Table S1: Volatiles identified in the bouquet from *Daldinia clutidae* MUCL 53761.

Compound	*I*	*I* (Lit.)	Identification[a]	Peak area[b]
4-Methylhexan-3-one (**6**)	846	842 [1]	ms, ri	1.9%
Cyclohexanol (**10**)	887	886 [2]	ms, ri, std	<0.1%
Cyclohexanone (**11**)	899	895 [2]	ms, ri, std	<0.1%
2,5-Dimethylpyrazine (**14**)	915	912 [3]	ms, ri, std	<0.1%
2-Acetylfuran (**12**)	916	911 [4]	ms, ri, std	<0.1%
Oct-1-en-3-ol (**9**)	982	974 [5]	ms, ri, std	0.2%
2,4,6-Trimethylpyridine (**15**)	992	993 [6]	ms, ri	<0.1%
2-Acetylthiazole (**13**)	1019	1014 [5]	ms, ri, std	0.8%
1-Phenylethanol (**16**)	1062	1057 [5]	ms, ri, std	<0.1%
Acetophenone (**17**)	1066	1059 [5]	ms, ri, std	<0.1%
cis-Linalool oxide (**32**)	1074	1067 [5]	ms, ri	0.2%
trans-Linalool oxide (**33**)	1089	1084 [5]	ms, ri	0.3%
2-Phenylethanol (**18**)	1113	1106 [5]	ms, ri, std	<0.1%
Manicone (**7**)	1139	1136 [7]	ms, ri, std	<0.1%
Methyl salicylate (**19**)	1194	1190 [8]	ms, ri, std	<0.1%
(4*R*,5*R*,6*S*)-5-Hydroxy-4,6-dimethyloctan-3-one (**8**)	1231	1228 [7]	ms, ri, std	0.5%
2-Methyl-4-chromanone (**21**)	1369	1366 [7]	ms, ri	<0.1%
Methyl 2,6-dihydroxybenzoate (**20**)	1388	1385 [8]	ms, ri	<0.1%
2-Nonylfuran (**25**)	1394		syn	1.9%
unknown furan (**X**)	1400		syn	<0.1%
Geosmin (**29**)	1403	1399 [5]	ms, ri, std	<0.1%

5-Hydroxy-2-methyl-4-chromanone (**22**)	1473		ms, std [9]	43.5%
trans-β-Bergamotene (**31**)	1490	1480 [10]	ms, ri	0.3%
β-Bisabolene (**30**)	1510	1505 [10]	ms, ri	0.1%
5-Hydroxy-2-methyl-4*H*-chromen-4-one (**23**)	1591	1591 [11]	ms, ri, std	0.2%
2-Undecylfuran (**26**)	1597		syn	0.1%
unknown furan (**Y**)	1604		syn	0.1%
1,8-Dimethoxynaphthalene (**24**)	1659	1657 [11]	ms, ri	22.0%
6-Heptyl-2*H*-pyran-2-one (**27**)	1672	1677 [12]	ms, ri, std	0.1%
6-Nonyl-2*H*-pyran-2-one (**28**)	1878	1875 [7]	ms, ri, std	2.7%

[a] Compound identification was based on ms: identical mass spectrum, ri: identical retention index, std: comparison to an authentic standard (isolated from liquid culture extracts, from a commercial supplier, or synthesised in our previous work), syn: comparison to an authentic standard synthesised in this study. [b] Peak area in % of total peak area. The sum of peak areas is <100%, because unidentified compounds, medium compounds and contaminants (e. g. plasticisers) are not listed.

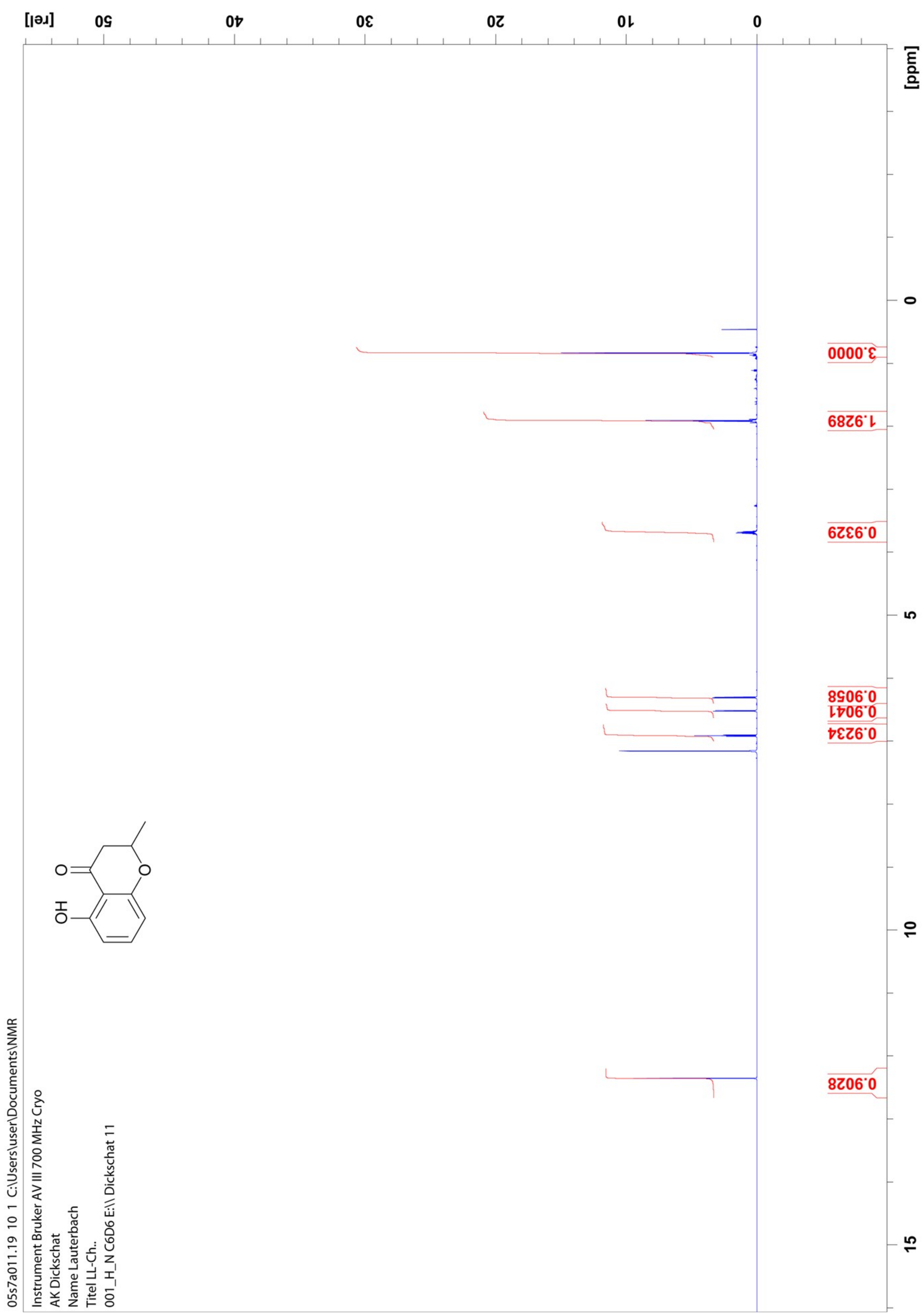


Figure S1. ^{1}H-NMR spectrum (700 MHz, C_6D_6) of **22** isolated from liquid culture extracts.

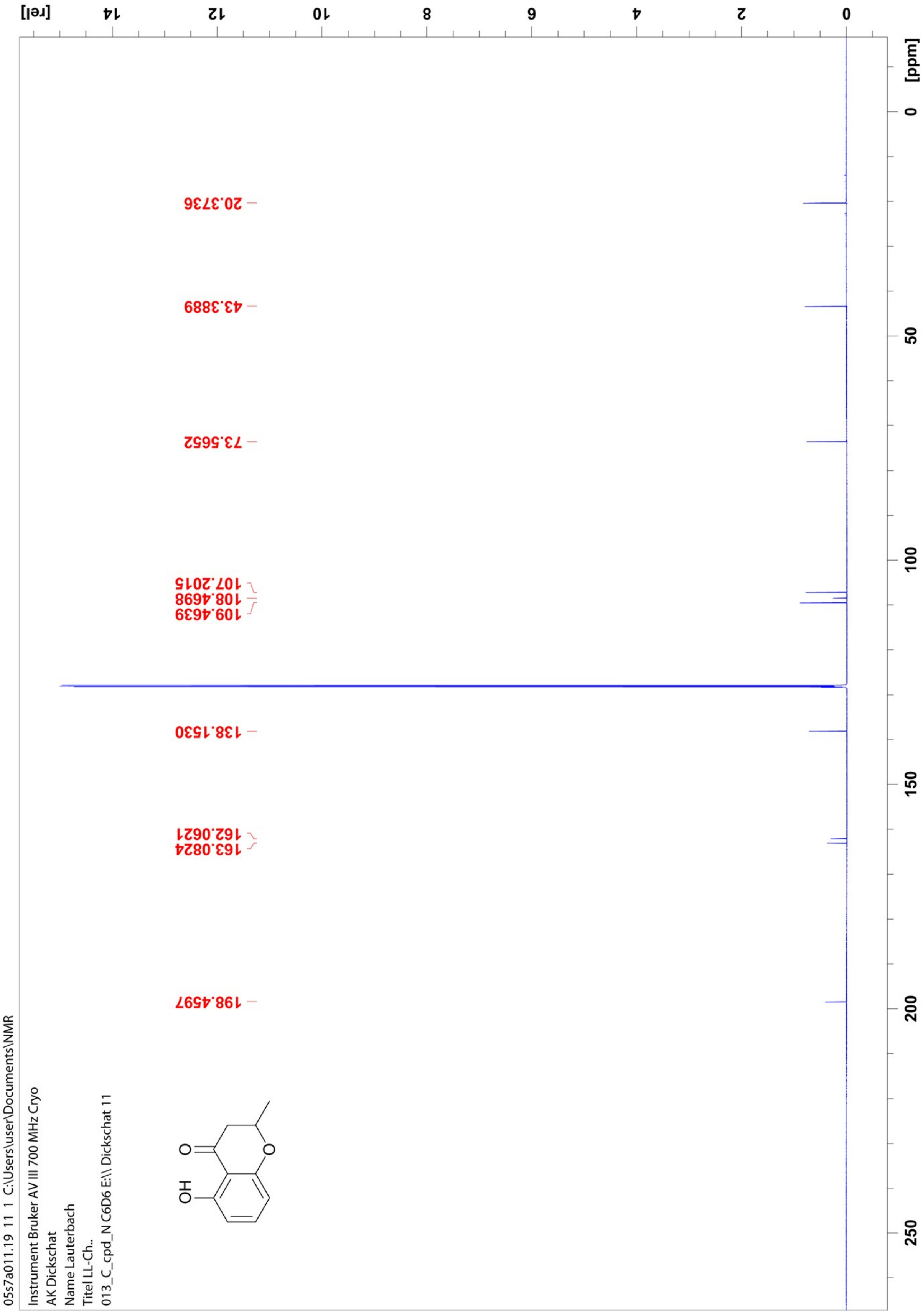


Figure S2. ^{13}C-NMR spectrum (175 MHz, C_6D_6) of **22** isolated from liquid culture extracts.

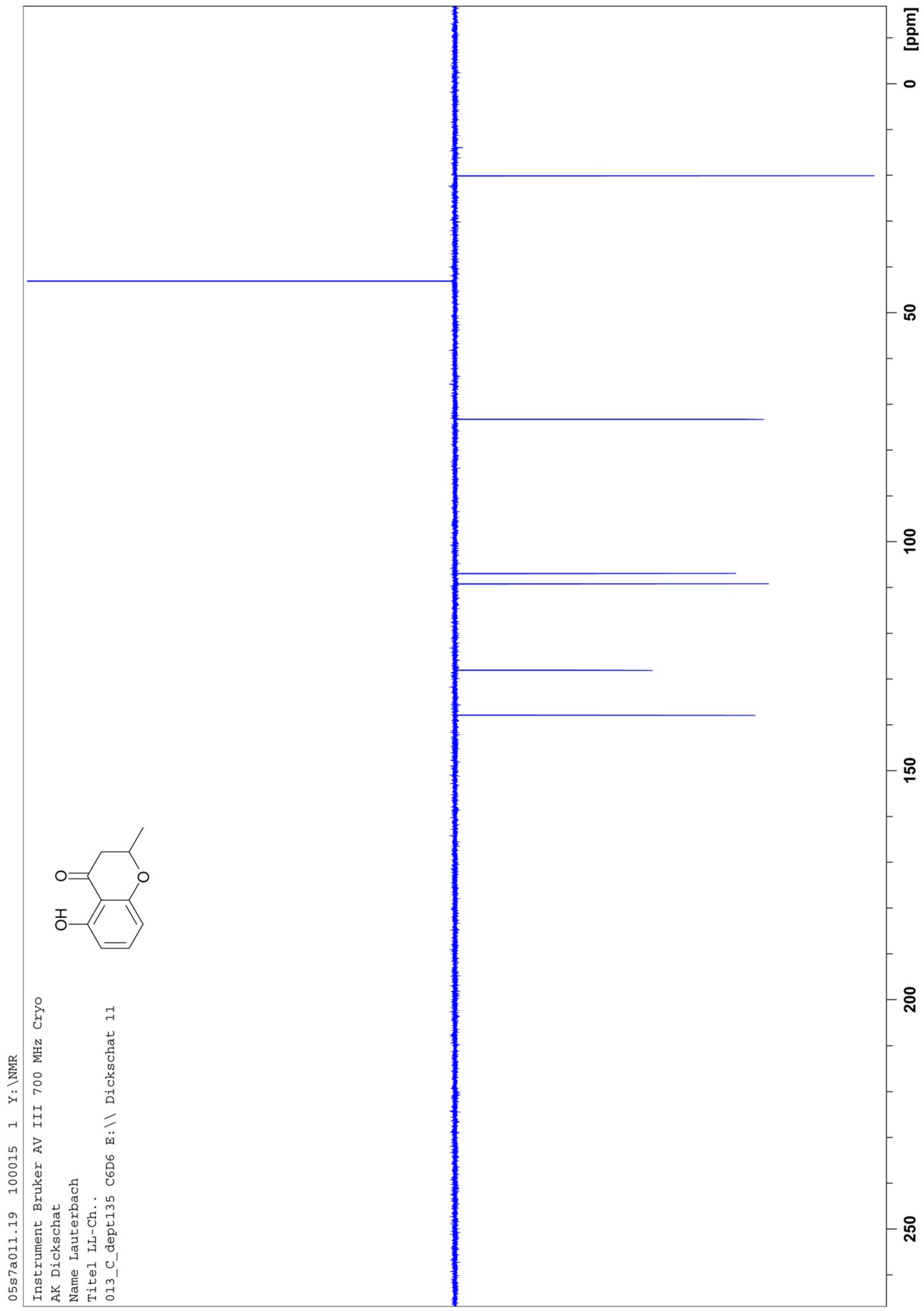


Figure S3. ^{13}C-DEPT spectrum (175 MHz, C_6D_6) of **22** isolated from liquid culture extracts.

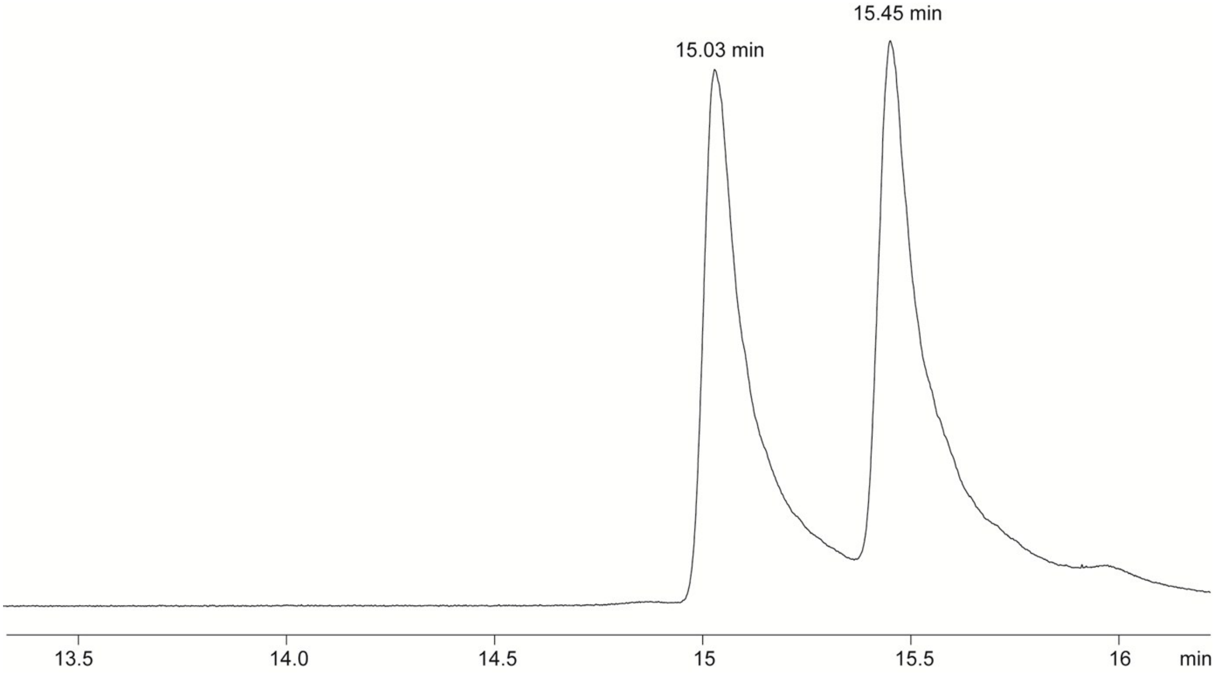


Figure S4. GC analysis of isolated **22** on a chiral stationary phase. Peak integration demonstrates that natural **22** from *Daldinia* cf. *childiae* is racemic.

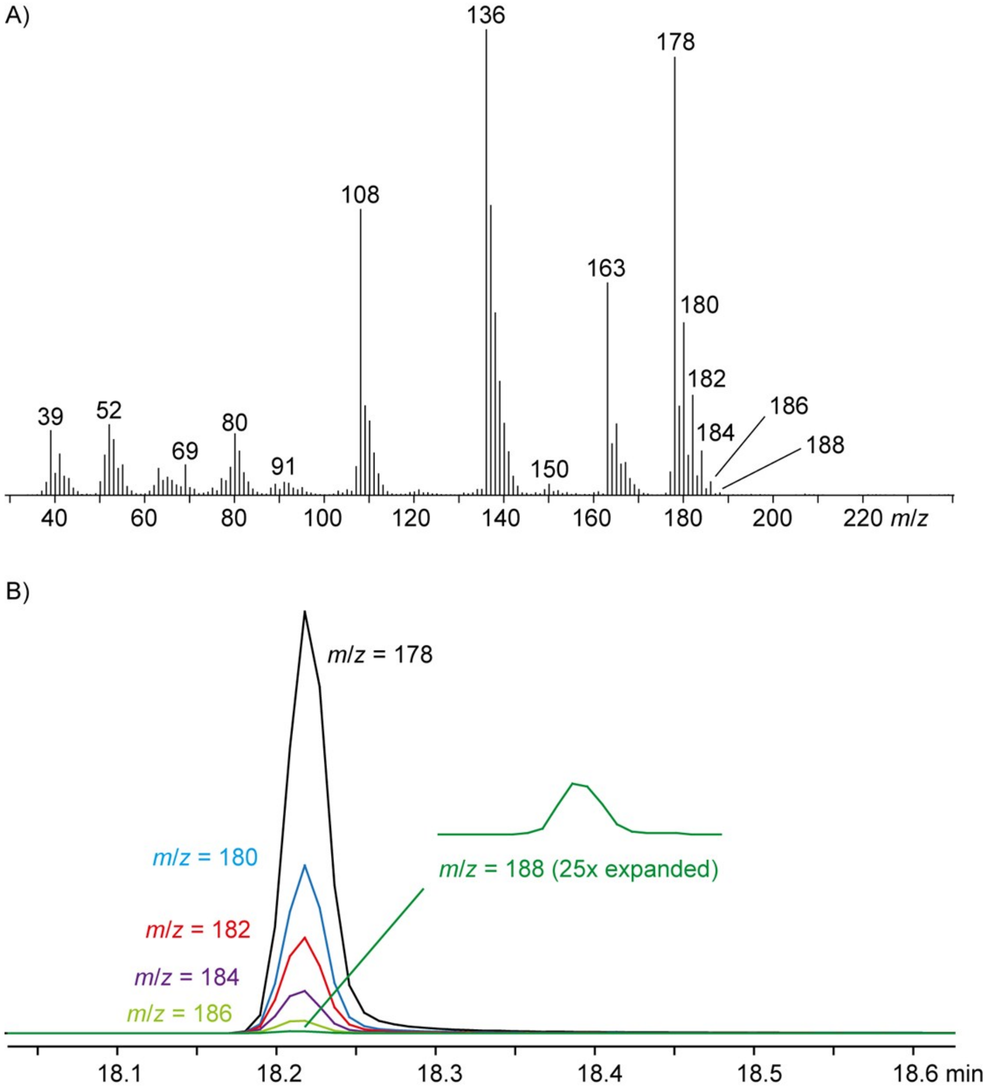


Figure S5. A) Mass spectrum of labelled **22** obtained in the feeding experiment with sodium (1,2-$^{13}C_2$)acetate showing the incorporation of up two five labelled C_2 units. B) Extracted ion chromatograms for non-labelled **22** (*m*/*z* = 178) and labelled **22** with one (*m*/*z* = 180), two (*m*/*z* = 182), three (*m*/*z* = 184), four (*m*/*z* = 186) and five (*m*/*z* = 188) incorporated (1,2-$^{13}C_2$)acetate units. The incorporation rate (14%) was determined from the peak integrals of these extracted ion chromatograms weighted by the number of labelled and unlabelled units they represent.

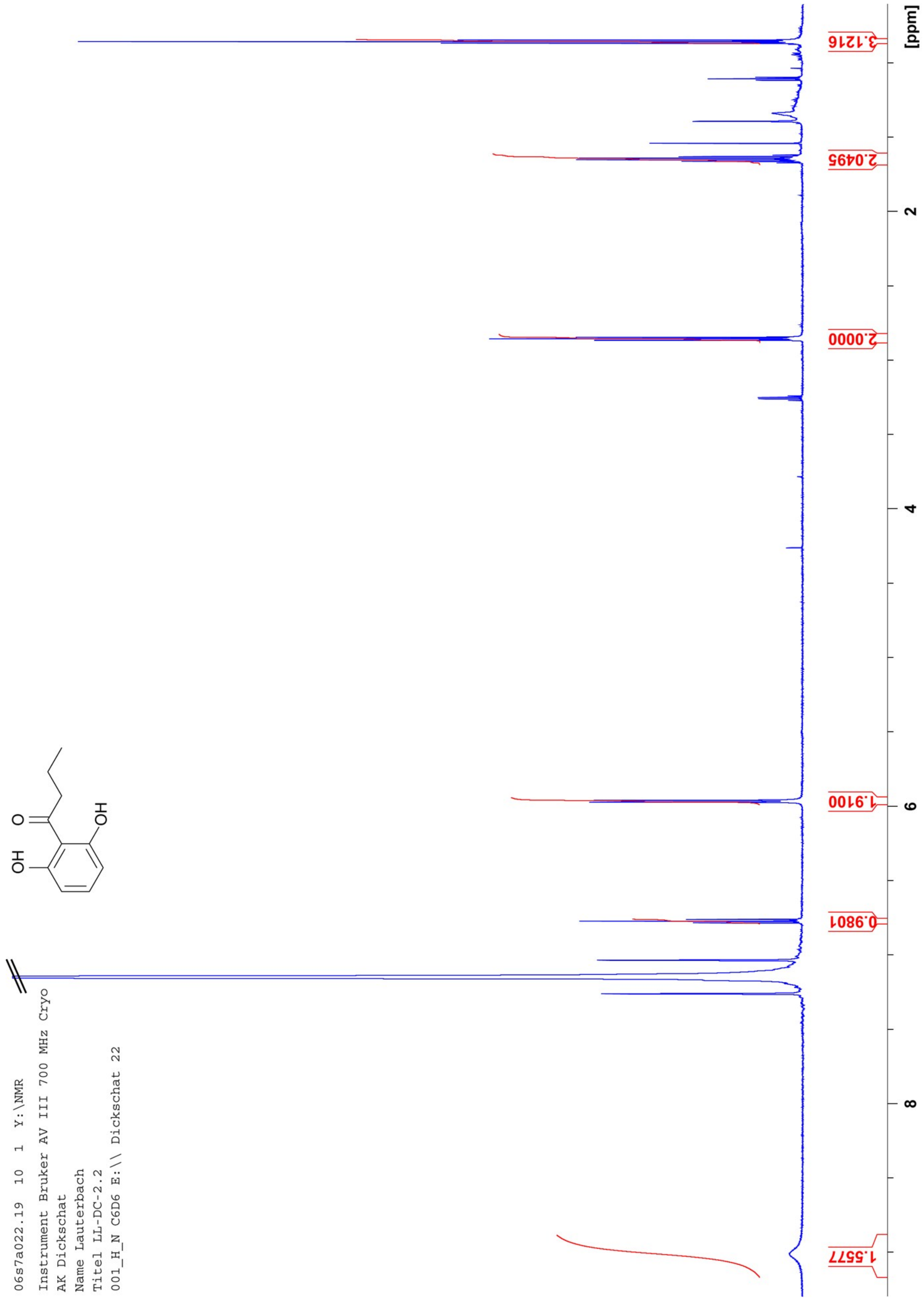


Figure S6. ^{1}H-NMR spectrum (700 MHz, C_6D_6) of **35**.

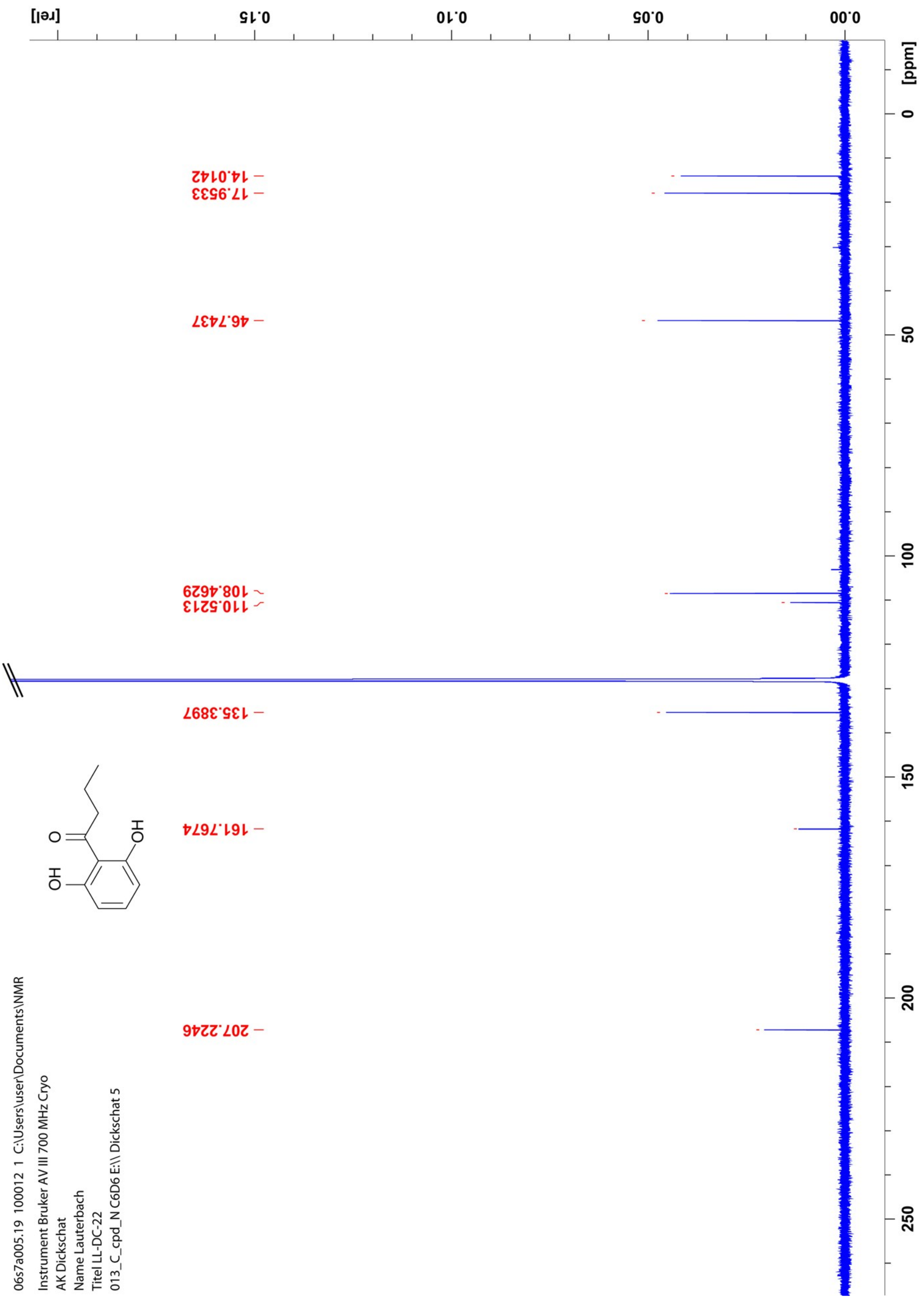


Figure S7. ^{13}C-NMR spectrum (175 MHz, C_6D_6) of **35**.

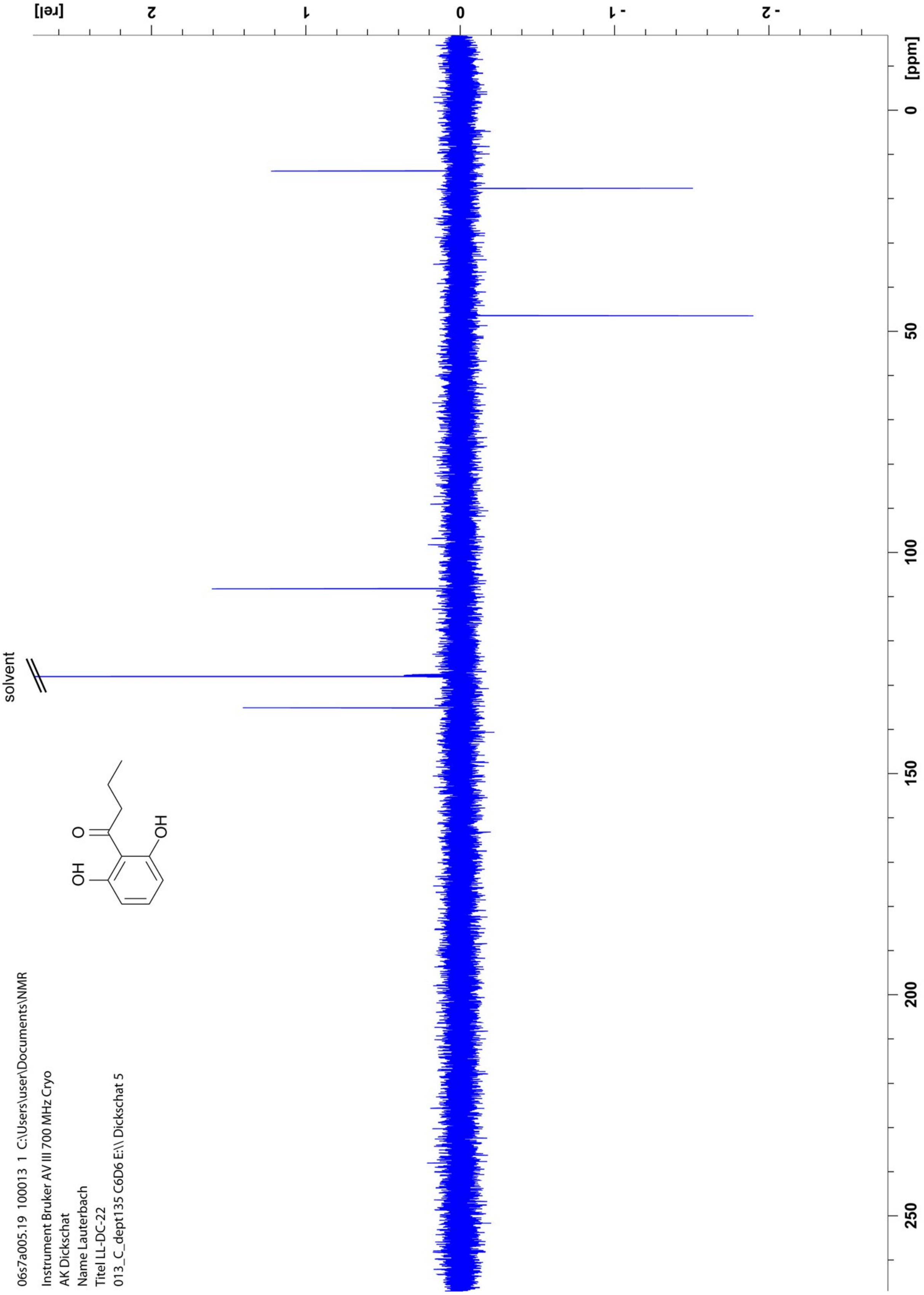
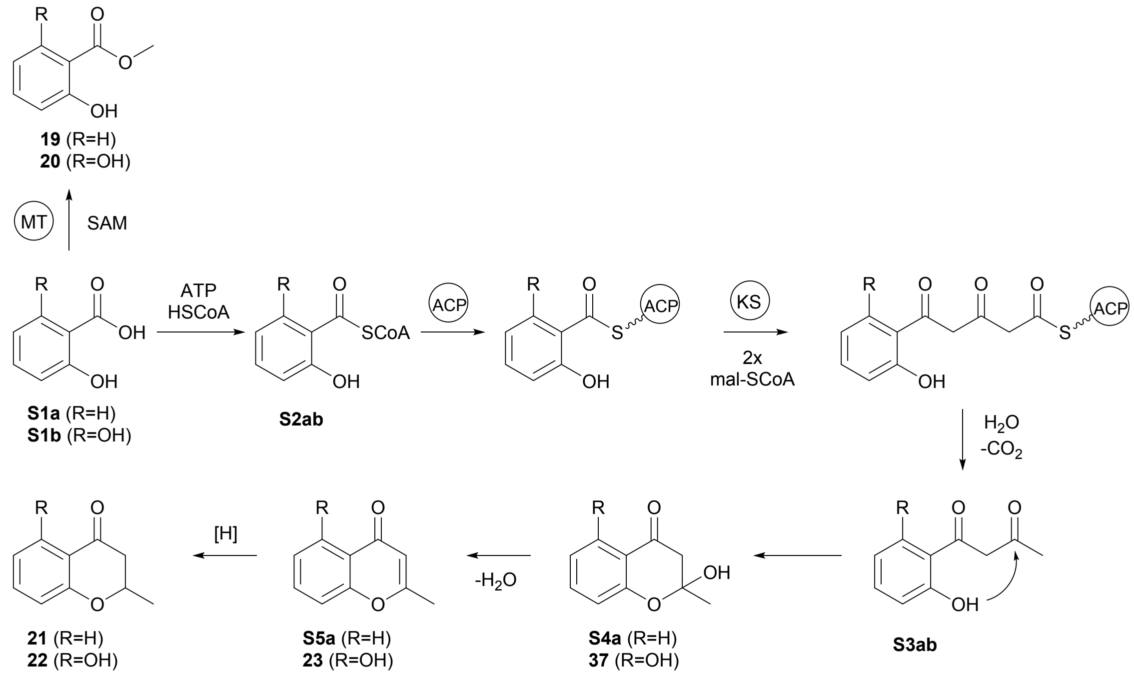


Figure S8. ^{13}C-DEPT spectrum (175 MHz, C_6D_6) of **35**.



Scheme S1. Alternative biosynthetic pathway to **22** and related natural products (excluded by the feeding experiment with sodium (1,2-$^{13}C_2$)acetate). This pathway would use salicylic acid (**S1a**) and 2,6-dihydroxybenzoic acid (**S1b**) as starter units. The corresponding methyl esters **19** and **20** are observed as trace compounds in the headspace extracts from *Daldinia clutidae* and could arise by *S*-adenosylmethionine (SAM) dependent methylation of **S1a** and **S1b** by a methyltransferase (MT). Instead of being biosynthetic starter units these benzoic acid derivatives may arise by degradation of the polyketides **21** and **22**. ACP: acyl carrier protein, KS: ketosynthase, mal-SCoA: malonyl-coenzyme A thioester.

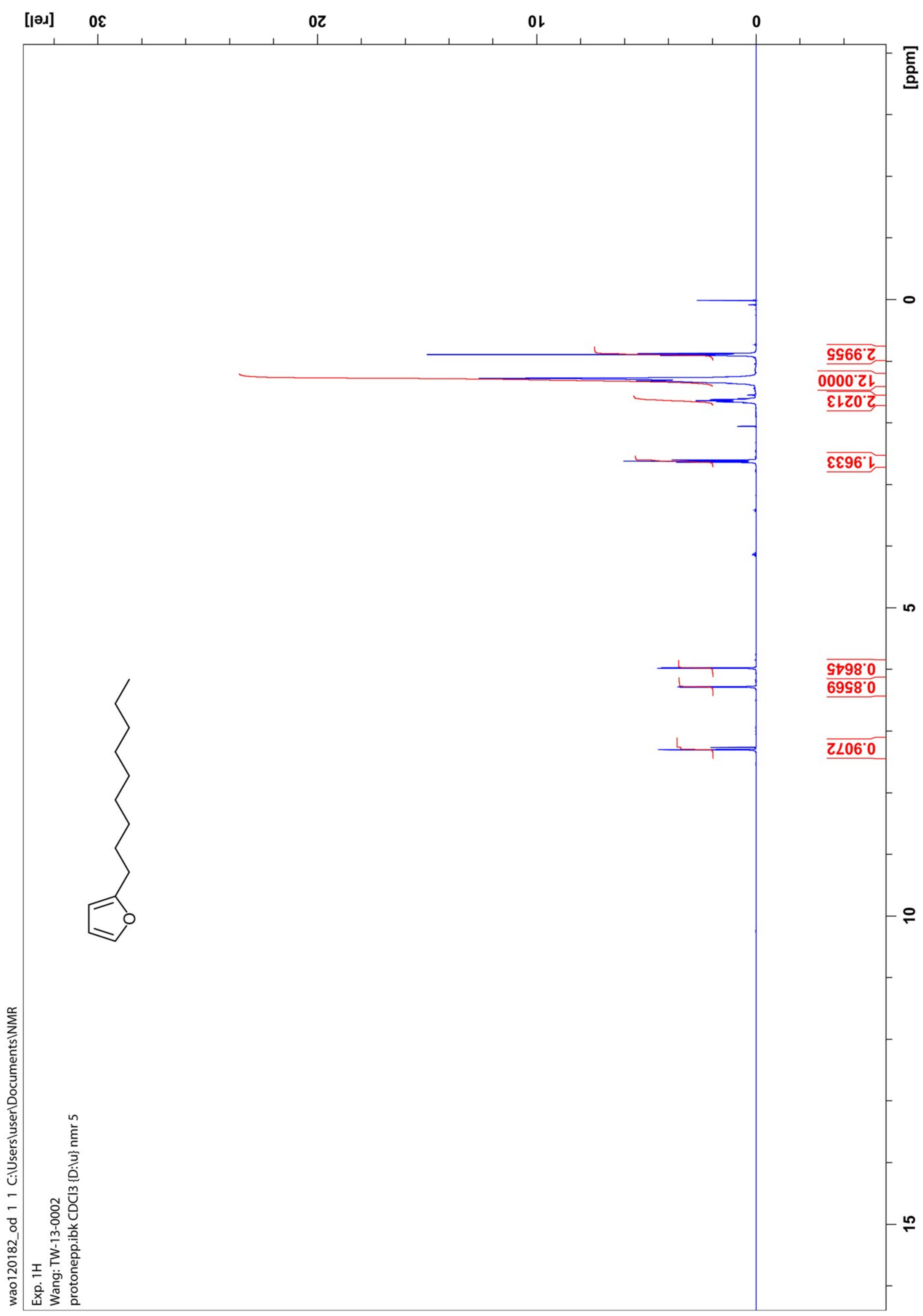


Figure S9. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **25**.

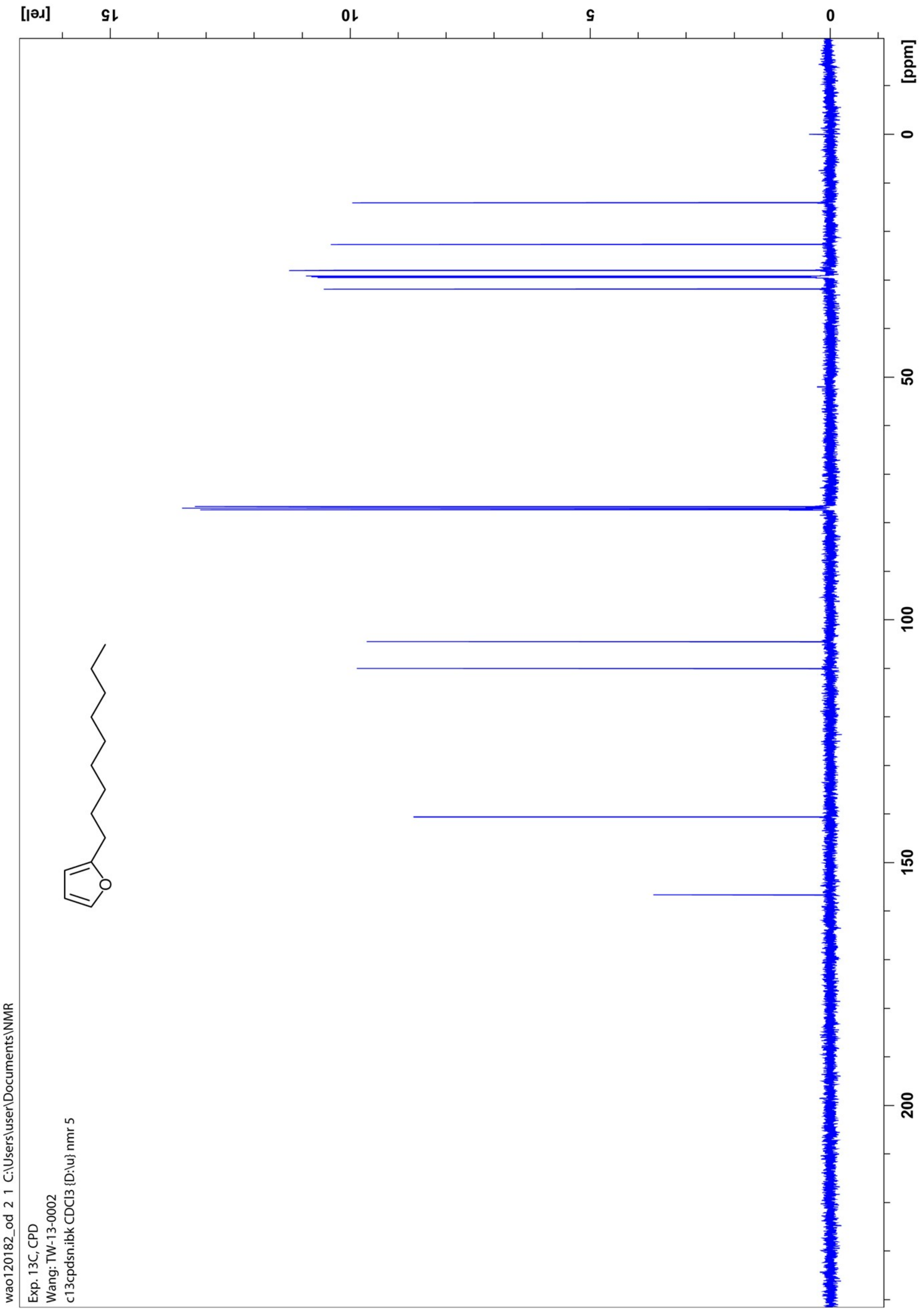


Figure S10. ^{13}C-NMR spectrum (100 MHz, $CDCl_3$) of **25**.

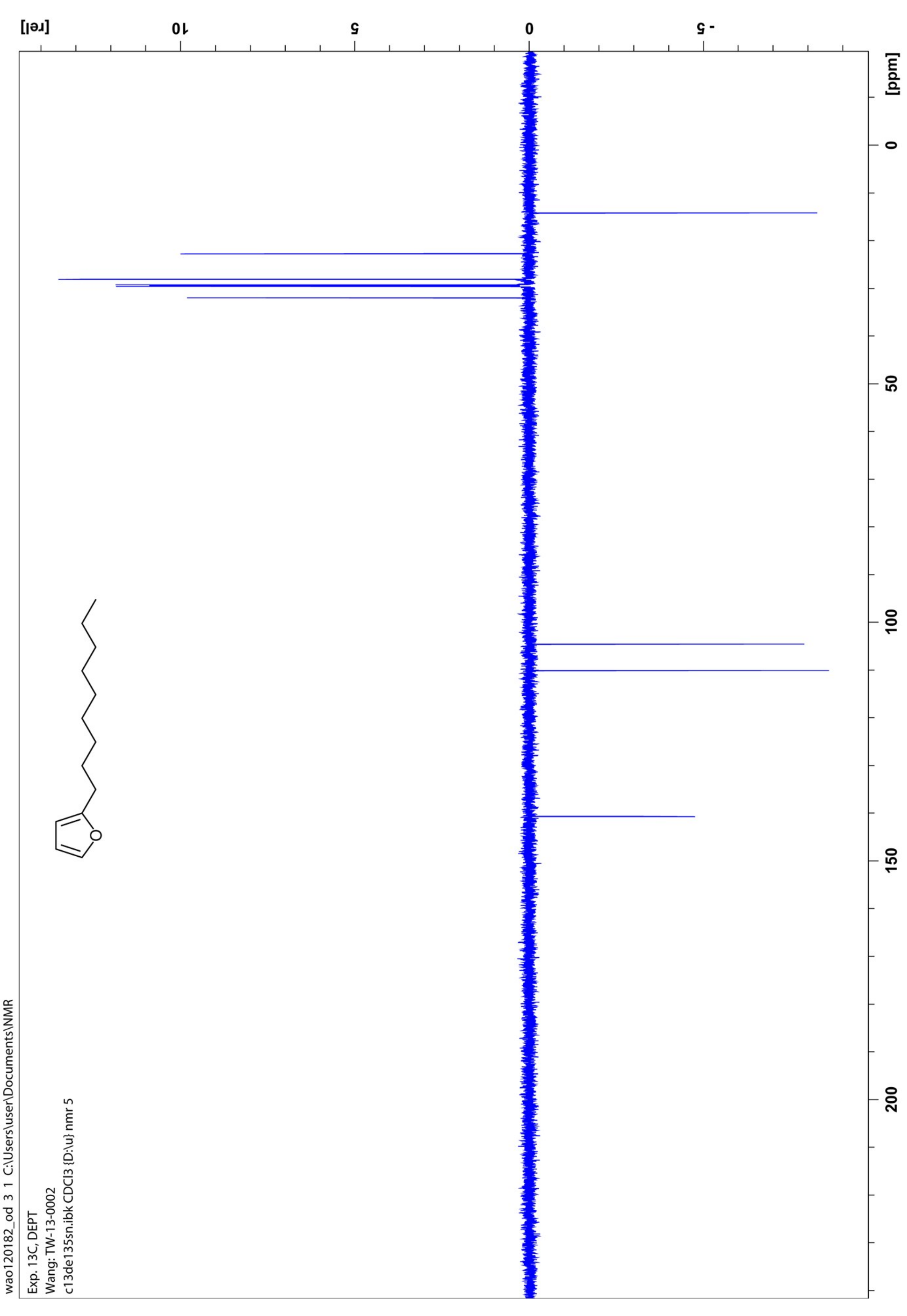


Figure S11. ^{13}C-DEPT spectrum (100 MHz, $CDCl_3$) of **25**.

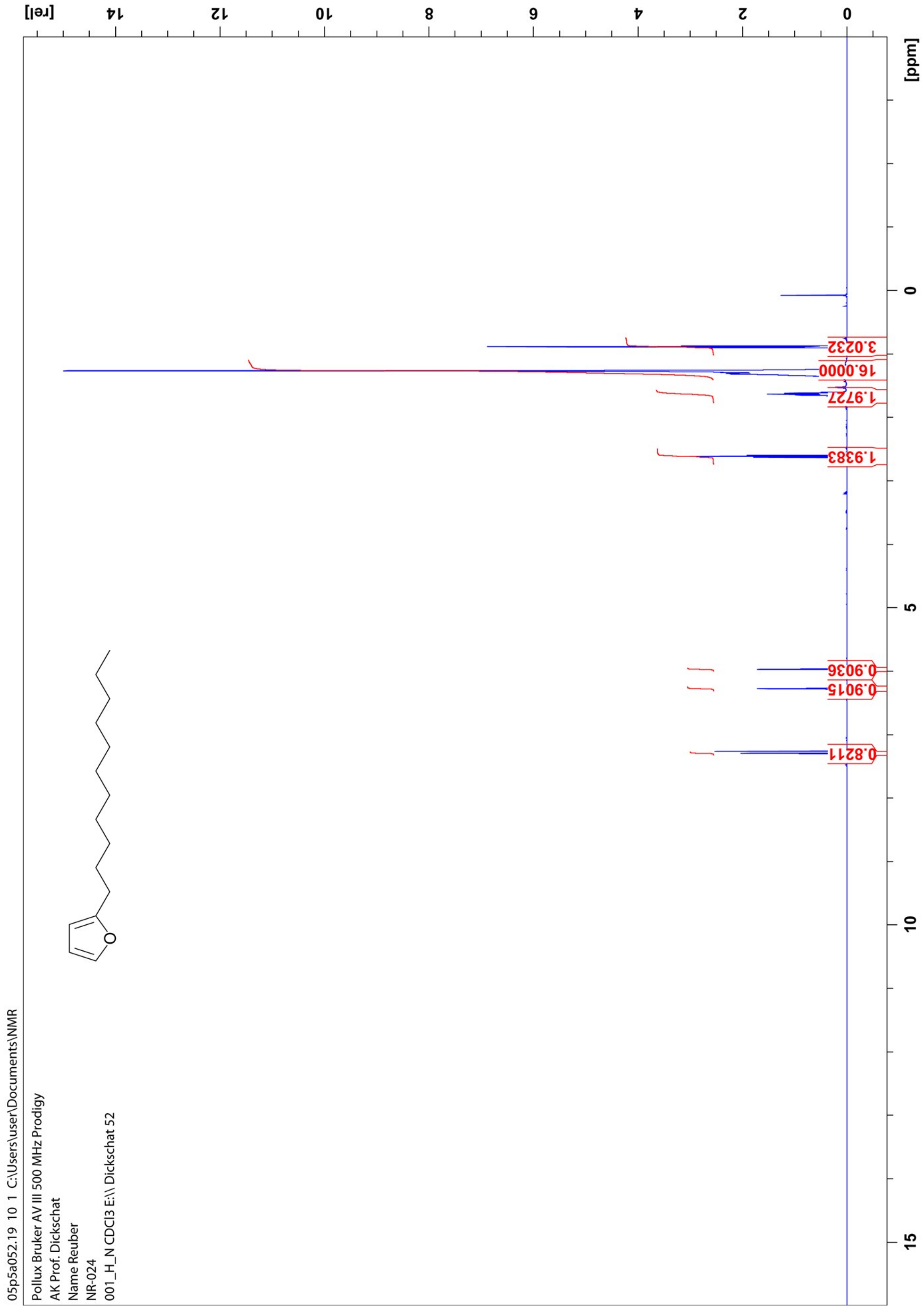


Figure S12. ^{1}H-NMR spectrum (500 MHz, CDCl$_3$) of **26**.

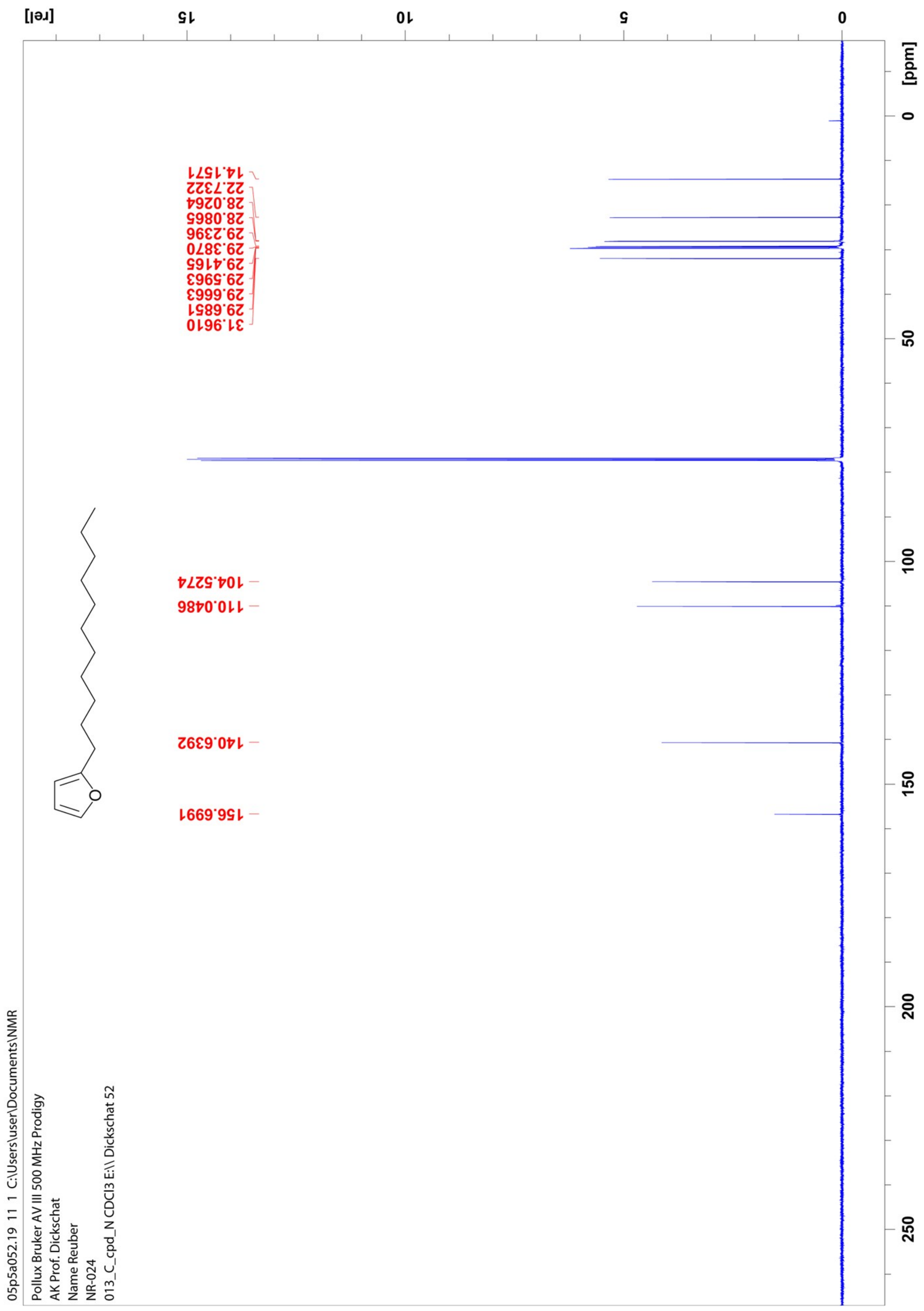


Figure S13. ^{13}C-NMR spectrum (125 MHz, $CDCl_3$) of **26**.

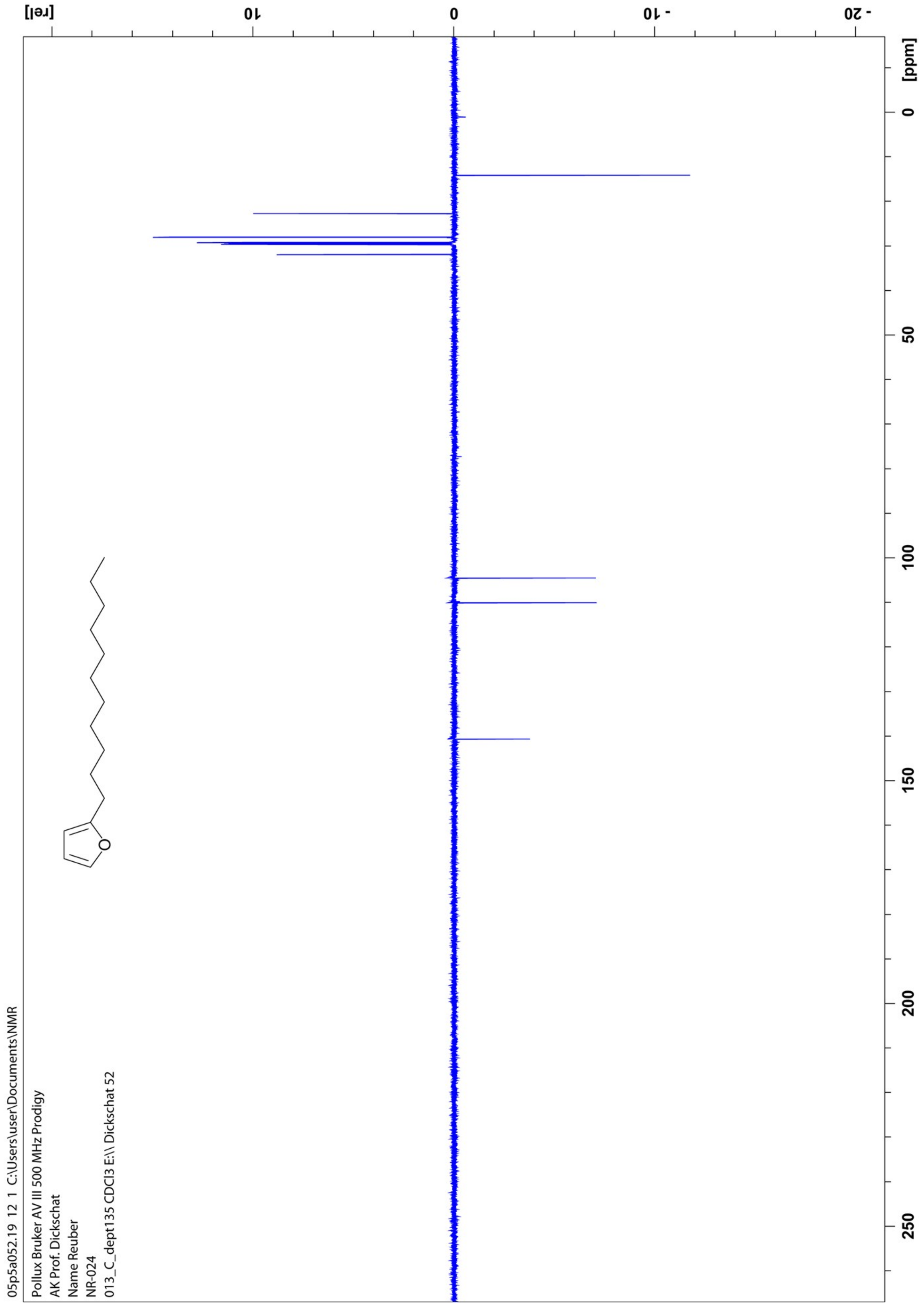


Figure S14. ^{13}C-DEPT spectrum (125 MHz, CDCl$_3$) of **26**.

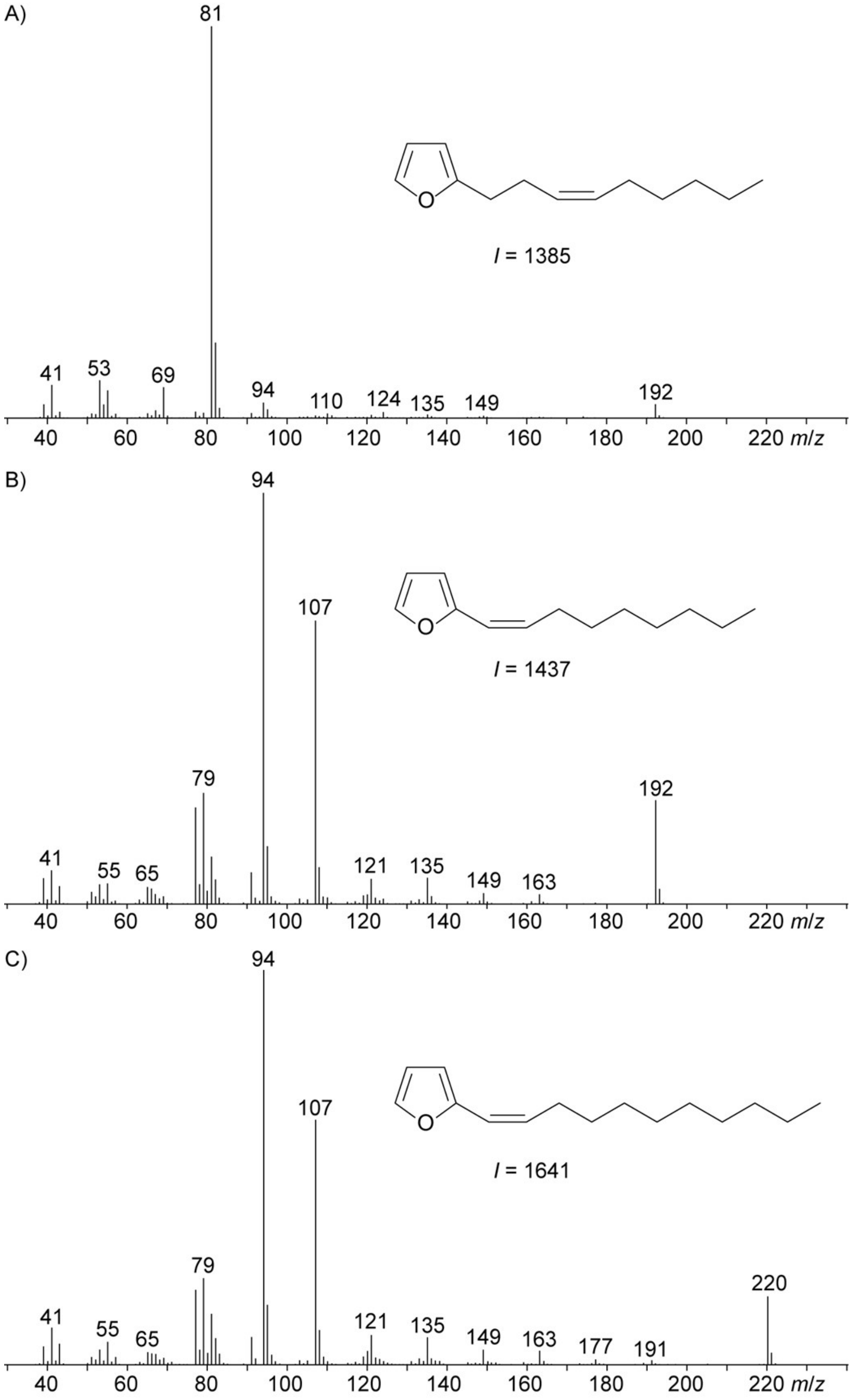


Figure S15. Synthetic candidate compounds that were considered for the alkenylfurans **X** and **Y**. EI mass spectra and retention indices of A) (*Z*)-2-(non-3-en-1-yl)furan (**41**), B) (*Z*)-2-(non-1-en-1-yl)furan (**45**) and C) (*Z*)-2-(undec-1-en-1-yl)furan (**46**). The mass spectra of (*E*)-**45** (*I* = 1466) and (*E*)-**46** (*I* = 1671) were very similar to those shown for the corresponding (*Z*)-isomers.

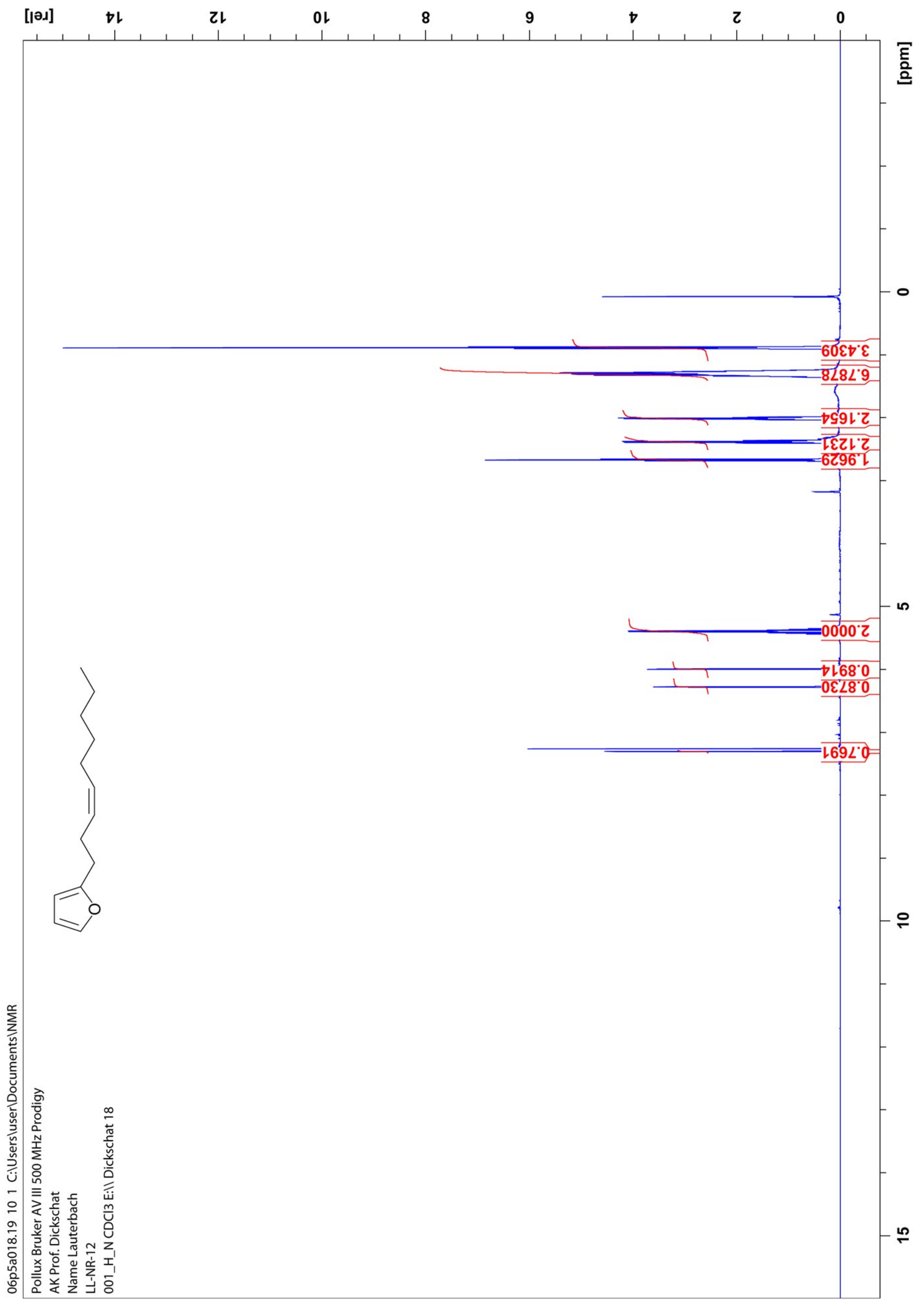


Figure S16. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **41**.

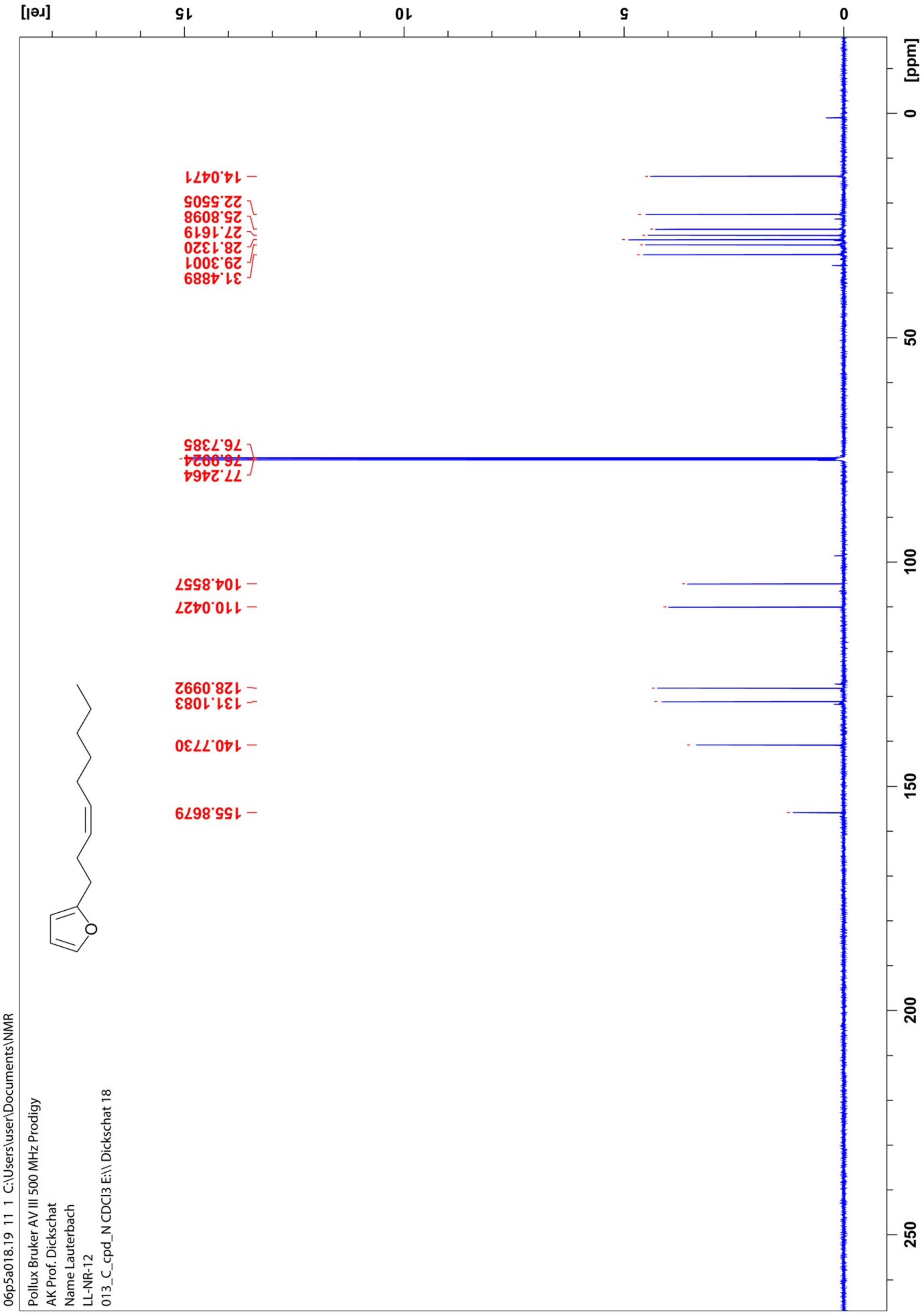


Figure S17. ^{13}C-NMR spectrum (125 MHz, $CDCl_3$) of **41**.

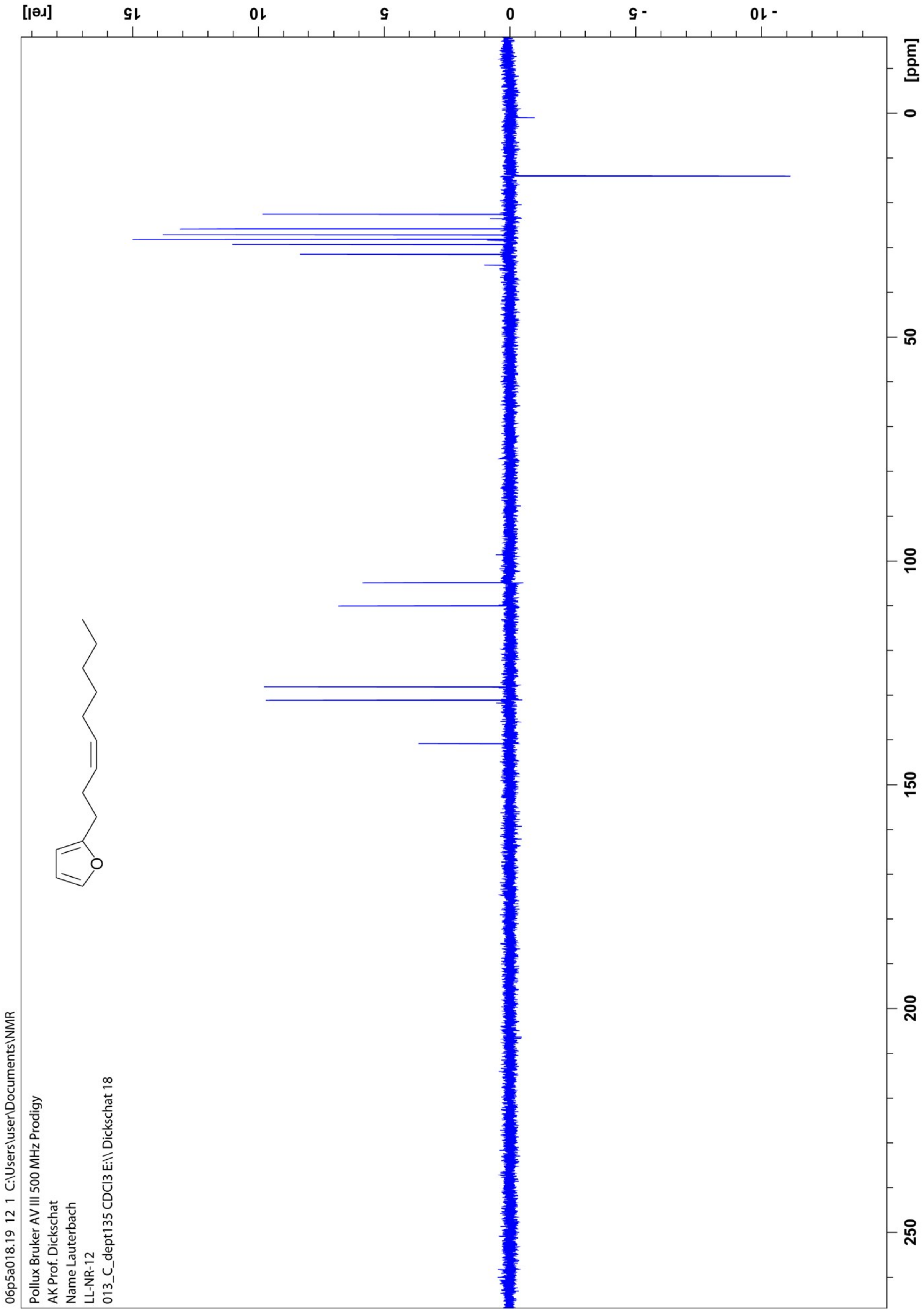


Figure S18. ^{13}C-DEPT spectrum (125 MHz, $CDCl_3$) of **41**.

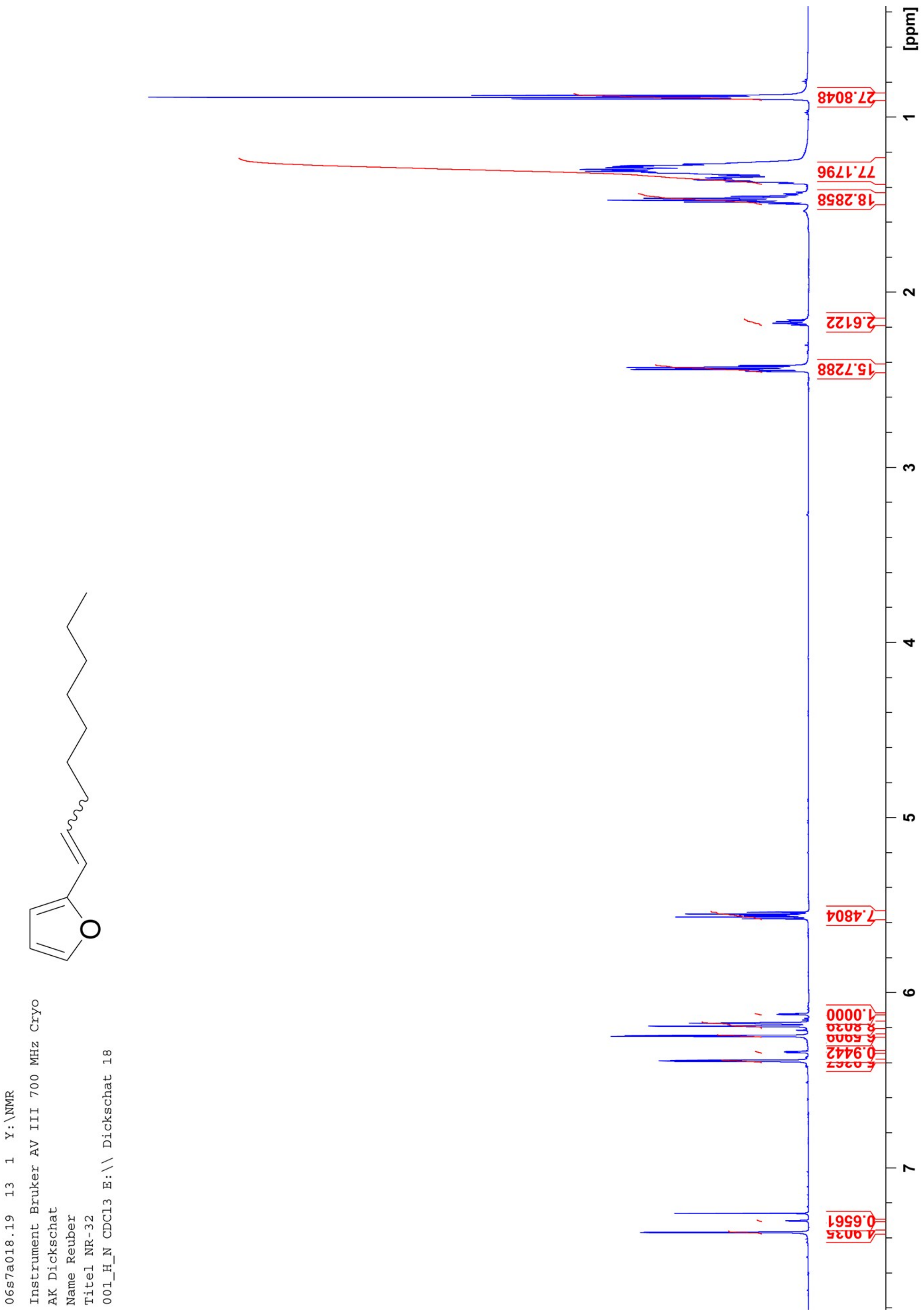


Figure S19. ^{1}H-NMR spectrum (700 MHz, $CDCl_3$) of **45**.

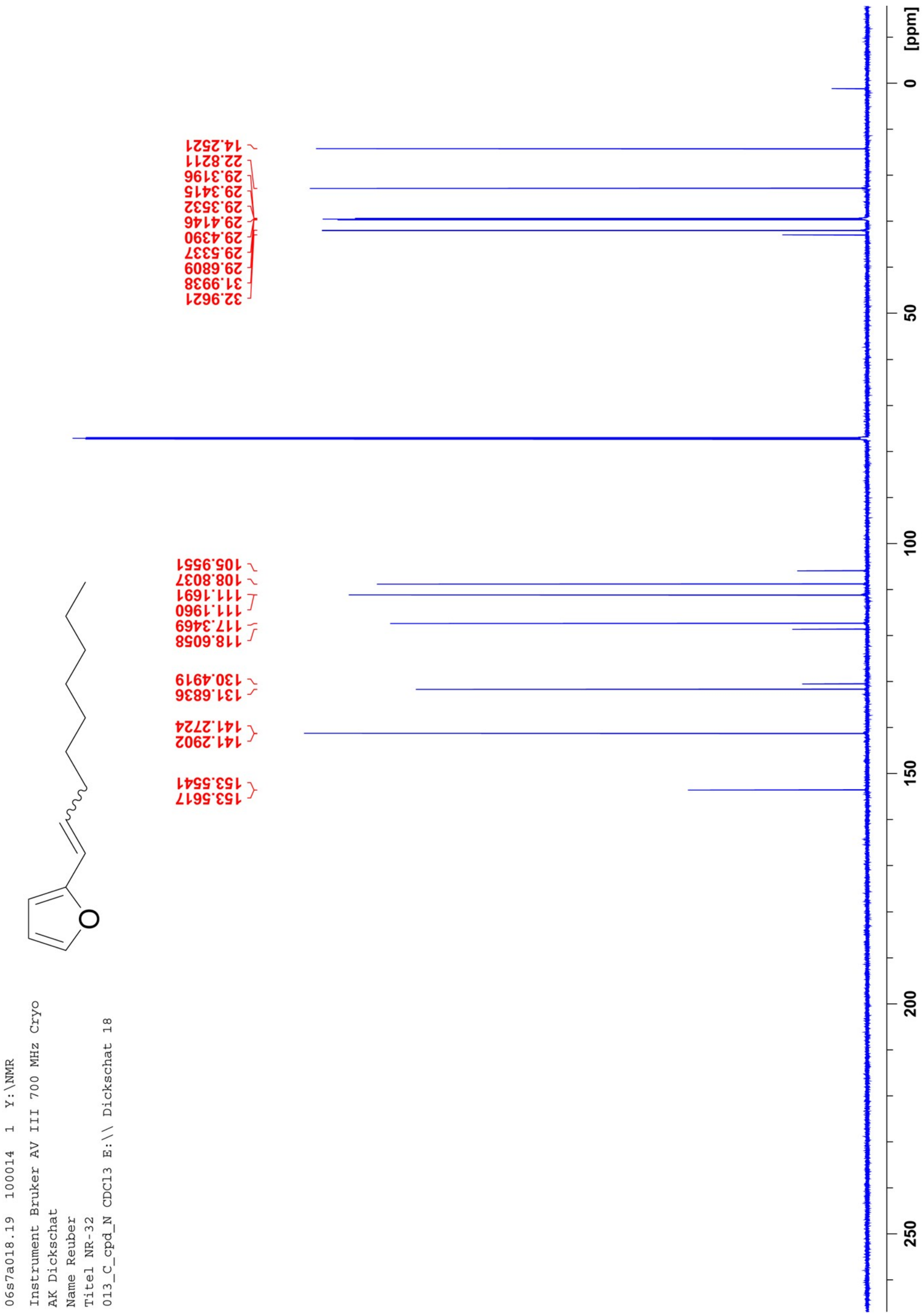


Figure S20. ^{13}C-NMR spectrum (175 MHz, $CDCl_3$) of **45**.

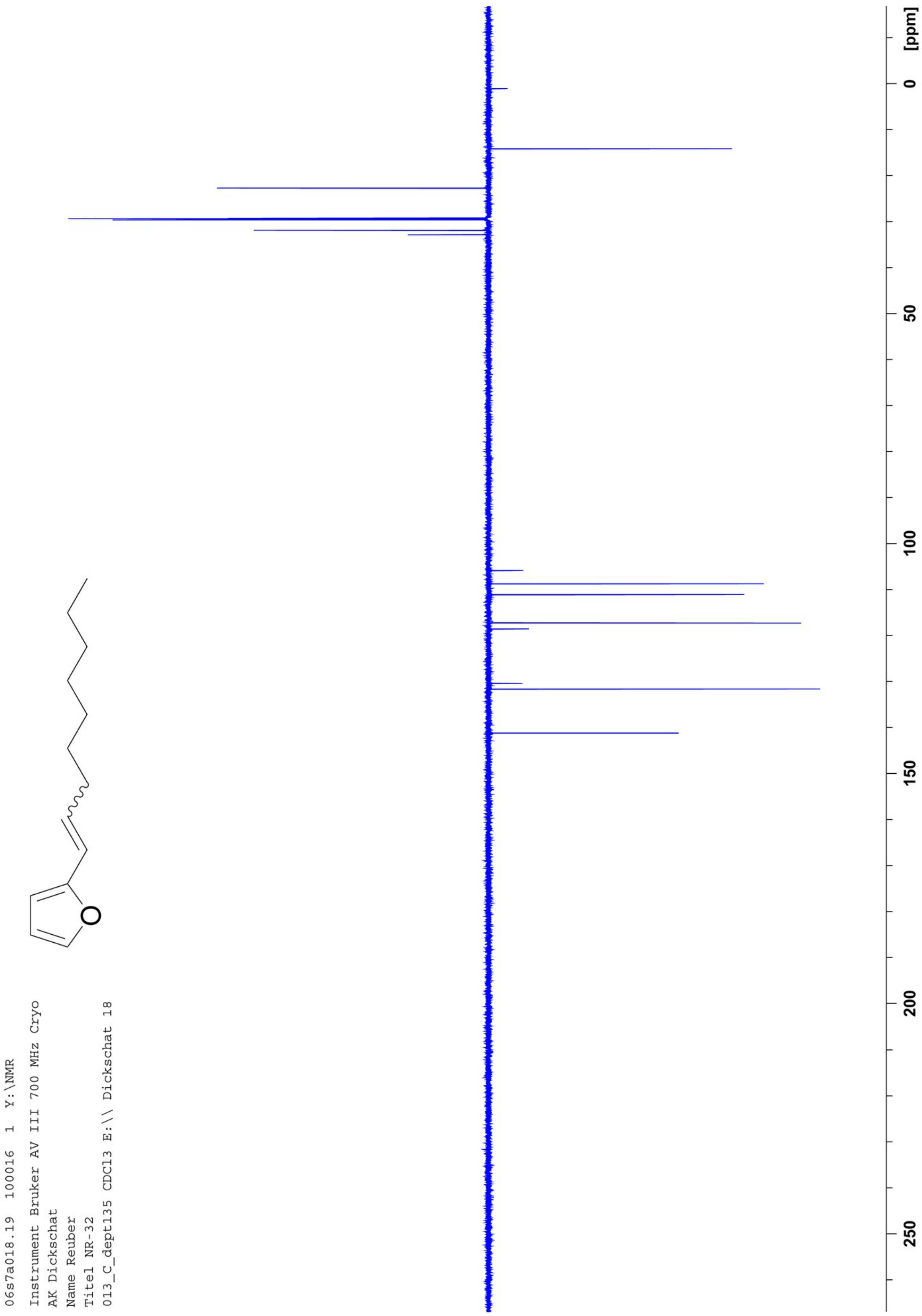


Figure S21. ^{13}C-DEPT spectrum (175 MHz, $CDCl_3$) of **45**.

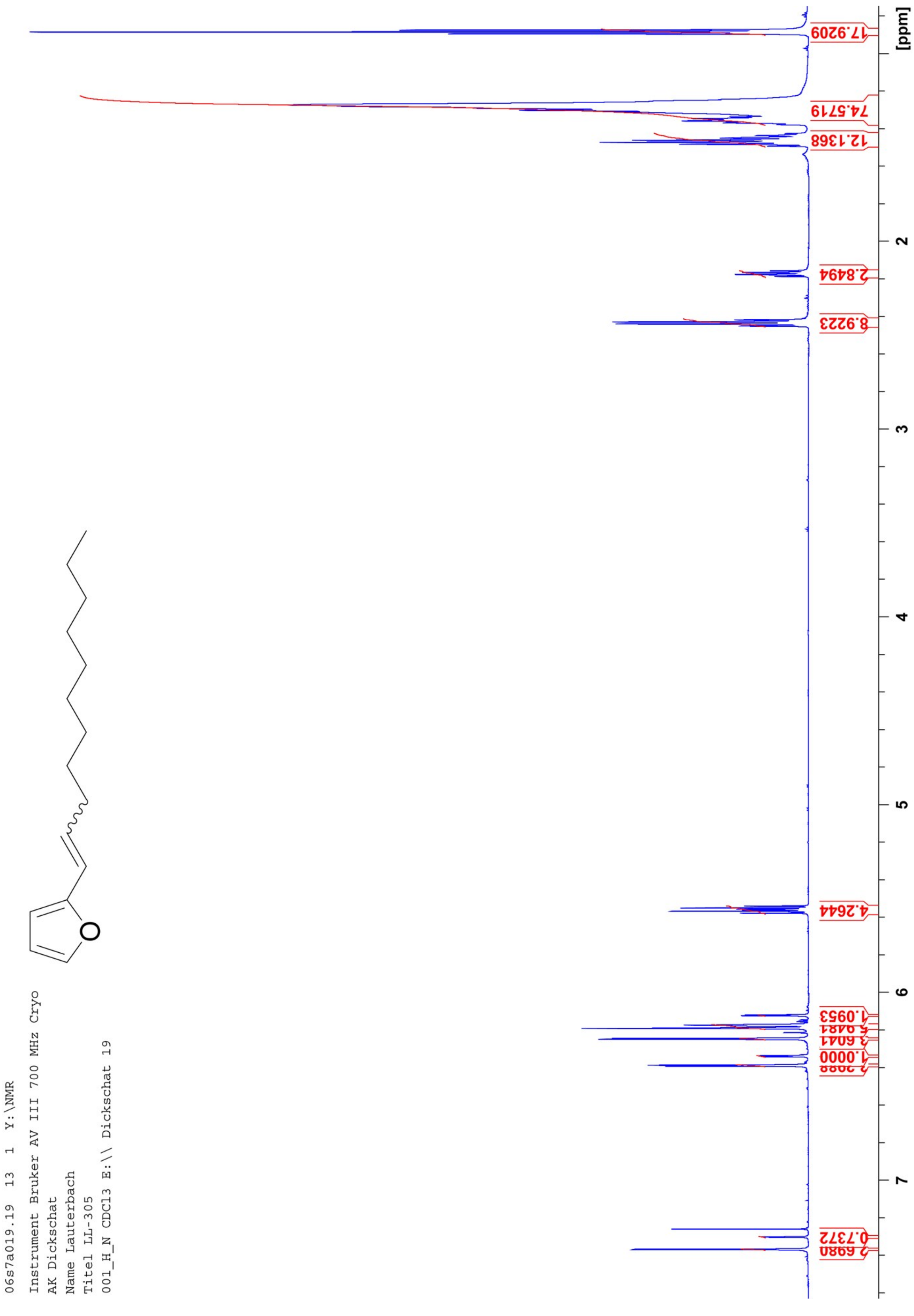


Figure S22. ^{1}H-NMR spectrum (700 MHz, $CDCl_3$) of **46**.

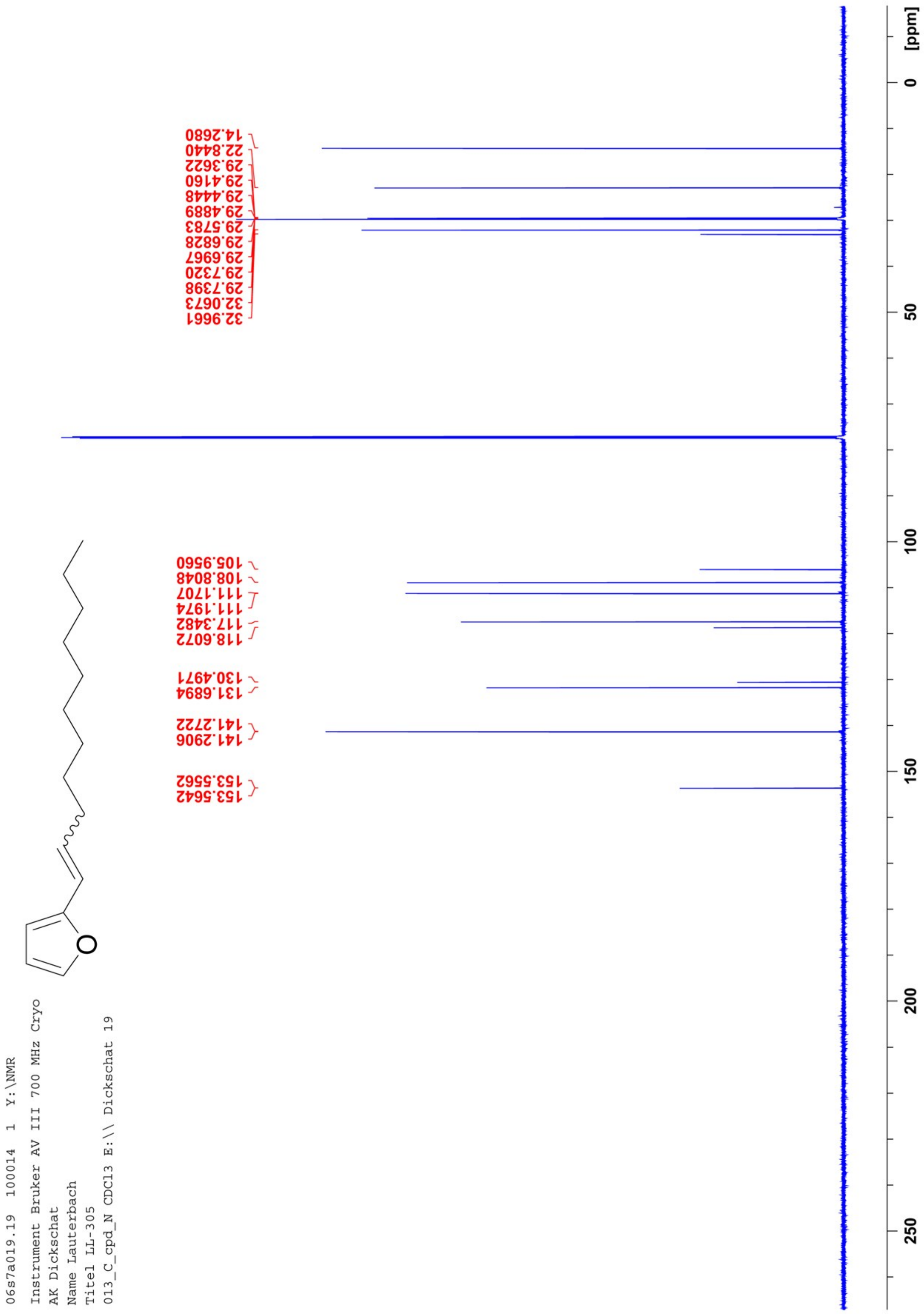


Figure S23. ^{13}C-NMR spectrum (175 MHz, $CDCl_3$) of **46**.

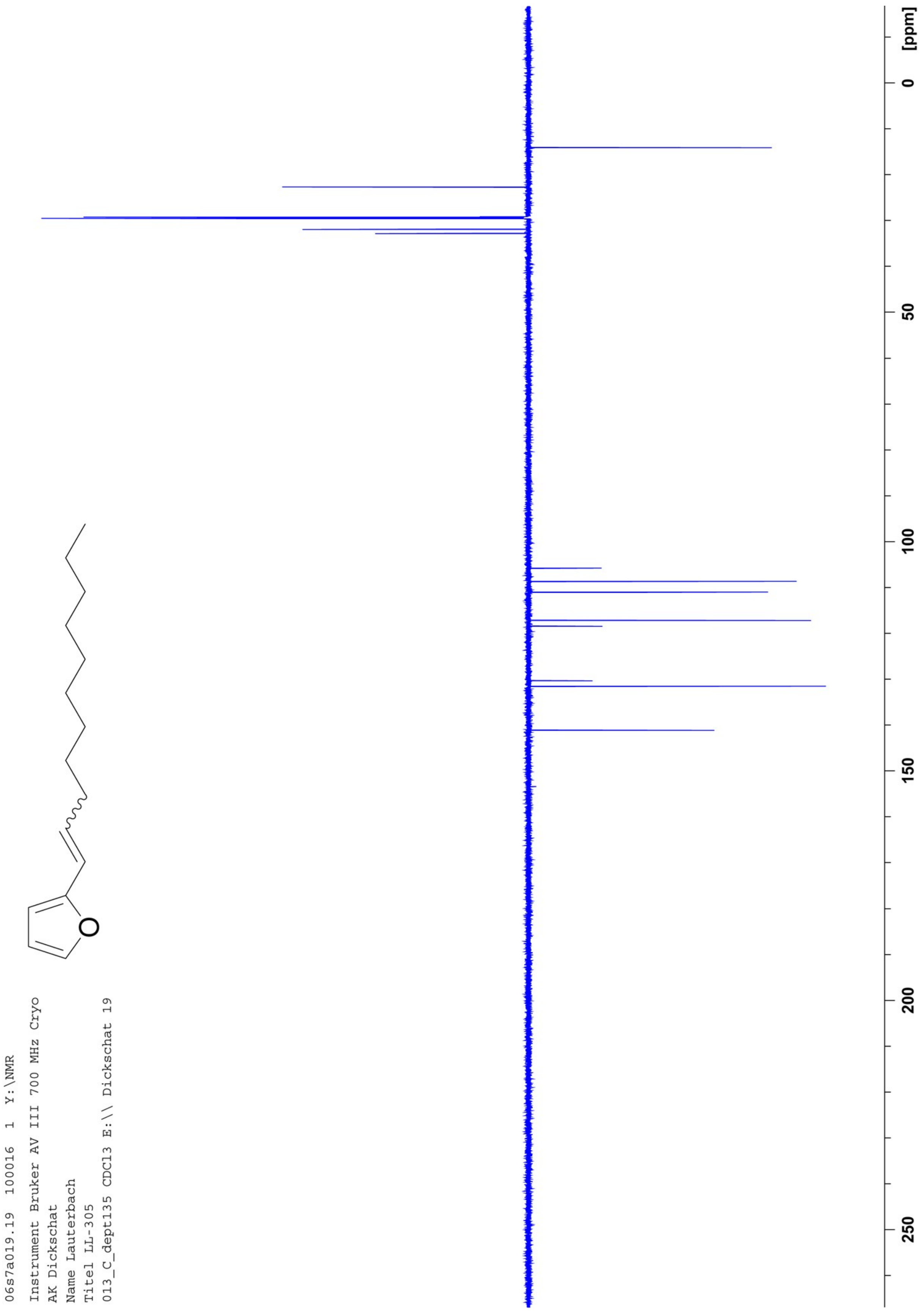


Figure S24. ^{13}C-DEPT spectrum (175 MHz, CDCl$_3$) of **46**.

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