Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Organocatalysts Wraped Around by Polyethylene Glycols (PEGs): A Unique Host-Guest System for Asymmetric Michael Addition Reactions

Dan Qian Xu, Shu Ping Luo, Yi Feng Wang, Ai Bao Xia,

Hua Dong Yue, Li Ping Wang, Zhen Yuan Xu*

State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology, Hangzhou 310014, china

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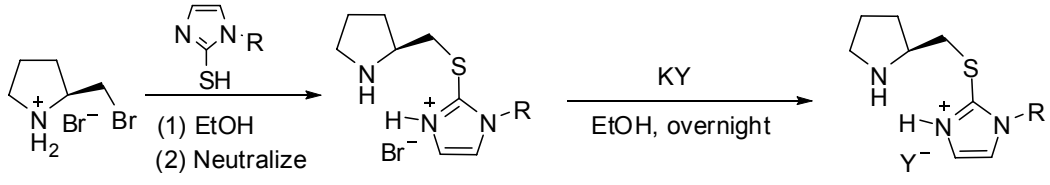
1. General Remarks

All starting chemicals were commercial products (Aldrich or J&K Chemica) with analytical grade. Organic solvents were dried and purified before use by usual methods.[1] (*S*)-2-Bromomethyl-pyrrolidine hydrobromide was synthesized according to literatures.[2] ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian NMR. Chemical shifts of ^{1}H and ^{13}C were given in δ relative to tetramethylsilane (TMS). Coupling constants *J* were given in Hz. IR spectra were obtained on a Bruker EQUINOX 55. Electrospray ionization (ESI) mass experiments were performed on a Finnigan LCQ Advantage. ESI-HRMS spectra were obtained on a Bruker APEX III FTICR mass spectrometer. GC-MS experiments were performed on an Angilent 6890N GC system with a 5973N mass selective detector. HPLC experiments were carried out using a JASCO LC-2000 Plus system consisting of MD and CD detectors.

2. General Procedure for the Preparation of Pyrrolidinyl-Thioimidazolium Salts 1-3



1-3 **1b-1i**

1or**1a**: R=CH_3
2: R=Ph
3: R=CH_2Ph

1b: R=Me, Y=BF_4
1c: R=Me, Y=PF_6
1d: R=Me, Y=CF_3COO
1e: R=Me, Y= $(CF_3SO_2)_2N$
1f: R=Me, Y=4-$MeC_6H_4SO_3$
1g: R=Me, Y=2-$C_{10}H_7SO_3$
1h: R=Me, Y=PhCOO
1i: R=Me, Y=$PhCH_2COO$

A mixture of 1-alkyl-2-mercaptoimidazole (10 mmol) and (*S*)-(+)-2-bromomethyl-pyrrolidine hydrobromide (10 mmol) in EtOH (30 mL) was heated with stirring at 80 °C for 8h. After completion, the solvent was removed by distillation and, the residue was recrystallized in EtOH and neutralized by NaOH (10 mmol) to afford the chiral pyrrolidinyl-thioimidazolium salts **1-3**.

The mixture of the chiral pyrrolidinyl-thioimidazolium salt **1** (or **1a**) (5 mmol), potassium salts of the corresponding acids (5 mmol), and EtOH (20 mL) was stirred for 24 h at room temperature. Then, the formed inorganic salt KBr was filtered off, the remained solution was evaporated under vacuum to afford the desired chiral pyrrolidinyl-thioimidazolium salts **1b-1i**.

3-Methyl-2-[(2*S*)-(pyrrolidinyl) methylthio]-3*H*-imidazol-1-ium bromide (**1** or **1a**)

^{1}H NMR (DMSO-d_6, δ ppm) : 1.68-1.77 (m, 1H), 1.83-1.98 (m, 2H), 2.07-2.16 (m, 1H), 3.19-3.22 (m, 2H), 3.35-3.42 (m, 2H), 3.61 (s, 3H), 3.81-3.84 (m, 1H), 7.01 (d, *J*= 1.6 Hz, 1H), 7.33 (d, *J*= 1.6 Hz, 1H), 9.36 (dr, 2H).

^{13}C NMR (DMSO-d_6, δ ppm): 23.363, 29.217, 33.153, 34.427, 44.581, 59.080, 123.635, 127.919, 139.718.

IR (film, cm^{-1}): 3418 [ν(N-H)], 3107 [ν(C-H) aromatic], 2953 and 2748 [ν(C-H) aliphatic], 1631 [ν(C=C)], 1461 [δ(C-H)], 1412 [δ(S-CH_2)].

ESI-MS: *m/z* 198 $[M-Br]^+$, 79 and 81 $[Br]^-$.

HRMS: (ESI+) *m/z* calcd for $[C_9H_{16}N_3S]^+$198.1059, found 198.1056.

3-Methyl-2-[(2*S*)-(pyrrolidinyl) methylthio]-3*H*-imidazol-1-ium tetrafluoroborate) (**1b**)

^{1}H NMR (DMSO-d_6, δ ppm) : 1.67-1.74 (m, 1H), 1.83-2.01 (m, 2H), 2.08-2.15 (m, 1H), 3.19-3.22 (m, 2H), 3.31 (dd, *J*= 8.0, 14.4 Hz, 1H), 3.41 (dd, *J*= 5.6, 14.4 Hz, 1H), 3.67 (s, 3H), 3.72-3.74 (m, 1H), 7.25 (s, 1H), 7.48 (s, 1H), 9.10 (dr, 2H).

^{13}C NMR (DMSO-d_6, δ ppm): 23.712, 29.468, 34.048, 35.170, 45.271, 59.444, 124.598, 126.038, 139.749.

IR (film, cm^{-1}): 3572 [ν(N-H)], 3149 [ν(C-H) aromatic], 2962 and 2745 [ν(C-H) aliphatic], 1621 [ν(C=C)], 1465 [δ(C-H)], 1413 [δ(S-CH_2)], 1062 [γ (BF)].

ESI-MS: *m/z* 198 $[M\text{-}BF_4]^+$, 87$[BF_4]^-$.

HRMS: (ESI+) *m/z* calcd for $[C_9H_{16}N_3S]^+$198.1059, found 198.1056. (ESI-) *m/z* calcd for $[C_9H_{16}N_3SB_2F_8]^-$ 372.1130, found 372.1115.

3-Methyl-2-[(2*S*)-(pyrrolidinyl) methylthio]-3*H*-imidazol-1-ium hexafluorophosphate (**1c**)

^{1}H NMR (DMSO-d_6, δ ppm) : 1.68-1.77 (m, 1H), 1.83-1.99 (m, 2H), 2.07-2.15 (m, 1H), 3.19 (t, *J*= 7.2 Hz, 2H), 3.28 (dd, *J*= 7.6, 14 Hz, 1H), 3.80 (dd, *J*= 5.2, 14 Hz, 1H), 3.59 (s, 3H), 3.79-3.86 (m, 1H), 6.99 (s, 1H), 7.30 (s, 1H), 9.21 (dr, 2H).

^{13}C NMR (DMSO-d_6, δ ppm): 23.674, 29.354, 33.252, 34.768, 45.112, 59.610, 123.870 128.245, 140.242.

IR (film, cm^{-1}): 3418 [ν(N-H)], 3157 [ν(C-H) aromatic], 2958 and 2928 [ν(C-H) aliphatic], 1630 [ν(C=C)], 1467 [δ(C-H)], 1414 [δ(S-CH_2)], 835 [γ (PF)].

ESI-MS: *m/z* 198 $[M\text{-}PF_6]^+$, 145 $[PF_6]^-$.

HRMS: (ESI+) *m/z* calcd for $[C_9H_{16}N_3S]^+$198.1059, found 198.1056. (ESI-) *m/z* calcd for $[PF_6]^-$ 144.9636, found 144.9641.

3-Methyl-2-[(2*S*)-(pyrrolidinyl) methylthio]-3*H*-imidazol-1-ium trifluoroacetate (**1d**)

^{1}H NMR (DMSO-d_6, δ ppm) : 1.69-1.76 (m, 1H), 1.83-1.98 (m, 2H), 2.08-2.14 (m, 1H), 3.21 (t, *J*= 6.8 Hz, 2H), 3.31-3.46 (m, 2H), 3.64 (s, 3H), 3.76-3.81 (m, 1H), 7.10 (s, 1H), 7.39 (s, 1H), 9.46 (dr, 2H).

^{13}C NMR (DMSO-d_6, δ ppm): 23.575, 29.475, 33.562, 34.715, 44.717, 59.118, 124.082, 127.206, 139.650, 158.942.

IR (film, cm^{-1}): 3440 [ν(N-H)], 3144 [ν(C-H) aromatic], 2973 and 2779 [ν(C-H) aliphatic], 1694 [ν(C=O)], 1465 [δ(C-H)], 1416 [δ(S-CH_2)], 1204 [γ (C-F)].

ESI-MS: *m/z* 198 $[M\text{-}CF_3COO]^+$, 113$[CF_3COO]^-$.

HRMS: (ESI+) *m/z* calcd for $[C_9H_{16}N_3S]^+$ 198.1059, found 198.1056. (ESI-) *m/z* calcd for $[C_2O_2F_3]^-$ 112.9845, found 112.9851.

3-Methyl-2-[(2*S*)-(pyrrolidinyl) methylthio]-3*H*-imidazol-1-ium trifluoromethanesulfonamide (**1e**)

^{1}H NMR (DMSO-d_6, δ ppm) : 1.68-1.77 (m, 1H), 1.83-1.98 (m, 2H), 2.08-2.16 (m, 1H), 3.20 (t, *J*= 7.2 Hz, 2H), 3.29-3.47 (m, 2H), 3.61 (s, 3H), 3.78-3.84 (m, 1H), 7.02 (d, *J*= 1.2 Hz, 1H), 7.33 (d, *J*= 1.2 Hz, 1H), 9.29 (dr, 2H).

^{13}C NMR (DMSO-d_6, δ ppm): 23.598, 29.392, 33.312, 34.654, 44.846, 59.345, 118.008, 121.208, 123.824, 128.086, 140.007.

IR (film, cm^{-1}): 3572 [ν(N-H)], 3207 [ν(C-H) aromatic], 2957 and 2752 [ν(C-H) aliphatic], 1465 [δ(C-H)], 1412 [δ(S-CH_2)], 1414 [δ(S-CH_2)], 1351 and 1137 [ν(S=O)], 1189 [γ (C-F)].

ESI-MS: *m/z* 198 [M-$(CF_3SO_2)_2N]^+$, 280 [$(CF_3SO_2)_2N]^-$.

HRMS: (ESI+) *m/z* calcd for $[C_9H_{16}N_3S]^+$ 198.1059, found 198.1056. (ESI-) *m/z* calcd for $[C_2F_6NO_4S_2]^-$ 279.9167, found 279.9177.

3-Methyl-2-[(2*S*)-(pyrrolidinyl) methylthio]-3*H*-imidazol-1-ium toluene-4-sulfonate (**1f)**

^{1}H NMR (DMSO-d_6, δ ppm) : 1.68-1.1.73 (m, 1H), 1.92-2.06 (m, 2H), 2.20-2.25 (m, 1H), 2.34 (s, 3H), 3.24-3.33 (m, 2H), 3.52-3.57 (m, 1H), 3.64-3.73 (m, 2H), 3.90 (s, 3H), 7.15 (d, *J*=8 Hz, 2H), 7.60 (d, *J*=8 Hz, 2H), 7.66 (s, 1H), 7.80 (s, 1H), 9.27 (dr, 2H).

^{13}C NMR (DMSO-d_6, δ ppm): 20.883, 23.886, 29.528, 33.570, 35.890, 45.756, 59.072, 124.317, 125.561, 128.344, 128.677, 138.285, 139.673, 144.973.

IR (film, cm^{-1}): 3458 [ν(N-H)], 3112 [ν(C-H) aromatic], 2971 and 2784 [ν(C-H) aliphatic], 1624 [ν(C=C)], 1461 [δ(C-H)], 1413 [δ(S-CH_2)], 1175 and 1010 [ν(S=O)].

ESI-MS: *m/z* 198 [M- *p*-$CH_3C_6H_4SO_3]^+$, 171 [*p*-$CH_3C_6H_4SO_3]^-$.

HRMS: (ESI+) *m/z* calcd for $[C_9H_{16}N_3S]^+$198.1059, found 198.1056. (ESI-) *m/z* calcd for $[C_7H_7O_3S]^-$ 171.0110, found 171.0111.

3-Methyl-2-[(2*S*)-(pyrrolidinyl) methylthio]-3*H*-imidazol-1-ium *β*-naphthalenesulfonate (**1g**)

^{1}H NMR (DMSO-d_6, δppm) : 1.60-1.65 (m, 1H), 1.78-1.88 (m, 2H), 2.01-2.04 (m, 1H), 3.07-3.11 (m, 2H), 3.18-3.30 (m, 2H), 3.58 (s, 3H), 3.65-3.68 (m, 1H), 6.96 (s, 1H), 7.28 (s, 1H), 7.51-7.54 (m, 2H), 7.71 (dd, *J*=2, 8.8 Hz, 1H), 7.86 (d, *J*=8.8 Hz, 1H), 7.89-7.92 (m, 1H), 7.96-7.98 (m, 1H), 8.15 (s, 1H).

^{13}C NMR (DMSO-d_6, δppm): 23.401, 29.422, 35.193, 35.360, 45.081, 58.875, 123.718, 124.256, 125.576, 126.592, 126.820, 127.585, 127.707, 128.571, 132.128, 132.924, 138.543, 144.708.

IR (film, cm^{-1}): 3450 [ν(N-H)], 3109 [ν(C-H) aromatic], 2968 and 2780 [ν(C-H) aliphatic], 1631 [ν(C=C)], 1461 [δ(C-H)], 1413 [δ(S-CH_2)], 1185 and 1030 [ν(S=O)].

ESI-MS: *m/z* 198 [M-$C_{10}H_7SO_3]^+$, 207 [$C_{10}H_7SO_3]^-$.

HRMS: (ESI+) *m/z* calcd for $[C_9H_{16}N_3S]^+$198.1059, found 198.1056. (ESI-) *m/z* calcd for $[C_{10}H_7O_3S]^-$ 207.0110, found 207.0109.

3-Methyl-2-[(2*S*)-(pyrrolidinyl) methylthio]-3*H*-imidazol-1-ium benzoate (**1h**)

^{1}H NMR (DMSO-d_6, δ ppm) : 1.68-1.77 (m, 1H), 1.84-2.00 (m, 2H), 2.08-2.16 (m, 1H), 3.21 (t, *J*=7.2, Hz, 2H), 3.31-3.43 (m, 2H), 3.61 (s, 3H), 3.79-3.86 (m, 1H), 7.01 (d, *J*=1.6 Hz, 1H), 7.33 (d, *J*=1.6 Hz, 1H), 7.49-53 (m, 2H), 7.61-7.65 (m, 1H), 7.95 (m, 2H), 9.34 (dr, 2H).

^{13}C NMR (DMSO-d_6, δ ppm): 23.575, 29.407, 33.411, 34.662, 44.732, 59.239, 123.847, 127.836, 128.624, 129.322, 130.816, 132.909, 139.862, 167.450.

IR (film, cm^{-1}): 3392 [ν(N-H)], 3107 [ν(C-H) aromatic], 2966 and 2755 [ν(C-H) aliphatic], 1597 [ν(C=C)], 1548 [ν(C=O)], 1460 and 1378 [δ(C-H)], 1412 [δ(S-CH_2)].

ESI-MS: *m/z* 198 [M-C_6H_5COO]$^+$, 121 [C_6H_5COO]$^-$.

HRMS: (ESI+) *m/z* calcd for [$C_9H_{16}N_3S$]$^+$198.1059, found 198.1056. (ESI-) *m/z* calcd for [$C_7H_5O_2$]$^-$ 121.0284, found 121.0290.

3-Methyl-2-[(2*S*)-(pyrrolidinyl) methylthio]-3*H*-imidazol-1-ium phenylacetate (**1i**)

^{1}H NMR (DMSO-d_6, δ ppm) : 1.47-1.54 (m, 1H), 1.66-1.80 (m, 2H), 1.87-1.93 (m, 1H), 2.88-2.99 (m, 2H), 3.15 (dd, *J*=14.8, 20 Hz, 2H), 3.38 (s, 2H), 3.41-3.44 (m, 1H), 3.57 (s, 3H), 6.38 (dr, 2H), 6.93 (s, 1H), 7.17-7.25 (m, 6H).

^{13}C NMR (DMSO-d_6, δ ppm): 23.871, 29.725, 33.100, 35.724, 44.543, 44.649, 58.336, 123.536, 125.508, 127.836, 128.321, 129.246, 138.346, 139.893, 175.298.

IR (film, cm^{-1}): 3393 [ν(N-H)], 3109 [ν(C-H) aromatic], 2951 and 2751 [ν(C-H) aliphatic], 1570 [ν(C=O)], 1458 and 1375 [δ(C-H)], 1411 [δ(S-CH_2)].

ESI-MS: *m/z* 198 [M- $C_6H_5CH_2COO$]$^+$, 135 [$C_6H_5CH_2COO$]$^-$.

HRMS: (ESI+) *m/z* calcd for [$C_9H_{16}N_3S$]$^+$198.1059, found 198.1056. (ESI-) *m/z* calcd for [$C_8H_7O_2$]$^-$ 135.0441, found 135.0444.

3-Phenyl-2-[(2*S*)-(pyrrolidinyl) methylthio]-3*H*-imidazol-1-ium bromide (**2**)

^{1}H NMR (DMSO-d_6, δ ppm) : 1.69-1.76 (m, 1H), 1.84-1.98 (m, 2H), 2.06-2.14 (m, 1H), 3.16-3.26 (m, 2H), 3.39-3.51 (m, 2H), 3.86-3.92 (m, 1H), 7.17 (d, *J*＝ 1.6 Hz, 1H), 7.47-7.53 (m, 3H), 7.55-7.60 (m, 3H), 9.27 (dr, 2H).

^{13}C NMR (DMSO-d_6, δ ppm): 23.538, 29.42k, 34.503, 44.922, 58.761, 123.339, 125.219, 128.541, 129.064, 129.527, 136.496, 140.515.

IR (film, cm^{-1}): 3427 [ν(N-H)], 3086 [ν(C-H) aromatic], 2961 and 2722 [ν(C-H) aliphatic], 1593 and 1498 [ν(C=C)], 1478 and 1344 [δ(C-H)], 1418 [δ(S-CH_2)], 767 [δ(Ar-H)].

ESI-MS: *m/z* 260 [M-Br]$^+$.

HRMS: (ESI+) *m/z* calcd for [$C_{14}H_{18}N_3S$]$^+$ 260.1216, found 260.1221.

3-Benzyl-2-[(2*S*)-(pyrrolidinyl) methylthio]-3*H*-imidazol-1-ium bromide (**3**)

^{1}H NMR (DMSO-d_6, δ ppm) : 1.68-1.76 (m, 1H), 1.83-1.98 (m, 2H), 2.06-2.12 (m, 1H), 3.18-3.24 (m, 2H), 3.34 (s, 2H), 3.35-3.49 (m, 2H), 3.87-3.91 (m, 1H), 7.17 (d, *J*=1.6 Hz, 1H), 7.46-7.53 (m, 3H), 7.56-7.60 (m, 1H), 9.20 (dr, 2H).

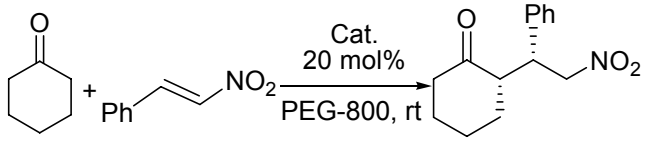
^{13}C NMR (DMSO-d_6, δ ppm): 23.629, 29.430, 35.162, 44.990, 49.623, 59.315, 123.164, 127.282, 127.942, 128.784, 128.882, 136.928, 140.158.

IR (film, cm^{-1}): 3388 [ν(N-H)], 3029 [ν(C-H) aromatic], 2928 and 2708 [ν(C-H) aliphatic], 1604 and 1496 [ν(C=C)], 1583 [ν(C=O)], 1519[ν(-NO_2)], 1454 and 1358 [δ(C-H)], 1430 [δ(S-CH_2)], 715 [δ(Ar-H)].

ESI-MS: *m/z* 274 [M-Br]$^+$.

HRMS: (ESI+) *m*/*z* calcd for $[C_{15}H_{20}N_3S]^+$ 274.1372, found 274.1380.

3. Typical Experimental Procedure for the Asymmetric Michael Addition Reaction



4 **5** **6**

To a mixture of nitrostyrene (0.5 mmol) and a chiral pyrrolidinyl-thioimidazolium salt catalyst (0.1 mmol) in PEG-800 (2 mL) was added cyclohexanone (1 mmol). The mixture was stirred at room temperature until completion of the reaction by monitoring on GC. The mixture was extracted four times with hexane/ether (6:1). The combined extracts were evaporated and purified by preparative TLC (hexane/$CHCl_3$ = 4:1) to give the Michael adduct. The ee value of the product was determined by chiral HPLC analysis.[3]

2-(2-Nitro-1-phenylethyl) cyclohexanone (**6**)

HPLC (Daicel Chiralpak AS-H, hexane/2-PrOH=95:5, flow rate 1.0 mL/min, λ=254nm): t_R=14.28 min (minor), 20.84 min (major).

^{1}H NMR ($CDCl_3$, δppm): 1.19-2.72 (m, 9H, cycl), 3.75 (ddd, *J*=10, 10, 4.8 Hz, 1H), 4.63 (dd, *J*=12.4, 10 Hz, 1H), 4.95 (dd, *J*=12.4, 4.8 Hz, 1H), 7.16-7.34 (m, 5H).

MS (EI): 55 (30), 77 (12), 91 (63), 104 (34), 115 (25), 141 (15), 157 (13), 171 (100), 183 (21), 200 (60), 247 (1).

2-(2-Nitro-1-(2-methoxyphenyl) ethyl) cyclohexanone (**7**)

HPLC (Daicel Chiralpak AS-H, hexane/2-PrOH=90:10, flow rate 1.0 mL/min, λ=254nm): t_R=10.19 min (minor), 18.09 min (major).

^{1}H NMR ($CDCl_3$, δppm): 1.16-1.25 (m, 1H), 1.56-1.79 (m, 4H), 2.05-2.09 (m, 1H), 2.35-2.49 (m, 2H), 2.94-3.01 (m, 1H), 3.84 (s, 3H)，3.95 (dt, *J*=9.2, 4.9 Hz, 1H), , 4.80-4.88 (m, 2H), 6.88 (t, *J*=8.4 Hz, 2H), 7.08 (d, *J*=7.6 Hz, 1H), 7.24 (dd, *J*=8.4, 7.6 Hz, 1H).

MS (EI): 55 (11), 77 (17), 91 (15), 105 (11), 121 (60), 134 (54), 145 (10), 159 (12), 171 (9), 187 (7), 201 (100), 213 (6), 230 (51), 277 (10).

2-(2-Nitro-1-(3-methoxyphenyl) ethyl) cyclohexanone (**8**)

HPLC (Daicel Chiralpak AS-H, hexane/2-PrOH=90:10, flow rate 1.0 mL/min, λ=254nm): t_R=14.16 min (minor), 22.20 min (major).

^{1}H NMR ($CDCl_3$, δppm): 1.21-1.27 (m, 1H), 1.55-1.81 (m, 4H), 2.07-2.10 (m, 1H), 2.35-2.49 (m, 2H), 2.62-2.70 (m, 1H), 3.70-3.77 (m, 1H), 3.79 (s, 3H), 4.62 (dd, *J*=10.4, 12.0 Hz, 1H), 4.92 (dd, *J*=12.0,

4.0 Hz, 1H), 6.71 (s, 1H), 6.75 (d, *J*=8.0 Hz, 1H), 6.79 (d, *J*=8.0 Hz, 1H), 7.25 (t, *J*=8.0 Hz, 1H).

MS (EI): 55 (5), 77 (16), 91 (26), 103 (14), 121 (39), 134 (27), 147 (11), 159 (18), 171 (10), 187 (14), 201 (100), 213 (33), 230 (38), 277 (19).

2-(2-Nitro-1-(4-methoxyphenyl) ethyl) cyclohexanone (**9**)

HPLC (Daicel Chiralpak AS-H, hexane/2-PrOH=90:10, flow rate 1.0 mL/min, λ=254nm): t_R=14.12 min (minor), 23.09 min (major).

^{1}H NMR ($CDCl_3$, δppm): 1.15-1.27 (m, 1H), 1.64-1.77 (m, 4H), 2.02-2.11 (m, 1H), 2.31-2.50 (m, 2H), 2.60-2.72 (m, 1H), 3.71 (ddd, *J*=9.6, 9.6, 4.6 Hz, 1H), 3.78 (s, 3H), 4.58 (dd, *J*=12.4, 9.6 Hz, 1H), 4.90 (dd, *J*=12.4, 4.6 Hz, 1H), 6.85 (d, *J*=6.7 Hz, 2H), 7.09 (d, *J*=6.7 Hz, 2H).

MS (EI): 55 (4), 77 (6), 91 (14), 103 (5), 121 (39), 134 (74), 147 (6), 176 (5), 187 (7), 201 (100), 213 (6), 230 (54), 277 (3).

2-(2-Nitro-1-(4-methylphenyl) ethyl) cyclohexanone (**10**)

HPLC (Daicel Chiralpak AS-H, hexane/2-PrOH=95:5, flow rate 1.0 mL/min, λ=254nm): t_R=8.79 min (minor), 13.70 min (major).

^{1}H NMR ($CDCl_3$, δppm): 1.18-1.28 (m, 1H), 1.52-1.79 (m, 4H), 2.04-2.10 (m, 1H), 2.33 (s, 3H), 2.35-2.50 (m, 2H), 2.63-2.70 (m, 1H), 3.69-3.75 (ddd, *J*=10, 10, 4.8 Hz, 1H), 4.60 (dd, *J*=12, 10 Hz, 1H), 4.91 (dd, *J*=12, 4.8 Hz, 1H), 7.04 (d, *J*=8.4 Hz, 2H), 7.12 (d, *J*=8.4 Hz, 2H).

MS (EI): 55 (6), 77 (7), 91 (17), 105 (47), 118 (36), 129 (16), 147 (13), 155 (11), 171 (11), 185 (100), 197 (13), 214 (53).

2-(2-Nitro-1-(4-chlorophenyl) ethyl) cyclohexanone (**11**)

HPLC (Daicel Chiralpak AS-H, hexane/2-PrOH=95:5, flow rate 1.0 mL/min, λ=254nm): t_R=11.10 min (minor), 15.03 min (major).

^{1}H NMR ($CDCl_3$, δppm): 1.19-1.30 (m, 1H), 1.61-1.82 (m, 4H), 2.08-2.10 (m, 1H), 2.34-2.50 (m, 2H), 2.63-2.67 (m, 1H), 3.75 (ddd, *J*=10, 10, 4.4 Hz, 1H), 4.61 (dd, *J*=12.4, 10 Hz, 1H), 4.93 (dd, *J*=12.4, 4.4 Hz, 1H), 7.15 (d, *J*=8.4 Hz, 2H), 7.34 (d, *J*=8.4 Hz, 2H).

MS (EI): 55 (13), 77 (10), 89 (7), 103 (16), 115 (23), 125 (57), 138 (37), 151 (11), 165 (12), 175 (7), 182 (8), 191 (13), 205 (100), 217 (14), 234 (50).

2-(2-Nitro-1-(4-trifluolomethylphenyl) ethyl) cyclohexanone (**12**)

HPLC (Daicel Chiralpak AS-H, hexane/2-PrOH=95:5, flow rate 1.0 mL/min, λ=254nm): t_R=8.14 min (minor), 11.86 min (major).

^{1}H NMR ($CDCl_3$, δppm): 1.25-2.70 (m, 9H, cycl), 3.98 (m, 1H), 4.66 (m, 1H), 4.99 (m, 1H), 7.59 (d, *J*=8.8 Hz, 2H), 8.31 (d, *J*=8.8 Hz, 2H).

MS (EI): 55 (30), 69 (12), 81 (8), 103 (8), 115 (15), 129 (17), 151 (14), 159 (68), 173 (35), 185 (24), 199 (16), 209 (15), 225 (19), 239 (100), 251 (34), 268 (53).

2-(2-Nitro-1-(2-nitrophenyl) ethyl) cyclohexanone (**13**)

HPLC (Daicel Chiralpak AD-H, hexane/2-PrOH=90:10, flow rate 1.0 mL/min, λ=254nm): t_R=20.68 min (minor), 24.94 min (major).

^{1}H NMR ($CDCl_3$, δppm): 1.24-2.66 (m, 9H, cycl), 4.09-4.13 (m, 1H), 4.30-4.35 (m, 1H), 4.93-4.95 (m, 1H), 7.38-7.47 (m, 2H), 7.54-7.65 (m, 1H), 7.84-7.90 (m, 1H).

MS (EI): 55 (49), 67 (22), 77 (41), 91 (31), 104 (20), 115 (39), 130 (36), 144 (19), 156 (17), 168 (13), 185 (91), 200 (20), 246 (100).

2-(2-Nitro-1-(furan-2-yl) ethyl) cyclohexanone (**14**)

HPLC (Daicel Chiralpak AS-H, hexane/2-PrOH=85:15, flow rate 1.0 mL/min, λ=254nm): t_R=13.01 min (minor), 15.55 min (major).

^{1}H NMR ($CDCl_3$, δppm): 1.25-2.79 (m, 9H, cycl), 3.98 (ddd, *J*=9.6, 9.6, 4.8 Hz, 1H), 4.67 (dd, *J*=12.4, 9.6 Hz, 1H), 4.80 (dd, *J*=12.4, 4.8 Hz, 1H), 6.18 (s, 1H), 6.29 (s, 1H), 7.34 (s, 1H).

MS (EI): 55 (11), 65 (9), 77 (14), 81 (29), 91 (15), 94 (33), 108 (10), 121 (9), 134 (9), 147 (14), 161 (100), 190 (63), 237 (1).

2-(2-Nitro-1-(thioan-2-yl) ethyl) cyclohexanone (**15**)

HPLC (Daicel Chiralpak AS-H, hexane/2-PrOH=90:10, flow rate 1.0 mL/min, λ=254nm): t_R=14.52 min (minor), 18.26 min (major).

^{1}H NMR ($CDCl_3$, δppm): 1.28-2.79 (m, 9H, cycl), 4.13 (ddd, *J*=8.8, 8.8, 4.4 Hz, 1H), 4.65 (dd, *J*=12.0, 8.8 Hz, 1H), 4.89 (dd, *J*=12.0, 4.4 Hz, 1H), 6.91-6.95 (m, 2H), 7.21-7.23 (m, 1H).

MS (EI): 55 (10), 65 (9), 77 (10), 97 (50), 110 (50), 123 (15), 135 (16), 150 (10), 163 (14), 177 (100), 189 (4), 206 (70).

2-(2-Nitro-1-(2-naphthyl) ethyl) cyclohexanone (**16**)

HPLC (Daicel Chiralpak AS-H, hexane/2-PrOH=85:15, flow rate 1.0 mL/min, λ=254nm): t_R=11.75 min (minor), 20.94 min (major).

^{1}H NMR ($CDCl_3$, δppm): 1.19-2.78 (m, 9H, cycl), 3.93 (ddd, *J*=10, 10, 4.4 Hz, 1H), 4.73 (t, *J*=12.4 Hz, 1H), 5.01 (dd, *J*=12.4, 4.4 Hz, 1H), 7.27-7.82 (m, 7H).

MS (EI): 55 (16), 73 (16), 81 (25), 115 (16), 128 (17), 141 (52), 154 (53), 165 (39), 179 (28), 191 (15), 207 (46), 221 (100), 250 (43), 281 (21), 297 (10).

3-(2-Nitro-1-phenylethyl) tetrahydro-pyran-4-one (**17**)

HPLC (Daicel Chiralpak AS-H, hexane/2-PrOH=90:10, flow rate 1.0 mL/min, λ=254nm): t_R=12.90 min (minor), 34.85 min (major).

^{1}H NMR ($CDCl_3$, δppm): 2.54-2.59 (m, 1H), 2.64-2.71 (m, 1H), 2.85-2.92 (m, 1H), 3.25-3.30 (m, 1H), 3.60-3.72 (m, 1H), 3.75-3.86 (m, 2H), 4.15 (m, 1H), 4.65 (dd, *J*=12.4, 10.4 Hz, 1H), 4.93 (dd, *J*=12.4,

4.8 Hz, 1H), 7.18 (d, *J*=7.6 Hz, 2H), 7.23-7.36 (m, 3H).

MS (EI): 51 (9), 65 (8), 77 (18), 91 (53), 104 (33), 115 (49), 131 (100), 145 (6), 157 (18), 172 (22), 187 (6), 202 (78).

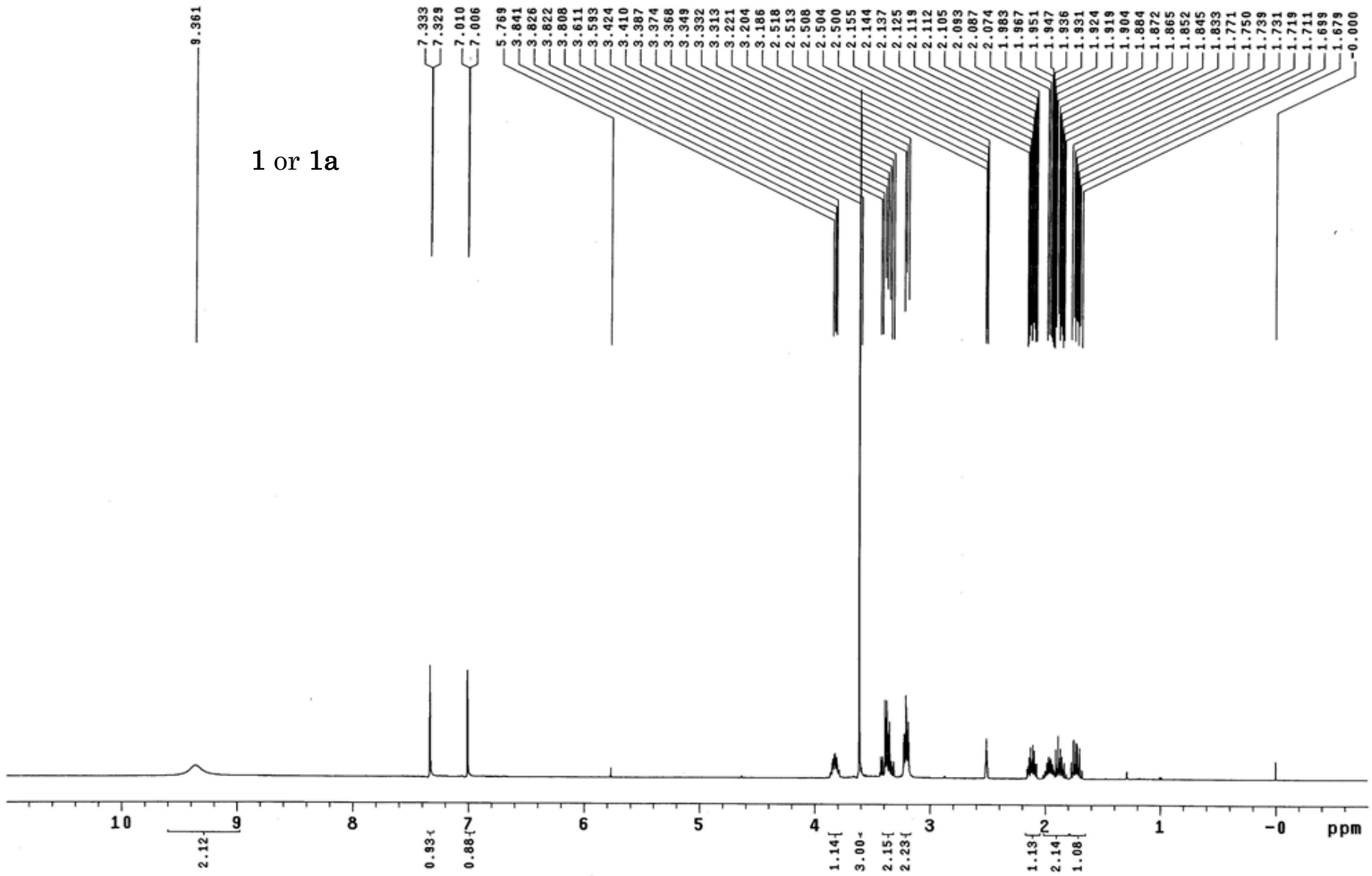
3-(2-Nitro-1-phenyl-ethyl) tetrahydro-thiopyran-4-one (**18**)

HPLC (Daicel Chiralpak AS-H, hexane/2-PrOH=90:10, flow rate 1.0 mL/min, λ=254nm): t_R=25.34 min (minor), 33.38 min (major).

^{1}H NMR ($CDCl_3$, δppm): 2.46 (dd, *J*=13.6, 10 Hz, 1H), 2.60-2.63 (m, 1H), 2.75-2.90 (m, 2H), 2.93-3.09 (m, 3H), 3.95-4.01 (m, 1H), 4.64 (dd, *J*=12.4, 10 Hz, 1H), 4.76 (dd, *J*=12.4, 4.4 Hz, 1H), 7.20 (d, *J*=6.8 Hz, 2H), 7.27-7.41 (m, 3H).

MS (EI): 65 (12), 77 (23), 91 (56), 104 (40), 115 (73), 131 (100), 147 (7), 157 (12), 162 (35), 171 (11), 190 (35), 218 (59), 265 (4).

4. NMR, ESI-MS and HRMS Spectra of Pyrrolidinyl-Thioimidazolium Salts 1-3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2.105
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1.967
1.951
1.947
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1.931
1.924
1.919
1.904
1.884
1.872
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1.750
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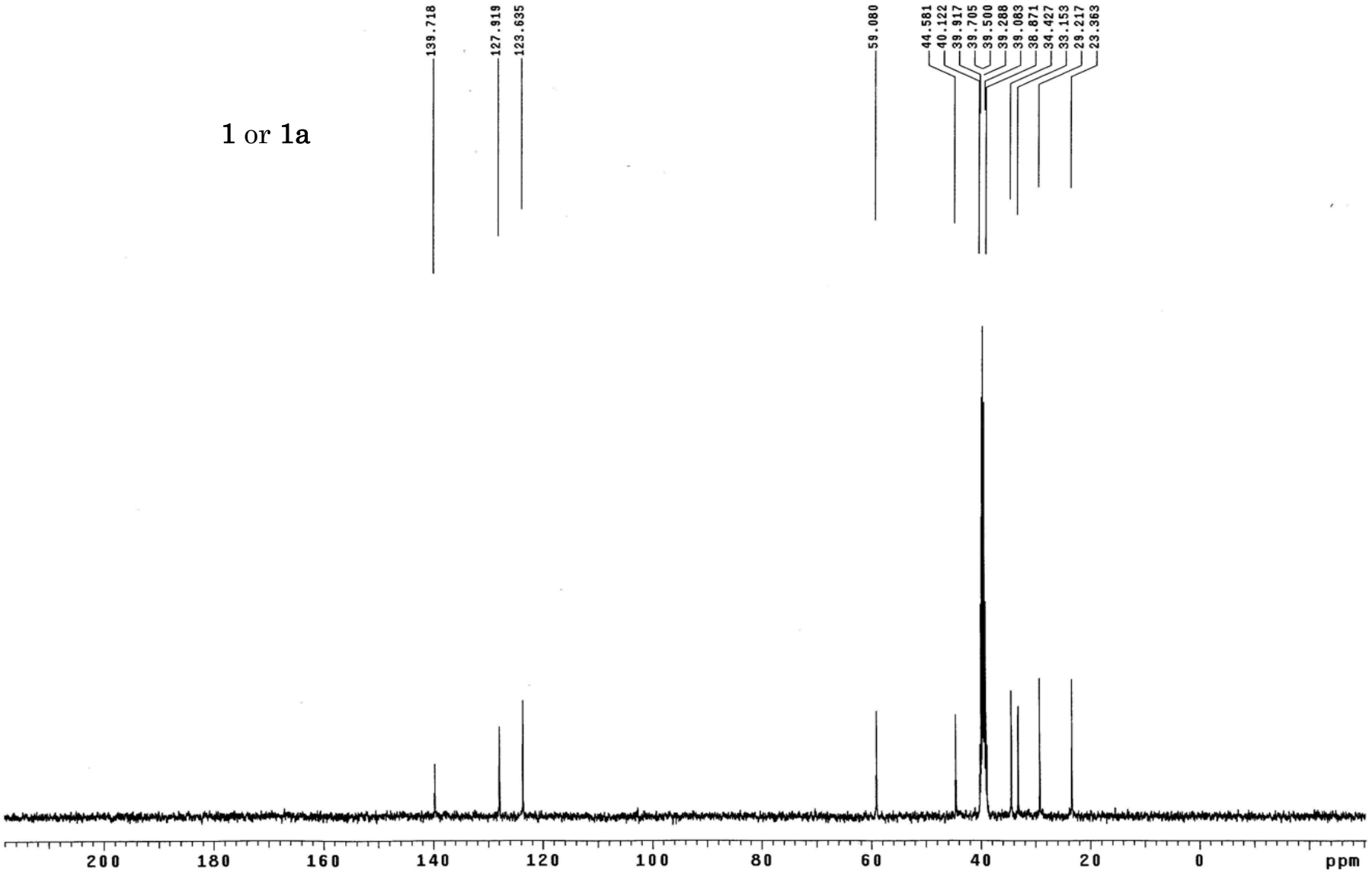
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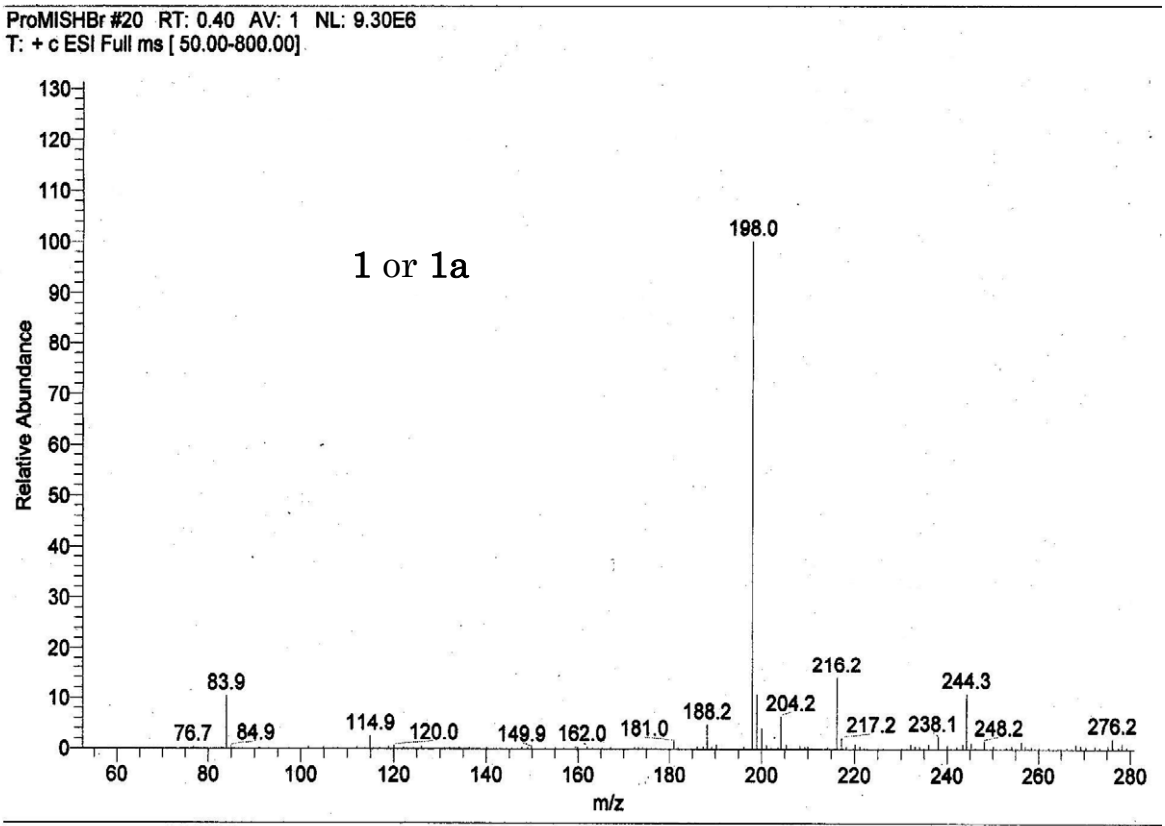
ppm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217.2
238.1
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276.2
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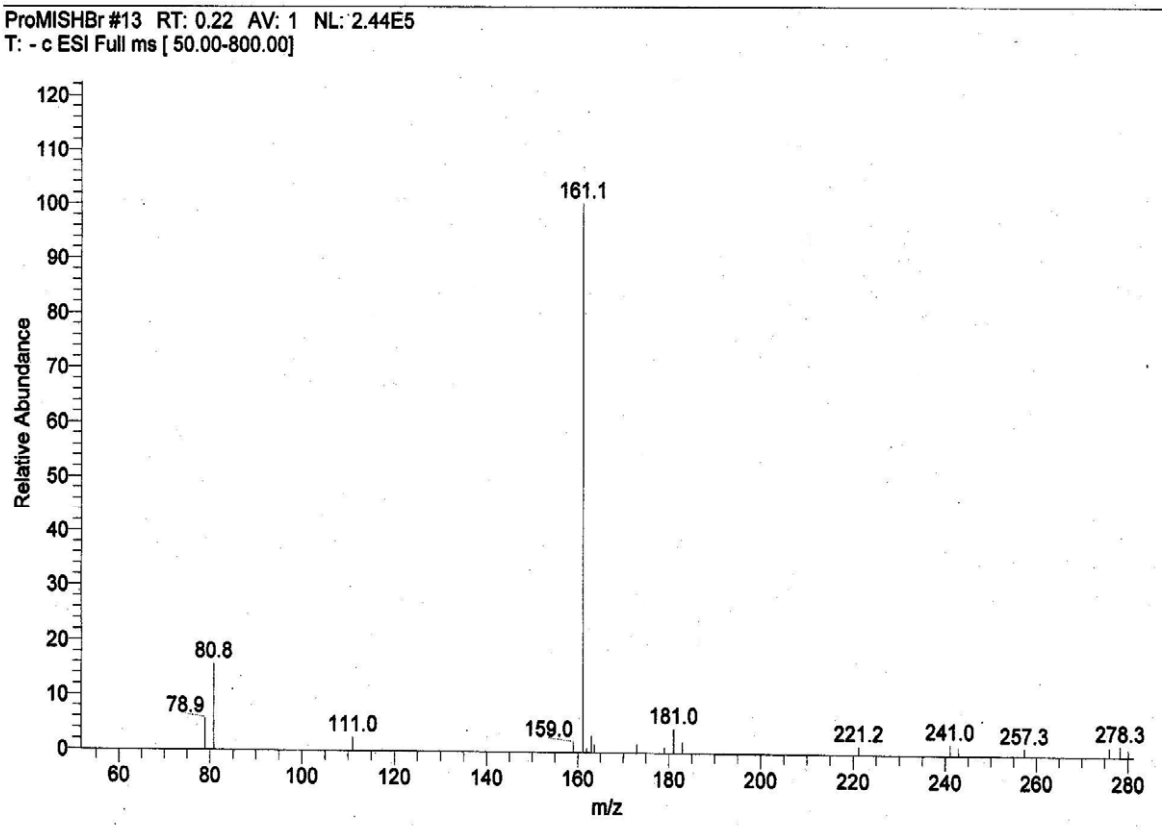
m/z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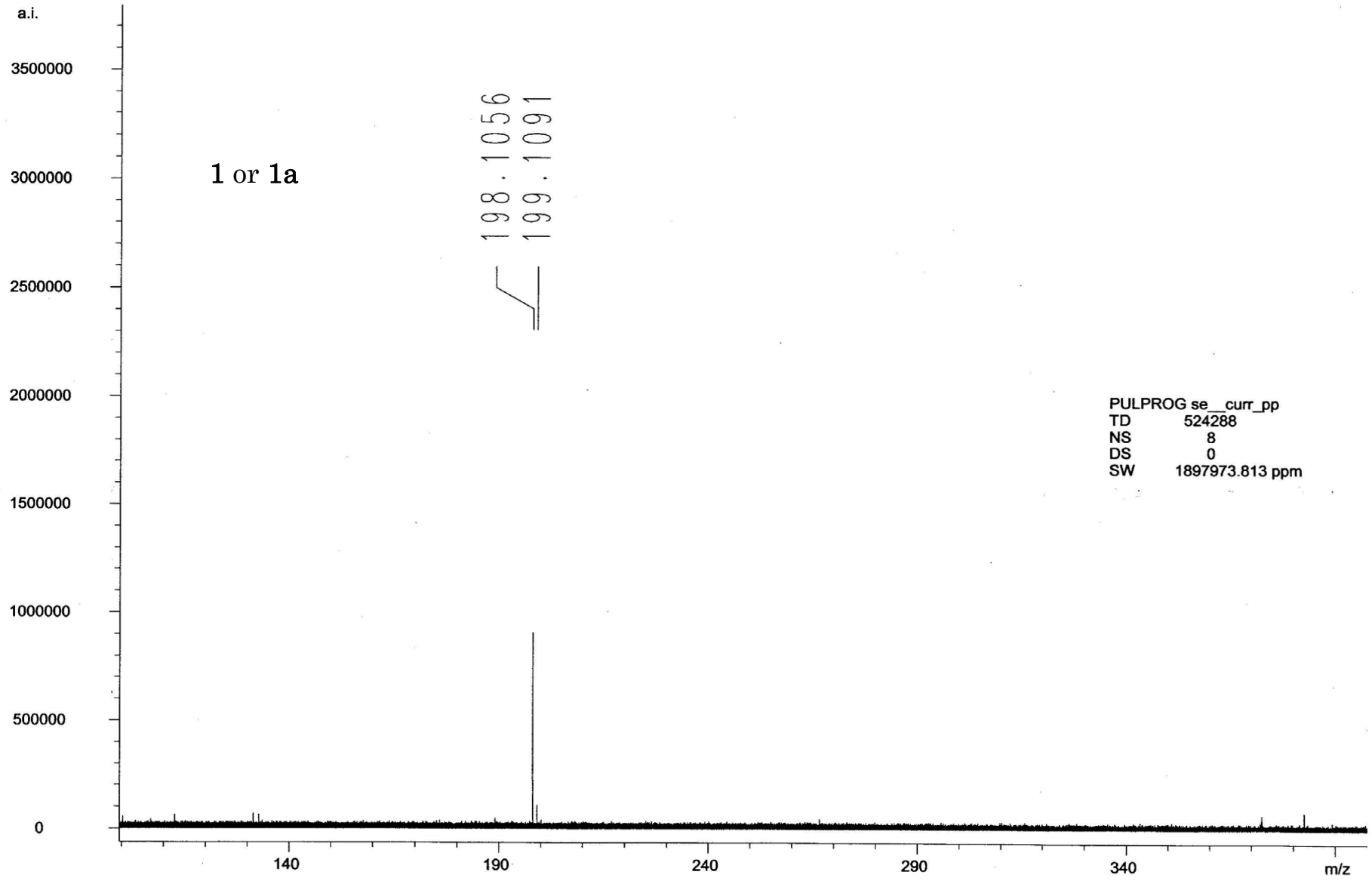
Relative Abundance
m/z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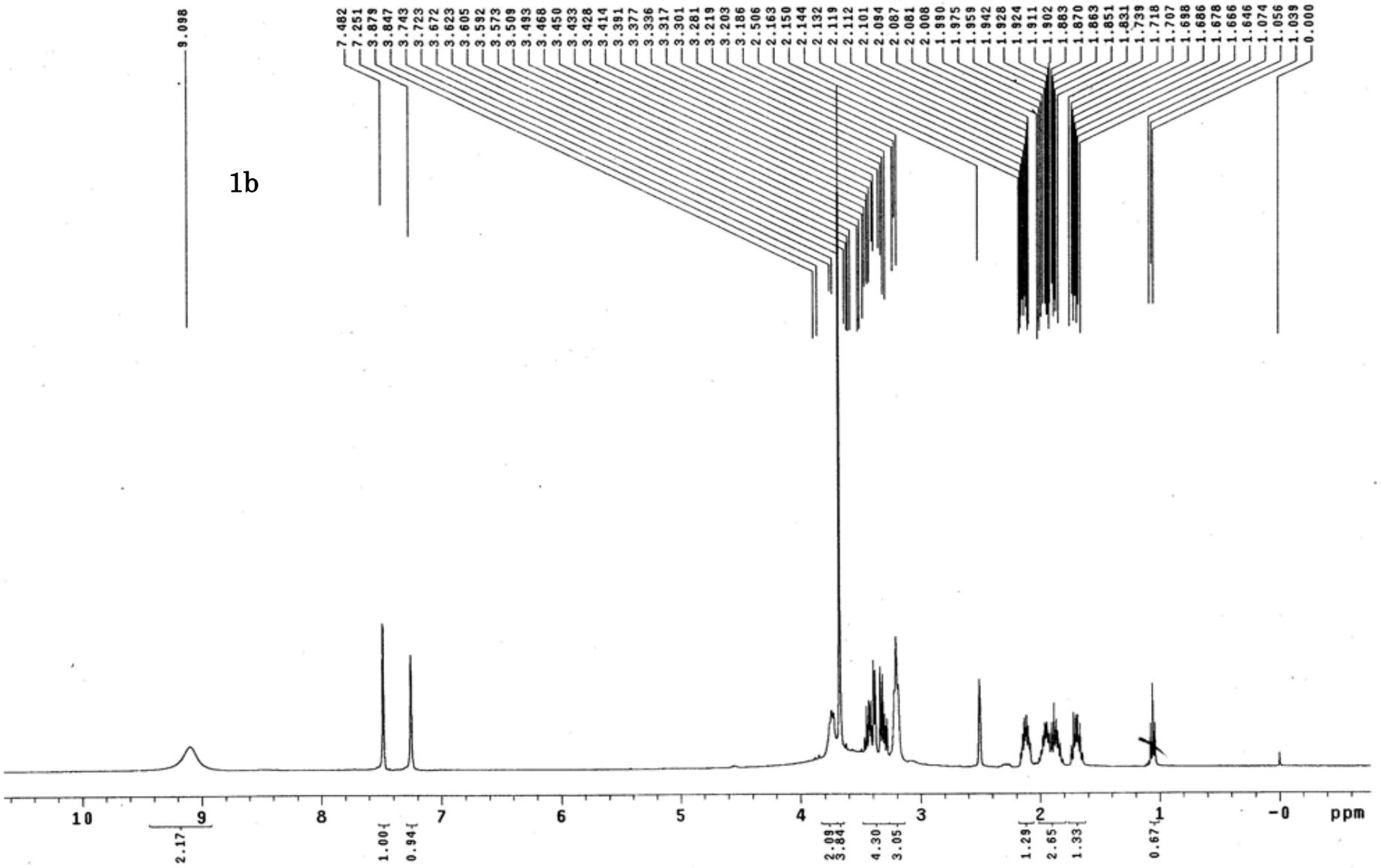
m/z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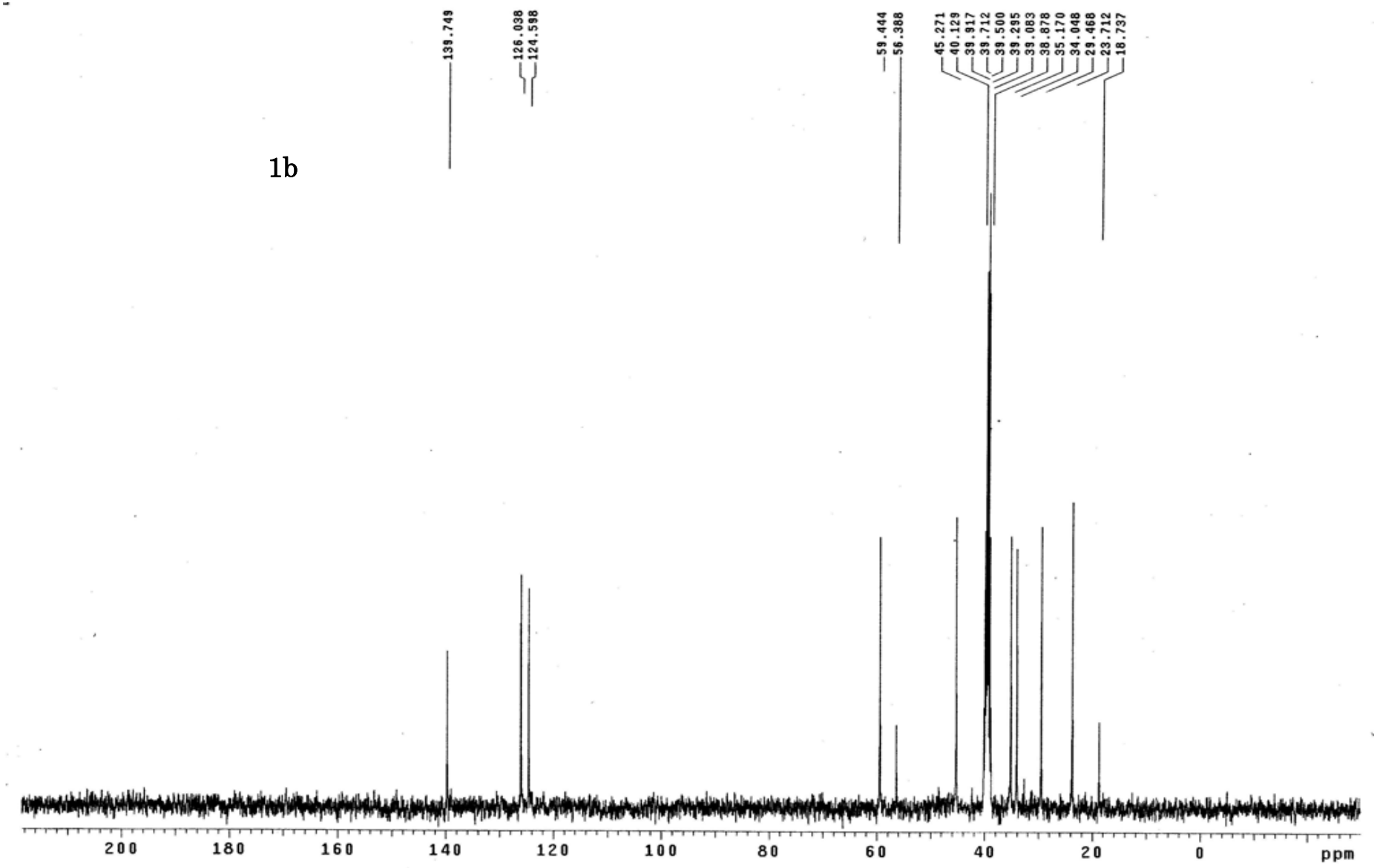
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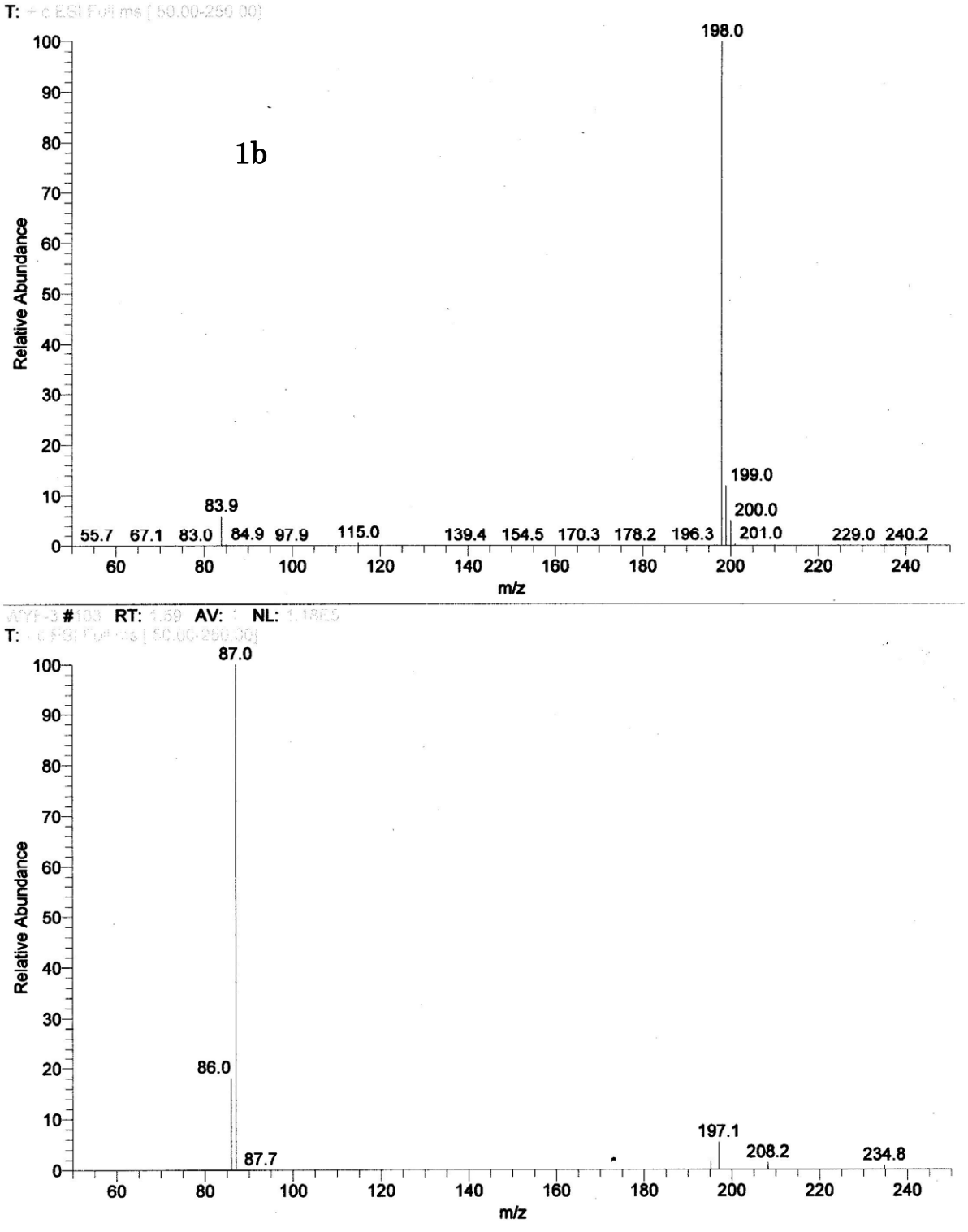
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97.9
115.0
139.4
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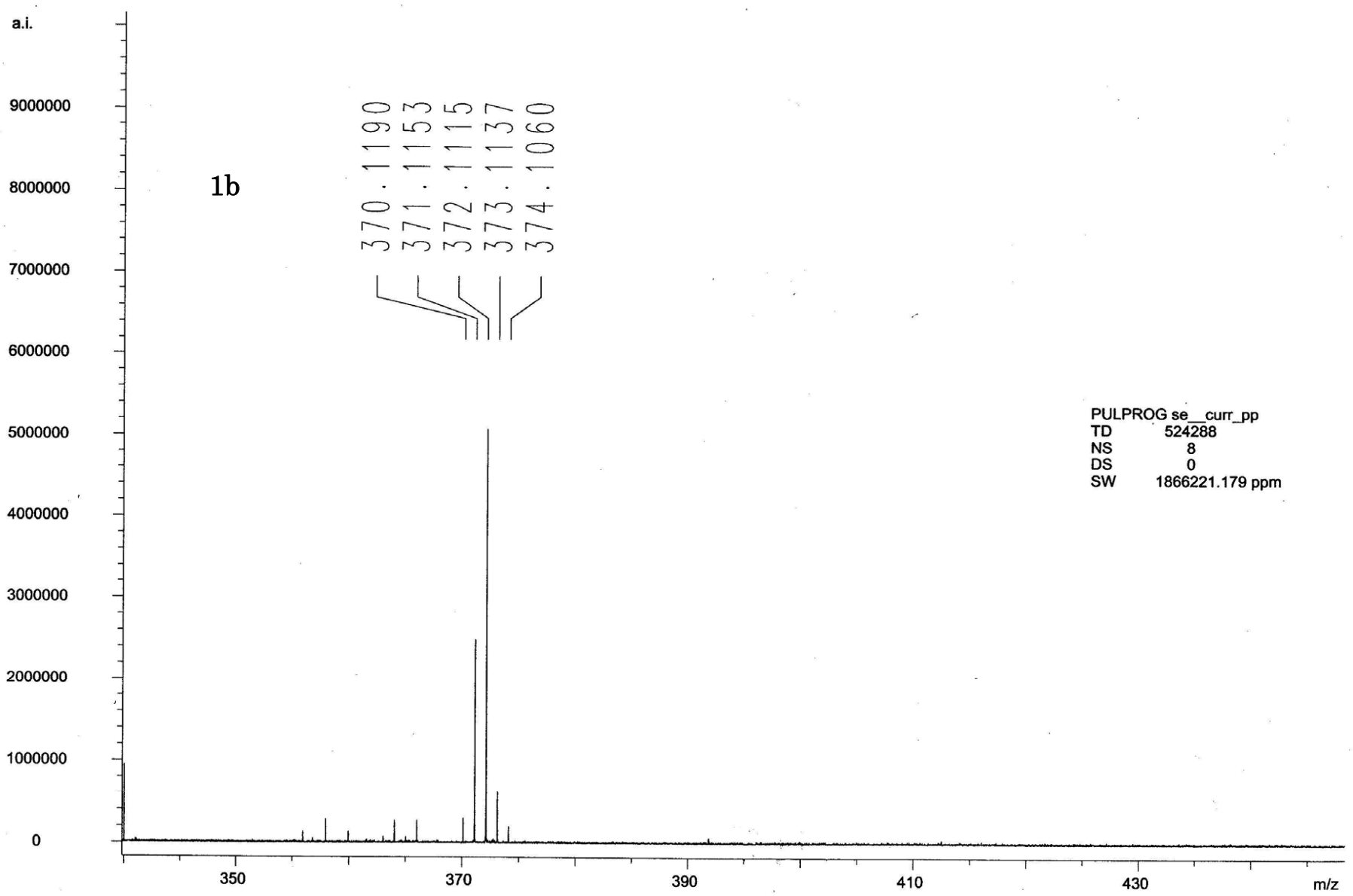
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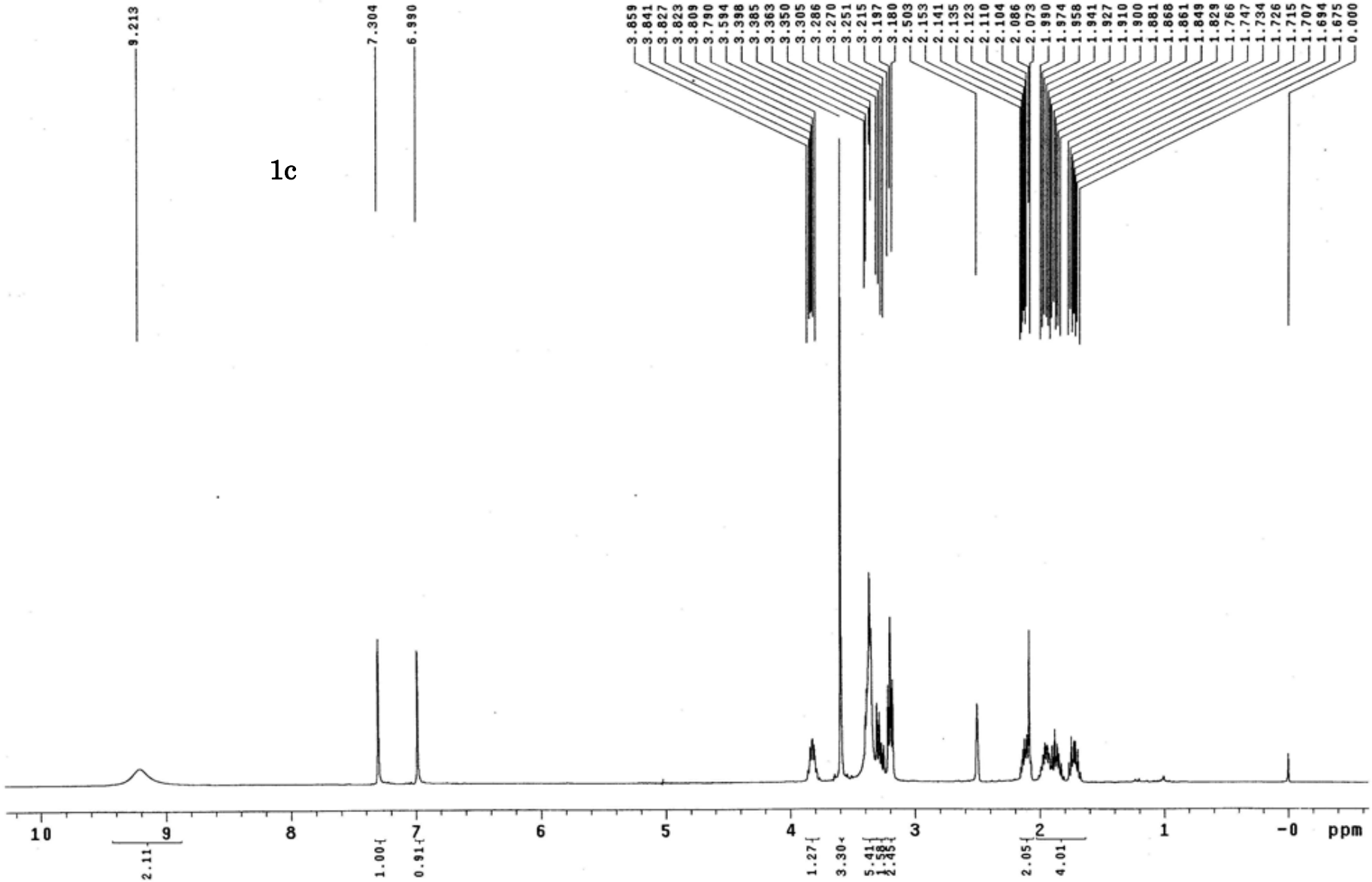
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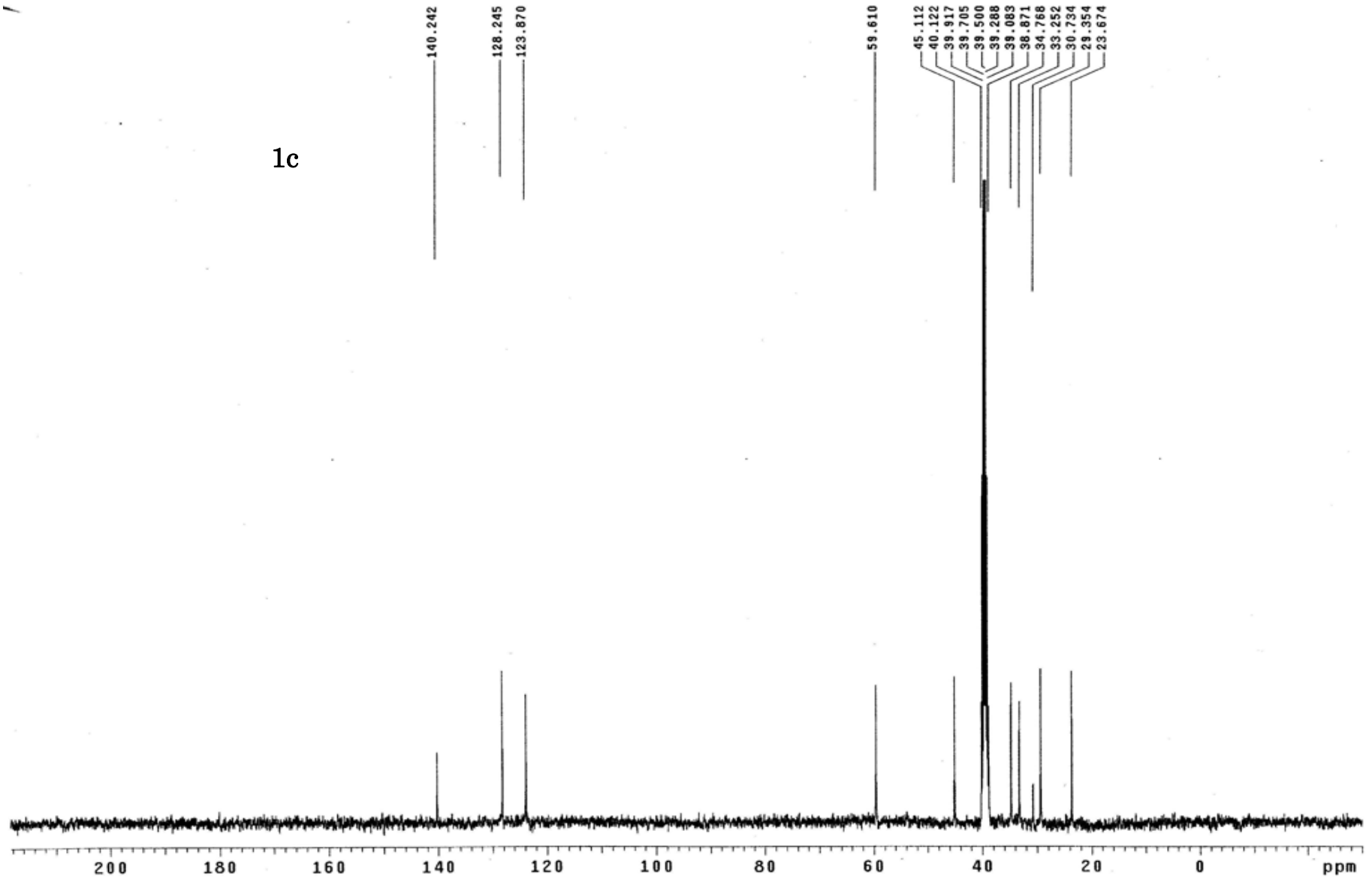
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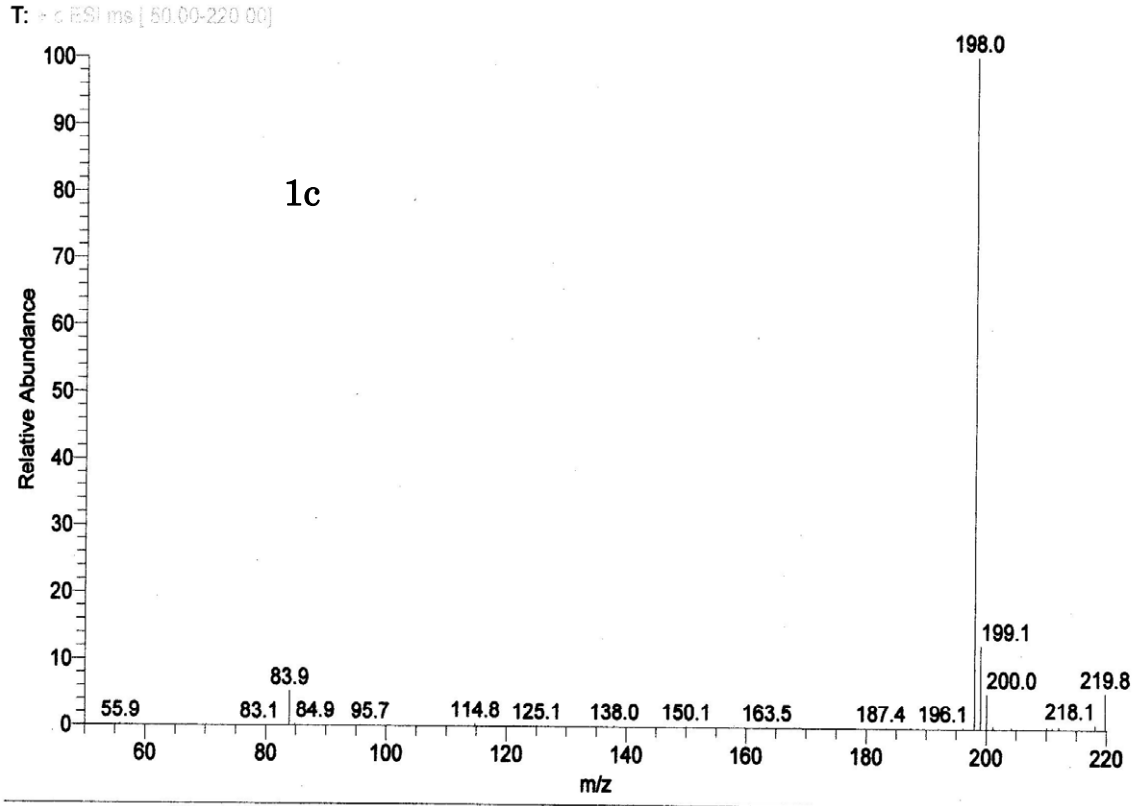
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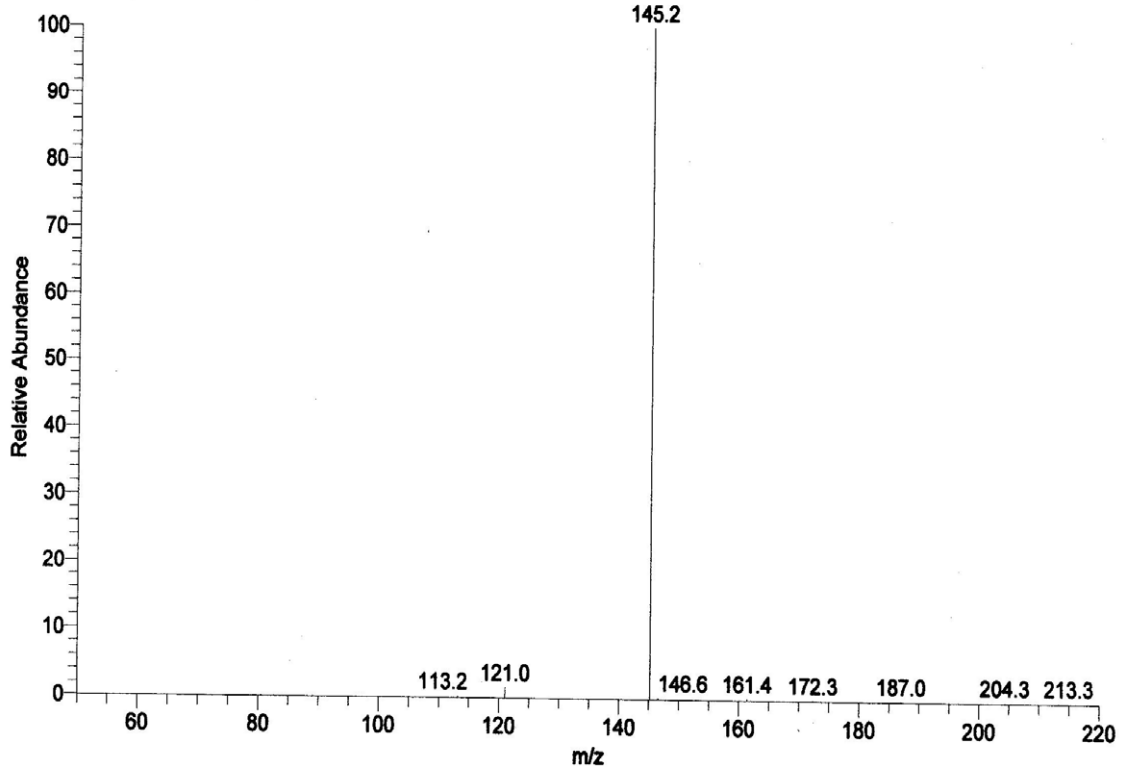
218.1
Relative Abundance
m/z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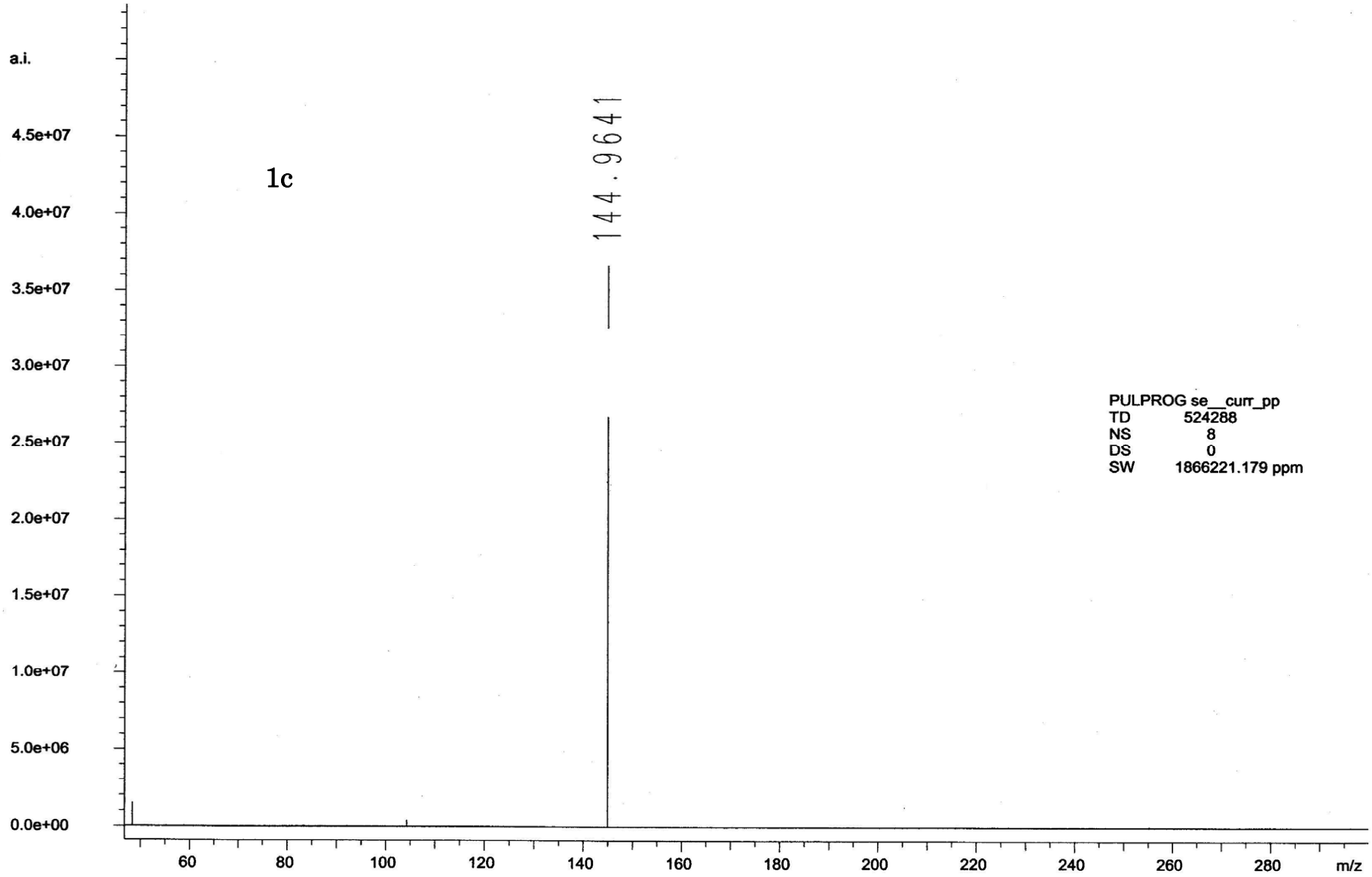
Relative Abundance
m/z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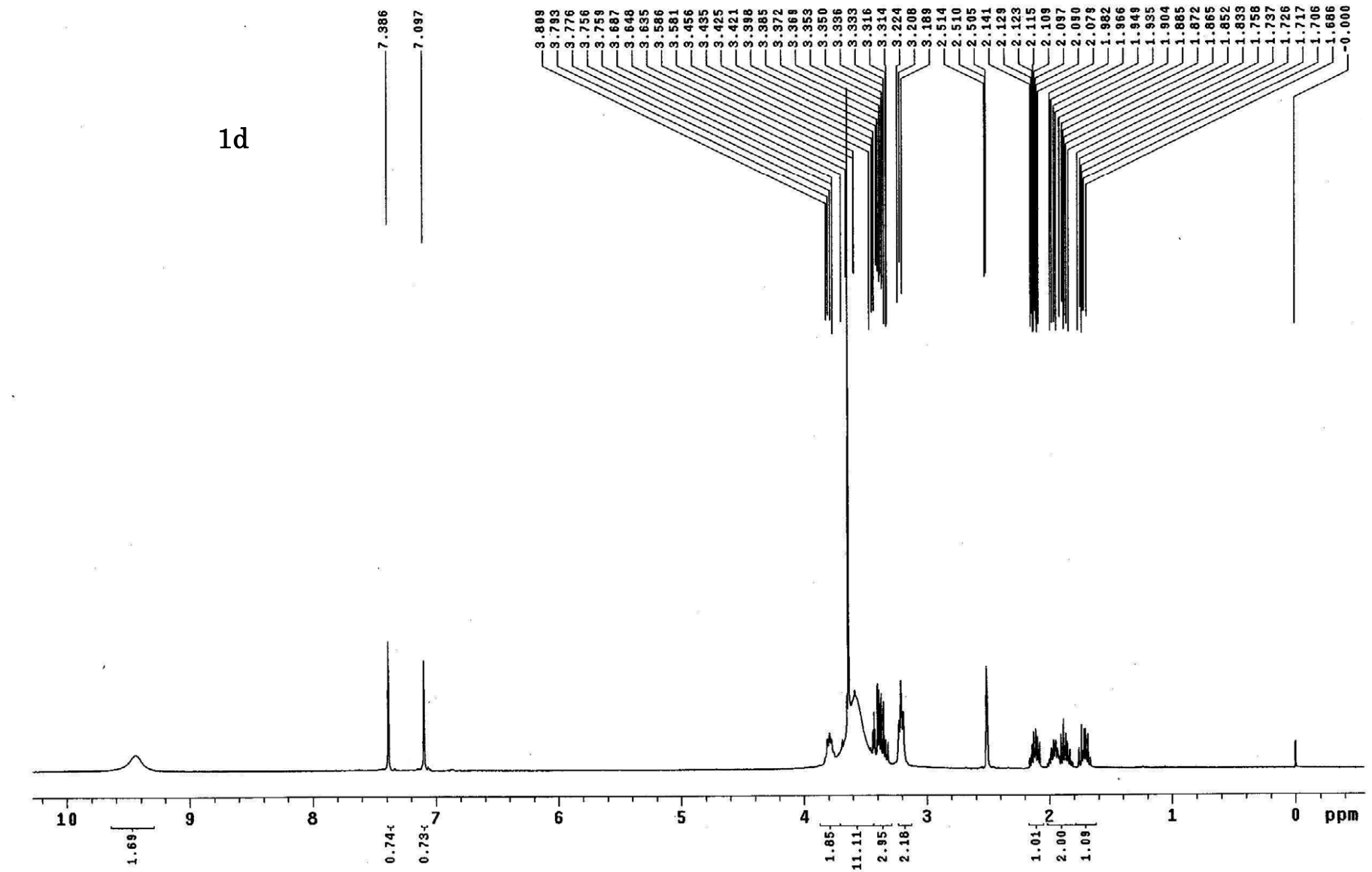
m/z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3.314
3.224
3.208
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2.505
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2.129
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2.109
2.097
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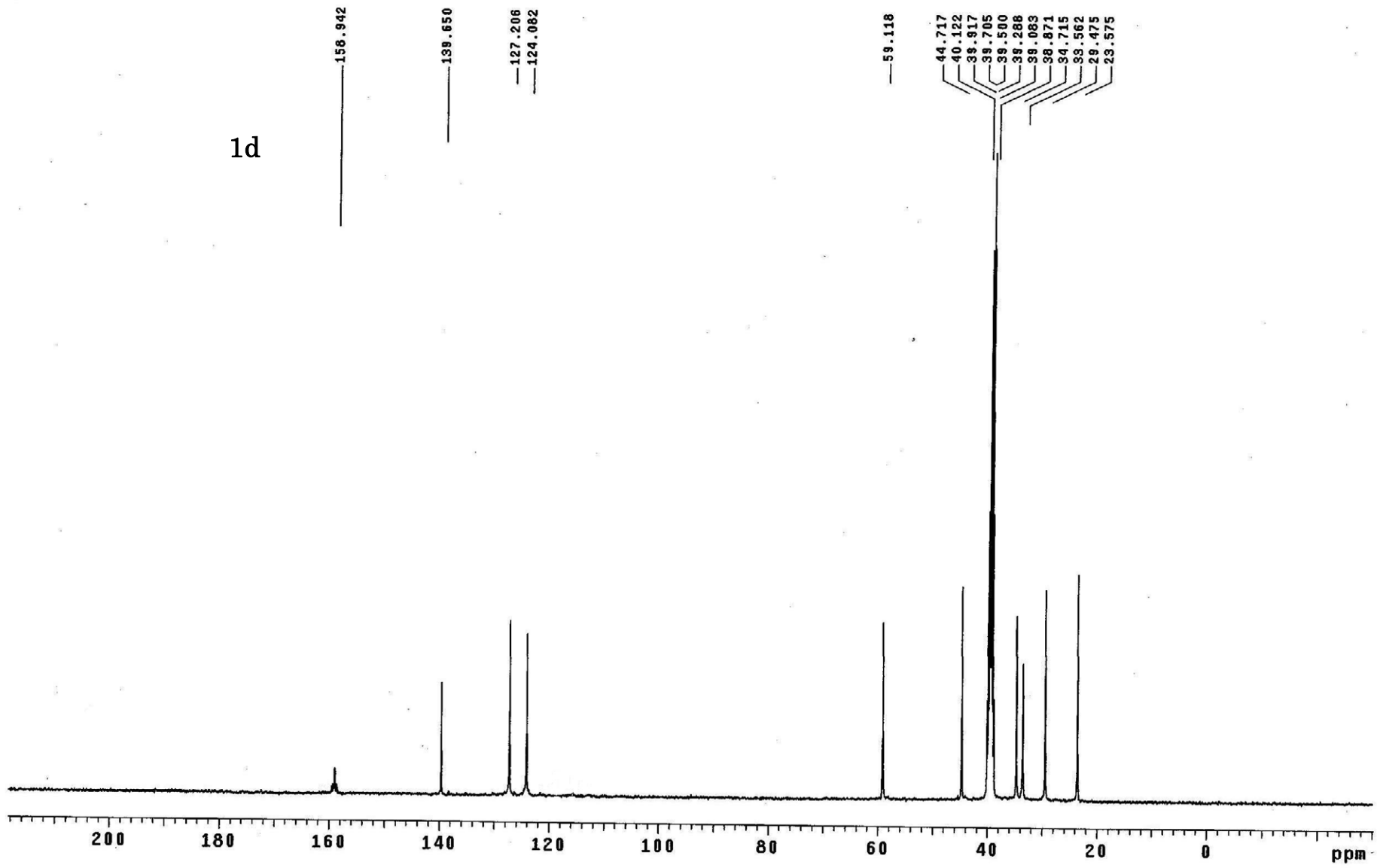
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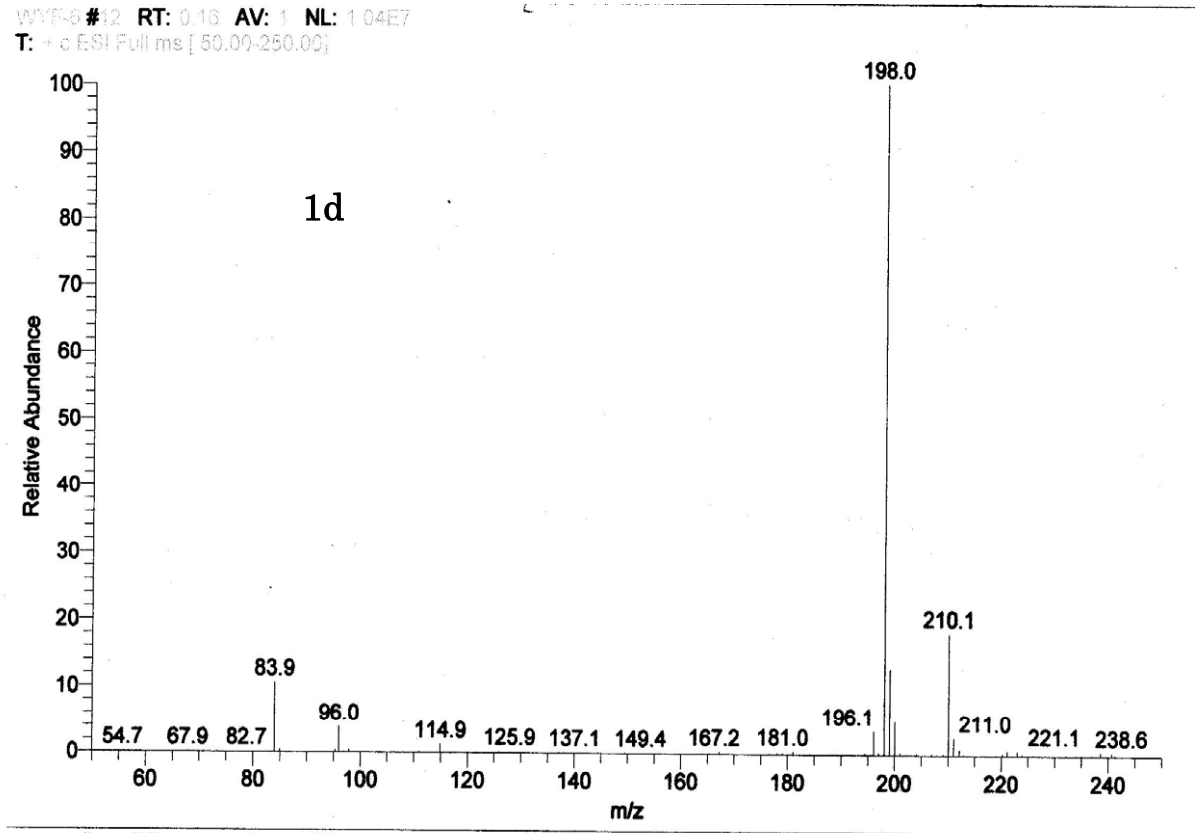
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Relative Abundance
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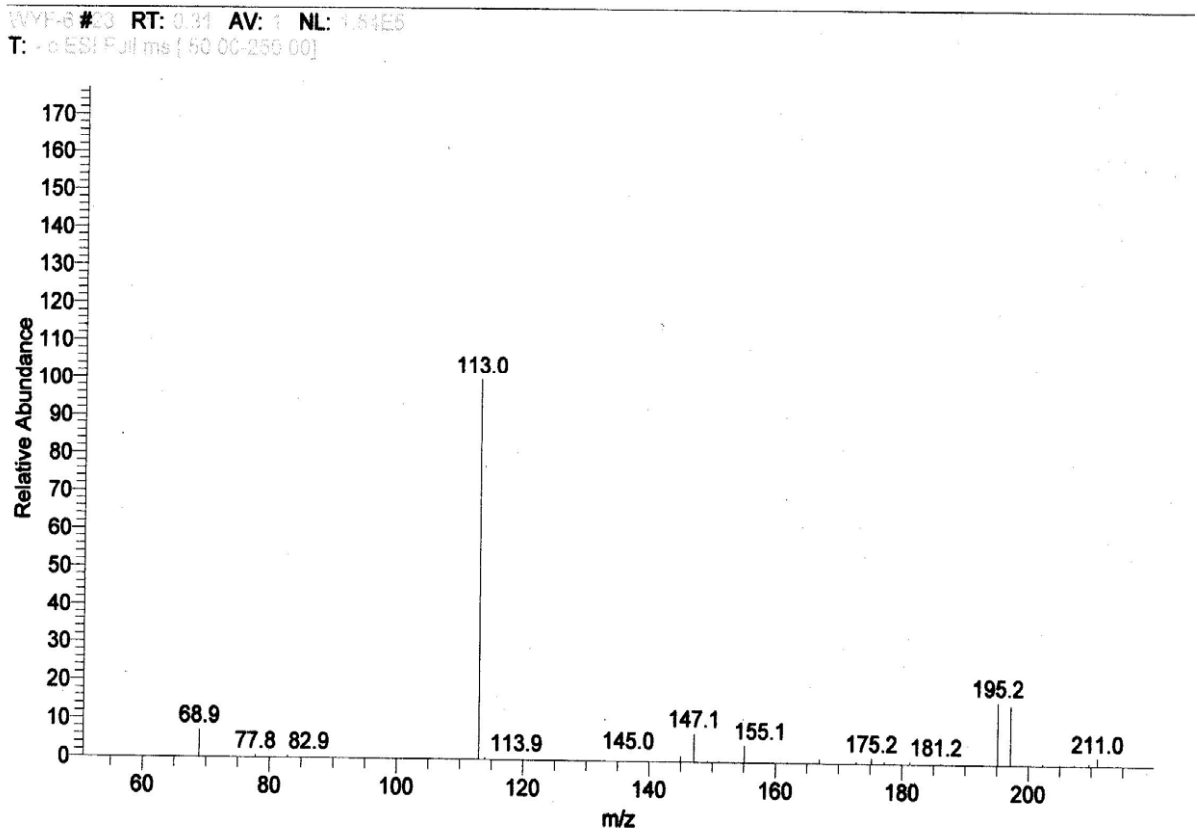
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Relative Abundance
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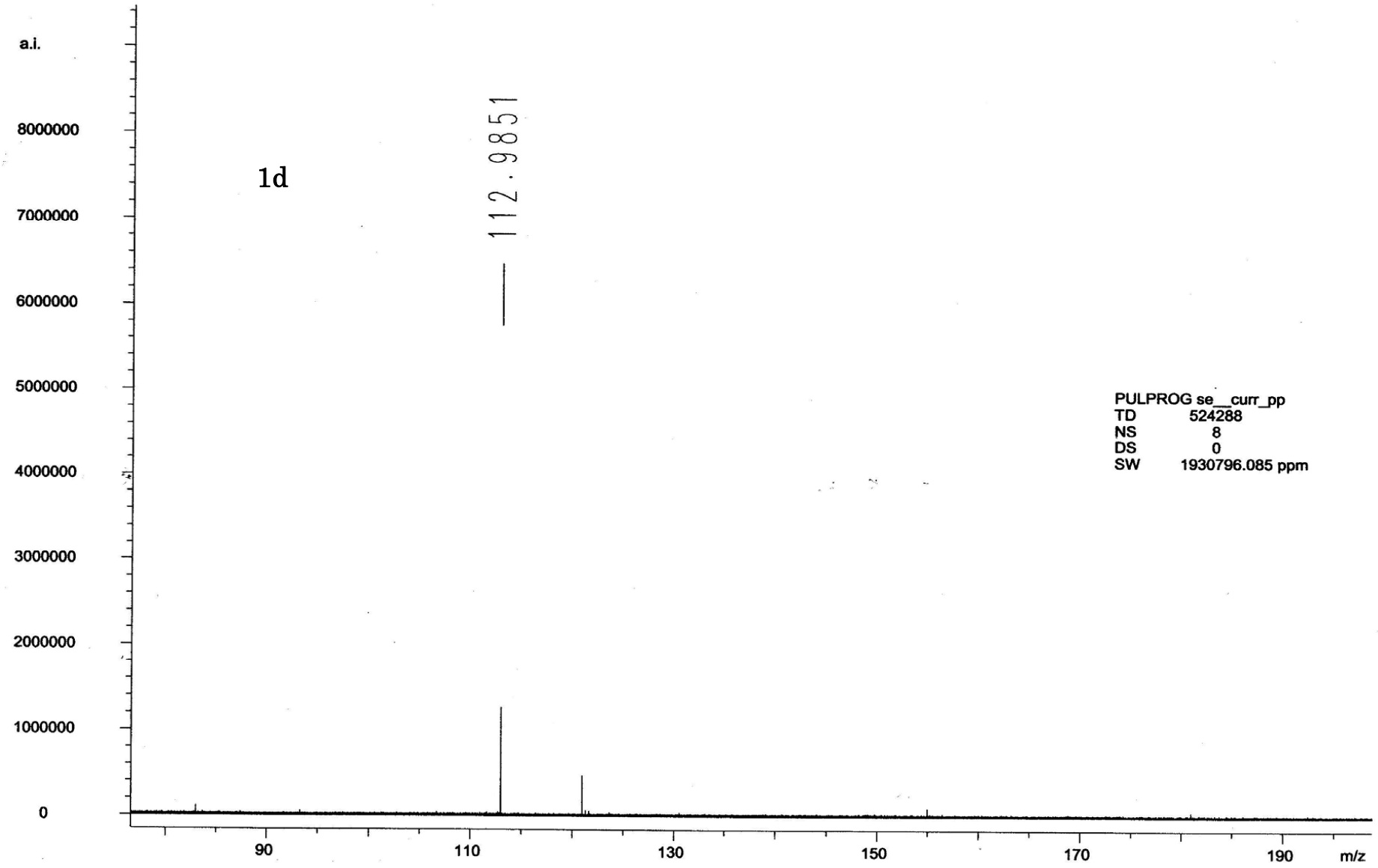
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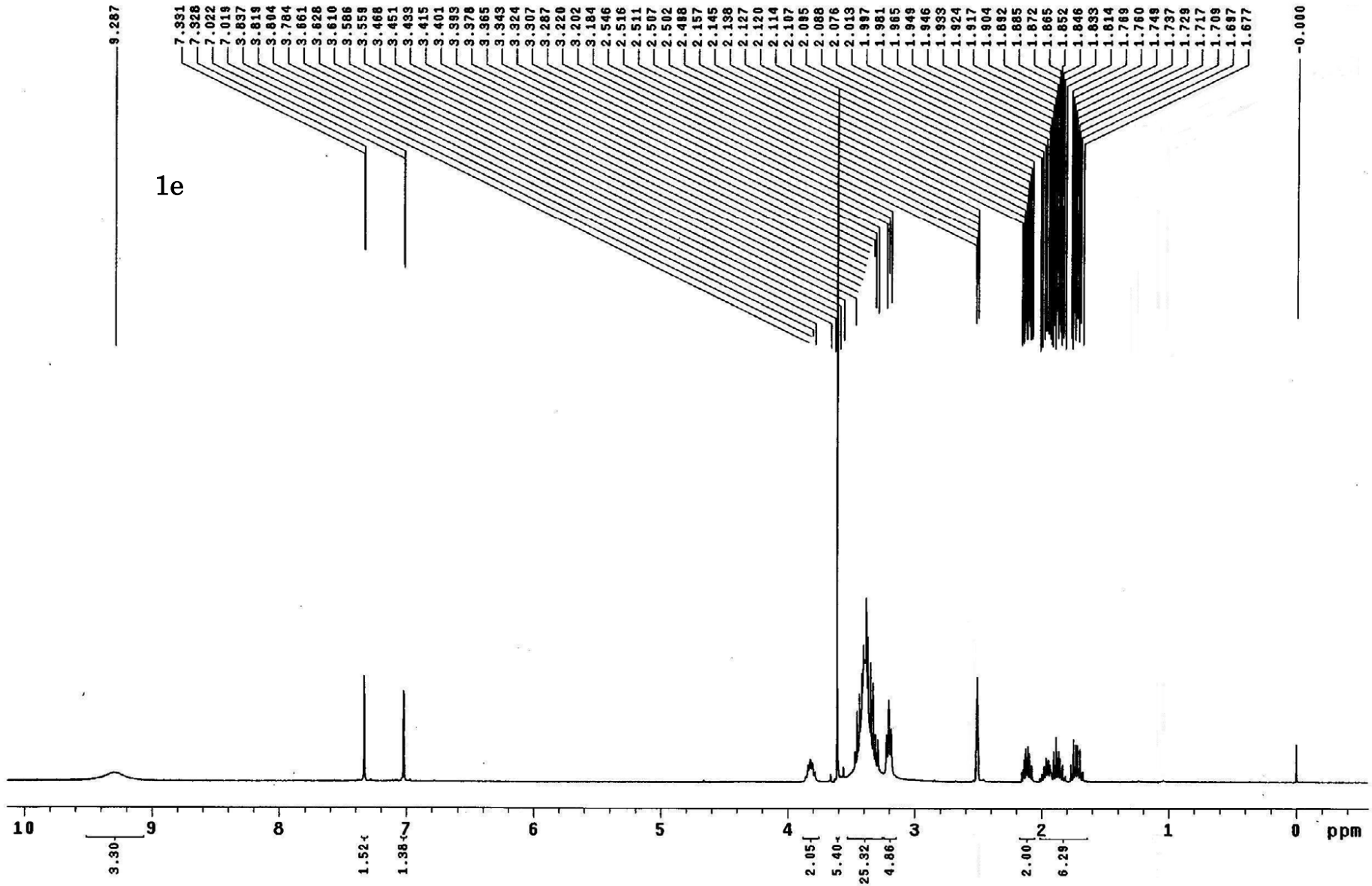
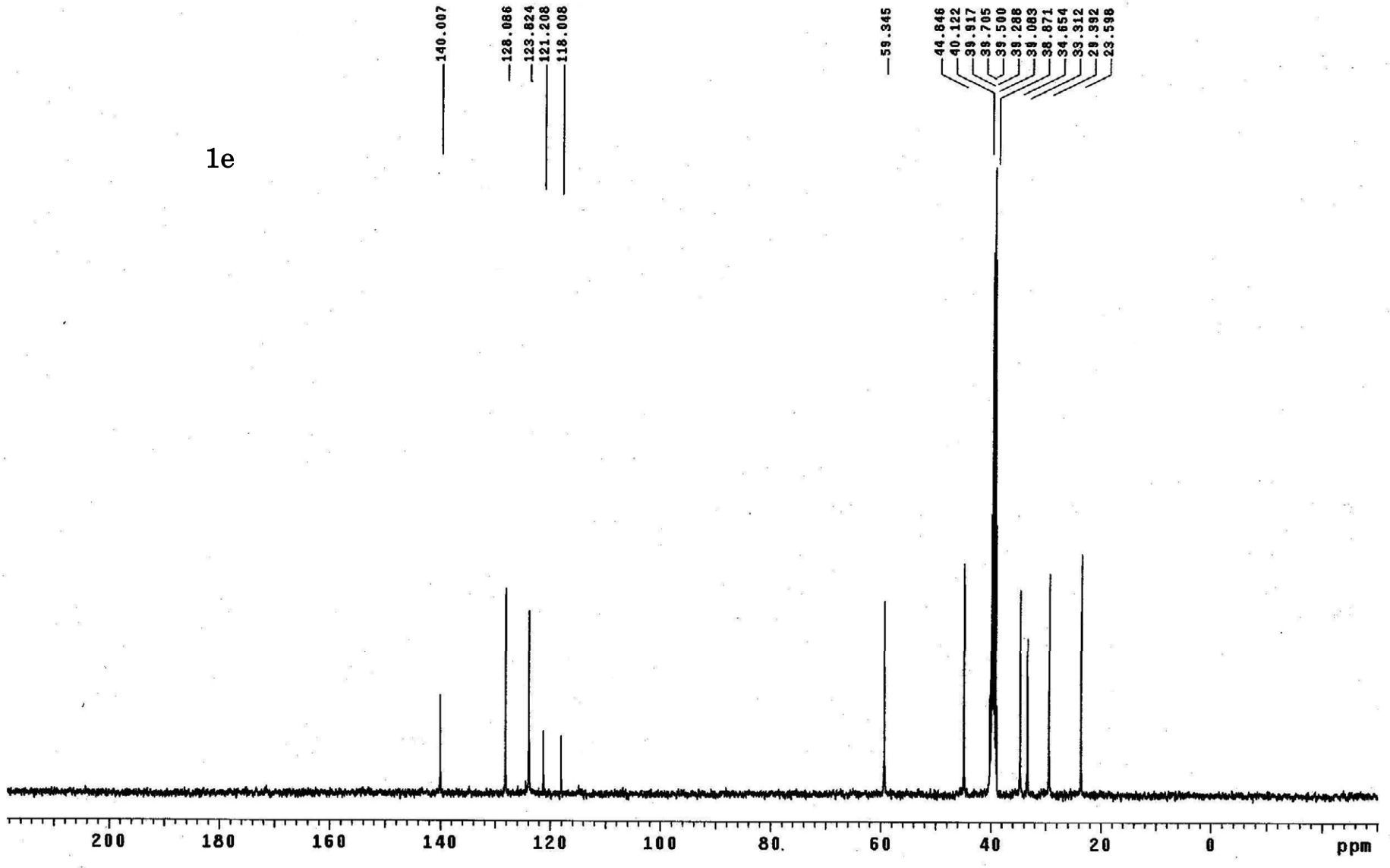
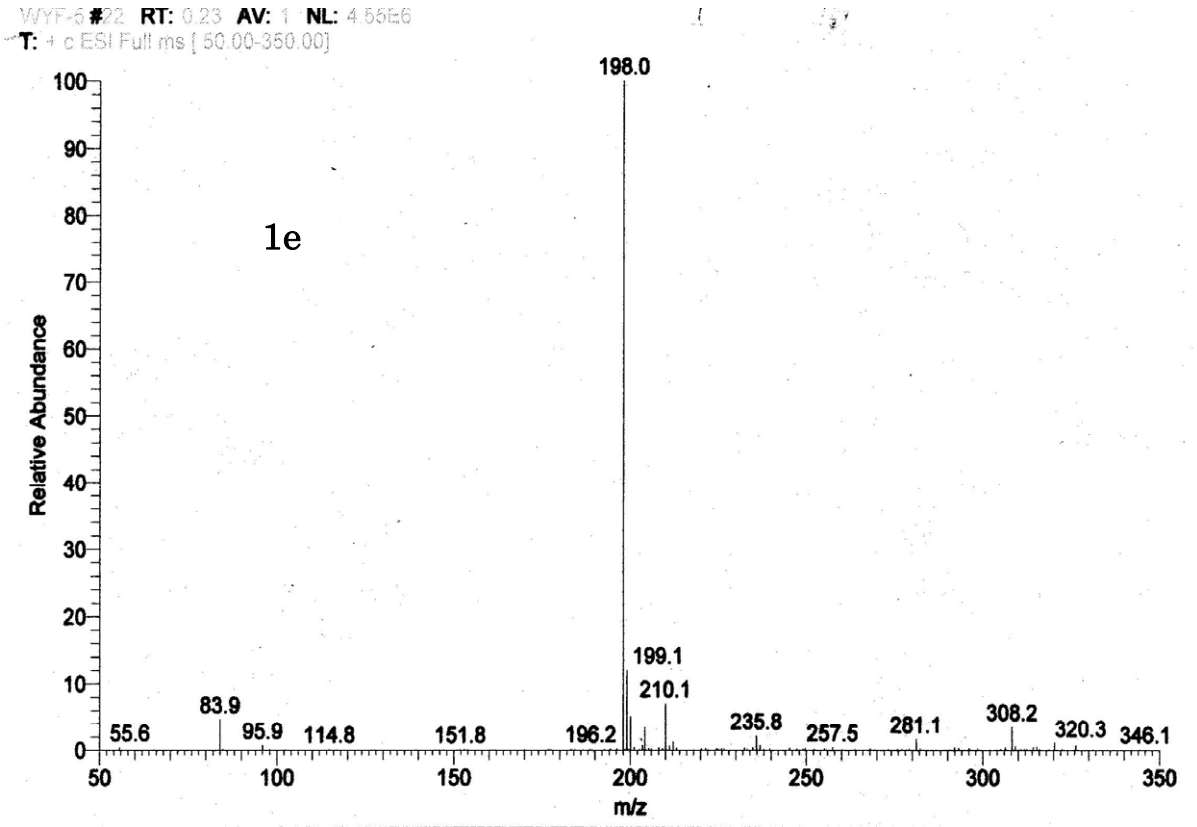
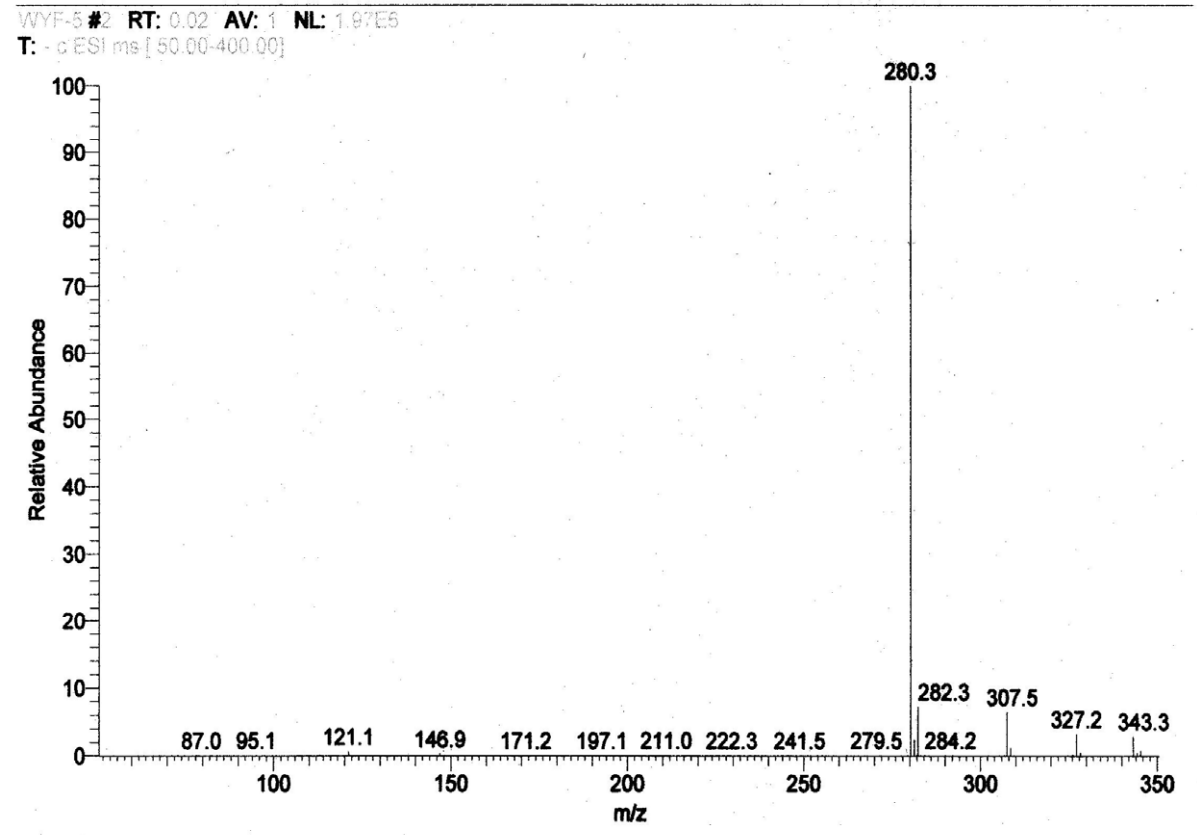
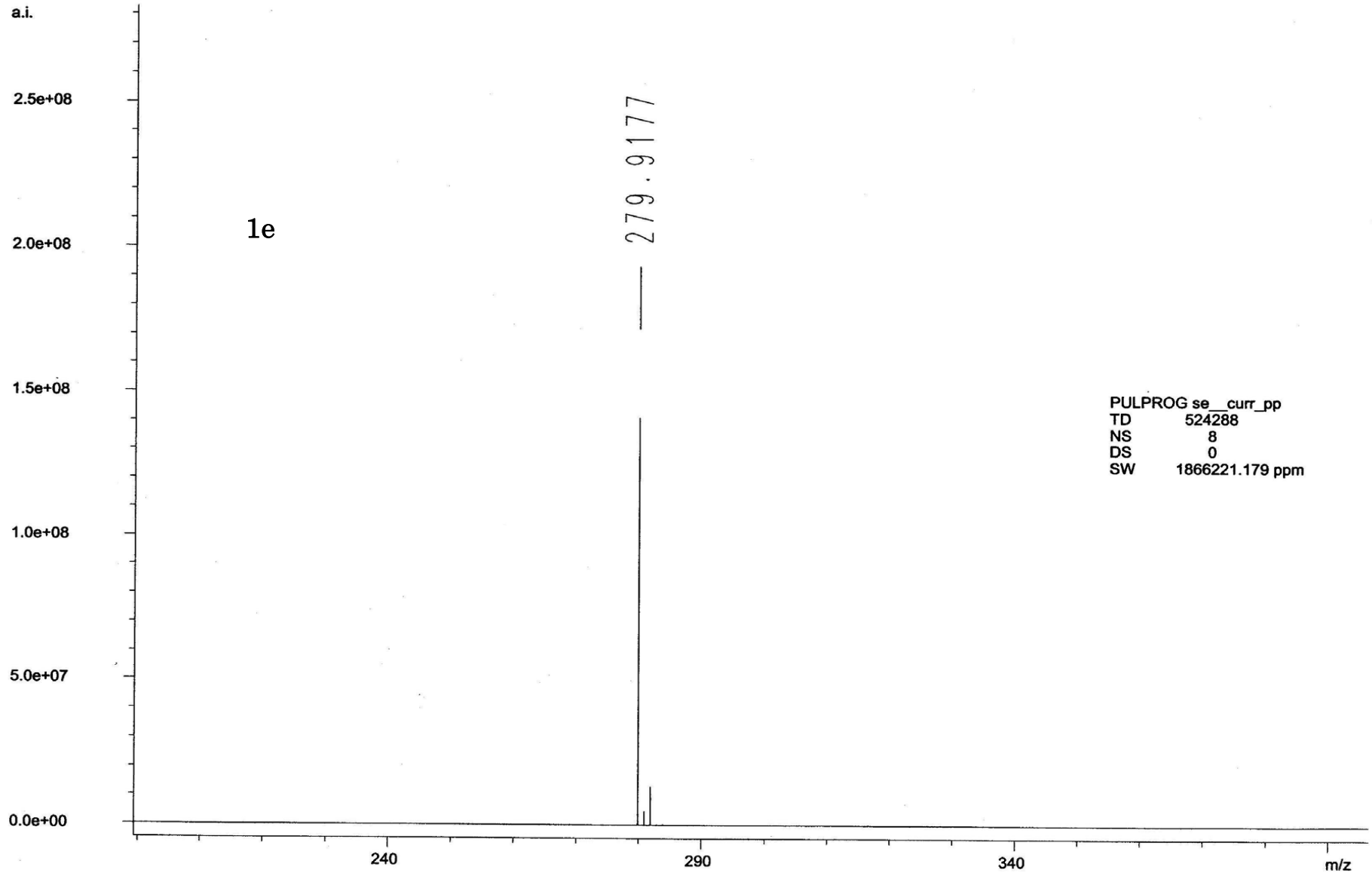
110
130
150
170
190
m/z

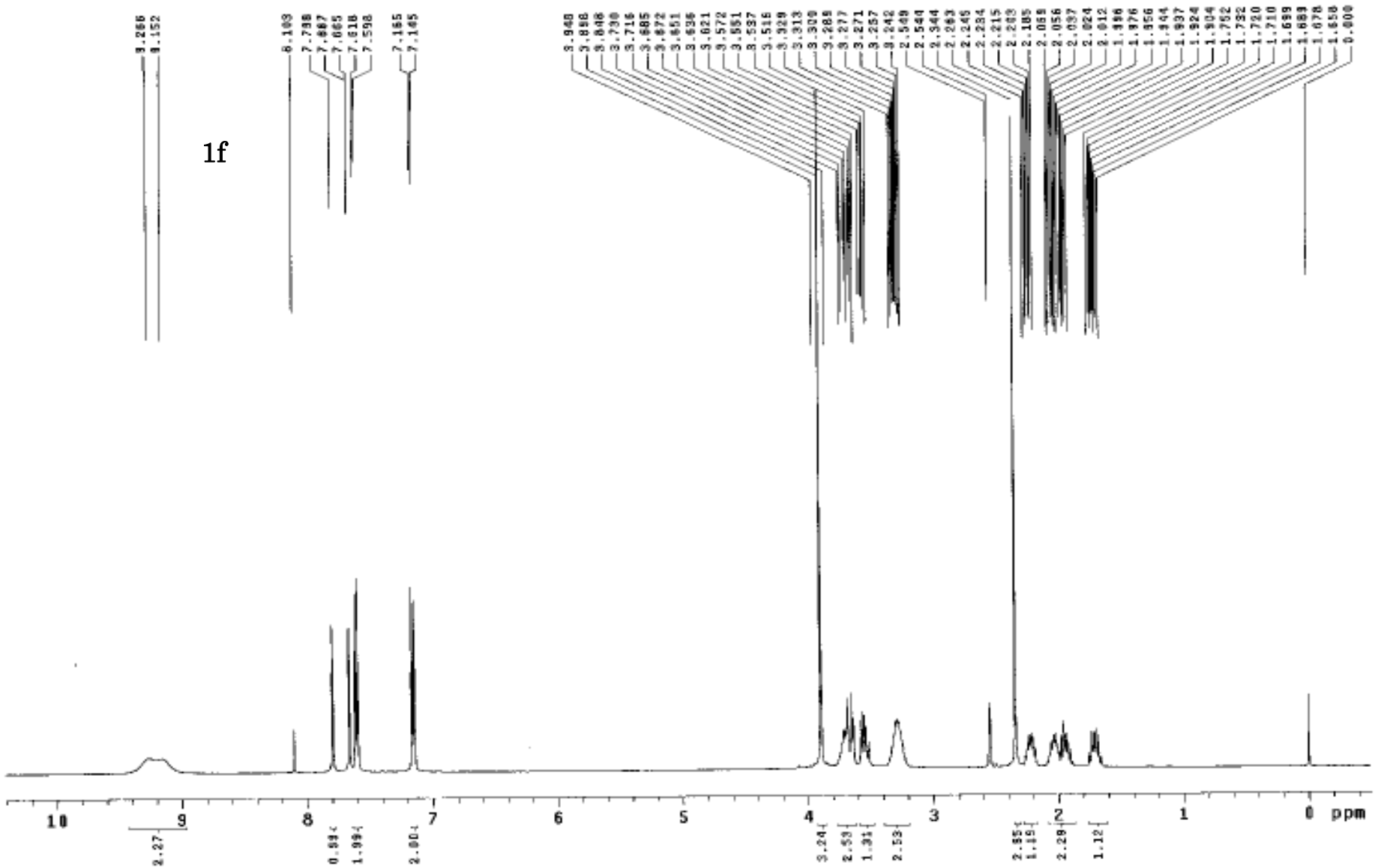

1e
9.287
7.331
7.328
7.022
7.019
3.837
3.819
3.804
3.784
3.661
3.628
3.610
3.586
3.559
3.468
3.451
3.433
3.415
3.401
3.393
3.378
3.365
3.343
3.324
3.307
3.287
3.220
3.202
3.184
2.546
2.516
2.511
2.507
2.502
2.488
2.157
2.145
2.138
2.127
2.120
2.114
2.107
2.095
2.088
2.076
2.013
1.987
1.981
1.965
1.949
1.946
1.933
1.924
1.917
1.904
1.892
1.885
1.872
1.865
1.852
1.846
1.833
1.814
1.769
1.760
1.749
1.737
1.729
1.717
1.709
1.687
1.677
-0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
3.30
1.52
1.38
2.05
5.40
25.32
4.86
2.00
6.29

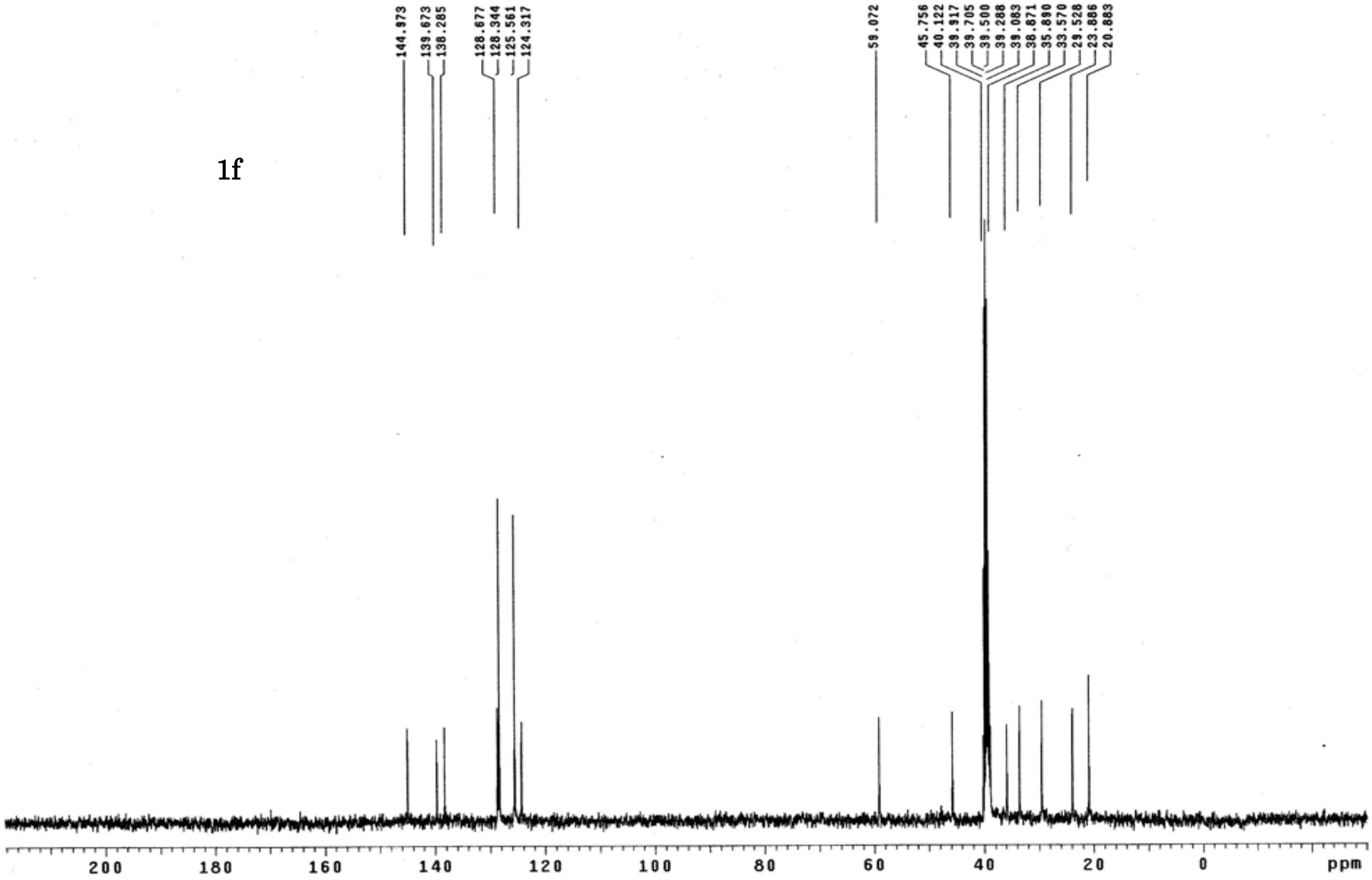

1e
140.007
128.086
123.824
121.208
118.008
59.345
44.846
40.122
39.917
39.705
39.500
39.288
39.083
38.871
34.654
33.312
29.392
23.598
200
180
160
140
120
100
80
60
40
20
0
ppm

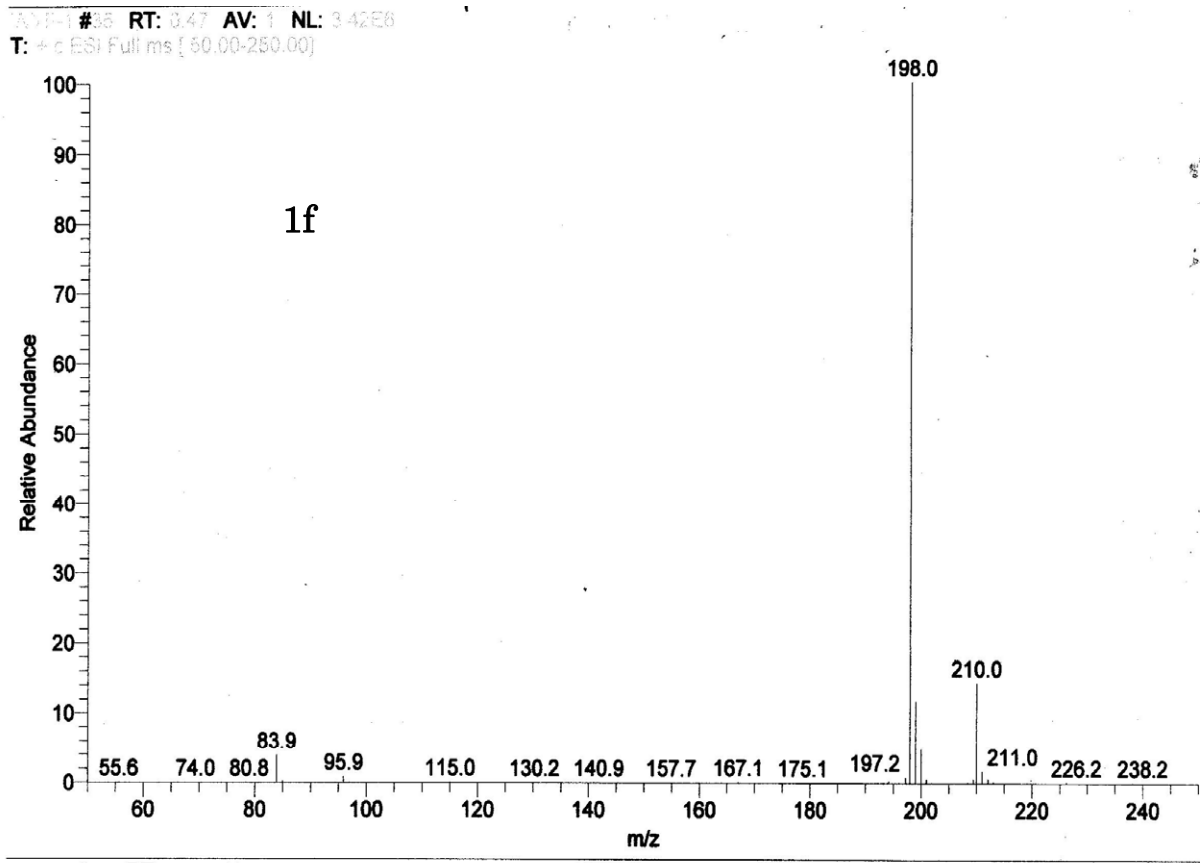

WYF-6 #22 RT: 0.23 AV: 1 NL: 4.55E6
T: + c ESI Full ms [50.00-350.00]
1e
198.0
199.1
210.1
83.9
55.6
95.9
114.8
151.8
196.2
235.8
257.5
281.1
308.2
320.3
346.1
Relative Abundance
m/z

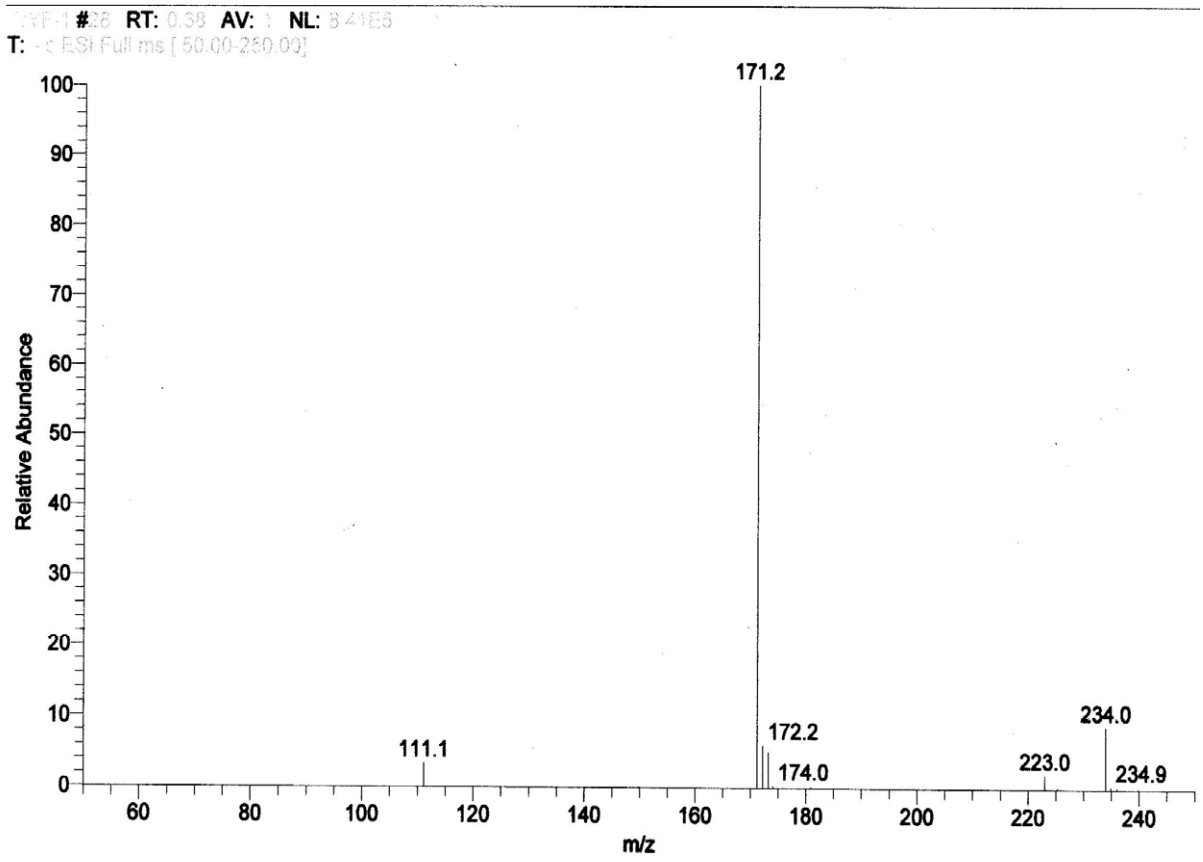

WYF-5 #2 RT: 0.02 AV: 1 NL: 1.97E5
T: - c ESI ms [50.00-400.00]
280.3
282.3
307.5
327.2
343.3
87.0
95.1
121.1
146.9
171.2
197.1
211.0
222.3
241.5
279.5
284.2
Relative Abundance
m/z

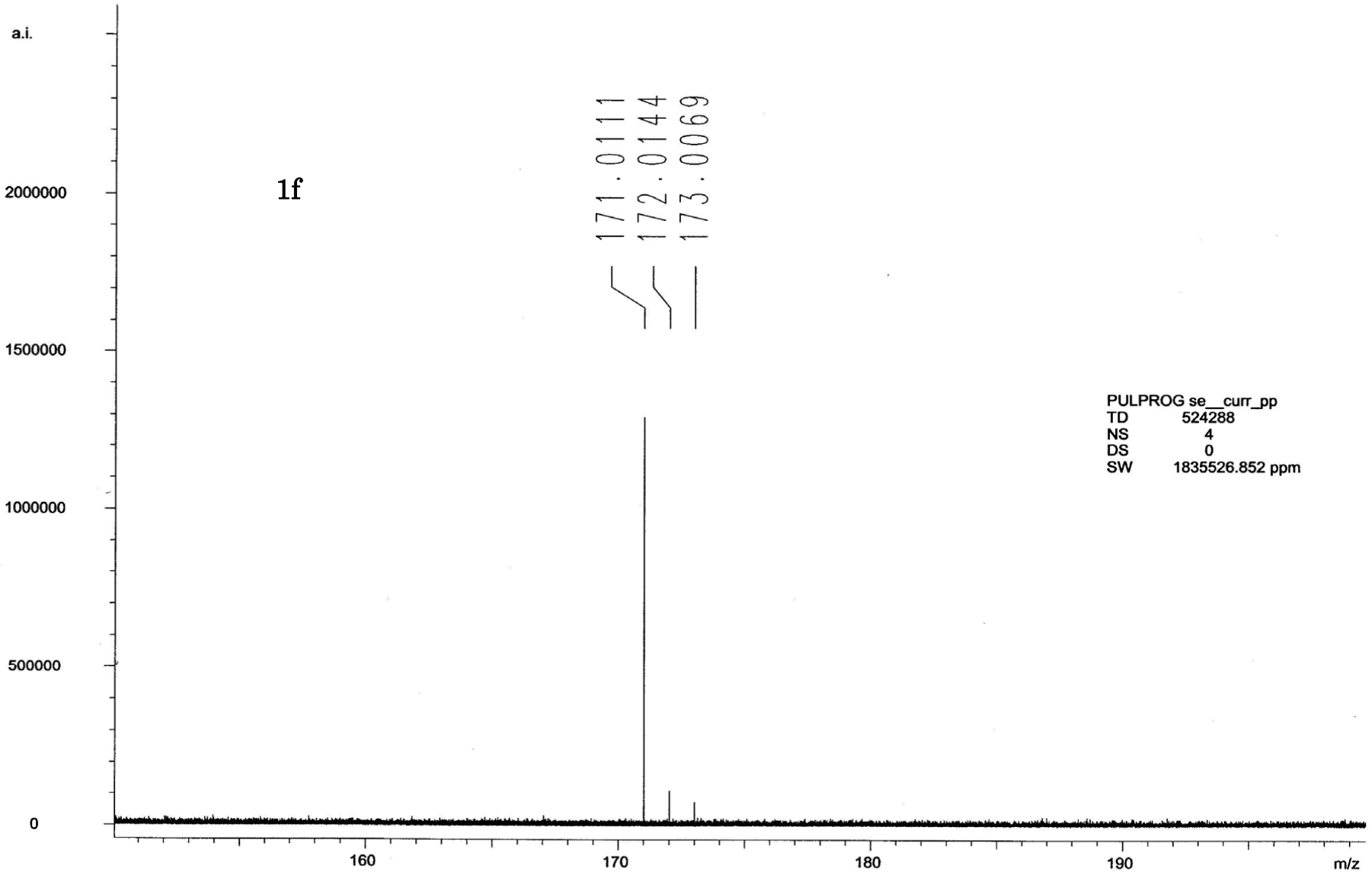

a.i.
2.5e+08
2.0e+08
1.5e+08
1.0e+08
5.0e+07
0.0e+00
1e
279.9177
PULPROG se__curr_pp
TD 524288
NS 8
DS 0
SW 1866221.179 ppm
240
290
340
m/z

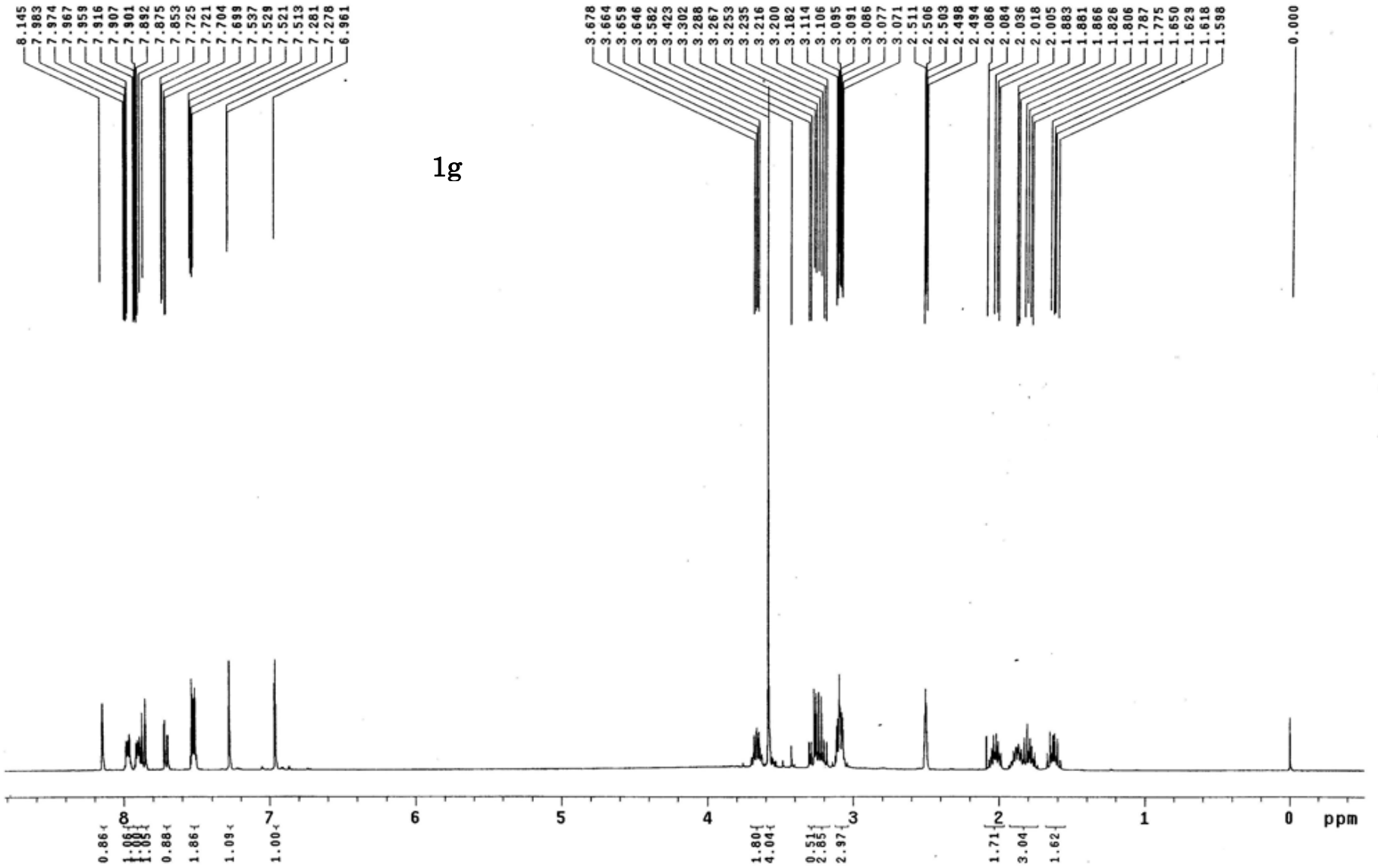

1f
9.266
9.152
8.103
7.738
7.687
7.665
7.618
7.598
7.165
7.145
3.948
3.888
3.848
3.730
3.716
3.685
3.672
3.651
3.636
3.621
3.572
3.551
3.537
3.516
3.329
3.313
3.309
3.288
3.277
3.271
3.257
3.242
2.569
2.544
2.344
2.263
2.245
2.234
2.215
2.203
2.185
2.059
2.056
2.037
2.024
2.012
1.996
1.976
1.956
1.944
1.937
1.924
1.904
1.752
1.732
1.720
1.710
1.699
1.689
1.678
1.658
0.000
10
9
8
7
6
5
4
3
2
1
0 ppm
2.27
0.99
1.99
2.00
3.24
2.53
1.31
2.53
2.85
1.85
2.28
1.12

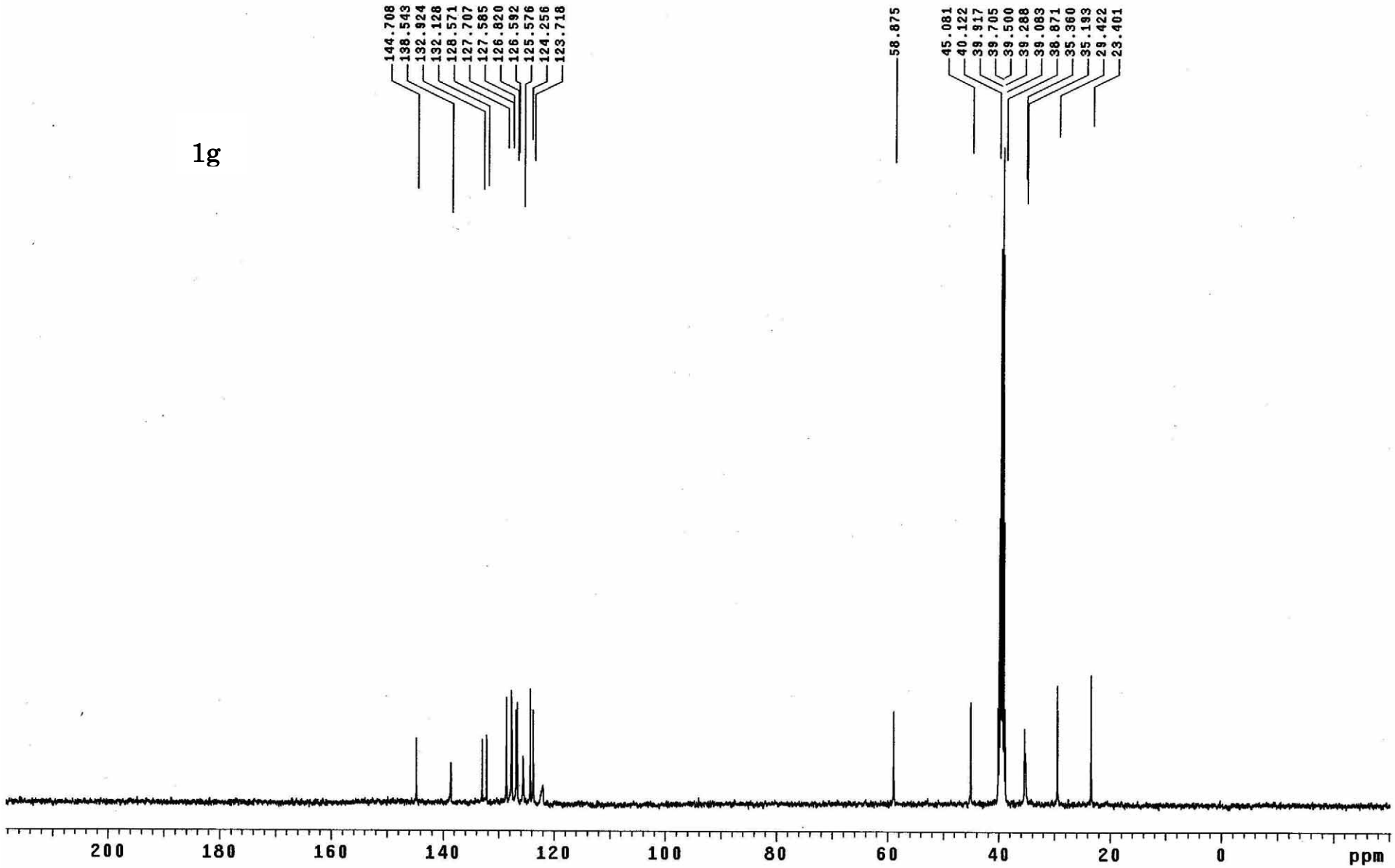

1f
144.873
139.673
138.285
128.677
128.344
125.561
124.317
59.072
45.756
40.122
39.917
39.705
39.500
39.288
39.083
38.871
35.880
33.570
29.528
23.886
20.883
200
180
160
140
120
100
80
60
40
20
0
ppm

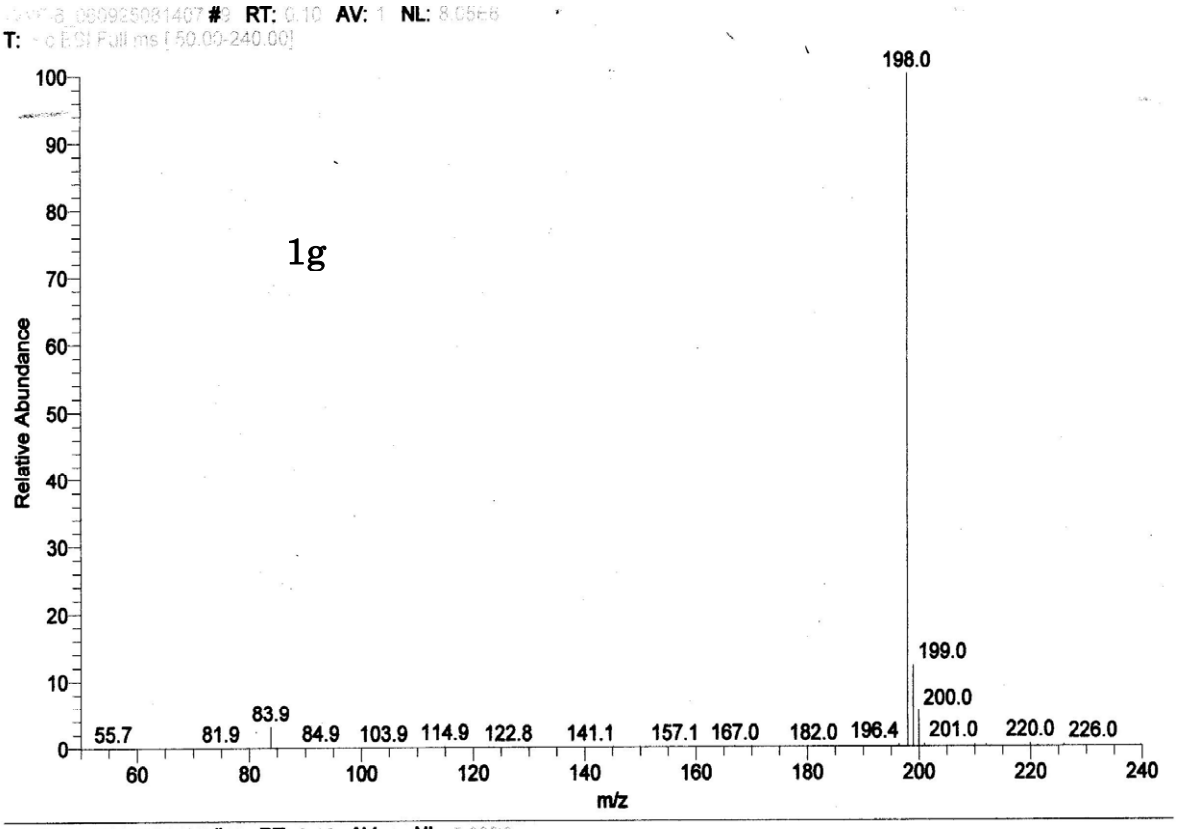

RT: 0.47 AV: 1 NL: 3.42E6
T: + c ESI Full ms [50.00-250.00]
1f
198.0
210.0
83.9
55.6
74.0
80.8
95.9
115.0
130.2
140.9
157.7
167.1
175.1
197.2
211.0
226.2
238.2
Relative Abundance
m/z

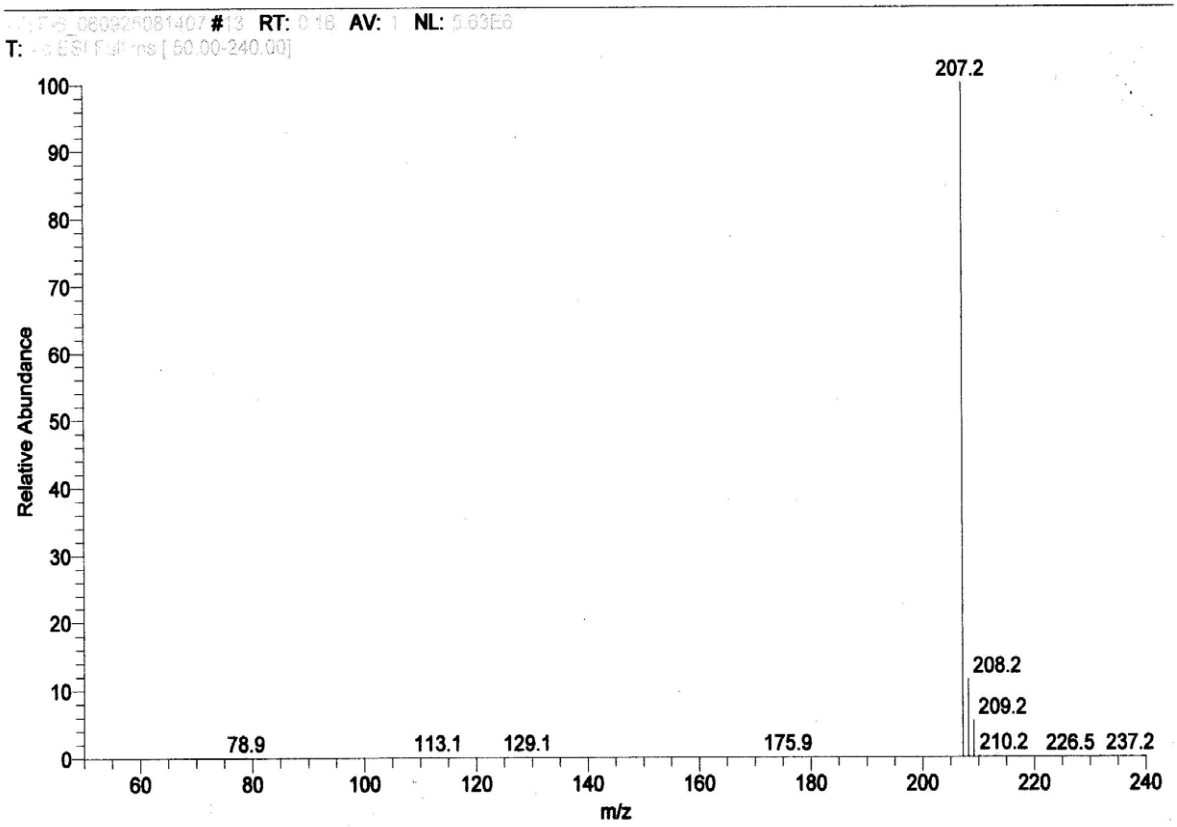

RT: 0.38 AV: 1 NL: 8.41E5
T: + c ESI Full ms [50.00-250.00]
171.2
111.1
172.2
174.0
223.0
234.0
234.9
Relative Abundance
m/z

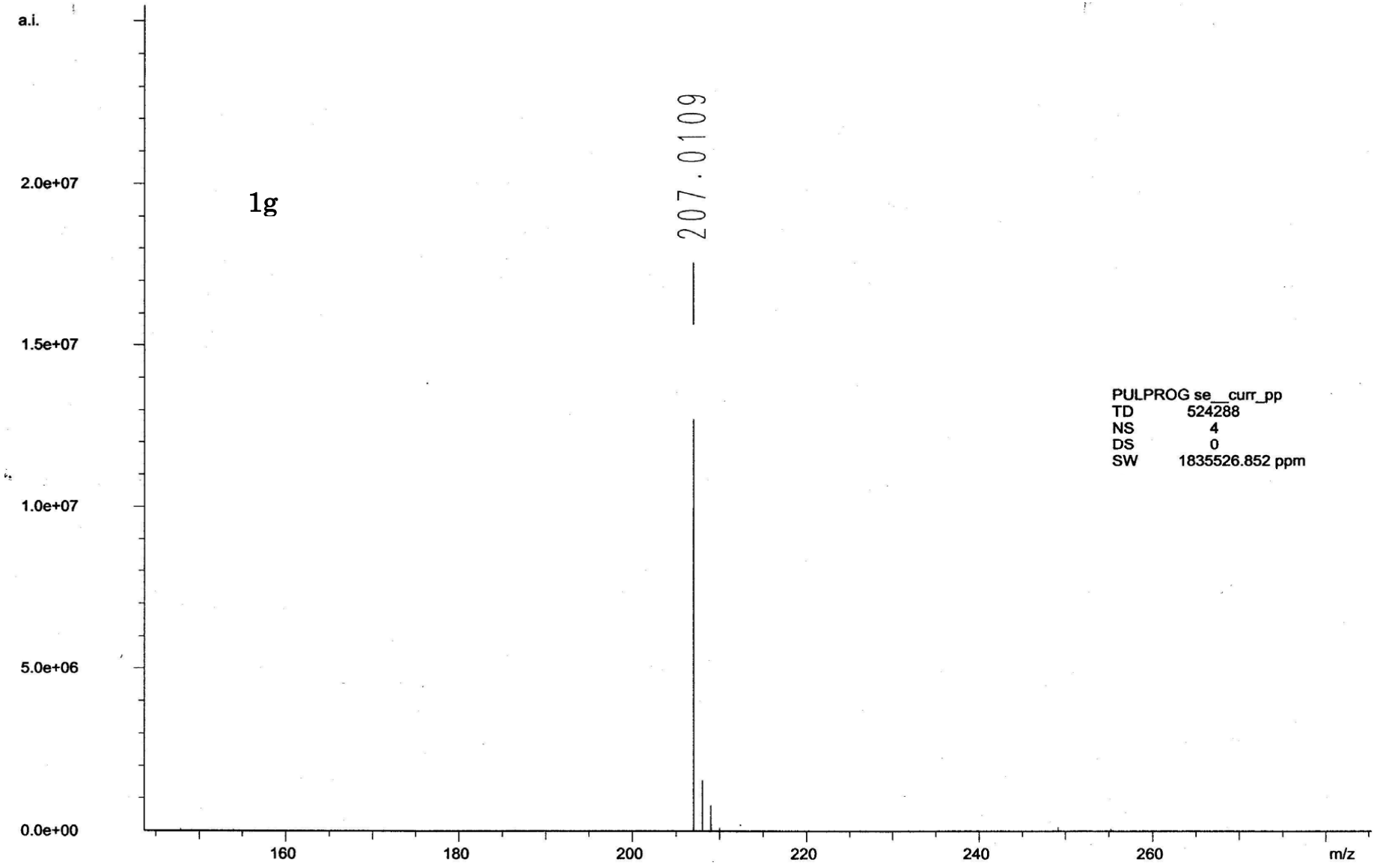

a.i.
2000000
1500000
1000000
500000
0
1f
171.0111
172.0144
173.0069
PULPROG se__curr_pp
TD 524288
NS 4
DS 0
SW 1835526.852 ppm
160
170
180
190
m/z

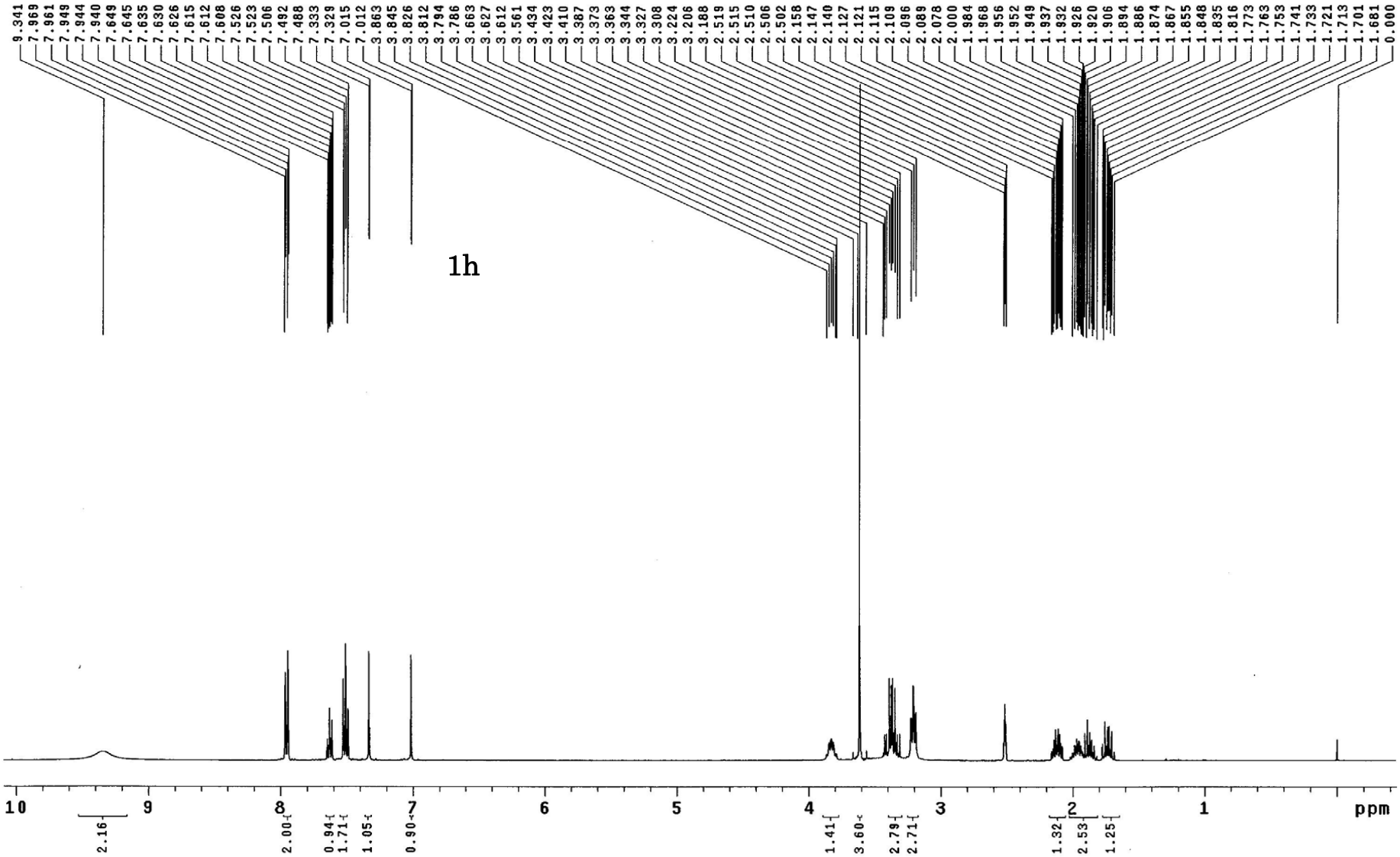

1g
8.145
7.983
7.974
7.967
7.959
7.916
7.907
7.901
7.892
7.875
7.853
7.725
7.721
7.704
7.699
7.537
7.529
7.521
7.513
7.281
7.278
6.961
3.678
3.664
3.659
3.646
3.582
3.423
3.302
3.288
3.267
3.253
3.235
3.216
3.200
3.182
3.114
3.106
3.095
3.091
3.086
3.077
3.071
2.511
2.506
2.503
2.498
2.494
2.086
2.084
2.036
2.018
2.005
1.883
1.881
1.866
1.826
1.806
1.787
1.775
1.650
1.629
1.618
1.598
0.000
ppm
0.86
1.06
1.00
1.05
0.88
1.86
1.09
1.00
1.80
4.04
0.51
2.85
2.97
1.71
3.04
1.62

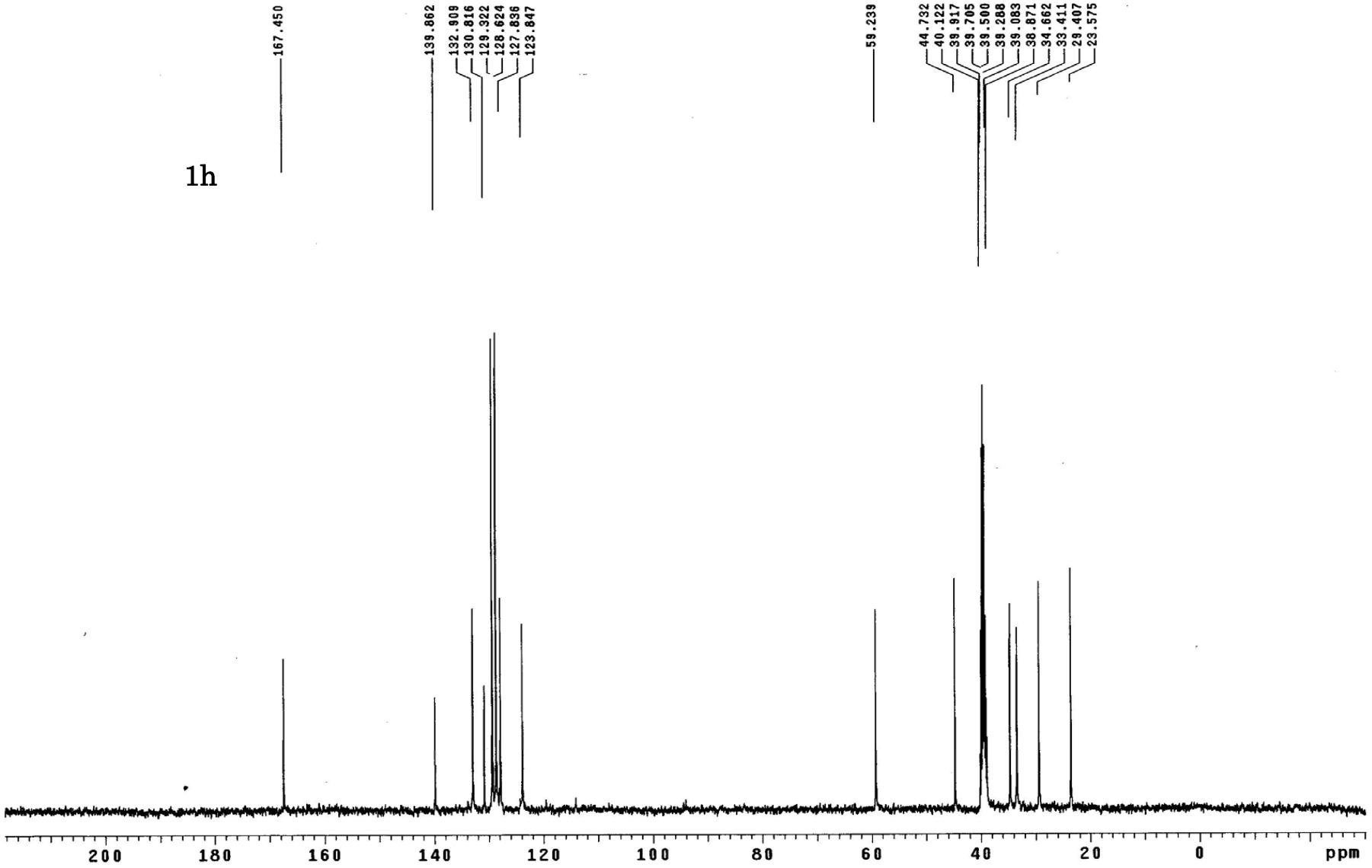

1g
144.708
138.543
132.924
132.128
128.571
127.707
127.585
126.820
126.592
125.576
124.256
123.718
58.875
45.081
40.122
39.917
39.705
39.500
39.288
39.083
38.871
35.360
35.193
29.422
23.401
200
180
160
140
120
100
80
60
40
20
0
ppm

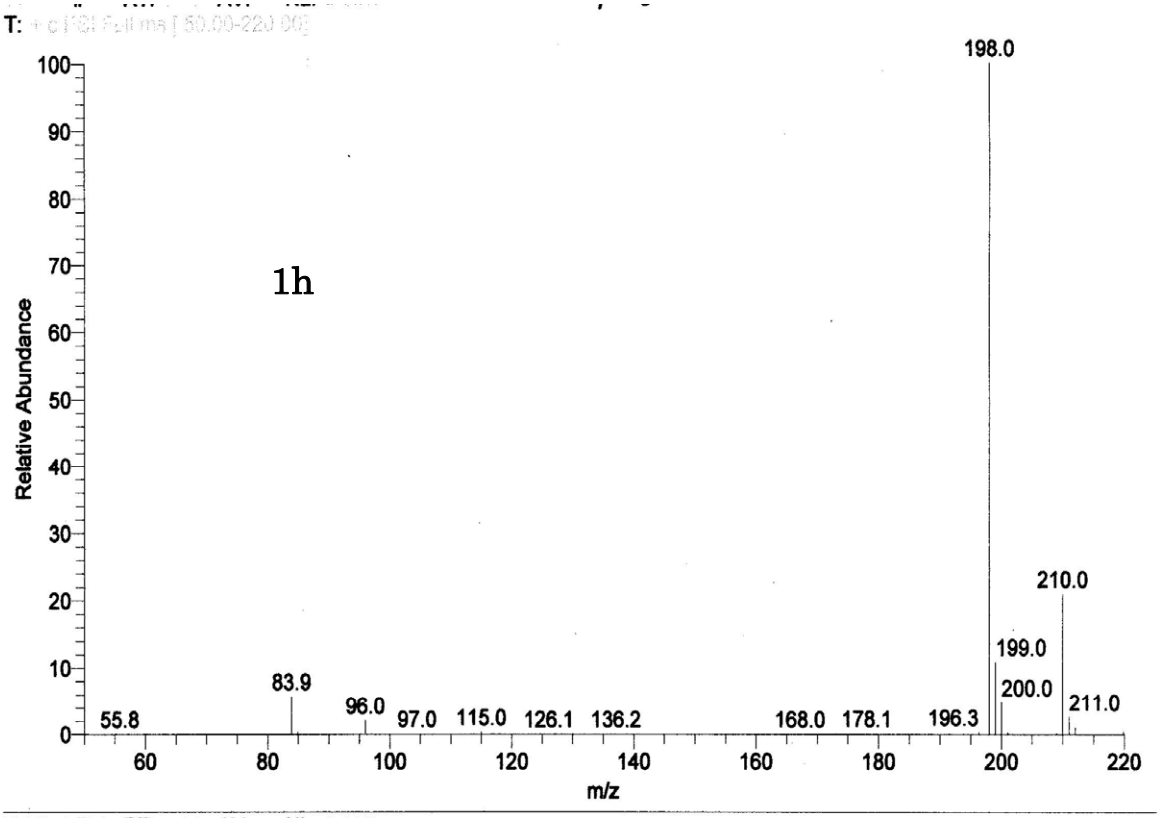

1g
198.0
199.0
200.0
201.0
83.9
55.7
81.9
84.9
103.9
114.9
122.8
141.1
157.1
167.0
182.0
196.4
220.0
226.0
Relative Abundance
m/z

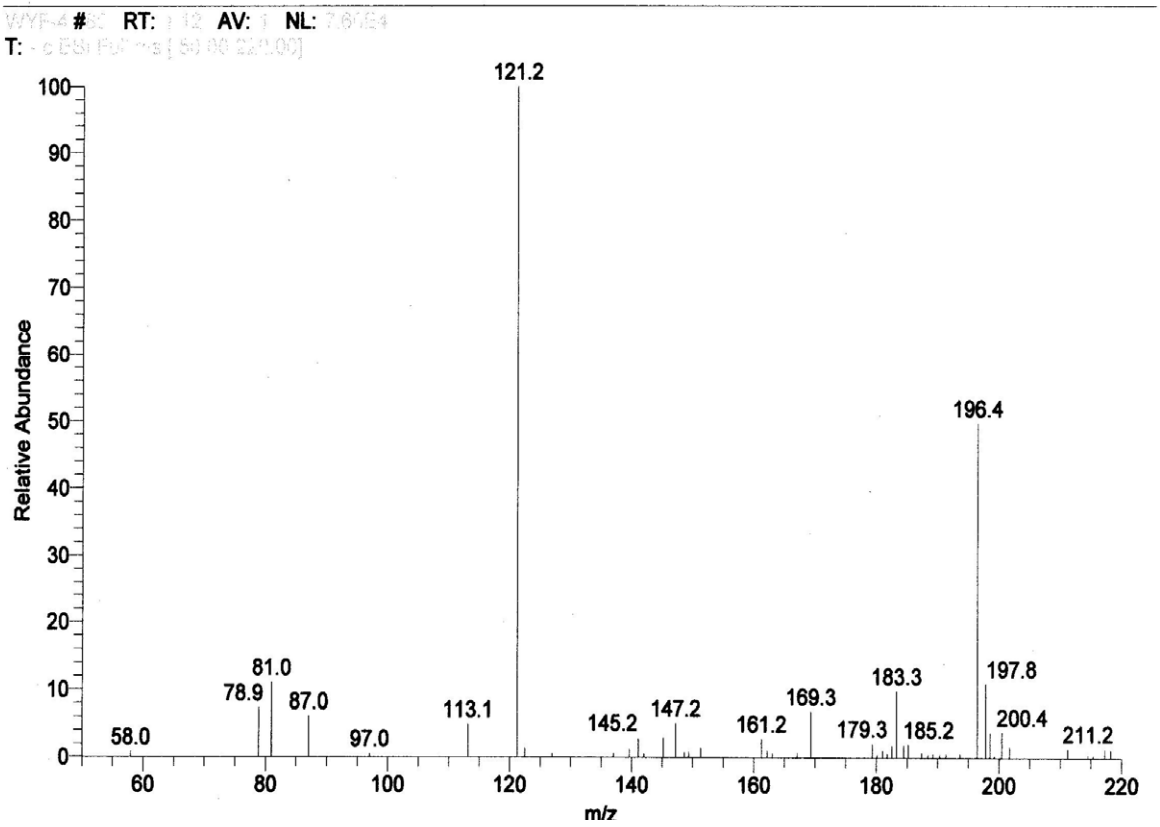

207.2
208.2
209.2
210.2
78.9
113.1
129.1
175.9
226.5
237.2
Relative Abundance
m/z

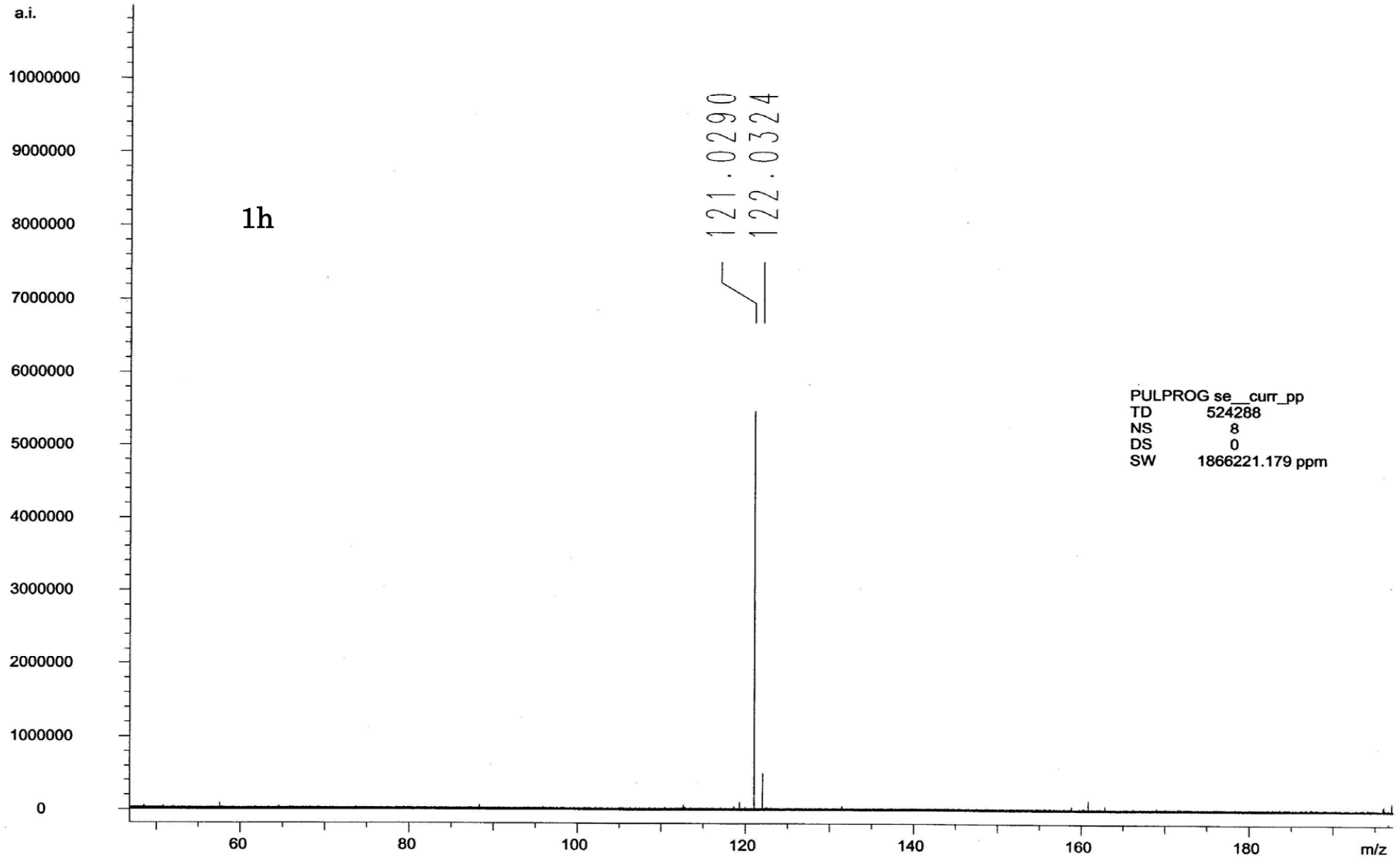

a.i.
2.0e+07
1.5e+07
1.0e+07
5.0e+06
0.0e+00
1g
207.0109
PULPROG se__curr_pp
TD 524288
NS 4
DS 0
SW 1835526.852 ppm
160
180
200
220
240
260
m/z

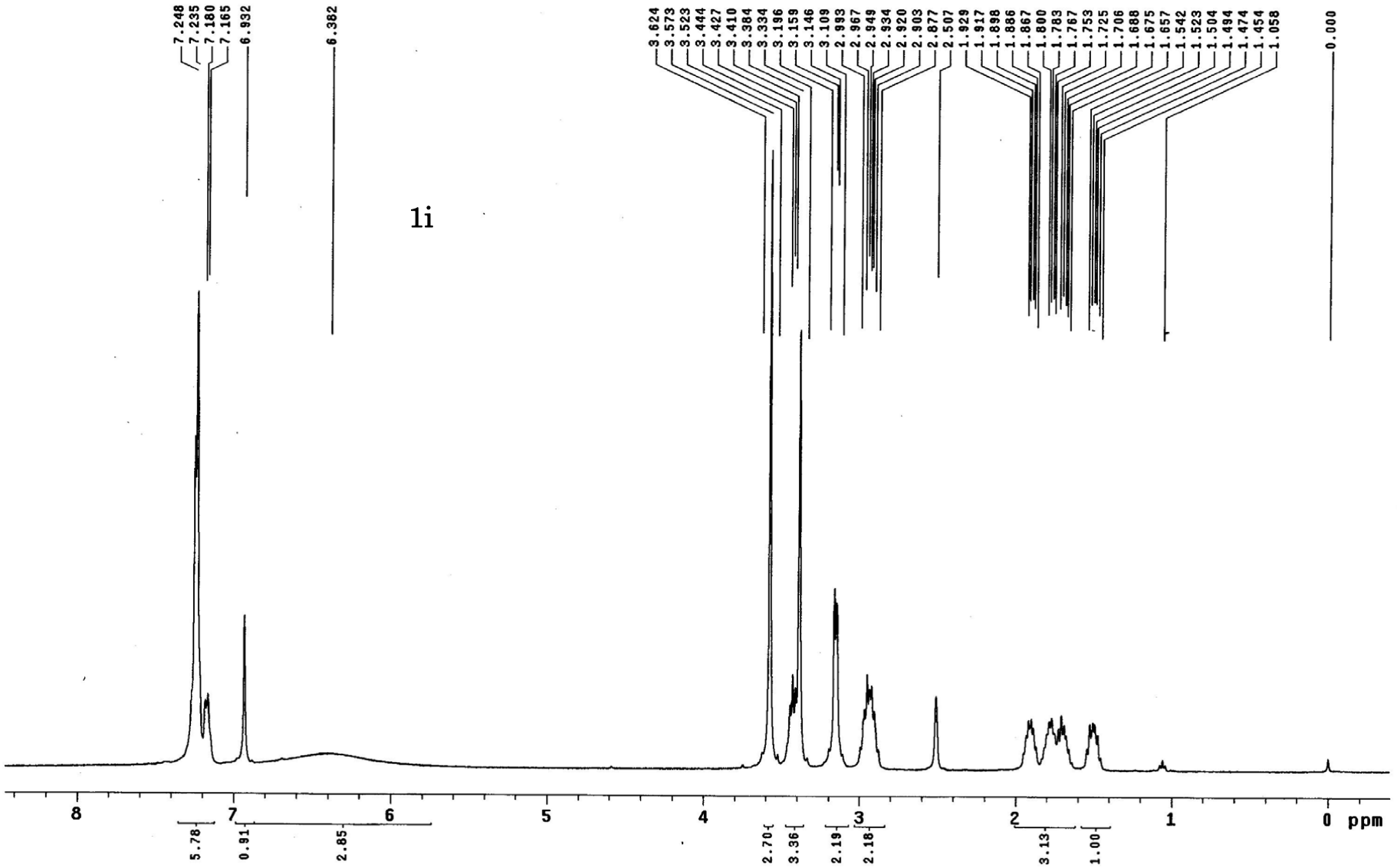

1h
9.341
7.969
7.961
7.949
7.944
7.940
7.649
7.645
7.635
7.630
7.626
7.615
7.612
7.608
7.526
7.523
7.506
7.492
7.488
7.333
7.329
7.015
7.012
3.863
3.845
3.826
3.812
3.794
3.786
3.663
3.627
3.612
3.561
3.434
3.423
3.410
3.387
3.373
3.363
3.344
3.327
3.308
3.224
3.206
3.188
2.519
2.515
2.510
2.506
2.502
2.158
2.147
2.140
2.127
2.121
2.115
2.109
2.096
2.089
2.078
2.000
1.984
1.968
1.956
1.952
1.949
1.937
1.932
1.926
1.920
1.906
1.894
1.886
1.874
1.867
1.855
1.848
1.835
1.816
1.773
1.763
1.753
1.741
1.733
1.721
1.713
1.701
1.681
0.000
10
9
8
7
6
5
4
3
2
1
ppm
2.16
2.00
0.94
1.71
1.05
0.90
1.41
3.60
2.79
2.71
1.32
2.53
1.25

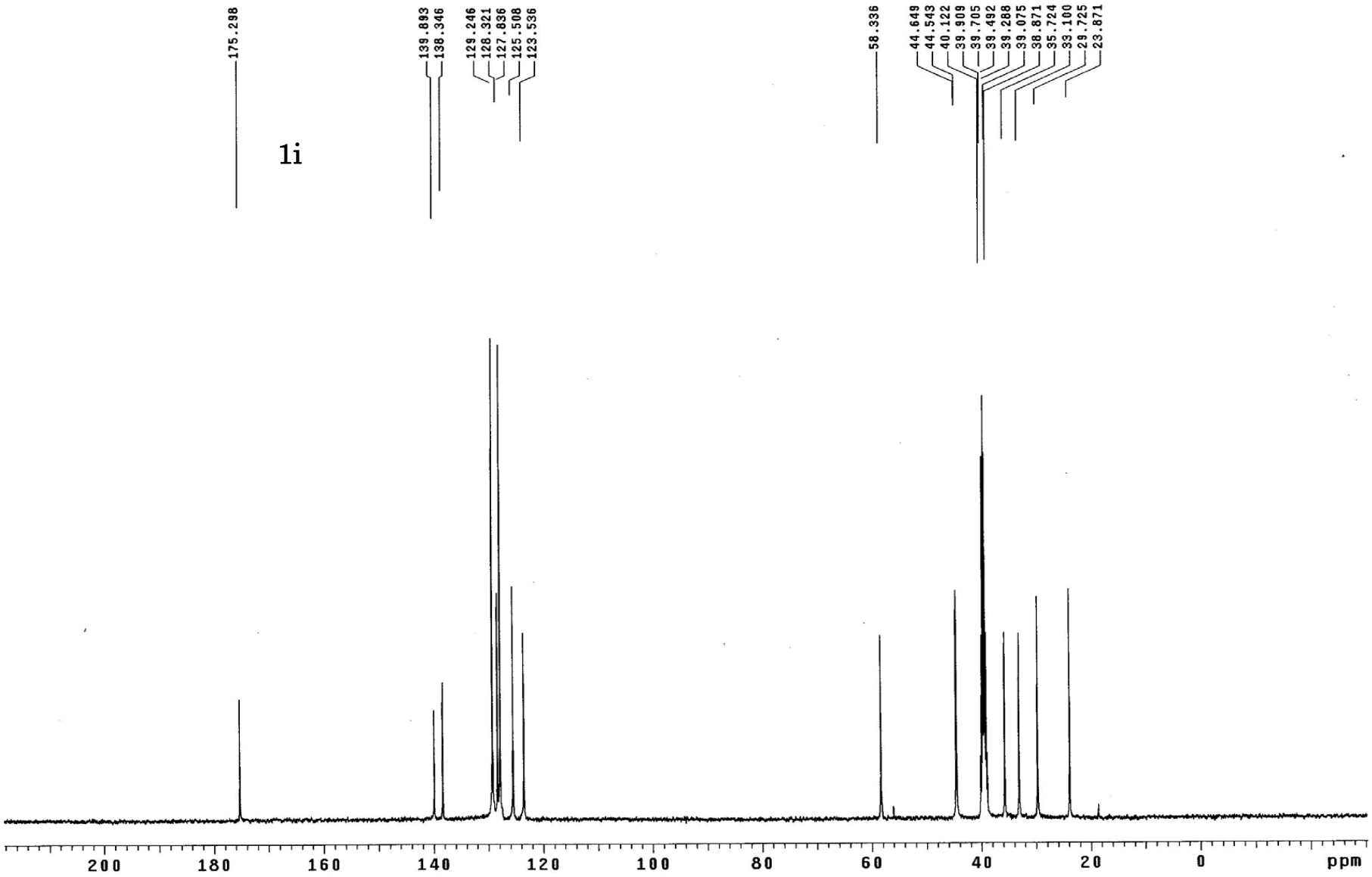

1h
167.450
139.862
132.909
130.816
129.322
128.624
127.836
123.847
59.239
44.732
40.122
39.917
39.705
39.500
39.288
39.083
38.871
34.662
33.411
29.407
23.575
200
180
160
140
120
100
80
60
40
20
0
ppm

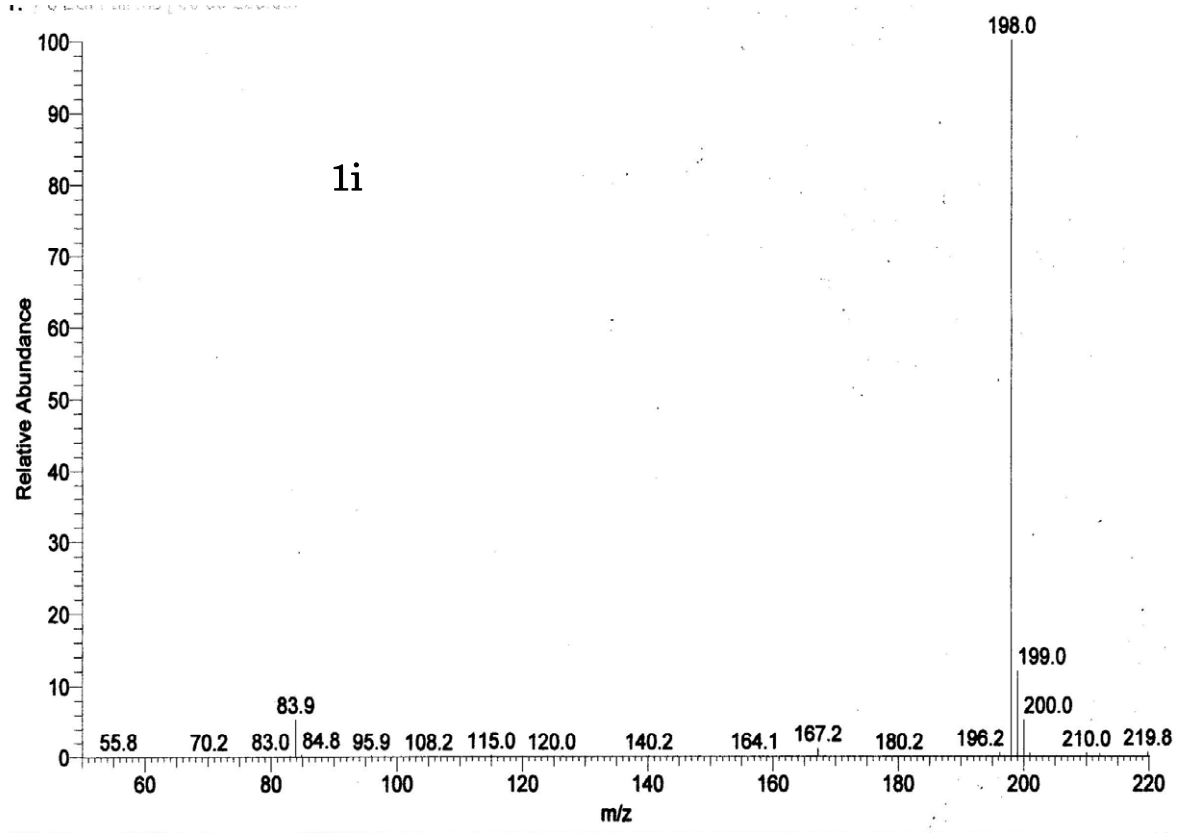

1h
Relative Abundance
m/z
198.0
210.0
199.0
200.0
211.0
83.9
96.0
55.8
97.0
115.0
126.1
136.2
168.0
178.1
196.3

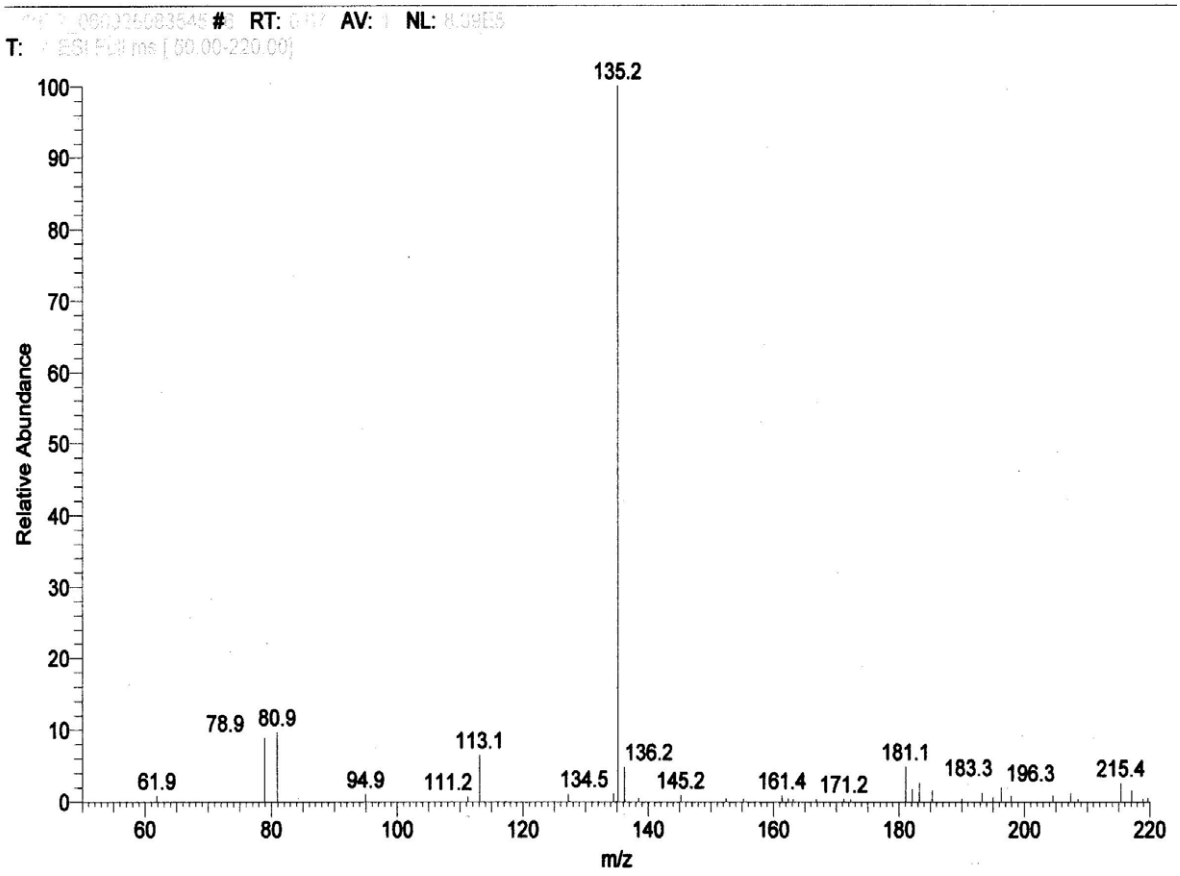

Relative Abundance
m/z
121.2
196.4
81.0
78.9
87.0
58.0
97.0
113.1
145.2
147.2
161.2
169.3
179.3
183.3
185.2
197.8
200.4
211.2

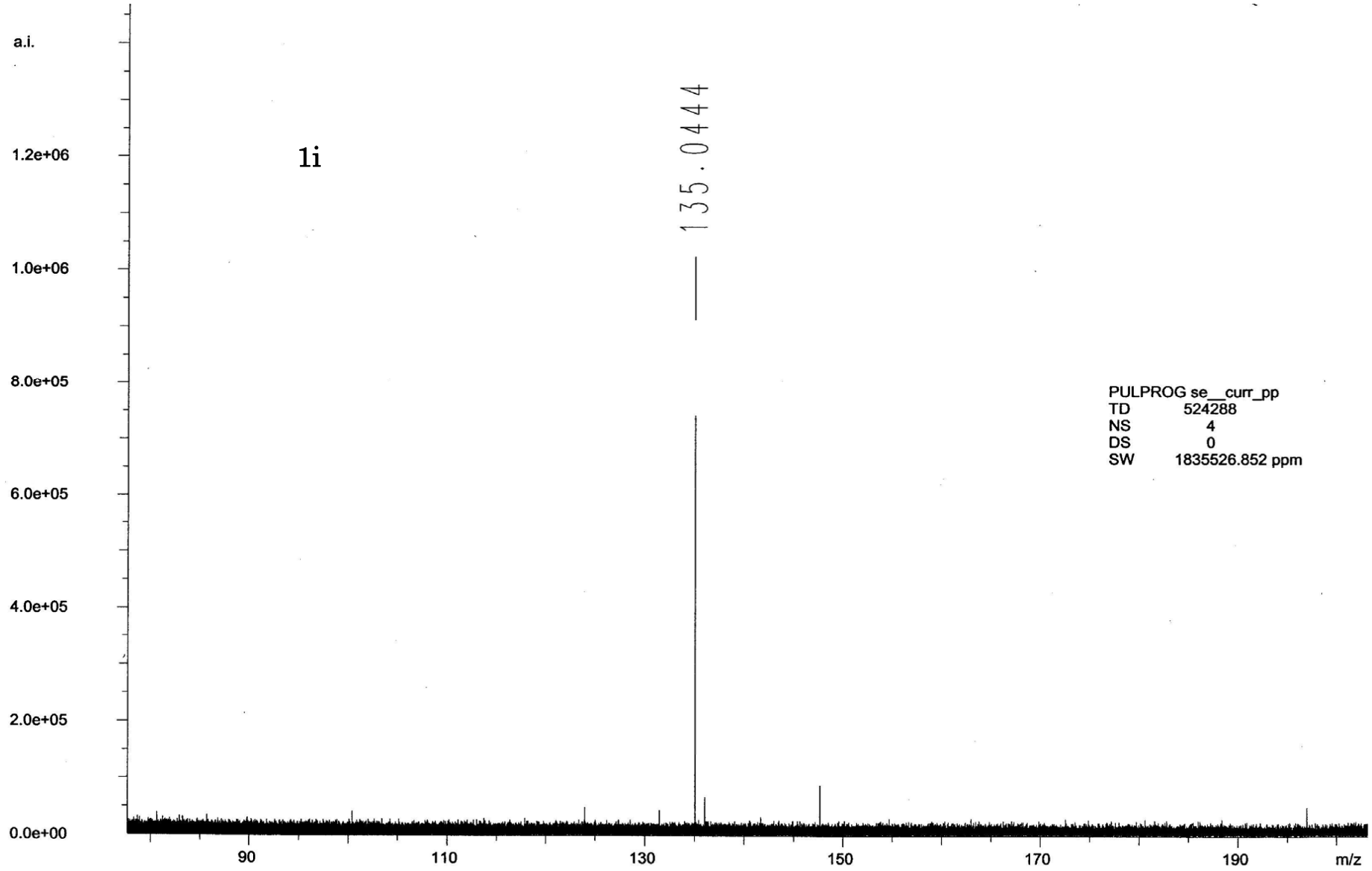

a.i.
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
1h
121.0290
122.0324
PULPROG se__curr_pp
TD 524288
NS 8
DS 0
SW 1866221.179 ppm
60
80
100
120
140
160
180
m/z

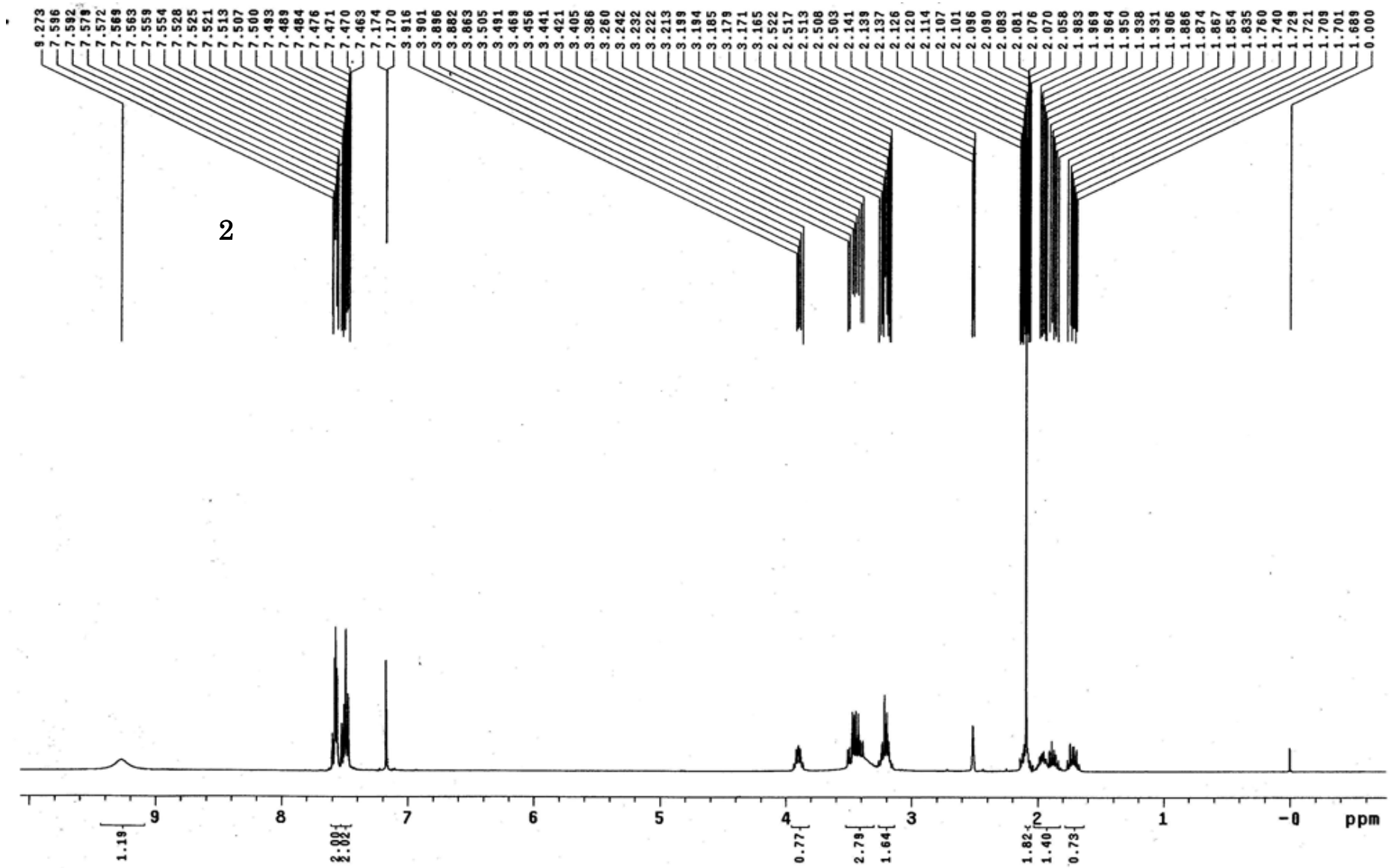

1i
7.248
7.235
7.180
7.165
6.932
6.382
3.624
3.573
3.523
3.444
3.427
3.410
3.384
3.334
3.196
3.159
3.146
3.109
2.993
2.967
2.949
2.934
2.920
2.903
2.877
2.507
1.929
1.917
1.898
1.886
1.867
1.800
1.783
1.767
1.753
1.725
1.706
1.688
1.675
1.657
1.542
1.523
1.504
1.494
1.474
1.454
1.058
0.000
8
7
6
5
4
3
2
1
0 ppm
5.78
0.91
2.85
2.70
3.36
2.19
2.18
3.13
1.00


1i
175.298
139.893
138.346
129.246
128.321
127.836
125.508
123.536
58.336
44.649
44.543
40.122
39.909
39.705
39.492
39.288
39.075
38.871
35.724
33.100
28.725
23.871
200
180
160
140
120
100
80
60
40
20
0
ppm


1i
198.0
199.0
200.0
83.9
55.8
70.2
83.0
84.8
95.9
108.2
115.0
120.0
140.2
164.1
167.2
180.2
196.2
210.0
219.8
Relative Abundance
m/z


135.2
78.9
80.9
113.1
61.9
94.9
111.2
134.5
136.2
145.2
161.4
171.2
181.1
183.3
196.3
215.4
Relative Abundance
m/z


a.i.
1i
135.0444
1.2e+06
1.0e+06
8.0e+05
6.0e+05
4.0e+05
2.0e+05
0.0e+00
90
110
130
150
170
190
m/z
PULPROG se__curr_pp
TD 524288
NS 4
DS 0
SW 1835526.852 ppm


9.273
7.596
7.592
7.579
7.572
7.569
7.563
7.559
7.554
7.528
7.525
7.521
7.513
7.507
7.500
7.493
7.489
7.484
7.476
7.471
7.470
7.463
7.174
7.170
3.916
3.901
3.896
3.882
3.863
3.505
3.491
3.469
3.456
3.441
3.421
3.405
3.386
3.260
3.242
3.232
3.222
3.213
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3.194
3.185
3.179
3.171
3.165
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2.517
2.513
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2.503
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1.867
1.854
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1.729
1.721
1.709
1.701
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9
8
7
6
5
4
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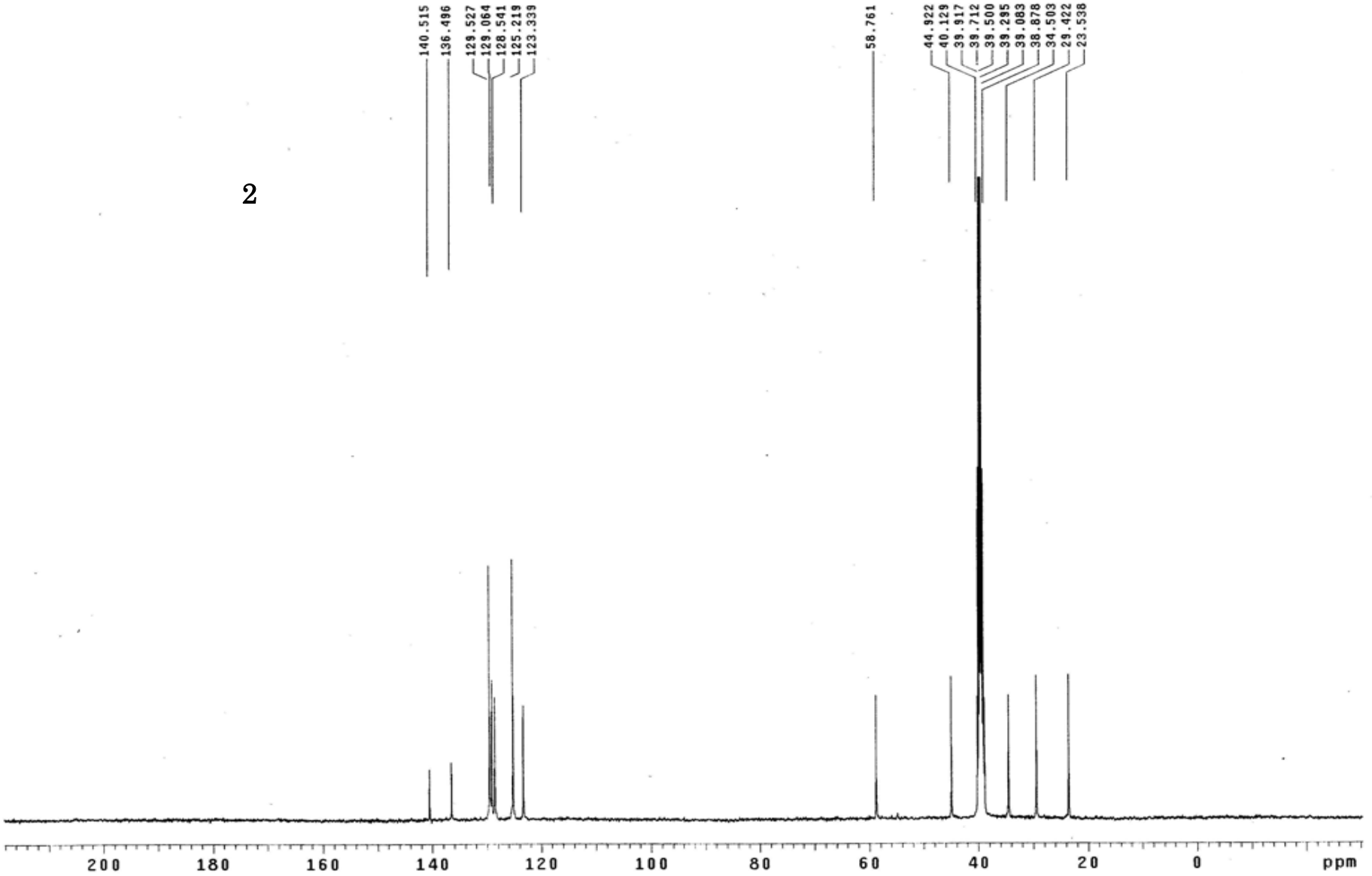
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44.922
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39.712
39.500
39.295
39.083
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200
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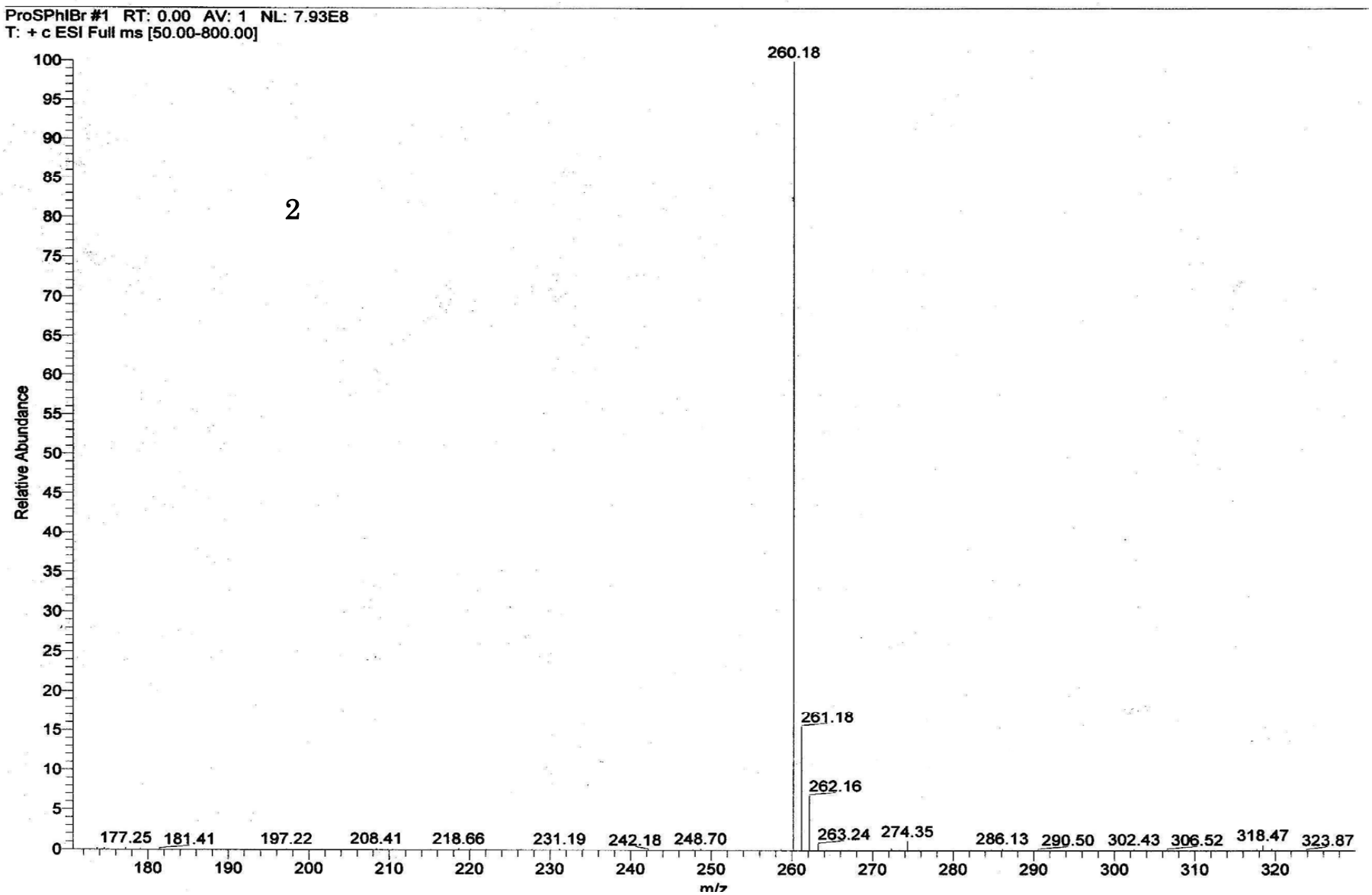
60
40
20
0
ppm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T: + c ESI Full ms [50.00-800.00]
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262.16
263.24
274.35
177.25
181.41
197.22
208.41
218.66
231.19
242.18
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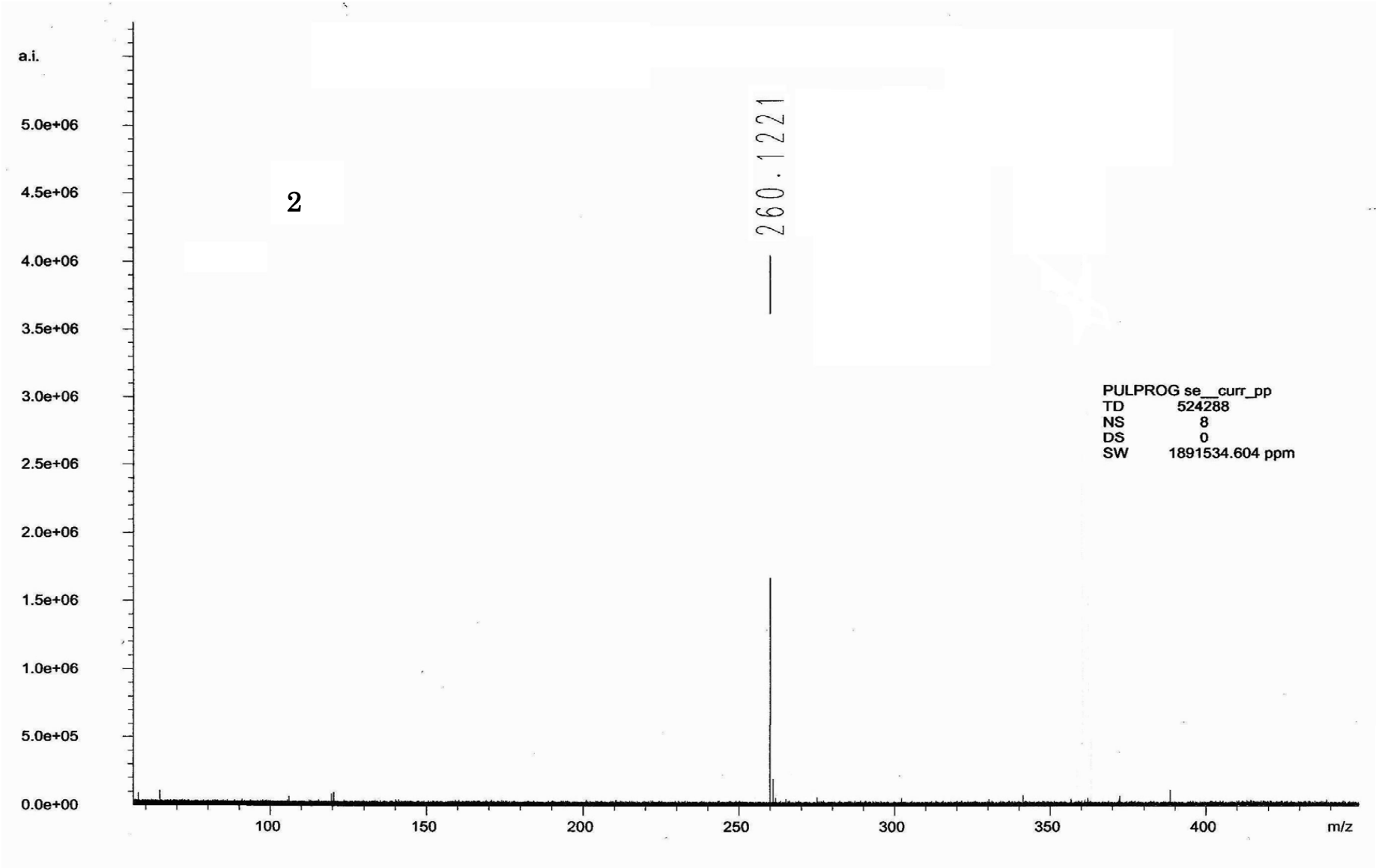
286.13
290.50
302.43
306.52
318.47
323.87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2
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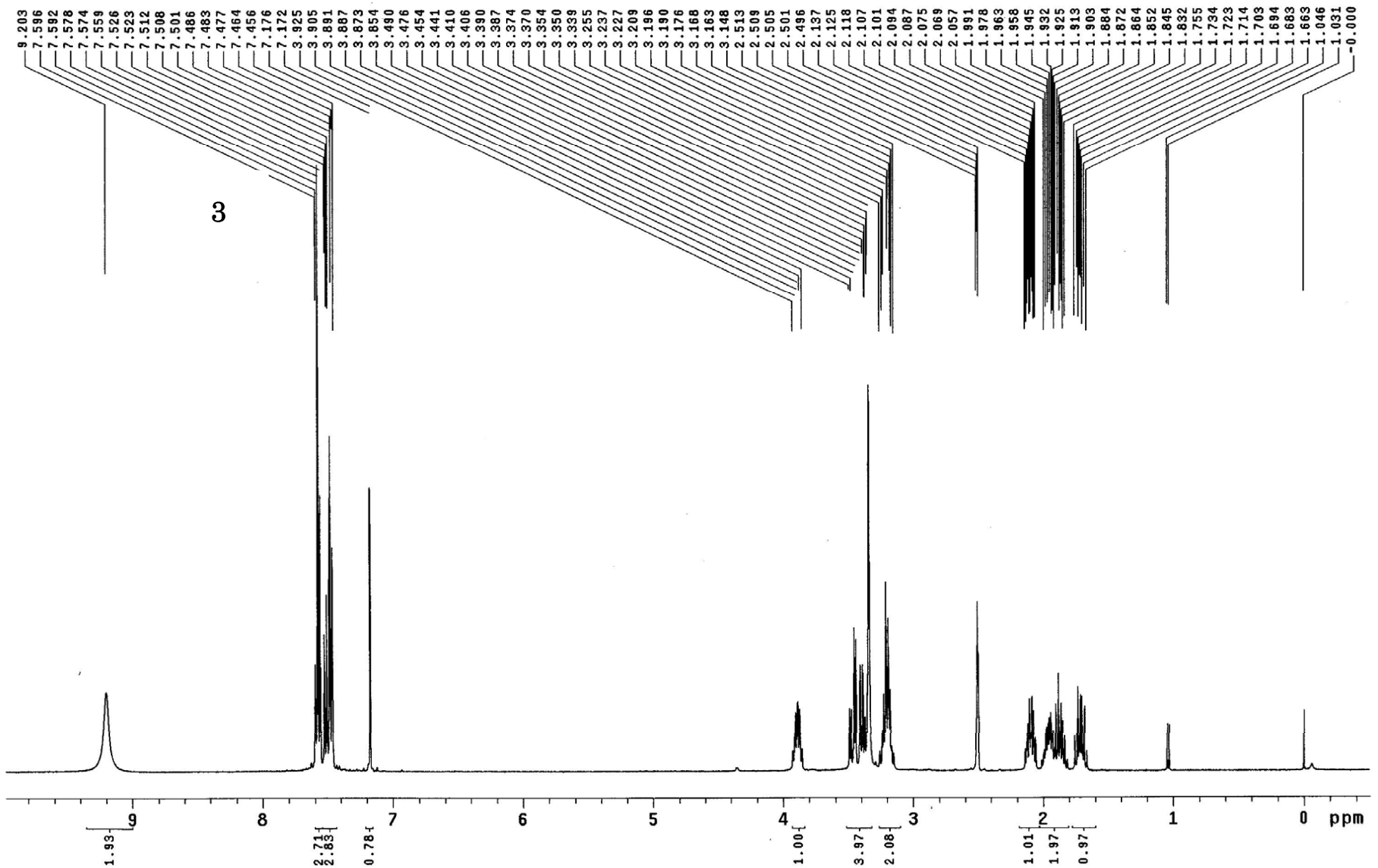
300
350
400
m/z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3.905
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3.190
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3.168
3.163
3.148
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2.509
2.505
2.501
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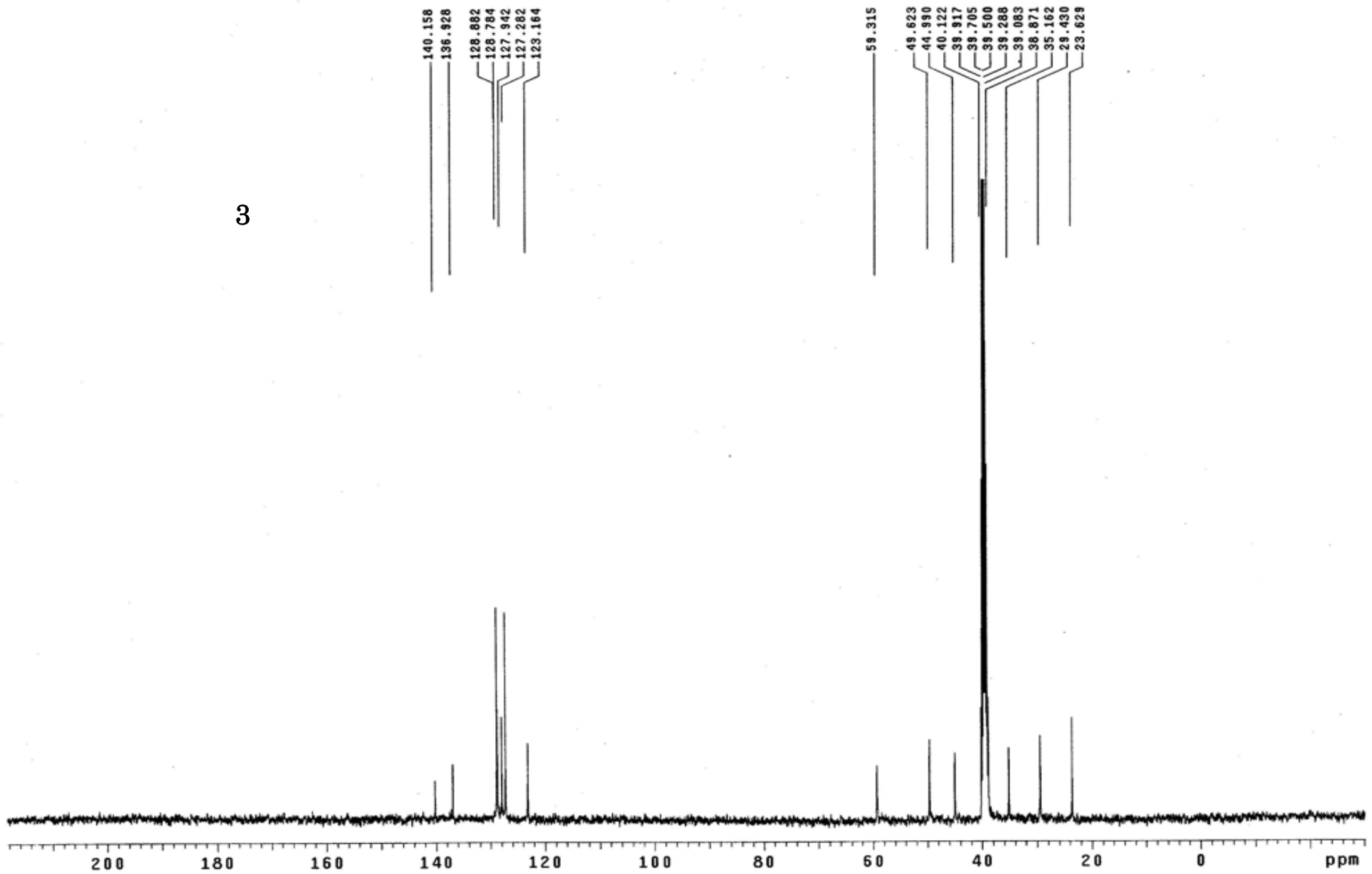
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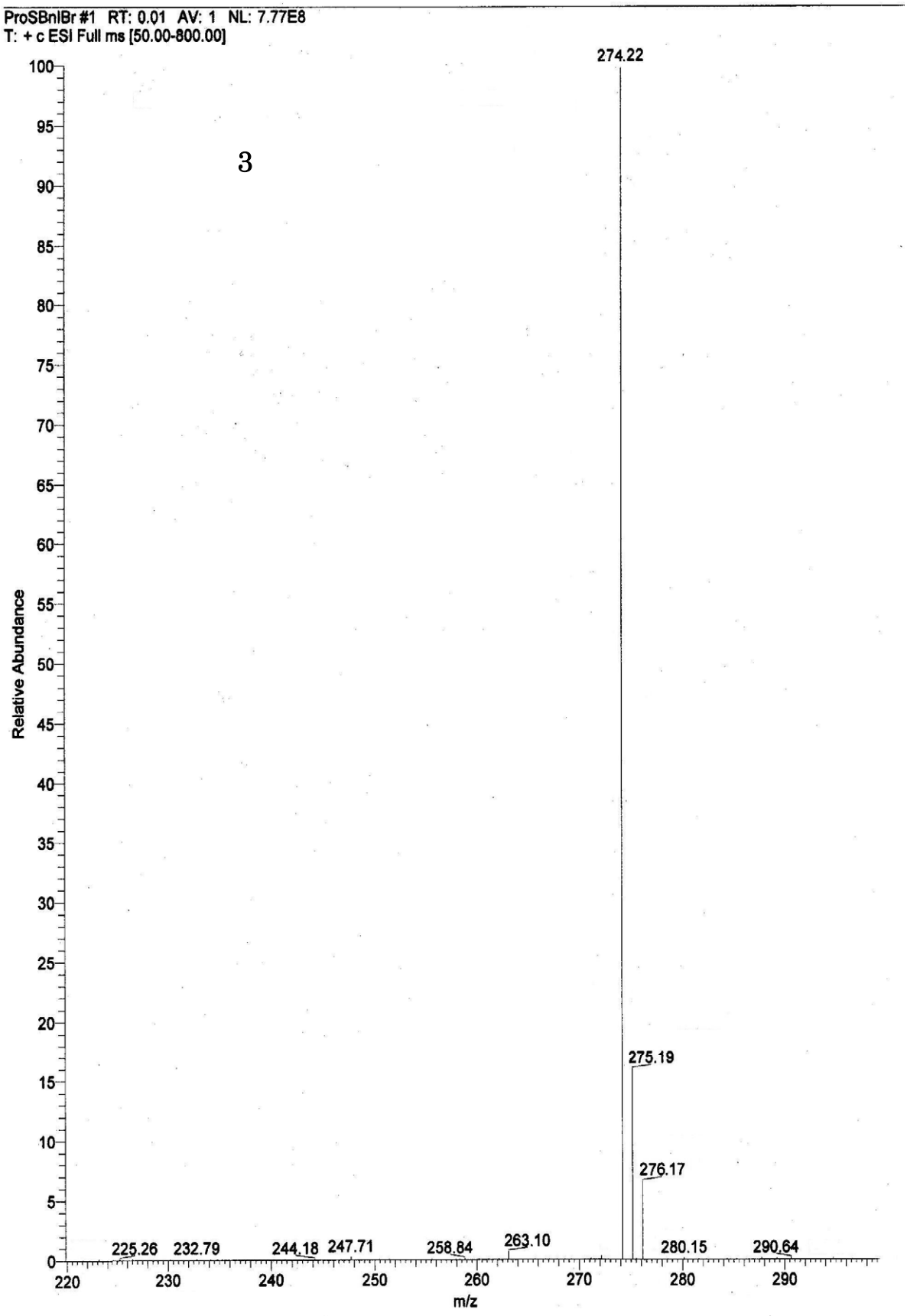
ppm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T: + c ESI Full ms [50.00-800.00]
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Relative Abundance
m/z
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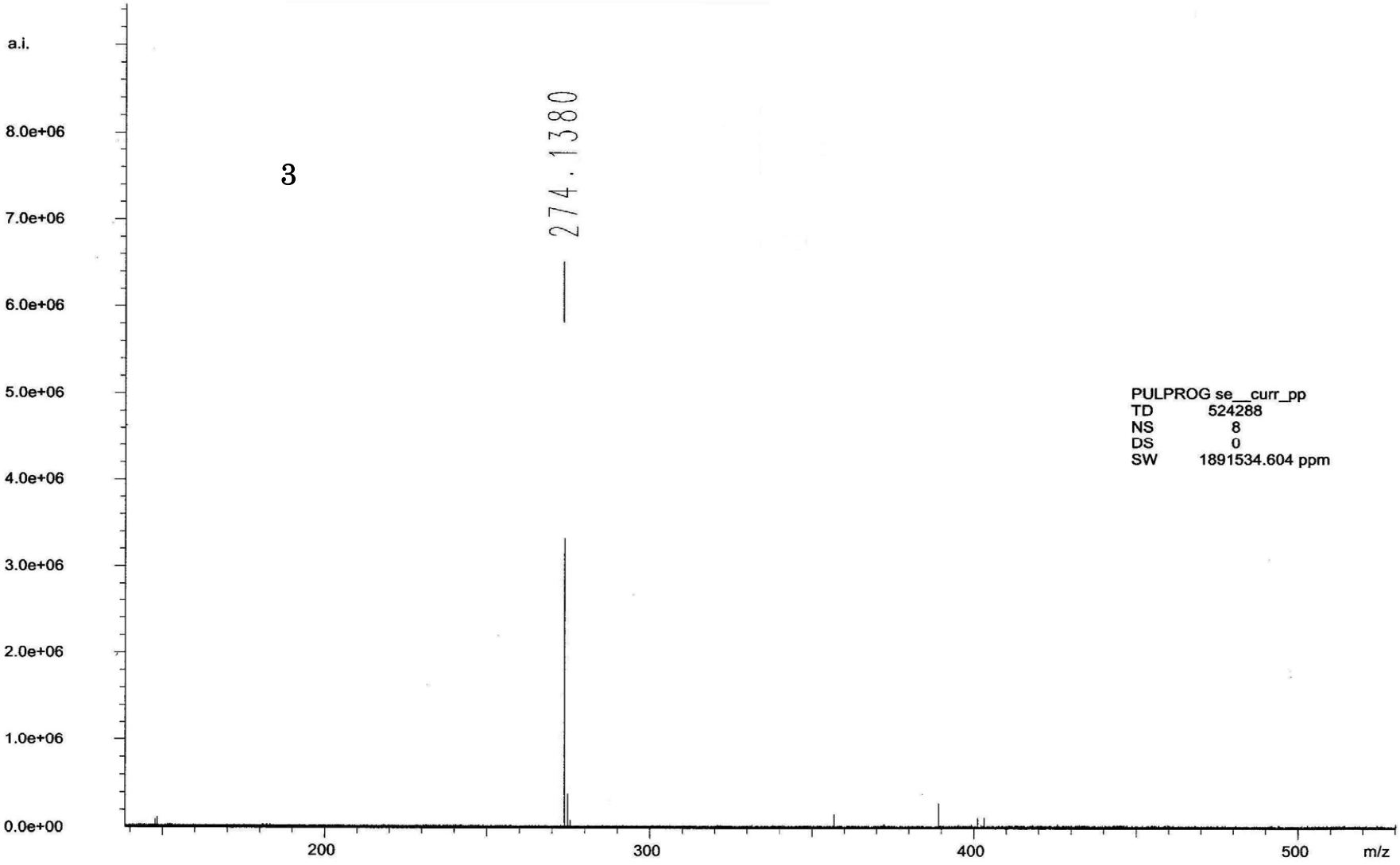
247.71
258.84
263.10
280.15
290.64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0.0e+00
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NS 8
DS 0
SW 1891534.604 ppm
200
300
400
500
m/z

5. X-Ray Crystal Data and Structure of 1f's Hydrobromide Salt

Table 1 Crystal data and structure refinement for **1f**'s hydrobromide salt

Empirical formula	C_{16} H_{24} Br N_3 O_3 S_2
Formula weight	450.41
Temperature	293 (2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2 (1) 2 (1) 2 (1)
Unit cell dimensions	a = 7.022 (7) A alpha = 90 deg.
	b = 7.332 (8) A beta = 90 deg.
	c = 38.75 (4) A gamma = 90 deg.
Volume	1995 (4) A^3
Z, Calculated density	4, 1.499 Mg/m^3
Absorption coefficient	2.289 mm^-1
F(000)	928
Crystal size	0.496 x 0.421 x 0.197 mm
Theta range for data collection	2.10 to 26.99 deg.
Limiting indices	-7<=h<=8, -9<=k<=8, -45<=l<=49
Reflections collected / unique	11718 / 4309 [R(int) = 0.1452]
Completeness to theta = 26.99	99.8 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.56229
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4309 / 0 / 233
Goodness-of-fit on F^2	0.918
Final R indices [I>2sigma(I)]	R1 = 0.0648, wR2 = 0.1477
R indices (all data)	R1 = 0.0869, wR2 = 0.1581
Absolute structure parameter	-0.004(14)
Extinction coefficient	0.0047(14)
Largest diff. peak and hole	0.935 and -0.760 e.A^-3

For crystallographic data in CIF or other electronic format see http://dx.doi.org/10.1039/b000000x. CCDC: 639780

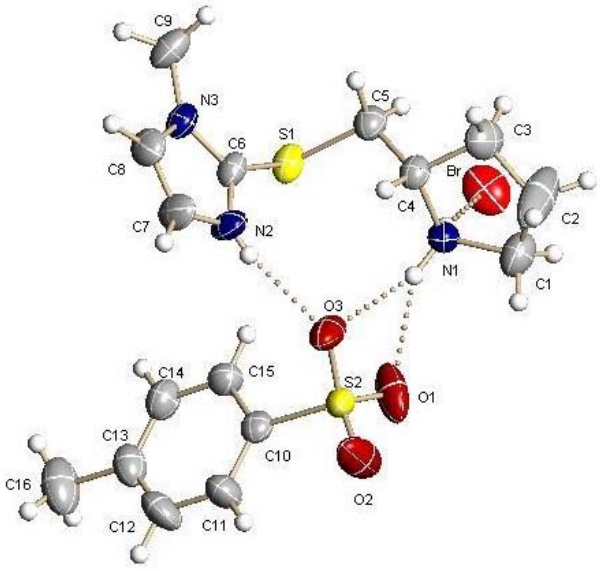
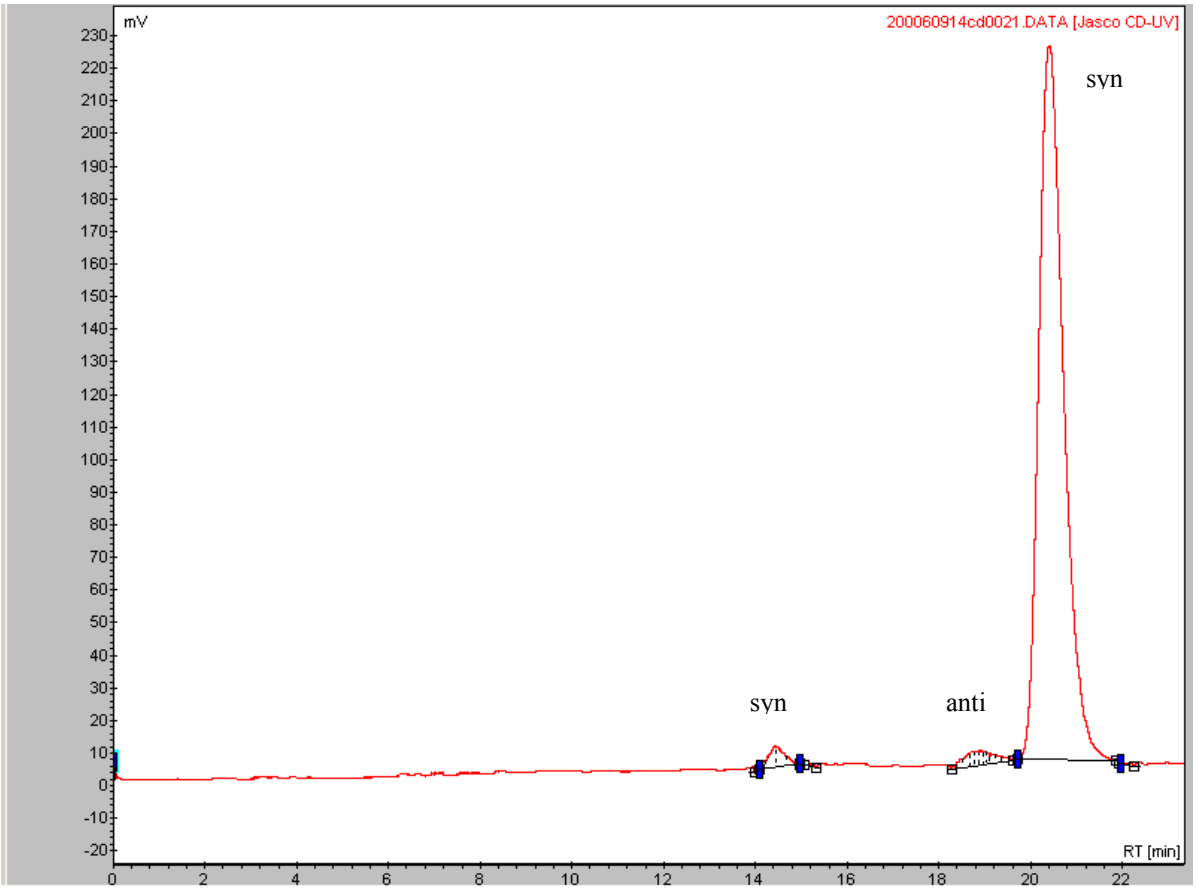


Figure 1 Molecular structure of **1f**'s hydrobromide salt

6. HPLC Chart for ee Value Determination and Crystal Structure of Michael Adduct 6

HPLC Chart of Michael Adduct **6**



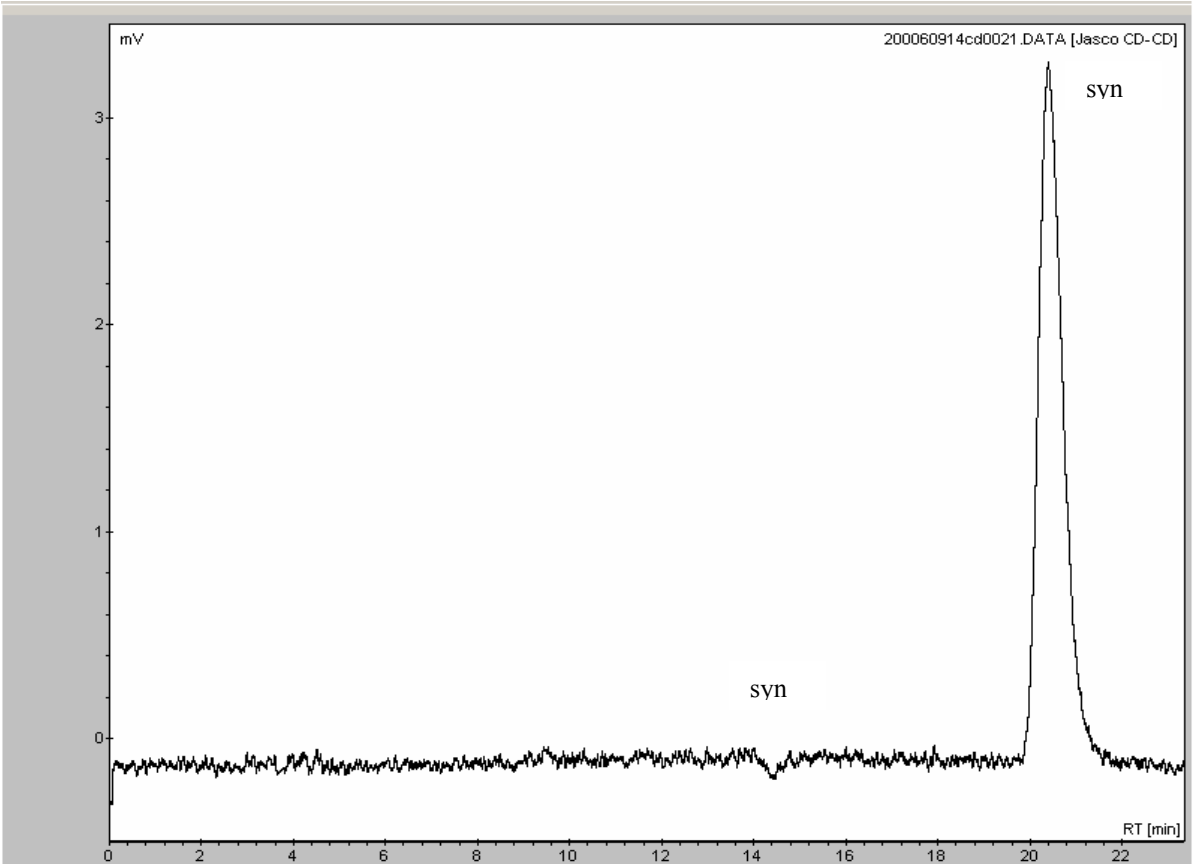


Table 2 Crystal data and structure refinement for Michael adduct **6**

Empirical formula	$C_{14}\ H_{17}\ N\ O_3$
Formula weight	247.29
Temperature	296 (1) K
Wavelength	0.71069 Å
Crystal system	orthorhombic
Space group	$P\ 2_1\ 2_1\ 2_1$
Unit cell dimensions	a = 5.578 (4) Å
	b = 8.563 (18) Å
	c = 27.852 (3) Å
Volume, z	1330(3) $Å^3$, 4
Density (calculated)	1.235 Mg/m^3
Absorption coefficient	0.087 mm^{-1}
F (000)	528.00
Crystal size	0.35 X 0.25 X 0.20 mm
Range for data collection	3.2 to 27.48°
Limiting indices	$-7 \le h \le 6$, $-10 \le k \le 11$, $-36 \le l \le 36$
Reflections collected	10339
Independent reflection	2937 (R_{int} = 0.033)
Absorption corrections	multi-scan
Max. and min. transmission	0.983 and 0.958
Refinement method	Full-matrix least-squares on F^2
Data / restrains / parameters	2937 / 0 / 165
Goodness-of-fit on F^2	1.004
Final R indices [I>2δ (I)]	R1 = 0.0369, wR2 = 0.0671
Largest diff. Peak and hole	0.25 and -0.24 e $Å^{-3}$
Absolute structure Flack	-0.0006(14)

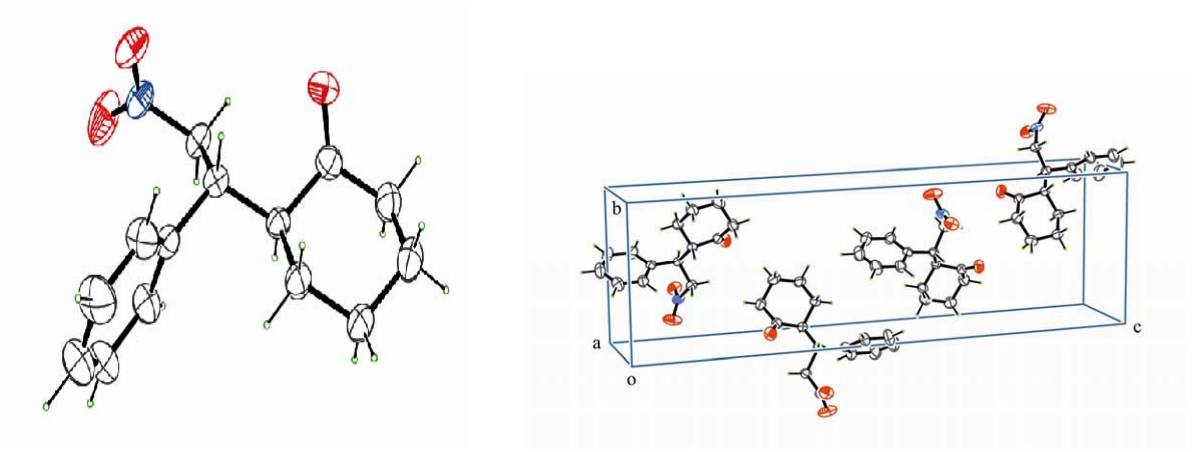


Figure 2 Molecular structure of Michael adduct **6** and its packing arrangement in unit cell

References:

(1) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, U. K., 1997.

(2) (a) Browden, K.; Green, P. N. *J. Chem. Soc.* **1952**, 1164. (b) Ikegami, S.; Uoji, K.; Akaboshi, S. *Tetrahedron* **1974**, *30*, 2077.

(3) Xu, D. Q.; Luo, S. P.; Yue, H. D.; Wang, L. P.; Liu, Y. K.; Xu, Z.Y. *Synlett* **2006**, 2569.