Supporting Information

Reactive Organogels: Self-assembled Support for Functional Materials

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Contents

Synthesis of compound 2.

A solution of p-nitrophenyl chloroformate (0.3 g, 1.5 mmol) in 25 mL of dry THF was added drop wise over a solution of *N,N'-bis*-(*L*-valyl) butylenediamine[8] (0.2 g, 0.7 mmol) and triethylamine (0.21 mL, 1.5 mmol) in 50 mL of dry THF at 0 ºC. After the addition, the mixture was stirred overnight at room temperature. The white solid was filtered and washed with 0.1 M HCl to eliminate triethylammonium chloride. The solid was further purified by gelation/filtration in acetonitrile. 92 % yield. ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm) 8.25 (d, 4H, J=8.4 Hz), 8.09 (d, 2H, J=8.4 Hz), 8.03 (m, 2H), 7.38 (d, 4H, J= 8.2 Hz), 3.83 (t, 2H, J=7.6 Hz), 3.2-3.0 (m, 4H), 2.03 (m, 2H), 1.42 (m, 4H), 0.90 (m, 12 H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm) 171.0, 156.9, 153.9, 144,8,125,9, 123.0, 61.3, 38.9, 30.9, 27.2, 19.9, 18.9; IR (KBr, cm^{-1}) 3290, 3099, 2962, 2867, 1718, 1647, 1524; ESI-MS (m/z) 639.1 ($M+Na^+$).

Gelation and gel-to-gel reaction procedure.

Compound **2** (3mg/mL) was dissolved in hot acetonitrile in a screw-capped vial of 2 cm diameter. A soft gel was formed after few minutes at room temperature. All samples were allowed to stand at rt for 30 minutes before the addition of reagents. Afterwards, 100 μL of a stock solution containing 4 equivalents of the amine were carefully added on top of the gel and let to diffuse and react for 2-3 h at room temperature. Then, the gel was filtered trough a filtering plate (pore 3) and dried under vacuum. The xerogels were studied by NMR in DMSO-d_6.

Compound 3a. ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm) 7.88 (m, 2H), 6.06 (m, 2H), 5.88 (d, 2H, J=8.9 Hz), 3.95 (t, J=6.9 Hz), 3.1-2.9 (m, 8H), 1.84 (m, 2H), 1.36 (m, 8H), 0.80 (m, 18H); ^{13}C NMR (DMSO-d_6, 75 MHz, T= 100 ºC) δ (ppm) 172.6, 158.7, 59.0, 55.3, 38.9, 31.7, 27.3, 23.8, 19.8, 18.5, 11.8; IR (KBr, cm^{-1}) 3345, 3278, 3106, 2964, 2933, 2873, 1630, 1563; ESI-MS (m/z) 457.5 ($M+H^+$), 479.6 ($M+Na^+$).

Compound 3b. ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm) 7.92 (t, 2H, J=5.4 Hz), 7.3-7.2 (m, 10H), 6.54 (t, 2H, J=5.8 Hz), 6.06 (d, 2H, J=9.1 Hz), 4.21 (dd, 4H, J=5.3 Hz), 4.01

(t, 2H, J=6.4 Hz), 3.1-3.0 (m, 4H), 1.86 (m, 2H), 1.39 (m, 4H), 0.84 (d, 6H, J=3.9 Hz), 0.80 (d, 6H, J=3.9Hz); ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm) 172.4, 158.5, 141.5, 128.9, 127.6, 127.3, 126.9, 116.5, 58.6, 43.5, 38.8, 32.0, 27.3, 20.0, 18.6; IR (KBr, cm^{-1}) 3336, 3277, 3107, 2962, 2931, 2870, 1629, 1564; ESI-MS (m/z) 553.4 ($M+H^+$), 575.4 ($M+Na^+$).

Compound 3c. ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm) see Figure 2 in main text; IR (cm^{-1}) 3338, 3276, 3099, 2956, 2867, 1630, 1568, 1226; ESI-MS (m/z) see Figure S1.

Compound 3d. ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm) 8.47 (d, 4H, J= 5.2 Hz), 7.95 (m, 2H), 7.21 (d, 4H, J=5.2 Hz), 6.66 (t, 2H, J=5.9 Hz), 6.18 (d, 2H, J=9.1 Hz), 4.24 (d, 4H, J=5.0 Hz), 4.0 (dd, 2H, J=6.2 Hz, J'=8.8 Hz), 3.1-3.0 (m, 4H), 1.86 (m, 2H), 1.39 (m, 4H), 0.82 (m, 12H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm) 171.5, 157.7, 149.9, 149.3, 126.1, 121.7, 115.8, 57.9, 41.8, 38.0, 31.2, 26.5, 19.2, 17.8; IR (KBr, cm^{-1}) 3345, 3269, 3106, 2956, 2867, 1630, 1562, 1225; ESI-MS (m/z) 555.5 ($M+H^+$), 577.3 ($M+Na^+$).

Compound 3e·*bis* (*p*-nitrophenolate). ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm) 8.02 (d, 4H, J= 9 Hz), 7.92 (m, 2H), 6.52 (d, 4H, J= 9 Hz), 6.12 (d, 2H, J= 9 Hz), 6.04 (d, 2H, J= 11 Hz), 4.05 (m, 2H), 3.2-3.0 (m, 8H), 2.7 (m, 8H), 2.0-1.9 (m, 4H), 1.8-1.4 (m, 8H), 1.1 (m, 4H), 0.9 (m,12H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ (ppm) 172.7, 157.7, 150.6, 139.8, 127.9, 119.4, 60.4, 48.0, 44.4, 38.3, 32.2, 30.9, 30.2, 27.6, 27.2, 20.1, 19.4; IR (KBr, cm^{-1}) 3372, 3297, 3092, 2956, 2922, 2867, 1636, 1555, 1229; ESI-MS (m/z) 567.5 ($M+H^+$).

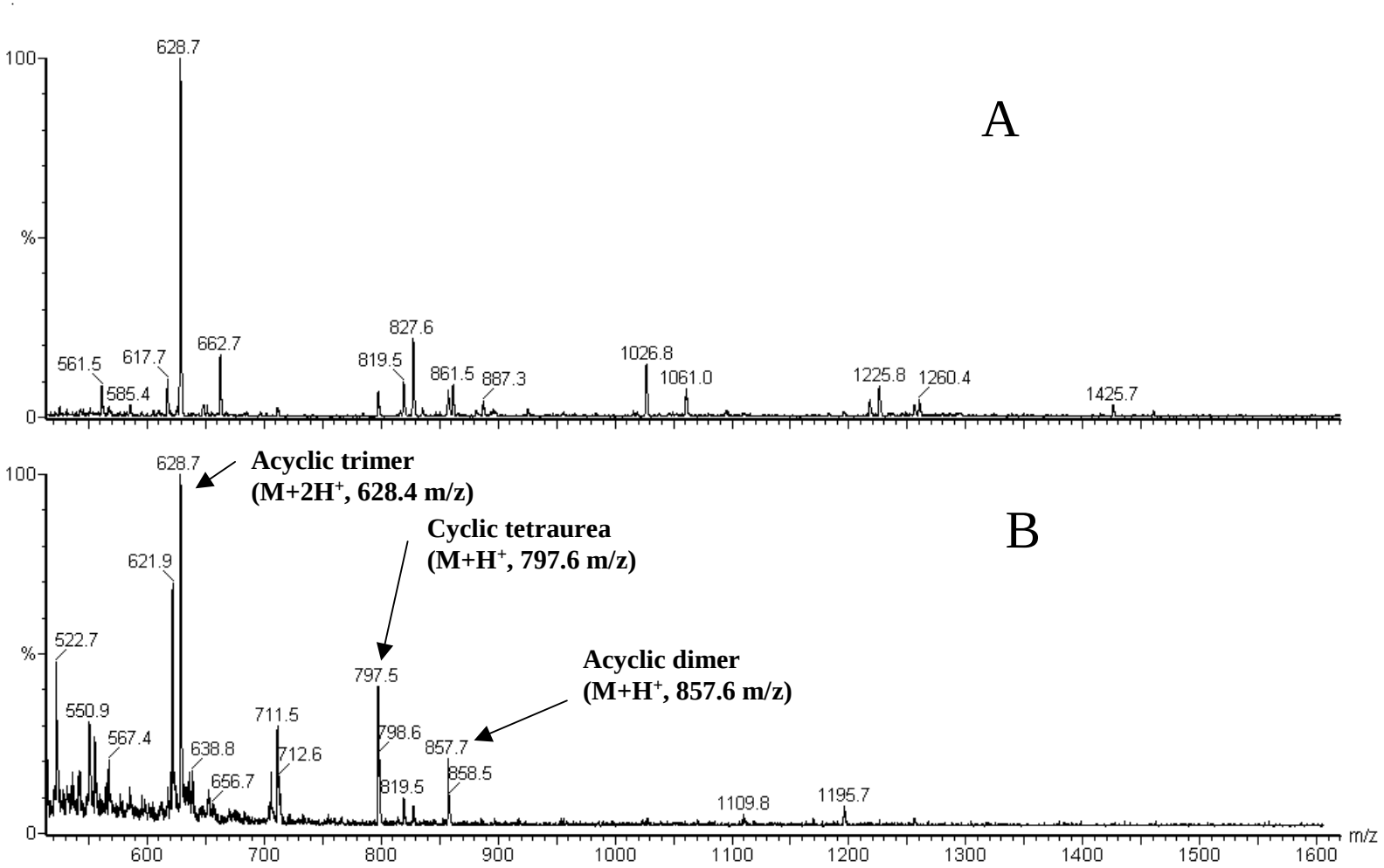
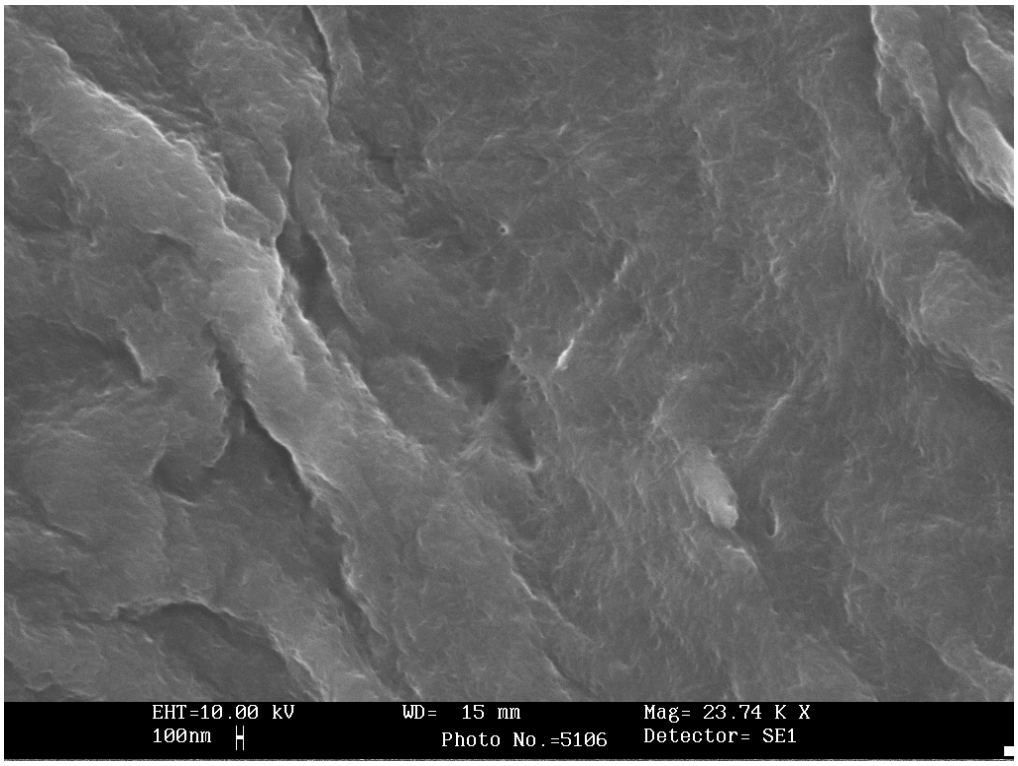


Fig S1. ESI-MS of compound **3c** obtained (A) in refluxing CH_3CN and (B) following the reactive-gel strategy.



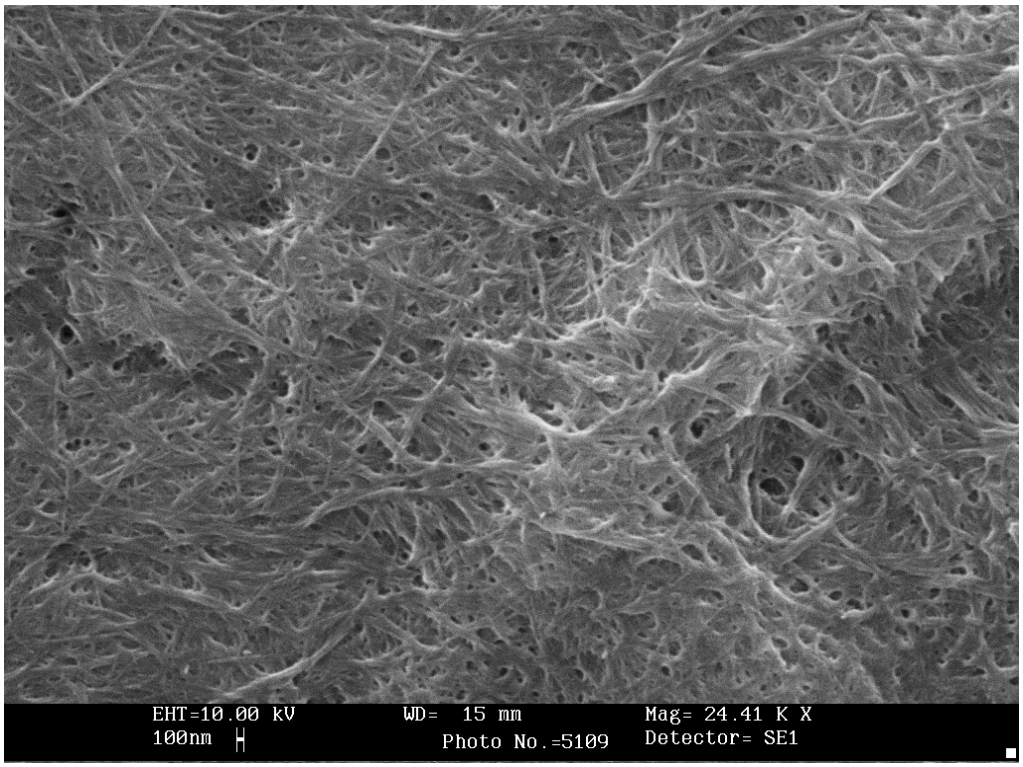


Fig. S2. Scanning electron micrographs of xerogels of compound **2** (top) and compound **3c** (bottom).

UV-vis spectroscopy:

Samples of 100 μL of the solution released from the gel after reaction were diluted in CH_3CN and analyzed in a Hewlett Packard 8453 spectrophotometer. The absorption band at 308 nm was monitored. Extinction coefficients at this wavelength were determined for stock solutions of the corresponding alkyl or aryl ammonium *p*-nitrophenolate in CH_3CN, in a concentration range similar to that of the unknown samples. All the experiments were performed in triplo. Large errors were found (ca. 20%) probably because the gel could retain some of the *p*-nitrophenolate in its matrix.

Table S1. UV-vis data for compounds **3a**-**3c** and **3e**.

Compound	**ε (308 nm)**	**Yield (%)**
3a	10616	85
3b	11219	>90
3c	8941	>90
3d	-	-
3e	9436	80

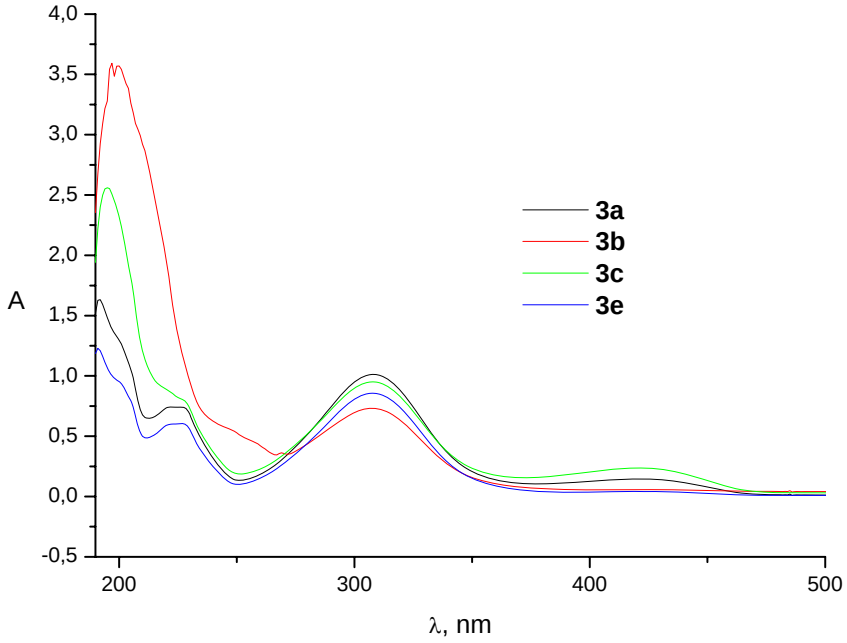


Fig. S3. UV-vis spectra of the solutions resulting from the reactions leading to compounds **3a**-**3c** and **3e**.

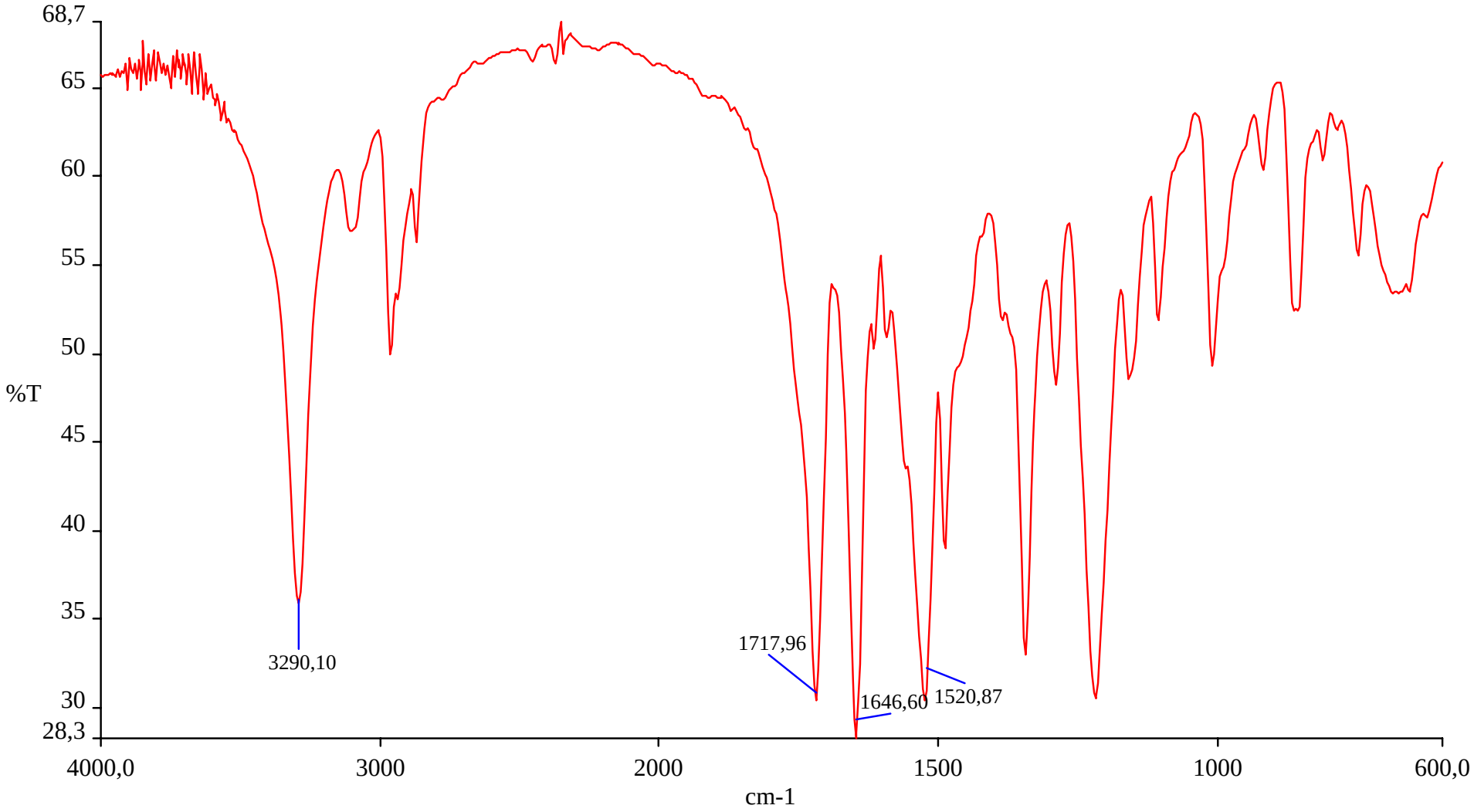


Fig. S4. FT-IR (KBr pellet) of the xerogel of compound **2**.

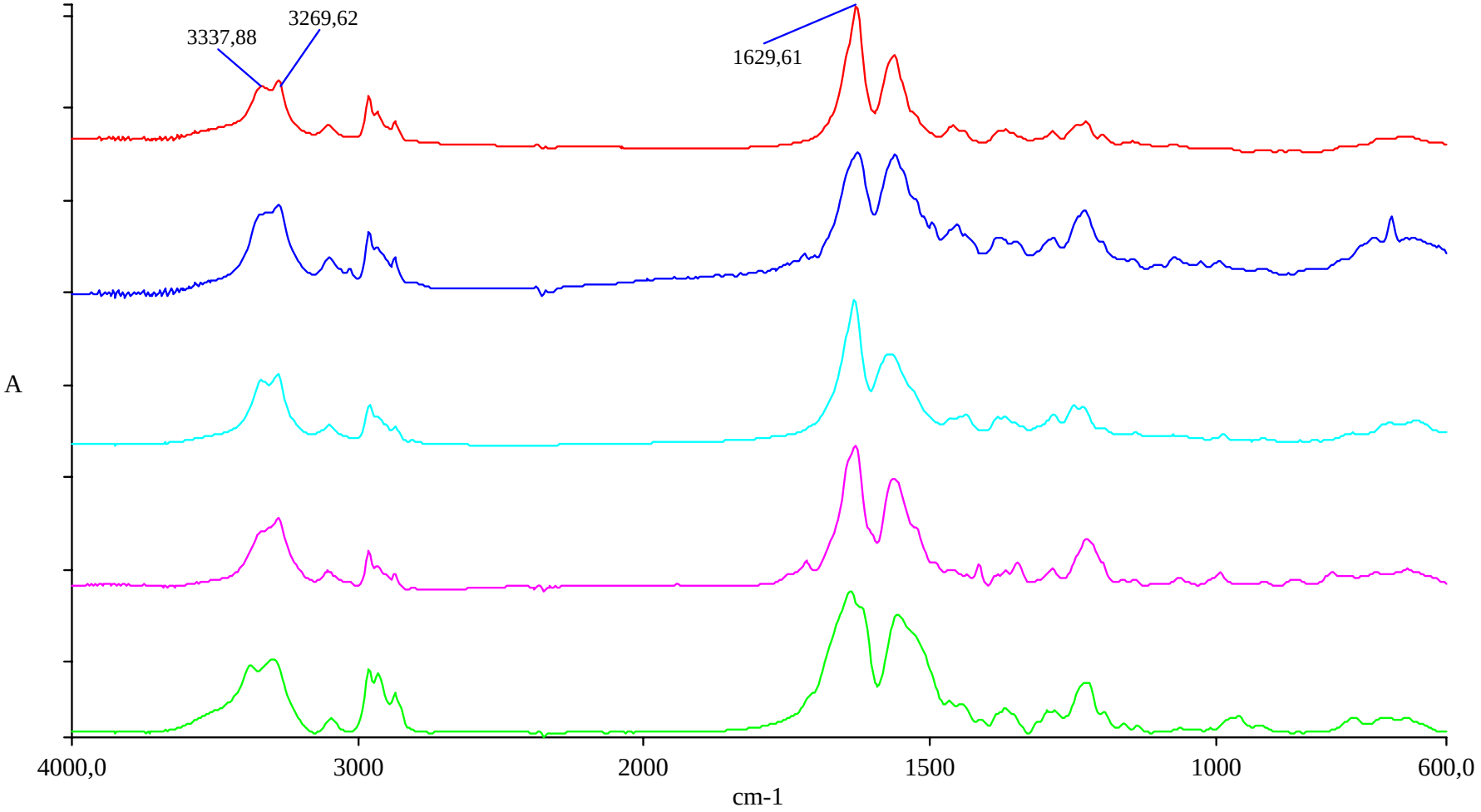


Fig. S5. FT-IR (KBr pellet) of the solids of compounds **3a, 3b, 3c, 3d** and **3e** (from top to bottom).

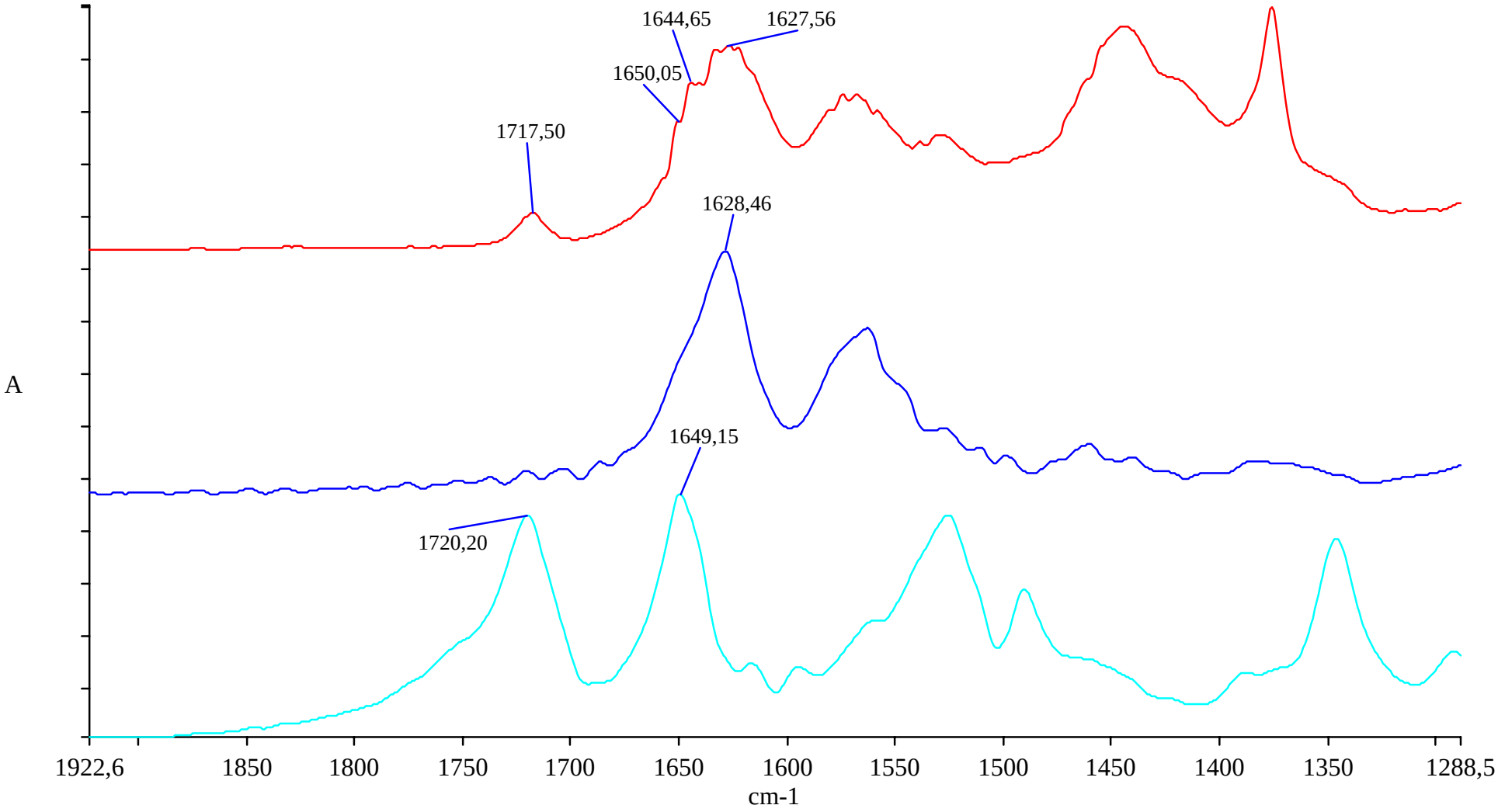
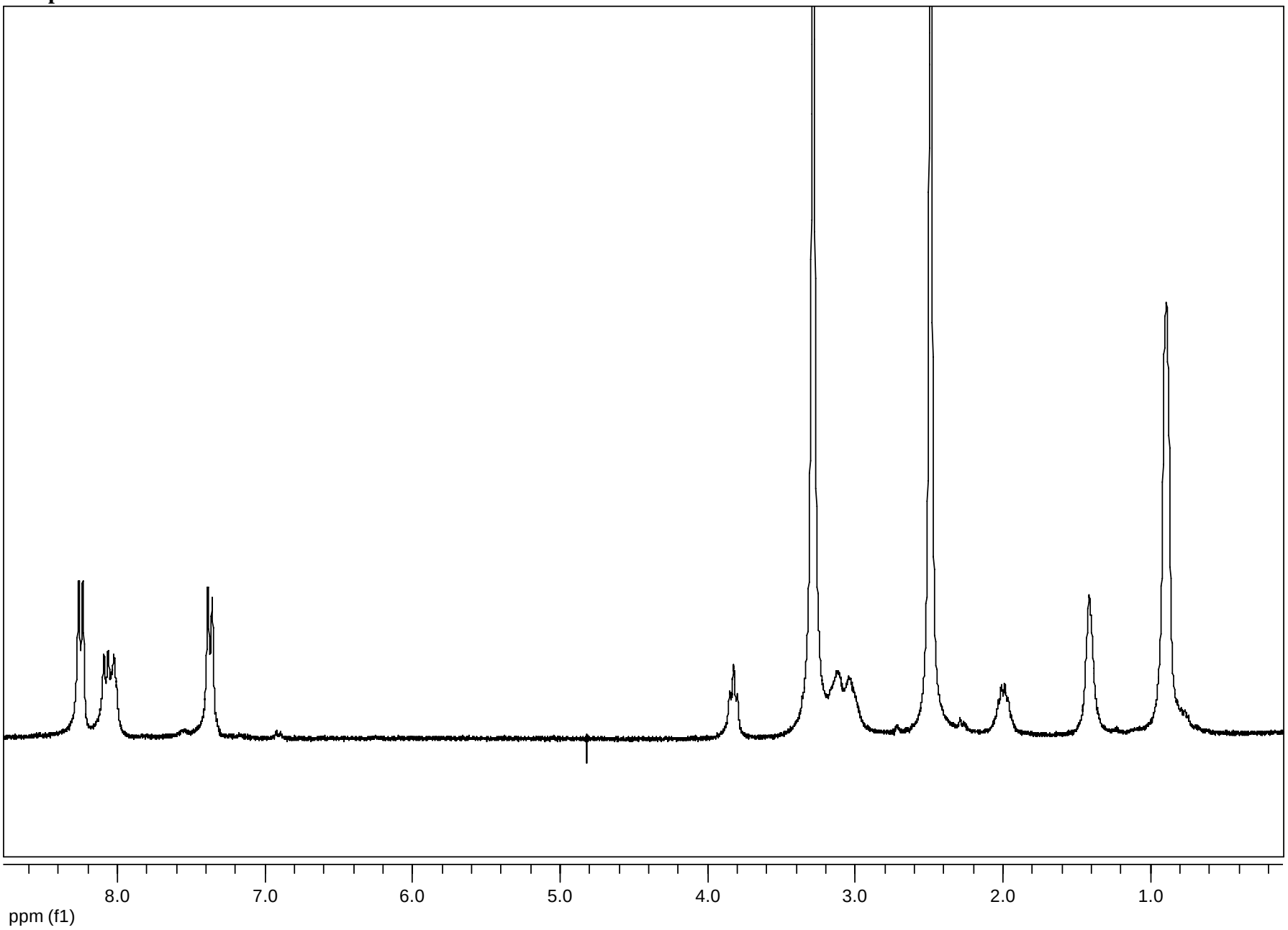
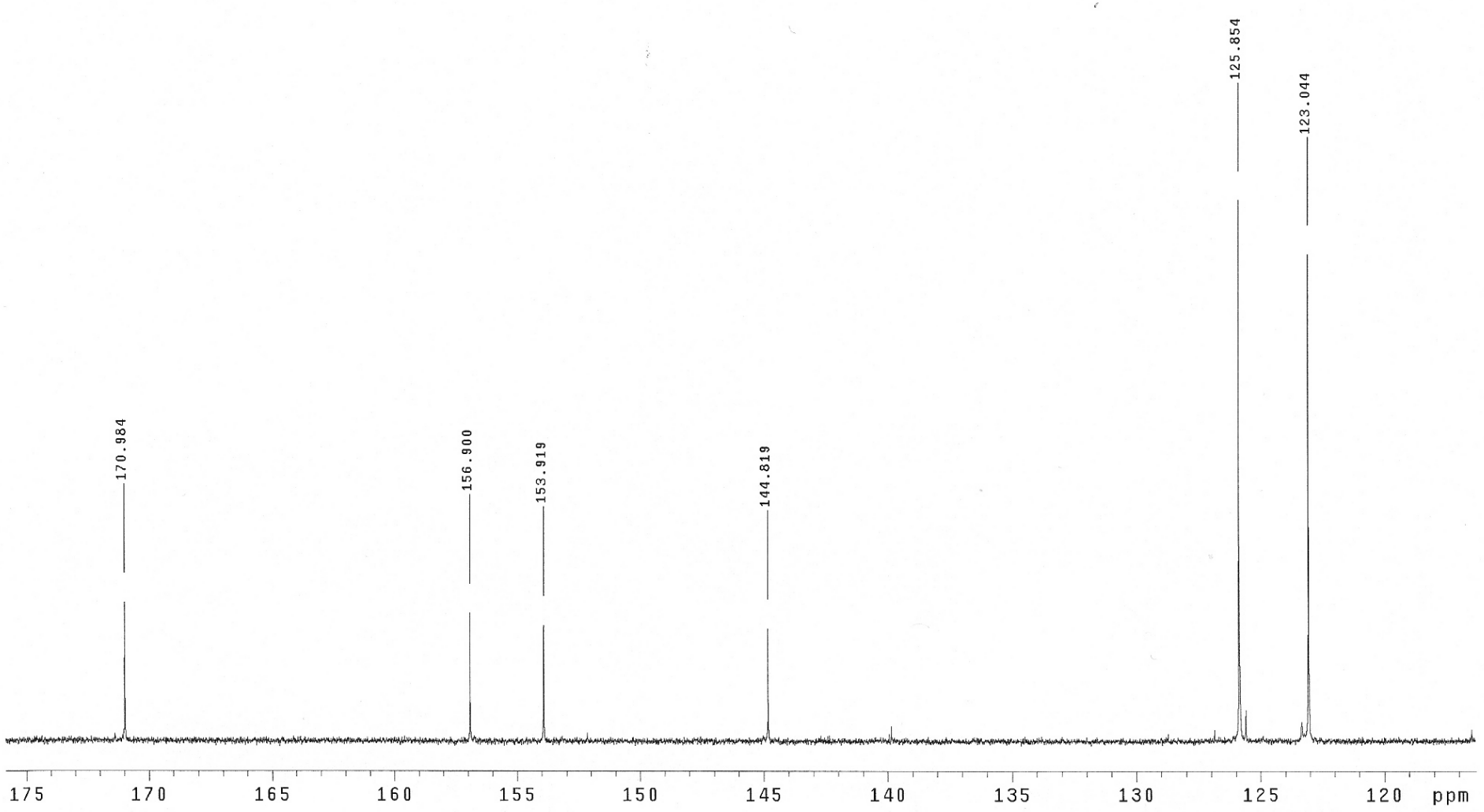


Fig. S6. FT-IR of xerogel of compound **2** (bottom, KBr), xerogel of compound **3a** (middle, KBr) and gel of **3a** directly after reaction (top, NaCl plates).

NMR spectra
Compound 2

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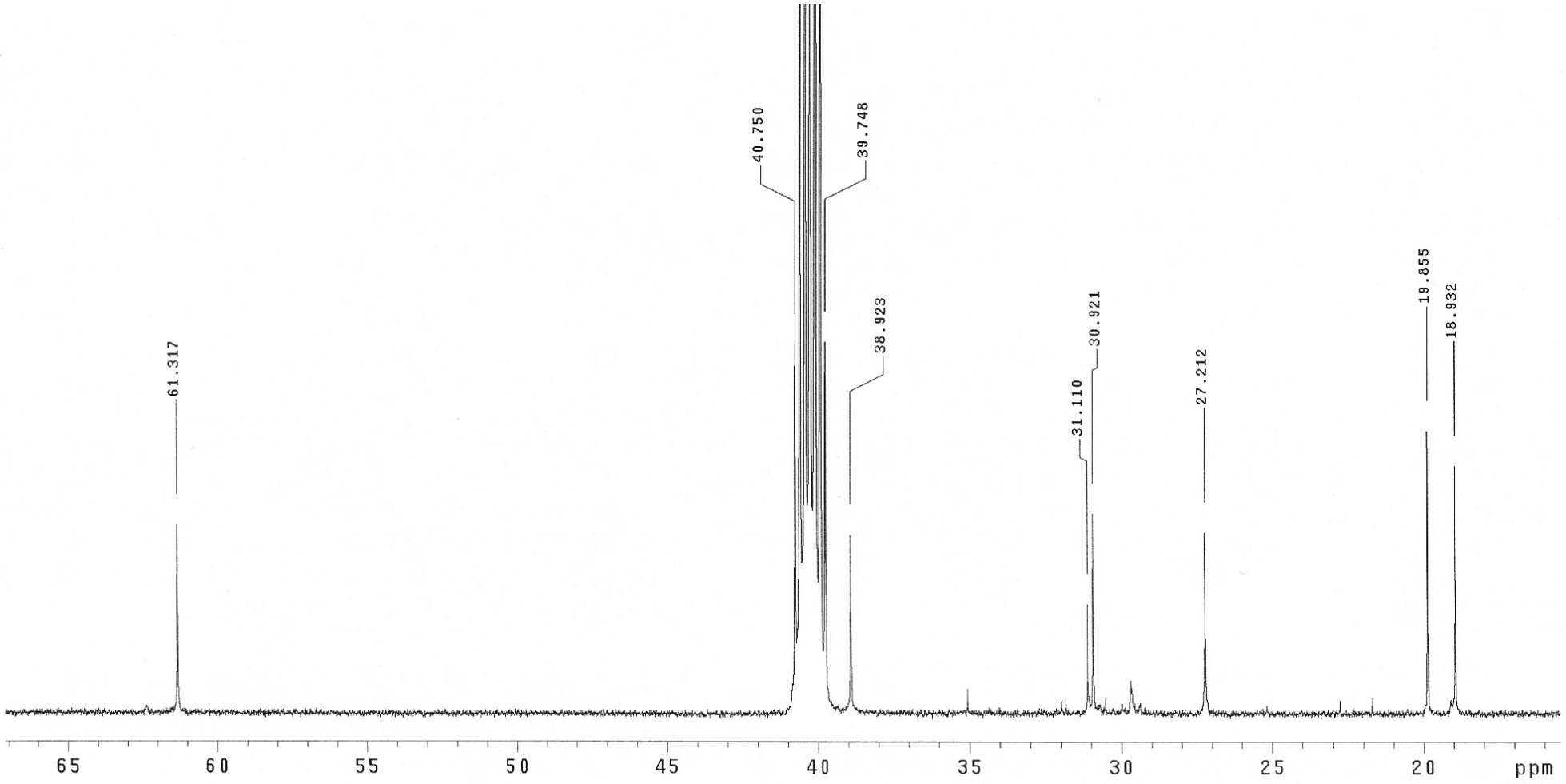
156.900
153.919
144.819
125.854
123.044
175
170
165
160
155
150
145
140
135
130
125
120
ppm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40.750
39.748
38.923
31.110
30.921
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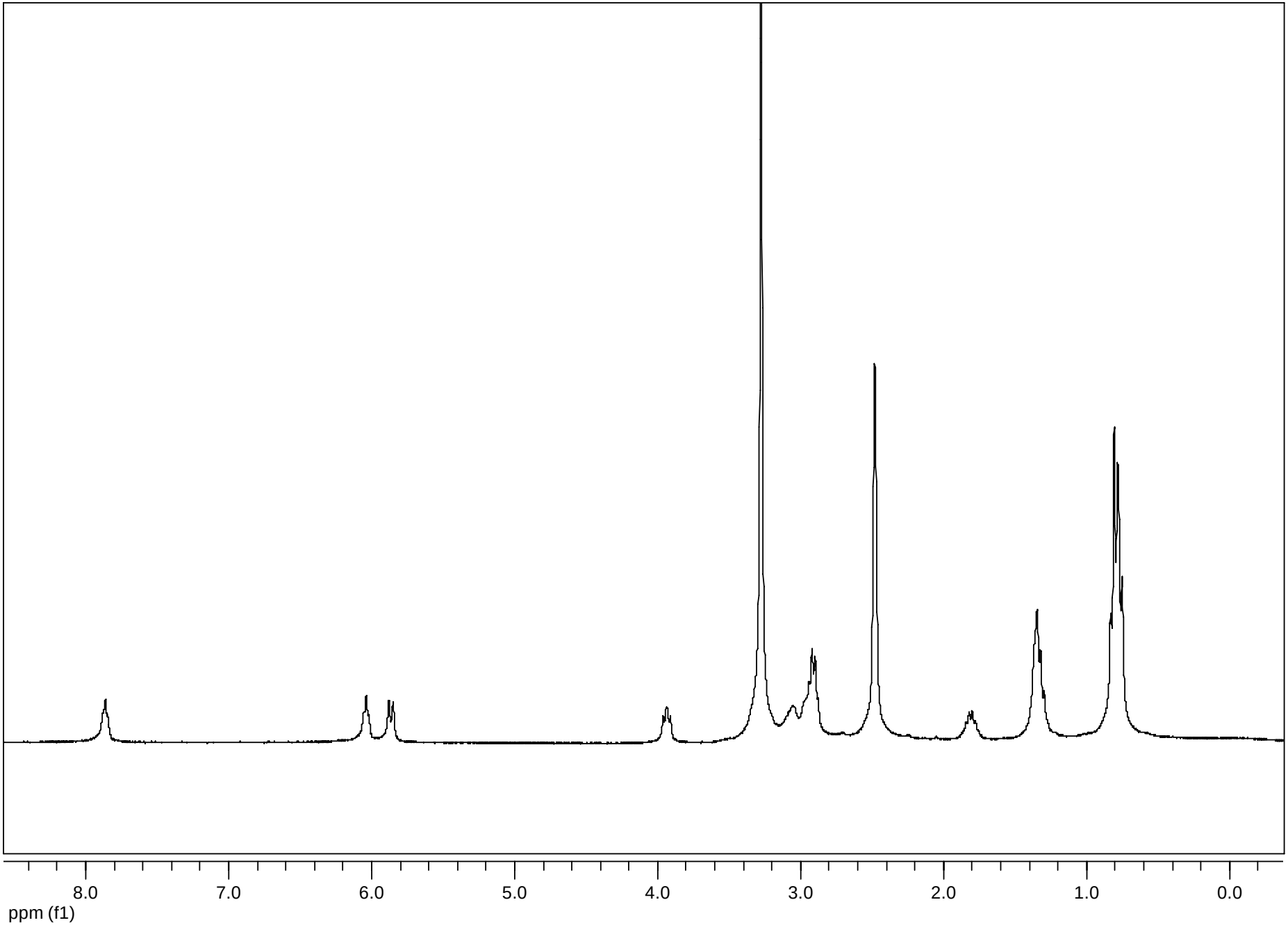
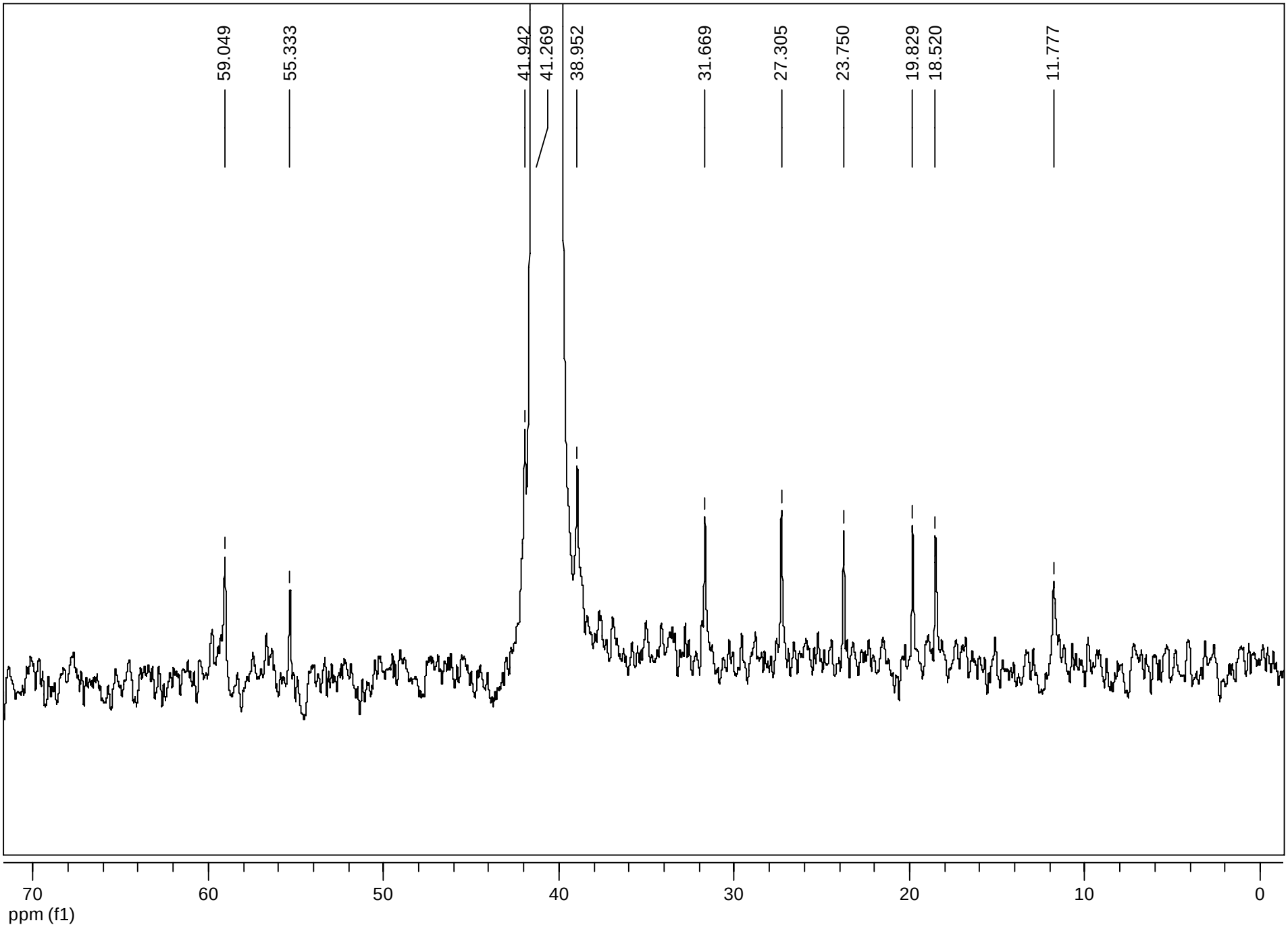
19.855
18.932
65
60
55
50
45
40
35
30
25
20
ppm

Compound 3a

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41.942
41.269
38.952
31.669
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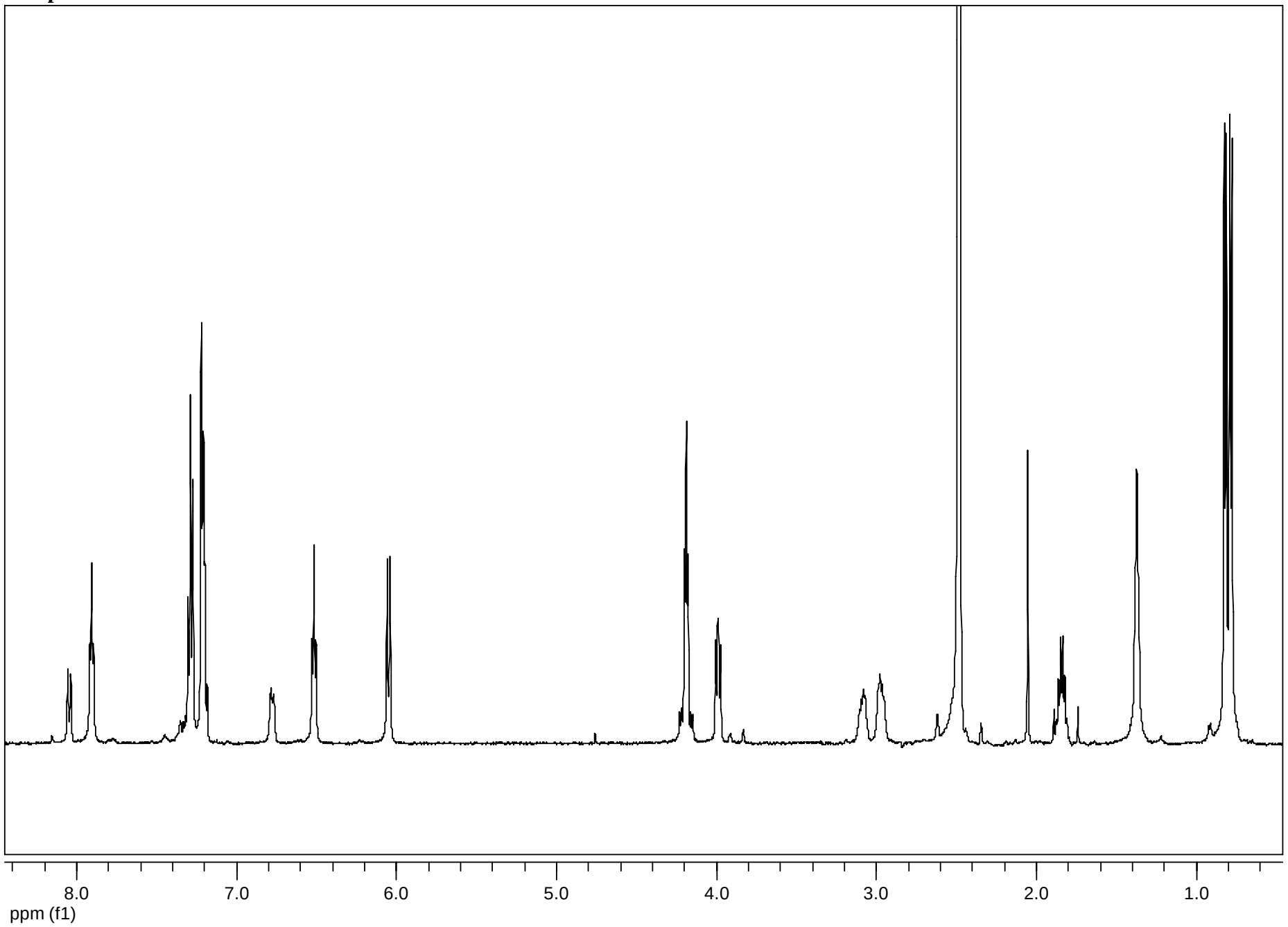
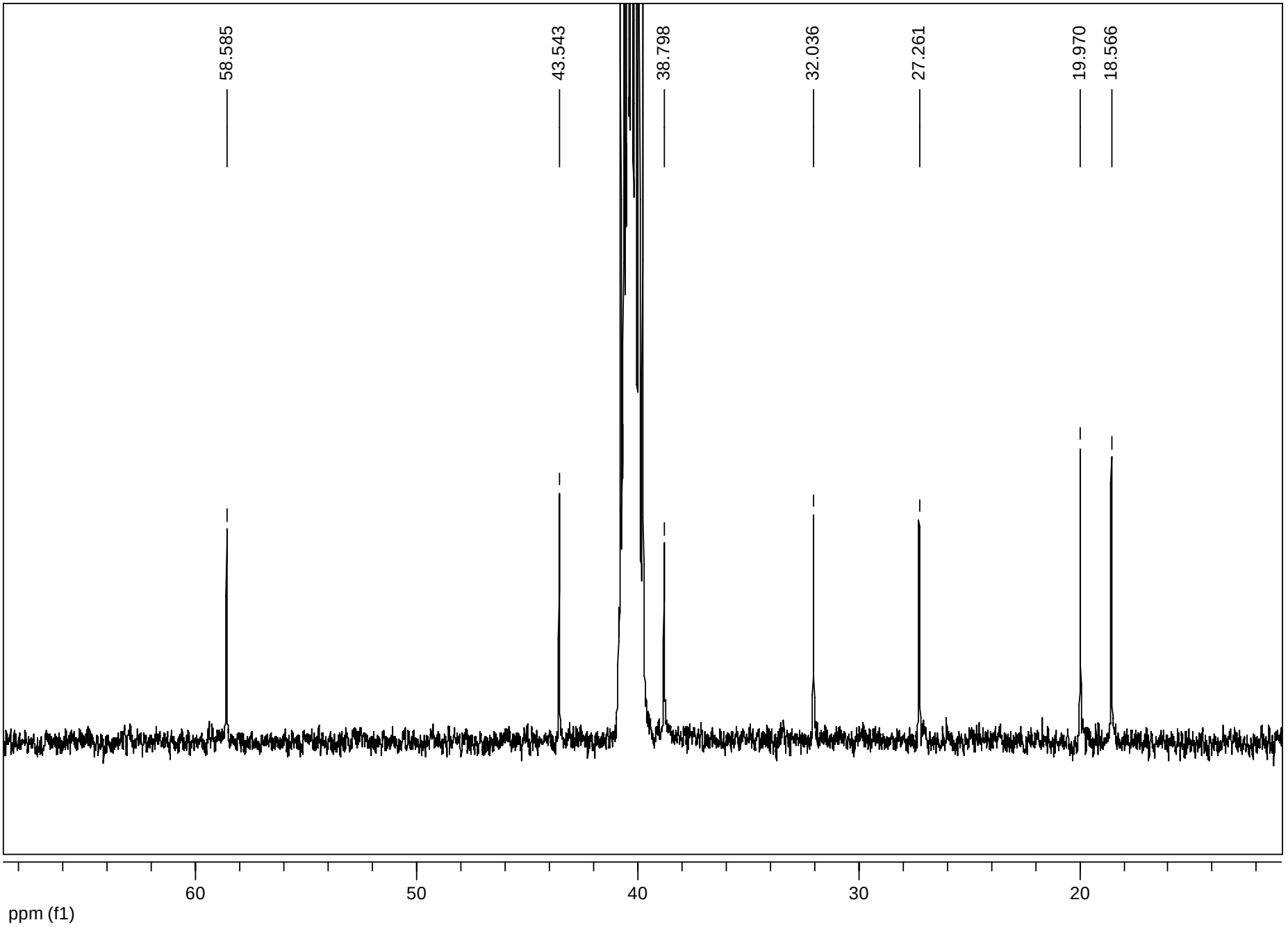
18.520
11.777
70
60
50
40
30
20
10
0
ppm (f1)

Compound 3b

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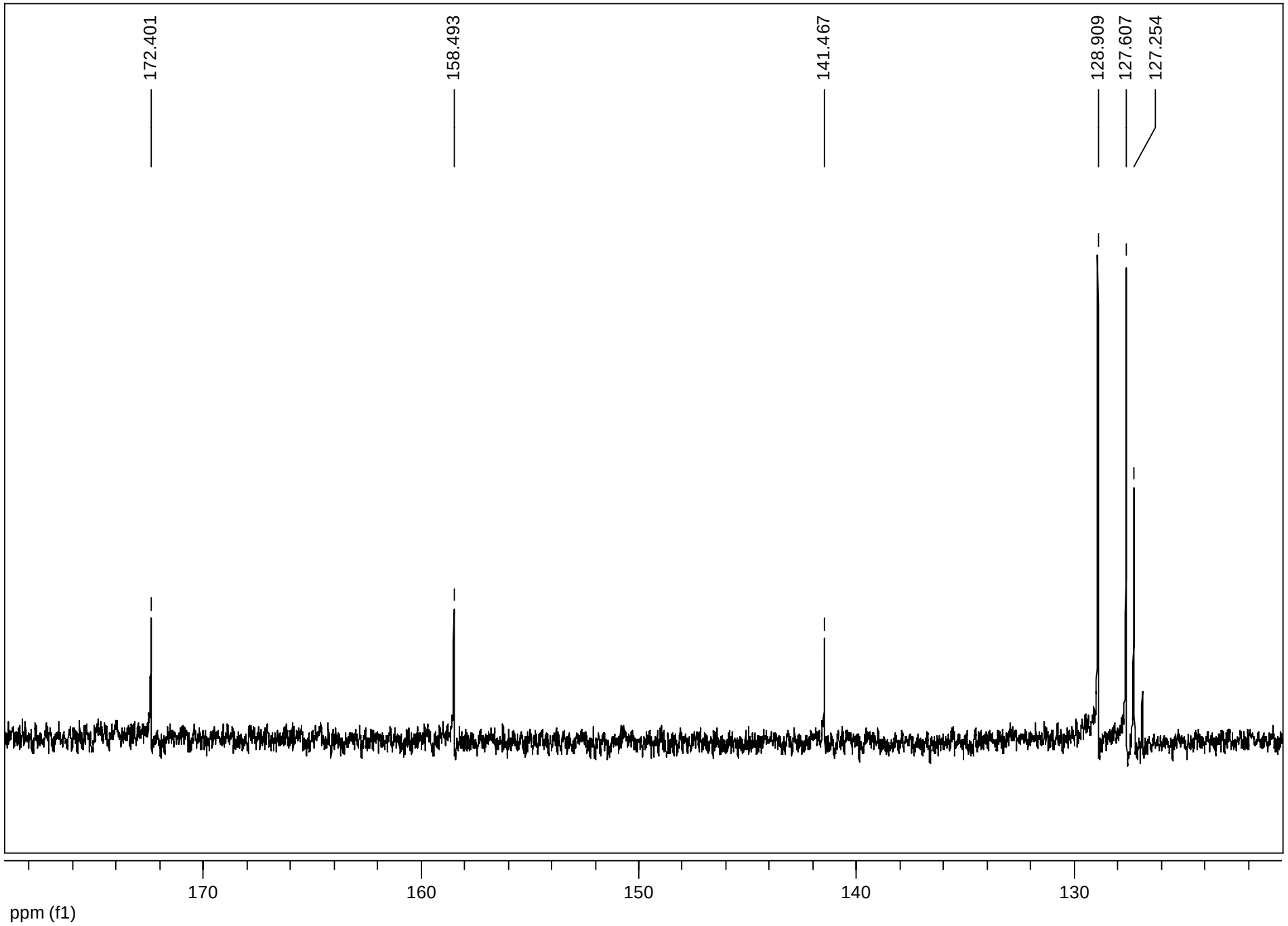
50
40
30
20
ppm (f1)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160
150
140
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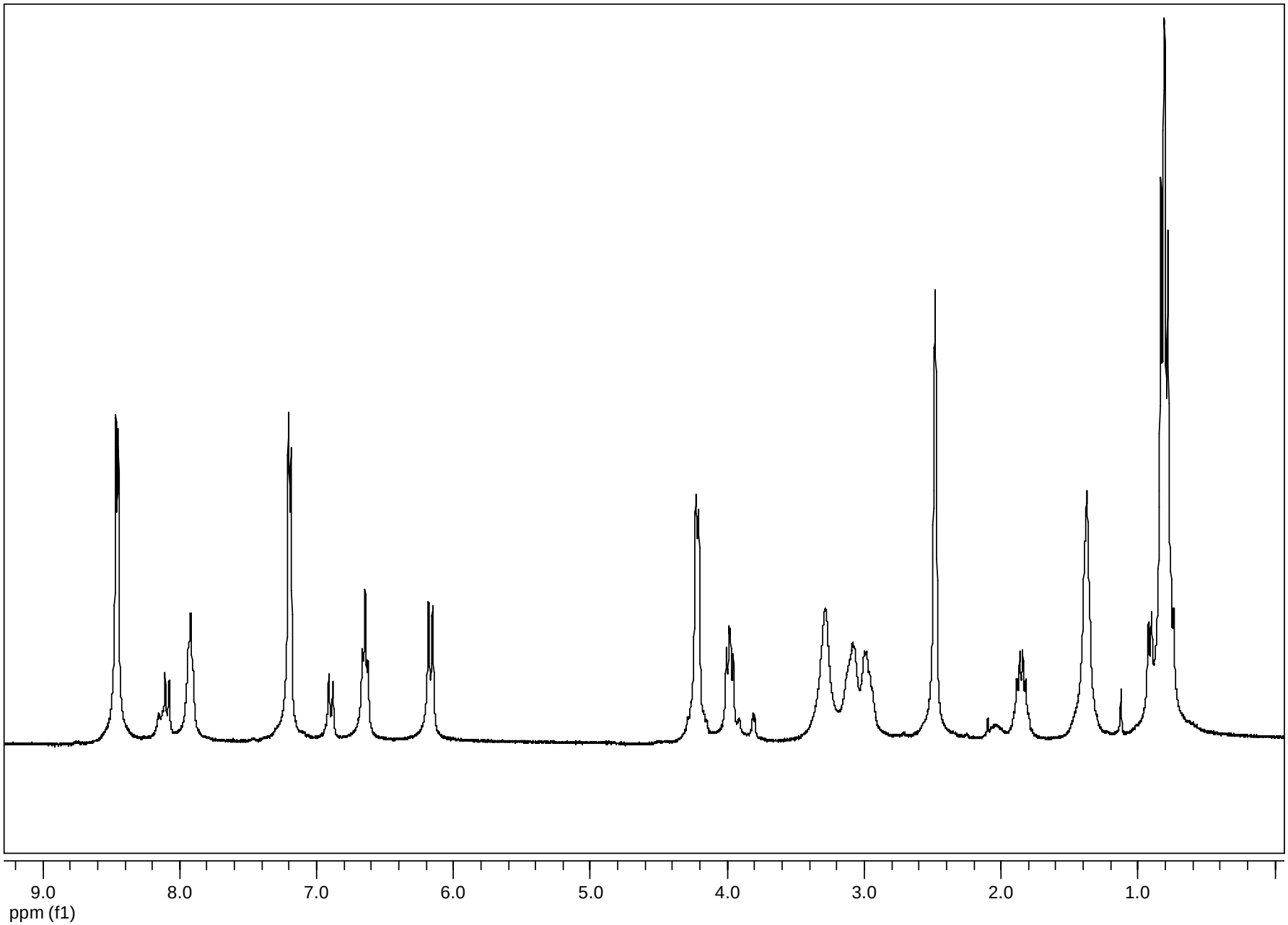
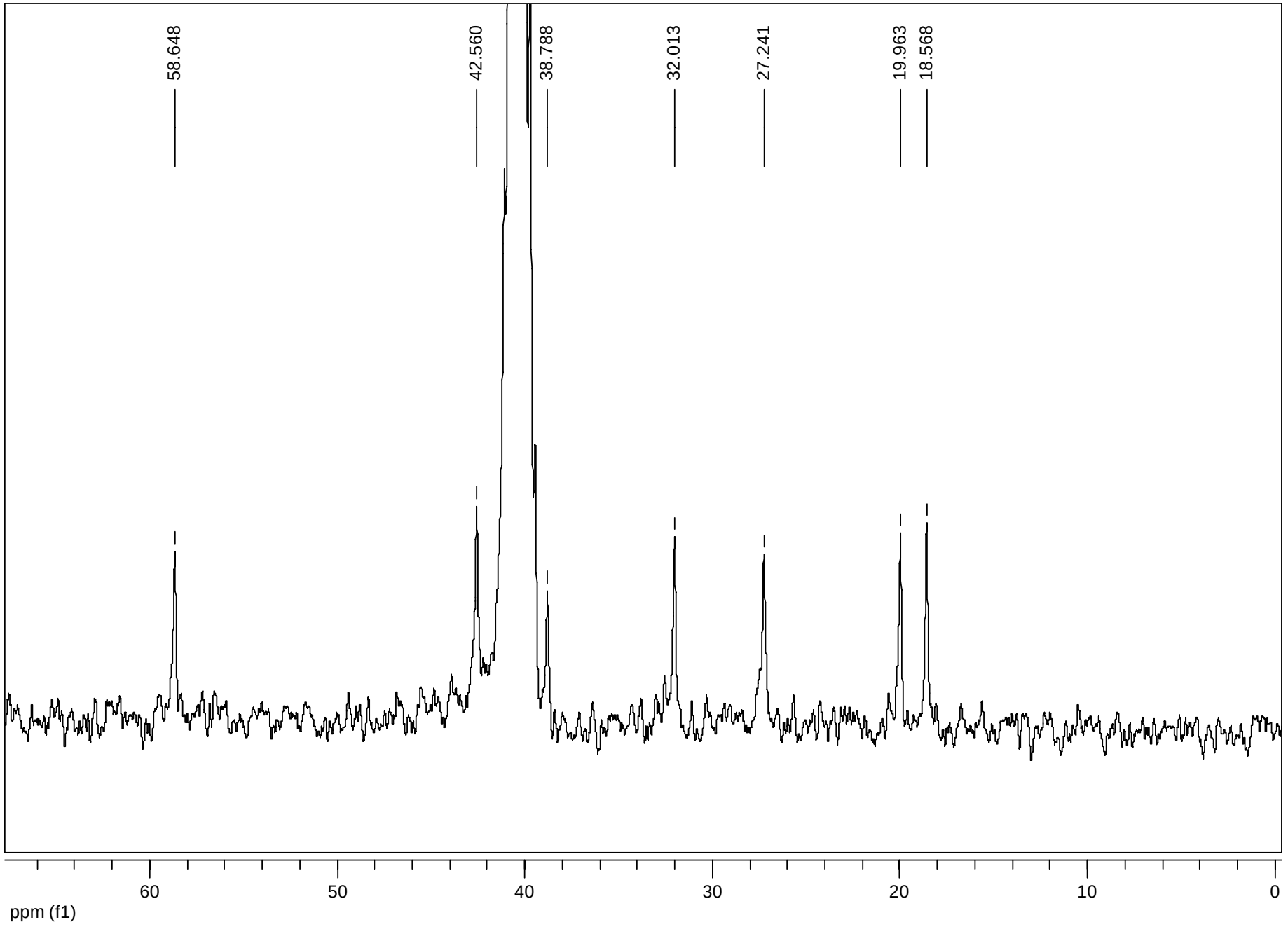
ppm (f1)

Compound 3d

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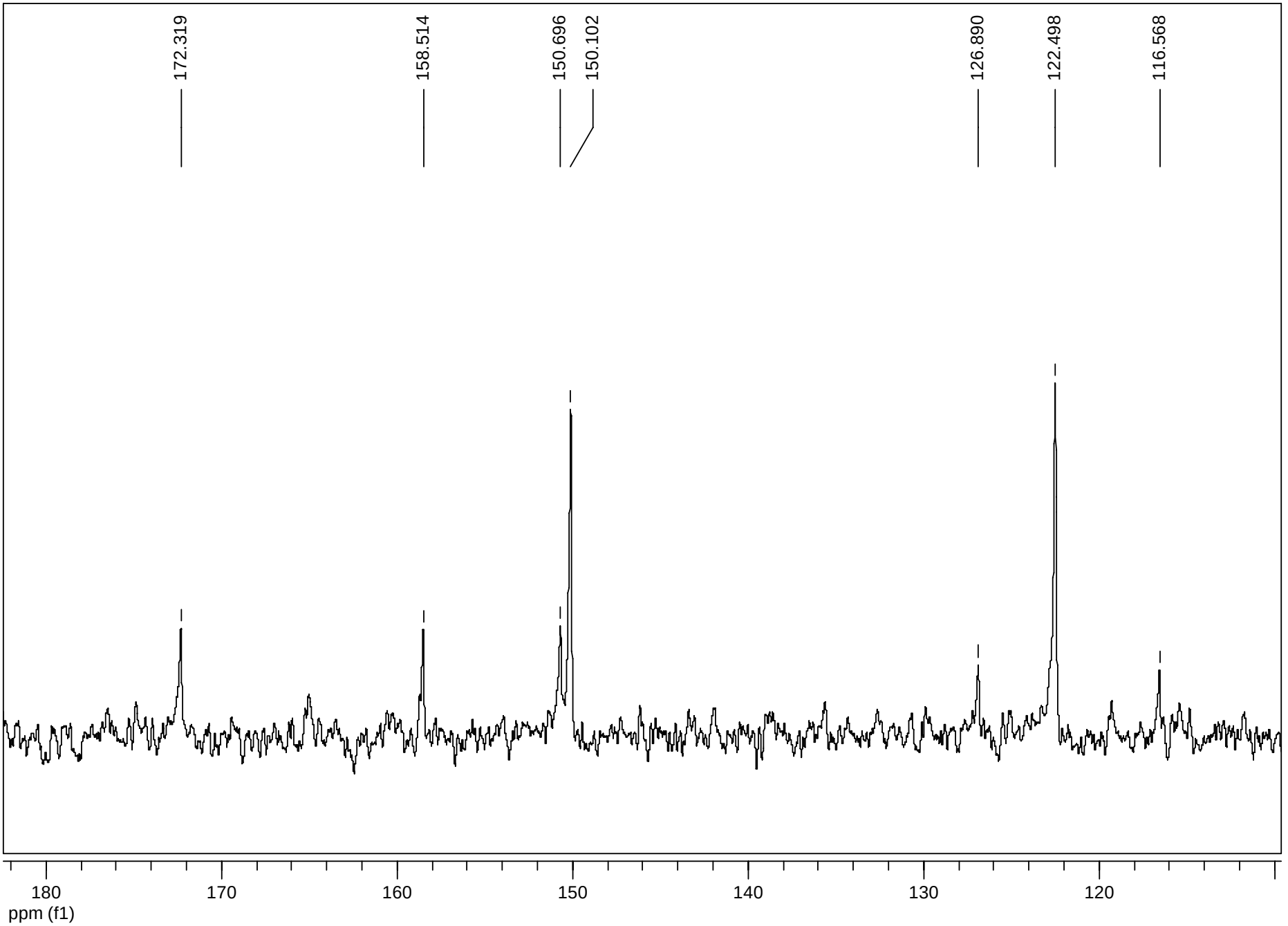
40
30
20
10
0
ppm (f1)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158.514
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160
150
140
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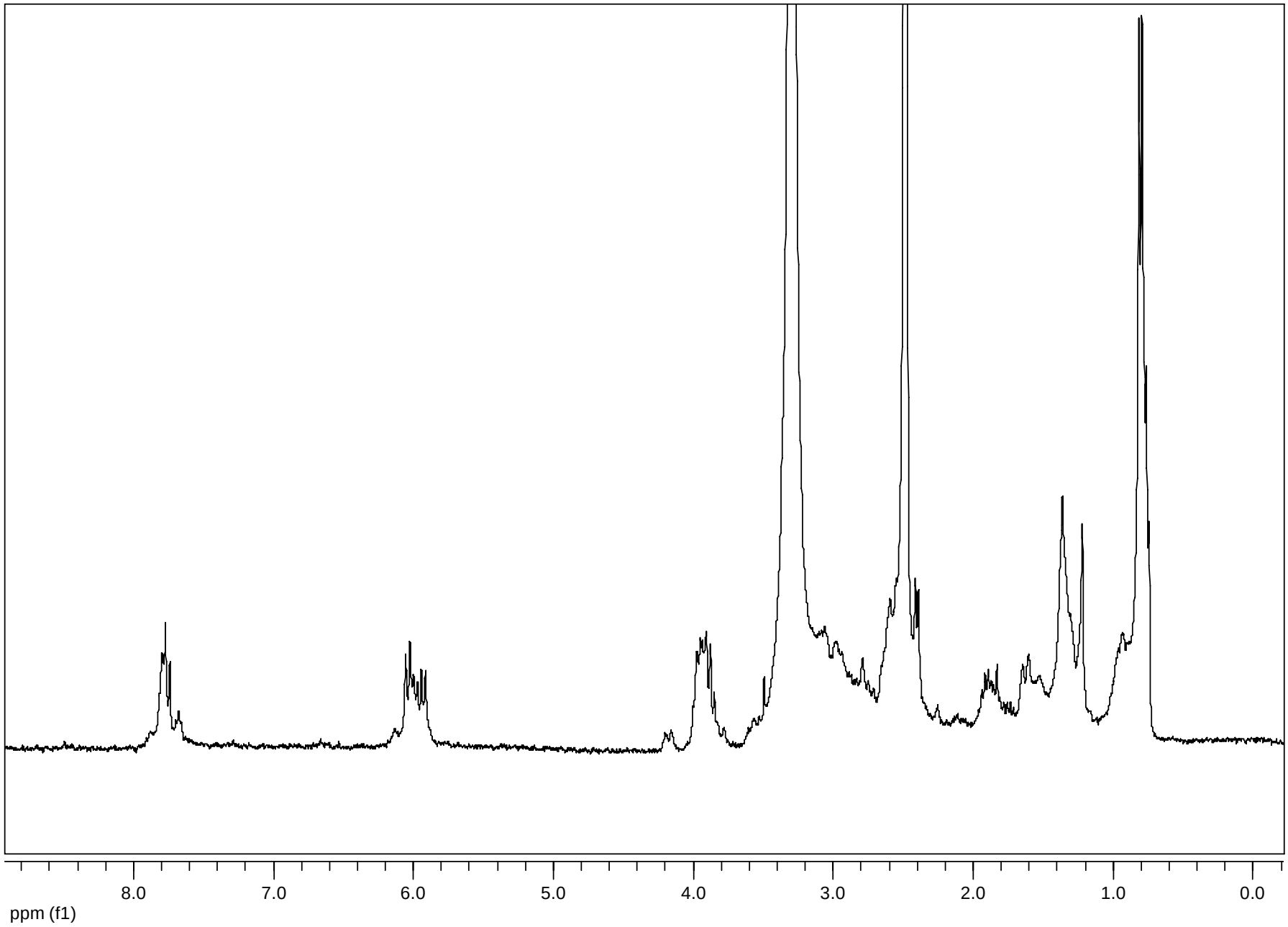
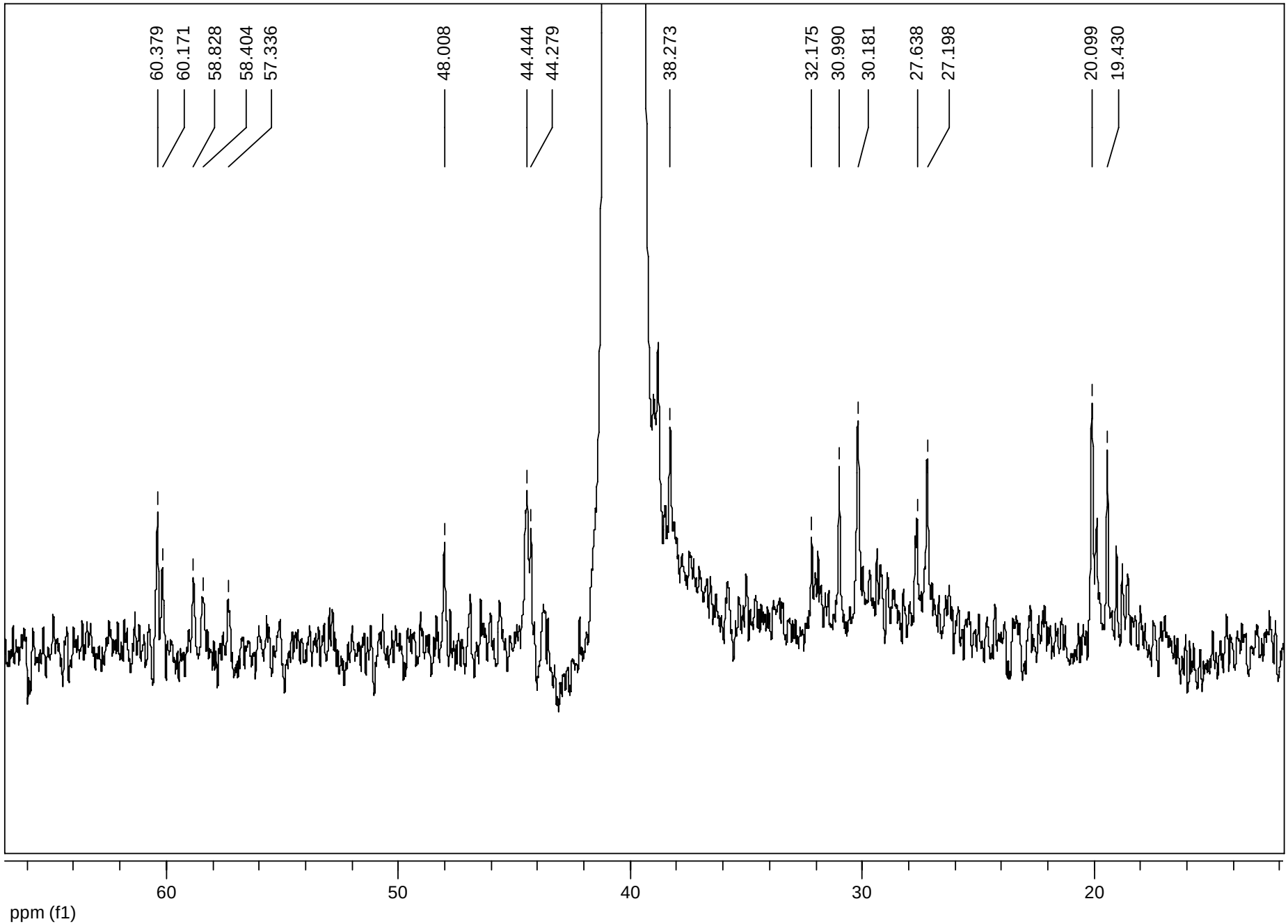
Compound 3e

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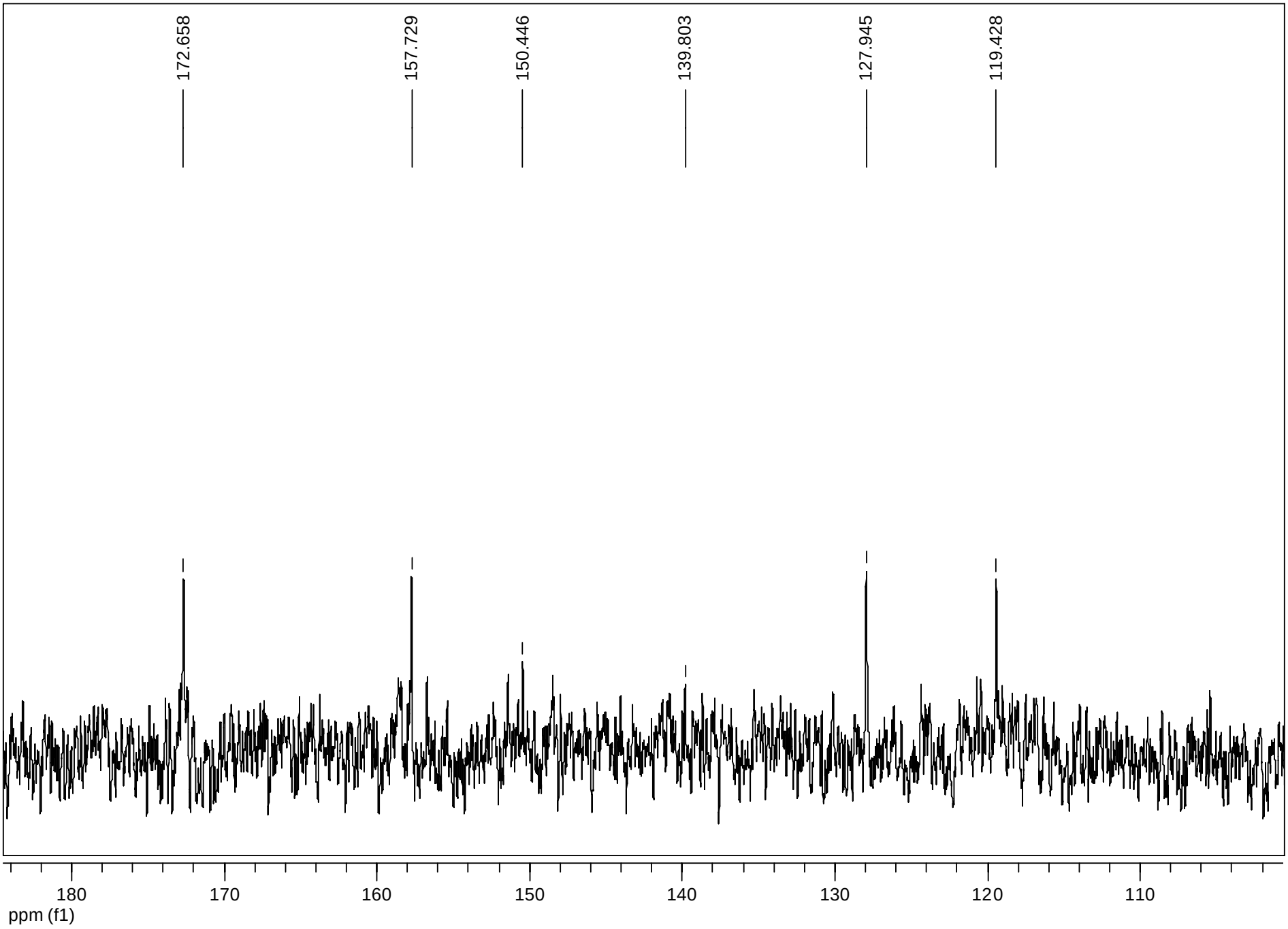
30
20
ppm (f1)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ppm (f1)