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## **Application of Cubane as an Internal Standard**

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## Experimental Details

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded for both 400MHz (400.13 MHz; 100.62 MHz) and 500MHz (500.13 MHz; 125.76 MHz). Coupling constants are given in hertz and chemical shifts are expressed as  $\delta$  values in parts per million. All experimental temperatures are reported to the nearest whole number in both Kelvin and degree Celsius. At each temperature the samples were allowed to equilibrate for 10 minutes before the data were collected. Chemical shifts for solvent peaks at 298 K were also recorded. GC/MS data were recorded under the following conditions: Ionisation at 70 eV, column: DB-5ms 30 m 0.25 mm, carrier-gas: He, total flow 32.2 mL/min, column flow 1.3 mL/min, injector temperature: 250 °C, standard program: 2 min at 40 °C, followed by a temperature increase of 16 °C/min and held at 250 °C for 5 min.

Solid cubane (**1**) (5 mg,  $4.8 \times 10^{-5}$  mol) prepared as per Eaton<sup>1</sup> was added to each NMR tube and the designated deuterated solvent (0.5 mL) was added to the tube. The filled NMR tube was placed in an ultrasonic bath to ensure all solid had completely dissolved. Each sample tube contained tetramethylsilane (TMS) (1 $\mu$ L).

1 P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.* , 1964, **86**, 3157-3158; P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.* , 1964, **86**, 962-964.

**Table 1- Deuterated NMR Solvent shifts to TMS = 0 ppm, on the Bruker AVANCE 400 at 25 °C.**

Solvent	<sup>1</sup> H (mult)	J <sub>HD</sub>	<sup>13</sup> C shifts	J <sub>CD</sub>
Acetic acid-d <sub>4</sub>	11.62(1) 2.03(5)	2.2	178.5(br) 20.1(7)	20
Acetone-d <sub>6</sub>	2.05(5)	2.2	206.1(br) 29.8(7)	19
Acetonitrile-d <sub>3</sub>	1.94(5)	2.5	118.4(br) 1.4(7)	21
Benzene-d <sub>6</sub>	7.16(br)		128.0(3)	24
Chloroform-d	7.26(1)		77.0(3)	32
Cyclohexane-d <sub>12</sub>	1.38(br)		26.4(5)	19
Dimethylformamide-d <sub>7</sub>	8.02(br) 2.91(5) 2.74(5)	1.9 1.9	162.7(3) 35.2(7) 30.1(7)	29 21 21
Dimethyl-d <sub>6</sub> Sulfoxide	2.5(5)	1.8	39.5(7)	21
Dioxane-d <sub>8</sub>	3.53(m)		66.5(5)	22
Methanol-d <sub>4</sub>	4.85(1) 3.31(5)	1.7	49.0(7)	21
Methylene Chloride-d <sub>2</sub>	5.32(3)	1.1	53.9(5)	27
Pyridine-d <sub>5</sub>	8.73(br) 7.58(br) 7.21(br)		149.9(3) 135.5(3) 123.5(3)	27 25 25
Tetrahydrofuran-d <sub>8</sub>	3.58(br) 1.72(br)		67.4(5) 25.3(5)	22 20
Toluene-d <sub>8</sub>	7.09(5) 7.01(5) 6.97(3) 2.09(5)	0.8 0.8 1.0 2.2	137.5(1) 128.9(3) 128.0(3) 125.1(3) 20.4(7)	24 24 24 19

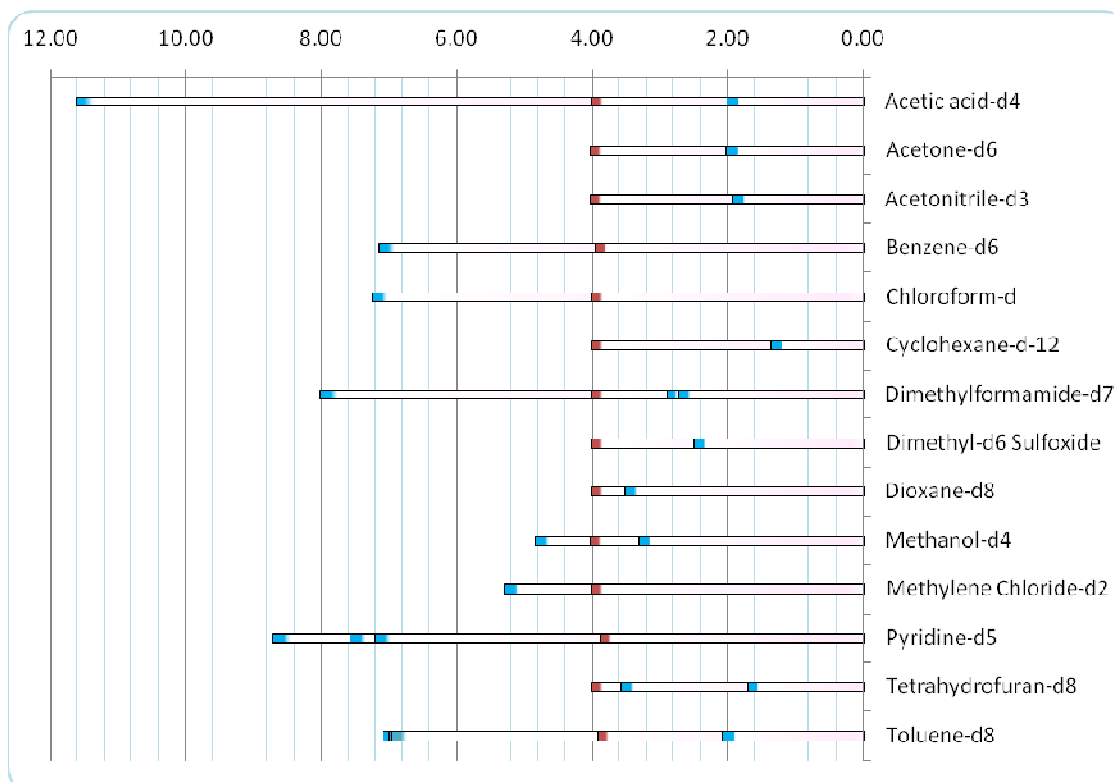


Figure 1. Proton shifts for cubane in deuterated solvents. Blue indicates solvent signals and red denotes the cubane signal.

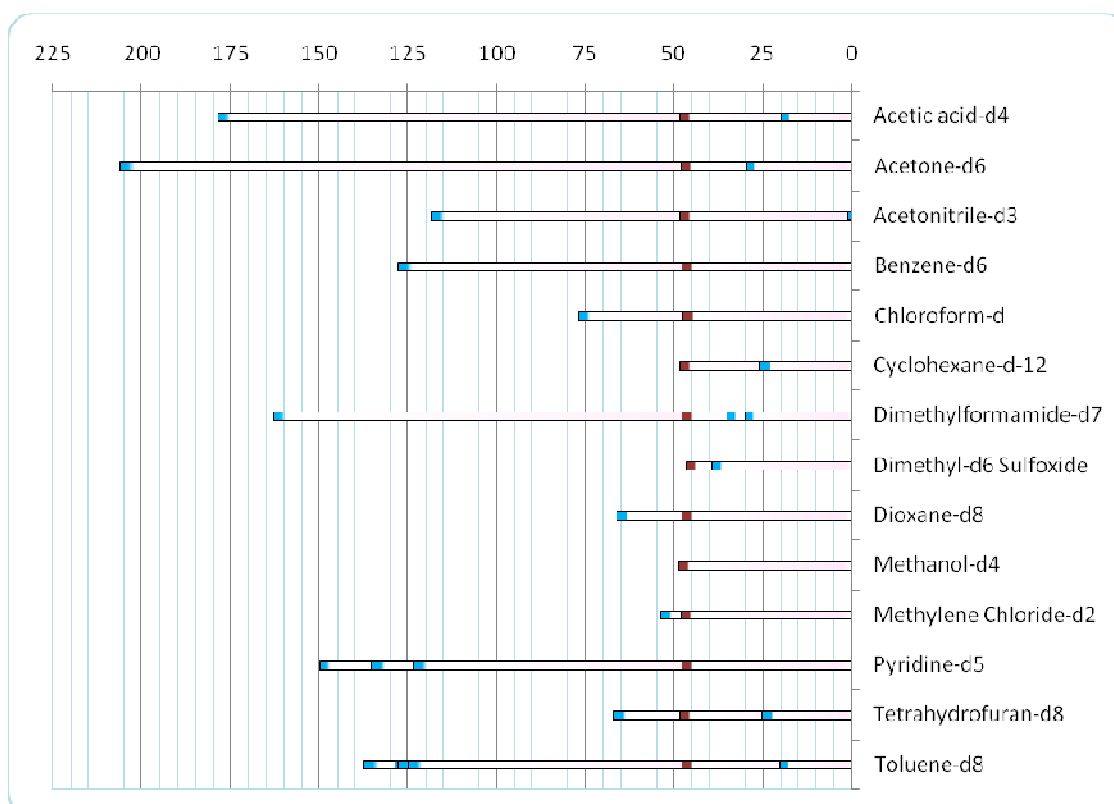
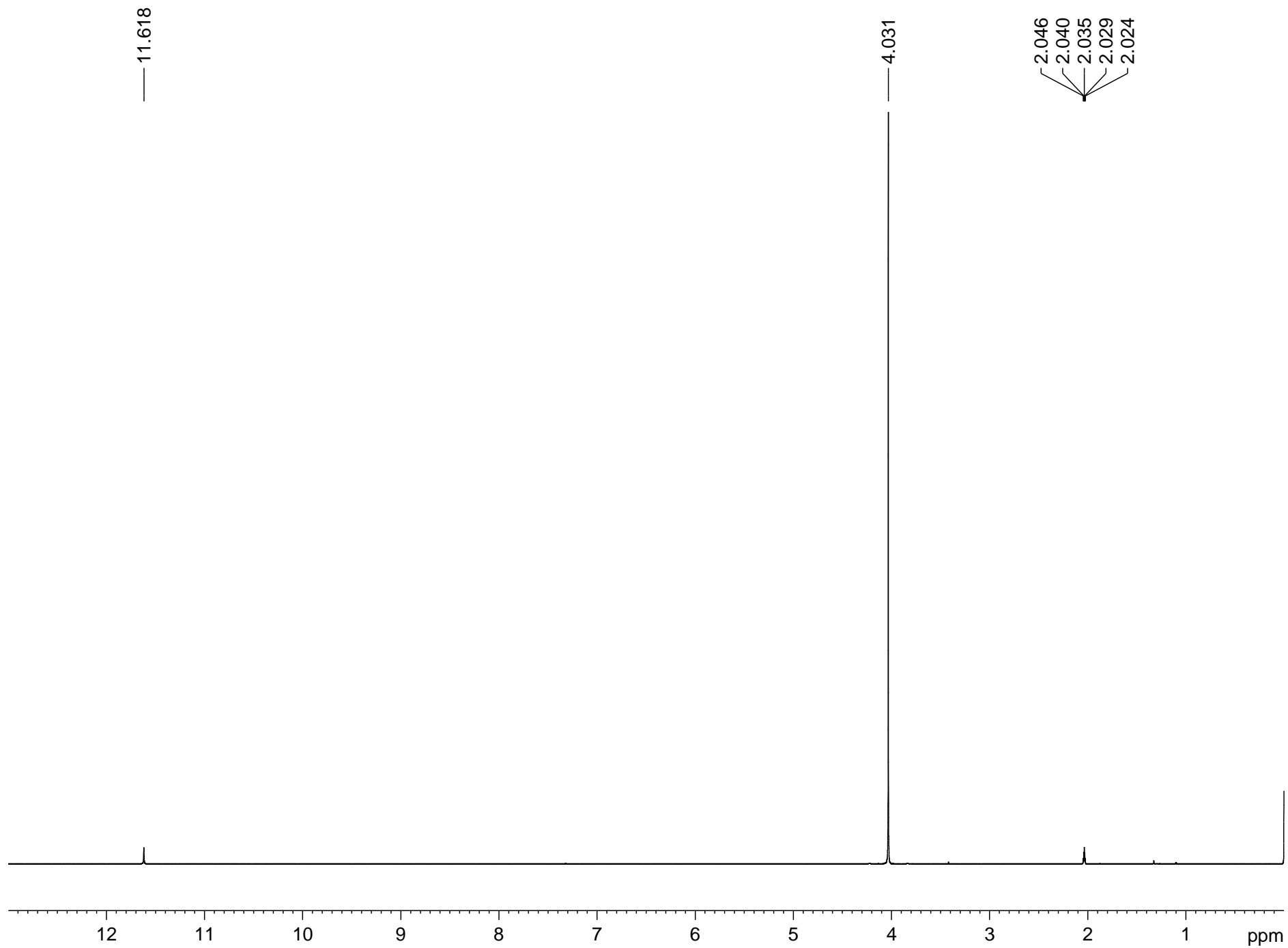
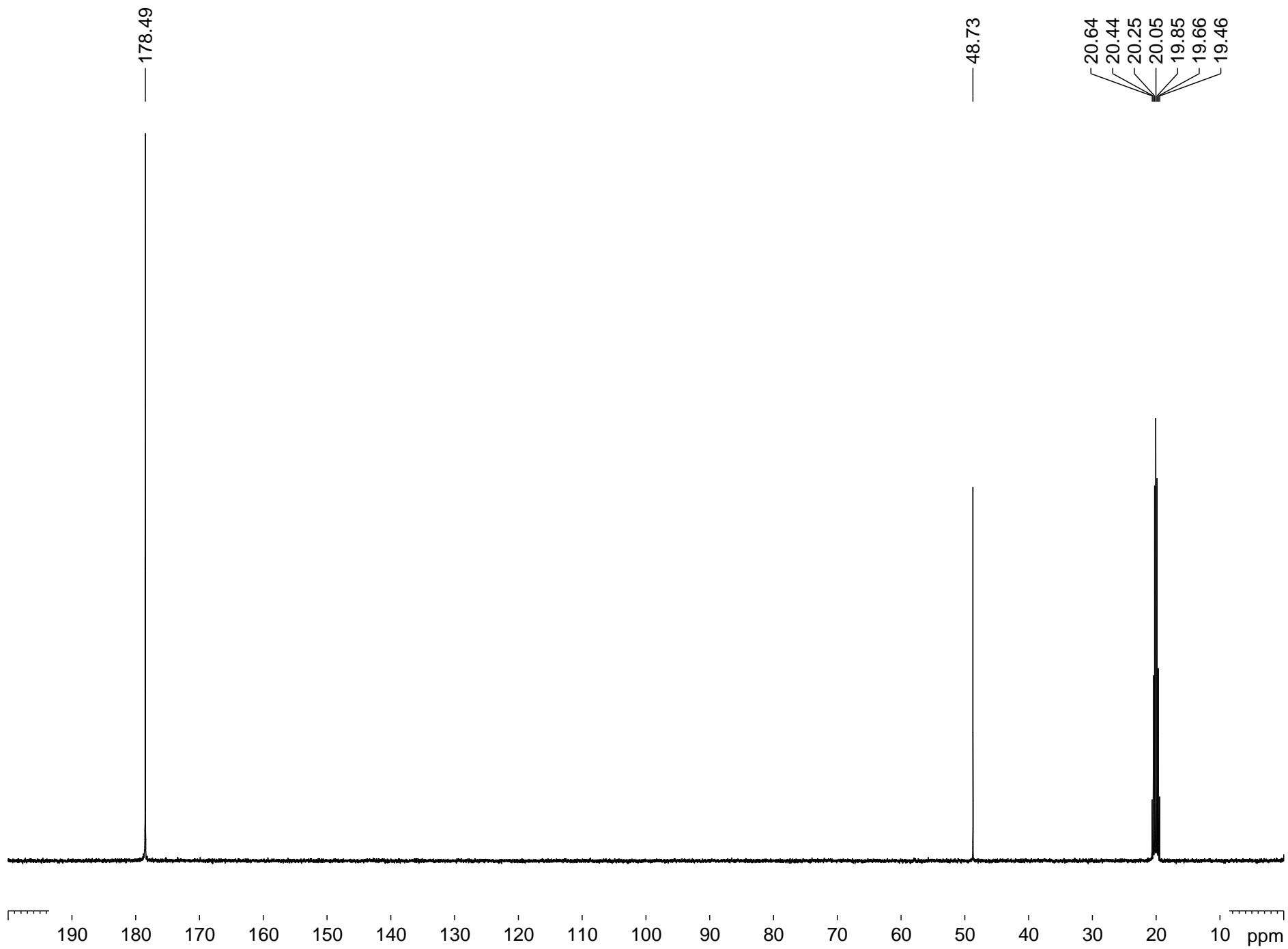


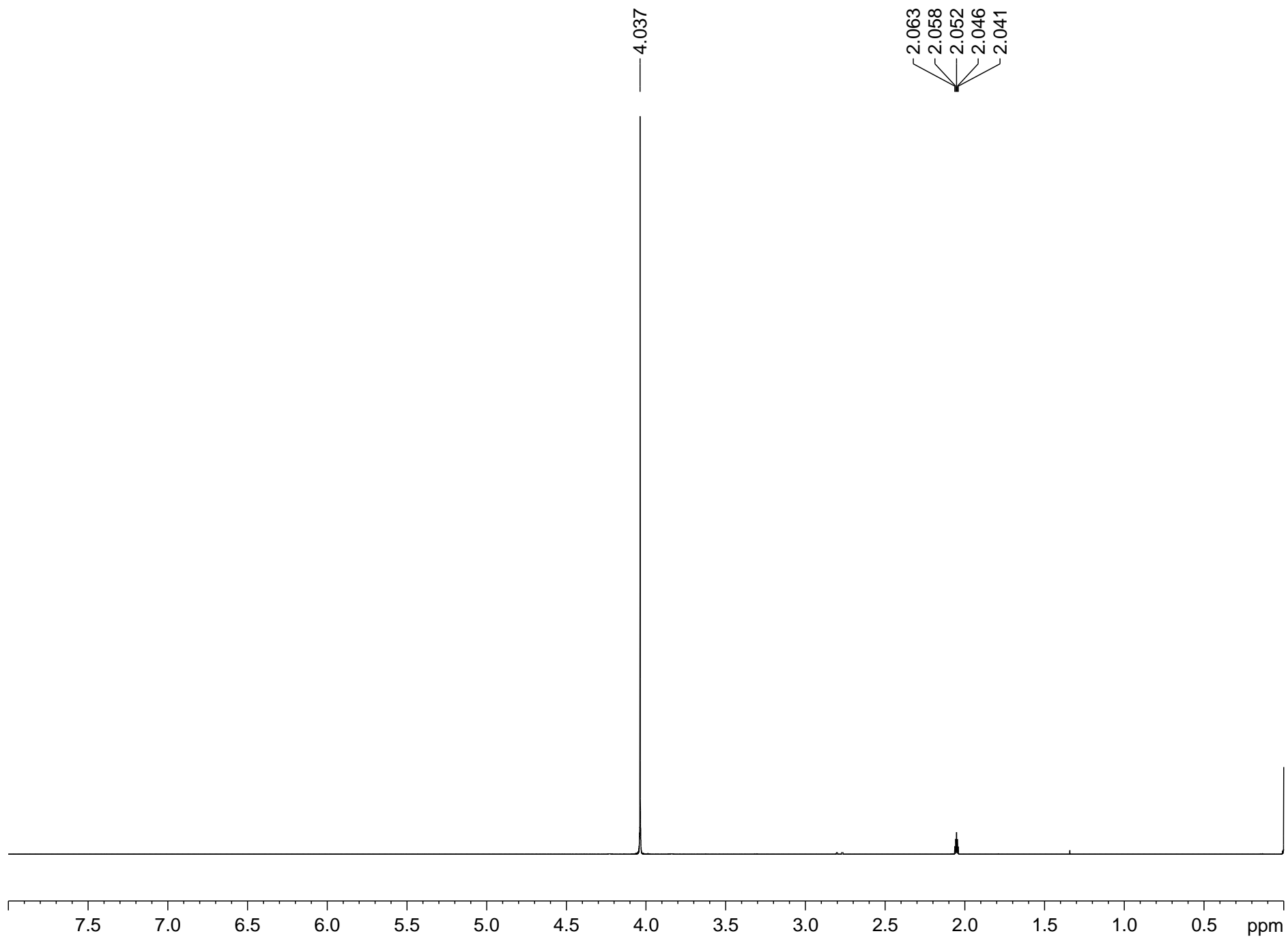
Figure 2. Carbon signals for cubane in deuterated solvents. Blue indicates solvent signals and red denotes the cubane signal.



1H, 400MHz, 298K, acetic acid-d4

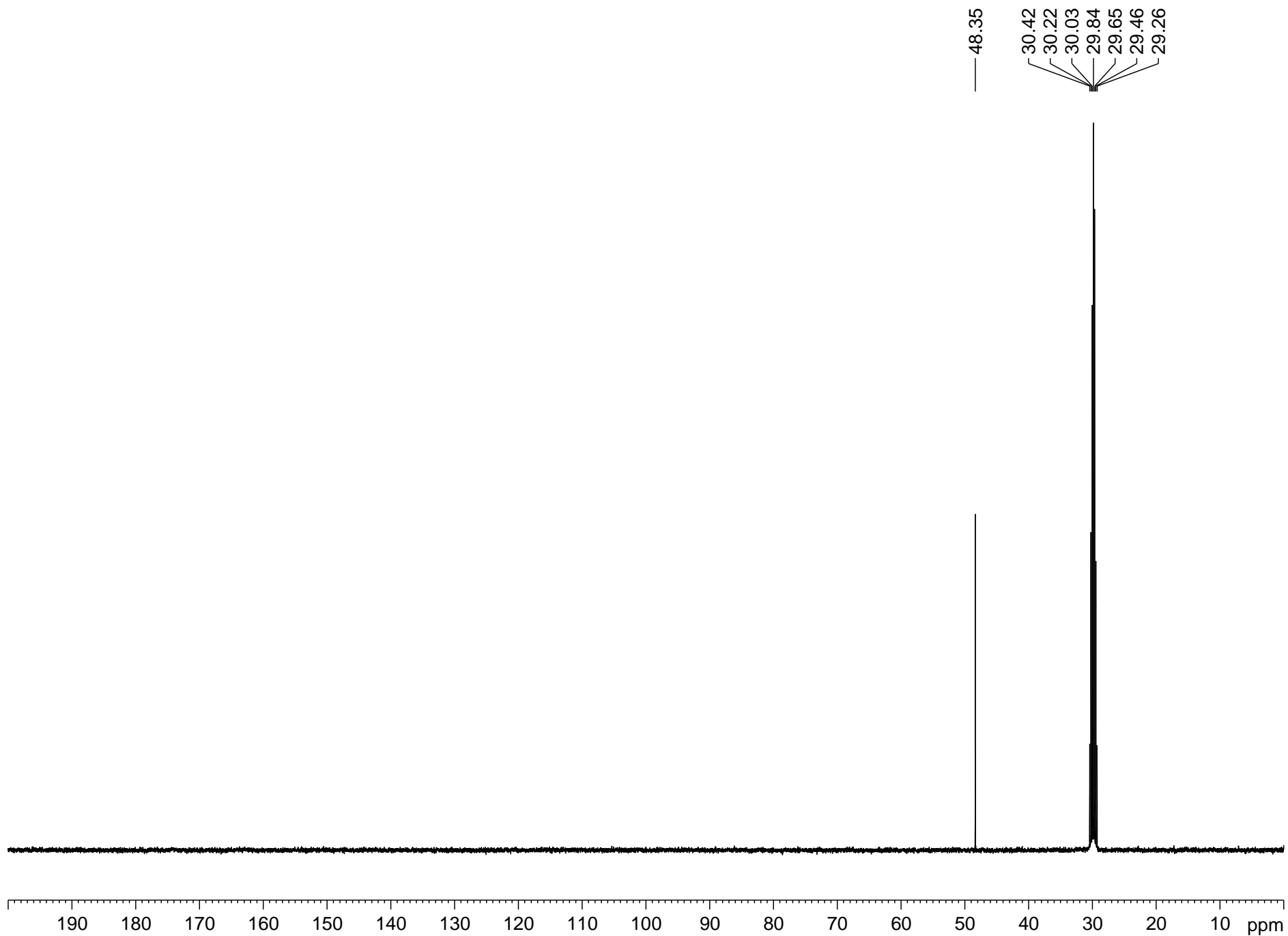


<sup>13</sup>C, 100MHz, 298K, acetic acid-d4

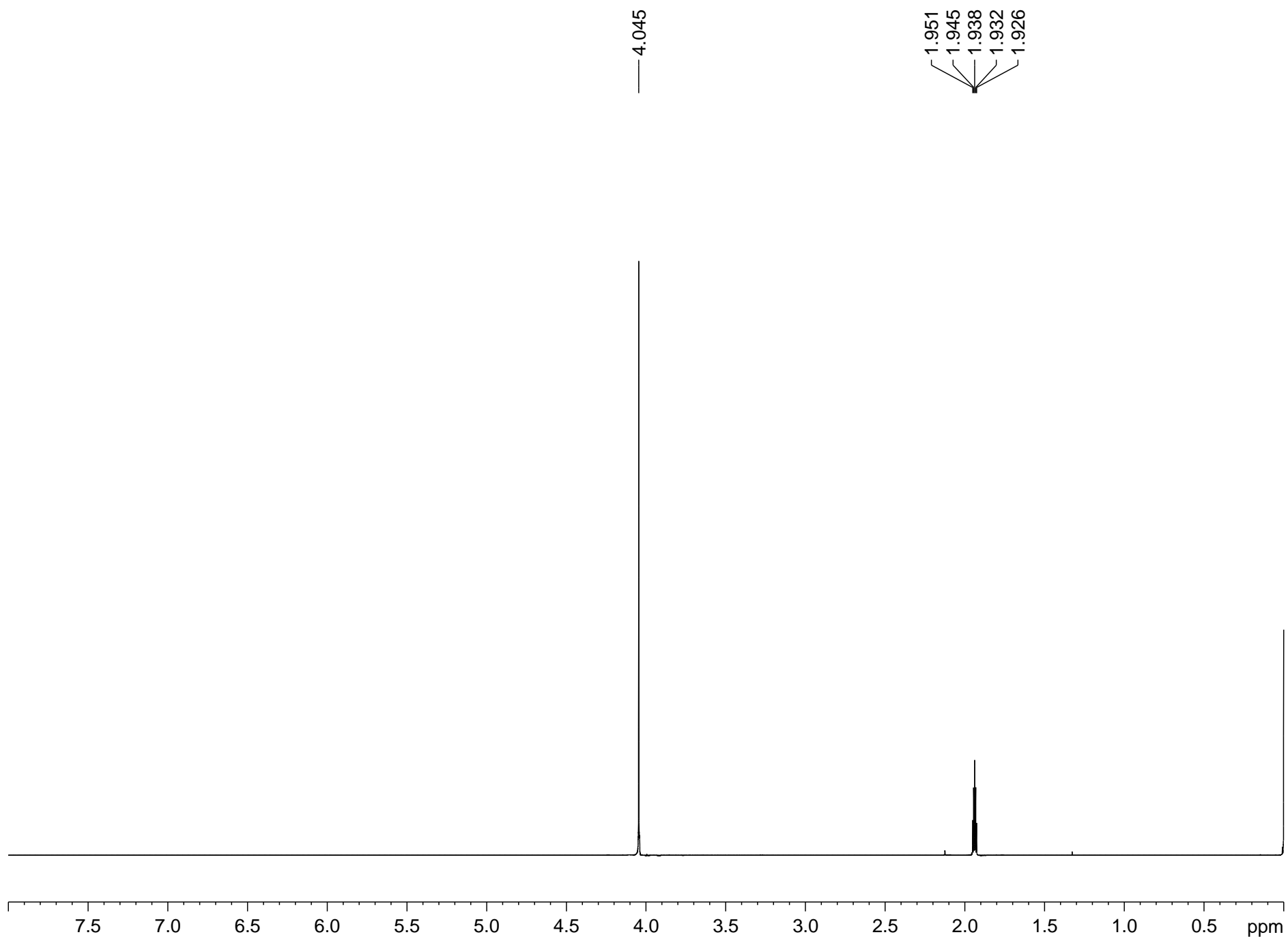


1H, 400MHz, 298K, acetone-d6

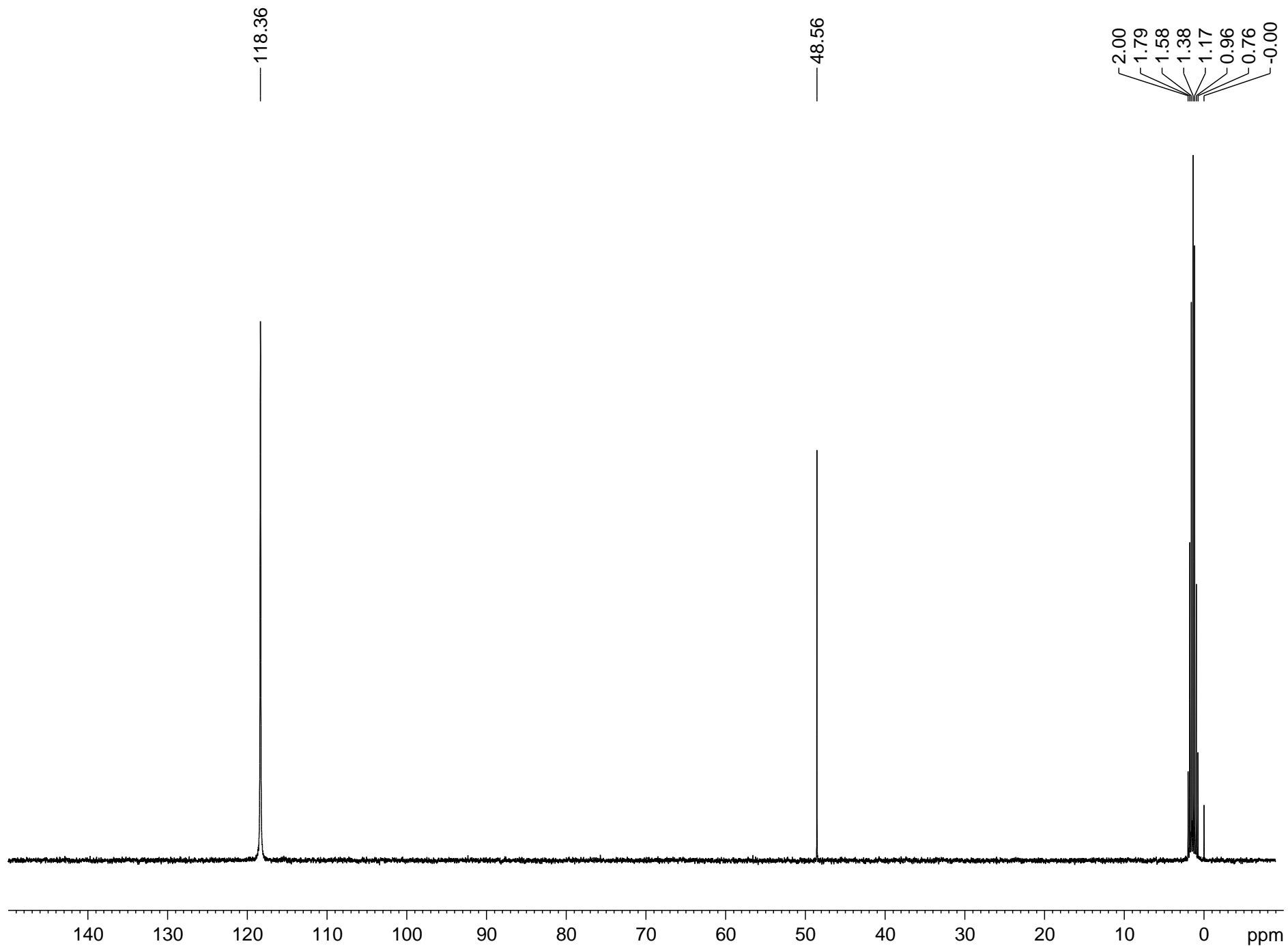




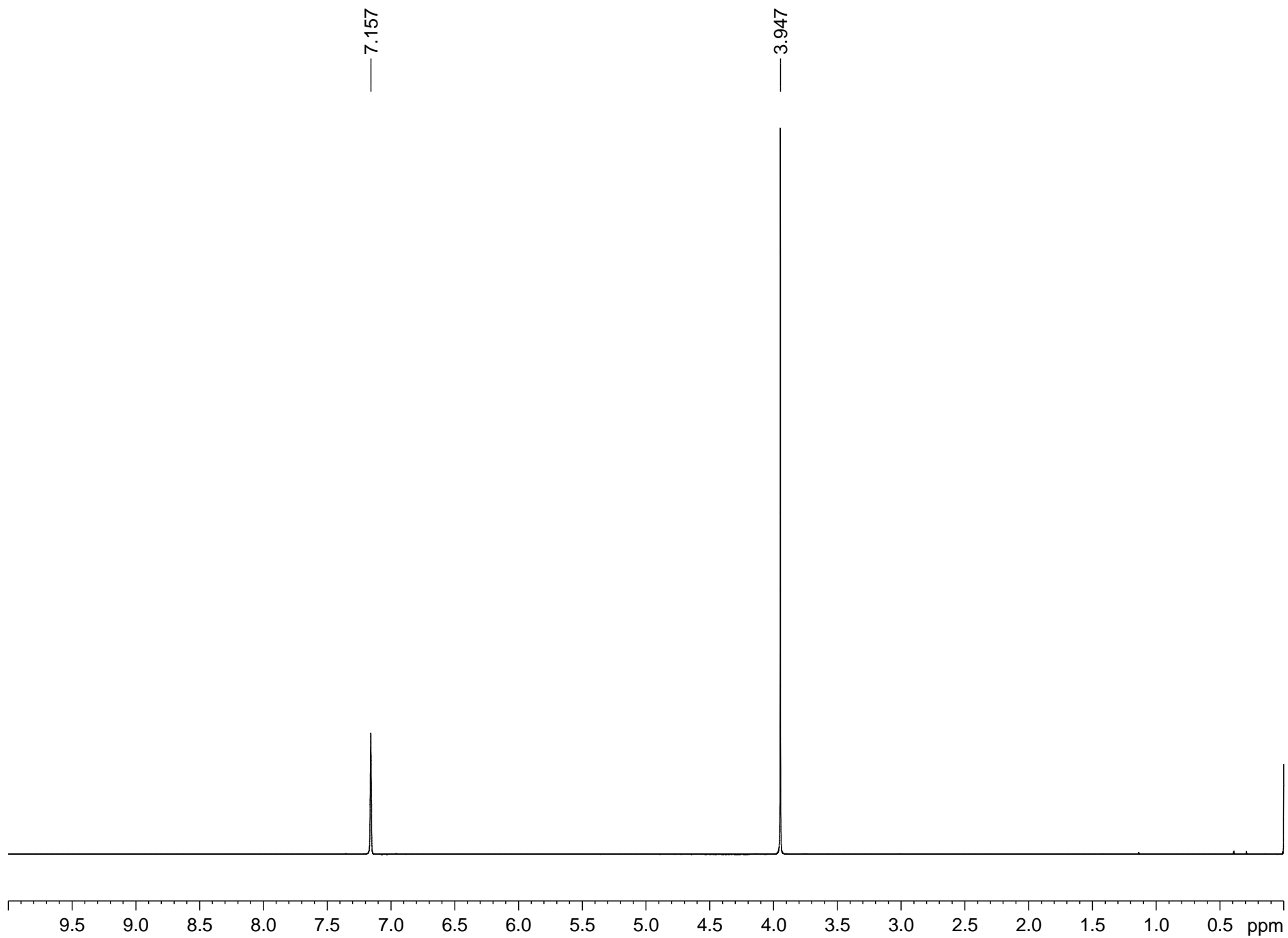
$^{13}\text{C}$ , 100MHz, 298K, acetone- $d_6$



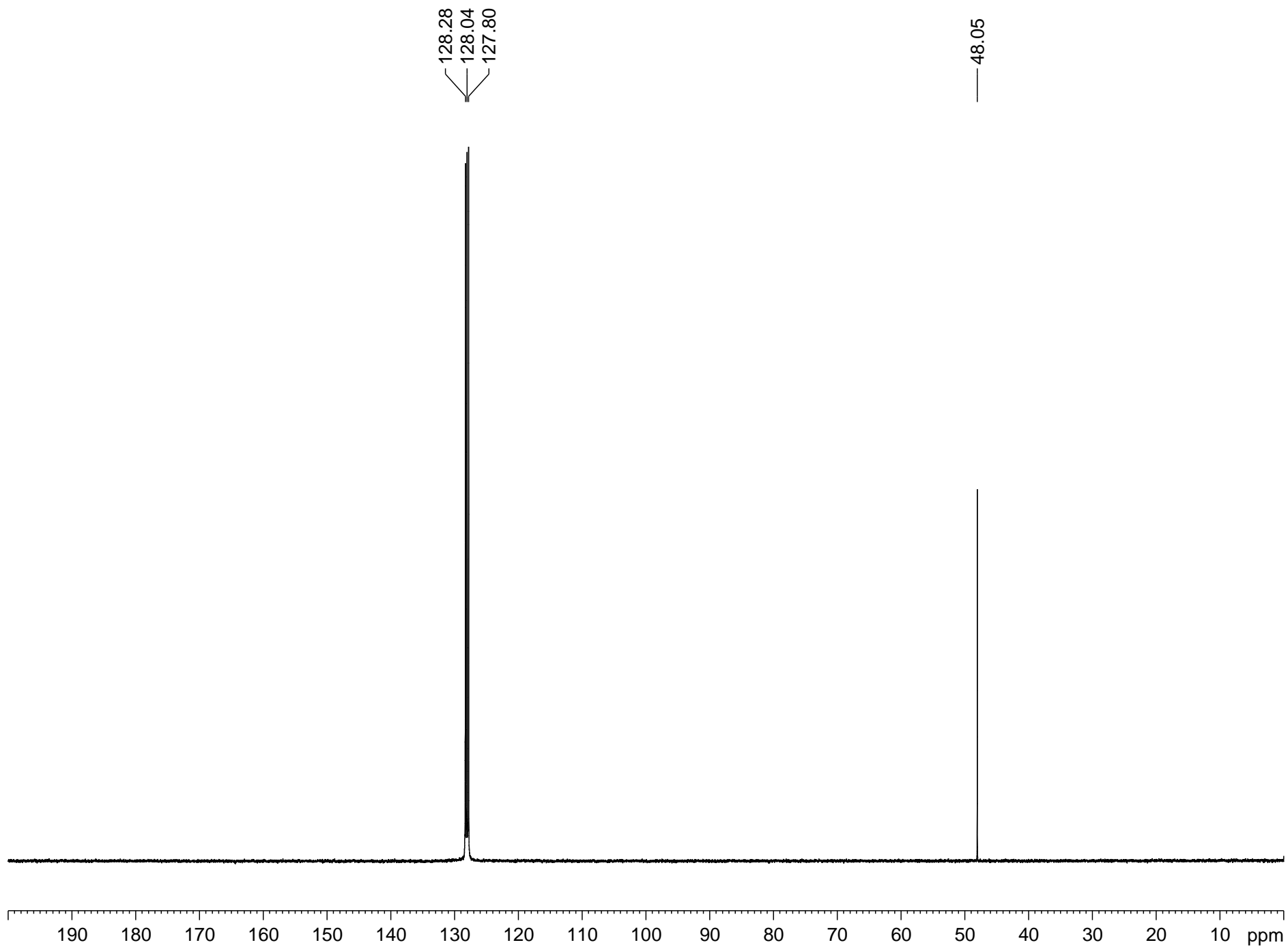
1H, 400MHz, 298K, acetonitrile-d3



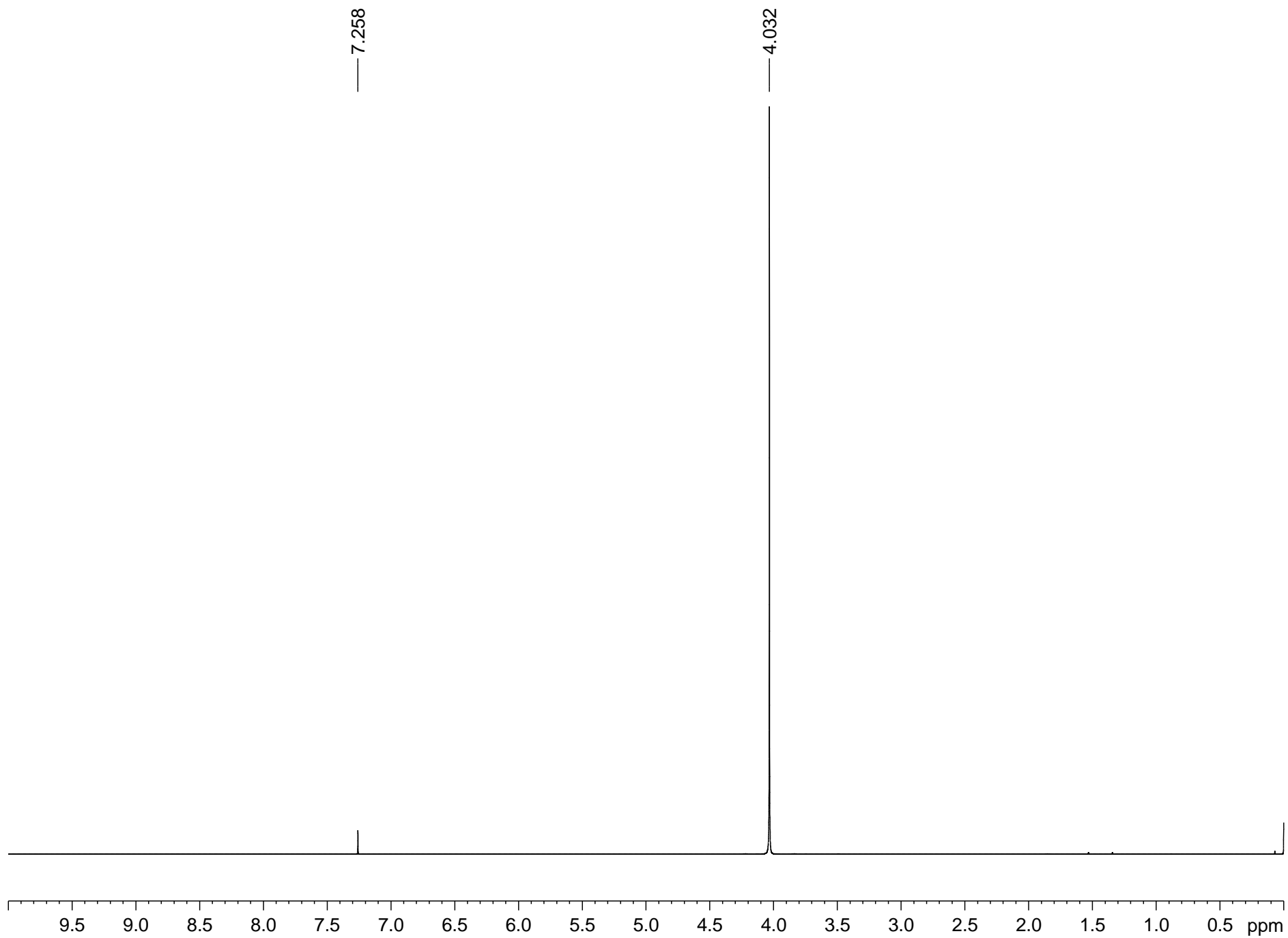
<sup>13</sup>C, 100MHz, 298K, acetonitrile-d<sub>3</sub>



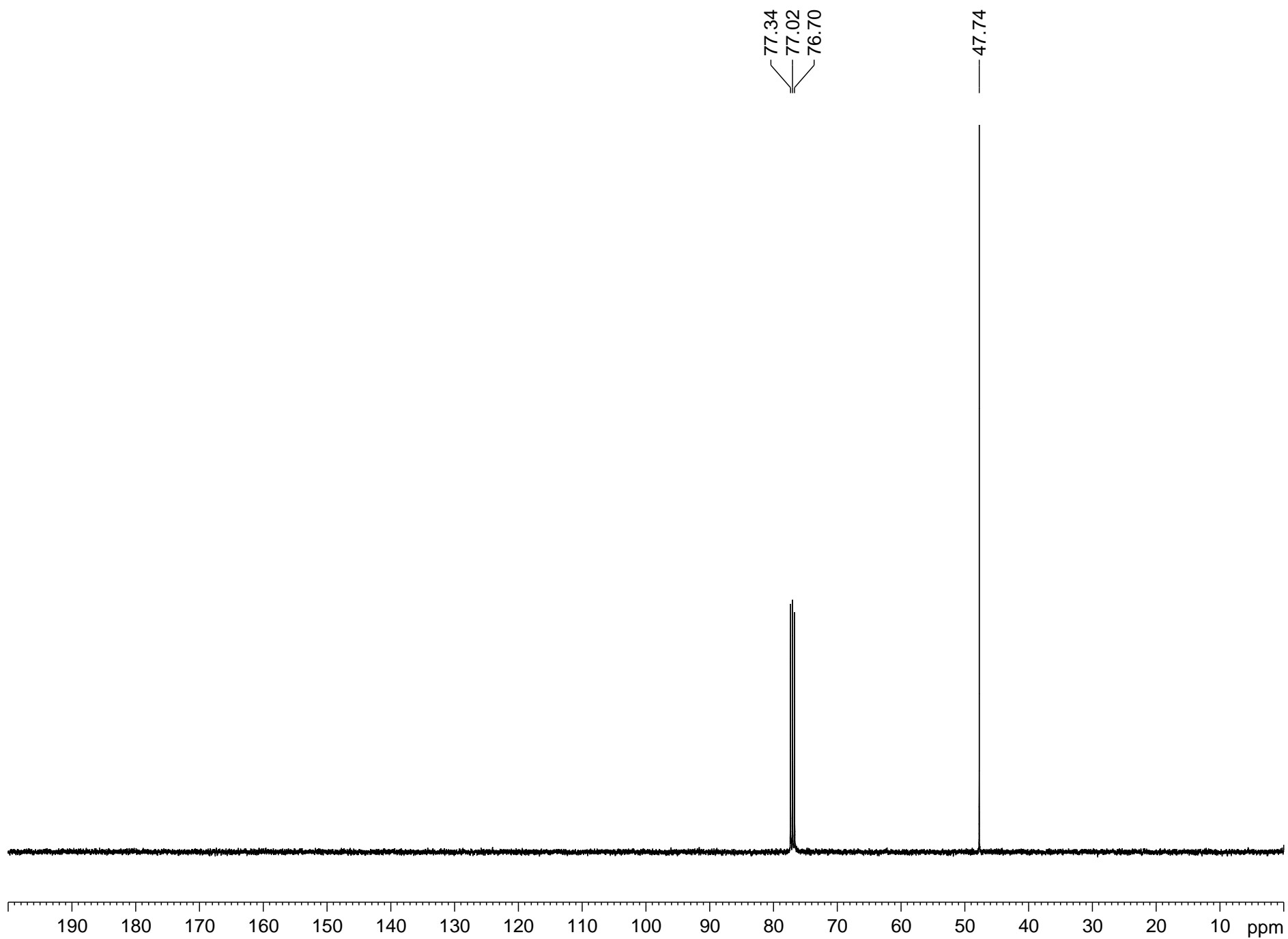
1H, 400MHz, 298K, benzene-d6



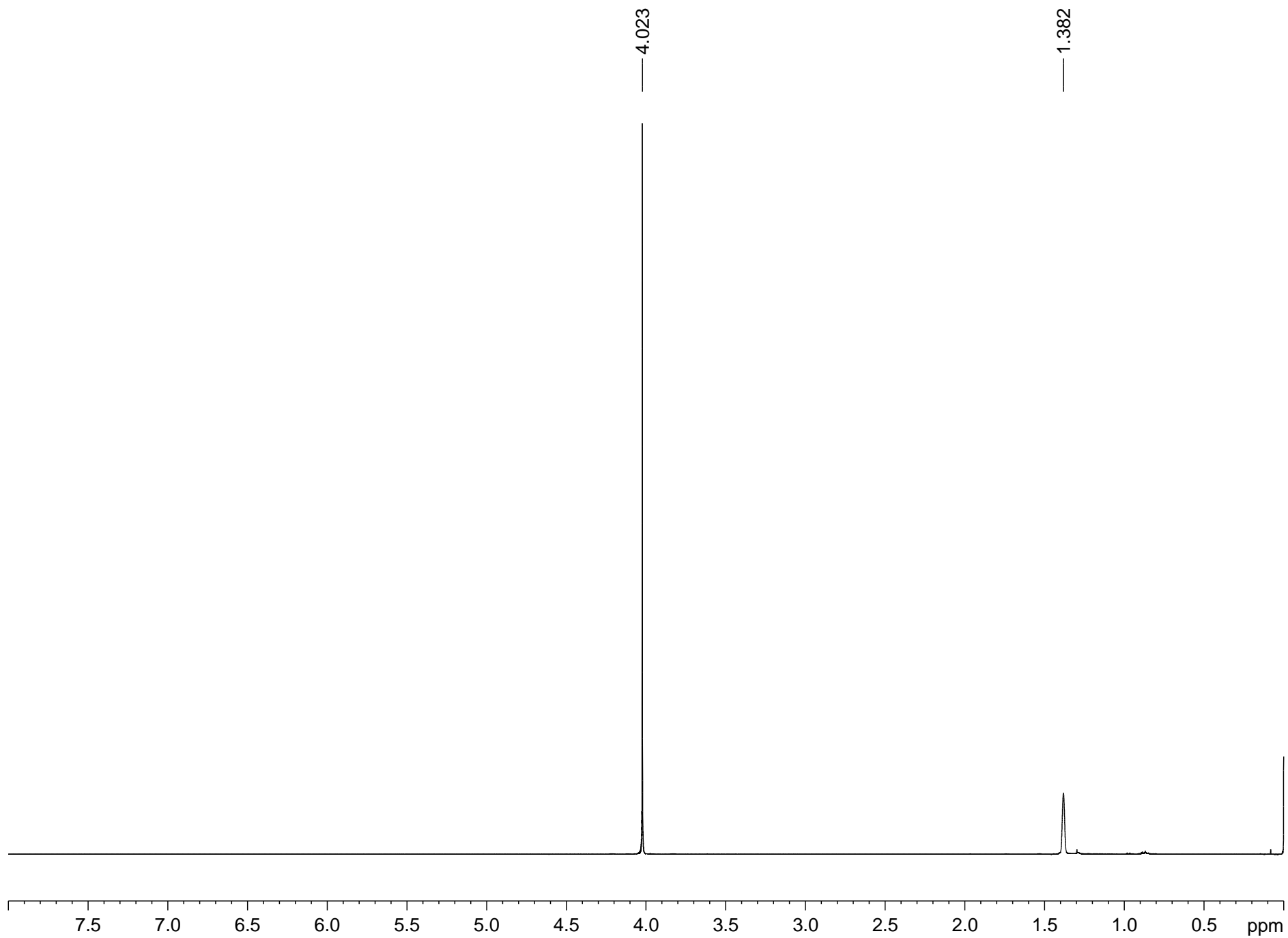
<sup>13</sup>C, 100MHz, 298K, benzene-d<sub>6</sub>



1H, 400MHz, 298K, chloroform-d

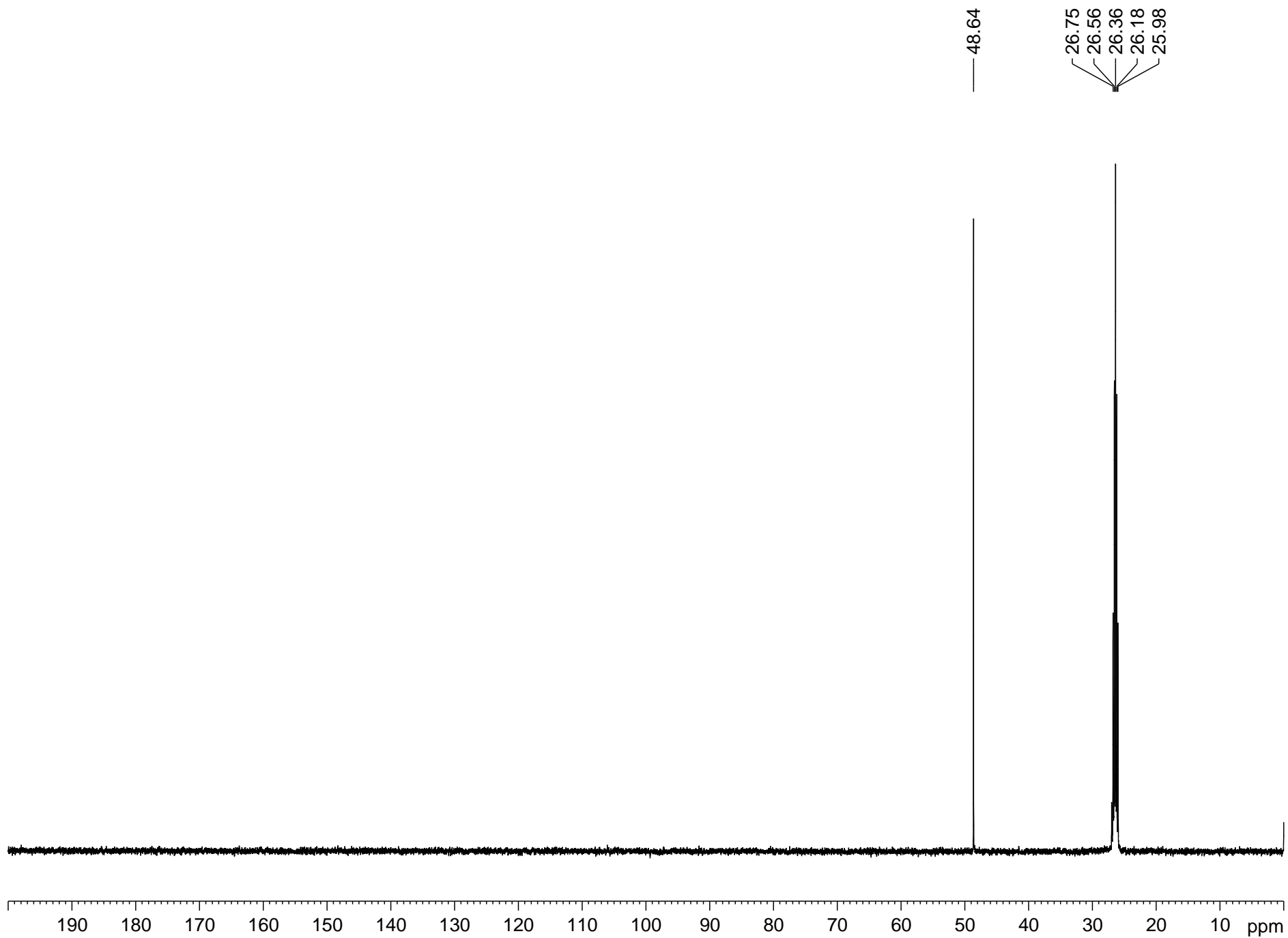


<sup>13</sup>C, 100MHz, 298K, chloroform-d

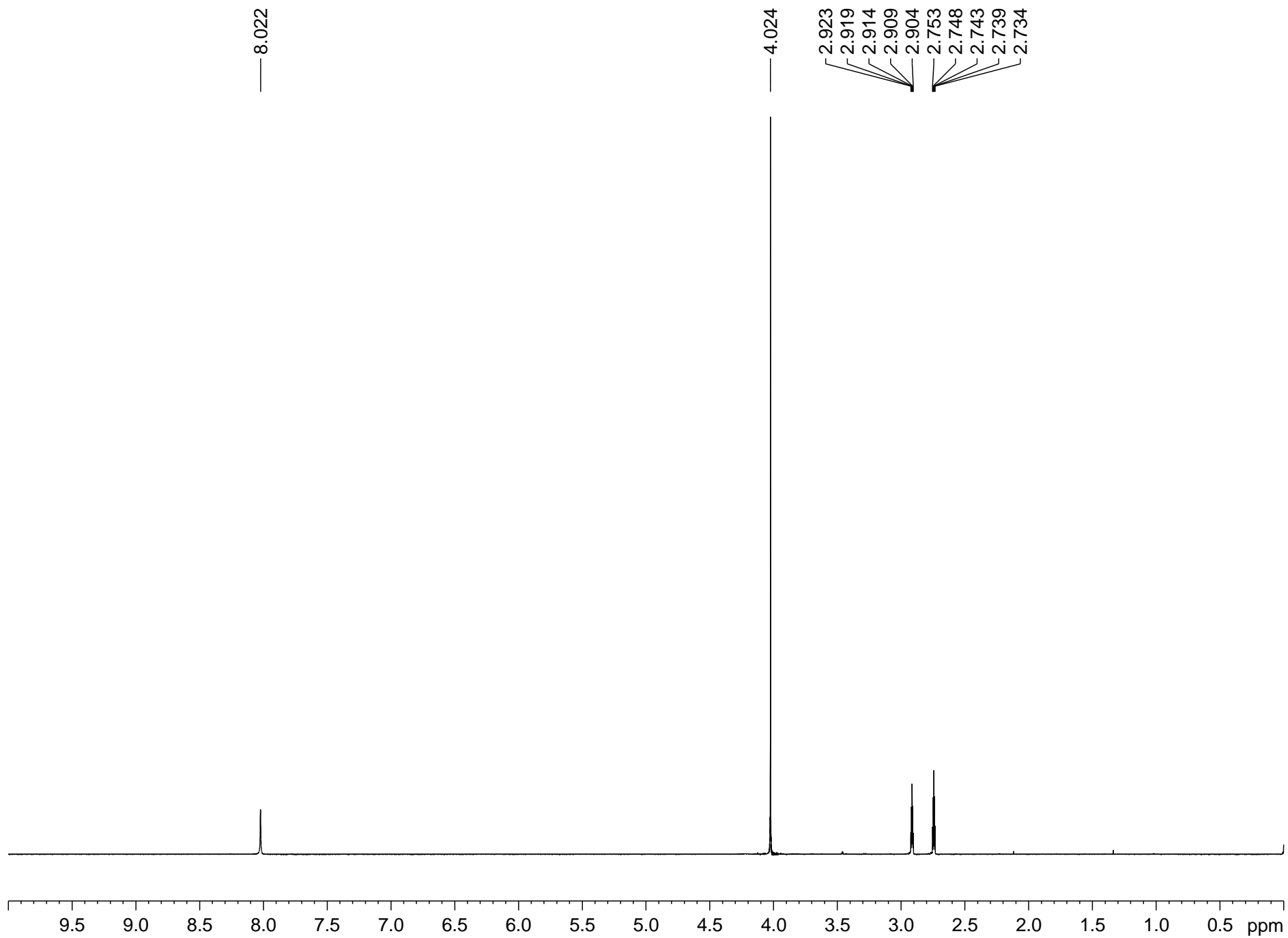


1H, 400MHz, 298K, cyclohexane-d12

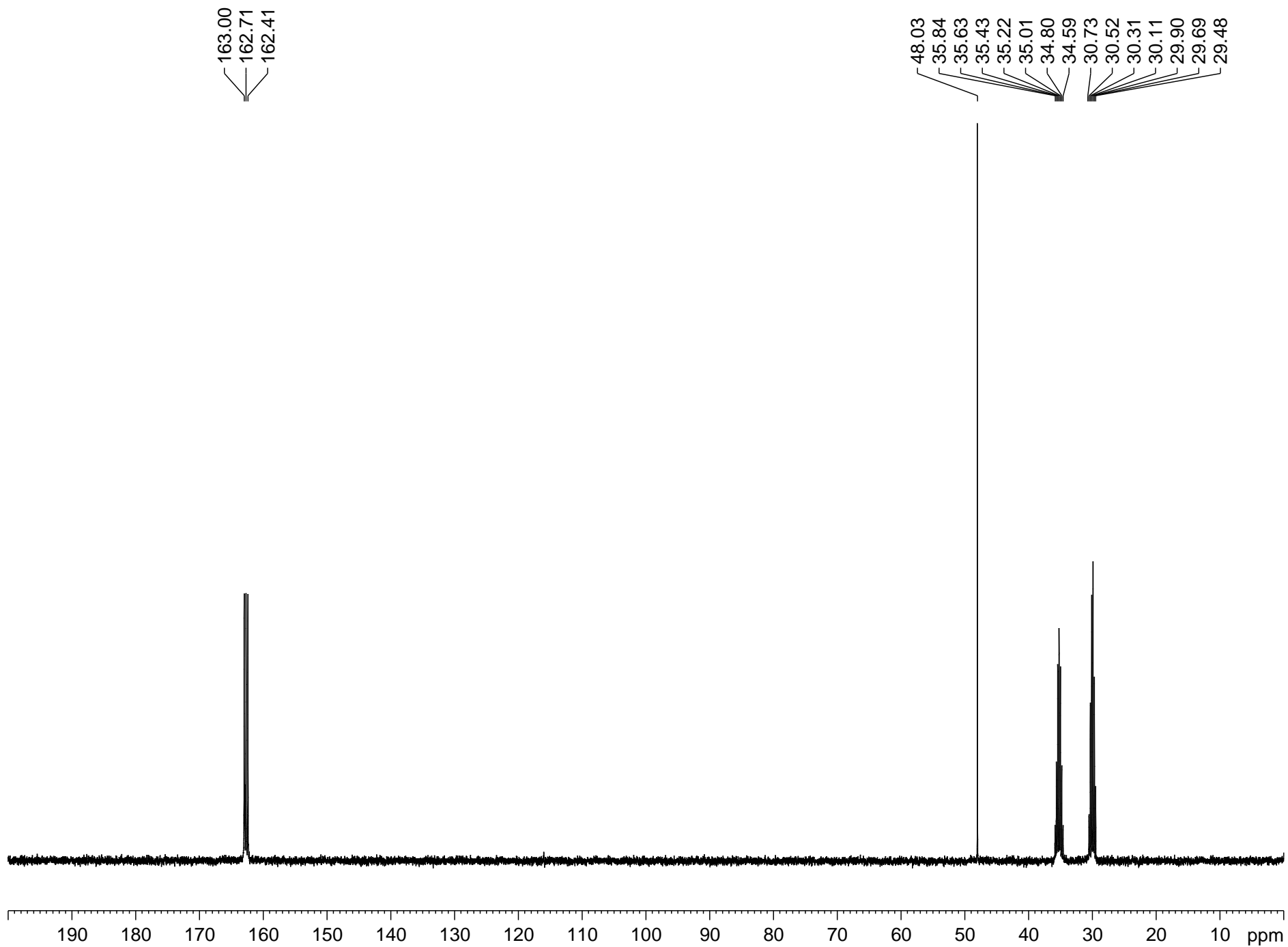




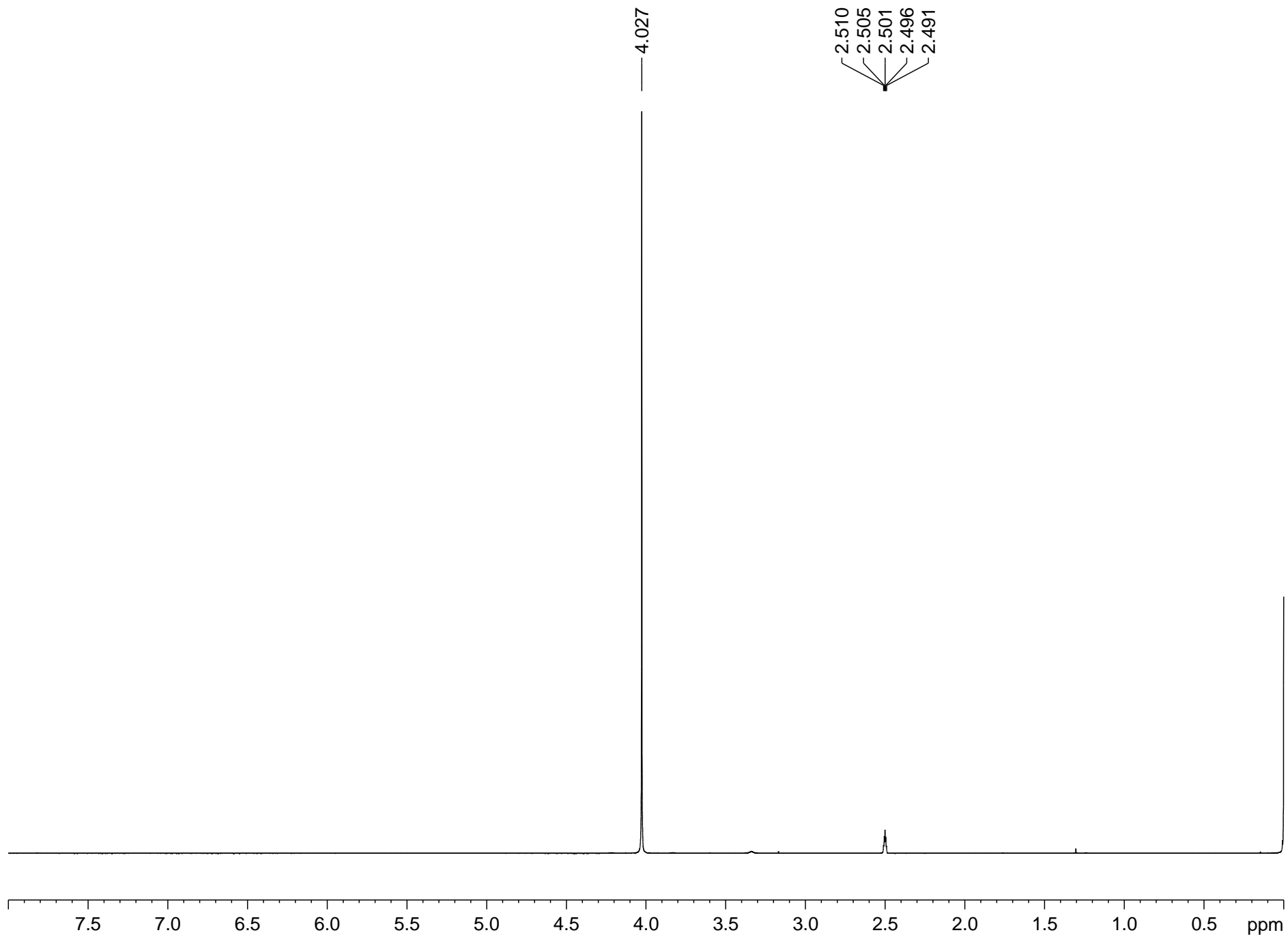
<sup>13</sup>C, 100MHz, 298K, cyclohexane-d12



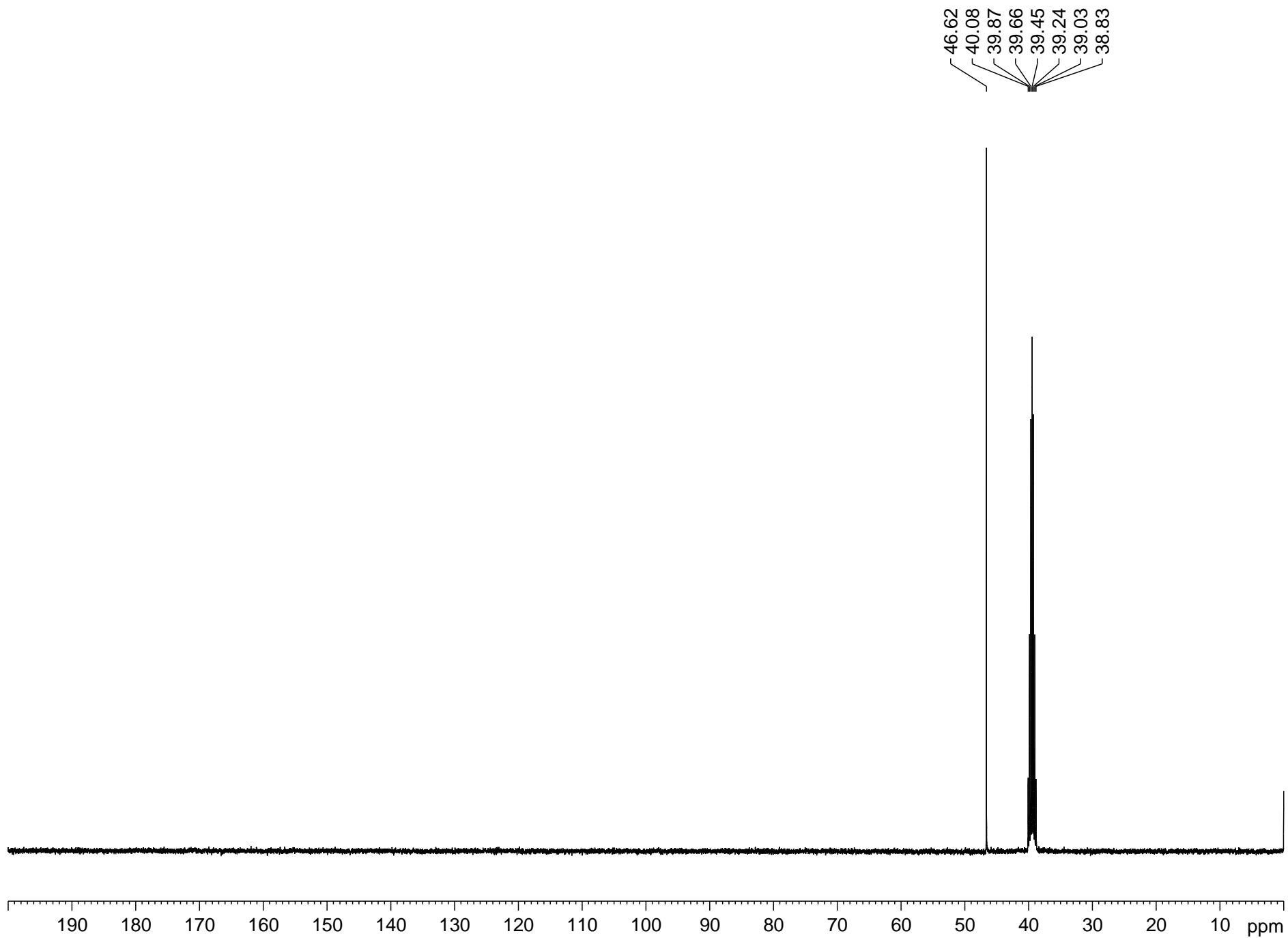
$^1\text{H}$ , 400MHz, 298K, dimethylformamide- $\text{d}_7$



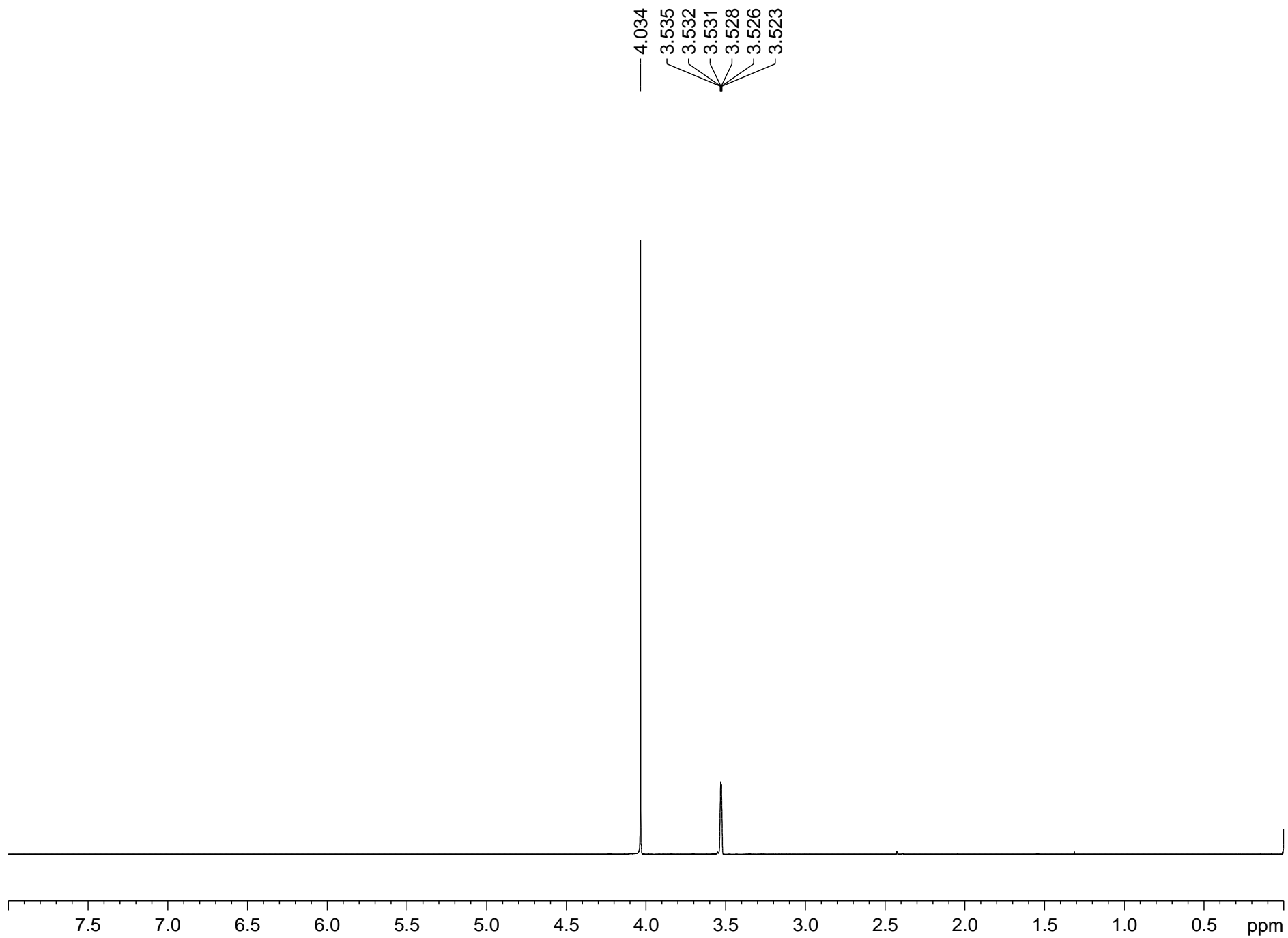
<sup>13</sup>C, 100MHz, 298K, dimethylformamide-d<sub>7</sub>



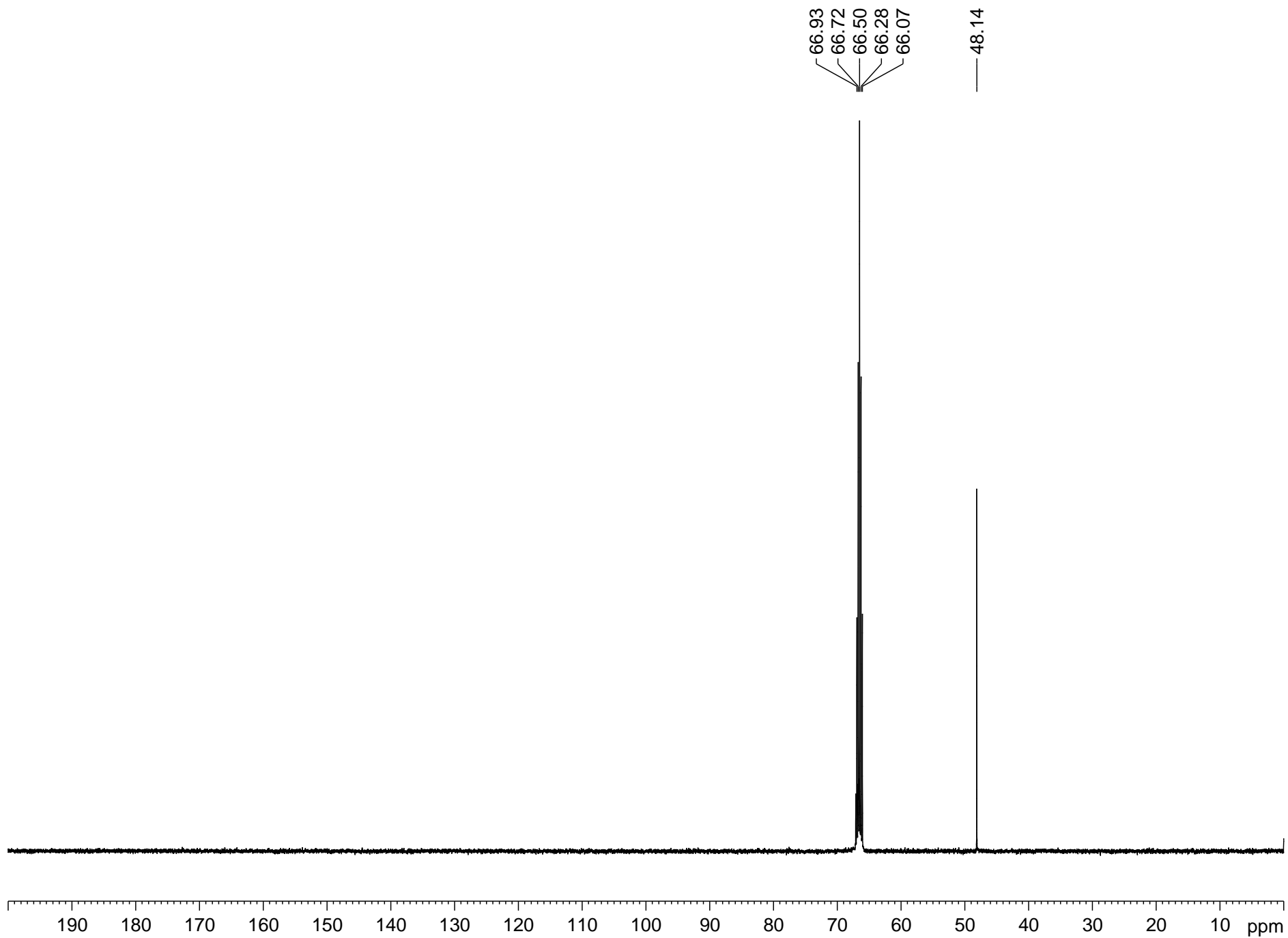
1H, 400MHz, 298K, dimethyl-d6 sulfoxide



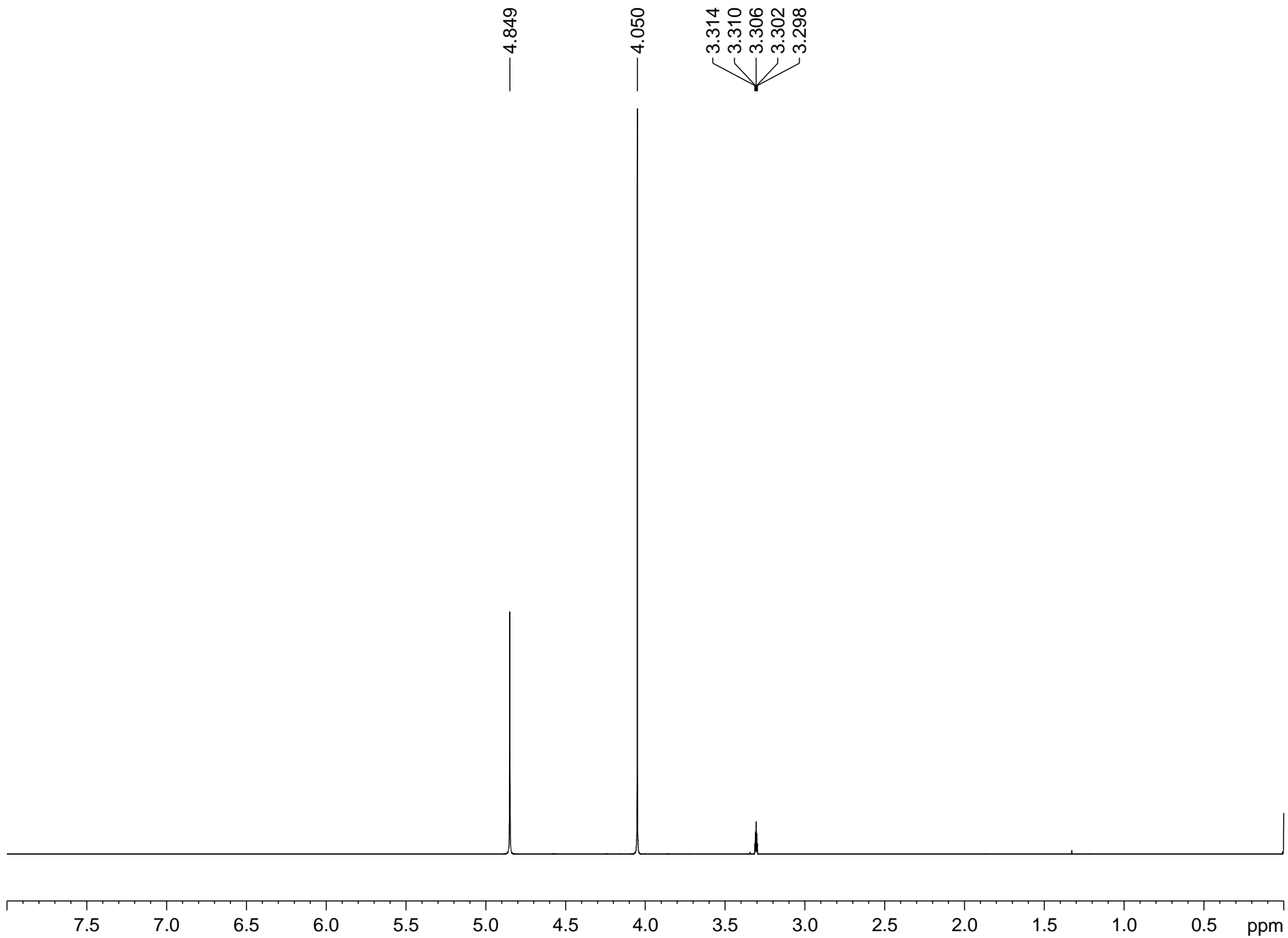
<sup>13</sup>C, 100MHz, 298K, dimethyl-d6 sulfoxide



1H, 400MHz, 298K, dioxane-d8

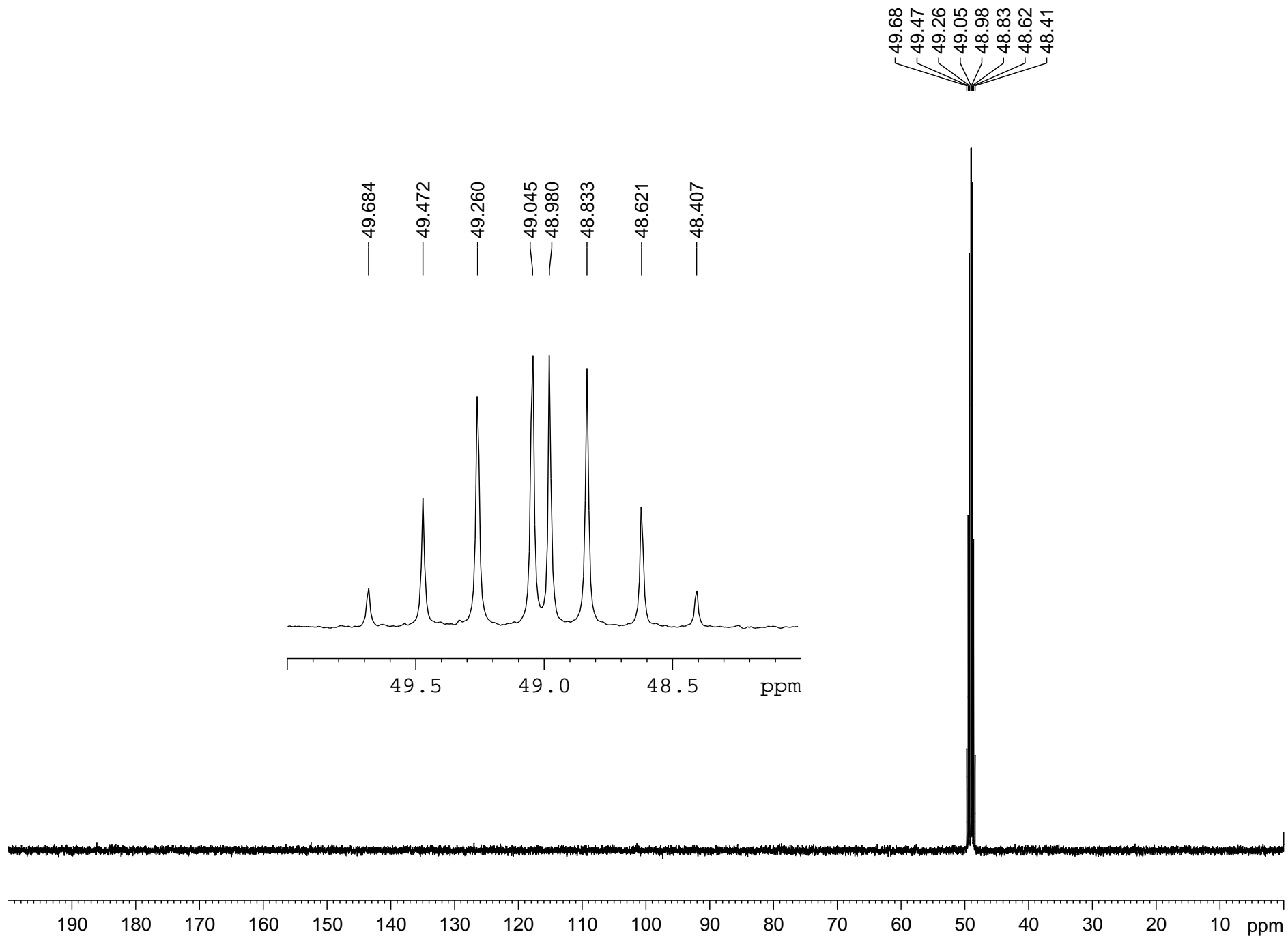


<sup>13</sup>C, 100MHz, 298K, dioxane-d<sub>8</sub>

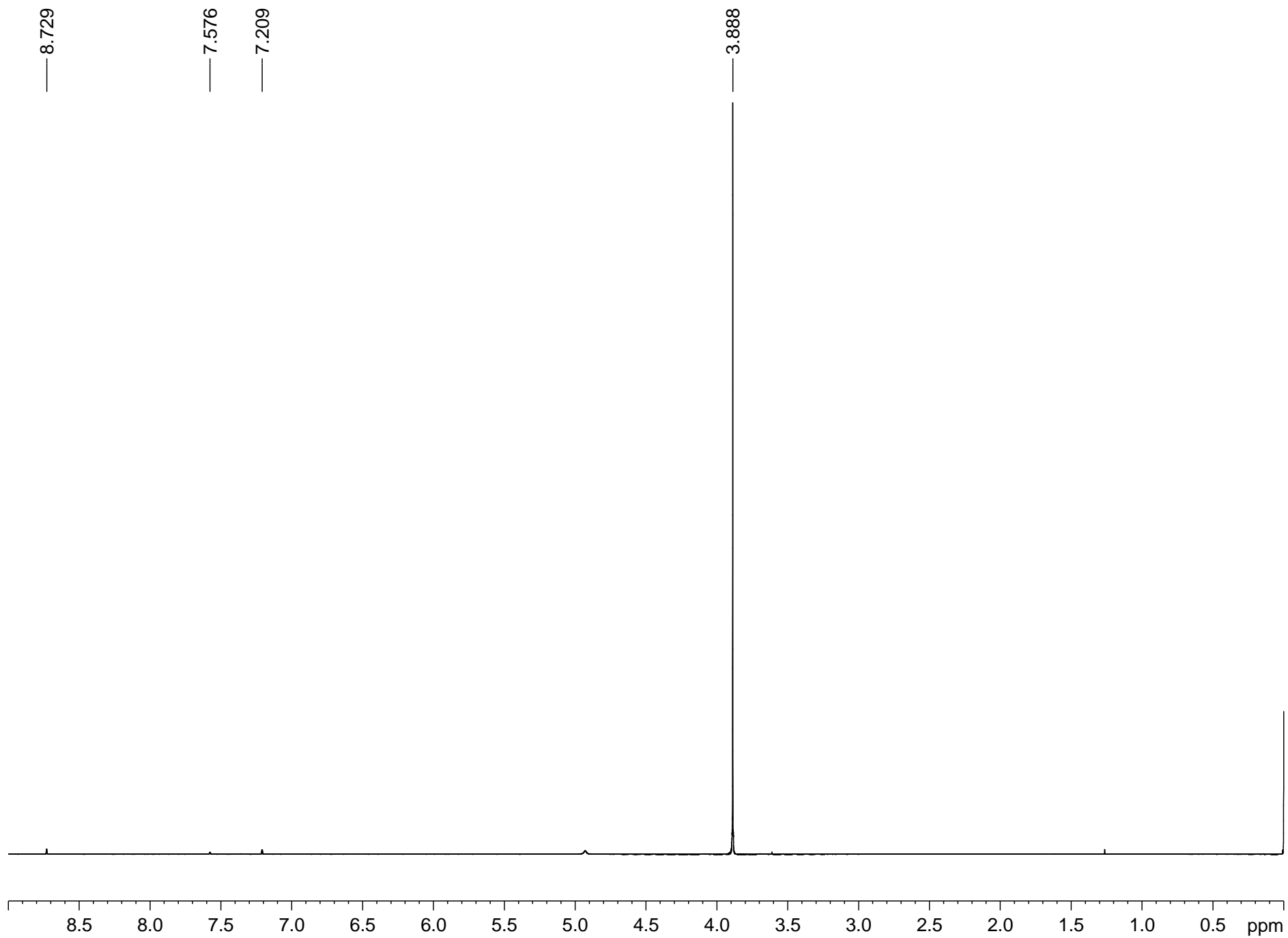


1H, 400MHz, 298K, methanol-d4

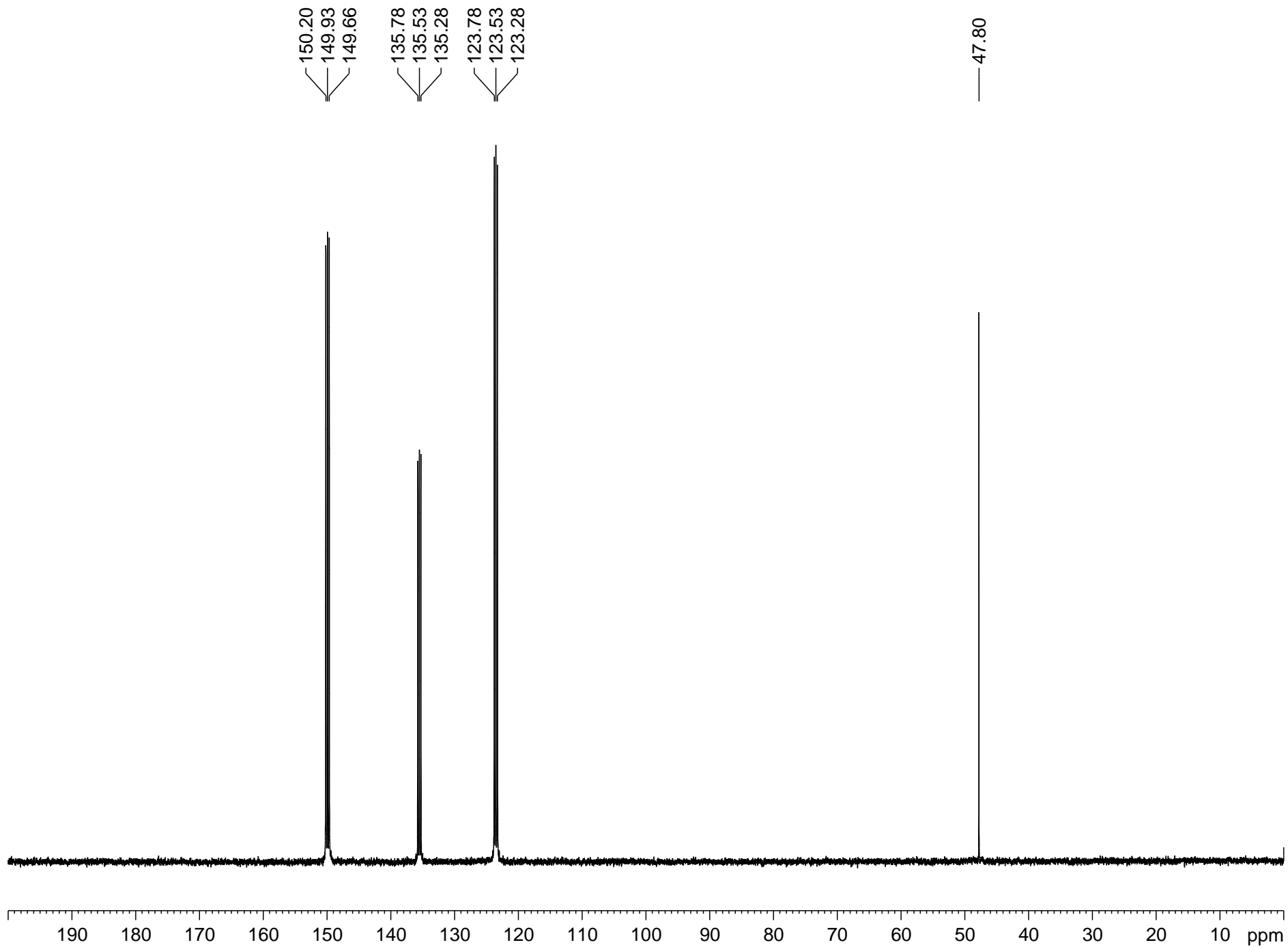




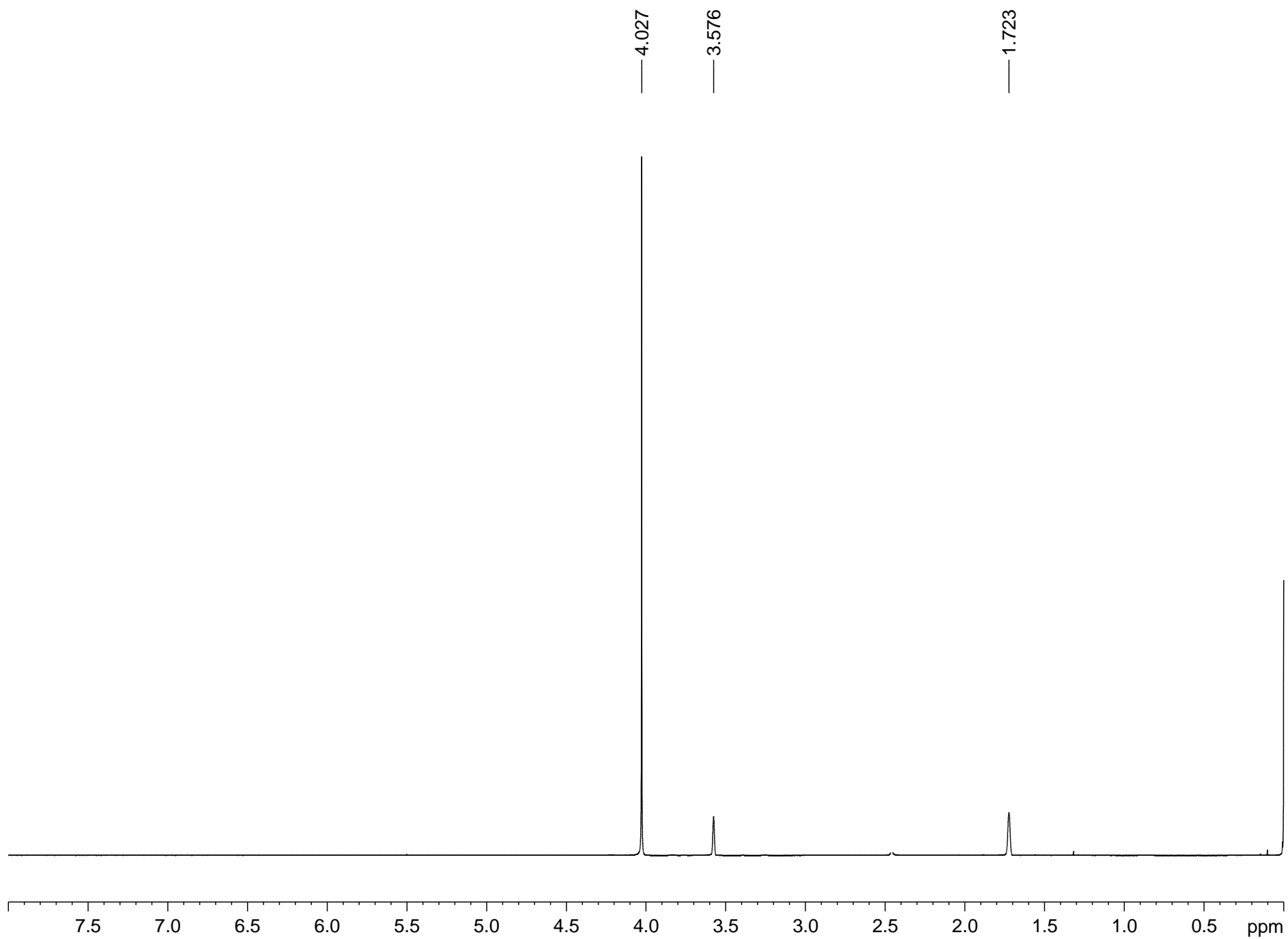
<sup>13</sup>C, 100MHz, 298K, methanol-d<sub>4</sub>



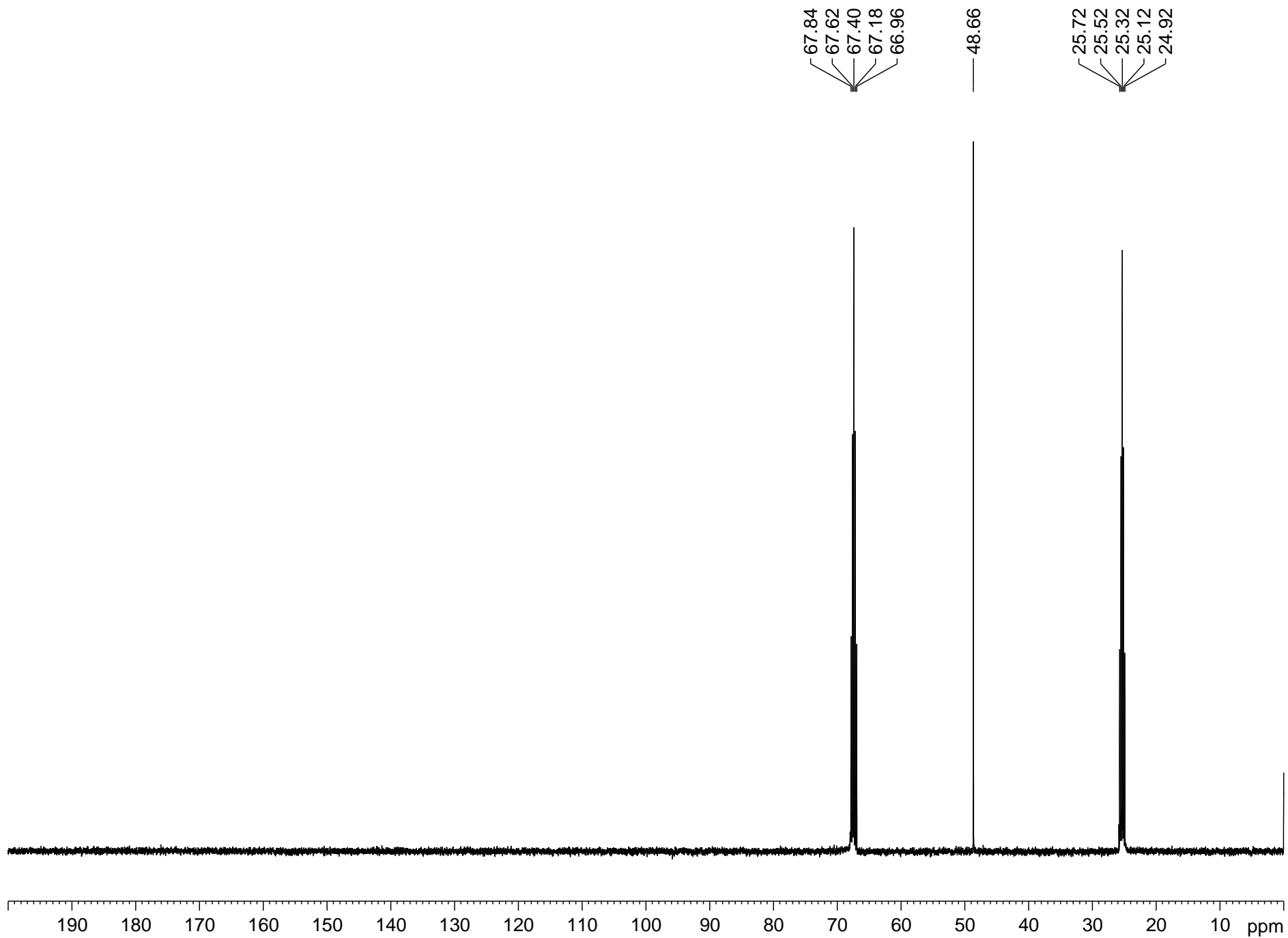
1H, 400MHz, 298K, pyridine-d5



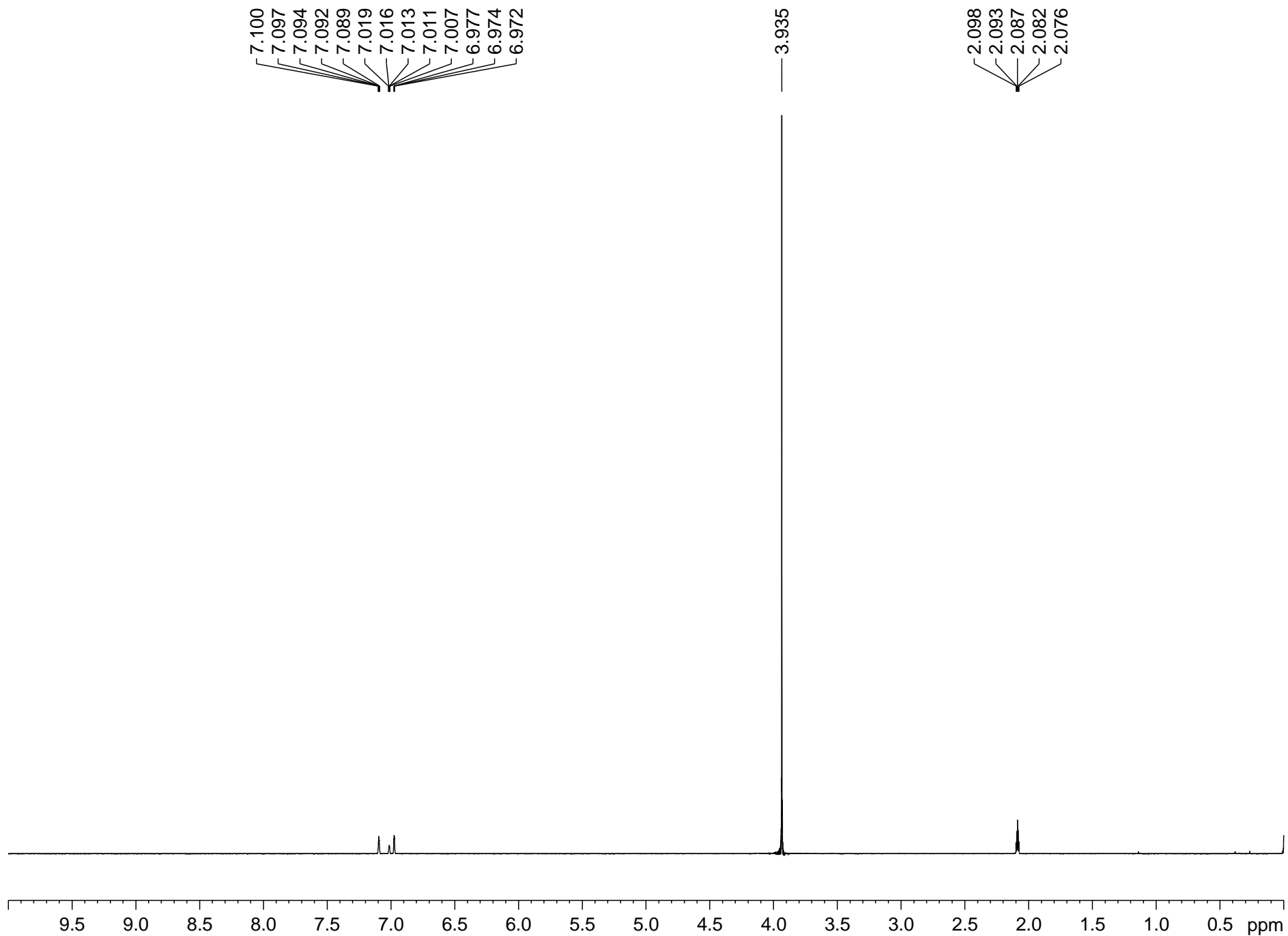
<sup>13</sup>C, 100MHz, 298K, pyridine-d<sub>5</sub>



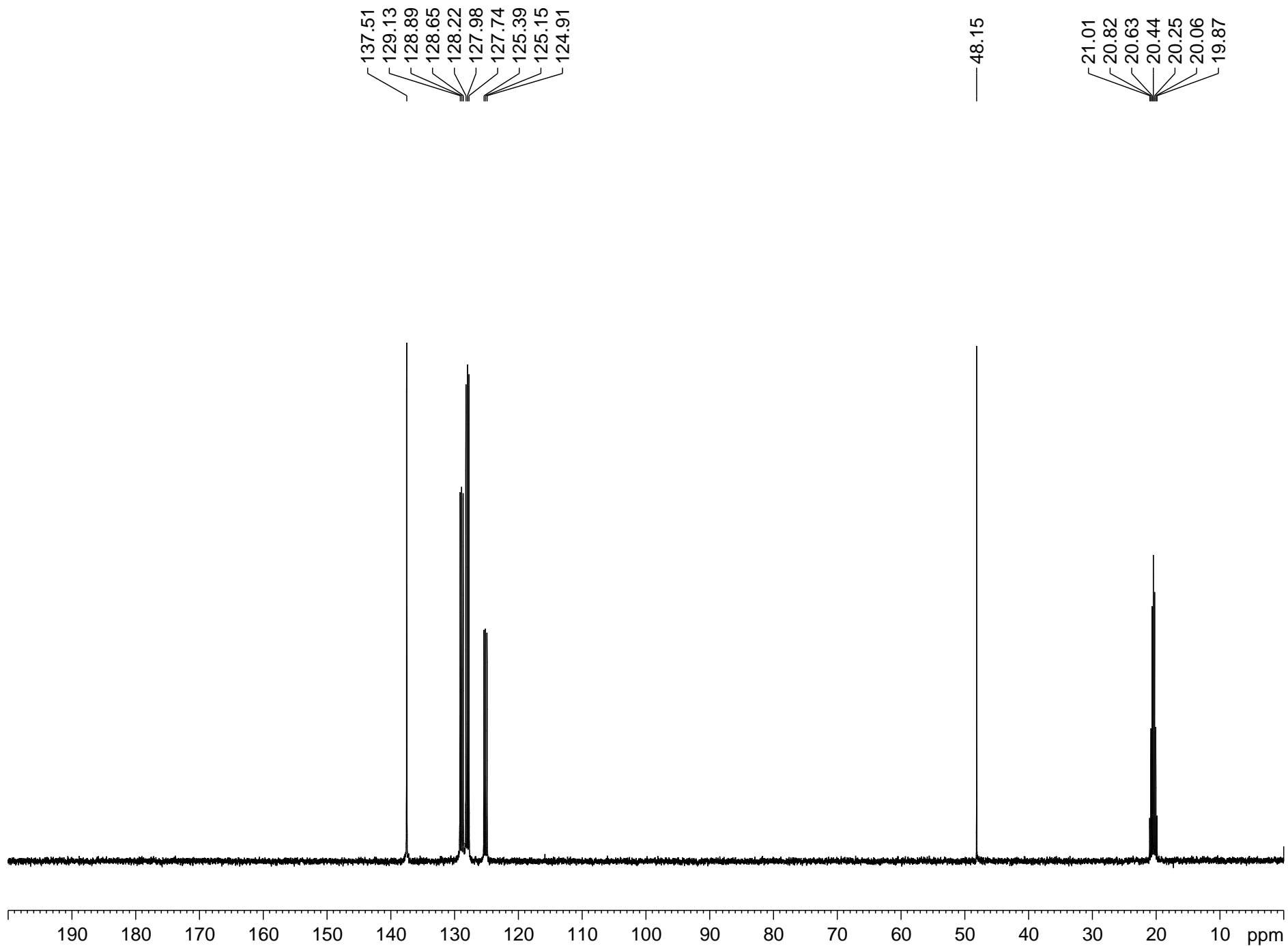
1H, 400MHz, 298K, tetrahydrofuran-d8



<sup>13</sup>C, 100MHz, 298K, tetrahydrofuran-d8



1H, 400MHz, 298K, toluene-d8



<sup>13</sup>C, 100MHz, 298K, toluene-d8