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„BioTechNan - the programme of interdisciplinary cross-institutional post gradual studies KNOW in the field of Biotechnology and Nanotechnology"

DESIGN, SYNTHESIS, AND BIOLOGICAL INVESTIGATION OF NEW PEPTIDES AND PEPTIDOMIMETICS OF COSMECEUTICAL INTEREST

Supplementary Information

DOCTORAL DISSERTATION

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Thesis in cotutelle prepared in the framework of the collaboration between Wroclaw University of Science and Technology and University of Florence (XXXV Ciclo)

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF DISCUSSED COMPOUNDS*

A	–	4-Methylpiperidine
B	–	Pyrrolidine
C	–	Morpholine
D	–	*N*-Ethylisopropylamine
1	–	Potassium cyanohydroxyamate
2	–	*N*-hydroxy-3-(hydroxyamino)-3-iminopropanamide
3	–	4,6-dimethylisoxazolo[3,4-*b*]pyridin-3(1*H*)-one
4	–	8-carboxy-4',5,7-trimethyl-3H-2λ^5-spiro[[1,2,4]triazolo[4,3-a]pyridine-2,1'-piperidin]-2-ylium (derivative with **A**)
4a	–	Fmoc-Lys[**N$^\varepsilon$(4)**]-OH
5	–	8-carboxy-5,7-dimethyl-3*H*-2λ^5-spiro[[1,2,4]triazolo[4,3-*a*]pyridine-2,1'-pyrrolidin]-2-ylium (derivative with **B**)
5a	–	Fmoc-Lys[**N$^\varepsilon$(5)**]-OH
6	–	8-carboxy-5,7-dimethyl-3*H*-2λ^5-spiro[[1,2,4]triazolo[4,3-a]pyridine-2,4'-morpholin]-2-ylium (derivative with **C**)
6a	–	Fmoc-Lys[**N$^\varepsilon$(6)**]-OH
7	–	8-carboxy-2-ethyl-5,7-dimethyl-2-(propan-2-yl)-2*H*,3*H*-[1,2,4]triazolo[4,3-*a*]pyridin-2-ium (derivative with **D**)
7a	–	Fmoc-Lys[**N$^\varepsilon$(7)**]-OH
8	–	Ac-MGKVV-NH_2
9	–	Ac-PGKVV-NH_2
10	–	**3**-PGKVV-NH_2
11	–	**4**-MGKVV-NH_2
12	–	**5**-MGKVV-NH_2
13	–	**6**-MGKVV-NH_2
14	–	**7**-MGKVV-NH_2
15	–	**4**-PGKVV-NH_2
16	–	**5**-PGKVV-NH_2
17	–	**6**-PGKVV-NH_2
18	–	**7**-PGKVV-NH_2
19	–	Ac-MGK[**N$^\varepsilon$(4)**]VV-NH_2
20	–	Ac-MGK[**N$^\varepsilon$(5)**]VV-NH_2
21	–	Ac-MGK[**N$^\varepsilon$(6)**]VV-NH_2
22	–	Ac-MGK[**N$^\varepsilon$(7)**]VV-NH_2
23	–	Ac-PGK[**N$^\varepsilon$(4)**]VV-NH_2
24	–	Ac-PGK[**N$^\varepsilon$(5)**]VV-NH_2
25	–	Ac-PGK[**N$^\varepsilon$(6)**]VV-NH_2
26	–	Ac-PGK[**N$^\varepsilon$(7)**]VV-NH_2
27-42	–	16 derivatives of (2*E*)-2-[1-(4-bromophenyl)ethylidene]hydrazine-1-carbothioamide
43	–	4-[(*E*)-(2-carbamothioylhydrazinylidene)methyl]benzoic acid
44	–	2-{3-[(*E*)-(2-carbamothioylhydrazinylidene)(phenyl)methyl]phenyl}propanoic acid
45	–	4-[(1*E*)-1-(2-carbamothioylhydrazinylidene)ethyl]benzoic acid
46	–	Ac-FFY-OH
47	–	Ac-FYY-OH
48	–	Ac-FWY-OH
49	–	TSC**43**-FFY-OH
50	–	TSC**43**-FYY-OH
51	–	TSC**43**-FWY-OH
52	–	TSC**44**-FFY-OH
53	–	TSC**44**-FYY-OH
54	–	TSC**44**-FWY-OH
55	–	TSC**45**-FFY-OH
56	–	TSC**45**-FYY-OH
57	–	TSC**45**-FWY-OH

Compounds marked with gray background were purchased (A-D**) or provided (**27-45**).*
Other compounds were synthesized and purified by the Author for the purpose of this thesis.

Chapter 1: High Performance Liquid Chromatography (HPLC) and Mass Spectrometry (MS) – LC-MS

1.1 Analyses of compounds 4a-7a, 8-26

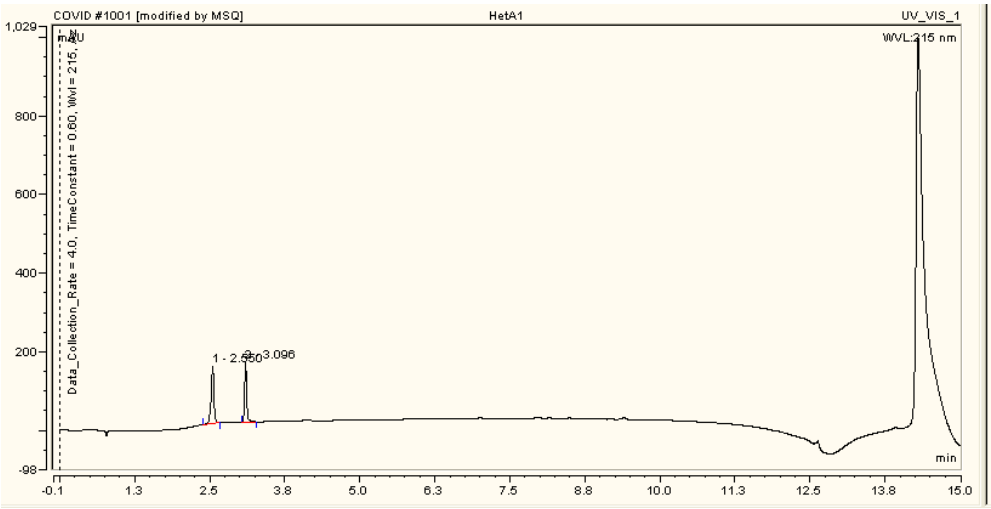


Figure SI 1. Chromatogram of **4** (crude product).

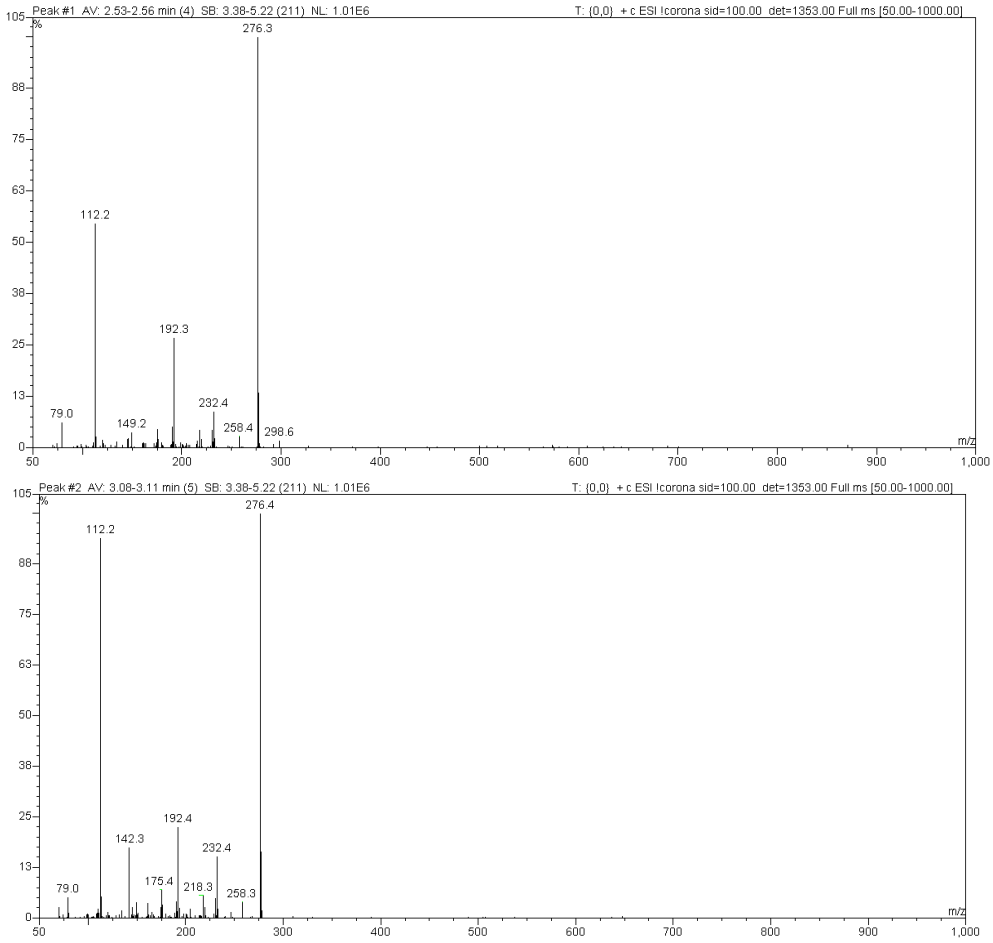


Figure SI 2. MS spectra of **4** of two visible peaks: 2.53-2.56 and 3.08-3.11 min (crude product).

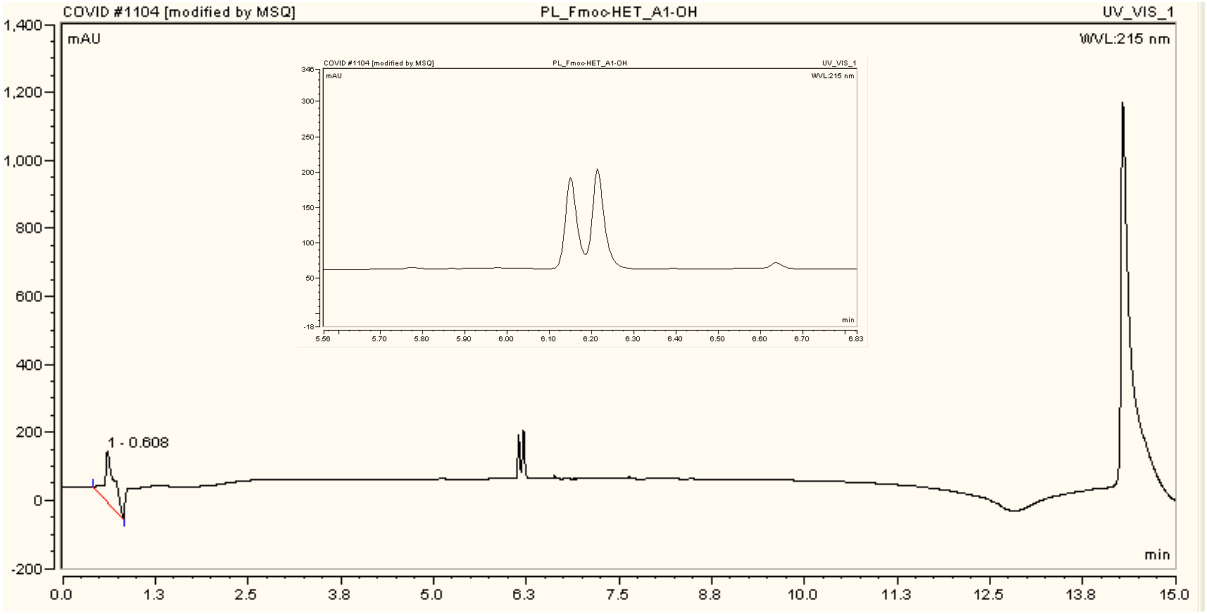


Figure SI 3. Chromatogram of **4a** with zoomed 6.10-6.30 retention time (crude product).

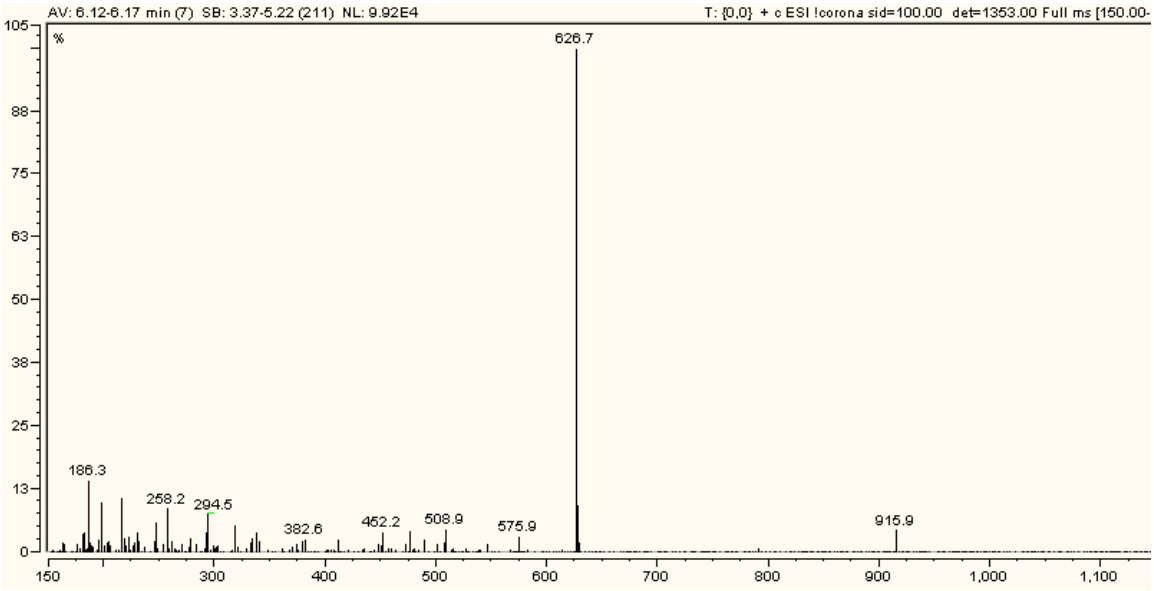


Figure SI 4. MS spectra of **4a** of the peak 6.12-6.17 min (crude product).

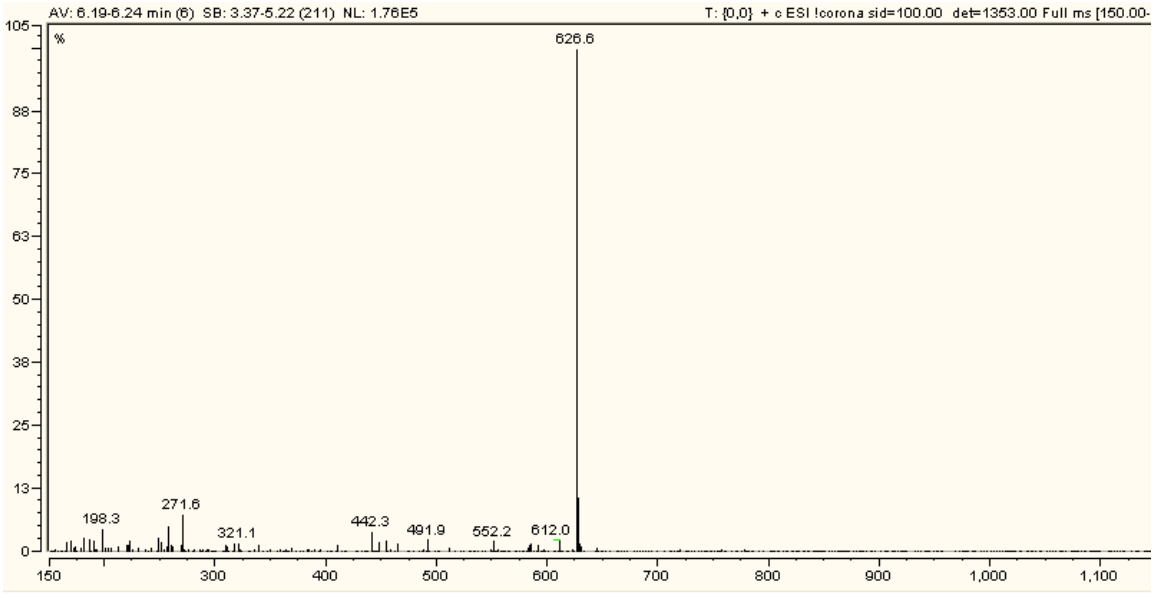


Figure SI 5. MS spectra of **4a** of the peak 6.19-6.24 min (crude product).

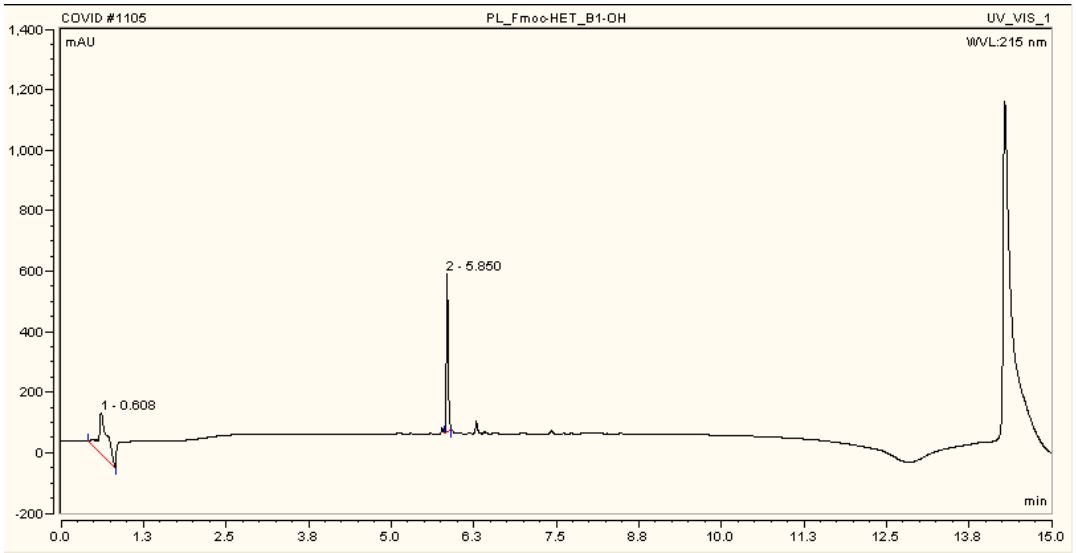


Figure SI 6. Chromatogram of **5a** (crude product).

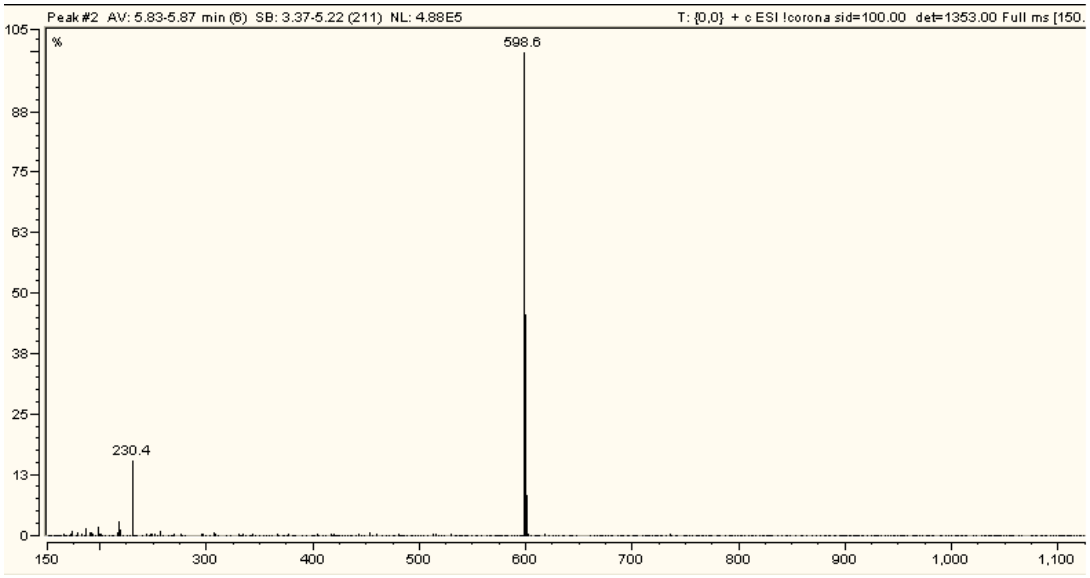


Figure SI 7. MS spectra of **5a** of the peak 5.83-5.87 min (crude product).

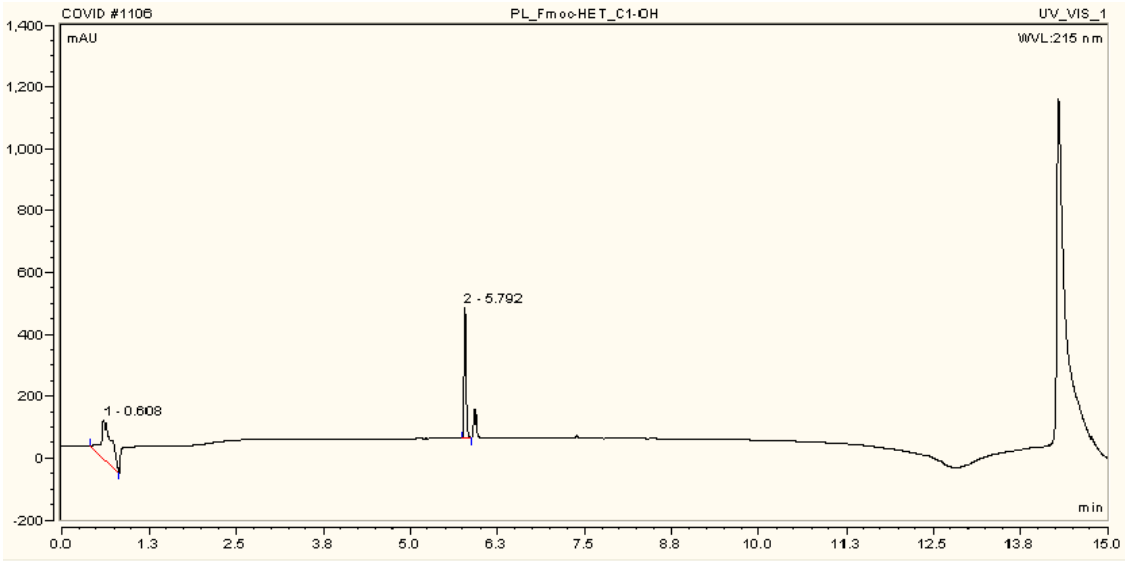


Figure SI 8. Chromatogram of **6a** (crude product).

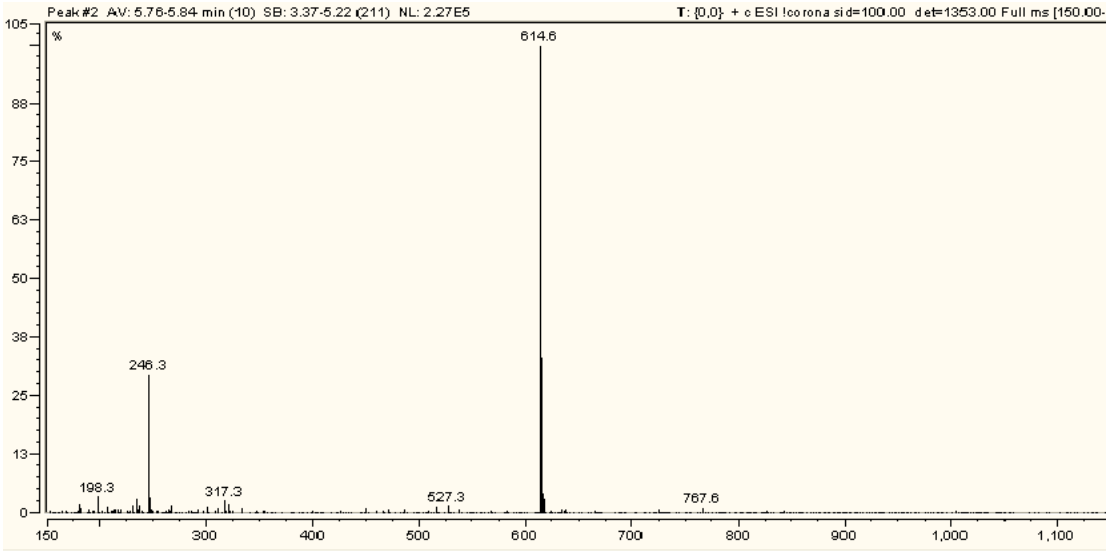


Figure SI 9. MS spectra of **6a** the peak 5.76-5.84 min (crude product).

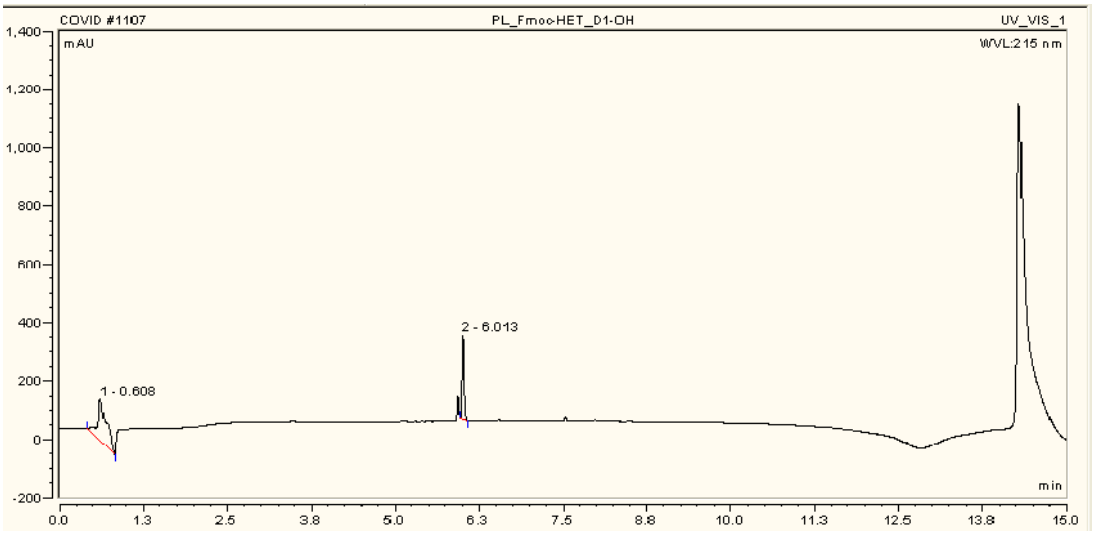


Figure SI 10. Chromatogram of **7a** (crude product).

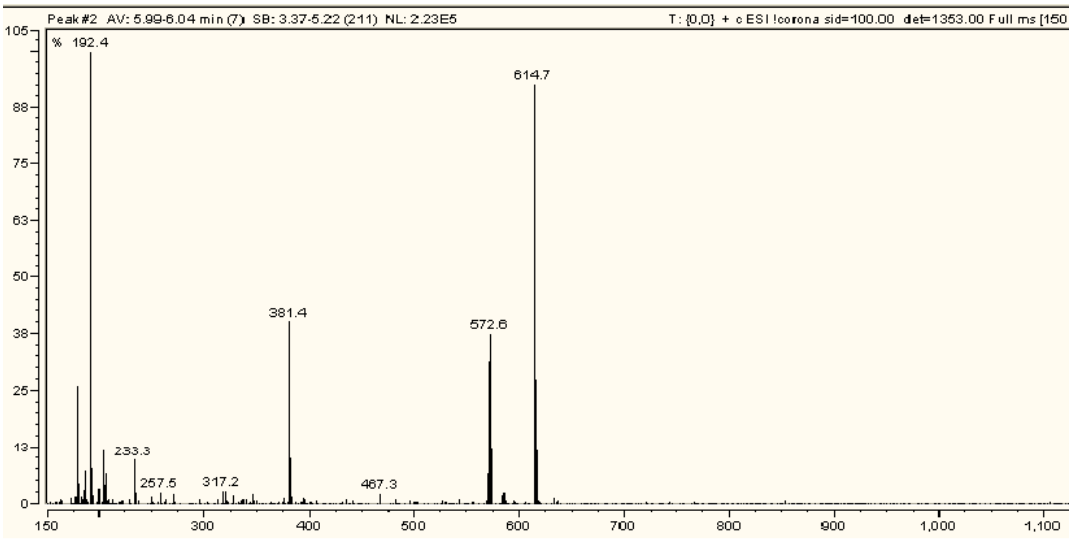


Figure SI 11. MS spectra of **7a** of the peak 5.99-6.04 min (crude product).

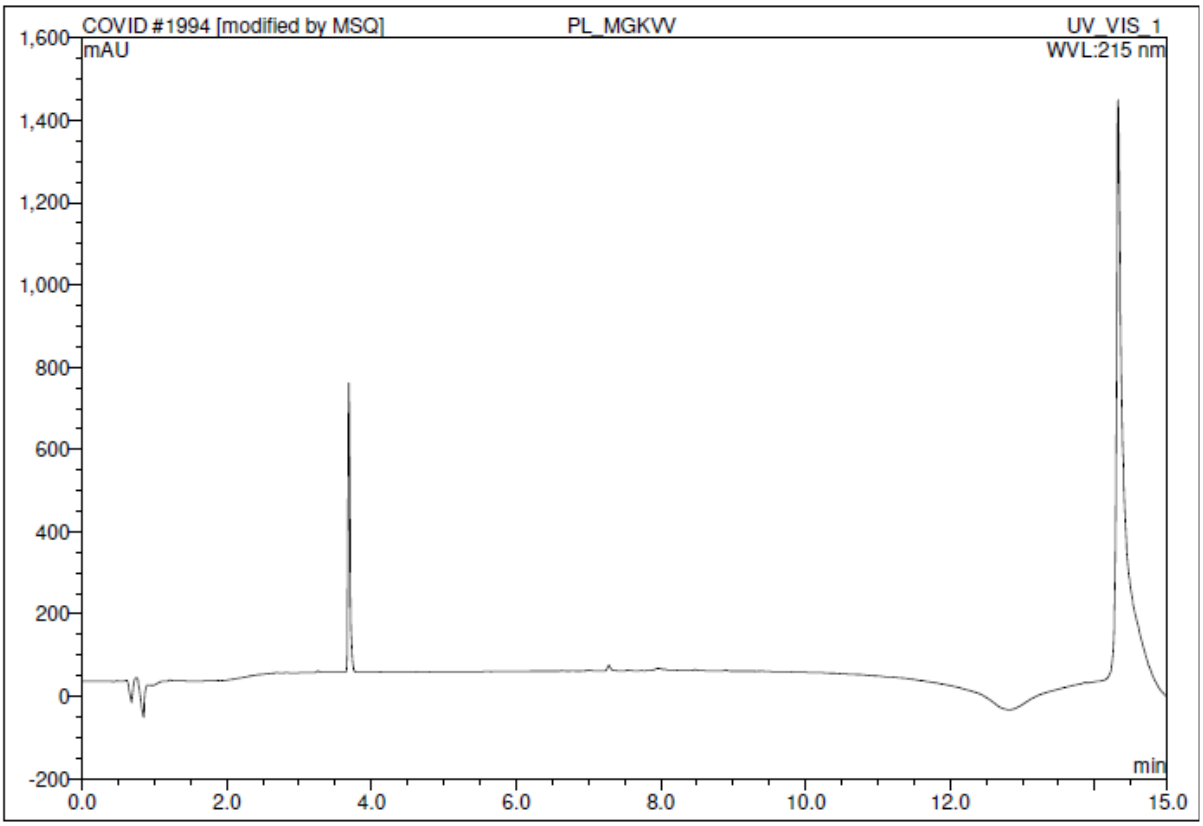


Figure SI 12. Chromatogram of **8** (pure product).

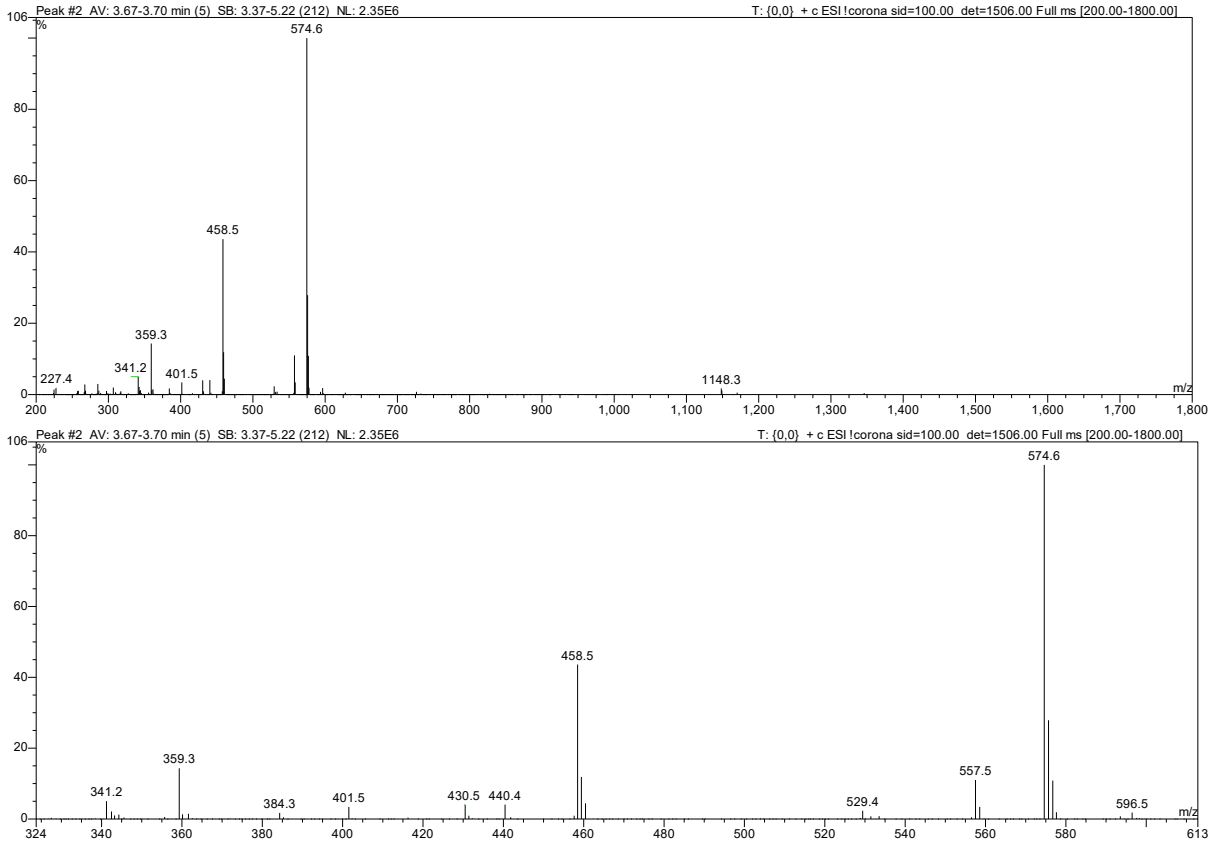


Figure SI 13. MS spectra of **8** of the peak 3.67-3.70 min (pure product). Zoom on the range 324-613 *m/z* was shown additionally.

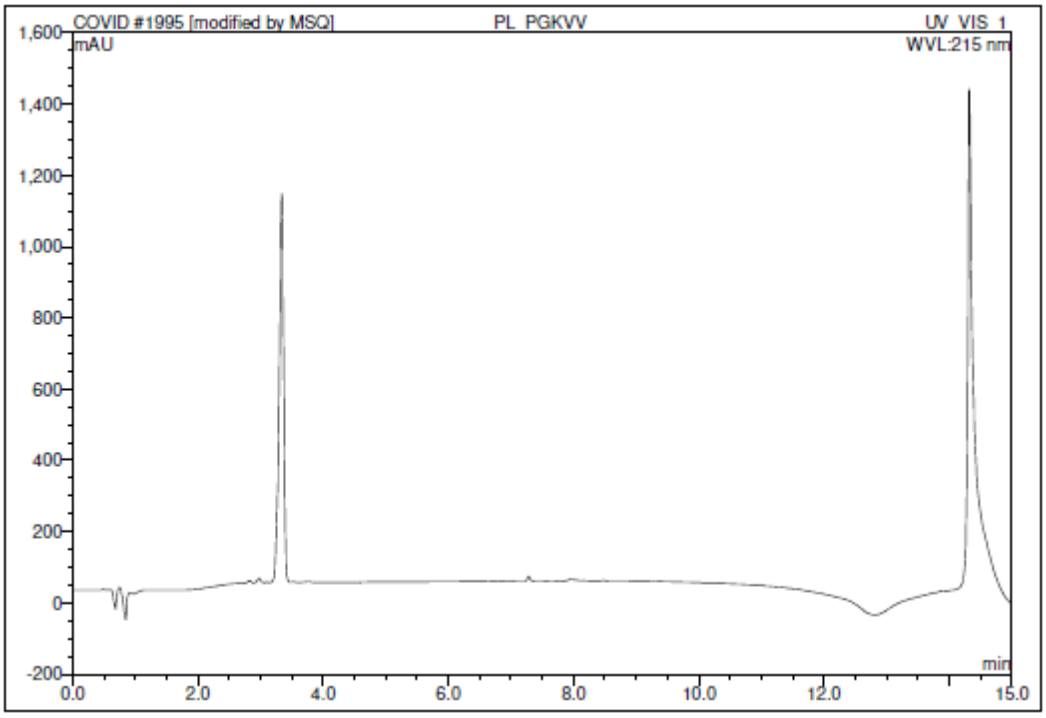


Figure SI 14. Chromatogram of **9** (pure product).

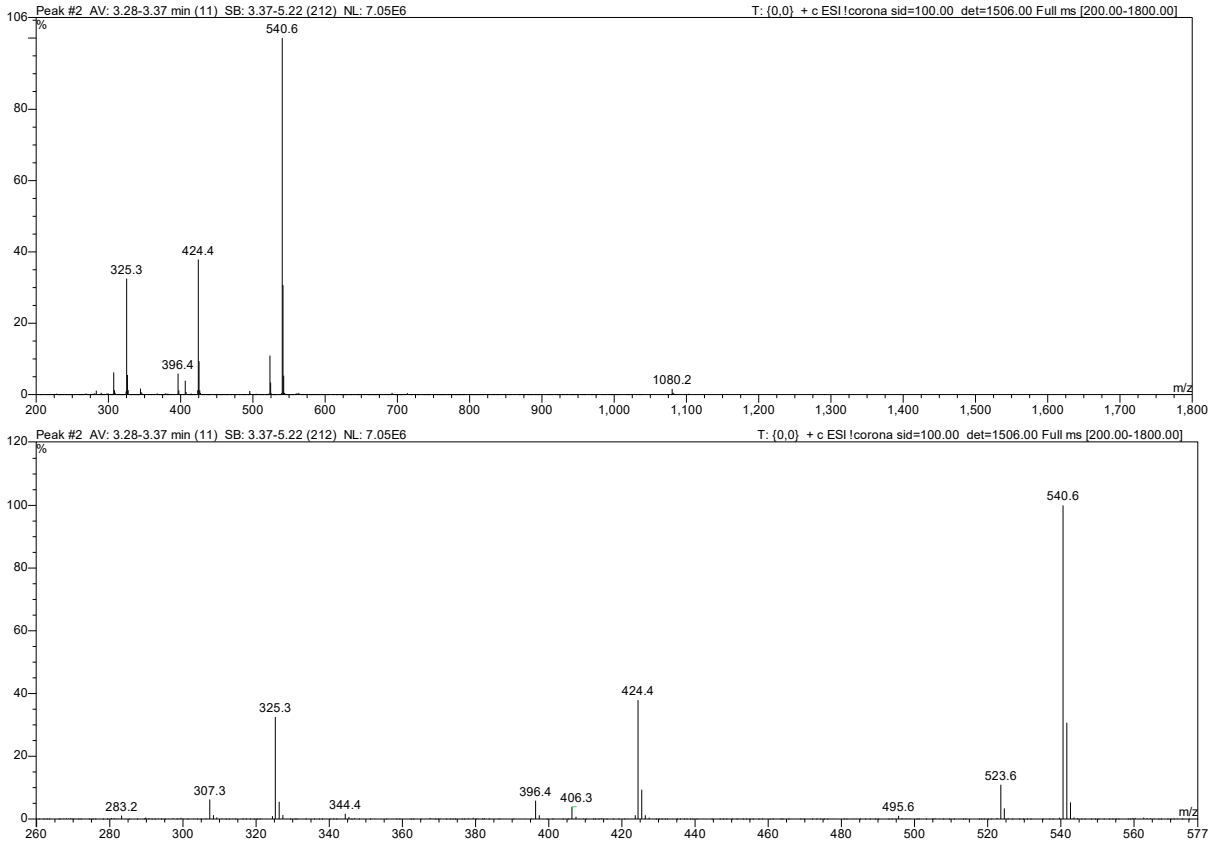


Figure SI 15. MS spectra of **9** of the peak 3.28-3.37 min (pure product). Zoom on the range 260-577 *m/z* was shown additionally.

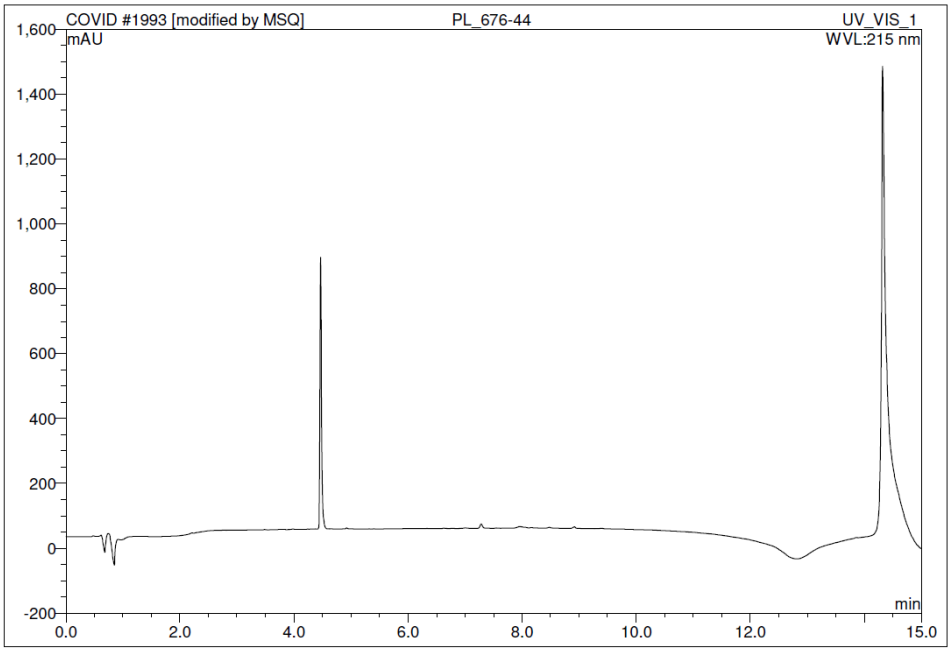


Figure SI 16. Chromatogram of **10** (pure product).

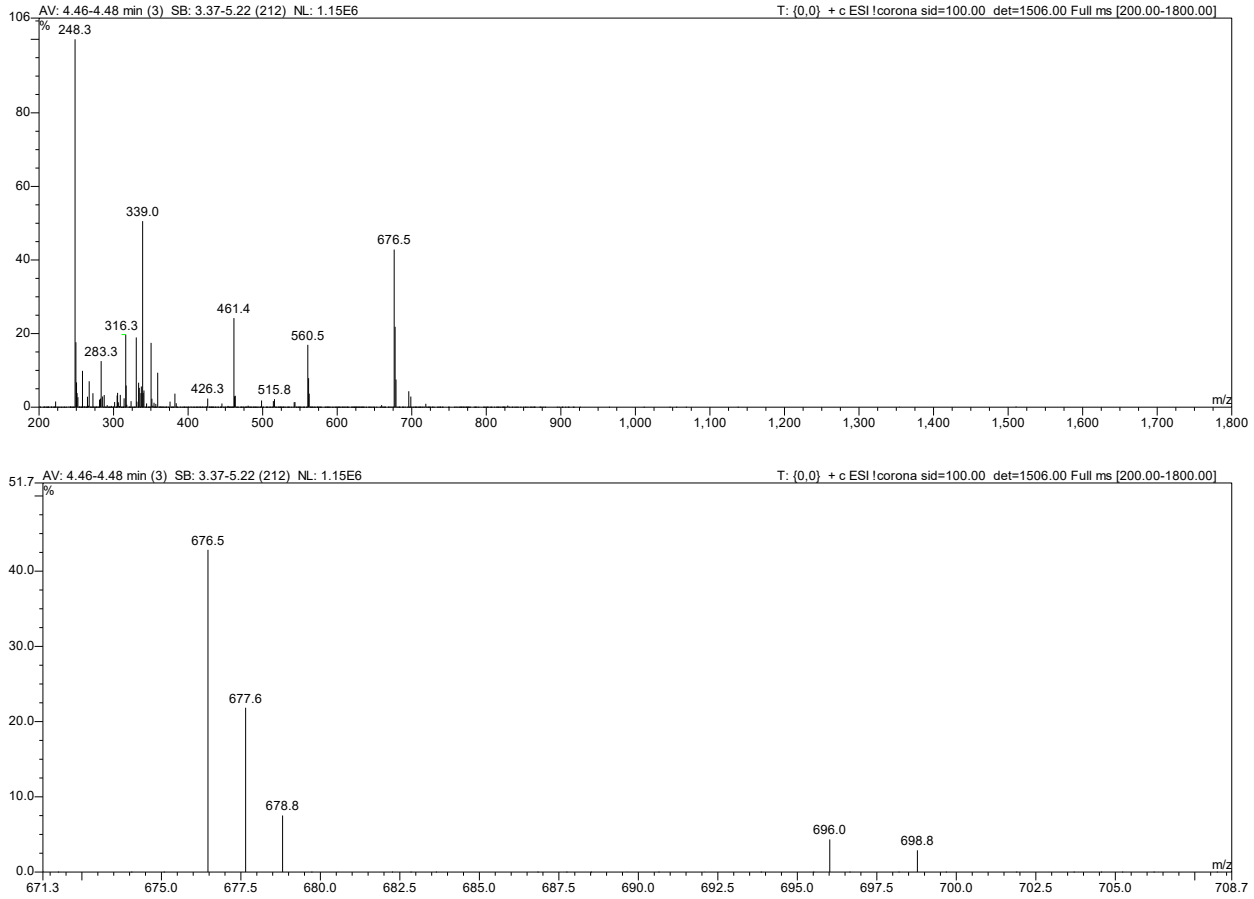


Figure SI 17. MS spectra of **10** of the peak 4.45 min (pure product). Zoom on the range 671-709 *m/z* was shown additionally.

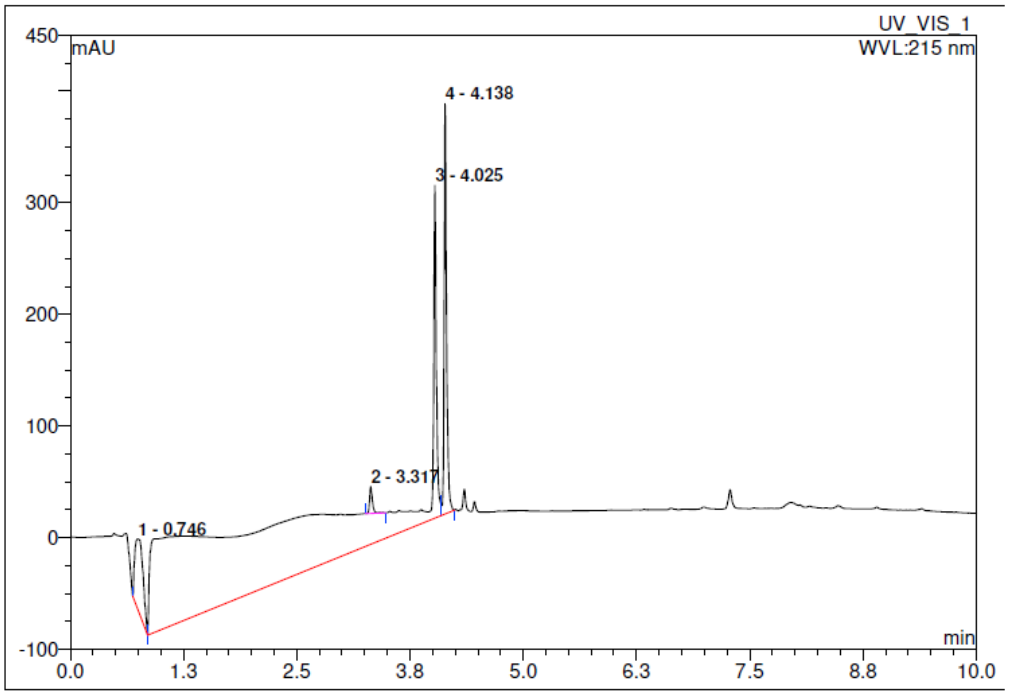


Figure SI 18. Chromatogram of **11** (pure product).

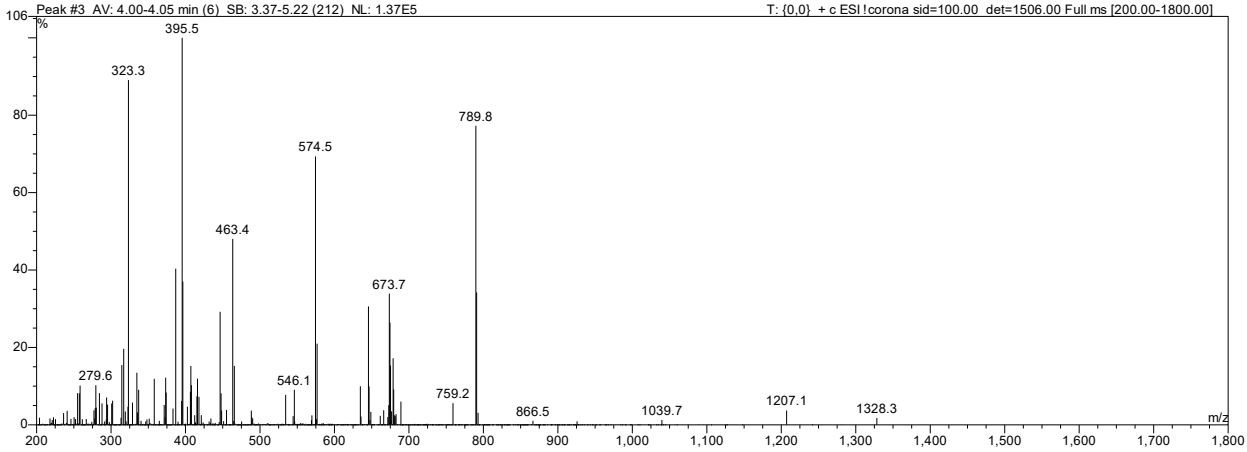


Figure SI 19. MS spectra of **11** of the peak 4.03 min (pure product).

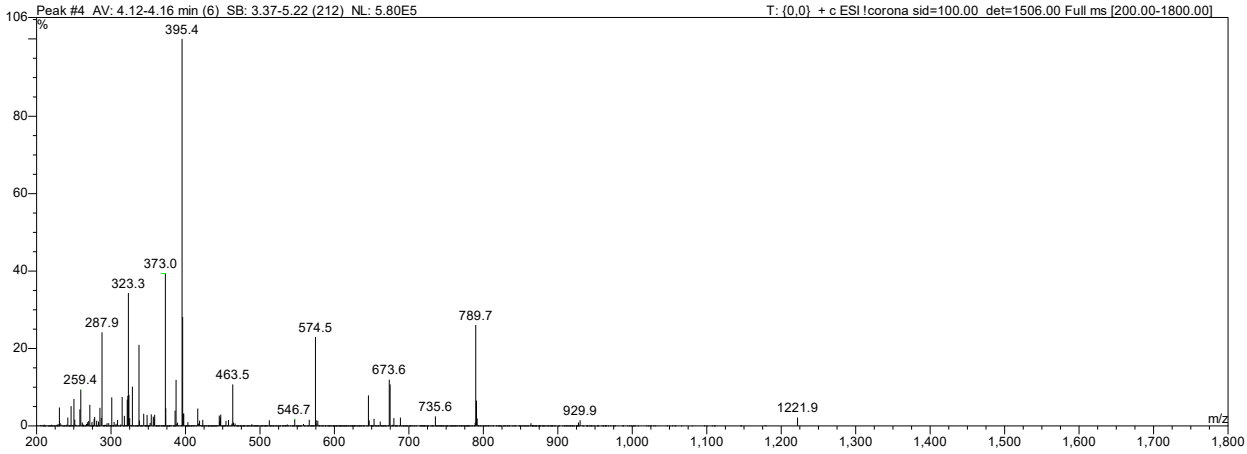


Figure SI 20. MS spectra of **11** of the peak 4.17 min (pure product).

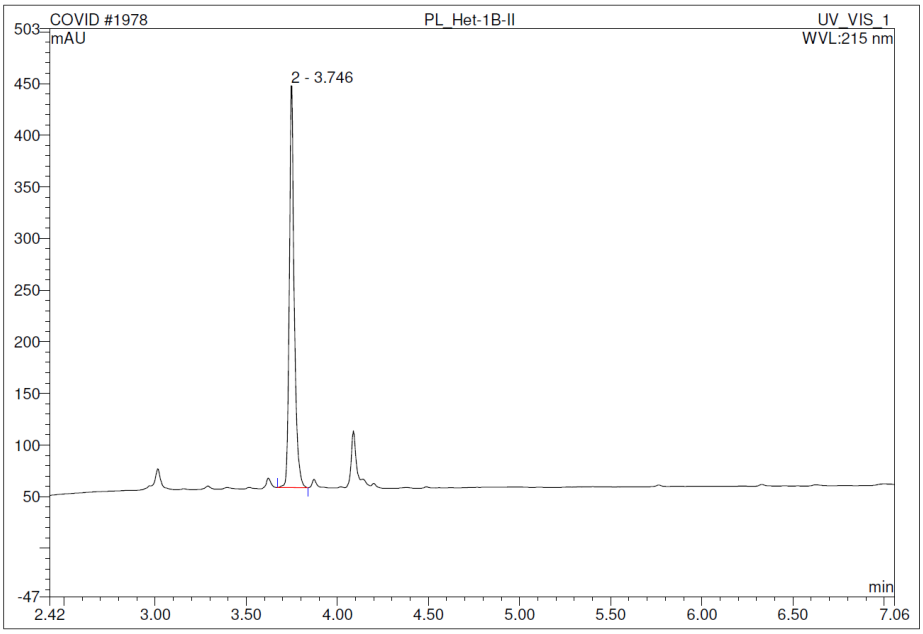


Figure SI 21. Chromatogram of **12** (pure product).

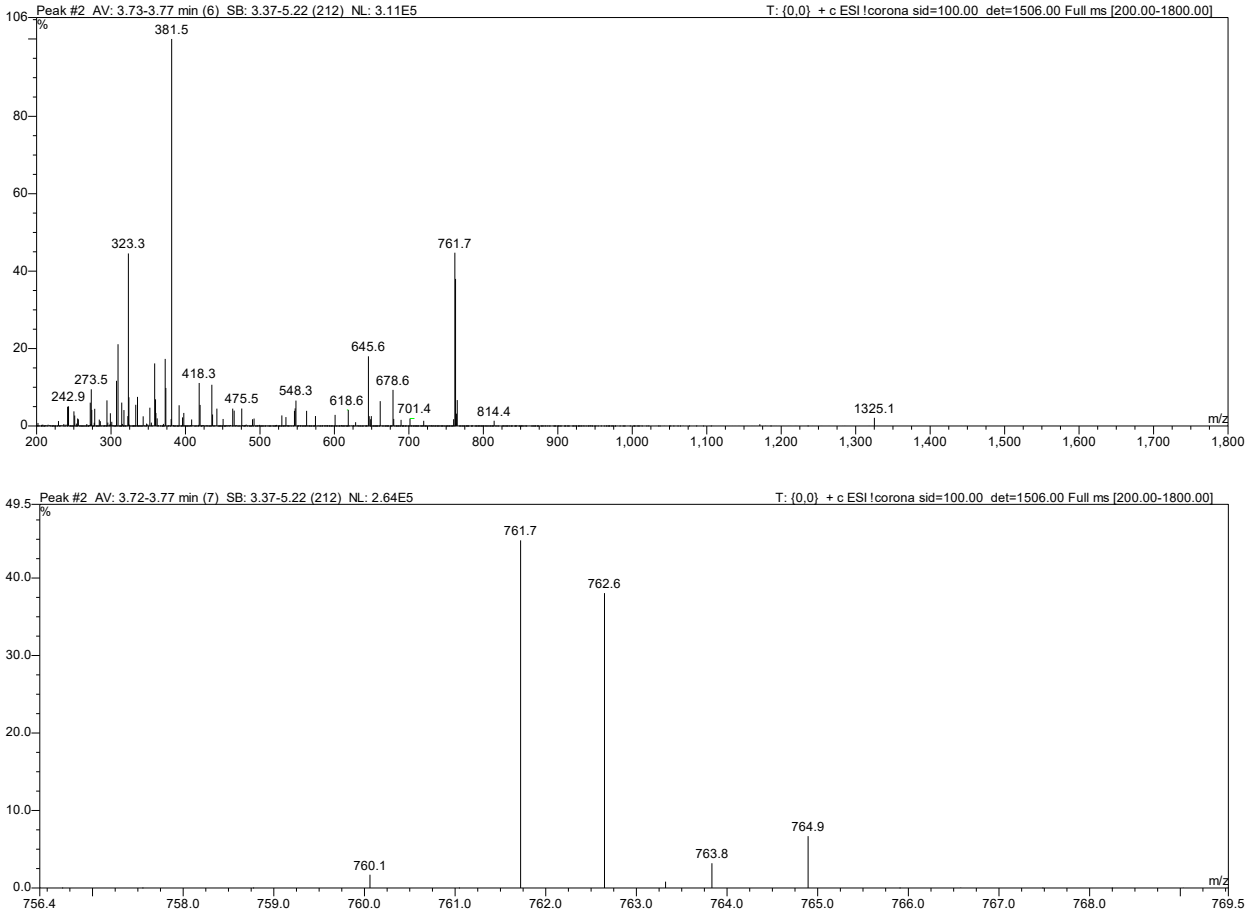


Figure SI 22. MS spectra of **12** of the peak 3.74 min (pure product). Zoom on the range 756-770 *m/z* was shown additionally.

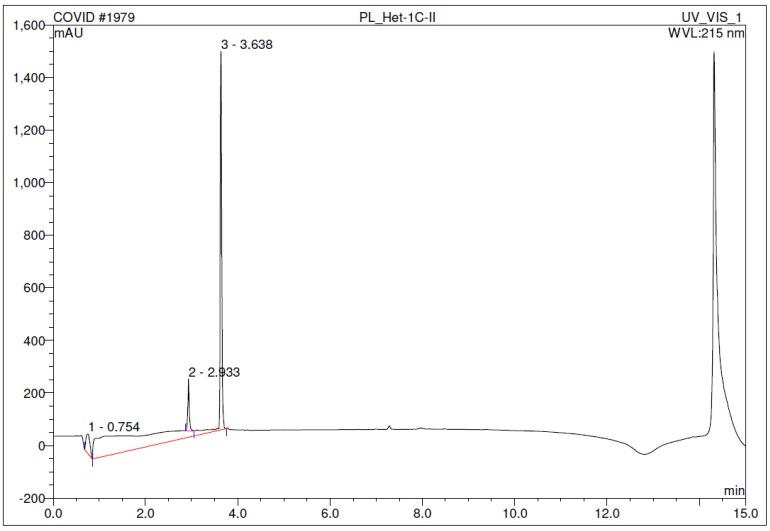


Figure SI 23. Chromatogram of **13** (pure product).

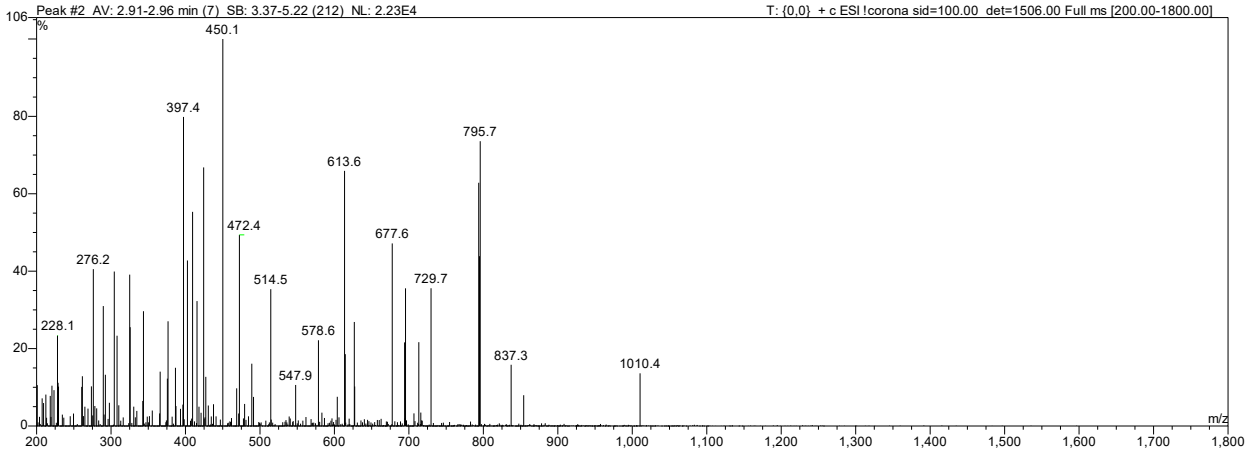
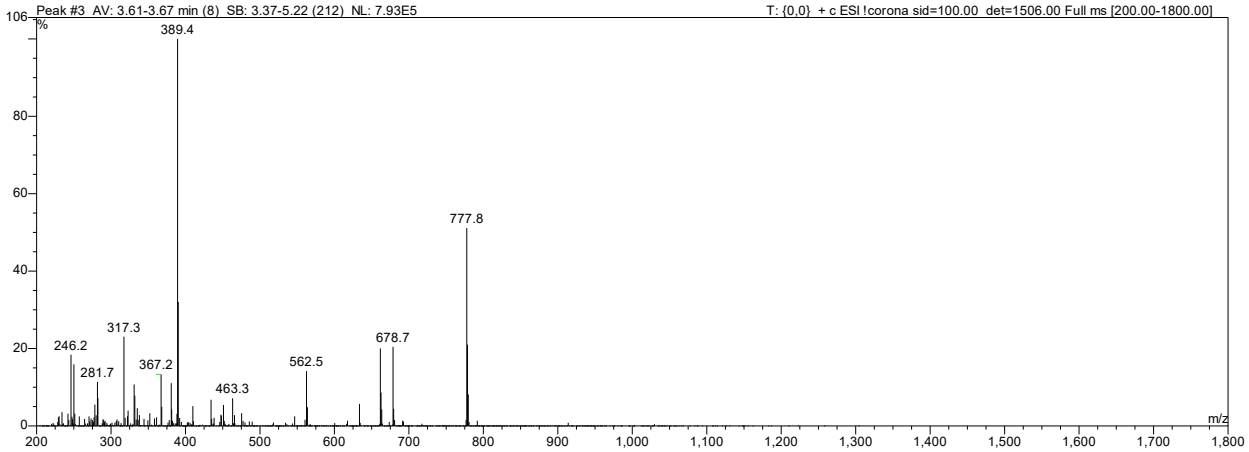


Figure SI 24. MS spectra of **13** of the peak 2.95 min (pure product).



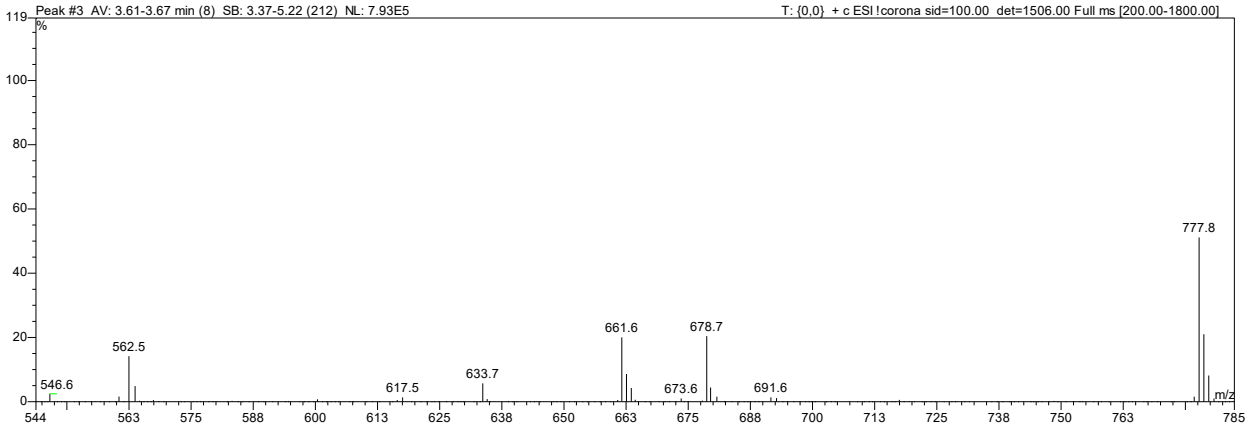


Figure SI 25. MS spectra of **13** of the peak 3.65 min (pure product). Zoom on the range 544-785 *m/z* was shown additionally.

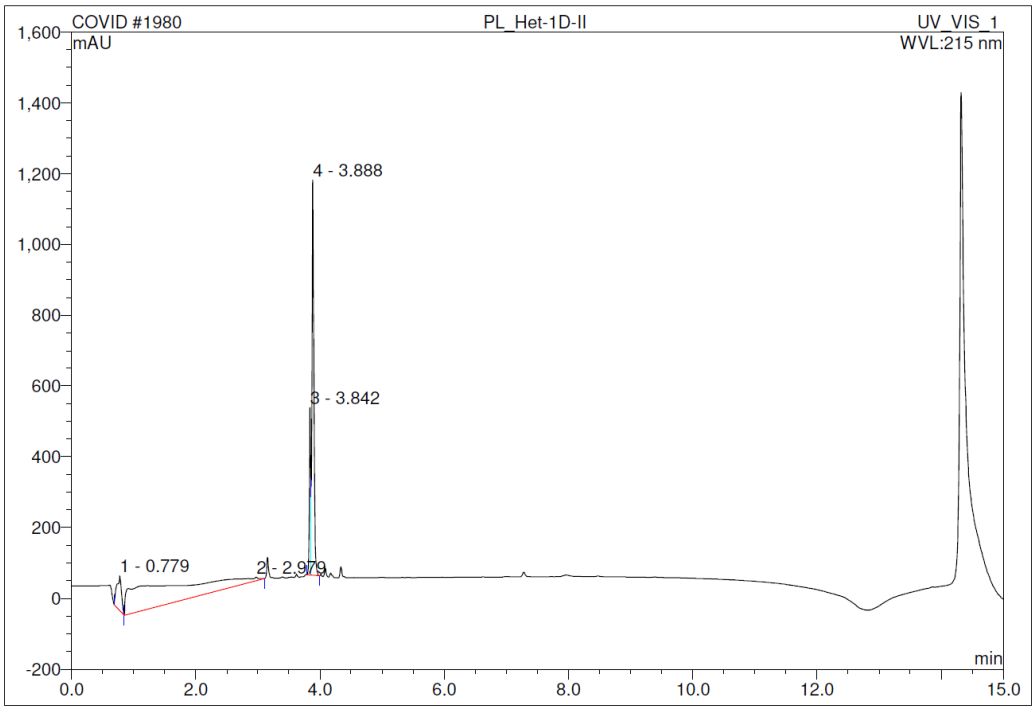
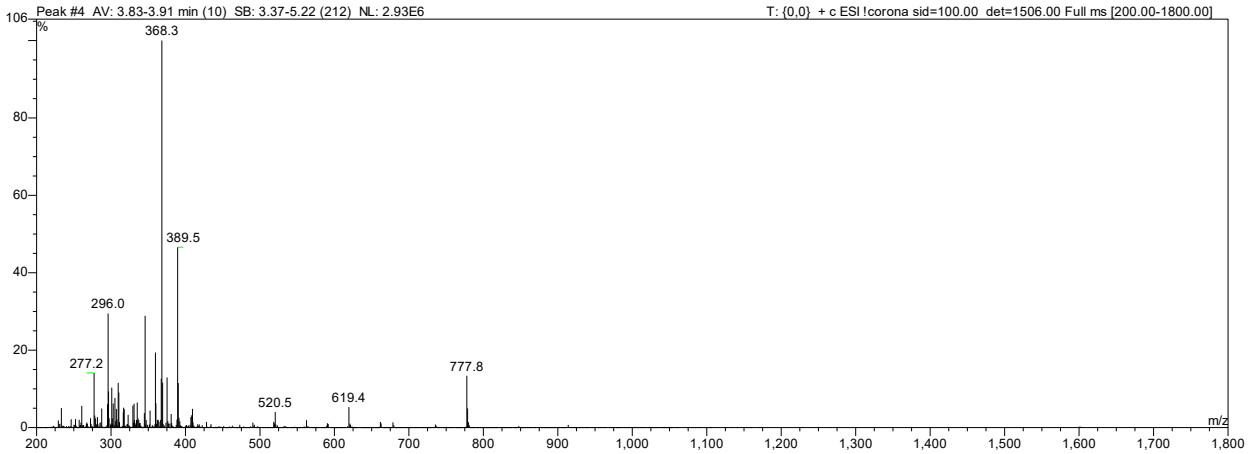


Figure SI 26. Chromatogram of **14** (pure product).



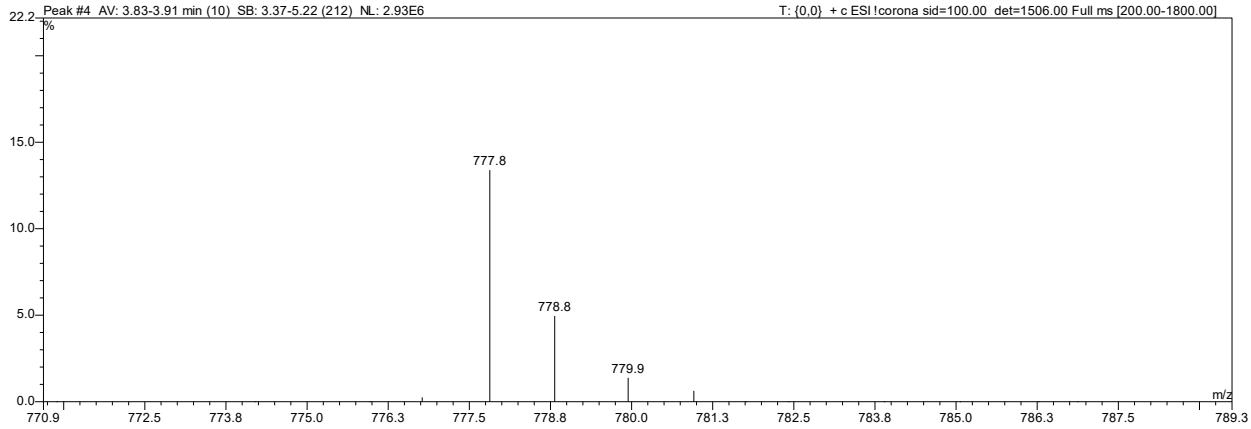


Figure SI 27. MS spectra of **14** of the peak 3.89 min (pure product). Zoom on the range 771-789 *m/z* was shown additionally.

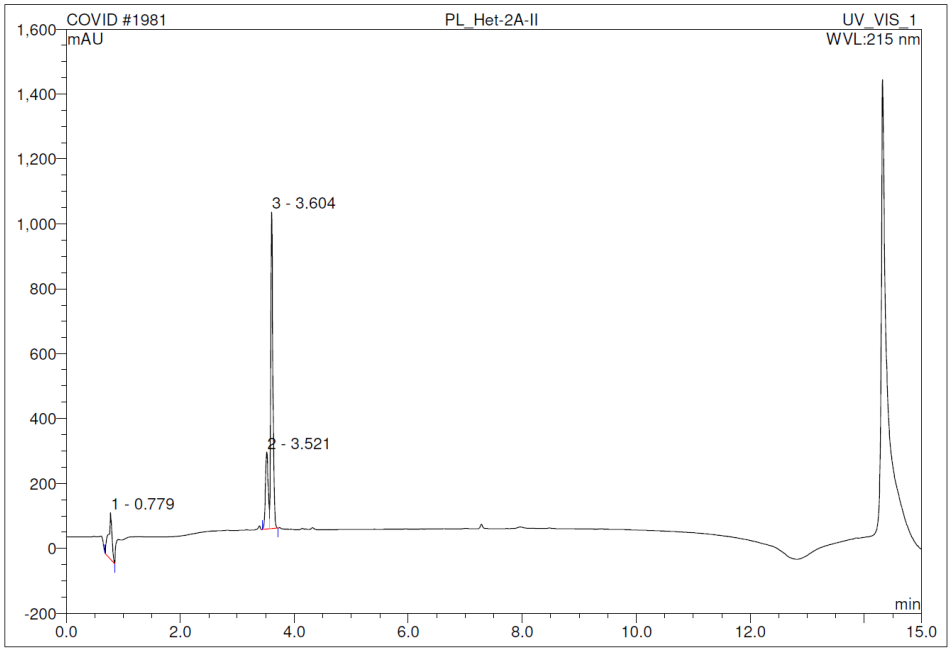


Figure SI 28. Chromatogram of **15** (pure product).

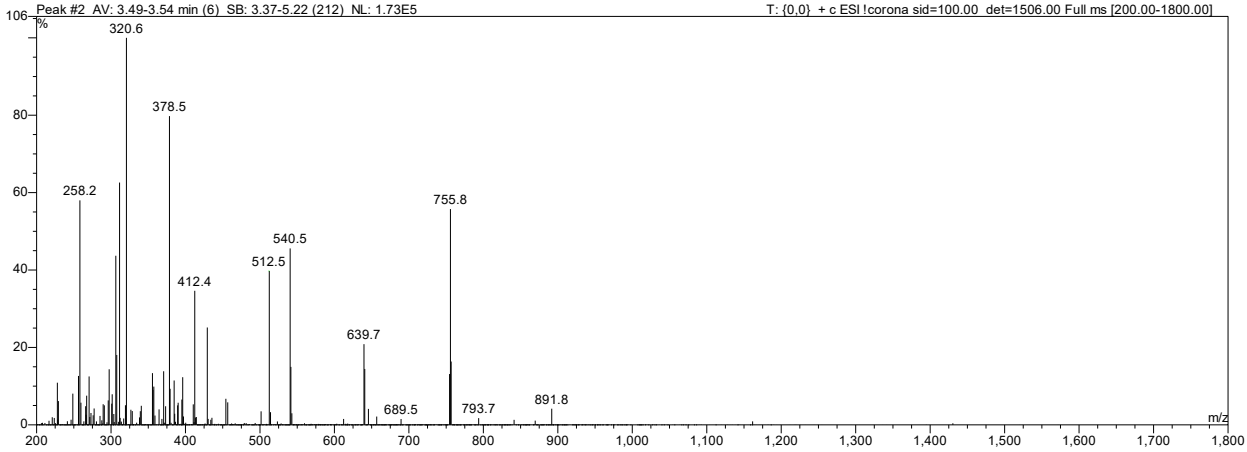


Figure SI 29. MS spectra of **15** of the peak 3.5 min (pure product).

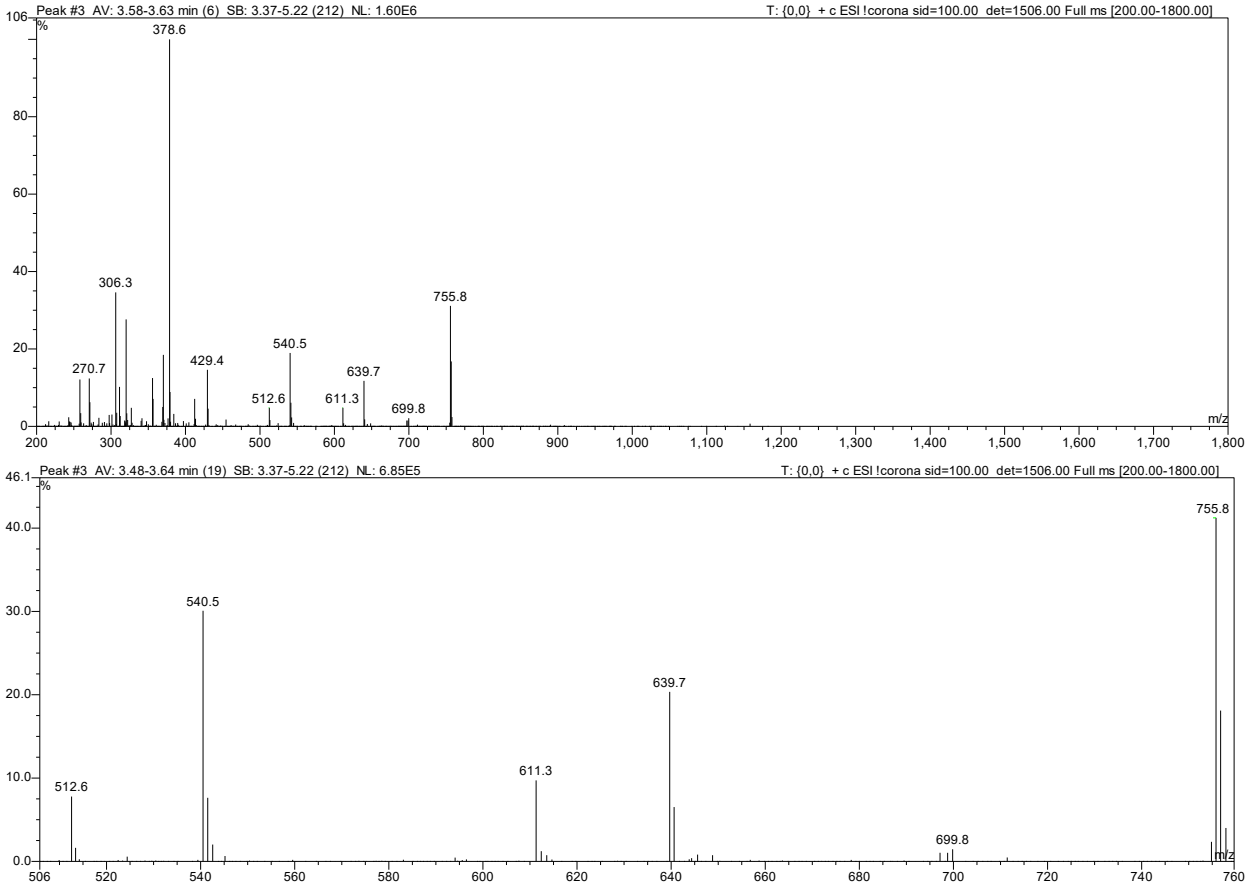


Figure SI 30. MS spectra of **15** of the peak 3.6 min (pure product). Zoom on the range 506-760 *m/z* was shown additionally.

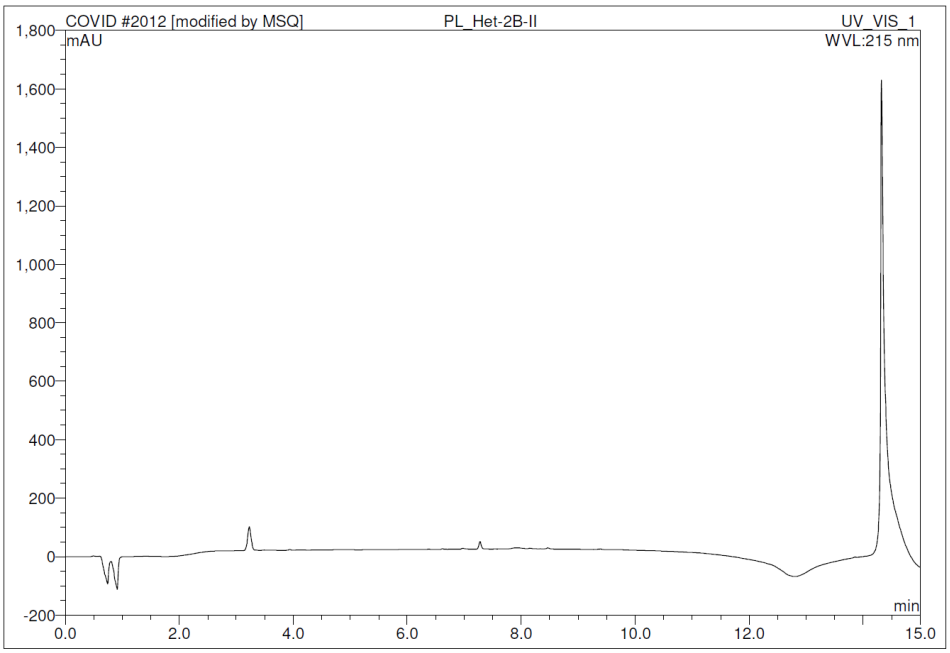


Figure SI 31. Chromatogram of **16** (pure product).

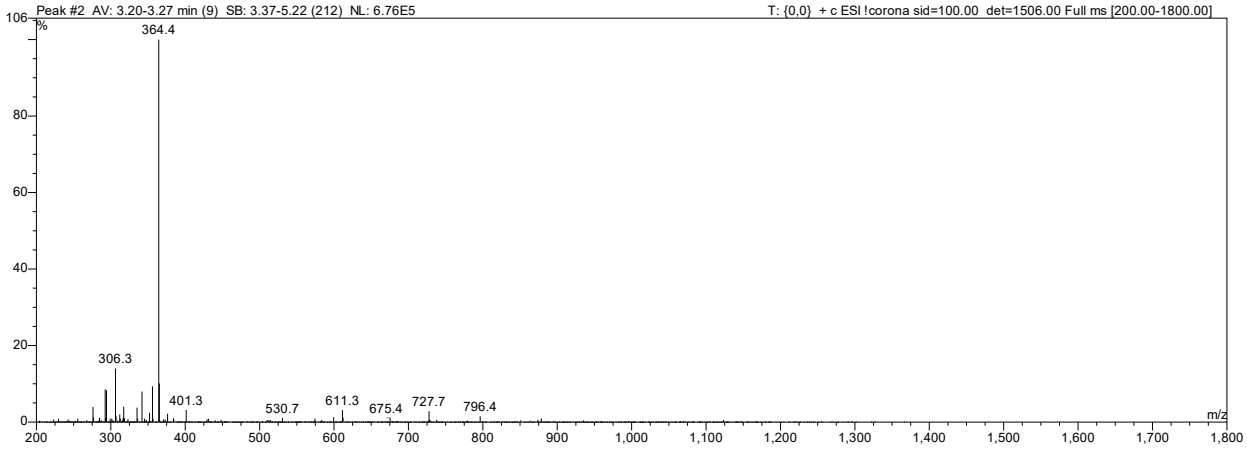


Figure SI 32. MS spectra of **16** of the peak 3.25 min (pure product).

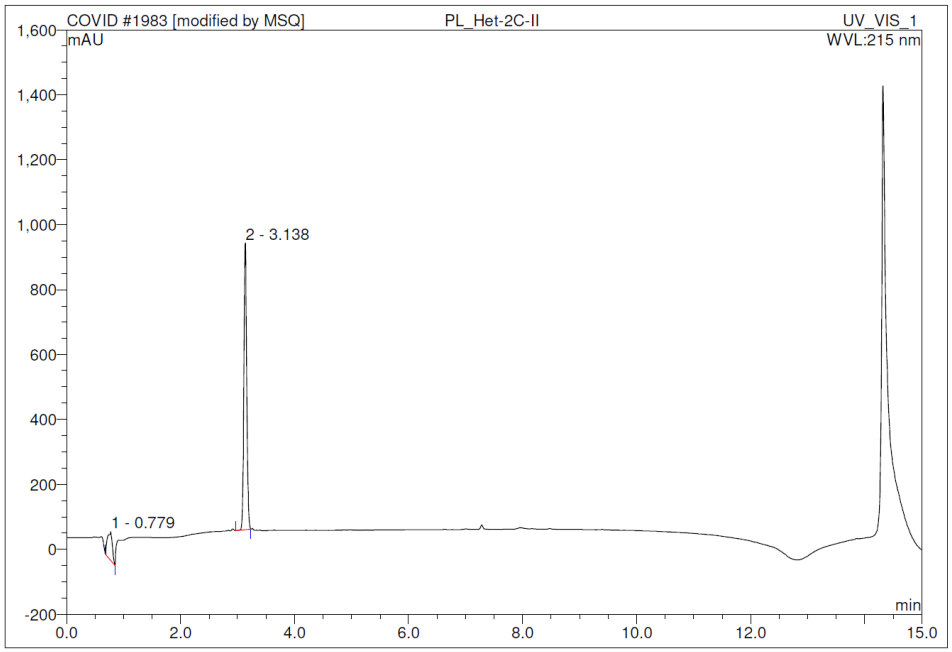


Figure SI 33. Chromatogram of **17** (pure product).

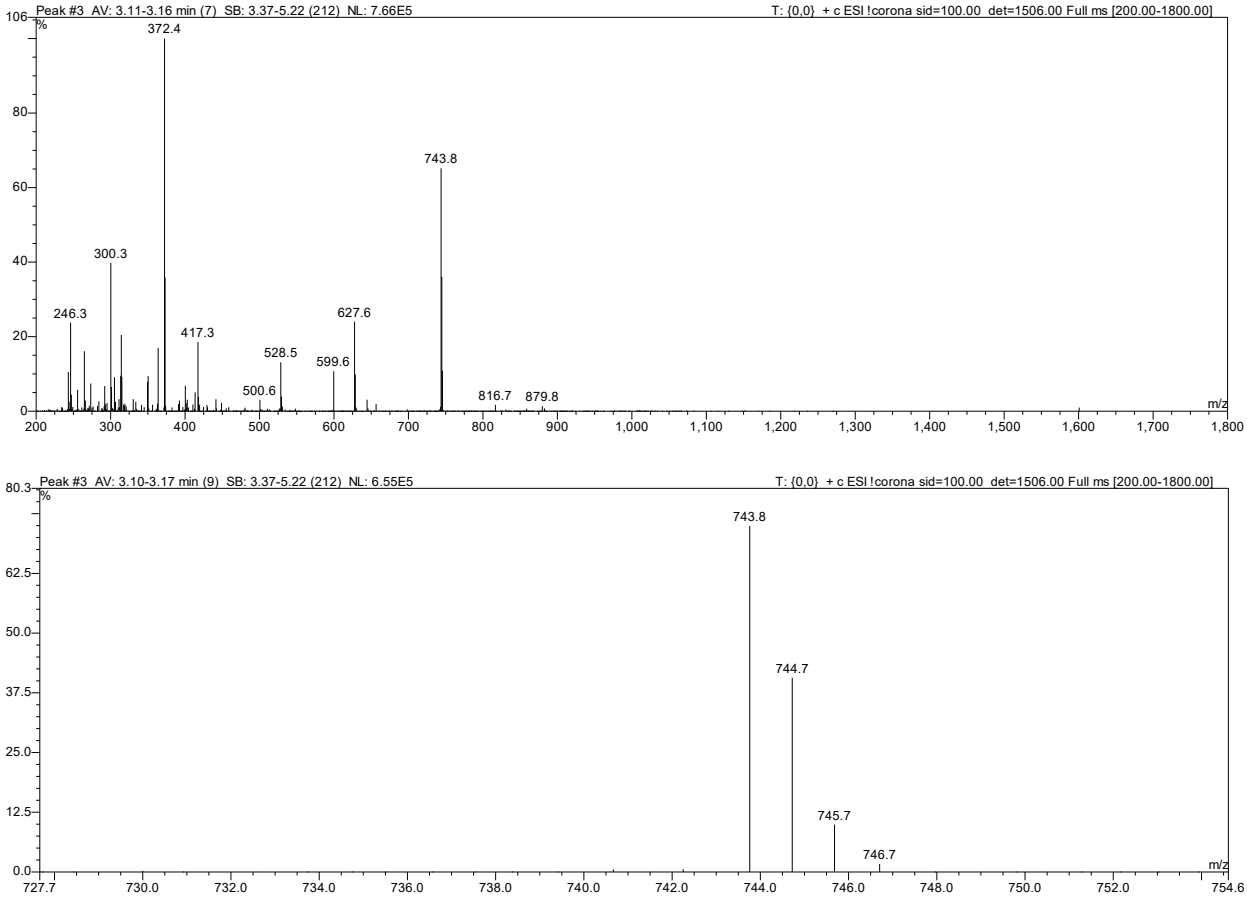


Figure SI 34. MS spectra of **17** of the peak 3.14 min (pure product). Zoom on the range 728-754 *m/z* was shown additionally.

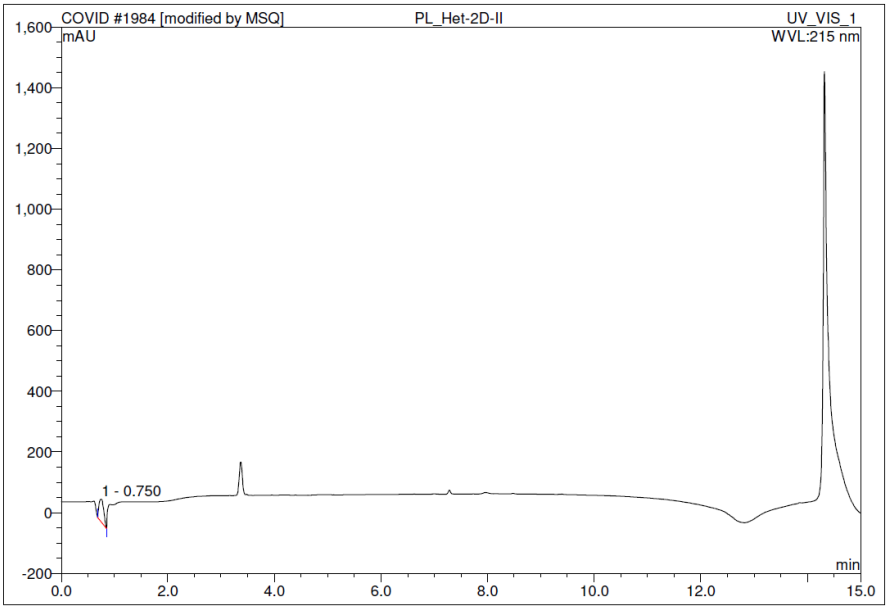


Figure SI 35. Chromatogram of **18** (pure product).

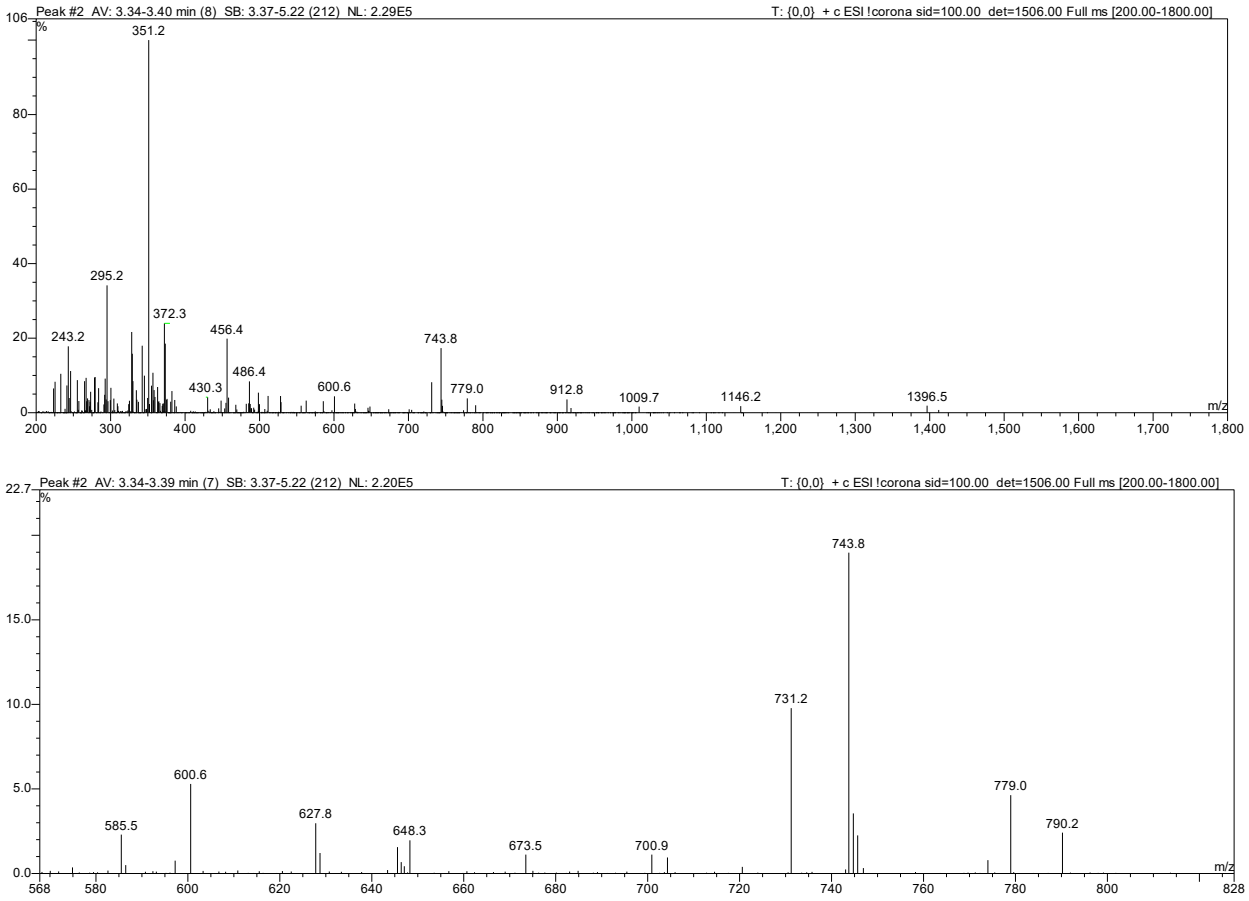


Figure SI 36. MS spectra of **18** of the peak 3.37 min (pure product). Zoom on the range 568-828 *m/z* was shown additionally.

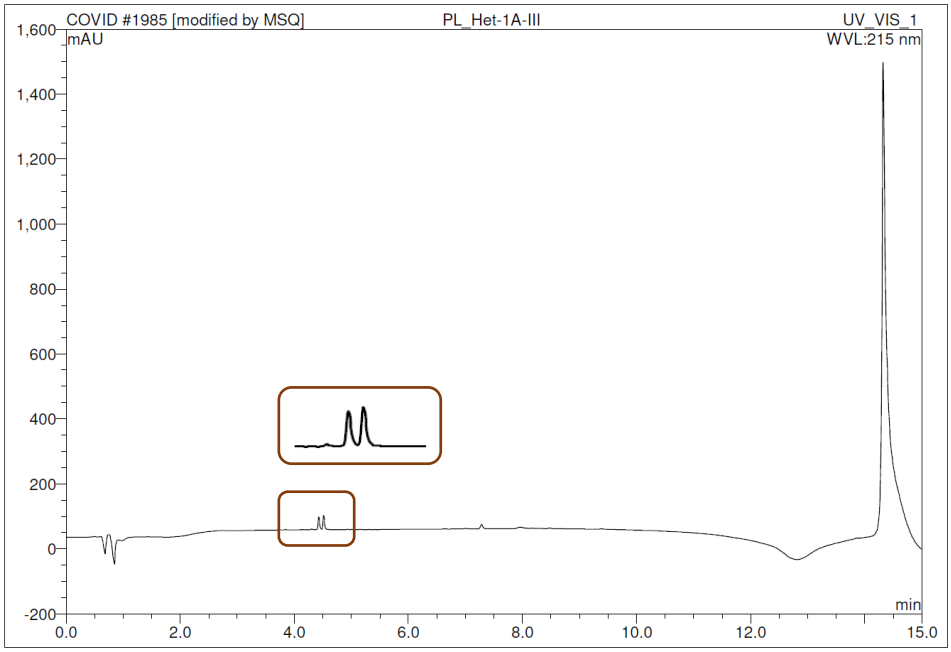


Figure SI 37. Chromatogram of **19** (pure product). Two separated peaks, with equal *m/z* value, are highlighted.

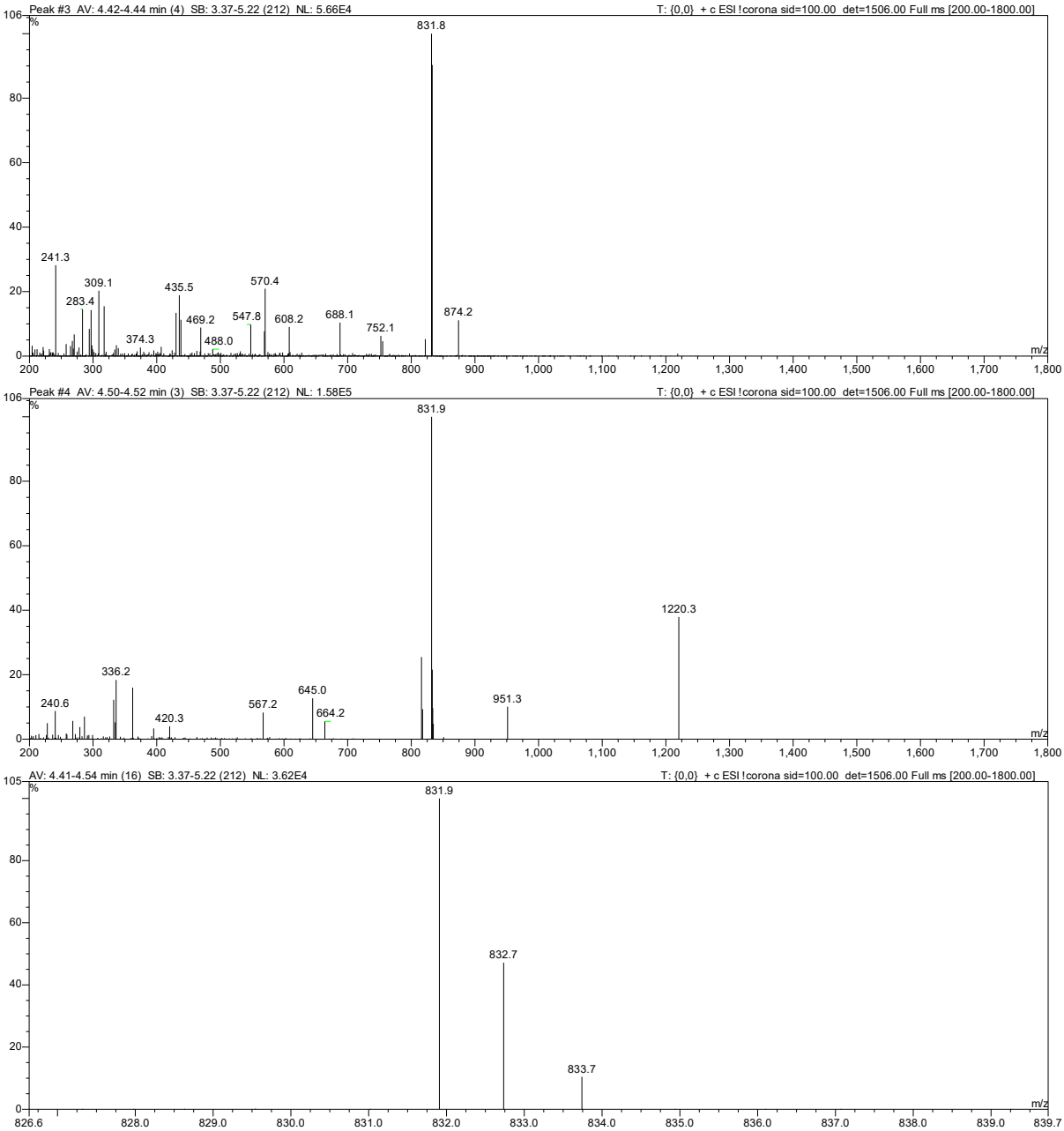


Figure SI 38. MS spectra of **19** of the peaks 4.42-4.44 (up) and 4.50-4.52 min (middle). Zoom on the range 826-840 *m/z* was shown additionally (down) (pure product).

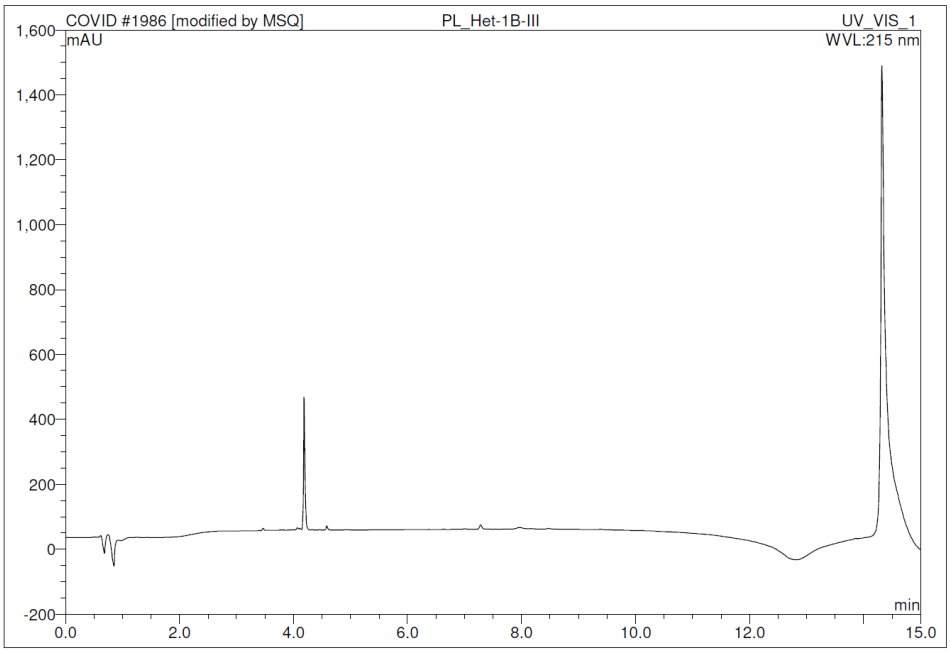


Figure SI 39. Chromatogram of **20** (pure product).

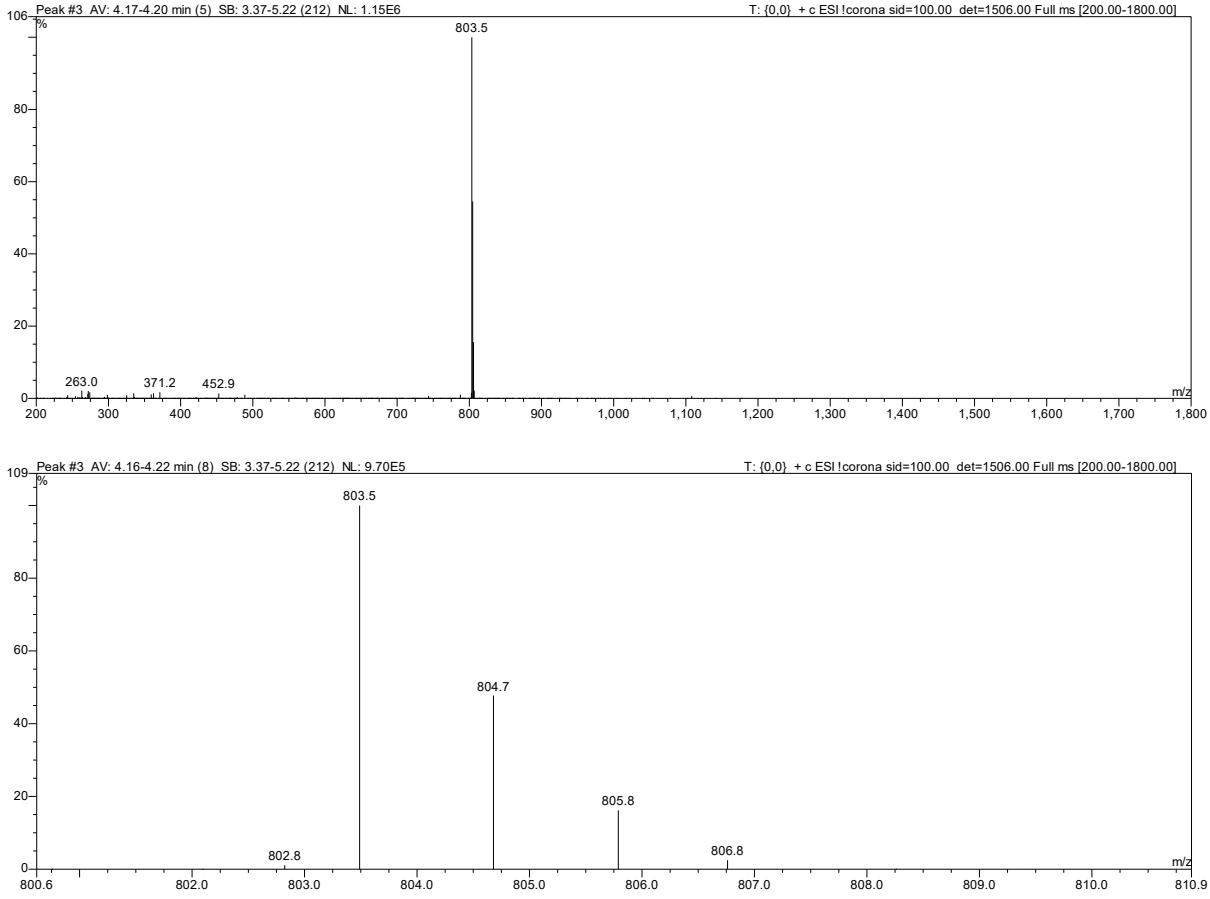


Figure SI 40. MS spectra of **20** of the peak 4.2 min (pure product). Zoom on the range 800-811 *m/z* was shown additionally.

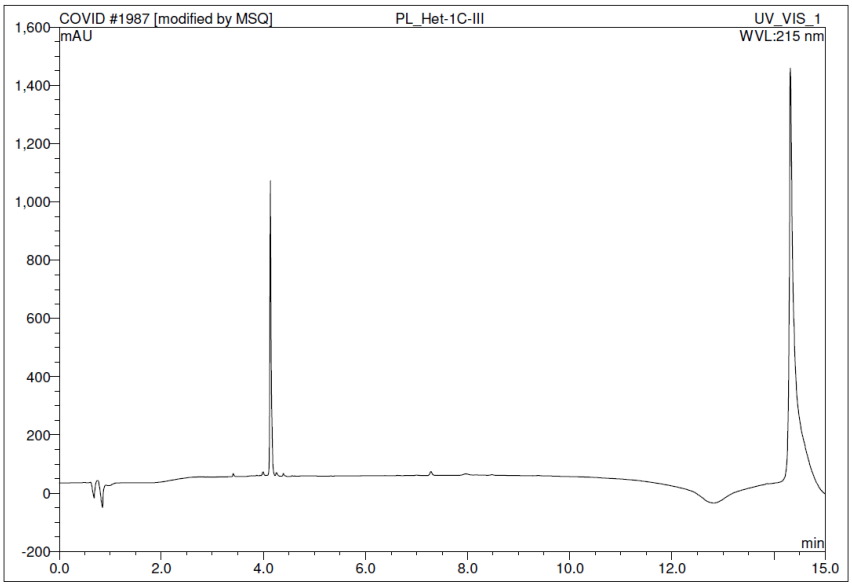


Figure SI 41. Chromatogram of **21** (pure product).

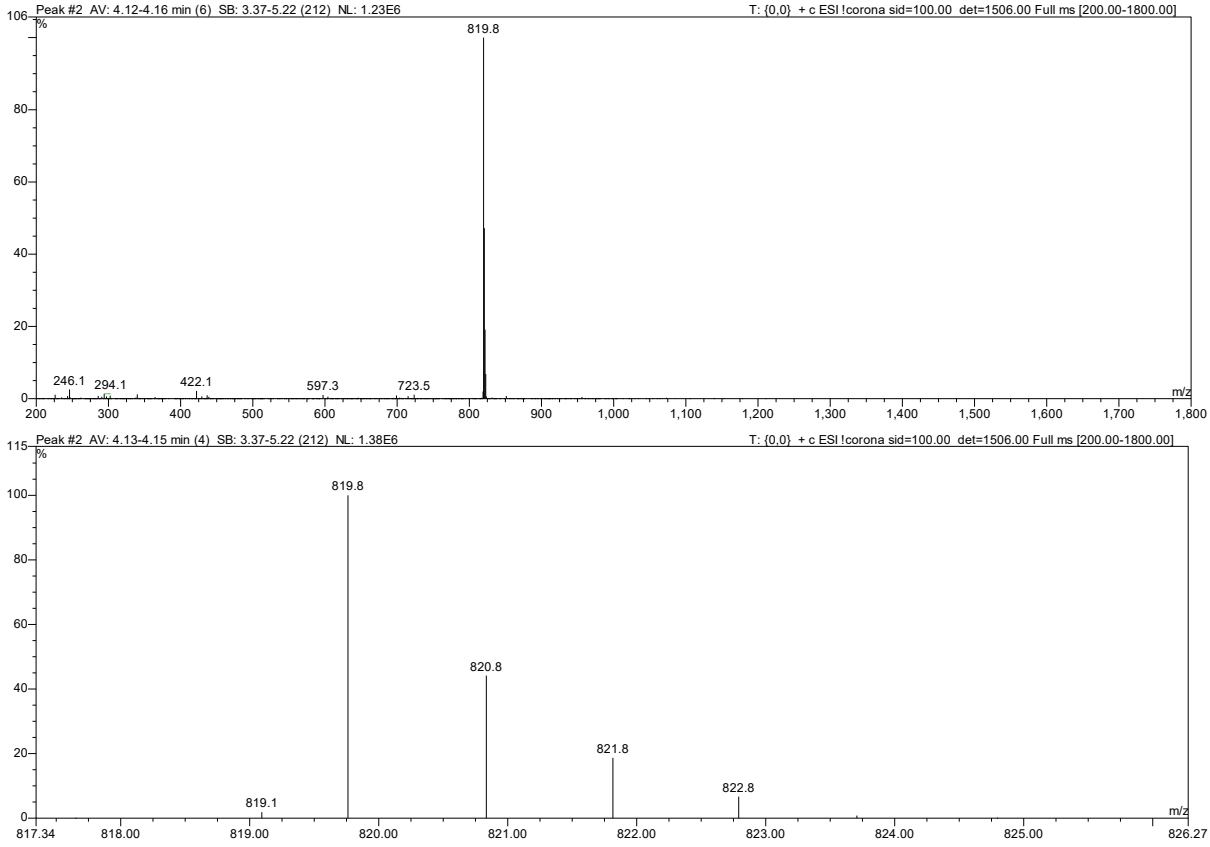


Figure SI 42. MS spectra of **21** of the peak 4.12-4.16 min (pure product). Zoom on the range 817-826 *m/z* was shown additionally.

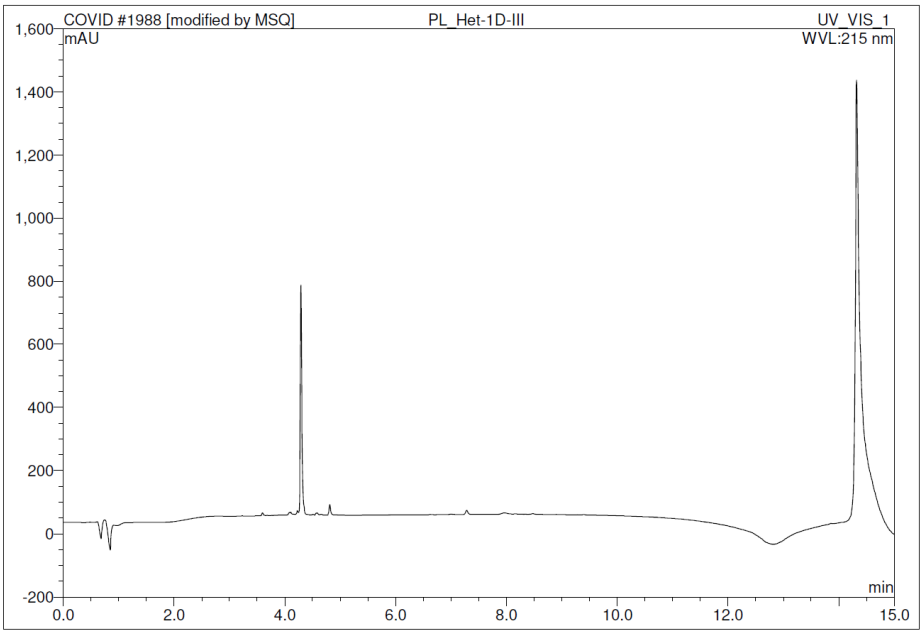


Figure SI 43. Chromatogram of **22** (pure product).

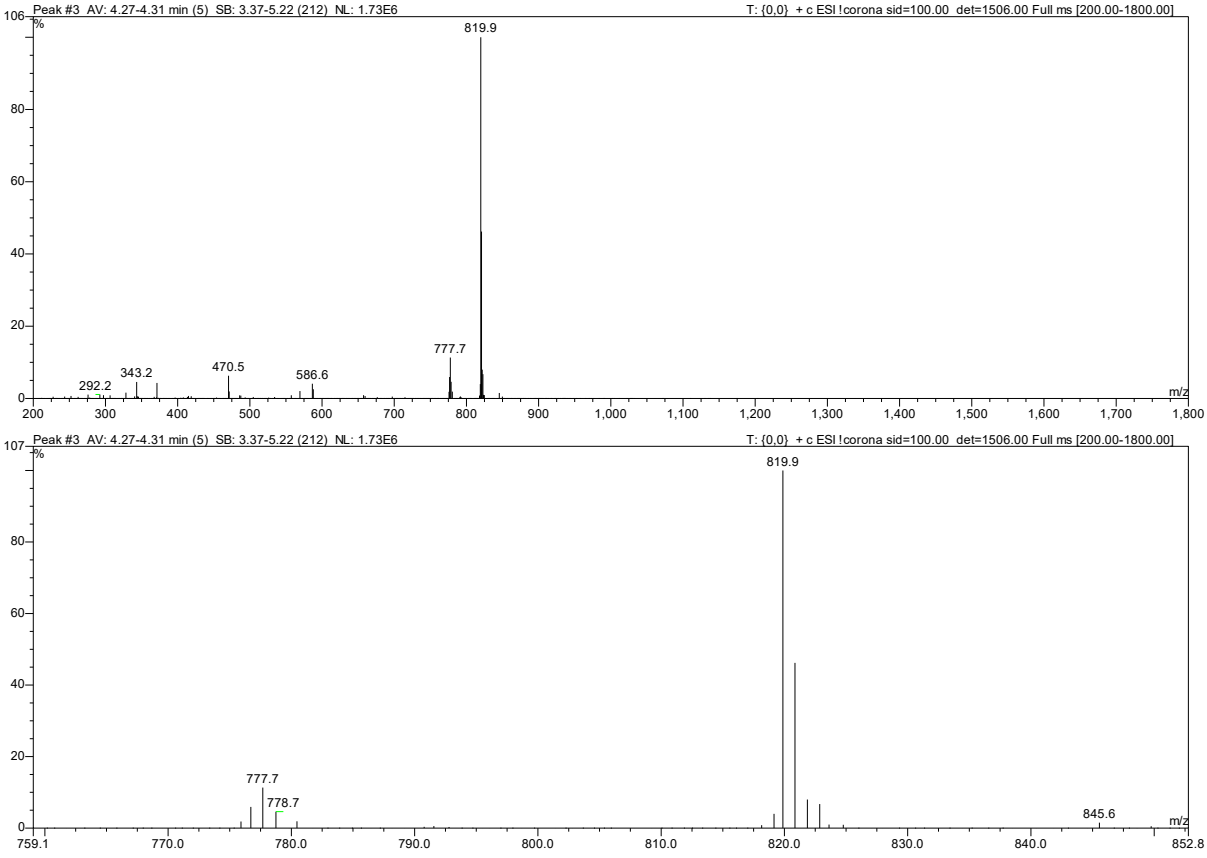


Figure SI 44. MS spectra of **22** of the peak 4.27-4.31 min (pure product). Zoom on the range 759-853 *m/z* was shown additionally.

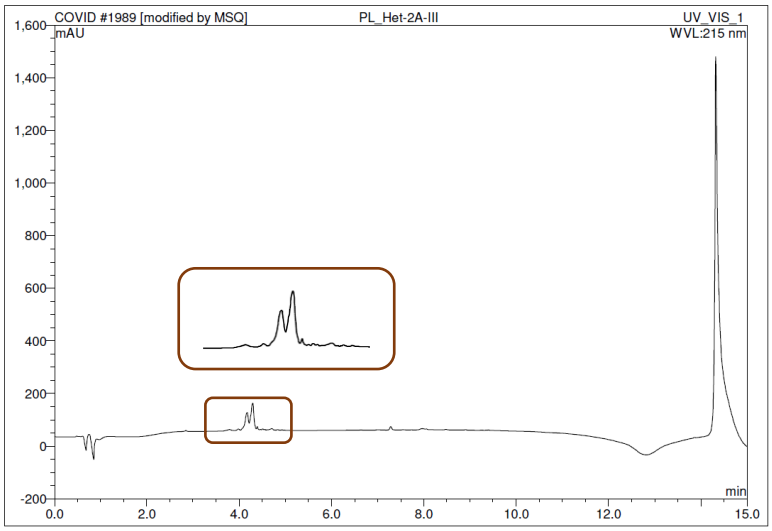


Figure SI 45. Chromatogram of **23** (pure product). Two separated peaks, with equal *m/z* value, are highlighted.

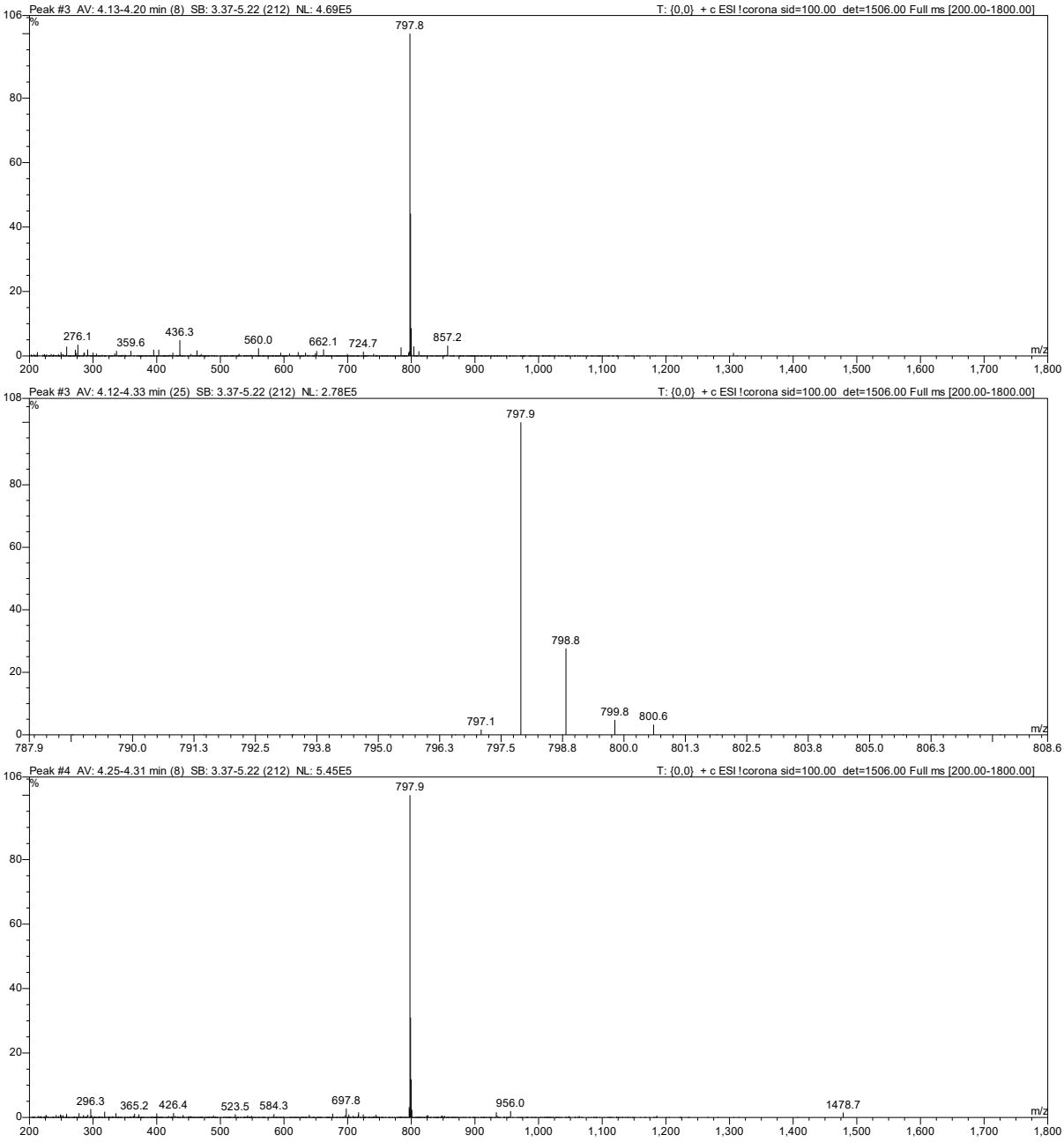


Figure SI 46. MS spectra of **23** of the peaks 4.13-4.20 (up) and 4.25-4.31 min (down) (pure product). Zoom on the range 788-809 *m/z* was shown additionally (middle).

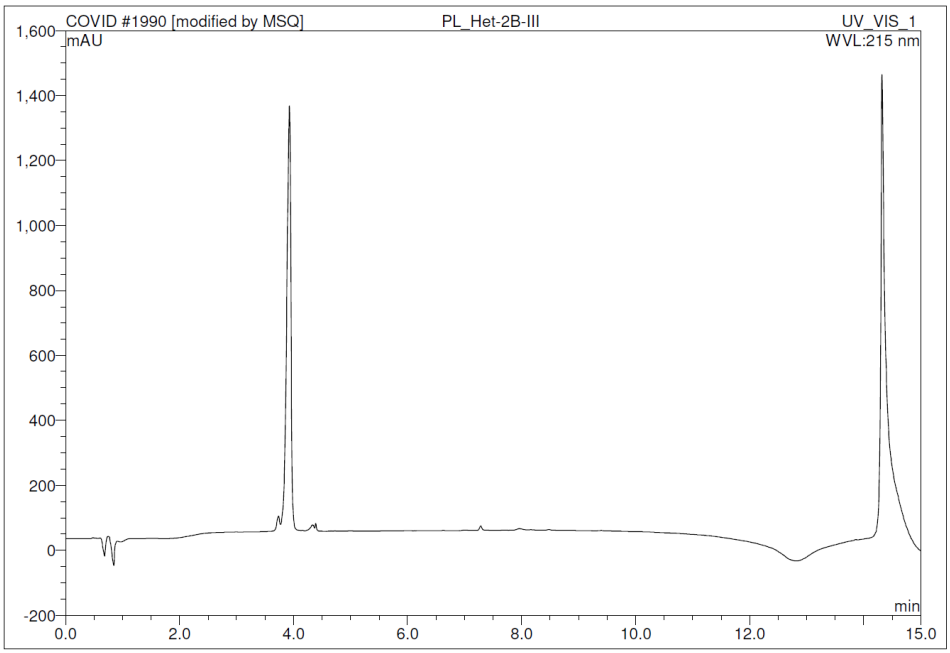


Figure SI 47. Chromatogram of **24** (pure product).

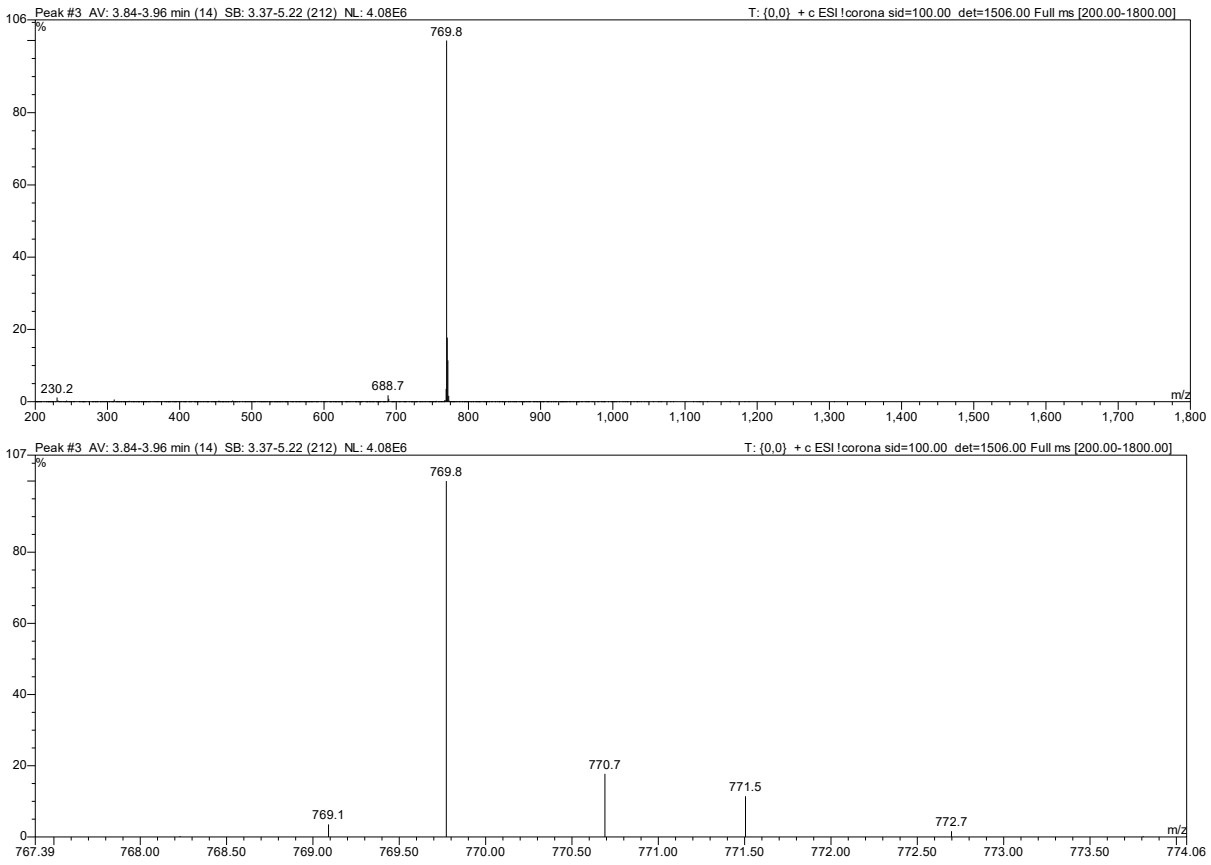


Figure SI 48. MS spectra of **24** of the peak 3.84-3.96 min (pure product). Zoom on the range 767-774 *m/z* was shown additionally.

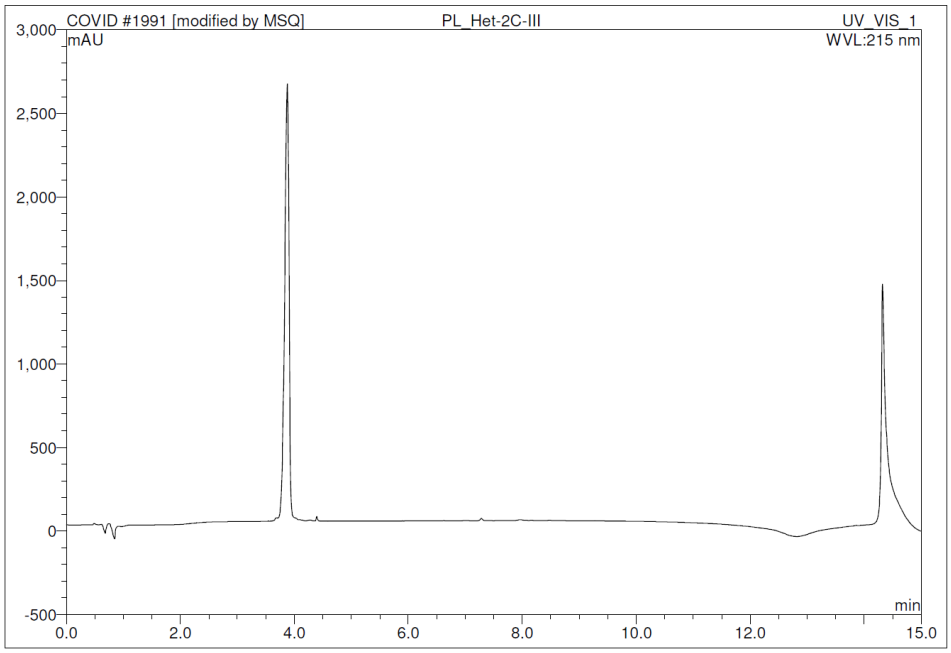


Figure SI 49. Chromatogram of **25** (pure product).

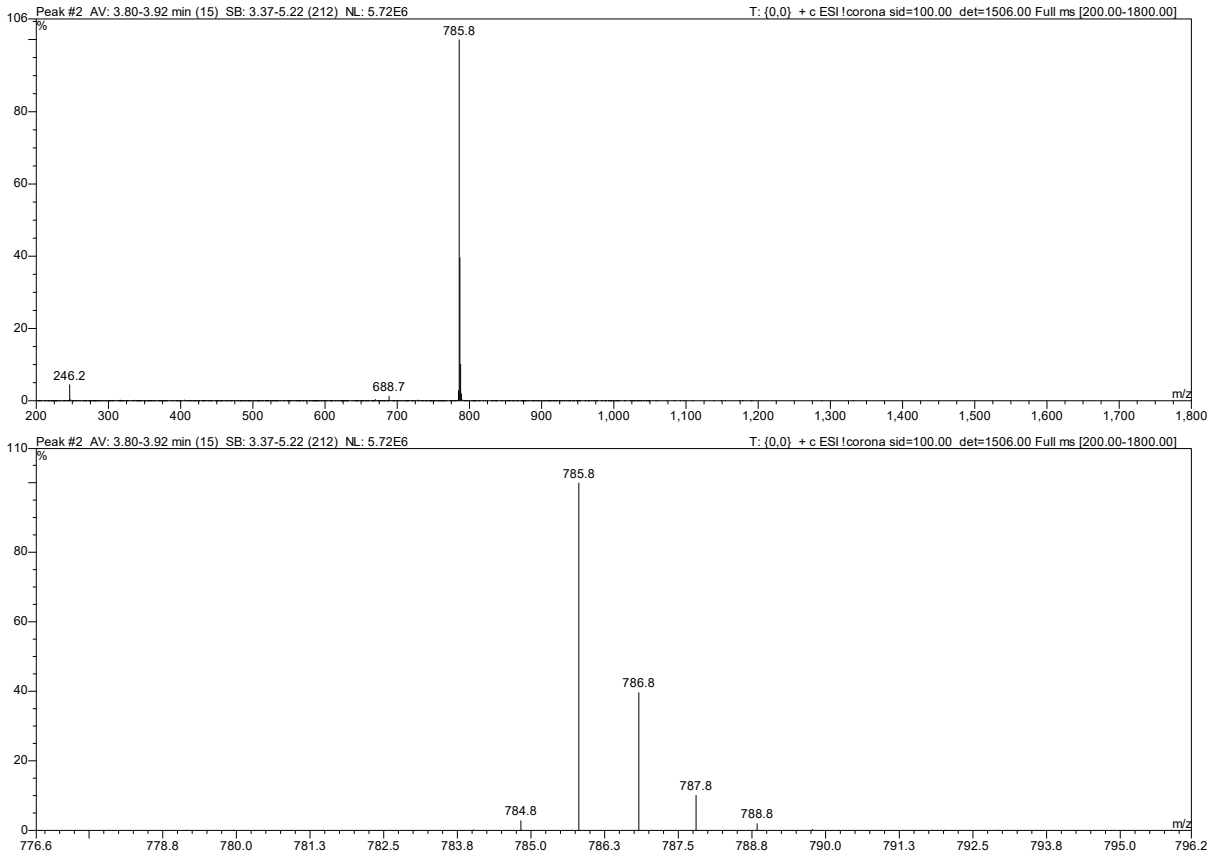


Figure SI 50. MS spectra of **25** of the peak 3.80-3.92 min (pure product). Zoom on the range 776-796 *m/z* was shown additionally.

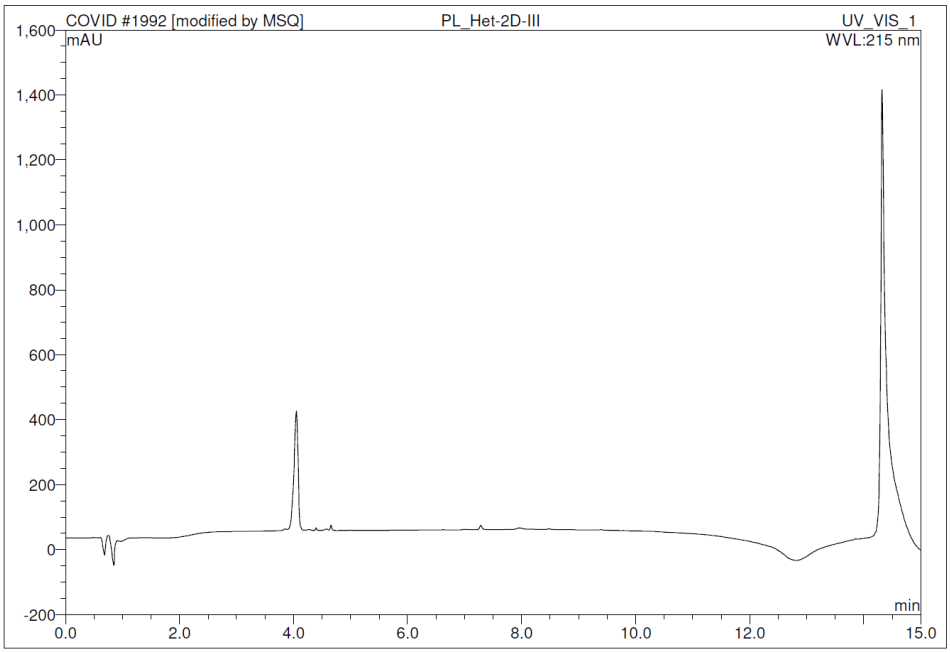


Figure SI 51. Chromatogram of **26** (pure product).

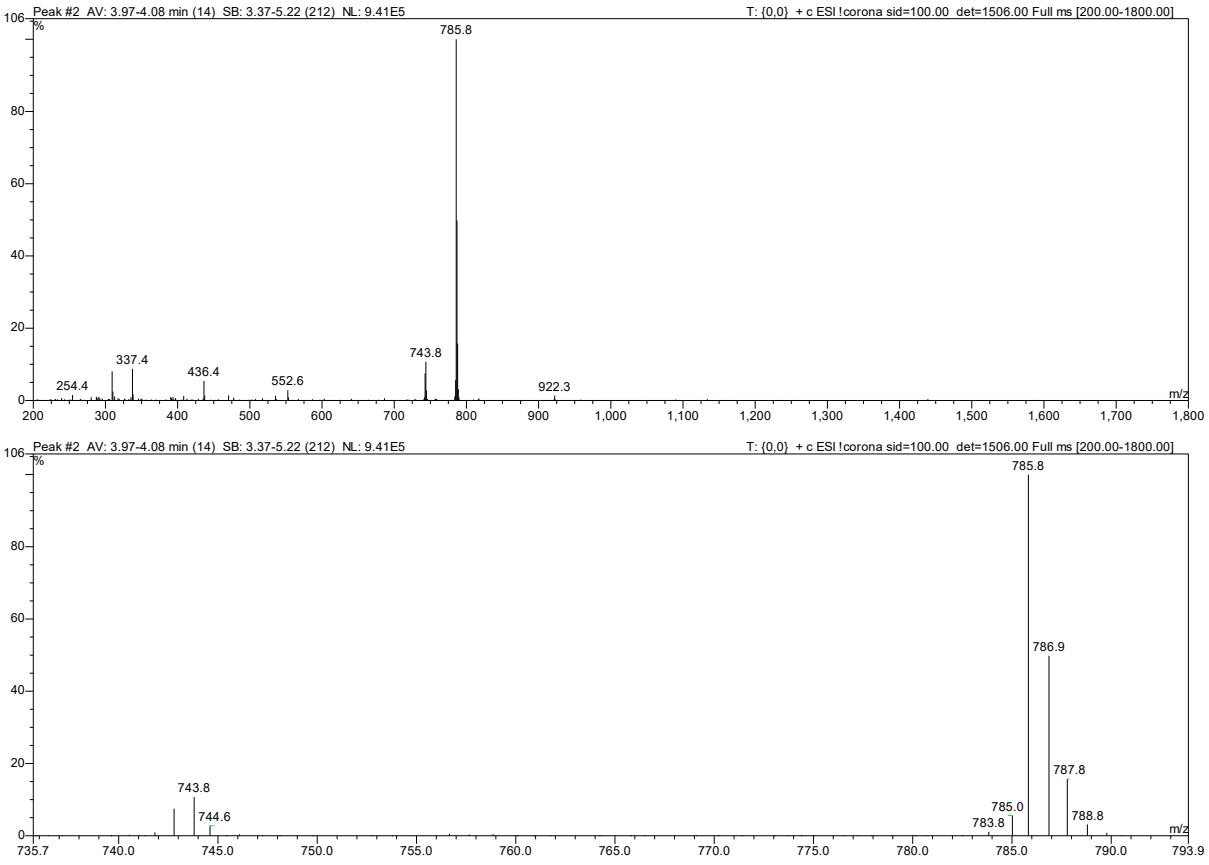


Figure SI 52. MS spectra of **26** of the peak 3.97-4.08 min (pure product). Zoom on the range 735-794 *m/z* was shown additionally.

1.2 Analyses of compounds 46-57

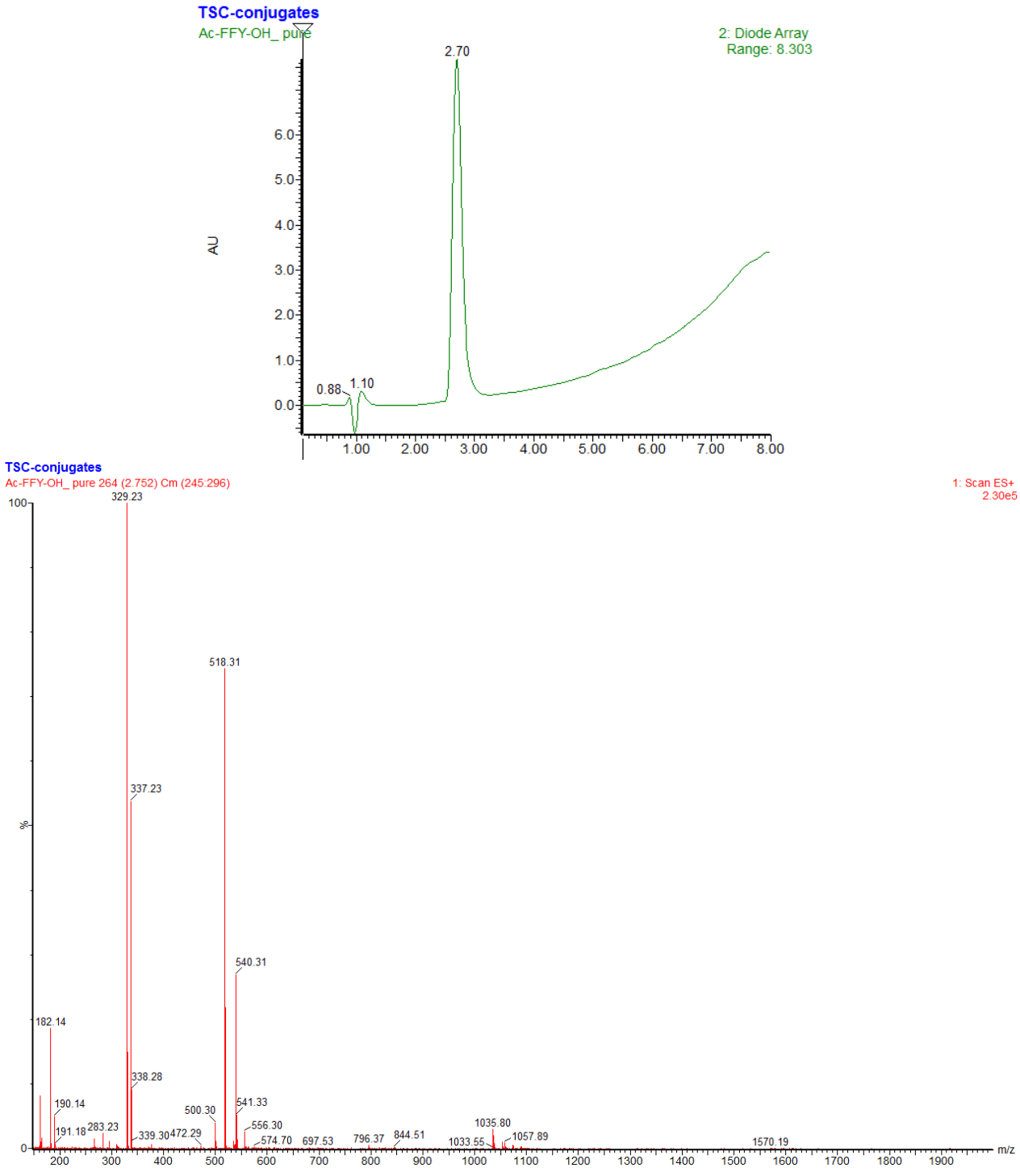


Figure SI 53. Chromatogram of **46** (Ac-FFY-OH) and MS spectra of the peak 2.7 min.

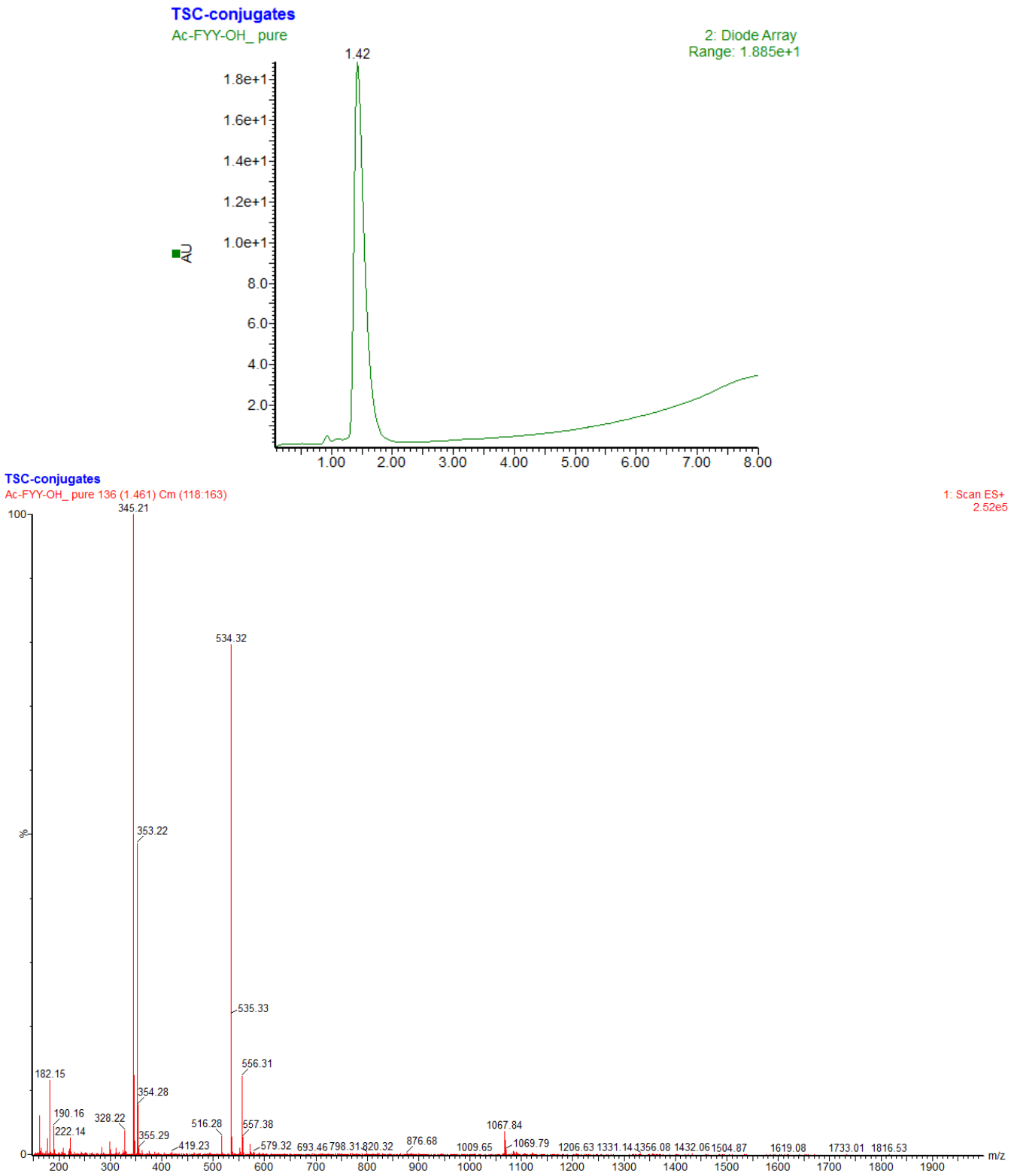


Figure SI 54. Chromatogram of **47** (Ac-FYY-OH) and MS spectra of the peak 1.4 min.

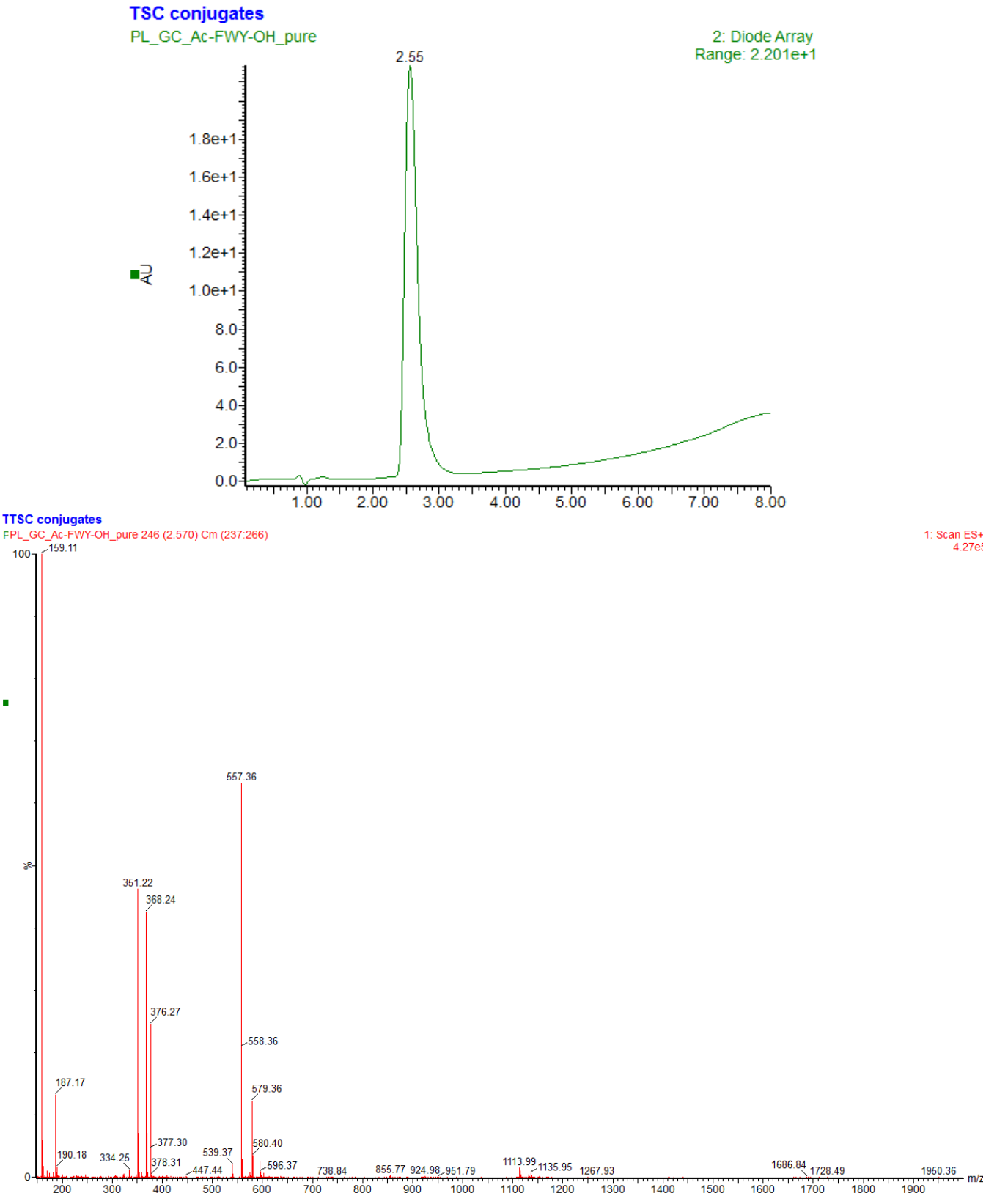


Figure SI 55. Chromatogram of **48** (Ac-FWY-OH) and MS spectra of the peak 2.5 min.

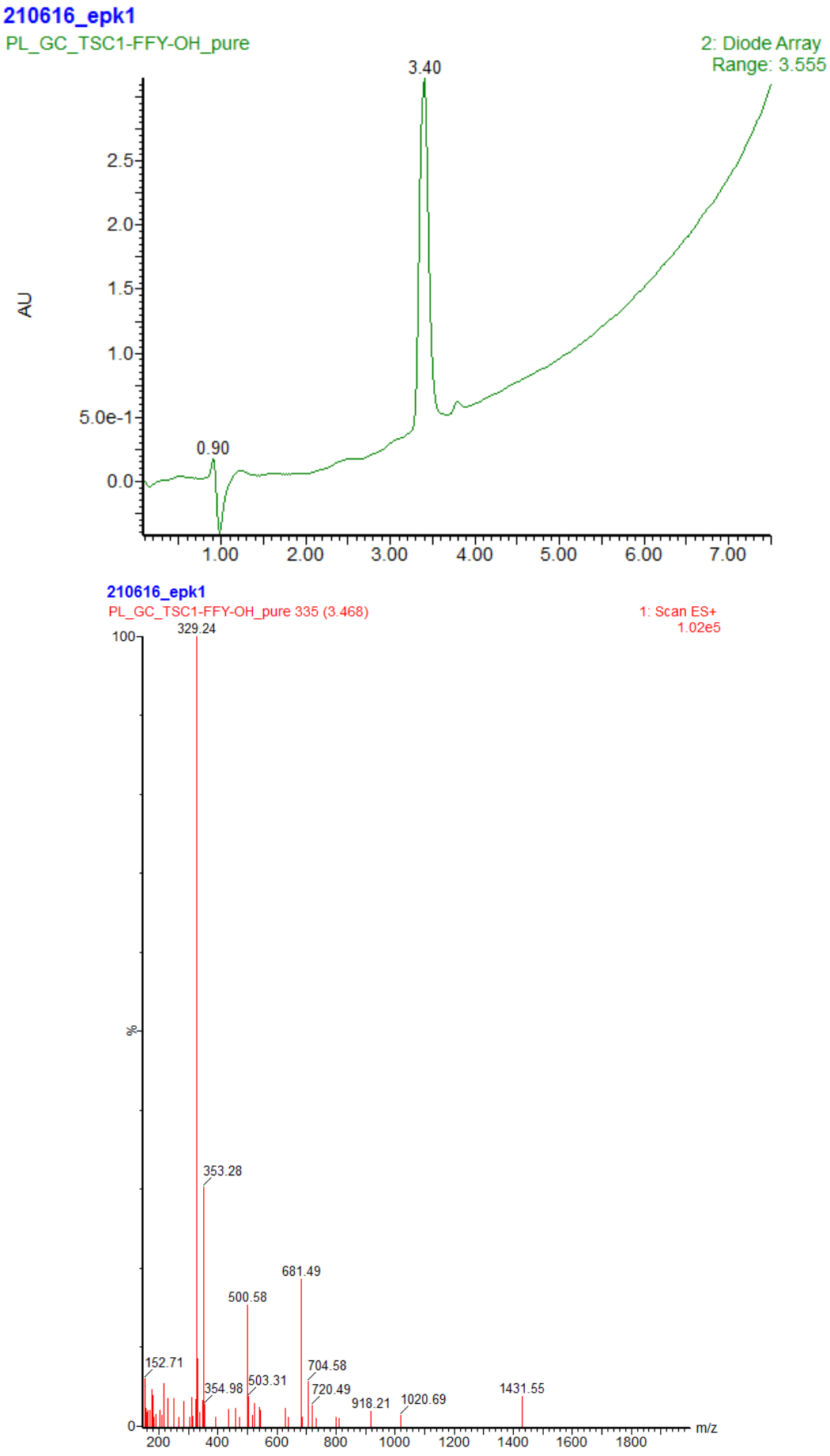


Figure SI 56. Chromatogram of **49** and MS spectra of the peak 3.4 min.

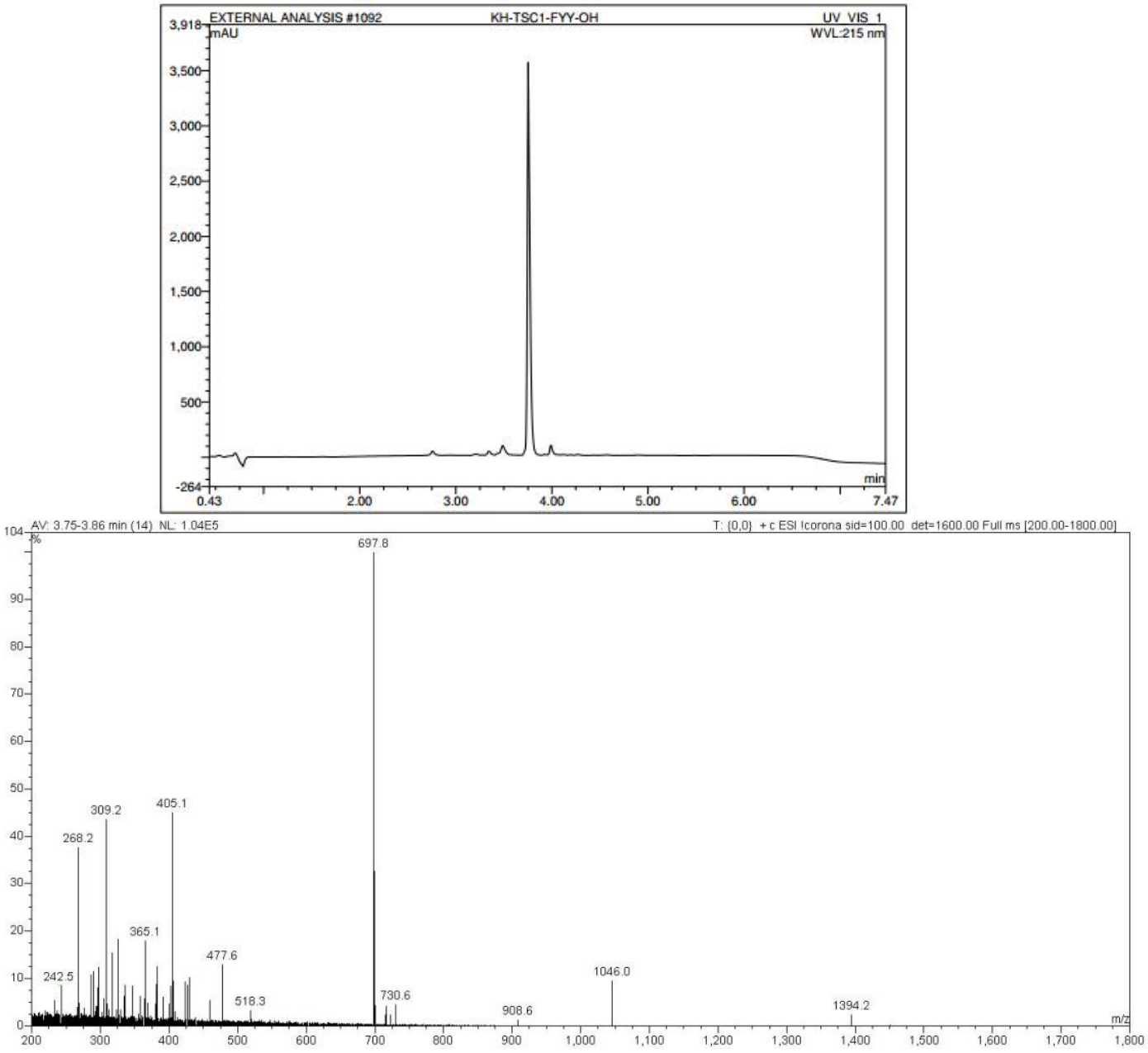


Figure SI 57. Chromatogram of **50** and MS spectra of the peak 3.8 min.

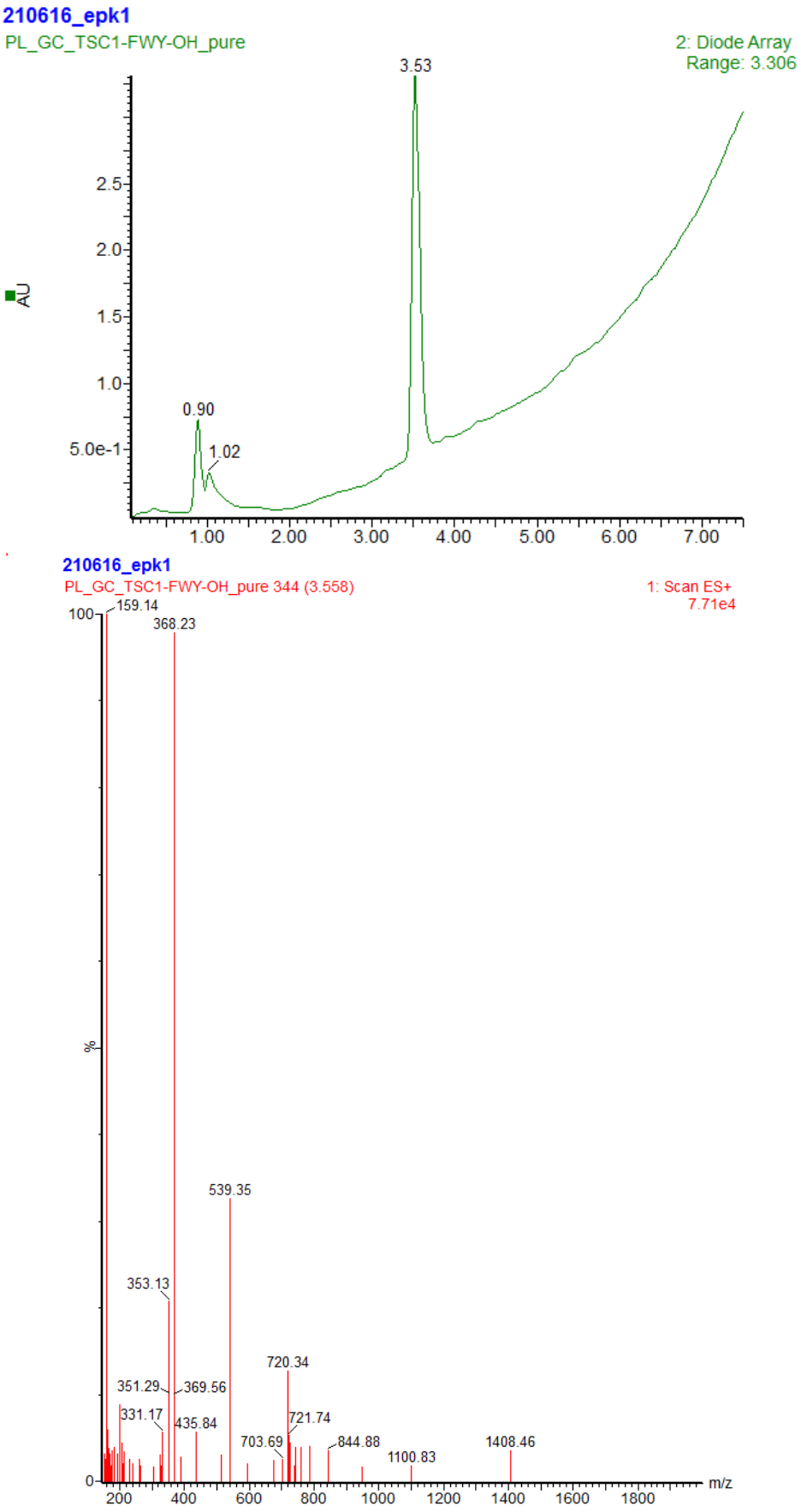


Figure SI 58. Chromatogram of **51** and MS spectra of the peak 3.5 min.

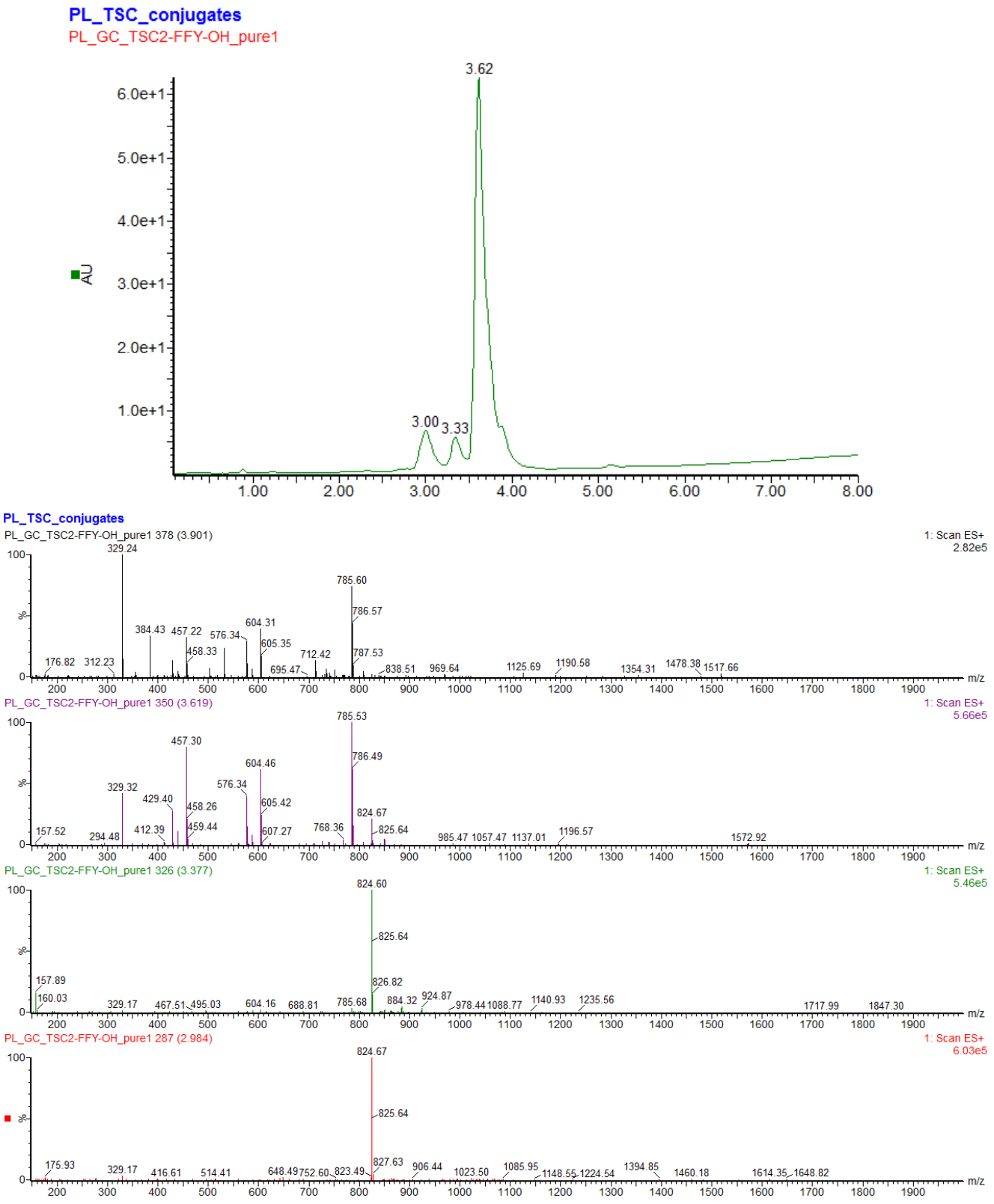


Figure SI 59. Chromatogram of **52** and MS spectra of the peaks found.

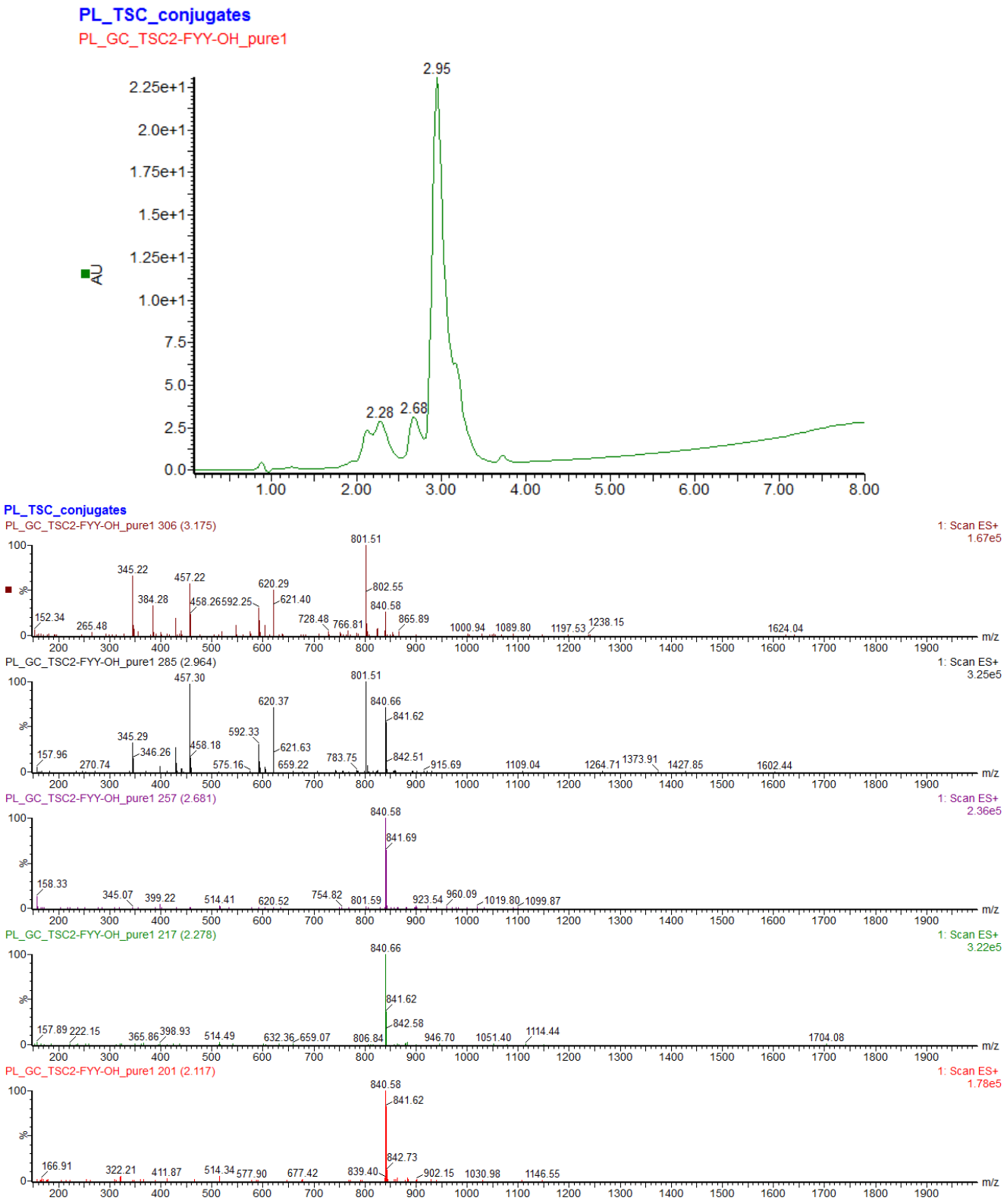


Figure SI 60. Chromatogram of **53** and MS spectra of the peaks found.

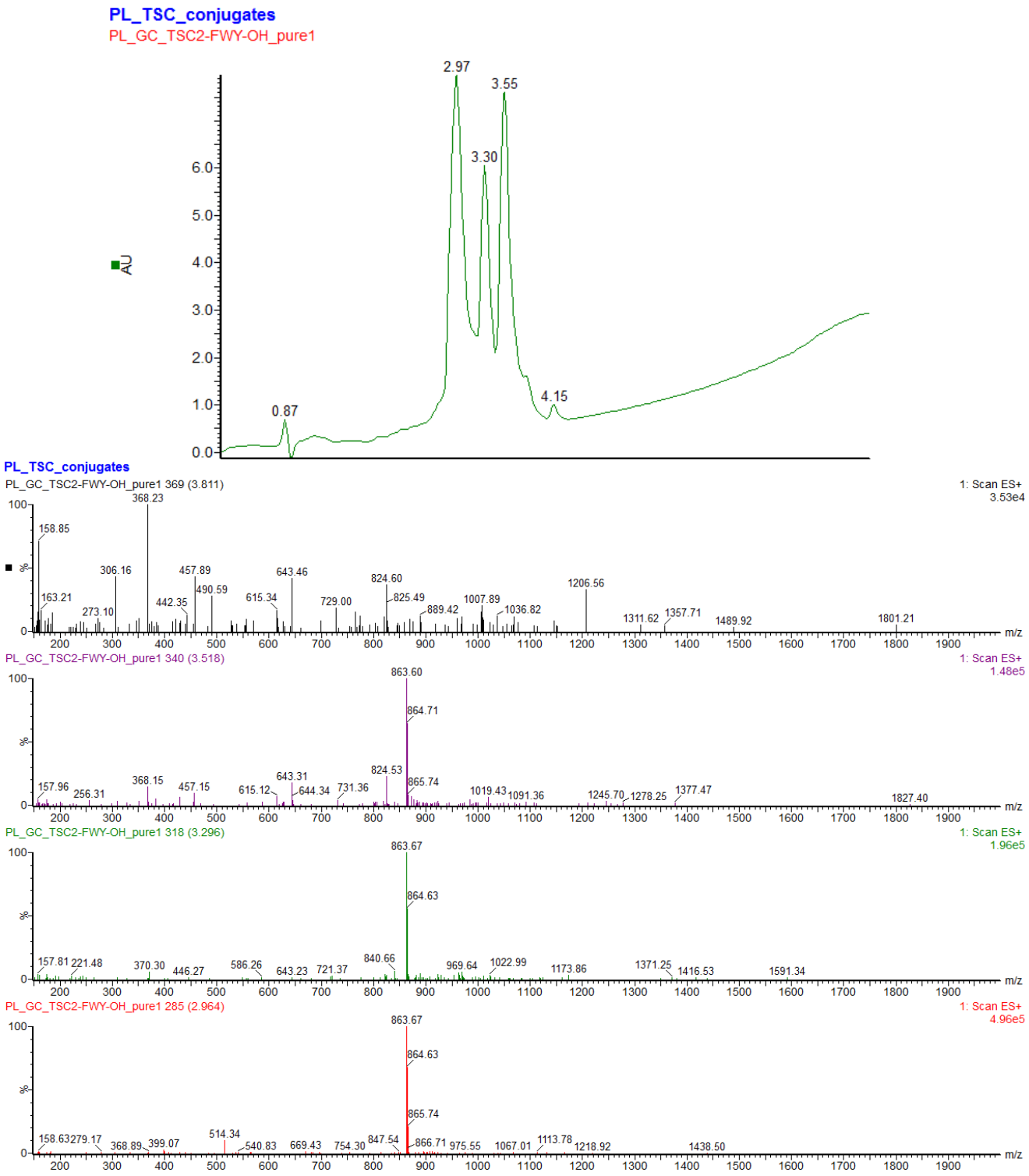


Figure SI 61. Chromatogram of **54** and MS spectra of the peaks found.

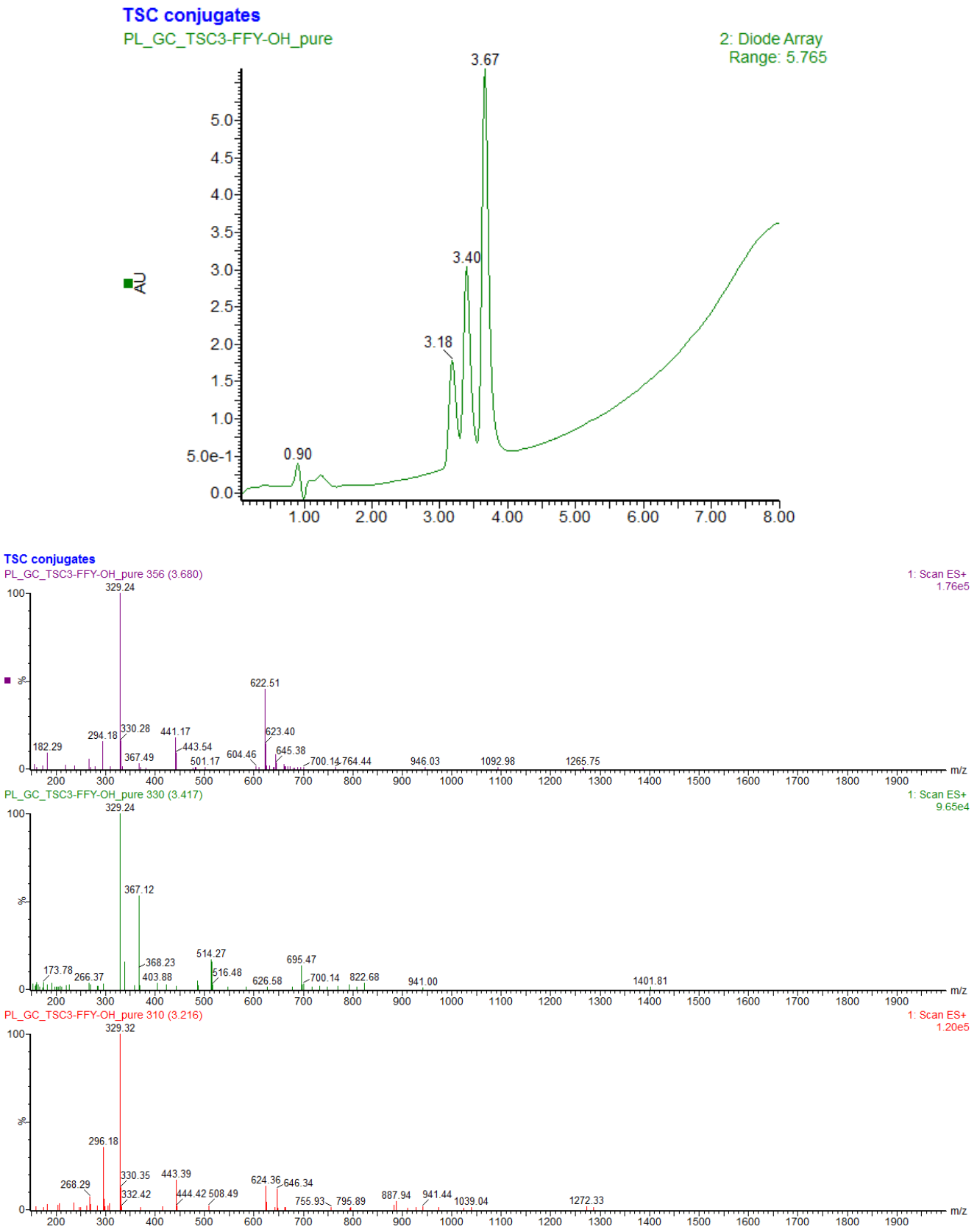


Figure SI 62. Chromatogram of **55** and MS spectra of the peaks found.

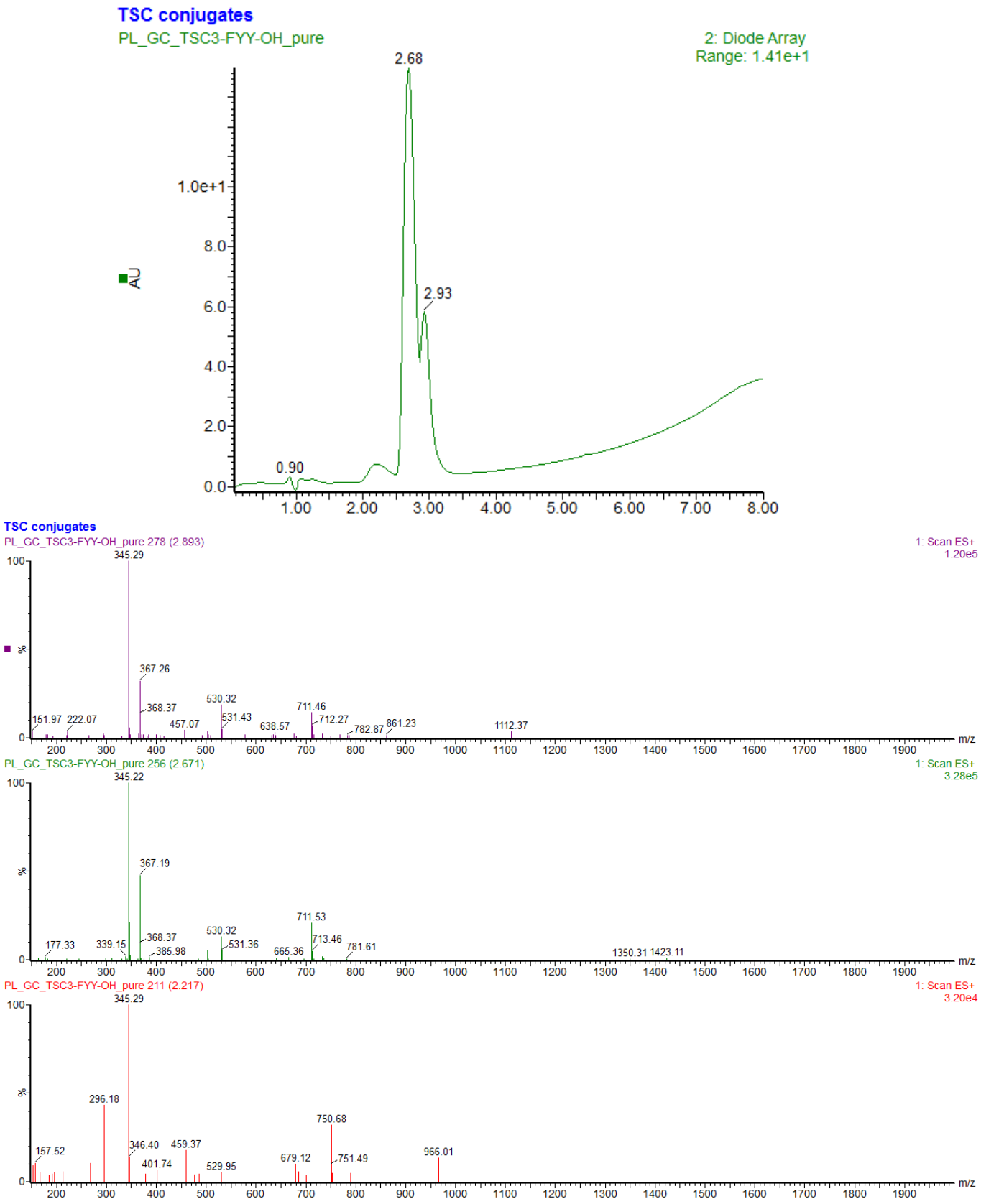
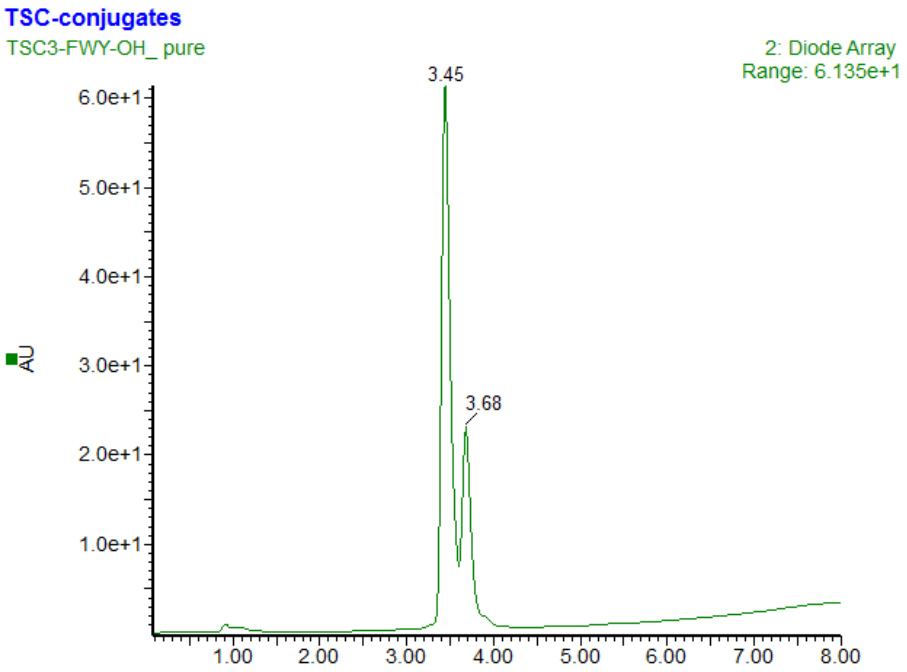
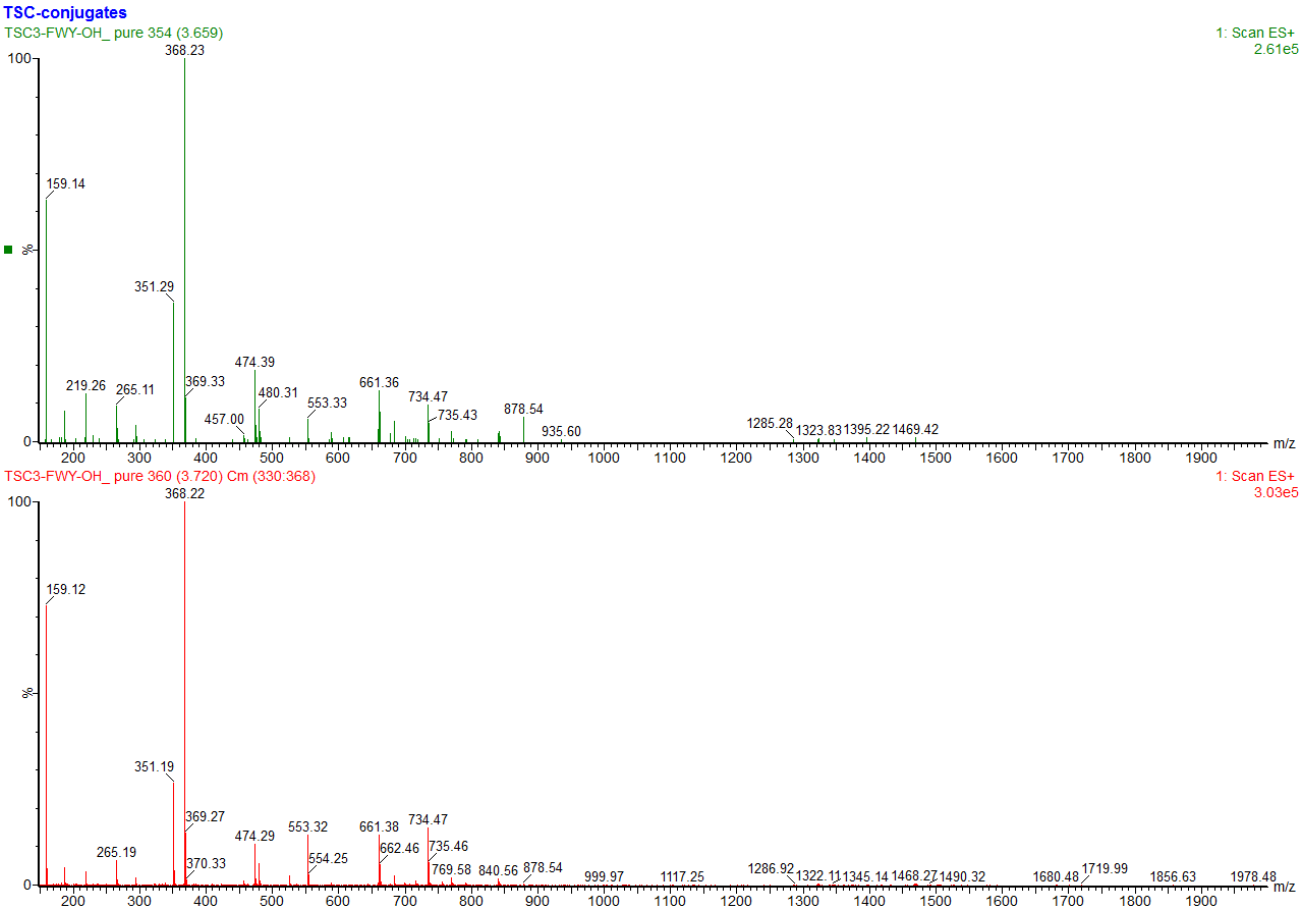


Figure SI 63. Chromatogram of **56** and MS spectra of the peaks found.


TSC-conjugates
TSC3-FWY-OH_ pure
2: Diode Array
Range: 6.135e+1
3.45
3.68
AU
6.0e+1
5.0e+1
4.0e+1
3.0e+1
2.0e+1
1.0e+1
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00


TSC-conjugates
TSC3-FWY-OH_ pure 354 (3.659)
1: Scan ES+
2.61e5
368.23
159.14
351.29
474.39
219.26
265.11
369.33
480.31
553.33
661.36
734.47
735.43
878.54
457.00
935.60
1285.28
1323.83
1395.22
1469.42
%
m/z
TSC3-FWY-OH_ pure 360 (3.720) Cm (330:368)
1: Scan ES+
3.03e5
368.22
159.12
351.19
369.27
474.29
553.32
661.38
734.47
265.19
370.33
554.25
662.46
735.46
769.58
840.56
878.54
999.97
1117.25
1286.92
1322.11
1345.14
1468.27
1490.32
1680.48
1719.99
1856.63
1978.48

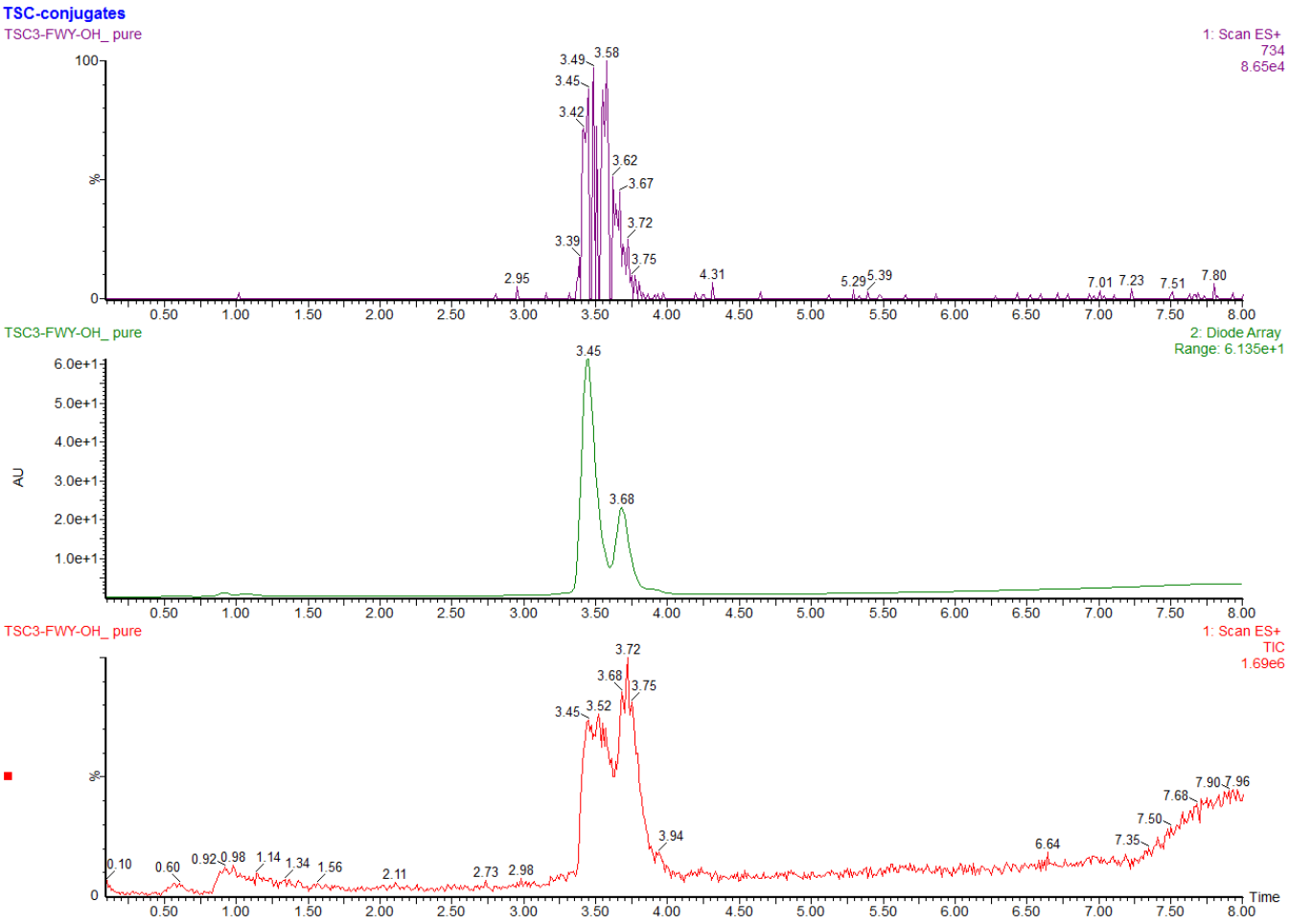


Figure SI 64. Chromatogram of **57** and MS spectra of the peaks found. The last set of spectra represents the search results of the signal *m/z*=734.

Chapter 2: Circular Dichroism (CD)

2.1 Analyses of compounds 8-9 and 11-26

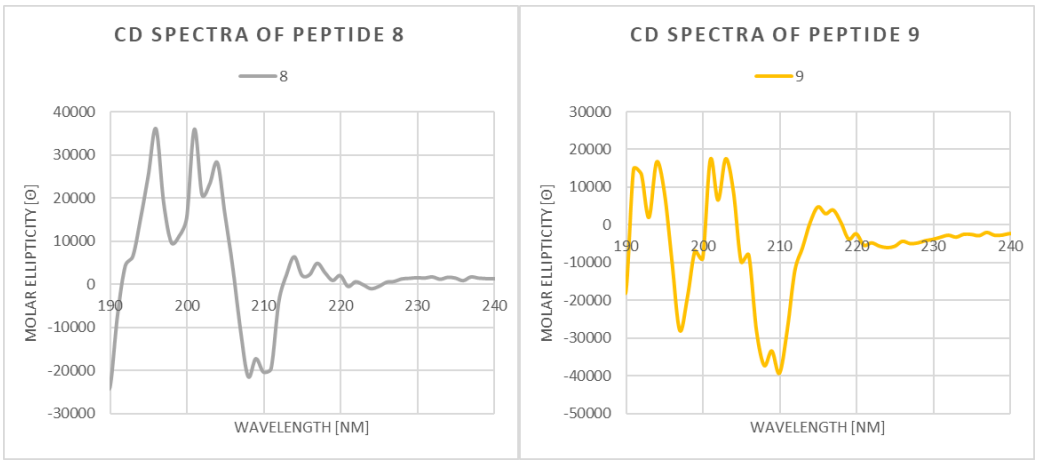


Figure SI 65. Single CD spectra registered for compounds **8** and **9**.

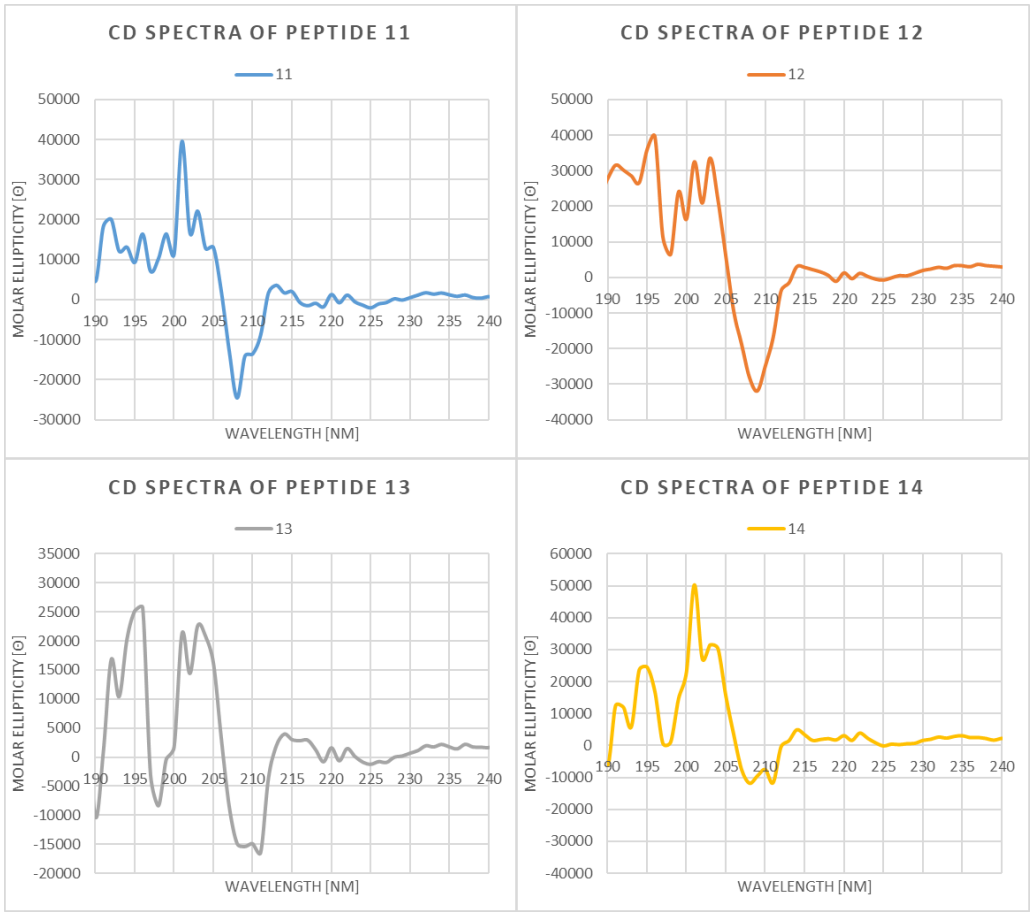


Figure SI 66. Single CD spectra registered for compounds **11-14**.

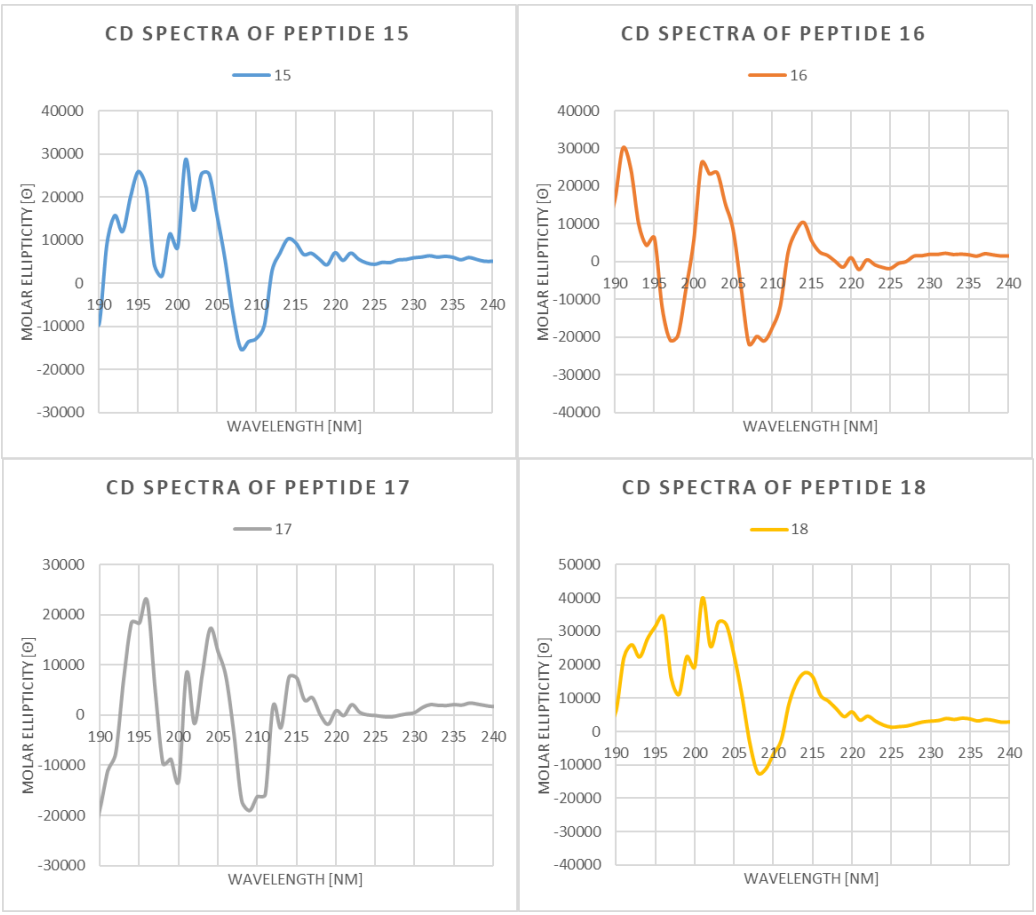


Figure SI 67. Single CD spectra registered for compounds **15-18**.

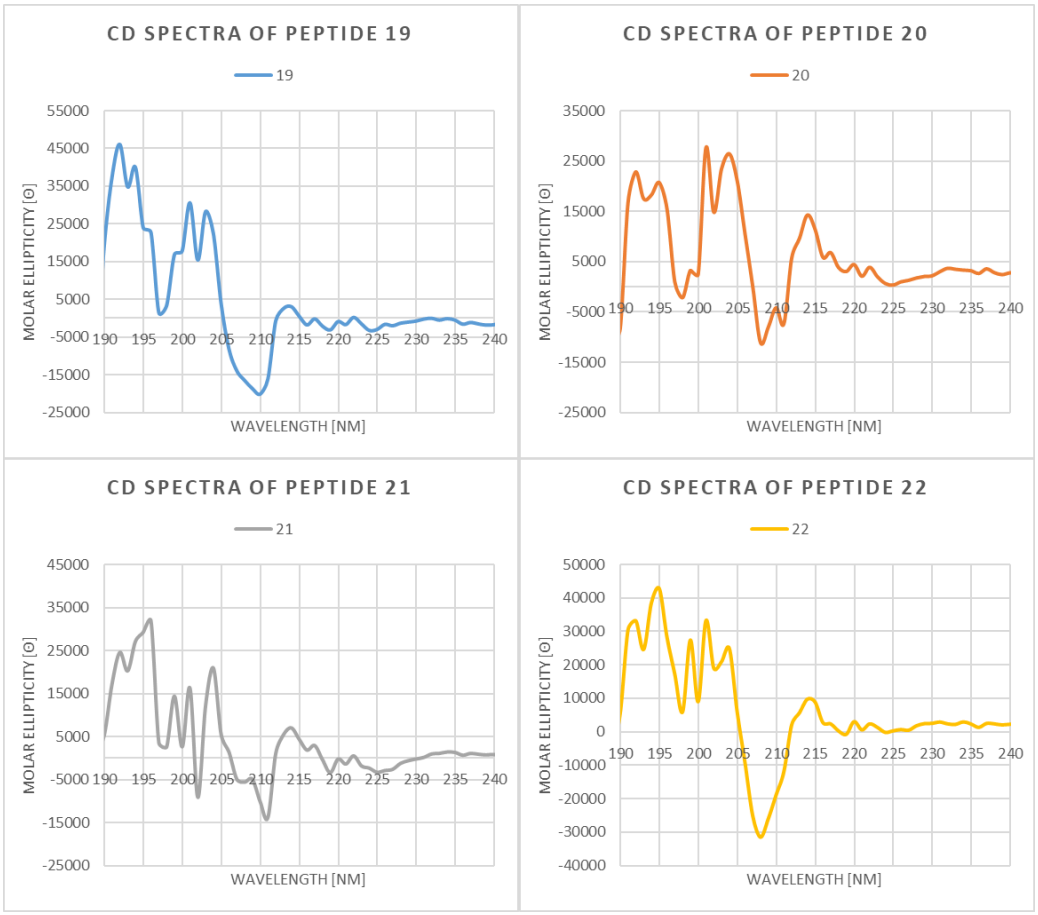


Figure SI 68. Single CD spectra registered for compounds **19-22**.

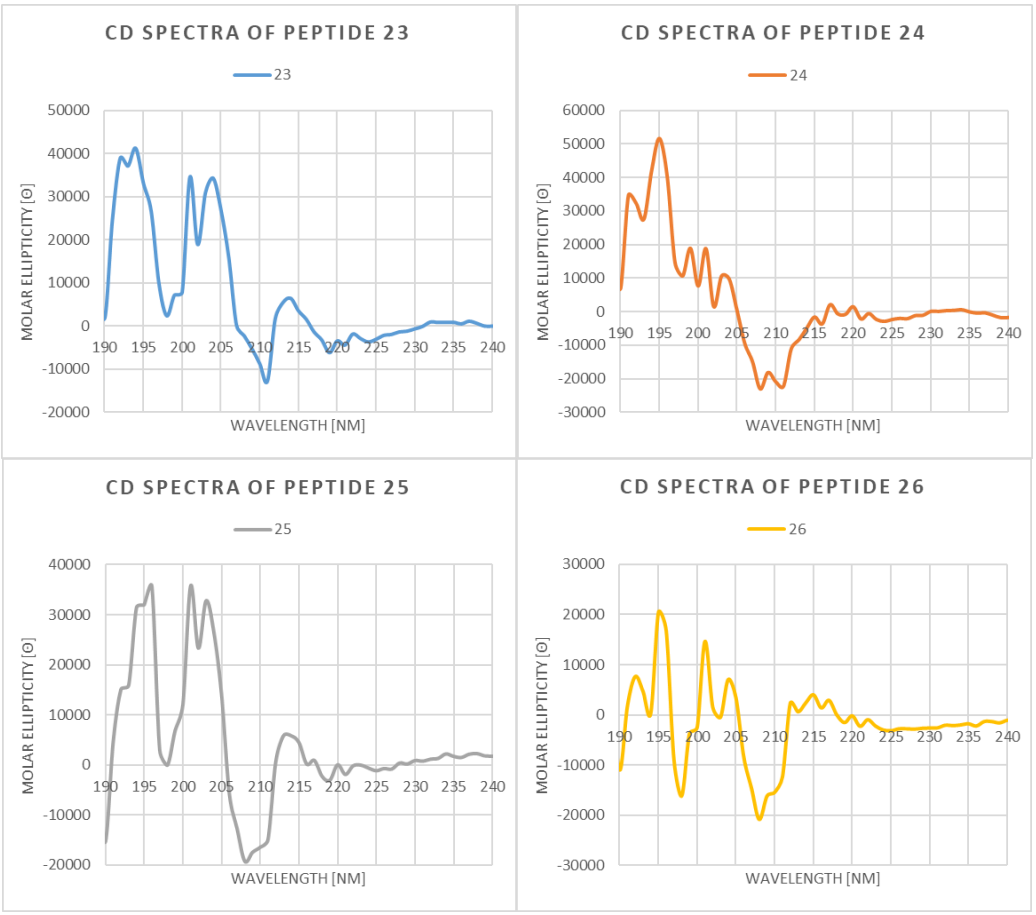


Figure SI 69. Single CD spectra registered for compounds **23-26**.

Chapter 3: Nuclear Magnetic Resonance (NMR)

3.1 ^{1}H-NMR of compound 3

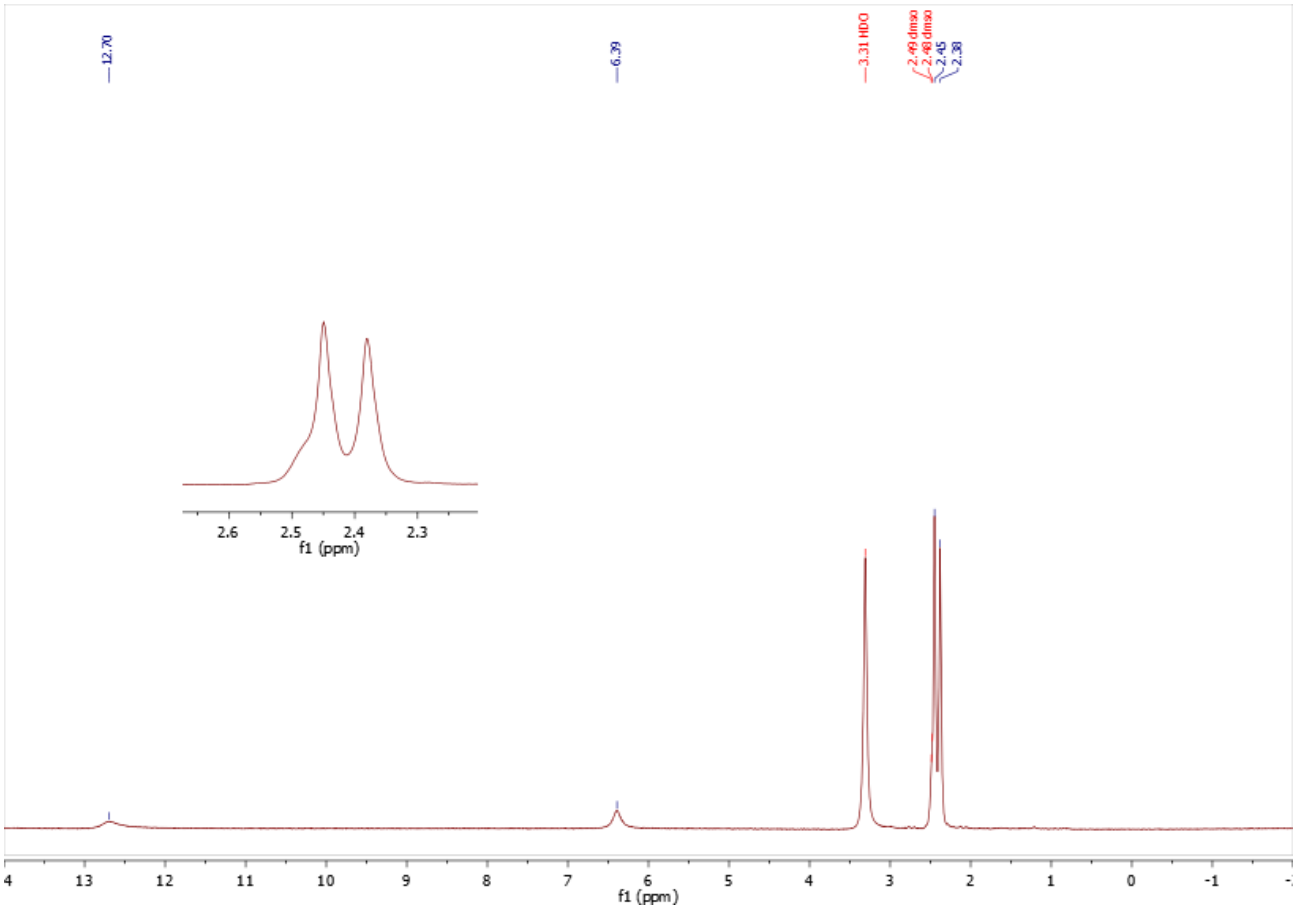


Figure SI 70. ^{1}H NMR spectra of 4,6-dimethylisoxazolo[3,4-*b*]pyridin-3(1*H*)-one **(3)** in DMSO-d_6.

Chemical shifts in ppm: δ=2.38 (s, 3H, CH_3), lit. 2.38; δ=2.45 (s, 3H, CH_3), lit. 2.45; δ=6.39 (s, 1H, CH), lit. 6.38; δ=12.70 (bs, 1H, NH), lit. 13.00. (b)s-(broad) singlet.

3.2 Chemical shifts values found in the spectra of compounds 4a-7a and 8-26

Table SI 1. Chemical shift values (ppm) from ^{1}H and ^{13}C spectra, assigned for building blocks **4a-7a.**

4a

	(C)H	(C)H2	(C)H3	C	C(H(3	C(H)	C(H)2	C(H)3	COO(H)	Ca	Cb	Cc	Cd	Ce	Cg	H	Ha	Hb	Hc	Hd	He	Hg	NH(Het)
A	-	-	17.78	-	-	-	-	2.290	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	109.7	-	-	-	-	6.103	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	19.39	-	2.168	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	76.96	-	-	-	-	5.750	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DMSO	-	-	-	39.45	-	-	-	-	-	-	-	-	-	-	-	2.501	-	-	-	-	-	-	-
E	-	72.32	-	-	-	-	5.771	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F	-	64.37	-	-	-	-	3.655	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fmoc	46.42	65.36	-	-	-	4.219	4.279	-	-	125.1	126.9	127.4	120.0	-	-	-	7.718	7.331	7.422	7.896	-	-	-
L	28.18	-	-	-	-	1.791	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Lys	-	-	-	-	-	-	-	-	8.207	38.07	28.19	-	30.20	53.58	22.74	-	3.204	1.613	-	1.727	3.853	1.438	7.627
M	-	-	20.21	-	-	-	-	0.9125	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

5a

	(C)H	(C)H2	(C)H3	C	C(H(3	C(H)	C(H)2	C(H)3	C2	COO(H)	Ca	Cb	Cc	Cd	Ce	Cg	H	Ha	Hb	Hc	Hd	He	Hg	NH(Het)
A	-	-	17.75	-	-	-	-	2.277	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	110.0	-	-	-	-	6.104	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	19.40	-	2.160	-	-	2.180	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	74.01	-	-	-	-	5.876	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DMSO	-	-	-	39.47	-	-	-	-	-	-	-	-	-	-	-	-	2.500	-	-	-	-	-	-	-
F	-	65.37	-	-	-	-	3.776	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fmoc	46.45	67.78	-	-	-	4.217	4.275	-	109.4	-	125.1	126.9	127.4	119.9	-	-	-	7.720	7.331	7.421	7.898	-	-	-
Lys	-	-	-	-	-	-	-	-	-	8.177	38.11	28.10	-	30.12	53.59	22.72	-	3.176	1.614	-	1.708	3.910	1.428	7.631

6a

	(C)H	(C)H2	(C)H3	C	C(H)	C(H)2	C(H)3	COO(H)	Ca	Cb	Cc	Cd	Ce	Cg	H	Ha	Hb	Hc	Hd	He	Hg	NH(Het)
A	-	-	17.77	-	-	-	2.296	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	110.4	-	-	-	6.152	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	19.44	-	-	-	2.195	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	75.98	-	-	-	5.854	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DMSO	-	-	-	39.49	-	-	-	-	-	-	-	-	-	-	2.498	-	-	-	-	-	-	-
E	-	61.13	-	-	-	3.934	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F	-	63.55	-	-	-	3.629	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fmoc	46.43	65.38	-	-	4.219	4.273	-	-	125.1	126.9	127.4	120.0	-	-	-	7.723	7.329	7.418	7.922	-	-	-
Lys	-	-	-	-	-	-	-	8.199	38.16	-	-	30.15	53.52	28.25	-	3.215	1.632	-	1.734	3.925	1.494	7.628

7a

	(C)H	(C)H2	(C)H3	C	C(H)	C(H)2	C(H)3	COO(H)	Ca	Cb	Cc	Cd	Ce	Cg	H	Ha	Hb	Hc	Hd	He	Hg	NH(Het)
A	-	-	17.72	-	-	-	2.327	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	109.6	-	-	-	6.074	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	19.23	-	-	-	2.143	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	69.33	-	-	-	5.761	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DMSO	-	-	-	39.48	-	-	-	-	-	-	-	-	-	-	2.499	-	-	-	-	-	-	-
Fmoc	46.44	65.38	-	-	4.219	4.275	-	-	125.1	126.9	127.4	120.0	-	-	-	7.721	7.327	7.418	7.923	-	-	-
G	59.10	-	-	-	3.518	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H+I	-	-	15.49	-	-	-	1.307	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
J	-	59.16	-	-	-	3.617	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
K	-	-	7.416	-	-	-	1.228	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Lys	-	-	-	-	-	-	-	8.283	38.24	28.38	-	30.12	53.60	22.71	-	3.168	1.614	-	1.713	3.904	1.440	7.616

Table SI 2. Chemical shift values (ppm) from ^{1}H and ^{13}C spectra, assigned for unmodified peptides **8-9**.

8

	(C)OCH	-(C)H3	-C(H)3	C	C=O	CO(C)H	COCH3	CONH2a	CONH2b	Ca	Cb	Cd	Cg	H	Ha	Hb	Hb*	Hd	He	Hg	NH	NH2
DMSO	-	-	-	39.51	-	-	-	-	-	-	-	-	-	2.500	-	-	-	-	-	-	-	-
Gly	-	-	-	-	168.6	-	-	-	-	41.83	-	-	-	-	3.697	-	-	-	-	-	8.222	-
Lys	-	-	-	-	171.4	-	-	-	-	38.60	26.48	31.47	21.95	-	2.736	1.503	-	1.642	4.316	1.261	7.630	7.851
Met	169.9	14.52	2.029	-	171.8	22.36	1.854	-	-	52.15	31.16	-	29.47	-	4.255	1.798	1.900	-	-	2.469	8.143	-
Val	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.8288	-	-
Val1	-	-	-	-	171.2	-	-	-	-	57.92	29.93	-	18.90	-	4.135	1.995	-	-	-	-	7.913	-
Val2	-	-	-	-	172.7	-	-	7.036	7.350	57.30	30.34	-	18.00	-	4.096	1.939	-	-	-	-	7.585	-

9

	C	C=O	CO(C)H	COCH3	CONH2a	CONH2b	Ca	Cb	Cd	Ce	Cg	H	Ha	Hb	Hb*	Hd	Hd*	He	Hg	NH	NH2
DMSO	39.47	-	-	-	-	-	-	-	-	-	-	2.499	-	-	-	-	-	-	-	-	-
Gly	-	168.8	-	-	-	-	41.84	-	-	-	-	-	3.699	-	-	-	-	-	-	8.308	-
Lys	-	171.3	-	-	-	-	38.60	26.47	31.13	51.97	21.95	-	2.731	1.507	-	1.643	-	4.332	1.265	7.694	7.906
Pro	-	172.3	22.17	1.888	-	-	59.41	22.26	47.47	-	31.39	-	4.226	1.779	1.833	3.558	3.486	-	2.120	-	-
Val	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.8352	-	-
Val1	-	170.6	-	-	-	-	57.80	29.96	-	-	18.81	-	4.139	1.994	-	-	-	-	-	8.008	-
Val2	-	172.5	-	-	7.039	7.339	57.25	30.52	-	-	17.84	-	4.093	1.945	-	-	-	-	-	7.578	-

Table SI 3. Chemical shift values (ppm) from ^{1}H and ^{13}C spectra, assigned for modified peptide **10**.

10

	(C)H	(C)H2	(C)H3	C(H)	C(H)2	C(H)3	CON(H(	COO(H)	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hd	He	Hg	N(H)2	NH
A	-	-	17.65	-	-	2.399	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	111.9	-	-	6.188	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	19.78	-	-	2.280	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	72.54	-	-	5.789	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	-	42.24	-	-	-	-	3.908	-	-	-	-	-	8.525
Het	-	-	-	-	-	-	-	8.917	-	-	-	-	-	-	-	-	-	-	-	-
Lys	-	-	-	-	-	-	-	-	39.32	26.31	30.40	53.44	21.87	2.947	1.660	1.740	4.302	1.385	8.160	7.479
Pro	-	-	-	-	-	-	-	-	69.88	-	42.90	-	29.86	4.046	1.994	3.876	-	2.041	-	-
Val	-	-	-	-	-	-	-	-	-	29.88	-	-	-	-	1.988	-	-	0.9330	-	-
Val1	-	-	-	-	-	-	-	-	59.61	-	-	-	18.16	4.109	-	-	-	0.9090	-	8.279
Val2	-	-	-	-	-	-	7.098	-	59.37	-	-	-	17.72	4.029	-	-	-	0.8910	-	8.226

Table SI 4. Chemical shift values (ppm) from ^{1}H and ^{13}C spectra, assigned for modified peptides **11-14**.

11

	(C)H	(C)H2	(C)H3	(C)ONH	-(C)H3	-C(H)3	C(H)	C(H)2	C(H)3	C1	C2	C3	C4	C=O	CONH2	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hb*	Hd	He	Hg	NH	NH2
A	-	-	17.81	-	-	-	-	-	2.312	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	111.8	-	-	-	-	-	6.192	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	19.11	-	-	-	-	-	2.221	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	77.82	-	-	-	-	-	5.711	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E	-	73.10	-	-	-	-	-	5.748	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F	-	65.47	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	-	-	-	-	-	-	173.8	-	42.48	-	-	-	-	3.965	-	-	-	-	-	8.543	-
L	28.49	-	-	-	-	-	1.860	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Lys	-	-	-	-	-	-	-	-	-	-	-	-	-	170.9	-	39.40	26.40	30.60	53.08	22.00	2.945	1.636	-	1.716	4.318	1.367	-	8.166
M	-	-	19.89	-	-	-	-	-	1.007	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Met	-	-	-	-	14.05	2.104	-	-	-	-	-	-	-	166.3	-	-	26.72	-	-	29.26	-	1.805	1.859	-	-	2.658	8.951	-
Ring	-	-	-	-	-	-	-	-	-	109.7	144.1	154.2	155.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Val	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	17.90	-	-	-	-	-	0.8978	-	-
Val1	-	-	-	-	-	-	-	-	-	-	-	-	-	173.5	-	59.65	30.22	-	-	-	4.094	2.171	-	-	-	-	8.238	-
Val2	-	-	-	175.7	-	-	-	-	-	-	-	-	-	-	7.090	59.41	29.89	-	-	17.85	4.045	2.014	-	-	-	-	7.623	-

12

	(C)H	(C)H2	(C)H3	(C)ONH	-(C)H3	-C(H)3	C(H)	C(H)2	C(H)3	C1	C2	C3	C4	C=O	CONH2	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hb*	Hd	He	Hg	NH	NH2
A	-	-	17.80	-	-	-	-	-	2.287	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	112.2	-	-	-	-	-	6.217	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	19.49	-	-	-	-	-	2.254	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	77.10	-	-	-	-	-	5.842	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E	-	-	-	-	-	-	-	6.360	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F	-	-	-	-	-	-	-	6.074	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	-	-	-	-	-	-	173.7	-	42.36	-	-	-	-	3.971	-	-	-	-	-	8.535	-
Lys	-	-	-	-	-	-	-	-	-	-	-	-	-	171.0	-	39.40	26.41	30.57	53.01	21.87	2.932	1.623	-	1.725	4.366	1.370	7.479	8.177
Met	-	-	-	-	14.13	2.122	-	-	-	-	-	-	-	166.5	-	64.16	30.41	-	-	29.24	3.862	2.048	2.373	-	-	2.676	8.949	-
Ring	-	-	-	-	-	-	-	-	-	109.8	144.2	155.1	155.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Val	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	17.88	-	-	-	-	-	0.8792	-	-
Val1	-	-	-	-	-	-	-	-	-	-	-	-	-	173.7	-	59.66	30.21	-	-	18.37	4.079	2.101	-	-	-	-	8.230	-
Val2	-	-	-	175.8	-	-	-	-	-	-	-	-	-	-	7.083	59.41	29.96	-	-	17.88	4.029	1.991	-	-	-	-	7.615	-

13

	(C)H	(C)H2	(C)H3	(C)ONH	-(C)H3	-C(H)3	C(H)	C(H)2	C(H)3	C1	C2	C3	C4	C=O	CONH2	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hb*	Hd	He	Hg	NH	NH2
A	-	-	19.67	-	-	-	-	-	2.287	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	112.2	-	-	-	-	-	6.217	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	19.02	-	-	-	-	-	2.254	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	77.10	-	-	-	-	-	5.842	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E	-	-	-	-	-	-	-	6.360	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F	-	-	-	-	-	-	-	6.074	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	-	-	-	-	-	-	173.7	-	42.36	-	-	-	-	3.971	-	-	-	-	-	8.535	-
Lys	-	-	-	-	-	-	-	-	-	-	-	-	-	171.0	-	39.40	26.41	30.57	53.01	21.87	2.932	1.623	-	1.725	4.366	1.370	7.479	8.177
Met	-	-	-	-	14.13	2.122	-	-	-	-	-	-	-	166.5	-	64.16	30.41	-	-	29.24	3.862	2.048	2.373	-	-	2.676	8.949	-
Ring	-	-	-	-	-	-	-	-	-	109.8	144.2	155.1	155.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Val	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	17.88	-	-	-	-	-	0.8792	-	-
Val1	-	-	-	-	-	-	-	-	-	-	-	-	-	173.7	-	59.66	30.21	-	-	18.37	4.079	2.101	-	-	-	-	8.230	-
Val2	-	-	-	175.8	-	-	-	-	-	-	-	-	-	-	7.083	59.41	29.96	-	-	17.88	4.029	1.991	-	-	-	-	7.615	-

14

	(C)H	(C)H2	(C)H3	C(H)	C(H)2	C(H)3	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hd	He	Hg	NH	NH2
A	-	-	-	-	-	2.303	-	-	-	-	-	-	-	-	-	-	-	-
B	111.6	-	-	6.174	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	70.27	-	-	5.720	-	-	-	-	-	-	-	-	-	-	-	-	-
G	60.36	-	-	3.582	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	42.41	-	-	-	-	3.952	-	-	-	-	8.549	-
H+I	-	-	15.53	-	-	1.372	-	-	-	-	-	-	-	-	-	-	-	-
J	-	60.37	-	-	3.711	-	-	-	-	-	-	-	-	-	-	-	-	-
K	-	-	7.262	-	-	1.290	-	-	-	-	-	-	-	-	-	-	-	-
Lys	-	-	-	-	-	-	39.40	26.27	30.56	53.42	21.96	2.935	1.628	1.720	4.310	1.354	7.492	8.159
Met	-	-	14.04	-	-	2.095	-	-	-	-	29.17	4.622	-	-	-	2.658	9.011	-
Val	-	-	-	-	-	-	-	-	-	-	17.80	-	-	-	-	0.9061	-	-
Val1	-	-	-	-	-	-	59.67	30.18	-	-	18.14	4.075	2.073	-	-	2.299	8.240	-
Val2	-	-	-	-	-	-	59.39	30.02	-	-	19.02	4.038	2.066	-	-	-	-	-

Table SI 5. Chemical shift values (ppm) from ^{1}H and ^{13}C spectra, assigned for modified peptides **15-18**.

15

	(C)H	(C)H2	(C)H3	C(H)	C(H)2	C(H)3	C2	C3	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hd	Hd*	He	Hg	NH	NH2
A	-	-	18.09	-	-	2.285	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	111.3	-	-	6.216	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	-	-	-	2.171	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	77.80	-	-	5.730	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E	-	72.99	-	-	5.768	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F	-	-	-	-	6.132	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	-	42.43	-	-	-	-	3.957	-	-	-	-	-	8.597	-
L	27.90	-	-	1.835	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Lys	-	-	-	-	-	-	-	-	39.40	26.50	30.76	53.42	21.94	2.937	1.629	1.721	-	4.317	1.366	7.496	8.121
M	-	-	19.59	-	-	0.9980	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pro	-	-	-	-	-	-	-	-	60.86	24.34	48.49	-	29.86	4.400	1.971	3.522	3.449	-	2.373	-	-
Ring	-	-	-	-	-	-	143.5	152.6	-	-	-	-	-	-	-	-	-	-	-	-	-
Val	-	-	-	-	-	-	-	-	-	-	-	-	17.91	-	-	-	-	-	0.9063	-	-
Val1	-	-	-	-	-	-	-	-	59.59	30.02	-	-	-	4.092	2.018	-	-	-	-	8.270	-
Val2	-	-	-	-	-	-	-	-	59.35	-	-	-	-	4.043	2.006	-	-	-	-	-	-

16

	(C)H	(C)H2	(C)H3	C(H)	C(H)2	C(H)3	C2	C3	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hd	Hd*	He	Hg	NH	NH2
A	-	-	18.25	-	-	2.323	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	110.7	-	-	6.233	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	21.34	-	-	2.234	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	75.53	-	-	5.873	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E	-	-	-	6.681	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F	111.4	-	-	6.173	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	-	42.36	-	-	-	-	3.894	-	-	-	-	-	8.594	-
Lys	-	-	-	-	-	-	-	-	39.38	26.29	30.79	54.19	21.84	2.945	1.640	1.724	-	4.315	1.367	7.508	8.160
Pro	-	-	-	-	-	-	-	-	60.80	24.24	48.48	-	-	4.397	1.981	3.509	3.450	-	2.062	-	-
Ring	-	-	-	-	-	-	143.7	153.7	-	-	-	-	-	-	-	-	-	-	-	-	-
Val	-	-	-	-	-	-	-	-	-	-	-	-	17.88	-	-	-	-	-	0.8784	-	-
Val1	-	-	-	-	-	-	-	-	59.58	29.98	-	-	-	4.085	2.017	-	-	-	-	8.278	-
Val2	-	-	-	-	-	-	-	-	59.03	-	-	-	-	4.065	2.009	-	-	-	-	8.271	-

17

	(C)H	(C)H2	(C)H3	C(H)	C(H)2	C(H)3	C1	C2	C3	Ca	Cb	Cd	Cd*	Ce	Cg	Ha	Ha*	Hb	Hb*	Hd	Hd*	He	Hg	NH	NH2
A	-	-	17.95	-	-	2.317	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	111.5	-	-	6.258	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	18.30	-	-	2.186	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	76.70	-	-	5.889	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E	-	-	-	6.264	6.252	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F	-	-	-	6.179	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	-	-	42.24	-	-	-	-	-	3.994	3.956	-	-	-	-	-	-	8.593	-
Lys	-	-	-	-	-	-	-	-	-	39.40	26.28	30.57	-	53.36	21.97	2.938	-	1.622	-	1.724	-	4.297	1.358	7.495	8.156
Pro	-	-	-	-	-	-	-	-	-	61.42	24.16	46.19	47.59	-	29.86	4.406	-	1.967	1.905	3.624	3.579	-	2.116	-	-
Ring	-	-	-	-	-	-	110.8	143.7	153.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Val	-	-	-	-	-	-	-	-	-	-	-	-	-	-	17.82	-	-	-	-	-	-	-	0.8984	-	-
Val1	-	-	-	-	-	-	-	-	-	59.68	30.26	-	-	-	18.31	4.080	-	2.022	-	-	-	-	-	8.266	-
Val2	-	-	-	-	-	-	-	-	-	59.46	29.95	-	-	-	17.96	4.032	-	2.004	-	-	-	-	-	-	-

18

	(C)H	(C)H2	(C)H3	C(H)	C(H)2	C(H)3	C2	C3	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hd	Hd*	He	Hg	NH	NH2
A	-	-	17.93	-	-	2.312	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	111.3	-	-	6.217	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	-	-	-	2.183	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	70.36	-	-	5.715	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
G	-	-	-	3.622	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	-	42.32	-	-	-	-	3.954	-	-	-	-	-	8.584	-
H+I	-	-	15.63	-	-	1.360	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
J	-	60.42	-	-	3.737	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
K	-	-	-	-	-	1.300	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Lys	-	-	-	-	-	-	-	-	39.41	26.27	30.53	53.29	21.91	2.930	1.618	1.713	-	4.311	1.392	7.497	8.142
Pro	-	-	-	-	-	-	-	-	-	24.25	48.65	-	29.96	4.434	1.970	3.537	3.489	-	2.396	-	-
Ring	-	-	-	-	-	-	143.2	152.6	-	-	-	-	-	-	-	-	-	-	-	-	-
Val	-	-	-	-	-	-	-	-	-	-	-	-	18.10	-	-	-	-	-	0.8994	-	-
Val1	-	-	-	-	-	-	-	-	59.58	30.00	-	-	-	4.085	2.013	-	-	-	-	8.269	-
Val2	-	-	-	-	-	-	-	-	59.40	-	-	-	-	4.040	1.994	-	-	-	-	-	-

Table SI 6. Chemical shift values (ppm) from ^{1}H and ^{13}C spectra, assigned for modified peptides **19-22**.

19

	(C)H	(C)H2	(C)H3	C(H)	C(H)2	C(H)3	COCH3	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hd	He	Hg	NH	NH(Het)
A	-	-	18.37	-	-	2.290	-	-	-	-	-	-	-	-	-	-	-	-	-
B	-	-	-	6.164	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	19.05	-	-	2.196	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	77.87	-	-	5.700	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E	-	73.08	-	-	5.757	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F	-	65.38	-	-	3.638	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	65.75	-	-	-	-	3.599	-	-	-	-	8.557	-
L	28.42	-	-	1.860	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Lys	-	-	-	-	-	-	-	39.60	27.83	30.70	53.61	22.33	3.315	1.593	1.790	4.353	1.391	8.503	8.367
M	-	-	20.09	-	-	0.9900	-	-	-	-	-	-	-	-	-	-	-	-	-
Met	-	-	14.32	-	-	2.037	1.967	42.78	-	-	-	29.50	3.813	2.037	-	-	2.571	8.489	-
Val	-	-	-	-	-	-	-	-	-	-	-	18.05	-	-	-	-	0.8998	-	-
Val1	-	-	-	-	-	-	-	59.78	30.14	-	-	-	4.065	2.030	-	-	-	8.211	-
Val2	-	-	-	-	-	-	-	59.59	-	-	-	-	4.086	1.992	-	-	-	8.168	-

20

	(C)H	(C)H2	(C)H3	C(H)	C(H)2	C(H)3	COCH3	CONH2	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hd	He	Hg	NH	NH(Het)
A	-	-	18.37	-	-	2.274	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	111.6	-	-	6.175	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	19.07	-	-	2.173	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	75.54	-	-	5.832	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F	-	69.21	-	-	3.819	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	8.532	-
Lys	-	-	-	-	-	-	-	-	-	27.77	30.96	53.65	22.37	3.298	1.581	1.745	4.347	1.354	8.024	8.372
Met	-	-	14.37	-	-	2.055	1.965	-	42.84	-	-	-	29.55	3.898	2.036	-	-	2.582	8.497	-
Val	-	-	-	-	-	-	-	-	-	-	-	-	18.11	-	-	-	-	0.9088	-	-
Val1	-	-	-	-	-	-	-	-	59.91	30.33	-	-	-	4.061	2.007	-	-	-	8.217	-
Val2	-	-	-	-	-	-	-	7.692	59.64	-	-	-	-	4.093	-	-	-	-	8.178	-

21

	(C)H	(C)H2	(C)H3	(CH)2	C(H)	C(H)2	C(H)3	COCH3	CONH2	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hd	He	Hg	NH	NH(Het)
A	-	-	18.16	-	-	-	2.247	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	111.8	-	-	-	6.163	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	18.79	-	-	-	2.147	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	76.84	-	-	-	5.796	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E	-	61.72	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E(a)	-	-	-	3.964	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E(b)	-	-	-	4.215	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F	-	64.16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F(a)	-	-	-	3.665	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F(b)	-	-	-	3.806	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.272	-	-	-	-	8.503	-
Lys	-	-	-	-	-	-	-	-	-	39.40	27.54	30.57	53.27	22.11	3.277	1.549	1.738	4.338	1.345	-	8.321
Met	-	-	14.08	-	-	-	2.005	1.969	-	42.57	-	-	-	29.13	3.849	2.002	-	-	2.520	8.444	-
Val	-	-	-	-	-	-	-	-	-	-	-	-	-	17.72	-	-	-	-	0.8675	-	-
Val1	-	-	-	-	-	-	-	-	-	59.73	30.03	-	-	-	4.012	1.976	-	-	-	8.169	-
Val2	-	-	-	-	-	-	-	-	7.978	59.36	-	-	-	-	4.044	1.972	-	-	-	8.127	-

22

	(C)H	(C)H2	(C)H3	C(H)	C(H)2	C(H)3	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hd	He	Hg	NH	NH(Het)
A	-	-	17.49	-	-	2.286	-	-	-	-	-	-	-	-	-	-	-	-
B	111.1	-	-	6.151	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	18.42	-	-	2.153	-	-	-	-	-	-	-	-	-	-	-	-
D	-	69.51	-	-	5.708	-	-	-	-	-	-	-	-	-	-	-	-	-
G	60.23	-	-	3.545	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	-	-	-	-	4.281	-	-	-	-	8.024	-
H+I	-	-	15.07	-	-	1.363	-	-	-	-	-	-	-	-	-	-	-	-
J	-	60.23	-	-	3.718	-	-	-	-	-	-	-	-	-	-	-	-	-
K	-	-	6.973	-	-	1.285	-	-	-	-	-	-	-	-	-	-	-	-
Lys	-	-	-	-	-	-	39.34	27.39	30.40	53.25	22.41	3.307	1.577	1.741	4.383	-	8.621	8.365
Met	-	-	-	-	-	1.993	42.36	-	-	-	29.09	3.913	-	-	-	2.578	8.491	-
Val	-	-	-	-	-	-	-	-	-	-	17.68	-	-	-	-	0.9463	-	-
Val1	-	-	-	-	-	-	-	29.76	-	-	-	4.032	-	-	-	-	8.213	-
Val2	-	-	-	-	-	-	59.28	-	-	-	-	4.084	-	-	-	-	8.166	-

Table SI 7. Chemical shift values (ppm) from ^{1}H and ^{13}C spectra, assigned for modified peptides **23-26**.

23

	(C)H	(C)H2	(C)H3	C(H)	C(H)2	C(H)3	CO(C)H	COC(H)	CONH2	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hb*	Hd	He	Hg	NH	NH(Het)
A	-	-	17.60	-	-	2.269	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	111.2	-	-	6.147	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	18.84	-	-	2.187	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	77.42	-	-	5.675	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E	-	72.67	-	-	5.708	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F	-	65.02	-	-	3.584	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	-	-	42.56	-	-	-	-	3.747	-	-	-	-	-	8.192	-
L	28.09	-	-	1.771	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Lys	-	-	-	-	-	-	-	-	-	39.34	27.57	30.87	54.90	22.35	3.299	1.575	-	1.675	4.107	1.331	8.525	7.657
M	-	-	19.61	-	-	0.9808	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pro	-	-	-	-	-	-	24.07	1.950	-	60.16	21.26	47.67	-	29.71	4.323	1.965	2.079	3.500	-	1.994	-	-
Val1	-	-	-	-	-	-	-	-	-	59.60	29.00	-	-	17.77	4.054	1.840	-	-	-	0.8803	8.055	-
Val2	-	-	-	-	-	-	-	-	7.722	59.32	29.54	-	-	16.38	4.021	1.917	-	-	-	0.9470	7.928	-

24

	(C)H	(C)H2	(C)H3	C(H)	C(H)2	C(H)3	CO(C)H	COC(H)	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hd	Hd*	He	Hg	NH
A	-	-	17.58	-	-	2.276	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	111.2	-	-	6.161	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	18.70	-	-	2.192	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	75.13	-	-	5.817	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F	-	68.77	-	-	3.606	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	-	42.34	-	-	-	-	3.836	-	-	-	-	-	8.465
Lys	-	-	-	-	-	-	-	-	39.36	27.42	30.43	53.60	22.27	3.284	1.574	1.734	-	4.227	1.341	8.529
Pro	-	-	-	-	-	-	24.16	1.965	59.45	21.20	48.52	-	29.70	4.361	2.026	3.493	3.445	-	1.999	8.212
Val	-	-	-	-	-	-	-	-	-	29.62	-	-	-	-	1.933	-	-	-	-	-
Val1	-	-	-	-	-	-	-	-	59.23	-	-	-	18.15	4.081	1.987	-	-	-	0.9263	8.160
Val2	-	-	-	-	-	-	-	-	60.24	-	-	-	17.69	4.036	1.911	-	-	-	0.9400	7.969

25

	(C)H	(C)H2	(C)H3	C(H)	C(H)2	C(H)3	CO(C)H	COC(H)	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hd	He	Hg	NH
A	-	-	17.37	-	-	2.285	-	-	-	-	-	-	-	-	-	-	-	-	-
B	111.5	-	-	6.210	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	18.64	-	-	2.189	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	77.35	-	-	5.813	-	-	-	-	-	-	-	-	-	-	-	-	-	-
E	-	62.67	-	-	3.907	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F	-	64.72	-	-	3.640	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	-	43.16	-	-	-	-	3.871	-	-	-	-	8.262
Lys	-	-	-	-	-	-	-	-	38.63	28.27	30.24	54.79	23.24	3.322	1.577	1.823	4.098	1.345	8.551
Pro	-	-	-	-	-	-	25.06	1.945	59.51	21.10	48.67	-	29.57	4.260	2.024	3.517	-	2.023	-
Val1	-	-	-	-	-	-	-	-	59.13	30.65	-	-	19.02	4.128	1.976	-	-	0.8760	-
Val2	-	-	-	-	-	-	-	-	60.05	30.39	-	-	17.45	4.032	1.915	-	-	0.9820	7.973

26

	(C)H	(C)H2	(C)H3	C(H)	C(H)2	C(H)3	CO(C)H	COC(H)	Ca	Cb	Cd	Ce	Cg	Ha	Hb	Hd	He	Hg	NH	NH(Het)
A	-	-	17.54	-	-	2.279	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B	111.0	-	-	6.141	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	18.51	-	-	2.142	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	-	69.40	-	-	5.710	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
G	-	-	-	3.600	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Gly	-	-	-	-	-	-	-	-	42.34	-	-	-	-	3.893	-	-	-	-	8.262	-
H+I	-	-	15.49	-	-	1.352	-	-	-	-	-	-	-	-	-	-	-	-	-	-
J	-	60.24	-	-	3.808	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
K	-	-	7.021	-	-	1.286	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Lys	-	-	-	-	-	-	-	-	39.42	27.43	30.44	53.65	22.36	3.296	1.573	1.712	4.274	1.365	8.624	8.397
Pro	-	-	-	-	-	-	24.19	1.972	60.24	21.30	48.56	-	29.57	4.301	2.082	3.512	-	2.251	-	-
Val1	-	-	-	-	-	-	-	-	59.46	29.80	-	-	18.16	4.088	2.007	-	-	0.8692	-	-
Val2	-	-	-	-	-	-	-	-	59.23	29.63	-	-	17.70	4.038	1.899	-	-	0.9020	7.976	-

3.3 ^{1}H and ^{13}C-NMR spectra of compounds 4a-7a and 8-26

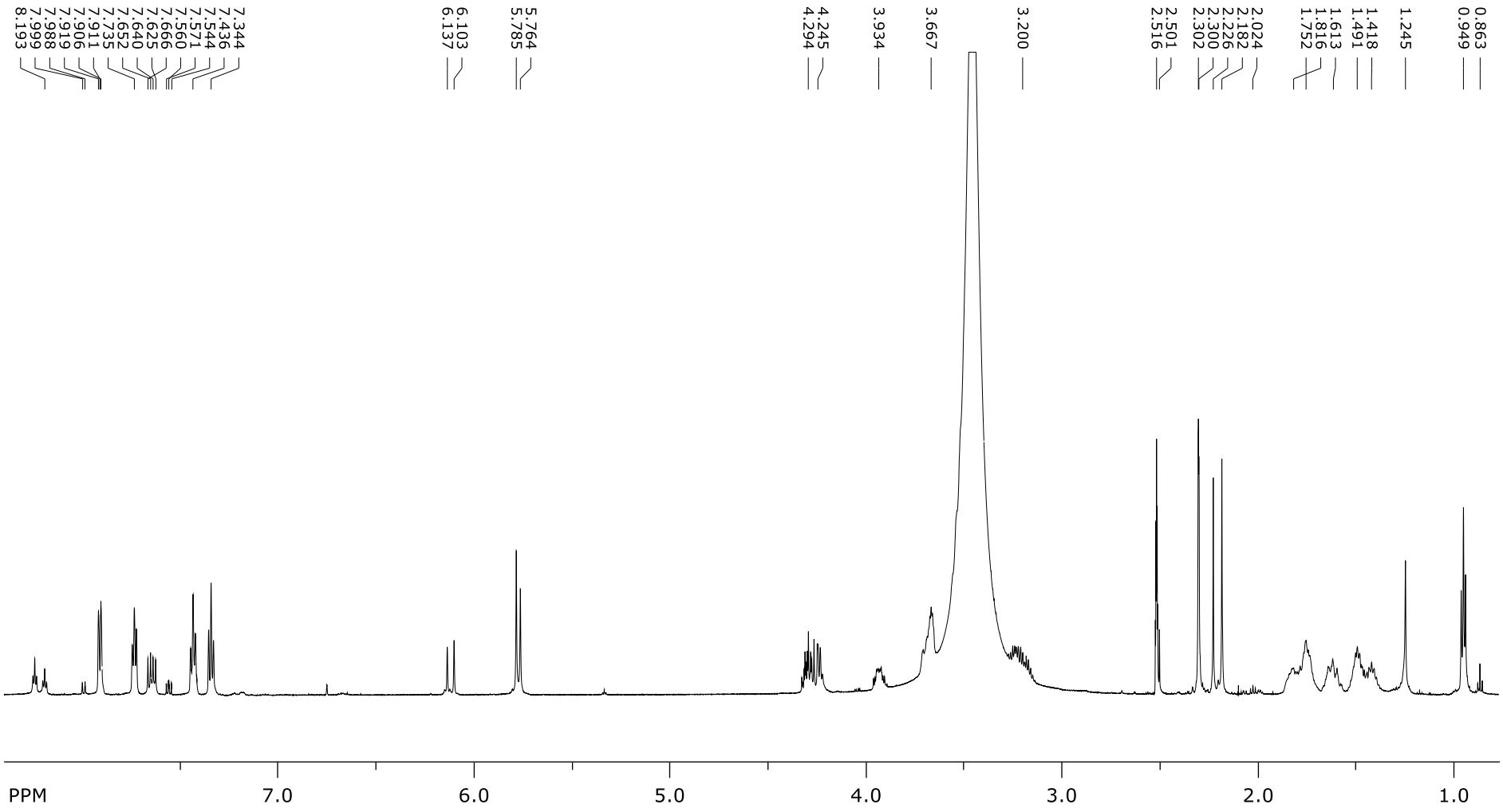


Figure SI 71. ^{1}H-NMR spectrum of **4a**.

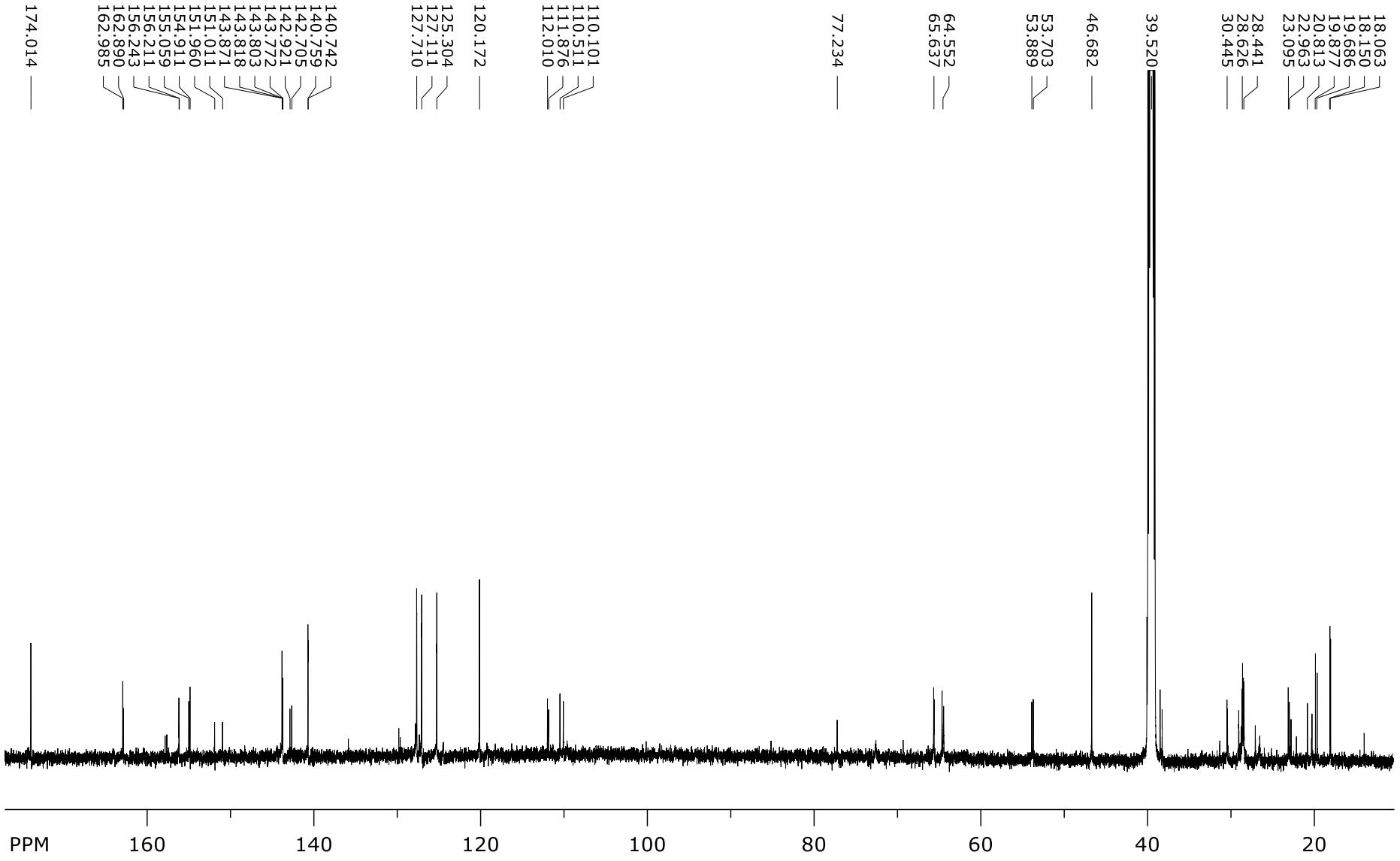


Figure SI 72. ^{13}C-NMR spectrum of **4a**.

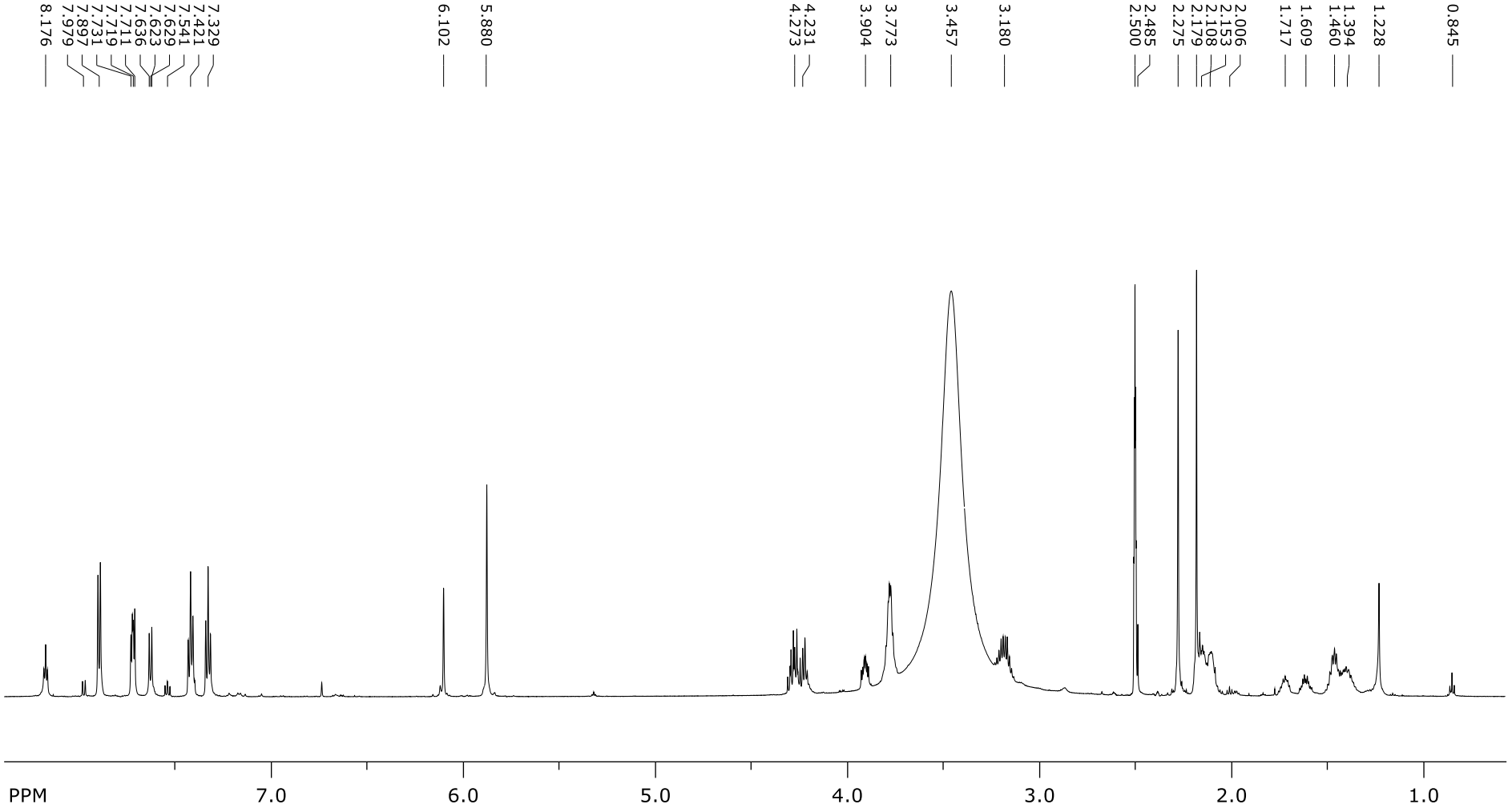


Figure SI 73. ^{1}H-NMR spectrum of **5a**.

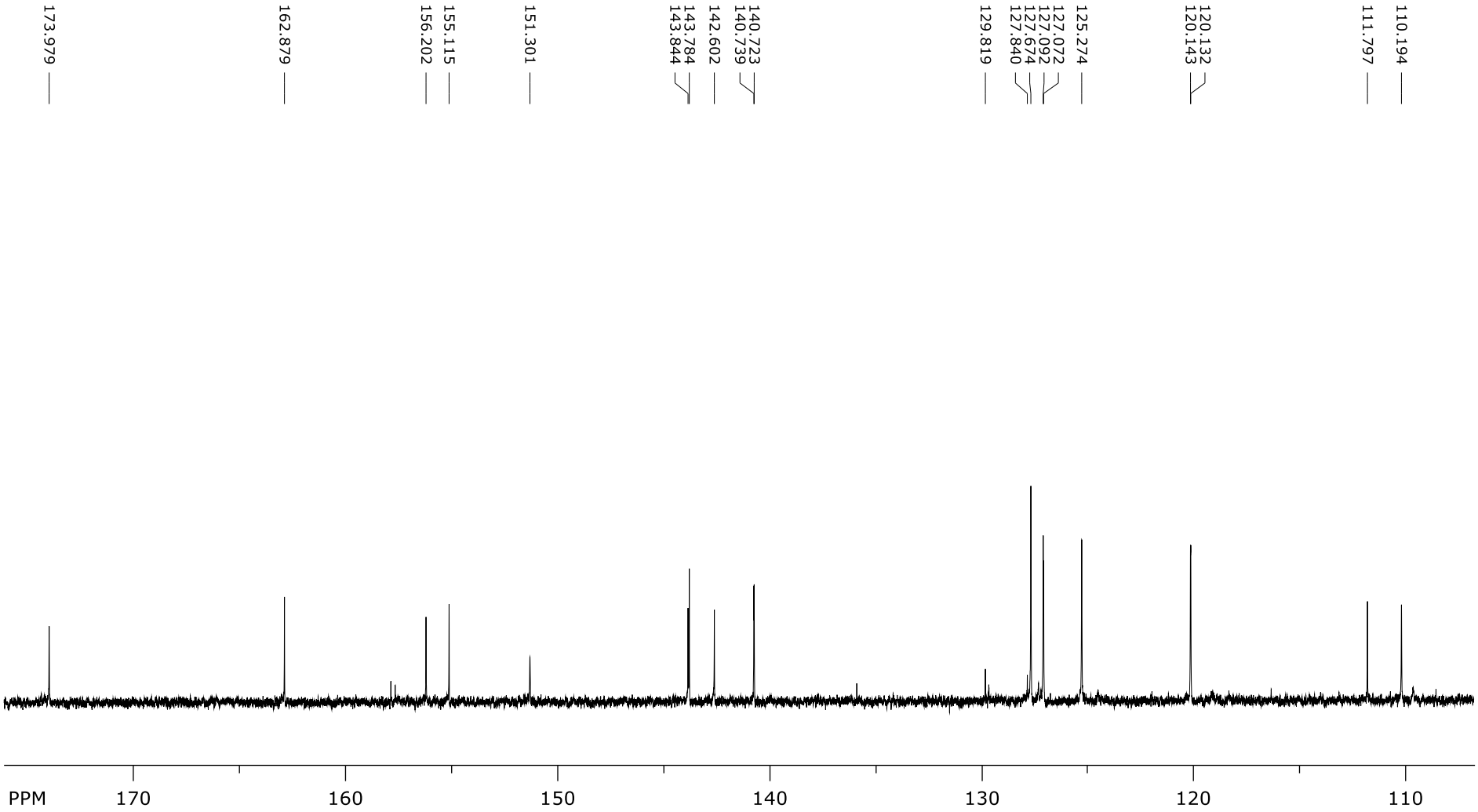


Figure SI 74. ^{13}C-NMR spectrum of **5a**.

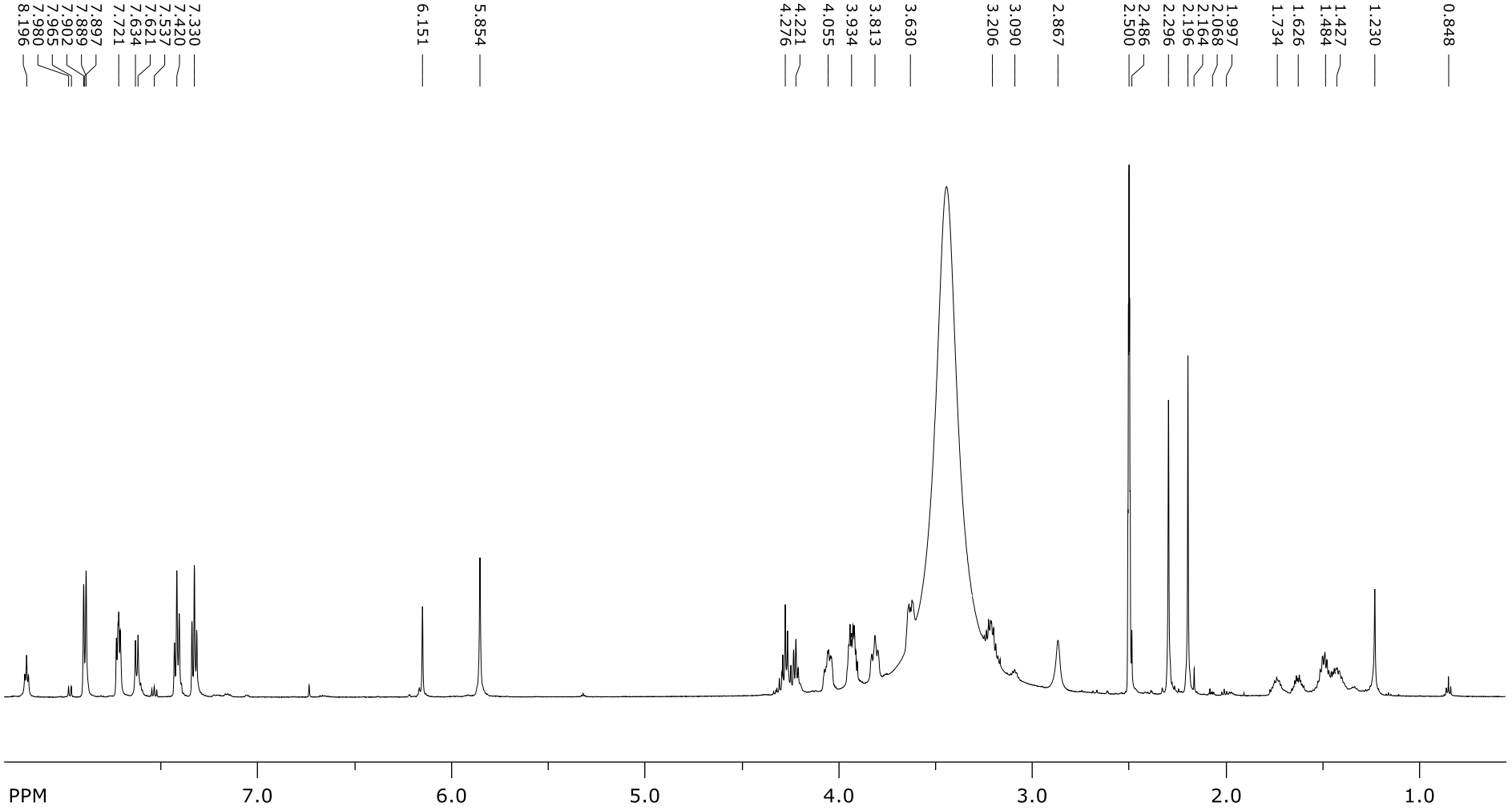


Figure SI 75. ^{1}H-NMR spectrum of **6a**.

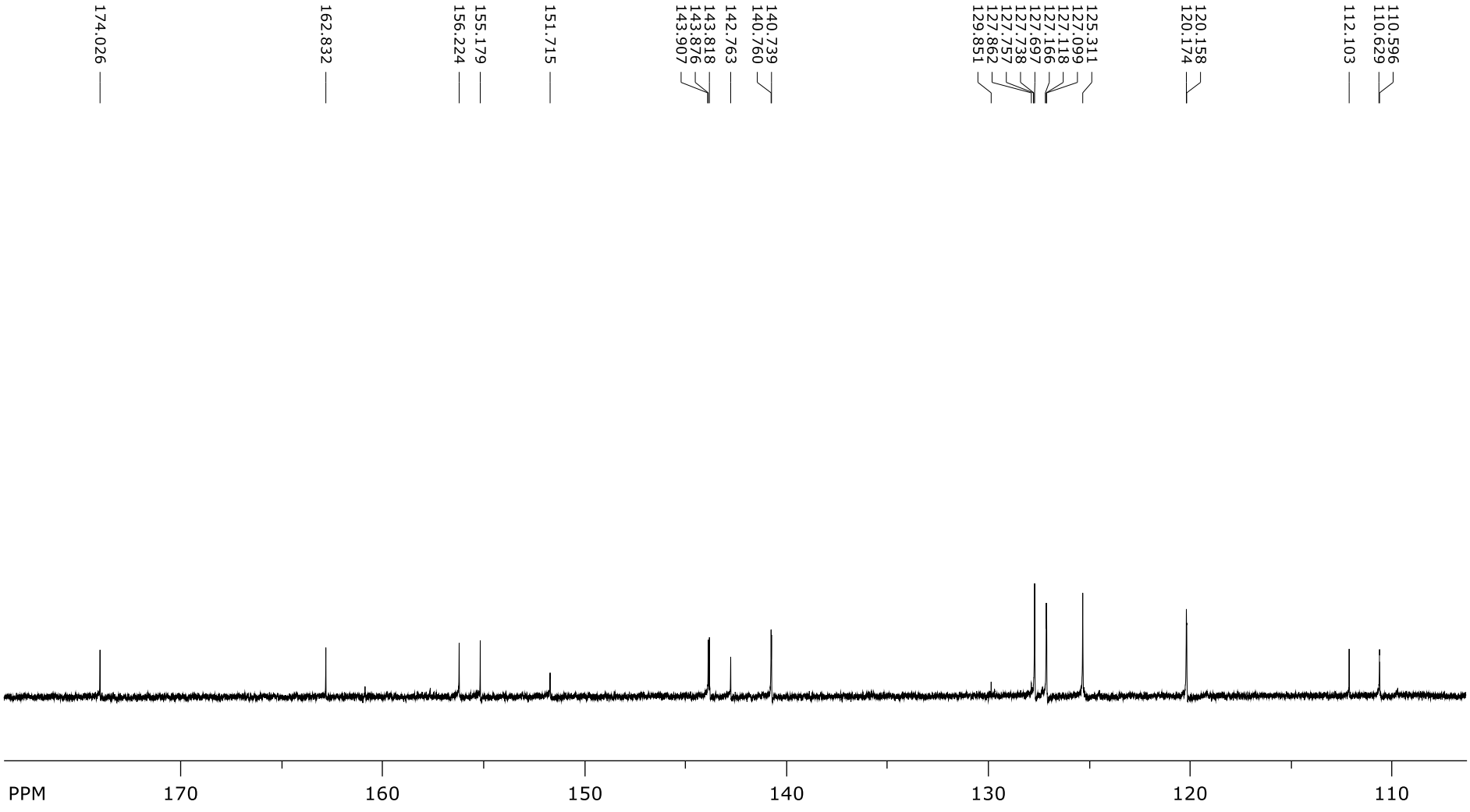


Figure SI 76. ^{13}C-NMR spectrum of **6a**.

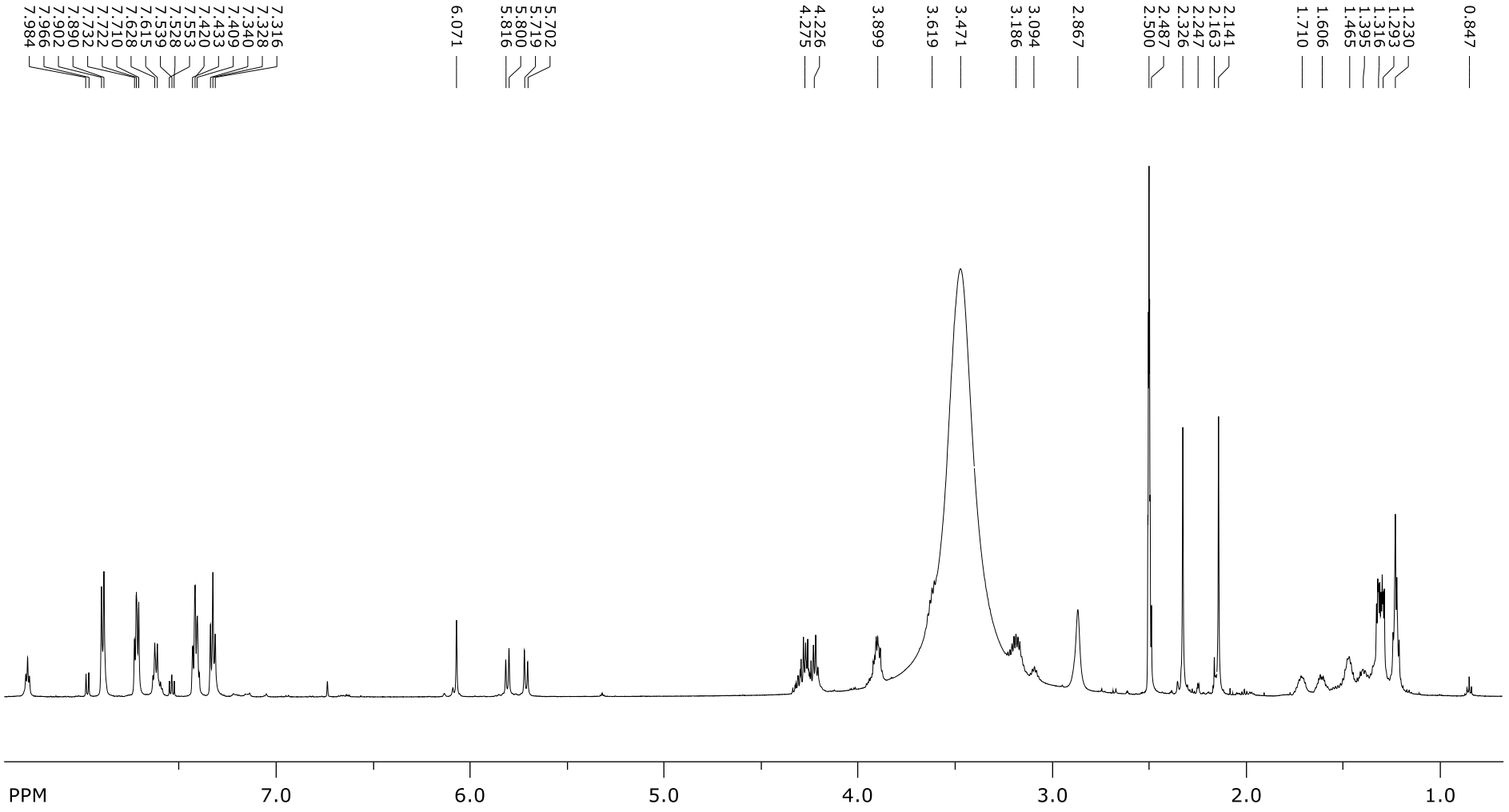


Figure SI 77. ^{1}H-NMR spectrum of **7a**.

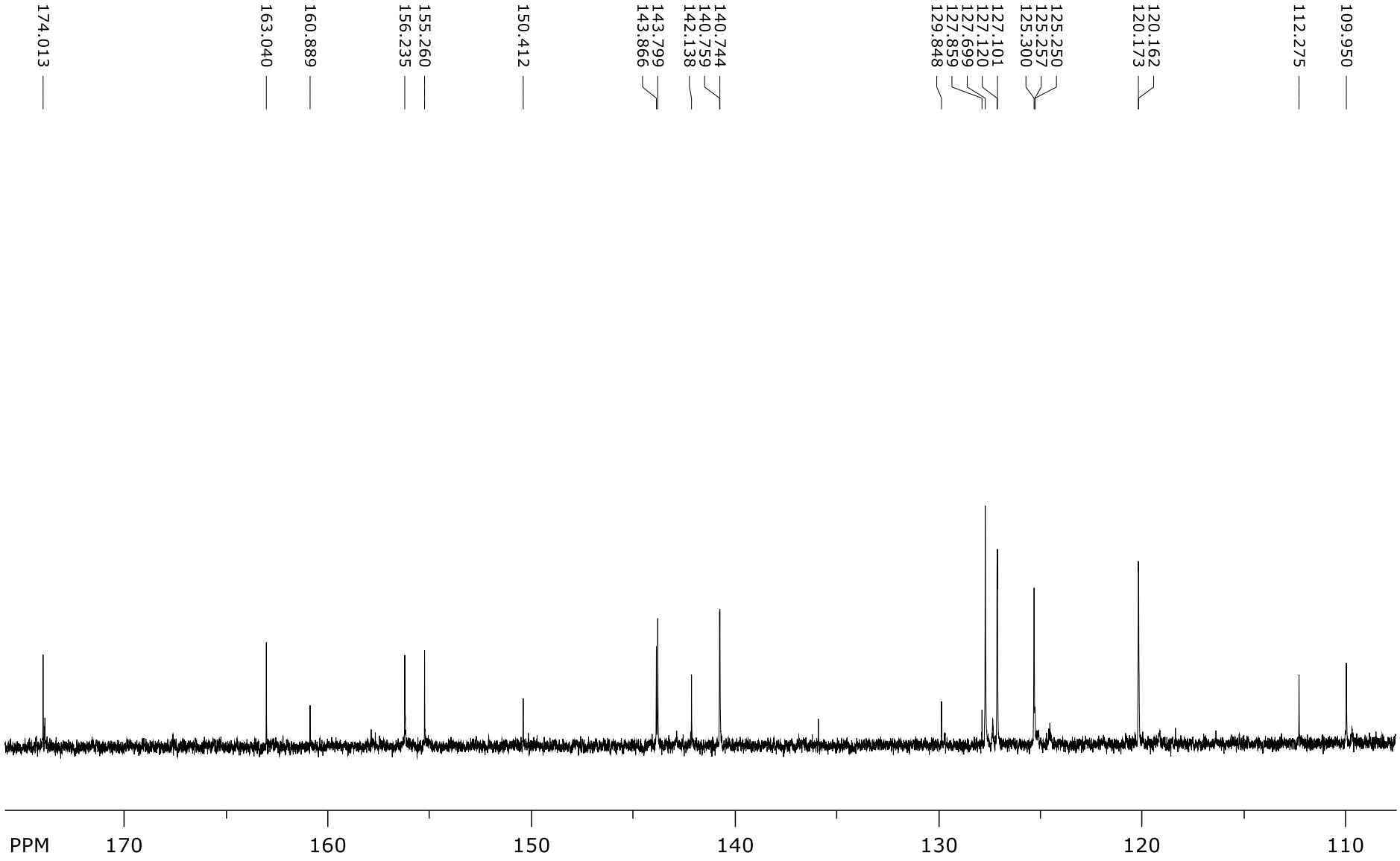


Figure SI 78. ^{13}C-NMR spectrum of **7a**.

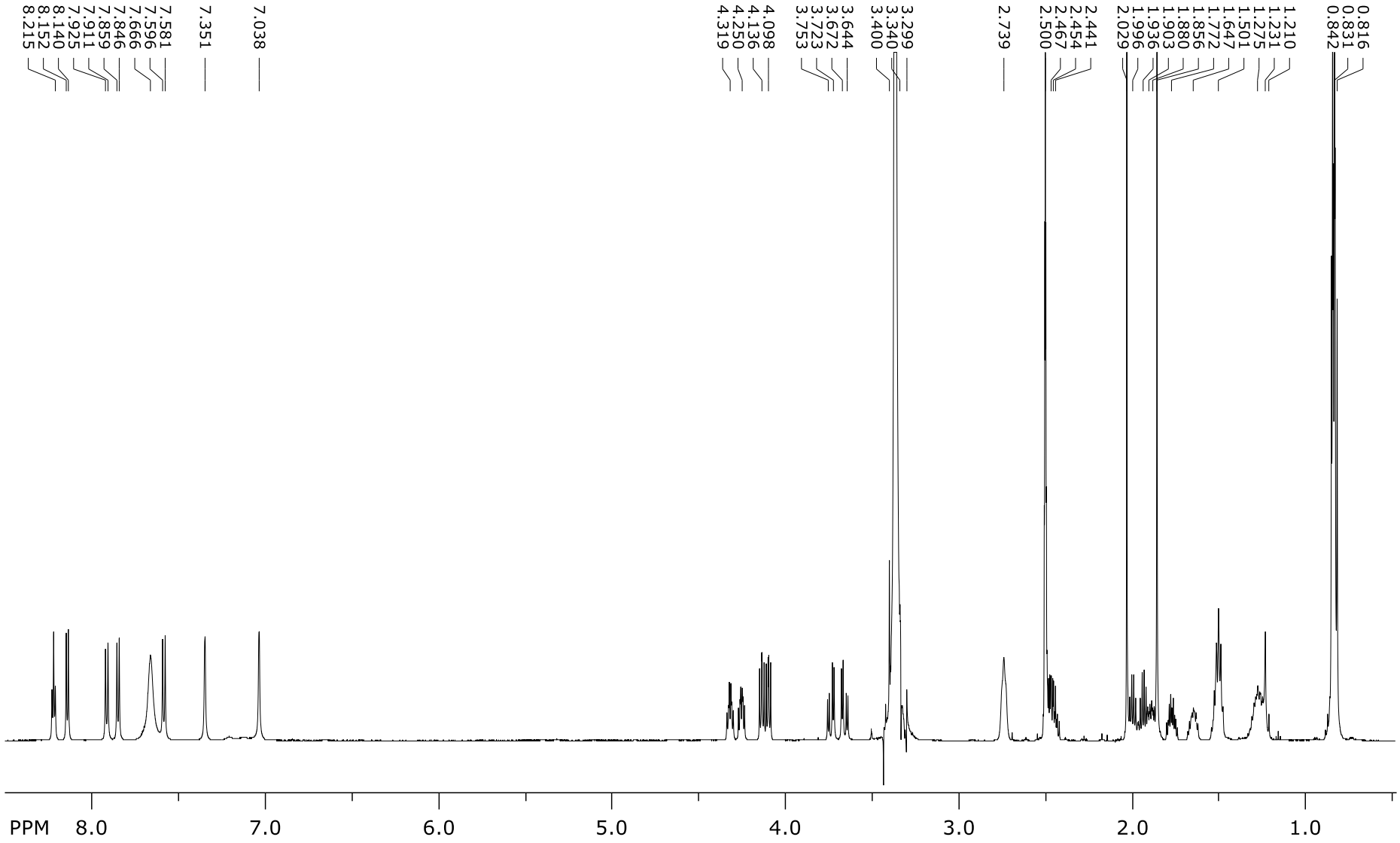


Figure SI 79. ^{1}H-NMR spectrum of **8**.

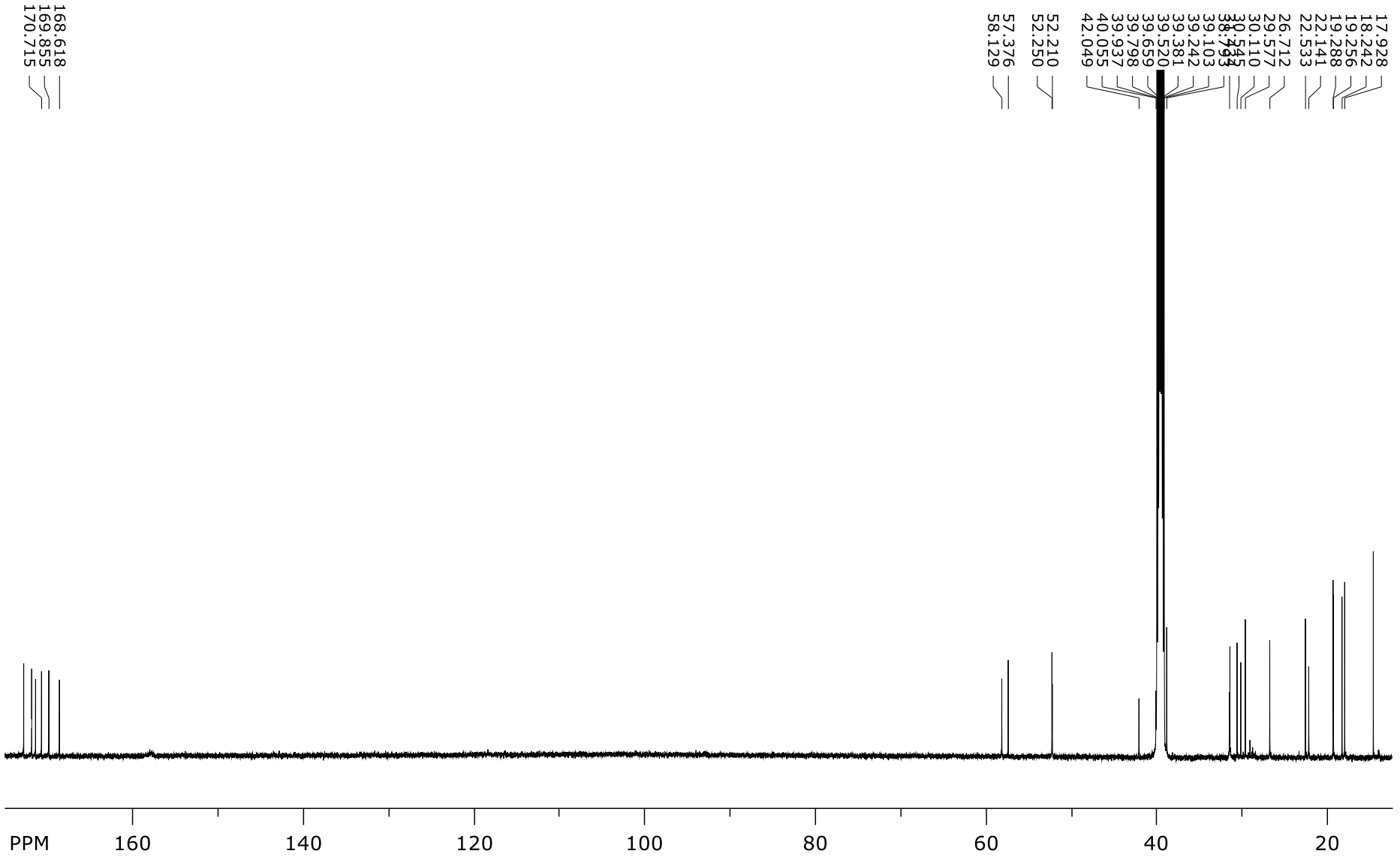


Figure SI 80. ^{13}C-NMR spectrum of **8**.

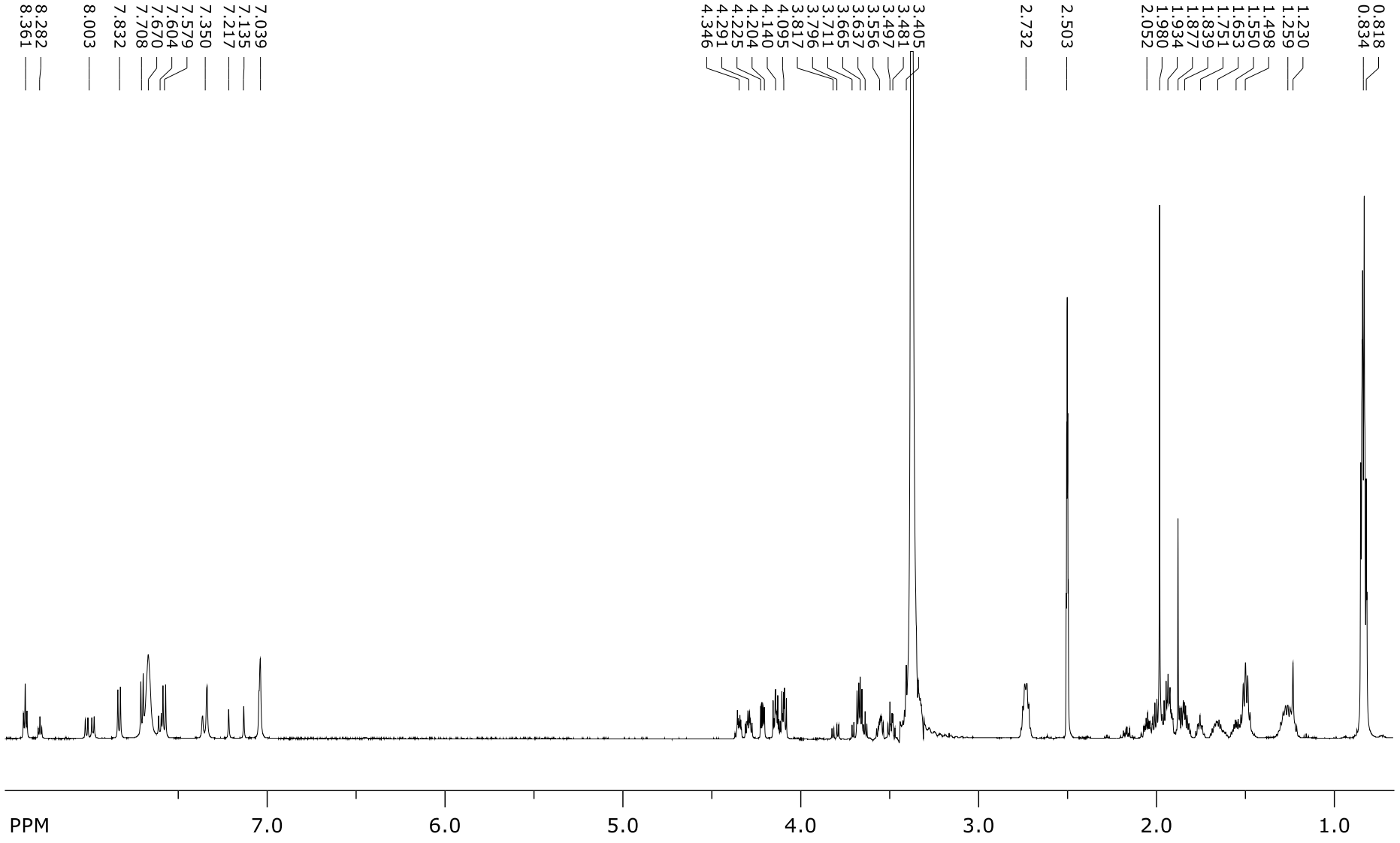


Figure SI 81. ^{1}H-NMR spectrum of **9**.

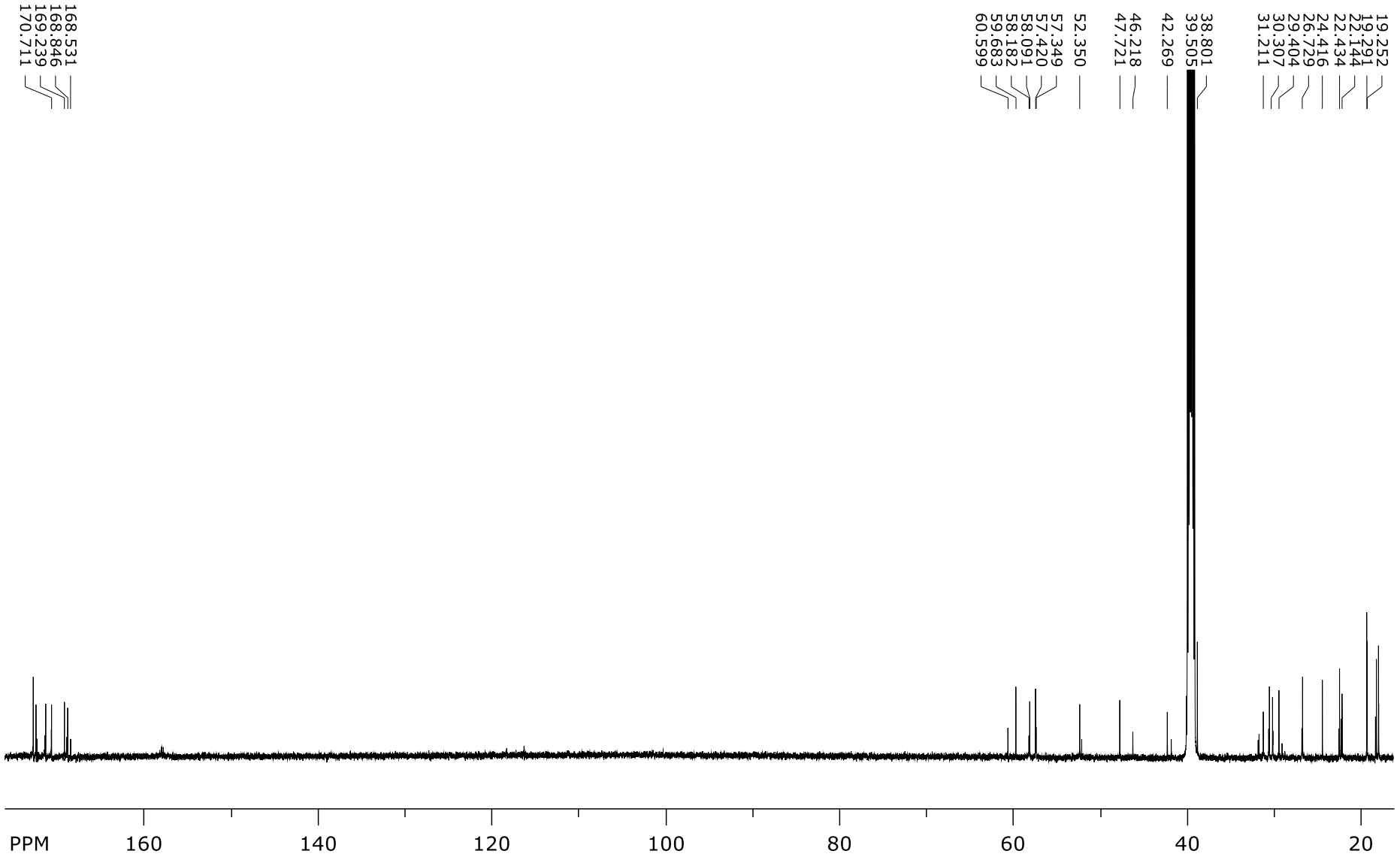


Figure SI 82. ^{13}C-NMR spectrum of **9**.

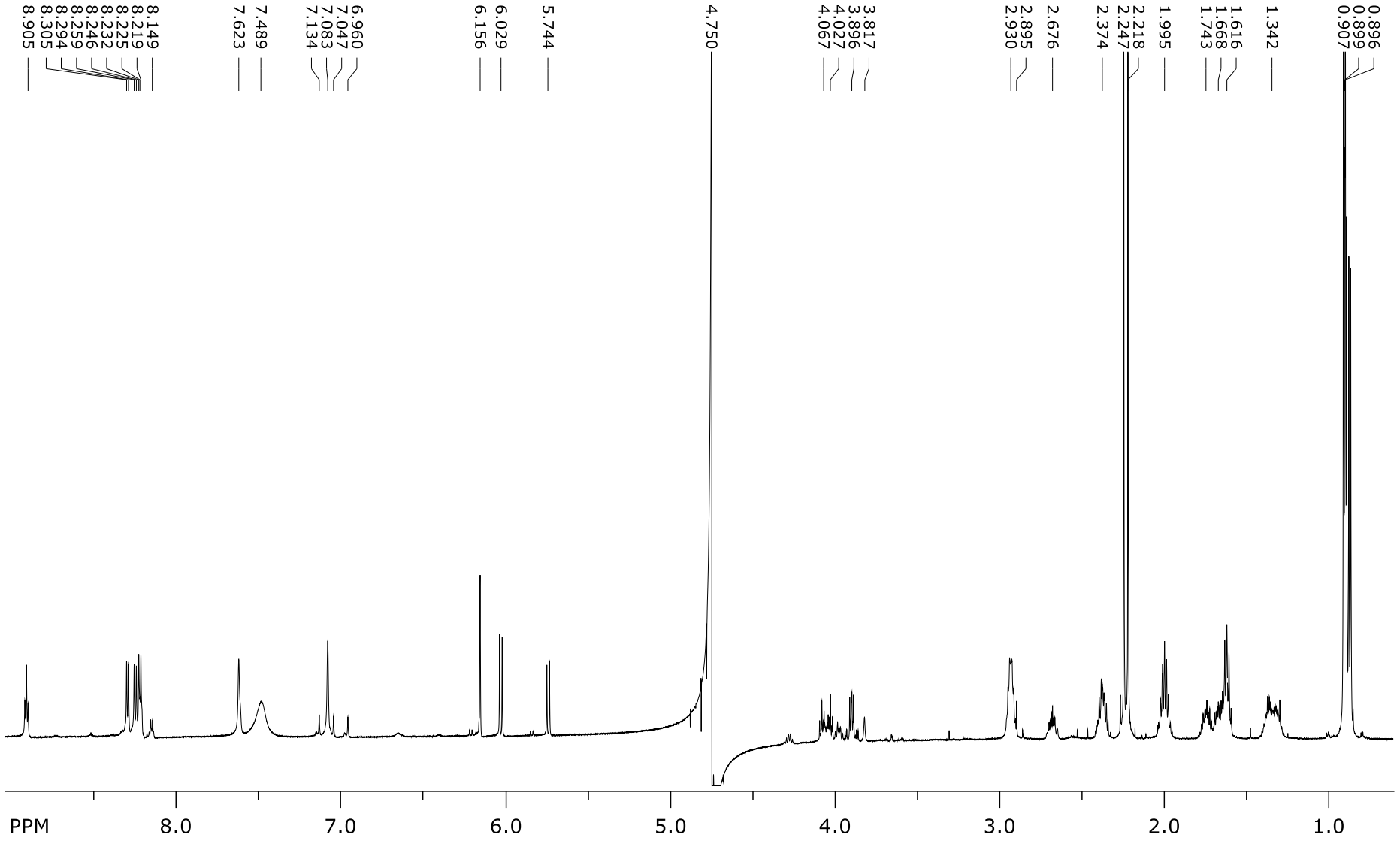


Figure SI 83. ^{1}H-NMR spectrum of **10**.

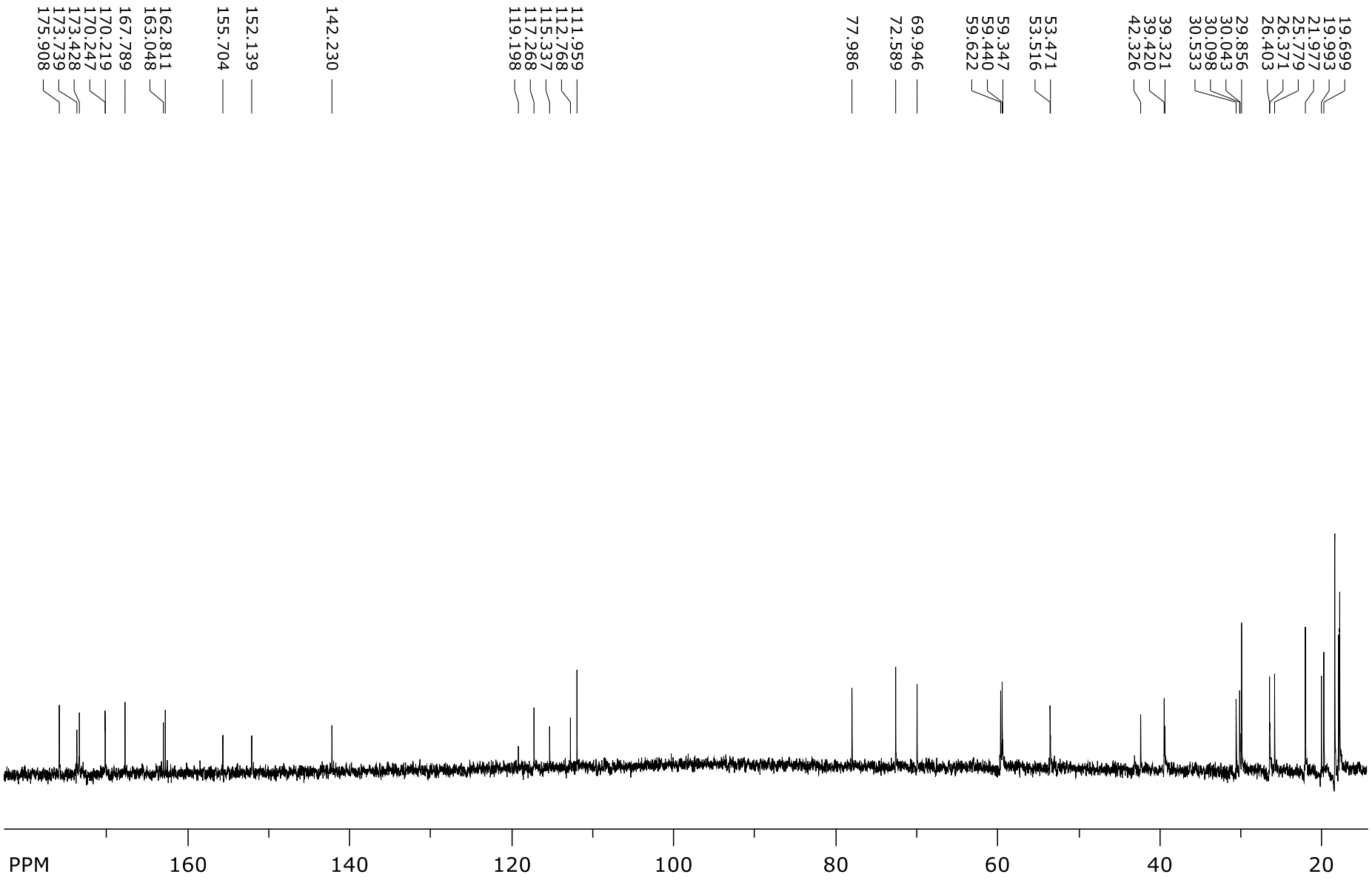


Figure SI 84. ^{13}C-NMR spectrum of **10**.

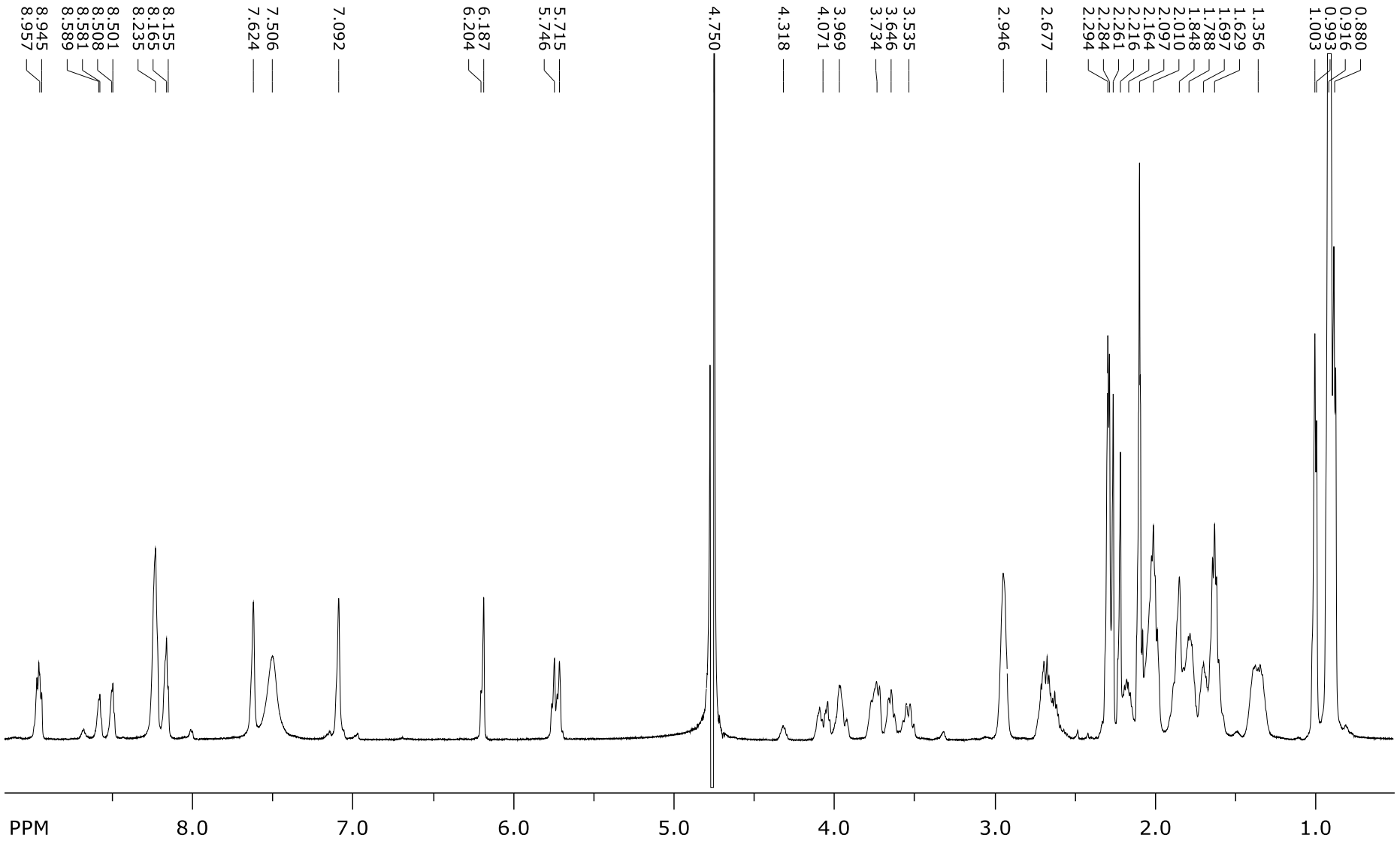


Figure SI 85. ^{1}H-NMR spectrum of **11**.

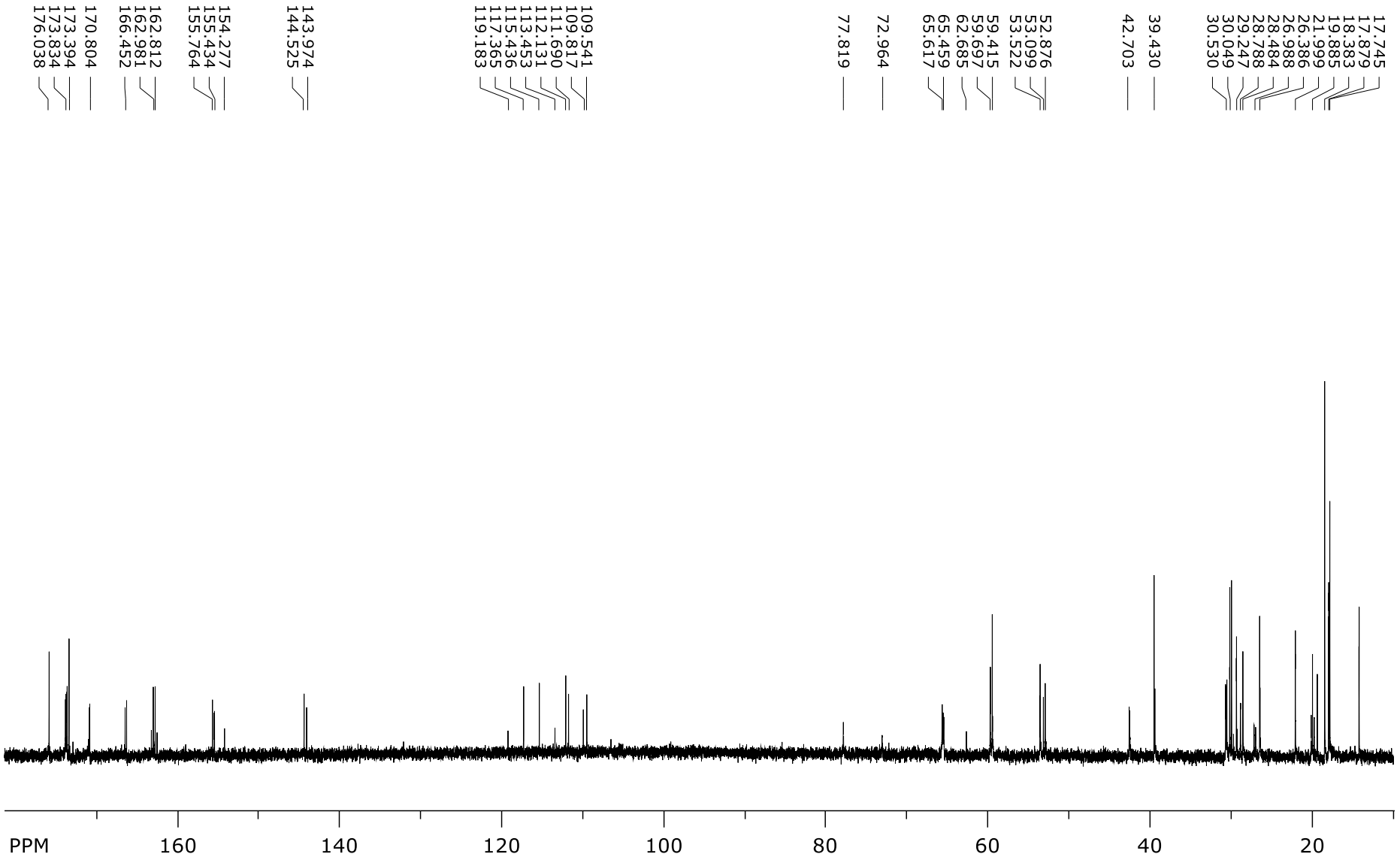


Figure SI 86. ^{13}C-NMR spectrum of **11**.

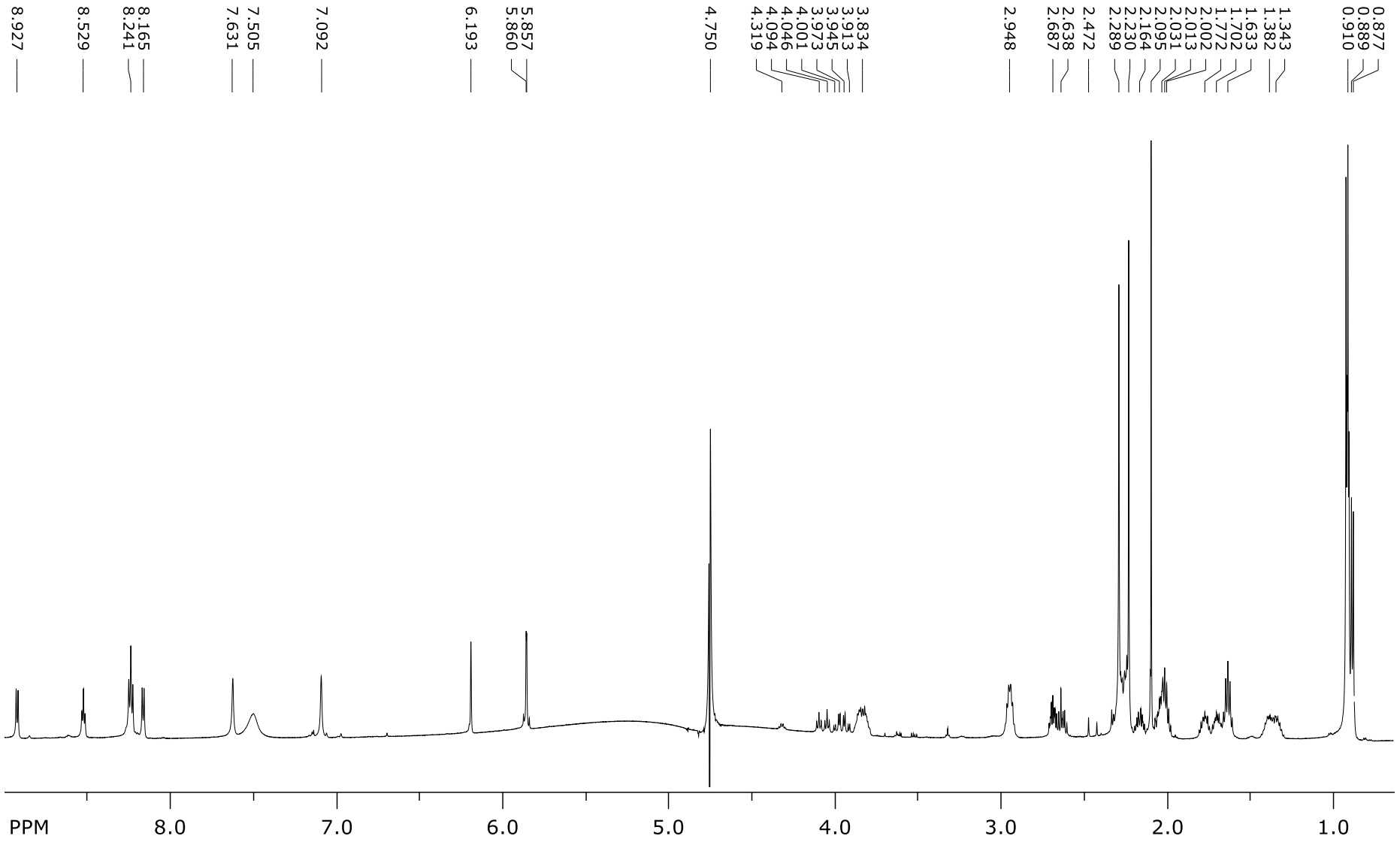


Figure SI 87. ^{1}H-NMR spectrum of **12**.

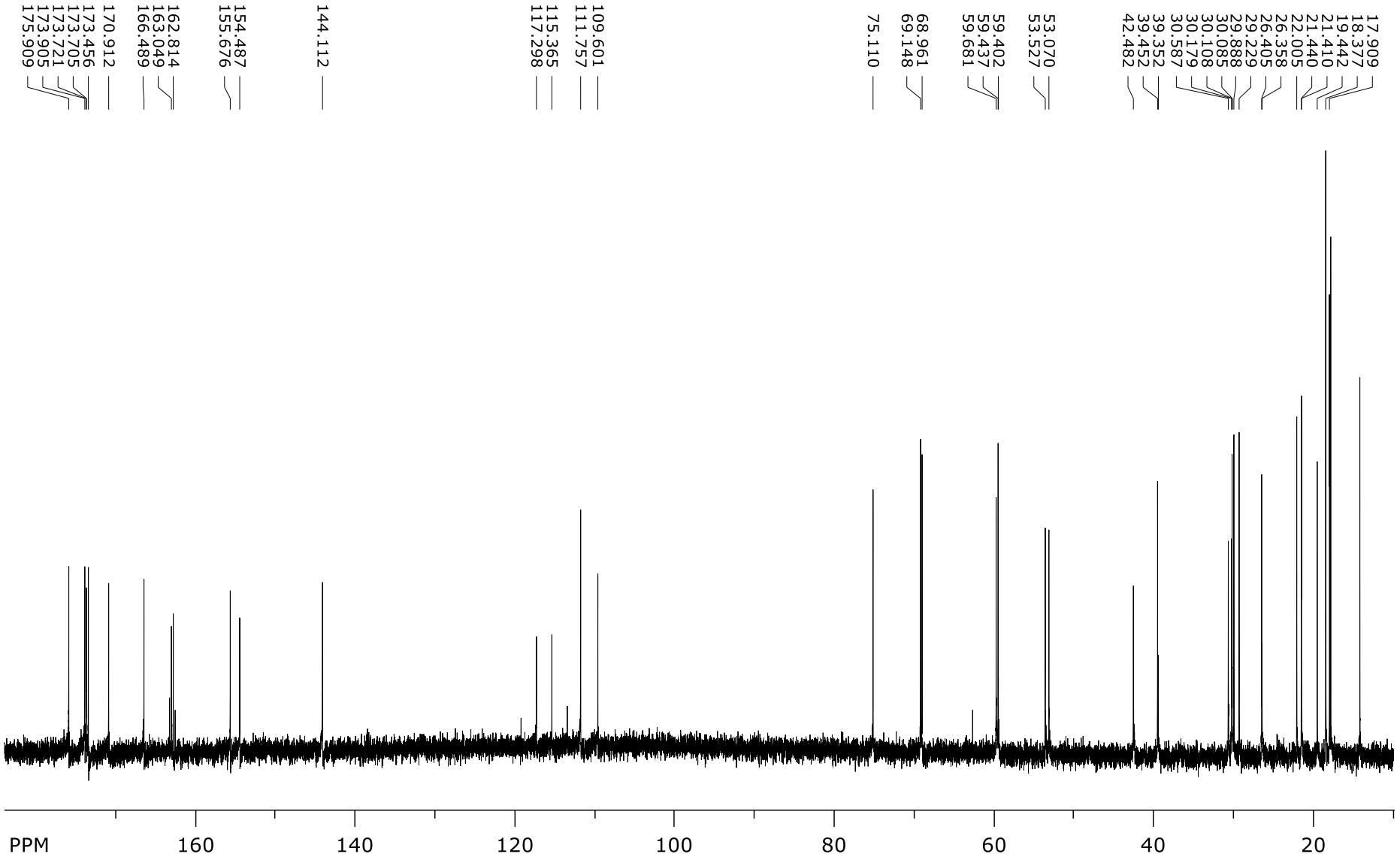


Figure SI 88. ^{13}C-NMR spectrum of **12**.

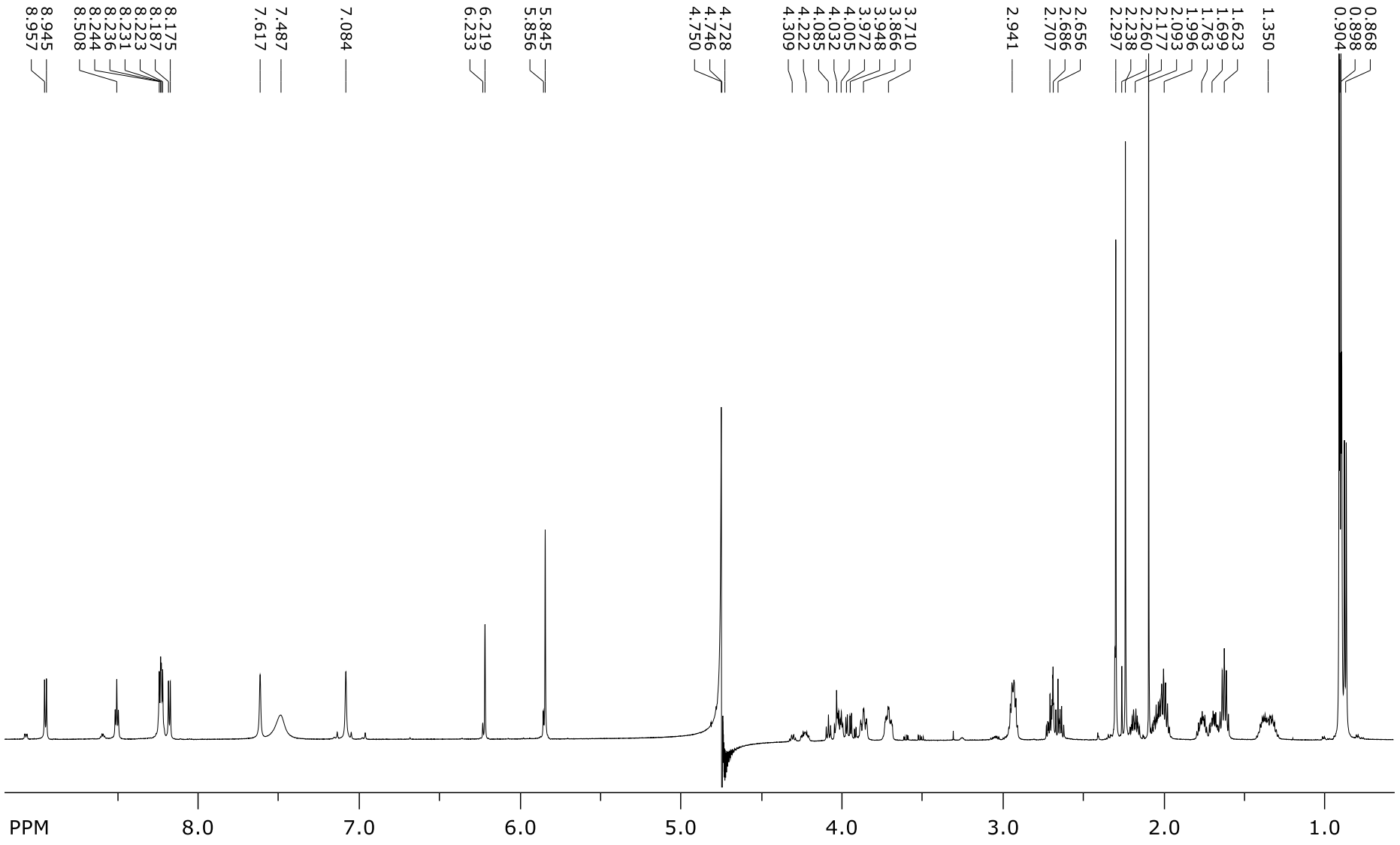


Figure SI 89. ^{1}H-NMR spectrum of **13**.

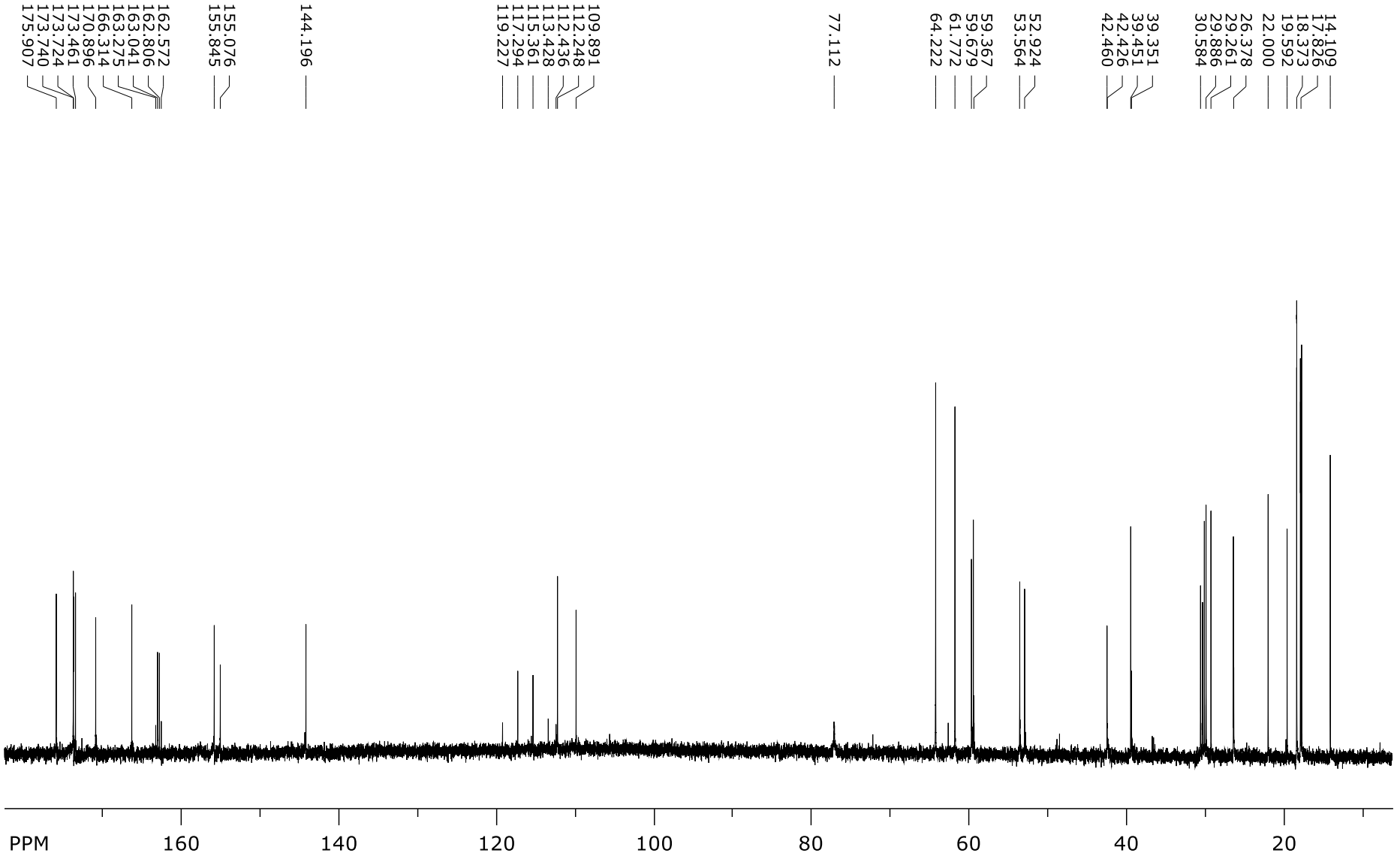


Figure SI 90. ^{13}C-NMR spectrum of **13**.

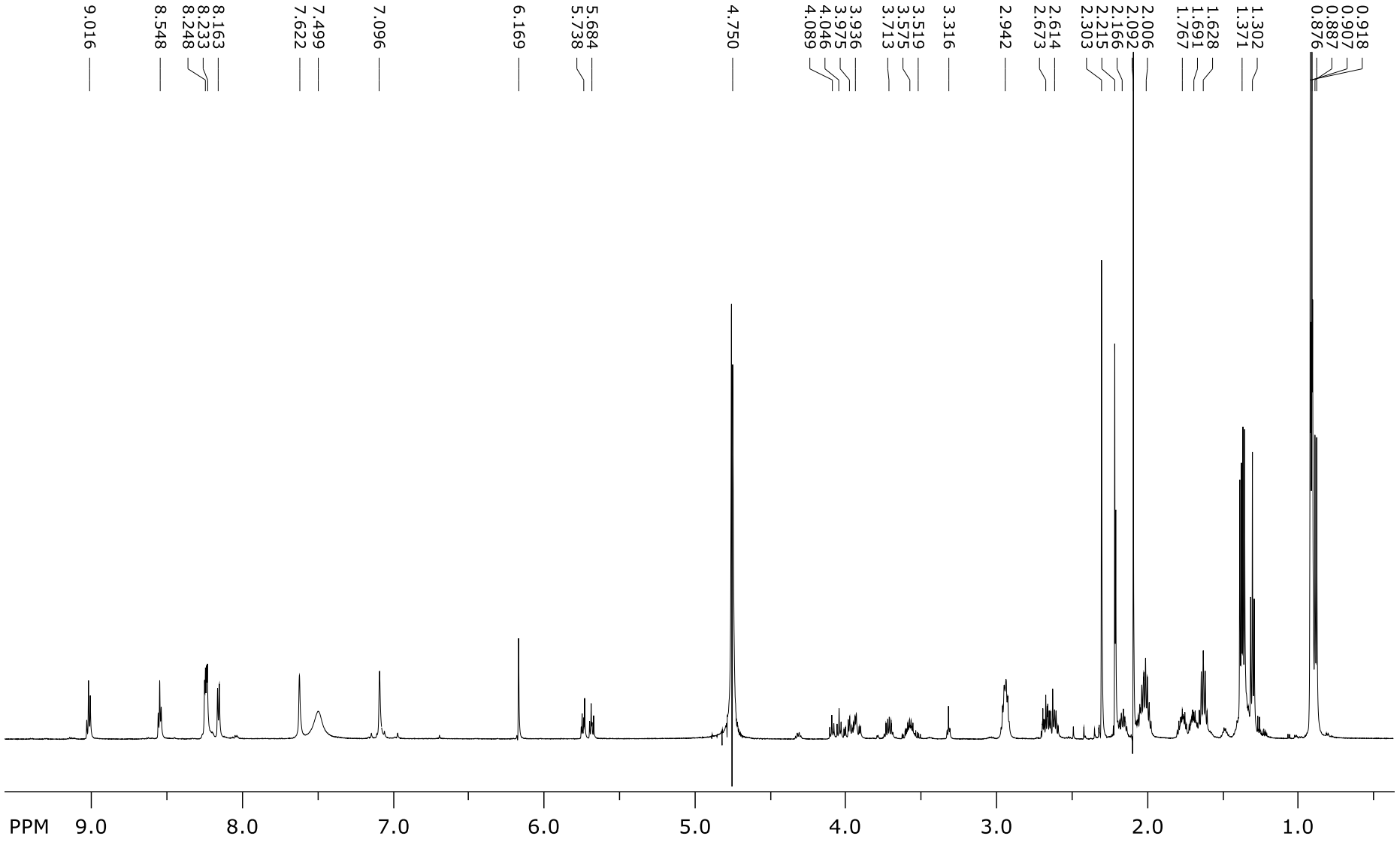


Figure SI 91. ^{1}H-NMR spectrum of **14**.

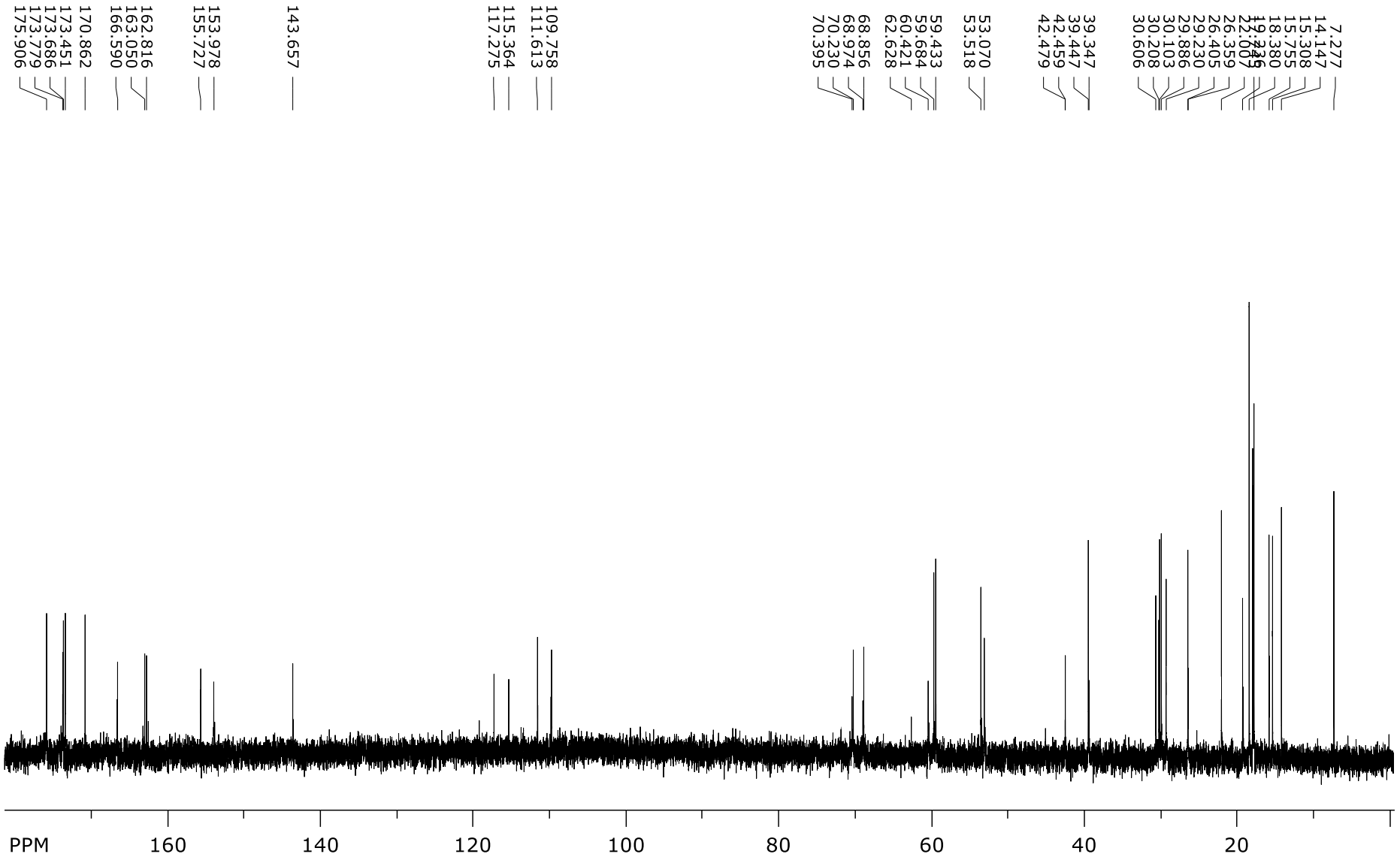


Figure SI 92. ^{13}C-NMR spectrum of **14**.

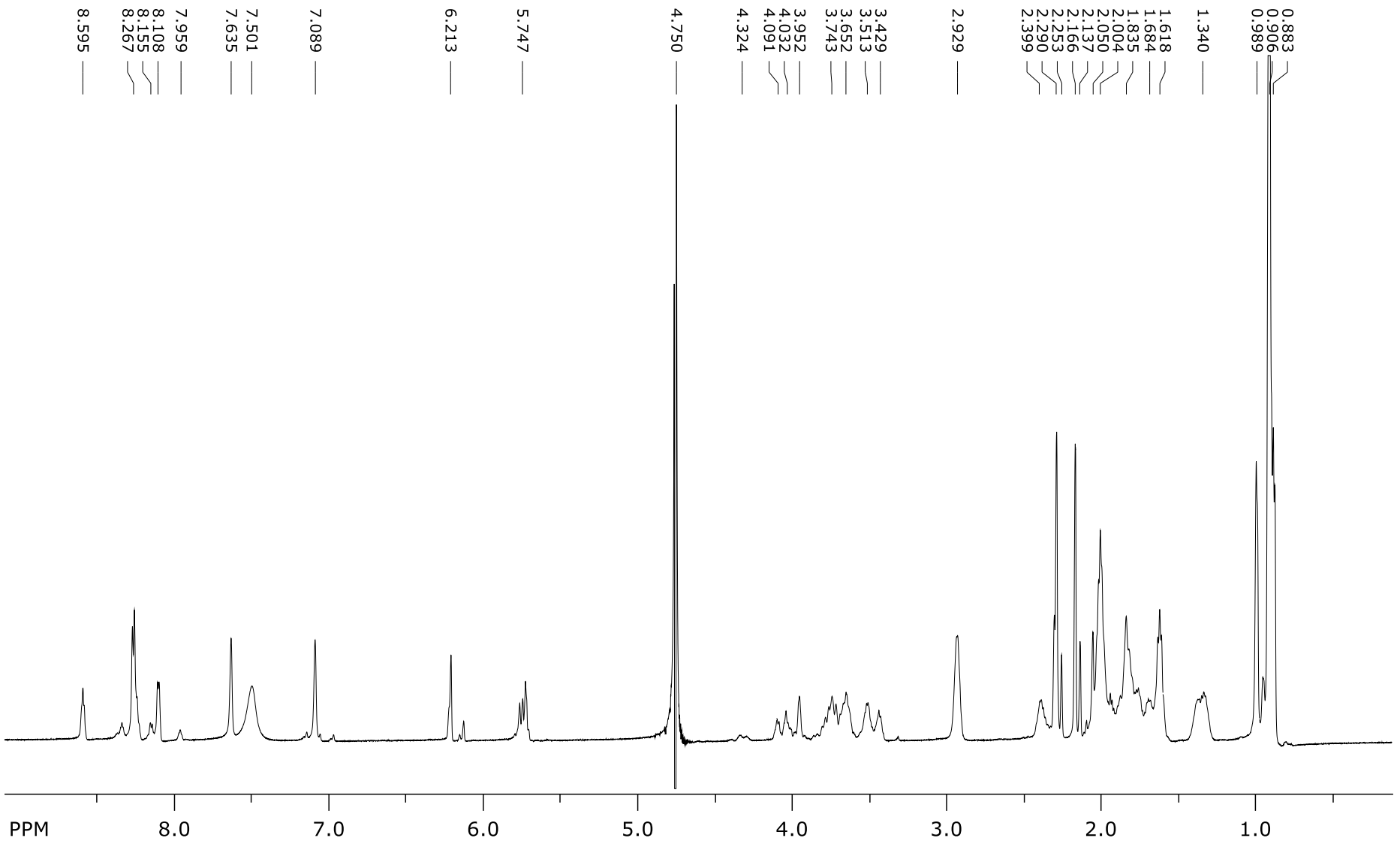


Figure SI 93. ^{1}H-NMR spectrum of **15**.

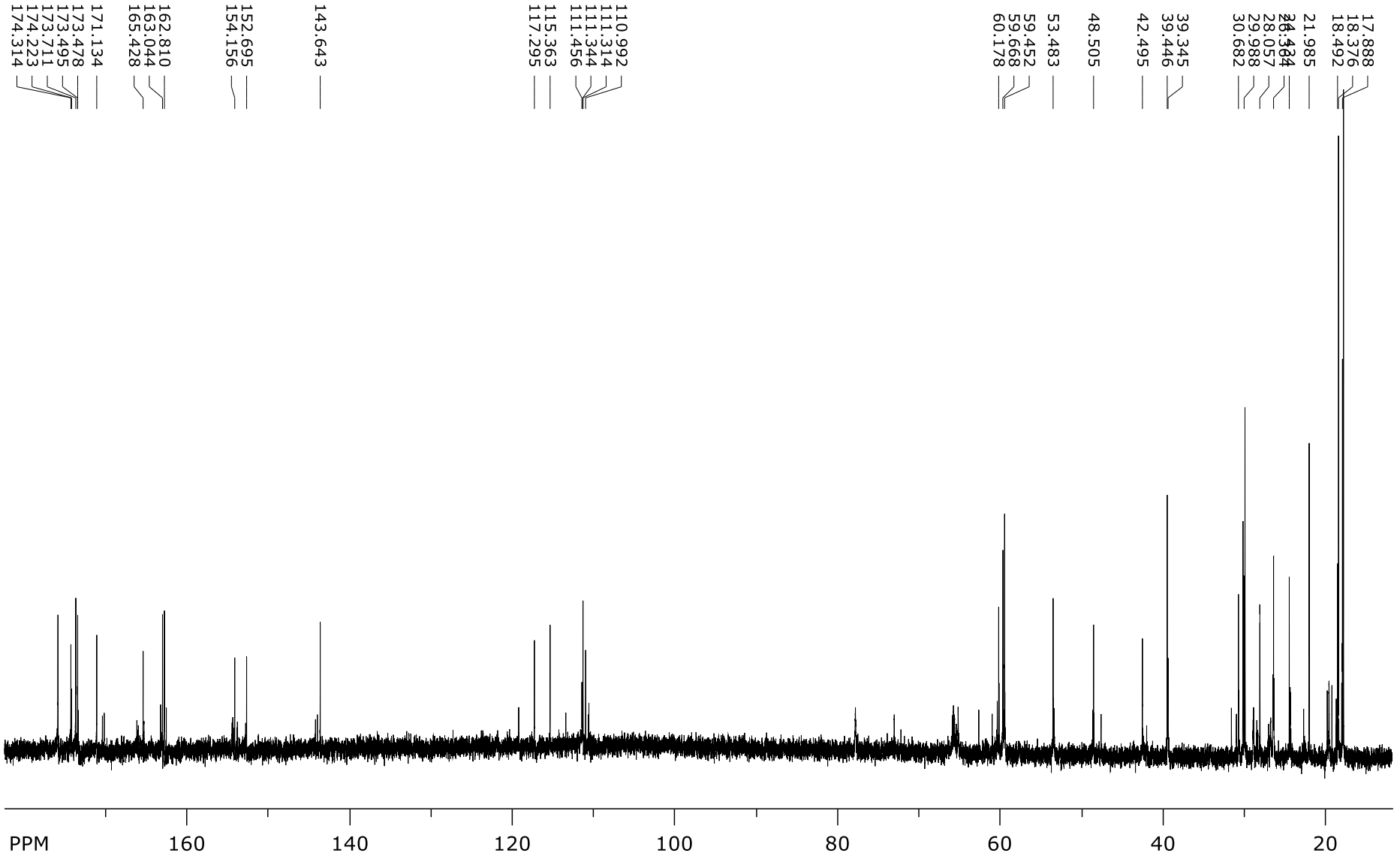


Figure SI 94. ^{13}C-NMR spectrum of **15**.

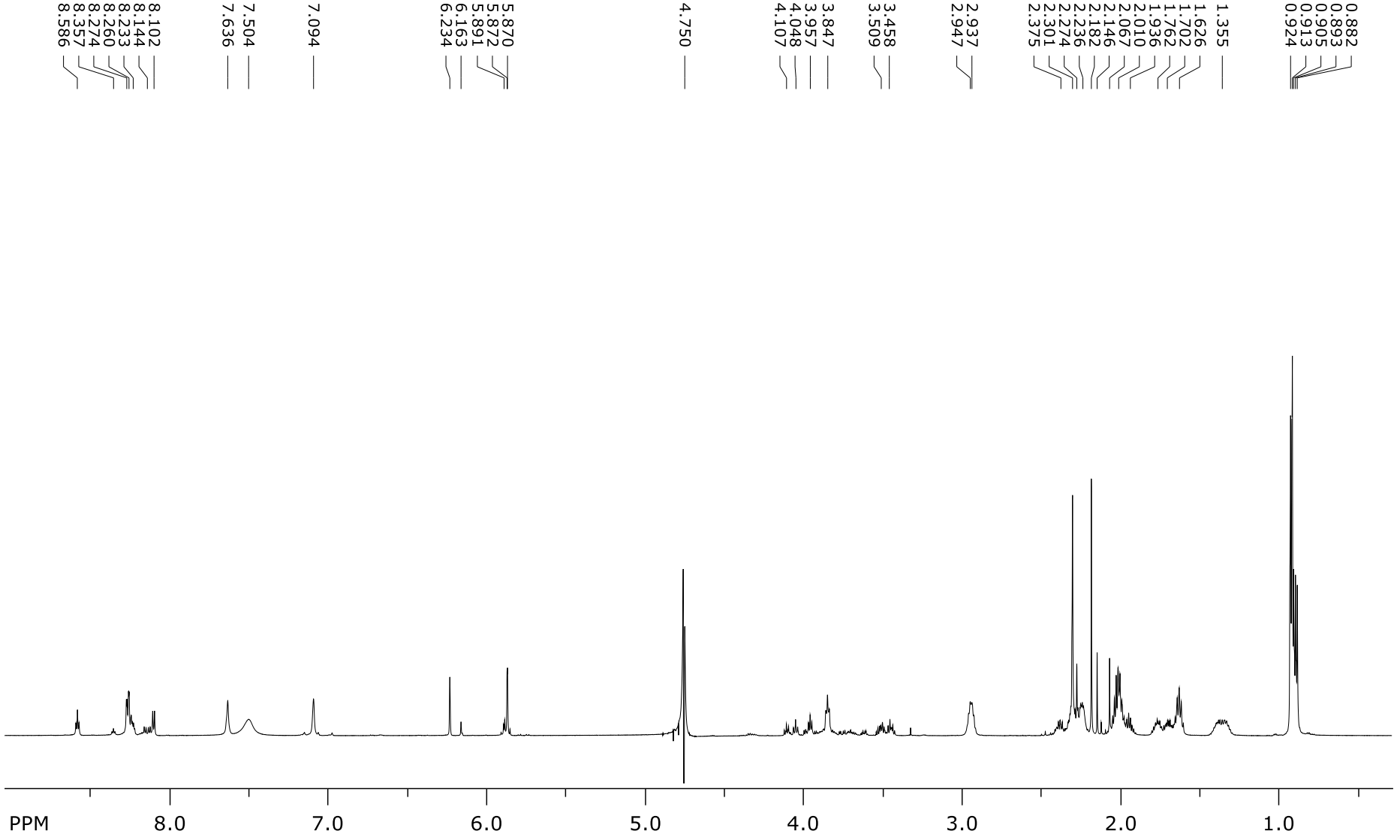


Figure SI 95. ^{1}H-NMR spectrum of **16**.

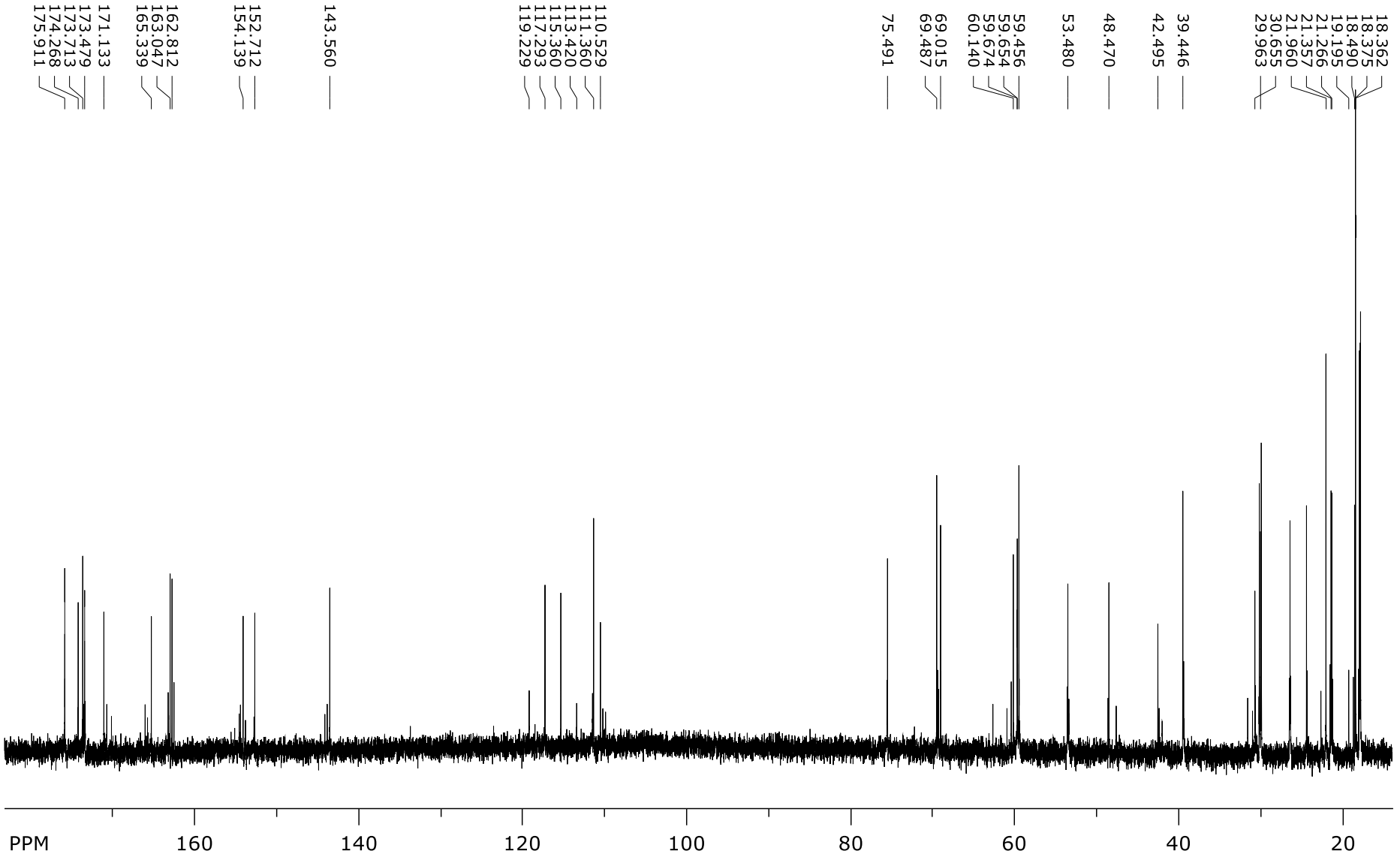


Figure SI 96. ^{13}C-NMR spectrum of **16**.

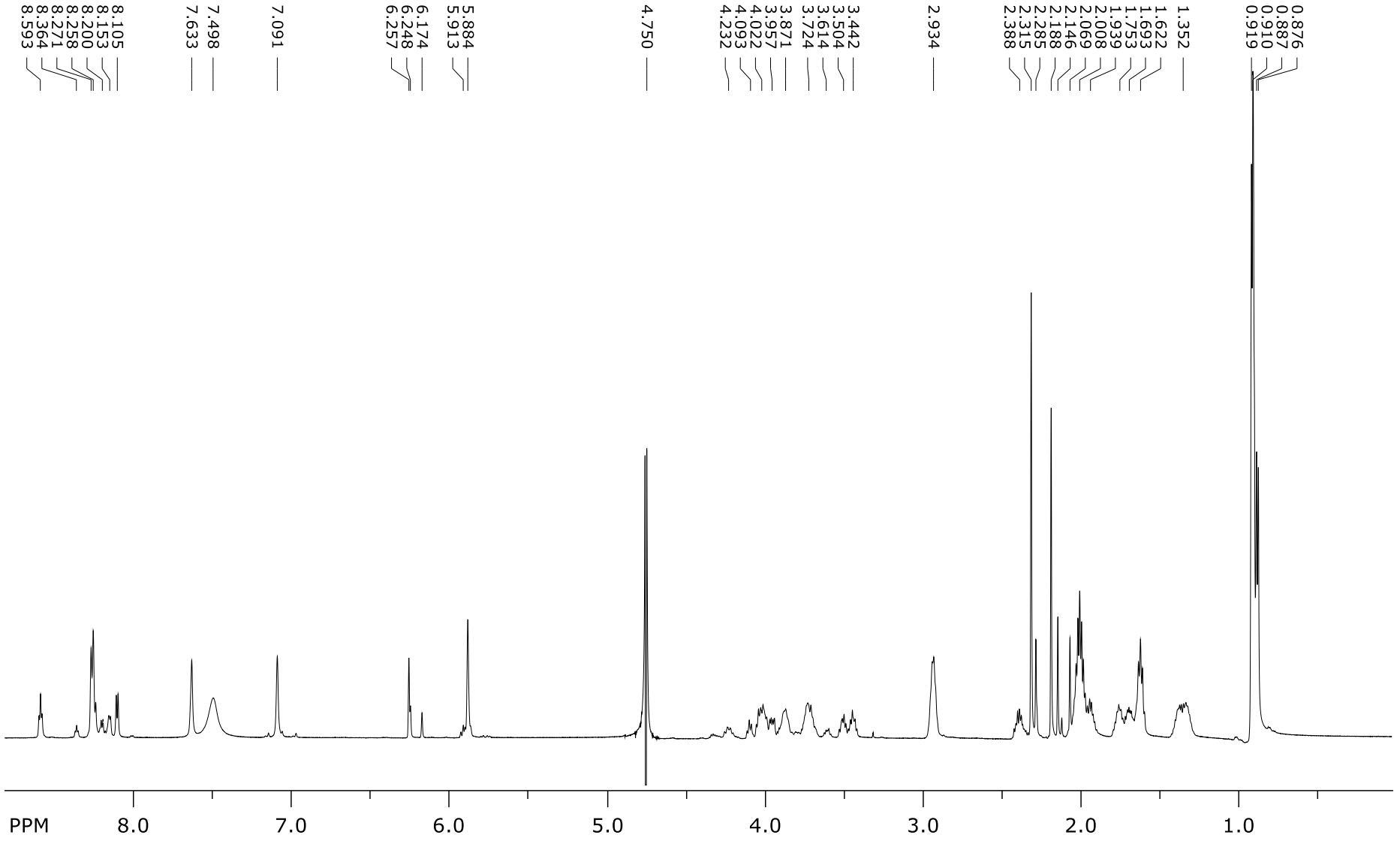


Figure SI 97. ^{1}H-NMR spectrum of **17**.

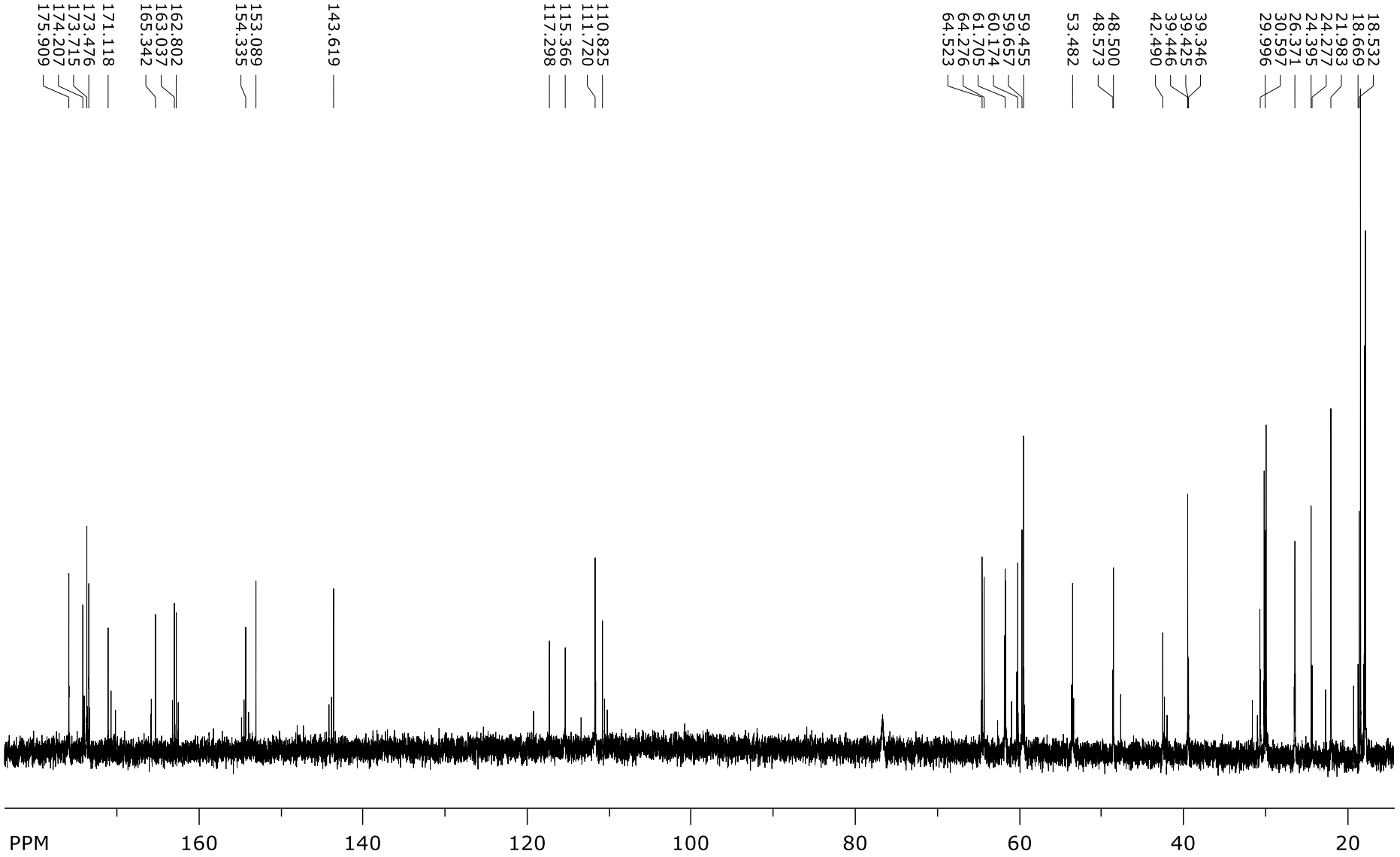


Figure SI 98. ^{13}C-NMR spectrum of **17**.

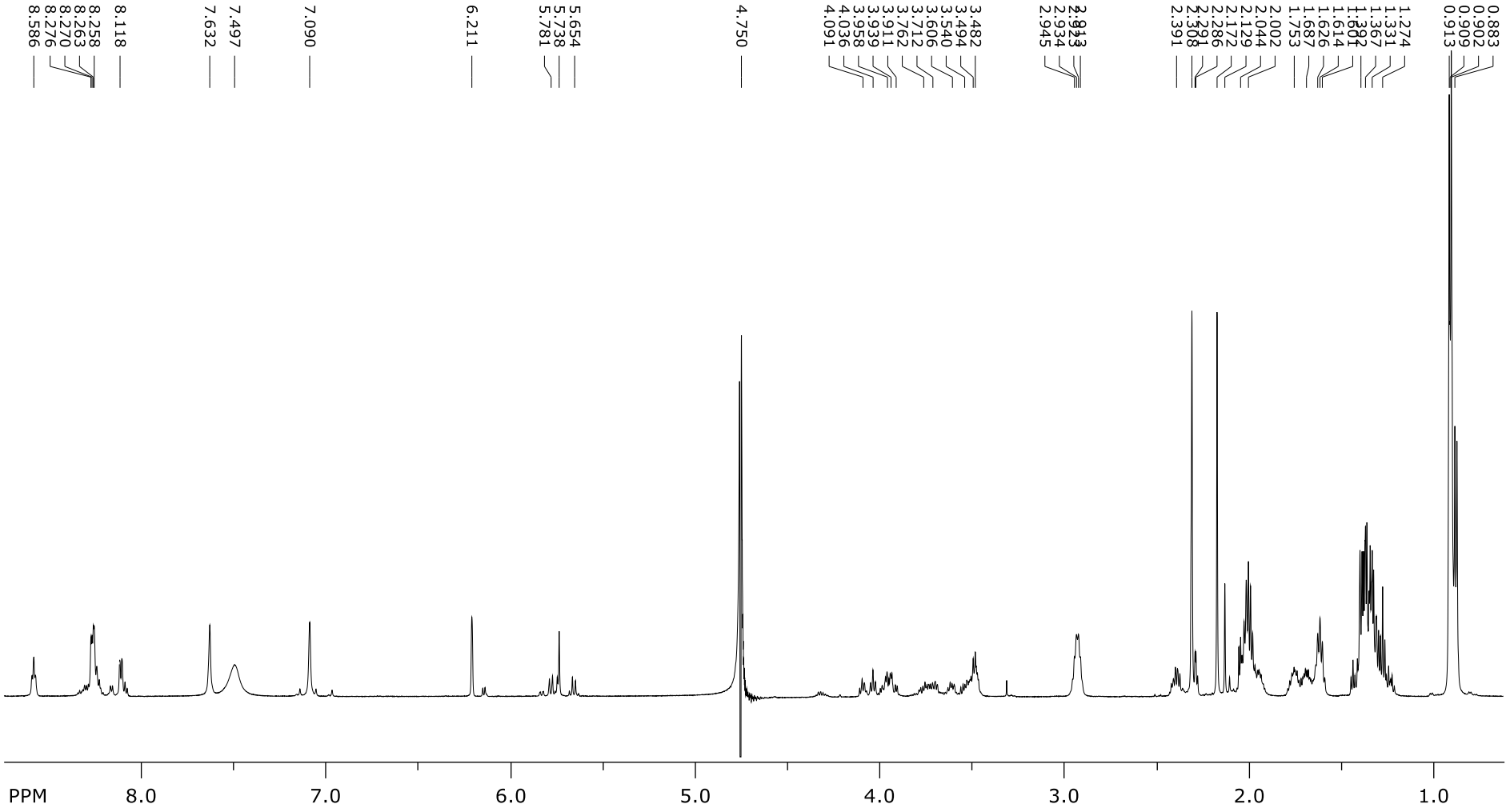


Figure SI 99. ^{1}H-NMR spectrum of **18**.

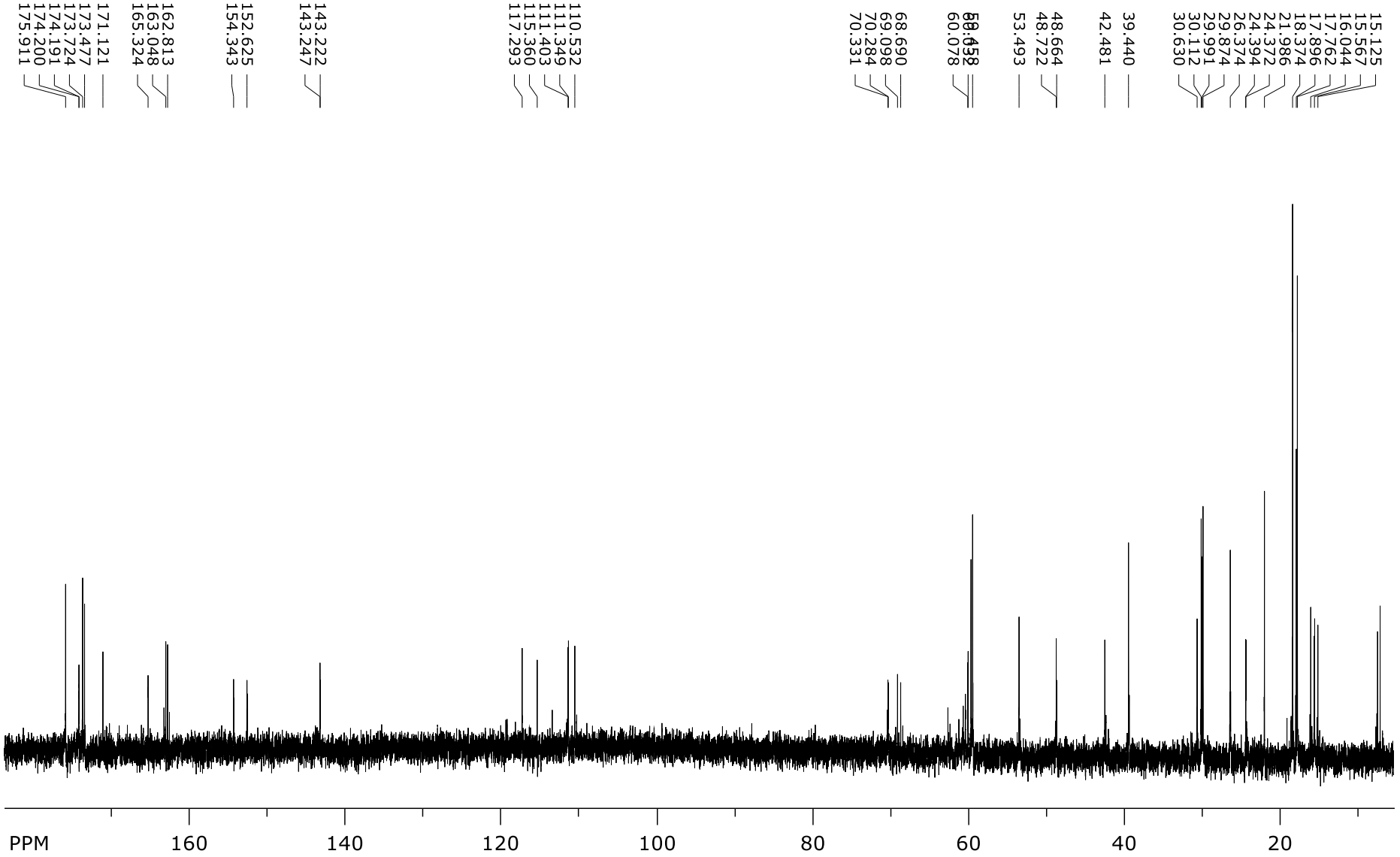


Figure SI 100. ^{13}C-NMR spectrum of **18**.

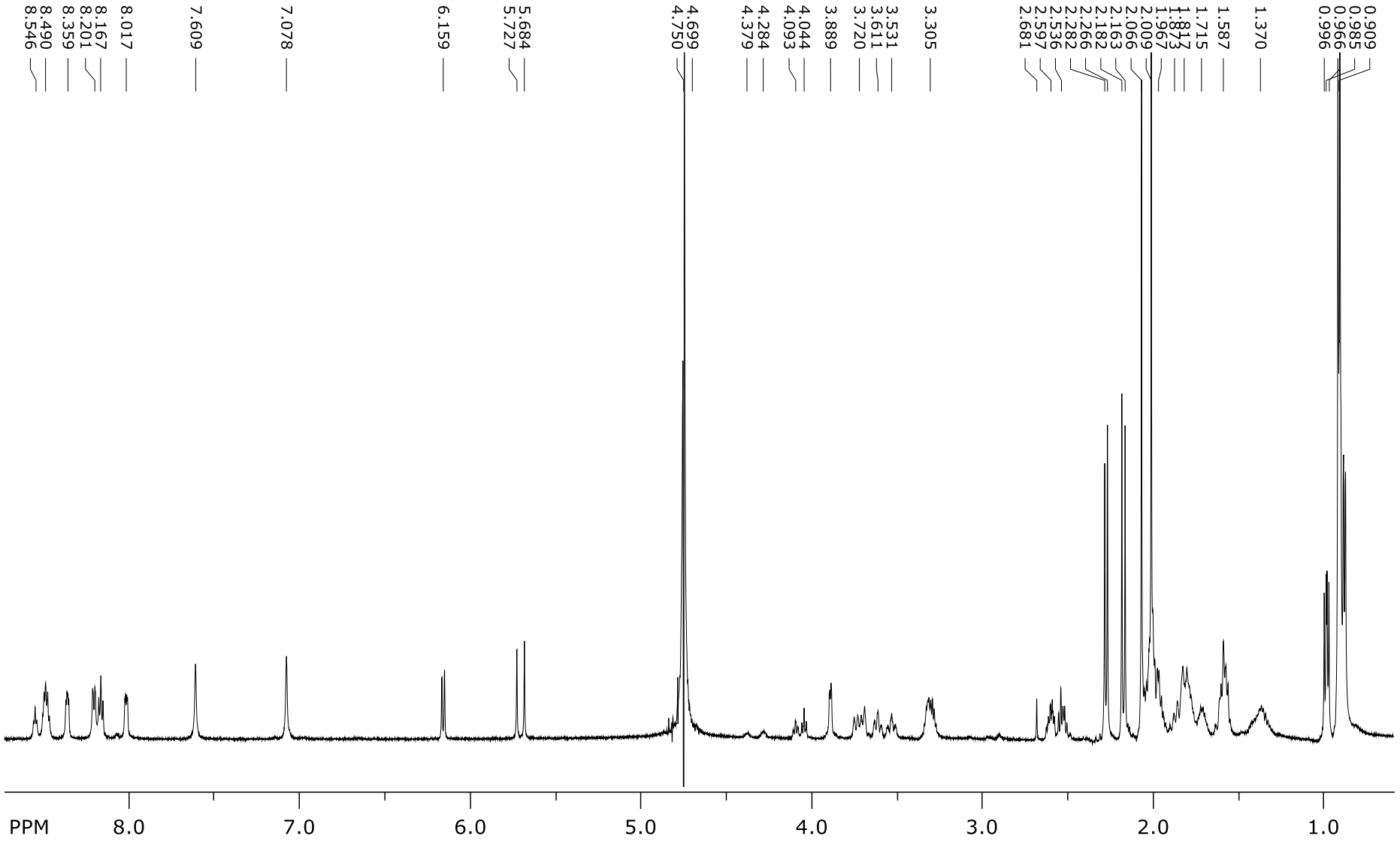


Figure SI 101. ^{1}H-NMR spectrum of **19**.

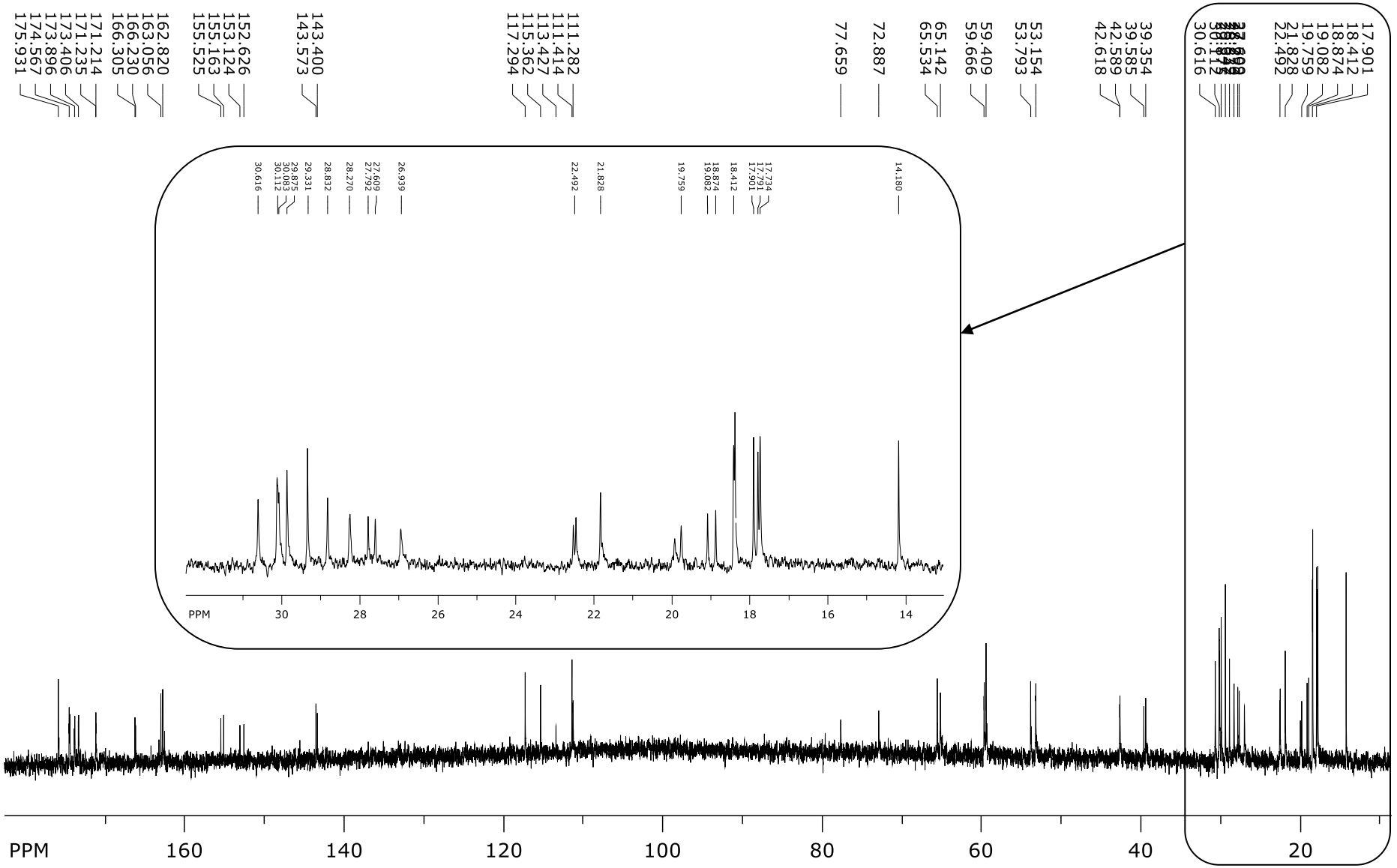


Figure SI 102. ^{13}C-NMR spectrum of **19**. Zoom on the fragment 15-32 ppm was added.

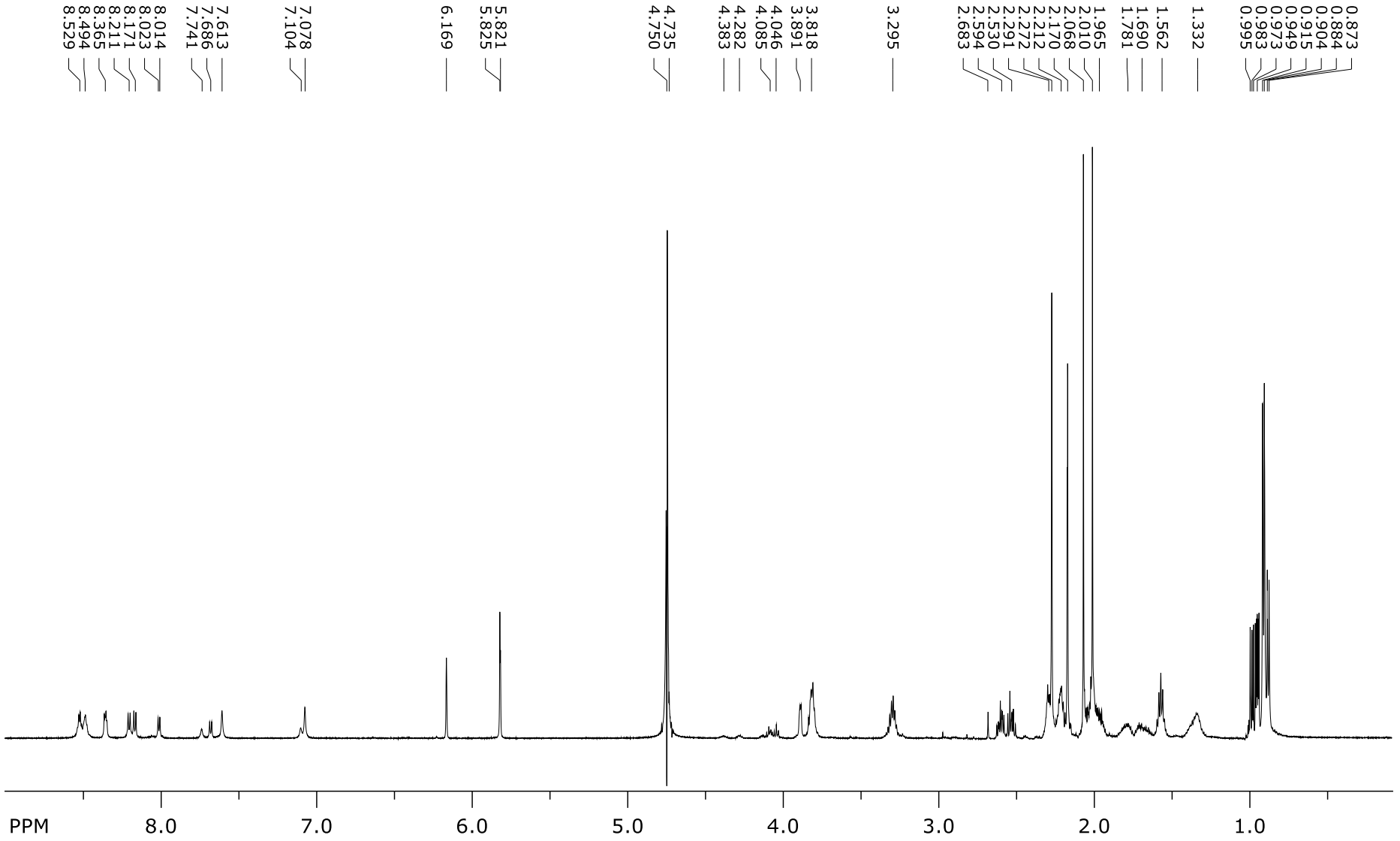


Figure SI 103. ^{1}H-NMR spectrum of **20**.

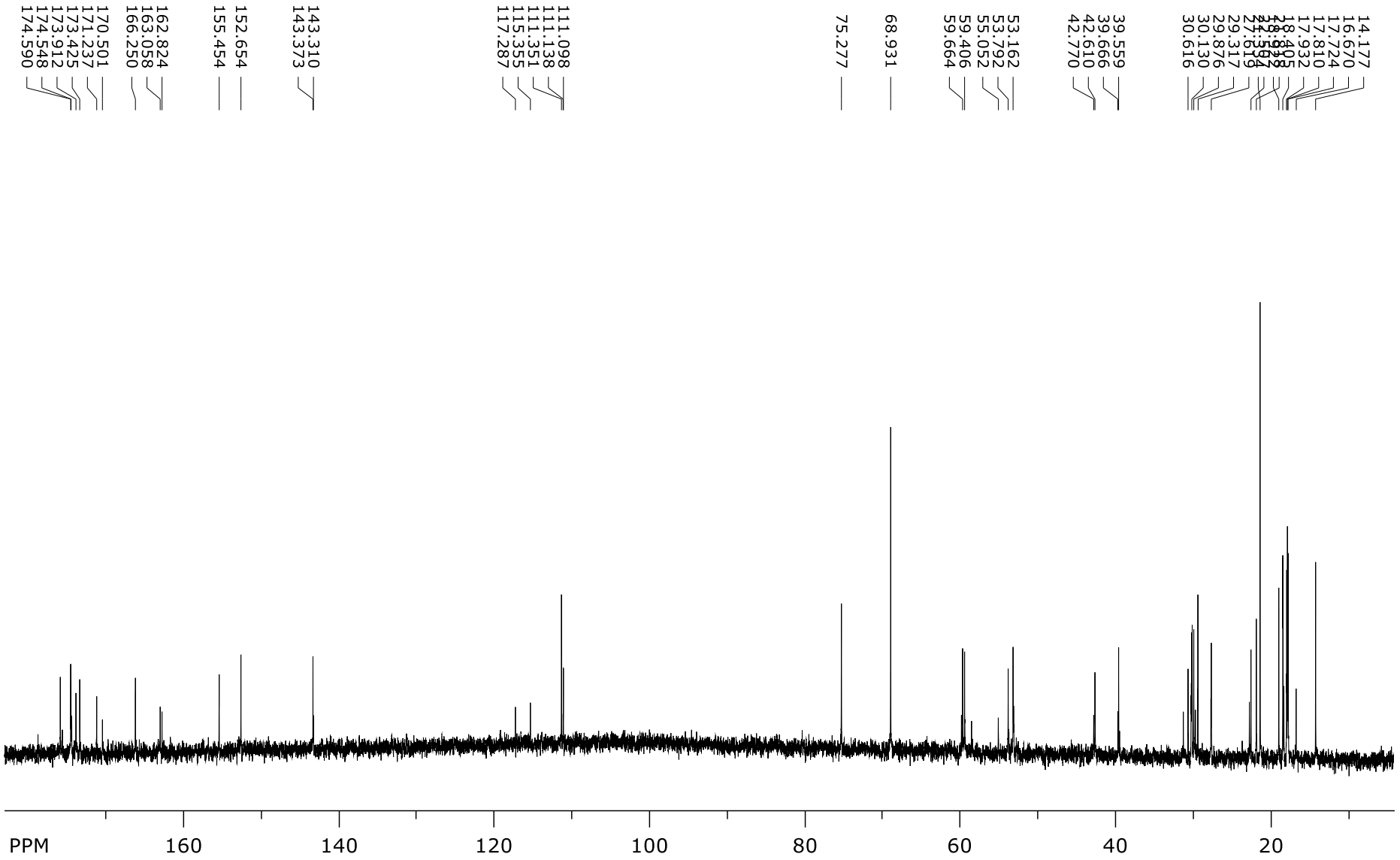


Figure SI 104. ^{13}C-NMR spectrum of **20**.

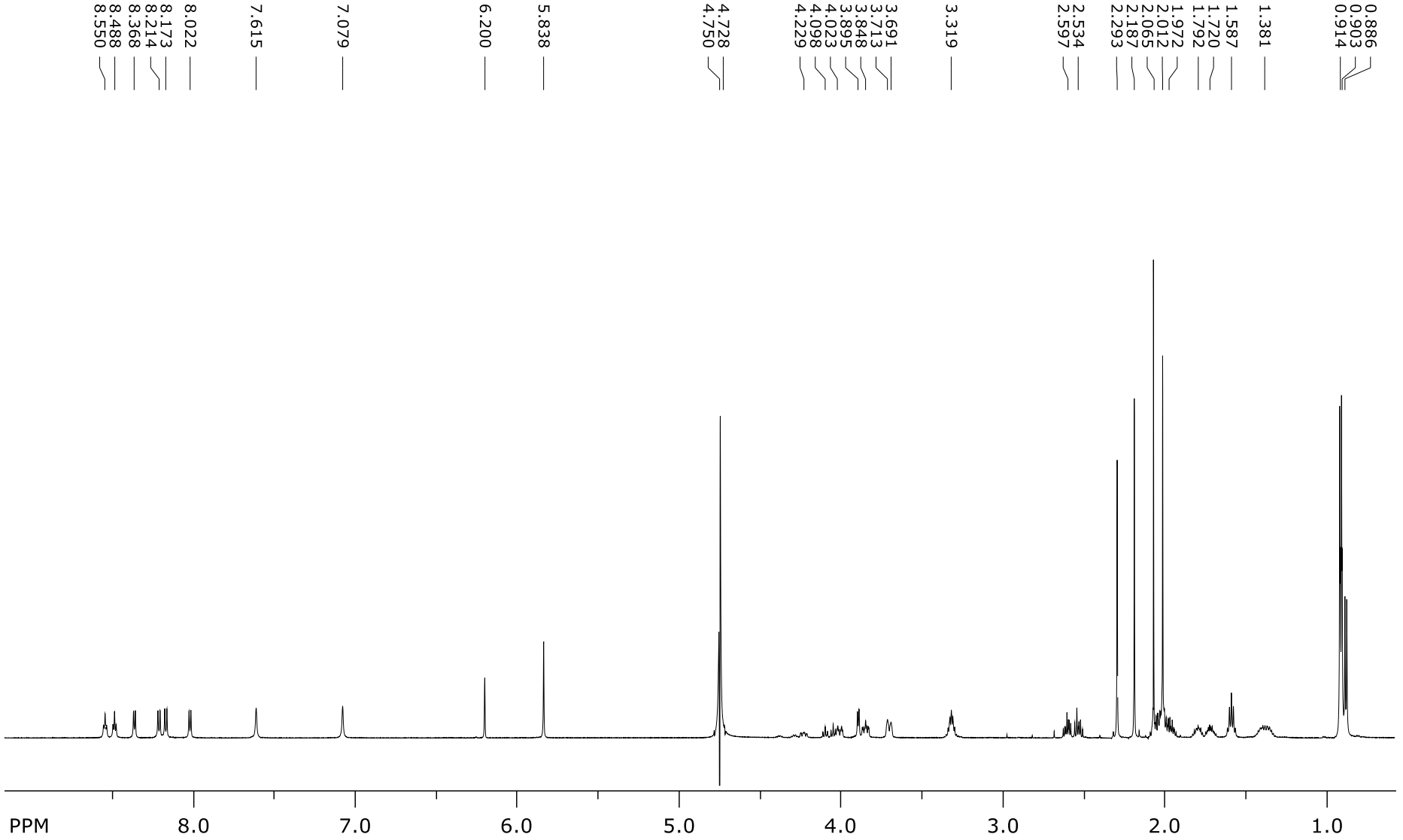


Figure SI 105. ^{1}H-NMR spectrum of **21.**

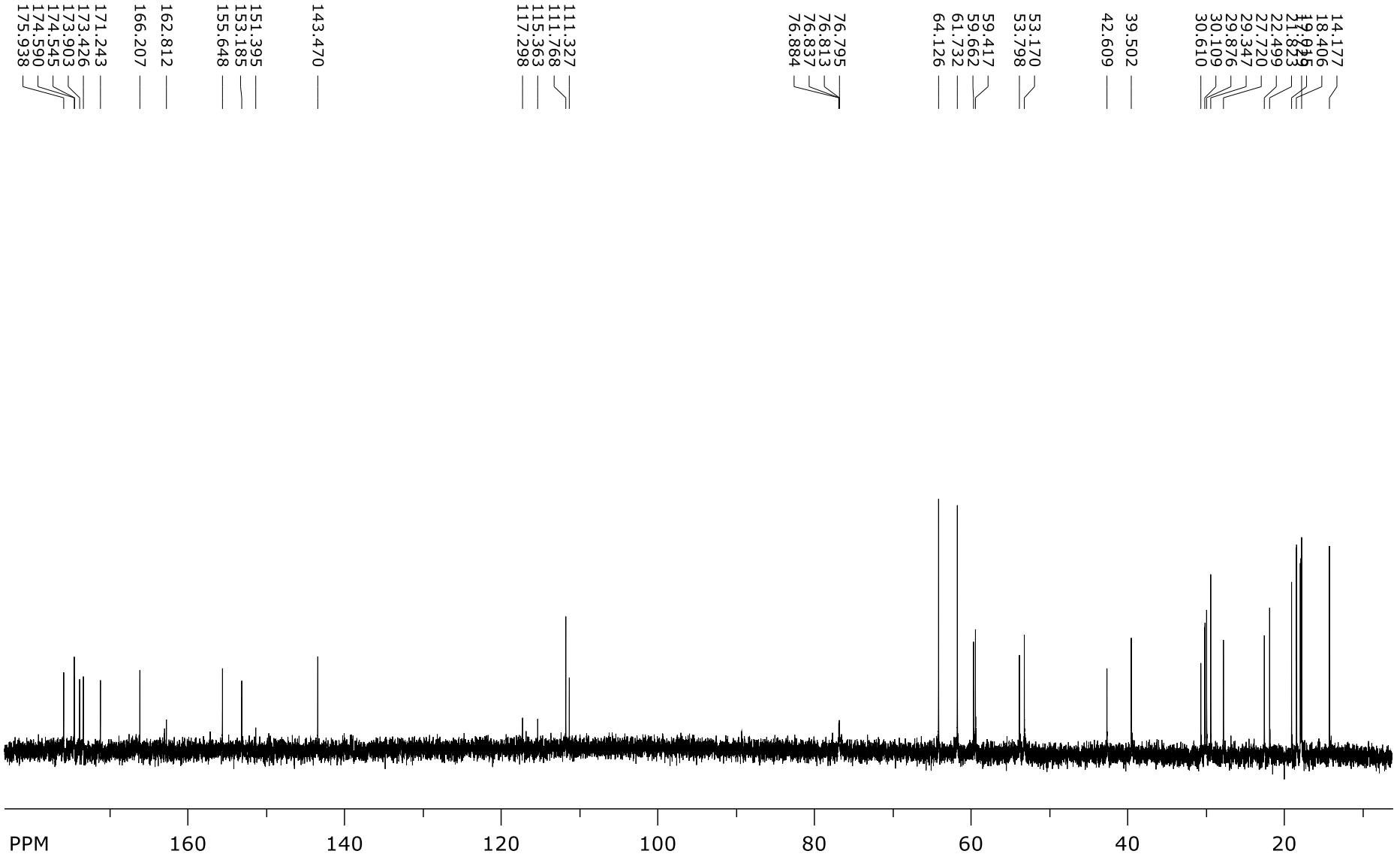


Figure SI 106. ^{13}C-NMR spectrum of **21**.

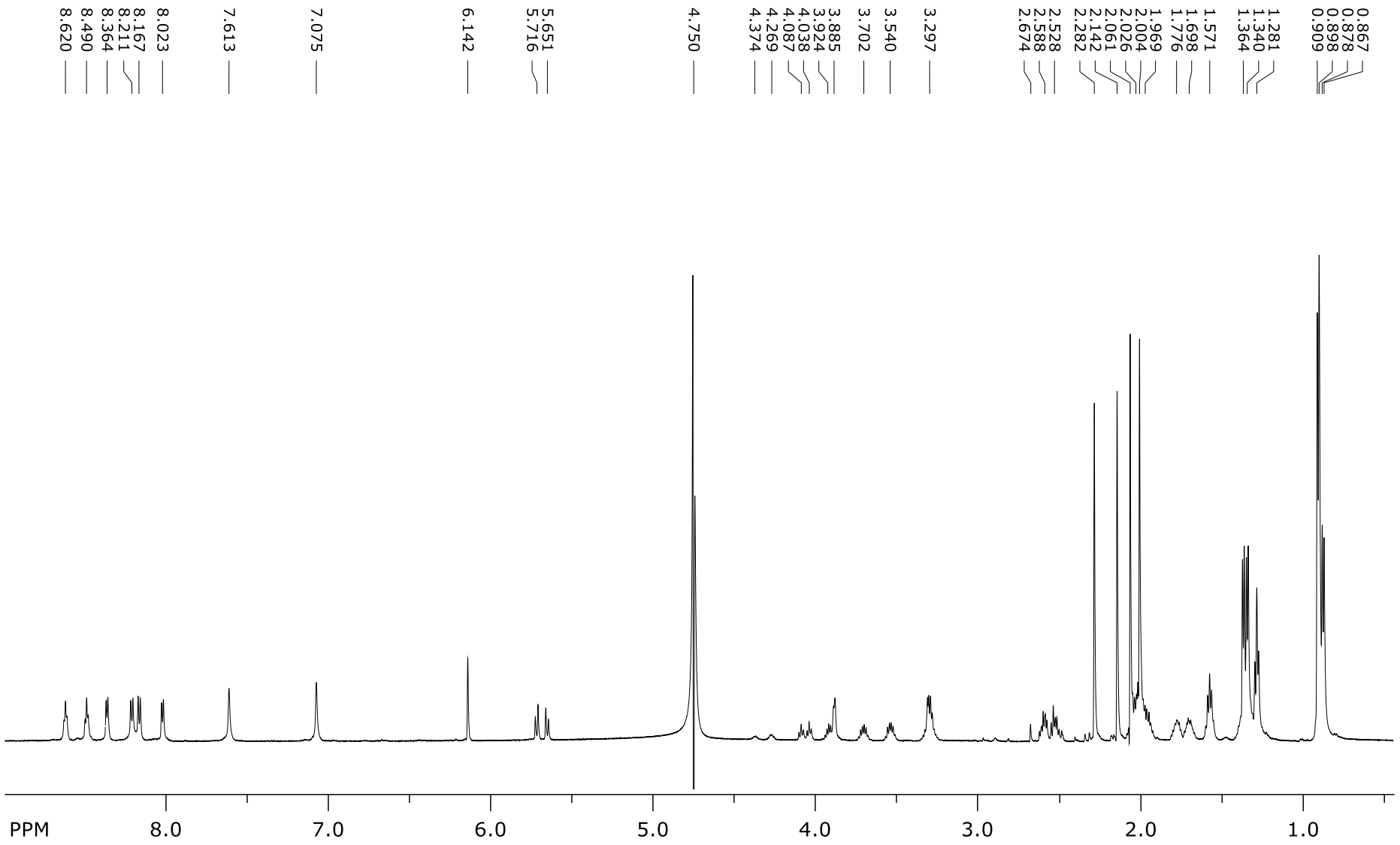


Figure SI 107. ^{1}H-NMR spectrum of **22**.

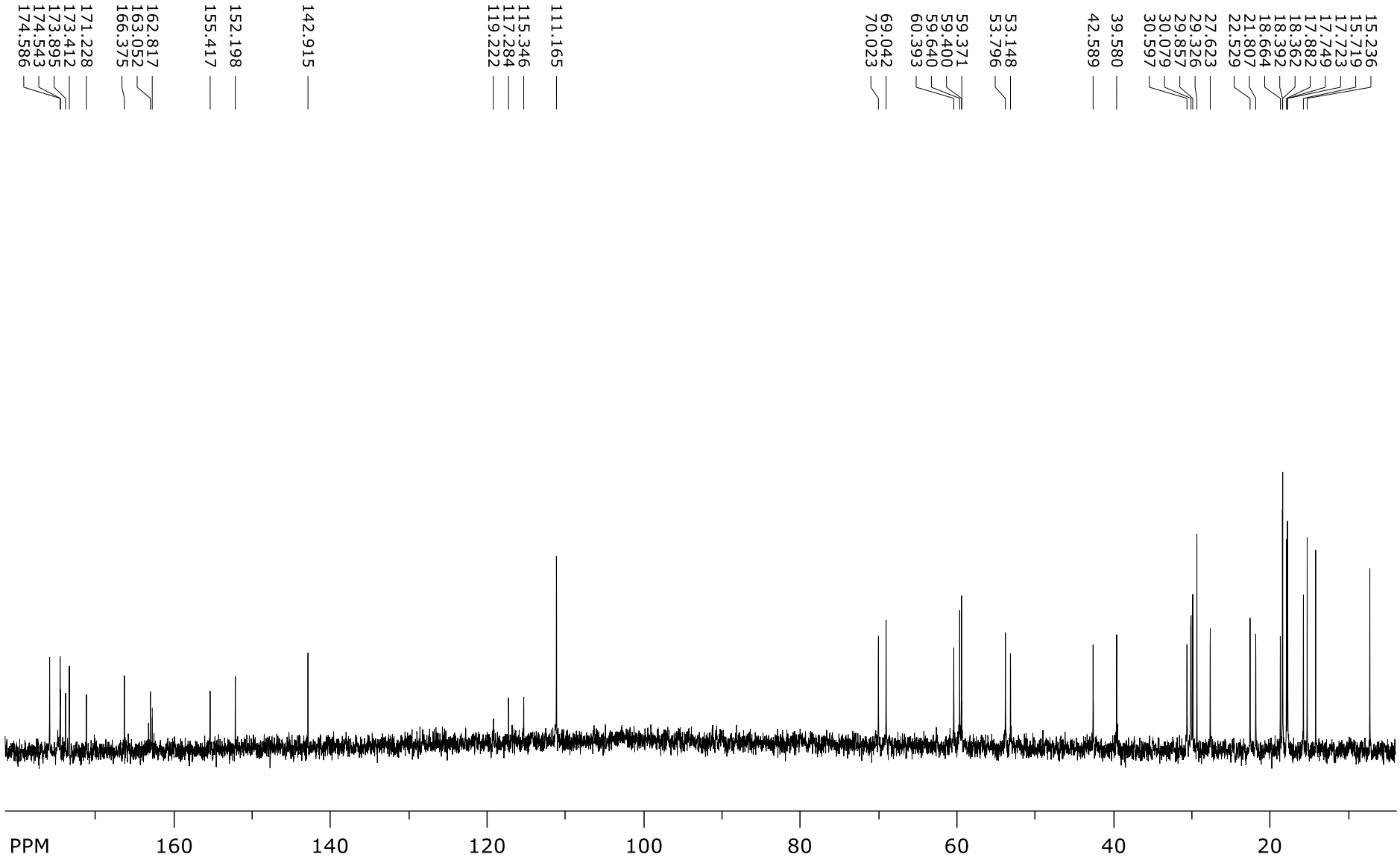


Figure SI 108. ^{13}C-NMR spectrum of **22**.

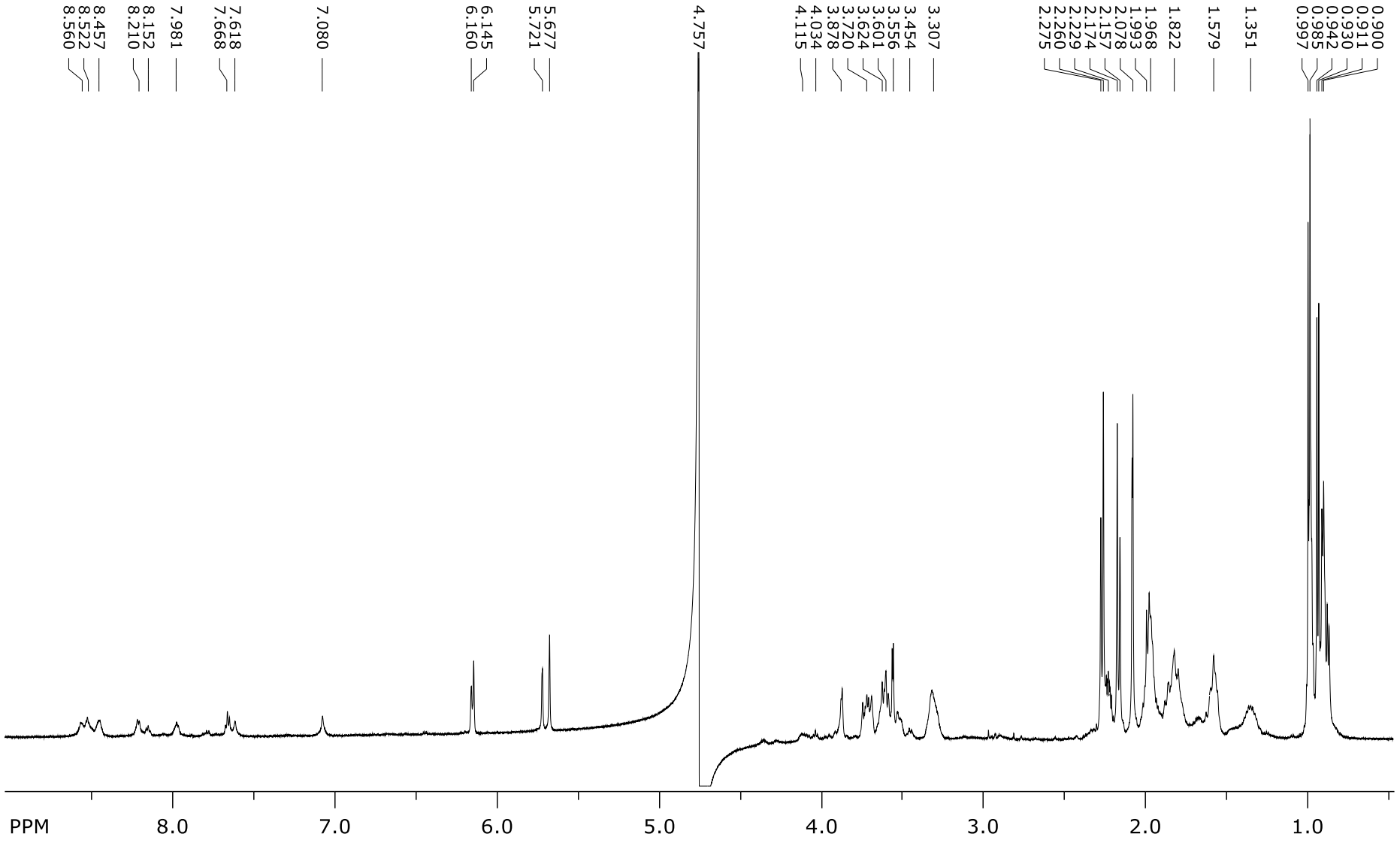


Figure SI 109. ^{1}H-NMR spectrum of **23**.

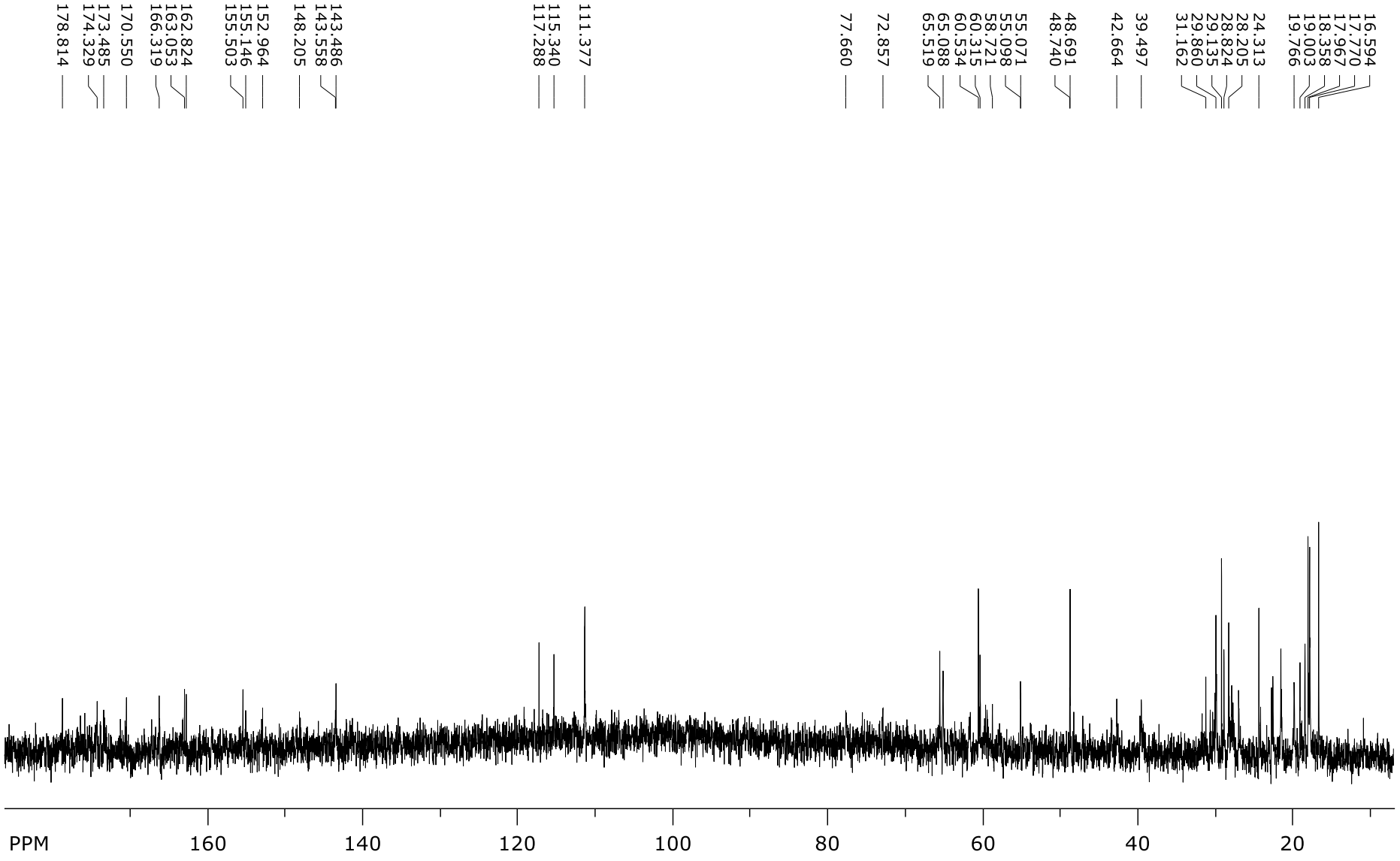


Figure SI 110. ^{13}C-NMR spectrum of **23**.

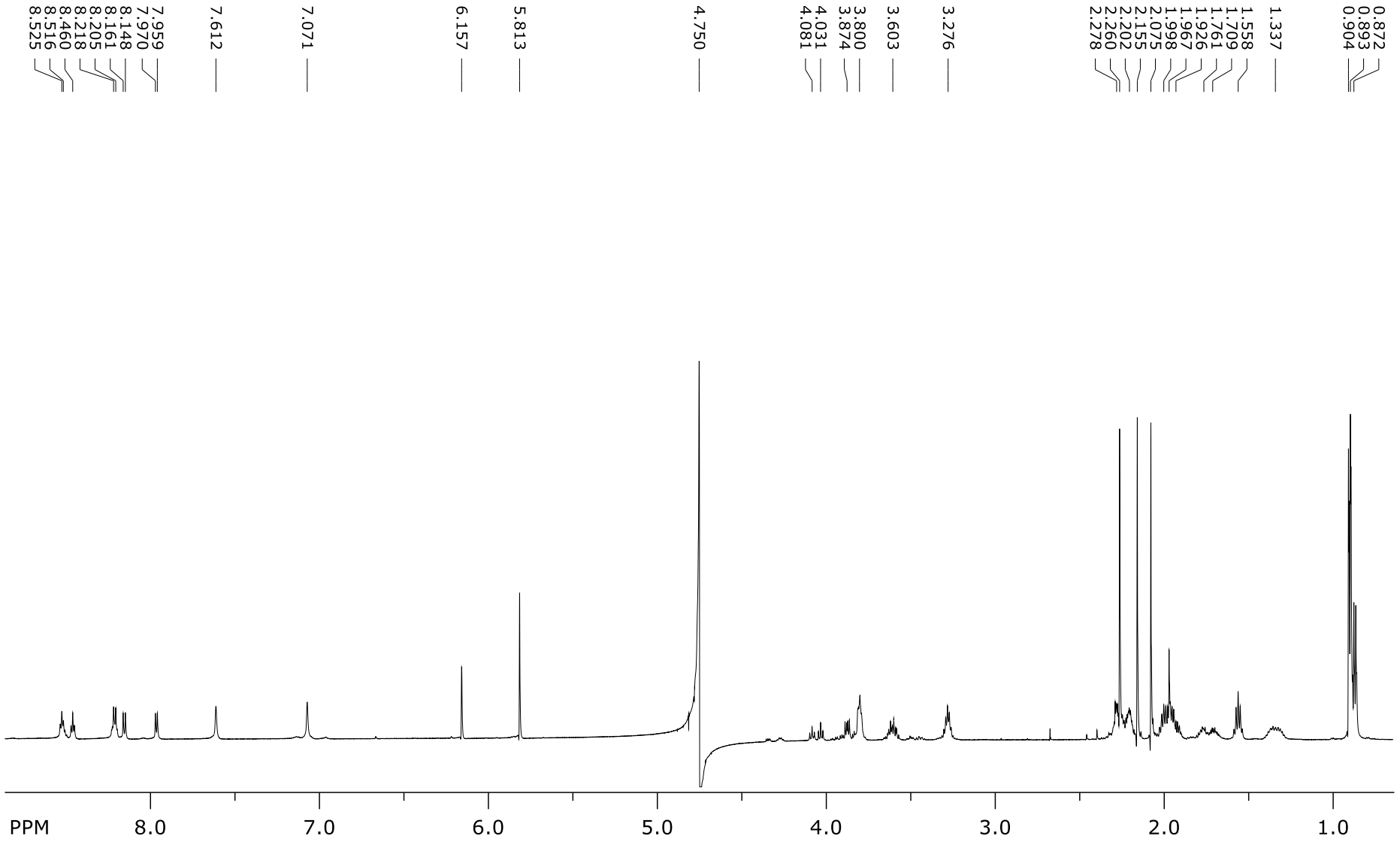


Figure SI 111. ^{1}H-NMR spectrum of **24**.

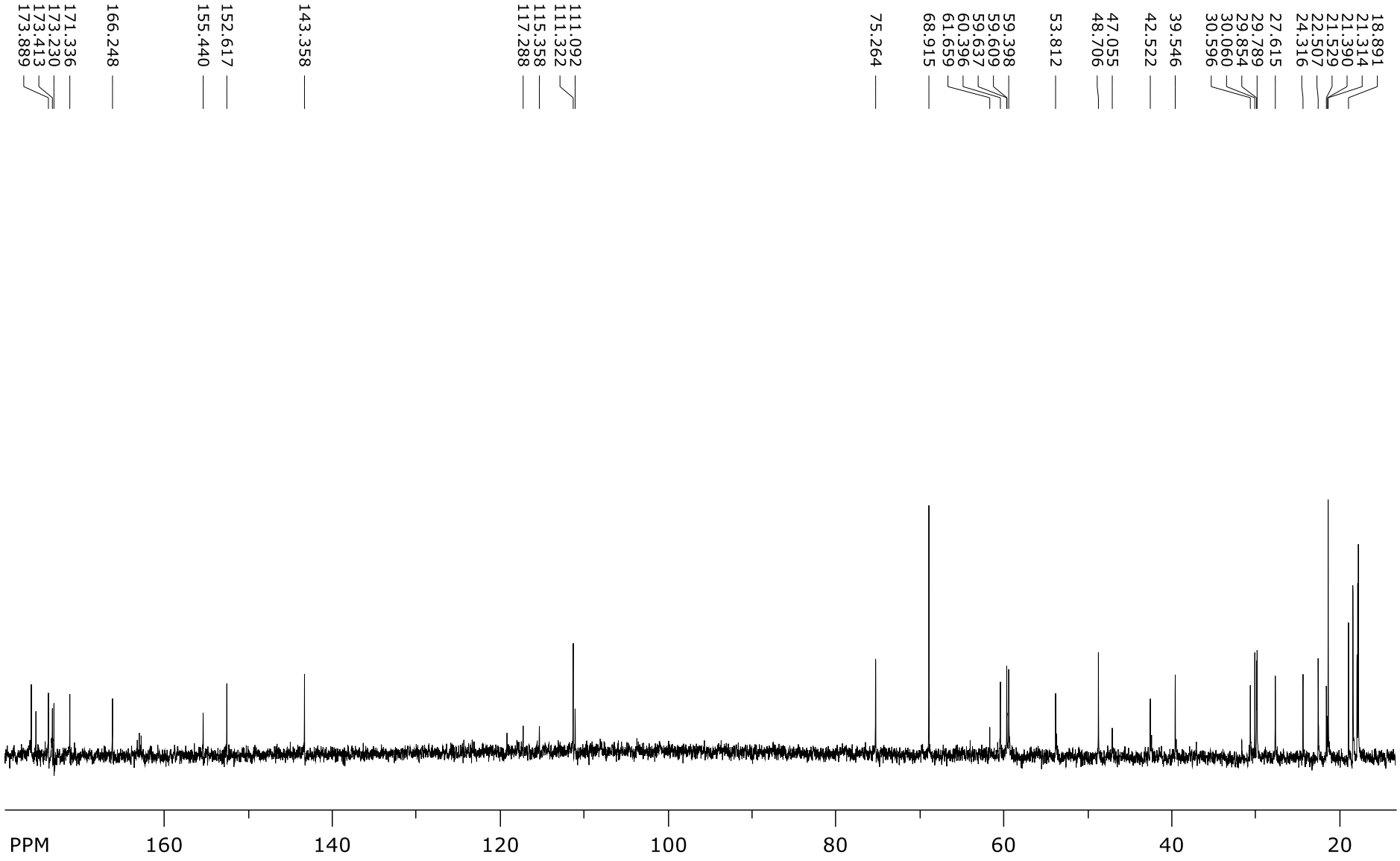


Figure SI 112. ^{13}C-NMR spectrum of **24**.

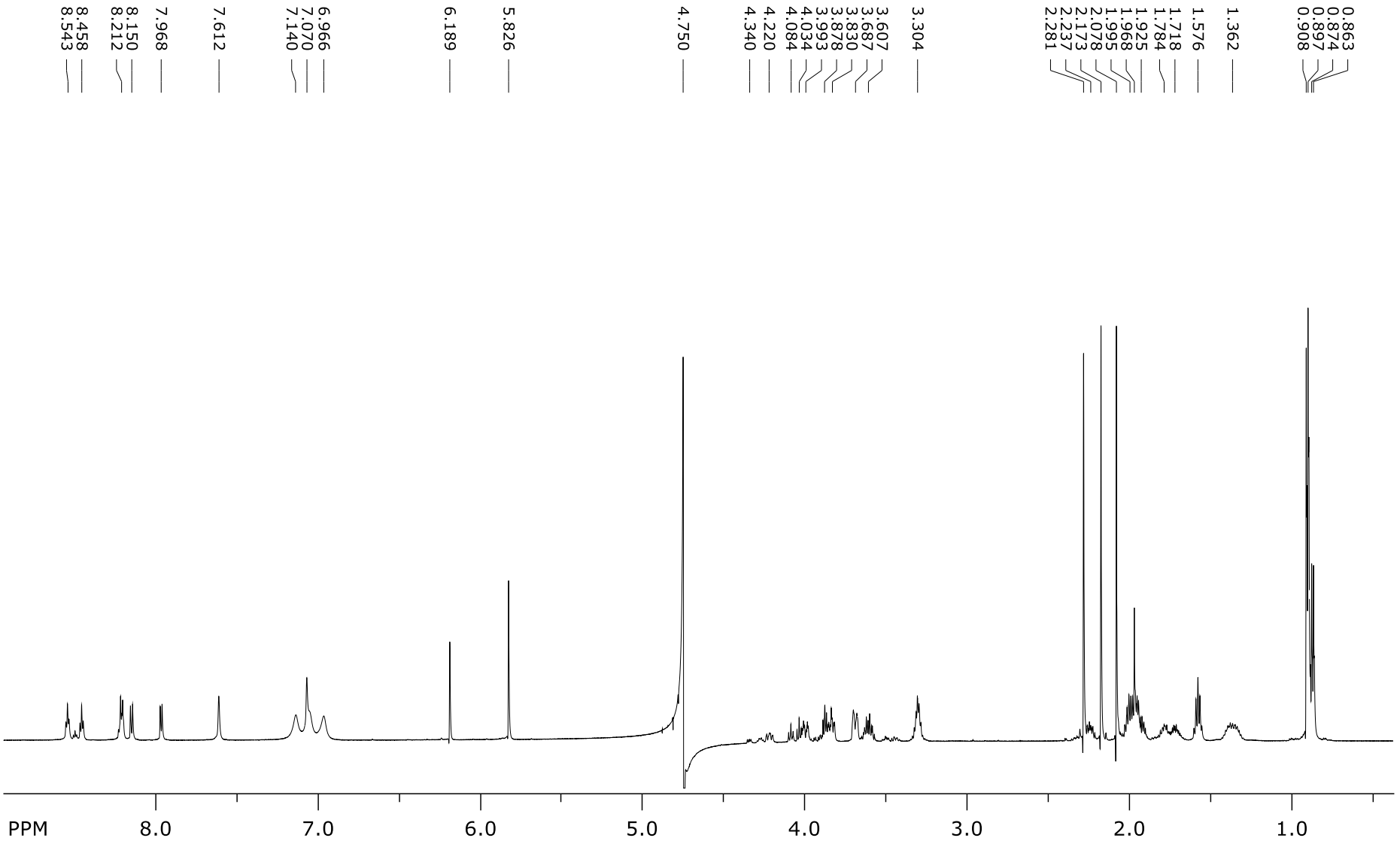


Figure SI 113. ^{1}H-NMR spectrum of **25**.

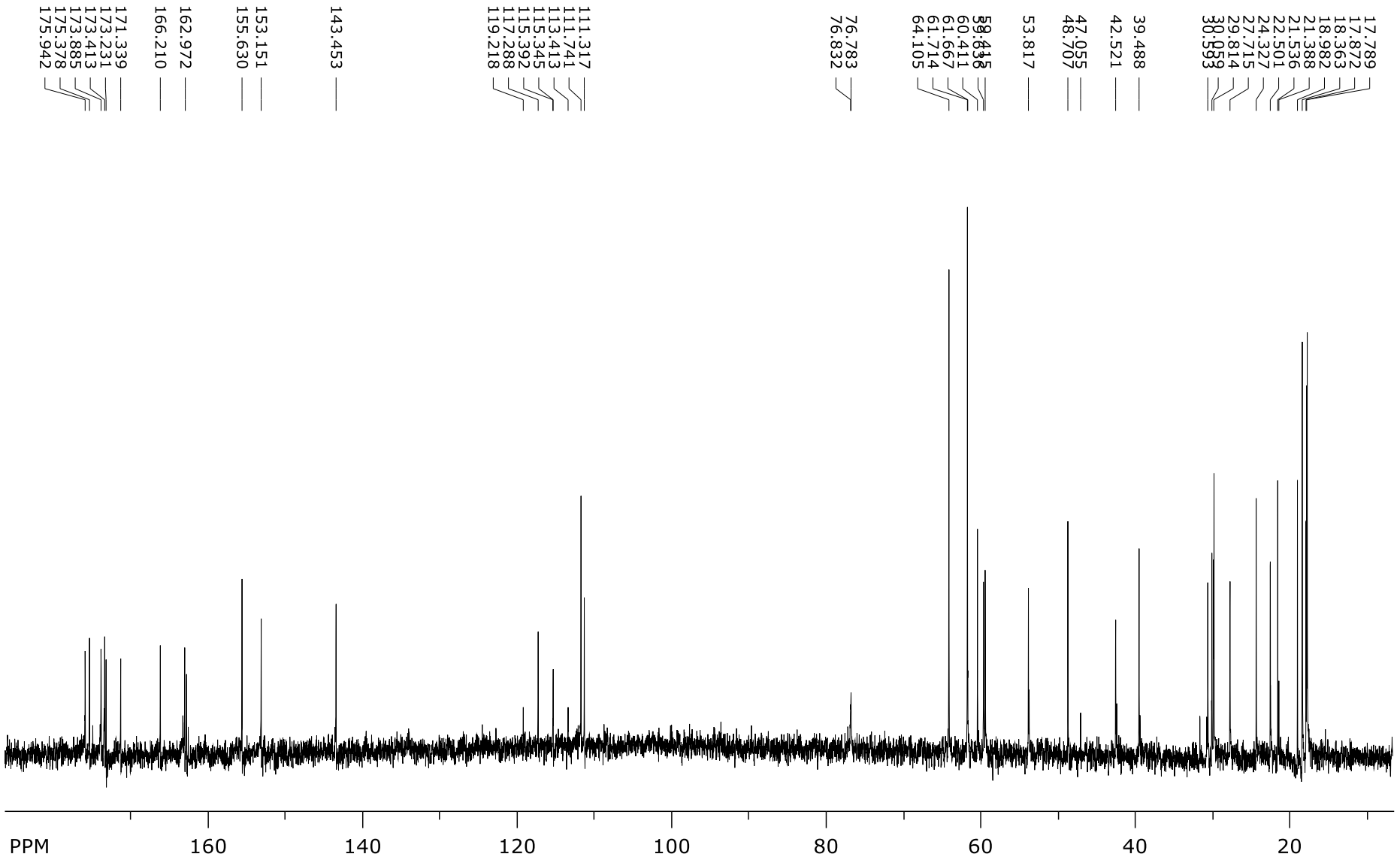


Figure SI 114. ^{13}C-NMR spectrum of **25**.

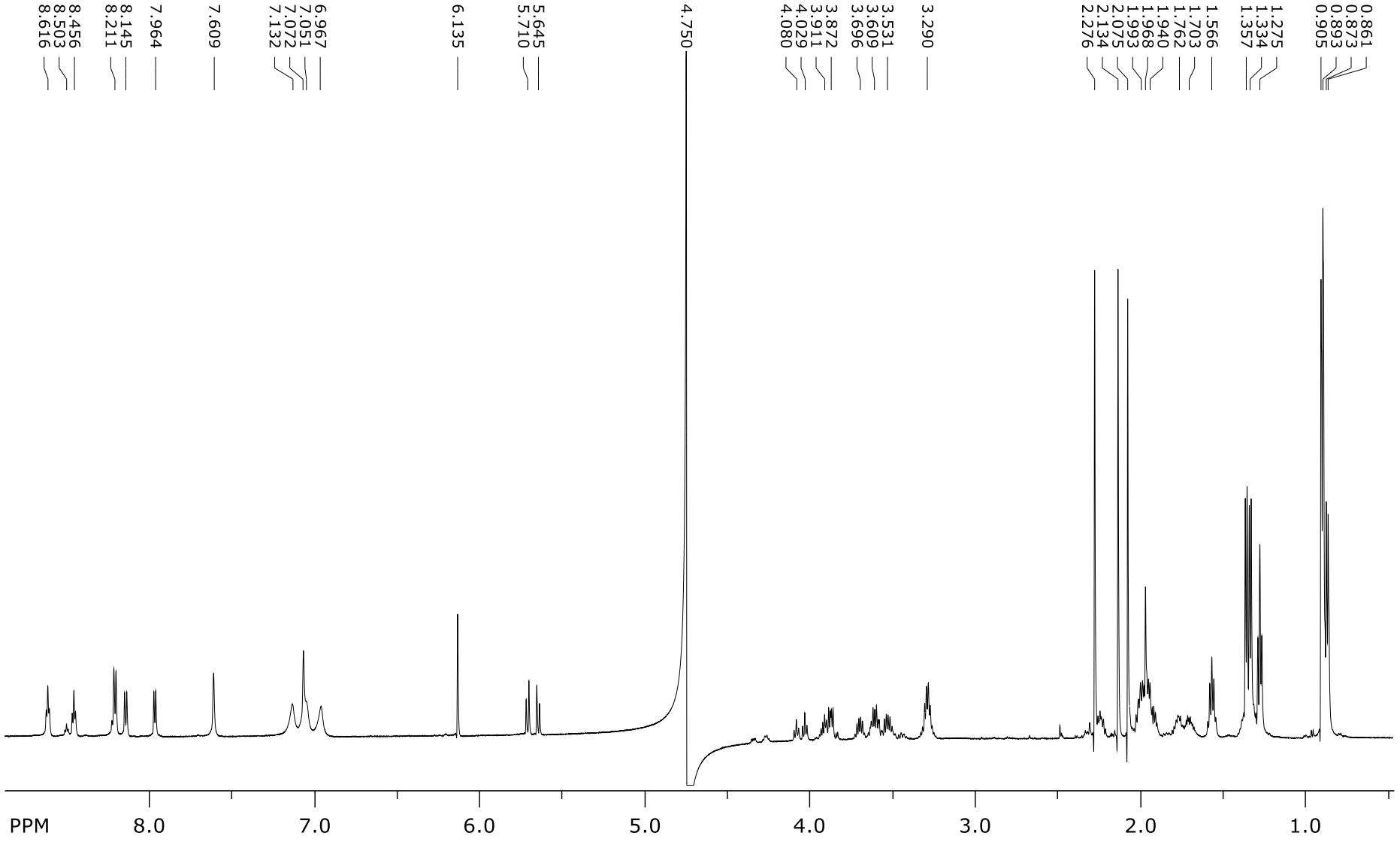


Figure SI 115. ^{1}H-NMR spectrum of **26**.

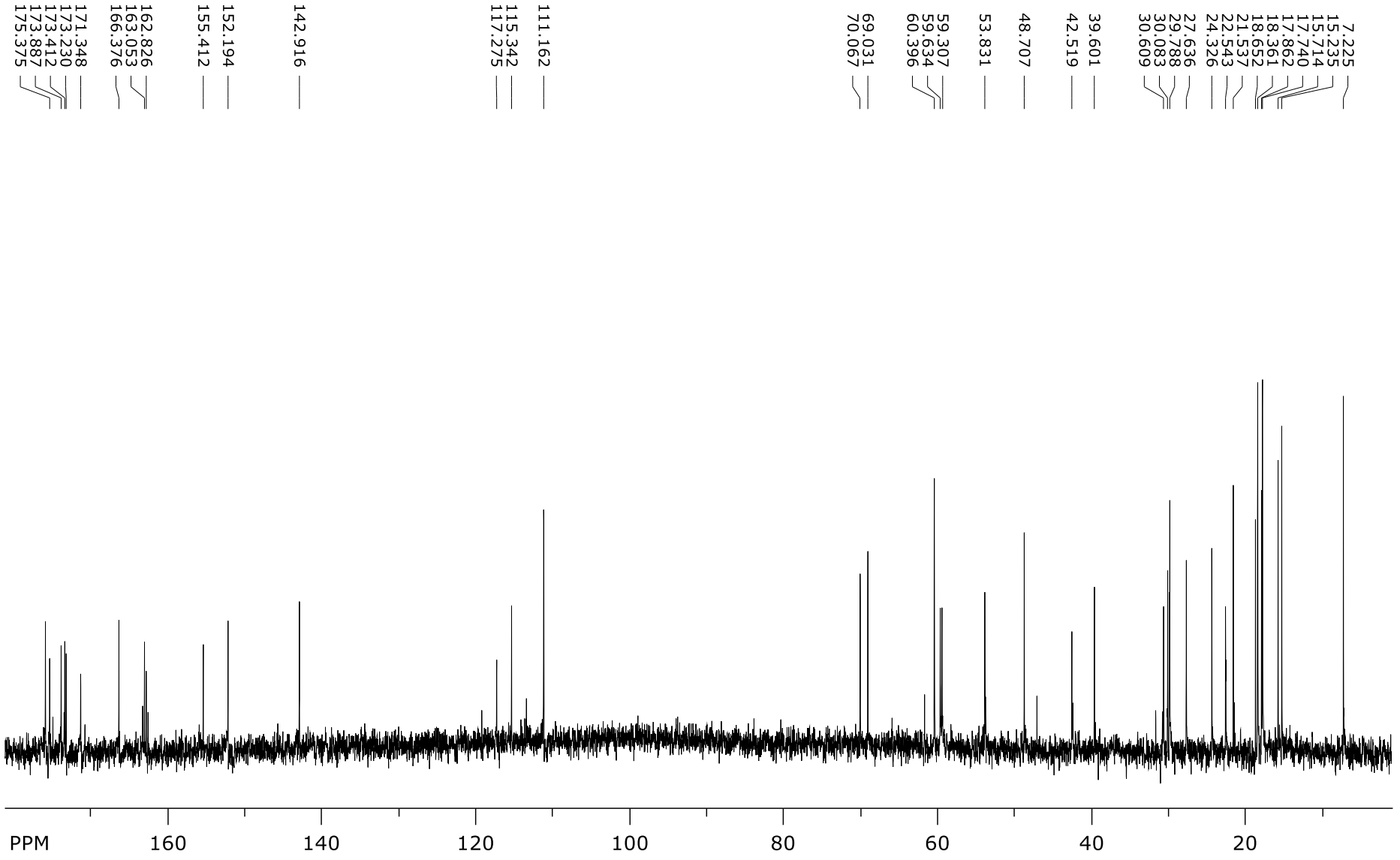


Figure SI 116. ^{13}C-NMR spectrum of **26**.