Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary material

Recyclable aluminium oxy-hydroxide supported Pd nanoparticles for selective hydrogenation of nitro compounds via sodium borohydride hydrolysis

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Table S1 Different methods in hydrogenation of 3-nitro phenol to 3-amino phenol

Catalyst	Reaction Condition	Time	Yield (%)	Refs
SAC[a]	Substrate (1 mmol), catalyst (300 mg), $NaBH_4$ (4 mmol), EtOH/H_2O (20 mL), 5 ^oC	4 h	87	1
G-PdCu	Substrate (1 mmol), catalyst (6 mg, 2 mol% Pd), $NaBH_4$ (2 mmol), EtOH/H_2O (3 mL), 50 ^oC	1.5 h	81	2
Ag-MPTA-1[b]	Substrate (0.2 mmol), catalyst (0.05 g), NaOH (0.5 mmol), iPrOH (20 mL), 80 ^oC, N_2 atmosphere	8 h	98	3
G-NiPd	Substrate (1 mmol), catalyst (4 mg), NH_3BH_3 (3 mmol), H_2O/MeOH (10 mL), RT	5 min	>99	4
SiO_2-Pd	Substrate (17.5 mmol), catalyst (5 μmol), H_2 (1 atm), H_2O (5 mL), 30 ^oC	12.5 h	100	5
MoS_2	Substrate (1 mmol), catalyst (0.1 mmol, 16 mg),$N_2H_4.H_2O$ (3 mmol), 60 ^oC	6 h	>99	6
Fe_3O_4@C@Pt	Substrate (0.25 mmol), catalyst (10 mg), H_2 (1 atm), EtOH (5 mL), RT	1 h	>99	7
Rh/C	Substrate (1 mmol), catalyst (0.1 mol%) ,$N_2H_4.H_2O$ (2 mmol), 60 ^oC	1 h	96	8
GO-Pt	Substrate (48.9 mmol), catalyst, H_2 (1 MPa), EtOH (30 mL), 40 ^oC	2 h	98	9
Pt/PICP[c]	Substrate (1 mmol), catalyst (0.5 mol%), H_2 (1 MPa), THF (2 mL), RT	3 h	99	10
Pd/AlO(OH)	**Substrate (1 mmol), catalyst (25 mg), $NaBH_4$ (3 mmol), H_2O/MeOH (1 mL), RT**	**1.15 min**	**>99**	**This study**

[a] Scrap automobile catalyst [b] Mesoporous poly-triallylamine [c] Porous ionic copolymer

Table S2 The reduction of some nitroarenes in the presence different commercial catalyst.

Catalyst	Substrate	Reaction Condition	Time	Yield (%)	Refs
Pd/C	Nitrobenzene	Substrate (17.5 mmol), catalyst (5 μmol), H_2 (1 atm), H_2O (5 mL), 30 ^oC	24 h	38	5
	4-bromo nitrobenzene	Substrate (1 mmol), catalyst (13 mg, 10 wt% mol% Pd), $N_2H_4.H_2O$ (10 mmol), MeOH (5 mL), 80 ^oC	5 min.	92	11
	Nitrobenzene	Substrate (5 mmol), catalyst (5 mol%), 1,4-cyclohexadiene (6 equiv), MeOH (10 mL), MW, 120 ^oC	5 min.	70	12
	Nitrobenzene	Substrate (1 mmol), catalyst (15 mg), $B_{10}H_{14}$ (10 mg), MeOH (5 mL), AcOH (two drops), N_2 atmosphere, reflux	1.5 h	90	13
Fe_3O_4	3-nitroaniline	Substrate (1 mmol), catalyst (0.003 mmol), $NaBH_4$, RT	5 min.	12	14
$Cu(Acac)_2$	3-nitroaniline	Substrate (1 mmol), catalyst (0.003 mmol), $NaBH_4$, RT	5 min.	69	14

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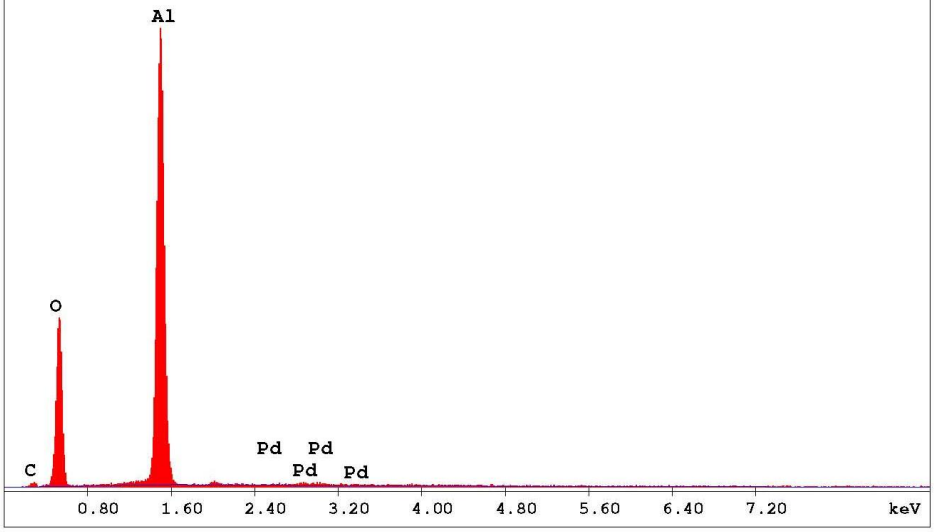
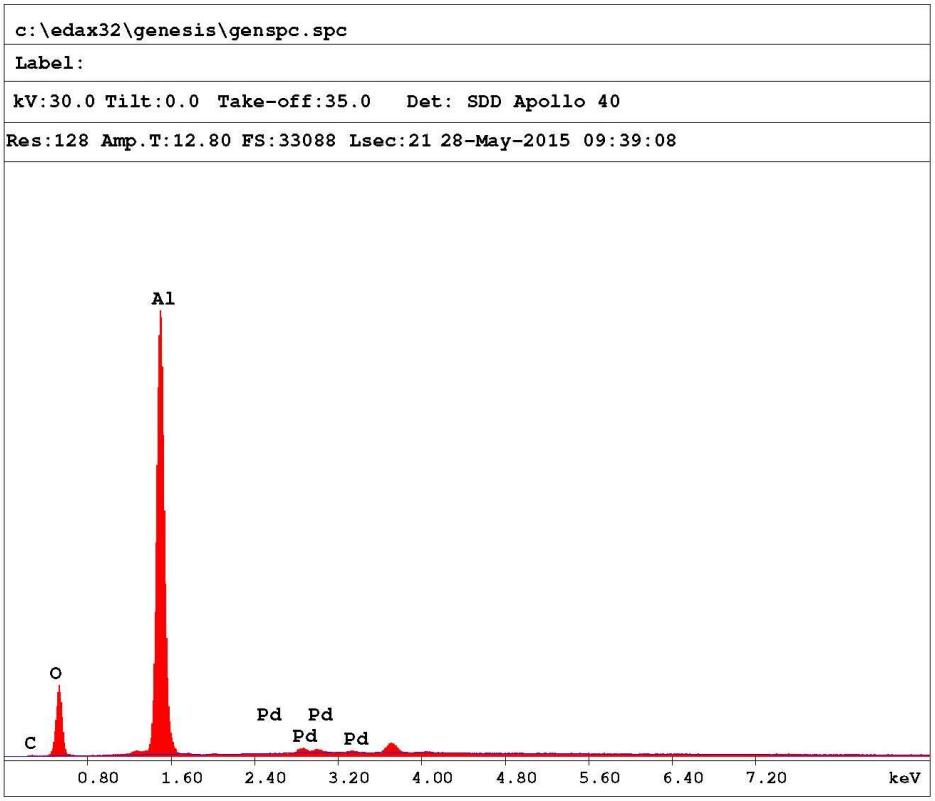


EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
C K	3.99	6.78	0.0056	1.0573	0.1336	1.0005
O K	40.98	52.28	0.1469	1.0396	0.3446	1.0008
AlK	53.80	40.70	0.4009	0.9681	0.7696	1.0001
PdL	1.23	0.24	0.0091	0.7855	0.9411	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	29.75	3.63	9.75	8.19
O K	1345.90	7.27	1.31	185.19
AlK	4695.44	31.80	0.70	147.67
PdL	31.34	29.53	14.46	1.06

Figure S1 EDX spectrum before the reaction of Pd/AlO(OH) NPs.



EDAX ZAF Quantification (Standardless)
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Element	Wt %	At %	K-Ratio	Z	A	F
C K	2.31	4.18	0.0028	1.0593	0.1133	1.0005
O K	33.18	45.18	0.0881	1.0444	0.2540	1.0011
AlK	62.10	50.14	0.3993	0.9782	0.6570	1.0003
PdL	2.41	0.49	0.0161	0.8146	0.8217	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	12.80	5.17	8.18	2.48
O K	897.87	9.53	0.73	94.26
AlK	7671.30	49.33	0.25	155.50
PdL	94.55	97.86	3.92	0.97

Figure S2 EDX spectrum after using ten times of Pd/AlO(OH) NPs.

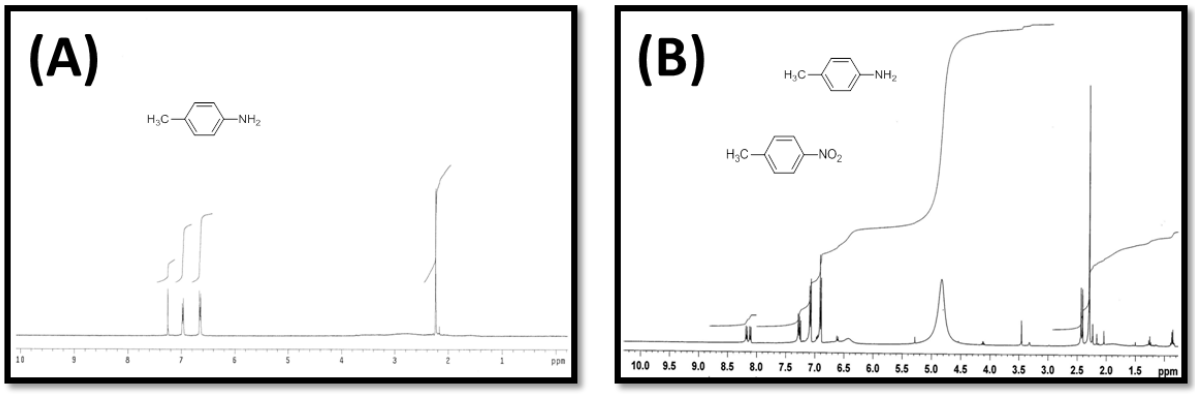


Figure S3 [1]H-NMR spectra of 1-methyl-4-aminobenzene (A) The reduction in the presence of Pd/C; (B) The reduction in the presence of PdAlO(OH) NPs.

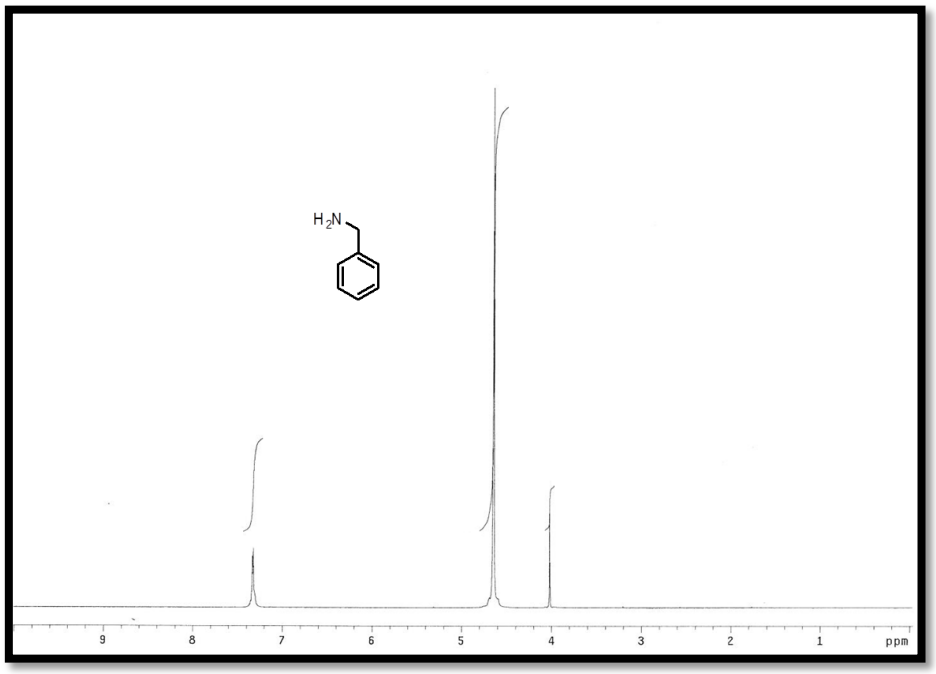
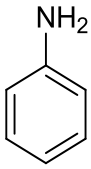


Figure S4 [1]H-NMR spectrum of the phenylmethanamine.

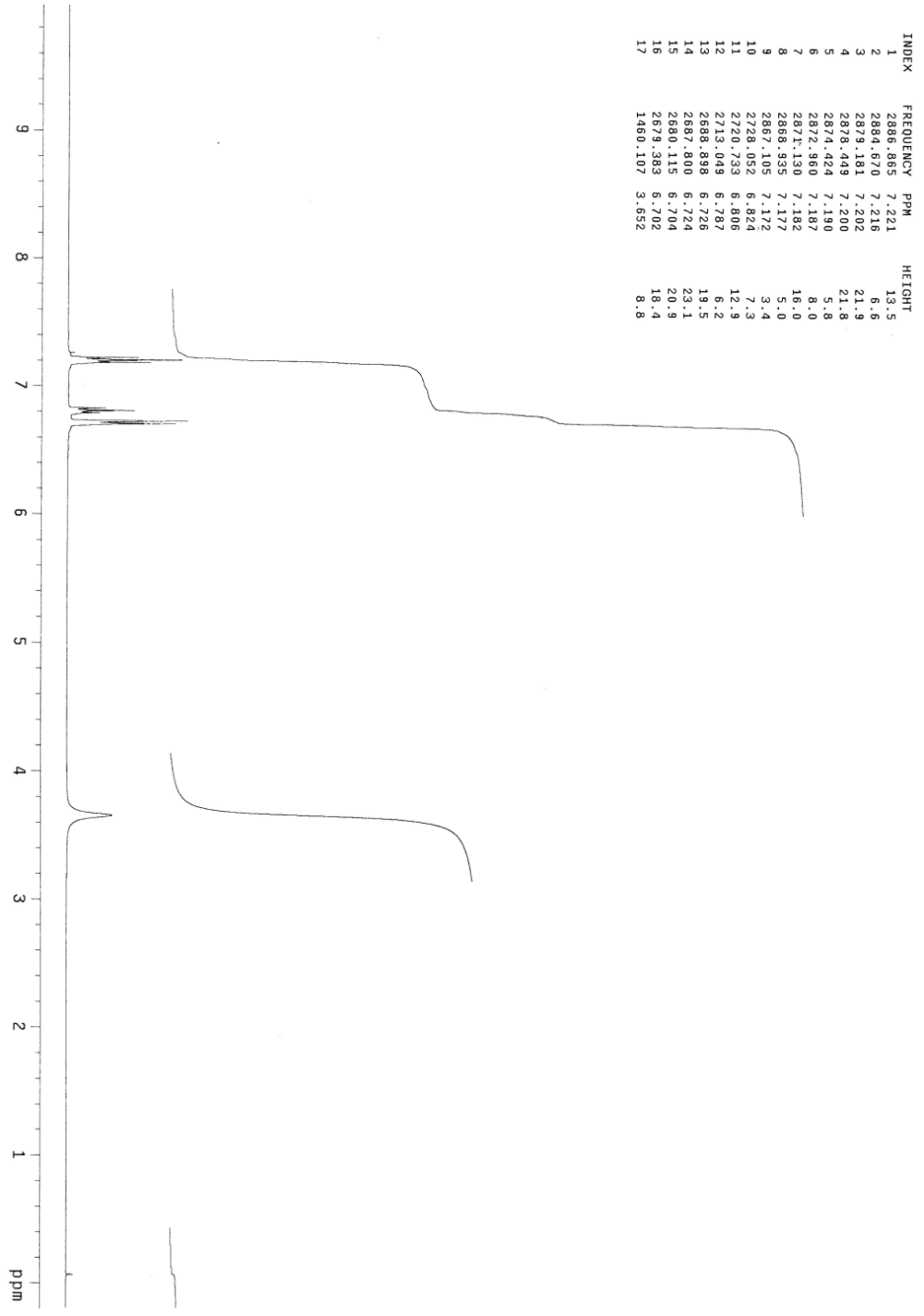
References

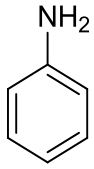
1. H. Genc, *Catal. Commun*., 2015, **67**, 64-67.
2. Y.-S. Feng, J.-J. Ma, Y.-M. Kang and H.-J. Xu, *Tetrahedron*, 2014, **70**, 6100-6105.
3. N. Salam, B. Banerjee, A. S. Roy, P. Mondal, S. Roy, A. Bhaumik and Sk. M. Islam, *Appl. Catal. A,* 2014, **477**, 184-194.
4. H. Goksu, S. F. Ho, O. Metin, K. Korkmaz, A. M. Garcia, M. S. Gultekin and S. Sun, *ACS Catal.*, 2014, **4**, 1777-1782.
5. J. Li, X.-Y. Shi, Y.-Y. Bi, J.-F. Wei and Z.-G. Chen, *ACS Catal*., 2011, **1**, 657-664.
6. L. Huang, P. Luo, M. Xiong, R. Chen, Y. Wang, W. Xing and J. Huang, *Chin. J. Chem*., 2013, **31**, 987-991.
7. M. Xie, F. Zhang, Y. Long and J. Ma, *RSC Adv*., 2013, **3**, 10329-10334.
8. P. Luo, K. Xu, R. Zhang, L. Huang, J. Wang, W. Xing and J. Huang, *Catal. Sci. Technol*., 2012, **2**, 301-304
9. R. Nie, J. Wang, L. Wang, Y. Qin, P. Chen and Z. Hou, *Carbon*, 2012, **50**, 586-596.
10. K. Xu, Y. Zhang, X. Chen, L. Huang and R. Zhang, *Adv. Synth. Catal*. 2011, **353**, 1260-1264.
11. F. Li, B. Frett and H. Li, *Synlett*, 2014, **25**, 1403-1408.
12. J. F. Quinn, C. E. Bryant, K. C. Golden and B. T. Gregg, *Tetrahedron Letters*, 2010, **51**, 786-789.
13. J. W. Bae, Y. J. Cho, S. H. Lee and C. M. Yoon, *Tetrahedron Lett*., 2000, **41**, 175-177.
14. R. K. Sharma, Y. Monga, A. Puri, *J. Mol. Catal. A: Chem*., 2014, **393**, 84-95.

^{1}H-NMR and ^{13}C-NMR spectra and spectral data for the amine products

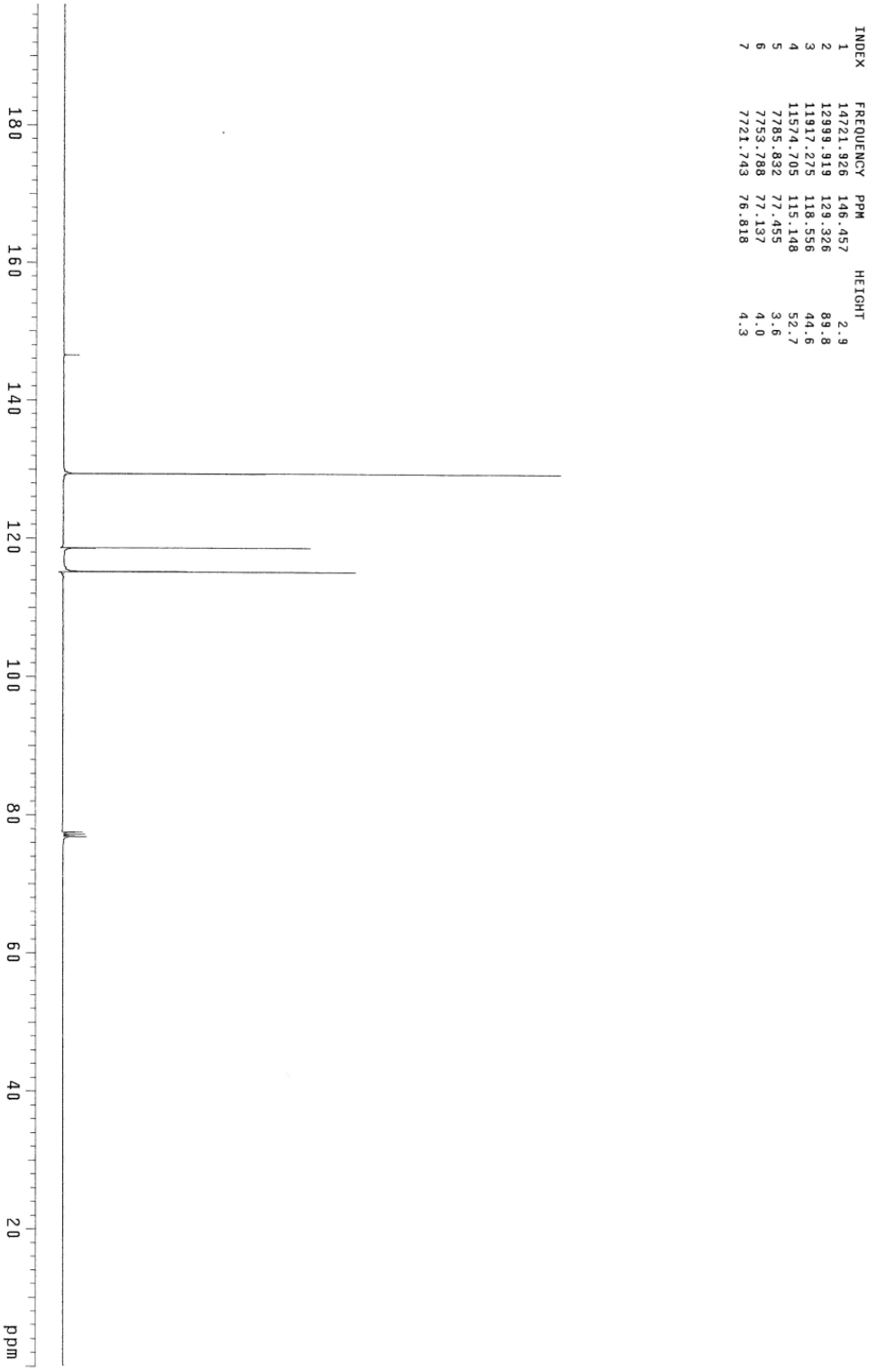


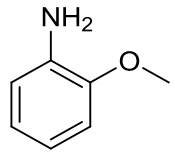
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, J = 9.0 Hz, 2H), 6.80 (t, J = 9.0 Hz, 1H), 6.72 (d, J = 9.0 Hz, 2H), 3.64 (s, 2H).



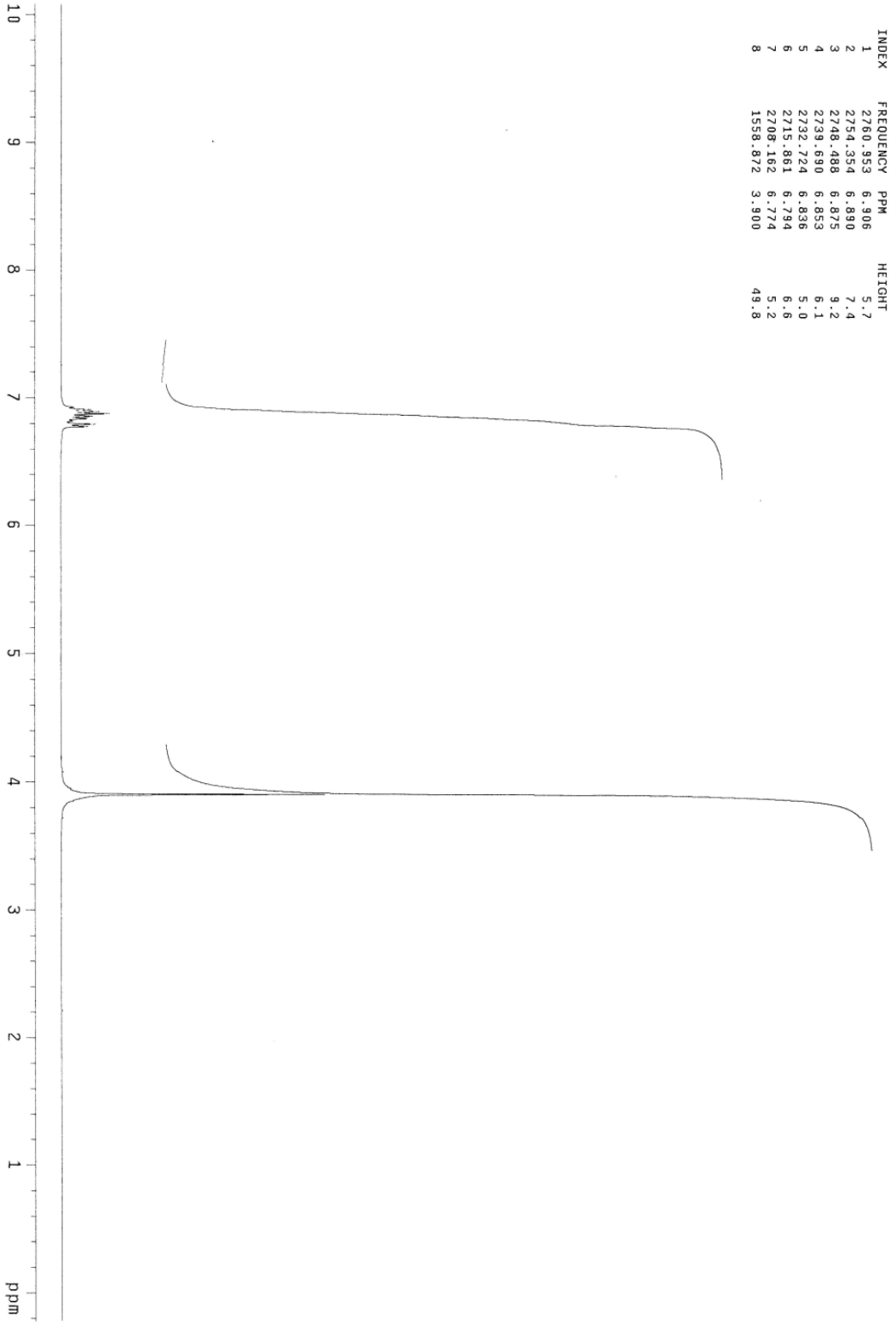


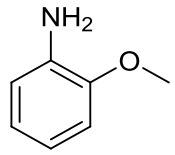
^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 129.3, 118.5, 115.1.



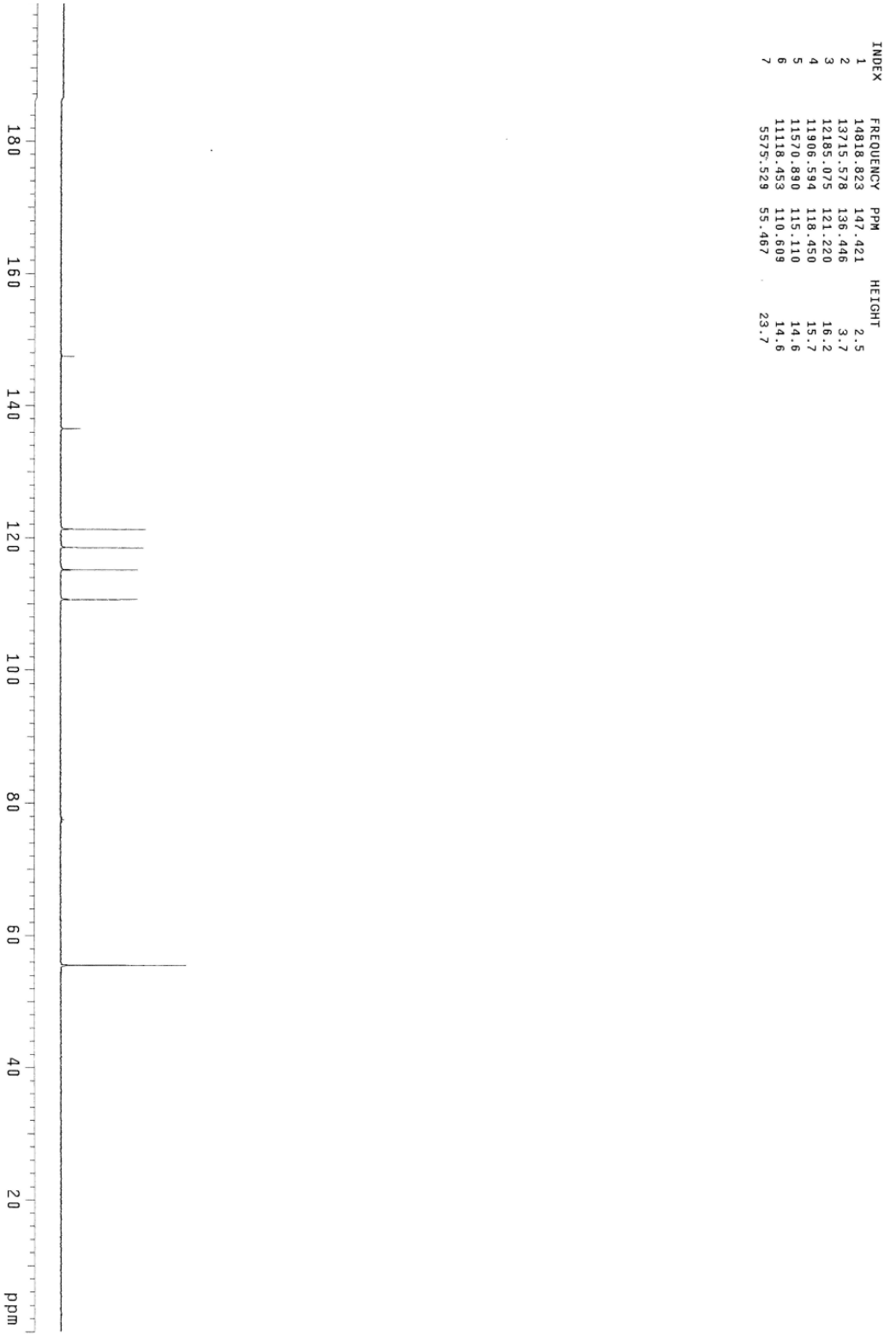


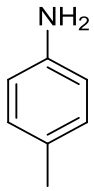
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90-6.77 (m, 4H), 3.90 (s, 3H).



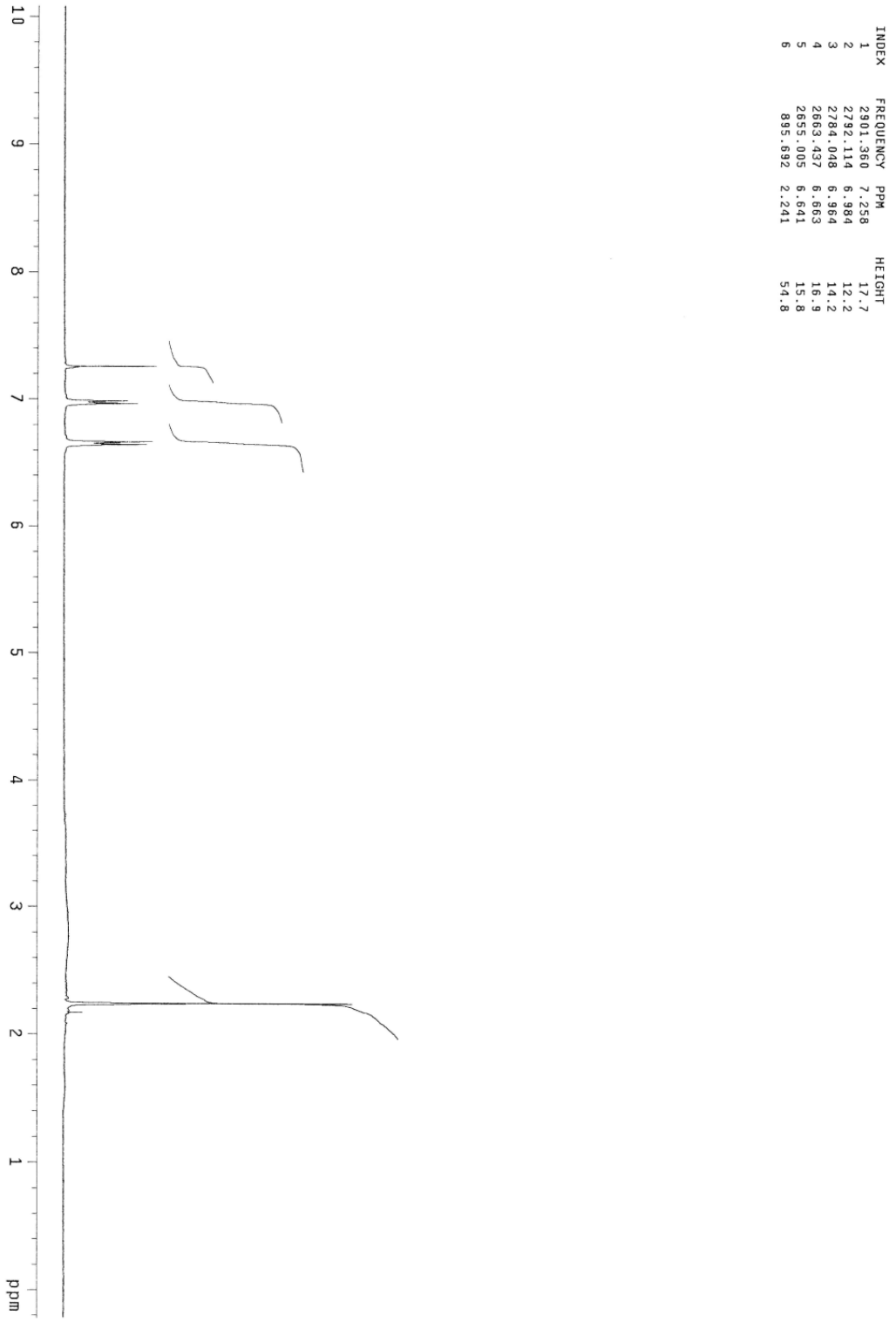


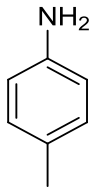
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 136.4, 121.2, 118.4, 115.1, 110.6, 55.5.



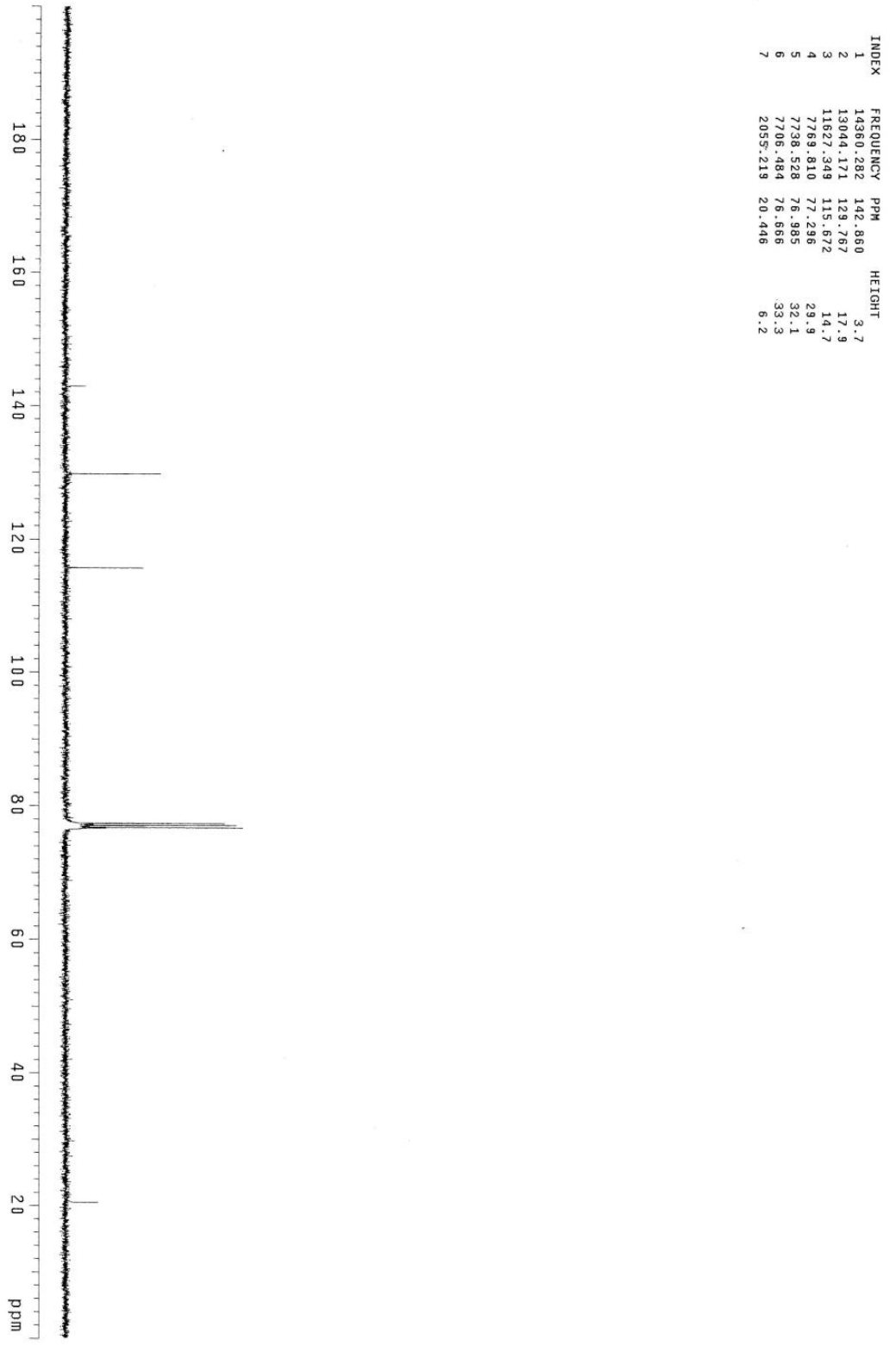


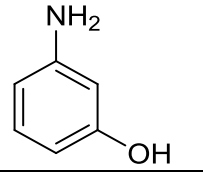
^{1}H NMR(400 MHz, $CDCl_3$) δ 6.98 (d, J = 7.9 Hz, 2H), 6.65 (d, J = 8.3 Hz,2H), 2.24 (s, 3H).



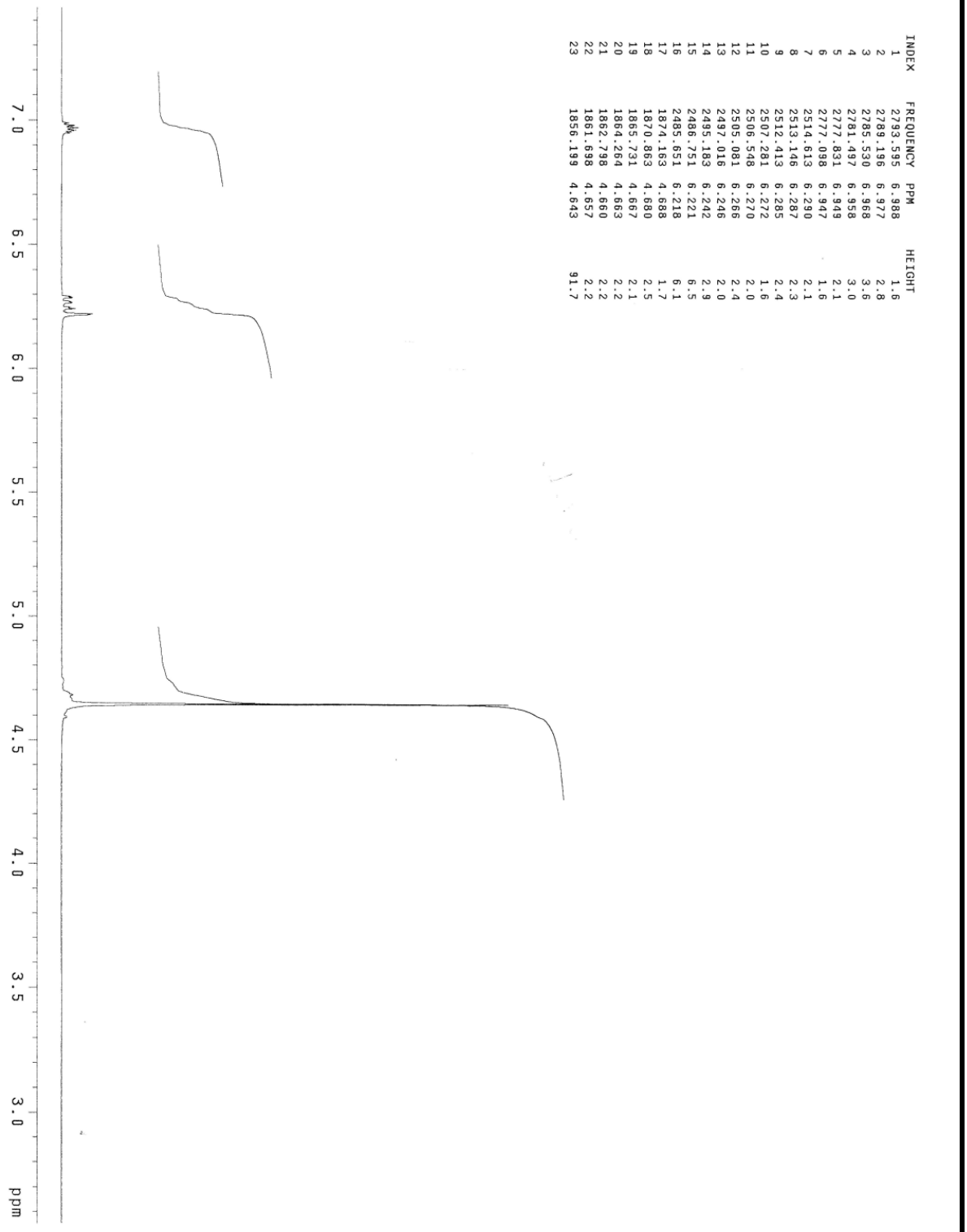


^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 129.7, 127.8, 115.7, 20.4.





^{1}H NMR (400 MHz, D_2O) δ 6.96 (m, 1H), 6.26 (m, 3H).



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5	2777.831	6.949	2.1
6	2777.098	6.947	1.6
7	2514.613	6.290	2.1
8	2513.146	6.287	2.3
9	2512.413	6.285	2.4
10	2507.281	6.272	1.6
11	2506.548	6.270	2.0
12	2505.081	6.266	2.4
13	2497.016	6.246	2.0
14	2495.183	6.242	2.9
15	2486.751	6.221	6.5
16	2485.651	6.218	6.1
17	1874.163	4.688	1.7
18	1870.863	4.680	2.5
19	1865.731	4.667	2.1
20	1864.264	4.663	2.2
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22	1861.698	4.657	2.2
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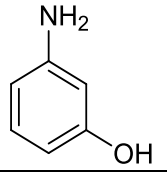
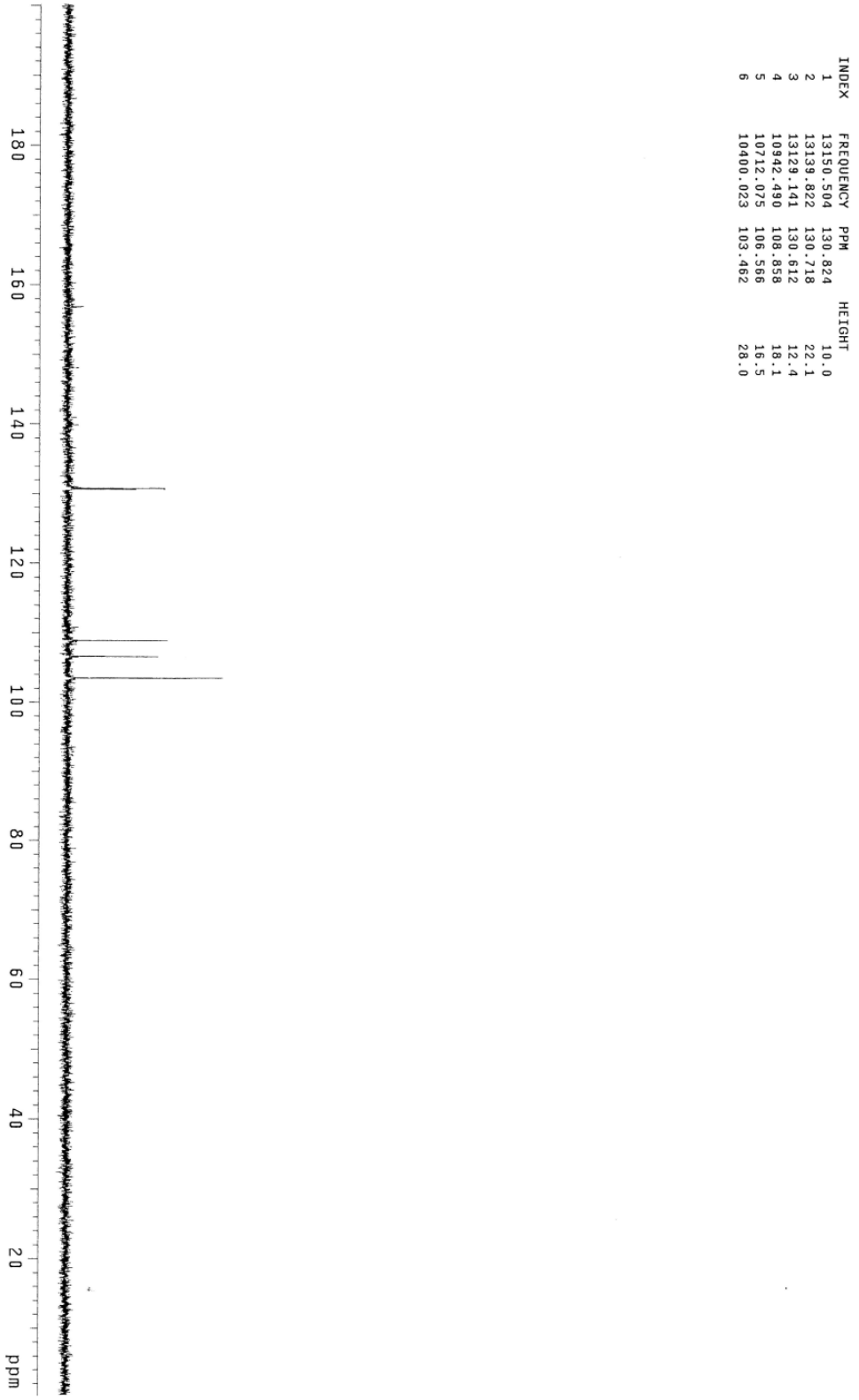
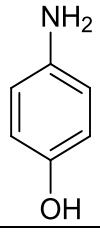
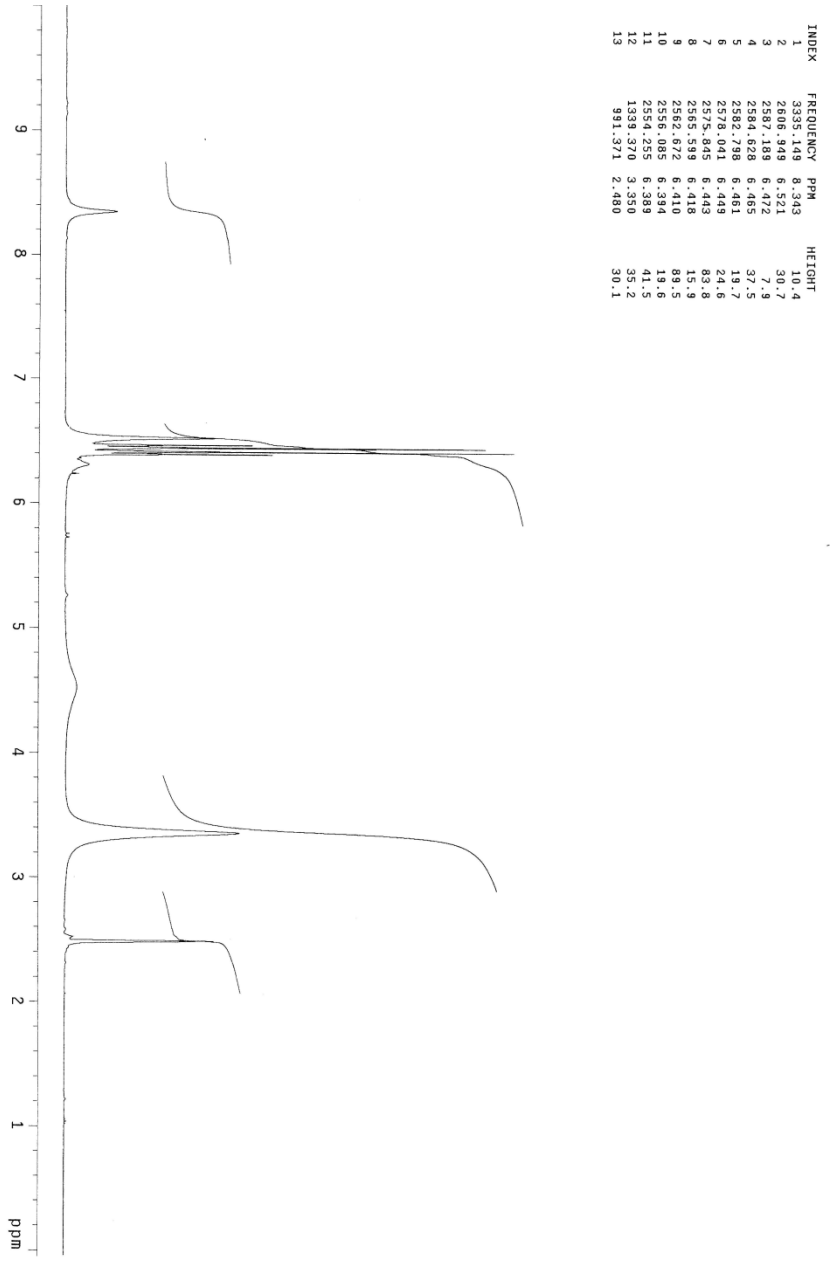


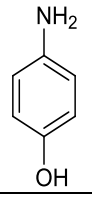
^{13}C NMR (100 MHz, D_2O) δ 130.8, 130.7, 130.6, 108.8, 106.6, 103.5



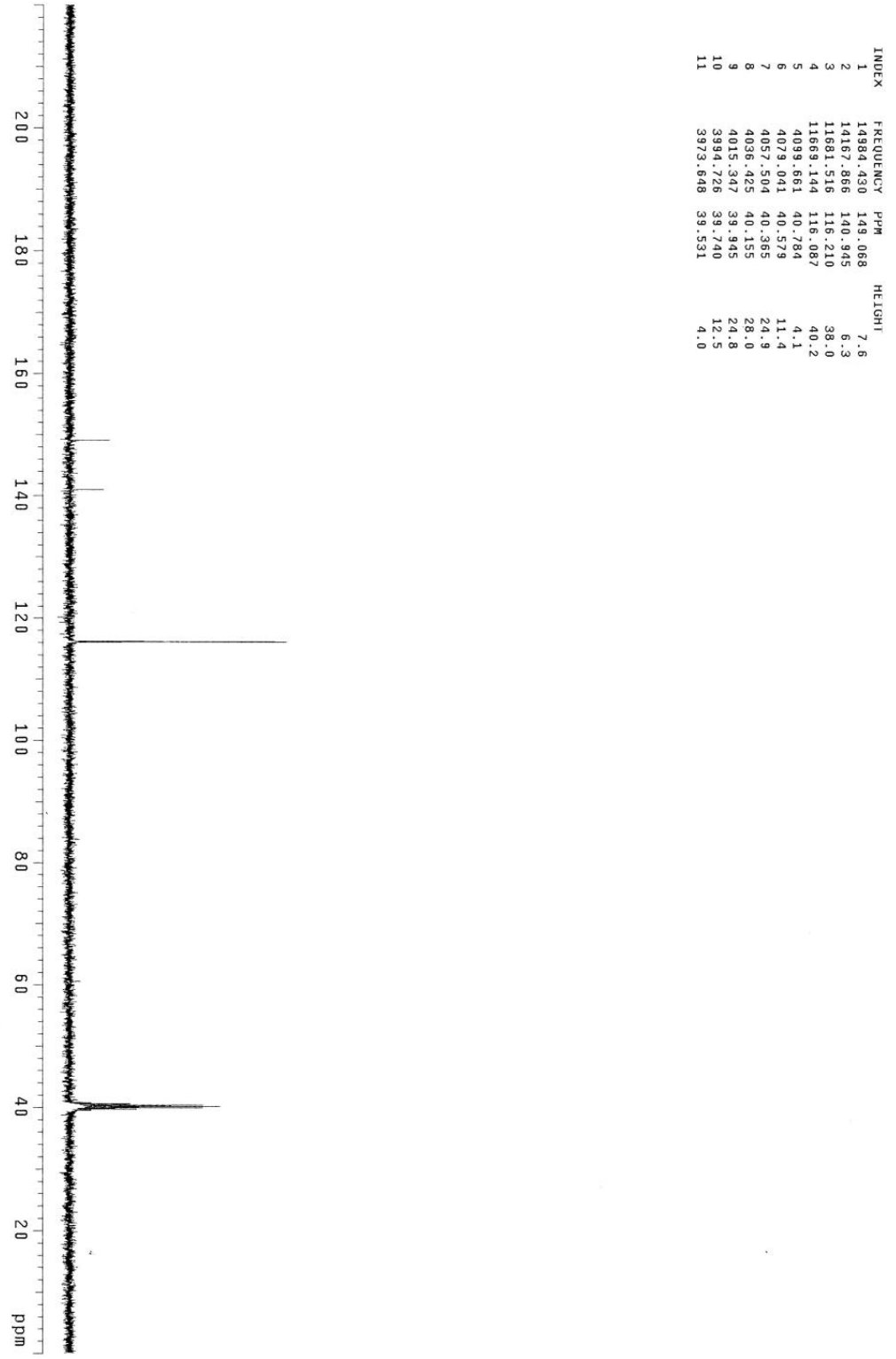


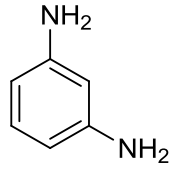
^{1}H NMR (400 MHz, DMSO) δ 8.34 (s, 1H), 6.46 (d, J = 8.7 Hz, 2H), 6.39 (d, J = 8.7 Hz, 2H).



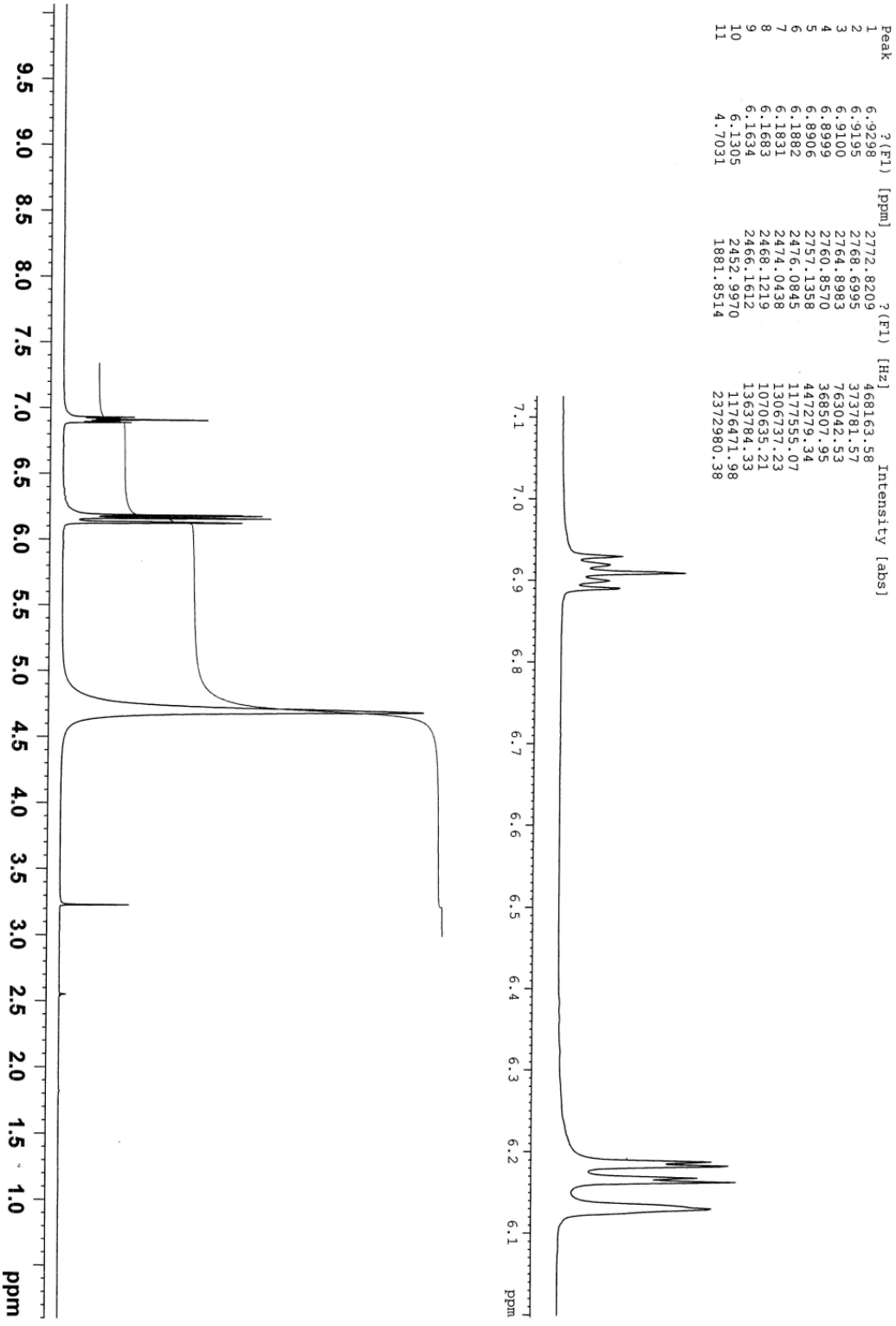


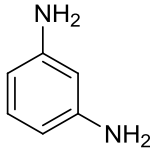
^{13}C NMR (100 MHz, DMSO) δ 149.1, 140.9, 116.2, 116.1.



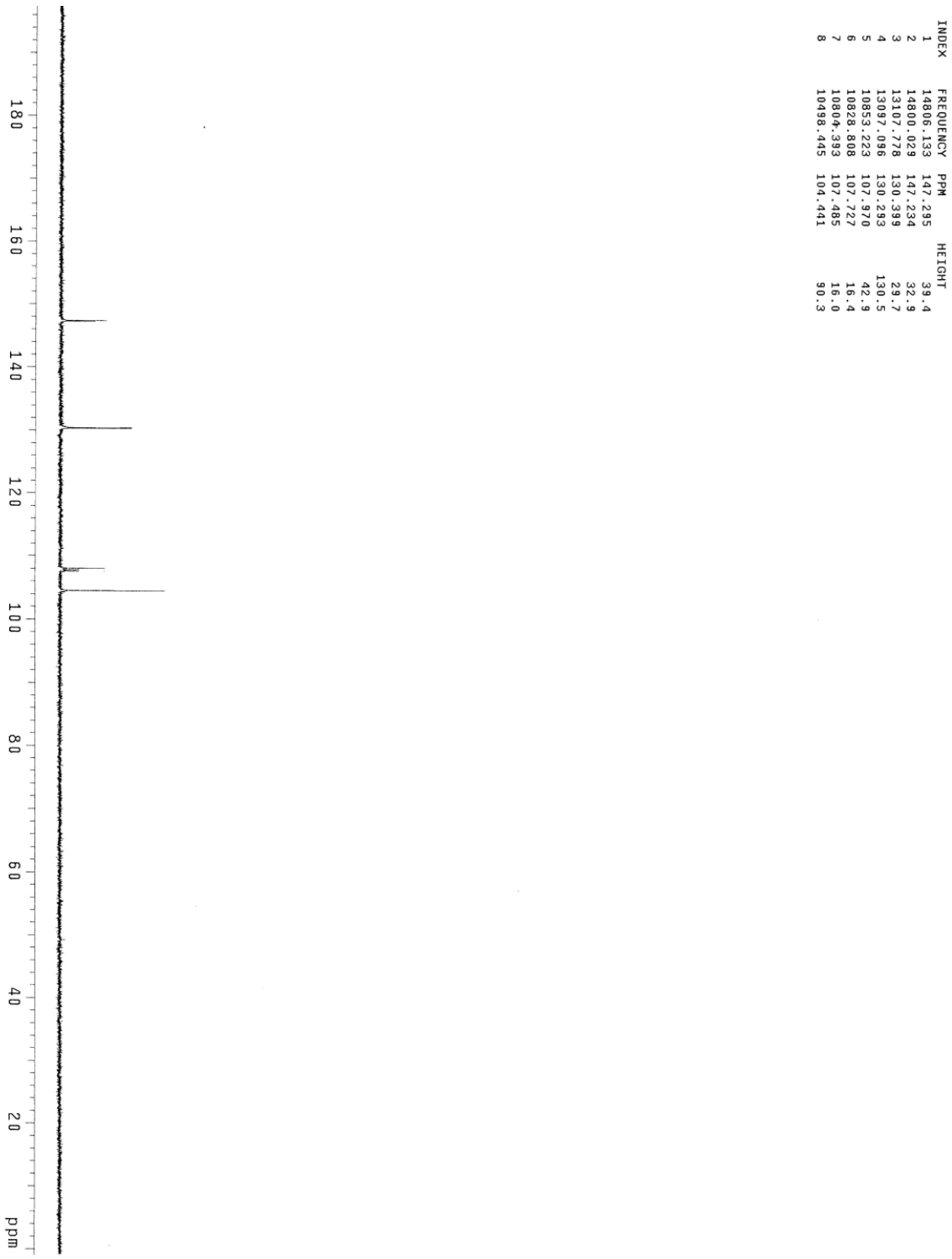


^{1}H NMR (400 MHz, D_2O) δ 6.91 (m, 1H), 6.17 (dd, J = 7.9, 2.0 Hz, 2H), 6.13 (s, 1H).





^{13}C NMR (100 MHz, D_2O) δ 147.2, 130.4, 130.3, 104.4.



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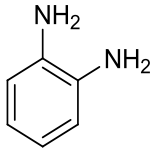
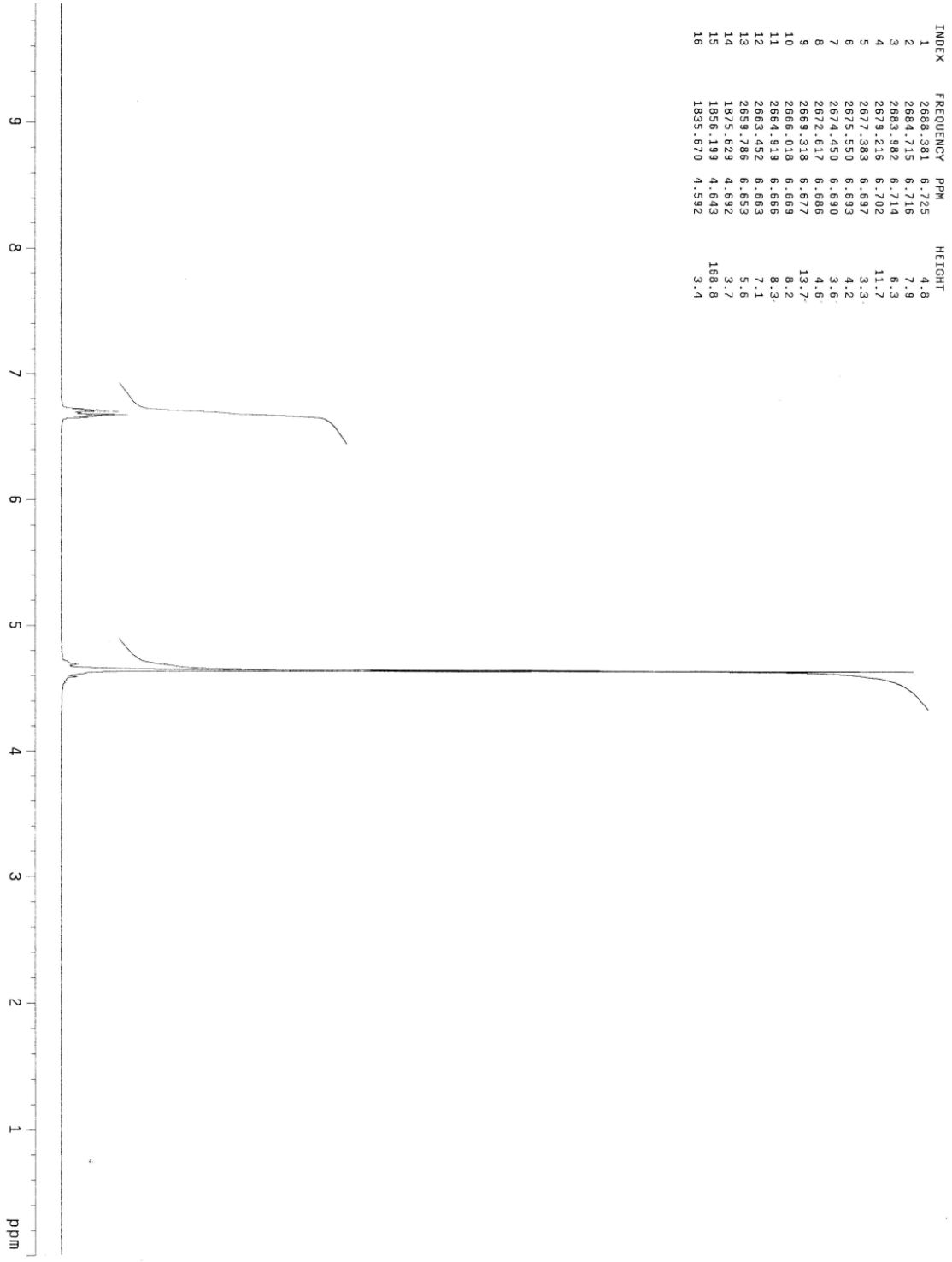
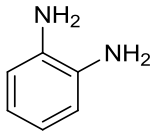
4	13097.096	130.293	130.5
5	10853.223	107.970	42.9
6	10828.808	107.727	16.4
7	10804.393	107.485	16.0
8	10498.445	104.441	90.3

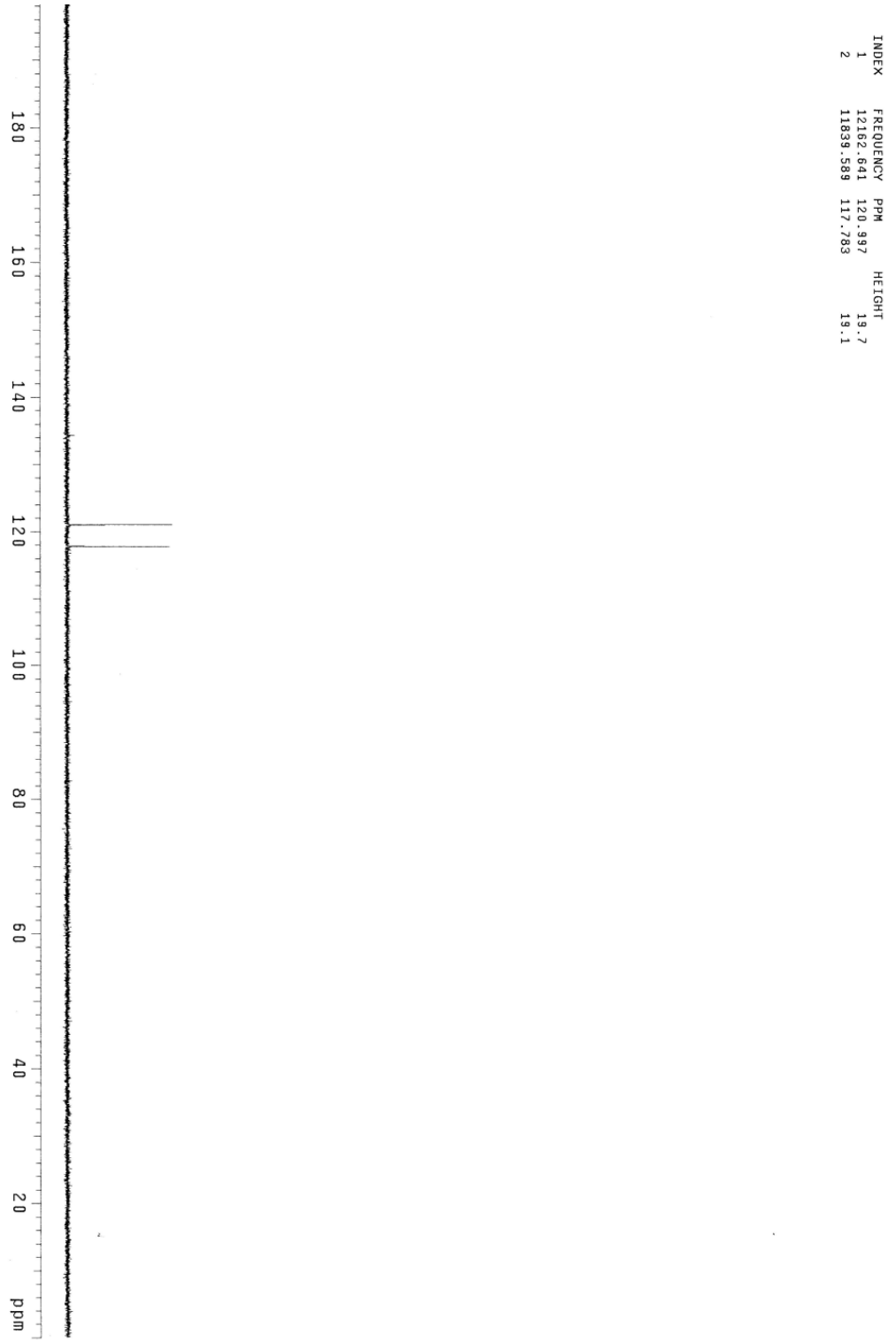


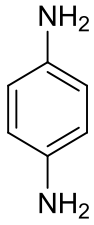
^{1}H NMR (400 MHz, D_2O) δ 6.72-6.65 (m, 4H).



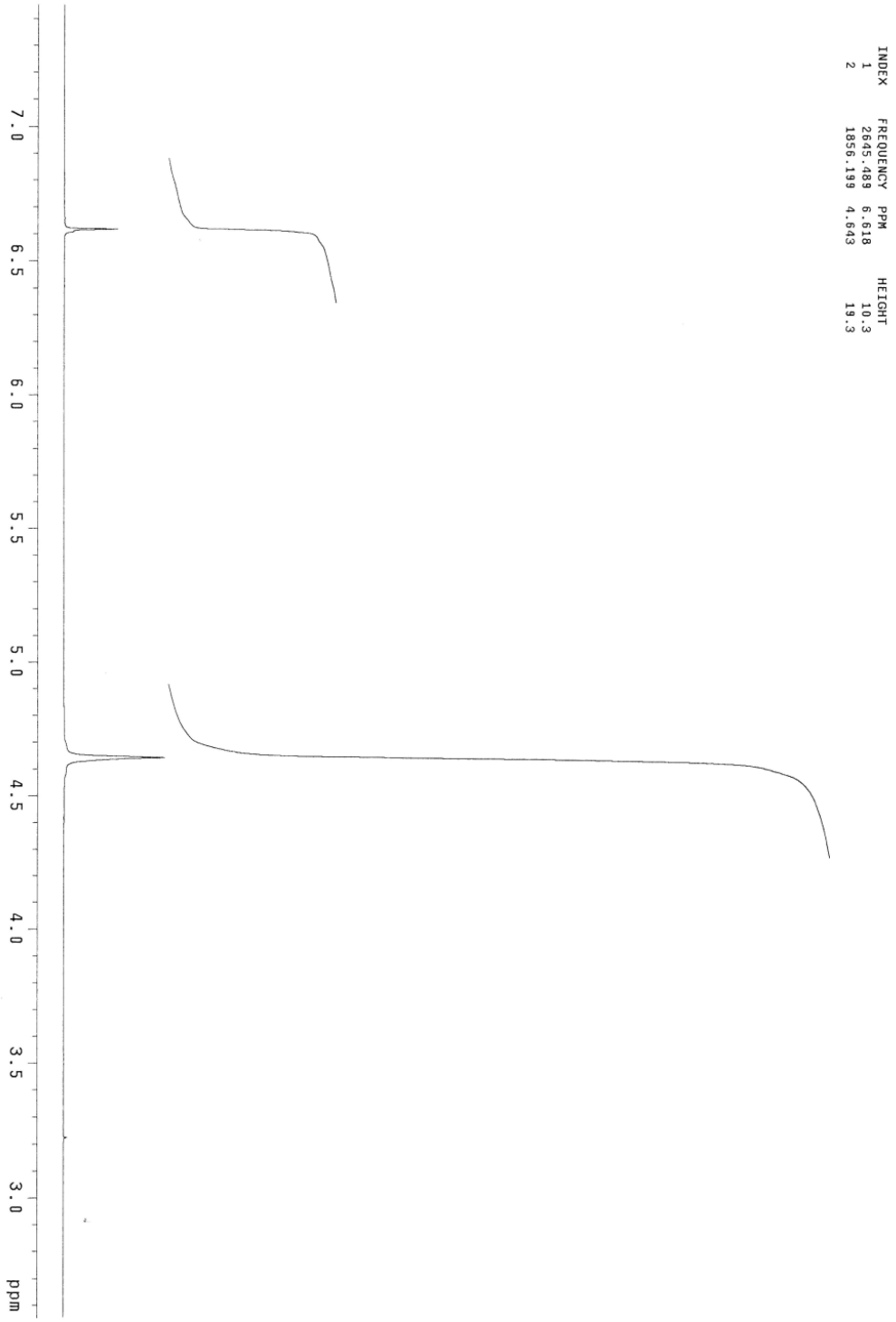


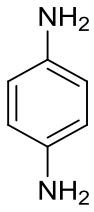
^{13}C NMR (100 MHz, D_2O) δ 134.2, 120.9, 117.8



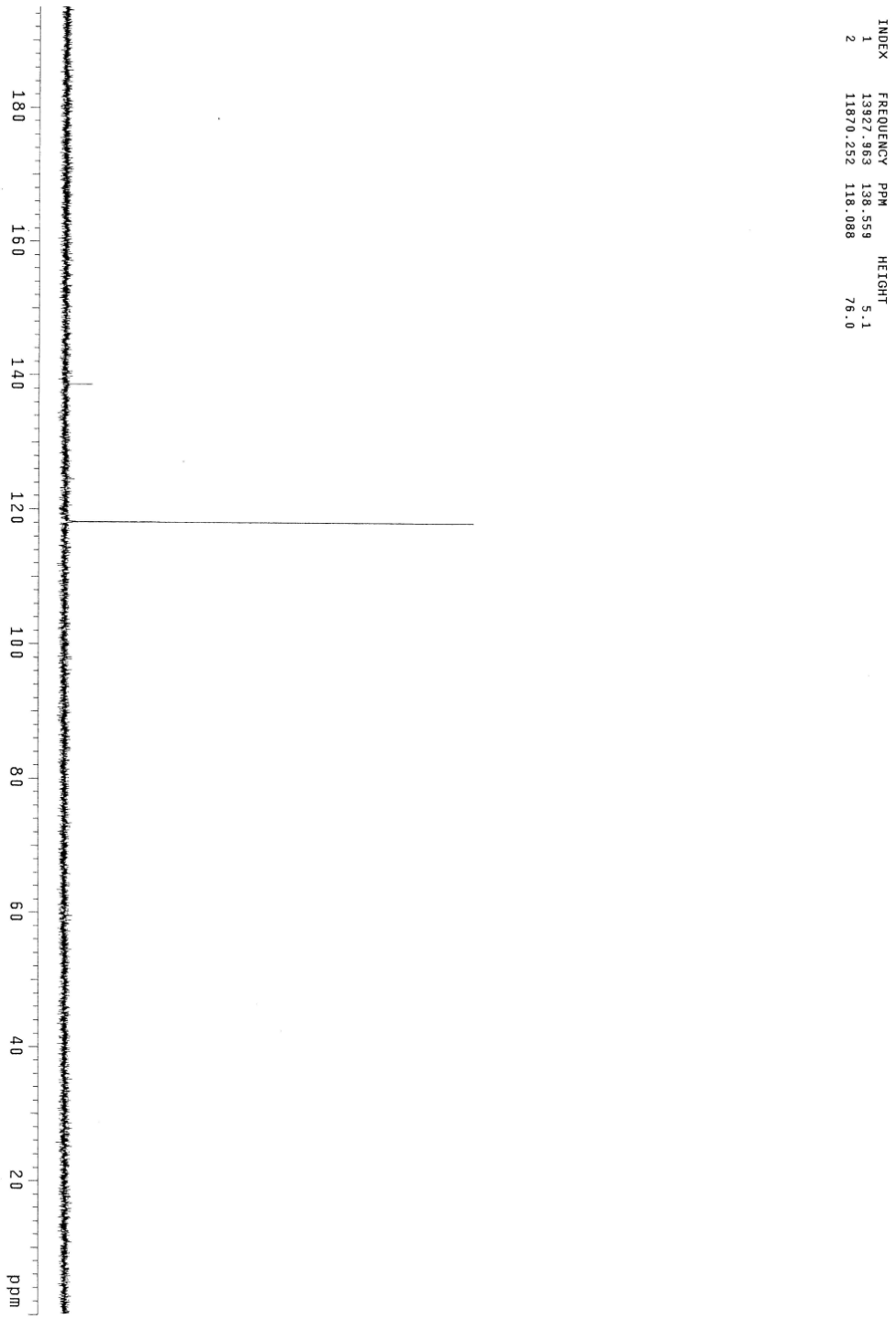


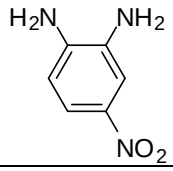
^{1}H NMR (400 MHz, D_2O) δ 6.62 (s, 4H), 4.64 (s, 4H).



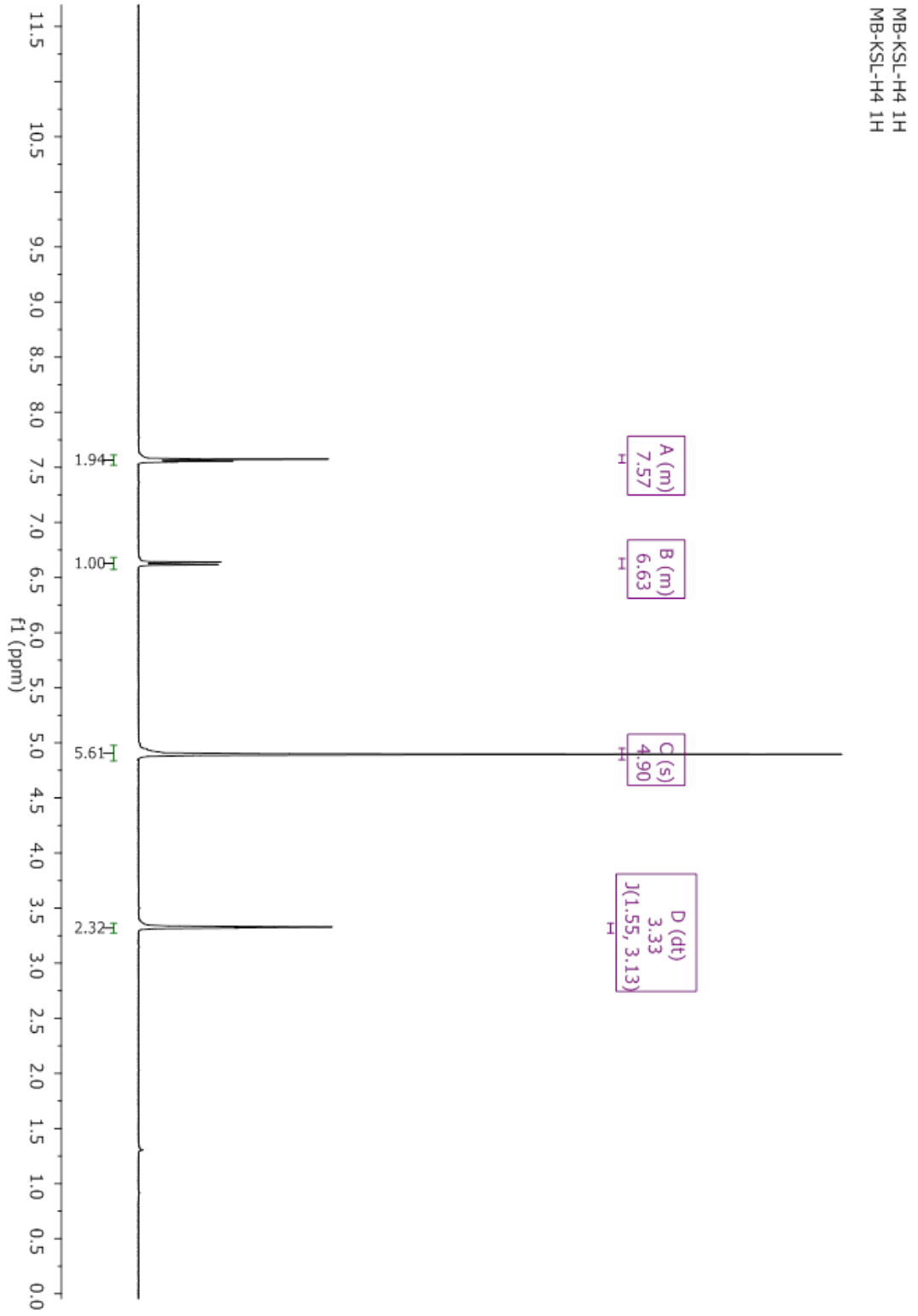


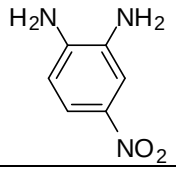
^{13}C NMR (100 MHz, D_2O) δ 138.6, 118.1.



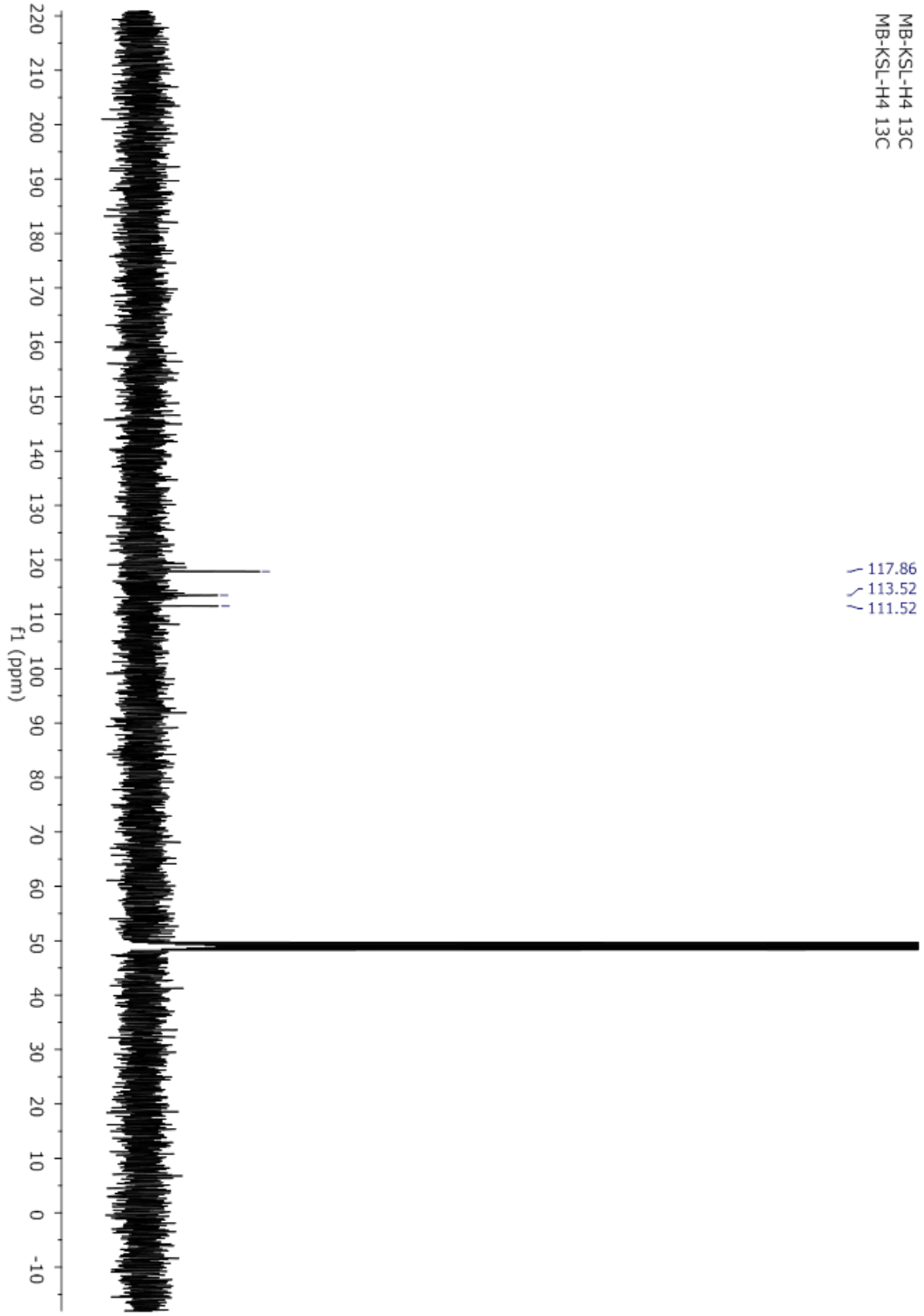


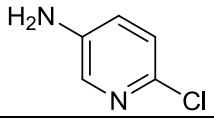
^{1}H NMR (400 MHz, CD_3OD) δ 7.57 (m, 2H), 6.63 (m, 1H), 4.90 (s, 4H).



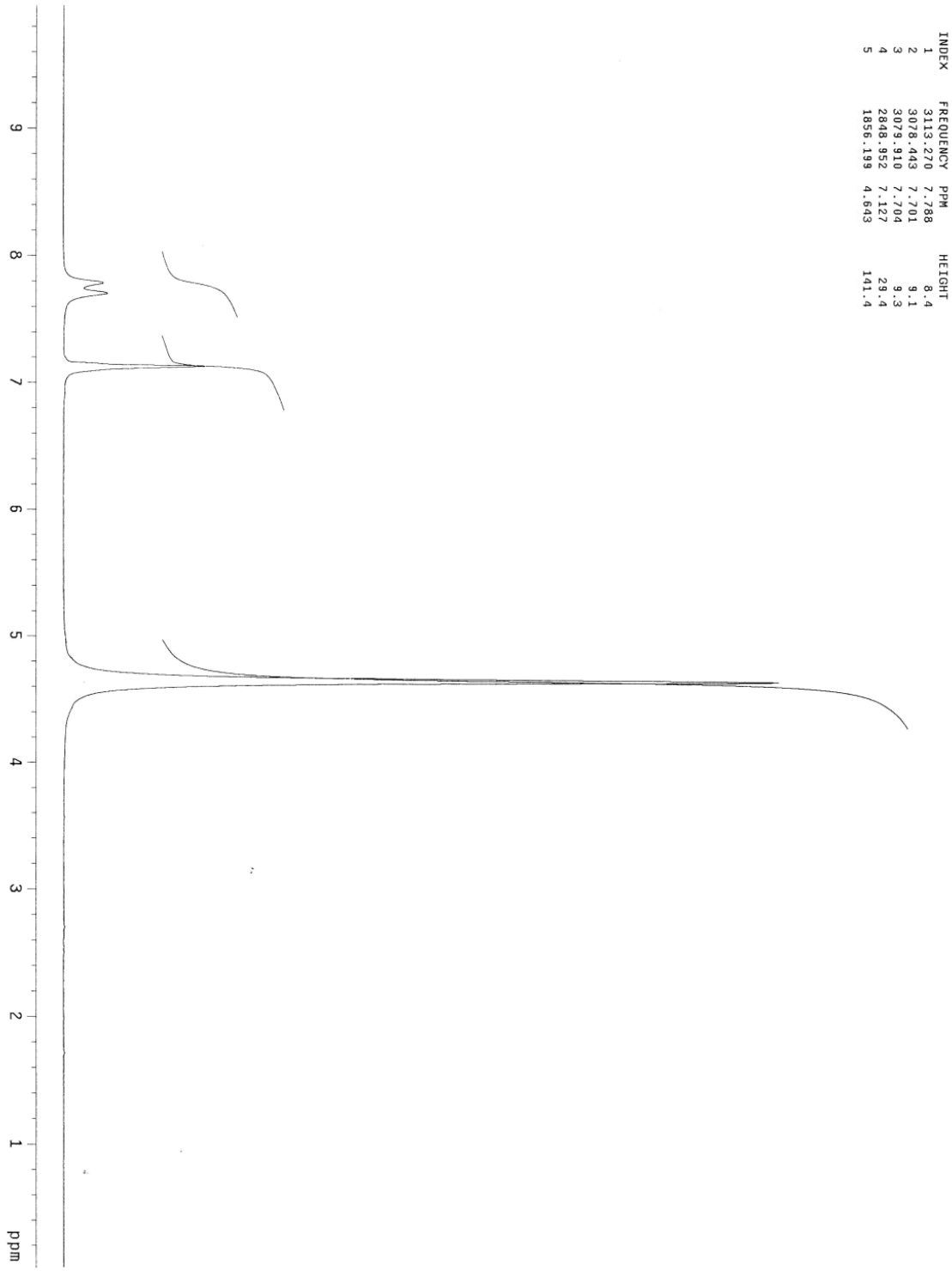


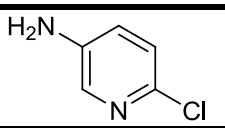
^{13}C NMR (100 MHz, CD_3OD) δ 142.3, 138.6, 137.1, 117.9, 113.5, 111.5.



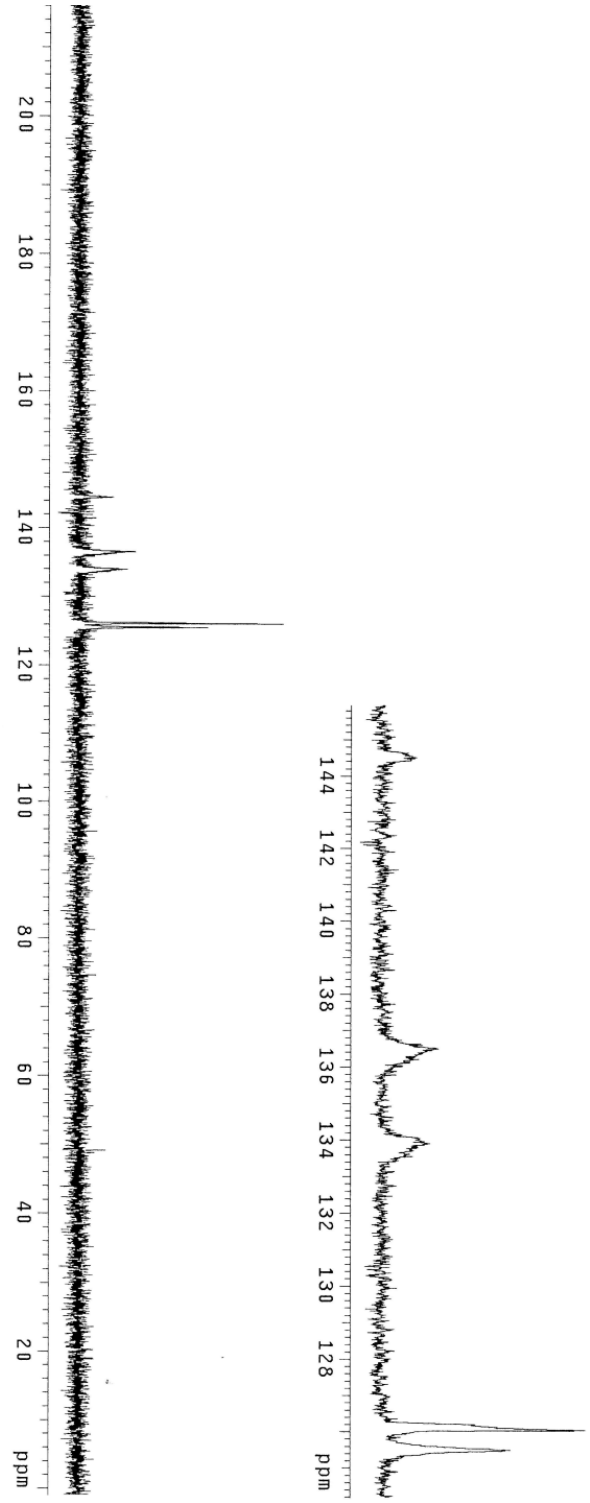


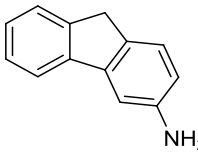
^{1}H NMR (400 MHz, D_2O) δ 7.74 (d, J = 2.9 Hz, 1H), 7.13 (bs, 2H).



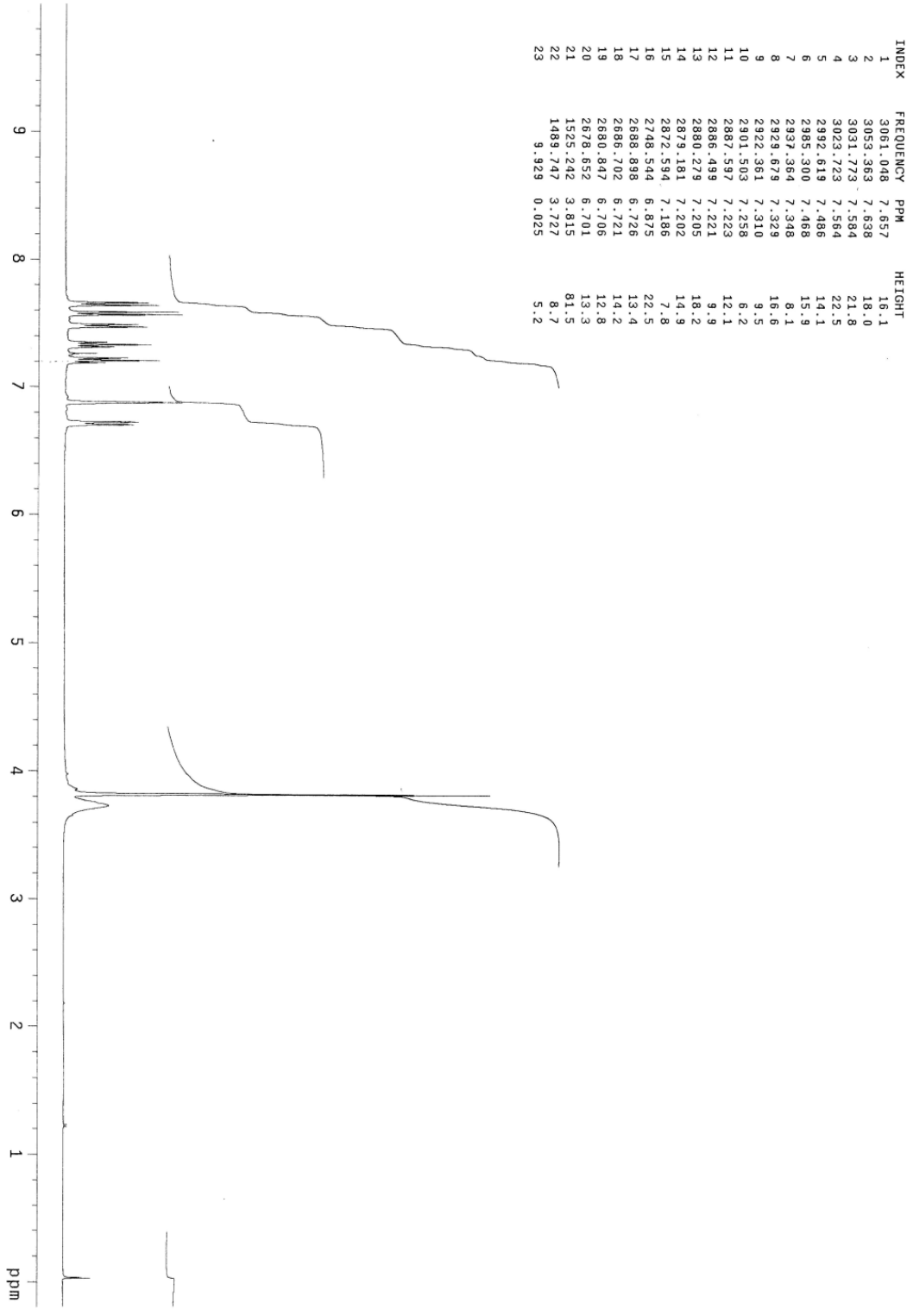


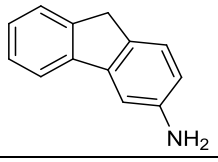
^{13}C NMR (100 MHz, D_2O) δ 144.5, 136.5, 133.9, 126.0, 125.5.



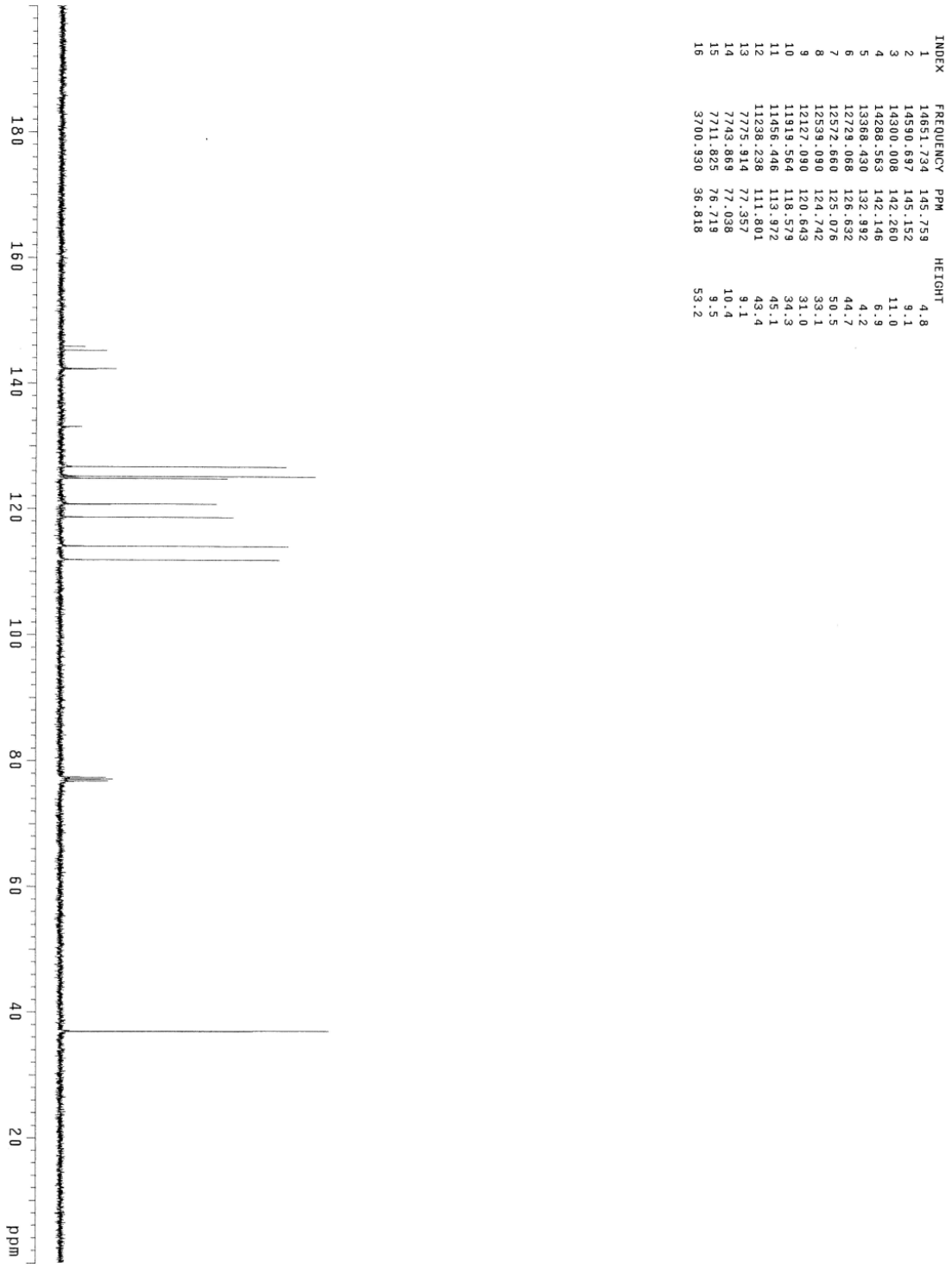


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 6.87 (s, 1H), 6.71 (dd, J = 8.1, 2.2 Hz, 1H), 3.72 (s, 2H).

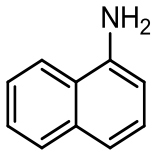




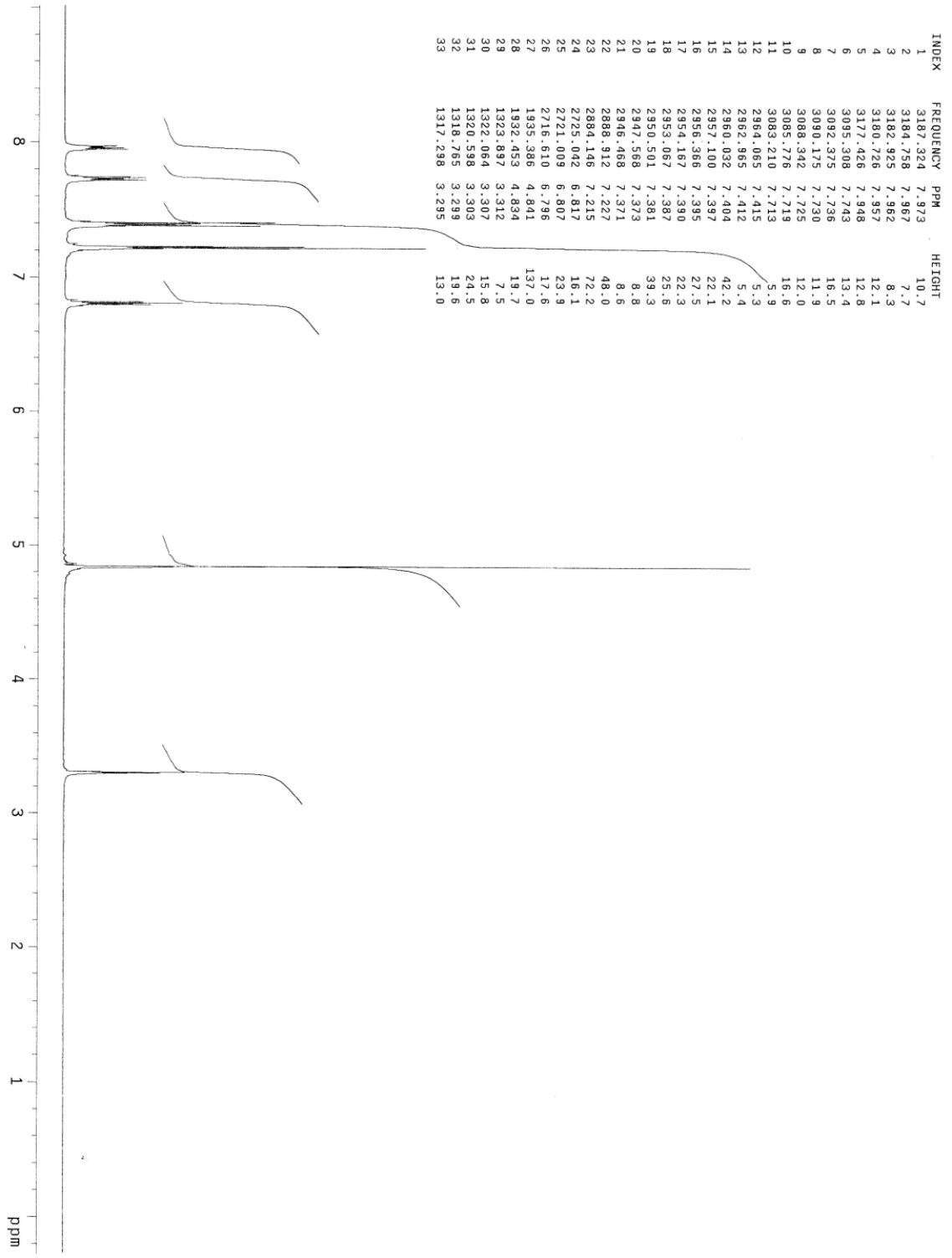
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 145.1, 142.3, 142.1, 132.9, 126.6, 125.1, 124.7, 120.6, 118.6, 113.9, 11.8, 36.8.

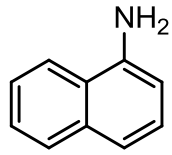


INDEX	FREQUENCY	PPM	HEIGHT
1	14651.734	145.759	4.8
2	14590.697	145.152	9.1
3	14300.008	142.260	11.0
4	14288.563	142.146	6.9
5	13368.430	132.992	4.2
6	12729.068	126.632	44.7
7	12572.660	125.076	50.5
8	12539.090	124.742	33.1
9	12127.090	120.643	31.0
10	11919.564	118.579	34.3
11	11456.446	113.972	45.1
12	11238.238	111.801	43.4
13	7775.914	77.357	9.1
14	7743.869	77.038	10.4
15	7711.825	76.719	9.5
16	3700.930	36.818	53.2



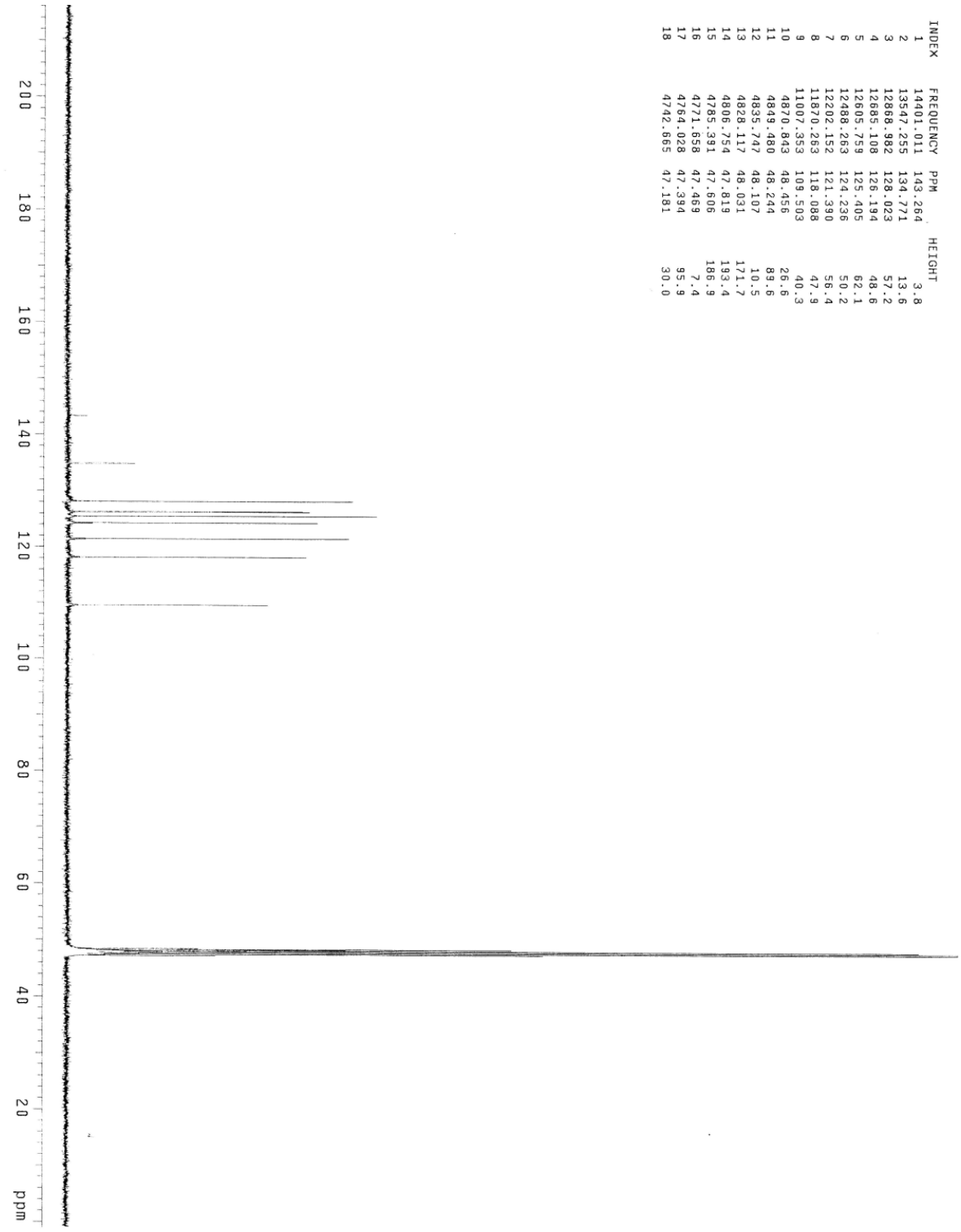
^{1}H NMR (400MHz, CD_3OD) δ 7.95 (m, 1H), 7.73 (m, 1H), 7.39 (m, 2H), 7.22 (m, 2H), 6.80 (m, 1H).

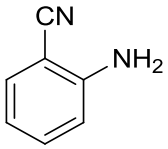




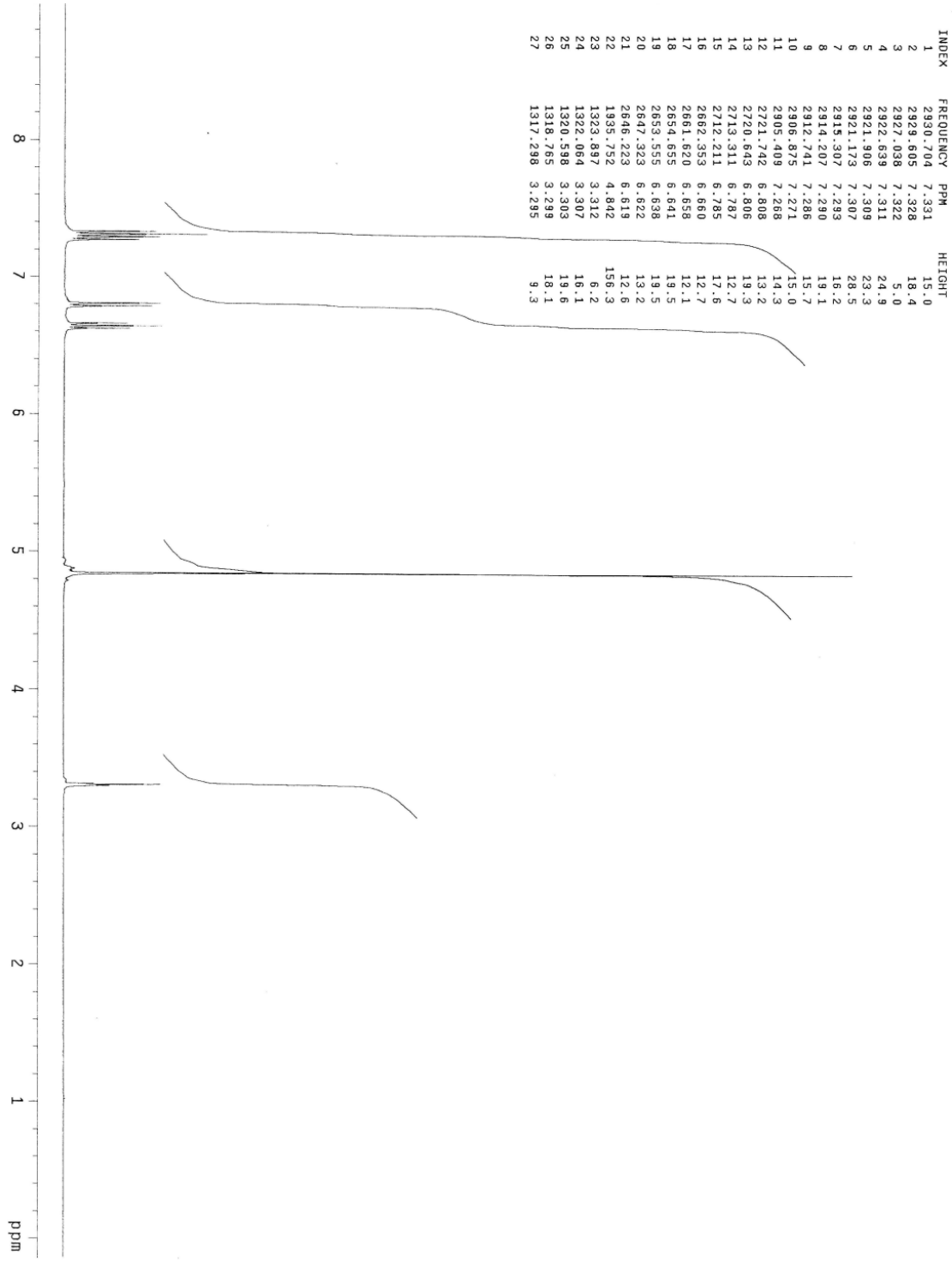
^{13}C NMR (100MHz, CD_3OD) δ 143.3, 134.8, 128.0, 126.2, 125.4, 124.2, 121.4, 118.1, 109.5.

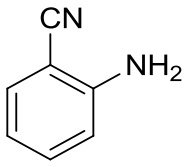
INDEX	FREQUENCY	PPM	HEIGHT
1	14401.011	143.264	3.8
2	13547.255	134.771	13.6
3	12868.982	128.023	57.2
4	12685.108	126.194	48.6
5	12605.759	125.405	62.1
6	12488.263	124.236	50.2
7	12202.152	121.390	56.4
8	11870.263	118.088	47.9
9	11007.353	109.503	40.3
10	4870.843	48.456	26.6
11	4849.480	48.244	89.6
12	4835.747	48.107	10.5
13	4828.117	48.031	171.7
14	4806.754	47.819	193.4
15	4785.391	47.606	186.9
16	4771.658	47.469	7.4
17	4764.028	47.394	95.9
18	4742.665	47.181	30.0



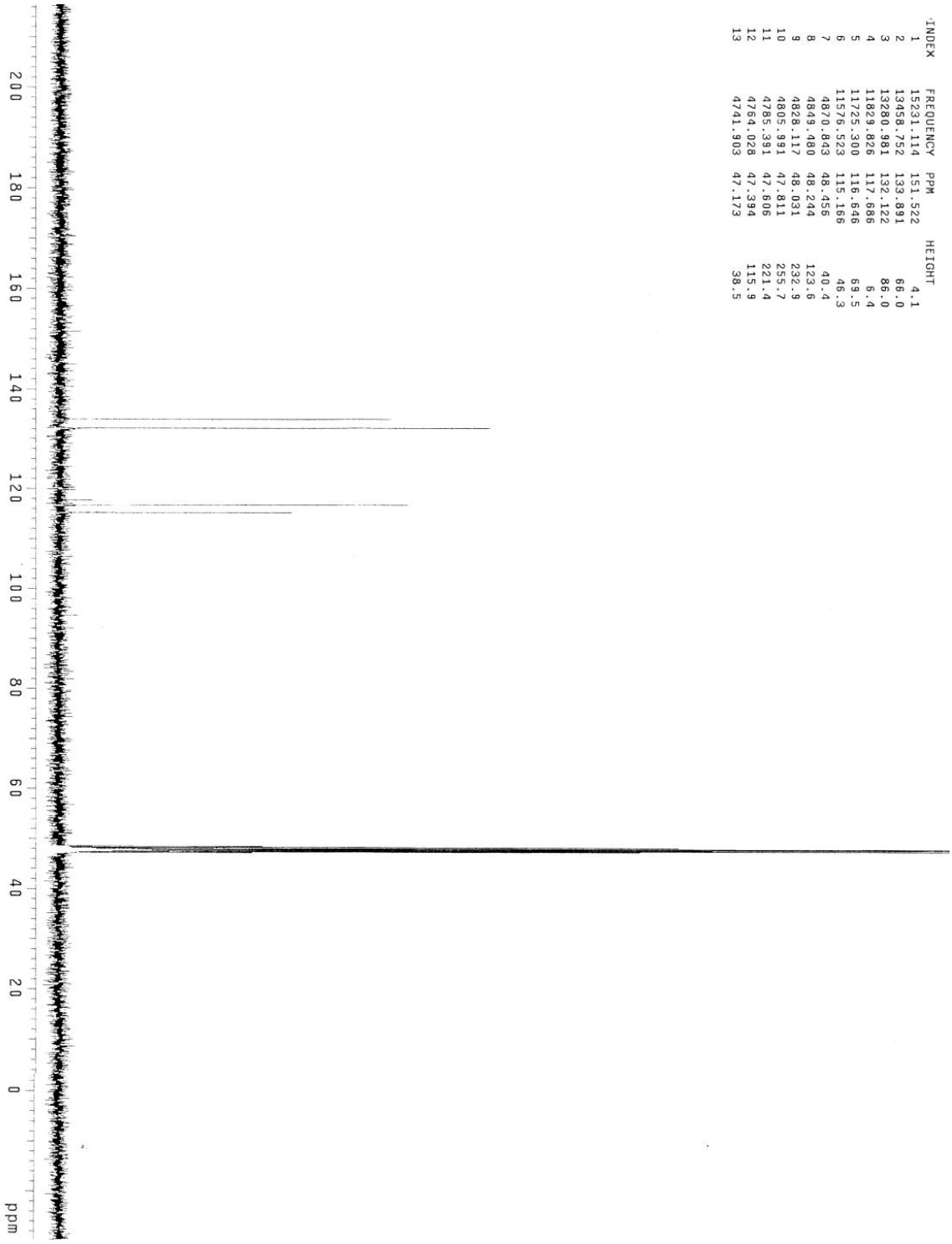


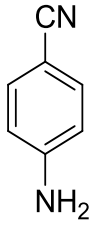
^{1}H NMR (400MHz, CD_3OD) δ 7.33–7.26 (m, 2H), 6.70 (m, 2H), 3.31 (bs, 2H).



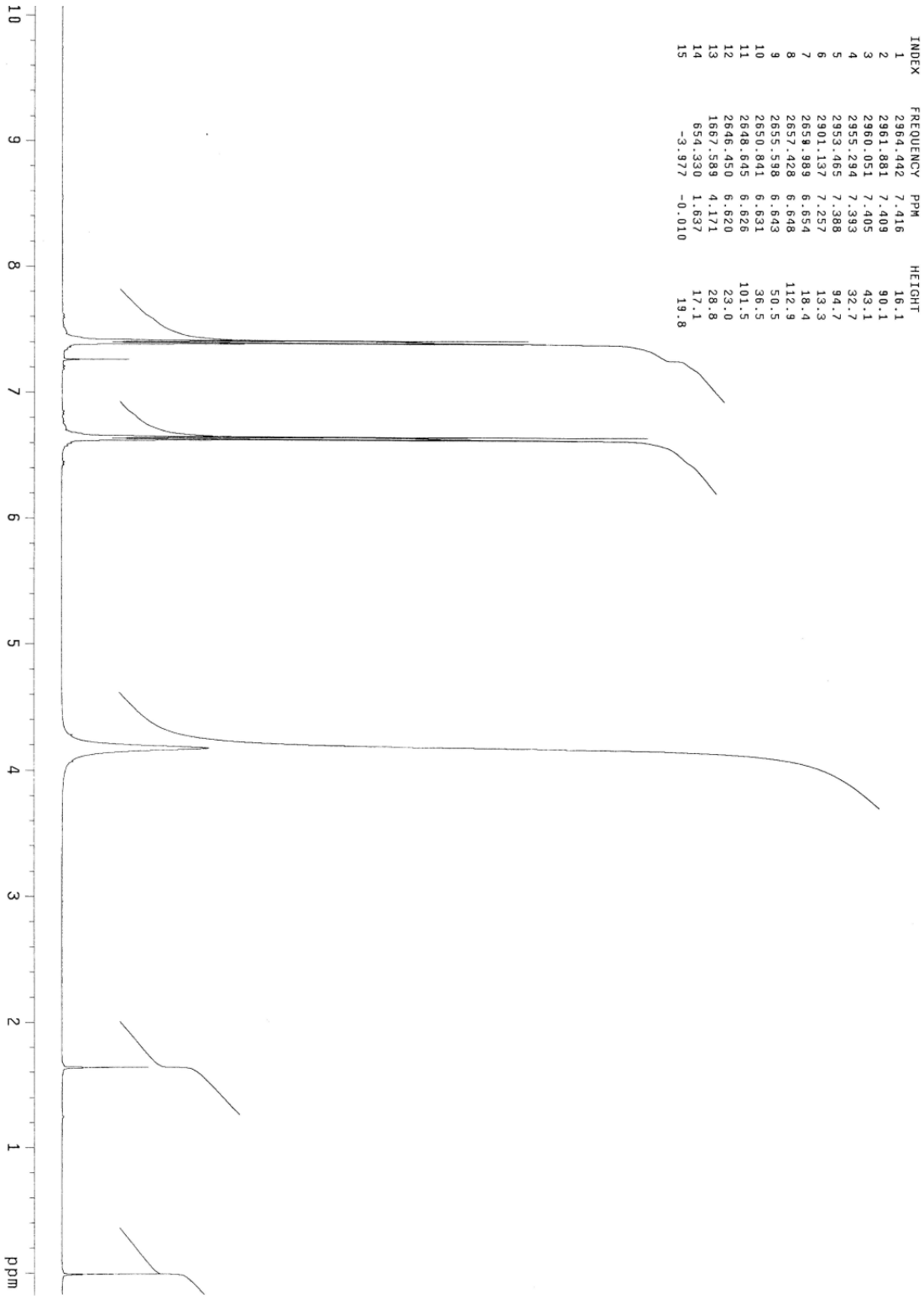


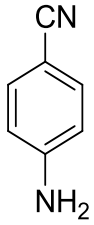
^{13}C NMR (100MHz, CD_3OD) δ 151.5, 133.9, 132.1, 117.7, 116.4, 115.2.



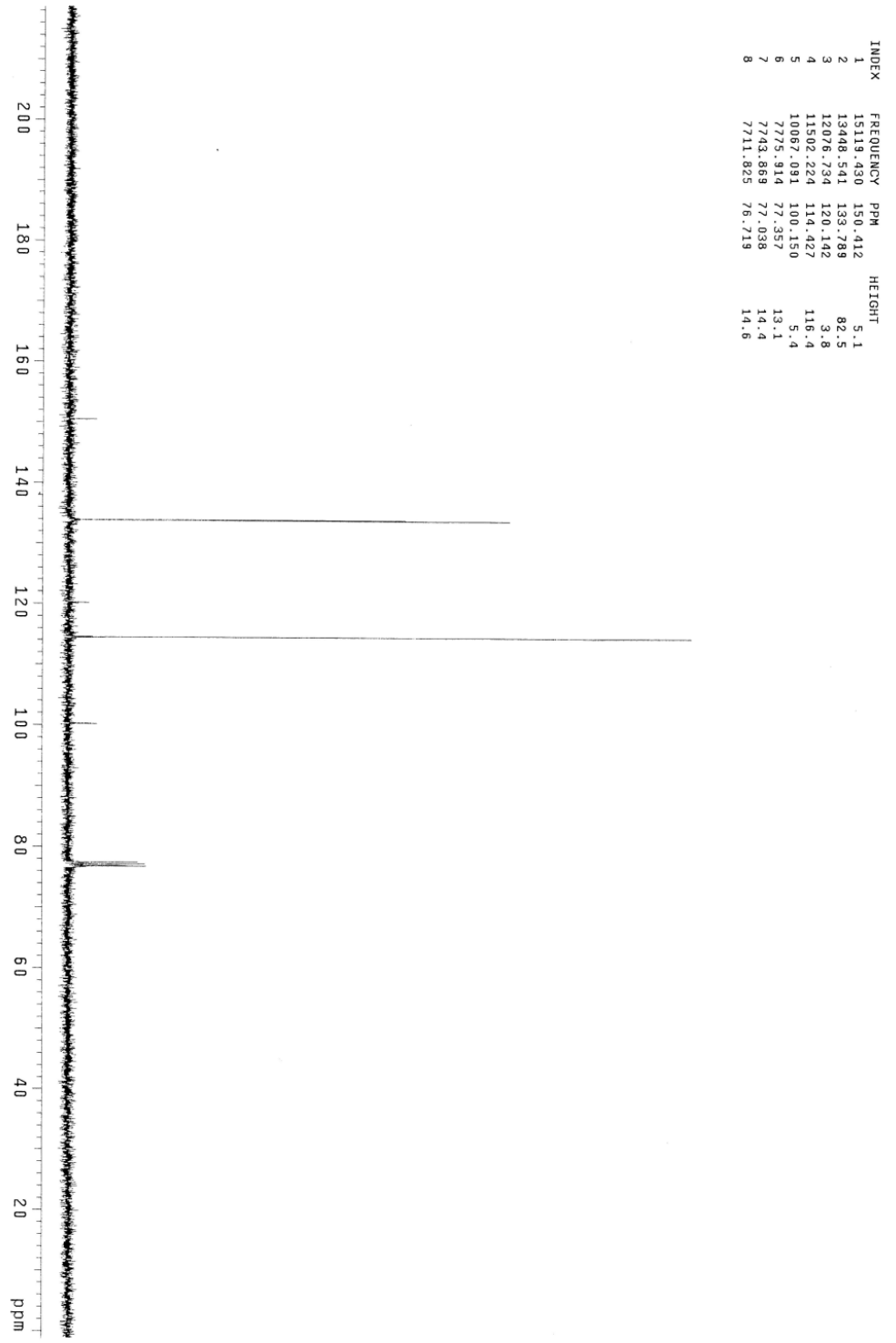


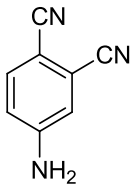
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.6 Hz, 2H), 6.63 (d, J = 8.6 Hz, 2H), 4.17 (bs, 2H).



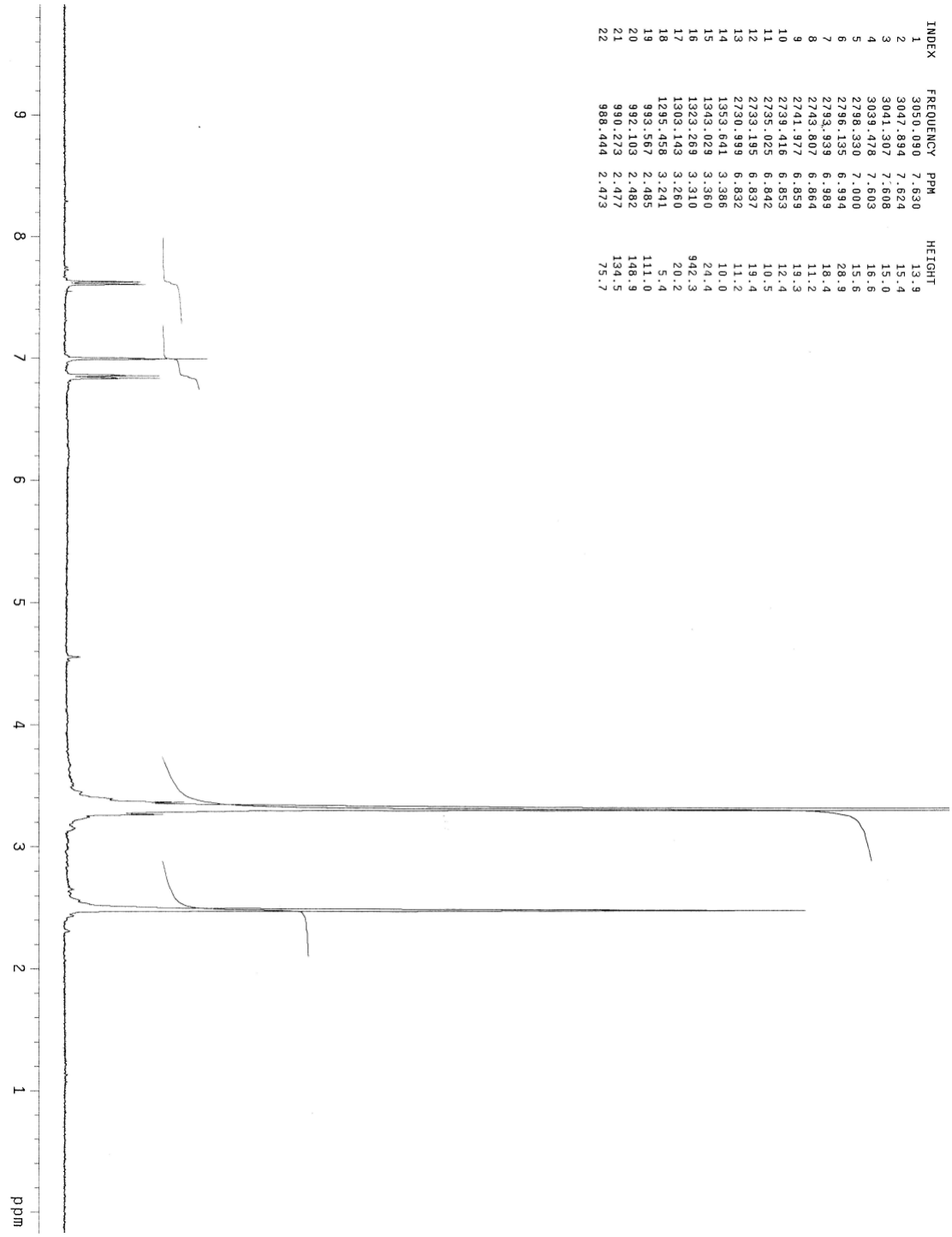


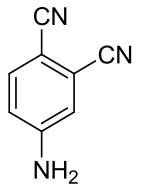
^{13}C NMR (100MHz, $CDCl_3$) δ 150.4, 133.8, 120.1, 114.4, 100.1.



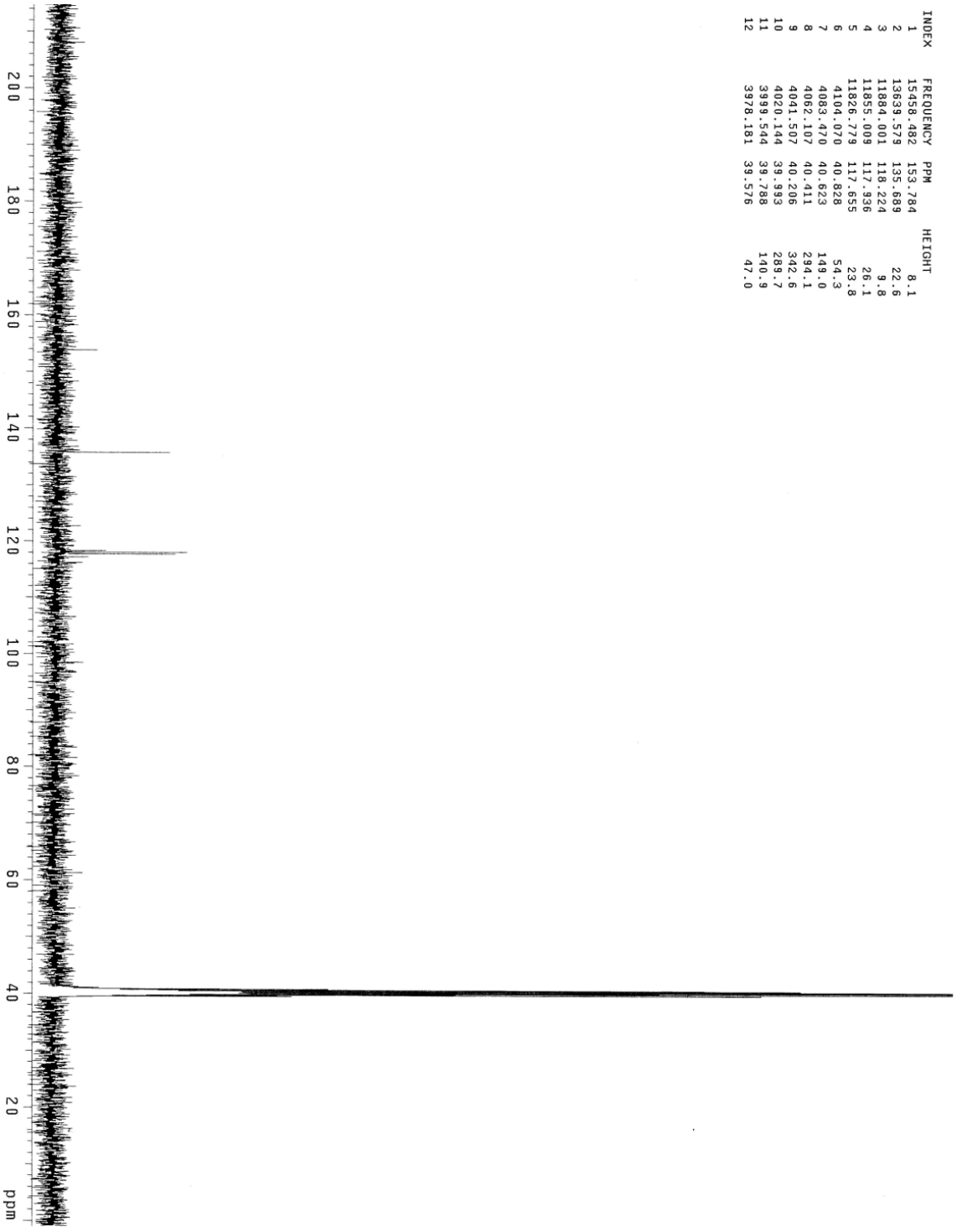


^{1}H NMR (400 MHz, DMSO) δ 7.61 (m, 1H), 6.99 (m, 1H), 6.85 (m, 1H).

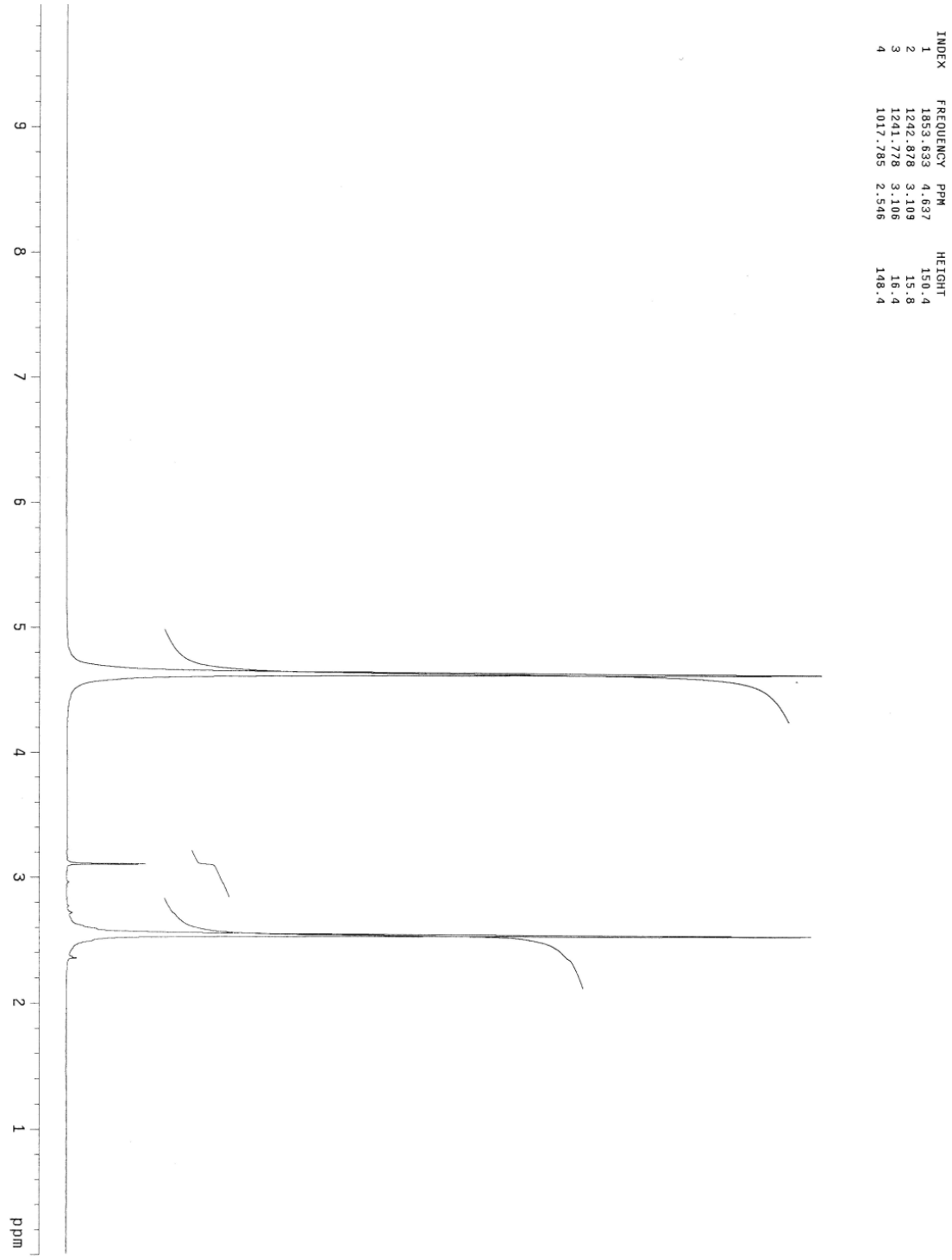




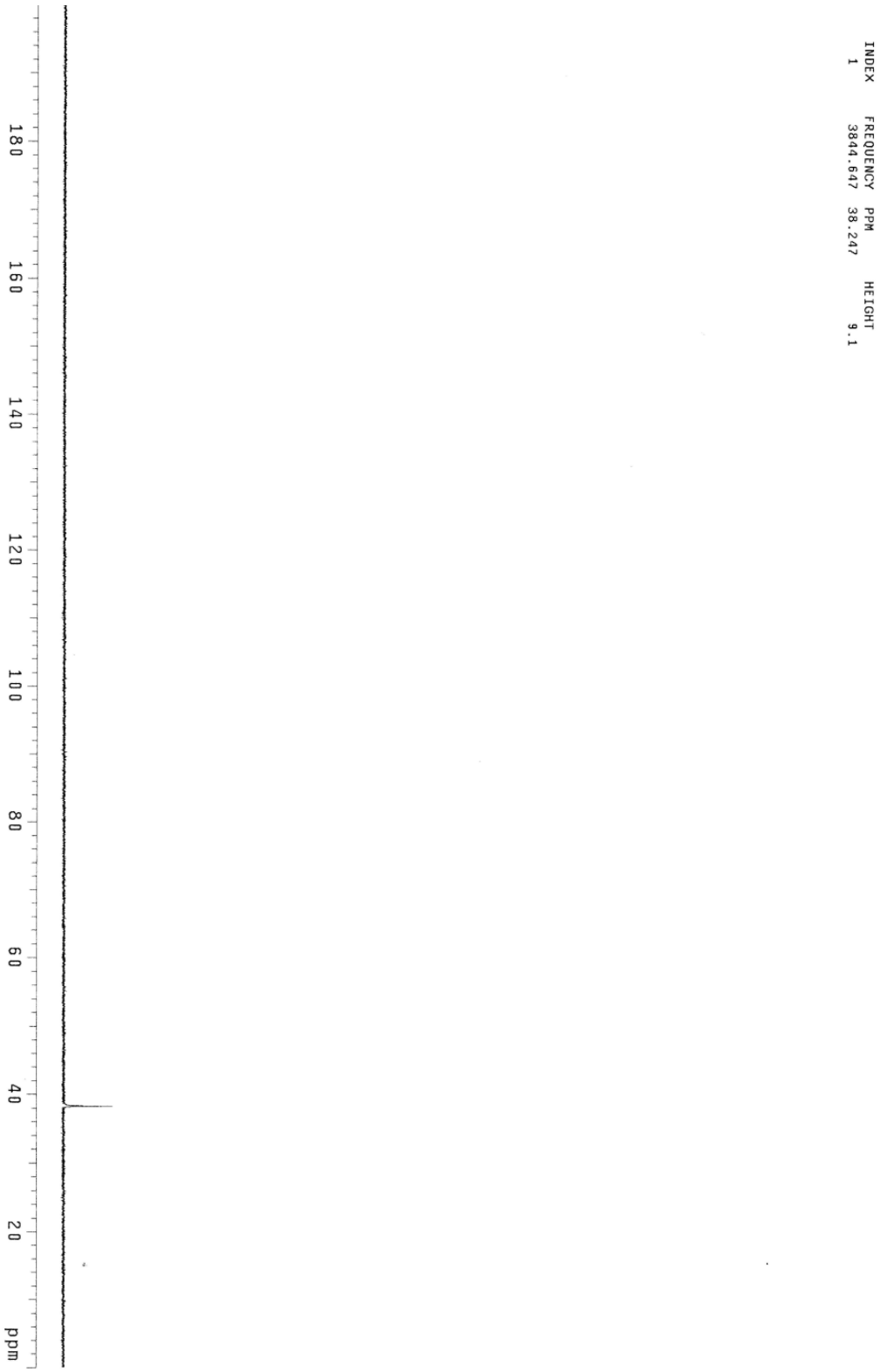
^{13}C NMR (100 MHz, DMSO) δ 153.8, 135.7, 118.2, 117.9, 117.6.

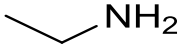


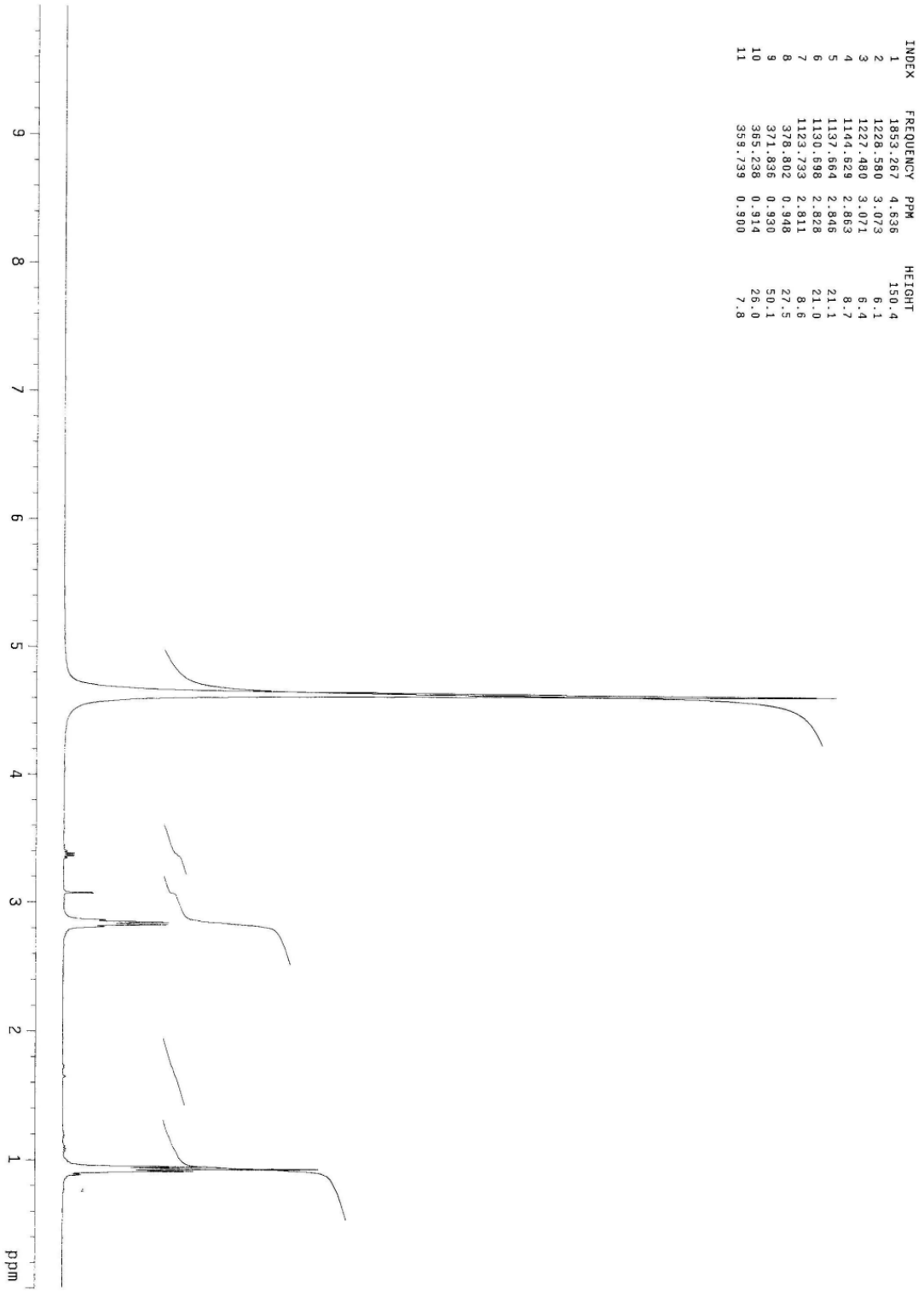
H_3C–NH_2	**^{1}H NMR (400 MHz, D_2O)** δ 2.55 (s, 3H).

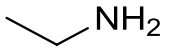


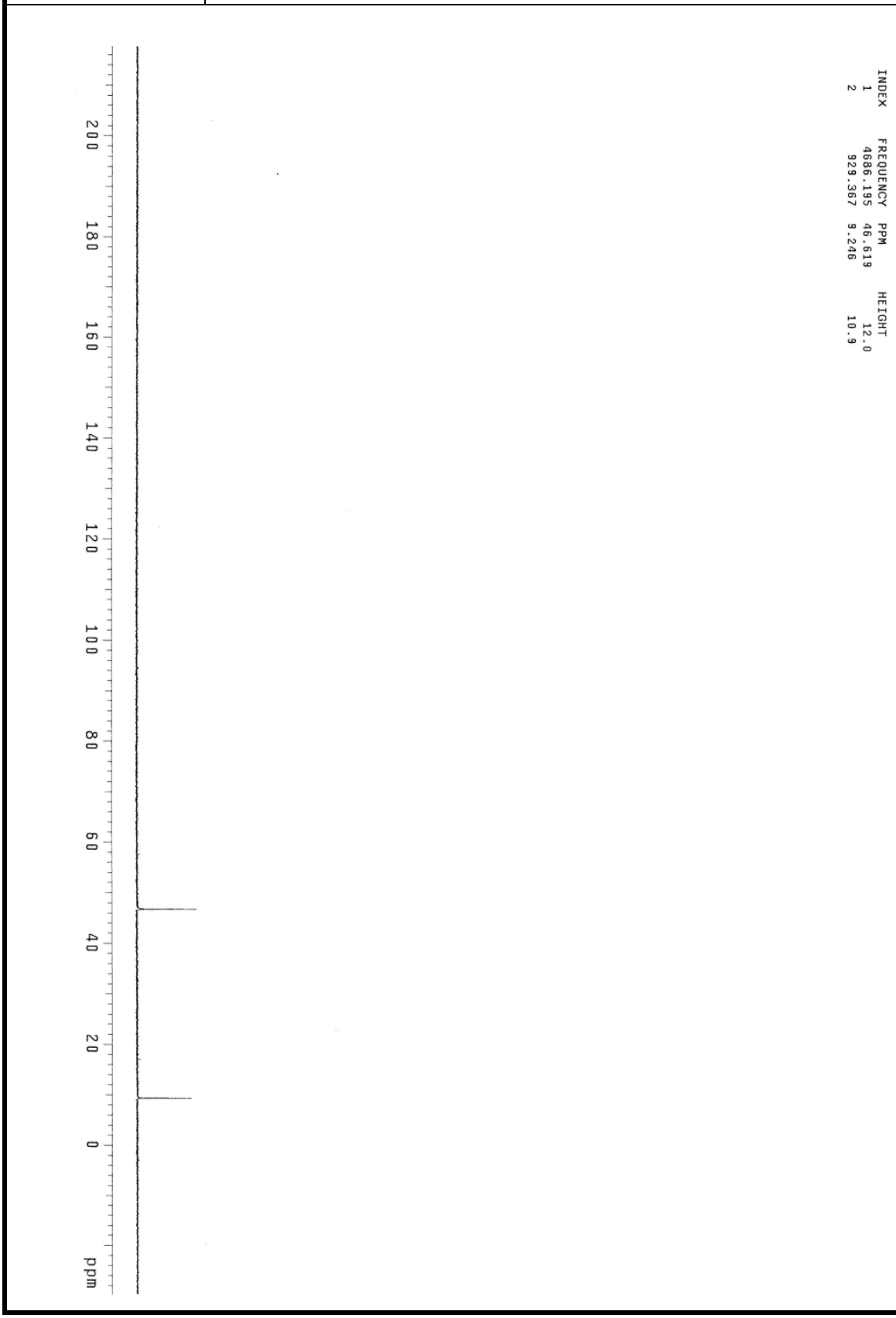
H_3C–NH_2	**^{13}C NMR (100MHz, D_2O)** δ 38.2.

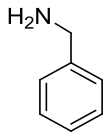


	**^{1}H NMR (400 MHz, D_2O)** δ 2.84 (q, J = 6.9 Hz, 2H), 0.92 (t, J = 6.9 Hz, 3H).

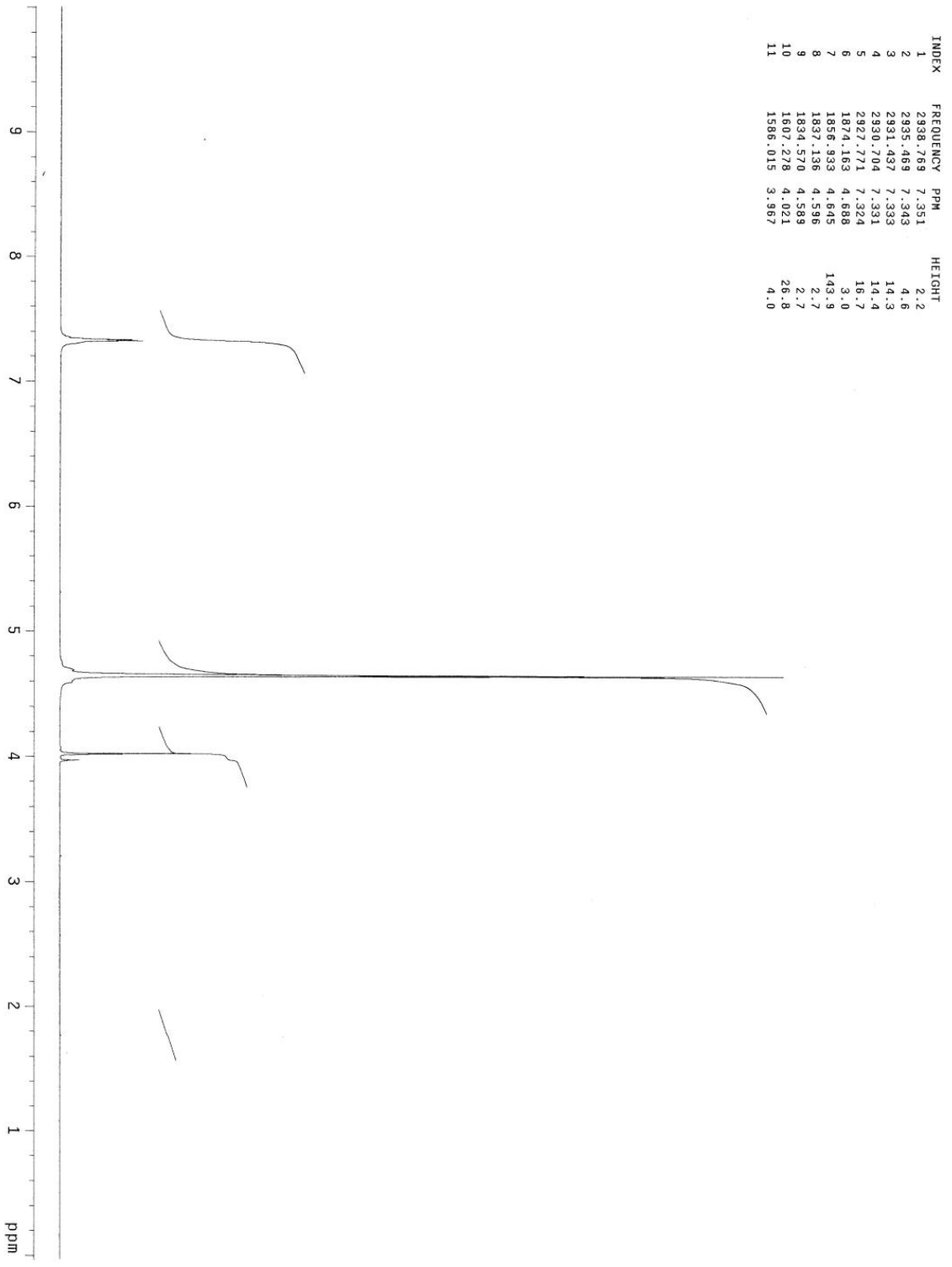


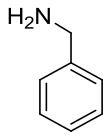
	**^{13}C NMR (100MHz, D_2O)** δ 46.6, 9.2.





^{1}H NMR (400MHz, D_2O) δ 7.35−7.32 (m, 5H), 3.97 (s, 2H).





^{13}C NMR (100MHz, D_2O) δ 143.5, 129.3, 129.2, 128.5, 43.4.