**Gel Permeation Chromatography.** The analytical gel permeation chromatography (GPC) experiments were performed on a Waters system equipped with a Waters 1515 isocratic pump, a Waters 2414 refractive index detector, a Waters 2998 photodiode array detector, and a miniDAWN TREOS 3-angle laser light scattering detector (MALLS, Wyatt Technology, CA). The separations were performed at 50 °C using DMF containing 0.1 M LiBr as the eluent at a 1.0 ml/min. flow rate. Relative molecular weights and PDIs were calculated with Astra software (version 5.1.7.3, Wyatt Technology, CA) based on conventional calibration method using polyethylene glycol standards (1.5 kDa to 128 kDa).

**NMR Experiments.** NMR spectra were recorded using a Varian U400, UI400, U500, VXR500 or UI500NB spectrometer in the NMR Laboratory in the School of Chemical Science at the University of Illinois. Chemical shifts (δ) and coupling constants (J) are reported in parts per million (ppm) and hertz (Hz), respectively. $^{1}$H NMR chemical shifts were referenced to the residual solvent peak at 4.87 ppm in methanol-$d_4$ ($CD_3OD$) and 4.79 ppm in water-$d_2$ ($D_2O$). The data was processed in MestReNova (version 8.1.1-11591, Mestrelab Research S. L.)

**Table 1. Sample H1.**

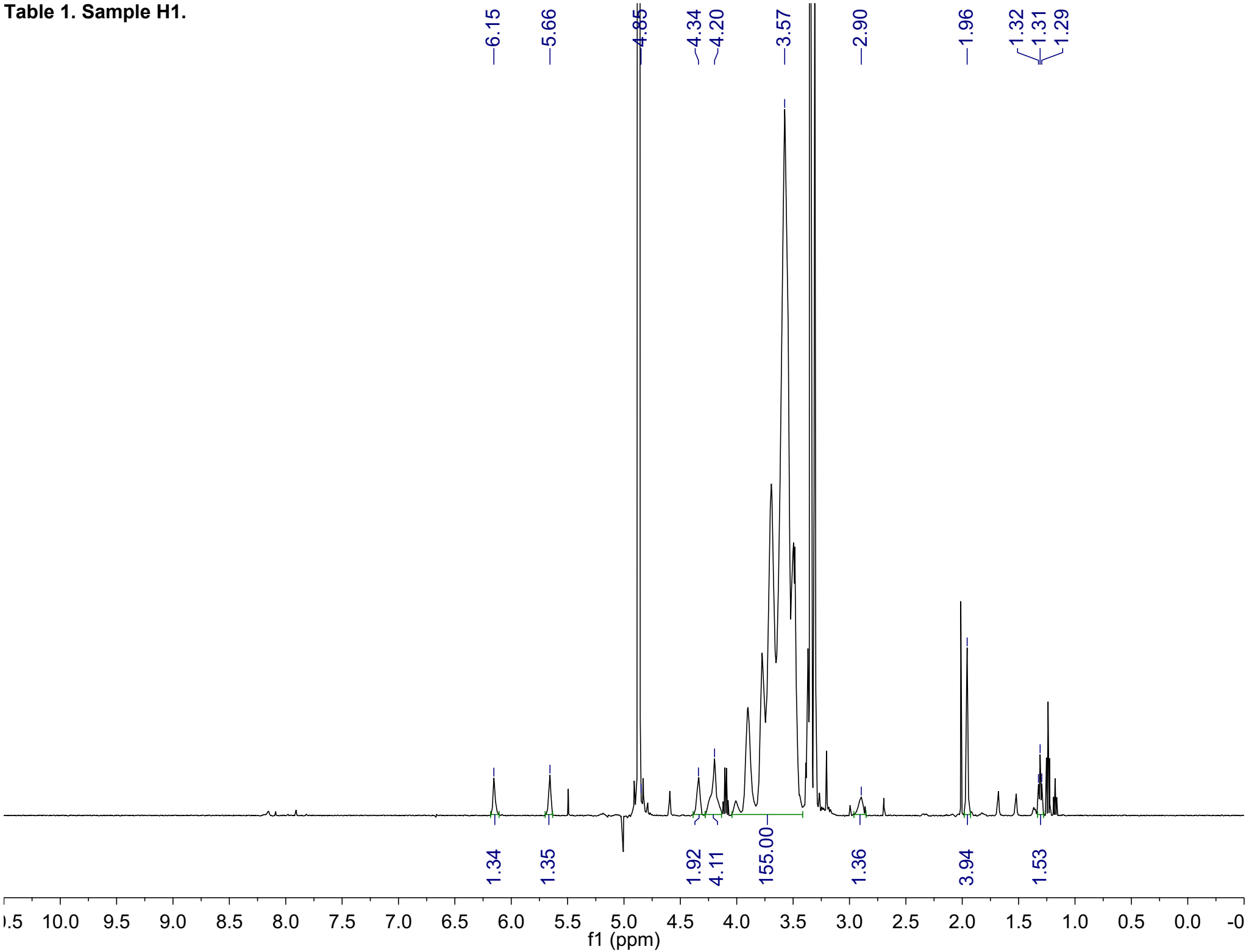


**Table 1. Sample H1**

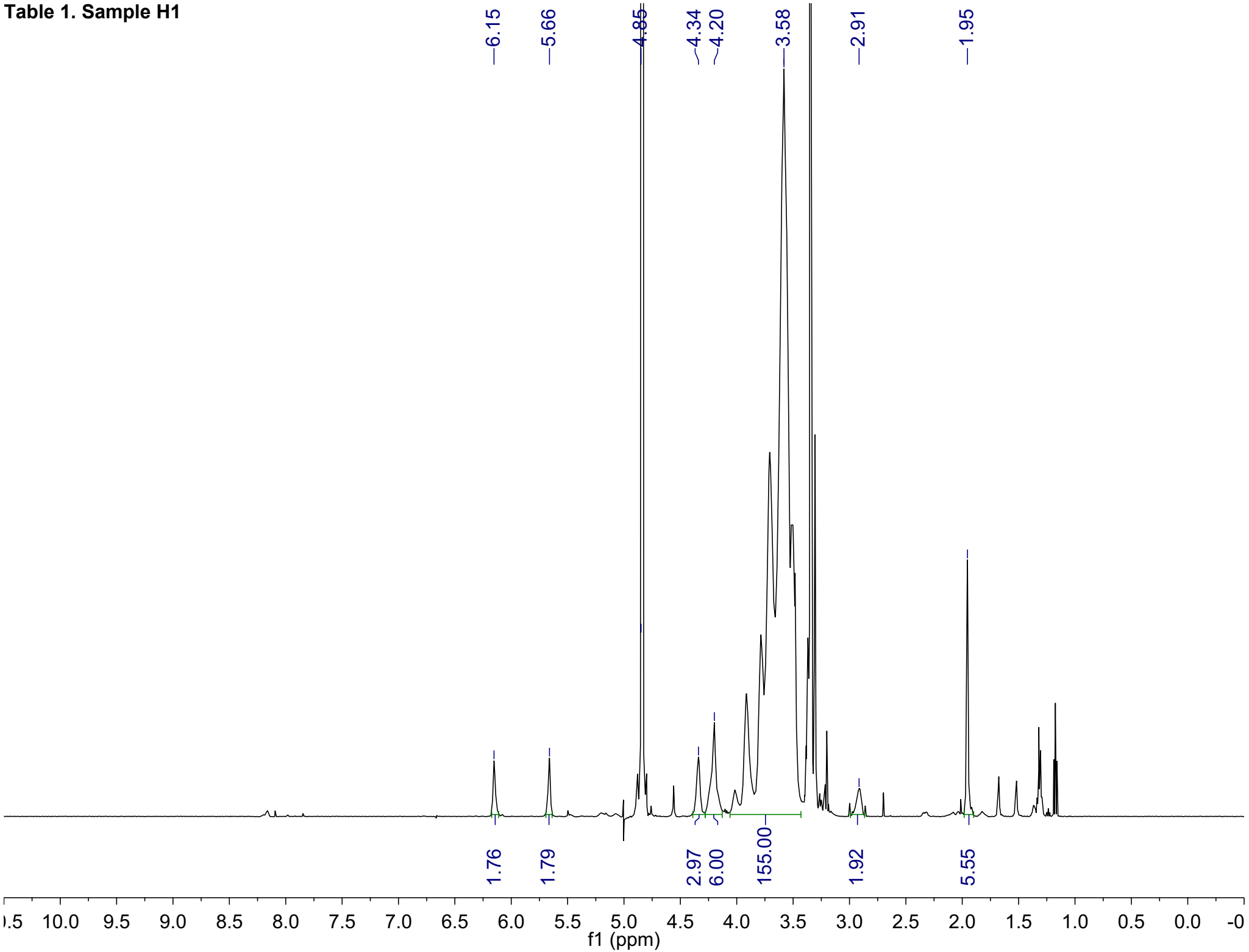


**Table 1. Sample H2.**

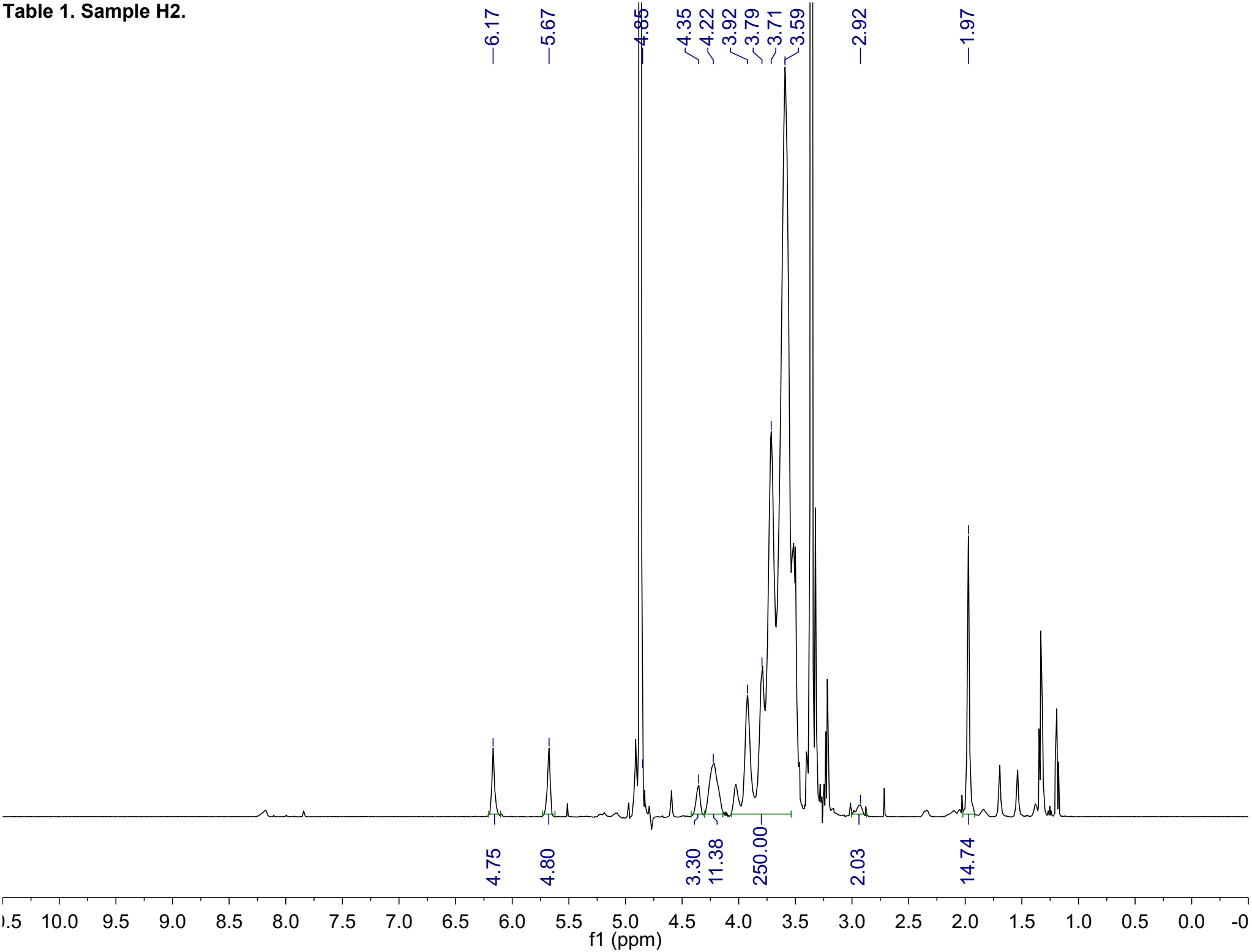


**Table 2. Sample 1.**

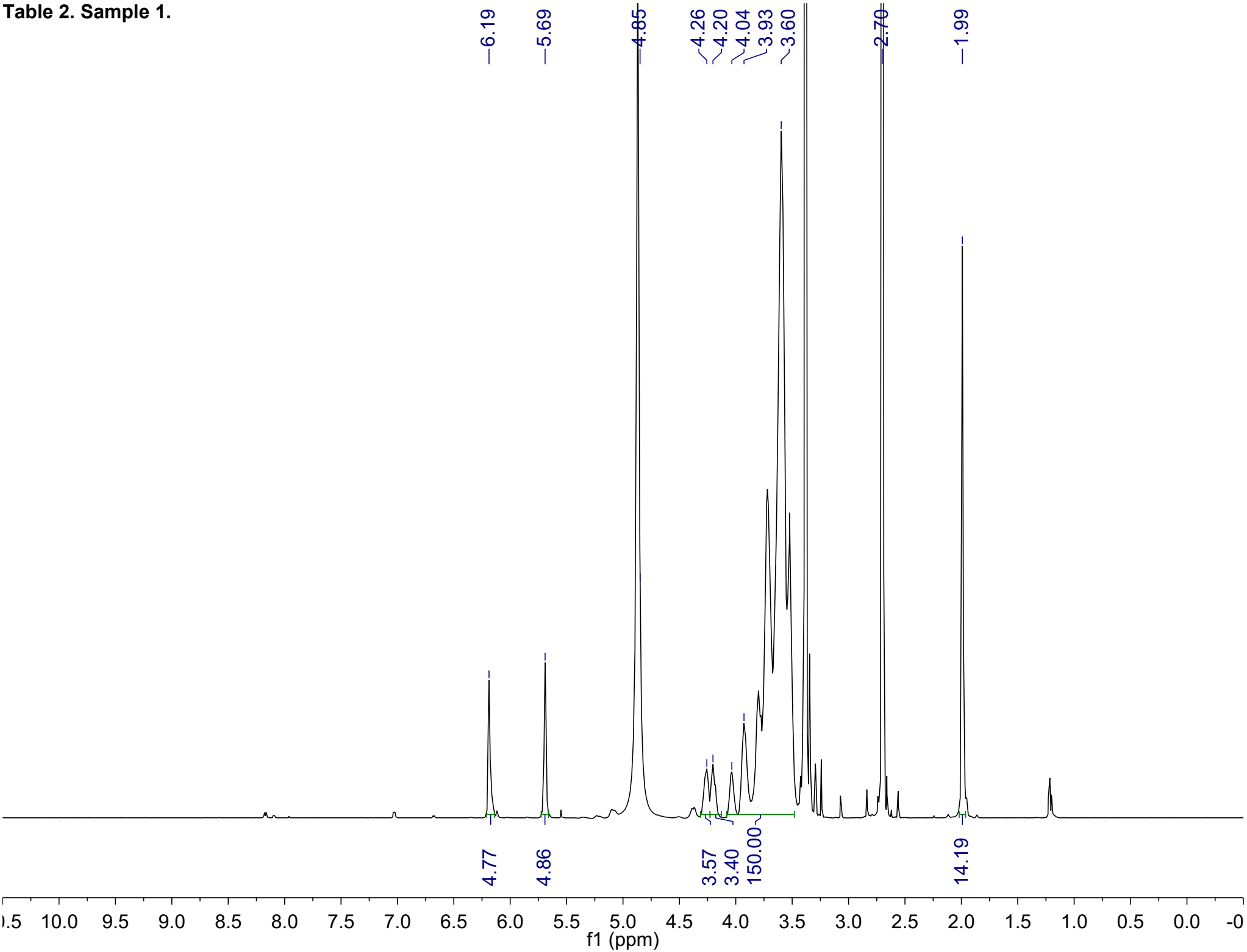


**Table 2. Sample 2**

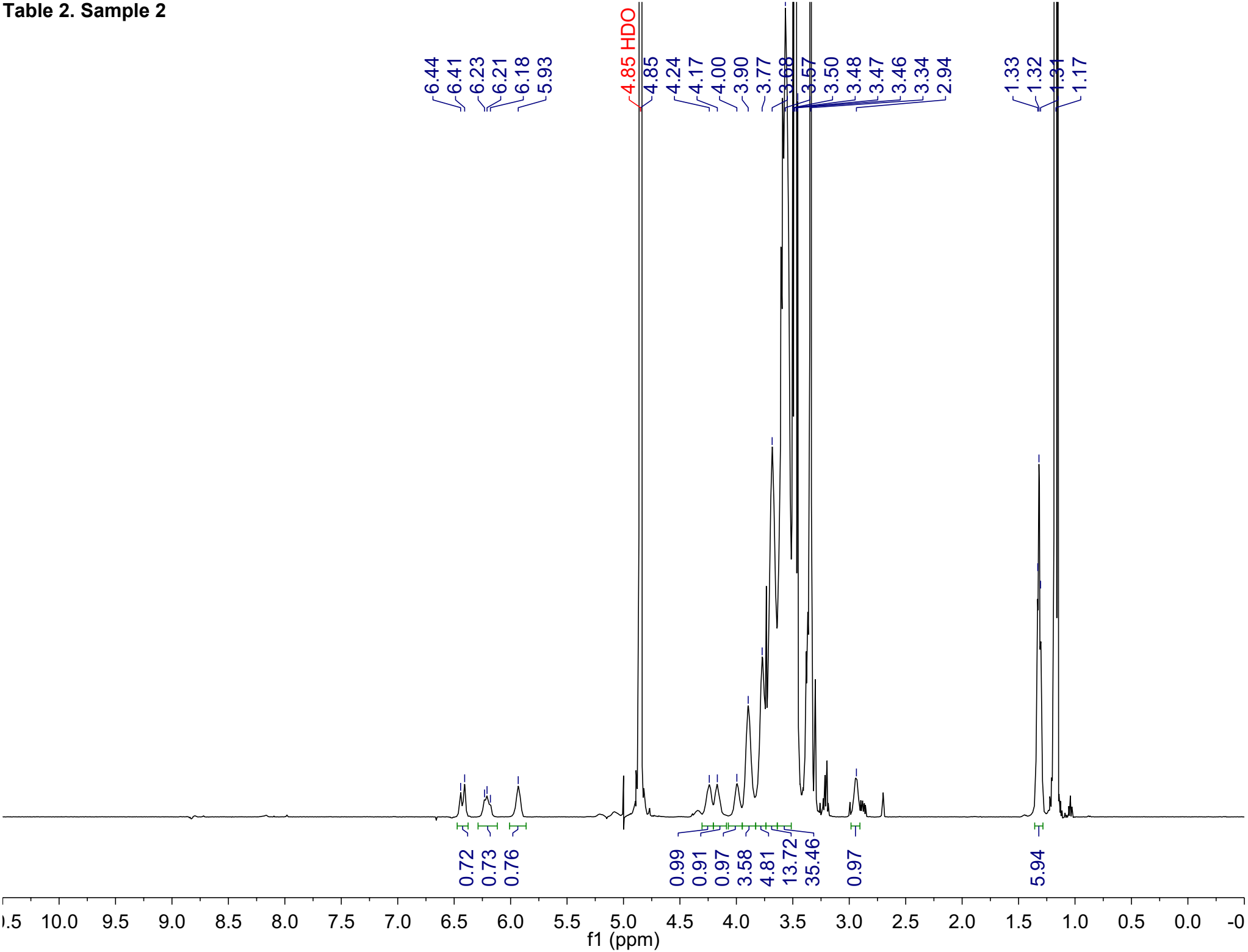


**Table 2. Sample 3.**

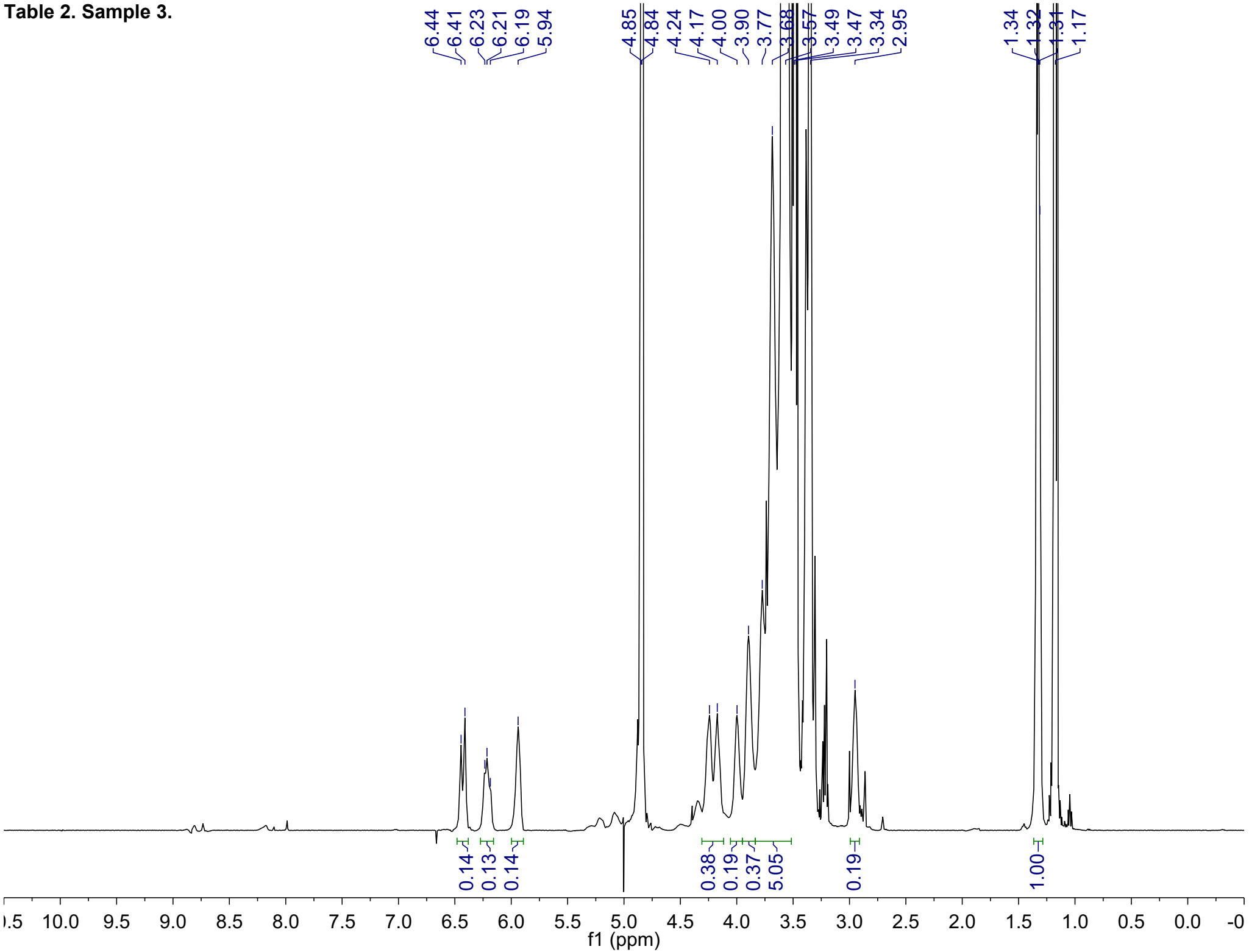


**Table 2. Sample 4.**

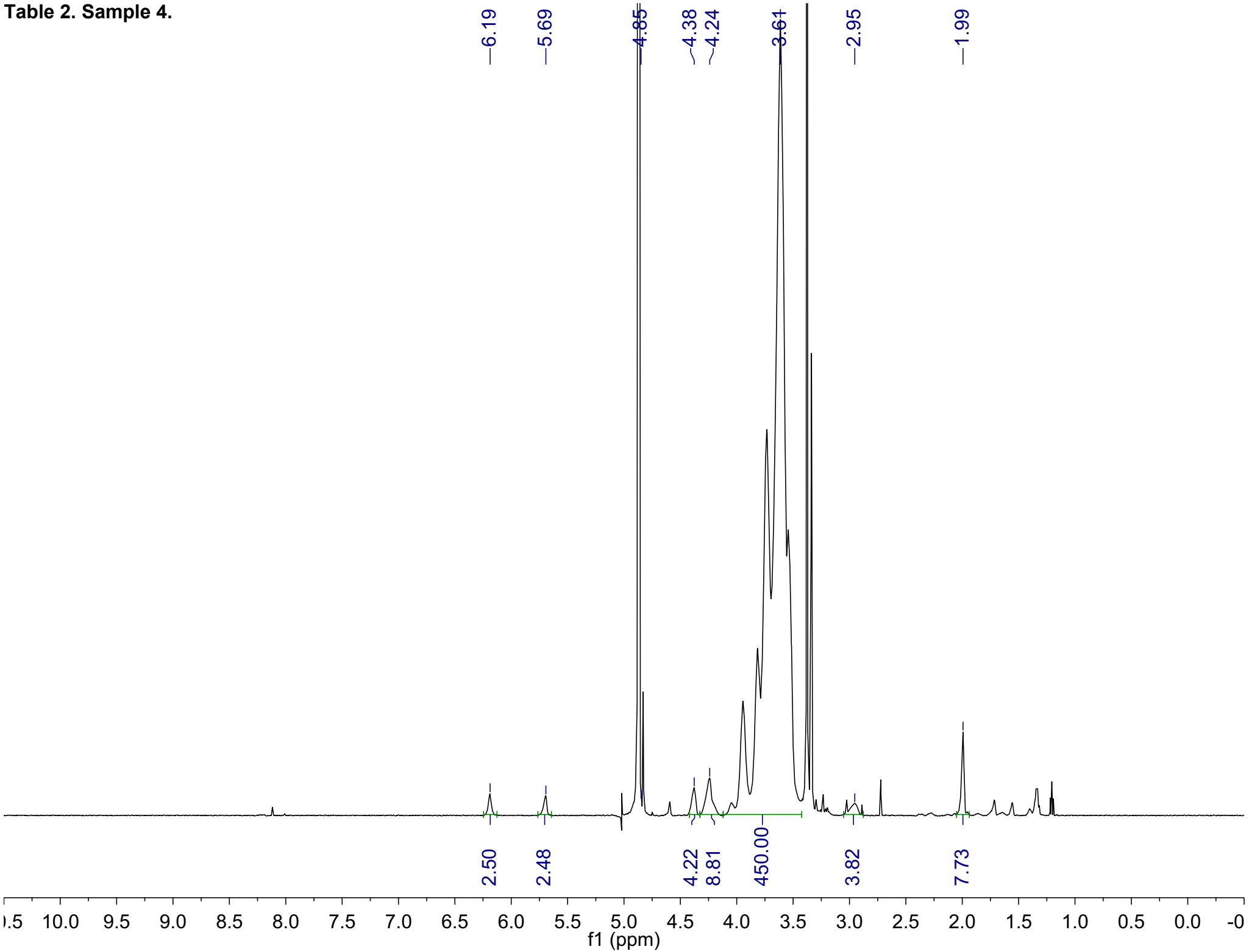


**Table 2. Sample 5.**

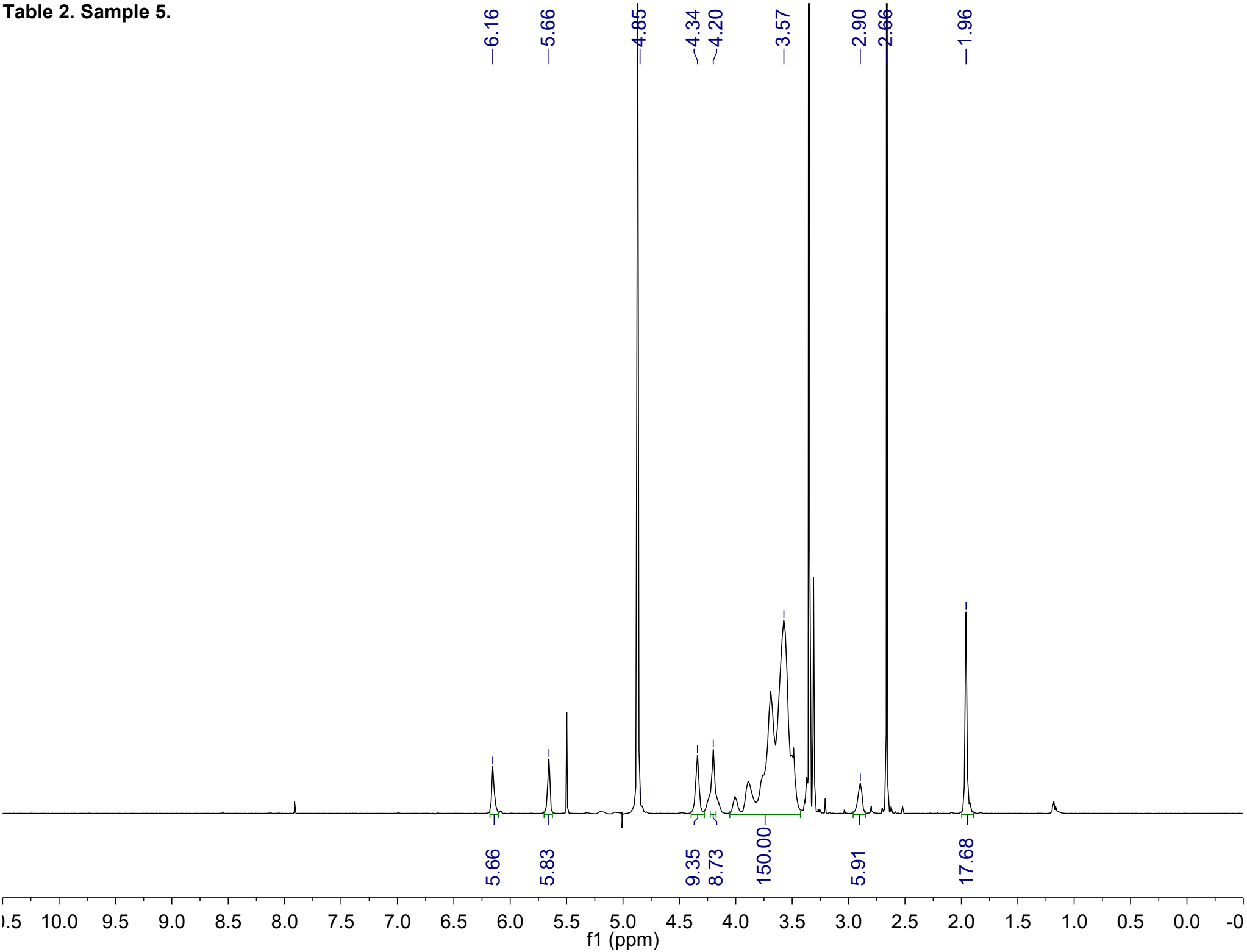


**Table 2. Sample 6.**

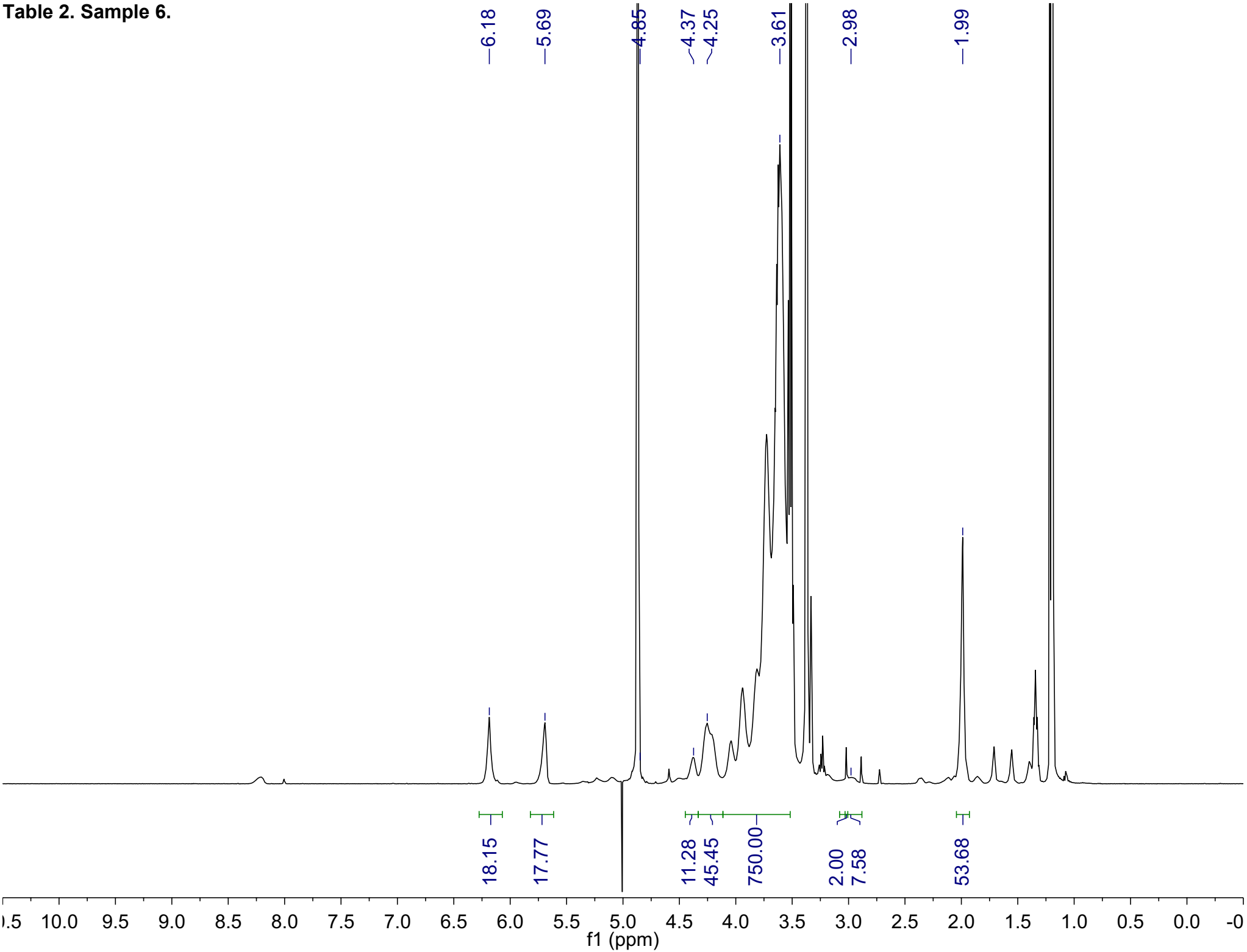


**Table 2. Sample 7.**

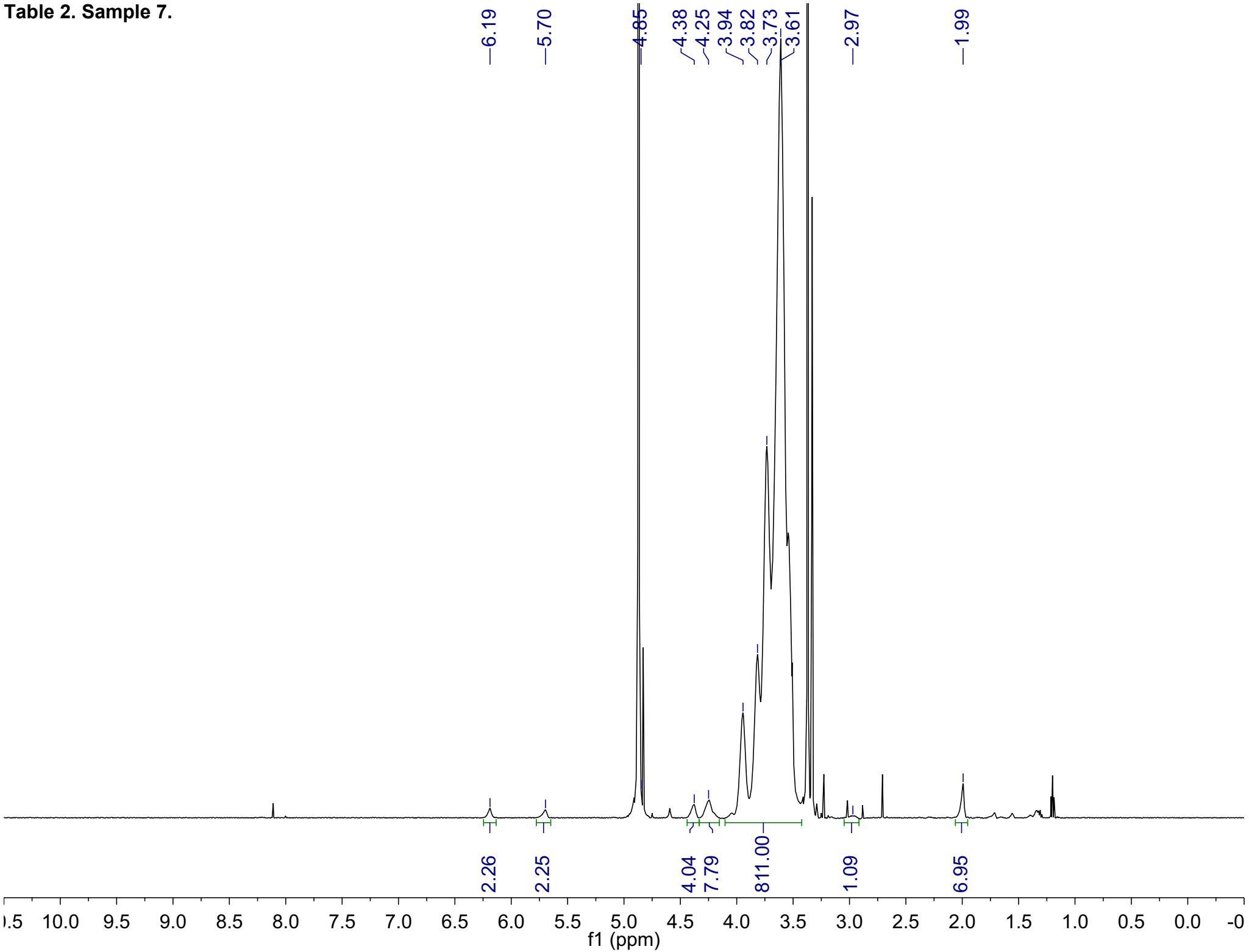


**Table 2. Sample 8.**

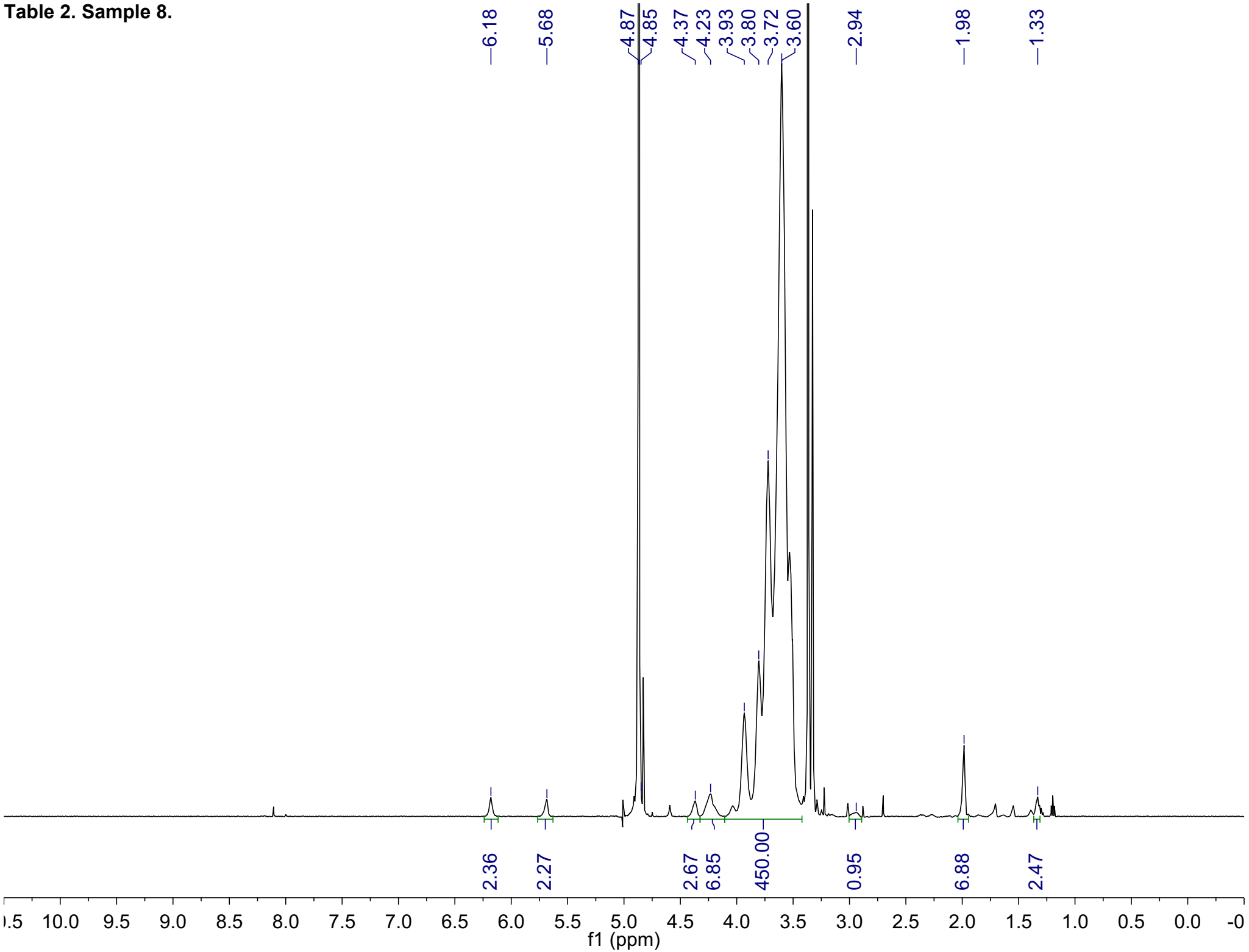


**Table 2. Sample 9.**

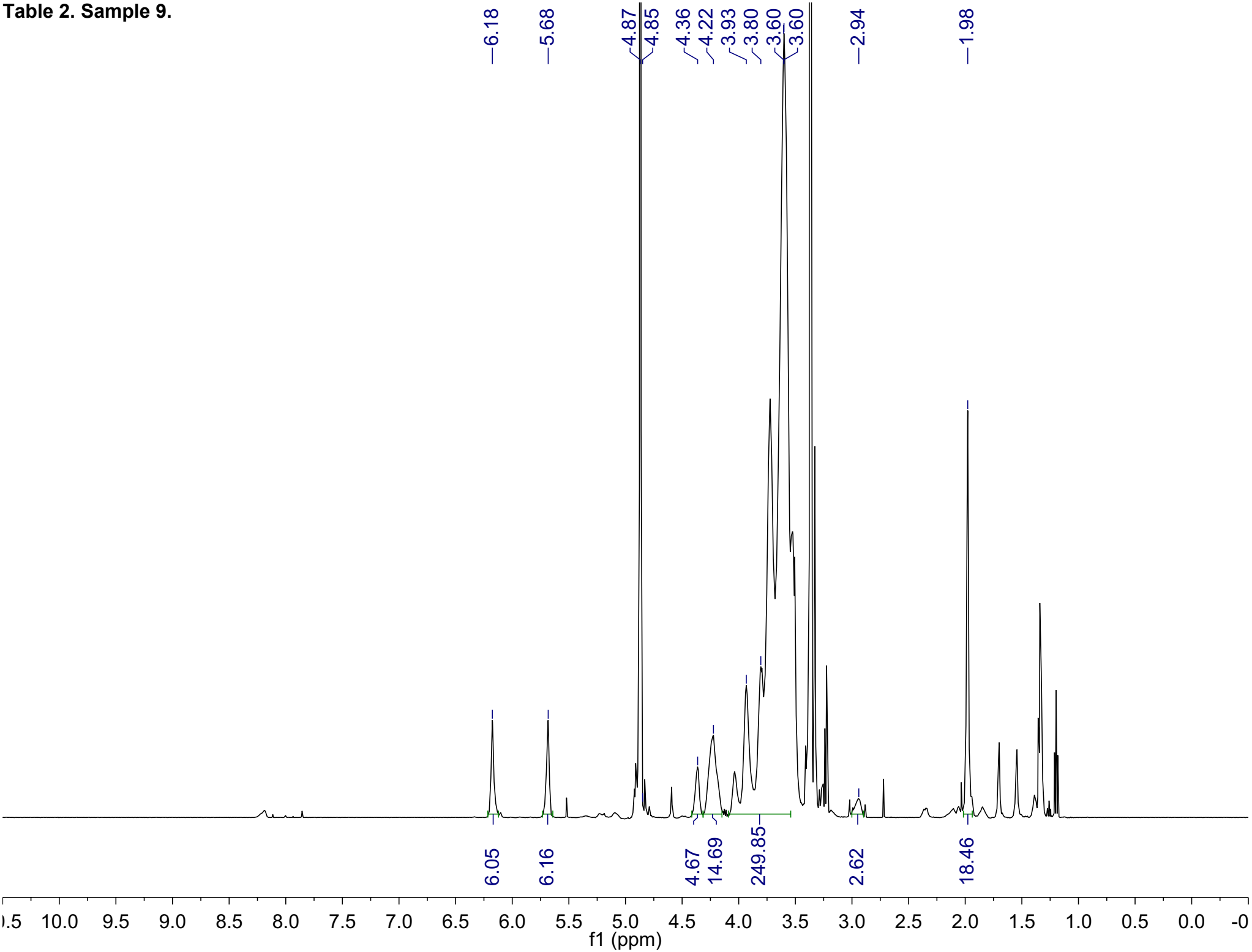


Table 1. Sample H1.
$^1$H NMR (500 MHz; CD3OD): δ 6.15 (bs, 1.3H, -C=C**H**$_2$), 5.66 (bs, 1.4H, -C=C**H**$_2$), 4.34 (bs, 1.9H, O-C**H**$_2$CCH), 4.20 (bs, 4H), 3.43-4.04 (bm, 155H), 2.90 (bs, 1.6H, -CC**H)**, 1.96 (s, 3.9H,–CC**H**$_3$).

Table 1. Sample H1.
$^1$H NMR (500 MHz; CD3OD): δ 6.15 (bs, 1.8H, -C=C**H**$_2$), 5.66 (bs, 1.8H, -C=C**H**$_2$), 4.34 (bs, 3H, O-C**H**$_2$CCH), 4.20 (bs, 6H), 3.46-4.08 (bm, 155H), 2.91 (bs, 1.9H, -CC**H)**, 1.95 (s, 5.6H, -CC**H**$_3$).

Table 1. Sample H2.
$^1$H NMR (500 MHz; CD3OD): δ 6.17 (bs, 4.8H, -C=C**H**$_2$), 5.67 (bs, 4.8H, -C=C**H**$_2$), 4.35 (bs, 3.3H, O-C**H**$_2$CCH), 4.22 (bs, 11H), 3.45-4.08 (bm, 250H), 2.92 (bs, 2.0H, -CC**H)**, 1.97 (s, 14.7H, -CC**H**$_3$).

Table 2. Sample 1.
$^1$H NMR (500 MHz; CD3OD): δ 6.19 (bs, 4.8H, -C=C**H**$_2$), 5.69 (bs, 4.9H, -C=C**H**$_2$), 4.26 (bm, 4H), 4.20 (bm, 3H), 3.45-4.08 (bm, 150H), 2.70 (DMSO imp.), 1.99 (s, 14.2H –CC**H**$_3$).

Table 2. Sample 2.
$^1$H NMR (500 MHz; CD3OD): δ 6.20 (bs, 4.3H, -C=C**H**$_2$), 5.71 (bs, 4.3H, -C=C**H**$_2$), 4.39 (bs, 3.2H, O-C**H**$_2$CCH), 4.26 (bs, 14H), 3.44-4.12 (bm, 450H), 2.98 (bs, 2.0H, -CC**H)**, 2.00 (s, 12.9H, -CC**H**$_3$).

Table 2. Sample 3.
$^1$H NMR (500 MHz; CD3OD): δ 6.21 (bs, 7.0H, -C=C**H**$_2$), 5.71 (bs, 7.0H, -C=C**H**$_2$), 4.39 (bs, 5.4H, O-C**H**$_2$CCH), 4.26 (bs, 20H), 3.47-4.13 (bm, 450H), 2.97 (bs, 3.6H, -CC**H)**, 2.01 (s, 21.1H, -CC**H**$_3$).

Table 2. Sample 4.
$^1$H NMR (500 MHz; CD3OD): δ 6.19 (bs, 2.5H, -C=C**H**$_2$), 5.69 (bs, 2.5H, -C=C**H**$_2$), 4.38 (bs, 4.2H, O-C**H**$_2$CCH), 4.24 (bs, 9H), 3.43-4.12 (bm, 450H), 2.95 (bs, 3.8H, -CC**H)**, 1.99 (s, 7.7H, -CC**H**$_3$).

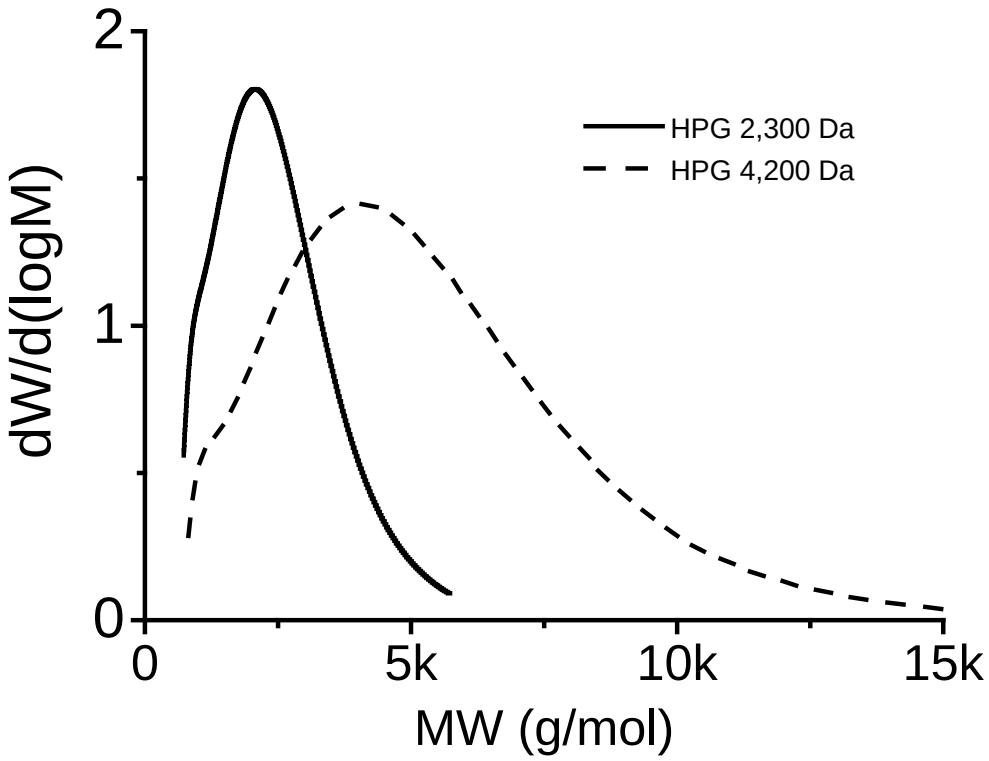
Table 2. Sample 5.
$^1$H NMR (500 MHz; CD3OD): δ 6.16 (bs, 5.7H, -C=C**H**$_2$), 5.66 (bs, 5.8H, -C=C**H**$_2$), 4.34 (bs, 9H, O-C**H**$_2$CCH), 4.20 (bs, 9H), 3.43-4.05 (bm, 150H), 2.90 (bs, 5.9H, -CC**H)**, 2.66 (DMSO imp.), 1.96 (s, 17.7H,–CC**H**$_3$).

Table 2. Sample 6.
$^1$H NMR (500 MHz; CD3OD): δ 6.18 (bs, 18.2H, -C=C**H**$_2$), 5.69 (bs, 17.8H, -C=C**H**$_2$), 4.37 (bs, 11.3H, O-C**H**$_2$CCH), 4.25 (bs, 45H), 3.45-4.09 (bm, 750H), 2.98 (bs, 5.5H, -CC**H)**, 1.99 (s, 53.7H, -CC**H**$_3$).

Table 2. Sample 7.
$^{1}$H NMR (500 MHz; CD3OD):δ 6.19 (bs, 2.1H, -C=C**H**$_2$), 5.70 (bs, 2.1H, -C=C**H**$_2$), 4.38 (bs, 3.7H, O-C**H**$_2$CCH), 4.25 (bs, 7H), 3.45-4.09 (bm, 750H), 2.97 (bs, 1.0H, -CC**H)**, 1.99 (s, 6.4H, -CC**H**$_3$).

Table 2. Sample 8.
$^{1}$H NMR (500 MHz; CD3OD): δ 6.18 (bs, 2.3H, -C=C**H**$_2$), 5.68 (bs, 2.3H, -C=C**H**$_2$), 4.37 (bs, 2.7H, O-C**H**$_2$CCH), 4.23 (bs, 7H), 3.43-4.12 (bm, 450H), 2.94 (bs, 1.5H, -CC**H)**, 1.98 (s, 6.7H, -CC**H**$_3$).

Table 2. Sample 9.
$^{1}$H NMR (500 MHz; CD3OD): δ 6.18 (bs, 6.0H, -C=C**H**$_2$), 5.68 (bs, 6.1H, -C=C**H**$_2$), 4.36 (bs, 4.7H, O-C**H**$_2$CCH), 4.22 (bs, 15H), 3.47-4.12 (bm, 250H), 2.94 (bs, 2.6H, -CC**H)**, 1.98 (s, 18.5H, -CC**H**$_3$).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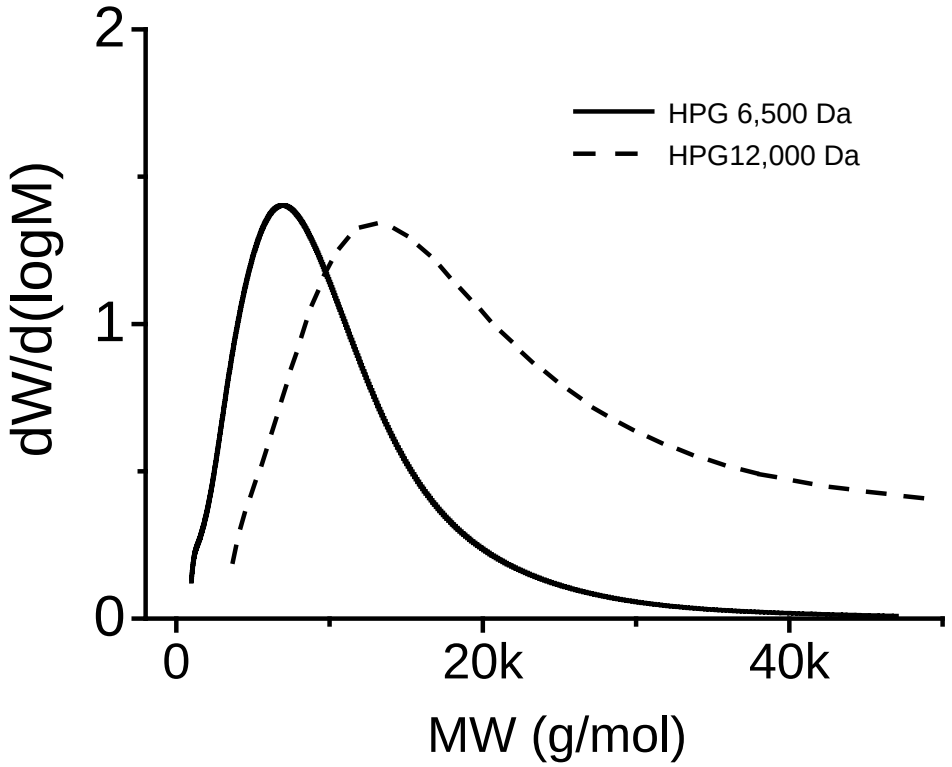
1
0
dW/d(logM)
HPG 2,300 Da
HPG 4,200 Da
0
5k
10k
15k
MW (g/mol)


2
1
0
dW/d(logM)
HPG 6,500 Da
HPG12,000 Da
0
20k
40k
MW (g/mol)

# Supplementary figures

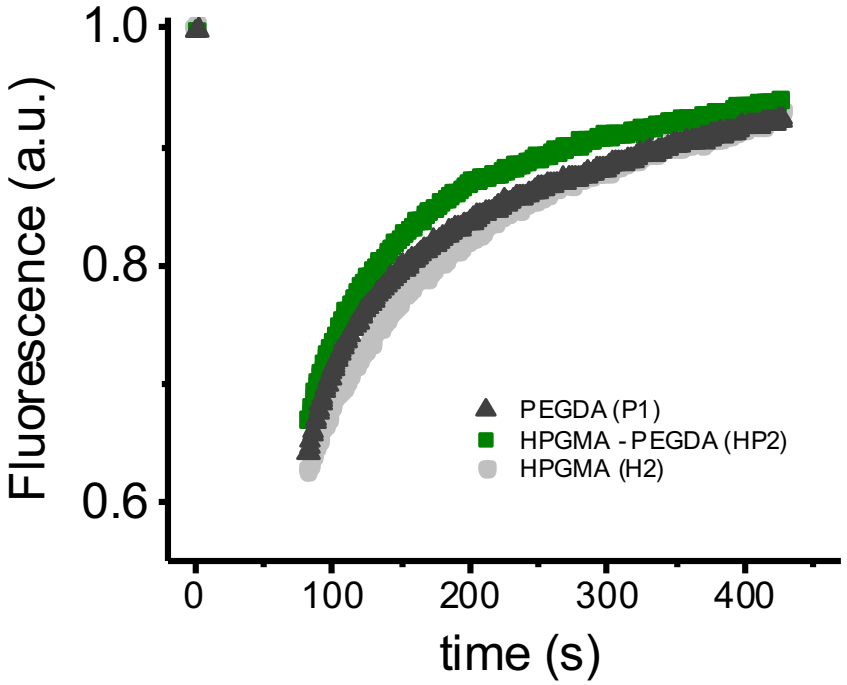



**Figure S1. FRAP raw data** showing recovery curves fluorescence versus time. H2, HP2 and P1 hydrogels contained 40kDa dextran molecules labelled with FITC probes. The fitting goodness was evaluated with reduced chi-squared statistics. The values are: P1 0.96, HP2 0.87, H2 1.4.

**Table S1.** Diffusivity ($\mu m^2/s$) of H2, HP2 and P1 hydrogels containing 40kDa and 4kDa dextran molecules labelled with FITC probes. Short bleaching times (3 to 5 s) as compared to normal times (80 s) are used to prove the lack of diffusion during photobleaching.

| Sample | 40kDa | 40kDa<br>Short bleaching | 4kDa |
|---|---|---|---|
| P1 | 39 ± 1 | 37 ± 1 | 78 ± 3 |
| HP2 | 40 ± 1 | 39 ± 2 | 73 ± 2 |
| H2 | 34 ± 1 | 26 ± 4 | 65 ± 2 |

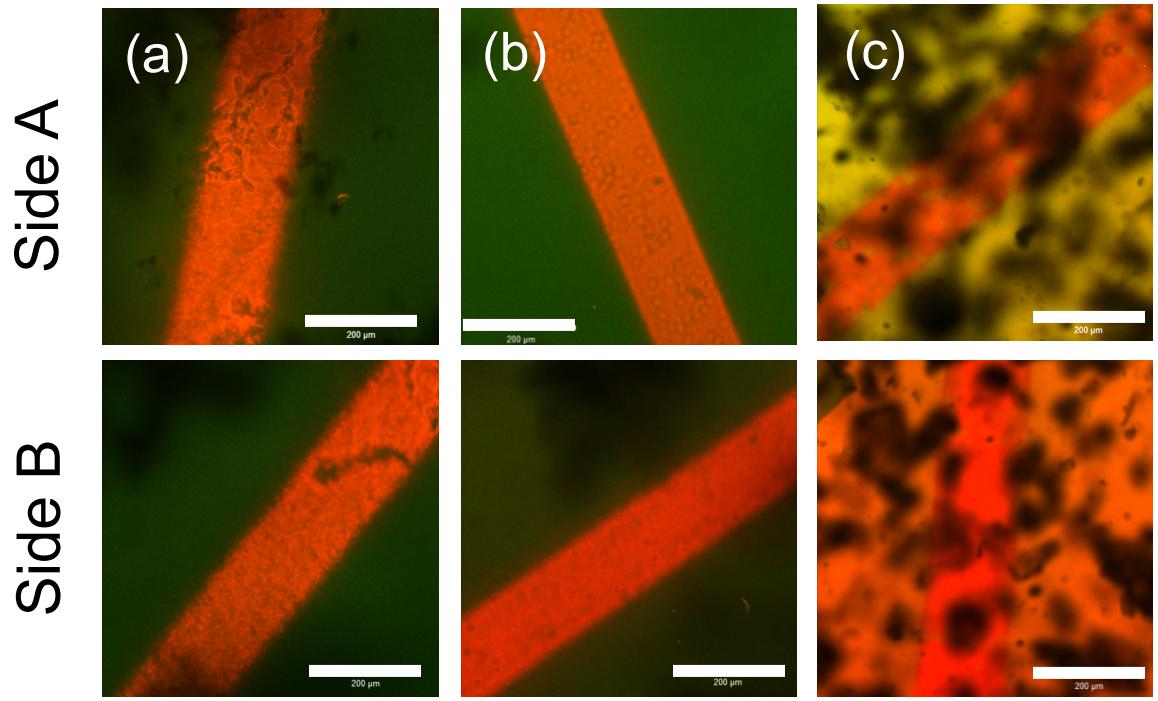



**Figure S2. Three dimensional hydrogel patterning with FITC and TAMRA-RGDSC peptides.** TAMRA-RGDSC was covalently added to 1mm-thick hydrogels in a stripe pattern, then FITC-RGDSC was attached to the rest of the hydrogel in an additional step. (a) PEGDA, (b) PEGDA – HPGMA and (c) HPGMA hydrogels. Scale bar 200 μm.

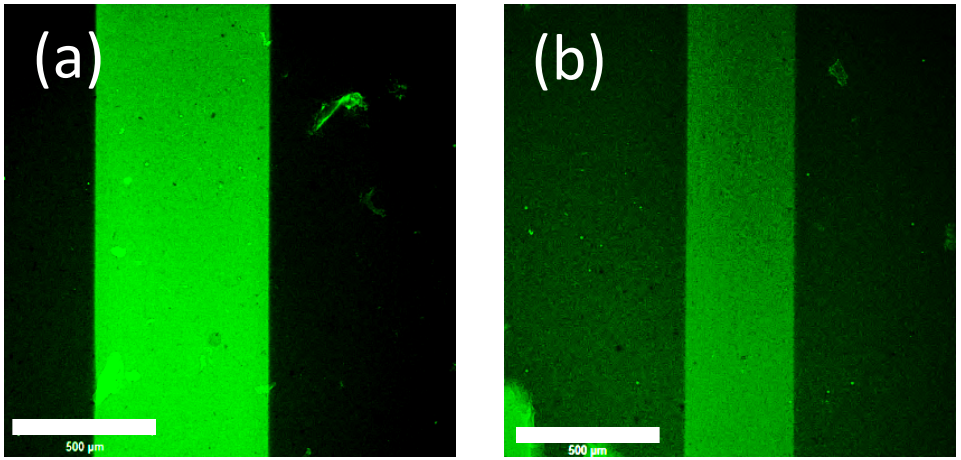



**Figure S3. Hydrogel patterning with FITC-RGDSC peptides.** FITC-RGDSC was covalently added in a stripe pattern to 20 wt% hydrogels. (a) HPGMA (H1), (b) PEGDA – HPGMA (HP1). Scale bar 200 μm. H1 characteristics are MW 2,300, 0.43 M MA and 0.5 M yne.

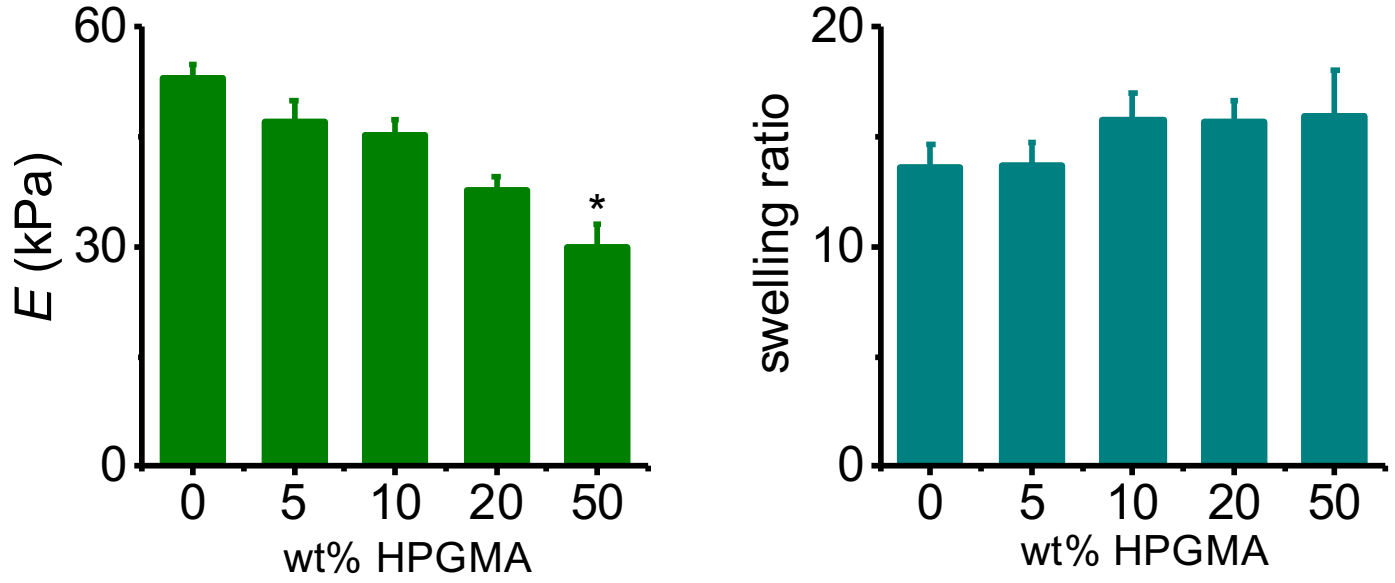



**Figure S4. Hydrogel physical properties of PEGDA hydrogels containing increasing amounts of HPGMA.** Young modulus of PEGDA (P1) hydrogels decreases as H2 HPGMA concentration increases for 10 wt% hydrogels, up to 50 wt% (HP2). No significant difference is observed between corresponding swelling ratios. * $p < 0.05$.