Stereodynamics and Edge-to-Face CH-π Aromatic Interactions in Imino Compounds Containing Heterocyclic Rings

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Supplementary Information

Page:

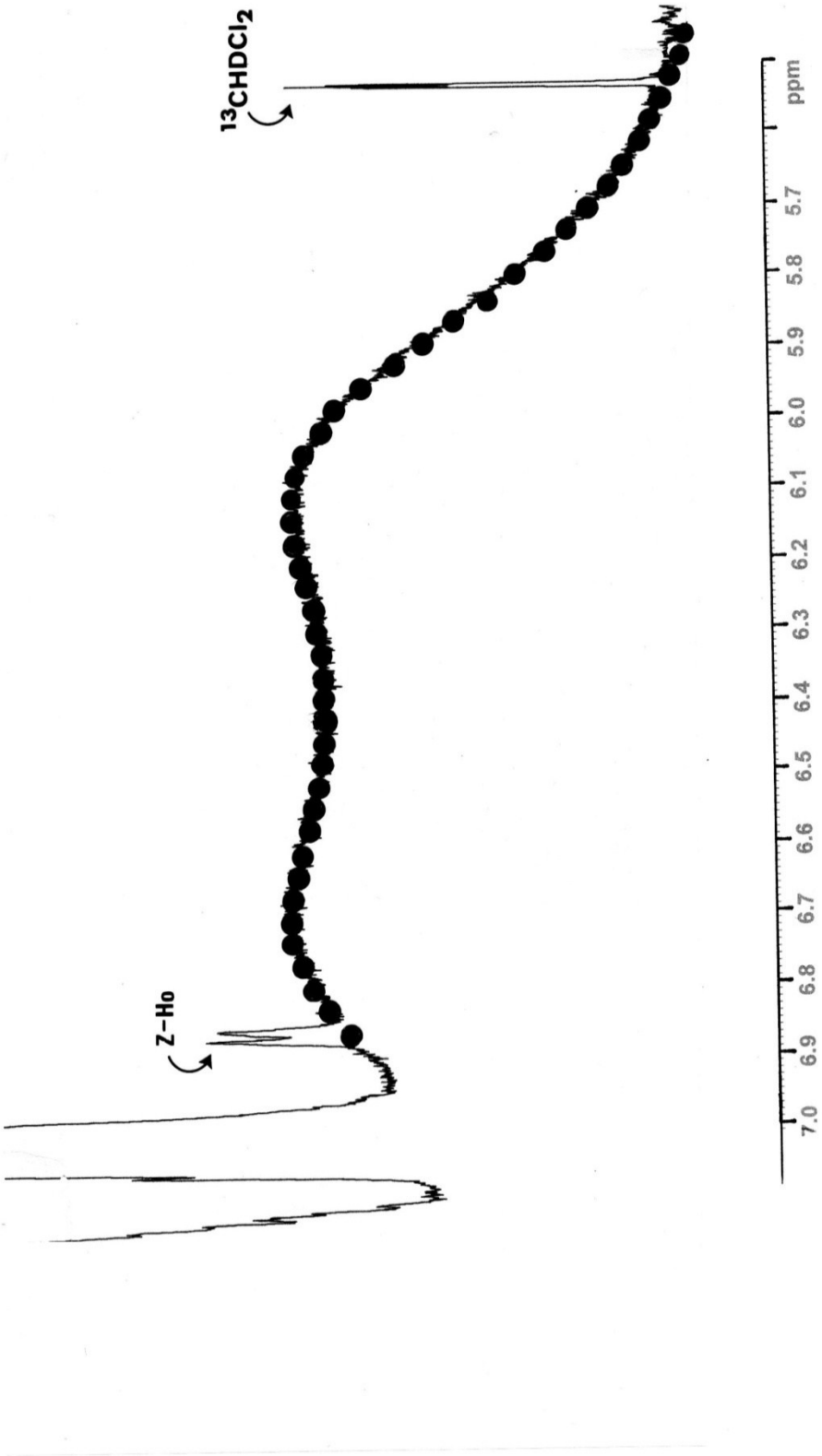


Fig. S-3: Experimental (-) and best fit computed (●) exchange broadened ^{1}H NMR (500 MHz) lineshape of the imino phenyl 2Ho signal of **1**-***E*** at -46 ^{o}C in CD_2Cl_2; k = 1031 s^{-1}.

Barrier to rotation around the phenyl-imino bond in 1-*E*

T/°K	Δν/Hz	St. Dev./%[a]	k/s^{-1}	$\Delta G^{\ddagger}$/kcal mol^{-1}
193	626	1.63	56	9.59
199	610	0.97	96	9.69
203	600	0.83	128	9.77
208	590	0.48	215	9.81
213	570	0.61	349	9.85
227	548	0.86	1031	10.03
233	523	0.54	1813	10.05

[a] St. Dev. is the standard deviation between best fit computed spectrum and the experimental spectrum.

$\Delta H^{\ddagger} = 7.6 \pm 0.4$ kcal mol^{-1} ; $\Delta S^{\ddagger} = -10.5 \pm 2.0$ cal mol^{-1} K^{-1}

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

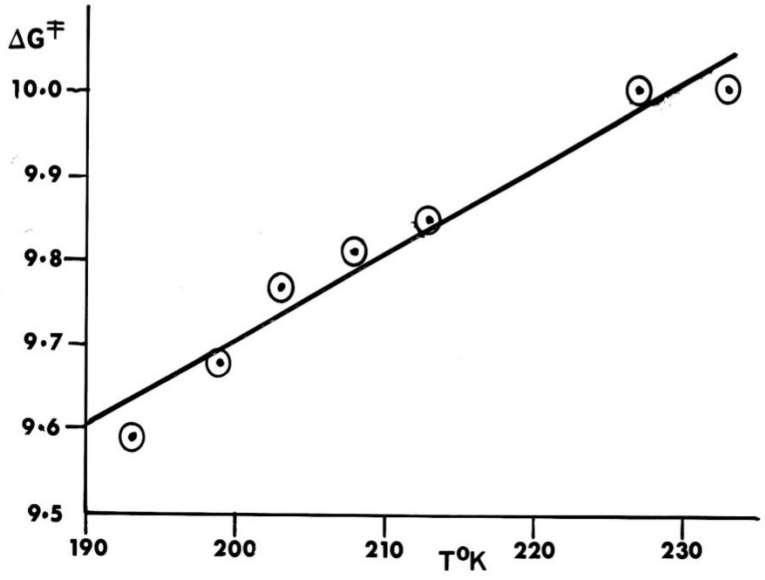


Fig. S-4: Calculated rates of rotation around the phenyl-imino bond in **1-*E*** at various temperatures and estimated free energy ($\Delta G^{\ddagger}$), enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation.

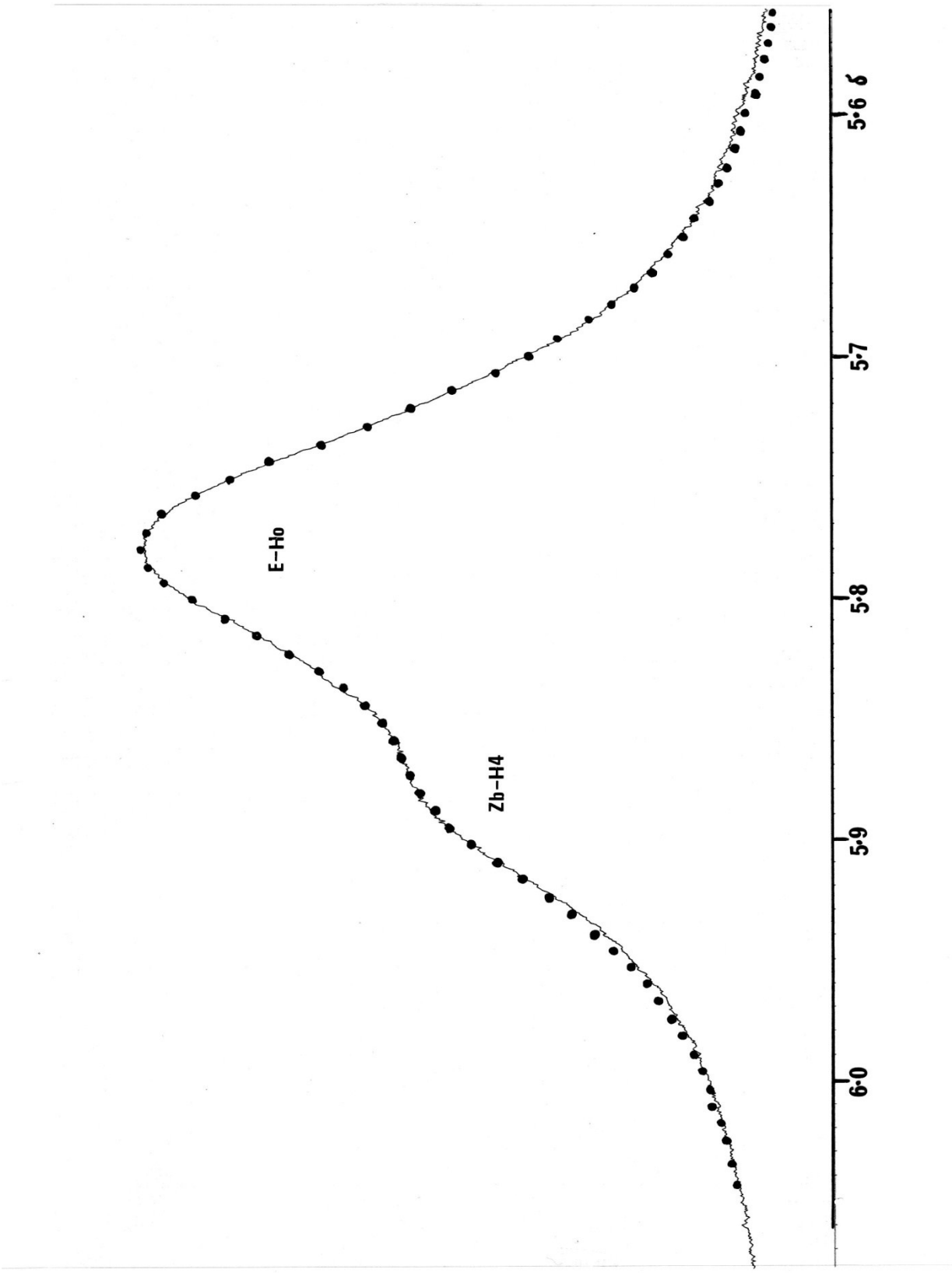


Fig. S-5: Experimental (-) and best fit computed (●) exchange broadened ^{1}H NMR lineshape of the overlapping shielded **1-*E*** Ho and **1-*Z*** pyridyl H-2 signals at -65°C in CD_2Cl_2 (500MHz).

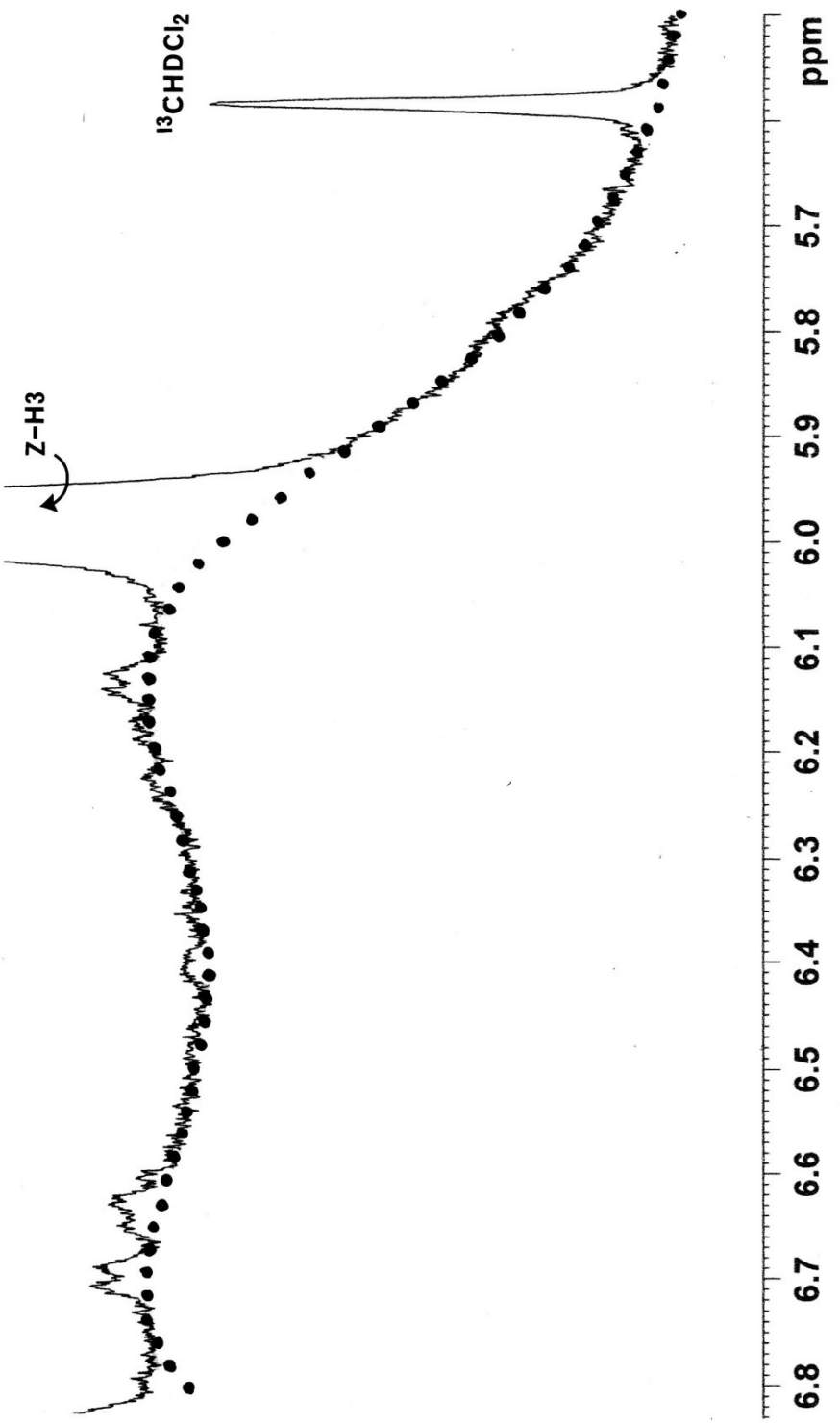
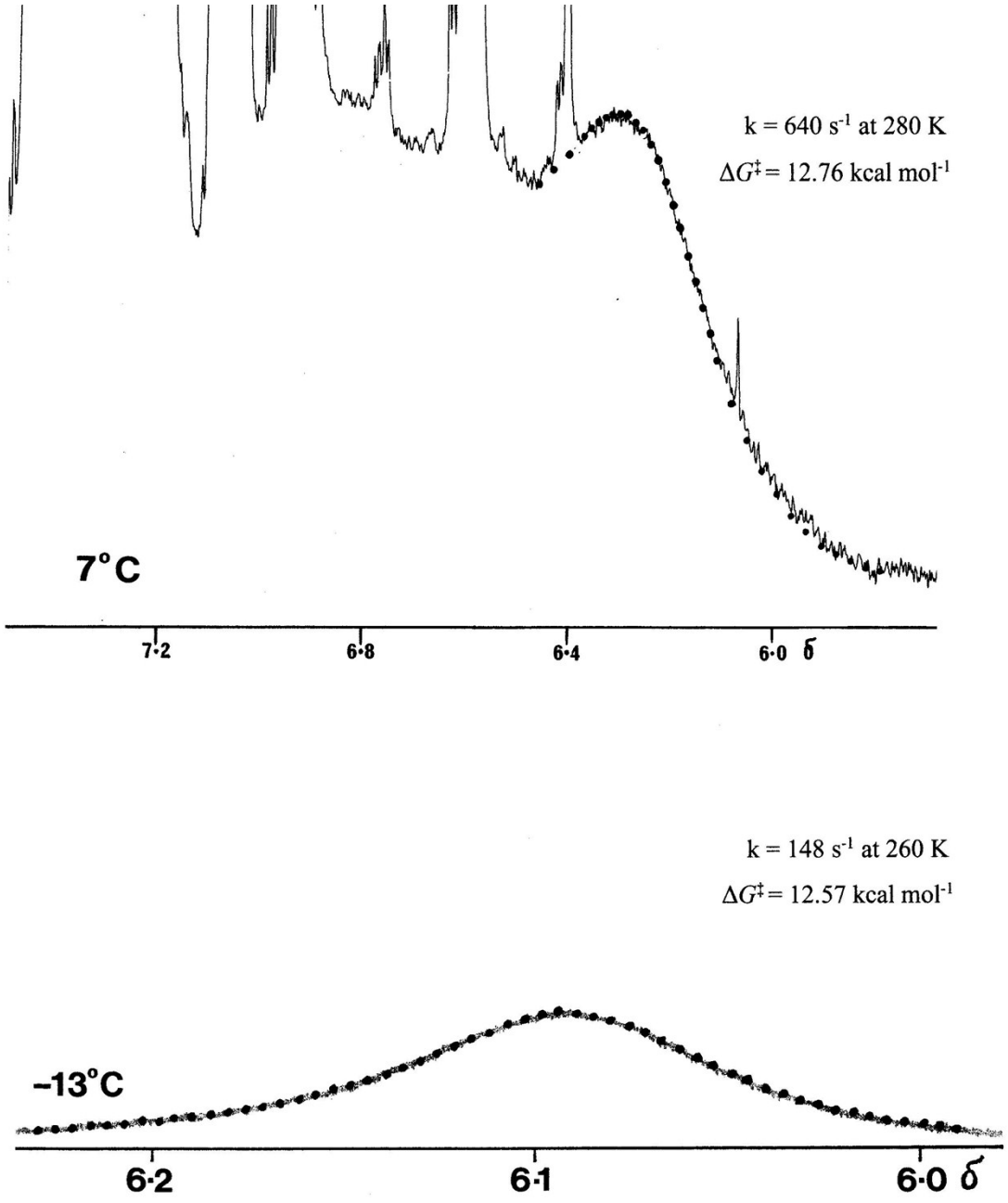


Fig. S-6: Experimental (-) and best fit computed (●) ^{1}H NMR lineshape of the exchange broadened imino phenyl 2Ho signal of **3-*E*** at -52 ^{o}C in CD_2Cl_2 (500 MHz); k = 731 s^{-1}.



Combination of the above $\Delta G^{\ddagger}$ data gives: $\Delta H^{\ddagger} = 10.1 \pm 1.2$ kcal mol^{-1}

$\Delta S^{\ddagger} = -9.5 \pm 4$ cal mol^{-1} K^{-1}

Fig. S-7: Experimental (-)) and best fit computed (●) ^{1}H NMR lineshapes of the exchange broadened imino phenyl 2Ho signal of **5-*E*** at -13 ºC and 7 ºC in CD_2Cl_2 (500 MHz); k = 148 s^{-1} and 640 s^{-1} respectively.

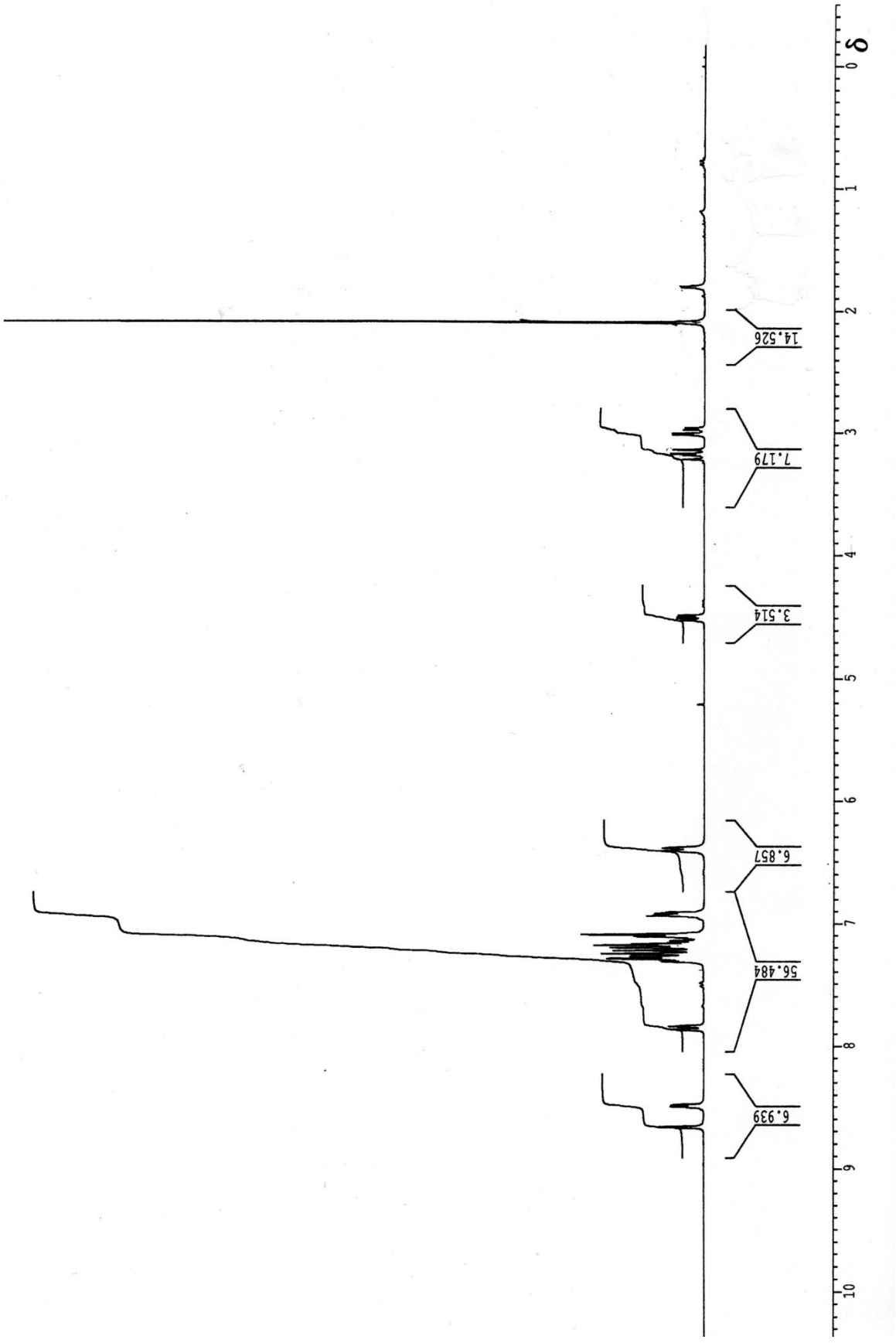


Fig. S-8: ^{1}H NMR (300 MHz) of compound **1*E*** in $CDCl_3$.

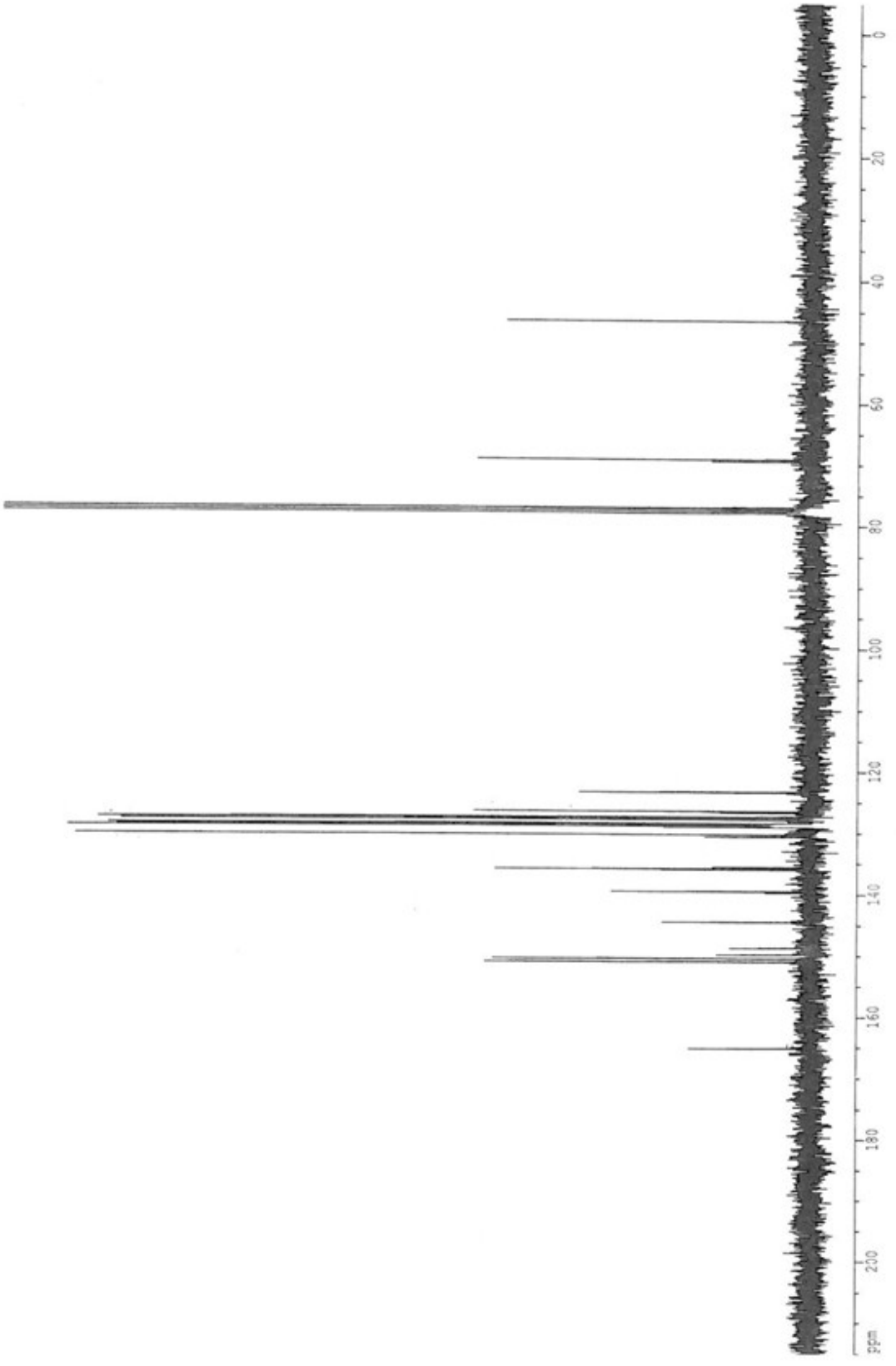


Fig. S-9: ^{13}C NMR (75.4 MHz) of compound **1** (*E* and Z) in $CDCl_3$.

Sample Report (continued):

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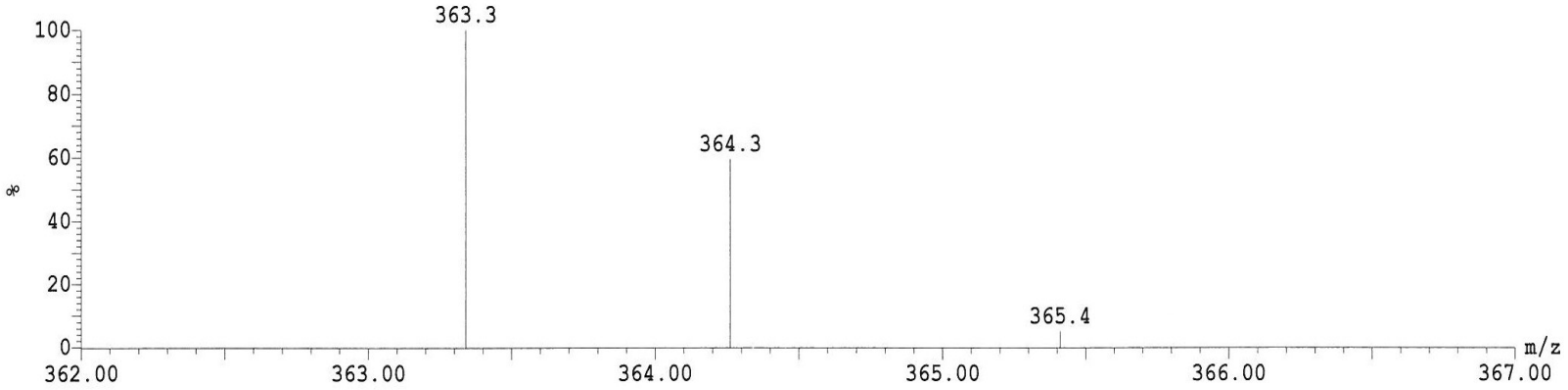
1:MS ES+
7.0e+007



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8.3e+004

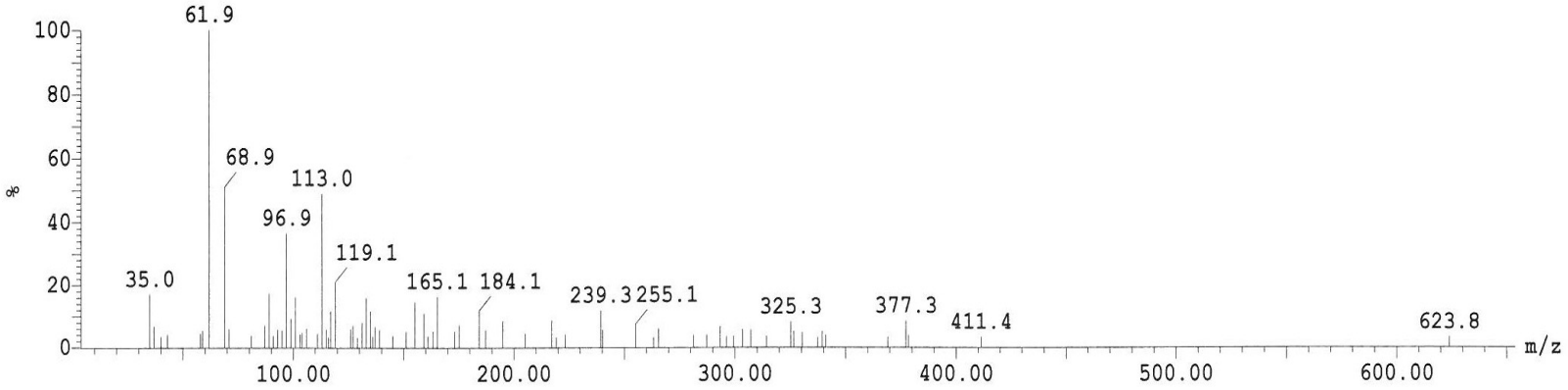


Fig. S-10: Mass Spectrum of compound **1**.

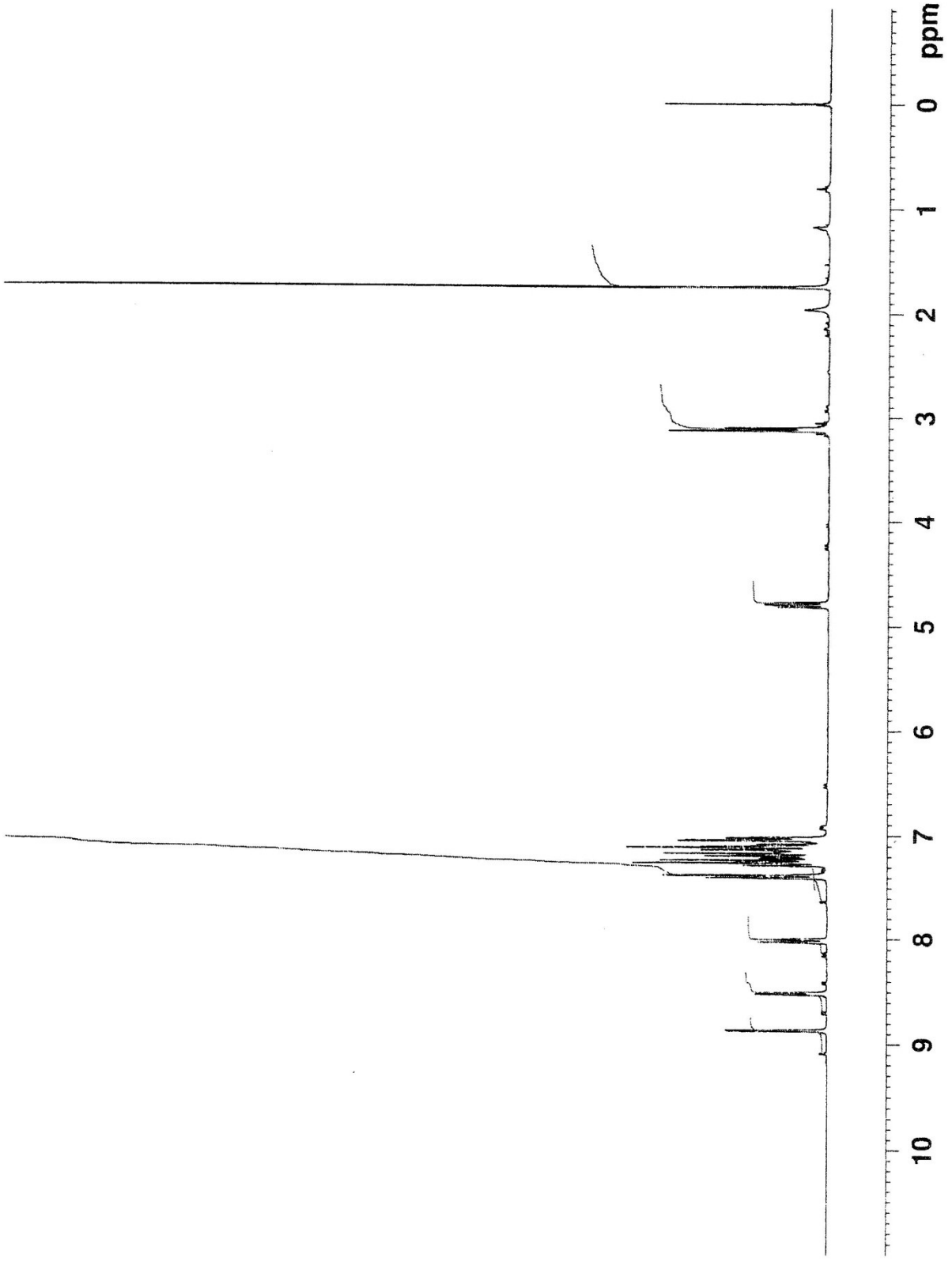


Fig. S-11: ^{1}H NMR (300 MHz) of compound **2** in $CDCl_3$.

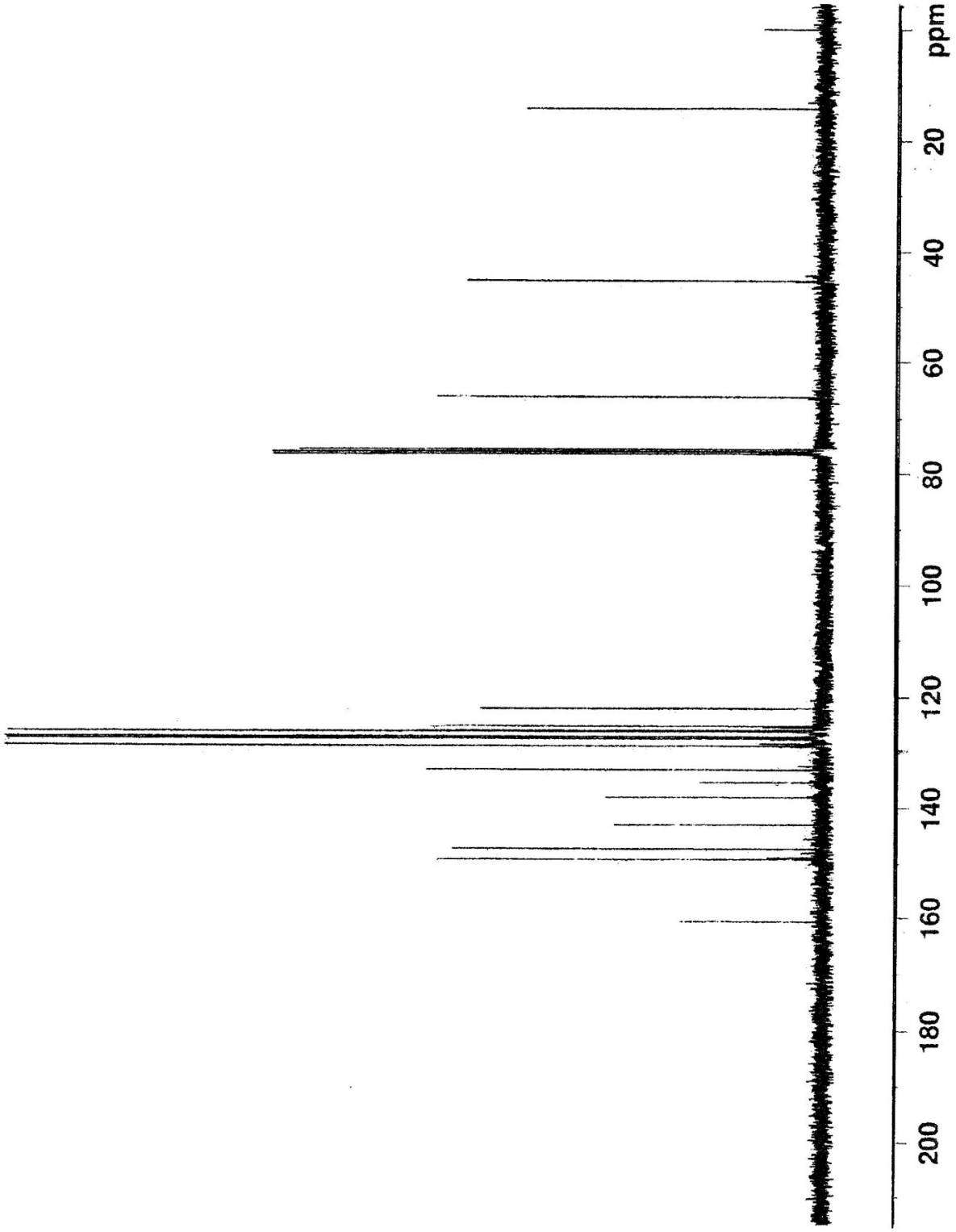
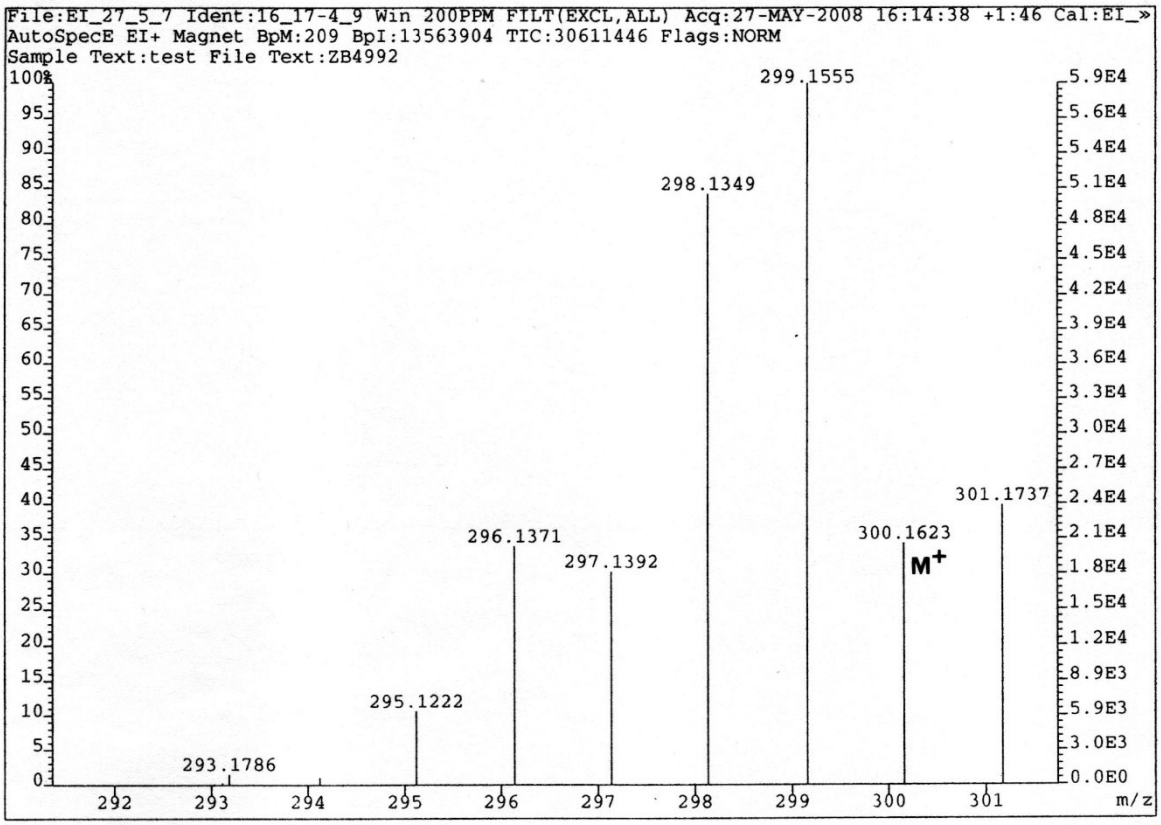


Fig. S-12: ^{13}C NMR (75.4 MHz) of compound **2** in $CDCl_3$.



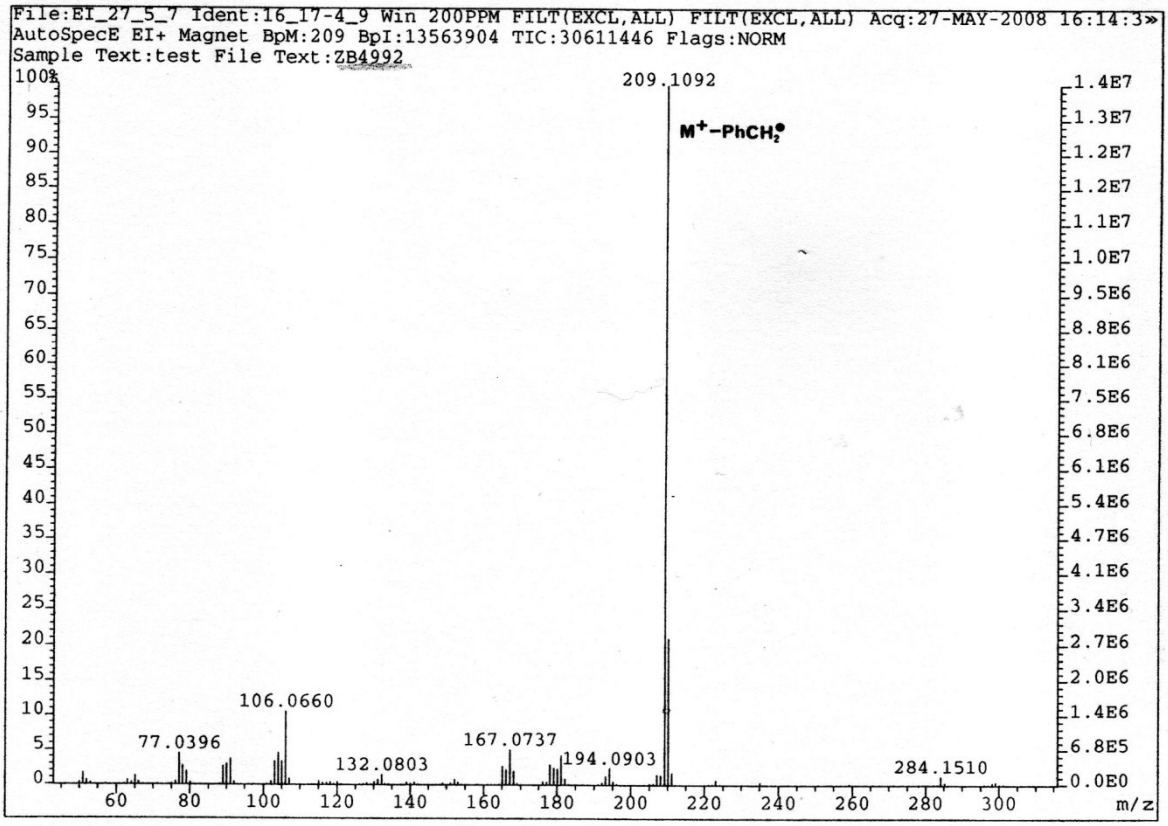


Fig. S-13: Mass Spectrum of compound **2**.

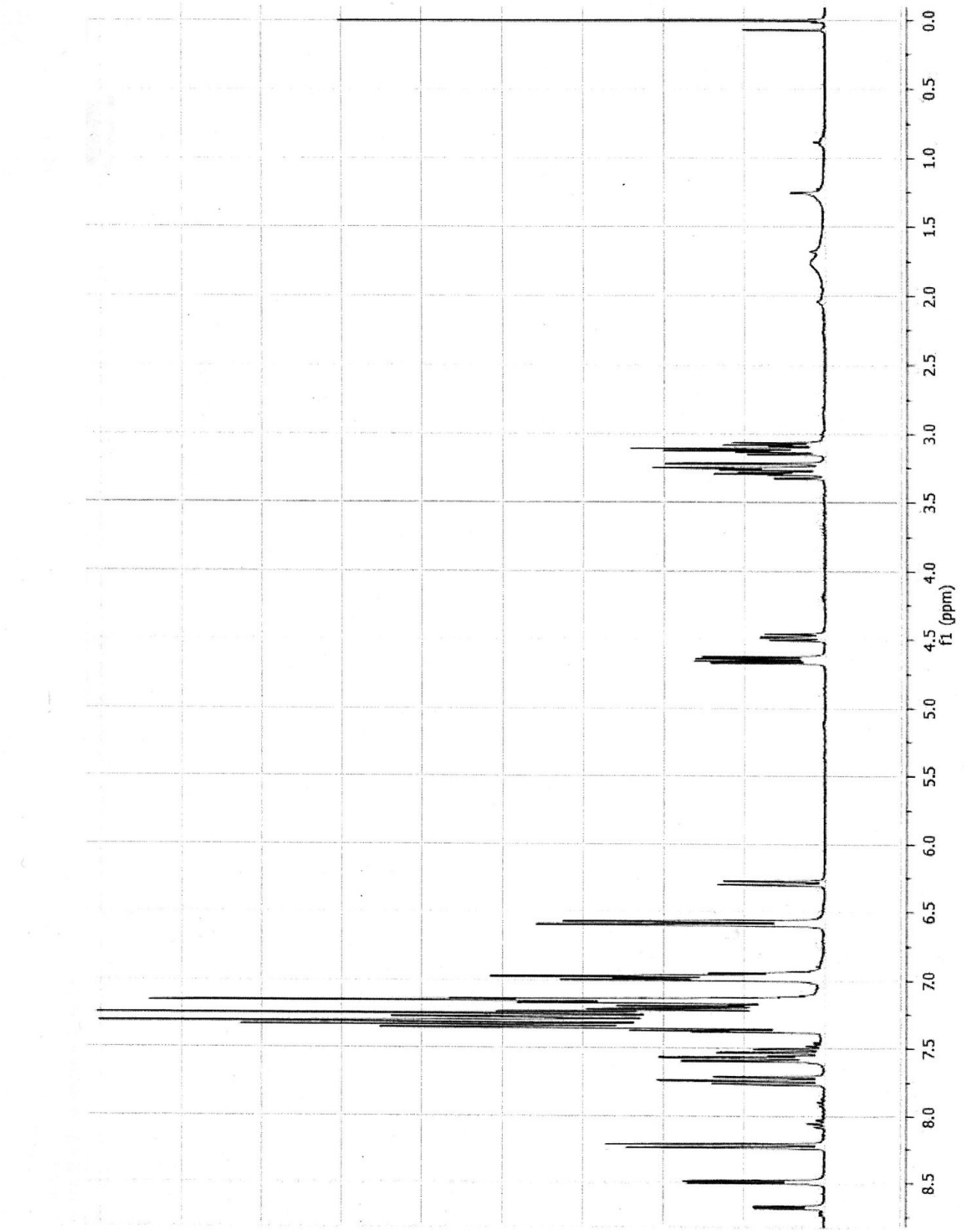


Fig. S-14: ^{1}H NMR (300 MHz) of compound **3** (*E* and *Z*) in $CDCl_3$.

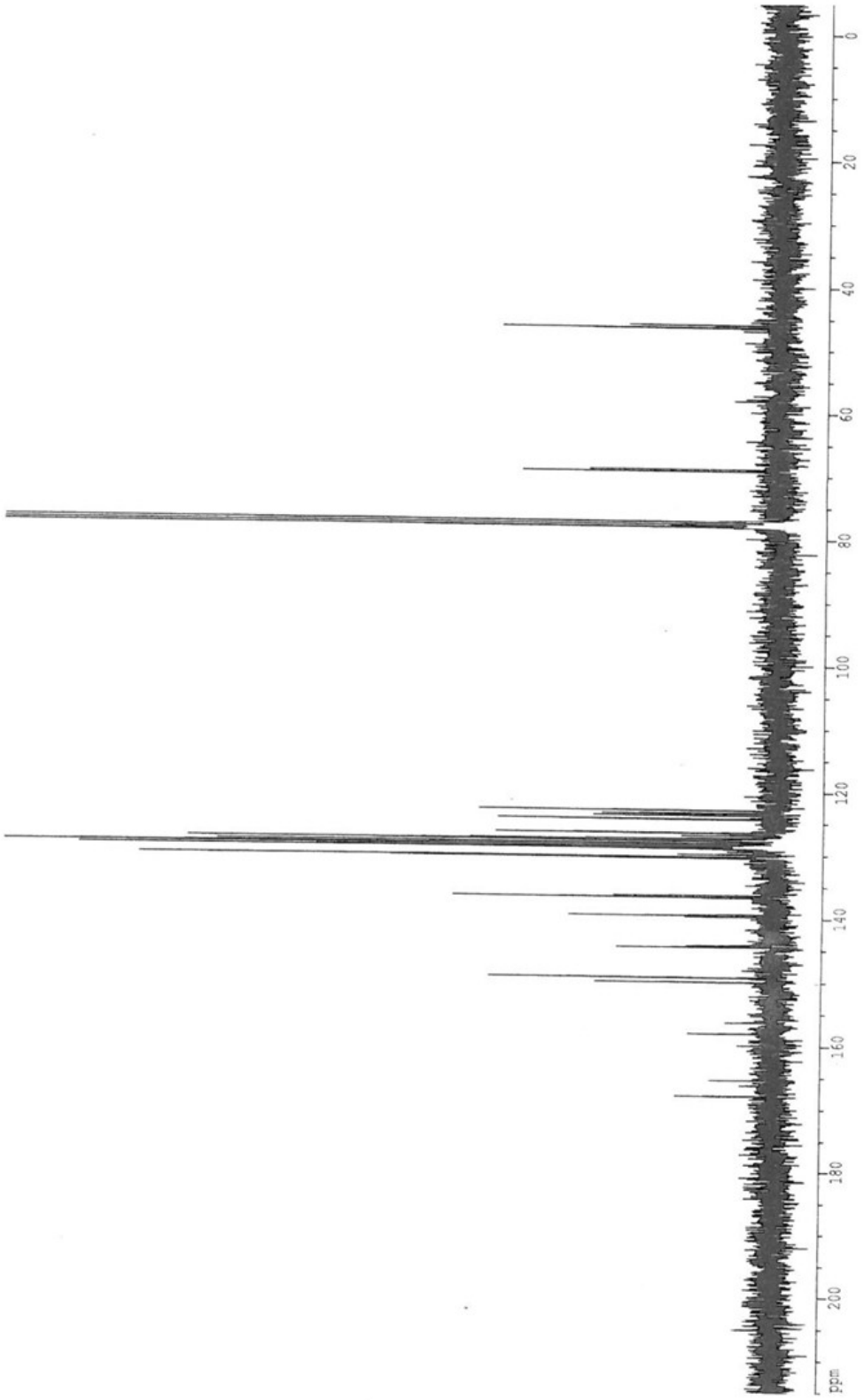


Fig. S-15: ^{13}C NMR (75.4 MHz) of compound **3** (*E* and *Z*) in $CDCl_3$.

S-16: Mass Spectrum of compound **3**.

Single Mass Analysis

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Selected filters: None

Monoisotopic Mass, Even Electron Ions

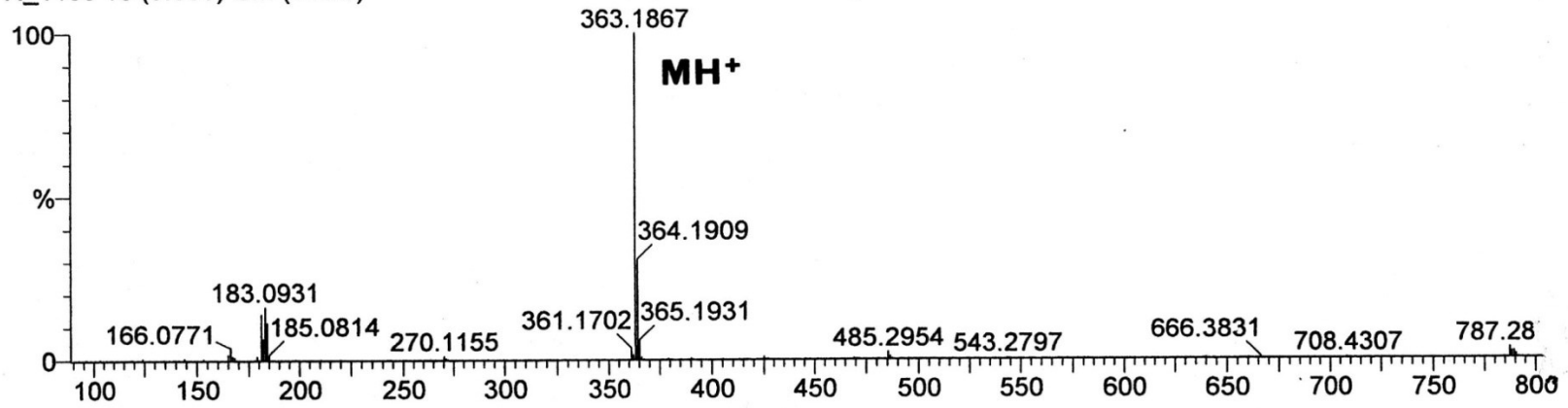
305 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-50 H: 0-50 N: 0-5 O: 0-5 Na: 0-1

EG 5

H_1199 15 (0.630) Cm (11:26)



Minimum:				-1.5						
Maximum:		5.0	10.0	50.0						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula				
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	363.1896	-2.9	-8.0	4.5	17461.8	C17	H28	N2	O5	Na
	363.1837	3.0	8.3	13.5	3938.5	C24	H24	N2	Na	

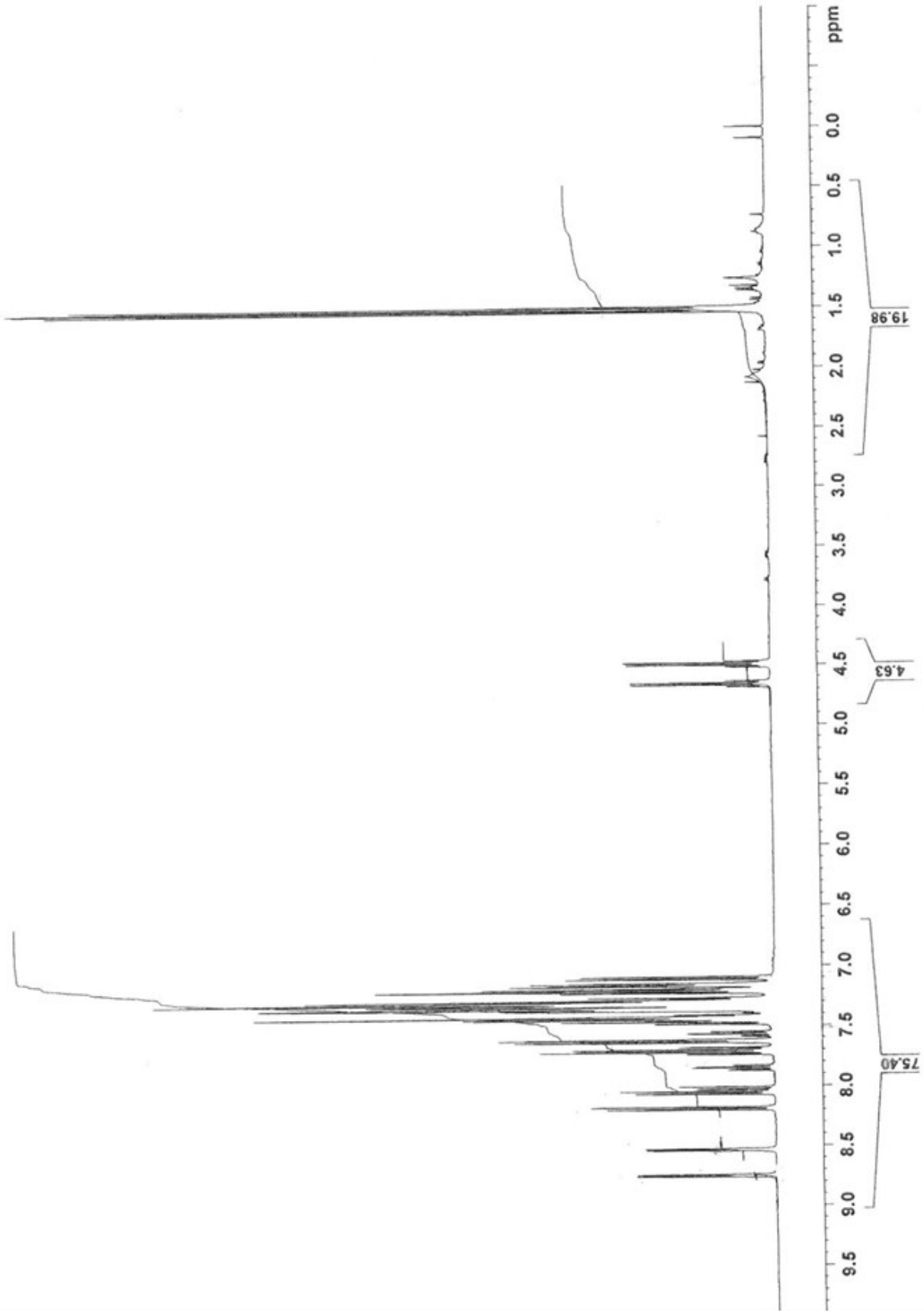

Fig. S-17: ^{1}H NMR (300 MHz) of compound **4** (*E* and *Z*) in $CDCl_3$.

Single Mass Analysis
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Selected filters: None

Monoisotopic Mass, Even Electron Ions
255 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
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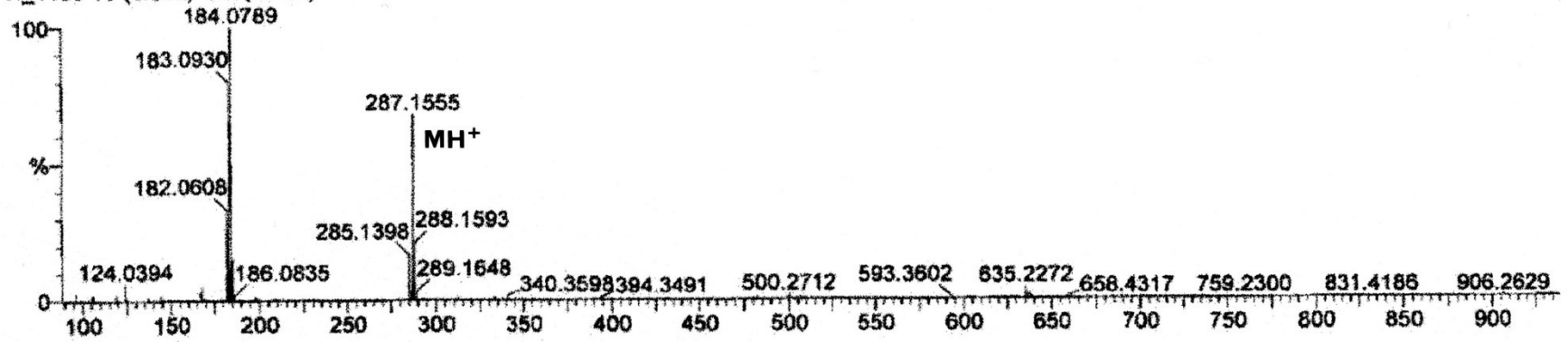
EG 4
H_1198 15 (0.630) Cm (10:32)



Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
287.1555	287.1548	0.7	2.4	12.5	1069.7	C20 H19 N2
	287.1583	-2.8	-9.8	0.5	5204.6	C11 H24 N2 O5 Na

Fig. S-18: Mass Spectrum of compound 4.

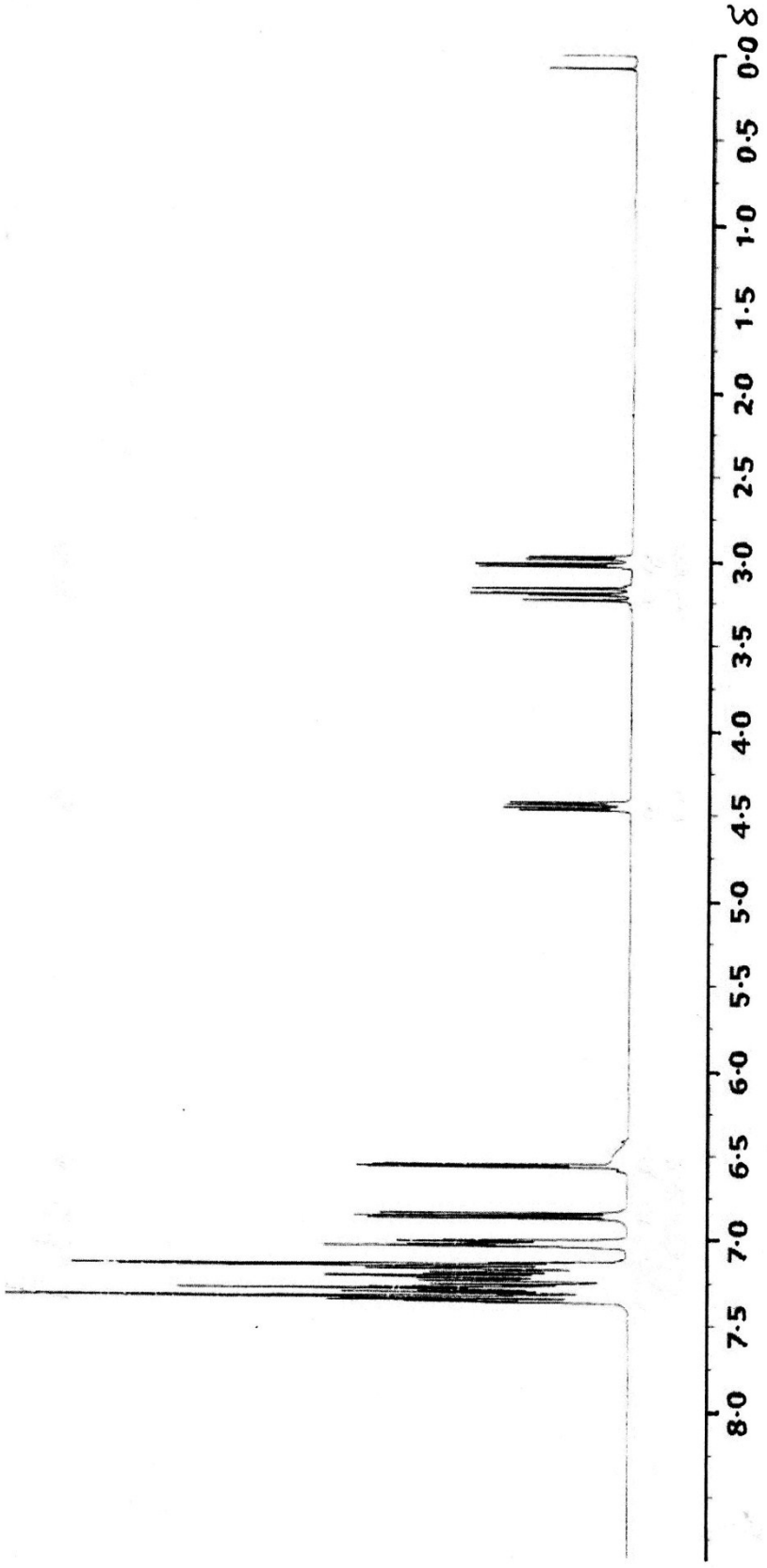


Fig. S-19: ^{1}H NMR (300 MHz) of compound **5** in $CDCl_3$.

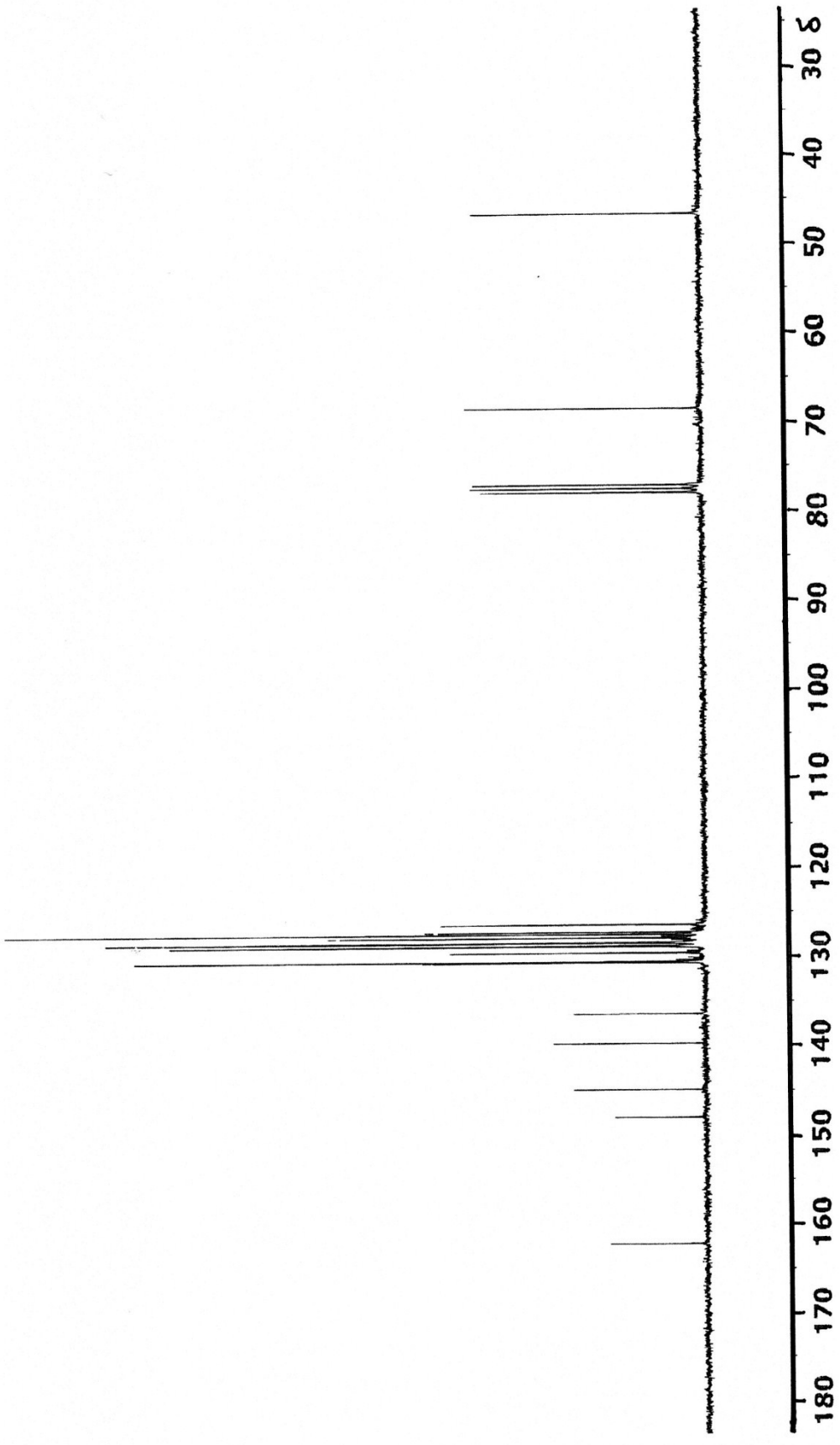
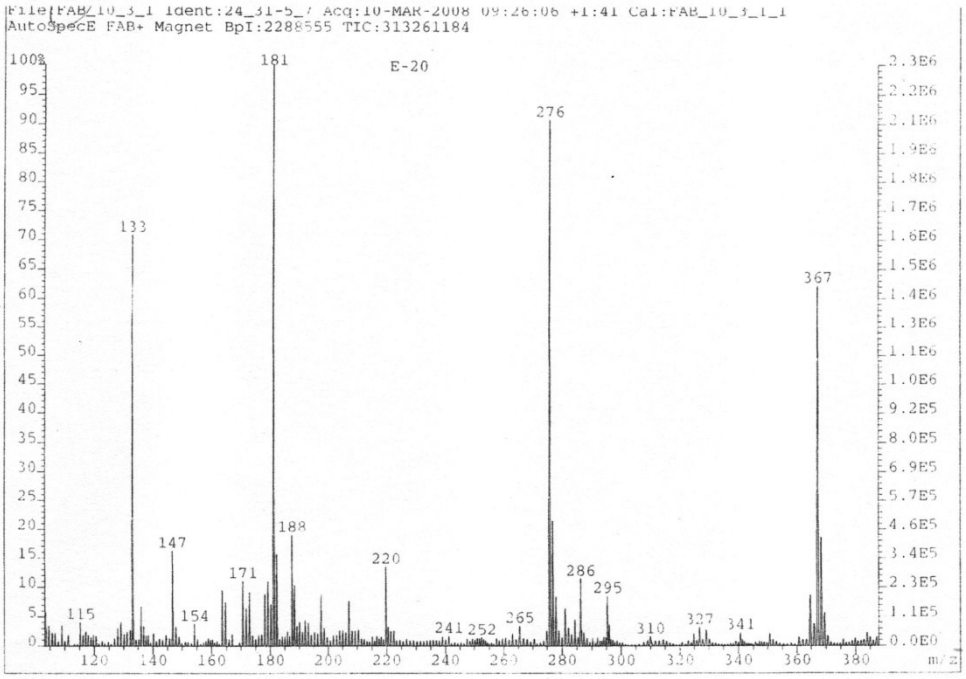


Fig. S-20: ^{13}C NMR (74.5 MHz) of compound **5** in $CDCl_3$.



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Mass	%RA	mDa	PPM	Calc. Mass	DBE	C	H	N	S
368.147577	2.4	-0.3	-0.8	368.147297	15.5	25	22	1	1

Statistic calculations

	mDa	PPM	
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Fig. S-21: Mass Spectrum of compound **5**.

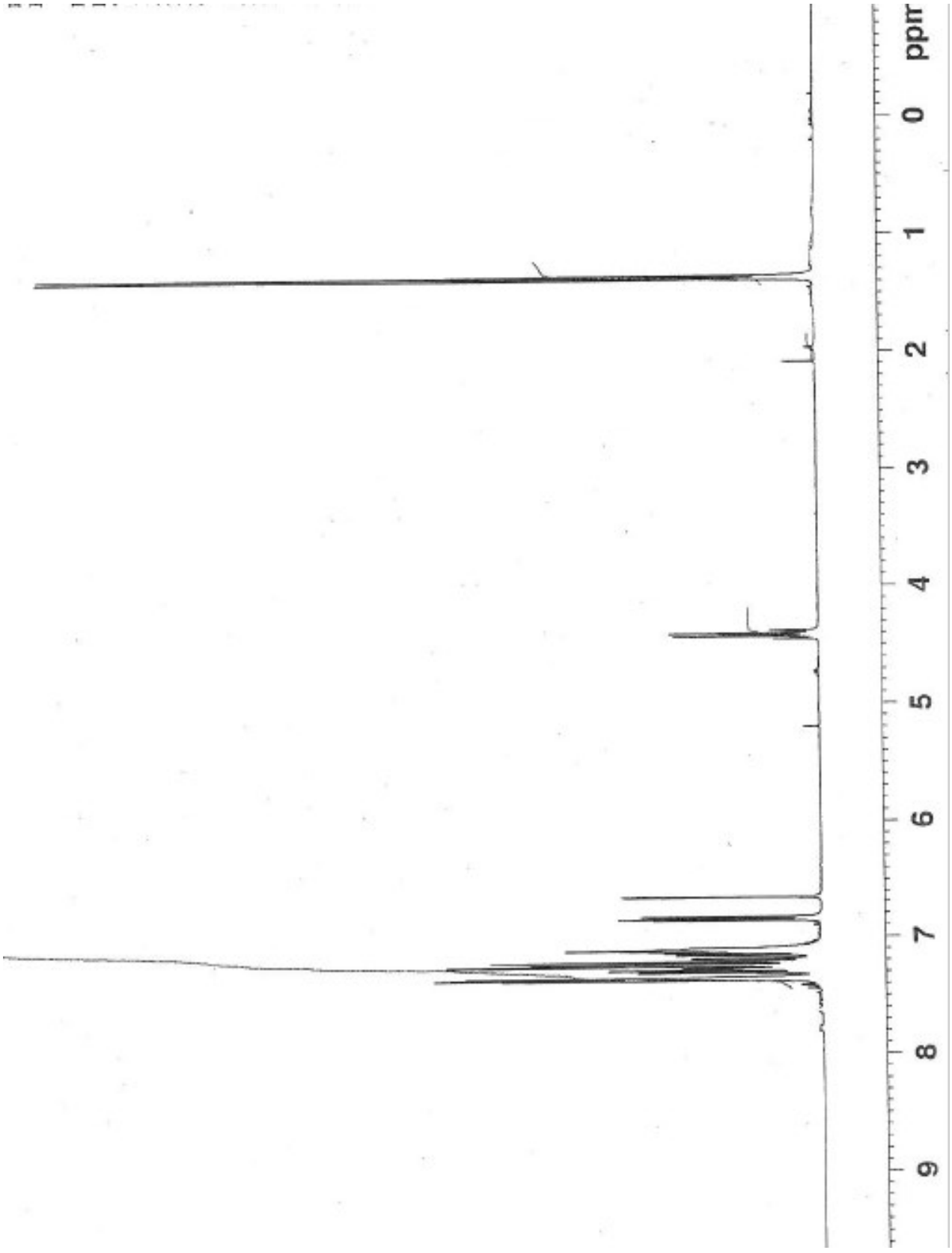


Fig. S-22: ^{1}H NMR (300 MHz) of compound **6** in $CDCl_3$.

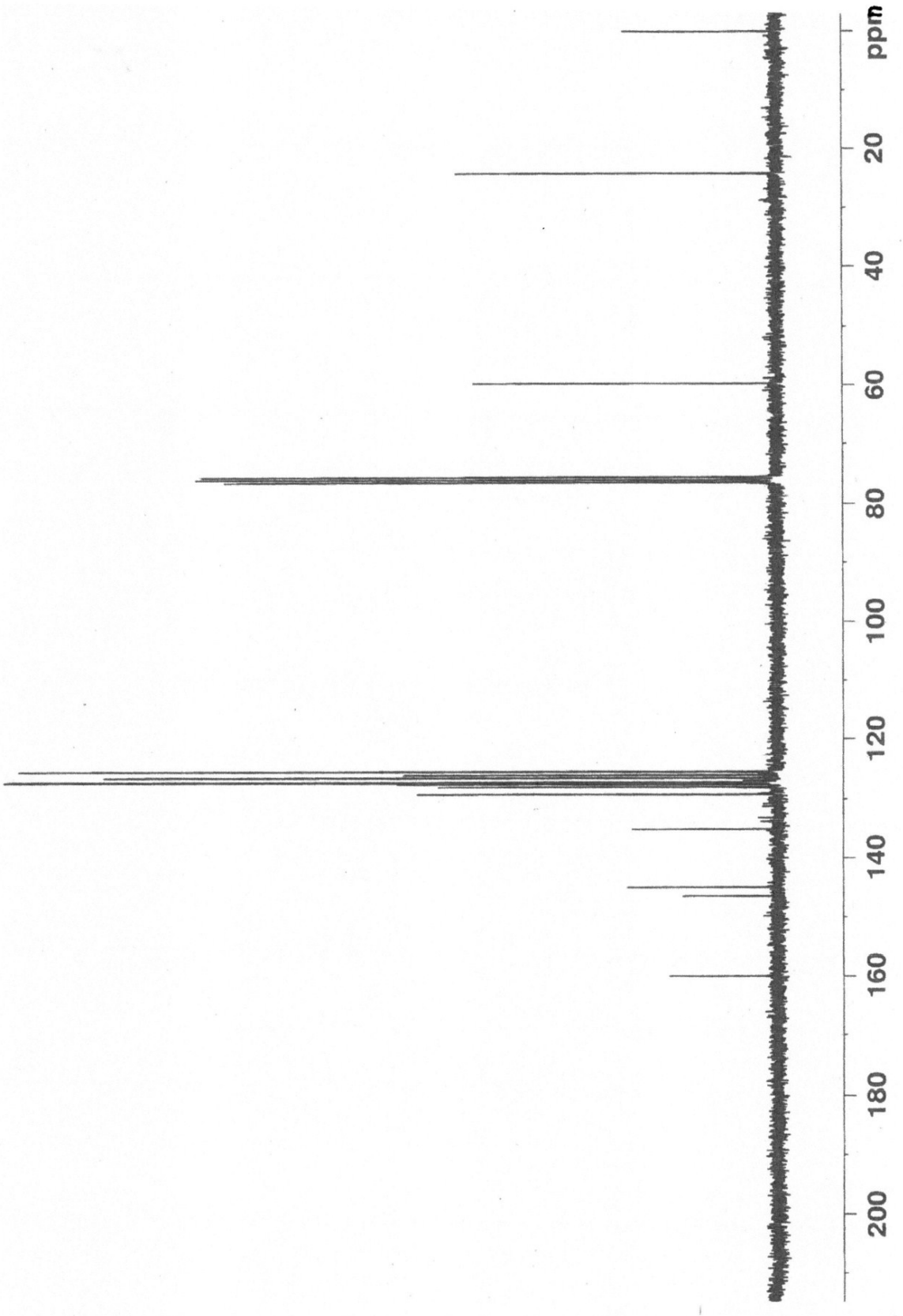


Fig. S-23: ^{13}C NMR (75.4 MHz) of compound **6** in $CDCl_3$.

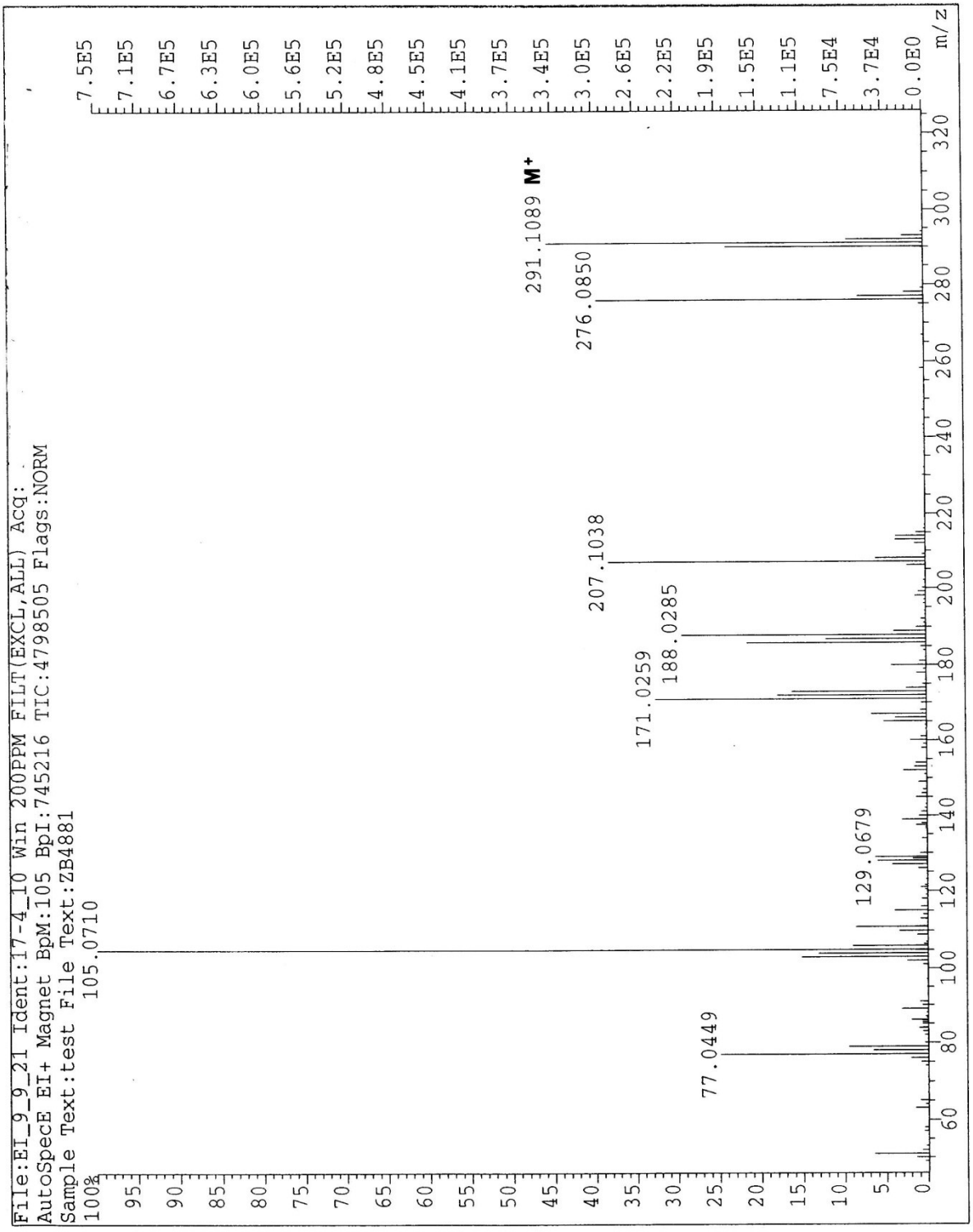


Fig. S-24: Mass Spectrum of compound **6**.

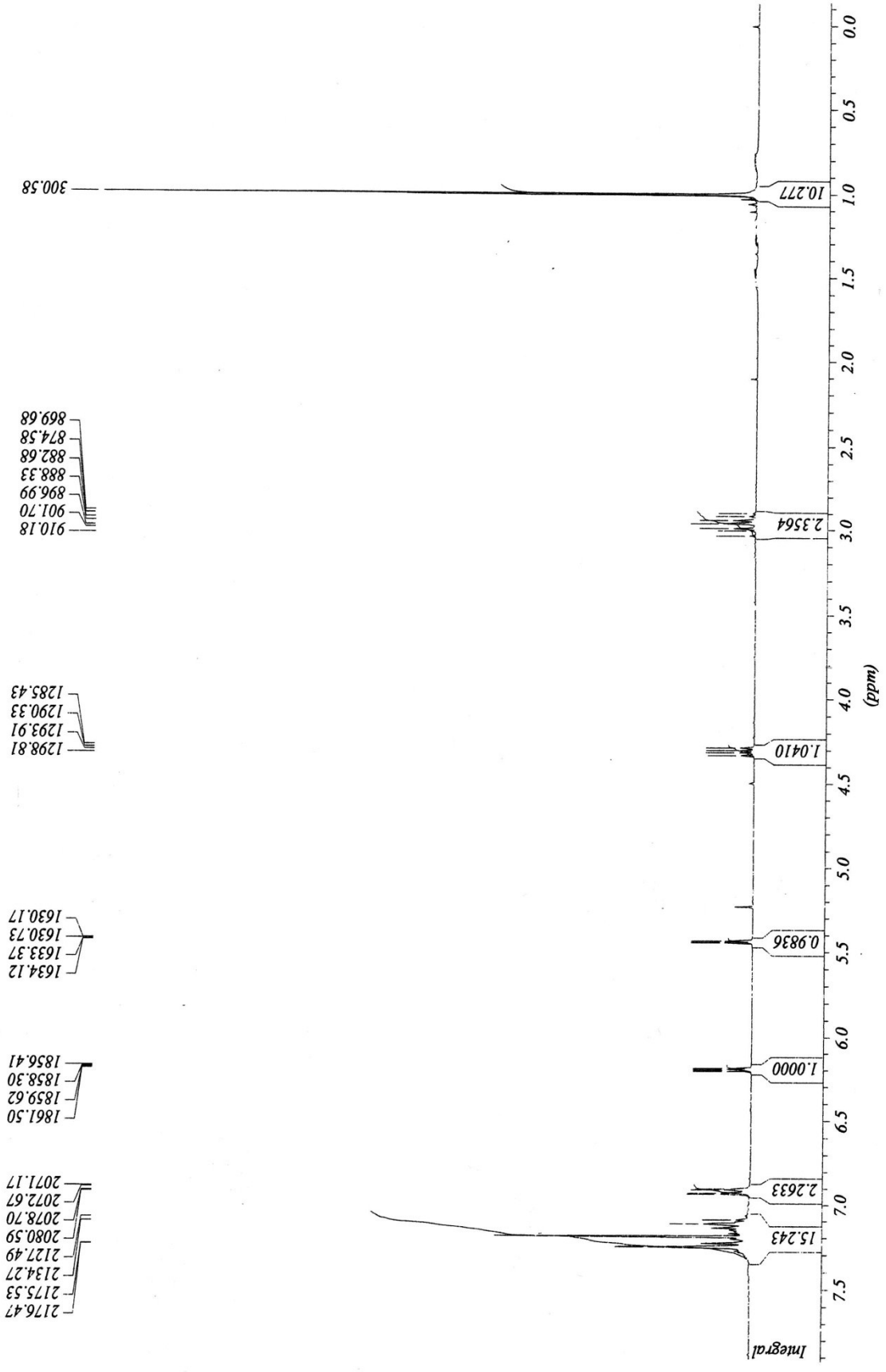


Fig. S-25: ^{1}H NMR (300 MHz) of compound **7** in $CDCl_3$.

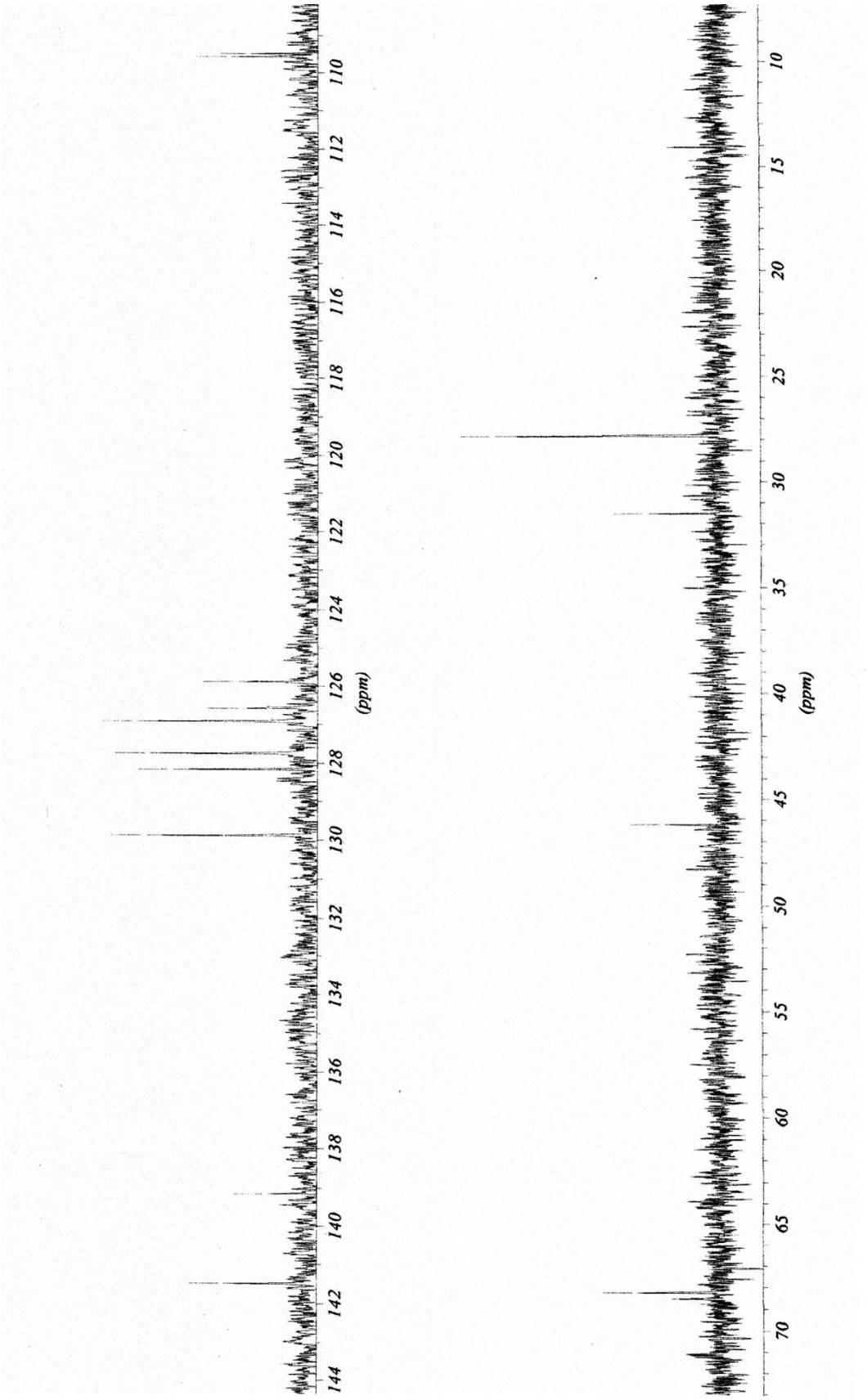


Fig. S-26: ^{13}C NMR (75.4 MHz) of compound **7** in $CDCl_3$.

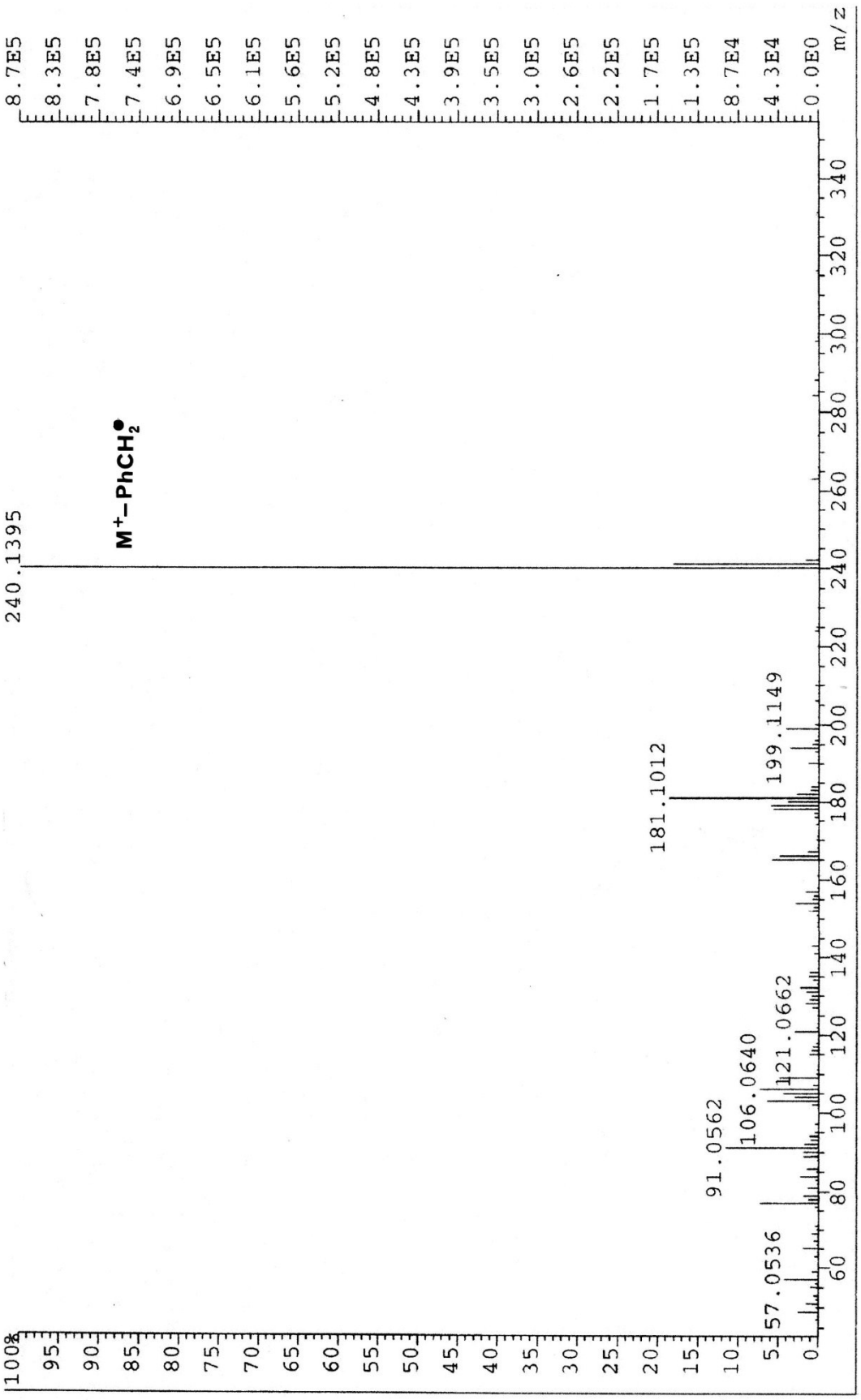


Fig. S-27 Mass Spectrum of compound **7.**

Fig. S-28: ^{1}H NMR (300 MHz) of compound **8** in $CDCl_3$.

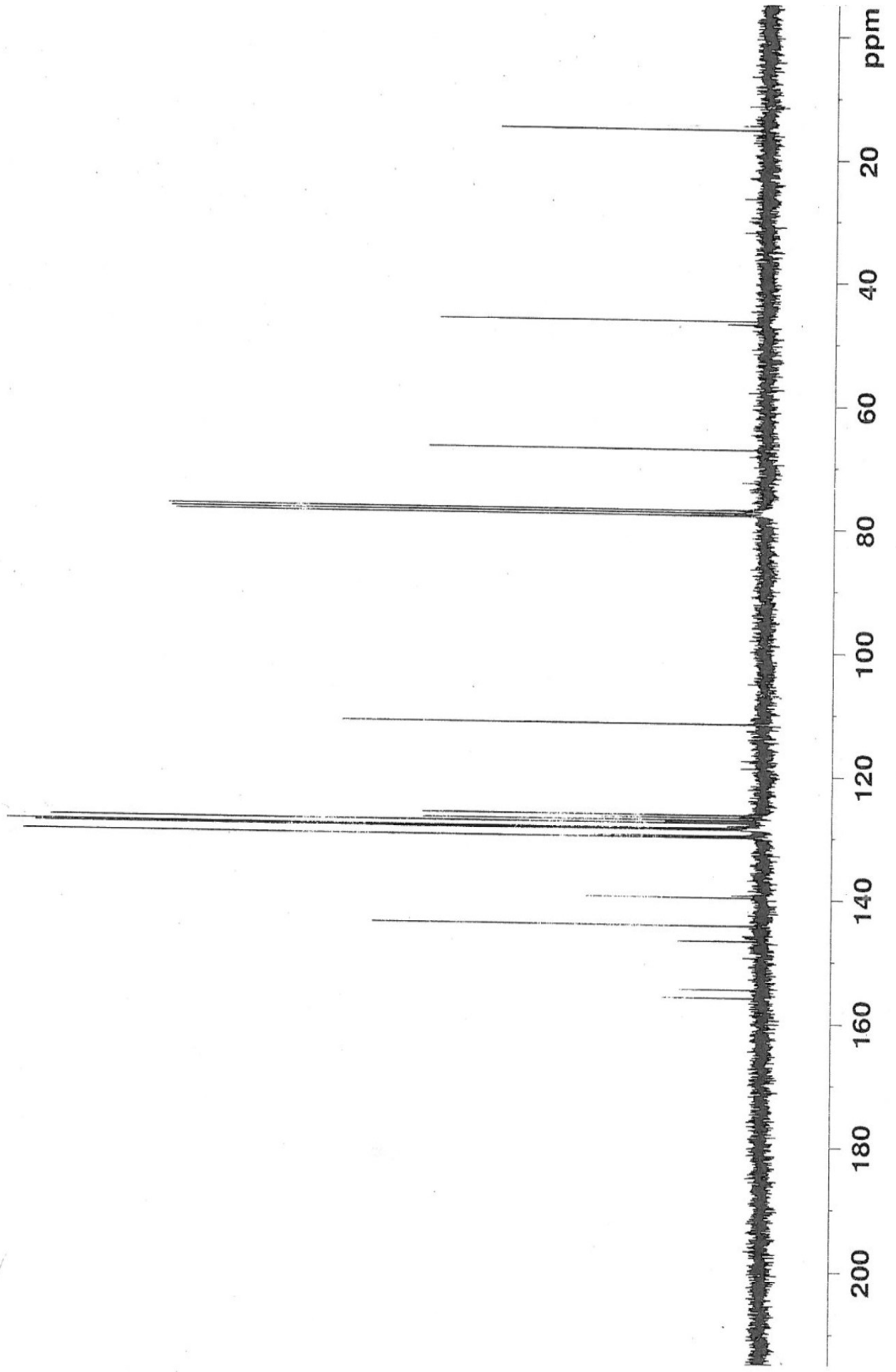
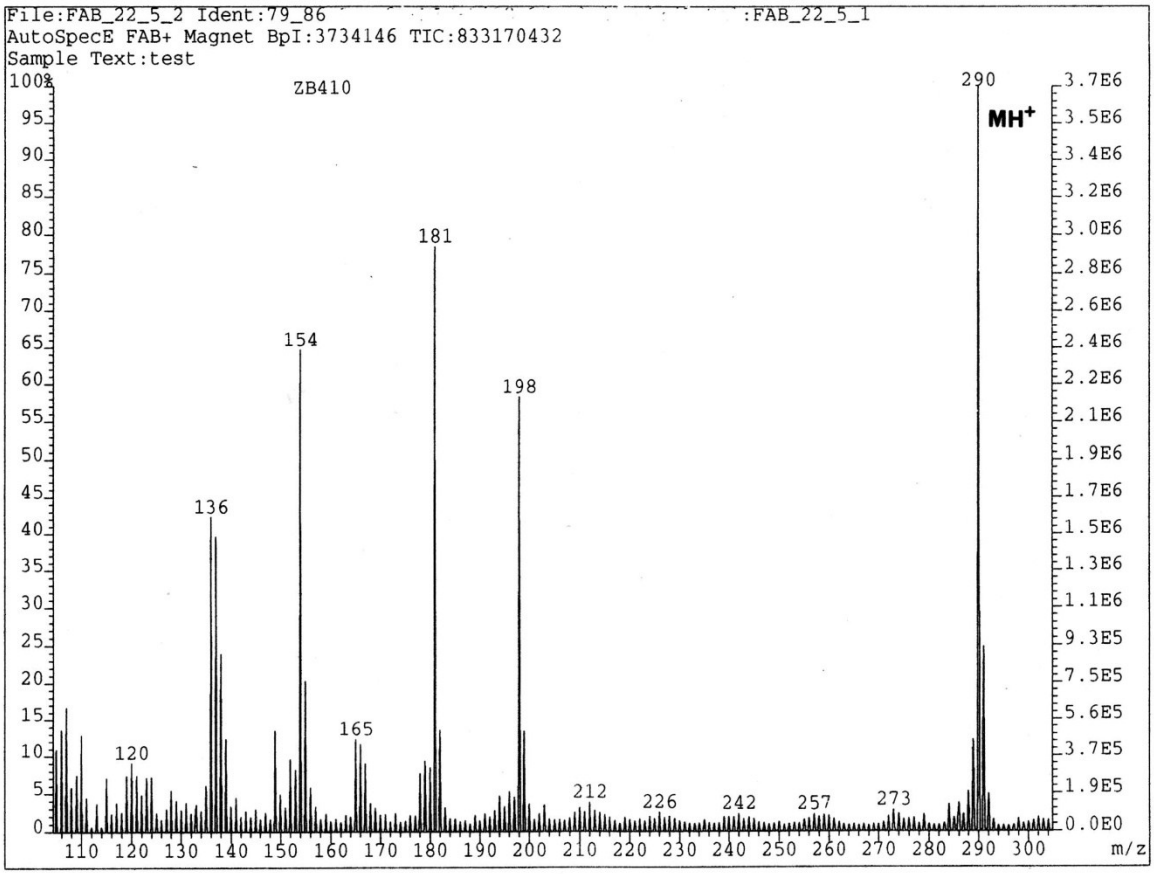


Fig. S-29: ^{13}C NMR (75.4 MHz) of compound **8** in $CDCl_3$.



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288.138814	0.1	0.0	0.1	288.138839	12.5	20	18	1	1

Statistic calculations

	mDa	PPM	
Mean	0.18	0.64	n = 2
RMS	0.24	0.84	
SD	0.23	0.78	

Fig. S-30: Mass spectrum of compound **8**.