SUPPORTING INFORMATION

New 6-Oxa-2-silabicyclo[2.2.0]hexanes by Photochemical Conversion of acyl(allyl)(dimethyl)silanes

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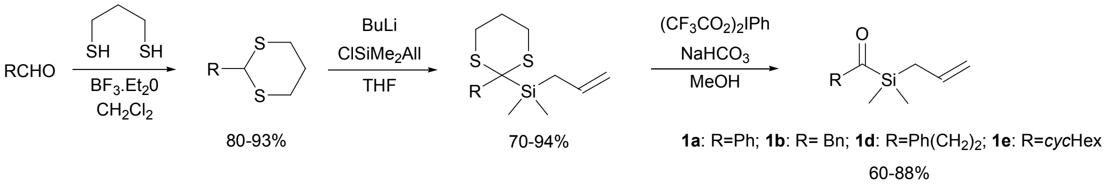
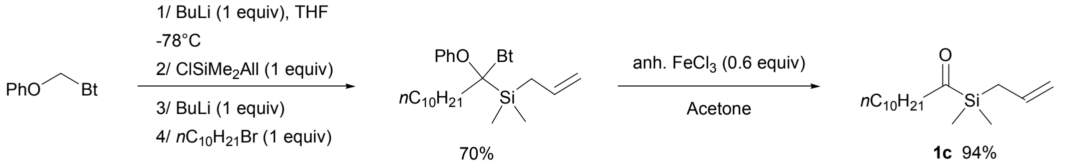
General: CH_3CN was distilled on calcium hydride, THF was distilled from sodium-benzophenone. Precoated aluminium backed plates Merck Kieselgel 60F254 and Macherey-Nagel GmbH & Co KG 40-63 µm were used for thin layer and column chromatography, respectively. GC analyses were performed on a polydimethylsiloxane DB-1 capillary column (30m x 0.25 mm ID x 0.25 µm). Melting points (mp) were determined on a Tottoli apparatus and were uncorrected. NMR spectra were recorded in $CDCl_3$, at frequencies of 250 MHz for ^1H, 235.3 MHz for ^{19}F and 62.9 MHz for ^{13}C NMR. Chemicals shifts (δ) are reported in ppm relative to TMS. HRMS (ESI^+) was recorded on a on a Waters (Q-TOF) spectrometer, equipped with pneumatically assisted electrospray (Z-spray) ion source in positive mode. GC/MS analysis was performed with a TR 1 MS (Thermo Electron) spectrometer, with a capillary column (polydimethylsiloxane, 30m x 0.25 mm ID x 0.25µm) and using a chemical ionization (NH_3 g) mode. Infrared data (IR) are expressed in cm^{-1}.

Preparation of starting ally(acyl)silanes 1.

The substrates **1a**, **1b**, **1d** and **1e** were prepared according to a Brook/Corey[1] type methodology (eq 1). Substrate **1c** was prepared according to a Katritzky type methodology (eq. 2).[2] In both cases the conditions of the final step were modified. The detailed description of the acylsilanes will be reported in a forthcoming paper. Their NMR spectra are enclosed.



(eq. 1)



(eq. 2)

Irradiation of acylsilanes, preparation of 2-oxa-6-silabicyclo(2.2.0)hexanes 2: general procedure.

A solution of the acylsilane **1c**, **1d** or **1e** (0.75 mmol) in degassed freshly distilled CH_3CN (15 mL) was irradiated under UV-light (Rayonet, λ = 350 nm) for 40 min. The solvent was evaporated and product **2** was isolated pure after flash chromatography (SiO_2, Petroleum ether-AcOEt 97:3).

1-decyl-6,6-dimethyl-2-oxa-6-silabicyclo[2.2.0]hexane (2c). Colourless oil. Yield=99%. ^{1}H NMR δ = 0.25 (s, 3H), 0.49 (s, 3H), 0.88 (t, J=6.5 Hz, 3H), 1.1-1.5 (m, 18H), 1.6-2,0 (m, 2H), 2.94-3.03 (m, 1H), 4.46 (dd, J=6.6, J=3.7 Hz, 1H), 5.08 (dd, J=7.4 Hz, J=6.6 Hz). ^{13}C NMR δ = -3, -1.4, 14.1, 16.7, 22.7, 25.0, 29.3, 29.6, 29.7, 29.9, 31.9, 35.9, 38.1, 78.8, 97.6; IR (KBr): ν ~ = 2925, 2854, 1466, 1256, 1051, 840; GCMS (CI): *m/z* (%): 286 $(M+NH_4)^+$, 285, 255 (100%), 92; HRMS (ESI+): *m/z*: calcd for $C_{16}H_{32}OSi$ + Na: 291.2120; found: 291.2116.

1-phenethyl-6,6-dimethyl-2-oxa-6-silabicyclo[2.2.0]hexane (2d). Colourless oil. Yield=53%. ^{1}H NMR δ = 0.00 (s, 3H), 0.46 (s, 3H), 1.22 (d, J=6.8 Hz, 2H), 2.0-2.4 (m, 2H), 2.6-2,8 (m, 2H), 3.0-3.1 (m, 1H), 4.53 (dd, J=6.7 Hz, J=3.8 Hz, 1H), 5.16 (dd, J=6.7 Hz, J=6.7, 1H), 7.1-7.4 (m, 5H). ^{13}C NMR δ = -3, -1.9, 16.7, 30.9, 38.0, 38.1, 78.8, 96.3, 125.7, 128.3 (2C) 128.7 (2C), 142.3. IR (KBr): ν ~ = 2926, 1496, 1220, 1031. GCMS (CI): *m/z* (%): 250 $(M+NH_4)^+$, 208, 92 (100%), 91, 52.

1-cyclohexyl-6,6-dimethyl-2-oxa-6-silabicyclo[2.2.0]hexane (2e). Colourless oil. Yield=52%. ^{1}H NMR δ = 0.30 (s, 3H), 0.48 (s, 3H), 0.9-1.3 (m, 8H), 1.5-1.9 (m, 5H), 3.06-3.15 (m, 1H), 4.43 (dd, J=6.3 Hz, J=3.4 Hz, 1H), 5.05 (dd, J=6.3 Hz, J=6.3, 1H). ^{13}C NMR δ = -2.8, -0.4, 17.1, 26.2, 26.5, 26.7 (2C), 27.9, 36.2, 43.1, 79.3, 101.4. IR (KBr): ν ~ = 2921, 1456, 1259, 1032. GCMS (CI): *m/z* (%): 210 (M^+), 165, 152, 127, 99 (100%), 75 (The enclosed ^{13}C NMR spectrum was take from a sample containing the by-product and exhibit three additional peaks).

Oxidative desilylation of 2c

To a solution of **2c** (0.19 mmol, 50 mg) in DMF (1 mL) was added 30% H_2O_2 (12 equiv) and KF (4 equiv). The reaction mixture was heated under stirring for 7 h. Water (20 mL) was added before extraction with ether (5 x 10 mL). The organic phase was washed with 10% aq NaHSO3, then with saturated NaHCO3. Evaporation of the solvent under vacuum yielded the dihydroxyketone **4** (44 mg, 95%) as a white solid. Mp = 50-55°C.

^{1}H NMR δ = 0.87 (t, J=6.4 Hz, 3H), 1.1-1.4 (m, 16H), 1.5-1.7 (m, 2H), 2.56 (t, J=7.4 Hz, 1H), 3.99 (m, 4H). ^{13}C NMR δ = 14.2, 22.8, 23.5, 29.3, 29.4, 29.5, 29.6, 29.7, 32.0, 42.4, 54.6, 62.7 (2C), 213.6. IR ($CHCl_3$): ν ~ = 3520, 2931, 2854, 1722, 1447, 1260.

Conversion of 2c into the oxetane 5

To a solution of **2c** (0.19 mmol, 50 mg) in THF (3 mL) was added TBAF,$3H_20$ (120 mg, 0.38 mmol, 2 equiv). The mixture was stirred at rt until completion of the reaction (monitoring by TLC (SiO_2, Hexanes/AcOEt 97:3)). Aq NH_4Cl was added and after 5 min stirring the two phases were separated. The aqueous phase was extracted with ether (2x5mL). The organic extracts were dried over $MgSO_4$. After evaporation of the solvent, the residu was purified by chromatography over silica gel (Hexanes/AcOEt 96:4) yielding the oxetane **5** (25 mg, 64%) as a colourless oil.

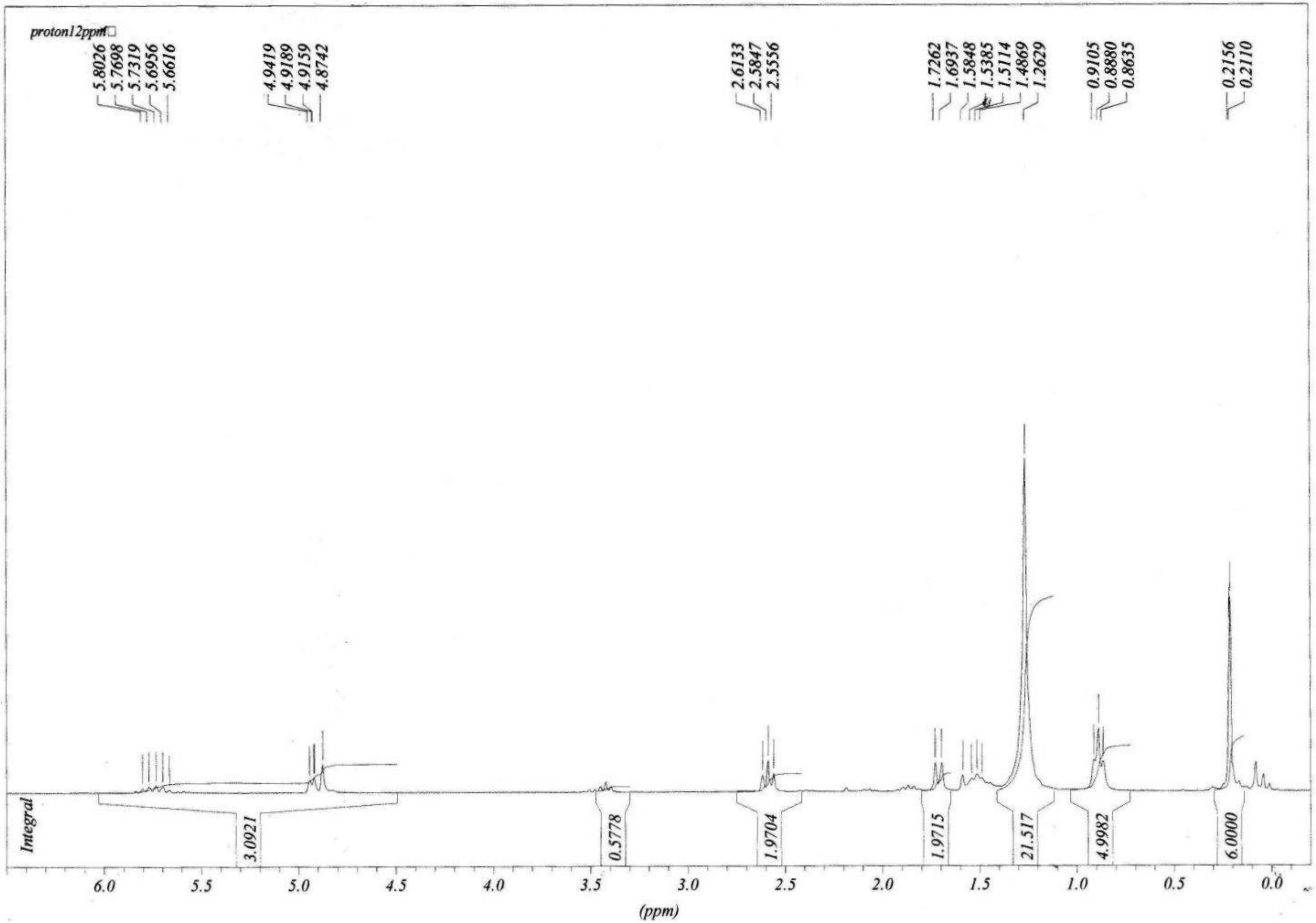
^{1}H NMR δ = 0.85 (t, J=6.4 Hz, 3H), 1.1-1.4 (m, 19H), 1.5-1.7 (m, 2H), 2.54-2.66 (m, 1H), 4.15 (dd, J=6.8 Hz, J=6.2 Hz, 1H), 4.31 (m, 1H), 4.46 (dd, J=6.8 Hz, J=6.3 Hz, 1H). ^{13}C NMR δ = 14.3, 16.2, 22.8, 24.4, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8 (2C), 37.3, 75.8, 91.7. IR ($CHCl_3$): ν ~ = 2926, 2855, 1467, 1042.

References

[1] A. G. Brook, J. M. Duff, P. F. Jones, and N R Davis, *J. Am. Chem. Soc.* 1967, **89**, 4431; E. J. Corey, D. Seebach, and R. Freedman, *J. Am. Chem. Soc.* 1967, **89**, 434.

[1] A. R. Katritzky, H. Lang, Z. Wang and Z. Lie, *J. Org. Chem.* 1996**,** **61**, 7551.

1c ^{1}H NMR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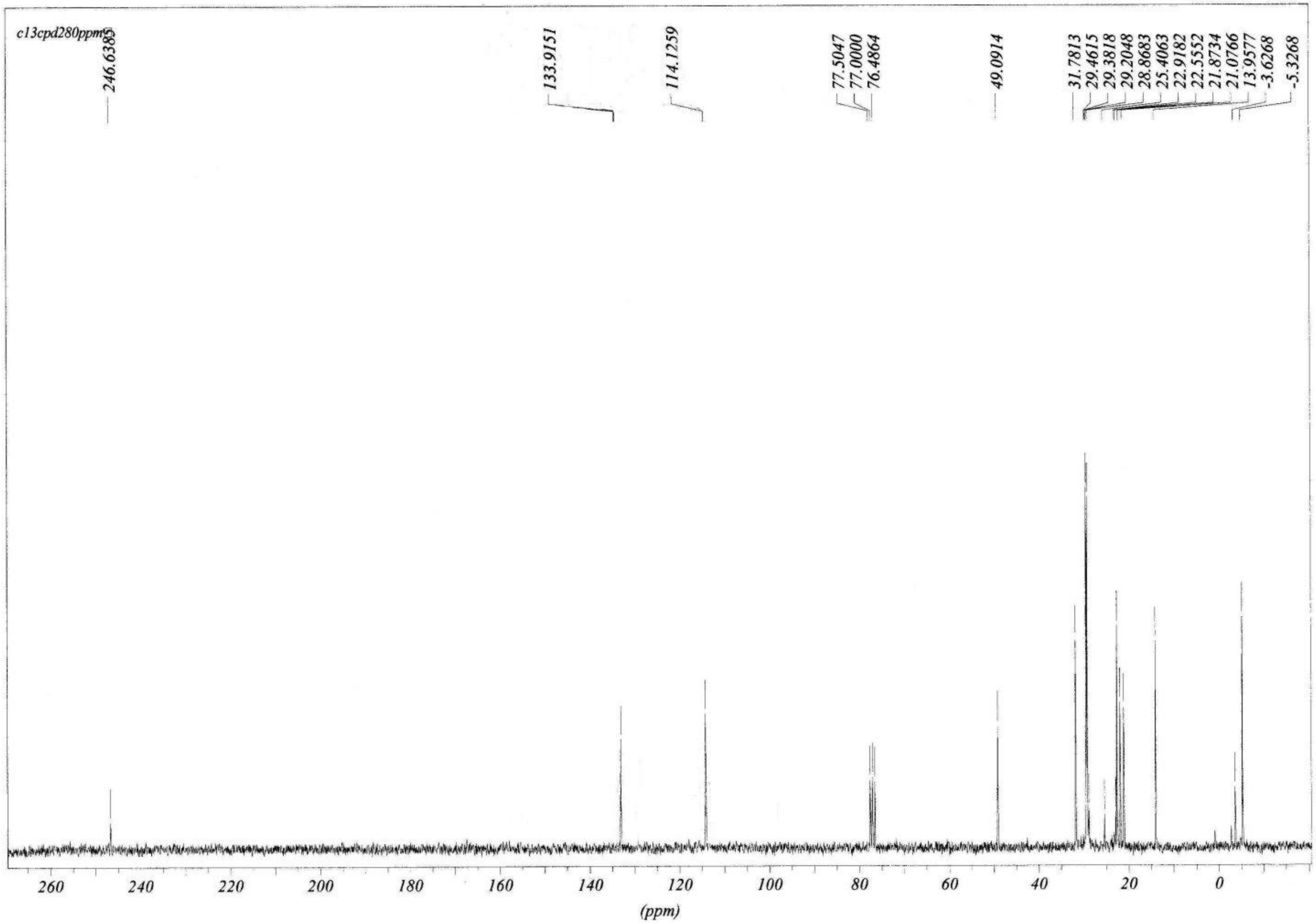
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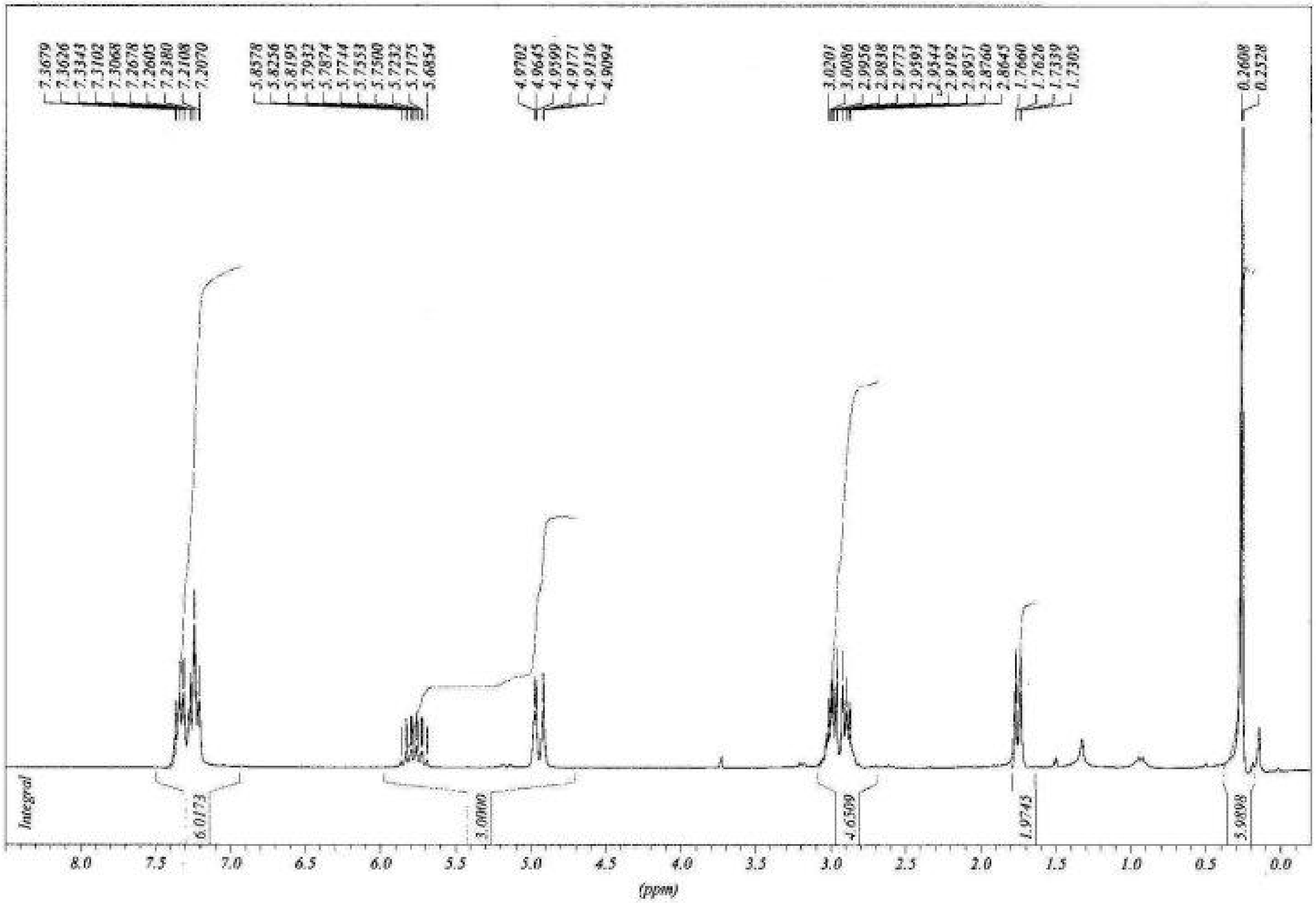
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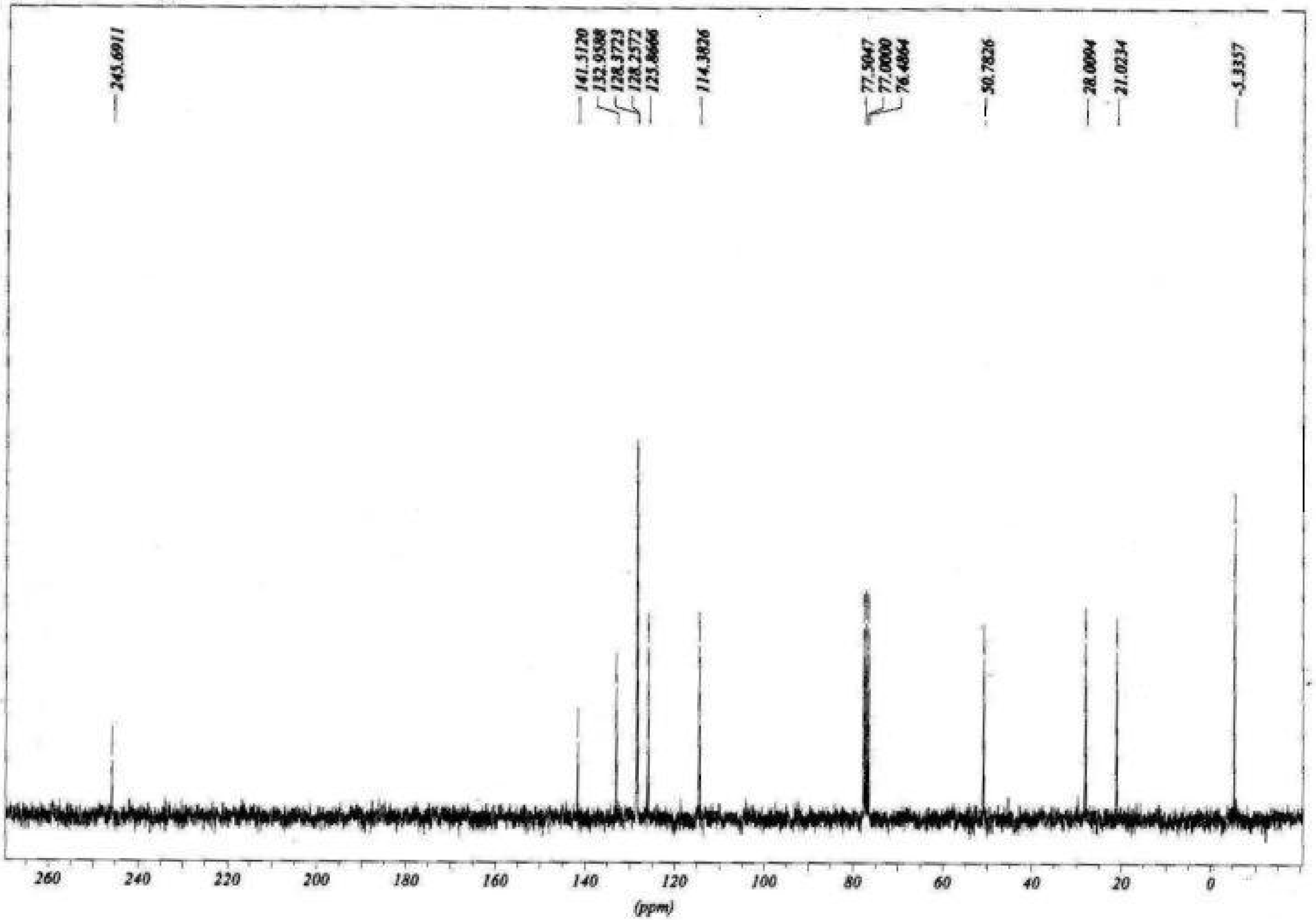
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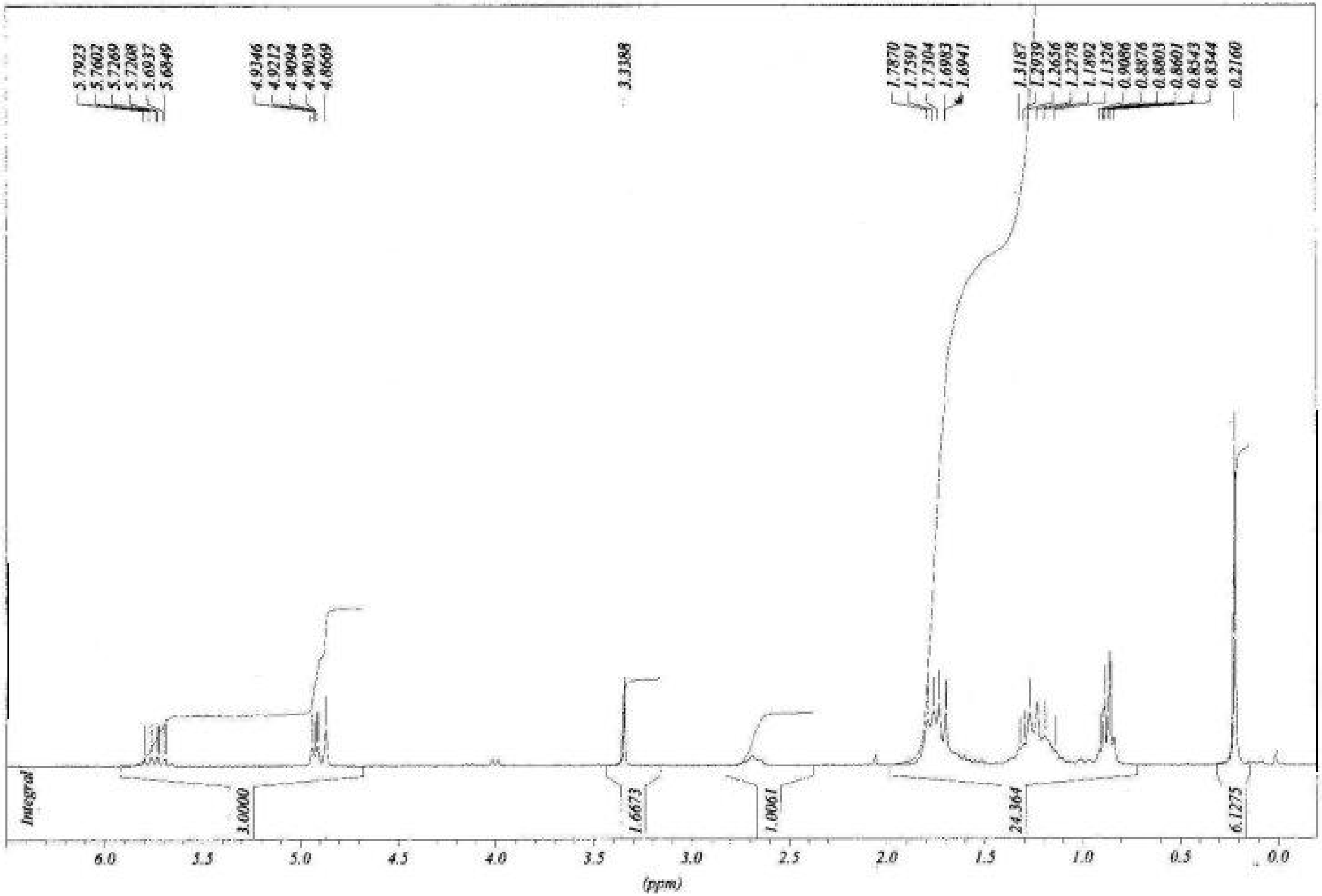

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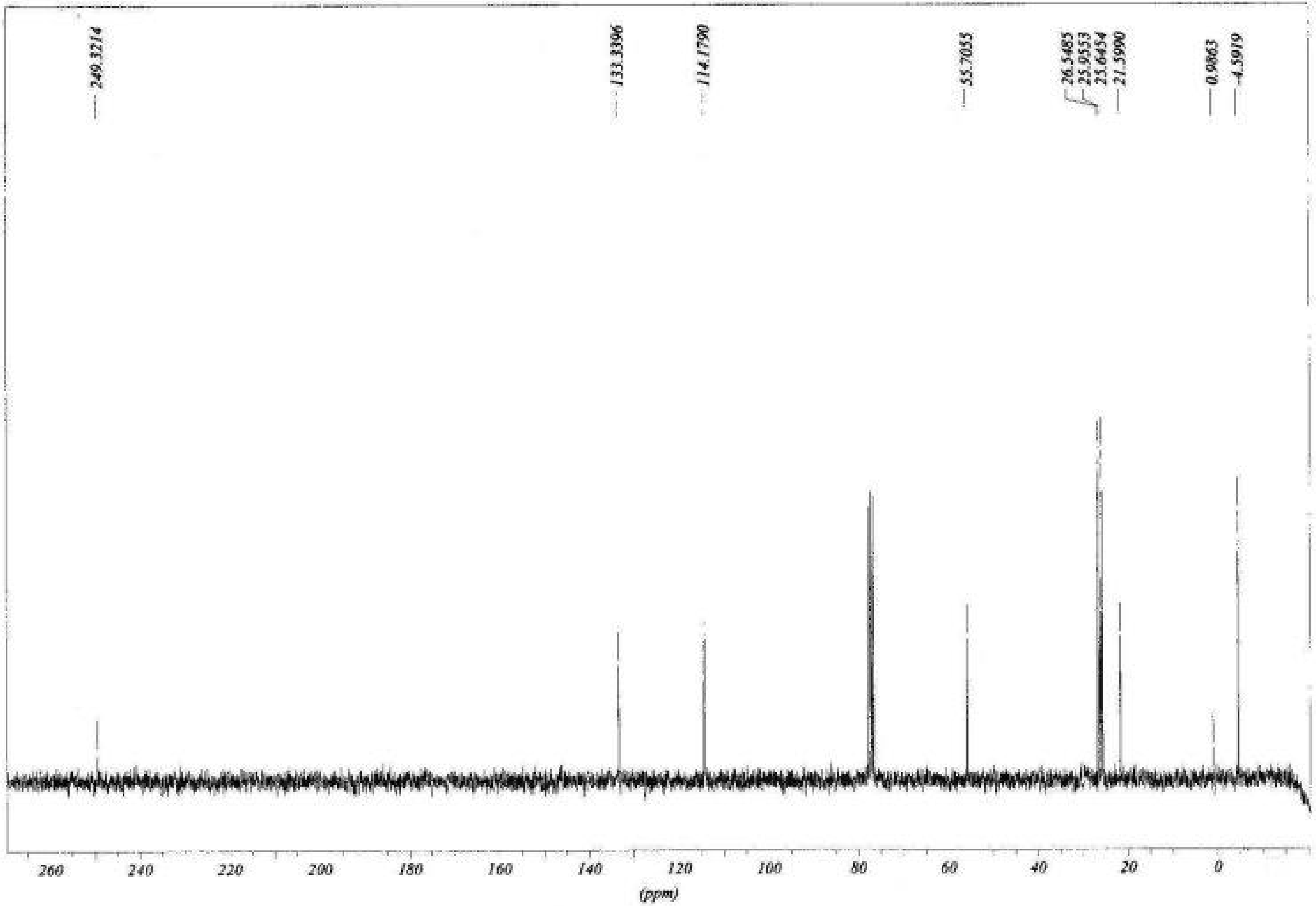

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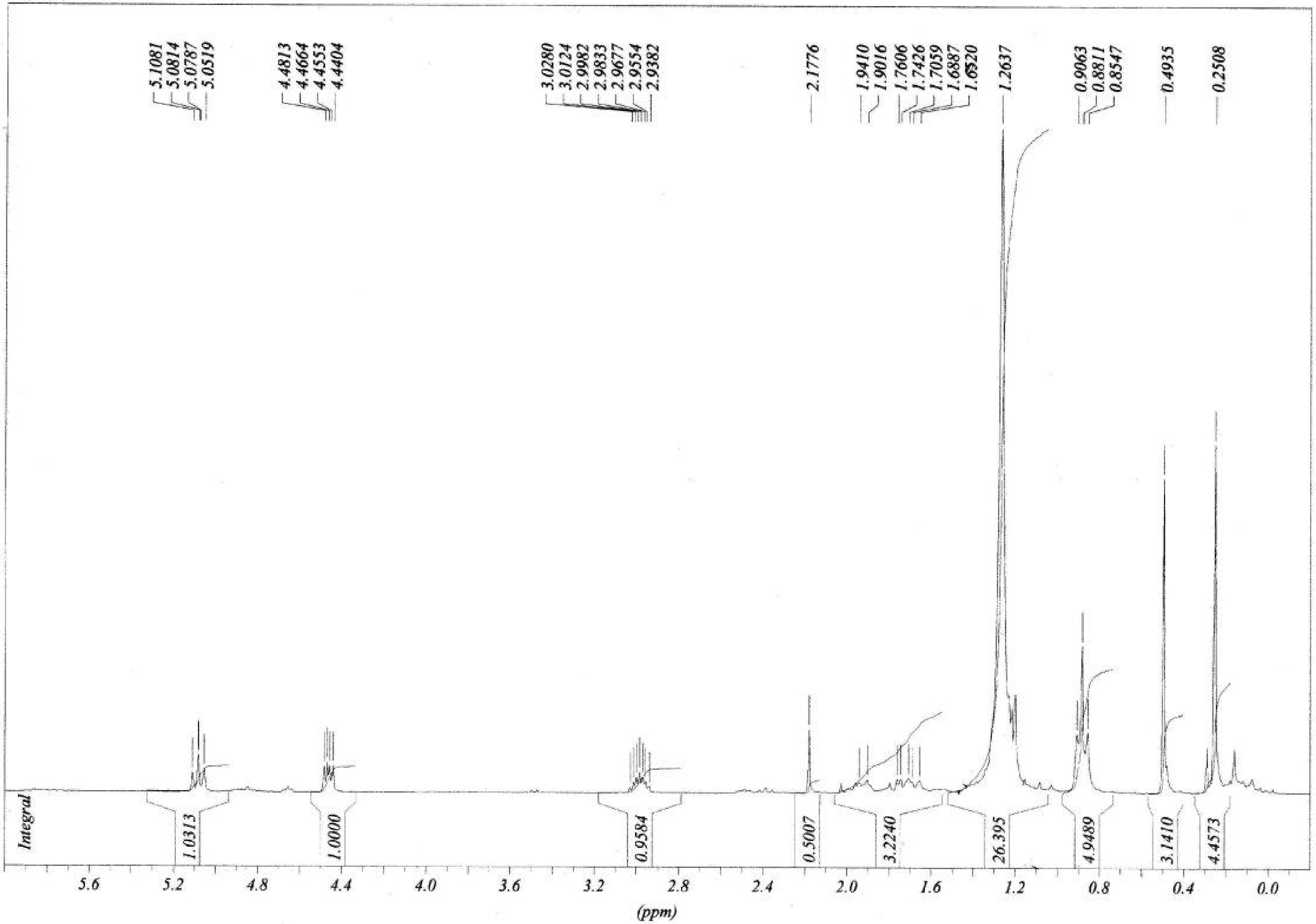
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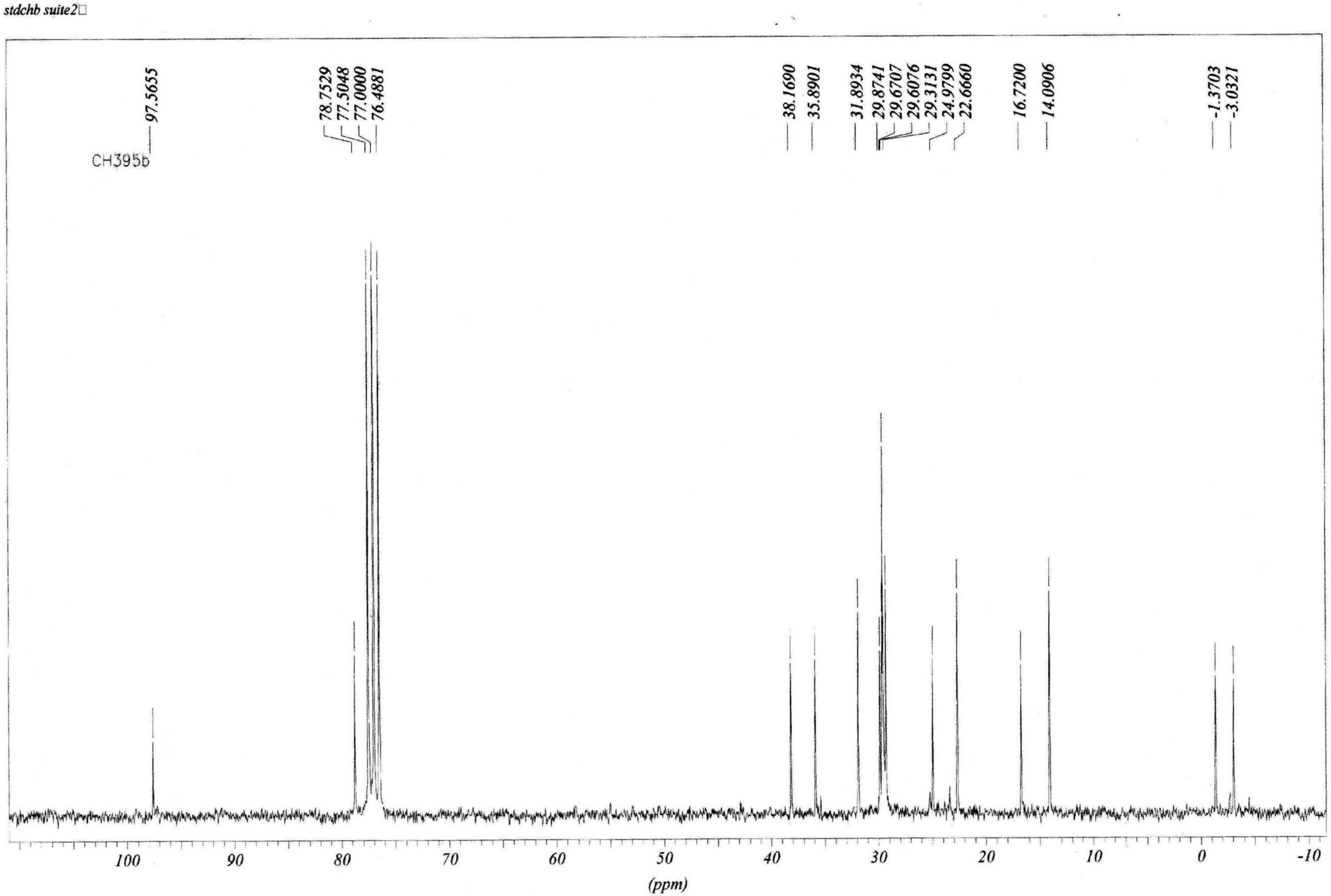
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2c HRMS

Elemental Composition Report **Page 1**

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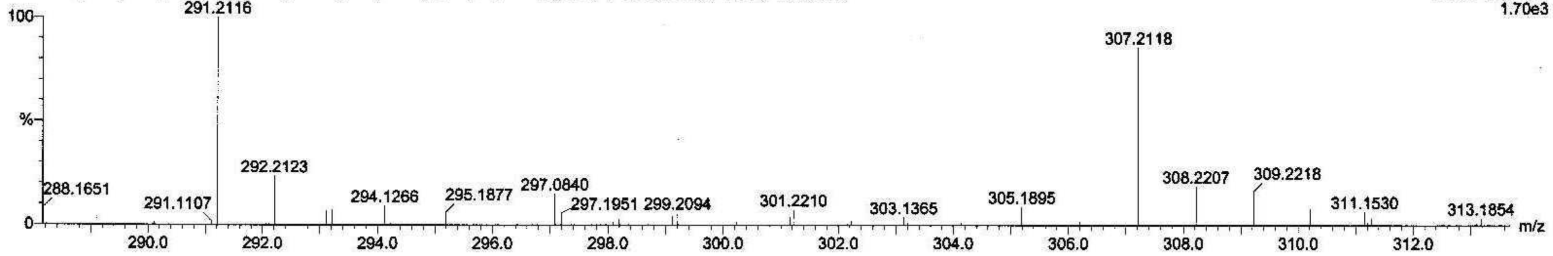

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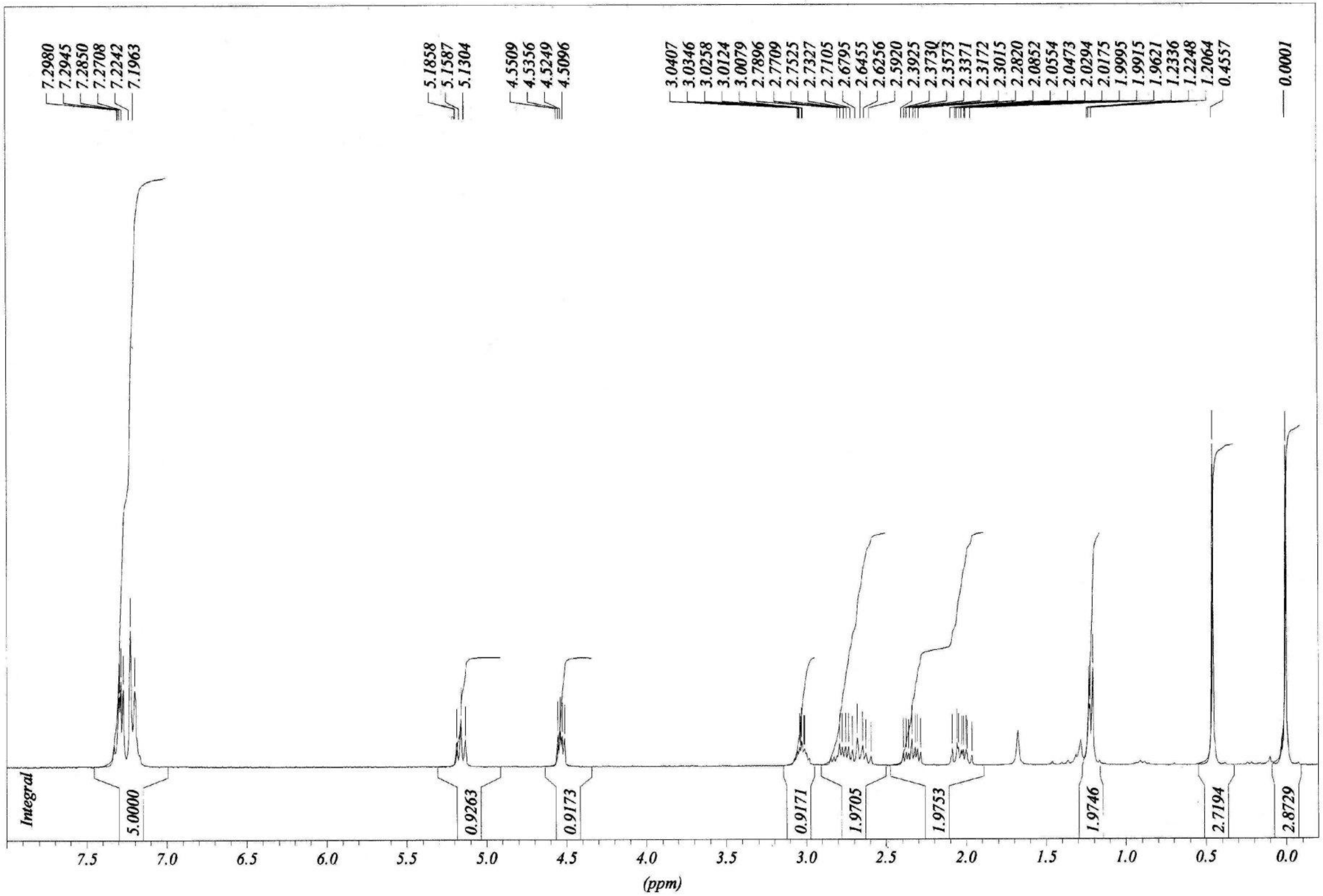
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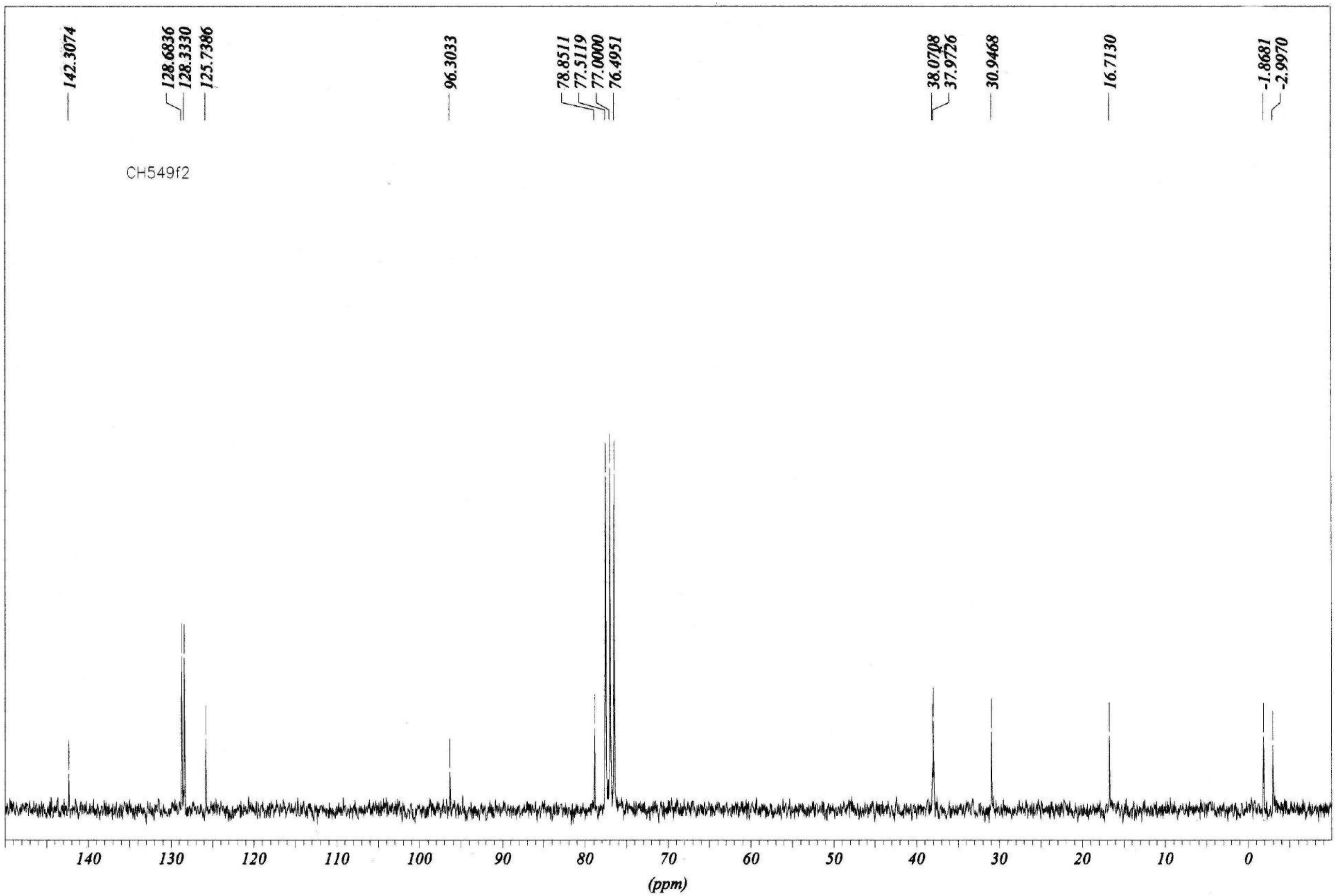
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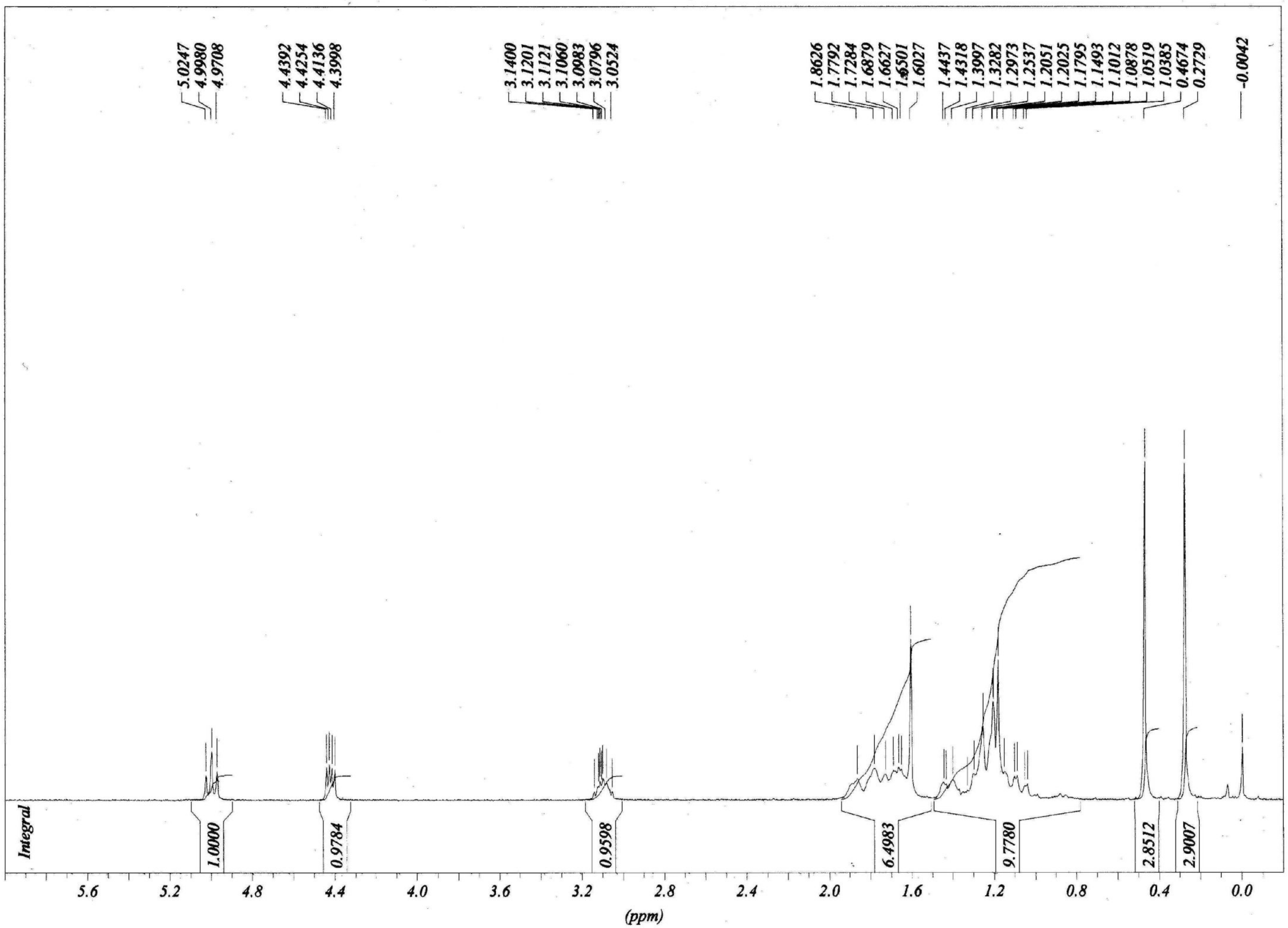
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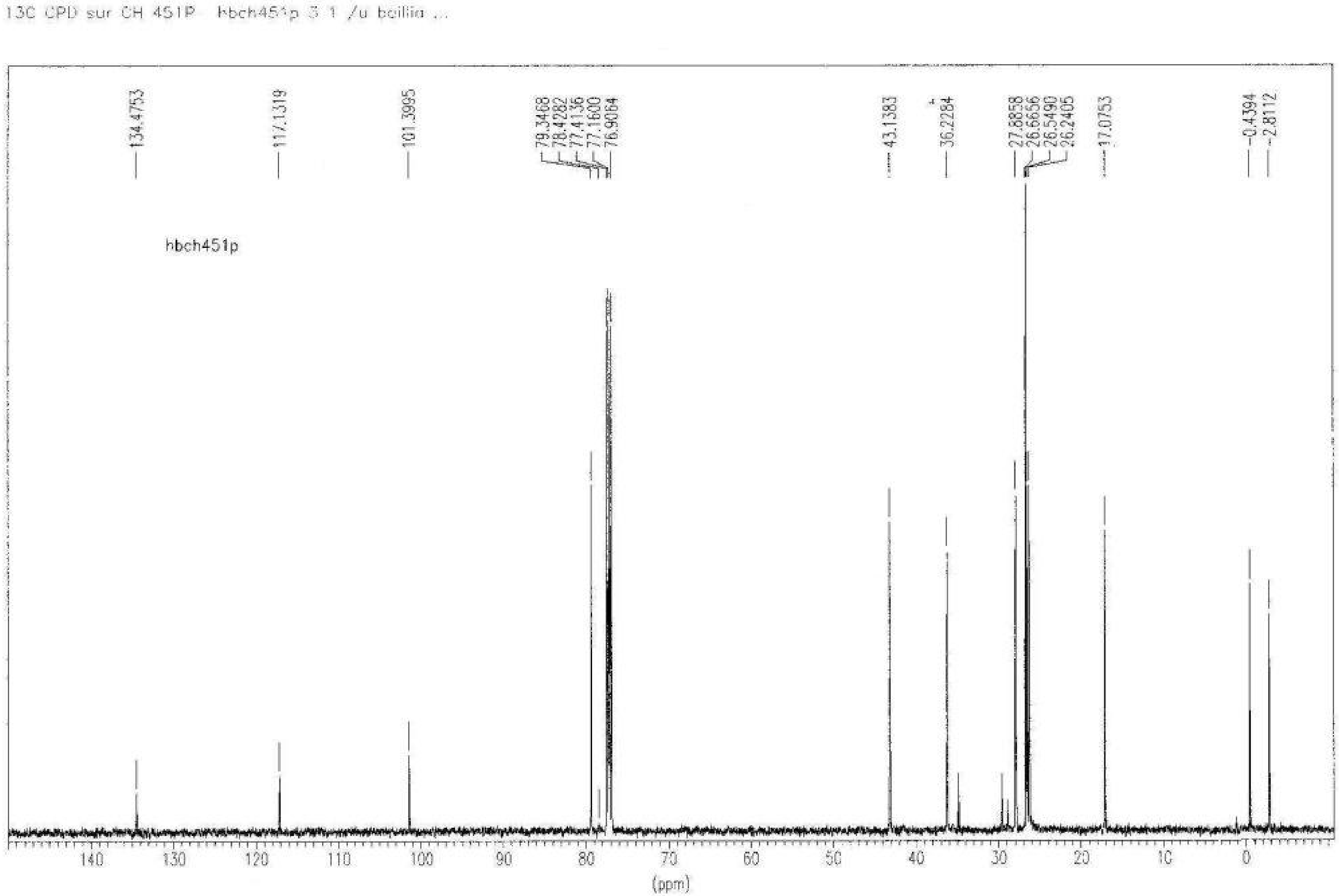
2e ^{13}C NMR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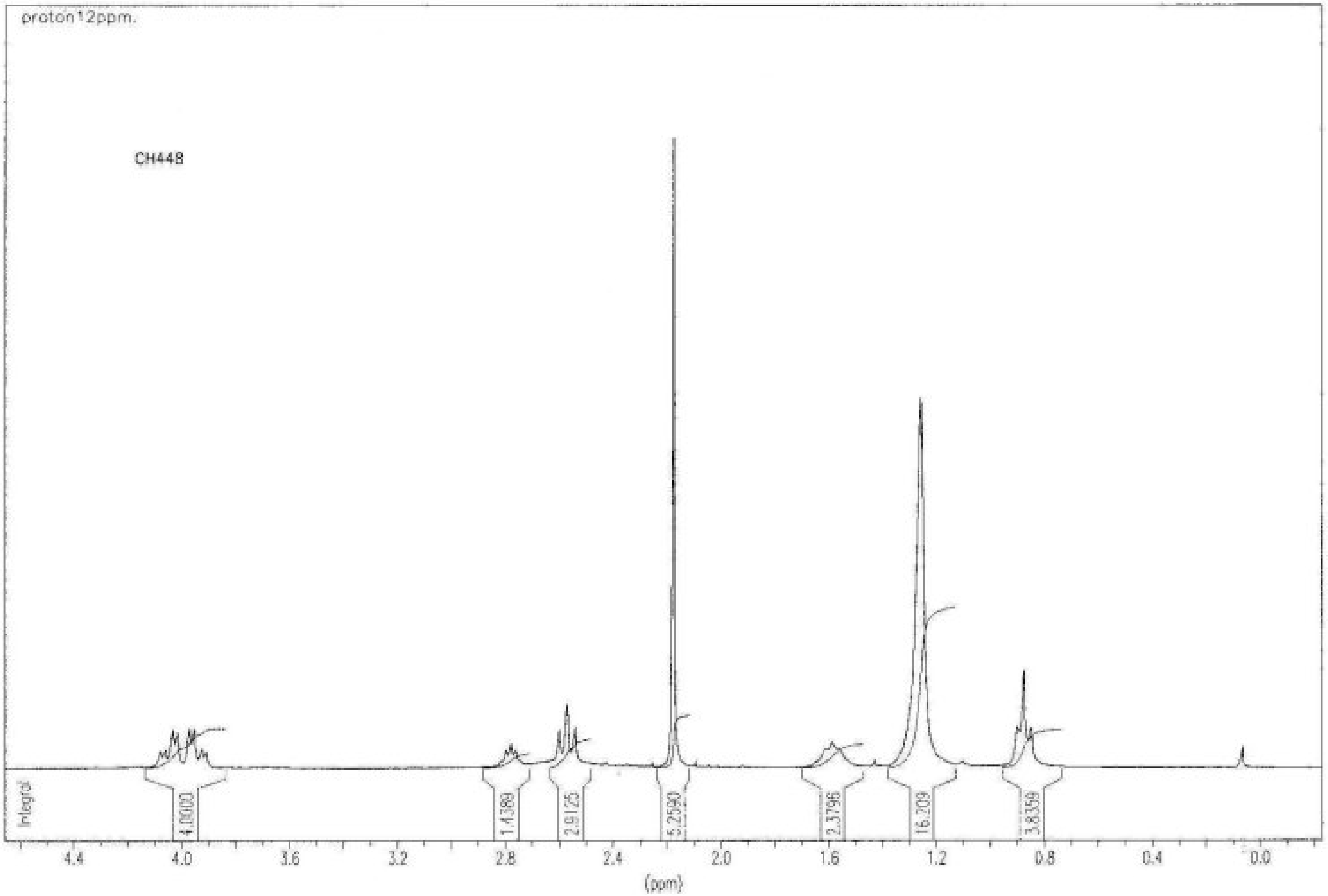
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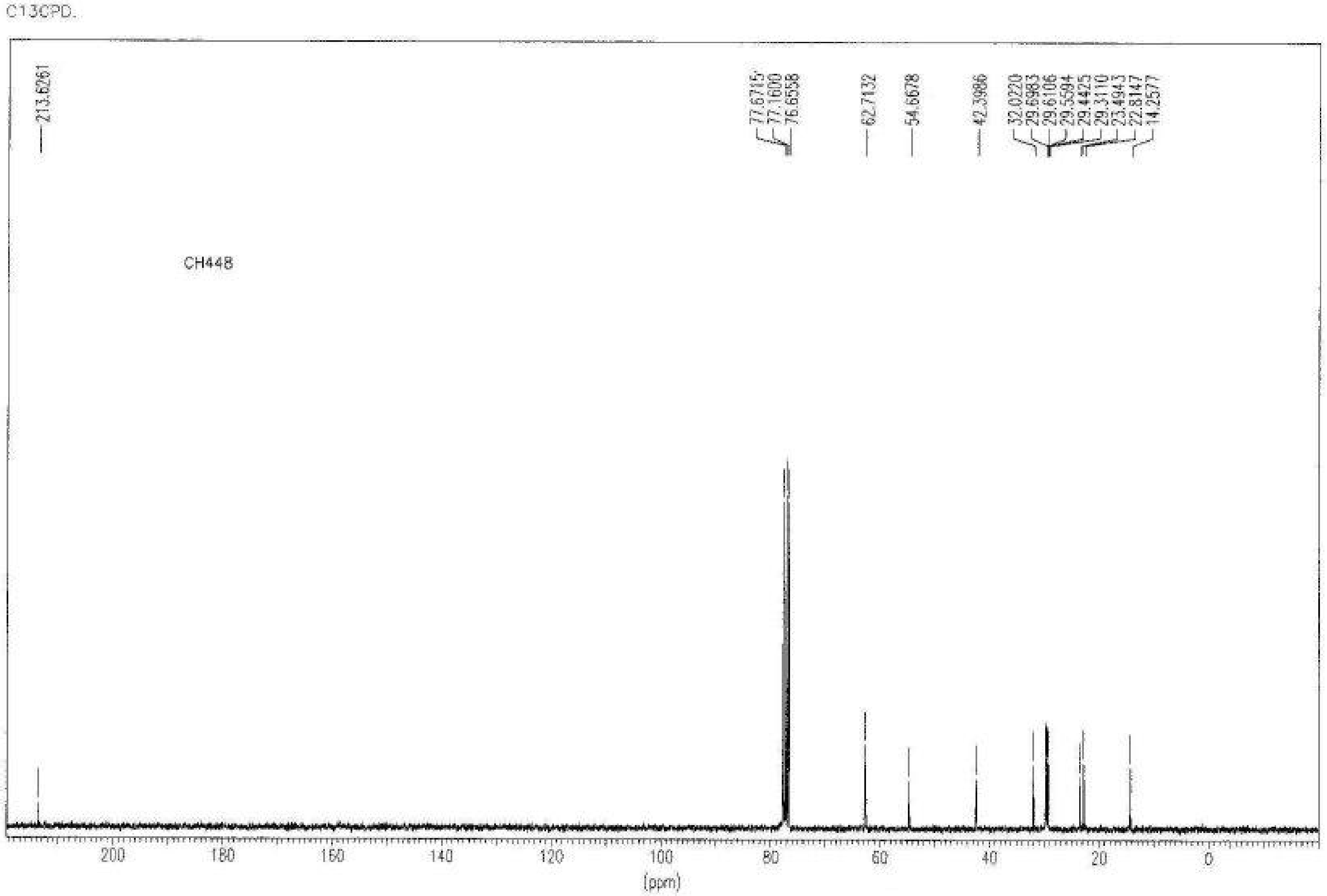
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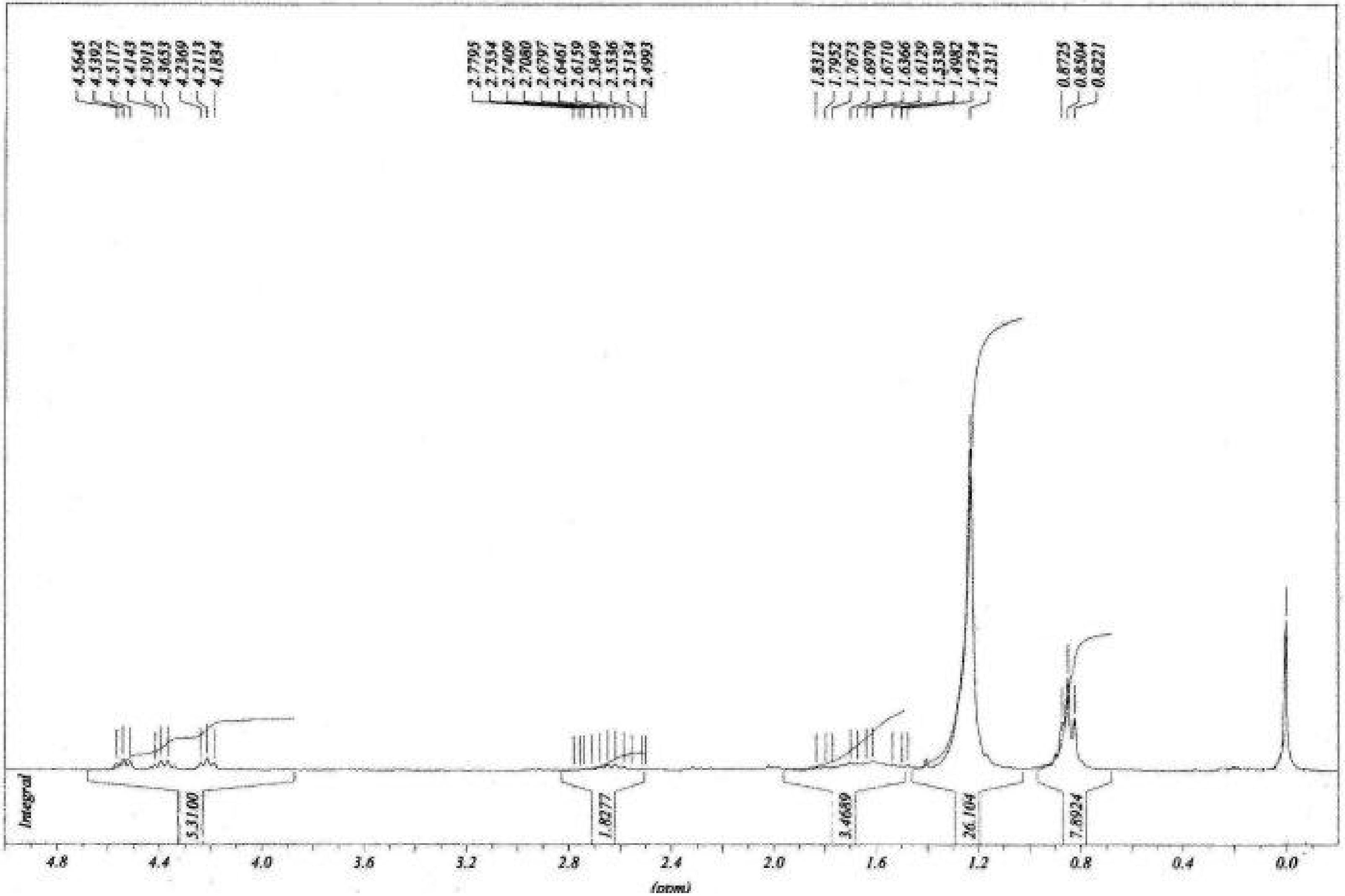
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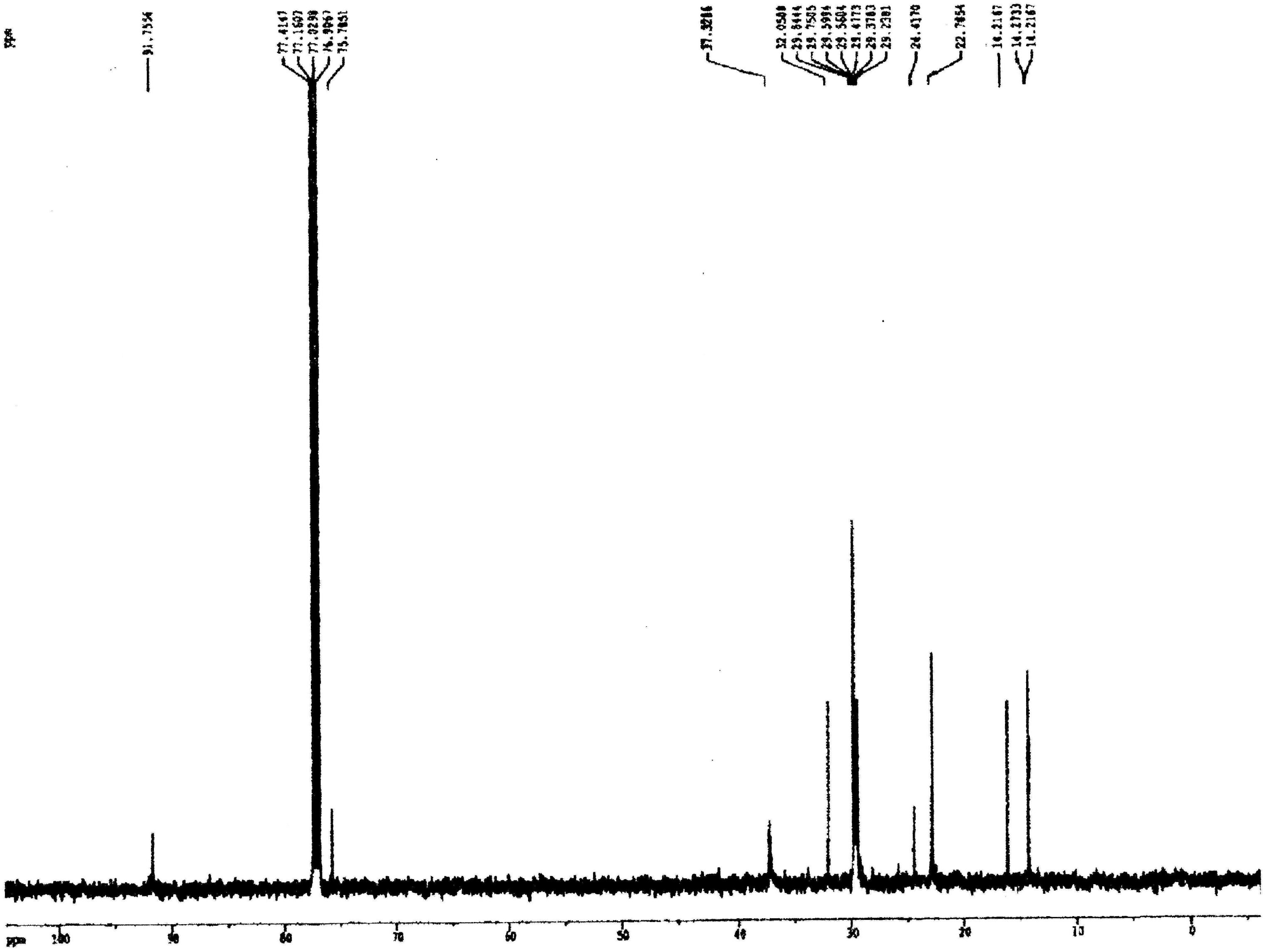
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
(ppm)

5 ^{13}C NMR


ppm
91.7554
77.4147
77.1607
77.0290
76.9067
75.7851
37.3286
32.0500
29.8444
29.7505
29.5994
29.5604
29.4173
29.3783
29.2381
24.4170
22.7054
16.2167
14.2733
14.2167
ppm
100
90
80
70
60
50
40
30
20
10
0