Supporting Information

Fluorinated alcohols as promoters for the metal-free direct substitution reaction of allylic alcohols with nitrogen, silyl and carbon nucleophiles

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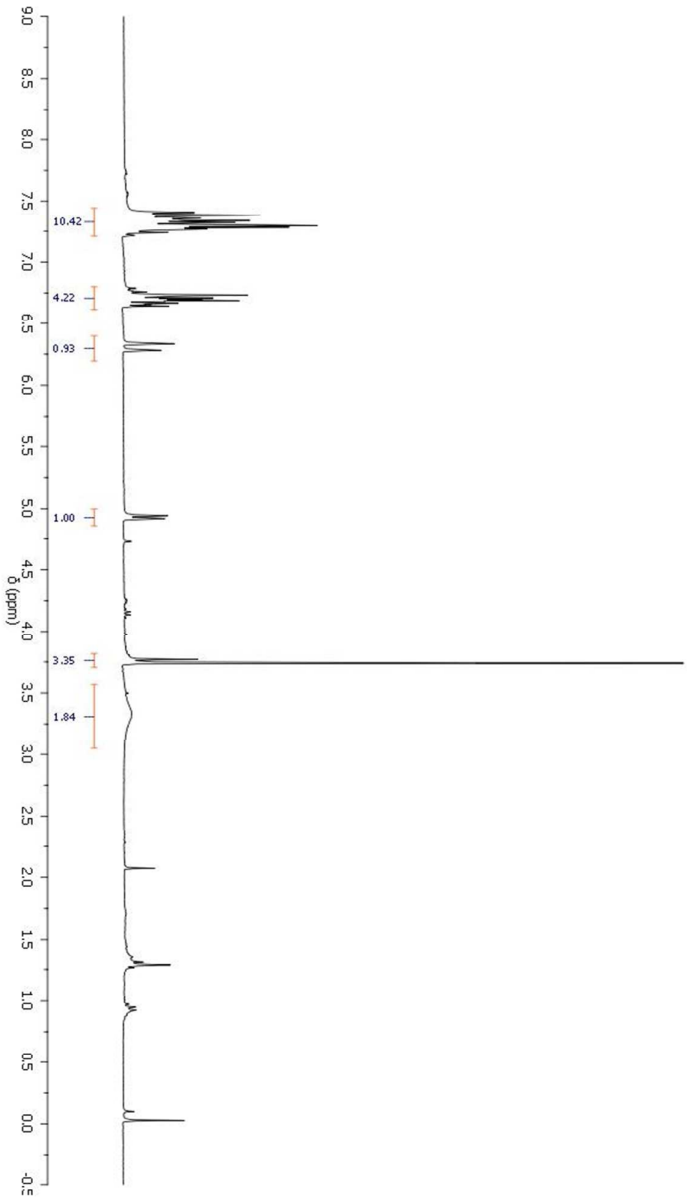
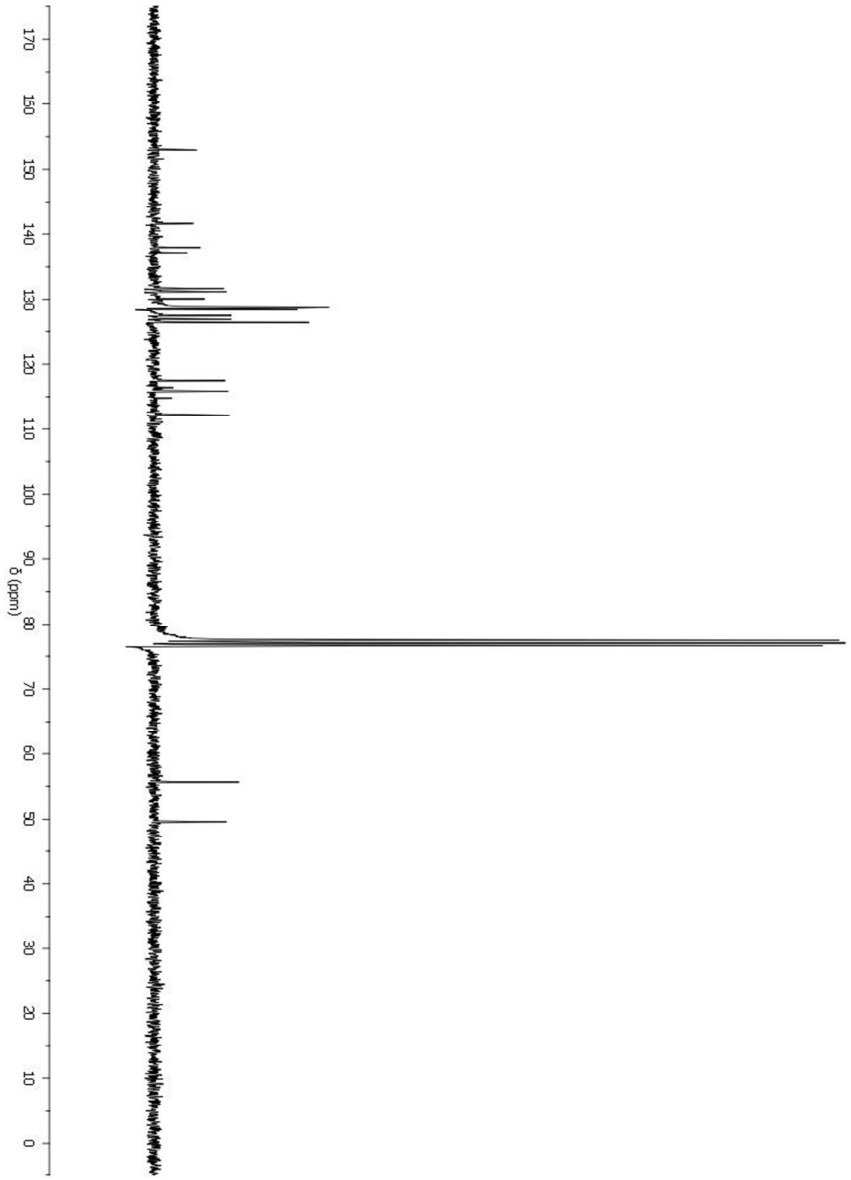
General Remarks

All the solvents and reagents were purchased from commercial sources and used without further purification. Substrates which were not commercially available were synthesized according to known literature procedures. Commercially available HFIP and TFE were used. Melting points are uncorrected. For IR only the structurally most relevant peaks are listed. NMR spectra were performed on 300 or 400 MHz apparatus using $CDCl_3$ as solvent and TMS as internal standard unless otherwise stated. Conversions and compound purities were determined by GC analyses. Low-resolution electron impact (EI) mass spectra were obtained at 70eV and only the structurally most relevant fragmentations are reported. Analytical TLC was performed on pre-coated commercially available silica gel plates and the spots visualized with UV light at 254 nm. Flash chromatography employed prepackaged columns (12 mm ∅ × 7.5 or 15 cm) using silica gel 60 (0.040-0.063 mm) and a chromatography pump. Enantiomeric excesses were determined by HPLC analyses with the corresponding chiral column, using mixtures of n-hexane/isopropyl alcohol as mobile phase.

3am ^{1}H NMR



3am ^{13}C NMR



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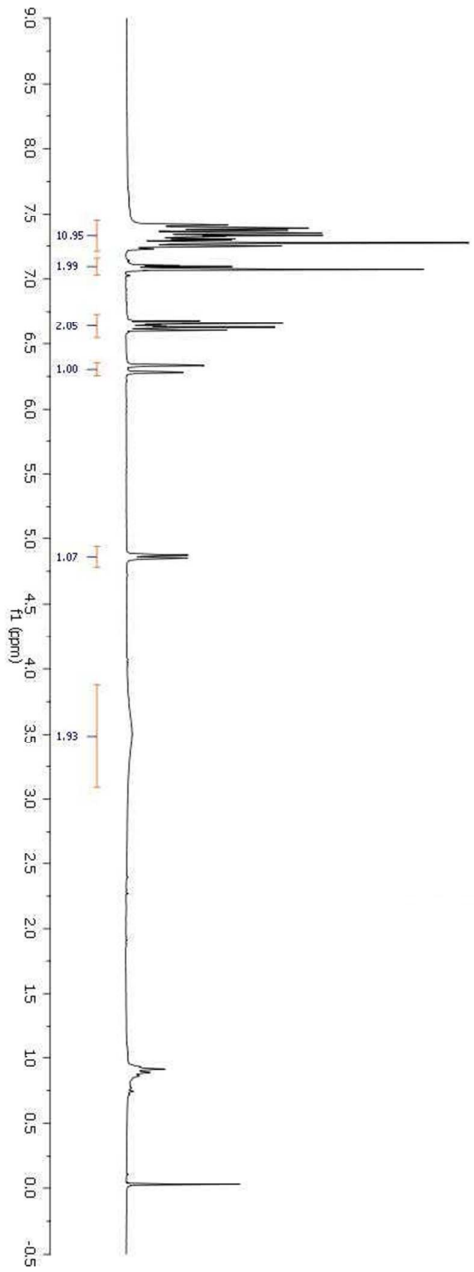

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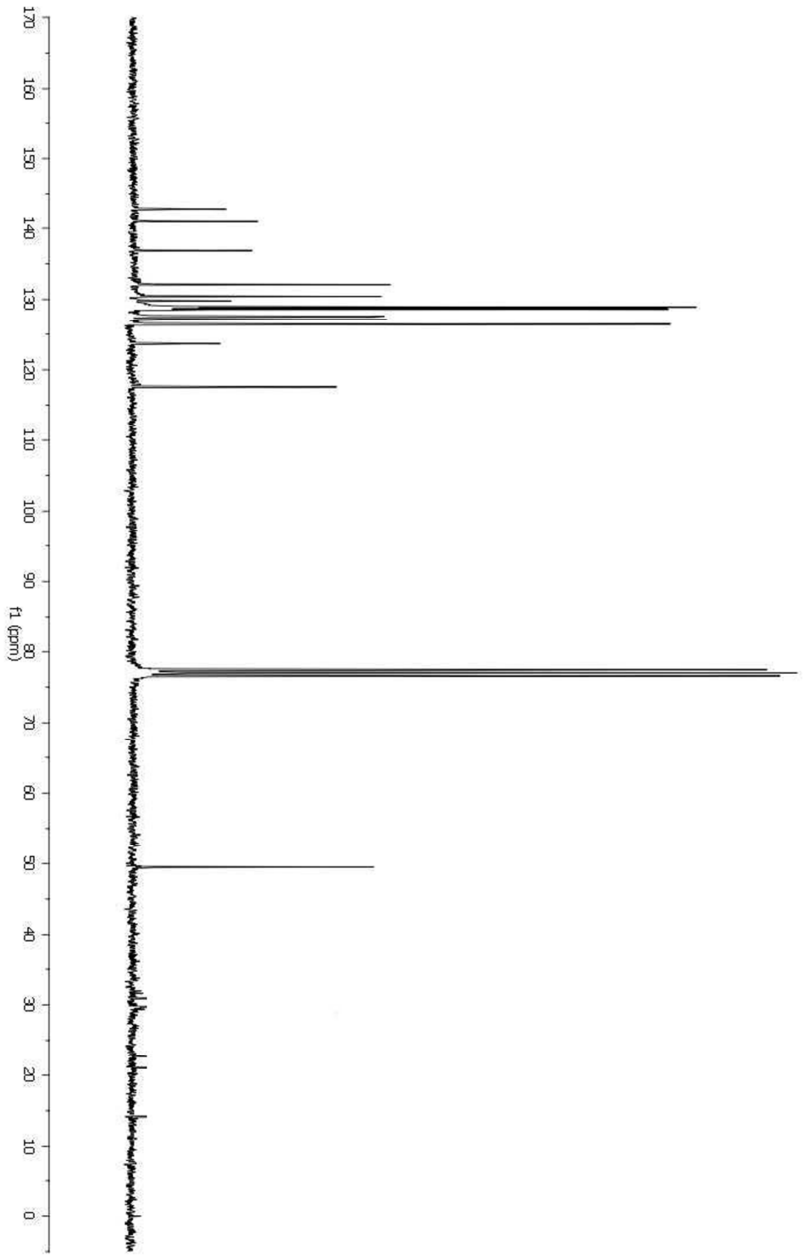

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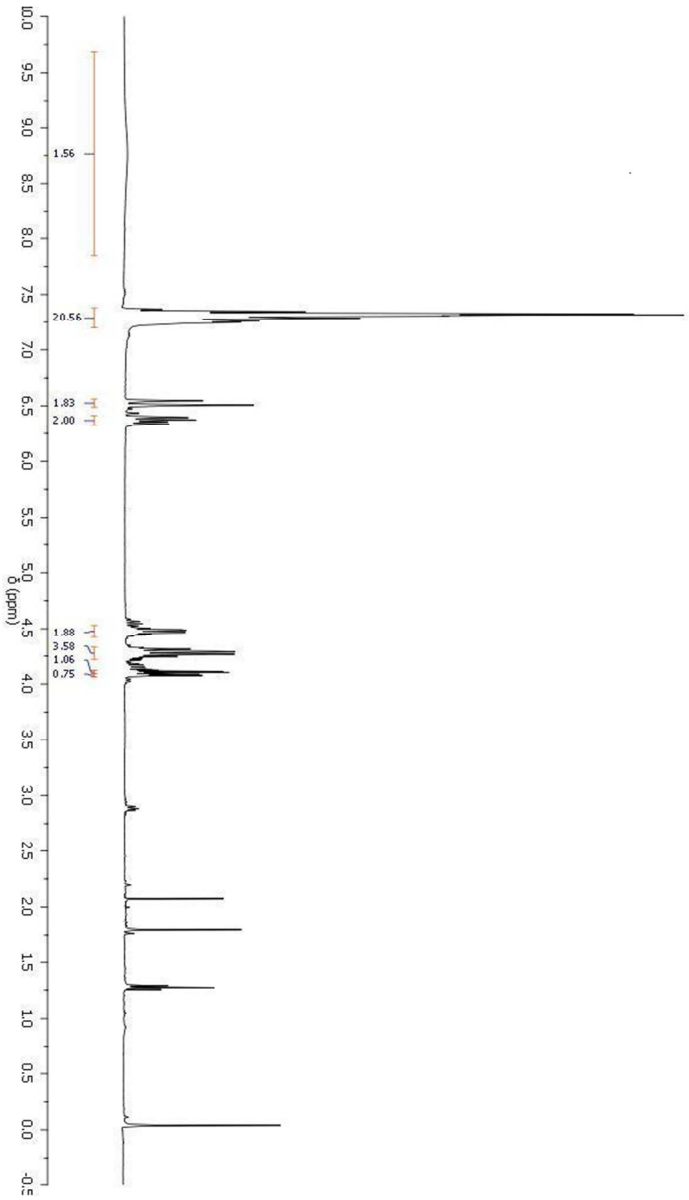

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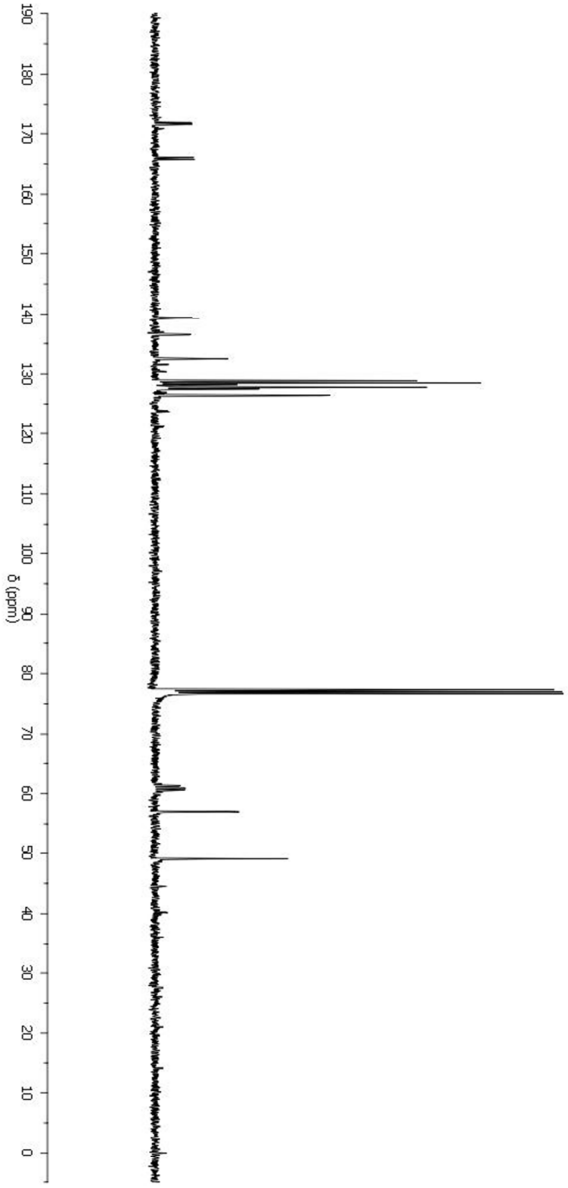
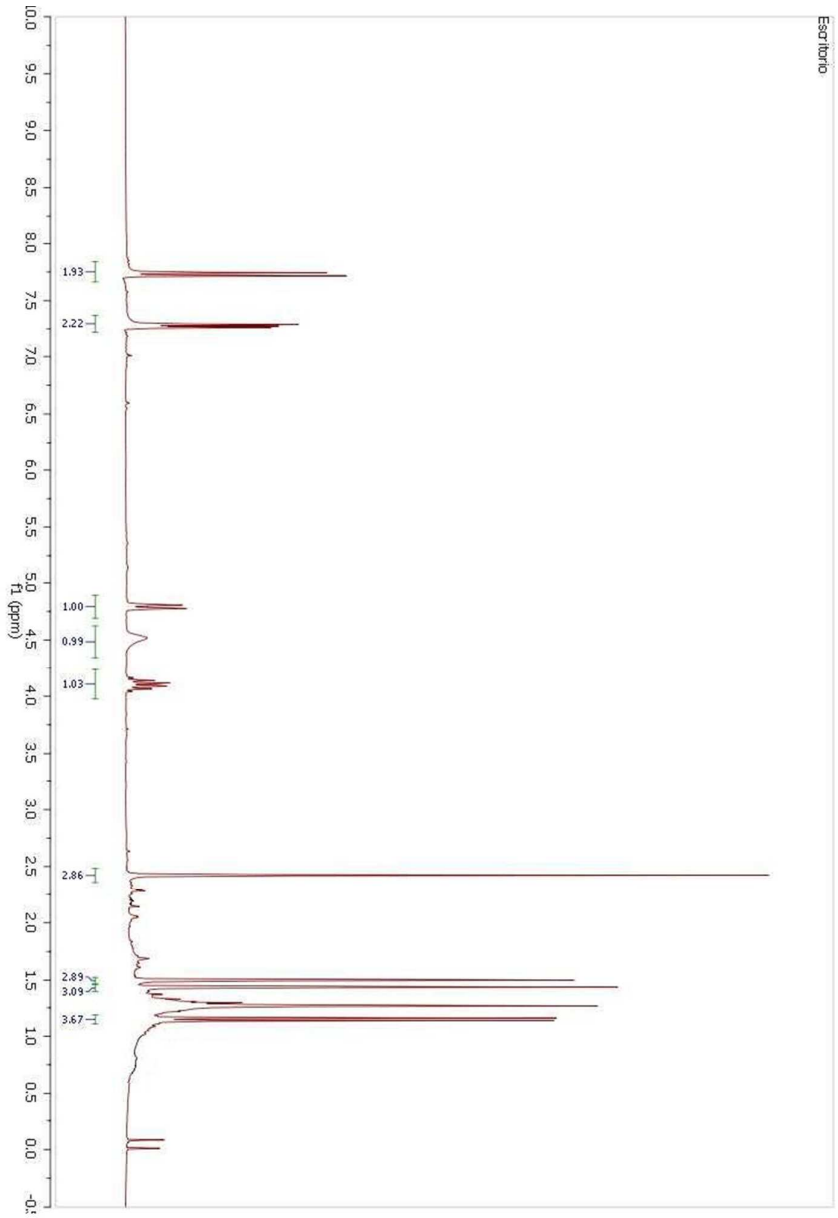

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

3ga ^{1}H NMR



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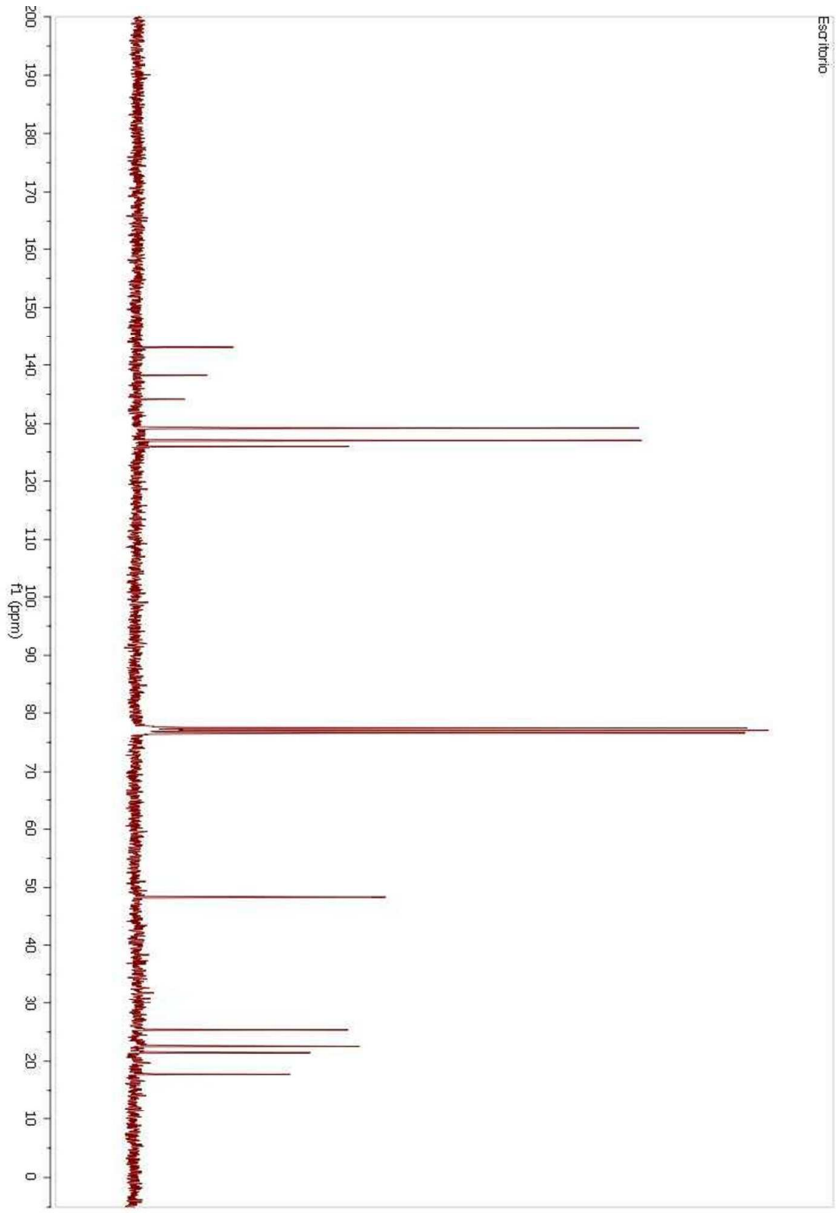
Escritorio
f1 (ppm)
200
190
180
170
160
150
140
130
120
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100
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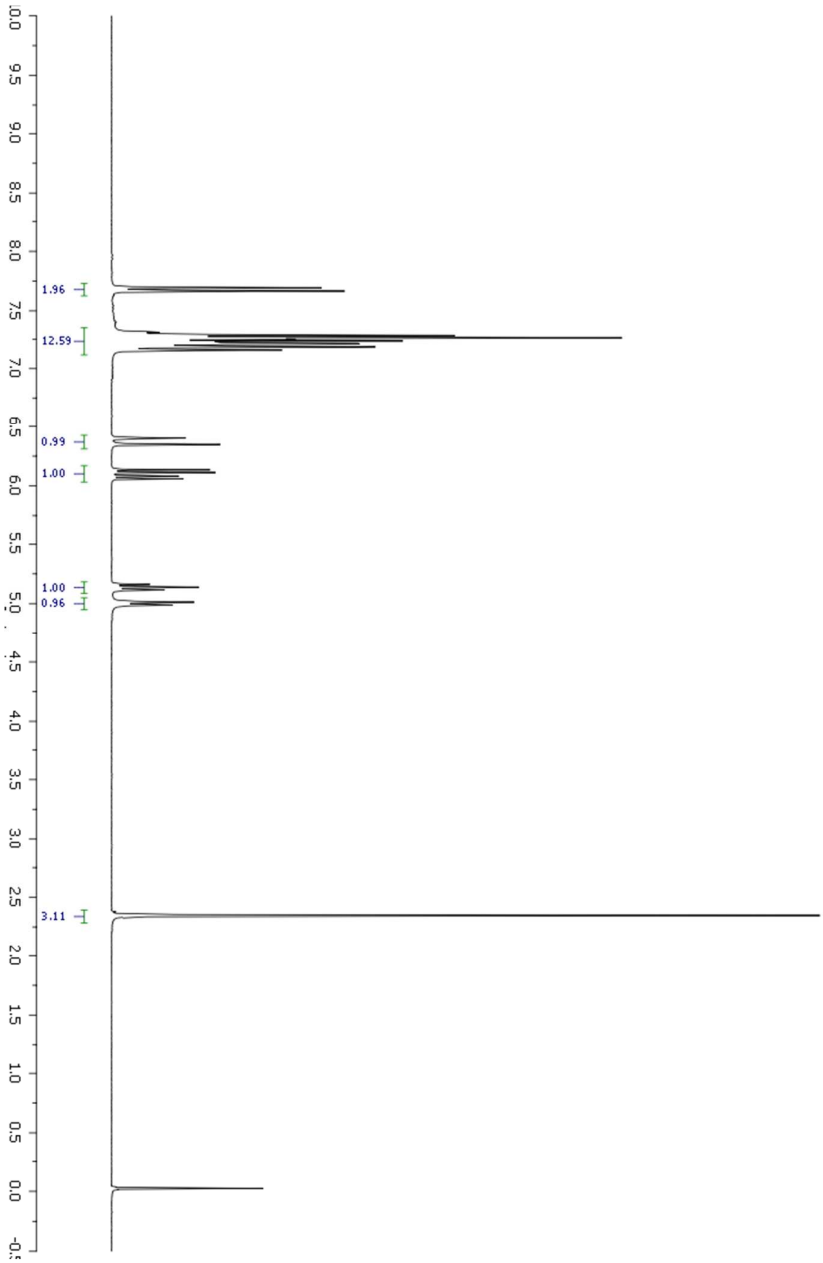
70
60
50
40
30
20
10
0

3aa ^{1}H NMR



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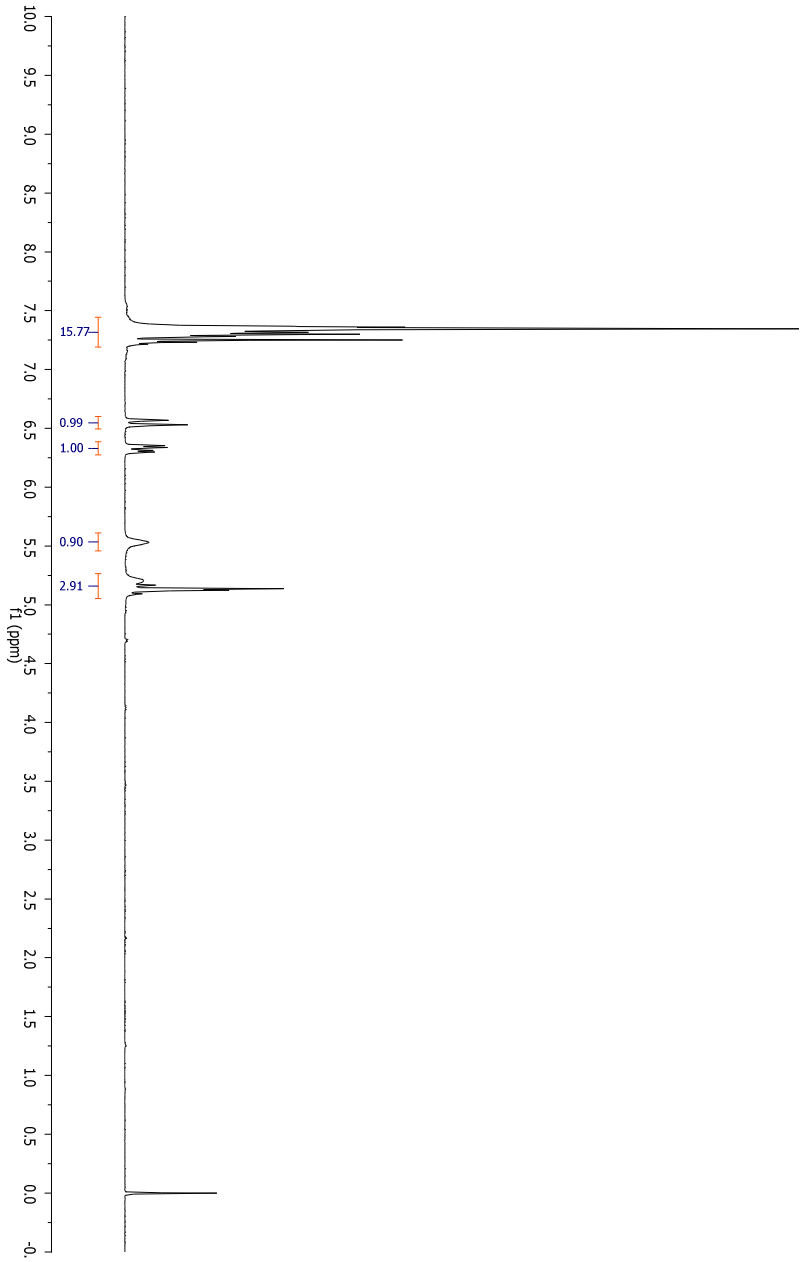

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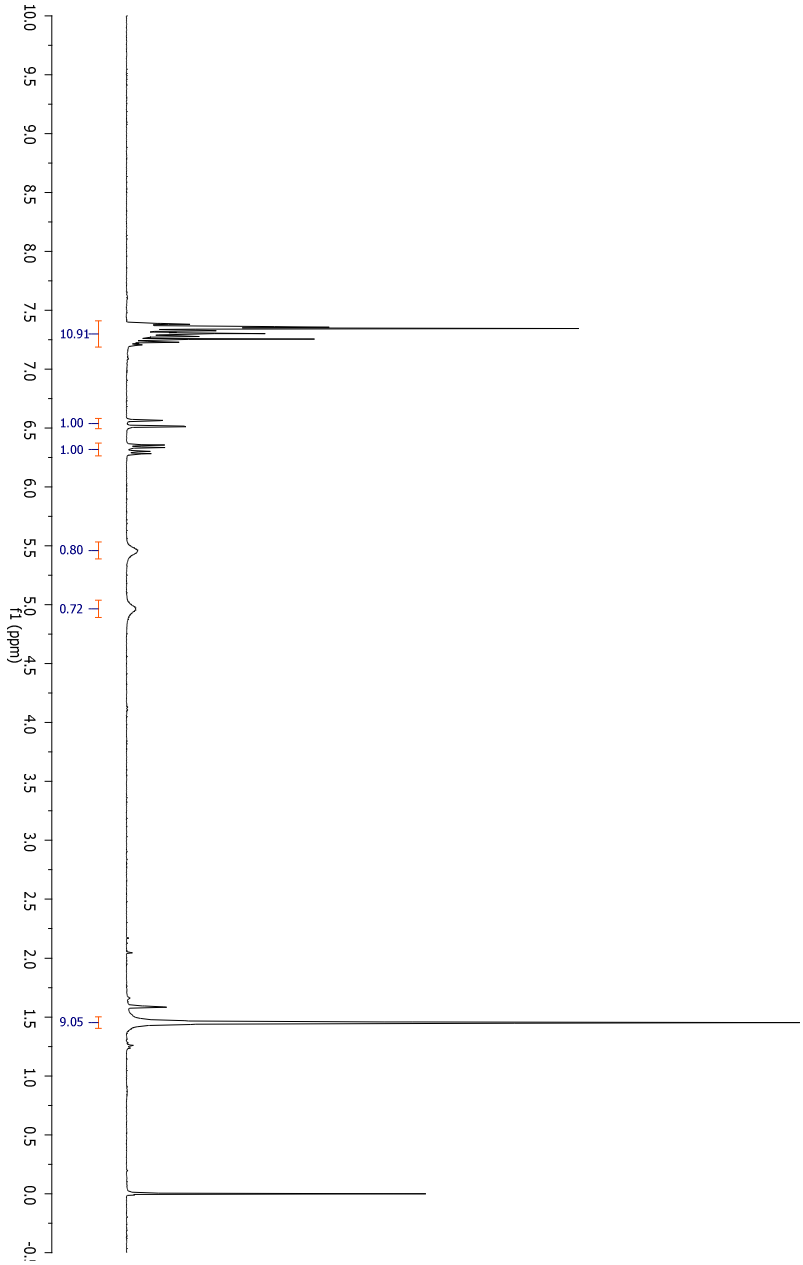

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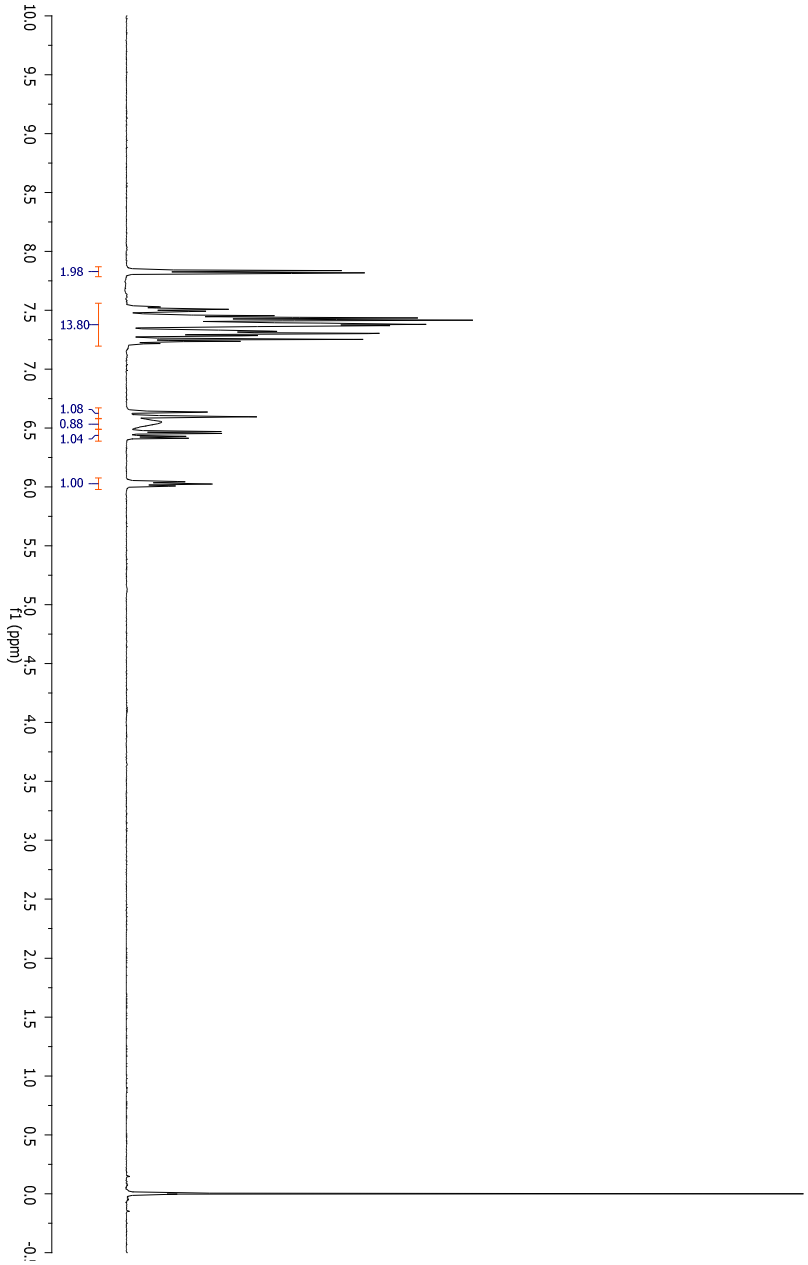

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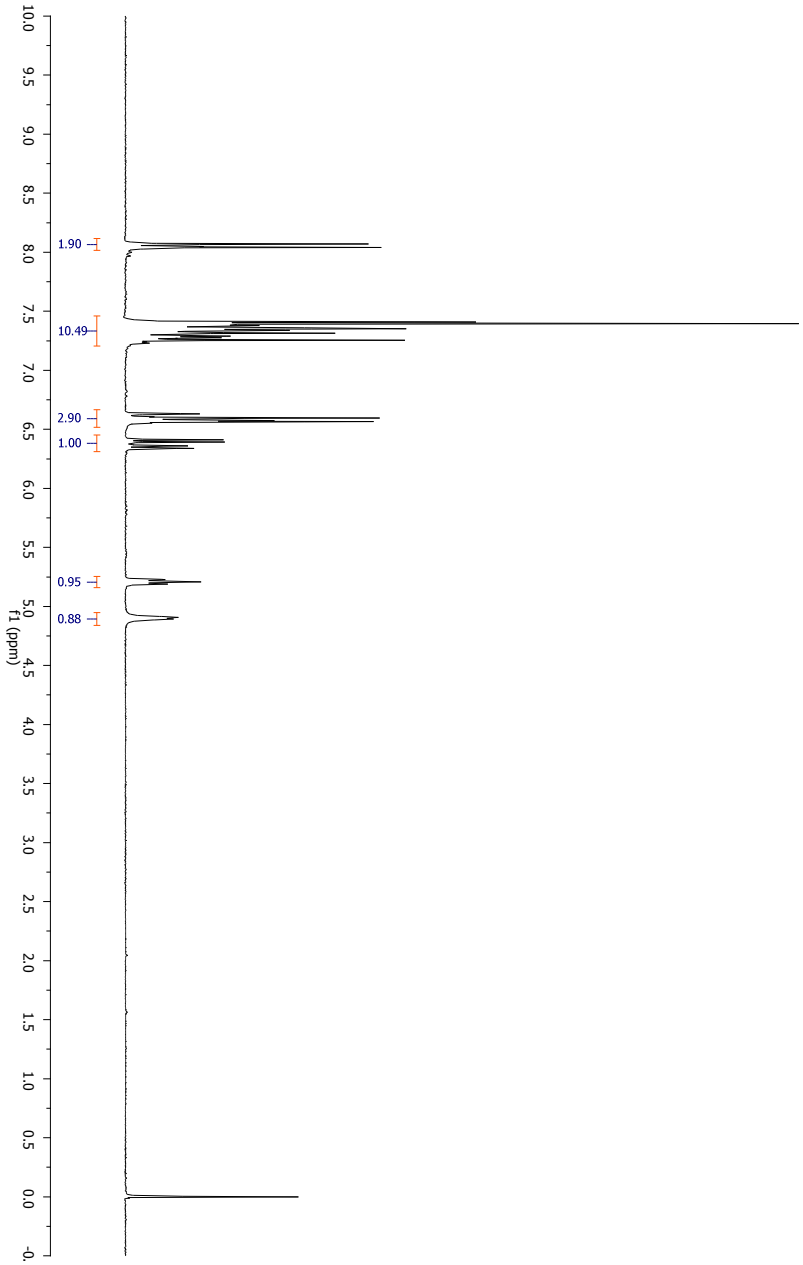

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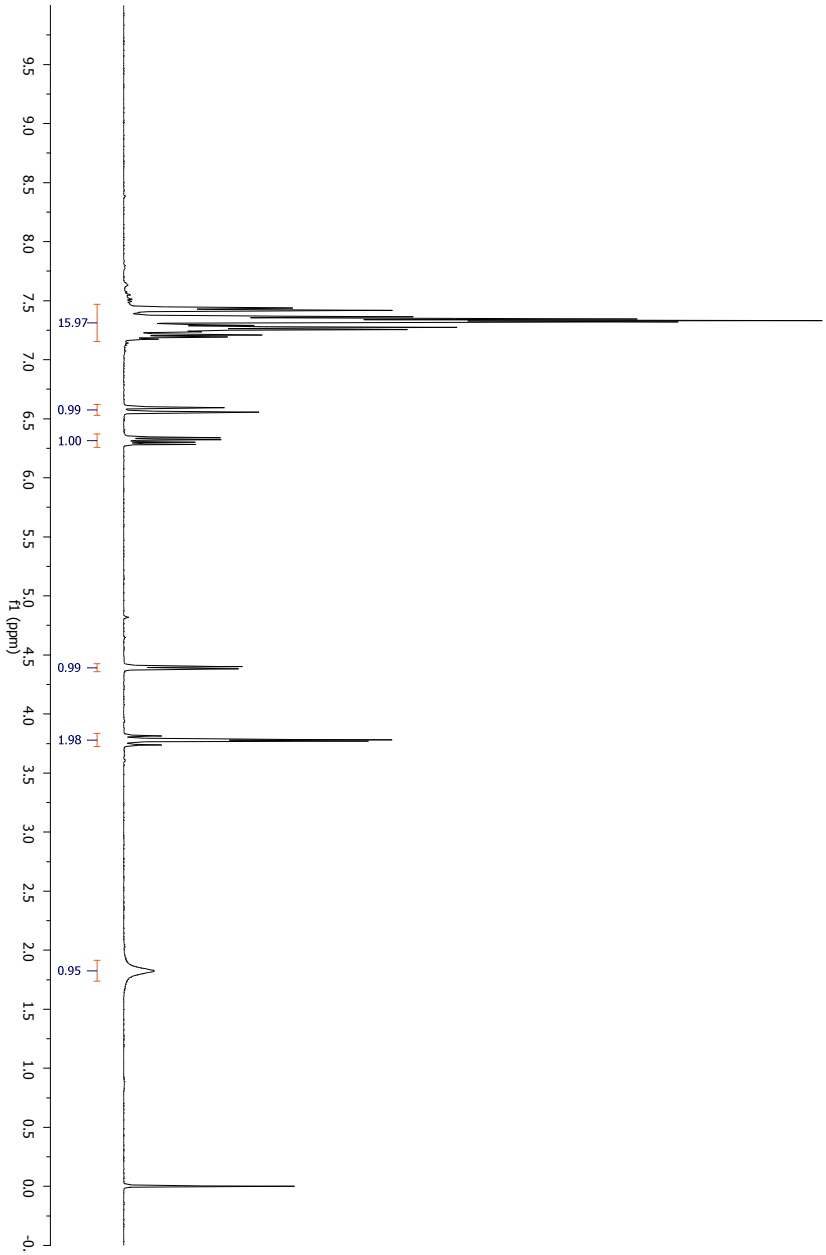

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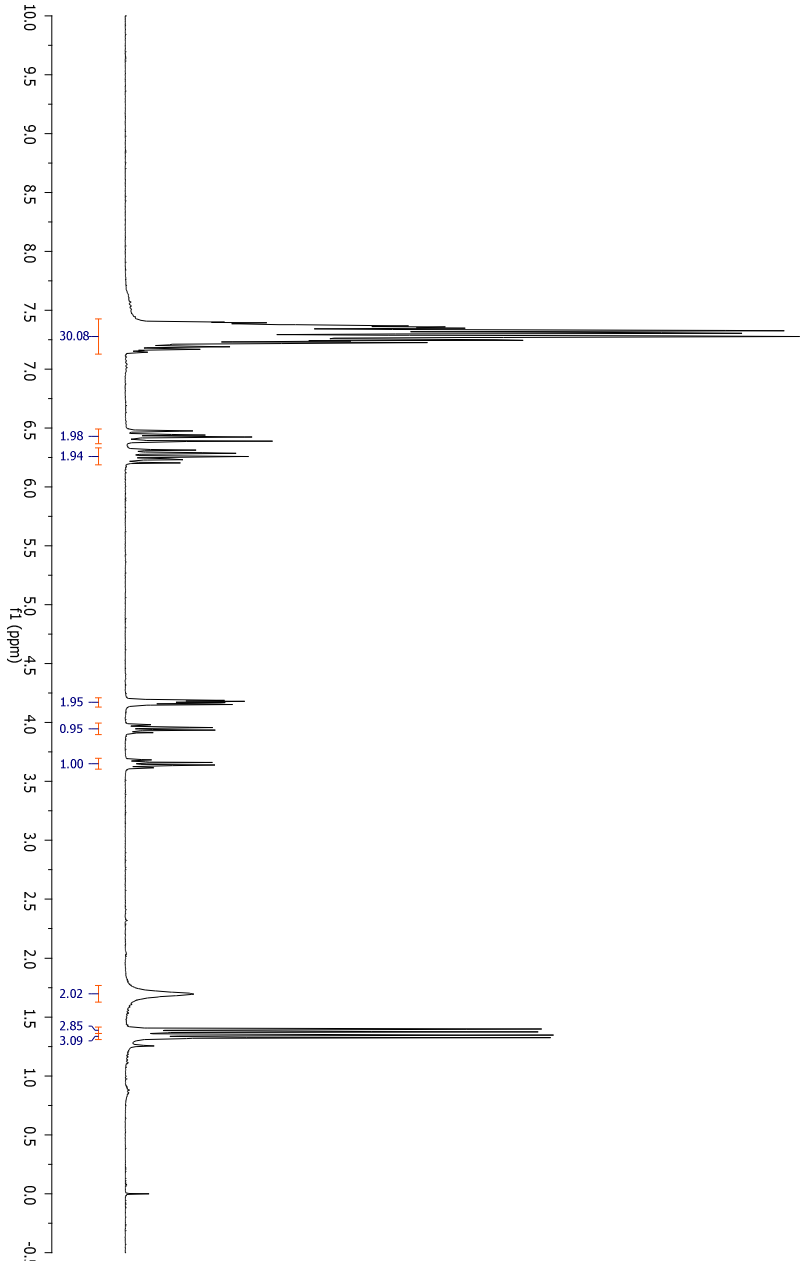

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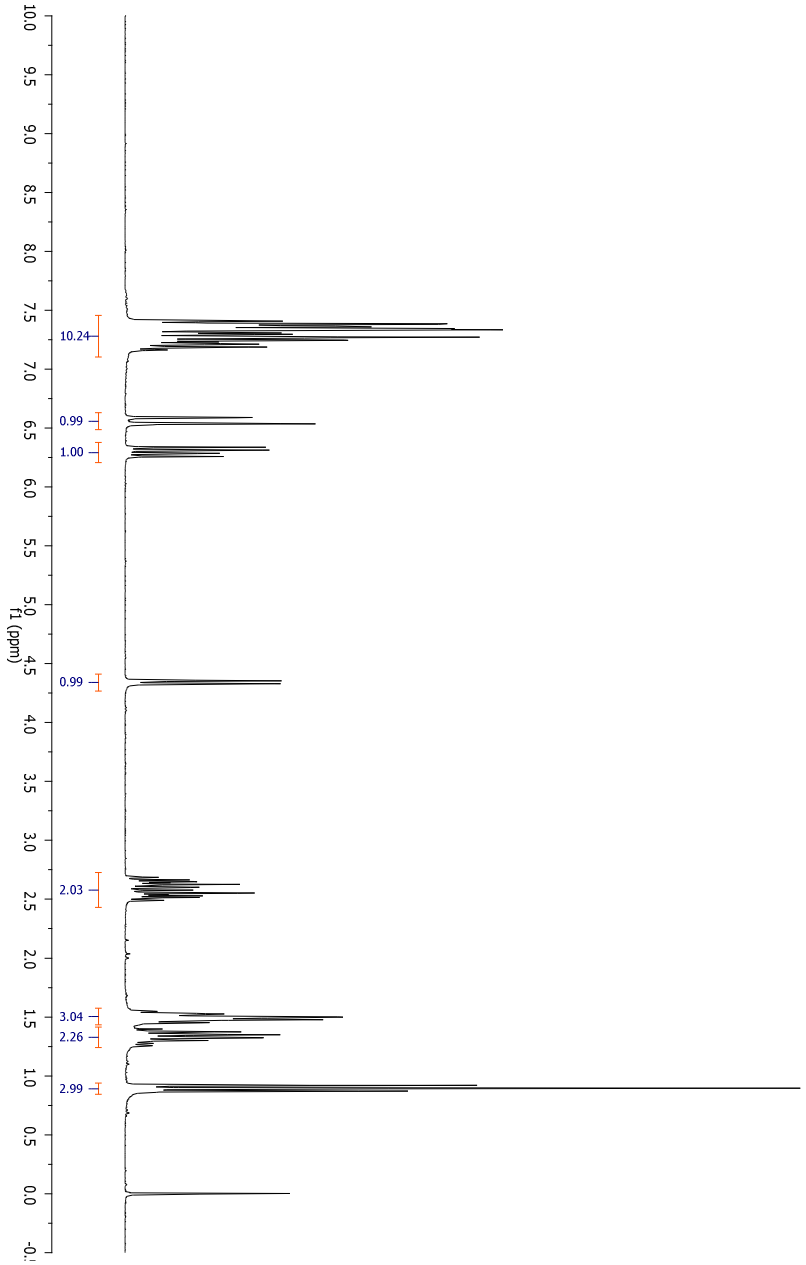

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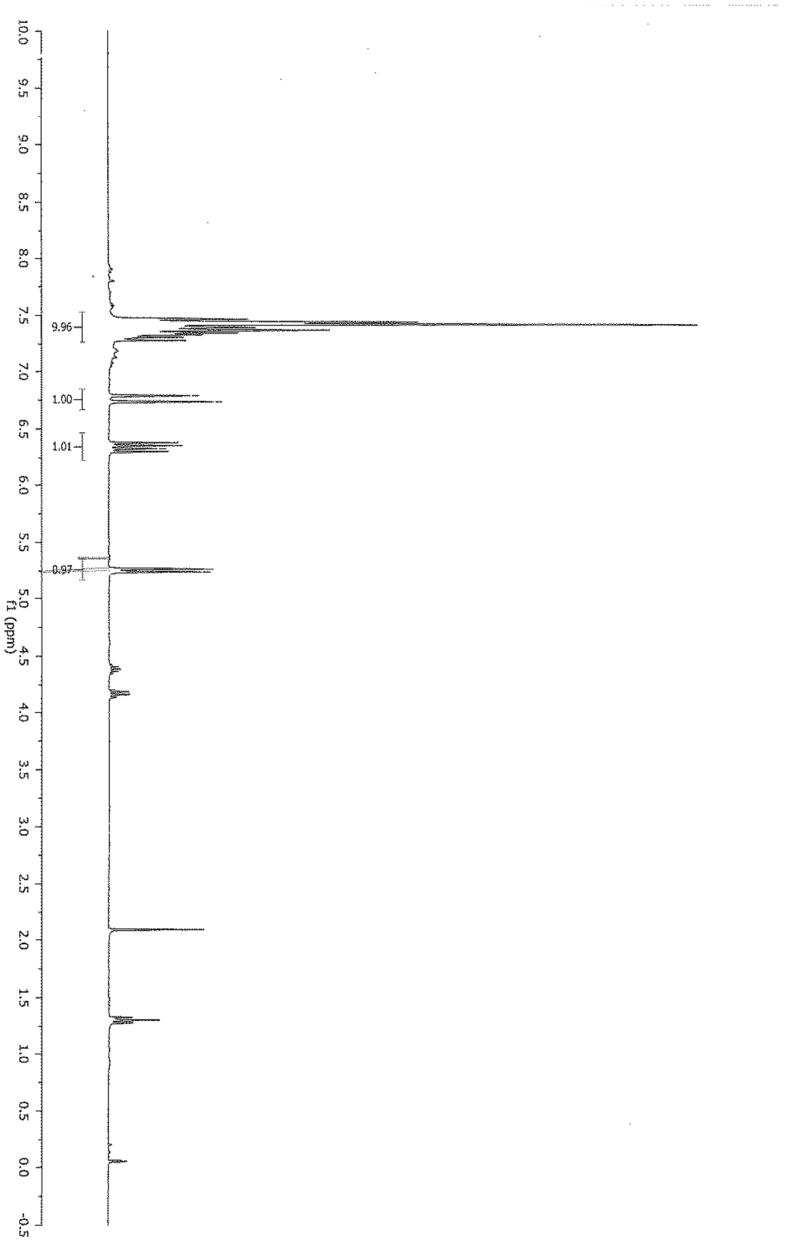

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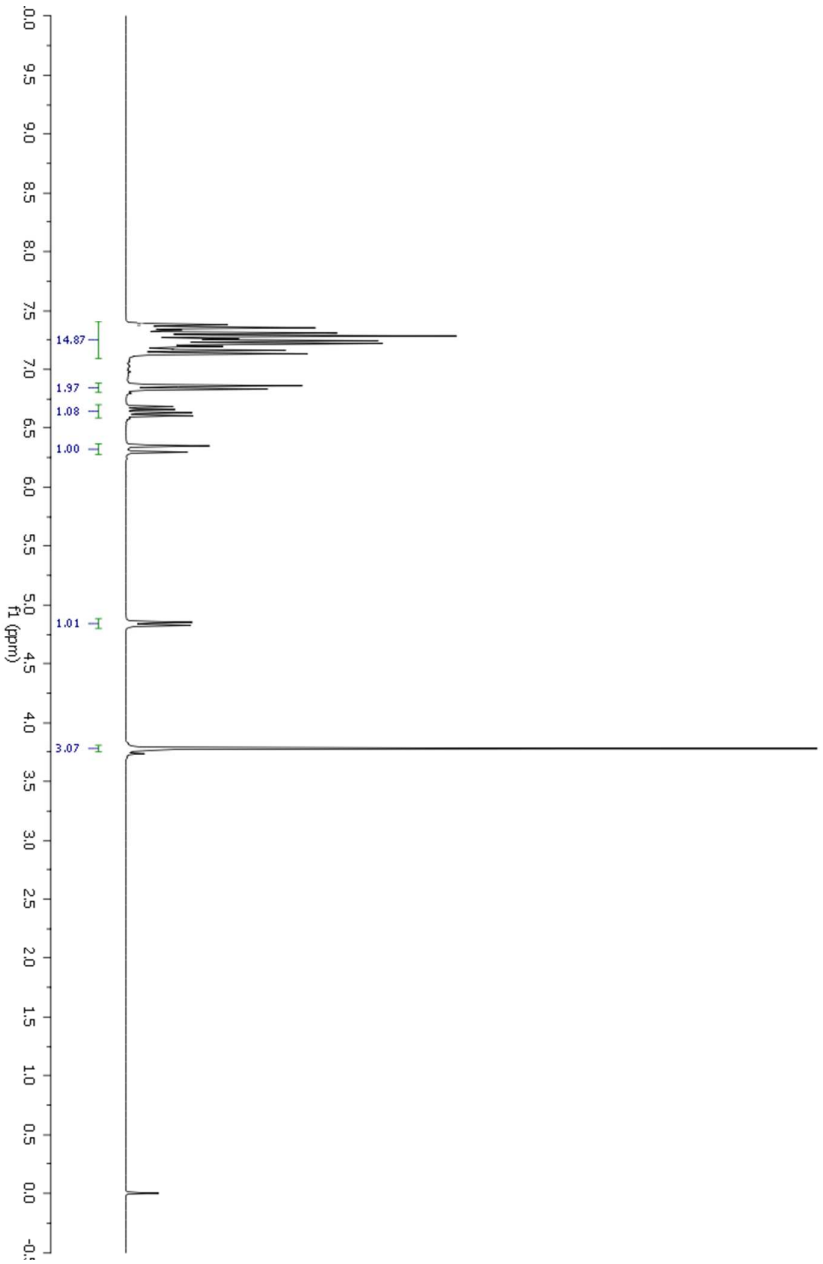

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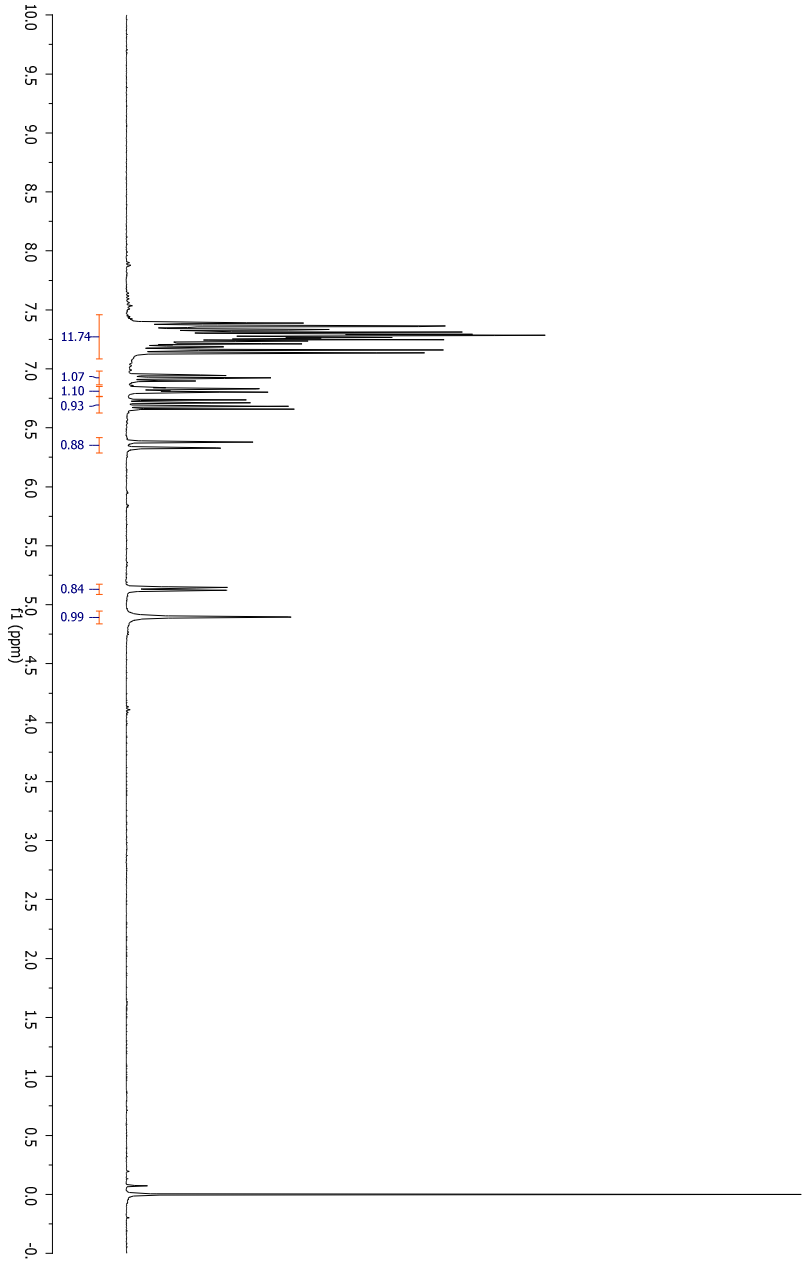
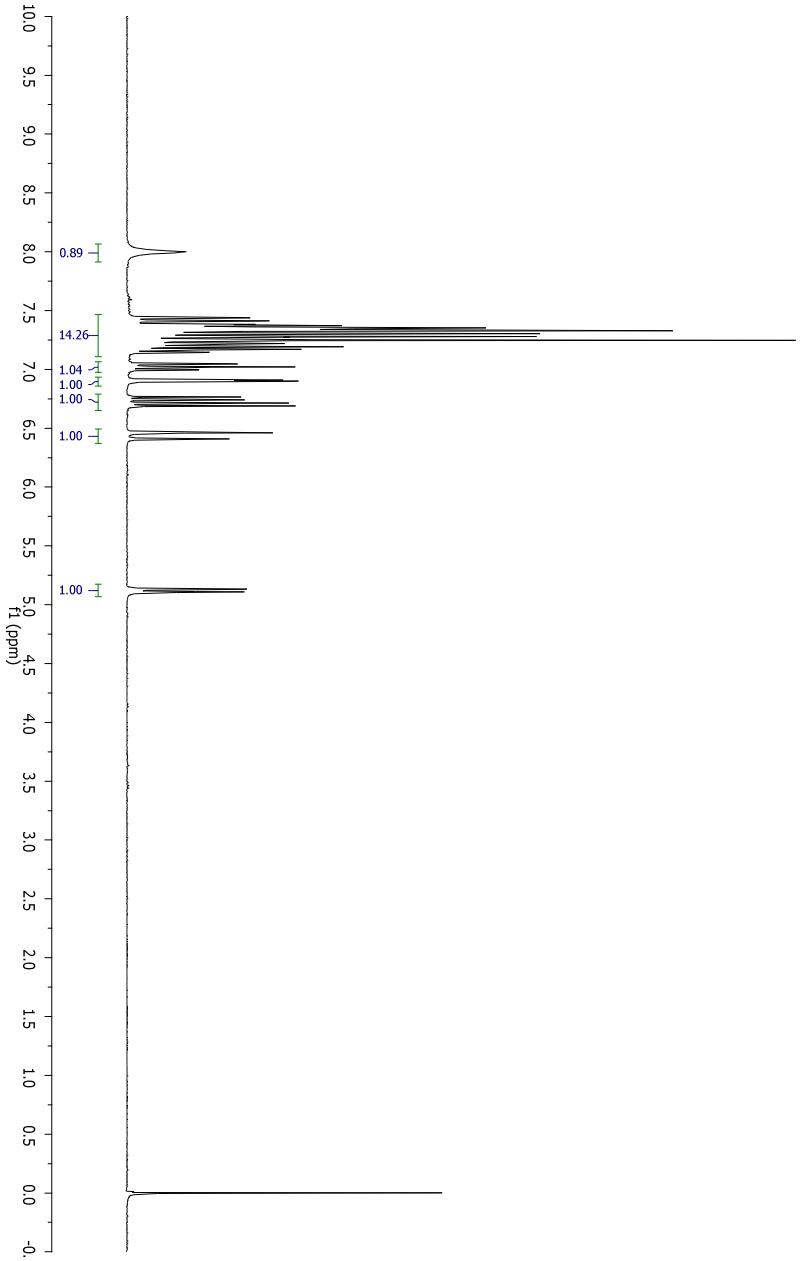


3al ^{1}H NMR



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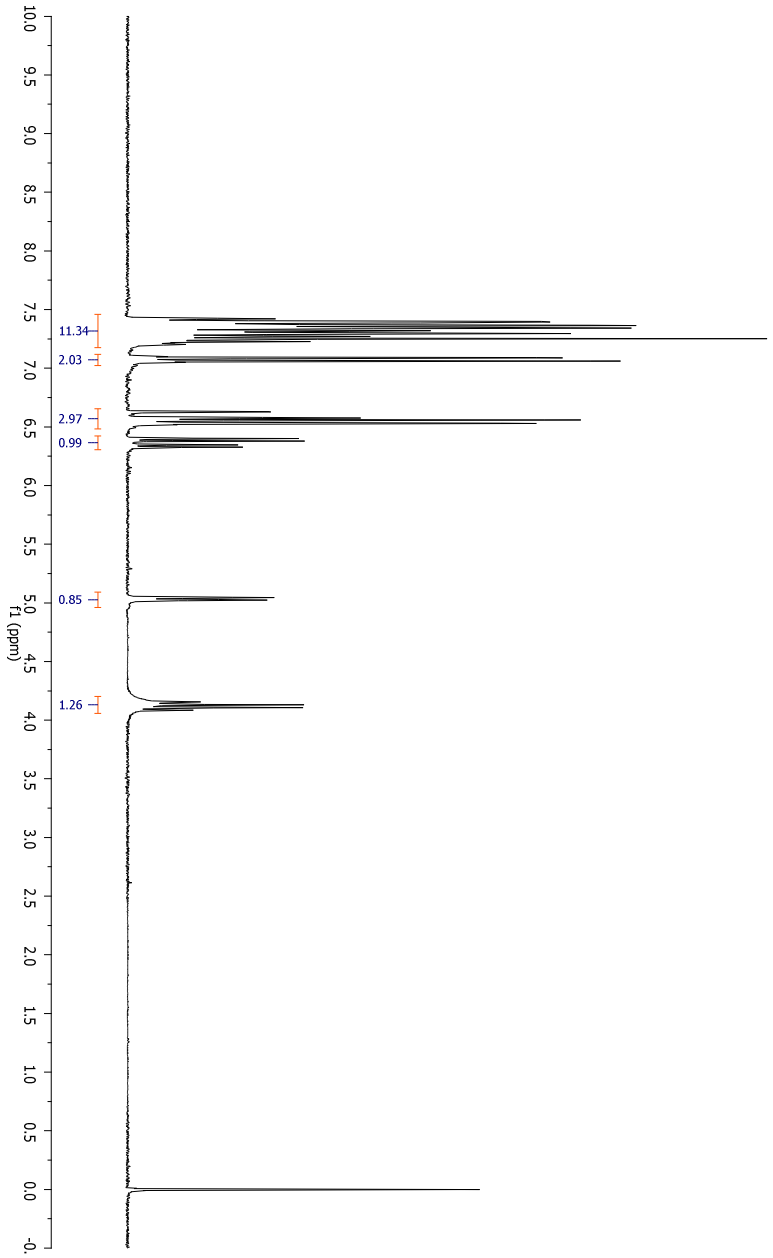

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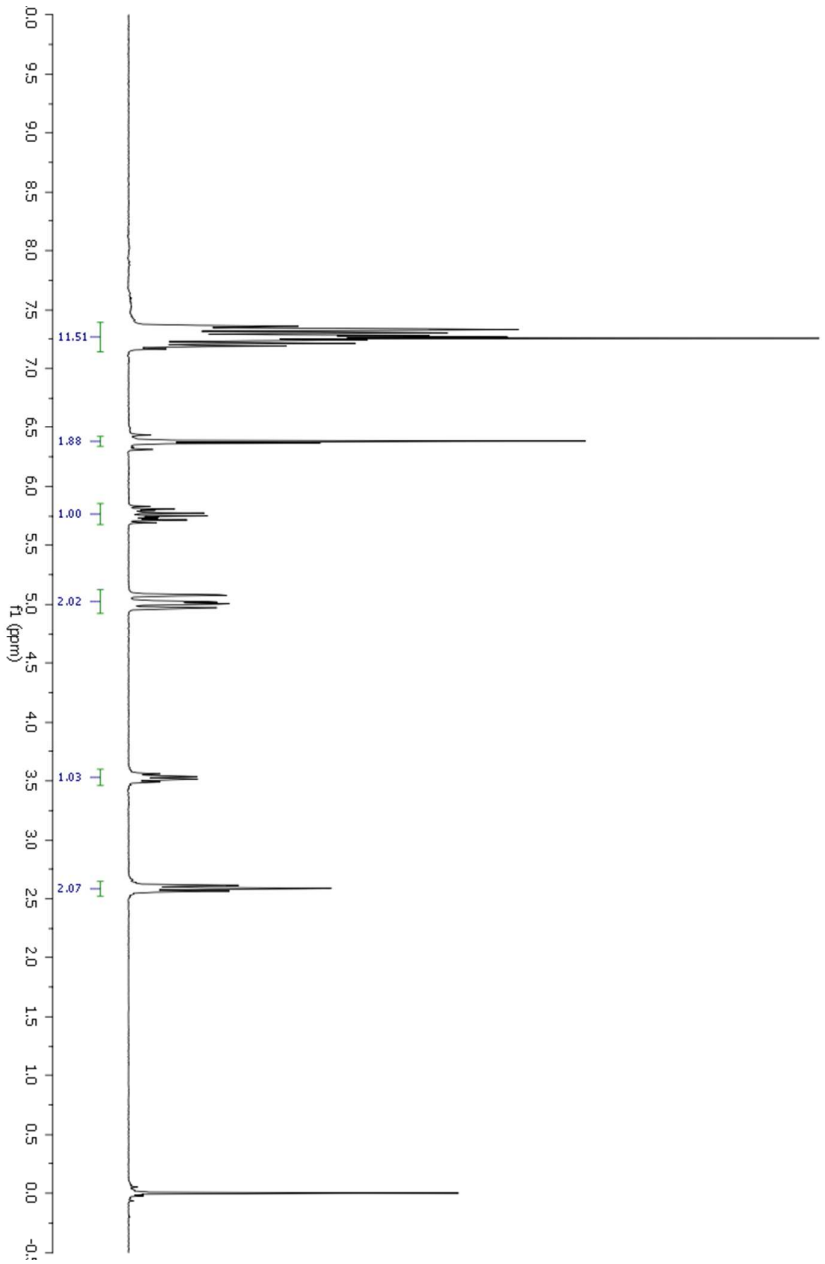

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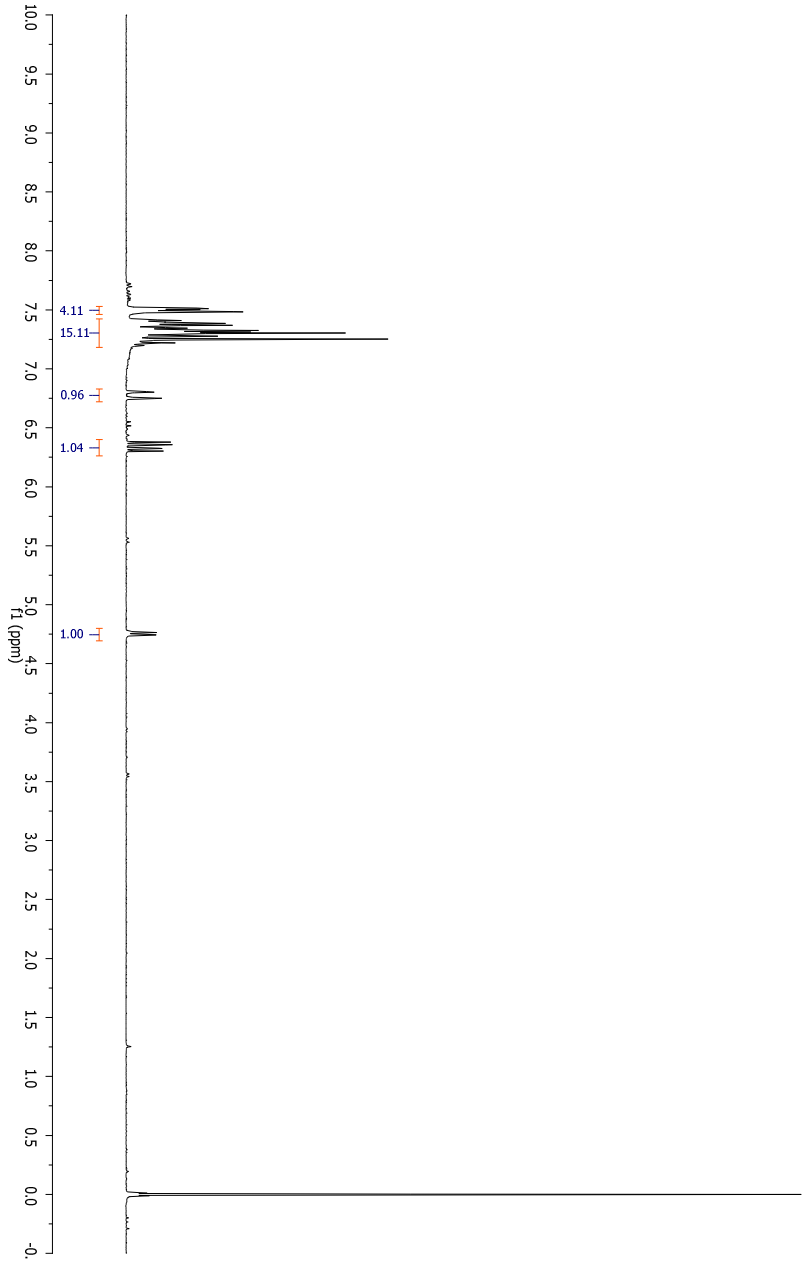

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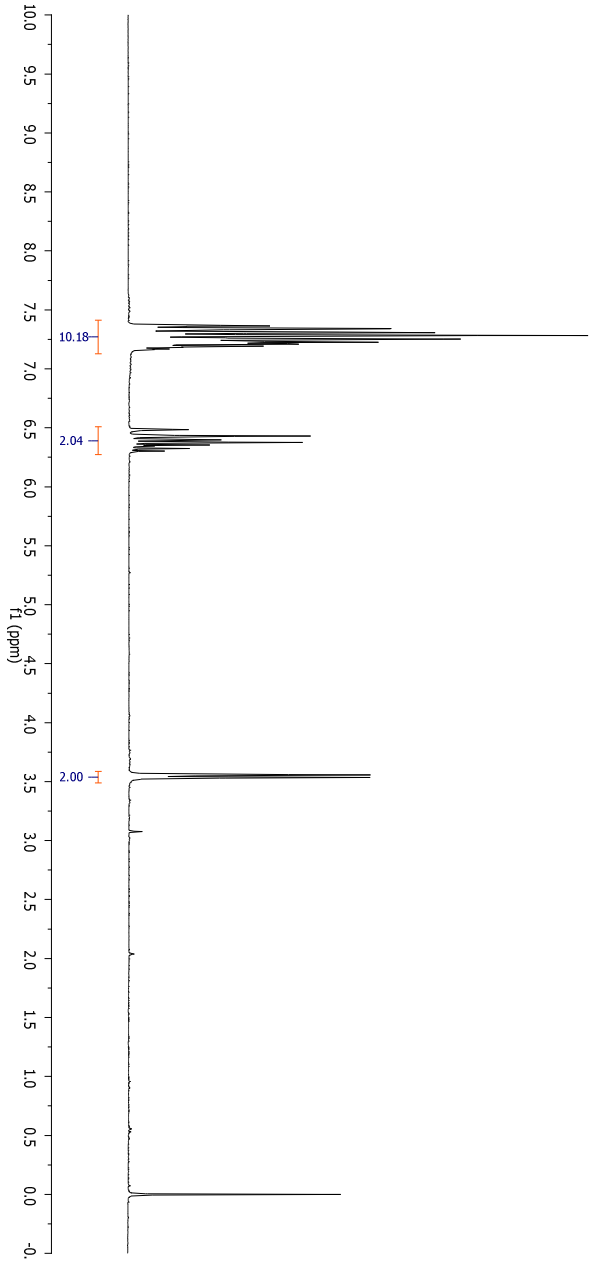

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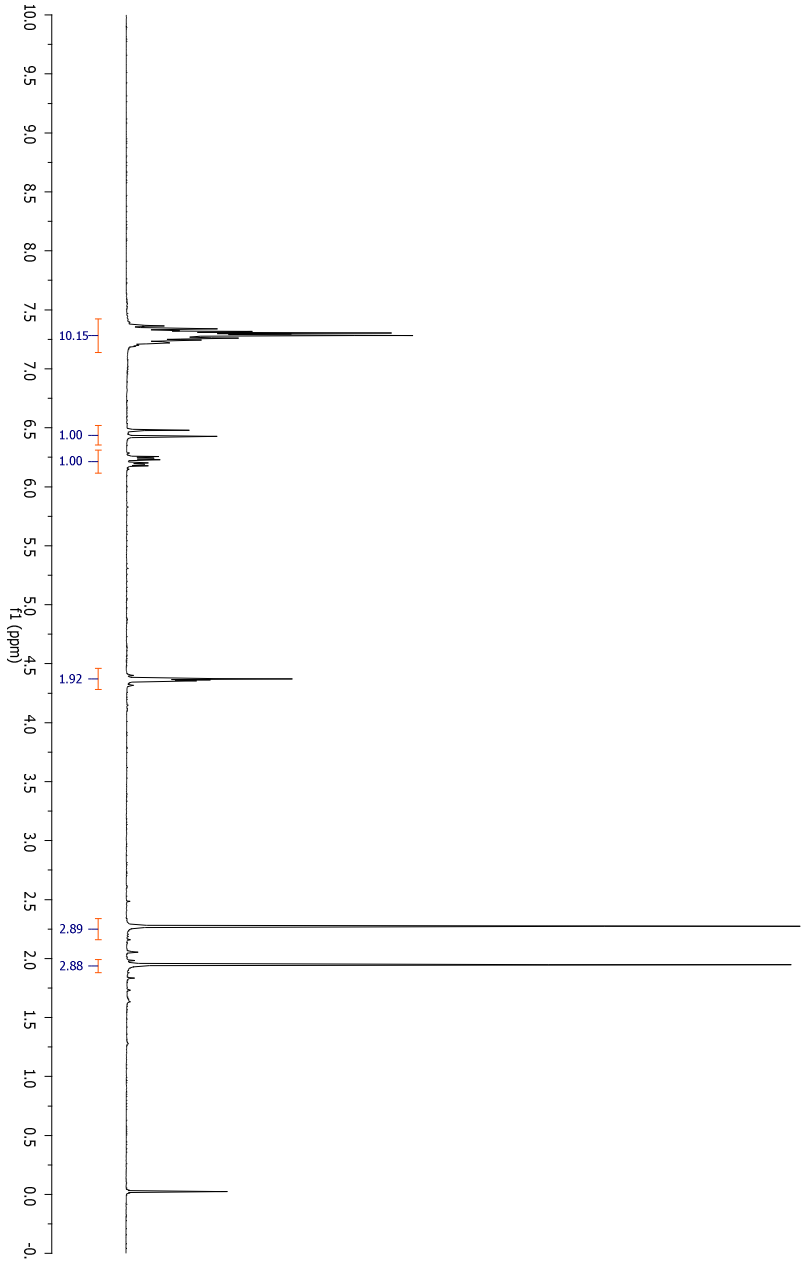

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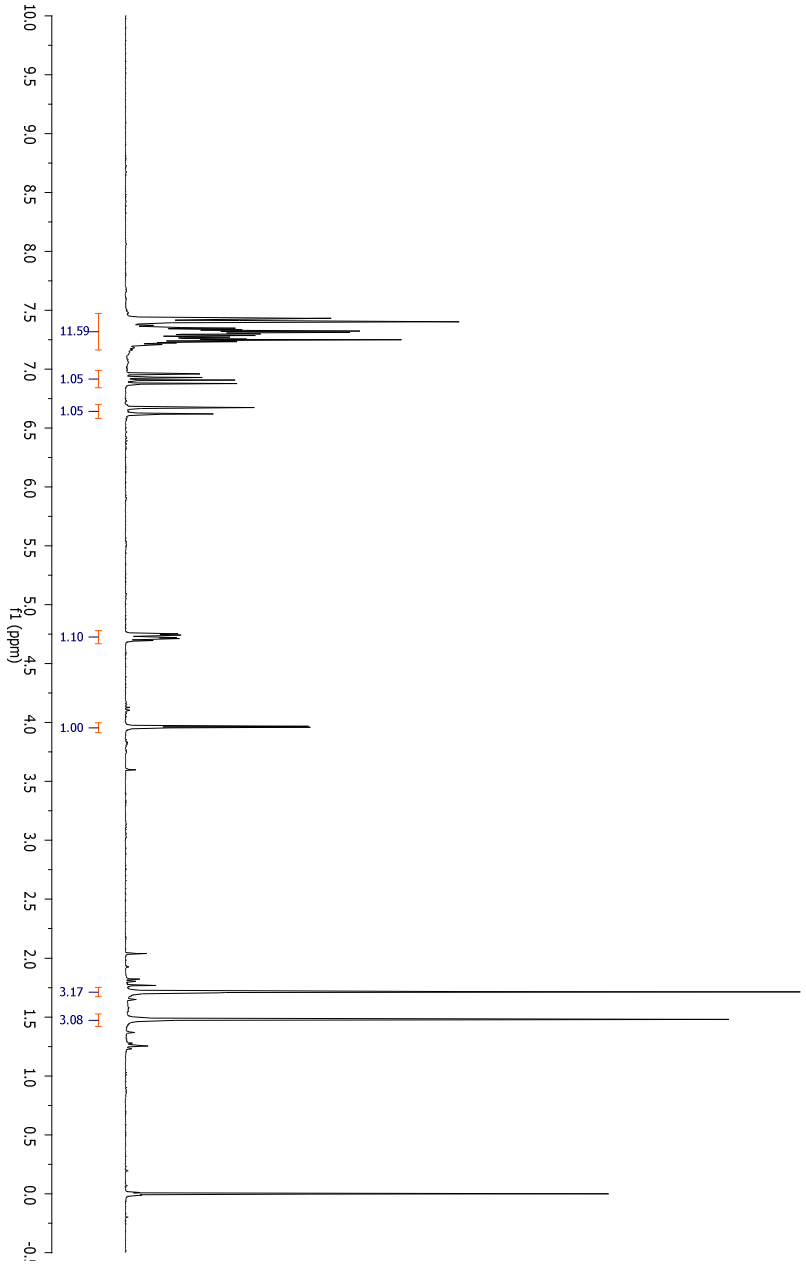

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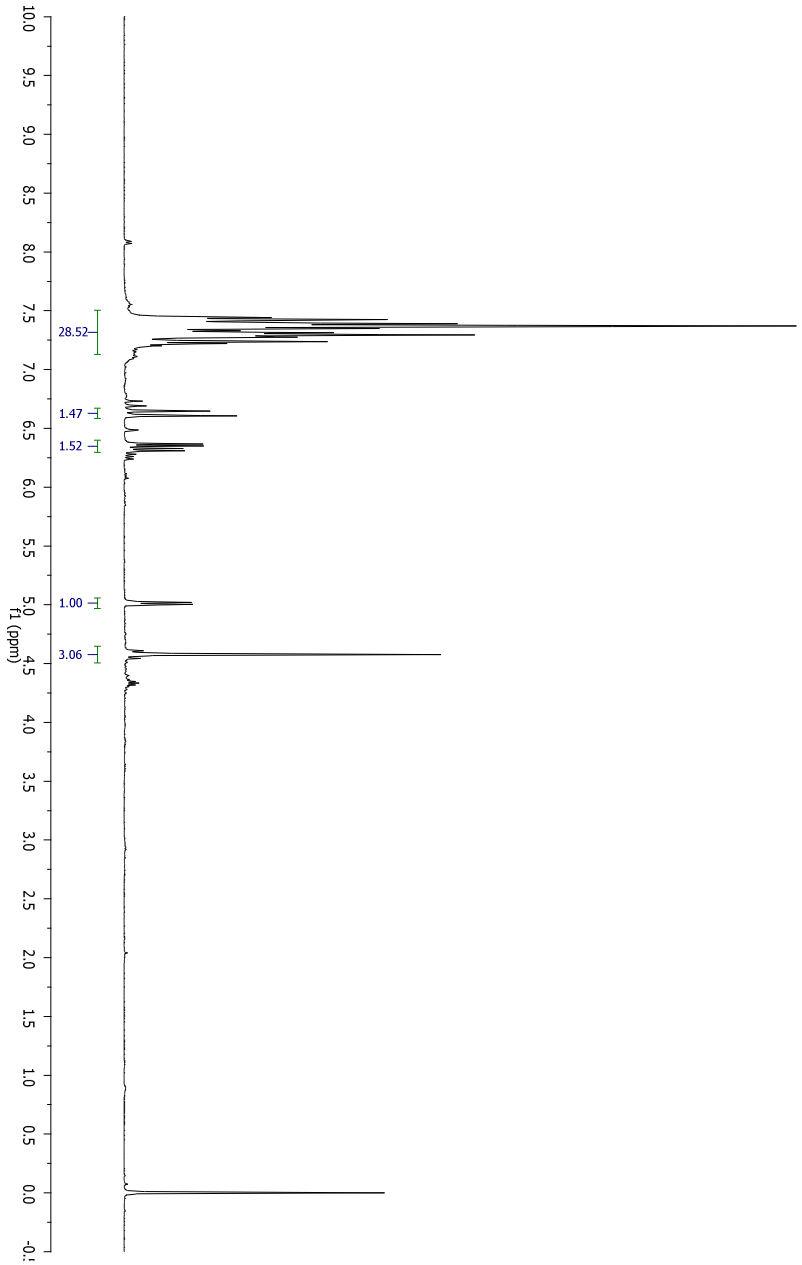

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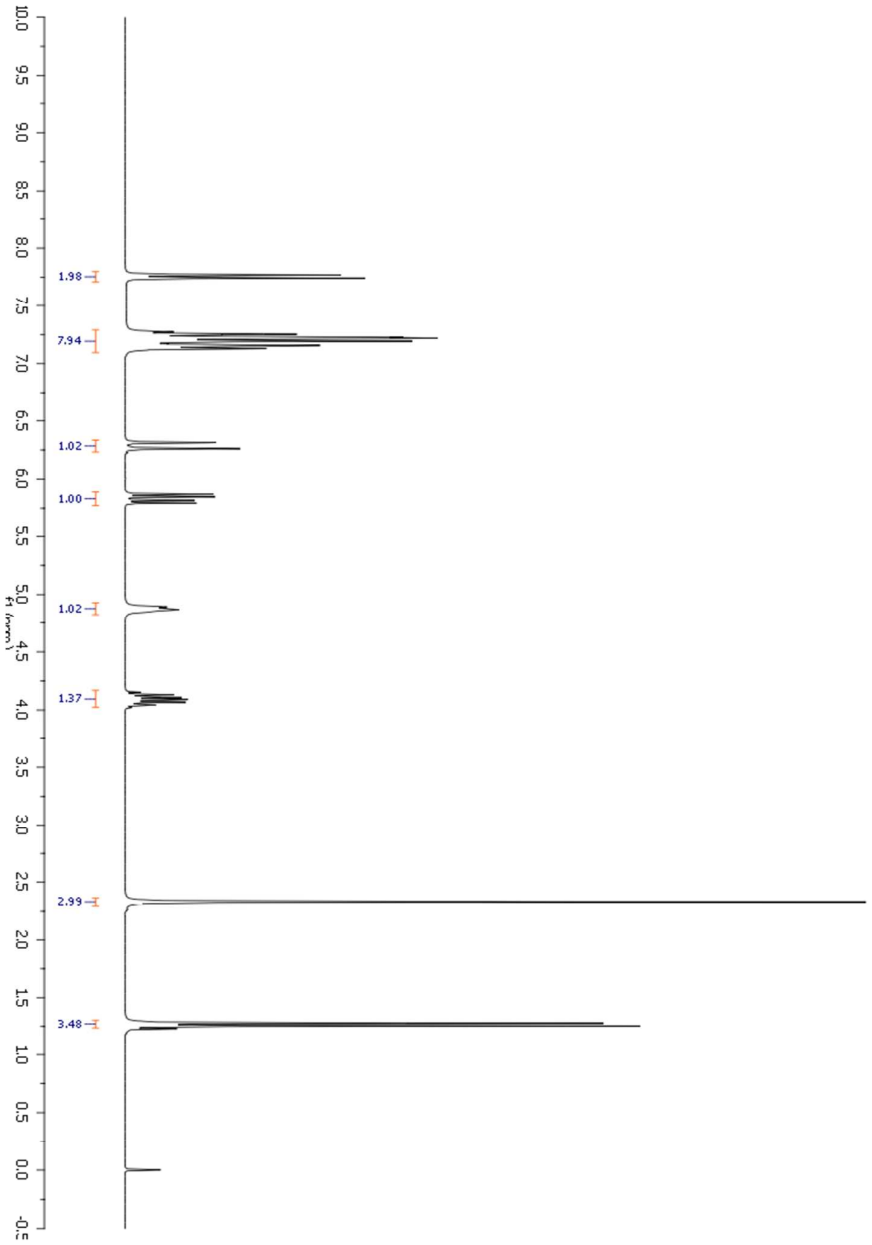

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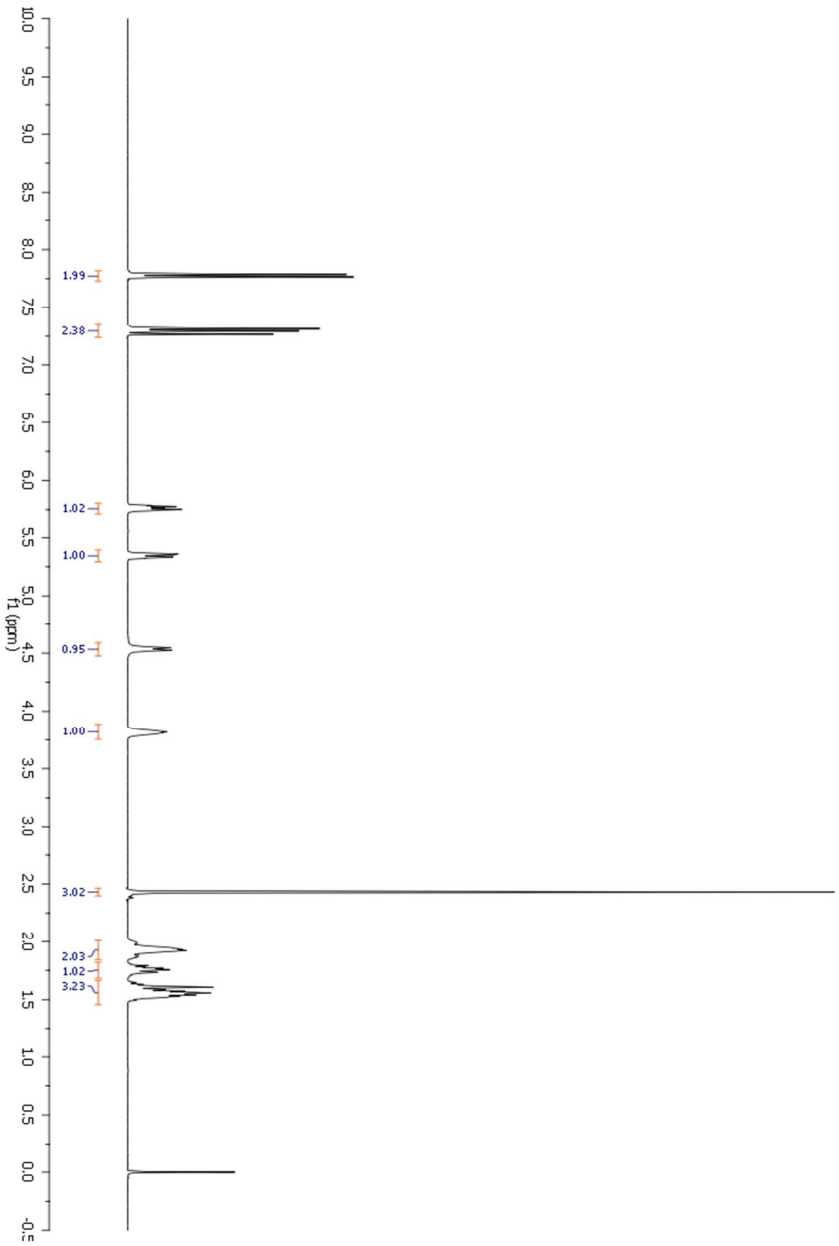

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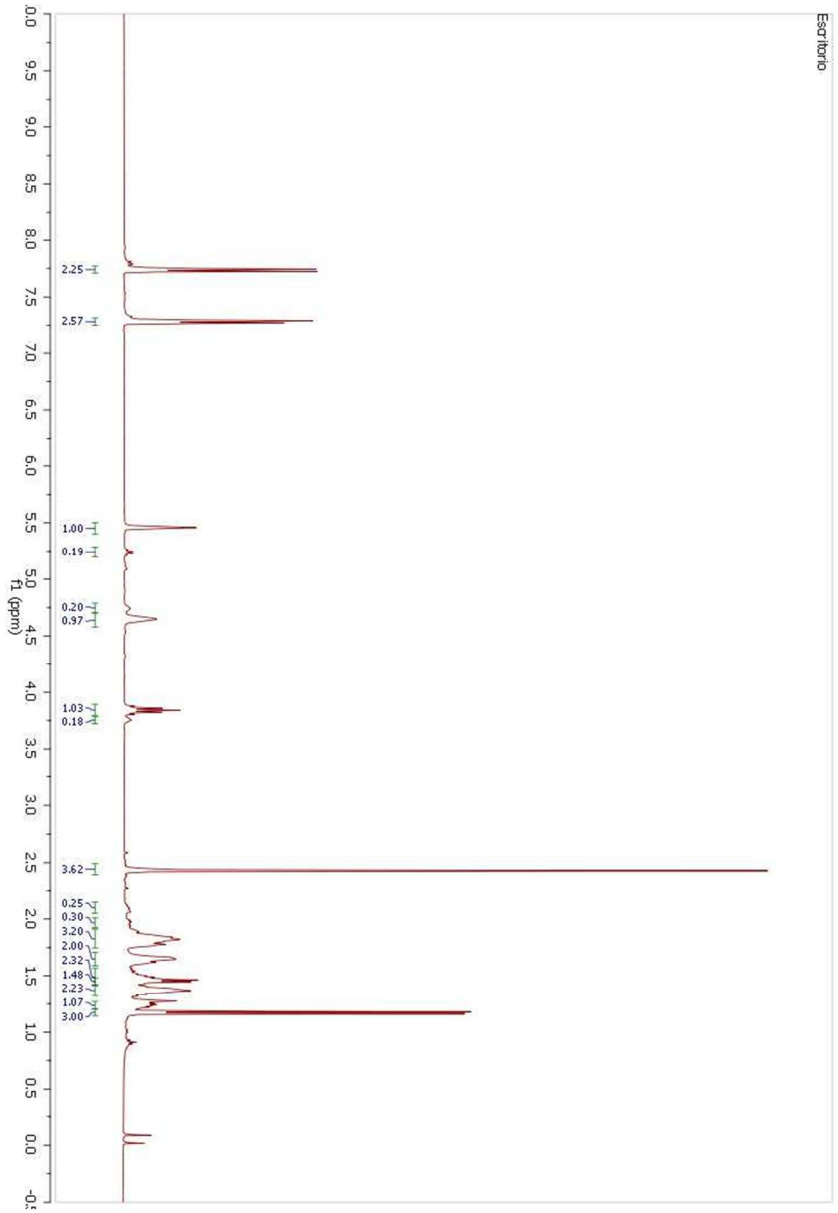
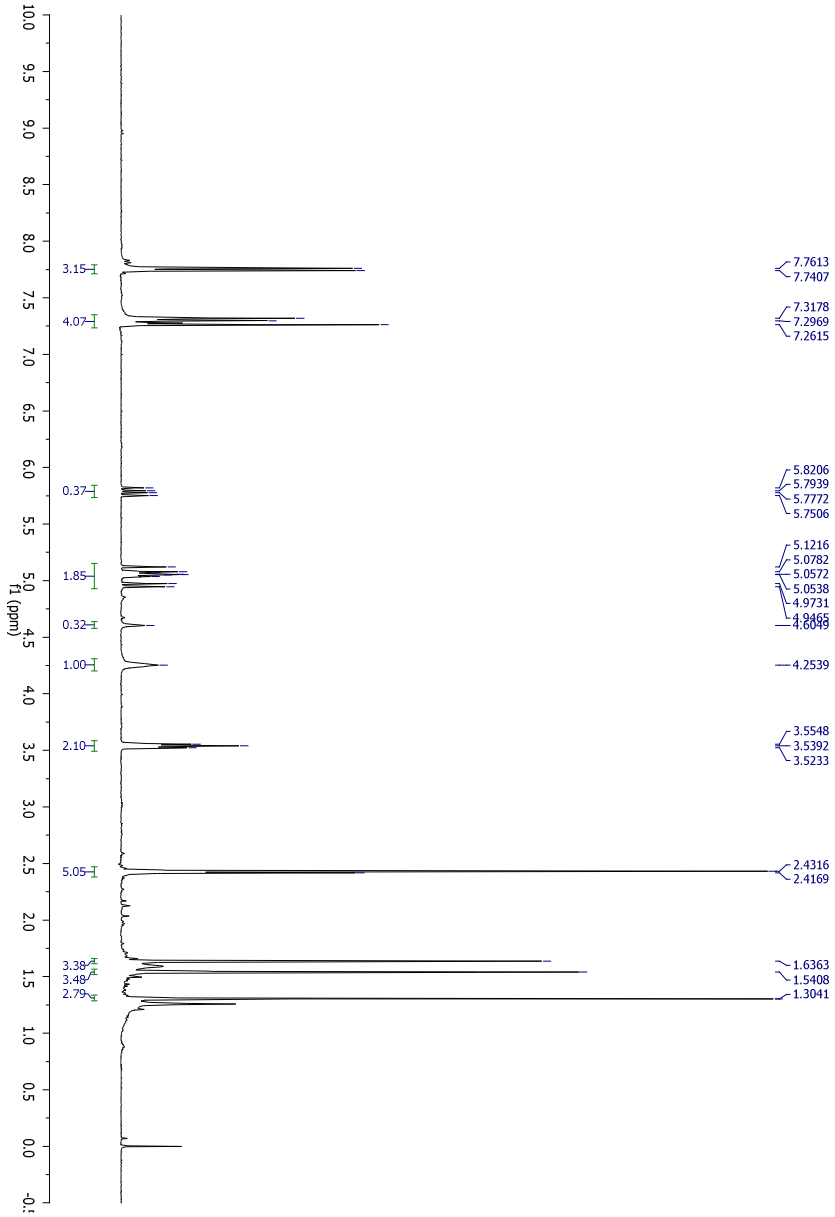

Escritorio
f1 (ppm)
2.25
2.57
1.00
0.19
0.20
0.97
1.03
0.18
3.62
0.25
0.30
3.20
2.00
2.32
1.48
2.23
1.07
3.00

3fa' ^{1}H NMR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0.37
1.85
0.32
1.00
2.10
5.05
3.38
3.48
2.79
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7.7407
7.3178
7.2969
7.2615
5.8206
5.7939
5.7772
5.7506
5.1216
5.0782
5.0572
5.0538
4.9731
4.9465
4.6049
4.2539
3.5548
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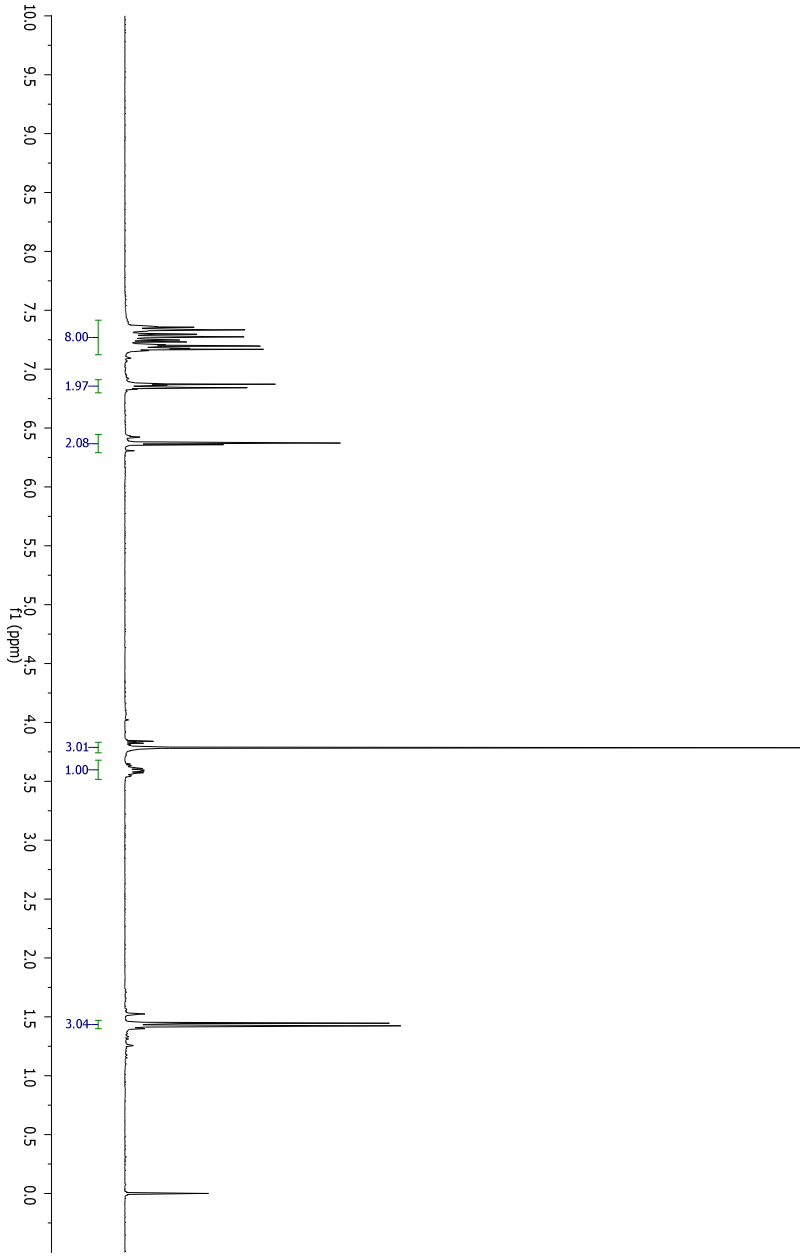
1.5408
1.3041

3bj ^{1}H NMR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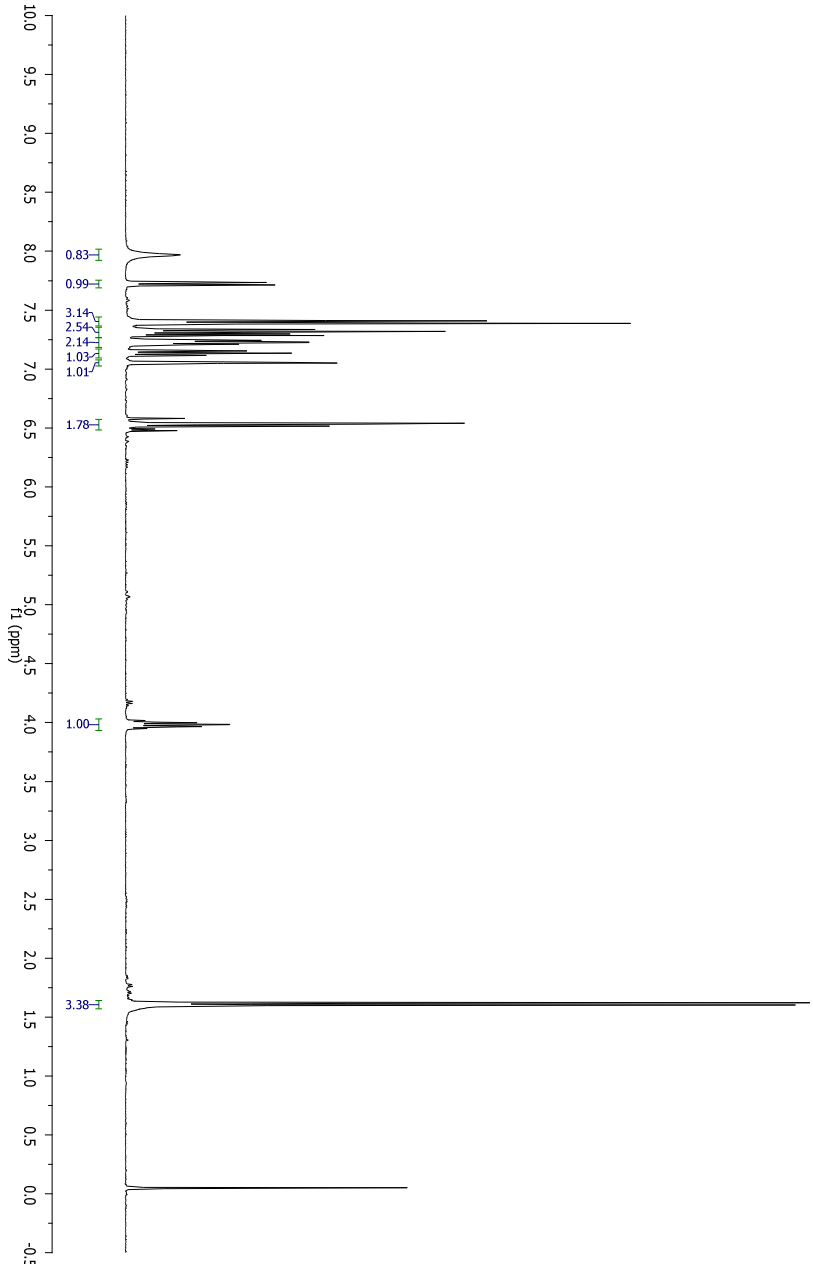
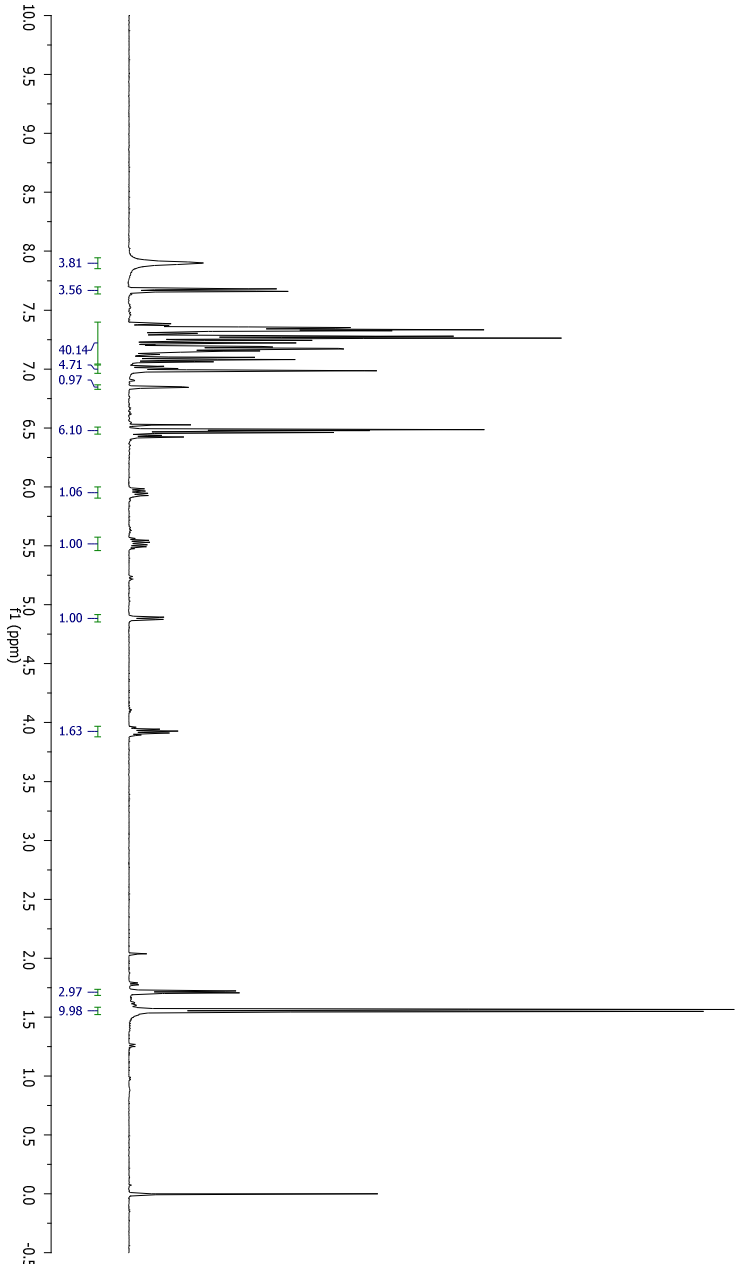
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
8.00
1.97
2.08
3.01
1.00
3.04

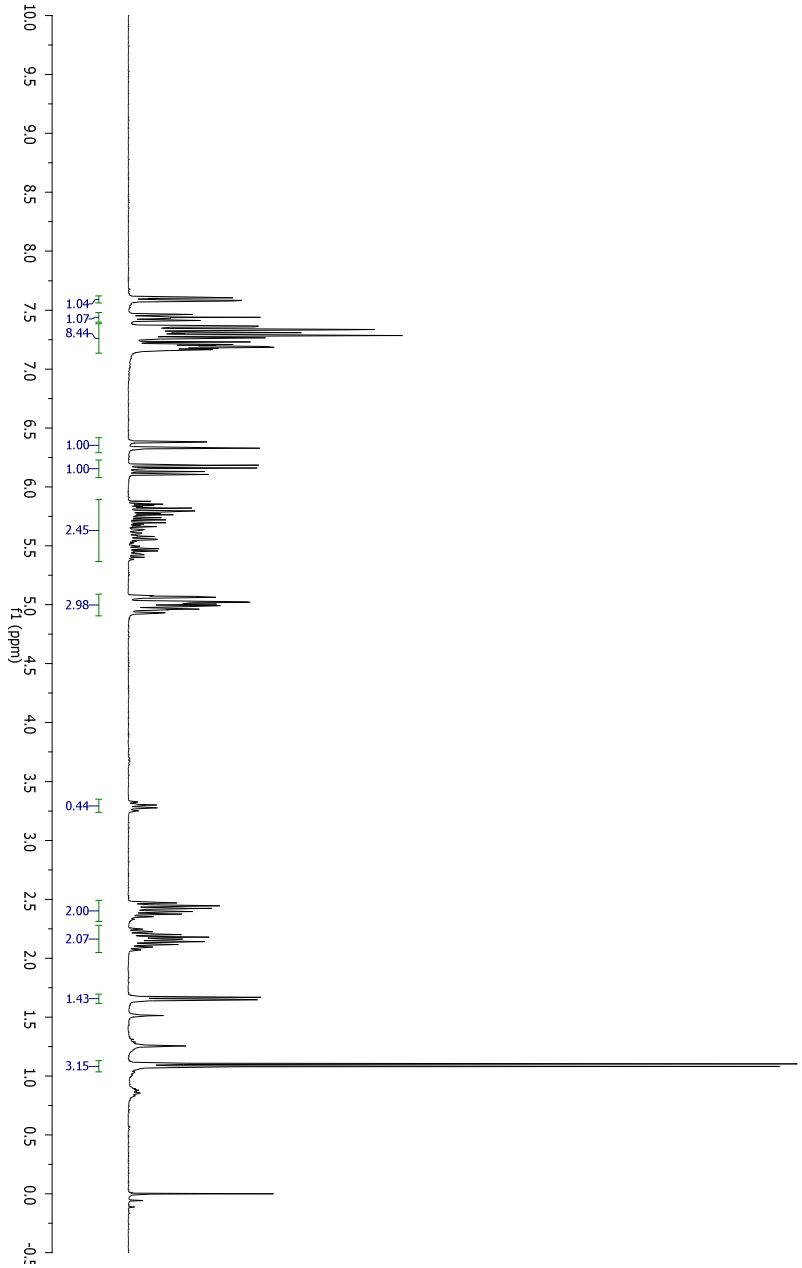
3bl ^{1}H NMR



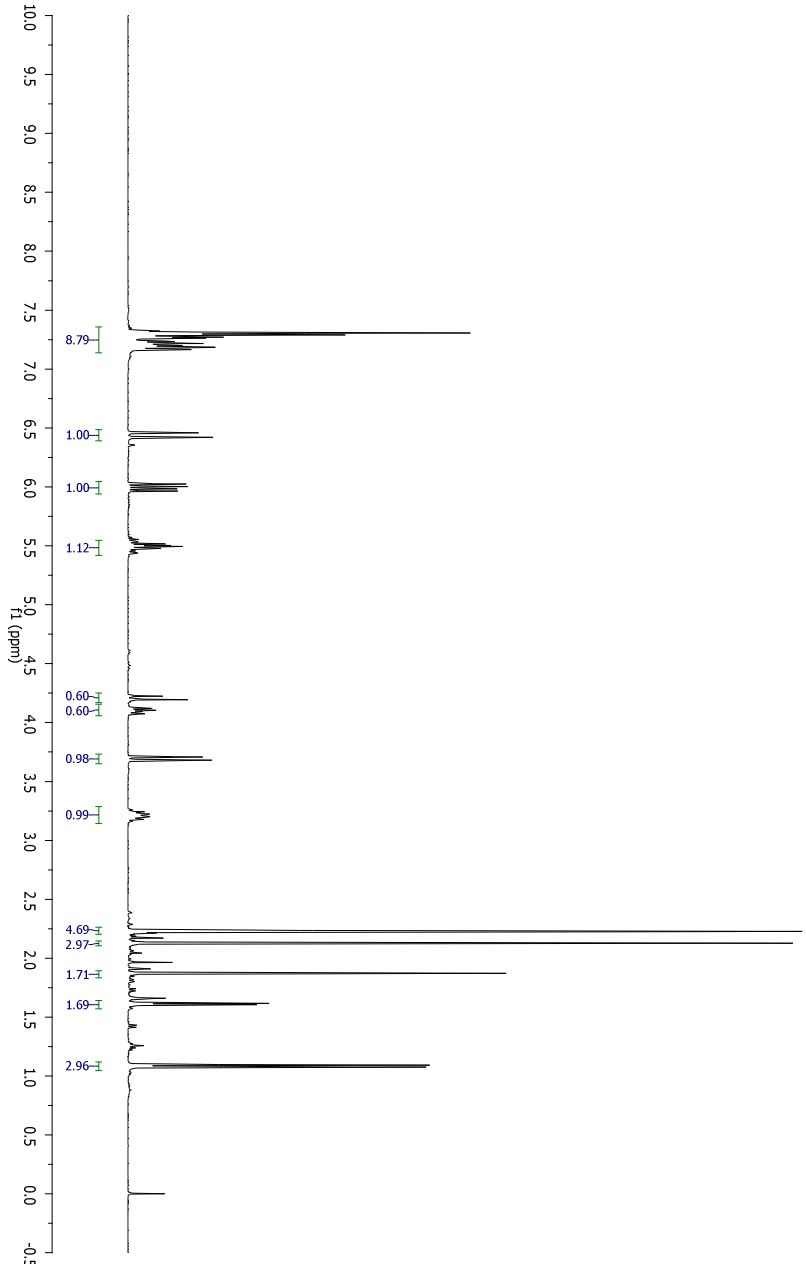
3bl + 3bl' ^{1}H NMR



3bo + 3bo' ^{1}H NMR



3br + 3br' ^{1}H NMR



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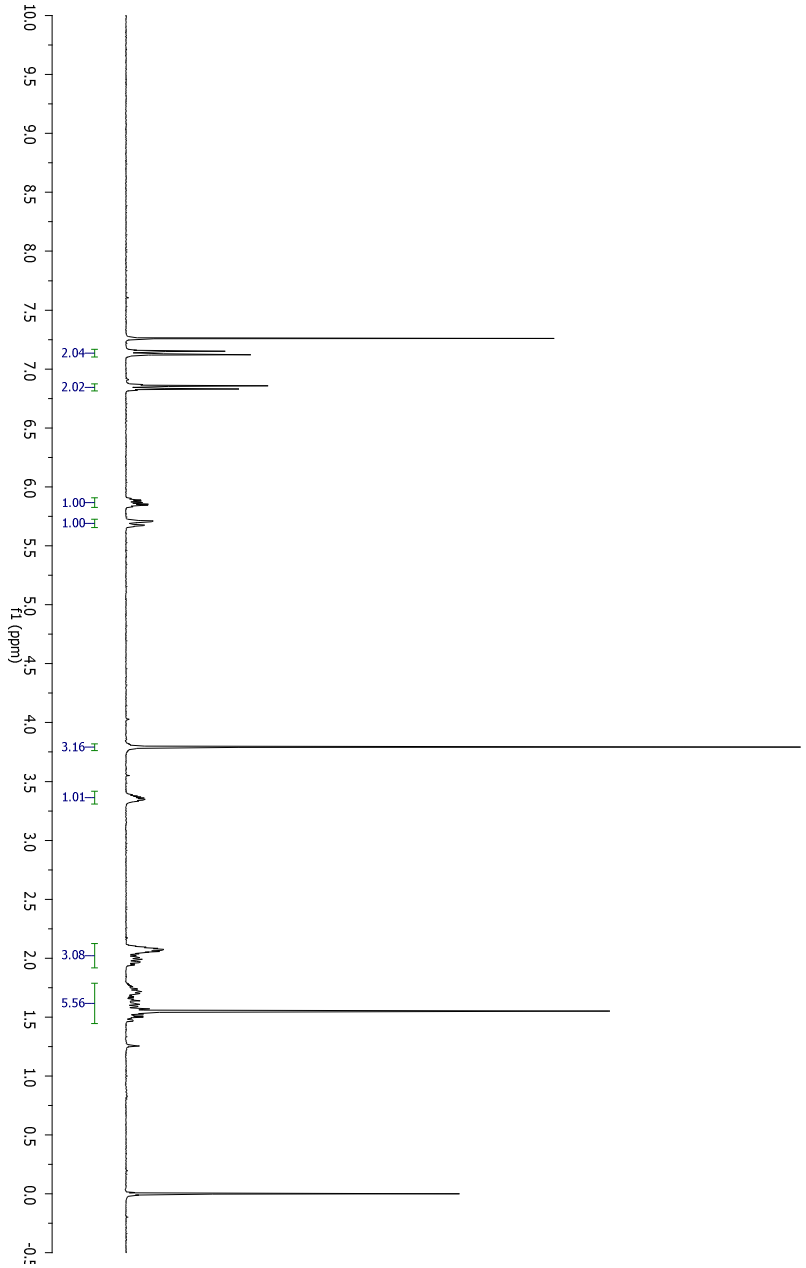
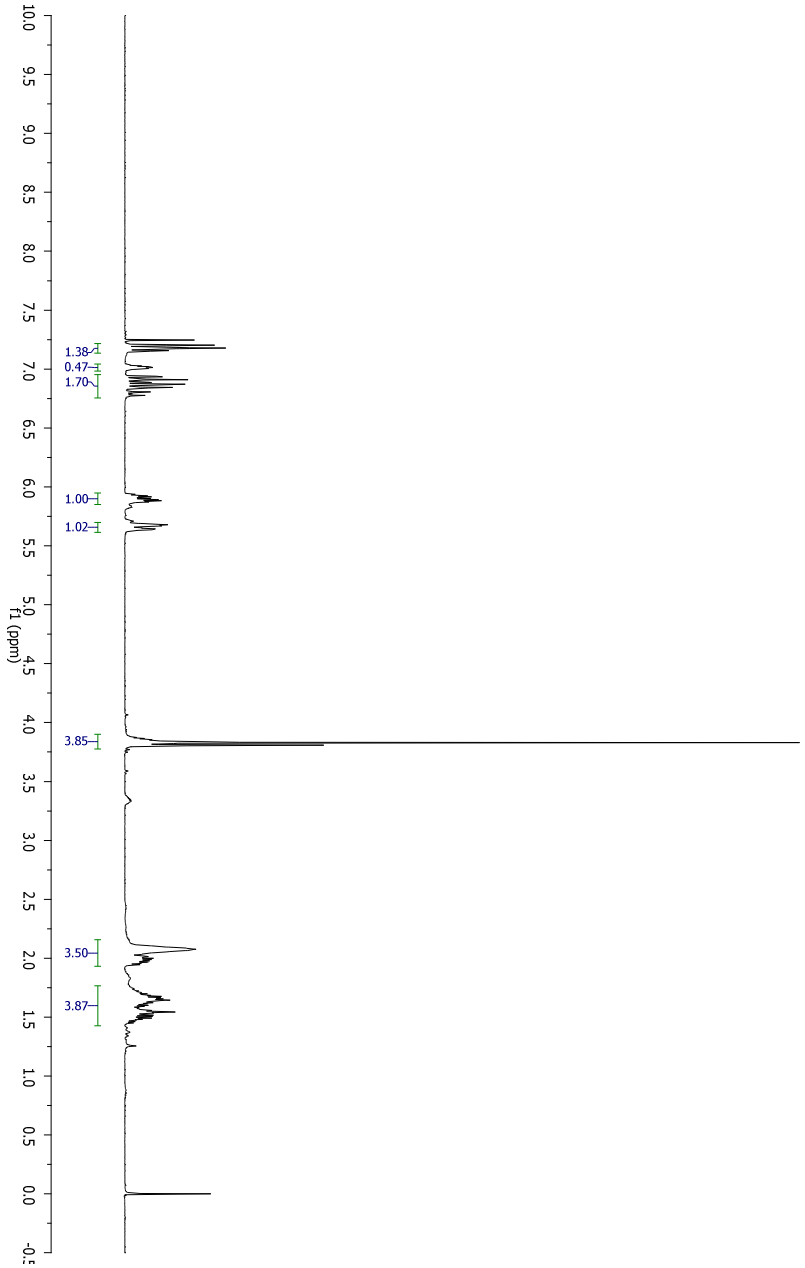


3dj + 3dj'' ^{1}H NMR



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Vial Number: 1
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