

Supporting Information

Photosensitizer-Promoted Photoaddition Reactions of α -Silyl Group Containing *N*-Alkyl Glycinates to Dimethyl Acetylenedicarboxylate (DMAD)

Suk Hyun Lim, Dae Won Cho*

Department of Chemistry, Yeungnam University, Gyeongsan, Gyeongbuk 712-749, Korea

(dwcho00@yu.ac.kr)

Table of Contents

1. Experimental	S2-S7
2. ¹ H and ¹³ C-NMR spectra	S8-S51

Experimental

General. The ^1H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded CDCl_3 , and chemical shifts were reported in parts per million (d, ppm) relative to CHCl_3 (7.24 ppm for ^1H and 77 ppm for ^{13}C) as an internal standard. HRMS data were obtained by using an either EI or FAB. All starting materials used in the synthetic sequences came from commercial sources. All new compounds described were isolated in > 95% purity (by NMR analysis) unless noted otherwise.

Preparation of *N*- α -trimethylsilyl-*N*-alkyl glycinate **8a-8e.** Individual MeCN solutions (100 mL) containing primary amines **6a-6e** and **9** (10 mmol), K_2CO_3 (30 mmol), and (iodomethyl)trimethylsilane (TMSCH_2I , 5 mmol) were stirred in 12 h at 80 °C. Then, the reaction mixtures were evaporated in vacuo to give residues that were triturated with CH_2Cl_2 . The resulting triturates were dried and concentrated in vacuo to afford residues, which were subjected to silica gel column chromatography (EtOAc: Hex = 1: 5 - 1:10) to yield corresponding *N*- α -trimethylsilyl-*N*-alkyl amines **7a** (57%), **7b** (48%), **7c** (60%), **7d** (89%), **7e** (62%) and **10** (52%). Similar to above synthetic sequences, individual MeCN solutions containing **7a-7e** and **10** (5 mmol), K_2CO_3 (10 mmol) and BrCH_2CN (5 mmol) were stirred for 12 h at room temperature. By employing nearly equal work-up processes mentioned above, all of glycinate **8a**¹ (78 %), **8b** (69 %), **8c** (72 %), **8d**² (77 %), **8e** (85 %) and **8f** (55 %) were successfully prepared.

8a: ^1H NMR δ 0.02 (s, 9H), 0.84 (t, 3H, $J = 6.6$ Hz), 1.21-1.25 (m, 6H), 1.34-1.41 (m, 2H), 2.11 (s, 2H), 2.52 (t, 2H, $J = 7.2$ Hz), 3.26 (s, 3H), 4.11 (q, 2H, $J = 6.9$ Hz); ^{13}C NMR δ -1.8, 13.8, 14.0, 22.4, 26.6, 27.3, 31.6, 45.5, 57.3, 57.6, 59.5, 170.9.

8b: ^1H -NMR 0.01 (s, 9H), 1.22 (t, 3H, $J = 7.2$ Hz), 2.19 (s, 2H), 2.79 (t, 2H, $J = 6$ Hz), 3.28 (s, 3H), 3.385 (s, 2H), 3.42 (t, 2H, $J = 6$ Hz), 4.10 (q, 2H, $J = 7.2$ Hz); ^{13}C -NMR -1.8, 14.0, 46.0, 56.3, 57.9, 58.3, 59.6, 71.0, 171.1; HRMS (EI) m/z 247.1605 (M^+ , $\text{C}_{11}\text{H}_{25}\text{NO}_3\text{Si}$ requires 247.1604).

8c: ^1H NMR δ 0.02 (s, 15H), 0.81 (s, 9H), 1.189 (t, 3H, $J = 7.2$ Hz), 2.18 (s, 2H), 2.70 (t, 2H, $J = 6.3$ Hz), 3.34 (s, 2H), 3.63 (t, 2H, $J = 6.3$ Hz), 4.07 (q, 2H, $J = 7.2$ Hz); ^{13}C NMR δ -5.5, -1.6, 14.2, 18.2, 25.8, 46.6, 58.5, 59.2, 59.9, 61.9, 171.4; HRMS (EI) m/z 347.2310 (M^+ , $\text{C}_{16}\text{H}_{37}\text{NO}_3\text{Si}_2$ requires 347.2312).

8d: ^1H NMR δ 0.01 (s, 9H), 1.20 (t, 3H, $J = 7.2$ Hz), 2.16 (s, 2H), 3.20 (s, 2H), 3.71 (s, 2H), 4.09 (q, 2H, $J = 7.2$ Hz), 7.17-7.31 (m, 5H); ^{13}C NMR δ -1.6, 14.2, 45.5, 56.9, 59.8, 61.4, 126.9, 128.1, 128.7, 139.4, 171.2.

8e: ^1H NMR δ 0.06 (s, 9H), 1.27 (t, 3H, $J = 7.2$ Hz), 2.24 (s, 2H), 2.73-2.78 (m, 2H), 2.83-2.88 (m, 2H), 3.38 (s, 2H), 4.16 (q, 2H, $J = 7.2$ Hz), 7.15-7.29 (m, 5H); ^{13}C -NMR -1.6, 14.2, 34.0, 45.6, 57.8, 59.3, 59.9, 125.7, 128.1, 128.6, 140.2, 171.1; HRMS (EI) m/z 293.1807 (M^+ , $\text{C}_{16}\text{H}_{27}\text{NO}_2\text{Si}$ requires 293.1811).

8f: ^1H NMR δ ^1H -NMR 0.03 (s, 9H), 1.90 (s, 2H), 2.59 (t, 2H, $J = 5.1$ Hz), 3.21 (s, 2H), 4.33 (t, 2H, $J = 5.1$ Hz); ^{13}C -NMR -1.6, 49.8, 52.6, 59.0, 68.6, 167.7; HRMS (EI) m/z 187.1026 (M^+ , $\text{C}_8\text{H}_{17}\text{NO}_2\text{Si}$ requires 187.1029).

General procedure of photoreactions of glycines 8a-8f with dimethyl acetylenedicarboxylate (DMAD). The individual solvent (220 mL) containing glycines (3.2 mM), DMAD (3.2 mM), and photosensitizers (0.27-0.32 mM) that were purged with oxygen before and during irradiations, were irradiated with a 450 W Hanovia medium pressure Hg lamp equipped by a flint glass filter (> 310 nm) for certain time periods to bring about 100% conversion of glycines. Then, the photolysates were concentrated in vacuo to yield residues, which were subjected to silica gel column chromatography to determine photoproducts and their yields.

Photoreaction of 8a with DMAD. In MeCN solution of DCA: 5 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12a** (10%), **13a** (9%) and **14a** (31%). In toluene solution of C_{60} : 10 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12a** (11 %),

13a (6%) and **14a** (36%). In MeCN solution of RB: 5 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12a** (31%), **13a** (8%) and **14a** (21%).

12a: $^1\text{H NMR}$ δ 0.38 (s, 9H), 0.86 (t, 3H, $J = 6.6$ Hz), 1.27-1.32 (m, 9H), 1.57-1.66 (m, 2H), 3.75 (s, 3H), 3.86 (s, 3H), 4.25 (q, 2H, $J = 10.5$ Hz), 4.39 (t, 2H, $J = 7.8$ Hz); $^{13}\text{C-NMR}$ 1.3, 13.9, 22.5, 26.2, 31.4, 33.1, 48.5, 51.5, 52.3, 60.9, 122.1, 123.4, 126.4, 144.1, 159.7, 164.3, 166.9; HRMS (EI) m/z 411.2079 (M^+ , $\text{C}_{20}\text{H}_{33}\text{NO}_6\text{Si}$ requires 411.2077).

13a: $^1\text{H NMR}$ δ 0.83 (t, 3H, $J = 6.3$ Hz), 1.23-1.33 (m, 9H), 1.68-1.75 (m, 2H), 3.78 (s, 3H), 3.90 (s, 3H), 4.21-4.28 (m, 4H), 7.33 (s, 1H); $^{13}\text{C-NMR}$ 14.0, 22.5, 26.2, 31.2, 31.3, 50.2, 51.6, 52.6, 60.9, 113.0, 120.2, 125.6, 130.9, 159.4, 163.0, 166.4; HRMS (EI) m/z 339.1680 (M^+ , $\text{C}_{17}\text{H}_{25}\text{NO}_6$ requires 339.1682).

14a: $^1\text{H NMR}$ δ 0.85 (t, 3H, $J = 6$ Hz), 1.23-1.27 (m, 9H), 1.55 (t, 2H, $J = 6.6$ Hz), 3.14 (t, 2H, $J = 7.8$ Hz), 3.59 (s, 3H), 3.80 (s, 2H), 3.88 (s, 3H), 4.18 (q, 2H, $J = 6$ Hz), 4.58 (s, 1H); $^{13}\text{C-NMR}$ 13.9, 14.1, 22.5, 26.4, 31.4, 50.9, 51.7, 52.5, 52.9, 61.6, 85.7, 154.1, 165.6, 167.8, 168.4; HRMS (EI) m/z 329.1839 (M^+ , $\text{C}_{16}\text{H}_{27}\text{NO}_6$ requires 329.1838).

Photoreaction of 8b with DMAD. In MeCN solution of DCA: 5 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12b** (5%), **13b** (4%) and **14b** (40%). In toluene solution of C_{60} : 10 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12b** (5 %) and **14b** (45%). In MeCN solution of RB: 5 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12b** (24%), **13b** (1%) and **14b** (45%).

12b: $^1\text{H NMR}$ δ 0.38 (s, 9H), 1.29 (t, 3H, $J = 7.2$ Hz), 3.22 (s, 3H), 3.52 (t, 2H, $J = 5.7$ Hz), 3.76 (s, 3H), 3.86 (s, 3H), 4.24 (q, 2H, $J = 7.2$ Hz), 4.67 (t, 2H, $J = 5.7$ Hz); $^{13}\text{C-NMR}$ 1.5, 14.0, 47.6, 51.5, 52.4, 59.0, 60.9, 72.4, 121.7, 122.9, 126.9, 146.4, 159.8, 164.1, 167.1; HRMS (EI) m/z 385.1554 (M^+ , $\text{C}_{17}\text{H}_{27}\text{NO}_7\text{Si}$ requires 385.1557).

13b: ^1H NMR δ 1.30 (t, 3H, $J = 7.2$ Hz), 3.27 (s, 3H), 3.61 (t, 2H, $J = 5.1$ Hz), 3.78 (s, 3H), 3.90 (s, 3H), 4.24 (q, 2H, $J = 7.2$ Hz), 4.46 (t, 2H, $J = 5.1$ Hz), 7.41 (s, 1H); ^{13}C -NMR 13.9, 49.8, 51.6, 52.7, 58.9, 61.0, 71.4, 113.1, 119.8, 125.7, 132.5, 159.7, 163.0, 166.4; HRMS (FAB) m/z 314.1233 ($M+1$, $\text{C}_{14}\text{H}_{20}\text{NO}_7$ requires 314.1234).

14b: ^1H NMR δ 1.25 (t, 3H, $J = 7.2$ Hz), 3.27 (s, 3H), 3.36 (t, 2H, $J = 5.1$ Hz), 3.51 (t, 2H, $J = 5.1$ Hz), 3.60 (s, 3H), 3.88 (s, 3H), 3.96 (s, 2H), 4.18 (q, 2H, $J = 7.2$ Hz), 4.59 (s, 1H); ^{13}C -NMR 14.1, 50.9, 52.0, 52.8, 53.0, 58.9, 61.4, 77.2, 86.1, 154.1, 165.6, 167.7, 168.3; HRMS (EI) m/z 303.1317 ($M+$, $\text{C}_{13}\text{H}_{21}\text{NO}_7$ requires 303.1318).

Photoreaction of 8c with DMAD In MeCN solution of DCA: 5 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12c** (7%), **13c** (5%) and **14c** (33%). In toluene solution of C_{60} : 10 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12c** (8%), **13c** (5%) and **14c** (34%). In MeCN solution of RB: 5 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12c** (27%) and **14c** (26%).

12c: ^1H NMR δ -0.06 (s, 6H), 0.39 (s, 9H), 0.80 (s, 9H), 1.29 (t, 3H, $J = 6$ Hz), 3.72-3.76 (m, 2H), 3.76 (s, 3H), 3.85 (s, 3H), 4.22 (q, 2H, $J = 6$ Hz), 4.61 (t, 2H, $J = 6.3$ Hz); ^{13}C NMR δ -5.6, 1.5, 13.9, 18.3, 25.8, 49.4, 51.6, 52.3, 60.9, 63.8, 122.1, 123.8, 126.5, 145.2, 159.8, 164.2, 166.9; HRMS (FAB) m/z 486.2345 ($M+H$, $\text{C}_{22}\text{H}_{40}\text{NO}_7\text{Si}$ requires 486.2343).

13c: ^1H NMR δ -0.09 (s, 6H), 0.81 (s, 9H), 1.29 (t, 3H, $J = 6.9$ Hz), 3.77 (s, 3H), 3.82 (t, 2H, $J = 4.8$ Hz), 3.89 (s, 3H), 4.23 (q, 2H, $J = 6.9$ Hz), 4.41 (t, 2H, $J = 4.8$ Hz), 7.40 (s, 1H); ^{13}C NMR δ -5.7, 13.9, 18.1, 25.7, 29.7, 51.6, 52.1, 52.6, 60.9, 62.2, 112.8, 119.7, 125.8, 132.8, 159.7, 163.0, 166.3; HRMS (FAB) m/z 414.1949 ($M+H$, $\text{C}_{19}\text{H}_{32}\text{NO}_7\text{Si}$ requires 414.1948).

14c: ^1H NMR δ 0.02 (s, 6H), 0.85 (s, 9H), 1.25 (t, 3H, $J = 7.2$ Hz), 3.32 (t, 2H, $J = 5.7$ Hz), 3.60 (s, 3H), 3.74 (t, 2H, $J = 5.7$ Hz), 3.88 (s, 3H), 3.98 (s, 2H), 4.18 (q, 2H, $J = 7.2$ Hz), 4.58 (s, 1H); ^{13}C

NMR δ -5.6, 14.1, 18.1, 25.8, 50.9, 53.0, 54.1, 61.5, 77.2, 85.9, 154.1, 165.6, 167.8, 168.4; HRMS (EI) m/z 403.2029 (M+H, C₁₈H₃₃NO₇Si requires 403.2026).

Photoreaction of 8d with DMAD. In MeCN solution of DCA: 5 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12d** (6%) and **14d** (50%). In toluene solution of C₆₀: 10 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12d** (38%) and **14d** (21%). In MeCN solution of RB: 5 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12d** (11%) and **14d** (49%).

12d: ¹H NMR δ 0.26 (s, 9H), 1.19 (t, 3H, J = 7.2 Hz), 3.80 (s, 3H), 3.88 (s, 3H), 4.12 (q, 2H, J = 7.2 Hz), 5.77 (s, 2H), 6.78 (d, 2H, J = 7.2 Hz), 7.18-7.31 (m, 3H); ¹³C-NMR 1.2, 14.0, 51.5, 51.8, 52.6, 61.1, 122.7, 124.4, 125.2, 126.7, 127.3, 128.8, 138.4, 145.6, 159.6, 164.4, 166.9; HRMS (FAB) m/z 418.1680 (M+H, C₂₁H₂₈NO₆Si requires 418.1686).

14d: ¹H-NMR δ 1.23 (t, 3H, J = 6.9 Hz), 3.59 (s, 3H), 3.70 (s, 2H), 3.89 (s, 3H), 4.16 (q, 1H, J = 6.9 Hz), 4.38 (s, 2H), 4.70 (s, 1H), 7.22-7.34 (m, 5H); ¹³C-NMR δ 14.2, 50.2, 51.1, 53.2, 55.2, 61.7, 87.0, 128.1, 128.3, 129.0, 134.9, 154.5, 165.9, 167.9, 168.3; HRMS (FAB) m/z 336.1445 (M+H, C₁₇H₂₂NO₆ requires 336.1447).

Photoreaction of 8e with DMAD. In MeCN solution of DCA: 5 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12e** (9%), **13e** (6%) and **14e** (35%). In toluene solution of C₆₀: 10 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12e** (5%), **13e** (8%) and **14e** (40%). In MeCN solution of RB: 5 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12e** (19%), **13e** (6%) and **14e** (25%).

12e: ¹H NMR δ 0.38 (s, 9H), 1.30 (t, 3H, J = 7.2 Hz), 2.94 (t, 2H, J = 8.1 Hz), 3.77 (s, 3H), 3.87 (s, 3H), 4.25 (q, 2H, J = 7.2 Hz), 4.67 (t, 2H, J = 8.1 Hz), 7.17-7.31 (m, 5H); ¹³C-NMR 1.4, 14.0, 39.0, 49.4, 51.6, 52.4, 61.0, 122.1, 123.2, 126.7, 126.8, 128.7, 128.8, 137.4, 144.5, 159.6, 164.2, 166.9; HRMS (EI) m/z 431.1761 (M+, C₂₂H₂₉NO₆Si requires 431.1764).

13e: ^1H NMR δ 1.32 (t, 3H, $J = 6.9$ Hz), 3.02 (t, 2H, $J = 7.8$ Hz), 3.76 (s, 3H), 3.91 (s, 3H), 4.28 (q, 2H, $J = 6.9$ Hz), 4.48 (t, 2H, $J = 7.8$ Hz), 7.11-7.14 (m, 3H), 7.21-7.30 (m, 3H); ^{13}C -NMR 14.0, 37.9, 51.6, 51.7, 52.6, 61.0, 113.1, 120.0, 125.8, 126.9, 128.7, 128.8, 131.1, 137.3, 159.5, 162.9, 166.3; HRMS (EI) m/z 359.1367 (M^+ , $\text{C}_{19}\text{H}_{21}\text{NO}_6$ requires 359.1369).

14e: ^1H NMR δ 1.25 (t, 3H, $J = 6.9$ Hz), 2.88 (t, 2H, $J = 7.2$ Hz), 3.41 (t, 2H, $J = 7.2$ Hz), 3.63 (s, 3H), 3.67 (s, 2H), 3.90 (s, 3H), 4.18 (q, 2H, $J = 6.9$ Hz), 4.68 (s, 1H), 7.14 (d, 2H, $J = 6.6$ Hz), 7.21-7.31 (m, 3H); ^{13}C -NMR 14.1, 50.9, 52.5, 53.0, 54.2, 61.2, 86.2, 126.7, 128.6, 128.7, 137.9, 153.7, 165.6, 167.7, 168.3; HRMS (EI) m/z 349.1528 (M^+ , $\text{C}_{18}\text{H}_{23}\text{NO}_6$ requires 349.1525).

Photoreaction of 8f with DMAD. In MeCN solution of DCA: 5 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12f** (51%) and **13f** (2%). In toluene solution of C_{60} : 10 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12f** (44 %) and **13f** (1%). In MeCN solution of RB: 5 min irradiation, column chromatography (EtOAc: hexane = 1: 5) to yield **12f** (48%) and **13f** (1%).

12f: ^1H NMR δ 0.40 (s, 9H), 3.78 (s, 3H), 3.93 (s, 3H), 4.27 (t, 2H, $J = 5.4$ Hz), 4.58 (t, 2H, $J = 5.4$ Hz); ^{13}C -NMR 0.8, 44.8, 51.9, 53.0, 65.6, 120.8, 123.6, 126.7, 142.5, 156.8, 163.7, 165.6; HRMS (EI) m/z 325.0984 (M^+ , $\text{C}_{14}\text{H}_{19}\text{NO}_6\text{Si}$ requires 325.0982).

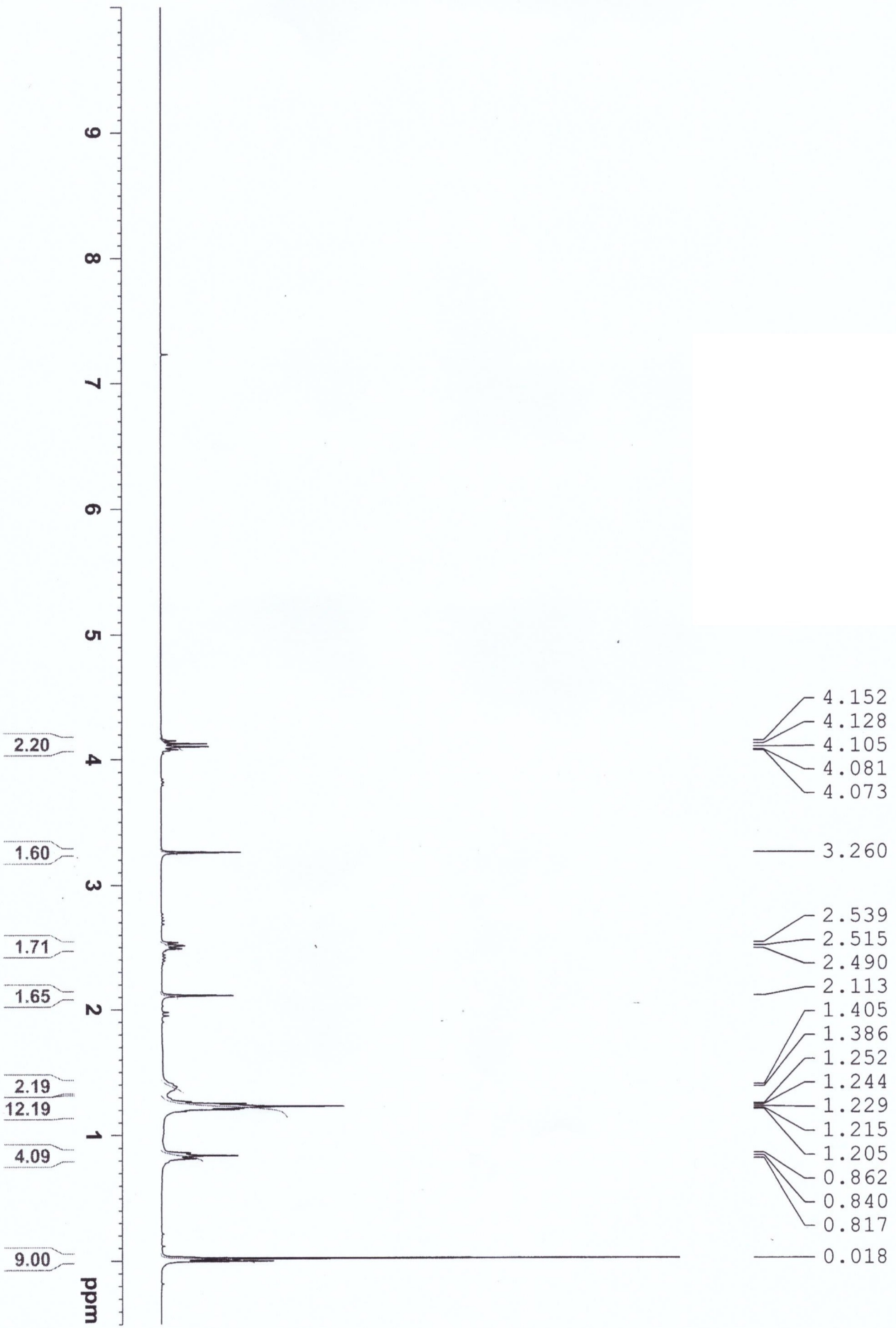
13f: ^1H NMR δ 3.79 (s, 3H), 3.94 (s, 3H), 4.23 (t, 2H, $J = 5.4$ Hz), 4.61 (t, 2H, $J = 5.4$ Hz), 7.38 (s, 1H); ^{13}C NMR δ 43.6, 51.9, 53.1, 65.8, 115.8, 117.9, 125.2, 127.1, 156.4, 162.4, 164.7; HRMS (EI) m/z 253.0583 (M^+ , $\text{C}_{11}\text{H}_{11}\text{NO}_6$ requires 253.0586).

Reference

1. Lim, S. H.; Yi, J.; Moon, G. M.; Ra, C. S.; Nahm, K.; Cho, D. W.; Kim, K.; Hyung, T. G.; Yoon, U. C.; Lee, G. Y.; Kim, S.; Kim, J.; Mariano, P. S. *J. Org. Chem.* **2014**, *79*, 6946-6958.
2. Lim, S. H.; Atar, A. B.; Bae, G.; Wee, K. -R.; Cho, D. W. *RSC Adv.* **2019**, *9*, 5639-5648.

8a

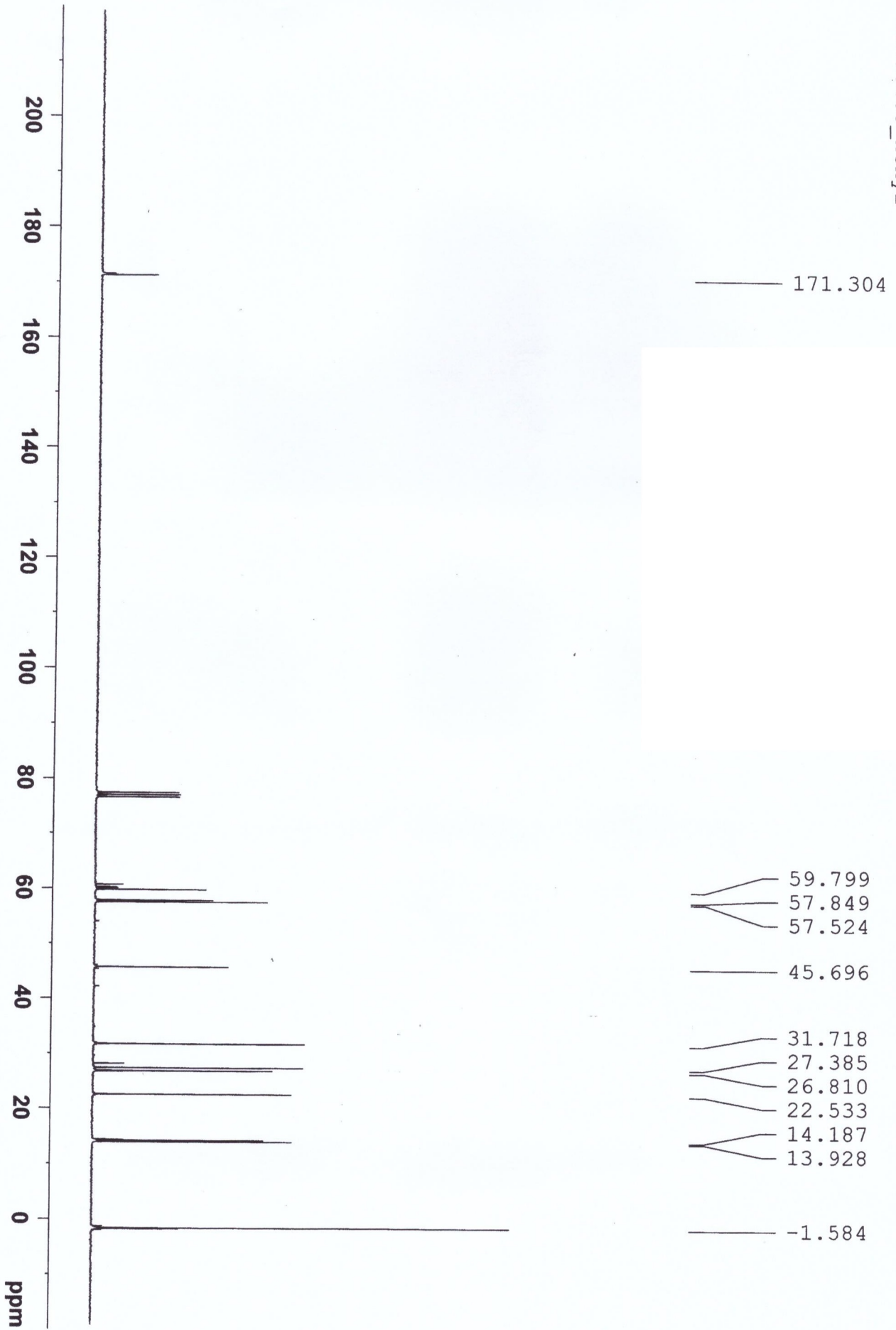
20130603moon



S8

8a

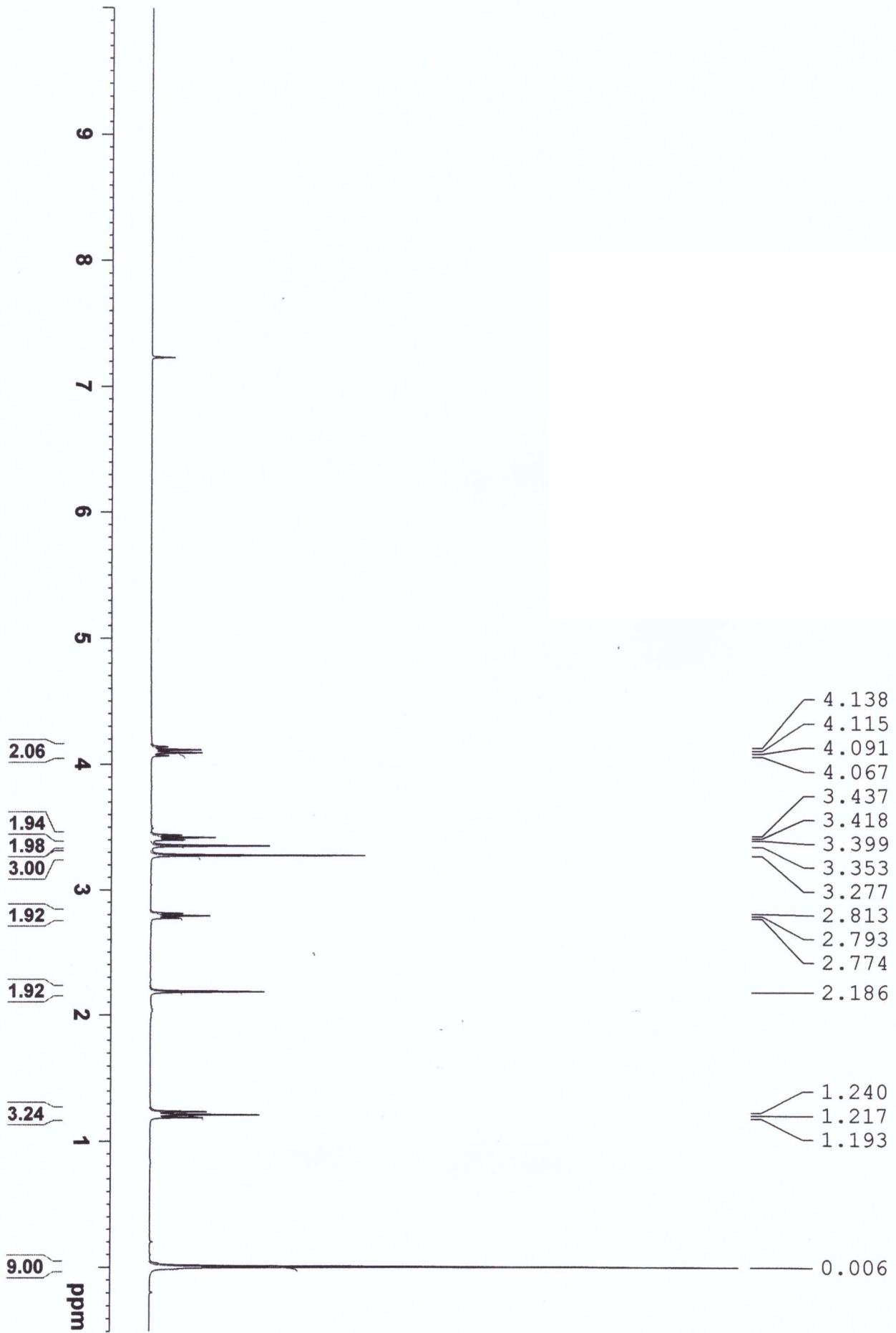
20190403_hexyl1



S9

8b

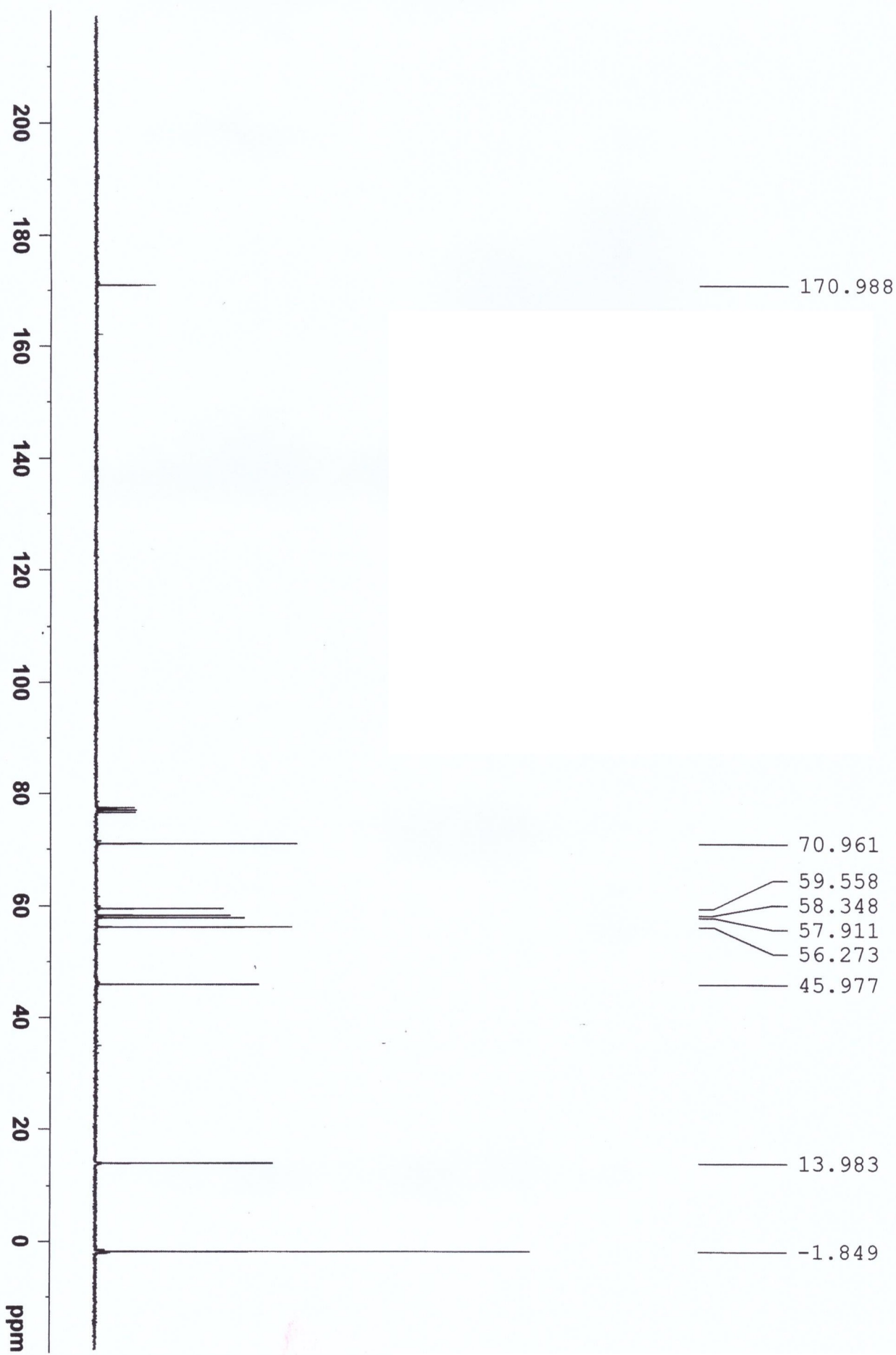
20161226 (9H)



S10

8b

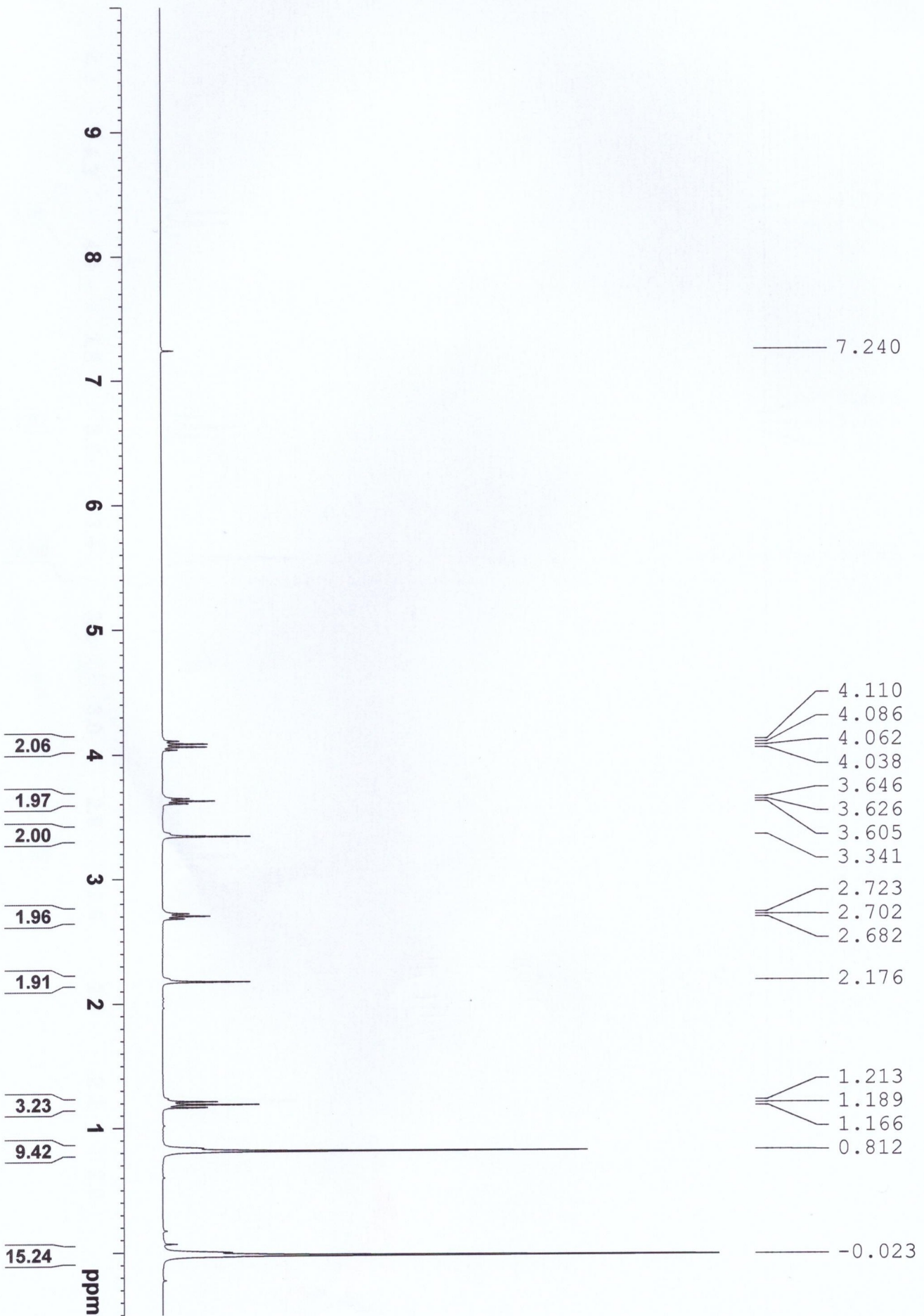
20161226(9C)



S11

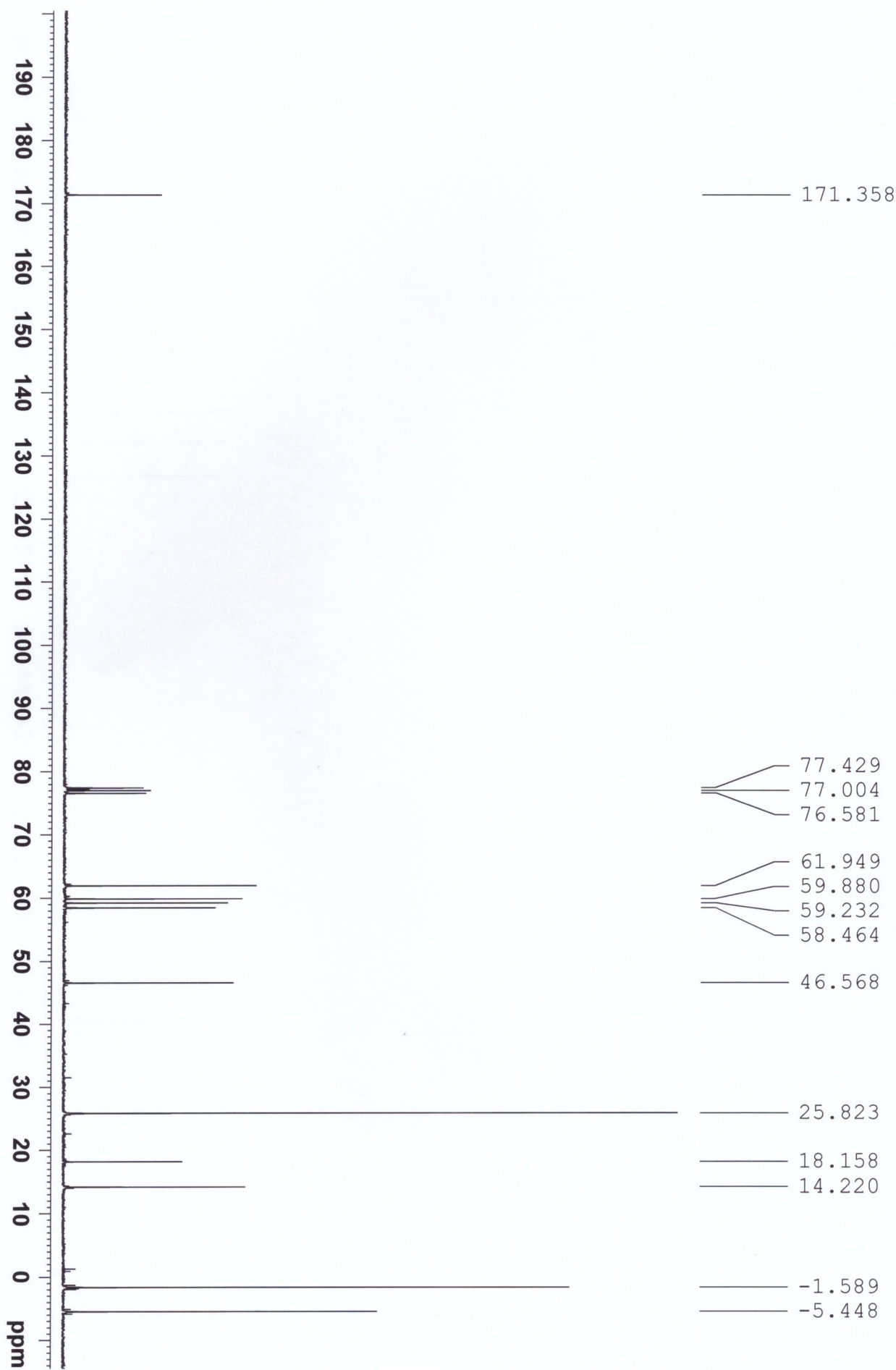
8c

2015-10-13-04



S12

2015-10-13-05

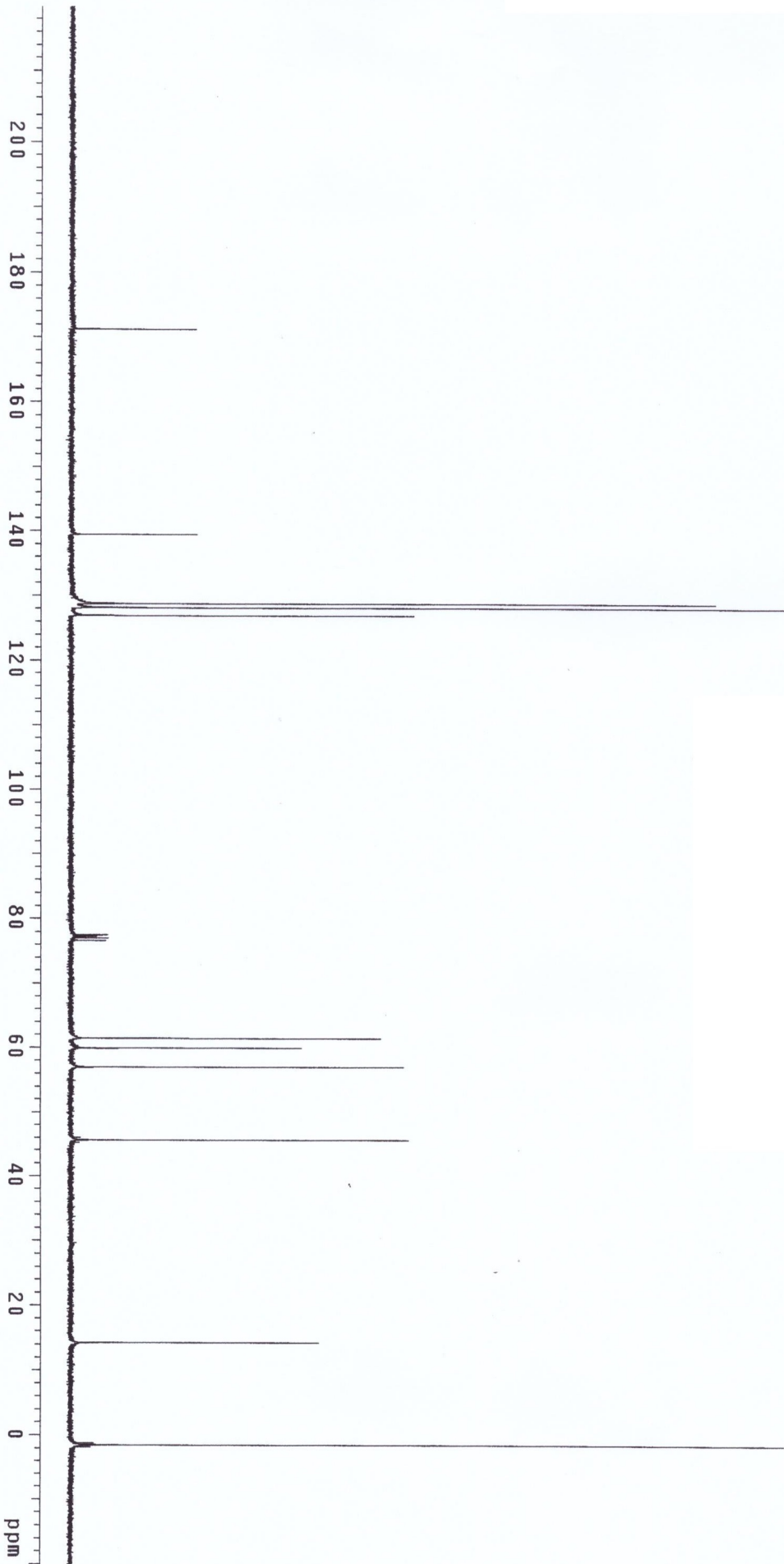


8d

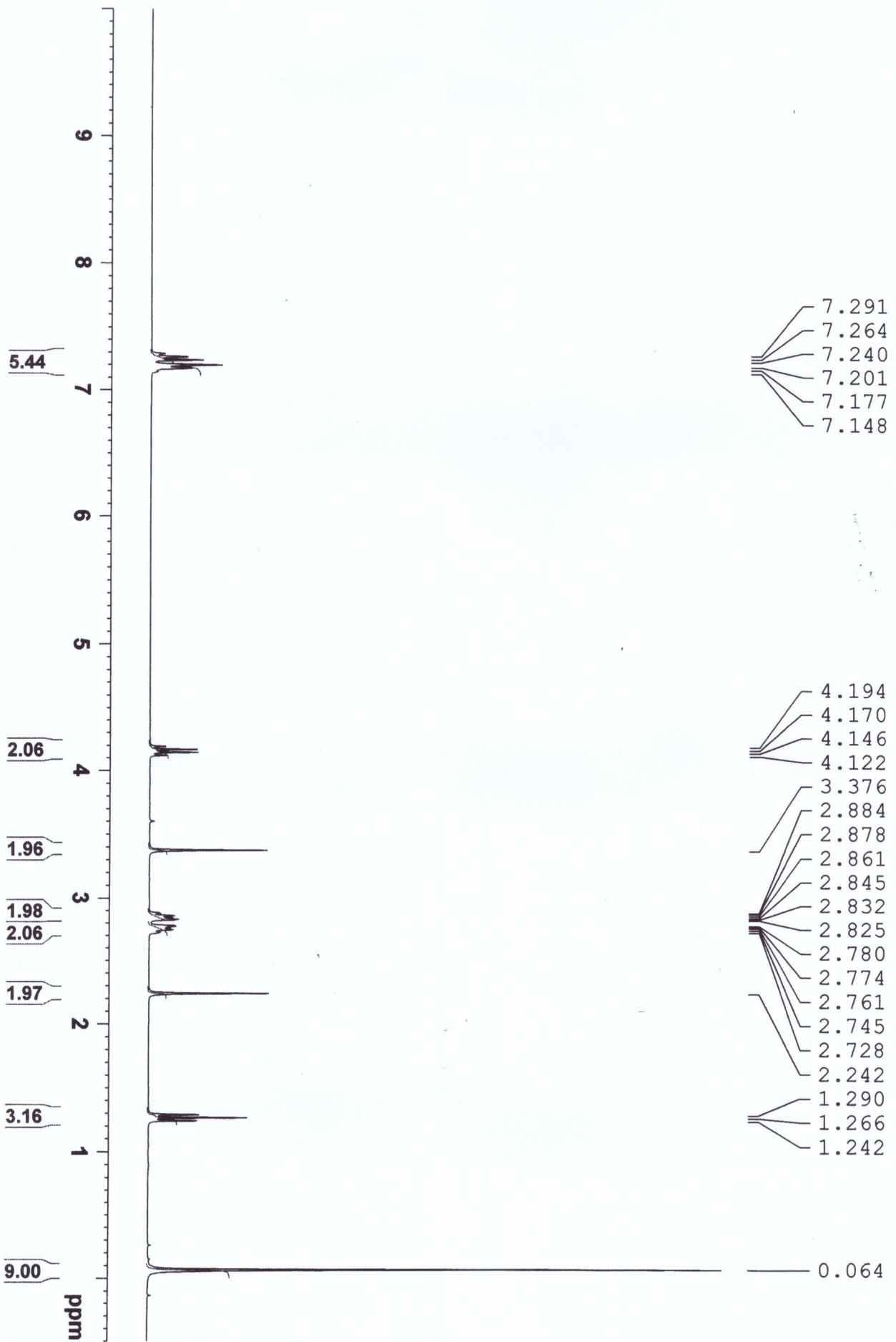


S14

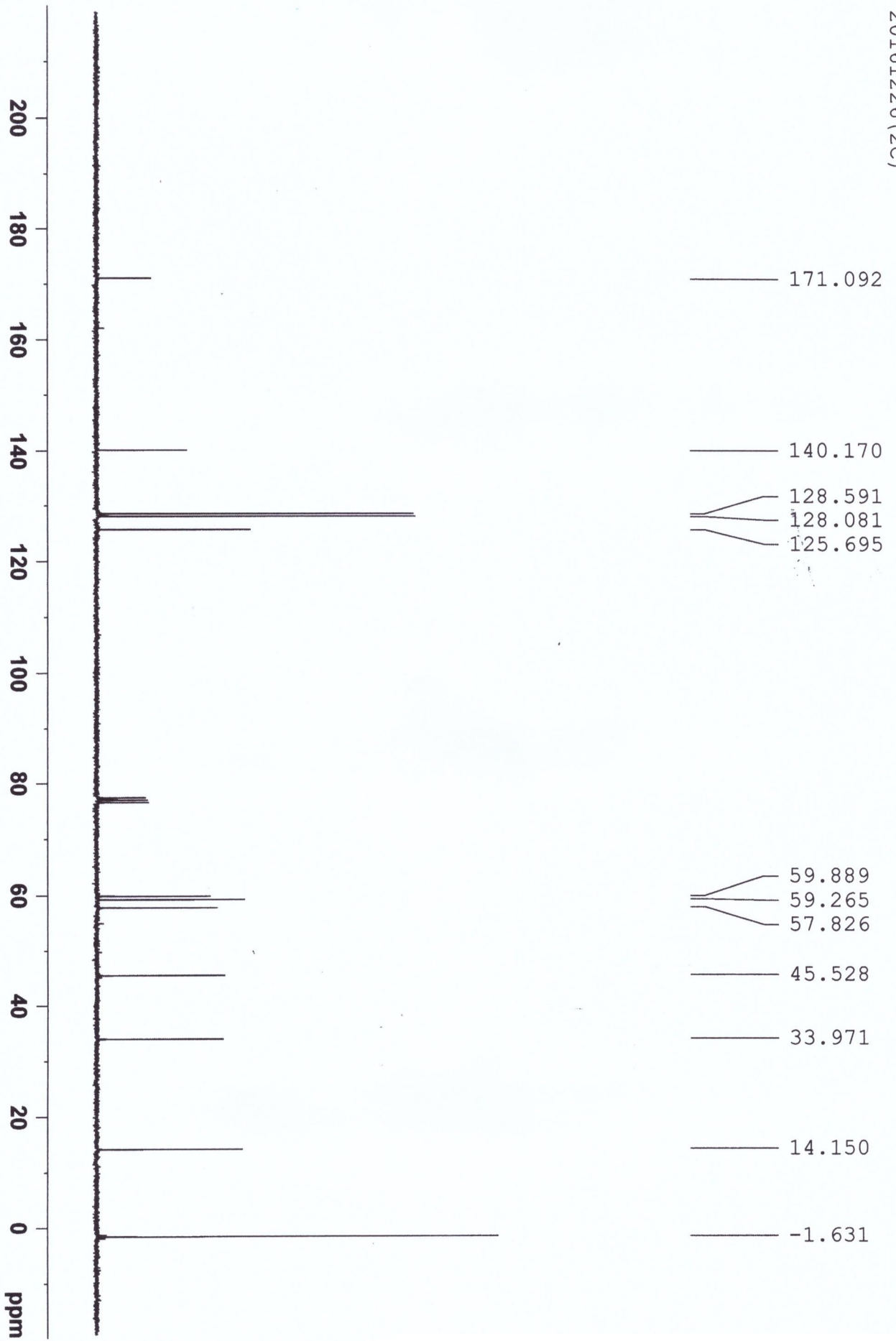
8d

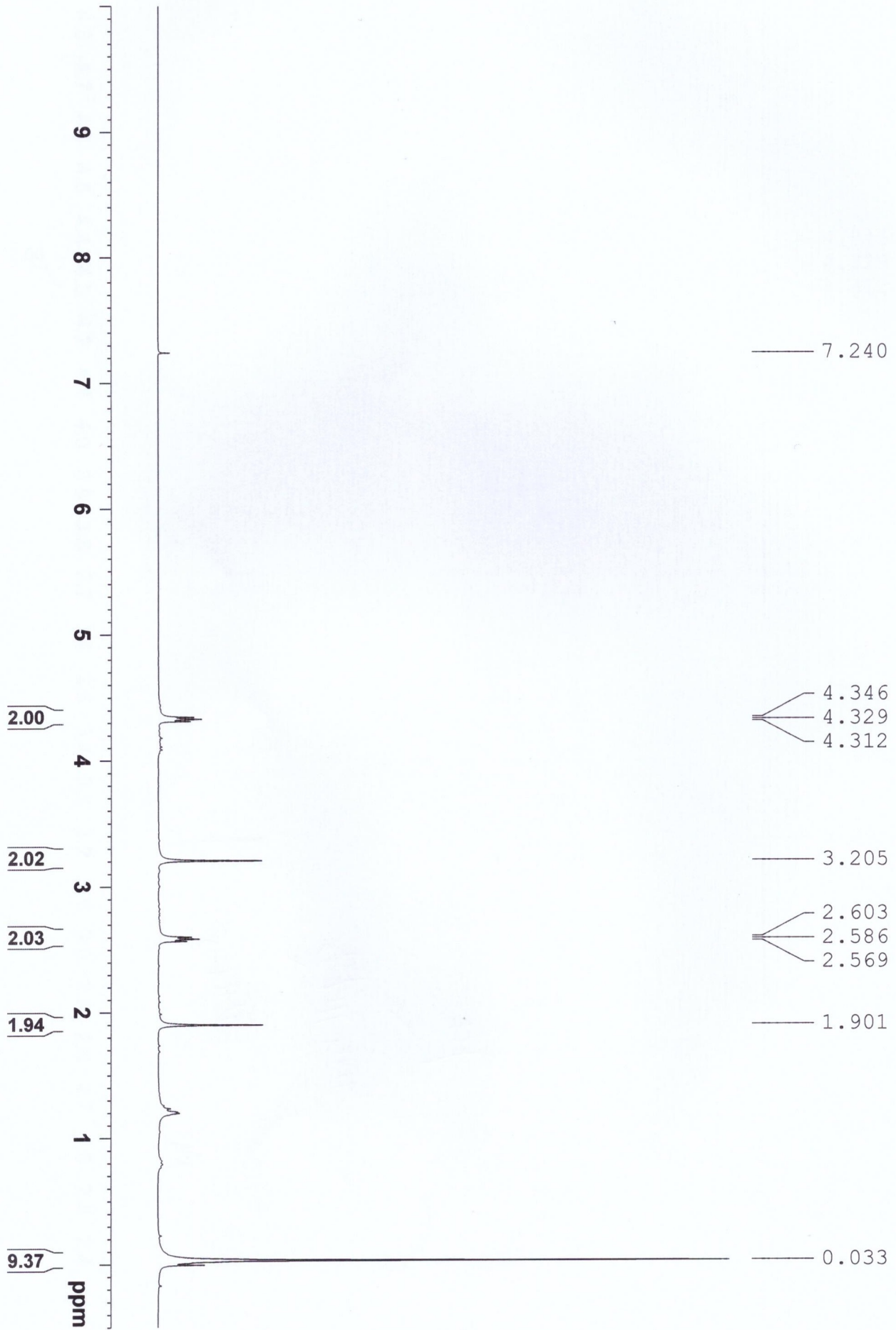


S15

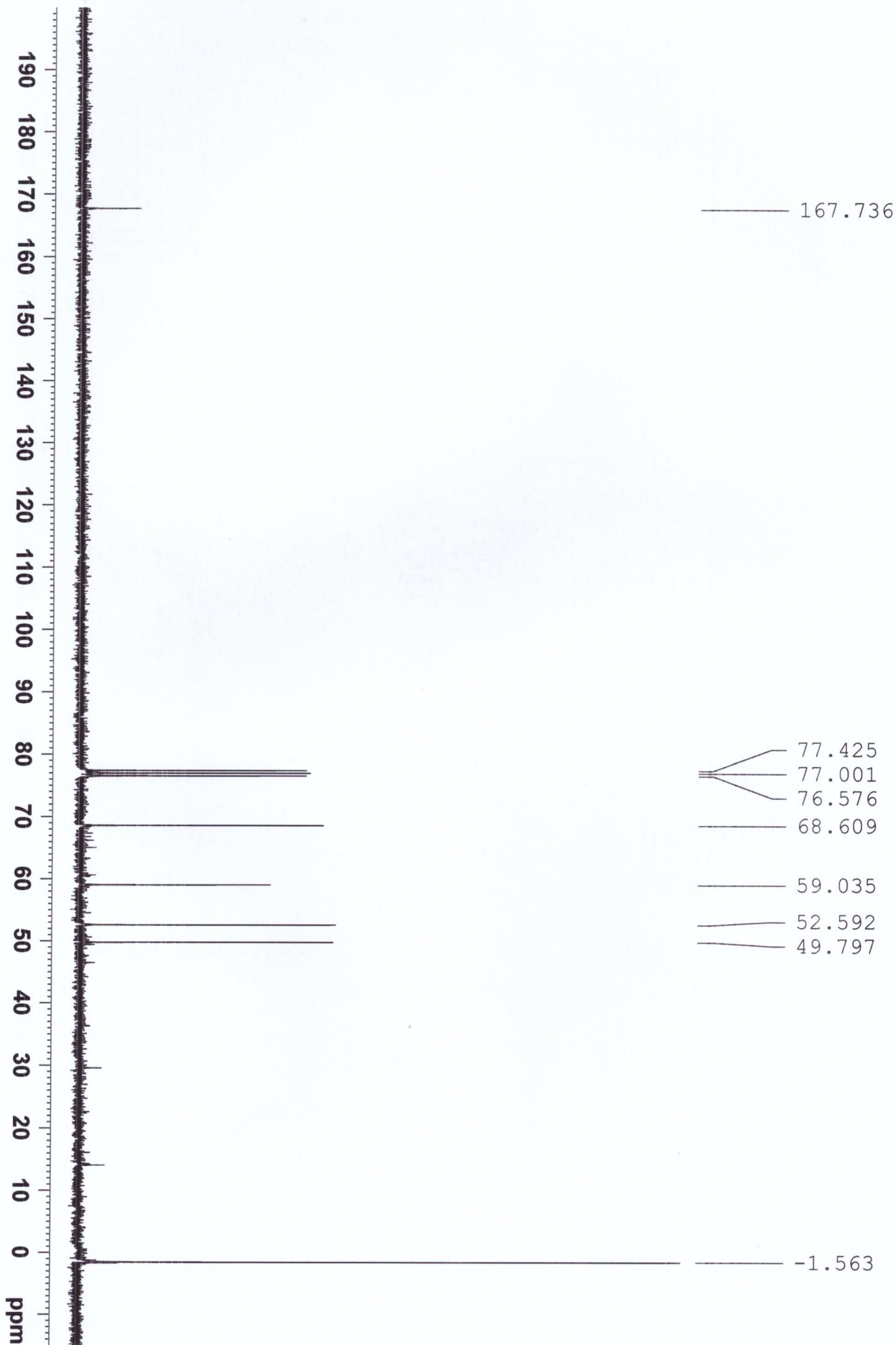


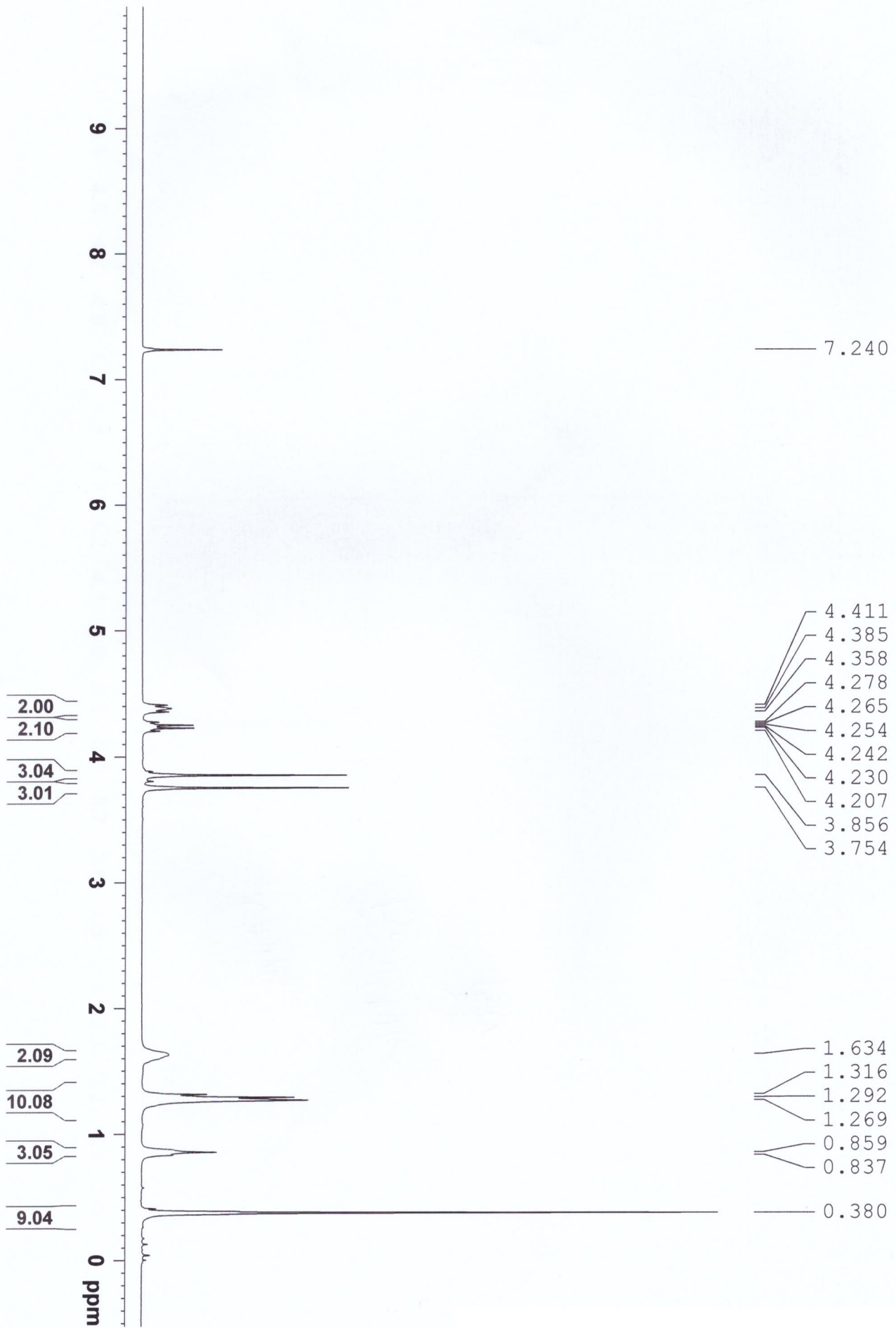
20161226 (2C)





2016-01-26-05





. pyrrole

Sample Name:

Data Collected on:
Agilent-MSR-ymmr600
Archive directory:

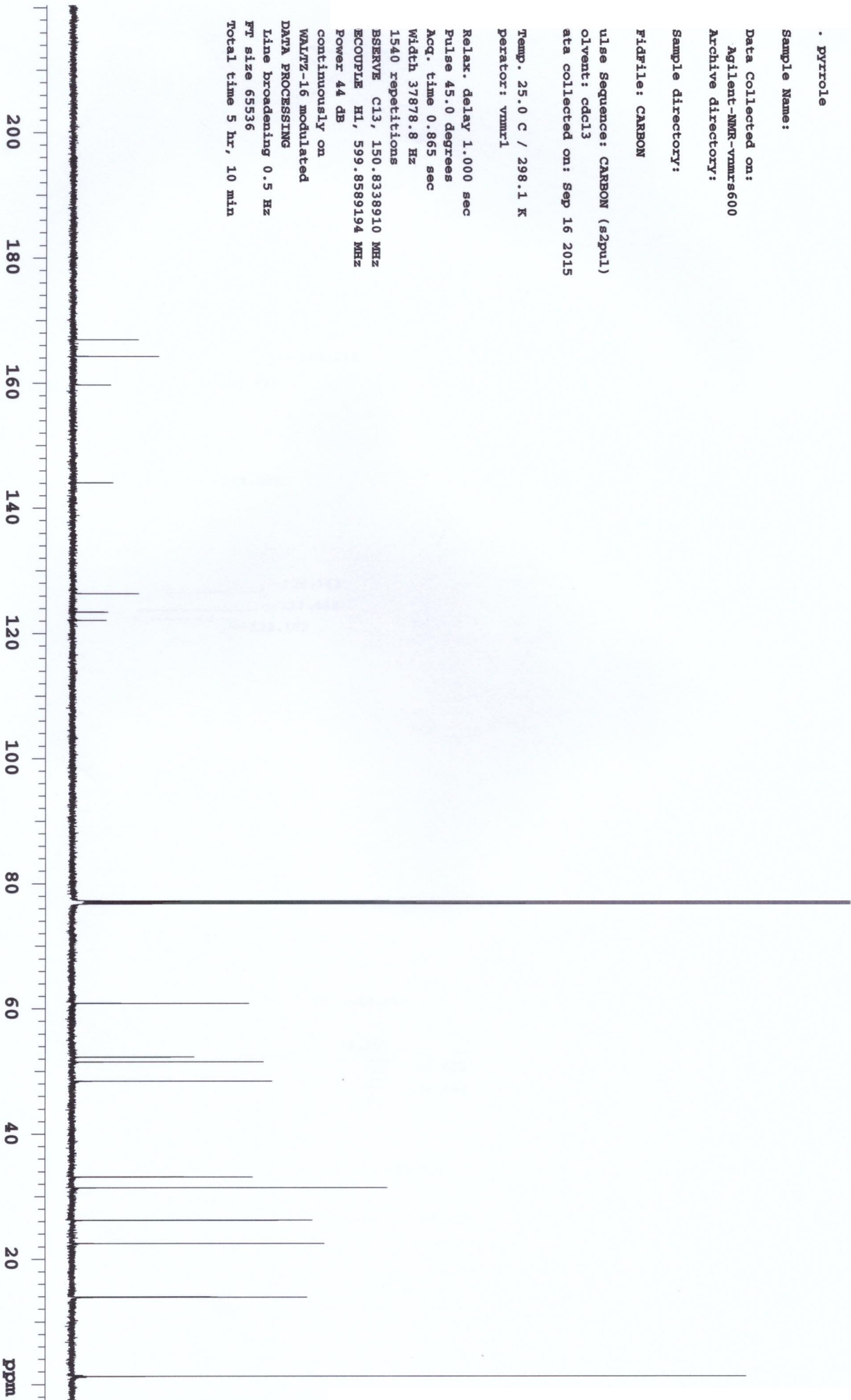
Sample directory:

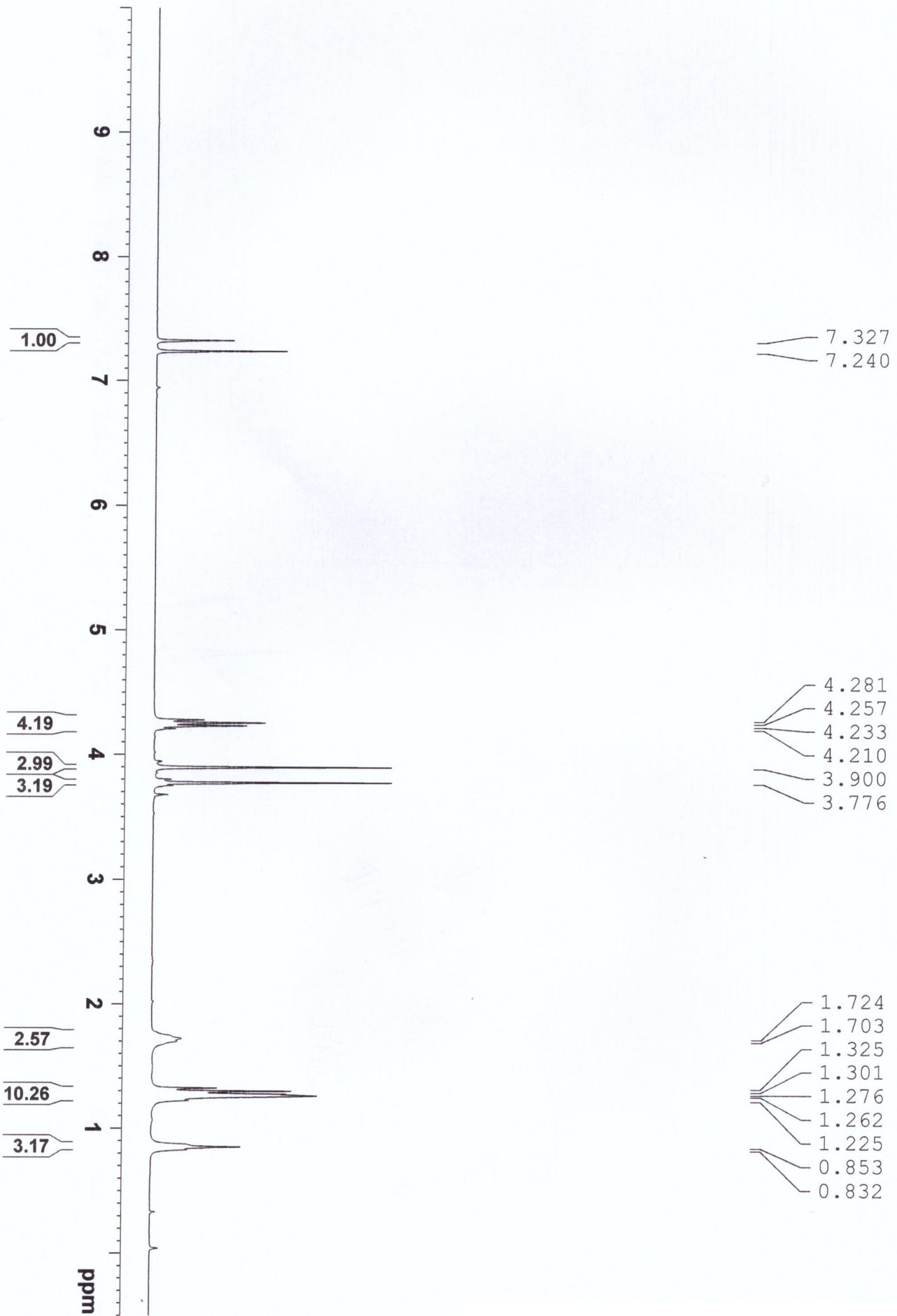
Fidfile: CARBON

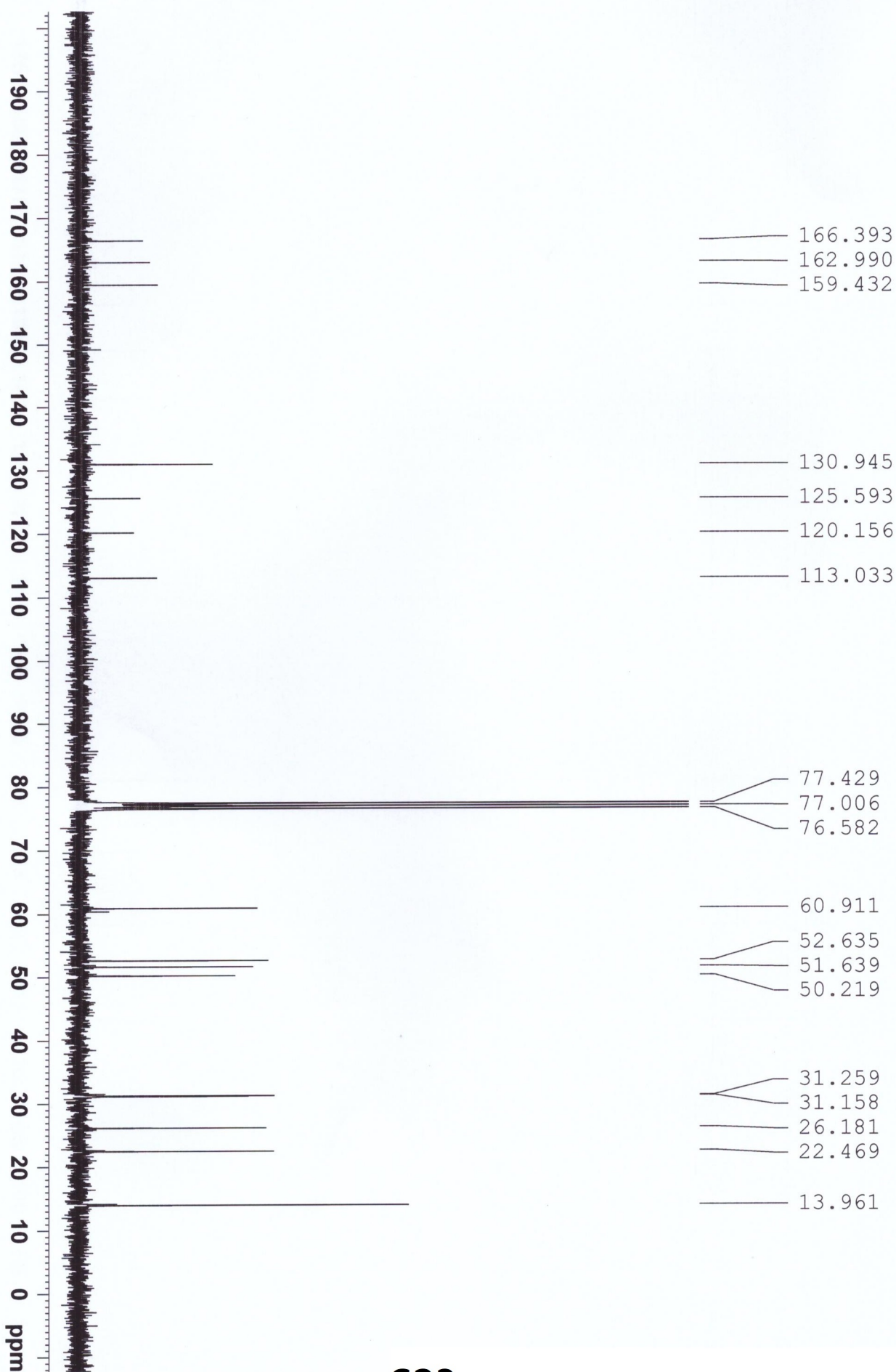
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 16 2015

Temp. 25.0 C / 298.1 K
Operator: ymmr1

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.865 sec
Width 37878.8 Hz
1540 repetitions
BSERVE C13, 150.8338910 MHz
ECOUPLE H1, 599.8589194 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 5 hr, 10 min

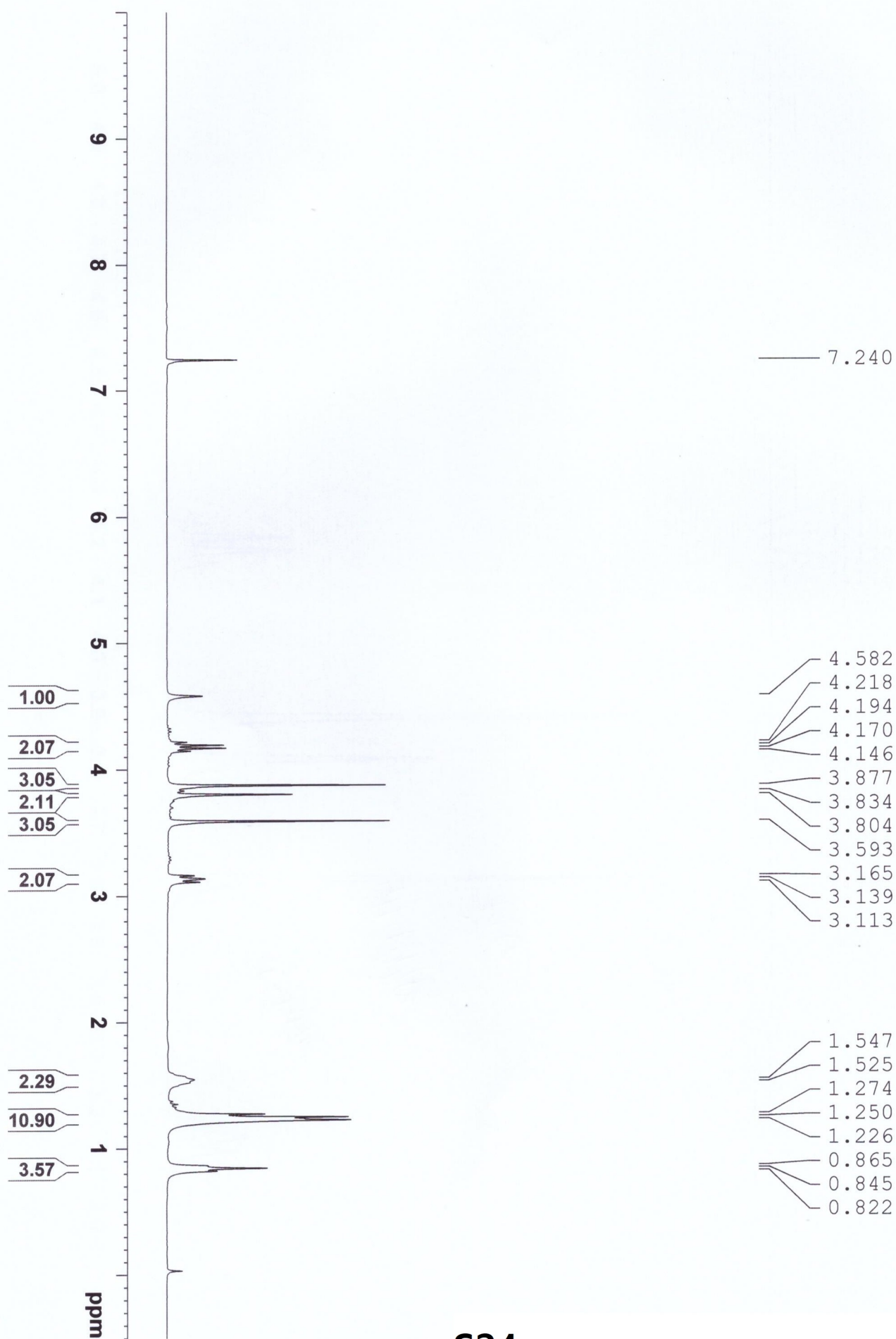




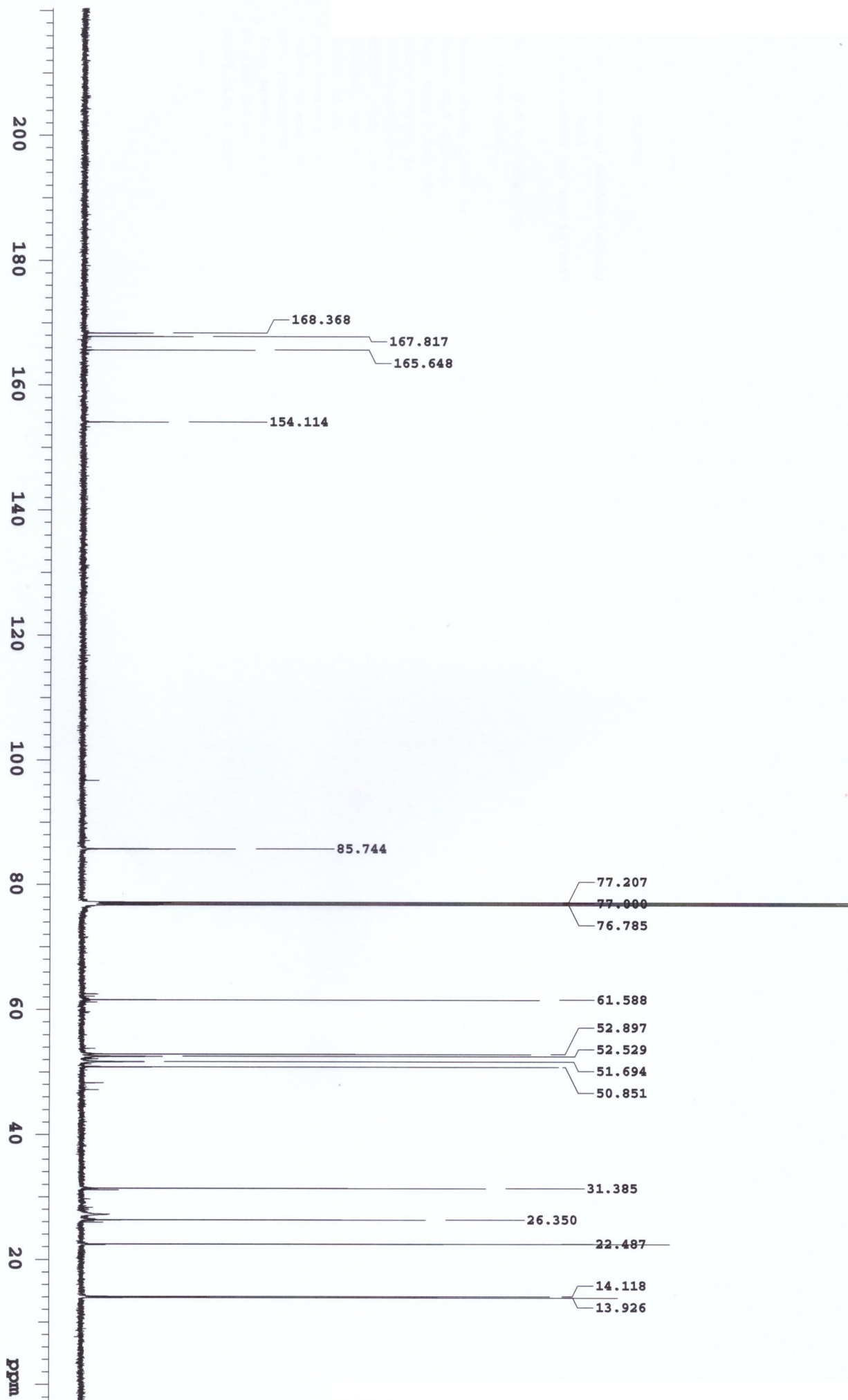


14a

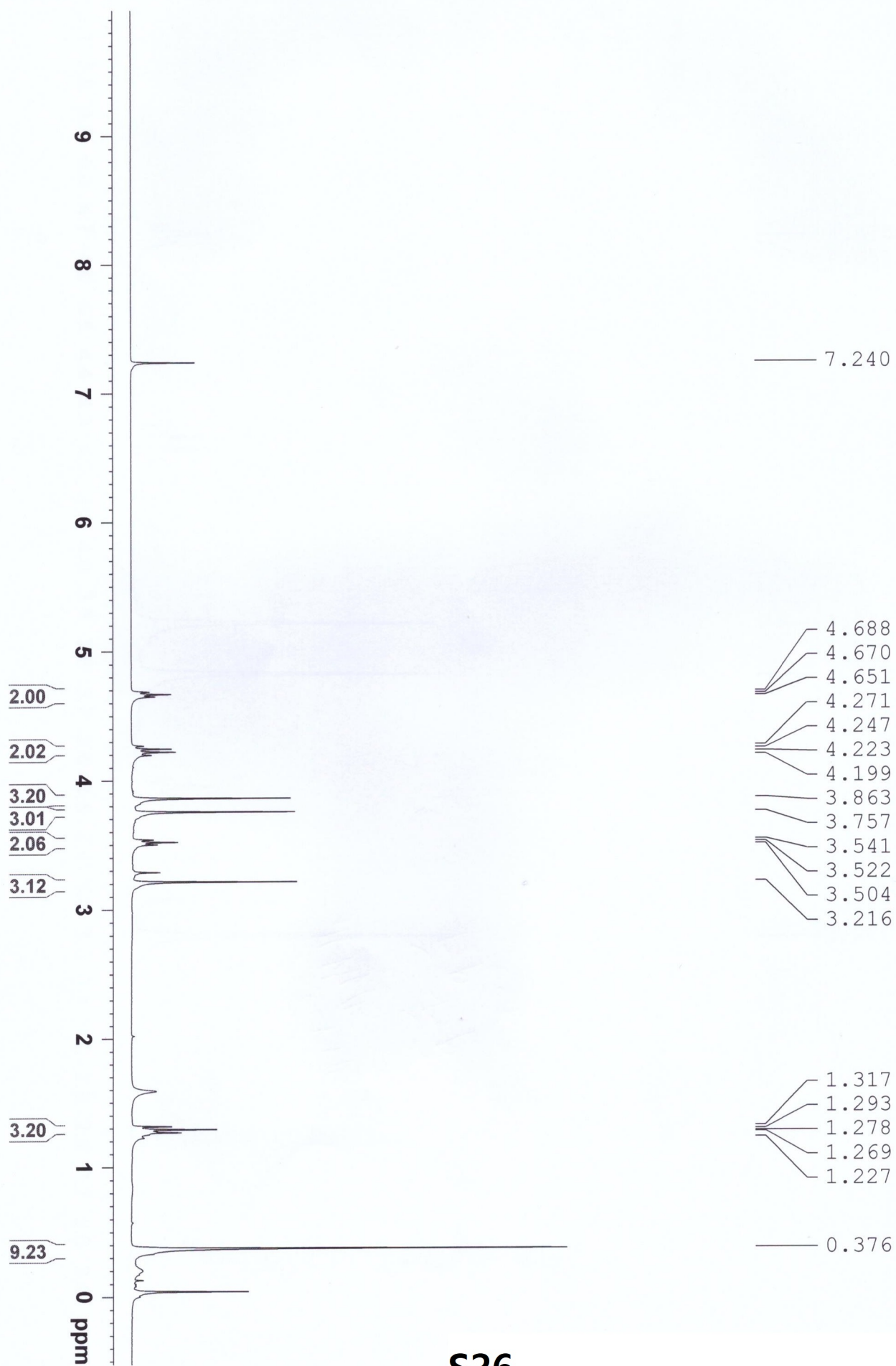
2015-12-07-04



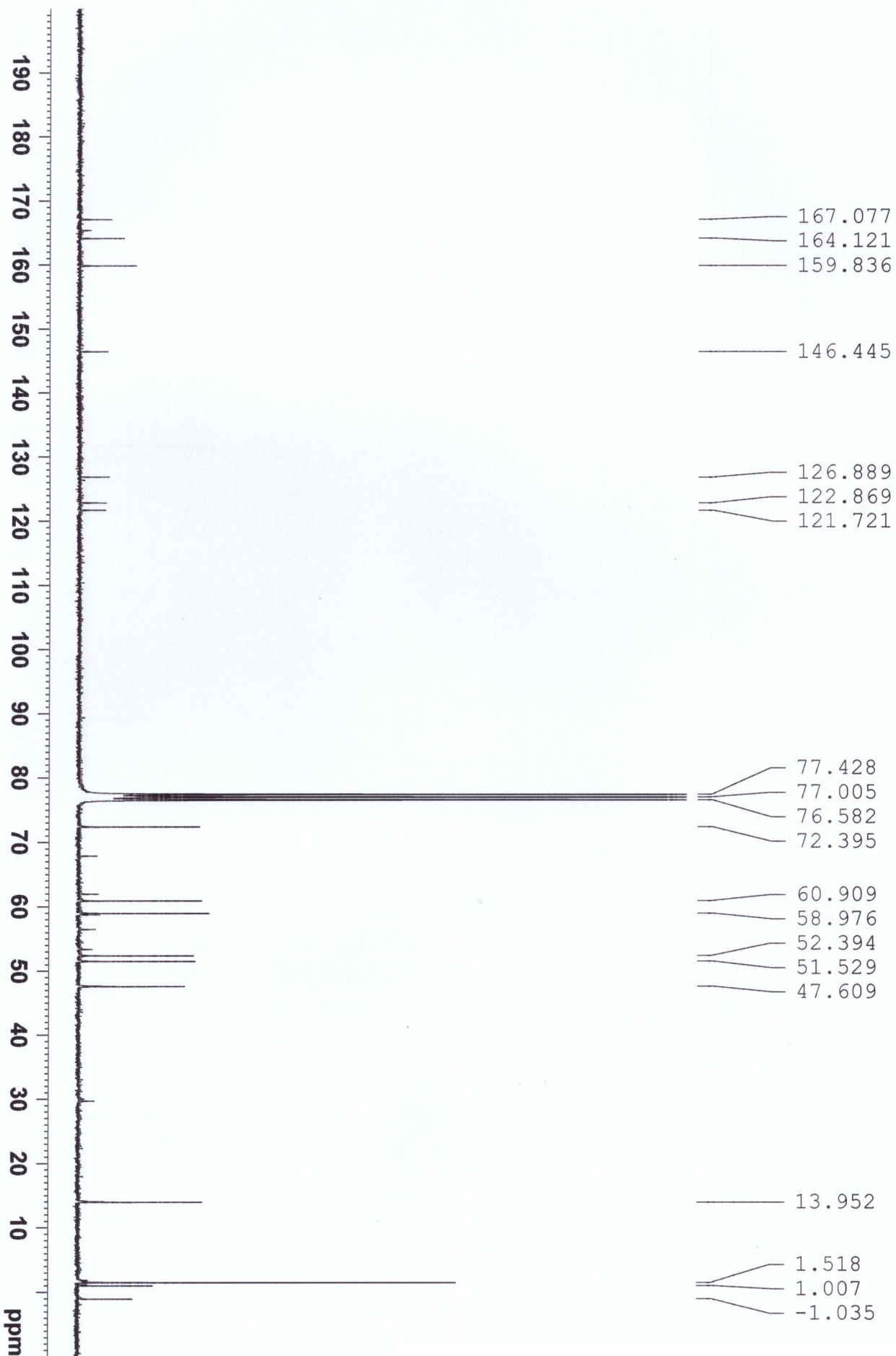
14a

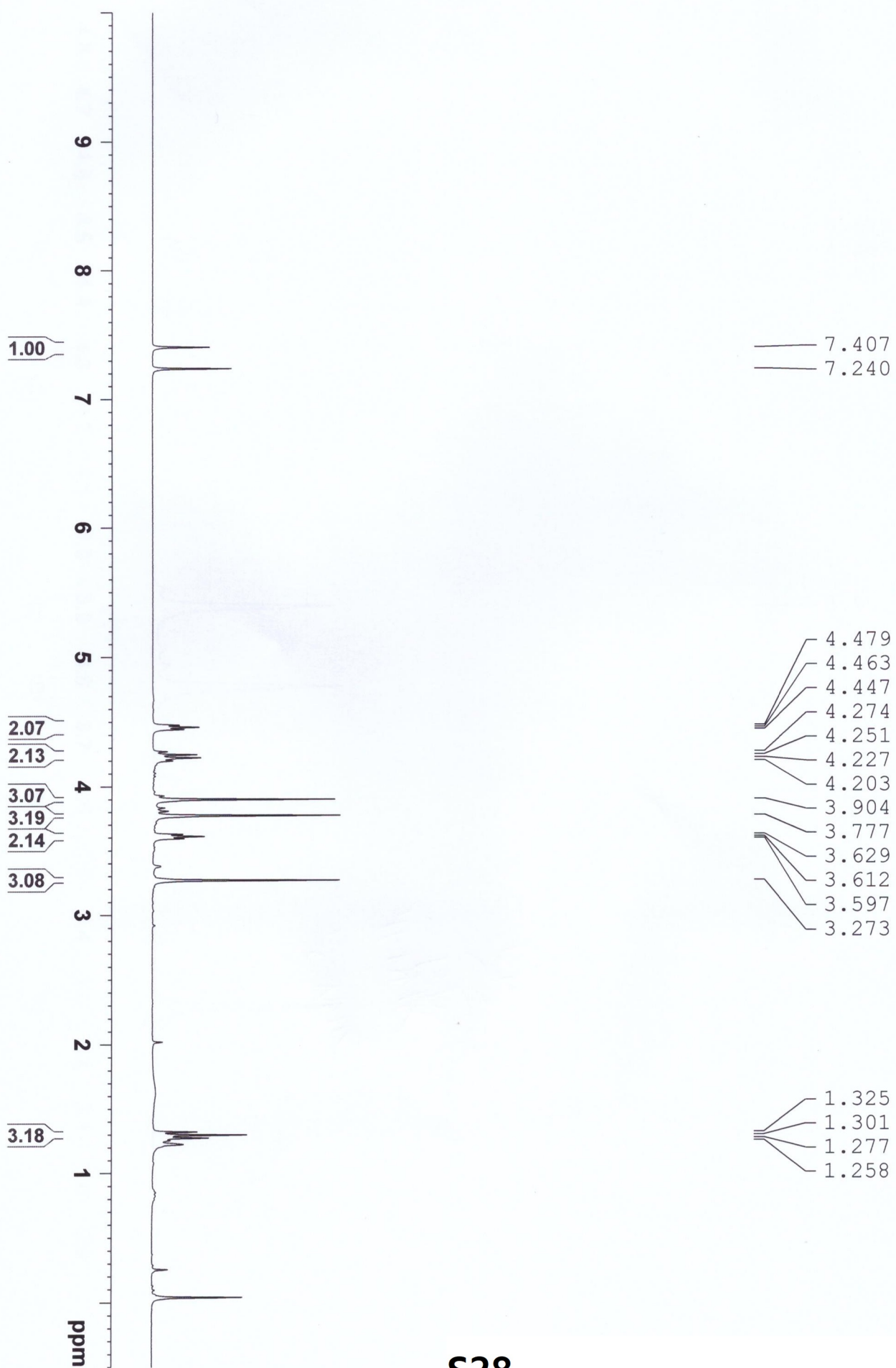


S25

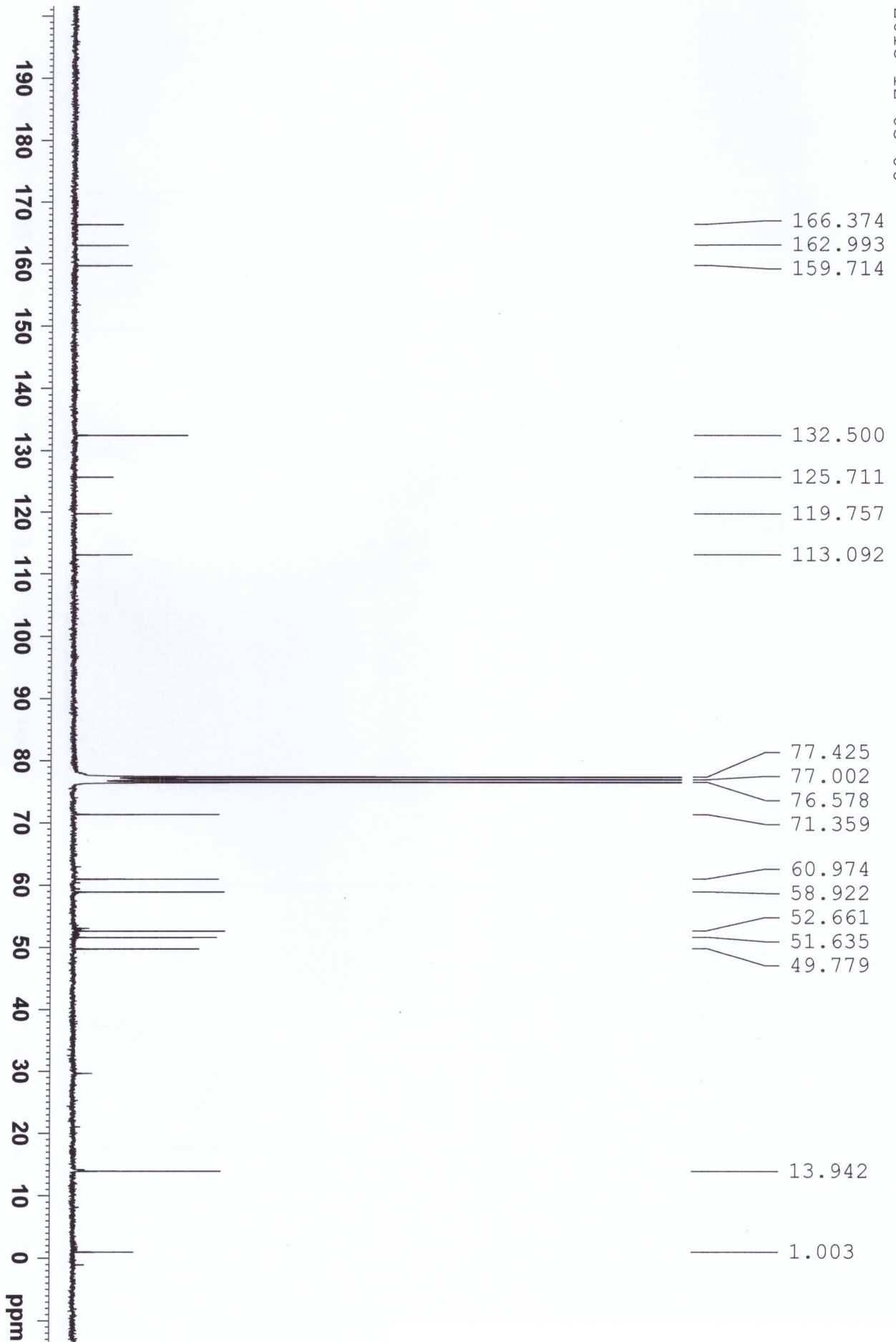


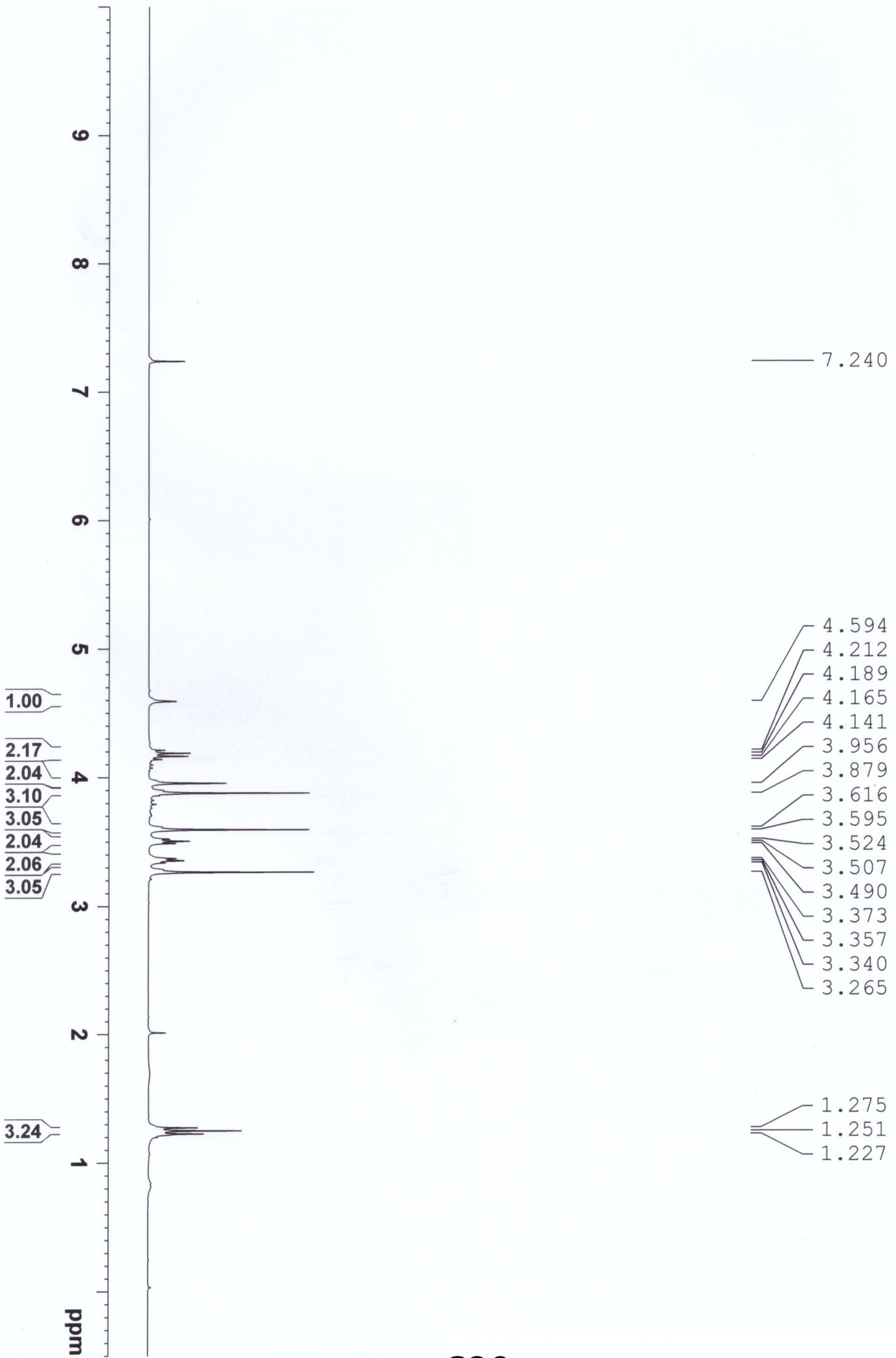
2016-02-02-02

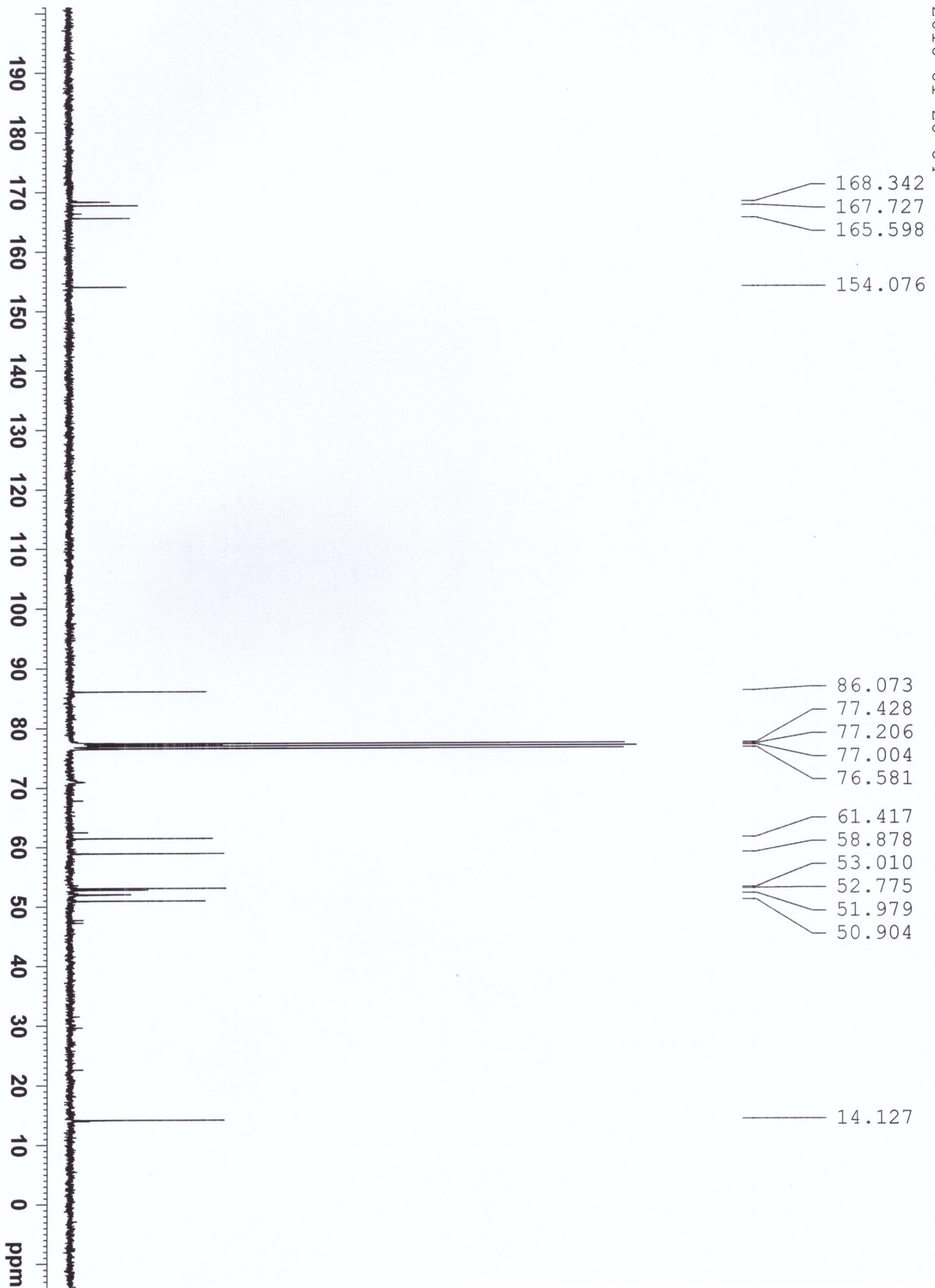


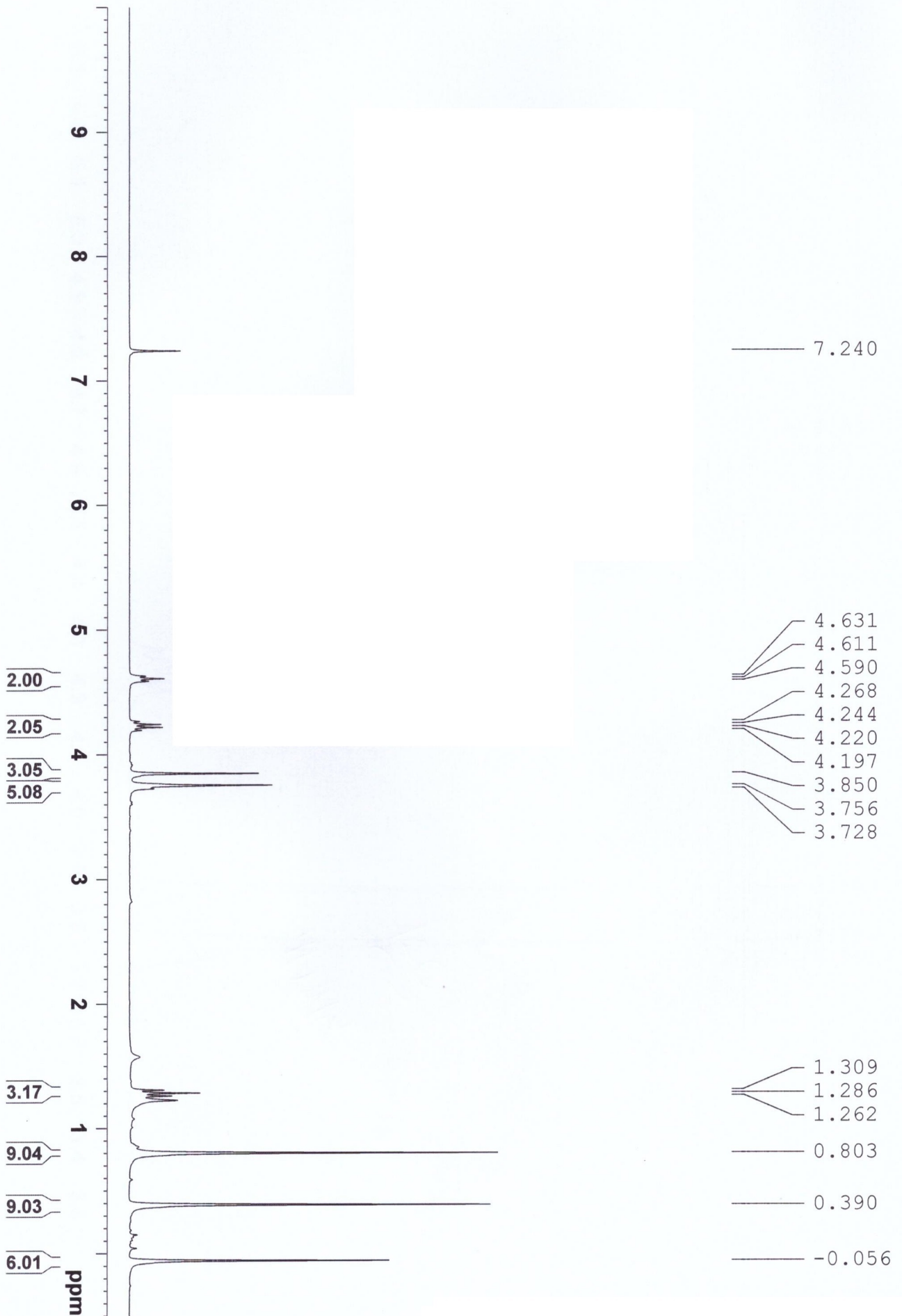


2015-12-03-06

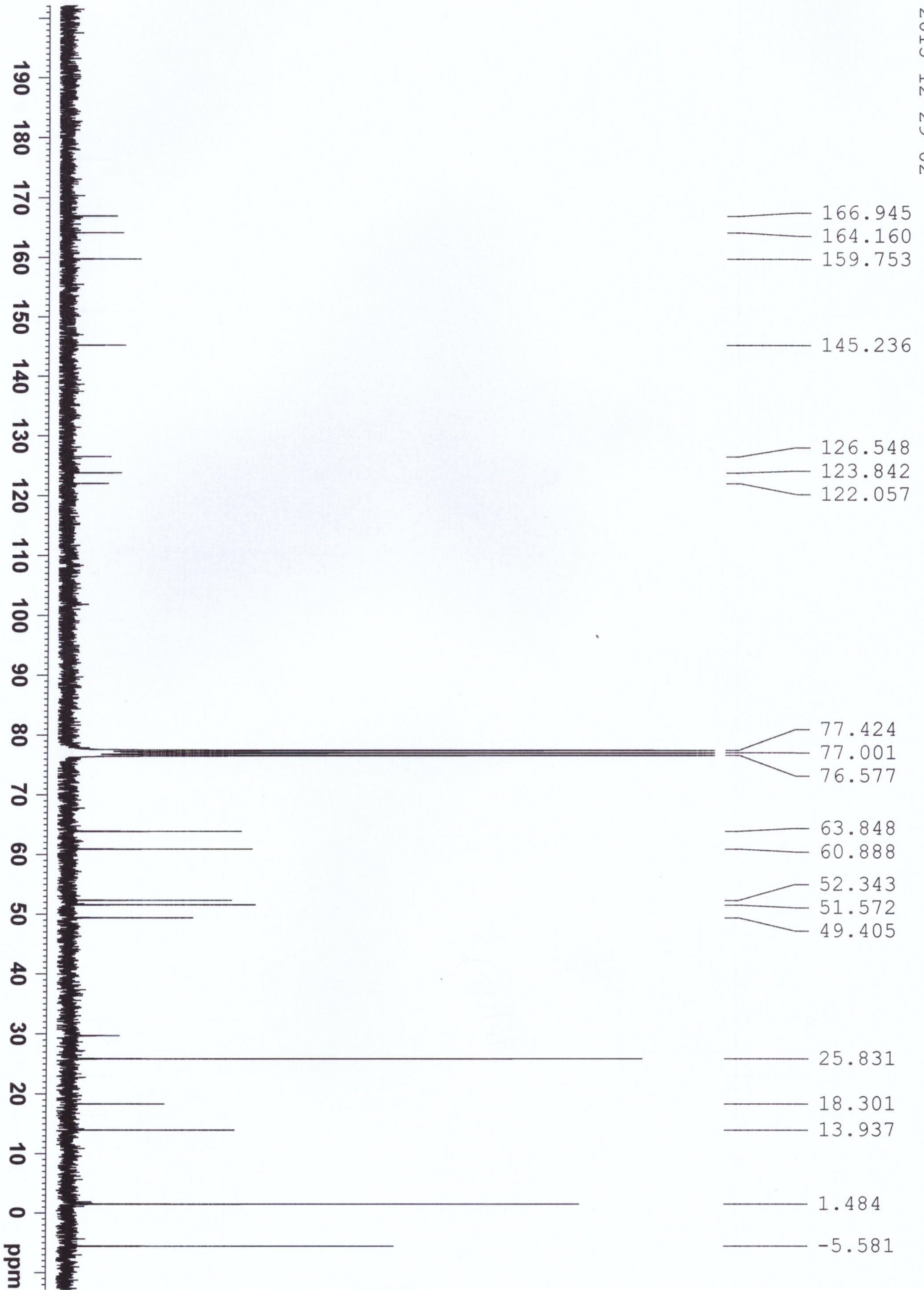






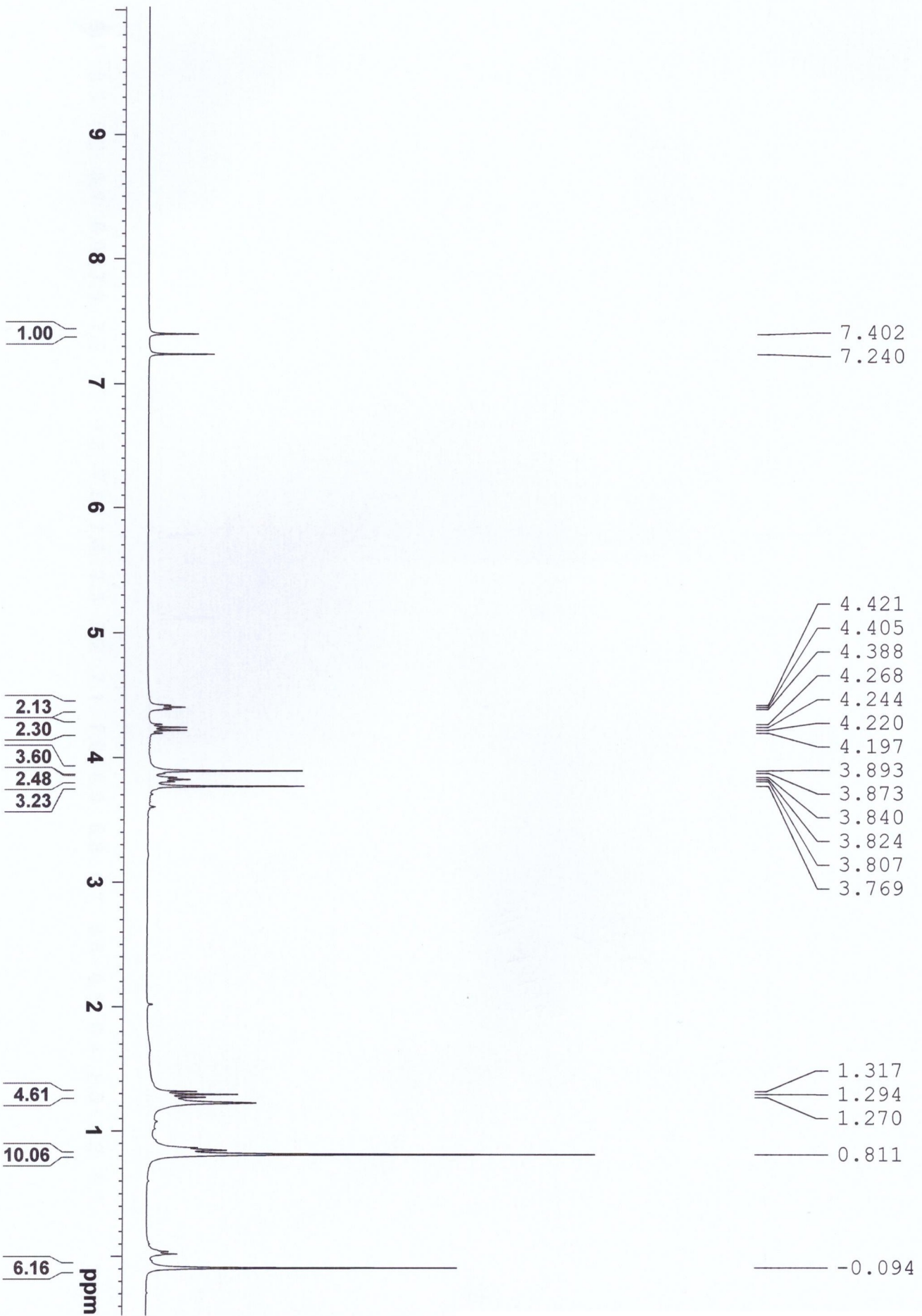


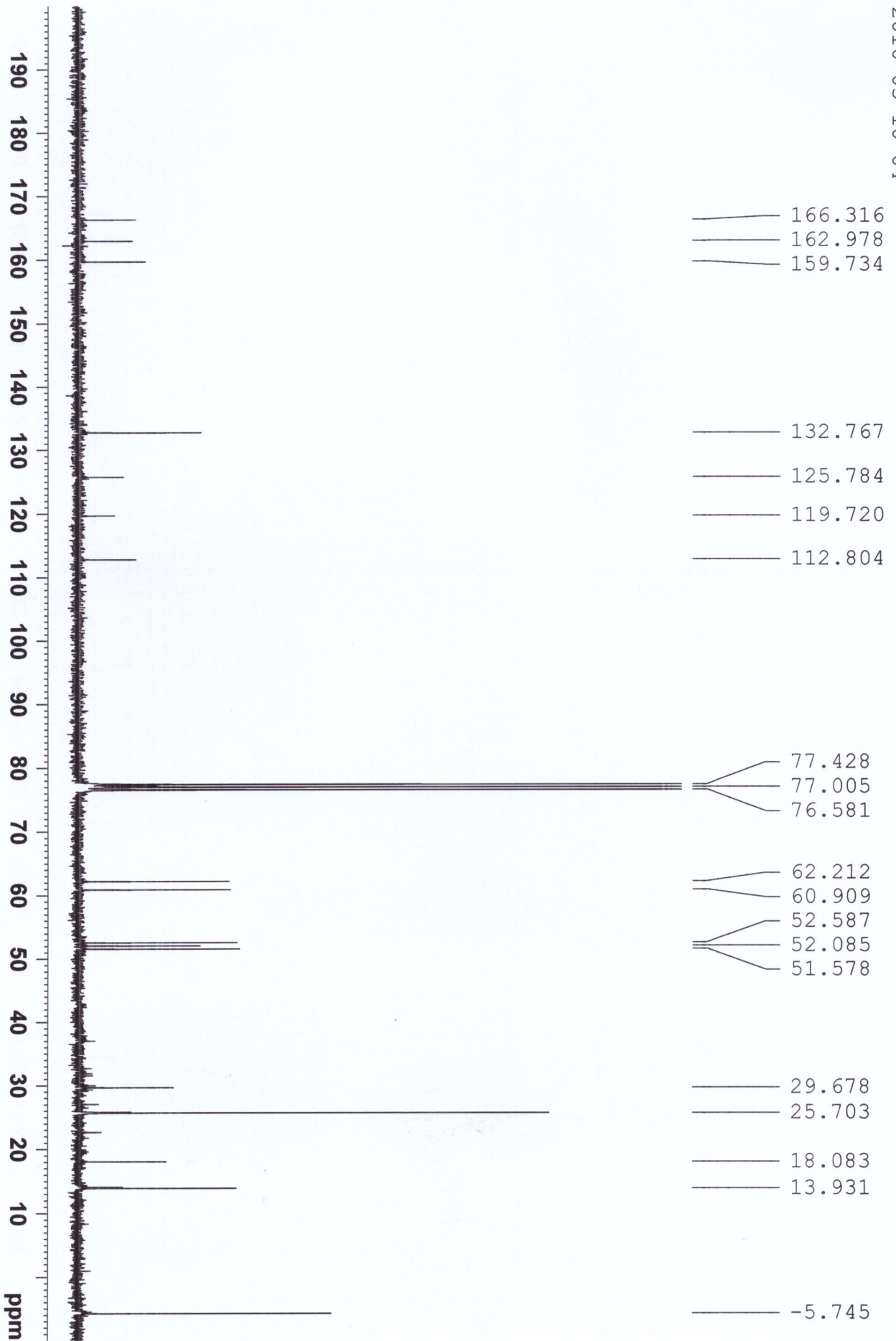
2015-12-29-02

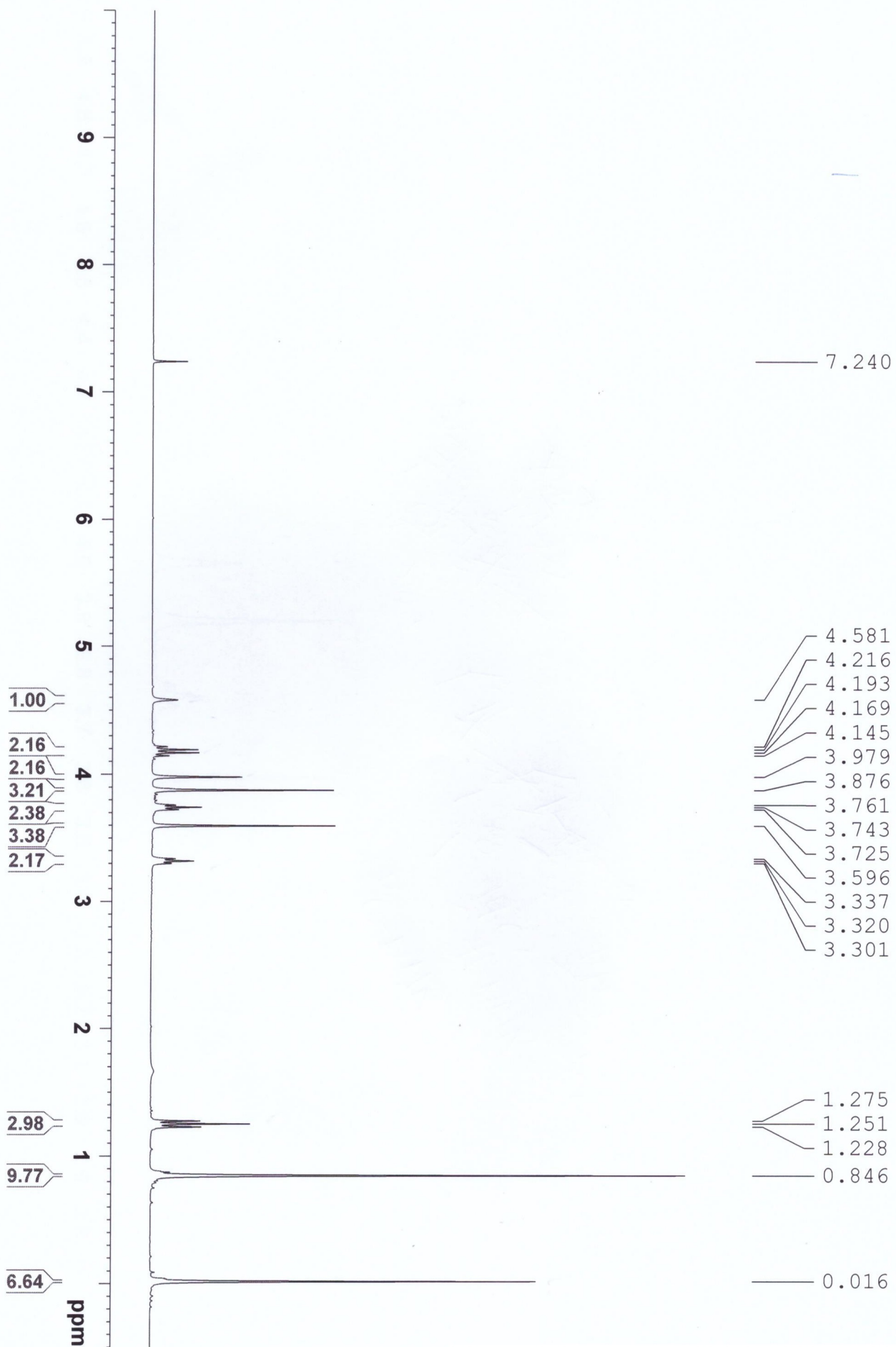


13c

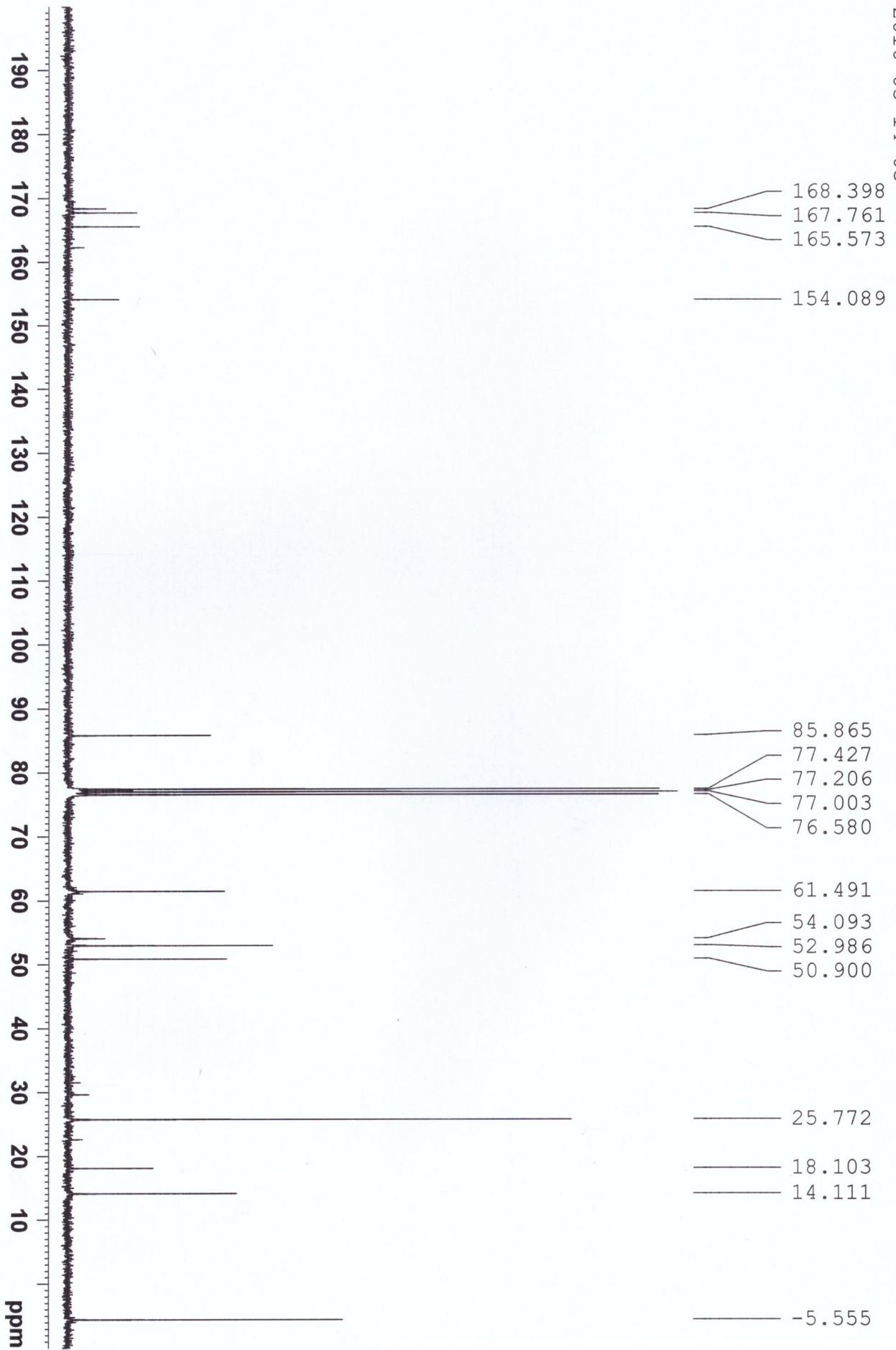
2016-03-08-02

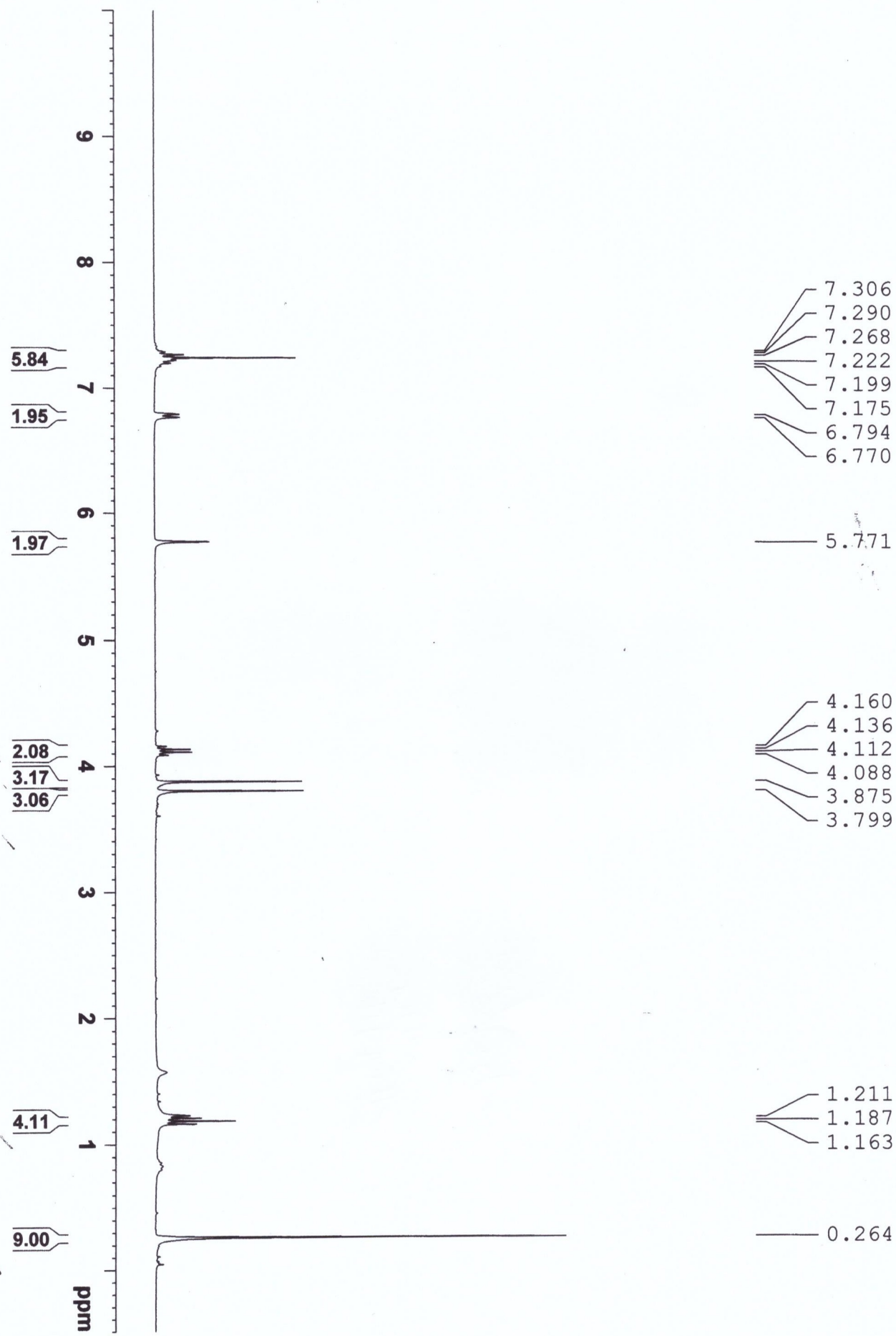




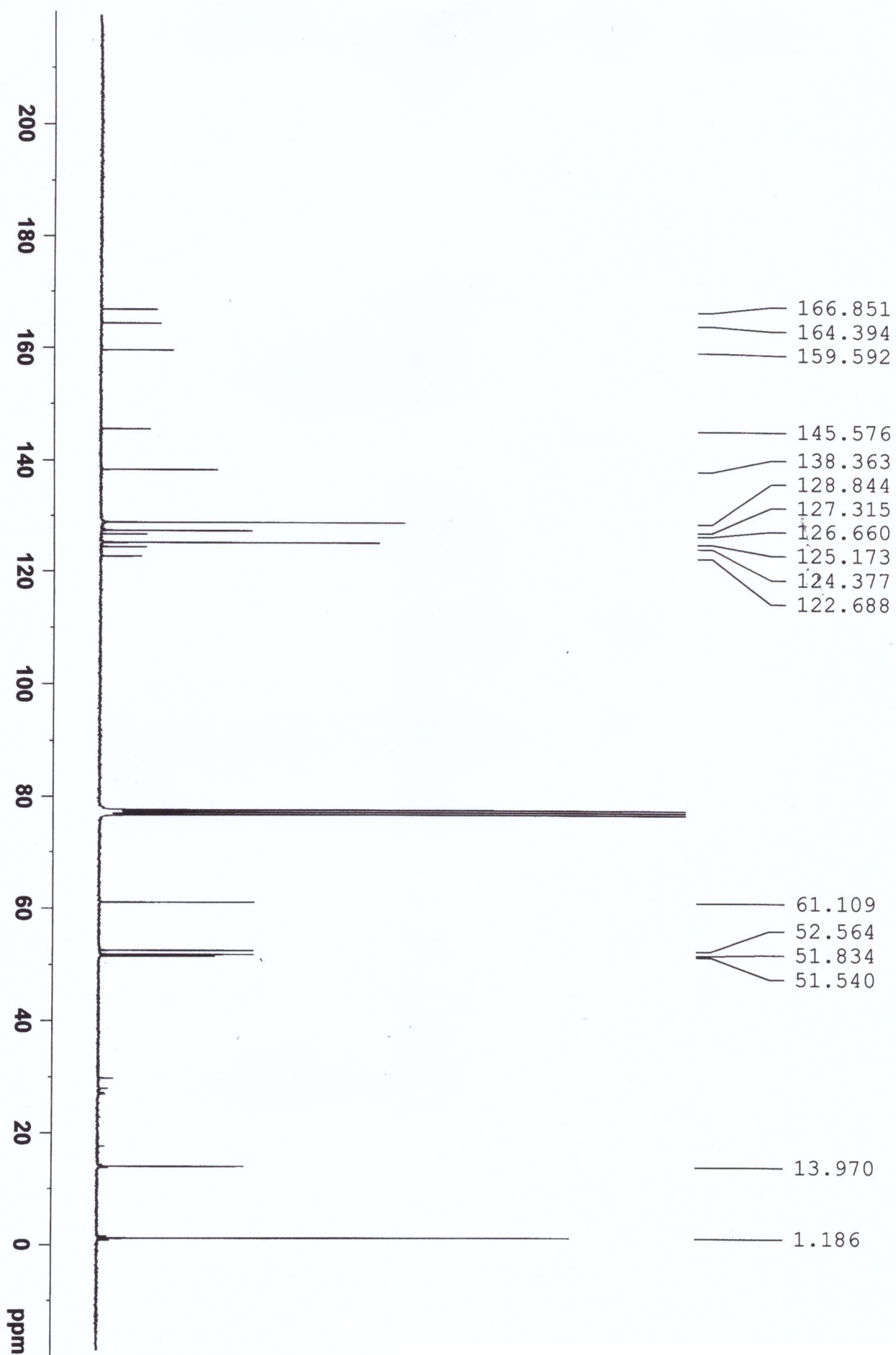


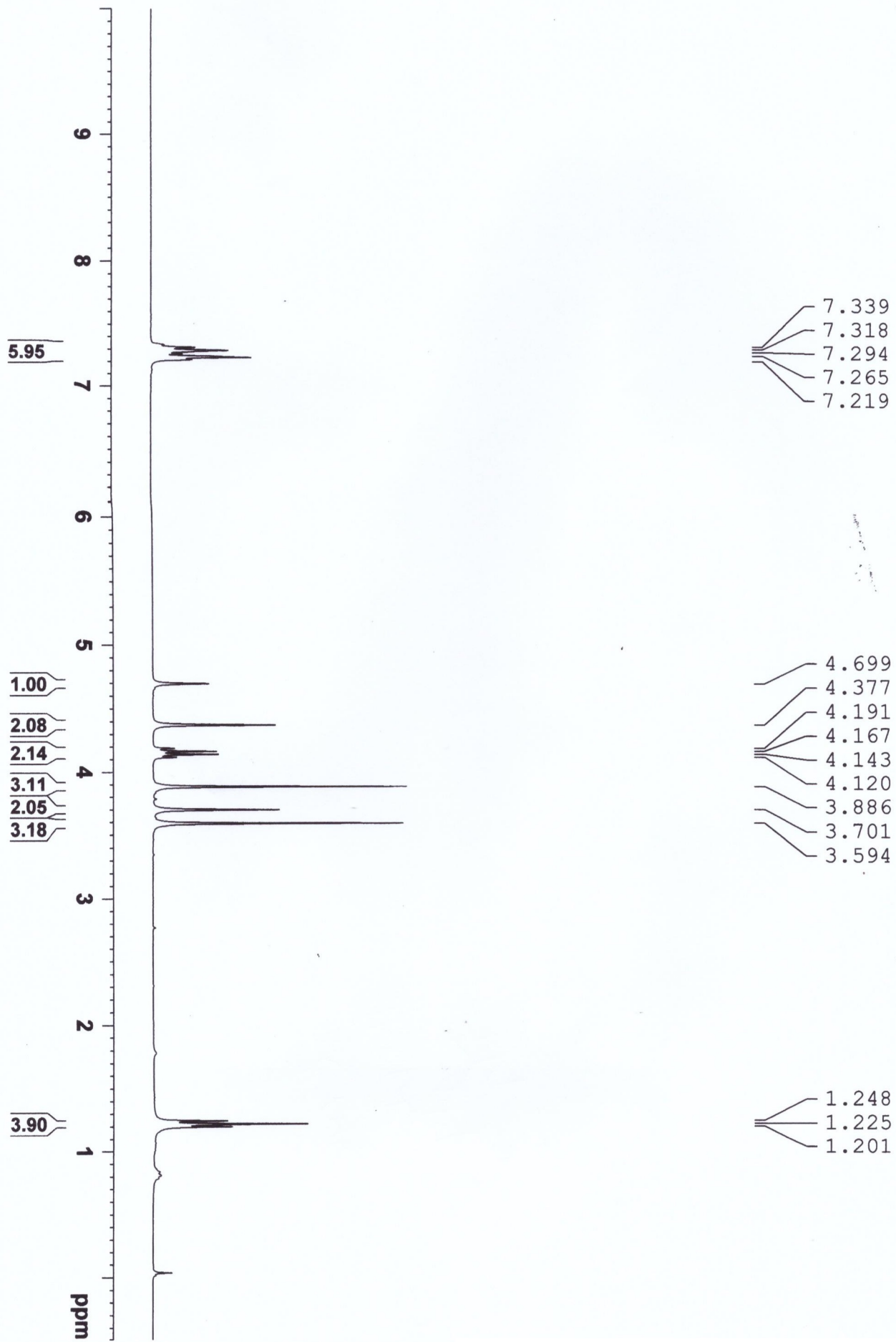
2016-03-14-03



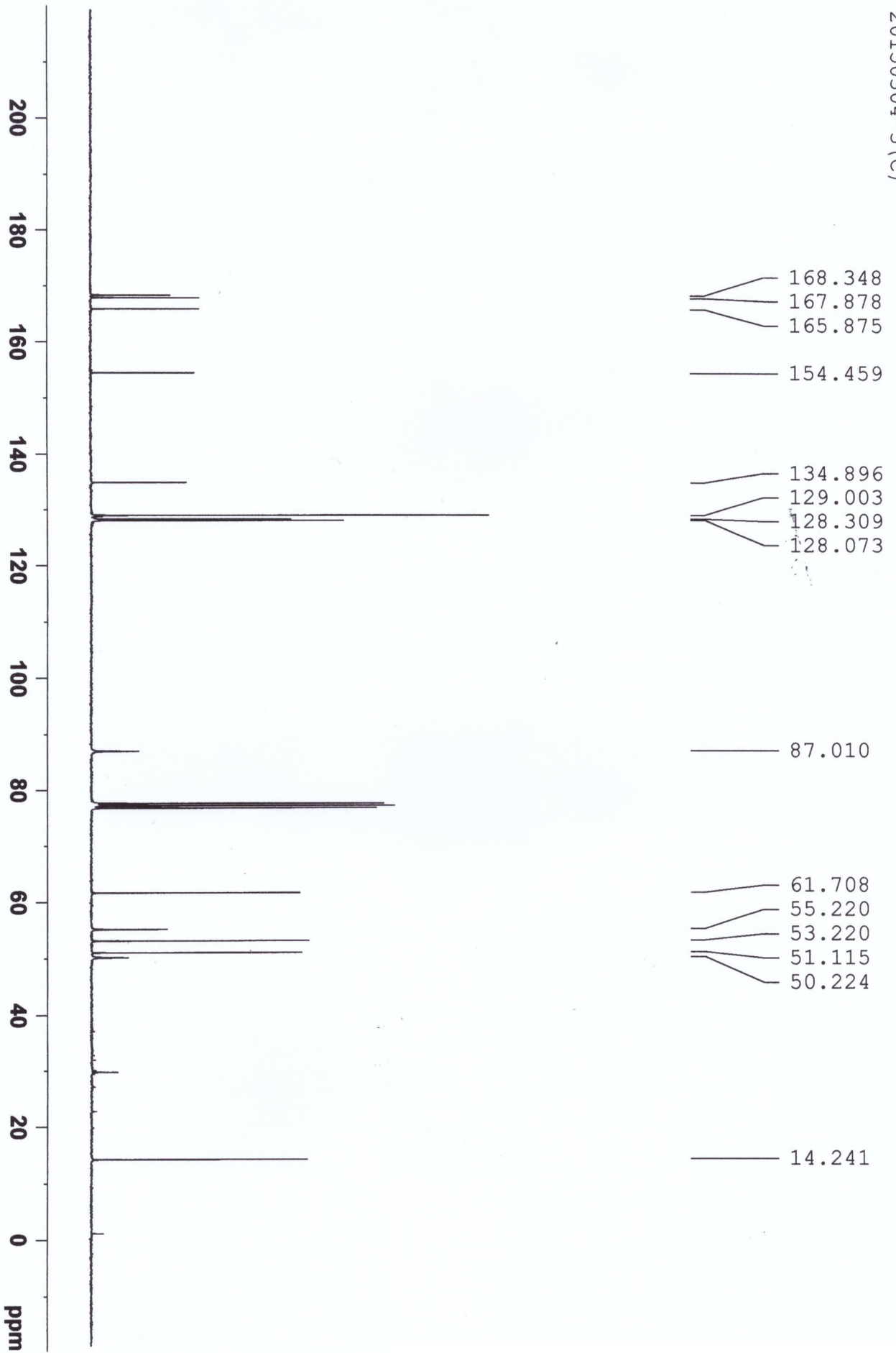


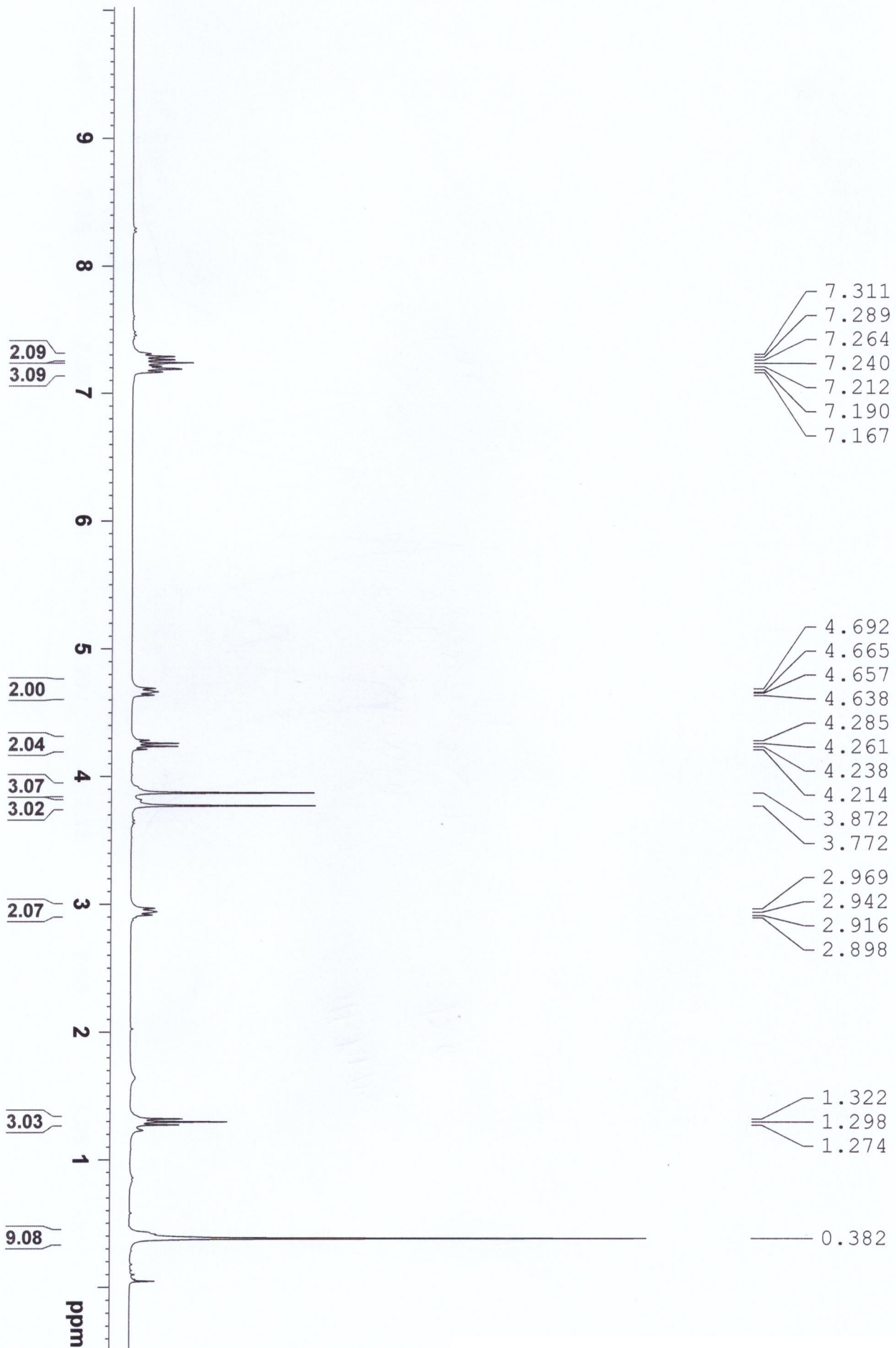
20150224-1 (C)



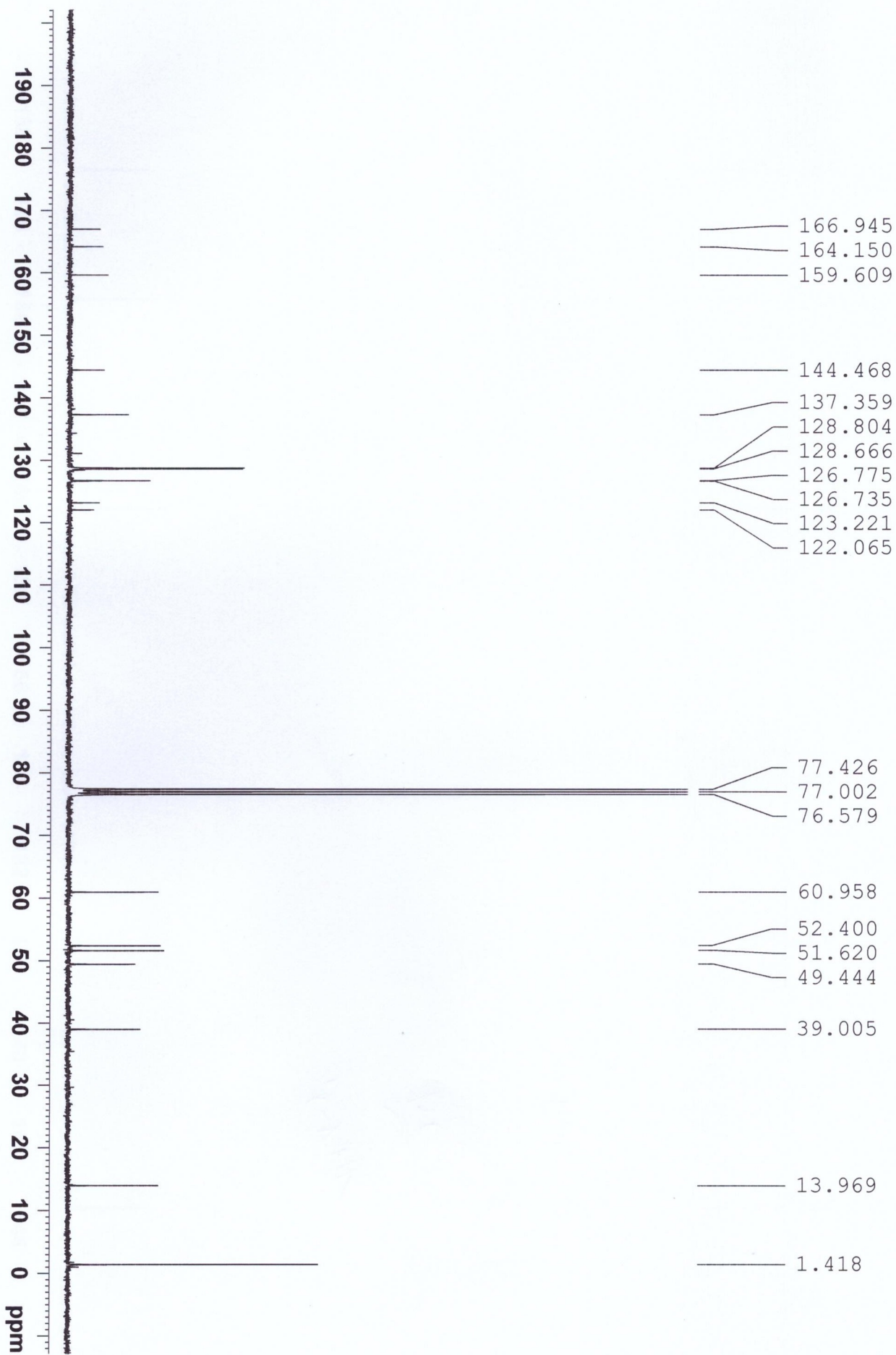


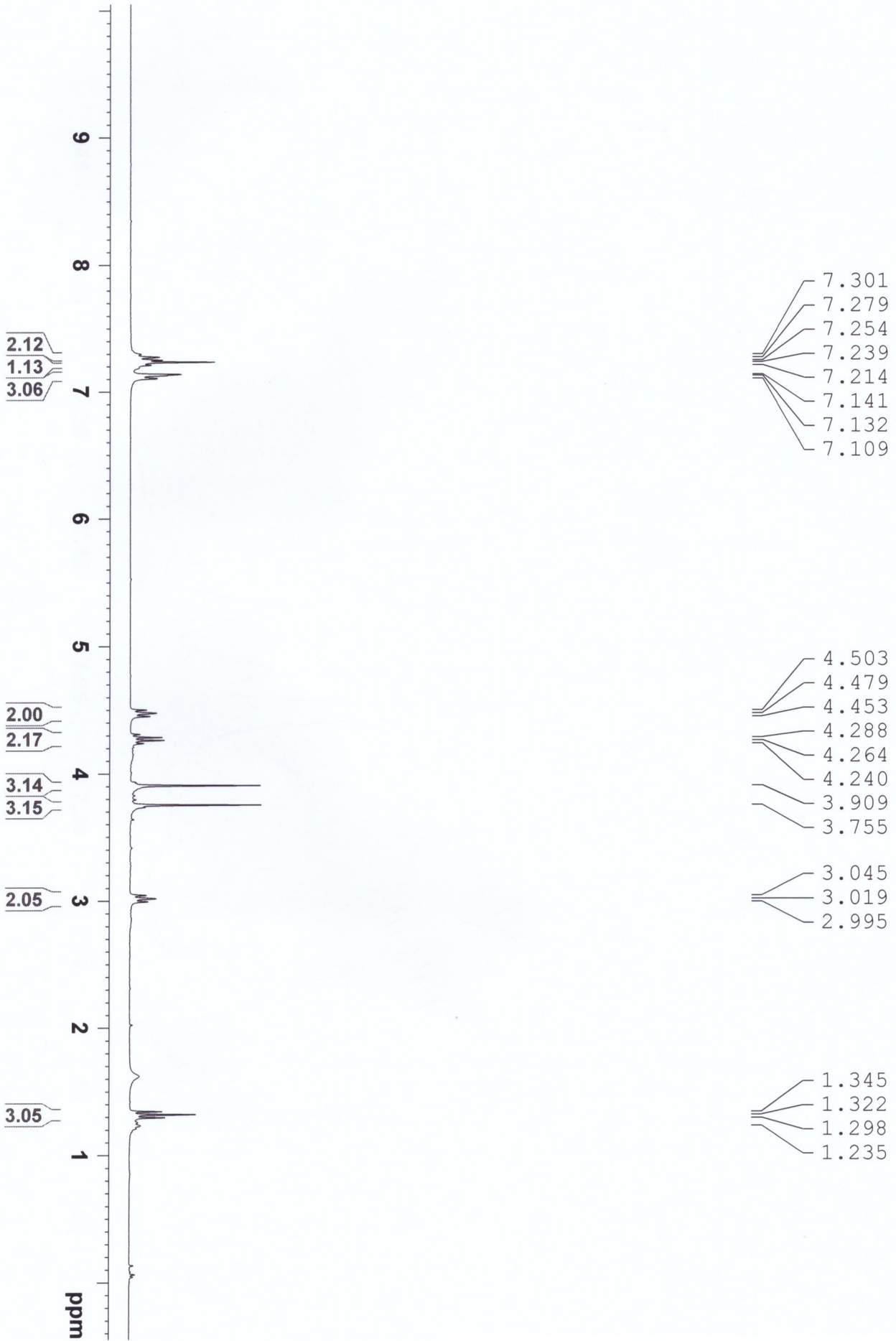
20150304-3 (C)



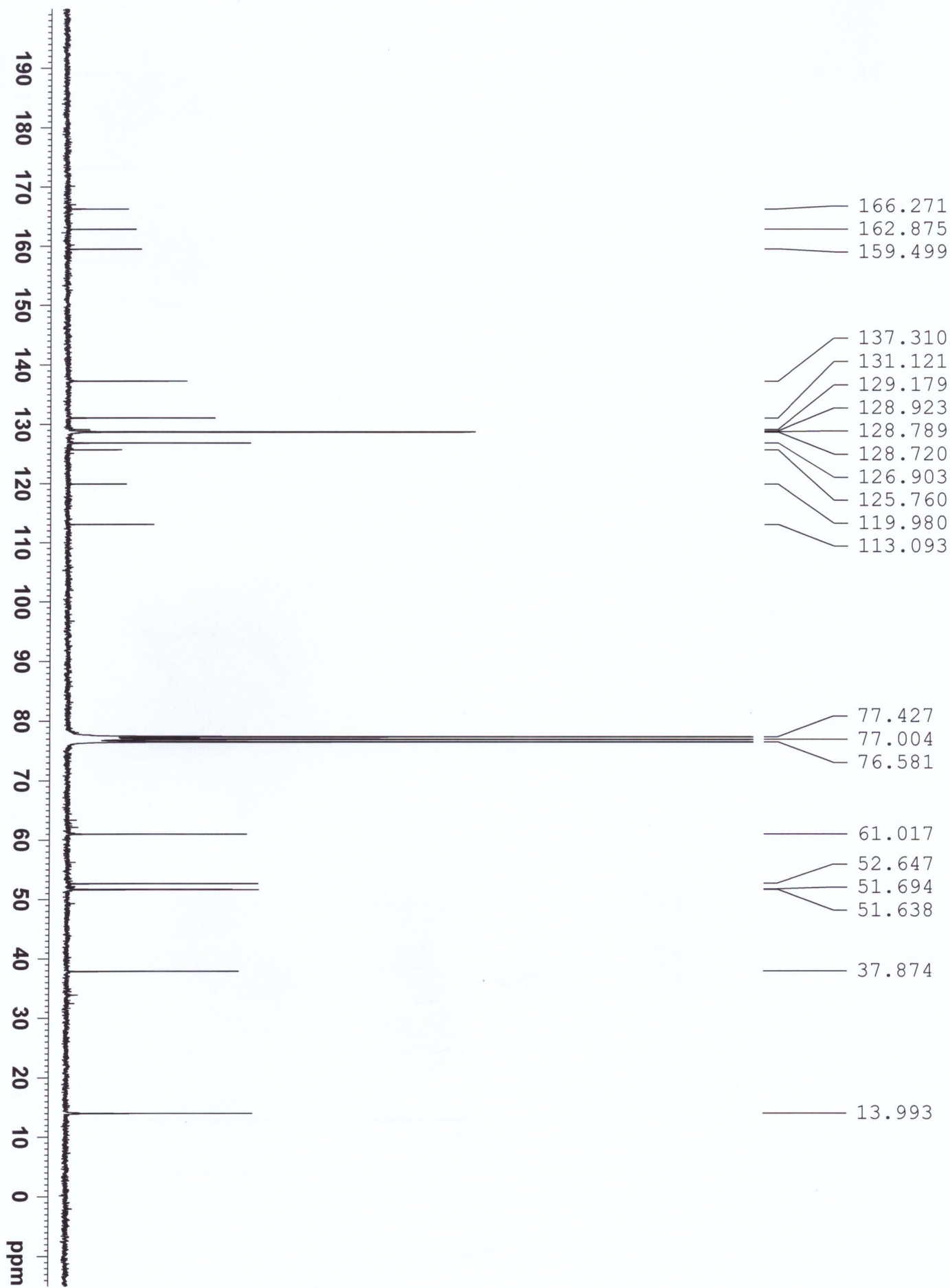


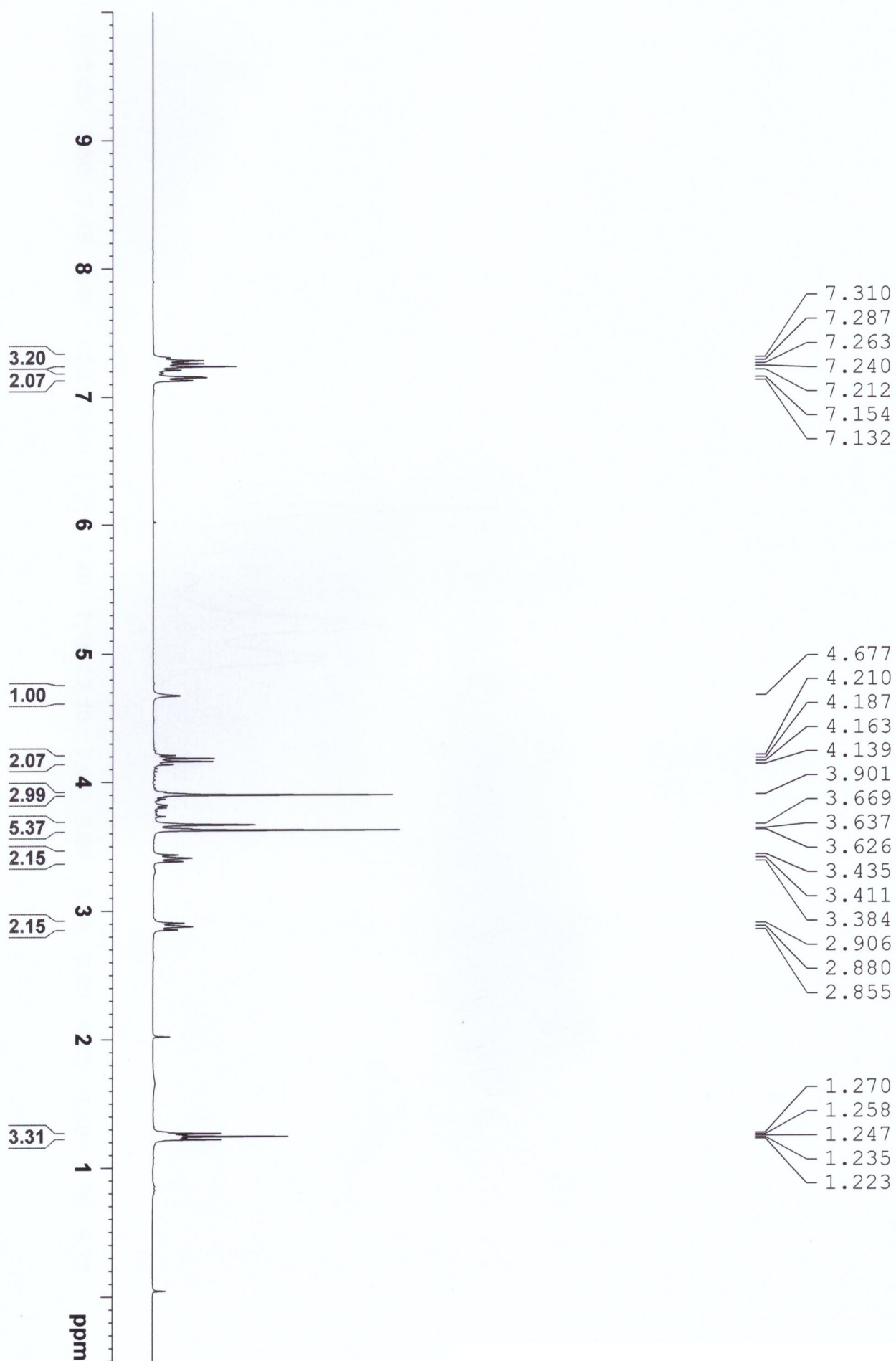
2015-12-16-02

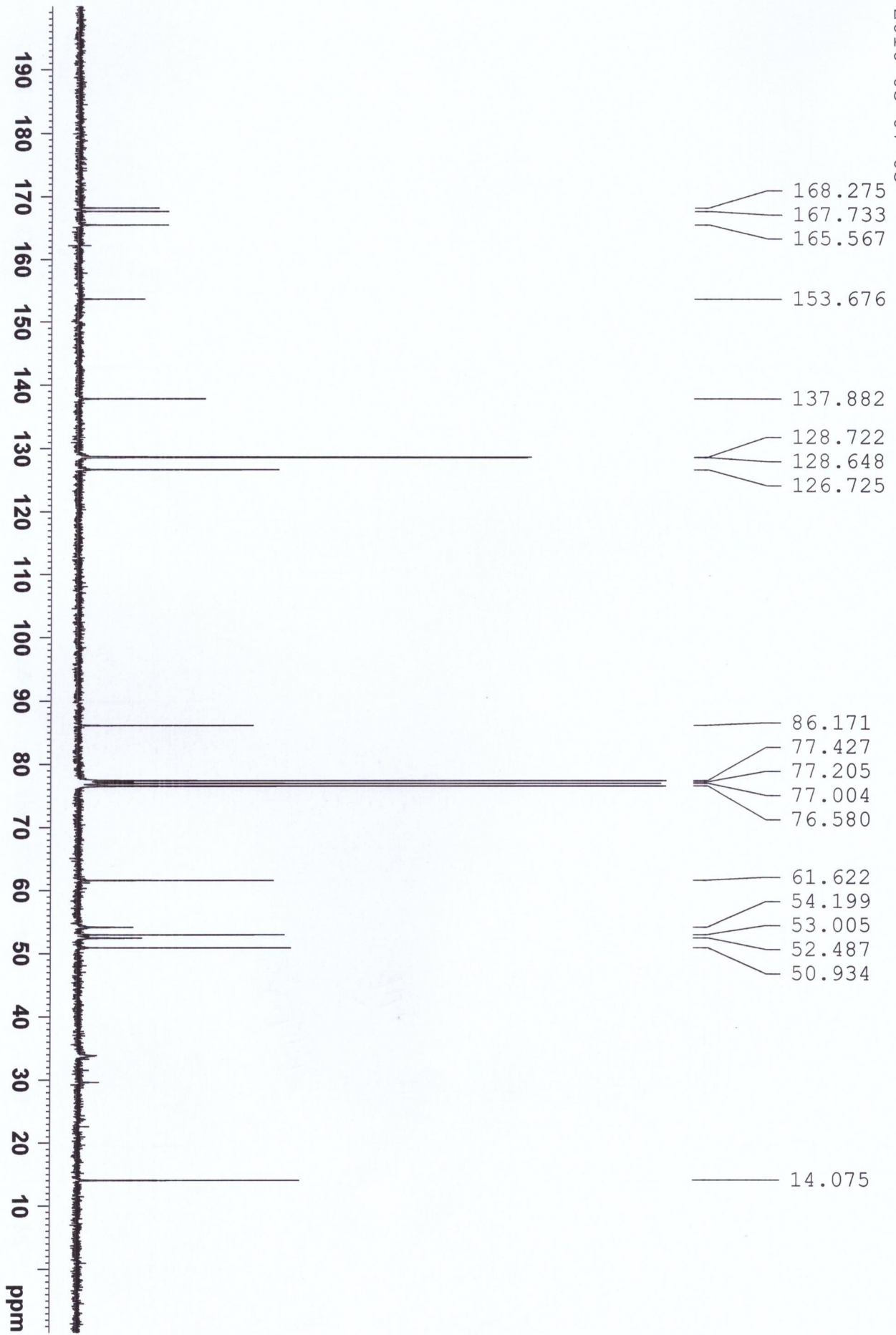


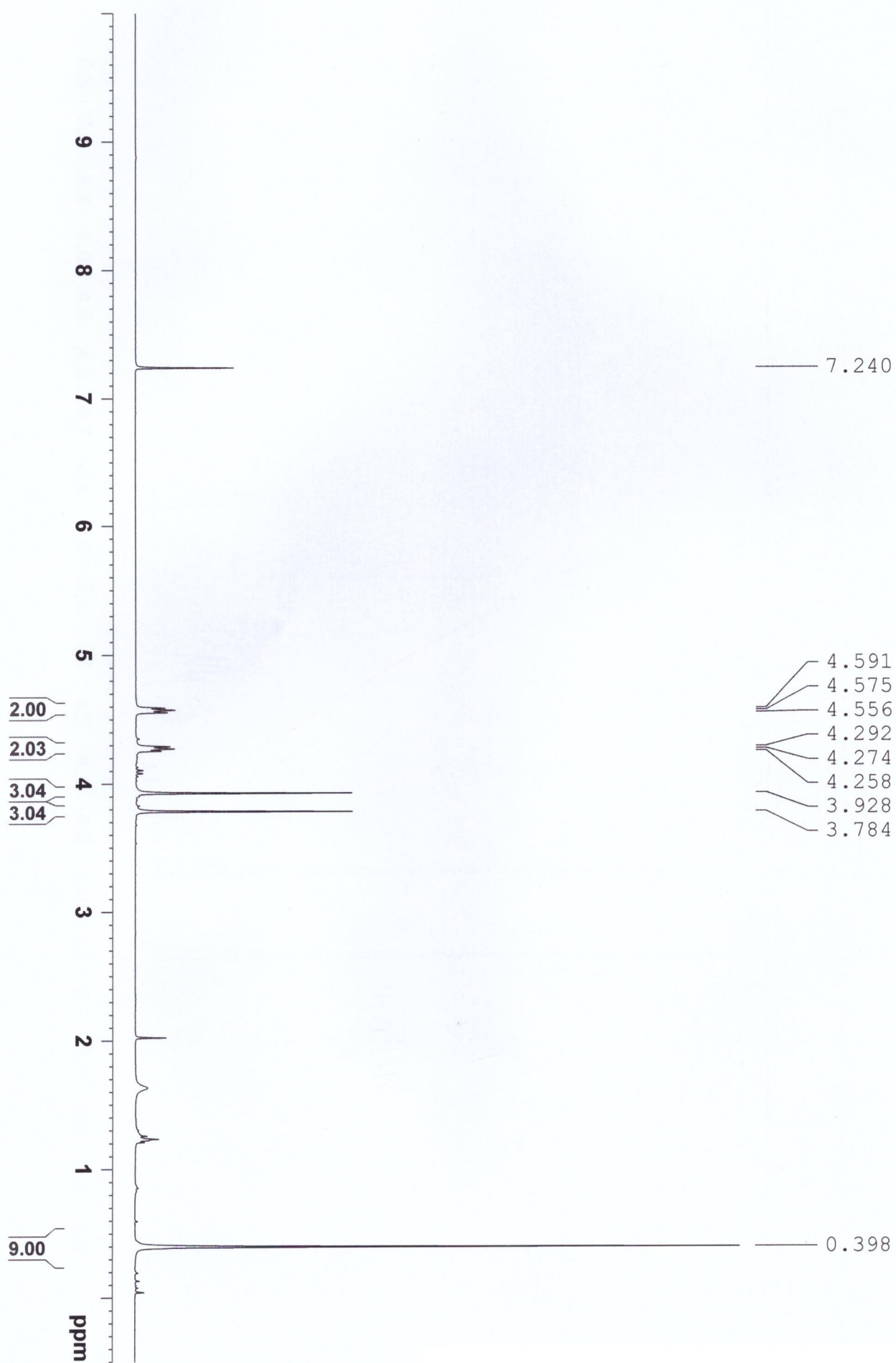


2015-11-19-01

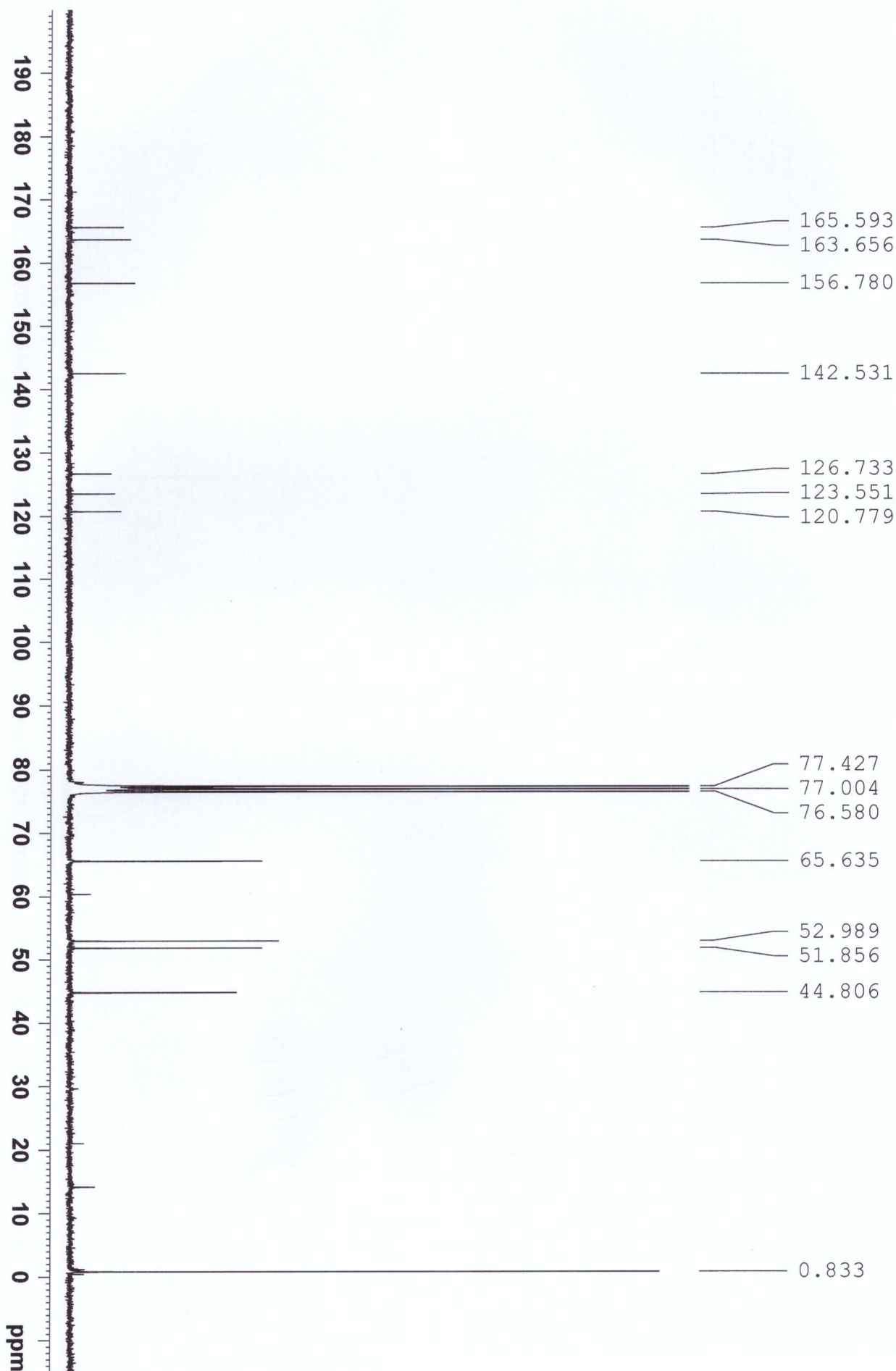


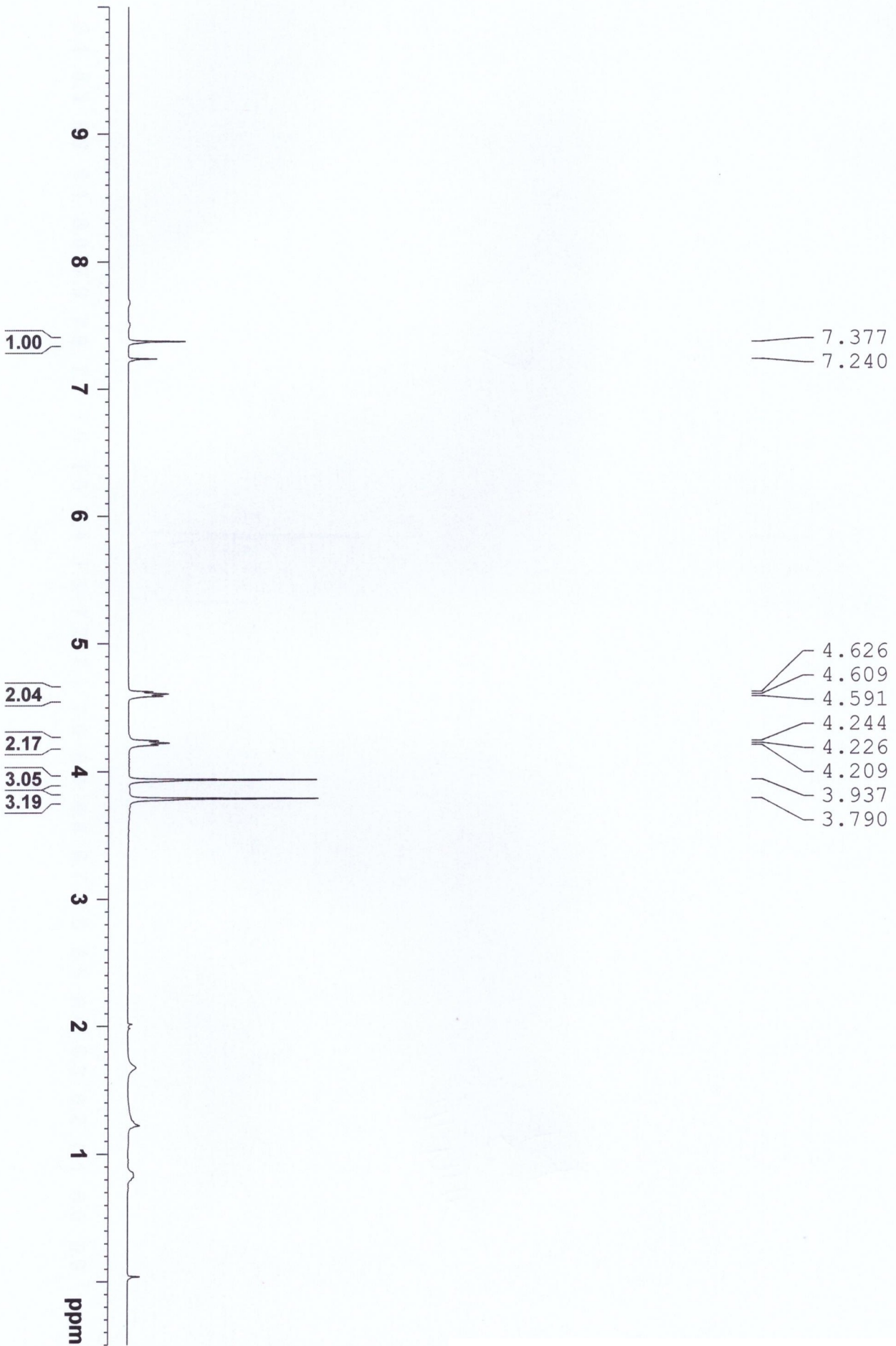






2015-12-08-05





2015-10-12-01

