Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

SUPPORTING INFORMATION

Volatiles from the fungal microbiome of the marine sponge *Callyspongia* cf. *flammea*

Lena Barra,[a] Paul Barac,[b] Gabriele M. König,[b] Max Crüsemann[b] and Jeroen S. Dickschat*[a]

a. Kekulé-Institute for Organic Chemistry and Biochemistry, University of Bonn, Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany

E-mail: dickschat@uni-bonn.de

b. Institute of Pharmaceutical Biology, University of Bonn, Nußallee 6, D-53115 Bonn, Germany

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1. LIST OF IDENTIFIED VOLATILES

Table S1. Identified volatile compounds and their occurrence in the investigated strains.

Compound[a]	***I***[b]	***I* (Lit.)**[c]	**Ident.**[d]	**occurrence (strain)**[e]
furan-3-carbaldehyde (**34**)	816		ms, std	St
butyl acetate (**35**)	819	814[1]	ms, ri, std	St
furan-2-carbaldehyde	835	835[2]	ms, ri, std	St
2-furanmethanol	854	850[3]	ms, ri, std	D, St
ethyl 2-methylbutyrate (**45**)	856	861[4]	ms, ri	E
ethylbenzene	860	858[5]	ms, ri, std	E, B
m-xylene	868	866[5]	ms, ri, std	E, B
protoanemonin (**6**)	881	880[6]	ms, ri	D
cyclohexanol (**46**)	886	886[7]	ms, ri, std	E
2-acetylfuran	909	909[8]	ms, ri, std	D, Sp
2,5-hexanedione	927	931[9]	ms, ri, std	St,
2-hydroxy-5-methylhexan-3-one (**36**)	942	944[10]	ms, ri	St
4-methyl-γ-butyrolactone (**37**)	954	958[11]	ms, ri	St
benzaldehyde	959	952[8]	ms, ri, std	B, Sp
1-octen-3-ol (**38**)	978	975[12]	ms, ri, std	St, E
1-ethyl-4-methylbenzene	968	965[13]	ms, ri, std	B
3-octanon (**39**)	986	983[14]	ms, ri, std	St, E
6-methylhept-5-en-2-one (**51**)	987	981[8]	ms, ri, std	B
1,3,4-trimethylbenzene	993	995[8]	ms, ri, std	E, B
2-acetylpyrrole	1058	1054[8]	ms, ri, std	D, St, Sp
3,4-dimethylpentan-4-olid (**47**)	1064	1063[15]	ms, ri, std	E
acetophenone	1066	1059[8]	ms, ri, std	St, Sp
linalool (**40**)	1100	1095[8]	ms, ri, std	St, B
nonanal (**7**)	1104	1101[16]	ms, ri, std	D, St, E, B, Sp
2-phenylethanol	1114	1107[8]	ms, ri, std	St, Sp
phenylacetonitrile (**10**)	1138	1134[8]	ms, ri, std	D
1,2-dimethoxybenzene (**41**)	1146	1146[17]	ms, ri, std	St
2-methylisoborneol (**42**)	1184	1178[8]	ms, ri, std	St, B
decanal (**8**)	1202	1201[8]	ms, ri, std	D, St, E, B, Sp

2-phenyloxyethanol	1219	1221[8]	ms, ri	St, B, Sp
benzothiazole (**43**)	1224	1223[18]	ms, ri	St, E, Sp
undecanal (**9**)	1307	1305[14]	ms, ri, std	D, E
3,4-dimethoxystyrene (**11**)	1364	1368[19]	ms, ri, std	D
1,3,4-trimethoxybenzene (**44**)	1368	1373	ms, std	St
dodecanal (**48**)	1418	1411[20]	ms, ri, std	E, B
geranylactone (**12**)	1454	1455[21]	ms, ri, std	D, St, B
dauca-4(11),8-diene (**13**)	1539	1537[22]	ms, ri	D
hexadecane (**49**)	1600	1600[8]	ms, ri, std	E
(1(10)*E*,5*E*)-germacradien-11-ol (**14**)	1649	1638[23]	ms, ri, std	D
tetradecanol (**50**)	1676	1676[8]	ms, ri, std	E
isotorquatone (**15**)	1808		ms, std	D
chartabomone (**16**)	1853		ms, std	D
dichotomone (**17**)	1884		ms, std	D

[a]Compound numbers refer to compound numbers in main text. Unidentified compounds and artifacts are not listed. Compounds which have also been identified from the medium are marked in italics. [b]Retention index on a HP5-MS fused silica capillary column. [c]Retention index on the same or a similar column from tabulated data in the literature. [d]Identification based on ms: mass spectrum (mass spectral match factor >850), ri: retention index on same or similar column (maximum deviation of 10 points), std: comparison to a synthetic or commercially available standard. [e]Letters refer to fungal strains: *D. cejpii* (D), *Stachylidium* sp. (St), *Emericella* sp. (E), *Sporormiella* sp. (Sp), *Botrytis* sp. (B).

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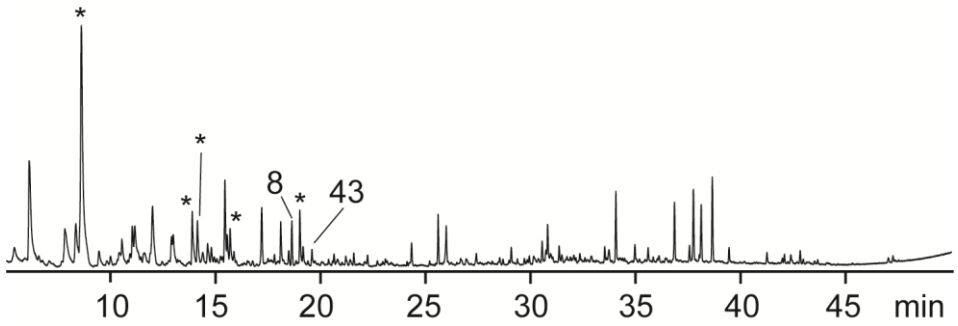
2. HEADSPACE EXTRACT OF *Sporormiella* sp. 293 K05

A)



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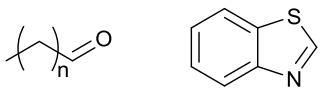
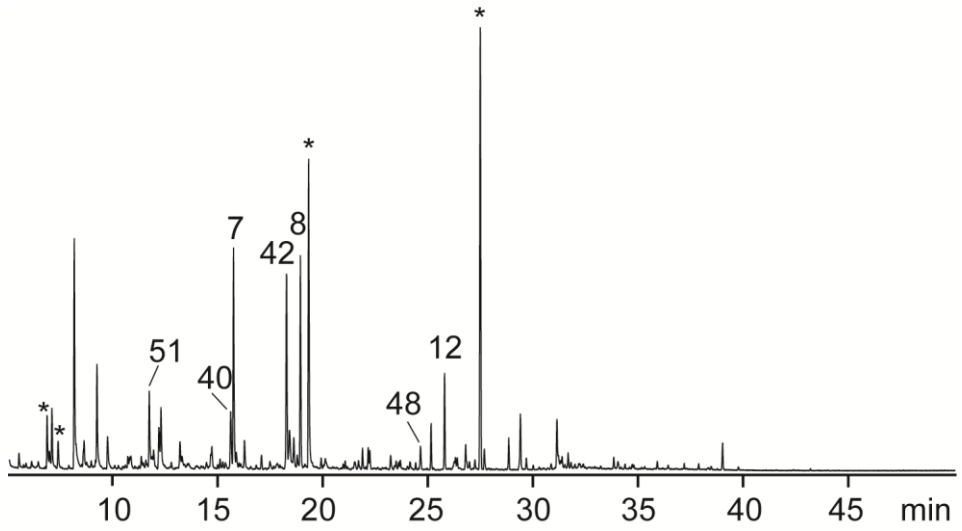


n = 8 (**8**) **43**

Figure S1. Volatiles produced by *Sporormiella*. A) Gas chromatogram of the headspace extract, B) structures of the detected volatiles. Asterisks indicate compounds originating from the medium.

3. HEADSPACE EXTRACT OF *Botrytis* sp. 293 K02

A)



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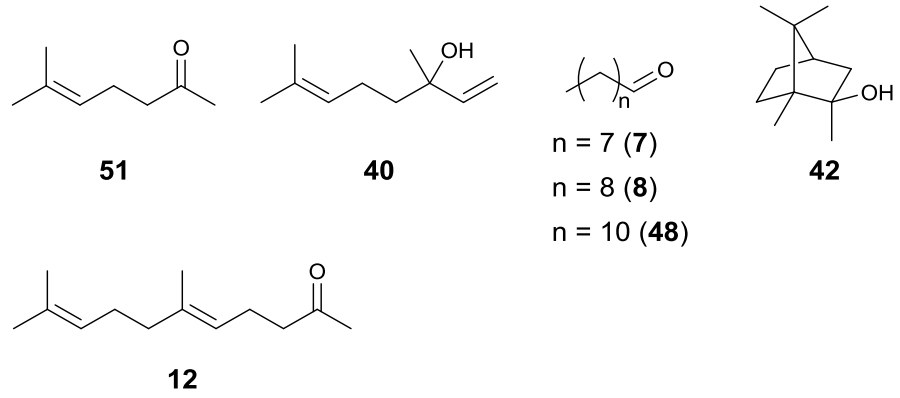
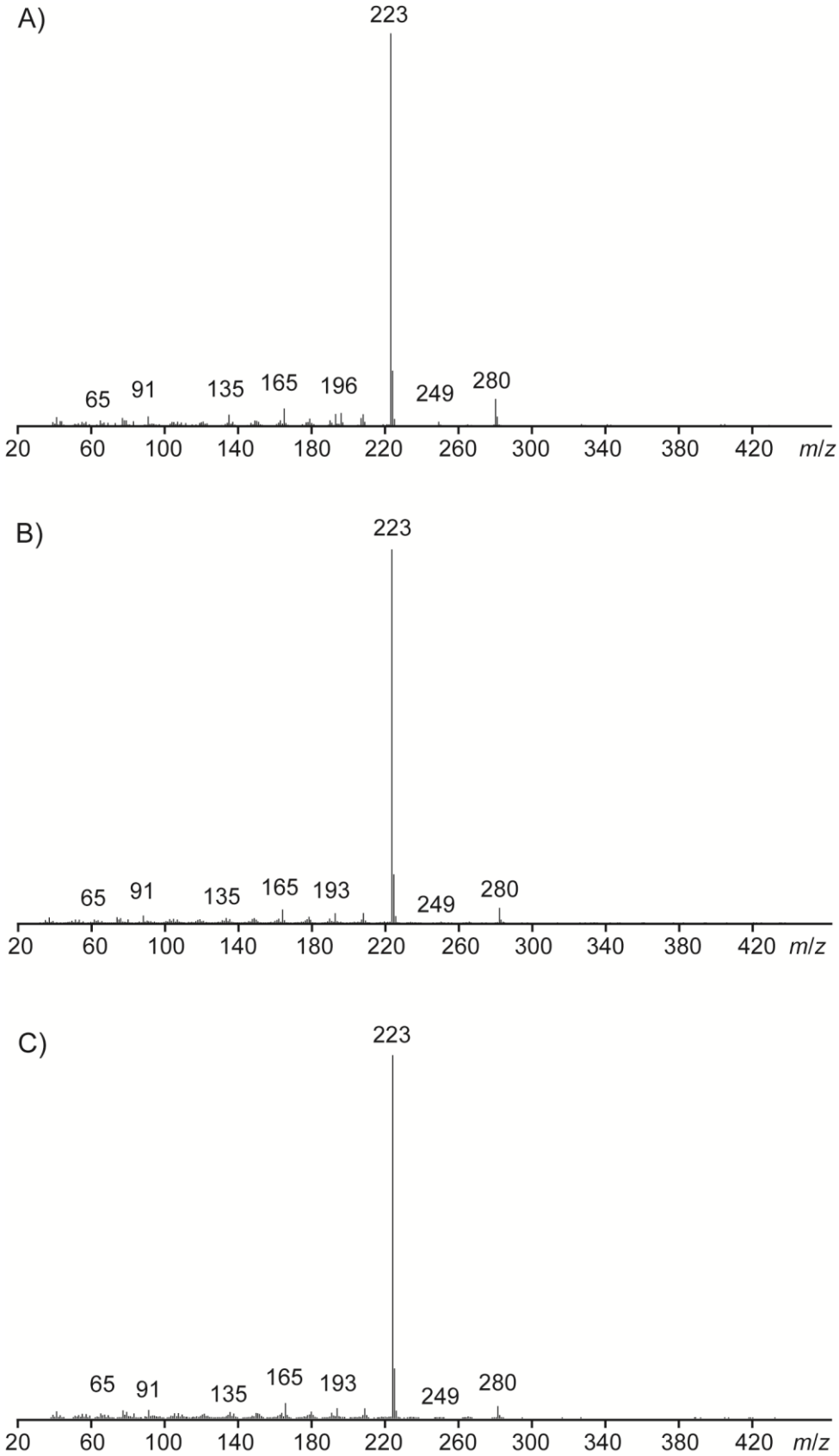


Figure S2. Volatiles produced by *Botrytis*. A) Gas chromatogram of the headspace extract, B) structures of the detected volatiles. Asterisks indicate compounds originating from the medium.

4. MASS SPECTRA OF ISOTORQUATONE (15) AND TORQUATONE (18)



F**igure S3.** Mass spectra of A) synthetic isotorquatone (**15**), B) synthetic torquatone (**18**), C) natural product from *D. cejpii* (identified as **15**).

5. IDENTIFICATION OF ISOTORQUATONE BY GC-MS

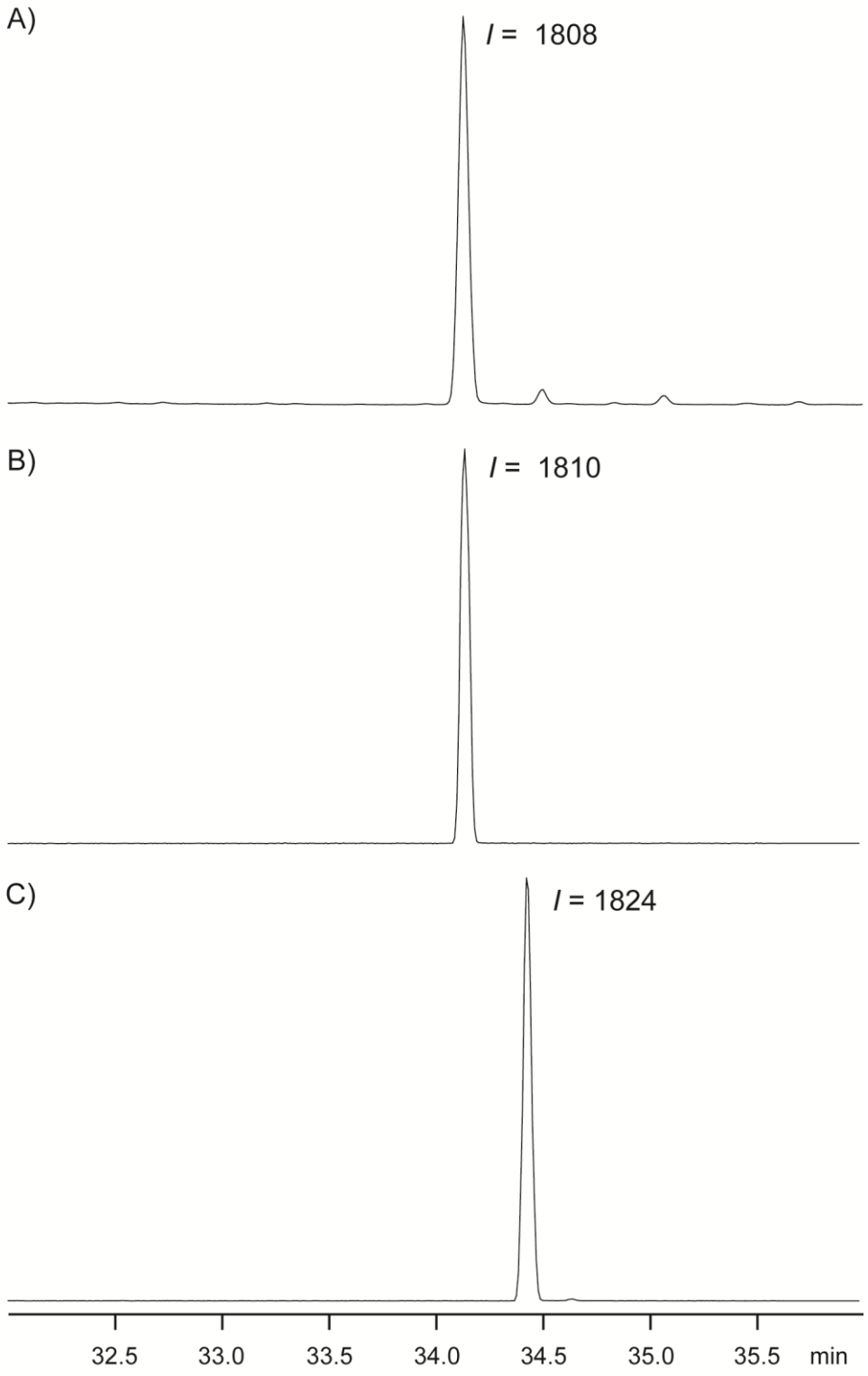


Figure S4. Total ion chromatograms of A) headspace extract of *D. cejpii*, B) synthetic **15**, C) synthetic **18**.

6. DETERMINATION OF THE ABSOLUTE CONFIGURATION OF 15

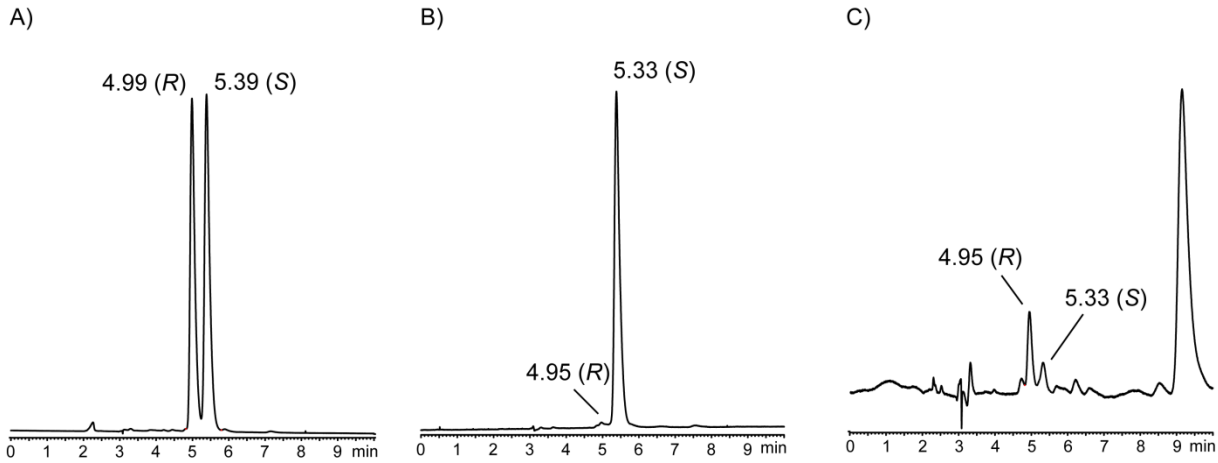


Figure S5. Analysis of the absolute configuration of **15** by HPLC on a homochiral stationary phase. A) mixture of synthetic (*R*)-**15** and (*S*)-**15**, B) synthetic (*S*)-**15**, C) natural product from *D. cejpii*.

7. MASS SPECTRA OF DESMETHYL ANALOGS 16, 17 and 19

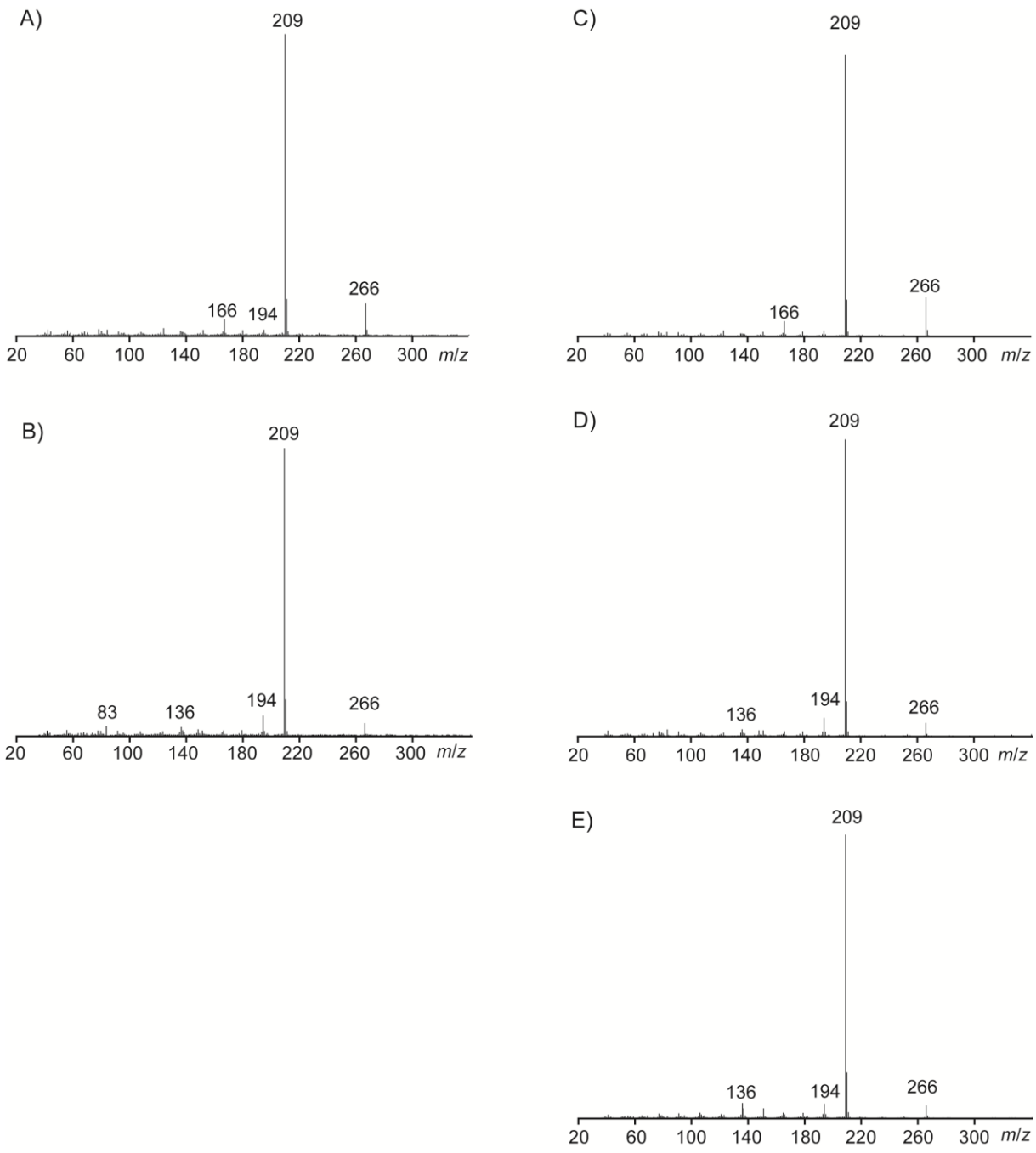


Figure S6. Mass spectra of A) natural desmethyl analogue **16**, B) natural desmethyl analogue **17**, C) synthetic **16**, D) synthetic **17**, E) synthetic **19**.

8. RESULTS OF FEEDING EXPERIMENTS

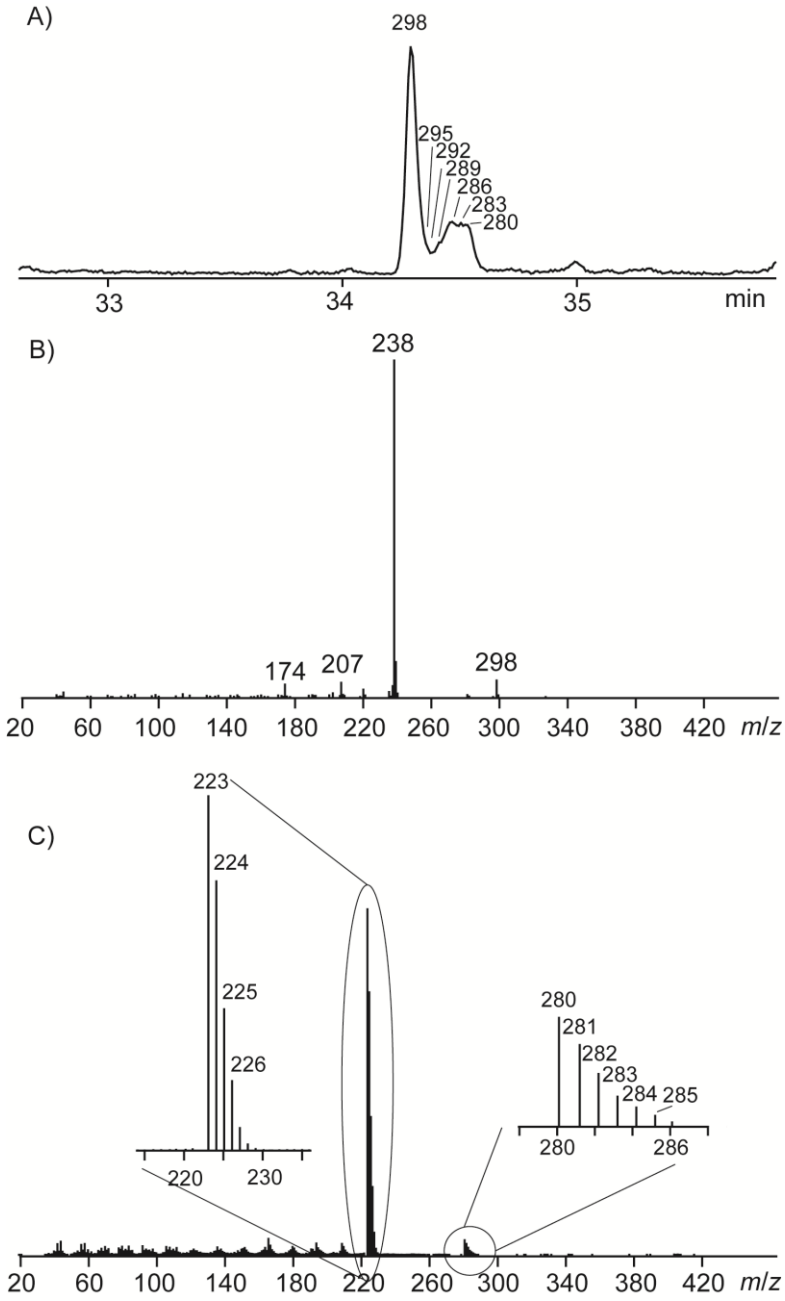


Figure S7. Results of feeding experiments in *D. cejpii*. A) Total ion chromatogram of the headspace-extract of *D. cejpii* after feeding of (*methyl*-$^{2}H_3$)-L-methionine, B) mass spectrum of ($^{2}H_{18}$)-**15** after feeding of (*methyl*-$^{2}H_3$)-L-methionine, C) mass spectrum of **15** after feeding of (2-^{13}C)acetate.

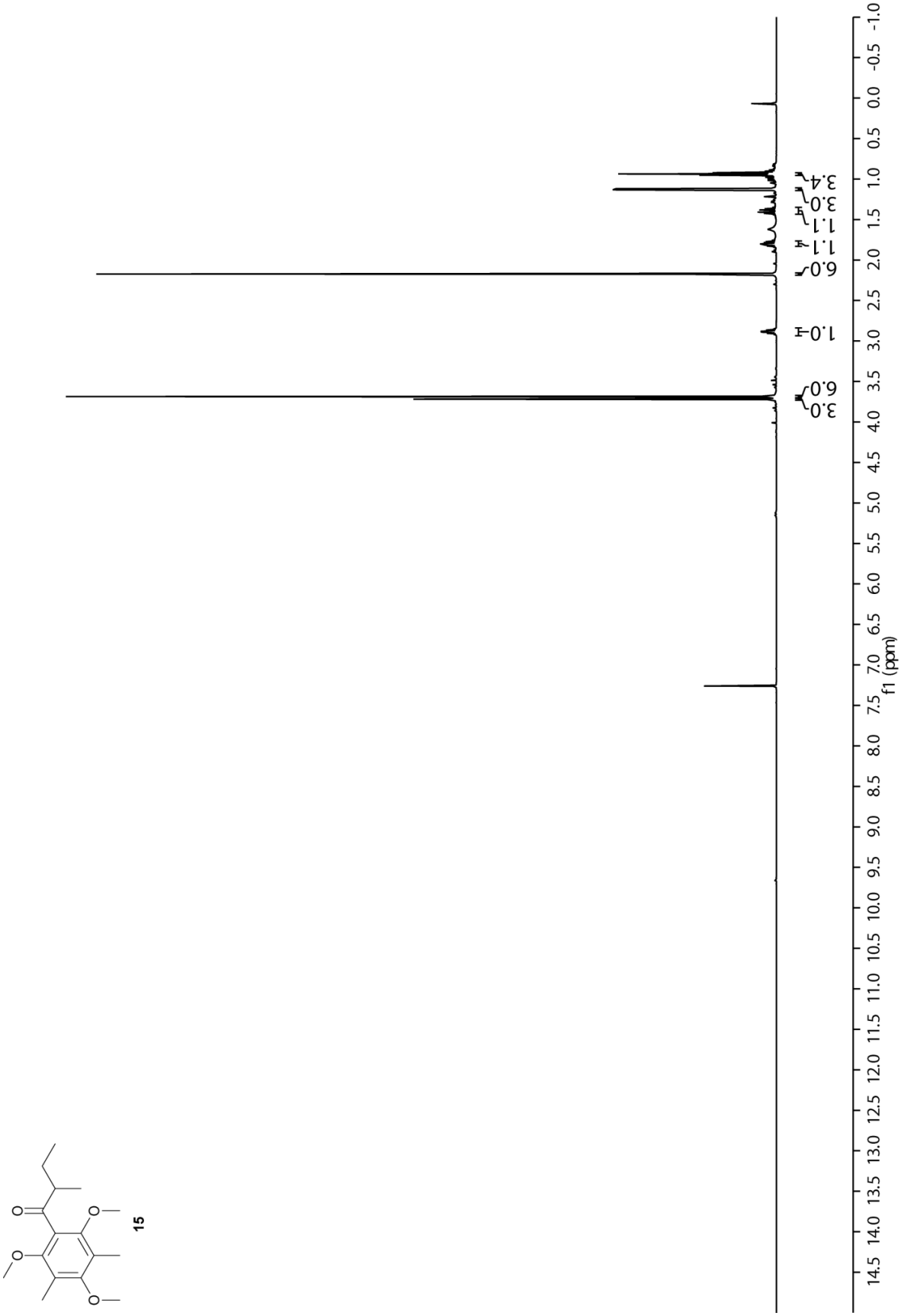
9. BIOACTIVITY TESTS AGAINST BACTERIA

Table S2. Bioactivity tests against bacteria.

Compound	***B. megaterium* DSM 32[a]**	***E. coli* DSM 498[a]**
15	0	0
(*S*)-**15**	0	0
16	3	0
17	3	2[b]
18	0	0
19	2[b]	1[b]
25	2[b]	0
pos. control (ertapenem)	10	8

[a] Radii of inhibition zones in mm, [b] partial inhibition.

10. NMR SPECTRA OF SYNTHETIC COMPOUNDS



15

Figure S8. ^{1}H NMR spectrum of **15** (500 MHz, $CDCl_3$).

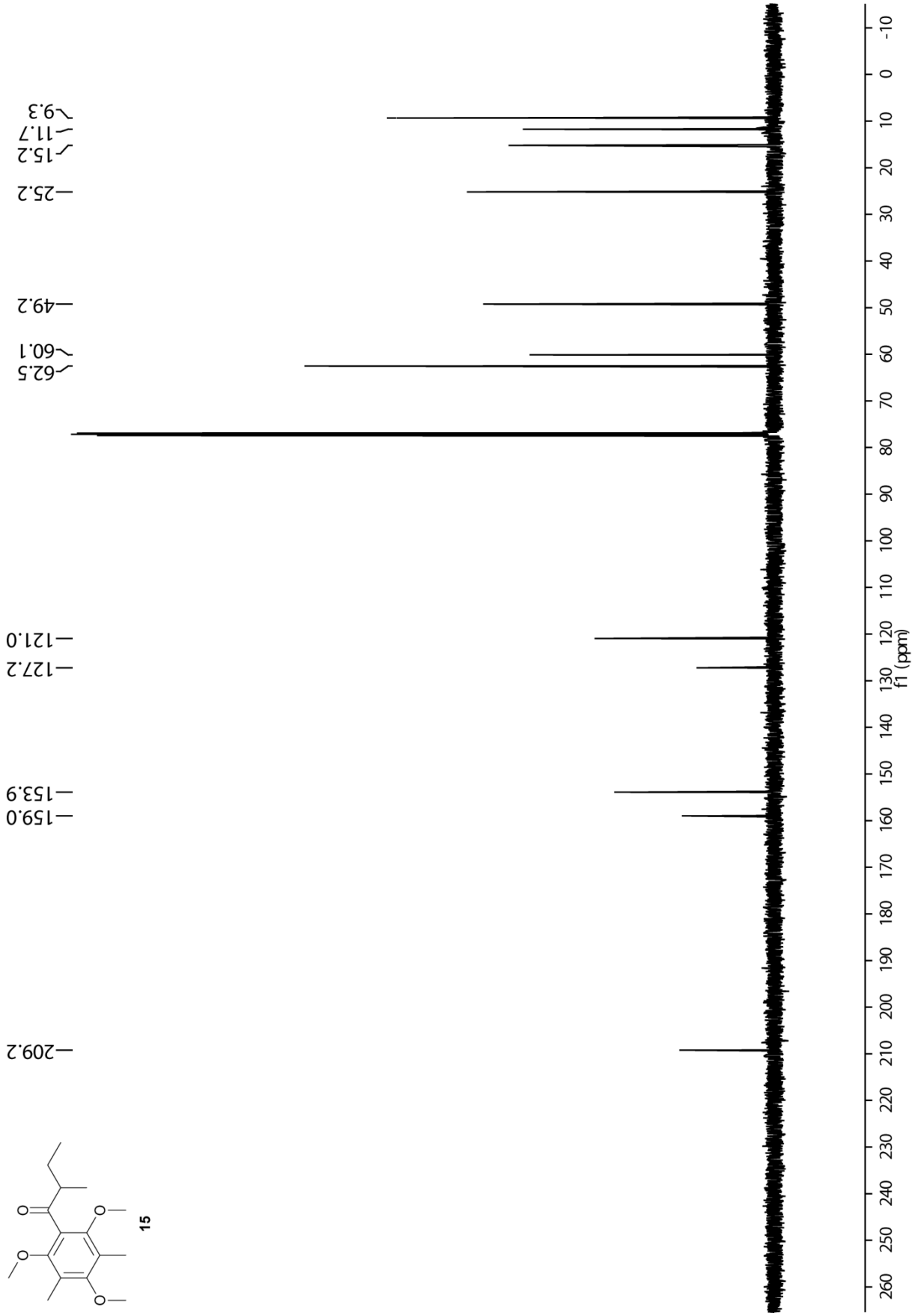


Figure S9. ^{13}C NMR spectrum of **15** (125 MHz, $CDCl_3$).

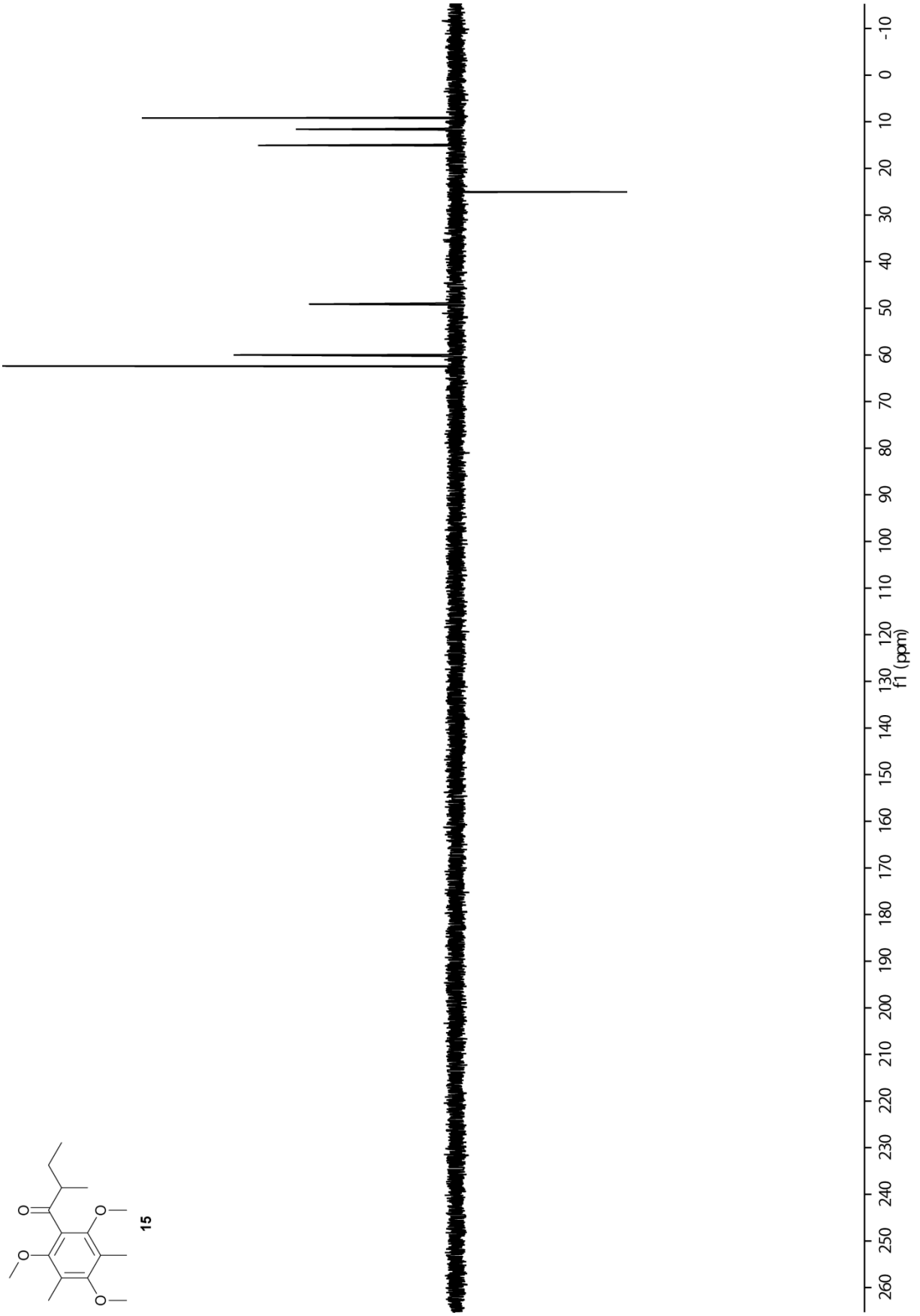


Figure S10. ^{13}C DEPT 135 spectrum of **15** (125 MHz, $CDCl_3$).

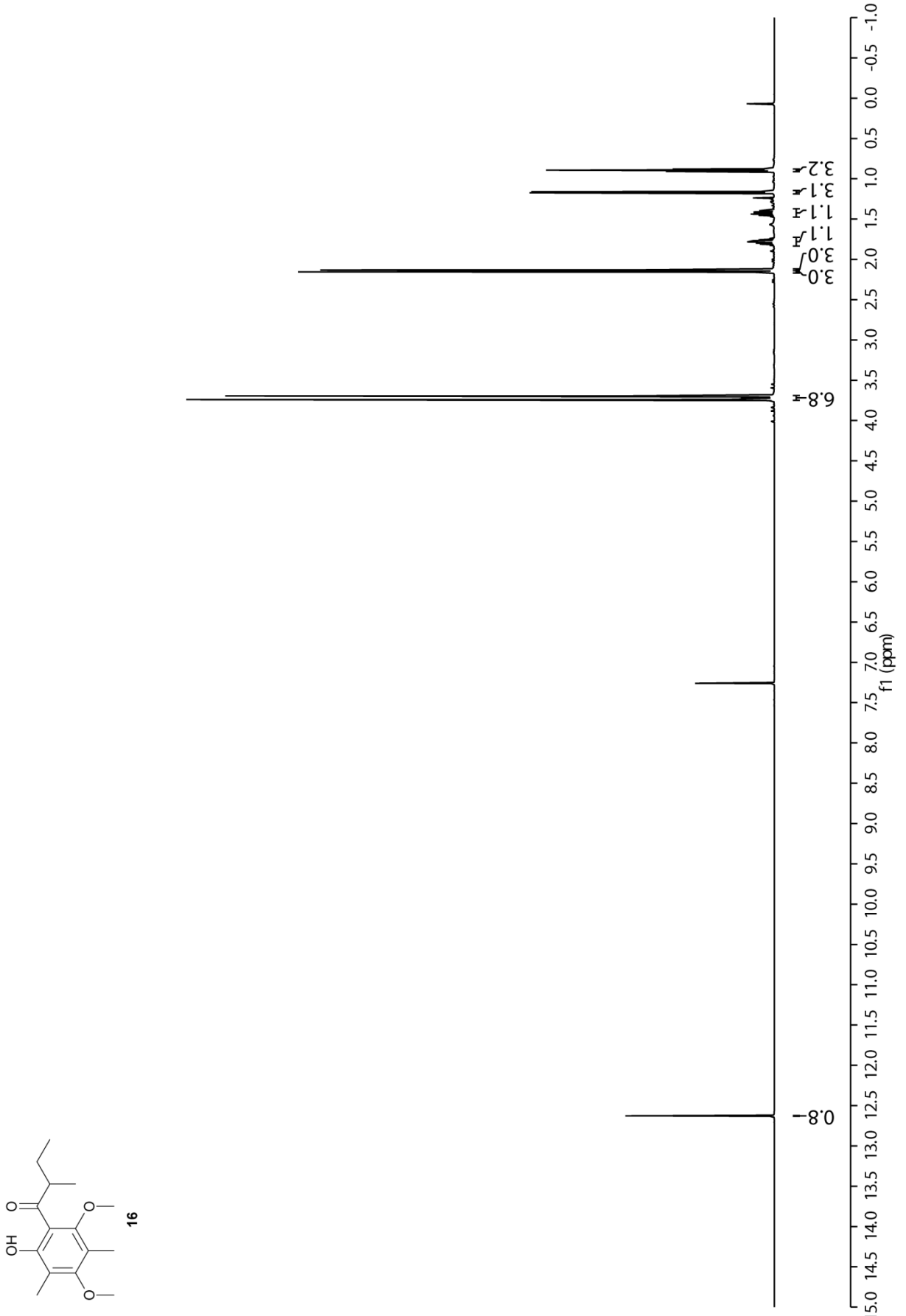


Figure S11. ^{1}H NMR spectrum of **16** (500 MHz, $CDCl_3$).

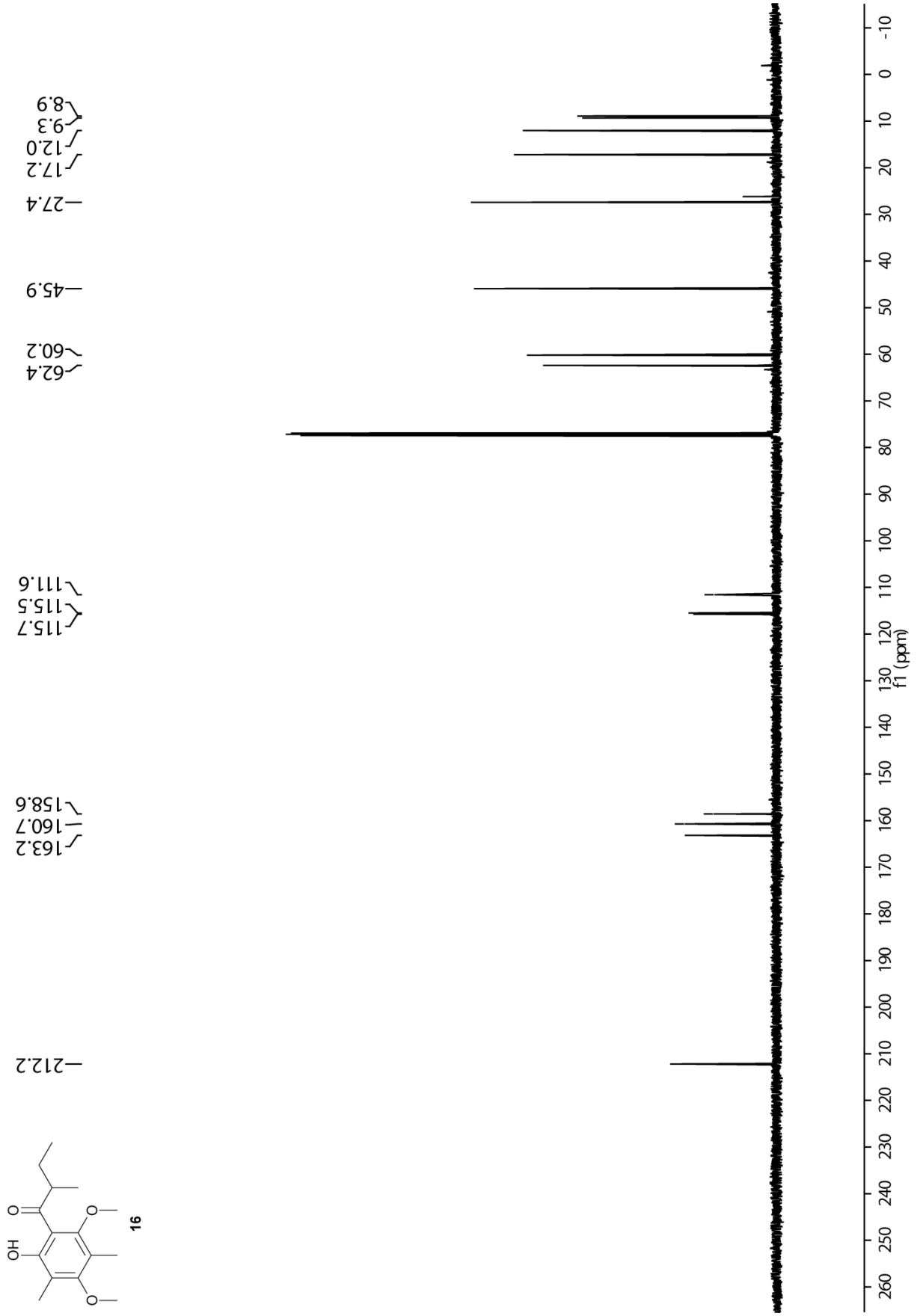


Figure S12. ^{13}C NMR spectrum of **16** (125 MHz, $CDCl_3$).

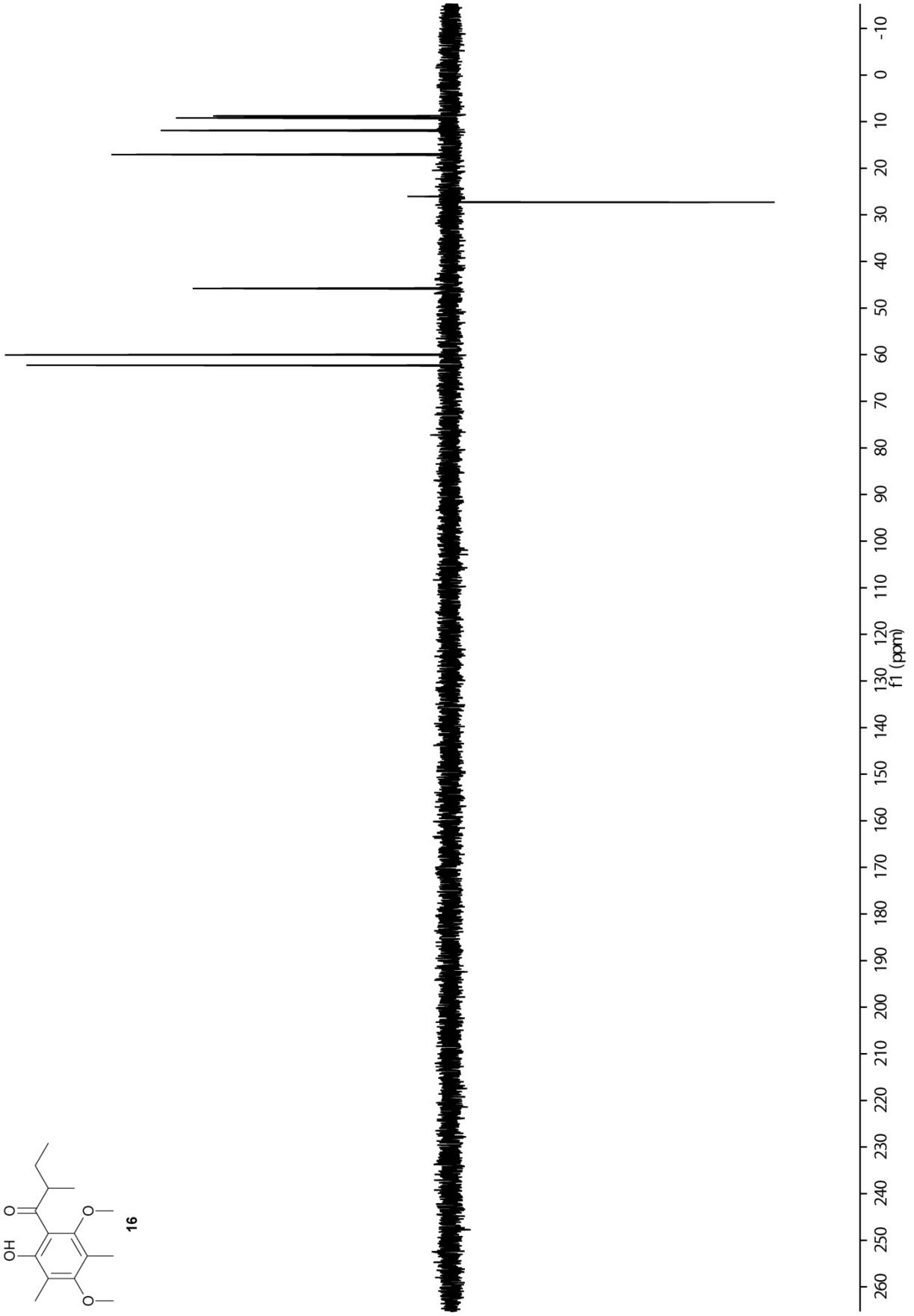


Figure S13. ^{13}C DEPT 135 spectrum of **16** (125 MHz, $CDCl_3$).

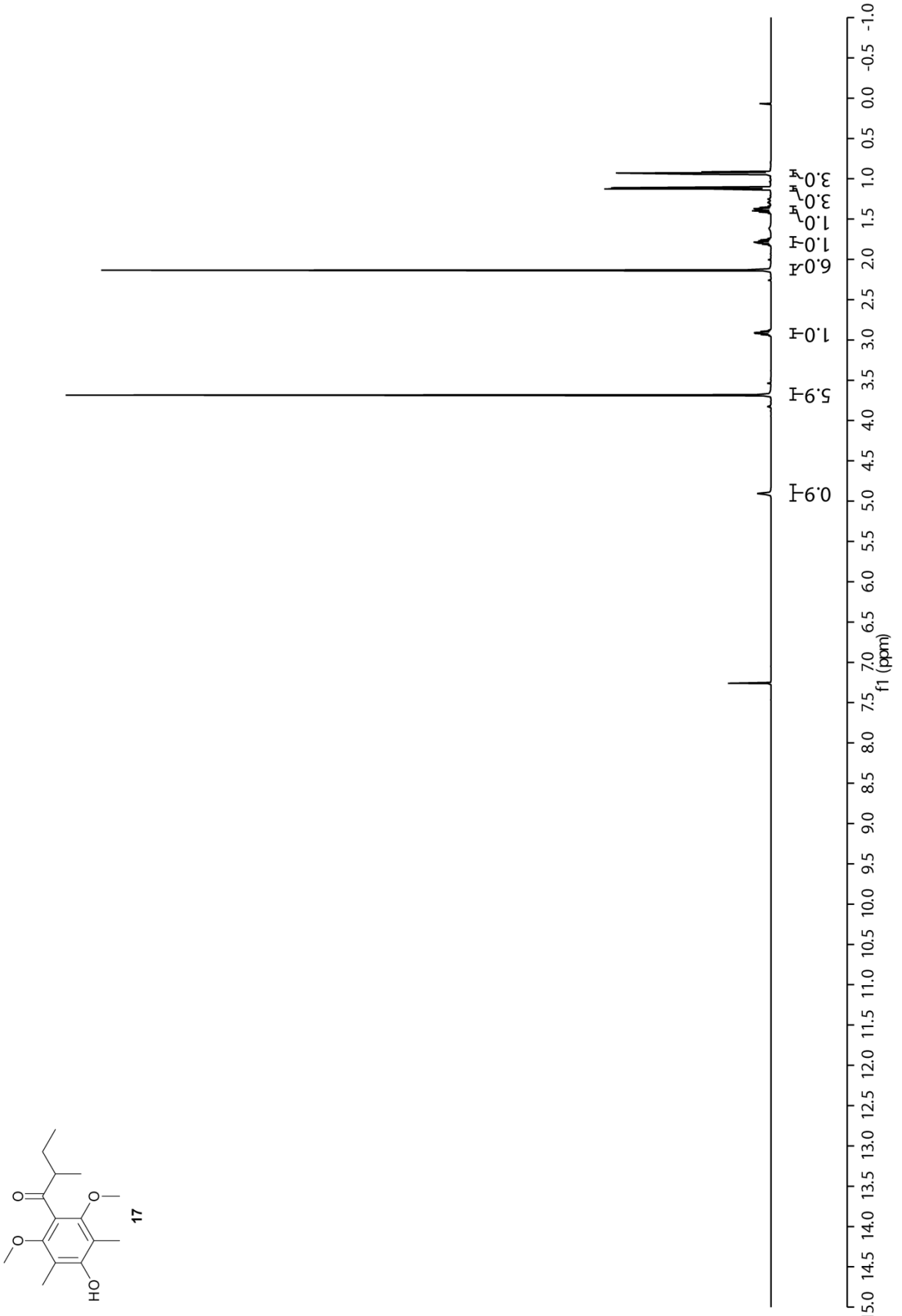


Figure S14. ^{1}H NMR spectrum of **17** (500 MHz, $CDCl_3$).

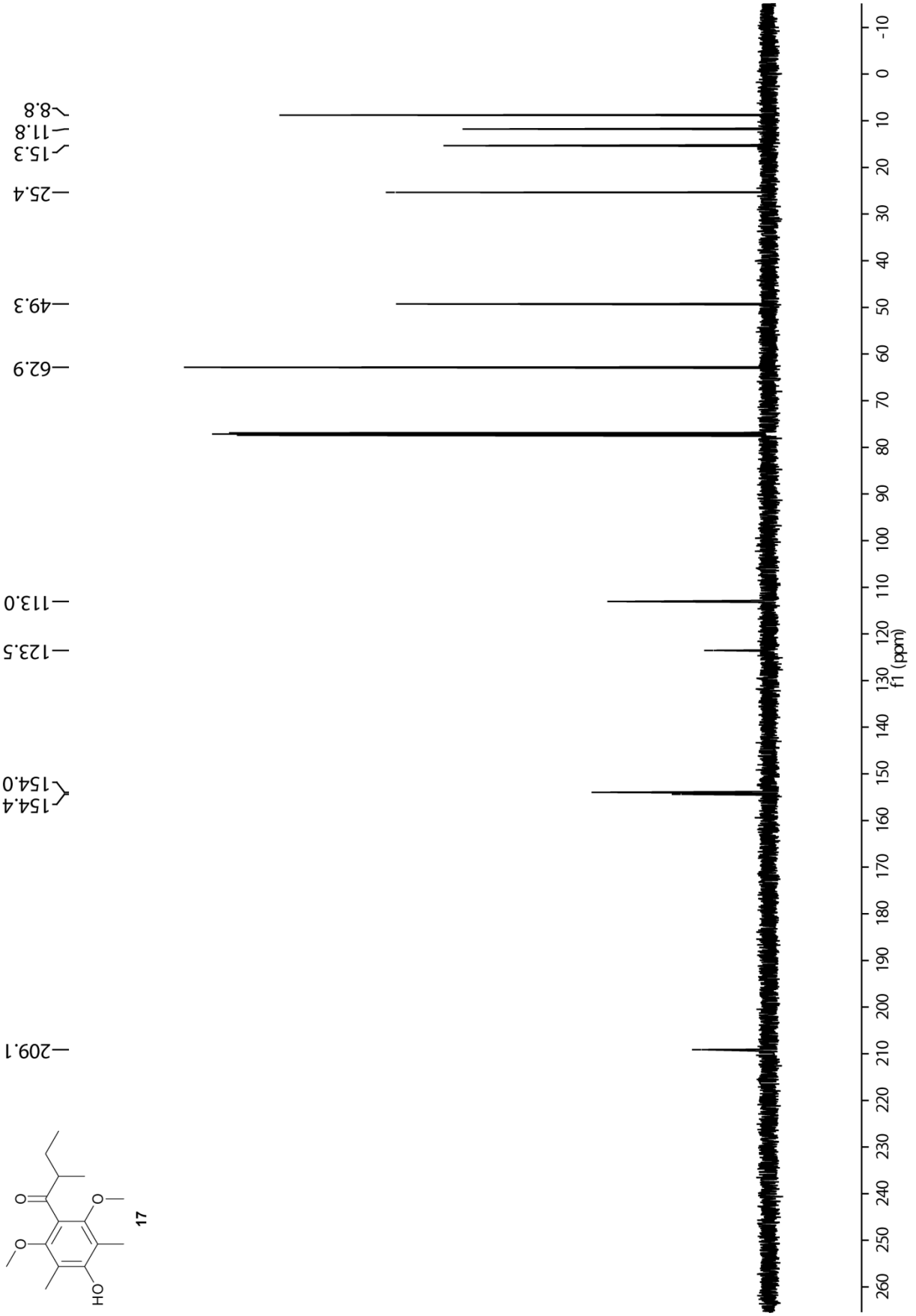


Figure S15. ^{13}C NMR spectrum of **17** (125 MHz, $CDCl_3$).

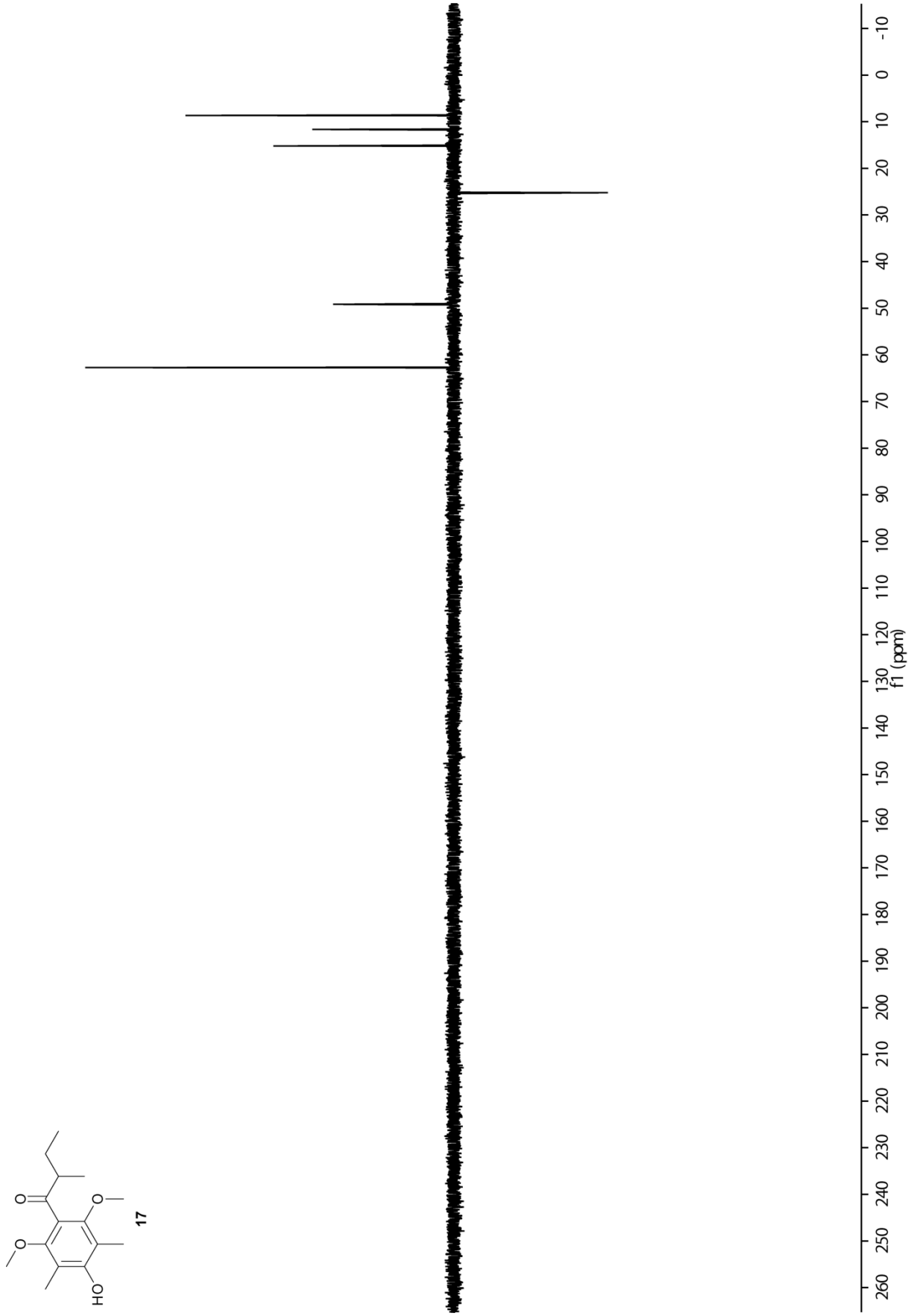


Figure S16. ^{13}C DEPT 135 spectrum of **17** (125 MHz, $CDCl_3$).

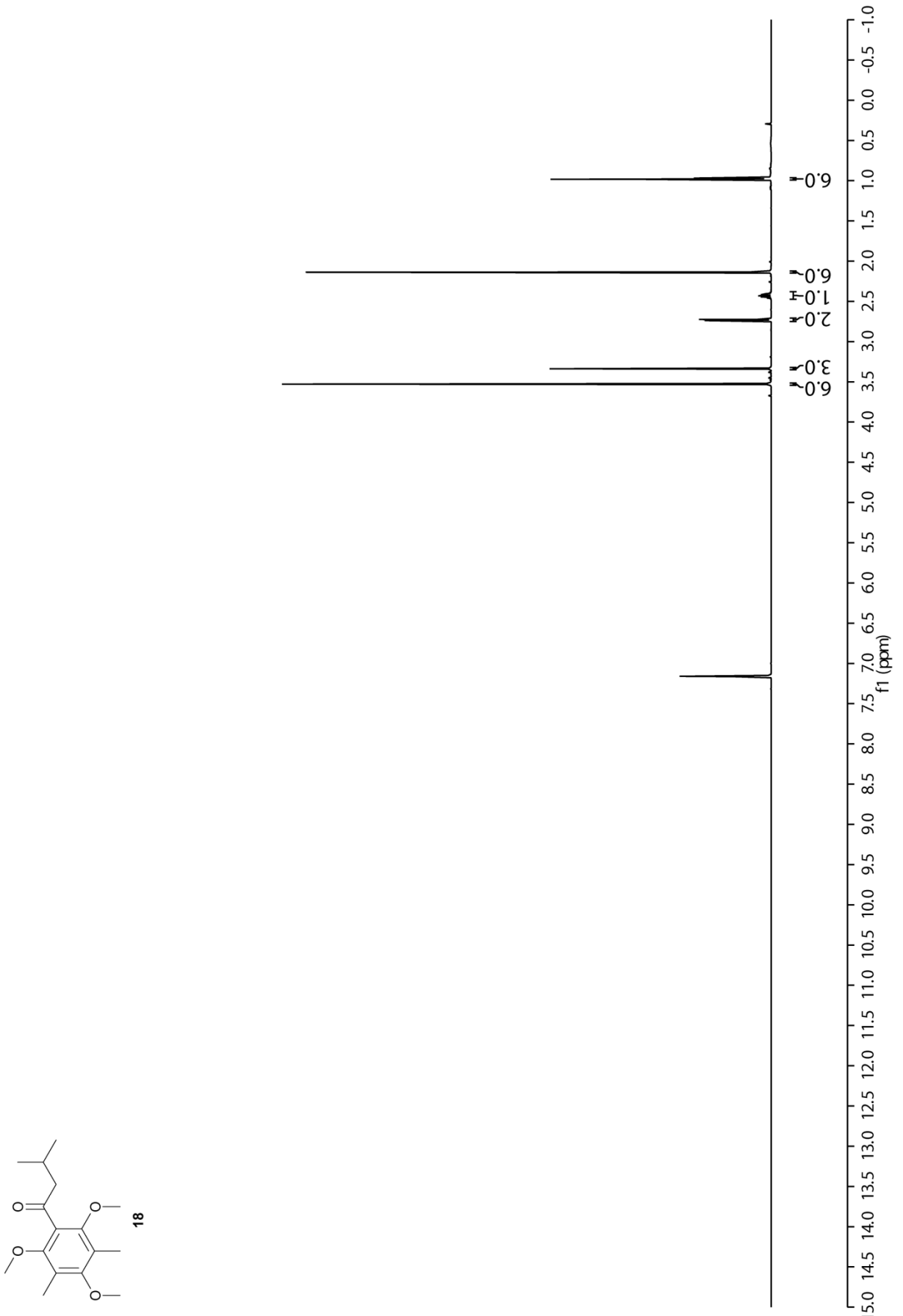


Figure S17. ^{1}H NMR spectrum of **18** (500 MHz, C_6D_6).

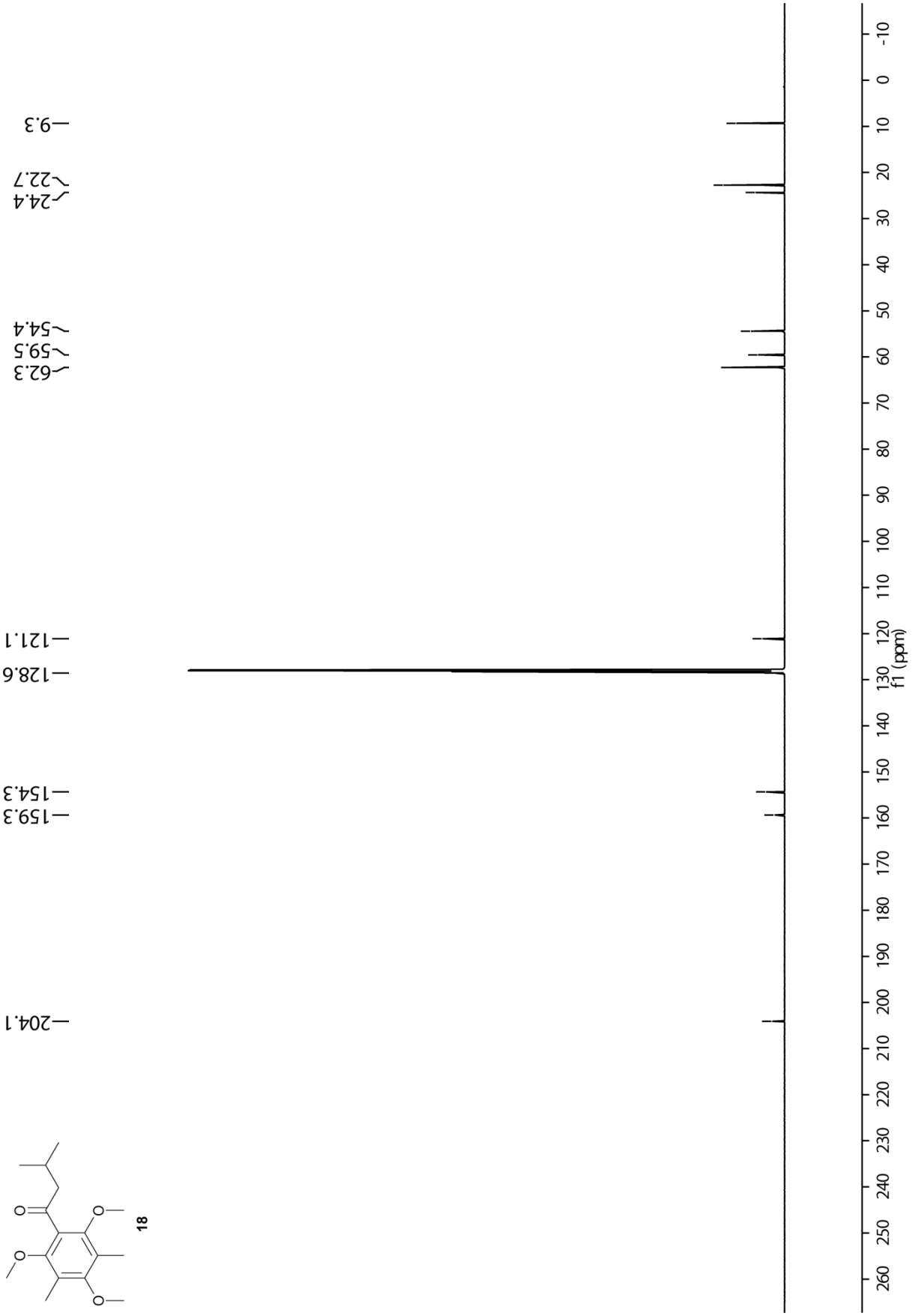


Figure S18. ^{13}C NMR spectrum of **18** (125 MHz, C_6D_6).

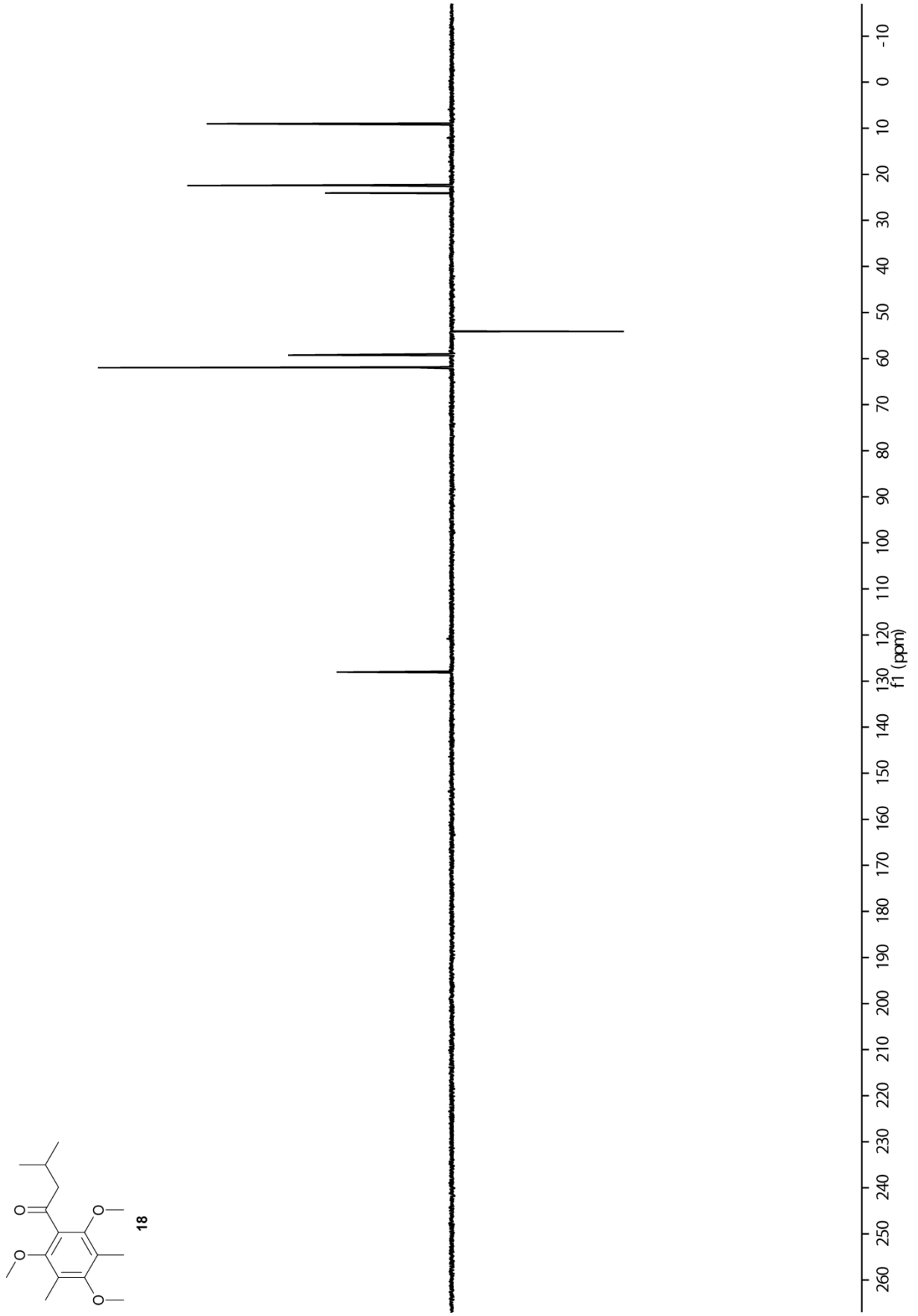


Figure S19. ^{13}C DEPT 135 spectrum of **18** (125 MHz, C_6D_6).

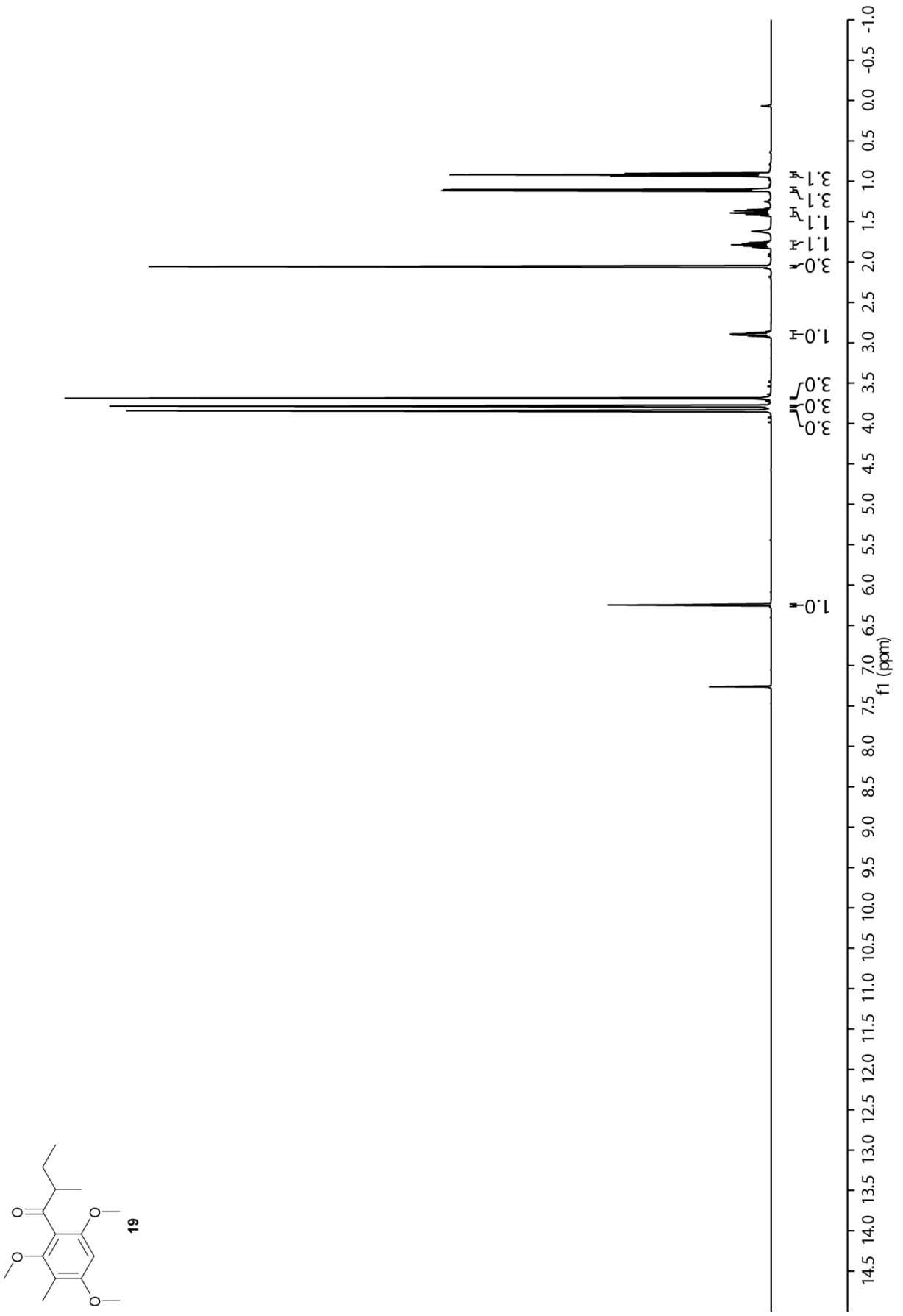


Figure S20. ^{1}H NMR spectrum of **19** (500 MHz, $CDCl_3$).

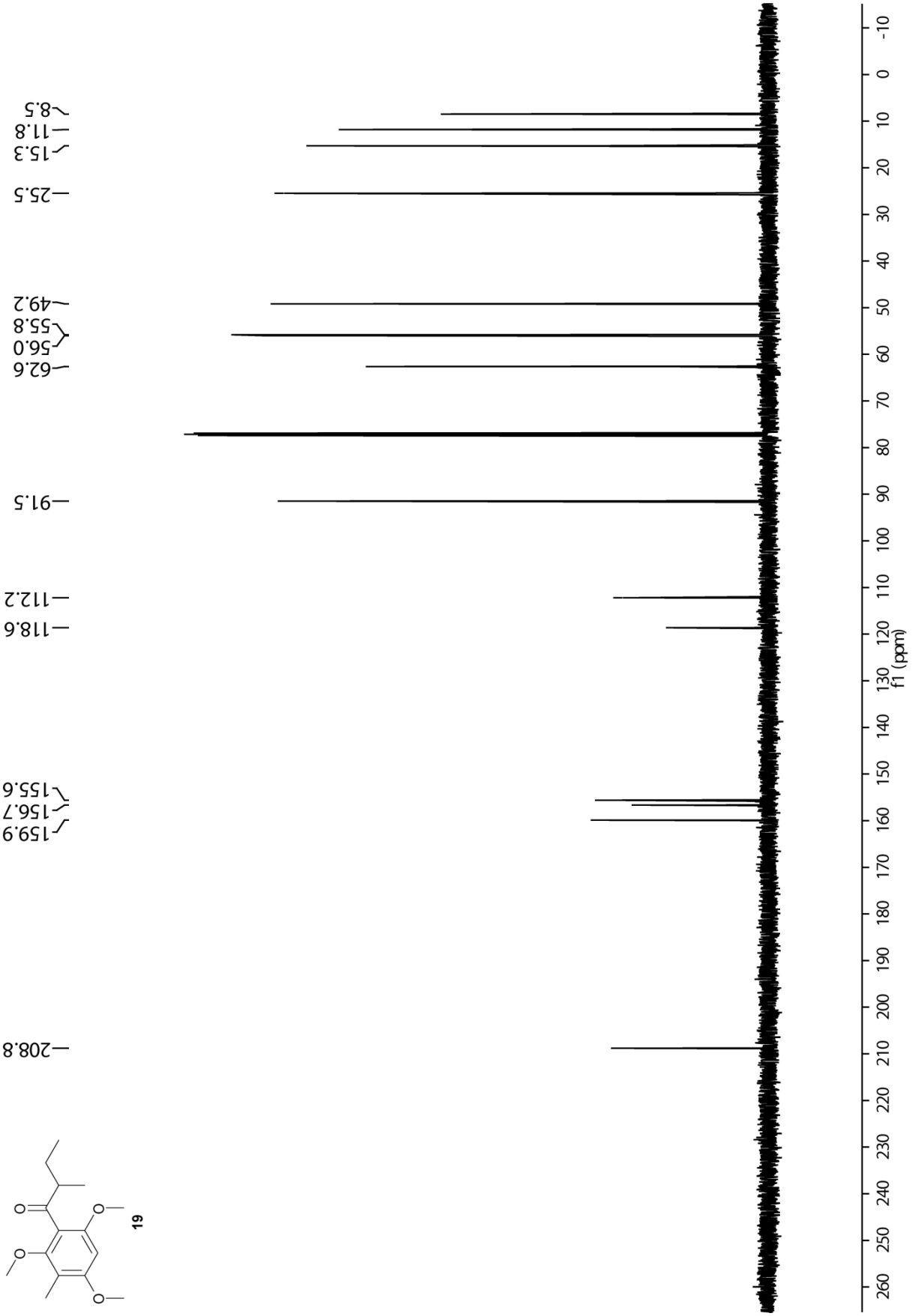


Figure S21. ^{13}C NMR spectrum of **19** (125 MHz, $CDCl_3$).

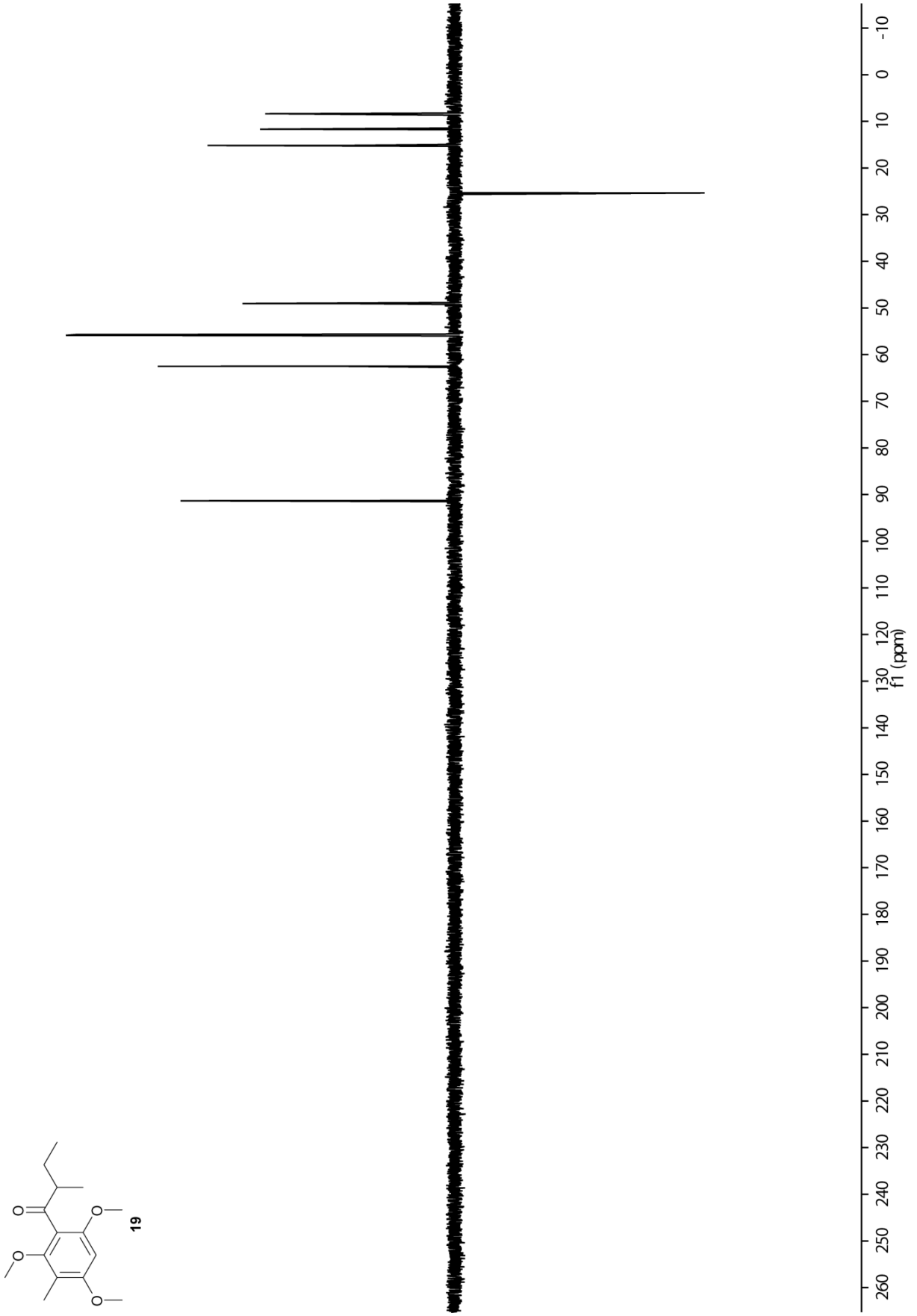


Figure S22. ^{13}C DEPT 135 spectrum of **19** (125 MHz, $CDCl_3$).

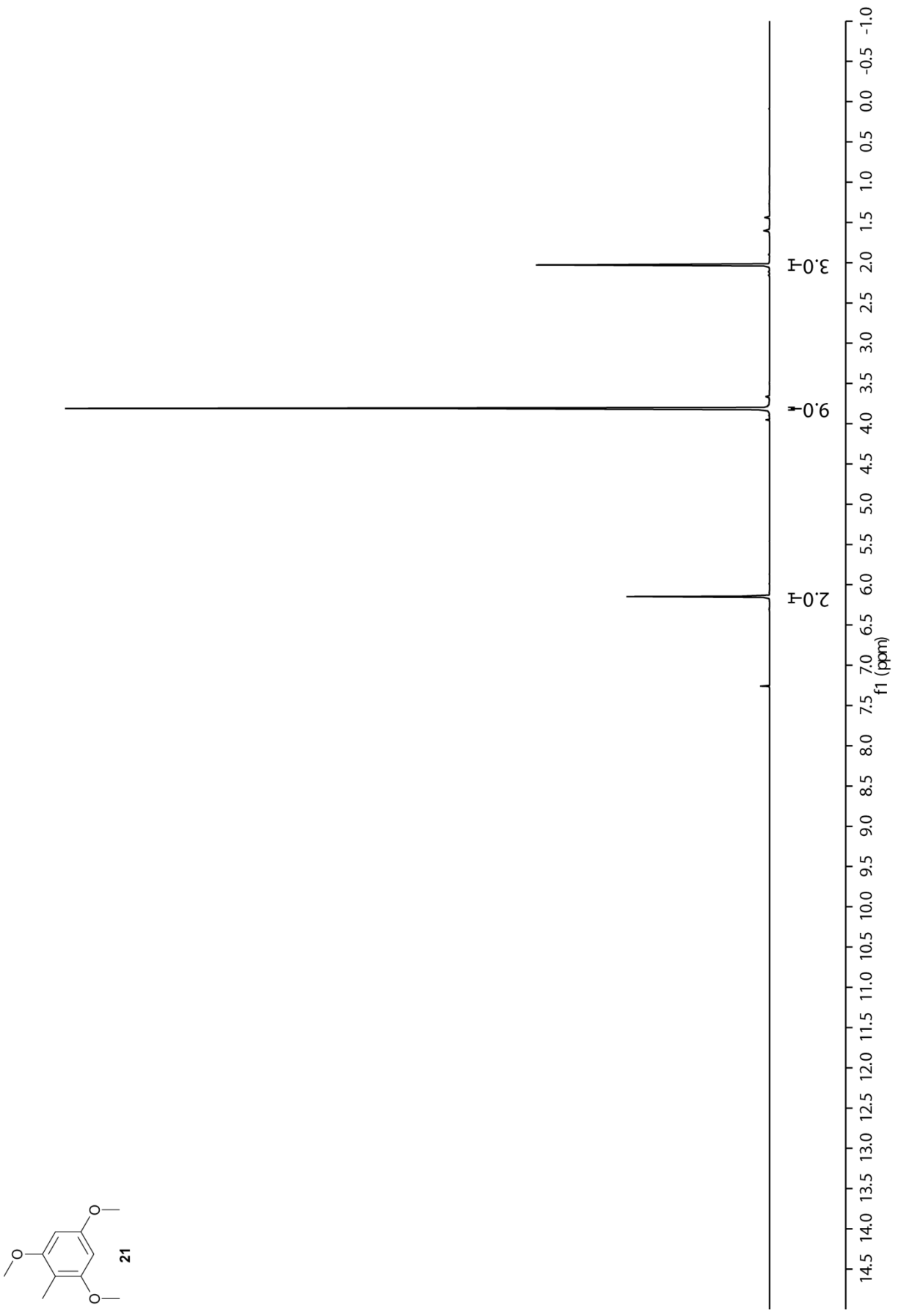


Figure S23. ^{1}H NMR spectrum of **21** (500 MHz, $CDCl_3$).

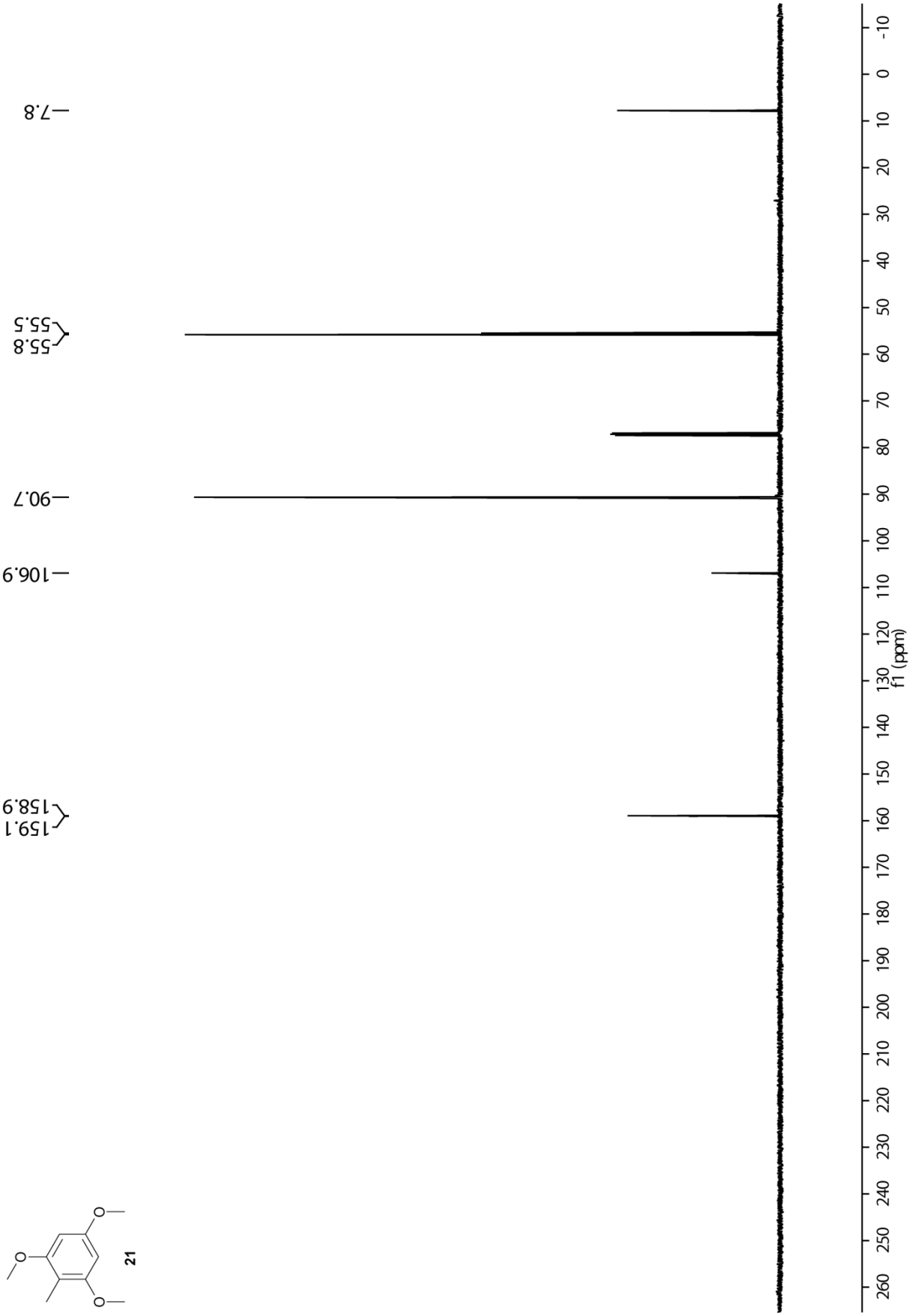


Figure S24. ^{13}C NMR spectrum of **21** (125 MHz, $CDCl_3$).

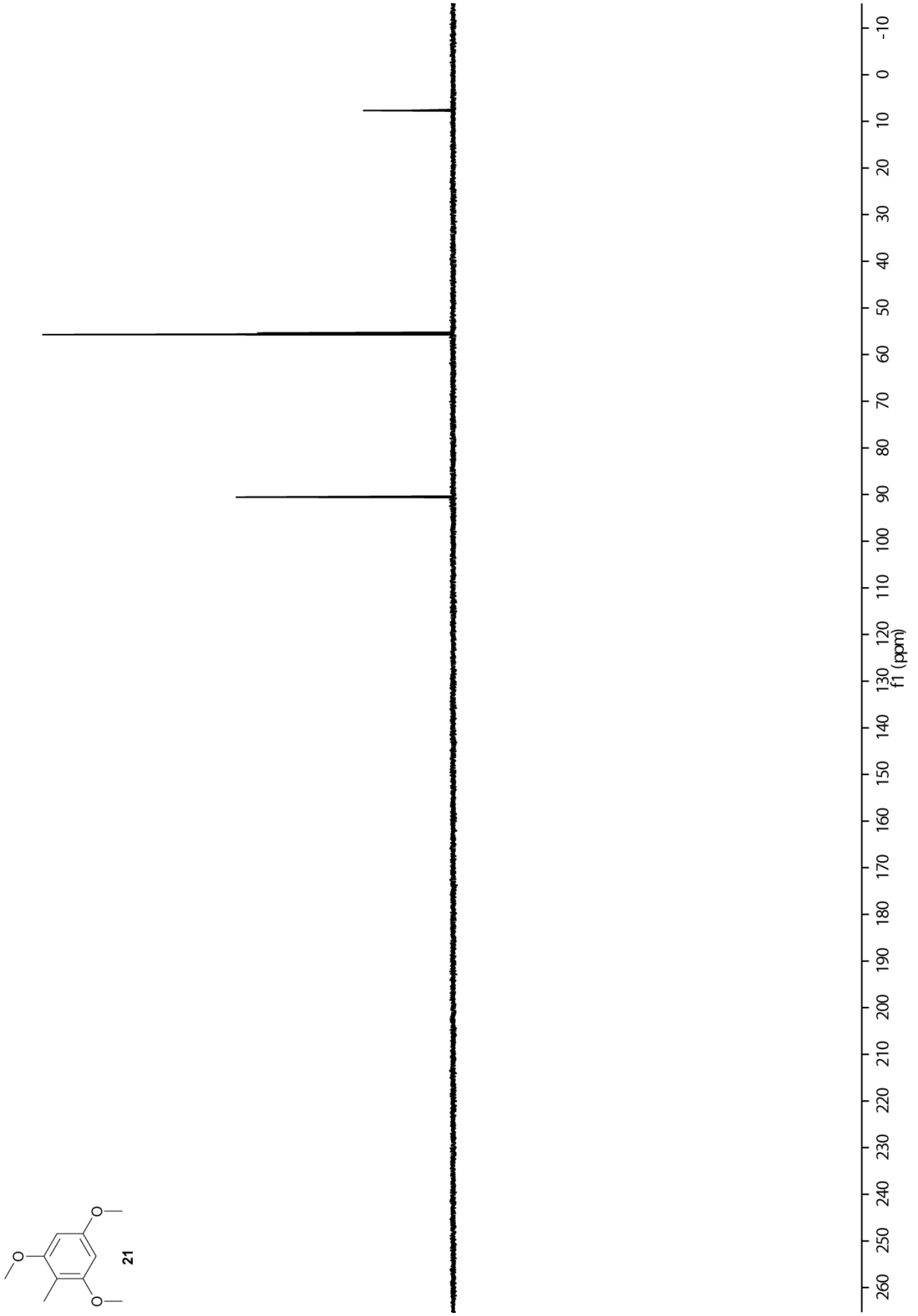


Figure S25. ^{13}C DEPT 135 spectrum of **21** (125 MHz, $CDCl_3$).

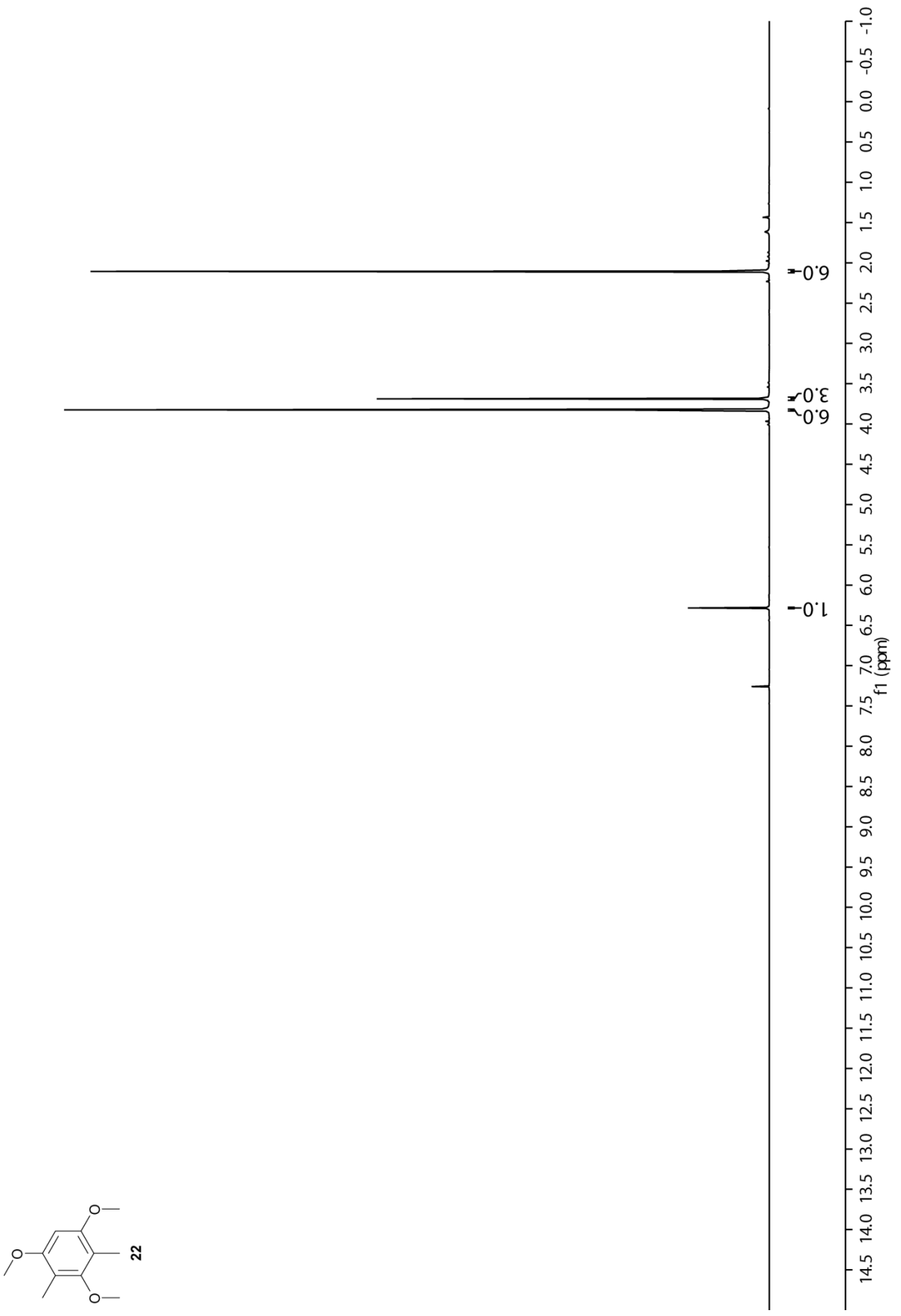


Figure S26. ^{1}H NMR spectrum of **22** (500 MHz, $CDCl_3$).

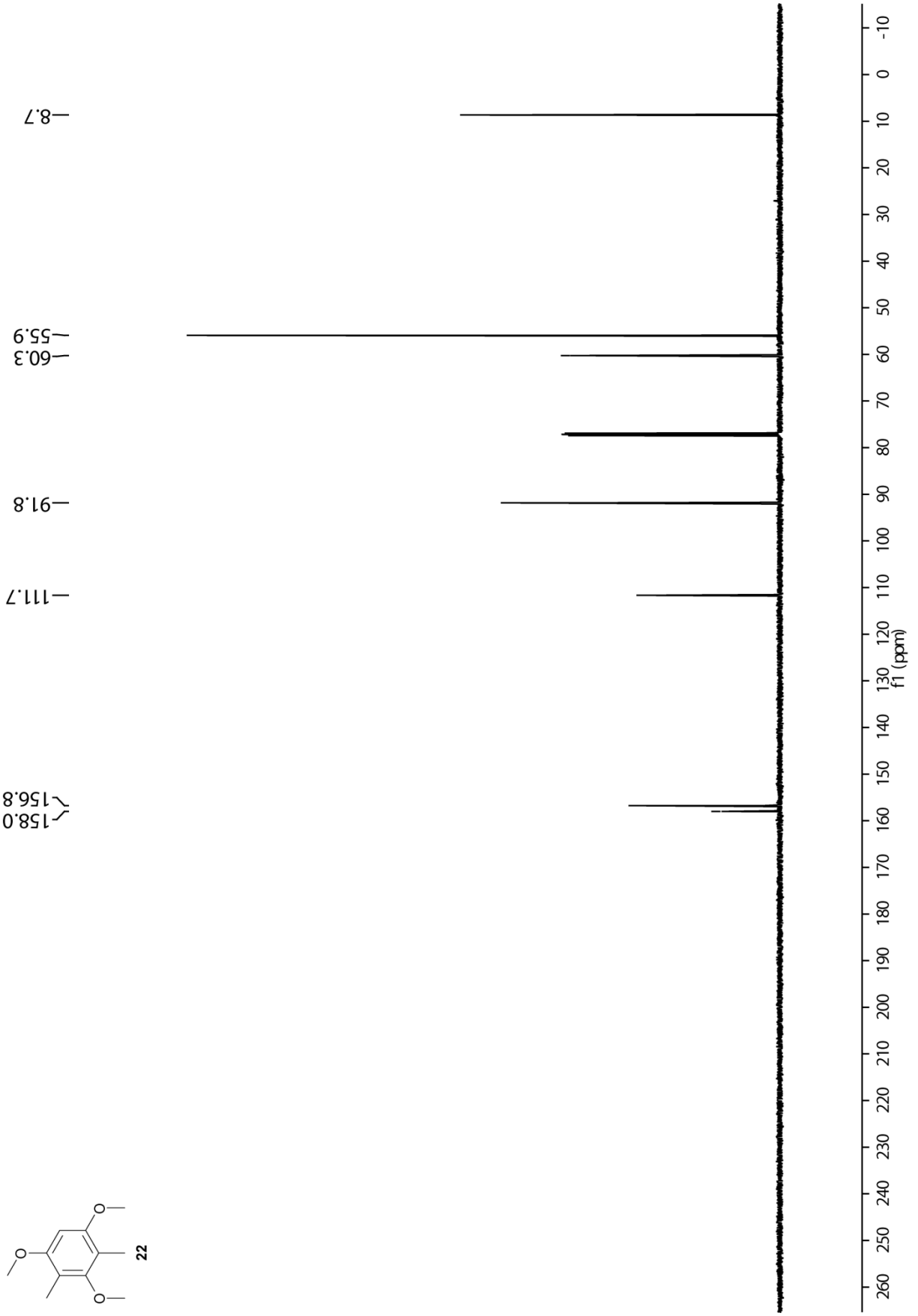


Figure S27. ^{13}C NMR spectrum of **22** (125 MHz, $CDCl_3$).

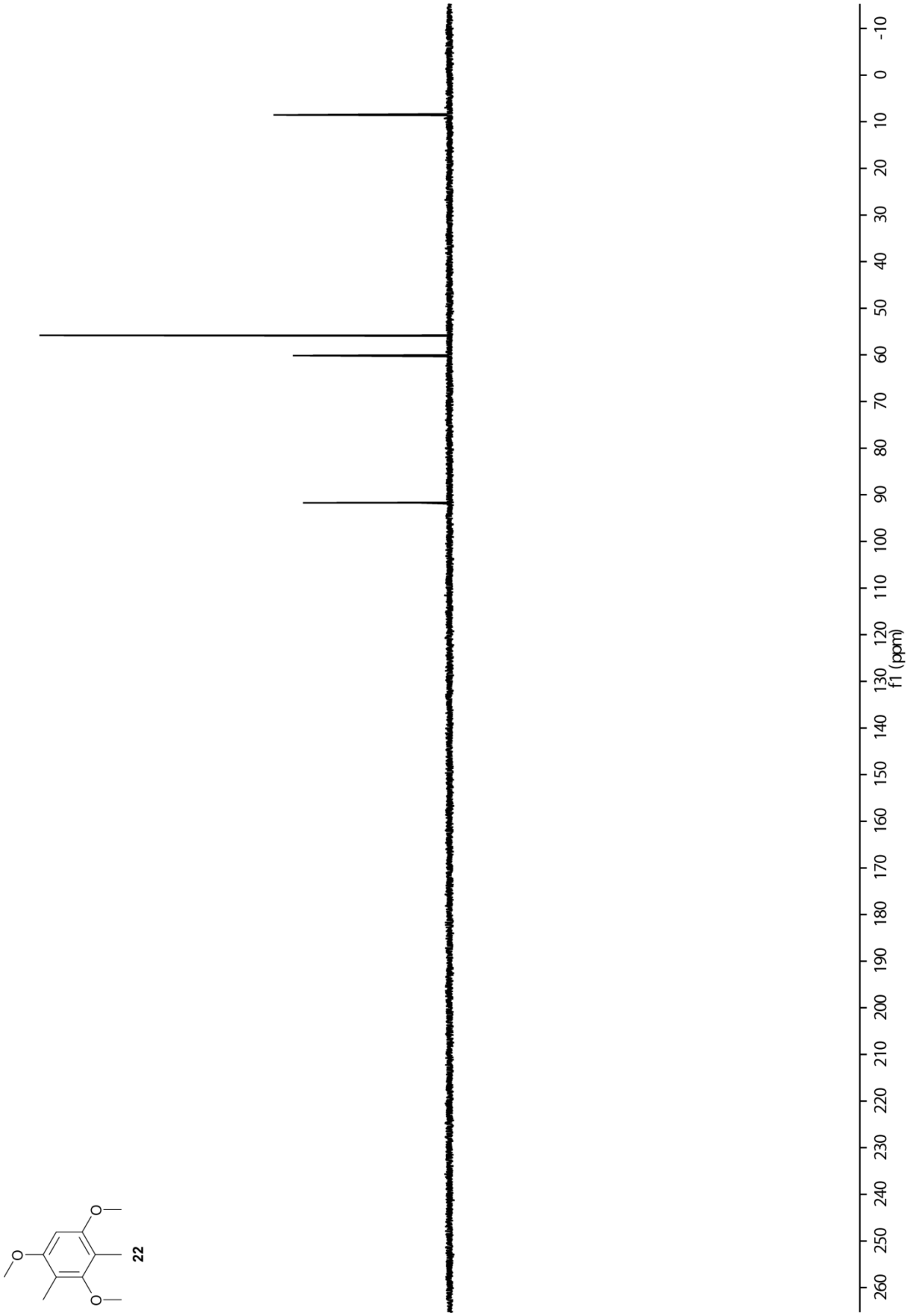


Figure S28. ^{13}C DEPT 135 spectrum of **22** (125 MHz, $CDCl_3$).

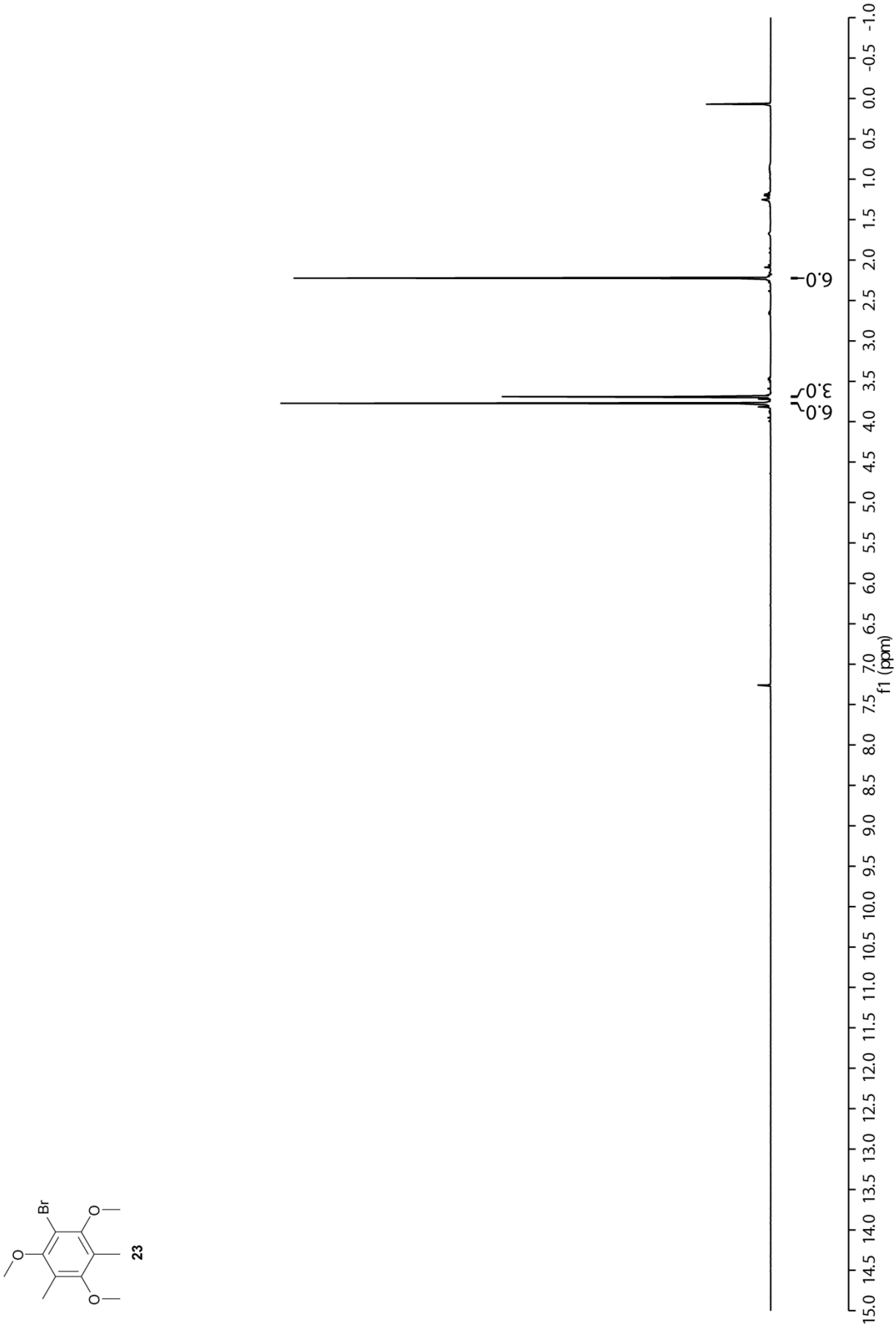


Figure S29. ^{1}H NMR spectrum of **23** (400 MHz, $CDCl_3$).

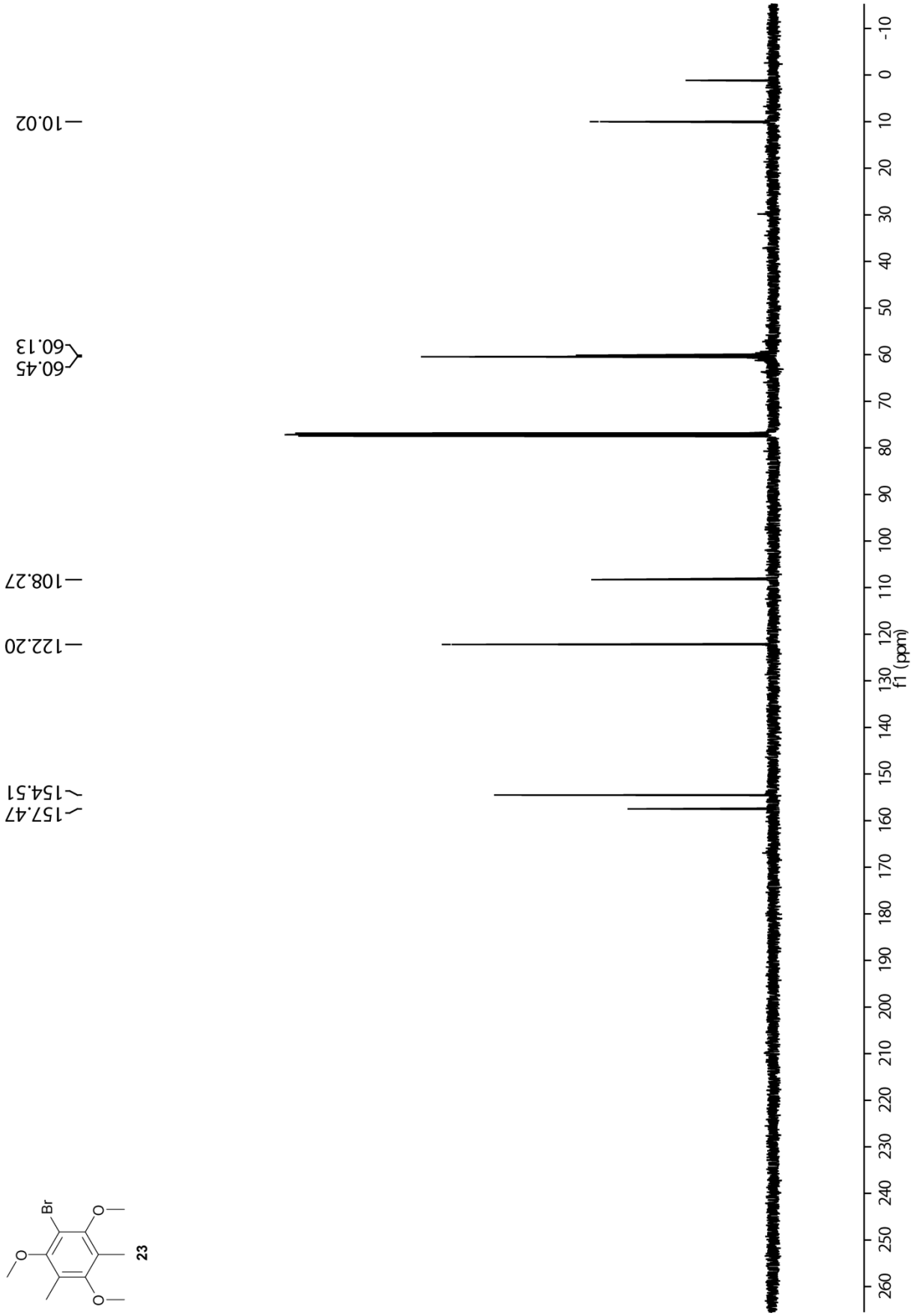


Figure S30. ^{13}C NMR spectrum of **23** (100 MHz, $CDCl_3$).

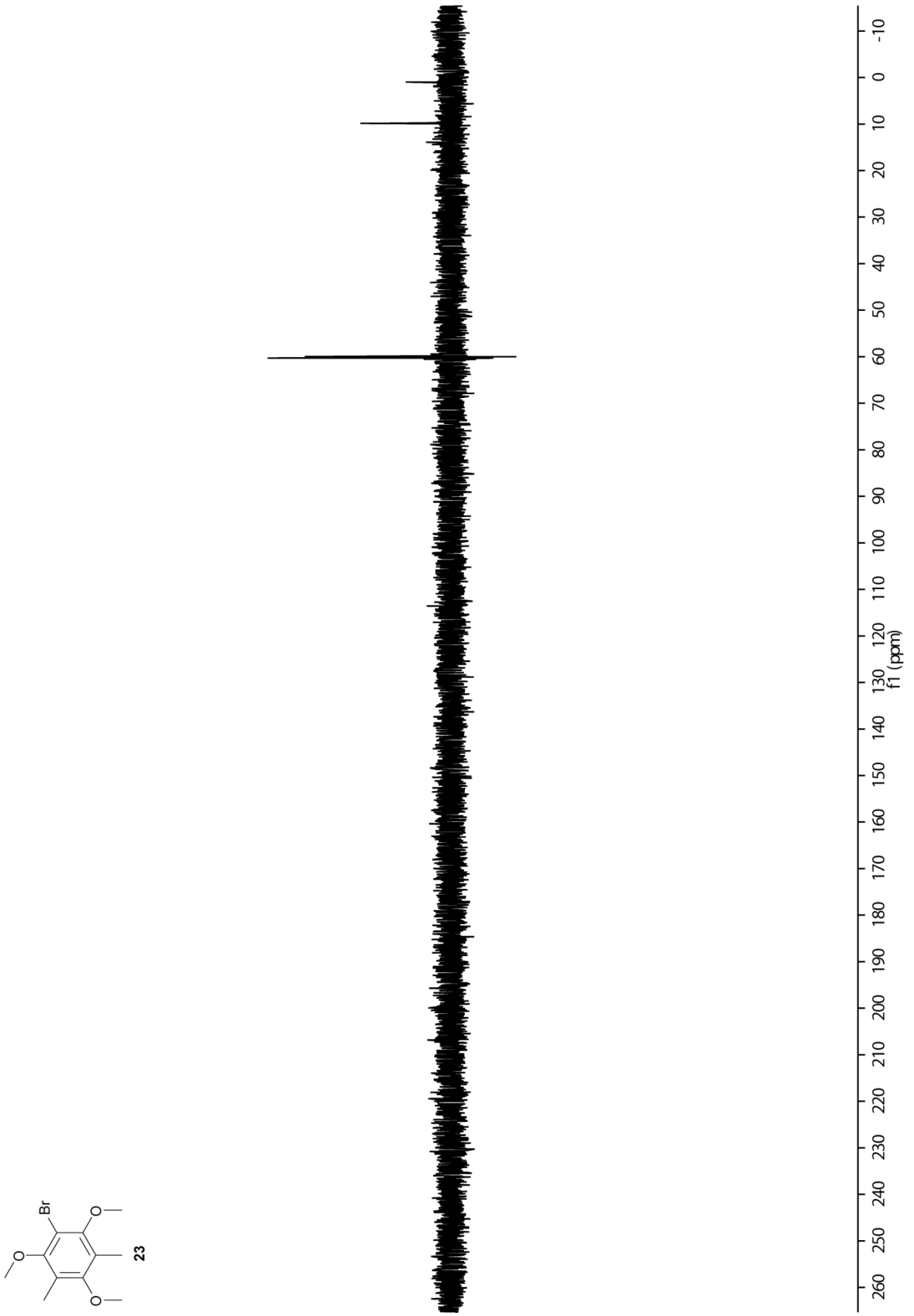


Figure S31. ^{13}C DEPT 135 spectrum of **23** (100 MHz, $CDCl_3$).

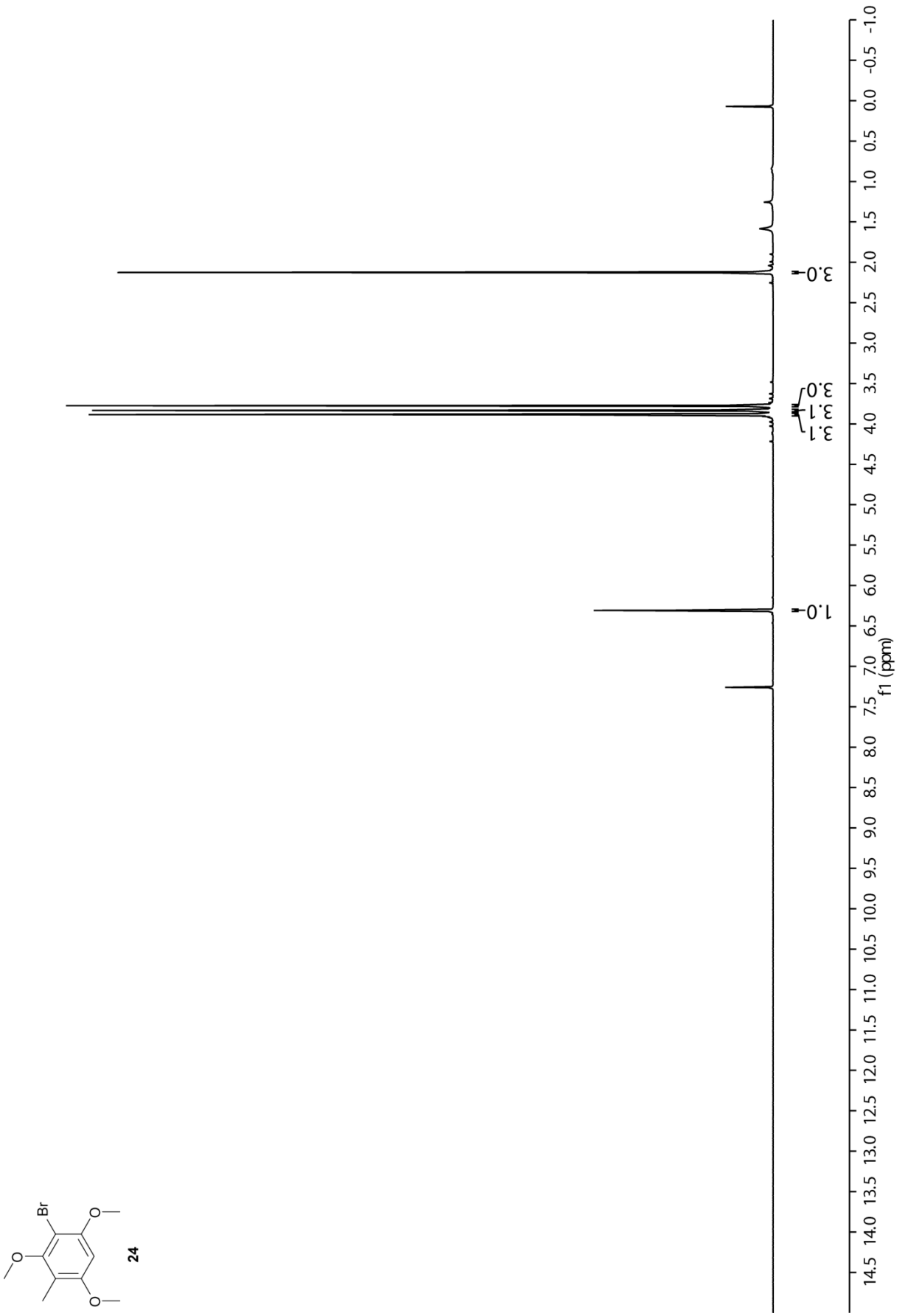


Figure S32. ^{1}H NMR spectrum of **24** (500 MHz, $CDCl_3$).

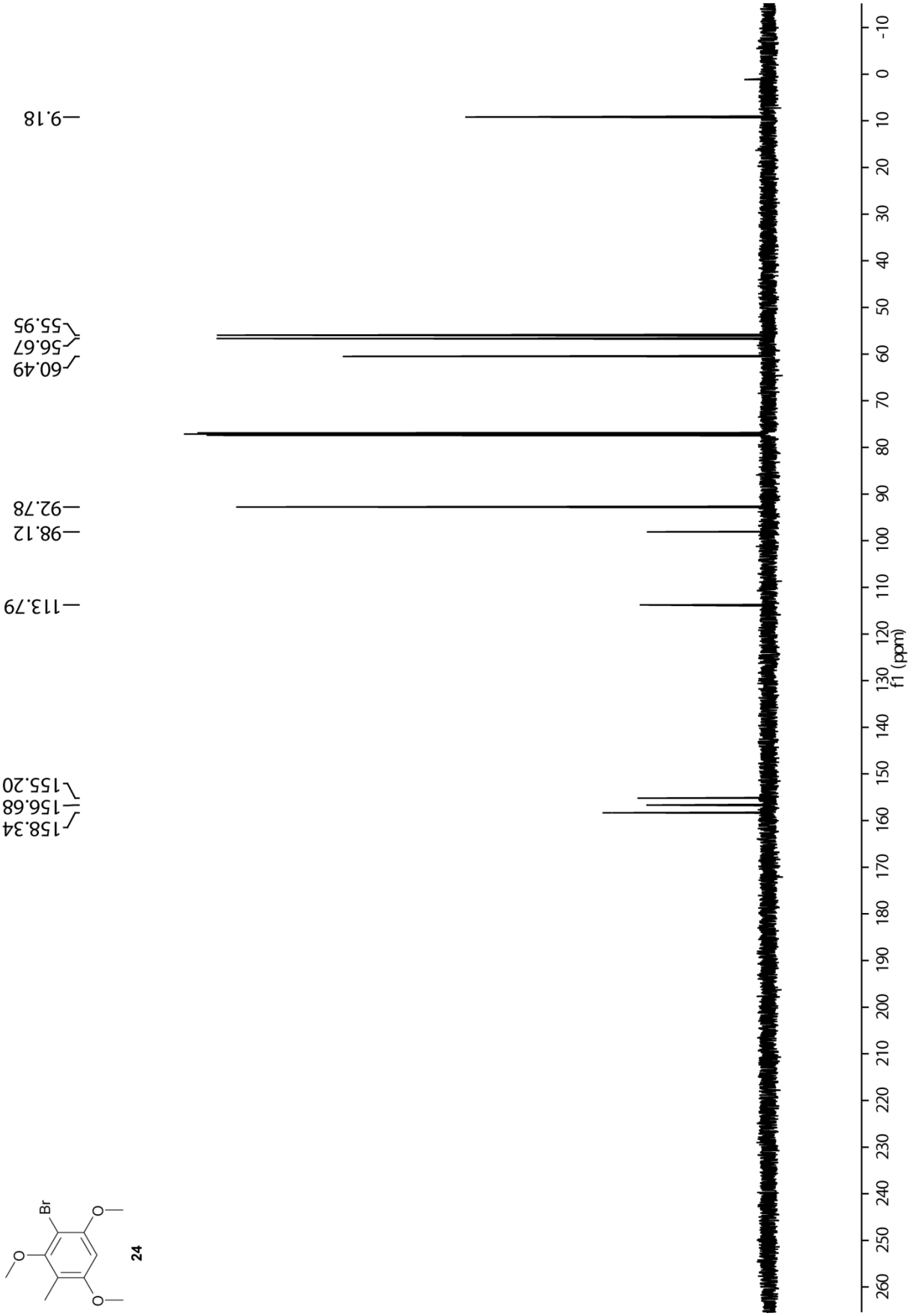


Figure S33. ^{13}C NMR spectrum of **24** (125 MHz, $CDCl_3$).

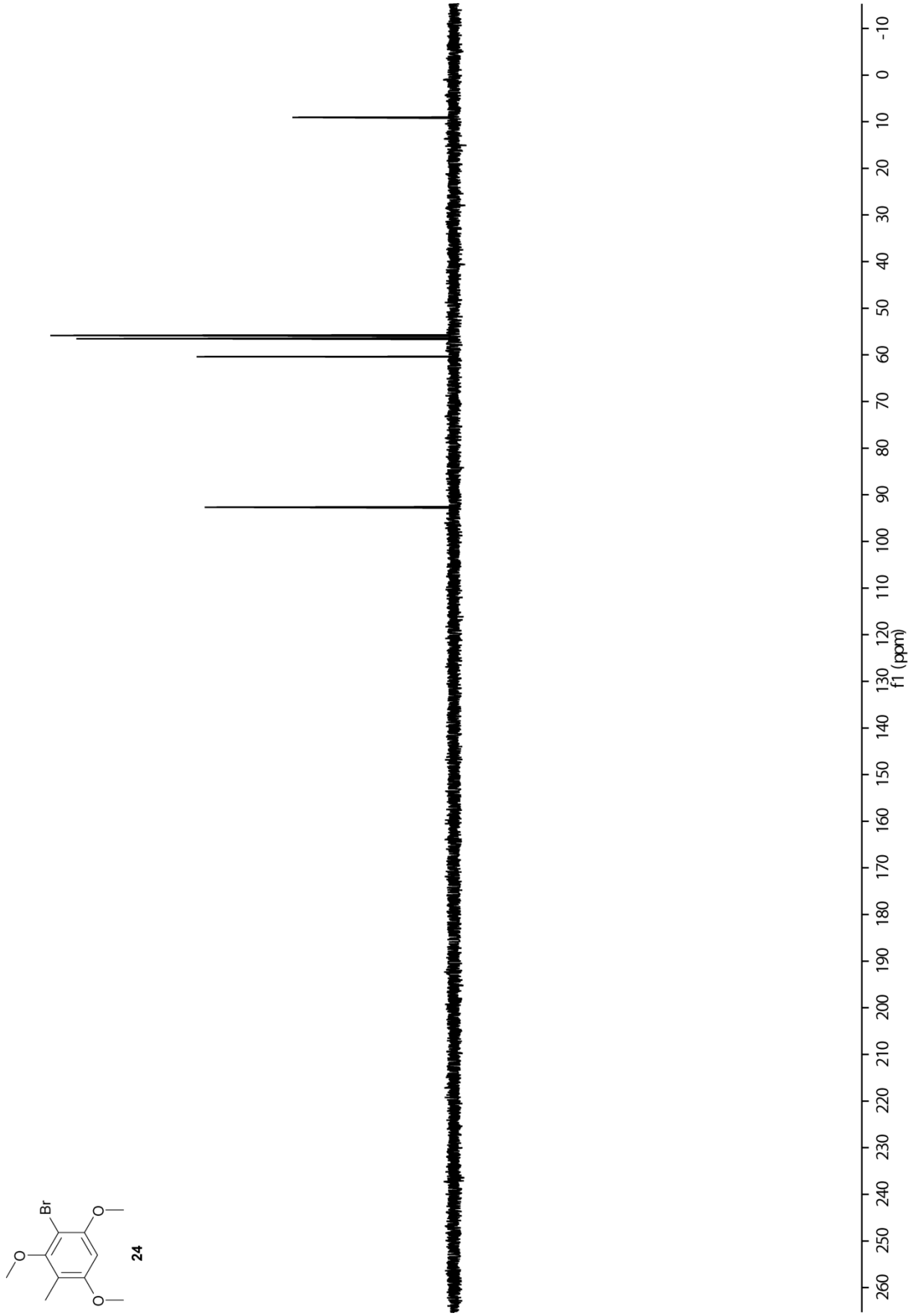


Figure S34. ^{13}C DEPT 135 spectrum of **24** (125 MHz, $CDCl_3$).

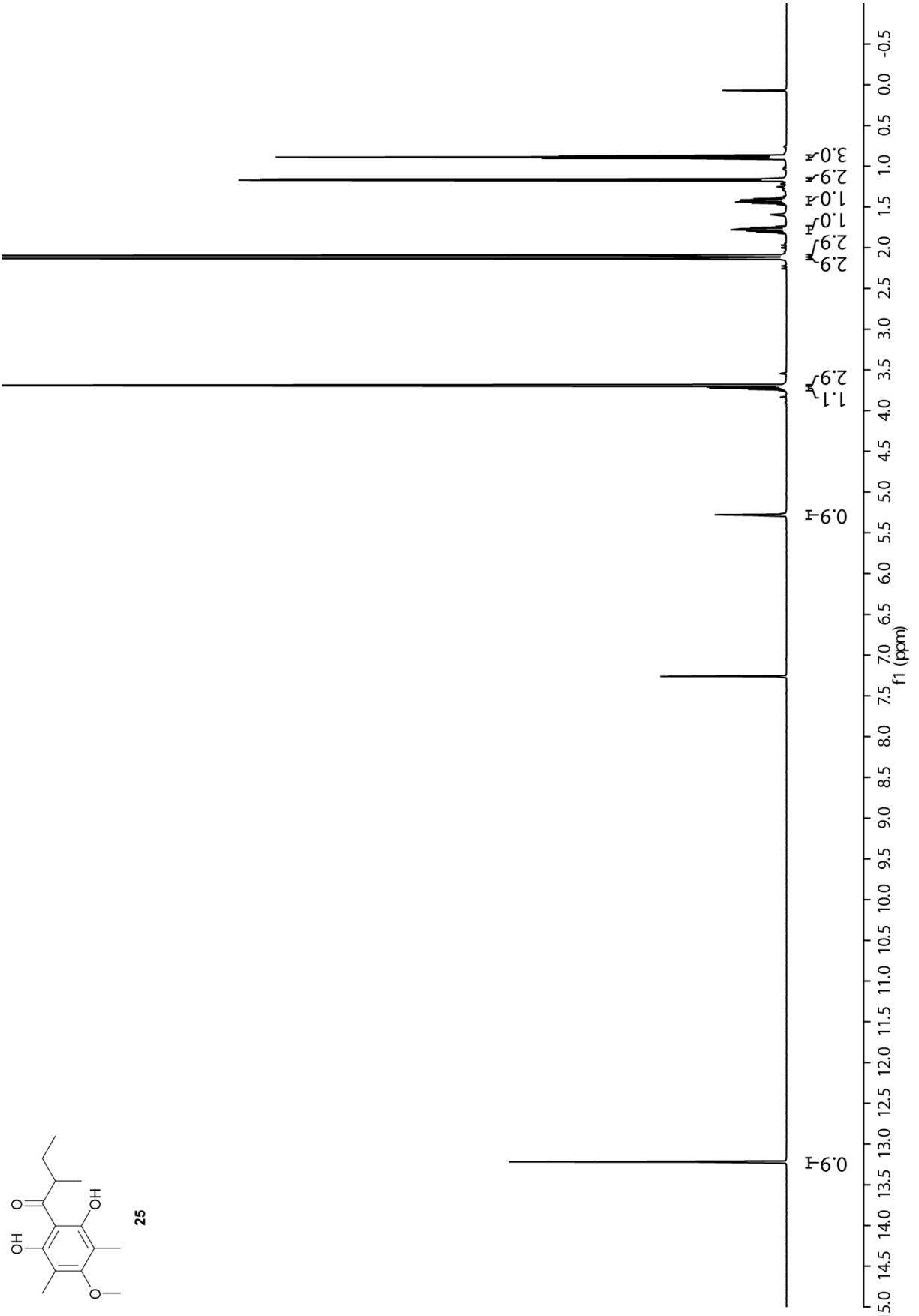


Figure S35. ^{1}H NMR spectrum of **25** (500 MHz, $CDCl_3$).

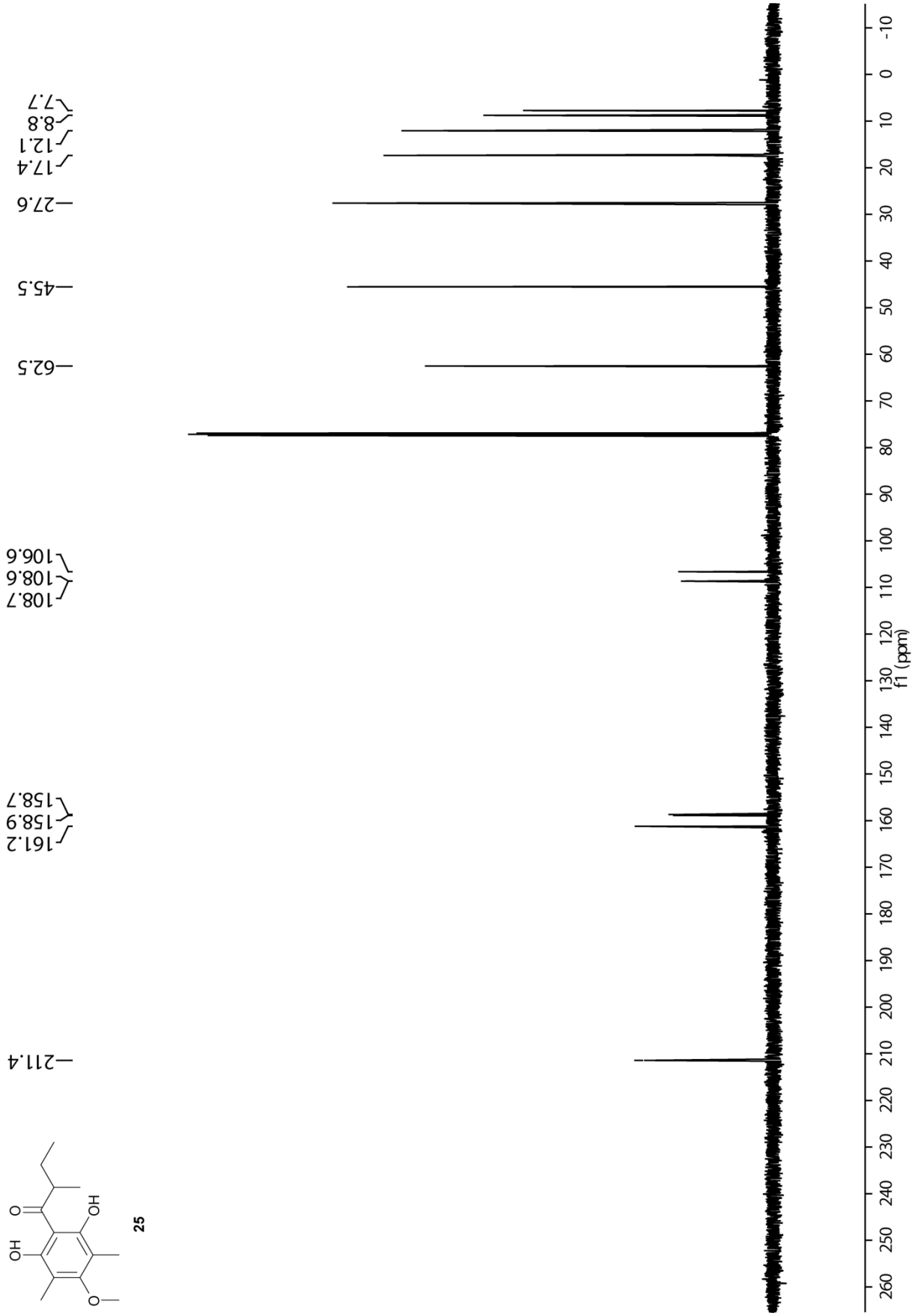


Figure S36. ^{13}C NMR spectrum of **25** (125 MHz, $CDCl_3$).

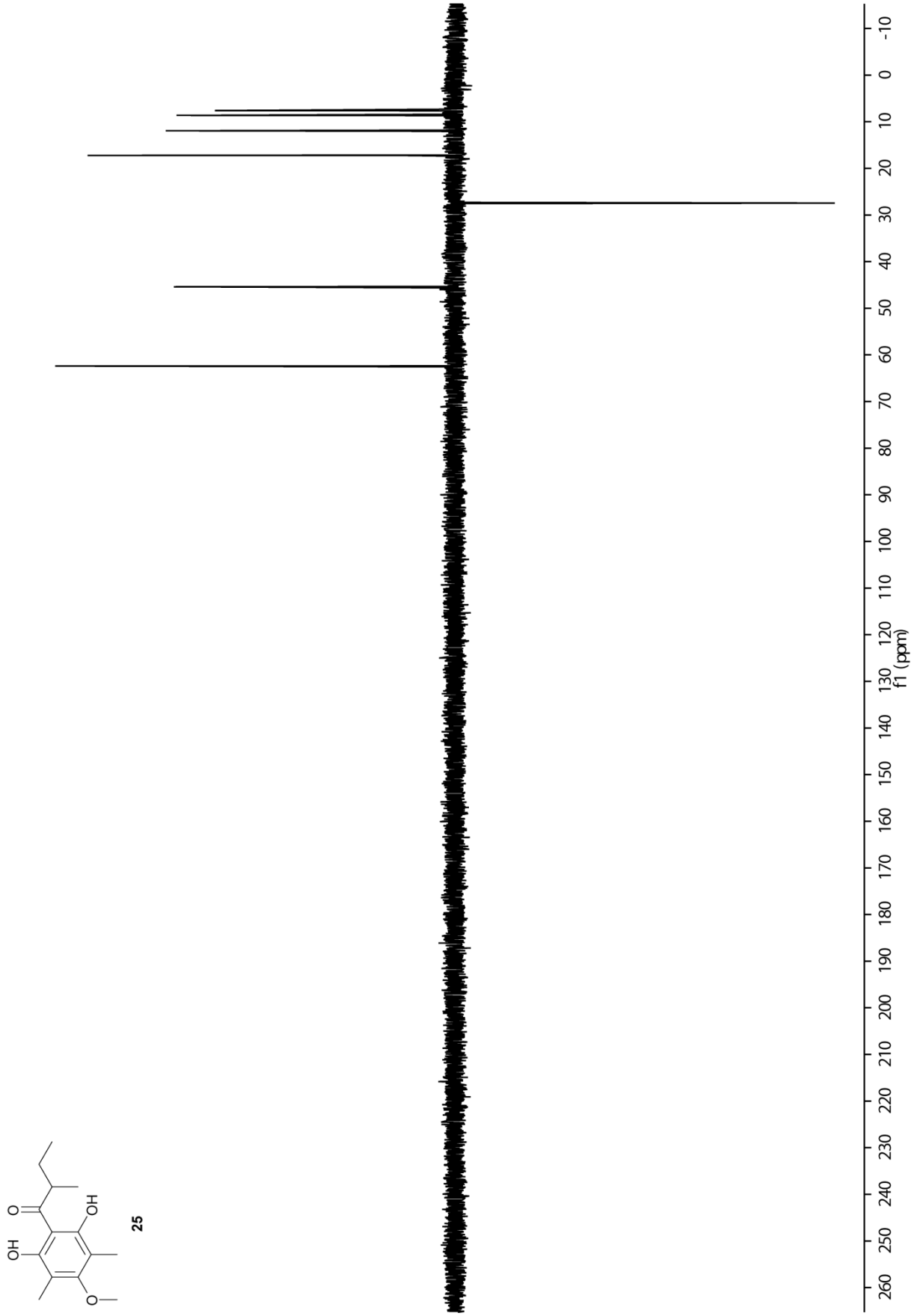


Figure S37. ^{13}C DEPT 135 spectrum of **25** (125 MHz, $CDCl_3$).