

Supporting Information

Heteroditopic *p*-tert-butyl thiacalix[4]arenes for creating supramolecular self-assemblies by cascade or commutative mechanisms

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Table S1. Size of aggregates (average hydrodynamic diameters, d_1 , d_2 , d_3 (nm)), and peak area intensity, S_1 , S_2 , S_3 (%), for peaks 1, 2, 3, respectively, obtained with *p*-*tert*-butyl thiacalix[4]arene derivative 5-10 and silver cations, dicarboxylic acids in CH_2Cl_2 (HPLC), and polydispersity index (PDI)^a

System	d ₁ , nm/S ₁ , %	d ₂ , nm/S ₂ , %	d ₃ , nm/S ₃ , %	PDI
1,3-alternate (5)+AgNO ₃	-	69.8±1.0/100	-	0.06±0.02
1,3- alternate (5)+oxalic acid	-	120.8±17.2/100	-	0.42±0.38
cone (6a)	-	189.8±63.8/96.4±8.5	5354.0±1182.8/3.6±8.5	0.50±0.20
cone (6a)+AgNO ₃	-	86.0±5.8/100	-	0.14±0.02
cone (6a)+ oxalic acid	-	131.6±25.0/97.6±2.0	5034.0±408.4/2.4±2.0	0.22±0.03
cone (6a)+ malonic acid	-	239.4±70.4/80.6±9.3	4411.4±613.2/19.4±9.3	0.28±0.11
partial cone (6b)	-	333.6±202.4/92.8±10.9	5448.4±136.8/7.2±10.9	0.84±0.25
partial cone (6b)+AgNO ₃	-	51.6±0.8/100	-	0.09±0.01
partial cone (6b)+ oxalic acid	-	168.6±16.8/100	-	0.15±0.05
1,3-alternate (6c)	-	482.4±156.4/88.7±19.0	3844.8±1182.8/11.3±19.0	0.39±0.14
1,3-alternate (6c)+AgNO ₃	-	232.2±72.6/97.3±2.2	4979.4±353.0/2.7±2.2	0.24±0.06
1,3-alternate (6c)+ oxalic acid	-	182.6±13.8/100	-	0.19±0.08
cone (7a)+AgNO ₃	-	75.0±4.4/100	-	0.15±0.02
partial cone (7b)+AgNO ₃	-	52.4±6.8/97.6±2.7	4173.4±1044.2/3.3±2.7	0.24±0.11
1,3- alternate (7c)+AgNO ₃	-	104.4±5.4/100	-	0.23±0.03
cone (8a)	8.2±5.6/59.8±32.3	-	4446.4±1271.2/40.2±32.3	0.76±0.68
cone (8a)+AgNO ₃	9.2±4.0/2.4±3.6	81.0±41.0/93.9±5.0	3894.0±725.8/3.6±3.4	0.31±0.14
cone (8a)+ oxalic acid	7.2±3.4/12.1±3.8	65.4±21.6/87.9±3.8	-	0.45±0.21
cone (8a)+ malonic acid	11.0±1.6/3.3±4.5	127.8±33.4/94.0±5.5	4905.2±122.0/2.7±1.8	0.18±0.14
cone (8a)+ succinic acid	-	220.6±108.6/95.4±9.4	4733.0±883.8/4.6±9.4	0.27±0.17
partial cone (8b)	31.0±8.6/57.2±20.8	795.4±538.2/37.0±24.3	4784.6±849.8/5.8±4.9	0.26±0.14
partial cone (8b)+AgNO ₃	38.2±22.4/24.0±32.2	288.6±96.8/76.0±32.2	-	0.56±0.12
partial cone (8b)+ oxalic acid	-	93.2±21.8/98.1±2.7	4951.6±644.4/1.9±2.7	0.35±0.27
1,3-alternate (8c)	-	92.4±17.6/100	-	0.08±0.04
1,3-alternate (8c)+AgNO ₃	-	51.8±9.4/96.6±2.5	4925.8±358.0/3.4±2.5	0.15±0.14
1,3-alternate (8c)+ oxalic acid	-	183.0±19.6/100	-	0.14±0.06
1,3-alternate (8c)+ malonic acid	-	203.4±44.8/100	-	0.10±0.05
cone (9a)	94.4±34.4/10.9±10.1	308.0±108.4/89.1±10.1	-	0.55±0.17
cone (9a)+AgNO ₃	-	157.6±43.0/98.1±3.0	4756.0±633.8/1.9±3.0	0.23±0.09
cone (9a)+ oxalic acid	-	54.6±33.4/100	-	0.73±0.29
cone (9a)+ malonic acid	7.6±6.6/8.6±2.6	118.6±51.6/83.0±9.6	5032.6±573.6/8.3±8.8	0.32±0.23
cone (9a)+ succinic acid	-	174.6±58.4/96.5±2.5	4569.2±330.4/3.5±2.5	0.19±0.10

<i>partial cone (9b)</i> +AgNO ₃	-	65.2±6.4/96.1±3.3	3668.0±1340.6/4.0±3.3	0.22±0.09
<i>partial cone (9b)</i> + oxalic acid	-	53.4±1.2/99.4±1.1	4812.8±384.4/0.6±1.1	0.16±0.03
<i>1,3-alternate (9c)</i>	-	343.2±215.6/88.0±21.8	5560.0±1356.0/12.0±21.8	0.66±0.70
<i>1,3-alternate (9c)</i> +AgNO ₃	-	137.0±27.6/100	-	0.10±0.02
<i>1,3-alternate (9c)</i> + oxalic acid	-	134.6±21.0/100	-	0.22±0.16
<i>1,3-alternate (9c)</i> + malonic acid	-	140.4±23.2/100	-	0.14±0.02
<i>cone (10a)</i> +AgNO ₃	-	246.4±17.6/100	-	0.20±0.05
<i>partial cone (10b)</i> +AgNO ₃	-	84.4±58.0/94.6±4.7	3917.2±699.6/5.4±4.7	0.19±0.10
<i>partial cone (10b)</i> + malonic acid	-	153.0±41.2/98.5±1.4	5333.0±194.4/1.5±1.4	0.19±0.12
<i>1,3-alternate (10c)</i> +AgNO ₃	-	84.8±21.0/96.6±3.1	4064.4±584.6/3.4±3.1	0.22±0.10
<i>1,3-alternate (10c)</i> + oxalic acid	-	60.8±46.6/98.8±2.7	4728.0±495.4/1.2±2.7	0.57±0.50

^a ±, standard deviation; -, no aggregates are formed

Table S2. Size of aggregates (average hydrodynamic diameters, d_1 , d_2 , d_3 (nm)), peak area intensity, S_1 , S_2 , S_3 (%), for peaks 1, 2, 3, respectively, obtained with *p*-tert-butylthiacalix[4]arene derivatives and silver cations, dicarboxylic acids in CH_2Cl_2 (HPLC) at 20°C^a, and polydispersity index (PDI)^a

System	d_1 , nm/ S_1 , %	d_2 , nm/ S_2 , %	d_3 , nm/ S_3 , %	PDI
<i>cascade systems</i>				
[<i>partial cone</i> (6b)+oxalic acid] _{agr.} +AgNO ₃		124.4±25.6/100		0.23±0.09
[1,3- <i>alternate</i> (6c)+AgNO ₃] _{agr.} + succinic acid	10.8±1.2/6.1±2.6	86.6±4.4/93.9±2.6		0.27±0.01
[<i>cone</i> (8a)+AgNO ₃] _{agr.} + succinic acid		40.4±8.8/95.5±4.6	3526.0±1495.0/4.5±4.6	0.23±0.12
[1,3- <i>alternate</i> (8c)+ malonic acid] _{agr.} +AgNO ₃	10.6±3.8/0.7±1.7	80.8±16.2/98.6±1.9	5421.2±86.0/0.7±1.1	0.21±0.15
[<i>partial cone</i> (9b)+AgNO ₃] _{agr.} + oxalic acid		95.8±6.0/99.4±1.2	4730.0±368.2/0.6±1.2	0.16±0.03
[1,3- <i>alternate</i> (9c)+AgNO ₃] _{agr.} + oxalic acid	15.0±3.4/6.9±9.7	80.4±5.8/93.2±9.7		0.31±0.01
[<i>cone</i> (10a)+AgNO ₃] _{agr.} + oxalic acid		79.2±32.4/98.9±1.5	5034.4±444.8/1.1±1.5	0.30±0.20
[<i>cone</i> (10a)+AgNO ₃] _{agr.} + malonic acid		73.8±31.8/98.8±1.7	4685.4±1085.4/1.2±1.7	0.20±0.15
[<i>cone</i> (10a)+AgNO ₃] _{agr.} + succinic acid		74.6±18.0/98.0±1.4	5009.6±241.4/2.0±1.4	0.26±0.06
[<i>partial cone</i> (10b)+AgNO ₃] _{agr.} + oxalic acid		37.4±11.0/100		0.67±0.37
[1,3- <i>alternate</i> (10c)+AgNO ₃] _{agr.} + malonic acid	30.6±7.6/14.4±14.1	121.6±41.4/84.0±13.4	5240.6±308.4/1.6±1.9	0.18±0.10
<i>intermediate systems</i>				
[1,3- <i>alternate</i> (8c)+AgNO ₃] _{agr.} + oxalic acid		87.8±10.6/100		0.21±0.10
[1,3- <i>alternate</i> (8c)+oxalic acid] _{agr.} +AgNO ₃		131.4±2.4/100		0.06±0.02
[<i>cone</i> (9a)+ succinic acid] _{agr.} +AgNO ₃	5.2±0.6/11.0±0.9	54.4±4.6/87.4±0.8	4977.0±194.0/1.6±0.9	0.39±0.14
[<i>cone</i> (9a)+AgNO ₃] _{agr.} +succinic acid	14.8±4.4/3.2±4.6	86.6±11.0/96.8±4.6		0.25±0.08
<i>commutative systems</i>				
[1,3- <i>alternate</i> (6c)+AgNO ₃] _{agr.} + oxalic acid		87.2±4.2/100		0.21±0.05
[1,3- <i>alternate</i> (6c)+oxalic acid] _{agr.} +AgNO ₃		84.8±4.0/100		0.23±0.14
[<i>cone</i> (8a)+ malonic acid] _{agr.} +AgNO ₃	3.2±0.4/11.9±2.6	46.4±4.8/85.0±2.4	4716.0±405.6/3.1±2.1	0.38±0.14
[<i>cone</i> (8a)+AgNO ₃] _{agr.} + malonic acid	4.6±0.2/35.8±2.8	52.4±2.2/64.2±2.8		0.39±0.01
[1,3- <i>alternate</i> (9c)+ malonic acid] _{agr.} +AgNO ₃	16.8±4.4/10.6±2.4	95.4±21.4/88.9±2.6	5202.6±326.6/0.5±1.0	0.25±0.14
[1,3- <i>alternate</i> (9c)+AgNO ₃] _{agr.} + malonic acid		94.0±3.4/100		0.24±0.01

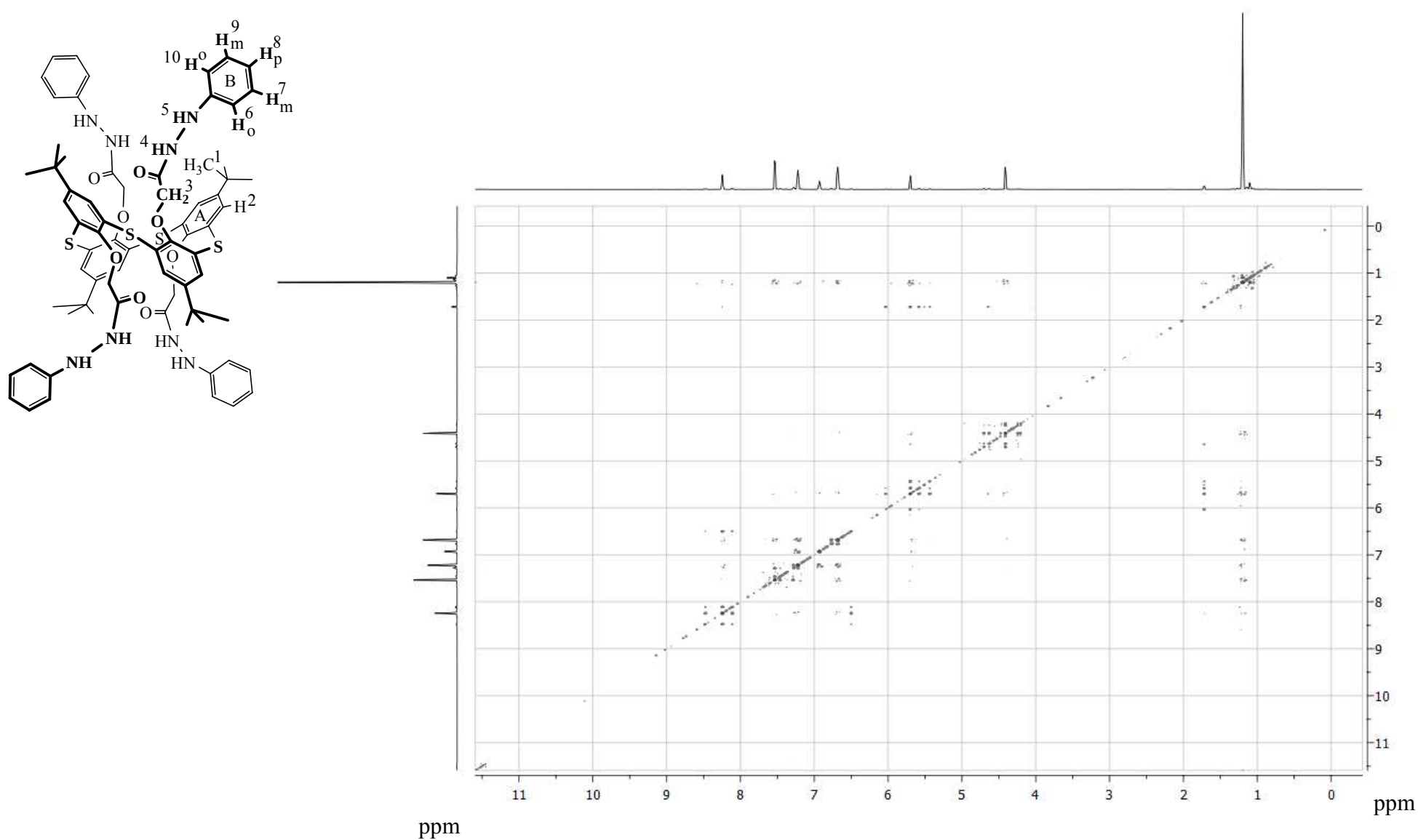
^a±, standard deviation; -, no aggregates are formed.

Table S3. Logarithms of the association constants ($\lg K_{\text{ass}}$) and stoichiometry of (n ("guest" / "host")) nanoscale aggregates based on compounds **6b, **6c**, **8a**, **8c**, **9a-c**, **10a-c** and silver ions (**I**), dicarboxylic acids^a**

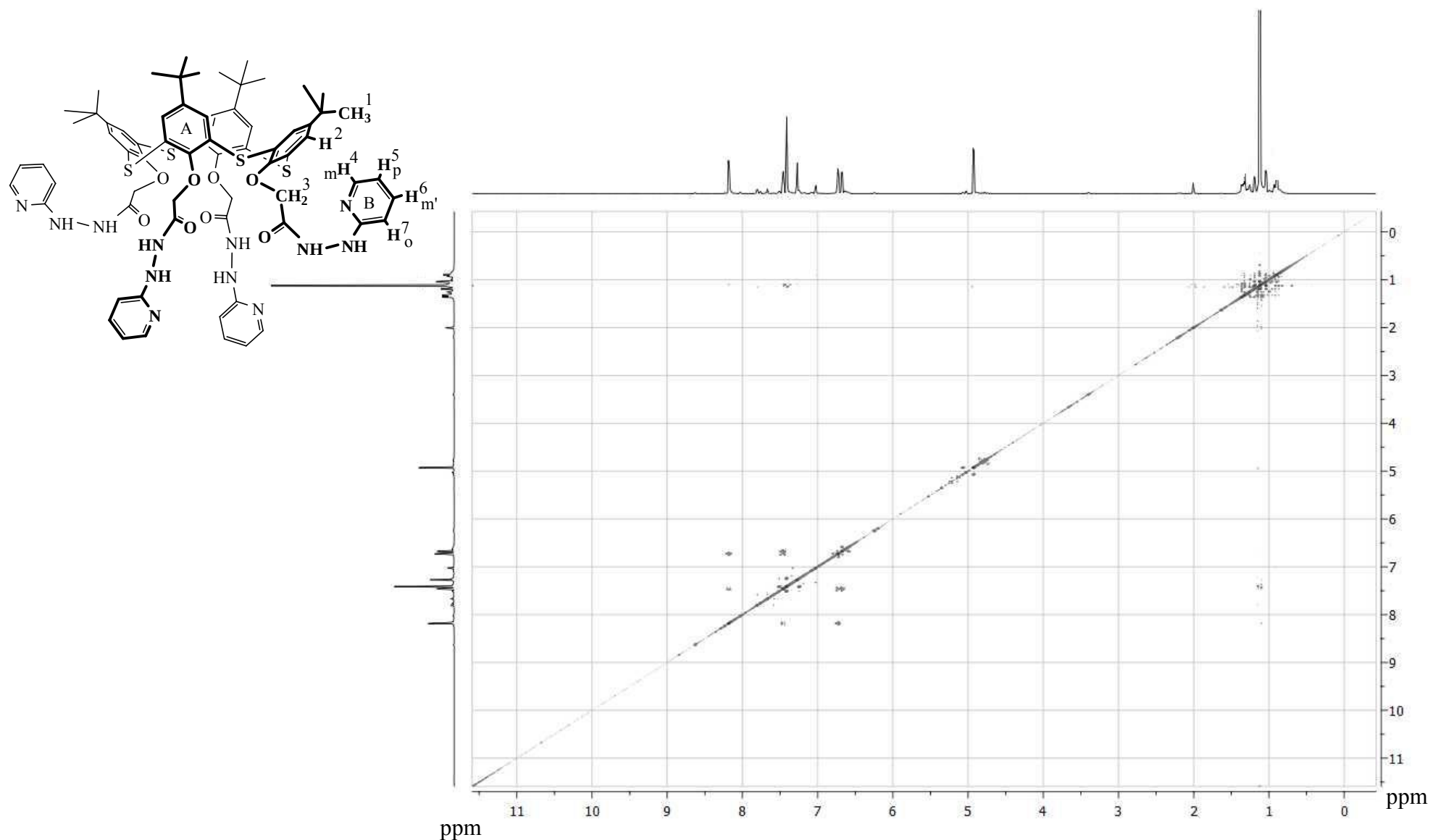
System	n	$\lg K_{\text{ass}}$
[<i>partial cone</i> (6b)+oxalic acid] _{agr.} +AgNO ₃ ^a	0.52±0.10	2.32±0.52
[1,3- <i>alternate</i> (6c)+AgNO ₃] _{agr.} + succinic acid ^a	0.48±0.05	1.13±0.24
[1,3- <i>alternate</i> (6c)+AgNO ₃] _{agr.} + oxalic acid ^b	0.49±0.04	1.52±0.19
[1,3- <i>alternate</i> (6c)+ oxalic acid] _{agr.} +AgNO ₃ ^b	0.97±0.04	5.46±0.20
[<i>cone</i> (8a)+AgNO ₃] _{agr.} + succinic acid ^a	0.37±0.03	0.78±0.14
[<i>cone</i> (8a)+ malonic acid] _{agr.} +AgNO ₃ ^b	1.22±0.04	6.58±0.18
[<i>cone</i> (8a)+AgNO ₃] _{agr.} + malonic acid ^b	0.40±0.02	1.15±0.09
[1,3- <i>alternate</i> (8c)+ malonic acid] _{agr.} +AgNO ₃ ^a	1.10±0.03	6.32±0.15
[1,3- <i>alternate</i> (8c)+AgNO ₃] _{agr.} + oxalic acid ^c	0.56±0.03	1.83±0.17
[1,3- <i>alternate</i> (8c)+ oxalic acid] _{agr.} +AgNO ₃ ^c	1.04±0.05	5.76±0.26
[<i>cone</i> (9a)+ succinic acid] _{agr.} +AgNO ₃ ^b	1.10±0.05	5.40±0.27
[<i>cone</i> (9a)+AgNO ₃] _{agr.} + succinic acid ^c	0.51±0.04	1.02±0.23
[<i>partial cone</i> (9b)+AgNO ₃] _{agr.} + oxalic acid ^a	0.56±0.03	2.04±0.14
[1,3- <i>alternate</i> (9c)+AgNO ₃] _{agr.} + oxalic acid ^a	0.95±0.05	3.68±0.21
[1,3- <i>alternate</i> (9c)+AgNO ₃] _{agr.} + malonic acid ^b	0.51±0.08	1.26±0.41
[1,3- <i>alternate</i> (9c)+ malonic acid] _{agr.} +AgNO ₃ ^b	1.10±0.1	6.89±0.33
[<i>cone</i> (10a)+AgNO ₃] _{agr.} + oxalic acid ^a	0.67±0.03	2.23±0.17
[<i>cone</i> (10a)+AgNO ₃] _{agr.} + malonic acid ^a	1.71±0.08	6.62±0.40
[<i>cone</i> (10a)+AgNO ₃] _{agr.} + succinic acid ^a	1.58±0.11	6.13±0.54
[<i>partial cone</i> (10b)+AgNO ₃] _{agr.} + oxalic acid ^a	1.40±0.14	5.88±0.73
[1,3- <i>alternate</i> (10c)+AgNO ₃] _{agr.} + malonic acid ^a	1.15±0.06	3.86±0.30

^a – cascade systems; ^b – commutative systems; ^c – intermediate systems.

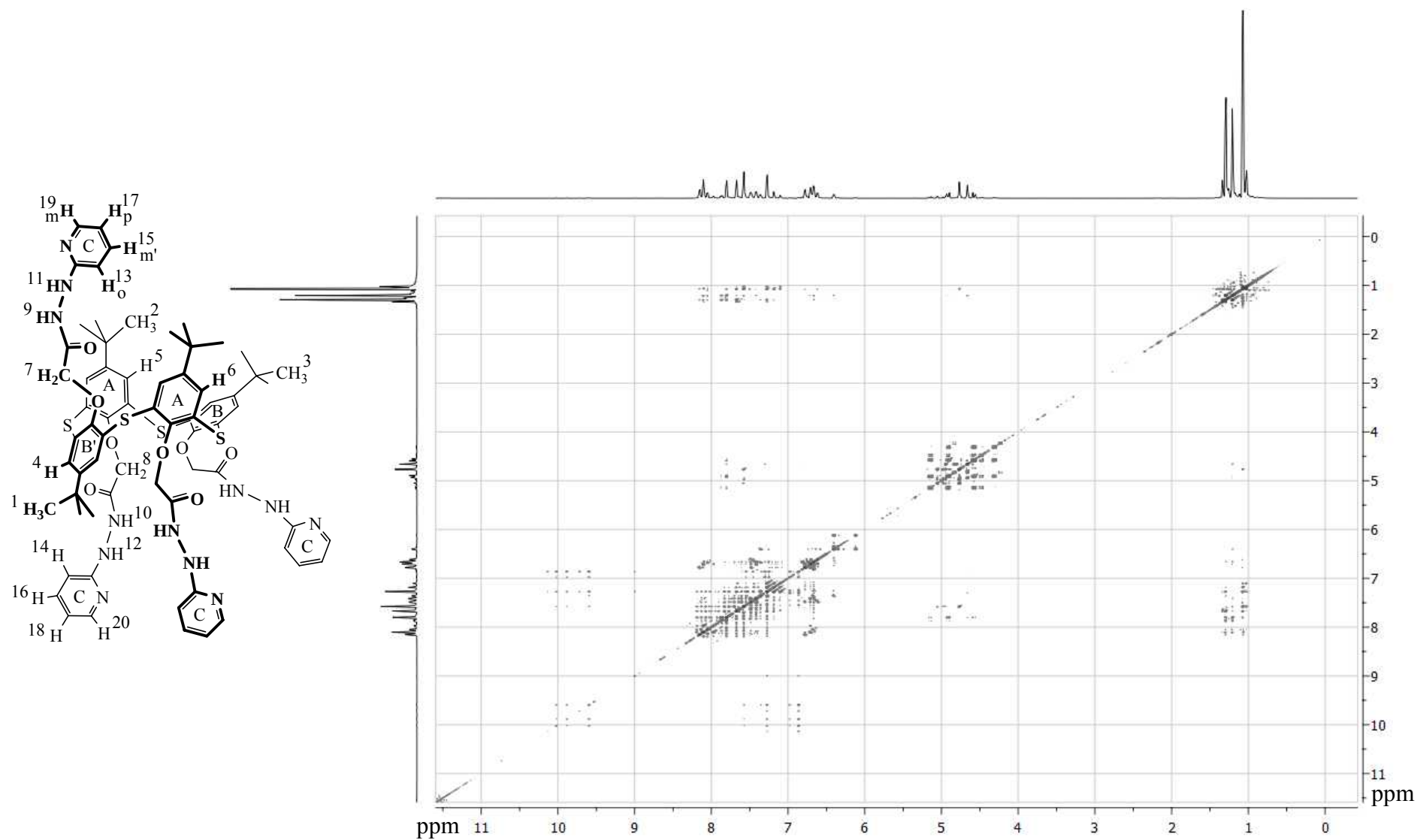
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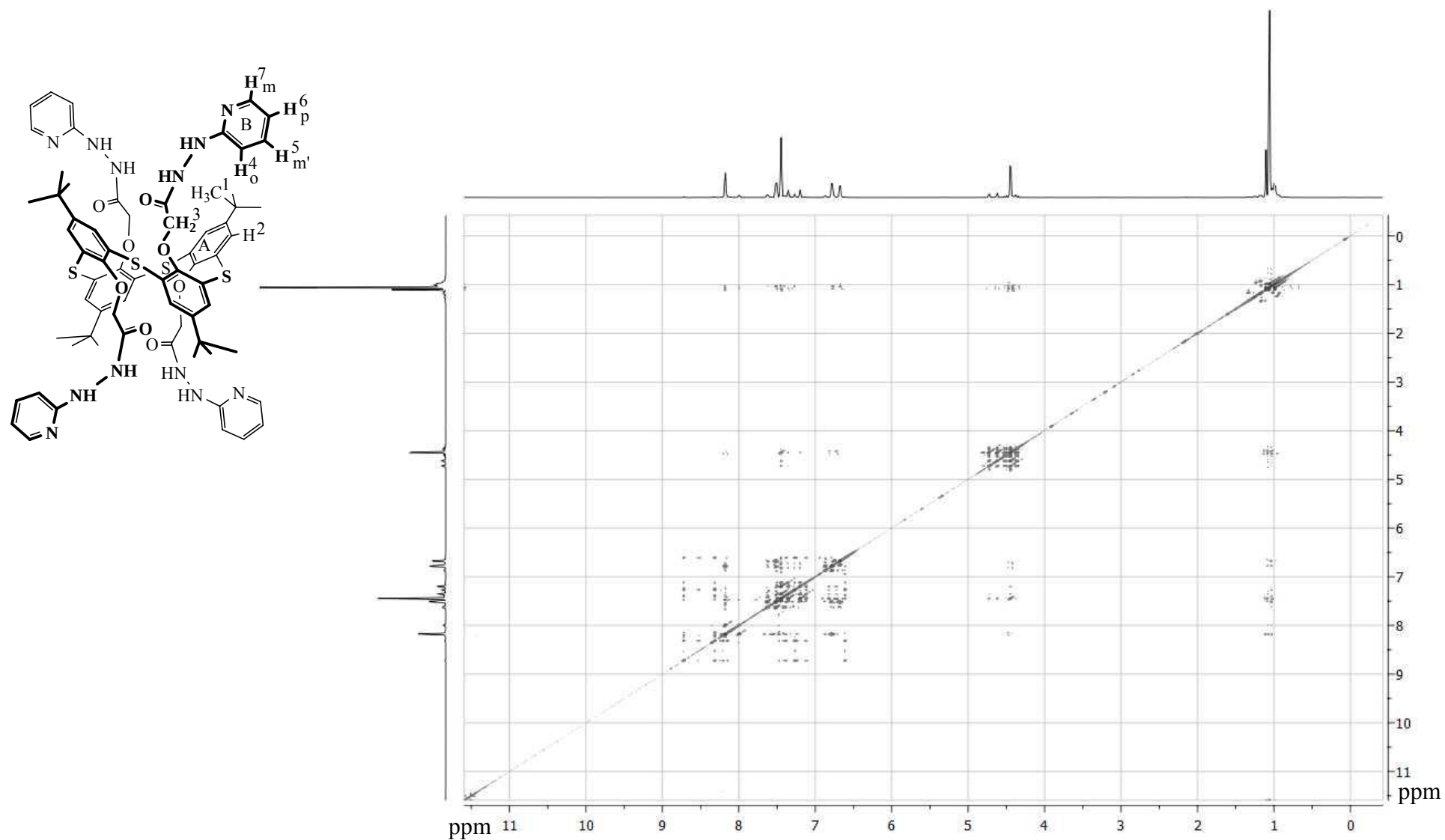
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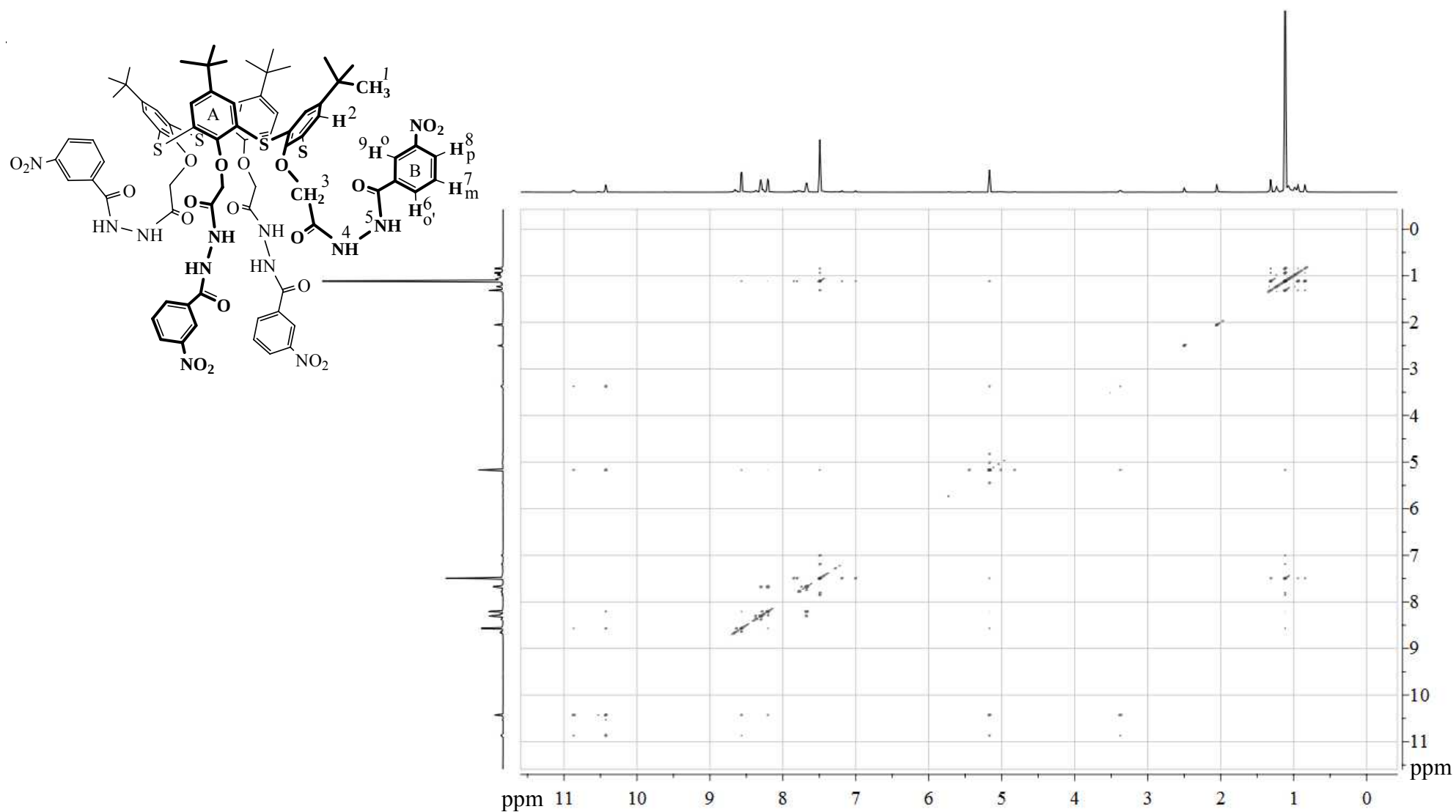
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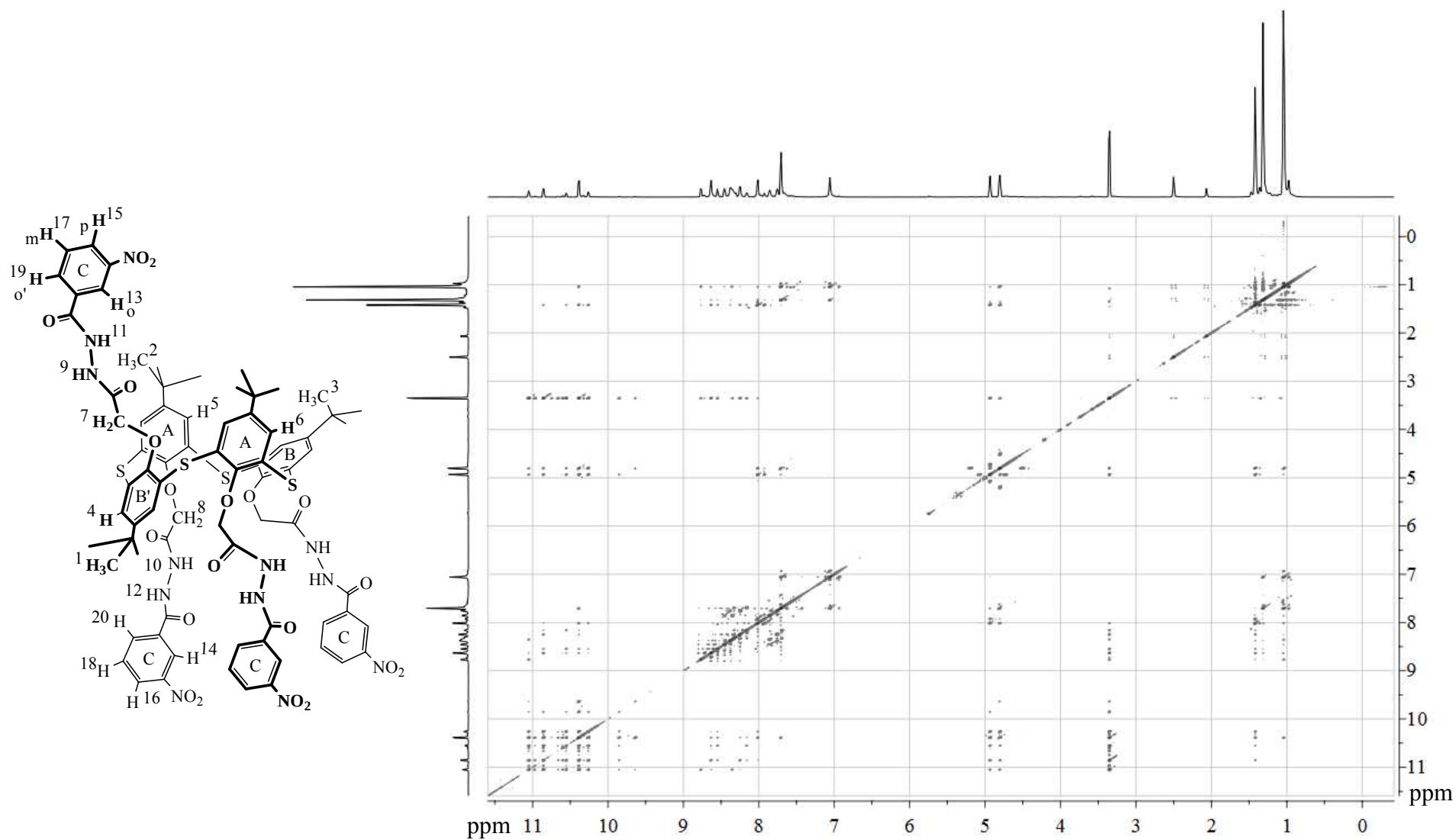
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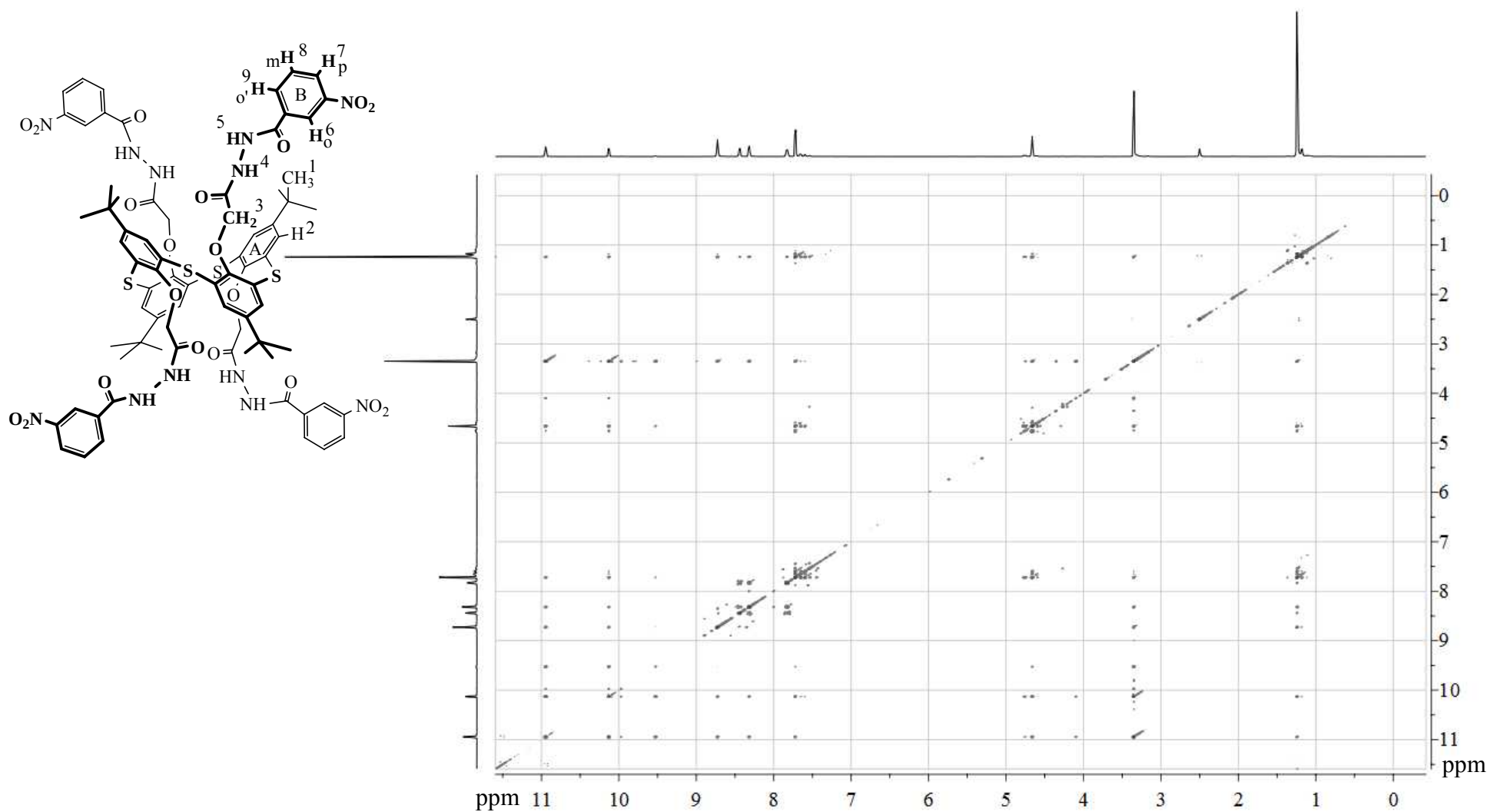
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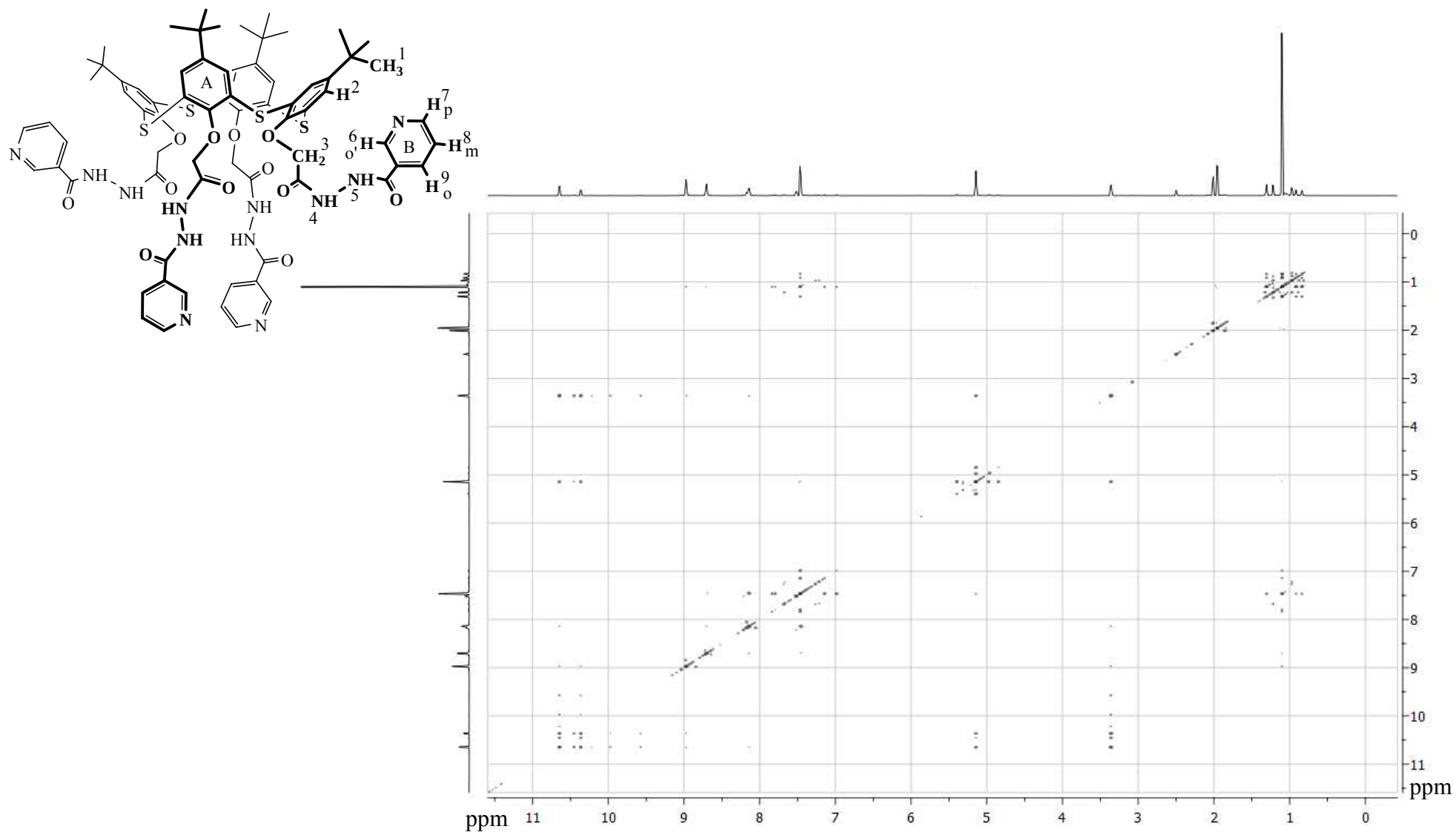
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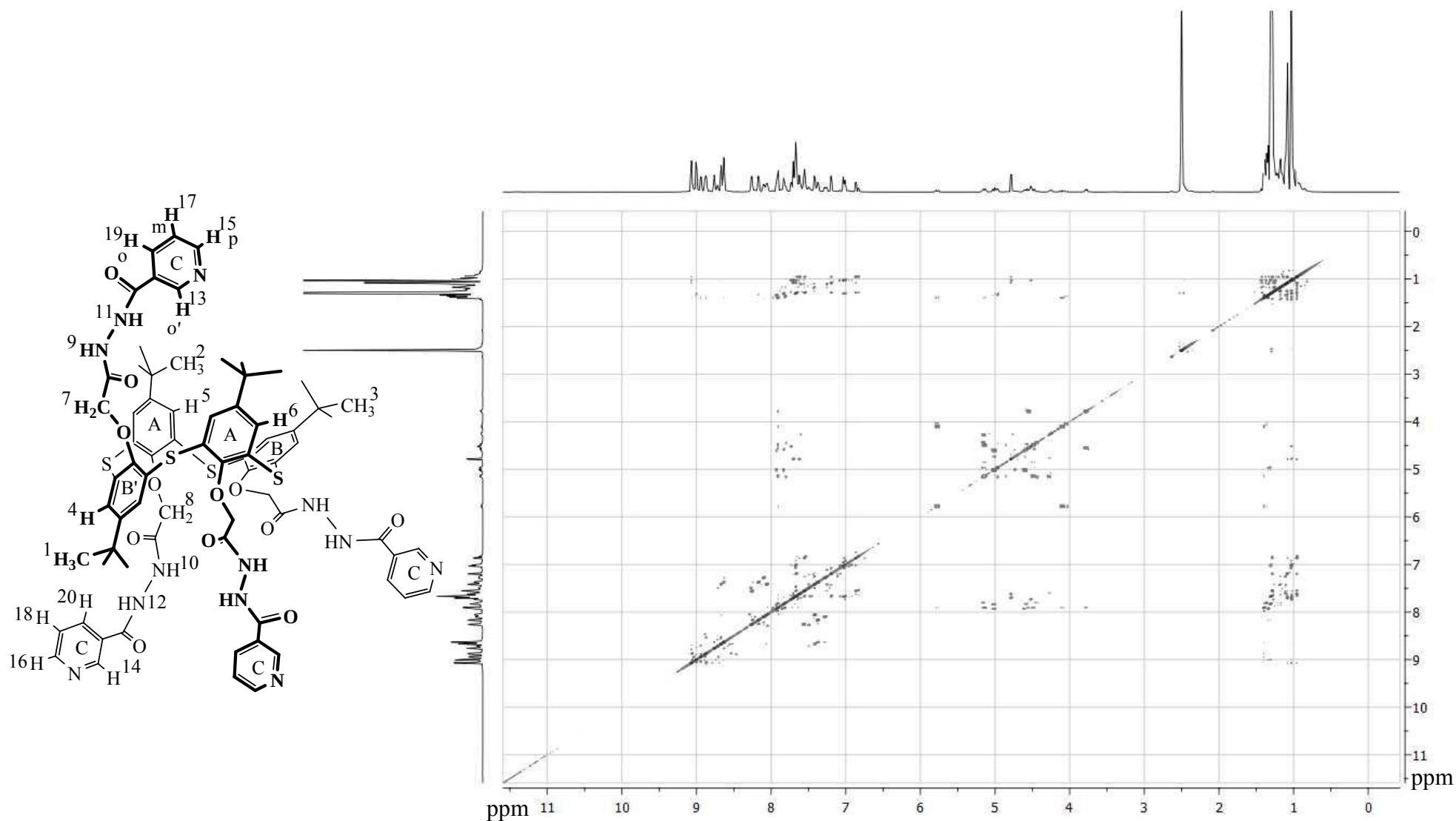
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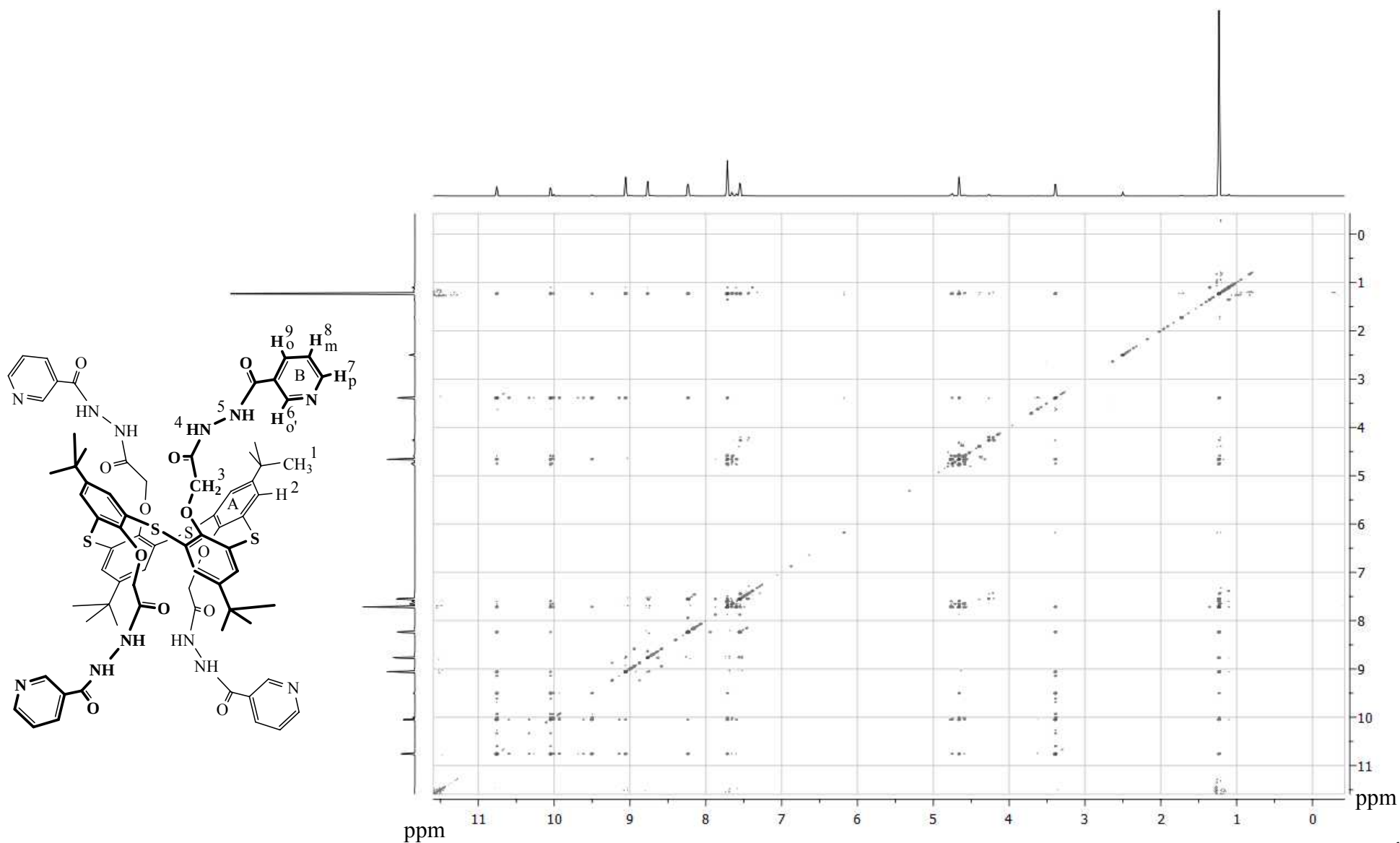
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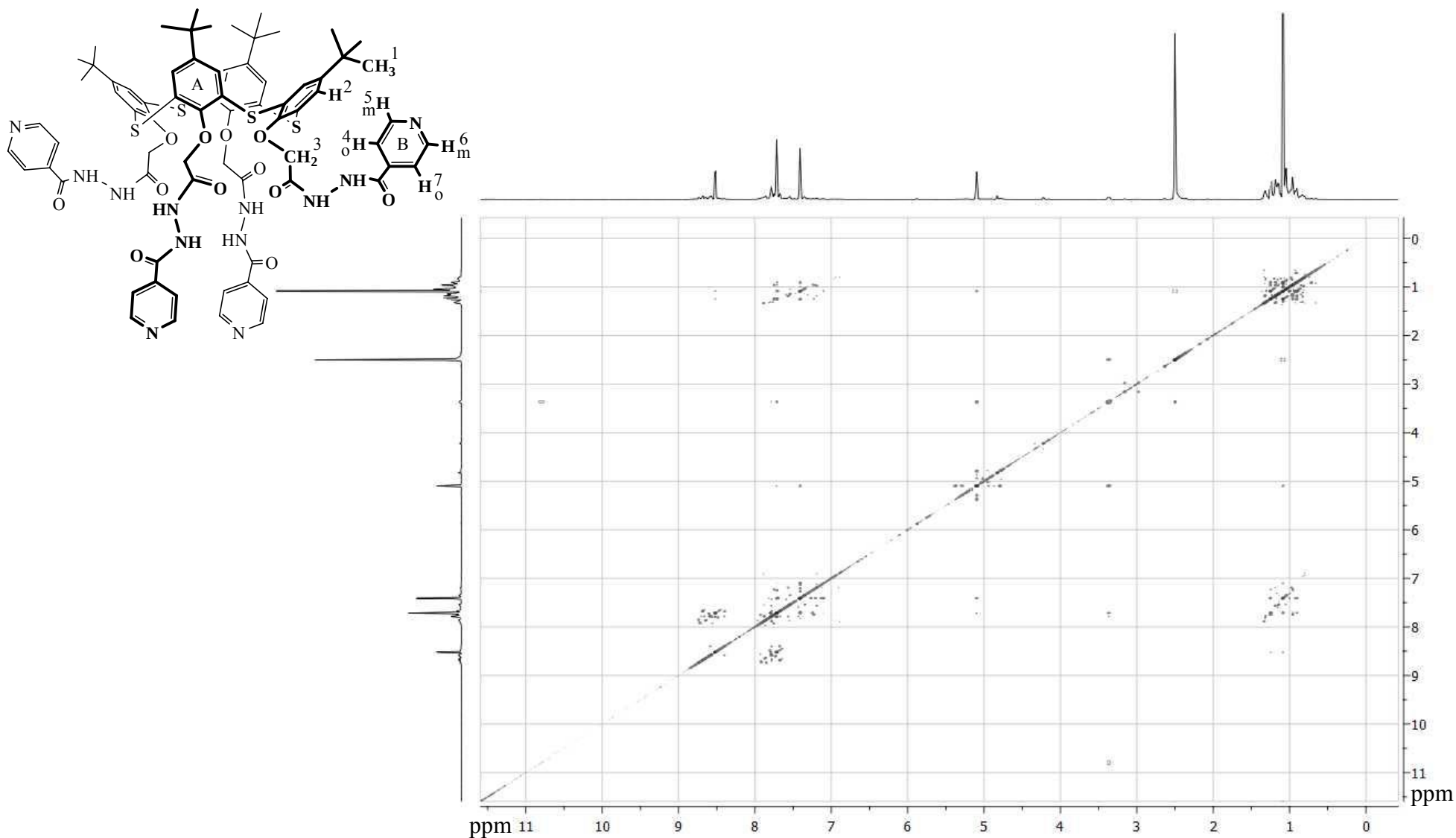
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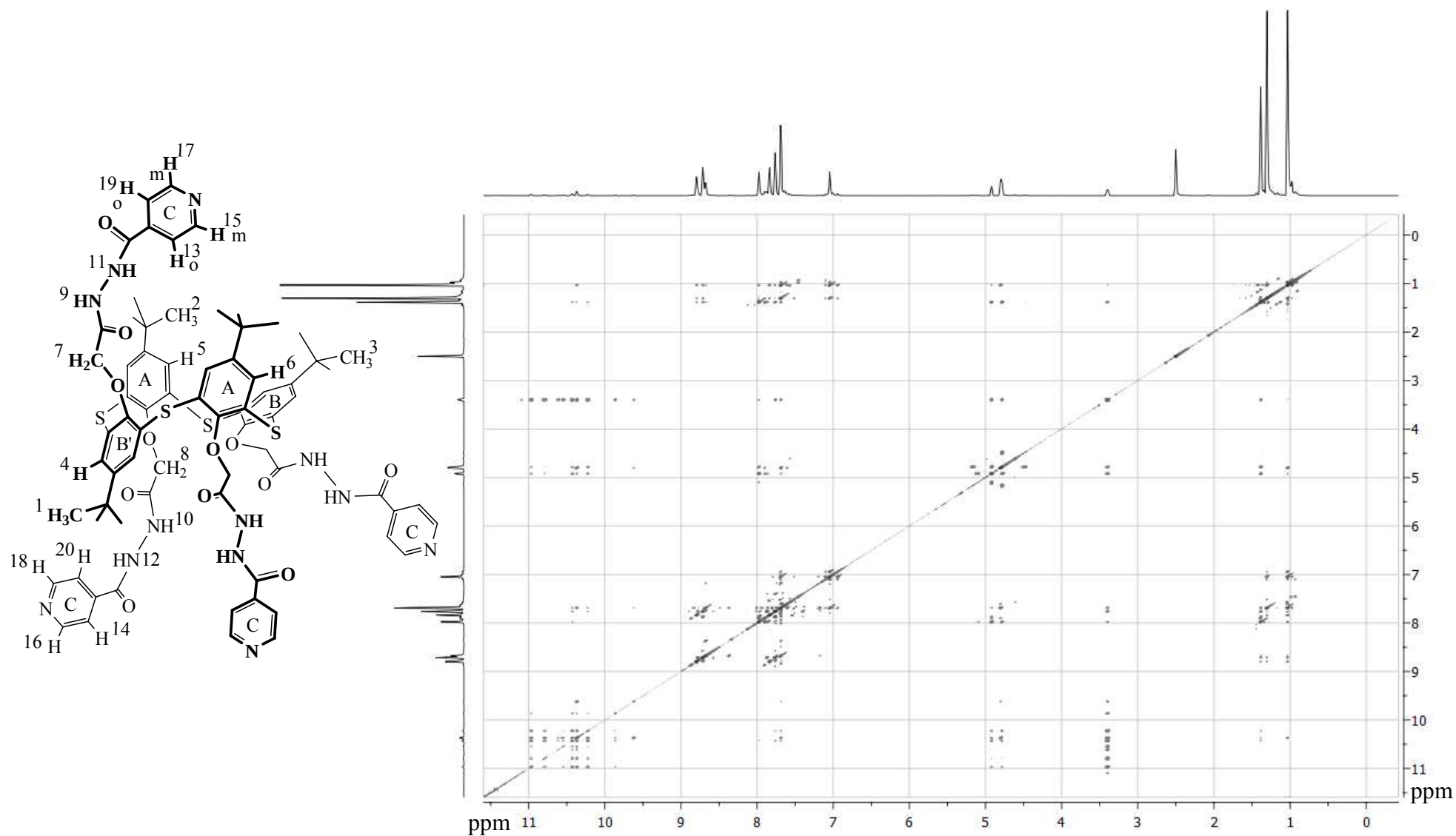
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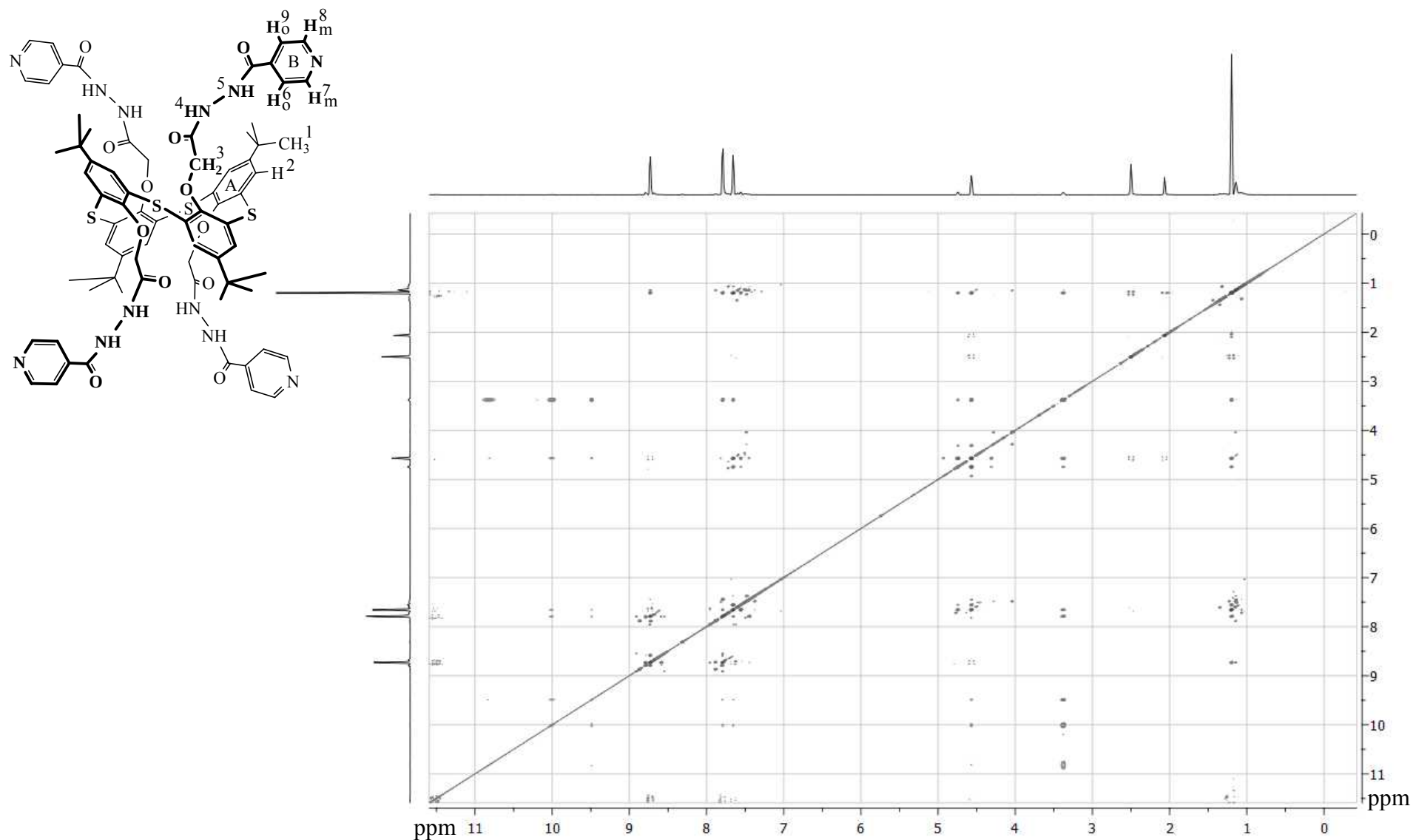
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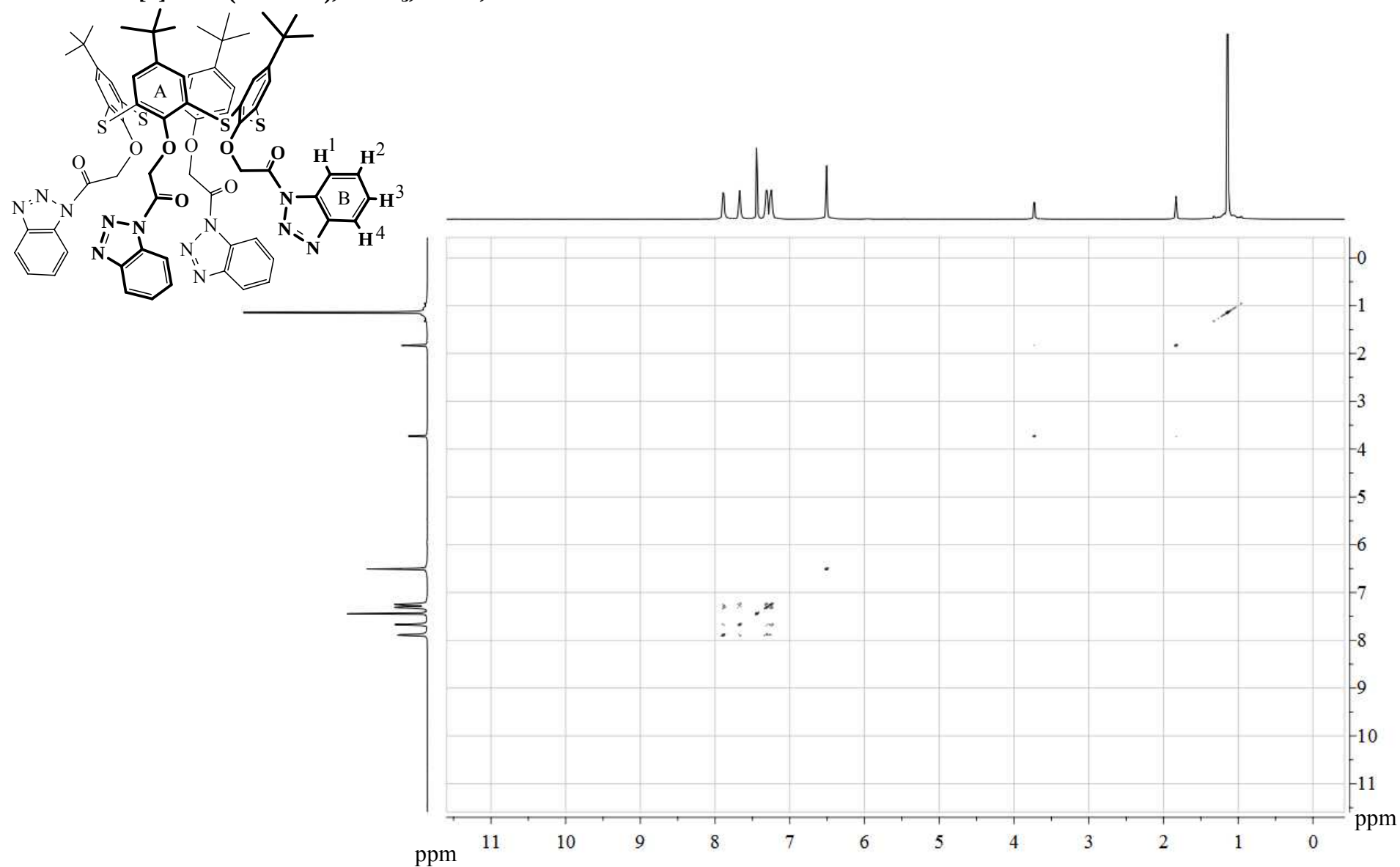
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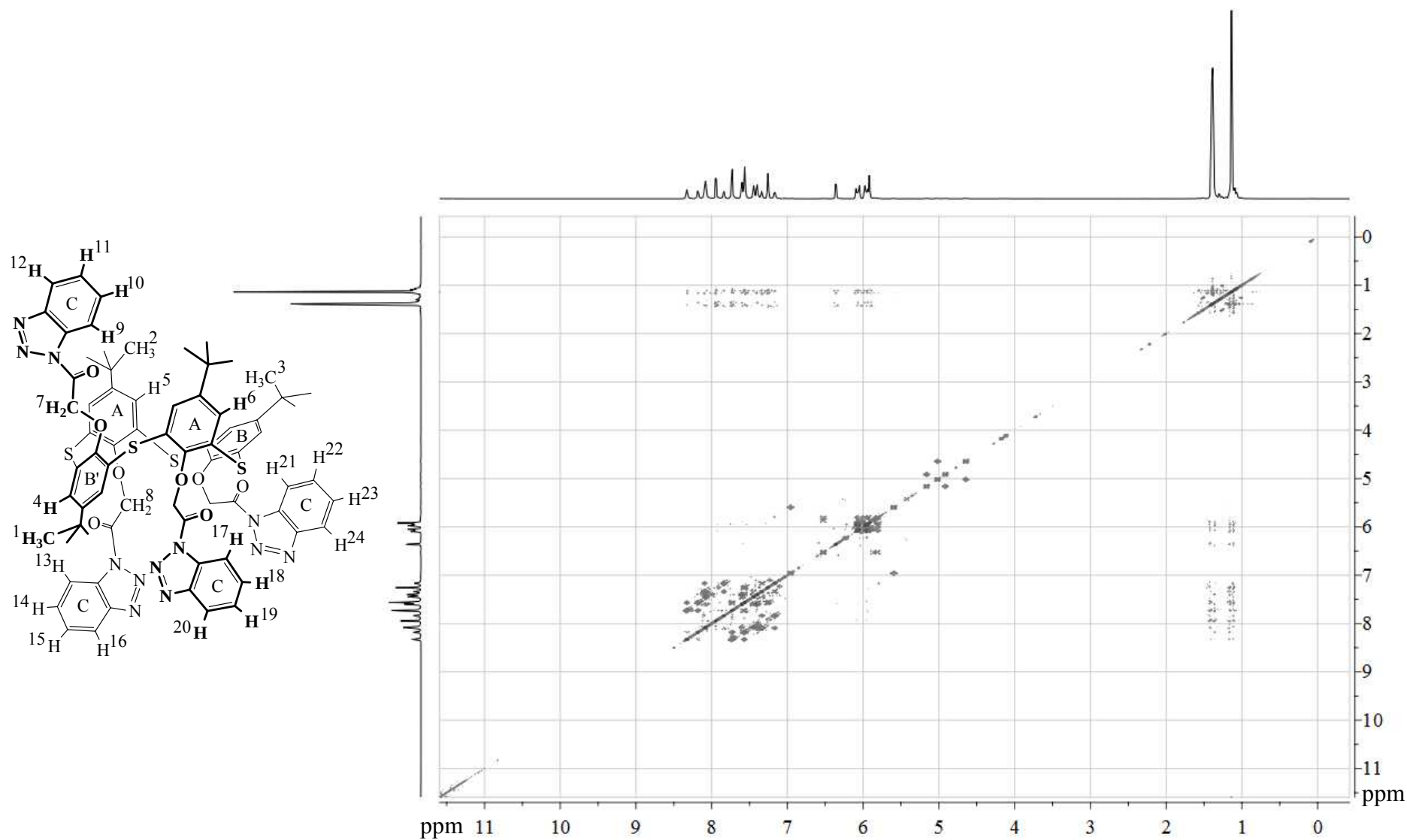
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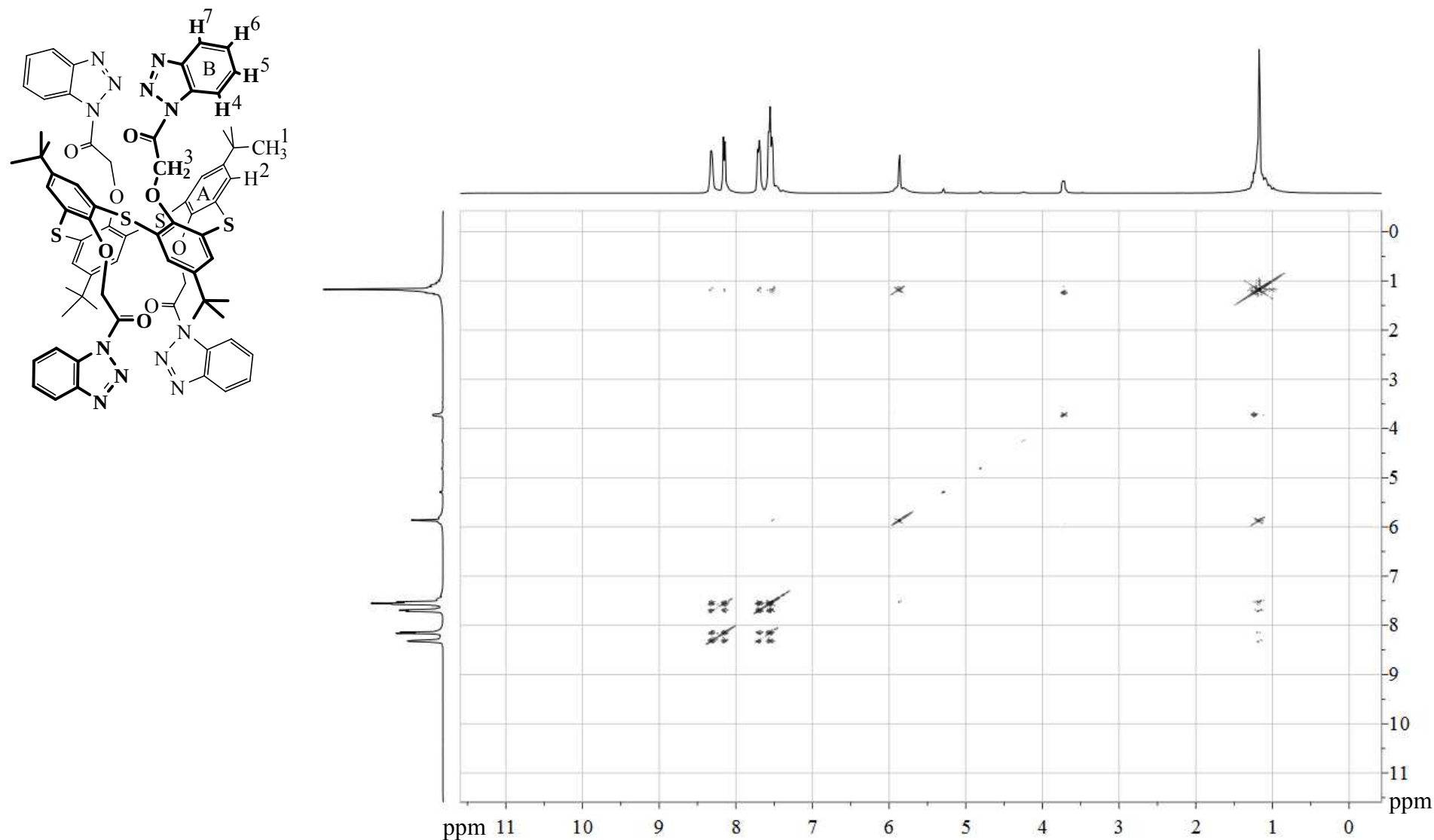
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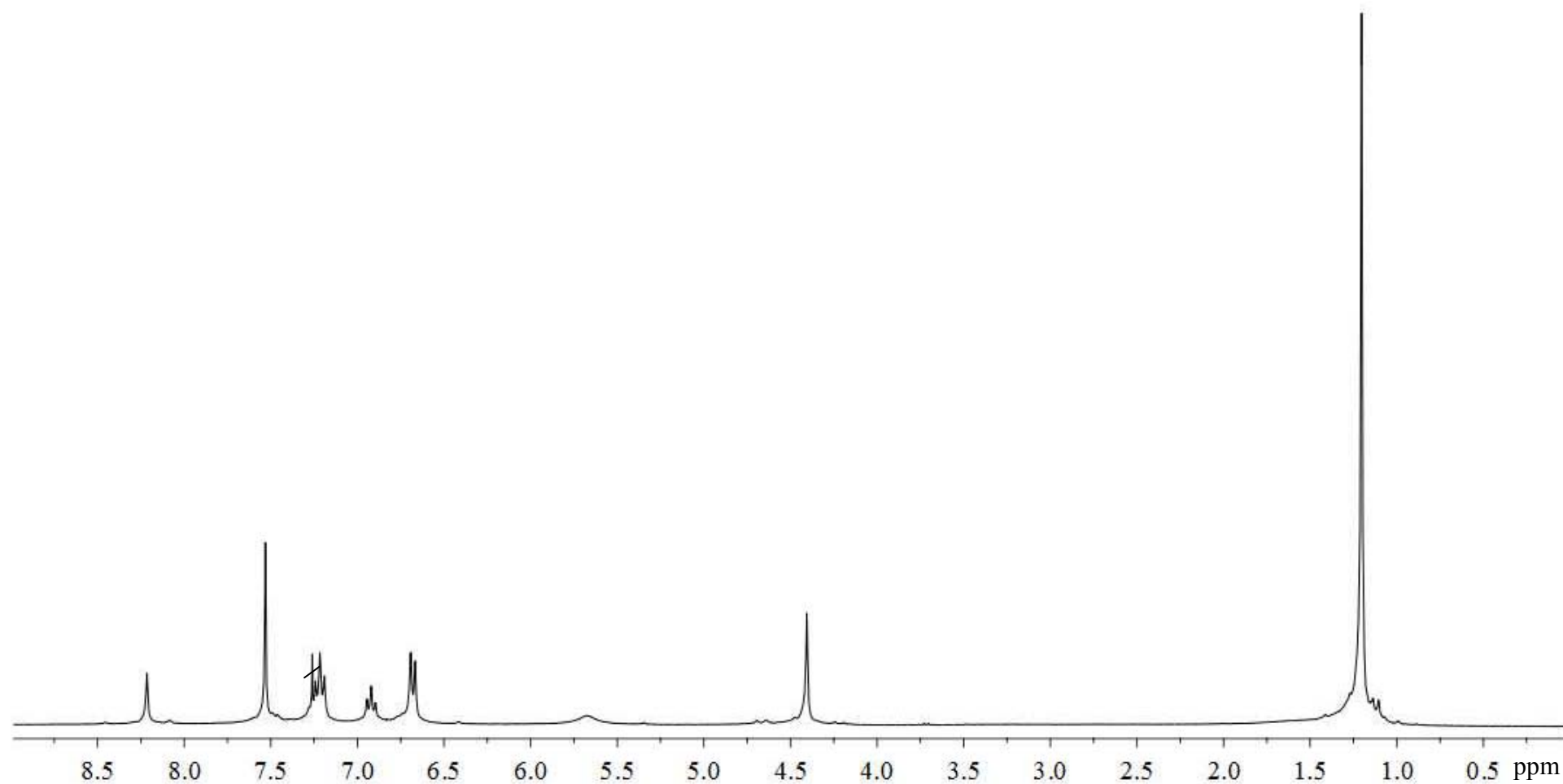
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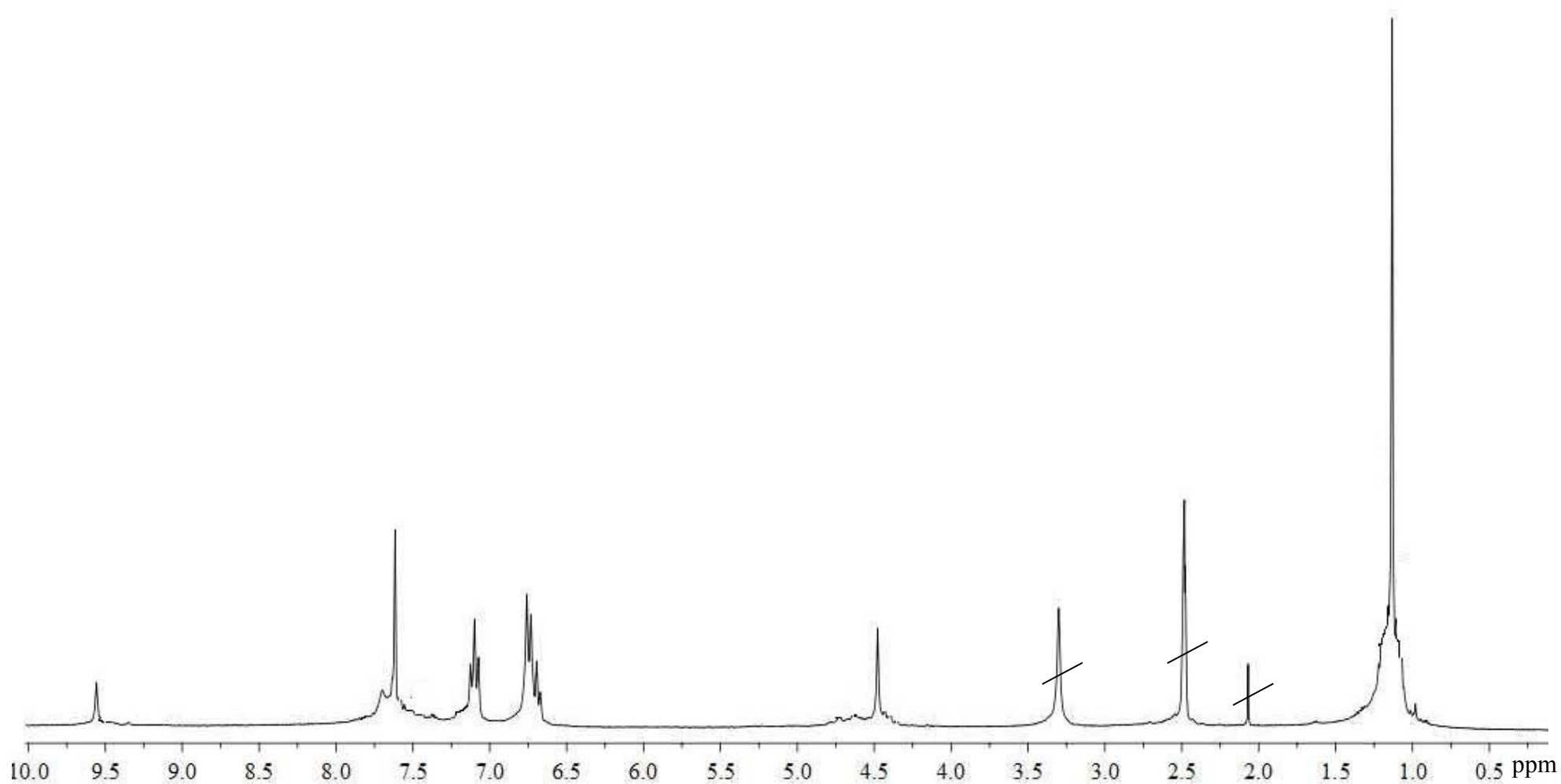
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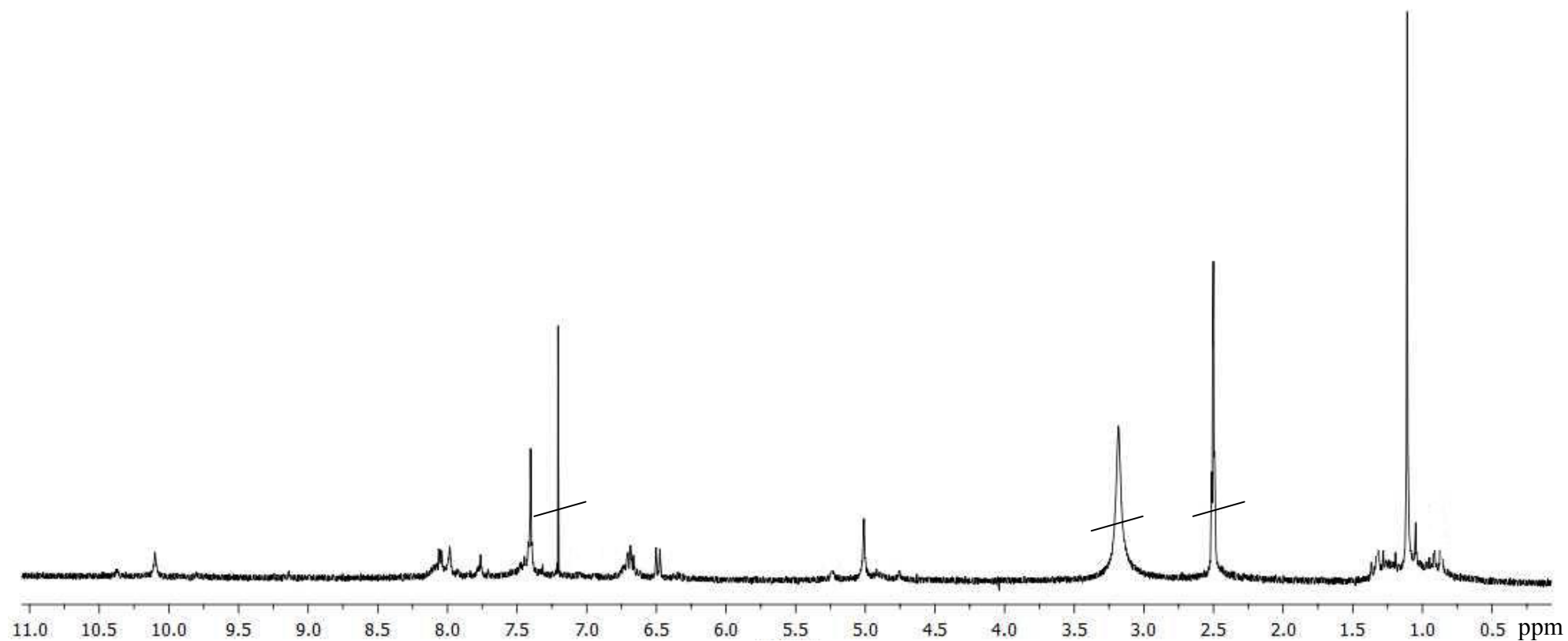
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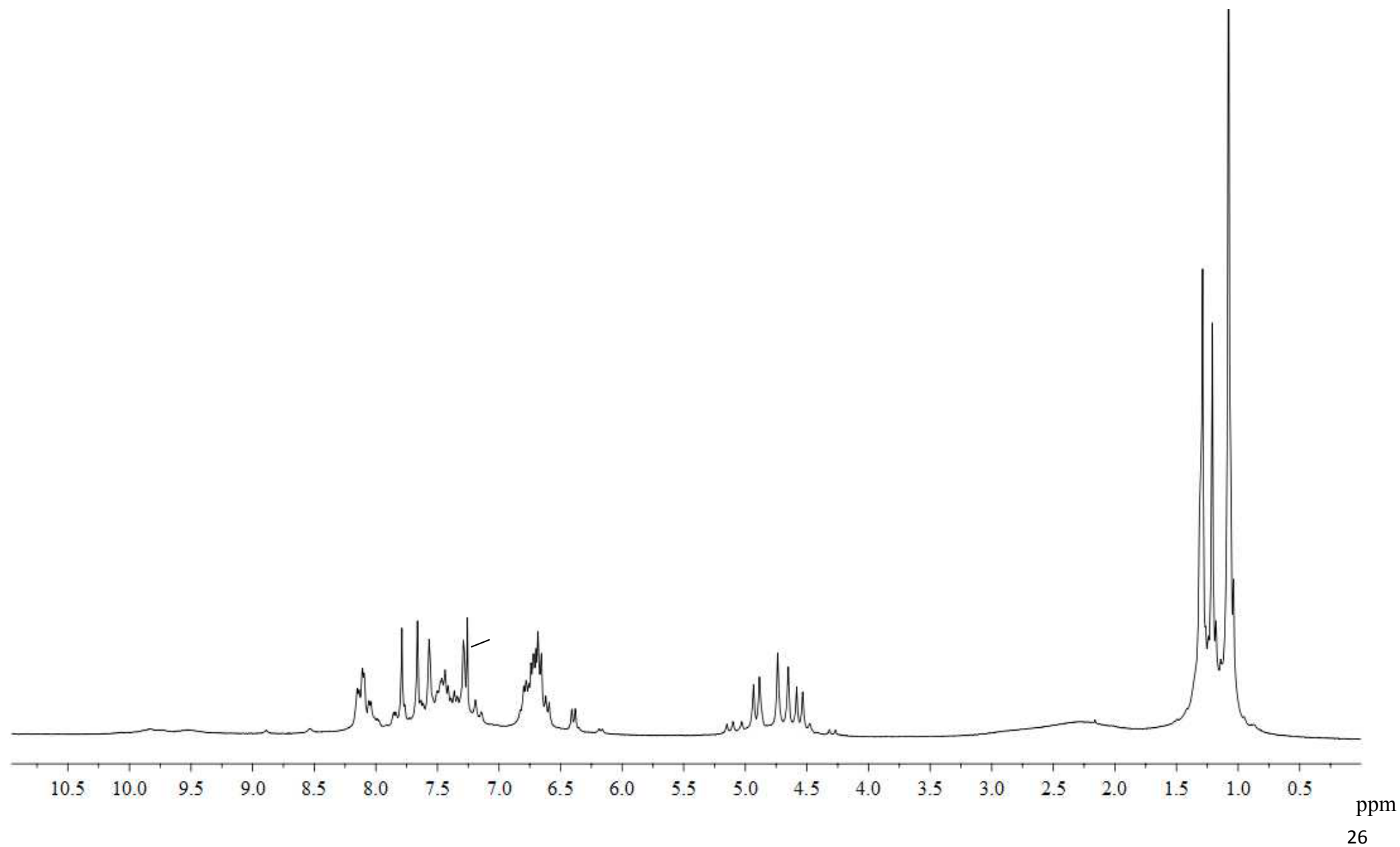
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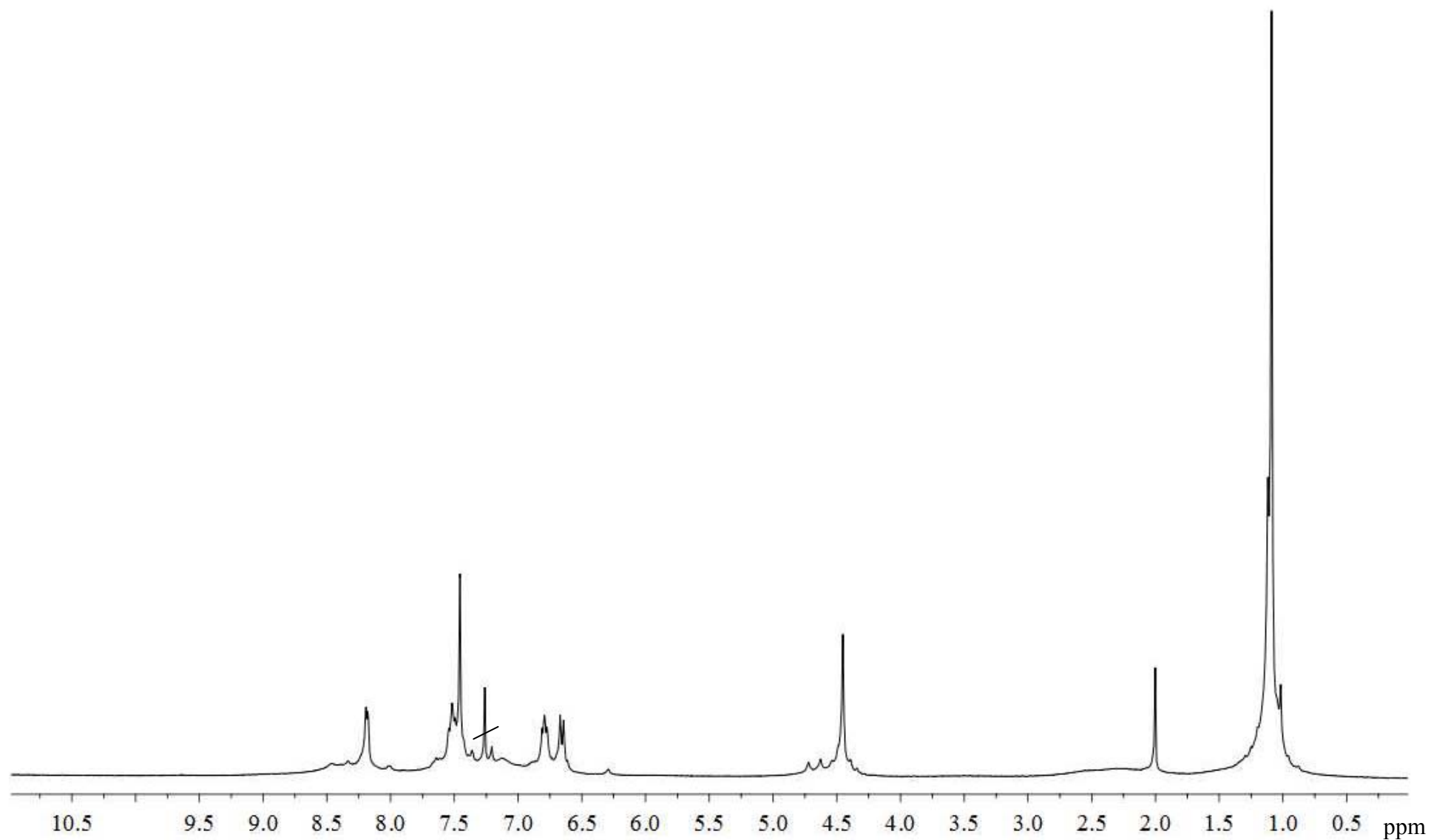
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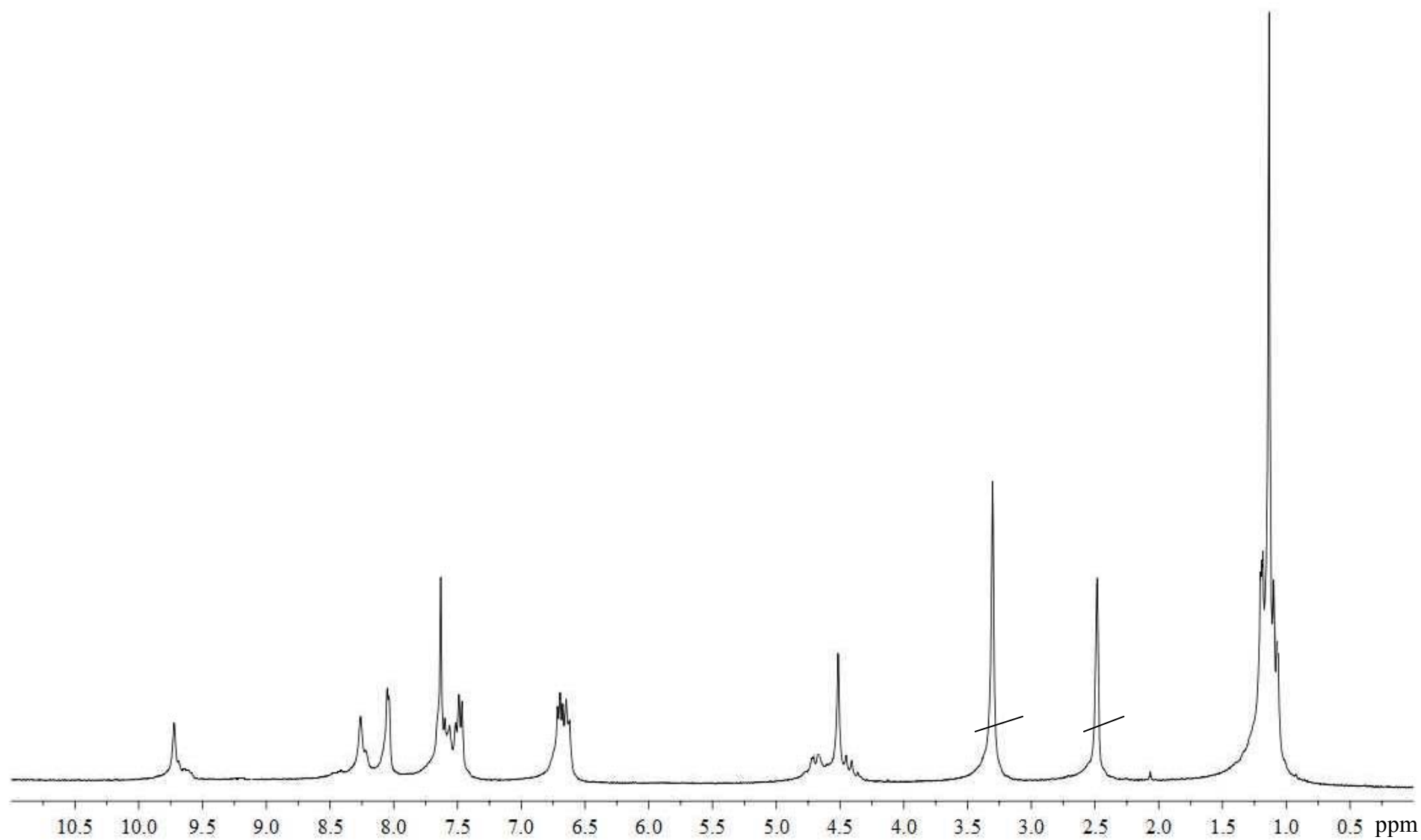
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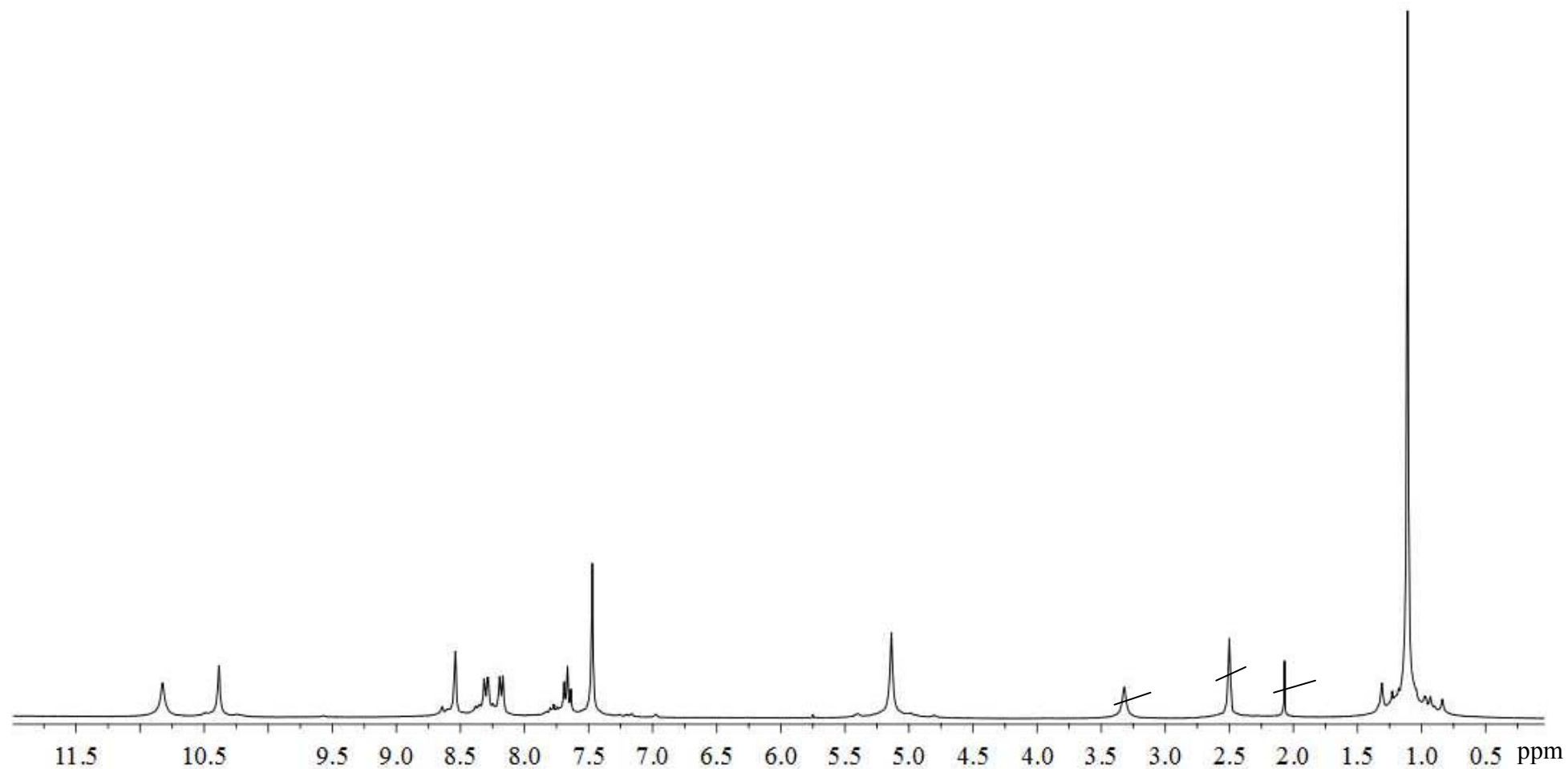
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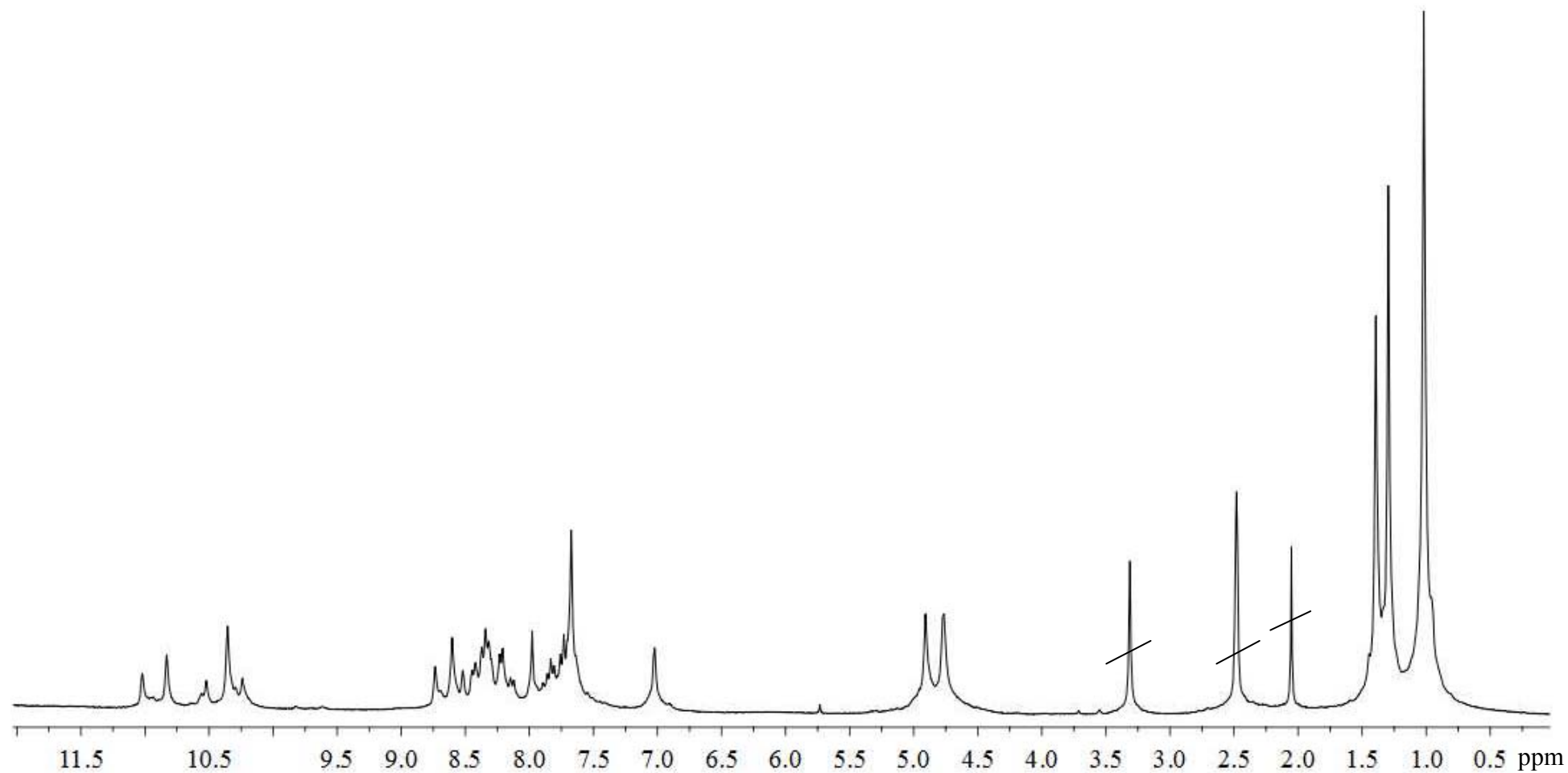
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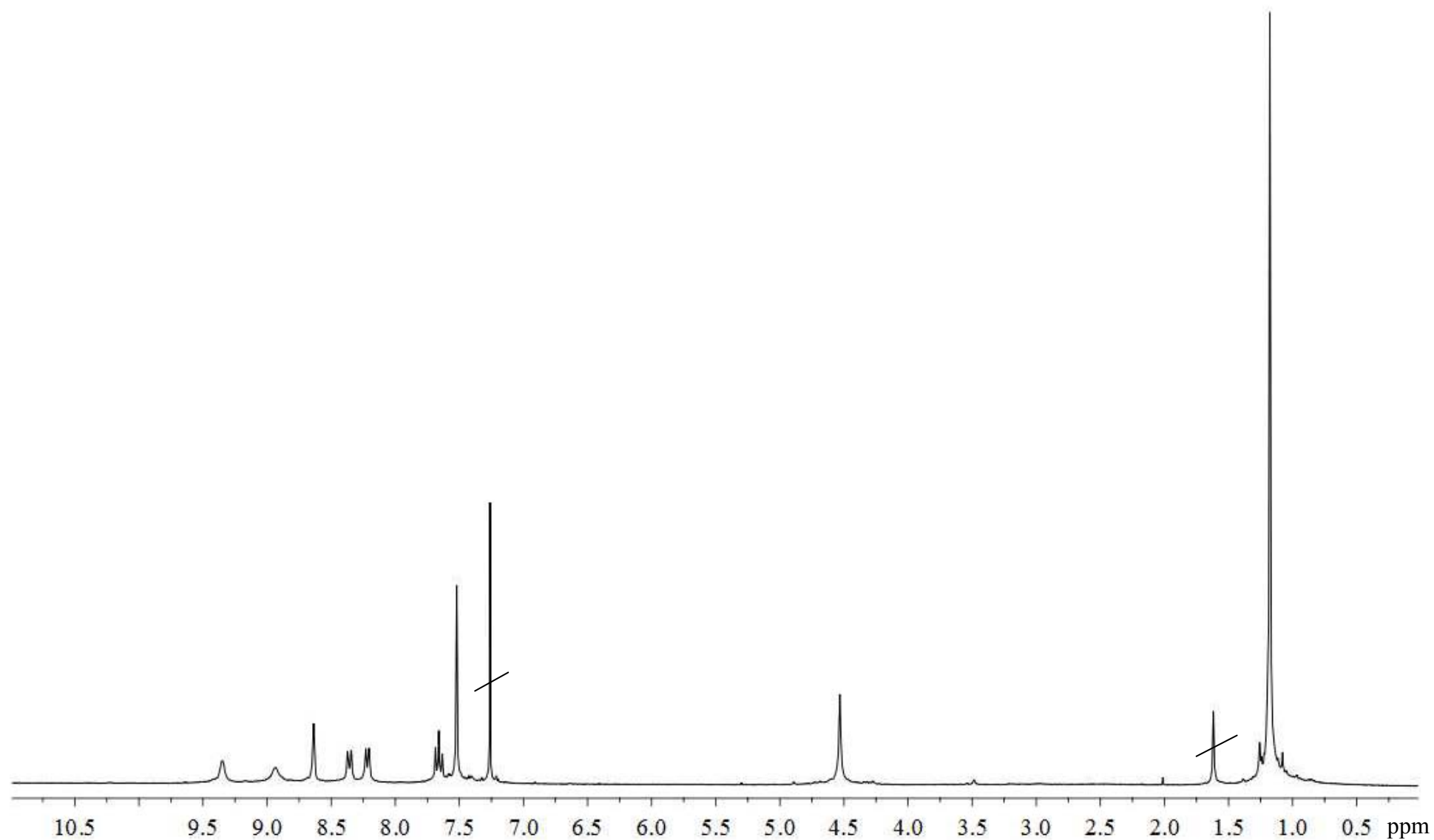
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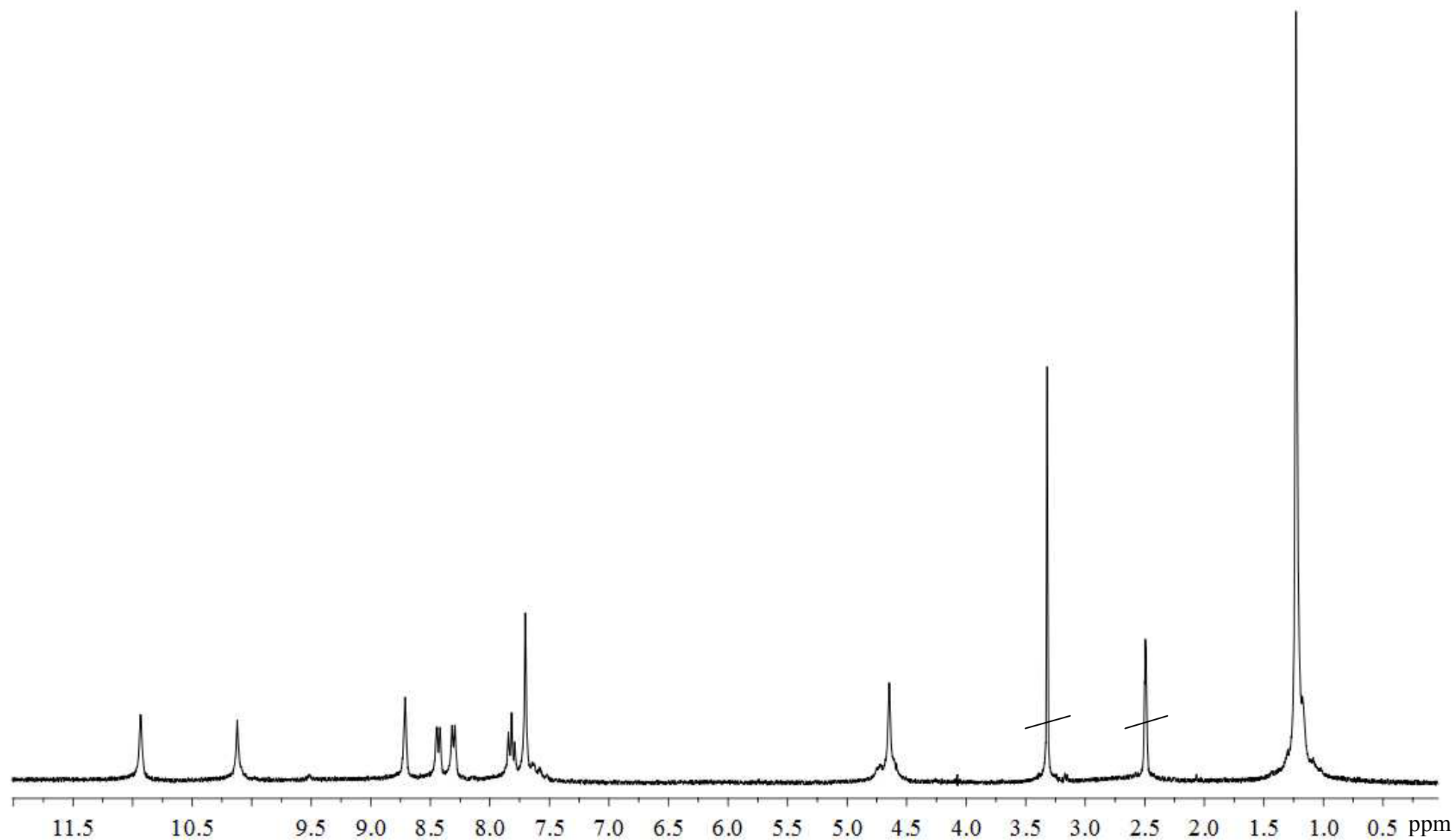
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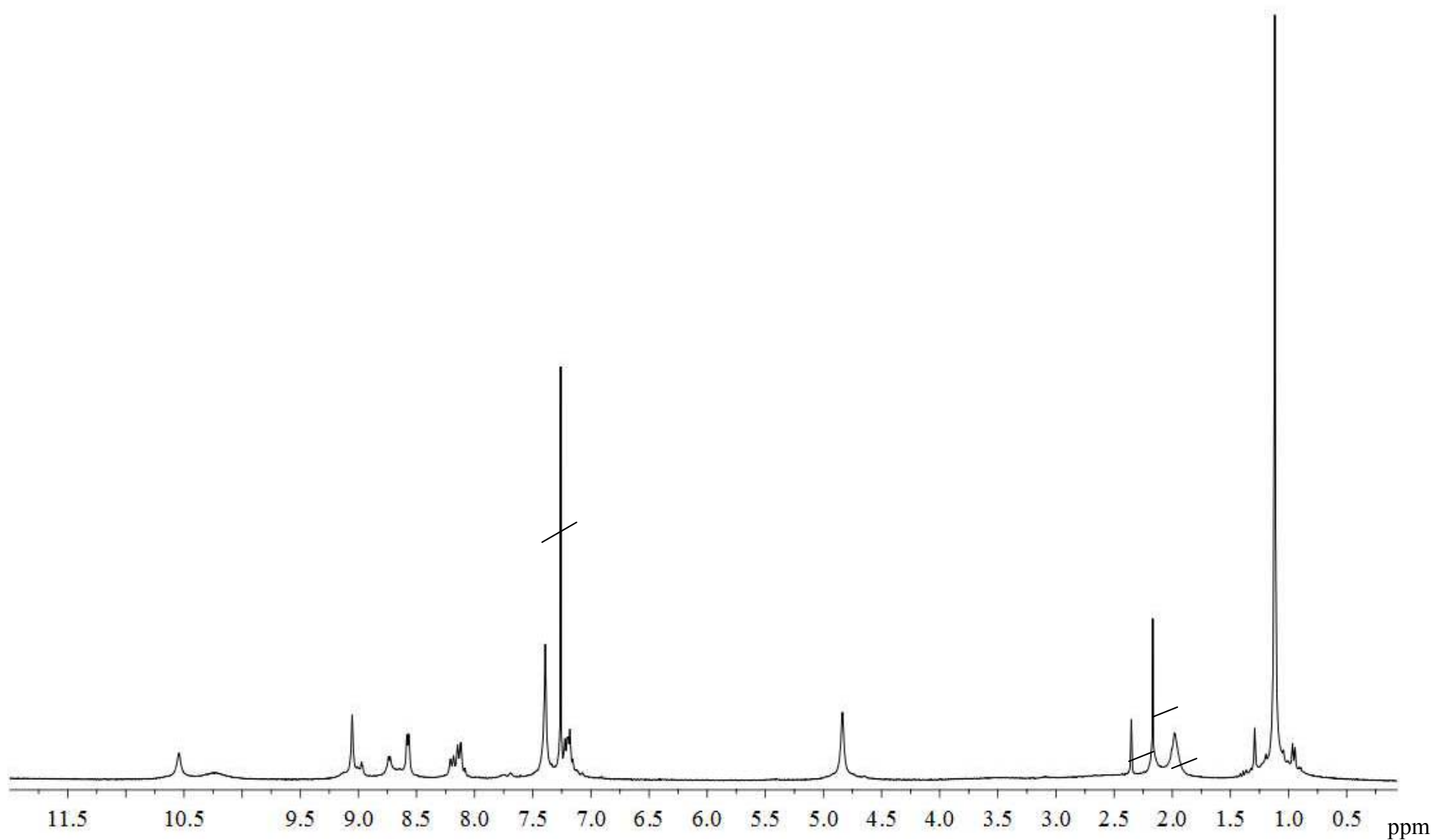
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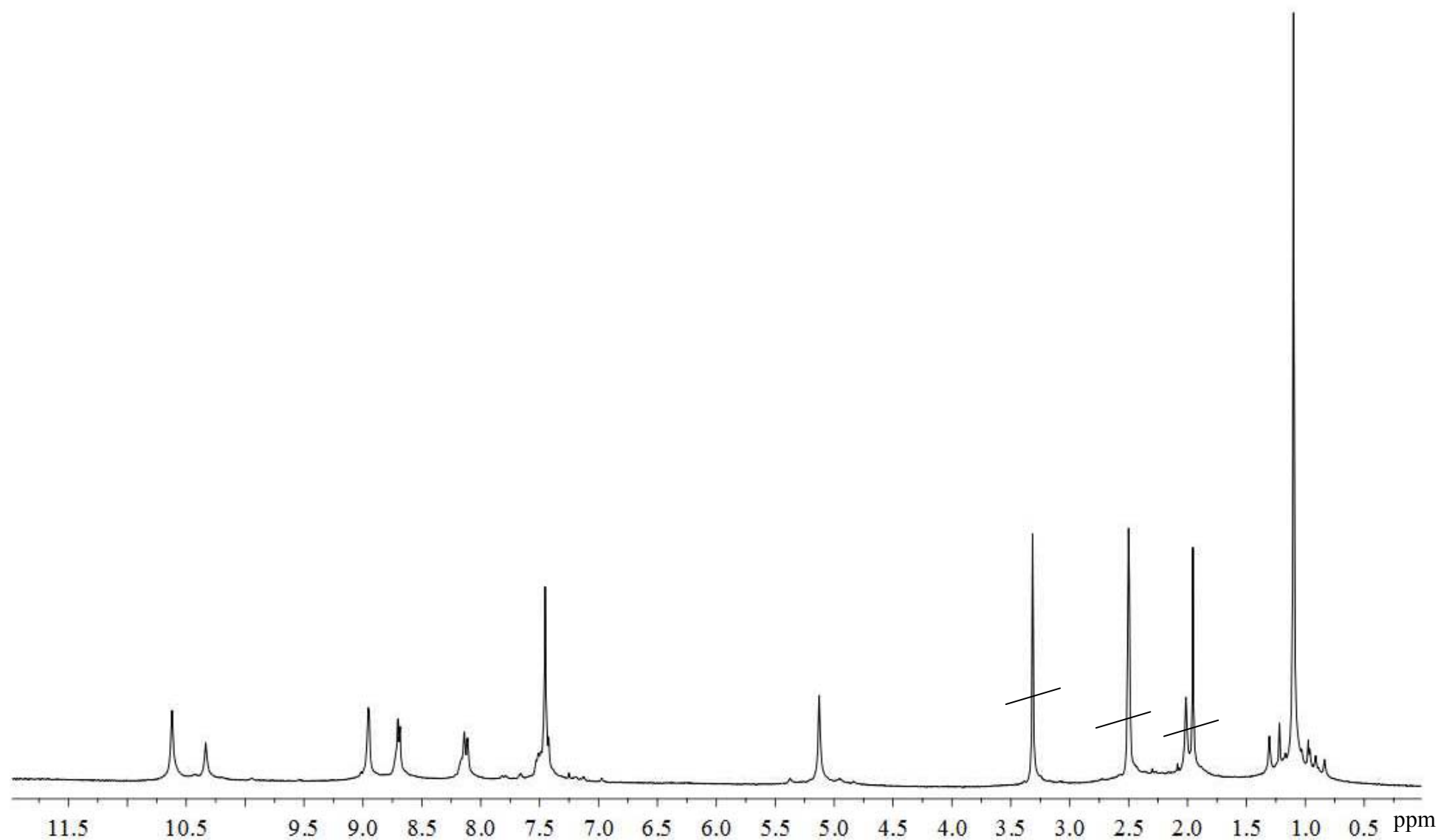
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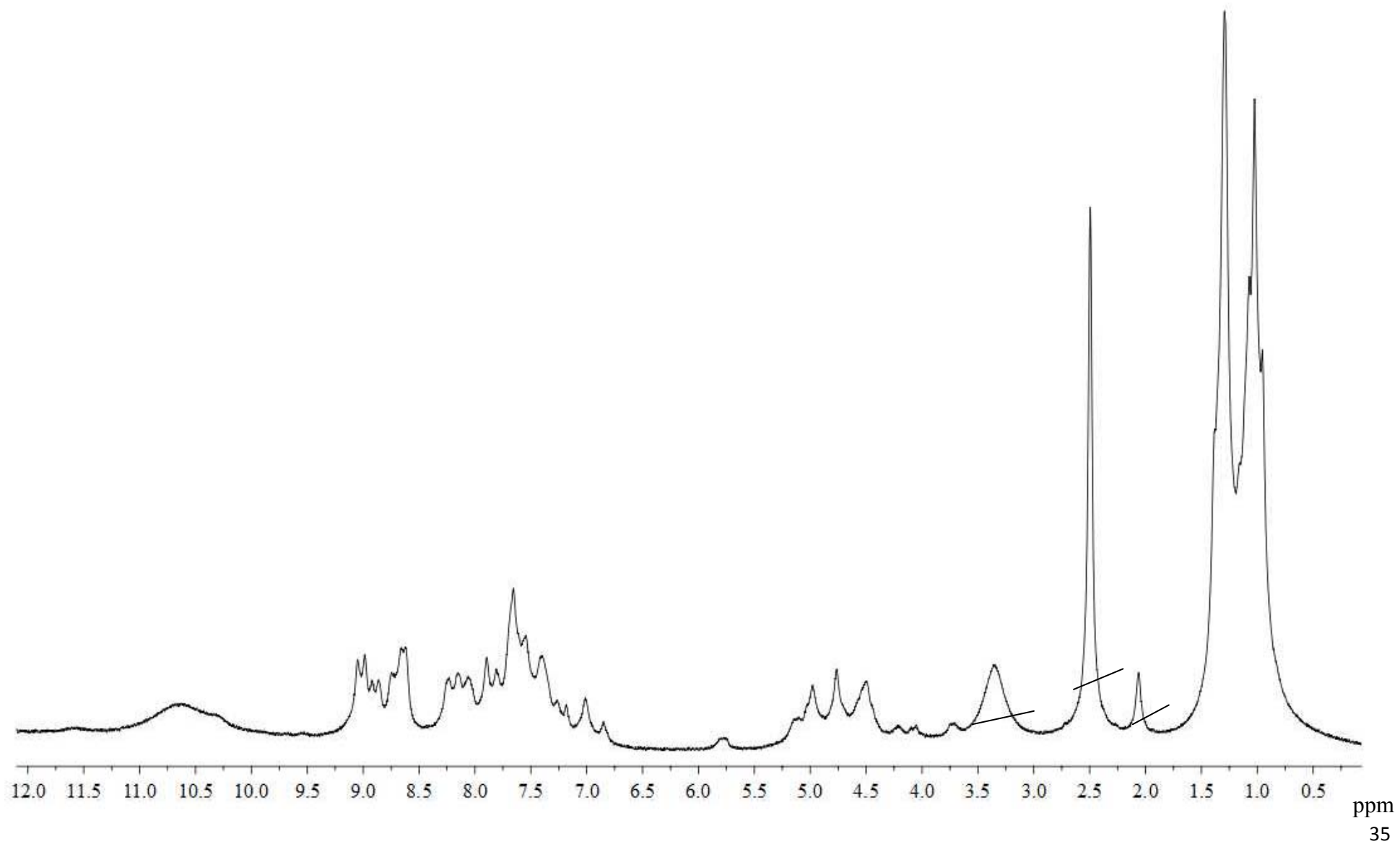
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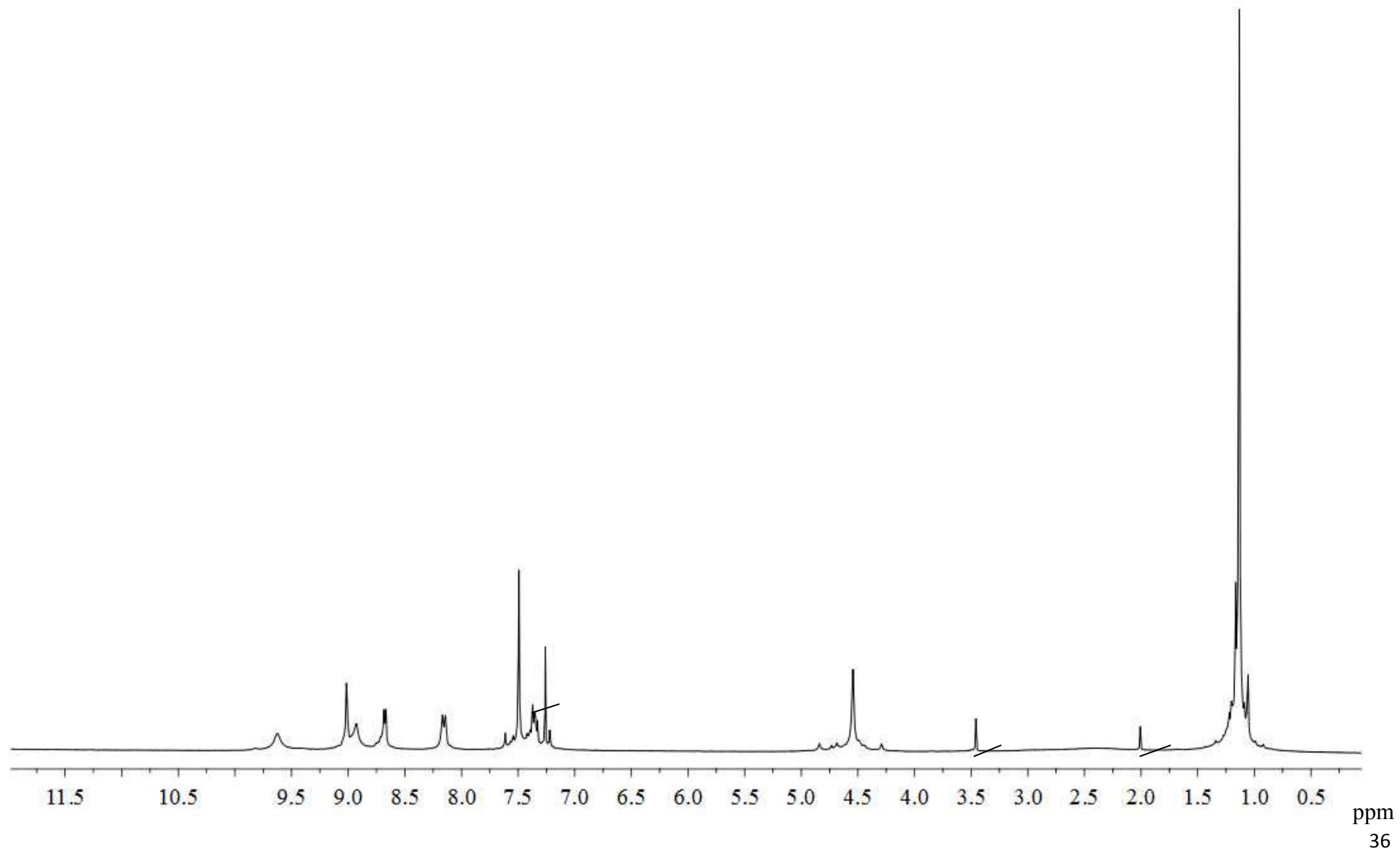
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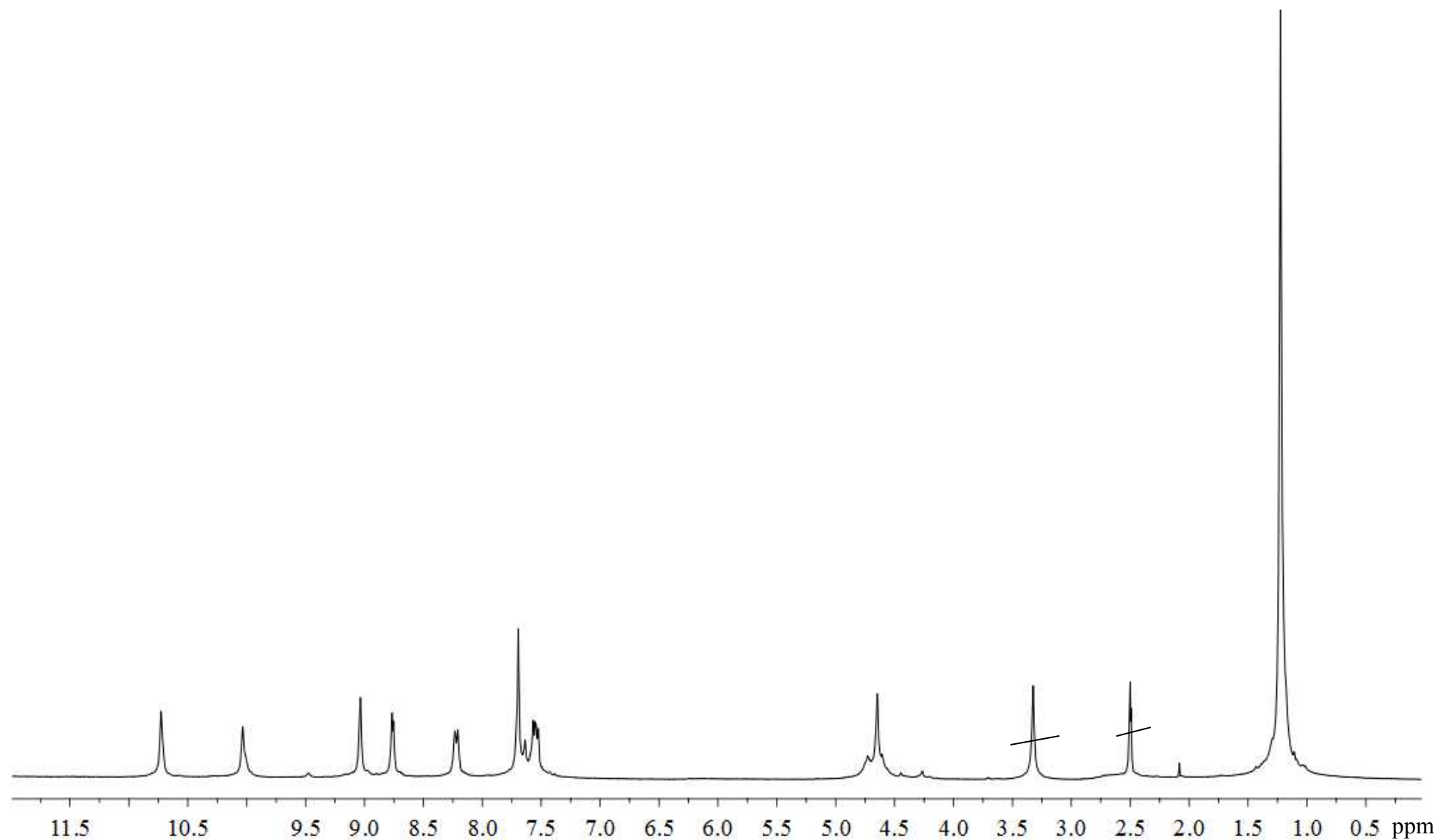
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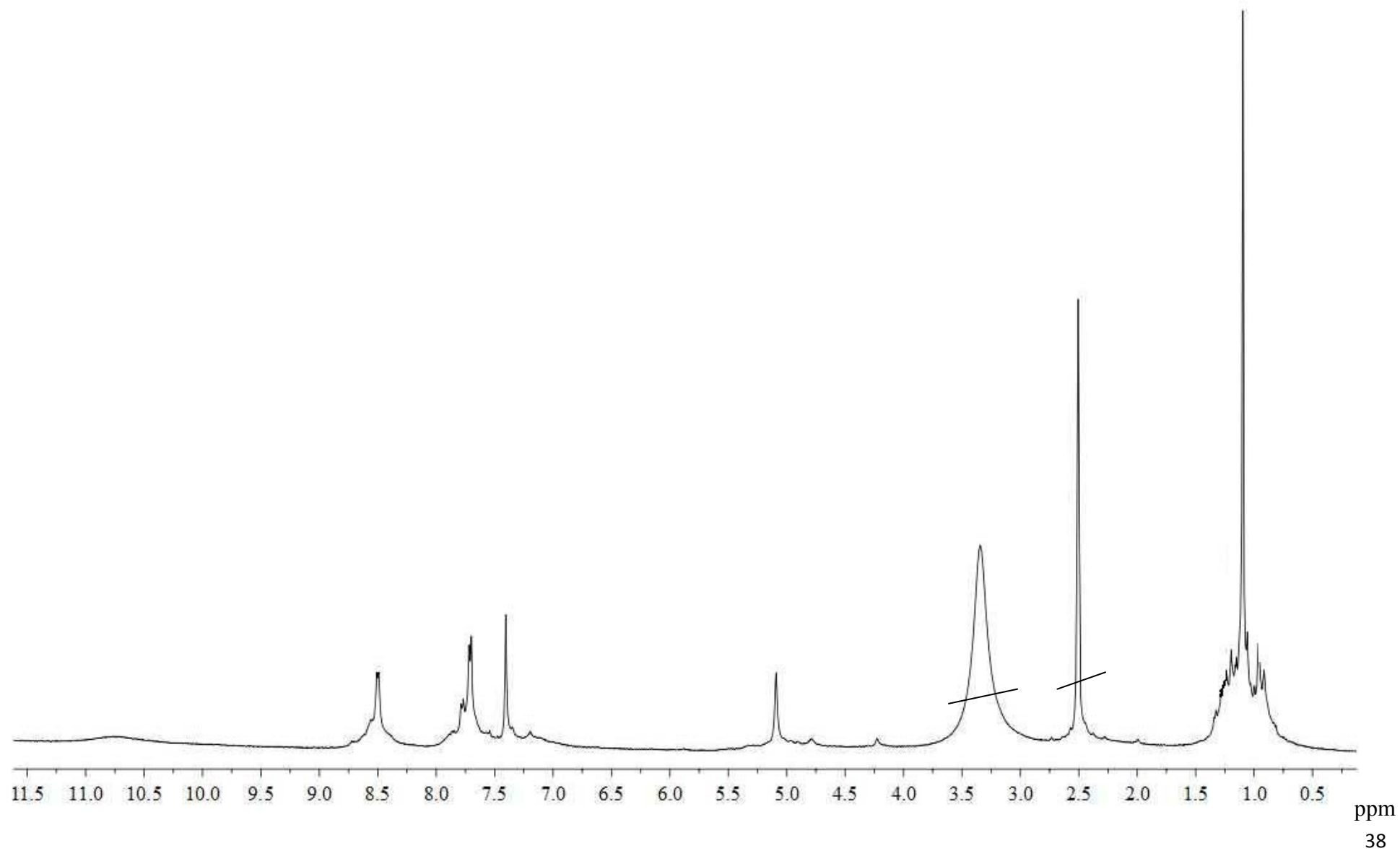
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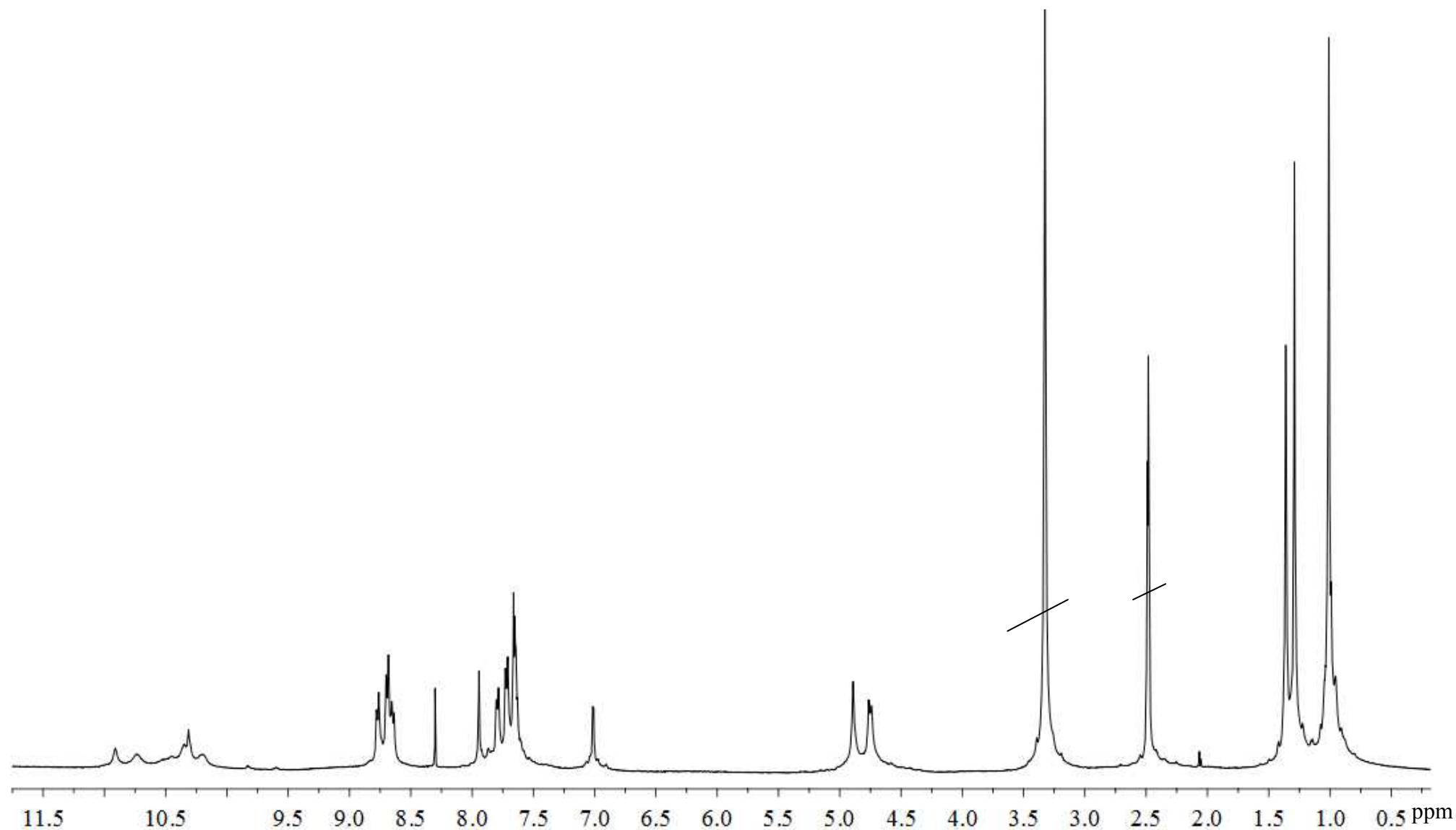
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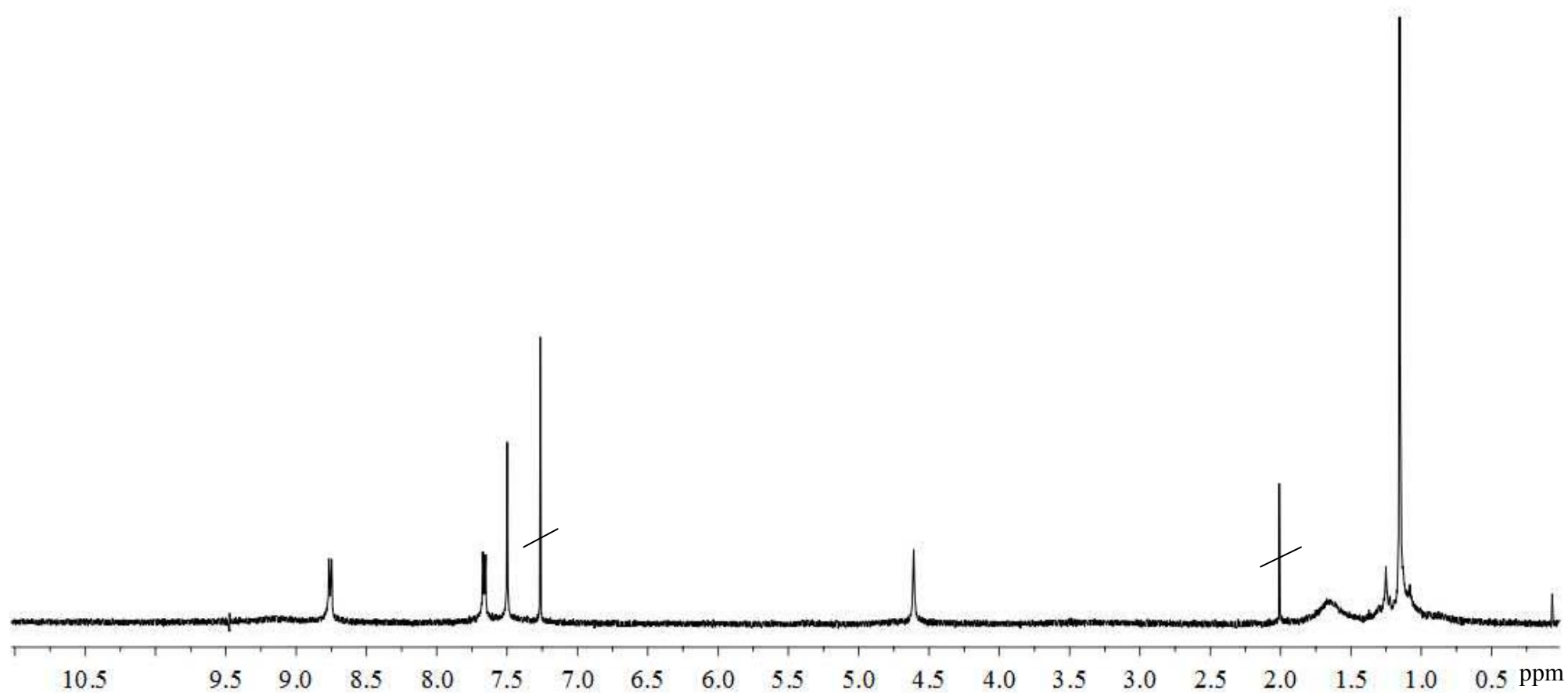
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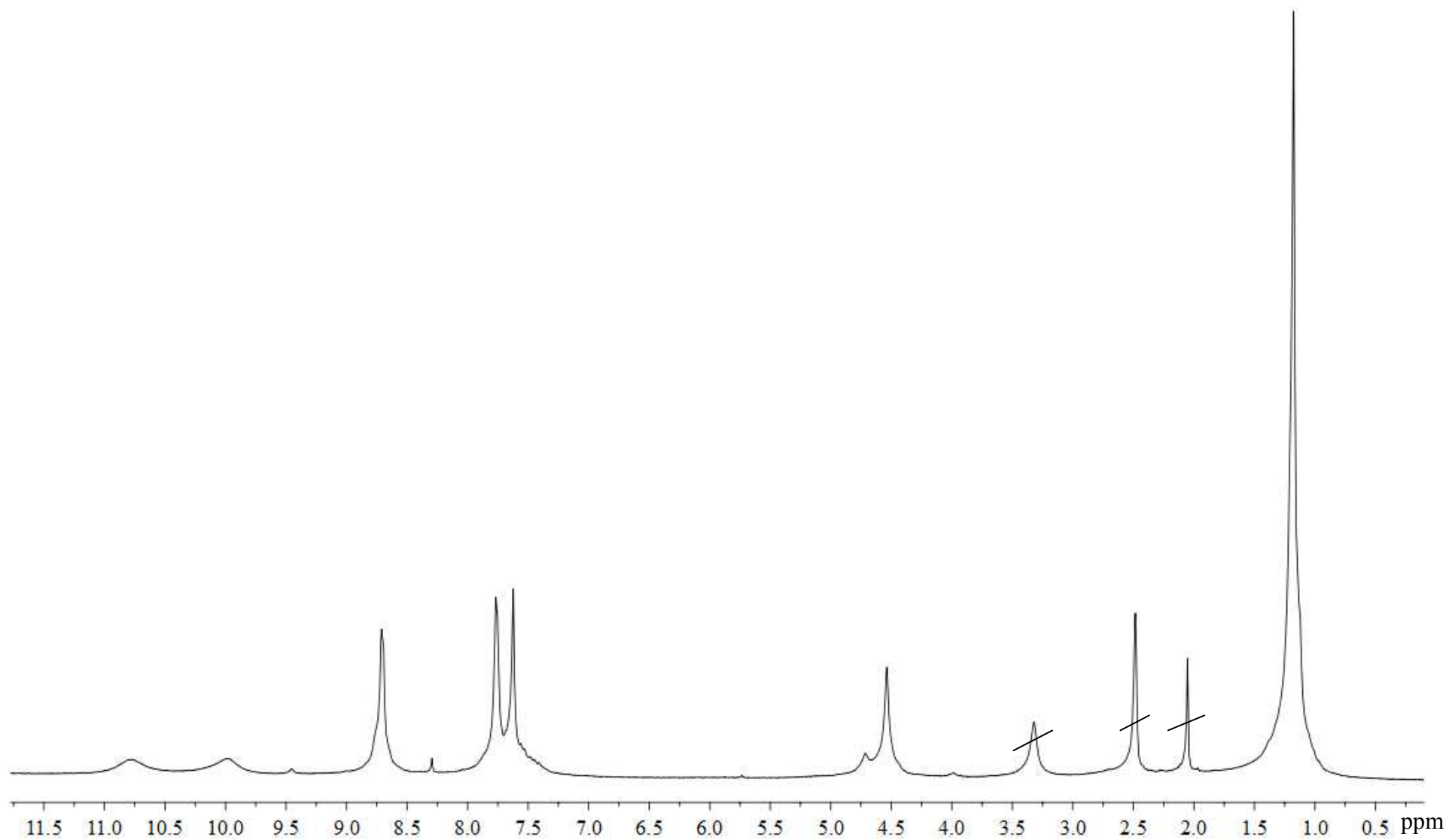
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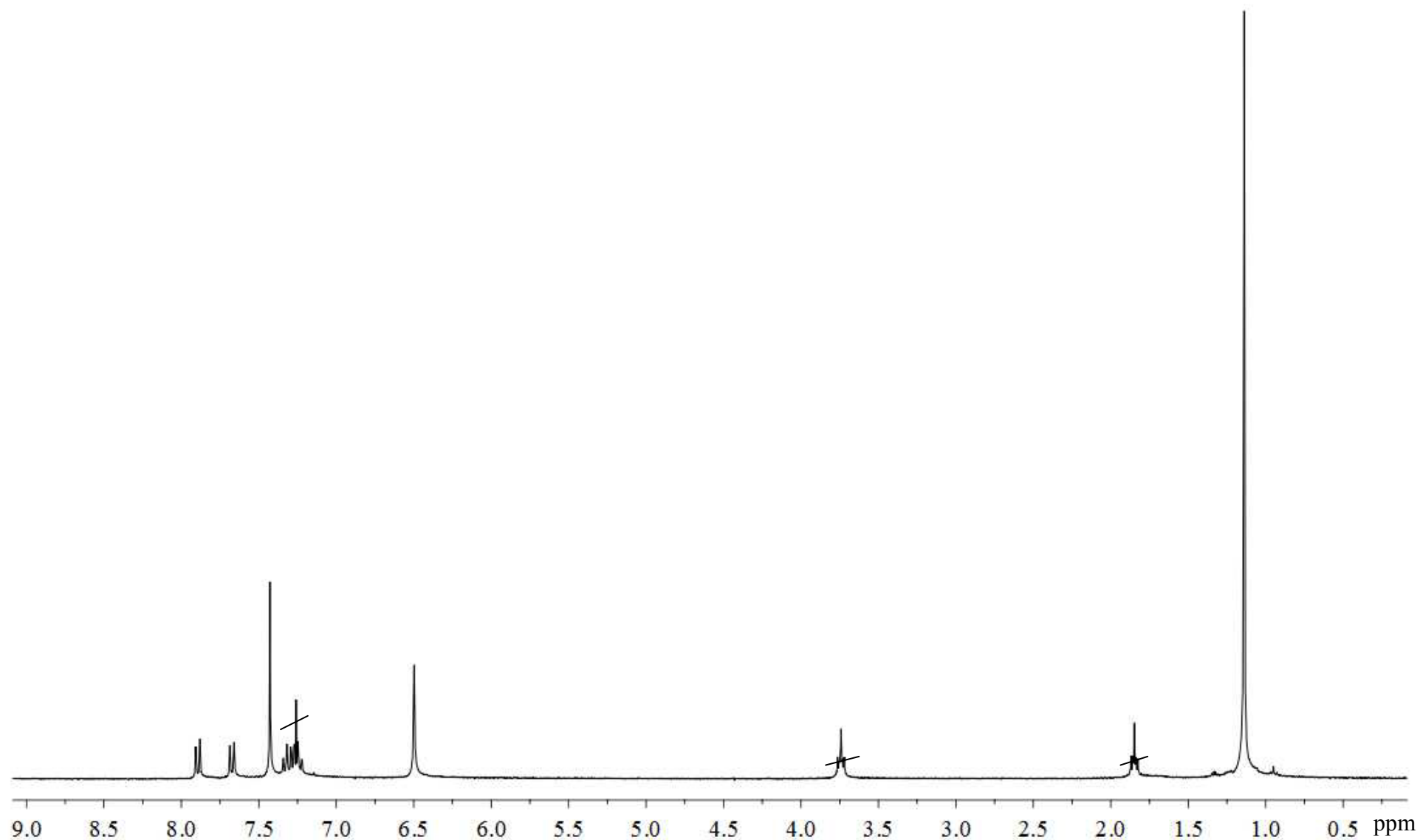
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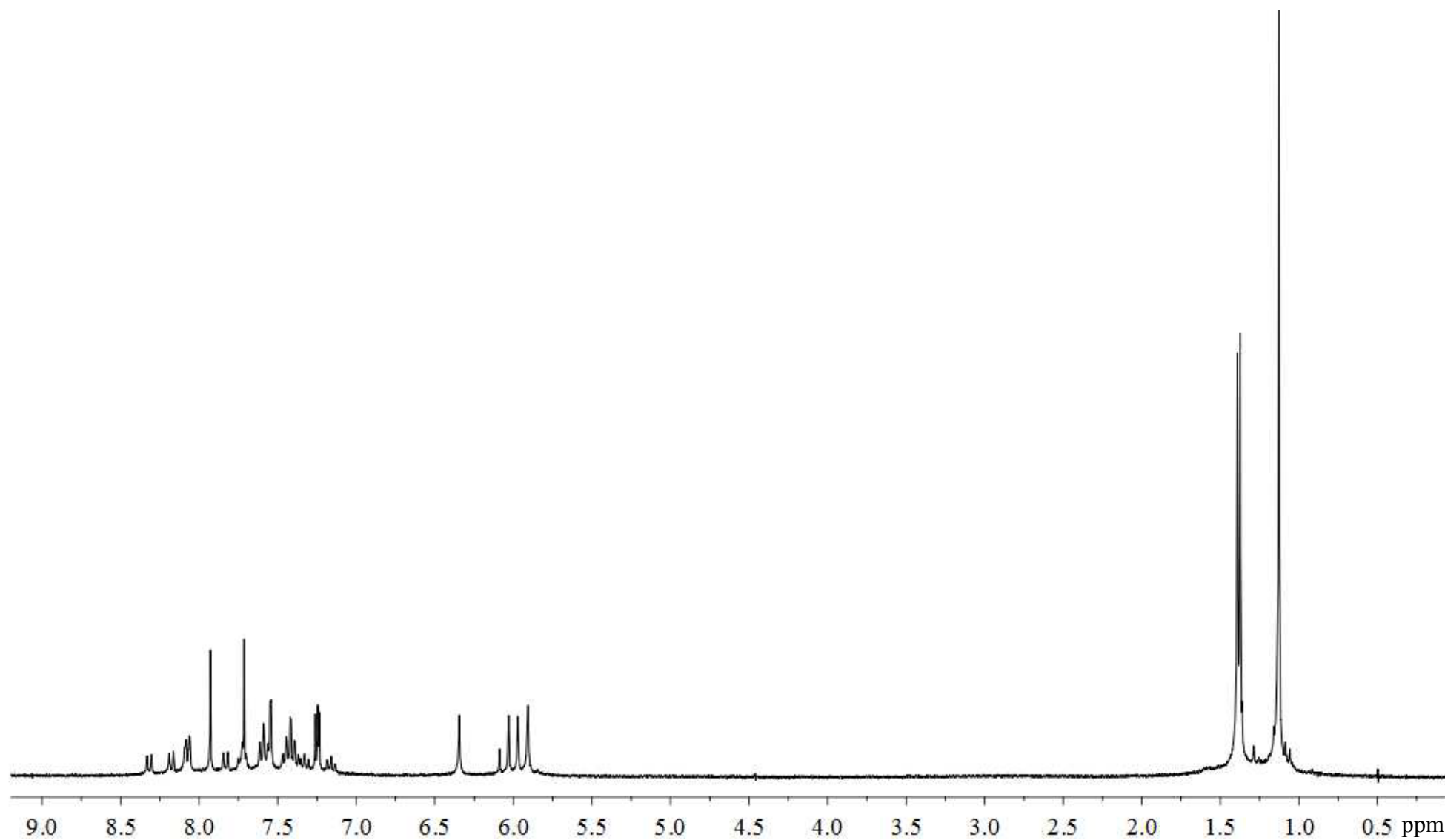
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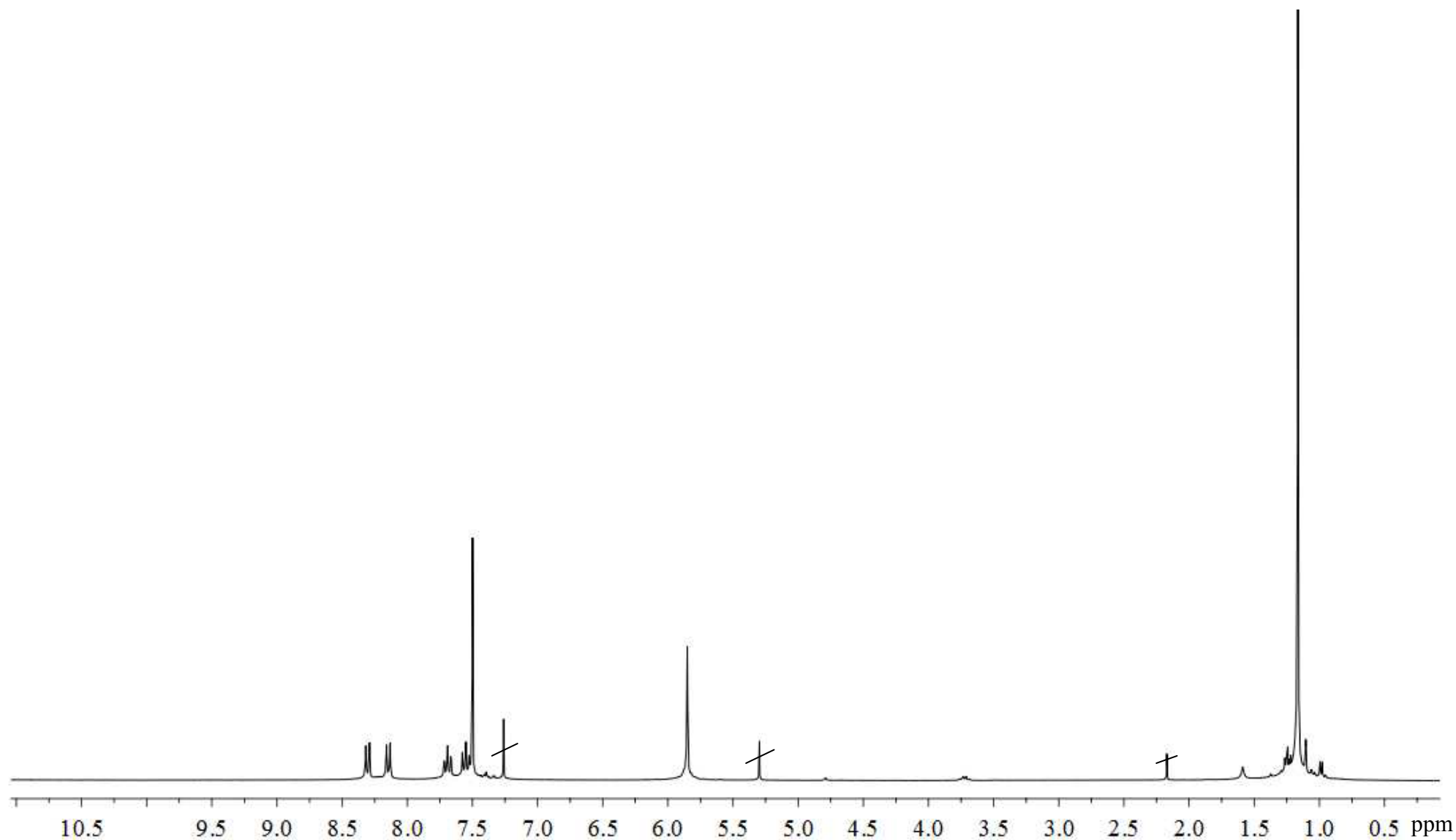
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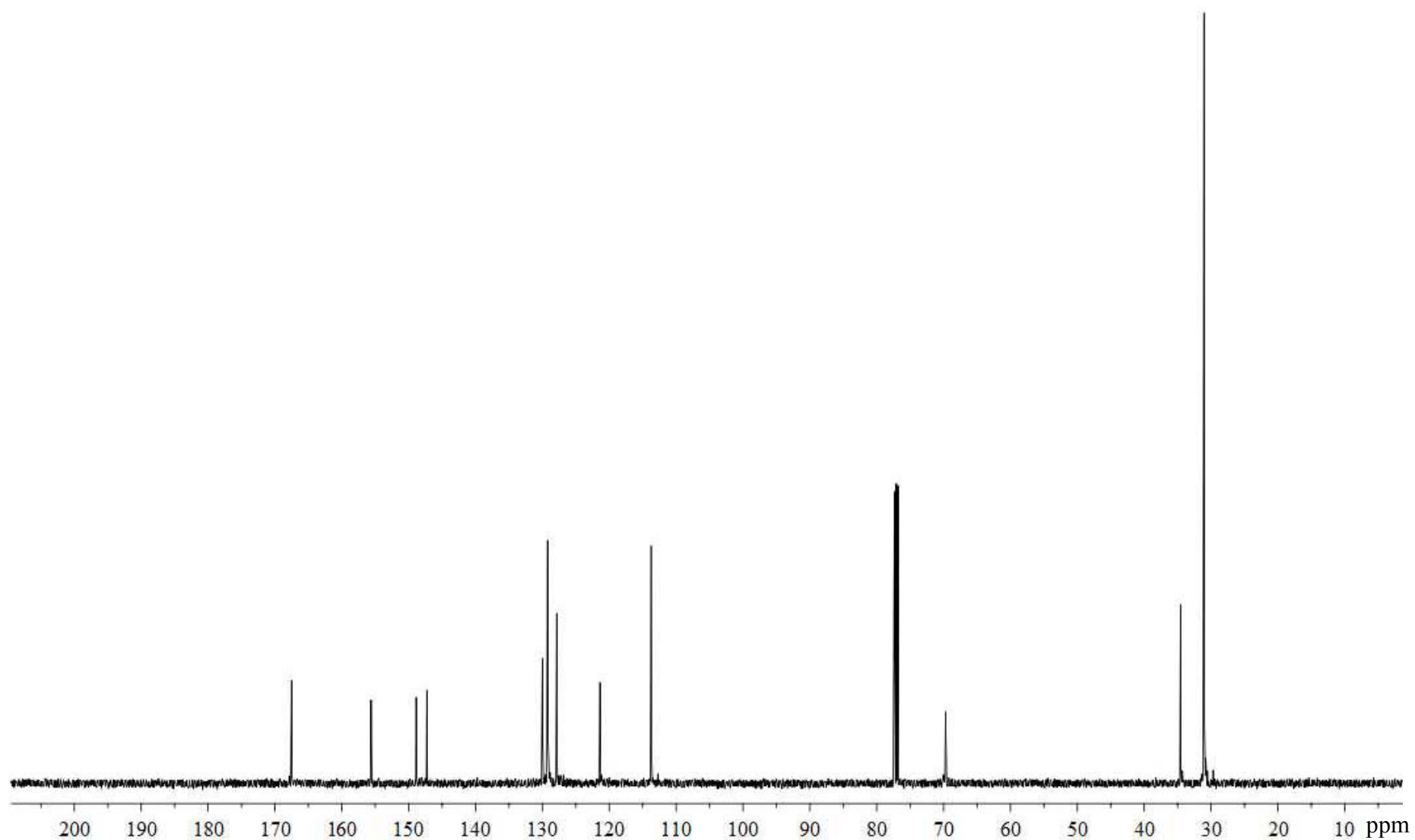
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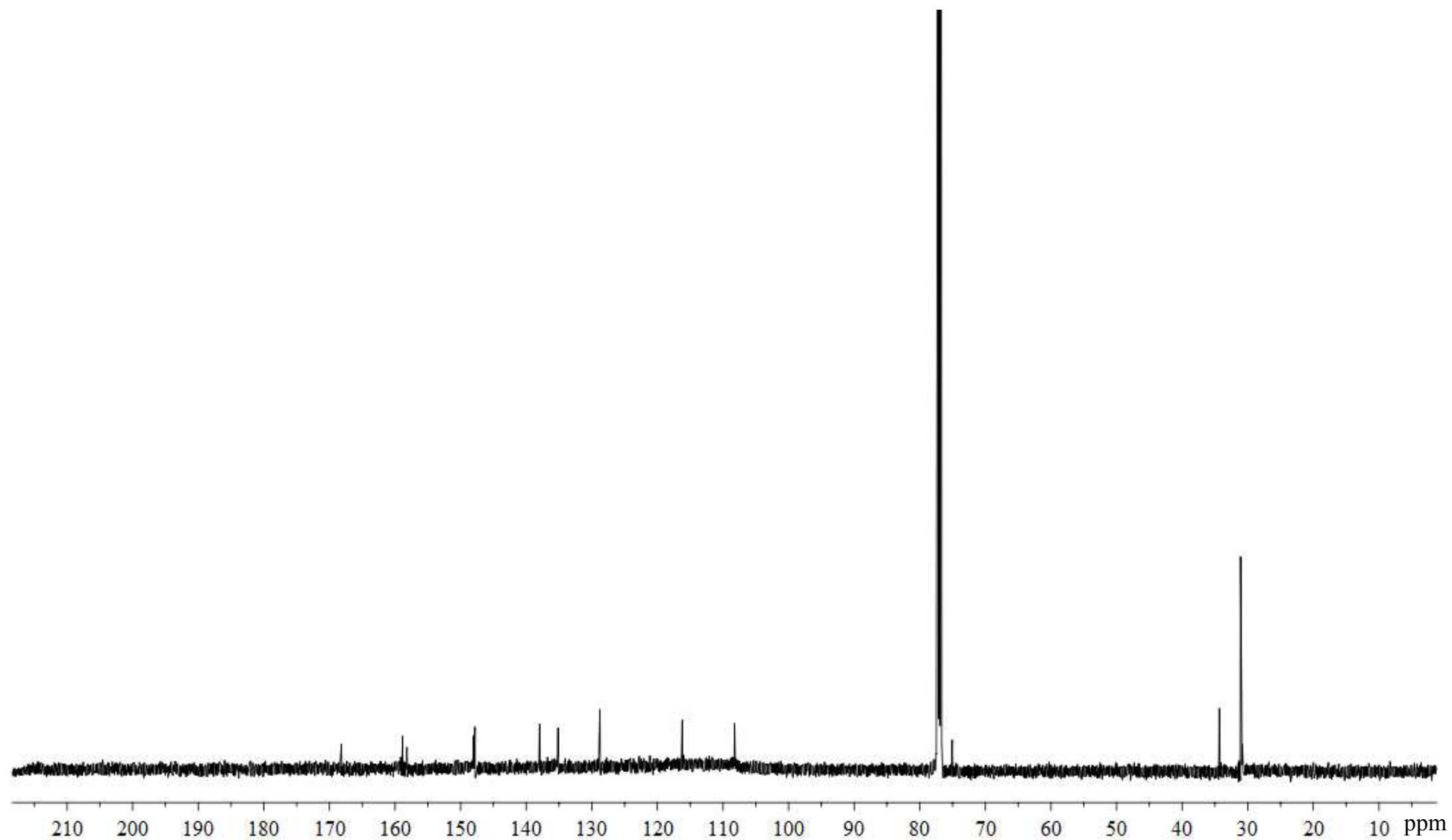
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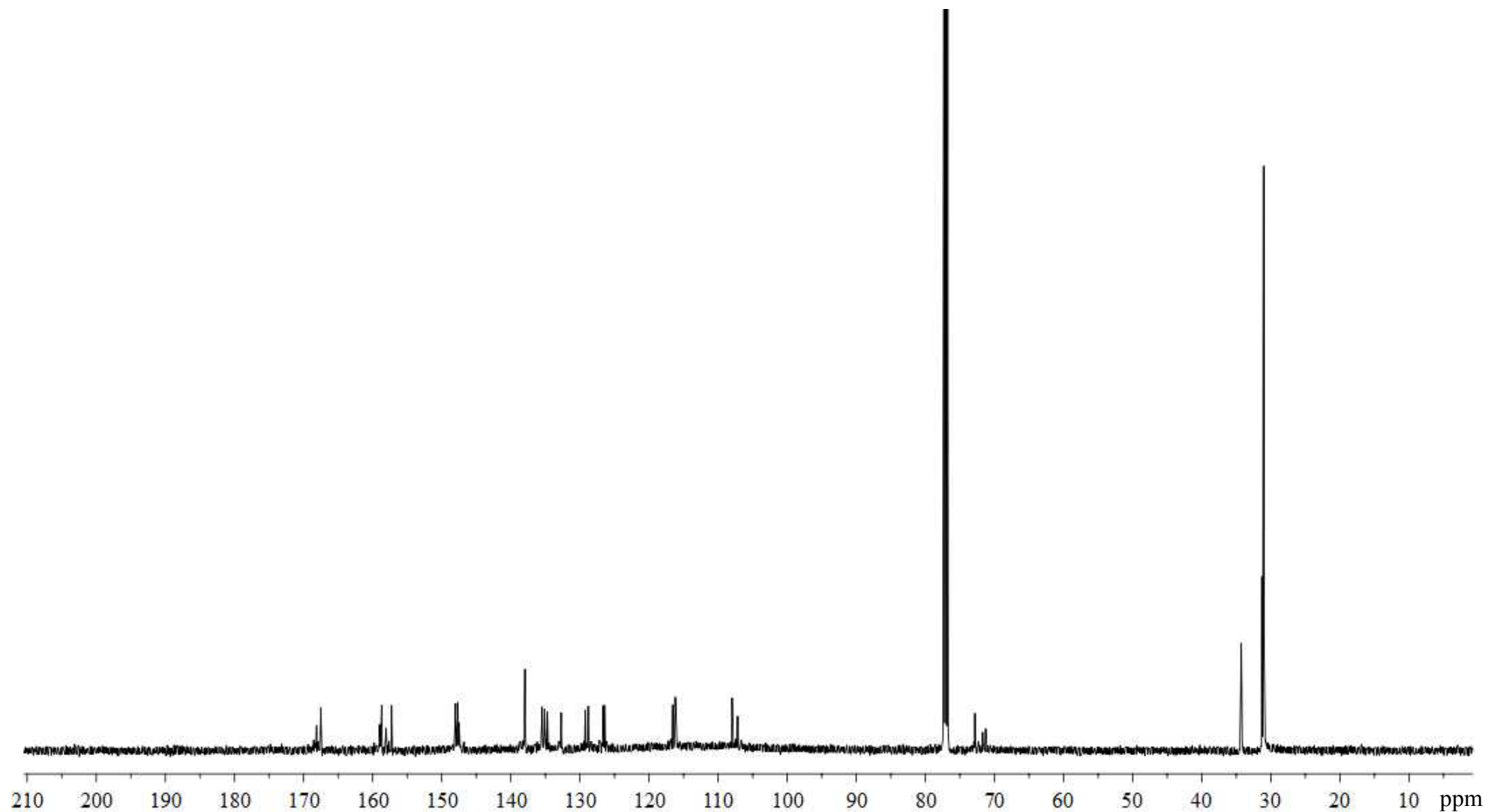
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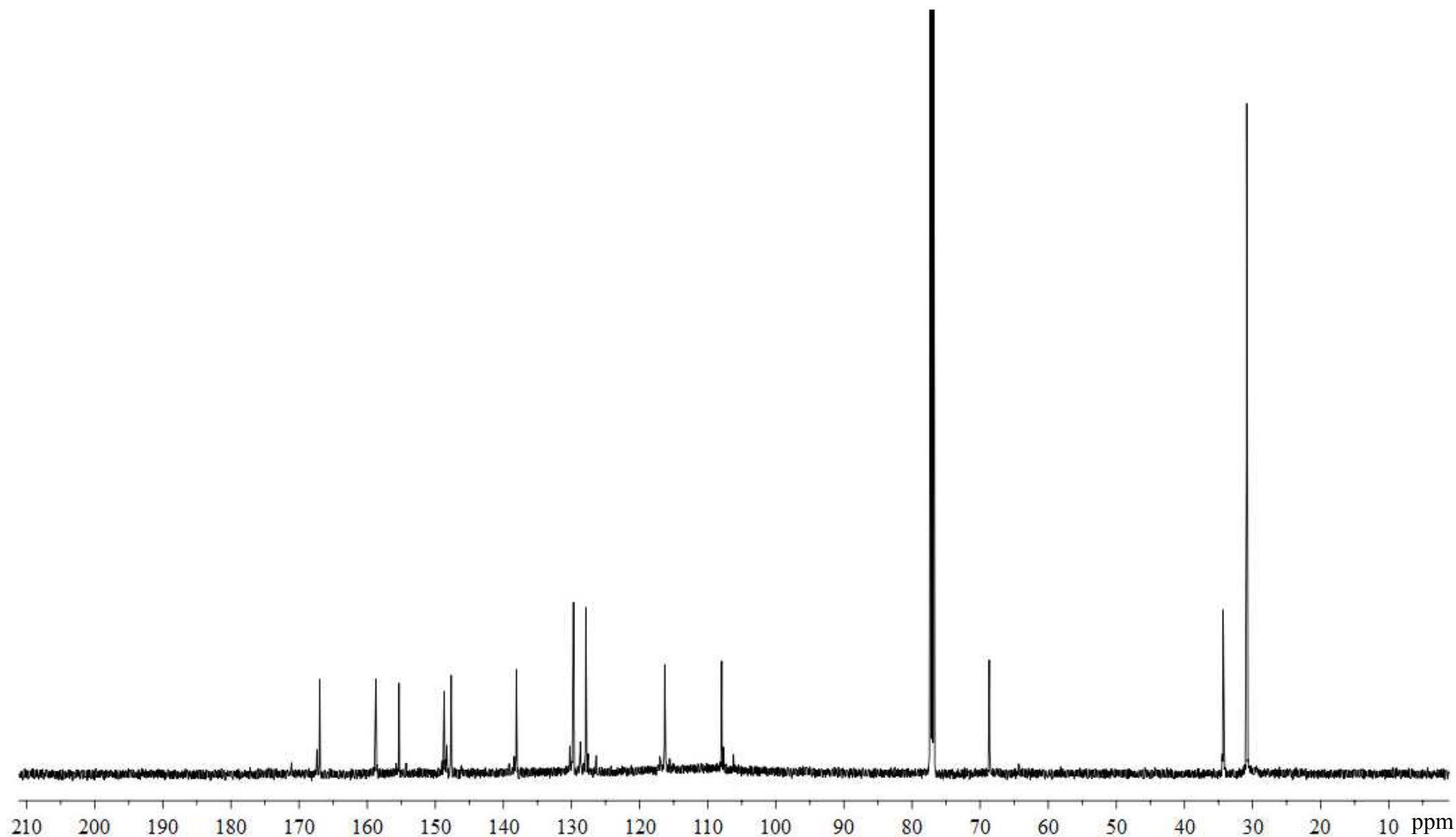
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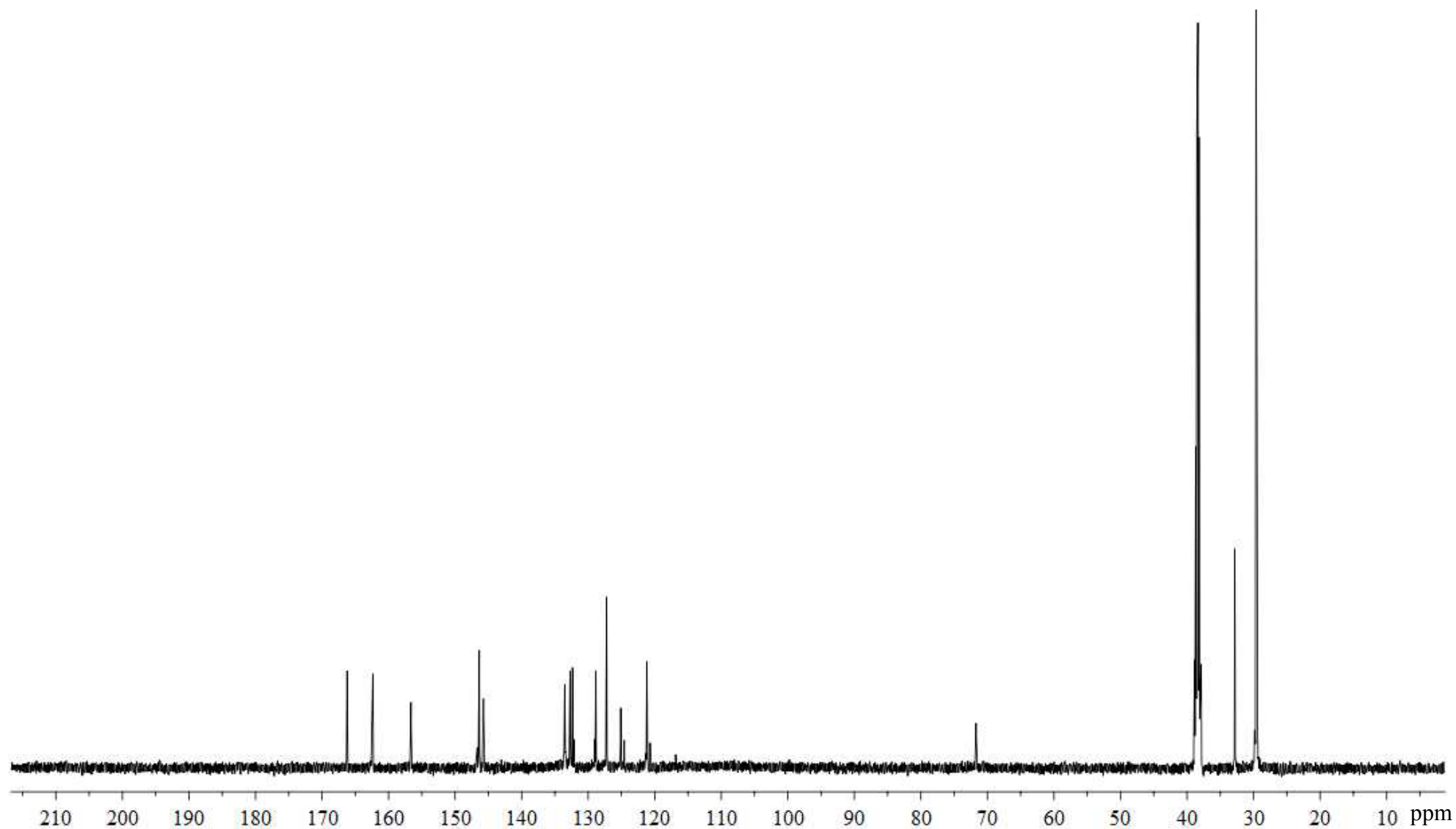
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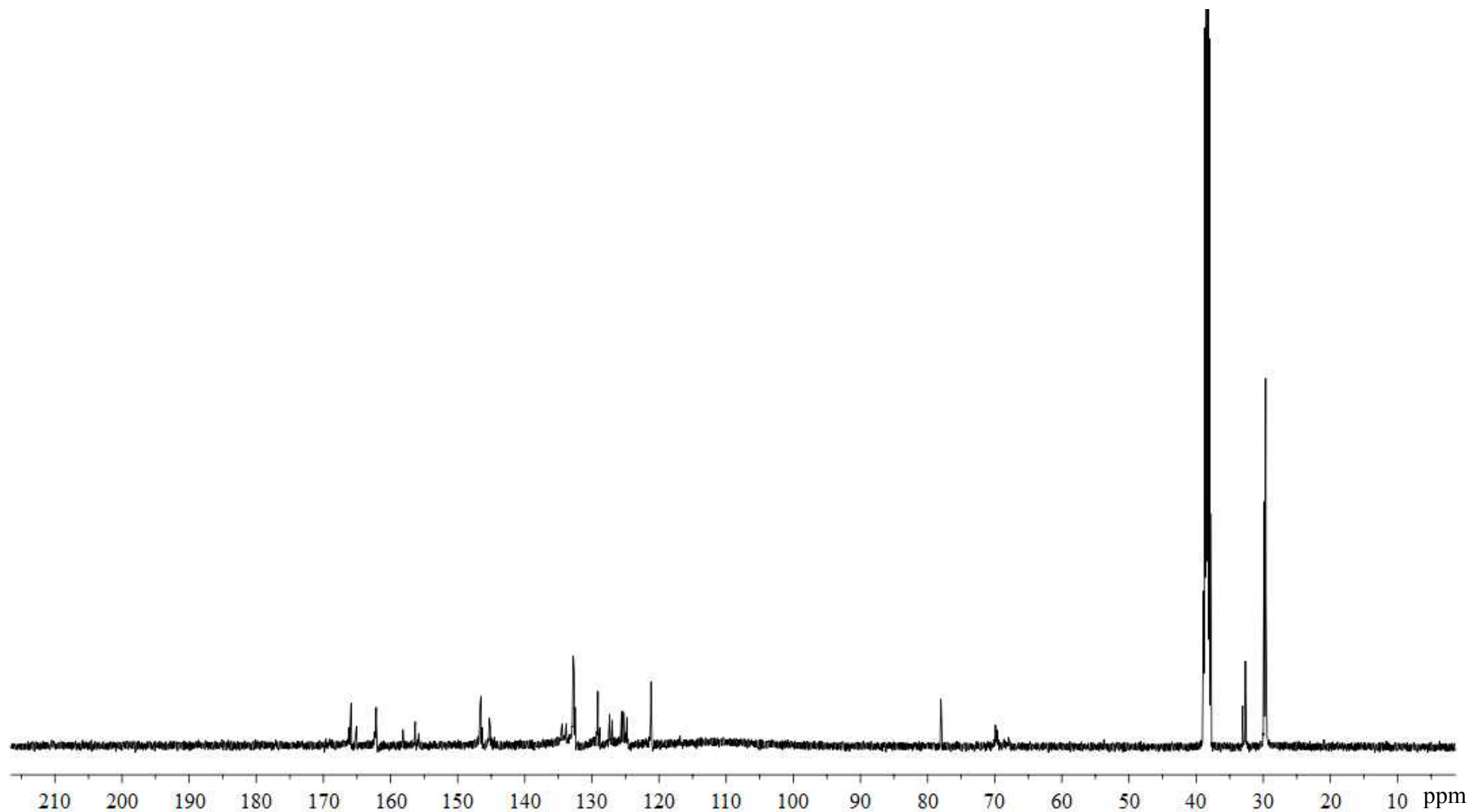
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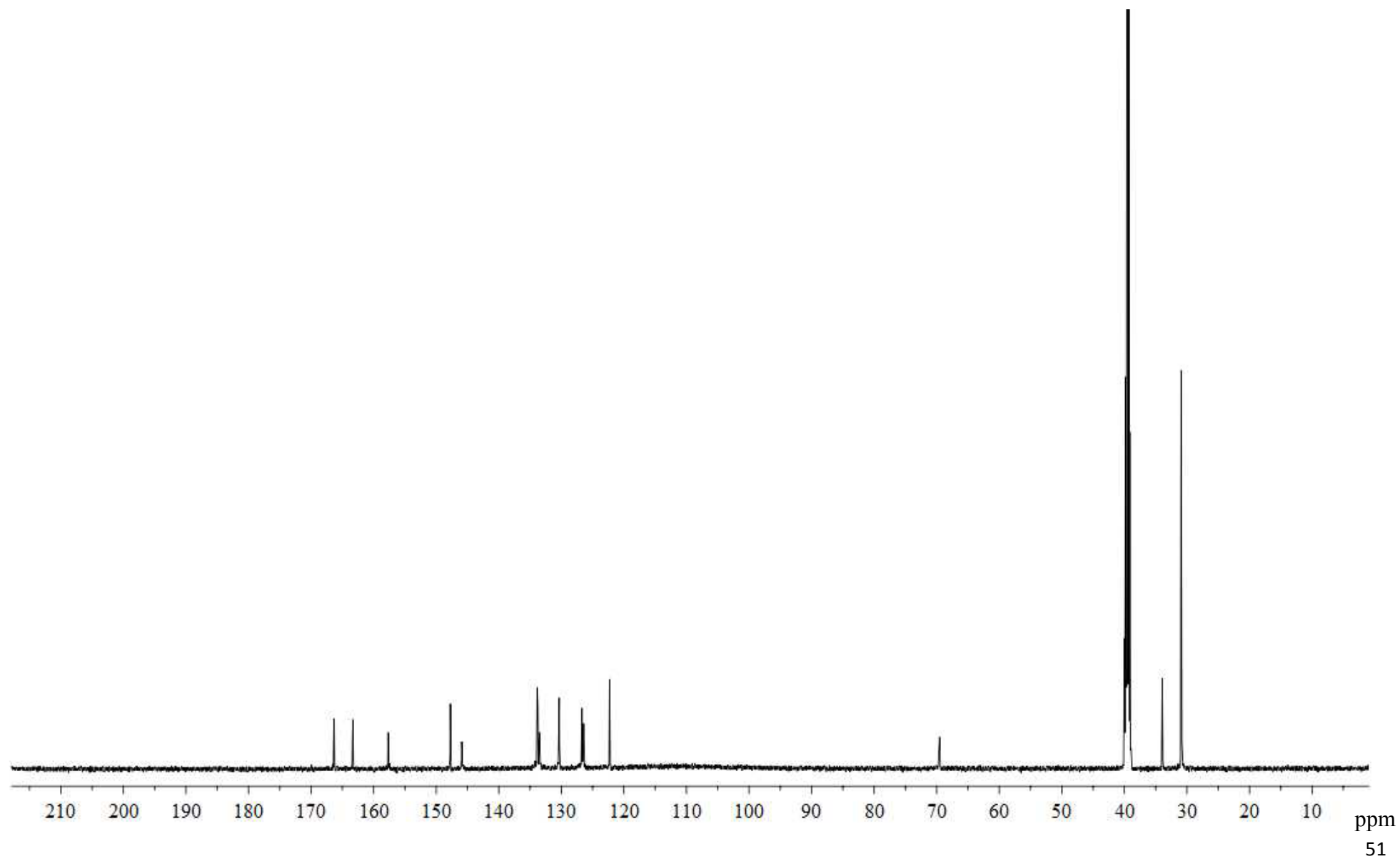
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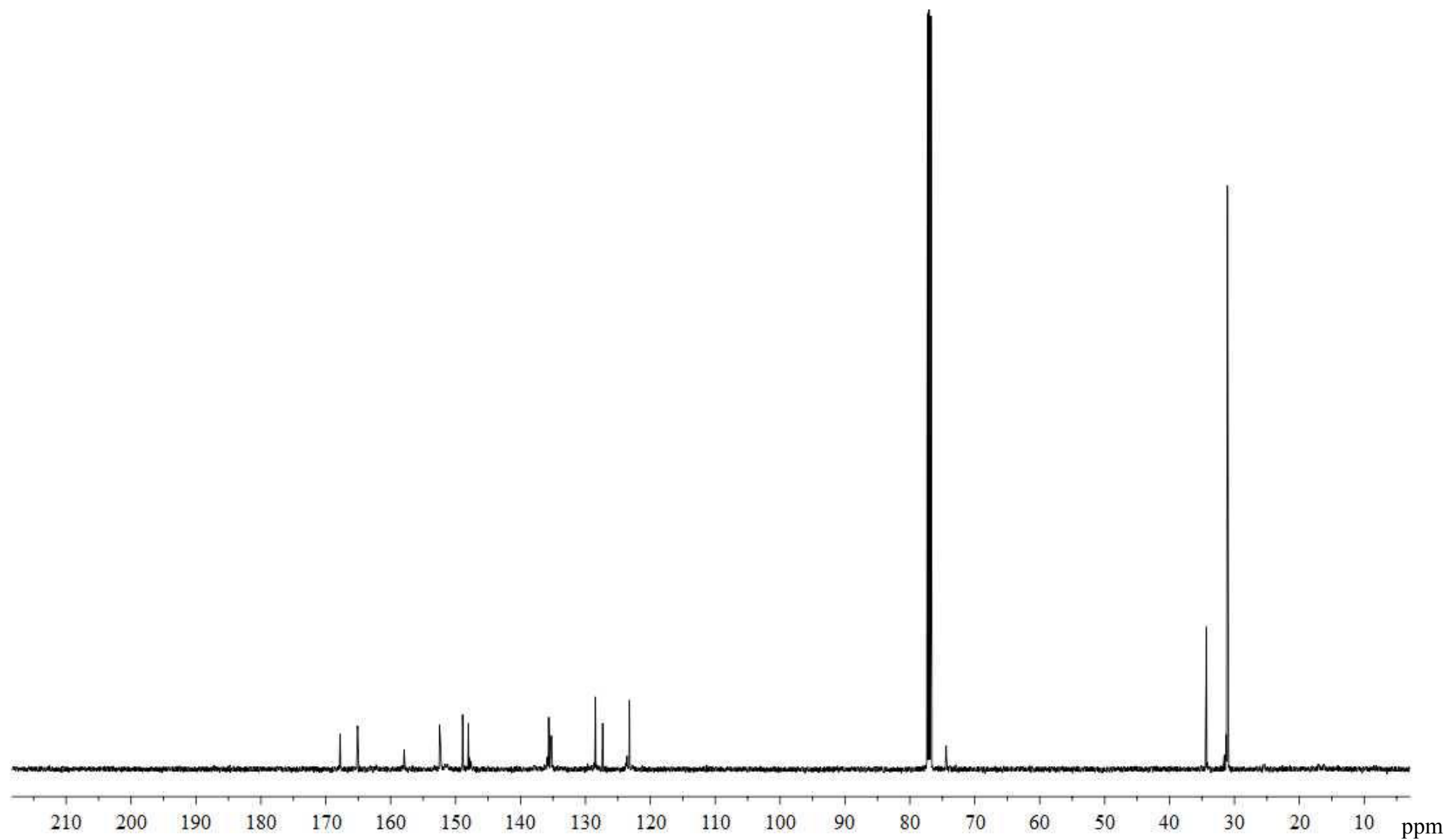
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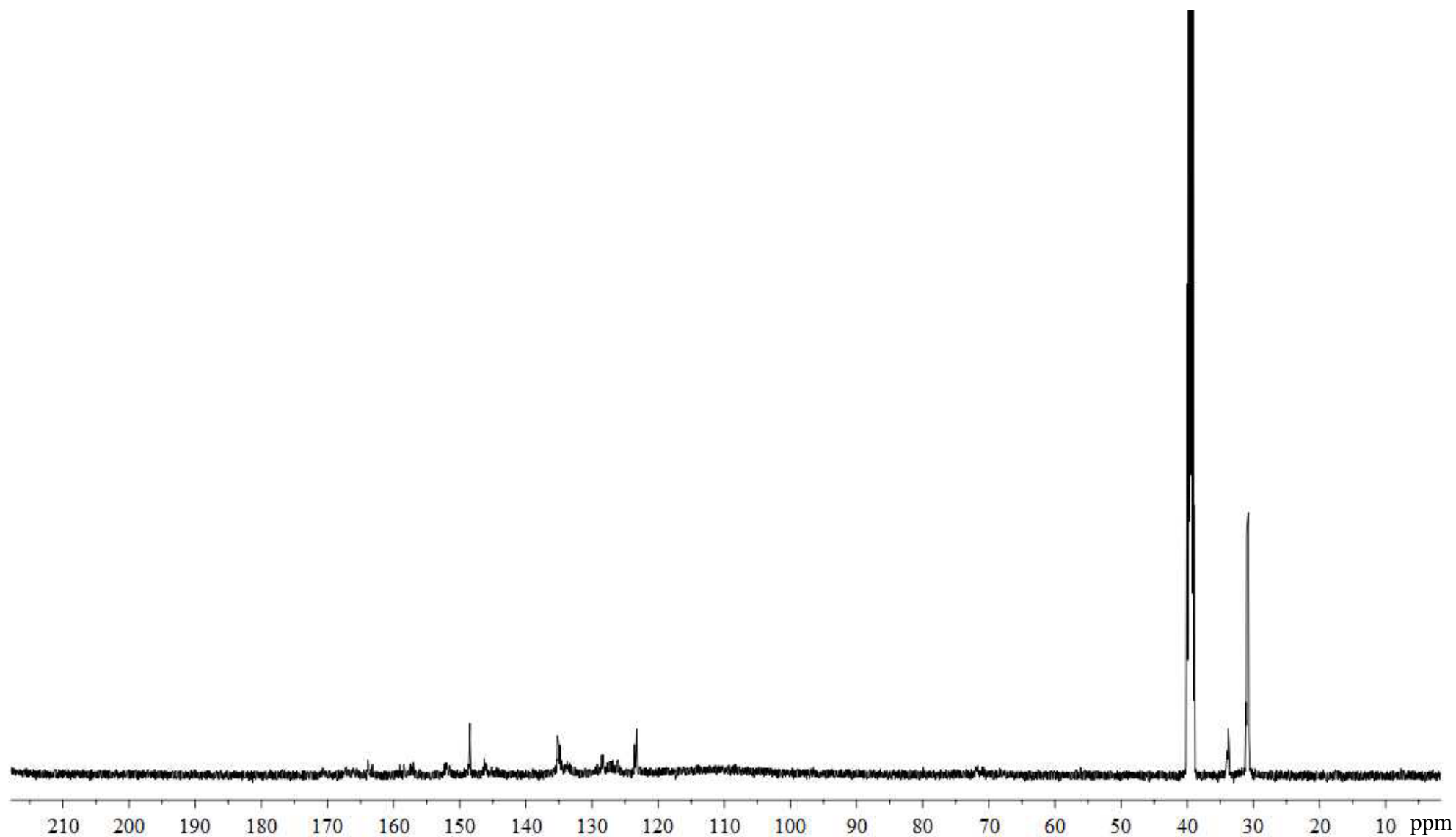
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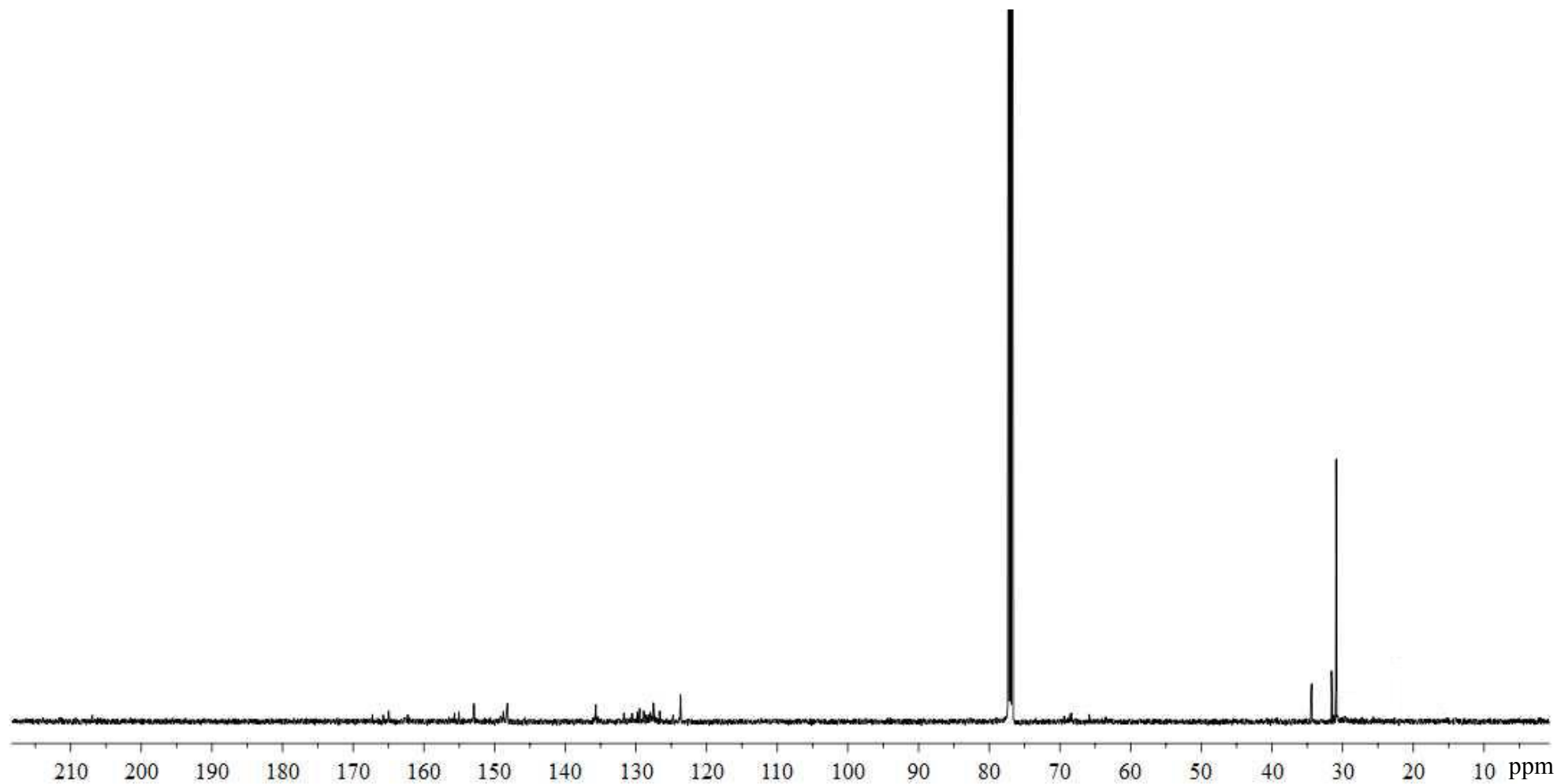
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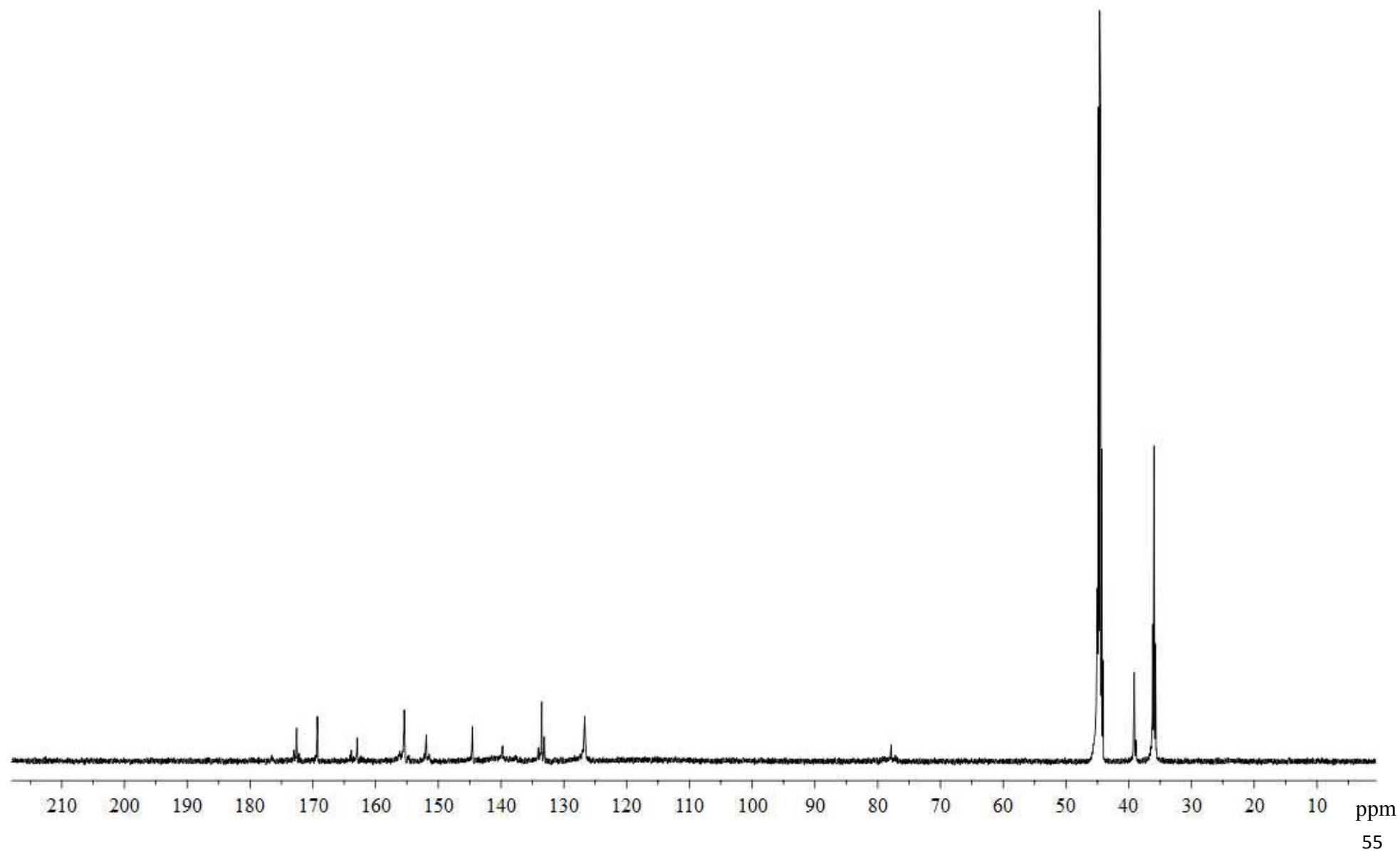
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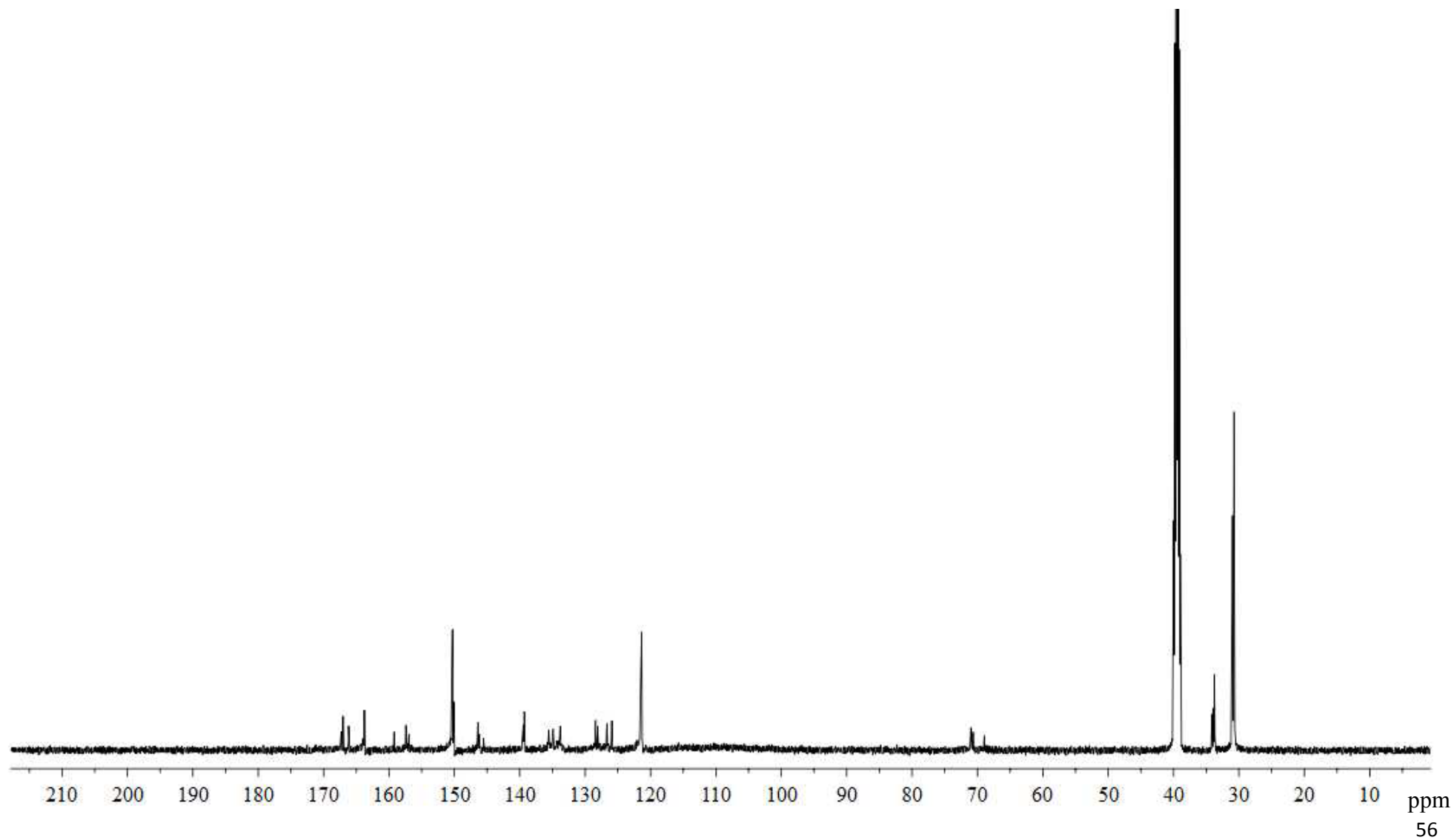
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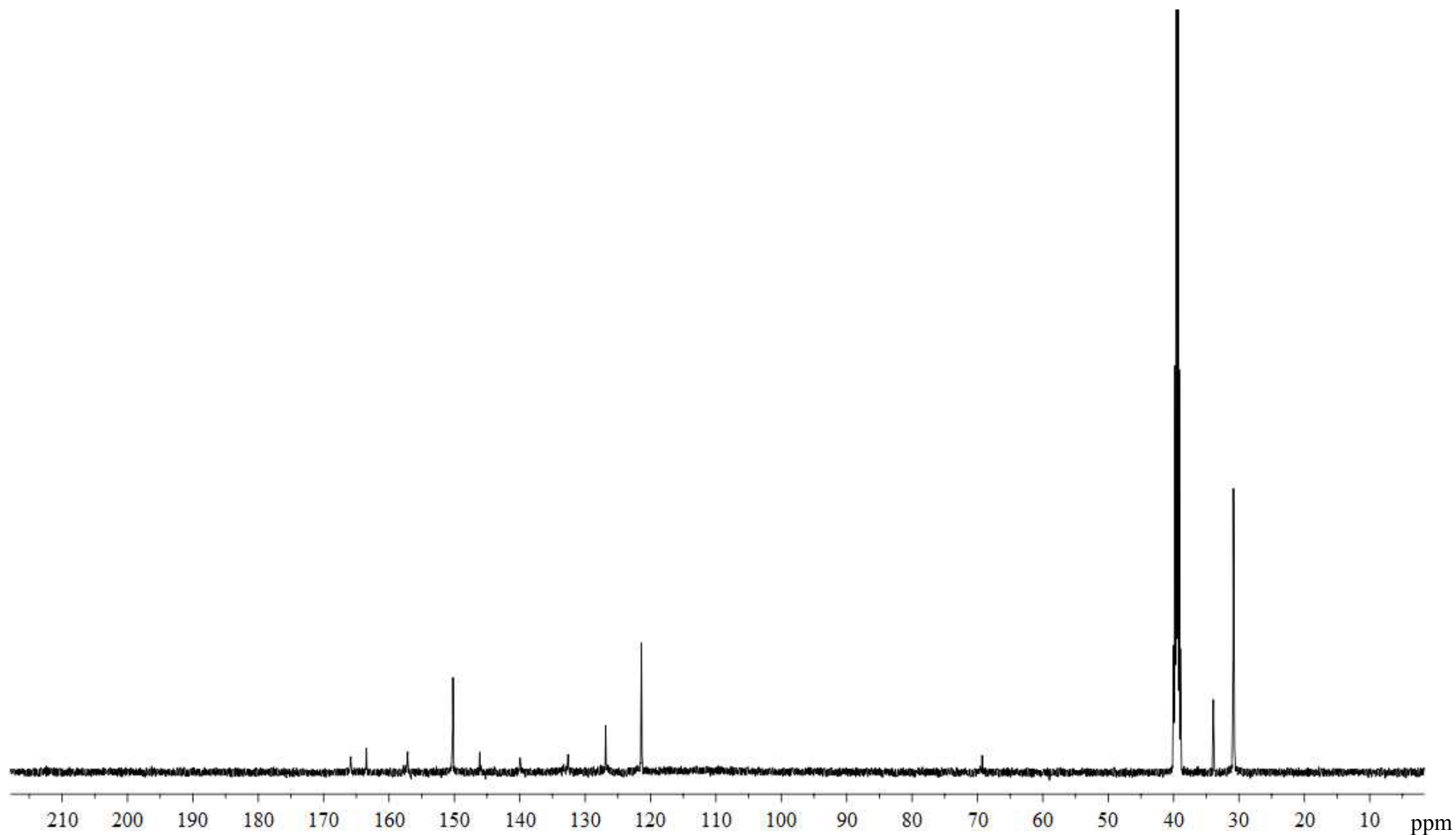
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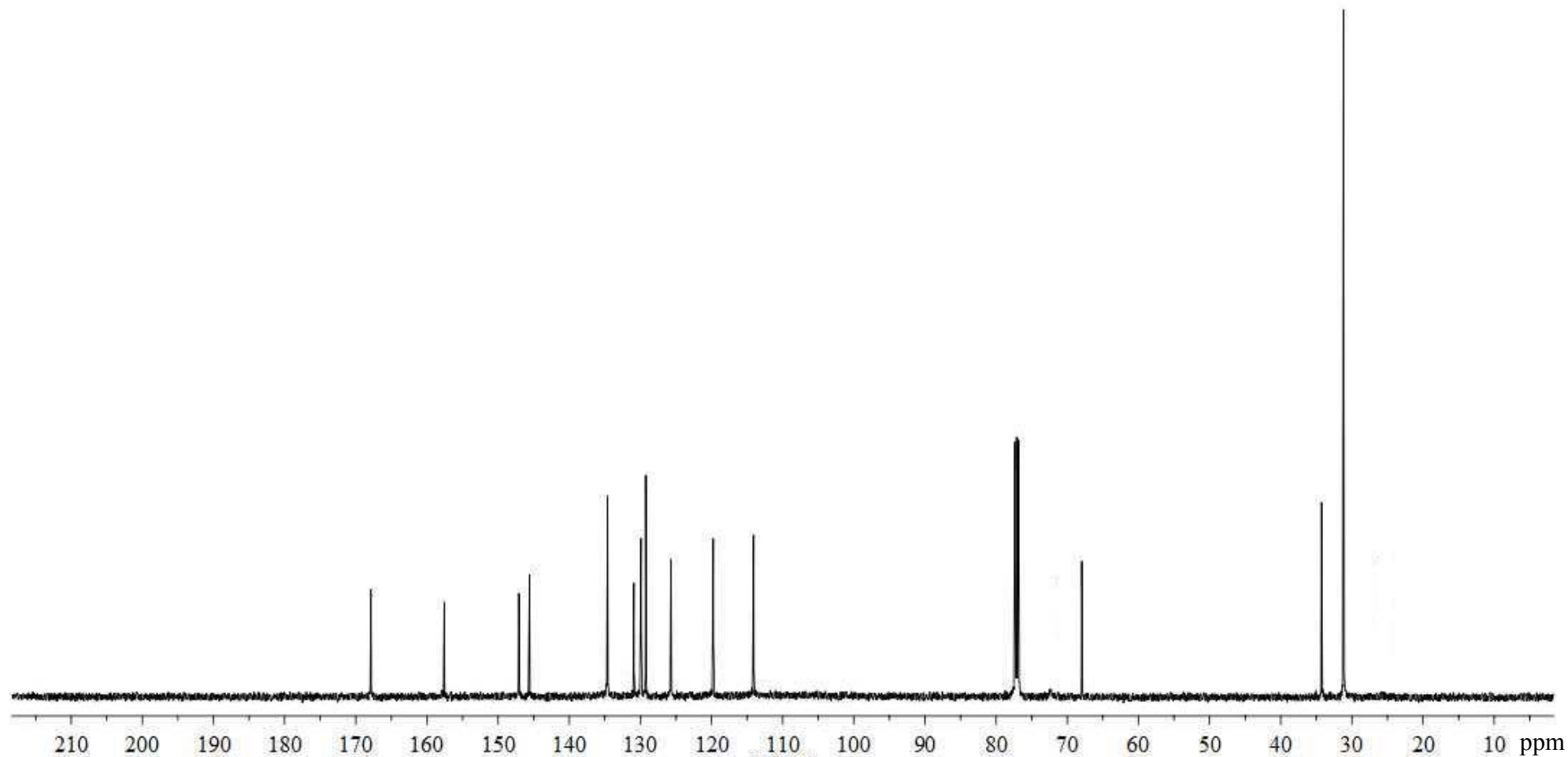
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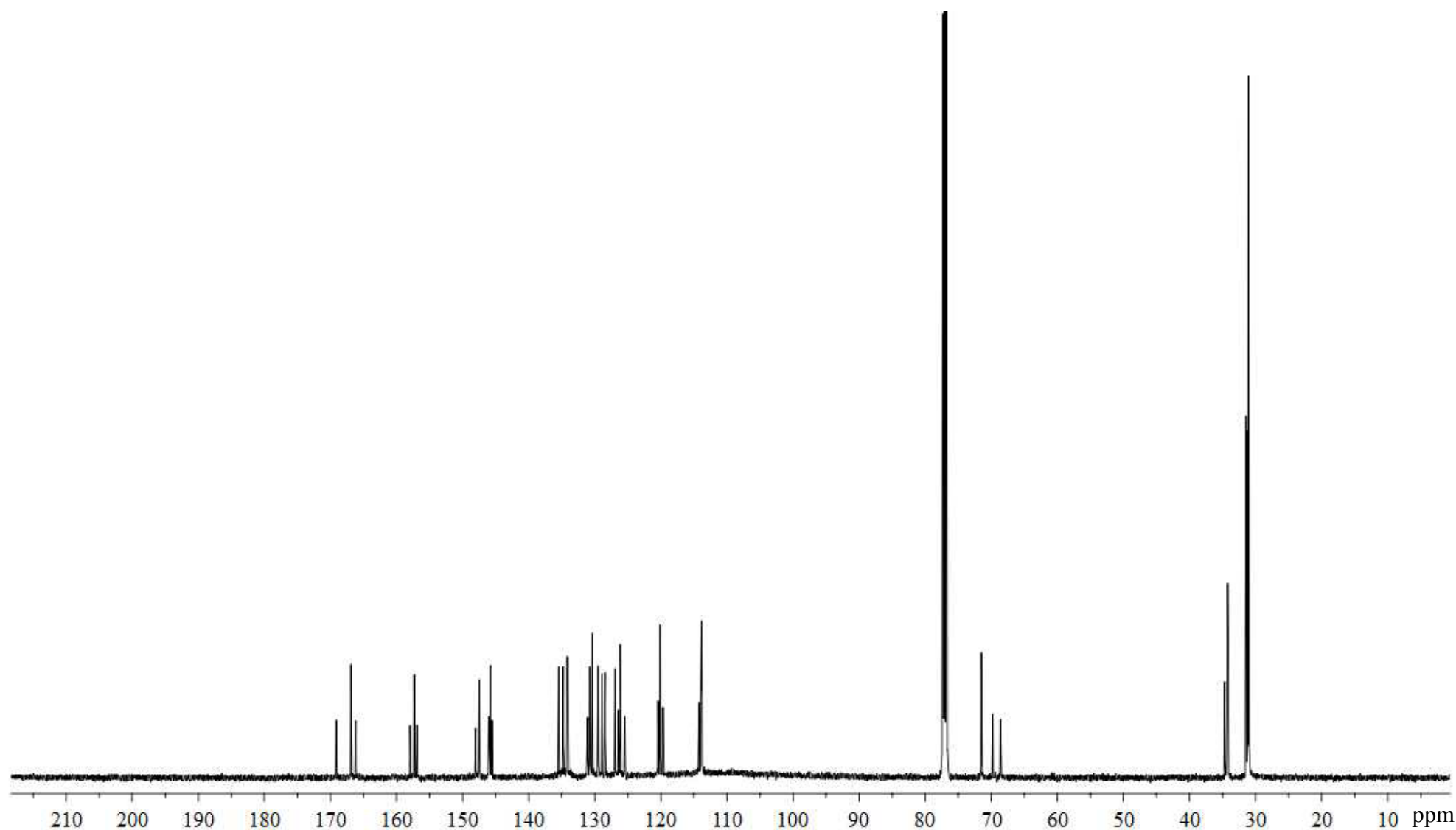
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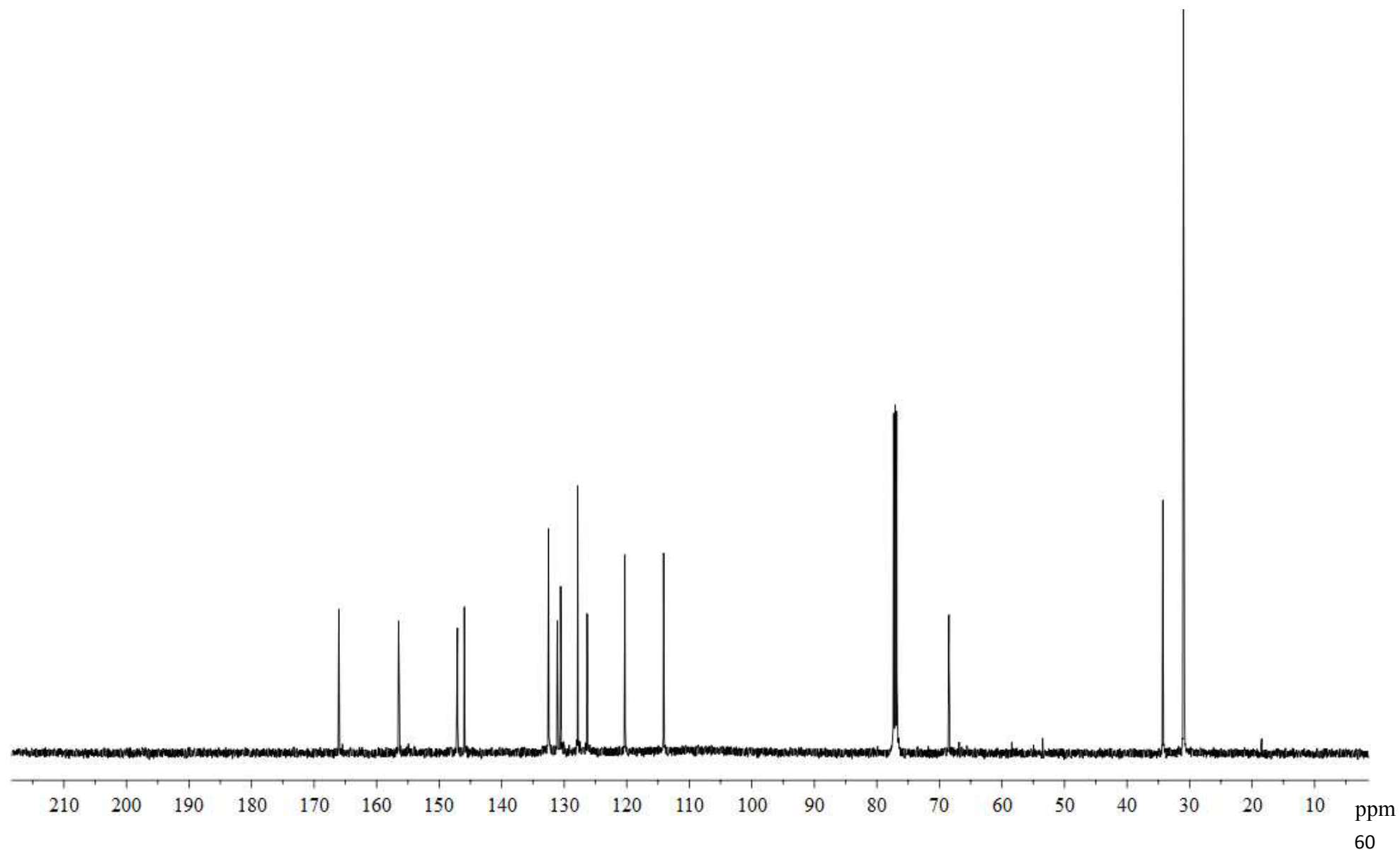
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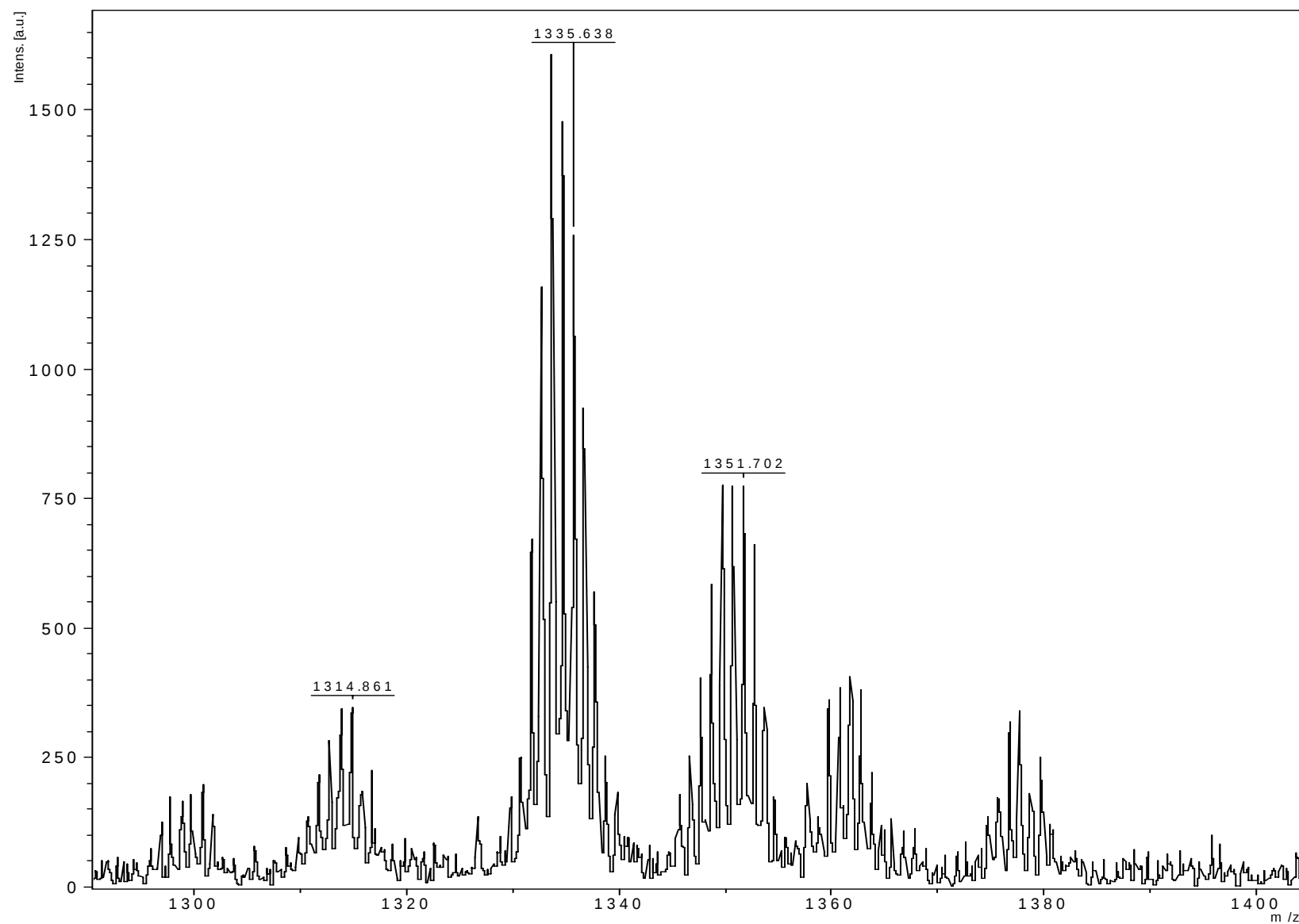
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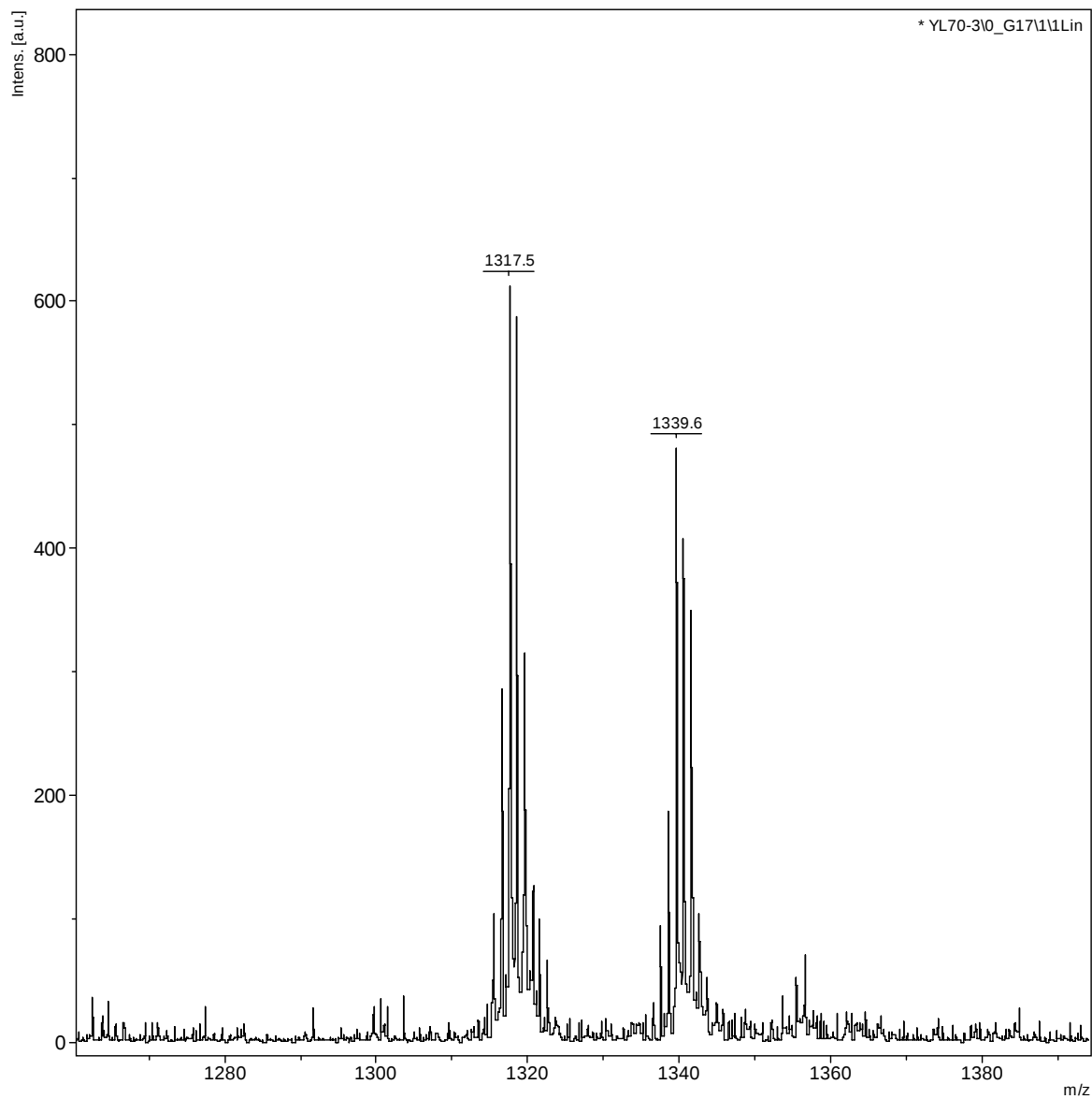
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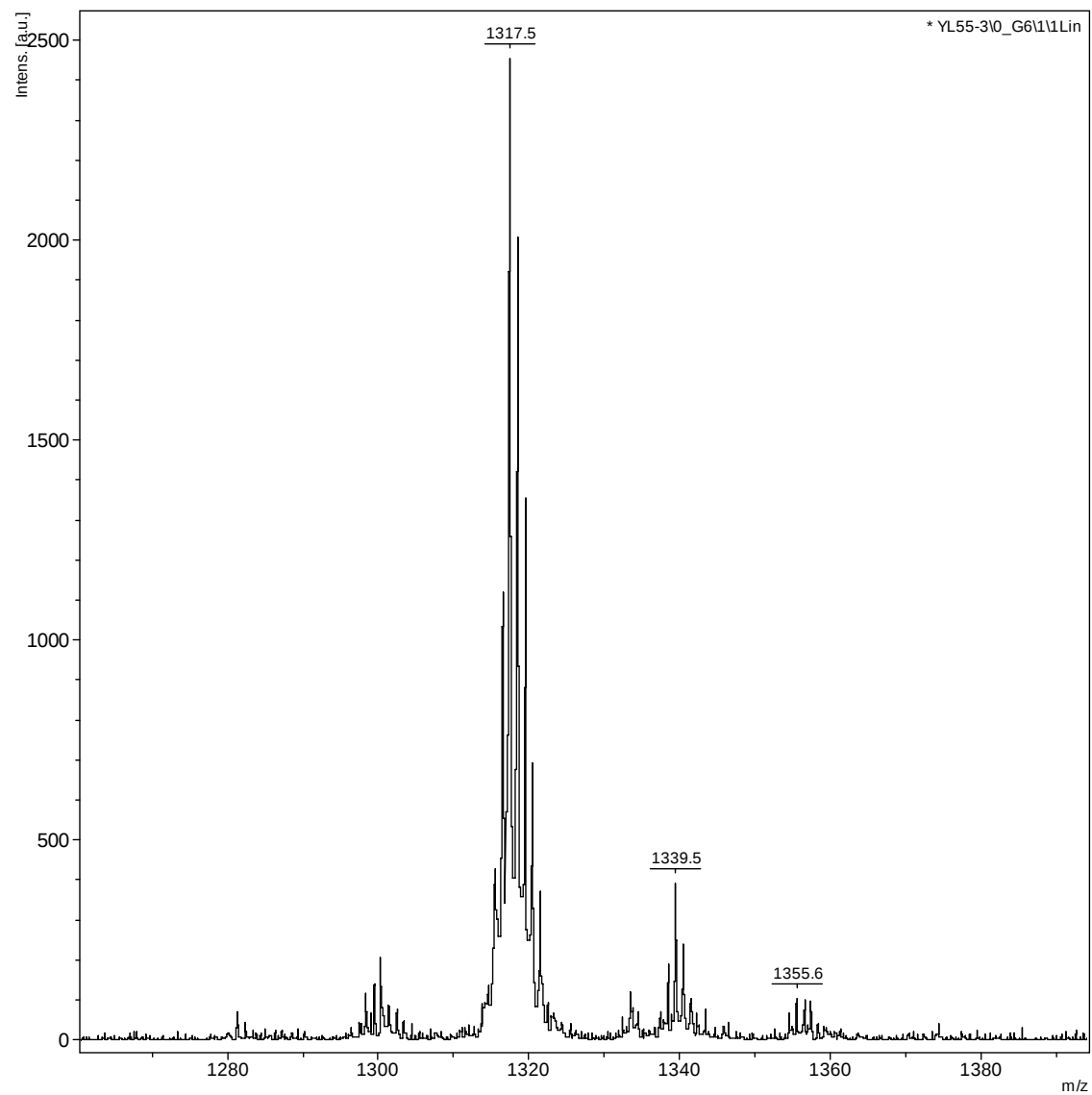
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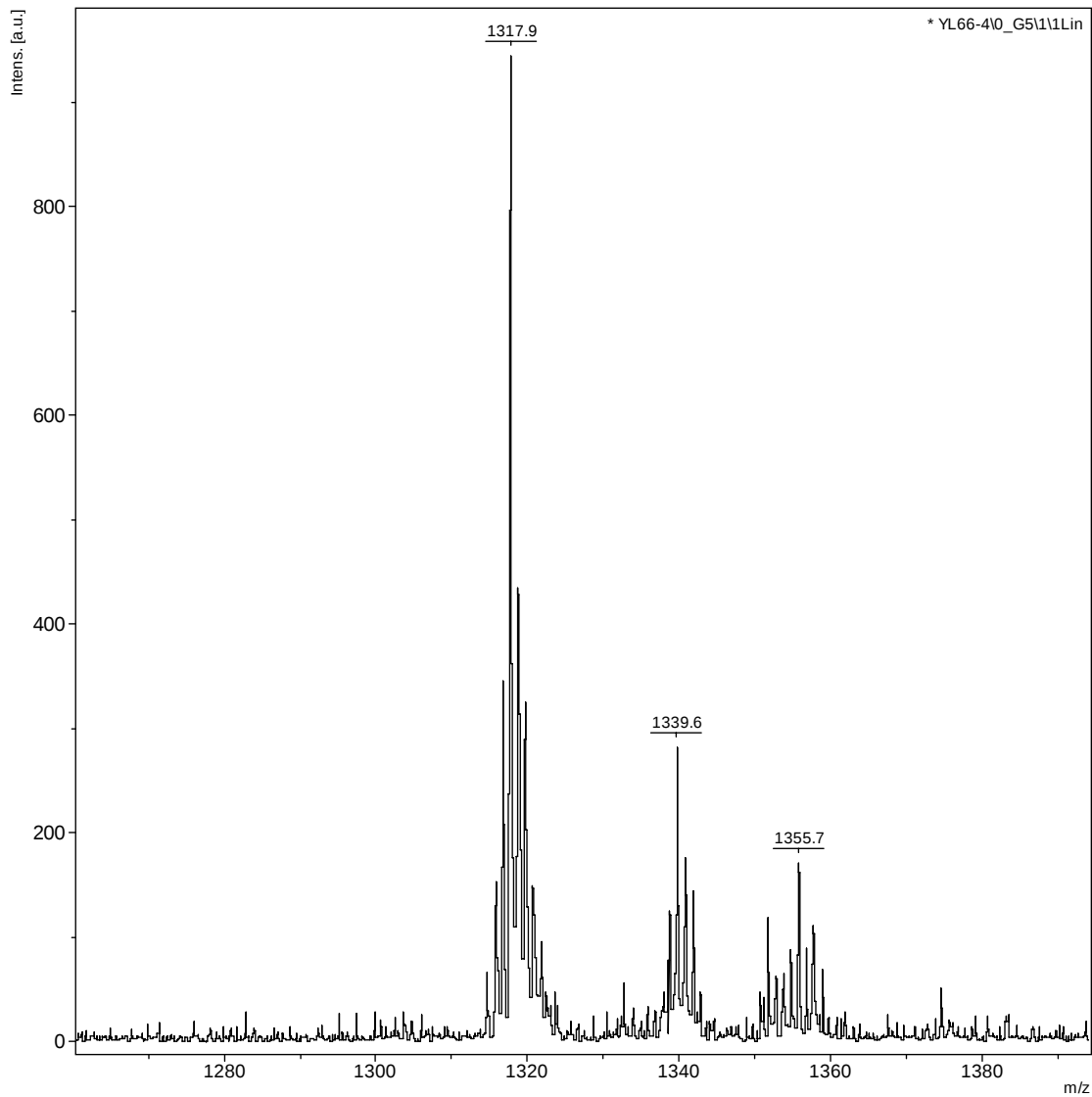
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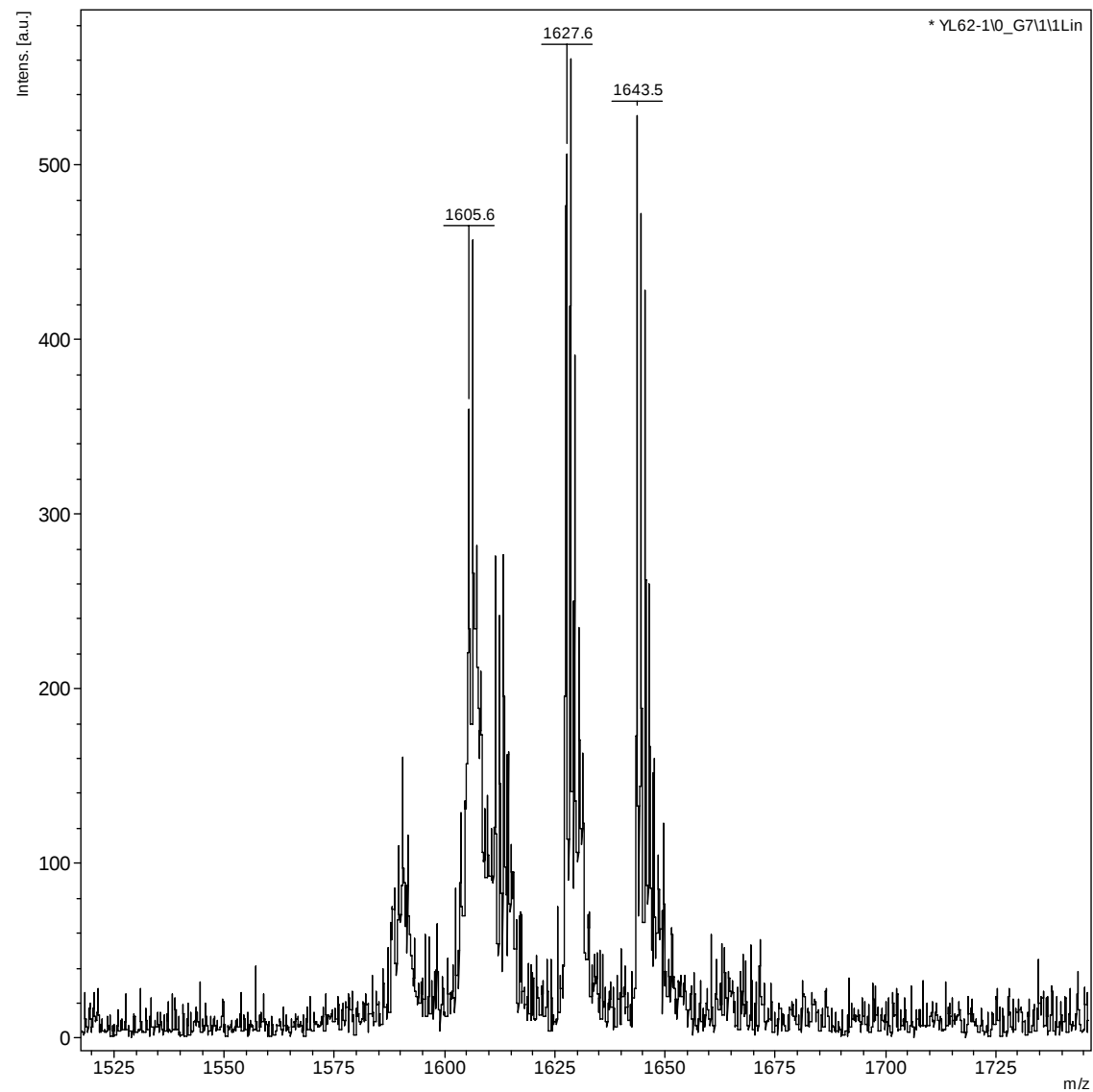
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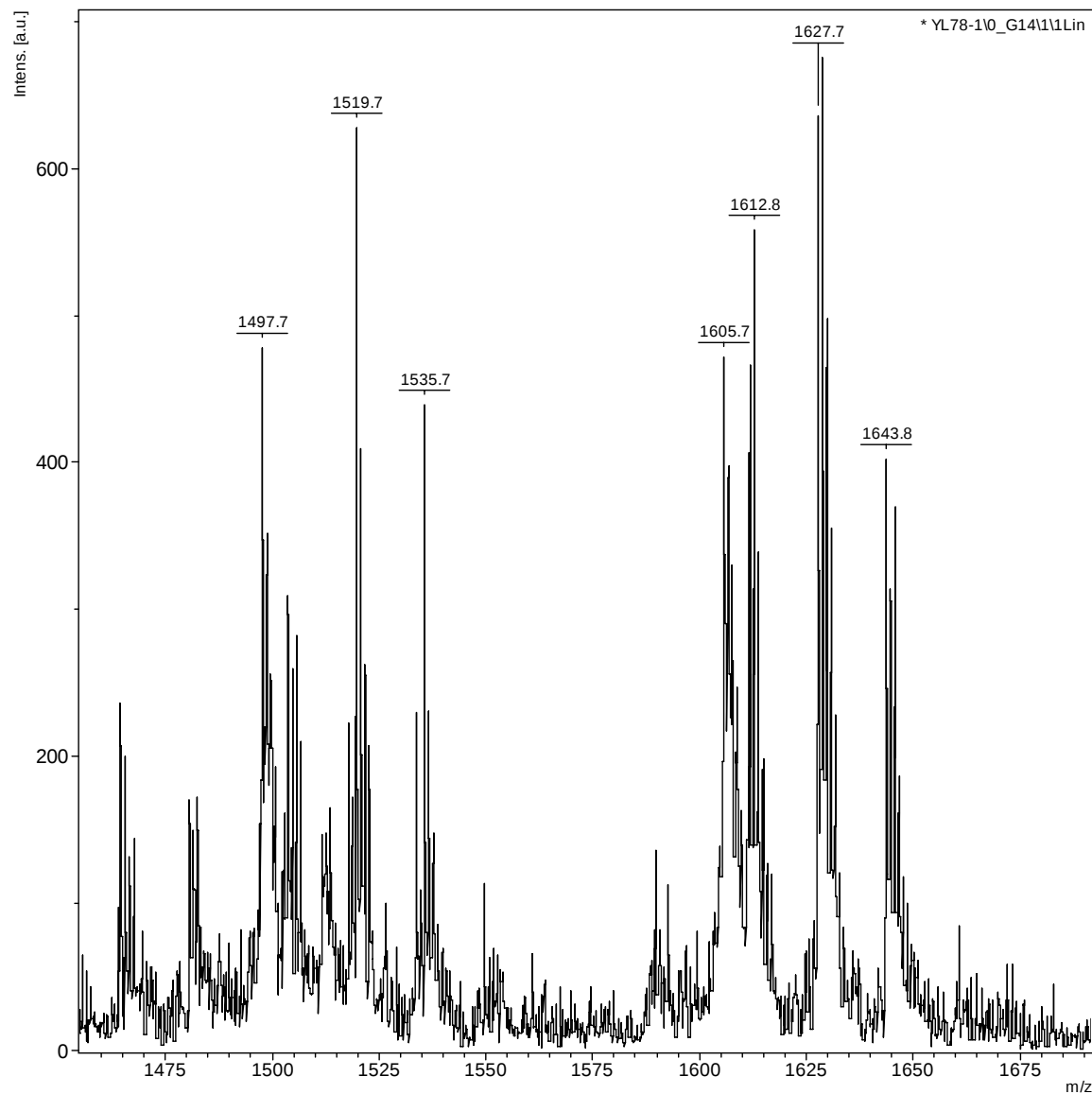
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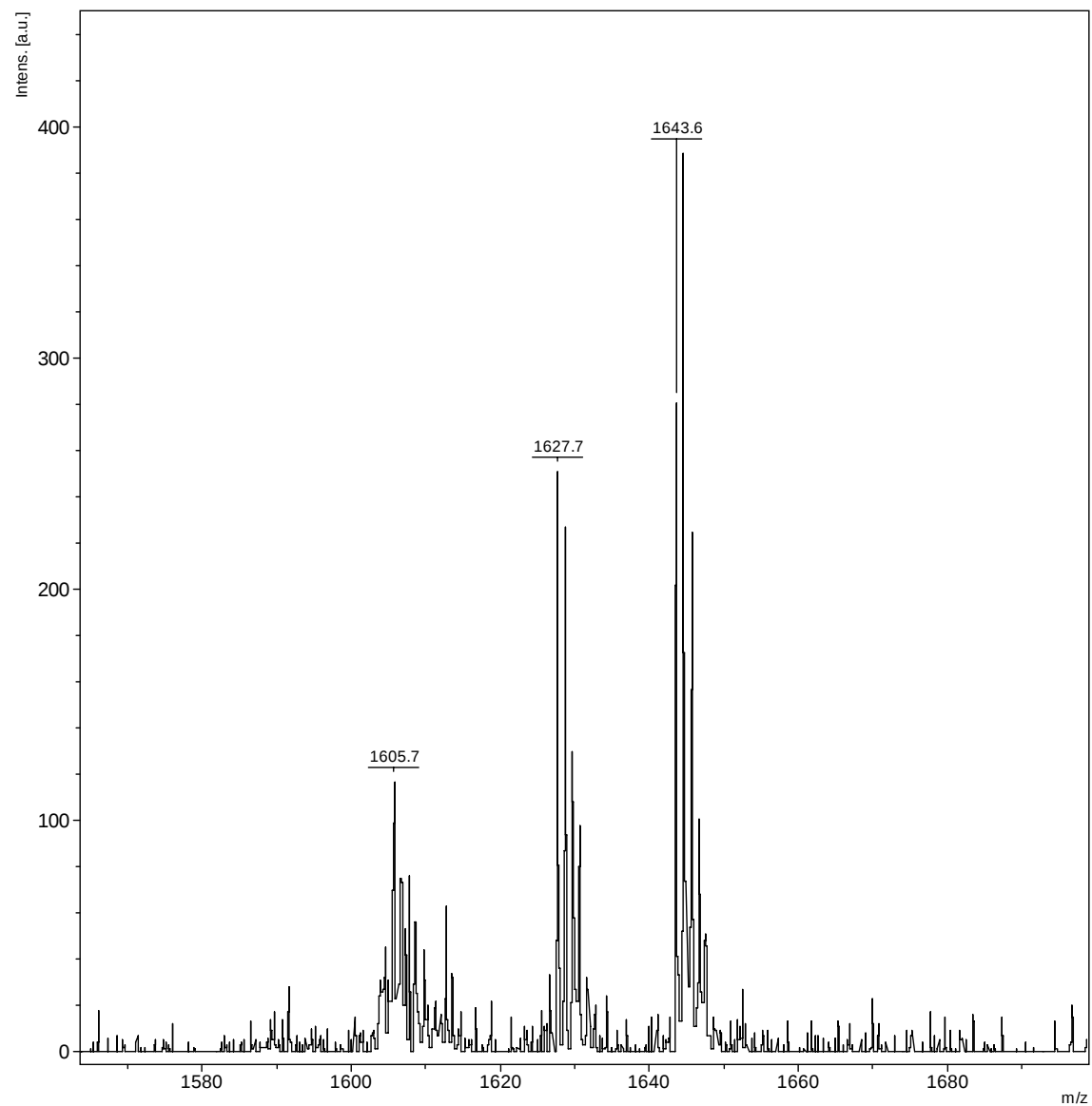
Mass spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis[(((3-nitrophenyl)carbonyl-hydrazidocarbonyl)-methoxy]-2,8,14,20-tetrathiacalix[4]arene (*cone-7a*)



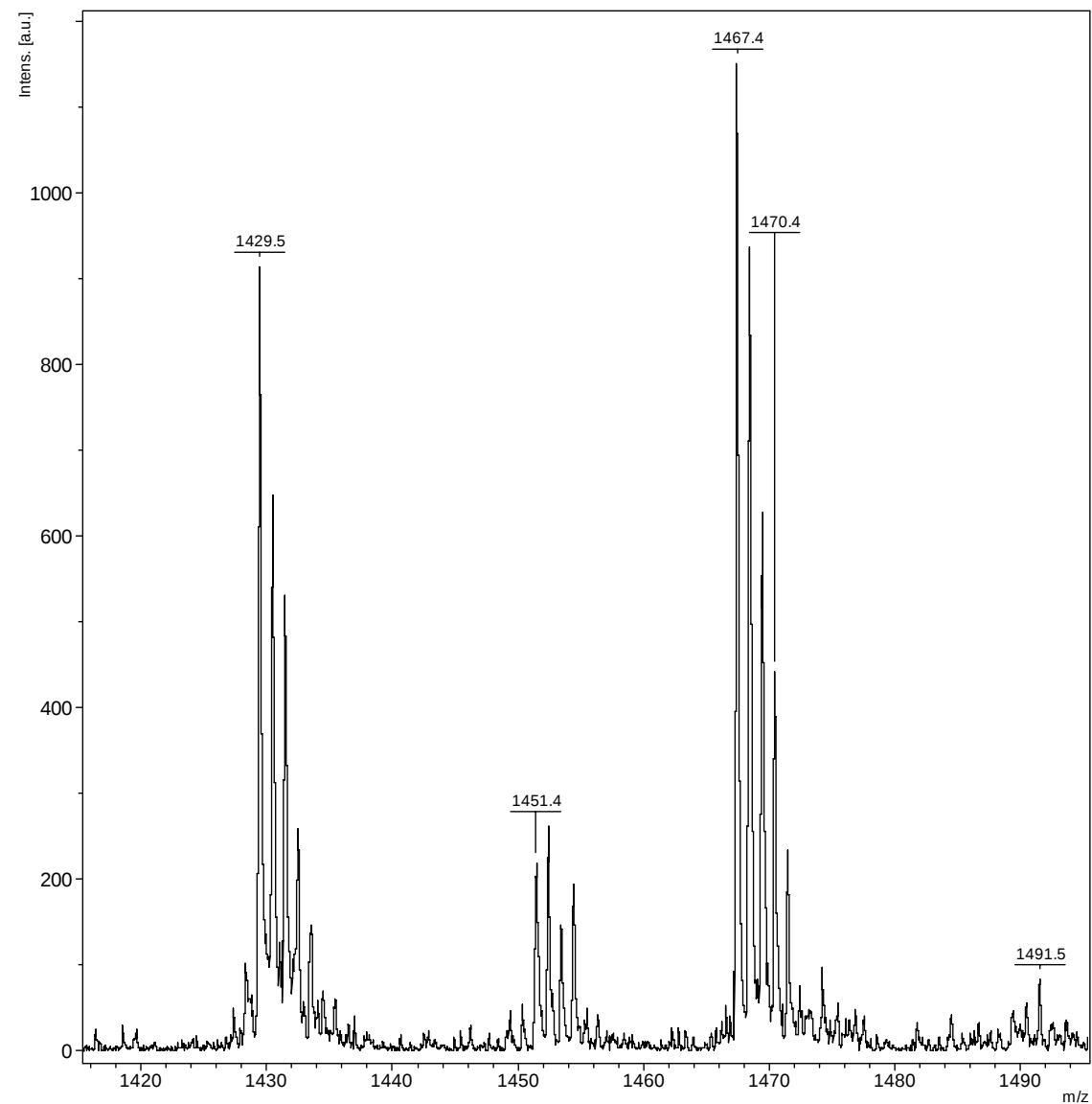
Mass spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis[(((3-nitrophenyl)carbonyl-hydrazidocarbonyl)-methoxy)-2,8,14,20-tetrathiacalix[4]arene (*partial cone*-7b)



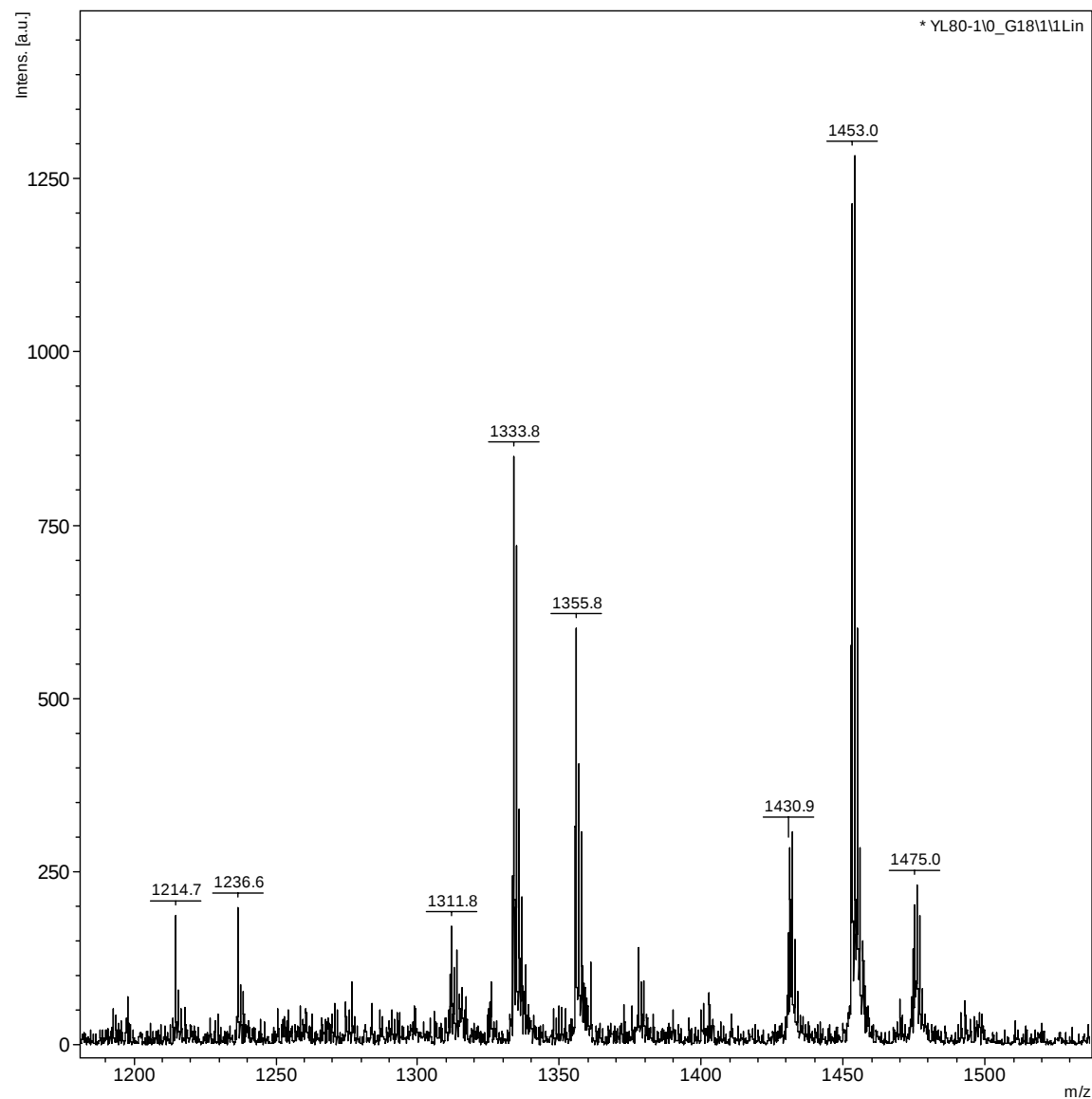
Mass spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis[(((3-nitrophenyl)carbonyl-hydrazidocarbonyl)-methoxy)-2,8,14,20-tetrathiacalix[4]arene (1,3-*alternate*-7c)



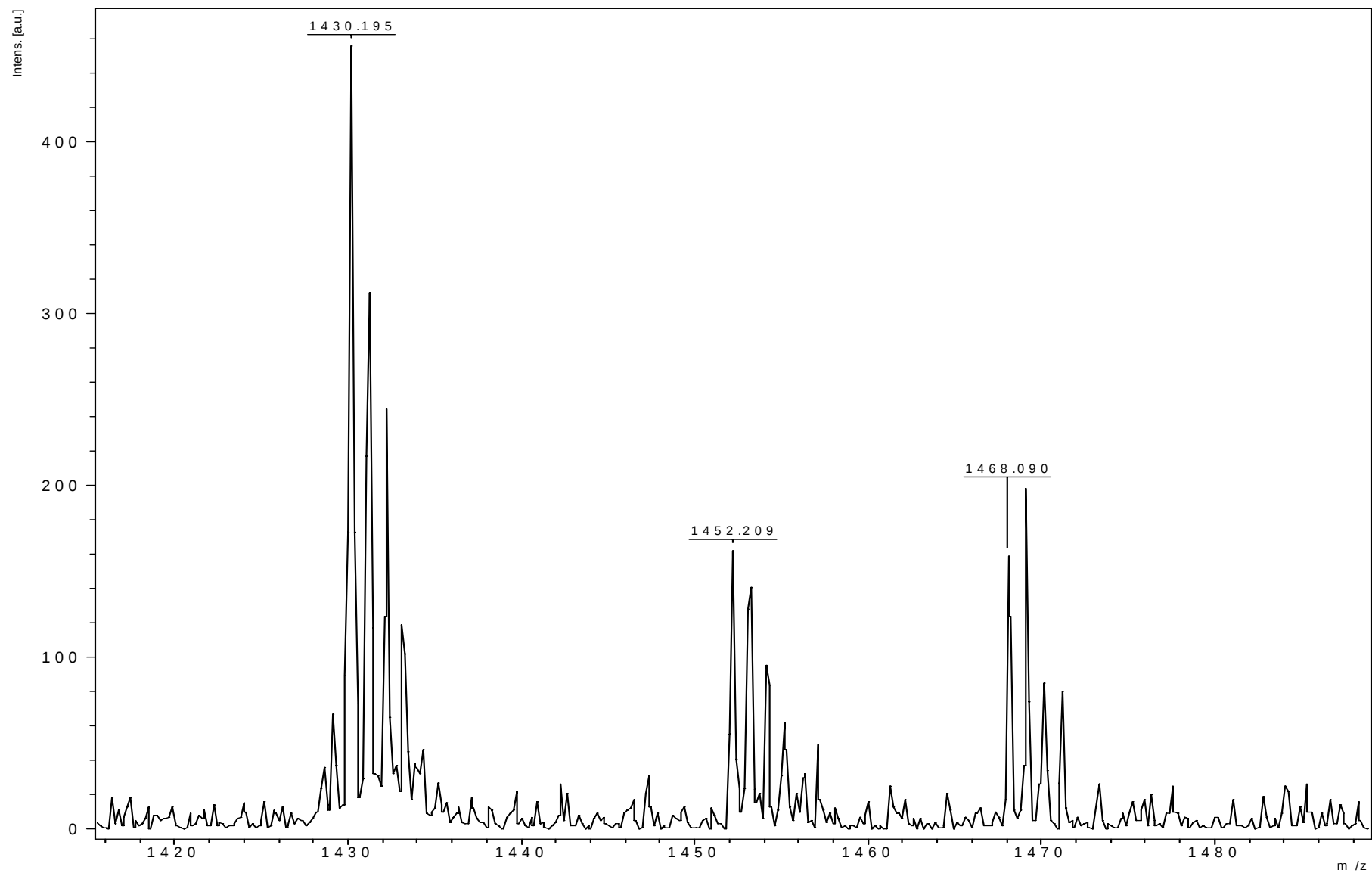
Mass spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(((3-pyridyl)carbonyl-hydrazidocarbonyl)-methoxy)-2,8,14,20-tetrathiacalix[4]arene (*cone-8a*)



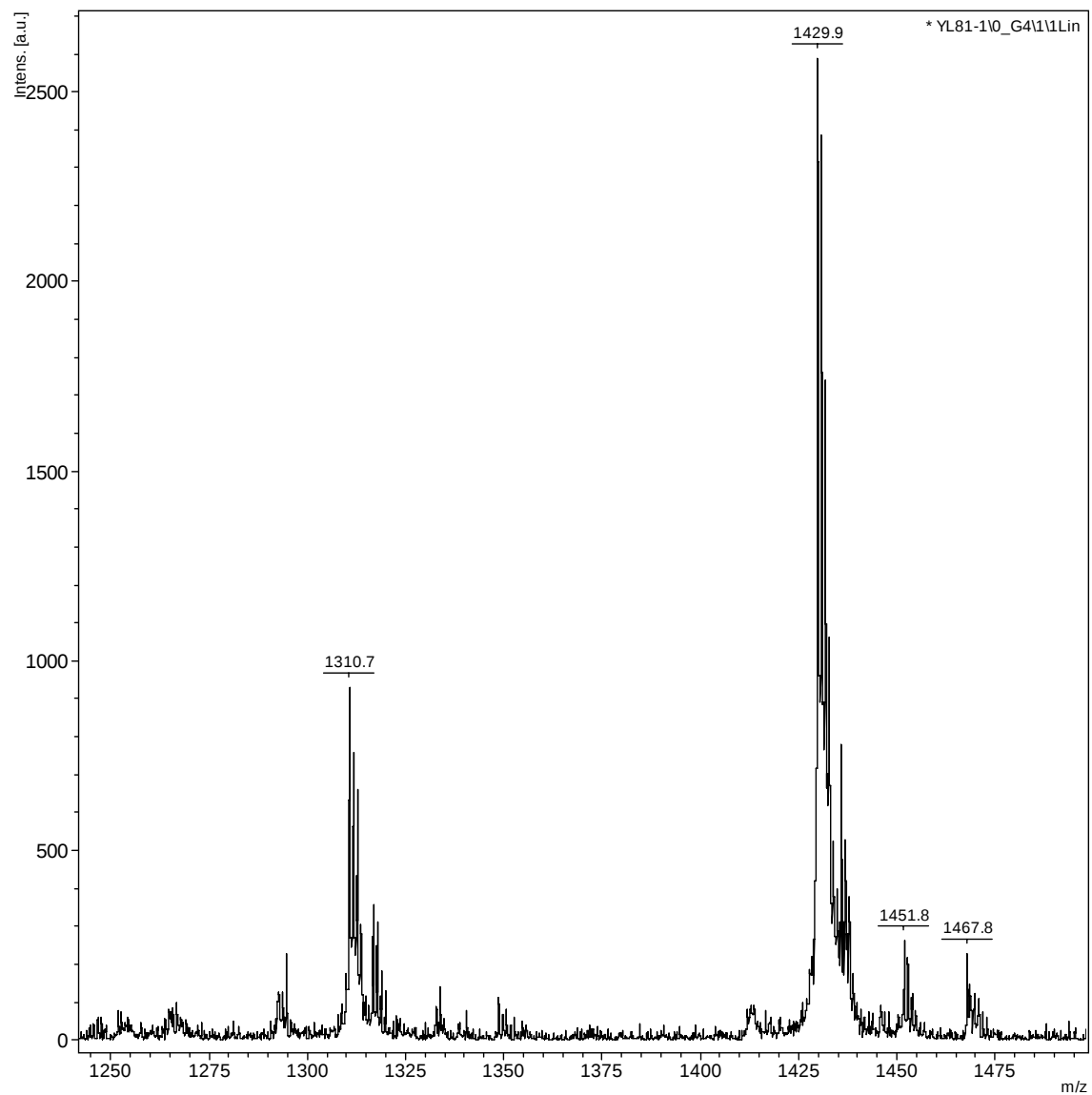
Mass spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(((3-pyridyl)carbonyl-hydrazidocarbonyl)-methoxy)-2,8,14,20-tetrathiacalix[4]arene (*partial cone-8b*)



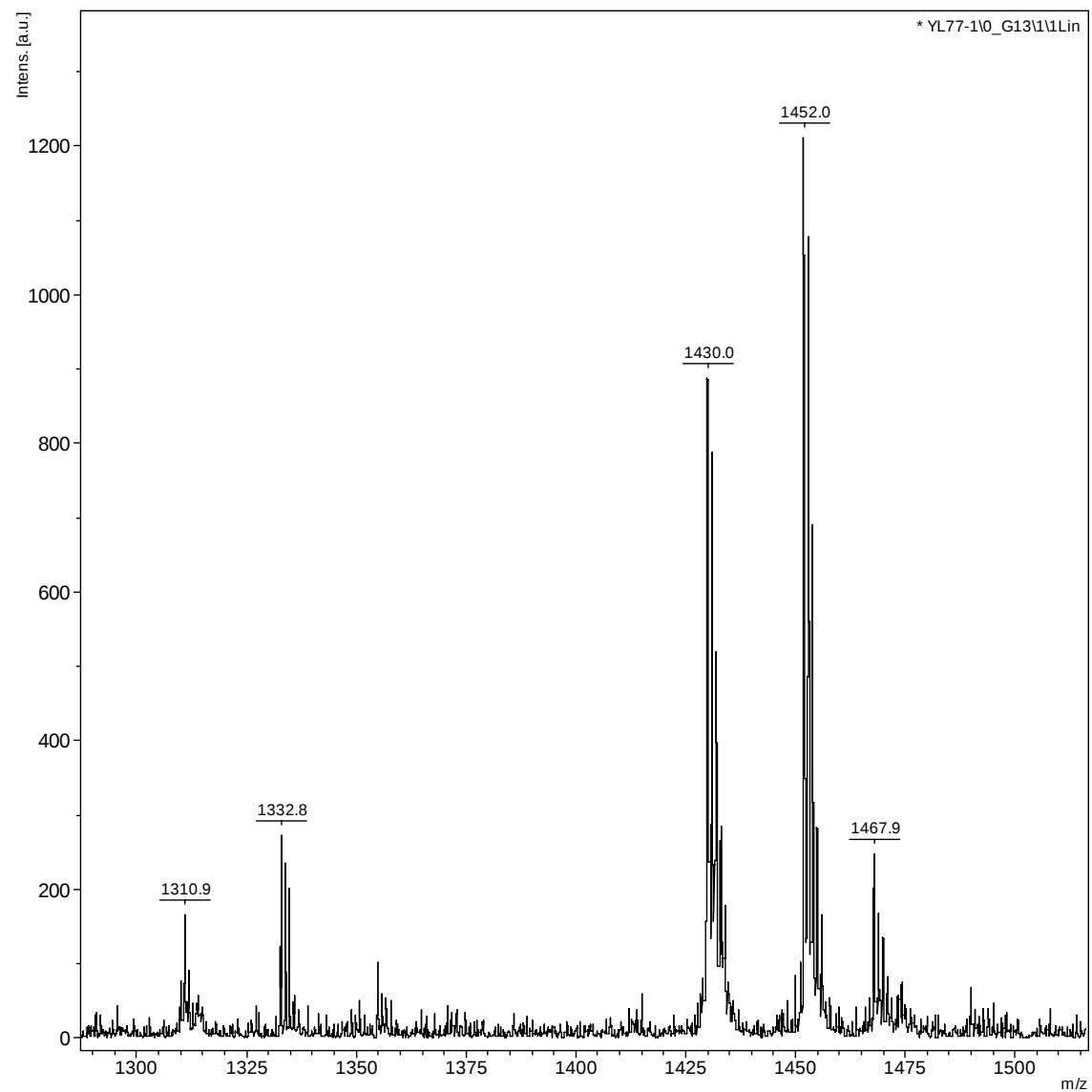
Mass spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(((3-pyridyl)carbonyl-hydrazidocarbonyl)-methoxy)-2,8,14,20-tetrathiacalix[4]arene (1,3-*alternate*-8c)



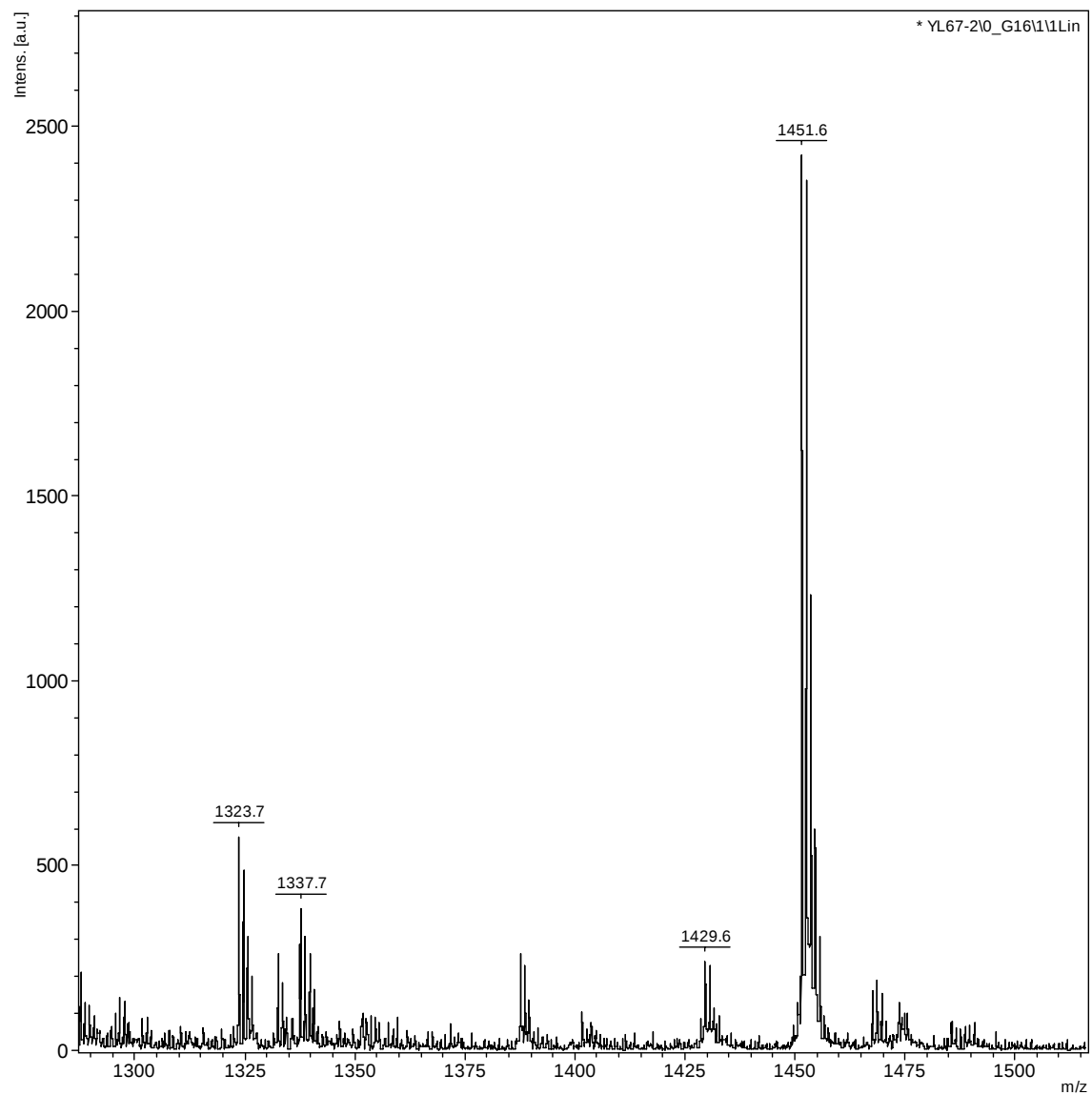
Mass spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis[[(4-pyridyl)carbonyl-hydrazidocarbonyl]-methoxy]-2,8,14,20-tetrathiacalix[4]arene (*cone*-9a)



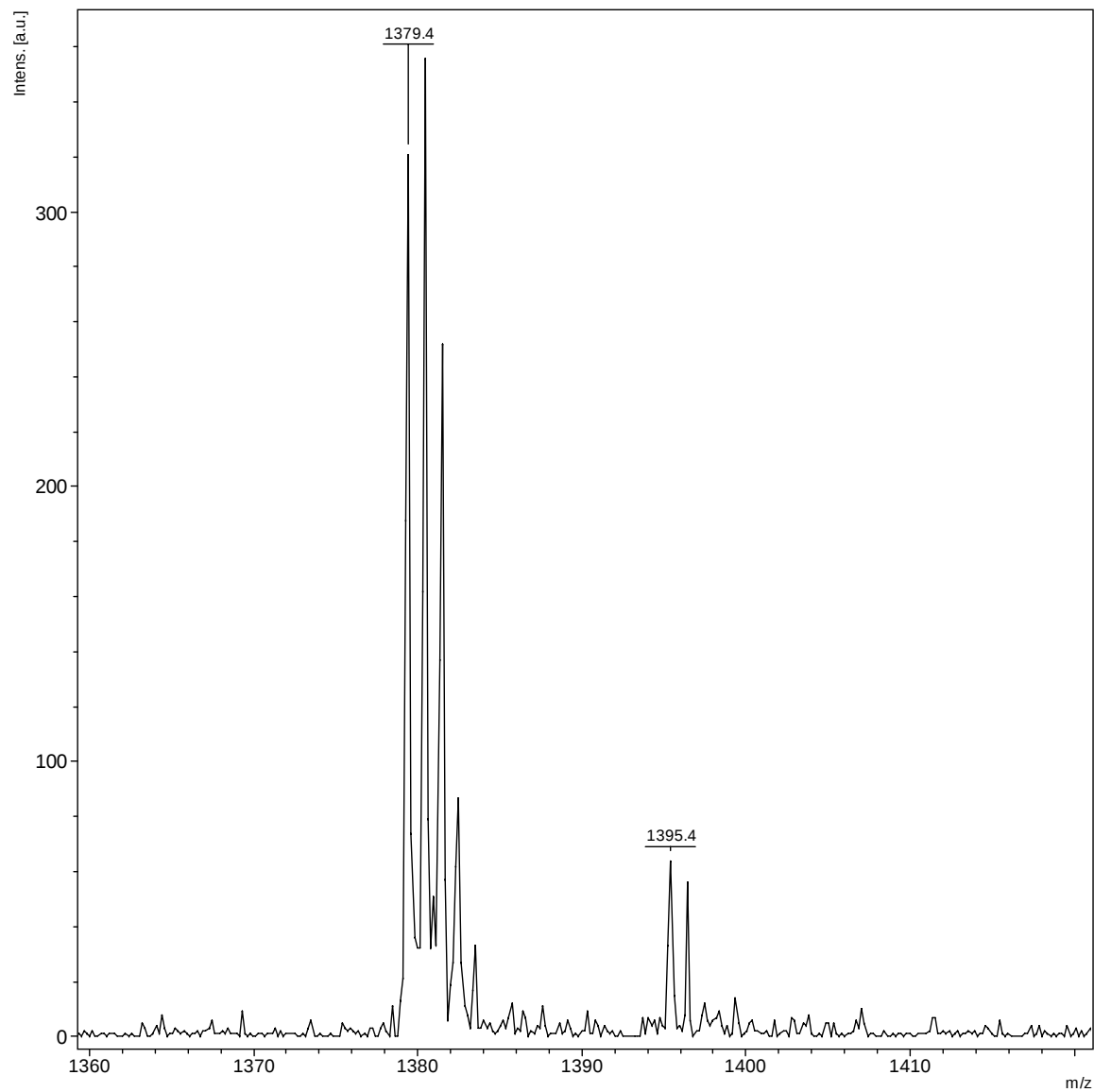
Mass spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(((4-pyridyl)carbonyl-hydrazidocarbonyl)-methoxy)-2,8,14,20-tetrathiacalix[4]arene (*partial cone*-9b)



Mass spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(((4-pyridyl)carbonyl-hydrazidocarbonyl)-methoxy)-2,8,14,20-tetrathiacalix[4]arene (1,3-*alternate*-9c)



Mass spectrum of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis[(1-carbonylbenzotrianol)-methoxy]-2,8,14,20-tetrathiacalix[4]arene (*cone*-10a)



Mass spectrum of ,11,17,23-t etra-*tert*-butyl-25,26,27,28-tetrakis[(1-carbonylbenzotrianol)-methoxy]-2,8,14,20-tetrathiacalix[4]arene (1,3-*alternate*-10c)

