Electronic Supplementary Information

Selective *N*-Alkylation of Amines Using Nitriles under Hydrogenation Conditions: Facile Synthesis of Secondary and Tertiary Amines

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General: All reagents, unless otherwise specified, were purchased from commercial sources (Aldrich, TCI, Wako, Kanto, Kishida, Nacalai, etc.) and used without further purification. dist. RCNs represent purified nitriles, the purification of which were achieved by washing commercial nitriles with half volume of conc. HCl and saturated $NaHCO_3$ solution, drying with $MgSO_4$ or K_2CO_3 and distilling from CaH_2 or P_4O_{10}.[1)] 10% Pd/C was purchased from Aldrich (20,569-9) or N.E. Chemcat (K type). 5% Rh/C was obtained from WAKO (186-01011). MeOH for HPLC (WAKO 138-06473) was used without purification as a solvent. All reactions were monitored by thin-layer chromatography (TLC) on glass-backed silica gel 60 F_{254}, 0.2 mm plates (Merck), and compounds were visualized under UV light (254 nm), *p*-anisaldehyde solution with subsequent heating. The silica gel (200-300 mesh) for column chromatography was purchased from the Merck. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ solution on a JEOL EX 400 and AL 400 instrument. Spectra data are reported in ppm relative to tetramethylsilane (TMS) as internal standard. Low and high-resolution mass spectra analysis (HRMS) data were measured on a JEOL JMS-SX 102A machine. Microanalyses were accomplished at the Microanalytical Laboratory of Gifu Pharmaceutical University, Japan. Melting points were determined on a Yanagimoto melting point apparatus and were uncorrected. All new compounds were further characterized by elemental analysis or HRMS. Compounds known in the literature were characterized by comparing their ^{1}H NMR data with the previously reported data.

Preparation of *N*-Benzyloxycarbonyl-4-triethylsilyloxypiperidine (1) (eq 7)**:** An oven-dried round bottom flask was charged with 4-hydroxypiperidine (1.0 g, 10 mmol) and *N*-(benzyloxycarbonyloxy)succinimide (2.9 g, 12 mmol) and was evacuated and backfilled with nitrogen. After THF (10 mL) was added, the mixture was stirred for 30 h at room temperature. The reaction mixture was concentrated under reduced pressure and the residue was partitioned between EtOAc (50 mL) and water (50 mL). The organic phase was washed with brine (50 mL), dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography ($CHCl_3$) to provide *N*-benzyloxycarbonyl-4-hydroxypiperidine as a colorless oil (1.7 g, 71%, commercially available). ^{1}H NMR ($CDCl_3$): δ 7.38−7.26 (m, 5H), 5.12 (s, 2H) , 3.92−3.81 (m, 3H), 3.17−3.10 (m, 2H), 1.98 (brs, OH), 1.84 (brs, 2H), 1.55−1.41 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 155.3, 136.7, 128.4, 128.0, 127.8, 67.3, 67.1, 41.3, 34.0; MS (EI) *m/z* 235 (M^+, 18%), 91 (100); HRMS (EI) Calcd for $C_{13}H_{17}NO_3$ (M^+): 235.1209. Found: 235.1213.

N-Benzyloxycarbonyl-4-hydroxypiperidine (700 mg, 3.0 mmol) and DMAP (73 mg, 0.60 mmol) was loaded into the round bottom flask. The flask was evacuated and backfilled with nitrogen and pyridine (10 mL) and triethylsilyl chloride (680 mg, 4.5 mmol) was added into the mixture and stirred for 23 h. The reaction mixture was partitioned between Et_2O (50 mL) and water (50 mL). The organic phase was washed with double diluted saturated solution of $NaHCO_3$ and brine (50 mL), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude

mixture was purified by flash silica gel column chromatography (hexane/Et_2O = 20 : 1) to provide the titled compound **1** as a colorless oil (1.0 g, 95%). ^{1}H NMR ($CDCl_3$): δ 7.36−7.30 (m, 5H), 5.12 (s, 2H) , 3.88−3.85 (m, 1H), 3.82−3.72 (m, 2H), 3.31−3.25 (m, 2H) , 1.72 (brs, 2H), 1.51 (brs, 2H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.59 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 155.2, 136.9, 128.4, 127.9, 127.7, 67.0, 66.9, 40.9, 34.4, 6.8, 4.8; MS (FAB, NBA) *m/z* 350 (M^++H, 34%); HRMS (FAB, NBA) Calcd for $C_{19}H_{32}NO_3Si$ (M^++H) 350.2152. Found 350.2145.

***N*-Ethyl-4-triethylsilyloxypiperidine (2)** (eq 7): After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of *N*-benzyloxycarbonyl-4-triethylsilyloxypiperidine (**1**) (87 mg, 0.25 mmol), 10% Pd/C [8.7 mg (Aldrich 20,569-9), 10 wt% of the substrate] in MeCN (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for appropriate time (see Tables 1 and 2). The reaction mixture was filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm) and the filtrate was concentrated under reduced pressure to provide the titled compound (**2**) as a pale yellow oil (60 mg, 98%). ^{1}H NMR ($CDCl_3$): δ 3.67 (brs, 1H), 2.73 (brs, 2H), 2.38 (q, *J* = 7.2 Hz, 2H), 2.10 (brs, 2H), 1.82−1.74 (m, 2H), 1.65−1.56 (m, 2H), 1.07 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.58 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 68.3, 52.3, 50.8, 35.0, 12.3, 6.8, 4.9; MS (FAB, NBA) *m/z* 244 (M^++H, 22%); HRMS (FAB, NBA) Calcd for $C_{13}H_{30}NOSi$ (M^++H) 244.2097. Found 244.2090.

General Procedure for Reductive Alkylation of Aromatic Amines Using Nitriles (Tables 1–5, eqs 8 and 9): Unless otherwise specified, the reaction was carried out as follows. After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of the aromatic amine (**3**) (1.0 or 0.50 mmol), metal-supported catalyst (10 wt% of the amine) and RCN (5.0 equiv) [and additive (1.0 equiv)] in MeOH (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for appropriate time (see Tables). The reaction mixture was filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm) and the filtrate was concentrated under reduced pressure. [When water soluble additive such as NH_4OAc, AcOH, etc. was added to the reaction, the residue was partitioned between Et_2O (10 mL) and water (10 mL). The aqueous phase was extracted with Et_2O (10 mL×3), and then combined the organic phases were washed with brine (10 mL), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure.] The ratio of the primary amine, secondary amine and tertiary amine was confirmed by ^{1}H NMR of the crude mixture in $CDCl_3$. The crude mixture was purified by flash silica gel column chromatography, if necessary.

***N*-Ethylaniline (4a)** (Table 1, Entries 3, 9 and 10, commercially available): 85−97 % yields as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.17 (t, *J* = 6.5 Hz, 2H), 6.69 (t, *J* = 6.5 Hz, 1H), 6.63 (d, *J* = 6.5 Hz, 2H), 3.15 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

***N*-Ethyl-4-anisidine (4b)**[2] (Table 2, Entry 2): 99% as a black oil contaminated with 1% *N*,*N*-diethyl-4-anisidine (**5b**). ^{1}H NMR ($CDCl_3$): δ 6.78 (d, *J* = 9.3 Hz, 2H), 6.58 (d, *J* = 9.3 Hz, 2H), 3.74 (s, 3H), 3.11 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); HRMS (EI) Calcd for $C_9H_{13}NO$ (M^+) 151.1001. Found 151.0997.

***N*-Ethyl-3,4,5-trimethoxyaniline (4c)**[3] (Table 2, Entry 3): 100% as a dark blue oil. ^{1}H NMR ($CDCl_3$): δ 5.85 (s, 2H), 3.83 (s, 6H), 3.76 (s, 3H), 3.13 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 153.9, 145.2, 130.0, 90.3, 61.1, 55.9, 38.9, 14.8; MS (EI) *m/z* 211 (M^+, 40%), 196 (100); HRMS (EI) Calcd for $C_{11}H_{17}NO_3$ (M^+) 211.1196. Found 211.1209.

4-Ethylaminoacetanilide (4d)[3] (Table 2, Entry 4): 97% as a colorless solid. mp 123−124 °C; ^{1}H NMR ($CDCl_3$): δ 7.25 (d, *J* = 8.5 Hz, 2H), 6.55 (d, *J* = 8.5 Hz, 2H), 3.50 (brs, NH), 3.12 (q, *J* = 7.1 Hz, 2H), 2.11 (s, *3*H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 168.3, 145.6, 128.1, 122.4, 112.8, 38.7, 24.1, 14.8; MS (EI) *m/z* 167 (M^+, 100%), 163 (40), 121 (65); Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.39; H, 7.92; N, 15.72. Found C, 67.39; H, 8.08; N, 15.67.

4-Ethylaminobenzoic acid (4e)[3] (Table 2, Entry 5): 94% as a colorless solid. mp 179−180 °C; ^{1}H NMR ($CDCl_3$): δ 7.92 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 3.23 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 171.7, 152.6, 132.3, 117.1, 111.3, 37.9, 14.6; MS (EI) *m/z* 165 (M^+, 45%), 150 (100); Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found C, 65.22;

H, 6.67; N, 8.32.

***N*-Ethylanthranilic acid (4f)**[3] (Table 2, Entry 6): 91% as a light brown solid. mp 156−157 °C; ^{1}H NMR ($CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.60 (t, *J* = 8.0 Hz, 1H), 3.26 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 173.0, 151.8, 135.5, 132.6, 114.5, 111.3, 108.5, 37.4, 14.5; MS (EI) *m/z* 165 (M^+, 50%), 132 (100), 150 (25), 77 (19), 57 (15); Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found C, 65.58; H, 6.65; N, 8.26.

***N*-Ethyl-4-fluoroaniline (4g)**[3] (Table 2, Entry 8): 93% as a brown oil. ^{1}H NMR ($CDCl_3$): δ 6.93−6.86 (m, 2H), 6.55−6.52 (m, 2H), 3.41 (brs, NH), 3.11 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 156.9, 154.6, 144.8, 115.7, 115.5, 113.5, 39.1, 14.9; MS (EI) *m/z* 139 (M^+, 38%), 124 (100); HRMS (EI) Calcd for $C_8H_{10}FN$ (M^+) 139.0797. Found 139.0792.

***N*-Ethyl-4-trifluoromethylaniline (4h)**[3] (Table 2, Entry 9 and Table 3, Entry 8): 52% conversion and 99% product isolated as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.39 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 8.5 Hz, 2H), 3.89 (brs, NH), 3.22−3.15 (m, 2H), 1.27 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 150.8, 126.7, 126.62, 126.65, 111.7, 38.1, 14.6; MS (EI) *m/z* 189 (M^+, 30%), 174 (100); HRMS (EI) Calcd for $C_9H_{10}F_3N$ (M^+) 189.0765. Found 189.0771.

Methyl 4-ethylaminobenzoate (4i)[3] (Table 2, Entry 10 and eq 8): 78% conversion and 99% product isolated as a colorless solid. ^{1}H NMR ($CDCl_3$): δ 7.86 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 8.7 Hz, 2H), 4.03 (brs, NH), 3.85 (s, 3H), 3.21 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 167.4, 152.0, 131.6, 118.2, 111.3, 51.5, 37.9, 14.6; MS (EI) *m/z* 179 (M^+, 55%), 164 (100), 148 (25); Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found C, 66.85; H, 7.27; N, 7.75.

***N*-Ethyl-2-isopropylaniline (4j)** (Table 2, Entry 11): 85% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.15−7.10 (m, 2H), 6.73 (t, *J* = 7.8 Hz, 1H) , 6.65 (d, *J* = 7.8 Hz, 1H), 3.55 (brs, NH), 3.19 (q, *J* = 7.1 Hz, 2H), 2.90−2.83 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.25 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 145.1, 131.9, 126.7, 124.8, 117.1, 110.4, 38.6, 27.1, 22.3, 15.0; MS (EI) *m/z* 163 (M^+, 54%), 148 (100), 134 (30); HRMS (EI) Calcd for $C_{11}H_{17}N$ (M^+): 163.1361. Found: 163.1366.

2-Ethylaminobiphenyl (4k)[4] (Table 2, Entry 12): 95% product contaminated with 2% 2-diethylaminobiphenyl (**5k**).[5] ^{1}H NMR ($CDCl_3$): δ 7.45−7.07 (m, 7H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.70 (t, *J* = 7.2 Hz, 1H), 3.82 (brs, NH), 3.14 (q, *J* = 7.1 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H).

***N*-Ethyl-2-naphthylamine (4m)**[3] (Table 2, Entry 14): 97% product contaminated with 3%

N,*N*-diethyl-2-naphthylamine (**5m**).[6] ^{1}H NMR ($CDCl_3$): δ 7.66–7.60 (m, 3H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.80 (s, 1H), 3.71 (brs, NH), 3.26 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 146.6, 135.3, 128.9, 127.6, 127.5, 126.3, 125.9, 121.8, 118.0, 104.3, 38.5, 14.8; MS (EI) *m/z* 171 (M^+, 75%), 156 (100), 127 (40); HRMS (EI) Calcd for $C_{12}H_{13}N$ (M^+) 171.1048. Found 171.1038.

***N*-Ethyl-3-aminopyridine (4n)**[7] (Table 2, Entry 15): 79% product contaminated with 13% 3-aminopyridine (**3n**). ^{1}H NMR ($CDCl_3$): δ 8.01 (d, *J* = 2.9 Hz, 1H), 7.94 (dd, *J* = 4.6, 1.2 Hz, 1H), 7.09−7.06 (m, 1H), 6.87−6.84 (m, 1H), 3.20−3.14 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

***N*-Propylaniline (6a)** (Table 4, Entry 1, commercially available): 49% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.17 (t, *J* = 7.9 Hz, 2H), 6.68 (t, *J* = 7.9 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 2H), 3.08 (t, *J* = 7.2 Hz, 2H), 1.69−1.60 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H).

***N*-Butylaniline (6b)** (Table 4, Entry 3, commercially available): 78% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.17 (t, *J* = 7.8 Hz, 2H), 6.68 (t, *J* = 7.8 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 2H), 3.11 (t, *J* = 7.2 Hz, 2H), 1.64−1.57 (m, 2H), 1.48−1.39 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H).

***N*-Amylaniline (6c)** (Table 4, Entry 4, commercially available): 89% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.17 (t, *J* = 7.5 Hz, 2H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 2H), 3.59 (brs, NH), 3.10 (t, *J* = 7.1 Hz, 2H), 1.64−1.55 (m, 2H), 1.39−1.36 (m, 4H), 0.92 (t, *J* = 7.1 Hz, 3H).

***N*-Dodecylaniline (6d)** (Table 4, Entry 6, commercially available): The reaction mixture was treated with $LiAlH_4$ to separate with dodecyl nitrile from reaction mixture. 90% as a colorless solid. ^{1}H NMR ($CDCl_3$): δ 7.17 (t, *J* = 7.6 Hz, 2H), 6.68 (t, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 7.6 Hz, 2H), 3.58 (brs, NH), 3.10 (t, *J* = 7.1 Hz, 2H), 1.65−1.58 (m, 2H), 1.39−1.26 (m, 18H), 0.88 (d, *J* = 6.8 Hz, 3H).

***N*-Isobutylaniline (6e)**[8] (Table 4, Entry 8): 88% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.16 (t, *J* = 7.7 Hz, 2H), 6.67 (t, *J* = 7.7 Hz, 1H), 6.59 (d, *J* = 7.7 Hz, 2H), 3.67 (brs, NH), 2.93 (d, *J* = 6.8 Hz, 2H), 1.94−1.84 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 6H).

***N*-Isoamylaniline (6f)**[3] (Table 4, Entry 10): 85% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.17 (t, *J* = 7.6 Hz, 2H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 2H), 3.54 (brs, NH), 3.12 (t, *J* = 7.3 Hz, 2H), 1.74−1.69 (m, 1H), 1.52 (q, *J* = 7.3 Hz, 2H), 0.95 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 148.5, 129.2, 117.1, 112.7, 42.1, 38.6, 26.0, 22.6. MS (EI) *m/z* 163 (M^+, 20%), 106 (100), 77 (14); HRMS (EI) Calcd for $C_{11}H_{17}N$ (M^+) 163.1354. Found 163.1361.

***N*-(Cyclohexylmethyl)aniline (6g)**[9] (Table 4, Entry 12): 99% as a colorless oil. ^{1}H NMR ($CDCl_3$):

δ 7.17 (t, *J* = 7.6 Hz, 2H), 6.67 (t, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 7.6 Hz, 2H), 3.70 (brs, NH), 2.95 (d, *J* = 6.3 Hz, 2H), 1.84−1.54 (m, 6H), 1.30−1.13 (m, 3H), 1.02−0.93 (m, 2H).

***N*-(2,2-Dimethylpropyl)aniline (6h)**[3] (Table 4, Entry 14): 80% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.16 (t, *J* = 7.4 Hz, 2H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 7.4 Hz, 2H), 3.62 (brs, NH), 2.89 (s, 2H), 0.99 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 149.1, 129.2, 116.9, 112.6, 55.8, 31.8, 22.7; MS (EI) *m/z* 163 (M^+, 15%), 106 (100), 77 (13); HRMS (EI) Calcd for $C_{11}H_{17}N$ (M^+) 163.1365. Found 163.1361.

***N*-(3-Hydroxypropyl)aniline (6i)**[10] (Table 4, Entry 15): 81% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.18 (t, *J* = 7.4 Hz, 2H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 7.4 Hz, 2H), 3.82 (t, *J* = 6.1 Hz, 2H), 3.29 (t, *J* = 6.1 Hz, 2H), 1.92−1.86 (m, 2H).

***N*-(4,4-Dimethoxybutyl)aniline (6j)**[3] (Table 4, Entry 16): 14% as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.16 (t, *J* = 7.5 Hz, 2H), 6.68 (t, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 7.5 Hz, 2H), 4.40 (t, *J* = 5.4 Hz, 1H), 3.43 (brs, NH), 3.33 (s, 6H), 3.14 (t, *J* = 6.6 Hz, 2H), 1.70−1.67 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 148.3, 129.2, 117.1, 112.7, 104.3, 52.8, 43.6, 30.1, 24.6; MS (EI) *m/z* 209 (M^+, 29%), 146 (100), 106 (80); HRMS (EI) Calcd for $C_{12}H_{19}NO_2$ (M^+) 209.1416. Found 209.1418.

***N*-(2-Phenylethyl)aniline (6k)**[11] (Table 4, Entry 17): 24% product contaminated with 9% BnCN. ^{1}H NMR ($CDCl_3$): δ 7.34−7.16 (m, 7H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.3 Hz, 1H), 3.67 (brs, NH), 3.41 (t, *J* = 7.1 Hz, 2H), 2.92 (t, *J* = 7.1 Hz, 2H).

***N*-(3-Cyanopropyl)aniline (6l)**[3] (Table 4, Entry 18): 86% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.19 (t, *J* = 7.3 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.3 Hz, 2H), 3.69 (brs, NH), 3.32 (t, *J* = 6.7 Hz, 2H), 2.48 (t, *J* = 6.7 Hz, 2H), 2.00−1.94 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 147.5, 129.4, 119.3, 118.0, 112.8, 42.3, 25.3, 14.8; MS (EI) *m/z* 160 (M^+, 25%), 106 (100), 77 (15); HRMS (EI) Calcd for $C_{10}H_{12}N_2$ (M^+) 160.0992. Found 160.1001.

***N*-Cyclohexylaniline (8)** (eq 9, commercially available)**:** 67% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.15 (t, *J* = 7.5 Hz, 2H), 6.28 (t, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 7.5 Hz, 2H), 3.50 (brs, NH), 3.29−3.22 (m, 1H), 2.08−2.03 (m, 2H), 1.78−1.73 (m, 2H), 1.66−1.62 (m, 1H), 1.42−1.32 (m, 2H), 1.27−1.10 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 147.4, 129.2, 116.8, 113.1, 51.7, 33.5, 25.9, 25.0; MS (EI) *m/z* 175 (M^+, 40%), 132 (100), 106 (35); HRMS (EI) Calcd for $C_{12}H_{17}N$ (M^+) 175.1361. Found 175.1363.

Procedure for Study of Temperature Effect (Table 6): The mixture of 4-trifluoromethylaniline (**3h**) (1.0 mmol), 10% Pd/C (10 wt%, Aldrich 20,569-9) and MeCN (5.0 equiv) in MeOH (1.0 mL) was warm up (or cool down) to given temperature in Table 6. After two vacuum/H_2 cycles to

remove air from the reaction tube, the mixture was hydrogenated under ambient pressure (balloon) for appropriate time (Table 6). The reaction mixture was filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm) and the filtrate was concentrated under reduced pressure. The ratio of **3h**, *N*-ethyl-4-trifluoromethylaniline (**4h**) was confirmed by ^{1}H NMR of the crude mixture in $CDCl_3$.

Procedure for Reductive Cyclization of 2-Aminobenzylcyanide (9) (eq 10): After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of 2-aminobenzylcyanide (**9**) (81 mg, 0.50 mmol) and 10% Pd/C [8.1 mg (Aldrich 20,569-9), 10 wt % of **9**] in MeOH (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for 22 h. The reaction mixture was filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm) and the filtrate was concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane : Et_2O = 20 : 1) to afford indole (**10**) as a colorless solid (62 mg, 98% commercially available): ^{1}H NMR ($CDCl_3$): δ 7.87 (brs, NH), 7.63 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.20−7.07 (m, 3H), 6.52 (s, 1H).

Procedure for Dialkylation of *p*-Phenetidine (3o) (Scheme 2): After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of *p*-phenetidine (**3o**) (128 μL, 1.0 mmol), 10% Pd/C [14 mg (N.E. Chemcat, K-type), 10 wt% of **3o**], MeCN (158 μL, 3.0 mmol) and $AcONH_4$ (231 mg, 3.0 equiv) in MeOH (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for 24 h. The reaction mixture was filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm) and the filtrate was partitioned between Et_2O (10 mL) and water (10 mL). The aqueous phase was extracted with Et_2O (10 mL×3), and then combined the organic phases were washed with brine (10 mL), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The ratio of **4o** and **5o** was confirmed by ^{1}H NMR of the crude mixture in $CDCl_3$. Into the resulted crude mixture of **4o** and **5o** was added 10% Pd/C [14 mg (N.E. Chemcat, K-type)], MeCN (158 μL, 3.0 mmol) and $AcONH_4$ (231 mg, 3.0 equiv) in MeOH (1.0 mL) and then hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for 24 h. The reaction mixture was filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm) and the filtrate was partitioned between Et_2O (10 mL) and water (10 mL). The aqueous phase was extracted with Et_2O (10 mL×3), and then combined the organic phases were washed with brine (10 mL), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to provide *N*,*N*-diethylphenetidine (**5o**) as a brown oil (185 mg, 96%).[12] ^{1}H NMR($CDCl_3$) δ: 6.82 (d, *J* = 8.9 Hz, 2H), 6.72 (d, *J* = 8.9 Hz, 2H), 3.98 (q, *J* = 6.9 Hz, 2H), 3.27 (q, *J* = 7.0 Hz, 4H),1.39 (t, *J* = 6.9 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ: 142.6, 115.4, 115.1, 63.8, 45.1, 14.8, 12.3; MS (FAB, NBA) m/z 194 (M^++H, 19.8 %), 193 (29.3 %); HRMS (FAB, NBA) Calcd for $C_{12}H_{19}NO$ (M^++H) 194.1545. Found 194.1549.

Procedure for Dialkylation of Aniline (3a) (Table 7): After two vacuum/H_2 cycles to remove air

from the reaction tube, the stirred mixture of **3a** (91 μL, 1.0 mmol), 10% Pd/C [9.3 mg (N.E. Chemcat, K type), 10 wt% of **3a**], MeCN (158 μL, 3.0 mmol) [and $AcONH_4$ (1.0, 3.0 or 5.0 equiv) for entries 2–4 or MS 13X (20 wt%) for Entry 5] in MeOH (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for given reaction time. The reaction mixture was filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm) [and the filtrate was partitioned between Et_2O (10 mL) and water (10 mL). The aqueous phase was extracted with Et_2O (10 mL×3), and then combined the organic phases were washed with brine (10 mL), dried with anhydrous Na_2SO_4, filtered for entries 2–4] and concentrated under reduced pressure. The ratio of **3a**, **4a** and **5a** was confirmed by ^1H NMR of the crude mixture in $CDCl_3$.

General Procedure for Preparation of Aromatic Secondary Amines from Nitro Aromatic Compounds 11 (Tables 8 and 9): Unless otherwise specified, the reaction was carried out as follows. After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of the nitro aromatic compound **11** (1.0 or 0.50 mmol), 10% Pd/C (Aldrich 20,569-9, 10 wt% of the amine) and RCN (5.0 equiv) [and NH_4OAc (1.0 equiv)] in MeOH (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for appropriate time (see Table 8 and 9). The reaction mixture was filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm) and the filtrate was concentrated under reduced pressure. [When NH_4OAc was added to the reaction, the residue was partitioned between Et_2O (10 mL) and water (10 mL). The aqueous phase was extracted with Et_2O (10 mL×3), and then combined the organic phases were washed with brine (10 mL), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure.] The ratio of the primary amine, secondary amine and tertiary amine was confirmed by ^{1}H NMR of the crude mixture in $CDCl_3$. The crude mixture was purified by flash silica gel column chromatography, if necessary.

***N*-Ethyl-4-methylaniline (4p)**: 97% as a blue oil (Table 8, Entry 7, commercially available). ^{1}H NMR ($CDCl_3$): δ 6.98 (d, *J* = 8.3 Hz, 2H), 6.54 (d, *J* = 8.3 Hz, 2H), 3.13 (q, *J* = 7.1 Hz, 2H), 2.04 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 146.2, 129.7, 126.4, 113.0, 38.8, 20.3, 14.9; MS (EI) *m/z* 135 (M^+, 40%), 120 (100), 91 (16).

***N*-Ethyl-2-methylaniline (4q)**: 81% (Table 8, Entry 8, commercially available) product contaminated with 11% *N*,*N*-diethyl-2-methylaniline (commercially available). ^{1}H NMR ($CDCl_3$): δ 7.12 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 7.01−6.60 (m, 2H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.80 (s, 1H), 3.71 (brs, NH), 3.26 (q, *J* = 7.2 Hz, 2H), 2.13 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H).

General Procedure for Selective Mono-*N*-Alkylation of Aliphatic Primary Amines (12) (Tables 10 and 11): Unless otherwise specified, the reaction was carried out as follows. After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of the nitro aromatic compound (1.0 or 0.50 mmol), metal-supported catalyst (10 wt% of the amine) and RCN (2.0 equiv) in MeOH (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for appropriate time (see Table 11). The reaction mixture was filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm) and the filtrate was concentrated under reduced pressure. The ratio of the primary amine (**12**), secondary amine (**13**) and tertiary amine (**14**) was confirmed by ^{1}H NMR of the crude mixture in $CDCl_3$. The crude mixture was purified by flash silica gel column chromatography, if necessary.

***N*-Ethyldecylamine (13a)**[3)] (Table 10, Entry 6): 96% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.64 (q, *J* = 7.2 Hz, 2H), 2.59 (t, *J* = 7.1 Hz, 2H), 1.48−1.46 (m, 2H), 1.28−1.26 (m, 14H), 1.11 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 50.0, 44.2, 31.9, 30.3, 29.6, 29.3, 27.4, 22.6, 15.4, 14.1; MS (FAB, NBA) *m/z* 186 (M^++H, 20%); HRMS (FAB, NBA) Calcd for $C_{12}H_{27}N$ (M^++H) 186.2228. Found 186.2222.

***N*-Propyldecylamine (13b)**[13)] (Table 11, Entry 1): 89% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.63−2.57 (m, 4H), 1.57−1.50 (m, 4H), 1.30−1.26 (m, 14H), 0.92 (t, *J* = 7.3 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 51.7, 49.8, 31.9, 29.7, 29.6, 29.3, 27.4, 22.8, 22.6, 14.1, 11.7; MS (FAB, NBA) *m/z* 200 (M^++H, 53%); HRMS (FAB, NBA) Calcd for $C_{13}H_{30}N$ (M^++H) 200.2378. Found 200.2372.

***N*-Butyldecylamine (13c)**[3)] (Table 11, Entry 2): 82% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.62−2.58 (m, 4H), 1.52−1.44 (m, 4H), 1.39−1.26 (m, 16H), 0.92 (t, *J* = 7.3 Hz, 3H), 0.88 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 49.9, 49.5, 31.9, 31.8, 29.7, 29.6, 29.3, 27.4, 22.6, 20.5, 14.1, 13.9; MS (FAB, NBA) *m/z* 214 (M^++H, 15%); HRMS (FAB, NBA) Calcd for $C_{14}H_{32}N$ (M^++H) 214.2535. Found 214.2543.

***N*-Amyldecylamine (13d)**[3)] (Table 11, Entry 3): 71% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.58 (t, *J* = 7.1 Hz, 4H), 1.52−1.45 (m, 4H), 1.36−1.26 (m, 18H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 50.2, 31.9, 30.2, 29.9, 29.6, 29.3, 27.4, 22.6, 14.0; MS (EI) *m/z* 227 (M^+, 10%), 170 (100), 100 (100); HRMS (EI) Calcd for $C_{15}H_{33}N$ (M^+) 227.2613. Found 227.2600.

***N*-Isobutyldecylamine (13e)** (Table 11, Entry 4): 39% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.59 (t, *J* = 7.2 Hz, 2H), 2.43 (d, *J* = 6.7 Hz, 2H), 1.82−1.72 (m, 1H), 1.51−1.48 (m, 2H), 1.31−1.22 (m, 14H), 0.91 (d, *J* = 6.7 Hz, 6H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 58.2, 50.2, 31.9, 30.2, 29.6, 29.6, 29.6, 29.3, 28.3, 27.4, 22.7, 20.7, 14.1; MS (FAB, NBA) *m/z* 214 (M^++H, 68%); HRMS (FAB, NBA) Calcd for $C_{14}H_{32}N$ (M^++H) 214.2535. Found 214.2543.

***N*-(2,2-Dimethylpropyl)decylamine (13f)** (Table 11, Entry 5): 61% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.61 (t, *J* = 7.3 Hz, 2H), 2.36 (s, 2H), 1.52−1.48 (m, 2H), 1.28−1.26 (m, 14H), 0.92 (s, 9H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 62.4, 51.1, 31.9, 31.4, 29.8, 29.6, 29.6, 29.3, 27.9, 27.3, 22.7, 14.1. MS (EI) *m/z* 227 (M^+, 3%), 212 (9), 198 (25), 170 (100), 100 (7), 72 (15); HRMS (EI) Calcd for $C_{15}H_{33}N$ (M^+) 227.2613. Found 227.2608.

***N*-Ethyl-2-phenylethylamine (13g)**[14] (Table 11, Entry 6): 80% product contaminated with 5% 2-phenylethylamine (commercially available). ^{1}H NMR ($CDCl_3$): δ 7.32−7.21 (m, 5H), 2.91−2.80 (m, 4H), 2.66 (q, *J* = 7.2 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H).

***N*-Ethyl-4-phenylbutylamine (13h)** (Table 11, Entry 7): 98% as colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.29−7.25 (m, 2H), 7.19−7.17 (m, 3H), 2.66−2.61 (m, 6H), 1.69−1.62 (m, 2H), 1.57−1.49 (m, 2H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 142.4, 128.3, 128.2, 128.6, 49.8, 44.2, 35.8, 29.8, 29.2, 15.3; MS (FAB, NBA) *m/z* 178 (M^++H, 40%); HRMS (FAB, NBA) Calcd for $C_{12}H_{20}N$ (M^+) 178.1596. Found 178.1587.

***N*-Ethyl-cyclohexylmethylamine (13i)**[15] (Table 11, Entry 8): 56% product contaminated with 5% corresponding imine. ^{1}H NMR ($CDCl_3$): δ 2.62 (q, *J* = 7.1 Hz, 2H), 2.43 (d, *J* = 6.8 Hz, 2H), 1.74−1.65 (m, 5H), 1.48−1.41 (m, 1H), 1.29−1.14 (m, 3H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.99−0.85 (m, 2H).

***N*-Ethyl-4-methoxybenzylamine (13j)**[16] (Table 11, Entry 9): 98 % as colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.23 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 3.80 (s, 3H), 3.73 (s, 2H), 2.67 (q, *J* = 7.2 Hz, 2H), 1.12 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 158.5, 132.7, 129.3, 128.2, 55.2, 53.4, 43.6, 15.3.

***N*-(2-Cyclohexylethyl)-*N*-ethylamine (13k')** (Table 11, Entry 10): 97% as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 2.67−2.60 (m, 4H), 1.71−1.68 (m, 5H), 1.38 (q, *J* = 7.2 Hz, 2H), 1.31–1.16 (m, 4H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.95−0.87 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 47.6, 44.3, 37.9, 35.8, 33.5, 26.6, 26.3, 15.4; MS (EI) *m/z* 155 (M^+, 10%); HRMS (EI) Calcd for $C_{10}H_{21}N$ (M^+) 155.1683. Found 155.1674.

***N*-Ethyl-2-morpholinoethanamine (13l)**[17] (Table 11, Entry 12): 90% product contaminated with 5% corresponding imine and 4% 2-morpholinoethanamine. ^{1}H NMR ($CDCl_3$): δ 3.72−3.70 (m, 4H), 2.71 (t, *J* = 6.1 Hz, 2H), 2.66 (q, *J* = 7.3 Hz, 2H) , 2.50 (t, *J* = 6.1 Hz, 2H), 2.45 (brs, 4H), 1.21 (t, *J* = 7.3 Hz, 3H).

***N*-Ethyl-6-hydroxyhexylamine (13m)** (Table 11, Entry 13): 99% as a colorless oil. ^{1}H NMR

($CDCl_3$): δ 3.64 (t, *J* = 6.6 Hz, 2H), 2.65 (q, *J* = 7.1 Hz, 2H), 2.61 (t, *J* = 7.3 Hz, 2H), 1.61−1.42 (m, 4H), 1.38−1.36 (m, 4H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 62.4, 49.5, 44.0, 32.6, 29.8, 27.0, 25.6, 15.0; MS (FAB, NBA) *m/z* 146 (M^++H, 52%); HRMS (FAB, NBA) Calcd for $C_8H_{20}NO$ (M^++H) 146.1545. Found 146.1551.

Procedure for the Reductive *N,N*-Dialkylation of Primary Alkylamine (12) and *N*-Alkylation of Secondary Amine (15) (Tables 12−14 and 16): After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of **12a** (1.0 mmol), 10% Pd/C (Aldrich, 10 wt% of **12 or 15**), RCN (2.0 or 3.0 mmol) and additive (1.0–5.0 equiv) in solvent (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for a given reaction time. The reaction mixture was filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm) and the filtrate was concentrated under reduced pressure. [When water soluble additive such as NH_4OAc, AcOH, etc. was added to the reaction, the residue was partitioned between Et_2O (10 mL) and water (10 mL). The aqueous phase was extracted with Et_2O (10 mL×3), and then combined the organic phases were washed with brine (10 mL), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure.] The ratio of **12a**, **13a** and **14a** (**15** and **16**) was confirmed by ^{1}H NMR of the crude mixture in $CDCl_3$. The crude mixture was purified by flash silica gel column chromatography, if necessary.

***N,N*-Diethyldecylamine (14a)**[3] (Table 10, Entry 1; Table 12, Entry 8 and 9): 97% and 99% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.51 (t, *J* = 7.2 Hz, 4H), 2.40 (t, *J* = 7.8 Hz, 2H), 1.47−1.42 (m, 2H), 1.38−1.20 (m, 14H), 1.02 (t, *J* = 7.2 Hz, 6H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 53.1, 46.9, 31.9, 29.6, 29.6, 29.3, 27.8, 27.0, 22.7, 14.1, 11.7; MS (FAB, Gly) *m/z* 214 (M^++H, 17%); HRMS (FAB, Gly) Calcd for $C_{14}H_{32}N$ (M^++H) 214.2535. Found 214.2530.

***N,N*-Dipropyldecylamine (14b)**[18] (Table 13, Entry 1): 89% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.40−2.34 (m, 6H), 1.49−1.30 (m, 6H), 1.26 (brs, 14H), 0.90−0.85 (m, 9H). ^{13}C NMR ($CDCl_3$): δ 56.3, 54.3, 31.9, 29.6, 29.3, 27.7, 27.1, 22.6, 20.2, 14.1, 12.0; MS (EI) *m/z* 241 (M^+, 6%), 240 (5), 212 (100), 114 (75), 86 (24).

***N,N*-Dibutyldecylamine (14c)**[3] (Table 13, Entry 2): 82% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.40−2.36 (m, 6H), 1.44−1.37 (m, 6H), 1.33−126 (m, 18H), 0.93−0.86 (m, 9H); ^{13}C NMR ($CDCl_3$): δ 54.3, 54.0, 31.9, 29.6, 29.2, 27.7, 27.0, 22.6, 20.8, 14.1; MS (FAB, NBA) *m/z* 270 (M^++H, 52%); HRMS (EI) Calcd for $C_{18}H_{40}N$ (M^++H) 270.3161. Found 270.3158.

***N,N*-Diamyldecylamine (14d)**[3] (Table 13, Entry 3): 71% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.37 (t, *J* = 7.6 Hz, 6H), 1.46−1.20 (m, 24H), 0.89−0.86 (m, 9H); ^{13}C NMR ($CDCl_3$): δ 54.1, 31.9, 29.8, 29.6, 29.3, 27.6, 26.9, 22.6, 14.1; MS (FAB, Gly) *m/z* 298 (M^++H, 95%); HRMS (FAB, Gly)

Calcd for $C_{20}H_{44}N$ (M^++H) 298.3468. Found 298.3474.

***N,N*-Diethyloctylamine (14n)**[19] (Table 13, Entry 5)**:** 97% as a colorless oil. ^{1}H NMR($CDCl_3$) δ: 2.47 (q, *J* = 7.2 Hz, 4H), 2.35 (dd, *J* = 9.0, 5.6 Hz, 2H), 1.44–1.28 (m, 12H), 0.97 (t, *J* = 7.2 Hz, 6H), 0.84 (t, *J* = 6.8 Hz, 3H); MS (FAB, NBA) m/z 186 (M^++H, 32.6 %).

***N,N*-Dibutyloctylamine (14o)**[20] (Table 13, Entry 6)**:** 100% as a colorless oil. ^{1}H NMR($CDCl_3$) δ: 2.40-2.36 (m, 6H), 1.43-1.27 (m, 20H), 0.91 (t, *J* = 7.3 Hz, 6H), 0.88 (t, *J* = 3.9 Hz, 3H); ^{13}C NMR($CDCl_3$)δ: 54.1, 53.8, 31.8, 29.5, 29.3, 28.9, 27.6, 26.7, 22.6, 20.7, 14.0; MS (FAB, NBA) m/z 242 (M^++H, 26.1 %); HRMS (FAB, NBA) Calcd for $C_{16}H_{35}N$ (M^++H) 242.2848. Found 242.2842.

***N,N*-Diamyloctylamine (14p)** (Table 13, Entry 7)**:** 97% as a colorless oil. ^{1}H NMR($CDCl_3$) δ: 2.40–2.36 (m, 6H), 1.47–1.21 (m, 24H), 0.90 (t, *J* = 7.0 Hz, 6H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR($CDCl_3$) δ: 54.1, 31.8, 29.7, 29.5, 29.2, 27.5, 27.0, 26.7, 22.5, 13.9; MS (FAB, NBA) m/z 270 (M^++H, 99.7 %); HRMS (FAB, NBA) Calcd for $C_{18}H_{39}N$ (M^++H) 270.3161. Found 270.3167.

***N,N*-Diethyl-2-phenylethylamine (14g)**[21] (Table 13, Entry 8): 90% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.30−7.17 (m, 5H), 2.78−2.67 (m, 4H), 2.61 (q, *J* = 7.1 Hz, 4H), 1.07 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 140.5, 128.7, 128.4, 126.0, 54.7, 46.8, 33.0, 11.5; MS (FAB, NBA) *m/z* 178 (M^++H, 85%); HRMS (FAB, NBA) Calcd for $C_{12}H_{19}N$ (M^++H) 178.1596. Found 178.1602.

***N,N*-Diethylcyclohexylmethylamine (14i)**[22] (Table 13, Entry 9): 75% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 2.48 (q, *J* = 7.1 Hz, 4H), 2.16 (t, *J* = 6.8 Hz, 2H), 1.78−1.75 (m, 2H), 1.71−1.64 (m, 3H), 1.44−1.36 (m, 1H), 1.25−1.13 (m, 3H), 0.99 (t, *J* = 7.1 Hz, 6H), 0.88−0.79 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 61.0, 45.0, 36.3, 32.1, 26.8, 26.3; MS (FAB, NBA) *m/z* 170 (M^++H, 50%); HRMS (FAB, NBA) Calcd for $C_{11}H_{23}N$ (M^++H) 170.1909. Found 170.1917.

***N,N*-Diethylcyclohexylamine (14q)** (Table 13, Entry 10, commercially available): 69% product contaminated with 7% *N*-ethylcyclohexylamine. ^{1}H NMR ($CDCl_3$): δ 2.54 (q, *J* = 7.1 Hz, 4H), 2.53−2.48 (m, 1H), 1.86−1.60 (m, 5H), 1.31−1.08 (m, 5H), 1.03 (t, *J* = 7.1 Hz, 6H).

***N,N*-Diethyl-6-hydroxyhexylamine (14m)**[23] (Table 13, Entry 11): 100% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 3.63 (t, *J* = 6.3 Hz, 2H), 2.86 (q, *J* = 7.1 Hz, 4H), 2.73 (t, *J* = 8.1 Hz, 2H), 1.65−1.53 (m, 4H), 1.47−1.36 (m, 4H), 1.16 (t, *J* = 7.1 Hz, 6H).

Dibutylethylamine (16a) (Table 14, Entry 1, commercially available): 76% as a colorless oil. ^{1}H

NMR ($CDCl_3$): δ 2.50 (q, *J* = 7.1 Hz, 2H), 2.40 (t, *J* = 7.5 Hz, 4H), 1.46−1.25 (m, 8H), 1.00 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.5 Hz, 6H).

***N*-Ethylpiperizine (16b)** (Table 14, Entries 2 and 3, commercially available): 76% and 74% yields were determined by GC and decylamine was used as an internal standard.

***N*-Ethylmorphorine (16c)** (Table 14, Entry 4, commercially available): 82% and 88% yields were determined by GC and decylamine was used as an internal standard.

***N*-Butylmorphorine (16d)**[24] (Table 14, Entry 5): 51% as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 3.72 (t, *J* = 4.9 Hz, 4H), 2.43−2.30 (m, 8H), 1.51–1.19 (m, 4H), 0.92 (t, *J* = 7.3 Hz, 3H).

***N*-Ethyl-4-hydroxypiperidine (16e)**[25] (Table 14, Entry 6): 98% as a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 3.72−3.69 (m, 1H), 2.80−2.77 (m, 2H), 2.40 (q, *J* = 7.2 Hz, 2H), 2.14−2.09 (m, 2H), 1.94−1.89 (m, 2H), 1.78 (brs, OH), 1.65−1.56 (m, 2H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 68.0, 52.2, 50.6, 34.4, 12.2; MS (EI) *m/z* 129 (M^+, 28%), 114 (100), 69 (28); HRMS (EI) Calcd for $C_7H_{15}NO$ (M^+) 129.1156. Found 129.1154.

1-Ethyl-4-(3'-phenylpropyl)piperazine (16f') (Table 14, Entry 7): 80% product contaminated with 4% 4-(3'-phenylpropyl)piperazine (**15e'**). ^{1}H NMR ($CDCl_3$): δ 7.29−7.15 (m, 5H), 2.63 (t, *J* = 7.8 Hz, 2H), 2.49 (brs, 8H), 2.41 (q, *J* = 7.3 Hz, 2H), 2.38 (t, *J* = 7.7 Hz, 2H), 1.86−1.79 (m, 2H), 1.08 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 142.2, 128.3, 128.2, 125.7, 58.0, 53.2, 52.8, 52.3, 33.7, 28.6, 11.9; MS (EI) *m/z* 232 (M^+, 53%), 127 (100), 91 (30); HRMS (EI) Calcd for $C_{15}H_{24}N_2$ (M^+) 232.1940. Found 232.1936.

Synthesis of Unsymmetrical Tertiary Amines (Table 15):

***N*-Butyl-*N*-ethyldecylamine (17a)** (Table 15, Entry 1): After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of decylamine (**12a**) (79 mg, 0.50 mmol), 5% Rh/C (7.9 mg, 10 wt% of the amine) and PrCN (87 μL, 1.0 mmol) in MeOH (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for 34 h. The reaction mixture was filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm) and the filtrate was concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography ($CHCl_3$/MeOH = 50:1) to provide *N*-butyldecylamine (**13c**) (87 mg, 82%). The resulted **13c** was used as a substrate for the following reaction. After two vacuum/H_2 cycles to

remove air from the reaction tube, the stirred mixture of **13c** (53 mg, 0.25 mmol), MeCN (65 μL, 1.3 mmol), $AcONH_4$ (19 mg, 0.25 mmol), 10% Pd/C [10 mg (Aldrich 20,569-9), 20 wt% of the amine] in MeOH (0.50 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for 34 h. The reaction mixture was filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm) and the filtrate was partitioned between Et_2O (10 mL) and water (10 mL). The aqueous phase was extracted with Et_2O (10 mL×3), and then combined the organic phases were washed with brine (10 mL), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography ($CHCl_3$/MeOH = 100:1) to provide the titled compound (**17a**) (53.3 mg, 88% as a pale yellow oil). ^{1}H NMR ($CDCl_3$): δ 2.68 (q, *J* = 7.1 Hz, 2H), 2.58−2.54 (m, 4H), 1.50−1.46 (m, 4H), 1.35−1.26 (m, 16H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H) , 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 51.9, 51.6, 46.9, 31.8, 31.7, 29.4, 29.2, 29.1, 27.0, 25.8, 23.7, 22.6, 20.3, 14.0, 13.6, 9.2; MS (FAB, NBA) *m/z* 242 (M^++H, 100%); HRMS (FAB, NBA) Calcd for $C_{16}H_{36}N$ (M^++H) 242.2848. Found 242.2846.

***N*-Ethyl-*N*-propyldecylamine (17b)** (Table 15, Entry 2): After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of decylamine (**12a**) (79 mg, 0.50 mmol), 5% Rh/C (7.9 mg, 10 wt% of the amine) and EtCN (71 μL, 1.0 mmol) in MeOH (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for 24 h. The reaction mixture was added MeOH (20 mL) and filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm). The filtrate was concentrated under reduced pressure and the crude mixture was used for the following reaction without purification. After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of the above crude mixture, MeCN (130 μL, 2.5 mmol), $AcONH_4$ (39 mg, 0.50 mmol), 10% Pd/C [20 mg (Aldrich 20,569-9), 25 wt% of the amine] in MeOH (0.50 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for 34 h. The reaction mixture was filtrated through a membrane filter (Millipore, Millex®-LH, 0.45 μm) using MeOH (20 mL) and concentrated under reduced pressure. The filtrate was partitioned between EtOAc (10 mL) and water (10 mL). The aqueous phase was extracted with EtOAc (10 mL×3), and then combined the organic phases were washed with brine (10 mL), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (CH_2Cl_2/MeOH = 10:1) to provide the titled compound (**17b**) (78 mg, 69%). ^{1}H NMR ($CDCl_3$): δ 3.10 (q, *J* = 7.2 Hz, 2H), 2.96–2.89 (m, 4H), 1.87–1.82 (m, 2H), 1.78 (brs, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.32–1.24 (m, 14H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 53.1, 51.5, 46.9, 31.5, 29.1, 29.1, 28.9, 28.8, 26.6, 22.8, 22.3, 16.7, 13.8, 11.0, 8.5. MS (EI) m/z 227 (M^+ 10%), 212 (10), 198 (60), 100 (100), 86 (12), 72 (16), 43 (10). HRMS (EI) Calcd for $C_{15}H_{33}N$ (M^+): 227.2613. Found: 227.2615.

***N*-Ethyl-*N*-pentyldecylamine (17c)** (Table 15, Entry 3): After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of decylamine (**12a**) (79 mg, 0.50 mmol), 5% Rh/C (7.9

mg, 10 wt% of the amine) and BuCN (100 μL, 1.0 mmol) in MeOH (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for 24 h. The reaction mixture was added MeOH (20 mL) and filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm). The filtrate was concentrated under reduced pressure and the crude mixture was used for the following reaction without purification. After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of the above crude mixture, MeCN (130 μL, 2.5 mmol), $AcONH_4$ (39 mg, 0.50 mmol), 10% Pd/C [20 mg (Aldrich 20,569-9), 25 wt% of the amine] in MeOH (0.50 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for 34 h. The reaction mixture was filtrated through a membrane filter (Millipore, Millex®-LH, 0.45 μm) using MeOH (20 mL) and concentrated under reduced pressure. The filtrate was partitioned between EtOAc (10 mL) and water (10 mL). The aqueous phase was extracted with EtOAc (10 mL×3), and then combined the organic phases were washed with brine (10 mL), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (CH_2Cl_2/MeOH = 10:1) to provide the titled compound **17c** (68 mg, 53%). ^{1}H NMR ($CDCl_3$):δ3.10 (q, *J* = 7.5 Hz, 2H), 2.96–2.93 (m, 4H), 1.83–1.78 (m, 4H), 1.40 (t, *J* = 7.5 Hz, 3H), 1.38–1.25 (m, 18H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ51.5, 46.9, 31.6, 29.1, 29.1, 29.0, 28.8, 28.6, 26.6, 22.9, 22.6, 22.4, 21.9, 13.8, 13.6, 8.5 (one signal could not be located because of it's overlap with another signal). MS (EI) m/z 255 (M^+, 5%), 240 (10), 224 (10), 198 (60), 154 (10), 128 (70), 98 (8), 84 (8), 72 (100). HRMS (EI) Calcd for $C_{17}H_{37}N$ (M^+): 255.2926. Found: 255.2931.

***N*-Ethyl-*N*-propyl-2-phenetylamine (17d)**[26] (Table 15, Entry 4): After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of 2-phenethylamine (**12b**) (121 mg, 1.0 mmol), 5% Rh/C (24 mg, 20 wt% of the amine) and MeCN (100 μL, 2.0 mmol) in MeOH (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for 28 h. The reaction mixture was added MeOH (20 mL) and filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm). The filtrate was concentrated under reduced pressure and the crude mixture was used for the following reaction without purification. After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of the above crude mixture, EtCN (360 μL, 5.0 mmol), $AcONH_4$ (77 mg, 1.0 mmol), 10% Pd/C [33 mg (Aldrich 20,569-9), 27 wt% of the amine] in MeOH (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for 7.0 h. The reaction mixture was filtrated through a membrane filter (Millipore, Millex®-LH, 0.45 μm) using MeOH (20 mL) and concentrated under reduced pressure. The filtrate was partitioned between EtOAc (10 mL) and water (10 mL). The aqueous phase was extracted with EtOAc (10 mL×3), and then combined the organic phases were washed with brine (10 mL), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (CH_2Cl_2/MeOH = 30:1) to provide the titled compound (**17d**) (179 mg, 94% as a pale yellow oil). ^{1}H NMR ($CDCl_3$): δ 7.30−7.17 (m, 5H), 2.77−2.64 (m, 4H), 2.63−2.58 (m, 2H), 2.48−2.43 (m, 2H), 1.54−1.42 (m, 2H), 1.05 (t, *J* = 7.1 Hz,

3H), 0.89 (t, *J* = 7.3 Hz, 3H).

***N*-Ethyl-*N*-pentyl-2-phenetylamine (17e)** (Table 15, Entry 5): After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of 2-phenethylamine (**12b**) (60 mg, 0.50 mmol), 5% Rh/C (6.0 mg, 10 wt% of the amine) and BuCN (105 μL, 1.00 mmol) in MeOH (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for 28 h. The reaction mixture was added MeOH (20 mL) and filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm). The filtrate was concentrated under reduced pressure and the crude mixture was used for the following reaction without purification. After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of the above crude mixture, MeCN (130 μL, 2.5 mmol), $AcONH_4$ (39 mg, 0.50 mmol), 10% Pd/C [20 mg (Aldrich 20,569-9), 33 wt% of the amine] in MeOH (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for 7.0 h. The reaction mixture was filtrated through a membrane filter (Millipore, Millex®-LH, 0.45 μm) using MeOH (20 mL) and concentrated under reduced pressure. The filtrate was partitioned between EtOAc (10 mL) and water (10 mL). The aqueous phase was extracted with EtOAc (10 mL×3), and then combined the organic phases were washed with brine (10 mL), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (CH_2Cl_2/MeOH = 30:1) to provide the titled compound (**17e**) (71.8 mg, 66%). ^{1}H NMR ($CDCl_3$): δ7.31 (m, 2H), 7.26–7.22 (m, 3H), 3.13–3.09 (m, 6H), 2.96 (t, *J* = 8.3 Hz, 2H), 1.73 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.35–1.29 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ136.4, 128.8, 128.5, 127.0, 53.3, 51.7, 47.0, 30.2, 28.8, 22.9, 22.0, 13.7, 8.7. MS (FAB, NBA) m/z 220 (M^++H, 8%), 89 (12). HRMS (FAB, NBA) Calcd for $C_{15}H_{26}N$ (M^++H): 220.2065. Found: 220.2073.

Synthesis of phenylacetamidine (18a)[27] (eq 11): An oven-dried round bottom flask was evacuated and backfilled with nitrogen. Anhydrous MeCN (5.7 mL, 110 mmol) and aniline (9.8 g, 100 mmol) was added to the flask. $AlCl_3$ (14 g, 100 mmol) was added slowly with stirring over a period of 1.0 h, and stirred for 1.0 h at 100 °C. 0.20 N HCl solution (200 mL) and activated carbon (250 mg) was added to the reaction mixture. The mixture was filtered through a celite cake and the filtrate was slowly poured into 4.0 N NaOH solution (180 mL). The mixture was extracted from $CHCl_3$ (300 mL). The organic phase was washed with water and brine, dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography ($CHCl_3$/MeOH = 5 : 1) to provide a colorless oil. The material was triturated with hexane and then recrystallized from benzene (50 mL) to provide the titled compound (**18a**) (100 mg, 74%). ^{1}H NMR ($CDCl_3$): δ 7.30−7.28 (m, 2H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.89−6.87 (m, 2H), 4.45 (brs, NH), 2.11 (s, 3H), 1.83 (brs, NH); ^{13}C NMR ($CDCl_3$): δ 154.8, 149.2, 129.4, 122.8, 121.8, 22.8; MS (EI) *m/z* 134 (M^+, 100%), 119 (46), 93 (72), 77 (70); Anal. Calcd for $C_8H_{10}N_2$: C, 71.61; H, 7.51; N, 20.88. Found C, 71.66; H, 7.51; N, 20.79.

Reaction of Phenylacetamidine (18a) under 10%Pd/C-Catalyzed Hydrogenation Conditions (eq 11): After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of **18a** (67.2 mg, 0.50 mmol), 10% Pd/C [6.7 mg (Aldrich 20,569-9), 10 wt% of **18a**] in MeOH (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for 24 h. To the reaction mixture was added MeOH (20 mL) and filtrated using a membrane filter (Millipore, Millex®-LG, 0.20 μm). The filtrate was concentrated under reduced pressure to give starting material **18a** quantitatively.

Reaction of BuCN under 10%Pd/C-Catalyzed Hydrogenation Conditions (eq 12): After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of *N*,*N*-dimethylaniline (**22**) (26 μL, 1.0 mmol), 10% Pd/C (8.3 mg, Aldrich 20,569-9) and BuCN (105 μL, 1.00 mmol) in MeOH (1.0 mL) was hydrogenated under ambient pressure (balloon) at room temperature (ca. 20 °C) for 28 h. To the reaction mixture was added MeOH (20 mL) and filtrated using a membrane filter (Millipore, Millex®-LH, 0.45 μm). The filtrate was concentrated under reduced pressure and the ratio of BuCN (77%), secondary amine (20%) and tertiary amine (3%) was confirmed by GC analysis.

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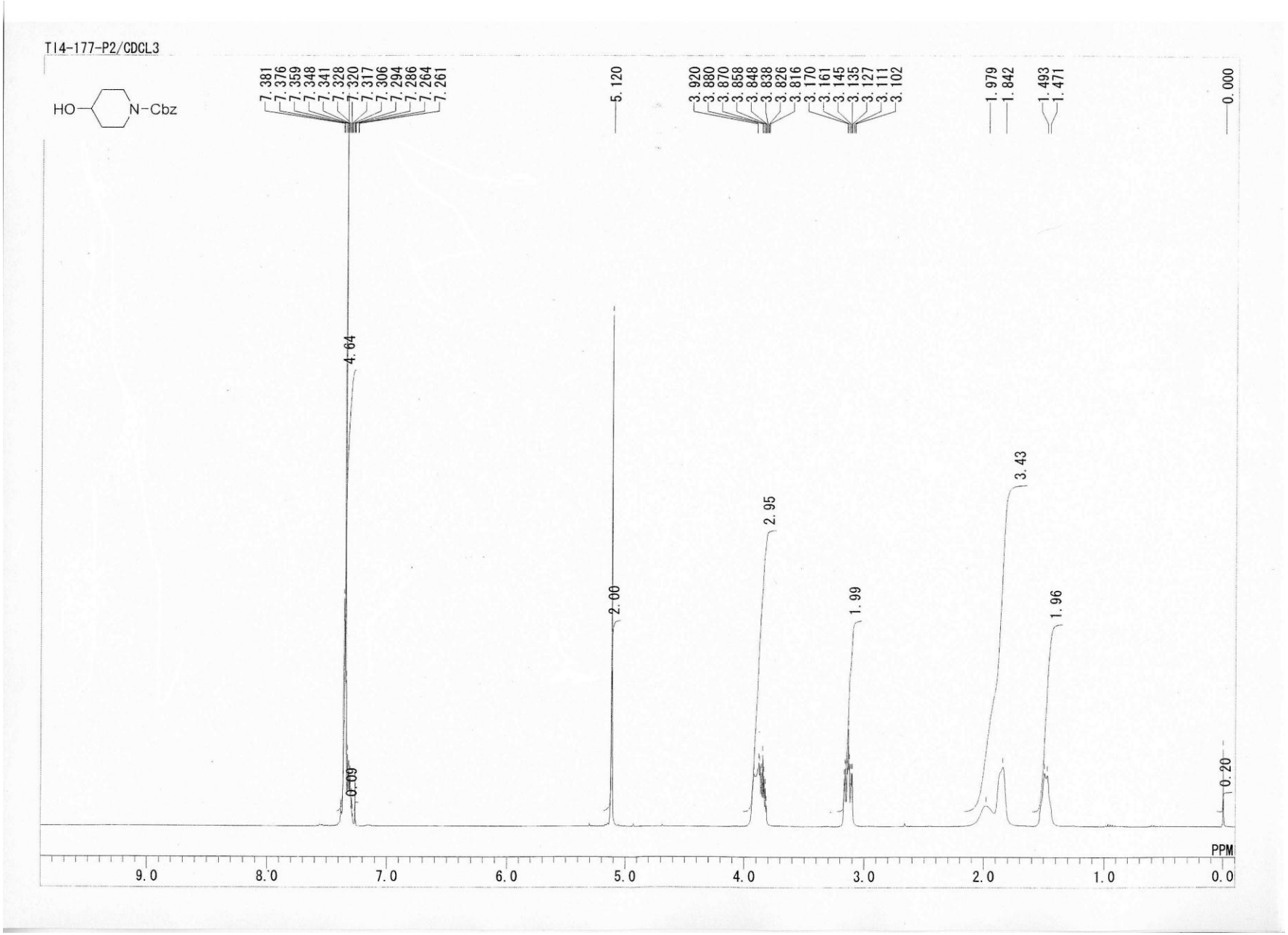

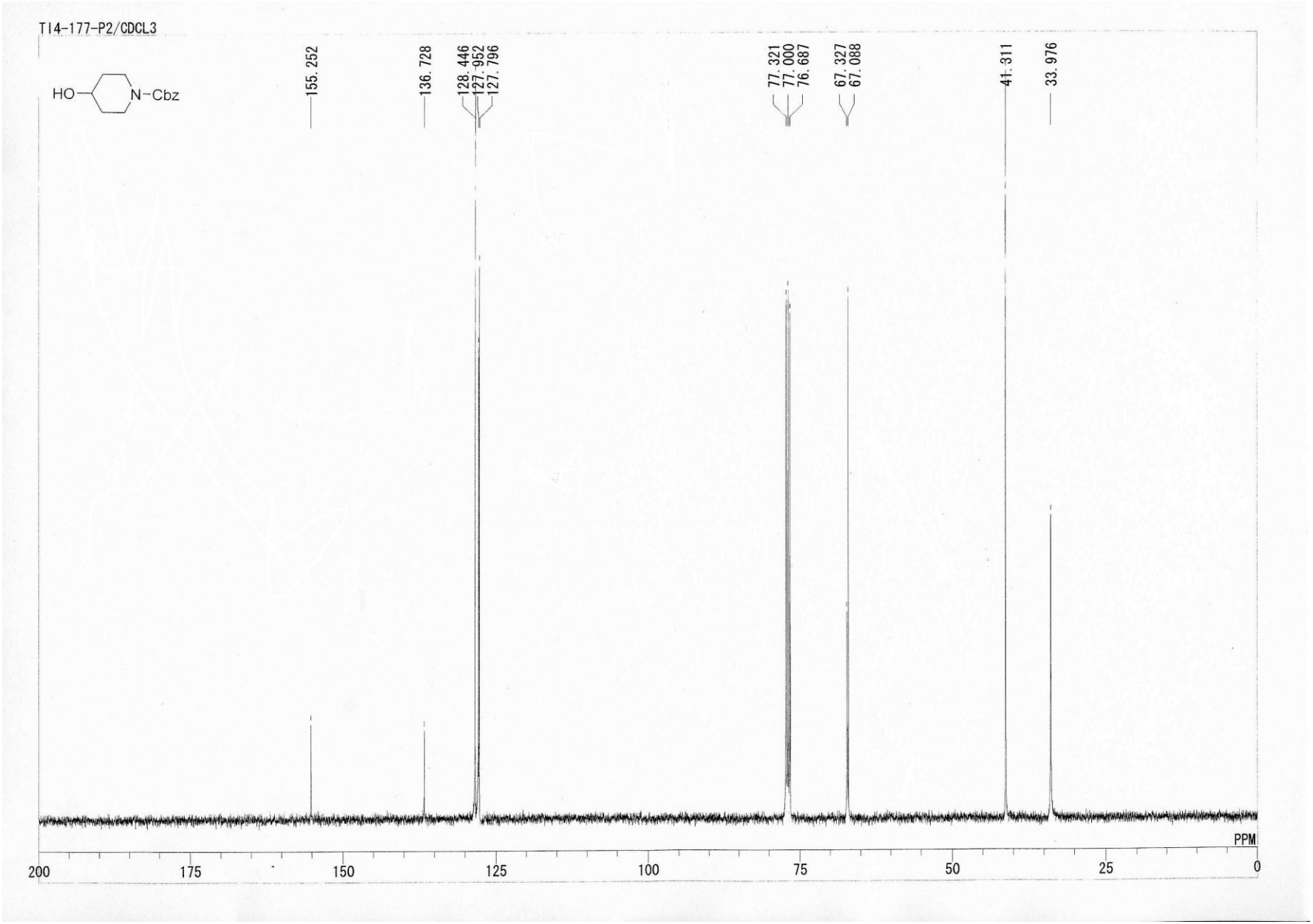

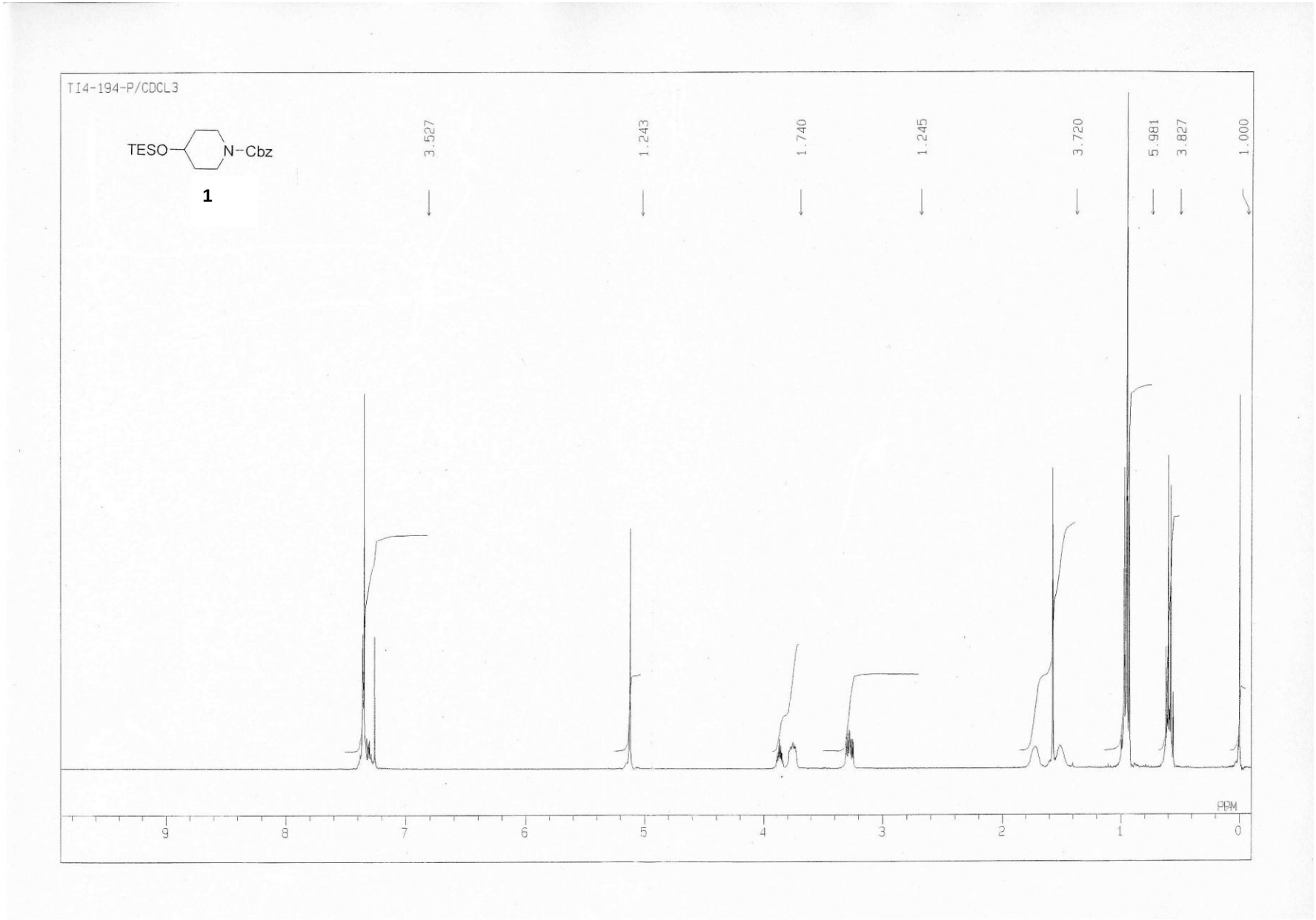

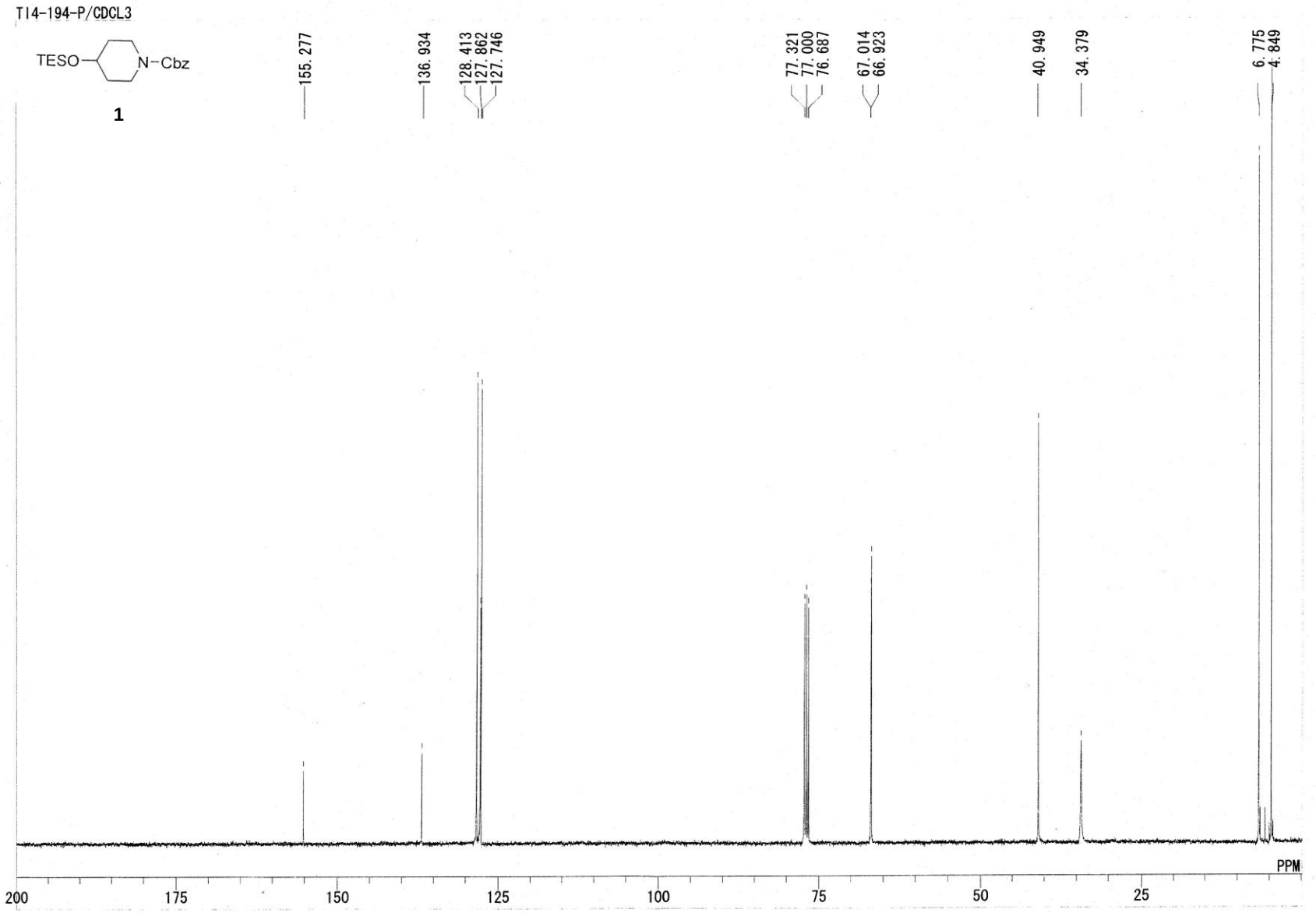

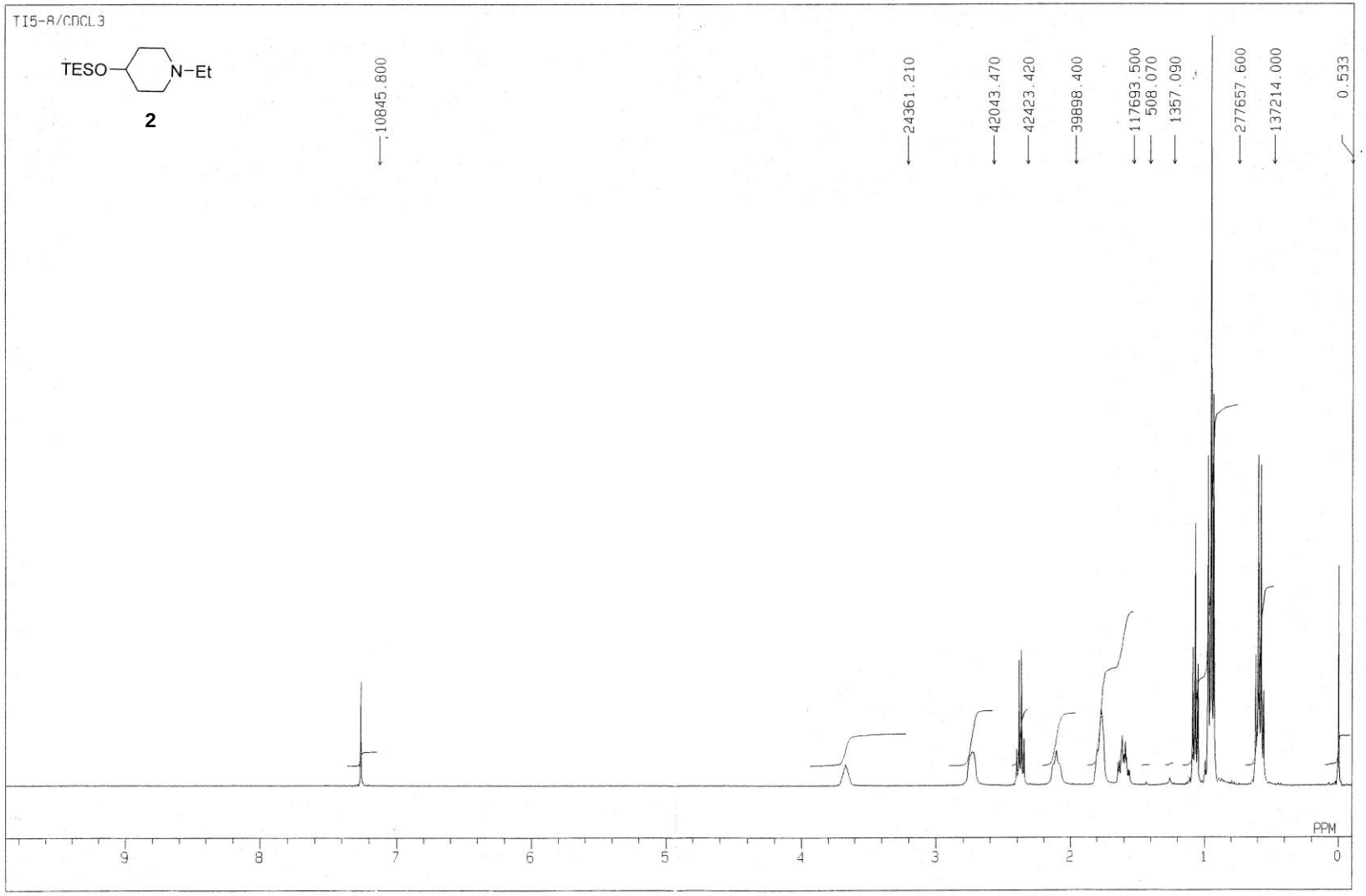

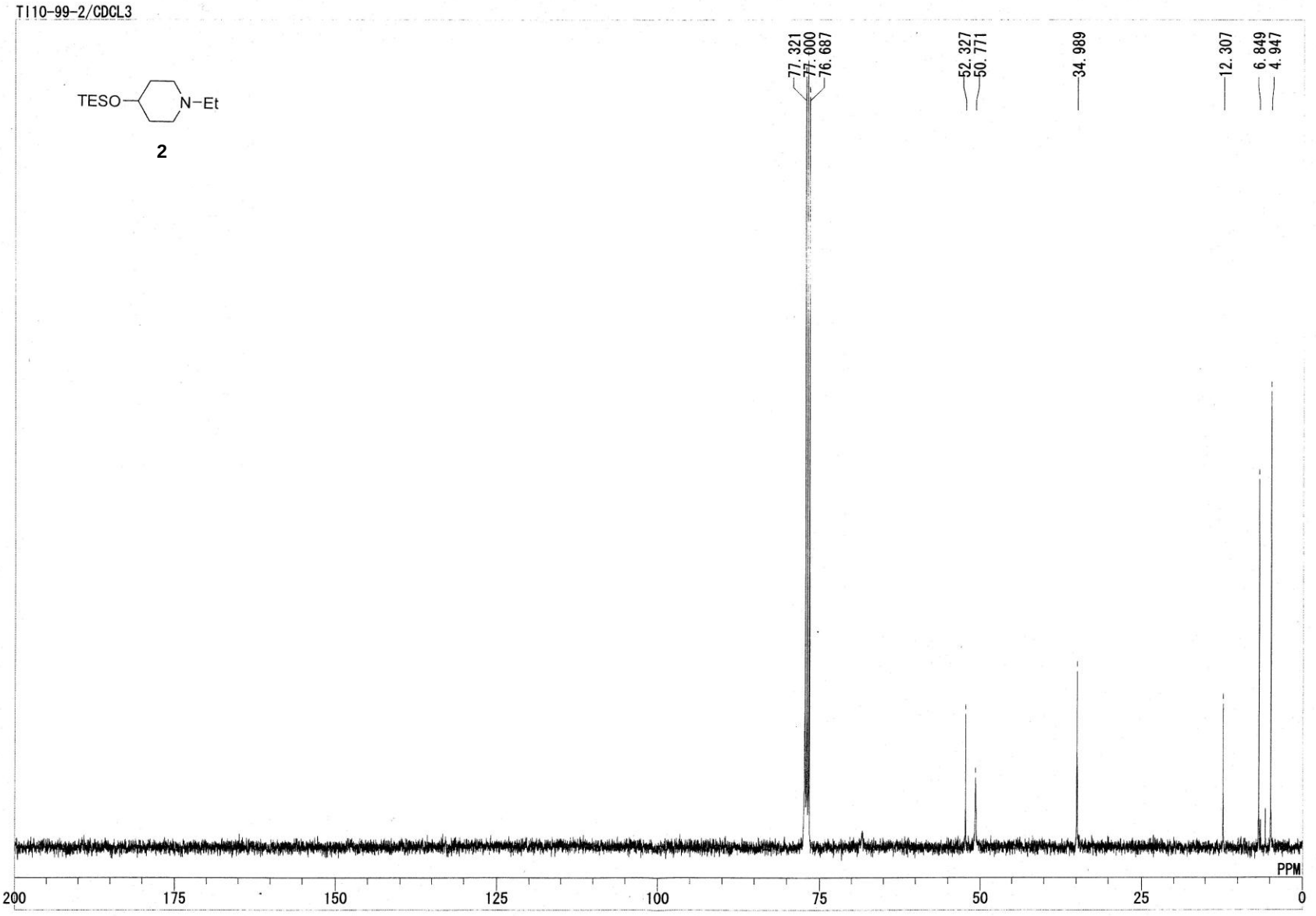

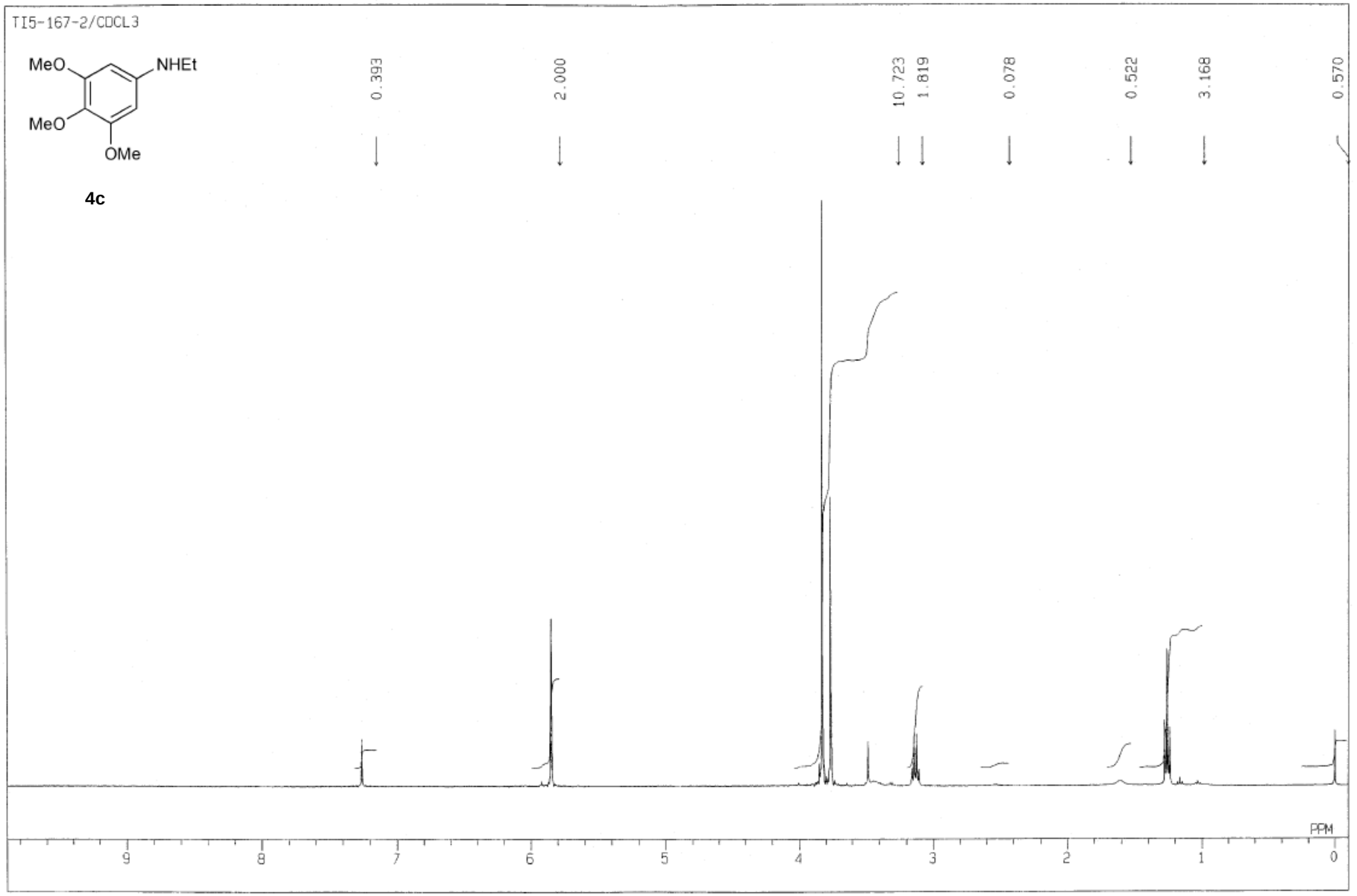

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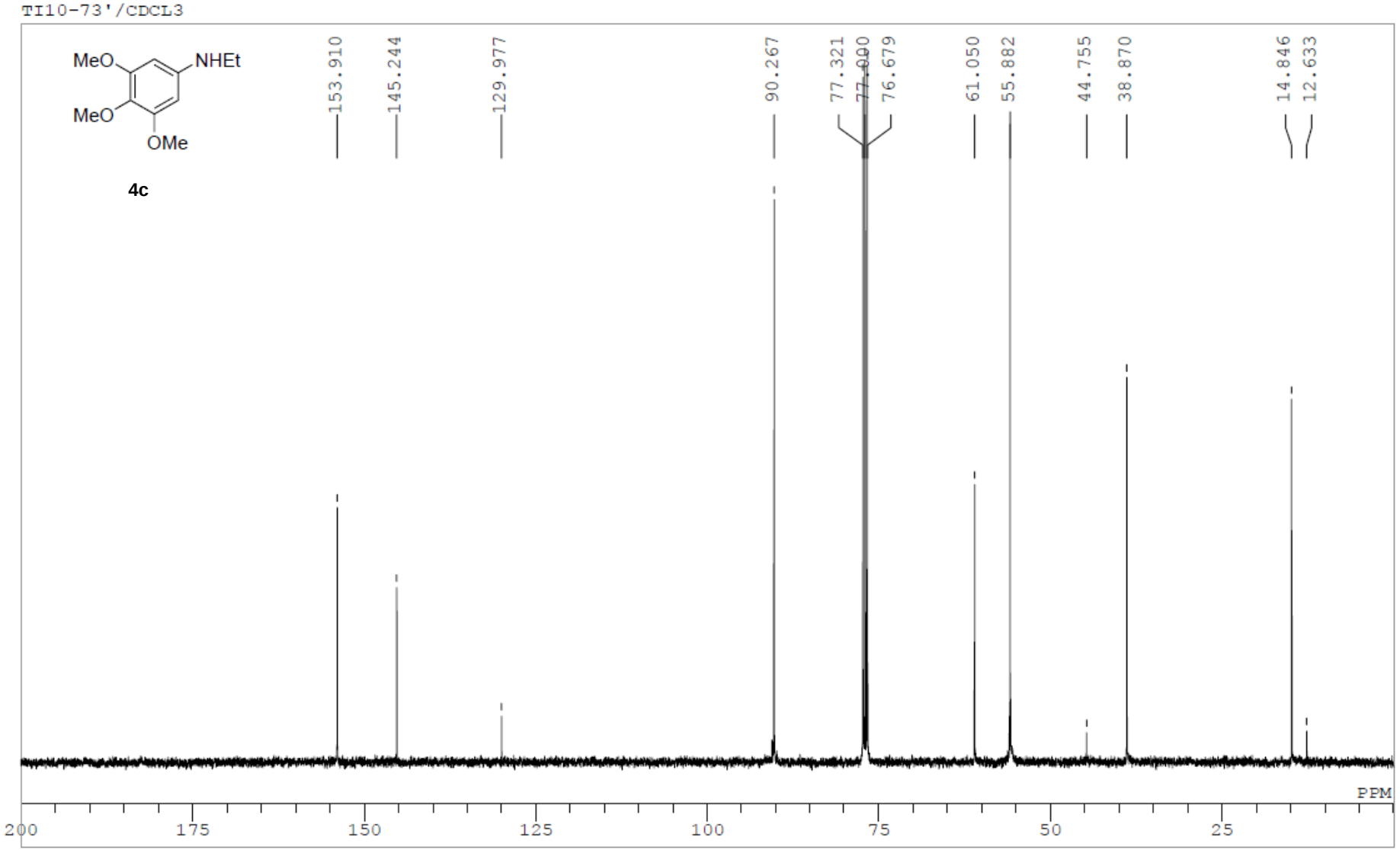

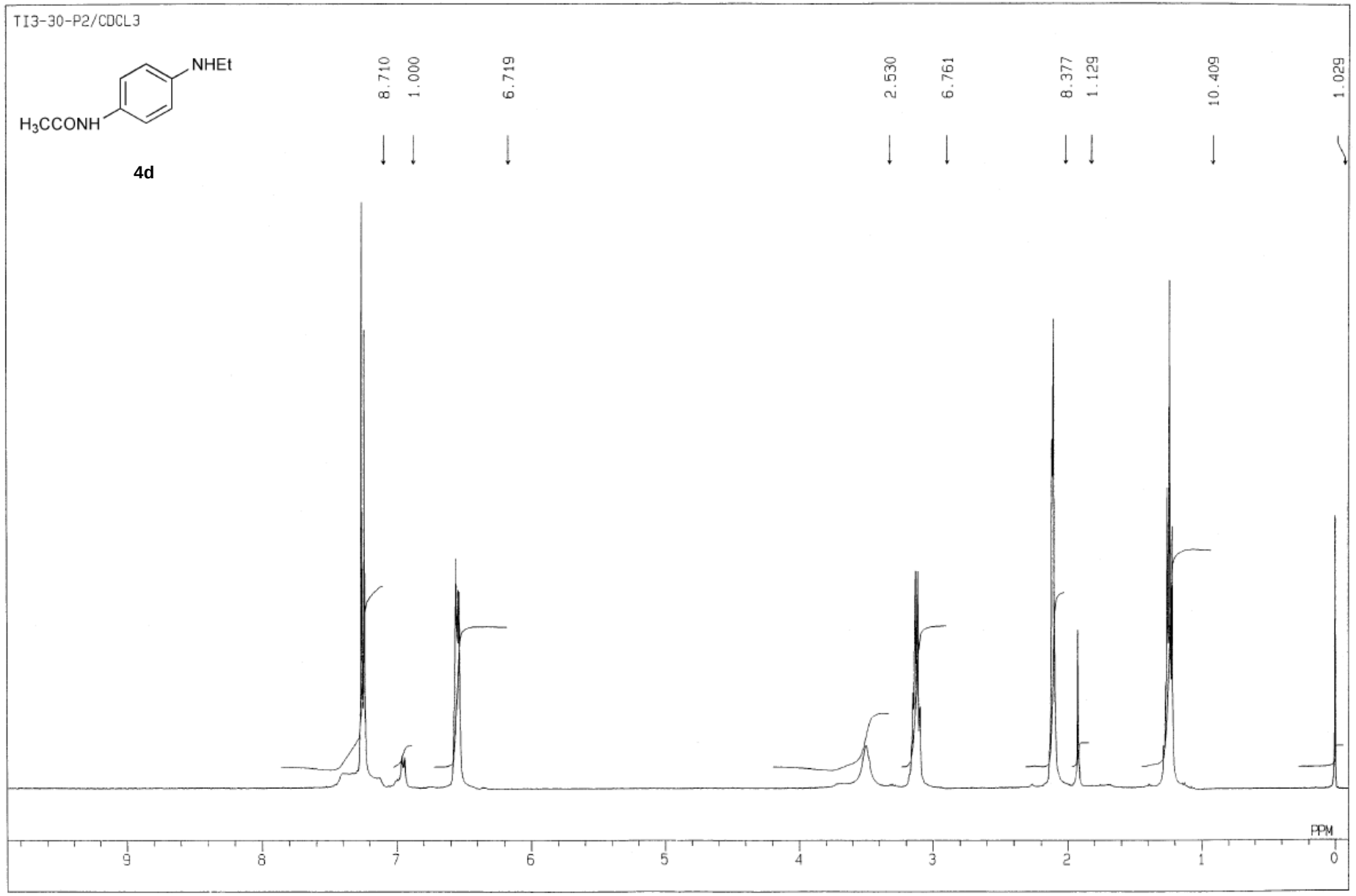

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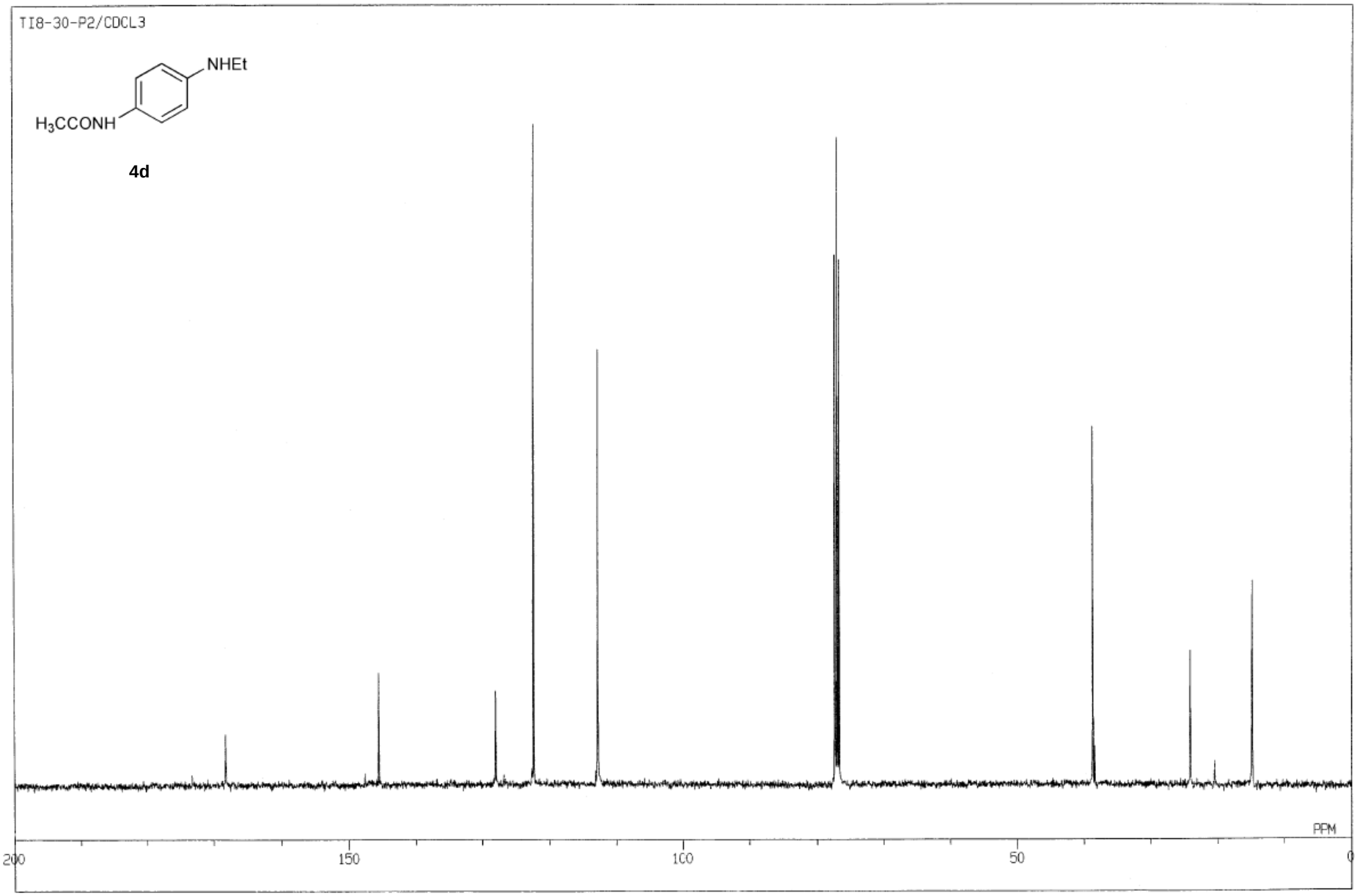

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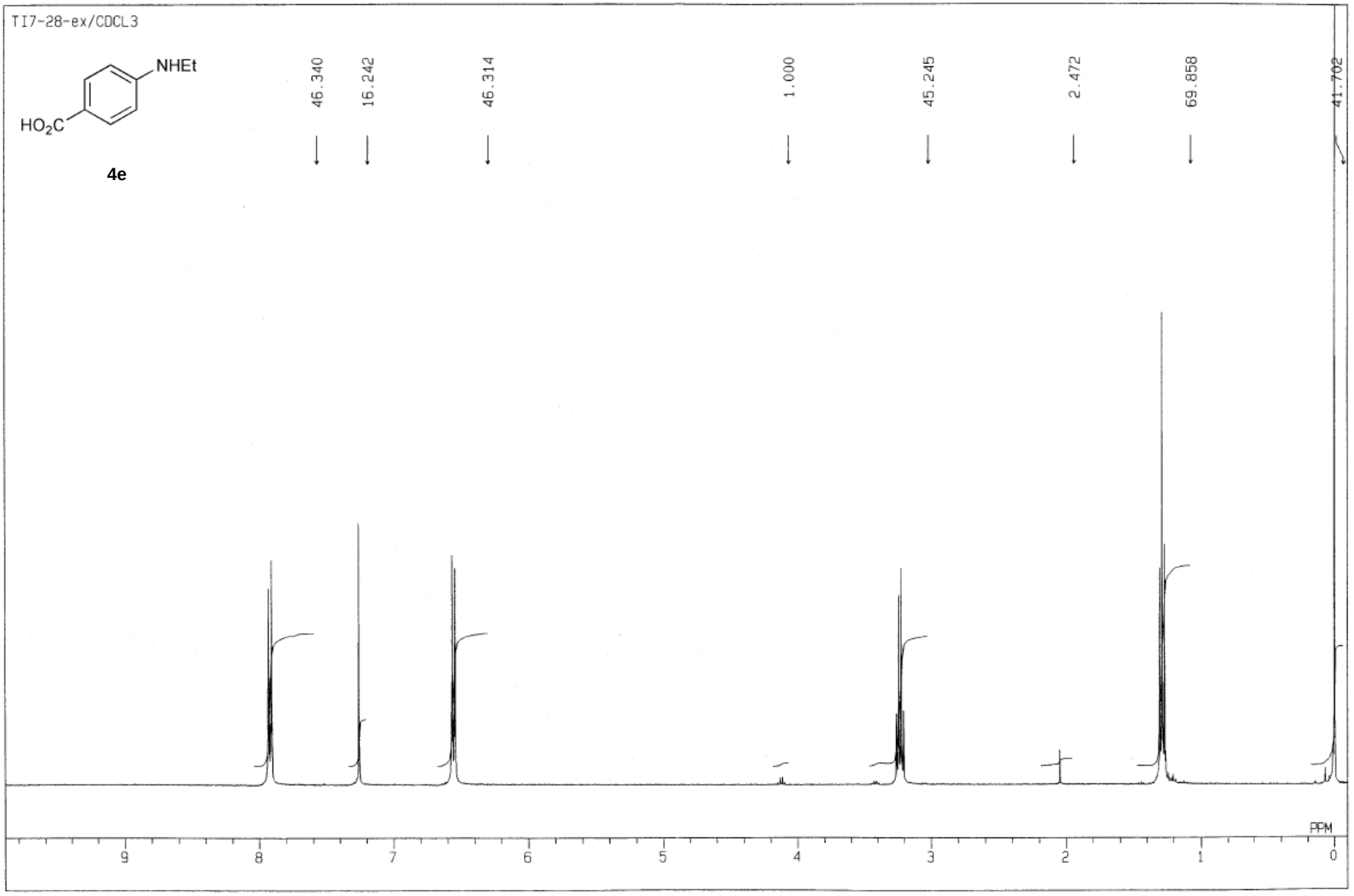

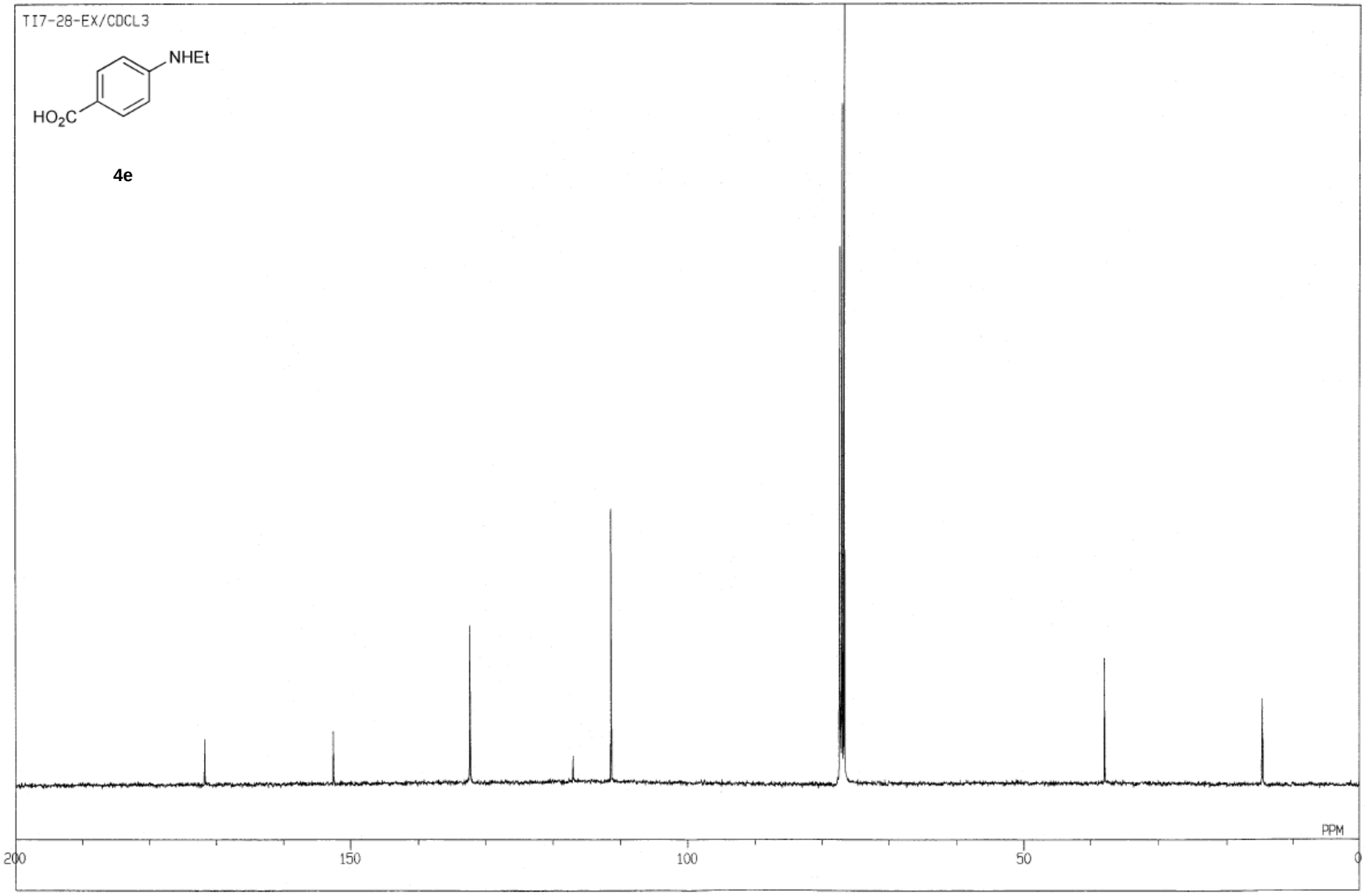

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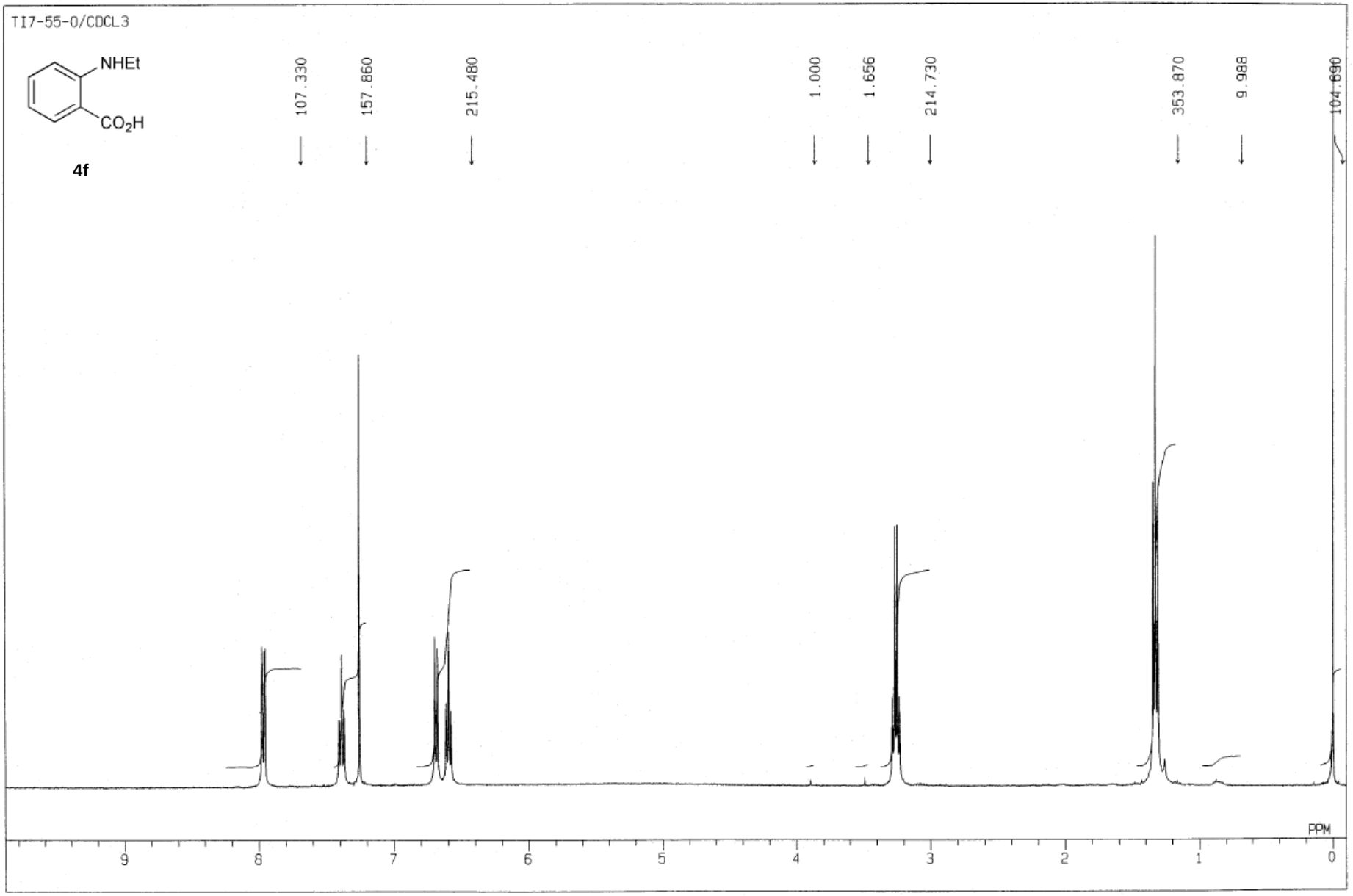

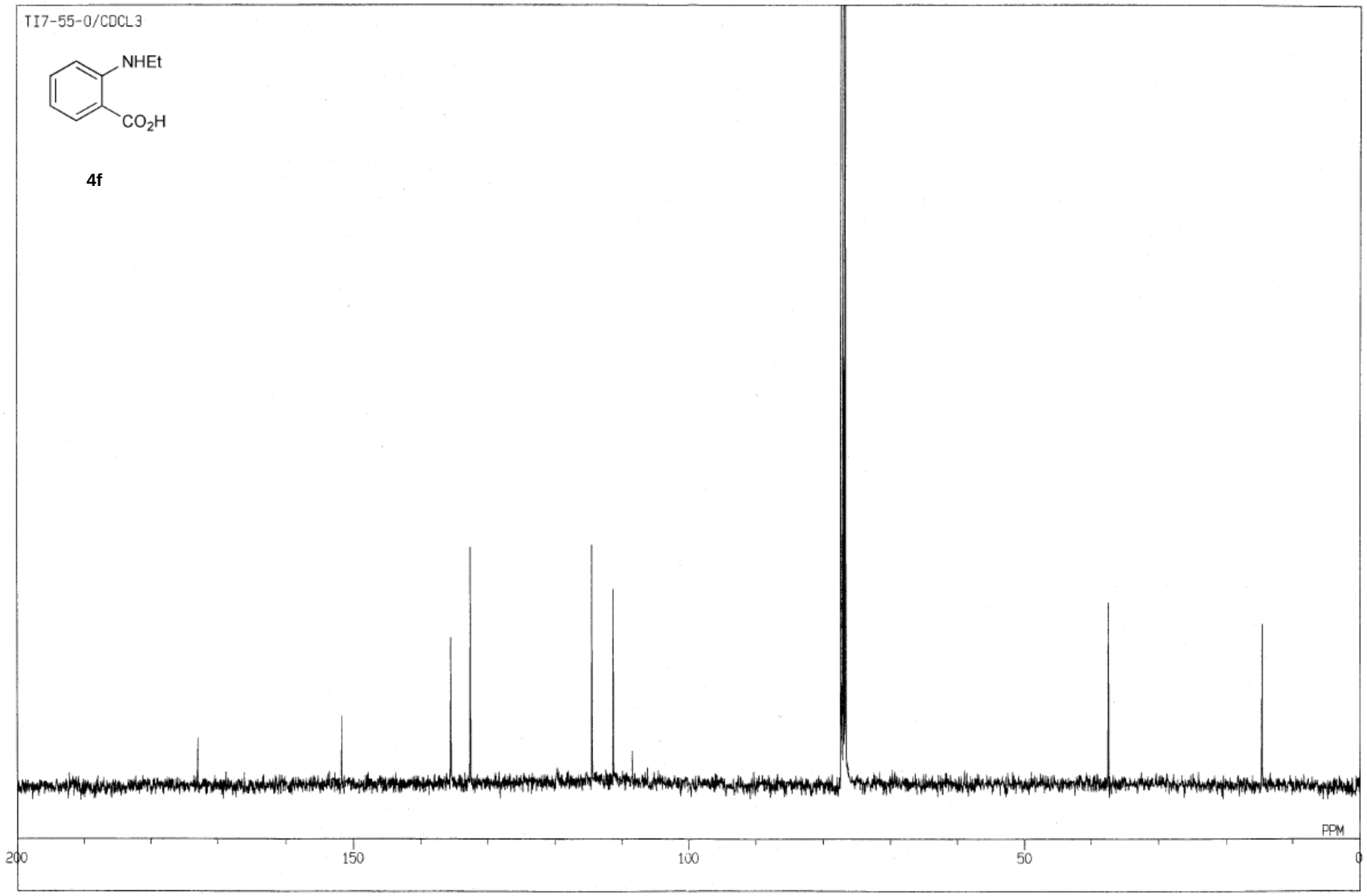

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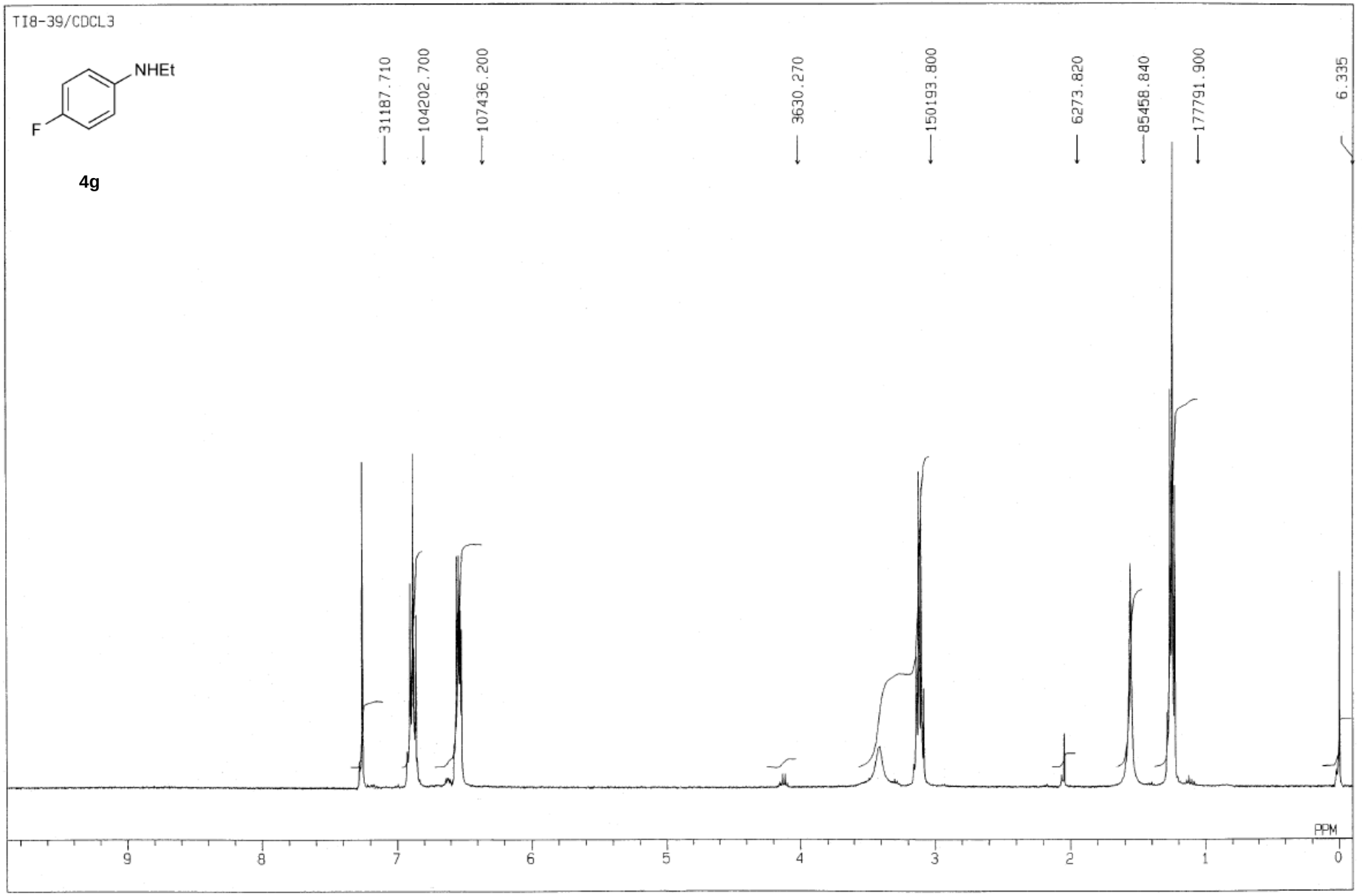

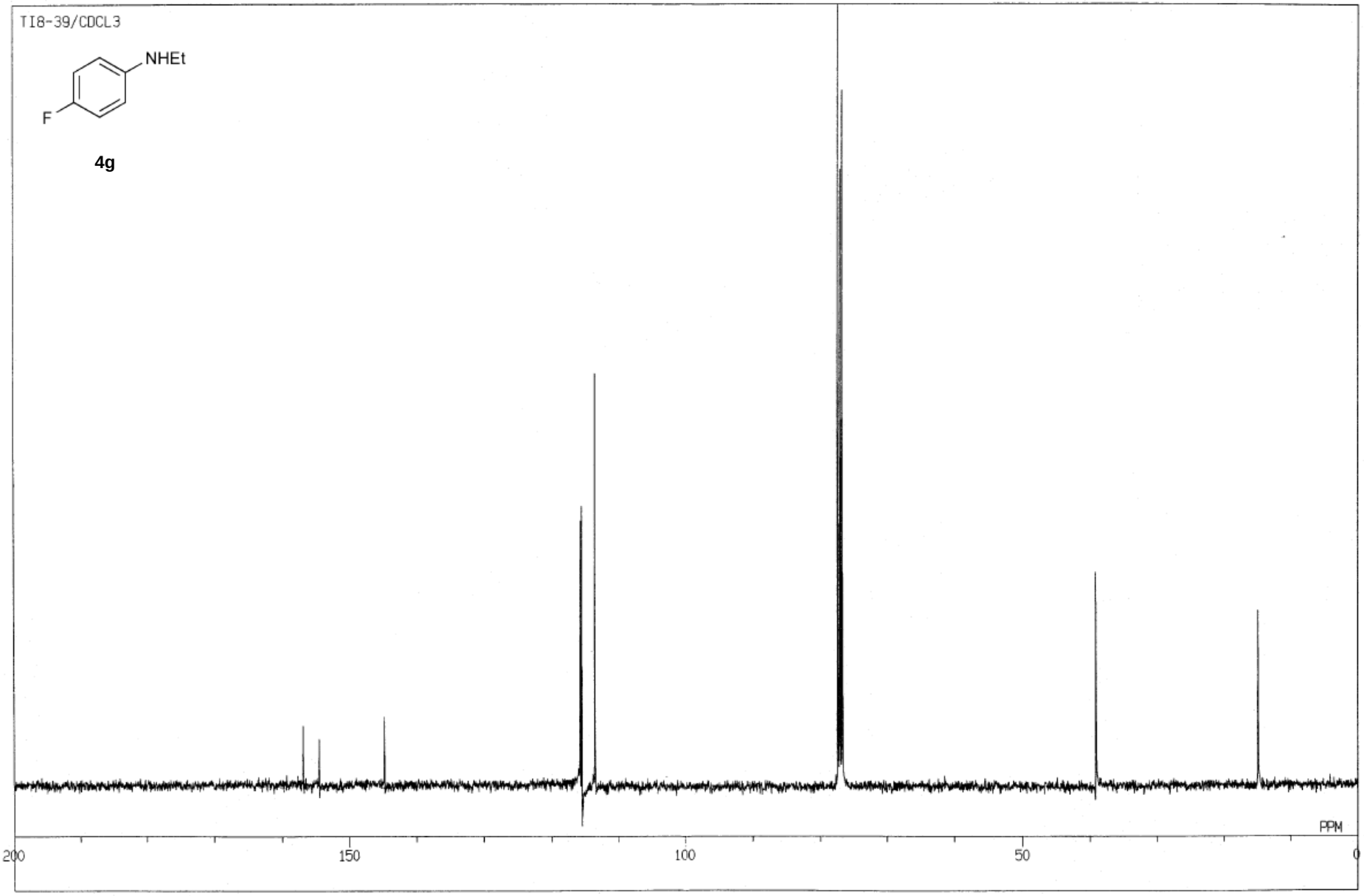

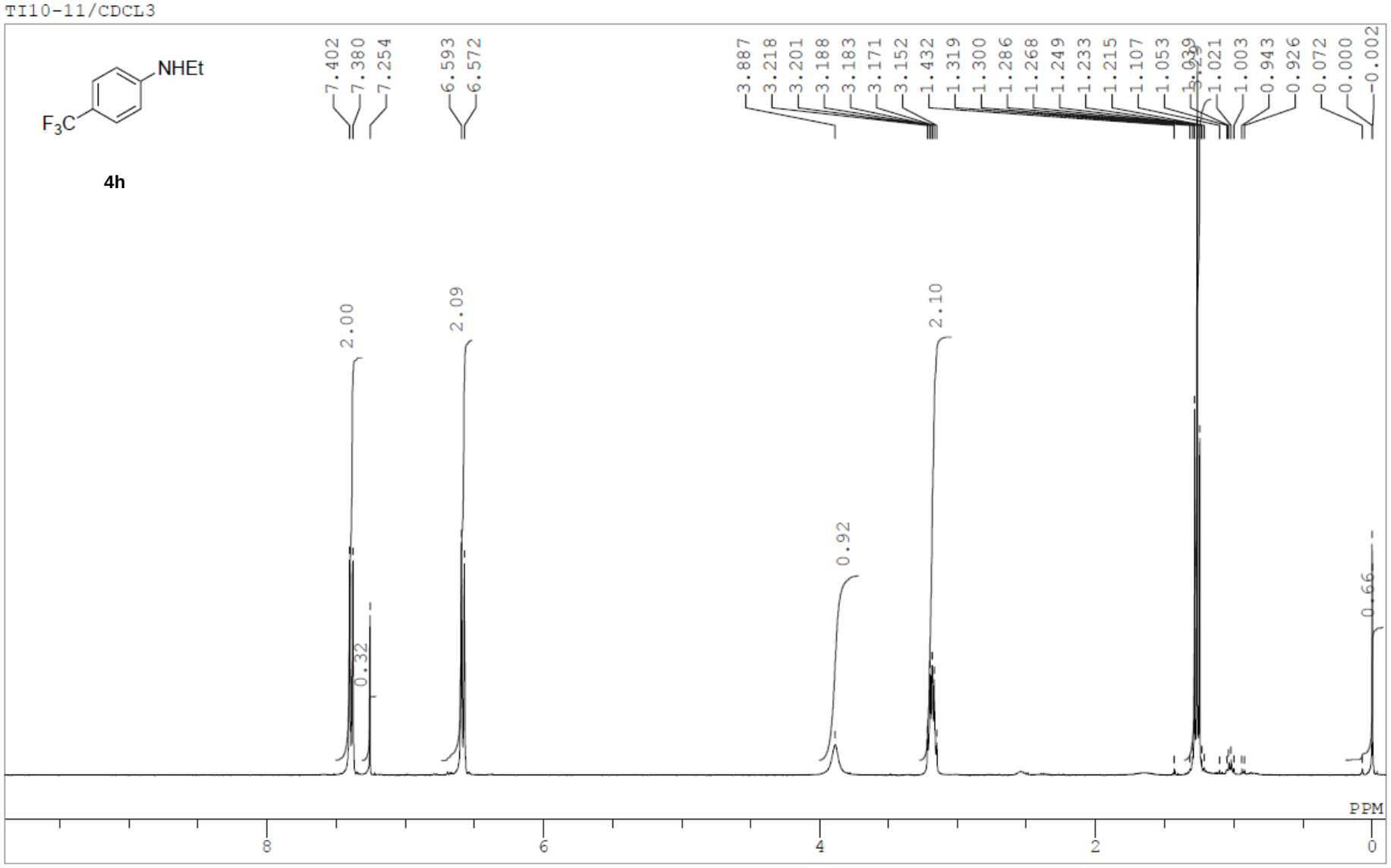

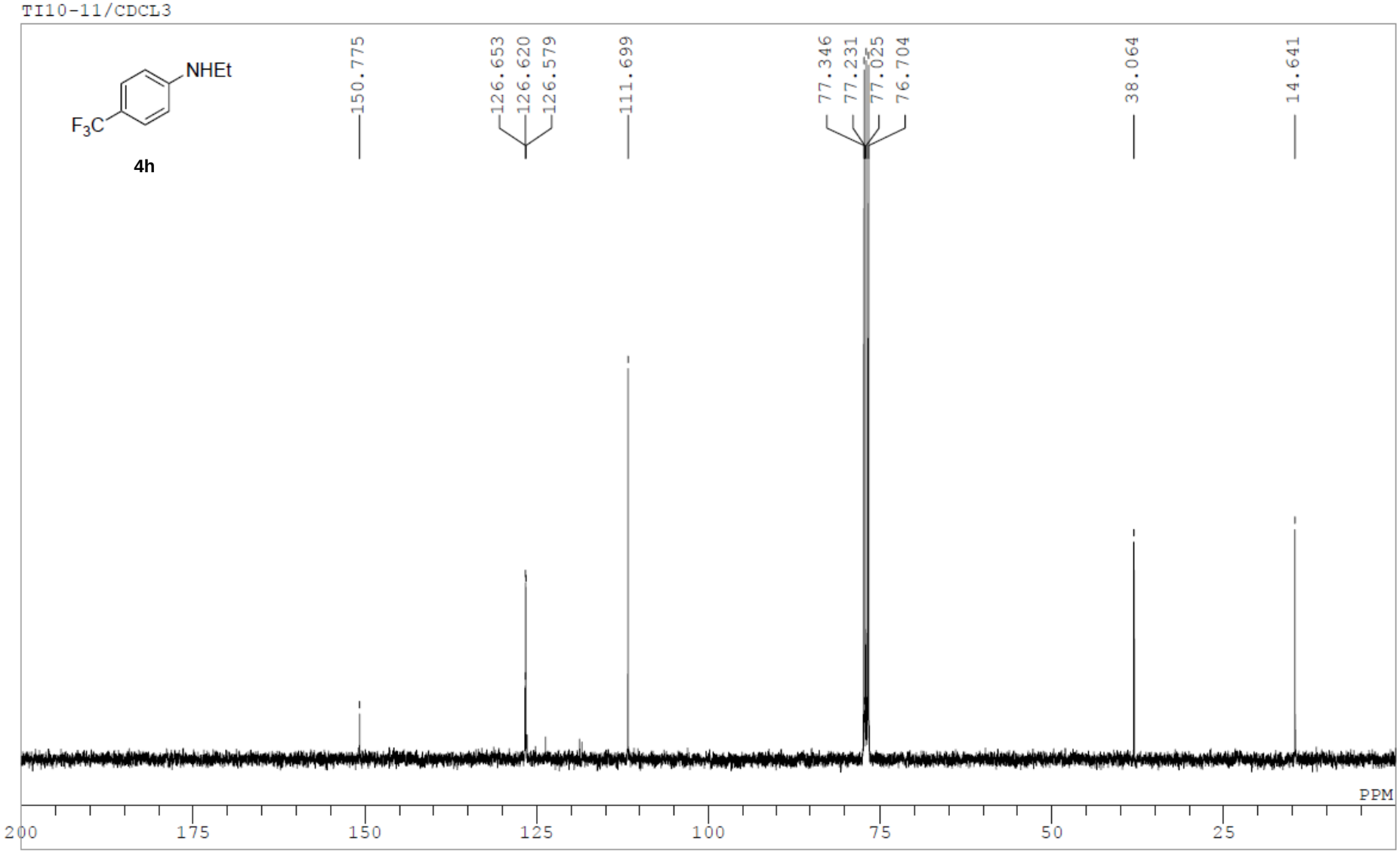

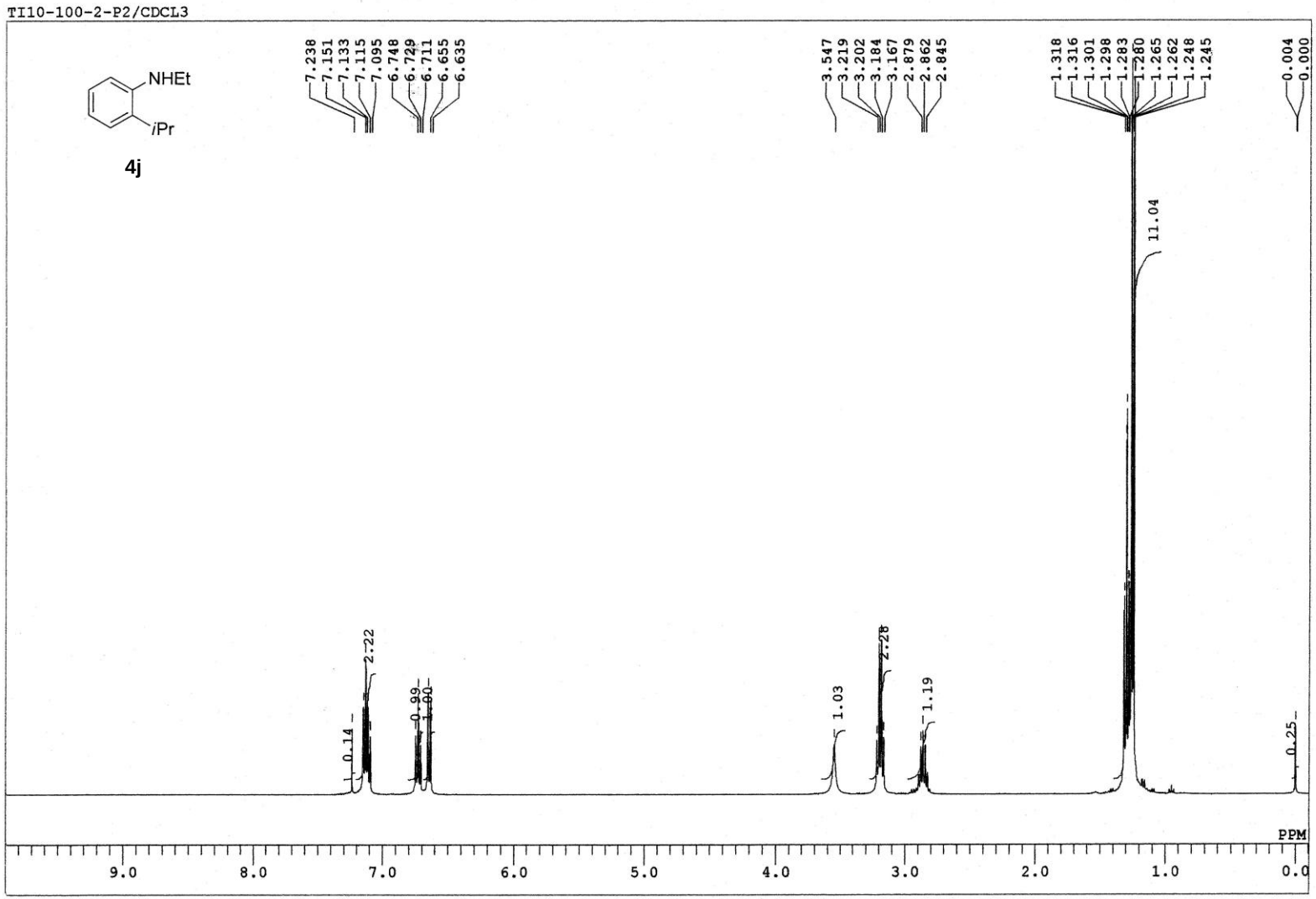

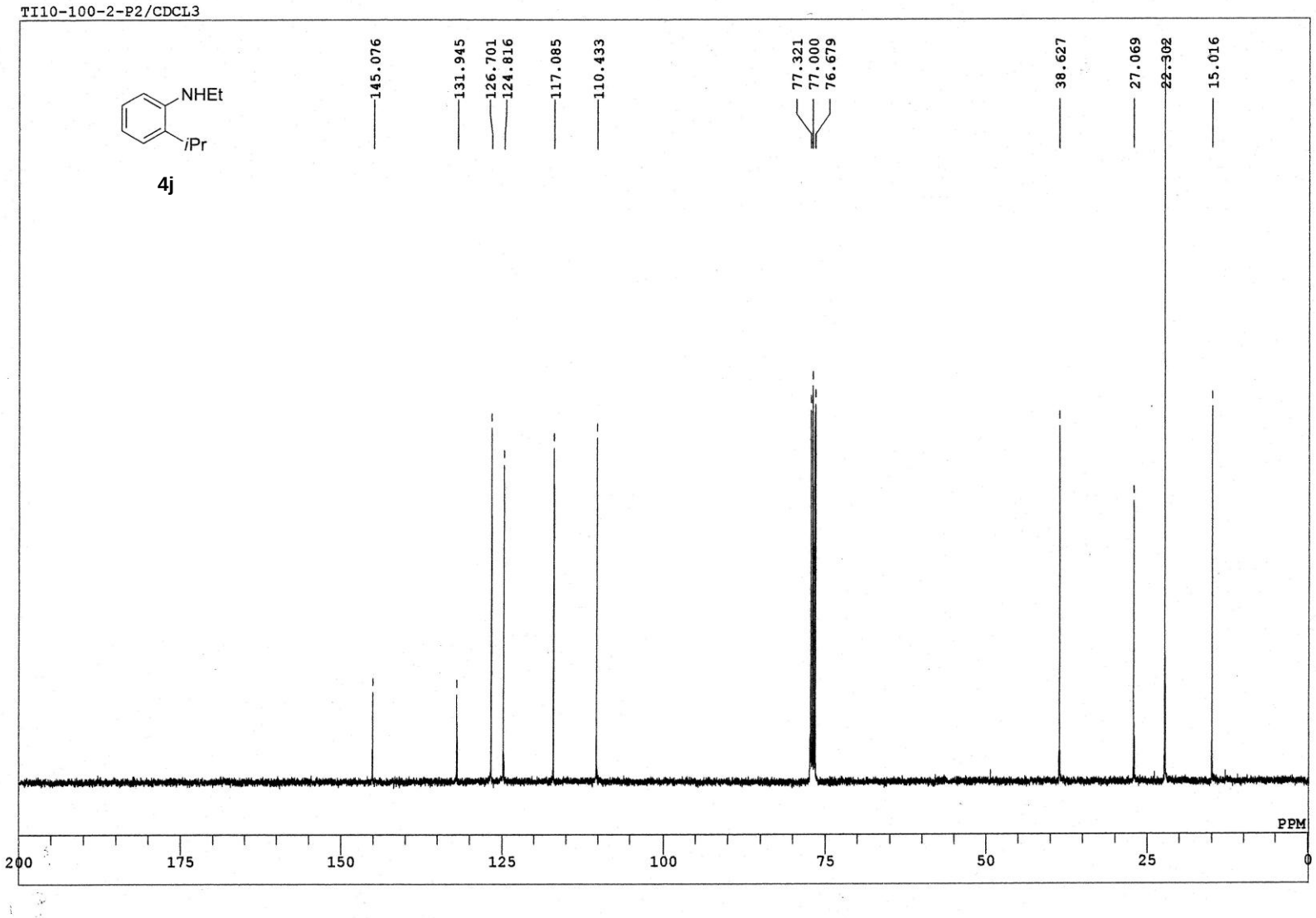

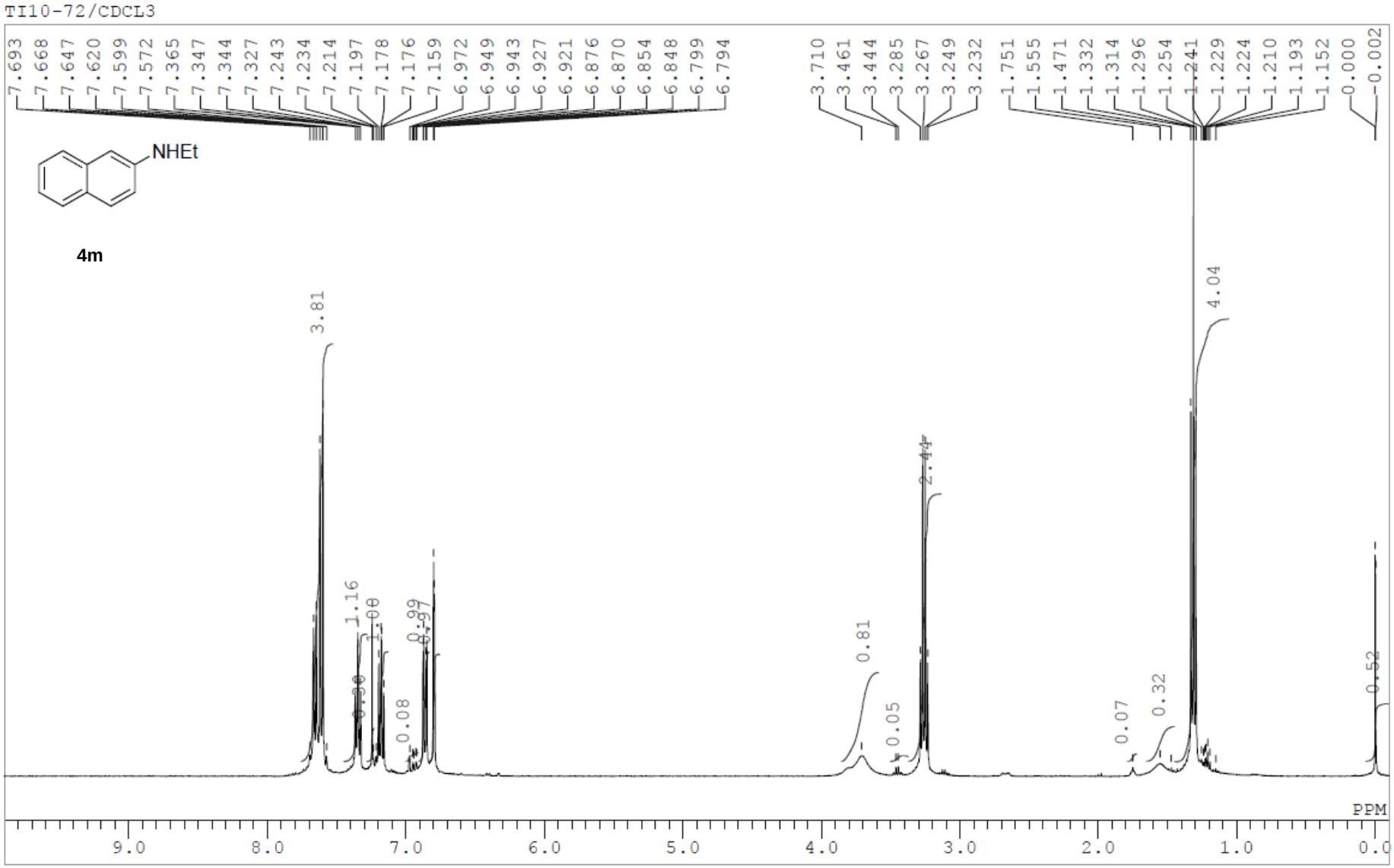

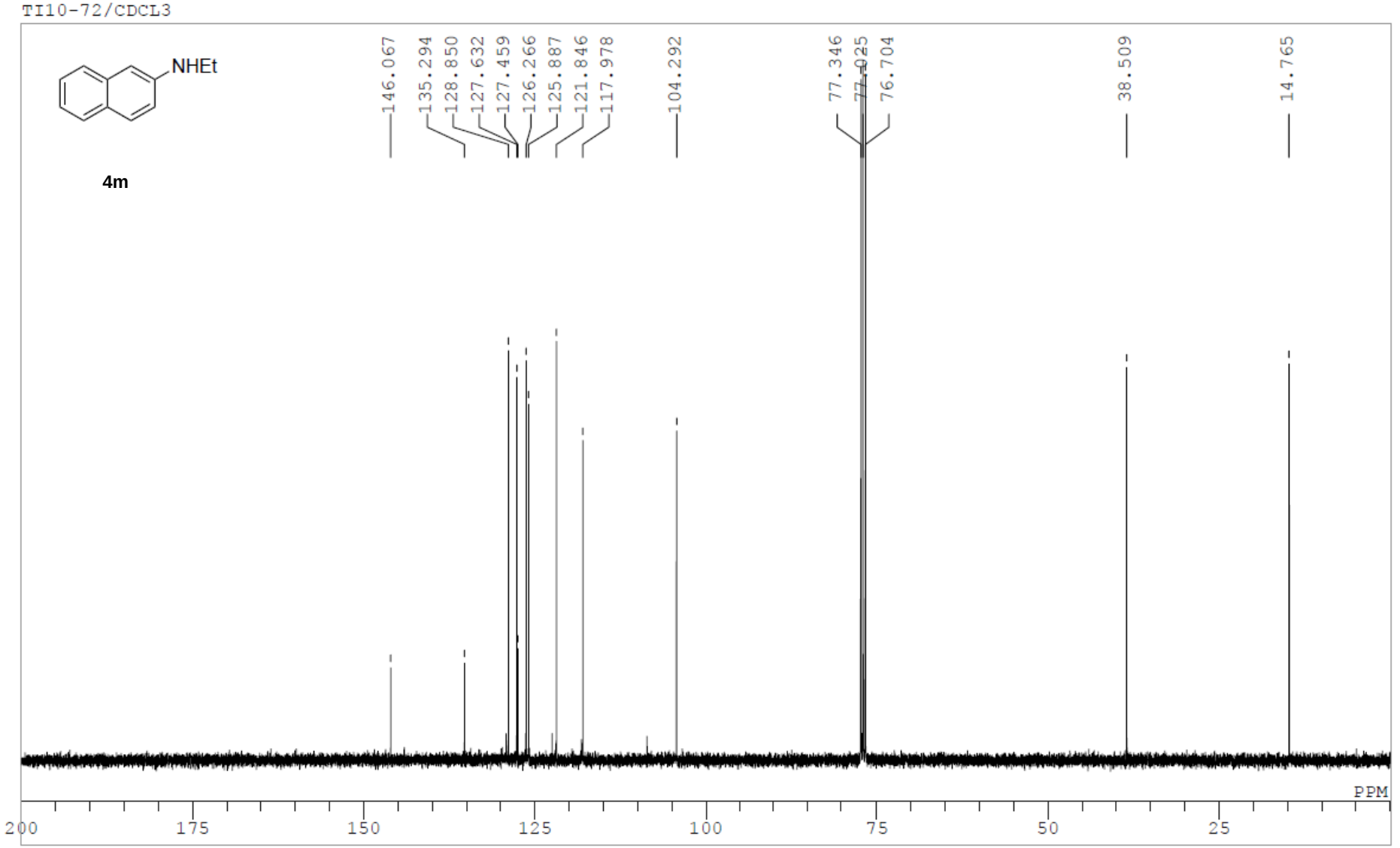

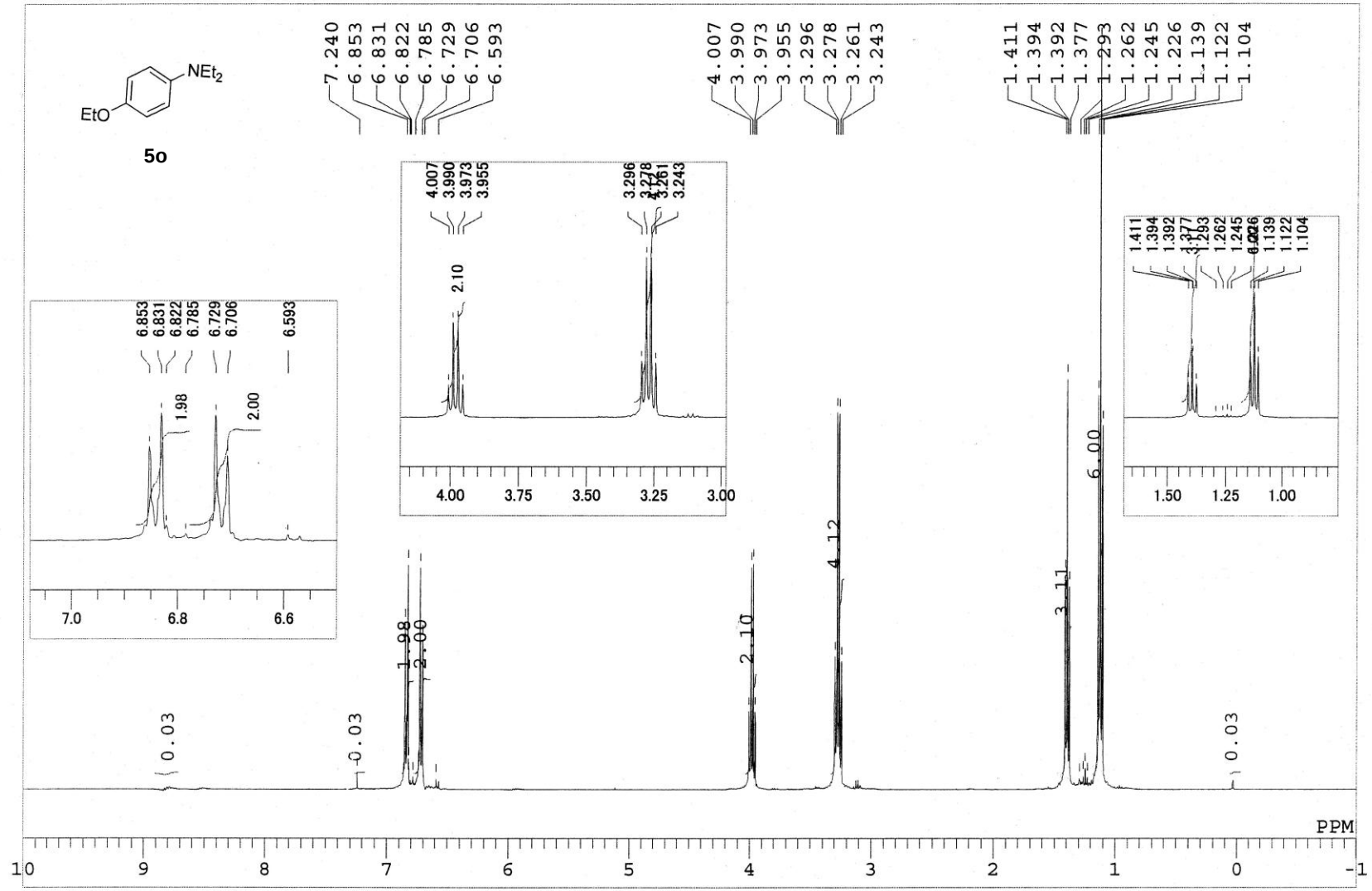

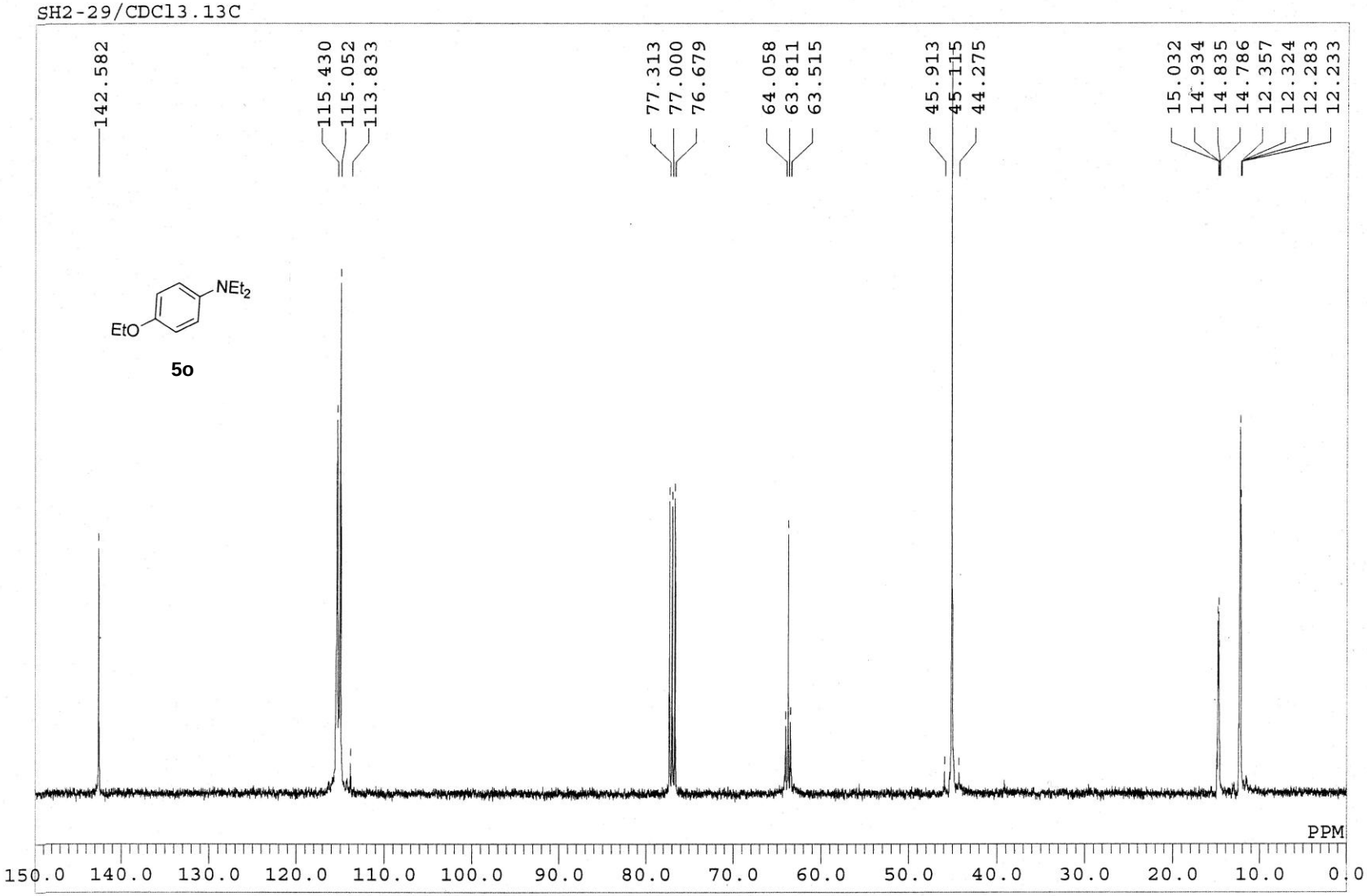

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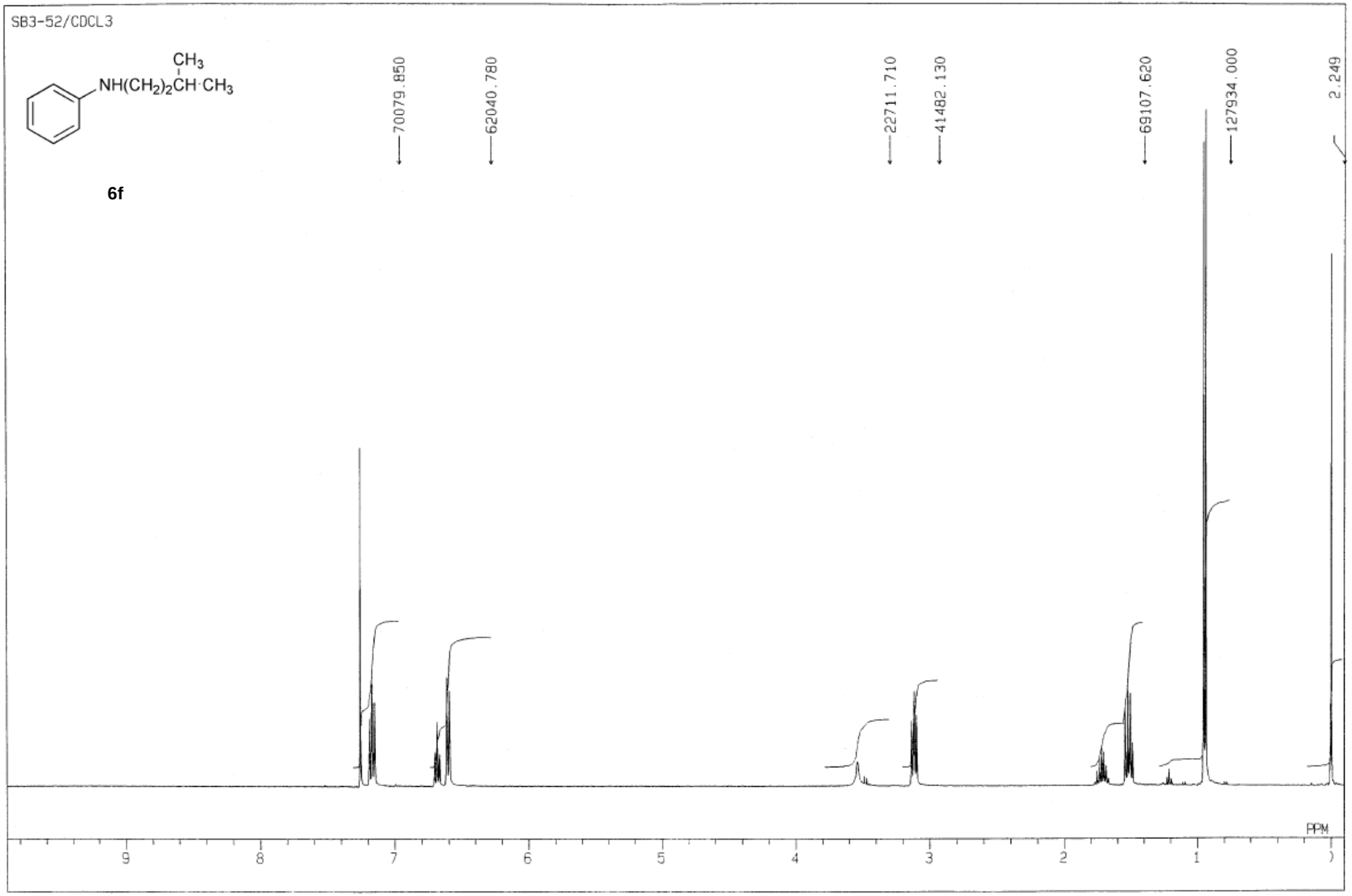

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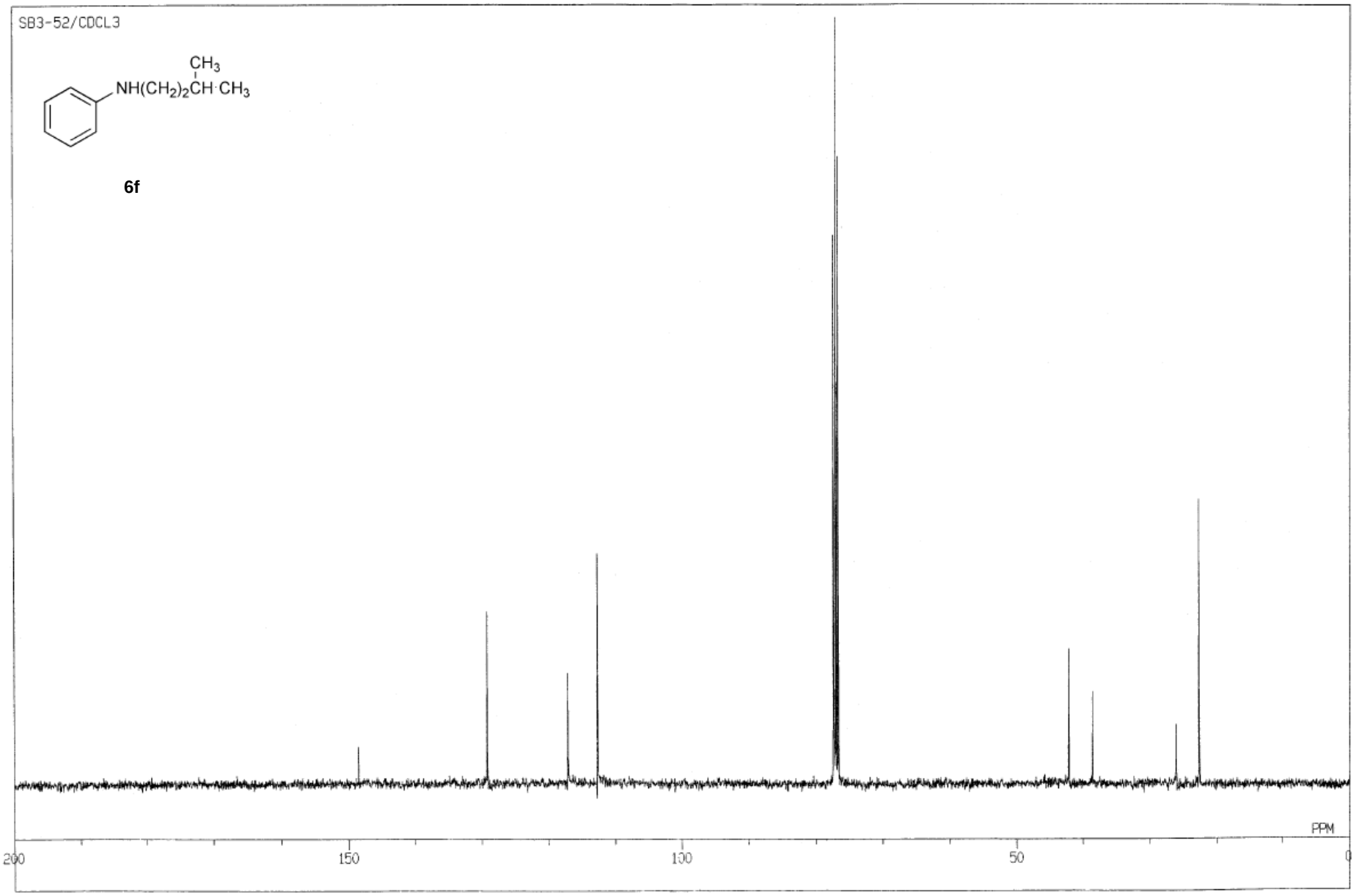

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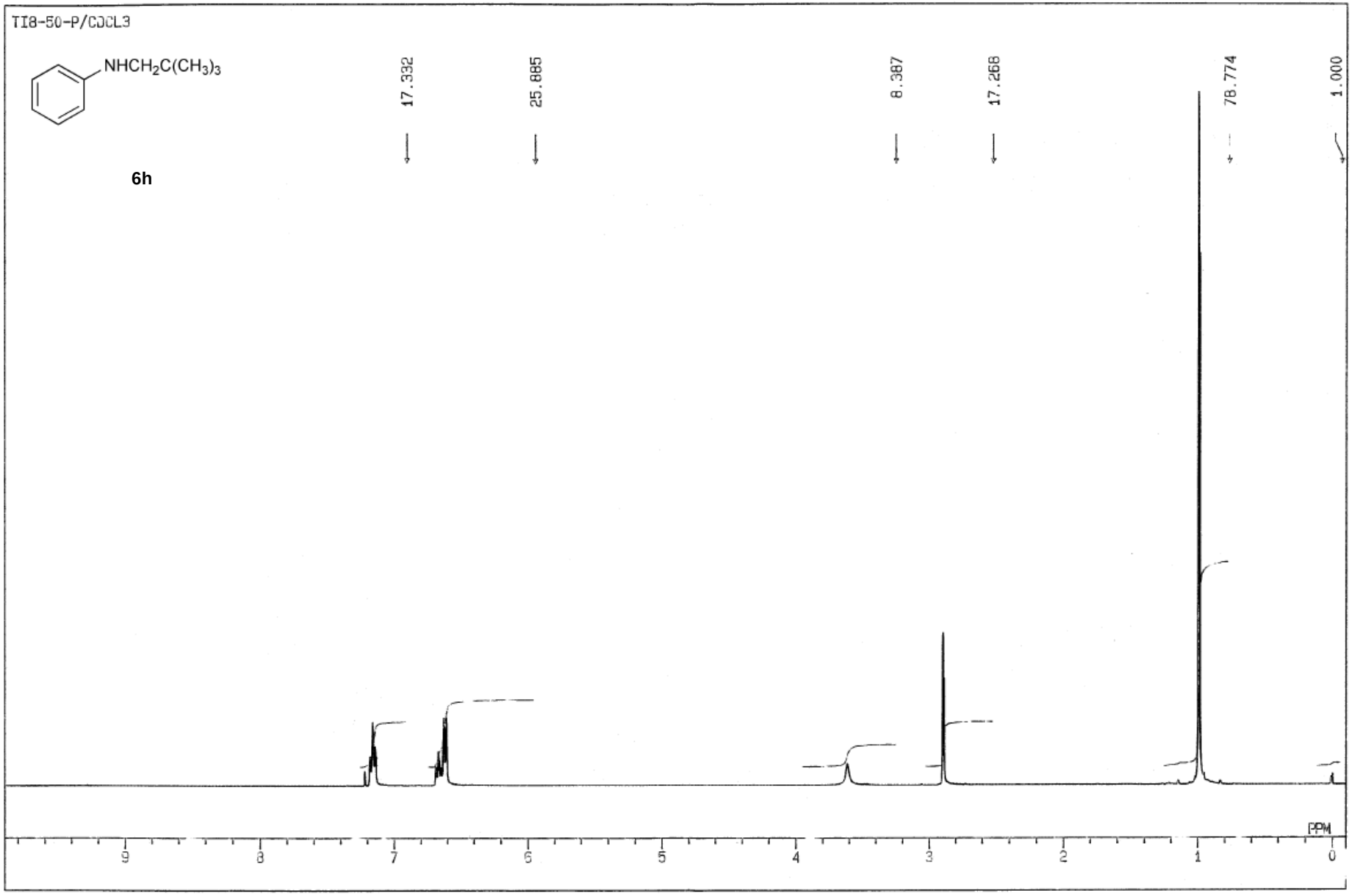

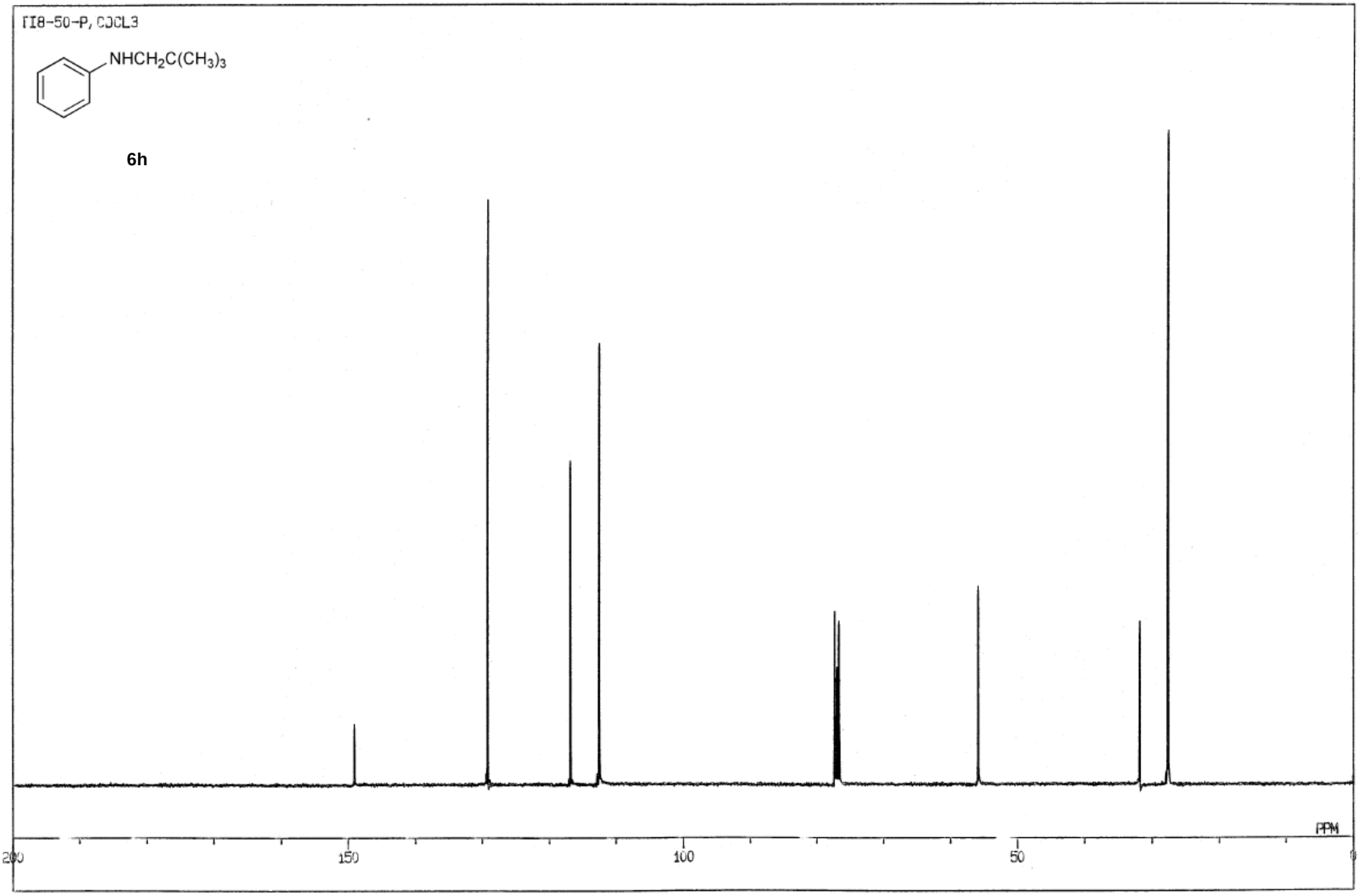

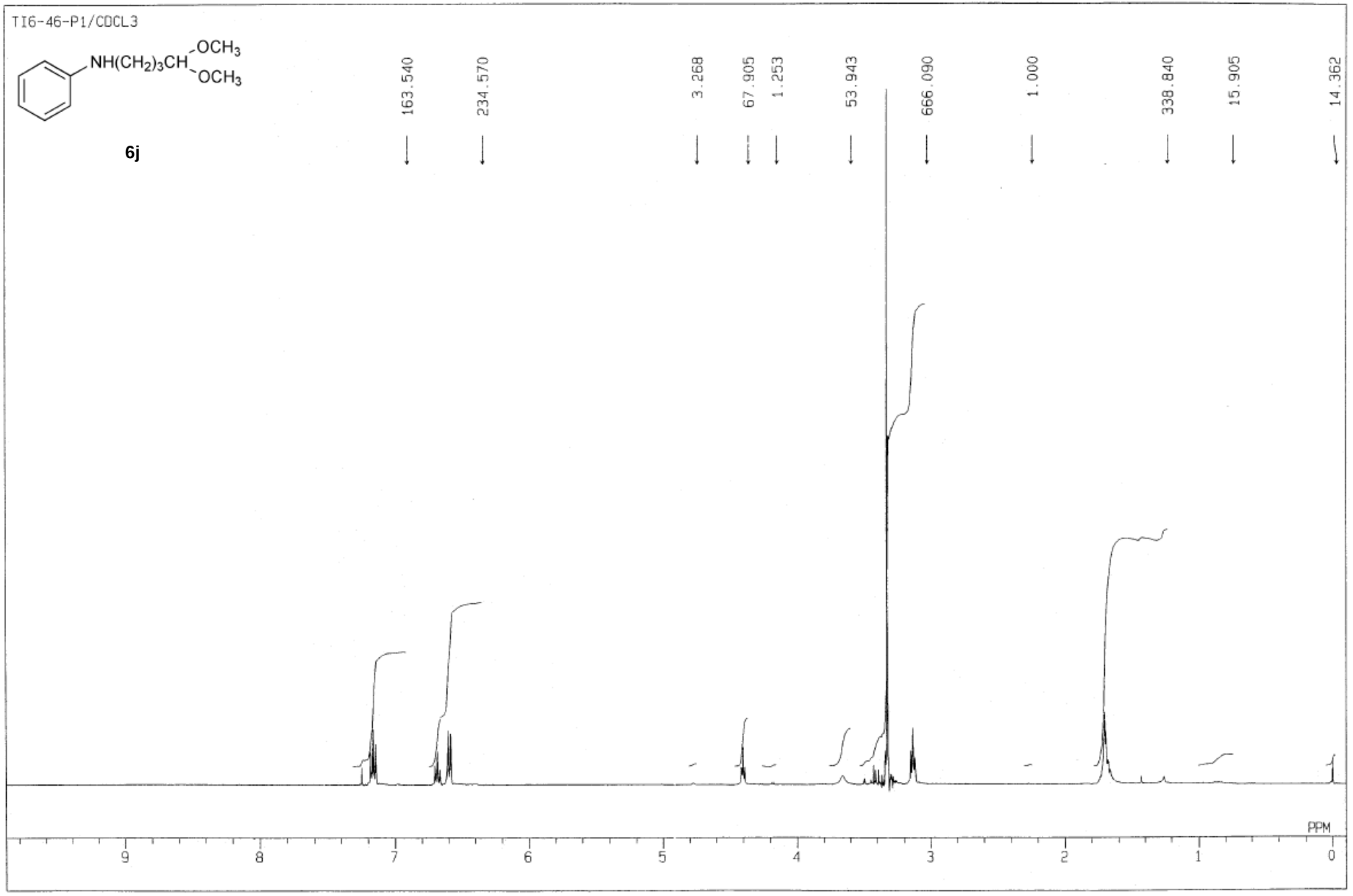

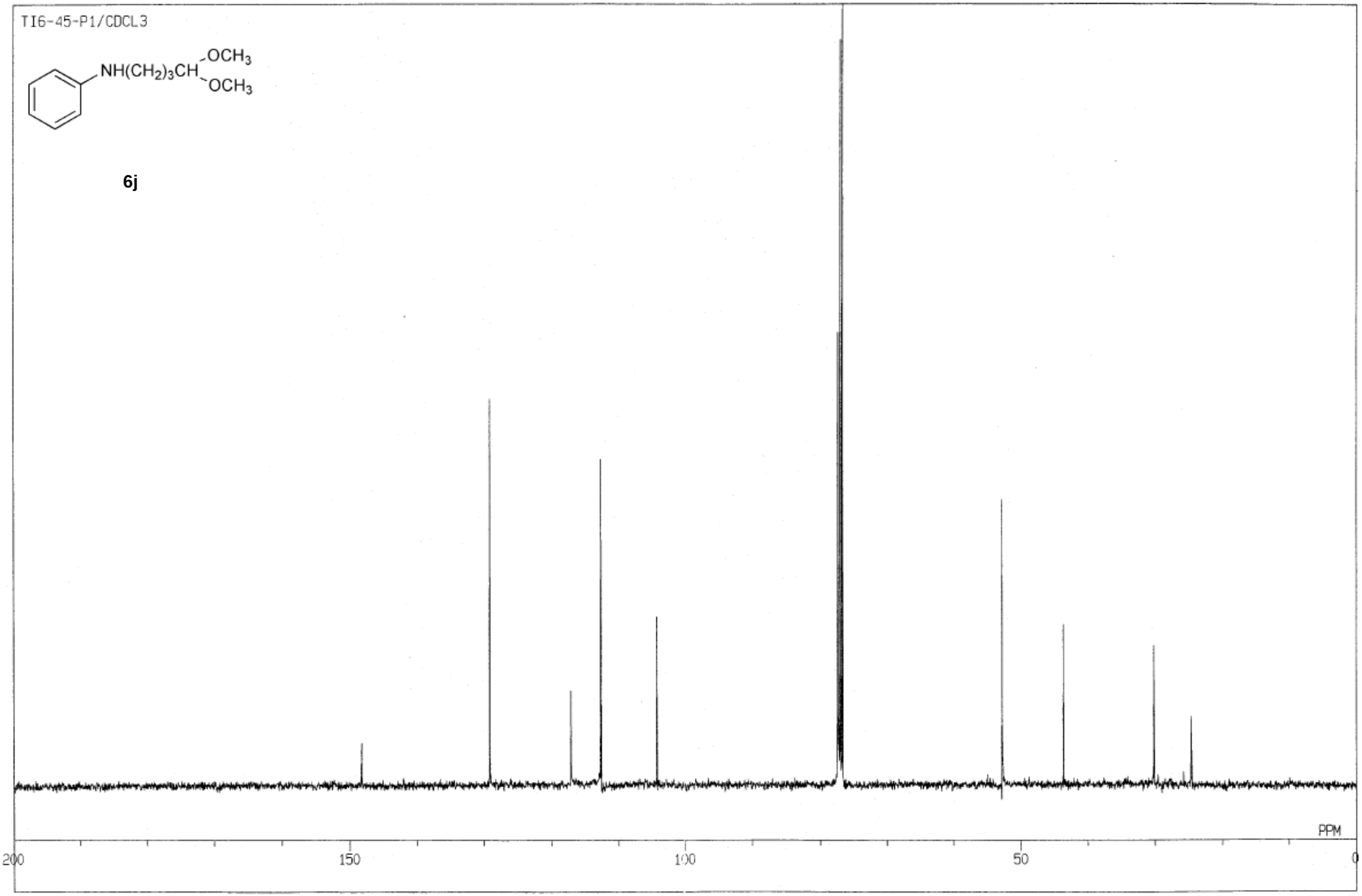

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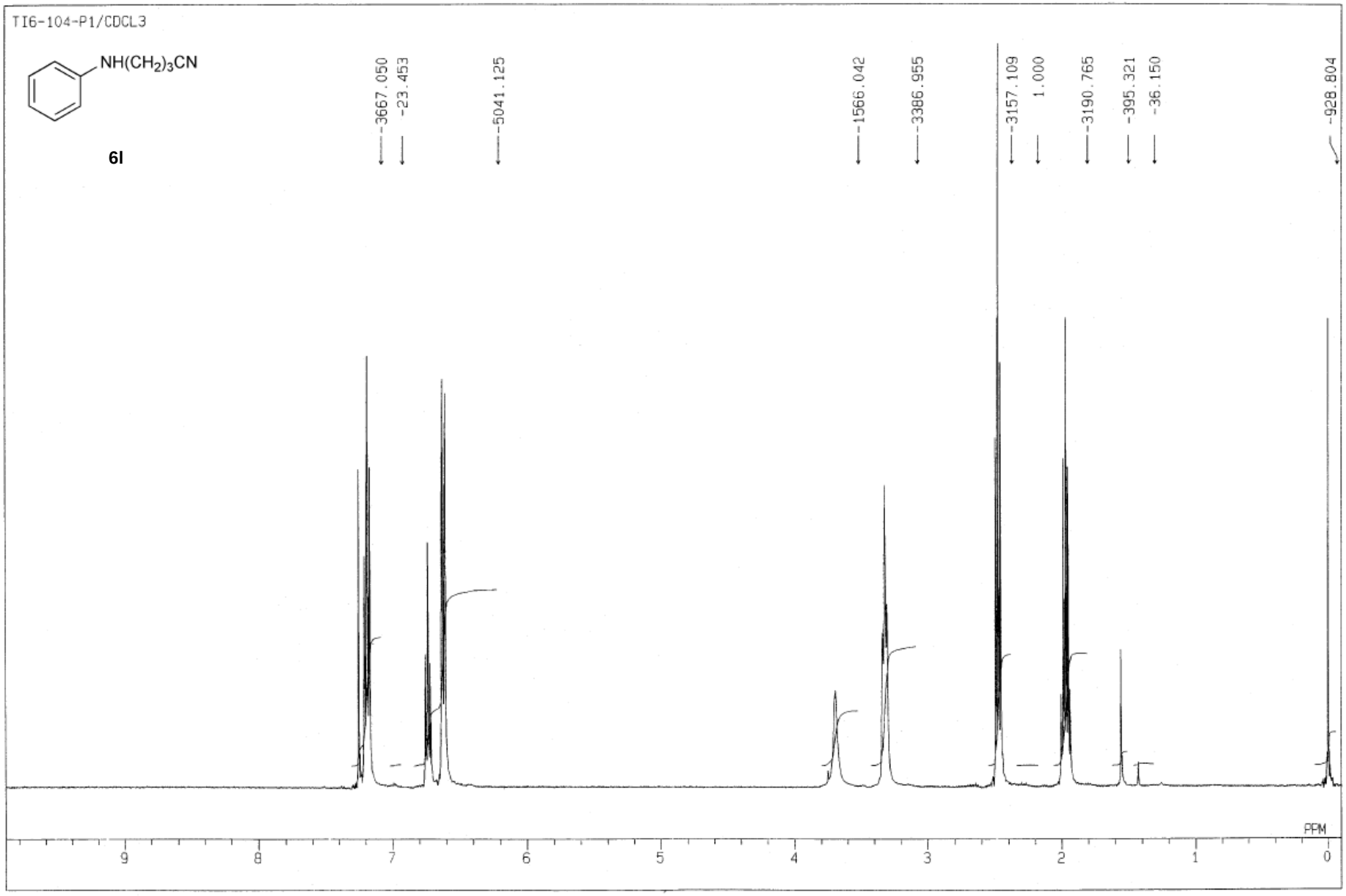

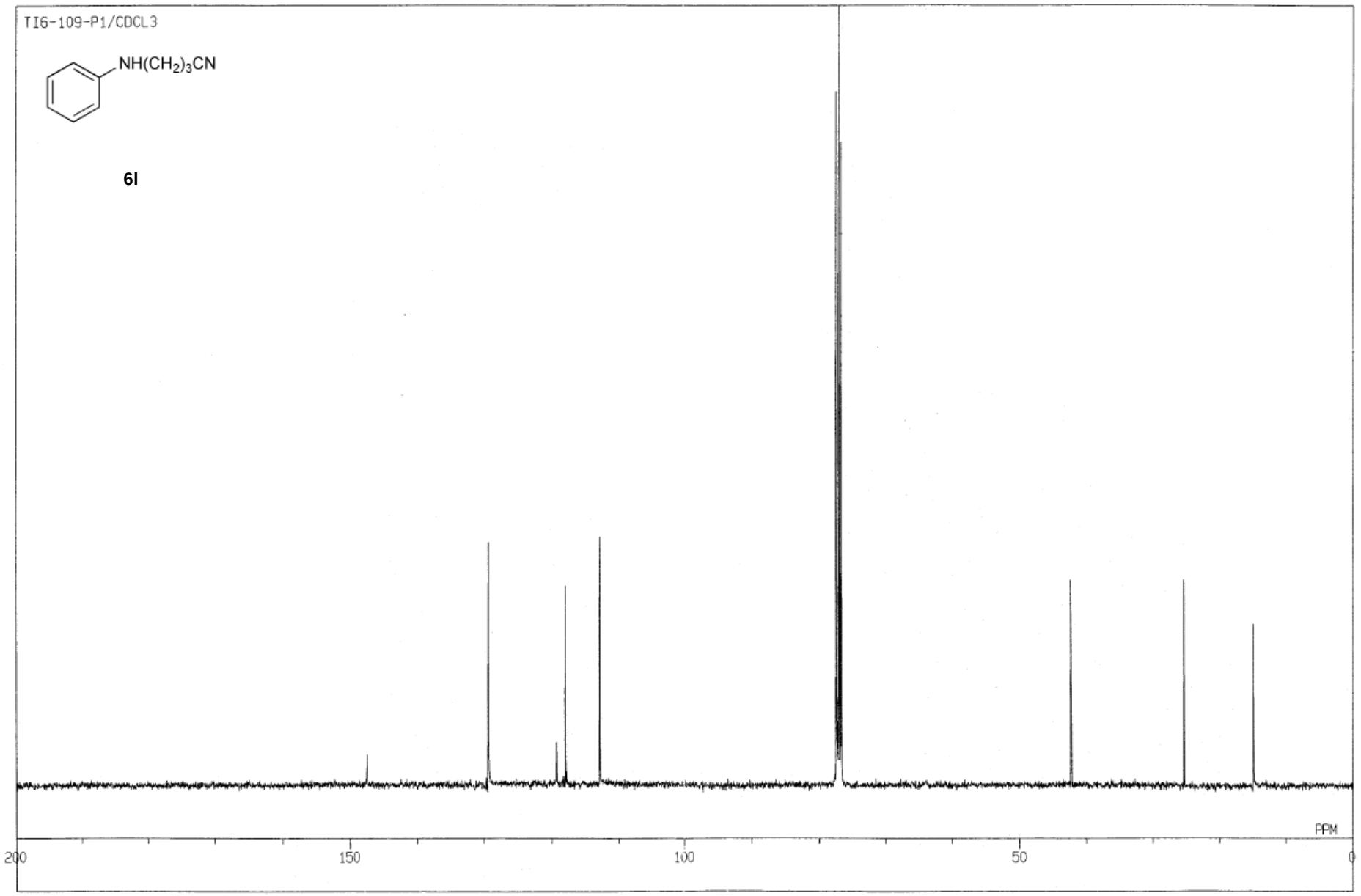

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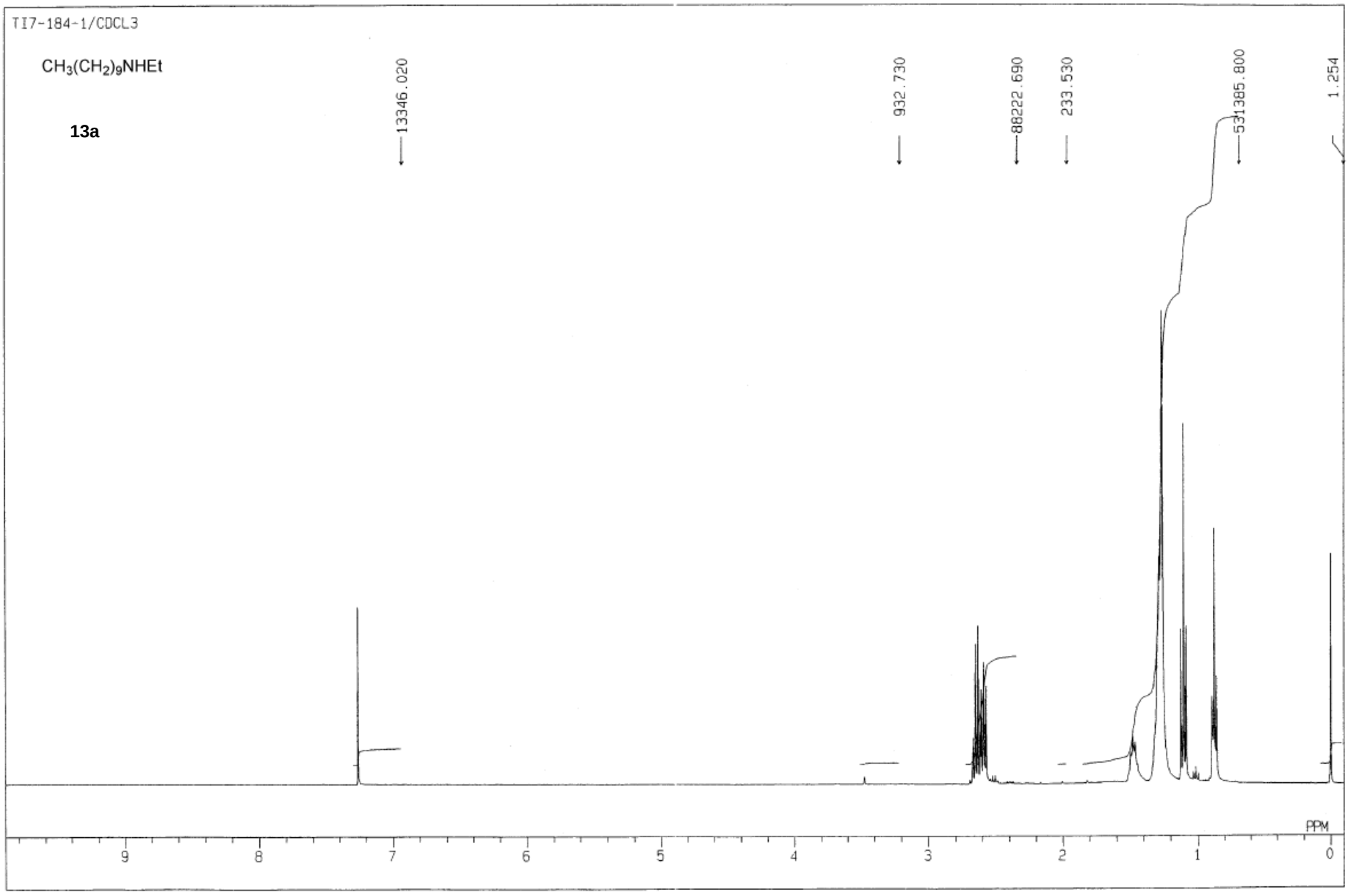

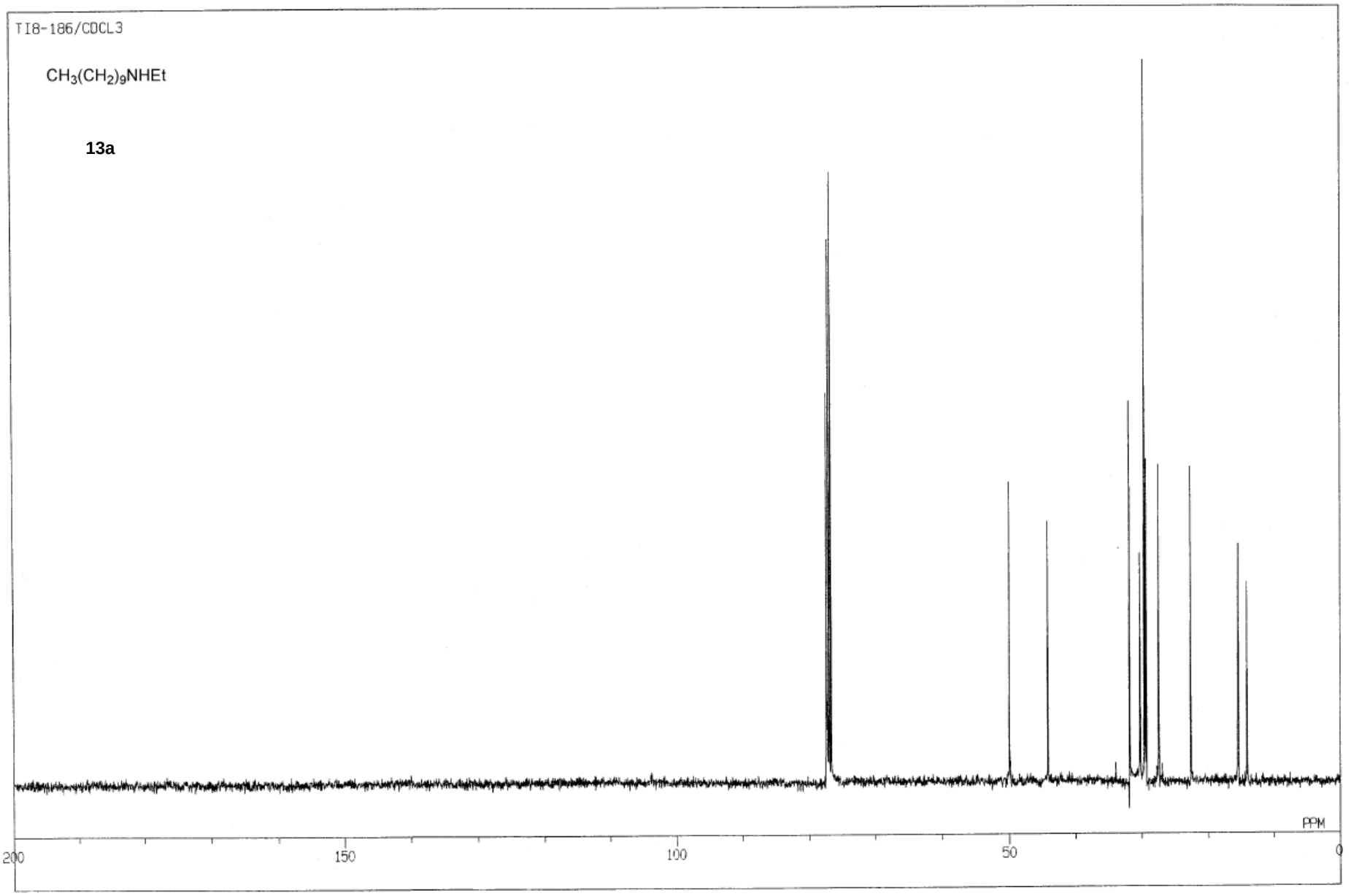

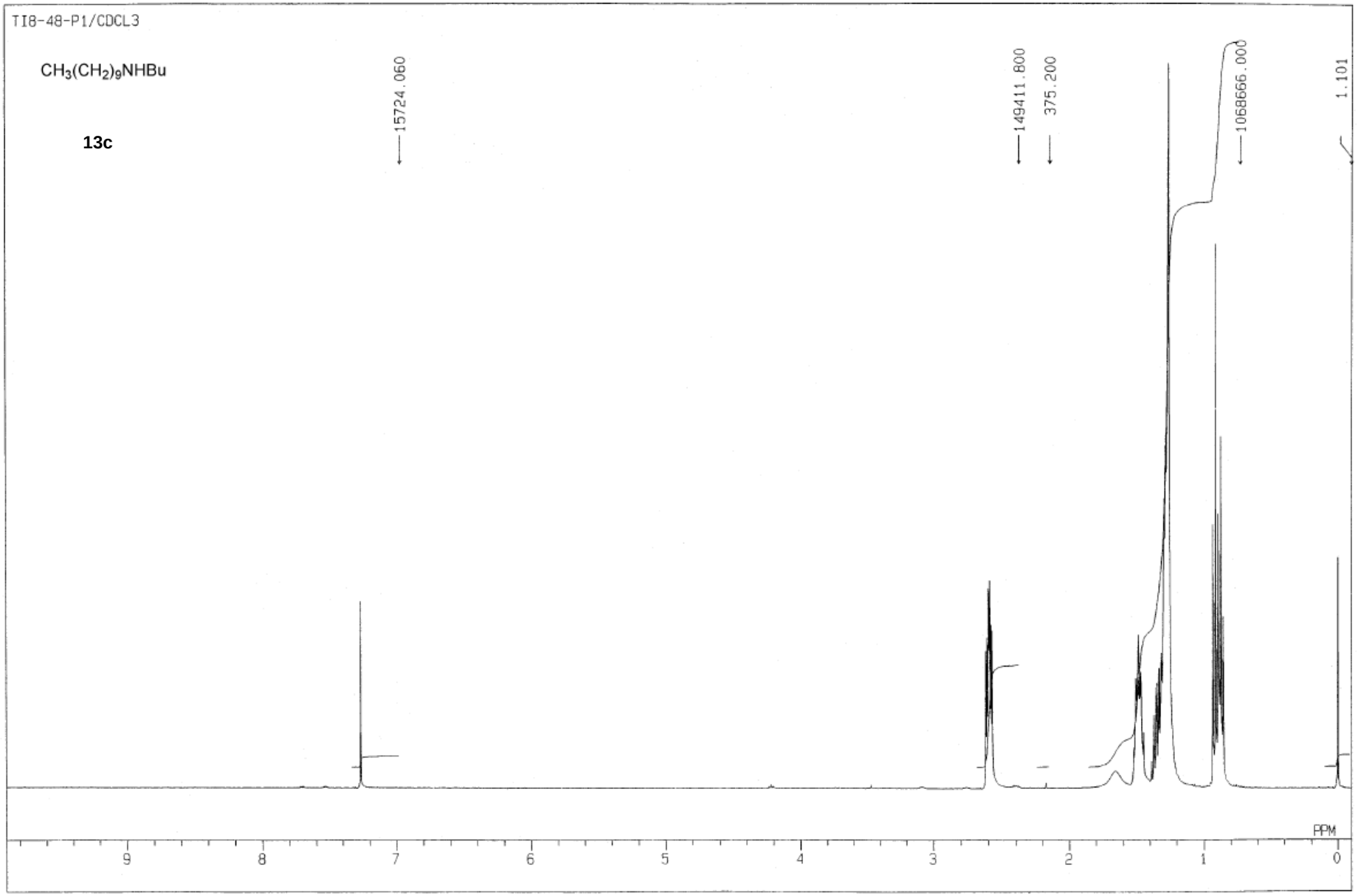

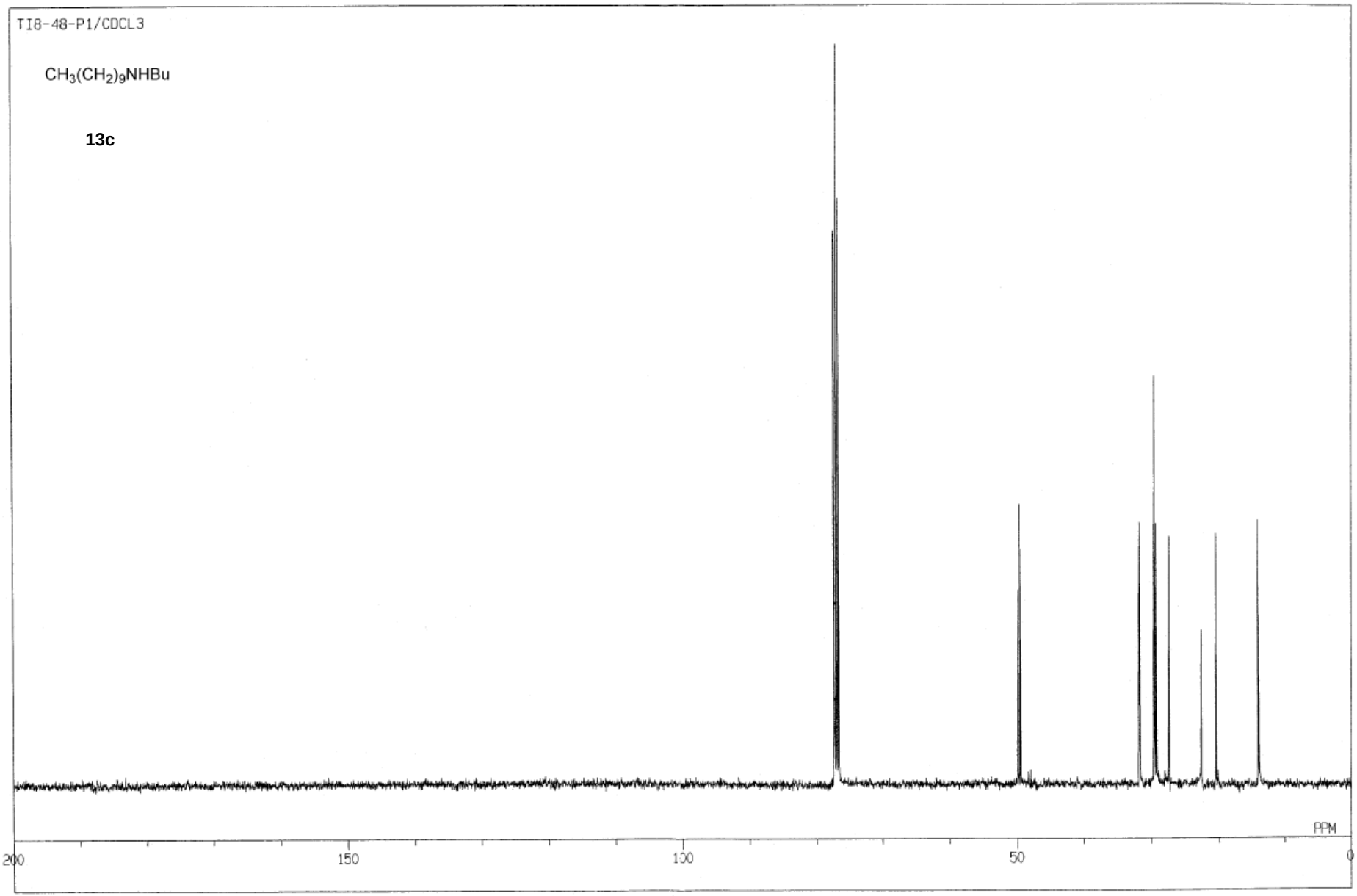

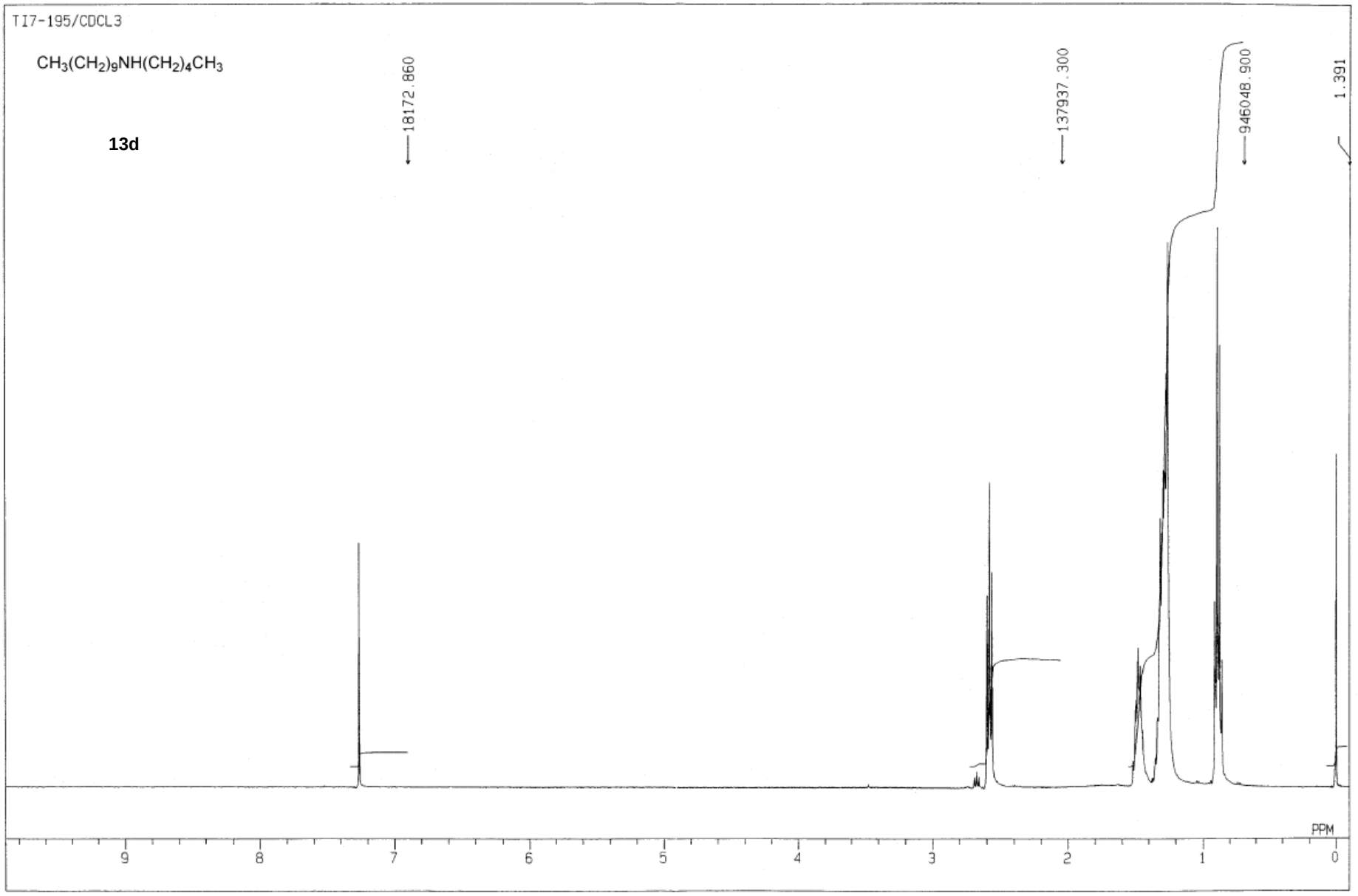

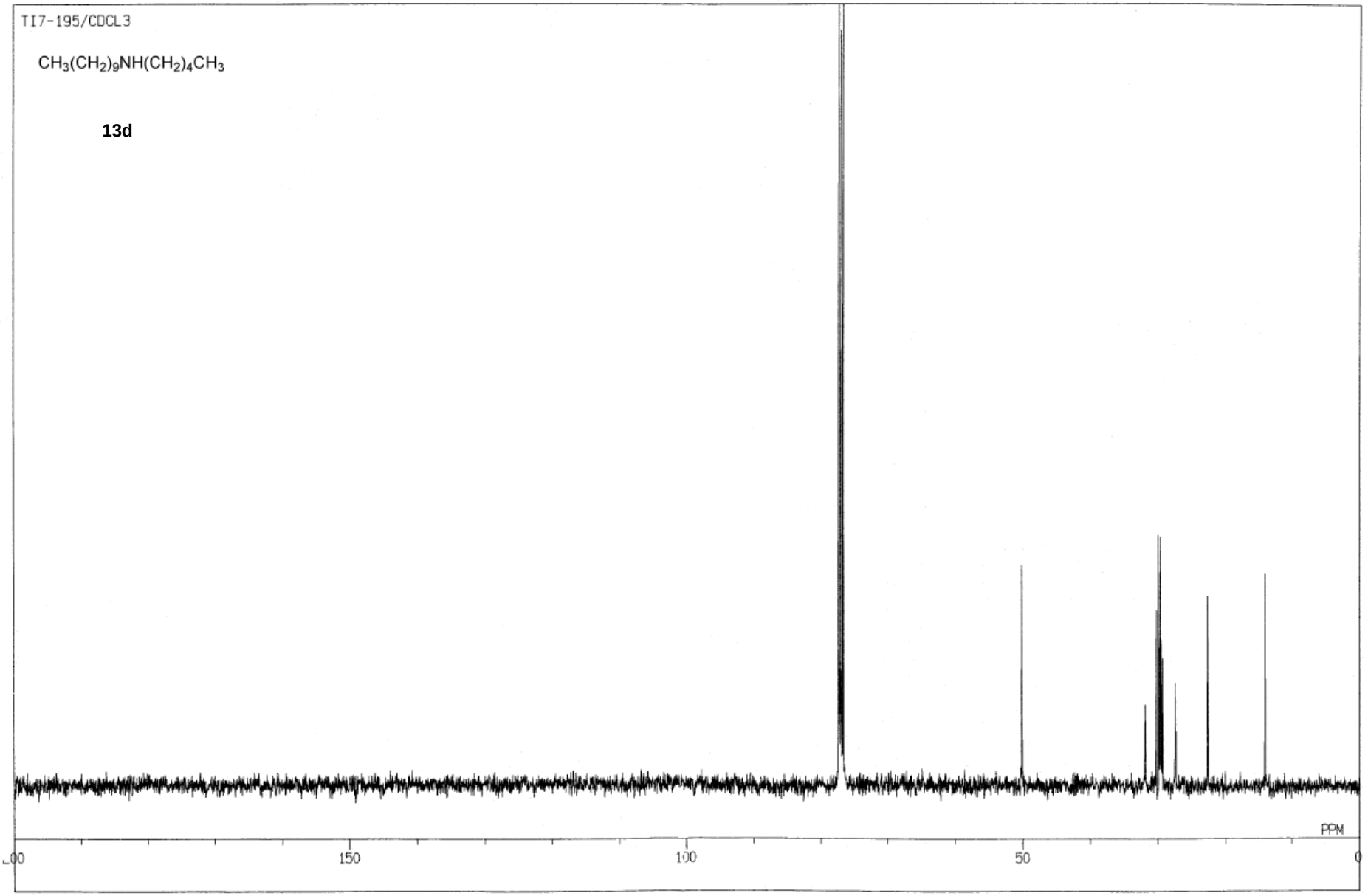

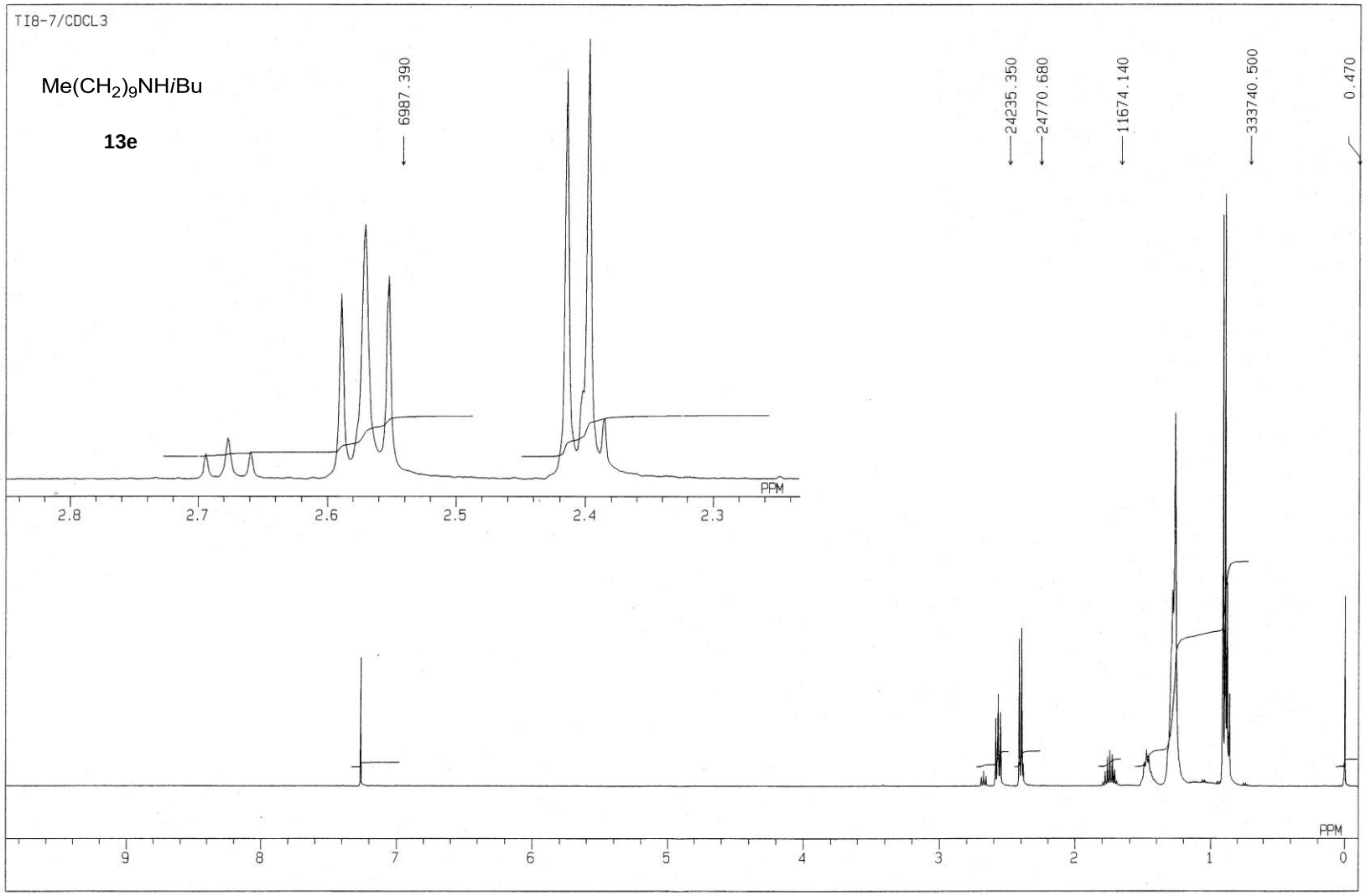

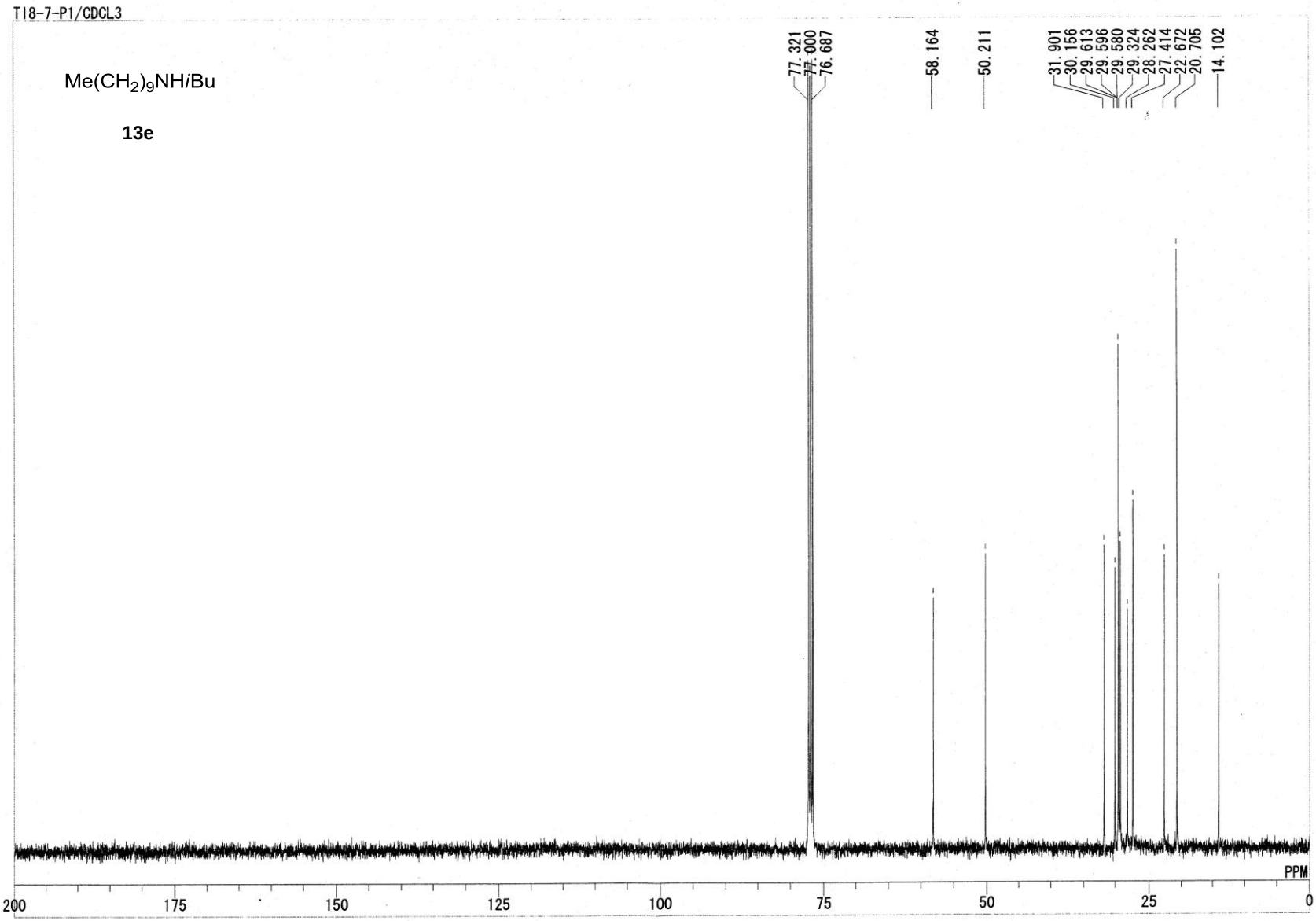

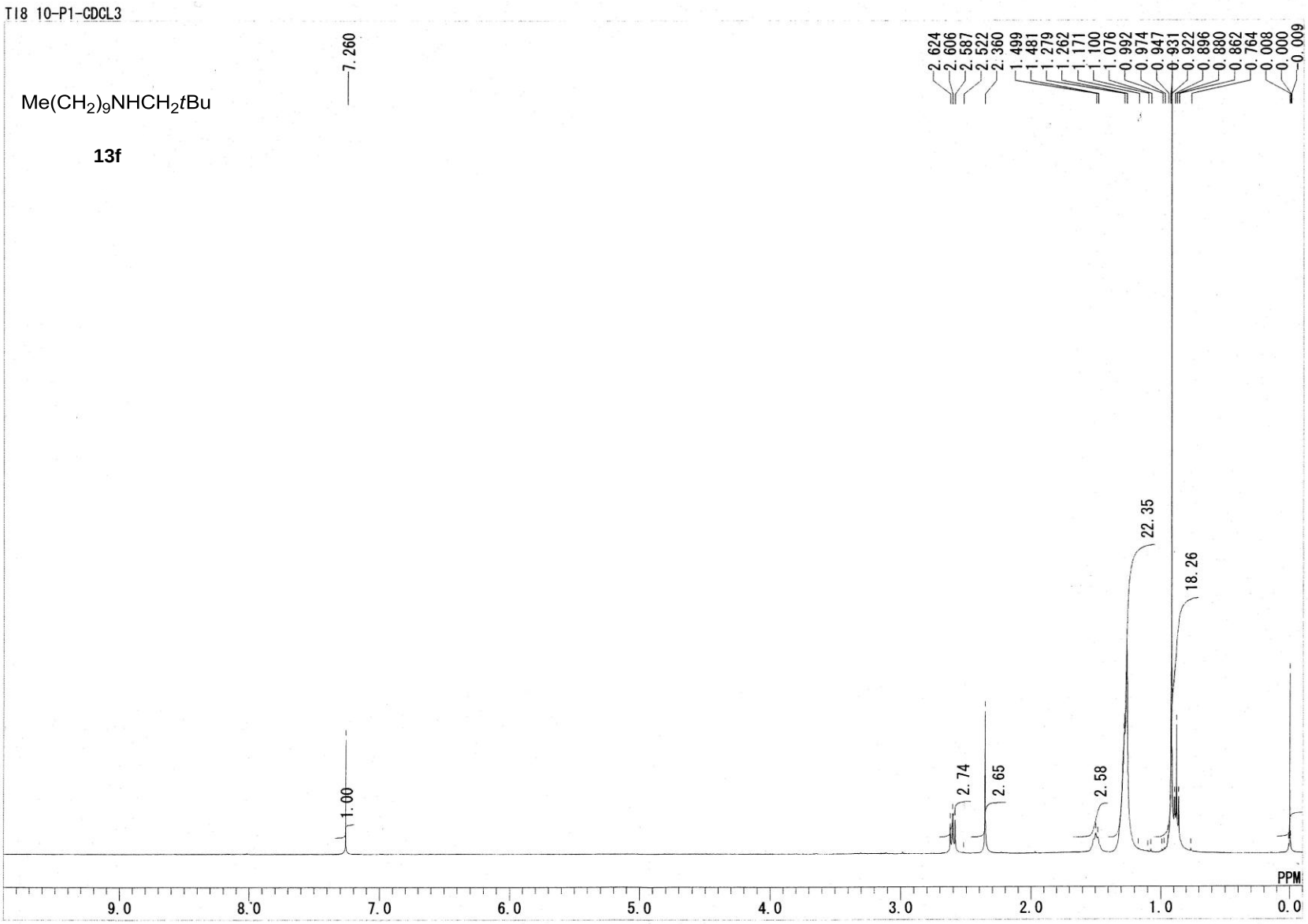

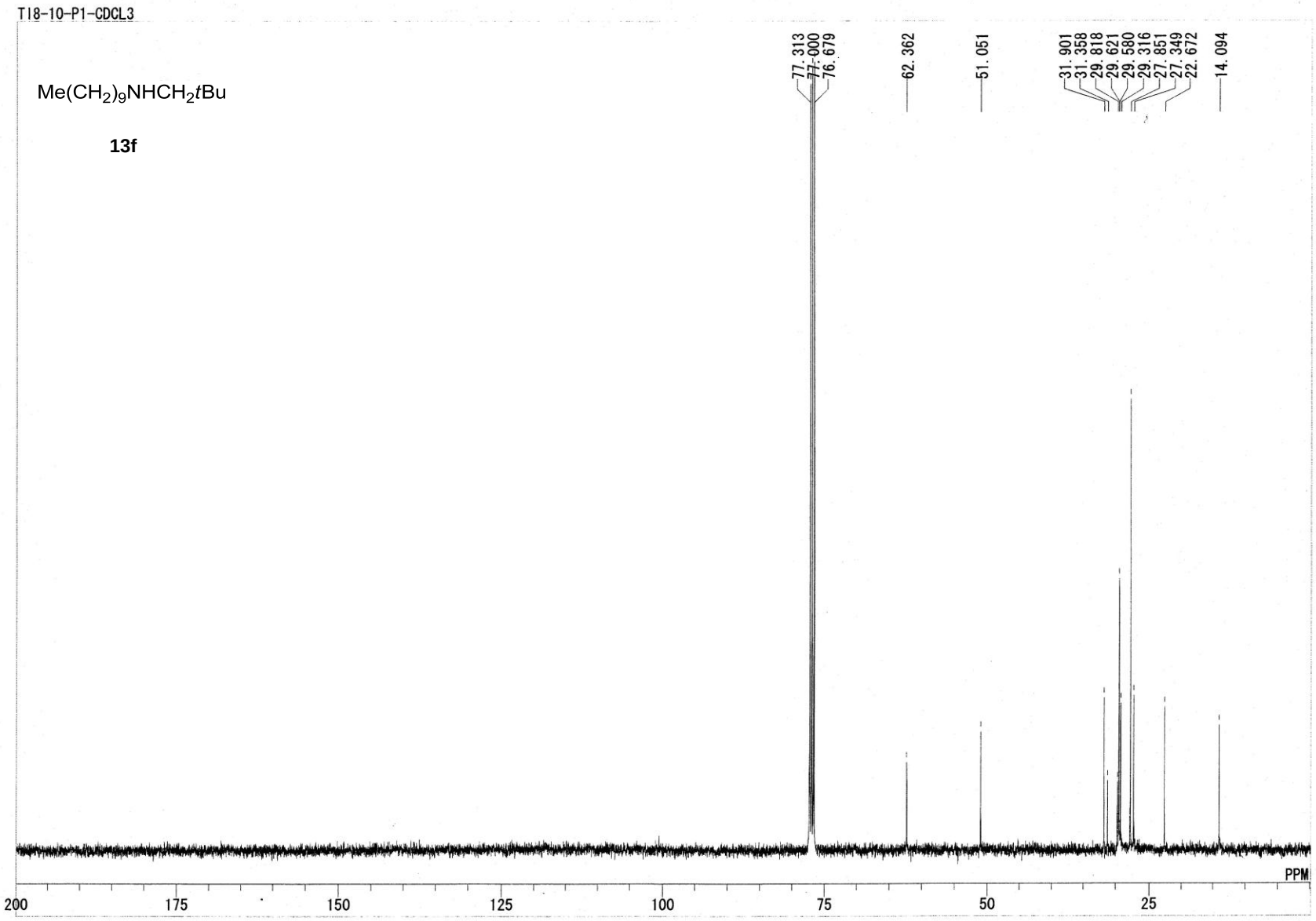

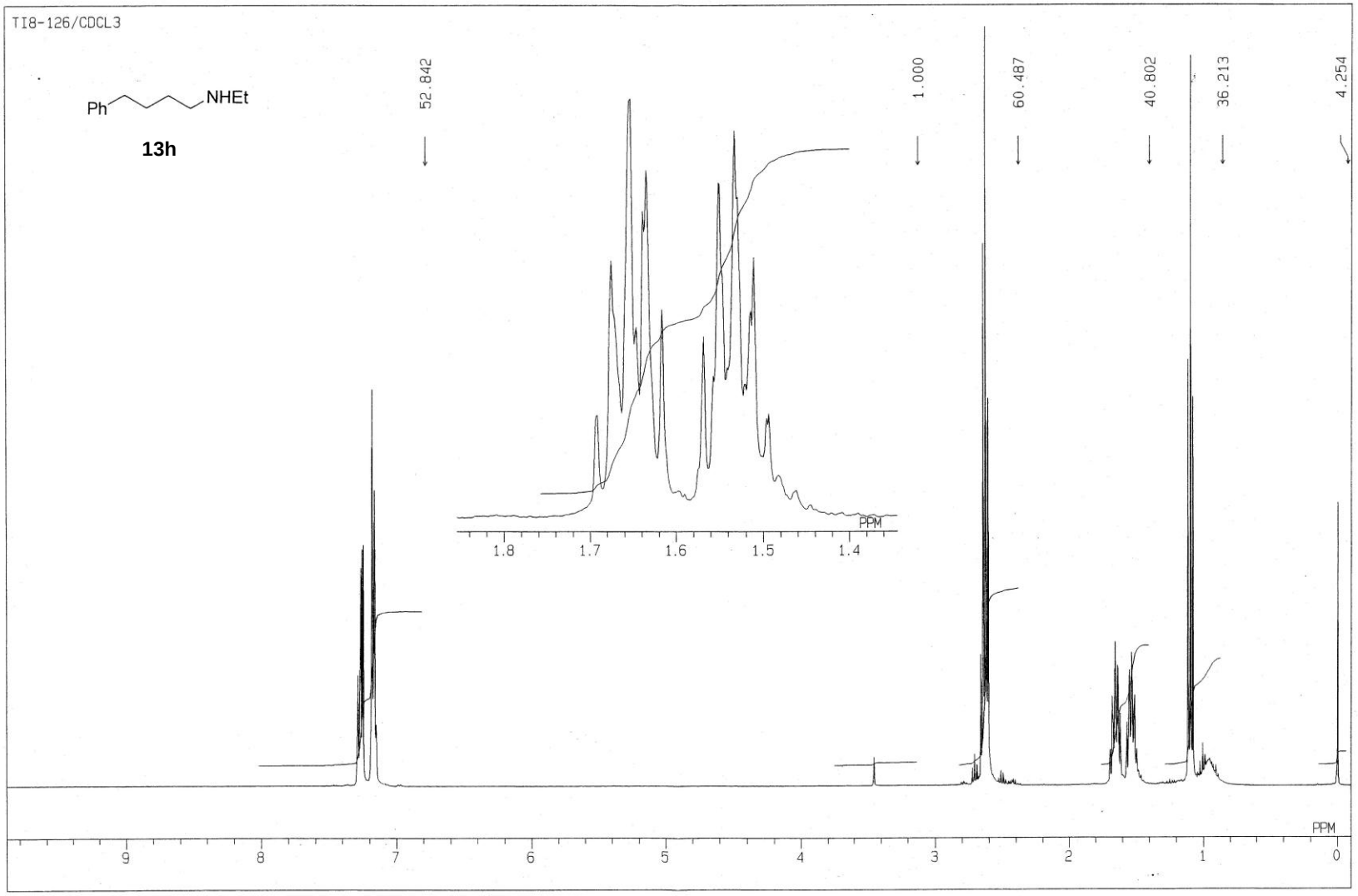

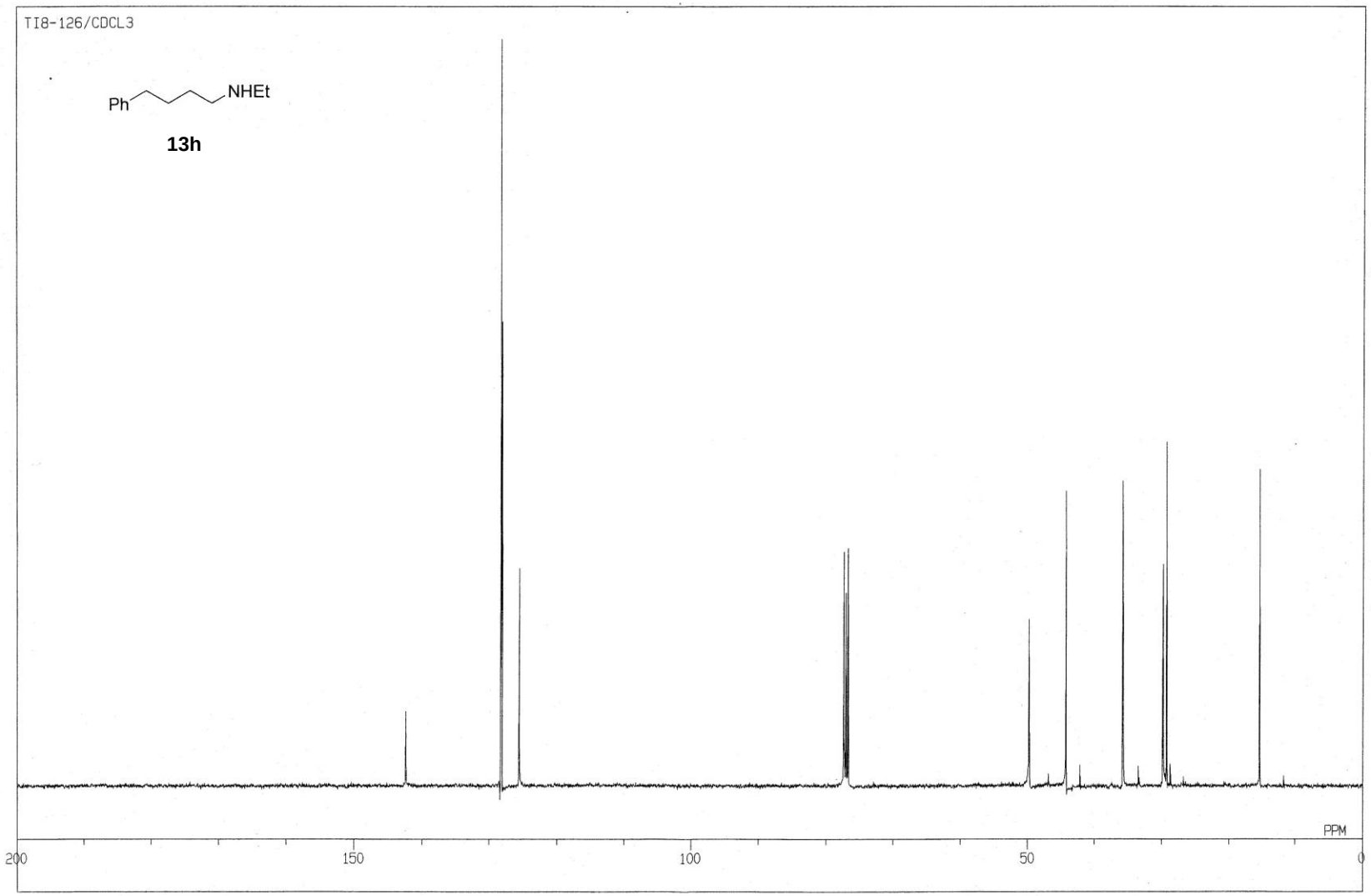

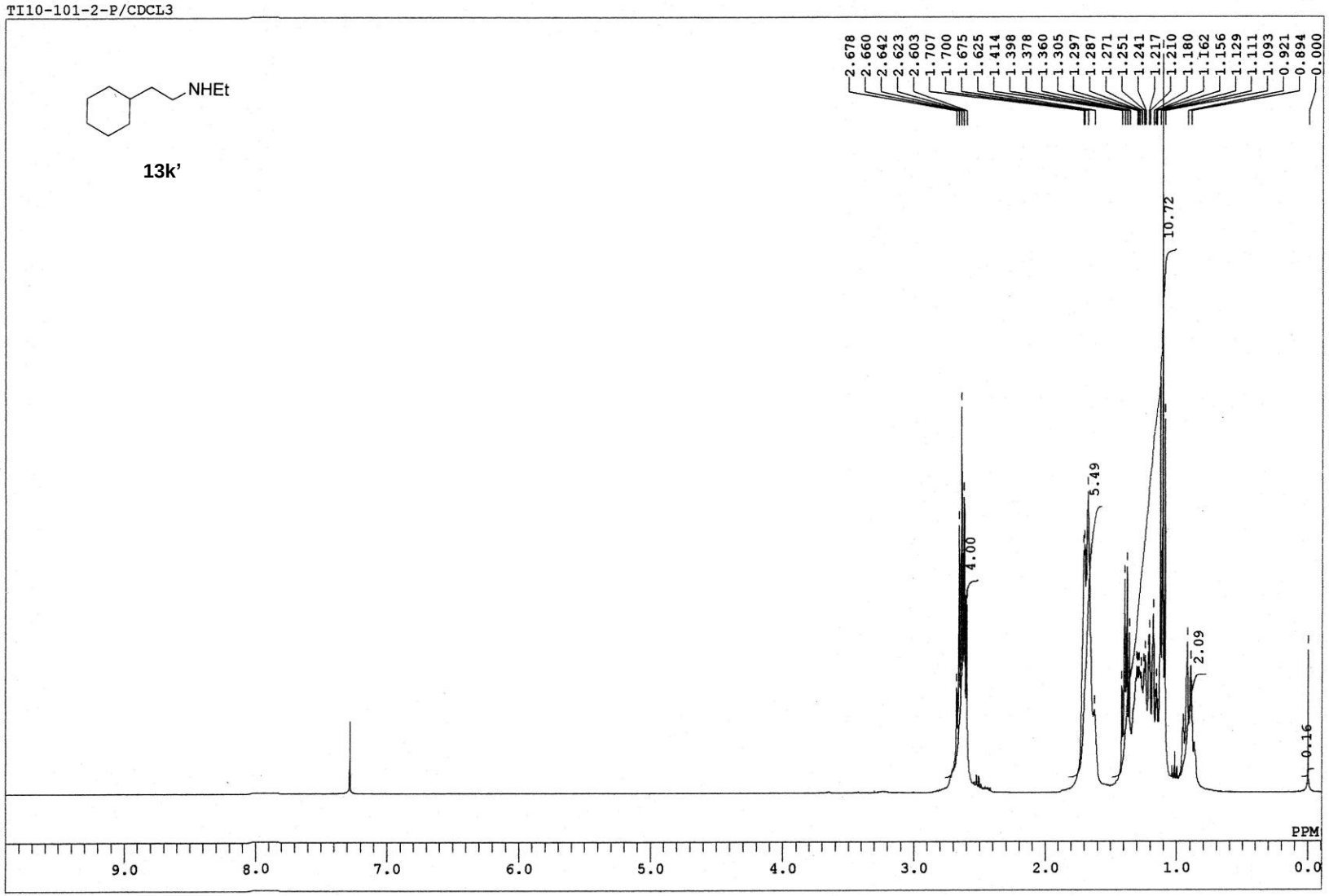

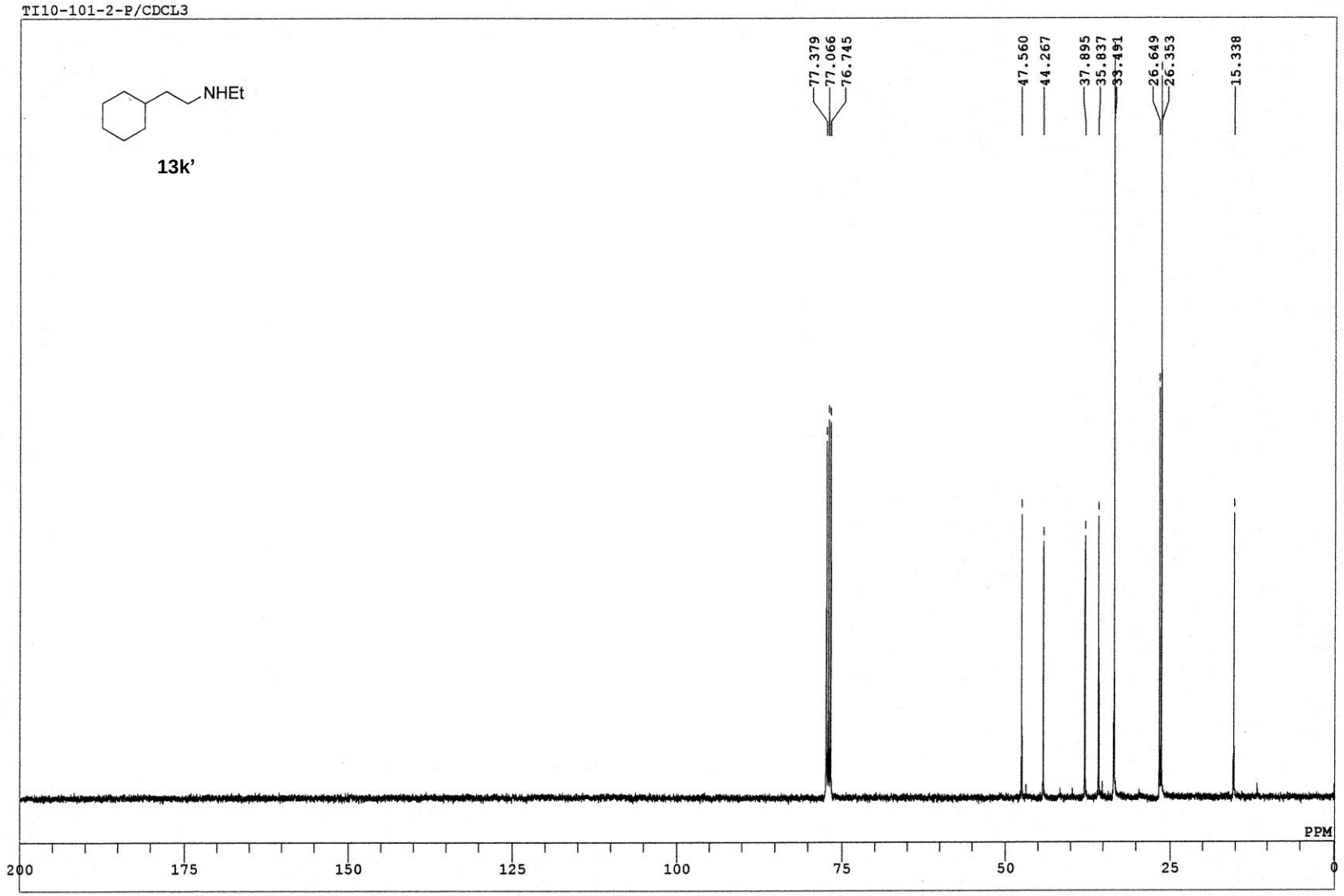

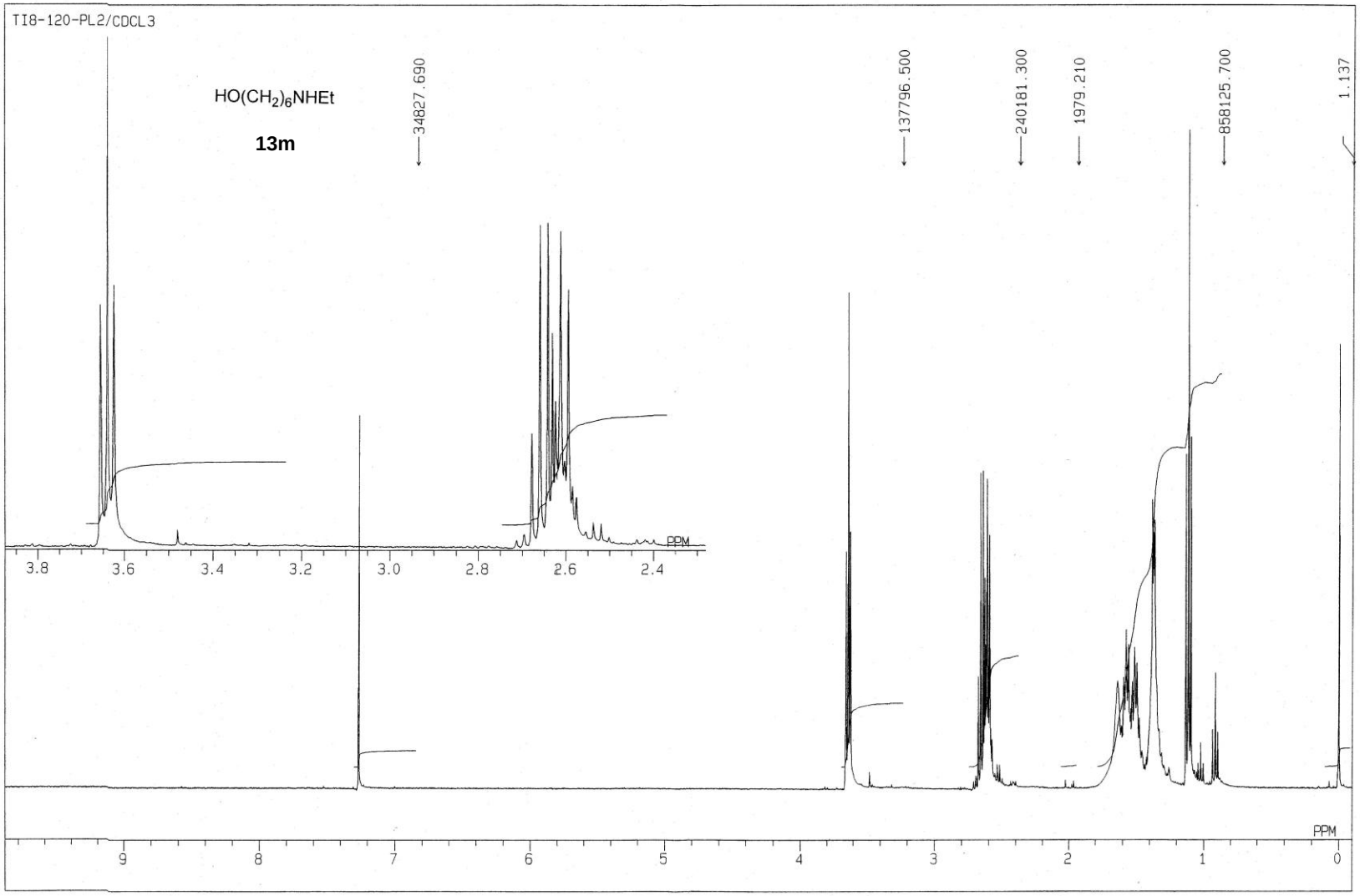

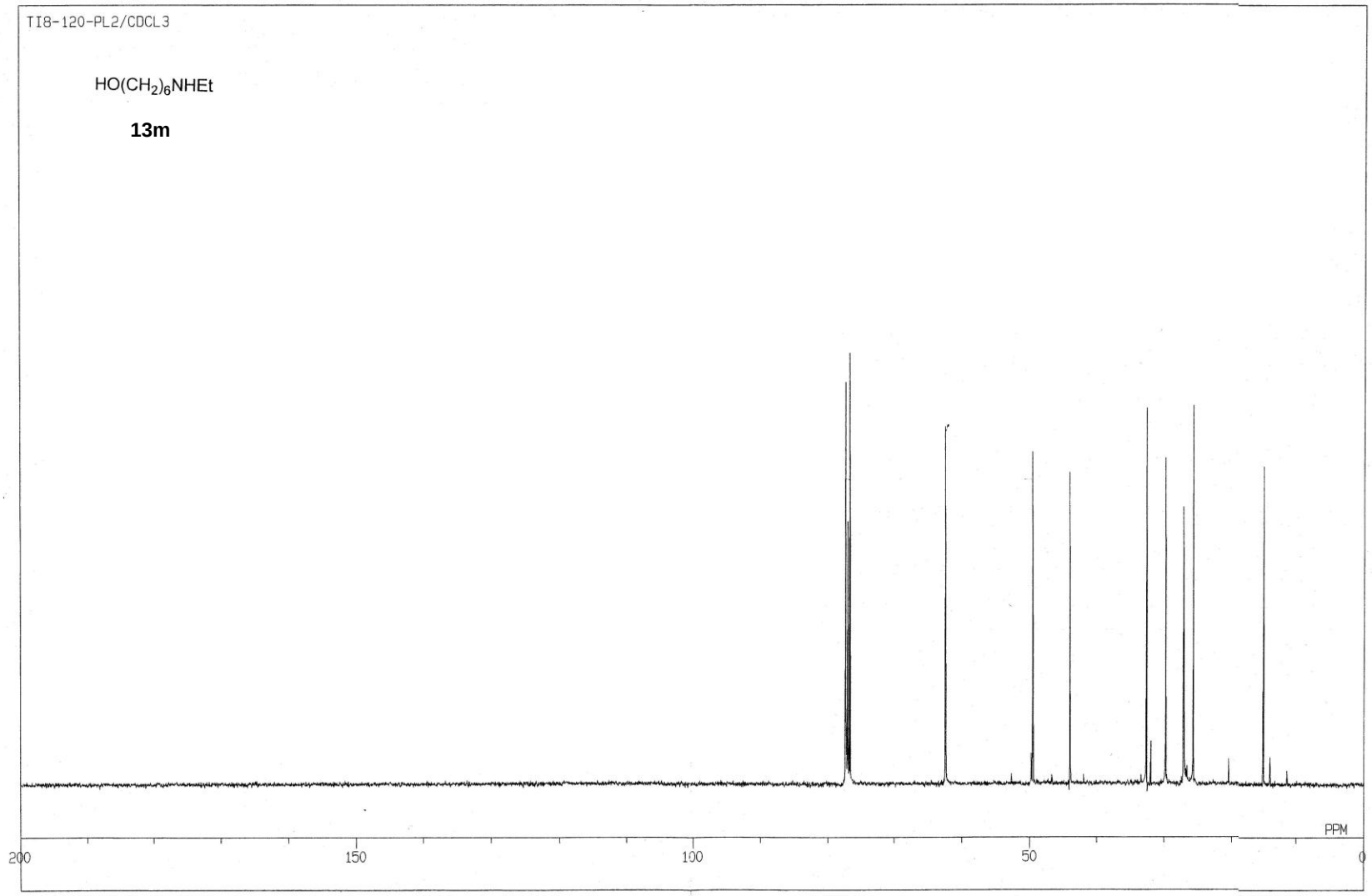

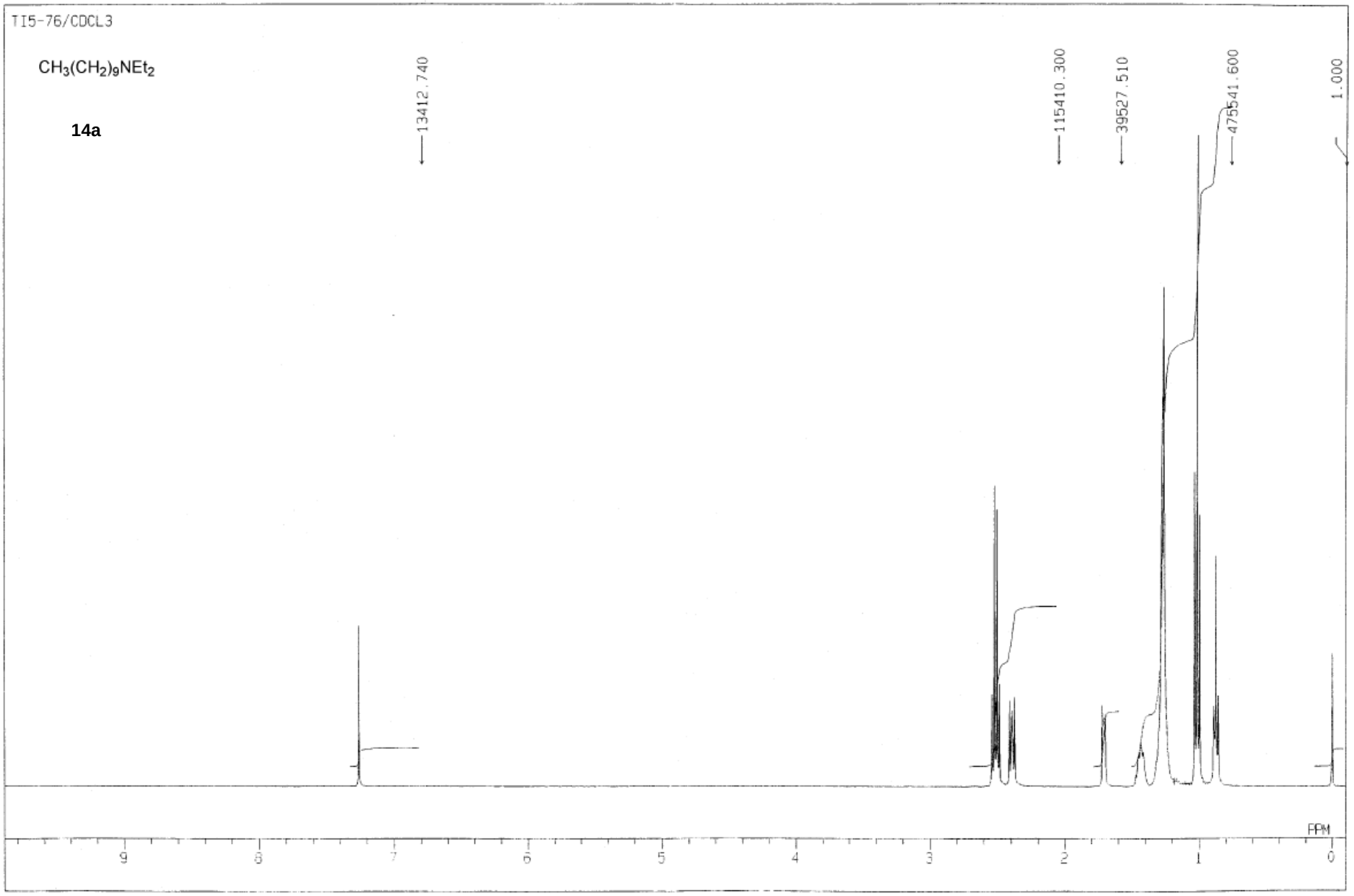

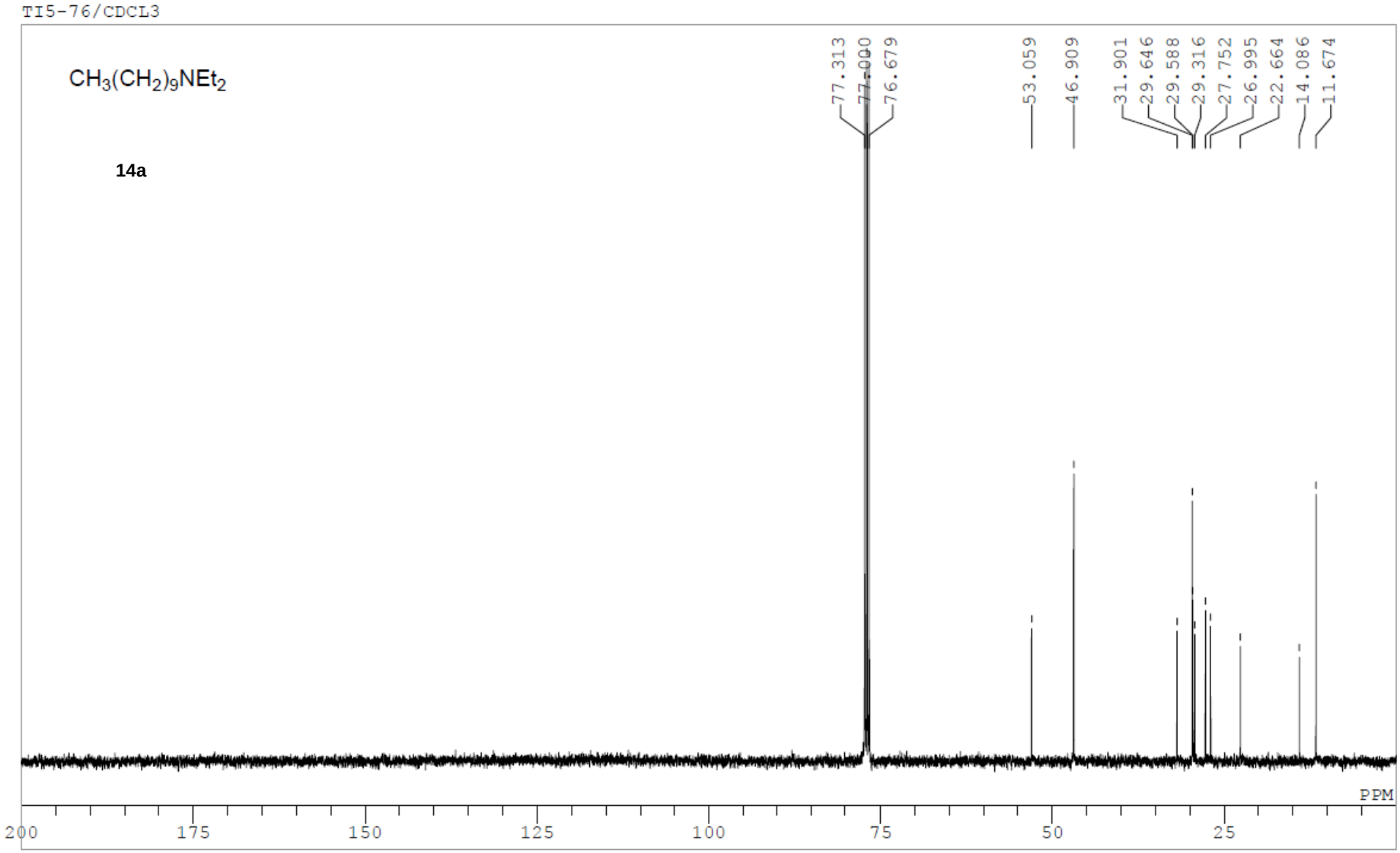

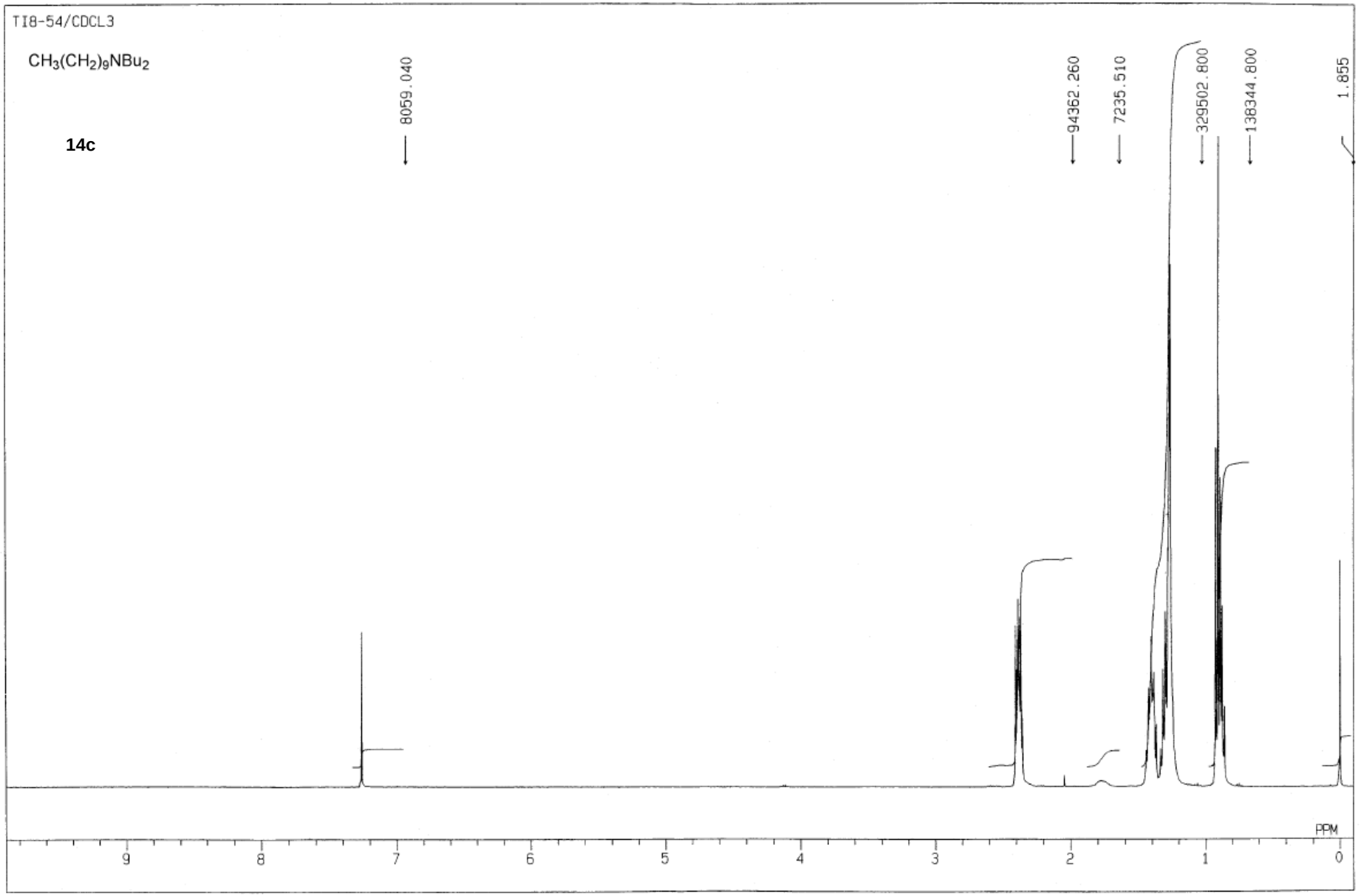

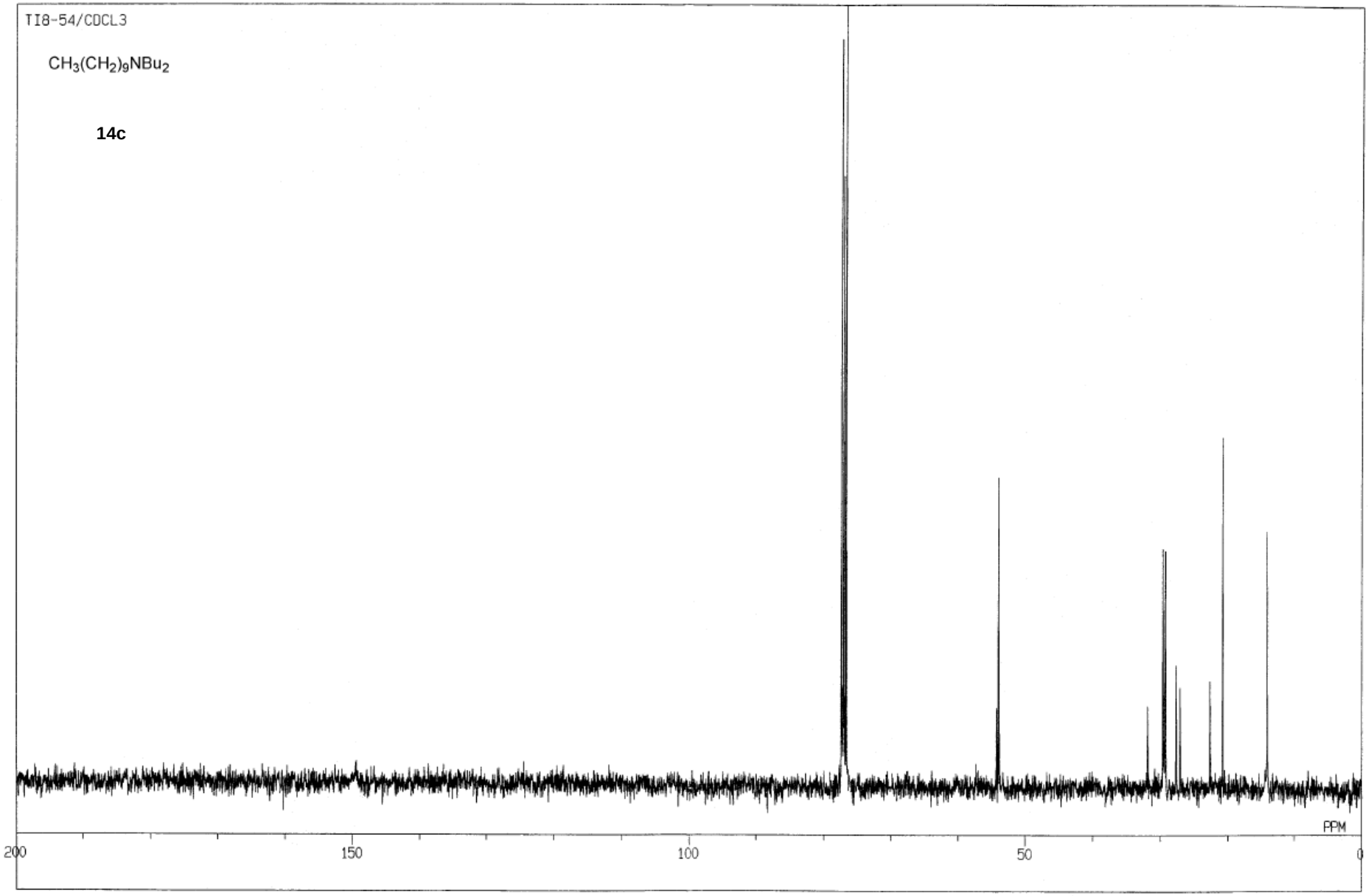

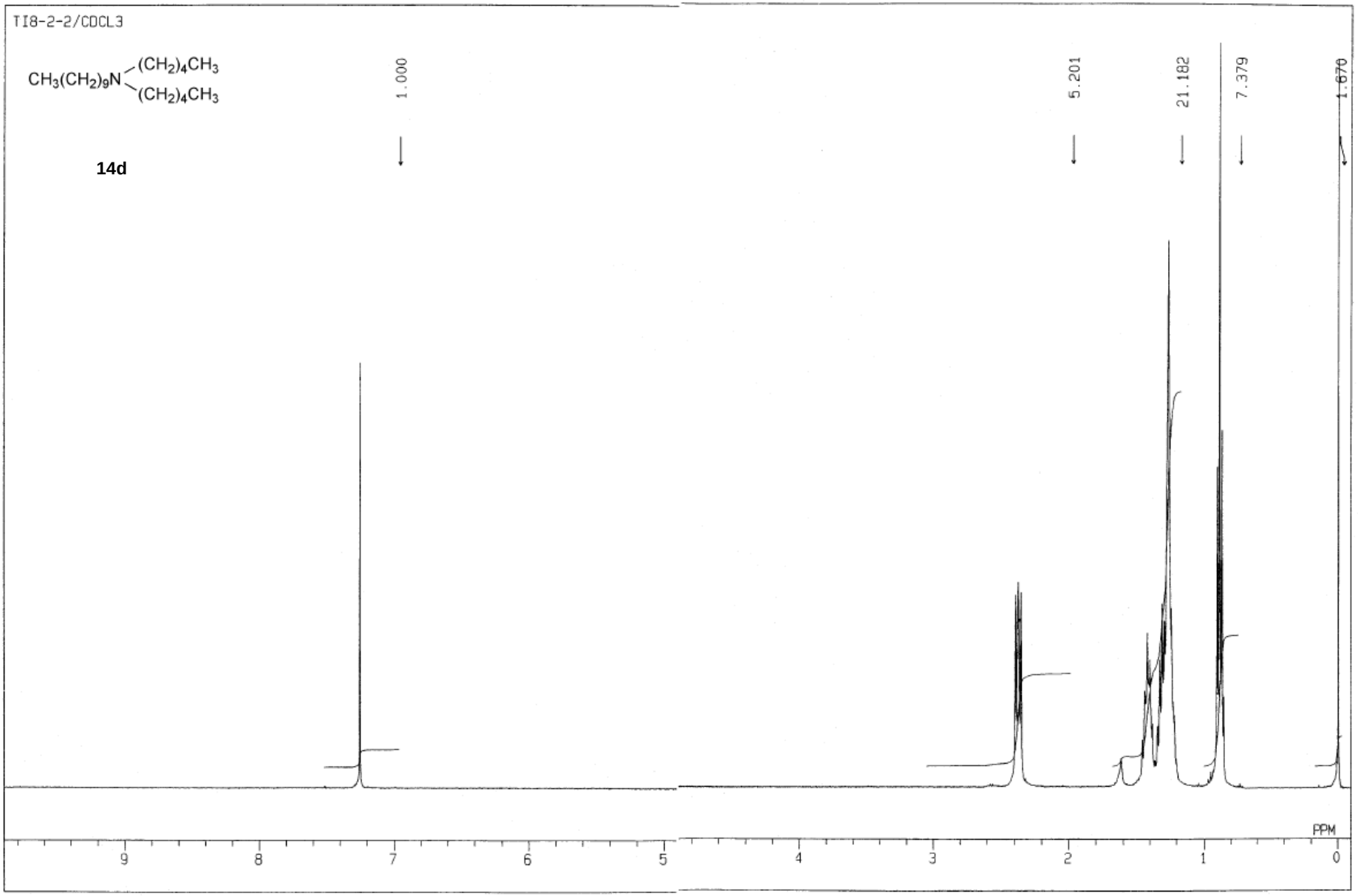

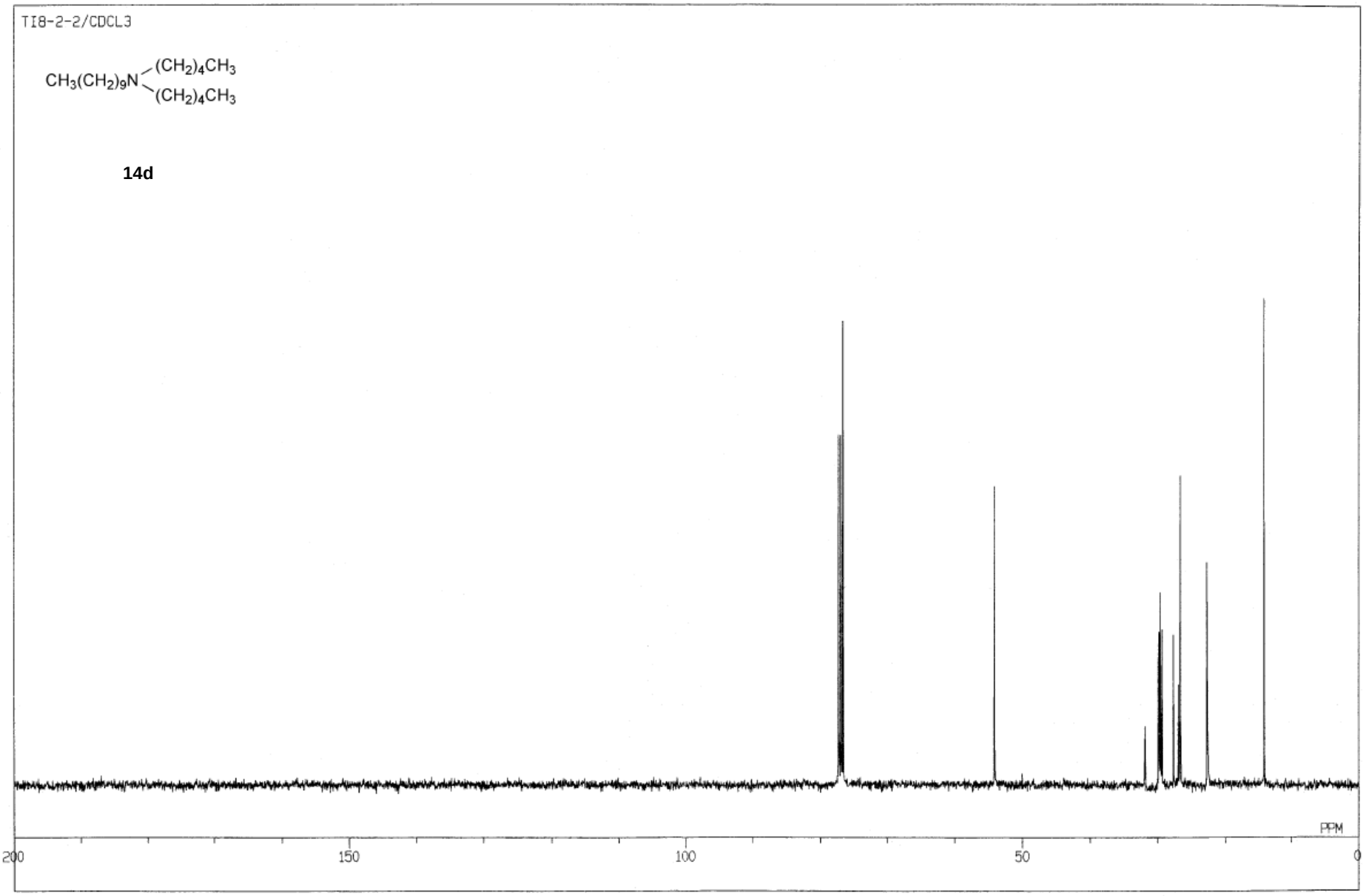

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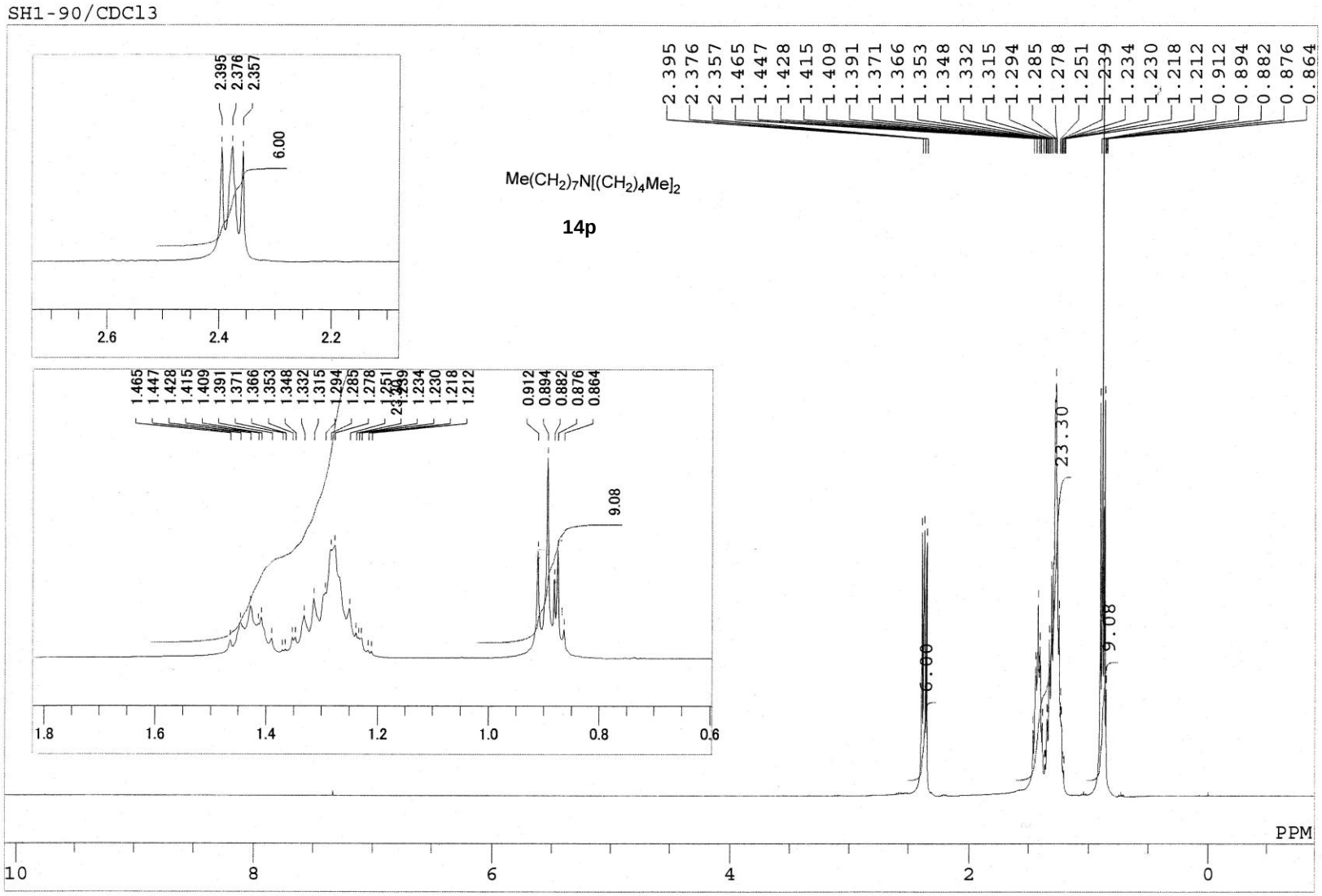

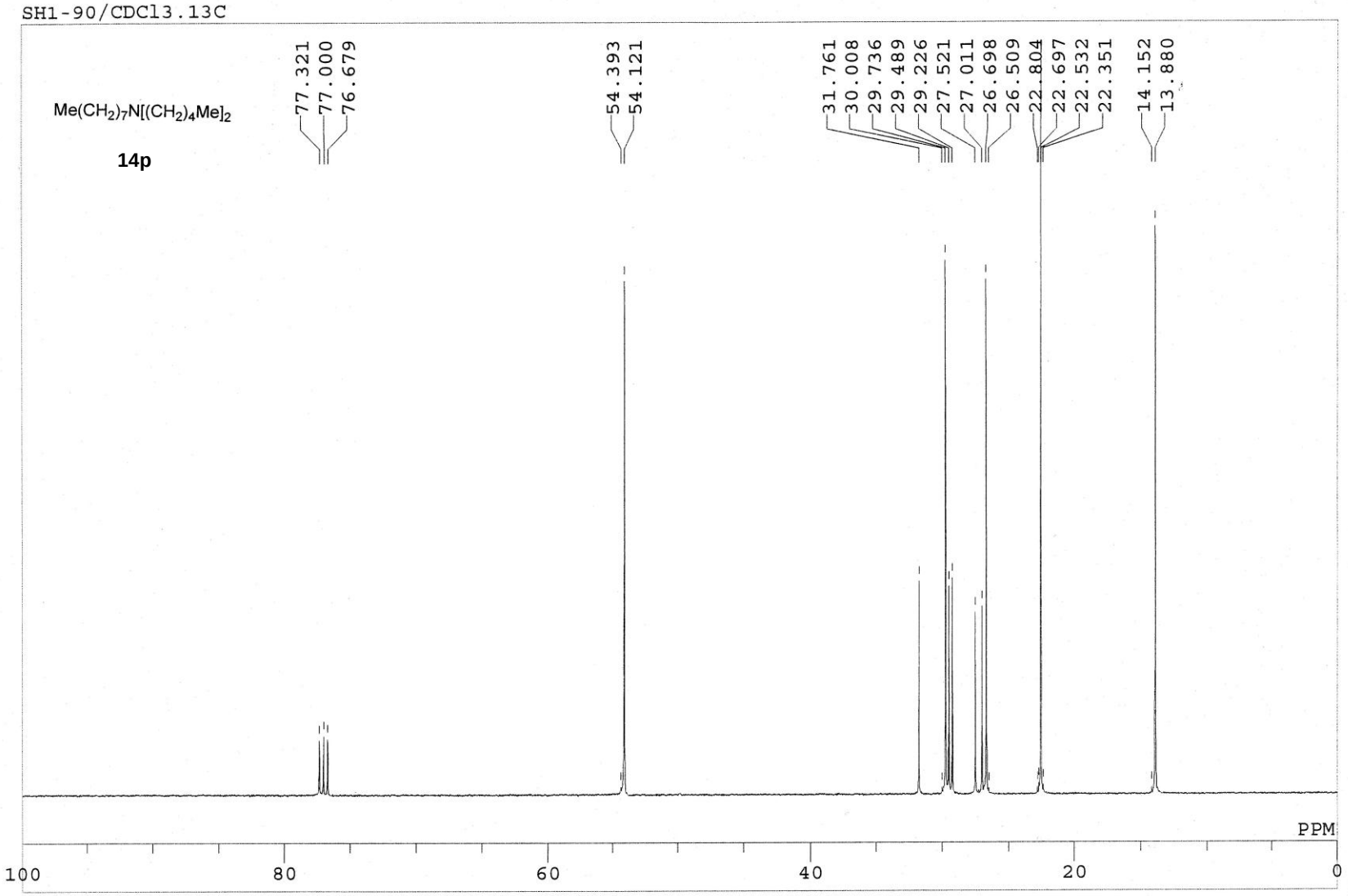

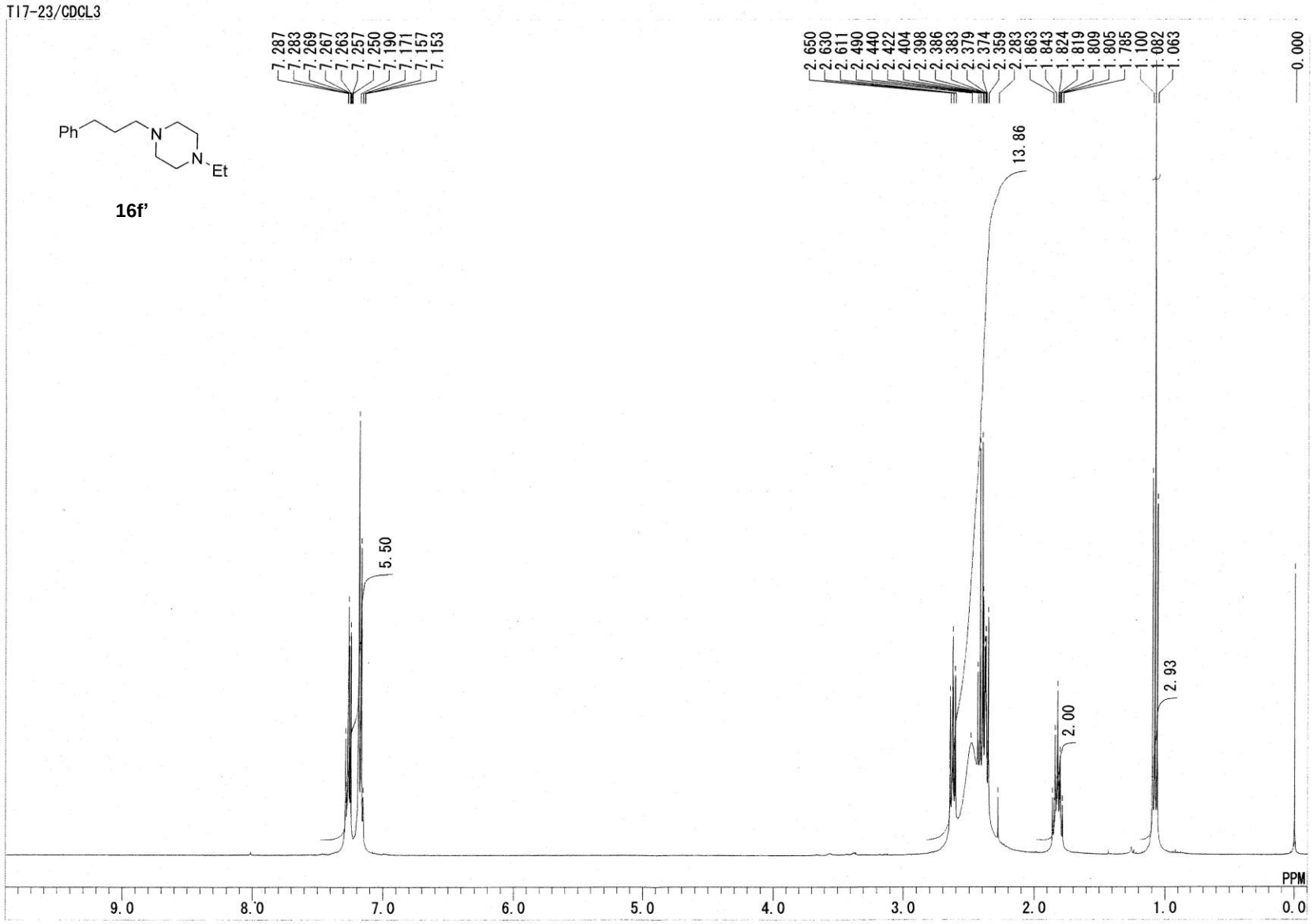

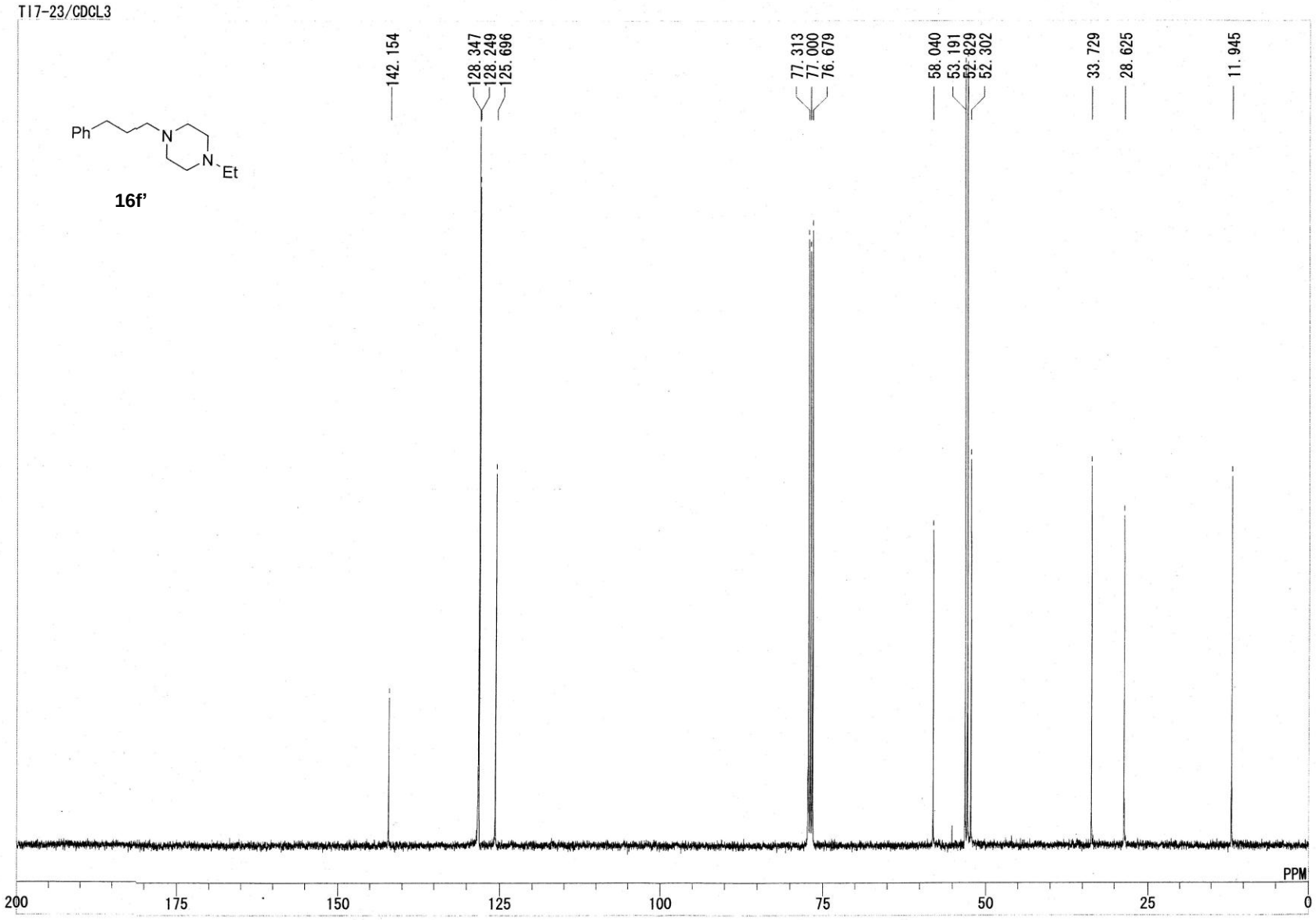

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