SUPPORTING INFORMATION

‘‘Dihydroxylation of Olefins Catalyzed by Zeolite-Confined Osmium Nanoclusters: A Novel, Effective, Reusable and Eco-Friendly Method for Preparation of 1,2-*cis*-Diols’’

Önder Metin,*[,a] Nurdan Alcan Alp,[a] Serdar Akbayrak,[b] Abdullah Biçer,[a] Mehmet Serdar Gültekin,*[,a] Saim Özkar,[b] Uğur Bozkaya[a]

[a]Department of Chemistry, Faculty of Science, Ataturk University, 25240 Erzurum, Turkey
[b]Department of Chemistry, Middle East Technical University, 06800 Ankara, Turkey
E-mail: ometin@atauni.edu.tr; gultekin@atauni.edu.tr

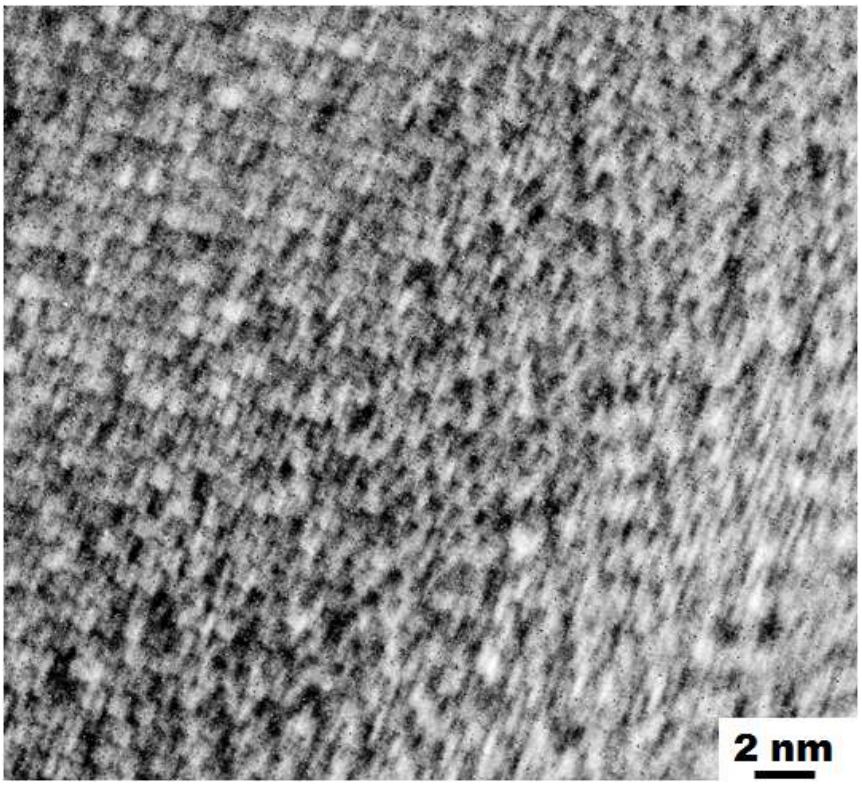


Figure S1. A representative HRTEM image of zeolite-confined osmium(0) nanoclusters

Geometry optimizations for theoretical molecular volume computations are carried out using Gaussian 03 program package.

Benzoil-cyclohexene
Optimized geometry at B3LYP/6-31G(d) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.947820	1.145369	-0.551817
2	6	0	4.545520	0.130236	0.079828
3	1	0	4.550885	1.913002	-1.033934
4	1	0	5.633134	0.073658	0.093733
5	8	0	0.331152	0.339404	-0.093013
6	6	0	-0.573129	-0.644340	-0.307200
7	8	0	-0.273395	-1.776328	-0.638119
8	6	0	-1.975511	-0.181076	-0.095548
9	6	0	-3.007494	-1.105588	-0.307041
10	6	0	-2.283652	1.127093	0.302946
11	6	0	-4.334628	-0.726069	-0.123347
12	1	0	-2.746580	-2.112867	-0.614618
13	6	0	-3.613303	1.502701	0.487148
14	1	0	-1.482244	1.838650	0.466286
15	6	0	-4.639082	0.578559	0.274362
16	1	0	-5.131818	-1.445457	-0.289236
17	1	0	-3.849935	2.517019	0.796748
18	1	0	-5.674863	0.874734	0.418512
19	6	0	2.448612	1.300449	-0.649628
20	1	0	2.160888	1.606079	-1.664111
21	1	0	2.104544	2.105685	0.016956
22	6	0	3.791589	-0.968797	0.786883
23	1	0	4.261951	-1.182001	1.756125
24	1	0	3.875045	-1.902432	0.209174
25	6	0	2.310343	-0.610607	0.996999
26	1	0	2.214067	0.118136	1.812308
27	1	0	1.734601	-1.499289	1.273059
28	6	0	1.731523	0.003995	-0.276710
29	1	0	1.796611	-0.721067	-1.093183

E = -654.2704013 a.u., ZPVE = 152.57 (Kcal/Mol)

Acetyl-cyclohexen

Optimized geometry at B3LYP/6-31G(d) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.136871	0.232880	-0.696965
2	6	0	-1.132164	1.339316	-0.480254
3	6	0	-2.353141	1.132710	0.023805
4	6	0	-0.760698	-1.159131	-0.555827
5	6	0	-1.713462	-1.226353	0.642691
6	6	0	-2.856862	-0.214309	0.477311
7	8	0	0.918249	0.422288	0.305939
8	6	0	2.160802	0.002610	-0.027551
9	6	0	3.132852	0.271857	1.099524
10	8	0	2.446765	-0.514603	-1.086358
11	1	0	0.343288	0.324770	-1.675259
12	1	0	-0.815427	2.341485	-0.762439
13	1	0	-3.037896	1.974871	0.118677
14	1	0	0.037043	-1.905305	-0.484286
15	1	0	-1.313141	-1.374938	-1.481129
16	1	0	-1.152481	-0.994107	1.556870
17	1	0	-2.114894	-2.239641	0.759874
18	1	0	-3.592773	-0.589812	-0.252192
19	1	0	-3.410067	-0.100983	1.419378
20	1	0	4.128338	-0.066535	0.809978
21	1	0	3.154258	1.341783	1.331064
22	1	0	2.810903	-0.250557	2.006418

E = -462.5282638 a.u., ZPVE = 118.92 (Kcal/Mol)

Cis-diphenyl-eten

Optimized geometry at B3LYP/6-31G(d) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.390234	-1.461390	-0.862408
2	6	0	1.416817	-0.467553	-0.791614
3	6	0	1.646829	0.716492	-0.066842
4	6	0	2.898001	0.876280	0.556220
5	6	0	3.869052	-0.121699	0.493274
6	6	0	3.618011	-1.297757	-0.215232
7	1	0	2.192617	-2.365091	-1.433234
8	1	0	0.473777	-0.599844	-1.311381
9	1	0	3.103619	1.794728	1.101538
10	1	0	4.824131	0.022594	0.991696
11	1	0	4.375134	-2.075180	-0.272643
12	6	0	0.674879	1.823967	0.000728
13	1	0	1.142020	2.808314	0.042377
14	6	0	-0.674839	1.824151	-0.000322
15	1	0	-1.141728	2.808596	-0.042204
16	6	0	-1.646919	0.716749	0.066869
17	6	0	-1.417223	-0.466955	0.792420
18	6	0	-2.897669	0.876116	-0.557005
19	6	0	-2.390557	-1.460854	0.863081
20	1	0	-0.474538	-0.598800	1.312932
21	6	0	-3.868677	-0.121953	-0.494163
22	1	0	-3.103083	1.794257	-1.102924
23	6	0	-3.617964	-1.297630	0.215036
24	1	0	-2.193276	-2.364262	1.434484
25	1	0	-4.823465	0.021994	-0.993243
26	1	0	-4.375061	-2.075087	0.272349

E = -540.7019669 a.u., ZPVE = 135.36 (Kcal/Mol)

Trans-diphenyl-eten
Optimized geometry at B3LYP/6-31G(d) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.209738	-1.087251	-0.054711
2	6	0	2.829235	-1.276525	-0.051025
3	6	0	1.939970	-0.186622	0.001977
4	6	0	2.493596	1.108204	0.055431
5	6	0	3.871558	1.298221	0.051668
6	6	0	4.739020	0.202647	-0.003842
7	1	0	4.871731	-1.948251	-0.096996
8	1	0	2.424495	-2.285405	-0.091204
9	1	0	1.840875	1.974838	0.104020
10	1	0	4.273396	2.307311	0.094130
11	1	0	5.814775	0.355400	-0.005757
12	6	0	0.498591	-0.454044	0.000711
13	1	0	0.242392	-1.512627	-0.006452
14	6	0	-0.498593	0.454022	0.000843
15	1	0	-0.242384	1.512605	-0.006045
16	6	0	-1.939964	0.186610	0.002077
17	6	0	-2.493612	-1.108213	0.055532
18	6	0	-2.829216	1.276520	-0.050985
19	6	0	-3.871574	-1.298211	0.051677
20	1	0	-1.840897	-1.974845	0.104250
21	6	0	-4.209726	1.087264	-0.054757
22	1	0	-2.424465	2.285396	-0.091151
23	6	0	-4.739024	-0.202626	-0.003917
24	1	0	-4.273431	-2.307294	0.094135
25	1	0	-4.871702	1.948276	-0.097072
26	1	0	-5.814780	-0.355375	-0.005931

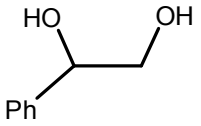
E = -540.7099648 a.u., ZPVE = 135.11 (Kcal/Mol)

Diacetyl-cyclohexen
Optimized geometry at B3LYP/6-31G(d) level.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.789994	-0.004392	-0.871381
2	6	0	0.244095	-1.074140	-1.093242
3	6	0	1.531854	-0.924872	-0.769410
4	6	0	-0.171875	1.336793	-0.461299
5	6	0	0.985271	1.148769	0.525423
6	6	0	2.096444	0.317997	-0.115485
7	8	0	-1.667488	-0.509077	0.188350
8	6	0	-2.949352	-0.072904	0.177125
9	6	0	-3.728157	-0.683418	1.320174
10	8	0	-3.399257	0.699622	-0.641804
11	1	0	-1.415787	0.130512	-1.758311
12	1	0	-0.109296	-2.006646	-1.529478
13	1	0	2.232528	-1.733770	-0.969029
14	1	0	-0.953211	1.982188	-0.048677
15	1	0	0.193020	1.832231	-1.372013
16	1	0	0.636134	0.617375	1.418529
17	1	0	1.388529	2.112877	0.852894
18	1	0	2.609476	0.929270	-0.881920
19	1	0	-4.758013	-0.325971	1.290219
20	1	0	-3.708944	-1.775770	1.248335
21	1	0	-3.267069	-0.412530	2.275663
22	8	0	3.036500	-0.013918	0.906676
23	6	0	4.334298	-0.309725	0.433984
24	1	0	4.761274	0.533742	-0.132638
25	1	0	4.956292	-0.497393	1.313393
26	1	0	4.361524	-1.203776	-0.208068

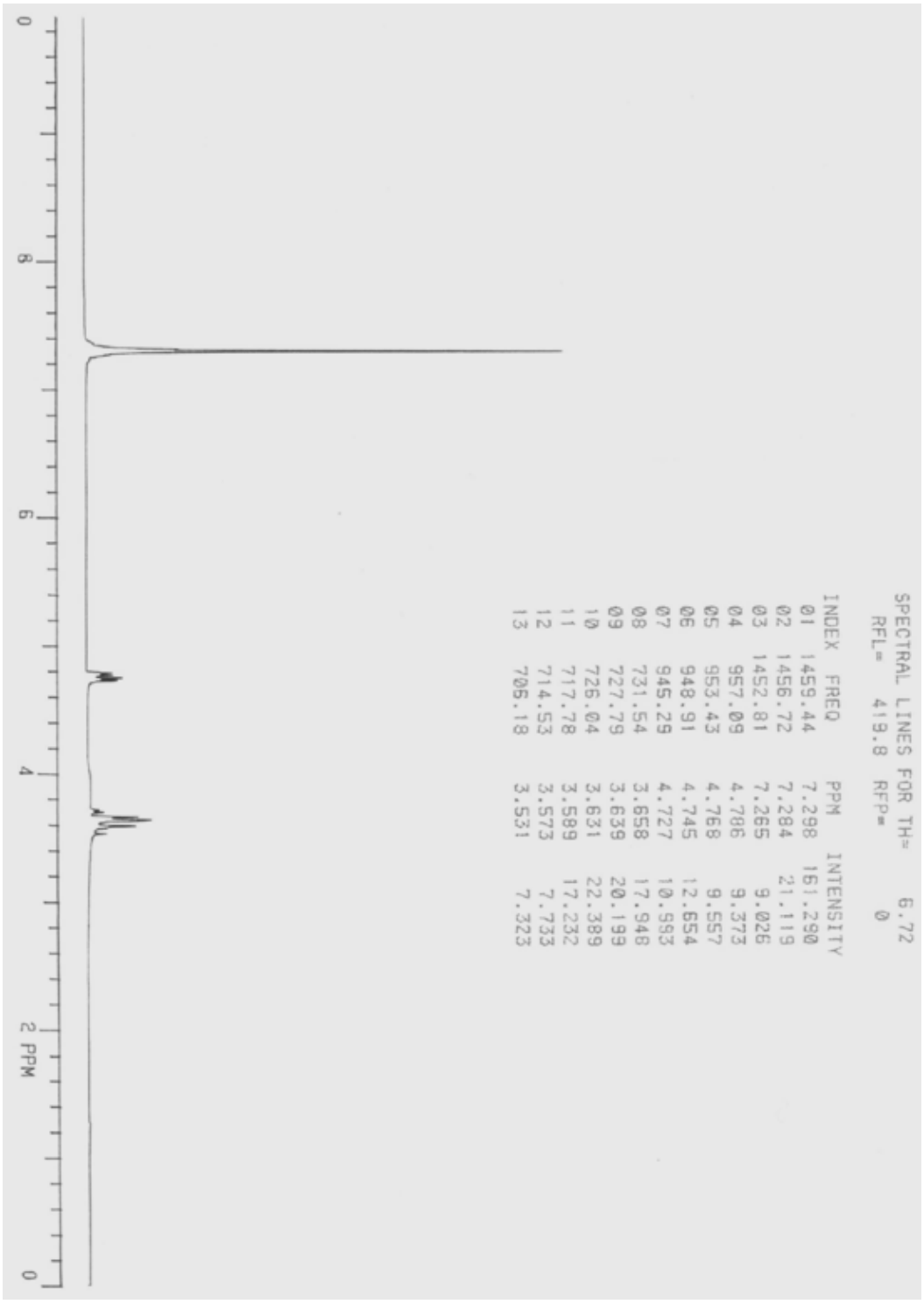
E = -577.0422057 a.u., ZPVE = 139.35 (Kcal/Mol)

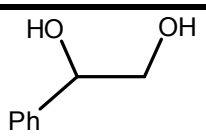
^{1}H-NMR and ^{13}C-NMR spectra and spectral data for *cis*-diols



1b

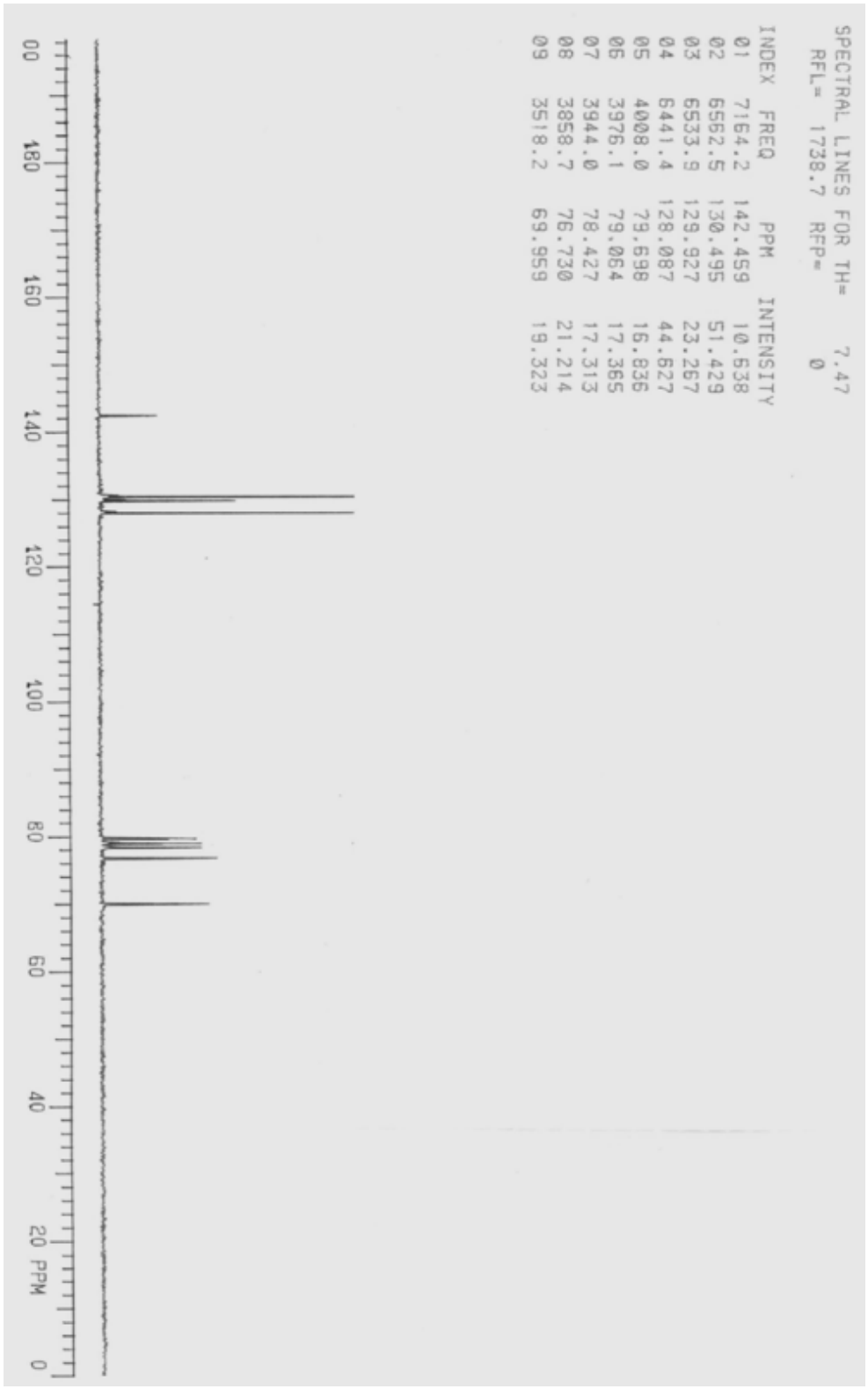
^{1}H -NMR (200 MHz, $CDCl_3$, ppm): δ= 7.26–7.29 (5 H, m), 4.75 (1 H,dd, *J* 8.2, 3.65), 3.63 (1 H, dd, *J* 11.01, 3.65,), 3.54 (1 H, dd, *J* 11.01, 8.0).

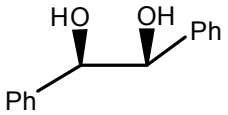




1b

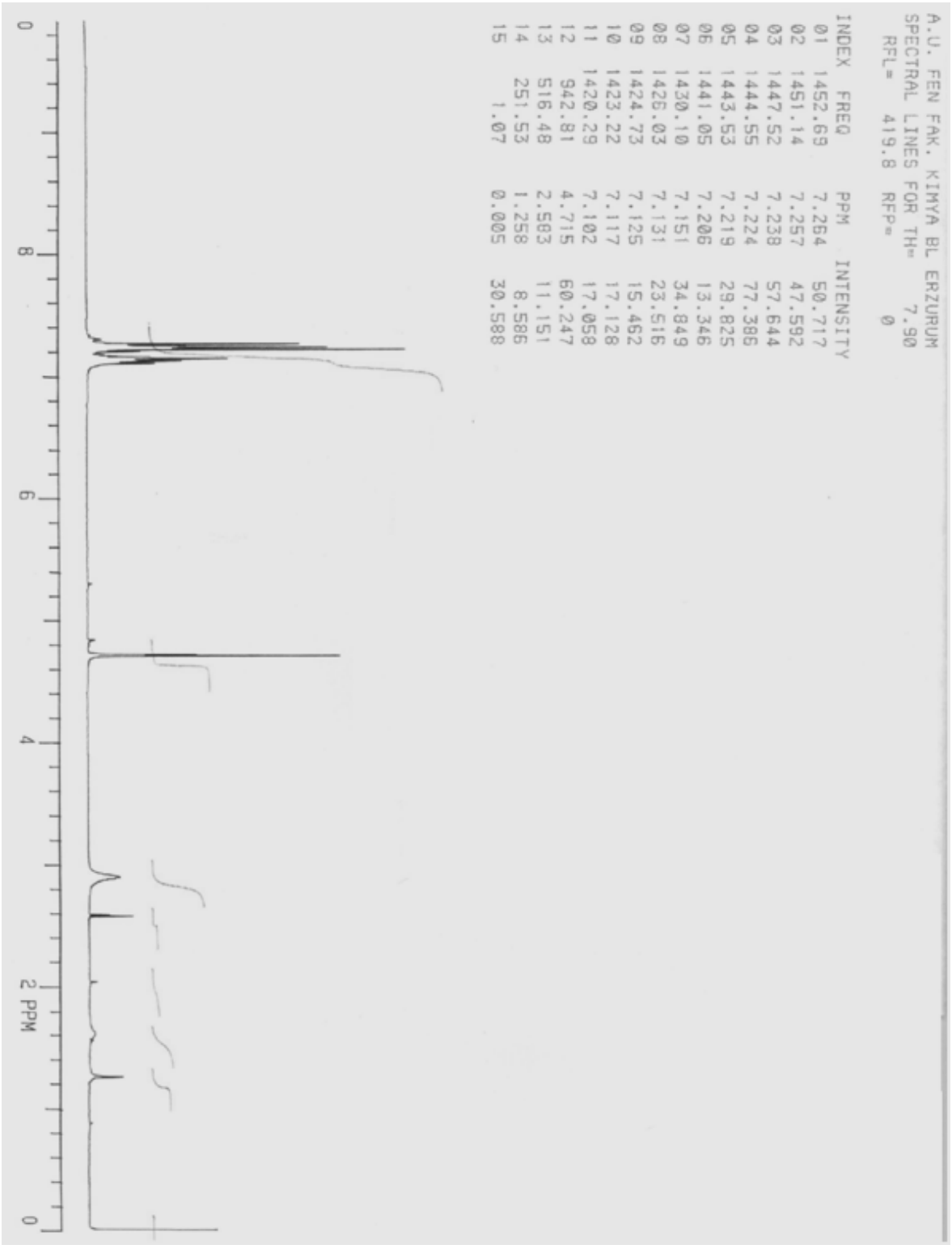
^{13}C-NMR (50 MHz, $CDCl_3$, ppm): δ= 142.5, 130.5, 129.9, 128.1, 76.7, 69.9.

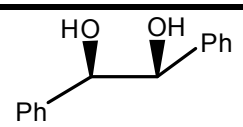




2b

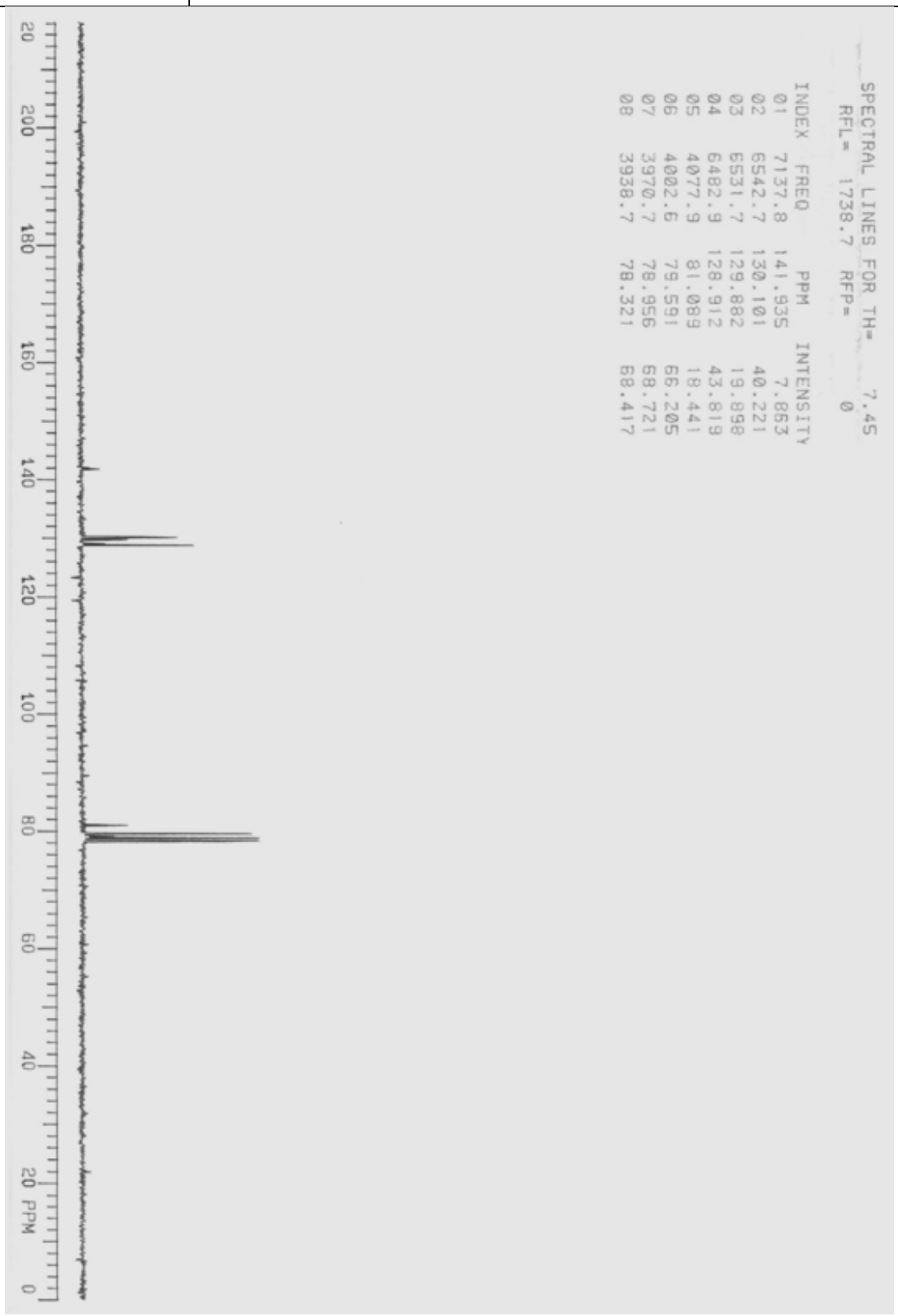
^{1}H -NMR (200 MHz, $CDCl_3$, ppm): δ=7.26-7.10 (10 H, m), 4.71 (2H, br s)

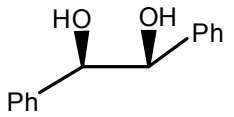




2b

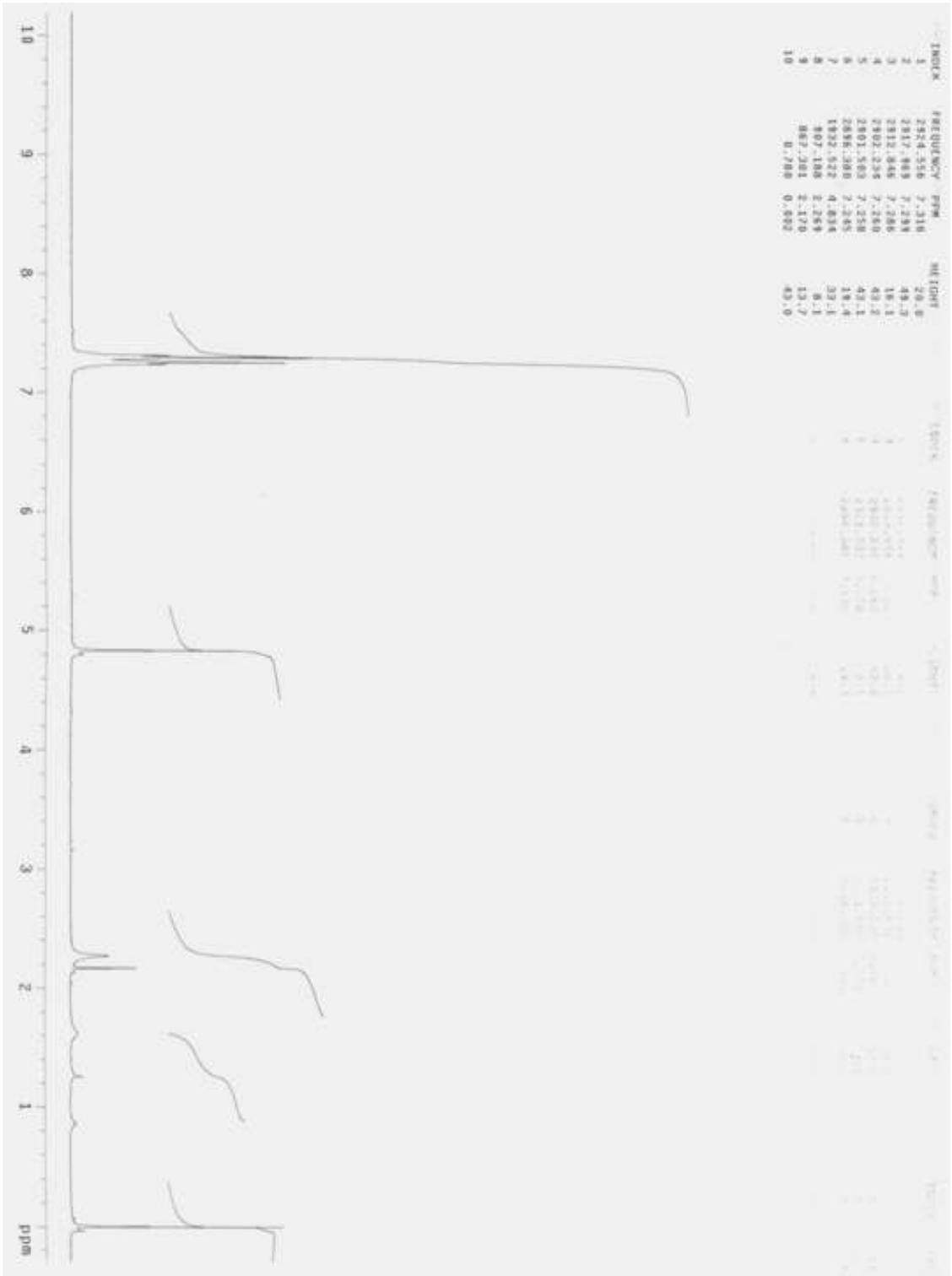
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 141.9, 130.1, 129.9, 128.9, 81.1.

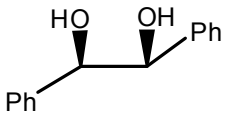




3b

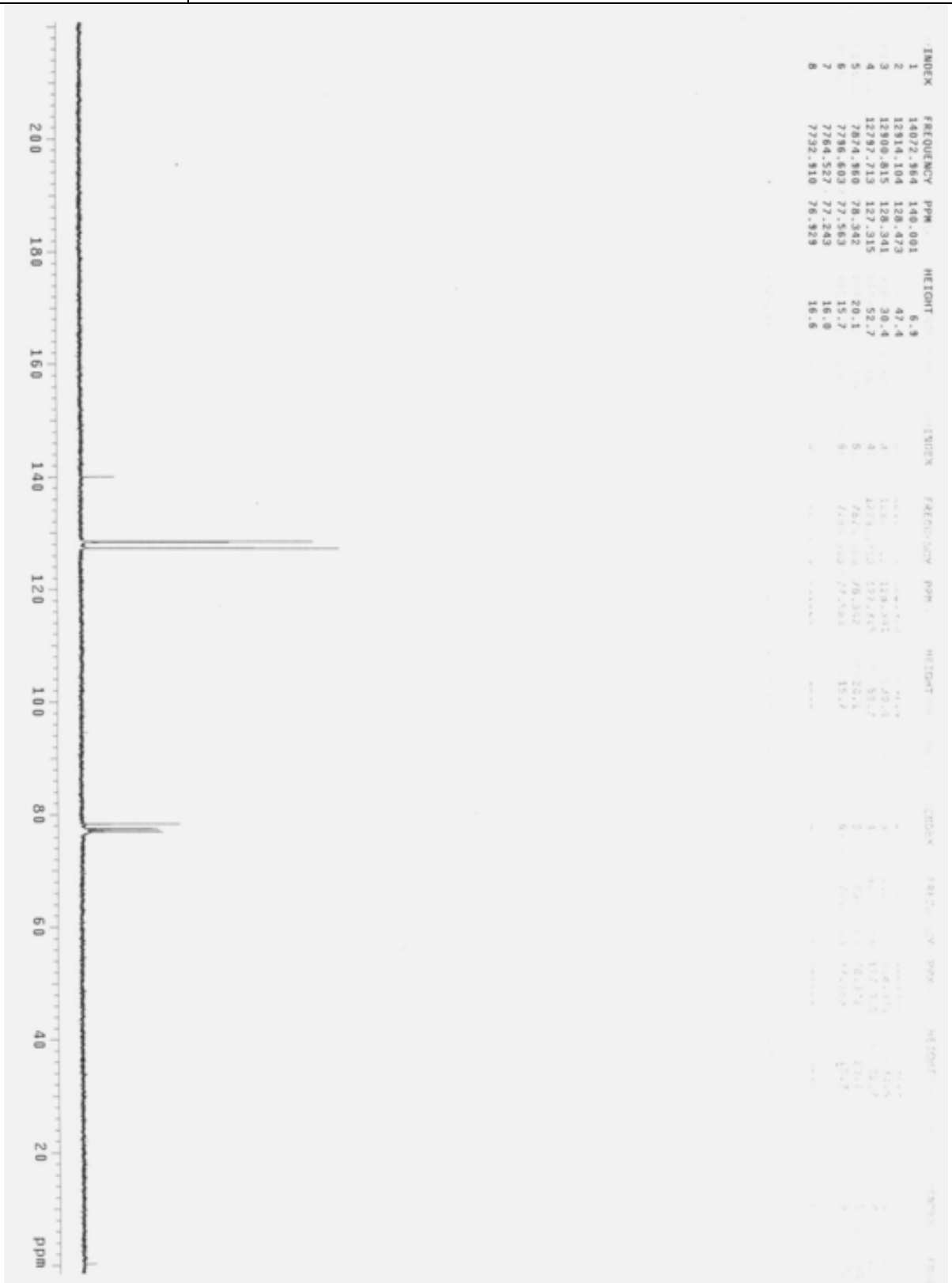
^{1}H -NMR (400 MHz, $CDCl_3$, ppm): δ= 7.31-7.24 (10H, m), 4.83 (2H, brs), (2OH, 2.20 brs)

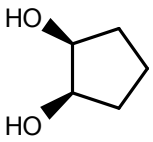




3b

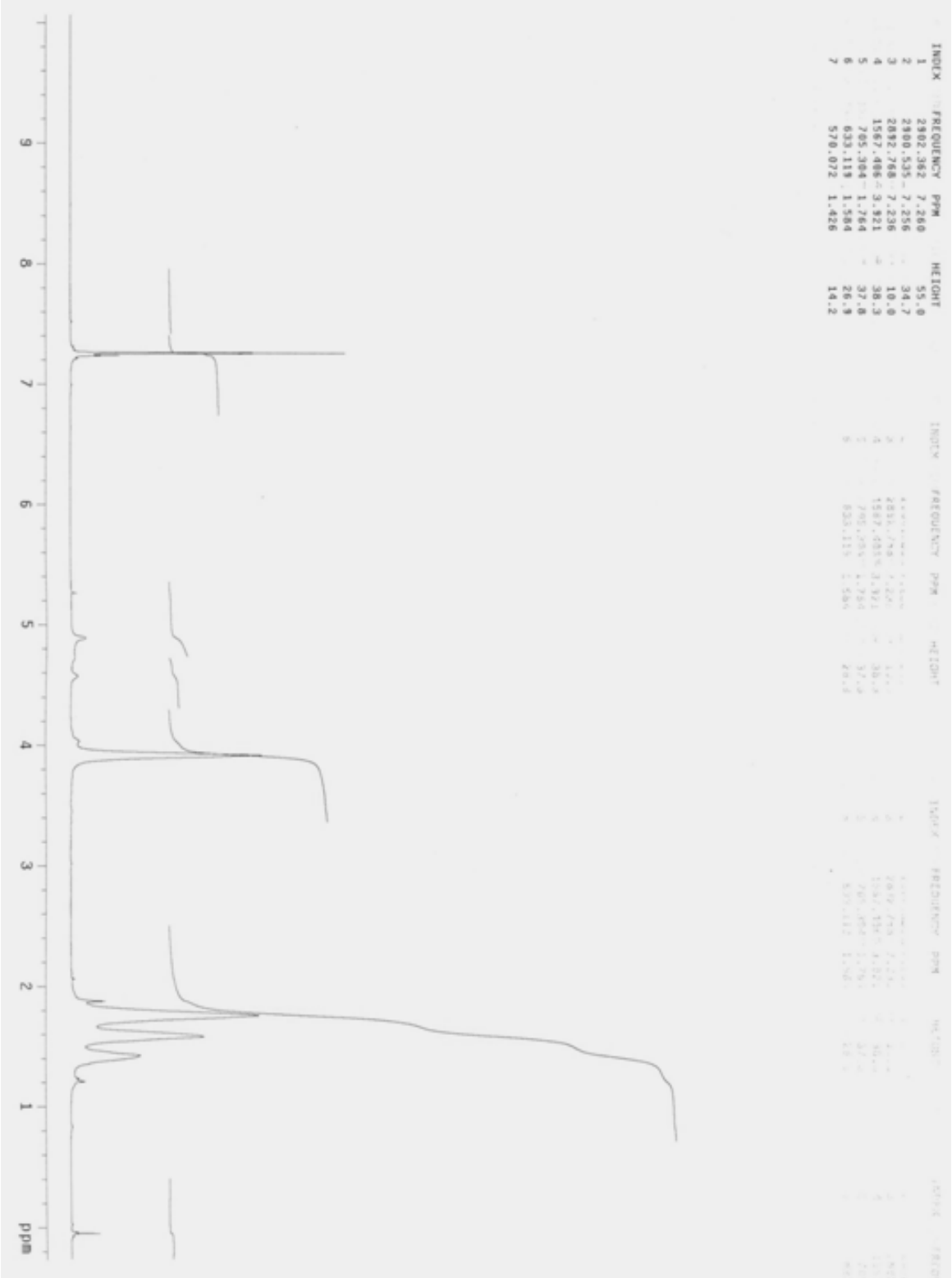
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 140.0, 128,5, 128.3, 127,3, 78.3.

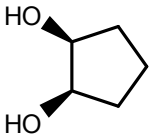




4b

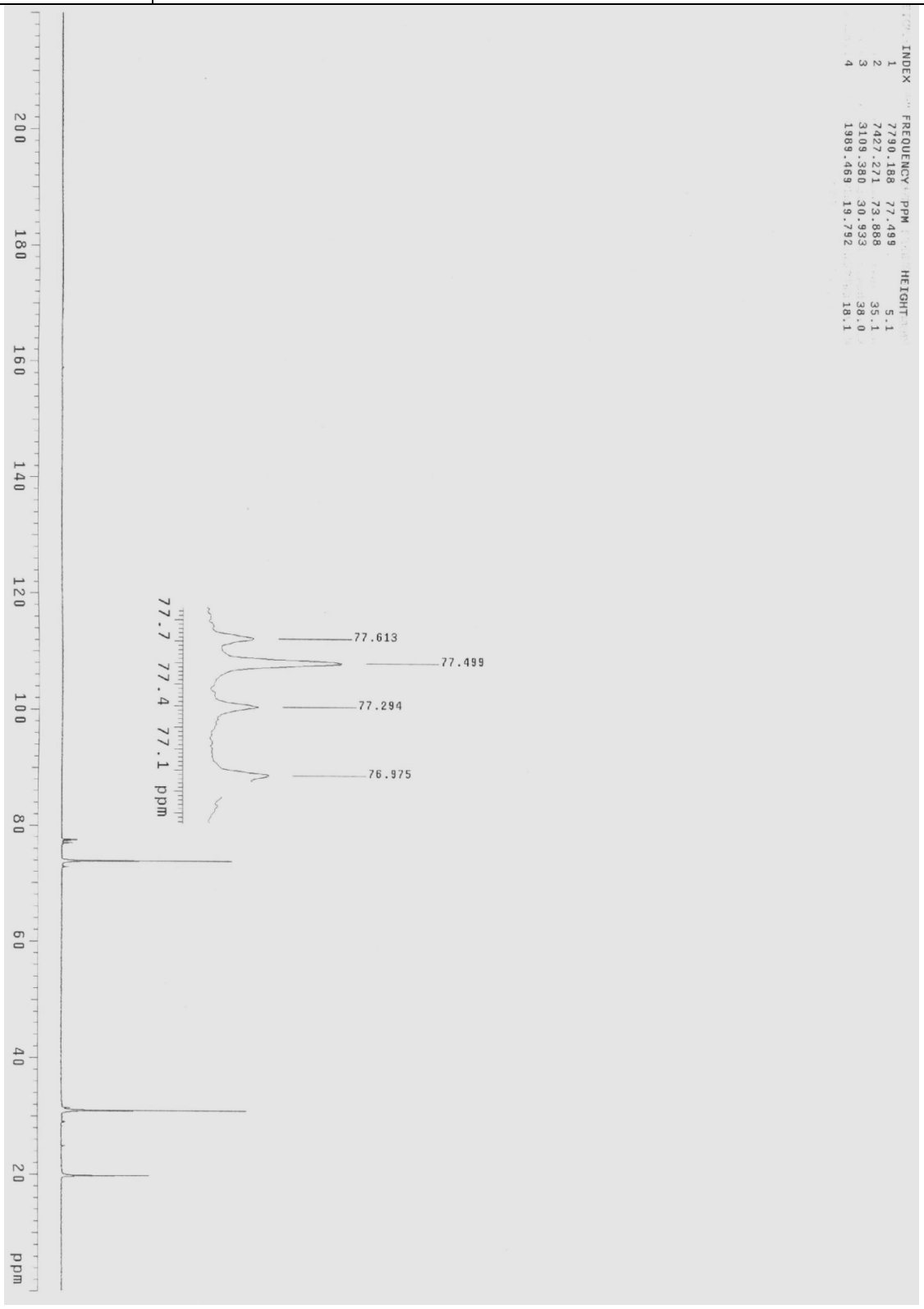
^{1}H -NMR (400 MHz, $CDCl_3$, ppm): δ= 3,9 (2H, m), 1.87 (2H, m), 1.58 (2H, m), 1.42 (2H, m).

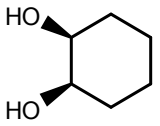




4b

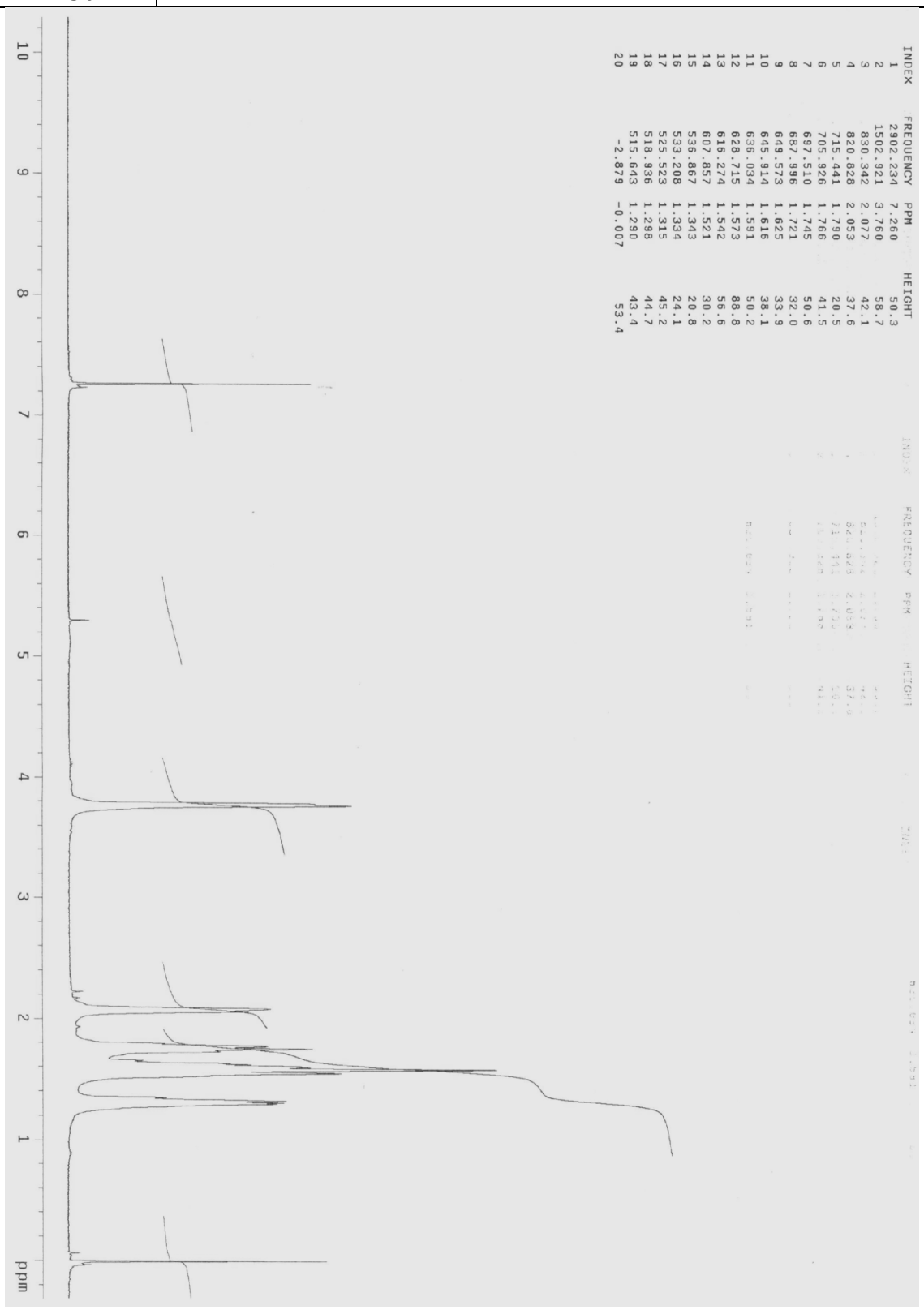
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 77.5, 30.9, 19.8.

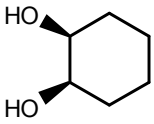




5b

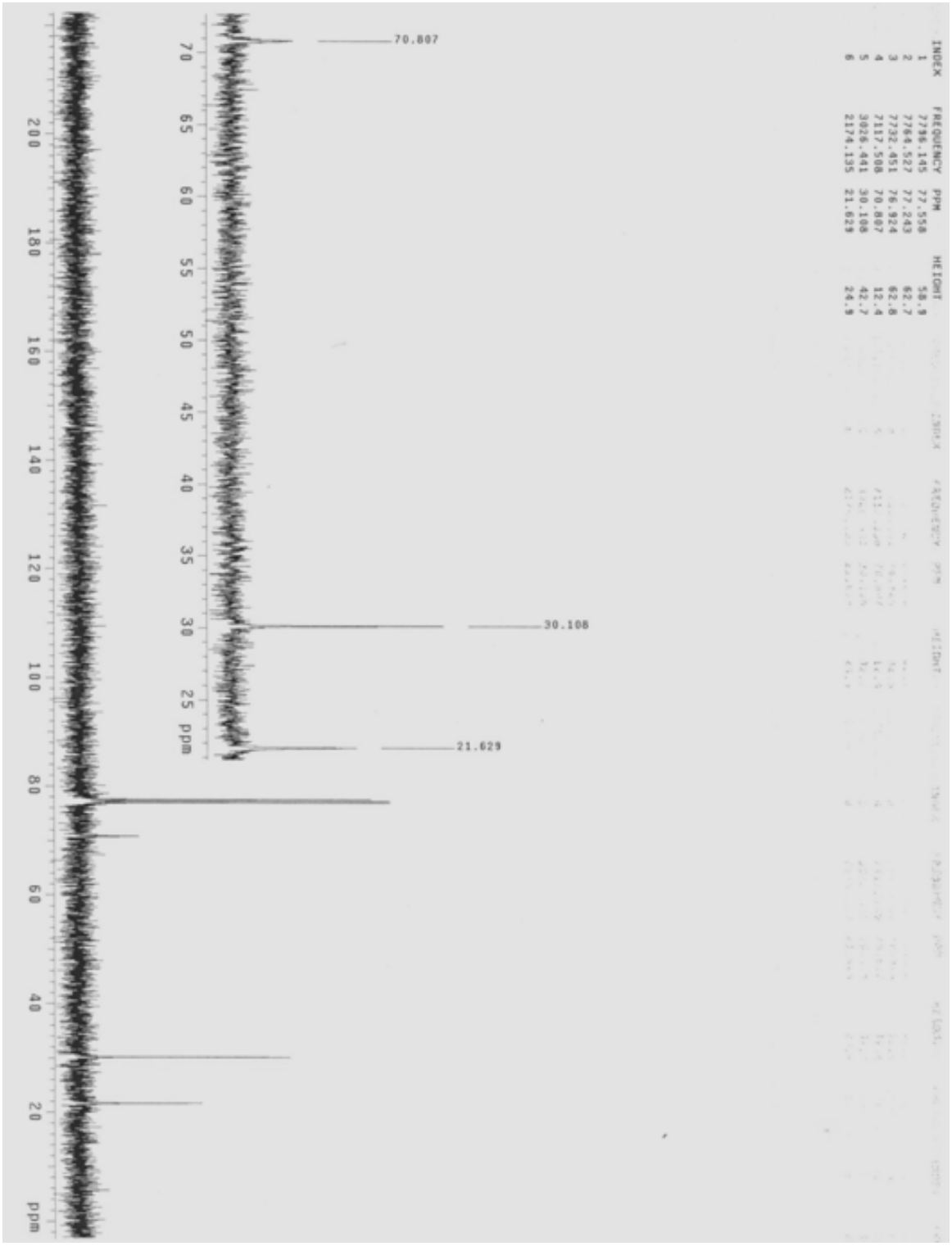
^{1}H -NMR (400 MHz, $CDCl_3$, ppm): δ= 3.76 (2H, m), 2.06 (2H, br s, 2OH), 1.79-1.29 (8H, m)

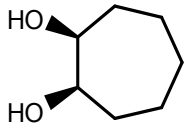




5b

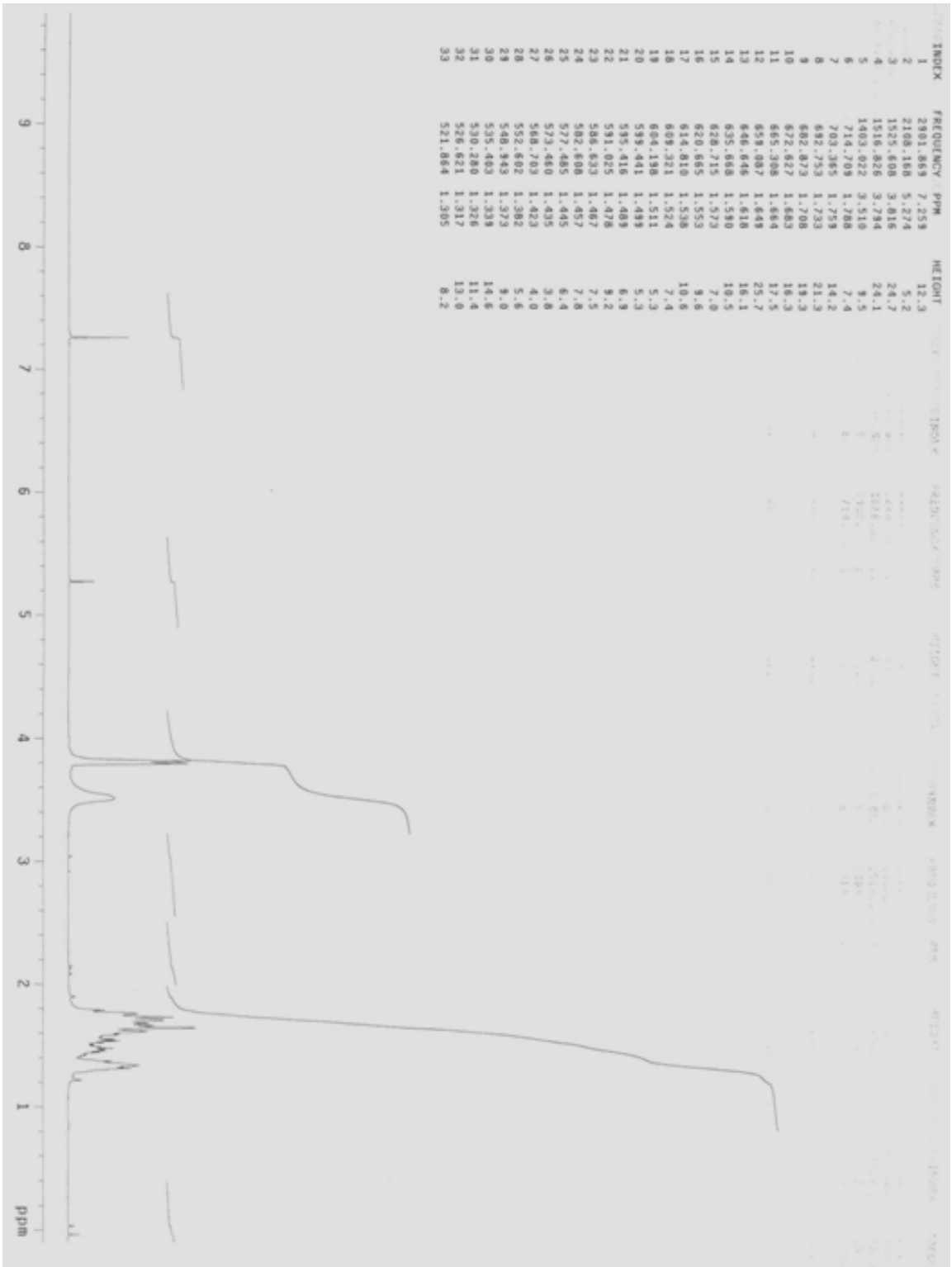
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 70.8, 30.1, 21.6.

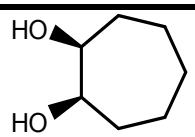




6b

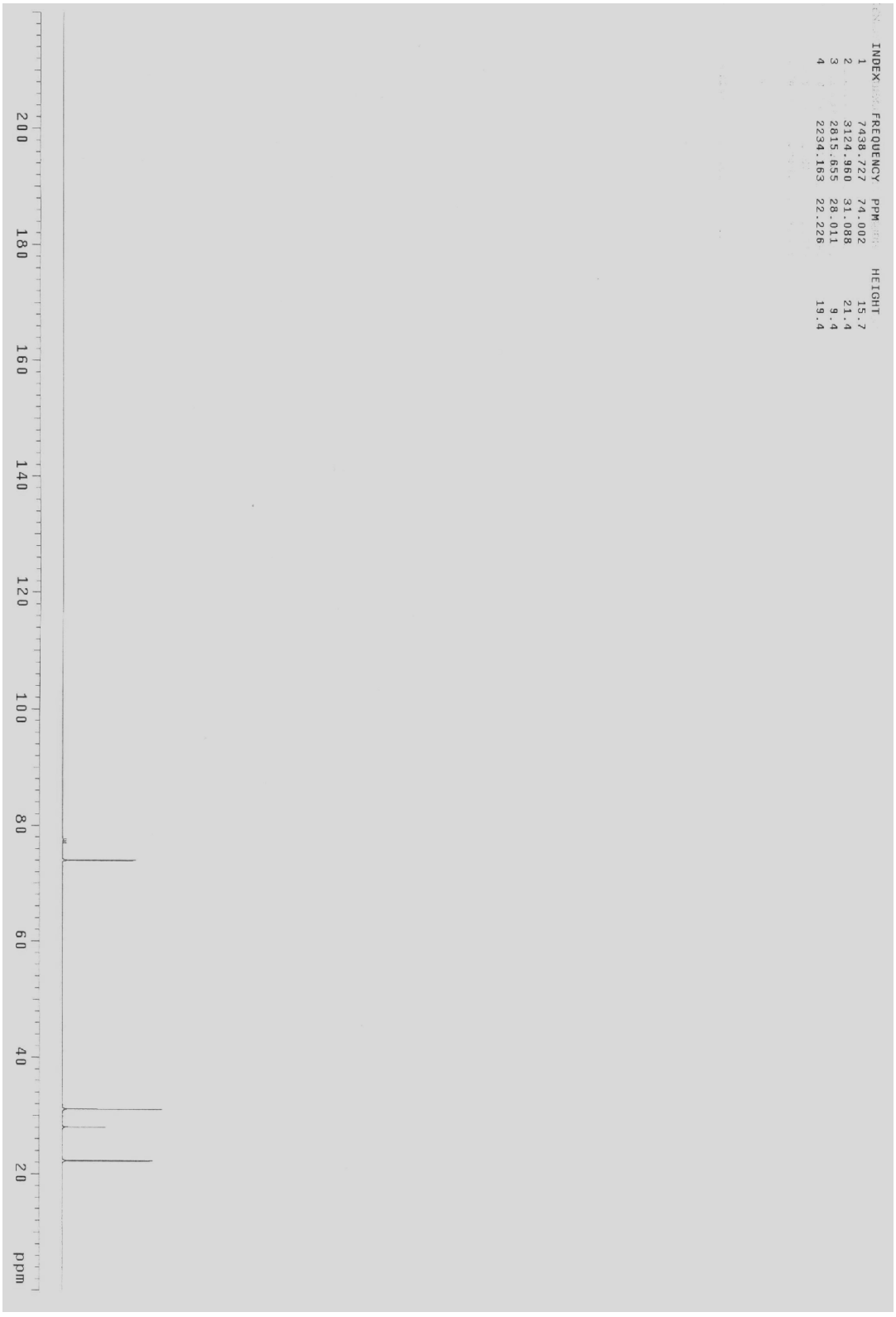
^{1}H -NMR (400 MHz, $CDCl_3$, ppm): δ= 3.80 (2H, d, J=8.8 Hz), 3.50 (2H, br s, 2OH), 1.78-1.30 (10H, m).

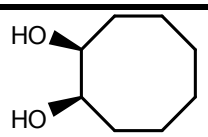




6b

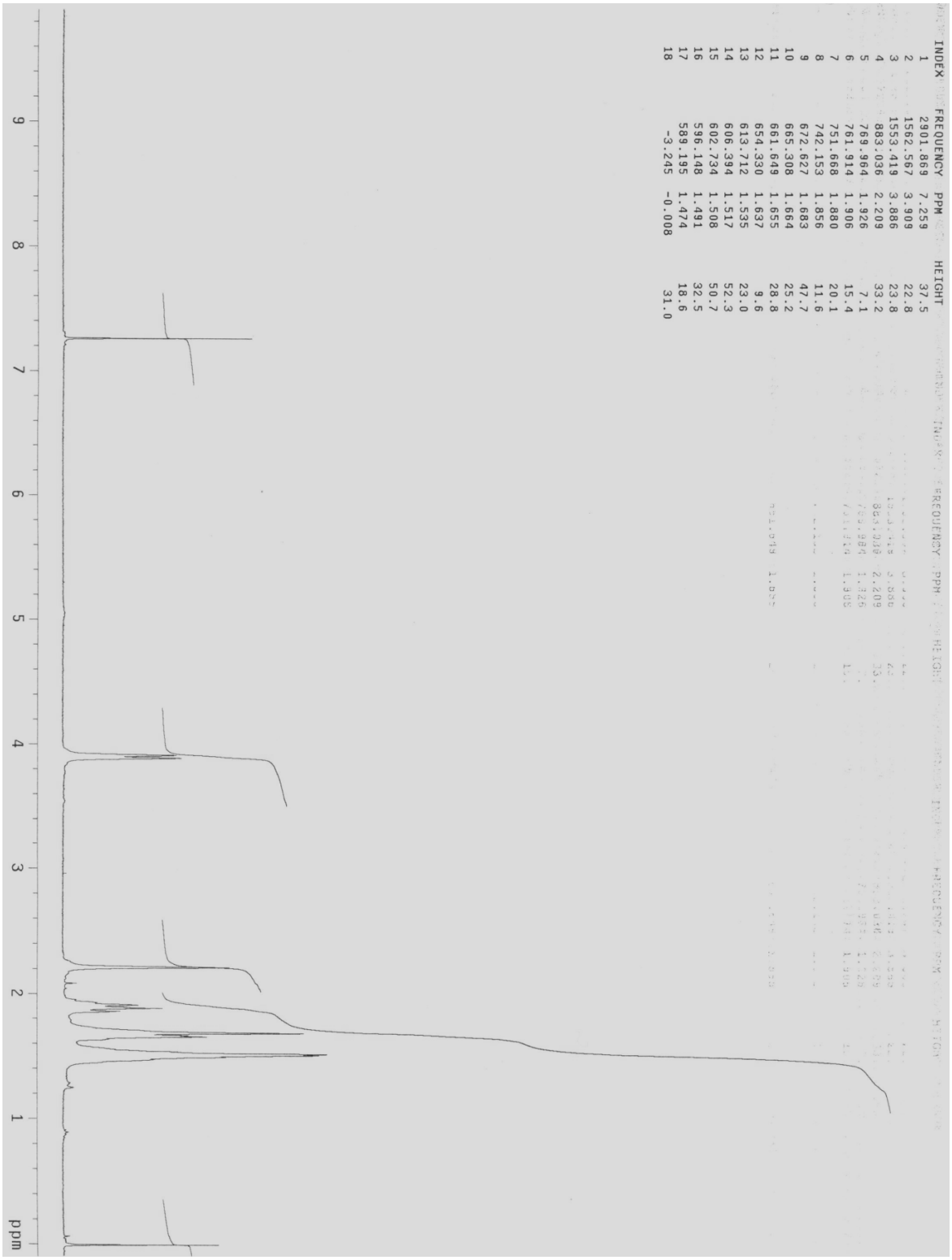
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 74.0, 31.1, 28.0, 22.2.

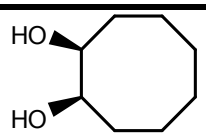




7b

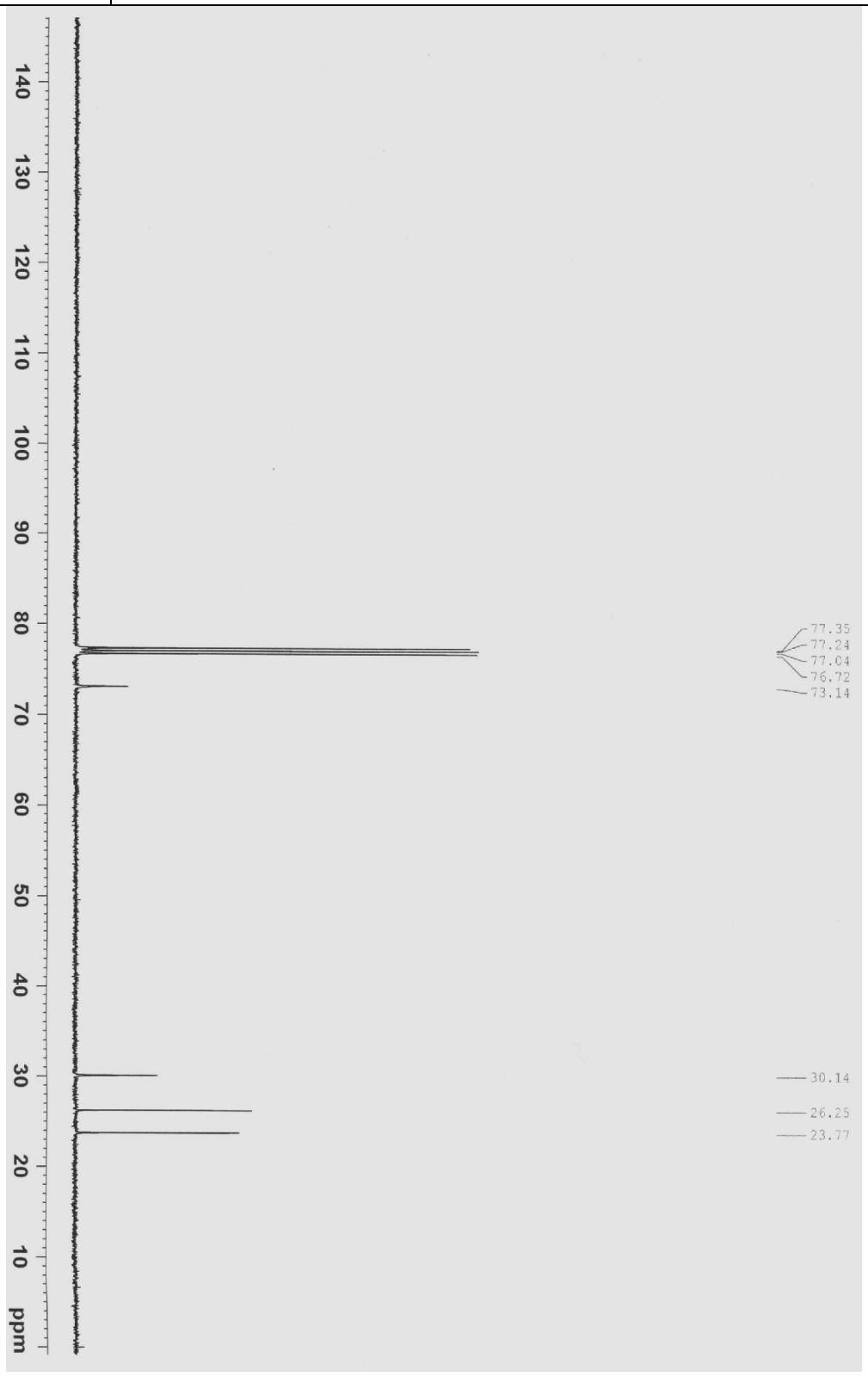
^{1}H -NMR (400 MHz, $CDCl_3$, ppm): δ=3.89 (2H, d, J=9.1Hz), 2.2 (2H, br s, 2OH), 1.89 (4H, m), 1.68-1.47 (8H, m).

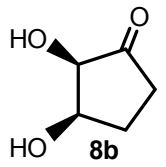




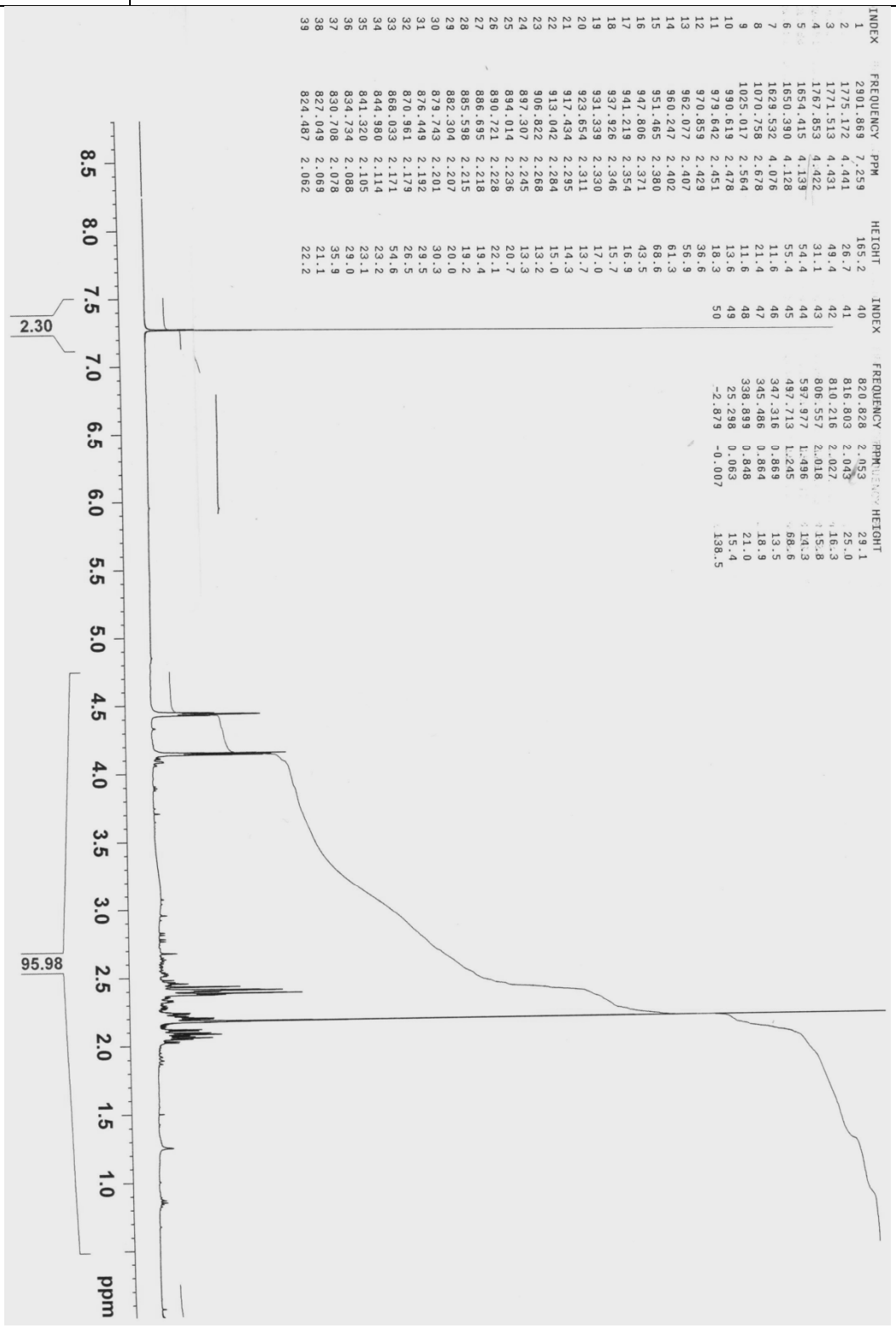
7b

^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 73.1, 30.1, 26.2, 23.8



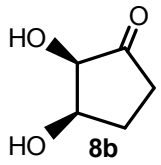


^{1}H -NMR (400 MHz, $CDCl_3$, ppm): δ=4.43 (1H, t, m), 4.12 (1H, m), 2.47 (2H, m), 2.38-2.16 (2H, m).

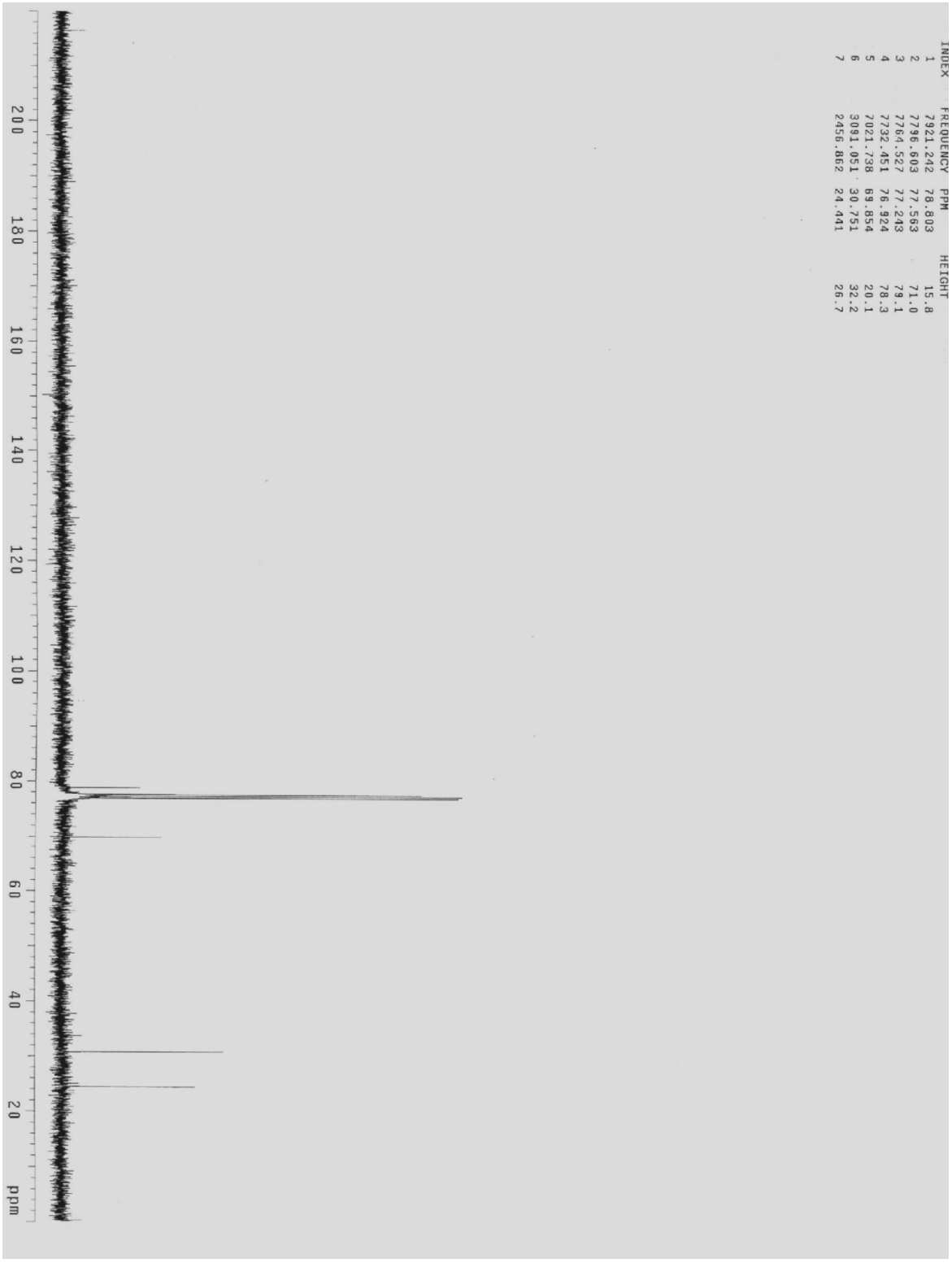


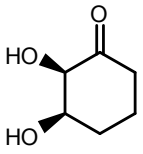
INDEX	FREQUENCY	PPM	HEIGHT
1	2901.869	7.259	165.2
2	1775.172	4.441	26.7
3	1771.513	4.431	49.4
4	1767.853	4.422	31.1
5	1654.415	4.139	54.4
6	1650.390	4.128	55.4
7	1629.532	4.076	11.6
8	1070.758	2.678	21.4
9	1025.017	2.564	11.6
10	990.619	2.478	13.6
11	979.642	2.451	18.3
12	970.859	2.429	36.6
13	962.077	2.407	56.9
14	960.247	2.402	61.3
15	951.465	2.380	68.6
16	947.806	2.371	43.5
17	941.219	2.354	16.9
18	937.926	2.346	15.7
19	931.339	2.330	17.0
20	923.654	2.311	13.7
21	917.434	2.295	14.3
22	913.042	2.284	15.0
23	906.822	2.268	13.2
24	897.307	2.245	13.3
25	894.014	2.236	20.7
26	890.721	2.228	22.1
27	886.695	2.218	19.4
28	885.598	2.215	19.2
29	882.304	2.207	20.0
30	879.743	2.201	30.3
31	876.449	2.192	29.5
32	870.961	2.179	26.5
33	868.033	2.171	54.6
34	844.980	2.114	23.2
35	841.320	2.105	23.1
36	834.734	2.088	29.0
37	830.708	2.078	35.9
38	827.049	2.069	21.1
39	824.487	2.062	22.2

INDEX	FREQUENCY	PPM	HEIGHT
40	820.828	2.053	29.1
41	816.803	2.043	25.0
42	810.216	2.027	16.3
43	806.557	2.018	15.8
44	597.977	1.496	14.3
45	497.713	1.245	68.6
46	347.316	0.869	13.5
47	345.486	0.864	18.9
48	338.899	0.848	21.0
49	25.298	0.063	15.4
50	-2.879	-0.007	138.5



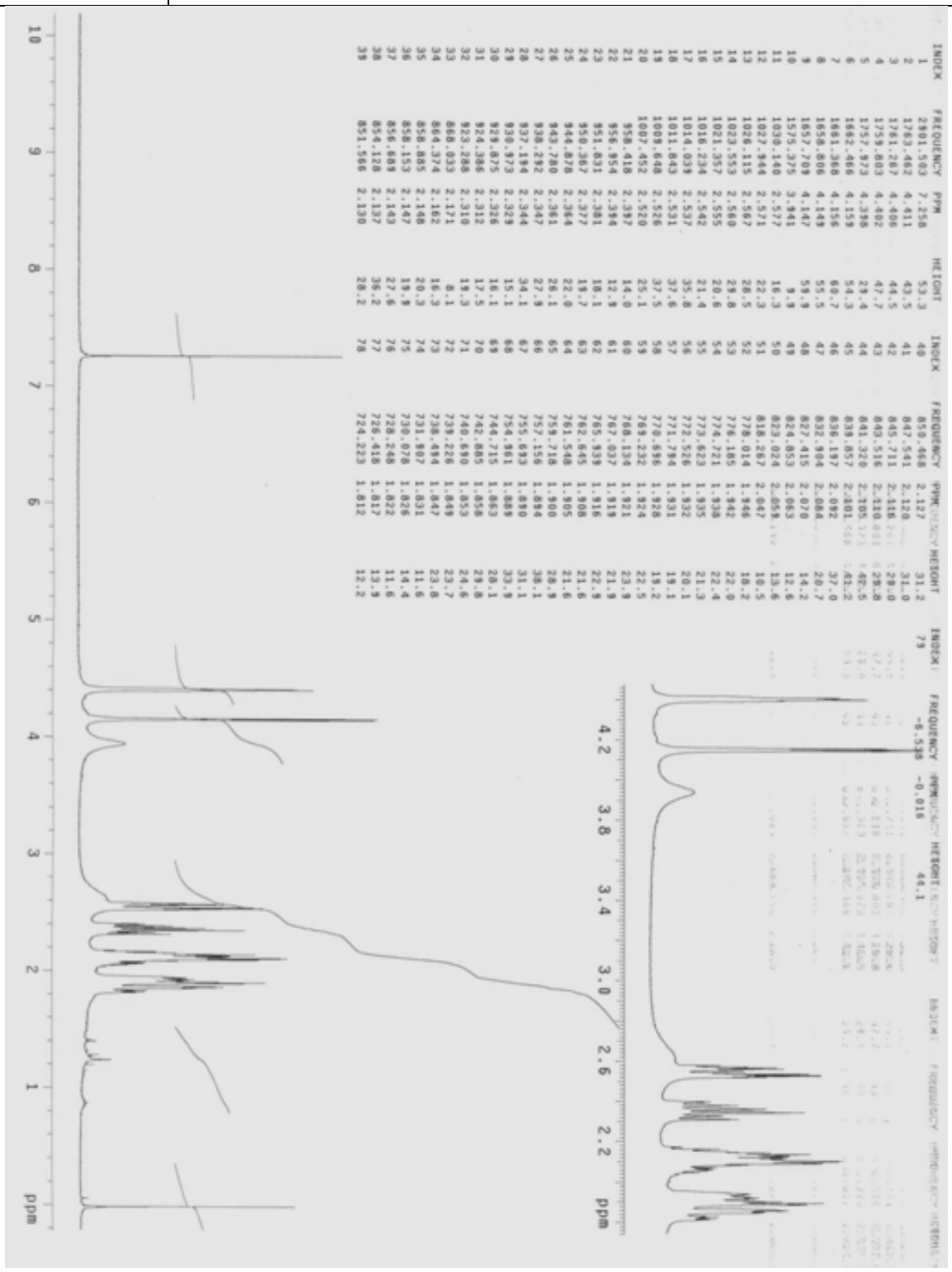
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ=213.1, 78.8, 69.9, 30.7, 26.7

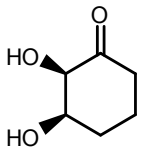




9b

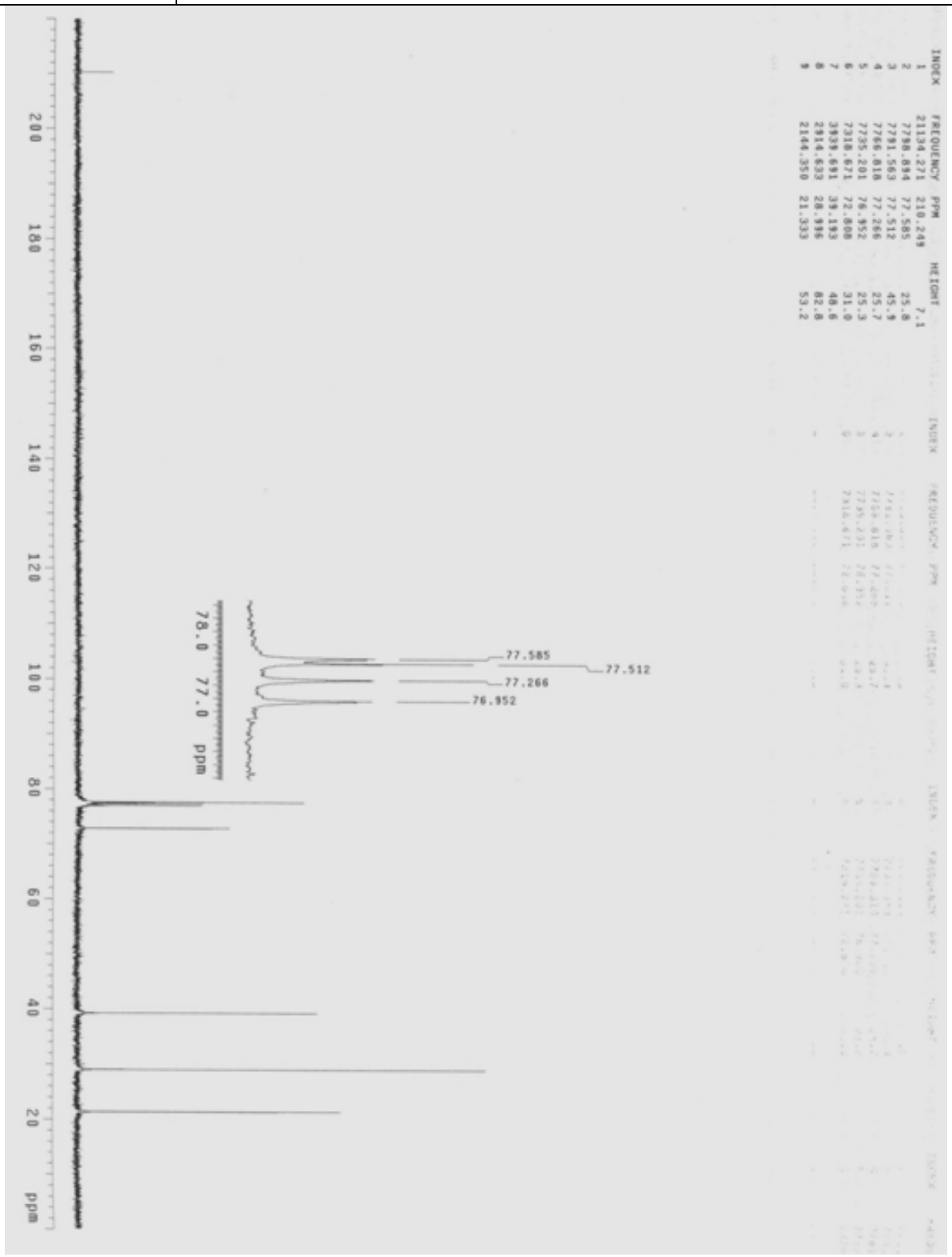
^{1}H -NMR (400 MHz, $CDCl_3$, ppm): δ=4.40 (1H, dd, J=2.2, 3.5, Hz), 4.14 (1H, m), 2.56 (1H, m), 2.38 (1H, m), 2.16 (2H, m), 1.85 (2H, m).

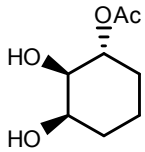




9b

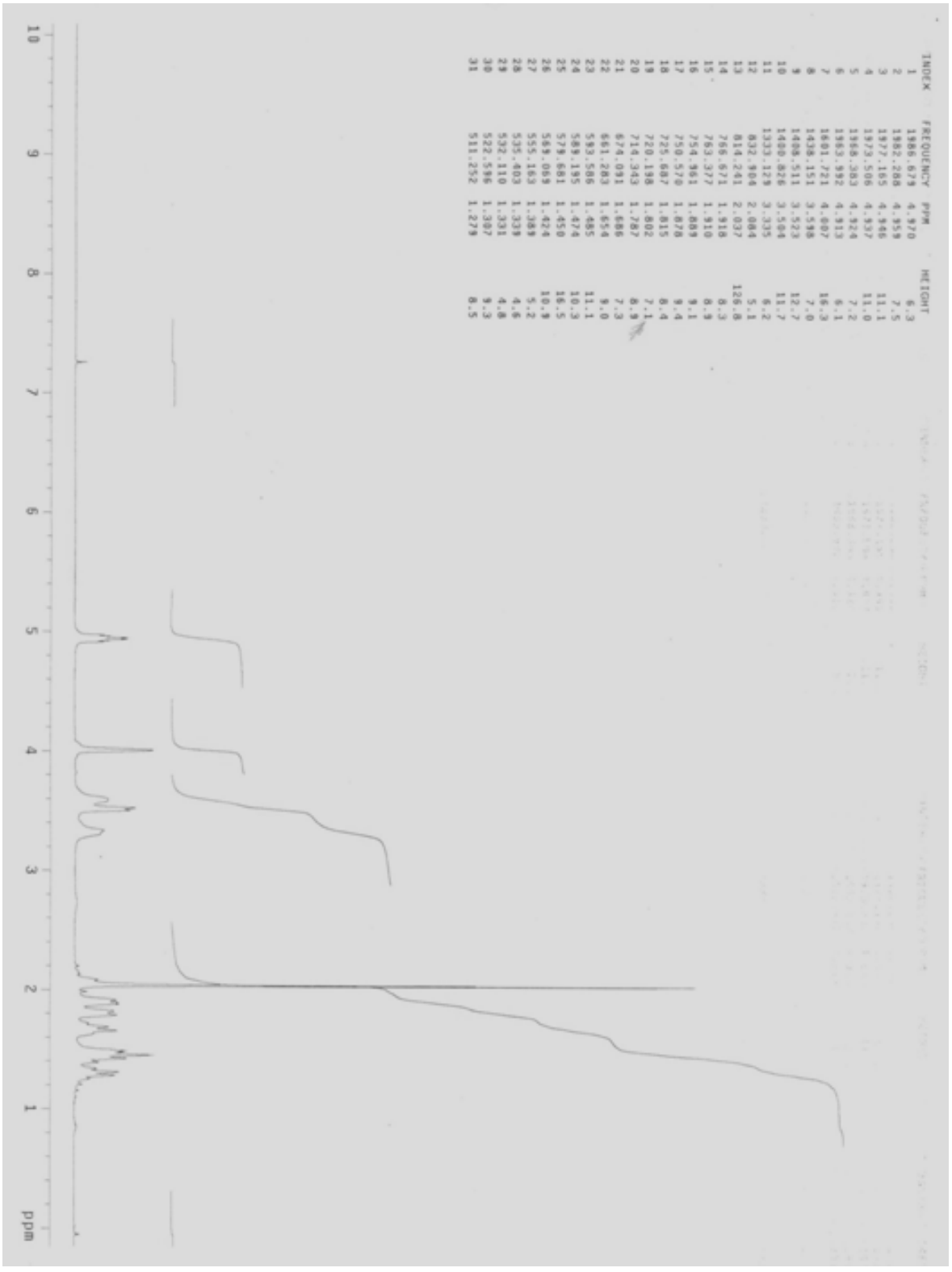
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 210.2, 77.5, 72.8, 39.2, 28.9, 21.3.

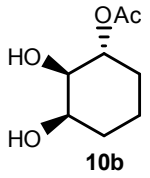




10b

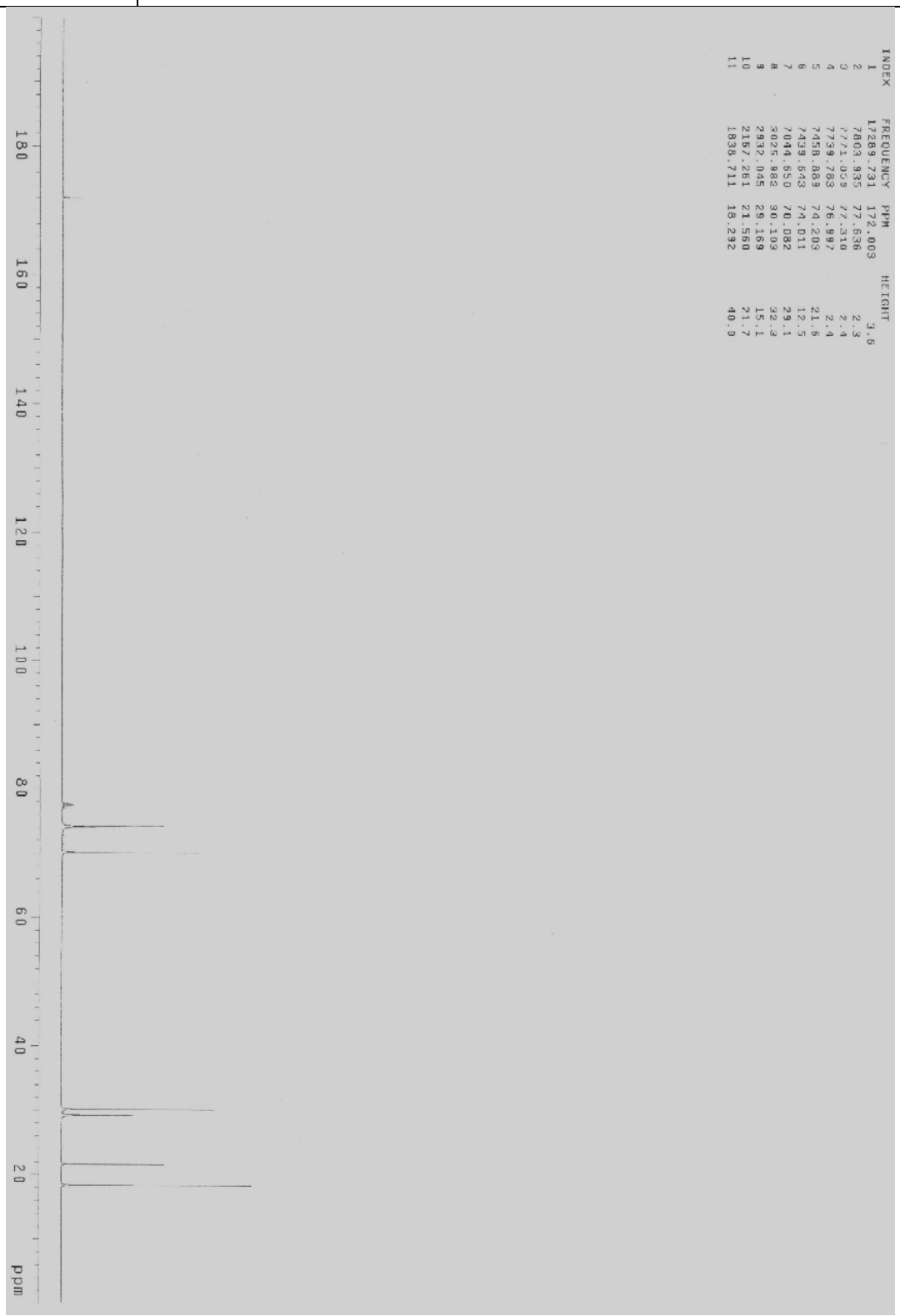
^{1}H -NMR (400 MHz, $CDCl_3$, ppm): δ=4.93 (1H, m), 4.00, (1H, m), 3.55 (1H, m), 3.59 (1H, OH brs), 3.33 (1H, OH brs), 1.91-1.27 (6H, m), 2.03 (3H, s).

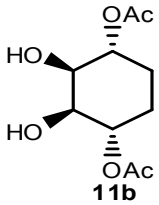




10b

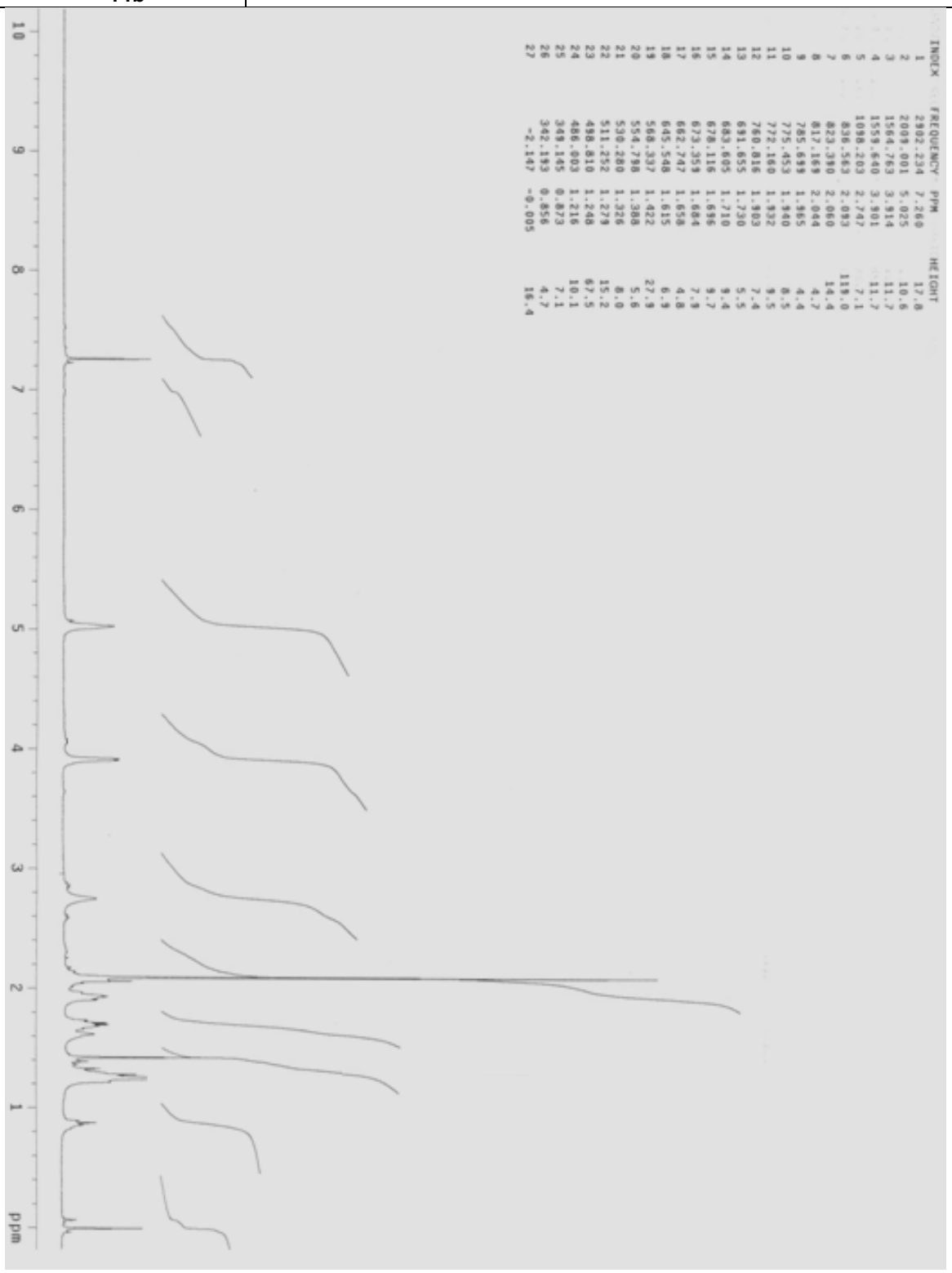
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 172.0, 74.2, 74.0, 70.1, 30.1, 29.2, 21.6, 18.3.

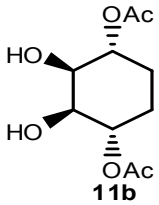




11b

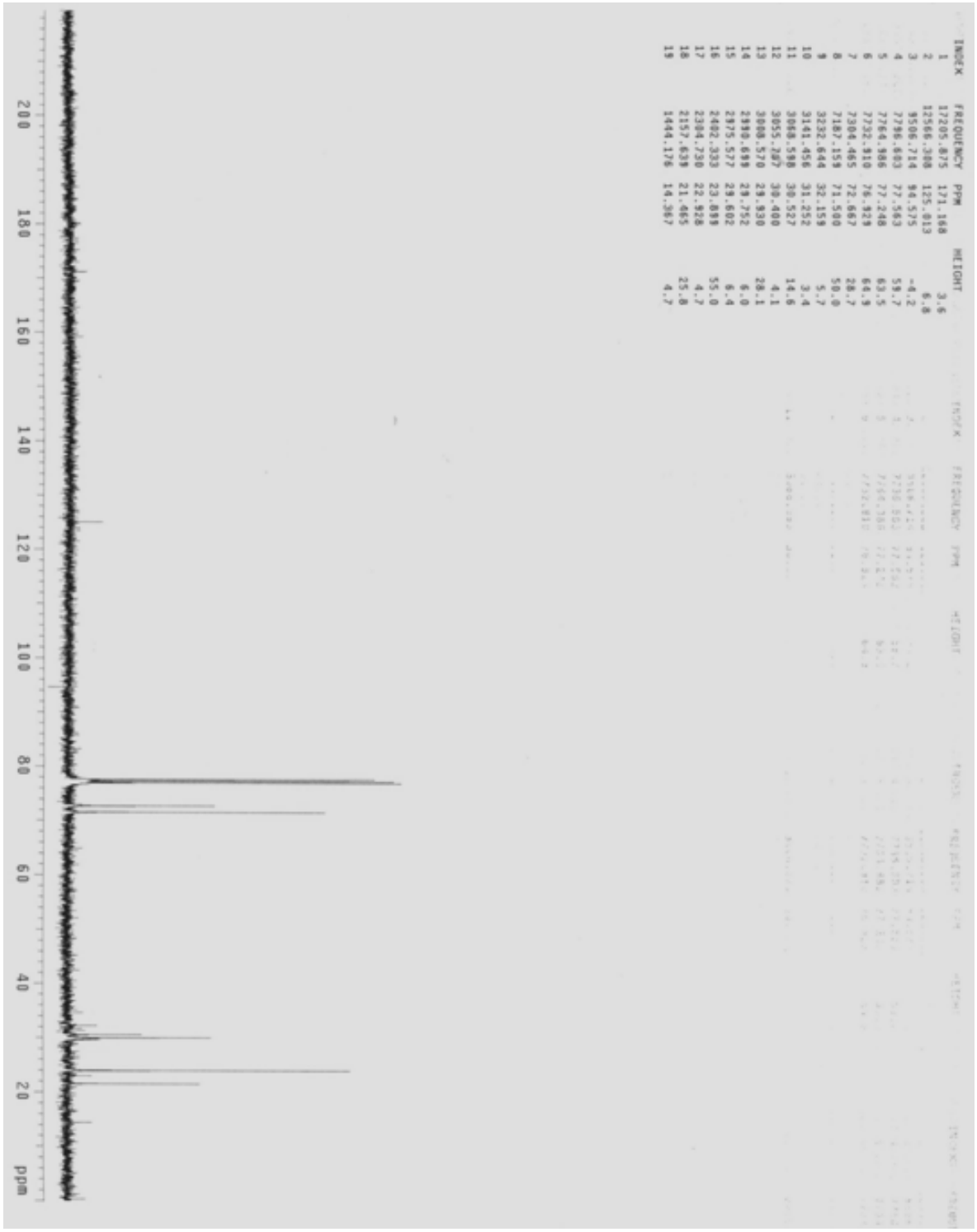
^{1}H -NMR (400 MHz, $CDCl_3$, ppm): δ=5.05 (2H, m), 3.90 (2H, m), 2.65 (2H, OH brs), 1.95 (2(H, m), 1.70)2H, m), 2.10 (6H, s).

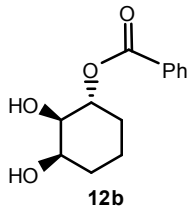




11b

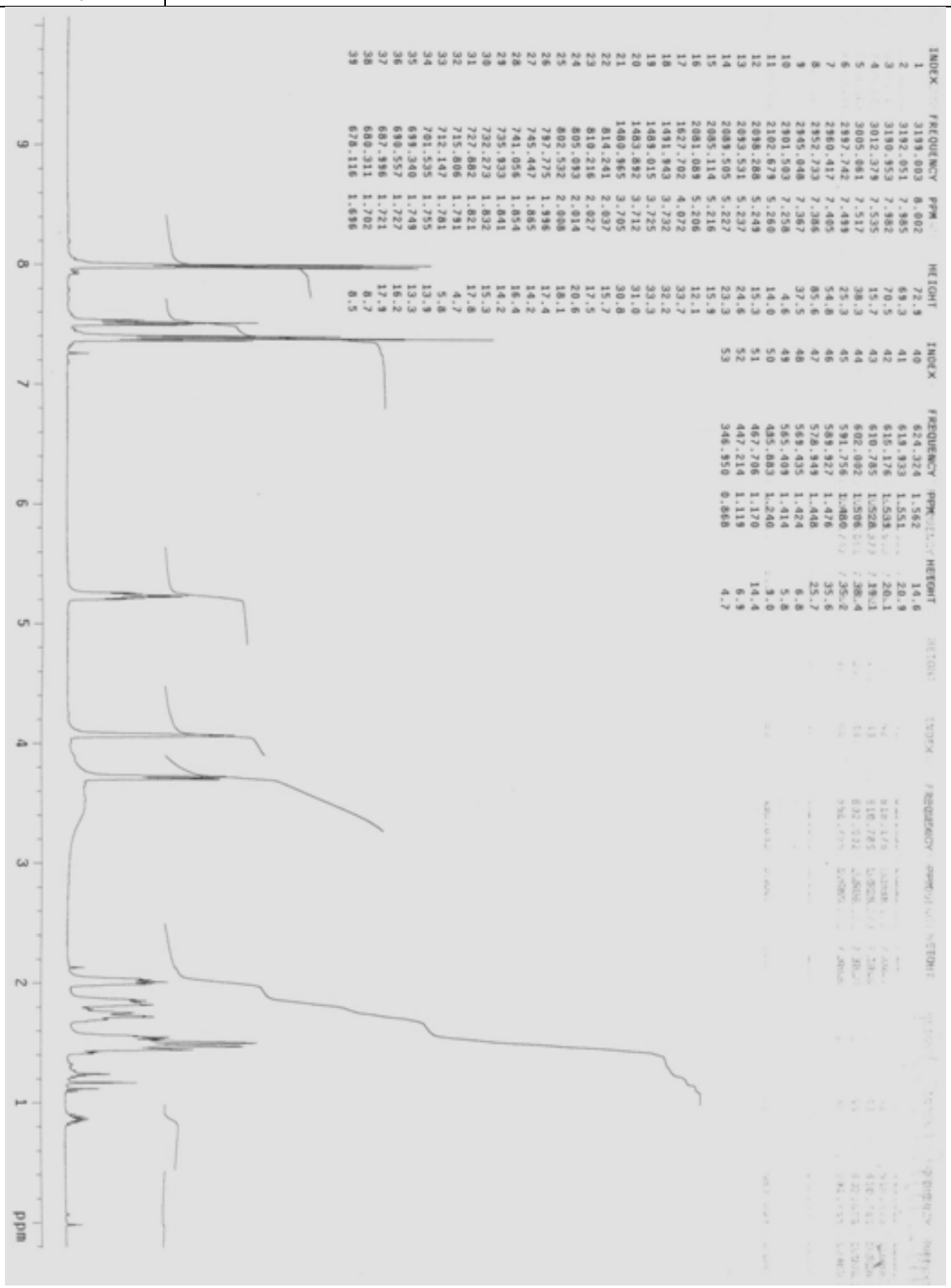
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ=171.1, 72.8, 71.5, 29.9, 23.9,

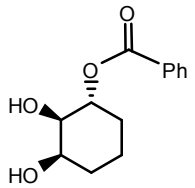




12b

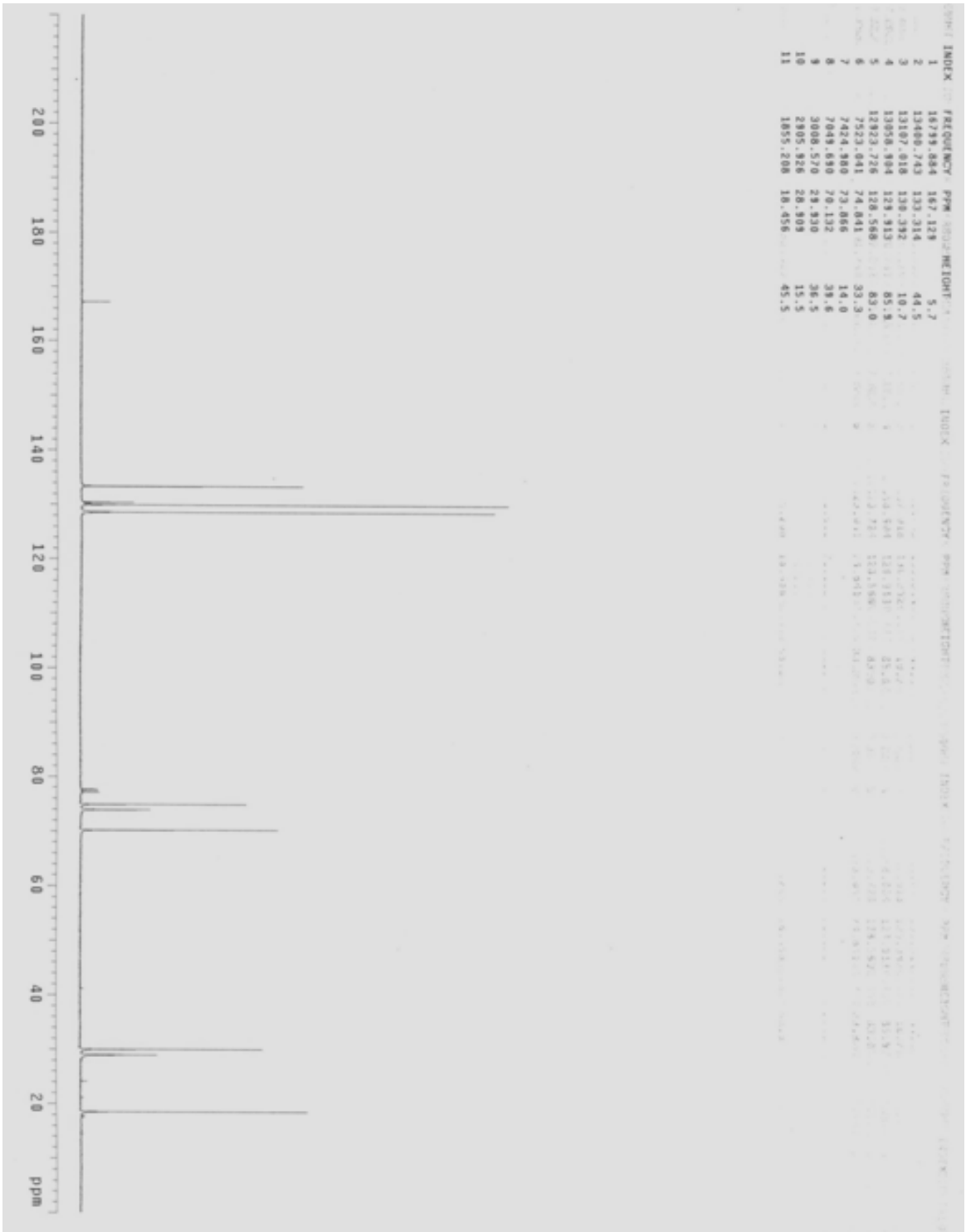
^{1}H -NMR (400 MHz, $CDCl_3$, ppm): δ= 8.00 (2H, m aryl), 7.49 (1H, m aryl), 7.38 (2H, m aryl), 5.22 (2H, m), 4.07 (1H,m), 3.72 (1H, m), 2.03-1.40 (6H, m).



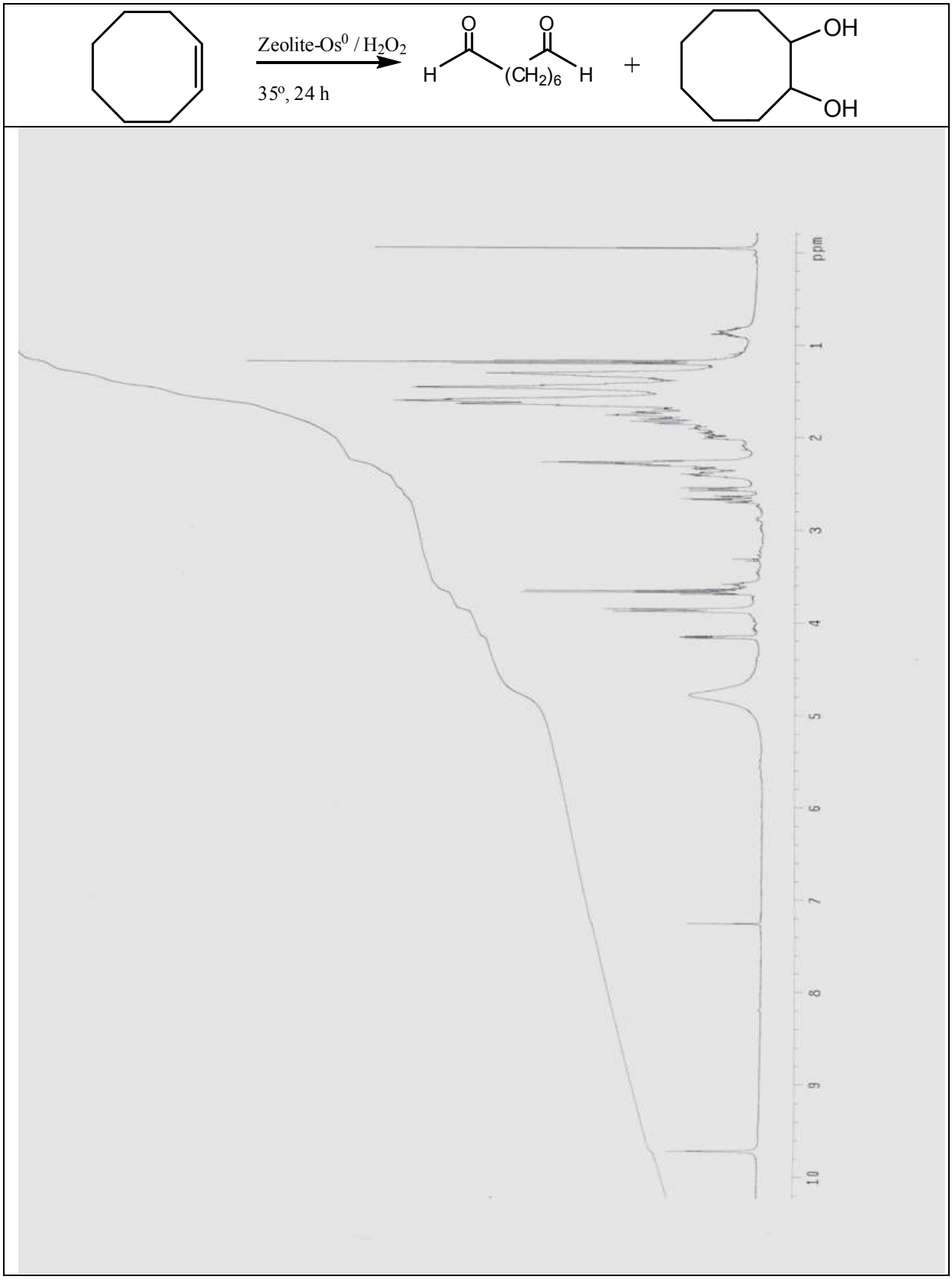


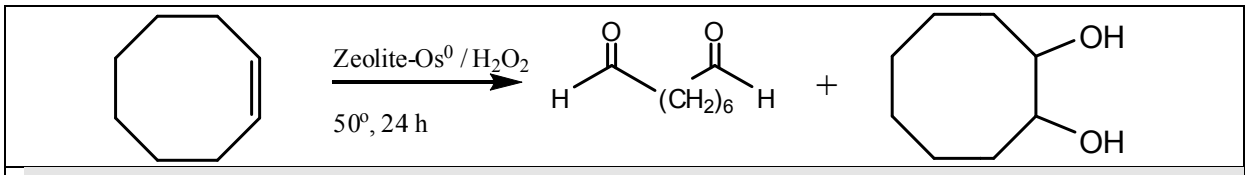
12b

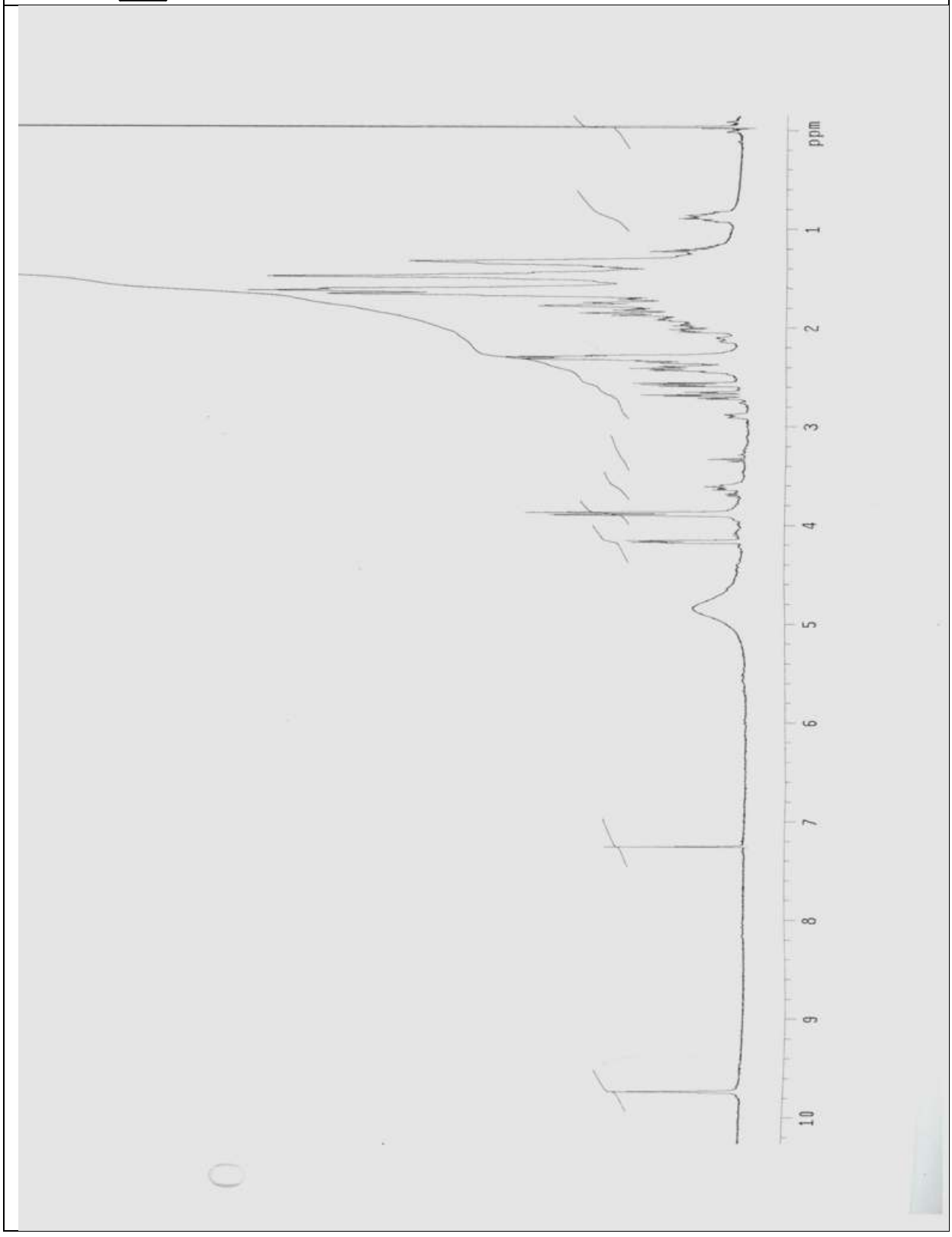
^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ= 167.1, 133.3, 130.4, 129.9, 128.7, 74.8, 73.9, 70.1, 29.9, 28.9, 18.5.

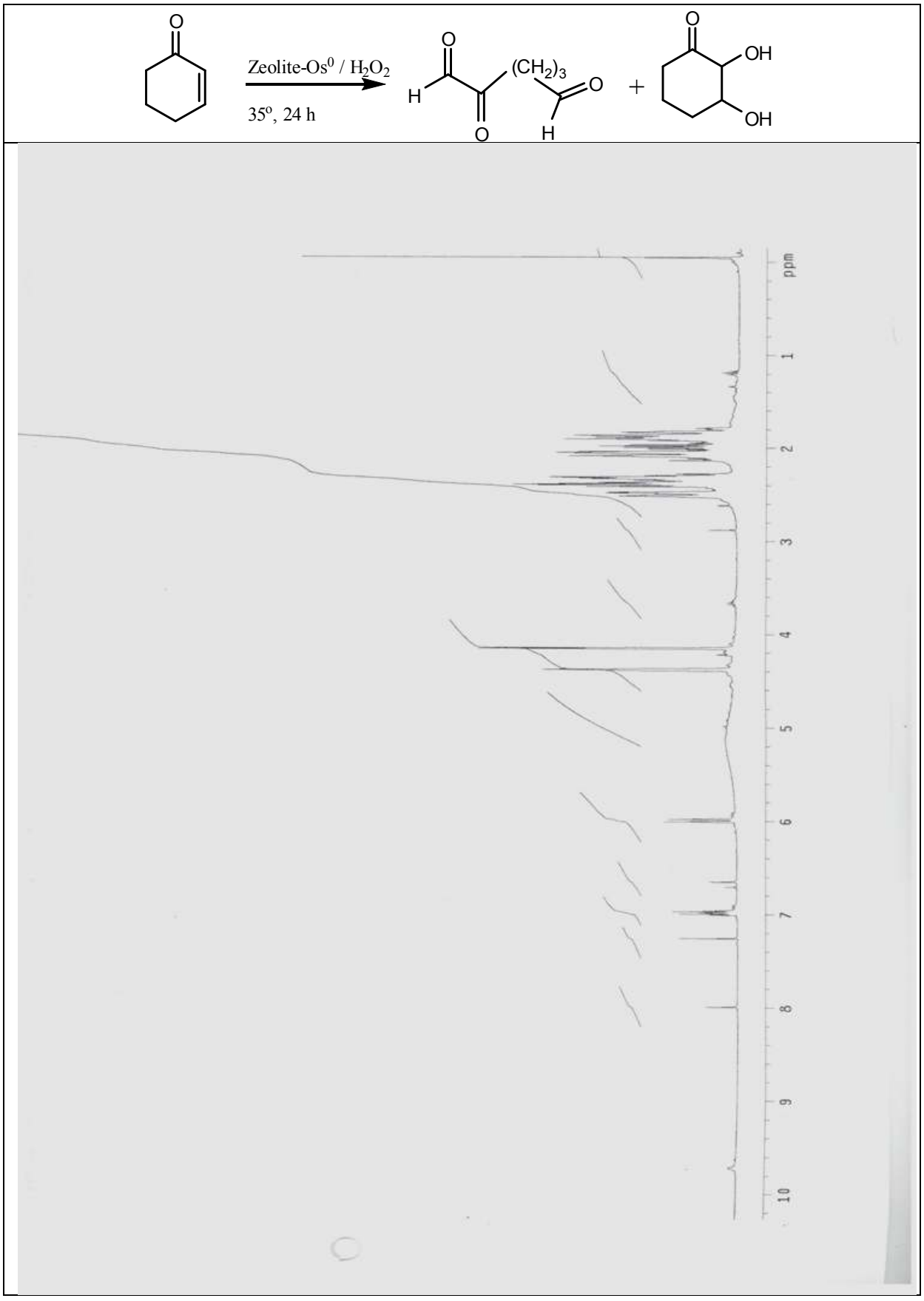


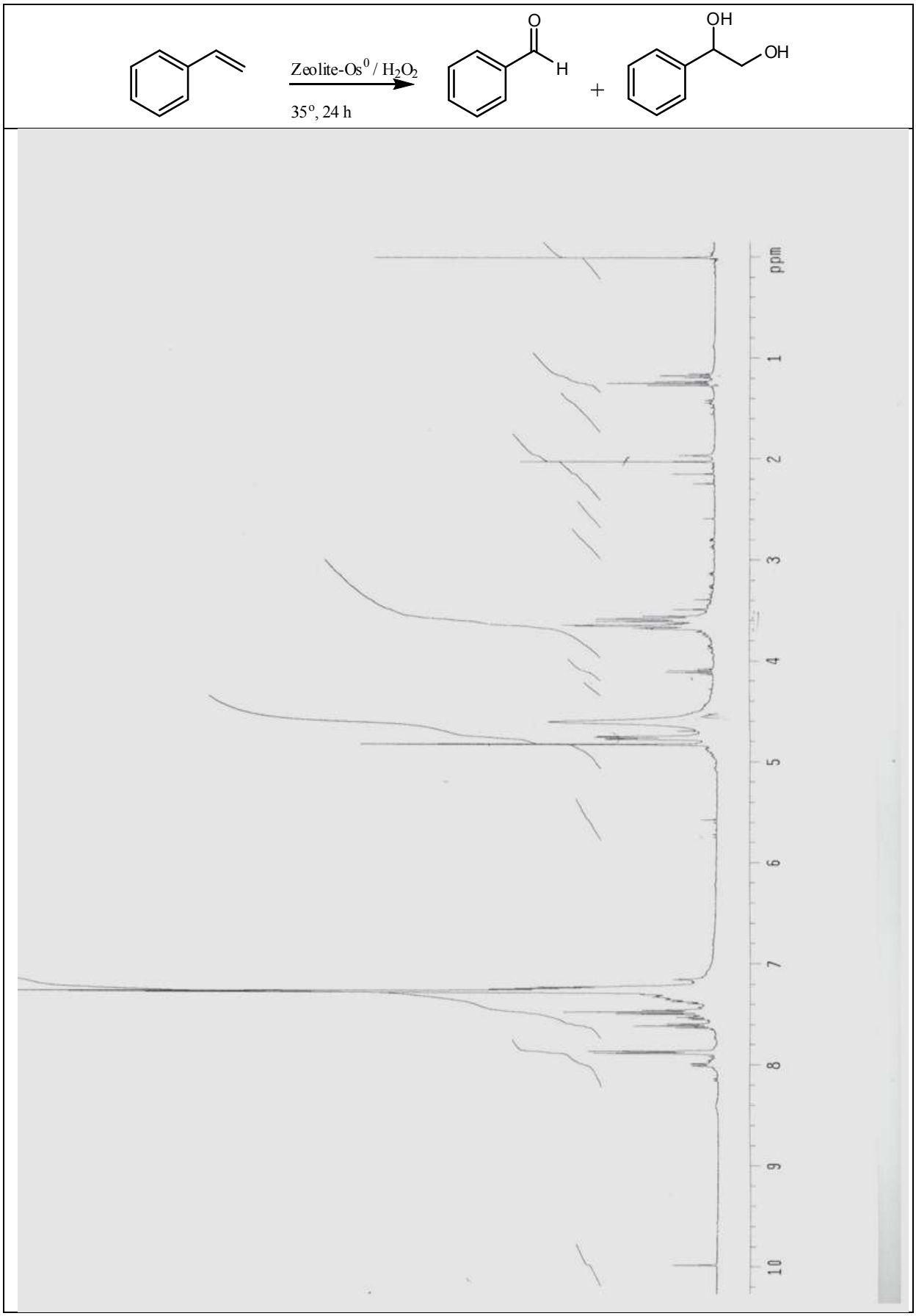
^{1}H-NMR spectra of the products obtained by catalytic dihydroxylation of olefins at different temperatures










Zeolite-Os^0 / H_2O_2
35°, 24 h
O
H
OH
OH
ppm
1
2
3
4
5
6
7
8
9
10