Supplementary Material (ESI) for Chemical Communications

Supporting Materials to

The Use of Calcium Carbide in One-pot Synthesis of Symmetric Diaryl Ethynes

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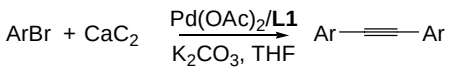
EXPERIMENTAL SECTION:

General: All reactions and manipulations were conducted under nitrogen atmosphere using standard Schlenk techniques. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). ^{1}H NMR, and ^{13}C NMR were recorded on a 300 MHz spectrometer. Chemical shifts were reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard. EA, IR, and MS spectra were recorded in analytical center in Wenzhou University.

Materials: *Caution: CaC_2 may cause fire when exposed in moisture.* THF was direct used without any dryness. K_2CO_3, $Pd(OAc)_2$ and aryl bromides were used directly as obtained commercially material unless otherwise noted. CaC_2 was grind into powder prior to use. **L1** was prepared according to literature.[1]

Table 1. Screen of the base ratio[a]



2 **1** **3**

entry	K_2CO_3 mol%	yield[b]
1	10	32
2	50	36
3	100	39
4	200	78
5	300	80

[a]All reactions were run with *p*-bromoanisole (376mg, 2 mmol), calcium carbide (236mg, 4 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), **L1** (43.1mg, 0.15 mmol)**,** with indicated ratio of K_2CO_3 in 5 ml of undried THF, refluxing for 12 h. [b]Isolated yield.

[1] R. Contreras, J. M. Grevy, Z. Garcia-Hernandez, M. Gueizado-Rodriguez and B. Wrackmeyer, Heteroat. Chem. 2001, **12**, 542.

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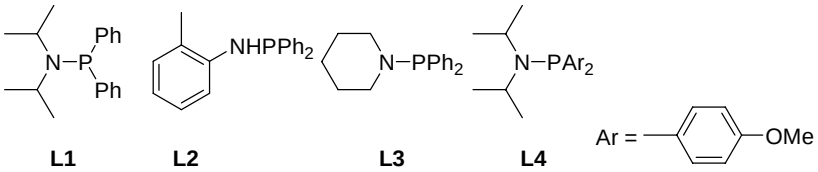
Table 2. Screen of the ligand[a]



L1 **L2** **L3** **L4**

entry	ligand	yield[b]
1	**L1**	78
2	**L2**	trace
3	**L3**	30
4	**L4**	82

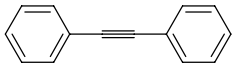
[a]All reactions were run with *p*-bromoanisole (376 mg, 2 mmol), calcium carbide (236mg, 4 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), indicated **L** (0.15 mmol)**,** with K_2CO_3 (552mg, 4 mmol) in 5 ml of undried THF , refluxing for 12 h. [b]Isolated yield.

Table 2. Screen of the bases, solvents[a]

entry	base	solvent	yield[b]
1	K_2CO_3	THF	78
2	$K_3PO_4 \cdot 3H_2O$	THF	56
3	$KF \cdot 2H_2O$	THF	26
4	Et_3N	THF	44
5	KOH	THF	35
6	Na_2CO_3	THF	49
7	K_2CO_3	dioxane	34
8	K_2CO_3	DMF	N.R.

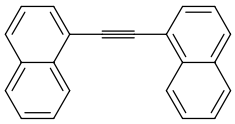
[a]All reactions were run with *p*-bromoanisole (376mg, 2 mmol), calcium carbide (236mg, 4 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), **L1** (43.1mg, 0.15 mmol)**,** with indicated bases (4 mmol) in 5 ml of indicated undried solvents, 65 °C for 12 h. [b]Isolated yield.

3a 1, 2-diphenylethyne[2]



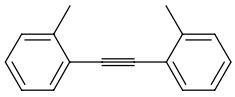
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60-7.51 (m, 4H), 7.34-7.31 (m, 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 131.6, 128.3, 128.2, 123.3, 89.4.

3b 1,2-di(naphthalen-1-yl)ethyne[3]



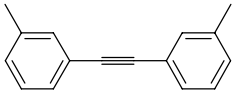
^{1}H NMR (300 MHz, $CDCl_3$): δ8.58-8.55 (m, 2H), 7.86-7.61 (m, 6H), 7.51-7.40 (m, 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 133.3, 130.5, 128.8, 128.3, 126.9, 126.4, 126.2, 125.3, 121.0, 92.5.

3c 1,2-di-*o*-tolylethyne[4]



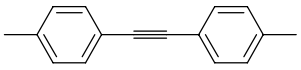
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53-7.50 (m, 2H), 7.23-7.17 (m, 6H), 2.49 (s, 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 139.9, 131.8, 129.5, 128.2, 125.6, 123.3, 92.3, 20.9.

3d 1,2-di-m-tolylethyne[5]



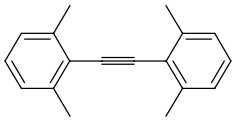
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.31 (m,4H), 7.25-7.21 (m,2H), 7.25-7.11 (m, 2H), 2.35 (s, 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 138.0, 132.2, 129.1, 128.6, 128.0, 123.2, 89.2, 21.2.

3e 1,2-di-*p*-tolylethyne[6]



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.8 Hz, 4H), 7.14 (d, *J* = 7.8 Hz, 4H), 2.36 (s, 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 138.2, 131.4, 129.1, 120.4, 88.9, 21.5.

3f 1,2-bis(2,6-dimethylphenyl)ethyne



[2] J. Cheng, Y. Sun, F. Wang, M. Guo, J.-H. Xu, Y. Pan and Z. Zhang, J. Org. Chem. 2004, **69**, 5428.

[3] A. Poloukhtine and V. V. Popik, J. Org. Chem. 2003, **68**, 7833.

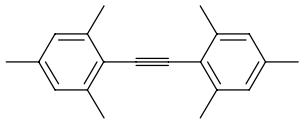
[4] J. Kowalik, and L. M .Tolbert, J. Org. Chem. 2001, **66**, 3229.

[5] G. R. Newkome, J. M. Roper and M. J. Robinson, J. Org. Chem. 1980, **45**, 4380.

[6] N. E. Leadbeater, M. Marco and B. J .Tominack, Org. Lett. 2003, **5**, 3919.

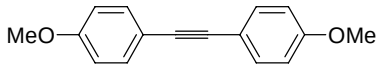
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12-7.09 (m, 6H), 2.54 (s, 12H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 140.1, 127.6, 126.8, 123.6, 95.8, 21.6. MS (EI) m/z 234 (M^+); IR (KBr, cm^{-1}) 3022 (w), 2917 (m), 2371 (w), 1463 (s), 765 (s). Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.20; H, 7.60.

3g 1,2-dimesitylethyne[7]



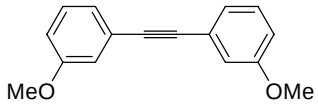
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.91 (s, 4H), 2.50 (s, 12H), 2.29 (s, 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 139.8, 137.4, 127.7, 120.8, 95.2, 21.5. MS (EI) m/z 262 (M^+); IR (KBr, cm^{-1}) 3022 (w), 2917 (m), 2371 (w), 1463 (s), 765 (s). Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.41; H, 8.66.

3h 1,2-bis(4-methoxyphenyl)ethyne[8]



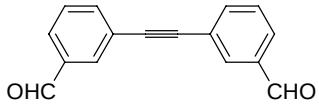
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, *J* = 9.0 Hz, 4H), 6.85 (d, *J* = 9.0 Hz, 4H), 3.81 (s, 6H). ^{13}CNMR (300 MHz, $CDCl_3$): δ 159.4, 132.8, 115.8, 114.0, 87.9, 55.3.

3i 1,2-bis(3-methoxyphenyl)ethyne[9]



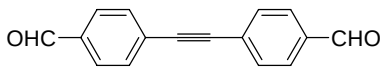
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25-7.23 (m, 2H), 7.11-7.06 (m, 4H), 6.91-6.88 (m, 2H), 3.82 (s, 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 159.4, 129.4, 124.2, 116.4, 115.0, 89.1, 55.3. MS (EI) m/z 238 (M^+); IR (KBr, cm^{-1}) 3027 (w), 2860 (w), 2359 (w), 1692 (s), 1155 (m), 787 (m). Anal. Calcd for $C_{18}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.44; H, 6.13.

3j 3,3'-(ethyne-1,2-diyl)dibenzaldehyde



^{1}H NMR (300 MHz, $CDCl_3$): δ 10.04 (s, 2H), 8.06 (s, 2H), 7.90-7.87 (m,2H), 7.78-7.76 (m, 2H), 7.59-7.54 (m, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 191.3, 137.1, 136.6, 132.9, 129.4, 129.2, 123.9, 89.3. MS (EI) m/z 234 (M^+); IR (KBr, cm^{-1}) 3027 (w), 2860 (w), 2359 (w), 1692 (s), 1155 (m), 787 (m). Anal. Calcd for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30. Found: C, 82.24; H, 4.13.

3k 4,4'-(ethyne-1,2-diyl)dibenzaldehyde[9]



^{1}H NMR (300 MHz, $CDCl_3$): δ 10.03 (s, 2H), 7.88 (d, *J* = 8.4 Hz, 4H), 7.70 (d, *J* = 8.4 Hz, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 191.3, 135.9, 132.3, 129.6, 128.6, 92.1.

3l 1,2-di(pyridin-3-yl)ethyne[10]

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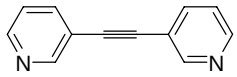
[7] C. J. Cooksey, J. L. Courtneidge, A. G. Davies, P. S. Gregory, J. C. Evans and C. C. Rowlands, J. Chem. Soc. Perkin Trans. 2 1988, 807.

[8] W. Zhang, S. Kraft and J. S. Moore, J. Am. Chem. Soc. 2004, **126**, 329.

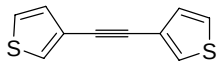
[9] N. G. Pschirer and U. H. F. Bunz, Tetrahedron Lett. 1999, **40**, 2481.

[10] D. A. Alonso, L. Botella, C. Najera and M. C. Pacheco, Synthesis 2004, 1713.



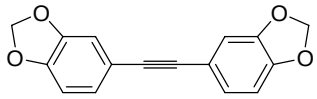
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.77 (s, 2H), 8.57 (d, *J* = 4.0 Hz, 2H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.32-7.26 (m, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 152.3, 149.0, 138.5, 123.1, 119.8, 89.1.

3m 1,2-di(thiophen-3-yl)ethyne[11]



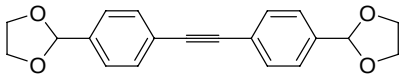
^{1}HNMR (300 MHz, $CDCl_3$): δ 7.50-7.48 (m, 2H), 7.30-7.26 (m, 2H), 7.19-7.16 (m, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 129.8, 128.4, 125.3, 122.2, 84.0.

3n 5-(2-(benzo[o][1,3]dioxol-5-yl)ethynyl)benzo[o][1,3]dioxole[12]



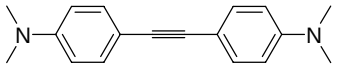
^{1}HNMR (300 MHz, $CDCl_3$): δ 7.04-7.401 (m, 2H), 6.96-6.94 (m, 2H), 6.79-6.76 (m, 2H), 5.99 (s, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 147.7, 147.4, 126.1, 116.6, 111.4, 108.4, 101.3, 87.6.

3p 2-(4-(2-(4-(1, 3-dioxolan-2-yl)phenyl)ethynyl)phenyl)-1, 3-dioxolane



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.1 Hz, 4H), 7.11(d, *J* = 8.1 Hz, 4H), 5.81 (s, 2H), 4.13-4.10 (m, 4H), 4.06-4.03 (m, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 138.0, 131.6, 126.5, 124.0, 103.3, 89.6, 65.3. MS (EI) m/z 322 (M^+); IR (KBr, cm^{-1}) 2947 (w), 2882 (m), 1635 (m), 1110 (s). Anal. Calcd for $C_{18}H_{14}O_2$: C, 74.52; H, 5.63. Found: C, 74.47; H, 5.88.

3q 4-(2-(4-(dimethylamino)phenyl)ethynyl)-*N, N*-dimethylaniline [7]



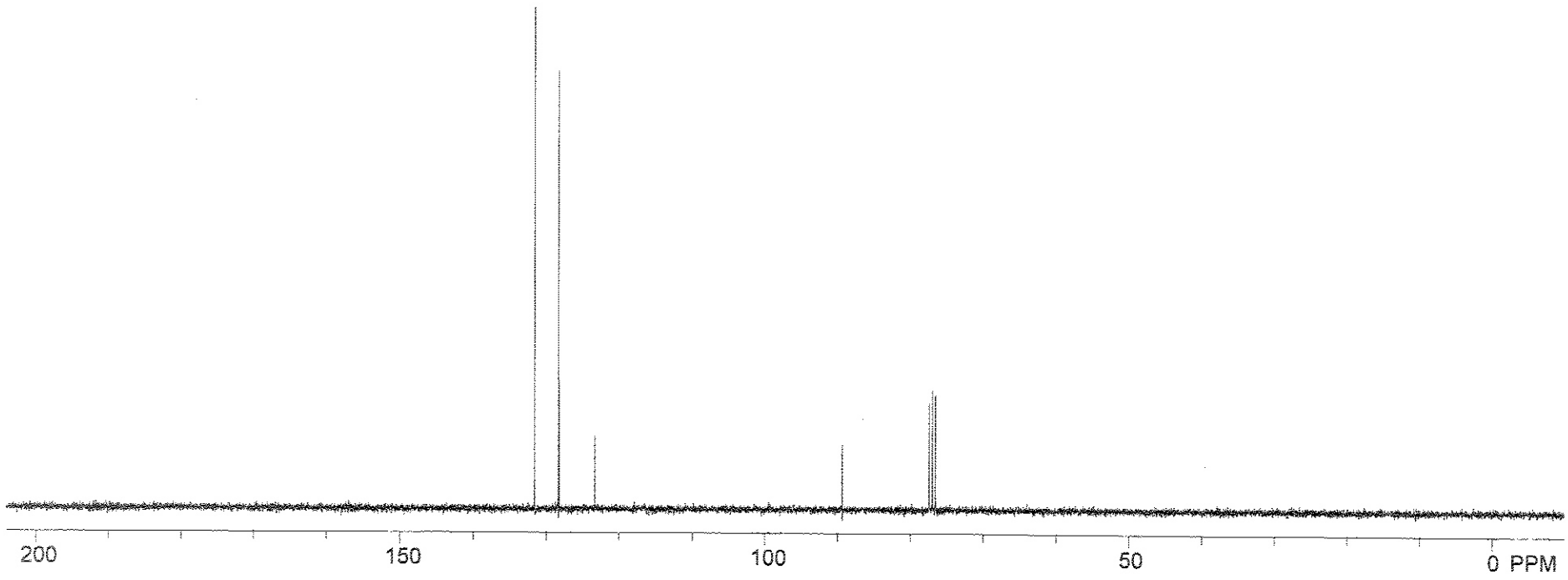
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.8 Hz, 4H), 6.64 (d, *J* = 8.8 Hz, 4H), 2.98 (s, 12H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 149.7, 132.4, 115.7, 111.9, 88.1, 40.3.

[11] S. C. Ng, I. Novak, L. Wang, H. H .Huang and W. Huang, Tetrahedron 1997, **53**, 13339.

[12] A. P. Rudenko and A. V. Vasil'ev, Russ. J. Org. Chem. 1995, **31**, 1360.


131.587
128.312
128.217
123.287
89.390
77.421
77.000
76.573

3a C NMR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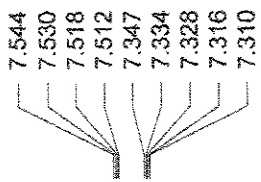

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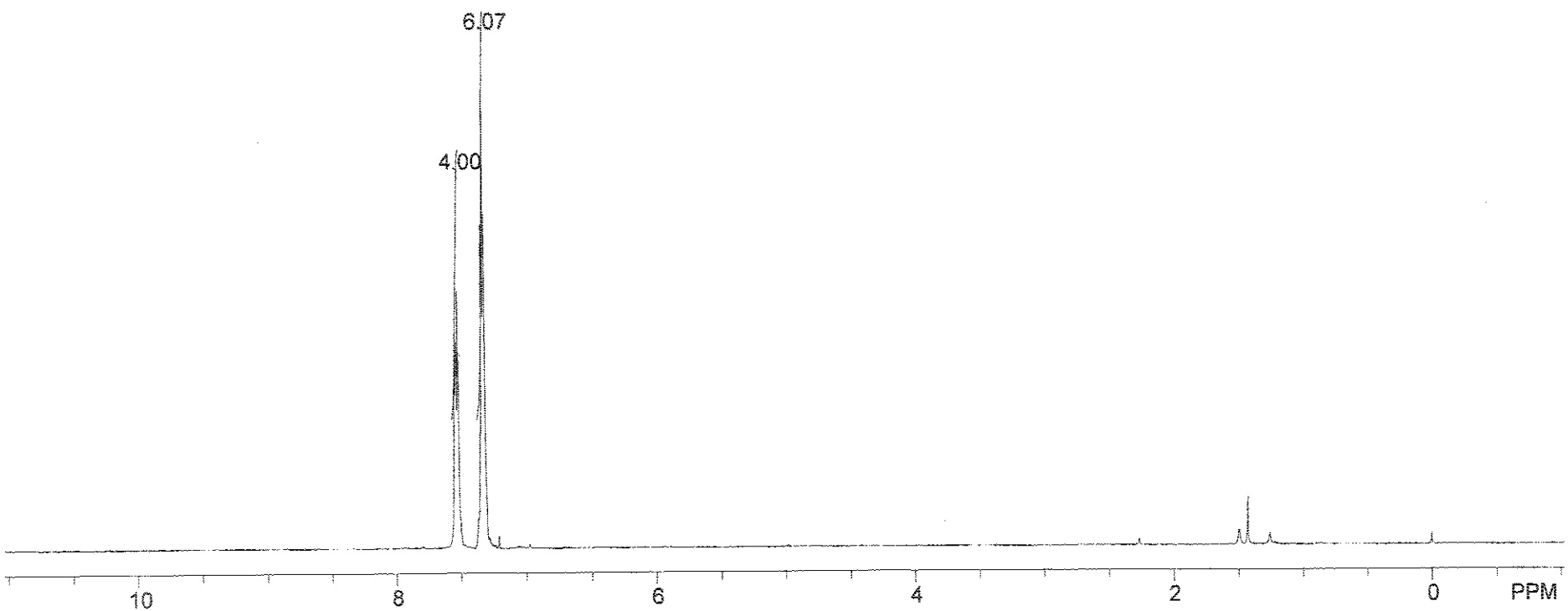

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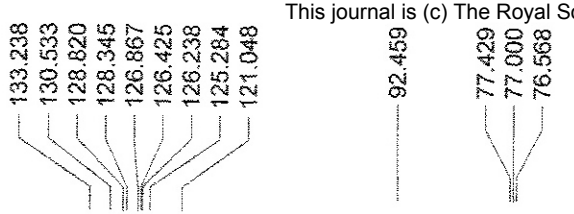
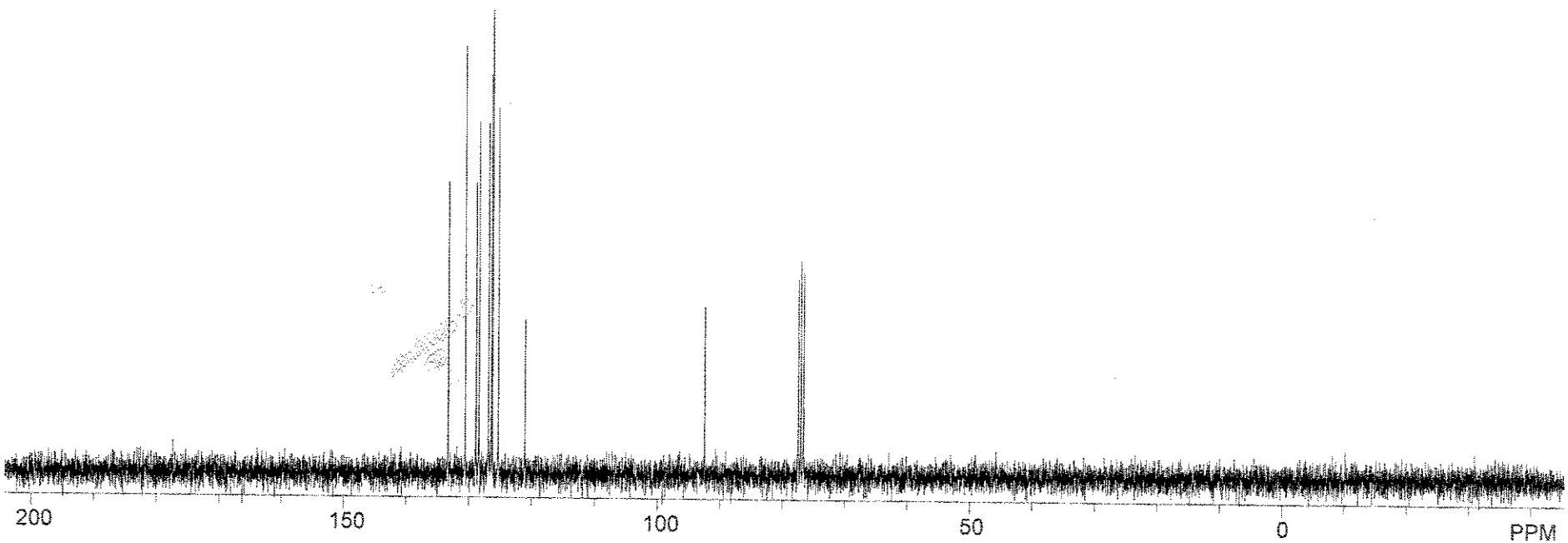


3b C NMR



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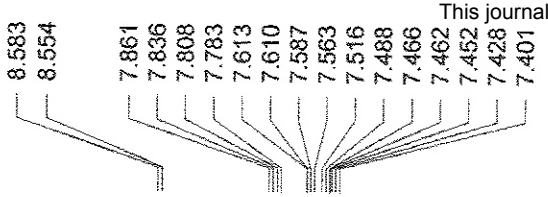
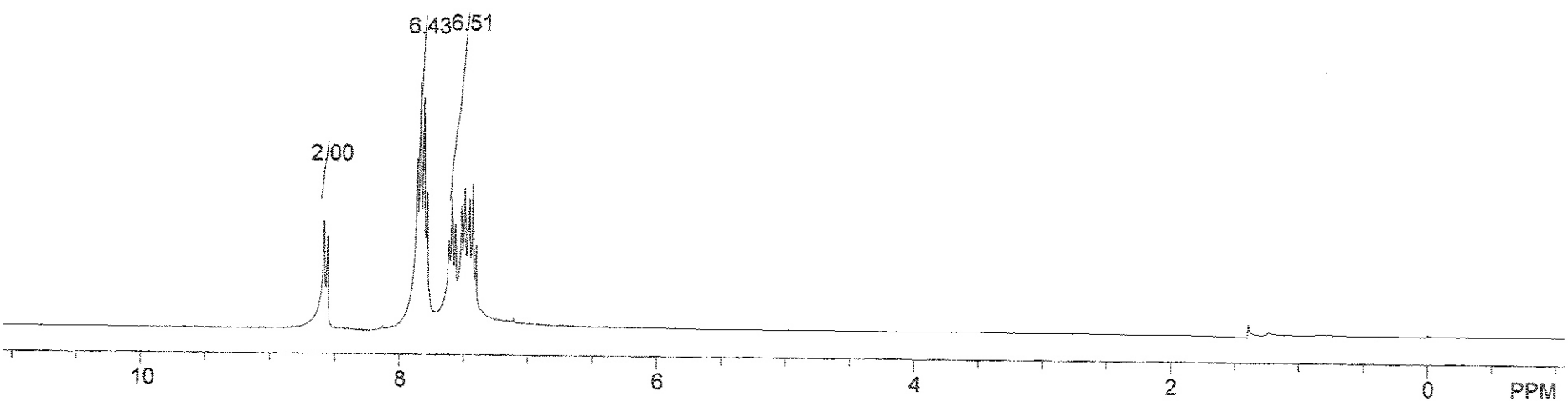


3b H NMR



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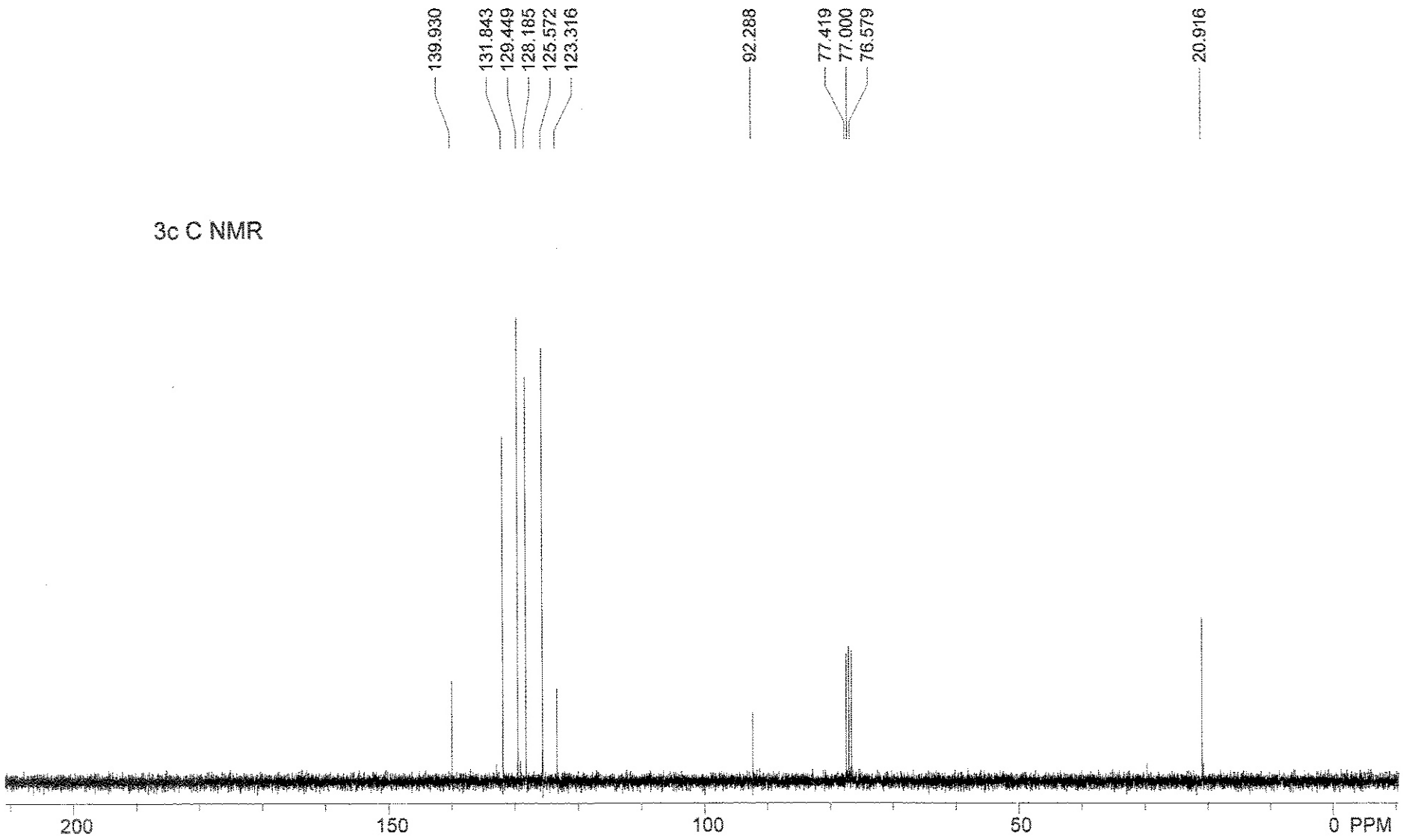

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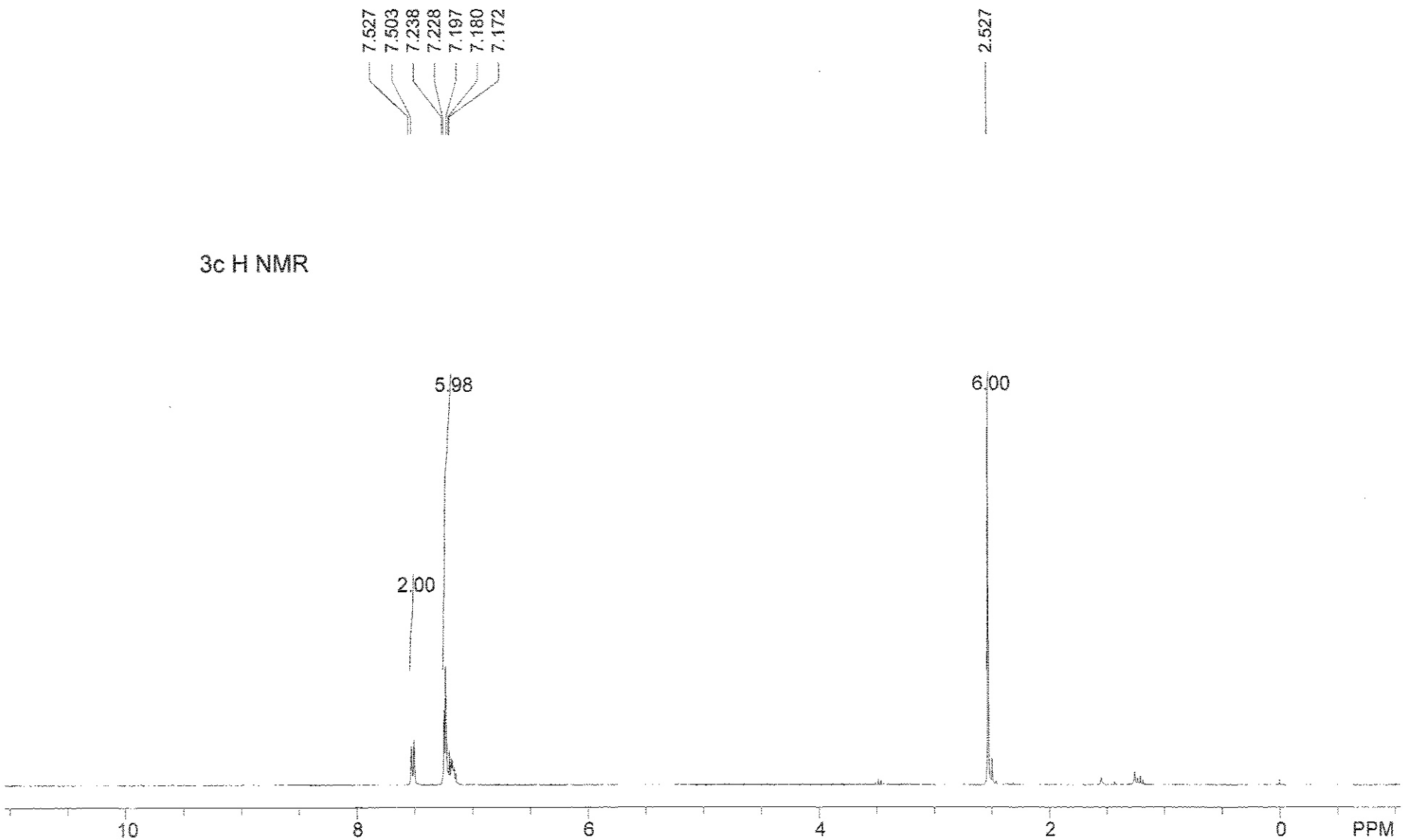

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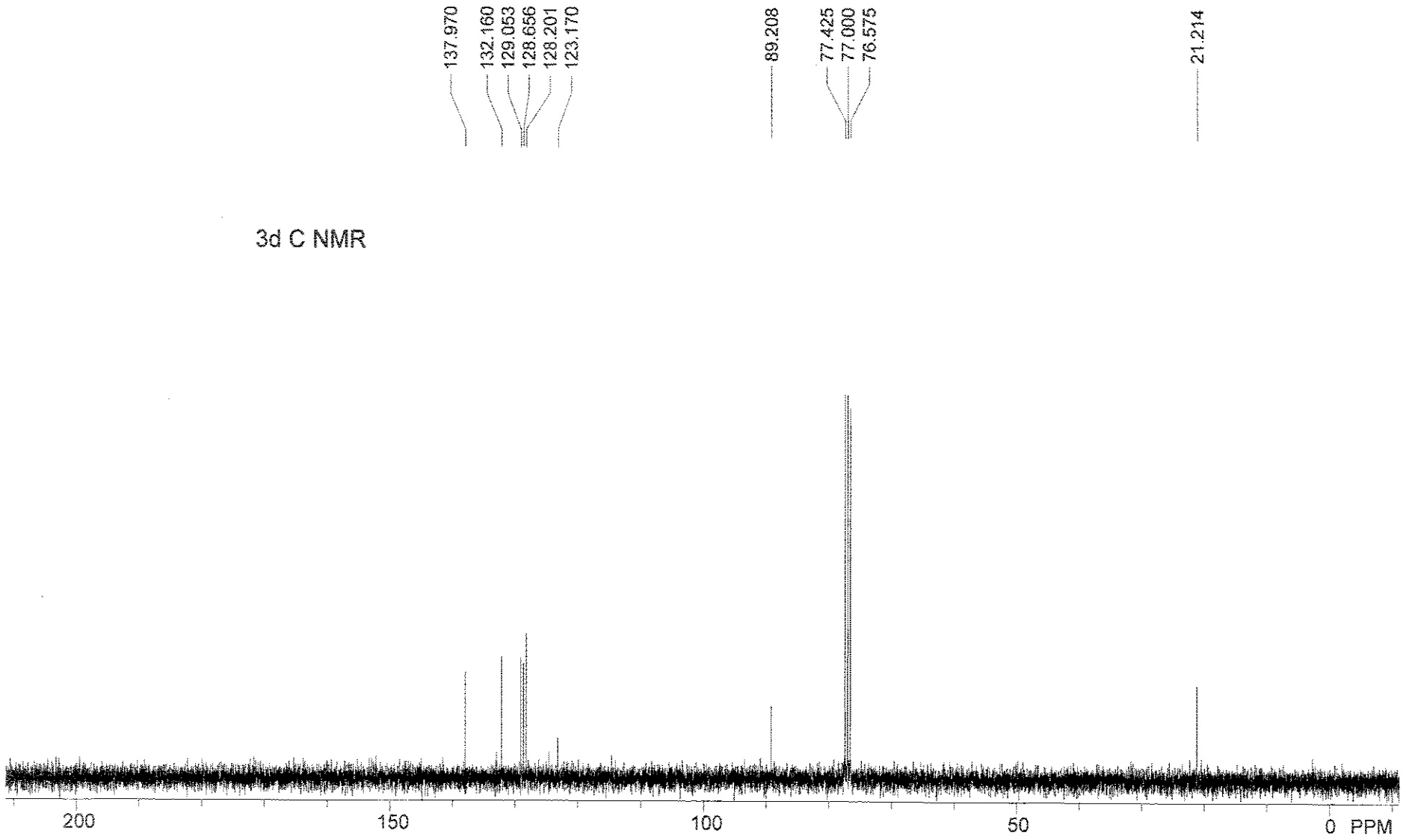

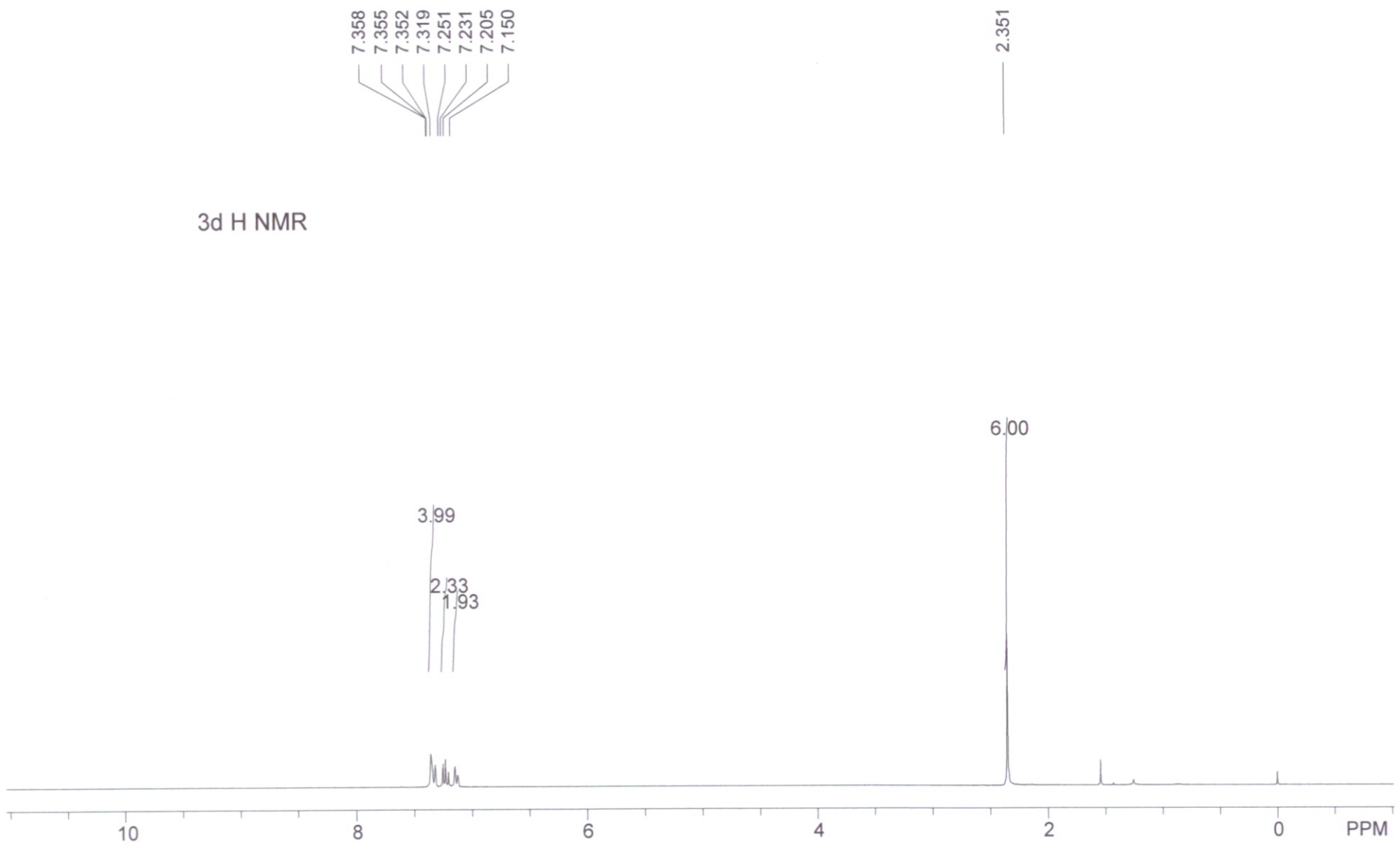
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7.355
7.352
7.319
7.251
7.231
7.205
7.150
2.351
3d H NMR
6.00
3.99
2.33
1.93
10
8
6
4
2
0
PPM

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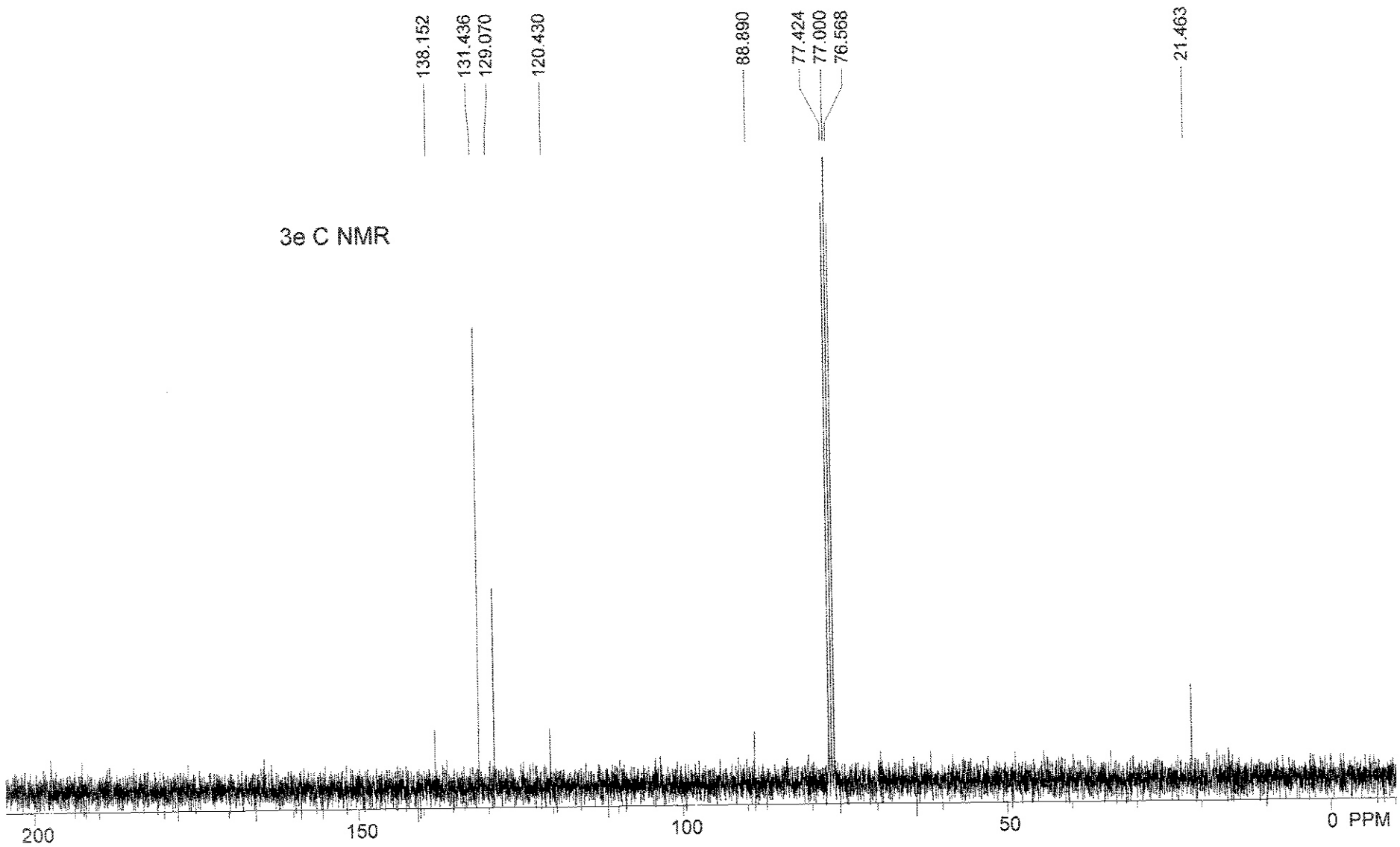

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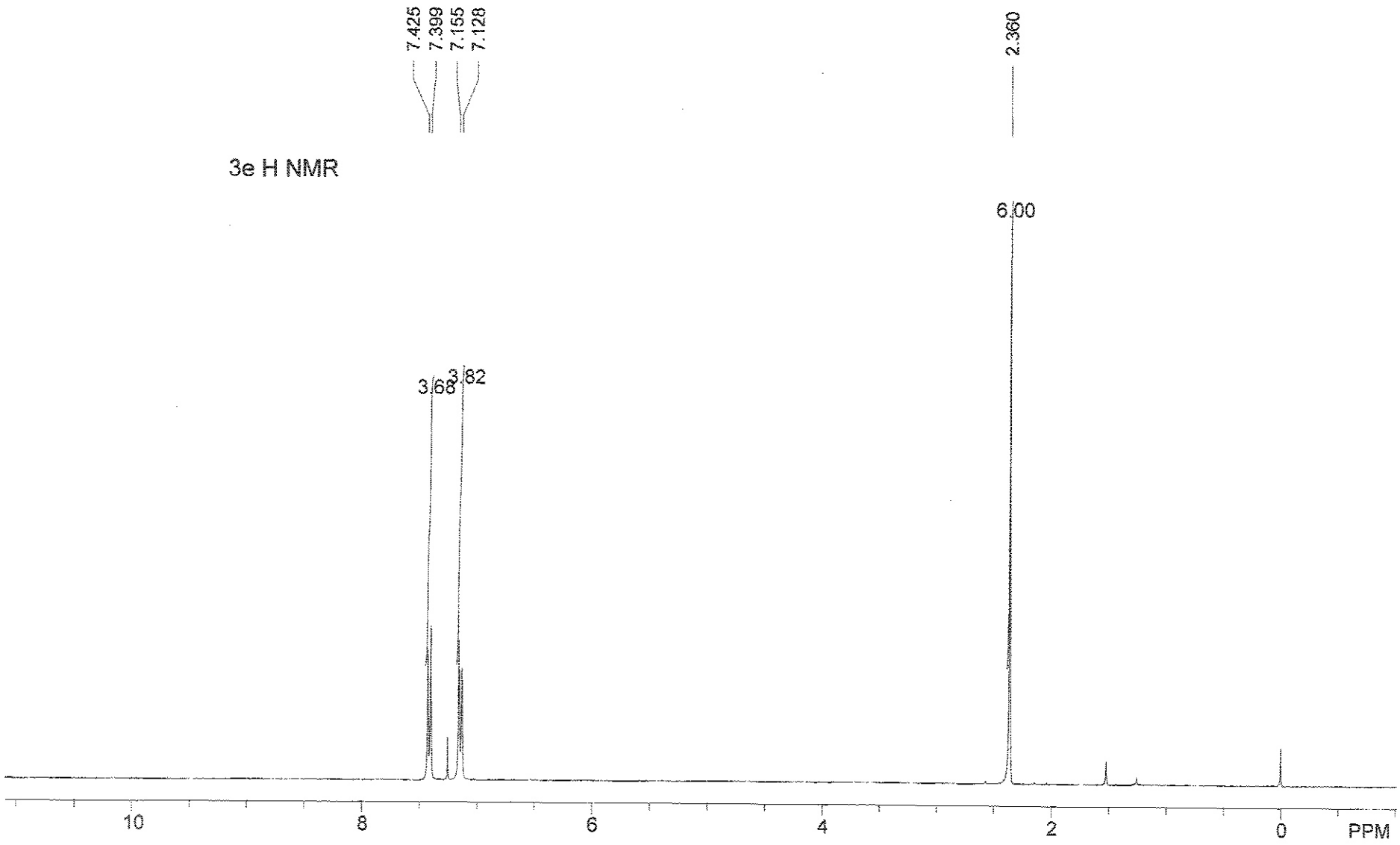

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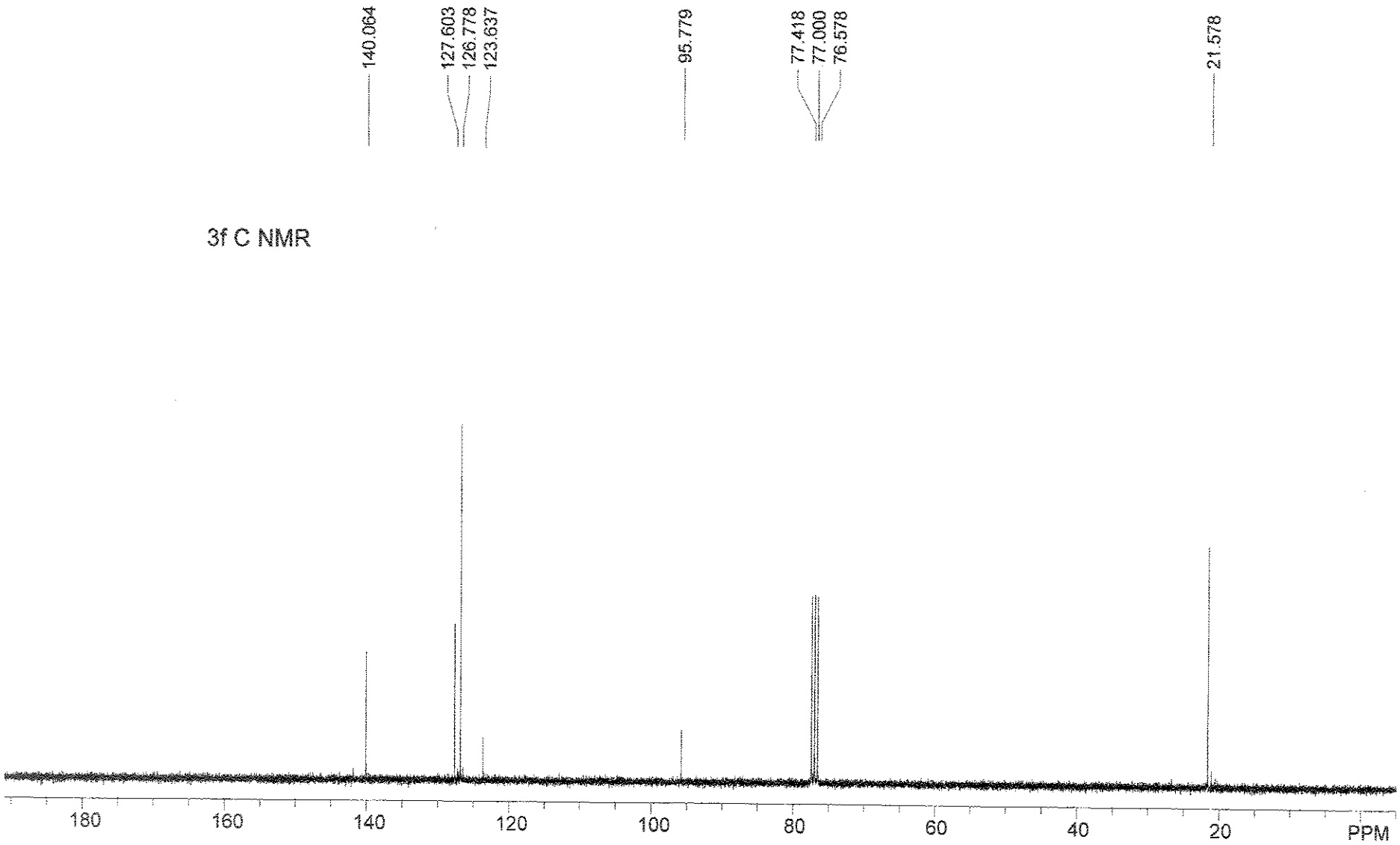

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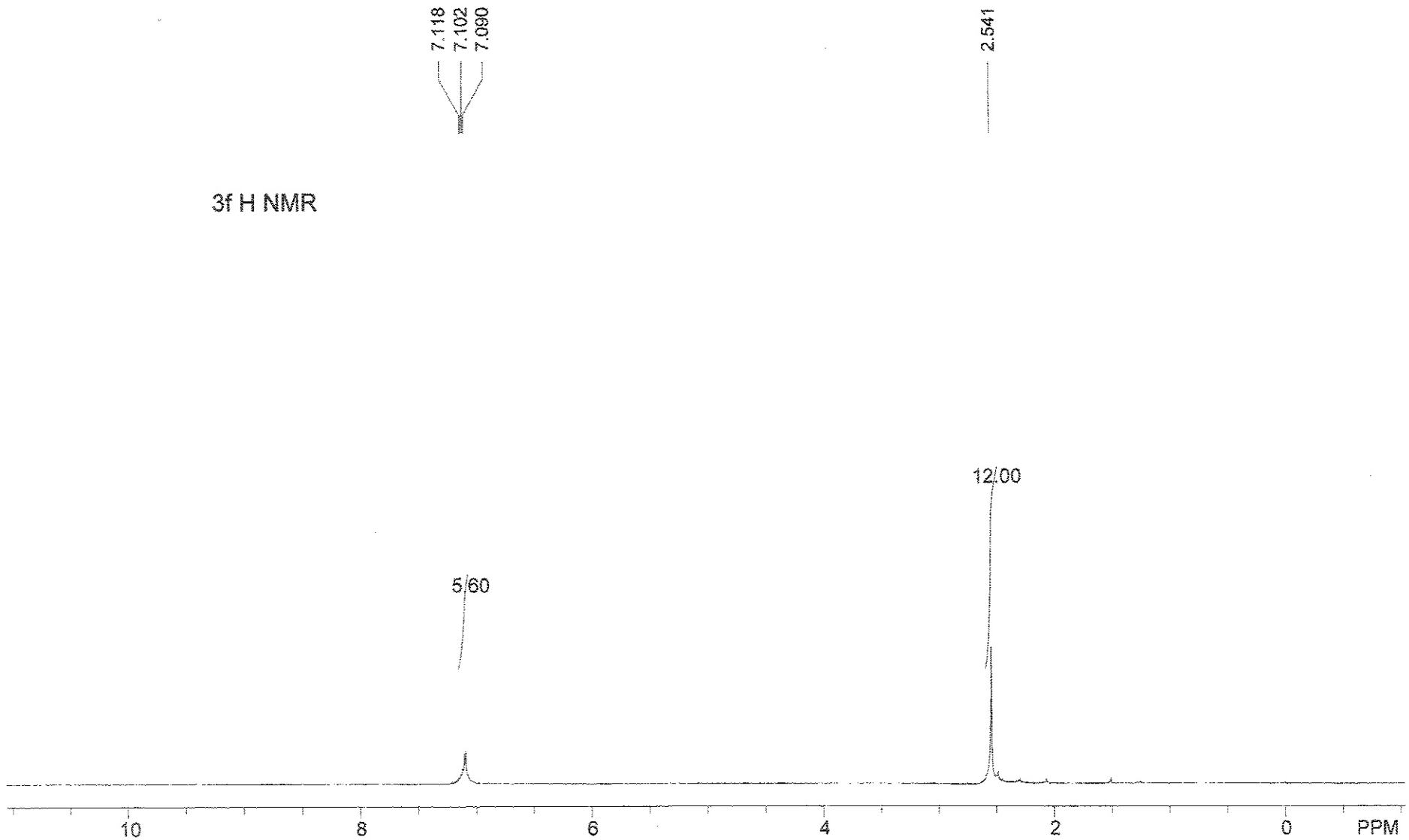

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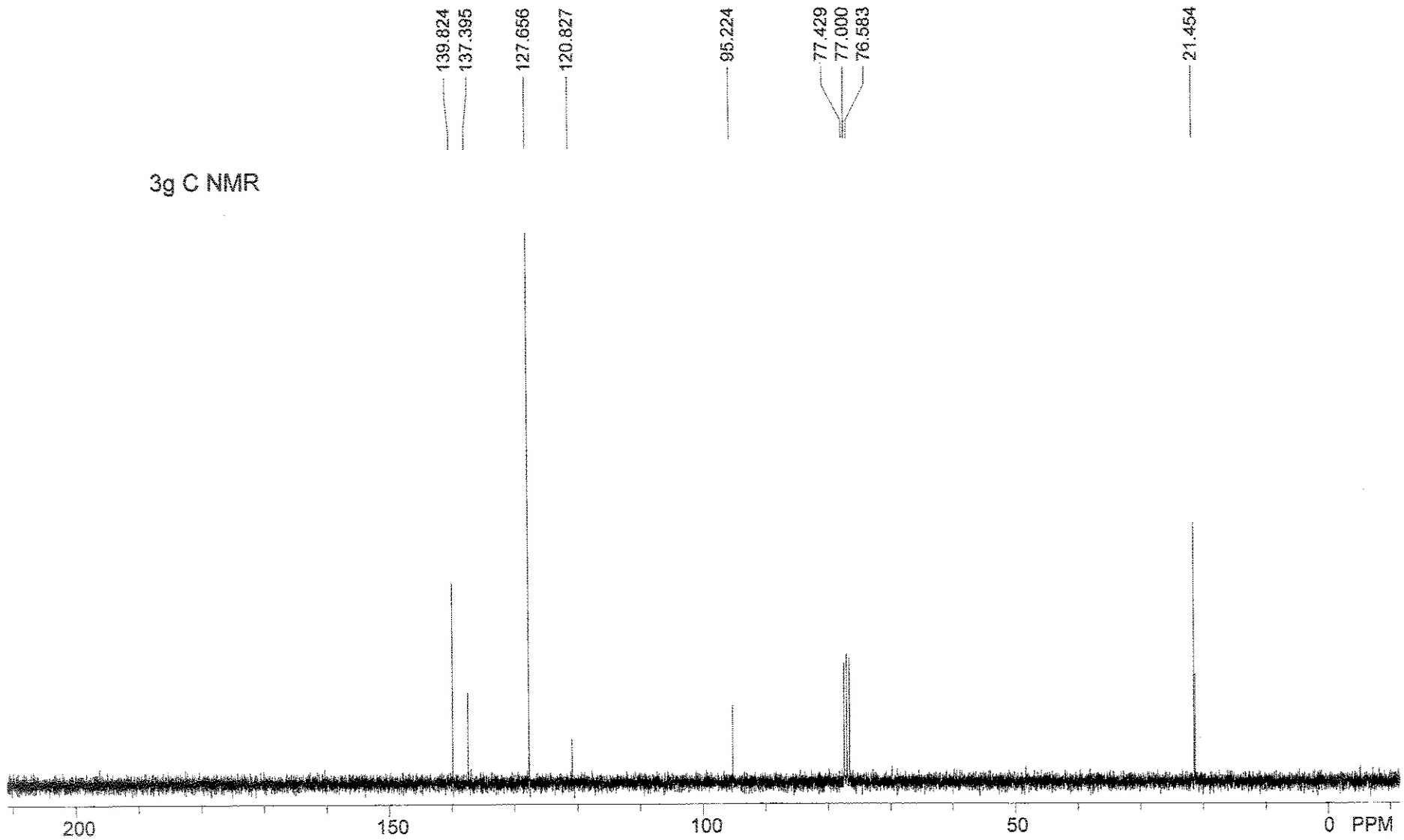

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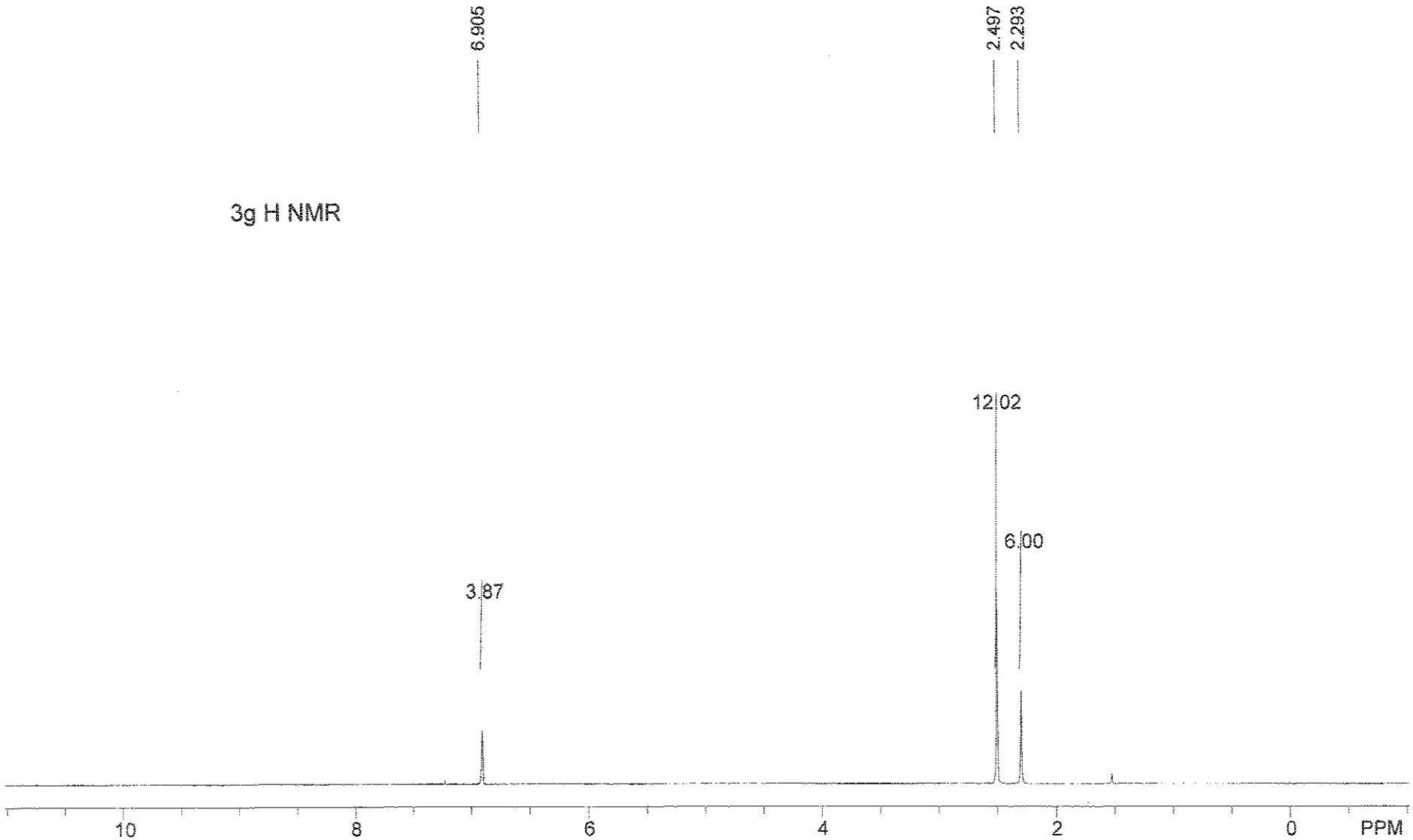

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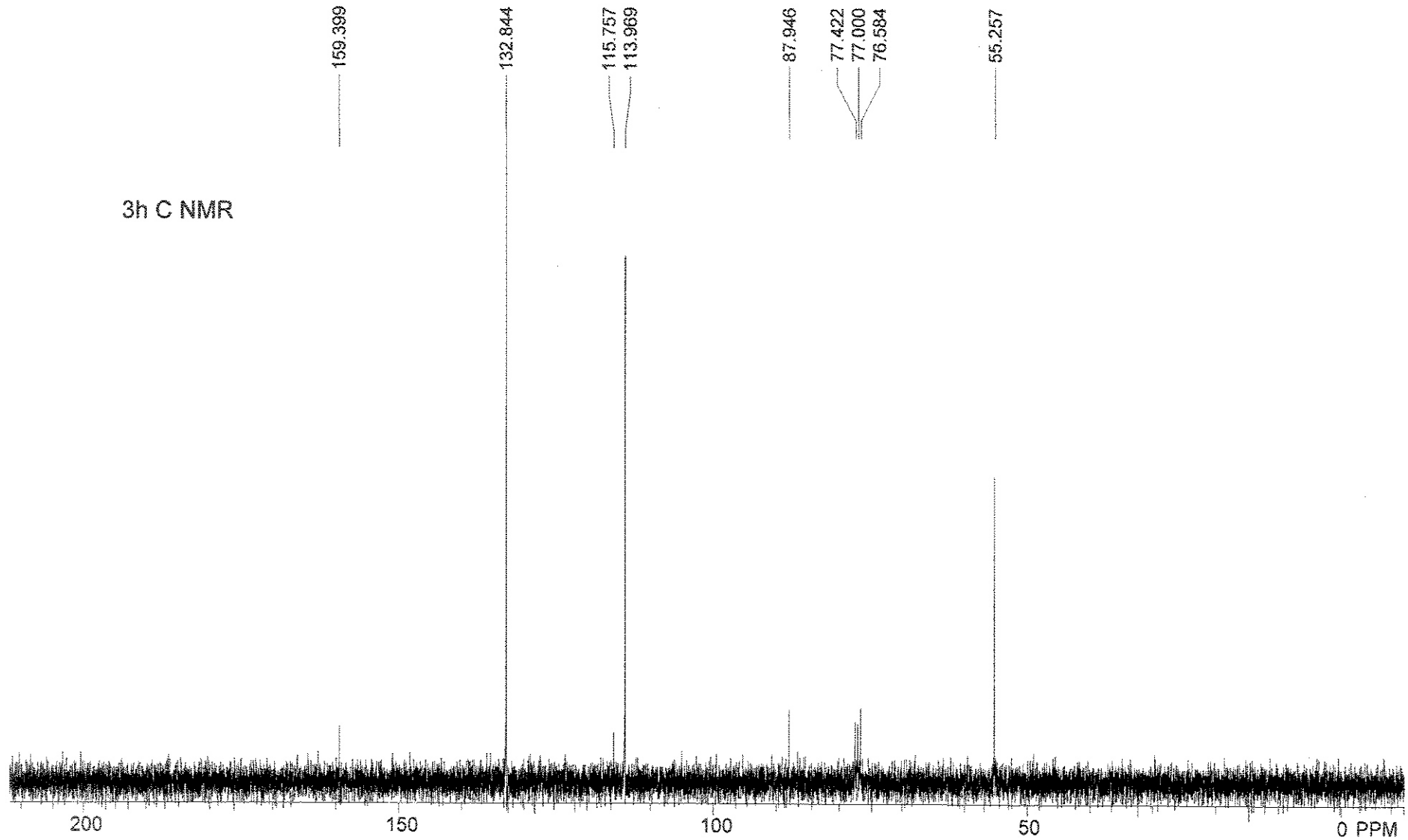

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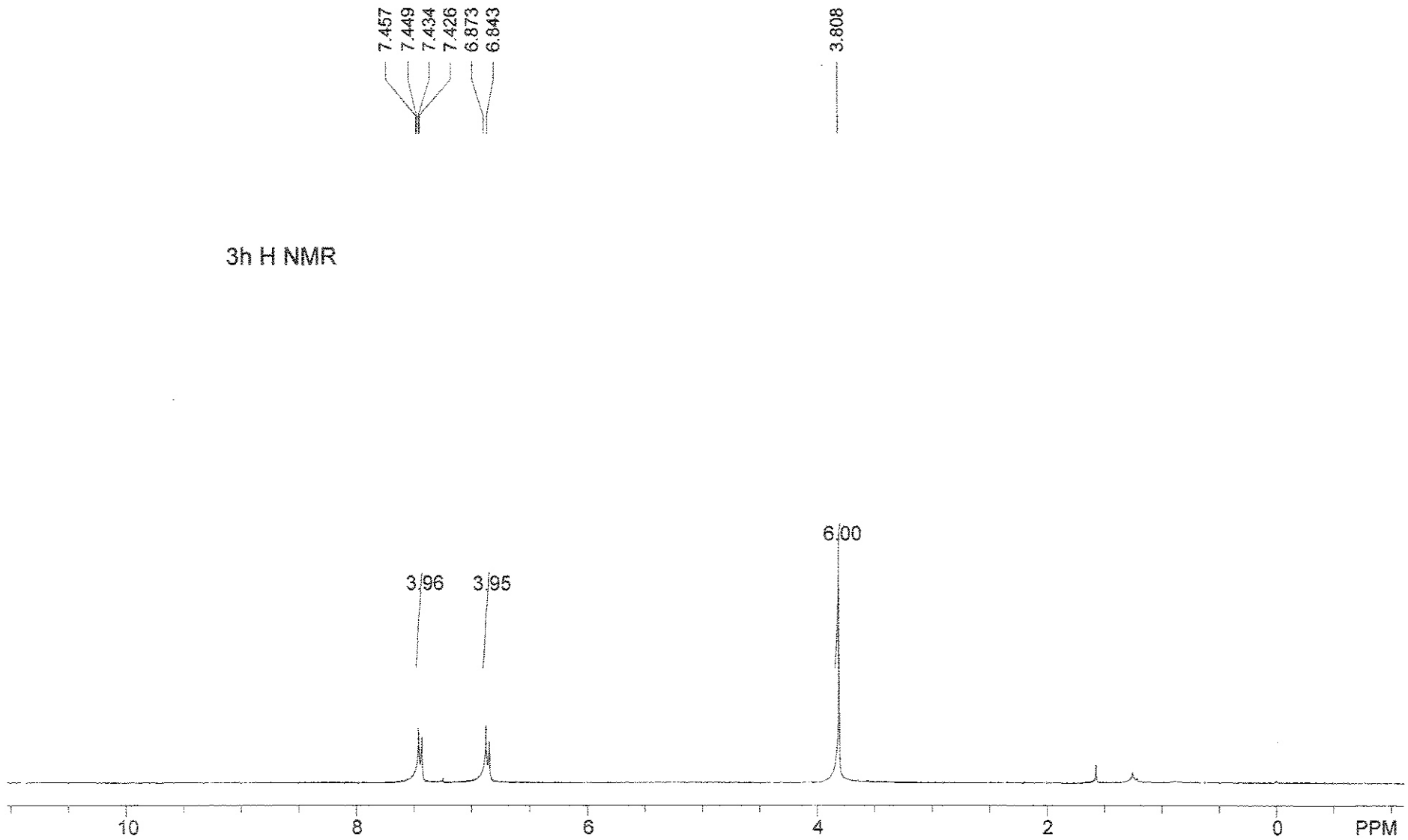

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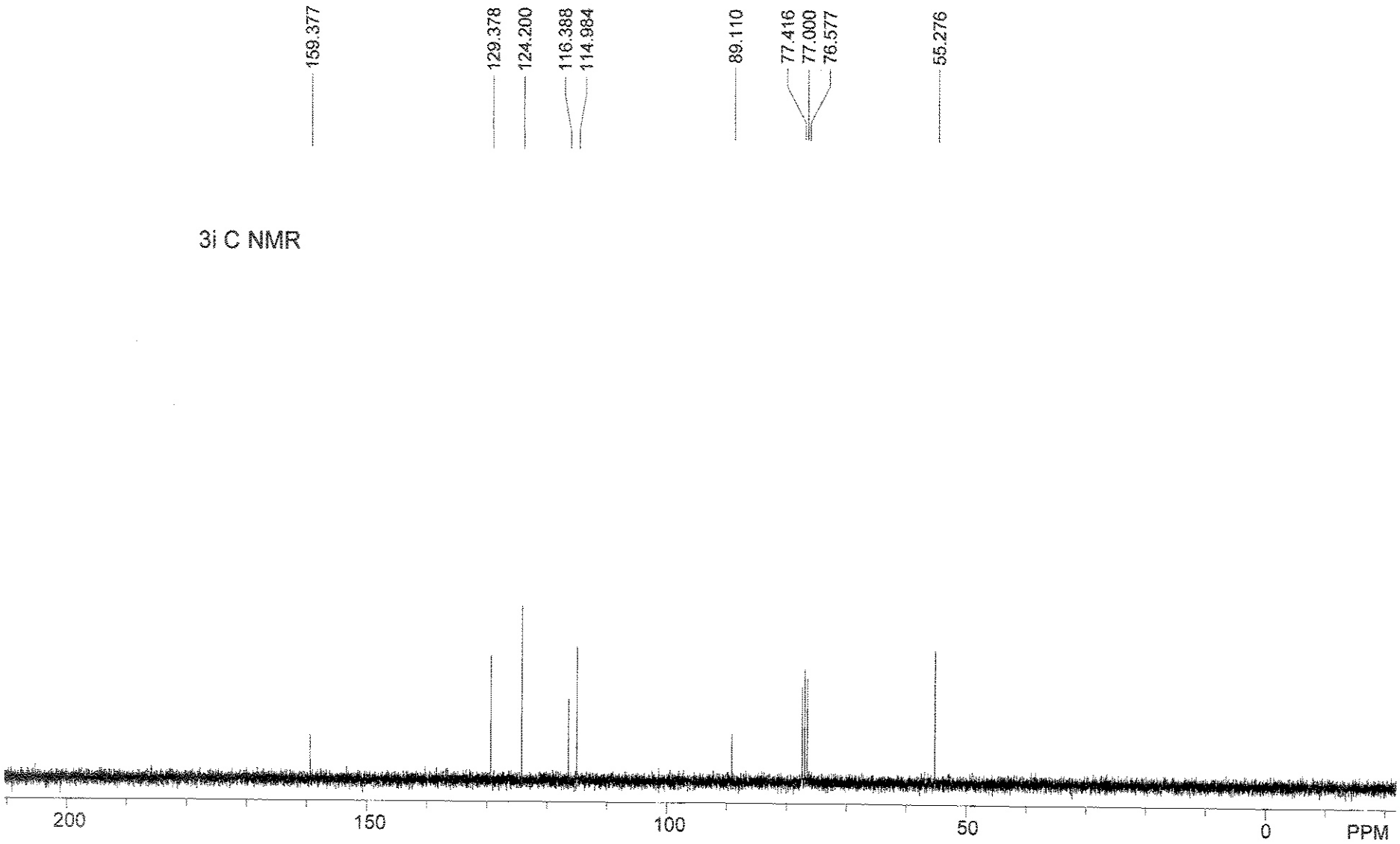

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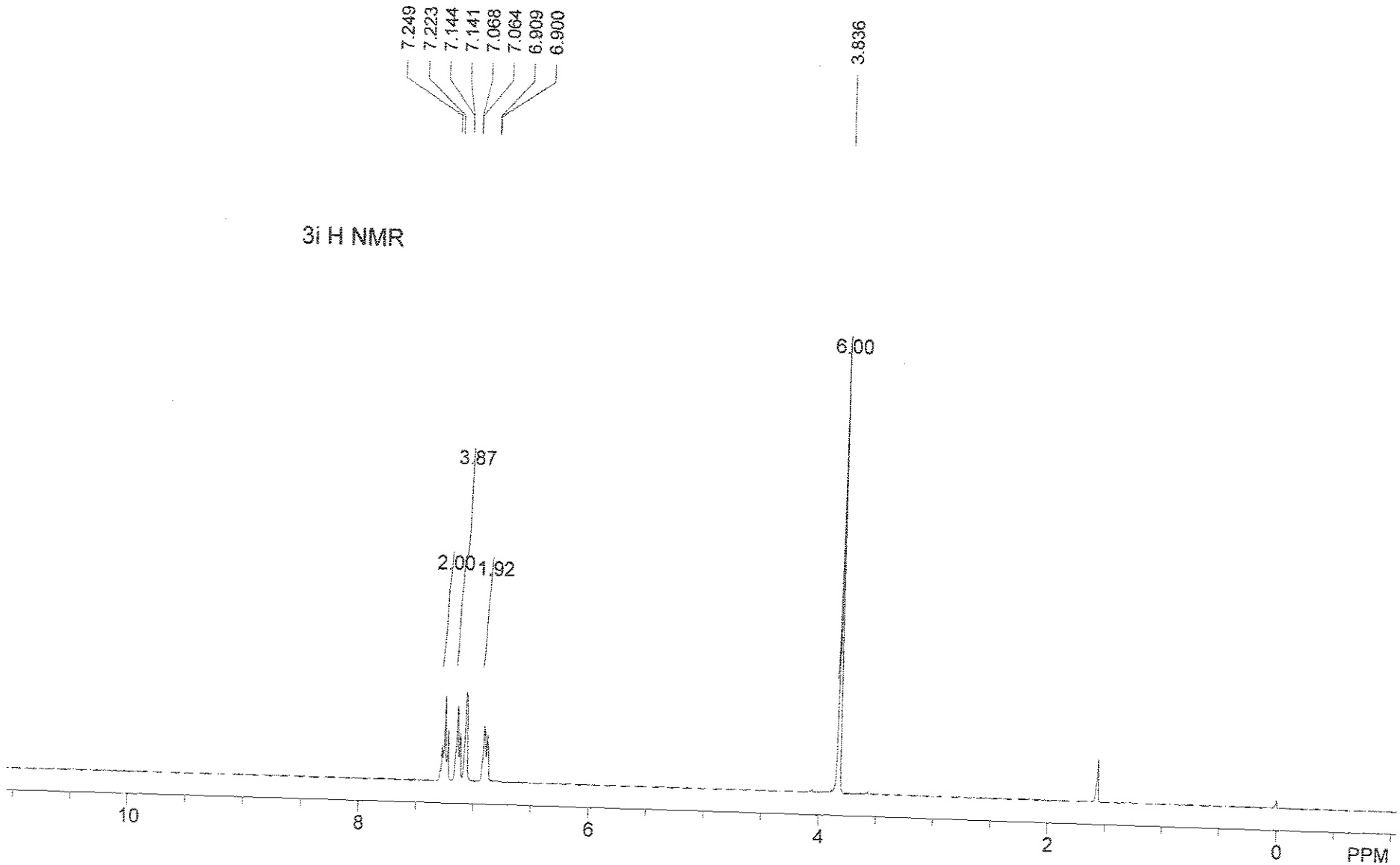

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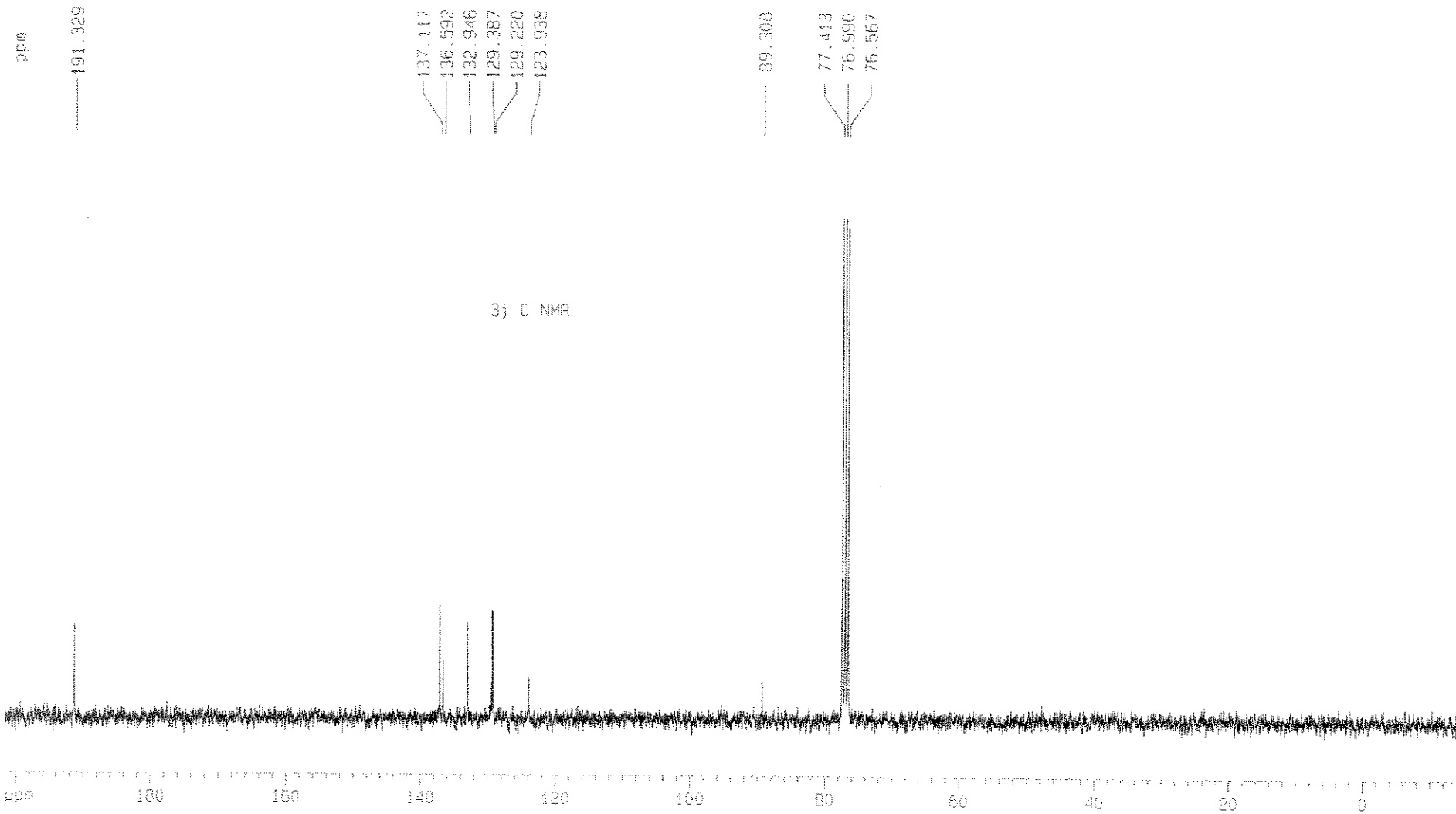

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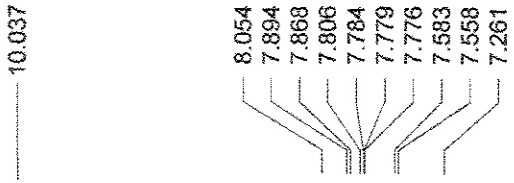
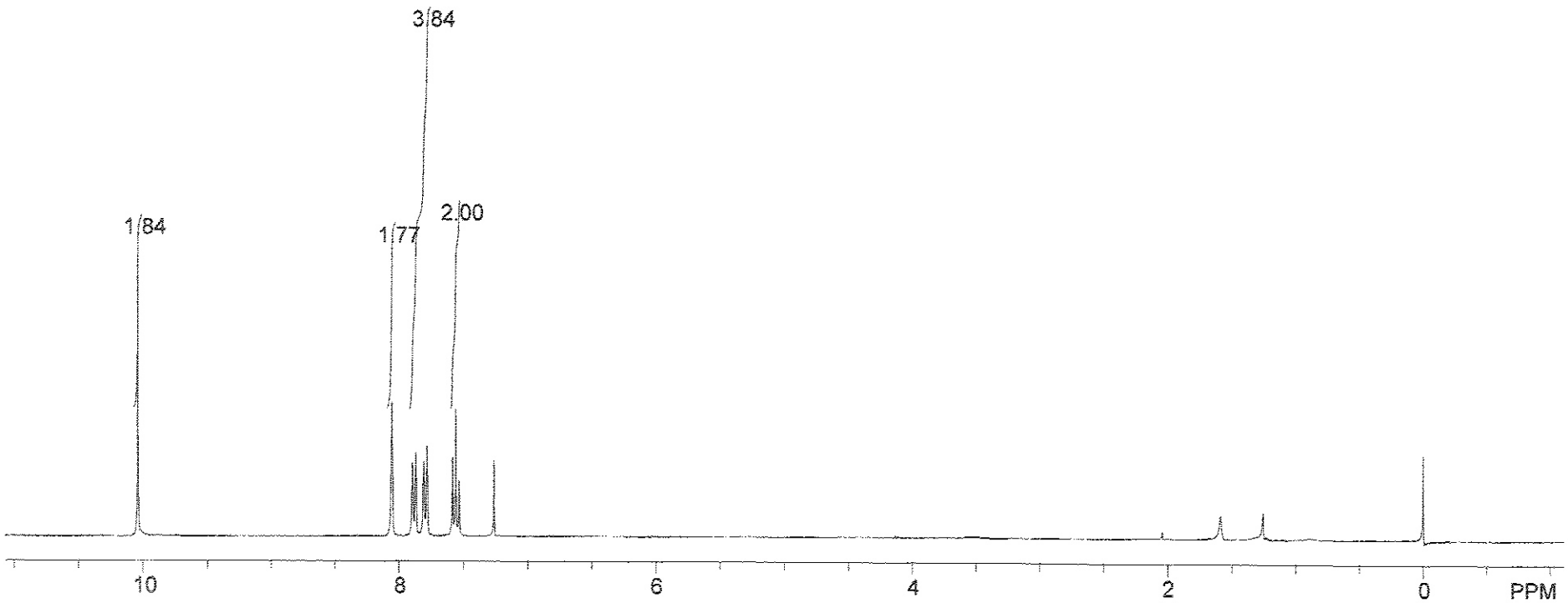


3j H NMR



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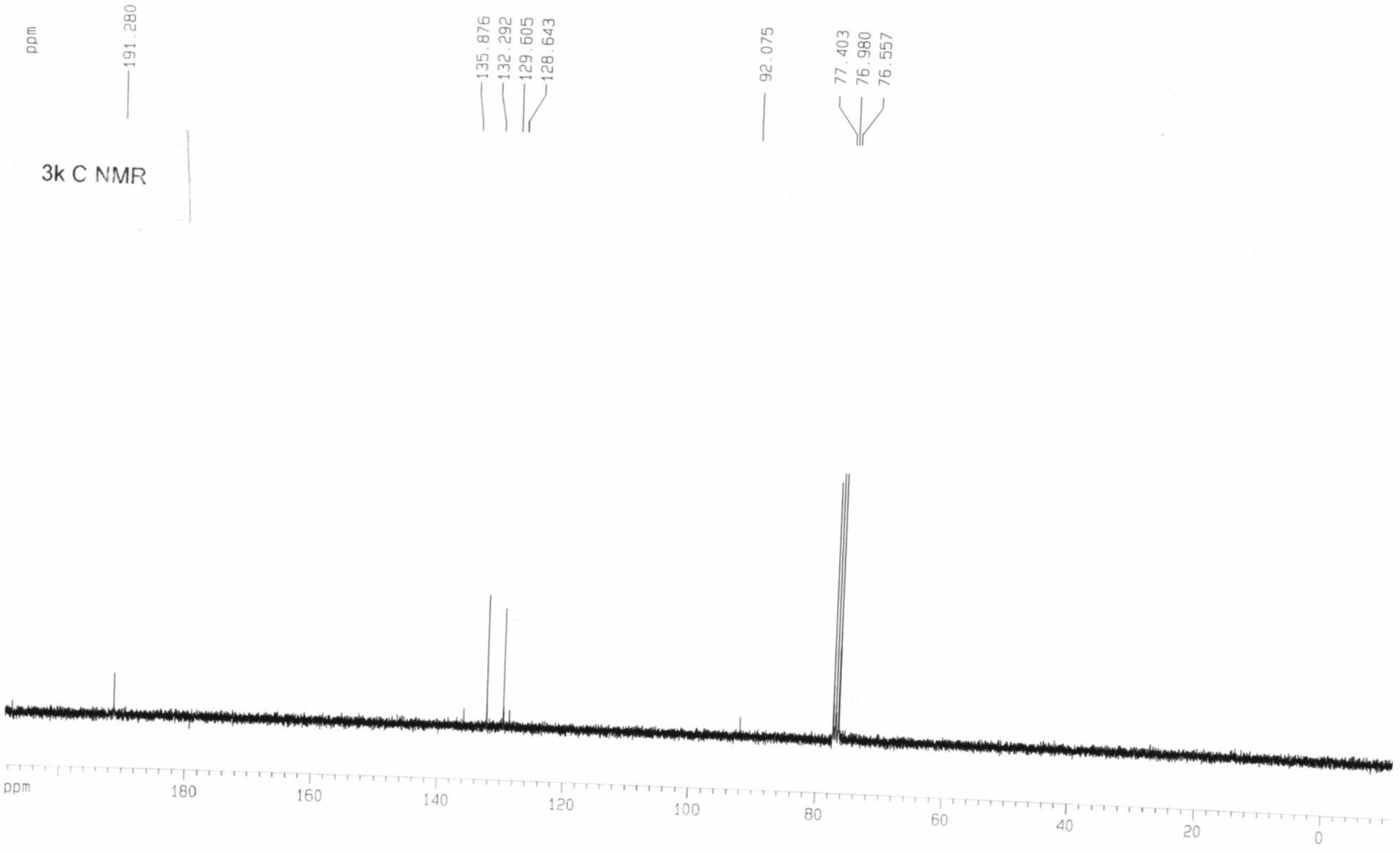

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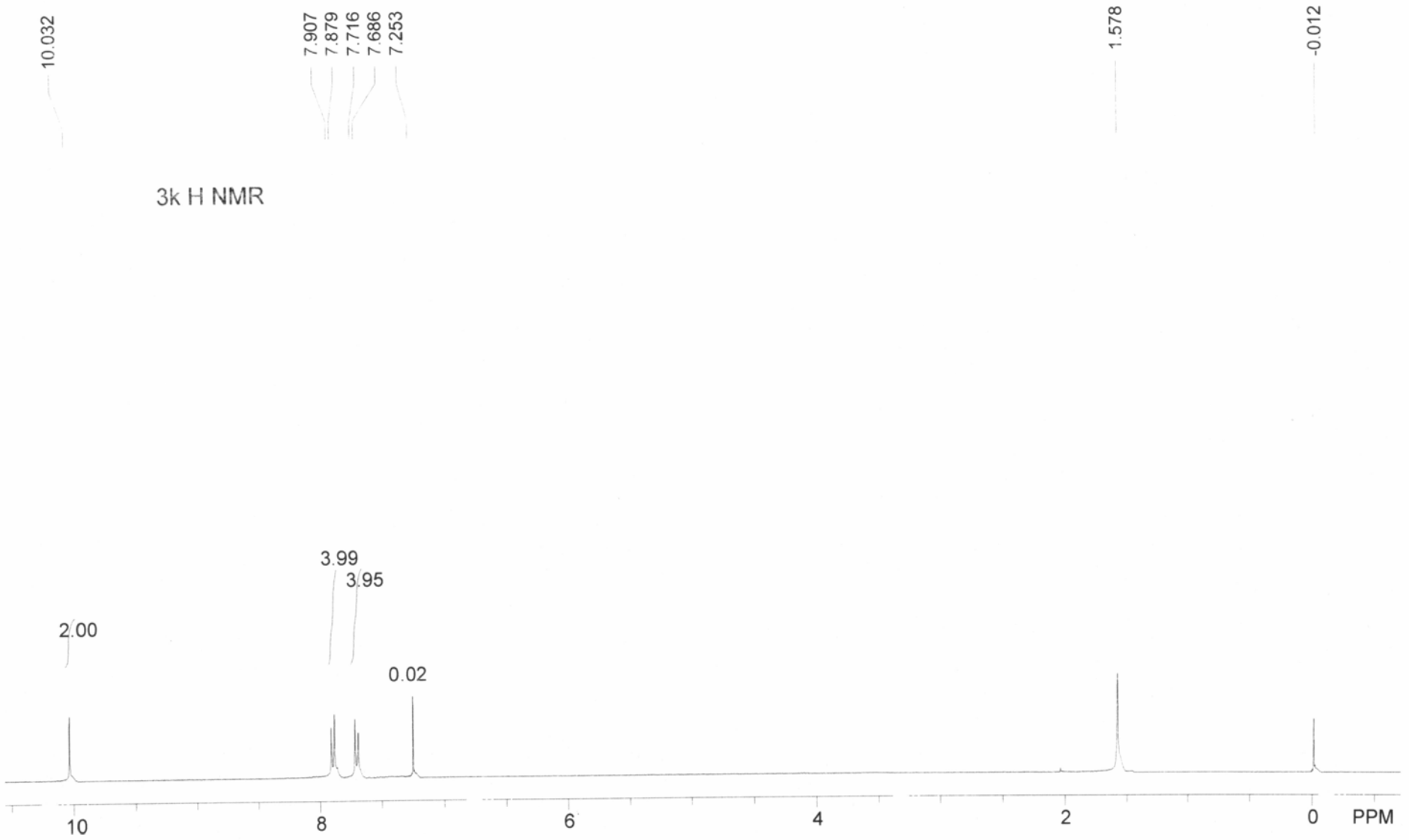

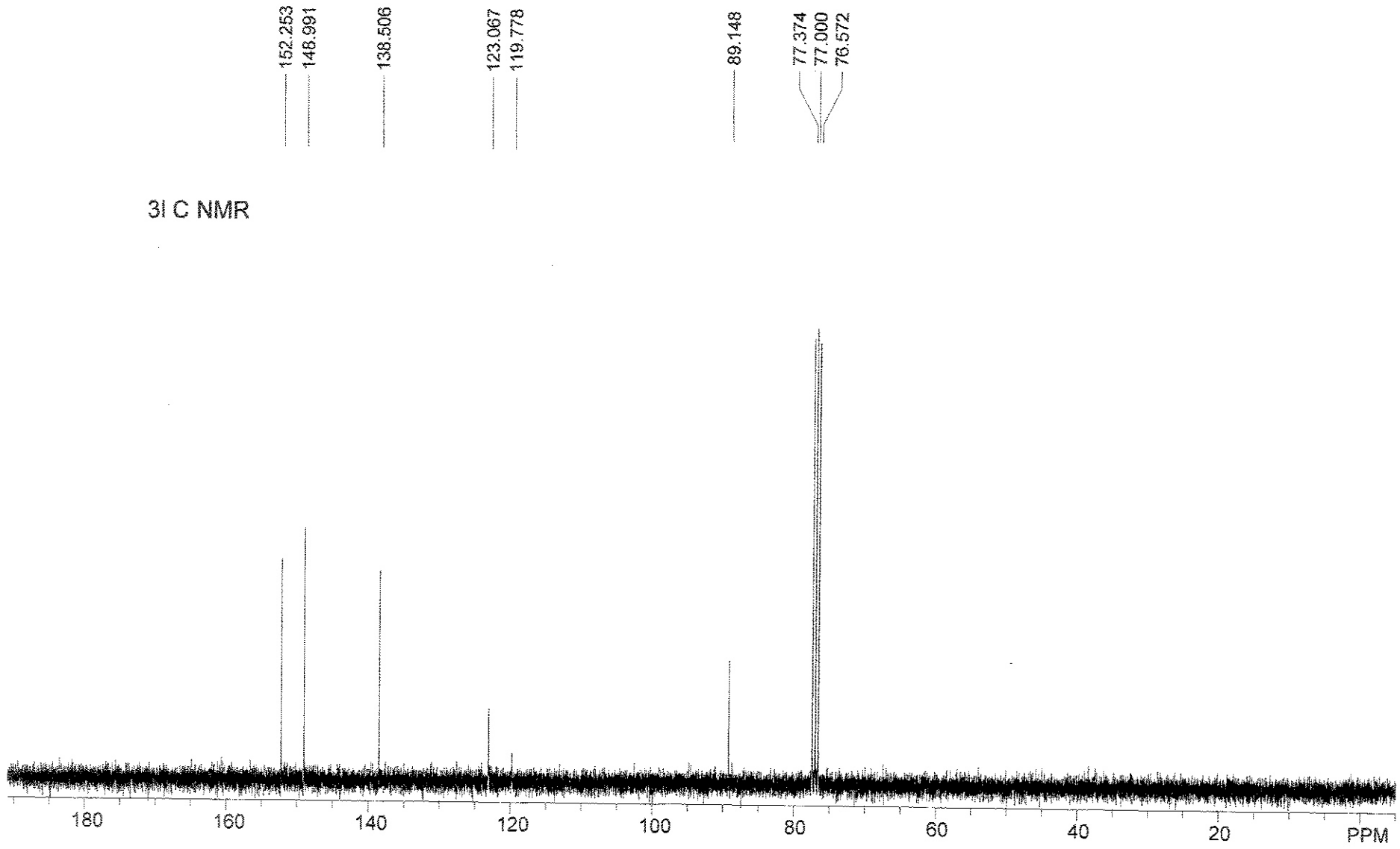
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3l C NMR
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140
120
100
80
60
40
20
PPM

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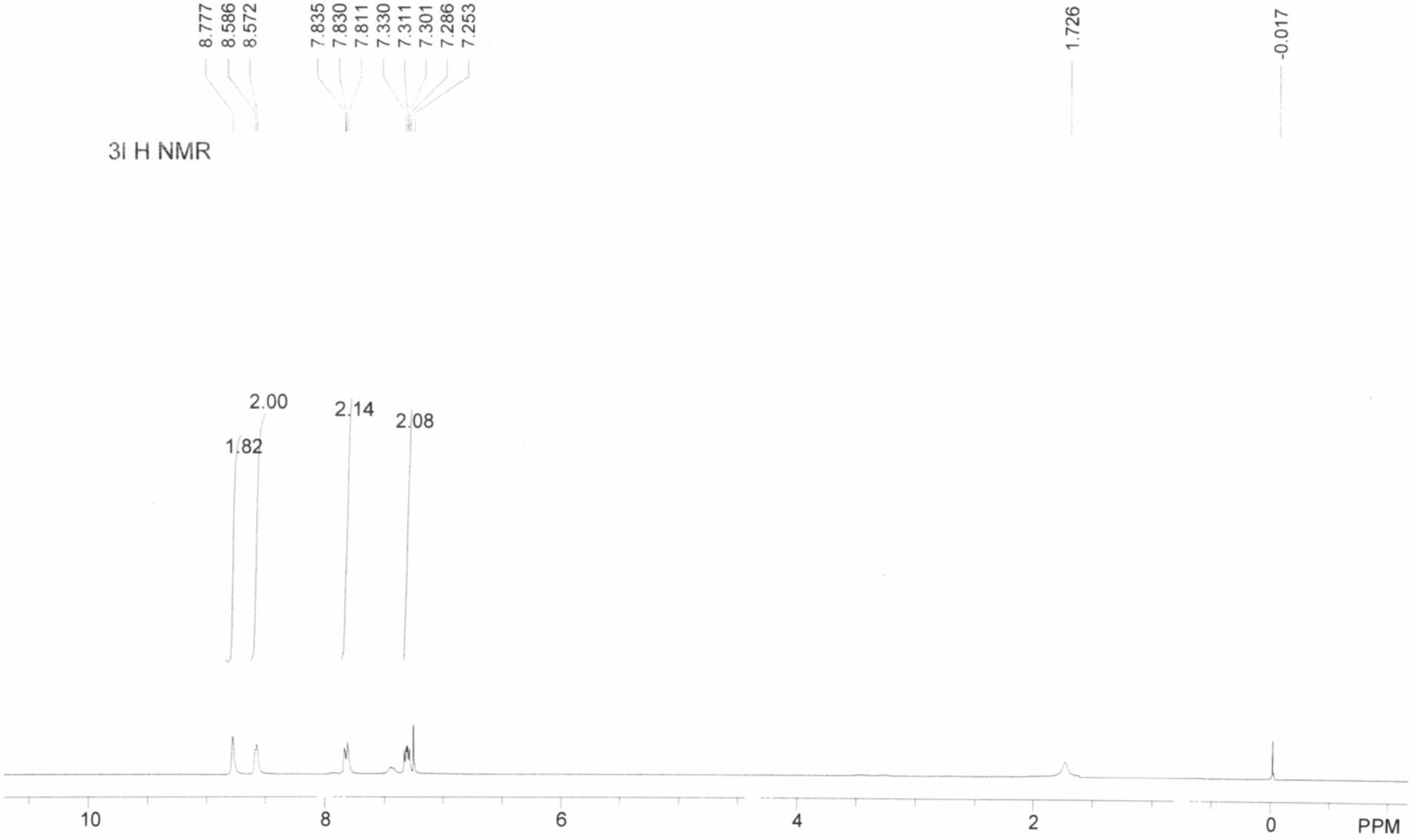

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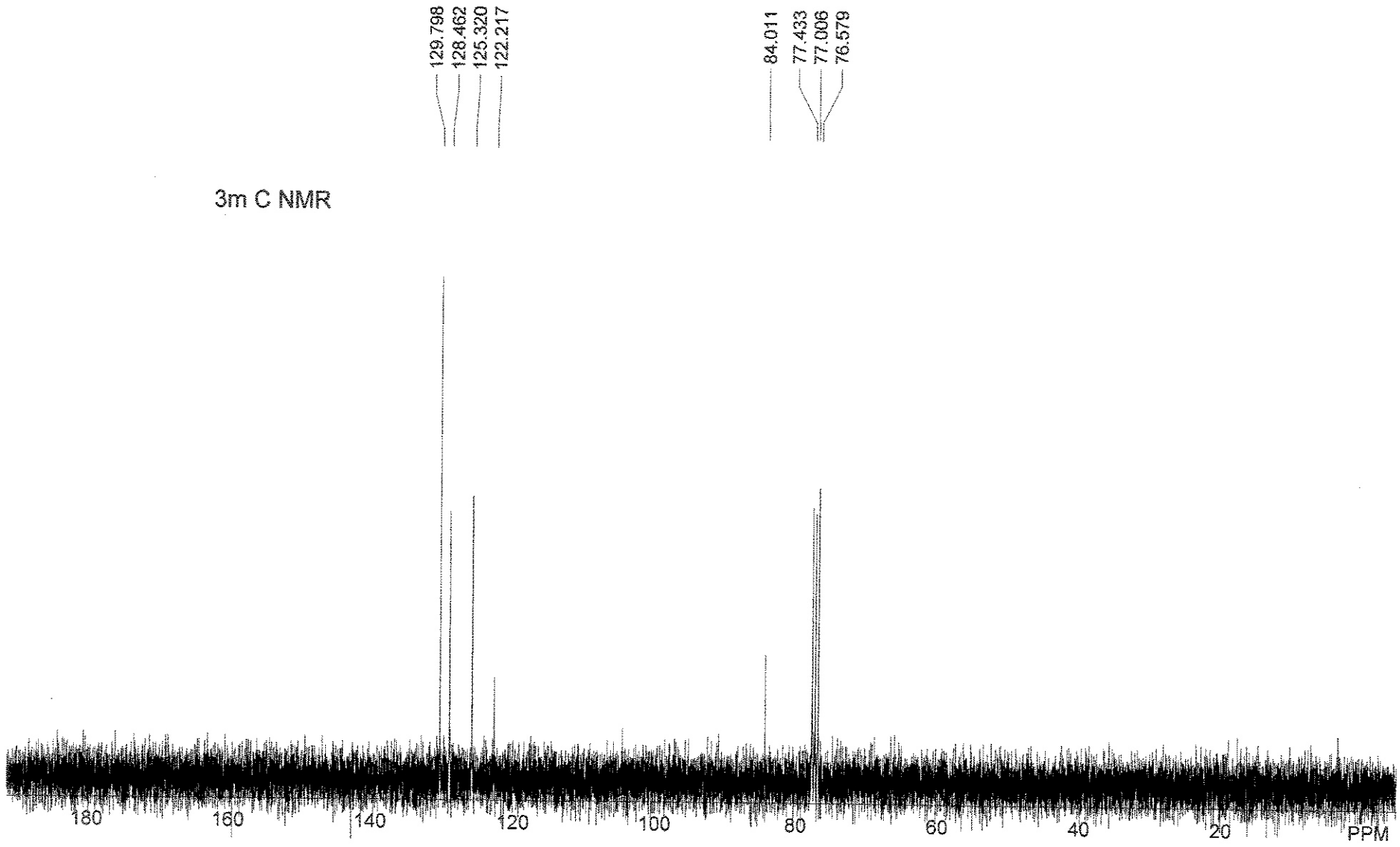

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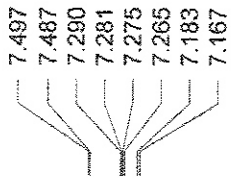
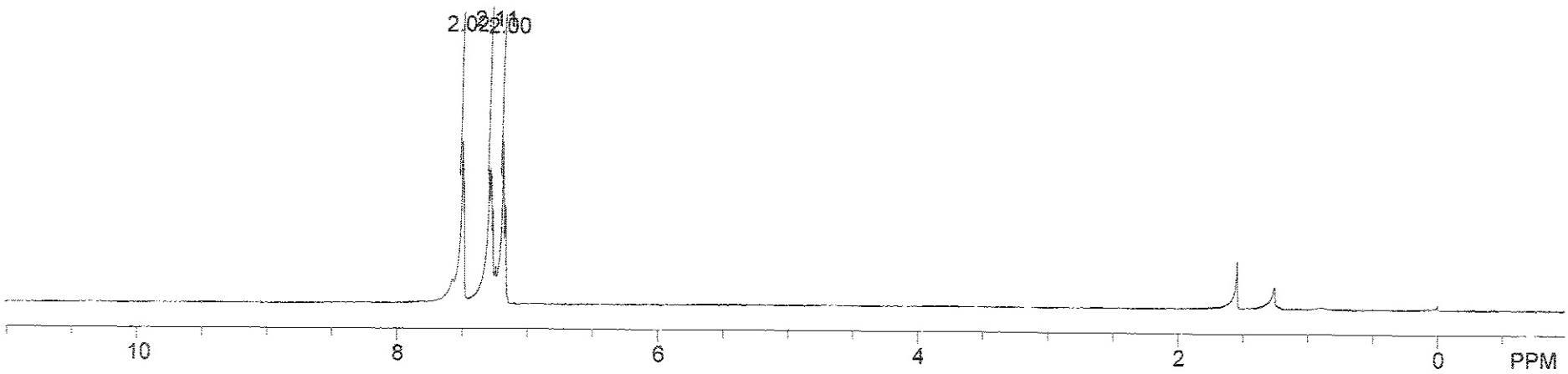


3m H NMR



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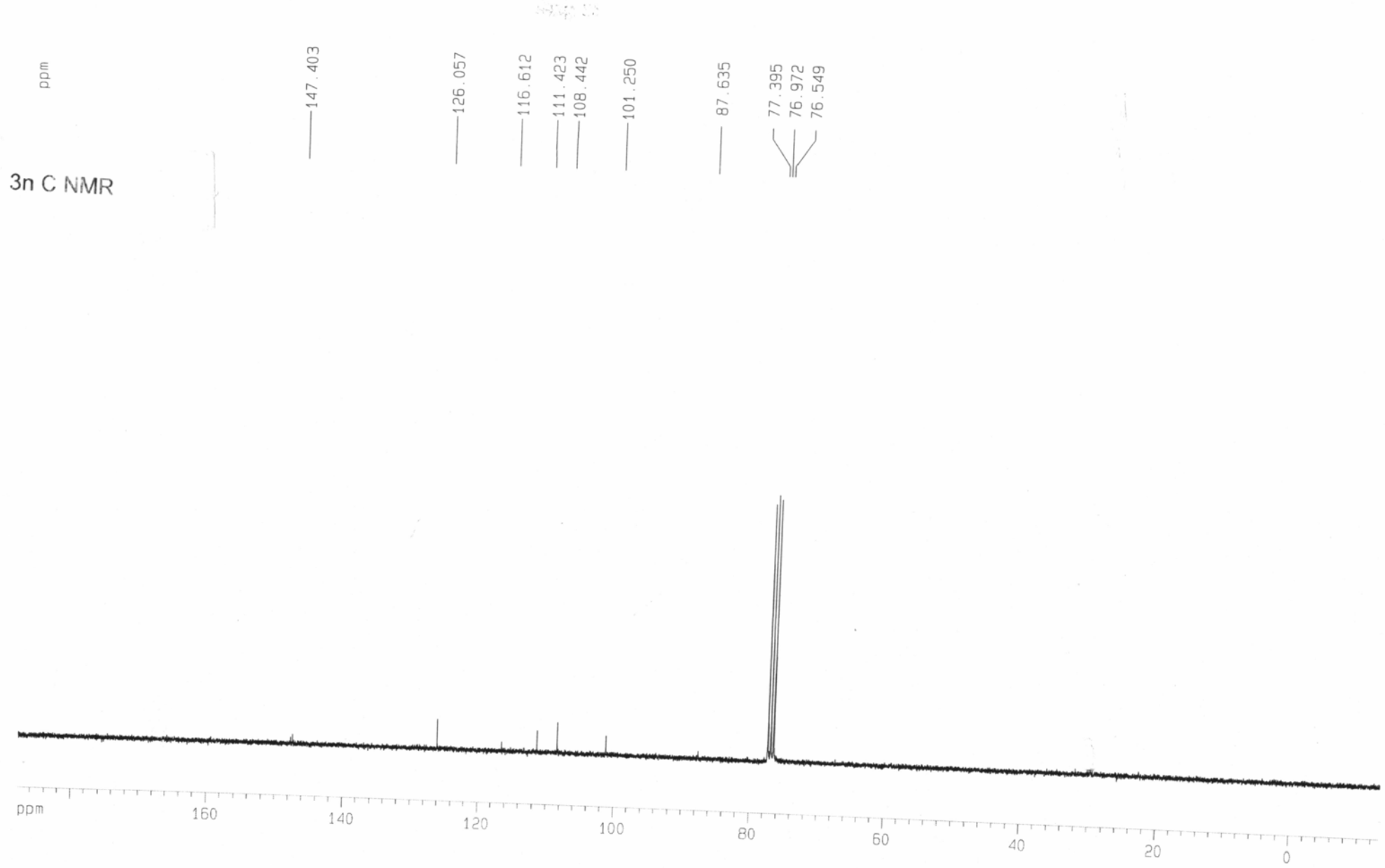

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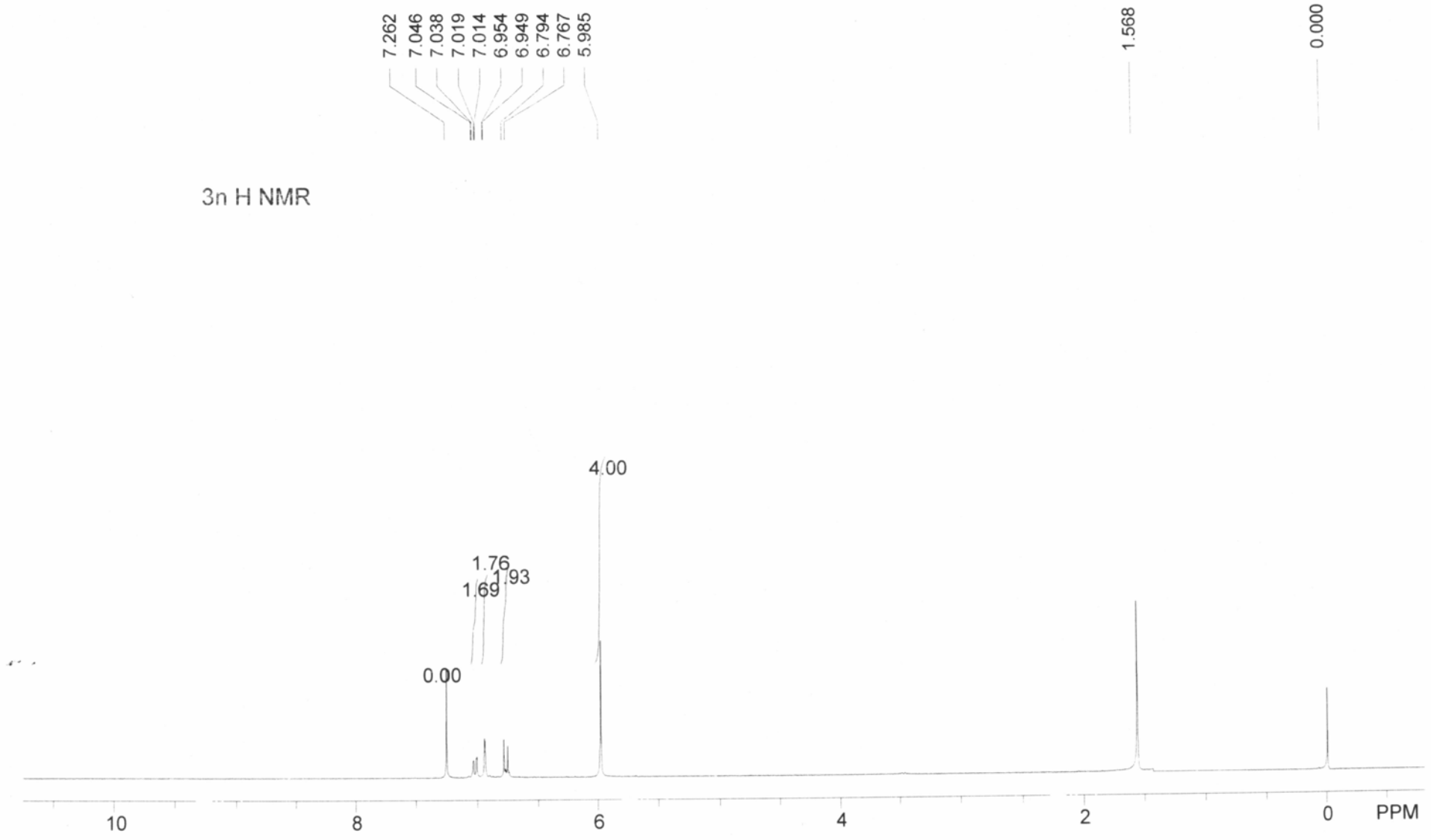

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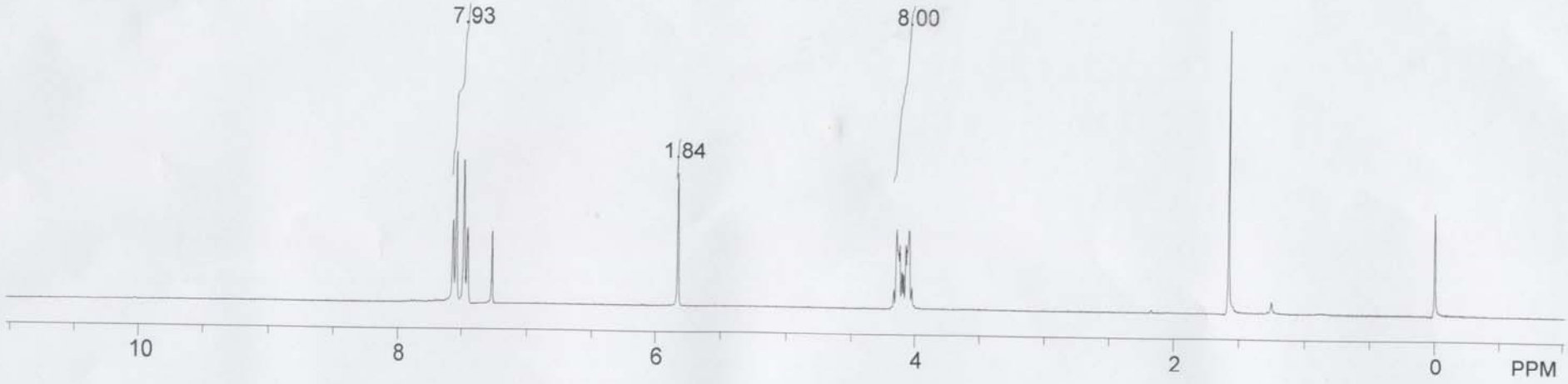
3p H NMR



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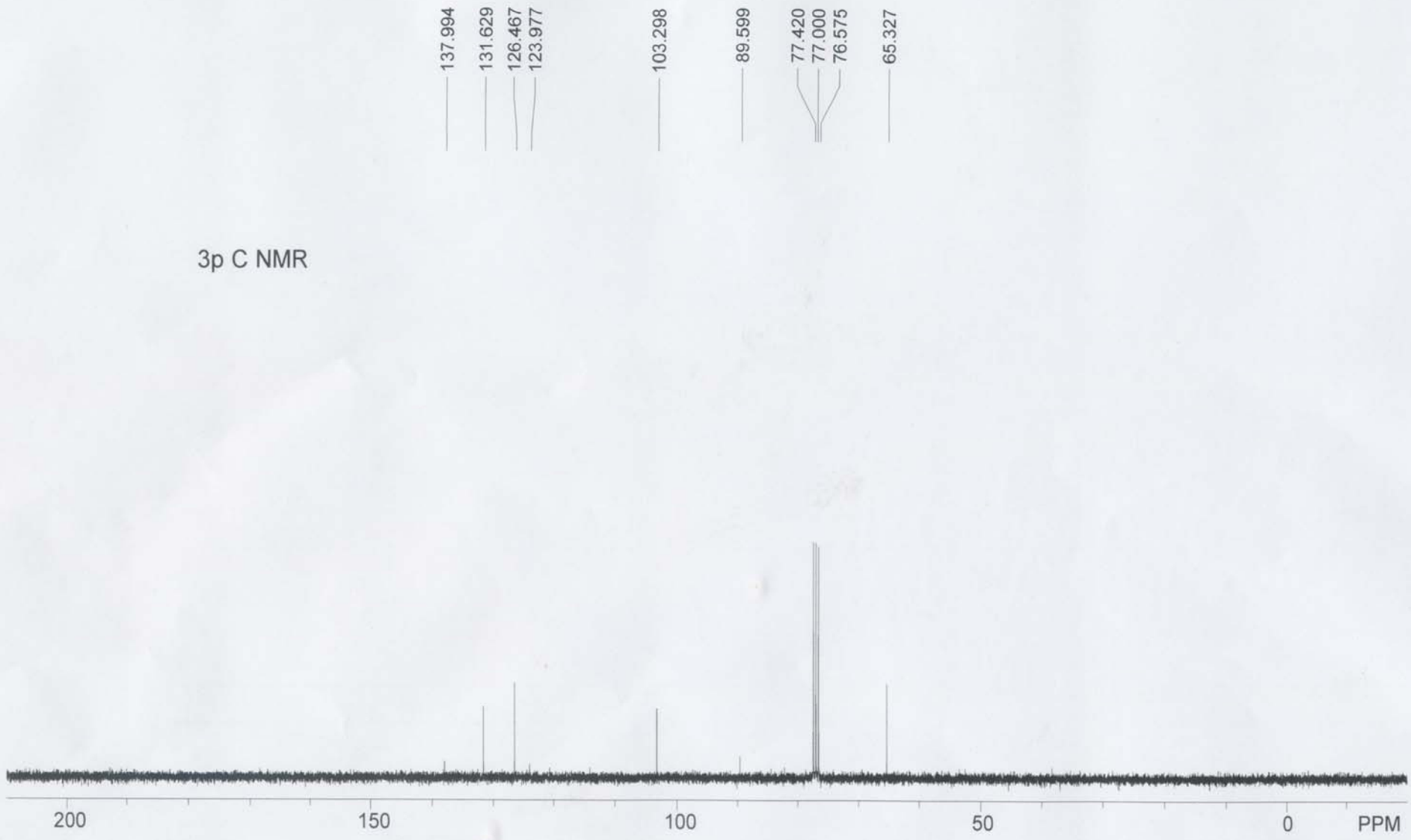

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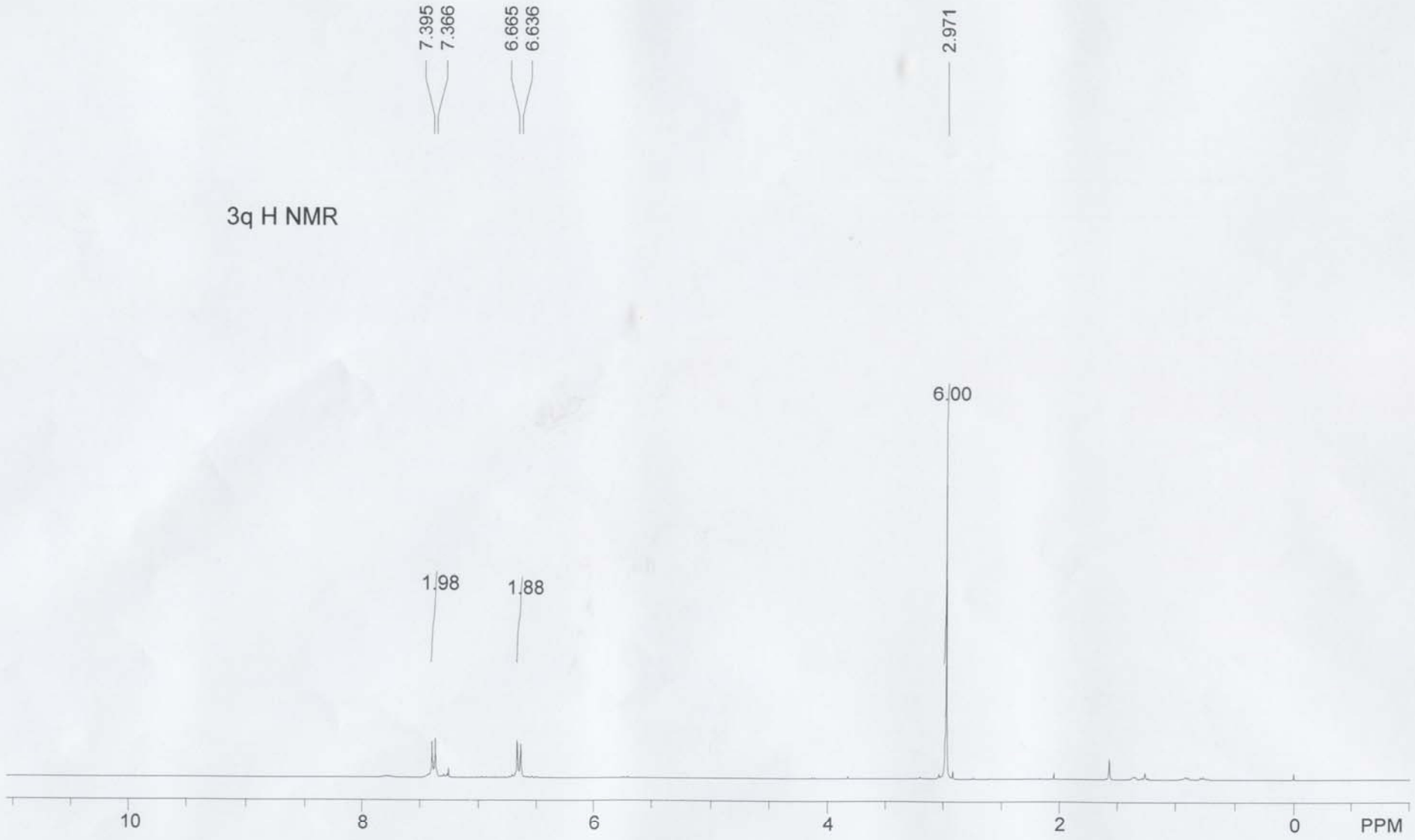

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