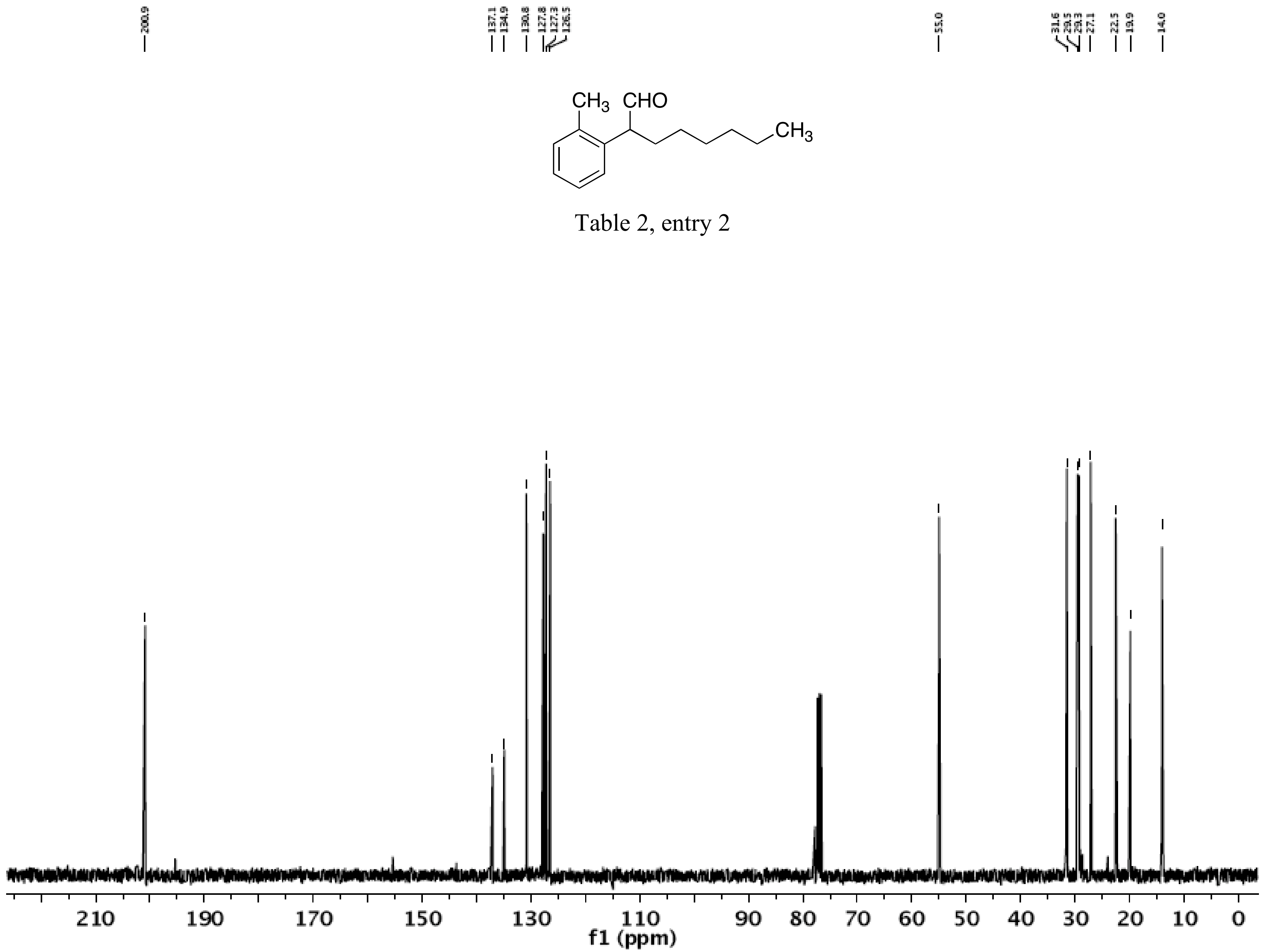

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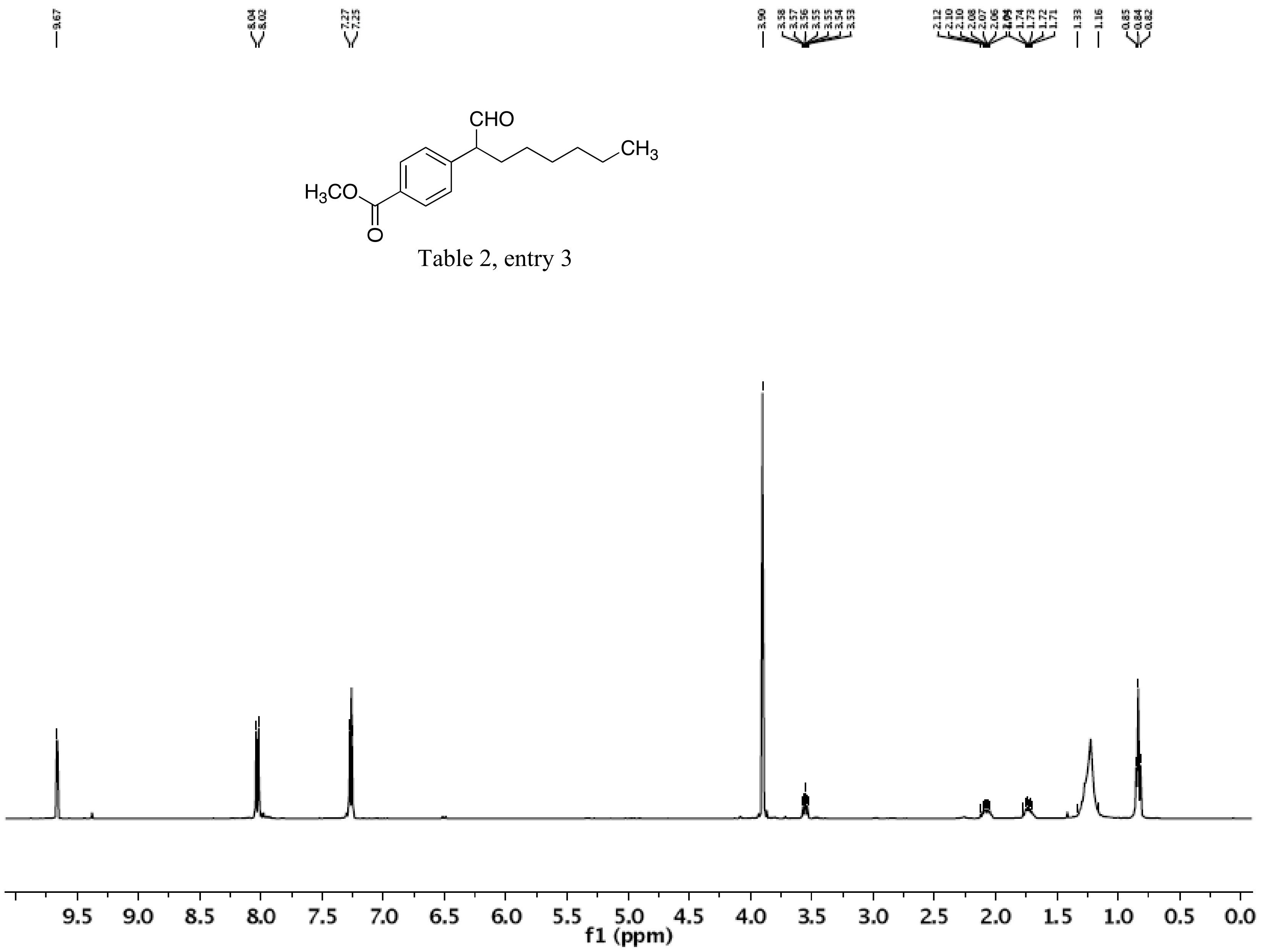

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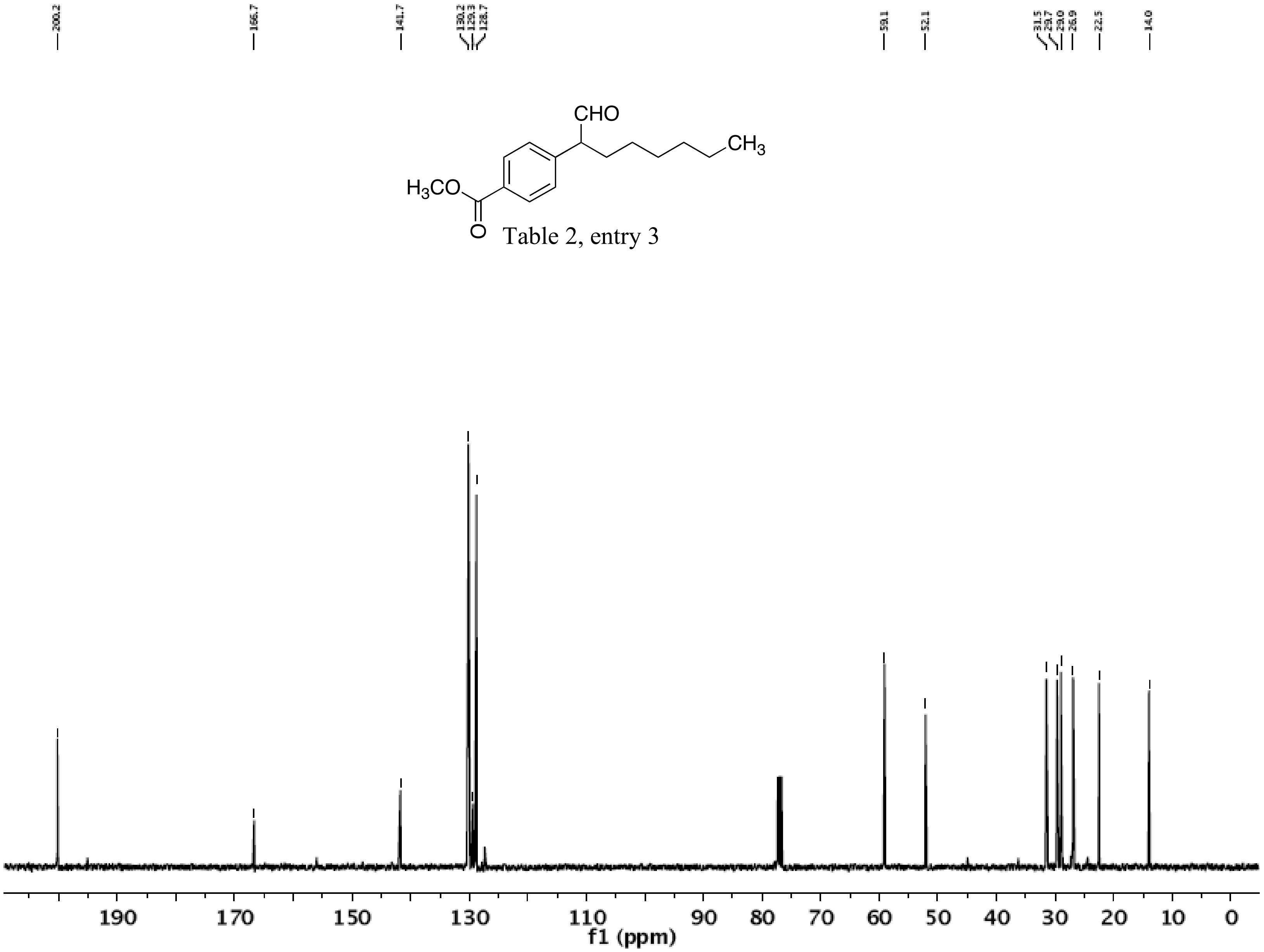
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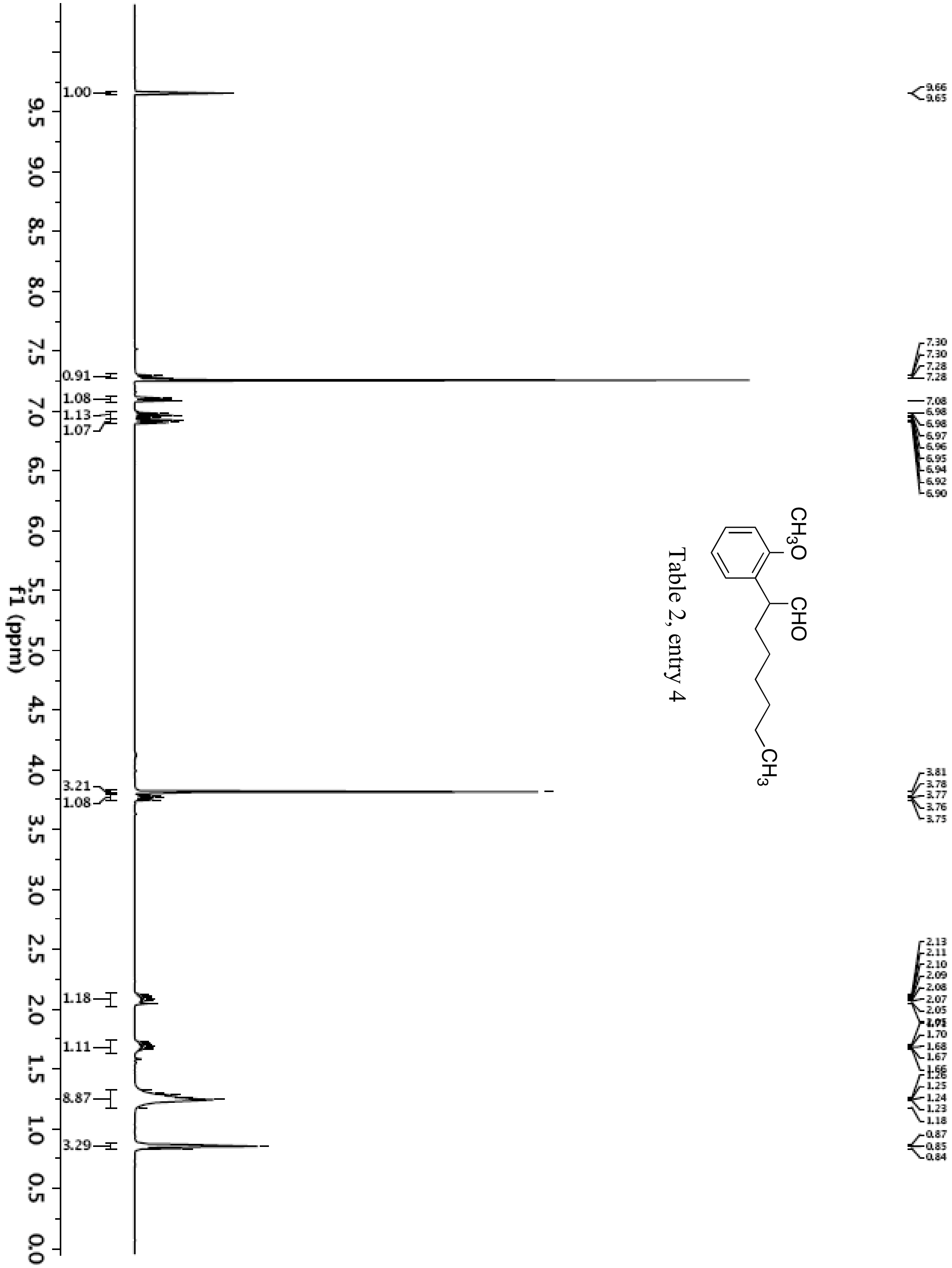

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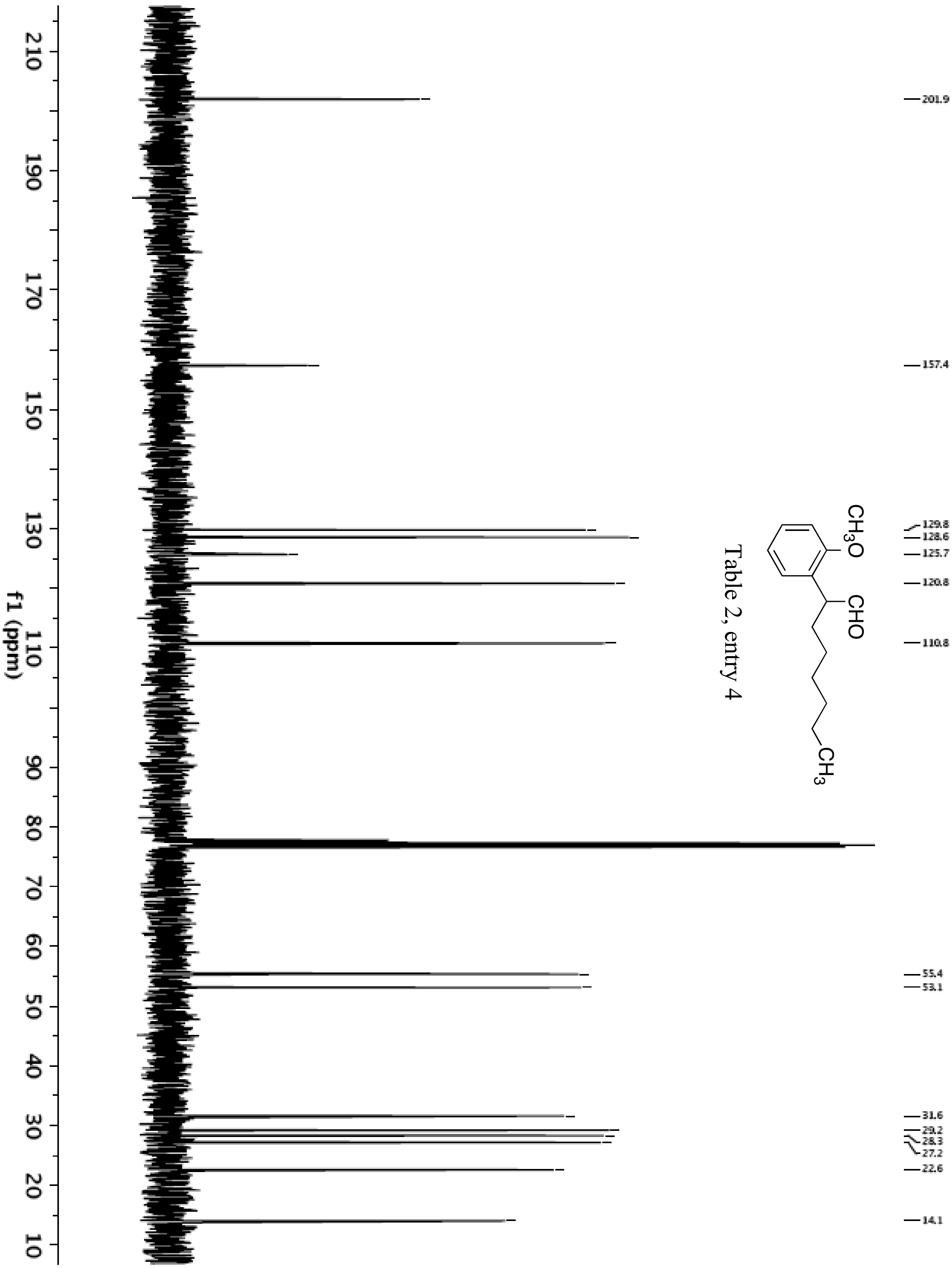

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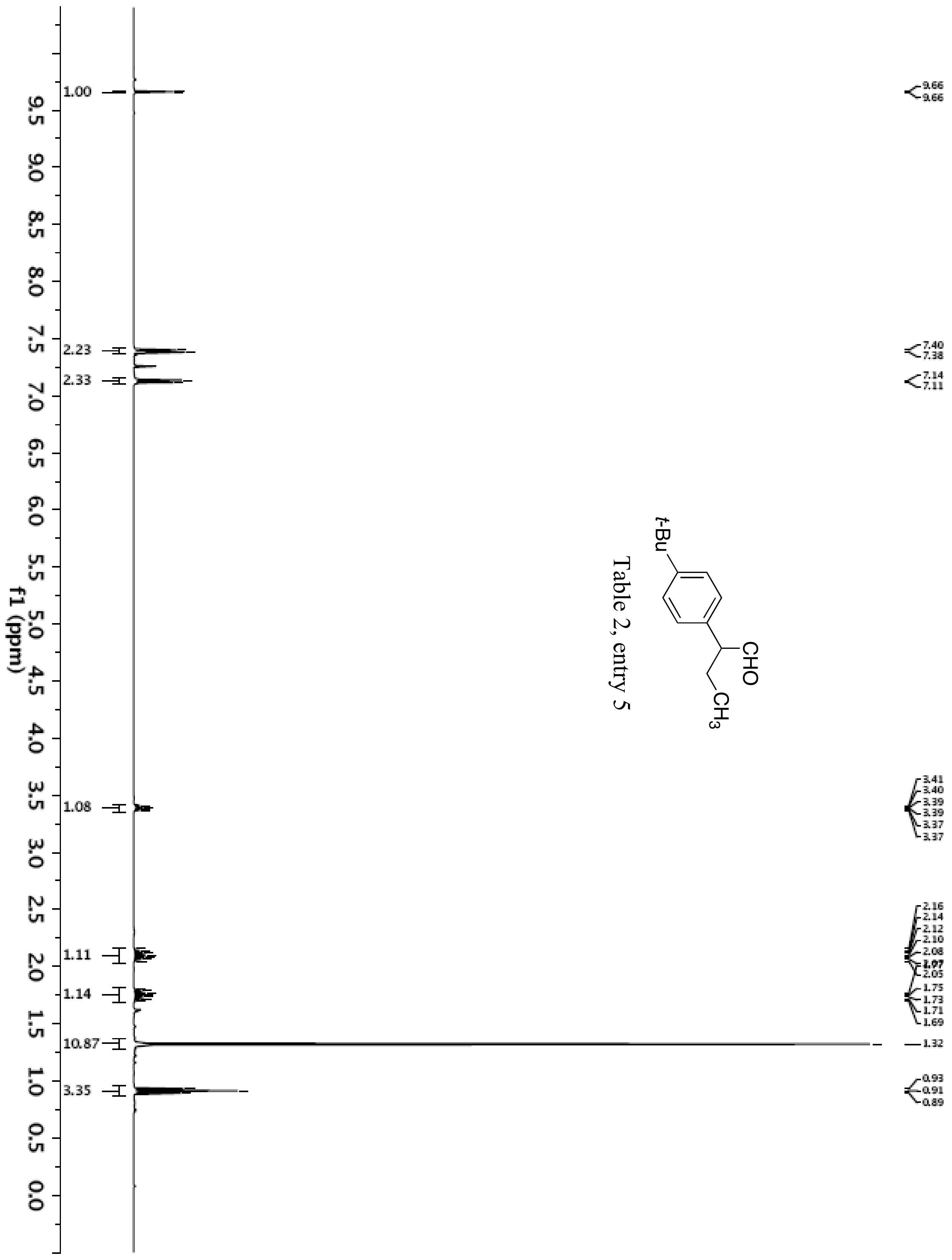

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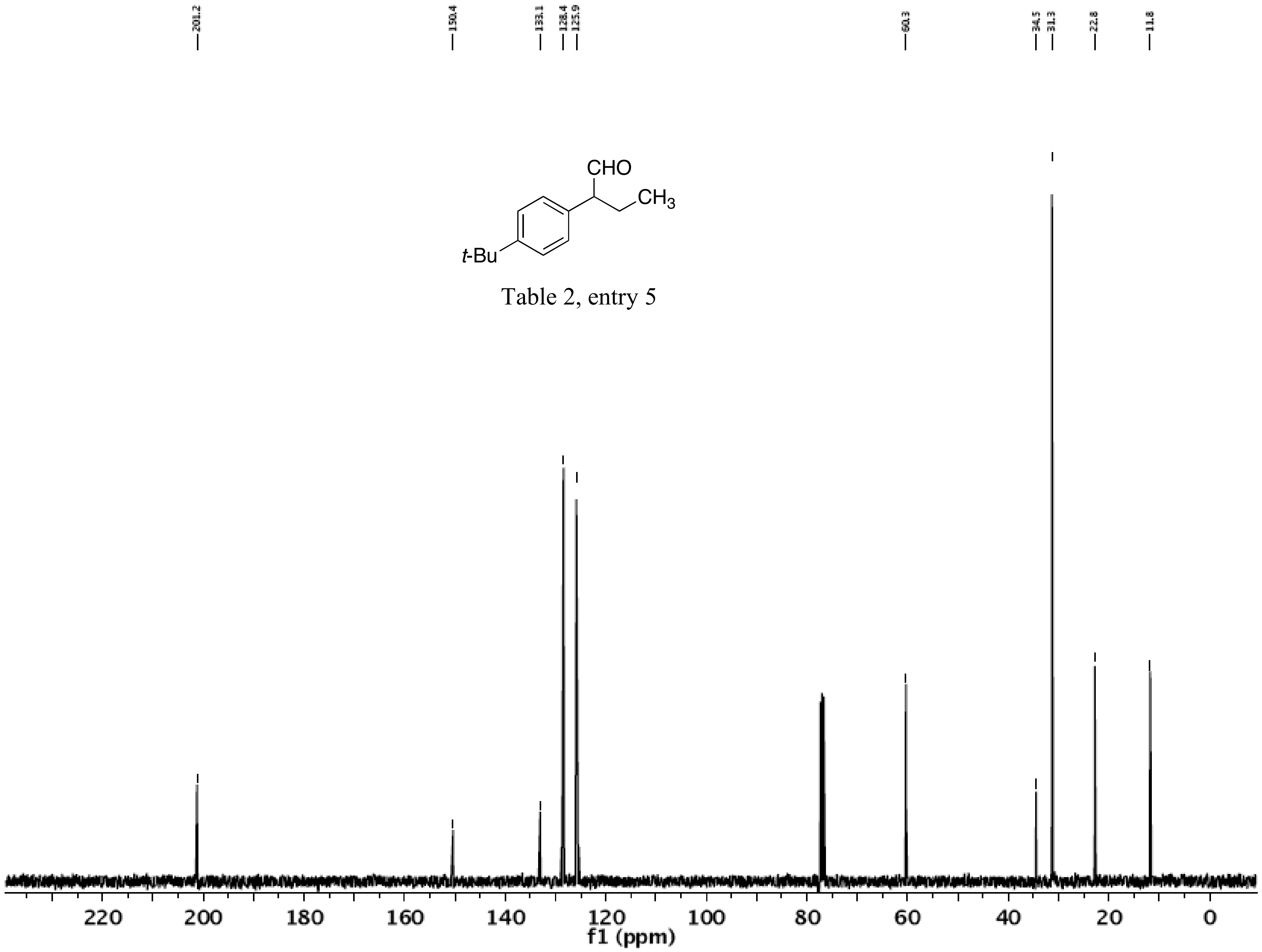

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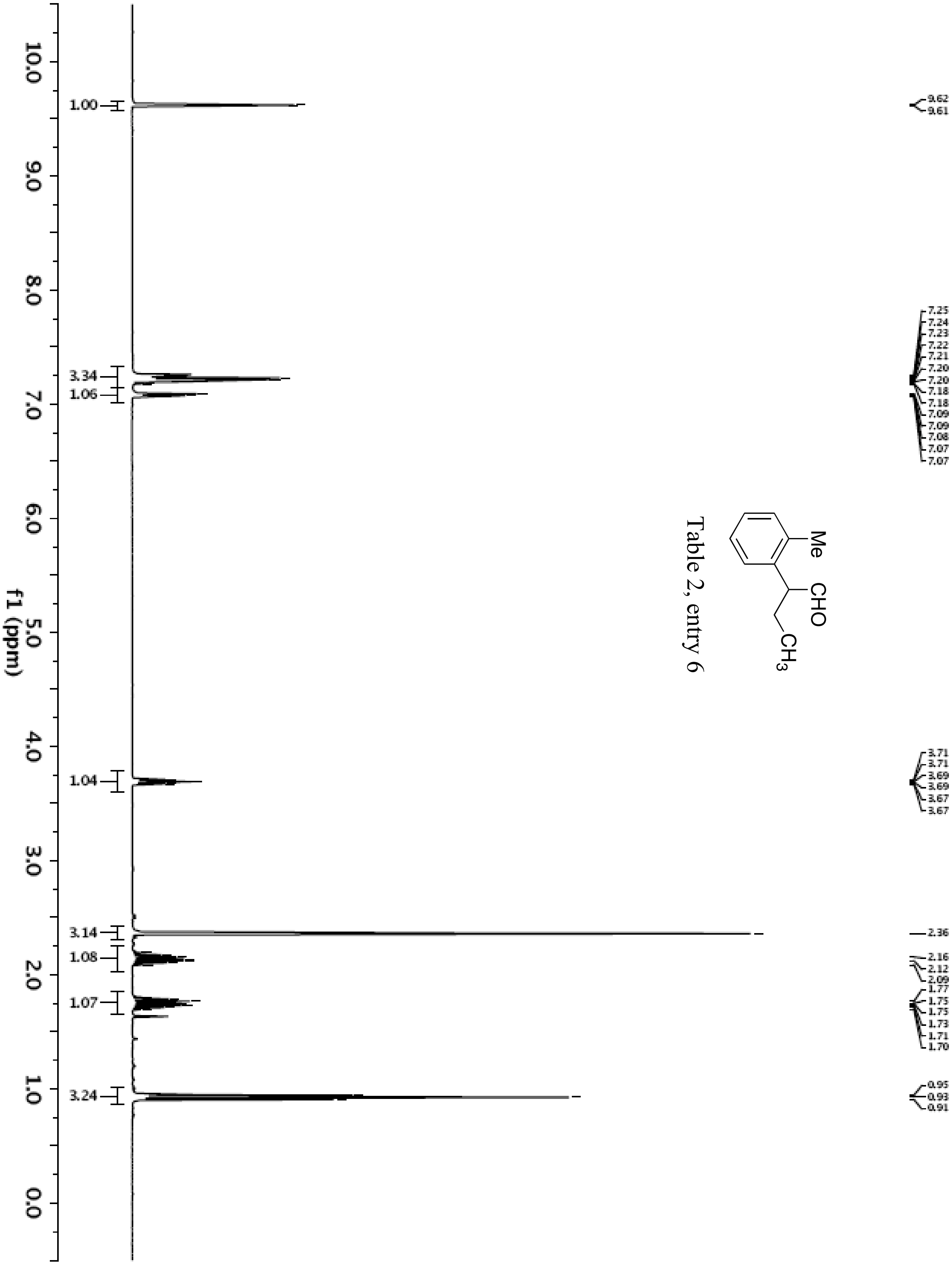

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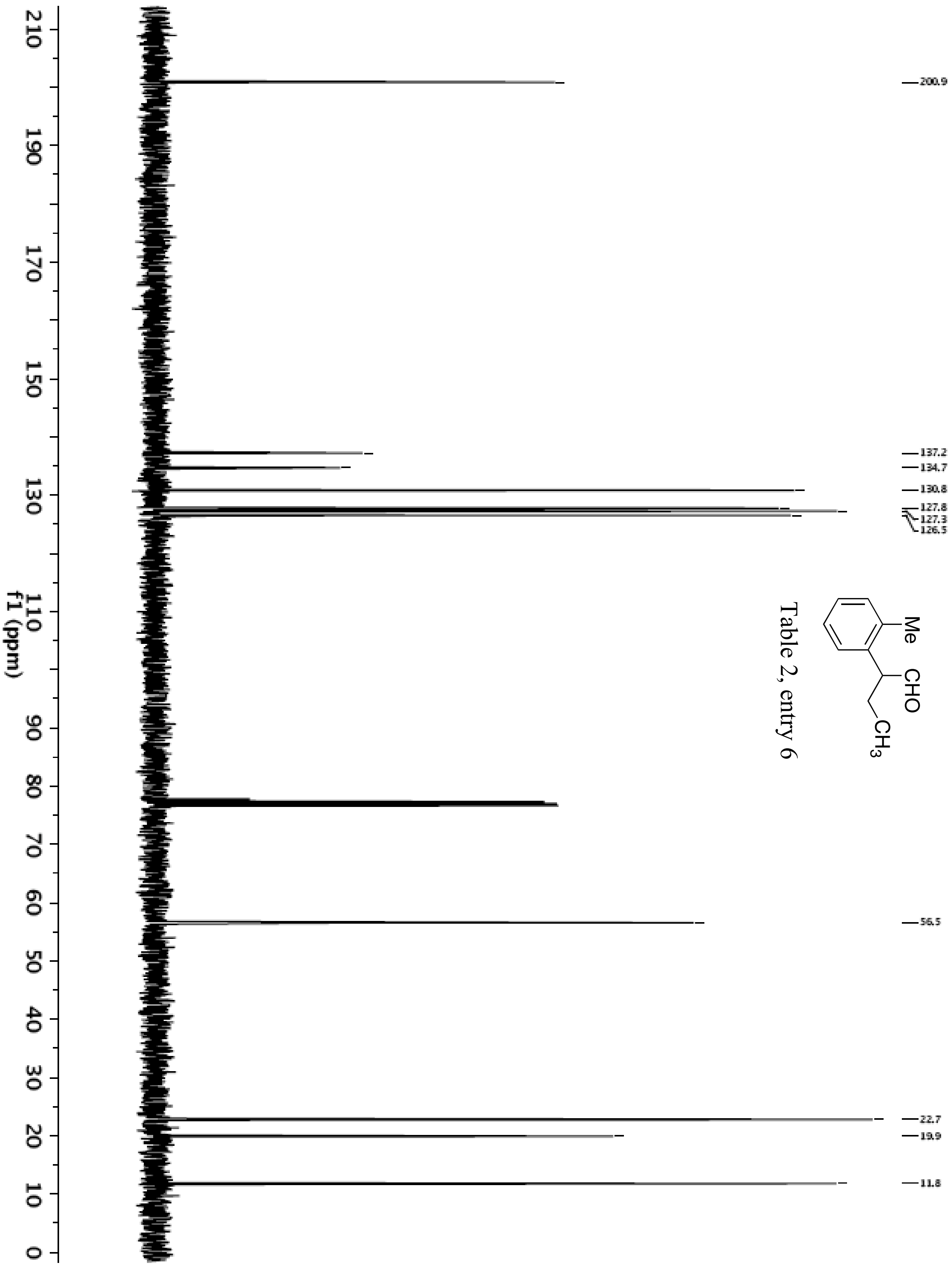

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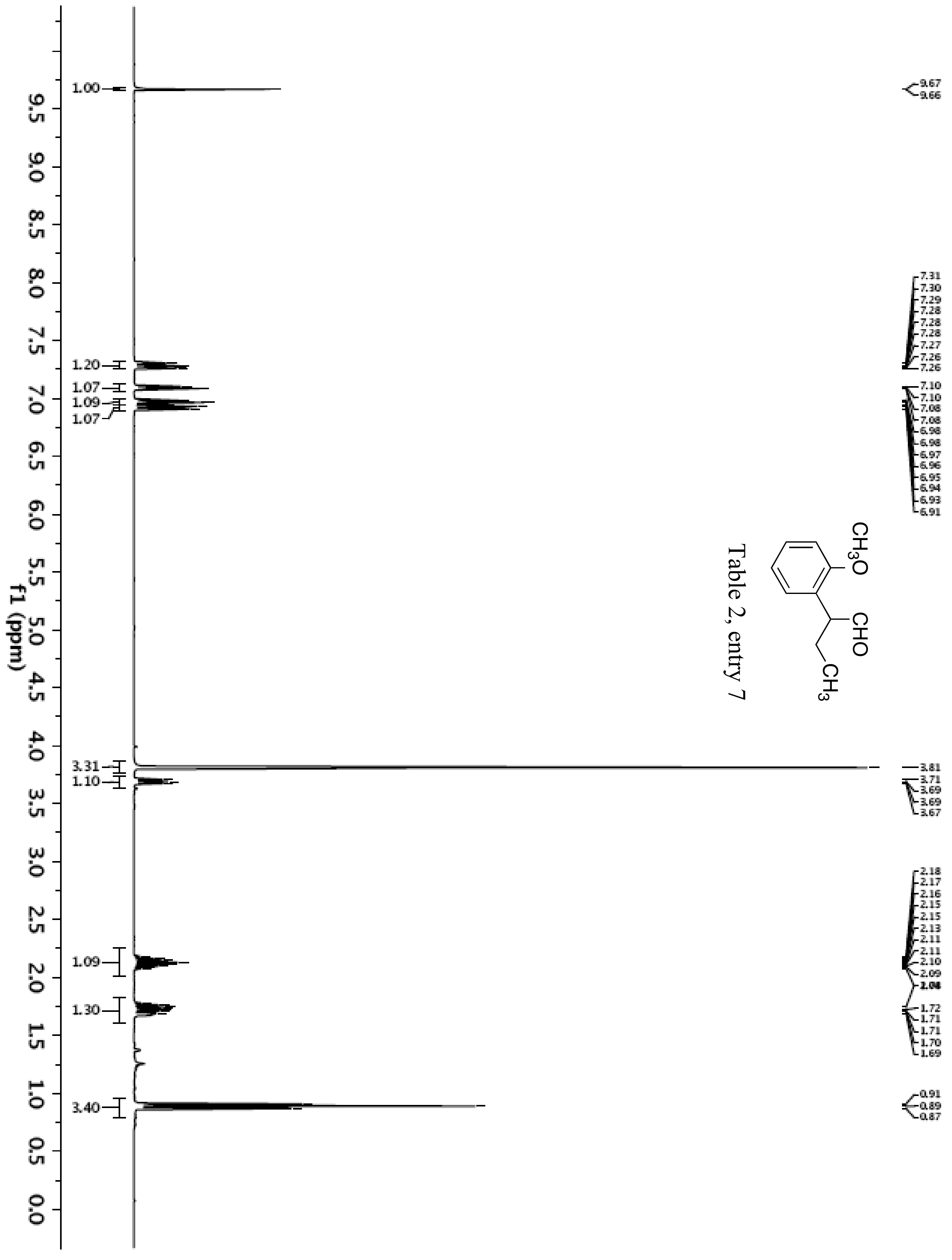

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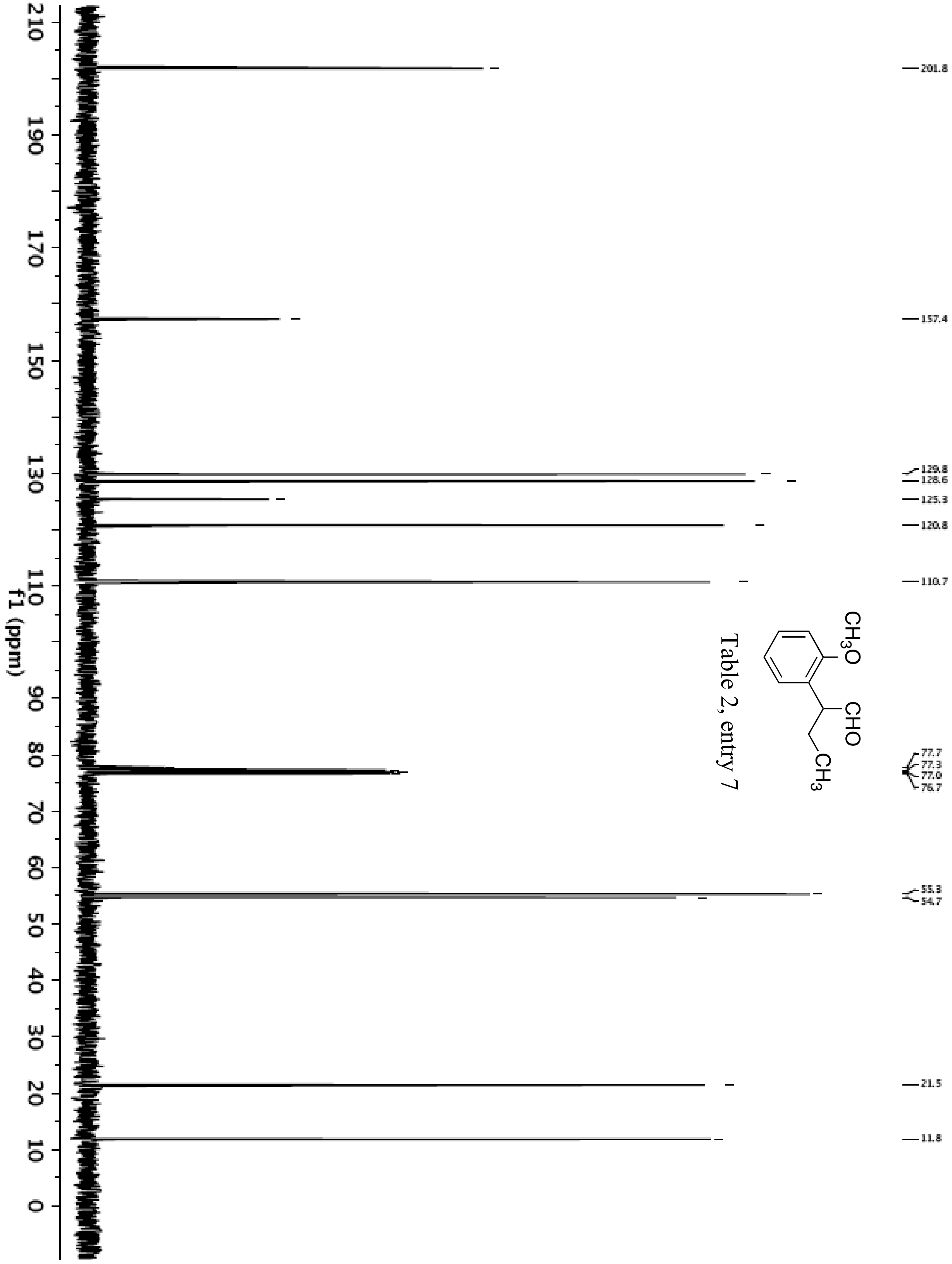

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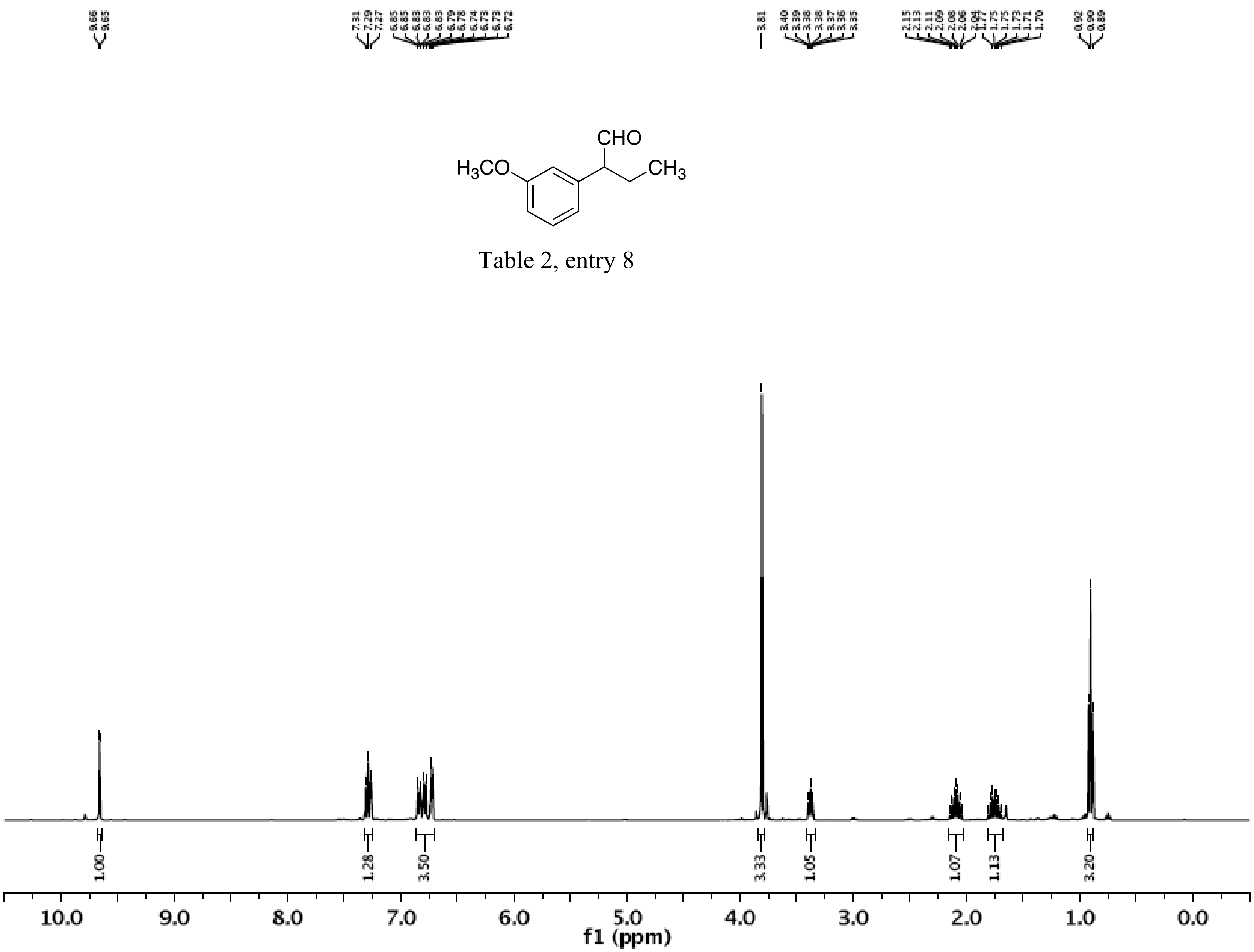

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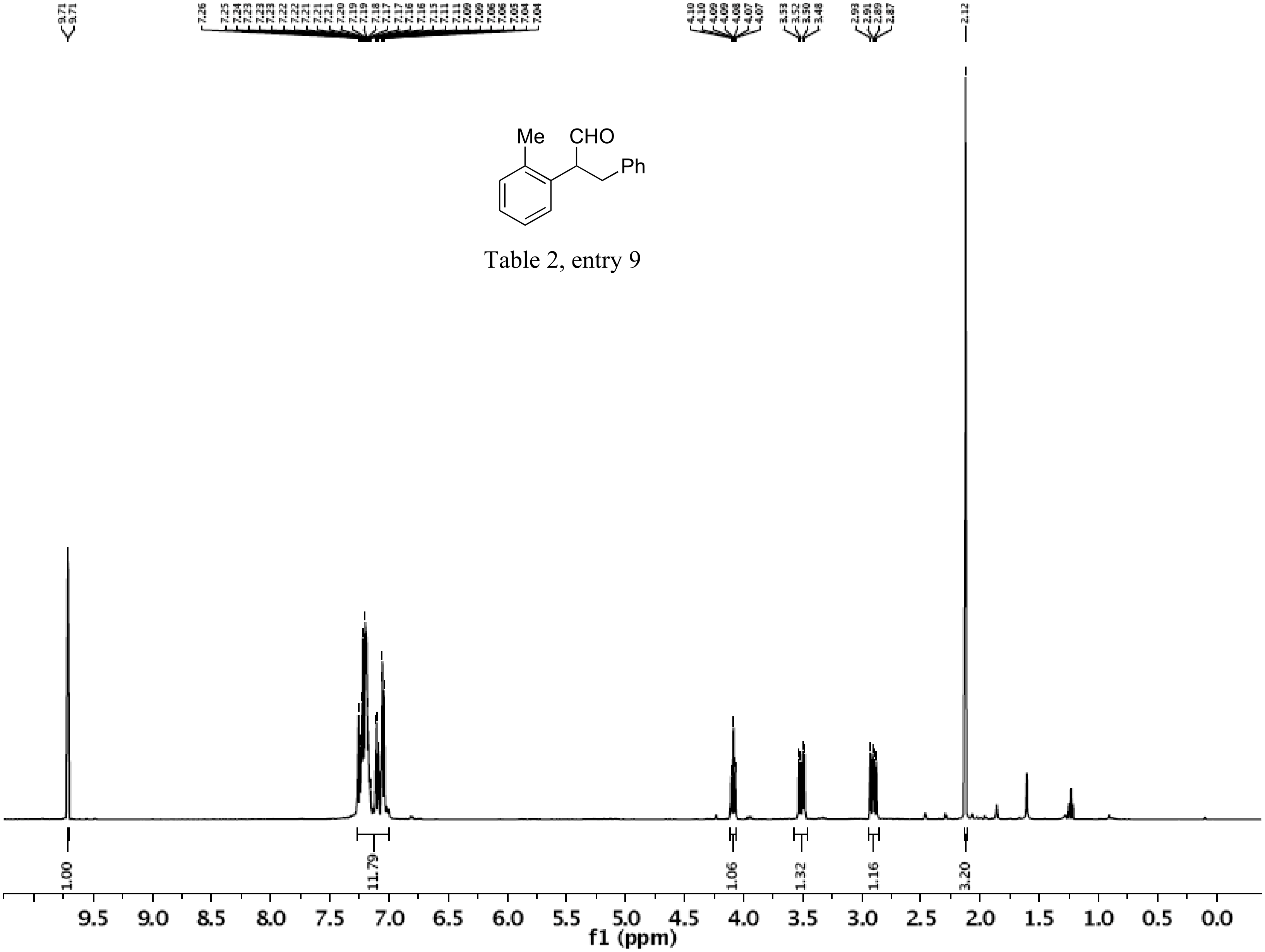

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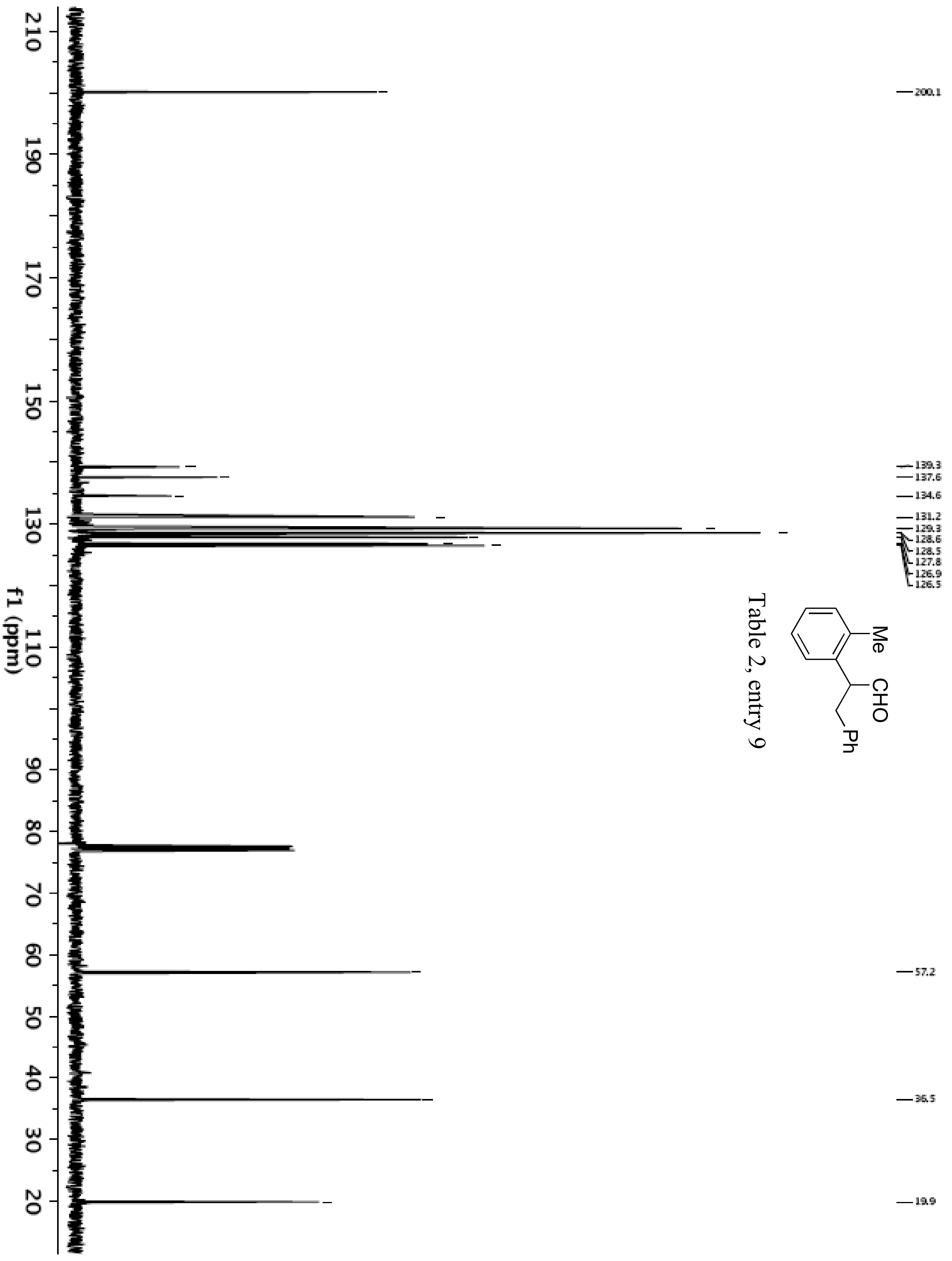

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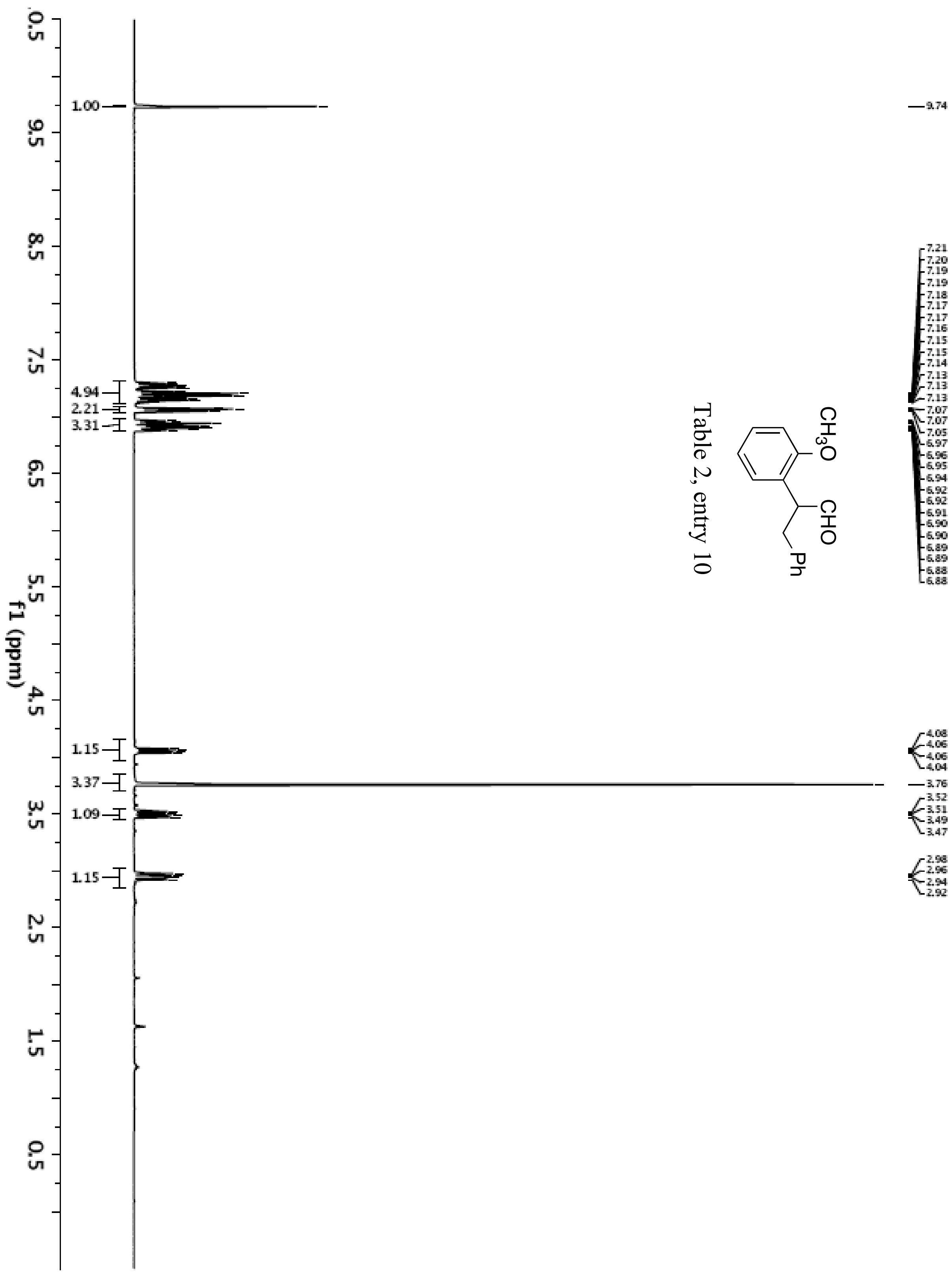

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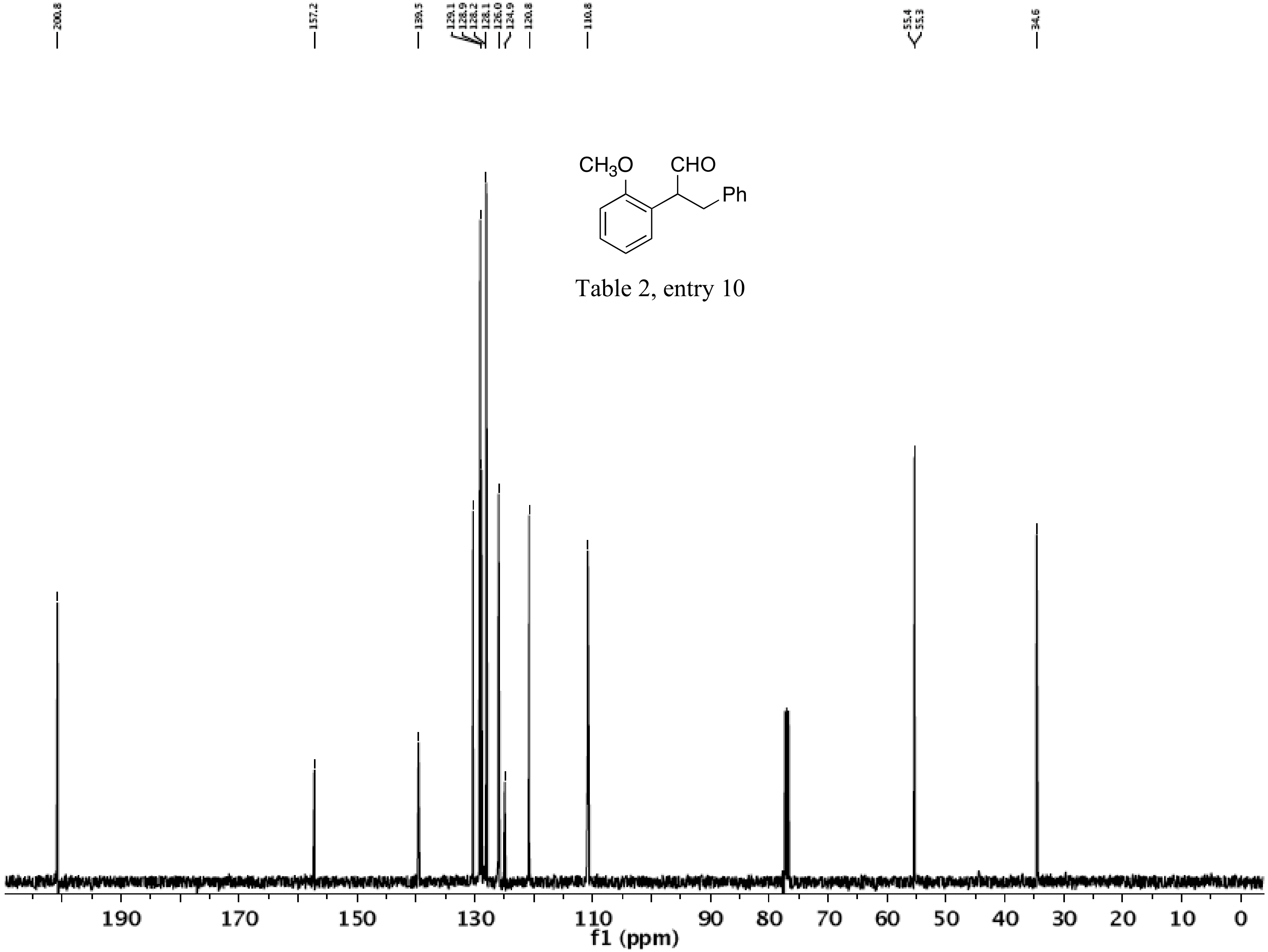

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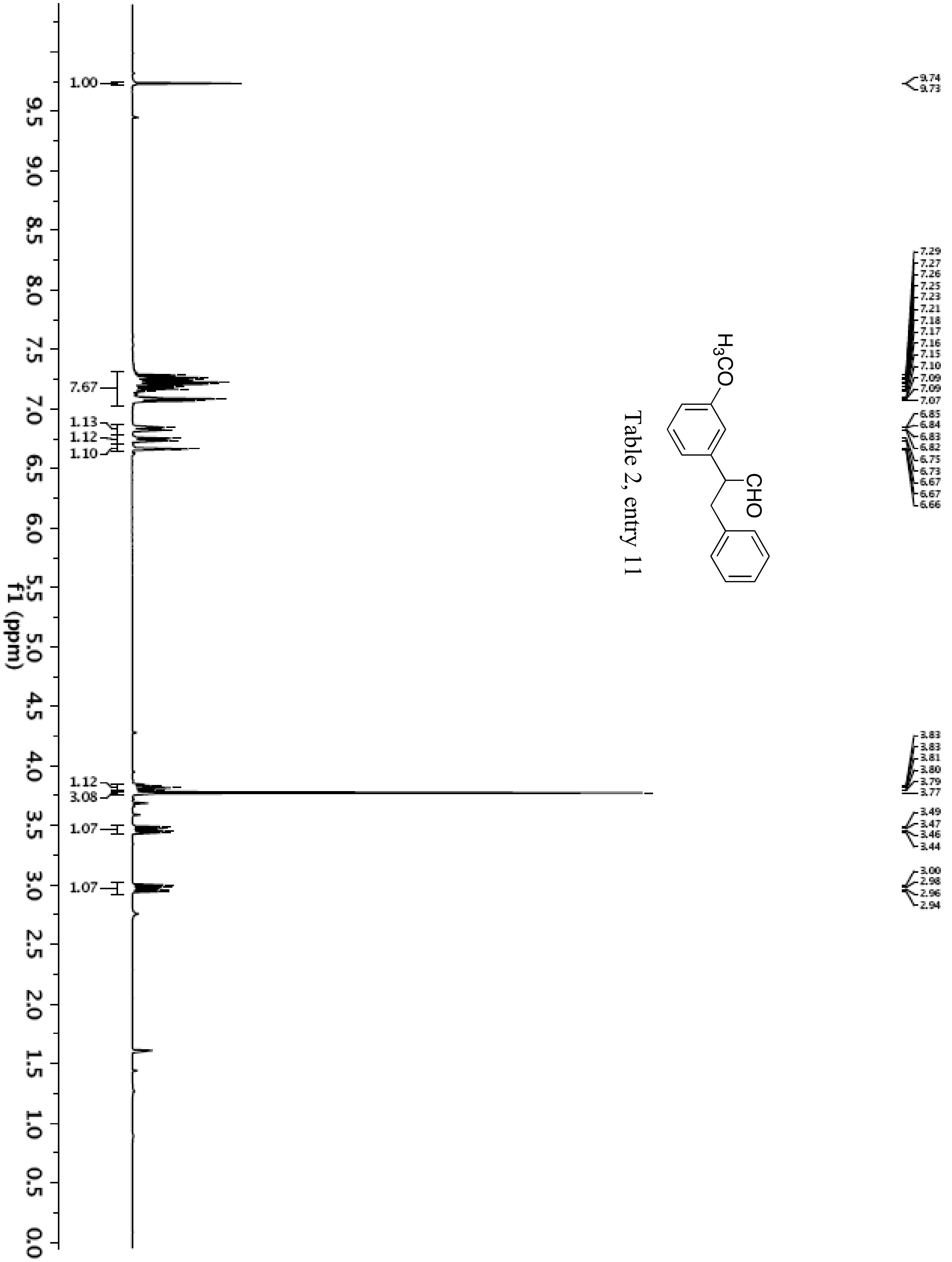

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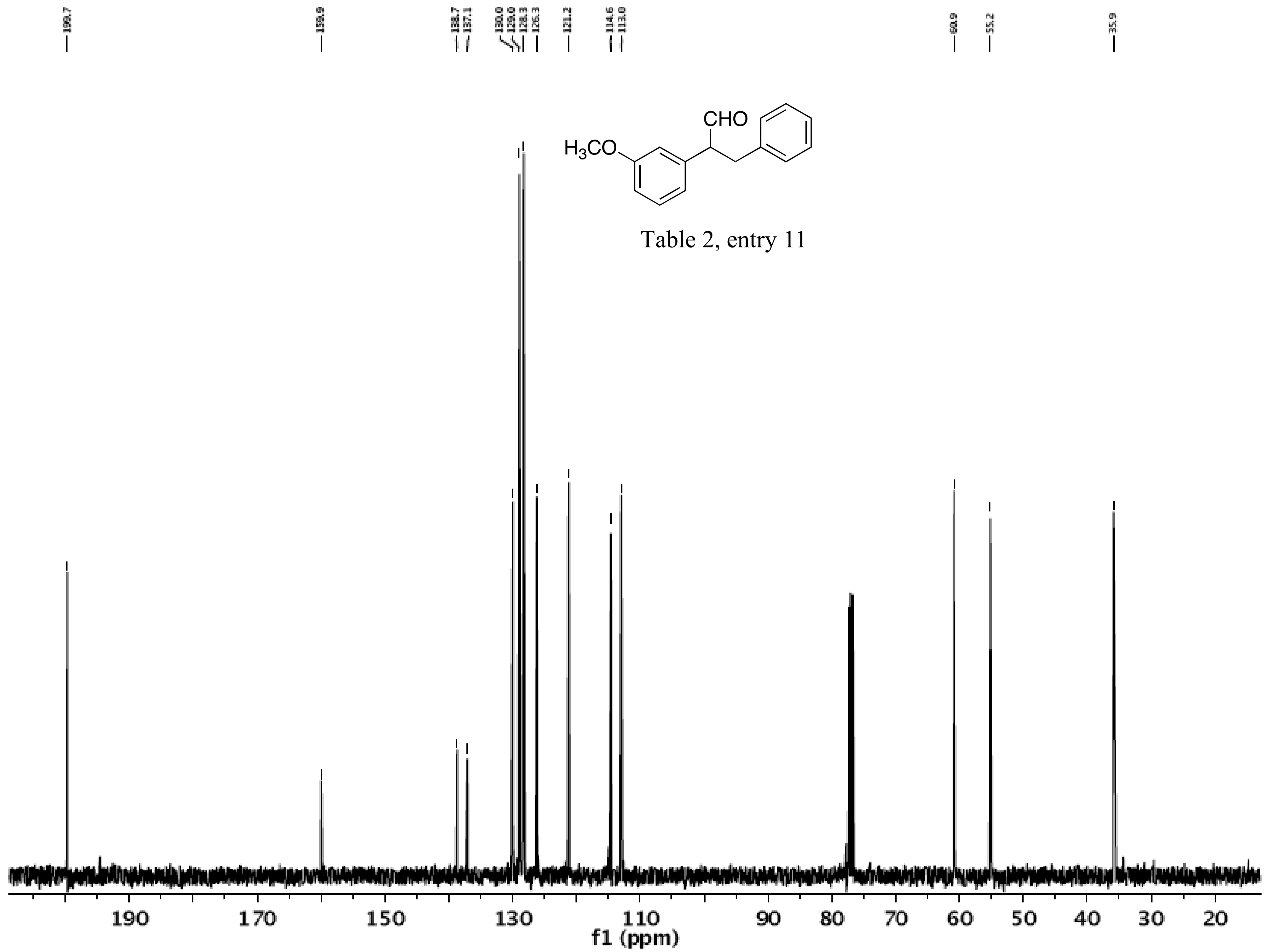

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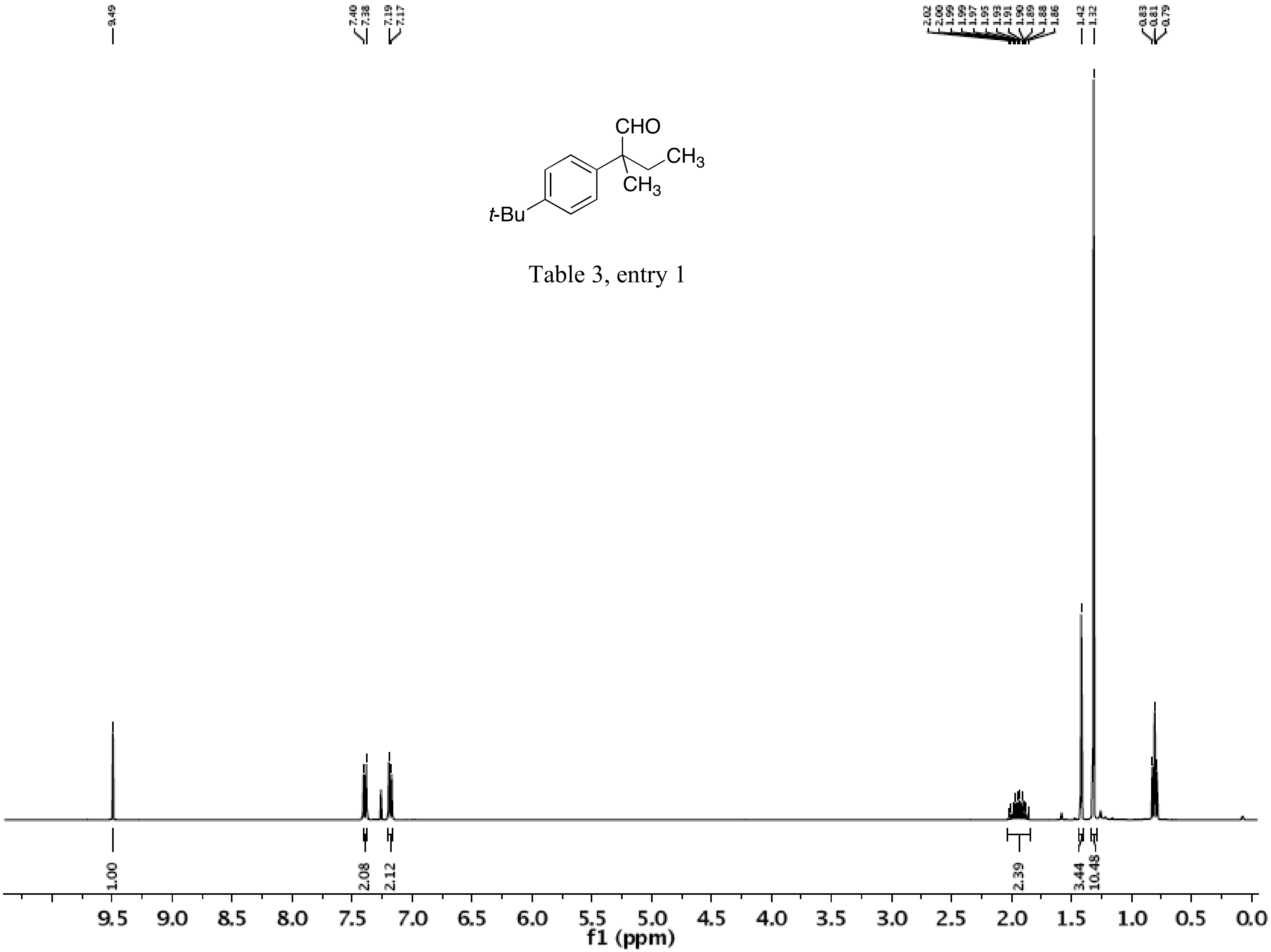

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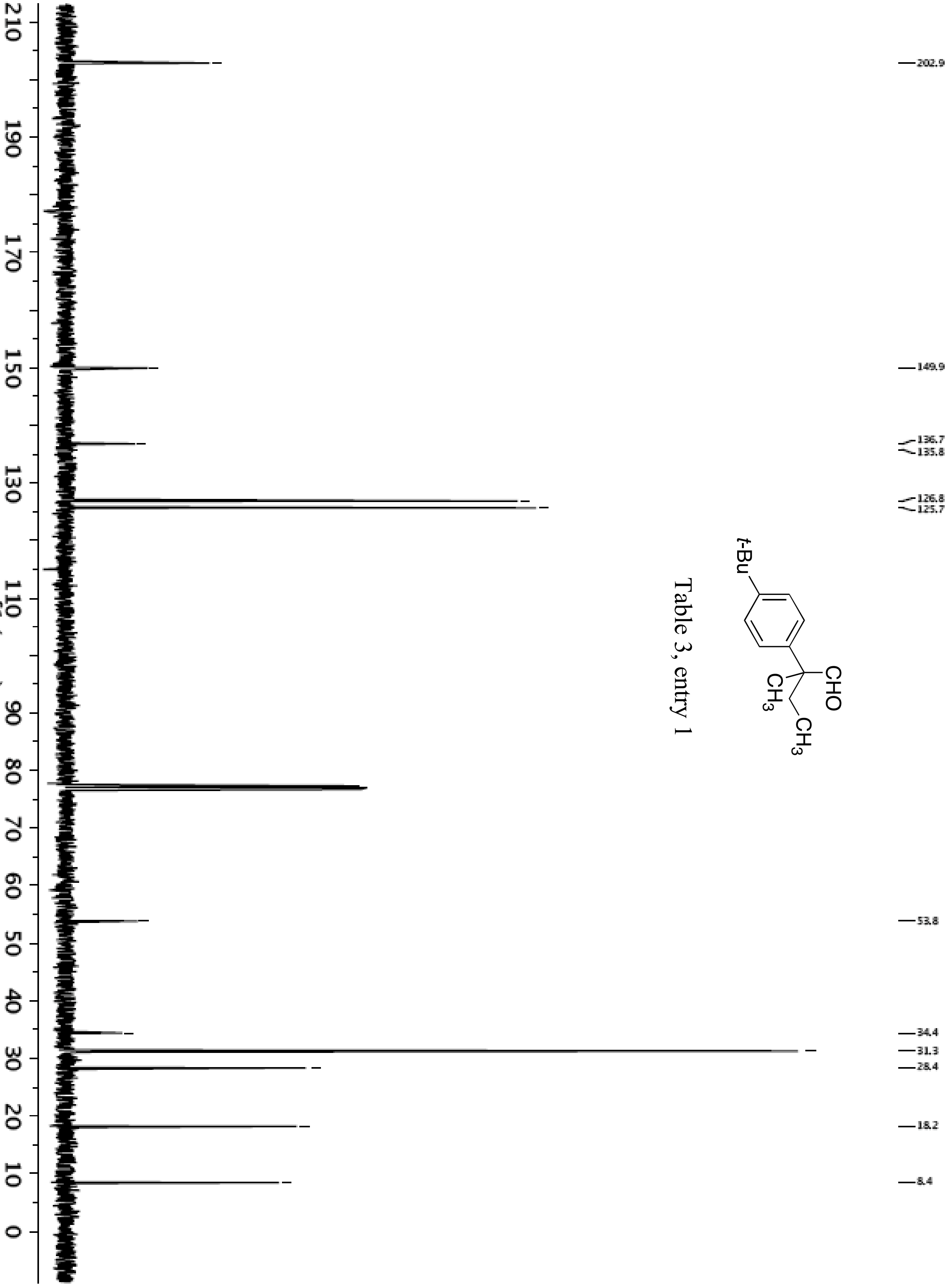

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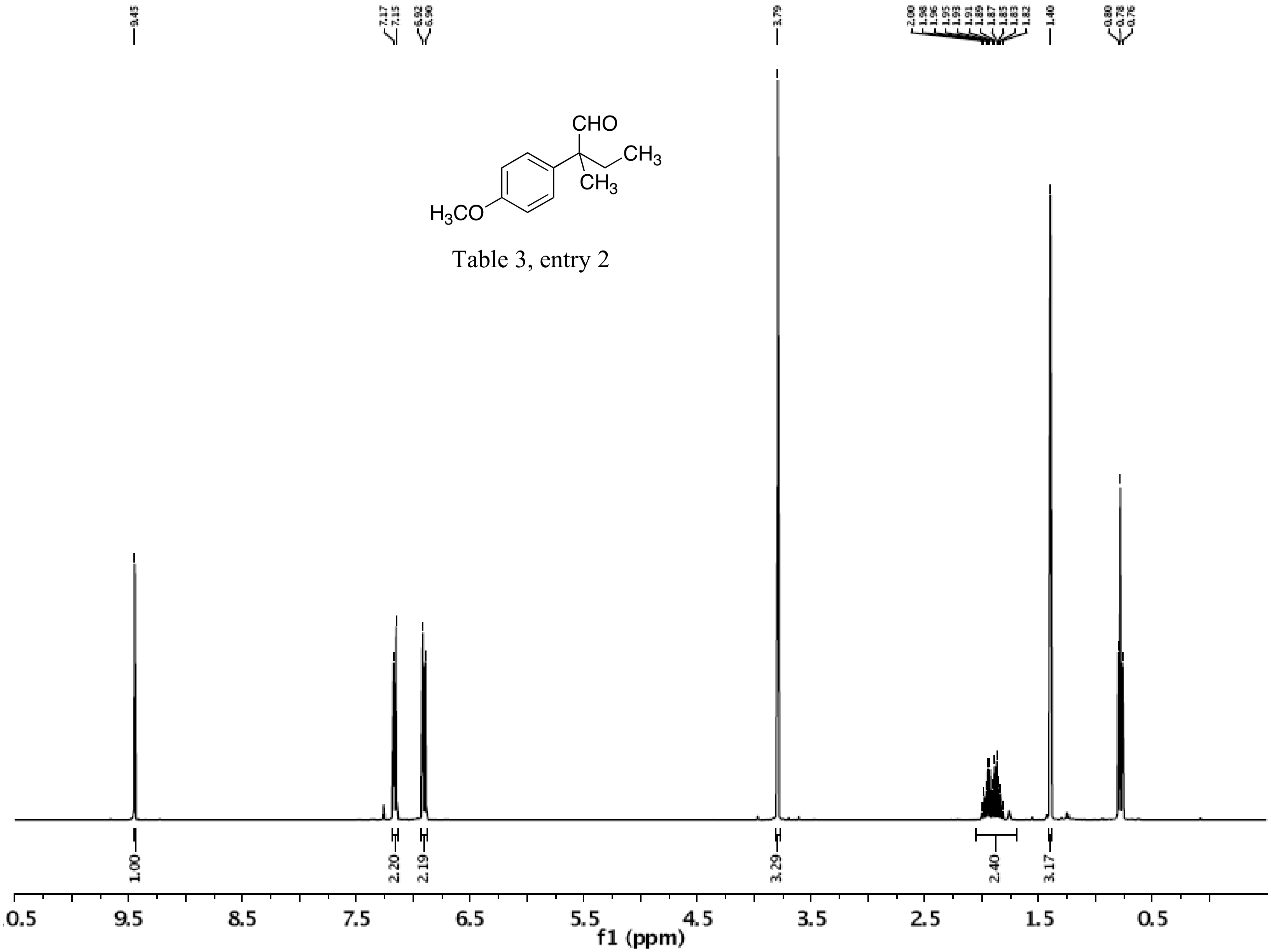

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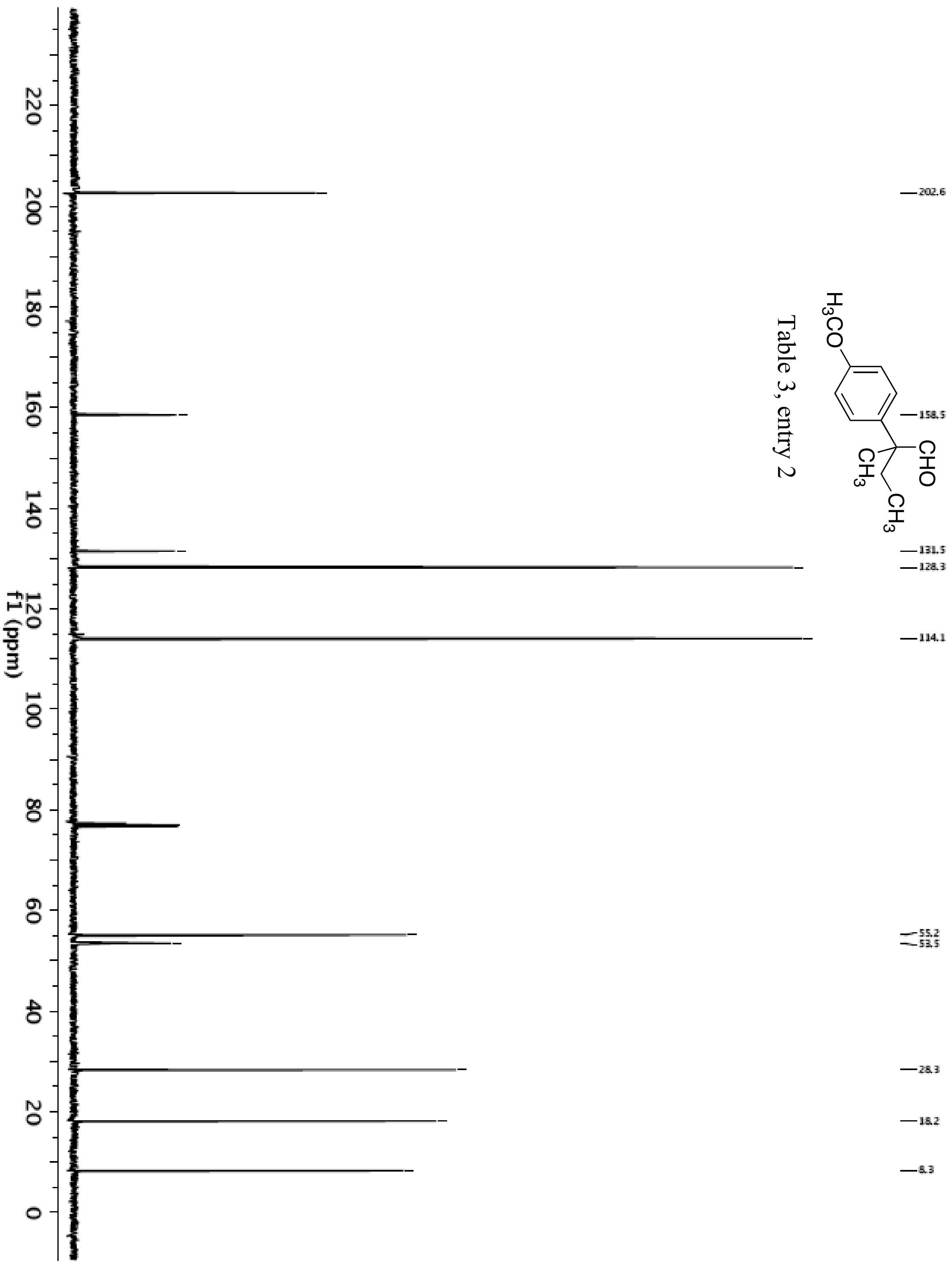
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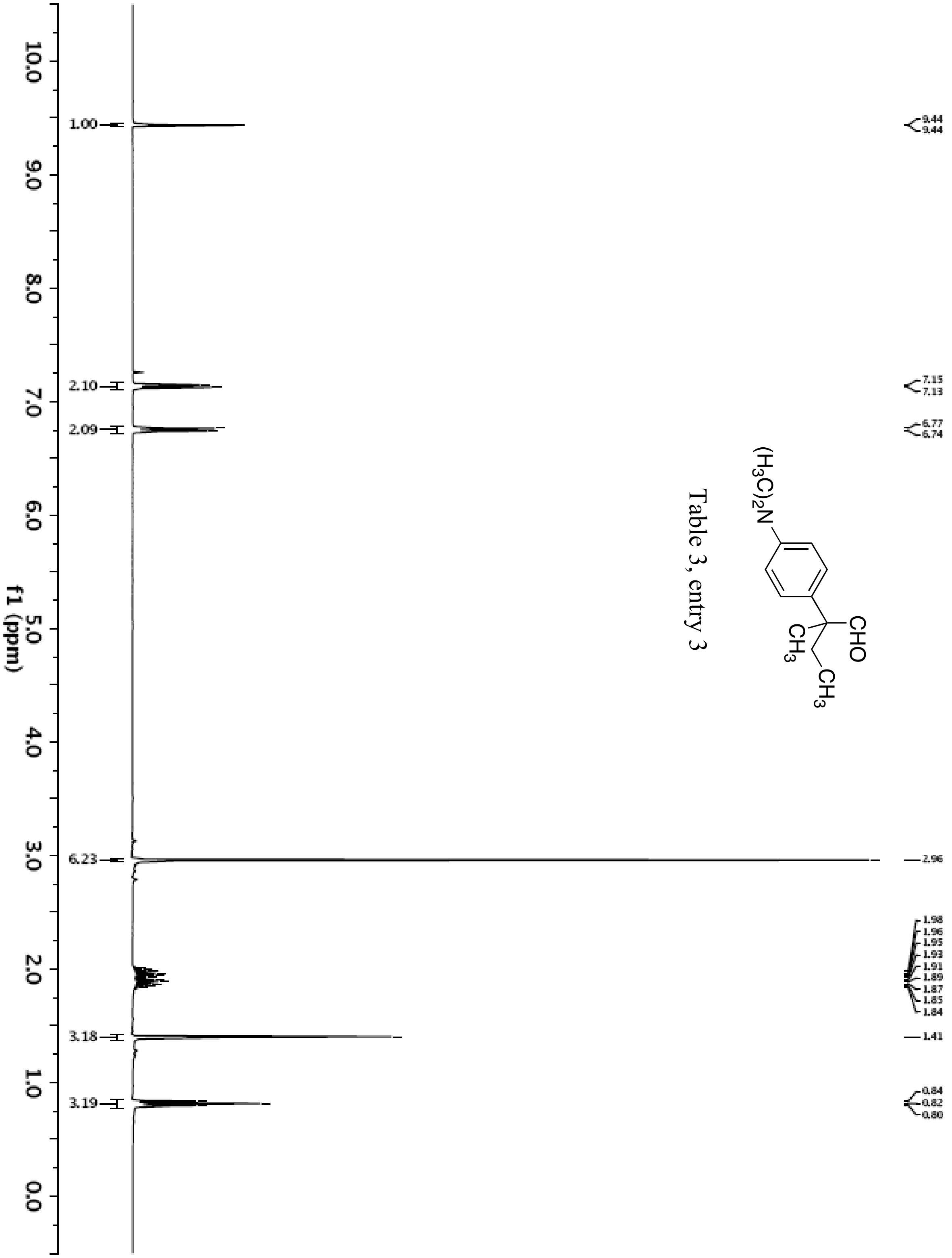

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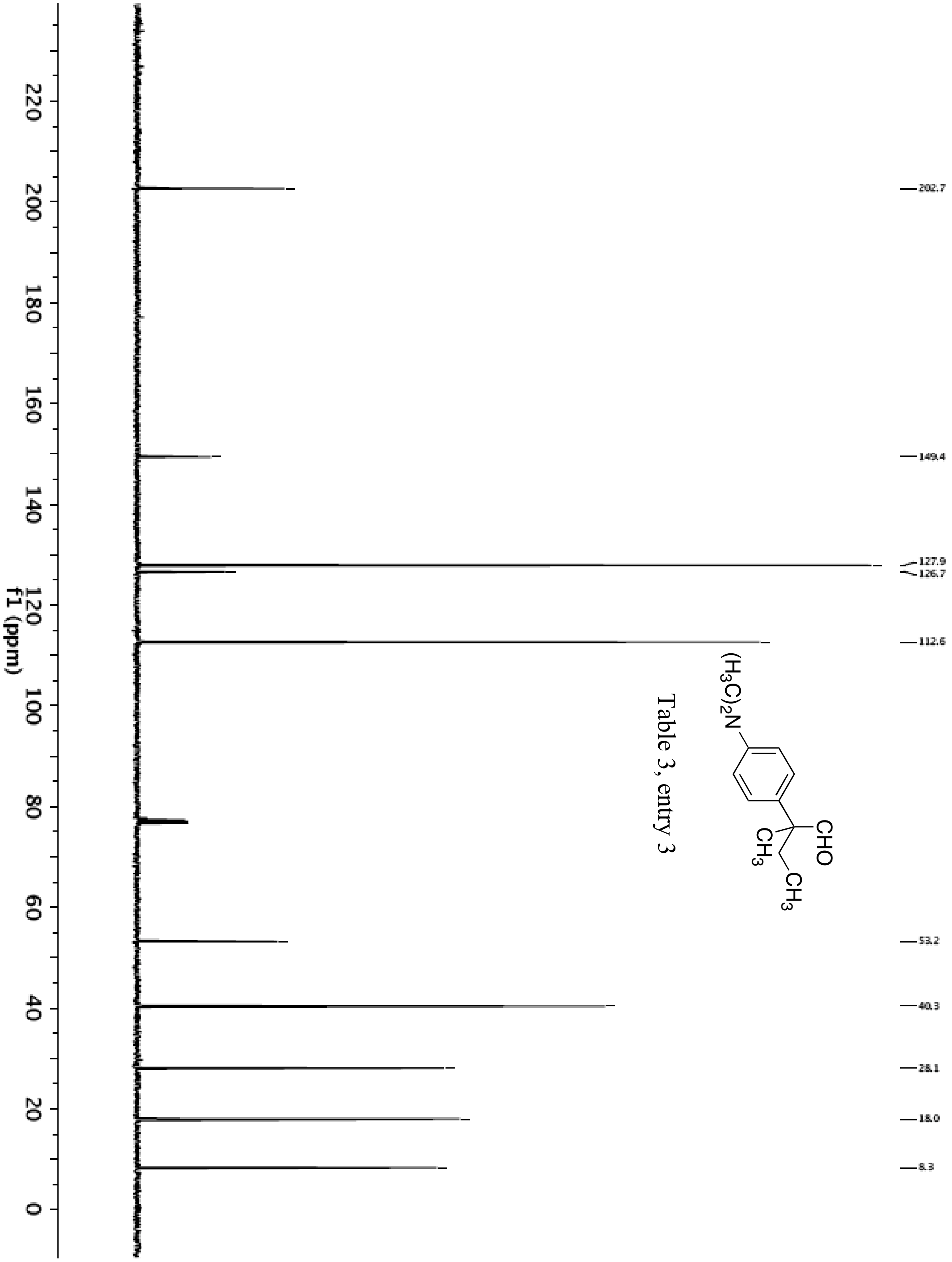

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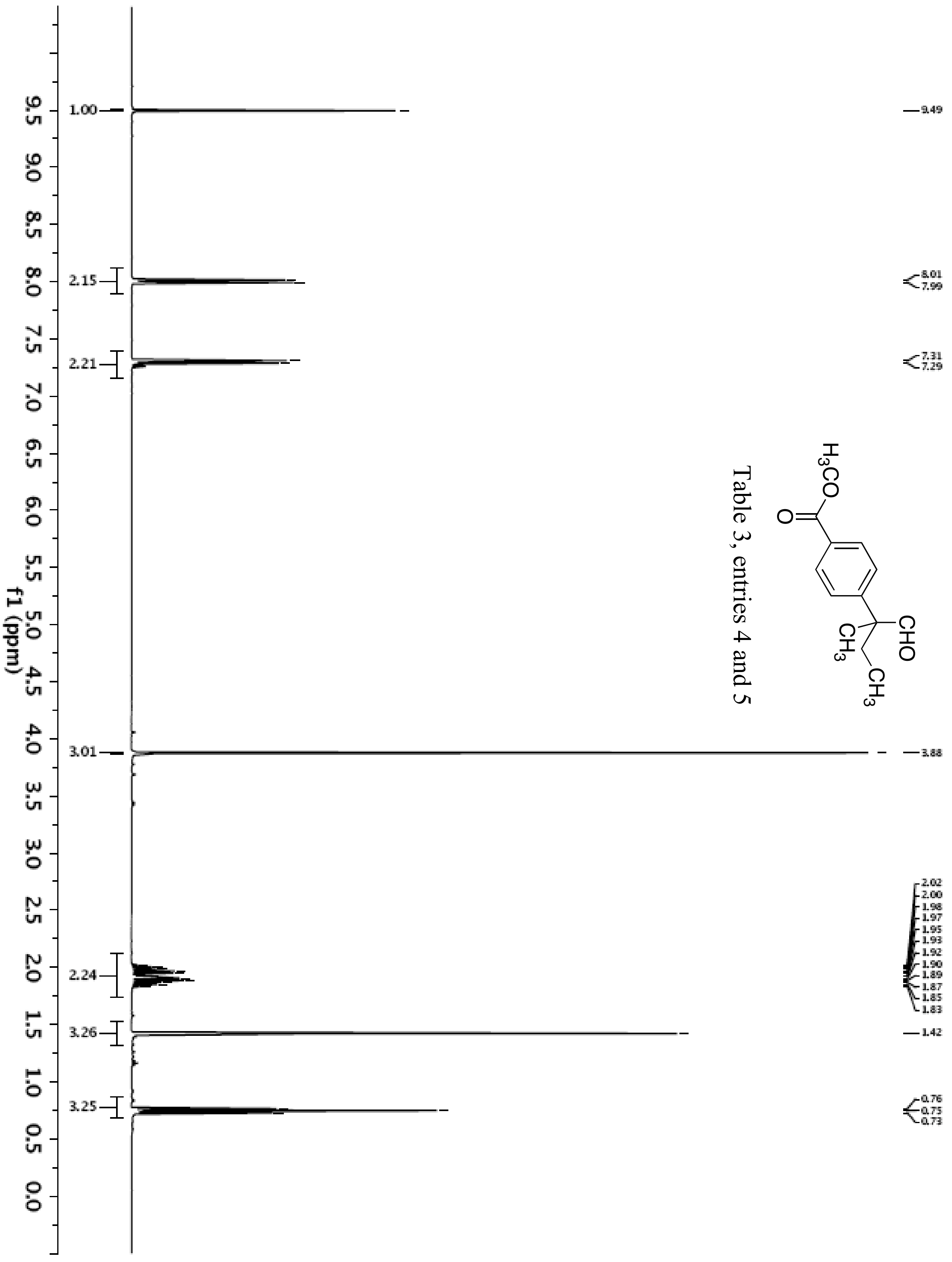
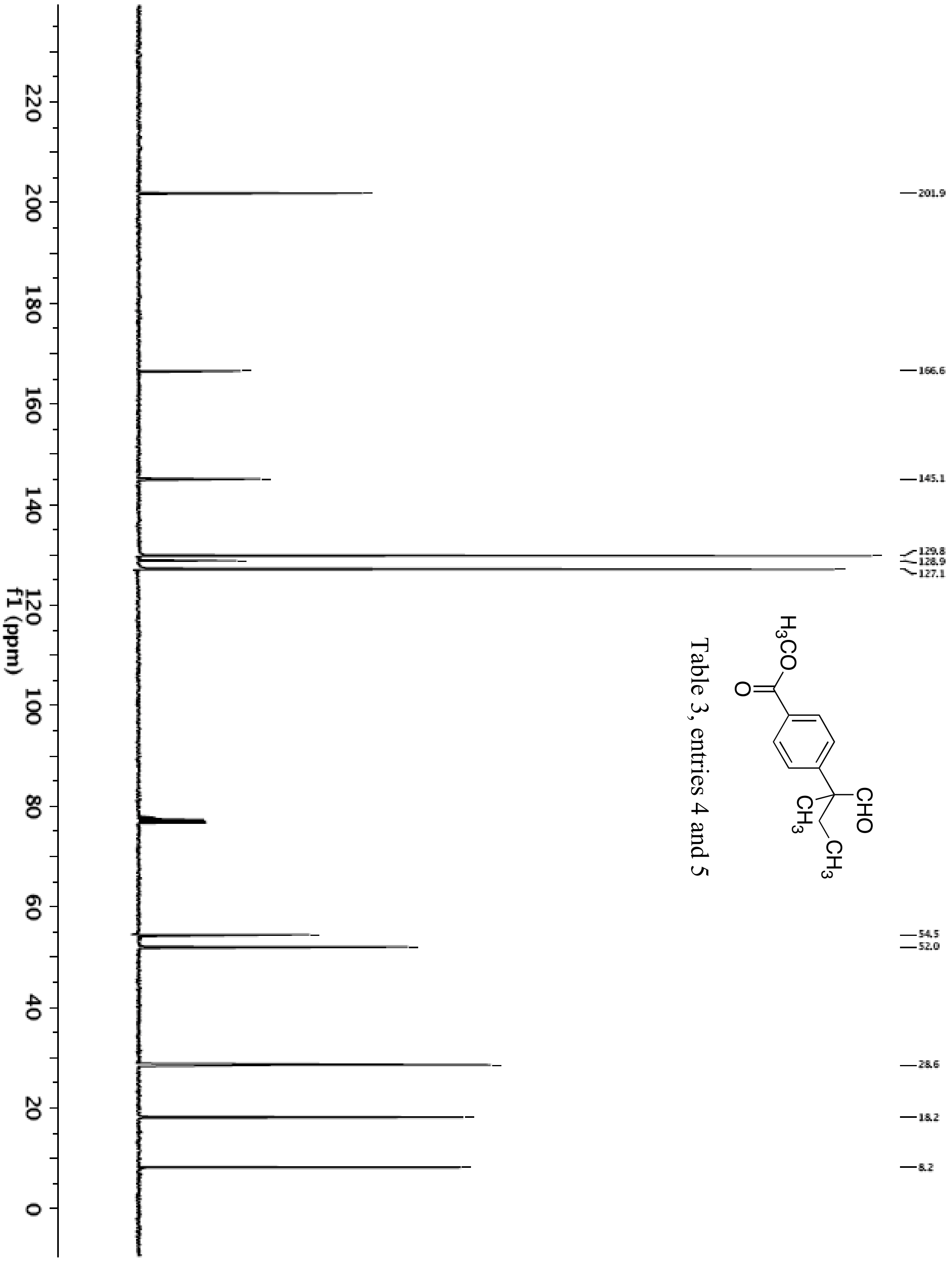


Table 3, entries 4 and 5



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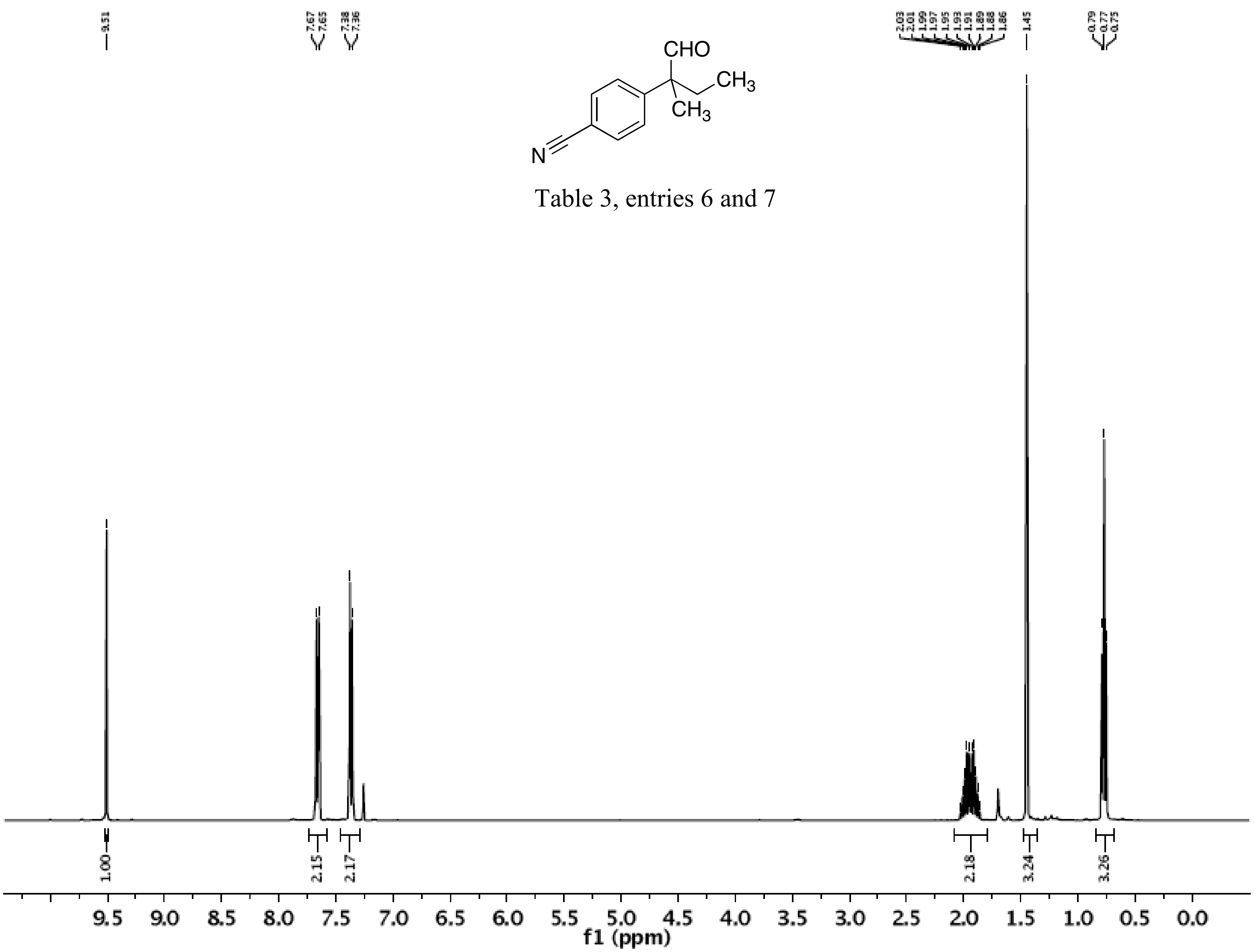

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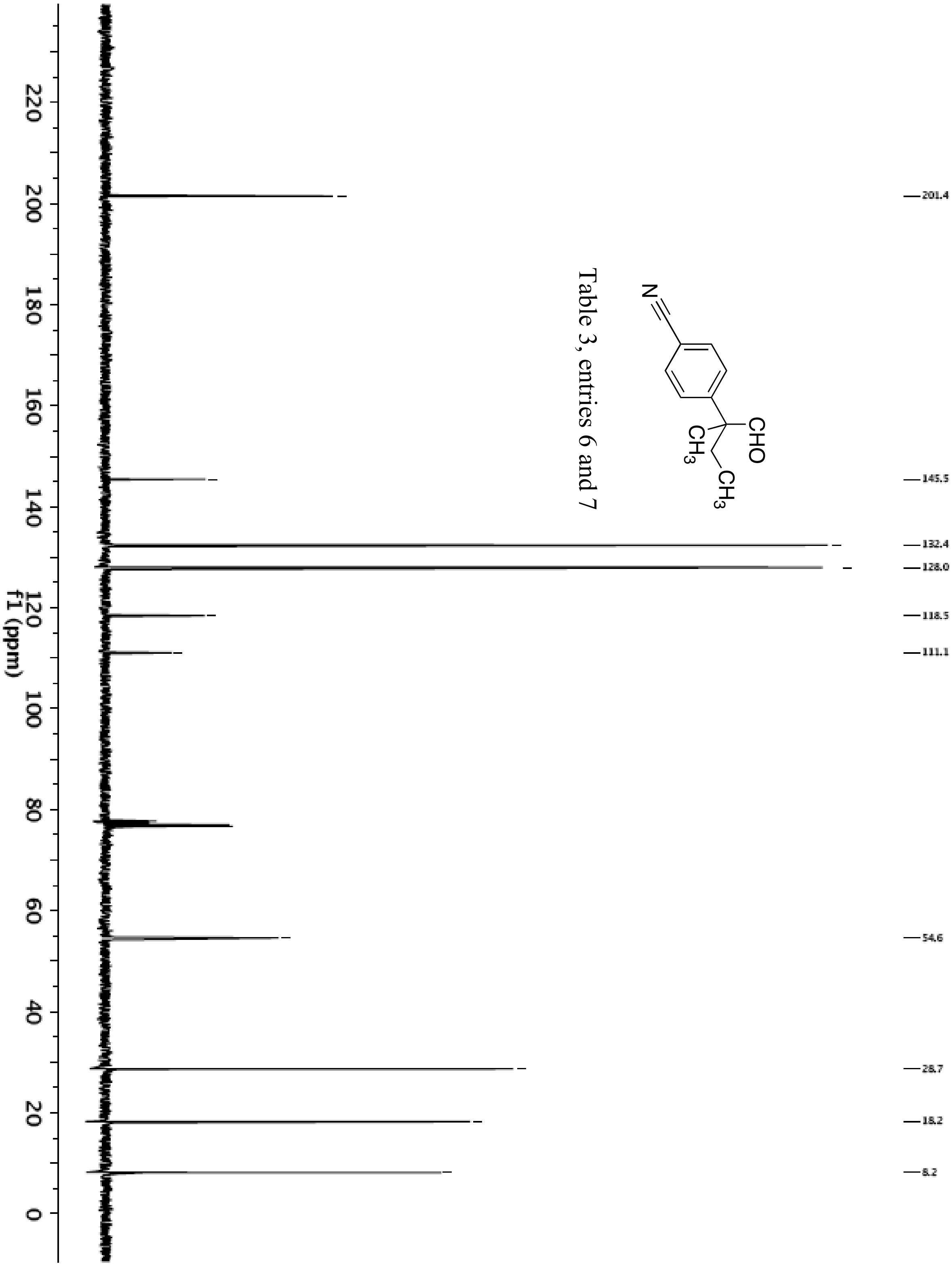
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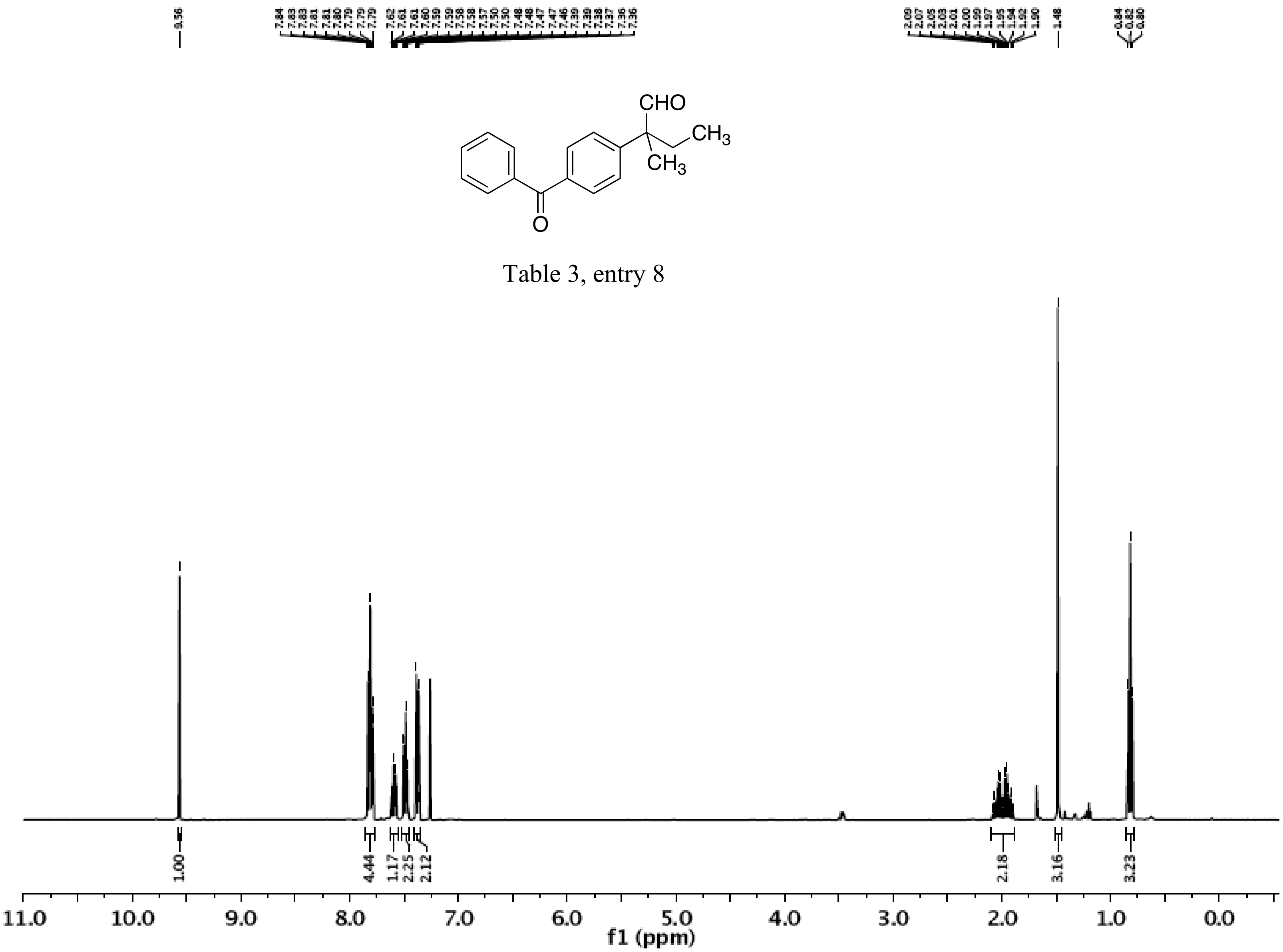

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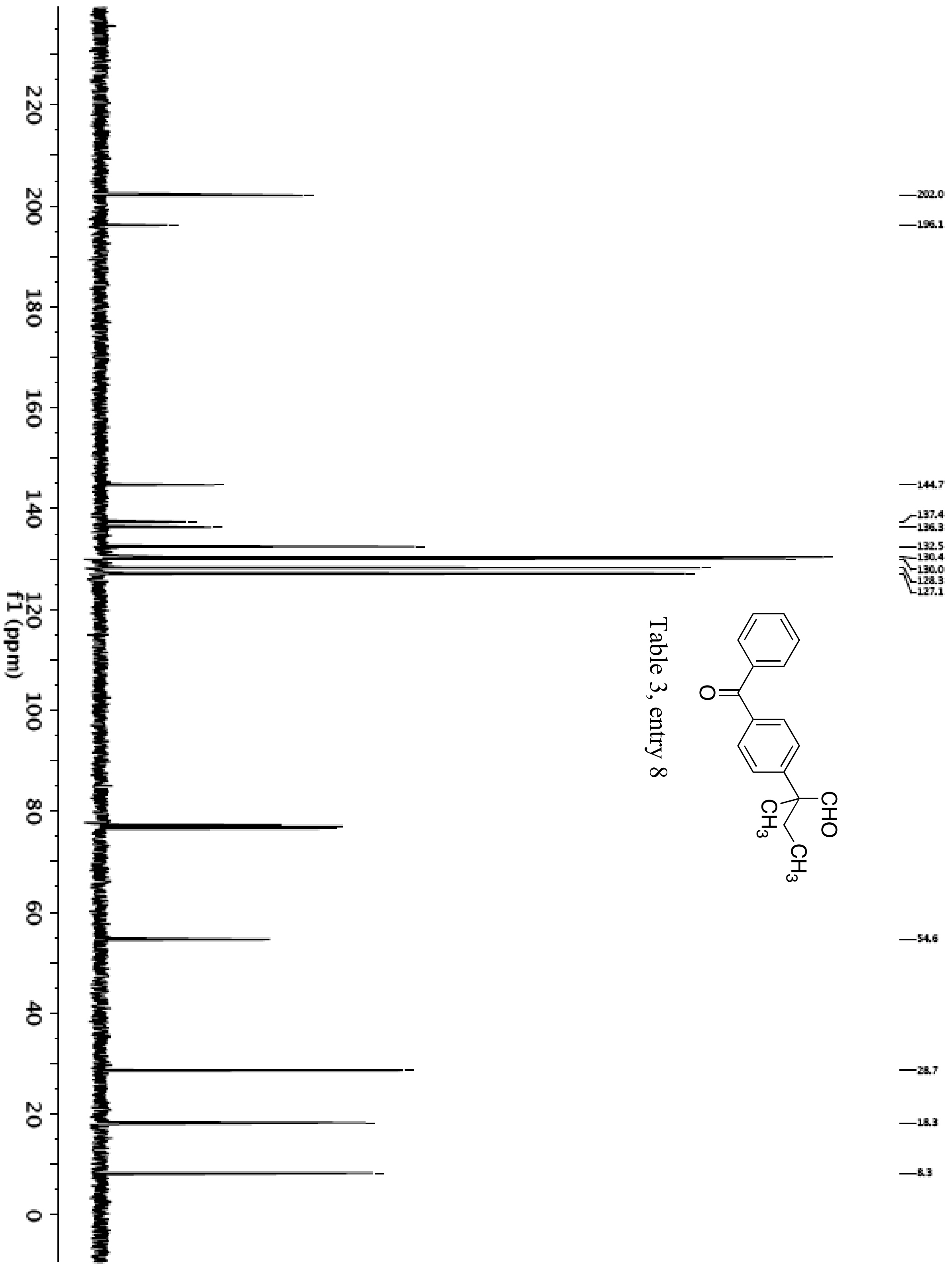

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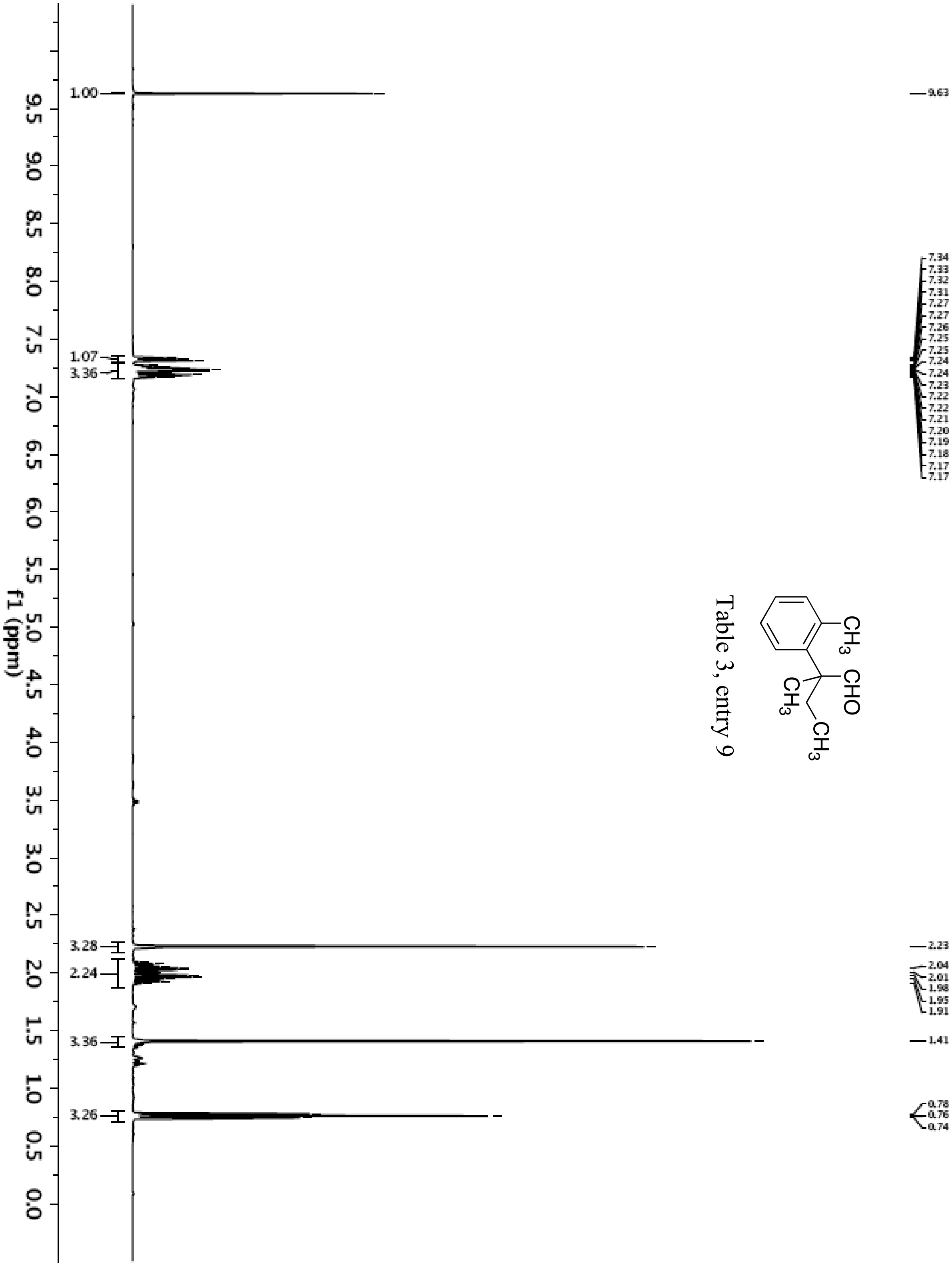

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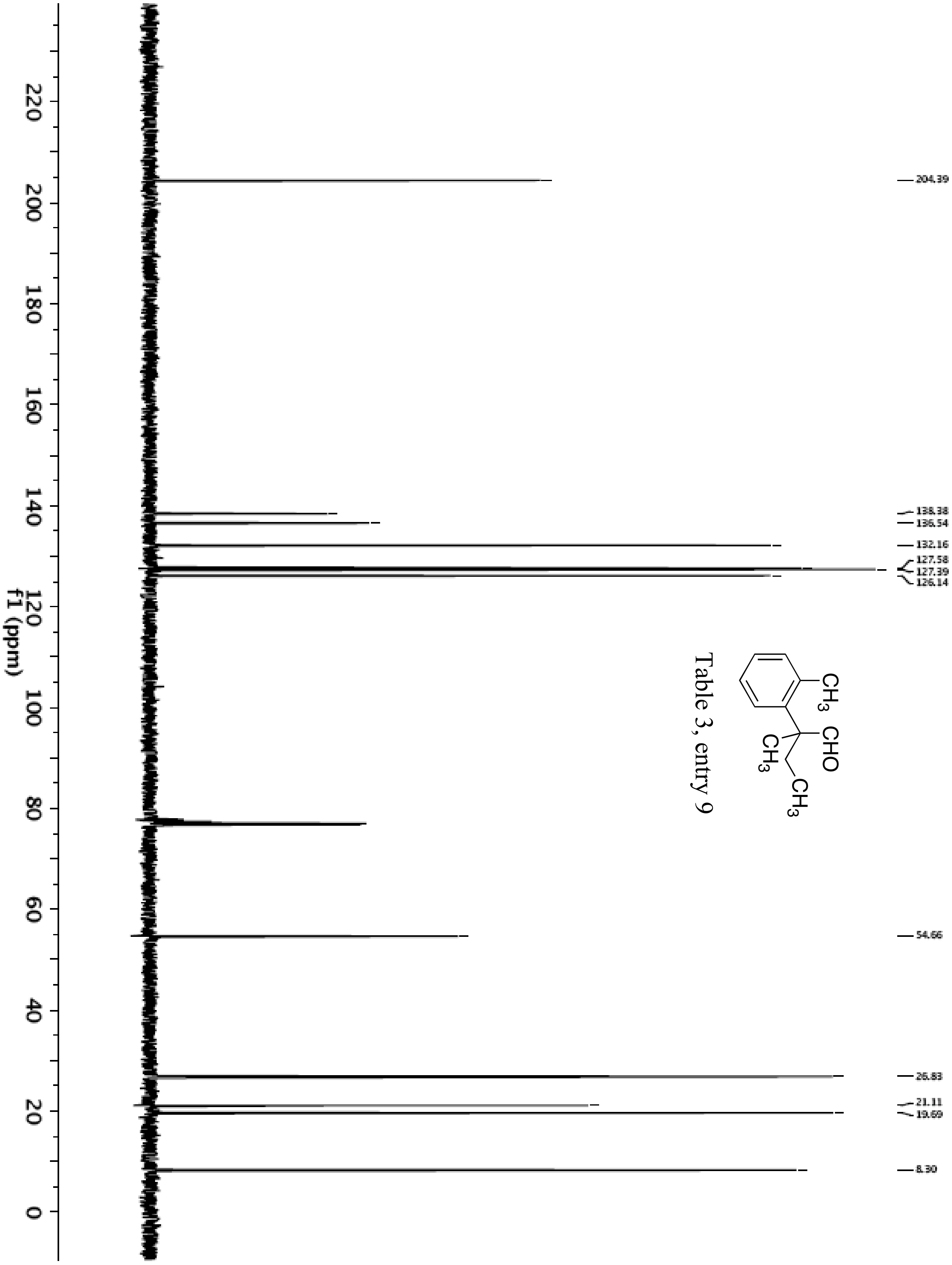

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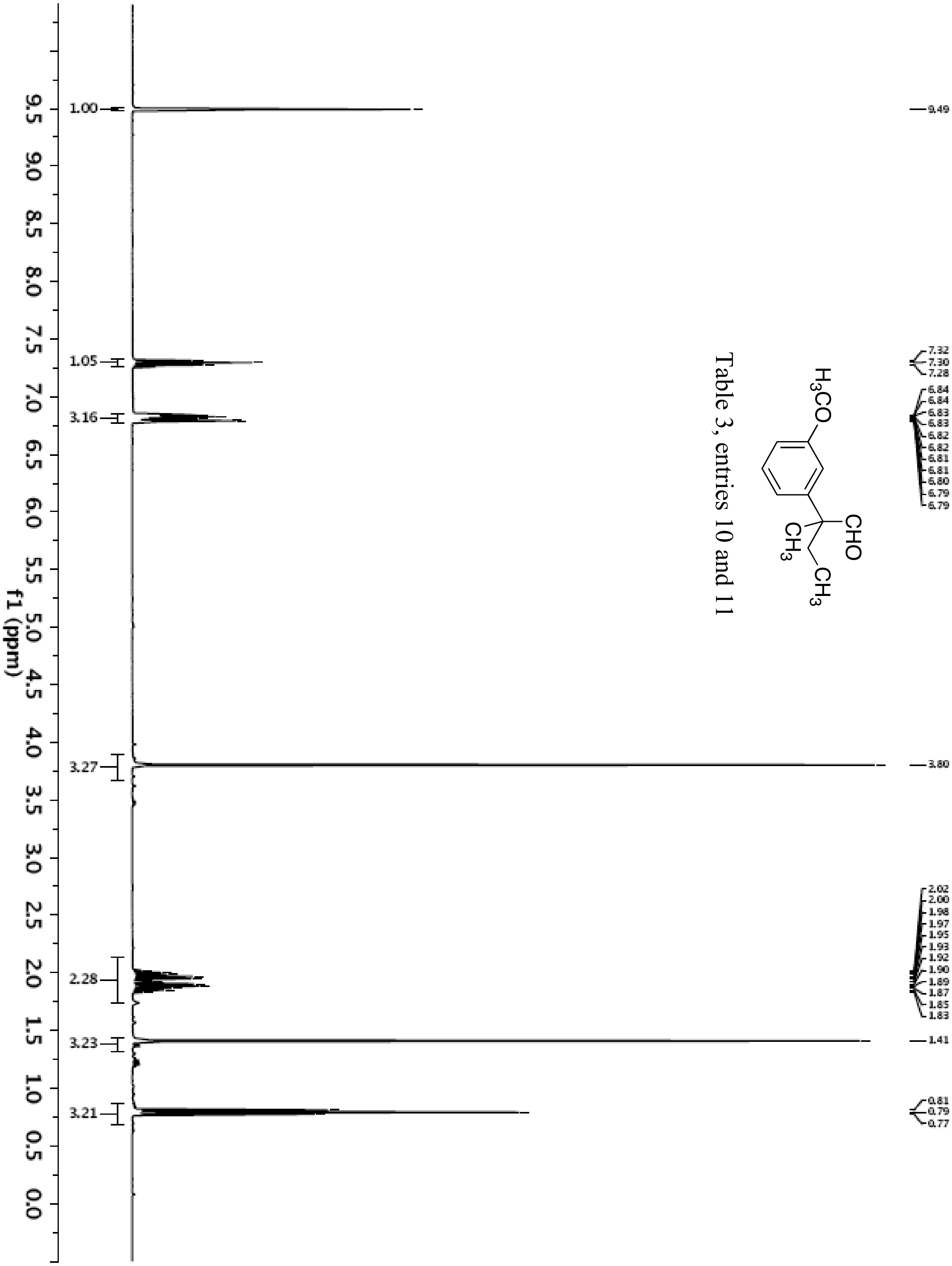
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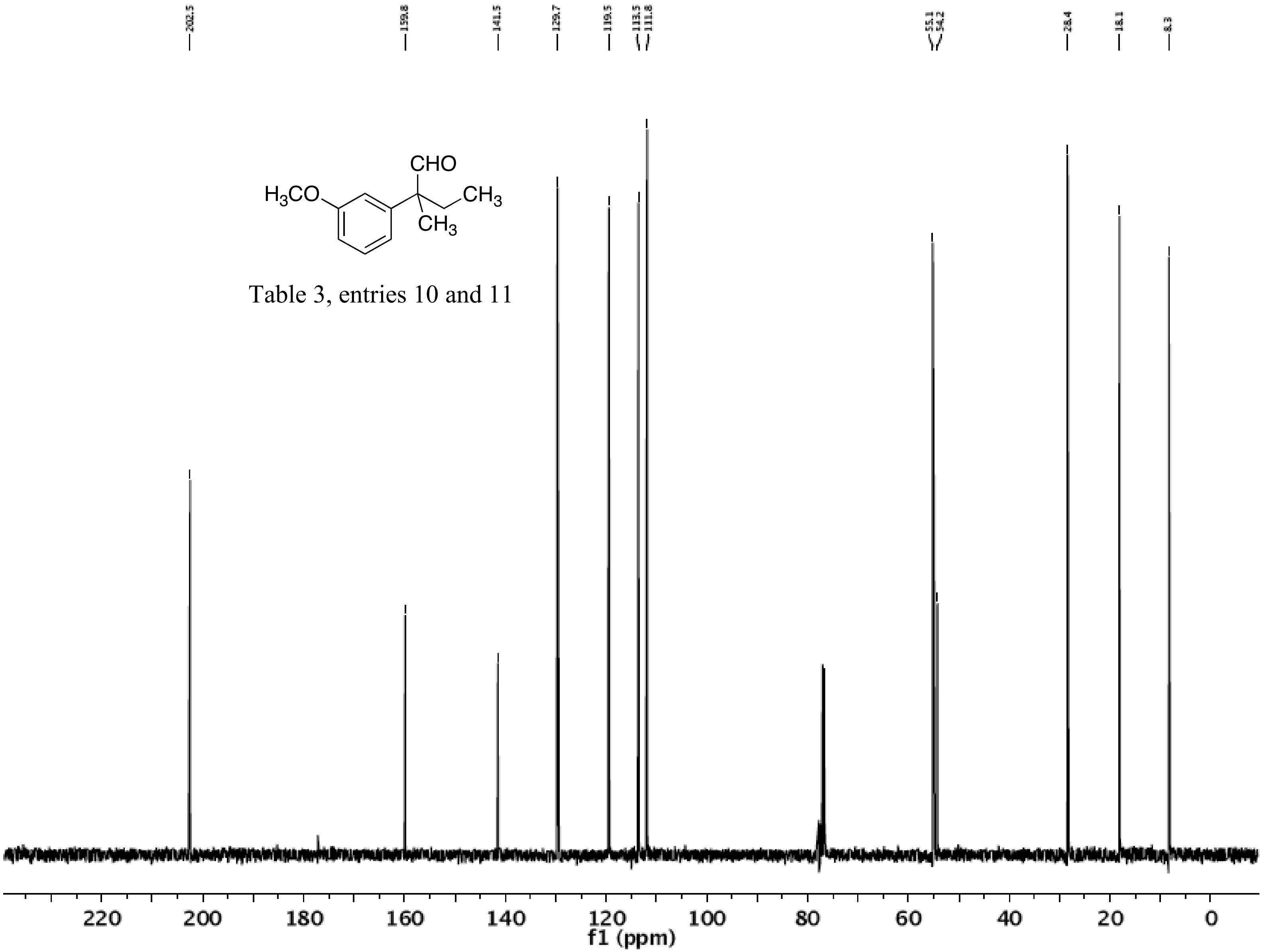

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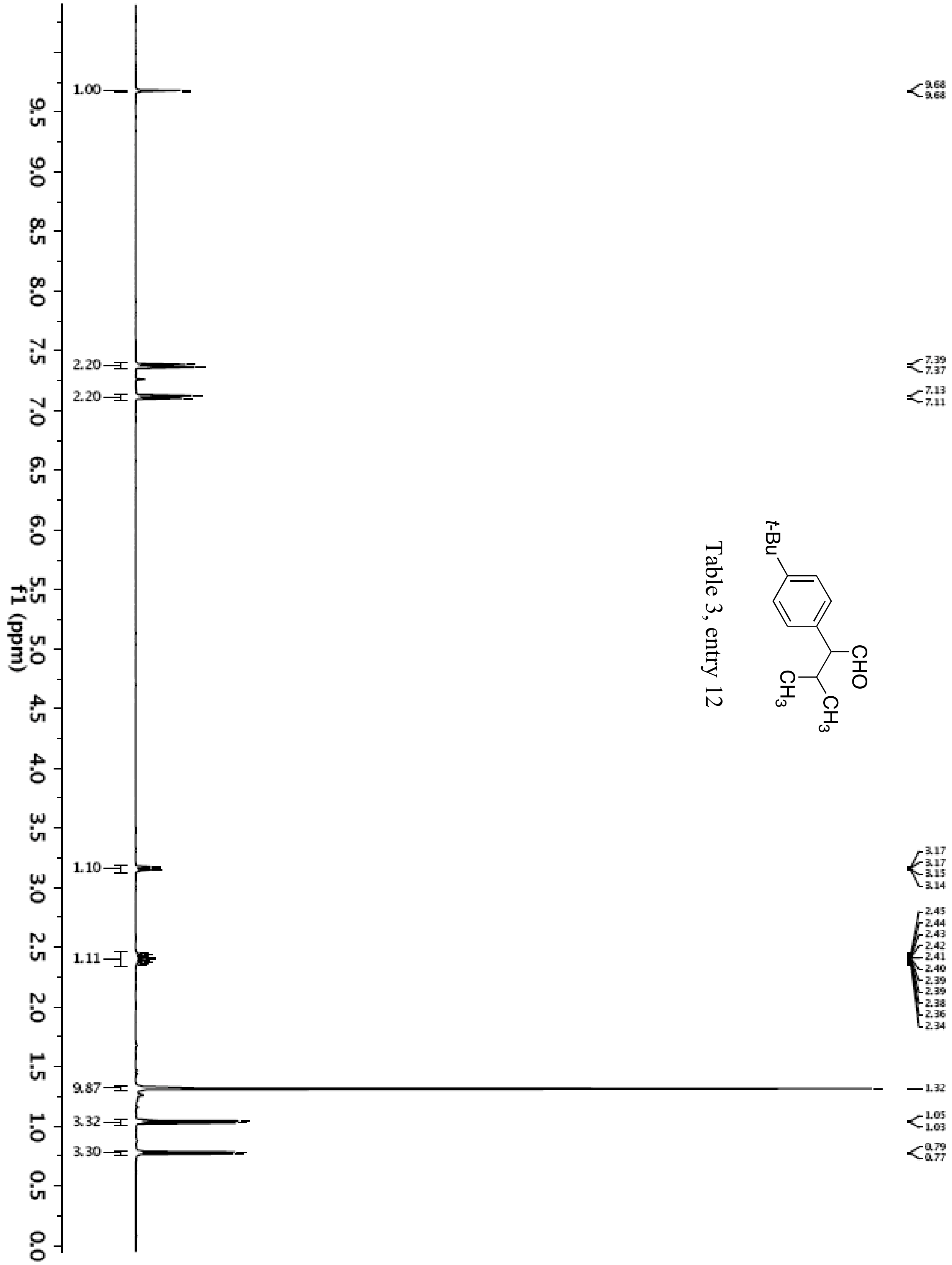
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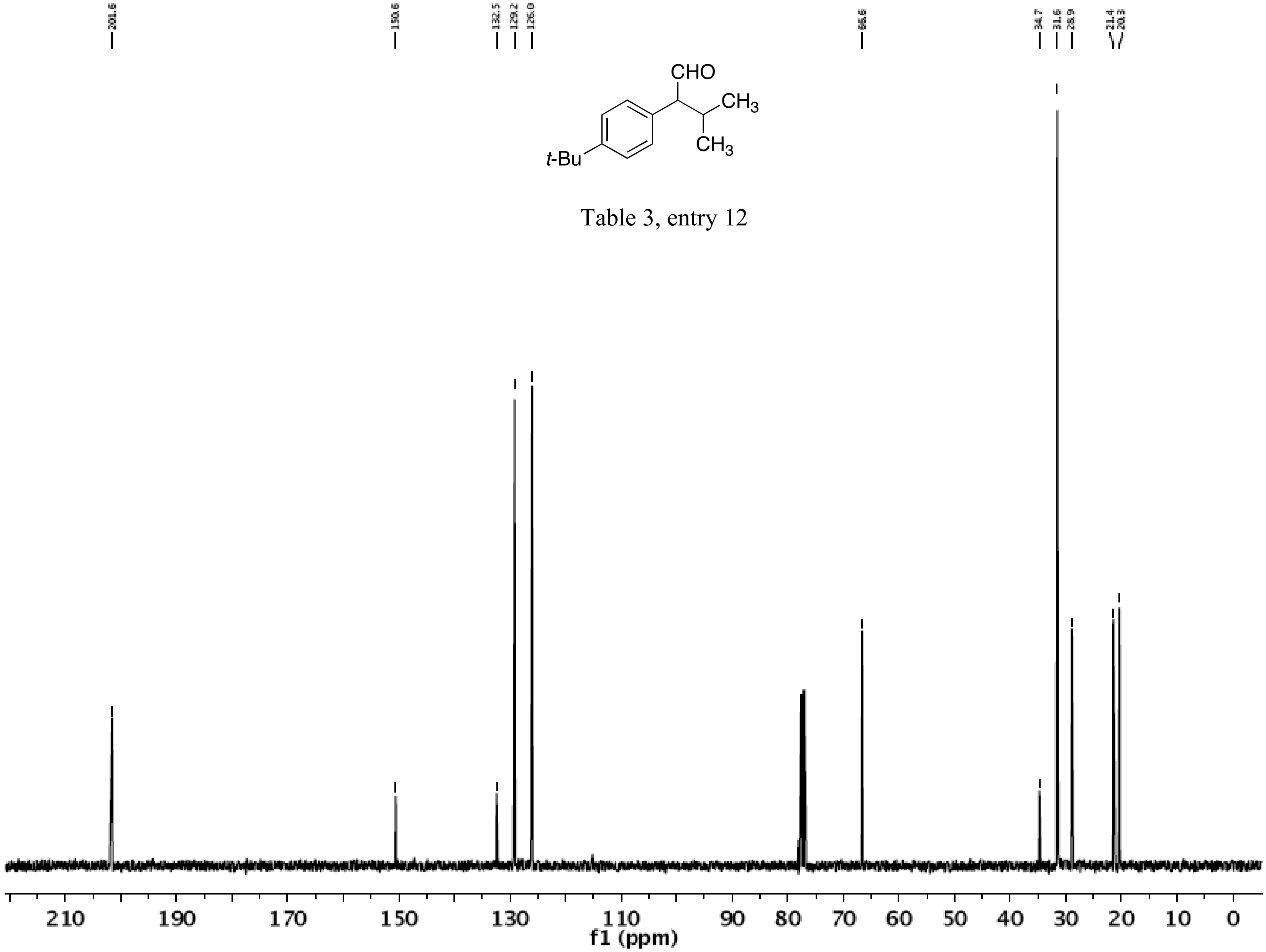

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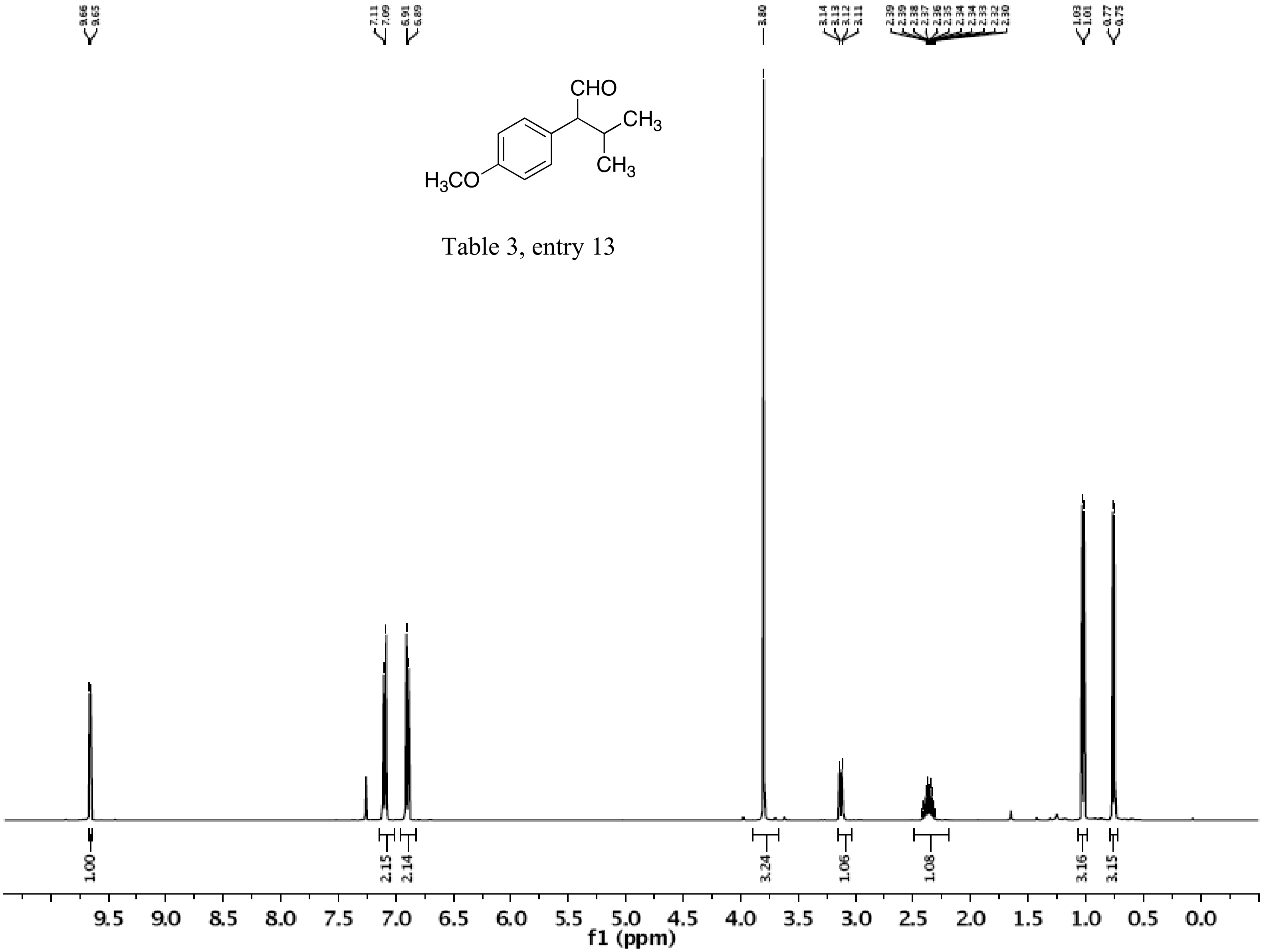
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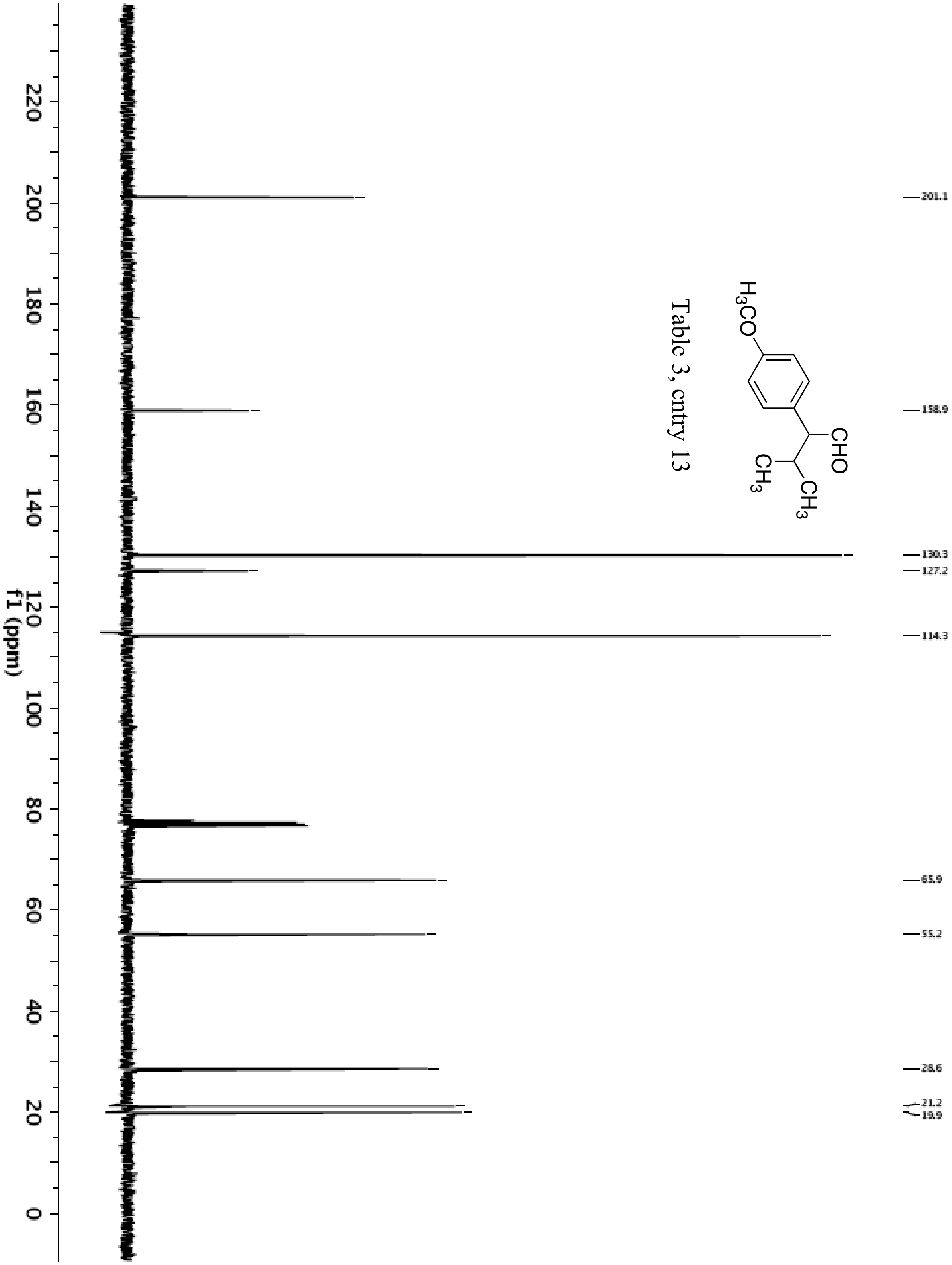

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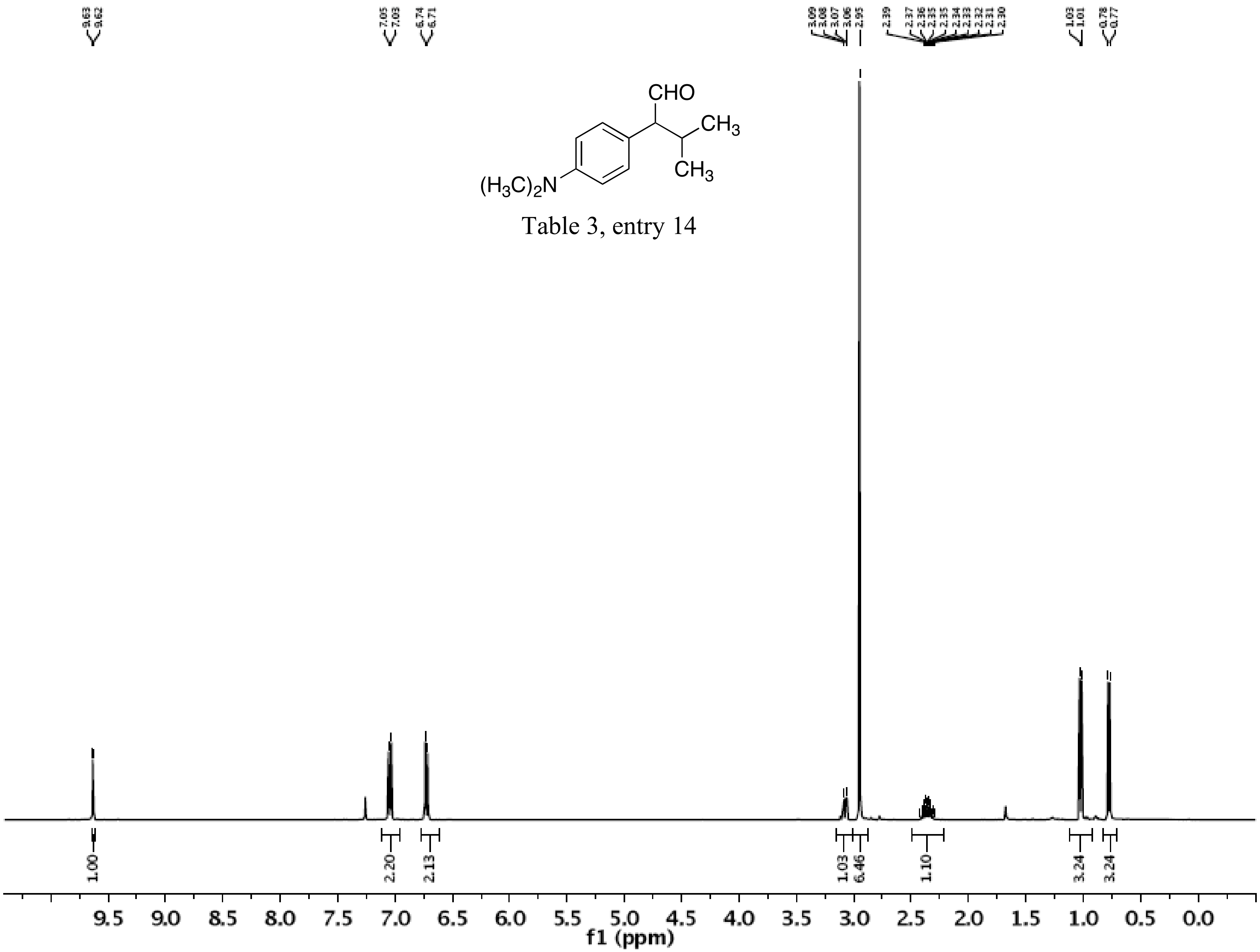

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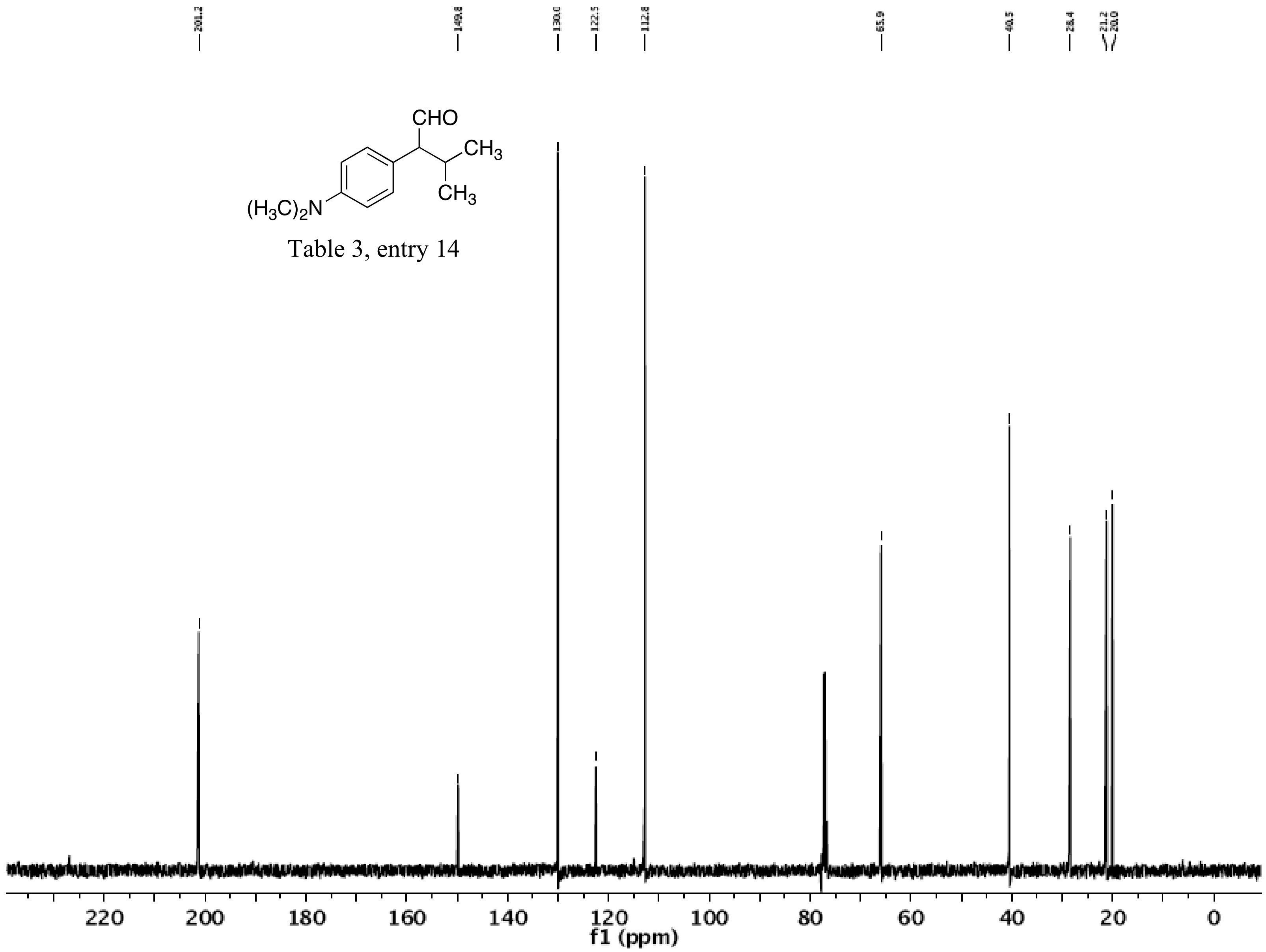
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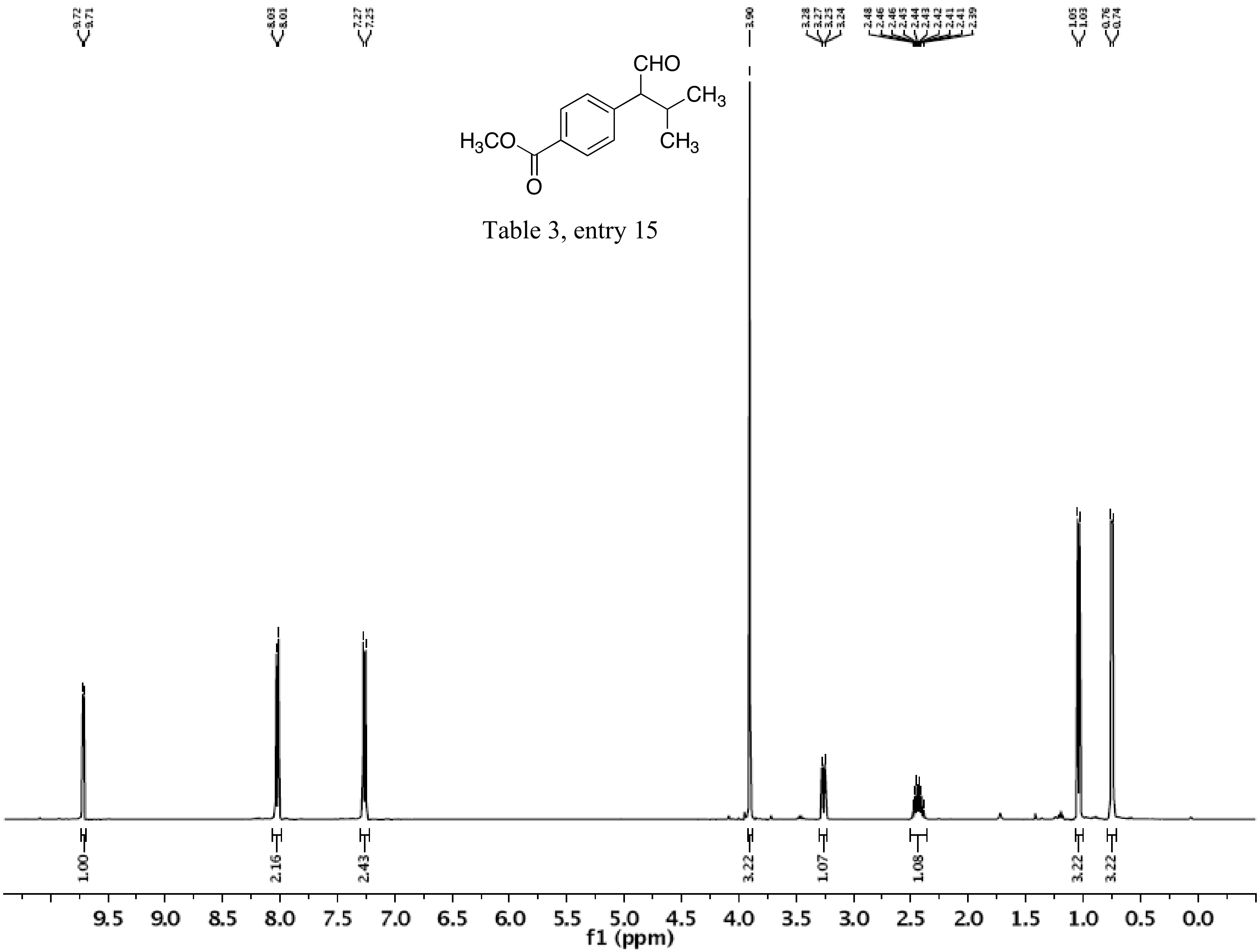

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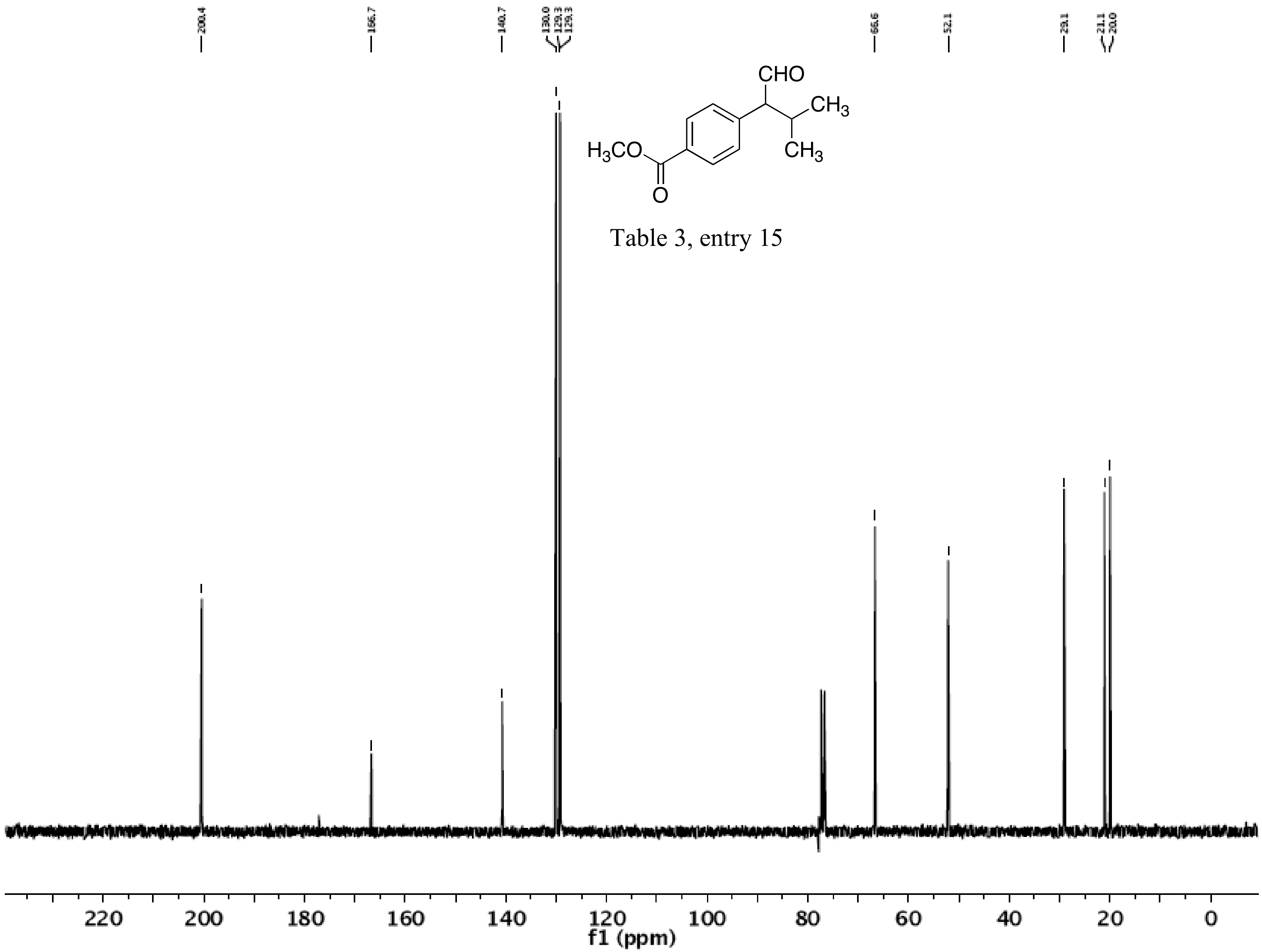
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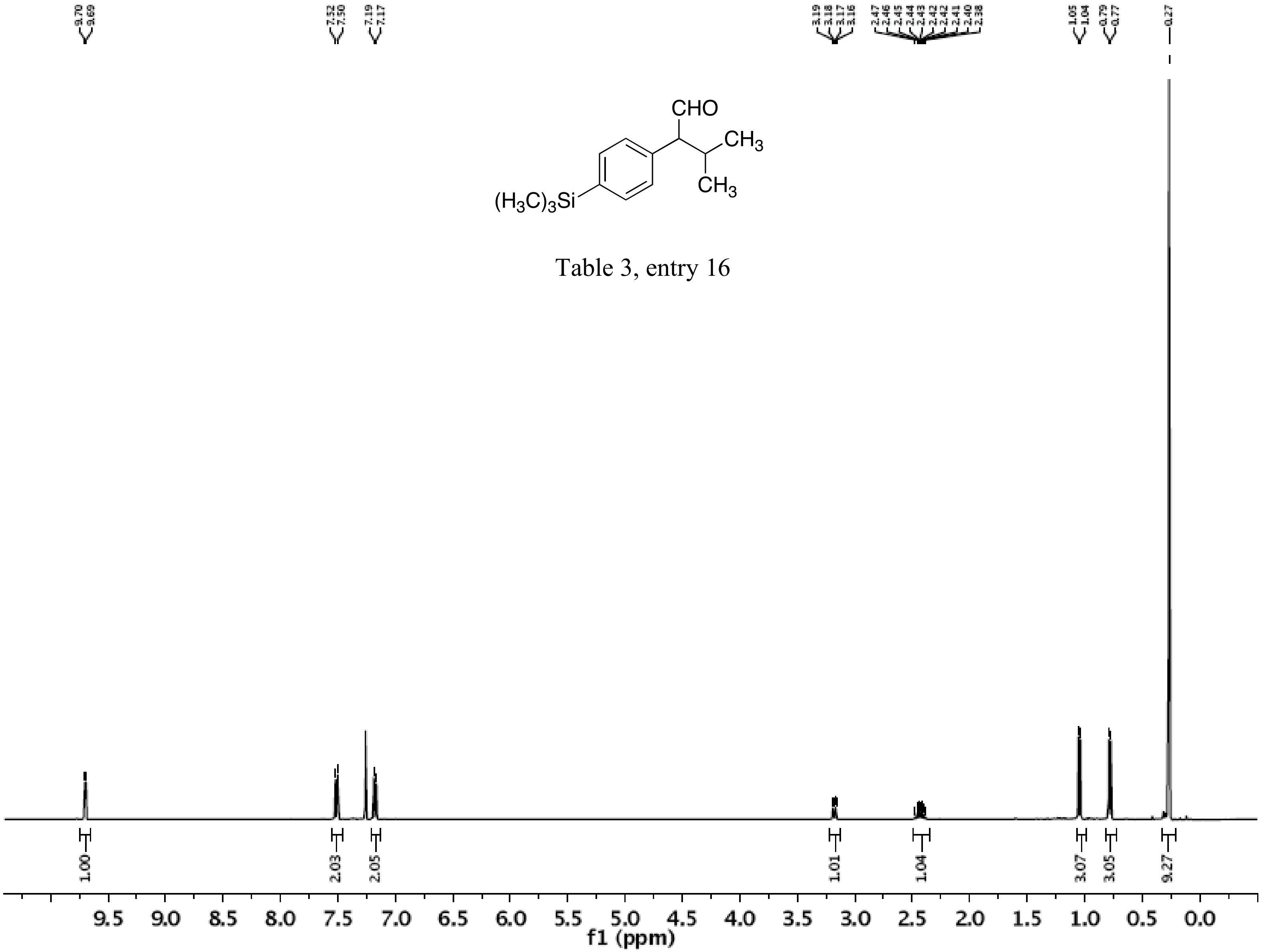

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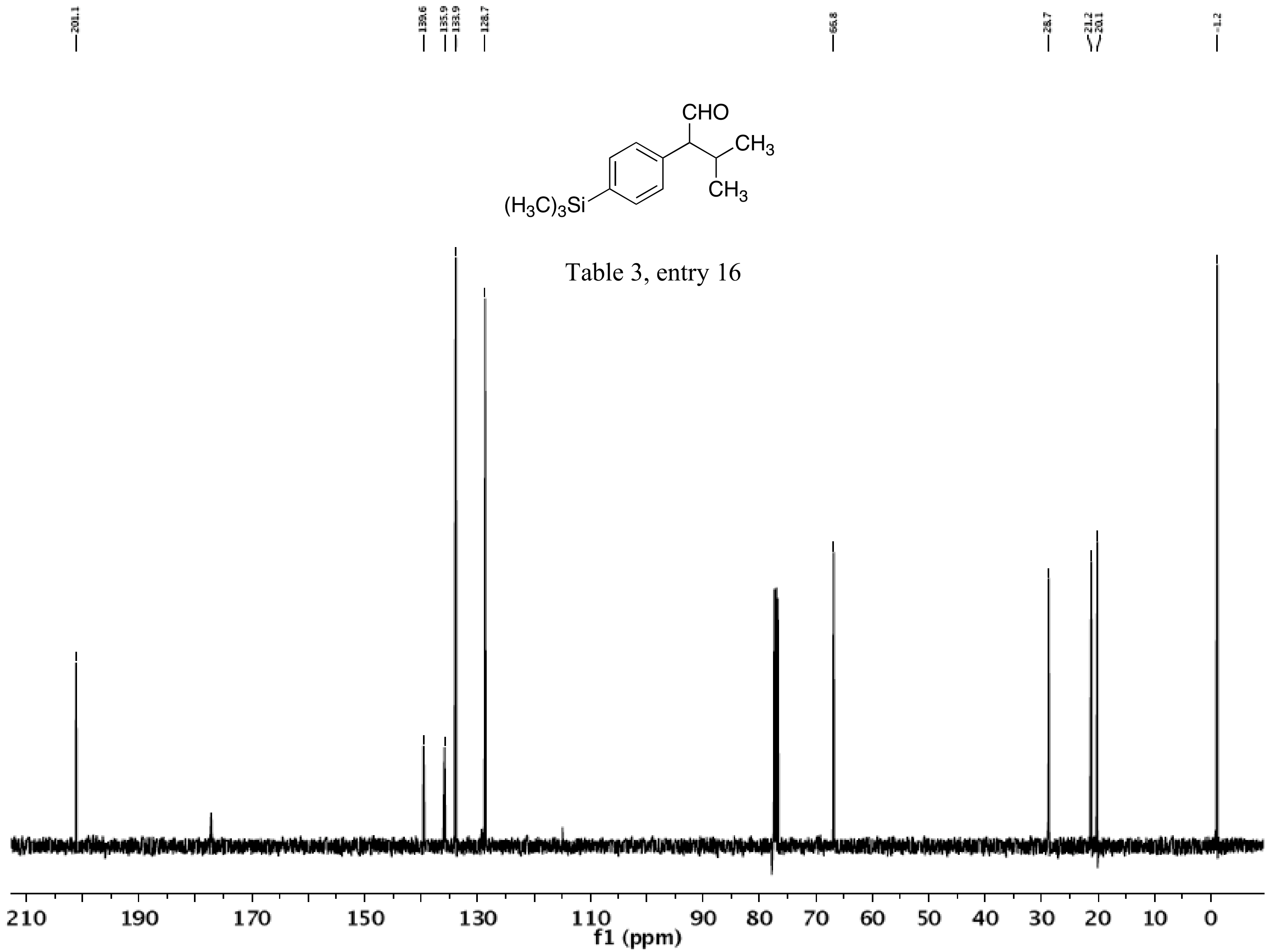

Table 3, entry 16