

Palladium-Catalyzed Coupling of Functionalized Primary and Secondary Amines with Aryl and Heteroaryl Halides: Two Ligands Suffice in Most Cases

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Supporting Information

General Reagent Information

All reactions were carried out under an argon atmosphere. 1,4-dioxane (dioxane), *tert*-butanol (*t*-BuOH) and 1,2-dimethoxyethane (DME) were purchased from Aldrich Chemical Co. in Sure-Seal bottles and were used as received. Anhydrous toluene and tetrahydrofuran (THF) were purchased from J. T. Baker in CYCLE-TAINER® solvent delivery kegs and vigorously purged with argon for 2 h. The solvent was further purified by passing it through two packed columns of neutral alumina under argon. Both potassium carbonate (K₂CO₃) and sodium *tert*-butoxide (NaOt-Bu) were purchased from Aldrich Chemical Co. Potassium *tert*-butoxide (KOt-Bu) was purchased from Acros. Powdered K₃PO₄ was purchased from Riedel-de Haën. *Anhydrous finely powdered* Cs₂CO₃ was a generous gift from Chemetall. The bulk of the bases were stored under nitrogen in a Vacuum Atmospheres glovebox. Small portions (~3 g) were removed from the glovebox in glass vials, stored in the air in a desiccator filled with anhydrous calcium sulfate, and weighed in the air. Lithium bis(trimethylsilyl)amide (LHMDS) solution (1.0 M) in THF was purchased from Aldrich. A solution in 1,4-dioxane was prepared freshly from solid LHMDS (Aldrich) prior to use. Aryl halides and amines were purchased from commercial sources (unless otherwise stated) and, when necessary, filtered through neutral alumina or distilled prior to use. Flash column chromatography was performed using a Biotage SP4 Flash Purification System using KP-Sil silica cartridges. In all cases, ethyl acetate was used to transfer the crude reaction material onto the silica gel sample. A gradient elution using hexane and ethyl acetate was performed, based on the recommendation from the Biotage TLC Wizard.

General Analytical Information. All compounds were characterized by ¹H NMR, ¹³C NMR spectroscopy. Copies of the ¹H NMR, ¹³C NMR can be found at the end of the Supporting Information. Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 MHz instrument. All ¹H NMR experiments are reported in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ¹³C NMR spectra are reported in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (77.23 ppm), unless otherwise stated, and all were obtained with ¹H decoupling. All IR spectra was taken on a Perkin – Elmer 2000 FTIR. All GC analyses were performed on a Agilent 6890 gas chromatograph with an FID detector using a J & W DB-1 column (10 m, 0.1 mm I.D.). Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA 30091.

Experimental Procedure.

General procedure for the Pd-catalyzed C-N bond formation between Primary Amine and Aryl Halides.

General procedure A. An oven-dried screw cap test tube was charged with a magnetic stir bar, BrettPhos precatalyst¹ **3** (2 mg, 0.0025 mmol, 0.25 mol% or as indicated), BrettPhos¹ **1** (1.3 mg, 0.0025 mmol, 0.25 mol% or as indicated), 1.0 mmol (if solid) aryl chloride (or, as indicated) and primary amine (1.2 mmol). The tube was evacuated and refilled with argon (three times). Under a counterflow of argon, remaining liquid reagents were added, followed by 2 mL (or, as indicated) 1,4-dioxane solution (or, as indicated) of LHMDS (2.4 mmol or, as indicated) by syringe. The tube was placed in a preheated oil bath at 100 °C (or, at indicated temperature) and the reaction mixture was stirred vigorously for 2 h (or, for indicated period of time). The reaction mixture was then cooled to room temperature, diluted with CH₂Cl₂, washed with water, dried over Na₂SO₄, concentrated in vacuo, and purified via the Biotage SP4 (silica- packed SNAP cartridge, KP-Sil, 10 g) eluting with a mixture of hexane and ethyl acetate.

General procedure B. An oven-dried screw cap test tube was charged with a magnetic stir bar, BrettPhos precatalyst¹ **3** (as indicated), BrettPhos **1** (as indicated), 1.0 mmol (if solid) aryl chloride (or, as indicated), primary amine (1.2 mmol) and K₂CO₃ (2.4 mmol or, as indicated). The tube was evacuated and refilled with argon (three times). Under a counterflow of argon, remaining liquid reagents were added, followed by *t*-BuOH (2 mL) by syringe. The tube was placed in a preheated oil bath at 110 °C (or, at indicated temperature) and the reaction mixture was stirred vigorously for 24 h (or, for indicated period of time). The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, washed with water, dried over Na₂SO₄, concentrated in vacuo, and purified via the Biotage SP4 (silica- packed SNAP cartridge, KP-Sil, 10 g) using mixture of hexane and ethyl acetate.

General procedure C. An oven-dried screw cap test tube was charged with a magnetic stir bar, BrettPhos precatalyst **3** (2 mg, 0.0025 mmol, 0.25 mol% or as indicated), BrettPhos **1** (1.3 mg, 0.0025 mmol, 0.25 mol% or as indicated), 1.0 mmol (if solid) aryl chloride (or, as indicated), primary amine (1.2 mmol) and NaO*t*-Bu (1.2 mmol or, as indicated). The tube was evacuated and refilled with argon (three times). Under a counterflow of argon, remaining liquid reagents were added, followed by 1,4-dioxane (2 mL) by syringe. The tube was placed in a preheated oil bath at 110 °C (or, at indicated temperature) and the reaction mixture was stirred vigorously for 2 h (or, for indicated period of time). The reaction mixture was then cooled to room temperature, diluted with CH₂Cl₂, washed with water, dried over Na₂SO₄, concentrated in vacuo, and purified via the Biotage SP4 (silica- packed SNAP cartridge, KP-Sil, 10 g) using mixture of hexane and ethyl acetate.

General procedure D. An oven-dried test tube, which was equipped with a magnetic stir bar, was charged with the precatalyst was charged with the BrettPhos precatalyst **3** (8.0 mg, 0.01 mmol, 1 mol%), BrettPhos **1** (5.4 mg, 0.01 mmol, 1 mol%), and base (2.4 mmol) and aminoacid (1.2 -1.4 mmol). The vessel was evacuated and backfilled with nitrogen (this process was repeated a total of 3 times) and then solven, and the aryl chloride (1.0 mmol) were added via syringe. The solution was heated to 110

°C (or, as indicated) until the starting material was completely consumed as monitored by HPLC. The reaction mixture then was allowed to cool to room temperature. To the reaction mixture were added water and 1 M HCl to adjust the pH *ca* 4. Then, the mixture was extracted with CH₂Cl₂ (3 x 20.0 mL). The organic layer was dried over Na₂SO₄. The solvent was evaporated, and the crude product was purified via the Biotage SP4 (silica-packed SNAP cartridge, KP-Sil, 10 g).

General procedure E. An oven-dried screw cap test tube was charged with a magnetic stir bar, (4 mg, 0.005 mmol, 0.5 mol% or as indicated), BrettPhos **1** (2.7 mg, 0.005 mmol, 0.5 mol% or as indicated), aryl iodide (if solid; 1.0 mmol), primary amine (1.2 mmol) and Cs₂CO₃ (2.4 mmol or, as indicated). The tube was evacuated and refilled with argon (three times). Under a counterflow of argon, remaining liquid reagents were added, followed by toluene (2 mL) by syringe. The tube was placed in a preheated oil bath at 110 °C (or, at indicated temperature) and the reaction mixture was stirred vigorously for 24 h (or, for indicated period of time). The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, washed with water, dried over Na₂SO₄, concentrated in vacuo, and purified via the Biotage SP4 (silica-packed SNAP cartridge, KP-Sil, 10 g) using mixture of hexane and ethyl acetate.

General procedure for the Pd-catalyzed C-N bond formation between Secondary Amine and Aryl Halides.

General procedure F. An oven-dried screw cap test tube was charged with a magnetic stir bar, RuPhos precatalyst² **4** (2.3 mg, 0.005 mmol, 0.5 mol% or as indicated), RuPhos **2** (3.6 mg, 0.005 mmol, 0.5 mol% or as indicated), 1.0 mmol (if solid) aryl chloride (or, as indicated), secondary amine (1.2 mmol) and NaOt-Bu (1.2 mmol or, as indicated). The tube was evacuated and refilled with argon (three times). Under a counterflow of argon, remaining liquid reagents were added, followed by THF (2 mL) by syringe. The tube was placed in a preheated oil bath at 85 °C and the reaction mixture was stirred vigorously for 24 h (or, for indicated period of time). The reaction mixture was then cooled to room temperature, diluted with CH₂Cl₂, washed with water, dried over Na₂SO₄, concentrated in vacuo, and purified via the Biotage SP4 (silica-packed SNAP cartridge, KP-Sil, 10 g) using mixture of hexane and ethyl acetate.

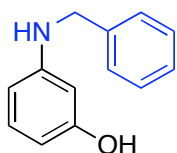
General procedure G. An oven-dried screw cap test tube was charged with a magnetic stir bar, RuPhos precatalyst **4** (2.3 mg, 0.005 mmol, 0.5 mol% or as indicated), RuPhos **2** (3.6 mg, 0.005 mmol, 0.5 mol% or as indicated), 1.0 mmol (if solid) aryl chloride (or, as indicated) and secondary amine (1.2 mmol) and Cs₂CO₃ (1.2 mmol or, as indicated). The tube was evacuated and refilled with argon (three times). Under a counterflow of argon, remaining liquid reagents were added, followed by 2 mL *t*-BuOH (or, as indicated) by syringe. The tube was placed in a preheated oil bath at 85 °C (or, at indicated temperature) and the reaction mixture was stirred vigorously for 16 h (or, for indicated period of time). The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, washed with water, dried over Na₂SO₄, concentrated in vacuo, and purified via the Biotage SP4 (silica-packed SNAP cartridge, KP-Sil, 10 g) using mixture of hexane and ethyl acetate.

General procedure H. An oven-dried screw cap test tube was charged with a magnetic stir bar, BrettPhos precatalyst **3** (2 mg, 0.0025 mmol, 0.25 mol% or as

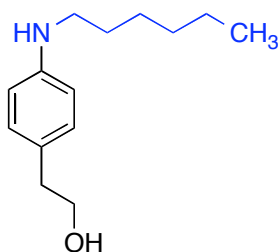
indicated), BrettPhos **1** (1.3 mg, 0.0025 mmol, 0.25 mol% or as indicated), 1.0 mmol (if solid) aryl chloride (or, as indicated) and primary amine (1.2 mmol). The tube was evacuated and refilled with argon (three times). Under a counterflow of argon, remaining liquid reagents were added, followed by 2.2 mL THF solution of LHMDS (2.2 mmol, 1.0 M in THF) by syringe. The tube was placed in a preheated oil bath at 65 °C (or, at indicated temperature) and the reaction mixture was stirred vigorously for 8 h (or, for indicated period of time). The reaction mixture was then cooled to room temperature, diluted with CH₂Cl₂, washed with water, dried over Na₂SO₄, concentrated in vacuo, and purified via the Biotage SP4 (silica- packed SNAP cartridge, KP-Sil, 10 g) using mixture of hexane and ethyl acetate.

General procedure I. To a screwcap vial was added RuPhos (**2**), RuPhos precatalyst (**4**), NaOt-Bu (115 mg, 1.2 mmol), aryl chloride (1 mmol, when solid) and amine (1.2 mmol, where solid). The vial was sealed with a teflon screwcap then evacuated and filled with argon for 3 cycles. THF (2 mL), aryl chloride (1 mmol, when liquid) and amine (1.2 mmol, when liquid) were added via syringe, and the reaction heated at 85 °C for 4 h. After cooling to room temperature the reaction was poured into sat. NaHCO₃ and extracted with 3 portions of EtOAc. The combined organic layers then washed with brine, dried over MgSO₄, filtered and concentrated, yielding the title compounds after purification.

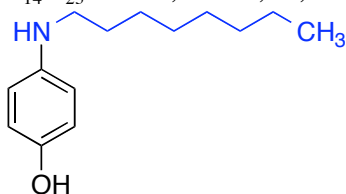
General procedure J. To a screwcap vial was added RuPhos (**2**) (1.15 mg, 0.25 mol%), RuPhos precatalyst (**4**) (1.8 mg, 0.25 mol%), K₃PO₄ (255 mg, 1.2 mmol) and aryl chloride (1 mmol, when solid). The vial was sealed with a teflon screwcap then evacuated and filled with argon for 3 cycles. *t*-Butanol (2 mL), benzyl piperazine-1-carboxylate (232 μL, 1.2 mmol) and aryl chloride (1 mmol, when liquid) were added via syringe, and the reaction heated at 110 °C for 16 h. After cooling to room temperature, the reaction was poured into 1M HCl (10 mL) and extracted with EtOAc. The acid layer was basified with NaOH, extracted with 3 portions of EtOAc and the combined organic layers then washed with brine, dried over MgSO₄, filtered and concentrated, yielding the title compounds after purification.



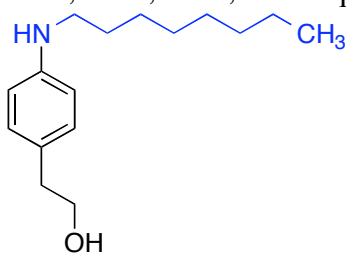
3-(benzylamino)phenol (Table 1, entries 1a and 1b).³ The general procedure A was followed for 5 h. Isolation and biotage purification afforded the title compound as a dark-brown oil (185 mg, 93%, entry **1a**). The general procedure A with aryl bromide for 5 h was followed. Isolation and biotage purification afforded the title compound in 92% yield (entry **1b**). ¹H NMR (400 MHz, CDCl₃) δ: 7.32 (d, 4H, J = 8.0), 7.29-7.27 (m, 1H), 7.00 (t, 1H, J = 8.0), 6.22-6.17 (m, 2H), 6.09 (t, 1H, J = 2.0), 4.24 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ: 156.8, 149.7, 139.2, 130.3, 128.7, 127.6, 127.3, 106.1, 104.9, 100.1, 48.3. IR (KBr disc, cm⁻¹): 3384, 1619, 1515, 1452, 1179, 1028, 909, 827, 731, 698.



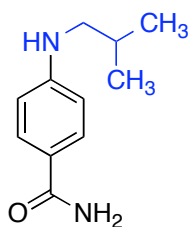
2-(4-Hexylaminophenyl)ethanol (Table 1, entry 1c). The general procedure A with 0.5 mol% catalyst and LHMDS (368 mg, 2.2 mmol) for 30 min at 90 °C was followed. Isolation and biotage purification afforded the title compound as a pale yellow solid (203 mg, 92%). ¹H NMR (400 MHz, CDCl₃) δ: 7.01 (d, 2H, J = 8.5), 6.55 (d, 2H, J = 8.5), 3.77 (t, 2H, J = 6.5), 3.53 (br-s, 1H), 3.06 (t, 2H, J = 7), 2.73 (t, 2H, J = 6.5), 1.54-1.63 (m, 2H), 1.25-1.41 (m, 6H), 0.88 (t, 3H, J = 6.9). ¹³C NMR (100 MHz, CDCl₃) δ: 147.4, 130.0, 126.8, 113.2, 64.1, 44.4, 38.4, 31.8, 29.7, 27.0, 22.8, 14.2. Anal. Calcd for C₁₄H₂₃NO: C, 75.97; H, 10.47. Found: C, 76.09; H, 10.44. m.p. 37-38 °C.



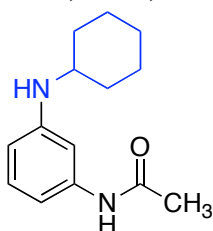
4-(octylamino)phenol (Table 1, entry 1d).³ The general procedure A with 0.5 mol% catalyst for 6 h was followed. Isolation and biotage purification afforded the title compound as a brown solid (155 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ: 6.65 (s, 2H), 6.53 (s, 2H), 4.47 (s, 2H), 3.01 (s, 2H), 1.56 (t, 2H, J = 8.0), 1.35-1.18 (m, 10H), 0.86 (t, 3H, J = 8.0). ¹³C NMR (100 MHz, CDCl₃) δ: 129.6, 117.0, 116.4, 115.1, 45.7, 32.0, 29.8, 29.6, 29.5, 27.4, 23.6, 22.9, 14.3. IR (KBr disc, cm⁻¹): 3315, 2926, 2855, 1603, 1515, 1468, 1376, 1237, 822. m.p. 73 °C (74-76 °C).



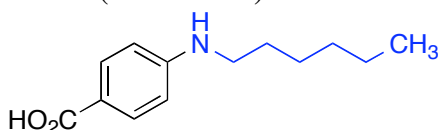
2-(4-(octylamino)phenyl)ethanol (Table 1, entry 1e).³ The general procedure A with 0.5 mol% catalyst for 20 min was followed. Isolation and biotage purification afforded the title compound as a reddish-yellow solid (210 mg, 84%). ¹H NMR (400 MHz, CDCl₃) δ: 7.00 (d, 2H, J = 8.0), 6.54 (d, 2H, J = 8.0), 3.74 (t, 2H, J = 8.0), 3.05 (t, 2H, J = 8.0), 2.71 (t, 2H, J = 8.0), 1.60-1.56 (m, 2H), 1.37-1.24 (m, 12H), 0.87 (t, 3H, J = 6.0). ¹³C NMR (100 MHz, CDCl₃) δ: 147.2, 129.9, 126.6, 113.0, 64.0, 44.2, 38.3, 31.9, 29.6, 29.5, 29.3, 27.2, 22.7, 14.2. IR (KBr disc, cm⁻¹): 3373, 2953, 2919, 2850, 1617, 1584, 1522, 1485, 1466, 1384, 1318, 1279, 1264, 1245, 1188, 1136, 1117, 1047, 1021, 824, 793, 756, 722, 606, 522, 444, 408. m.p. 50 °C.



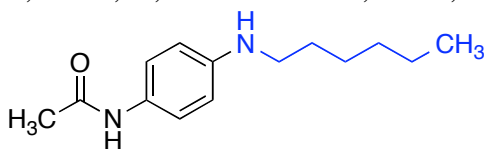
4-(isobutylamino)benzamide (Table 1, entry 1f).³ The general procedure A for 3 h was followed. Isolation and biotage purification afforded the title compound as a white solid (167 mg, 87%). ¹H NMR (400 MHz, CDCl₃) δ: 7.63-7.60 (m, 2H), 6.53-6.50 (m, 2H), 6.06 (s, 2H), 2.92 (t, 2H, J = 6.0), 1.84 (septet, 1H, J = 6.7), 0.94 (d, 6H, J = 4.0). ¹³C NMR (100 MHz, CDCl₃) δ: 169.7, 151.6, 129.3, 120.9, 111.5, 51.2, 28.0, 20.4. IR (KBr disc, cm⁻¹): 3402, 3192, 2961, 1643, 1614, 1570, 1529, 1471, 1397, 1332, 1263, 1189, 1152, 1123, 834, 791. m.p. 134 °C.



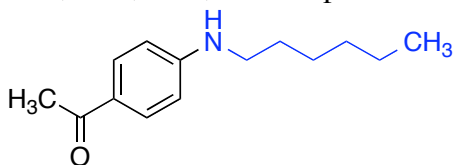
N-(3-(cyclohexylamino)phenyl)acetamide (Table 1, entry 1g).³ The general procedure A with 0.05 mol% catalyst for 16 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (187 mg, 80%). ¹H NMR (400 MHz, CDCl₃) δ: 7.57 (s, 1H), 7.03-6.98 (m, 2H), 6.58 (d, 1H, J = 8.0), 6.29 (dd, 1H, J = 8.0, J = 4.0), 3.55 (s, 1H), 3.21-3.15 (m, 1H), 2.09 (s, 2H), 1.98 (d, 2H, J = 8.0), 1.72-1.68 (m, 2H), 1.61-1.58 (m, 1H), 1.36-1.26 (m, 2H), 1.22-1.06 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 168.6, 148.1, 139.1, 129.6, 108.9, 108.1, 104.7, 51.6, 33.4, 25.9, 25.0, 24.7. IR (KBr disc, cm⁻¹): 3310, 2930, 2853, 1666, 1614, 1554, 1481, 1449, 1417, 1371, 1319, 1276, 1195, 1166, 1148, 1114, 1022, 991, 961, 910, 888, 846, 768, 732, 691. 405. m.p. 124 °C (124-125 °C).



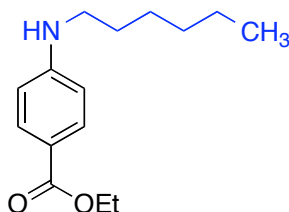
4-N-Hexylaminobenzoic acid (Table 1, entry 1h). The general procedure A with 0.5 mol% catalyst, LHMDS (368 mg, 2.2 mmol) and dioxane (1 mL) at 90 °C for 1 h was followed. Isolation and biotage purification afforded the title compound as a pale yellow solid (217 mg, 98%). ¹H NMR (400 MHz, d₆-DMSO) δ: 11.97 (s, 1H), 7.65 (d, 2H, J = 8.8), 6.54 (d, 2H, J = 8.8), 6.42 (t, 1H, J = 5.3), 3.04 (q, 2H, J = 6.5), 1.53 (quint, 2H, J = 7.2), 1.20-1.40 (m, 6H), 0.87 (t, 3H, J = 6.9). ¹³C NMR (100 MHz, d₆-DMSO) δ: 167.6, 152.7, 131.2, 116.6, 110.7, 42.4, 31.2, 28.5, 26.4, 22.2, 14.0. Anal. Calcd for C₁₃H₁₉NO₂: C, 70.56; H, 8.65. Found: C, 70.30; H, 8.64. m.p. 123-125 °C.



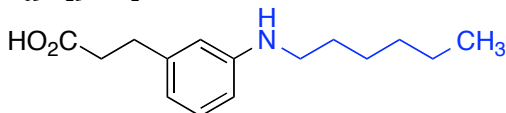
4-*N*-Hexylamino-acetanilide (Table 1, entry 1i). The general procedure A with 0.5 mol% catalyst and LHMDS (368 mg, 2.2 mmol) at 90 °C for 30 min was followed. Isolation and biotage purification (CH₂Cl₂/methanol) afforded the title compound as a pale yellow solid as a white solid (215 mg, 92%). ¹H NMR (400 MHz, d₆-DMSO) δ: 9.50 (s, 1H), 7.23 (d, 2H, J = 8.8), 6.46 (d, 2H, J = 8.8), 5.31 (t, 1H, J = 5.6), 2.93 (q, 2H, J = 6.6), 1.95 (s, 3H), 1.51 (quint, 2H, J = 7.2), 1.23-1.40 (m, 6H), 0.87 (t, 3H, J = 6.9). ¹³C NMR (100 MHz, d₆-DMSO) δ: 167.2, 145.4, 128.3, 120.9, 111.7, 43.2, 31.2, 28.8, 26.5, 23.7, 22.2, 14.0. m.p. 104-105 °C.



4'-*N*-Hexylamino-acetophenone (Table 1, entry 1j). The general procedure A with 0.5 mol% catalyst, LHMDS (368 mg, 2.2 mmol) and dioxane (1 mL) at 80 °C for 30 min. was followed. Isolation and biotage purification (CH₂Cl₂/methanol) afforded the title compound as a pale yellow solid as a yellow solid (191 mg, 87%). ¹H NMR (400 M, CDCl₃) δ: 7.80 (d, 2H, J = 8.8), 6.52 (d, 2H, J = 8.8), 4.16 (br-s, 1H), 3.13-3.18 (m, 2H), 2.48 (s, 3H), 1.55-1.65 (m, 2H), 1.25-1.45 (m, 6H), 0.87 (t, 3H, J = 6.9). ¹³C NMR (100 M, CDCl₃) δ: 196.5, 152.5, 131.0, 126.5, 111.4, 43.5, 31.7, 29.4, 26.9, 26.2, 22.8, 14.2. IR (neat, cm⁻¹): 3352, 2926, 1648, 1590, 1362, 1282, 1180, 954, 829. m.p. 76-77 °C.

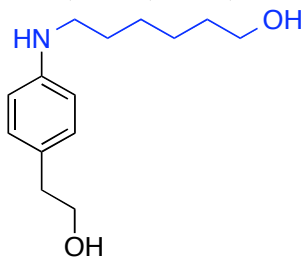


Ethyl 4-(hexylamino)benzoate (Table 1, entry 1k). The general procedure B with 1.2 mol% catalyst for 24 h was followed. Isolation and biotage purification afforded the title compound as a light-yellow solid (190 mg, 76%). ¹H NMR (400 MHz, CDCl₃) δ: 7.83 (d, 2H, J = 8.0), 6.50 (d, 2H, J = 8.0), 4.29 (q, 2H, J = 10.0), 4.07 (s, 1H), 3.12 (q, 2H, J = 10.0), 1.59 (pent, 2H, J = 8.0), 1.40-1.27 (m, 9H), 0.87 (t, 3H, J = 6.0). ¹³C NMR (100 MHz, CDCl₃) δ: 167.1, 152.3, 131.7, 118.5, 111.5, 60.3, 43.6, 31.8, 29.5, 26.9, 22.8, 14.7, 14.2. IR (KBr disc, cm⁻¹): 3375, 2933, 2854, 1680, 1603, 1577, 1533, 1476, 1423, 1369, 1343, 1312, 1282, 1266, 1174, 1108, 841, 773, 730, 701. Anal. Calcd for C₁₅H₂₃NO₂: C, 72.25; H, 9.30. Found: C, 72.46; H, 9.37. m.p. 90 °C.

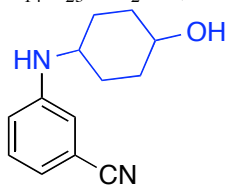


3-[3-(Hexylamino)phenyl]propanoic acid (Table 1, entry 1l). The general procedure A with 0.5 mol% catalyst, LHMDS (368 mg, 2.2 mmol) and dioxane (1 mL) for 30 min at 90 °C was followed. Isolation and biotage purification afforded the title compound as a pale yellow oil (197 mg, 79%). ¹H NMR (400 MHz, CDCl₃) δ: 7.08 (dd, 1H, J = 8.2 and 7.6), 6.52 (d, 1H, J = 7), 6.42-6.48 (m, 2H), 4.85 (br-s, 1H), 3.07 (t, 2H, J = 7), 2.86 (t, 2H, J = 8), 2.64 (t, 2H, J = 8), 1.59 (quint, 2H, J = 7.3), 1.25-1.42 (m, 6H), 0.88 (t, 3H,

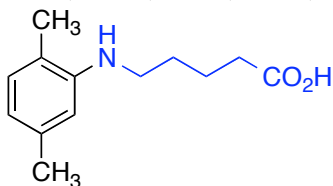
$J = 6.8$). ^{13}C NMR (400 MHz, CDCl_3) δ : 179.1, 148.6, 141.6, 129.5, 117.6, 113.2, 111.3, 44.4, 35.9, 31.8, 31.0, 29.6, 27.0, 22.8, 14.2. IR (neat, cm^{-1}): 3399, 2955, 2929, 2857, 1710, 1607, 1590, 1259, 697.



6-((4-(2-hydroxyethyl)phenyl)amino)hexan-1-ol (Table 2, entry 2a). The general procedure A with 1 mol% catalyst, LHMDS (3.4 mmol) and dioxane (3 mL) for 21 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (170 mg, 72%, entry 2a). ^1H NMR (400 MHz, CDCl_3) δ : 6.99 (d, 2H, $J = 8.0$), 6.54-6.51 (m, 2H), 3.74 (t, 2H, $J = 6.0$), 3.59 (t, 2H, $J = 6.0$), 3.05 (t, 3H, $J = 6.0$), 2.71 (t, 2H, $J = 6.0$), 1.60-1.50 (m, 6H), 1.38 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ : 147.3, 130.0, 126.9, 113.2, 64.1, 63.0, 44.3, 38.5, 32.8, 29.7, 27.1, 25.8. IR (KBr disc, cm^{-1}): 3382, 2931, 2855, 1691, 1658, 1614, 1519, 1479, 1317, 1044, 814, 697, 672. Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{NO}_2$: C, 70.85; H, 9.77. Found: C, 70.69; H, 9.73. m.p. 47 °C.



3-((4-hydroxycyclohexyl)amino)benzonitrile (Table 2, entry 2b). The general procedure A with 1 mol% catalyst and dioxane (3 mL) for 21 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (162 mg, 75%, entry 2a). ^1H NMR (400 MHz, CDCl_3) δ : 7.12-7.07 (m, 1H), 6.79 (d, 1H, $J = 8.0$), 6.67 (s, 2H), 4.05-3.97 (m, 1H), 3.58 (m, 1H), 3.13 (s, 1H), 2.97 (s, 1H), 2.02-1.93 (m, 4H), 1.39-1.30 (m, 2H), 1.18-1.09 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ : 171.7, 147.9, 130.2, 120.2, 119.9, 117.8, 115.1, 112.7, 69.9, 60.7, 51.0, 37.5, 34.0, 33.8, 30.8, 21.3, 14.4. IR (KBr disc, cm^{-1}): 3375, 2934, 2859, 2227, 1700, 1653, 1602, 1582, 1559, 1521, 1489, 1456, 1337, 1053, 991, 960, 778, 683.

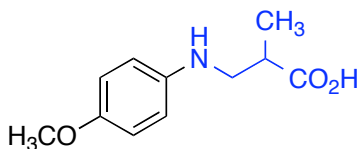


5-(2,5-Dimethoxyphenylamino)pentanoic acid (Table 2, entry 2c). The general procedure D with sodium tert-butoxide (230 mg, 2.4 mmol) and dioxane (5 mL) at 110 °C for 20 h was followed. Isolation and biotage purification afforded the title compound as a white solid (210 mg, 95%). ^1H NMR (400 MHz, CDCl_3) δ : 6.91 (d, 1H, $J = 7$), 6.46 (d, 1H, $J = 7$), 6.41 (s, 1H), 3.16 (t, 2H, $J = 7$), 2.42 (t, 2H, $J = 7$), 2.28 (s, 3H), 2.07 (s, 3H), 1.81-1.65 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ : 180.1, 146.1, 136.9, 130.1, 119.2, 117.8, 110.9, 43.7, 33.9, 29.1, 22.4, 21.8, 17.2. IR (neat, cm^{-1}): 3420, 2919, 2858,

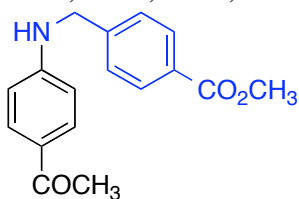
1703, 1616, 1584, 1521, 1297, 1279, 1215, 800. Anal. Calcd for C₁₃H₁₉NO₂: C, 70.56; H, 8.65. Found: C, 70.57; H, 8.61. m.p. 72-73 °C.



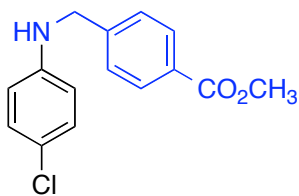
8-(2,5-Dimethoxyphenylamino)octanoic acid (Table 2, entry 2d). The general procedure D with sodium tert-butoxide (230 mg, 2.4 mmol) and dioxane (5 mL) at 110 °C for 20 h was followed. Isolation and biotage purification afforded the title compound as a white solid (247 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ: 6.91 (d, 1H, J = 7.4), 6.44 (d, 1H, J = 7.4), 6.41 (s, 1H), 3.11 (t, 2H, J = 7), 2.34 (t, 2H, J = 8), 2.27 (s, 3H), 2.07 (s, 3H), 1.65-1.60 (m, 4H), 1.43-1.35 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 180.4, 146.3, 136.9, 130.0, 119.0, 117.6, 110.9, 44.2, 34.3, 29.7, 29.3, 29.2, 27.2, 24.8, 21.8, 17.2. IR (neat, cm⁻¹): 3424, 2930, 2857, 1705, 1614, 1525, 1425, 1318, 1230, 1196, 790. Anal. Calcd for C₁₆H₂₅NO₂: C, 72.96; H, 9.57. Found: C, 72.54; H, 9.52. m.p. 77-78 °C.



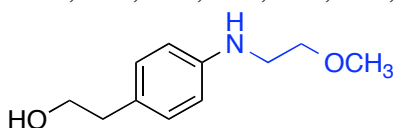
3-(4-Methoxyphenylamino)-2-methylpropanoic acid (Table 2, entry 2e). The general procedure D with potassium tert-butoxide (269 mg, 2.4 mmol) and toluene (1 mL) at 100 °C for 18 h was followed. Isolation and biotage purification afforded the title compound as a yellow oil (176 mg, 84%). ¹H NMR (400 MHz, CDCl₃) δ: 6.77 (d, 2H, J = 8.8), 6.66 (d, 2H, J = 8.8), 5.65 (br-s, 2H), 3.73 (s, 3H), 3.33 (dd, 1H, J = 13 and 8.8), 3.19 (dd, 1H, J = 13 and 5.1), 2.81-2.72 (m, 1H), 1.23 (d, 3H, J = 7.1). ¹³C NMR (100 MHz, CDCl₃) δ: 180.4, 153.4, 140.5, 116.0, 115.0, 55.8, 49.0, 38.9, 15.0. IR (neat, cm⁻¹): 3379, 2936, 1710, 1514, 1463, 1236, 1033, 822.



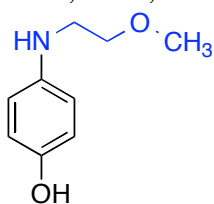
Methyl 4-(((4-acetylphenyl)amino)methyl)benzoate (Table 2, entry 2f). The general procedure E with toluene (3 mL) for 17 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (247 mg, 87%). ¹H NMR (400 MHz, CDCl₃) δ: 7.97 (d, 2H, J = 12.0), 7.76 (d, 2H, J = 8.0), 7.36 ((d, 2H, J = 8.0), 6.53 (d, 2H, J = 8.0), 4.85 (s, 1H), 4.44 (d, 2H, J = 4.0), 3.86 (s, 3H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 196.5, 166.8, 151.7, 143.7, 130.8, 130.1, 129.4, 127.2, 127.0, 111.7, 52.2, 47.2, 26.1. IR (KBr disc, cm⁻¹): 3339, 1708, 1656, 1595, 1527, 1423, 1361, 1335, 1283, 1180, 1113, 1019, 959, 850, 825, 764, 718. Anal. Calcd for C₁₇H₁₇NO₃: C, 72.07; H, 6.05. Found: C, 72.04; H, 5.99. m.p. 141 °C.



Methyl 4-(((4-chlorophenyl)amino)methyl)benzoate (Table 2, entry 2g). The general procedure E with toluene (3 mL) for 17 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (247 mg, 87%). ¹H NMR (400 MHz, CDCl₃) δ: 7.99-7.97 (m, 2H), 7.38 (d, 2H, J = 8.0), 7.08-7.06 (m, 2H), 6.49-6.47 (m, 2H), 4.34 (s, 2H), 4.19 (s, 1H), 3.88 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 167.1, 146.5, 144.6, 130.2, 129.4, 127.3, 122.5, 114.2, 52.3, 48.2. IR (KBr disc, cm⁻¹) 3388, 2955, 2848, 2361, 1714, 1598, 1506, 1466, 1437, 1416, 1316, 1278, 1179, 1103, 1081, 1019, 962, 845, 830, 805, 762, 701, 627, 508. m.p. 112 °C.

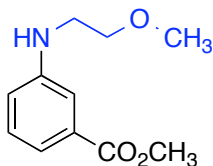


2-[4-(2-Methoxyethylamino)phenyl]ethanol (Table 2, entry 2h). An oven-dried test tube, which was equipped with a magnetic stir bar and fitted with a teflon septum, was charged with the BrettPhos precatalyst (4 mg, 0.05 mol%), BrettPhos (2.7 mg, 0.05 mol%). Then, the tube was taken into a glovebox (a needle was inserted in the septum) and the tube was charged with lithium bis(trimethylsilyl)amide (LHMDS) (3.68 g, 22 mmol). Then, dibutyl ether (nBu₂O) (5 mL), 4-chlorophenethyl alcohol (1.35 mL, 10 mmol), 2-methoxyethylamine (1.22 mL, 14 mmol) were added. The tube was resealed inside a glovebox and removed from the glovebox. The solution was heated to 90 °C for 18h. The reaction mixture then was allowed to cool to room temperature. To the reaction mixture was added 1 M HCl (20 mL). The mixture was stirred at room temperature for 20 min and was then extracted with CH₂Cl₂ (3 x 50.0 mL). The organic layer was separated and dried over Na₂SO₄. The solvent was evaporated, and the crude product was purified via the Biotage SP4 (silica-packed 40+M cartridge; EtOAc/hexanes) to provide the title compound as a pale yellow oil (1.48 g, 76%). ¹H NMR (400 MHz, CDCl₃) δ: 7.02 (d, 2H, J = 8), 6.58 (d, 2H, J = 8), 3.96 (br-s, 1H), 3.77 (q, 2H, J = 6), 3.58 (t, 2H, J = 5), 3.37 (s, 3H), 3.25 (t, 2H, J = 5), 2.74 (t, 2H, J = 7). ¹³C NMR (100 MHz, CDCl₃) δ: 146.7, 129.8, 127.4, 113.4, 71.0, 63.9, 58.7, 43.7, 38.3. IR (neat, cm⁻¹): 3376, 2931, 1617, 1521, 1321, 1118, 1046, 817.

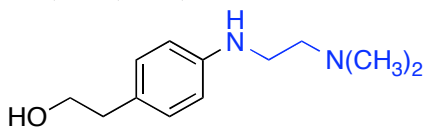


4-((2-methoxyethyl)amino)phenol (Table 2, entry 2i). The general procedure A with 0.5 mol% catalyst for 6h was followed. Isolation and biotage purification afforded the title compound as a brown liquid (130 mg, 78%). ¹H NMR (400 MHz, CDCl₃) δ: 6.65 (d, 2H, J = 8.0), 6.53 (d, 2H, J = 8.0), 4.61 (s, 2H), 3.57 (t, 2H, J = 4.0), 3.36 (s, 3H), 3.20 (t, 2H, J = 4.0). ¹³C NMR (100 MHz, CDCl₃) δ: 148.3, 142.0, 119.8, 116.2, 116.1, 115.2,

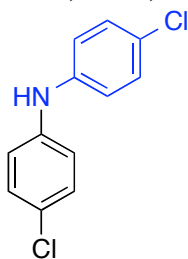
71.0, 58.8, 44.8. IR (KBr disc, cm^{-1}): 3351, 2932, 2284, 1658, 1598, 1514, 1366, 1236, 1118, 1022, 823.



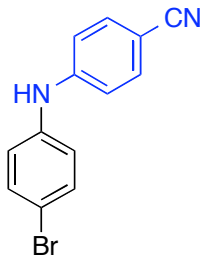
Methyl 3-((2-methoxyethyl)amino)benzoate (Table 2, entry 2j). The general procedure B with 1.5 mol% catalyst for 24 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (125 mg, 65%). ^1H NMR (400 MHz, d_6 -DMSO) δ : 7.34 (d, 1H, $J = 8.0$), 7.25 (s, 1H), 7.18 (t, 1H, $J = 8.0$), 6.77 (dd, 1H, $J = 8.0$, $J = 4.0$), 4.21 (s, 1H), 3.84 (s, 3H), 3.56 (t, 2H, $J = 6.0$), 3.34 (s, 3H), 3.28 (s, 2H). ^{13}C NMR (100 MHz, d_6 -DMSO) δ : 108.4, 101.7, 95.8, 95.1, 91.5, 91.2, 89.7, 75.0, 70.8, 68.5, 65.5. IR (KBr disc, cm^{-1}): 3394, 2950, 2929, 2893, 2360, 1719, 1606, 1588, 1513, 1491, 1439, 1385, 1334, 1286, 1245, 1193, 1108, 996, 938, 870, 846, 805, 754, 685, 546.



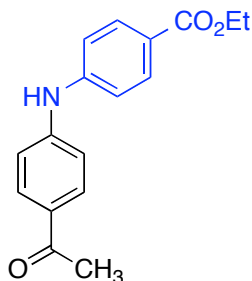
2-[[4-(2-Dimethylamino)ethylamino]phenyl]ethanol (Table 2, entry 2k). The general procedure A with 0.5 mol% catalyst, LHMDs (368 mg, 2.2 mmol) and dioxane (1 mL) for 30 min at 100 $^{\circ}\text{C}$ was followed. Isolation and biotage purification afforded the title compound as a yellow oil (192 mg, 92%). ^1H NMR (400 MHz, CDCl_3) δ : 7.02 (d, 2H, $J = 8$), 6.58 (d, 2H, $J = 8.4$), 4.20 (br-s, 1H), 3.77 (t, 2H, $J = 6.6$), 3.05-3.15 (m, 2H), 2.74 (t, 2H, $J = 6.5$), 2.52 (t, 2H, $J = 5.9$), 2.22 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 147.0, 129.8, 127.1, 113.1, 63.9, 58.1, 45.2, 41.3, 38.5. IR (neat, cm^{-1}): 3364, 2941, 2860, 2826, 1617, 1521, 1467, 1257, 1046, 818.



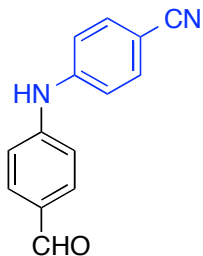
bis(4-chlorophenyl)amine (Table 3, entry 3a).⁴ The general procedure E with 0.1 mol% catalyst for 15 h was followed. Isolation and biotage purification afforded the title compound as a brownish-purple solid (236 mg, 99%). ^1H NMR (400 MHz, CDCl_3) δ : 7.22 (t, 2H, $J = 4.0$), 7.19 (t, 2H, $J = 4.0$), 6.49 (t, 2H, $J = 6.0$), 6.92 (t, 2H, $J = 6.0$), 5.62 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 141.6, 129.6, 126.2, 119.3. IR (KBr disc, cm^{-1}) 3416, 1591, 1505, 1322, 1093, 819, 677, 505, 406. m.p. 77 $^{\circ}\text{C}$ (77 $^{\circ}\text{C}$).



4-((4-bromophenyl)amino)benzonitrile (Table 3, entry 3b). The general procedure E with 0.5 mol% catalyst for 16 h was followed. Isolation and biotage purification afforded the title compound as a white-brown solid (217 mg, 80%). ^1H NMR (400 MHz, CDCl_3) δ : 7.47-7.41 (m, 4H), 7.03-7.01 (m, 2H), 6.95-6.92 (m, 2H), 6.08 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 147.6, 139.4, 134.0, 132.8, 122.7, 119.9, 116.4, 115.4, 102.3. IR (KBr disc, cm^{-1}): 3345, 2214, 1610, 1586, 1519, 1486, 1385, 1331, 1172, 1075, 1009, 815, 544, 488. Anal. Calcd for $\text{C}_{13}\text{H}_9\text{BrN}_2$: C, 57.17; H, 3.32. Found: C, 57.33; H, 3.25. m.p. 131 $^\circ\text{C}$.

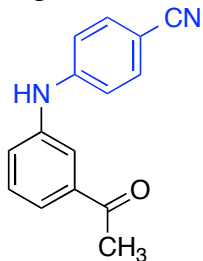


Ethyl 4-((4-acetylphenyl)amino)benzoate (Table 3, entries 3c and 3d). The general procedure E with 0.1 mol% catalyst for 15 h was followed. Isolation and biotage purification afforded the title compound as a white solid (249 mg, 88%, entry 3c). The general procedure B with 1 mol% catalyst for 21 h was followed. Isolation and biotage purification afforded the title compound as a white solid (271 mg, 96%, entry 3d). ^1H NMR (400 MHz, CDCl_3) δ : 7.95 (d, 2H, $J = 8.0$), 7.87 (d, 2H, $J = 8.0$), 7.13-7.10 (m, 4H), 6.82 (s, 1H), 4.32 (q, 2H, $J = 6.7$), 2.52 (s, 3H), 1.34 (t, 3H, $J = 8.0$). ^{13}C NMR (100 MHz, CDCl_3) δ : 196.9, 166.5, 146.6, 145.8, 131.6, 130.7, 130.6, 123.7, 117.4, 116.7, 60.9, 26.5, 14.6. IR (KBr disc, cm^{-1}): 3333, 1701, 1590, 1526, 1430, 1340, 1273, 1173, 1106, 958, 834, 768, 668, 591. Anal. Calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_3$: C, 72.07; H, 6.05. Found: C, 72.17; H, 6.11. m.p. 136 $^\circ\text{C}$.

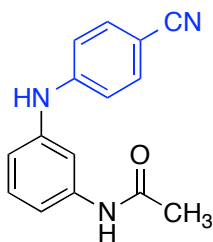


4-((4-formylphenyl)amino)benzonitrile (Table 3, entry 3e). The general procedure B with 1.5 mol% catalyst for 14 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (168 mg, 76%). ^1H NMR (400 MHz, d_6 -DMSO) δ : 9.76 (s, 1H), 9.48 (s, 1H), 7.77 (d, 2H, $J = 8.0$), 7.66 (d, 2H, $J = 8.0$), 7.24 (d, 4H, $J = 8.0$). ^{13}C NMR (100 MHz, d_6 -DMSO) δ : 191.3, 147.7, 146.3, 134.2, 132.1, 129.9, 120.0,

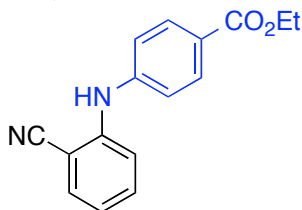
117.9, 102.5. IR (KBr disc, cm^{-1}): 3338, 2218, 1682, 1587, 1525, 1384, 1338, 1223, 1164, 822, 544. Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}$: C, 75.66; H, 4.54. Found: C, 75.62; H, 4.62. m.p. 162 °C.



4-((3-acetylphenyl)amino)benzonitrile (Table 3, entry 3f). The general procedure B with 1 mol% catalyst for 14 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (221 mg, 76%). ^1H NMR (400 MHz, CDCl_3) δ : 7.72 (t, 1H, $J = 2.0$), 7.62-7.60 (m, 1H), 7.47-7.34 (m, 4H), 7.00-6.98 (m, 2H), 6.51 (s, 1H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 198.1, 147.6, 141.1, 138.7, 134.0, 130.1, 125.1, 123.8, 120.0, 115.6, 114.6, 102.4, 27.0. IR (KBr disc, cm^{-1}): 3338, 2217, 1680, 1590, 1526, 1487, 1446, 1408, 1384, 1335, 1271, 1208, 1174, 908, 828, 789, 687, 587, 544, 501. Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$: C, 76.25; H, 5.12. Found: C, 75.85; H, 5.08. m.p. 103 °C.

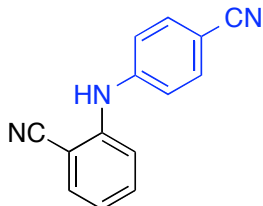


N-(3-((4-cyanophenyl)amino)phenyl)acetamide (Table 3, entry 3g). The general procedure A with 1.5 mol% catalyst for 24 h was followed. Isolation and biotage purification afforded the title compound as a dark-brown solid (176 mg, 70%). ^1H NMR (400 MHz, d_6 -DMSO) δ : 9.90 (s, 1H), 8.97 (s, 1H), 7.76-7.50 (m, 3H), 7.27 (t, 1H, $J = 10$), 7.24-6.93 (m, 3H), 6.86 (d, 1H, $J = 4.0$), 1.83 (s, 3H). ^{13}C NMR (100 MHz, d_6 -DMSO) δ : 169.0, 148.8, 141.6, 140.9, 134.3, 130.1, 120.6, 115.4, 115.0, 110.8, 99.8, 24.7. IR (KBr disc, cm^{-1}): 3317, 2216, 1672, 1597, 1529, 1434, 1339, 1173, 830, 780, 691, 544.

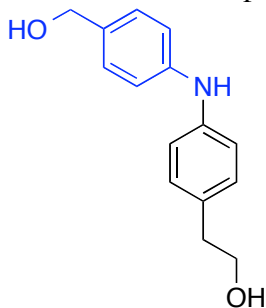


Ethyl 4-((2-cyanophenyl)amino)benzoate (Table 3, entry 3h). The general procedure B with 1 mol% catalyst for 21 h was followed. Isolation and biotage purification afforded the title compound as a brownish-yellow solid (253 mg, 95%). ^1H NMR (400 MHz, CDCl_3) δ : 7.98 (d, 2H, $J = 8.0$), 7.55-7.53 (m, 1H), 7.44-7.37 (m, 2H), 7.13 (d, 2H, $J = 8.0$), 6.98-6.94 (m, 1H), 6.53 (s, 1H), 4.34 (q, 2H, $J = 8.0$), 1.36 (t, 3H, $J = 8.0$). ^{13}C NMR (100 MHz, CDCl_3) δ : 166.1, 145.1, 144.8, 134.0, 133.4, 131.4, 124.6, 121.3, 118.1,

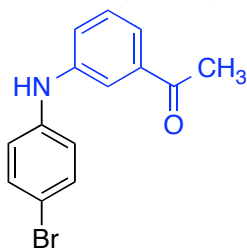
117.2, 116.6, 101.1, 60.8, 14.4. IR (KBr disc, cm^{-1}): 3330, 2982, 2221, 1708, 1611, 1593, 1573, 1520, 1470, 1454, 1367, 1324, 1278, 1176, 1106, 1020, 849, 757, 699. Anal. Calcd for $\text{C}_{30}\text{H}_{23}\text{N}_5\text{O}_2$: C, 72.16; H, 5.30. Found: C, 72.22; H, 5.14. m.p. 112-116 °C.



2-((4-cyanophenyl)amino)benzonitrile (Table 3, entry 3i).⁵ The general procedure B with 1.5 mol% catalyst for 14 h was followed. Isolation and biotage purification afforded the title compound as a pale-yellow solid (210 mg, 96%). ^1H NMR (400 MHz, CDCl_3) δ : 7.59-7.54 (m, 2H), 7.51-7.46 (m, 1H), 7.40-7.37 (m, 1H), 7.13 (d, 2H, $J = 8.0$), 7.04 (t, 1H, $J = 8.0$), 6.64-6.60 (m, 1H), 4.14 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 145.4, 144.3, 134.2, 134.0, 133.8, 122.7, 119.3, 118.2, 118.1, 117.1, 114.6, 105.1, 102.7. IR (KBr disc, cm^{-1}): 3318, 2221, 1609, 1591, 1571, 1518, 1489, 1471, 1453, 1325, 1294, 1174, 828, 757. m.p. 155 °C (156-157 °C).

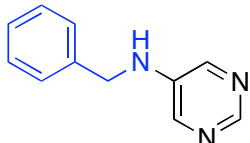


2-(4-((4-(hydroxymethyl)phenyl)amino)phenyl)ethanol (Table 3, entry 3j). The general procedure A with 0.5 mol% catalyst, LHMDS (3.4 mmol) for 24 h was followed. Isolation and biotage purification afforded the title compound as a brown solid (219 mg, 90%). ^1H NMR (400 MHz, d_6 -DMSO): 7.97 (s, 1H), 7.09 (t, 1H, $J = 8.0$), 7.03 (d, 2H, $J = 8.0$), 6.95 (t, 3H, $J = 8.0$), 6.83 (d, 1H, $J = 8.0$), 6.66 (d, 1H, $J = 8.0$), 5.08 (t, 1H, $J = 6.0$), 4.59 (t, 1H, $J = 4.0$), 3.51 (q, 2H, $J = 6.6$), 2.59 (t, 2H, $J = 8.0$). ^{13}C NMR (100 MHz, d_6 -DMSO) δ : 144.3, 140.0, 141.8, 131.3, 129.9, 129.2, 117.8, 114.9, 114.5, 63.5, 62.9, 38.9. IR (KBr disc, cm^{-1}): 3323, 2931, 1605, 1517, 1488, 1401, 1323, 1242, 1167, 1114, 1044, 937, 820, 781, 695, 668. Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2$: C, 74.05; H, 7.04. Found: C, 73.59; H, 7.09.

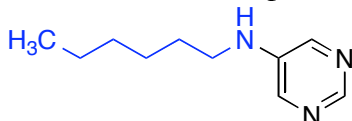


1-(3-((4-bromophenyl)amino)phenyl)ethanone (Table 3, entry 3k). The general procedure E with 0.1 mol% catalyst for 15 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (182 mg, 63%). ^1H NMR (400 MHz, CDCl_3) δ : 7.58 (t, 1H, $J = 2.0$), 7.48-7.46 (m, 1H), 7.35-7.29 (m, 3H), 7.22-7.18

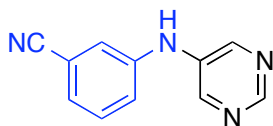
(m, 1H), 6.94-6.91 (m, 2H), 5.92 (s, 1H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 198.4, 143.4, 141.8, 138.6, 132.6, 129.8, 122.2, 121.6, 119.9, 117.0, 113.8, 27.0. IR (KBr disc, cm^{-1}): 3374, 3331, 1683, 1580, 1533, 1490, 1430, 1389, 1356, 1336, 1272, 1209, 1072, 982, 896, 830, 807, 771, 745, 683, 588, 496. Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{BrNO}$: C, 57.95; H, 4.17. Found: C, 58.17; H, 4.06. m.p. 117 °C.



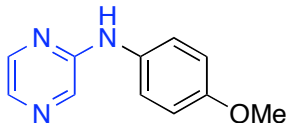
***N*-benzylpyrimidin-5-amine (Table 4, entry 4a).** The general procedure B with a mixture of 5-bromopyrimidine (0.5 mmol), benzylamine (0.6 mmol), K_2CO_3 (0.7 mmol), **5** (8 mg, 2 mol%), **1** (5 mg, 2 mol%), and *t*-BuOH (1 mL) at 110 °C for 24 h was followed. The crude product was purified via the biotage to provide the title compound as a white solid (87 mg, 94%). ^1H NMR (300 MHz, CDCl_3) δ : 8.58 (s, 1H), 8.11 (s, 2H) 7.33 (m, 5H), 4.42 (bs, 1H), 4.34 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ : 148.8, 141.9, 141.1, 137.8, 129.2, 128.1, 127.6, 47.7. IR (neat, cm^{-1}): 3246, 3044, 1575, 1435, 1418, 1309, 1200, 701. m.p. 109-110 °C.



***N*-hexylpyrimidin-5-amine (Table 4, entry 4b).** The general procedure B with a mixture of 5-bromopyrimidine (0.5 mmol), hexylamine (0.6 mmol), K_2CO_3 (0.7 mmol), **5** (8 mg, 2 mol%), **1** (5 mg, 2 mol%), and *t*-BuOH (1 mL) at 110 °C for 24 h was followed. The crude product was purified via the biotage to provide the title compound as a white solid (86 mg, 96%). ^1H NMR (300 MHz, CDCl_3) δ : 8.55 (s, 1H), 8.07 (s, 2H), 3.80 (s, 1H), 3.12 (q, $J = 7.0$ Hz, 2H), 1.62 (pentet, $J = 8.0$ Hz, 2H), 1.32 (m, 6H), 0.88 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ : 148.4, 142.2, 140.8, 43.4, 31.7, 29.4, 26.9, 22.8, 14.3. IR (neat, cm^{-1}): 3247, 3052, 2931, 2853, 1580, 1434, 1416, 1319, 1204, 870, 725, 629. m.p. 88-89 °C.

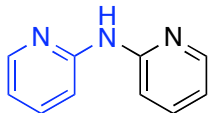


3-(pyrimidin-5-ylamino)benzonitrile (Table 4, entry 4c). The general procedure B with 5-bromopyrimidine (1 mmol), K_2CO_3 (1.4 mmol) at 110 °C for 2 h was followed. The crude product was purified via the biotage to provide the title compound as a white solid (185 mg, 94%). ^1H NMR (300 MHz, DMSO) δ : 8.86 (s, 1H), 8.72 (s, 1H), 8.61 (s, 2H), 7.44 (m, 3H), 7.30 (m, 3H). ^{13}C NMR (75 MHz, DMSO) δ : 151.5, 146.2, 143.5, 138.0, 131.4, 124.9, 122.0, 119.7, 119.5, 113.0. IR (neat, cm^{-1}): 3383, 2226, 1572, 1534, 1498, 1428, 1384, 1339, 797, 718. Anal. Calcd. for $\text{C}_{11}\text{H}_8\text{N}_4$: C, 67.34; H, 4.11. Found: C, 67.54; H, 4.15. m.p. 190-191 °C.

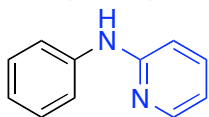


***N*-(4-methoxyphenyl)pyrazin-2-amine (Table 4, entry 4d).** The general procedure B with K_2CO_3 (1.4 mmol) at 110 °C for 4 h was followed. The crude product was purified

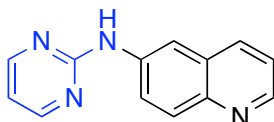
via the biotage to provide the title compound as a white solid (187 mg, 93%). ¹H NMR (300 MHz, CDCl₃) δ: 8.09 (s, 1H), 8.04 (m, 1H), 7.91 (d, *J* = 3.0 Hz, 1H), 7.30 (d, *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.76 (s, 1H), 3.81 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 156.9, 153.5, 142.2, 134.5, 132.4, 132.0, 124.0, 114.9, 55.8. IR (neat, cm⁻¹): 3200, 2949, 1584, 1547, 1427, 1334, 1245, 1144, 1035, 829. m.p. 131-133 °C.



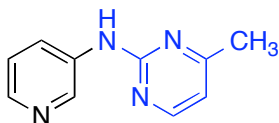
Dipyridin-2-ylamine (Table 4, entry 4e).⁶ The general procedure B with K₂CO₃ (1.4 mmol) at 110 °C for 2 h was followed. The crude product was purified via the biotage to provide the title compound as a white solid (156 mg, 93%). ¹H NMR (300 MHz, CDCl₃) δ: 8.95 (s, 1H), 8.28 (d, *J* = 5.0 Hz, 2H), 7.58 (m, 4H), 6.83 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ: 154.6, 147.9, 138.0, 116.5, 112.1. IR (neat, cm⁻¹): 3264, 3092, 3022, 1596, 1487, 1441, 1352, 763, 730. m.p. 89 °C (85-94 °C).



N-phenylpyridin-2-amine (Table 4, entry 4f).³ The general procedure A with 0.5 mol% catalyst, LHMDS (1.2 mmol) for 18 h was followed. Isolation and biotage purification afforded the title compound as a white solid (166 mg, 98%). ¹H NMR (400 MHz, CDCl₃) δ: 8.41 (d, 2H, *J* = 4.0), 8.13 (s, 1H), 7.62-7.59 (m, 2H), 7.35-7.31 (m, 2H), 7.06-7.02 (m, 1H), 6.68 (t, 1H, *J* = 6.0). ¹³C NMR (100 MHz, CDCl₃) δ: 160.5, 158.2, 139.7, 129.2, 123.0, 120.0, 112.6. IR (KBr disc, cm⁻¹): 3257, 3056, 1618, 1577, 1537, 1497, 1449, 1411, 1360, 1253, 1175, 1075, 1028, 996, 973, 900, 795, 780, 751, 696, 668, 641, 616, 598, 523, 503. m.p. 110 °C (109-110 °C).

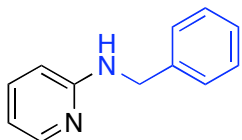


N-(pyrimidin-2-yl)quinolin-6-amine (Table 4, entry 4g). The general procedure B with K₂CO₃ (1.4 mmol) at 110 °C for 2 h was followed. The crude product was purified via the biotage to provide the title compound as a white solid (206 mg, 93%). ¹H NMR (300 MHz, CDCl₃) δ: 8.78 (d, *J* = 4.0 Hz, 1H), 8.50 (d, *J* = 4.5 Hz, 2H), 8.38 (d, *J* = 2.5 Hz, 1H), 8.10 (m, 3H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.34 (dd, *J* = 4.0 Hz, *J* = 8.5 Hz, 1H), 6.79 (t, *J* = 4.5 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ: 160.3, 158.3, 148.9, 145.2, 137.7, 135.7, 130.3, 129.3, 124.0, 121.7, 114.4, 113.3. IR (neat, cm⁻¹): 3270, 1580, 1540, 1501, 1448, 1430, 1413, 833, 795. Anal. Calcd. for C₁₃H₁₀N₄: C, 70.26; H, 4.54. Found: C, 70.08; H, 4.51. m.p. 152-154 °C.

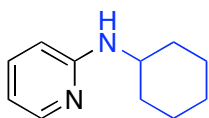


4-methyl-N-(pyridin-3-yl)pyrimidin-2-amine (Table 4, entry 4h). The general procedure A with 0.6 mol% catalyst, LHMDS (1.2 mmol) at 110 °C for 18 h was followed. Isolation and biotage purification afforded the title compound as a white solid (168 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ: 8.69-8.68 (m, 1H), 8.36 (s, 1H), 8.25-

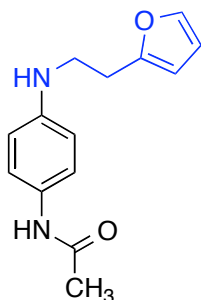
8.20 (m, 3H), 7.19 (dd, 1H, J = 8.0, J = 8.0), 6.58 (d, 1H, J = 4.0), 2.35 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 168.6, 160.1, 157.7, 143.3, 141.2, 136.9, 126.2, 123.6, 112.9, 24.4. IR (KBr disc, cm⁻¹): 3262, 3190, 3077, 2923, 1614, 1544, 1483, 1460, 1420, 1370, 1339, 1316, 1290, 1258, 1239, 1193, 1126, 1101, 1027, 990, 905, 797, 708, 677, 644, 609, 546. Anal. Calcd for C₁₀H₁₀N₄: C, 64.50; H, 5.41. Found: C, 64.58; H, 5.35. m.p. 90 °C.



N-benzylpyridin-2-amine (Table 4, entry 4i).³ The general procedure A with 0.25 mol% catalyst, LHMDS (1.2 mmol) for 5 min was followed. Isolation and biotage purification afforded the title compound as a white solid (160 mg, 87%). ¹H NMR (400 MHz, CDCl₃) δ: 8.07 (dd, 1H, J = 8.0, J = 4.0), 7.21-7.42 (m, 6H), 6.54-6.57 (m, 1H), 6.34 (d, 1H, J = 8.0), 5.00 (s, 1H), 2.27 (d, 2H, J = 8.0). ¹³C NMR (100 MHz, CDCl₃) δ: 158.7, 148.3, 139.2, 137.5, 128.7, 127.4, 127.2, 113.2, 106.8, 46.3. IR (KBr disc, cm⁻¹): 3225, 1602, 1575, 1530, 1455, 1442, 1338, 1292, 1162, 770, 748, 698. m.p. 92-94 °C (94-95 °C).

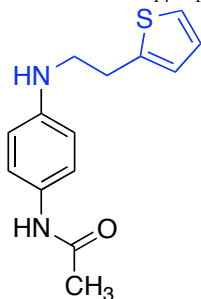


N-cyclohexylpyridin-2-amine (Table 4, entry 4j).³ The general procedure A with 0.25 mol% catalyst, LHMDS (1.2 mmol) for 12 h was followed. Isolation and biotage purification afforded the title compound as a light-yellow solid (140 mg, 80%). ¹H NMR (400 MHz, CDCl₃) δ: 8.03 (m, 1H), 7.31-7.37 (m, 1H), 6.46-6.49 (m, 1H), 6.31 (d, 1H, J = 8.0), 4.41 (s, 1H), 3.46-3.52 (m, 1H), 1.11-2.01 (m, 10H). ¹³C NMR (100 MHz, CDCl₃) δ: 158.2, 148.3, 137.3, 112.4, 106.7, 50.1, 33.4, 25.8, 24.9. IR (KBr disc, cm⁻¹): 3264, 2923, 1653, 1609, 1559, 1520, 1487, 1418, 731. m.p. 108 °C (105 °C).

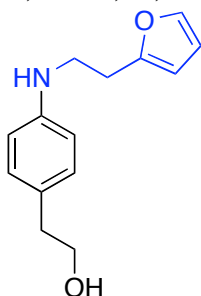


N-(4-((2-(furan-2-yl)ethyl)amino)phenyl)acetamide (Table 5, entry 5a). The general procedure A with 0.25 mol% catalyst, aryl bromide, LHMDS (2.25 mmol) and dioxane (5 mL) for 3 h was followed. Isolation and biotage purification afforded the title compound as a red liquid (220 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ: 7.96 (s, 1H), 7.30 (s, 1H), 7.25-7.22 (m, 2H), 6.51-6.48 (m, 2H), 6.27-6.26 (m, 1H), 6.04 (d, 1H, J = 4.0), 3.71 (s, 1H), 3.33 (t, 2H, J = 6.0), 2.87 (t, 2H, J = 6.0), 2.03 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 169.0, 153.5, 145.2, 141.7, 128.8, 122.7, 113.3, 110.5, 106.5, 42.9, 28.1, 24.3. IR (KBr disc, cm⁻¹): 3295, 3141, 2925, 1873, 1659, 1604, 1519, 1479, 1407, 1371,

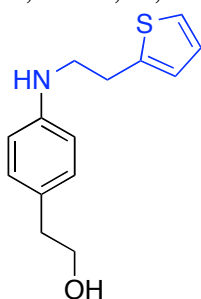
1314, 1272, 1212, 1178, 1145, 1121, 1079, 1006, 966, 924, 884, 823, 734, 600. Anal. Calcd for C₁₄H₁₆N₂O₂: C, 68.83; H, 6.60. Found: C, 68.22; H, 6.56.



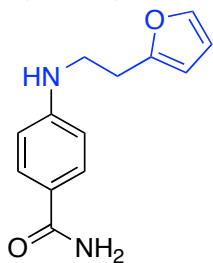
***N*-(4-((2-(thiophen-2-yl)ethyl)amino)phenyl)acetamide (Table 5, entry 5b).** The general procedure A with 0.5 mol% catalyst, aryl bromide for 12 h was followed. Isolation and biotage purification afforded the title compound as a brown solid (247 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ: 7.24 (d, 3H, J = 8.0), 7.14 (d, 1H, J = 4.0), 6.93-6.91 (m, 1H), 6.82 (d, 1H, J = 4.0), 6.56-6.53 (m, 2H), 3.71 (s, 1H), 3.37 (t, 2H, J = 6.0), 3.08 (t, 2H, J = 6.0), 2.09 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 168.4, 145.1, 141.9, 128.6, 127.2, 125.5, 124.1, 122.6, 113.5, 45.7, 29.8, 24.4. IR (KBr disc, cm⁻¹): 3293, 1657, 1604, 1517, 1406, 1370, 1313, 1249, 822, 698, 516. Anal. Calcd for C₁₄H₁₆N₂OS: C, 64.58; H, 6.19. Found: C, 64.47; H, 6.07. m.p. 76 °C.



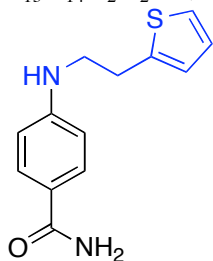
2-(4-((2-(furan-2-yl)ethyl)amino)phenyl)ethanol (Table 5, entry 5c). The general procedure A with 0.25 mol% catalyst, LHMDs (2.3 mmol) and dioxane (5 mL) for 12 h was followed. Isolation and biotage purification afforded the title compound as a red liquid (203 mg, 88%). ¹H NMR (400 MHz, CDCl₃) δ: 7.34-7.33 (m, 1H), 7.03 (d, 2H, J = 8.0), 6.59-6.56 (m, 2H), 6.31-6.30 (m, 1H), 6.08-6.07 (m, 1H), 3.74 (t, 2H, J = 4.0), 3.39 (t, 2H, J = 8.0), 2.92 (t, 2H, J = 8.0), 2.73 (t, 2H, J = 8.0). ¹³C NMR (100 MHz, CDCl₃) δ: 153.6, 146.7, 141.7, 130.1, 127.5, 113.5, 110.5, 106.5, 64.1, 42.8, 38.5, 28.2. IR (KBr disc, cm⁻¹): 3385, 3021, 2932, 1616, 1521, 1479, 1411, 1385, 1320, 1253, 1211, 1183, 1145, 1121, 1046, 1008, 924, 884, 814, 734, 600, 527. Anal. Calcd for C₁₄H₁₇NO₂: C, 72.70; H, 7.41. Found: C, 72.60; H, 7.47.



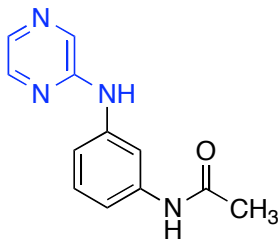
2-(4-((2-(thiophen-2-yl)ethyl)amino)phenyl)ethanol (Table 5, entry 5d). The general procedure A with 0.5 mol% catalyst, LHMDS (2.25 mmol) for 16 h was followed. Isolation and biotage purification afforded the title compound as a red solid (231 mg, 94%). ¹H NMR (400 MHz, CDCl₃) δ: 7.16 (dd, 1H, J = 4.0), 7.03 (d, 2H, J = 8.0), 6.95 (dd, 1H, J = 8.0, J = 4.0), 6.86-6.84 (m, 1H), 6.58 (d, 2H, J = 12.0), 3.76 (t, 2H, J = 8.0), 3.40 (t, 2H, J = 8.0), 3.10 (t, 2H, J = 8.0), 2.74 (t, 2H, J = 8.0). ¹³C NMR (100 MHz, CDCl₃) δ: 146.4, 141.8, 130.0, 127.3, 127.0, 125.4, 124.0, 113.4, 64.0, 45.4, 38.3, 29.7. IR (KBr disc, cm⁻¹): 3375, 3019, 2932, 2872, 1615, 1520, 1477, 1437, 1410, 1319, 1253, 1184, 1120, 1045, 848, 817, 699. Anal. Calcd for C₁₄H₁₇NOS: C, 67.98; H, 6.93. Found: C, 67.85; H, 6.85. m.p. 50 °C.



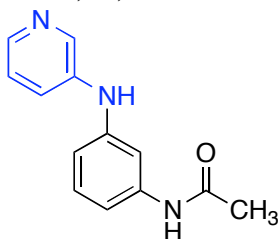
4-((2-(furan-2-yl)ethyl)amino)benzamide (Table 5, entry 5e). The general procedure A with 0.25 mol% catalyst and LHMDS (2.3 mmol) for 12 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (189 mg, 82%). ¹H NMR (400 MHz, d₆-DMSO) δ: 7.62 (d, 2H, J = 8.0), 7.55 (s, 1H), 7.49-7.48 (m, 1H), 6.87 (s, 1H), 6.51 (d, 2H, J = 8.0), 6.32 (dd, 1H, J = 4.0), 6.22 (t, 1H, J = 6.0), 6.15-6.14 (m, 1H), 3.29 (q, 1H, J = 6.7), 2.82 (t, 2H, J = 8.0). ¹³C NMR (100 MHz, d₆-DMSO) δ: 168.7, 153.9, 151.6, 142.1, 129.8, 121.6, 111.3, 111.1, 106.7, 41.8, 28.0. IR (KBr disc, cm⁻¹): 3381, 3171, 1639, 1608, 1529, 1397, 1333, 1192, 1152, 725. Anal. Calcd for C₁₃H₁₄N₂O₂: C, 67.81; H, 6.13. Found: C, 67.74; H, 6.05. m.p. 109 °C.



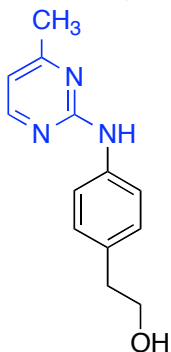
4-((2-(thiophen-2-yl)ethyl)amino)benzamide (Table 5, entry 5f). The general procedure A with 0.5 mol% catalyst for 21 h was followed. Isolation and biotage purification afforded the title compound as a brown solid (221 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ: 7.64 (d, 2H, J = 8.0), 7.15-7.14 (m, 1H), 6.94-6.91 (m, 1H), 6.82 (s, 1H), 6.55 (d, 2H, J = 8.0), 5.93 (s, 2H), 4.22 (t, 1H, J = 6.0), 3.44 (q, 2H, J = 6.7), 3.10 (t, 2H, J = 8.0). ¹³C NMR (100 MHz, CDCl₃) δ: 169.6, 151.0, 141.4, 129.5, 127.3, 125.7, 124.3, 121.8, 112.1, 44.8, 29.7. IR (KBr disc, cm⁻¹): 3380, 3175, 1640, 1607, 1572, 1527, 1483, 1434, 1395, 1331, 1279, 1189, 1151, 846, 830, 803, 702, 628, 535, 488. Anal. Calcd for C₁₃H₁₄N₂OS: C, 63.39; H, 5.73. Found: C, 63.30; H, 5.67. m.p. 102 °C.



***N*-(3-(pyrazin-2-ylamino)phenyl)acetamide (Table 5, entry 5g).** The general procedure A with 1 mol% catalyst, LHMDS (2.3 mmol) and dioxane (5 mL) for 16 h was followed. Isolation and biotage purification afforded the title compound as a brownish-white solid (204 mg, 89%). ¹H NMR (400 MHz, d₆-DMSO) δ: 9.87 (s, 1H), 9.45 (s, 1H), 8.20 (s, 1H), 8.05 (s, 1H), 7.93 (s, 1H), 7.85 (s, 1H), 7.42 (d, 1H, J = 8.0), 7.13-7.10 (m, 2H), 1.99 (s, 3H). ¹³C NMR (100 MHz, d₆-DMSO) δ: 168.8, 152.8, 141.4, 141.3, 140.2, 135.6, 133.9, 129.3, 113.6, 112.9, 109.5, 24.5. IR (KBr disc, cm⁻¹): 3304, 1667, 1612, 1550, 1523, 1484, 1428, 1355, 1165, 1144, 1005, 779. Anal. Calcd for C₁₂H₁₂N₄O: C, 63.15; H, 5.30. Found: C, 63.06; H, 5.20. m.p. 149 °C.

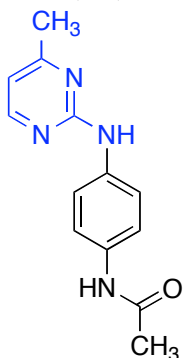


***N*-(3-(pyridin-3-ylamino)phenyl)acetamide (Table 5, entry 5h).** The general procedure A with 1 mol% catalyst, LHMDS (2.3 mmol) and dioxane (5 mL) for 20 h was followed. Isolation and biotage purification afforded the title compound as a brown solid (220 mg, 97%). ¹H NMR (400 MHz, d₆-DMSO) δ: 9.85 (s, 1H), 8.36 (s, 1H), 8.33 (d, 1H, J = 4.0), 7.98 (dd, 1H, J = 4.0, J = 4.0), 7.49 (t, 1H, J = 2.0), 7.43-7.41 (m, 1H), 7.18 (dd, 1H, J = 8.0, J = 4.0), 7.11 (t, 1H, J = 8.0), 7.02-6.98 (m, 1H), 6.72-6.68 (m, 1H), 1.98 (s, 3H). ¹³C NMR (100 MHz, d₆-DMSO) δ: 168.7, 153.9, 151.6, 142.1, 129.8, 121.6, 111.3, 111.1, 106.7, 28.0. IR (KBr disc, cm⁻¹): 3286, 1669, 1611, 1581, 1548, 1485, 1435, 1370, 1304, 1163, 1022, 782, 692. Anal. Calcd for C₁₃H₁₃N₃O: C, 68.70; H, 5.77. Found: C, 68.35; H, 5.97. m.p. 121 °C.

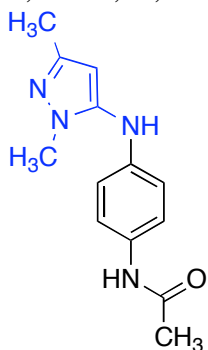


2-(4-((4-methylpyrimidin-2-yl)amino)phenyl)ethanol (Table 5, entry 5i). The general procedure A with 0.25 mol% catalyst, LHMDS (2.3 mmol) and dioxane (5 mL) for 5 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (200 mg, 87%). ¹H NMR (400 MHz, CDCl₃) δ: 8.18 (d, 1H, J = 8.0), 7.59 (s, 1H),

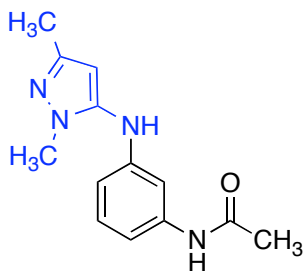
7.48 (d, 2H, J = 12.0), 7.12 (d, 2H, J = 8.0), 6.52 (d, 1H, J = 4.0), 3.77 (t, 2H, J = 6.0), 2.77 (t, 2H, J = 8.0), 2.58 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 168.4, 160.2, 157.6, 138.2, 132.9, 129.6, 120.1, 112.2, 63.8, 38.8, 24.4. IR (KBr disc, cm^{-1}): 3288, 3113, 2933, 1581, 1567, 1532, 1461, 1420, 1370, 1330, 1285, 1244, 1199, 1116, 1046, 794, 677, 575, 546, 521. Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{N}_3\text{O}$: C, 68.10; H, 6.59. Found: C, 68.30; H, 6.65. m.p. 59 °C.



***N*-(4-((4-methylpyrimidin-2-yl)amino)phenyl)acetamide (Table 5, entry 5j).** The general procedure A with 0.25 mol% catalyst, aryl bromide and LHMDS (2.3 mmol) and dioxane (5 mL) for 5 h was followed. Isolation and biotage purification afforded the title compound as a white solid (143 mg, 60%). ^1H NMR (400 MHz, d_6 -DMSO) δ : 9.76 (s, 1H), 9.40 (s, 1H), 8.23 (d, 1H, J = 8.0), 7.61 (d, 2H, J = 8.0), 7.40 (d, 2H, J = 8.0), 6.62 (d, 1H, J = 4.0), 2.28 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (100 MHz, d_6 -DMSO) δ : 168.4, 168.0, 160.5, 158.1, 136.7, 133.8, 120.1, 119.7, 112.1, 24.5, 24.3. IR (KBr disc, cm^{-1}): 3274, 1665, 1567, 1551, 1514, 1461, 1409, 1384, 1316, 840. Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$: C, 64.45; H, 5.82. Found: C, 63.98; H, 6.10. m.p. 164 °C.

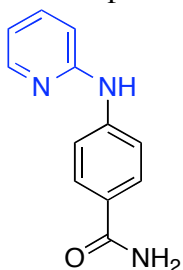


***N*-(4-((1,3-dimethyl-1H-pyrazol-5-yl)amino)phenyl)acetamide (Table 5, entry 5k).** The general procedure A with 0.5 mol% catalyst, aryl bromide and LHMDS (2.25 mmol) and dioxane (5 mL) for 18 h was followed. Isolation and biotage purification afforded the title compound as a brown solid (231 mg, 95%). ^1H NMR (400 MHz, CDCl_3) δ : 8.51 (s, 1H), 7.25 (d, 2H, J = 8.0), 6.62 (d, 2H, J = 12.0), 6.04 (s, 1H), 5.69 (s, 1H), 3.50 (s, 3H), 2.14 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 169.1, 147.6, 142.0, 141.5, 131.0, 122.3, 115.4, 97.4, 34.7, 24.2, 14.2. IR (KBr disc, cm^{-1}): 3261, 3041, 2243, 1664, 1611, 1563, 1514, 1445, 1417, 1371, 1305, 1272, 1249, 1177, 1114, 1015, 966, 910, 831, 732, 672. m.p. 55 °C.



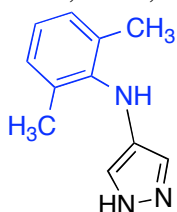
***N*-(3-((1,3-dimethyl-1*H*-pyrazol-5-yl)amino)phenyl)acetamide (Table 5, entry 5l).**

The general procedure A with 1 mol% catalyst, LHMDS (2.3 mmol) and dioxane (5 mL) for 3 h was followed. Isolation and biotage purification afforded the title compound as a brown solid (239 mg, 98%). ¹H NMR (400 MHz, CDCl₃) δ: 8.49 (s, 1H), 7.07-7.02 (m, 2H), 6.92 (d, 1H, J = 8.0), 6.41 (d, 1H, J = 8.0), 5.88 (s, 1H), 5.75 (s, 1H), 3.50 (s, 3H), 2.15 (s, 3H), 2.08 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 169.2, 147.7, 147.5, 145.7, 141.2, 139.6, 130.0, 111.5, 110.4, 106.3, 98.6, 34.7, 34.0, 24.6, 14.2, 13.9. IR (KBr disc, cm⁻¹): 3264, 3067, 1670, 1612, 1557, 1494, 1371, 1277, 1197, 1164, 1017, 910, 865, 777, 732, 691, 646. Anal. Calcd for C₁₃H₁₆N₄O: C, 63.91; H, 6.60. Found: C, 63.76; H, 6.88. m.p. 142 °C.



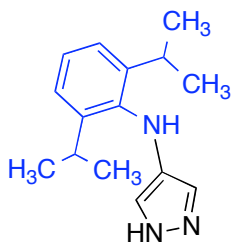
4-(pyridin-2-ylamino)benzamide (Table 5, entry 5m).⁷

The general procedure A with 0.25 mol% catalyst, LHMDS (2.3 mmol) and dioxane (5 mL) for 5 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (189 mg, 89%). ¹H NMR (400 MHz, d₆-DMSO) δ: 9.89 (s, 1H), 8.48 (d, 2H, J = 4.0), 7.78 (s, 6H), 7.15 (s, 1H), 6.85 (t, 1H, J = 6.0). ¹³C NMR (100 MHz, d₆-DMSO) δ: 168.1, 160.2, 158.6, 143.7, 128.7, 127.1, 117.9, 113.5. IR (KBr disc, cm⁻¹): 3414, 2252, 2126, 1668, 1579, 1530, 1449, 1418, 1386, 1247, 1189, 1027, 825, 763, 628.

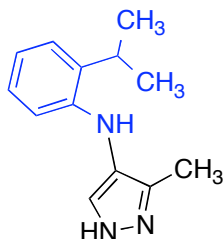


***N*-(2,6-dimethylphenyl)-1*H*-pyrazol-4-amine (Table 6, entry 6a).**

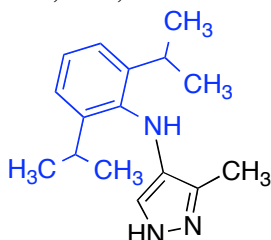
The general procedure A with 3 mol% catalyst, LHMDS (2.2 mL of 1.0 M solution in THF) and aryl bromide for 20 h was followed. Isolation and biotage purification afforded the title compound as a brown solid (166 mg, 89%). ¹H NMR (400 MHz, CDCl₃) δ: 7.07 (s, 2H), 7.03 (d, 2H, J = 8.0), 6.95-6.91 (m, 1H), 4.67 (s, 1H), 2.18 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 142.1, 131.9, 130.9, 129.0, 123.9, 18.5. IR (KBr disc, cm⁻¹): 3186, 2945, 1582, 1473, 1375, 1263, 1129, 1095, 1001, 942, 838, 767. m.p. 75 °C.



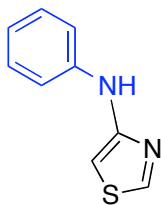
***N*-(2,6-diisopropylphenyl)-1*H*-pyrazol-4-amine (Table 6, entry 6b).** The general procedure A with 4 mol% catalyst, LHMDS (2.2 mL of 1.0 M solution in THF) and aryl bromide for 20 h was followed. Isolation and biotage purification afforded the title compound as a pale-white solid (183 mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ: 7.23-7.13 (m, 3H), 7.00 (s, 2H), 4.62 (s, 1H), 3.20 (septet, 2H, J = 7.3), 1.23 (d, 12H, J = 8.0). ¹³C NMR (100 MHz, CDCl₃) δ: 144.9, 138.9, 133.7, 125.9, 124.0, 28.1, 24.1. IR (KBr disc, cm⁻¹): 3190, 1962, 2868, 1582, 1459, 1383, 1256, 1129, 1057, 1002, 940, 835, 778, 498. Anal. Calcd for C₁₅H₂₁N₃: C, 74.03; H, 8.70. Found: C, 73.85; H, 8.66. m.p. 142 °C.



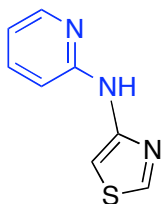
***N*-(2-isopropylphenyl)-3-methyl-1*H*-pyrazol-4-amine (Table 6, entry 6c).** The general procedure A with 3 mol% catalyst, LHMDS (2.2 mL of 1.0 M solution in THF) and aryl bromide for 20 h was followed. Isolation and biotage purification afforded the title compound as a red liquid (198 mg, 92%). ¹H NMR (400 MHz, CDCl₃) δ: 7.49 (s, 1H), 7.21-7.18 (m, 1H), 7.03-6.99 (m, 1H), 6.77 (t, 1H, J = 8.0), 6.53 (dd, 1H, J = 8.0), 4.91 (s, 1H), 3.02-2.98 (m, 1H), 2.19 (s, 3H), 1.34 (d, 6H, J = 4.0). ¹³C NMR (100 MHz, CDCl₃) δ: 144.2, 132.0, 126.7, 125.2, 121.5, 118.3, 112.3, 27.4, 22.6, 22.4, 9.8. IR (KBr disc, cm⁻¹): 3417, 3165, 2960, 1583, 1500, 1448, 1381, 1359, 1293, 1253, 1161, 1081, 1038, 993, 939, 749. Anal. Calcd for C₁₃H₁₇N₃: C, 72.52; H, 7.96. Found: C, 71.97; H, 8.10.



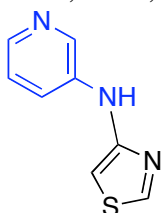
***N*-(2,6-diisopropylphenyl)-3-methyl-1*H*-pyrazol-4-amine (Table 6, entry 6d).** The general procedure A with 3 mol% catalyst, amine (0.6 mmol), aryl bromide (0.5 mmol), LHMDS (1.1 mL of 1.0 M solution in THF) for 20 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (86 mg, 67%). ¹H NMR (400 MHz, CDCl₃) δ: 7.13 (s, 3H), 6.70 (s, 1H), 4.32 (s, 1H), 3.15 (septet, 2H, J = 7.3), 2.23 (s, 3H), 2.13 (d, 12H, J = 4.0). ¹³C NMR (100 MHz, CDCl₃) δ: 143.8, 139.5, 129.8, 125.1, 123.7, 27.9, 23.8, 23.7, 10.2. IR (KBr disc, cm⁻¹): 3183, 2961, 2868, 1584, 1458, 1382, 1352, 1256, 1155, 1100, 1057, 938, 737, 668. Anal. Calcd for C₁₆H₂₃N₃: C, 74.67; H, 9.01. Found: C, 74.52; H, 8.98. m.p. 82 °C.



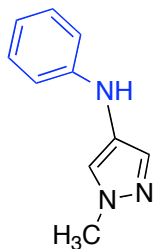
***N*-phenylthiazol-4-amine (Table 6, entry 6e).** The general procedure C with 3 mol% catalyst, amine (0.6 mmol), aryl bromide (0.5 mmol), NaO*t*-Bu (0.6 mmol) and dioxane (1 mL) for 23 h at 65 °C was followed. Isolation and biotage purification afforded the title compound as a black solid (60 mg, 68%). ¹H NMR (400 MHz, CDCl₃) δ: 8.59 (d, 1H, J = 4.0), 7.28 (t, 2H, J = 8.0), 7.11 (d, 2H, J = 8.0), 6.92 (t 1H, J = 8.0), 6.62 (s, 1H), 6.47 (d, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 154.3, 151.1, 142.4, 129.4, 121.1, 116.8, 91.3. IR (KBr disc, cm⁻¹): 3265, 3142, 3068, 1601, 1537, 1496, 1445, 1411, 1384, 1316, 1247, 1168, 878, 803, 756, 689, 645, 498, 481. m.p. 72 °C.



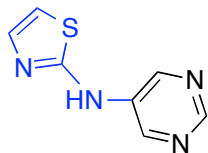
***N*-(pyridin-2-yl)thiazol-4-amine (Table 6, entry 6f).** The general procedure C with 4 mol% catalyst, amine (1 mmol), aryl bromide (0.5 mmol), NaO*t*-Bu (1 mmol) and dioxane (1 mL) for 20 h was followed. Isolation and biotage purification afforded the title compound as a light-yellow solid (64 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ: 9.76 (s, 1H), 8.70 (d, 1H, J = 4.0), 8.56 (d, 2H, J = 4.0), 7.71 (d, 1H, J = 4.0), 6.76 (t, 1H, J = 6.0). ¹³C NMR (100 MHz, CDCl₃) δ: 159.0, 158.1, 150.5, 150.0, 112.7, 97.2. IR (KBr disc, cm⁻¹): 3458, 3372, 3230, 3069, 1683, 1626, 1605, 1579, 1490, 1437, 1358, 1269, 1206, 1145, 997, 959, 886, 850, 786, 687. m.p. 145 °C.



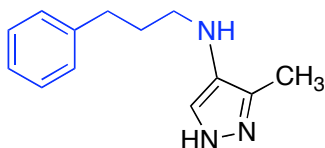
***N*-(pyridin-3-yl)thiazol-4-amine (Table 6, entry 6g).** The general procedure C with 4 mol% catalyst, amine (0.6 mmol), aryl bromide (0.5 mmol), NaO*t*-Bu (0.65 mmol) and dioxane (4 mL) for 20 h at 65 °C was followed. Isolation and biotage purification afforded the title compound as a brown solid (49 mg, 60%). ¹H NMR (400 MHz, CD₃CN) δ: 8.71 (s, 1H), 8.43 (s, 1H), 8.05 (s, 1H), 7.63-7.61 (m, 1H), 7.46 (s, 1H), 7.20-7.18 (m, 1H), 6.58 (s, 1H). ¹³C NMR (100 MHz, CD₃CN) δ: 151.9, 141.1, 139.7, 138.6, 123.6, 122.0, 117.3, 94.1. IR (KBr disc, cm⁻¹): 3254, 3059, 1589, 1552, 1484, 1432, 1411, 1283, 1238, 1128, 1049, 857, 800. Anal. Calcd for C₈H₇N₃S: C, 54.22; H, 3.98. Found: C, 54.21; H, 3.94. m.p. 100 °C.



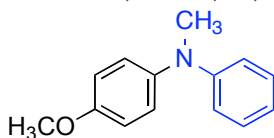
1-methyl-N-phenyl-1H-pyrazol-4-amine (Table 6, entry 6h). The general procedure C with 3 mol% catalyst, amine (0.6 mmol), aryl bromide (0.5 mmol), NaOt-Bu (0.6 mmol) and dioxane (1 mL) for 23 h was followed. Isolation and biotage purification afforded the title compound as a light-yellow solid (82 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ: 7.38 (s, 1H), 7.29 (s, 1H), 7.17-7.13 (m, 2H), 6.75-6.71 (m, 3H), 5.03 (s, 1H), 3.86 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 146.9, 135.5, 129.3, 124.8, 118.6, 113.5, 39.4. IR (KBr disc, cm⁻¹): 3281, 3105, 1595, 1574, 1520, 1499, 1381, 1362, 1316, 1257, 1169, 1021, 984, 858, 756, 696, 649. m.p. 124 °C.



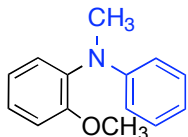
N-(pyrimidin-5-yl)thiazol-2-amine (Table 6, entry 6i). The general procedure B with 9 mol% catalyst, amine (0.6 mmol), aryl bromide (0.5 mmol), K₂CO₃ (1.2 mmol) and *t*-BuOH (2 mL) was followed. Isolation and biotage purification afforded the title compound as a brown solid (45 mg, 51%). ¹H NMR (400 MHz, d₆-DMSO) δ: 10.85 (s, 1H), 9.72 (s, 2H), 8.72 (s, 1H), 7.29 (d, 1H), 7.01 (d, 1H, J = 4.0). ¹³C NMR (100 MHz, d₆-DMSO) δ: 163.4, 151.6, 145.1, 139.6, 137.1, 111.0. IR (KBr disc, cm⁻¹): 2885, 1618, 1579, 1545, 1528, 1430, 1416, 1295, 1188, 864, 711. Anal. Calcd for C₇H₆N₄S: C, 47.18; H, 3.39. Found: C, 48.09; H, 3.27. m.p. 145 °C.



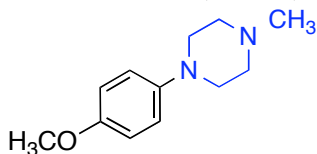
3-methyl-N-(3-phenylpropyl)-1H-pyrazol-4-amine (Table 6, entry 6j). The general procedure A with 3 mol% catalyst, LHMDS (2.2 mL of 1.0 M solution in THF) for 22 h at 90 °C was followed. Isolation and biotage purification afforded the title compound as a brown solid (159 mg, 74%). ¹H NMR (400 MHz, CDCl₃) δ: 7.27 (t, 3H, J = 6.0), 7.19 (d, 3H, J = 8.0), 7.02 (s, 1H), 2.98 (t, 2H, J = 6.0), 2.70 (t, 2H, J = 8.0), 2.14 (s, 3H), 1.95-1.89 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ: 141.9, 130.2, 128.5, 126.0, 48.0, 33.5, 31.4, 10.1. IR (KBr disc, cm⁻¹): 3177, 3025, 2933, 1653, 1602, 1522, 1496, 1454, 1384, 1355, 1184, 1090, 992, 938, 747, 700, 492. Anal. Calcd for C₁₃H₁₇N₃: C, 72.52; H, 7.96. Found: C, 71.84; H, 7.76.



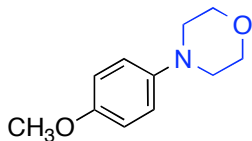
4-methoxy-*N*-methyl-*N*-phenylaniline (Table 7, entry 7a).⁸ General procedure F was followed using 4-chloroanisole (337 μ L, 2.5 mmol), *N*-methylaniline (327 μ L, 3 mmol), NaOt-Bu (288 mg, 3 mmol), THF (5 mL), RuPhos (**2**) (0.12 mg, 0.01 mol%) and RuPhos precatalyst (**4**) (0.18 mg, 0.01 mol%), with a reaction time of 4 h. Isolation afforded the title compound as a light yellow oil (529 mg, 99%). ¹H NMR (400 MHz, CDCl₃) δ 7.27 - 7.13 (m, 2H), 7.13 - 7.03 (m, 2H), 6.93 - 6.84 (m, 2H), 6.84 - 6.73 (m, 3H), 3.81 (d, *J* = 1.9 Hz, 4H), 3.25 (d, *J* = 0.5 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 156.22, 149.68, 142.16, 128.88, 126.22, 118.25, 115.61, 114.71, 55.46, 40.44. IR (KBr disc, cm⁻¹): 2951, 2834, 1596, 1507, 1341, 1241, 1181, 1131, 1034, 834, 791, 750, 694.



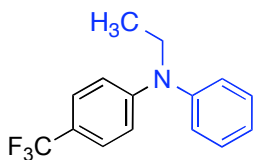
2-methoxy-*N*-methyl-*N*-phenylaniline (Table 7, entry 7b).⁹ The general procedure F with 0.05 mol% catalyst for 20 h was followed. Isolation and biotage purification afforded the title compound as a light-yellow liquid (202 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ : 7.28-7.22 (m, 4H), 7.04-7.01 (m, 2H), 6.77-6.70 (m, 3H), 3.81 (s, 3H), 3.27 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ : 156.3, 149.6, 137.1, 129.4, 129.0, 127.3, 121.6, 117.5, 113.7, 112.9, 55.9, 39.3. IR (KBr disc, cm⁻¹): 2918, 2048, 1918, 1700, 1576, 1497, 1341, 1109, 1027, 990, 872, 784, 744. Anal. Calcd for C₁₄H₁₅NO: C, 78.84; H, 7.09. Found: C, 79.01; H, 7.15.



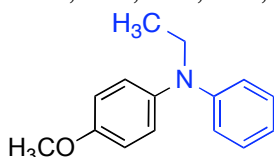
1-(4-methoxyphenyl)-4-methylpiperazine (Table 7, entry 7c).¹⁰ General procedure F was followed using 4-chloroanisole (135 μ L, 1 mmol), *N*-methylpiperazine (133 μ L, 1.2 mmol), NaOt-Bu (115 mg, 1.2 mmol), THF (2 mL), RuPhos (**2**) (0.42 mg, 0.1 mol%) and RuPhos precatalyst (**4**) (0.78 mg, 0.1 mol%), with a reaction time of 4 h. Isolation afforded the title compound as an orange solid (188 mg, 97%). ¹H NMR (400 MHz, CDCl₃) δ 6.86 - 6.79 (m, 2H), 6.79 - 6.63 (m, 2H), 3.68 (s, 3H), 3.02 (dd, *J* = 11.6, 6.6 Hz, 4H), 2.49 (dd, *J* = 17.8, 12.9 Hz, 4H), 2.27 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 153.45, 145.39, 117.83, 114.10, 55.20, 54.99, 50.27, 45.89. IR (KBr disc, cm⁻¹): 2791, 1513, 1451, 1287, 1250, 1148, 1037, 832. m.p. 65 °C



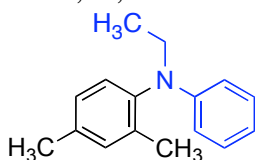
4-(4-methoxyphenyl)morpholine (Table 7, entry 7d).¹¹ General procedure F was followed using 4-chloroanisole (135 μ L, 1 mmol), morpholine (116 μ L, 1.2 mmol), NaOt-Bu (115 mg, 1.2 mmol), THF (2 mL), RuPhos (**2**) (0.21 mg, 0.05 mol%) and RuPhos precatalyst (**4**) (0.39 mg, 0.05 mol%), with a reaction time of 4 h. Isolation afforded the title compound as a colourless solid (188 mg, 97%). ¹H NMR (400 MHz, CDCl₃) δ 6.99 - 6.69 (m, 4H), 3.95 - 3.80 (m, 4H), 3.78 (s, 3H), 3.11 - 2.93 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 153.76, 145.46, 117.59, 114.29, 66.85, 55.34, 50.60. IR (KBr disc, cm⁻¹): 2971, 2854, 1517, 1453, 1266, 1121, 1030, 818. m.p. 70 °C



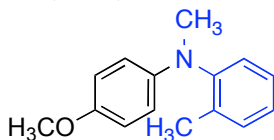
***N*-ethyl-*N*-phenyl-4-(trifluoromethyl)aniline (Table 7, entry 7e).**¹² The general procedure F with 0.01 mol% catalyst for 20 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (212 mg, 80%). ¹H NMR (400 MHz, CDCl₃) δ: 7.44 (t, 4H, J = 8.0), 7.24 (t, 3H, J = 6.0), 6.84 (d, 2H, J = 12.0), 3.86-3.81 (m, 2H), 1.29 (t, 3H, J = 6.0). ¹³C NMR (100 MHz, CDCl₃) δ: 150.8, 146.5, 130.2, 126.8, 126.6, 126.5, 125.6, 114.7, 46.8, 12.6. IR (KBr disc, cm⁻¹): 3061, 2977, 1617, 1594, 1522, 1495, 1452, 1383, 1328, 1272, 1241, 1195, 1163, 1119, 1071, 1026, 1005, 942, 825, 768, 711, 699, 621, 594, 568, 503.



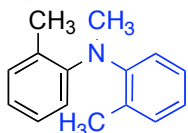
***N*-ethyl-4-methoxy-*N*-phenylaniline (Table 7, entry 7f).**¹² The general procedure F with 0.05 mol% catalyst for 16 h was followed. Isolation and biotage purification afforded the title compound as a light-yellow liquid (195 mg, 86%). ¹H NMR (400 MHz, CDCl₃) δ: 7.27 (t, 2H, J = 4.0), 7.17 (d, 2H, J = 8.0), 7.00-6.97 (m, 2H), 6.83 (d, 3H, J = 8.0), 3.87 (s, 3H), 3.79 (q, 2H, J = 6.0), 1.29 (t, 3H, J = 8.0). ¹³C NMR (100 MHz, CDCl₃) δ: 156.9, 149.0, 140.6, 129.3, 128.0, 118.0, 115.2, 55.7, 46.8, 12.9. IR (KBr disc, cm⁻¹): 3059, 3038, 2971, 2933, 2835, 2056, 1924, 1596, 1574, 1506, 1464, 1442, 1373, 1348, 1241, 1181, 1132, 1100, 1079, 1060, 1036, 991, 890, 870, 833, 776, 749, 694, 640, 578, 559, 521, 502. Anal. Calcd for C₁₅H₁₇NO: C, 79.26; H, 7.54. Found: C, 79.40; H, 7.61.



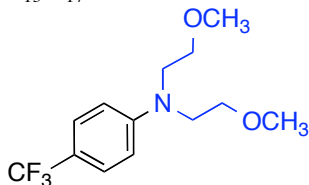
***N*-ethyl-2,4-dimethyl-*N*-phenylaniline (Table 7, entry 7g).** The general procedure F with 0.1 mol% catalyst for 20 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (158 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ: 7.23-7.16 (m, 3H), 7.07-7.00 (m, 2H), 6.72-6.70 (m, 1H), 6.55-6.52 (m, 2H), 3.68 (q, 2H, J = 6.0), 2.35 (s, 3H), 2.12 (s, 3H), 1.27 (t, 3H, J = 6.0). ¹³C NMR (100 MHz, CDCl₃) δ: 148.5, 145.0, 137.3, 134.3, 131.4, 130.5, 129.3, 127.5, 116.4, 112.8, 45.9, 21.2, 17.8, 13.1. IR (KBr disc, cm⁻¹): 3023, 2973, 2923, 2869, 1666, 1597, 1575, 1498, 1450, 1412, 1371, 1346, 1269, 1189, 1156, 1142, 1124, 1092, 1062, 1033, 993, 867, 811, 777, 747, 693. Anal. Calcd for C₁₆H₁₉N: C, 85.28; H, 8.50. Found: C, 85.10; H, 8.42.



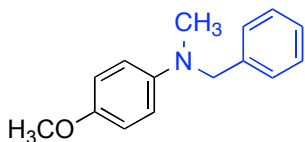
***N*-(4-methoxyphenyl)-*N*,2-dimethylaniline (Table 7, entry 7h).**¹³ The general procedure F with 0.3 mol% catalyst was followed. Isolation and biotage purification afforded the title compound as a brown liquid (207 mg, 91%). ¹H NMR (400 MHz, CDCl₃) δ: 7.30 (d, 1H, J = 8.0), 7.25 (d, 1H, J = 8.0), 7.18 (t, 2H, J = 8.0), 6.83-6.81 (m, 2H), 6.60-6.57 (m, 2H), 3.78 (s, 3H), 3.23 (s, 3H), 2.19 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 152.2, 148.1, 144.3, 136.5, 131.6, 127.6, 125.9, 115.3, 114.8, 56.0, 40.1, 18.3. IR (KBr disc, cm⁻¹): 2949, 1578, 1507, 1378, 1239, 1181, 1115, 1074, 1038, 875, 819, 776, 729, 677, 578, 522. Anal. Calcd for C₁₅H₁₇NO: C, 79.26; H, 7.54. Found: C, 79.26; H, 7.69.



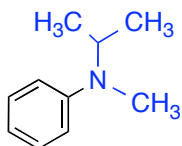
***N*,2-dimethyl-*N*-(*o*-tolyl)aniline (Table 7, entry 7i).** The general procedure F with 0.3 mol% catalyst was followed. Isolation and biotage purification afforded the title compound as an orange solid (196 mg, 93%). ¹H NMR (400 MHz, CDCl₃) δ: 7.19-7.15 (m, 4H), 7.02 (d, 2H, J = 8.0), 6.98 (d, 2H, J = 8.0), 3.13 (s, 3H), 2.11 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 150.3, 132.7, 131.7, 126.9, 123.2, 122.0, 41.6, 18.9. IR (KBr disc, cm⁻¹): 3065, 3018, 2950, 2864, 2802, 2361, 1599, 1578, 1490, 1474, 1376, 1315, 1287, 1268, 1235, 1193, 1129, 1102, 1052, 988, 874, 769, 753, 728, 719. Anal. Calcd for C₁₅H₁₇N: C, 85.26; H, 8.11. Found: C, 85.45; H, 8.08. m.p. 69 °C.



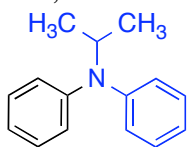
***N*,*N*-bis(2-methoxyethyl)-4-(trifluoromethyl)aniline (Table 7, entry 7j).** The general procedure F with 0.05 mol% catalyst for 2 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (263 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ: 7.41 (d, 2H, J = 12.0), 6.71 (d, 2H, J = 8.0), 3.60-3.52 (m, 8H), 3.33 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 150.4, 126.8, 126.7, 124.1, 117.7, 117.3, 111.1, 70.1, 59.1, 51.1. IR (KBr disc, cm⁻¹): 2930, 2891, 1721, 1616, 1572, 1532, 1452, 1401, 1331, 1279, 1198, 1164, 1116, 1071, 1014, 962, 819, 712, 638, 592, 509.



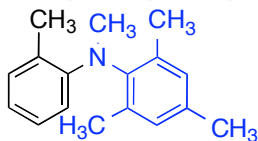
***N*-benzyl-4-methoxy-*N*-methylaniline (Table 7, entry 7k).**¹⁴ The general procedure F with 0.1 mol% catalyst for 20 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (216 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ: 7.37-7.28 (m, 5H), 6.88-6.78 (m, 4H), 4.47 (s, 2H), 3.78 (s, 3H), 2.96 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 152.0, 145.0, 139.5, 128.8, 127.4, 127.1, 115.0, 114.8, 58.2, 56.0, 39.3. IR (KBr disc, cm⁻¹): 3028, 2934, 2831, 1678, 1605, 1514, 1453, 1355, 1296, 1245, 1181, 1117, 1075, 1039, 947, 814, 734, 697. Anal. Calcd for C₁₅H₁₇NO: C, 79.26; H, 7.54. Found: C, 78.47; H, 7.57.



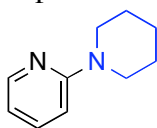
N-isopropyl-N-methylaniline (Table 7, entry 7l). The general procedure F with 2 mmol amine was followed. Isolation and biotage purification afforded the title compound as a colorless liquid (119 mg, 80%). ^1H NMR (400 MHz, CDCl_3) δ : 7.25-7.21 (m, 2H), 6.81-6.78 (m, 2H), 6.71-6.67 (m, 1H), 4.09 (q, 1H, $J = 8.0$), 2.72 (s, 3H), 1.16 (d, 6H, $J = 4.0$). ^{13}C NMR (100 MHz, CDCl_3) δ : 150.4, 129.3, 116.6, 113.6, 49.1, 30.0, 19.5. IR (KBr disc, cm^{-1}): 2917, 2849, 1713, 1673, 1598, 1503, 1450, 1287, 1232, 1111, 749, 698.



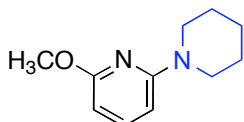
N-isopropyl-N-phenylaniline (Table 7, entry 7m).¹⁵ The general procedure F was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (186 mg, 88%). ^1H NMR (400 MHz, CDCl_3) δ : 7.38 (t, 4H, $J = 8.0$), 7.10 (t, 2H, $J = 8.0$), 6.98 (d, 4H, $J = 8.0$), 4.44 (m, 1H), 1.27 (d, 6H, $J = 4.0$). ^{13}C NMR (100 MHz, CDCl_3) δ : 146.5, 129.5, 123.2, 121.9, 48.1, 21.4. IR (KBr disc, cm^{-1}): 3069, 3035, 2972, 2933, 2874, 1662, 1588, 1573, 1494, 1460, 1386, 1364, 1347, 1291, 1233, 1195, 1171, 1125, 1072, 1038, 1026, 1000, 987, 890, 868, 770, 747, 703, 618, 563.



N,2,4,6-tetramethyl-N-(o-tolyl)aniline (Table 7, entry 7n). The general procedure F for 16 h was followed. Isolation and biotage purification afforded the title compound as a white solid (229 mg, 96%). ^1H NMR (400 MHz, CDCl_3) δ : 7.21 (d, 1H, $J = 8.0$), 6.98 (d, 2H, $J = 8.0$), 6.85 (s, 2H), 6.79 (d, 1H, $J = 4.0$), 3.19 (s, 3H), 2.29 (s, 3H), 2.07 (s, 6H), 1.62 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 149.4, 144.3, 136.1, 135.3, 132.3, 129.8, 127.0, 119.2, 115.7, 40.6, 21.1, 20.4, 19.1. IR (KBr disc, cm^{-1}): 2951, 2805, 2360, 1599, 1485, 1375, 1326, 1288, 1231, 1171, 1117, 1059, 1033, 990, 853, 762, 746, 715, 669, 607, 583. Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{N}$: C, 85.30; H, 8.84. Found: C, 85.08; H, 8.75. m.p. 79-83 $^\circ\text{C}$.



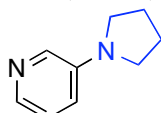
2-(piperidin-1-yl)pyridine (Table 8, entry 8a).¹⁶ The general procedure F with 0.1 mol% catalyst was followed. Isolation and biotage purification afforded the title compound as a colorless liquid (146 mg, 90%). ^1H NMR (400 MHz, CDCl_3) δ : 8.13-8.11 (m, 1H), 7.40-7.36 (m, 1H), 6.59 (d, 1H, $J = 8.0$), 6.51-6.48 (m, 1H), 3.47 (s, 4H), 1.59 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 159.9, 148.1, 137.5, 112.6, 107.3, 46.5, 52.7, 24.9. IR (KBr disc, cm^{-1}): 3002, 2933, 2853, 1717, 1596, 1562, 1484, 1438, 1385, 1360, 1311, 1269, 1246, 1224, 1165, 1130, 1094, 1051, 1025, 978, 954, 932, 854, 770, 731, 627, 524.



2-methoxy-6-(piperidin-1-yl)pyridine (Table 8, entry 8b). The general procedure F with 0.025 mol% catalyst was followed. Isolation and biotage purification afforded the title compound as a red oil (173 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ: 7.34 (t, 1H, J = 8.0), 6.13 (d, 1H, J = 8.0), 5.99 (d, 1H, J = 8.0), 3.84 (s, 3H), 3.48 (s, 4H), 1.60 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 163.2, 158.7, 140.2, 98.3, 97.2, 53.1, 46.5, 25.7, 25.0. IR (KBr disc, cm⁻¹): 2935, 2853, 1596, 1463, 1413, 1385, 1277, 1248, 1227, 1154, 1127, 1072, 1026, 981, 971, 854, 777, 721. Anal. Calcd for C₁₁H₁₆N₂O: C, 68.72; H, 8.39. Found: C, 68.58; H, 8.56.



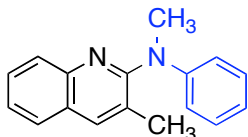
2-(pyrrolidin-1-yl)pyridine (Table 8, entry 8c).¹⁷ The general procedure F with 0.1 mol% catalyst was followed. Isolation and biotage purification afforded the title compound as a colorless liquid (138 mg, 93%). ¹H NMR (400 MHz, CDCl₃) δ: 8.12-8.10 (m, 1H), 7.40-7.35 (m, 1H), 6.46 (t, 1H, J = 6.0), 6.30 (d, 1H, J = 8.0), 3.40 (m, 4H), 1.96 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ: 157.5, 148.4, 137.1, 111.2, 106.7, 46.8, 25.7. IR (KBr disc, cm⁻¹): 2968, 2851, 2361, 1707, 1598, 1555, 1499, 1484, 1444, 1385, 1347, 1300, 1242, 1155, 993, 769, 733, 668, 467.



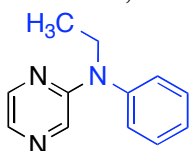
3-(pyrrolidin-1-yl)pyridine (Table 8, entry 8d).¹⁷ The general procedure F with 1 mol% catalyst for 12 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (129 mg, 87%). ¹H NMR (400 MHz, CDCl₃) δ: 7.95 (m, 1H), 7.89 (d, 1H, J = 4.0), 7.07 (dd, 1H, J = 8.0, J = 4.0), 6.78-6.75 (m, 1H), 3.28-3.24 (m, 4H), 2.01-1.96 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ: 143.9, 136.9, 134.4, 123.7, 117.9, 47.4, 25.6. IR (KBr disc, cm⁻¹): 3391, 3037, 2969, 2839, 1586, 1559, 1494, 1462, 1431, 1375, 1246, 1178, 1159, 1111, 1051, 1004, 959, 792, 708, 614.



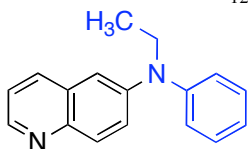
6-methoxy-N-methyl-N-phenylpyridin-2-amine (Table 8, entry 8e).¹⁶ The general procedure F with 0.025 mol% catalyst for 3 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (201 mg, 94%). ¹H NMR (400 MHz, CDCl₃) δ: 7.40-7.36 (m, 2H), 7.29-7.19 (m, 4H), 6.08-6.05 (m, 2H), 3.90 (s, 3H), 3.49 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 163.4, 157.8, 147.0, 139.6, 129.7, 126.6, 126.5, 125.4, 100.4, 97.5, 53.3, 38.3. IR (KBr disc, cm⁻¹): 3005, 2945, 1602, 1582, 1498, 1464, 1406, 1360, 1300, 1283, 1150, 1117, 1093, 1035, 982, 965, 811, 729. Anal. Calcd for C₁₃H₁₄N₂O: C, 72.87; H, 6.59. Found: C, 73.01; H, 6.59.



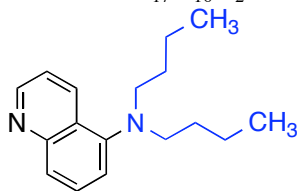
N,3-dimethyl-N-phenylquinolin-2-amine (Table 8, entry 8f). The general procedure F with 0.6 mol% catalyst was followed. Isolation and biotage purification afforded the title compound as a brown solid (211 mg, 85%). ¹H NMR (400 MHz, CDCl₃) δ: 7.91 (d, 1H, J = 8.0), 7.73 (s, 1H), 7.64 (d, 1H, J = 8.0), 7.57 (t, 1H, J = 8.0), 7.36 (t, 1H, J = 8.0), 7.25 (t, 2H, J = 6.0), 7.00 (t, 1H, J = 8.0), 6.93 (d, 2H, J = 8.0), 3.57 (s, 3H), 1.91 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 158.7, 149.5, 146.6, 138.3, 129.4, 128.6, 127.6, 127.1, 126.6, 126.2, 124.6, 122.9, 122.0, 41.6, 20.0. IR (KBr disc, cm⁻¹): 3059, 2963, 1621, 1595, 1560, 1492, 1471, 1431, 1400, 1353, 1298, 1283, 1170, 1137, 1106, 1046, 1010, 903, 858, 792, 727, 755, 698, 618, 585, 515, 481. Anal. Calcd for C₁₇H₁₆N₂: C, 82.22; H, 6.49. Found: C, 82.02; H, 6.53. m.p. 57 °C.



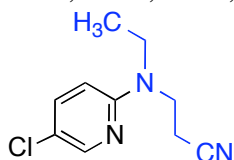
N-ethyl-N-phenylpyrazin-2-amine (Table 8, entry 8g). The general procedure F for 12 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (192 mg, 96%). ¹H NMR (400 MHz, CDCl₃) δ: 8.00-7.99 (m, 1H), 7.72 (t, 2H, J = 8.0), 7.39-7.35 (m, 2H), 7.24-7.22 (m, 1H), 7.19-7.17 (m, 2H), 3.90 (q, 2H, J = 8.0), 1.15 (t, 3H, J = 8.0). ¹³C NMR (100 MHz, CDCl₃) δ: 154.5, 143.7, 141.6, 133.1, 132.5, 130.4, 127.8, 127.0, 45.1, 12.9. IR (KBr disc, cm⁻¹): 3431, 3057, 2974, 2931, 2871, 1899, 1598, 1574, 1517, 1496, 1480, 1454, 1419, 1375, 1354, 1315, 1282, 1255, 1203, 1178, 1153, 1138, 1094, 1070, 1053, 1026, 997, 914, 825, 785, 767, 700, 637, 572. Anal. Calcd for C₁₂H₁₃N₃: C, 72.33; H, 6.58. Found: C, 72.44; H, 6.65.



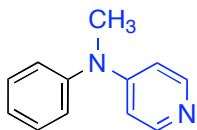
N-ethyl-N-phenylquinolin-6-amine (Table 8, entry 8h). The general procedure F with 0.2 mol% catalyst for 16 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (235 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ: 8.64 (s, 1H), 7.87-7.85 (m, 2H), 7.31-7.28 (m, 3H), 7.22-7.19 (m, 1H), 7.11-7.04 (m, 4H), 3.86-3.81 (m, 2H), 1.25-1.21 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 147.6, 147.2, 146.1, 144.1, 134.5, 130.1, 129.9, 129.8, 124.3, 124.2, 123.7, 121.5, 111.2, 47.0, 12.8. IR (KBr disc, cm⁻¹): 3391, 3034, 2972, 2932, 2871, 1936, 1620, 1591, 1494, 1465, 1436, 1384, 1349, 1253, 1180, 1155, 1120, 1091, 1032, 957, 929, 829, 767, 700, 617. Anal. Calcd for C₁₇H₁₆N₂: C, 82.22; H, 6.49. Found: C, 81.54; H, 6.70.



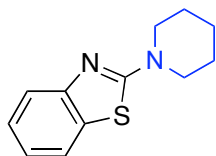
***N,N*-dibutylquinolin-5-amine (Table 8, entry 8i).** The general procedure F with 1 mol% catalyst was followed. Isolation and biotage purification afforded the title compound as a brown liquid (210 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ: 8.81-8.80 (m, 1H), 8.55 (d, 1H, J = 8.0), 7.76 (d, 1H, J = 8.0), 7.54 (t, 1H, J = 8.0), 7.29-7.27 (m, 1H), 7.12 (d, 1H, J = 8.0), 3.02 (t, 4H, J = 4.0), 1.42-1.37 (m, 4H), 1.24-1.16 (m, 4H), 0.81-0.75 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 150.2, 149.8, 149.0, 132.9, 129.2, 126.4, 124.6, 120.3, 118.5, 54.4, 29.3, 20.6, 14.1. IR (KBr disc, cm⁻¹): 3064, 3031, 2957, 2931, 2862, 1608, 1589, 1572, 1497, 1468, 1398, 1378, 1314, 1277, 1200, 1161, 1132, 1079, 1055, 1023, 925, 901, 802, 744, 692, 603, 585.



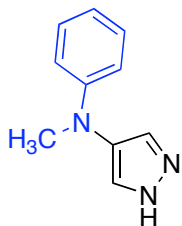
3-((5-chloropyridin-2-yl)(ethyl)amino)propanenitrile (Table 8, entry 8j). The general procedure G with 1 mol% catalyst, 2 mmol amine and 2 mmol Cs₂CO₃ for 24 h was followed. Isolation and biotage purification afforded the title compound as a light-yellow liquid (154 mg, 74%). ¹H NMR (400 MHz, CDCl₃) δ: 8.00 (s, 1H), 7.35 (dd, 1H, J = 8.0, J = 4.0), 6.42 (d, 1H, J = 8.0), 3.73 (t, 2H, J = 6.0), 3.44 (q, 2H, J = 6.7), 2.66 (t, 2H, J = 6.0), 1.14 (t, 3H, J = 8.0). ¹³C NMR (100 MHz, CDCl₃) δ: 155.4, 146.5, 137.4, 119.6, 119.2, 106.9, 45.3, 44.9, 16.8, 12.6. IR (KBr disc, cm⁻¹): 2975, 2248, 1592, 1552, 1495, 1412, 1373, 1324, 1283, 1218, 1186, 1138, 1114, 1078, 1044, 998, 920, 808, 776, 755, 638, 608, 515. Anal. Calcd for C₁₀H₁₂ClN₃: C, 57.28; H, 5.77. Found: C, 57.58; H, 5.80.



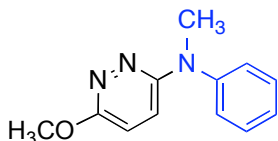
***N*-methyl-*N*-phenylpyridin-4-amine (Table 8, entry 8k).**¹⁸ The general procedure F was followed. Isolation and biotage purification afforded the title compound as a colorless liquid (130 mg, 71%). ¹H NMR (400 MHz, CDCl₃) δ: 7.44 (d, 2H, J = 4.0), 6.66 (t, 2H, J = 6.0), 6.50 (t, 1H, J = 8.0), 6.44 (d, 2H, J = 8.0), 5.78 (d, 2H, J = 8.0), 2.54 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 153.2, 149.3, 145.6, 129.4, 126.1, 125.9, 107.7, 38.9. IR (KBr disc, cm⁻¹): 3372, 3035, 1606, 1587, 1551, 1538, 1506, 1495, 1453, 1433, 1364, 1364, 1241, 1225, 1137, 1078, 1025, 991, 877, 810, 771, 700, 597, 570, 533.



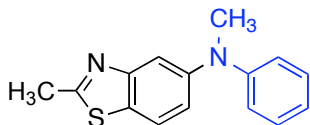
2-(piperidin-1-yl)benzo[*d*]thiazole (Table 8, entry 8l).¹⁹ The general procedure F with NaOt-Bu (1.4 mmol) at room temperature for 12 h was followed. Isolation and biotage purification afforded the title compound as a brown solid (181 mg, 83%). ¹H NMR (400 MHz, CDCl₃) δ: 7.56-7.49 (m, 2H), 7.26-7.22 (m, 1H), 7.01 (t, 1H, J = 8.0), 3.57 (s, 4H), 1.66 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 169.1, 153.2, 130.9, 126.1, 121.2, 120.8, 119.0, 49.8, 25.5, 24.5. IR (KBr disc, cm⁻¹): 2936, 2852, 1595, 1563, 1535, 1444, 1384, 1338, 1290, 1258, 1239, 1209, 1123, 1012, 751, 724. m.p. 93-95 °C (94 °C).



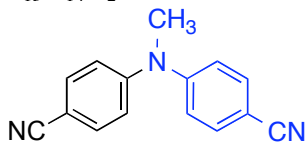
***N*-methyl-*N*-phenyl-1*H*-pyrazol-4-amine (Table 8, entry 8m).** The general procedure H with SPhos precatalyst² (2 mol%), SPhos (2 mol%), amine (0.6 mmol), aryl bromide (0.5 mmol), LHMDS (1.1 mL of 1.0 M solution in THF) for 24 h at 100 °C was followed. Isolation and biotage purification afforded the title compound as a yellow solid (73 mg, 84%). ¹H NMR (400 MHz, CDCl₃) δ: 7.51 (s, 2H), 7.22-7.18 (m, 3H), 6.85-7.83 (m, 2H), 6.79-6.76 (m, 1H), 3.22 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 149.5, 131.8, 129.0, 118.4, 114.6, 41.0. IR (KBr disc, cm⁻¹): 3175, 2949, 1599, 1580, 1498, 1372, 1294, 1154, 996, 942, 750, 693, 668. Anal. Calcd for C₁₀H₁₁N₃: C, 69.34; H, 6.40. Found: C, 68.44; H, 6.62. m.p. 53 °C.



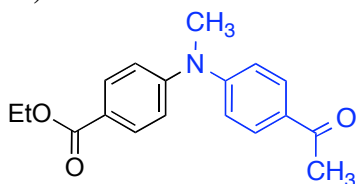
6-methoxy-*N*-methyl-*N*-phenylpyridazin-3-amine (Table 8, entry 8n).¹⁶ The general procedure G with 0.25 mol% catalyst for 18 h was followed. Isolation and biotage purification afforded the title compound as a white solid (196 mg, 91%). ¹H NMR (400 MHz, CDCl₃) δ: 7.31 (t, 2H, J = 8.0), 7.15-7.11 (m, 3H), 6.76 (d, 1H, J = 12.0), 6.60 (d, 1H, J = 12.0), 3.96 (s, 3H), 3.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 160.2, 156.9, 146.7, 130.1, 126.0, 125.9, 120.5, 118.9, 54.4, 39.3. IR (KBr disc, cm⁻¹): 2948, 1596, 1495, 1548, 1495, 1472, 1435, 1404, 1355, 1296, 1198, 1172, 1139, 1065, 1013, 871, 832, 807, 769, 700, 592. m.p. 80 °C (76-77 °C).



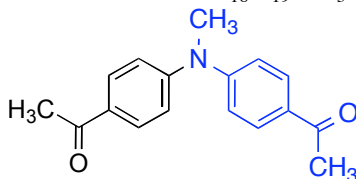
***N*,2-dimethyl-*N*-phenylbenzo[*d*]thiazol-5-amine (Table 8, entry 8o).** The general procedure G with 1.5 mol% catalyst for 18 h was followed. Isolation and biotage purification afforded the title compound as a white solid (226 mg, 89%). ¹H NMR (400 MHz, CDCl₃) δ: 7.61-7.58 (m, 2H), 7.28-7.24 (m, 2H), 7.05-7.02 (m, 3H), 6.95 (t, 1H, J = 8.0), 3.34 (s, 3H), 2.78 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 168.0, 155.0, 149.3, 148.2, 129.5, 128.3, 121.9, 121.8, 121.6, 120.9, 119.4, 113.4, 40.9, 20.4. IR (KBr disc, cm⁻¹): 3059, 2921, 2812, 1593, 1547, 1523, 1495, 1464, 1429, 1343, 1291, 1254, 1205, 1172, 1123, 1073, 1052, 1027, 1001, 942, 837, 806, 753, 699, 644. Anal. Calcd for C₁₅H₁₄N₂S: C, 70.83; H, 5.55. Found: C, 71.03; H, 5.50. m.p. 84 °C.



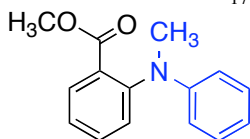
4,4'-((methylazanediyl)dibenzonitrile (Table 9, entry 9a).²⁰ The general procedure G with 0.2 mol% catalyst 20 h was followed. Isolation and biotage purification afforded the title compound as a white solid (198 mg, 85%). ¹H NMR (400 MHz, CDCl₃) δ: 7.52 (d, 4H, J = 6), 7.08 (d, 4H, J = 6), 3.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 150.8, 133.8, 120.8, 119.3, 105.1, 40.2. IR (KBr disc, cm⁻¹): 3081, 2916, 2221, 1611, 1594, 1553, 1504, 1344, 1306, 1275, 1259, 1178, 1142, 1104, 1066, 961, 909, 871, 827, 729. Anal. Calcd for C₁₅H₁₁N₃: C, 77.23; H, 4.75. Found: C, 77.04; H, 4.70. m.p. 151 °C (153 °C).



Ethyl 4-((4-acetylphenyl)(methyl)amino)benzoate (Table 9, entry 9b). The general procedure G with 0.2 mol% catalyst was followed. Isolation and biotage purification afforded the title compound as a yellow solid (290 mg, 98%). ¹H NMR (400 MHz, CDCl₃) δ: 7.95 (d, 2H, J = 8.0), 7.84 (d, 2H, J = 8.0), 7.09 (d, 2H, J = 8.0), 7.01 (d, 2H, J = 12.0), 4.31 (q, 2H, J = 8.0), 3.38 (s, 3H), 2.50 (s, 3H), 1.34 (t, 3H, J = 8.0). ¹³C NMR (100 MHz, CDCl₃) δ: 196.8, 166.4, 151.9, 151.5, 131.3, 130.3, 124.6, 121.0, 118.8, 61.0, 40.2, 26.5, 14.6. IR (KBr disc, cm⁻¹): 2981, 1709, 1673, 1611, 1591, 1562, 1509, 1475, 1428, 1357, 1312, 1273, 1181, 1106, 1064, 1019, 956, 875, 837, 772, 708, 595, 513. Anal. Calcd for C₁₈H₁₉NO₃: C, 72.71; H, 6.44. Found: C, 72.59; H, 6.41. m.p. 89 °C.

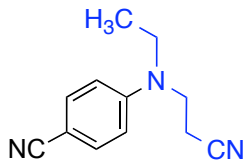


1,1'-((methylazanediyl)bis(4,1-phenylene))diethanone (Table 9, entry 9c). The general procedure G with 0.2 mol% catalyst was followed. Isolation and biotage purification afforded the title compound as a brown solid (248 mg, 93%). ¹H NMR (400 MHz, CDCl₃) δ: 7.87 (d, 4H, J = 8), 7.07 (d, 4H, J = 8), 3.40 (s, 3H), 2.52 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 196.8, 151.7, 131.1, 130.3, 120.0, 40.2, 26.6. IR (KBr disc, cm⁻¹): 1661, 1587, 1510, 1426, 1358, 1309, 1267, 1185, 1137, 1110, 956, 875, 831, 584. Anal. Calcd for C₁₇H₁₇NO₂: C, 76.36; H, 6.41. Found: C, 76.10; H, 6.37. m.p. 108 °C.

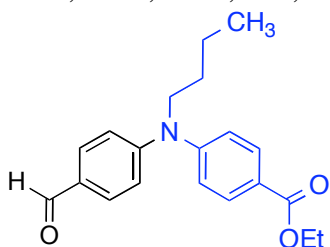


Methyl 2-(methyl(phenyl)amino)benzoate (Table 9, entry 9d). The general procedure G with 1.5 mol% catalyst for 18 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (169 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ: 7.81-7.78 (m, 1H), 7.52 (t, 1H, J = 8.0), 7.29-7.24 (m, 2H), 7.18-7.14 (m, 2H), 6.74 (t, 1H, J = 4.0), 6.65-6.62 (m, 2H), 3.58 (s, 3H), 3.28 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 167.7, 149.4, 148.3, 133.5, 131.6, 129.4, 129.2, 129.1, 125.4, 118.2, 114.5, 52.3, 40.6. IR (KBr disc, cm⁻¹): 3026, 2949, 1884, 2814, 1730, 1594, 1578, 1501, 1490, 1453, 1433, 1349, 1293, 1247, 1188, 1159, 1127, 1097, 1081, 1040, 991, 965, 871, 821,

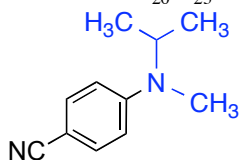
773, 750, 715, 694, 656. Anal. Calcd for C₁₅H₁₅NO₂: C, 74.67; H, 6.27. Found: C, 74.39; H, 6.25.



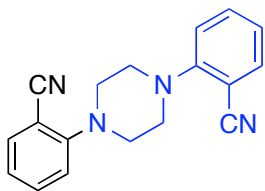
4-((2-cyanoethyl)(ethyl)amino)benzonitrile (Table 9, entry 9e). The general procedure G for 18 h was followed. Isolation and biotage purification afforded the title compound as a white solid (130 mg, 65%). ¹H NMR (400 MHz, CDCl₃) δ: 7.46 (d, 2H, J = 8.0), 6.62 (d, 2H, J = 12.0), 3.67 (t, 2H, J = 8.0), 3.50-3.47 (m, 2H), 2.60 (t, 2H, J = 6.0), 1.19 (t, 3H, J = 4.0). ¹³C NMR (100 MHz, CDCl₃) δ: 149.4, 134.1, 120.3, 117.9, 111.7, 99.0, 46.4, 45.7, 16.3, 12.3. IR (KBr disc, cm⁻¹): 2976, 2360, 2210, 1606, 1521, 1404, 1369, 1278, 1177, 1002, 816, 548. m.p. 85-88 °C.



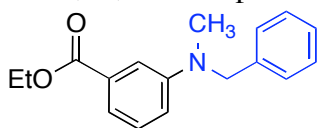
Ethyl 4-(butyl(4-formylphenyl)amino)benzoate (Table 9, entry 9f). The general procedure G with 0.2 mol% catalyst for 19 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (257 mg, 79%). ¹H NMR (400 MHz, CDCl₃) δ: 9.76 (s, 1H), 7.99 (d, 2H, J = 8.0), 7.69 (d, 2H, J = 10.0), 7.15 (d, 2H, J = 8.0), 6.92 (d, 2H, J = 6.0), 4.32 (q, 2H, J = 6.0), 3.76 (t, 2H, J = 8.0), 1.67-1.61 (m, 2H), 1.36-1.30 (m, 5H), 0.89 (t, 3H, J = 6.0). ¹³C NMR (100 MHz, CDCl₃) δ: 190.6, 166.2, 152.6, 150.4, 131.8, 131.5, 128.8, 126.0, 123.6, 117.5, 61.1, 52.4, 29.7, 20.4, 14.6, 14.0. IR (KBr disc, cm⁻¹): 2959, 2932, 2873, 2731, 1710, 1610, 1591, 1561, 1509, 1465, 1418, 1366, 1311, 1274, 1214, 1168, 1141. 1107, 1018, 879, 832, 772, 733, 704. Anal. Calcd for C₂₀H₂₃NO₃: C, 73.82; H, 7.12. Found: C, 73.76; H, 7.07.



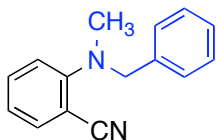
4-(isopropyl(methyl)amino)benzonitrile (Table 9, entry 9g).²¹ The general procedure G with 1 mol% catalyst for 12 h was followed. Isolation and biotage purification afforded the title compound as a white solid (130 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ: 7.30 (d, 2H, J = 8.0), 6.56 (d, 2H, J = 8.0), 4.04-4.00 (m, 1H), 2.66 (s, 3H), 1.07 (d, 6H, J = 4.0). ¹³C NMR (100 MHz, CDCl₃) δ: 152.3, 133.6, 120.9, 111.8, 96.9, 48.4, 29.9, 19.7. IR (KBr disc, cm⁻¹): 2974, 2212, 1605, 1519, 1483, 1394, 1350, 1219, 1182, 1127, 1046, 1004, 937, 817, 774. Anal. Calcd for C₁₁H₁₄N₂: C, 75.82; H, 8.10. Found: C, 75.84; H, 8.26. m.p. 47 °C (46 °C).



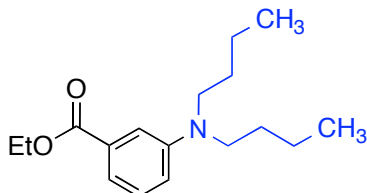
2,2'-(piperazine-1,4-diyl)dibenzonitrile (Table 9, entry 9h). The general procedure G with 1 mol% catalyst in THF for 20 h was followed. Isolation and biotage purification afforded the title compound as a white solid (207 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ: 7.56-7.54 (m, 2H), 7.49-7.47 (m, 2H), 7.06-7.00 (m, 4H), 3.38 (s, 8H). ¹³C NMR (100 MHz, CDCl₃) δ: 155.7, 134.5, 134.2, 122.5, 119.2, 118.6, 106.6, 51.9. IR (KBr disc, cm⁻¹): 2818, 2219, 1595, 1570, 1489, 1447, 1372, 1337, 1285, 1256, 1225, 1167, 1140, 1106, 1038, 941, 764, 718. Anal. Calcd for C₁₈H₁₆N₄: C, 74.98; H, 5.59. Found: C, 74.14; H, 5.89. m.p. 149 °C.



Ethyl 3-(benzyl(methyl)amino)benzoate (Table 9, entry 9i). The general procedure G with 1.5 mmol amine and 3 mol% catalyst in THF for 22 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (245 mg, 91%). Ethyl benzoate was found in 3% yield from this reaction. ¹H NMR (400 MHz, CDCl₃) δ: 7.52-7.51 (m, 1H), 7.44 (d, 1H, J = 8.0), 7.35-7.23 (m, 6H), 6.91 (dd, 1H, J = 8.0), 4.57 (s, 2H), 4.37 (q, 2H, J = 8.0), 3.07 (s, 3H), 1.39 (t, 3H, J = 8.0). ¹³C NMR (100 MHz, CDCl₃) δ: 167.3, 149.7, 138.6, 131.4, 129.2, 128.7, 127.1, 126.8, 117.6, 116.7, 113.1, 60.9, 56.5, 38.7, 14.5. IR (KBr disc, cm⁻¹): 3063, 3029, 2981, 2903, 1716, 1602, 1578, 1496, 1451, 1424, 1375, 1268, 1214, 1174, 1083, 1109, 1083, 1027, 988, 955, 863, 800, 753, 732, 697, 684, 668, 608, 555, 458. Anal. Calcd for C₁₇H₁₉NO₂: C, 75.81; H, 7.11. Found: C, 75.58; H, 7.14.

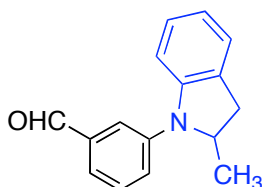


2-(benzyl(methyl)amino)benzonitrile (Table 9, entry 9j).²² The general procedure G with 1 mol% catalyst in THF for 19 h was followed. Isolation and biotage purification afforded the title compound as a colorless liquid (198 mg, 89%). ¹H NMR (400 MHz, CDCl₃) δ: 7.54-7.52 (m, 1H), 7.41-7.32 (m, 5H), 7.29-7.26 (m, 1H), 6.94-6.87 (m, 2H), 4.50 (s, 2H), 2.91 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 154.9, 137.4, 135.0, 133.7, 128.6, 127.9, 127.5, 120.1, 119.5, 118.4, 102.5, 59.7, 40.1. IR (KBr disc, cm⁻¹): 3584, 2214, 1595, 1487, 1451, 1423, 1358, 1180, 1113, 1046, 942.

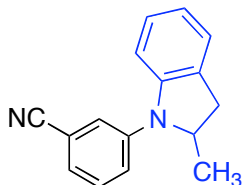


Ethyl 3-(dibutylamino)benzoate (Table 9, entry 9k). The general procedure G with 5 mol% catalyst in THF for 24 h was followed. Isolation and biotage purification afforded

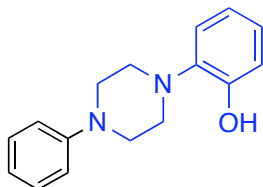
the title compound as a colorless liquid (211 mg, 76%). Ethyl benzoate was found in 6% yield from this reaction. ^1H NMR (400 MHz, CDCl_3) δ : 7.32-7.20 (m, 3H), 6.79-6.77 (m, 1H), 4.31 (q, 2H, $J = 8.0$), 3.29-3.25 (m, 4H), 1.58-1.51 (m, 4H), 1.38-1.31 (m, 7H), 0.94 (t, 6H, $J = 8.0$). ^{13}C NMR (100 MHz, CDCl_3) δ : 167.8, 148.3, 131.4, 129.2, 116.3, 116.0, 112.7, 60.9, 50.9, 29.5, 20.5, 14.5, 14.2. IR (KBr disc, cm^{-1}): 2958, 2933, 2873, 1718, 1602, 1576, 1497, 1456, 1367, 1289, 1265, 1217, 1179, 1110, 1084, 1032, 993, 933, 863, 798, 751, 686, 668. Anal. Calcd for $\text{C}_{17}\text{H}_{27}\text{NO}_2$: C, 73.61; H, 9.81. Found: C, 73.78; H, 9.99.



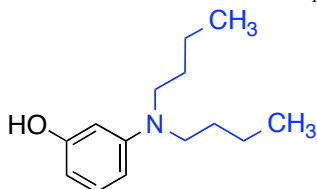
3-(2-methylindolin-1-yl)benzaldehyde (Table 9, entry 9l). The general procedure G with 1 mol% catalyst for 22 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (206 mg, 87%). Benzaldehyde was found in 3% yield from this reaction. ^1H NMR (400 MHz, CDCl_3) δ : 9.98 (s, 1H), 7.72 (s, 1H), 7.54-7.48 (m, 3H), 7.16 (d, 1H, $J = 8.0$), 7.06 (t, 1H, $J = 8.0$), 6.93 (d, 1H, $J = 8.0$), 6.78 (t, 1H, $J = 8.0$). ^{13}C NMR (100 MHz, CDCl_3) δ : 192.6, 147.2, 144.5, 137.8, 130.1, 127.4, 126.2, 125.5, 123.9, 120.1, 119.9, 109.0, 59.7, 37.2, 20.3. IR (KBr disc, cm^{-1}): 3049, 2968, 2845, 2727, 1699, 1592, 1489, 1462, 1392, 1284, 1248, 1224, 1182, 1156, 1106, 1058, 1027, 987, 931, 852, 816, 788, 747, 715, 692, 669, 648. Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}$: C, 80.98; H, 6.37. Found: C, 80.76; H, 6.33.



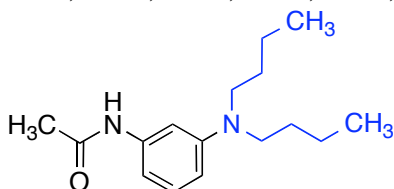
3-(2-methylindolin-1-yl)benzonitrile (Table 9, entry 9m). The general procedure G with 1 mol% catalyst for 24 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (220 mg, 94%). ^1H NMR (400 MHz, CDCl_3) δ : 7.47 (d, 1H, $J = 12.0$), 7.40 (t, 1H, $J = 8.0$), 7.21 (dd, 1H, $J = 14.0$, $J = 8.0$), 7.09 (t, 1H, $J = 8.0$), 6.96 (d, 1H, $J = 8.0$), 6.82 (t, 1H, $J = 8.0$), 4.40-4.35 (m, 1H), 3.37 (dd, 1H, $J = 12.0$, $J = 8.0$), 2.73 (dd, 1H, $J = 12.0$, $J = 8.0$), 1.33 (d, 2H, $J = 4.0$). ^{13}C NMR (100 MHz, CDCl_3) δ : 146.0, 144.2, 130.2, 127.3, 125.5, 124.7, 123.5, 122.1, 120.4, 119.1, 113.2, 109.3, 59.5, 37.0, 20.1. IR (KBr disc, cm^{-1}): 3072, 2969, 2849, 2229, 1590, 1574, 1489, 1461, 1432, 1376, 1309, 1284, 1249, 1224, 1179, 1162, 1091, 1057, 1028, 1002, 983, 905, 786, 748, 720, 686, 600, 498. Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2$: C, 82.02; H, 6.02. Found: C, 82.26; H, 5.94.



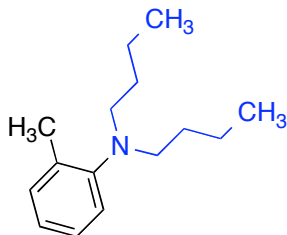
2-(4-phenylpiperazin-1-yl)phenol (Table 10, entry 10a). The general procedure H with 0.15 mol% catalyst for 20 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (178 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ: 7.31-7.27 (t, 2H), 7.21-7.19 (d, 1H), 7.12-7.08 (m, 1H), 6.99-6.96 (m, 4H), 6.92-6.86 (m, 2H), 3.33 (t, 4H, J = 6.0), 3.03 (t, 4H, J = 6.0). ¹³C NMR (100 MHz, CDCl₃) δ: 151.7, 151.4, 139.0, 129.4, 126.9, 121.6, 120.4, 116.6, 114.4, 52.9, 50.3. IR (KBr disc, cm⁻¹): 3174, 2831, 1594, 1505, 1493, 1453, 1378, 1315, 1262, 1225, 1180, 1134, 1095, 930, 774, 760, 701. Anal. Calcd for C₁₆H₁₈N₂O: C, 75.56; H, 7.13. Found: C, 75.61; H, 7.17.



3-(dibutylamino)phenol (Table 10, entry 10b).²³ The general procedure H with 1.5 mol% catalyst for 8 h was followed. Isolation and biotage purification afforded the title compound as a red liquid (195 mg, 88%). ¹H NMR (400 MHz, CDCl₃) δ: 7.01 (t, 1H, J = 8.0), 6.22 (d, 1H, J = 8.0), 6.09 (t, 2H, J = 8.0), 3.20 (t, 4H, J = 8.0), 1.57-1.49 (m, 4H), 1.36-1.28 (m, 4H), 0.92 (t, 7H, J = 8.0). ¹³C NMR (100 MHz, CDCl₃) δ: 156.9, 150.0, 130.2, 104.9, 102.4, 98.8, 51.1, 29.6, 20.6, 14.2. IR (KBr disc, cm⁻¹): 2958, 2932, 2872, 1620, 1512, 1462, 1402, 1367, 1243, 1197, 1110, 1029, 942, 821, 751, 689.

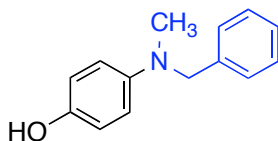


N-(3-(dibutylamino)phenyl)acetamide (Table 10, entry 10c). The general procedure H with 1.5 mol% catalyst for 8 h was followed. Isolation and biotage purification afforded the title compound as a brown solid (240 mg, 92%). ¹H NMR (400 MHz, CDCl₃) δ: 7.66 (s, 1H), 7.08-7.01 (m, 2H), 6.61 (d, 1H, J = 8.0), 6.35 (dd, 1H, J = 8.0), 3.22-3.18 (m, 4H), 2.12 (s, 3H), 1.56-1.45 (m, 4H), 1.35-1.28 (m, 4H), 0.91 (t, 6H, J = 6.0). ¹³C NMR (100 MHz, CDCl₃) δ: 168.7, 149.0, 139.4, 129.6, 108.0, 106.9, 103.5, 51.0, 29.6, 24.9, 20.6, 14.2. IR (KBr disc, cm⁻¹): 3302, 2957, 2932, 2872, 1662, 1613, 1583, 1554, 1499, 1457, 1369, 1322, 1273, 1177, 1147, 1111, 1035, 989, 930, 853, 764, 690, 535.

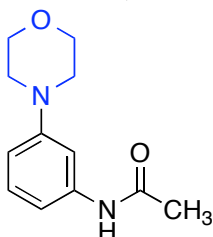


N,N-dibutyl-2-methylaniline (Table 10, entry 10d).²⁴ The general procedure H with 2 mol% SPhos precatalyst and 2 mol% SPhos for 12 h at room temperature was followed. Isolation and biotage purification afforded the title compound as a light-yellow liquid (164 mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ: 7.14 (t, 2H, J = 8.0), 7.07 (t, 1H, J = 8.0), 6.94 (t, 1H, J = 8.0), 2.88 (t, 4H, J = 8.0), 2.27 (s, 3H), 1.39-1.33 (m, 4H), 1.29-1.20 (m, 4H), 0.84 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 150.8, 135.2, 131.1, 126.2, 123.2,

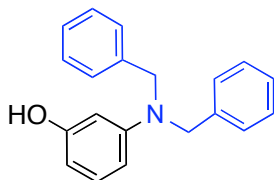
122.3, 54.0, 29.7, 20.7, 18.6, 14.3. IR (KBr disc, cm^{-1}): 2957, 2931, 2861, 1599, 1492, 1460, 1376, 1209, 1166, 1110, 765, 727.



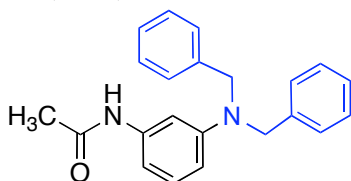
4-(benzyl(methyl)amino)phenol (Table 10, entry 10e). The general procedure H with 1 mol% catalyst for 24 h was followed. Isolation and biotage purification afforded the title compound as a black solid (151 mg, 71%). ^1H NMR (400 MHz, CDCl_3) δ : 7.34-7.27 (m, 5H), 6.73 (s, br, 2H), 5.77 (s, 1H), 4.42 (s, br, 1H), 2.89 (s, br, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ : 128.7, 128.5, 127.6, 127.4, 127.0, 115.2, 113.9, 39.1. IR (KBr disc, cm^{-1}): 3352, 3028, 2889, 2805, 1603, 1514, 1452, 1355, 1230, 1116, 1075, 1028, 1003, 947, 817, 732, 697, 601, 517, 458. Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}$: C, 78.84; H, 7.09. Found: C, 78.82; H, 7.09. m.p. 53 $^\circ\text{C}$.



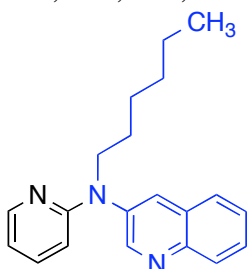
N-(3-morpholinophenyl)acetamide (Table 10, entry 10f).²³ The general procedure H with 0.15 mol% catalyst for 20 h was followed. Isolation and biotage purification afforded the title compound as a white solid (176 mg, 80%). ^1H NMR (400 MHz, CDCl_3) δ : 7.88 (s, 1H), 7.28 (s, 1H), 7.13 (t, 1H, $J = 8.0$), 6.84 (d, 1H, $J = 8.0$), 6.60 (d, 1H, $J = 8.0$), 3.76 (t, 4H, $J = 4.0$), 3.07 (t, 4H, $J = 4.0$), 2.10 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 169.0, 152.1, 139.3, 129.7, 111.6, 111.5, 107.5, 67.0, 49.3, 24.8. IR (KBr disc, cm^{-1}): 3296, 2857, 1662, 1610, 1554, 1497, 1424, 1372, 1301, 1251, 1198, 1121, 1024, 995, 941, 880, 772, 688. m.p. 160 $^\circ\text{C}$ (159-160 $^\circ\text{C}$).



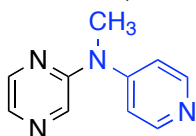
3-(dibenzylamino)phenol (Table 10, entry 10g).²⁵ The general procedure H with 1.5 mol% catalyst for 22 h was followed. Isolation and biotage purification afforded the title compound as a brown solid (250 mg, 87%). ^1H NMR (400 MHz, CDCl_3) δ : 7.34-7.24 (m, 10H), 7.00 (t, 1H, $J = 8.0$), 6.33 (dd, 1H, $J = 8.0$), 6.18-6.15 (m, 2H), 4.61 (s, 4H), 3.70 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 157.1, 151.0, 138.7, 130.4, 128.9, 128.8, 127.6, 127.1, 126.8, 105.3, 104.2, 99.8, 54.3, 52.7. IR (KBr disc, cm^{-1}): 3359, 3061, 3028, 2862, 1617, 1505, 1452, 1395, 1361, 1298, 1266, 1170, 1075, 1028, 990, 967, 911, 820, 736, 696.



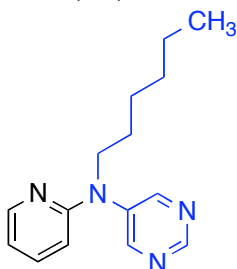
***N*-3-(dibenzylamino)phenylacetamide (Table 10, entry 10h).**²⁶ The general procedure H with 1.5 mol% catalyst for 22 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (258 mg, 78%). ¹H NMR (400 MHz, CDCl₃) δ: 7.04-7.24 (m, 12H), 7.04 (t, 2H, J = 8.0), 6.81-6.89 (m, 2H), 6.45 (d, 1H, J = 8.0), 4.60 (s, 4H), 2.10 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 168.6, 150.0, 139.2, 138.5, 129.9, 129.2, 128.9, 127.1, 126.8, 120.1, 108.8, 104.0, 54.3, 24.8. IR (KBr disc, cm⁻¹): 3300, 3029, 1663, 1610, 1552, 1495, 1451, 1363, 1320, 1254, 1176, 1028, 990, 963, 730, 695. m.p. 143 °C (143-144 °C).



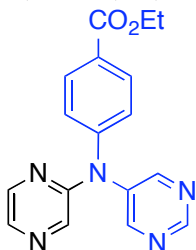
***N*-hexyl-*N*-(pyridin-2-yl)quinolin-3-amine (Table 11, entry 11a).** The general procedure F with 1 mol% catalyst, amine (1 mmol), aryl chloride (0.5 mmol), NaOt-Bu (0.6 mmol) for 20 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (107 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ: 8.81 (d, 1H, J = 4.0), 8.21-8.19 (m, 1H), 8.07 (d, 1H, J = 12.0), 7.92 (d, 1H, J = 4.0), 7.73 (d, 1H, J = 8.0), 7.66-7.62 (m, 1H), 7.53-7.49 (m, 1H), 7.35-7.31 (m, 1H), 6.66-6.63 (m, 1H), 6.49 (d, 1H, J = 8.0), 4.01 (t, 2H, J = 8.0), 1.70-1.66 (m, 2H), 1.35-1.22 (m, 6H), 0.84-0.80 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 158.2, 151.3, 148.3, 145.8, 139.4, 137.4, 130.7, 129.4, 129.0, 128.9, 127.5, 127.2, 114.4, 109.4, 50.8, 31.8, 28.2, 26.9, 22.8, 14.2. IR (KBr disc, cm⁻¹): 2928, 2857, 1591, 1561, 1477, 1428, 1390, 1331, 1305, 1259, 1224, 1197, 1141, 1072, 982, 786, 769, 752, 617. Anal. Calcd for C₂₀H₂₃N₃: C, 78.65; H, 7.59. Found: C, 78.38; H, 7.56.



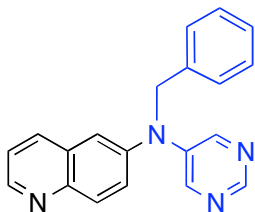
***N*-methyl-*N*-(pyridin-4-yl)pyrazin-2-amine (Table 11, entry 11b).** The general procedure F with 1 mol% catalyst for 12 h was followed. Isolation and biotage purification afforded the title compound as a white solid (152 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ: 8.43-8.40 (m, 3H), 8.20 (m, 1H), 8.04 (m, 1H), 7.06-7.05 (m, 2H), 3.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 153.7, 152.1, 151.1, 142.4, 136.9, 136.5, 115.3, 37.1. IR (KBr disc, cm⁻¹): 3394, 2361, 1597, 1574, 1518, 1502, 1478, 1403, 1360, 1304, 1272, 1226, 1154, 1079, 1052, 1000, 898, 823, 753, 640. Anal. Calcd for C₁₀H₁₀N₄: C, 64.50; H, 5.41. Found: C, 64.57; H, 5.51. m.p. 67 °C.



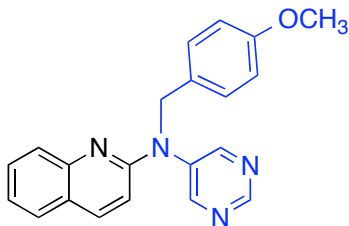
***N*-hexyl-*N*-(pyridin-2-yl)pyrimidin-5-amine (Table 11, entry 11c).** The general procedure F with 1 mol% catalyst, amine (1 mmol), aryl chloride (0.5 mmol), NaO*t*-Bu (0.6 mmol) for 18 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (122 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ: 8.87 (s, 1H), 8.60 (s, 2H), 8.15-8.13 (m, 1H), 7.42-7.38 (m, 1H), 6.70-6.67 (m, 1H), 6.58 (d, 1H, J = 8.0), 3.84 (t, 2H, J = 8.0), 1.64-1.58 (m, 2H), 1.27-1.21 (m, 6H), 0.80-0.77 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 157.1, 153.8, 153.3, 148.4, 140.9, 137.9, 115.8, 109.7, 50.4, 31.7, 27.9, 26.7, 22.7, 14.2. IR (KBr disc, cm⁻¹): 3046, 2956, 2929, 2858, 1590, 1564, 1476, 1441, 1420, 1373, 1306, 1257, 1226, 1189, 1154. Anal. Calcd for C₁₅H₂₀N₄: C, 70.28; H, 7.86. Found: C, 70.39; H, 7.88.



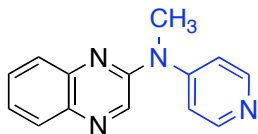
Ethyl 4-(pyrazin-2-yl(pyrimidin-5-yl)amino)benzoate (Table 11, entry 11d). The general procedure G with 0.25 mol% catalyst, amine¹⁹ (0.6 mmol), aryl chloride (0.5 mmol), Cs₂CO₃ (0.6 mmol) and *t*-BuOH (1.5 mL) for 18 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (145 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ: 8.96 (s, 1H), 8.58 (s, 2H), 8.17 (d, 2H, J = 8.0), 8.16 (s, 1H), 8.06 (d, 1H, J = 4.0), 7.23 (d, 2H, J = 8.0), 4.34 (q, 2H, J = 8.0), 1.36 (t, 3H, J = 8.0). ¹³C NMR (100 MHz, CDCl₃) δ: 165.7, 154.6, 153.5, 146.9, 142.2, 139.7, 138.4, 136.7, 132.2, 128.9, 125.8, 61.5, 14.5. IR (KBr disc, cm⁻¹): 2982, 1714, 1606, 1574, 1522, 1508, 1473, 1425, 1407, 1367, 1324, 1275, 1176, 1148, 1106, 1006, 853, 772, 724, 709.



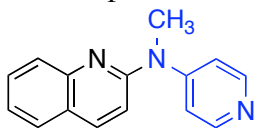
***N*-benzyl-*N*-(pyrimidin-5-yl)quinolin-6-amine (Table 11, entry 11e).** The general procedure F with 1 mol% catalyst, amine²⁷ (0.5 mmol), aryl chloride (0.5 mmol), NaO*t*-Bu (0.6 mmol) and THF (2 mL) for 18 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (137 mg, 88%). Quinoline was found in 3% yield from this reaction. ¹H NMR (400 MHz, CDCl₃) δ: 8.82-8.81 (m, 1H), 8.71 (s, 1H), 8.43 (s, 2H), 8.06 (d, 1H, J = 8.0), 7.98 (d, 1H, J = 8.0), 7.58 (dd, 1H, J = 8.0, J = 4.0), 7.53-7.52 (m, 1H), 7.37-7.24 (m, 6H), 5.09 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ: 151.0, 150.0, 146.3, 145.9, 144.1, 141.8, 136.9, 135.4, 131.8, 129.5, 129.3, 127.9, 126.7, 126.1, 122.0, 119.2, 56.4. IR (KBr disc, cm⁻¹): 3030, 1621, 1594, 1567, 1498, 1427, 1380, 1224, 1122, 839, 723, 696. Anal. Calcd for C₂₀H₁₆N₄: C, 76.90; H, 5.16. Found: C, 76.41; H, 5.27. m.p. 74 °C.



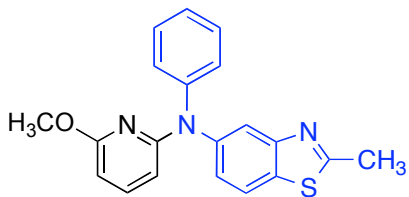
***N*-(4-methoxybenzyl)-*N*-(pyrimidin-5-yl)quinolin-2-amine (Table 11, entry 11f).** The general procedure F with 1.5 mol% catalyst, amine²⁸ (0.5 mmol), aryl chloride (0.5 mmol), NaOt-Bu (0.6 mmol) and THF (3 mL) for 12 h was followed. Isolation and biotage purification afforded the title compound as a white solid (128 mg, 75%). Quinoline was found in 4% yield from this reaction. ¹H NMR (400 MHz, CDCl₃) δ: 8.96 (s, 1H), 8.65 (s, 2H), 7.88 (d, 1H, J = 6.0), 7.77 (d, 1H, J = 6.0), 7.52-7.71 (m, 2H), 7.10-7.42 (m, 3H), 6.78 (t, 3H, J = 8.0), 5.32 (s, 2H), 3.72 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 159.2, 155.4, 154.8, 154.1, 147.5, 140.4, 138.2, 130.2, 129.7, 129.2, 127.5, 124.5, 124.0, 114.3, 111.5, 55.4, 52.9. IR (KBr disc, cm⁻¹): 1617, 1603, 1559, 1504, 1476, 1418, 1387, 1319, 1247, 1175, 1033, 812, 757, 730. Anal. Calcd for C₂₁H₁₈N₄O: C, 73.67; H, 5.30. Found: C, 73.46; H, 5.47. m.p. 121 °C.



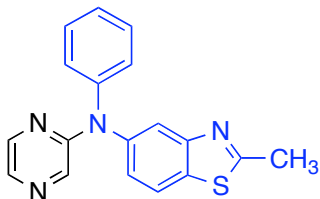
***N*-methyl-*N*-(pyridin-4-yl)quinoxalin-2-amine (Table 11, entry 11g).** The general procedure F with 1 mol% catalyst, amine (0.6 mmol), aryl chloride (0.5 mmol), NaOt-Bu (0.6 mmol) and THF (2 mL) for 24 h at 45 °C was followed. Isolation and biotage purification afforded the title compound as a yellow solid (87 mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ: 8.63 (s, 1H), 8.49 (d, 2H, J = 4.0), 7.90 (d, 1H, J = 8.0), 7.90 (d, 1H, J = 8.0), 7.61 (t, 1H, J = 8.0), 7.49 (t, 1H, J = 6.0), 7.12 (d, 2H, J = 4.0), 3.62 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 152.1, 151.3, 141.5, 139.4, 138.4, 130.6, 129.0, 127.5, 127.0, 116.2, 55.7, 37.4. IR (KBr disc, cm⁻¹): 3407, 3032, 2930, 1596, 1575, 1550, 1498, 1433, 1407, 1383, 1360, 1312, 1224, 1152, 1118, 1058, 992, 977, 923, 822, 763, 682, 612, 580, 563, 483. Anal. Calcd for C₁₄H₁₂N₄: C, 71.17; H, 5.12. Found: C, 70.93; H, 5.38. m.p. 85 °C.



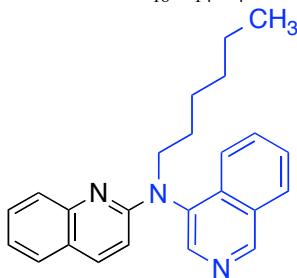
***N*-methyl-*N*-(pyridin-4-yl)quinolin-2-amine (Table 11, entry 11h).** The general procedure F with SPhos precatalyst (3 mol%), SPhos (3 mol%), amine (0.6 mmol), aryl chloride (0.5 mmol), NaOt-Bu (0.6 mmol) and THF (1.5 mL) for 24 h at 45 °C was followed. Isolation and biotage purification afforded the title compound as a white solid (103 mg, 88%). ¹H NMR (400 MHz, CDCl₃) δ: 8.42-8.40 (m, 2H), 7.91 (d, 1H, J=8.0), 7.84 (d, 1H, J = 8.0), 7.67 (d, 1H, J = 8.0), 7.62-7.58 (m, 1H), 7.36 (t, 1H, J = 8.0), 7.23-7.20 (m, 1H), 7.07-7.06 (m, 2H), 3.65 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 156.0, 153.0, 150.8, 147.8, 137.5, 130.1, 127.8, 127.6, 125.1, 124.9, 115.1, 115.0, 37.4. IR (KBr disc, cm⁻¹): 3046, 1618, 1606, 1588, 1551, 1498, 1472, 1430, 1383, 1364, 1310, 1223, 1142, 1114, 1068, 991, 922, 827, 811, 758. Anal. Calcd for C₁₅H₁₃N₃: C, 76.57; H, 5.57. Found: C, 76.40; H, 5.59. m.p. 93 °C.



***N*-(6-methoxypyridin-2-yl)-2-methyl-*N*-phenylbenzo[*d*]thiazol-5-amine (Table 11, entry 11i).** The general procedure G with 0.25 mol% catalyst, amine¹⁹ (0.6 mmol), aryl chloride (0.5 mmol), Cs₂CO₃ (0.6 mmol) and *t*-BuOH (1.5 mL) for 20 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (161 mg, 93%). ¹H NMR (400 MHz, CDCl₃) δ: 7.66-7.61 (m, 2H), 7.27-7.20 (m, 3H), 7.18-7.13 (m, 3H), 7.04 (t, 1H, J = 8.0), 6.14 (d, 2H, J = 6.0), 3.54 (s, 3H), 2.71 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 167.3, 162.2, 156.3, 153.8, 145.3, 143.9, 139.3, 130.7, 128.6, 126.3, 124.1, 123.6, 120.7, 119.5, 103.7, 101.0, 52.6, 19.6. IR (KBr disc, cm⁻¹): 1580, 1525, 1494, 1456, 1435, 1412, 1345, 1254, 1223, 1147, 1043, 1005, 783, 756, 723, 697, 550. Anal. Calcd for C₂₀H₁₇N₃OS: C, 69.14; H, 4.93. Found: C, 68.78; H, 4.88.

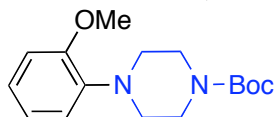


2-methyl-*N*-phenyl-*N*-(pyrazin-2-yl)benzo[*d*]thiazol-5-amine (Table 11, entry 11j). The general procedure G with 0.25 mol% catalyst, amine¹⁹ (0.6 mmol), aryl chloride (0.5 mmol), Cs₂CO₃ (0.6 mmol) and *t*-BuOH (1.5 mL) for 20 h was followed. Isolation and biotage purification afforded the title compound as a yellow solid (141 mg, 89%). ¹H NMR (400 MHz, CDCl₃) δ: 7.31 (s, 1H), 7.25 (s, 1H), 7.16 (s, 1H), 6.94-6.92 (m, 2H), 6.53 (t, 2H, J = 8.0), 6.42-6.35 (m, 4H), 1.96 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 167.9, 154.5, 153.9, 143.9, 142.5, 141.2, 135.5, 135.0, 132.1, 129.3, 126.0, 125.4, 123.0, 121.5, 119.5, 19.6. IR (KBr disc, cm⁻¹): 3424, 3057, 1592, 1571, 1552, 1516, 1493, 1473, 1456, 1408, 1340, 1322, 1304, 1274, 1233, 1196, 1174, 1146, 1068, 1003. Anal. Calcd for C₁₈H₁₄N₄S: C, 67.90; H, 4.43. Found: C, 67.93; H, 4.39. m.p. 89-92 °C.

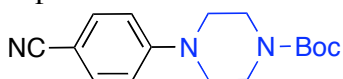


***N*-hexyl-*N*-(isoquinolin-4-yl)quinolin-2-amine (Table 11, entry 11k).** The general procedure F with 1 mol% catalyst, amine (0.6 mmol), aryl chloride (0.5 mmol), NaOt-Bu (0.6 mmol) and THF (2 mL) for 18 h was followed. Isolation and biotage purification afforded the title compound as a yellow liquid (135 mg, 76%). ¹H NMR (400 MHz, CDCl₃) δ: 9.27 (s, 1H), 8.53 (s, 1H), 8.06 (s, 1H), 7.83-7.77 (m, 2H), 7.61-7.50 (m, 5H), 6.16 (d, 1H, J = 12.0). ¹³C NMR (100 MHz, CDCl₃) δ: 157.1, 152.1, 148.1, 144.3, 137.1, 136.2, 134.7, 131.3, 130.1, 129.7, 128.5, 128.1, 127.5, 127.1, 123.5, 122.8, 122.6, 111.5, 50.7, 31.8, 28.3, 26.9, 22.8, 14.3. IR (KBr disc, cm⁻¹): 3049, 2954, 2928, 2856, 1619,

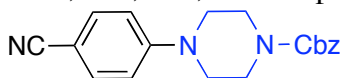
1605, 1579, 1559, 1503, 1479, 1455, 1425, 1402, 1333, 1296, 1259, 1229, 1160, 1143, 1118, 1017, 964, 901, 864, 815, 788, 753, 616. Anal. Calcd for C₂₄H₂₅N₃: C, 81.09; H, 7.09. Found: C, 80.47; H, 7.03.



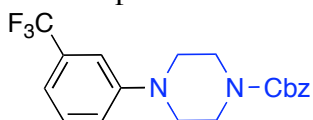
tert-butyl 4-(2-methoxyphenyl)piperazine-1-carboxylate (Table 12, entry 12a). The general procedure I using RuPhos (**2**) (1.15 mg, 0.25 mol%), RuPhos precatalyst (**4**) (1.8 mg, 0.25 mol%), 2-chloroanisole (127 μ L, 1mmol) and *tert*-butyl piperazine-1-carboxylate (223 mg, 1.2 mmol) was followed. Isolated as a light yellow solid (277 mg, 95%). ¹H NMR (400 MHz, CDCl₃) δ 7.09 - 6.93 (m, 2H), 6.93 - 6.70 (m, 2H), 3.82 (s, 3H), 3.60 (s, 4H), 2.99 (s, 4H), 1.45 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 154.44, 151.90, 140.07, 123.47, 120.75, 118.42, 111.04, 79.41, 55.11, 50.44, 43.41 (d, *J* = 117.1 Hz), 28.14. IR (KBr disc, cm⁻¹): 2975, 1696, 1501, 1421, 1242, 1173, 1029, 923, 747. m.p. 68 - 69 °C



tert-butyl 4-(4-cyanophenyl)piperazine-1-carboxylate (Table 12, entry 12b). The general procedure I using RuPhos (**2**) (0.92 mg, 0.2 mol%), RuPhos precatalyst (**4**) (1.44 mg, 0.2 mol%), 4-chlorobenzonitrile (138 mg, 1mmol) and *tert*-butyl piperazine-1-carboxylate (223 mg, 1.2 mmol) was followed. Isolated as a colourless solid (286 mg, 99%). ¹H NMR (400 MHz, CDCl₃) δ 7.38 (dd, *J* = 8.9, 1.5 Hz, 2H), 6.93 - 6.59 (m, 2H), 3.60 - 3.35 (m, 4H), 3.31 - 3.09 (m, 4H), 1.39 (d, *J* = 1.3 Hz, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 154.13, 152.78, 133.05, 119.52, 114.03, 99.97, 79.69, 46.58, 42.52 (d, *J* = 88.8 Hz), 27.98. IR (KBr disc, cm⁻¹): 2980, 2214, 1700, 1605, 1517, 1419, 1365, 1244, 1167, 1002, 918, 822, 546. m.p. 117-119 °C.

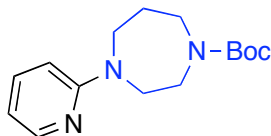


Benzyl 4-(4-cyanophenyl)piperazine-1-carboxylate (Table 12, entry 12c). The general procedure J using 4-chlorobenzonitrile (138 mg, 1mmol) was followed. The title compound was isolated as a light orange solid (311 mg, 97%). ¹H NMR (400 MHz, CDCl₃) δ 7.34 (dd, *J* = 8.8, 6.8 Hz, 2H), 7.31 - 7.16 (m, 5H), 6.70 (d, *J* = 8.8 Hz, 2H), 5.20 - 4.88 (s, 2H), 3.53 (d, *J* = 3.7 Hz, 4H), 3.17 (bs, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 154.58, 152.57, 136.10, 133.00, 128.12, 128.05, 127.70, 127.46, 119.49, 114.00, 99.94, 66.77, 46.38, 42.70. IR (KBr disc, cm⁻¹): 2859, 2215, 1700, 1604, 1517, 1429, 1238, 1179. m.p. 116 °C

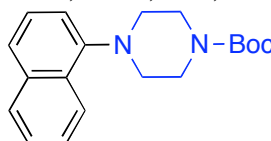


Benzyl 4-(3-(trifluoromethyl)phenyl)piperazine-1-carboxylate (Table 12, entry 12d). The general procedure J using 3-chlorobenzotrifluoride (136 μ L, 1mmol) was followed. The title compound was isolated as a yellow oil (298 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.47 - 7.29 (m, 6H), 7.13 (d, *J* = 7.1 Hz, 2H), 7.09 - 7.00 (m, 1H), 5.29 - 5.06 (m, 2H), 3.81 - 3.58 (m, 4H), 3.17 (s, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 155.03, 151.19, 136.52, 131.34 (q, *J* = 31.6 Hz), 129.60, 128.47, 128.05, 127.88, 124.23 (d, *J* =

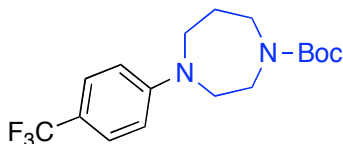
272.4 Hz), 119.28, 116.37, 112.61, 67.20, 48.66, 43.45. IR (KBr disc, cm^{-1}): 2830, 1702, 1609, 1497, 1431, 1320, 1233, 1164, 1122, 953, 697.



tert-butyl 4-(pyridin-2-yl)-1,4-diazepane-1-carboxylate (Table 12, entry 12e). The general procedure I using RuPhos (**2**) (2.3 mg, 0.5 mol%), RuPhos precatalyst (**4**) (3.6 mg, 0.5 mol%), 2-chloropyridine (97 μL , 1mmol) and *tert*-butyl 1,4-diazepane-1-carboxylate (236 μL , 1.2 mmol) was followed. Isolated as a light yellow oil (261 mg, 94%). ^1H NMR (400 MHz, CDCl_3) δ 8.08 (ddd, $J = 5.0, 1.9, 0.7$ Hz, 1H), 7.36 (t, $J = 7.8$ Hz, 1H), 6.46 (dd, $J = 12.4, 7.2$ Hz, 2H), 3.79 - 3.65 (m, 2H), 3.65 - 3.45 (m, 4H), 3.33 - 3.21 (m, 1H), 3.17 (t, $J = 6.2$ Hz, 1H), 1.90 (p, $J = 6.2$ Hz, 2H), 1.36 (d, $J = 21.5$ Hz, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.08, 157.03, 155.17, 154.90, 148.02, 147.93, 137.19, 111.55, 105.45, 105.39, 79.21, 48.69, 48.34, 47.09, 46.92, 46.45, 45.99, 45.62, 28.22, 28.13, 25.07, 24.74. IR (KBr disc, cm^{-1}): 2973, 1694, 1596, 1494, 1442, 1414, 1365, 1240, 1167, 928, 769.



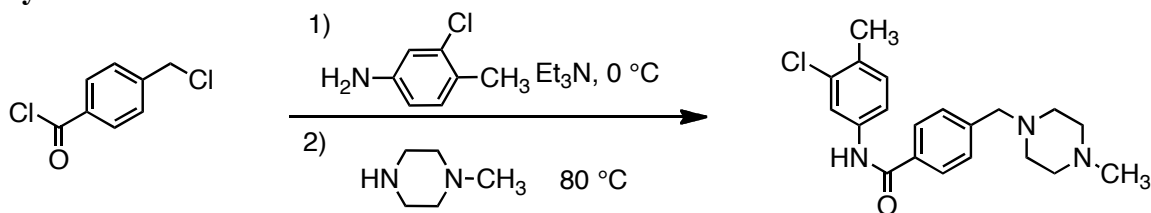
tert-butyl 4-(naphthalen-1-yl)piperazine-1-carboxylate (Table 12, entry 12f). The general procedure I using RuPhos (**2**) (0.46 mg, 0.1 mol%), RuPhos precatalyst (**4**) (0.72 mg, 0.1 mol%), 1-chloronaphthalene (136 μL , 1mmol) and *tert*-butyl piperazine-1-carboxylate (223 mg, 1.2 mmol) was followed. Isolated as a colourless oil (288 mg, 92%). ^1H NMR (400 MHz, CDCl_3) δ 8.30 - 8.16 (m, 1H), 7.90 - 7.77 (m, 1H), 7.59 (d, $J = 8.2$ Hz, 1H), 7.51 (dq, $J = 8.4, 6.8, 1.6$ Hz, 2H), 7.45 - 7.35 (m, 1H), 7.06 (dd, $J = 7.4, 0.9$ Hz, 1H), 4.32 - 3.30 (bs, 4H), 3.06 (s, 4H), 1.57 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 154.70, 149.16, 134.54, 128.61, 128.27, 125.73, 125.62, 125.34, 123.66, 123.12, 114.65, 79.57, 52.69, 44.48, 43.51, 28.30. IR (KBr disc, cm^{-1}): 2974, 1692, 1419, 1398, 1364, 1248, 1168, 1123, 1011, 773.



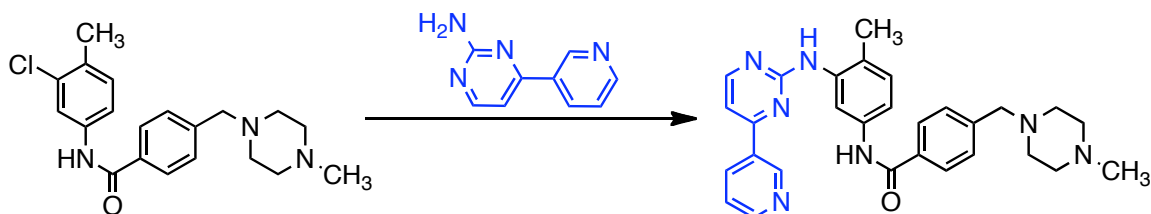
tert-butyl 4-(4-(trifluoromethyl)phenyl)-1,4-diazepane-1-carboxylate (Table 12, entry 12e). The general procedure I using RuPhos (**2**) (0.23 mg, 0.05 mol%), RuPhos precatalyst (**4**) (0.36 mg, 0.05 mol%), 4-chlorobenzotrifluoride (133 μL , 1mmol) and *tert*-butyl 1,4-diazepane-1-carboxylate (236 μL , 1.2 mmol) was followed. Isolated as a colourless solid by chromatography using Biotage SP4 system, eluting with 25% EtOAc in hexanes (301 mg, 88%). ^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, $J = 8.8$ Hz, 2H), 6.65 (d, $J = 8.5$ Hz, 2H), 3.62 - 3.41 (m, 6H), 3.27 (t, $J = 5.9$ Hz, 1H), 3.16 (t, $J = 6.1$ Hz, 1H), 2.03 - 1.72 (m, 2H), 1.37 (s, 5H), 1.29 (s, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.07, 154.69, 149.36, 149.25, 126.58, 126.28, 123.59, 117.82, 117.43, 117.11, 116.78, 110.74, 110.58, 79.48, 50.12, 49.82, 48.62, 47.87, 45.96, 45.89, 45.60, 45.41, 28.11, 27.96, 24.44,

24.19. ^{19}F NMR (376 MHz, CDCl_3) δ -61.50. IR (KBr disc, cm^{-1}): 2974, 1691, 1616, 1529, 1416, 1237, 1197, 1162, 1107, 1070. m.p. 70 °C

Synthesis of Gleevec®



***N*-(3-chloro-4-methylphenyl)-4-((4-methylpiperazin-1-yl)methyl)benzamide** A 20 mL schlenk flask, which was equipped with a magnetic stir bar and septum, was charged with 3-chloro-4-methylaniline (146 mL, 1.2 mmol), triethylamine (278 mL, 2.0 mmol), and THF (5 mL) and was evacuated and backfilled with argon. The reaction mixture was cooled to 0 °C and a solution of 4-(chloromethyl)benzoylchloride in THF (2 mL, 0.5 M, 1.0 mmol) was added over a ten minute period. The solution was stirred at 0 °C for 2 h and then 1-methylpiperazine (1.107 mL, 10 mmol) was added via syringe and the reaction vessel was sealed with a Teflon screw cap and heated to 80 °C for 12 h. The reaction was diluted with cold water and a white precipitate crashed out. The precipitate was filtered and washed with cold water (100 mL) to yield the product as a white solid (251 mg, 73%), mp 143-145 °C. ^1H NMR (300 MHz, CDCl_3) δ : 7.99 (s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.71 (s, 1H), 7.40 (d, J = 8.5 Hz, 3H), 7.16 (d, J = 8.0 Hz, 1H), 3.54 (s, 2H), 2.47 (bs, 8H), 2.32 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ : 165.9, 143.0, 137.0, 134.7, 133.6, 132.3, 131.2, 129.6, 127.3, 121.1, 118.8, 62.7, 55.3, 53.2, 46.2, 19.8. IR (neat, cm^{-1}): 2938, 2804, 1650, 1594, 1527, 1503, 1384, 1308, 1011, 815.



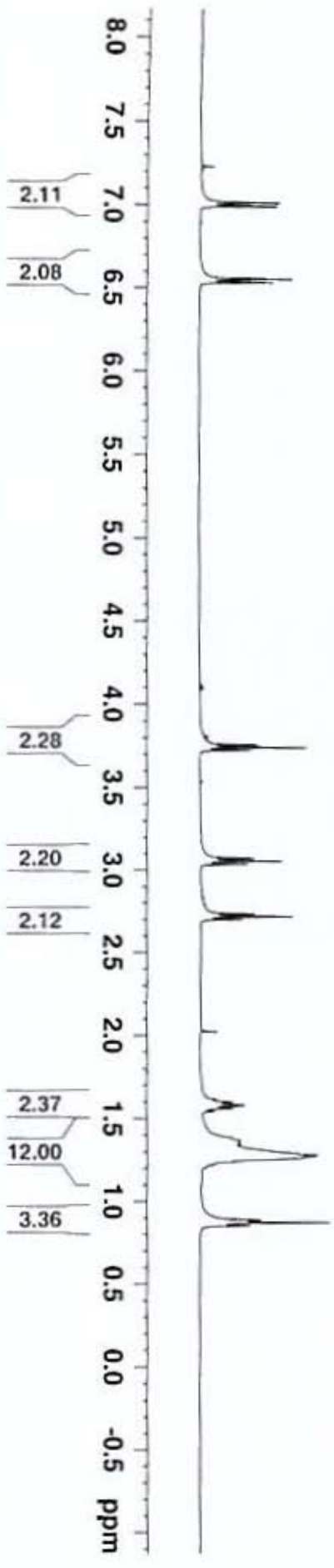
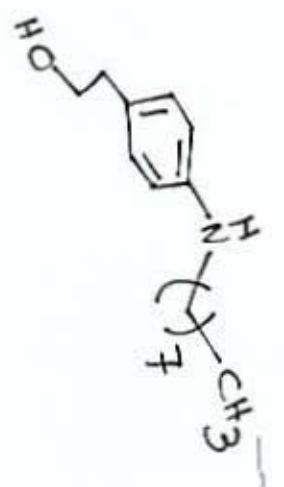
Imatinib Base An oven-dried test tube, which was equipped with a magnetic stir bar and fitted with a teflon septum, was charged with **3** (8 mg, 2 mol%), **1** (5 mg, 2 mol%), K_2CO_3 (152 mg, 1.1 mmol), aryl chloride (179 mg, 0.5 mmol), and 4-(pyridin-3-yl)pyrimidin-2-amine (103 mg, 0.6 mmol). The vessel was evacuated and backfilled with argon (this process was repeated a total of 3 times) and then *tert*-butanol (1 mL) was added via syringe. The solution was heated to 110 °C for 6 h. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, washed with water, concentrated in vacuo, and purified via the Biotage SP4 (30-100% MeOH/ H_2O , reverse phase 60 g cartridge) to provide the title compound as a white solid (207 mg, 84%), mp 206-208 °C (lit.^x mp 207-210). ^1H NMR (300 MHz, CDCl_3) δ : 9.20 (s, 1H), 8.65 (d, J = 5.0 Hz, 1H), 8.55 (s, 1H), 8.46 (m, 2H), 8.14 (s, 1H), 7.80 (d, J = 8.5 Hz, 2H), 7.38 (m, 3H), 7.28 (m, 1H), 7.13 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ : 165.8, 162.9, 160.8, 159.2, 151.7, 148.7, 142.7, 138.0, 136.9, 135.2, 134.1, 132.9, 131.0, 129.5, 127.3, 124.5,

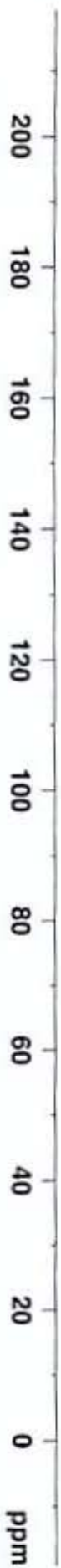
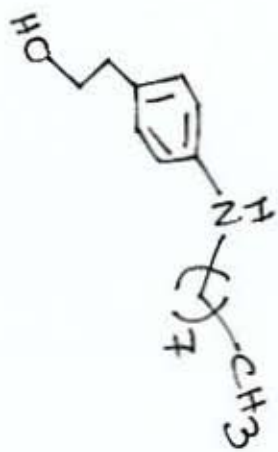
124.0, 115.7, 113.5, 108.5, 62.8, 55.3, 53.4, 46.3, 18.0. IR (neat, cm⁻¹): 3283, 2939, 2802, 1652, 1578, 1555, 1531, 1452, 1418, 1290, 731.

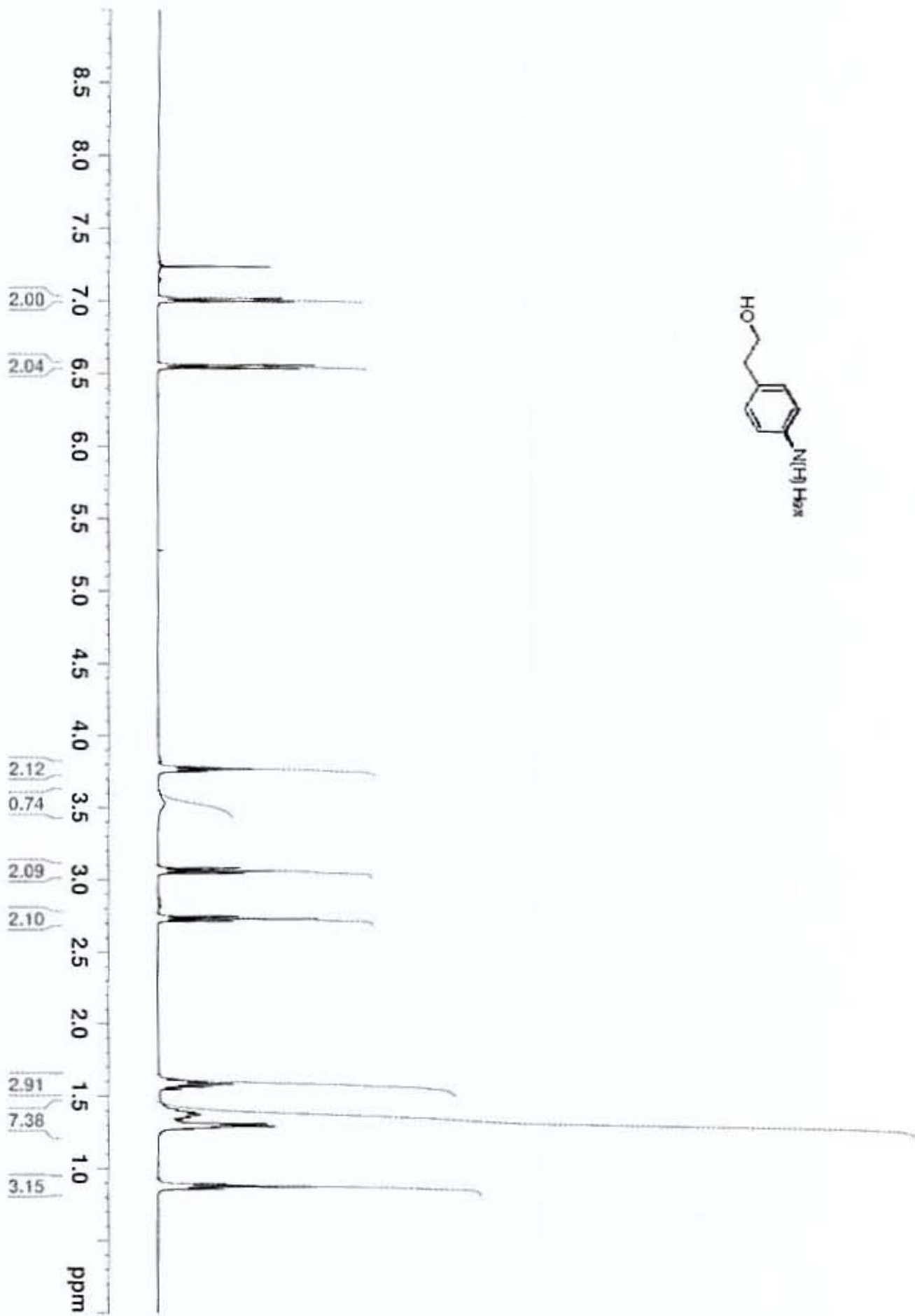
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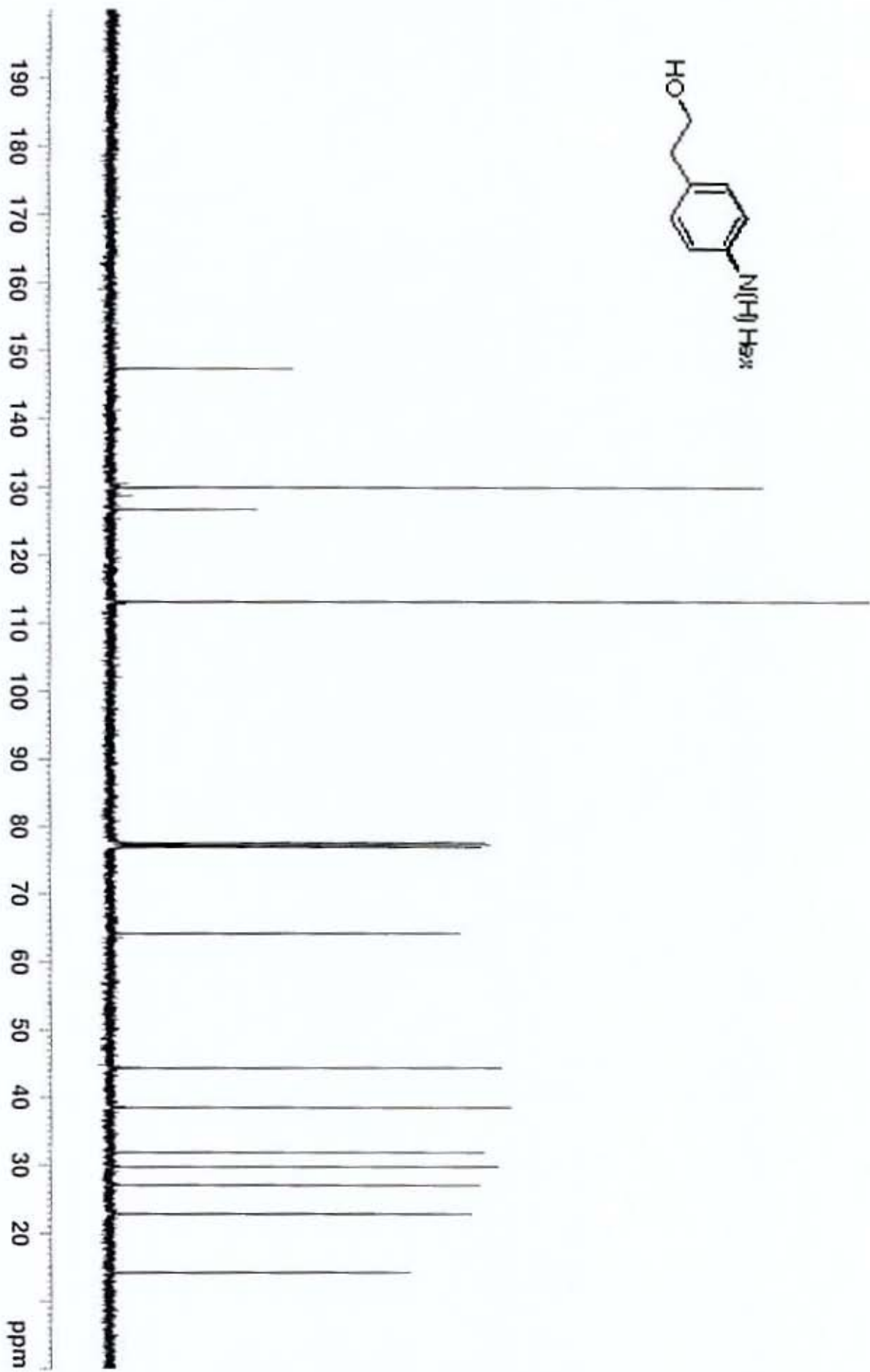
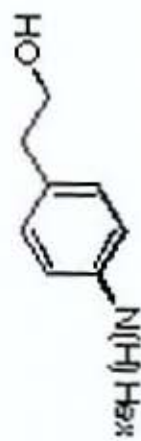
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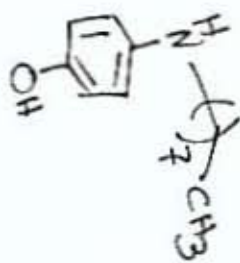
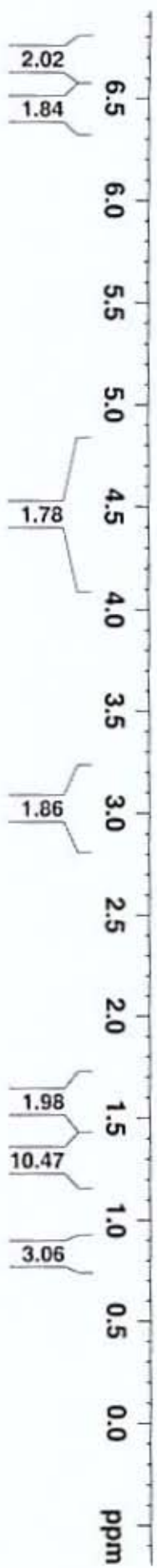
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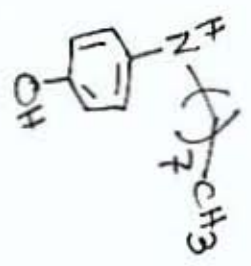
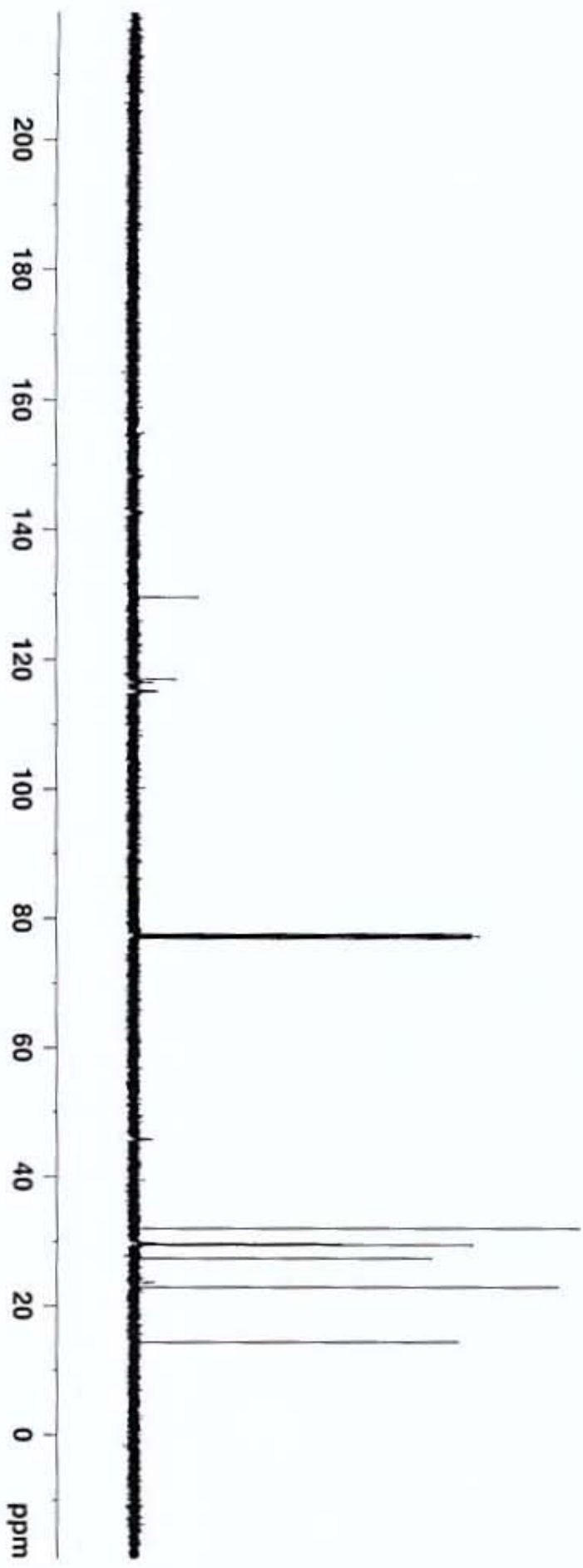


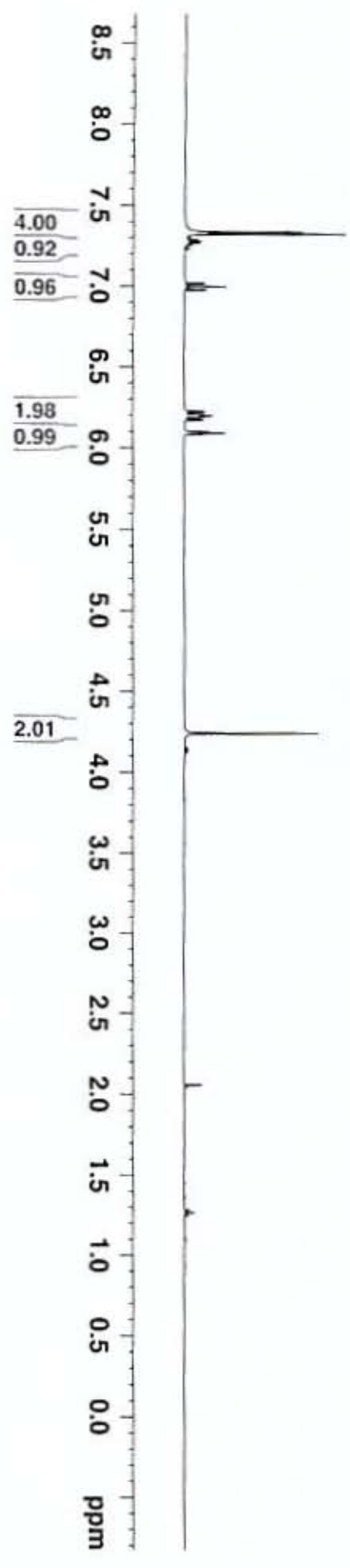
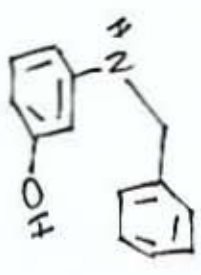


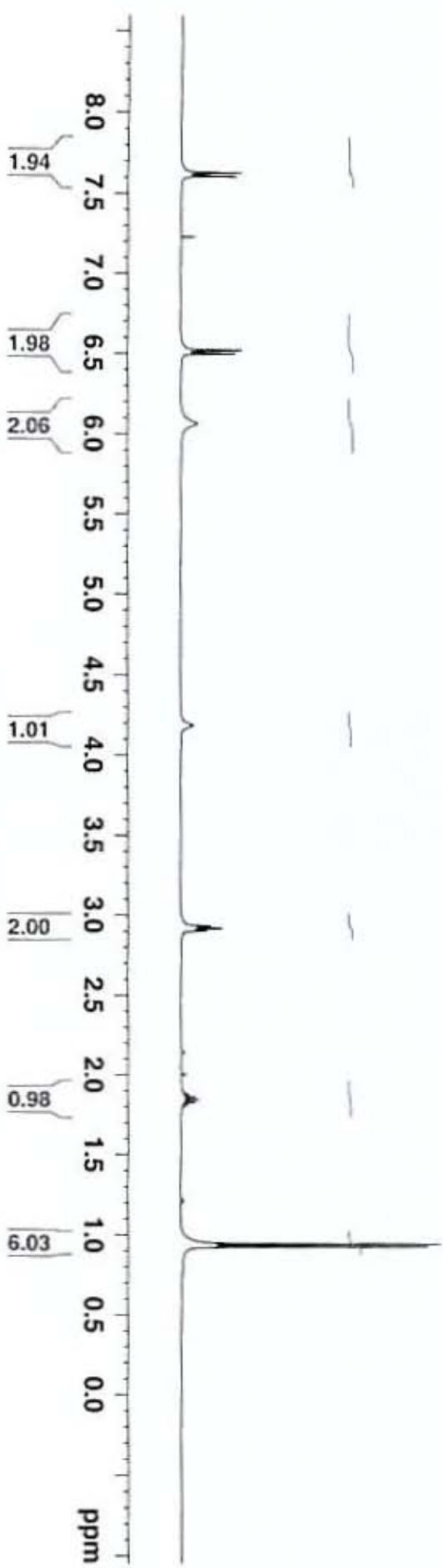
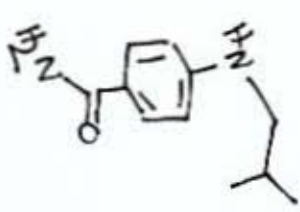




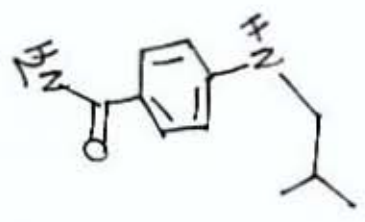




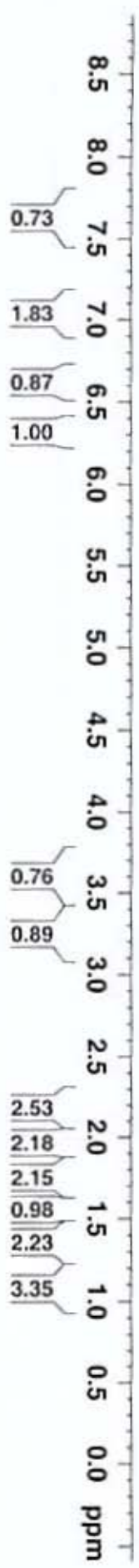
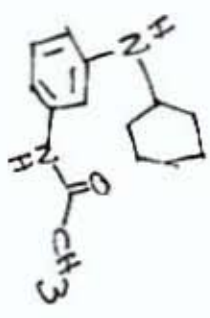


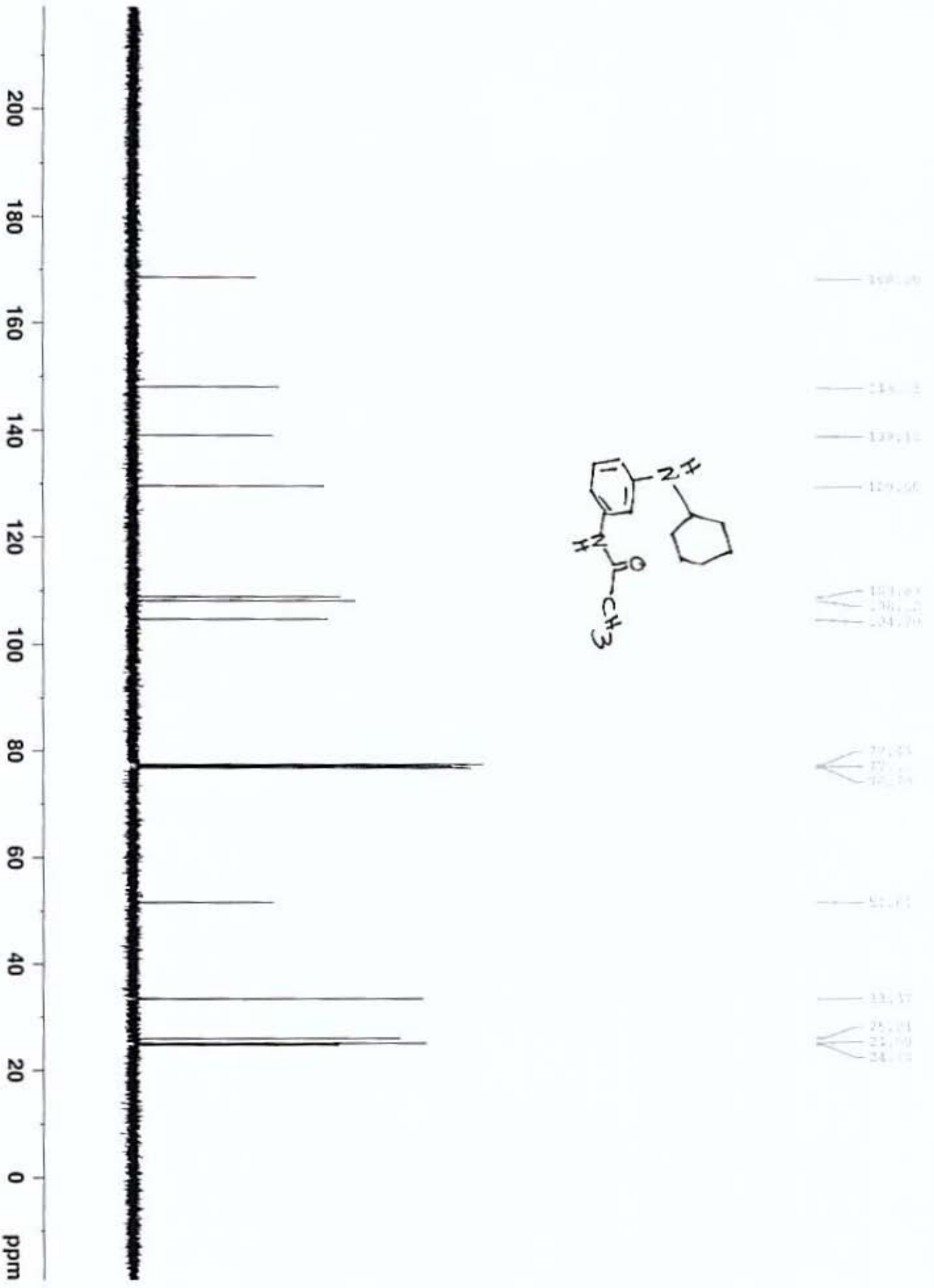


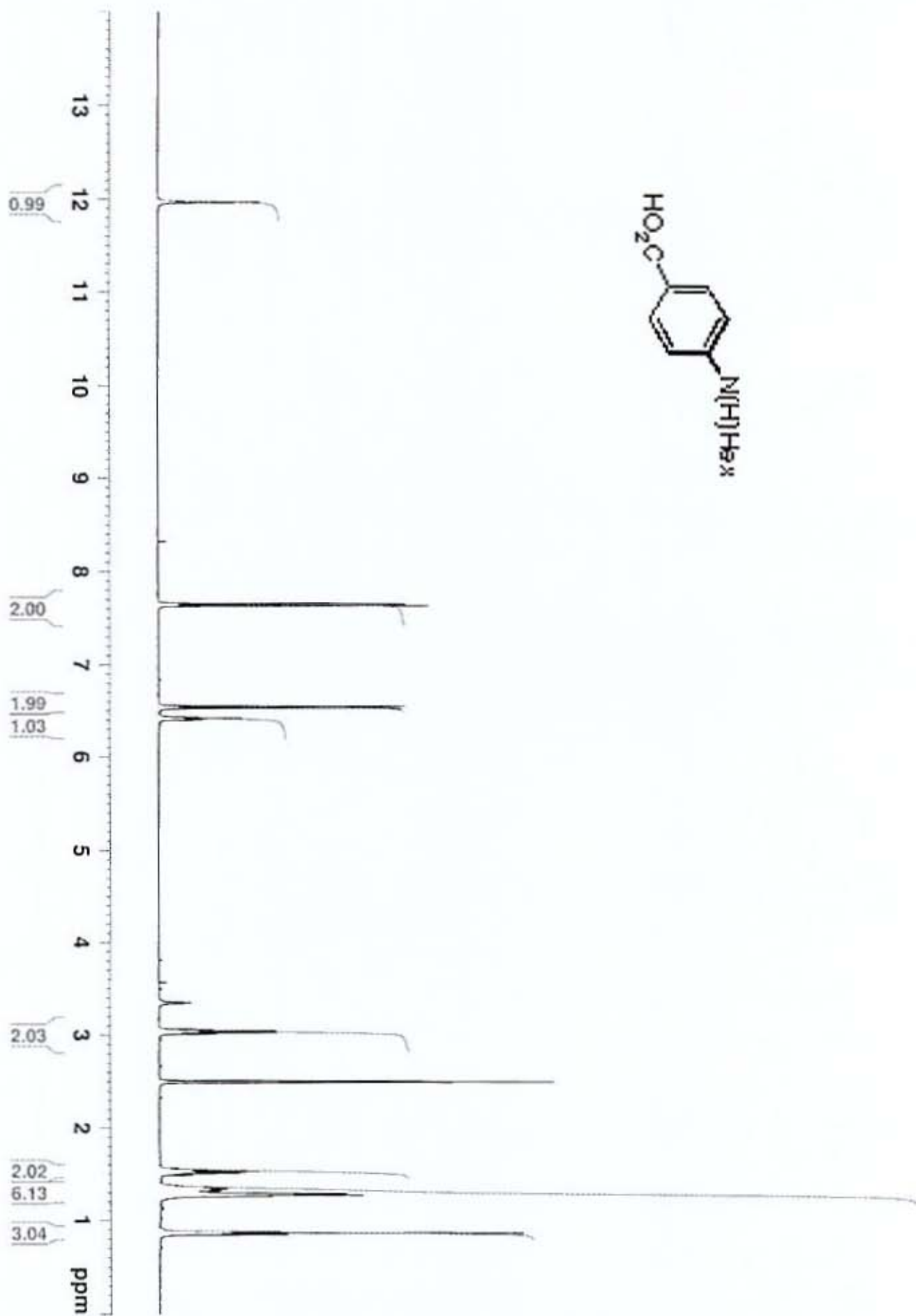
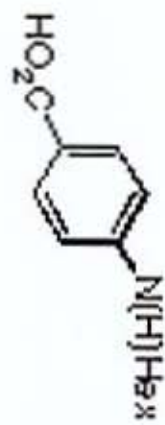
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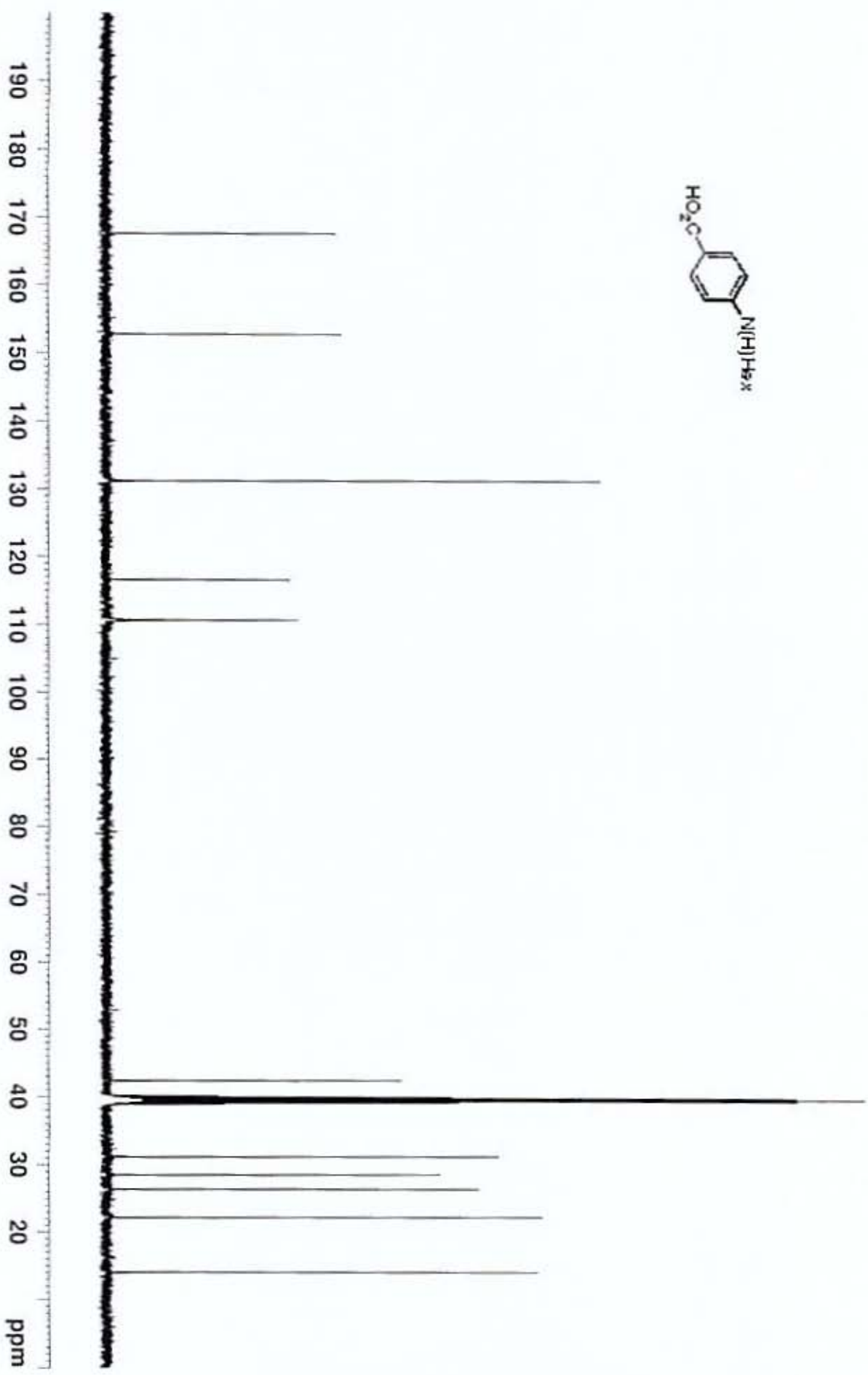
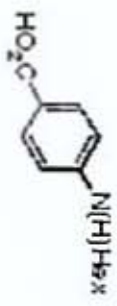


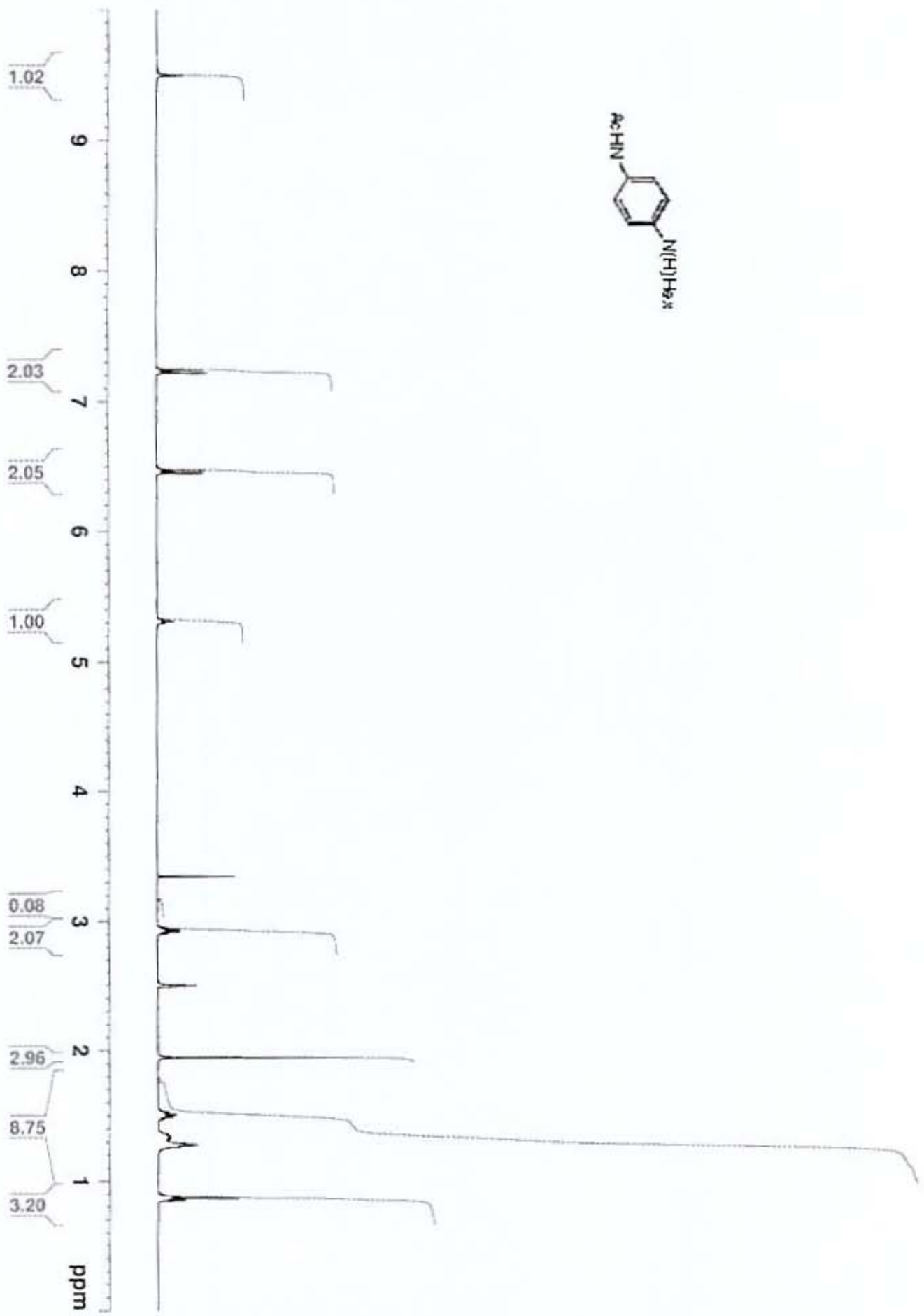
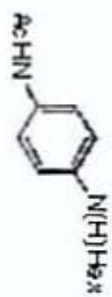
- 170.14
- 151.54
- 128.67
- 127.11
- 114.57
- 77.40
- 77.14
- 76.88
- 51.75
- 28.18
- 20.62

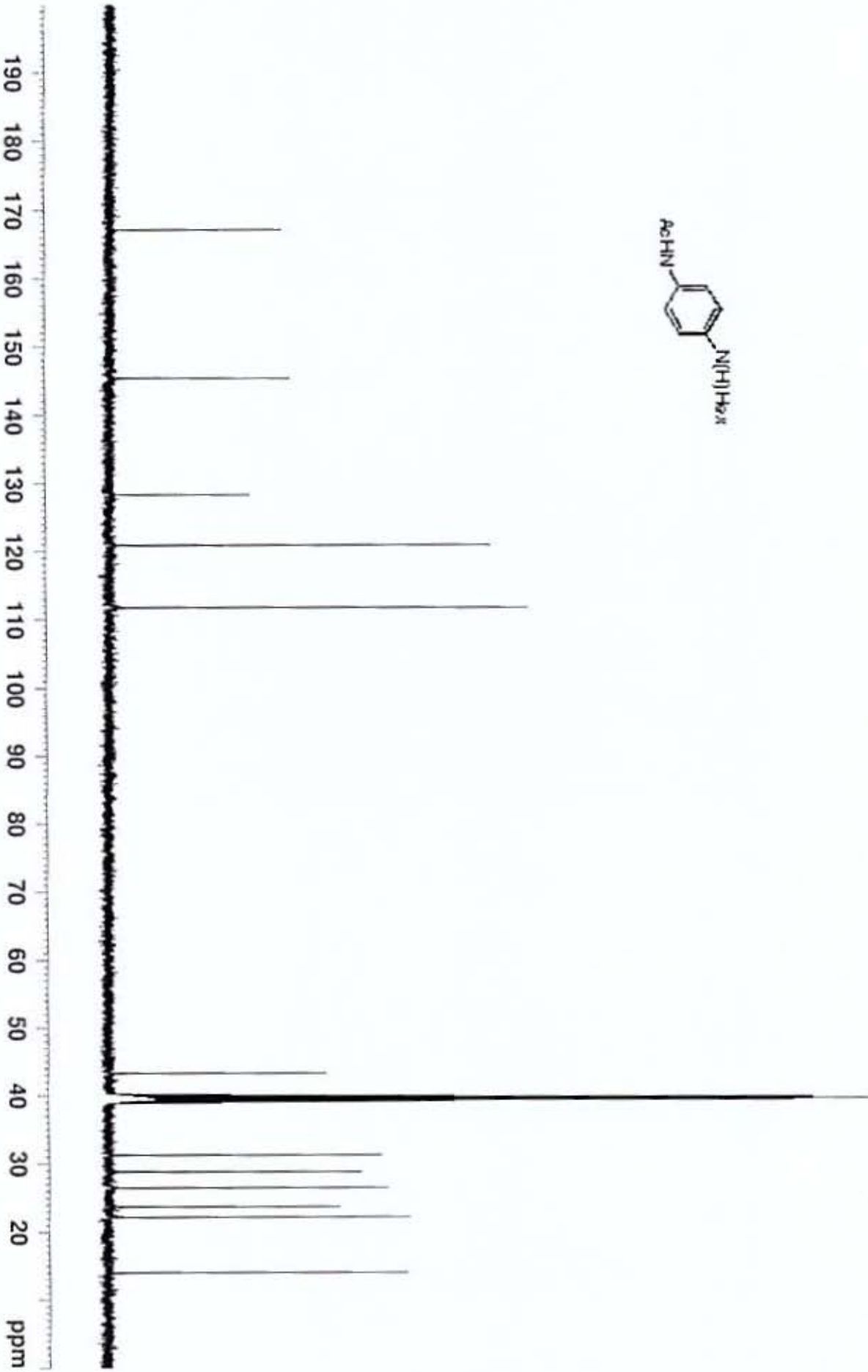
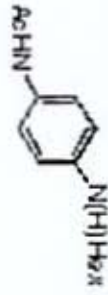


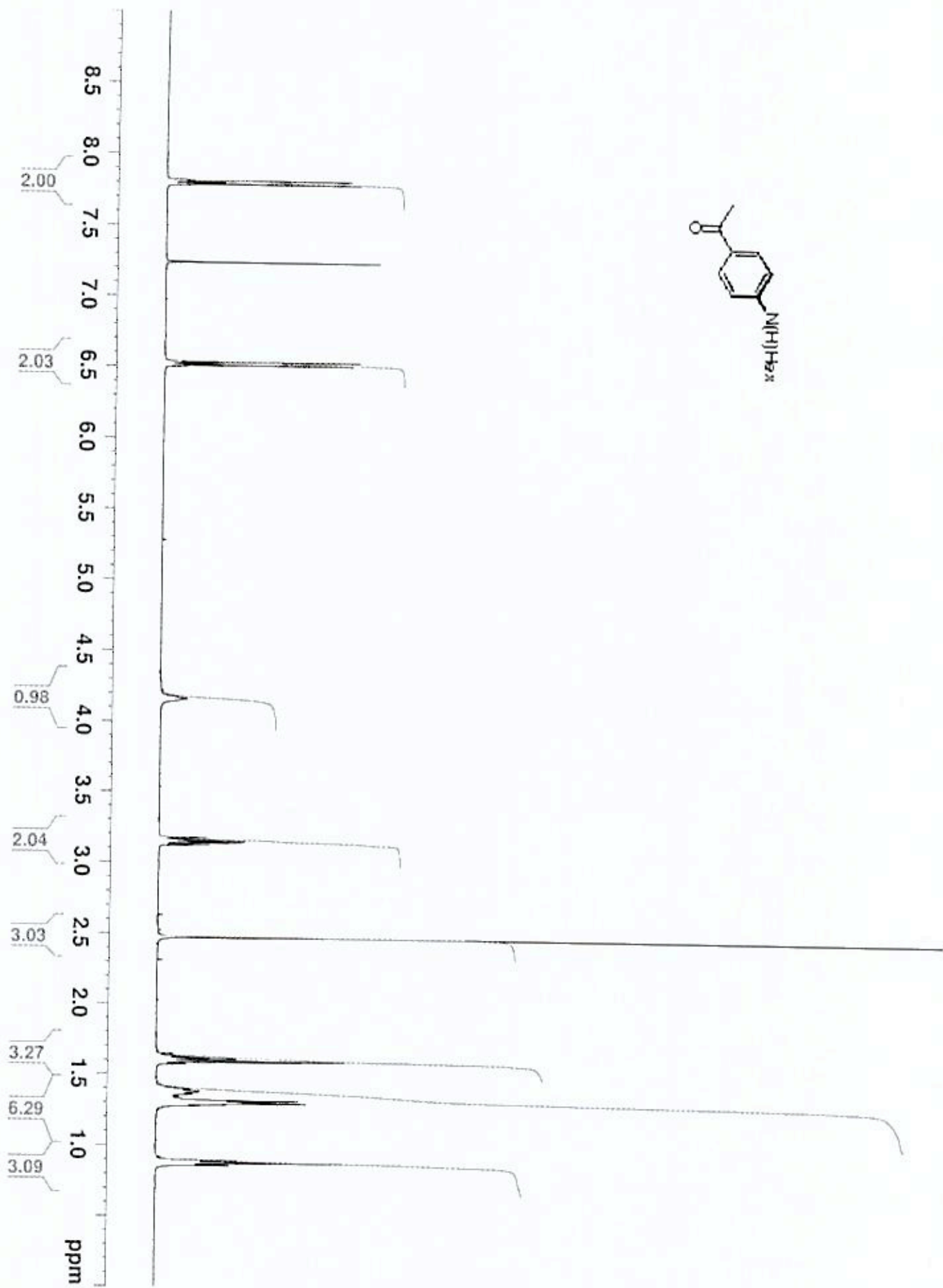
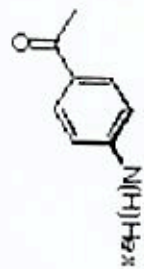


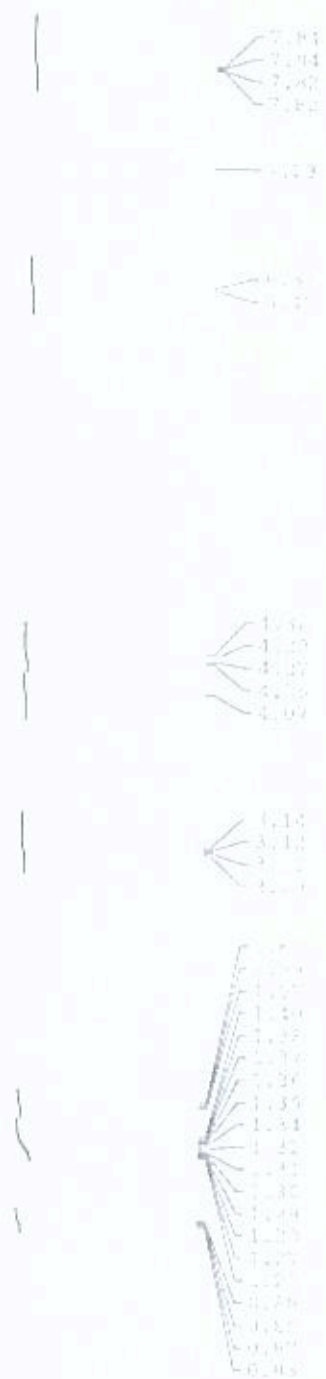
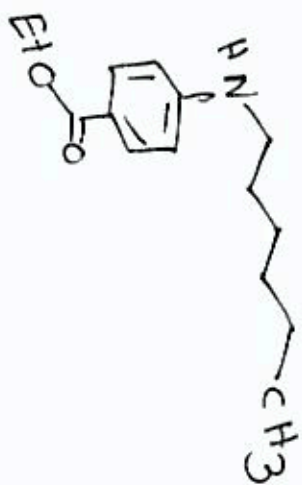
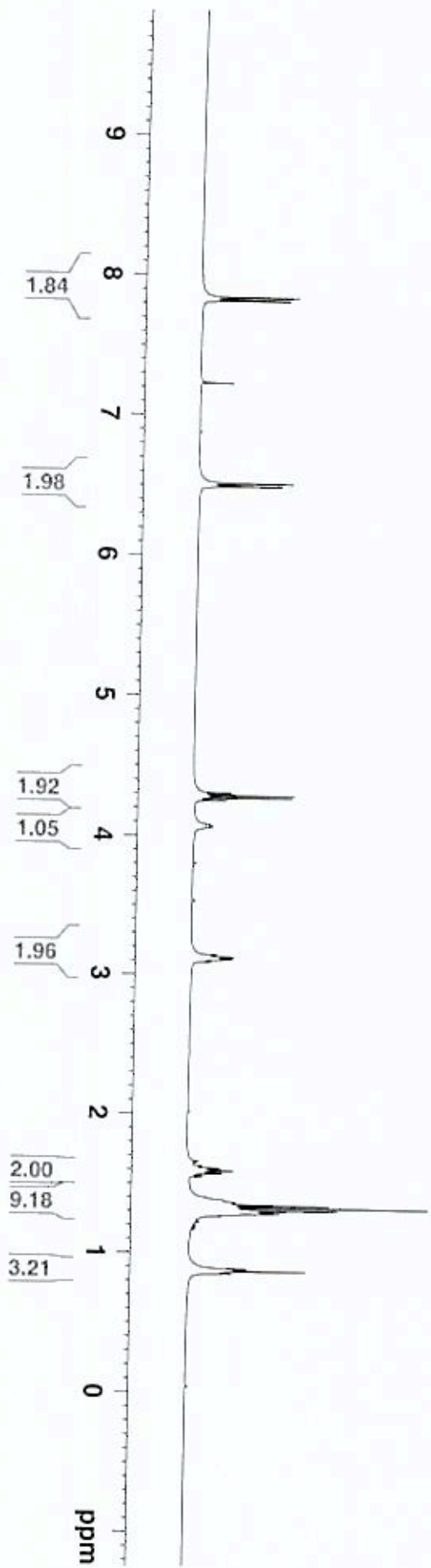


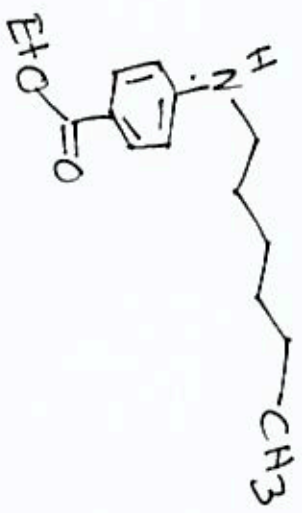
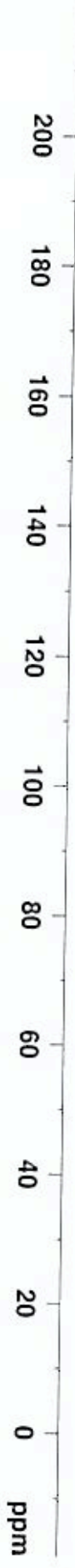


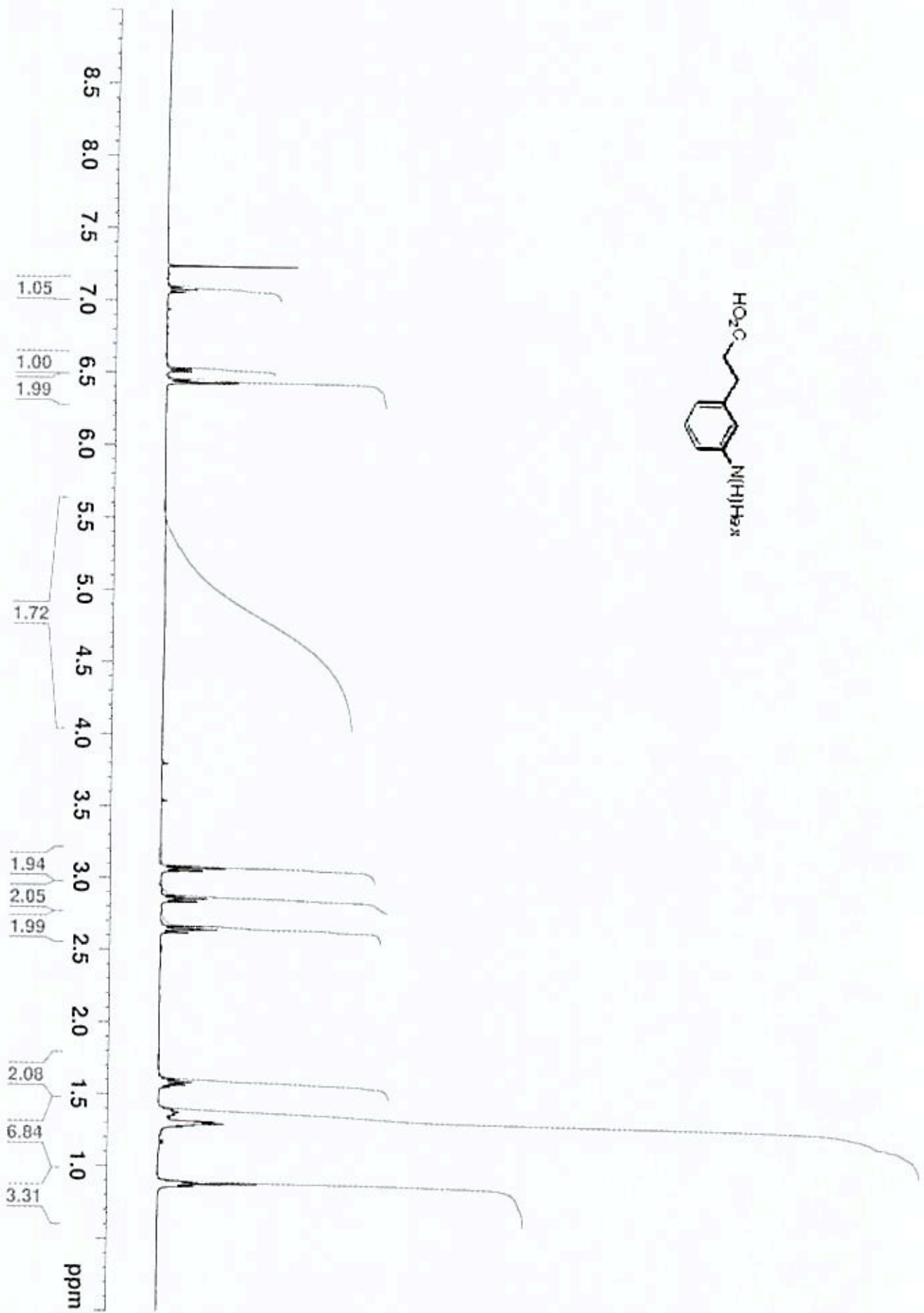
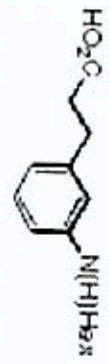


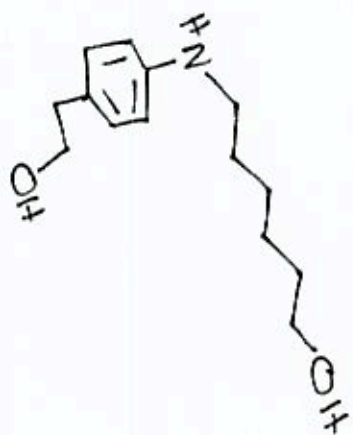
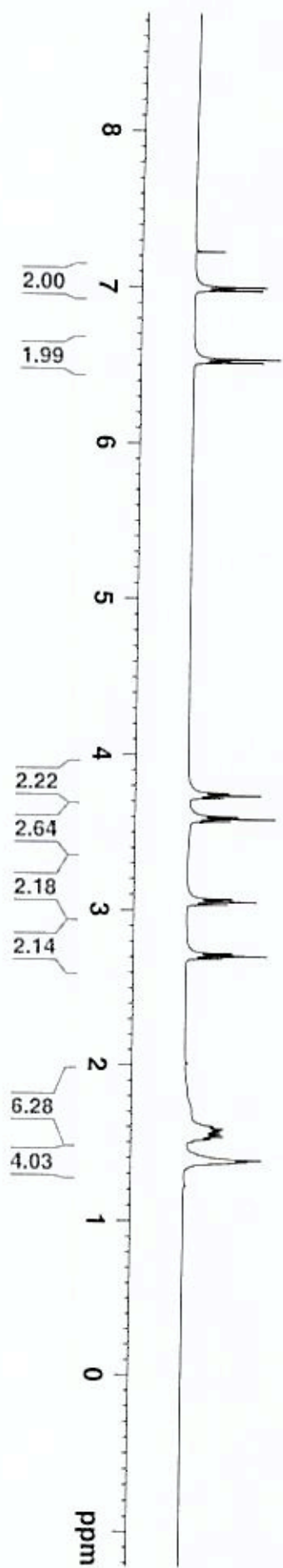


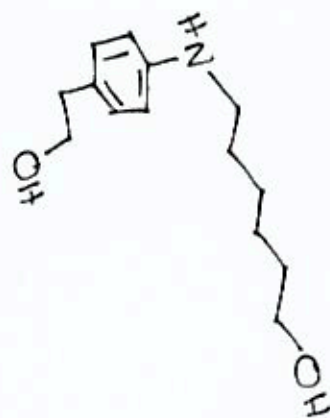
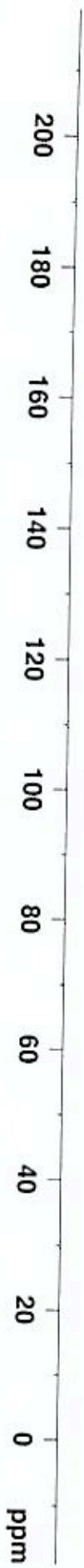




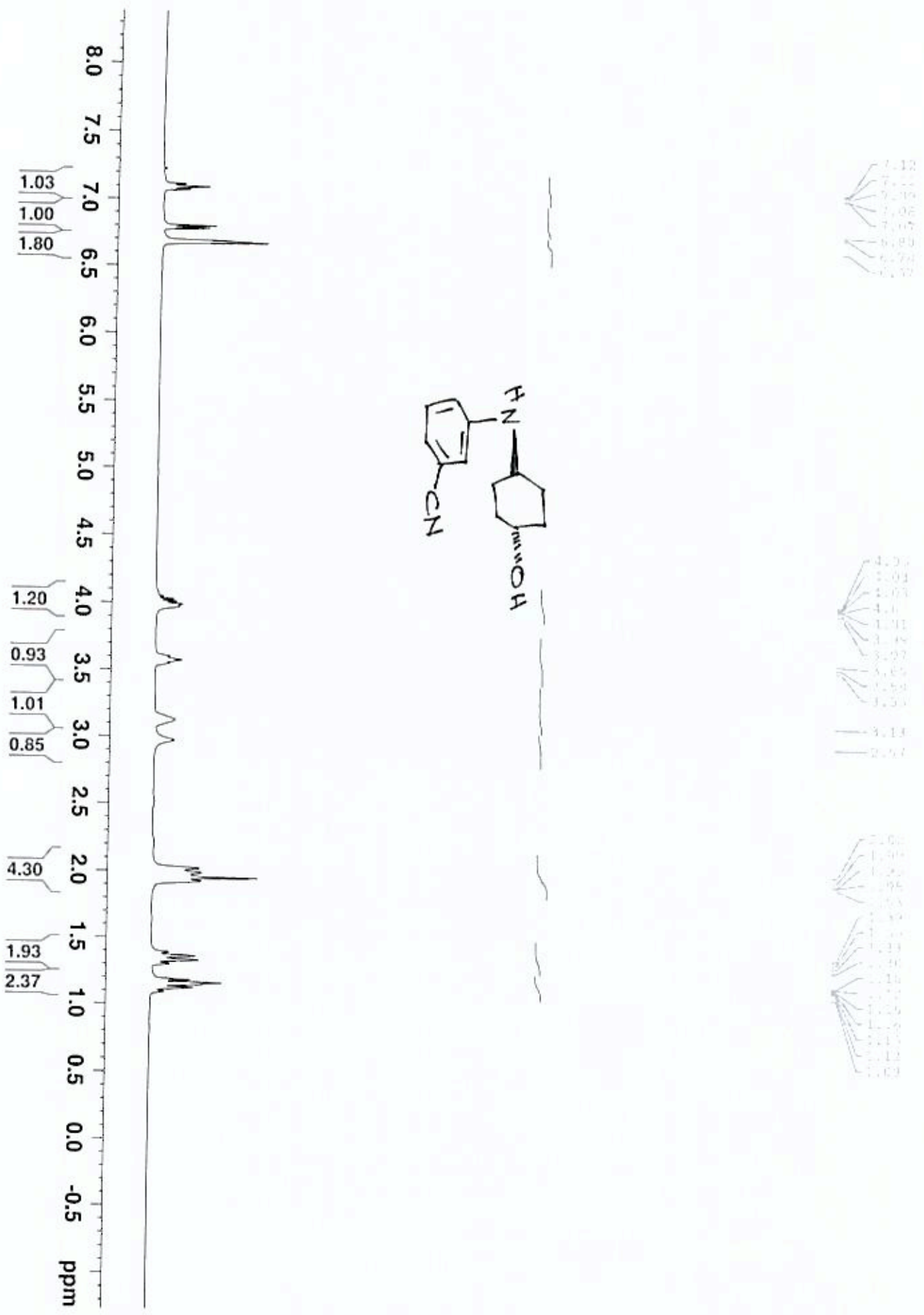


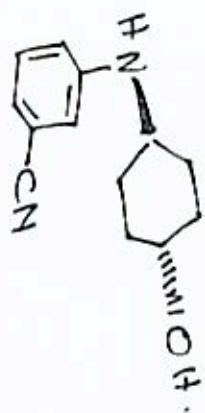






- 147.21
- 138.64
- 125.53
- 112.21
- 77.27
- 76.77
- 76.27
- 66.14
- 62.98
- 43.33
- 38.66
- 38.25
- 37.75
- 37.25
- 36.75
- 36.25

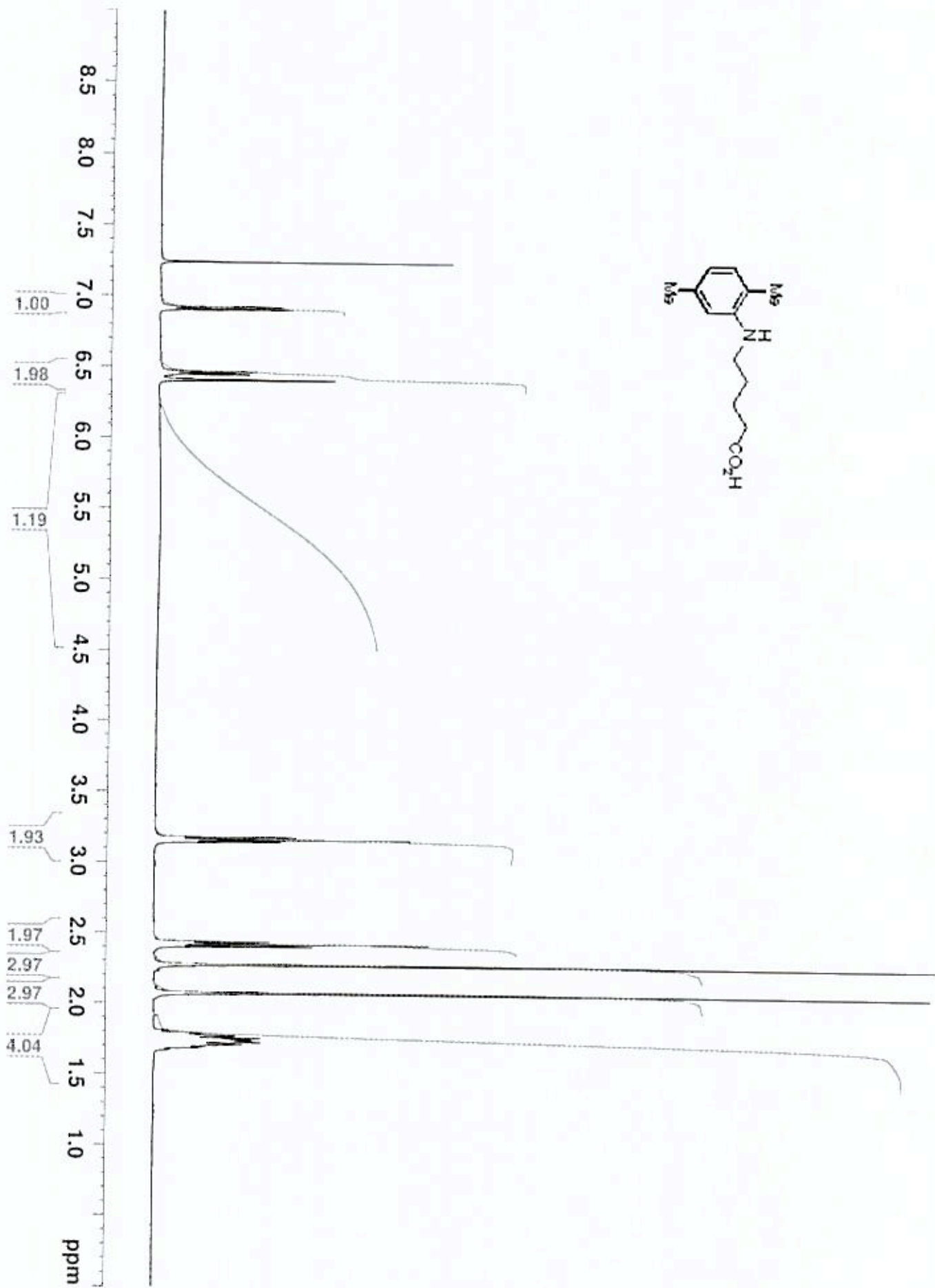
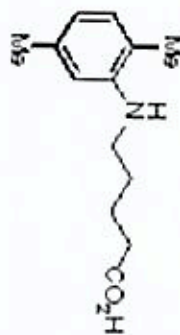


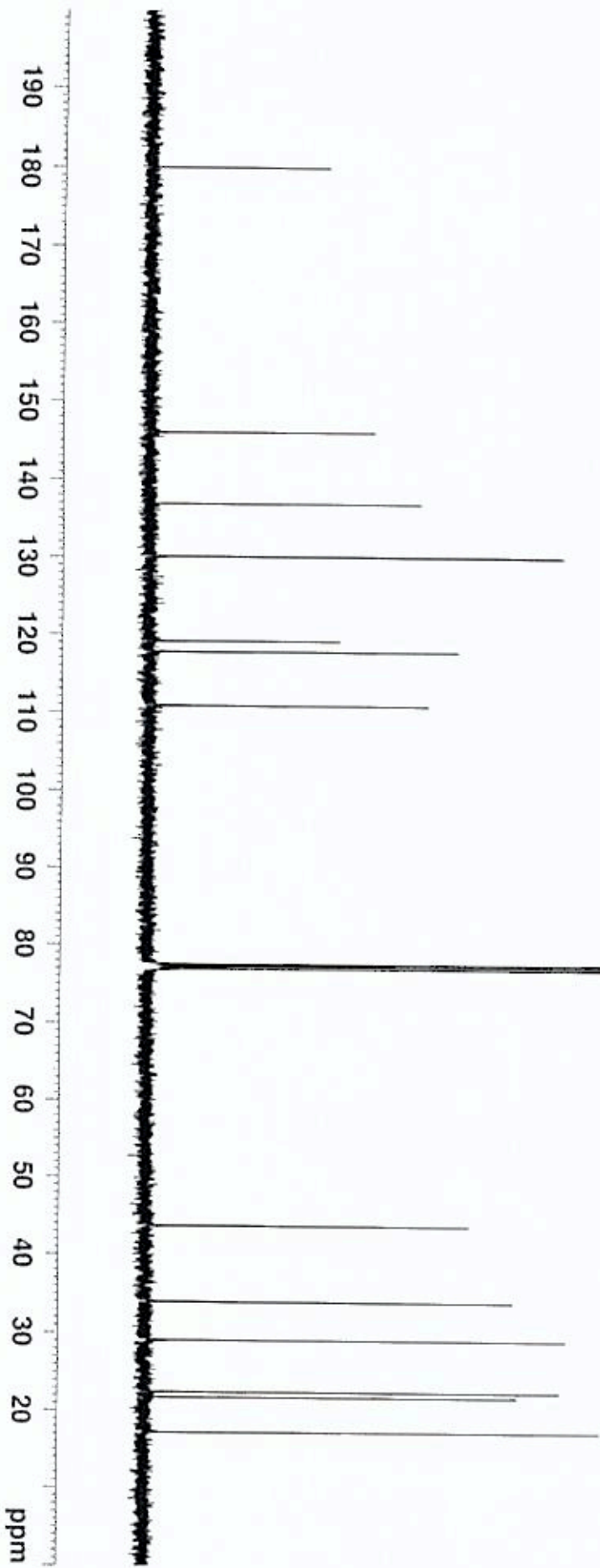
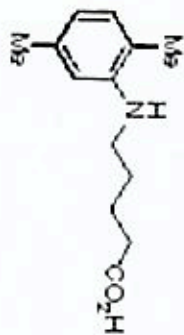


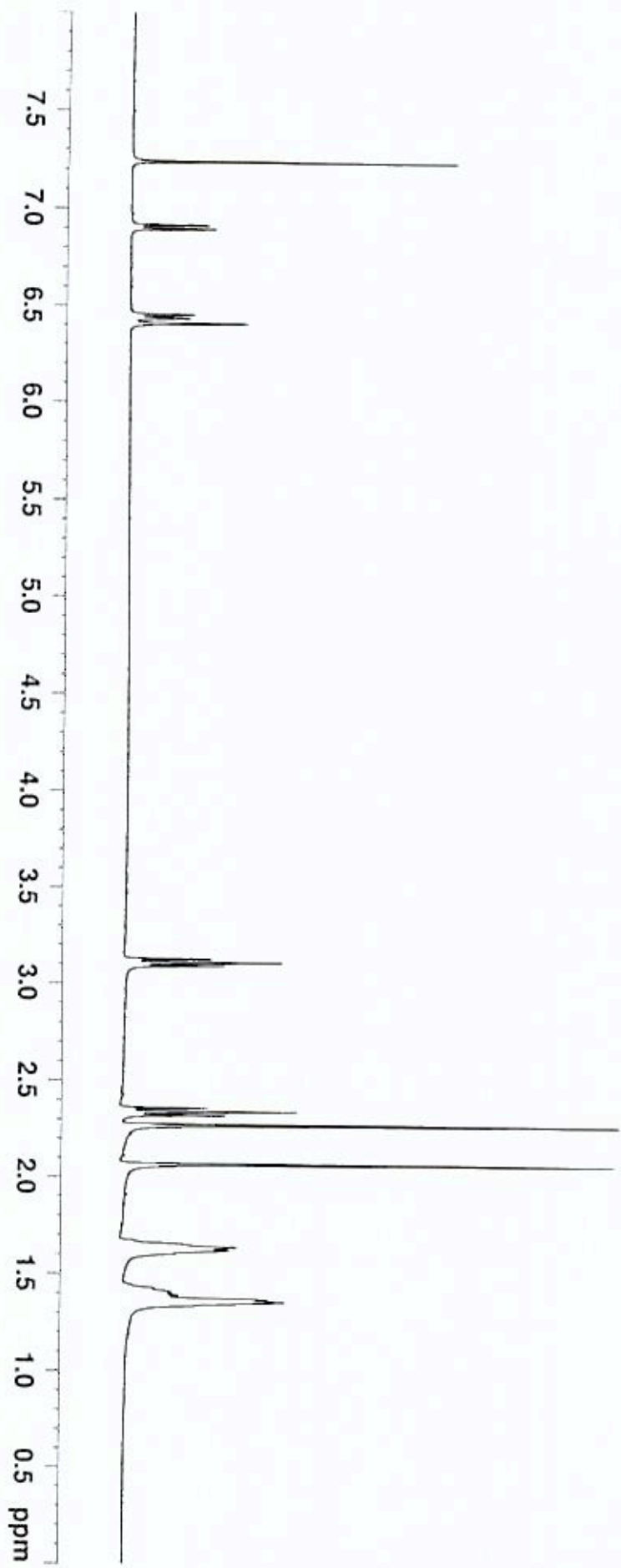
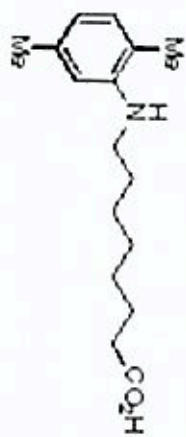
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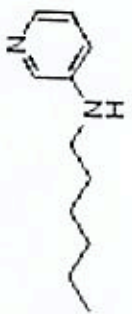


- 172.00
- 147.30
- 130.10
- 129.17
- 119.99
- 117.45
- 115.34
- 113.52
- 77.40
- 77.31
- 77.17
- 69.24
- 51.30
- 51.03
- 37.47
- 33.97
- 32.80
- 30.00
- 15.10
- 14.30





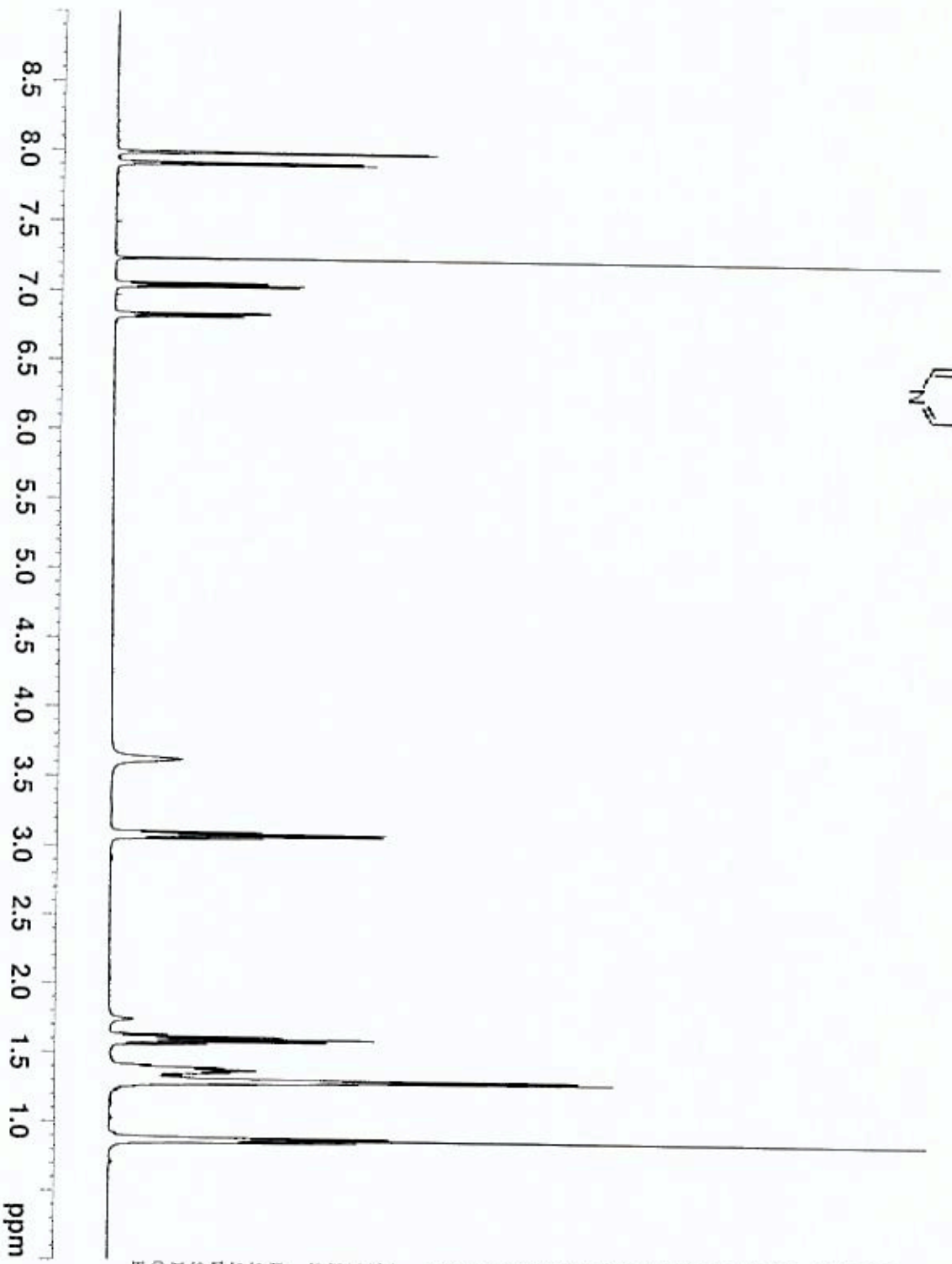


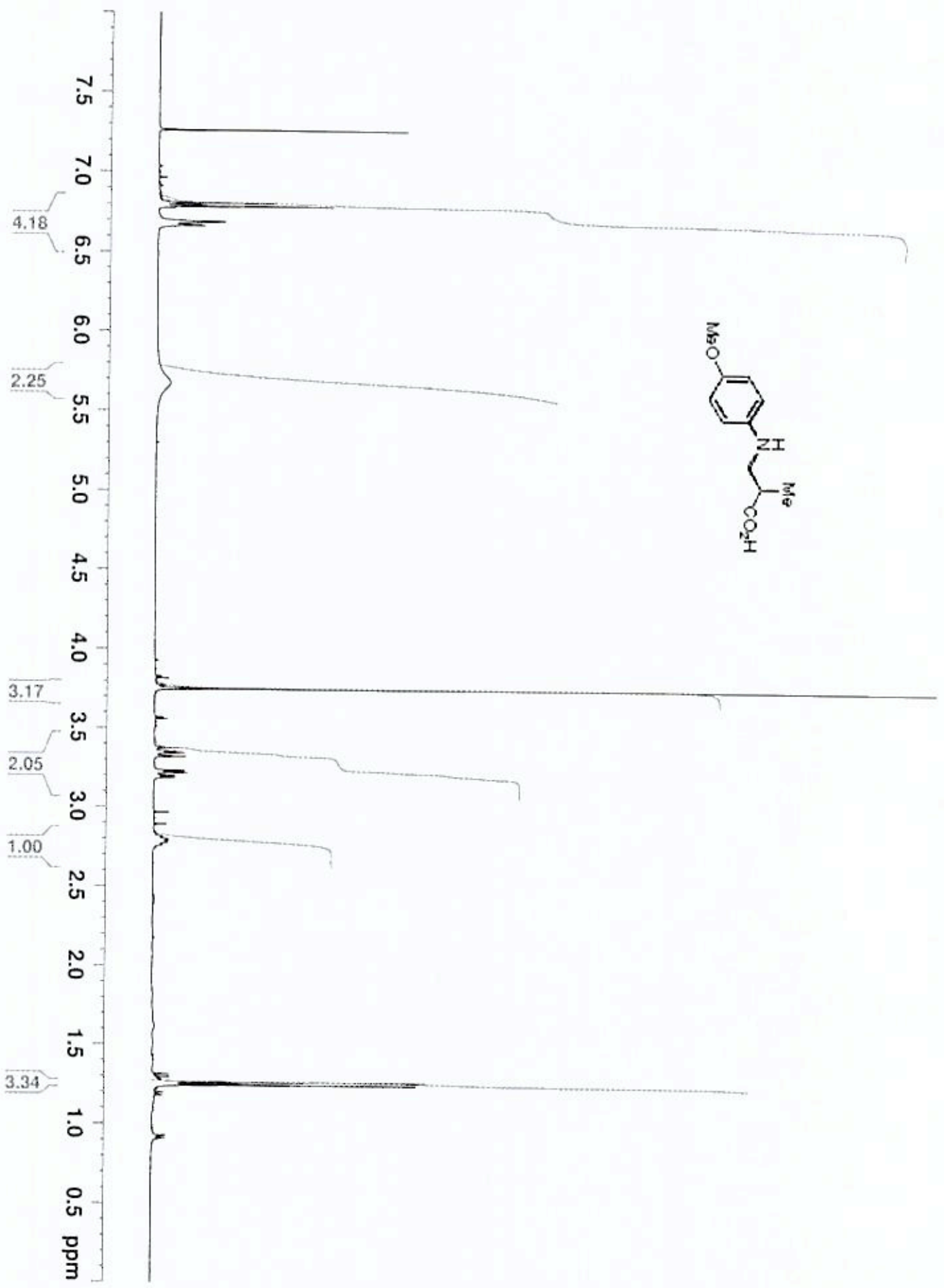
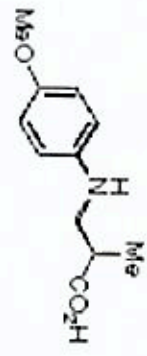


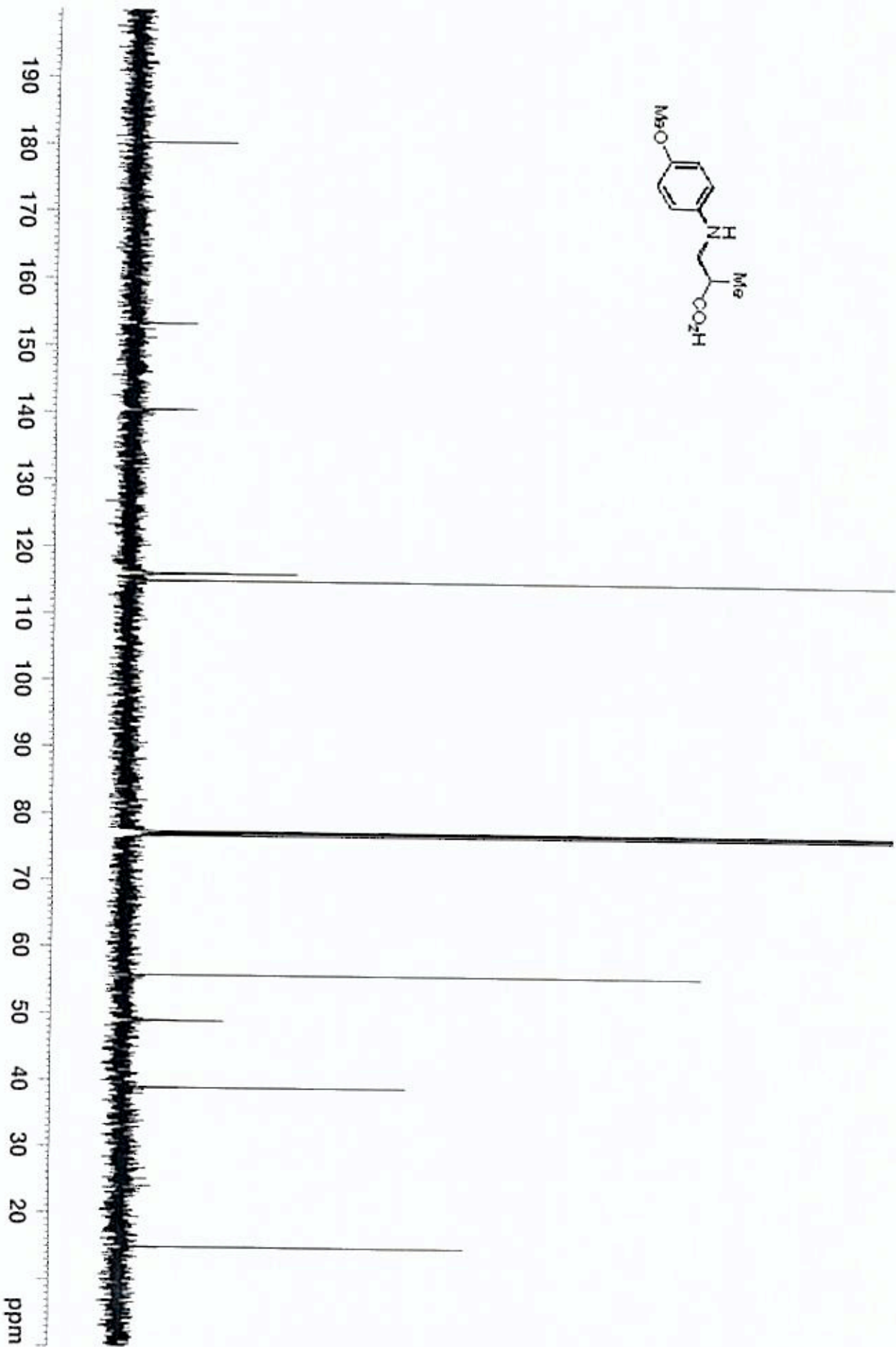
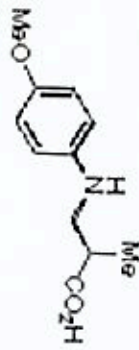
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 PROCNO 1

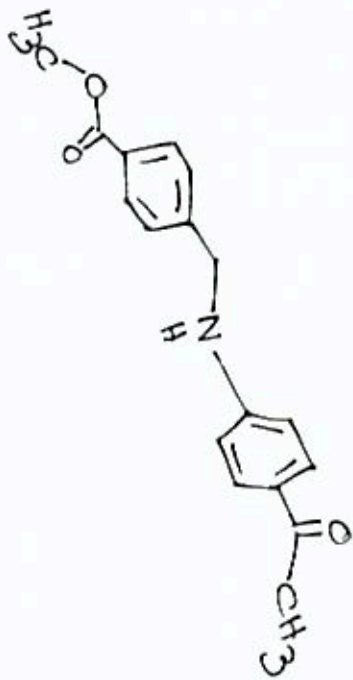
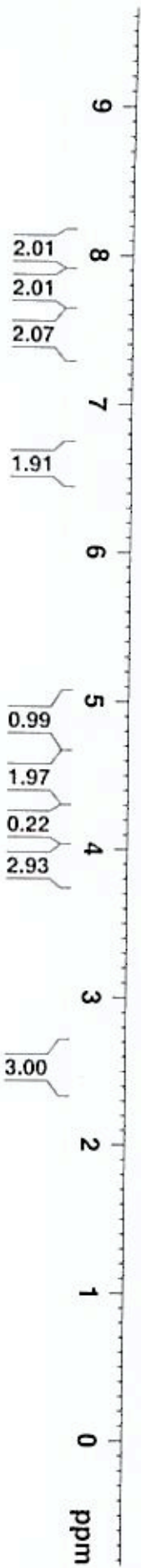
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 PULPROG zg30
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 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
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 DW 60.400 usec
 DE 6.00 usec
 TE 291.2 K
 D1 1.00000000 sec
 TD0 1

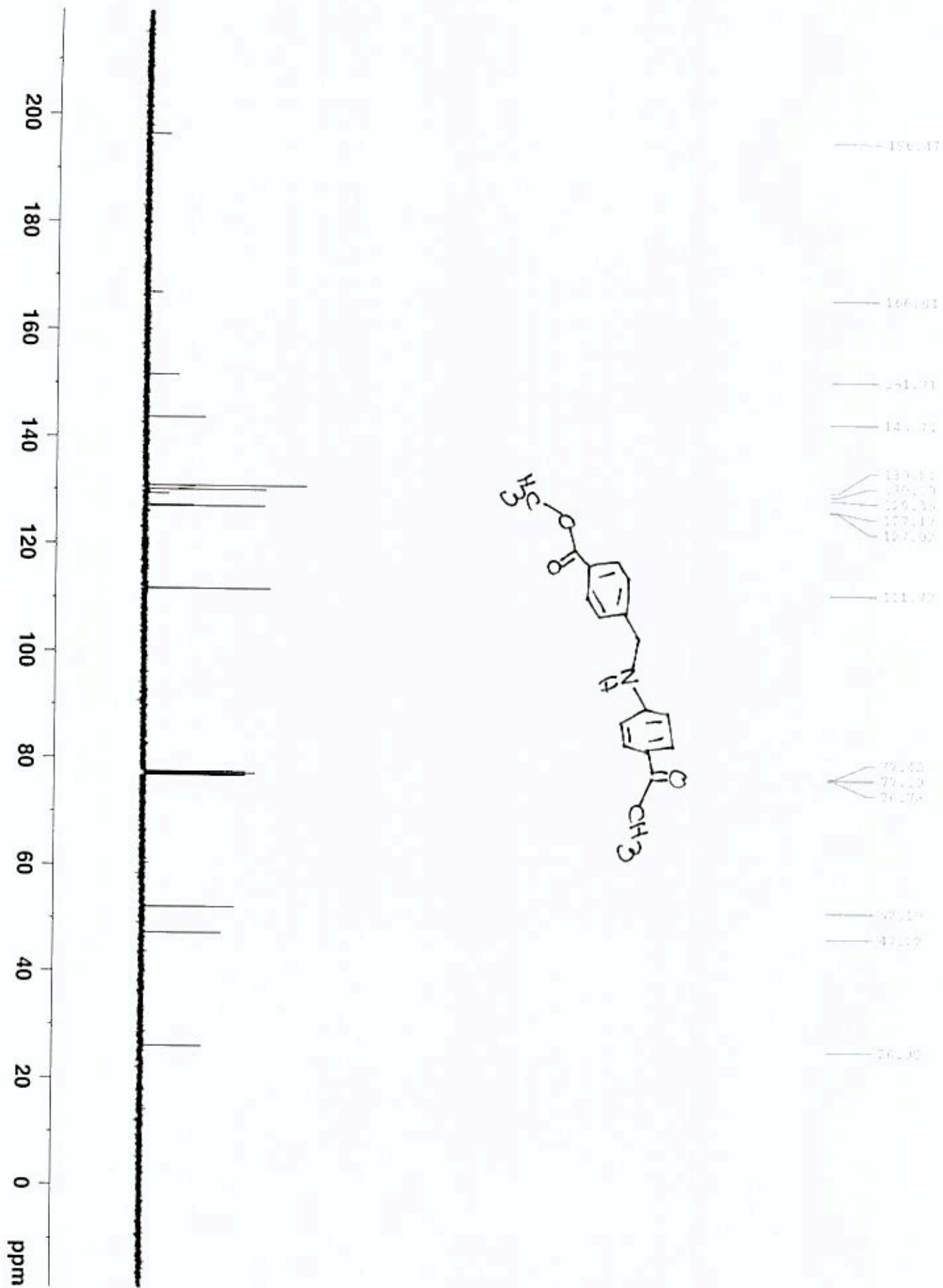
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 P1 14.00 usec
 PL1 0.00 dB
 SFO1 400.1324710 MHz
 F2 - Processing parameters
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 SF 400.1300190 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

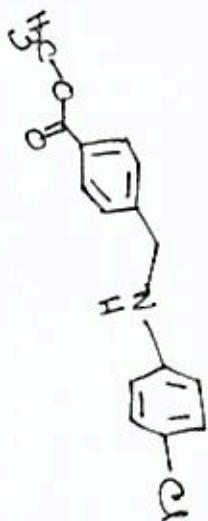
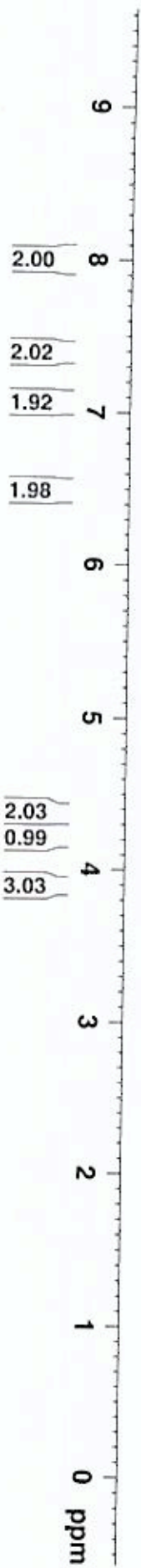


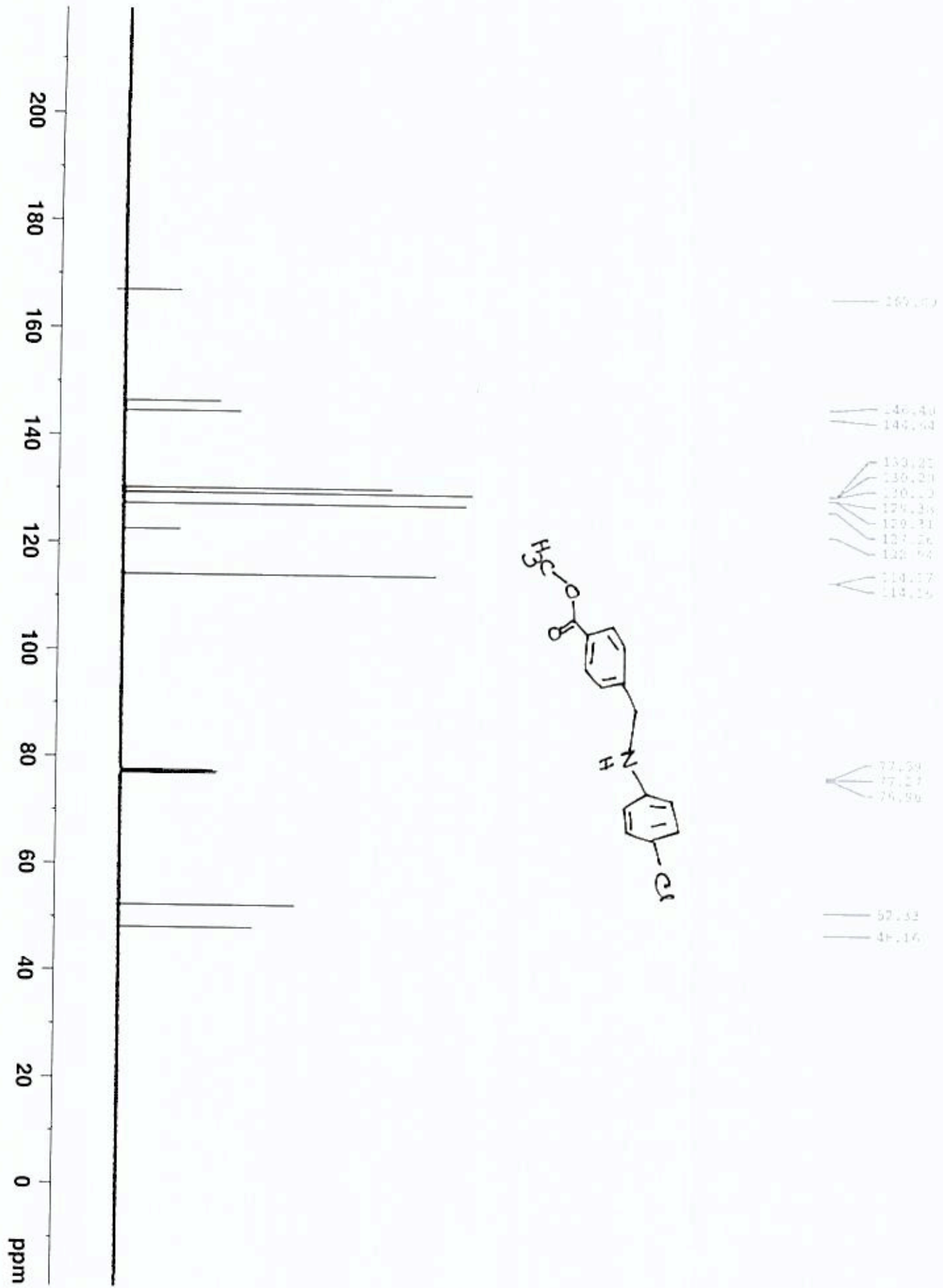
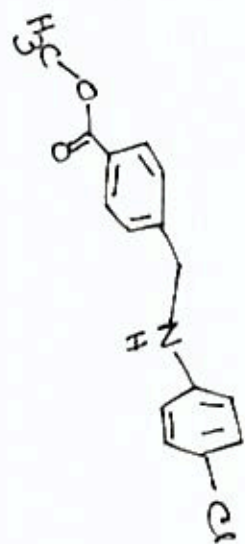


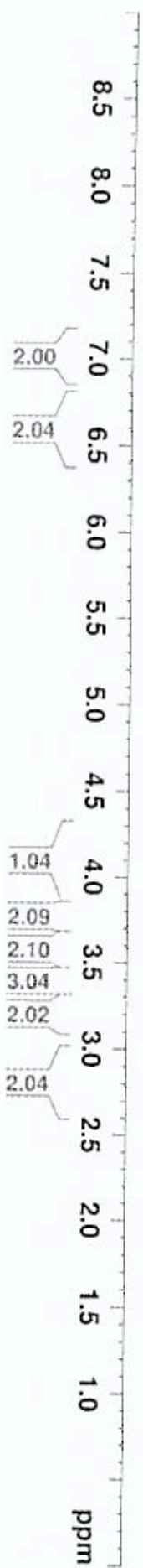
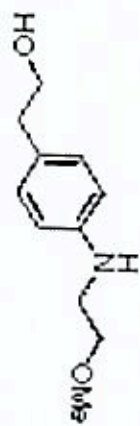


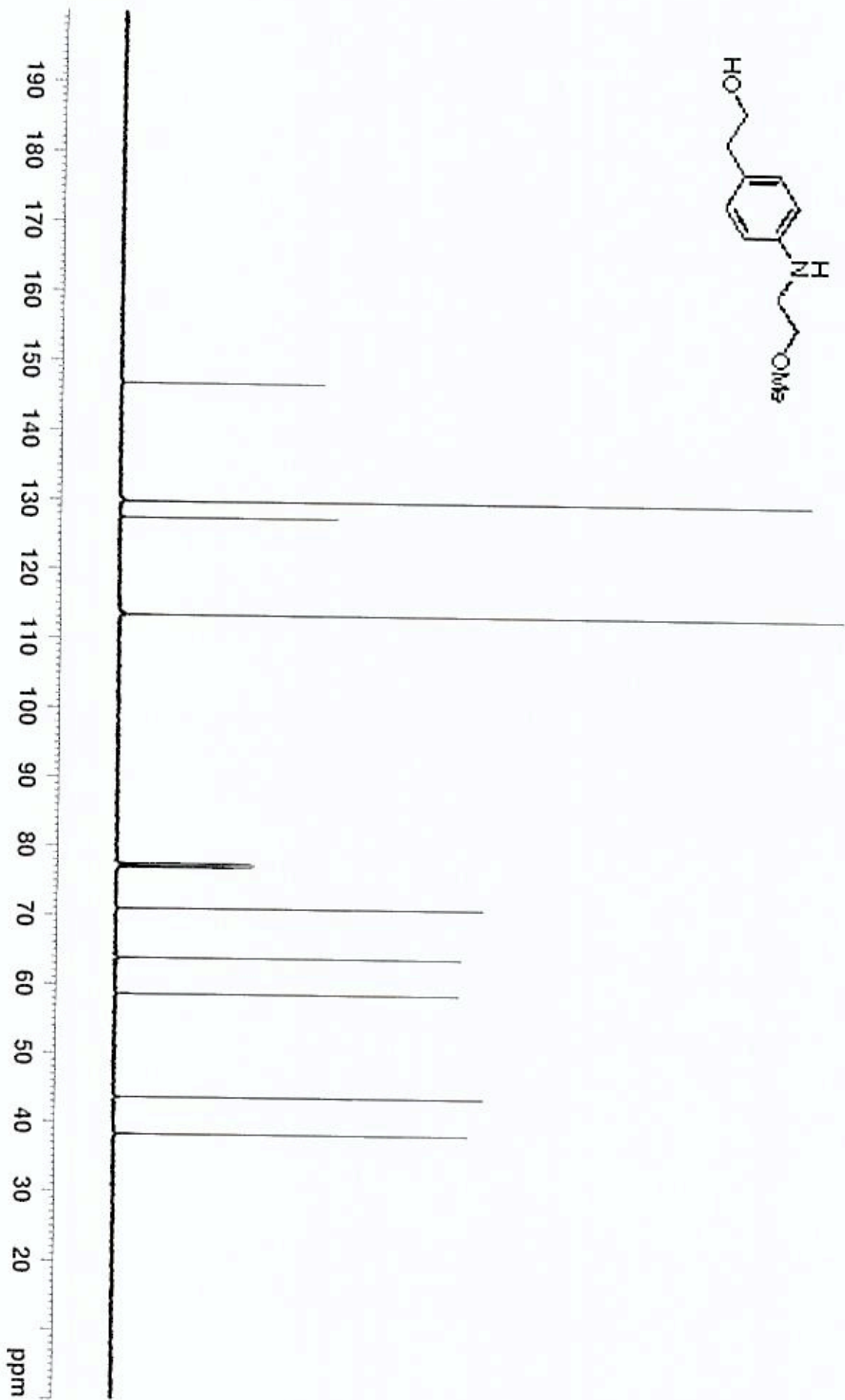
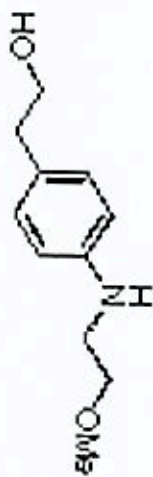


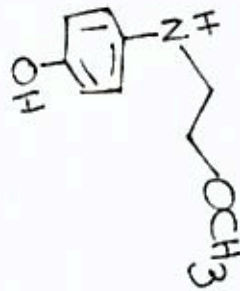
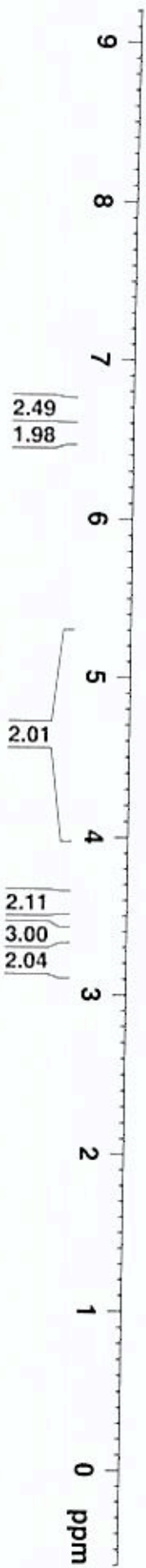








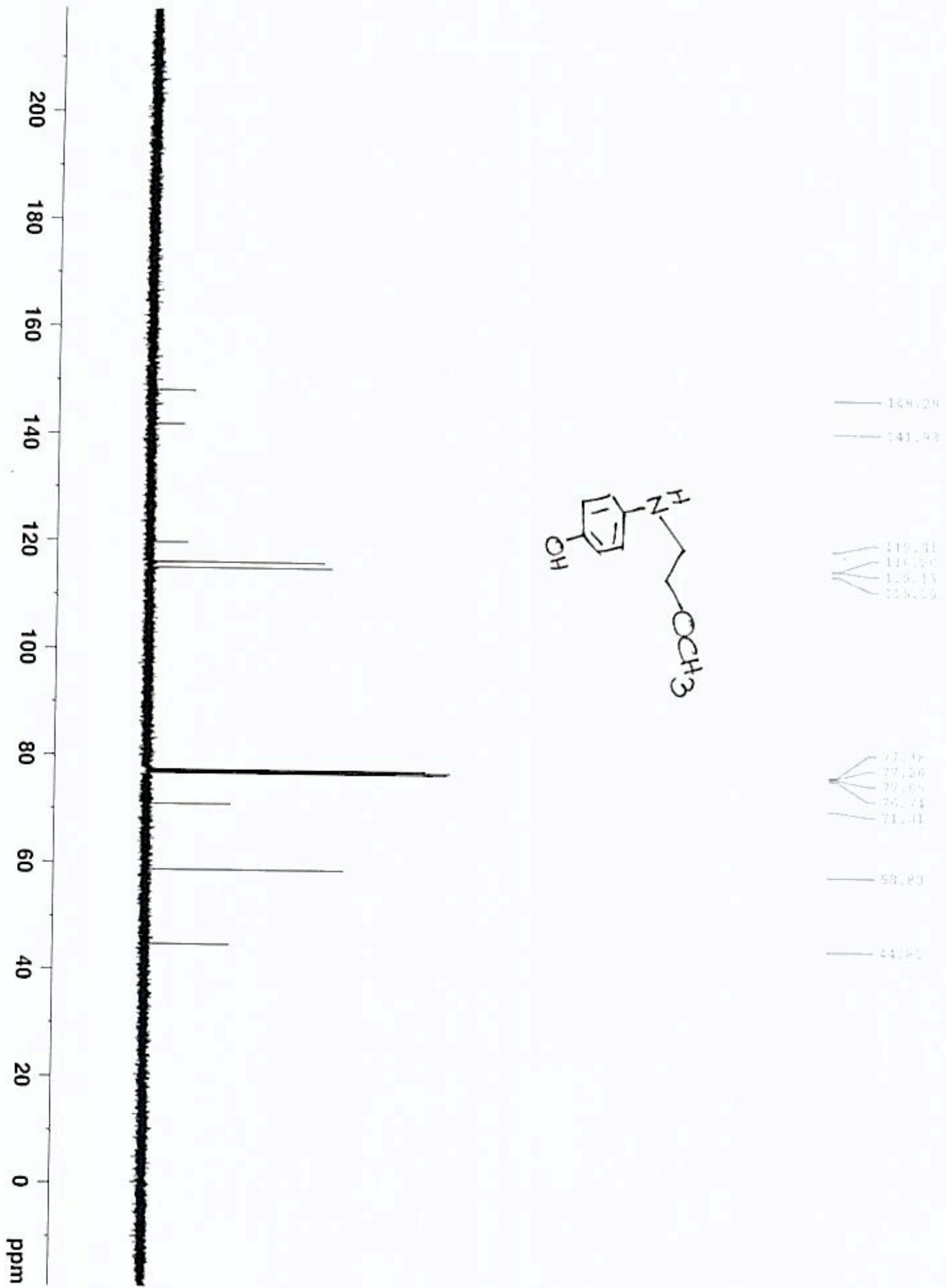


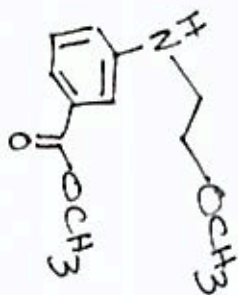
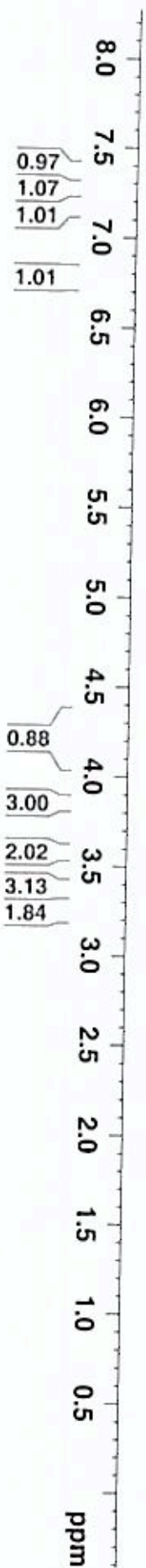


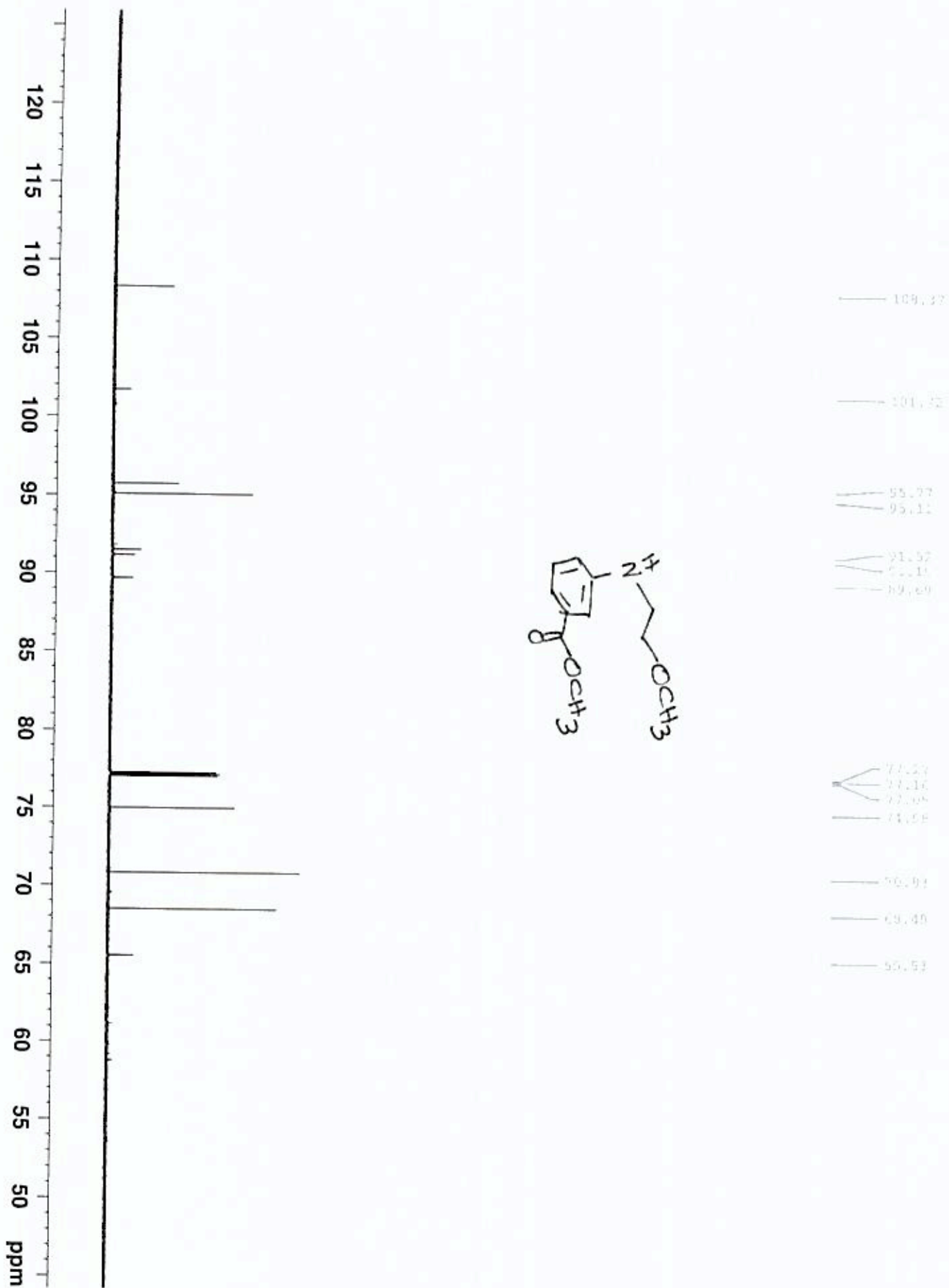
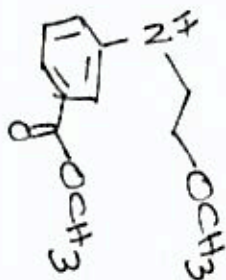
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7.23

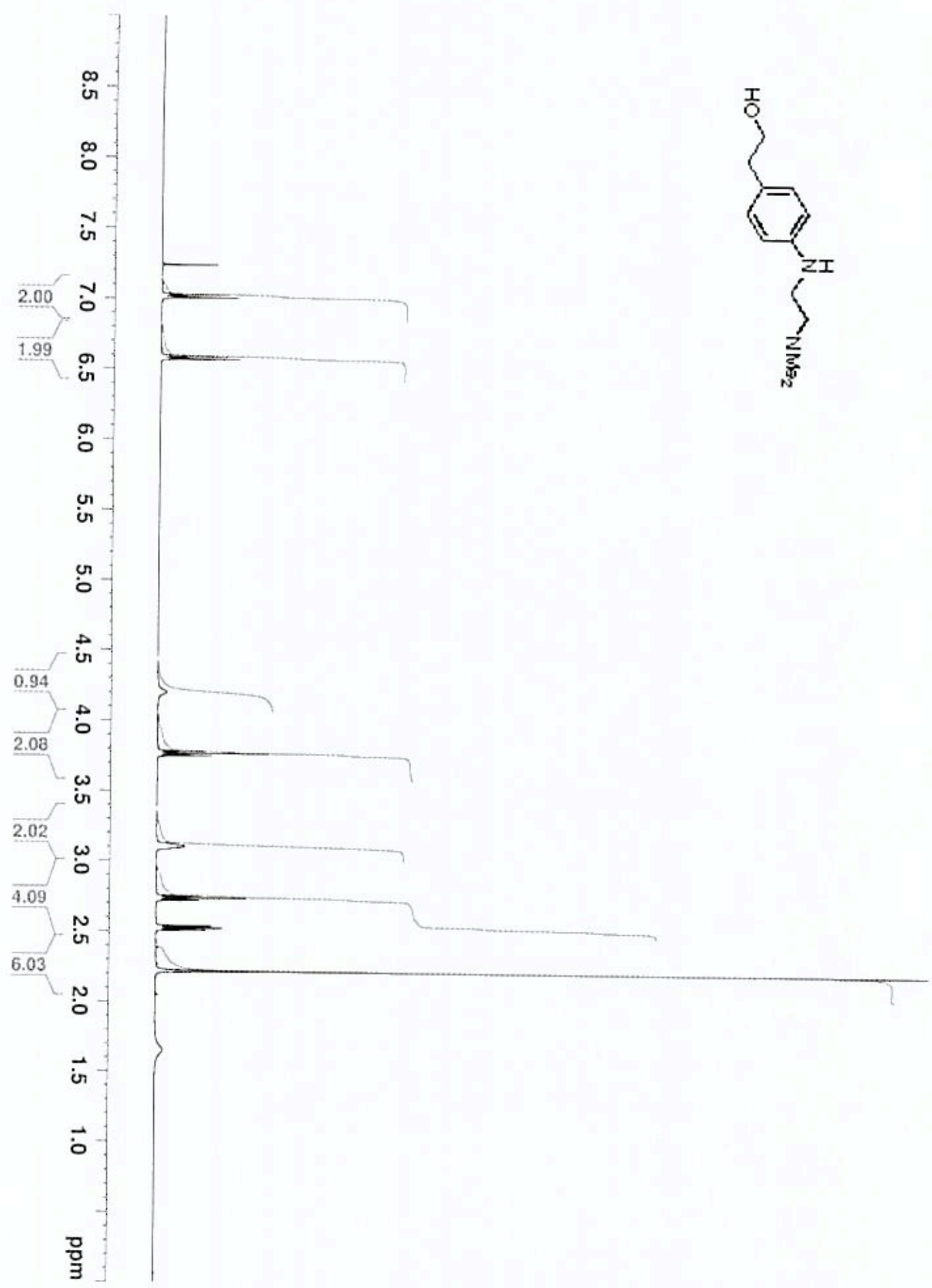
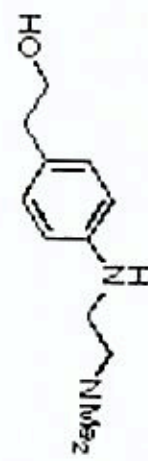
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6.84
6.82

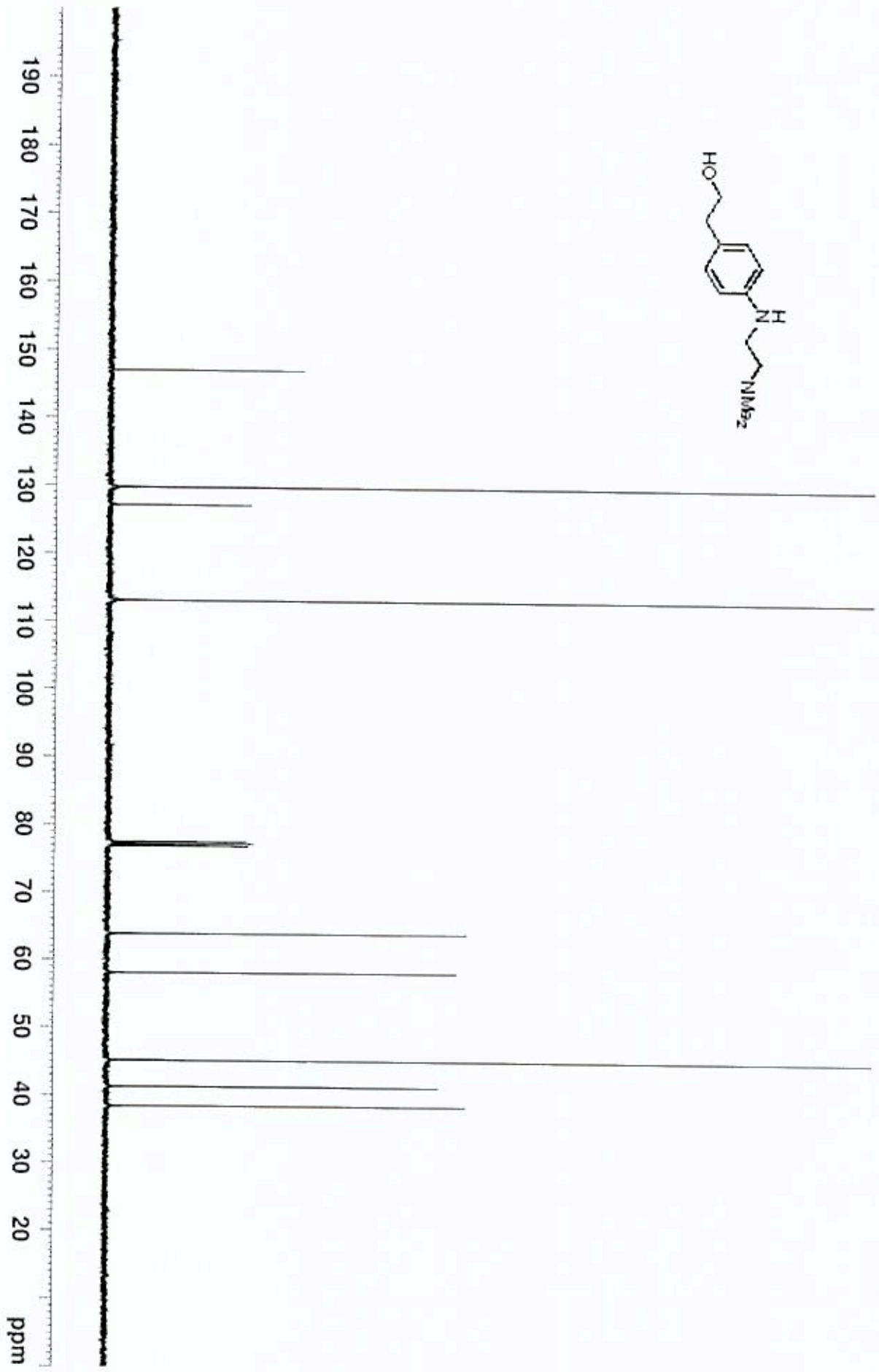
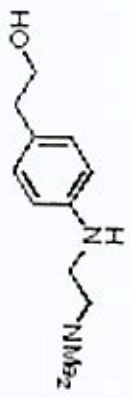
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3.77
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3.11
3.09
3.07

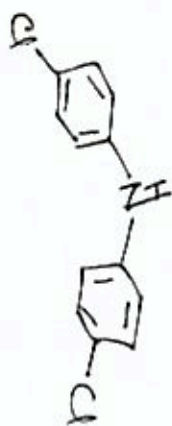


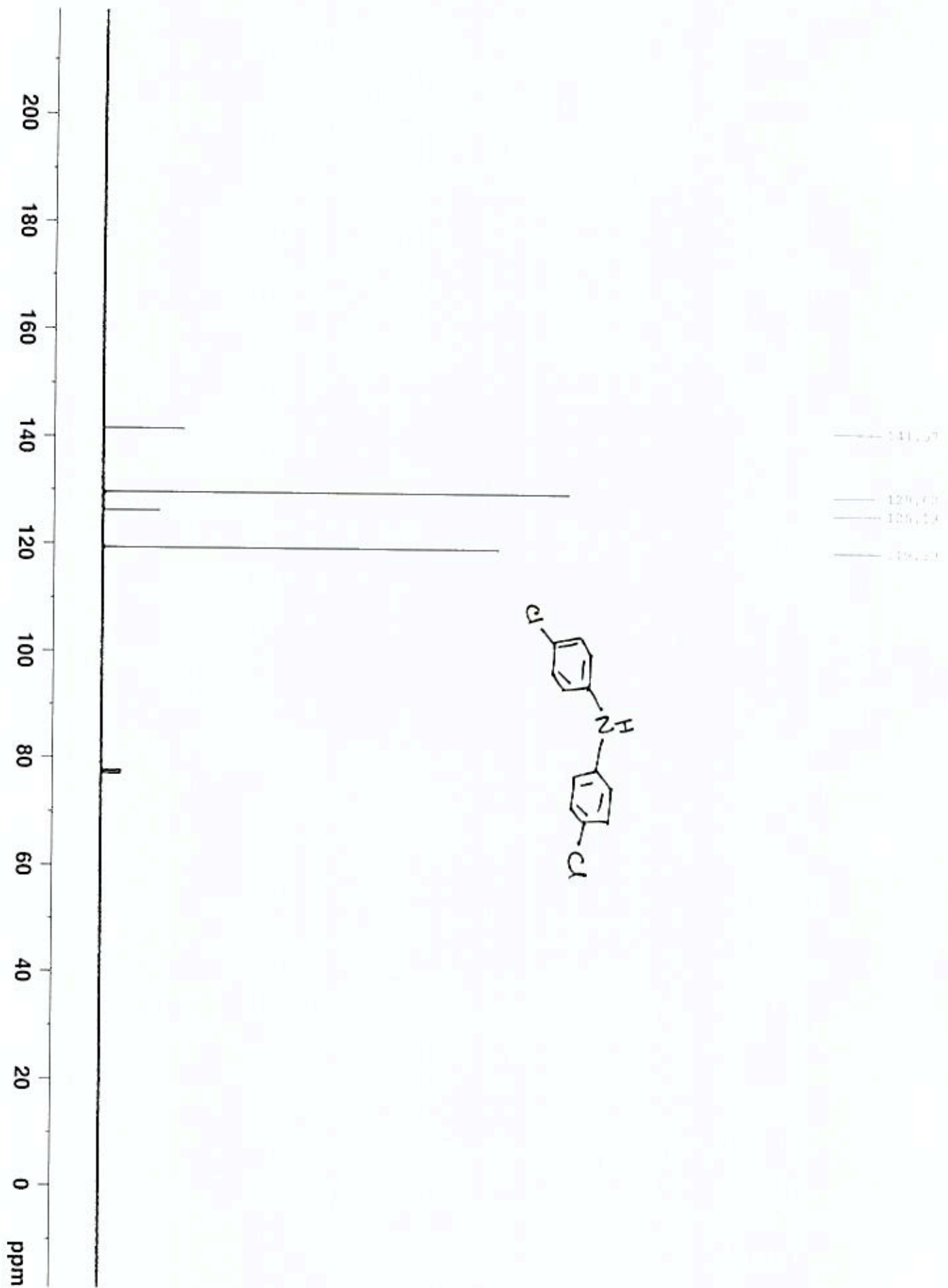


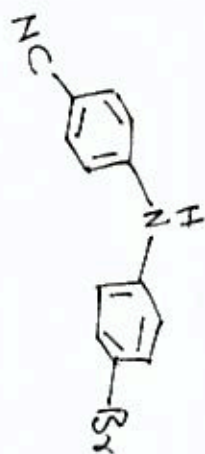


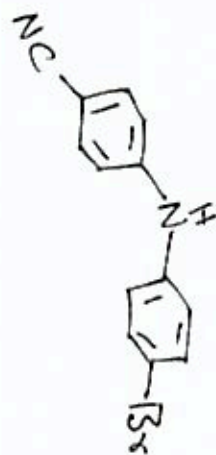




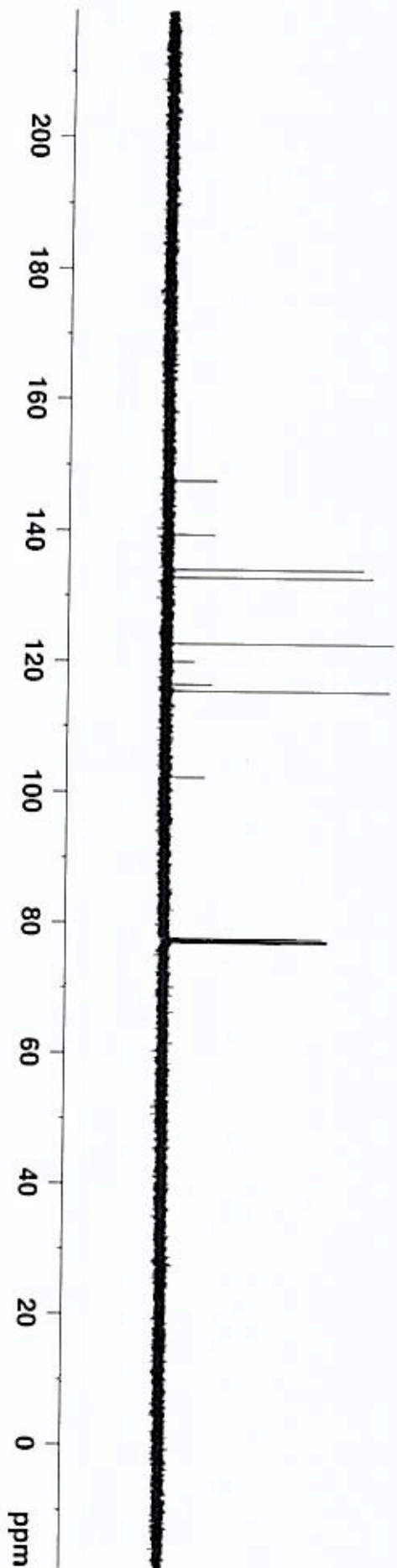


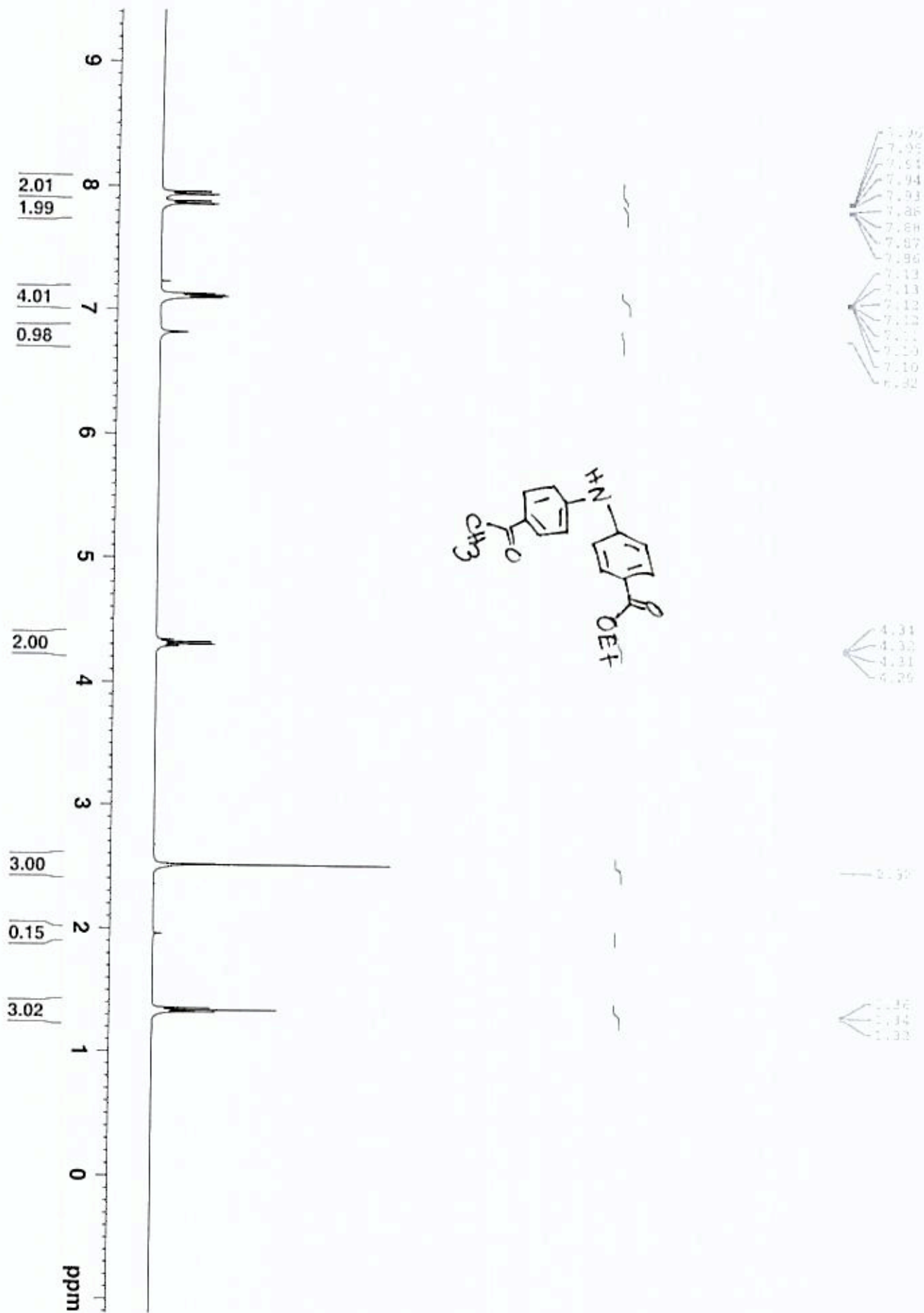


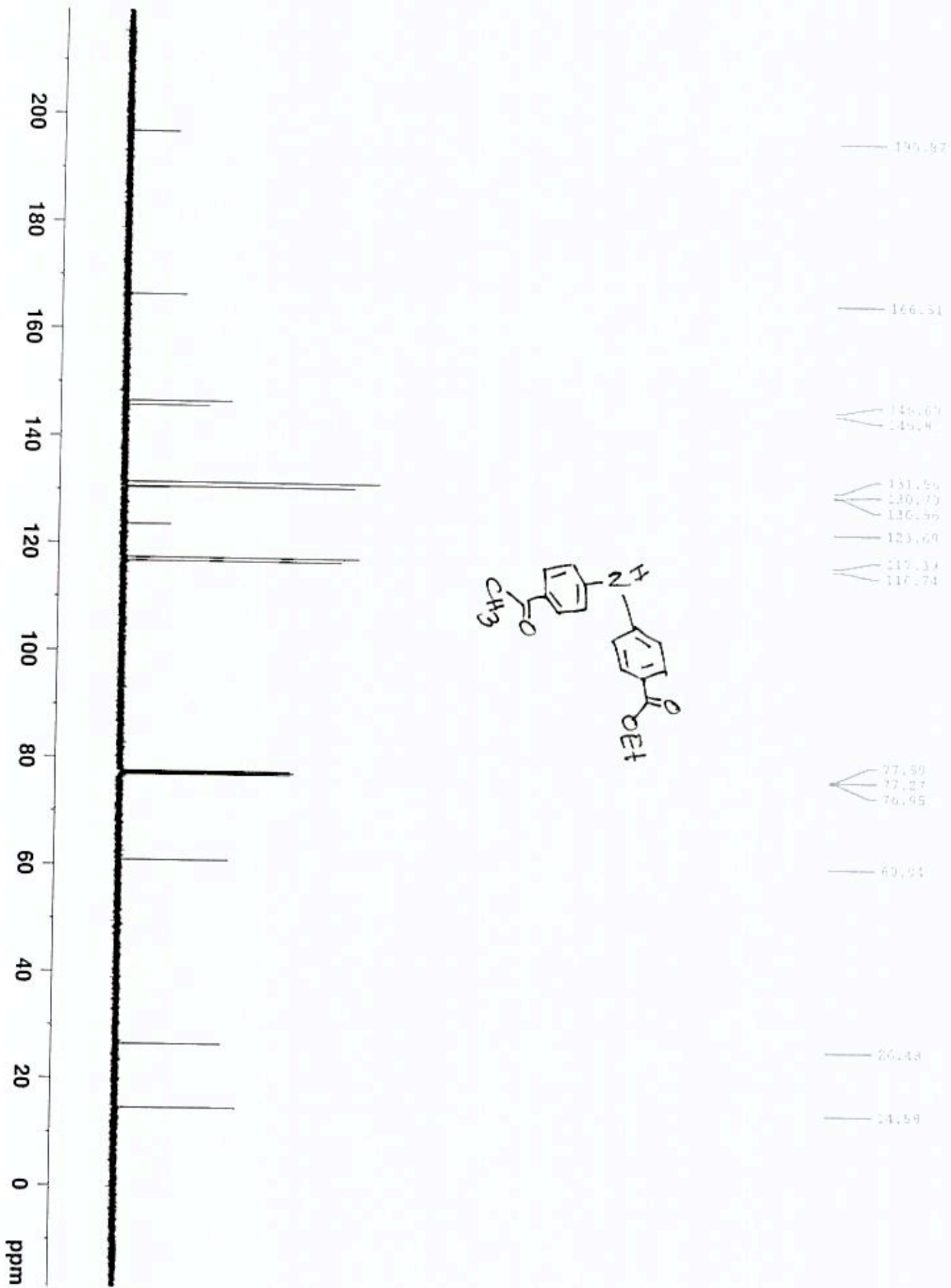


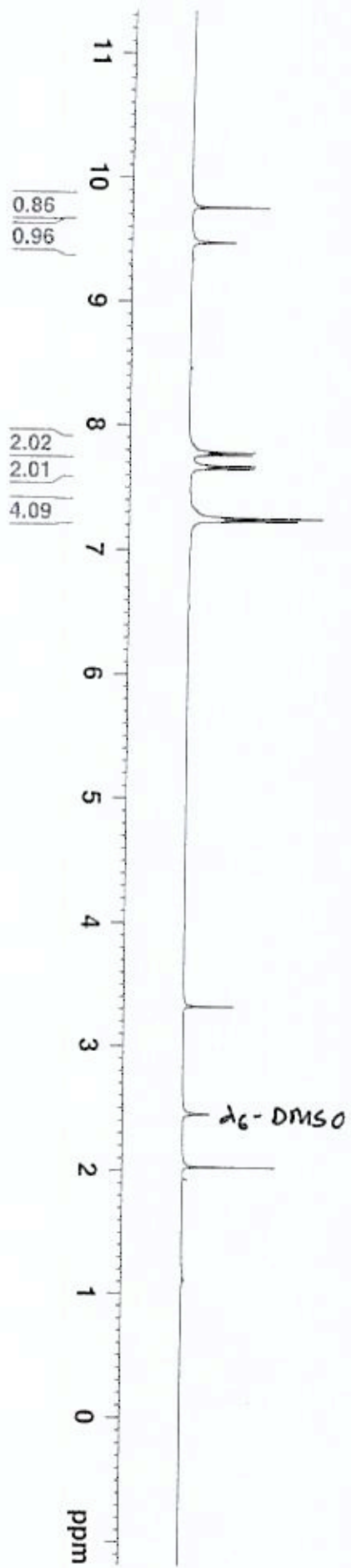
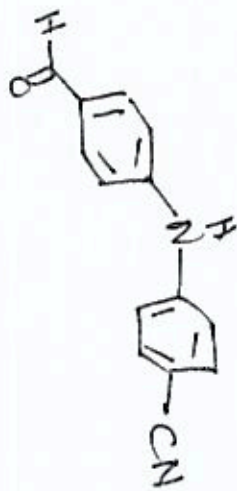


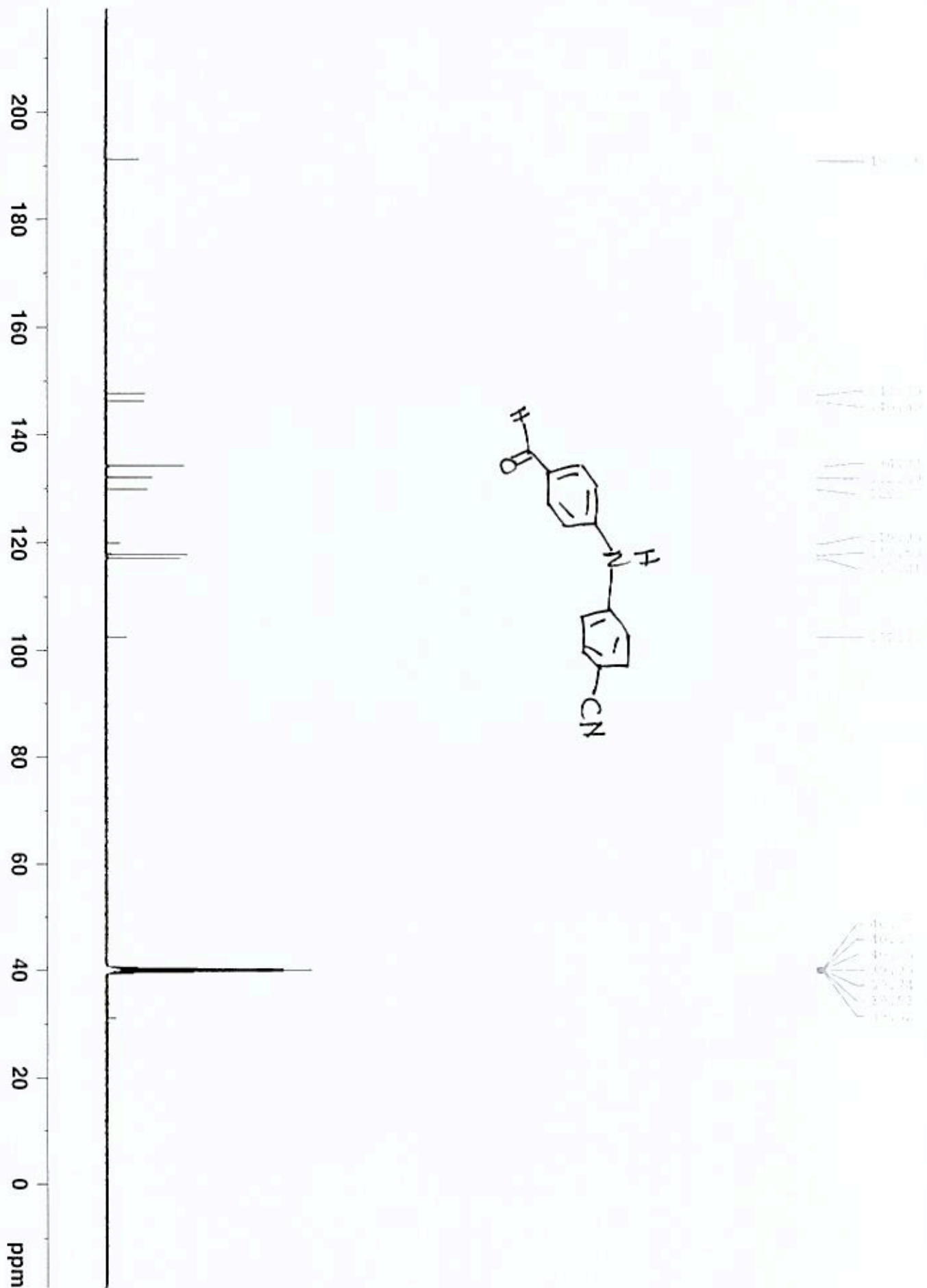
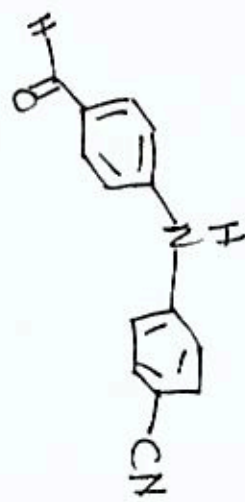
Chemical Shift (ppm)
147.30
139.40
134.04
132.05
132.81
122.75
119.93
116.41
112.42
102.10
77.30
77.24
76.92

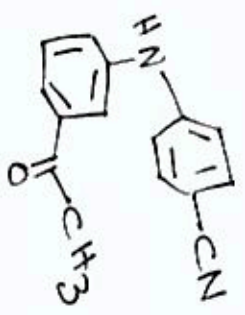
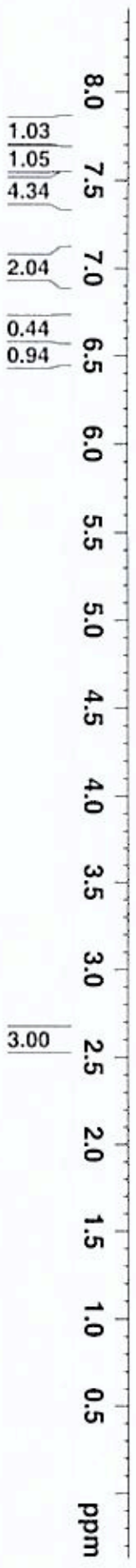


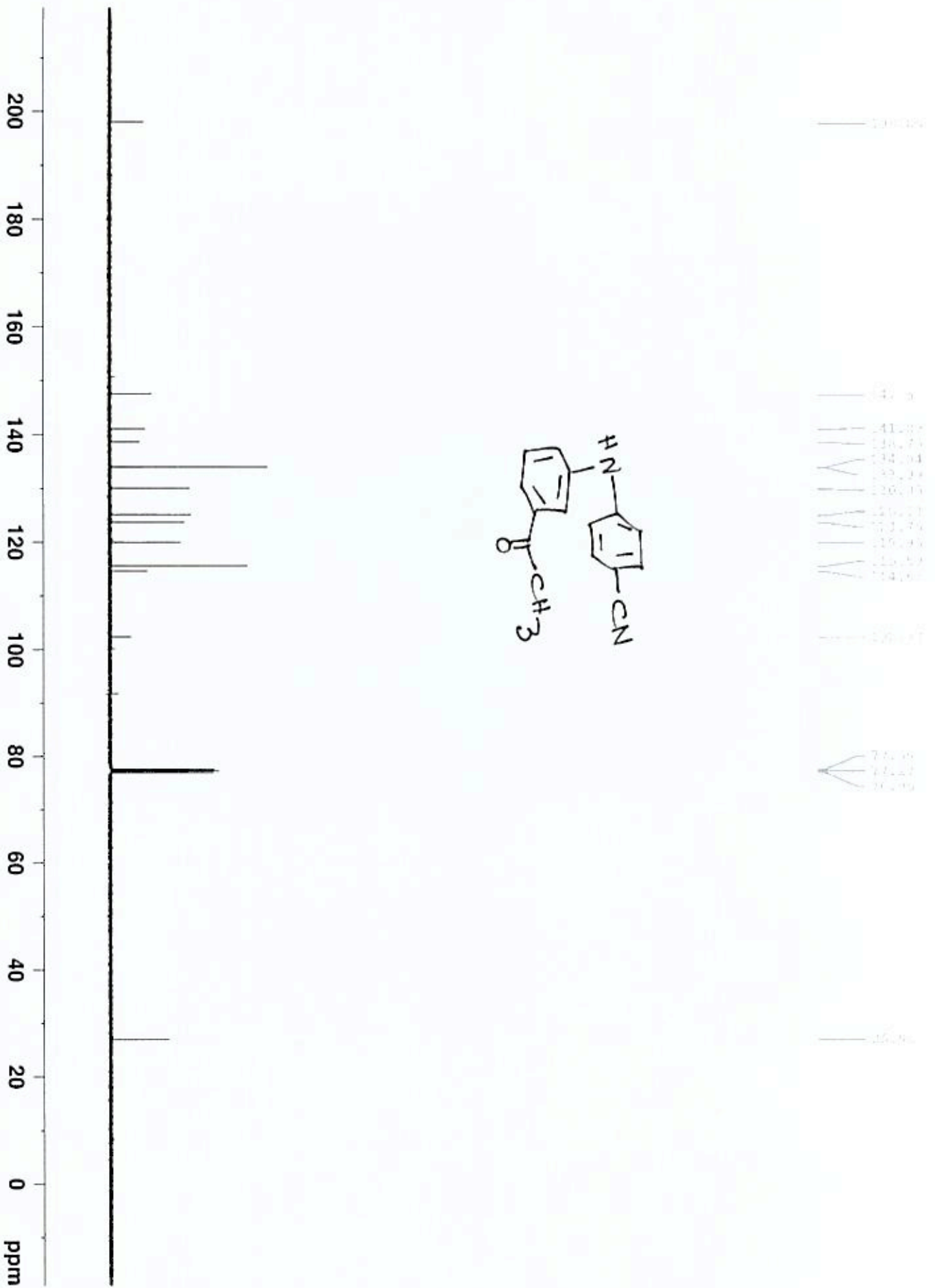
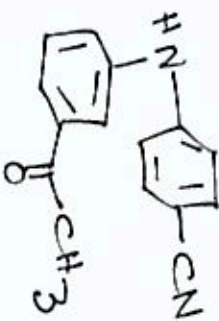


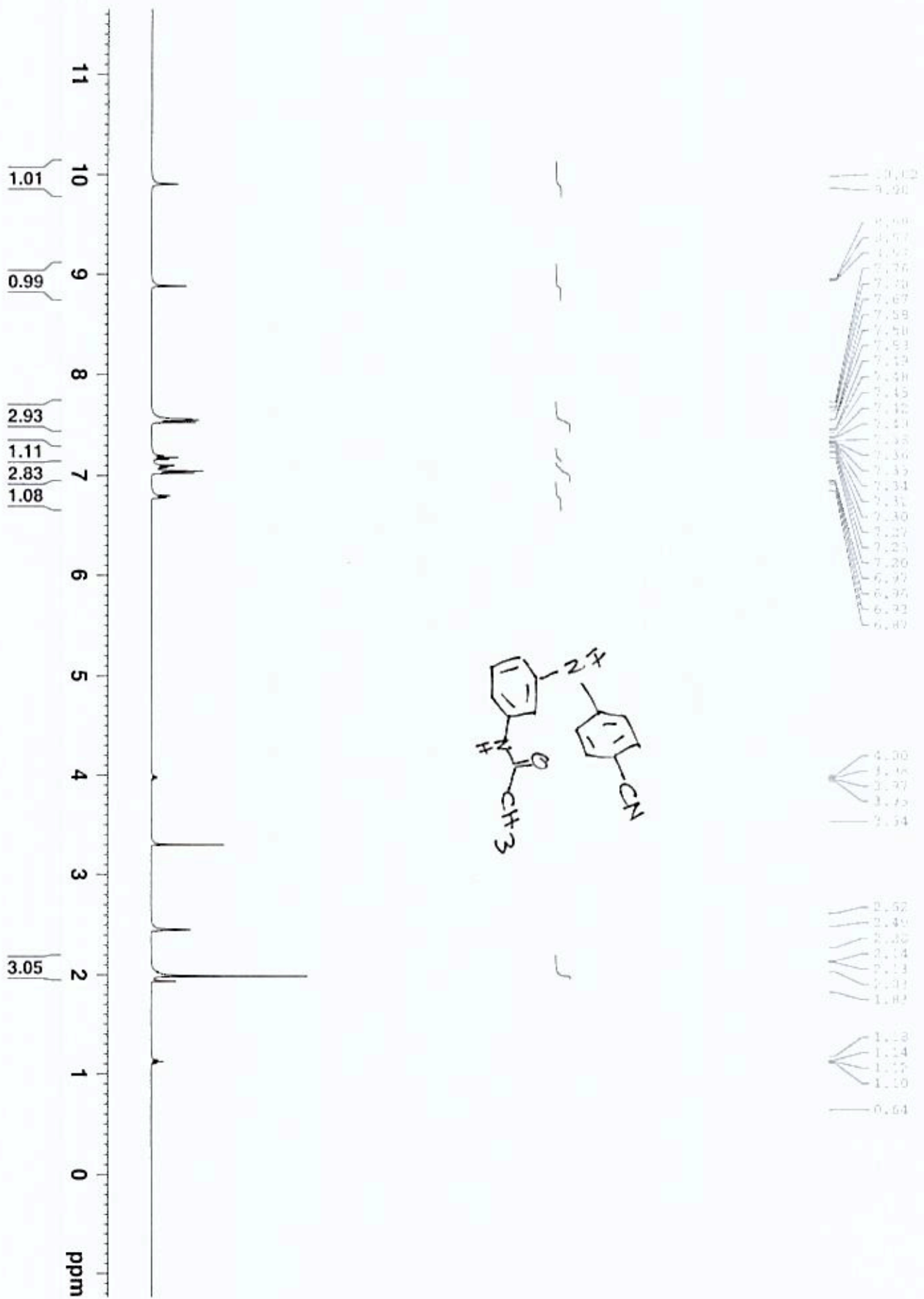


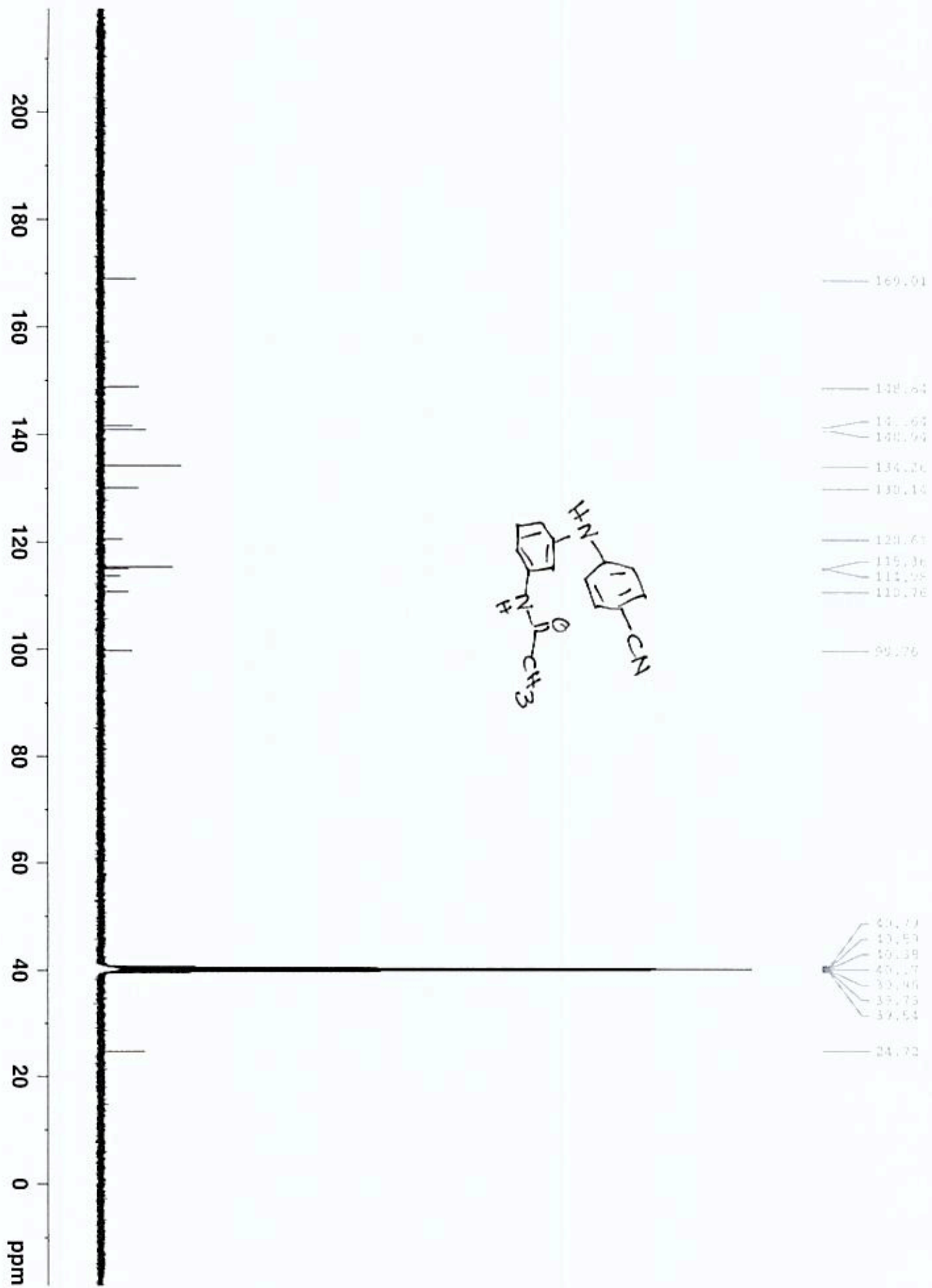


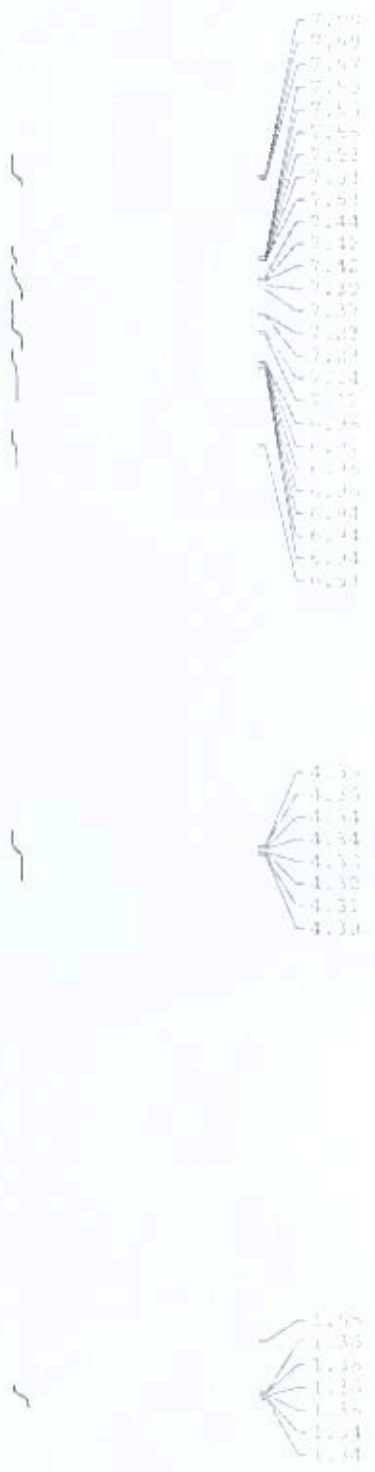
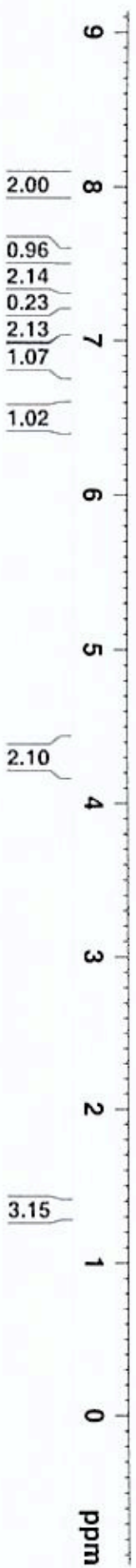


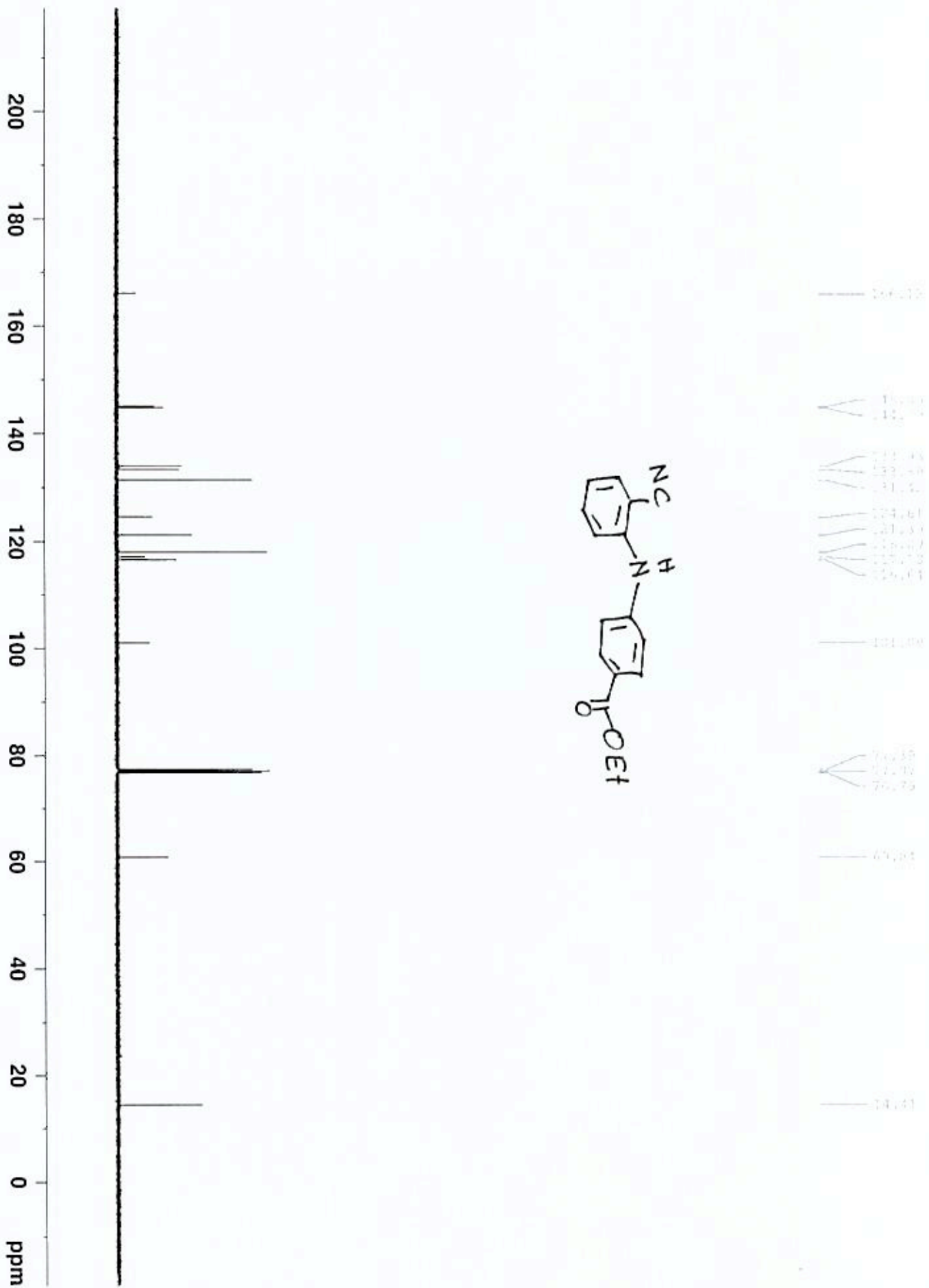
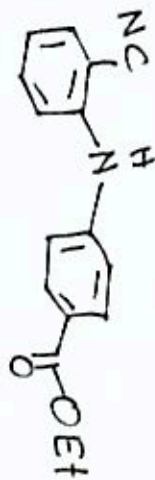


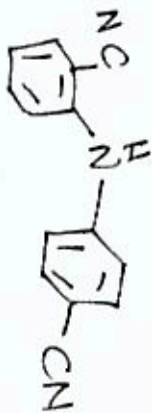
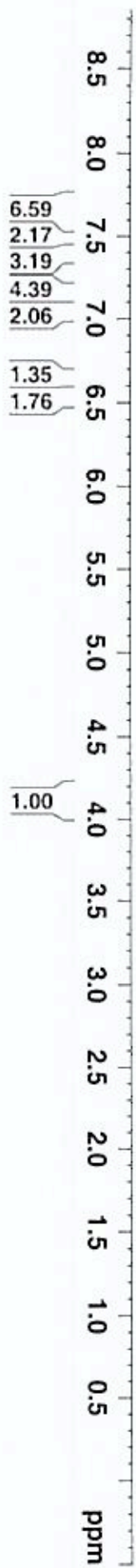


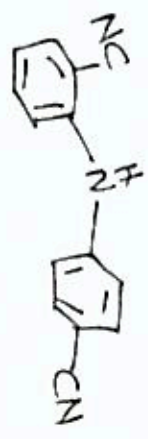




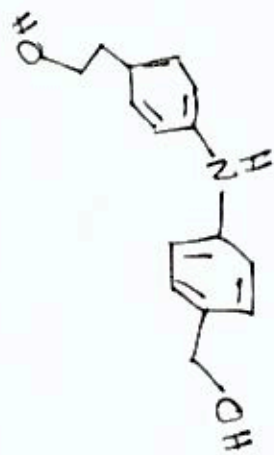
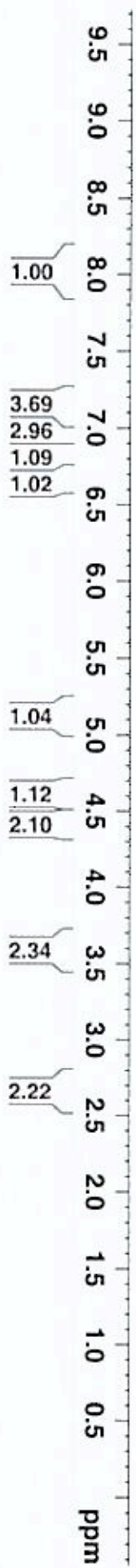


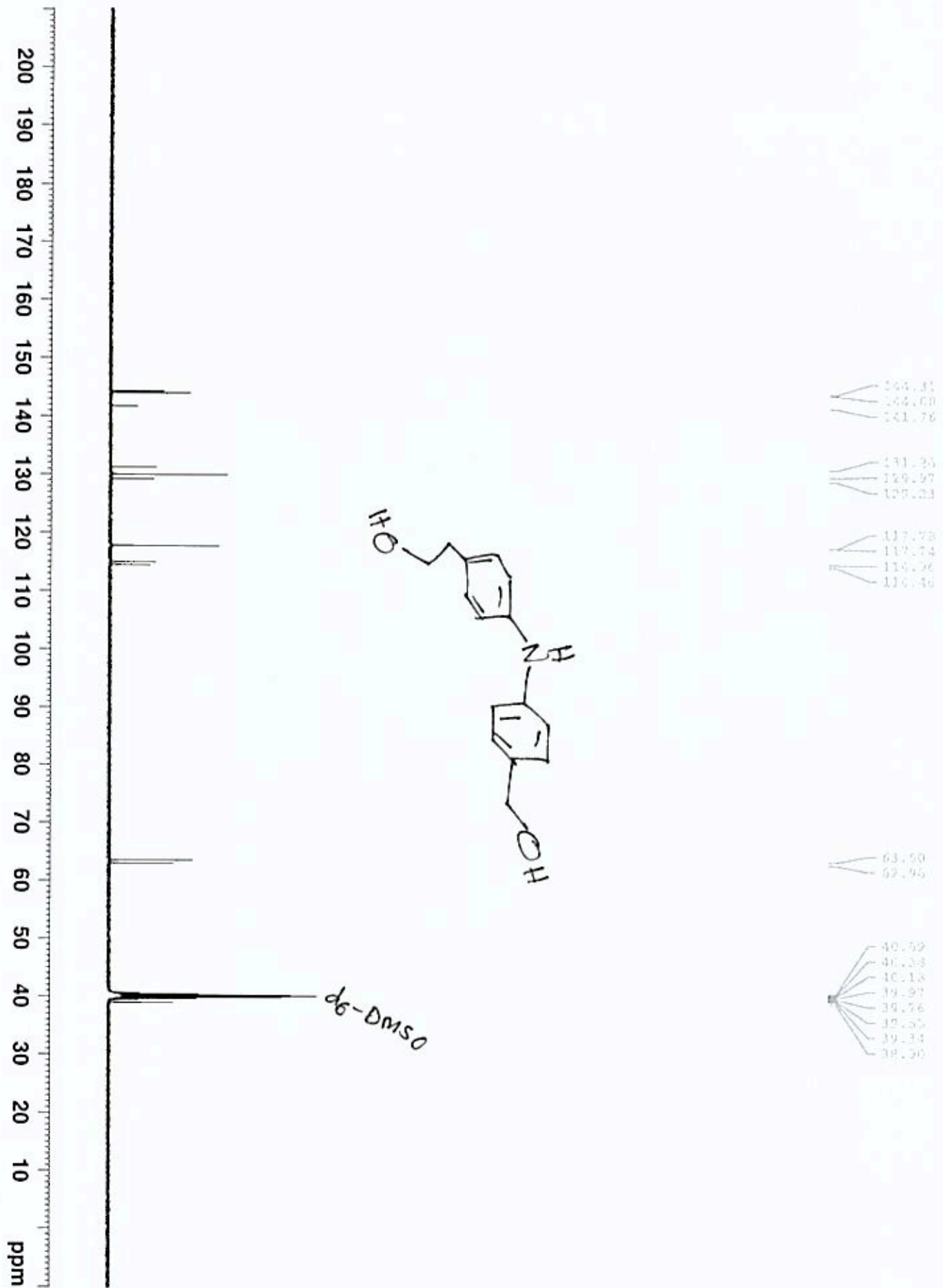


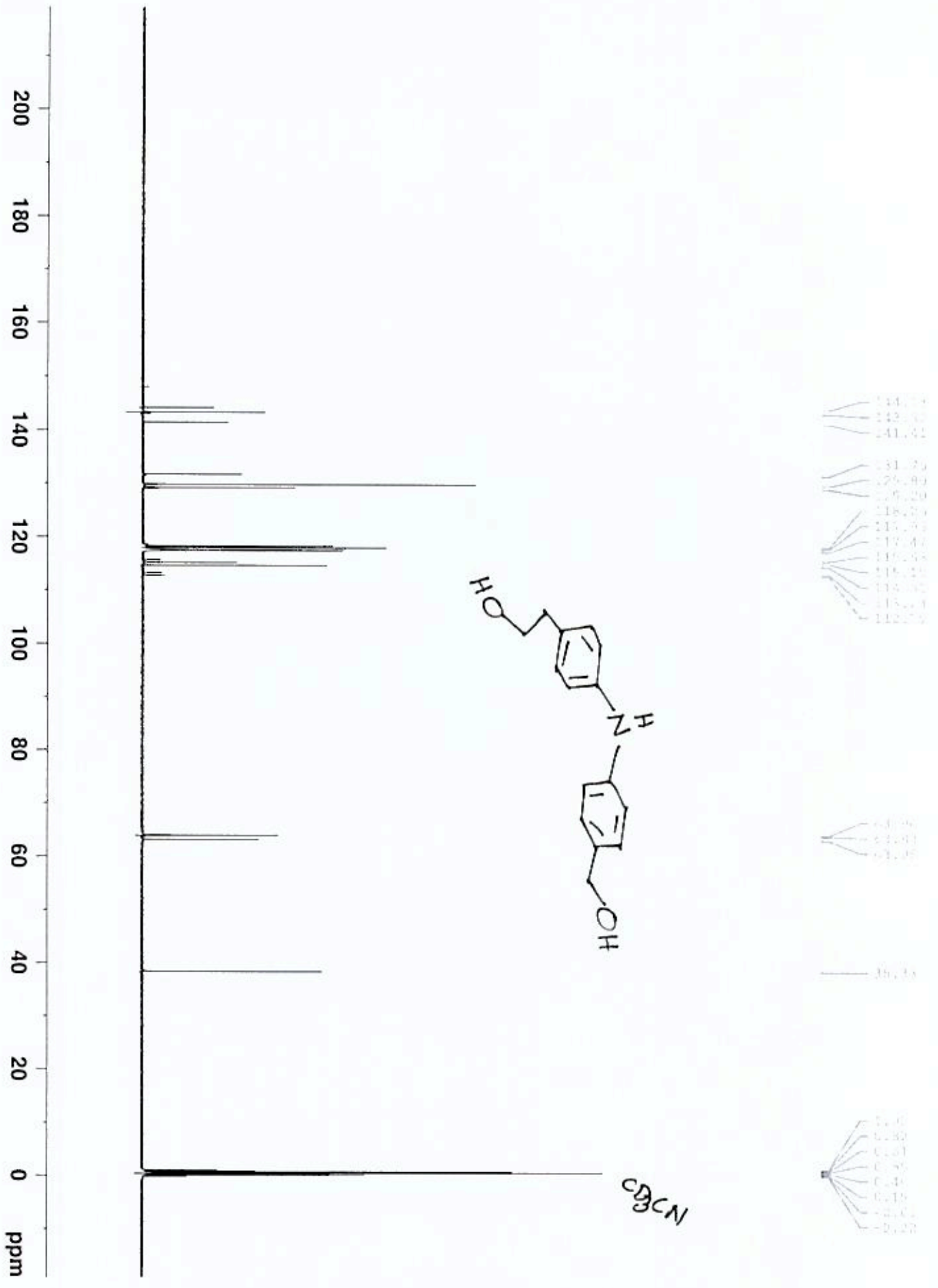


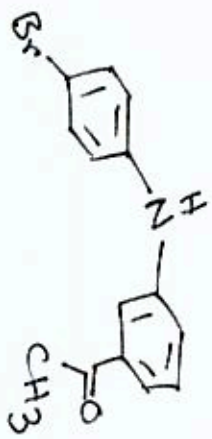


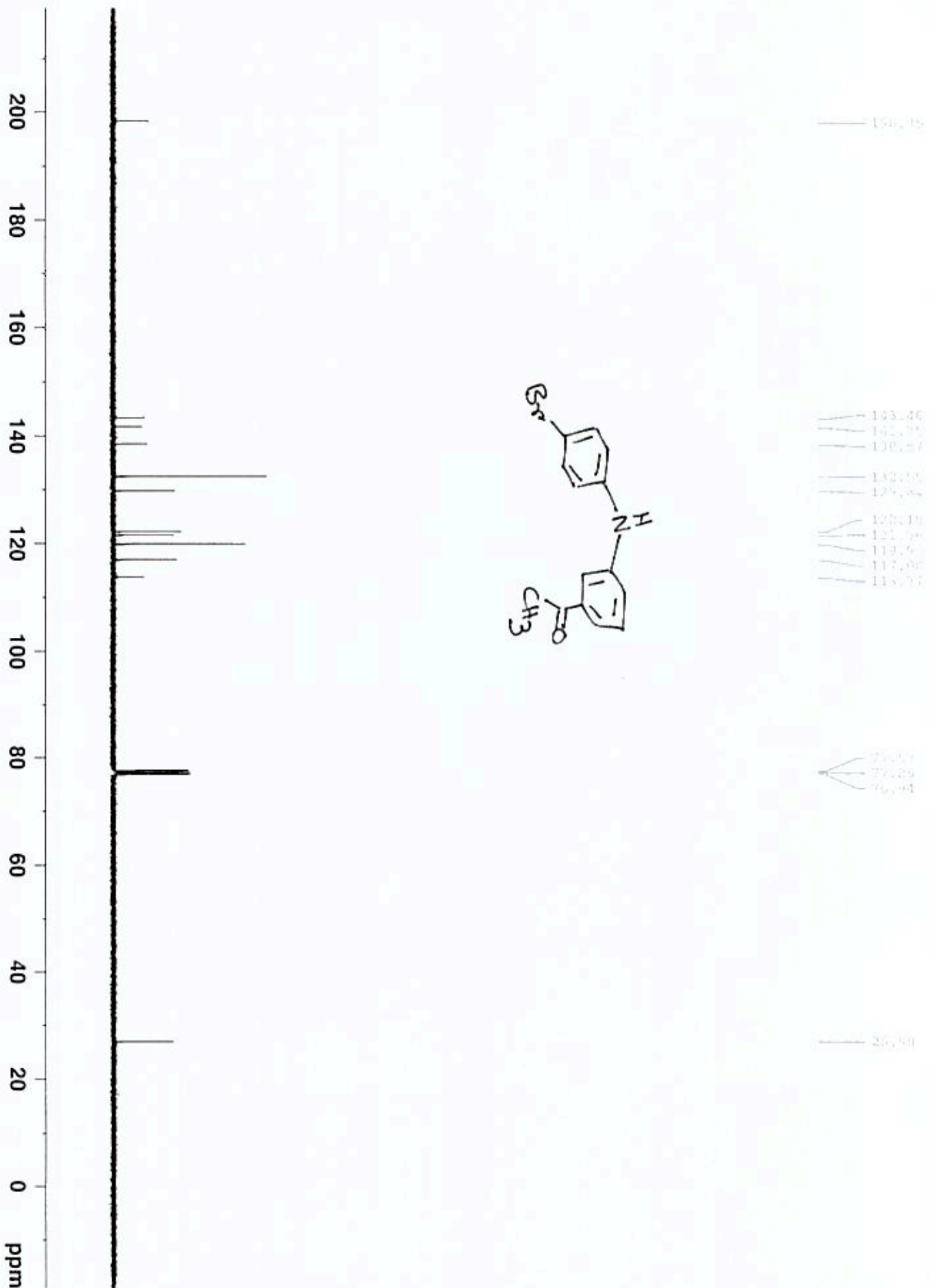
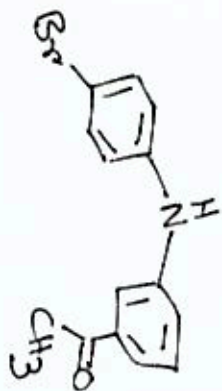
- 145.41
- 145.25
- 134.34
- 134.06
- 134.05
- 133.79
- 124.83
- 118.31
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- 118.10
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- 114.61
- 105.97
- 103.76
- 77.56
- 77.24
- 76.93

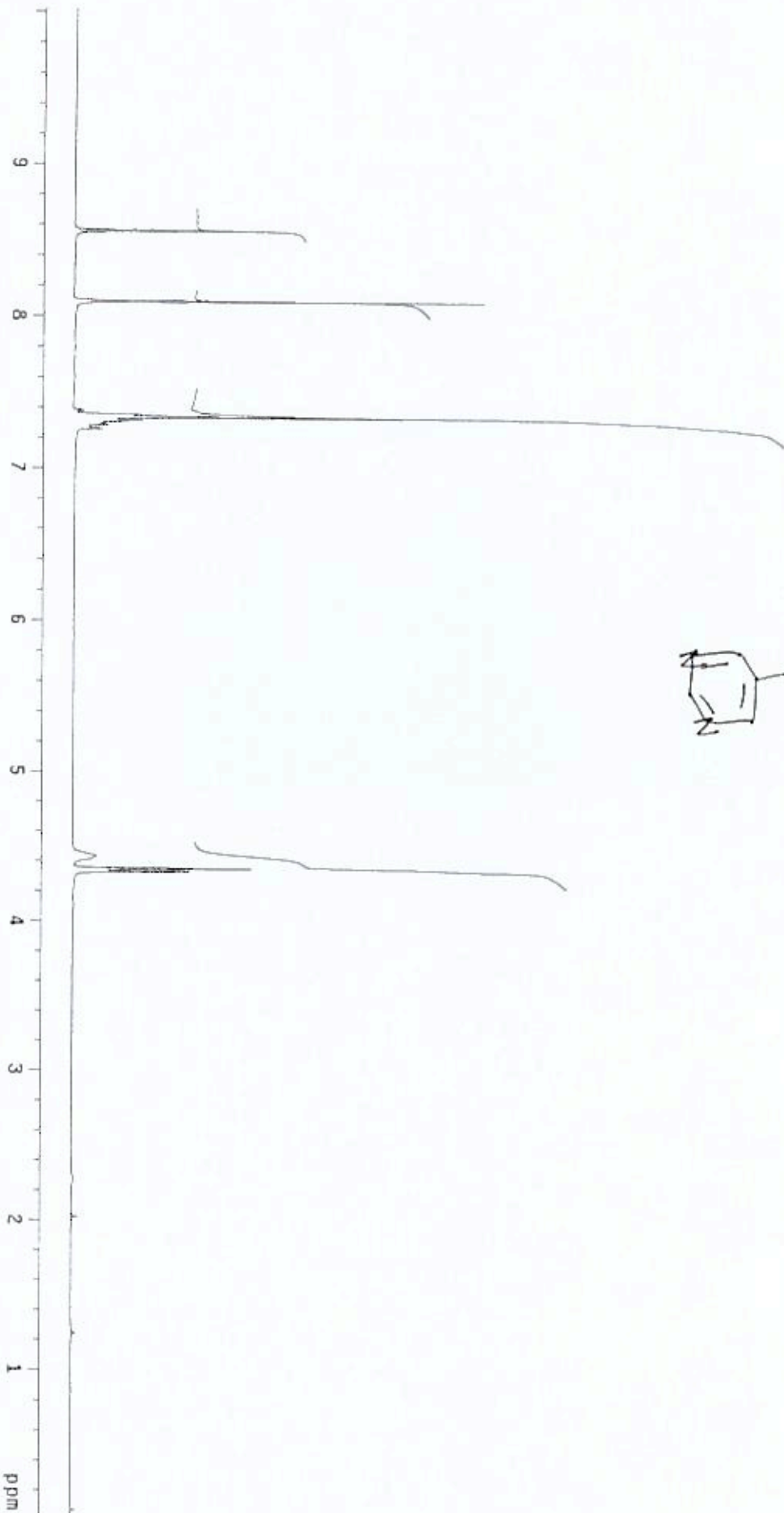
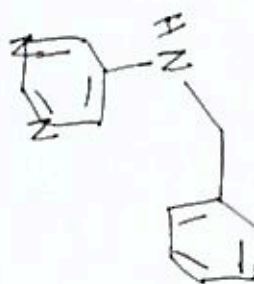


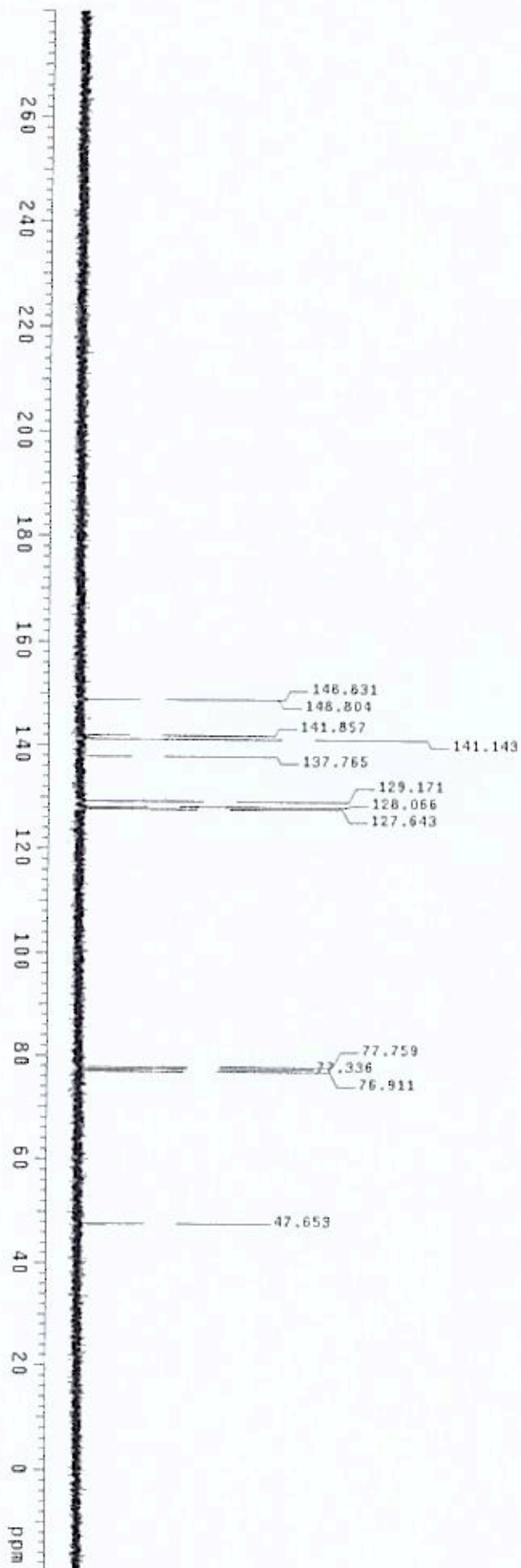
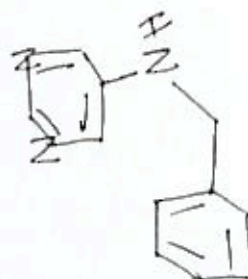


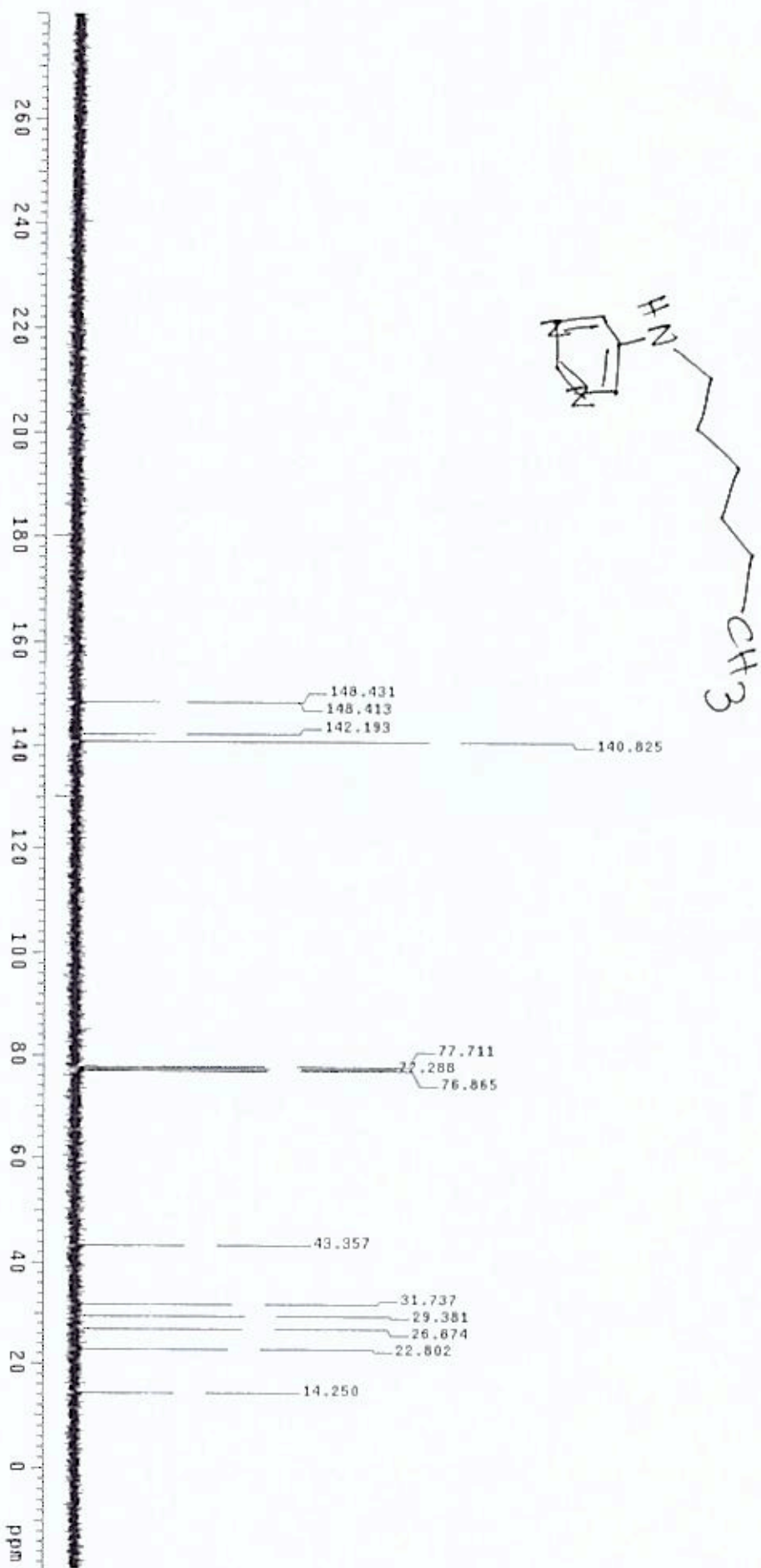


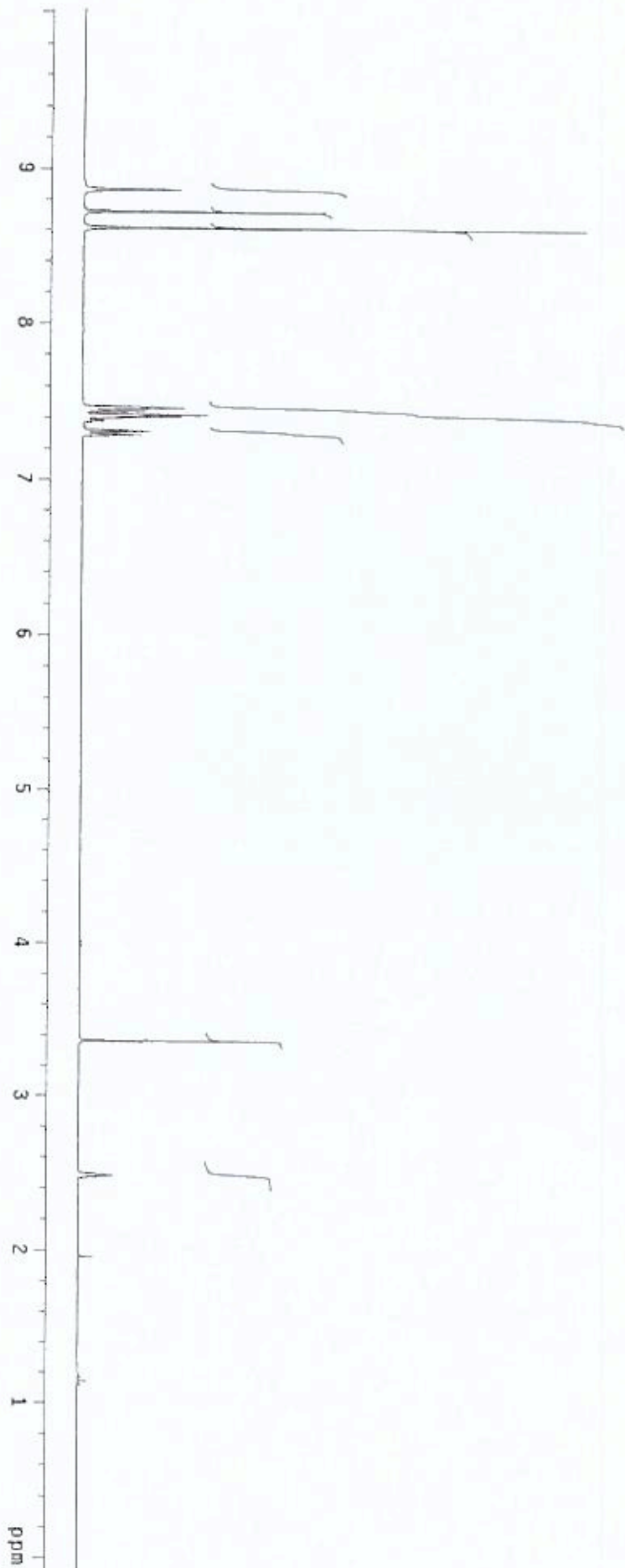
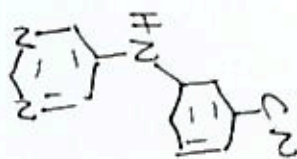


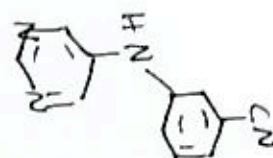
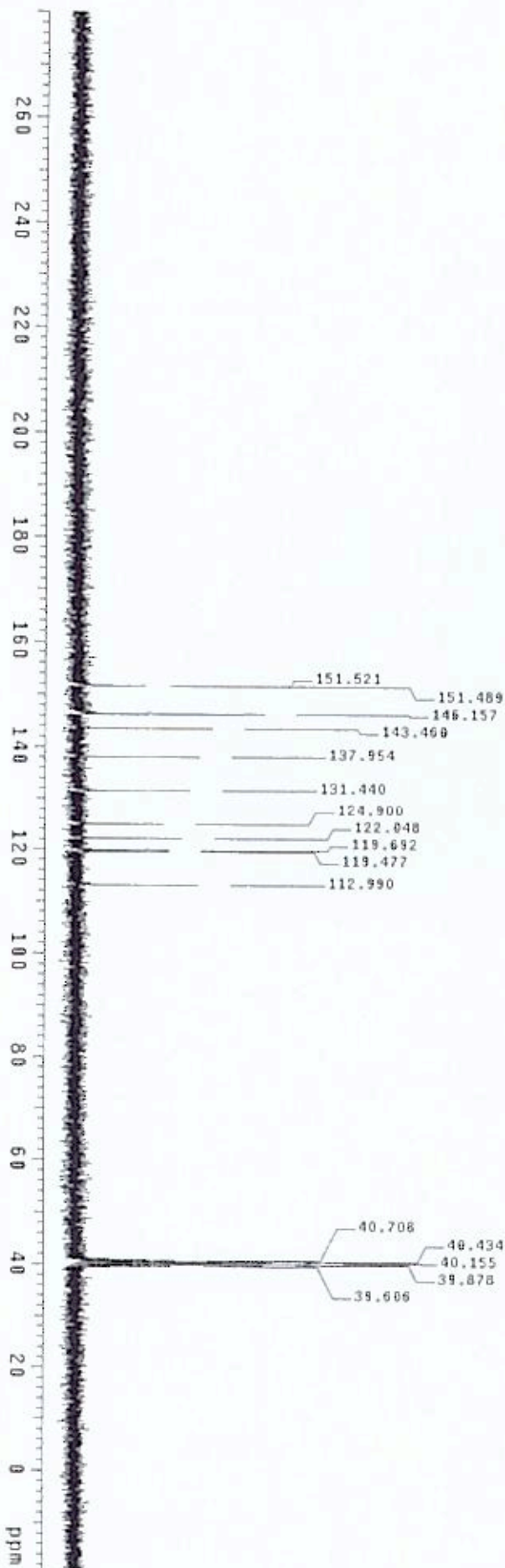


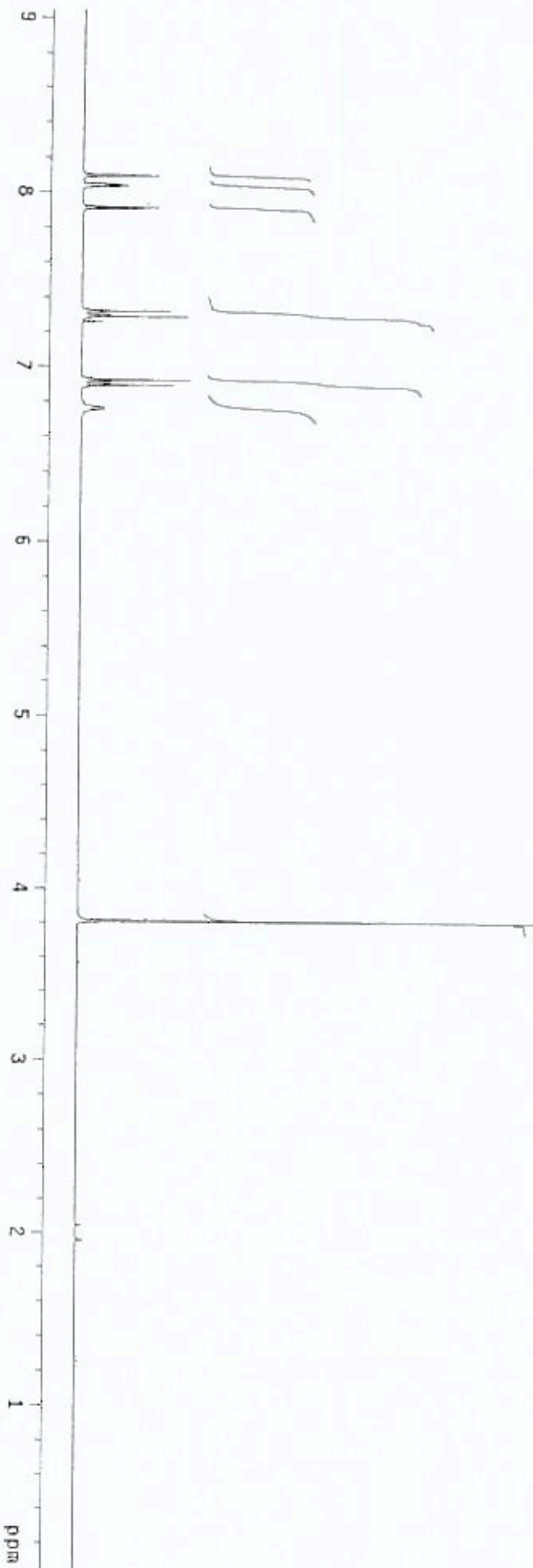
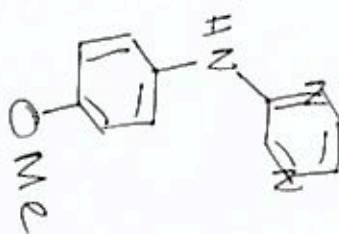


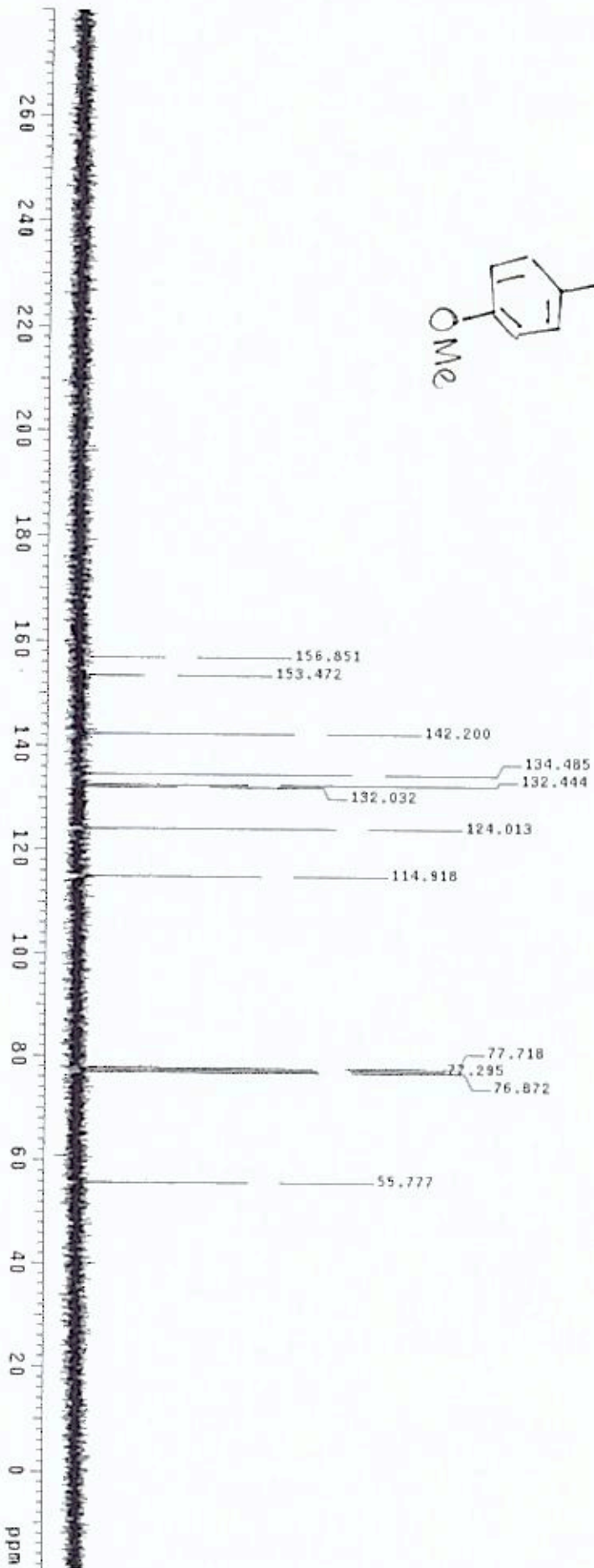
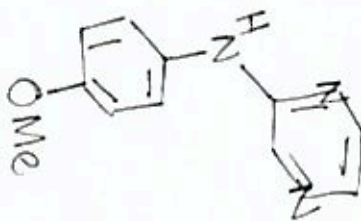


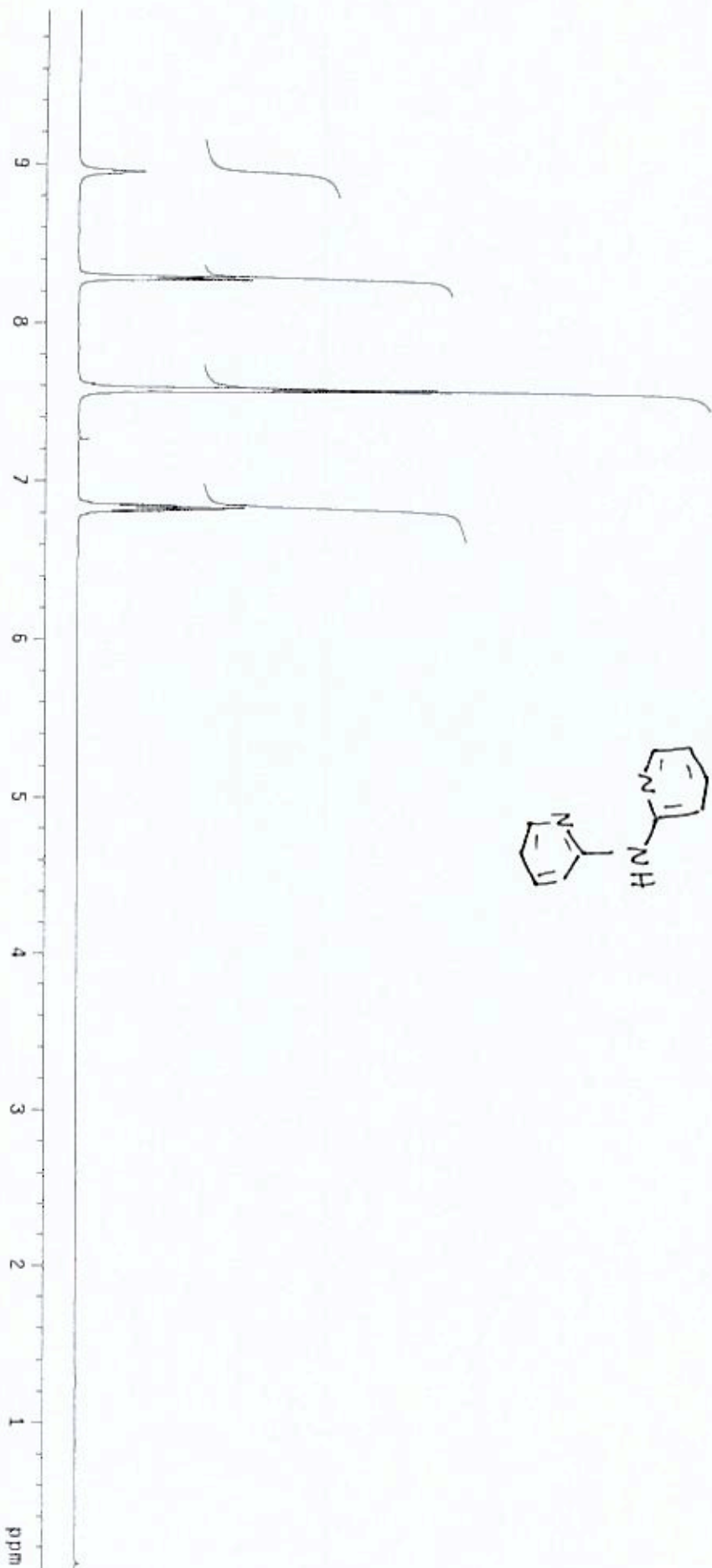


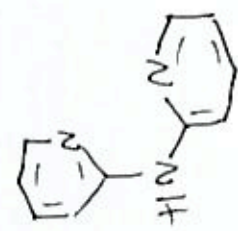
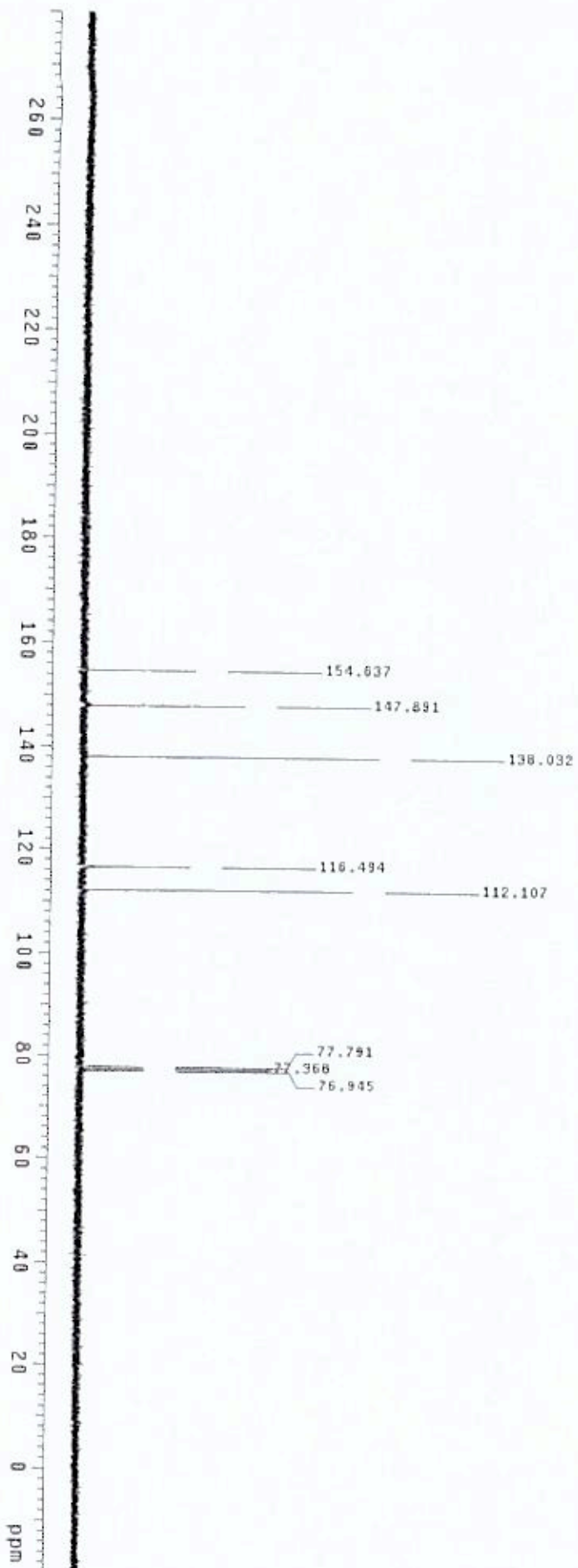


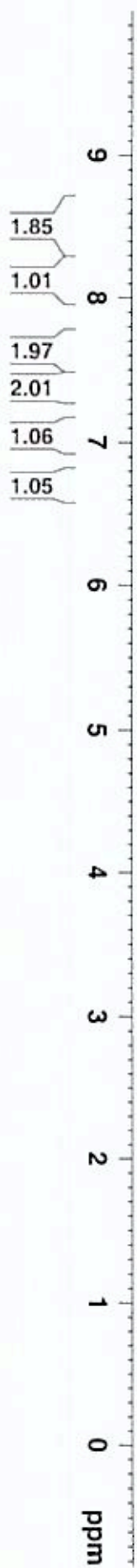


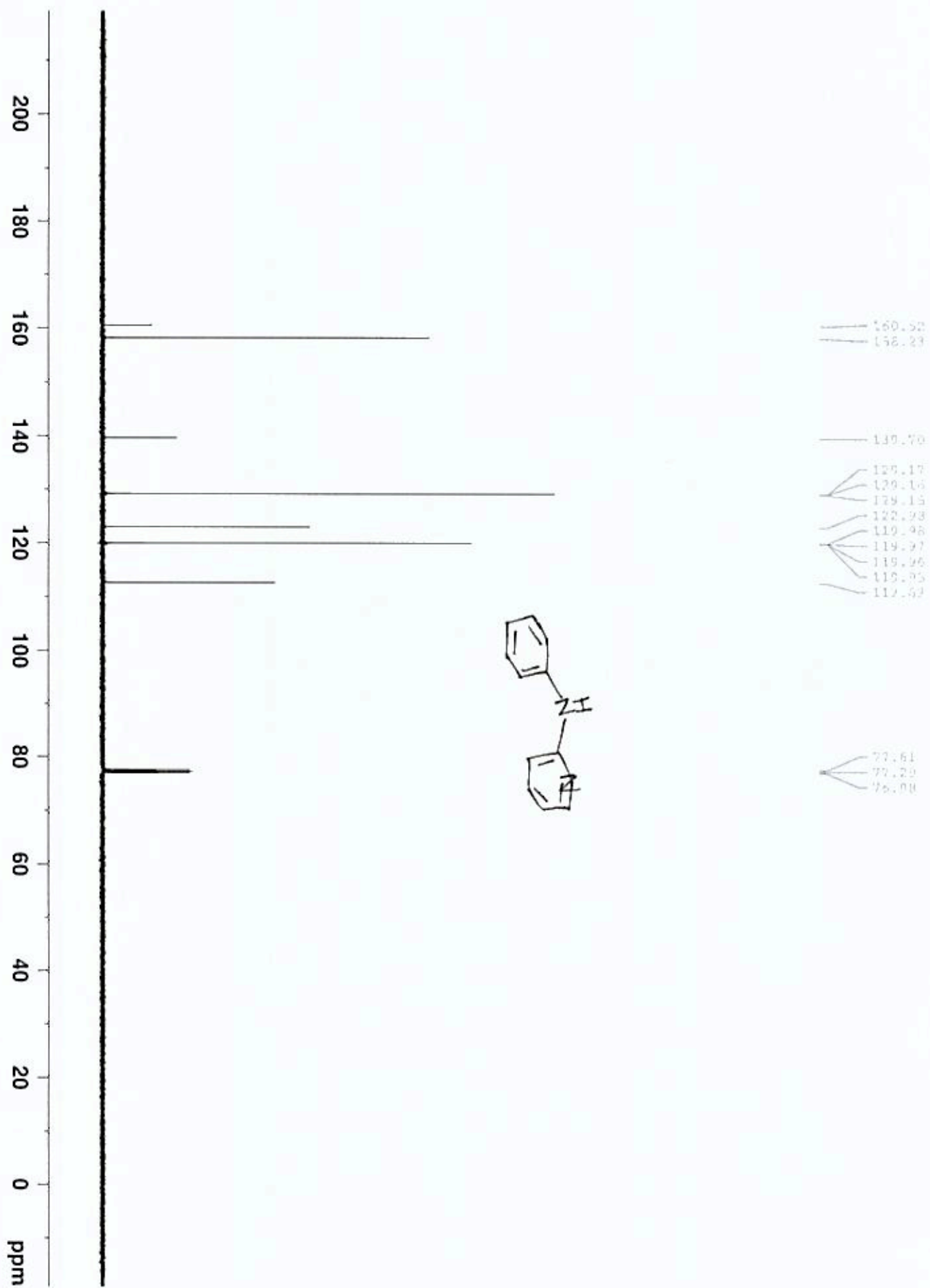
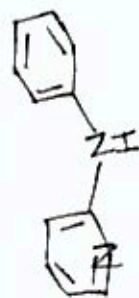


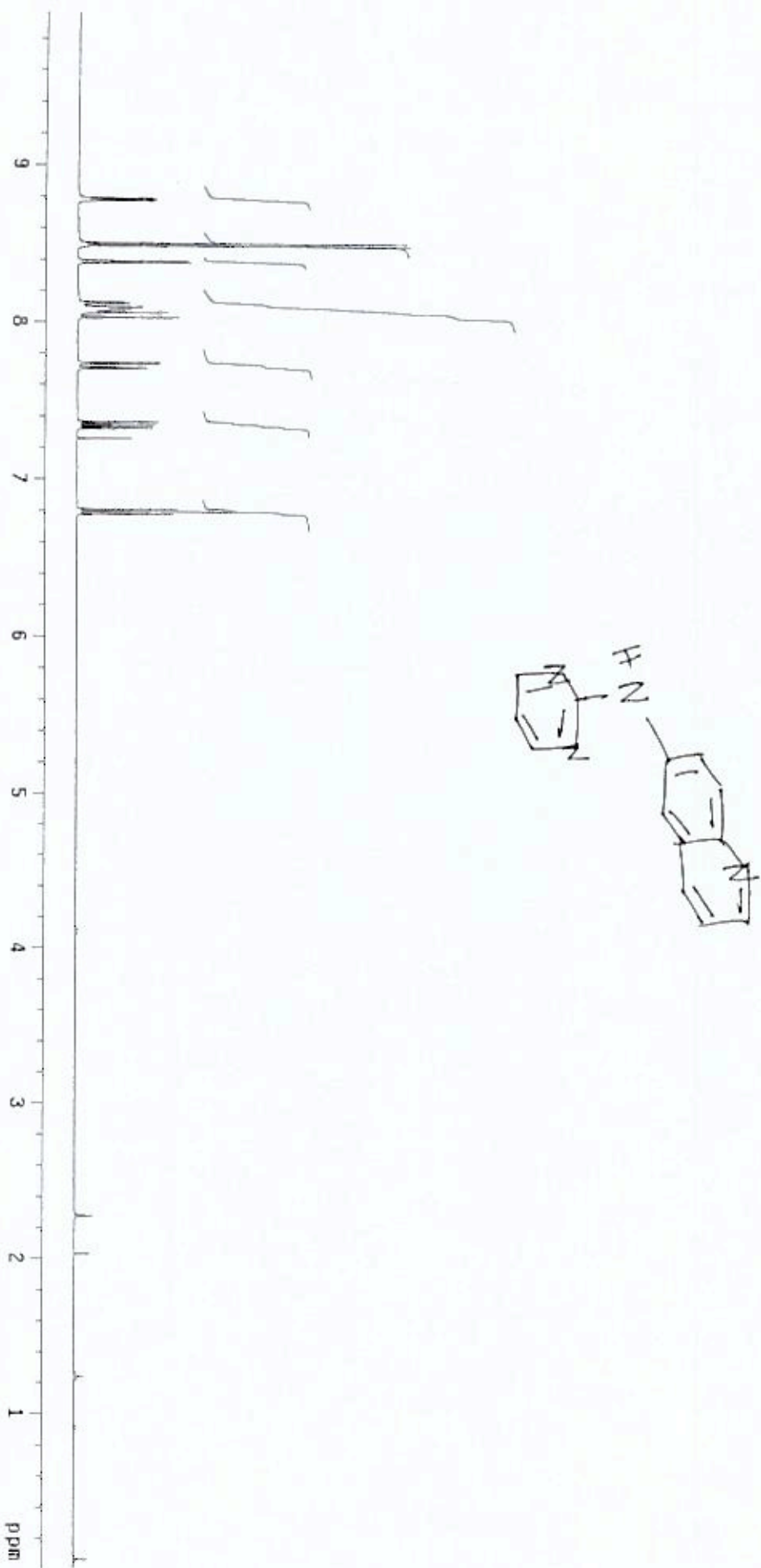


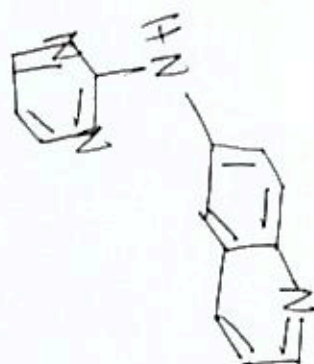
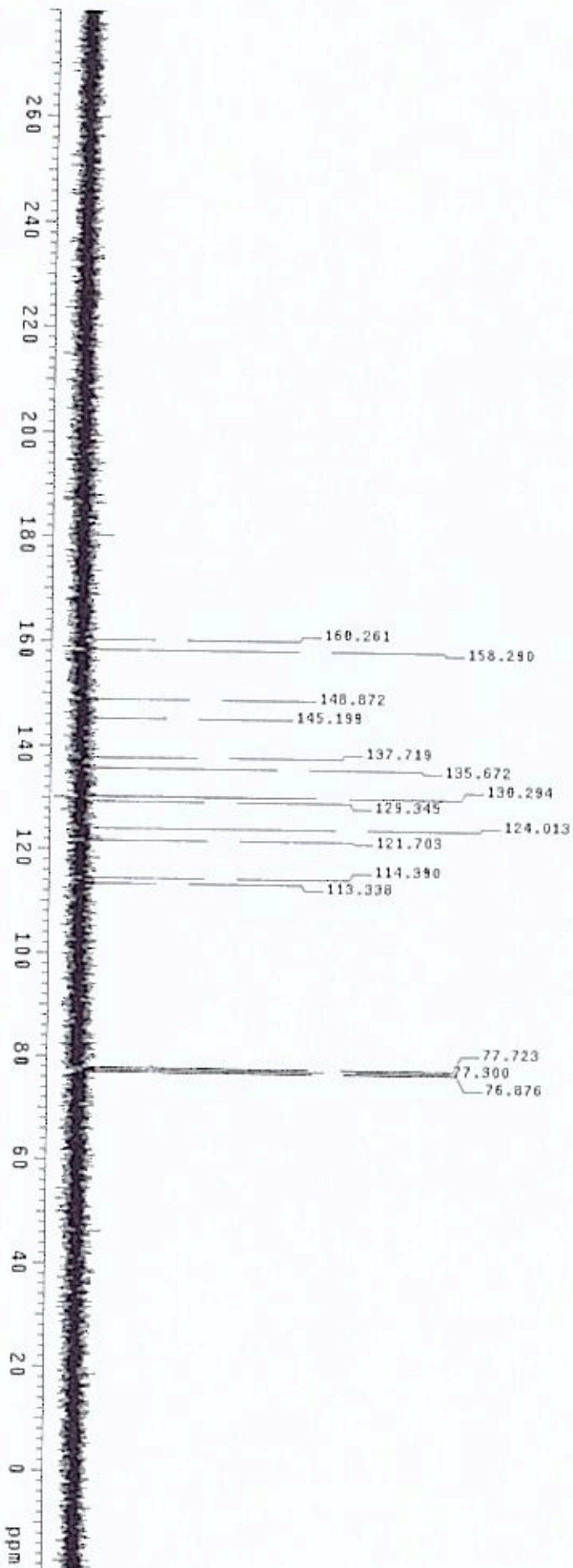


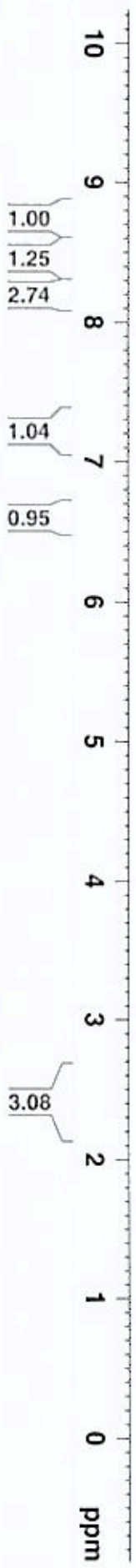


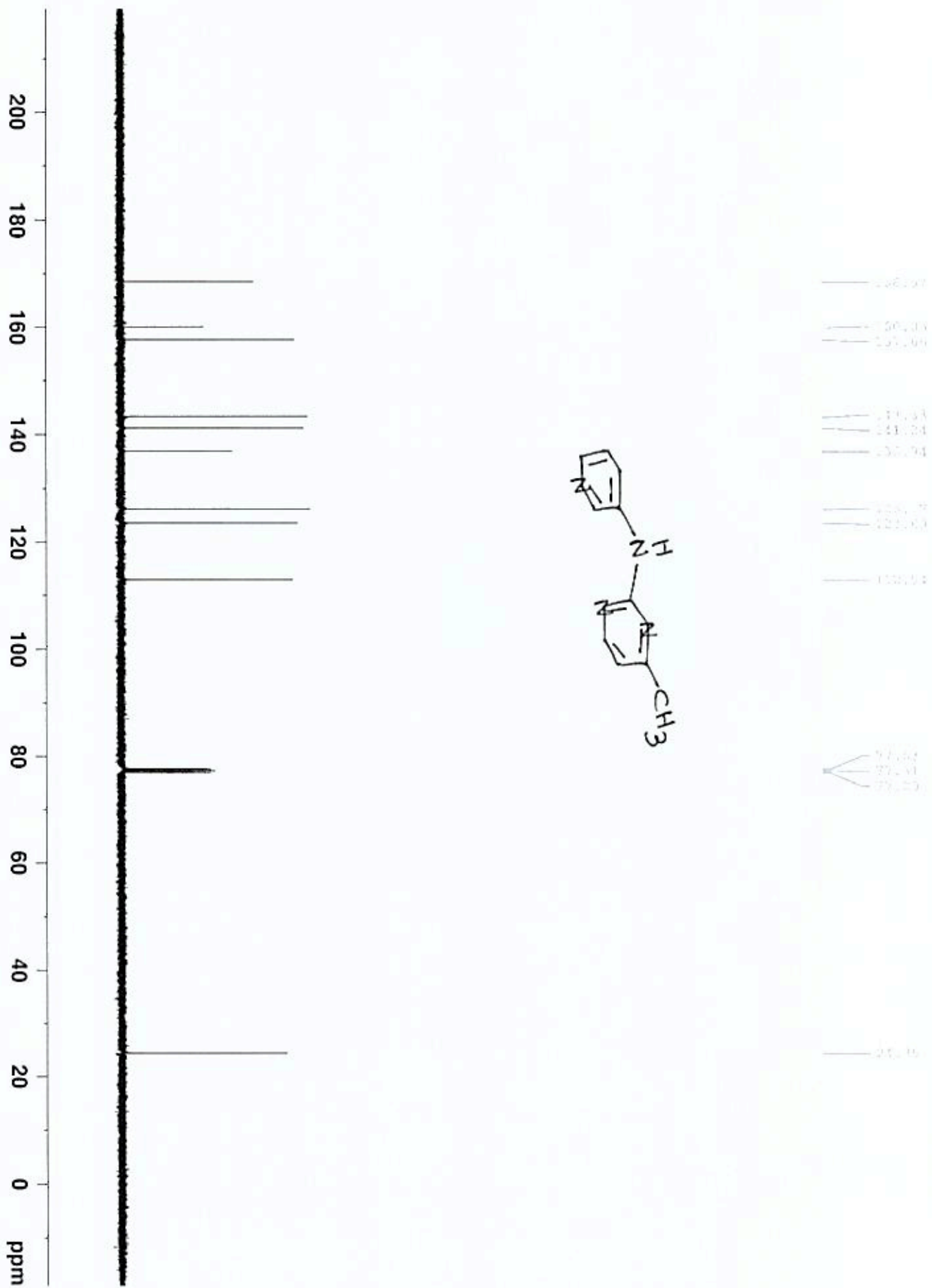


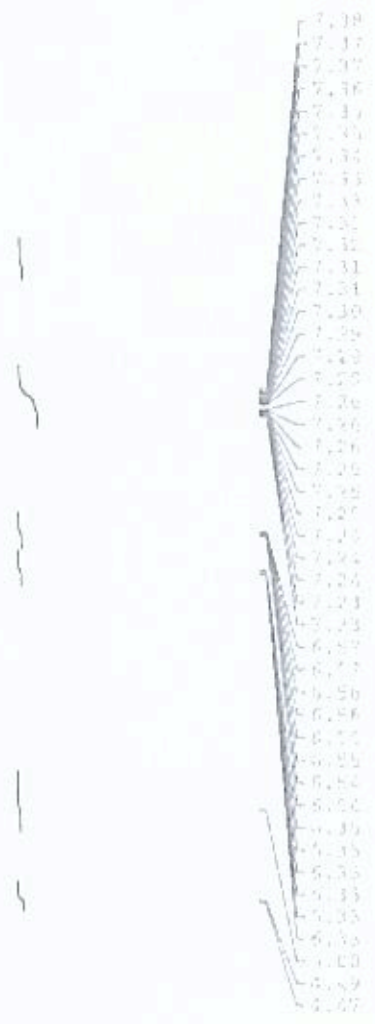
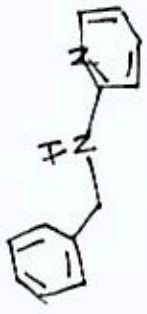
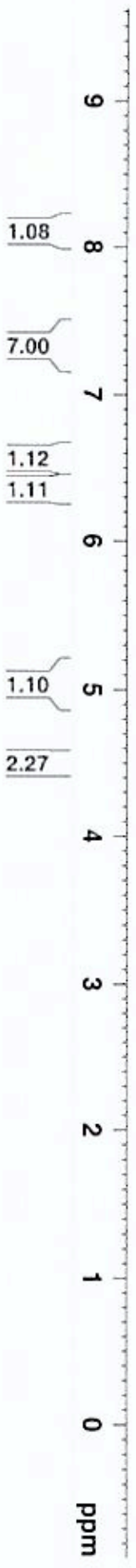


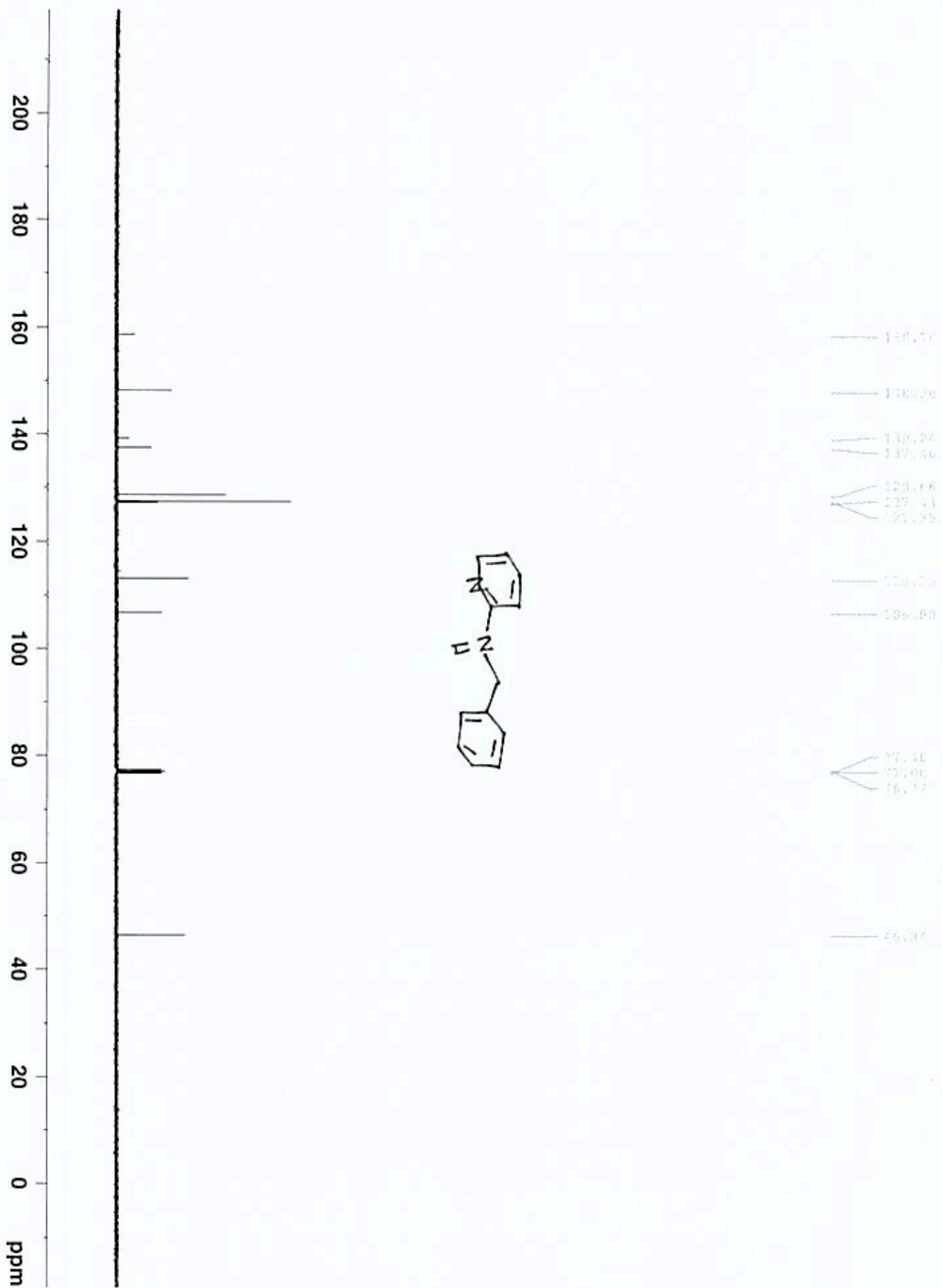


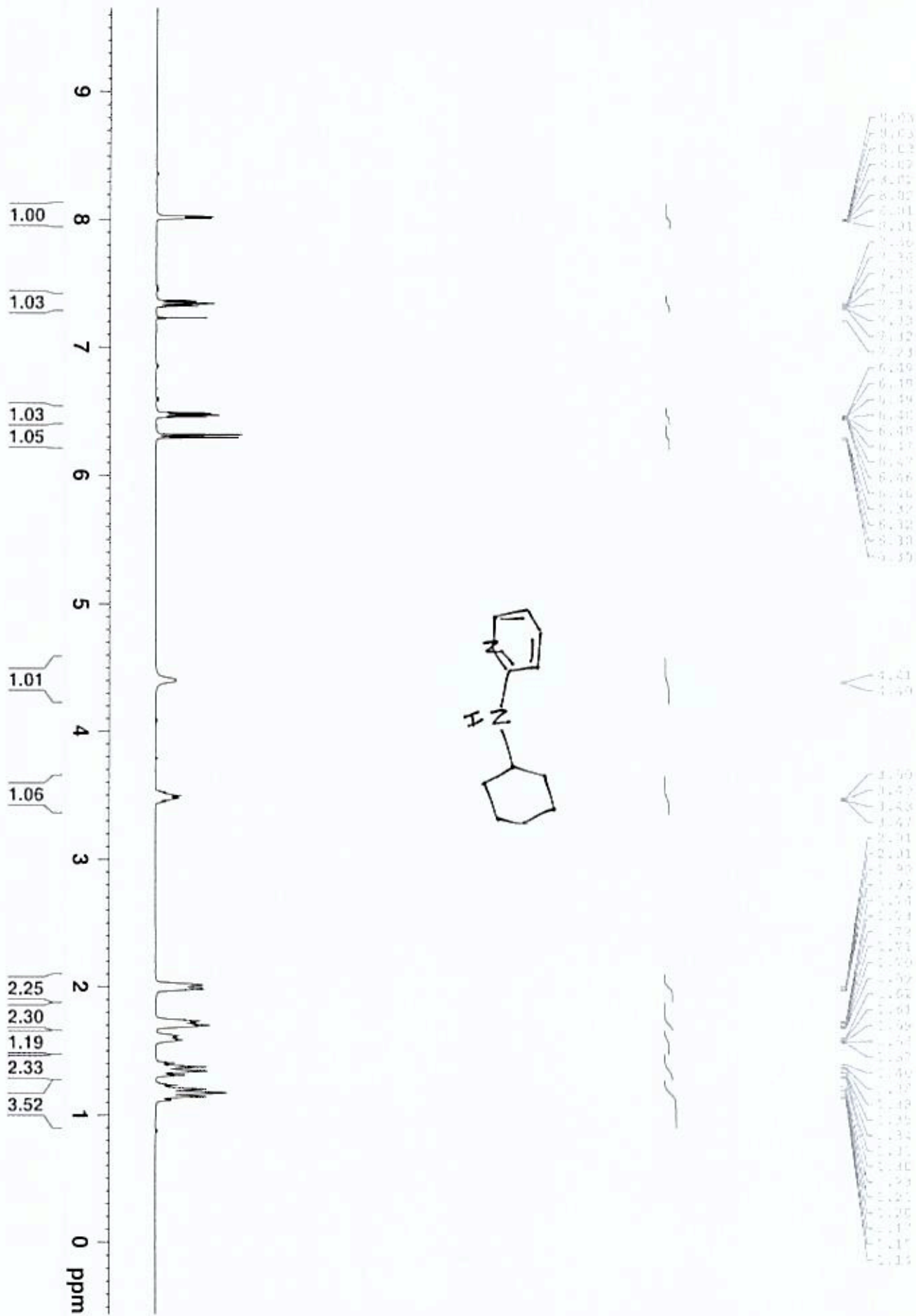


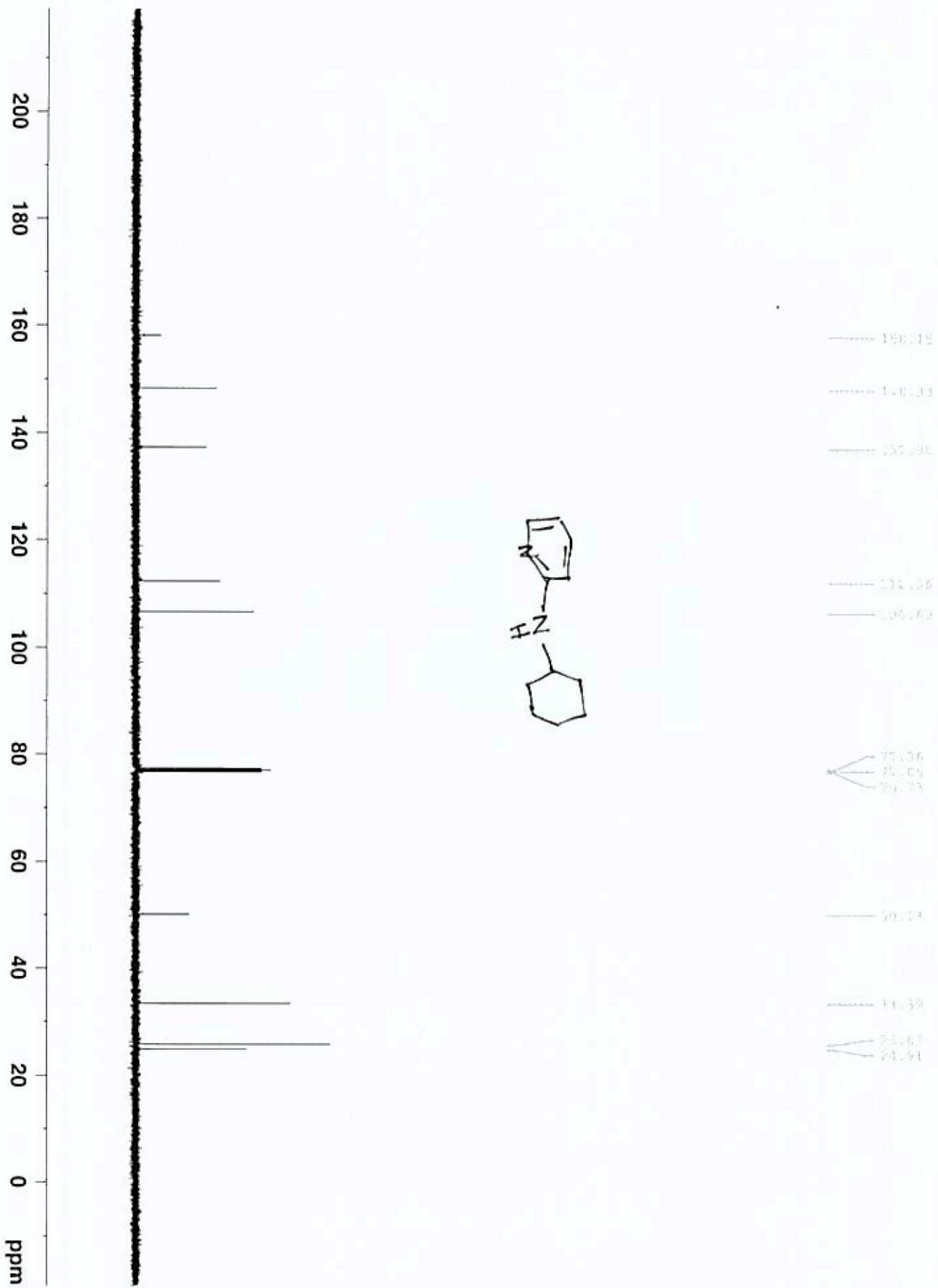


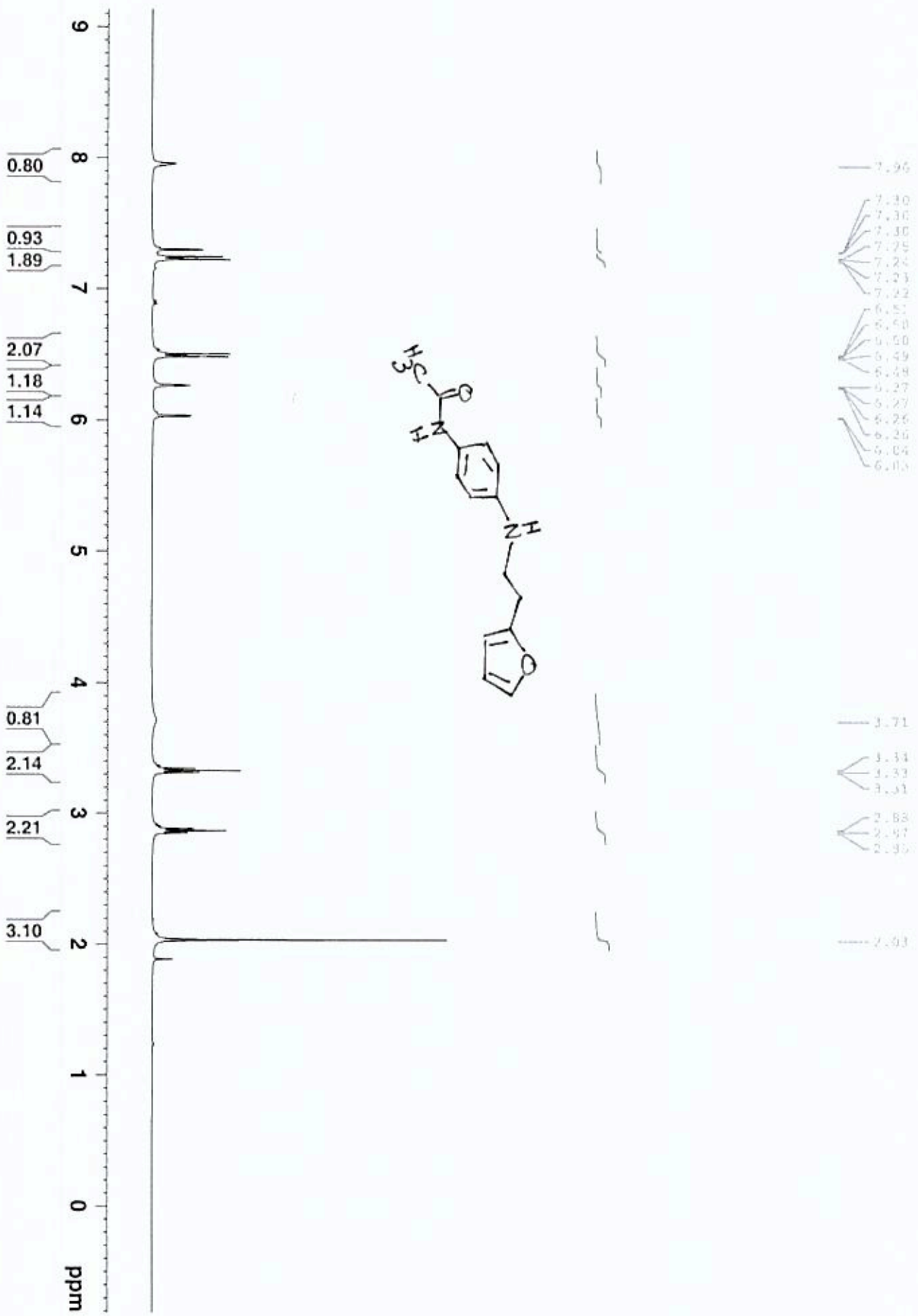


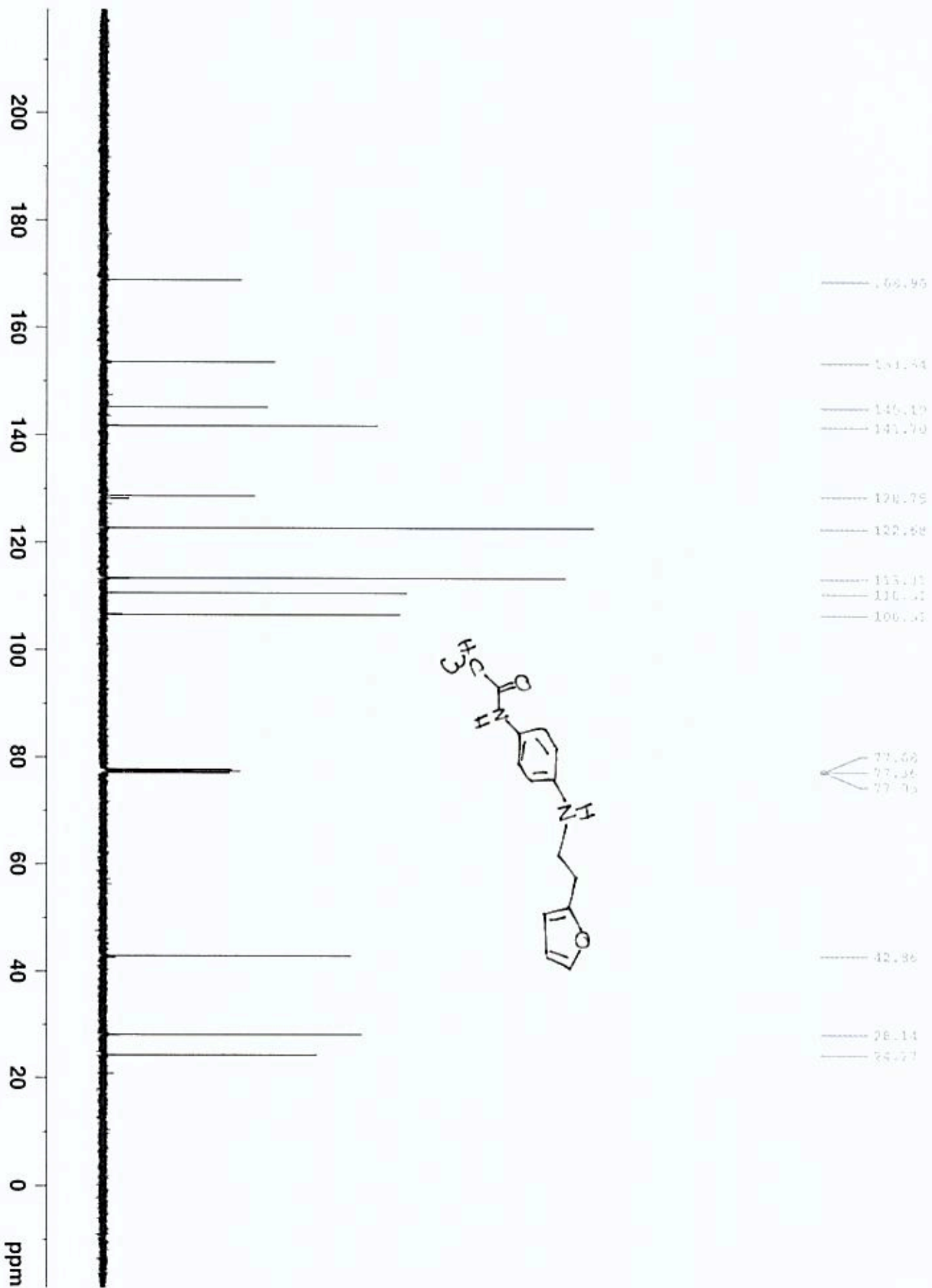


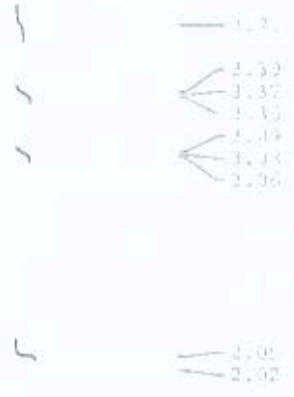
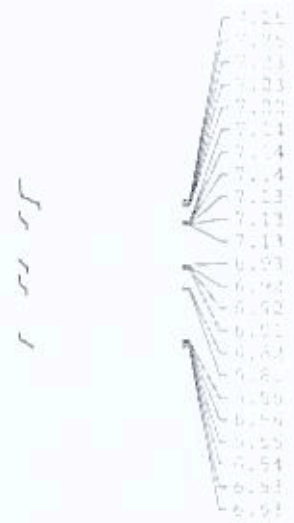
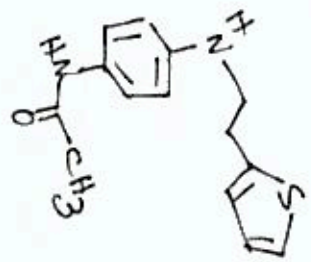
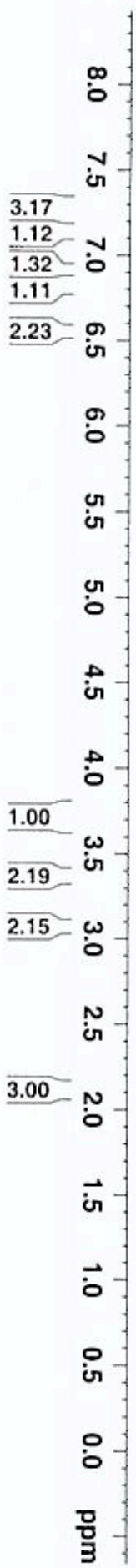


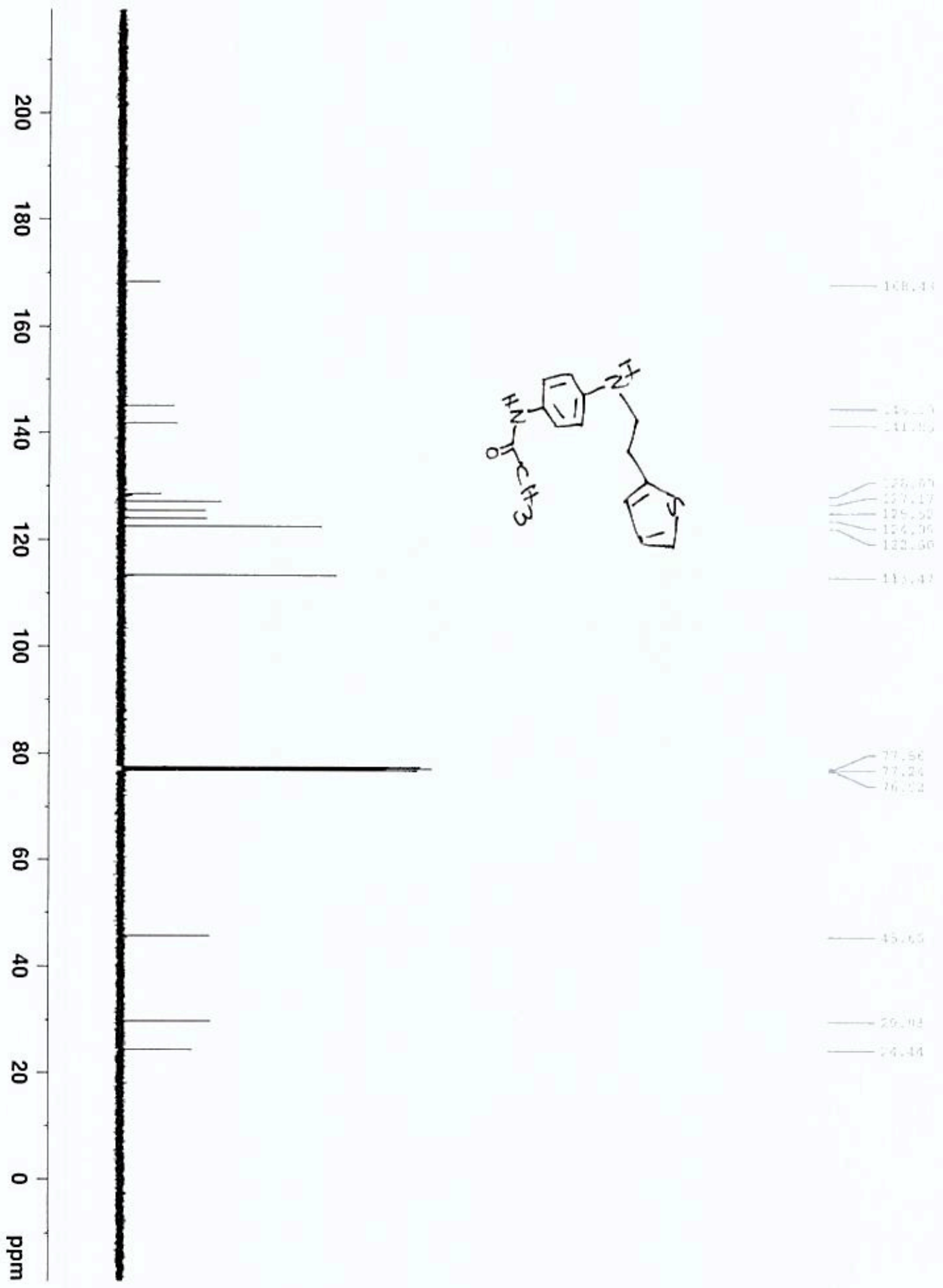


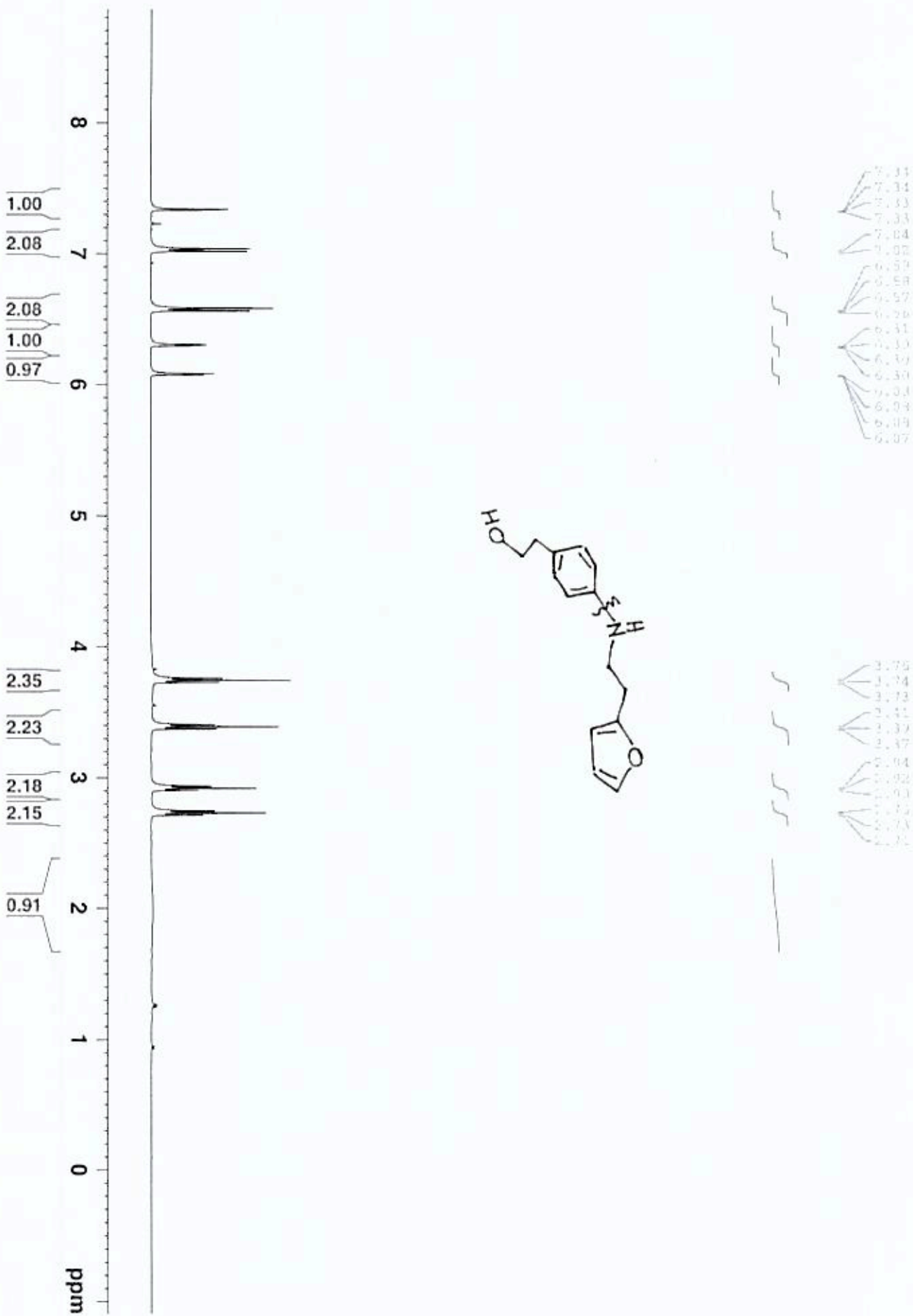


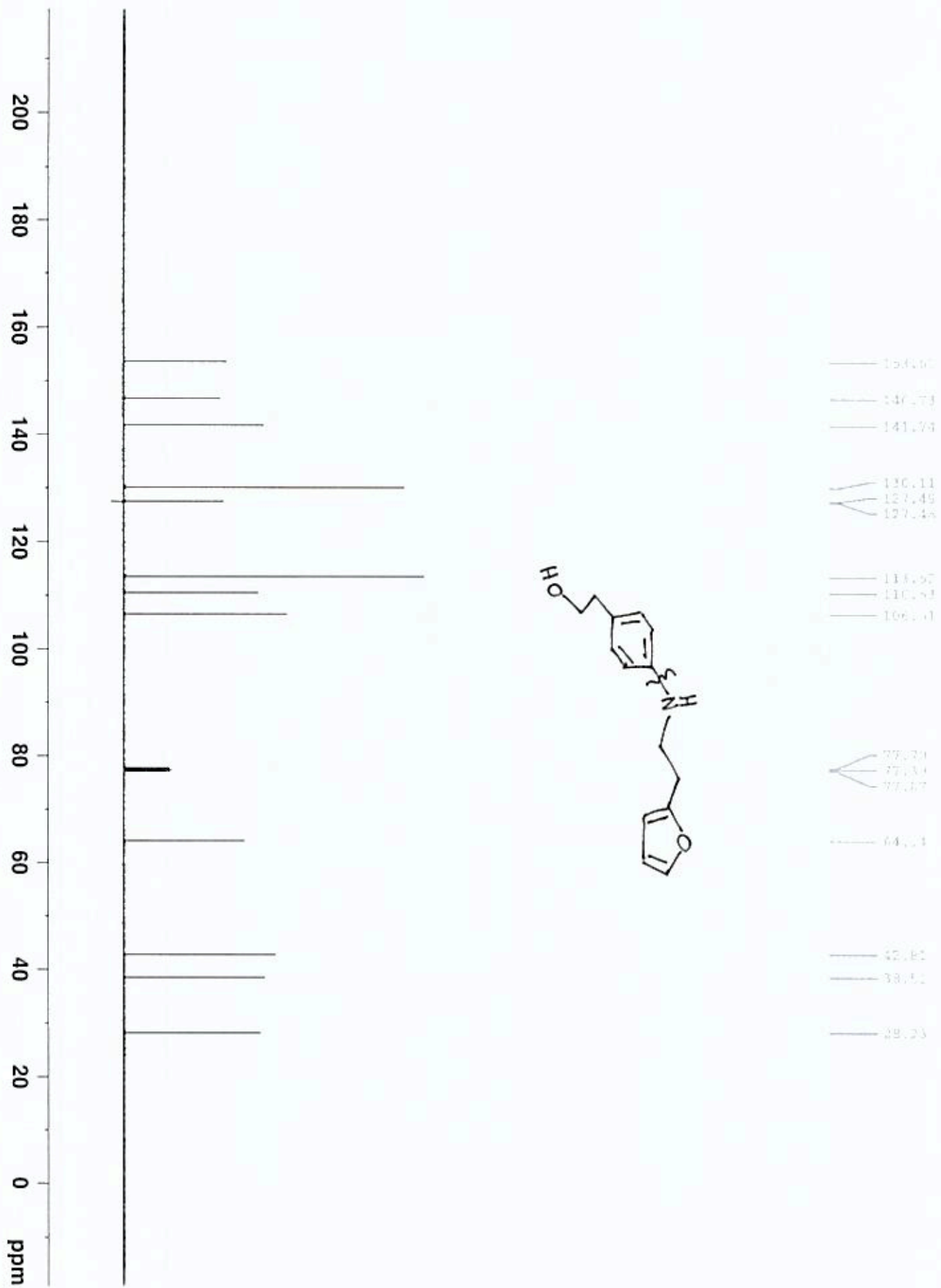
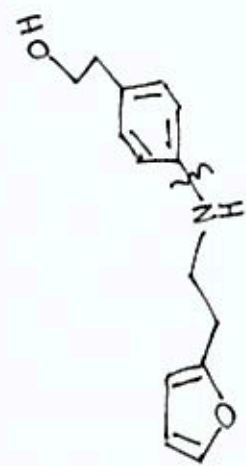


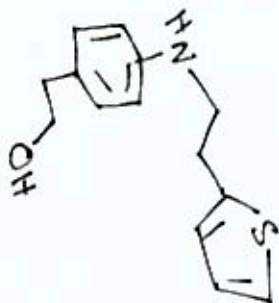
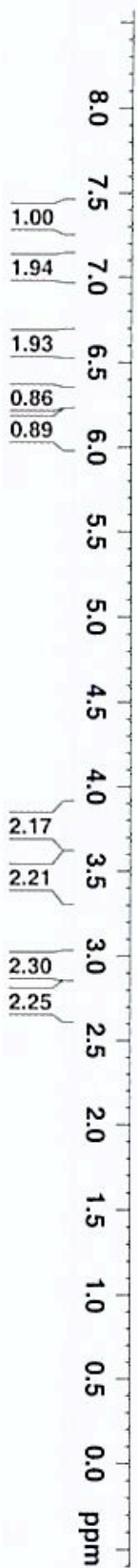


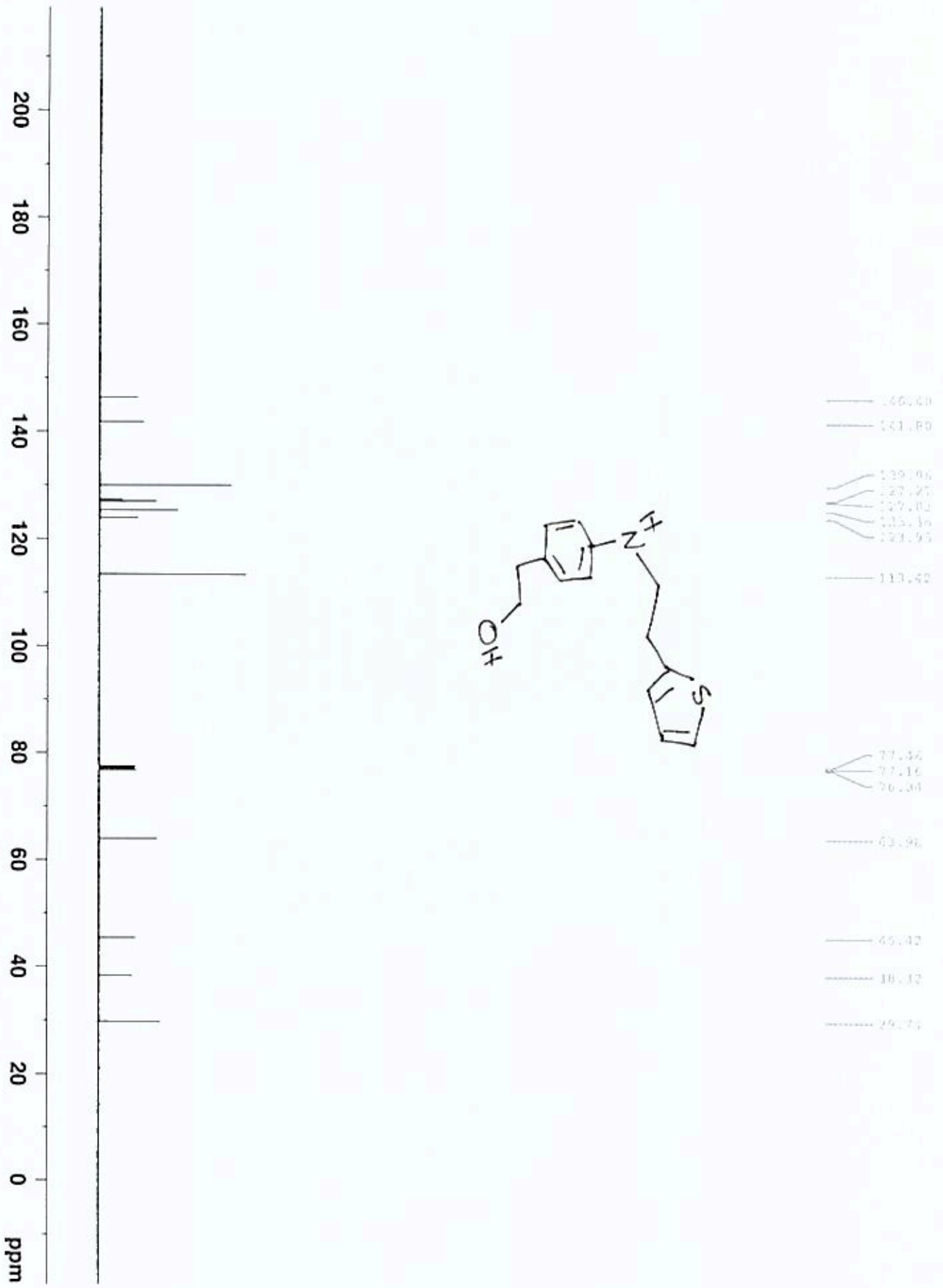


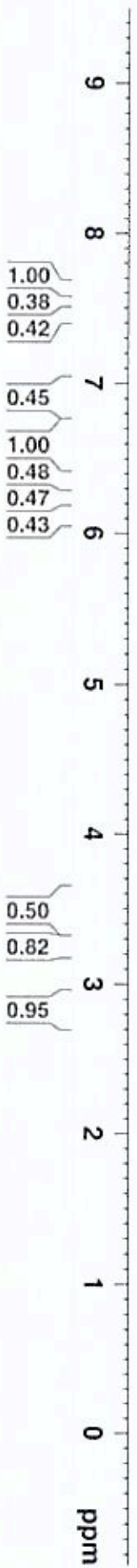


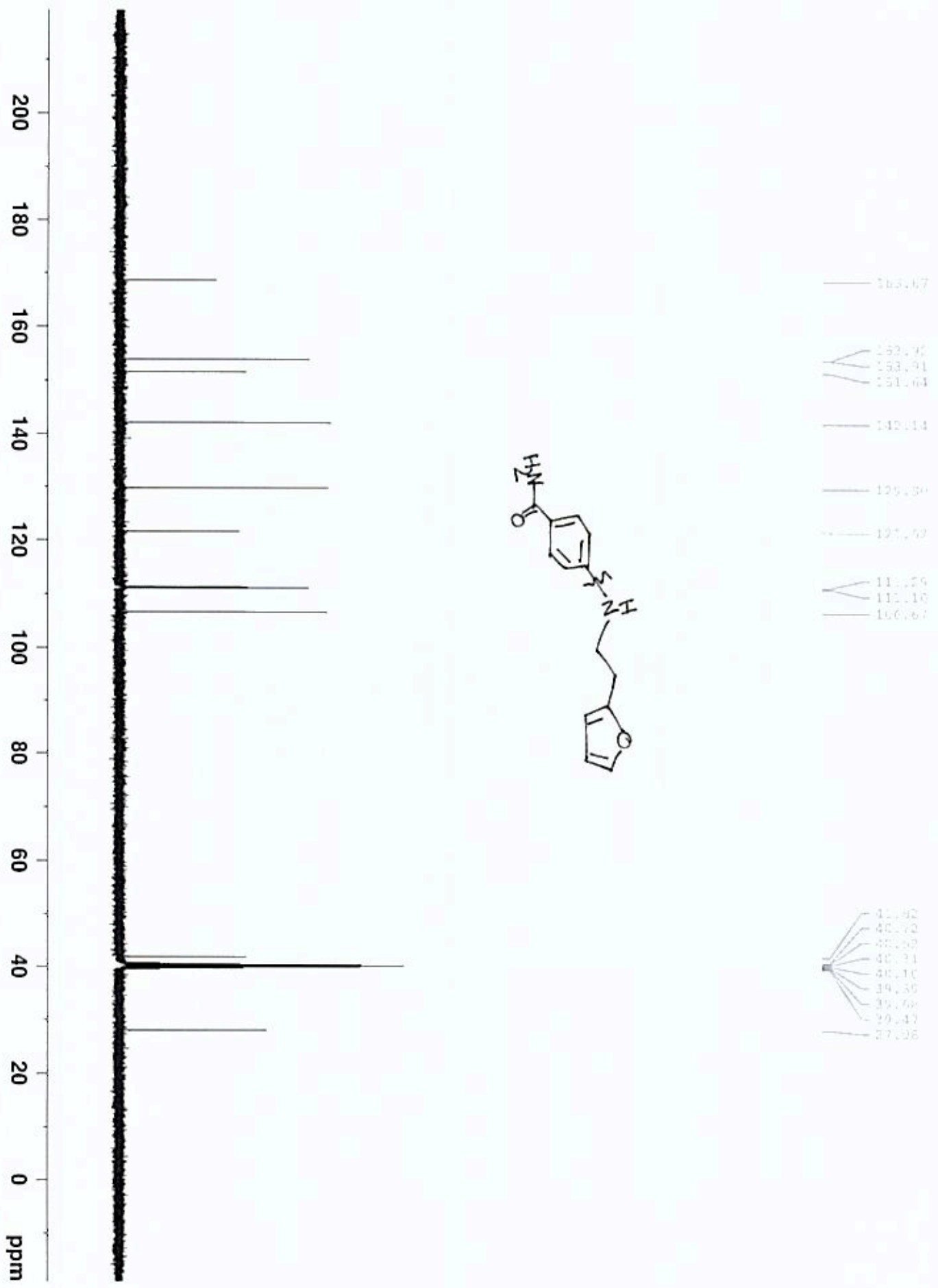


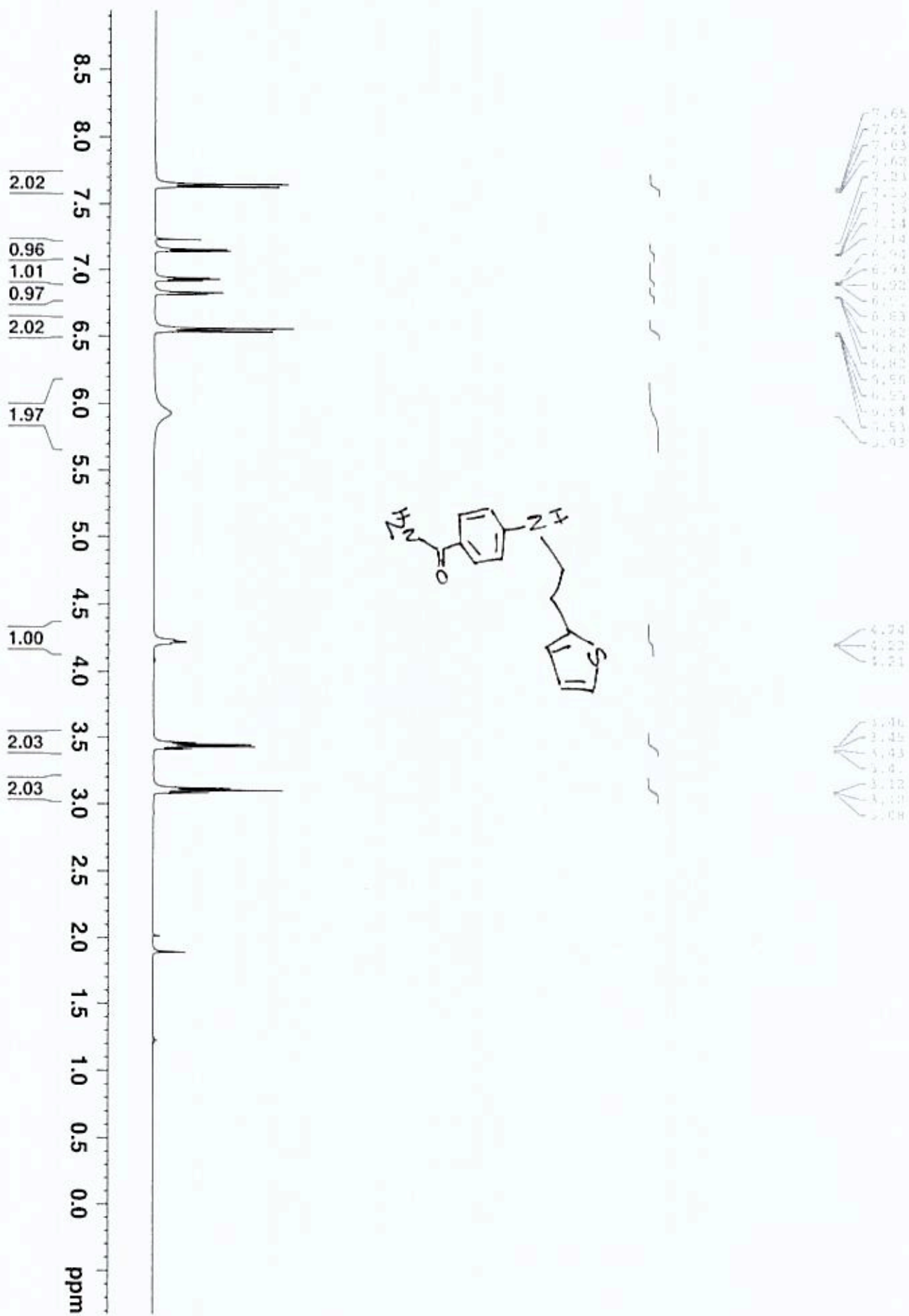


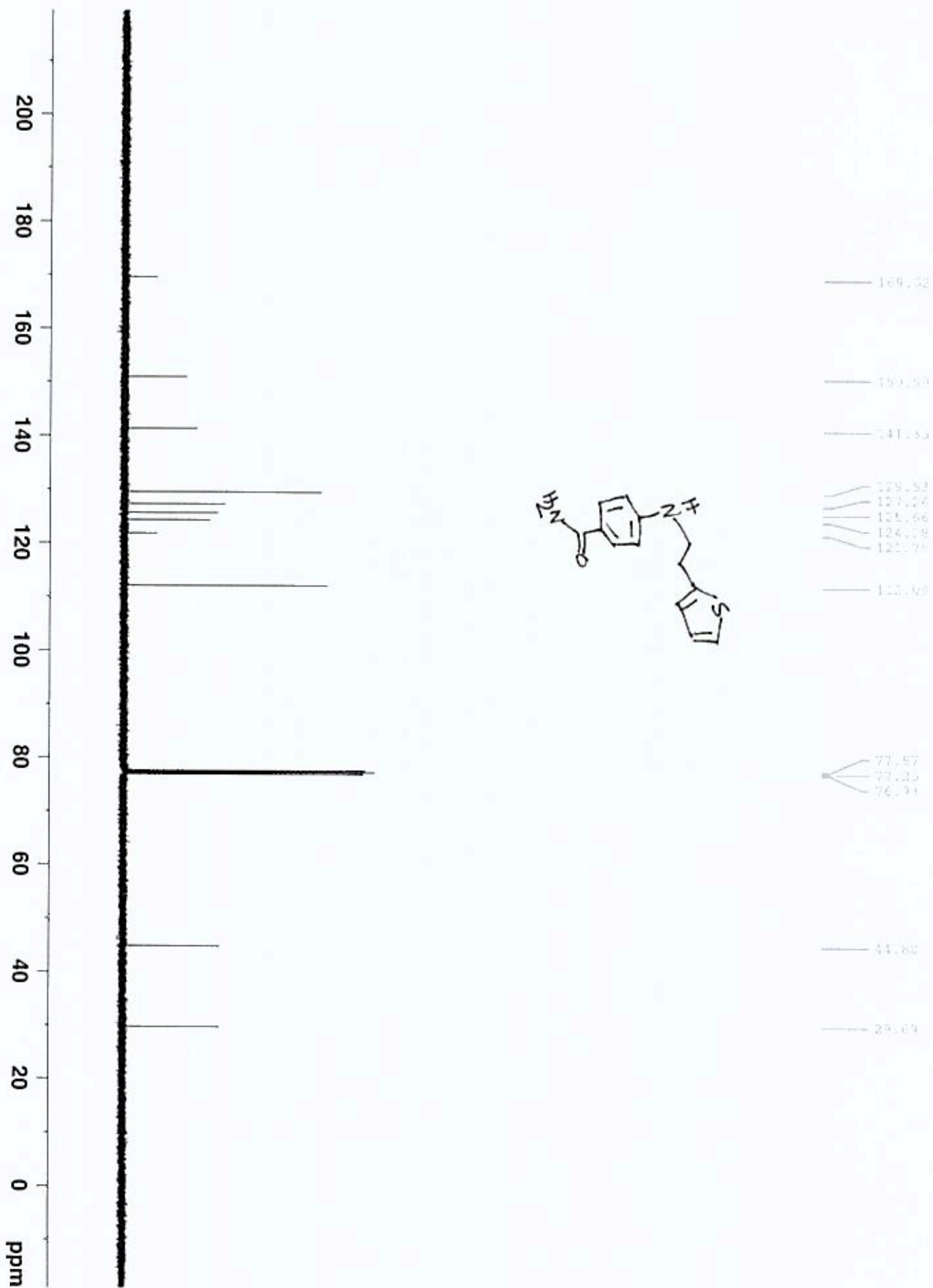
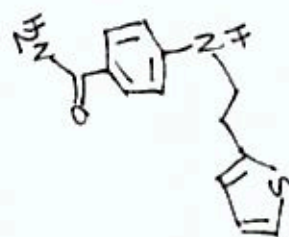


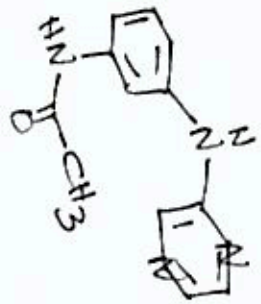
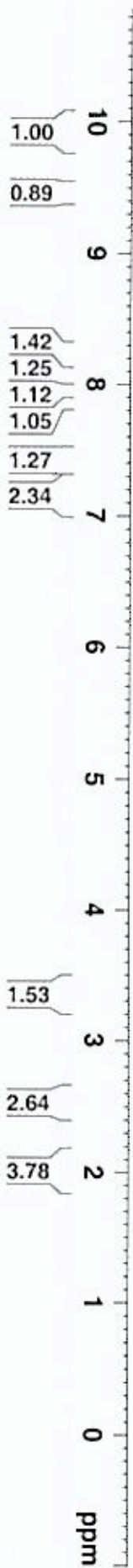


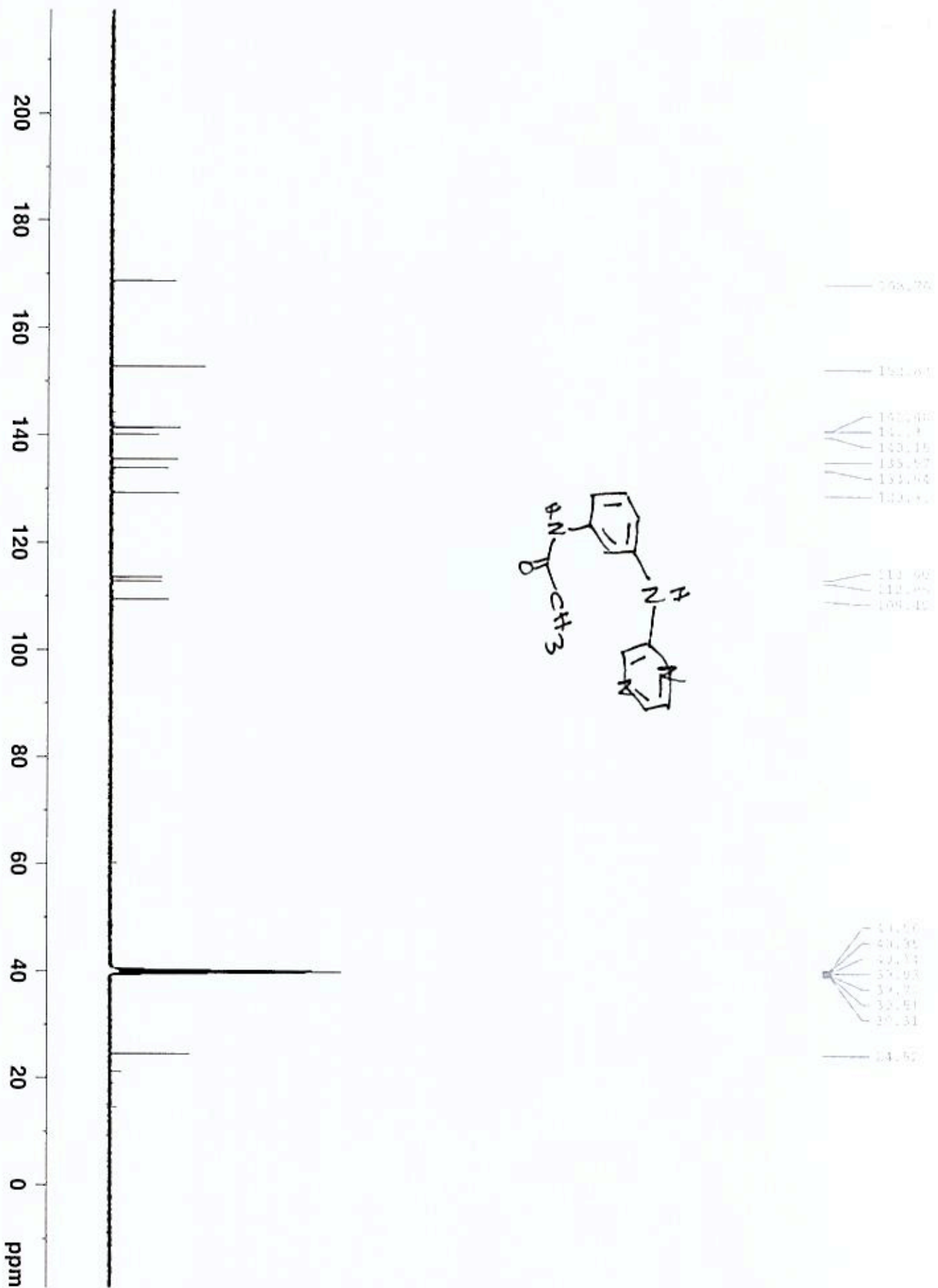
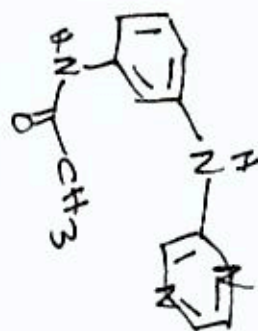


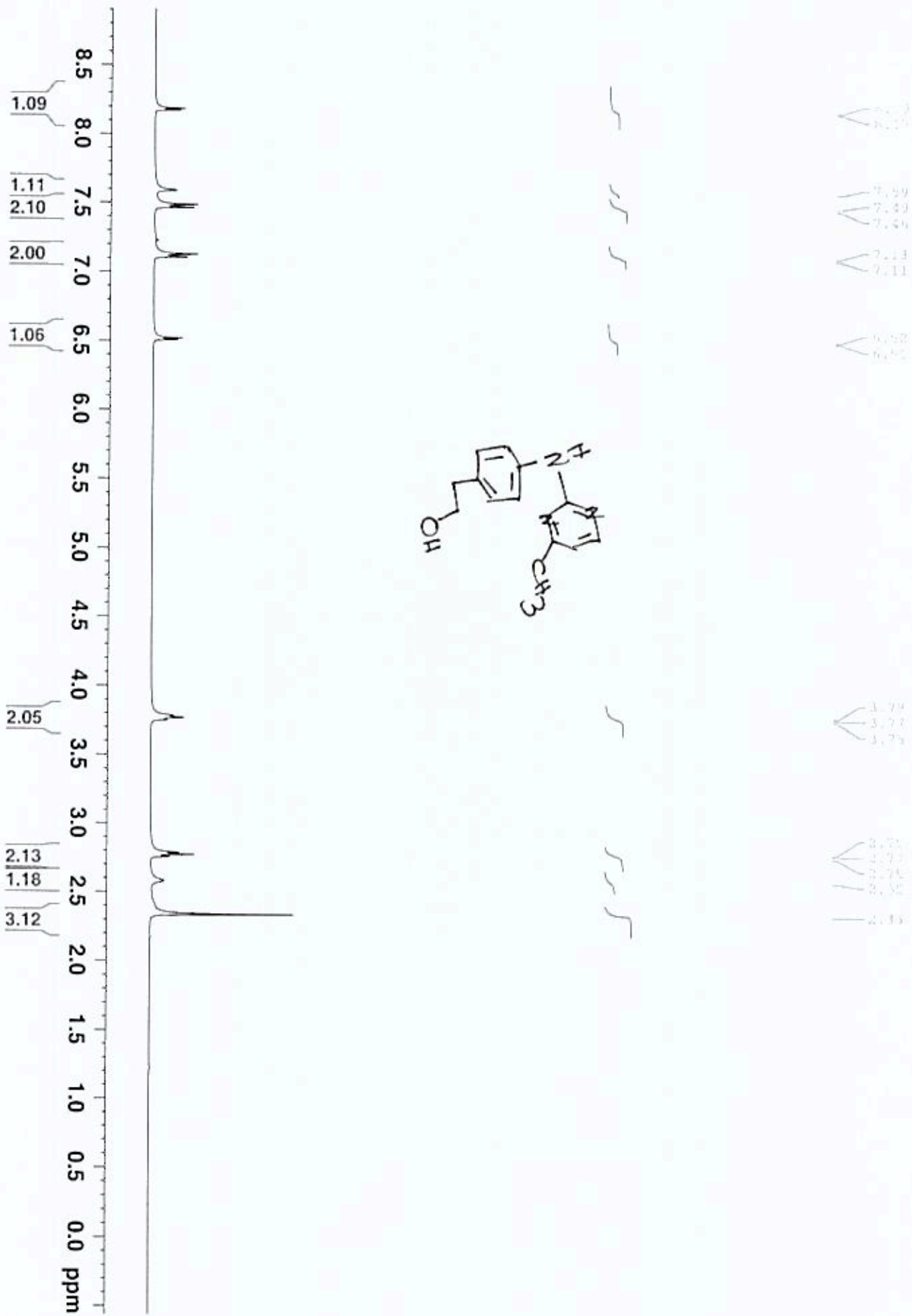




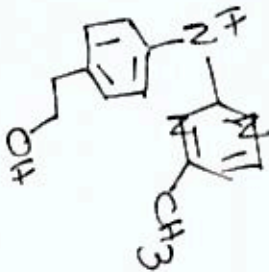
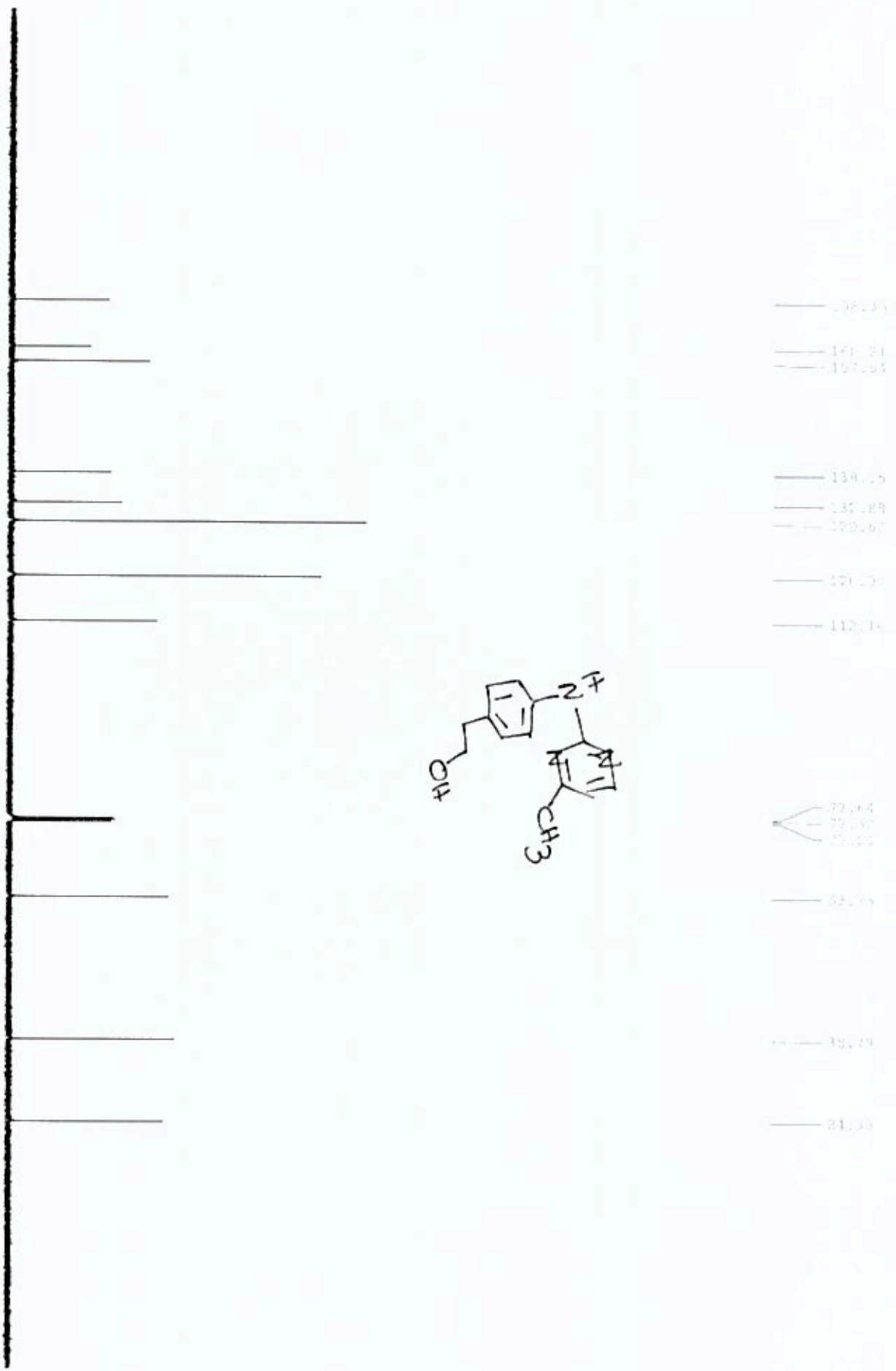


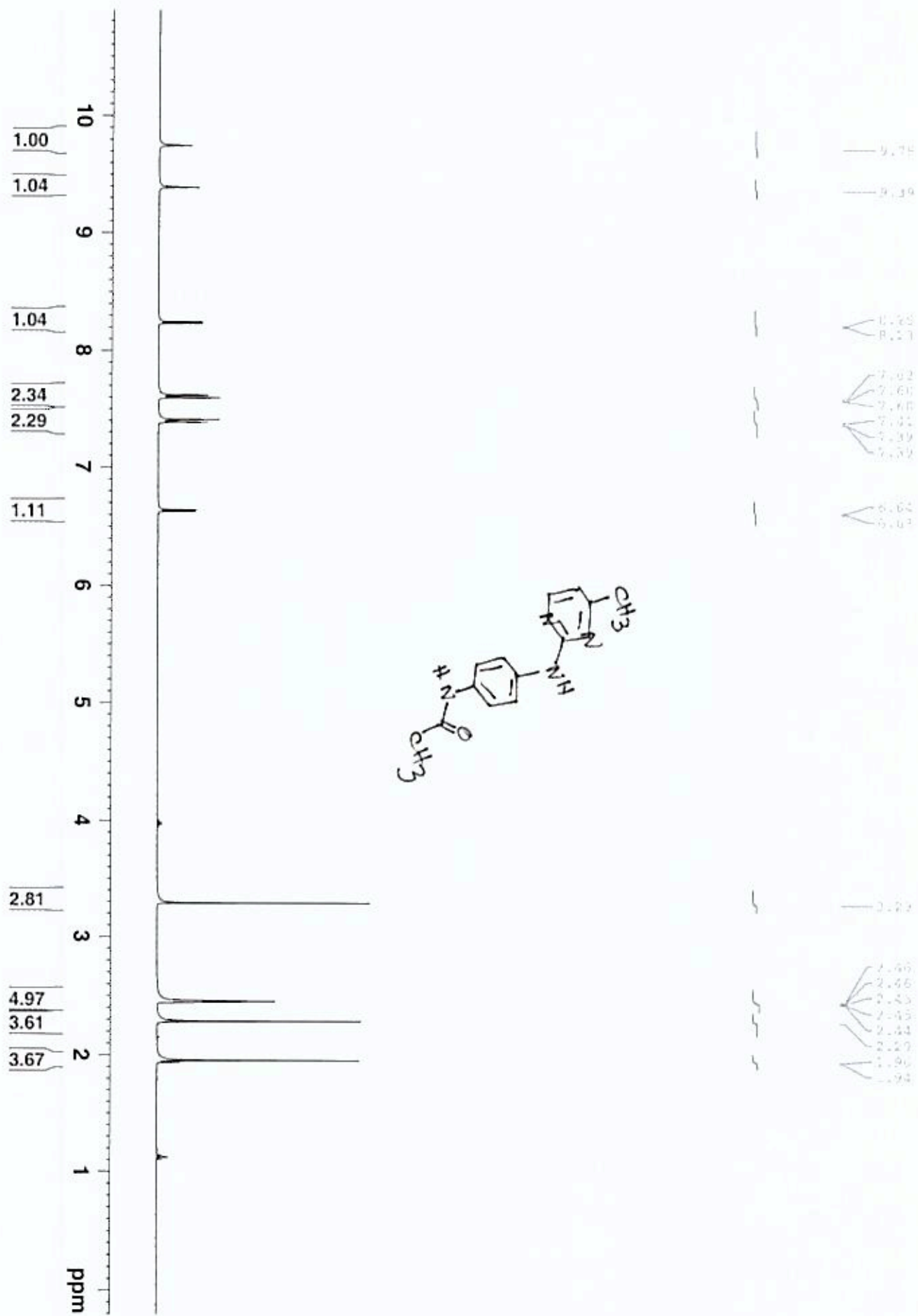


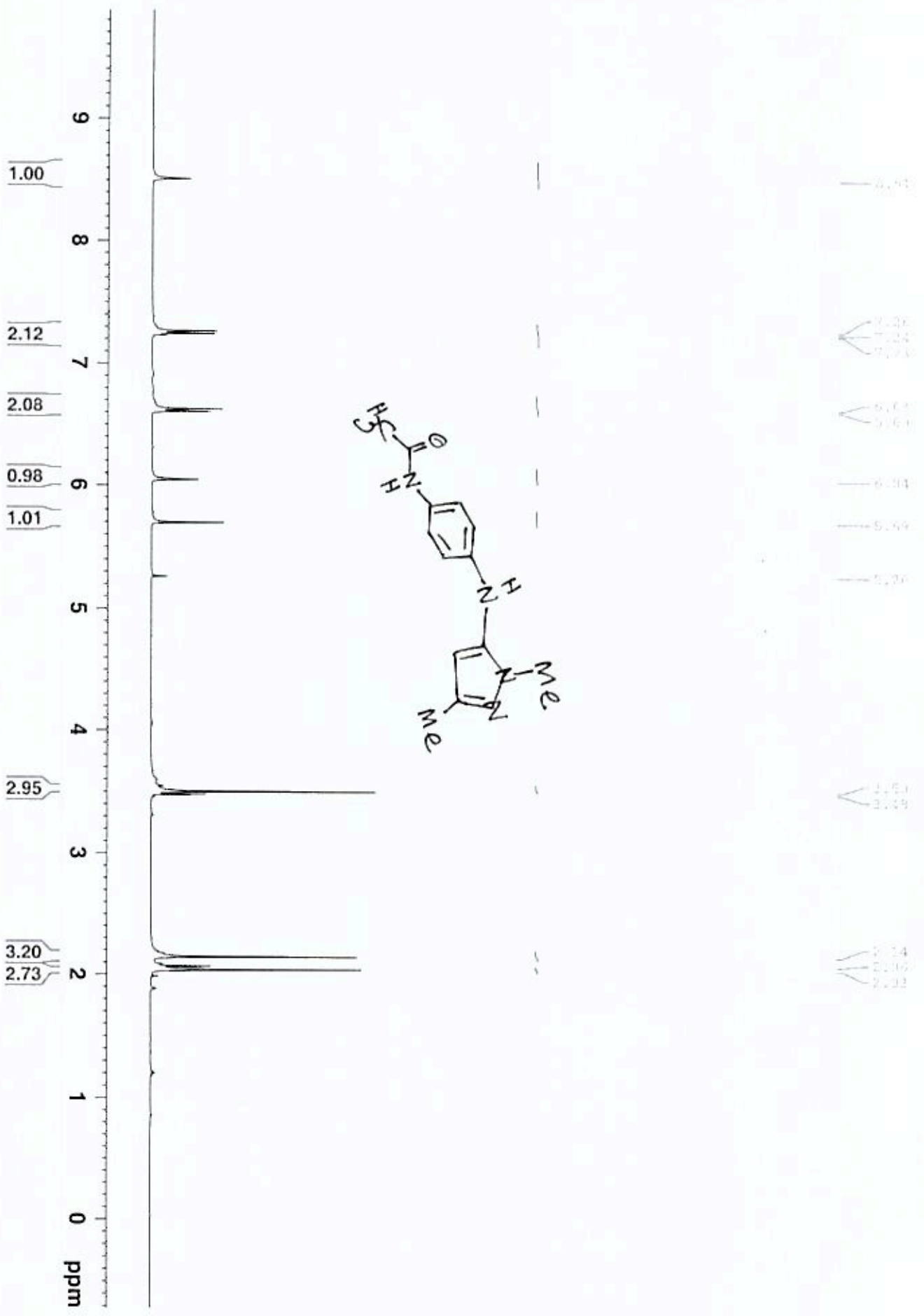


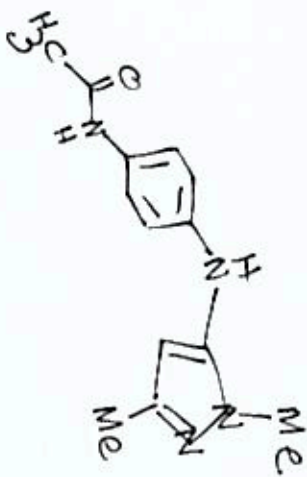
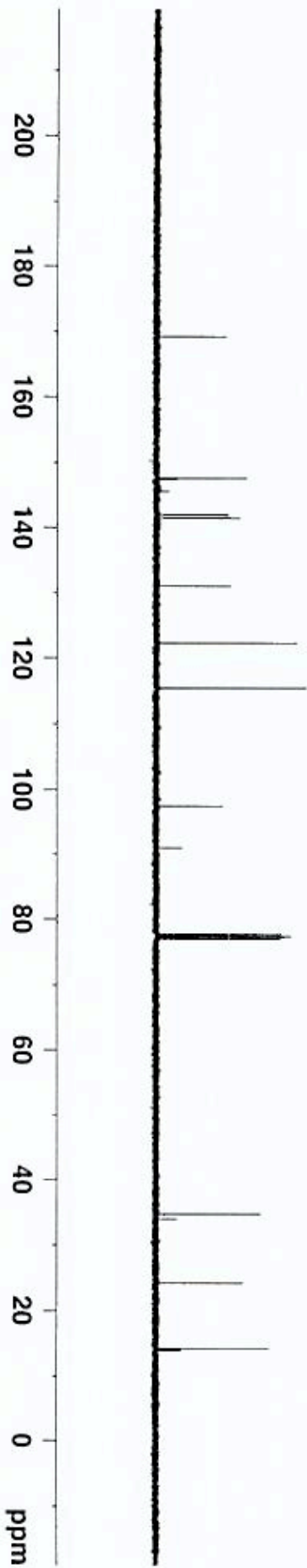


200
180
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120
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80
60
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20
0
ppm

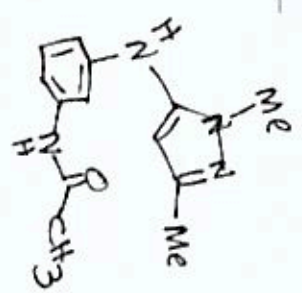


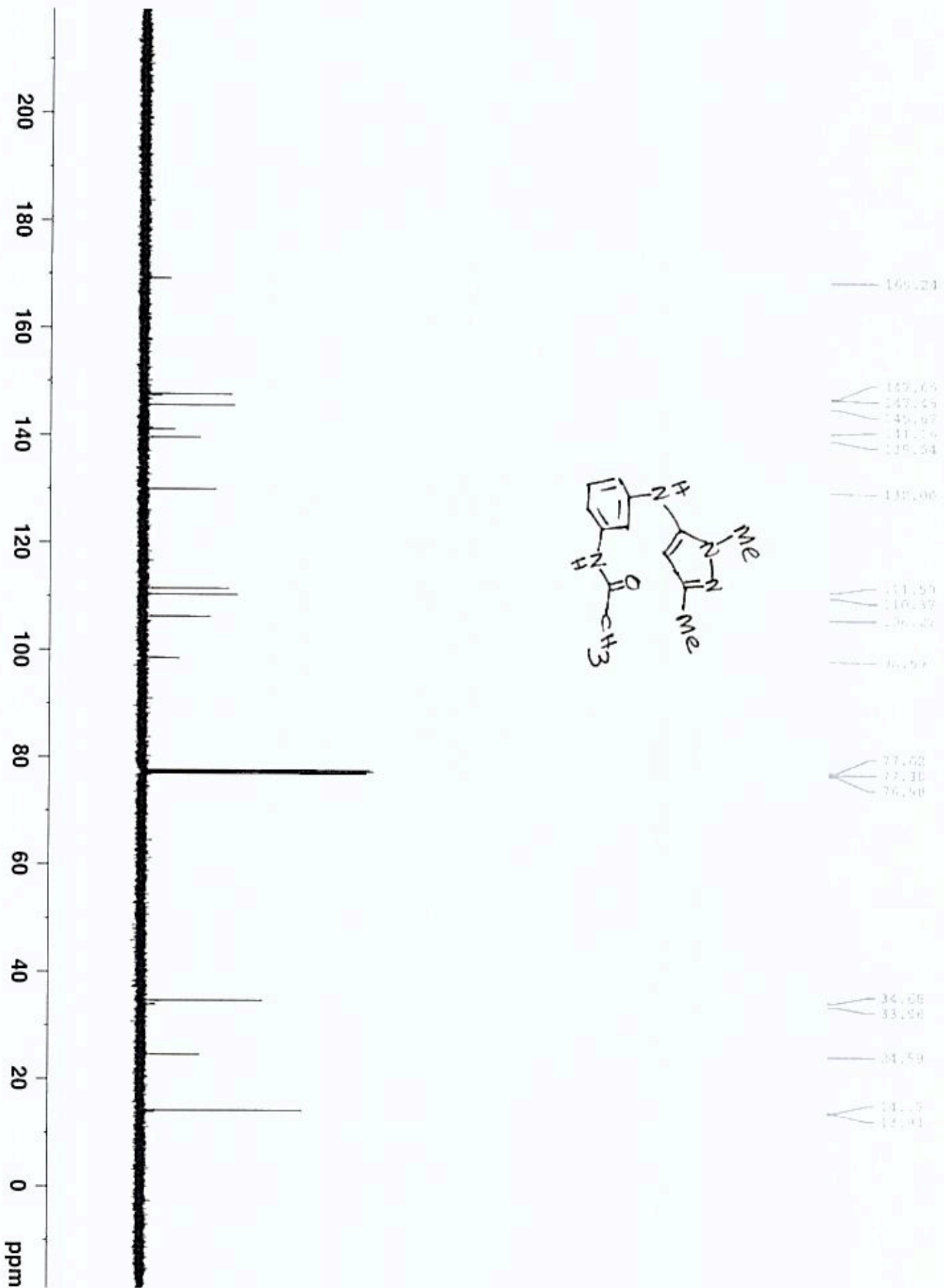


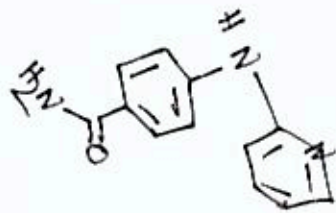
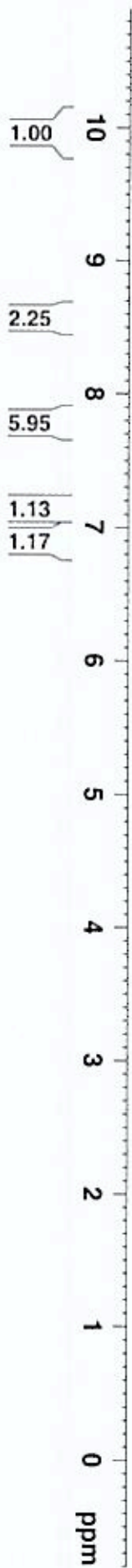


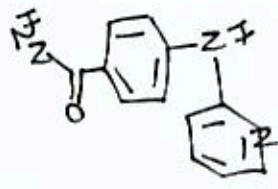


- 167.34
- 157.61
- 147.91
- 141.48
- 132.11
- 120.06
- 119.51
- 97.10
- 77.68
- 77.11
- 77.02
- 33.60
- 25.24
- 11.20



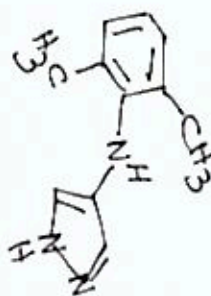
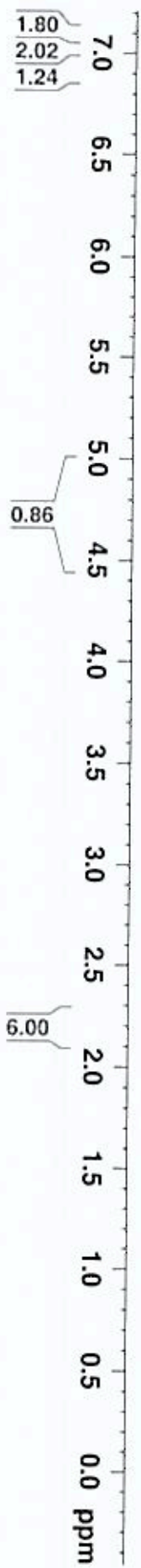


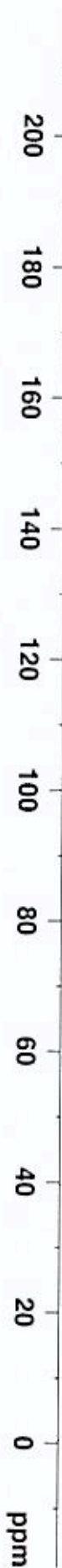
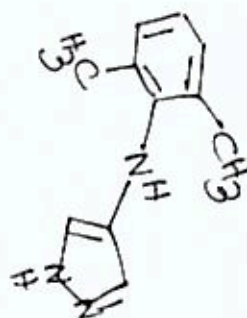




- 169.89
- 166.14
- 165.29
- 143.11
- 128.53
- 127.06
- 117.88
- 113.43

- 40.55
- 40.34
- 40.11
- 39.94
- 39.72
- 39.50
- 39.28
- 39.06

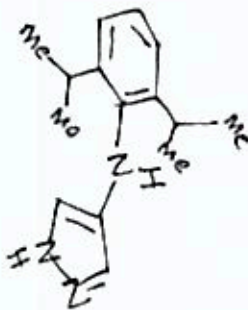
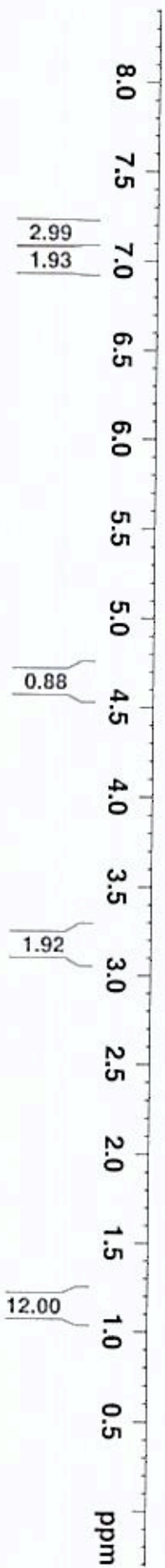


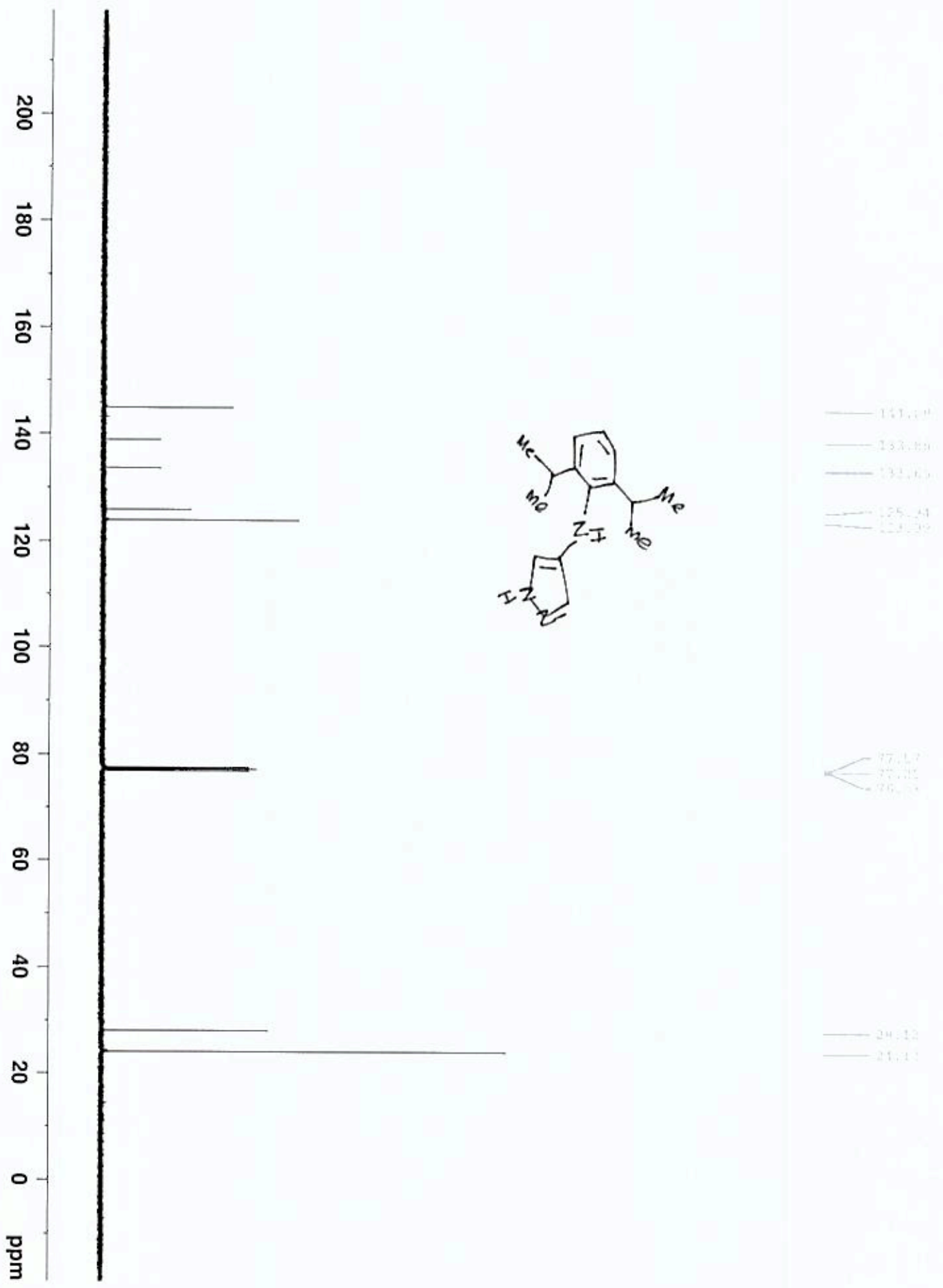


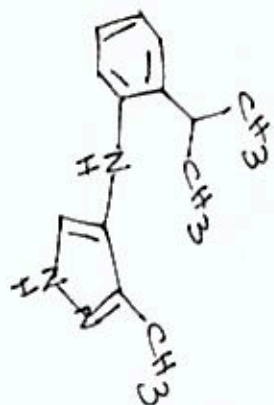
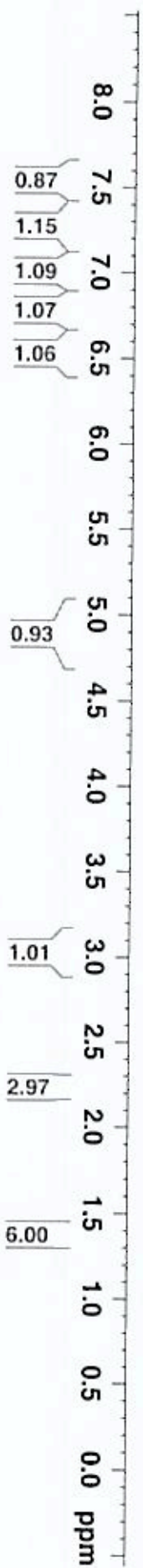
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 129.01
 121.94

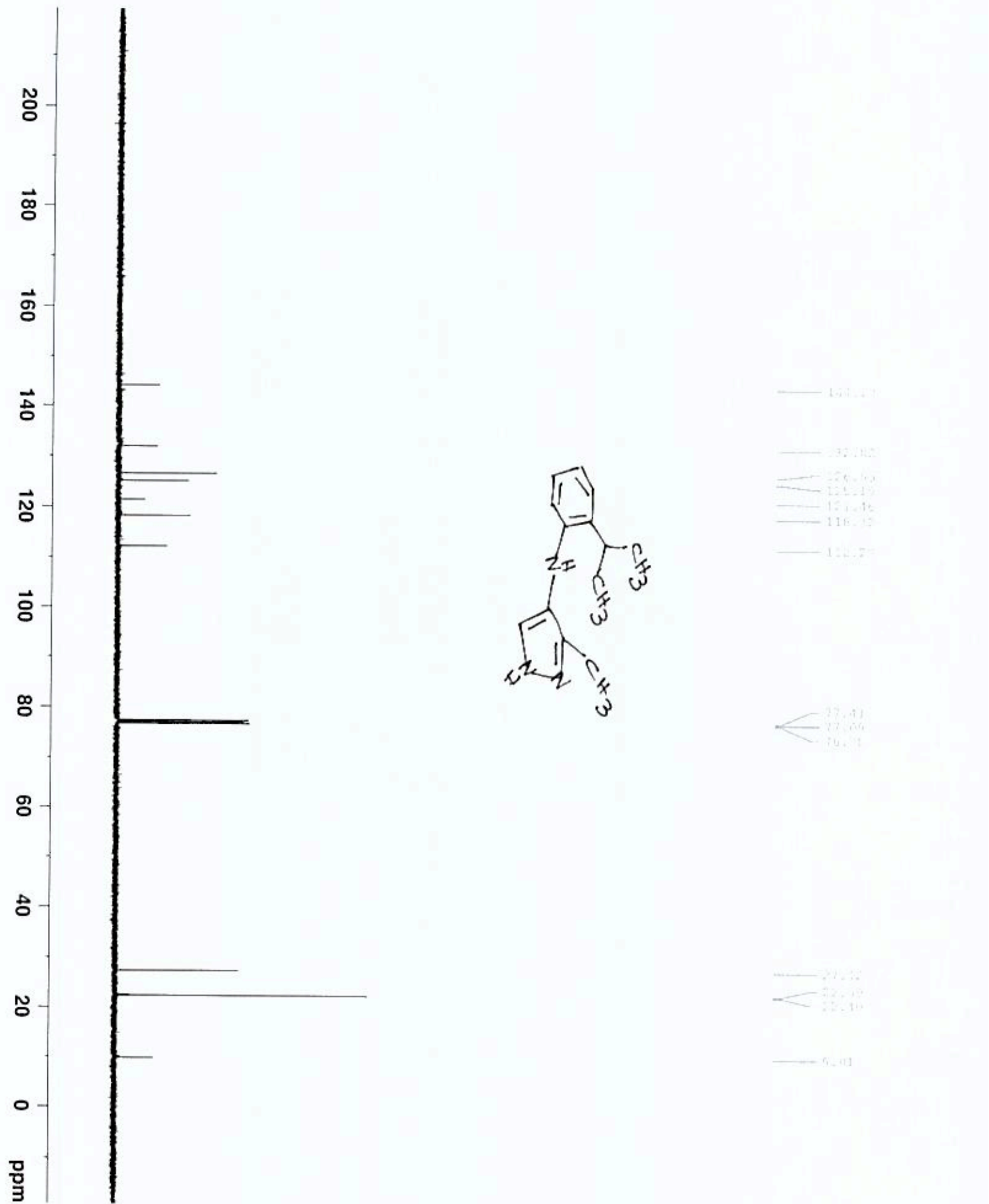
77.00
 77.00
 77.00

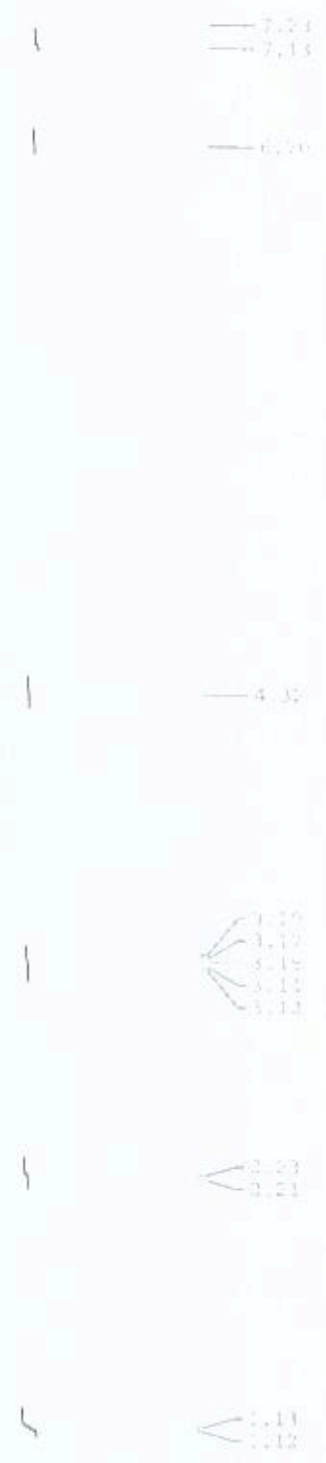
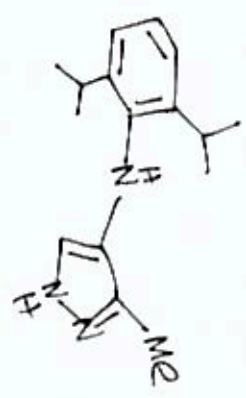
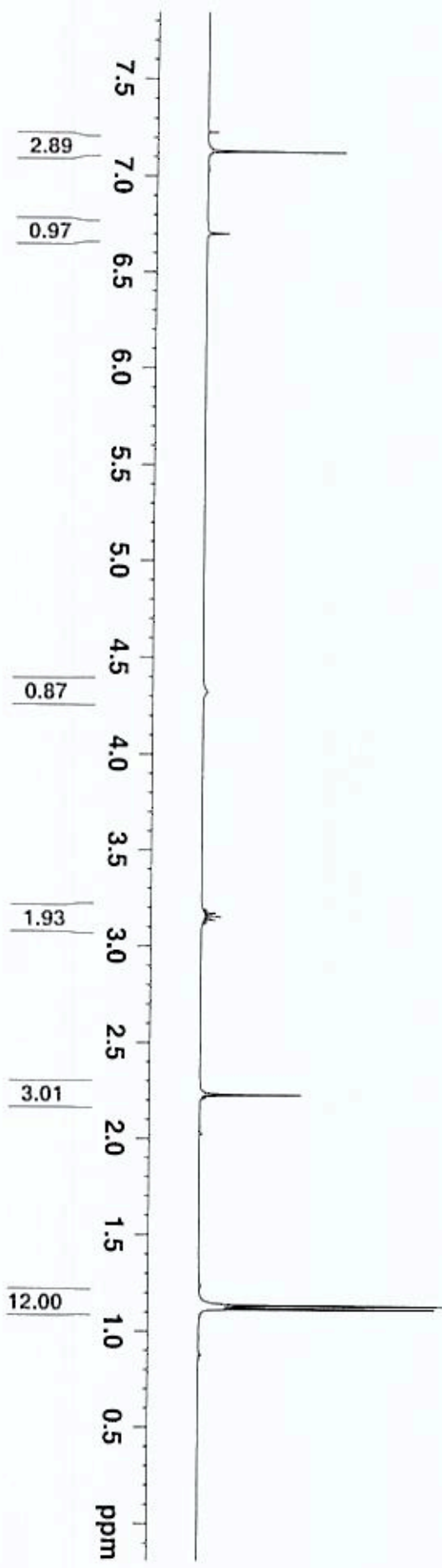
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 14.88

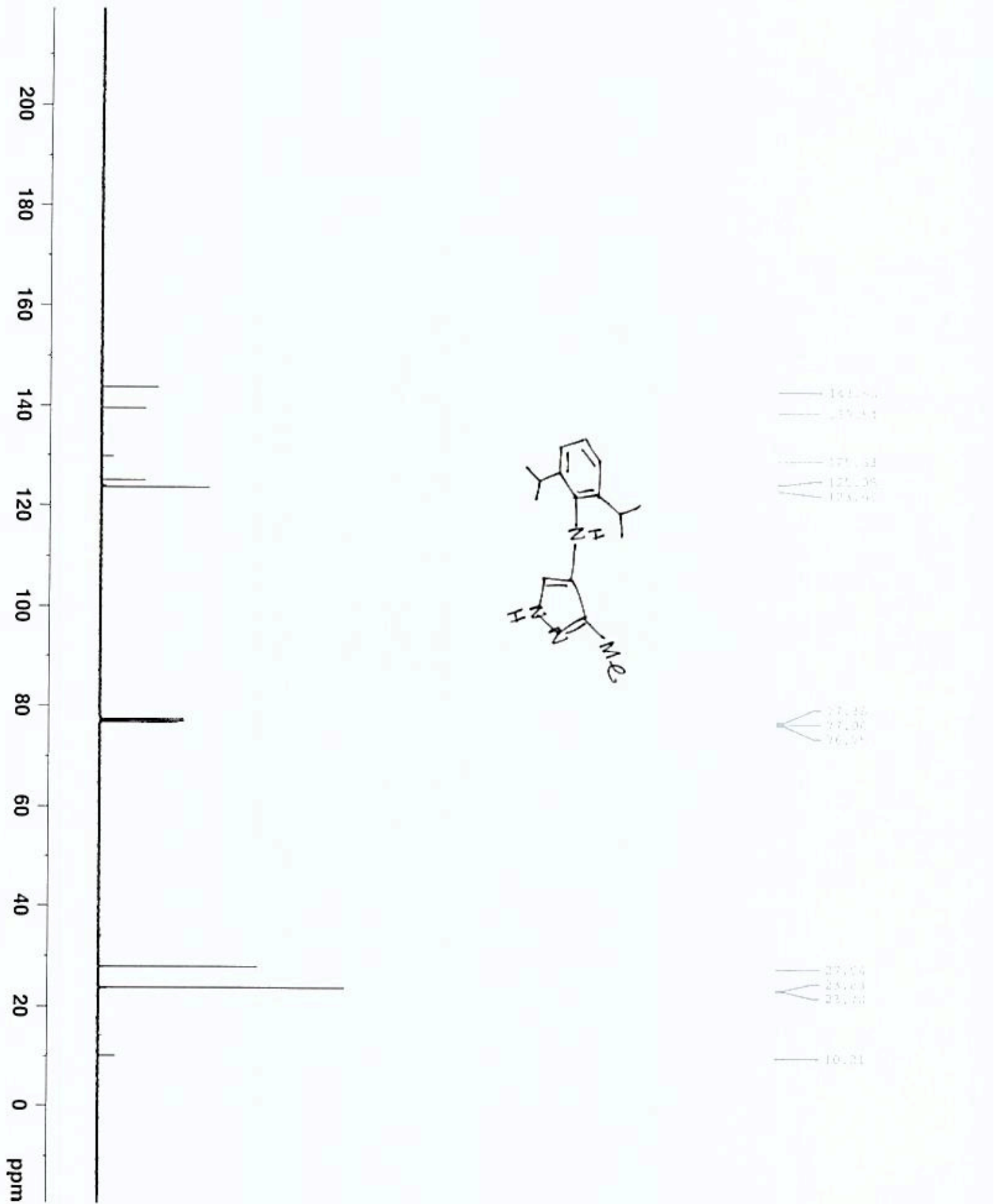










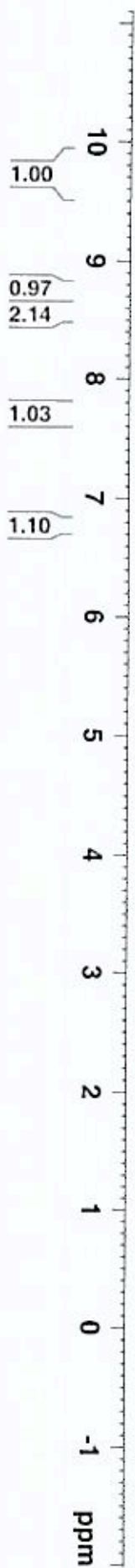


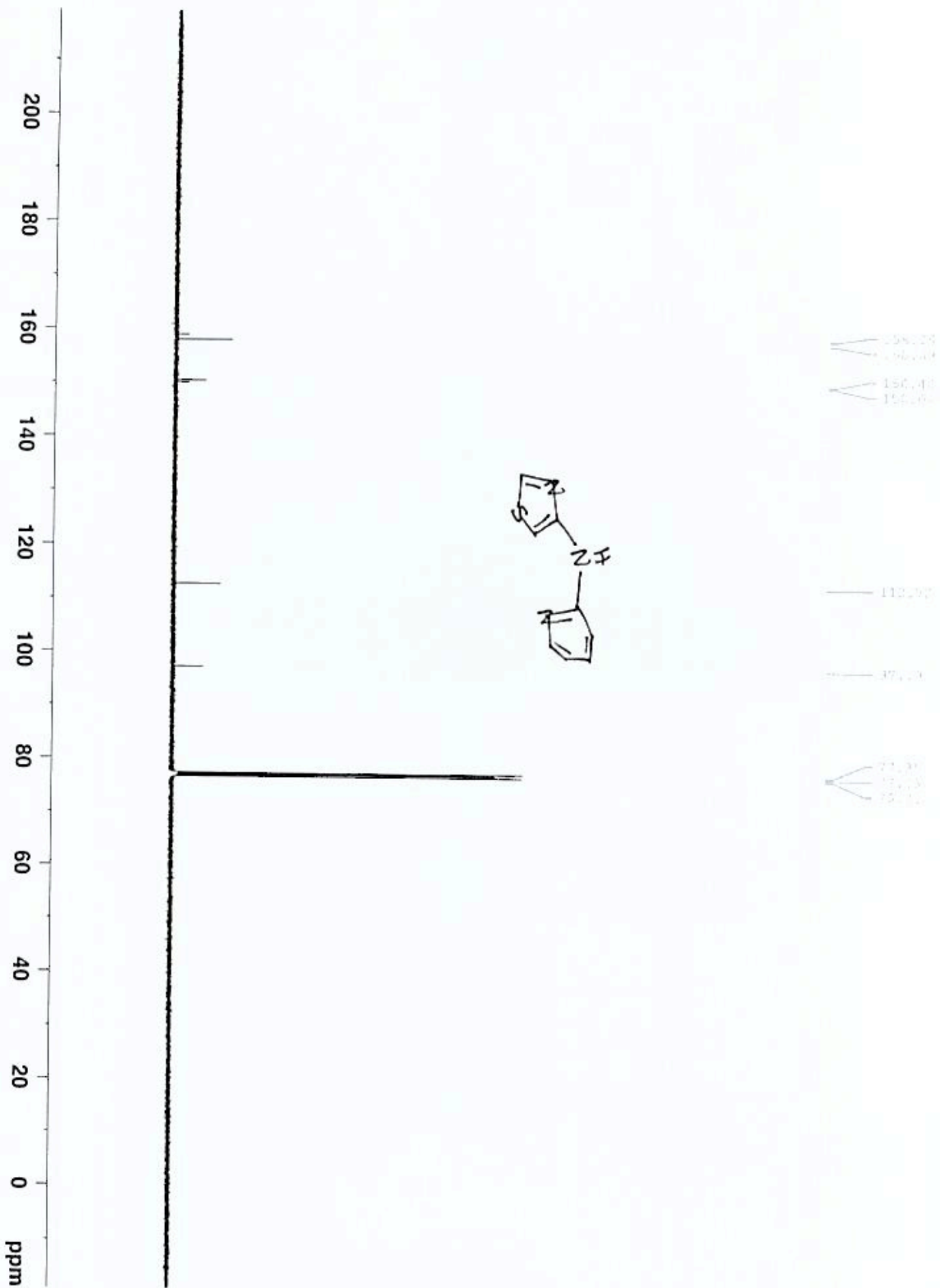


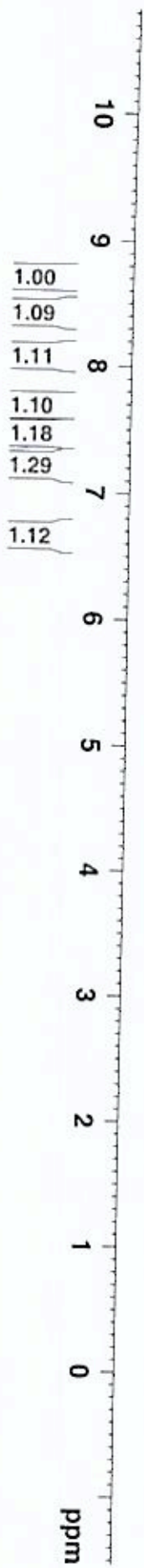
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20
0
ppm



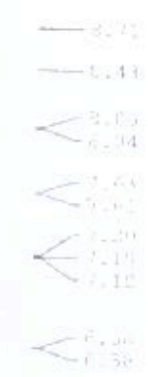
- 151.99
- 151.97
- 142.59
- 142.46
- 121.95
- 121.93
- 121.91
- 91.23
- 77.46
- 77.42
- 77.38

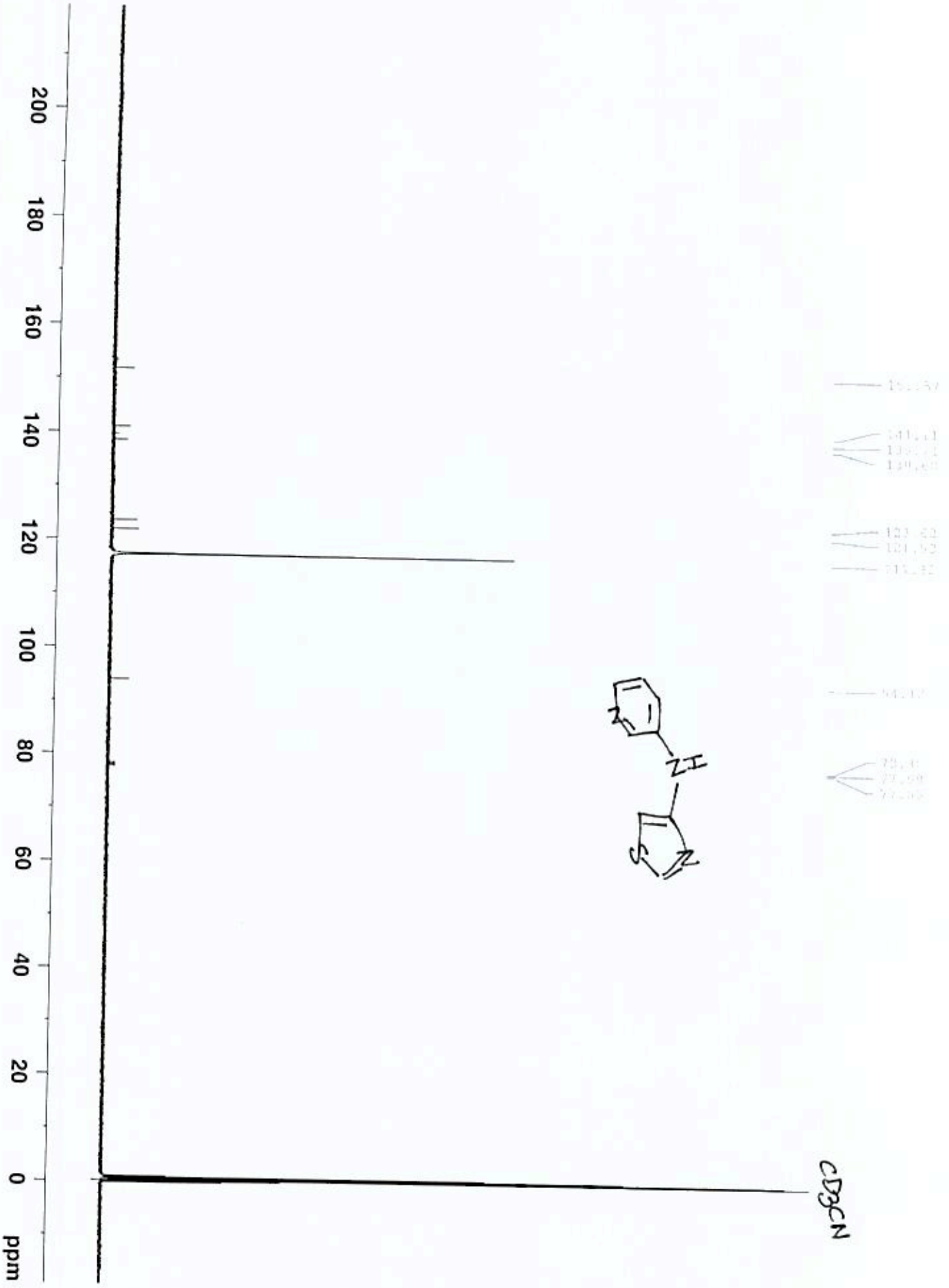


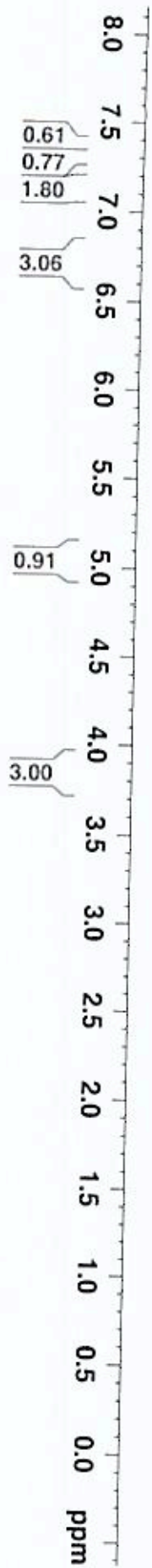




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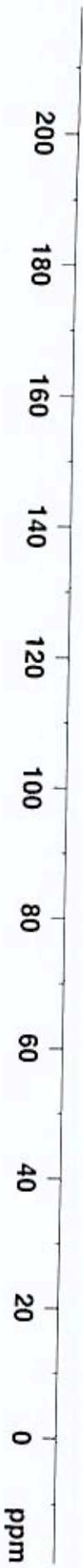




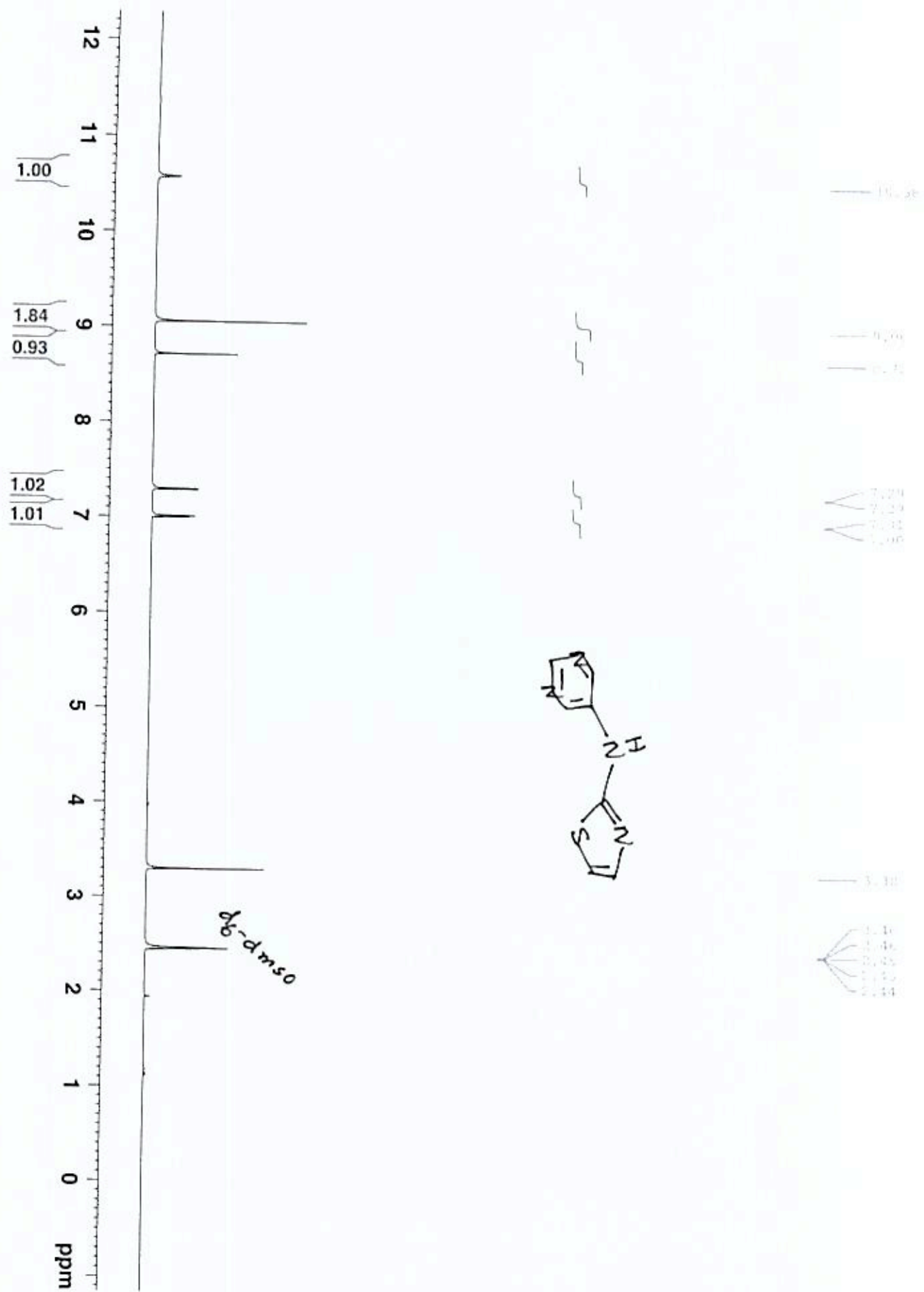


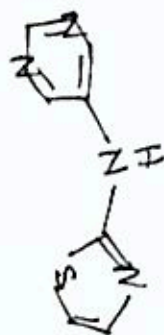
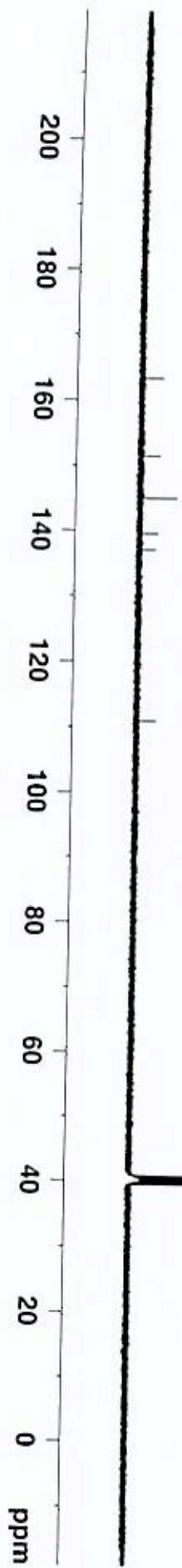
3.06

3.00



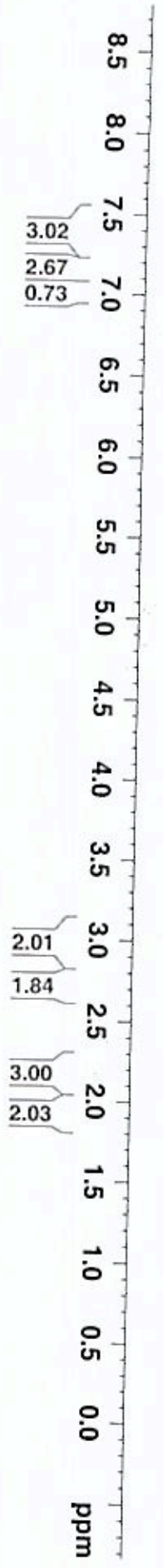
- 139.38
- 135.34
- 130.33
- 124.77
- 116.36
- 113.55
- 77.4
- 77.00
- 76.53
- 39.25

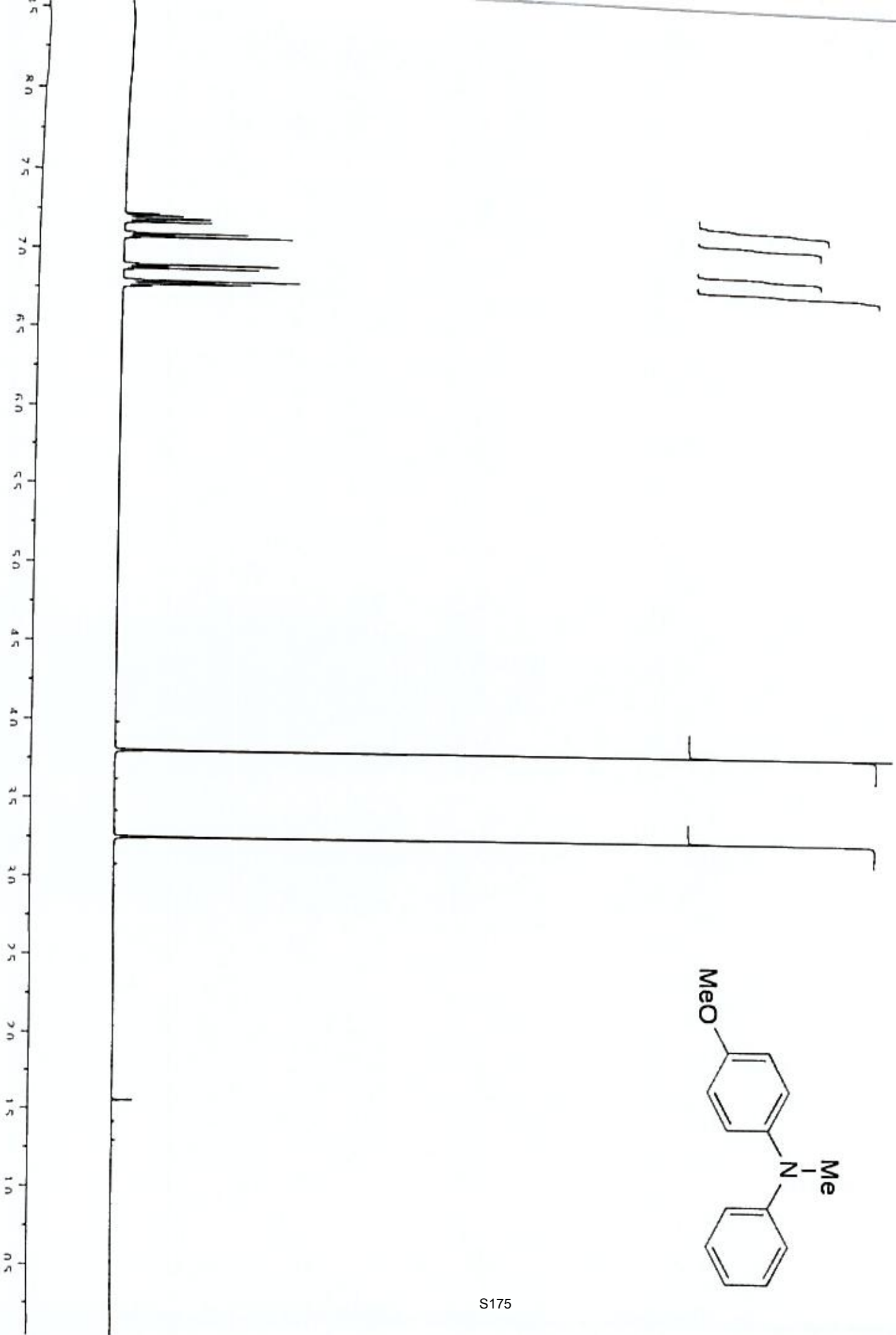
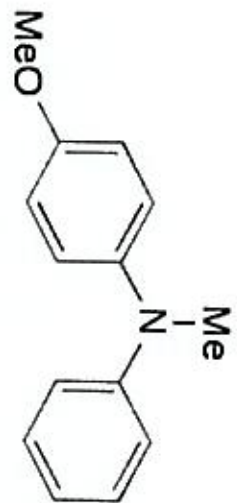




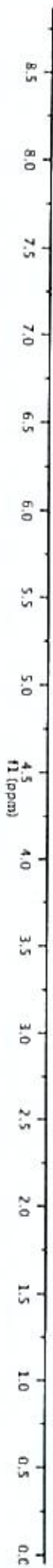
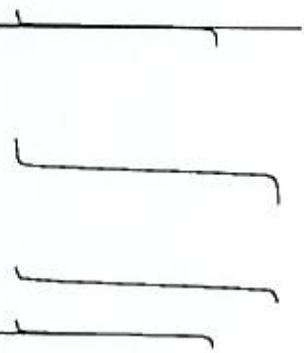
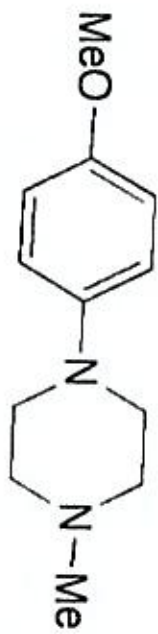
- 167.280
- 156.180
- 145.501
- 137.077
- 131.511
- 111.115

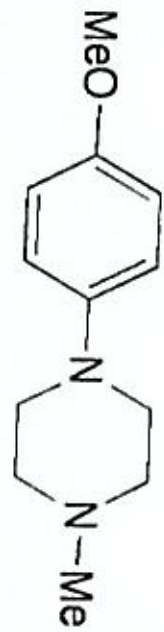
- 17.108
- 16.708
- 16.308
- 15.908
- 15.508
- 15.108
- 14.708
- 14.308
- 13.908
- 13.508
- 13.108
- 12.708
- 12.308
- 11.908
- 11.508
- 11.108
- 10.708
- 10.308
- 9.908
- 9.508
- 9.108
- 8.708
- 8.308
- 7.908
- 7.508
- 7.108
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- 4.708
- 4.308
- 3.908
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- 1.508
- 1.108
- 0.708
- 0.308
- 0.108





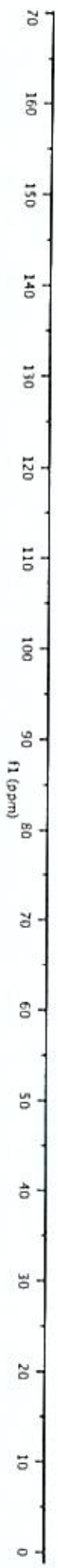


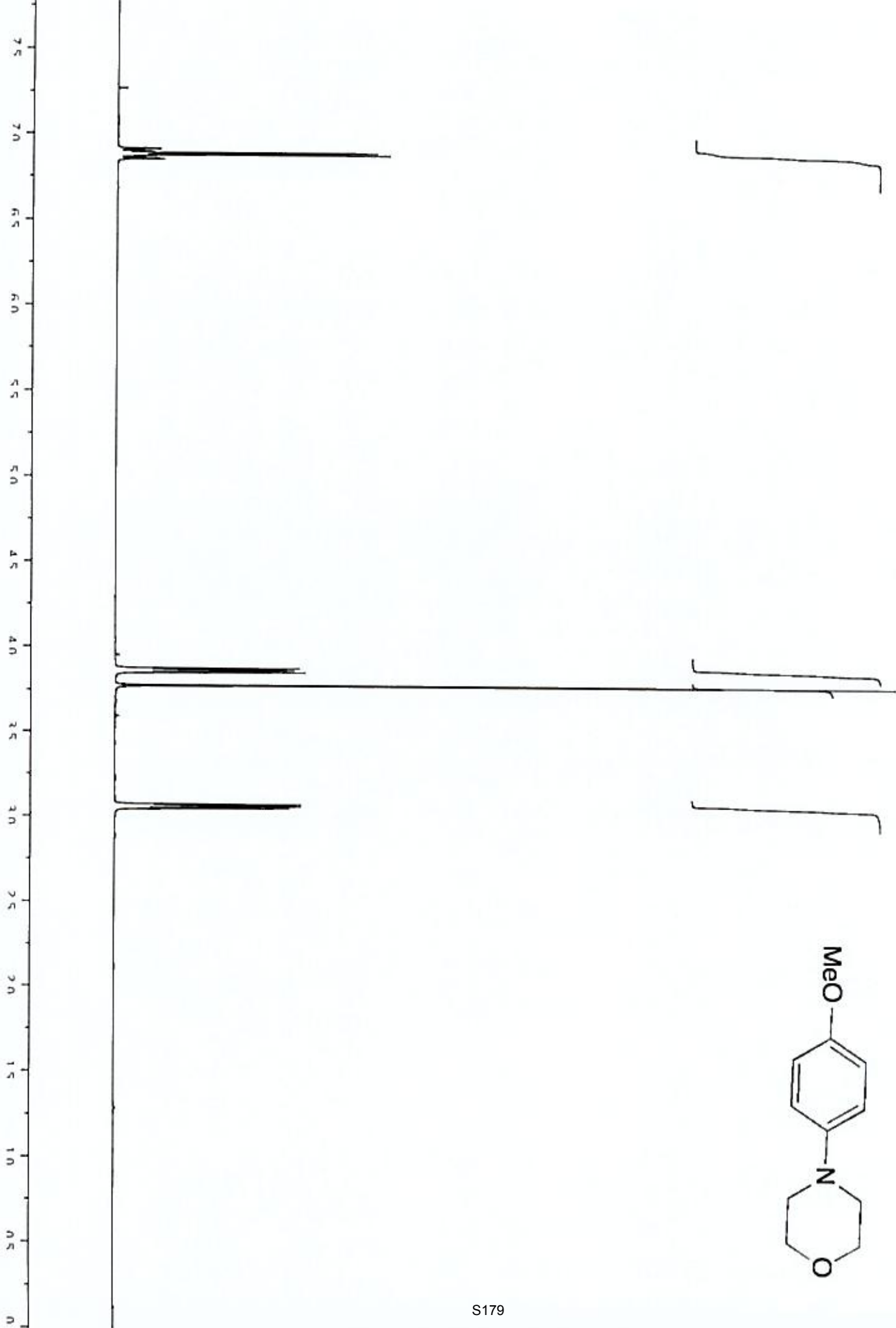
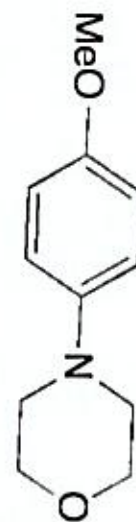


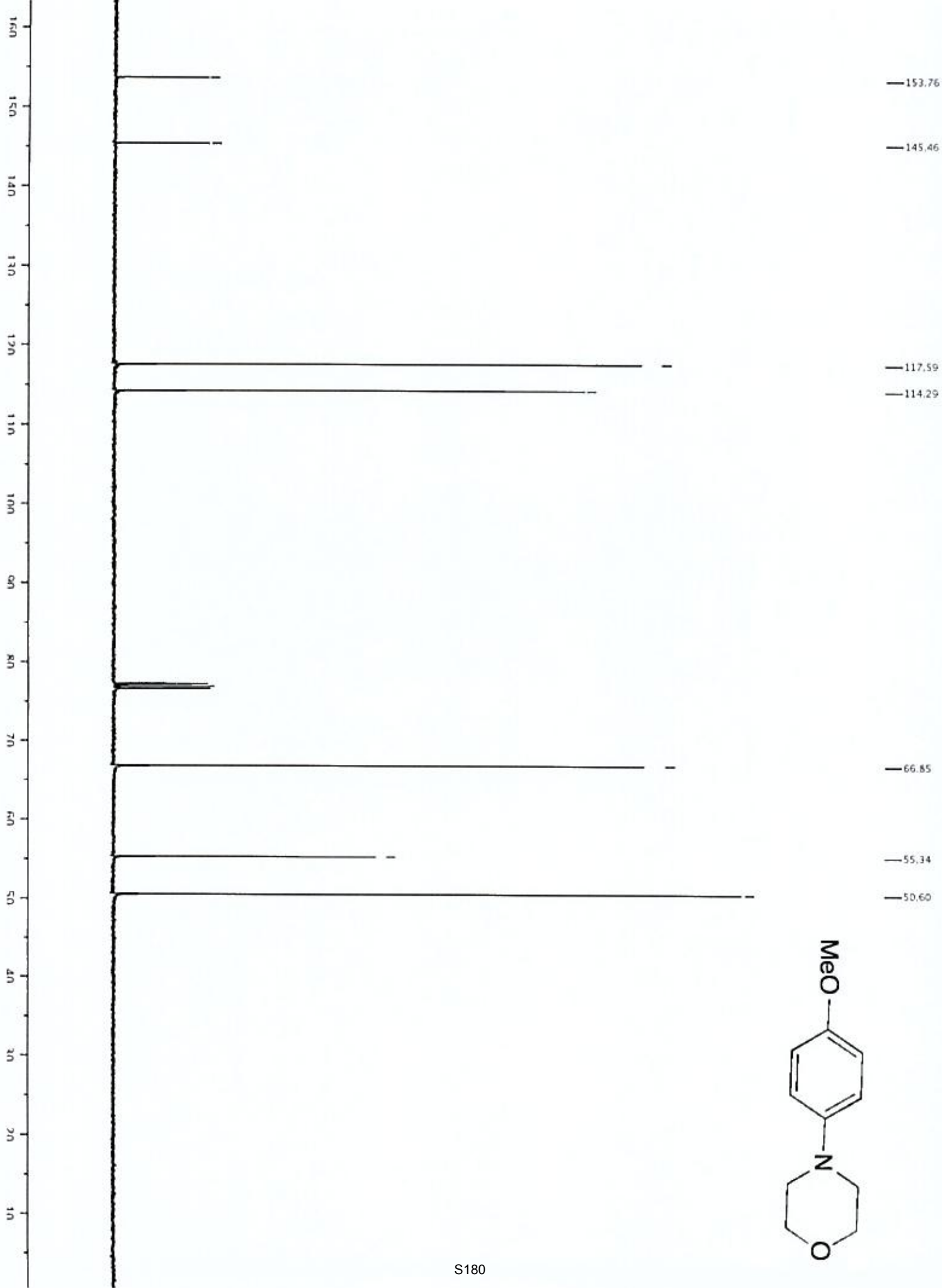


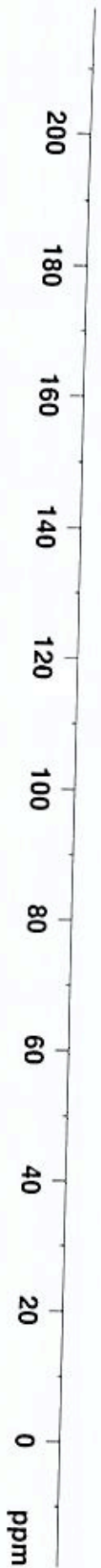
— 153.45
— 145.39
— 117.83
— 114.10

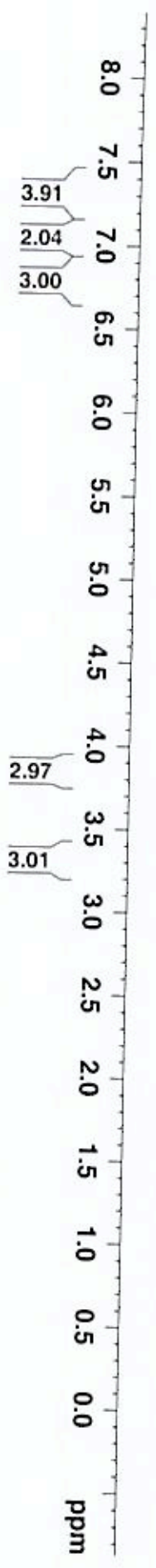
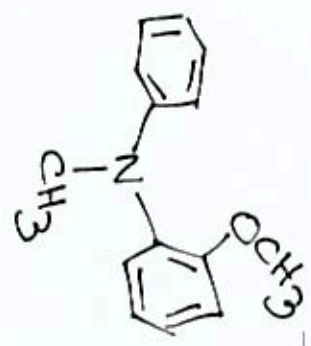
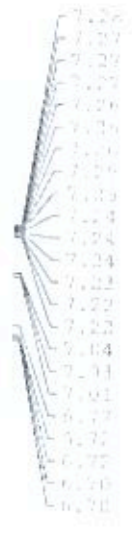
55.20
54.39
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45.89

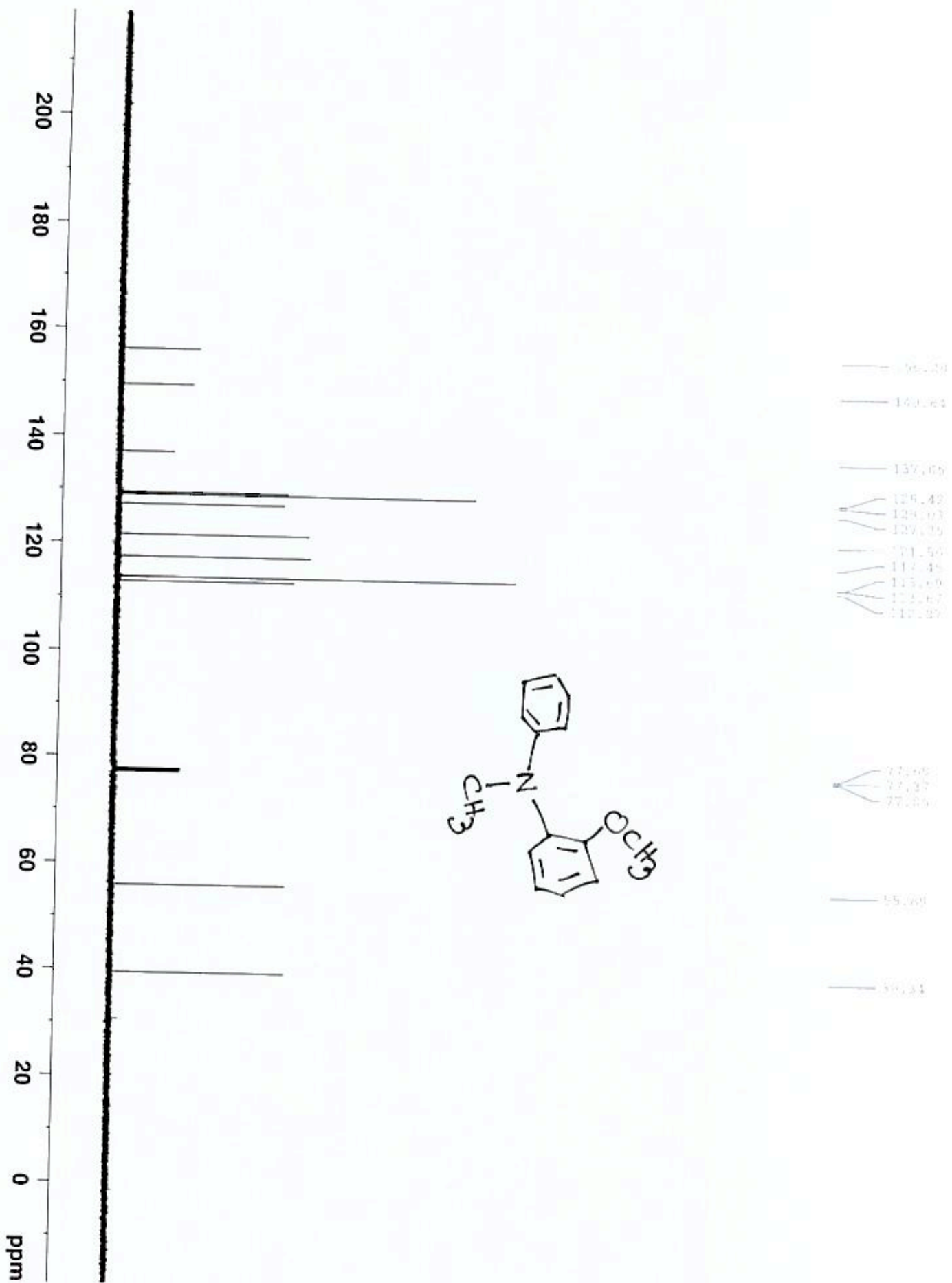


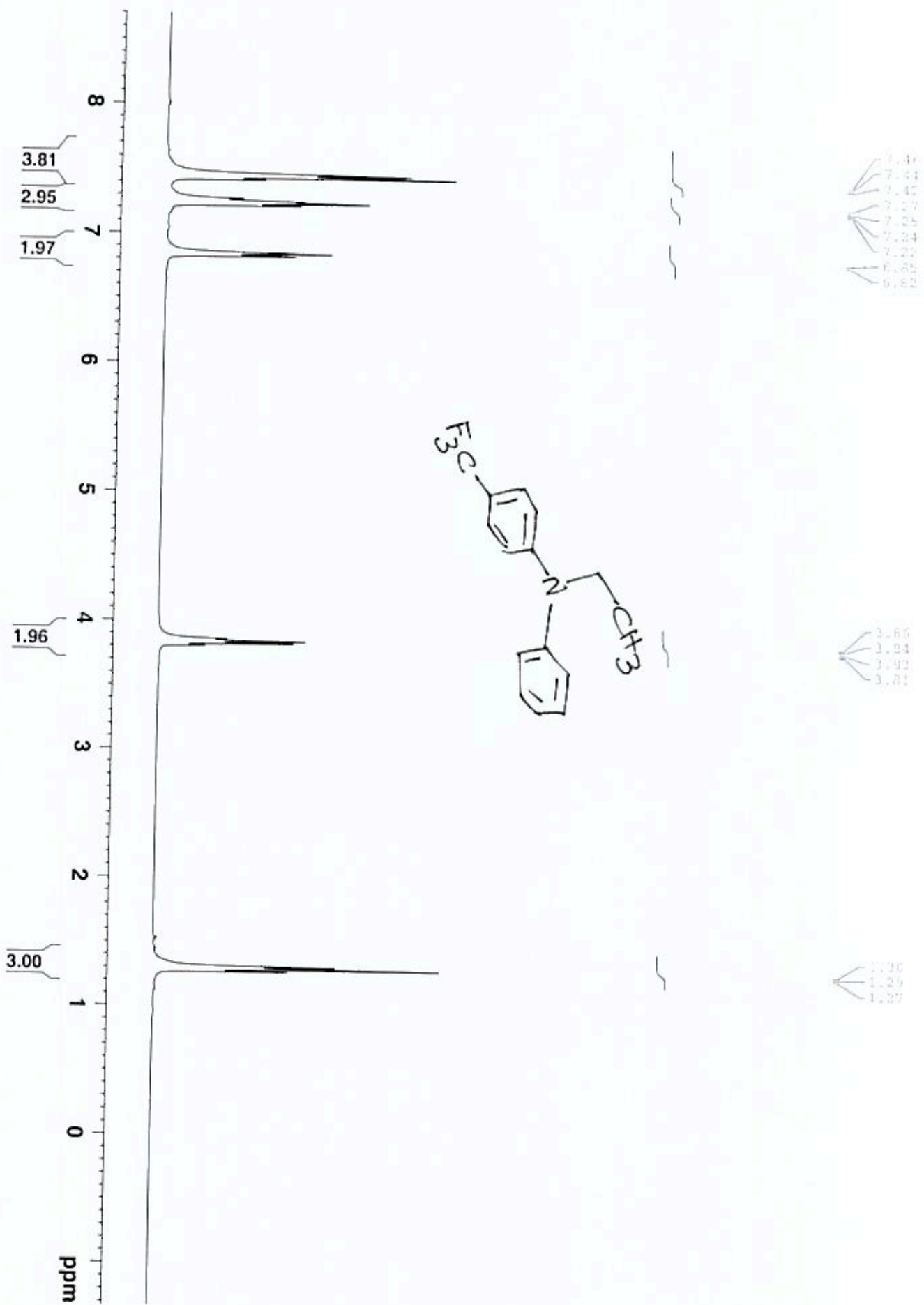


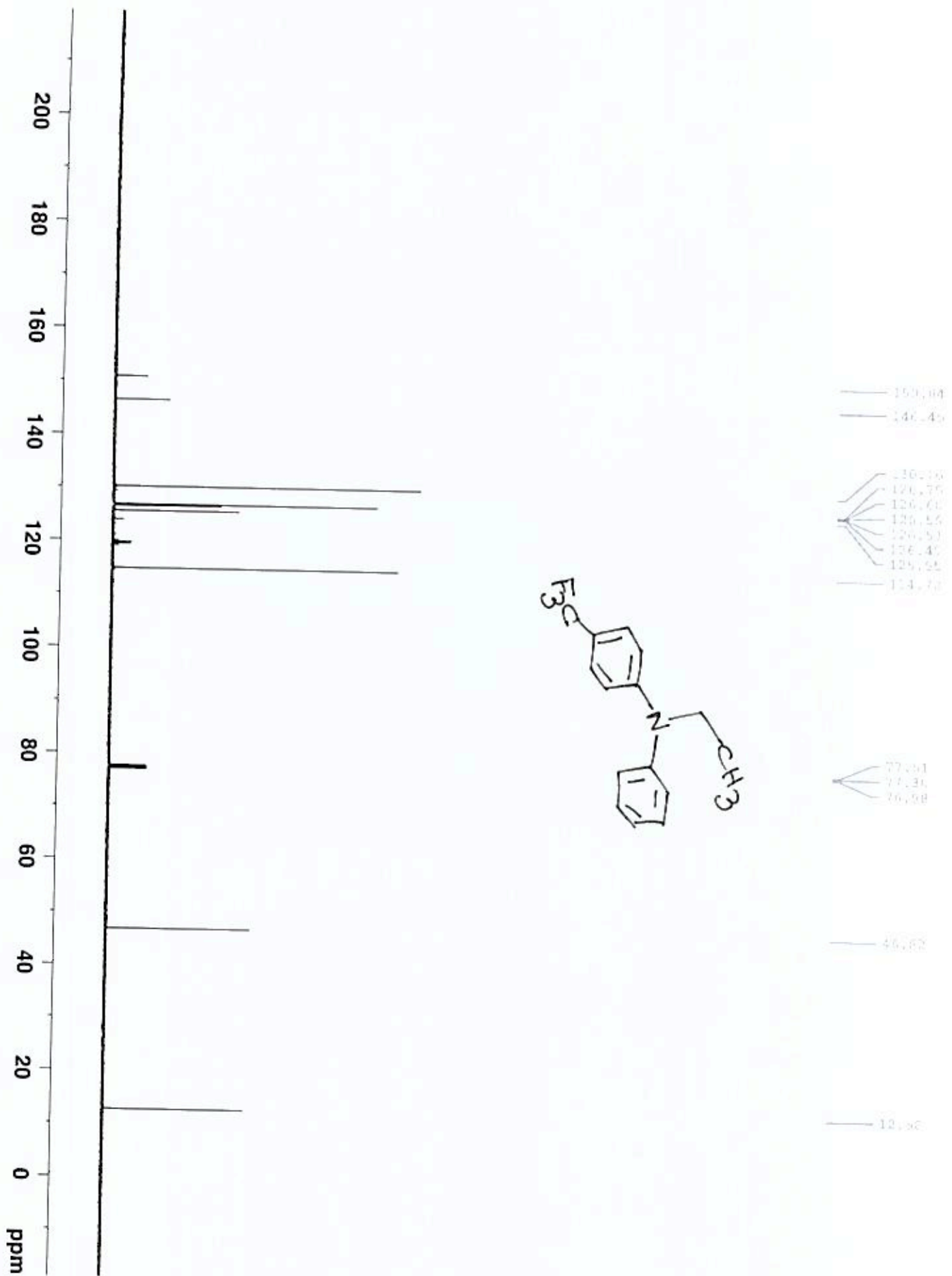


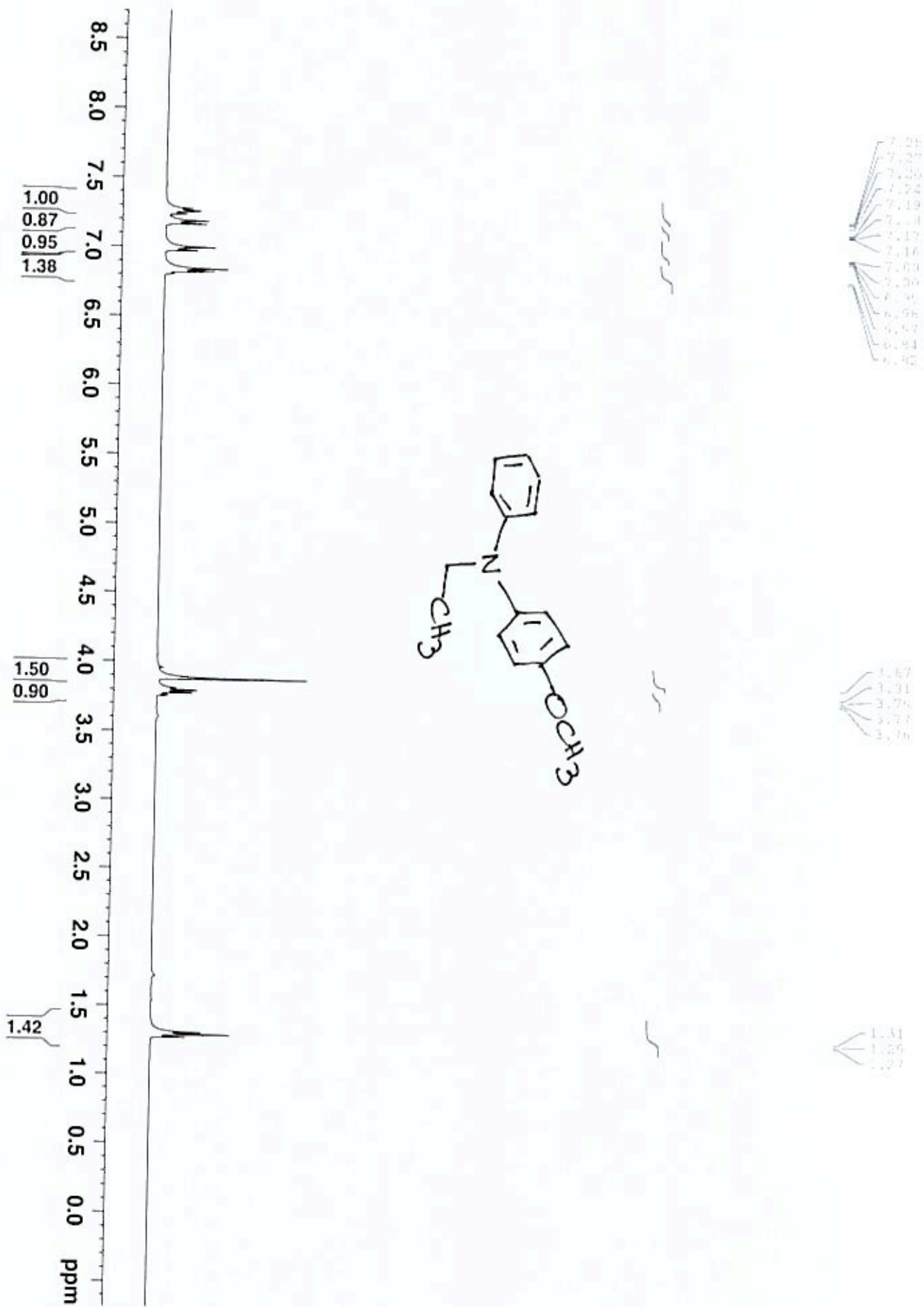


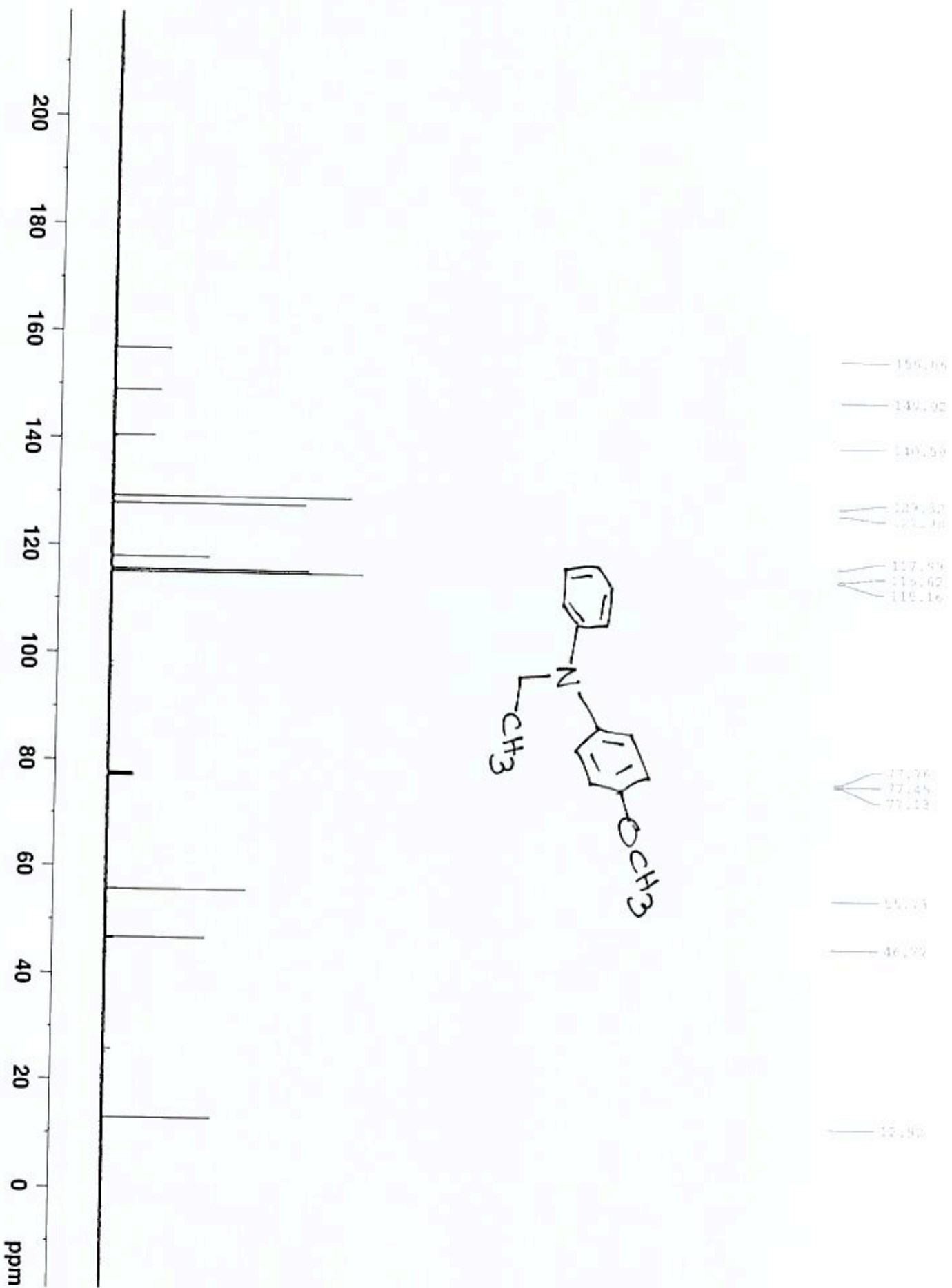


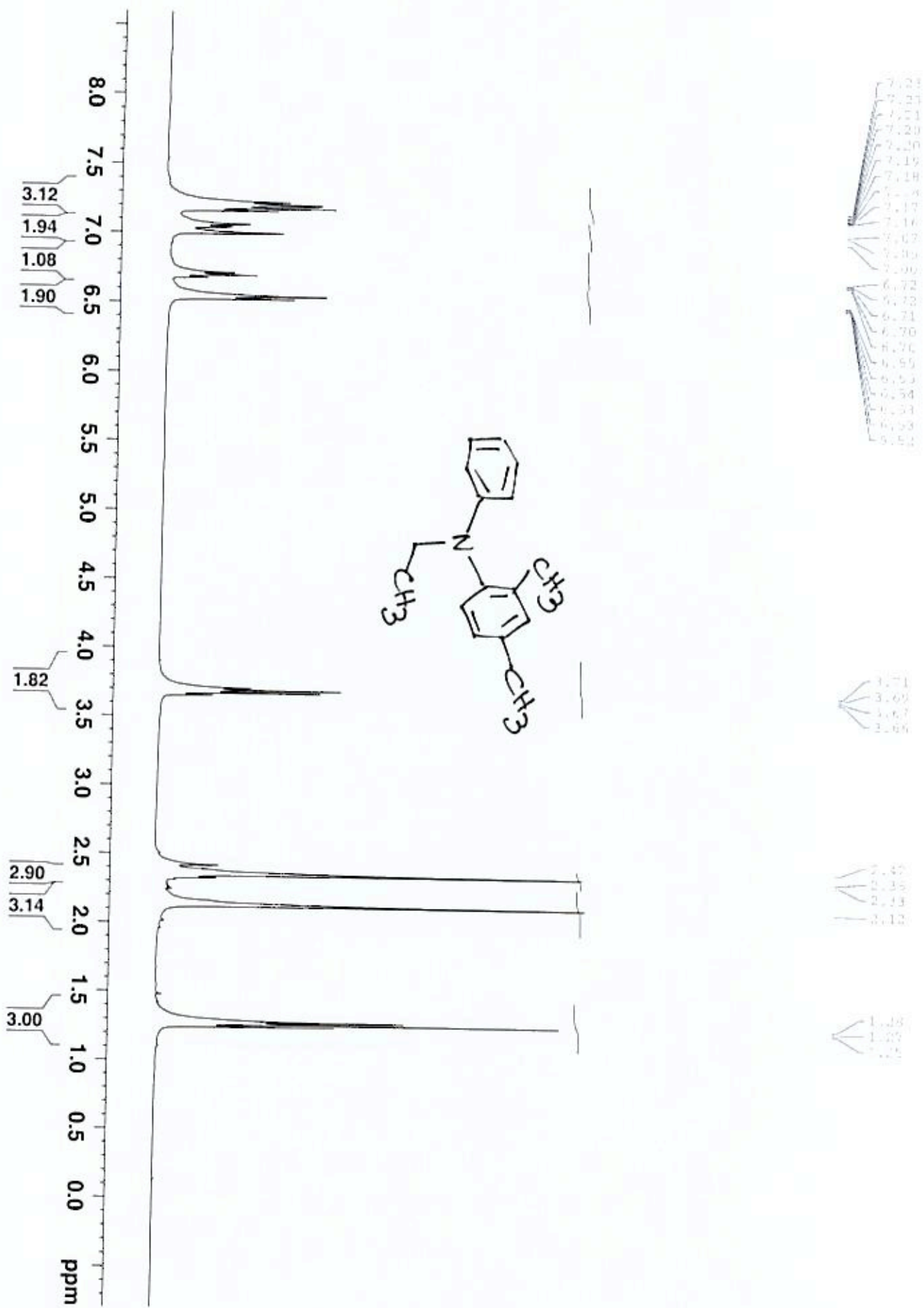


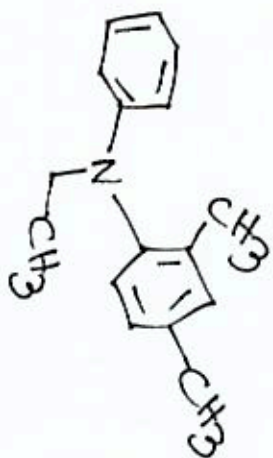
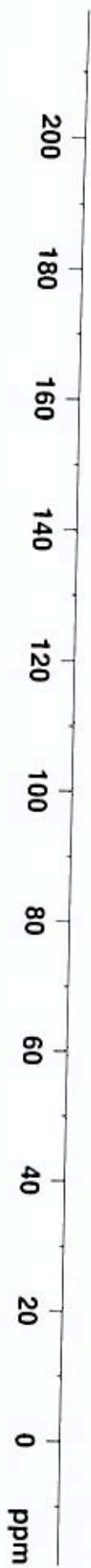




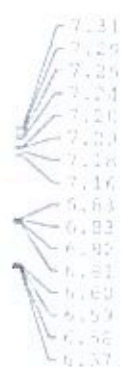
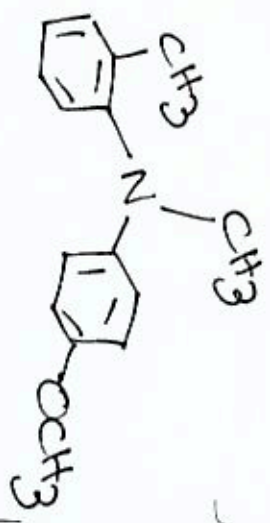
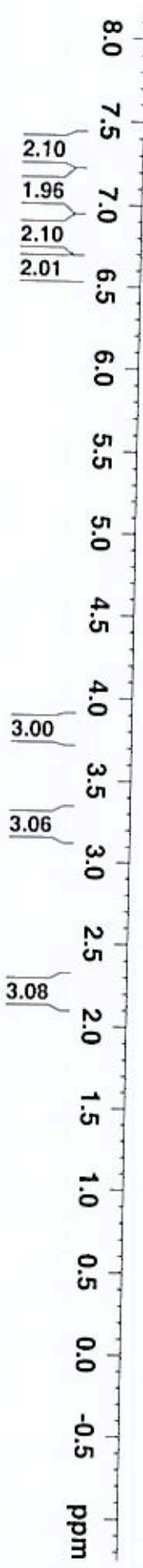


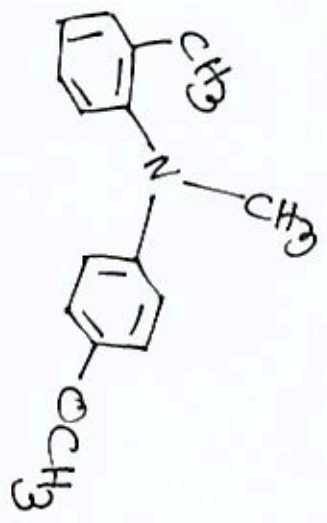
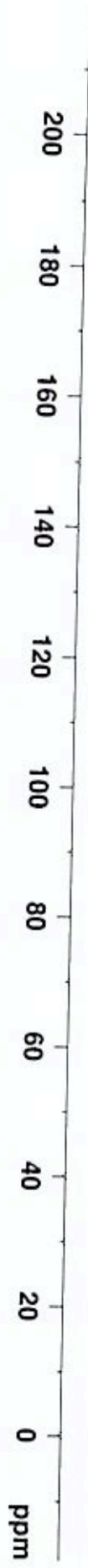




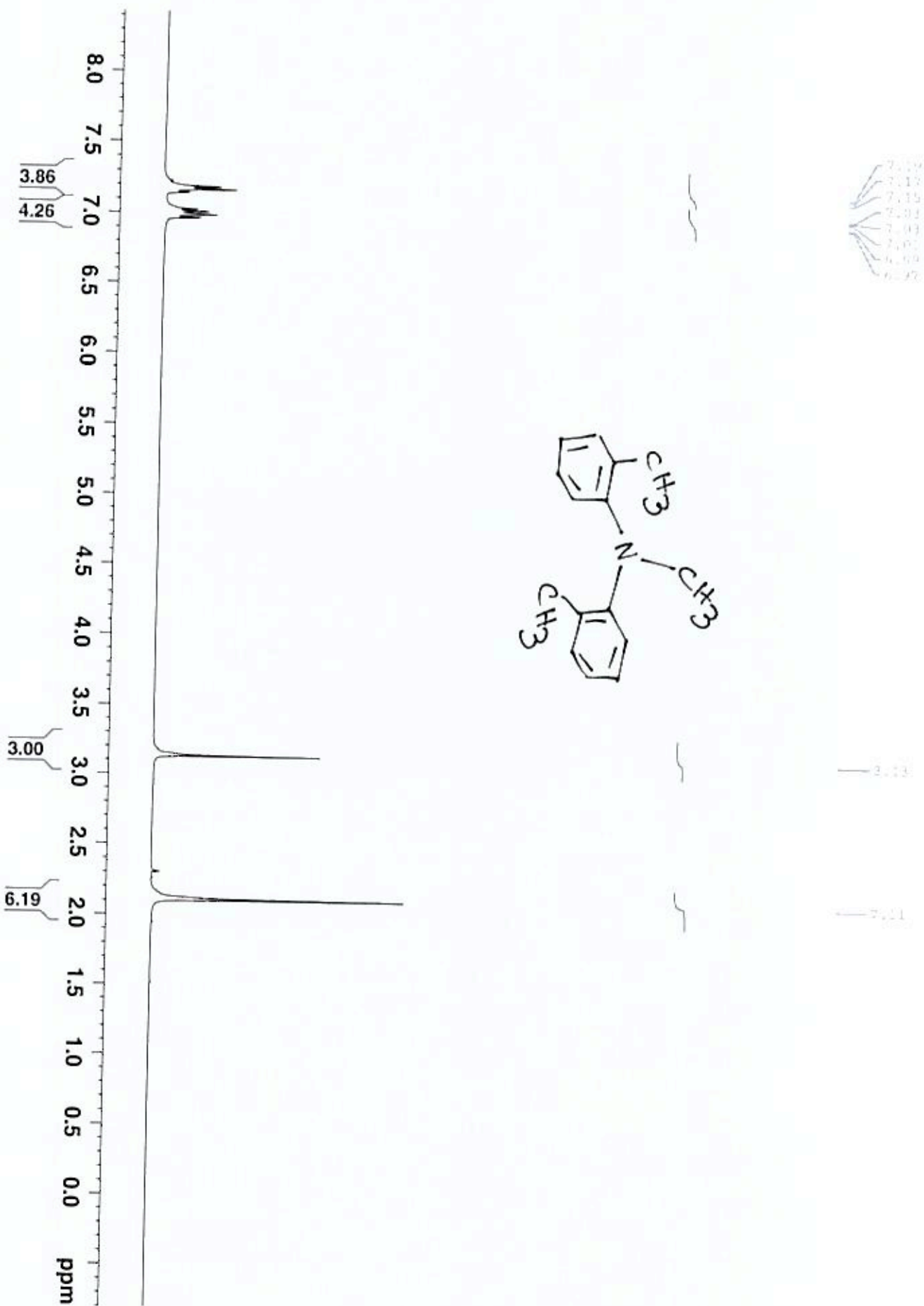
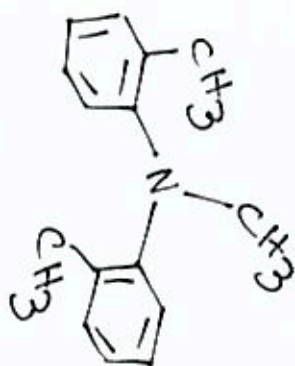


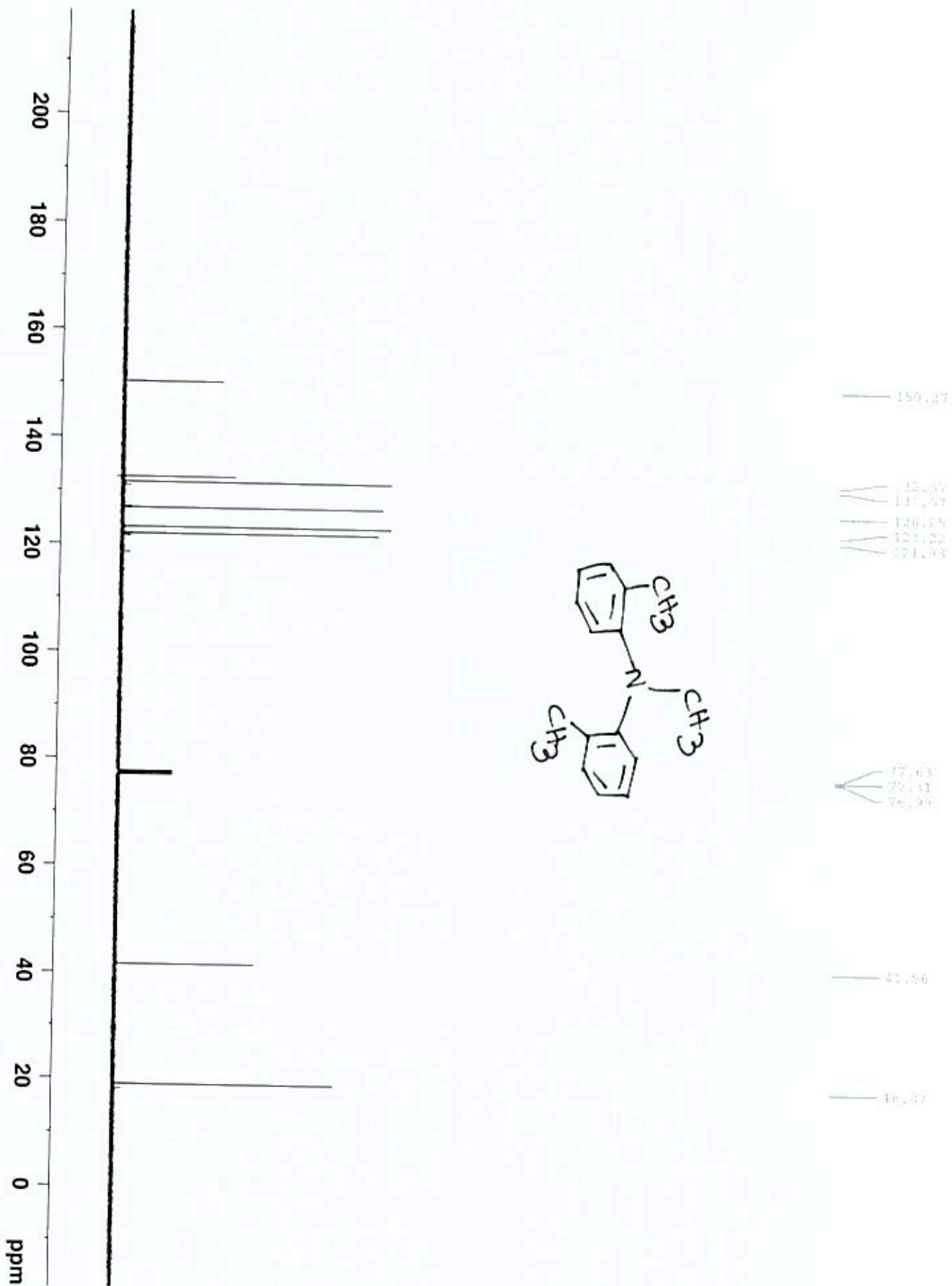
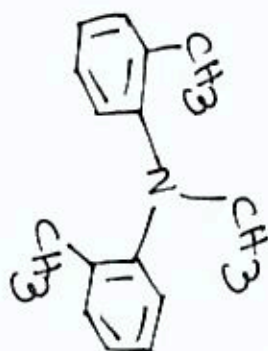
- 141.40
- 145.02
- 137.10
- 136.24
- 131.82
- 130.87
- 129.02
- 127.74
- 113.44
- 113.72
- 77.61
- 77.34
- 77.09
- 45.64
- 31.17
- 17.93
- 13.06

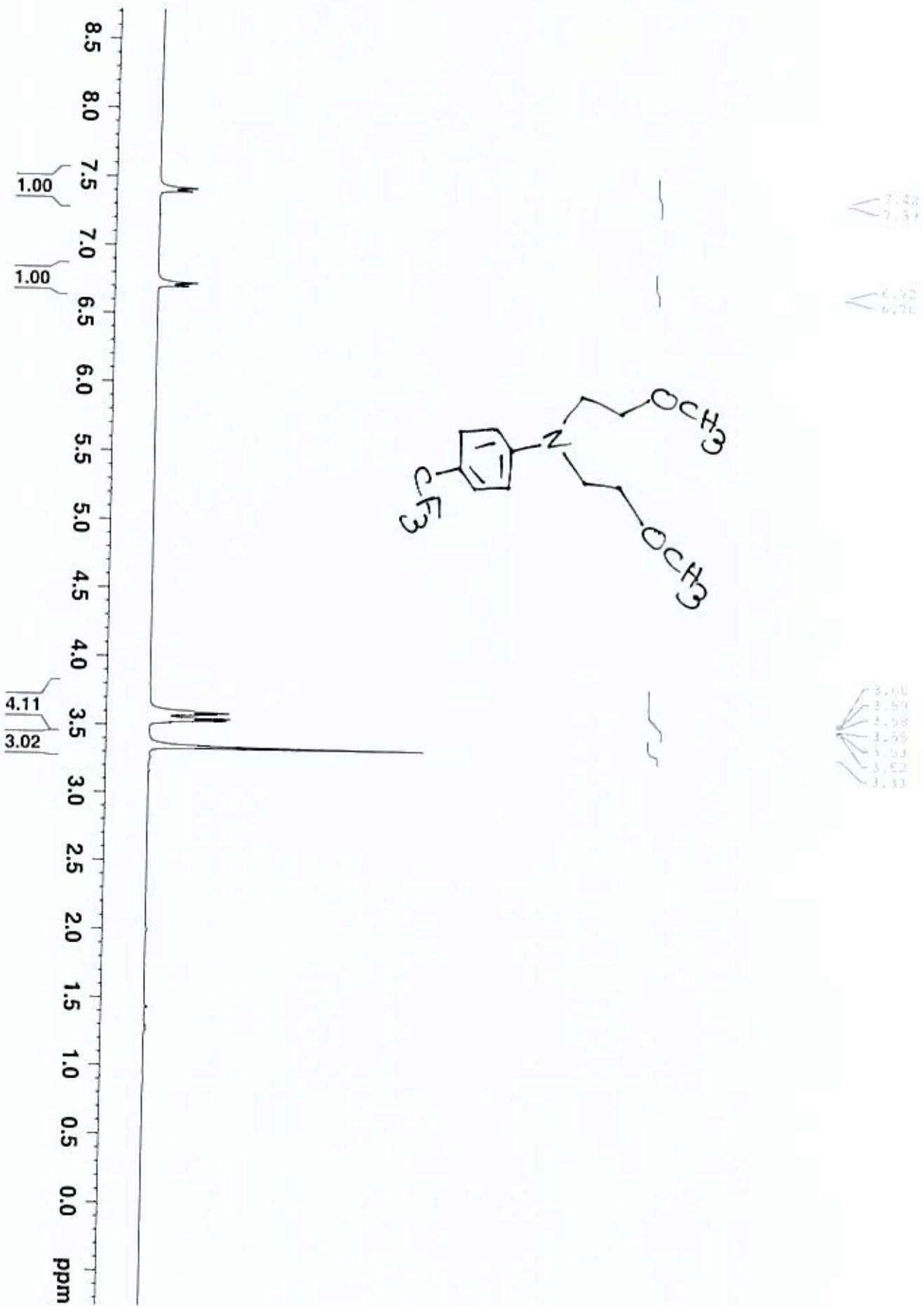


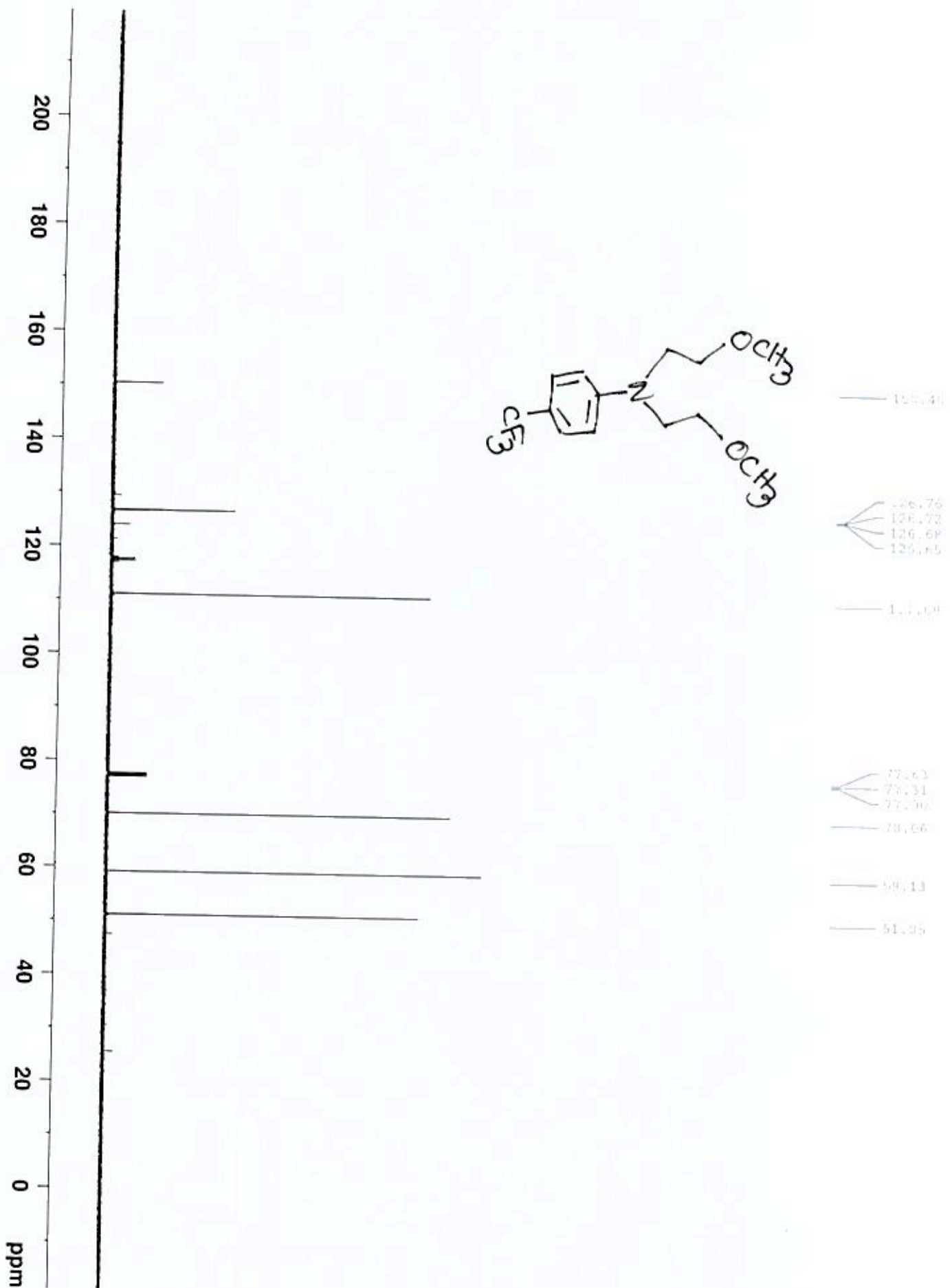


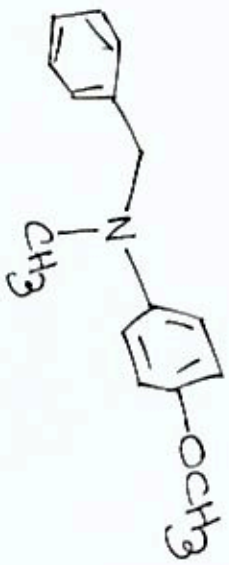
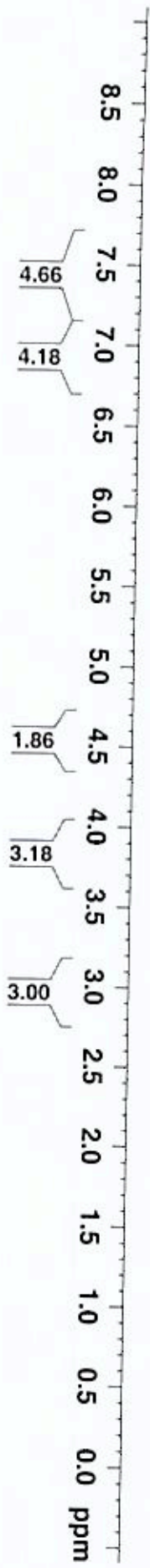
- 152.10
- 146.05
- 144.27
- 136.25
- 131.54
- 127.95
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- 115.20
- 114.90
- 77.68
- 77.35
- 77.16
- 55.37
- 39.10
- 19.35

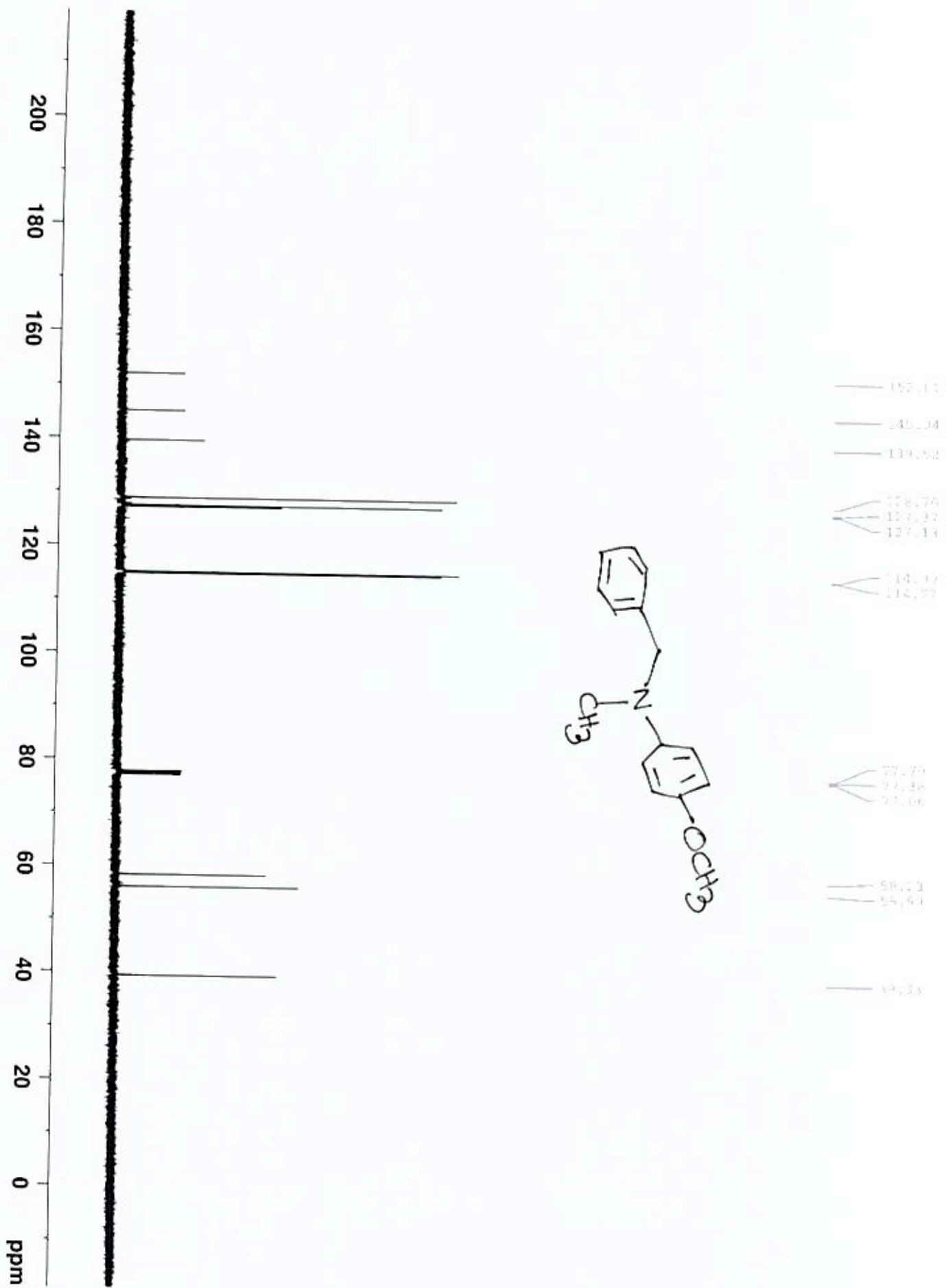
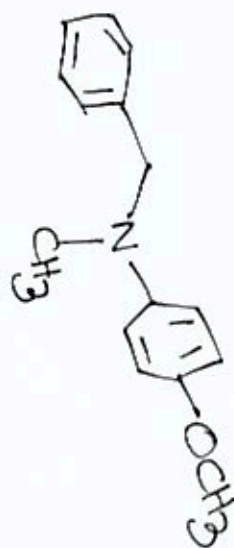


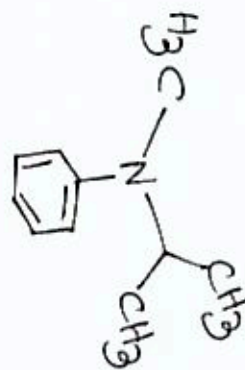
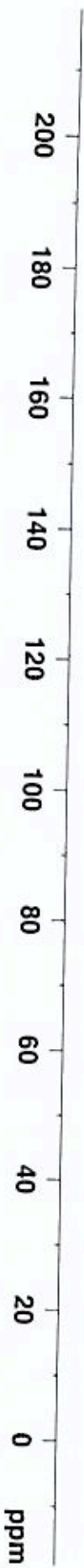












158.38

123.33

116.64

113.50

77.57

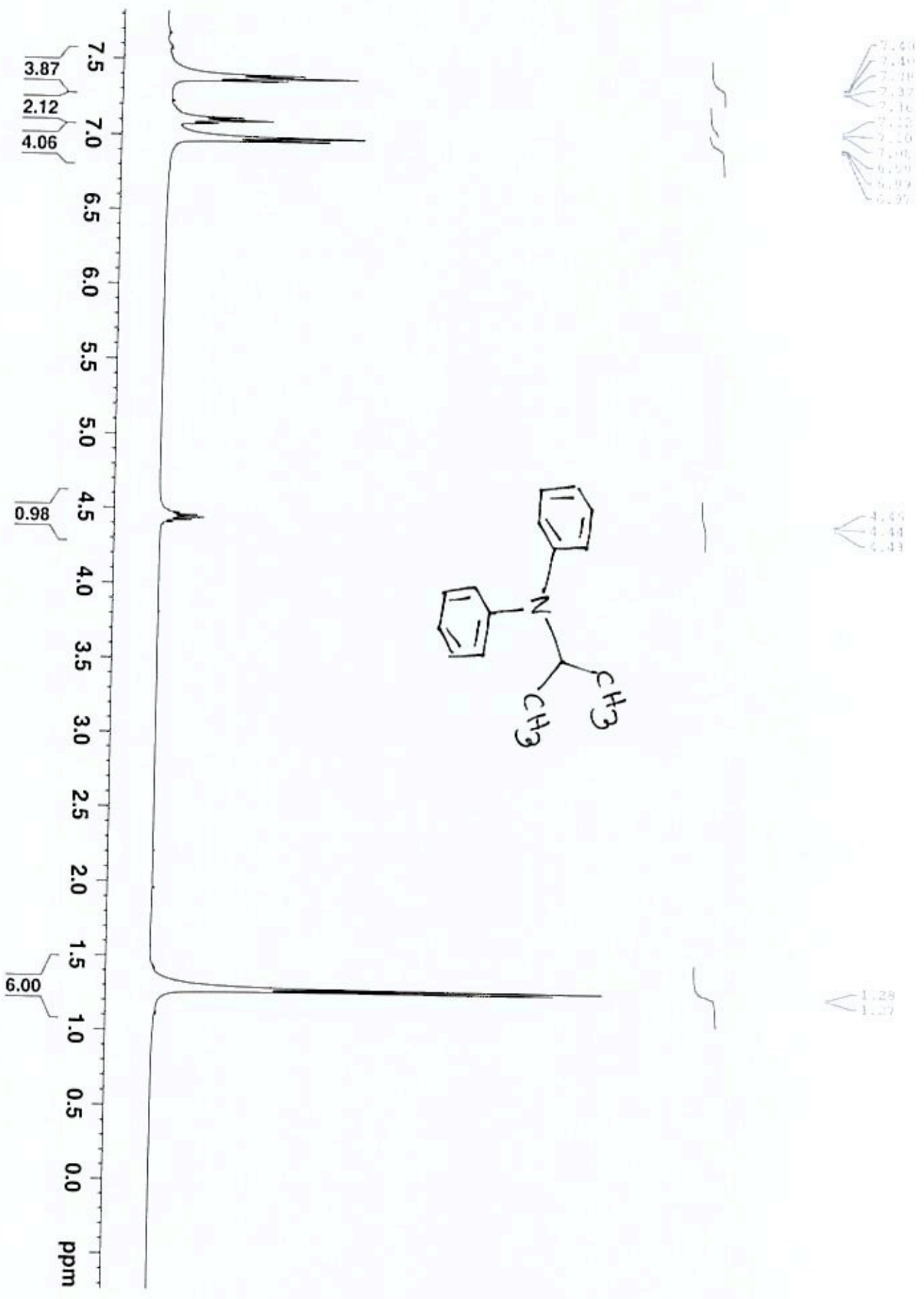
77.26

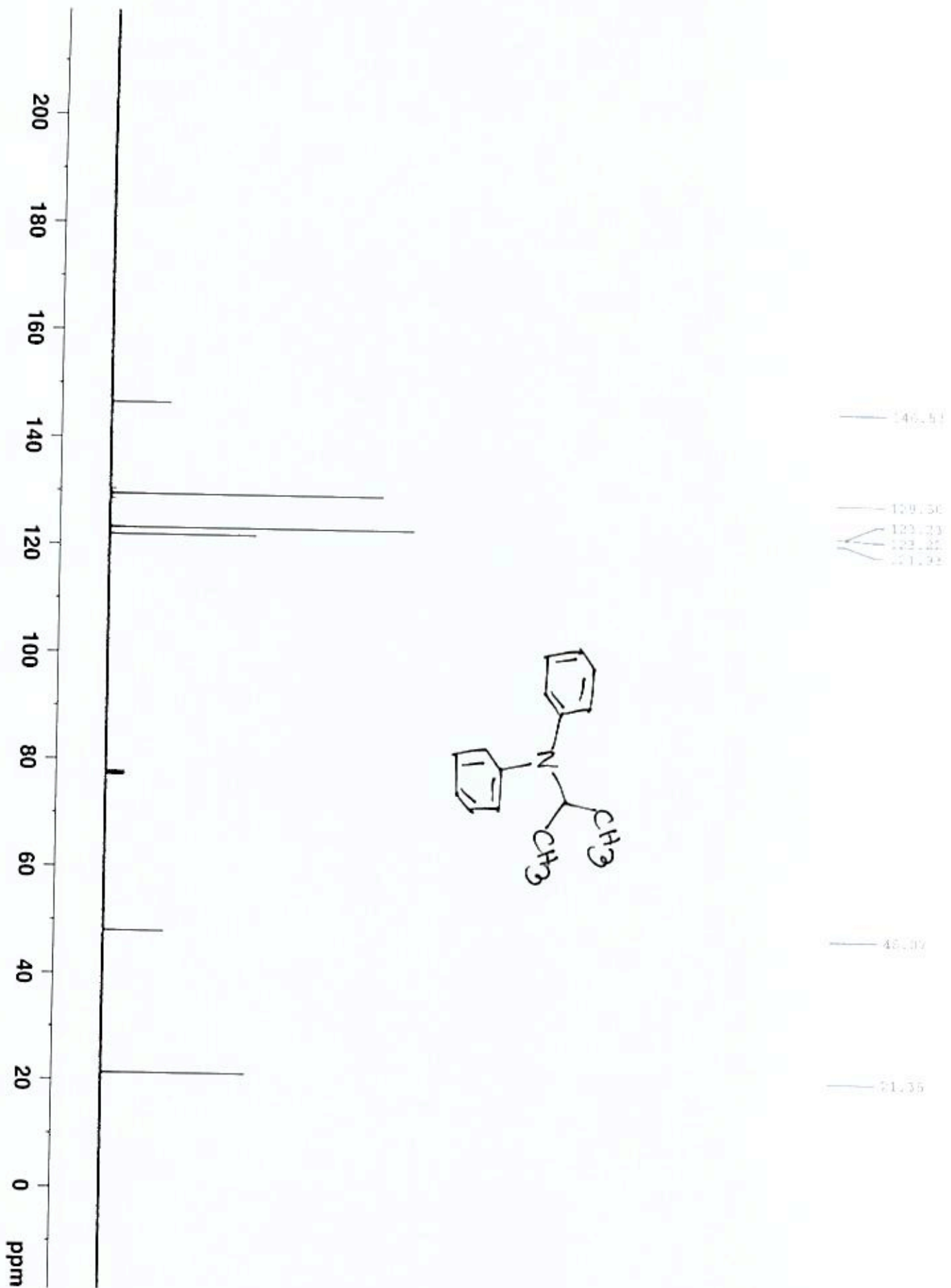
76.94

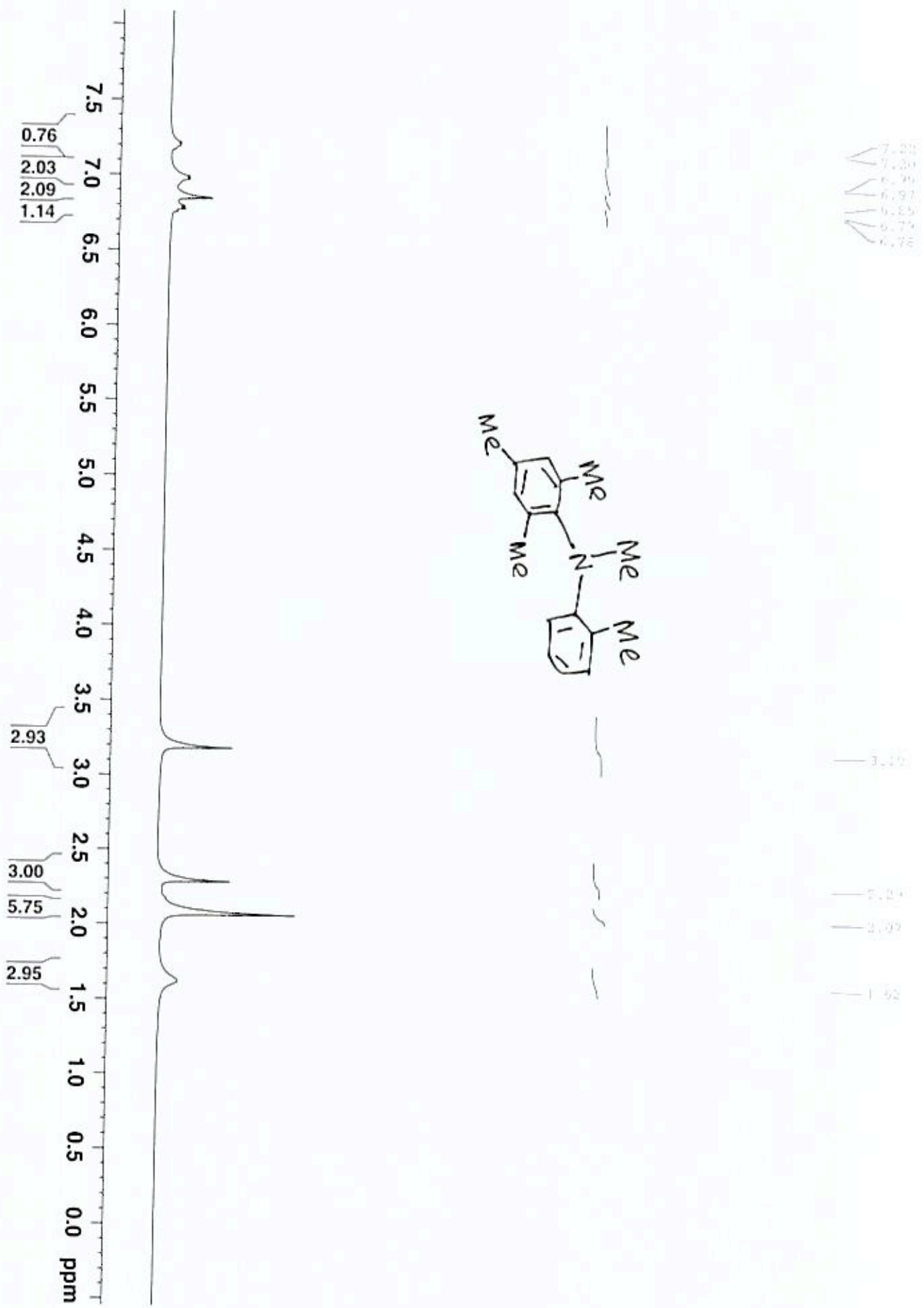
49.14

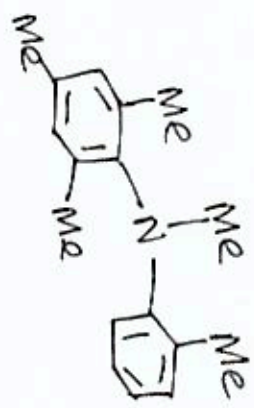
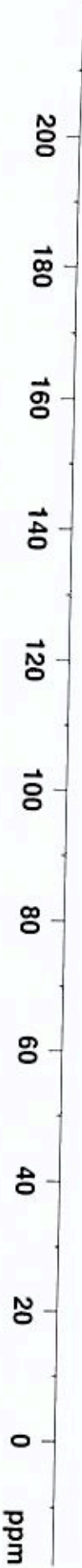
30.90

19.53

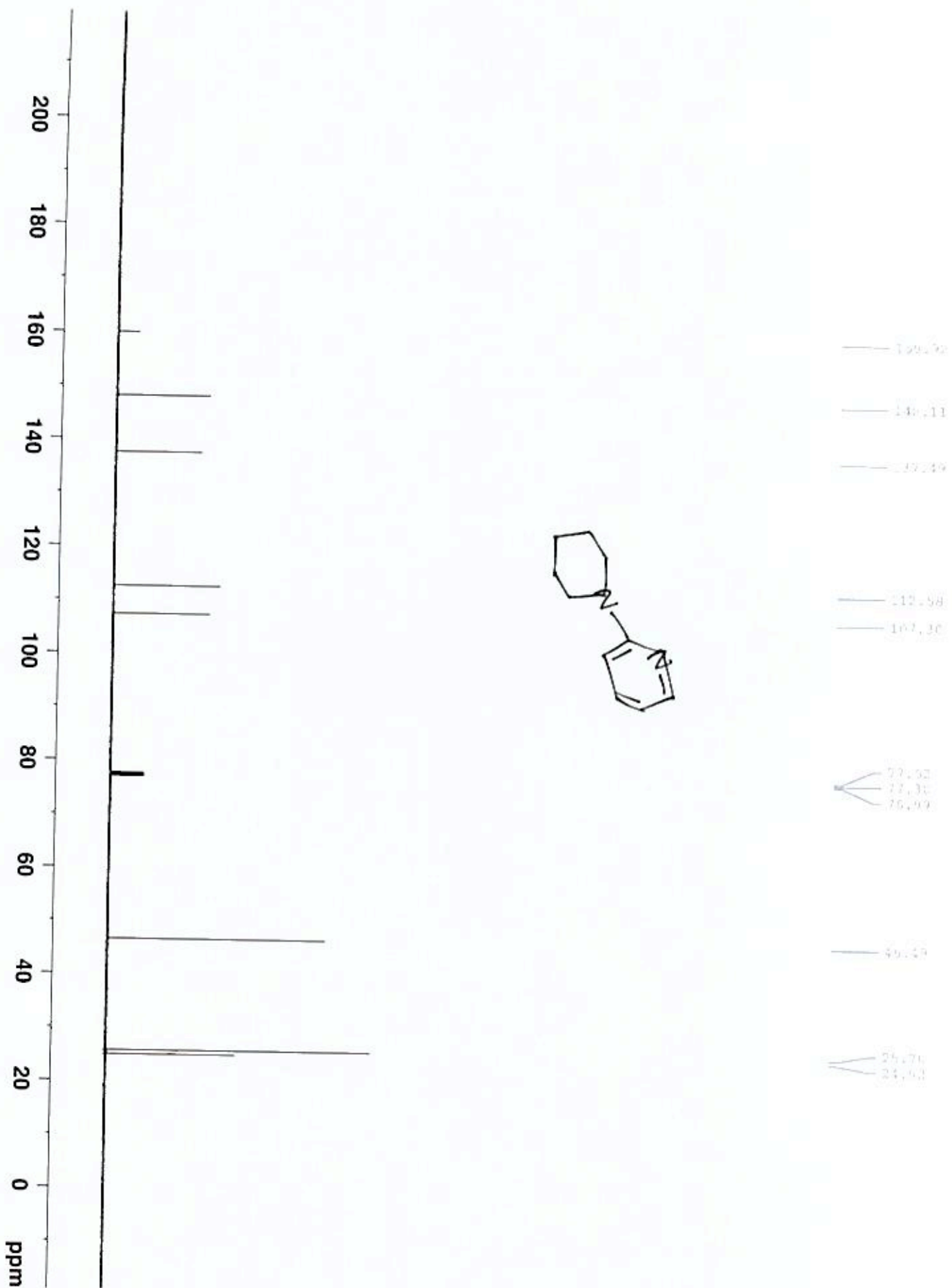


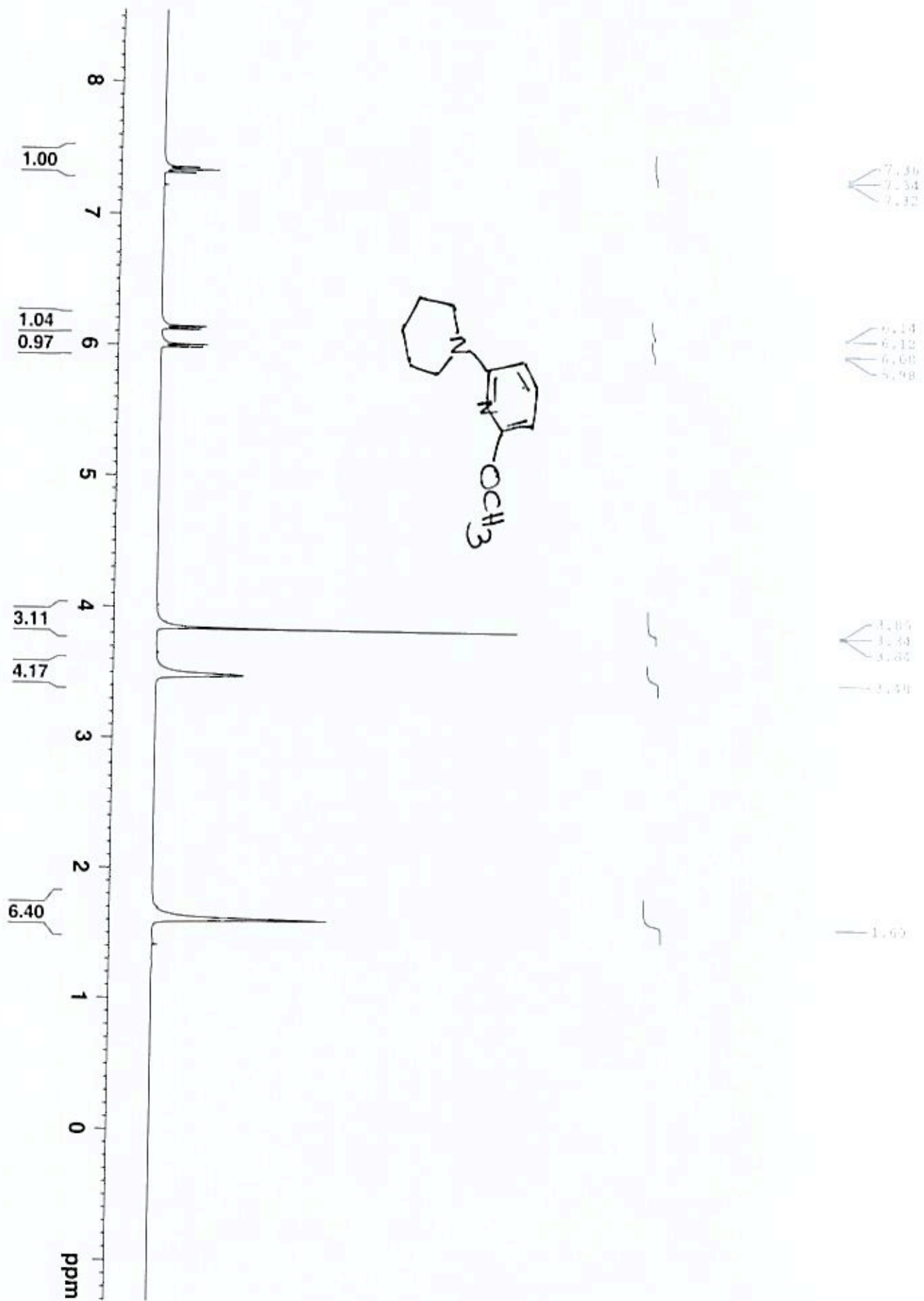


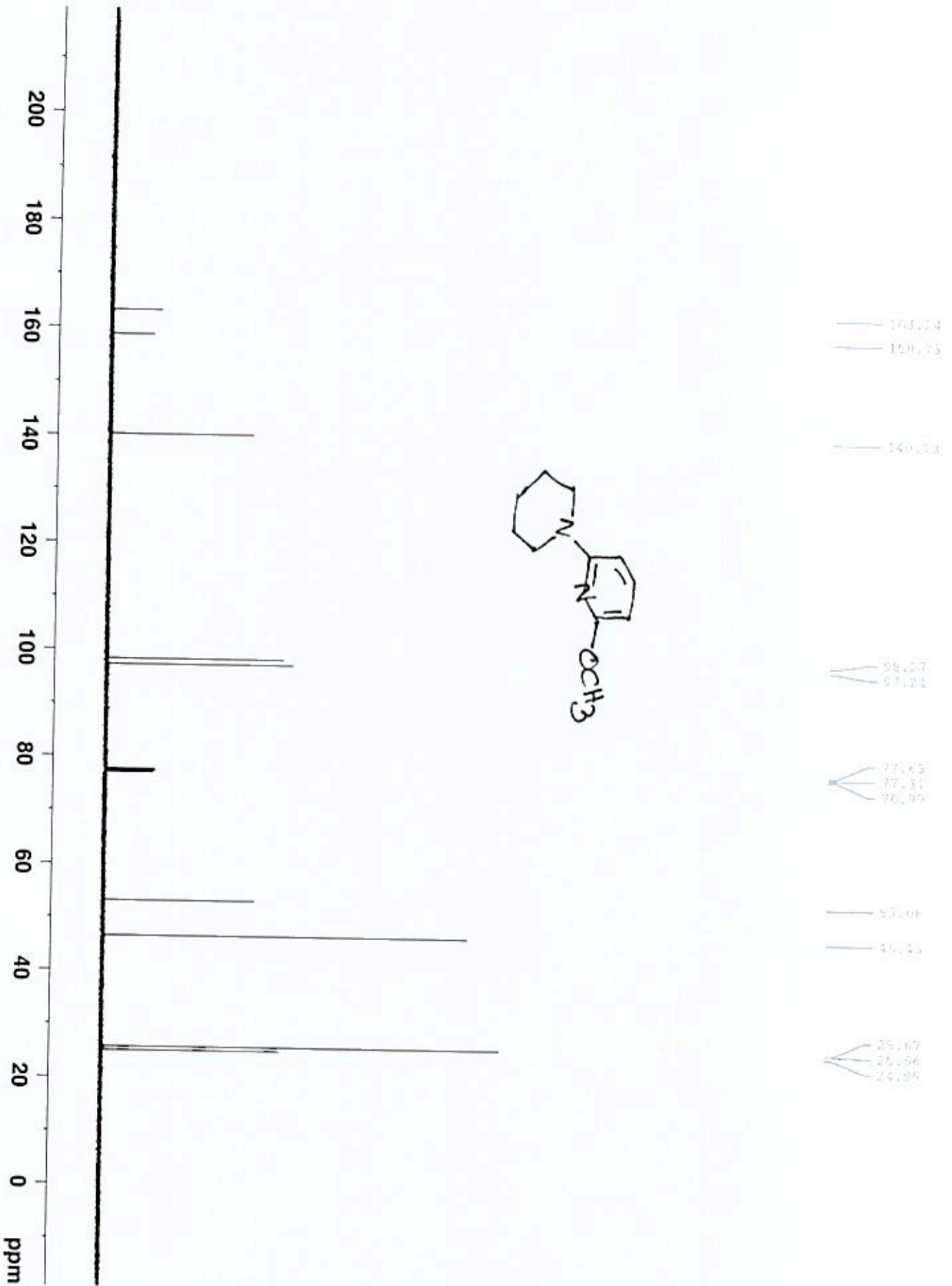
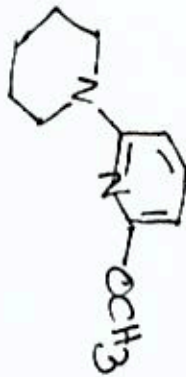


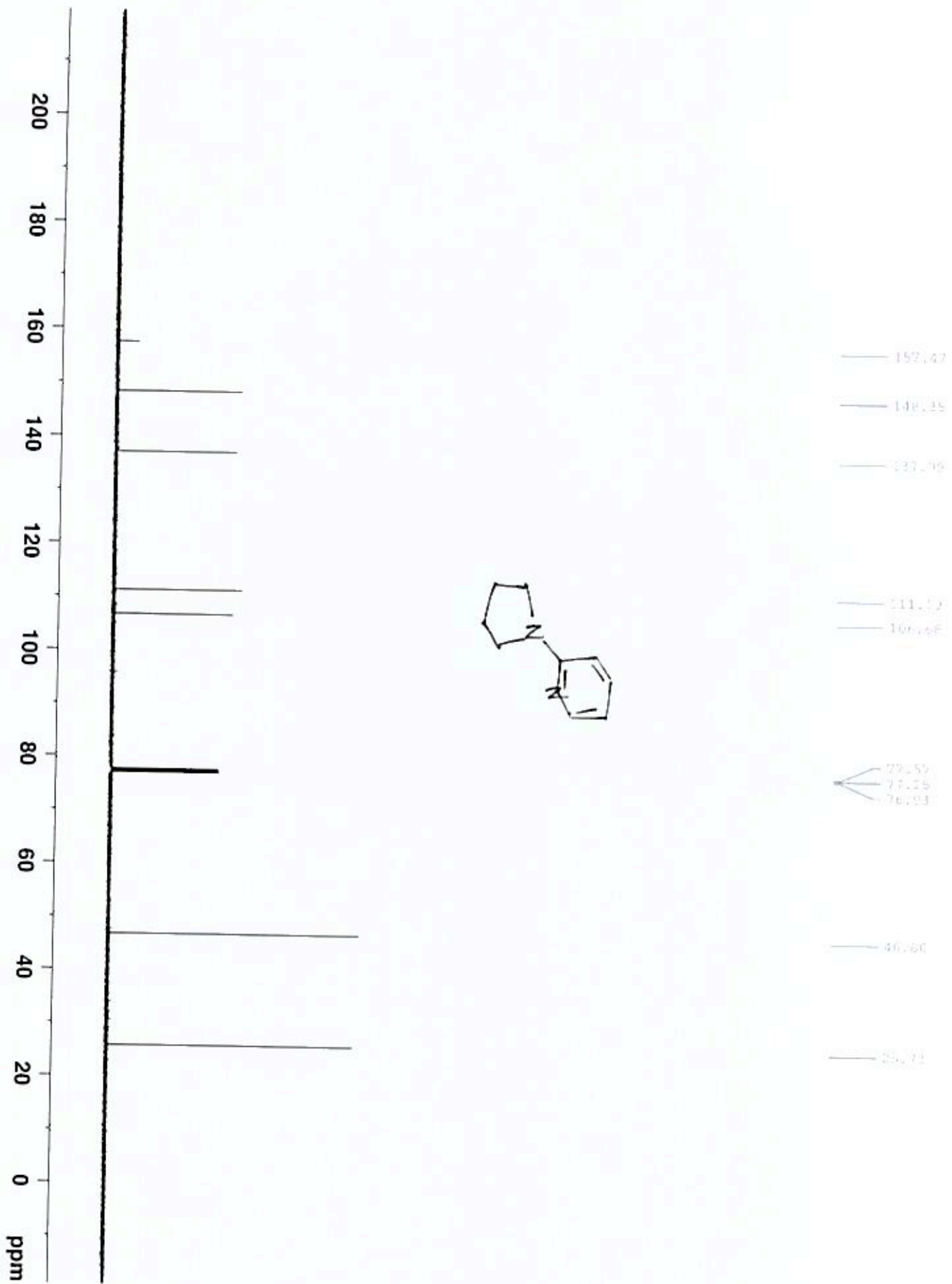


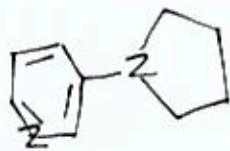
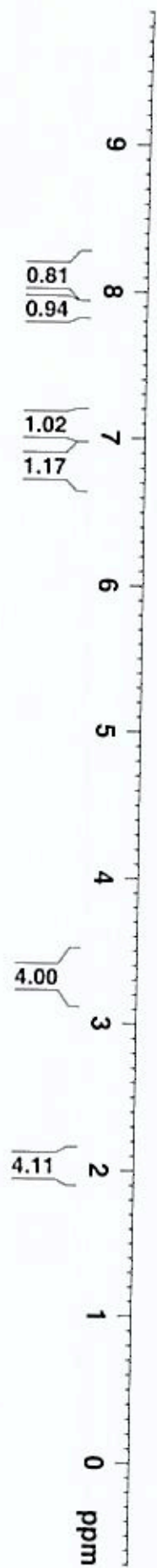
- 145.41
- 144.32
- 139.14
- 135.06
- 132.20
- 129.83
- 127.39
- 126.92
- 119.19
- 115.69
- 77.60
- 77.29
- 76.97
- 40.59
- 31.69
- 29.34
- 19.13

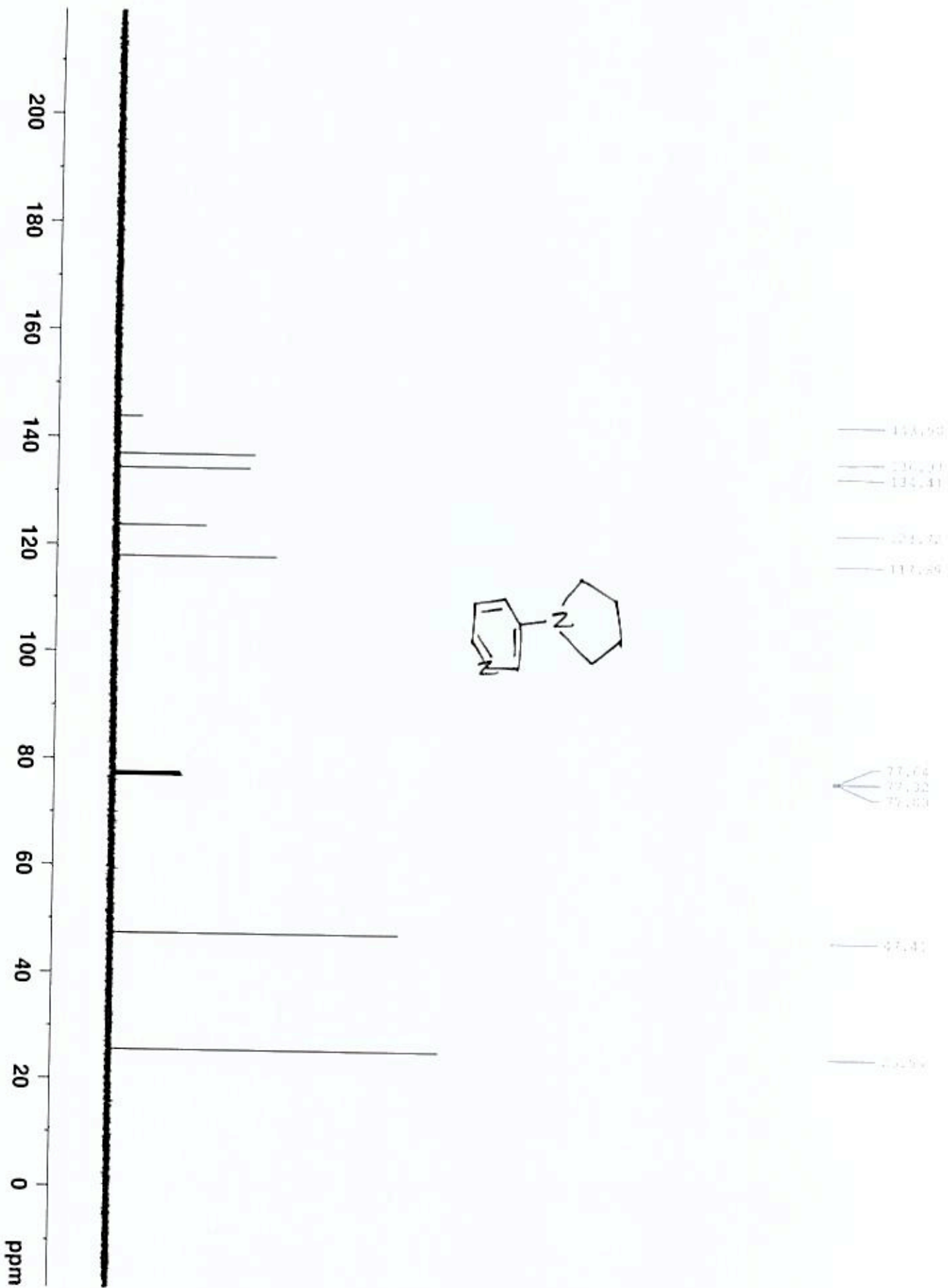




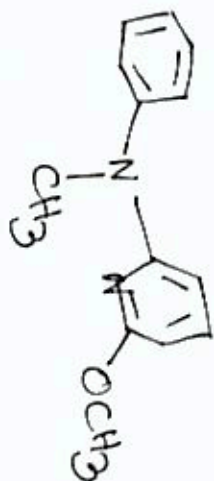
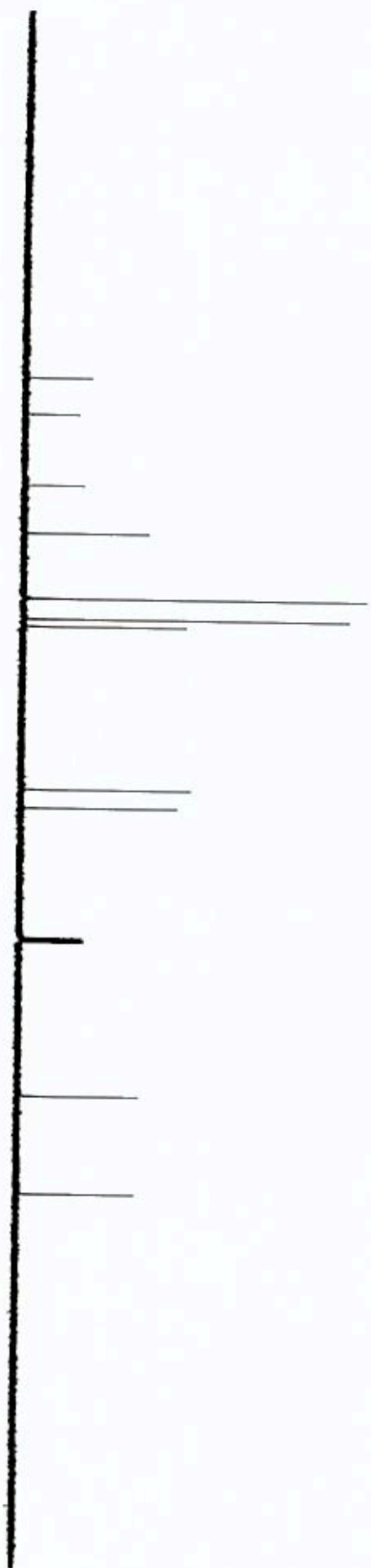




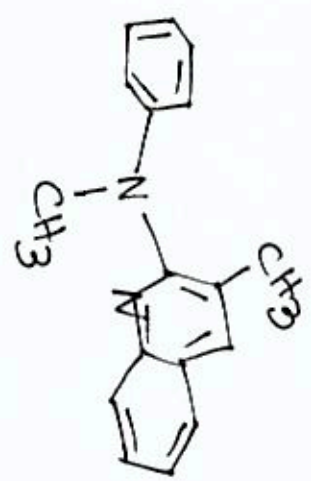
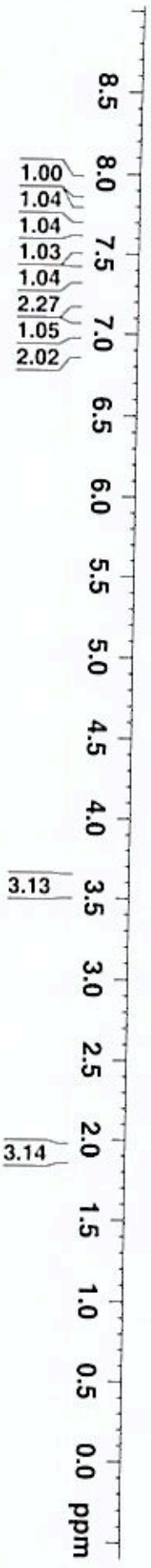


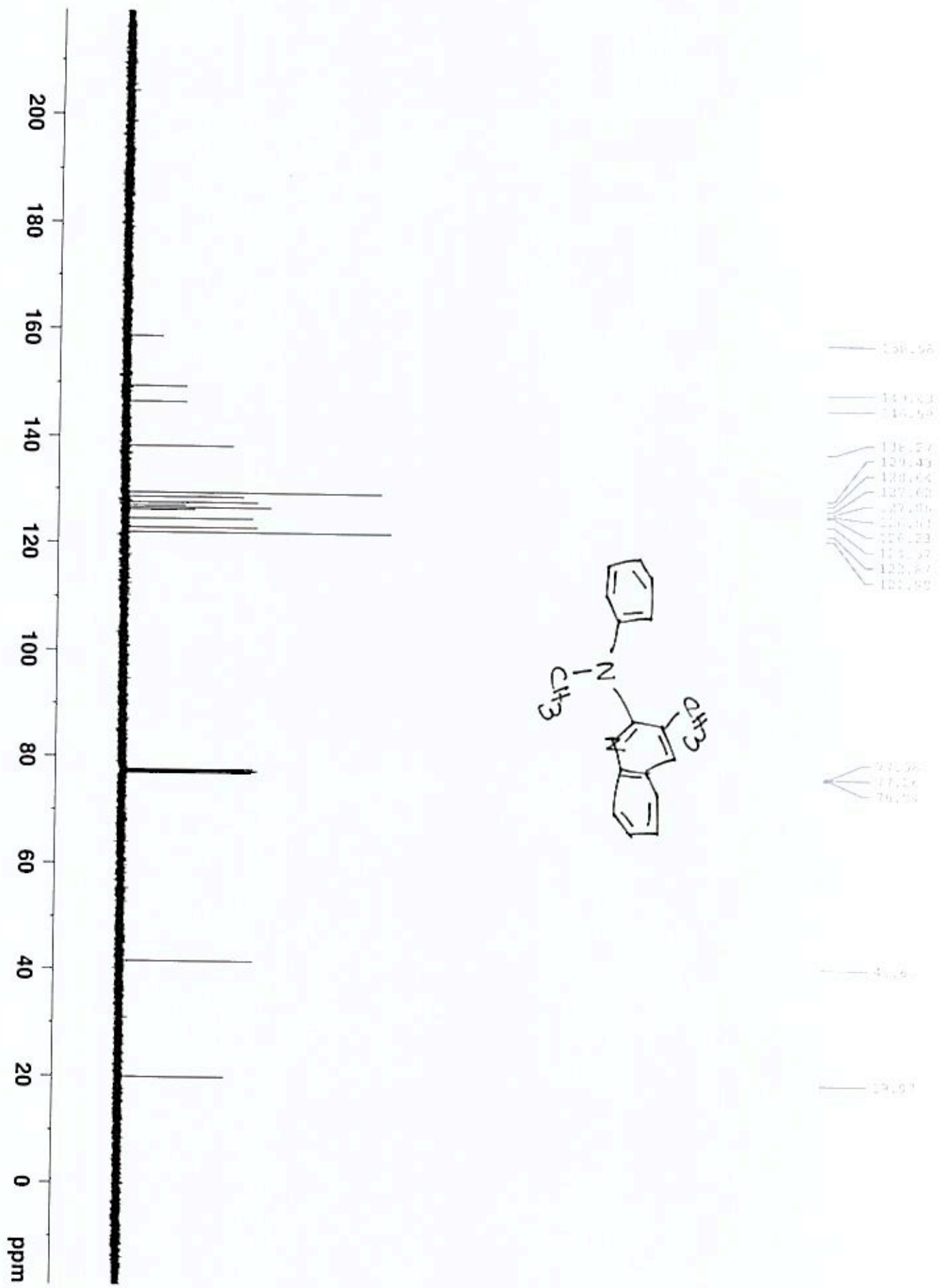


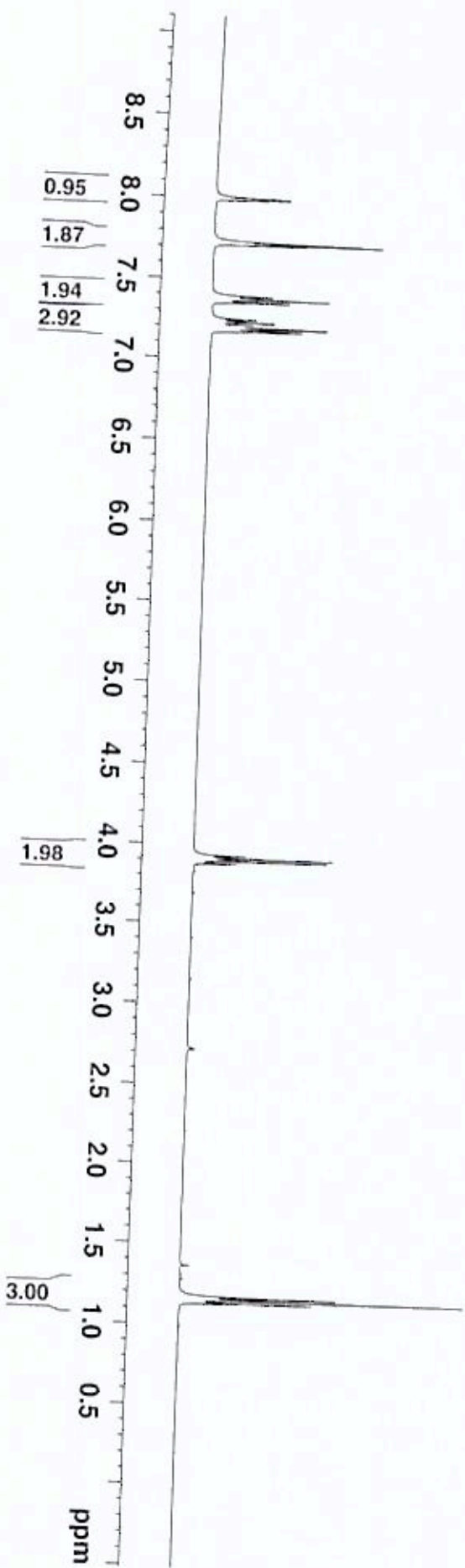
200 180 160 140 120 100 80 60 40 20 0 ppm

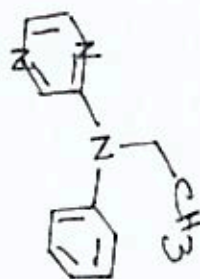
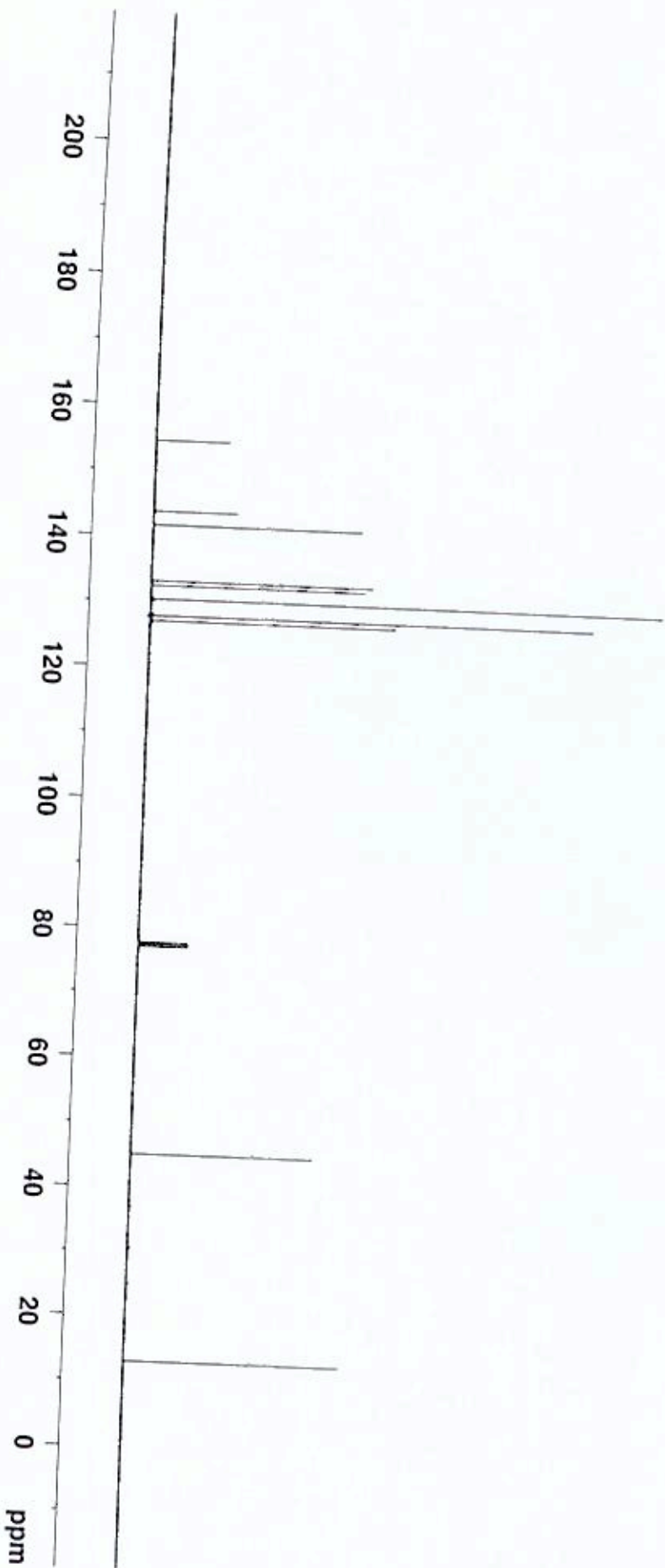


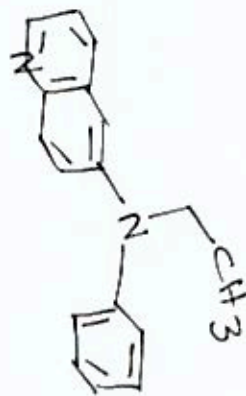
- 163.37
- 153.31
- 140.96
- 139.50
- 125.53
- 124.58
- 123.52
- 122.52
- 53.29
- 51.98
- 77.00
- 77.00
- 77.00
- 53.29
- 51.98

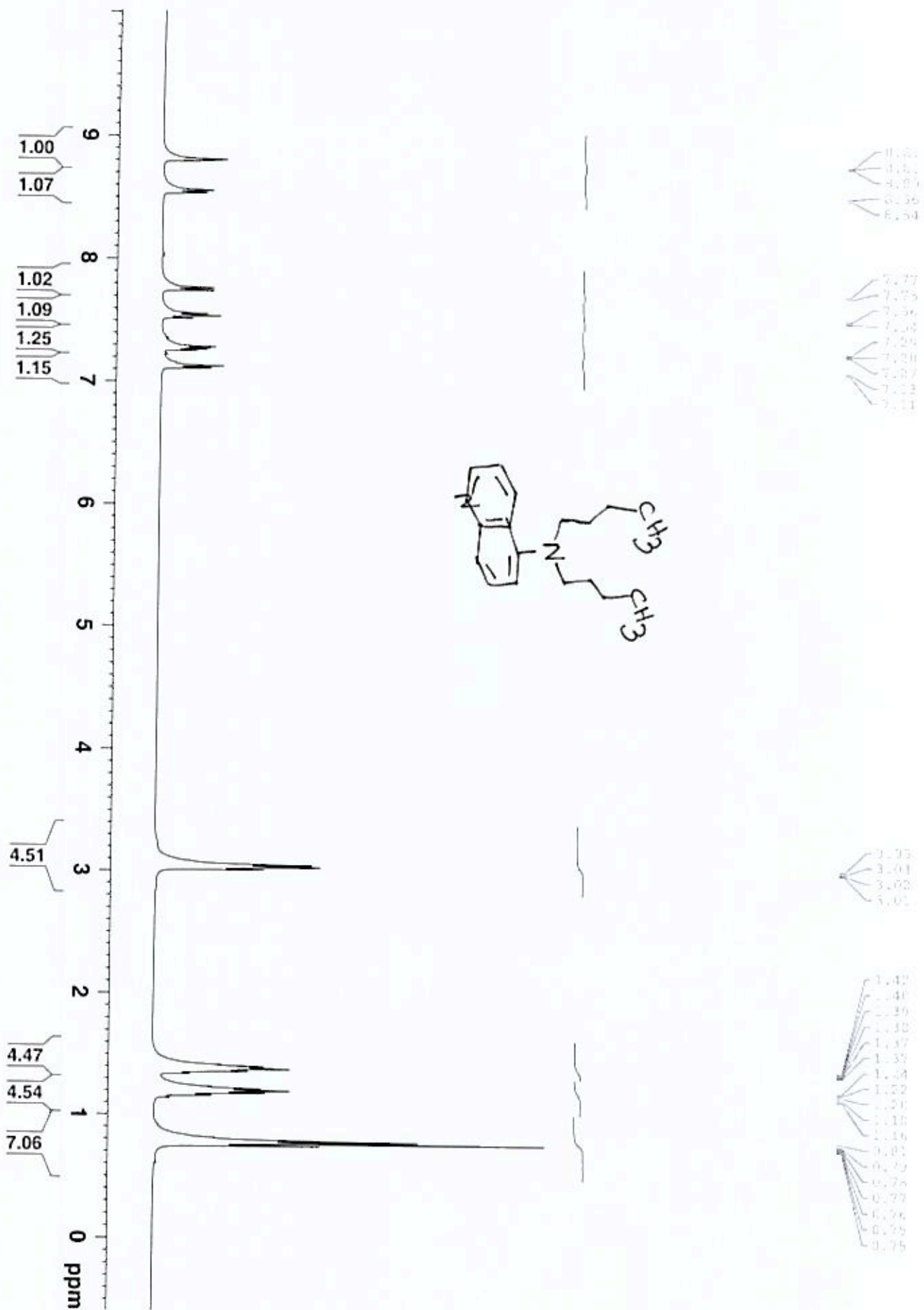


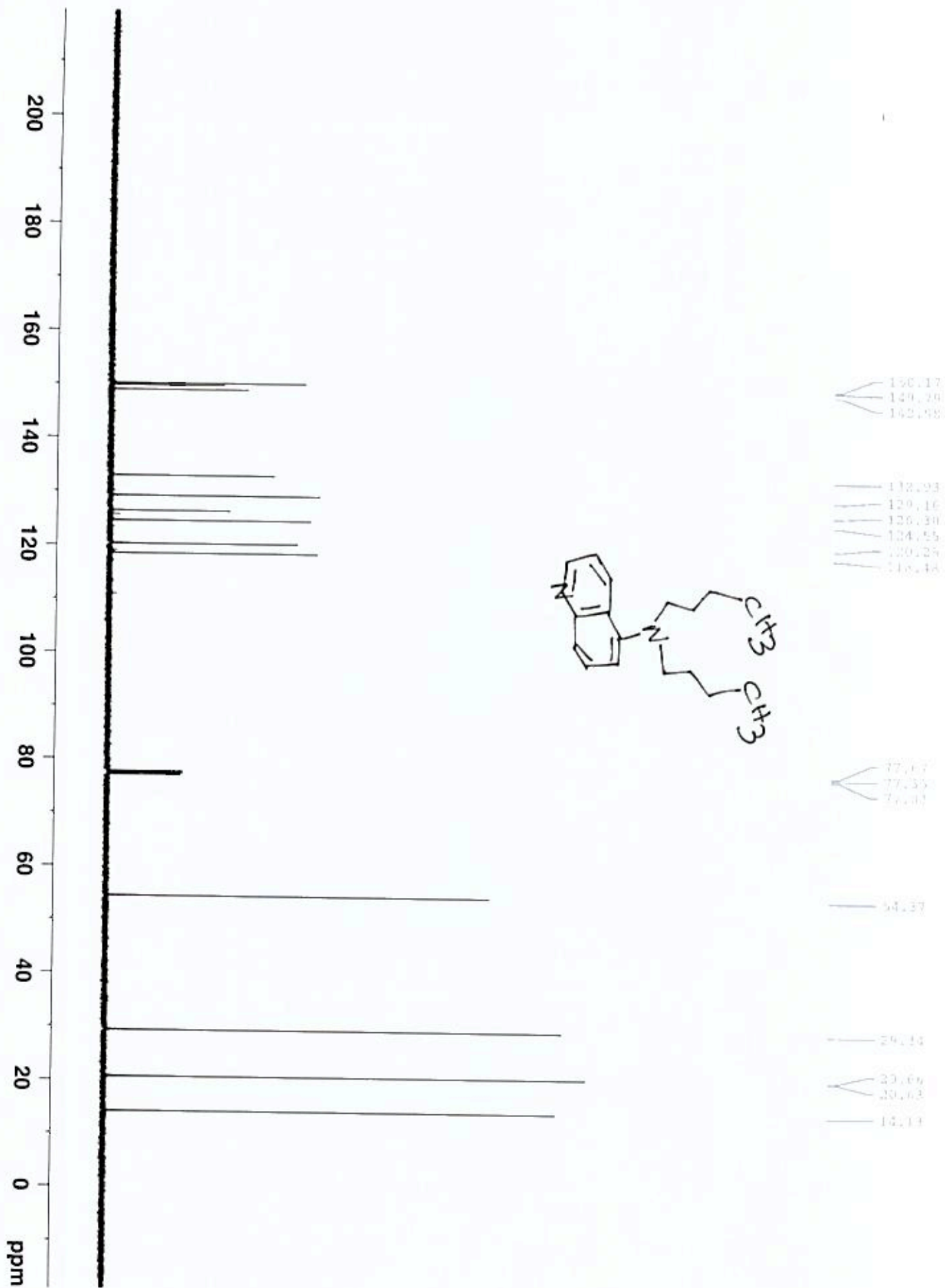


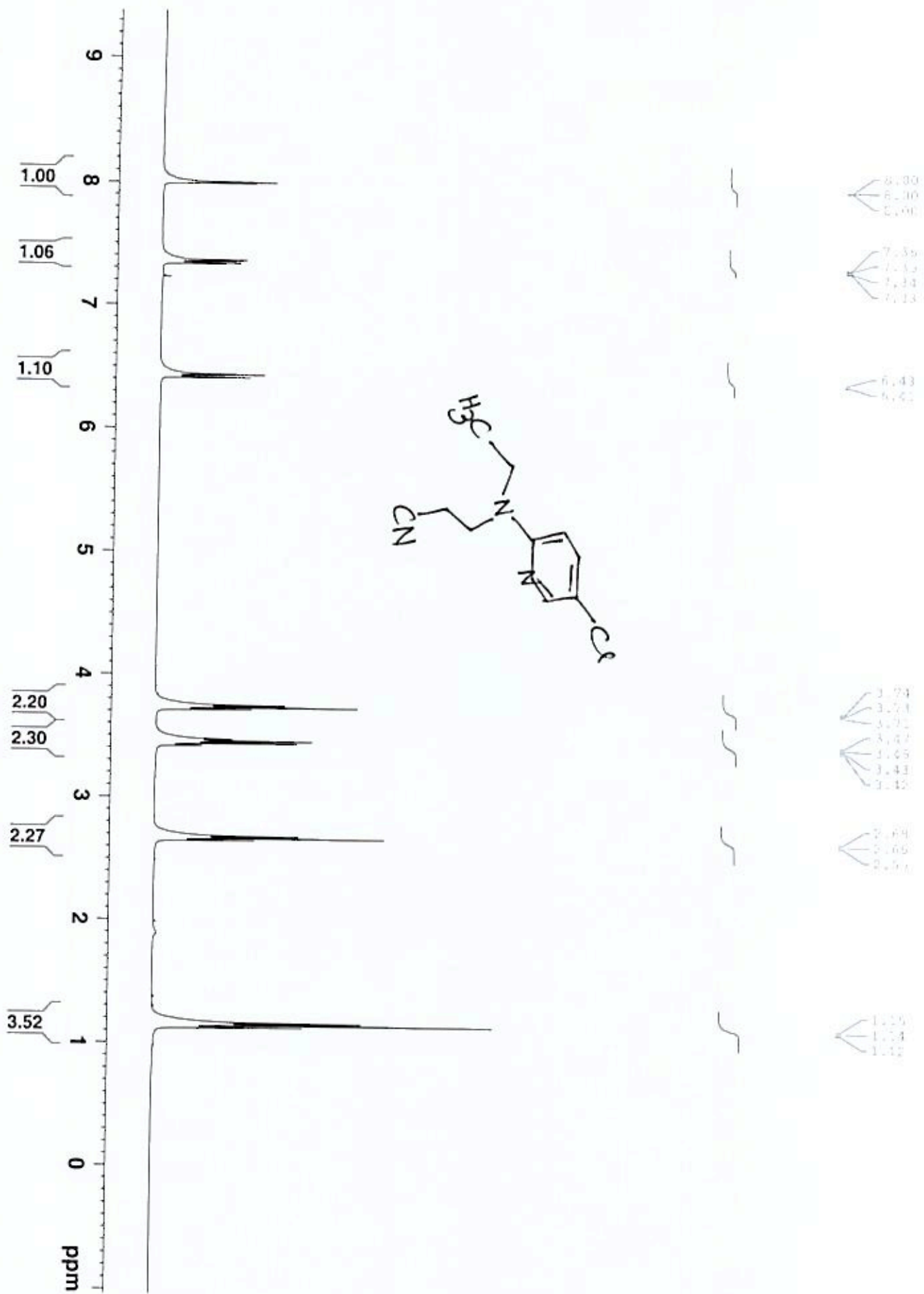


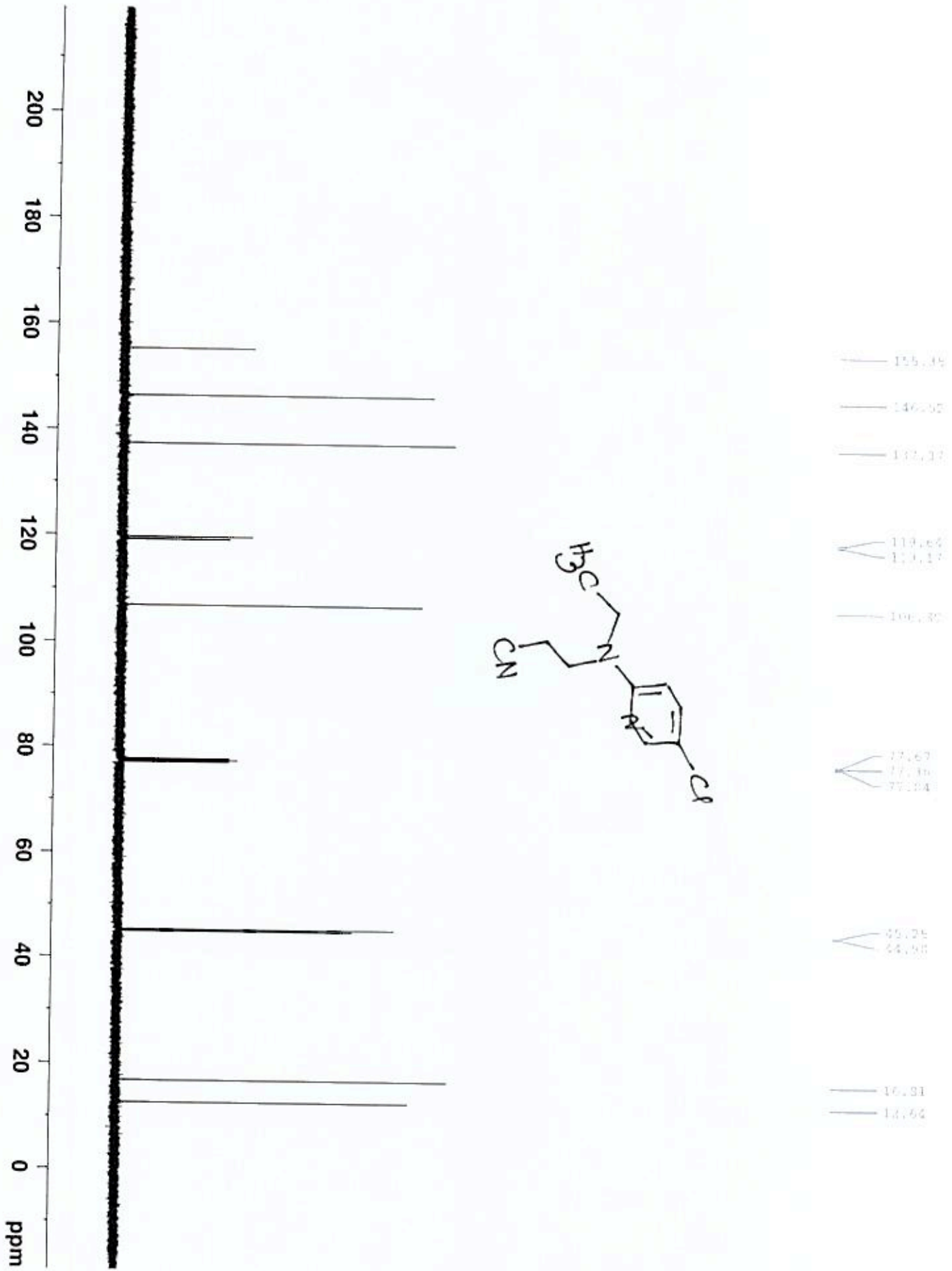


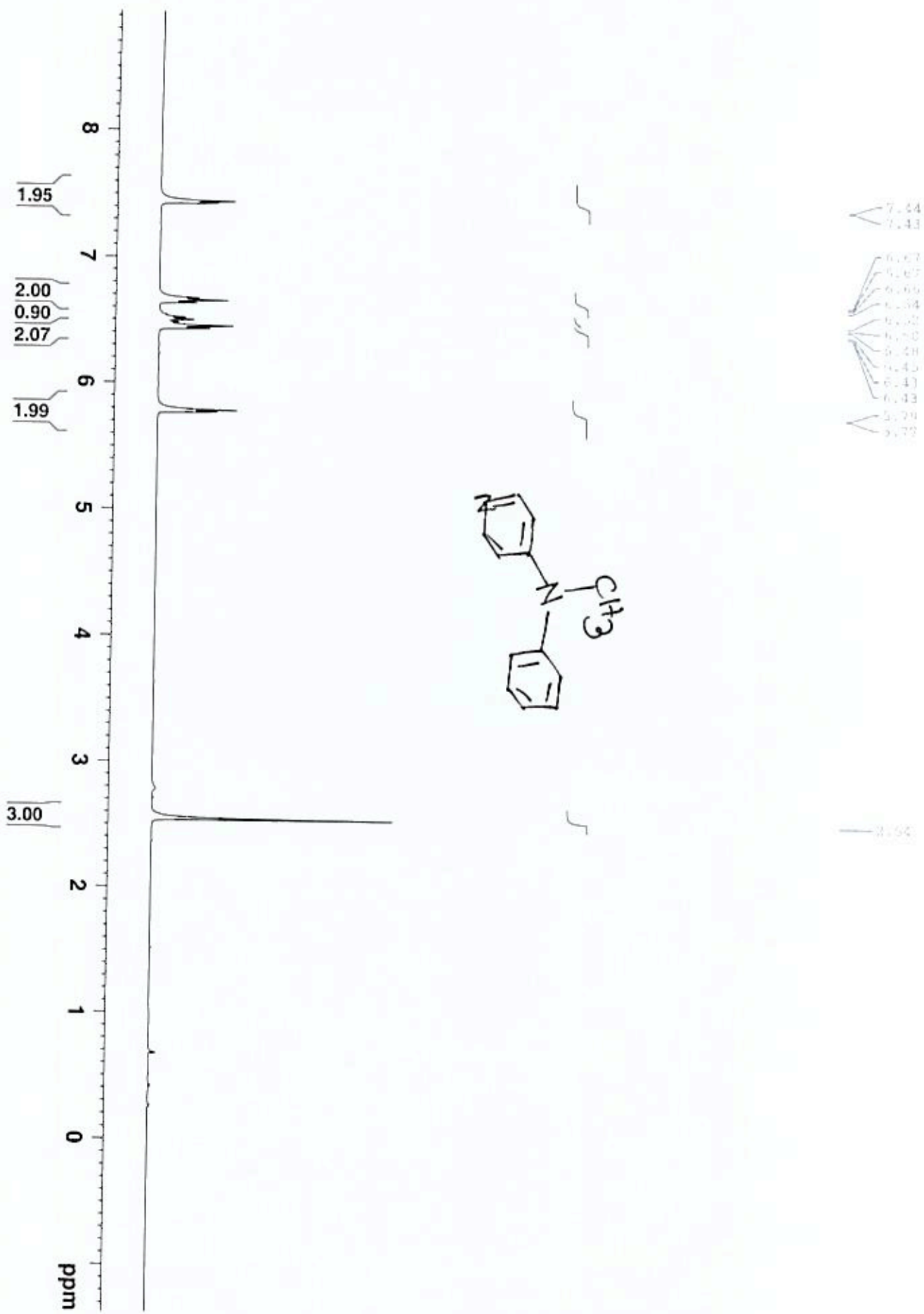


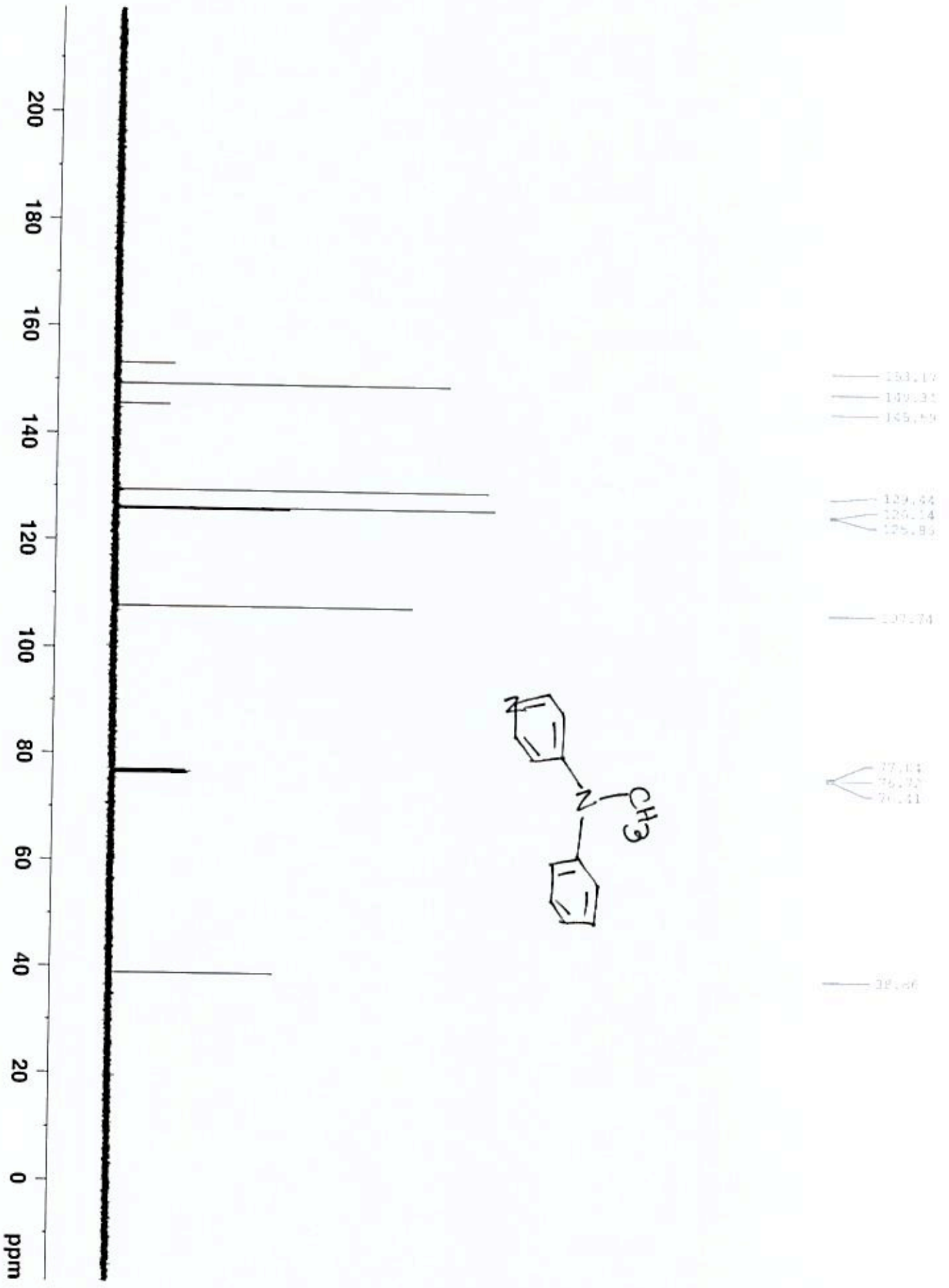
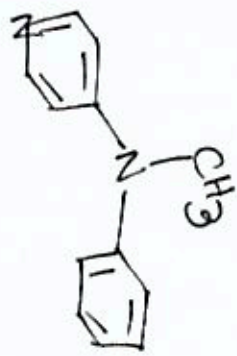


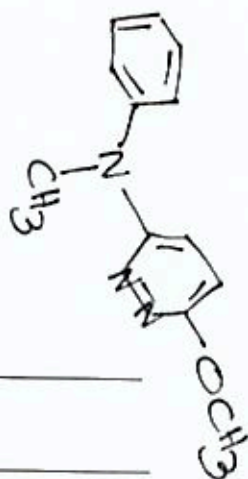
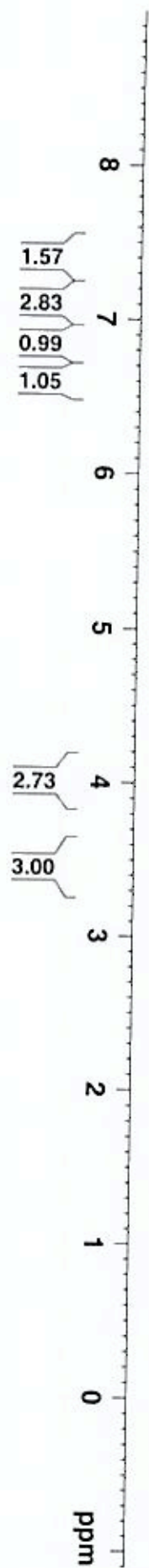


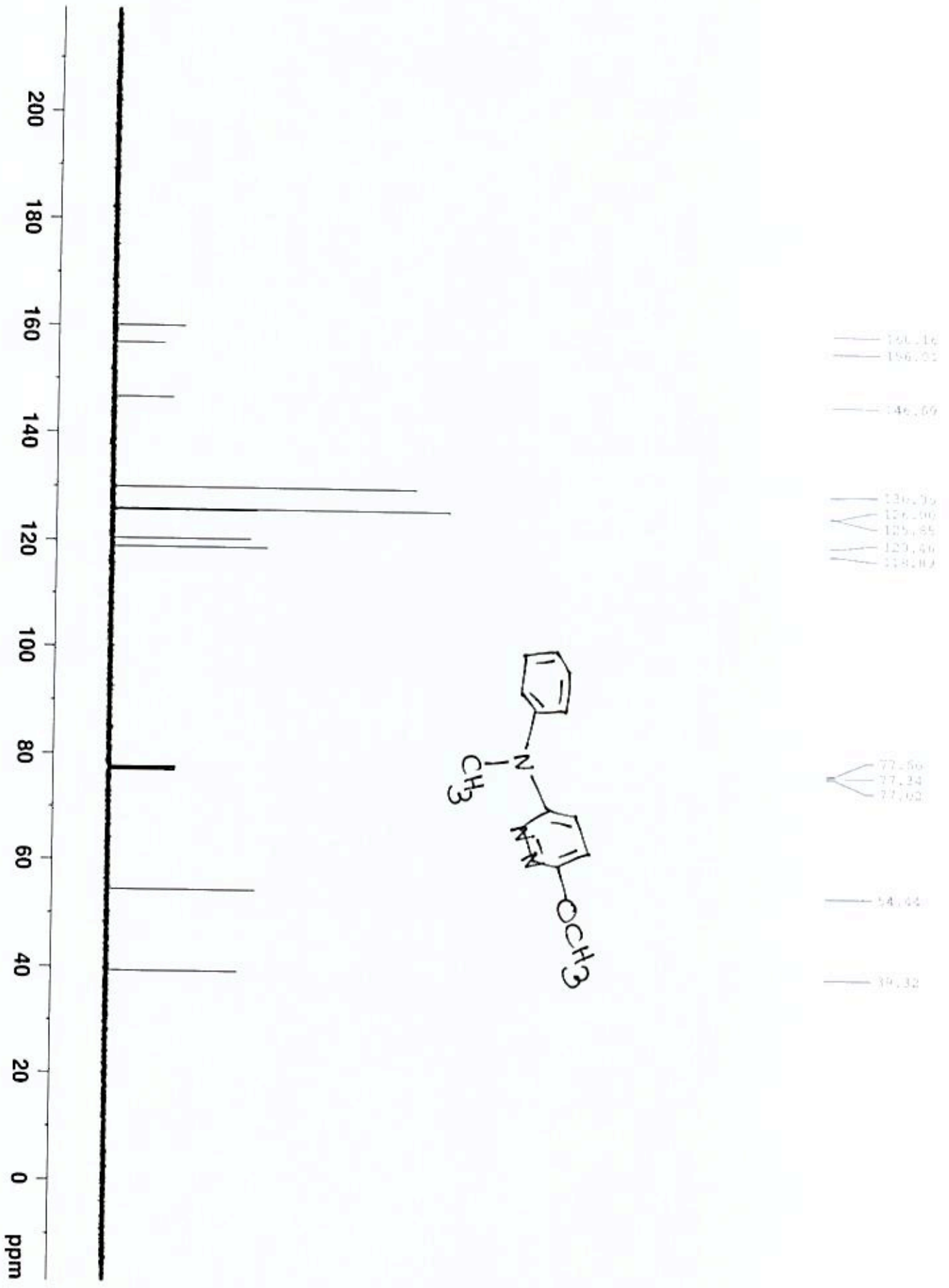


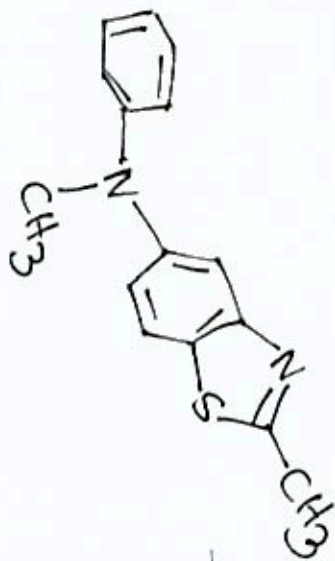
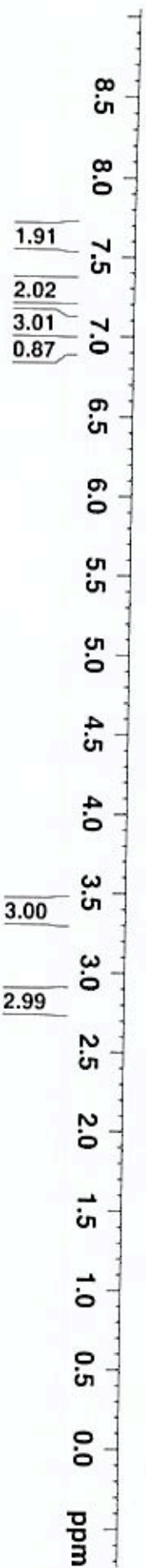






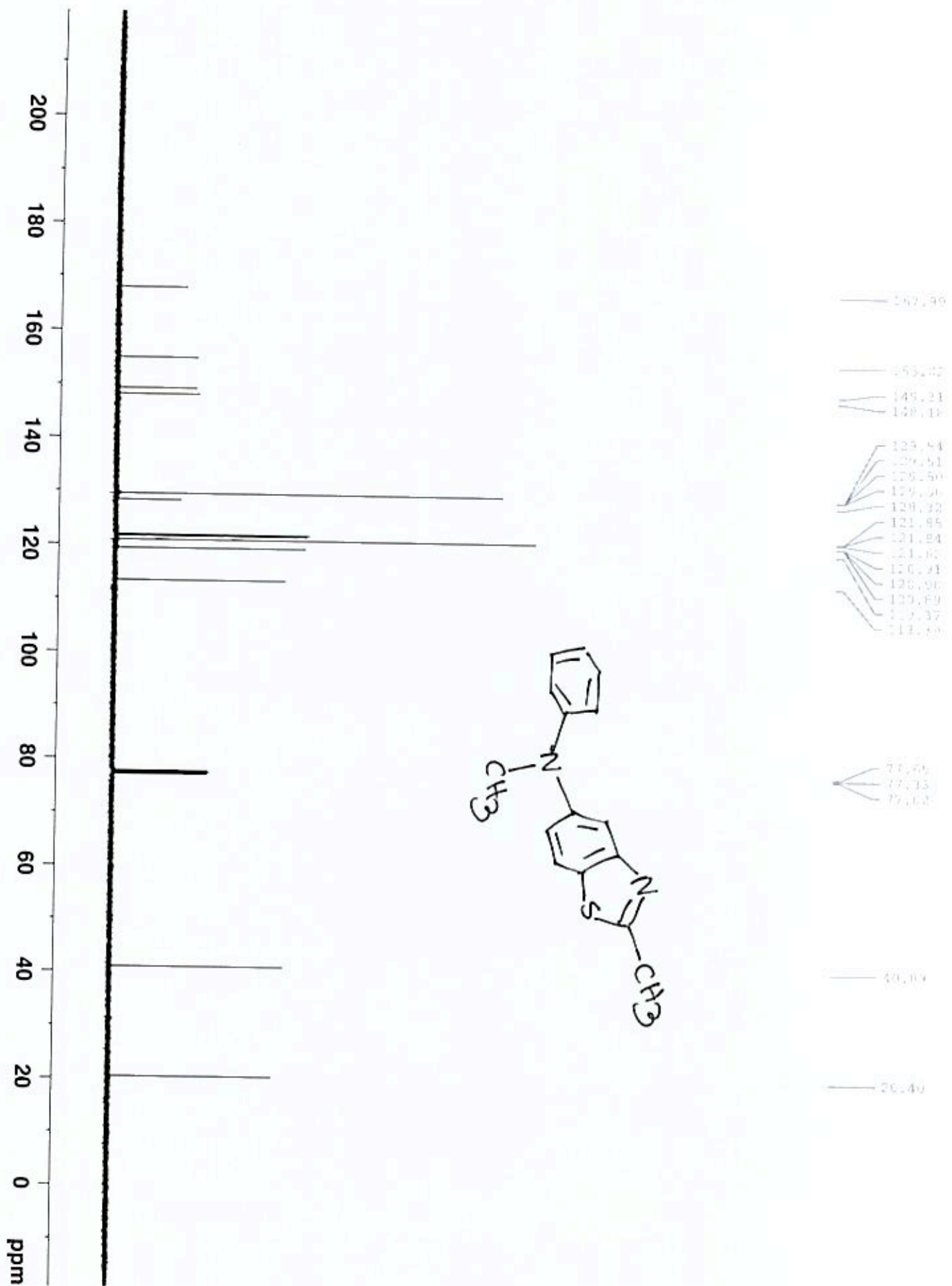






3.33

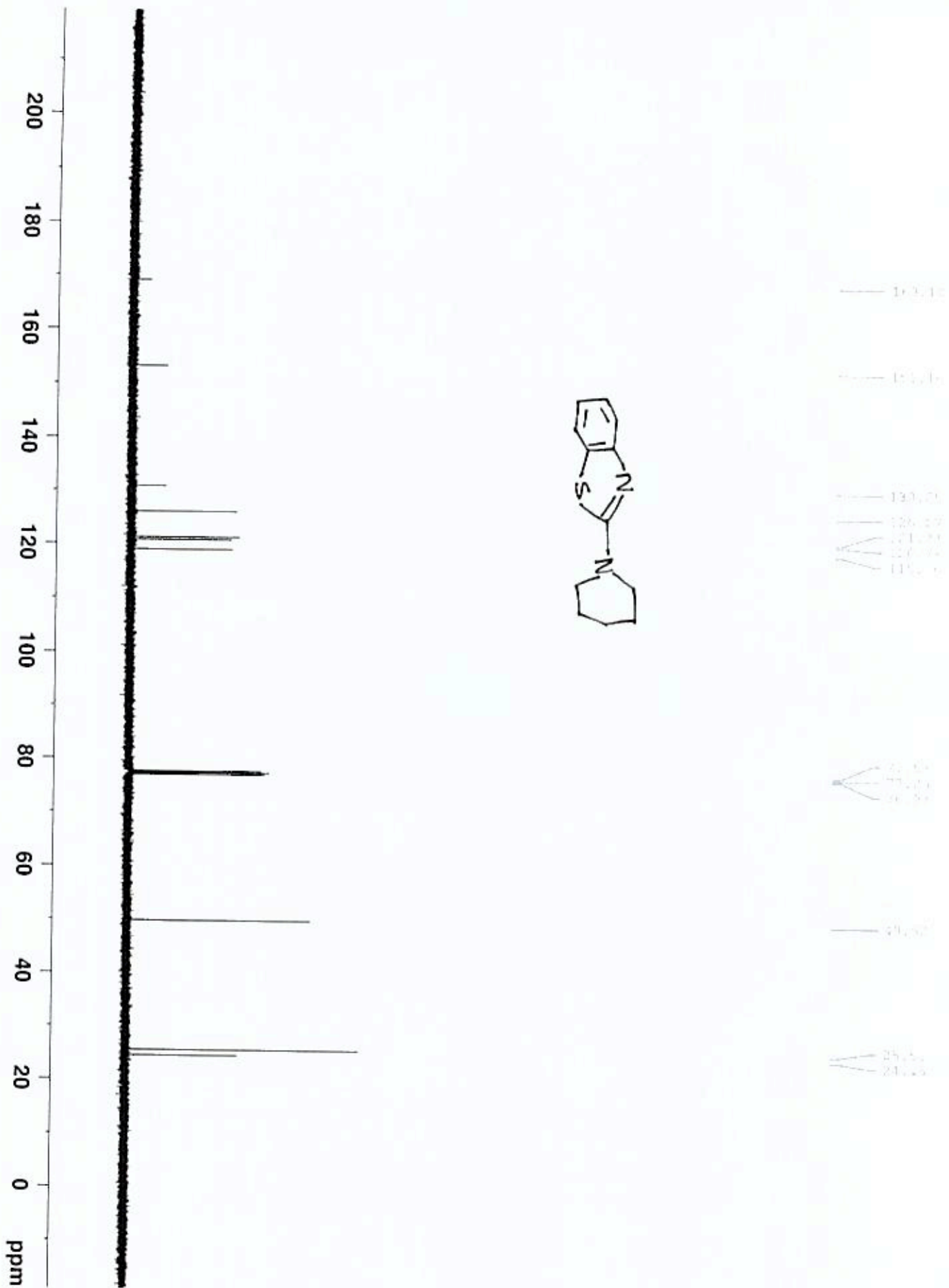
2.78

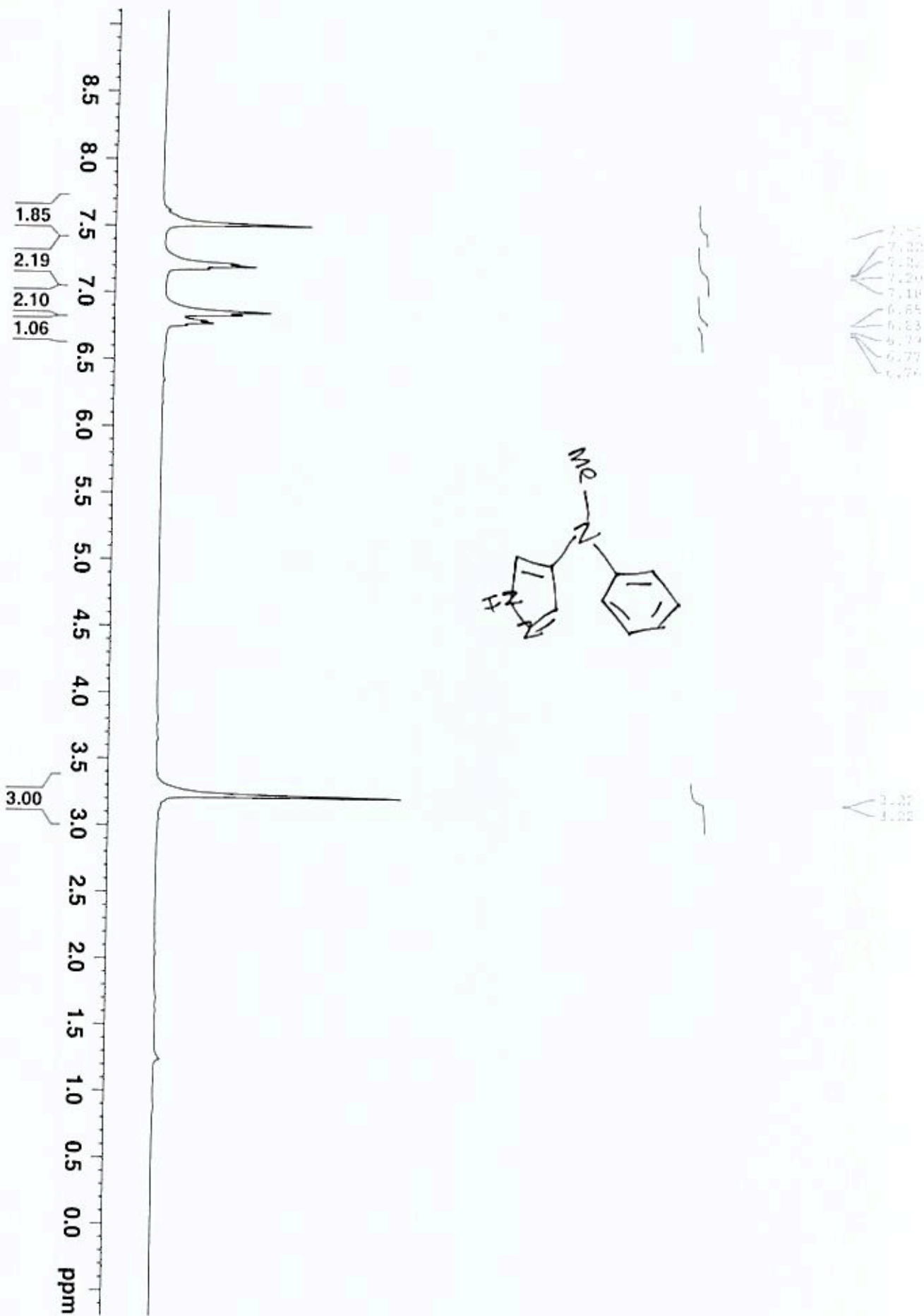


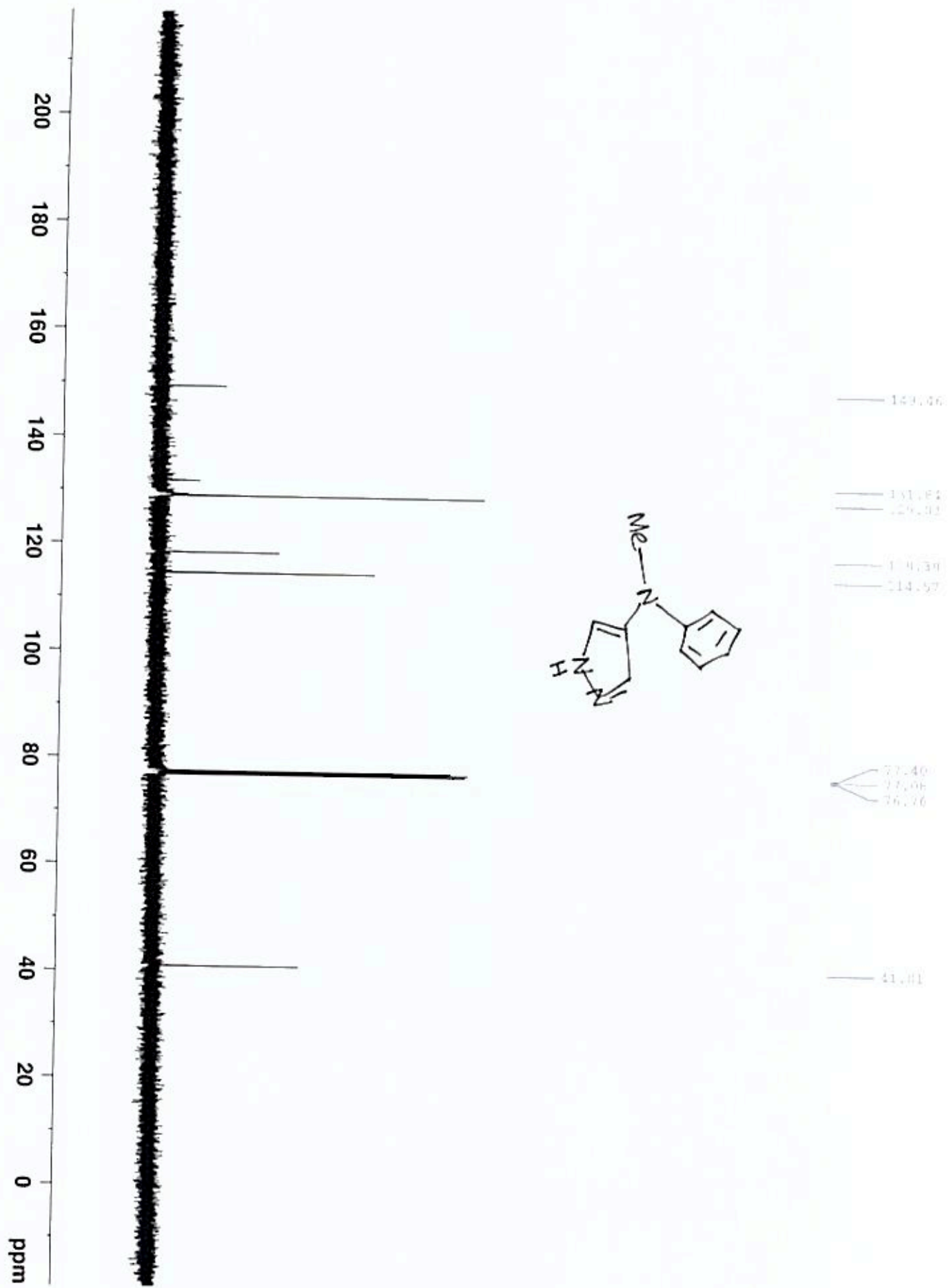


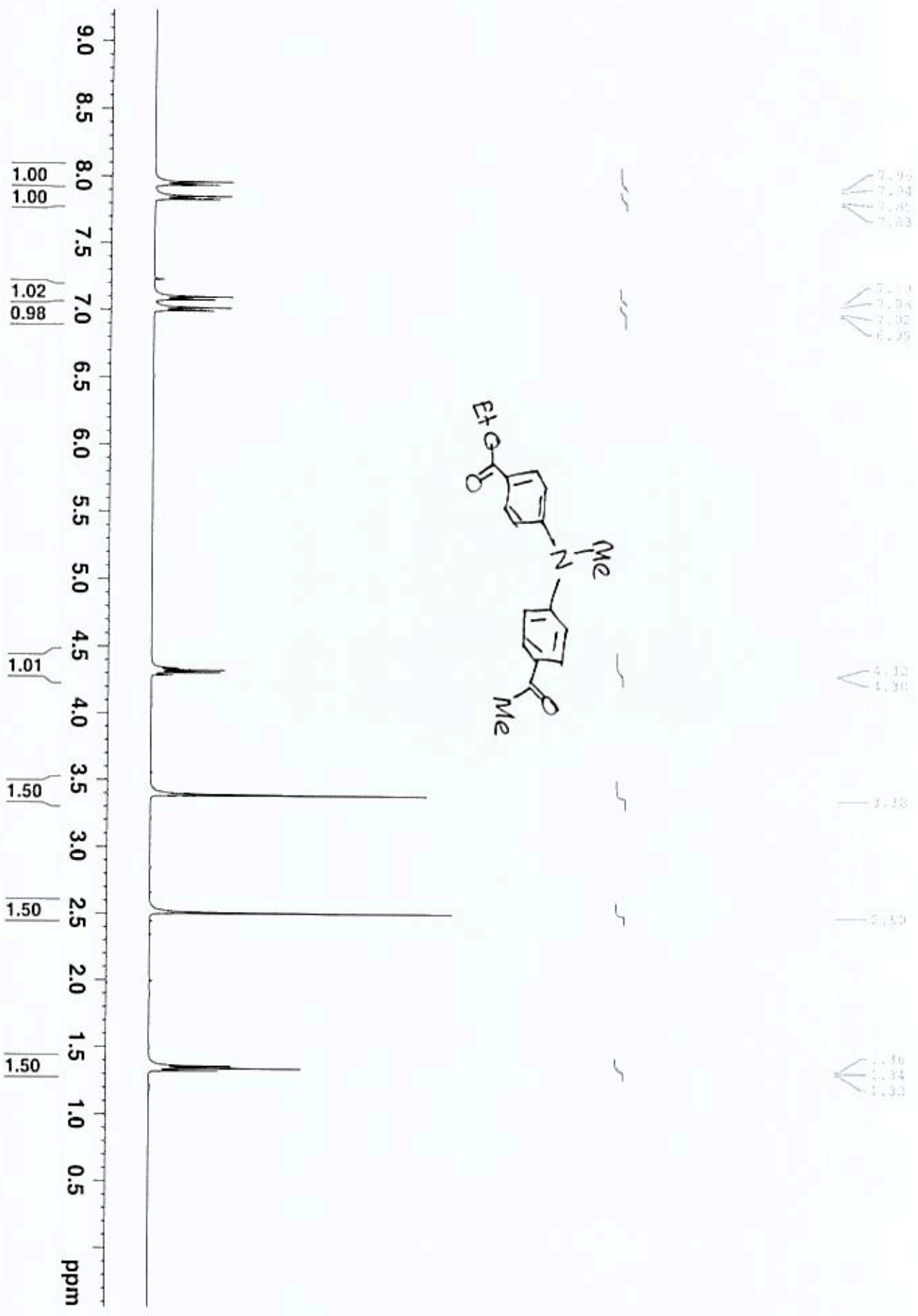
3.99

6.00

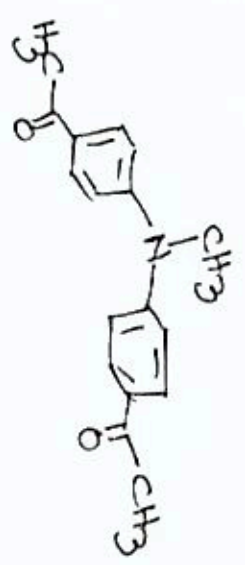










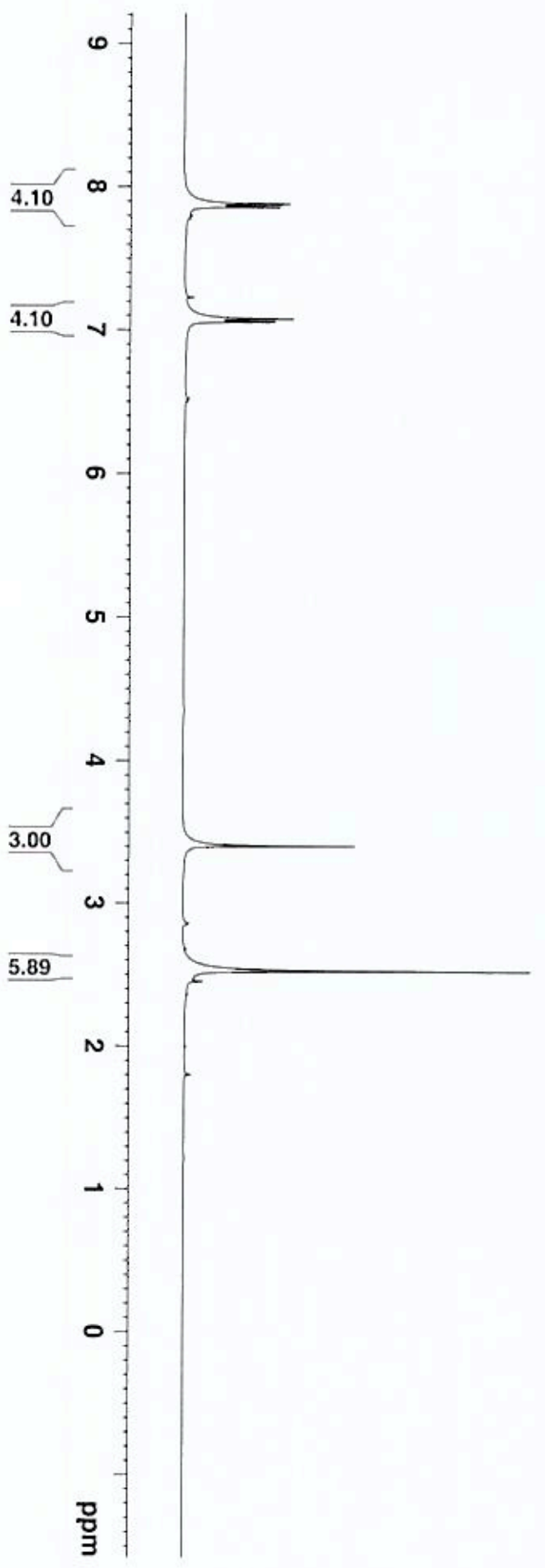


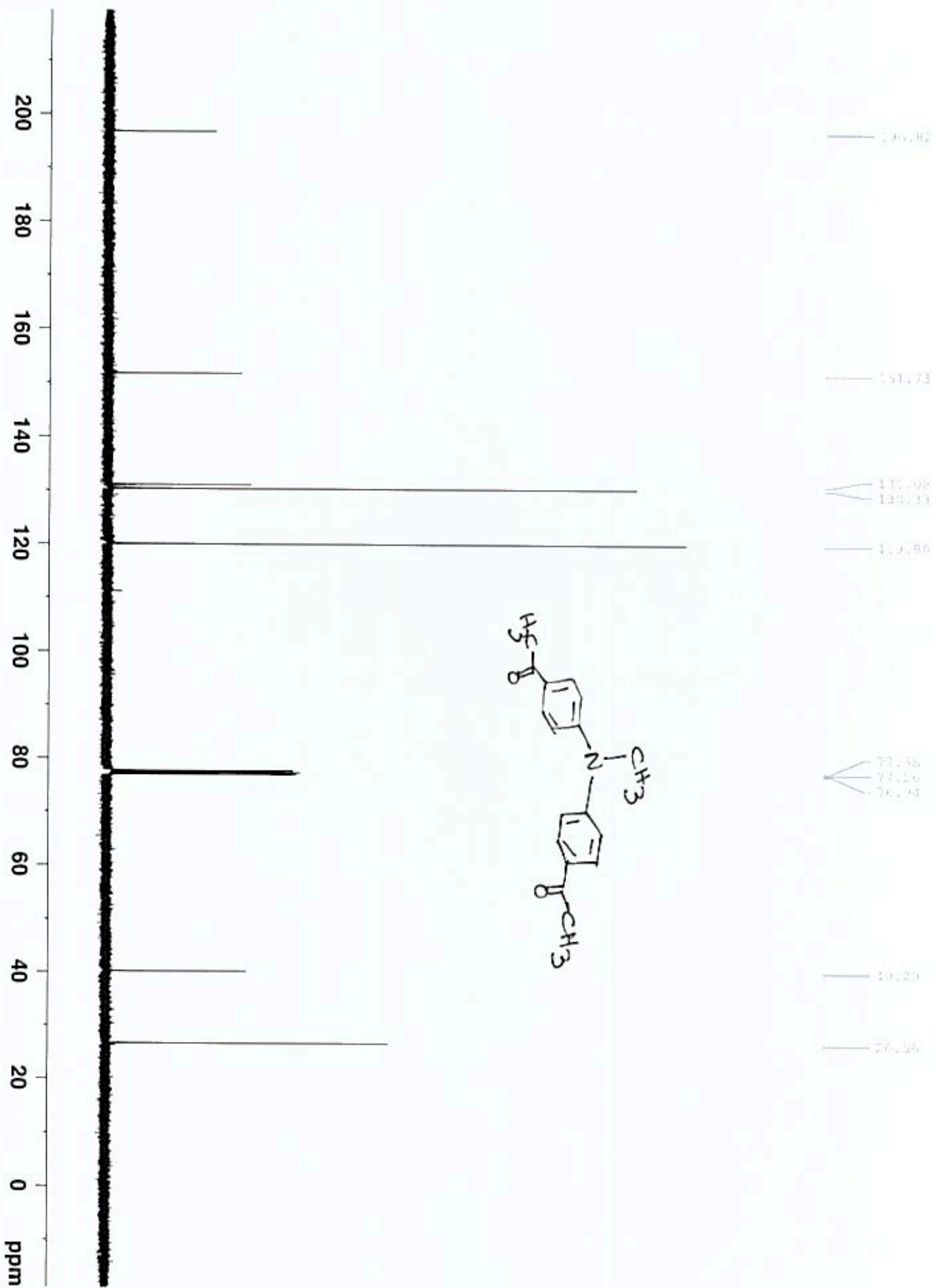
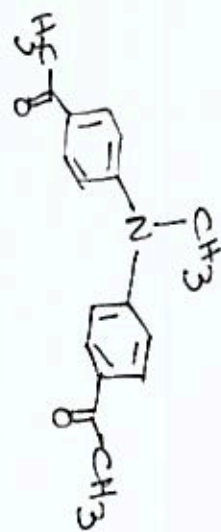
7.93
7.92

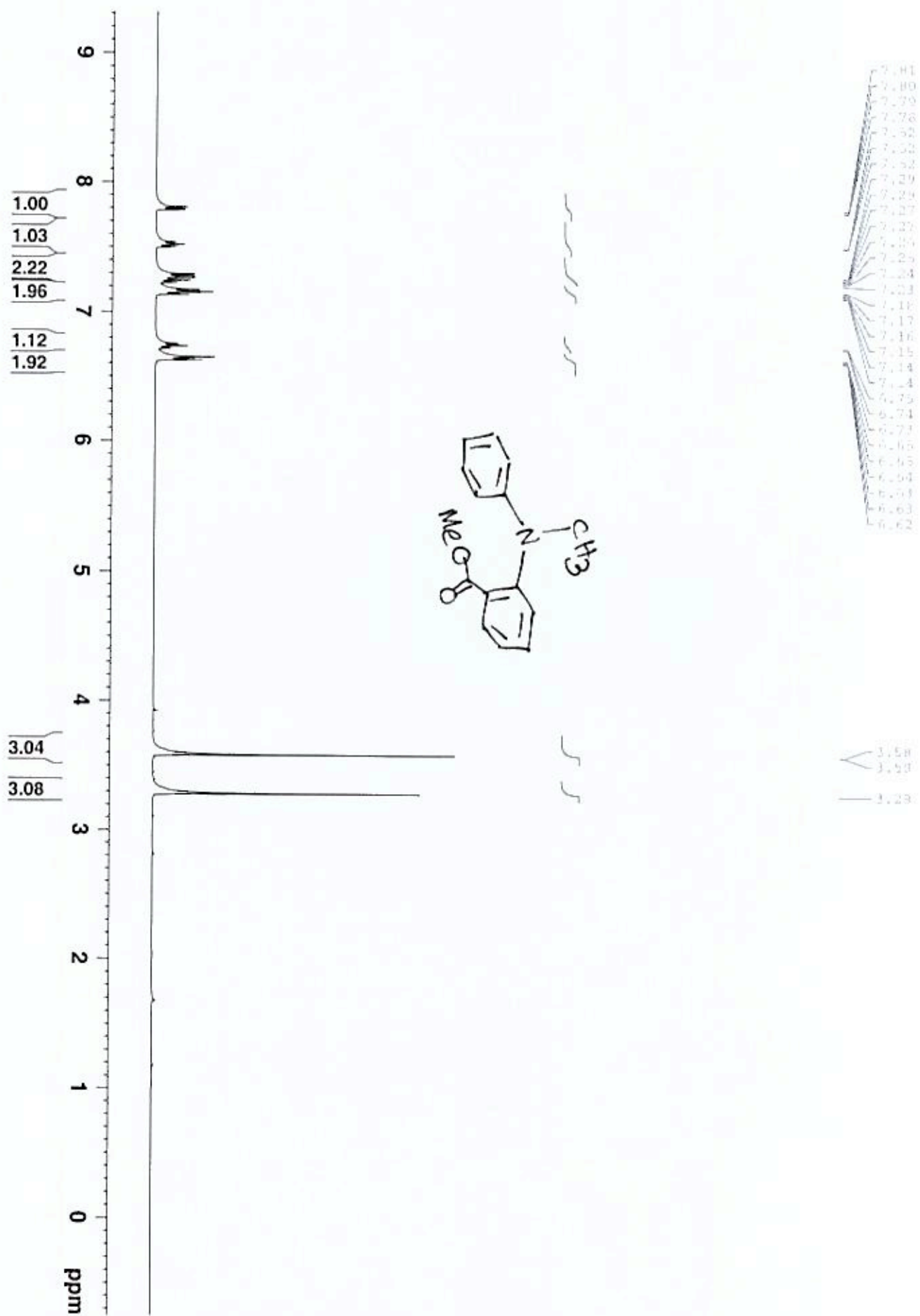
7.08
7.06

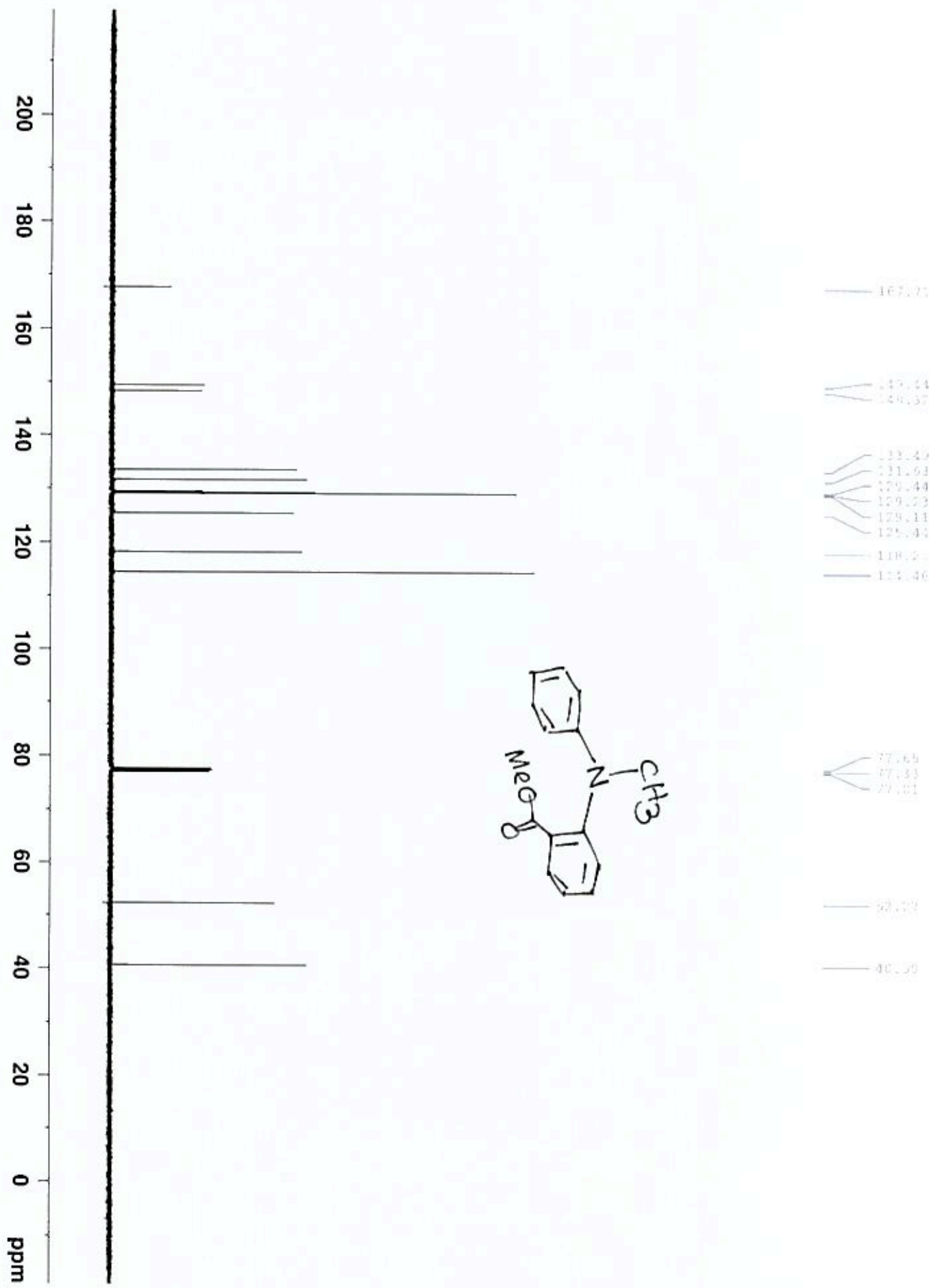
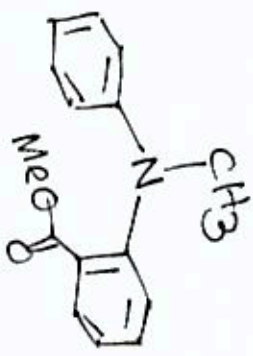
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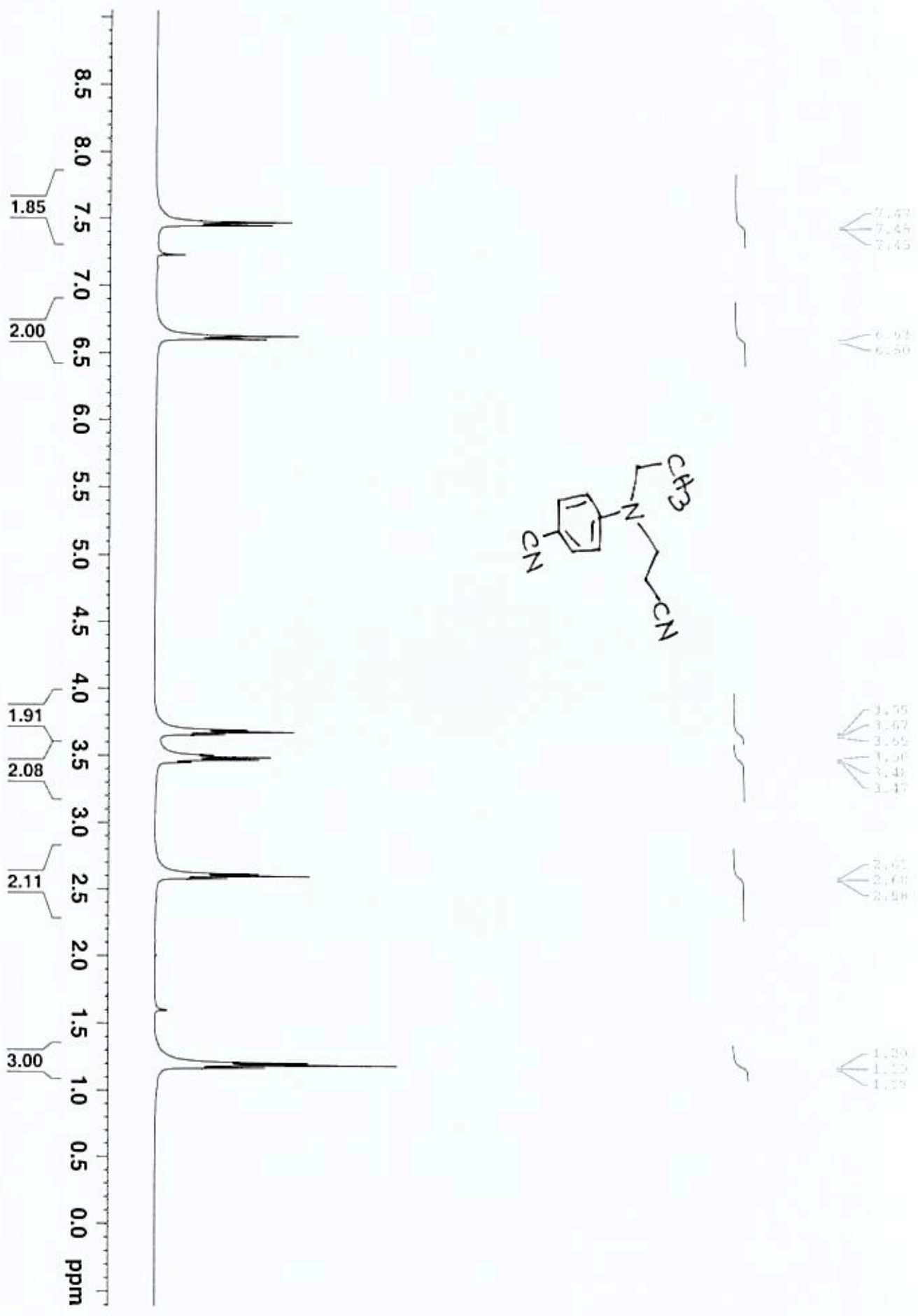
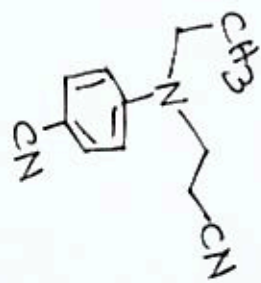
2.05

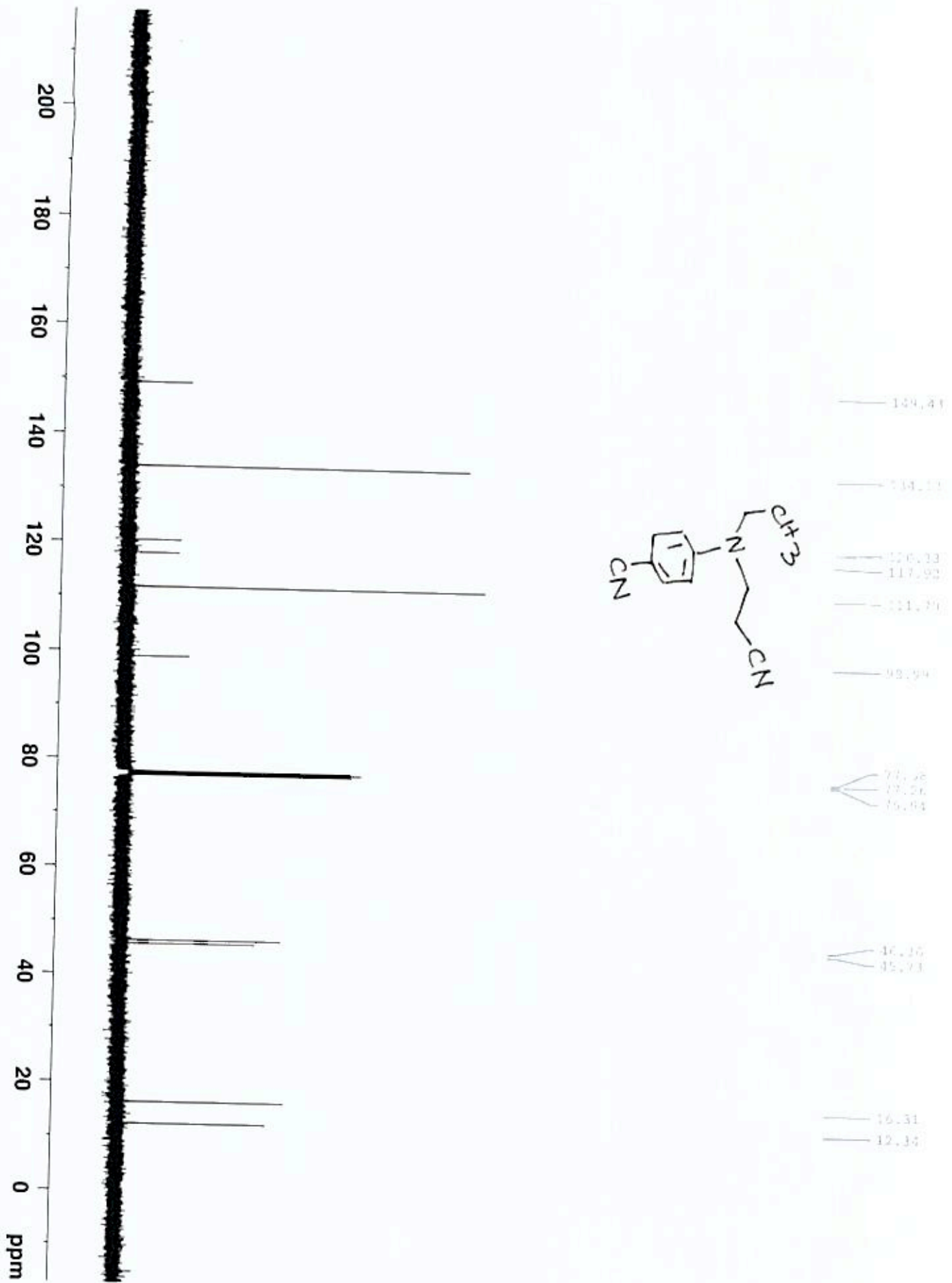


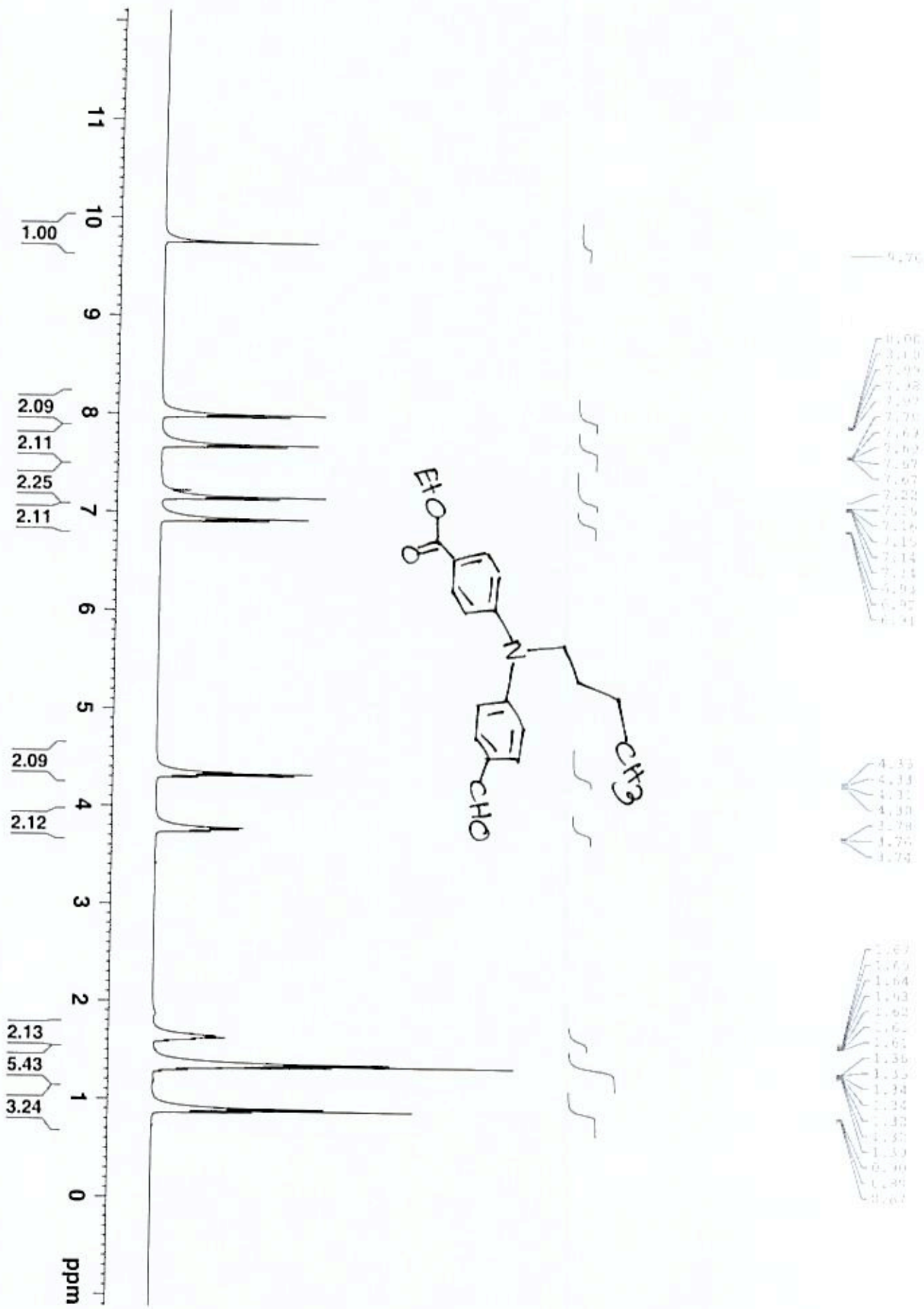


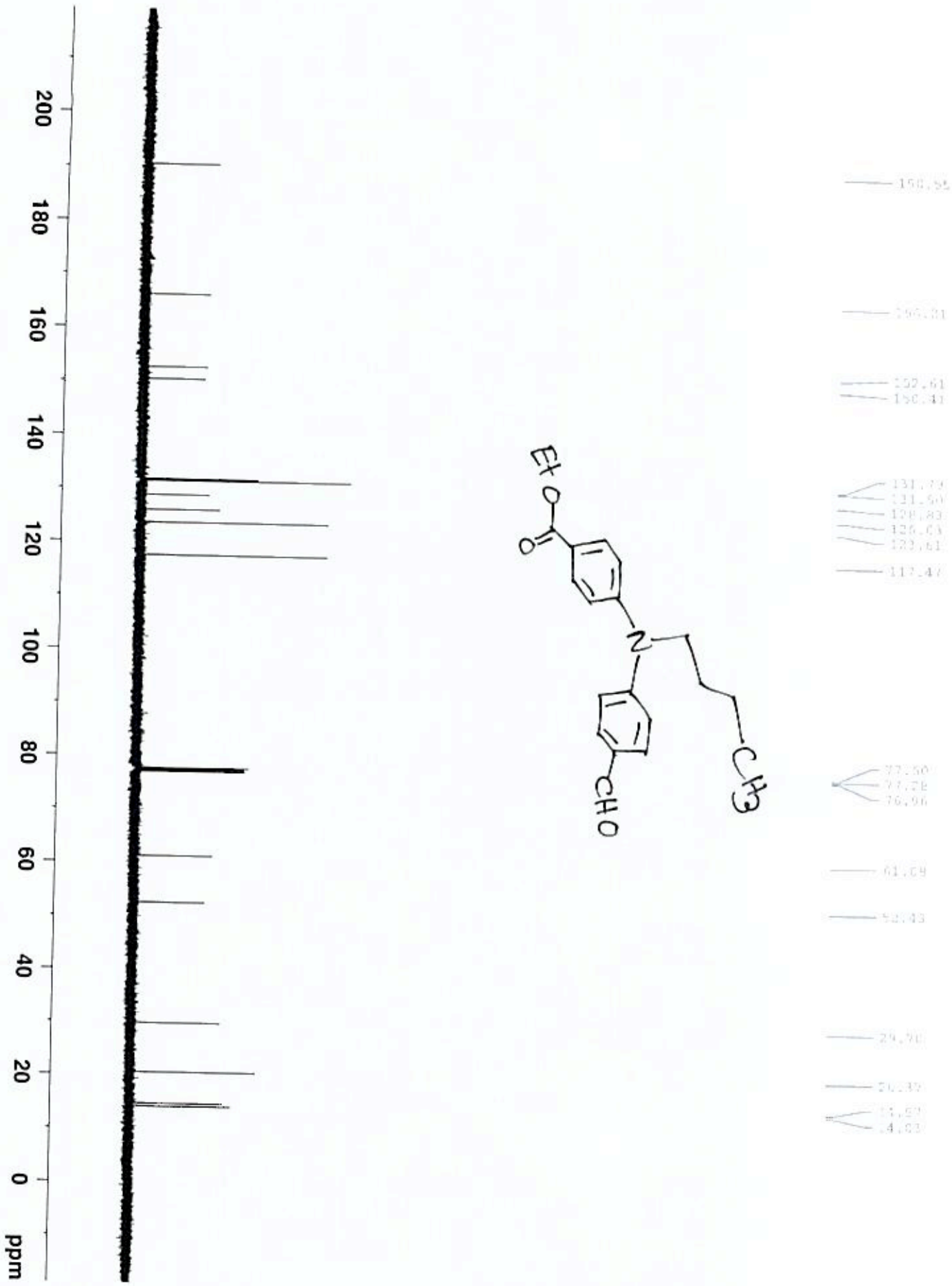


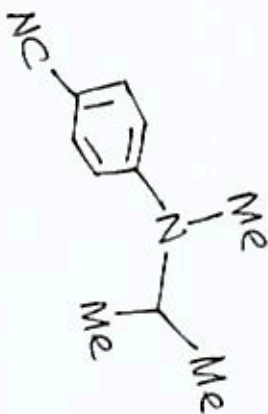












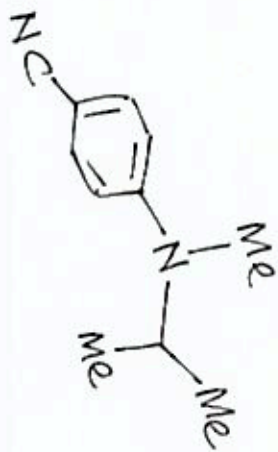
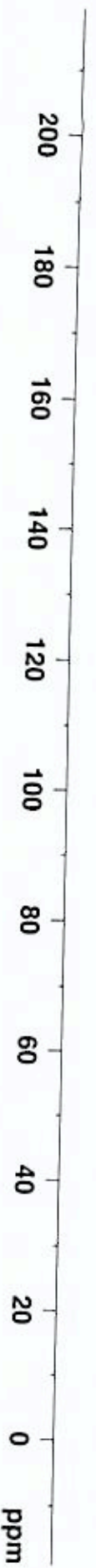
7.51
7.23

6.97
6.55

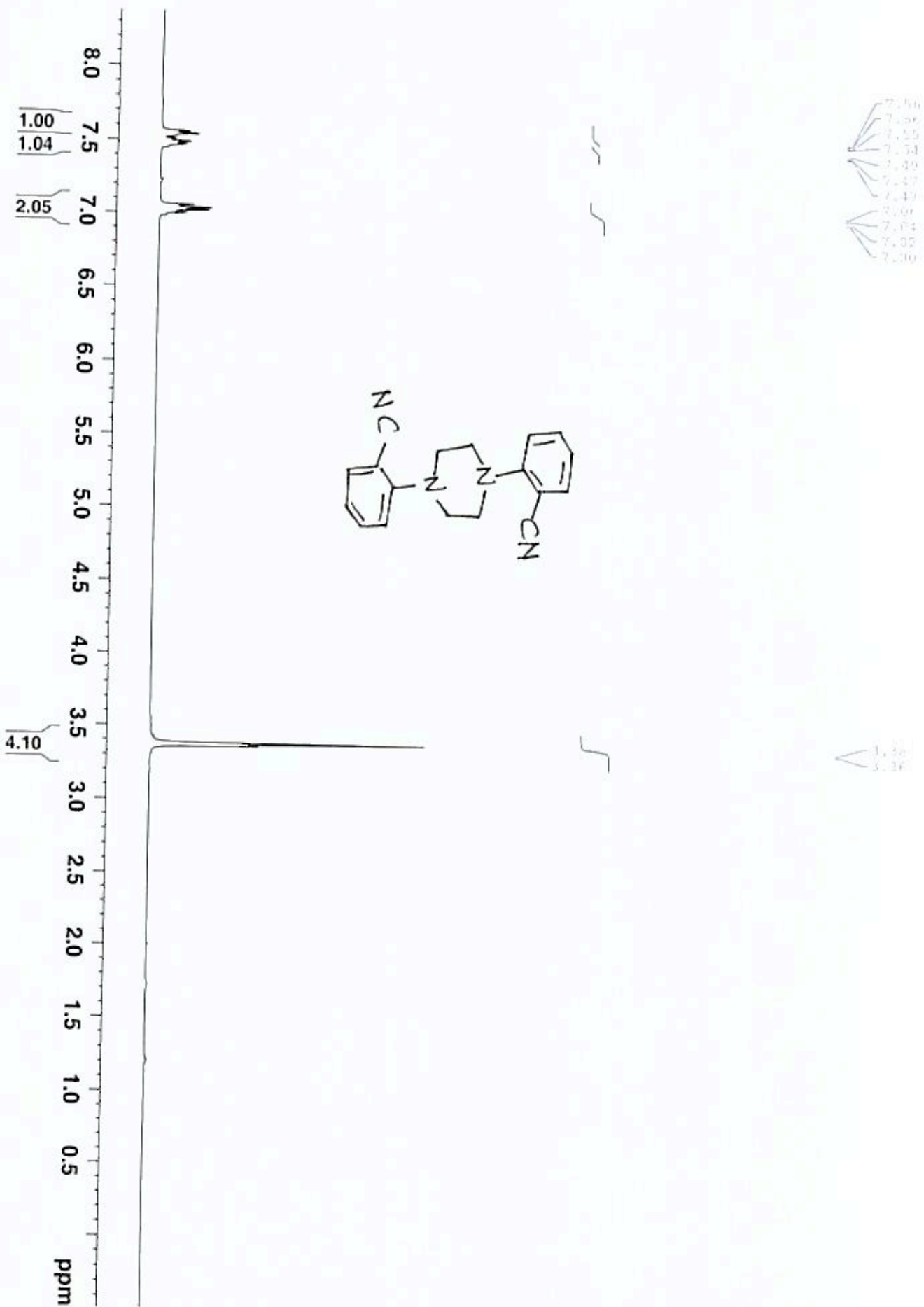
4.02
4.01

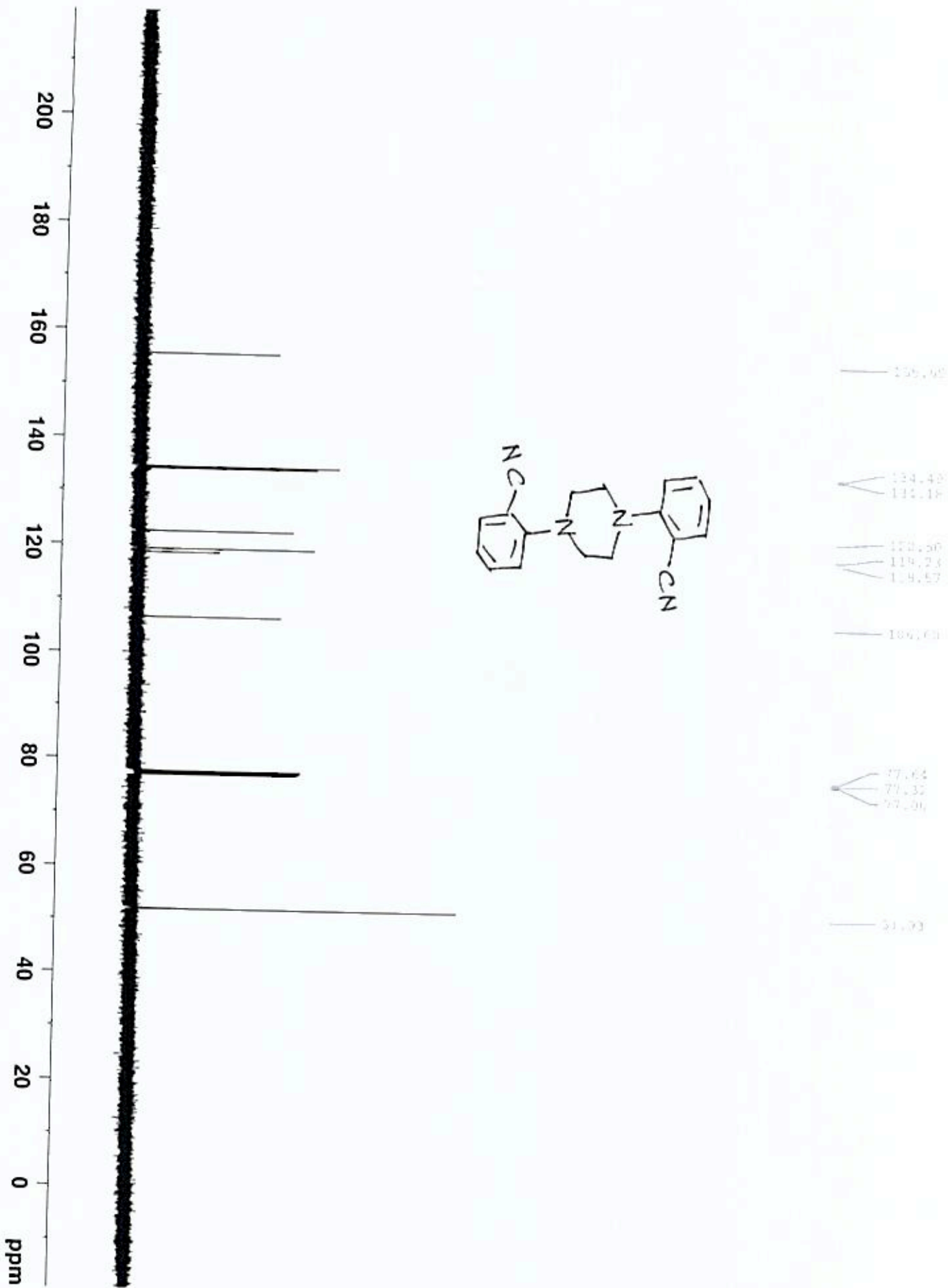
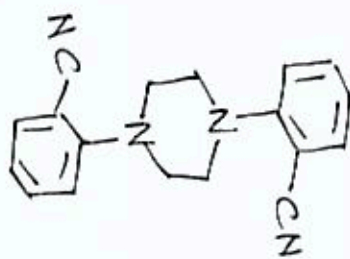
2.66

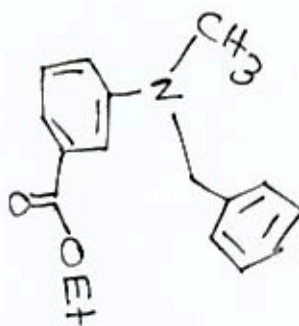
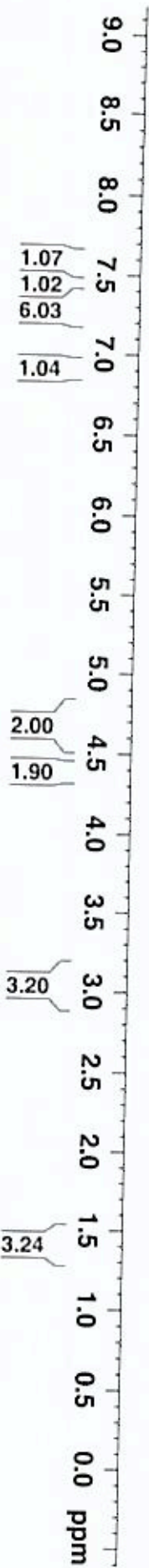
1.07
1.06

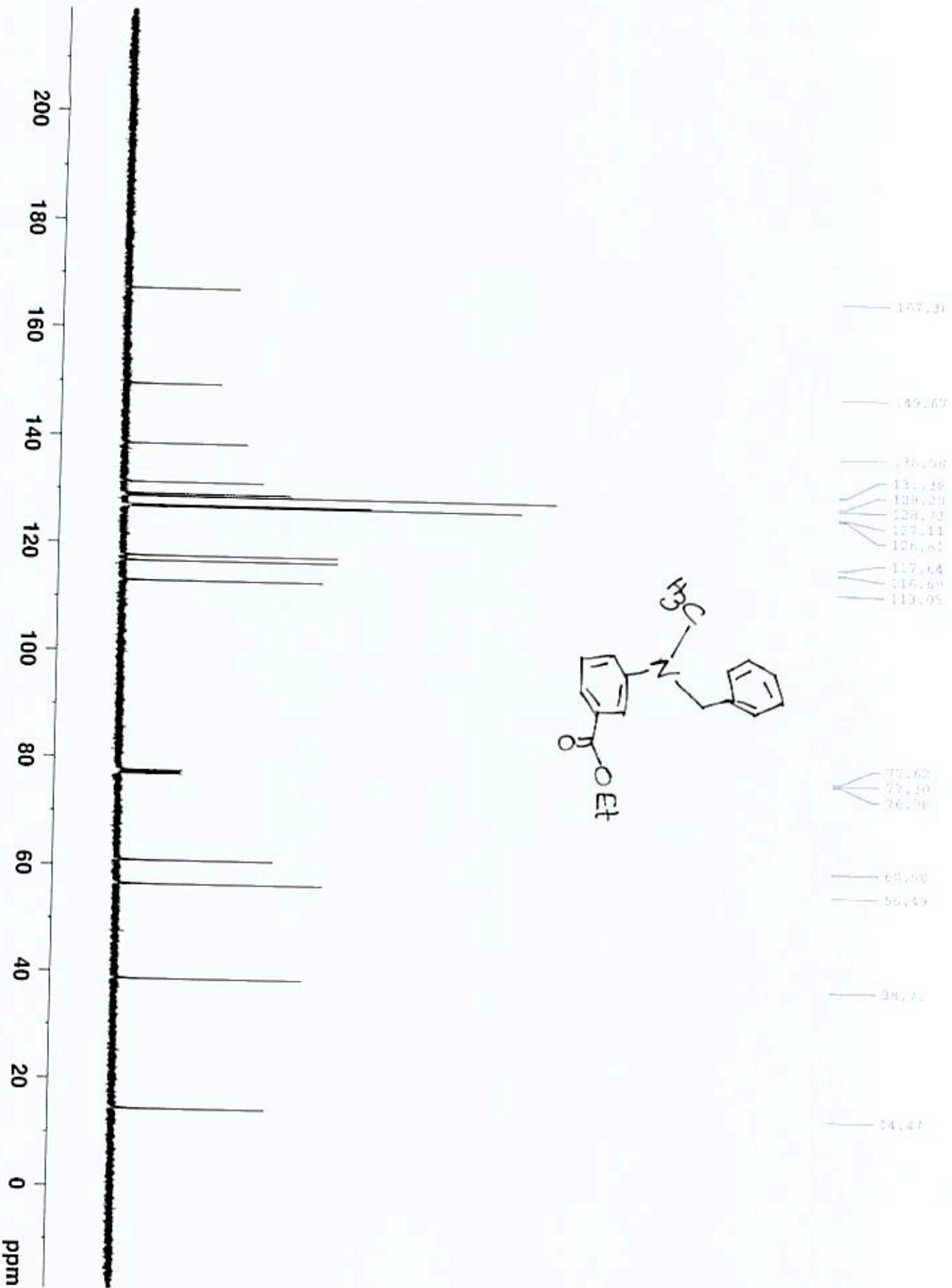


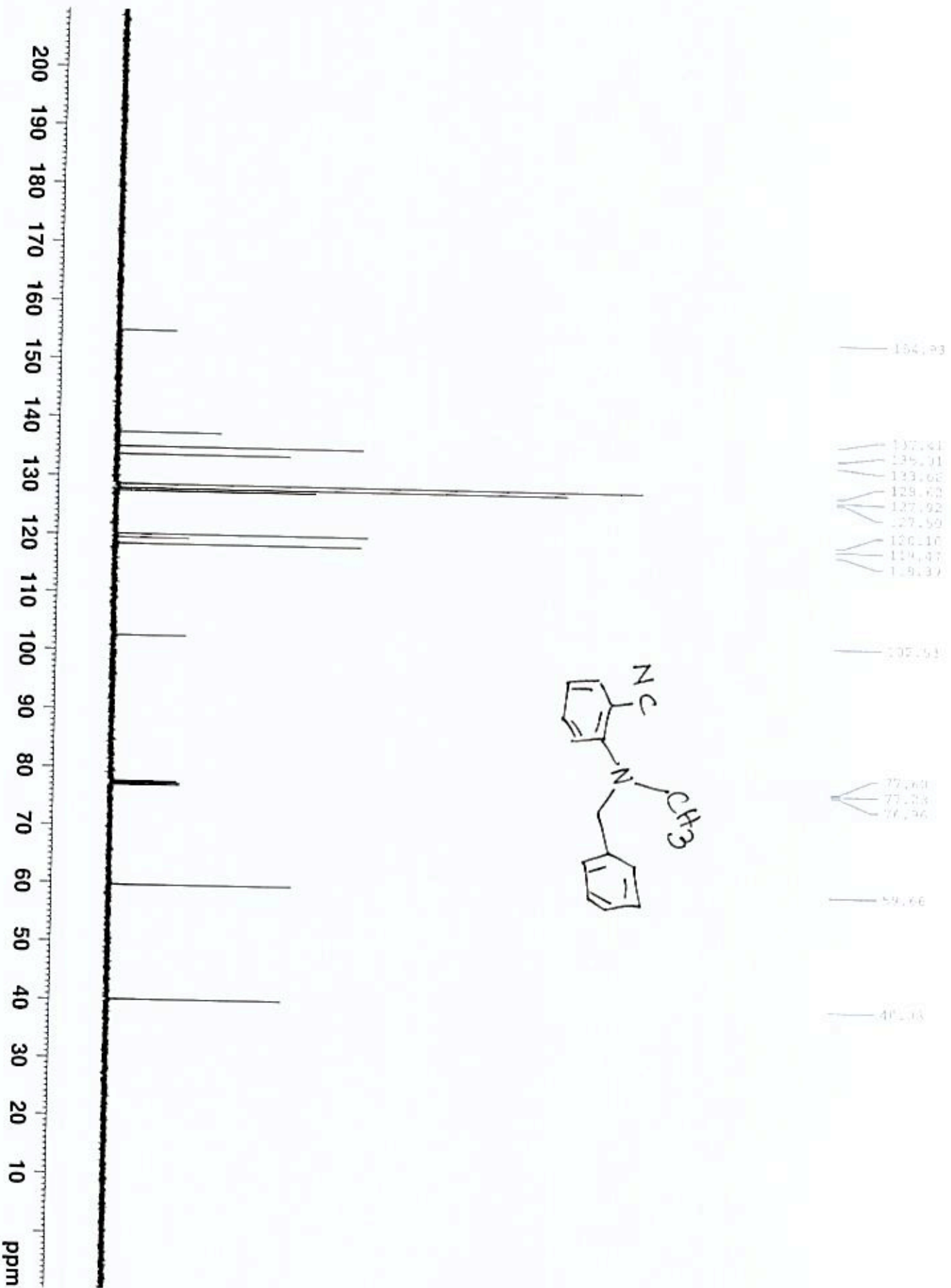
- 152.91
- 133.97
- 130.94
- 112.81
- 96.89
- 77.64
- 77.33
- 77.01
- 48.35
- 29.00
- 19.66

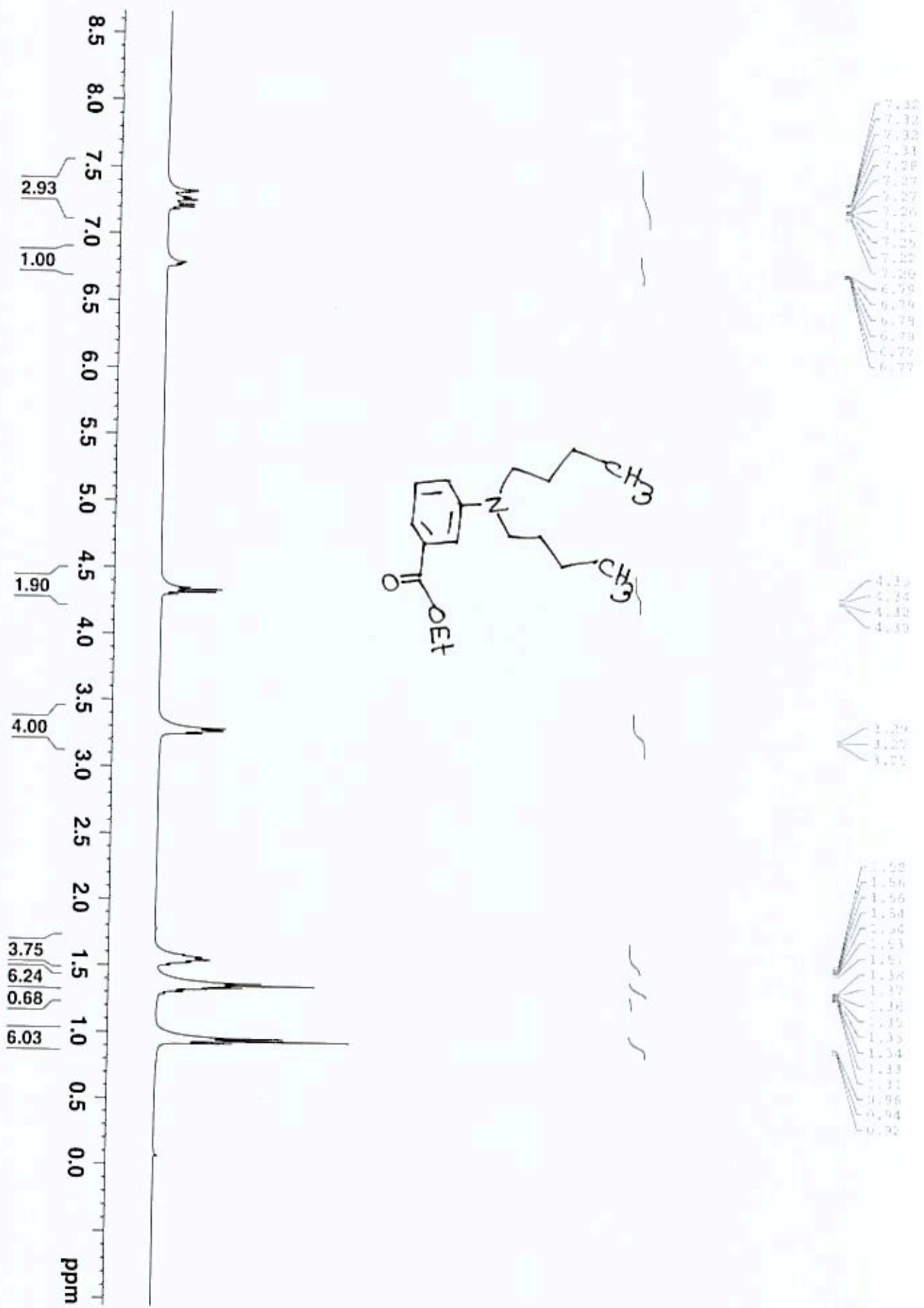


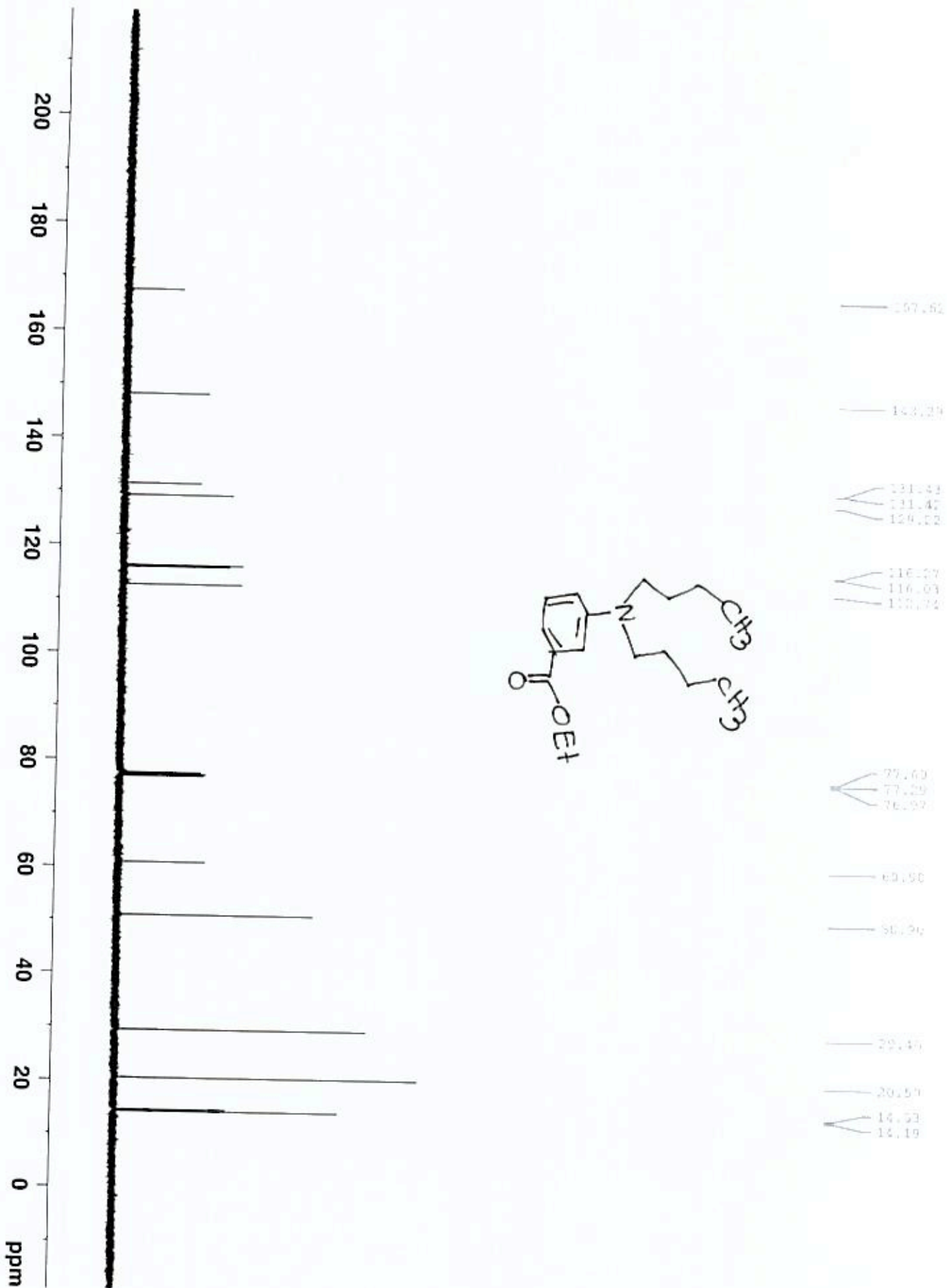
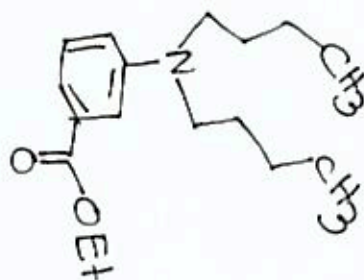


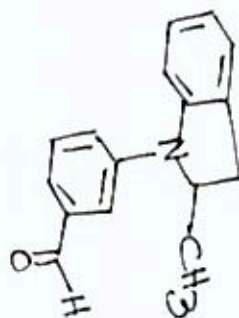
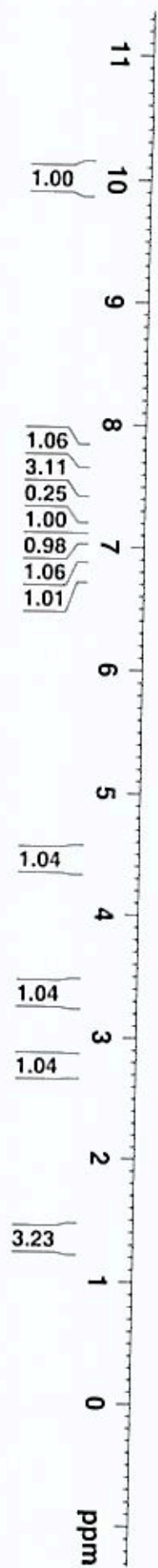


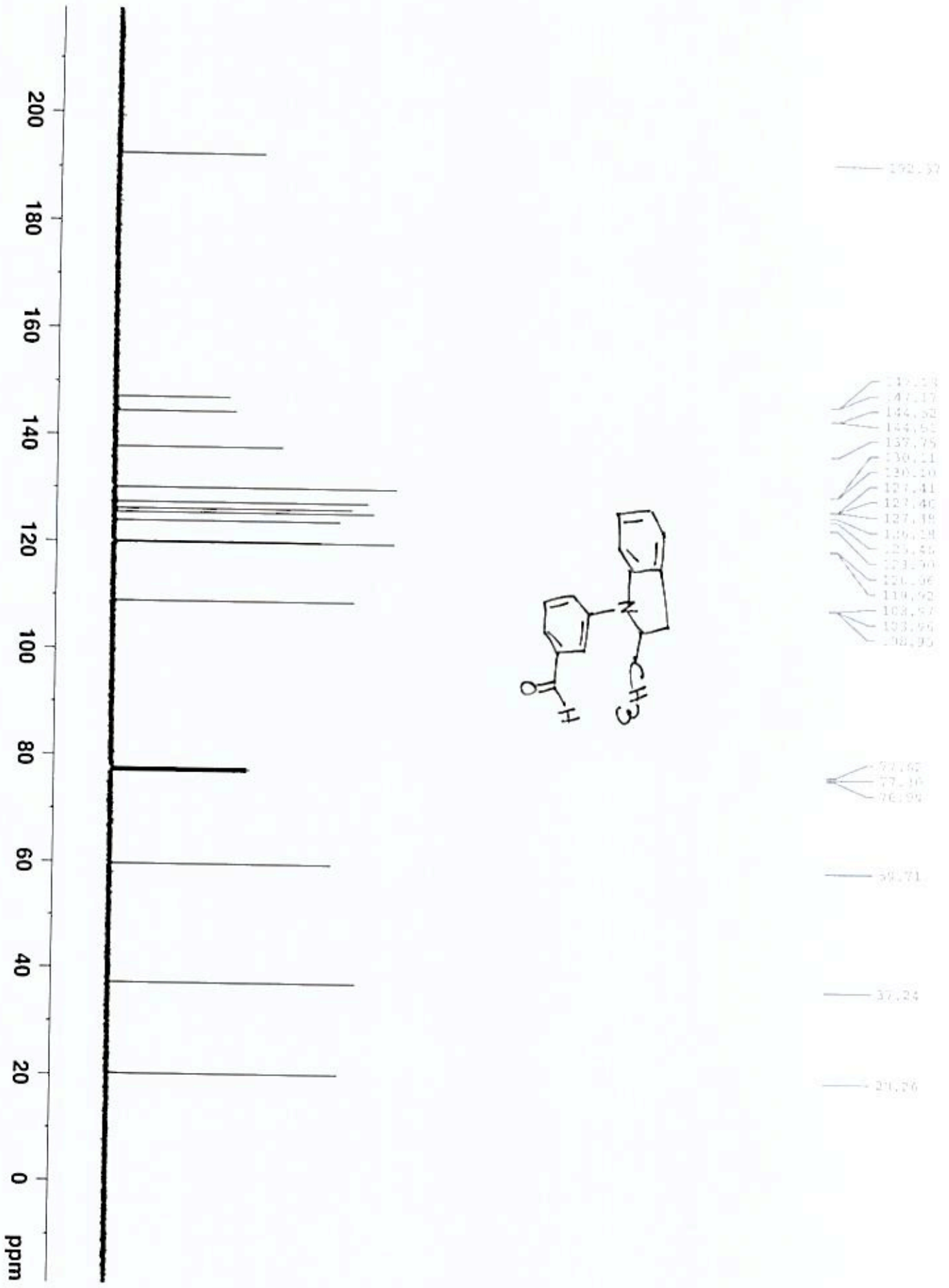
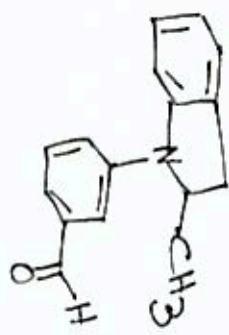


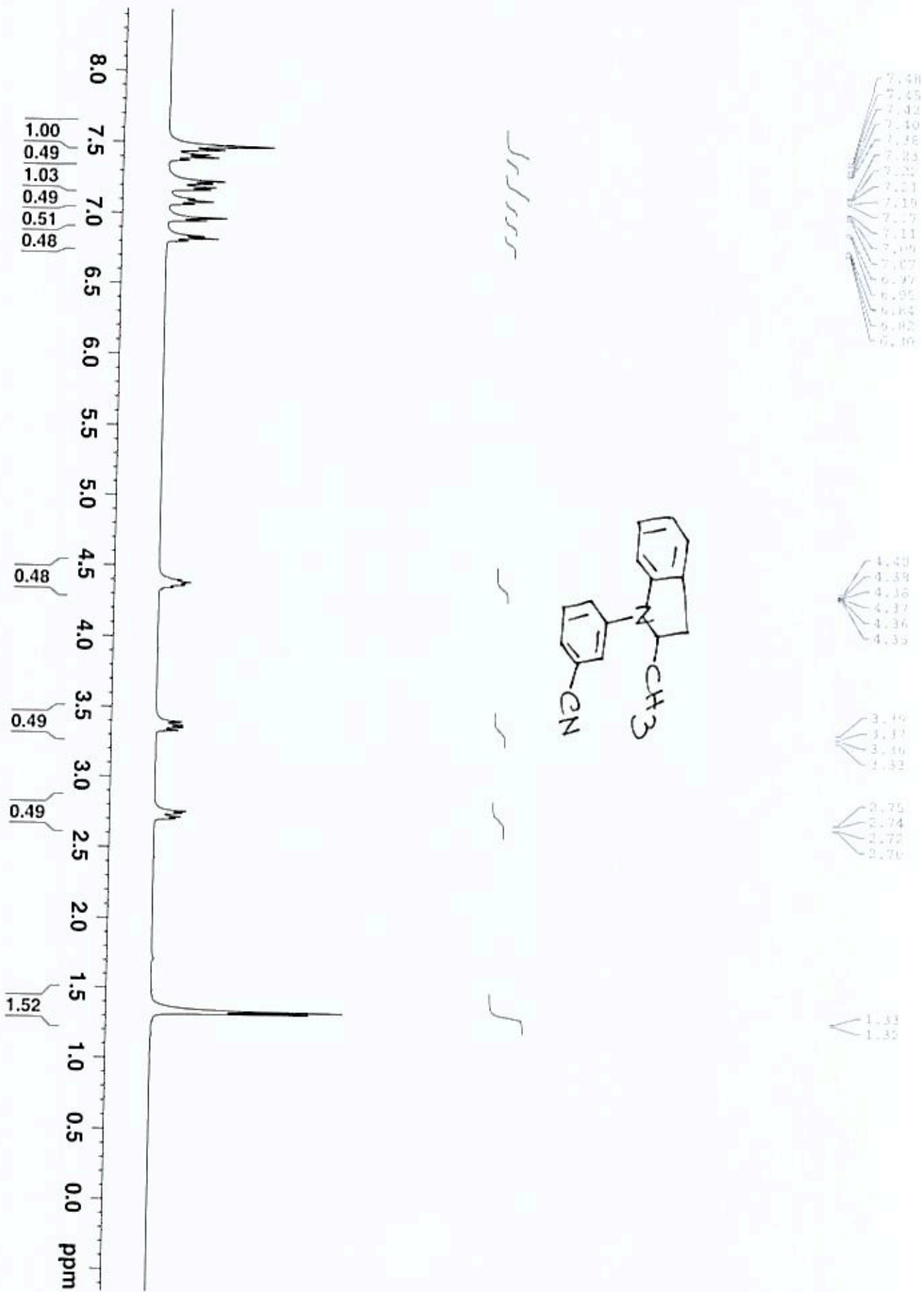




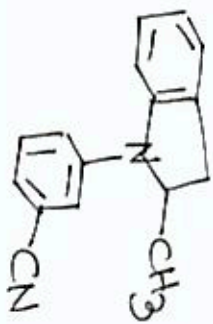
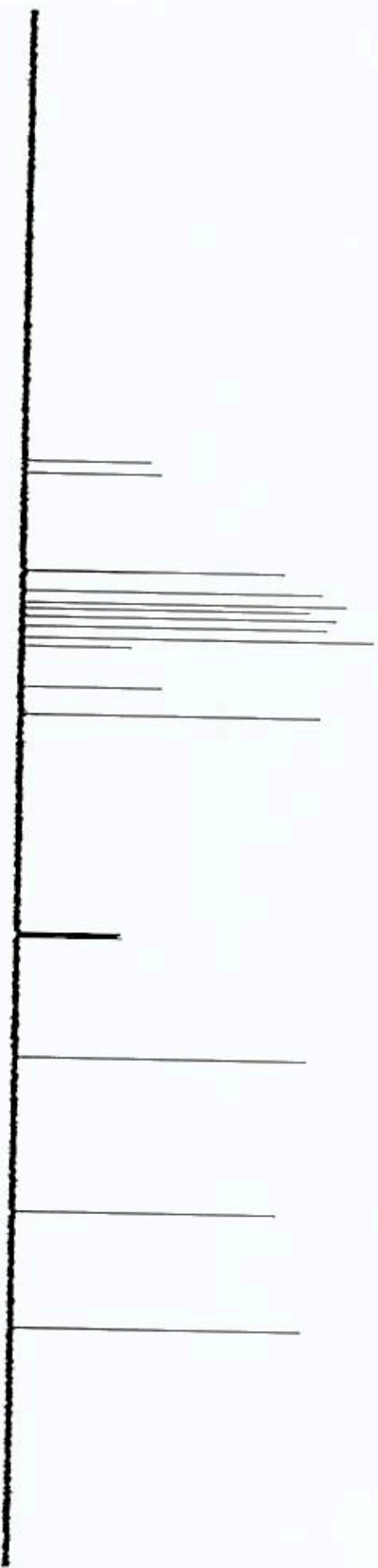






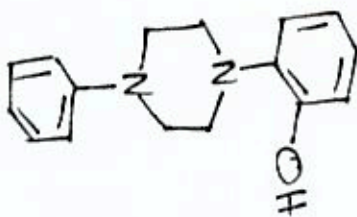
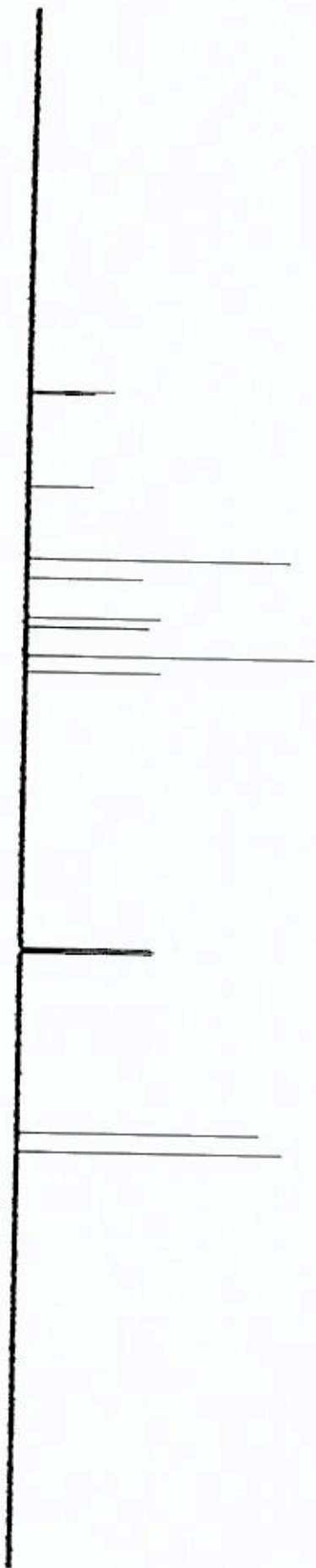


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



- 145.37
- 144.23
- 136.21
- 130.19
- 127.25
- 125.53
- 124.65
- 123.43
- 122.06
- 120.36
- 119.41
- 113.22
- 109.26
- 77.59
- 77.25
- 76.94
- 59.51
- 39.89
- 20.38

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



151.69
151.27

129.92

129.44

126.84

121.91

120.41

120.45

116.53

116.56

116.57

116.56

114.41

114.33

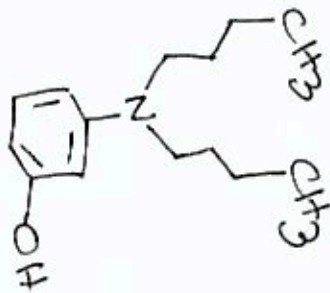
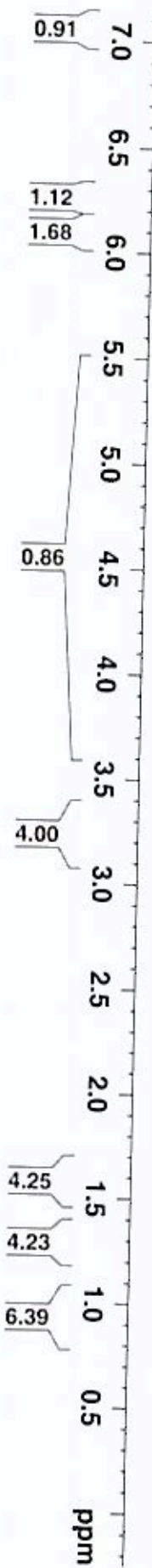
77.59

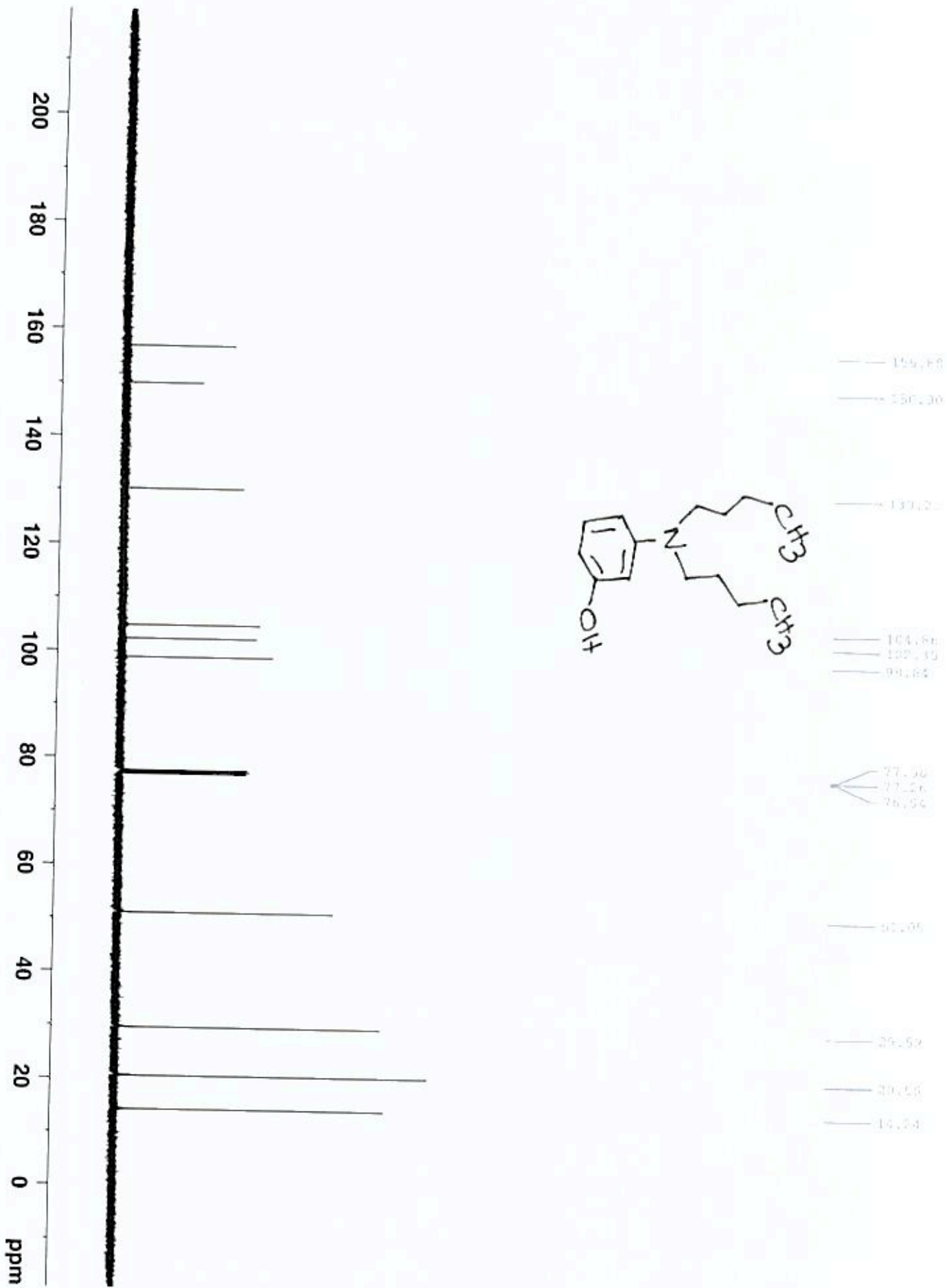
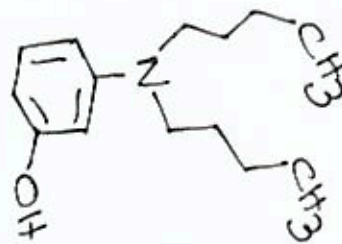
77.27

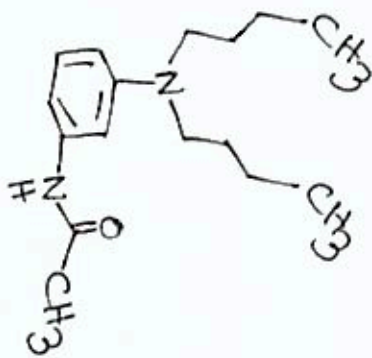
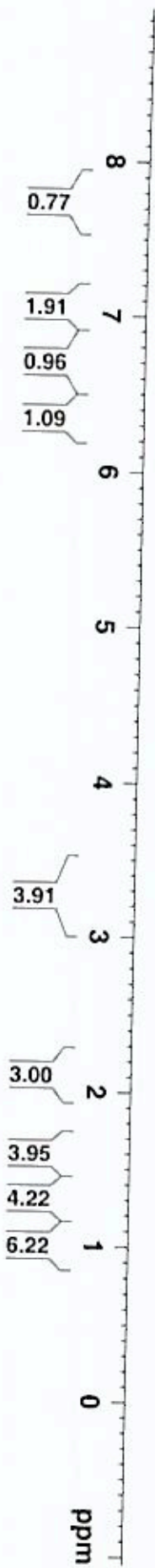
76.95

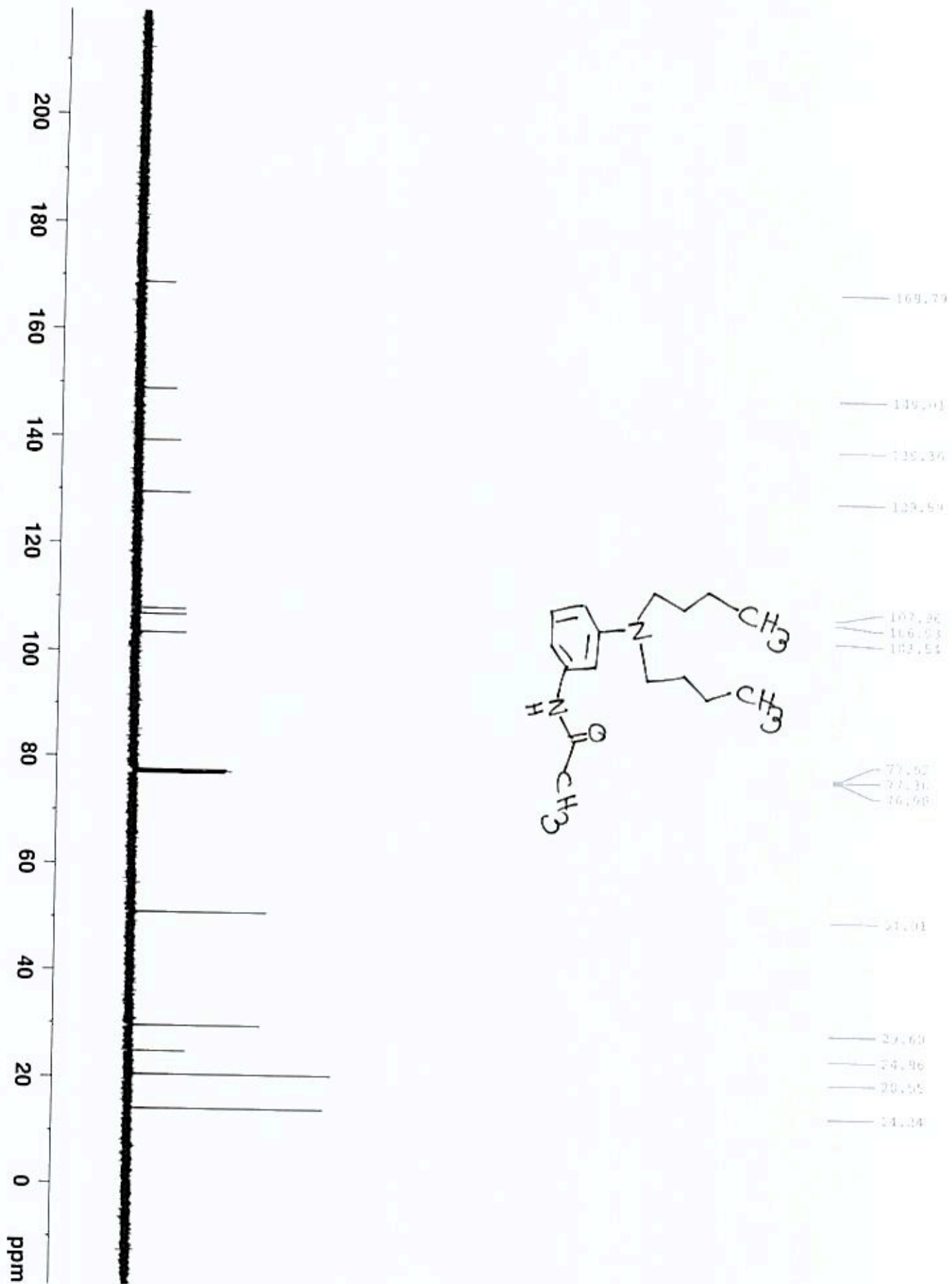
52.06

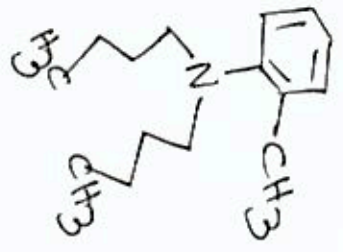
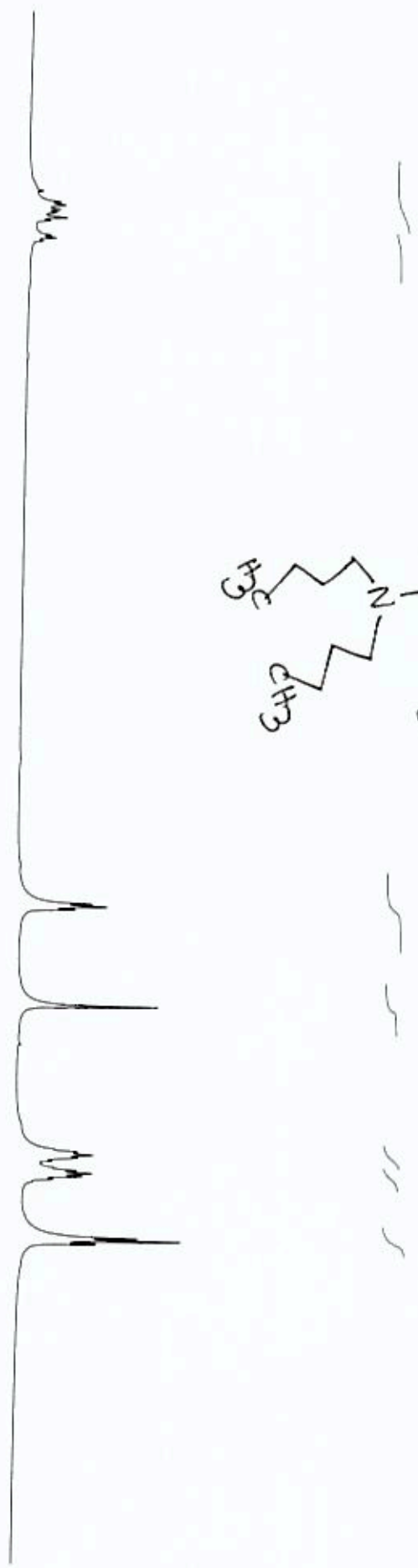
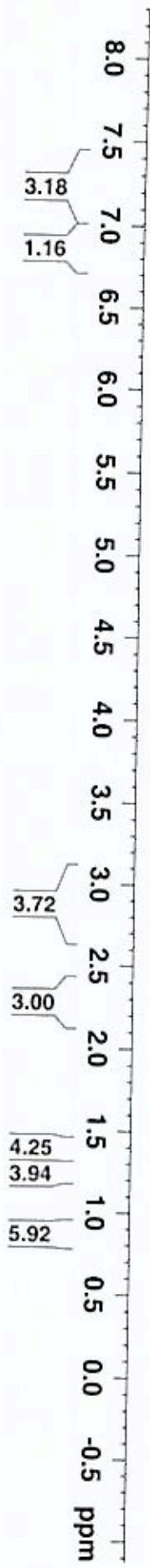
50.12

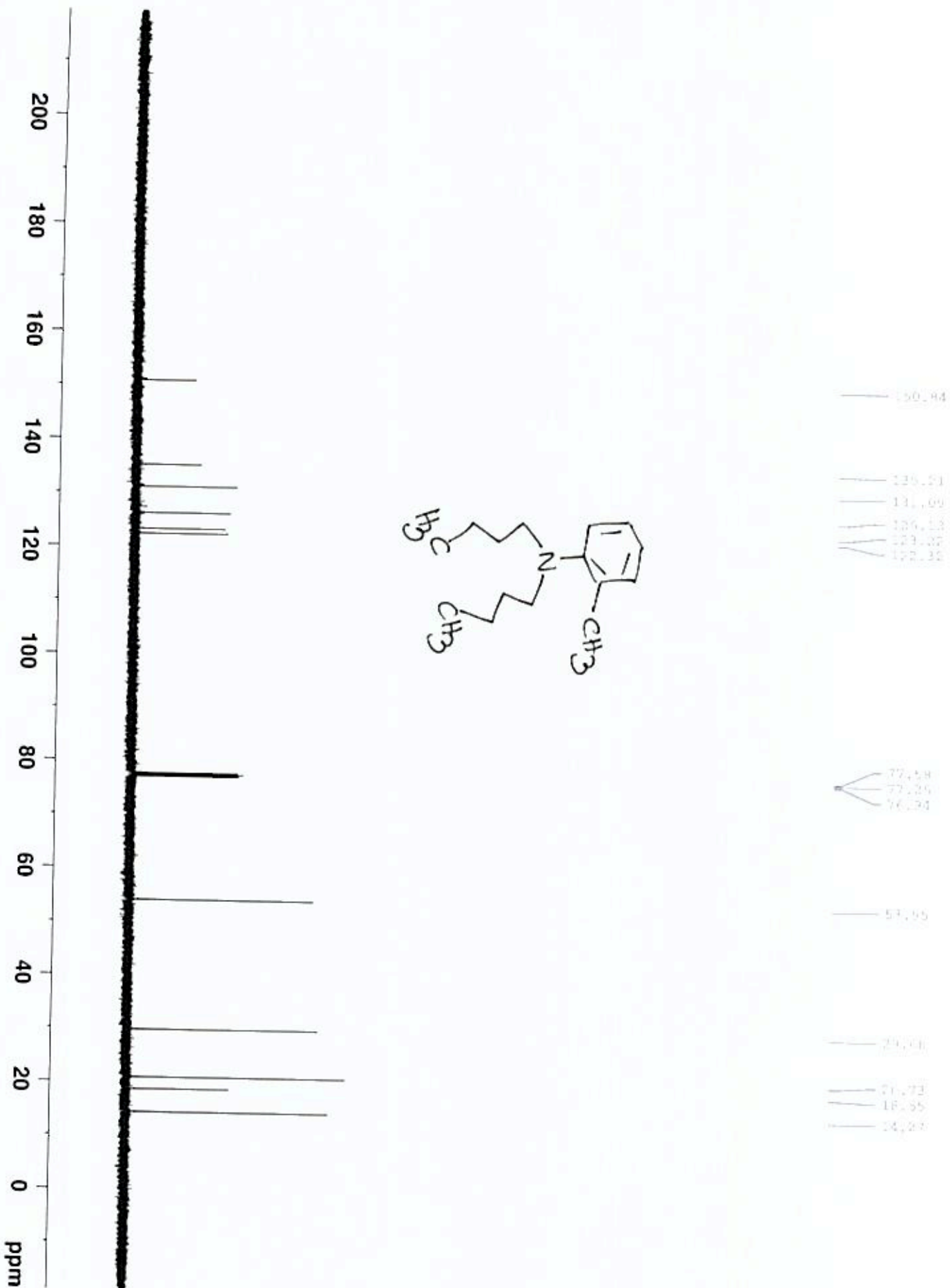


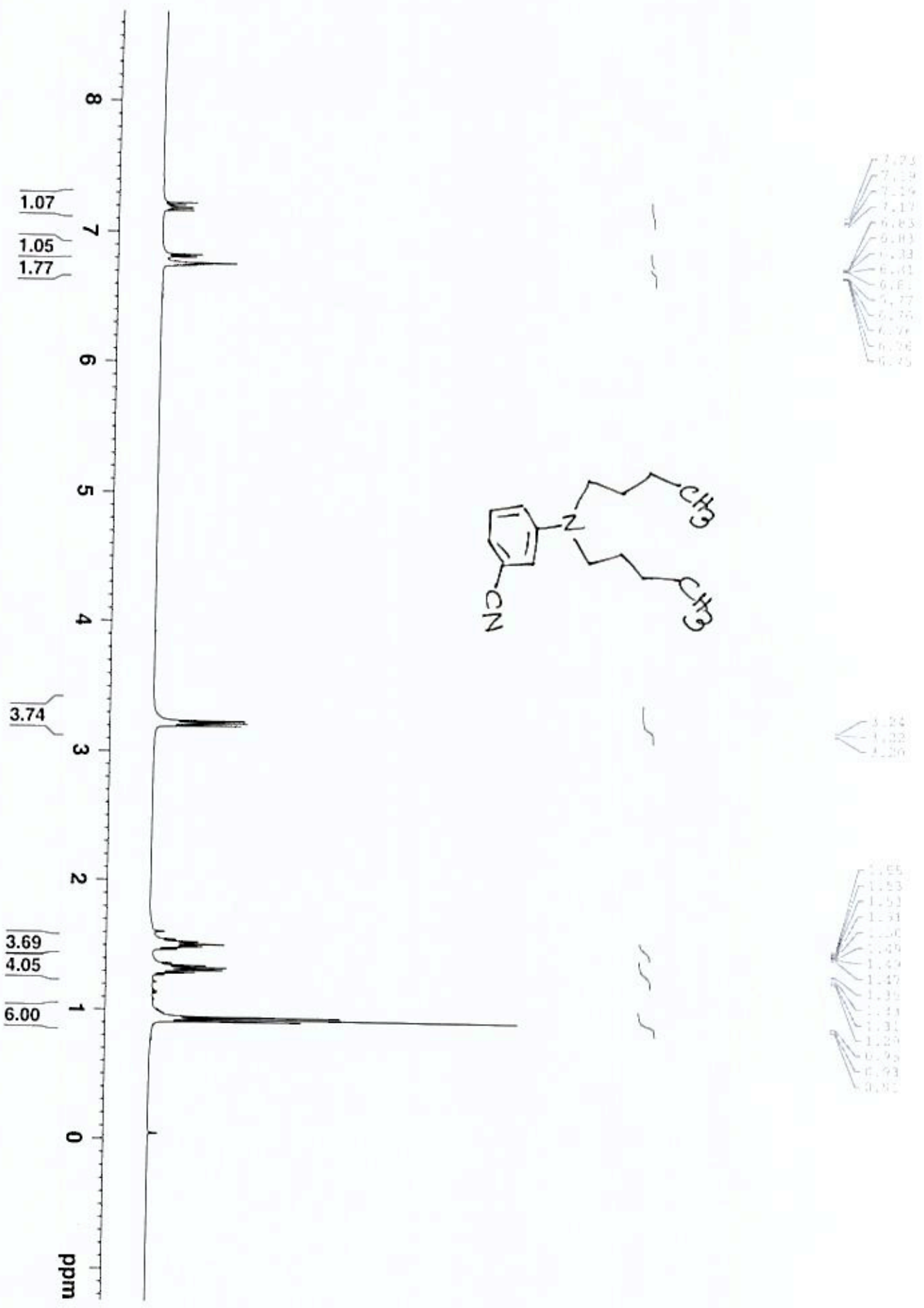


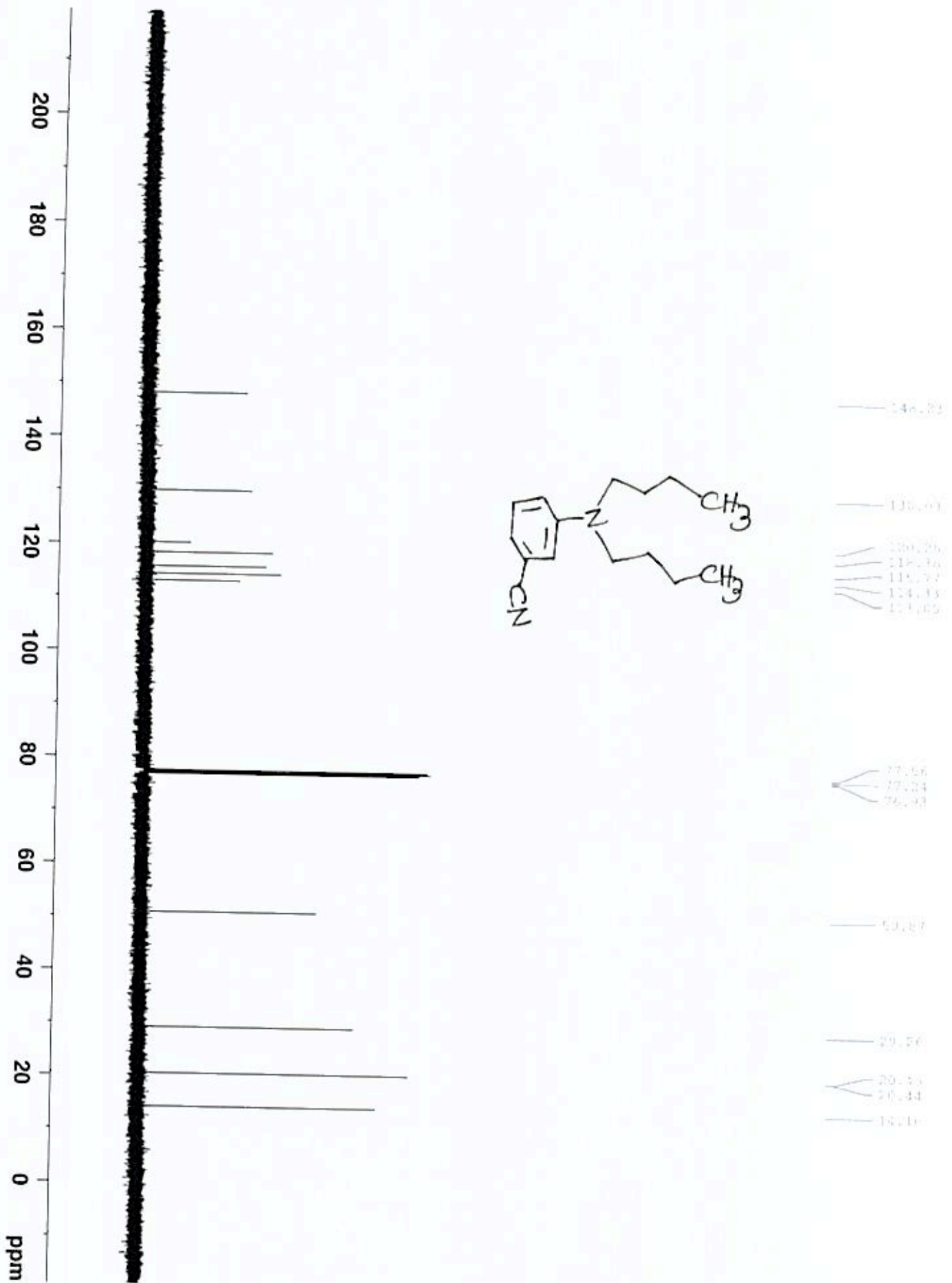


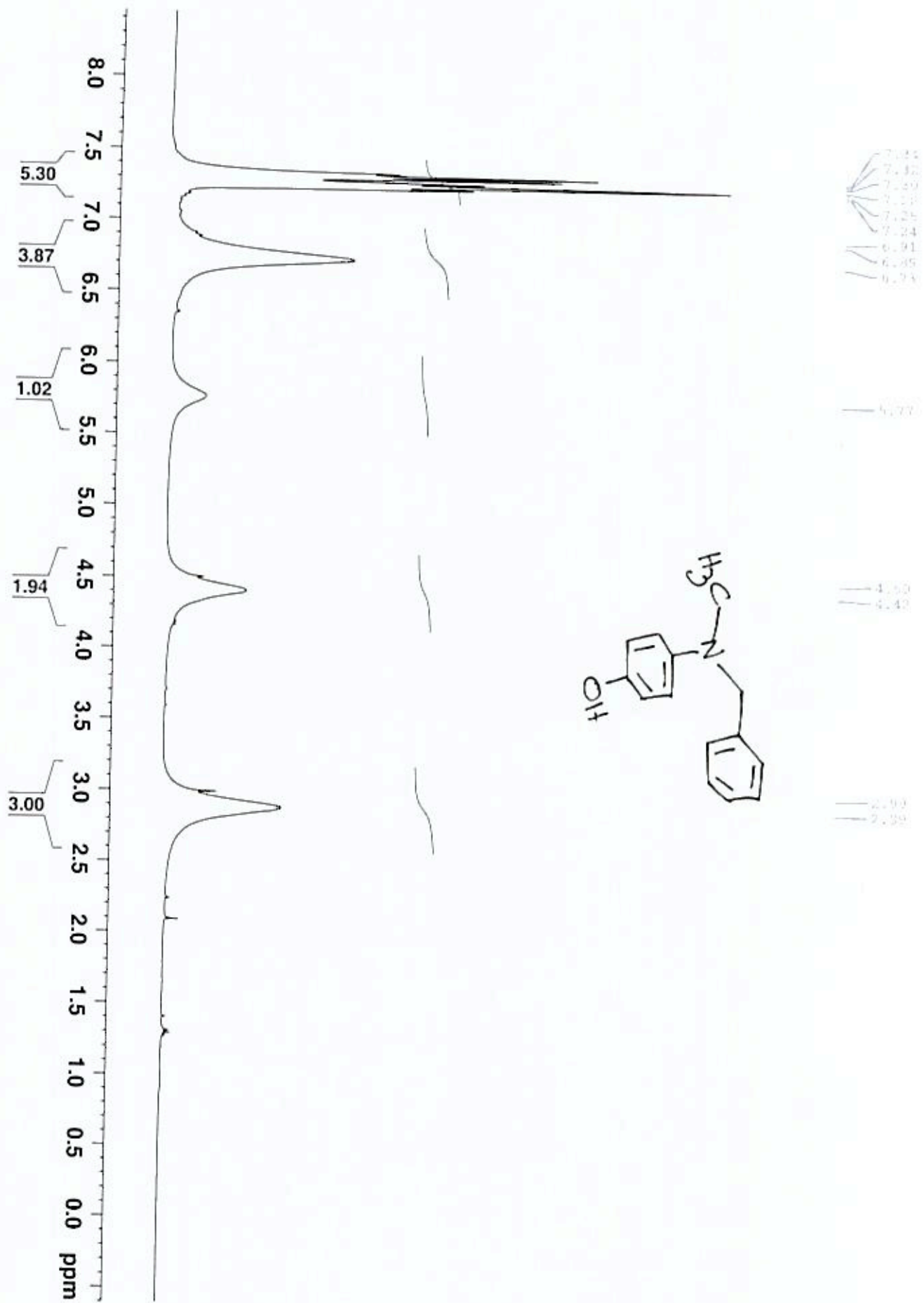


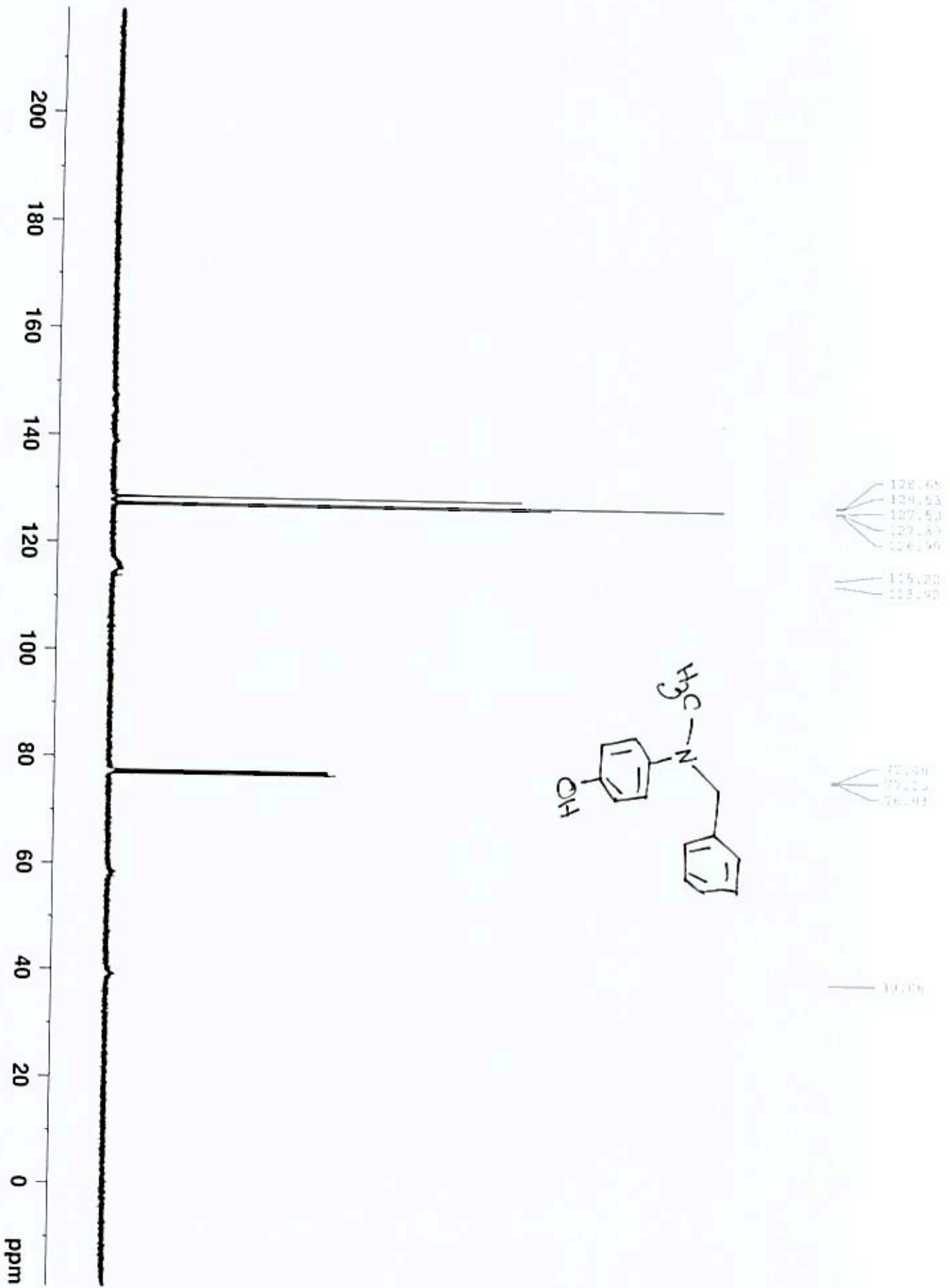


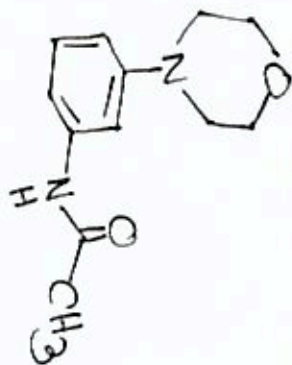


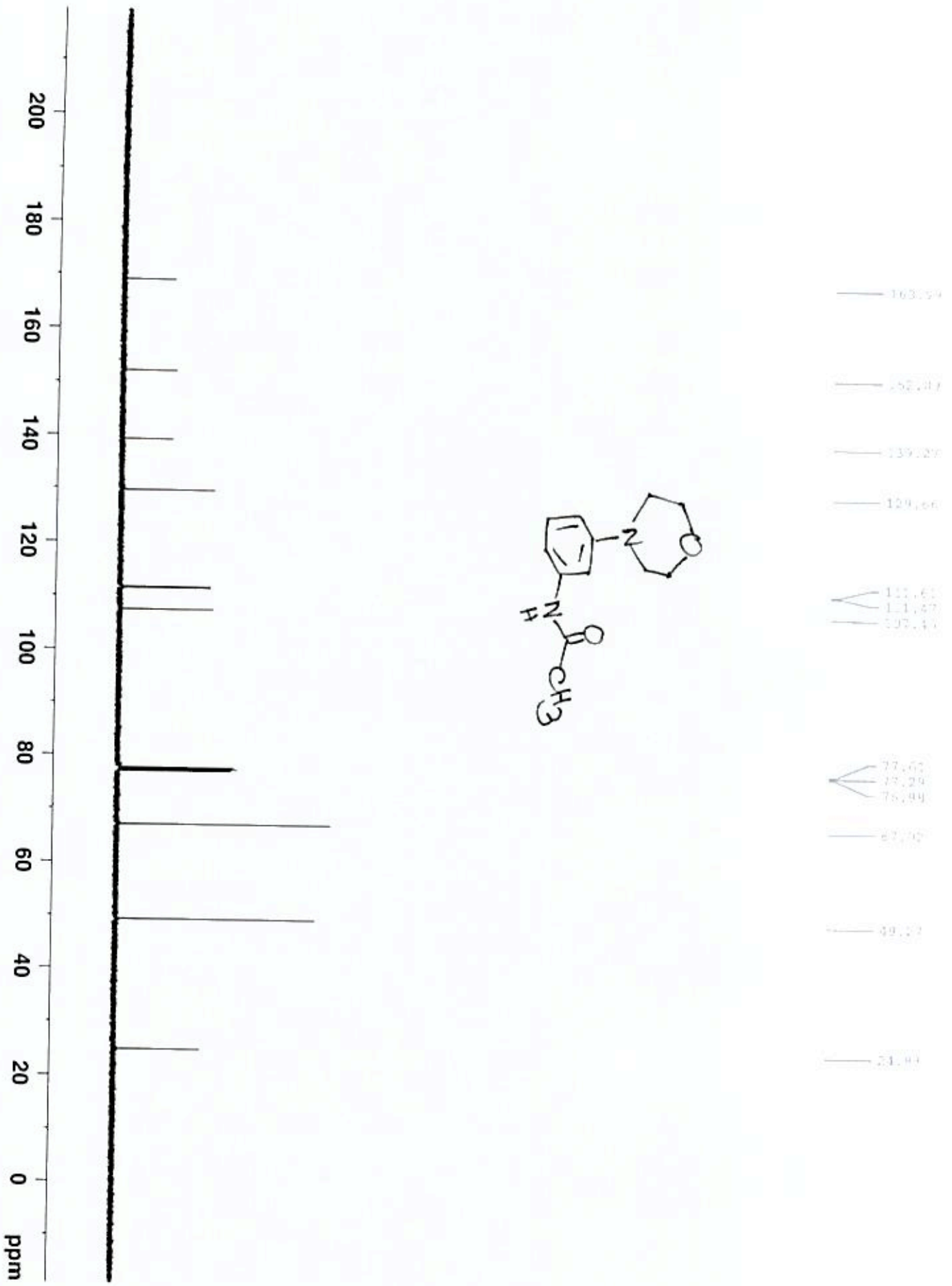
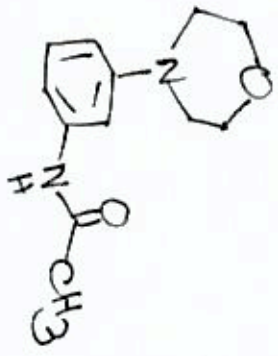


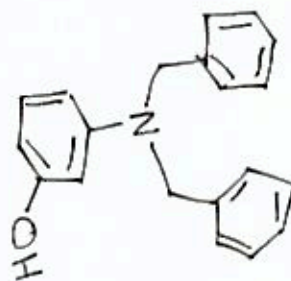






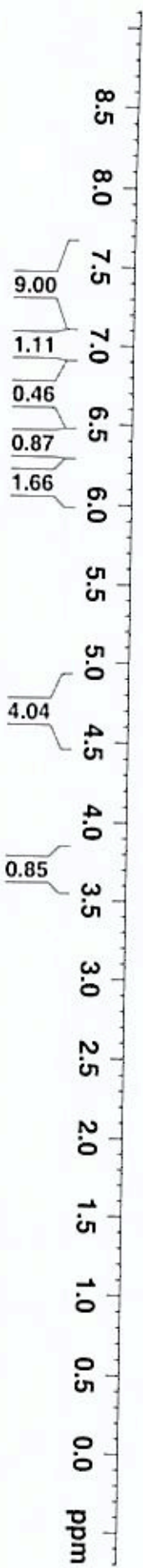


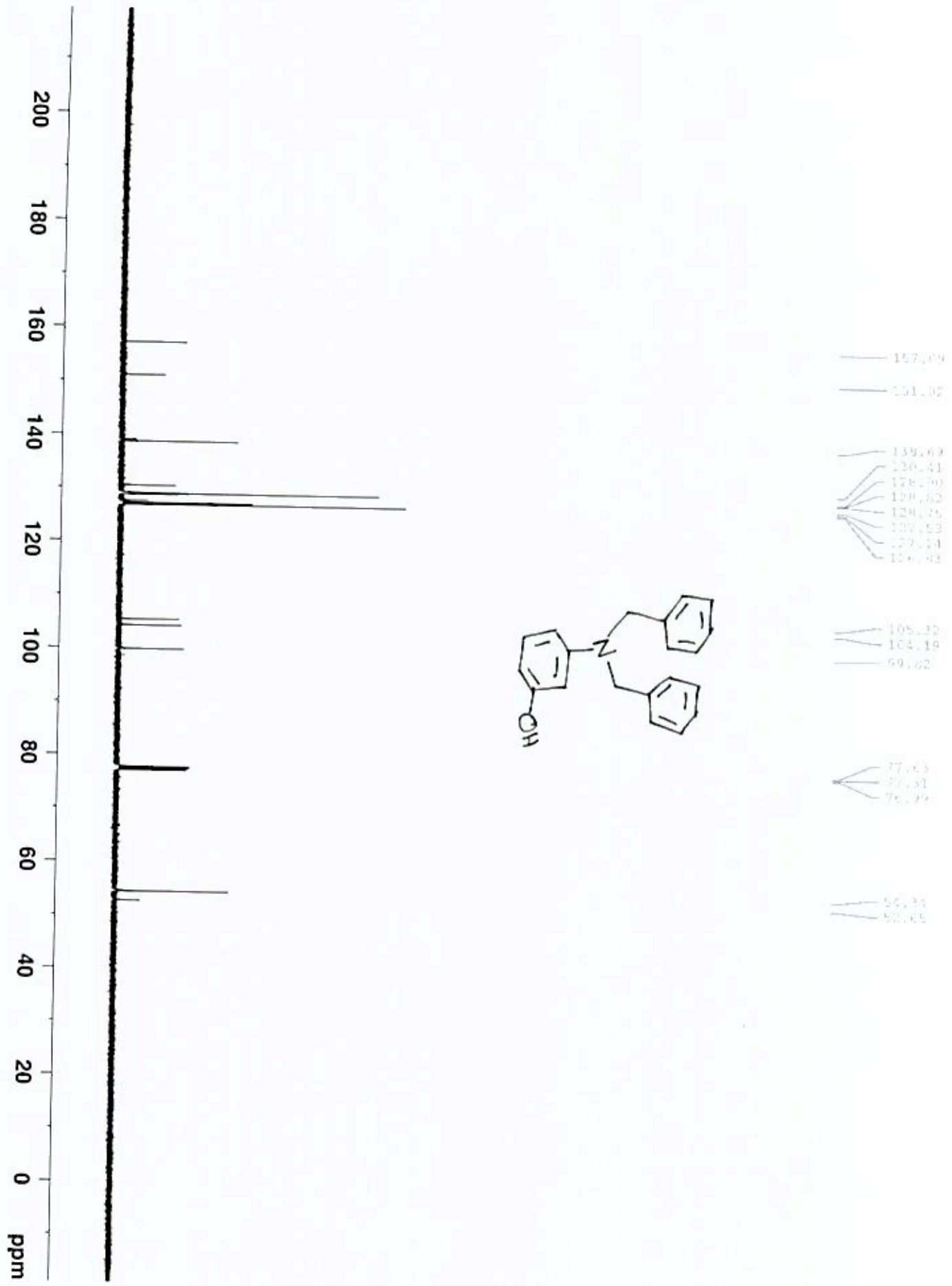


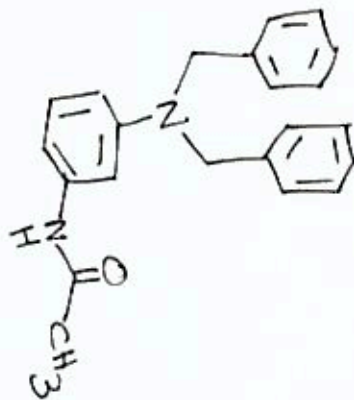
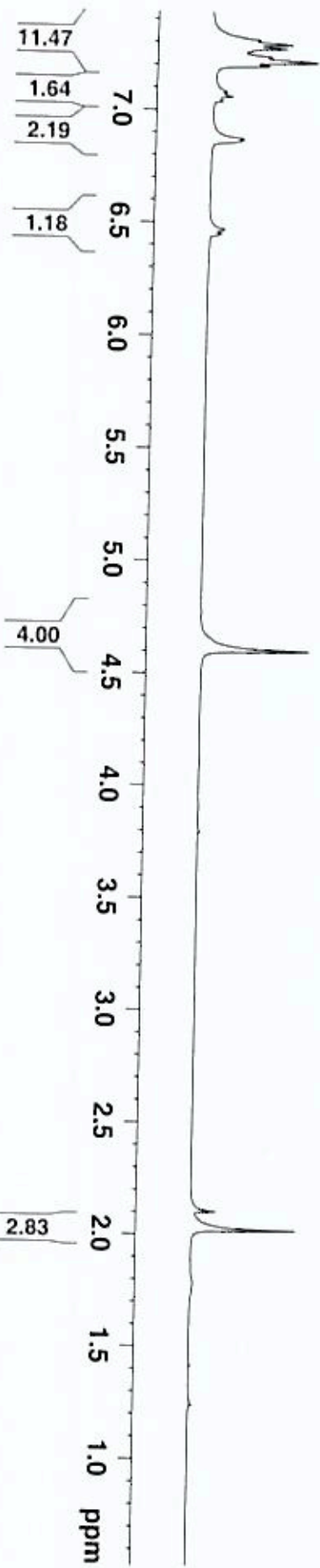


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3.78

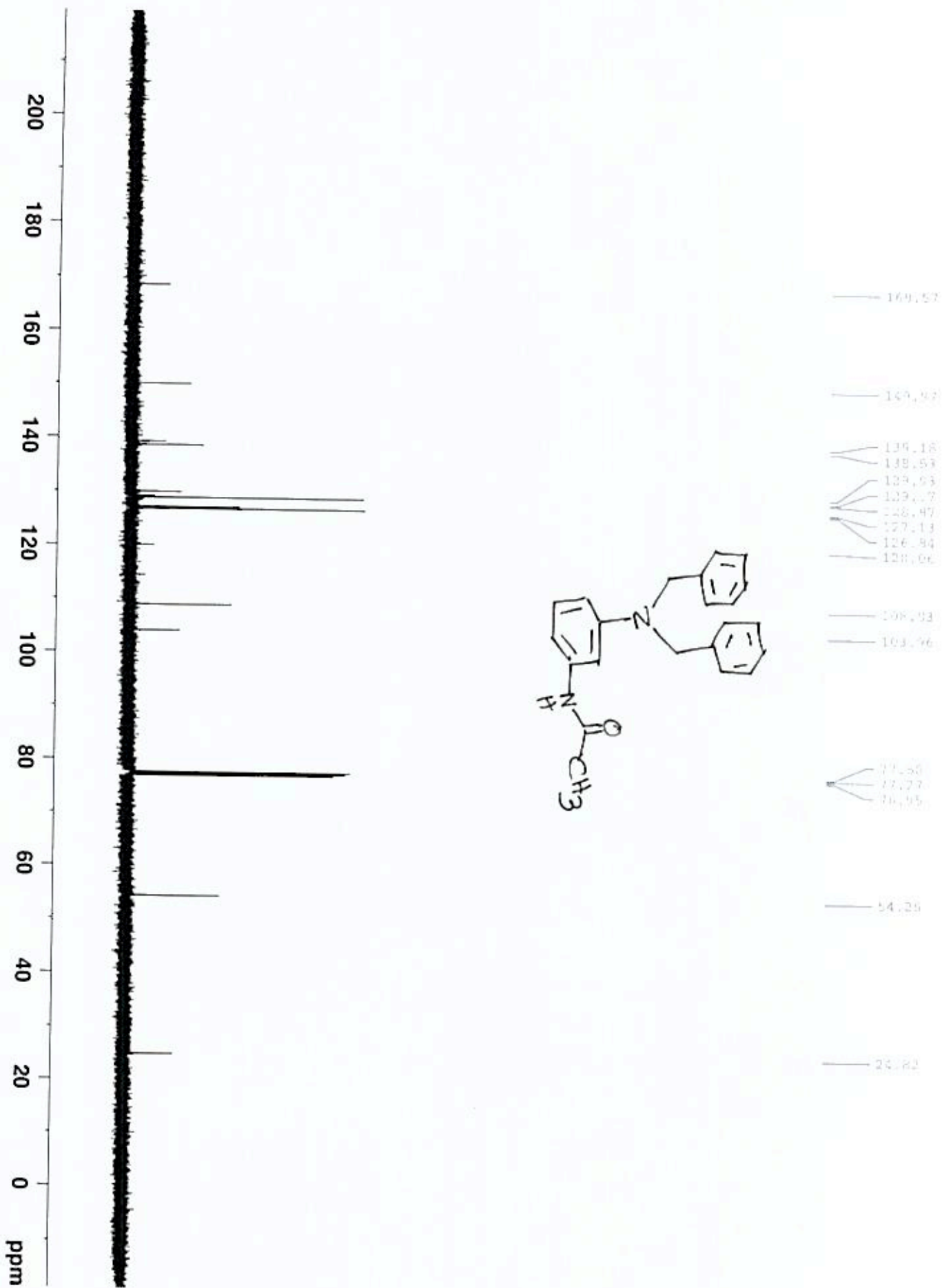


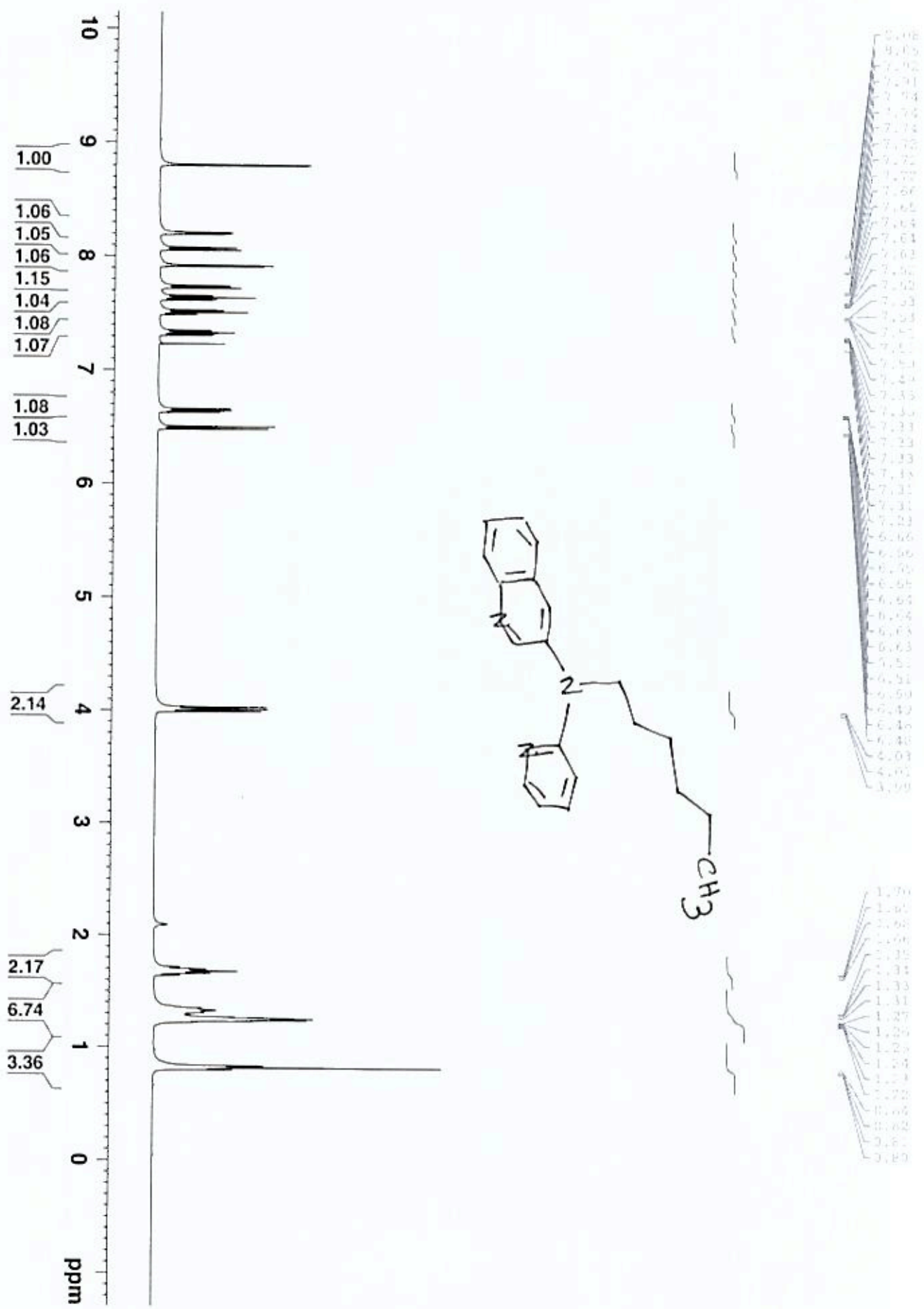


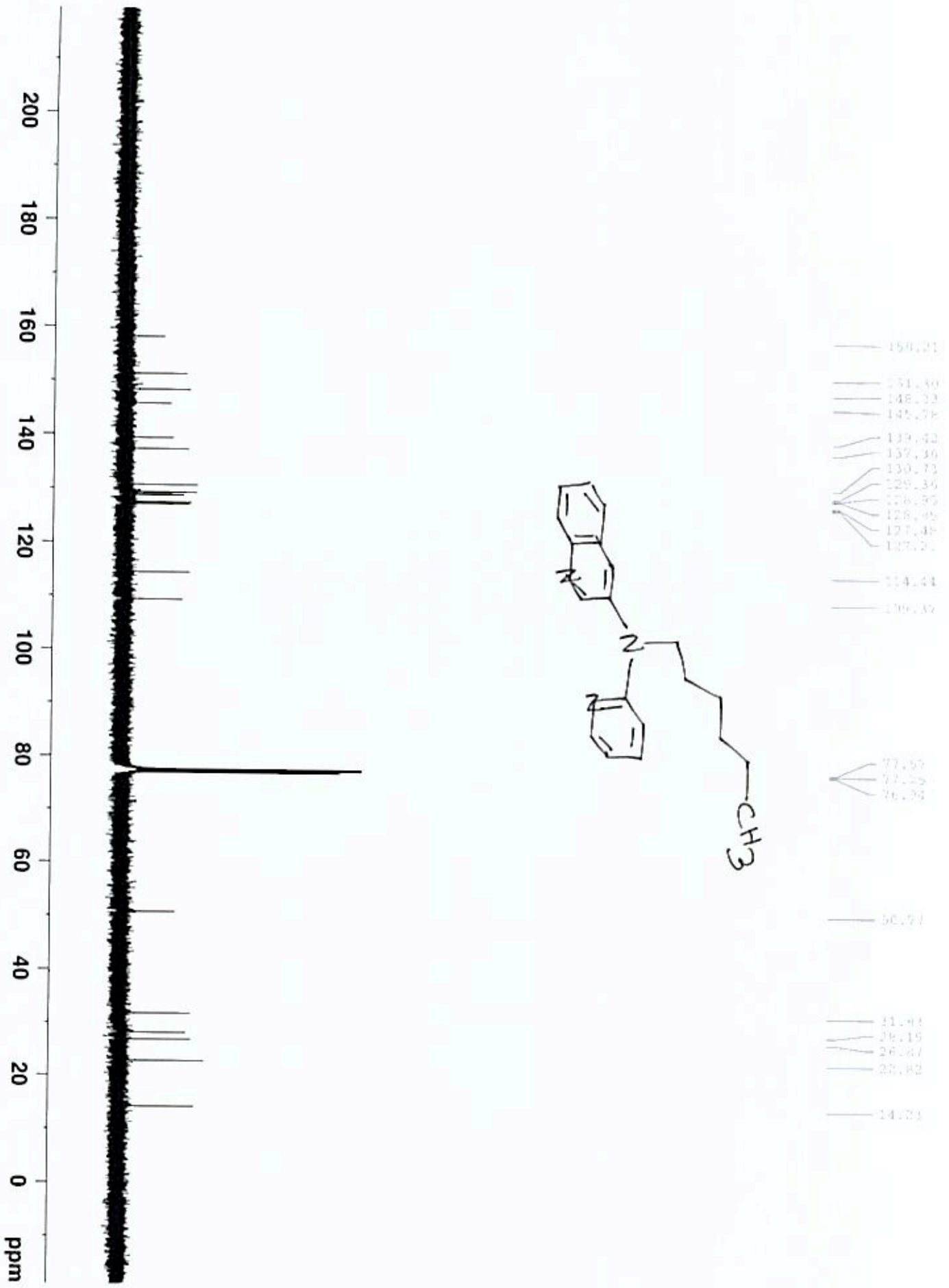


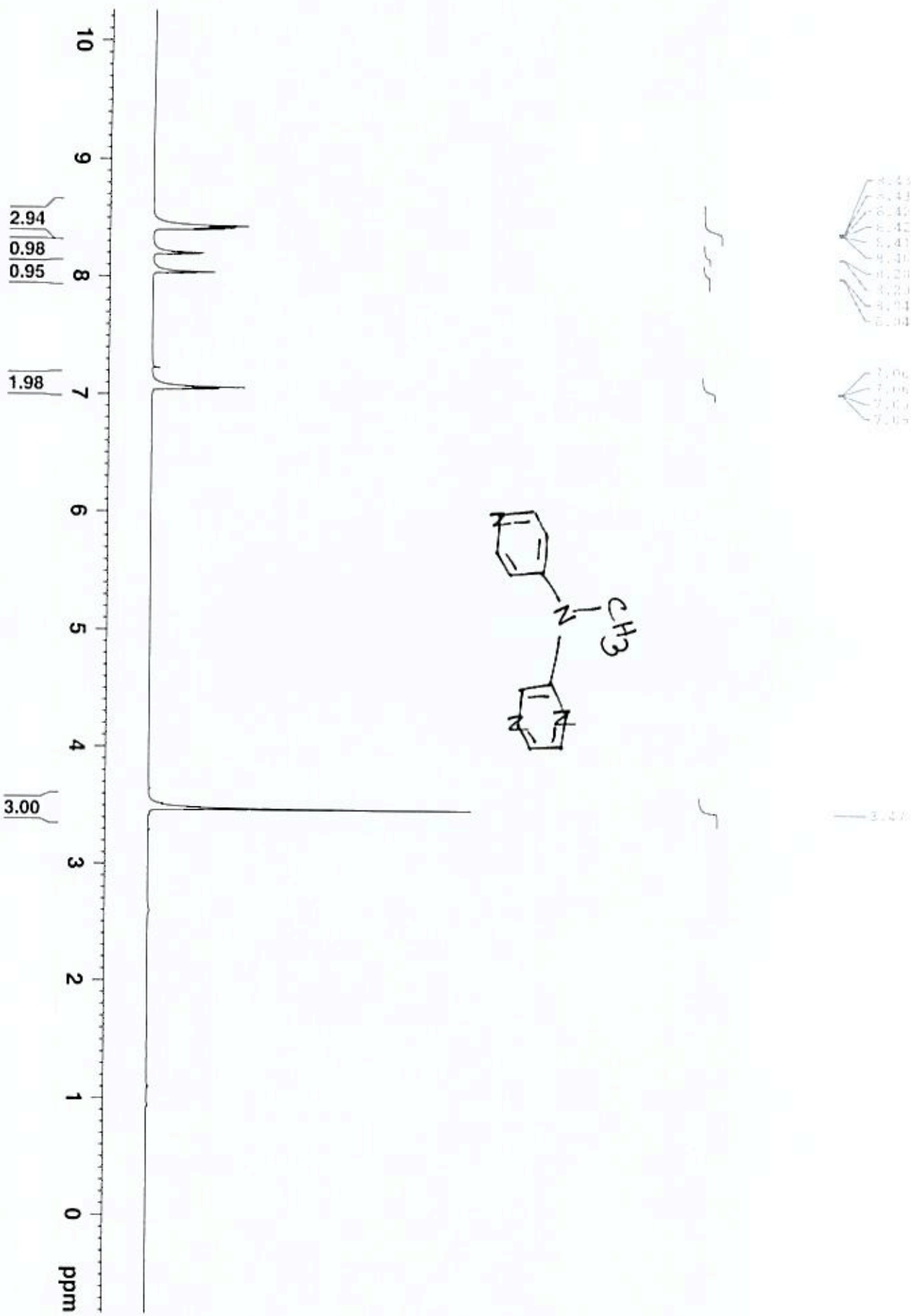
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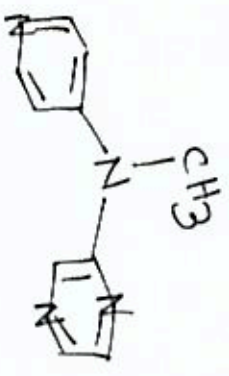
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2.02

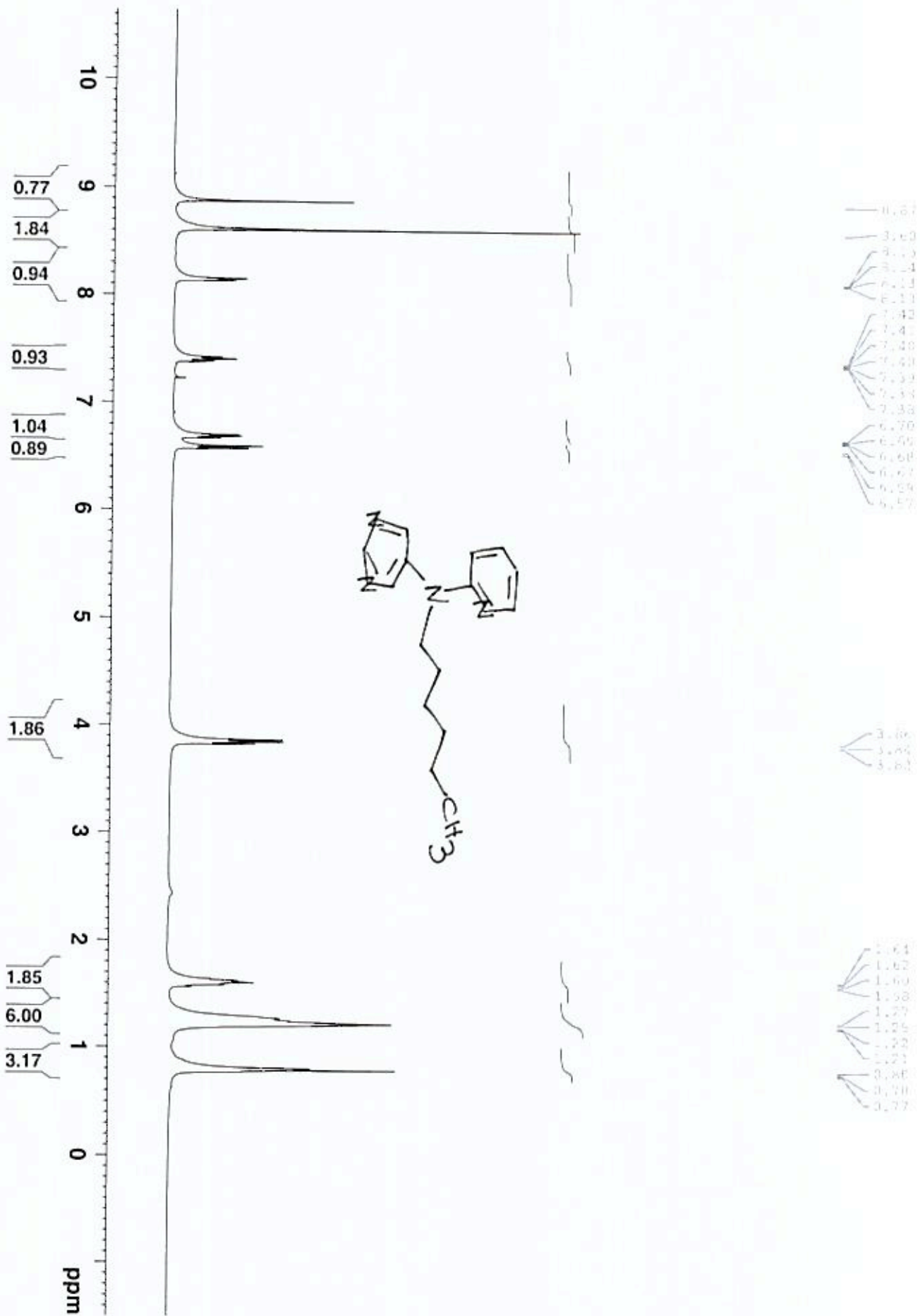




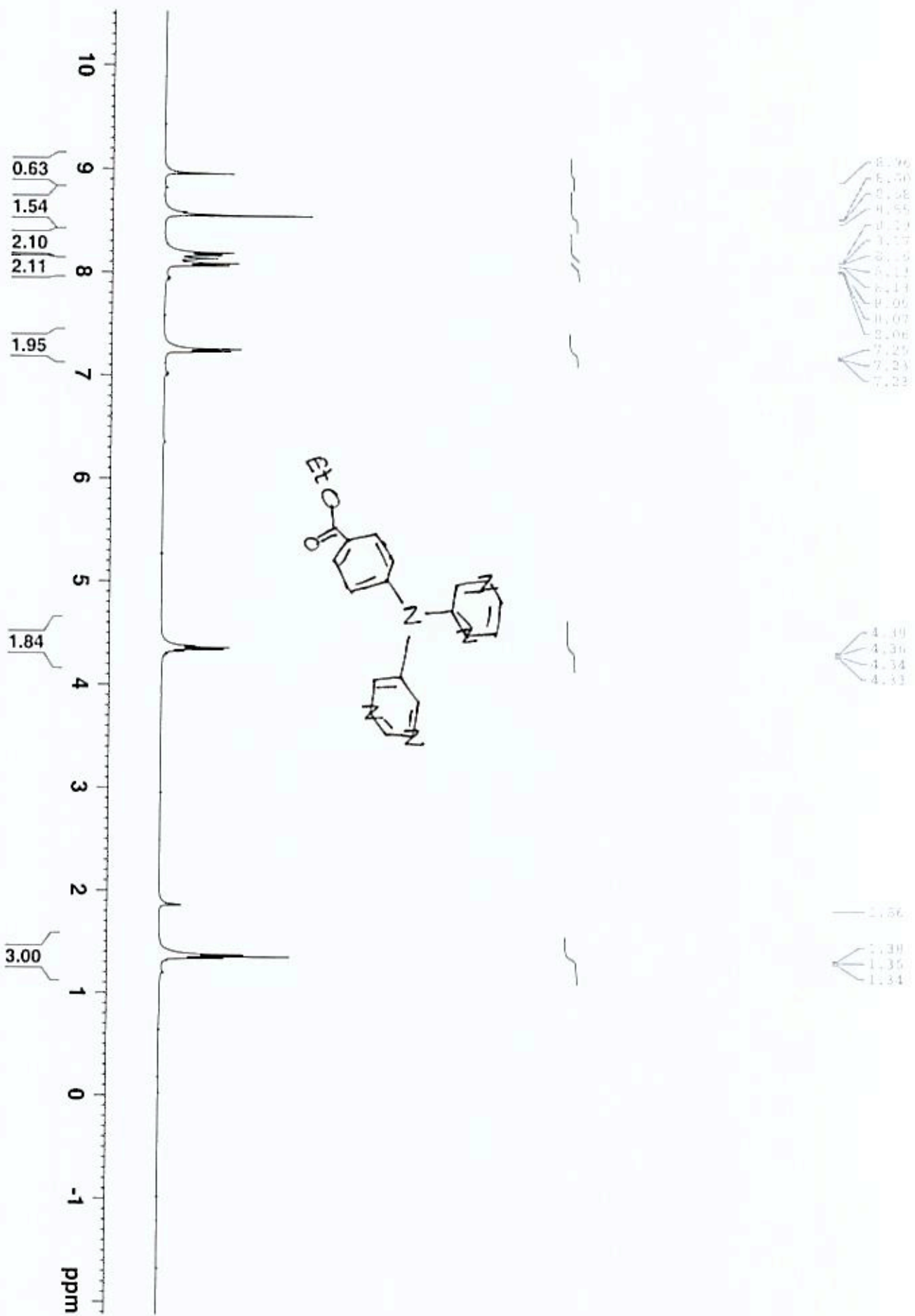




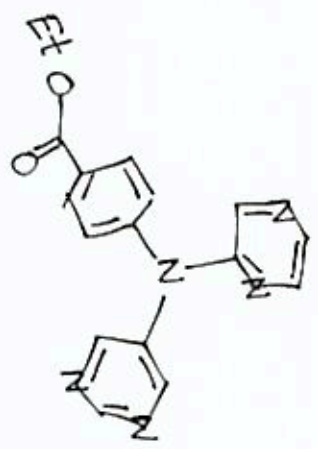








200 180 160 140 120 100 80 60 40 20 0 ppm

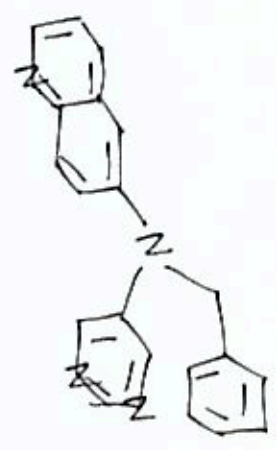
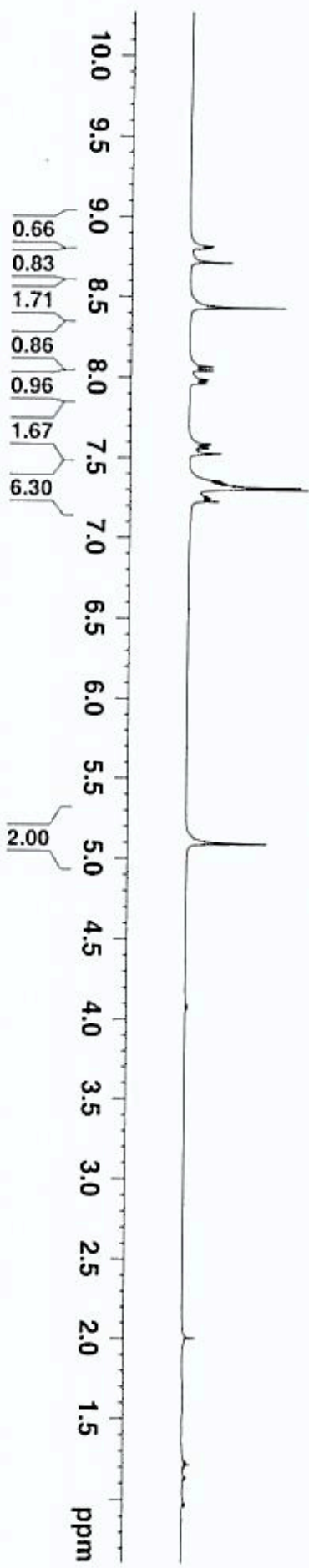


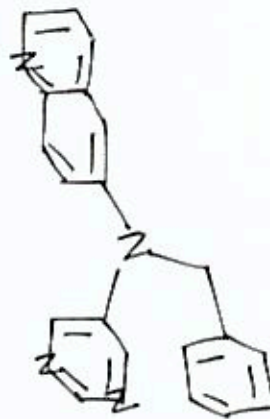
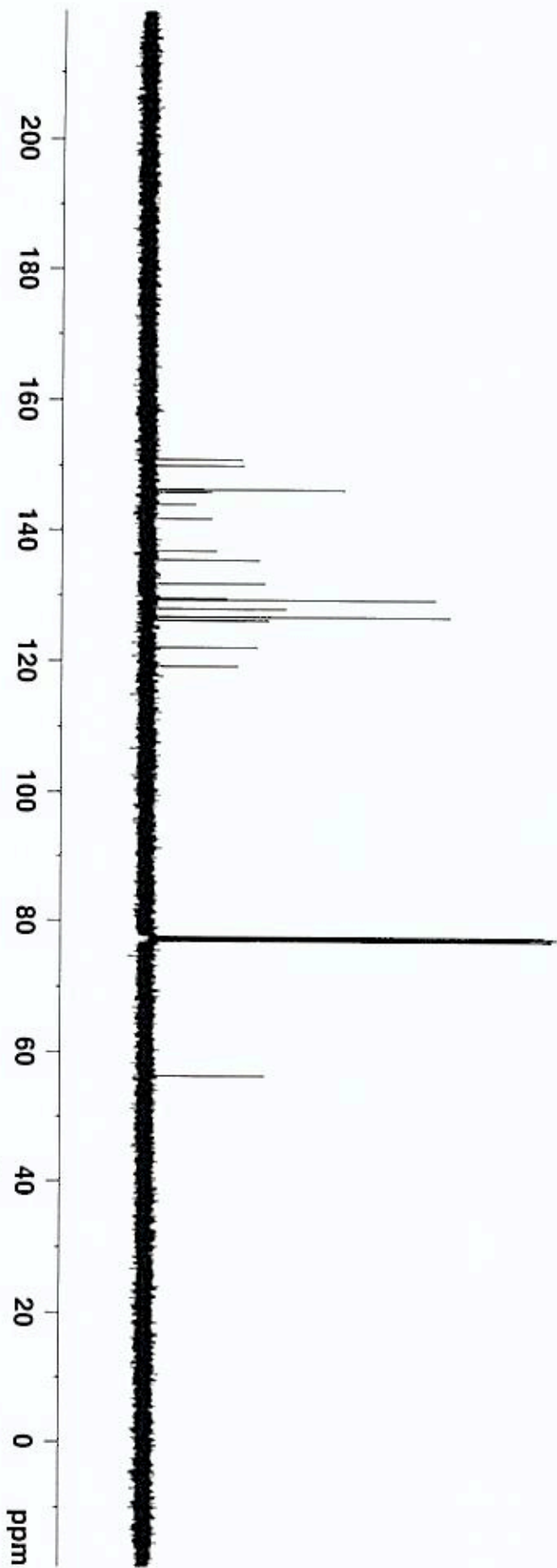
- 155.66
- 154.61
- 153.53
- 153.47
- 145.85
- 140.17
- 139.69
- 136.44
- 136.24
- 122.41
- 120.94
- 125.85

- 77.56
- 77.25
- 76.91

- 61.50

- 14.52

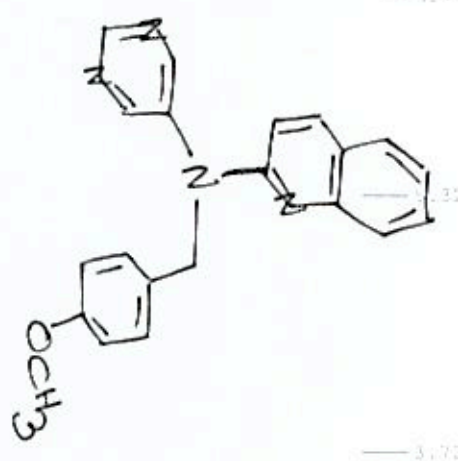
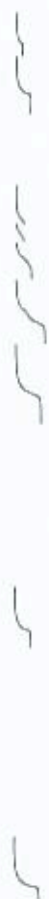
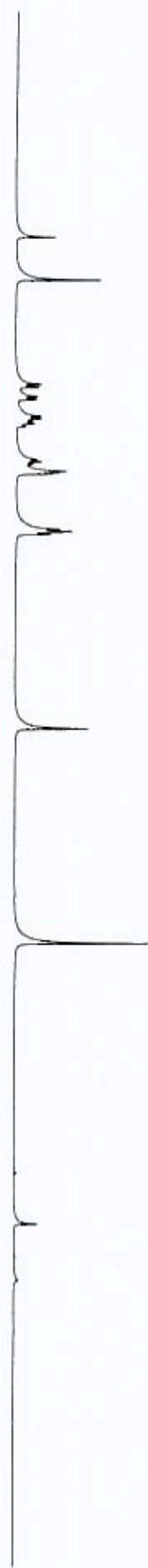
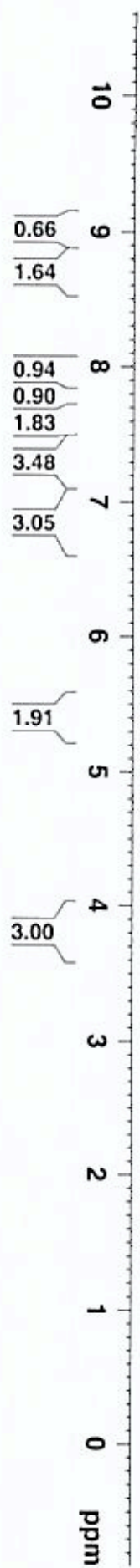




- 153.04
- 152.04
- 149.60
- 149.33
- 145.91
- 144.82
- 136.85
- 135.40
- 131.75
- 129.49
- 126.27
- 126.21
- 126.07
- 126.14
- 119.20

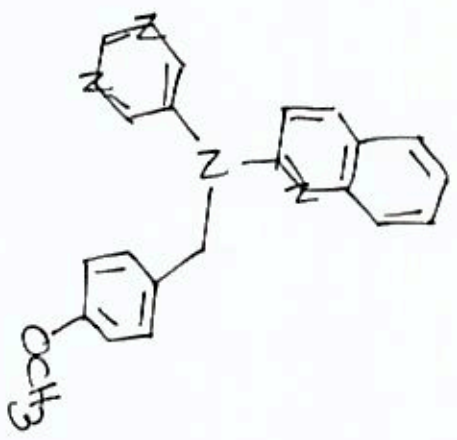
- 77.55
- 77.24
- 76.93

- 56.37

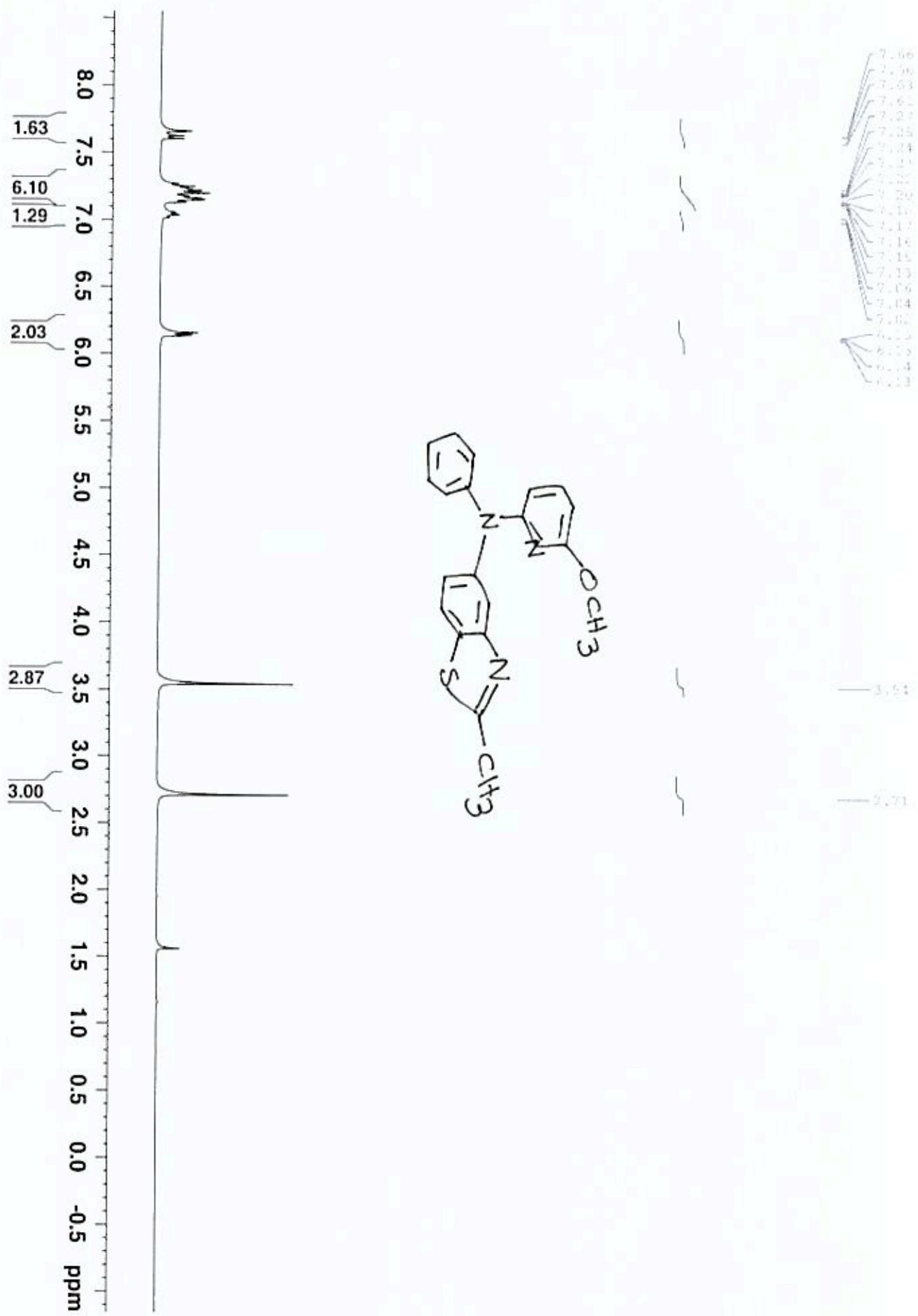


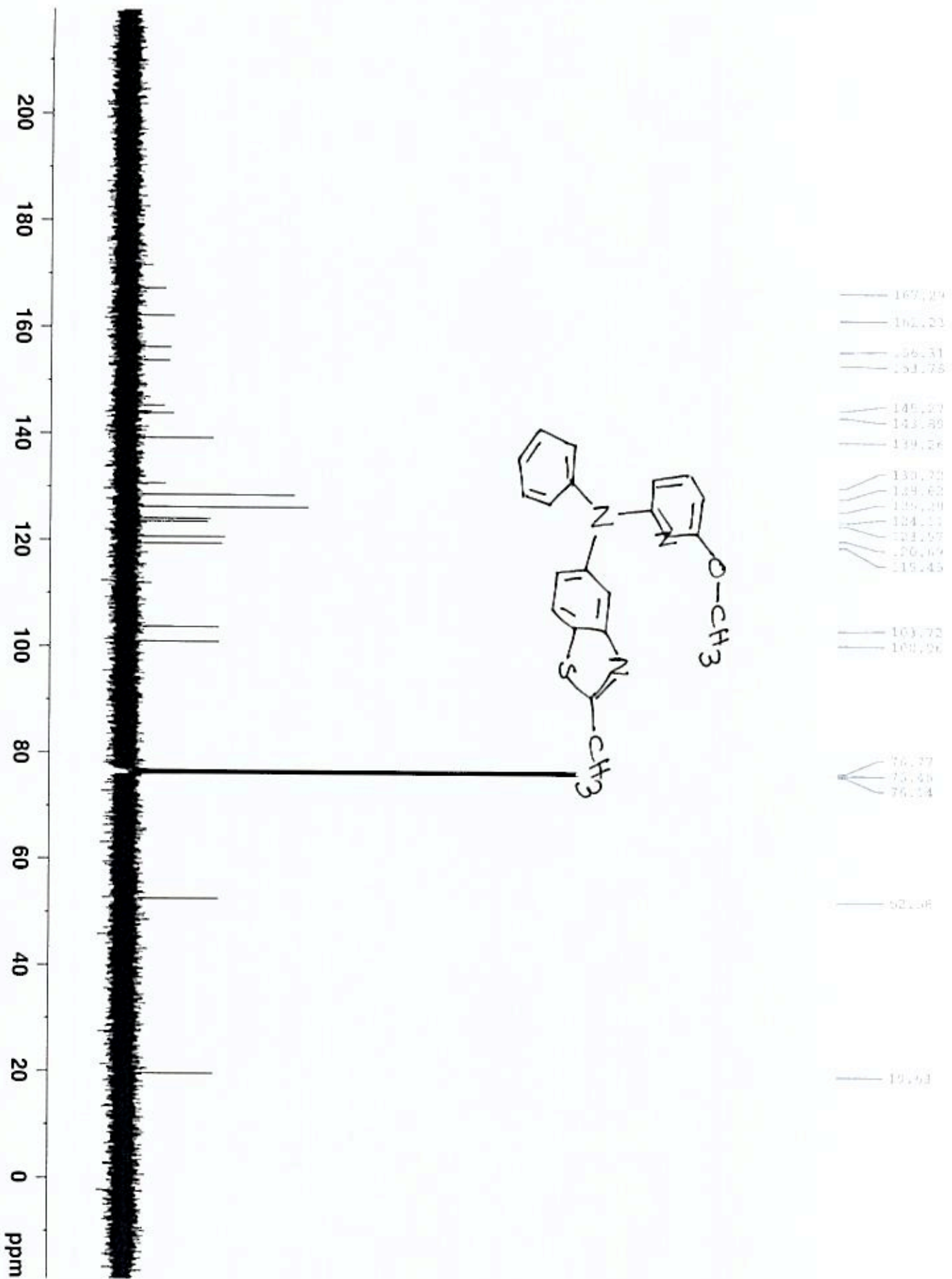
- 8.95
- 8.80
- 7.24
- 7.23
- 7.21
- 6.80
- 6.79
- 6.78
- 6.76
- 3.78

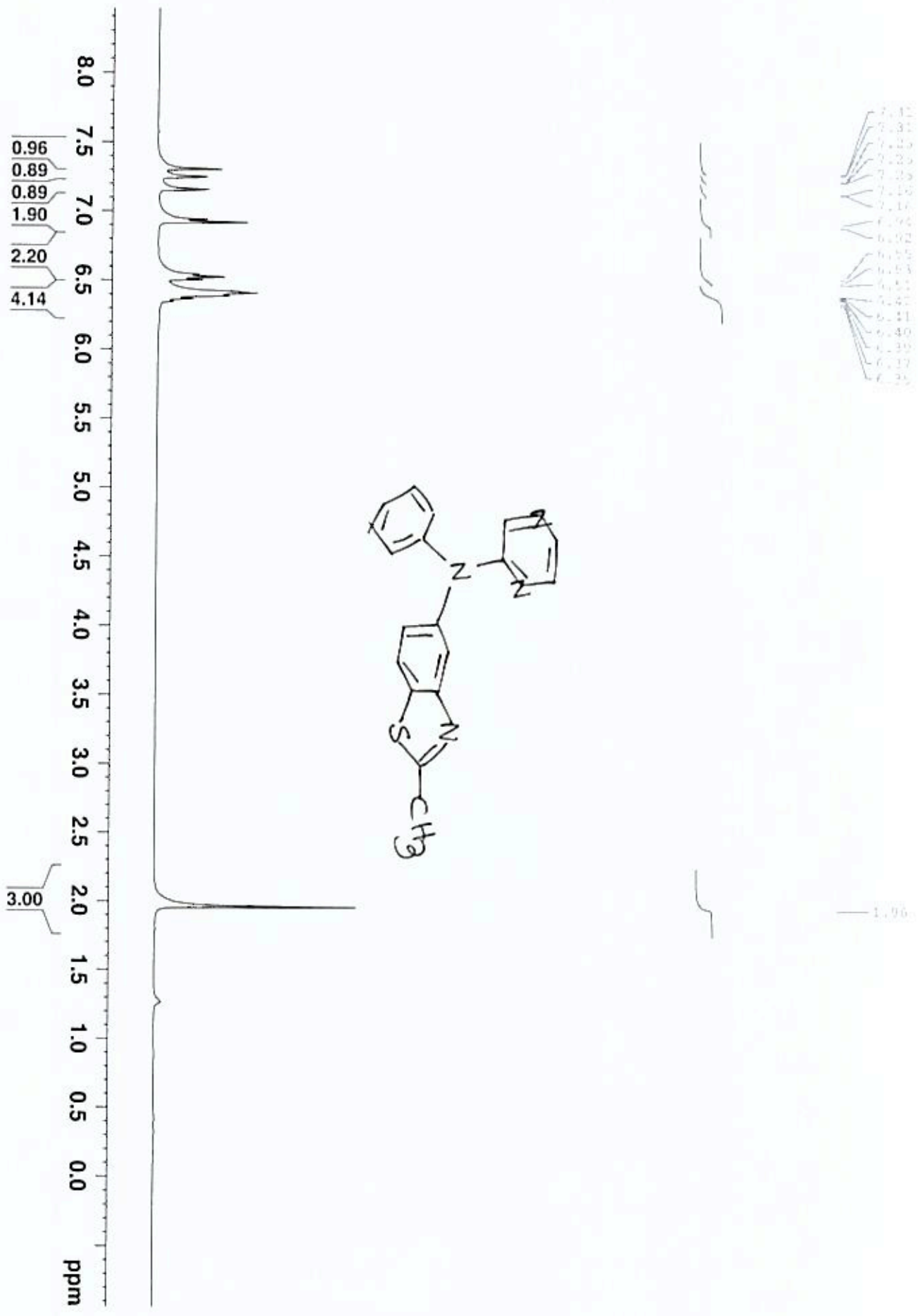
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

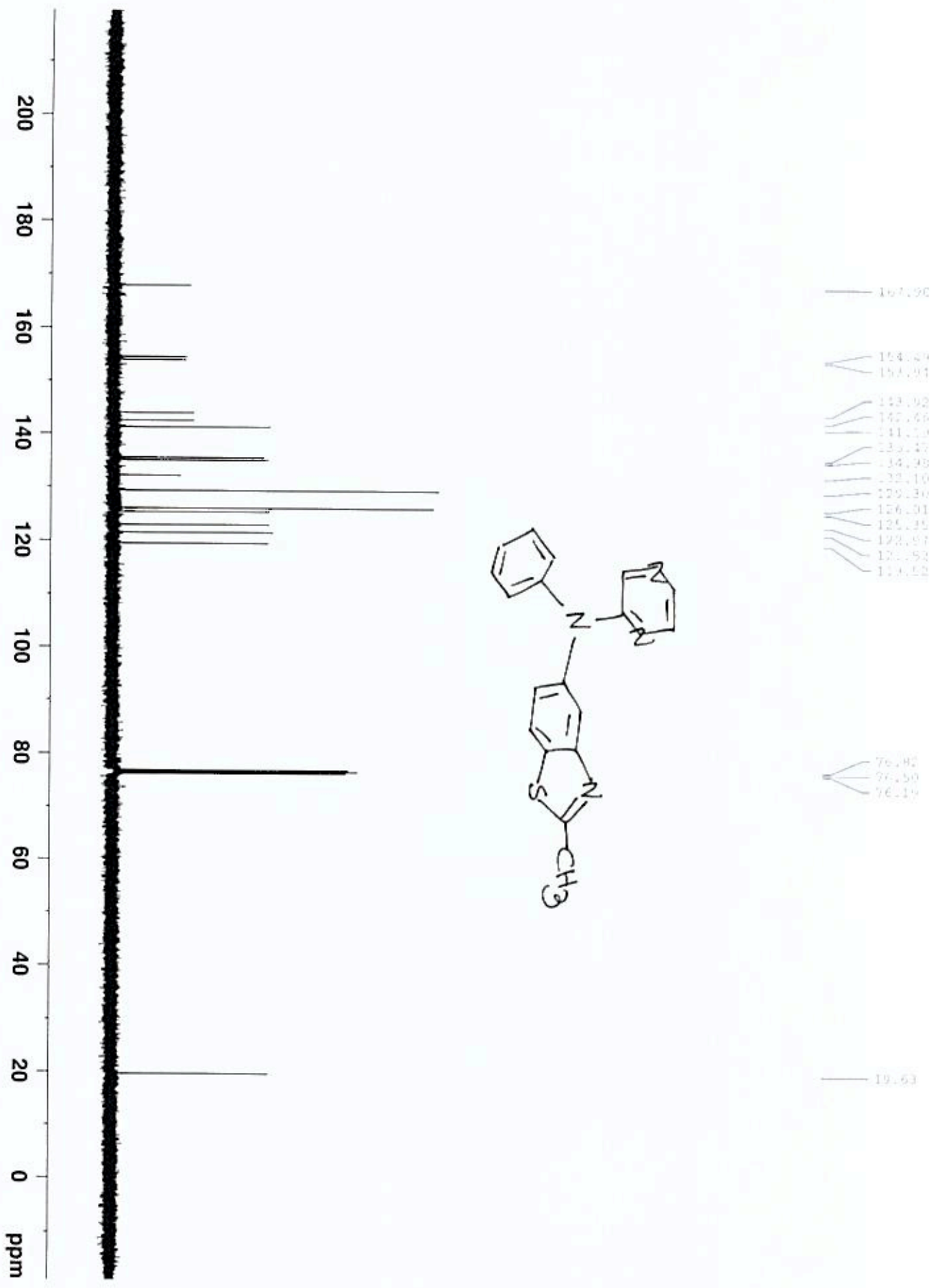


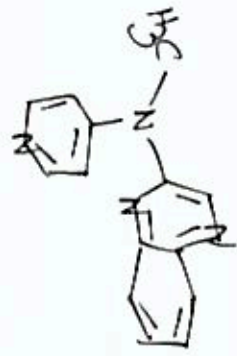
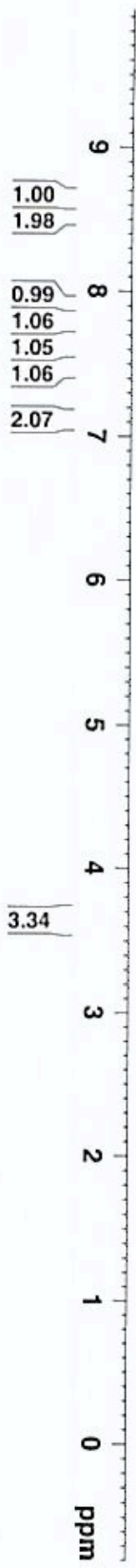
- 157.19
- 155.37
- 154.76
- 154.05
- 147.53
- 140.36
- 139.28
- 139.01
- 127.51
- 127.45
- 124.65
- 124.02
- 114.35
- 111.52
- 77.54
- 77.22
- 76.91
- 55.43
- 52.64



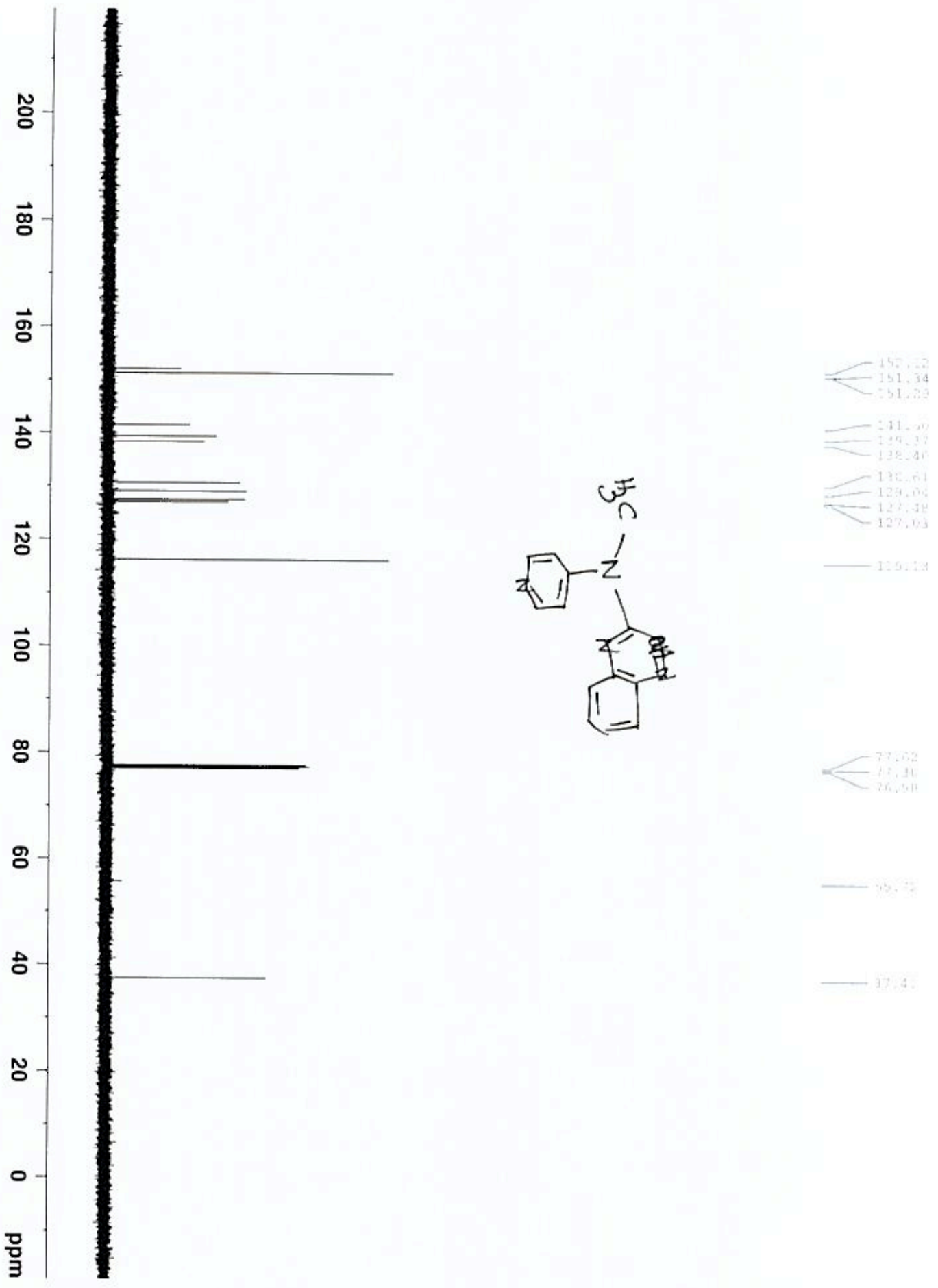
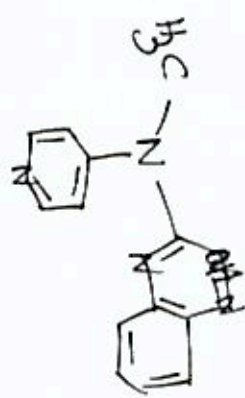


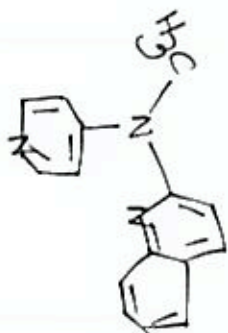
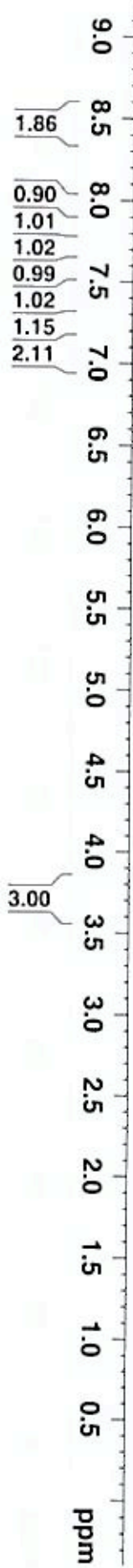




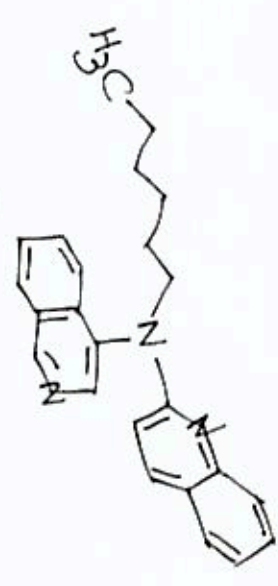
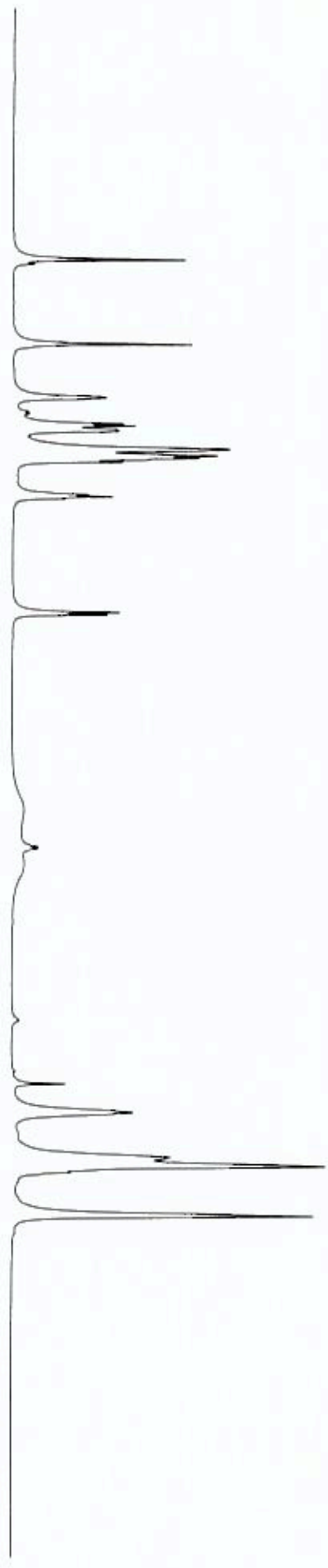
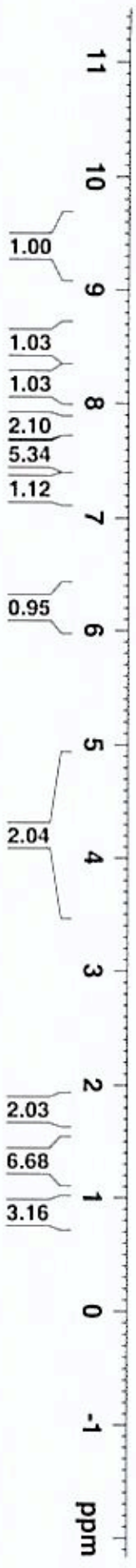


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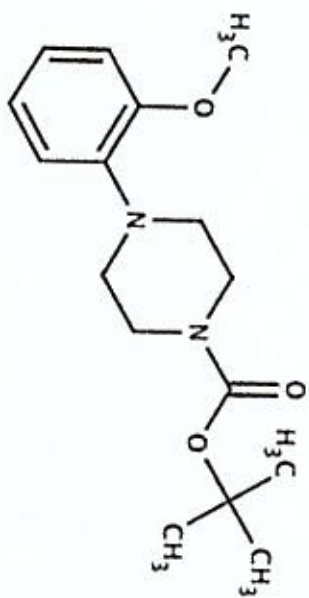




- 8.42
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- 1.04
- 1.02
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- 0.78
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- 0.68
- 0.66
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- 0.44
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- 0.10
- 0.08
- 0.06
- 0.04
- 0.02
- 0.00



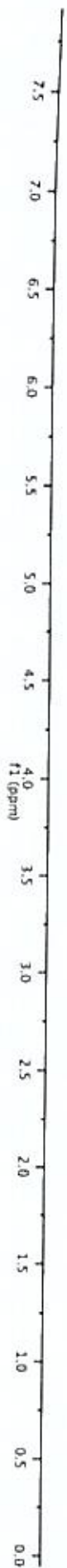


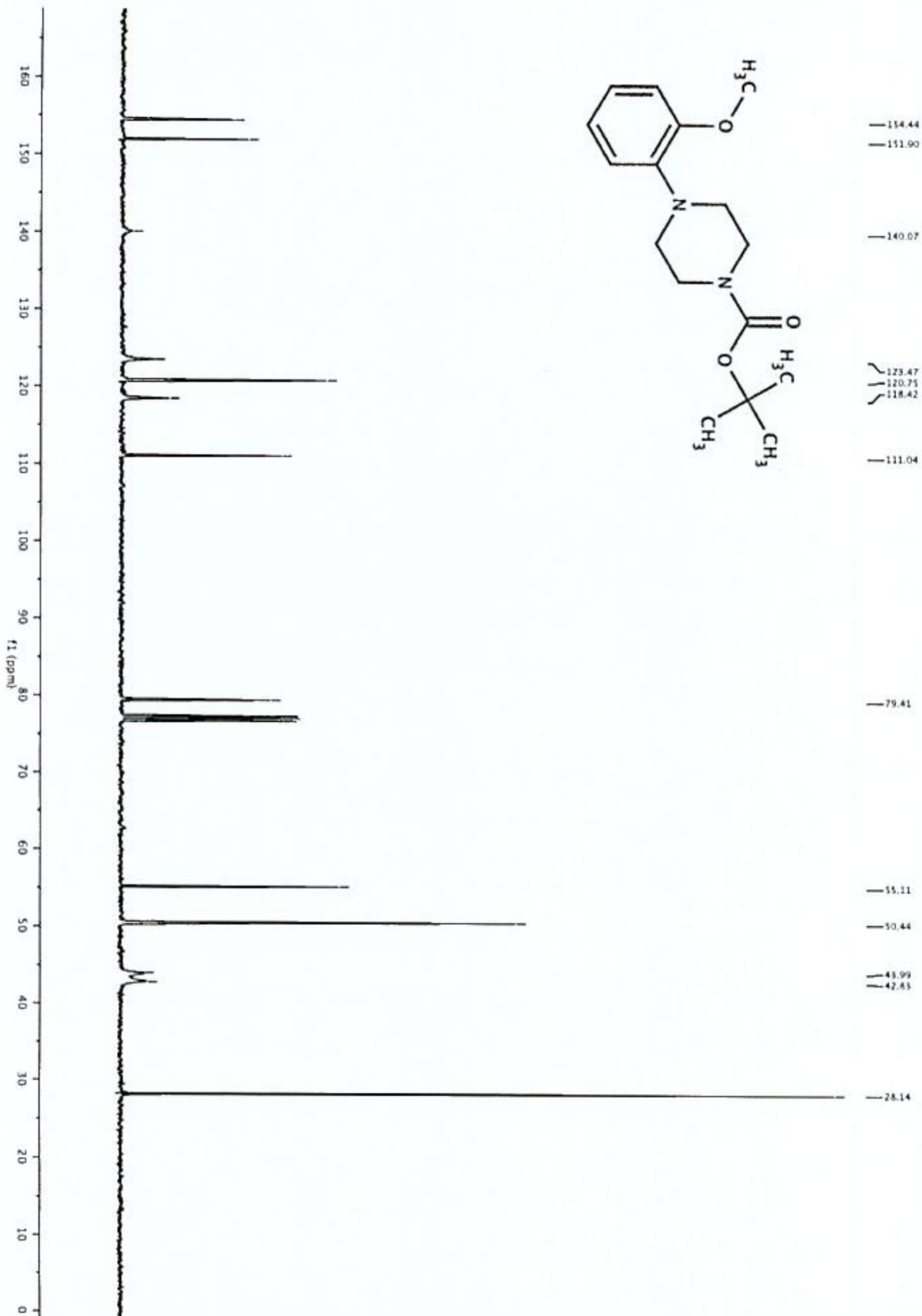


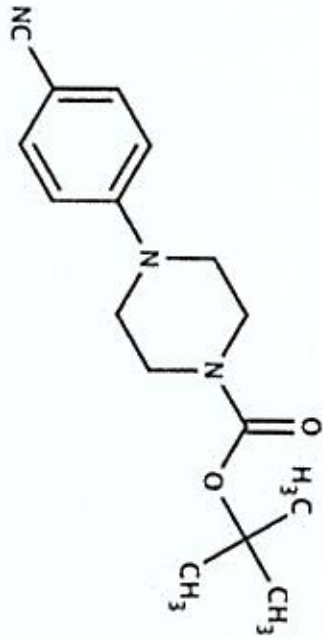
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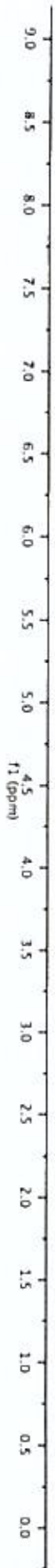


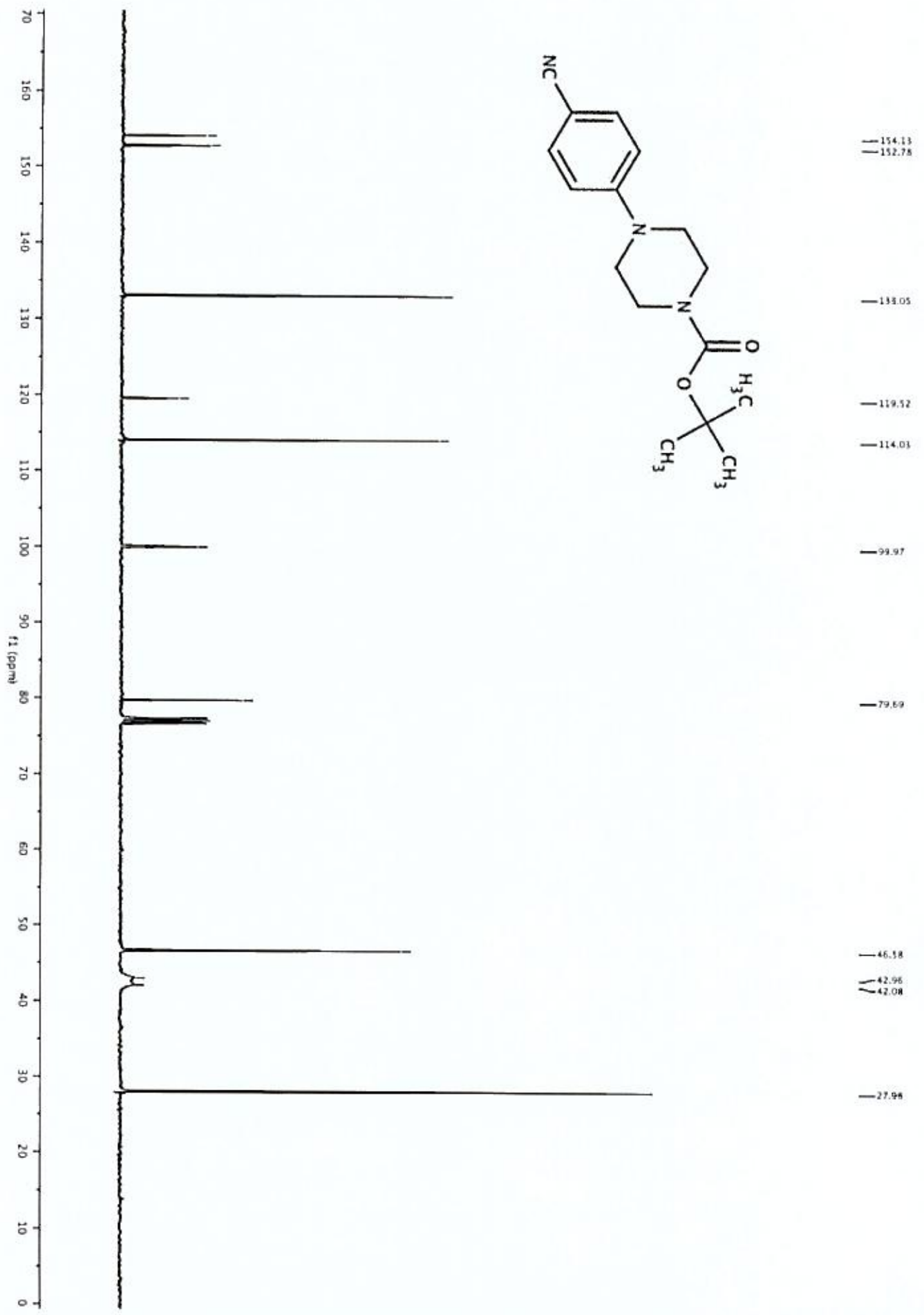
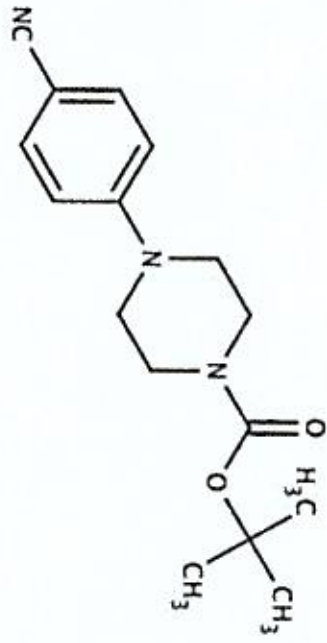


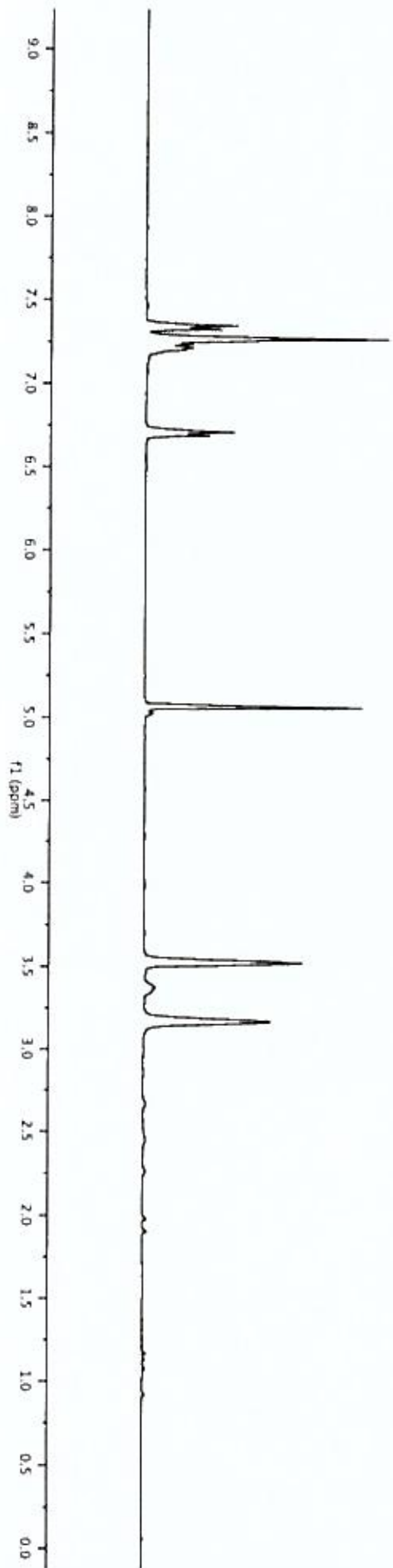
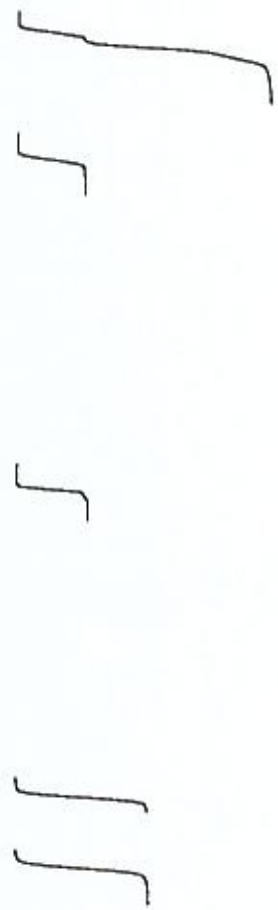
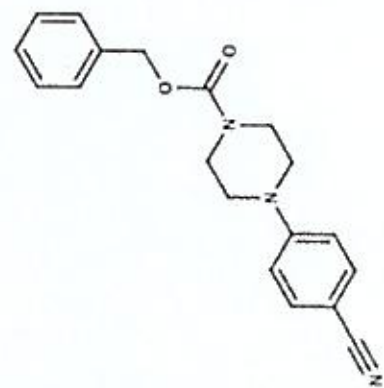


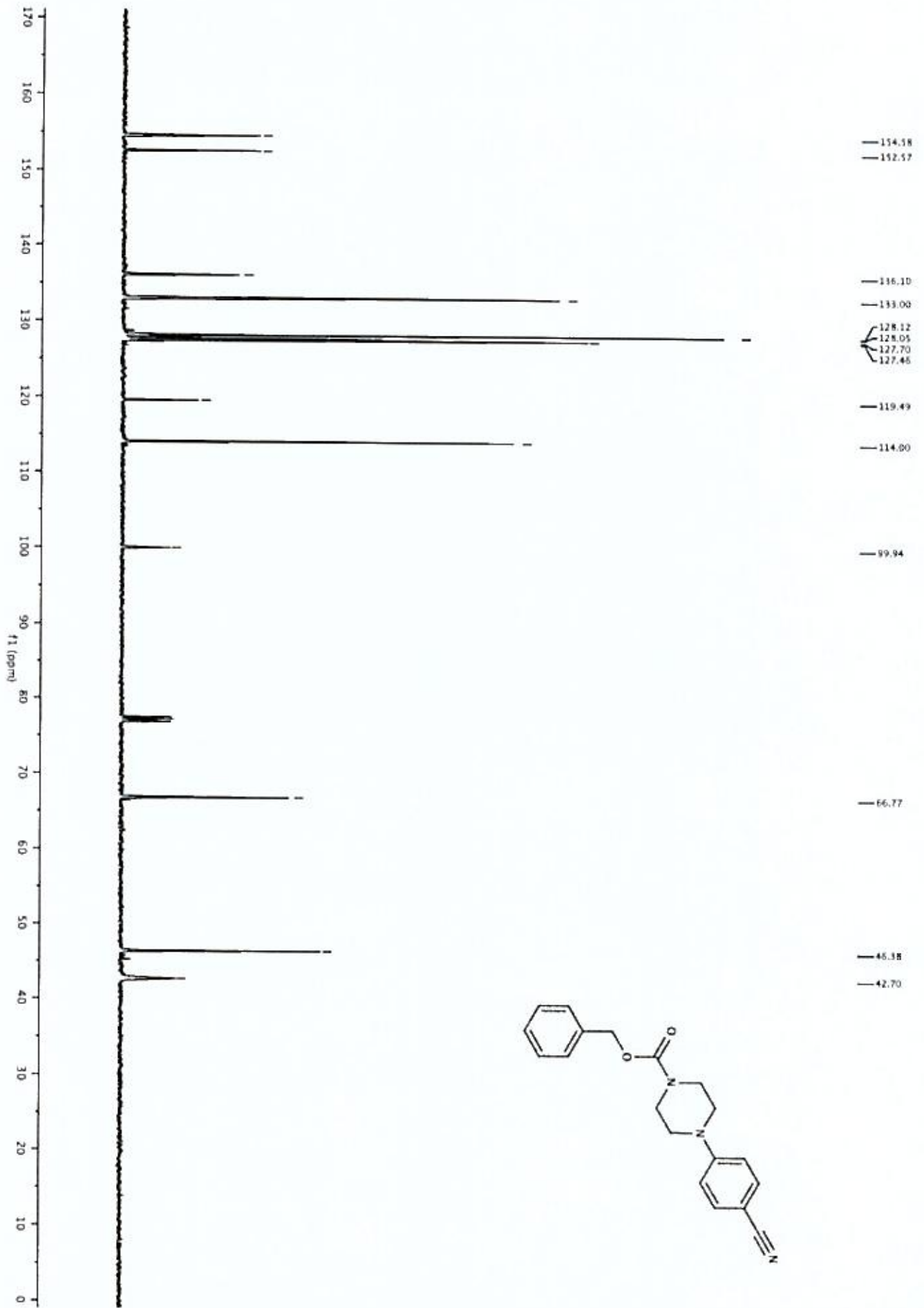
Handwritten integration marks: two sets of brackets, one above the aromatic region (7.2-7.5 ppm) and one above the methoxy region (3.4-3.6 ppm).

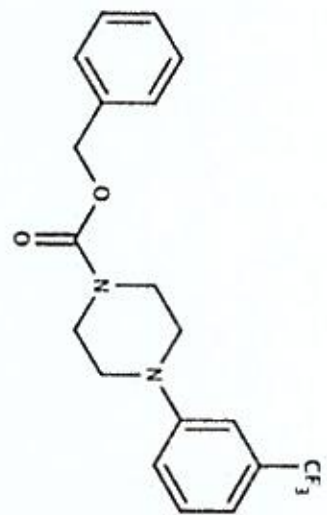
Handwritten integration marks: two sets of brackets, one above the methoxy region (3.4-3.6 ppm) and one above the tert-butyl methyl region (1.1-1.4 ppm).











Integration values for the aromatic region (7.0-7.5 ppm):

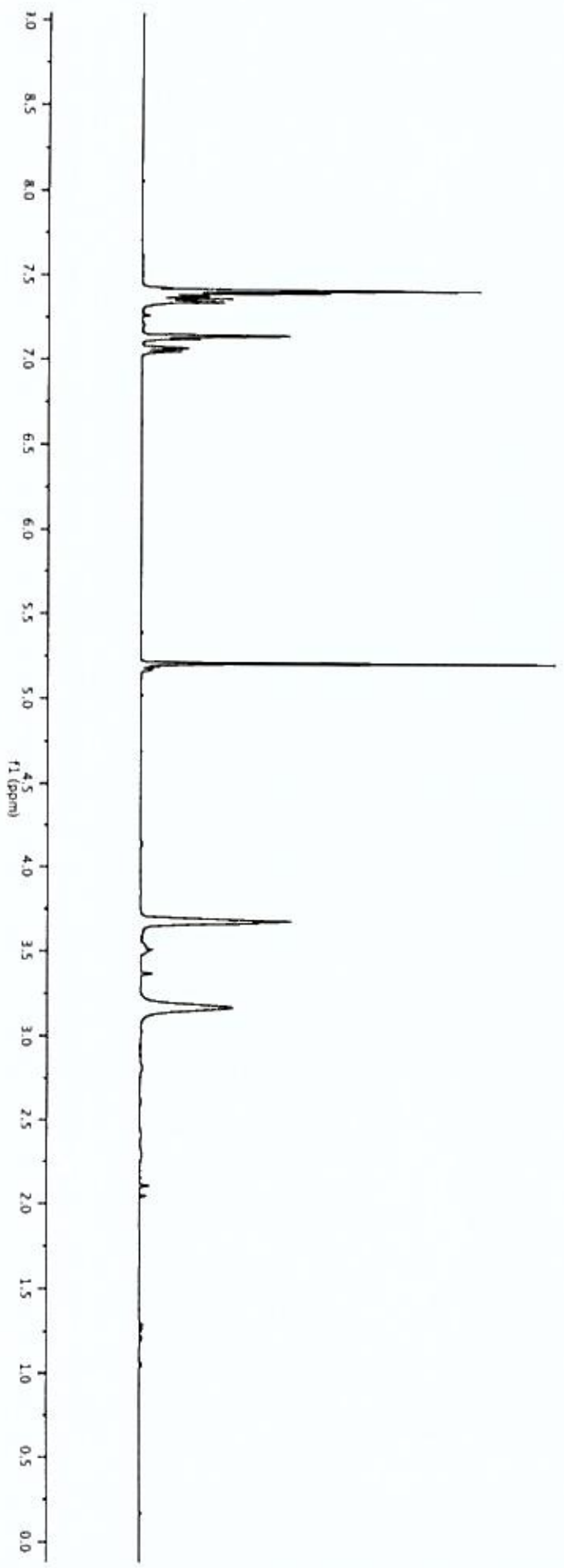
- 7.3-7.4 ppm: 1.00
- 7.1-7.2 ppm: 1.00

Integration value for the methylene region (4.3-4.5 ppm):

- 4.3-4.5 ppm: 1.00

Integration values for the methoxy region (3.5-3.8 ppm):

- 3.5-3.6 ppm: 1.00
- 3.7-3.8 ppm: 1.00



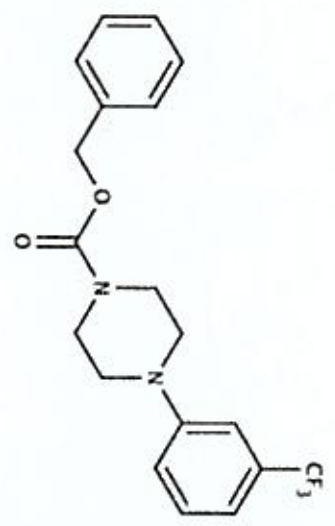
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

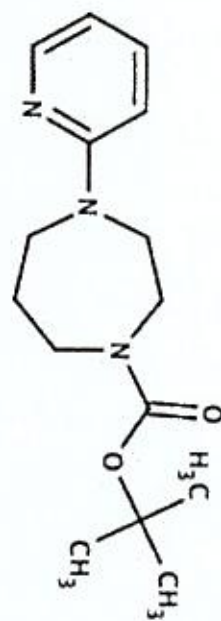
f1 (ppm)



- 155.03
- 153.19
- 136.52
- 131.81
- 131.50
- 131.18
- 130.87
- 129.60
- 128.47
- 128.05
- 127.88
- 125.58
- 122.87
- 119.28
- 116.37
- 112.61

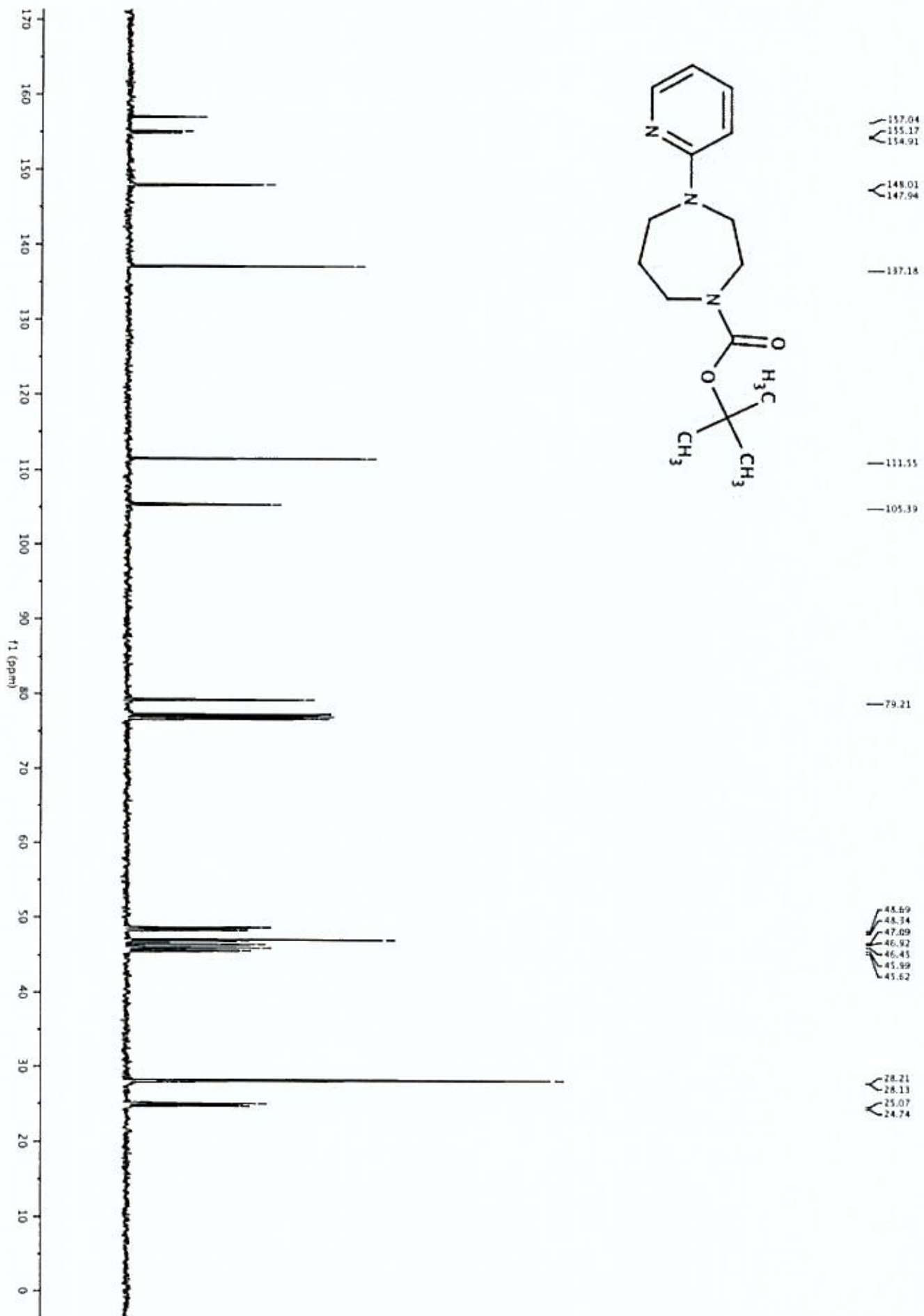
- 67.20
- 48.66
- 43.45

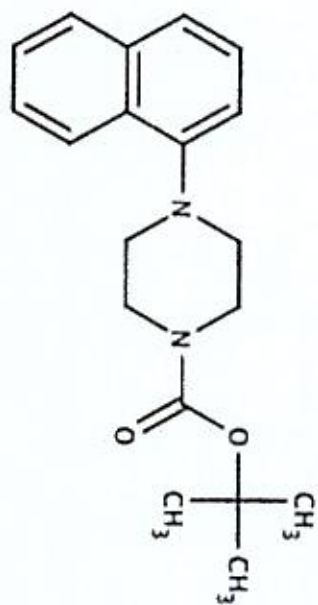




Handwritten annotations: "r r r r" and "r r r r" are written below the chemical structure, likely indicating integration values for the peaks in the spectrum.

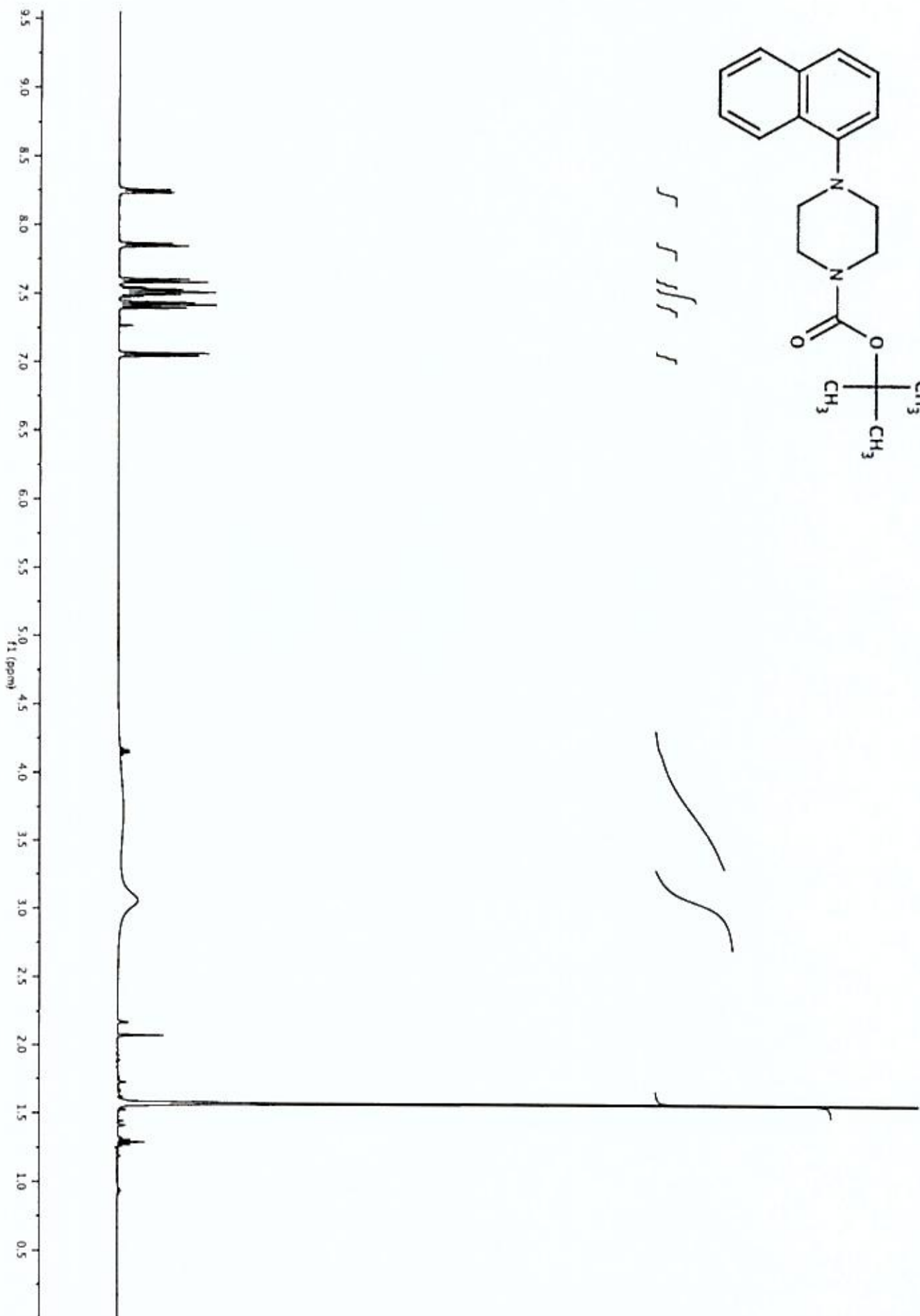




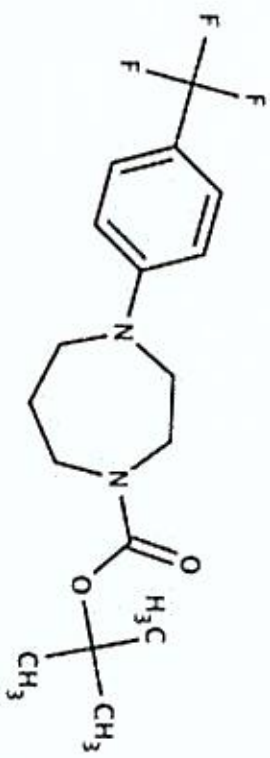


r r r r r

~ ~







Handwritten integration curves for the aromatic region (6.5-7.5 ppm).

Handwritten integration curves for the methoxy region (3.0-3.5 ppm).

Handwritten integration curves for the aliphatic region (1.0-2.0 ppm).

