

Supporting Information

for

C–C Bond Fragmentation by Grob/Eschenmoser reactions, an Enabling Methodology for Dendrimer Synthesis

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SI-1. Experimental Procedures

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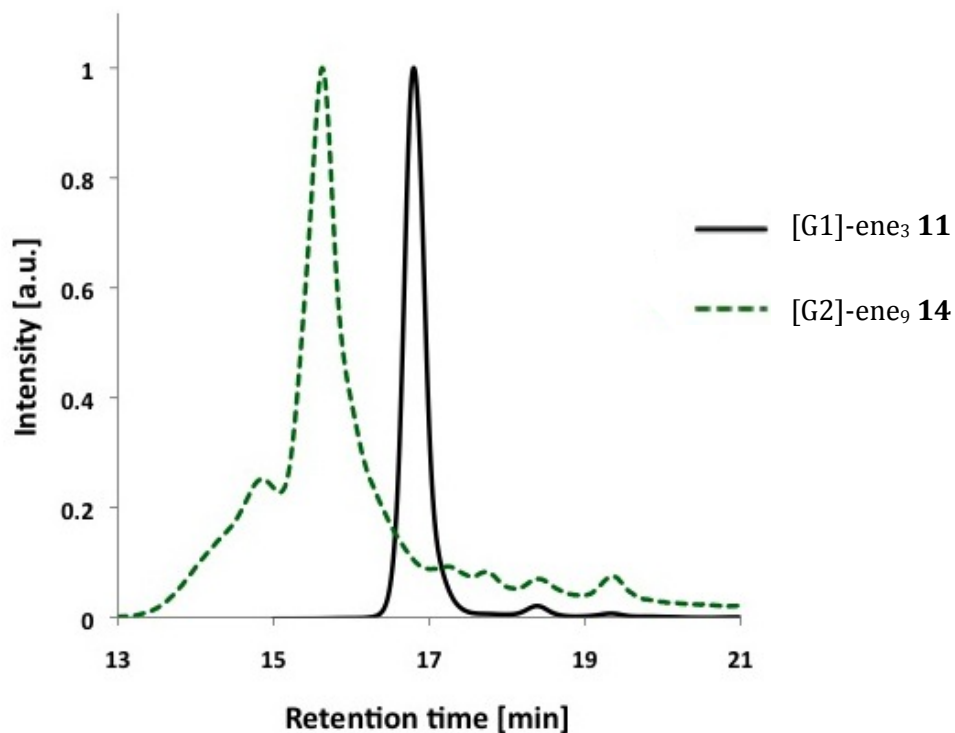
I. General Procedures

Proton (¹H) and carbon (¹³C) NMR spectra were recorded using a Bruker DPX300 operating at 300 MHz for proton and 75 MHz for carbon nuclei, a Bruker DRX400 (400 MHz and 100 MHz), or a Varian DRX 500 (500 MHz and 125 MHz). Infrared spectra (ν_{max}) were recorded on a Perkin-Elmer RXI FTIR Spectrometer. Low resolution mass spectrometry (ESI) was performed on a Micromass Platform QMS spectrometer. High resolution mass spectra (HRMS) were recorded on a Bruker BioApex 47e FTMS fitted with an Analytical electrospray source using NaI for accurate mass calibration. Melting points were measured on a Stuart Scientific Melting Point Apparatus in an open capillary. High-performance liquid chromatography (HPLC) analysis was performed using a Perkin-Elmer LC200 equipped with a Daicel AD-H column. Gel permeation chromatography (GPC) of solutions of the samples in chloroform was performed on a Tosoh EcosHLC-8320 GPC equipped with both refractive index (RI) and ultraviolet (UV) detectors (UV detection, $\lambda = 280$ nm) using Tosoh α 4000 and 2500 columns. Calibration curves were obtained using polystyrene standards. Flash column chromatography was performed on silica gel (Davisil LC60A, 40-63 μm silica media) using compressed air or nitrogen. Thin layer chromatography (TLC) was performed using aluminium-backed plates coated with 0.2 mm silica (Merck, DC-Platten, Kieselgel; 60 F₂₅₄ plates). Eluted plates were visualised using a 254 nm UV lamp and/or by treatment with a suitable stain followed by heating. Starting materials and reagents were purchased from Sigma-Aldrich, Oakwood or Alfa-Aesar and were used as supplied or, in case of some liquids, distilled. Acetonitrile and benzene were distilled from calcium hydride, tetrahydrofuran was distilled from sodium benzophenone ketyl,

dimethylformamide was distilled from magnesium sulphate, and toluene was distilled from sodium. Dimethylsulphoxide was dried over 4 Å molecular sieves.

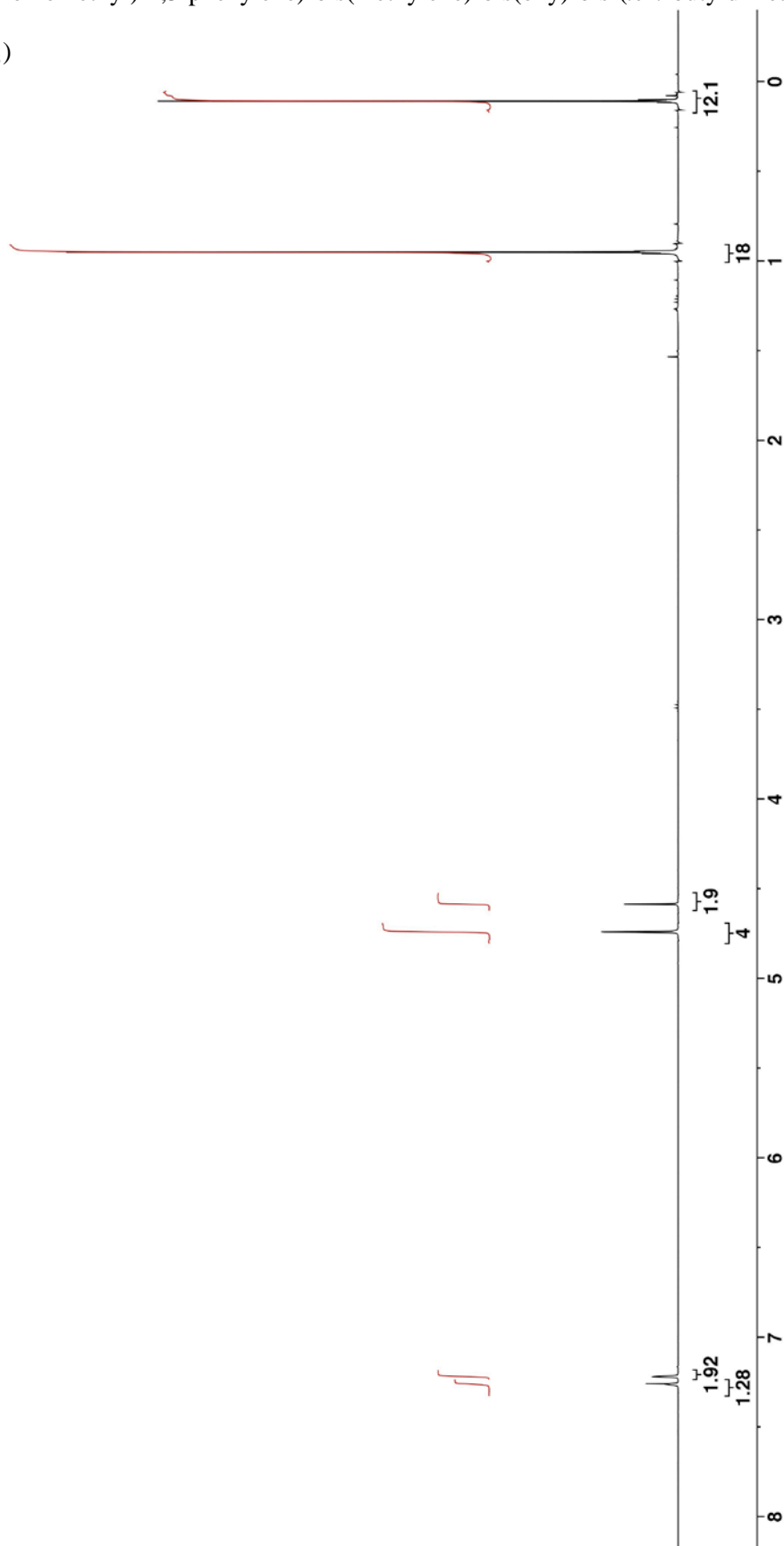
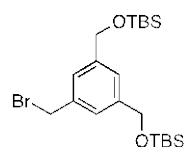
II. Gel Permeation Chromatography (GPC) Traces

Measured in chloroform against polystyrene standards. PDI [G1]-ene₃ **11** = 1.009, PDI [G2]-ene₉ **14** = 1.743.

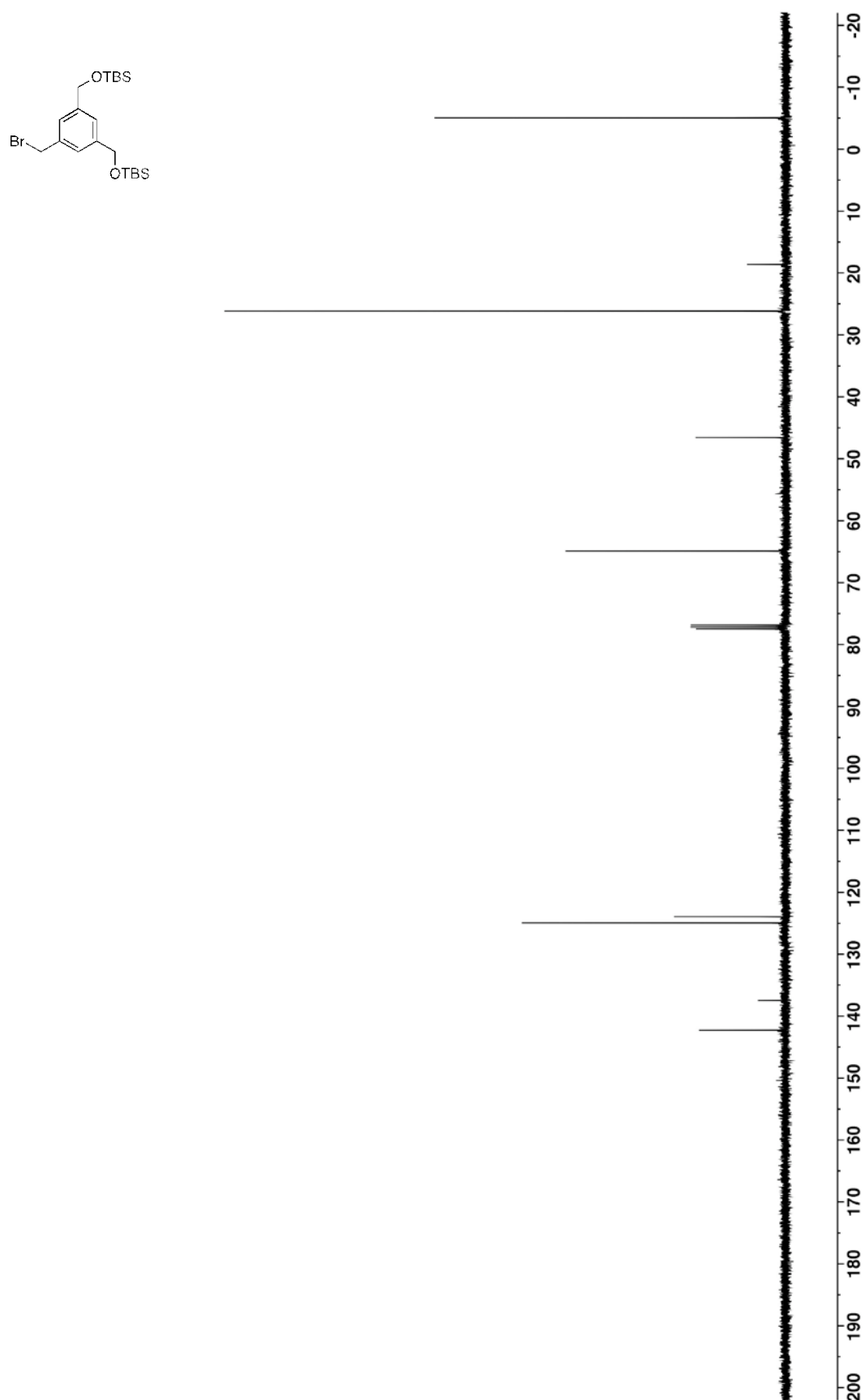


III. ^1H - and ^{13}C -NMR of new compounds

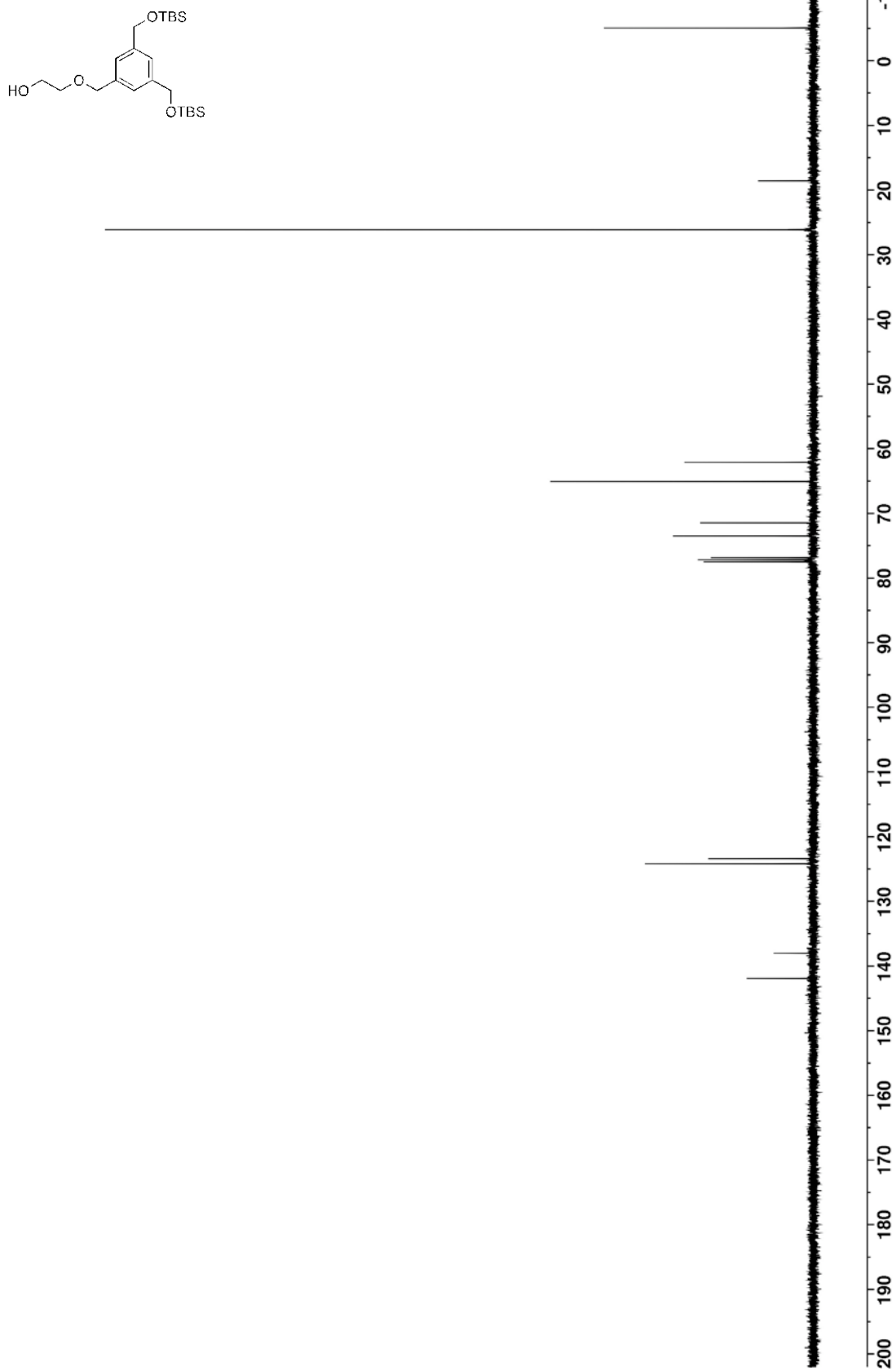
^1H -NMR of (5-(Bromomethyl)-1,3-phenylene) bis(methylene) bis(oxy) bis (*tert*-butyldimethylsilane)
(400 MHz, CDCl_3)



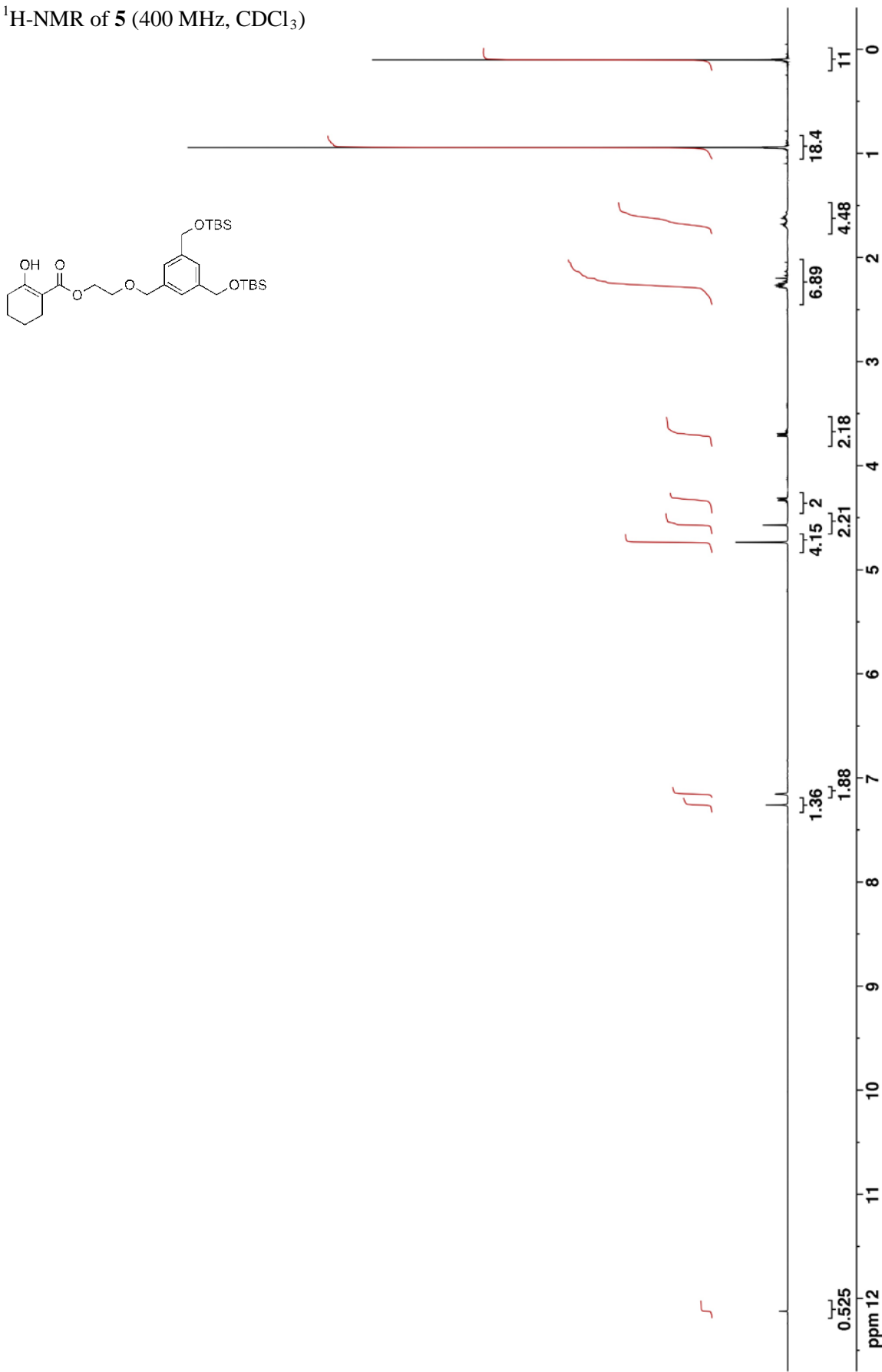
^{13}C -NMR of (5-(Bromomethyl)-1,3-phenylene) bis(methylene) bis(oxy) bis (*tert*-butyldimethylsilane)
(100 MHz, CDCl_3)



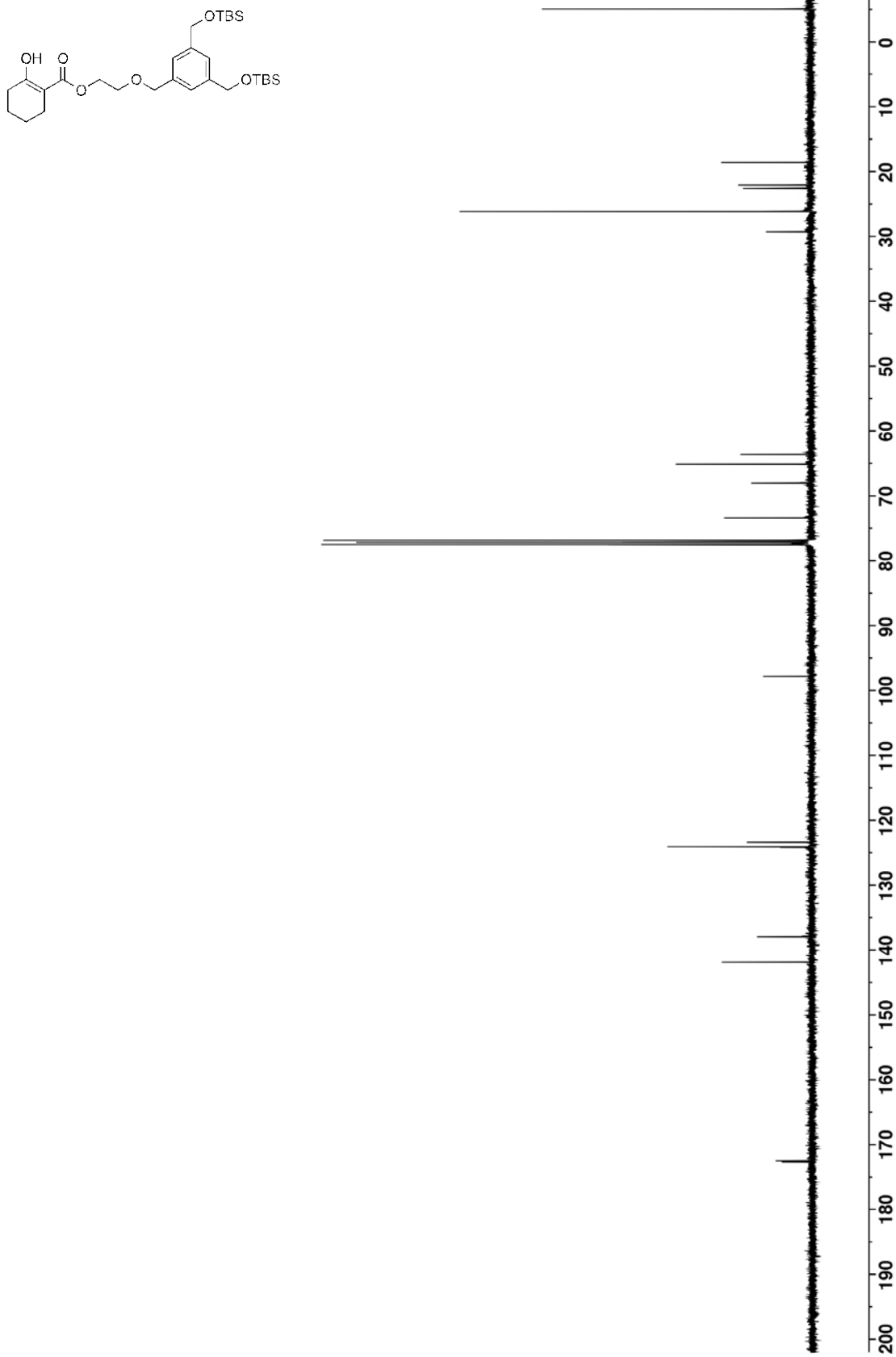
¹³C-NMR of **3** (100 MHz, CDCl₃)



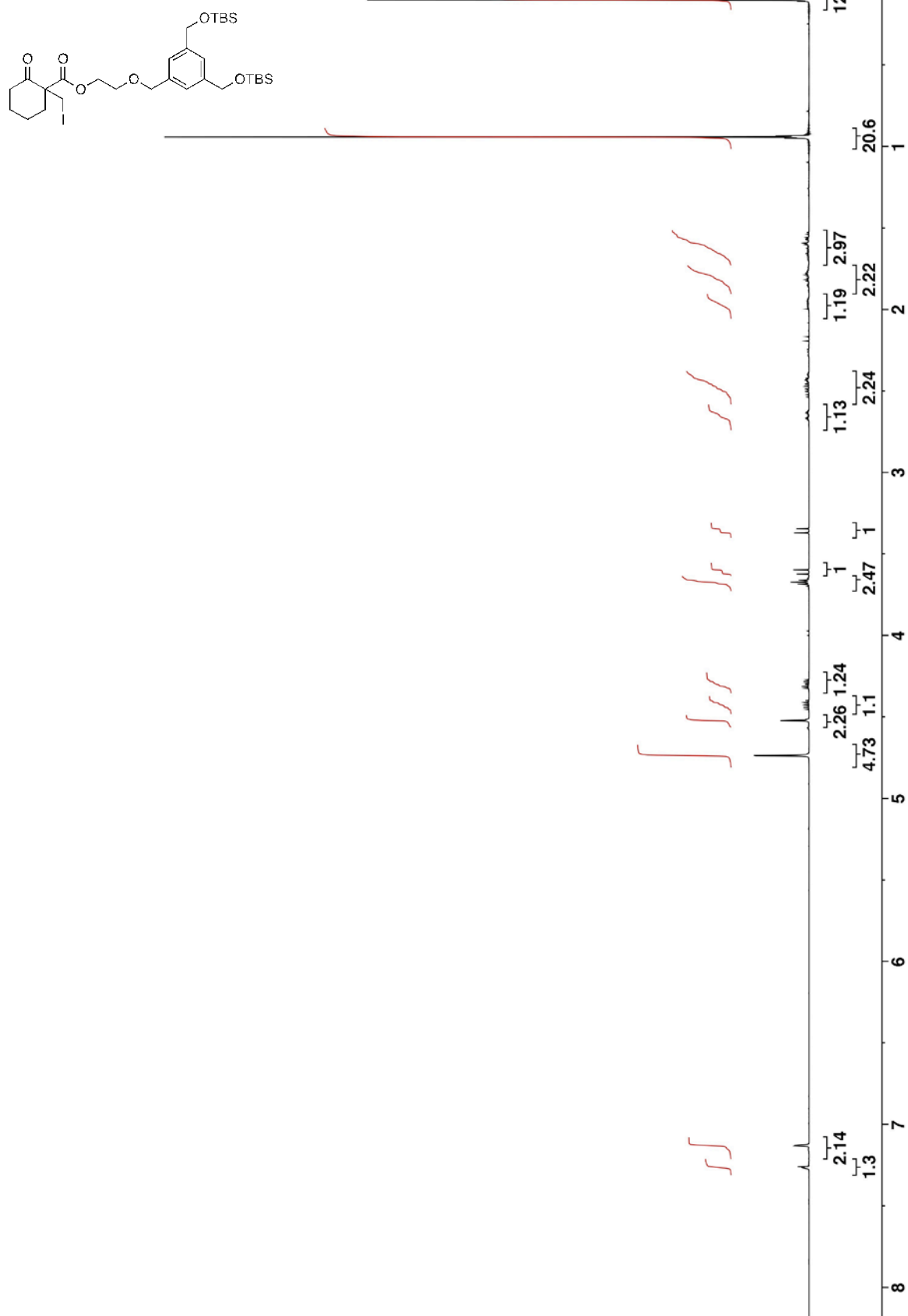
¹H-NMR of **5** (400 MHz, CDCl₃)



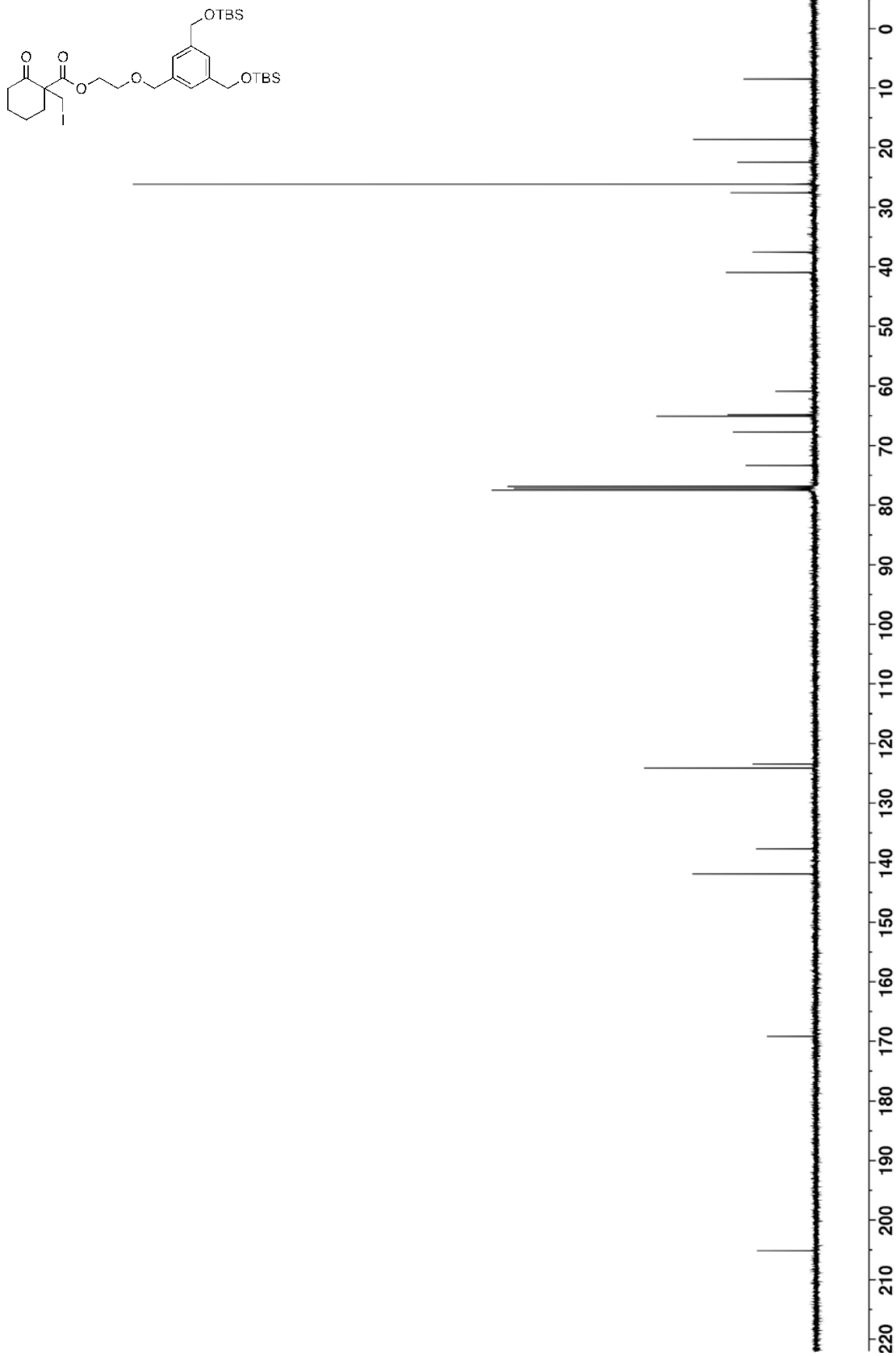
¹³C-NMR of **5** (100 MHz, CDCl₃)



^1H -NMR of **6** (400 MHz, CDCl_3)

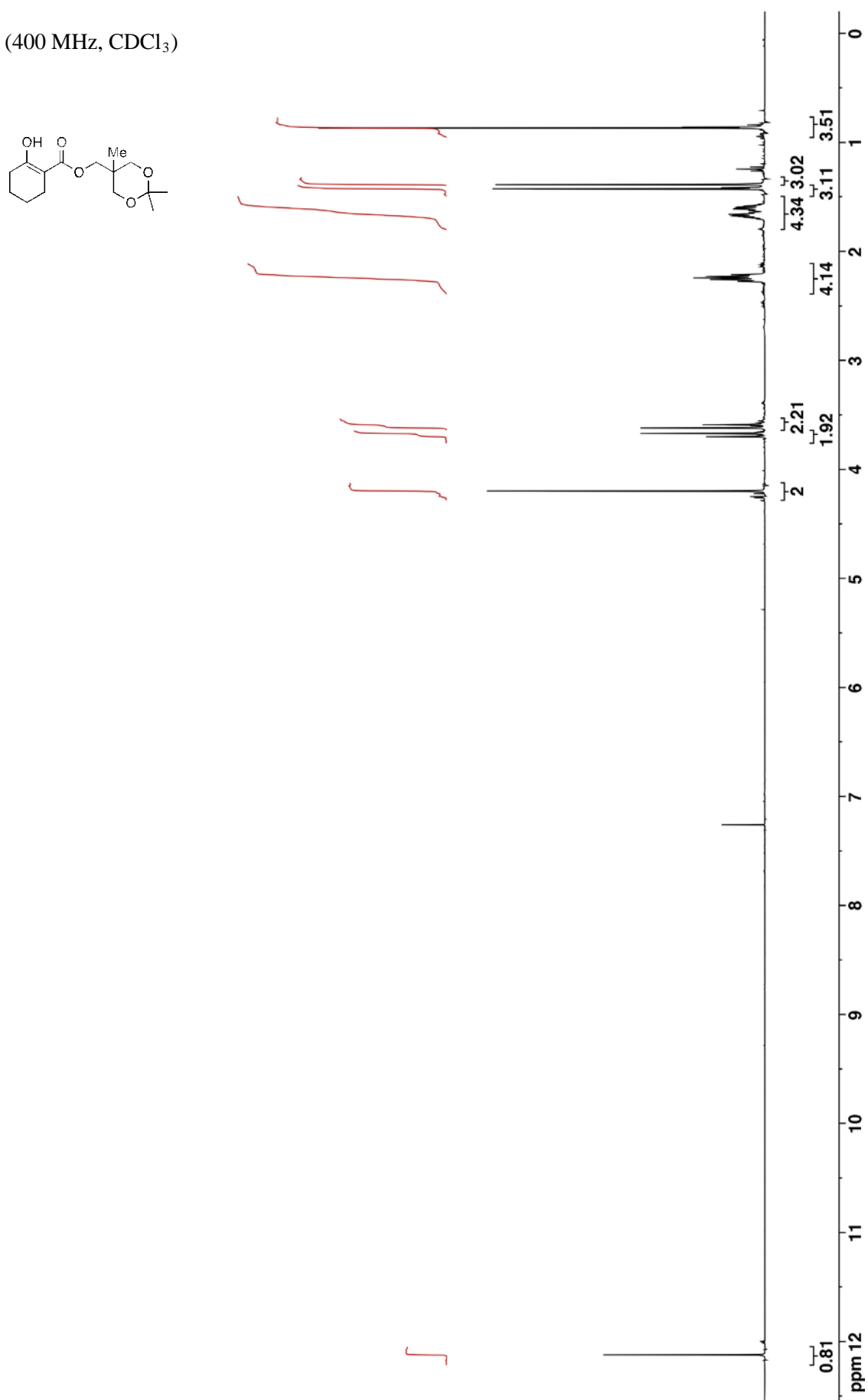


¹³C-NMR of **6** (100 MHz, CDCl₃)



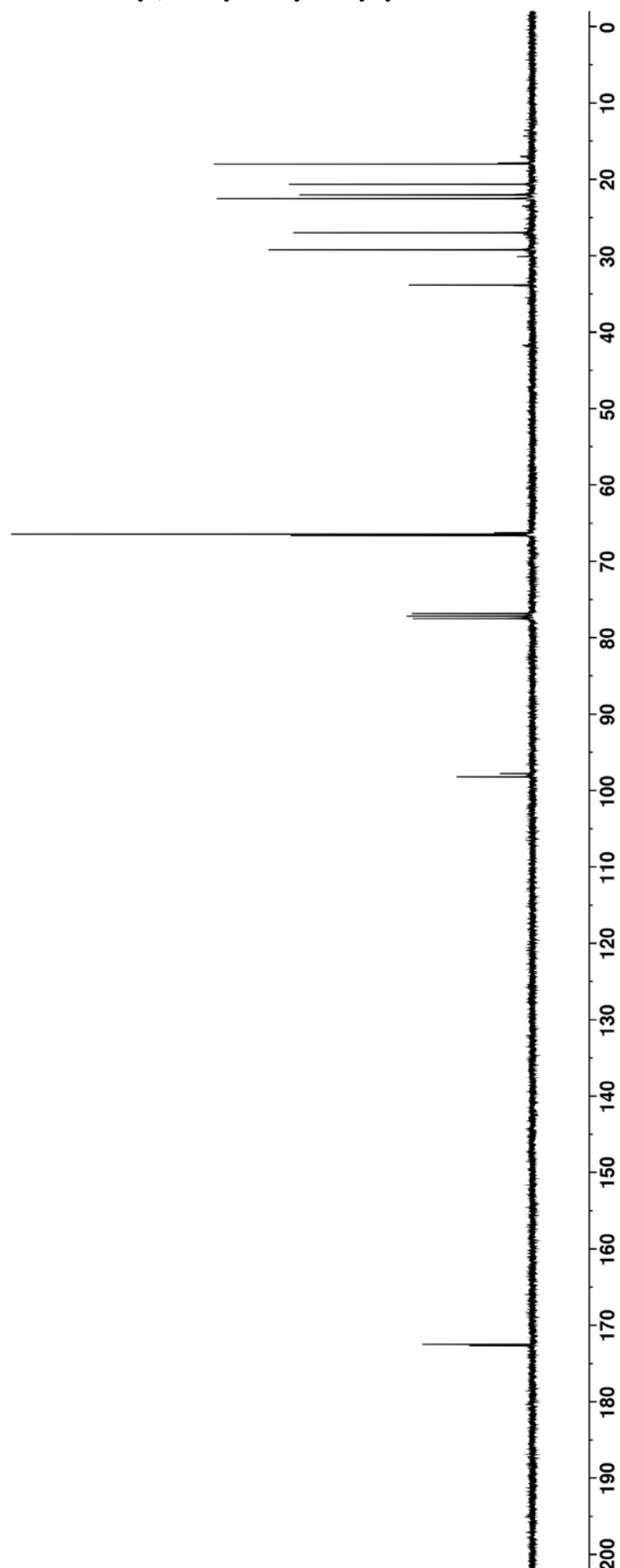
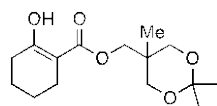
¹H-NMR of (2,2,5-trimethyl-1,3-dioxan-5-yl)methyl 2-hydroxycyclohex-1-ene-1-carboxylate

(400 MHz, CDCl₃)

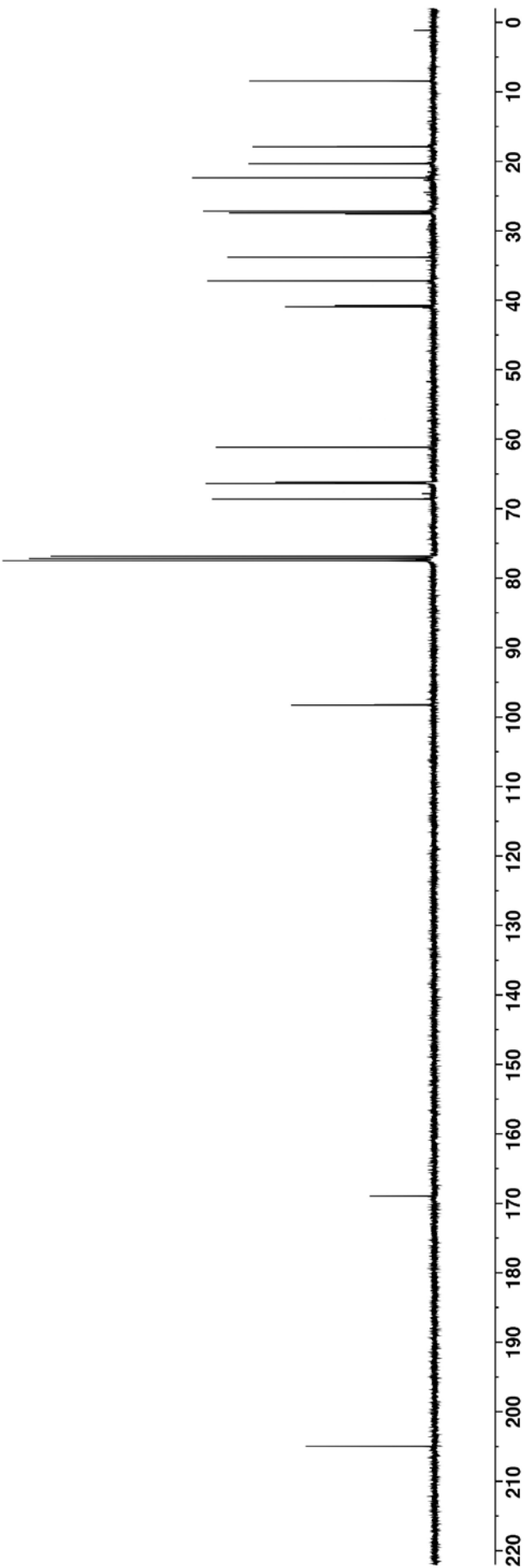
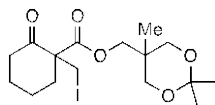


^{13}C -NMR of (2,2,5-trimethyl-1,3-dioxan-5-yl)methyl 2-hydroxycyclohex-1-ene-1-carboxylate

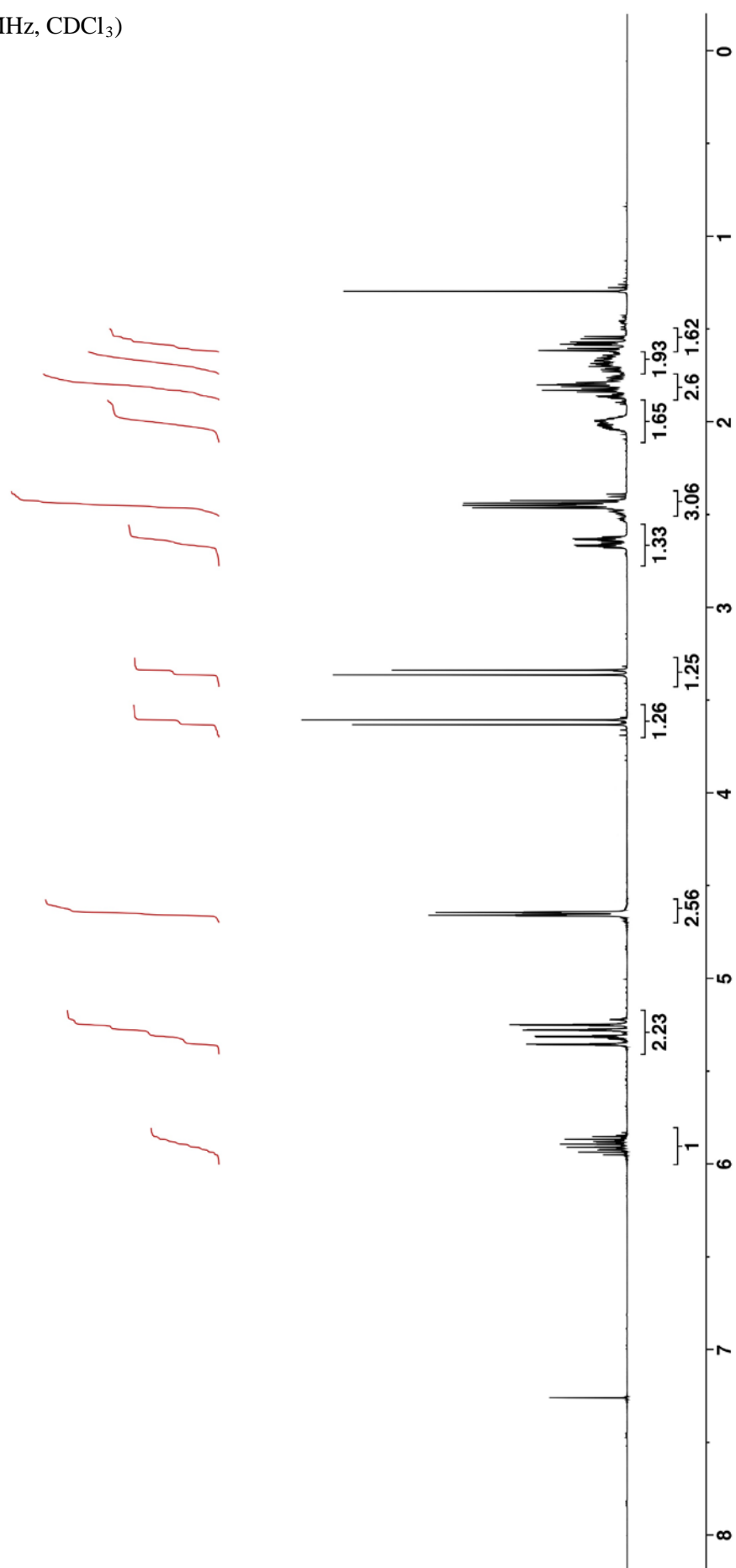
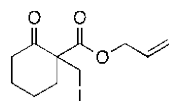
(100 MHz, CDCl_3)



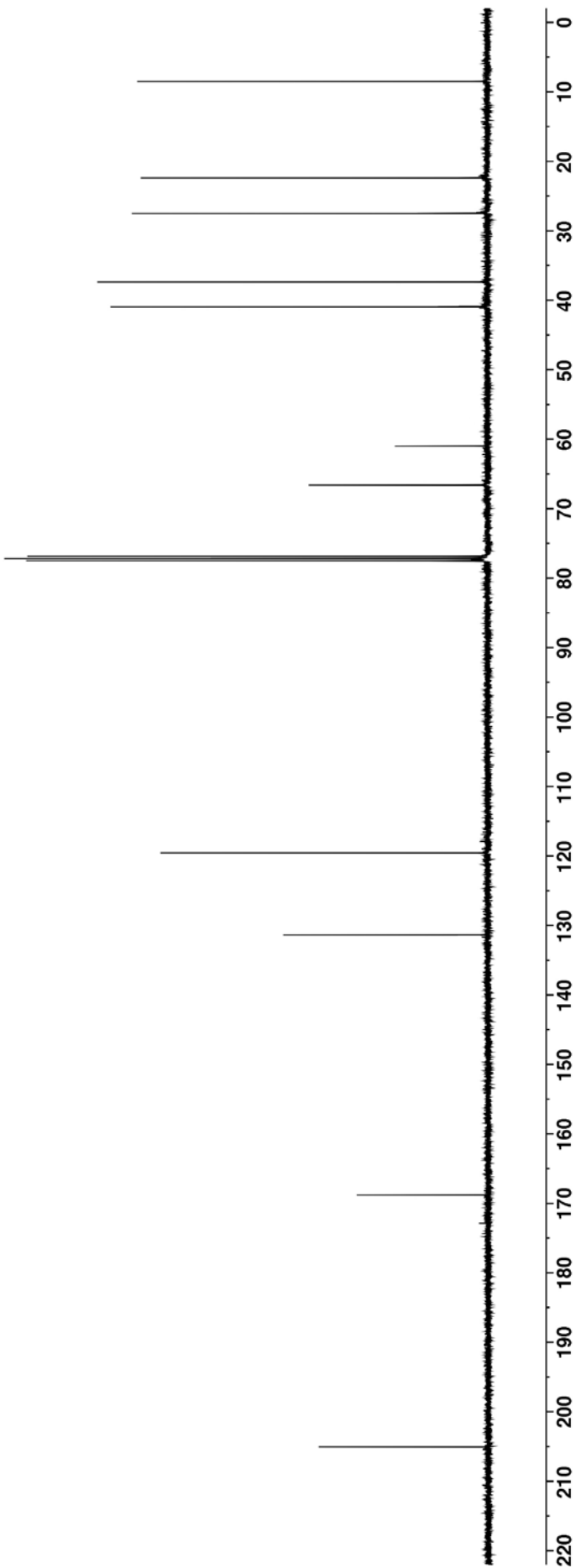
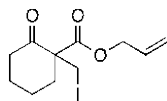
¹³C-NMR of **7** (100 MHz, CDCl₃)



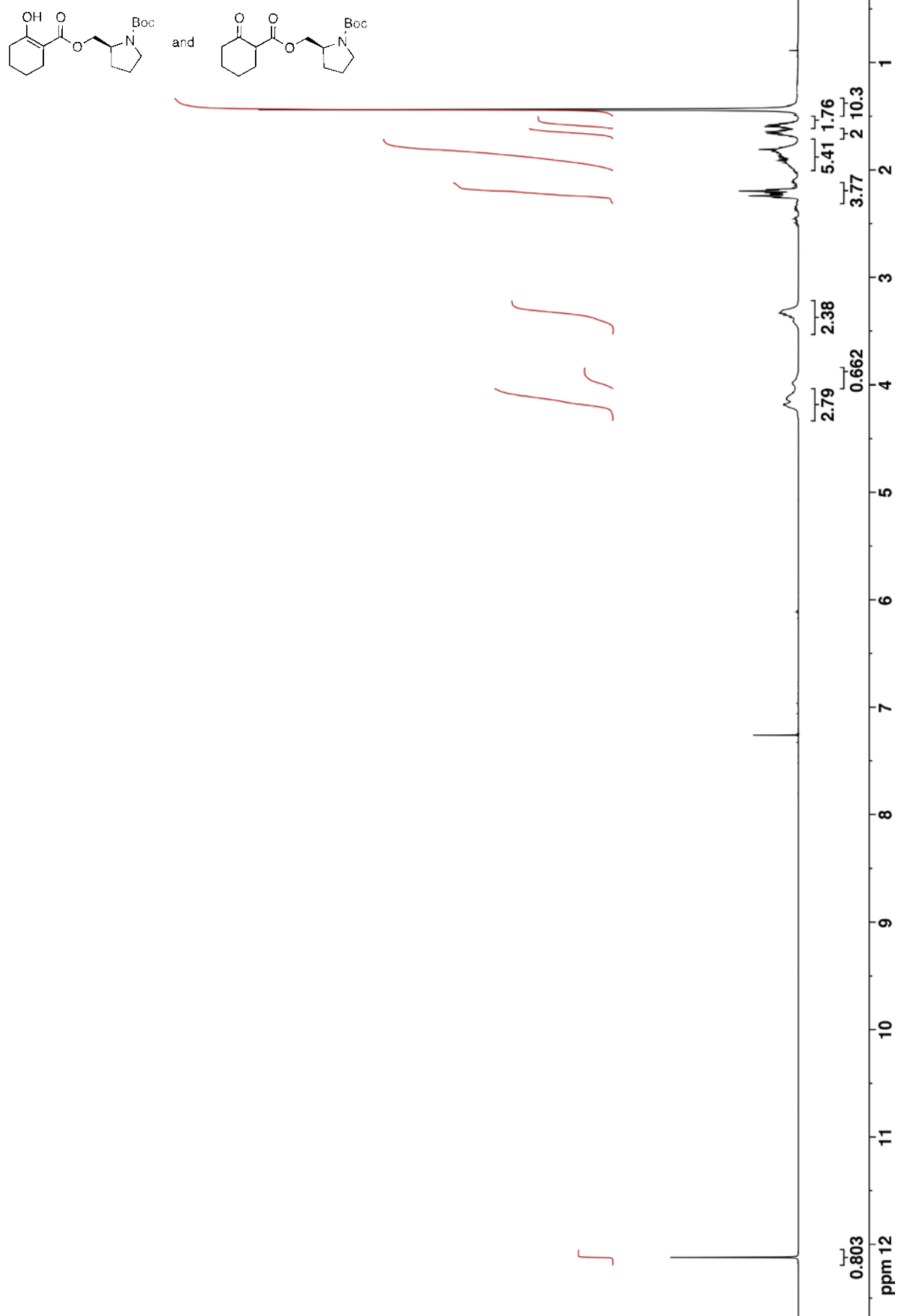
^1H -NMR of **20** (400 MHz, CDCl_3)



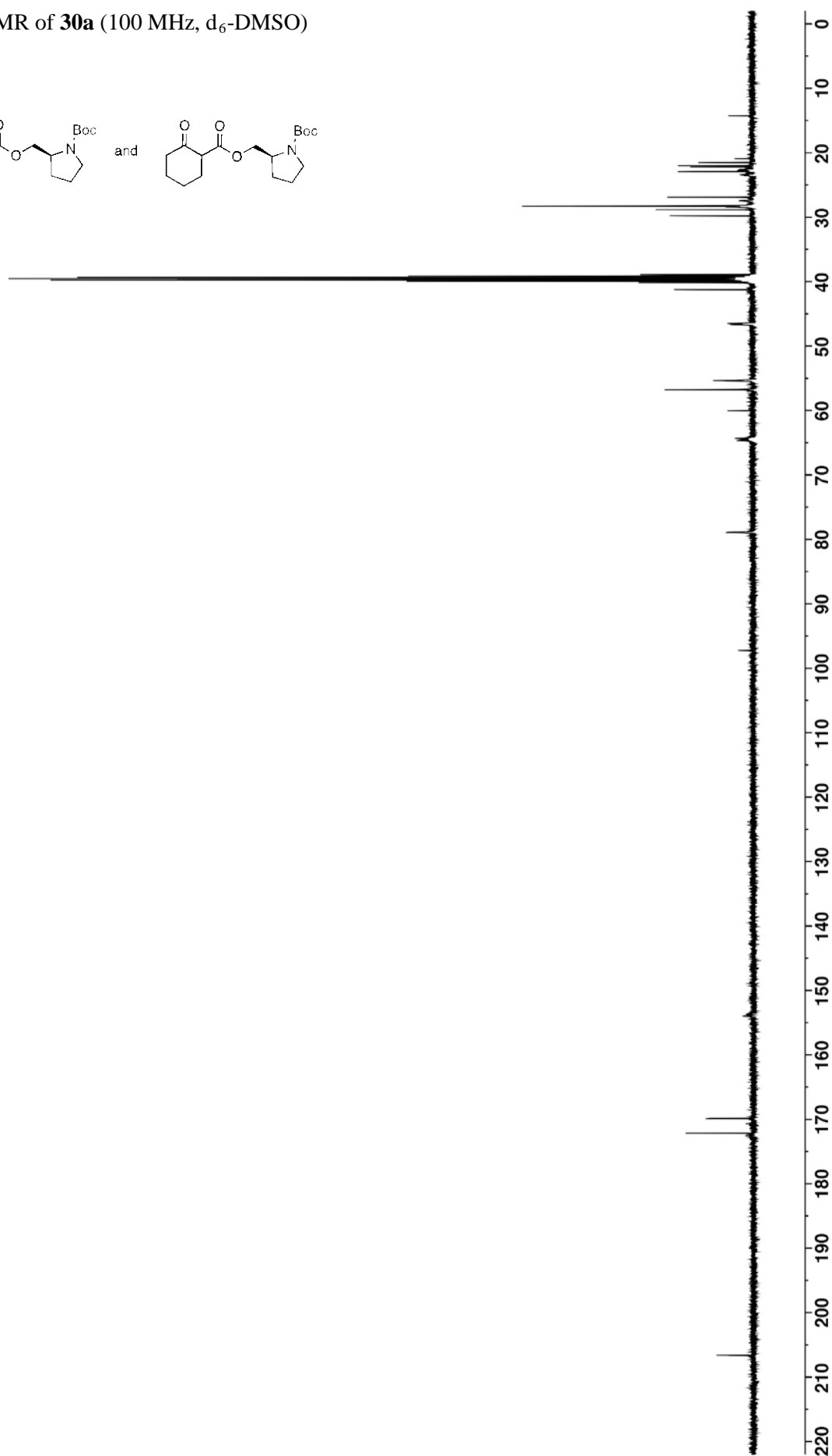
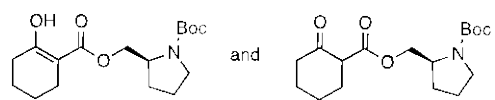
¹³C-NMR of **20** (100 MHz, CDCl₃)



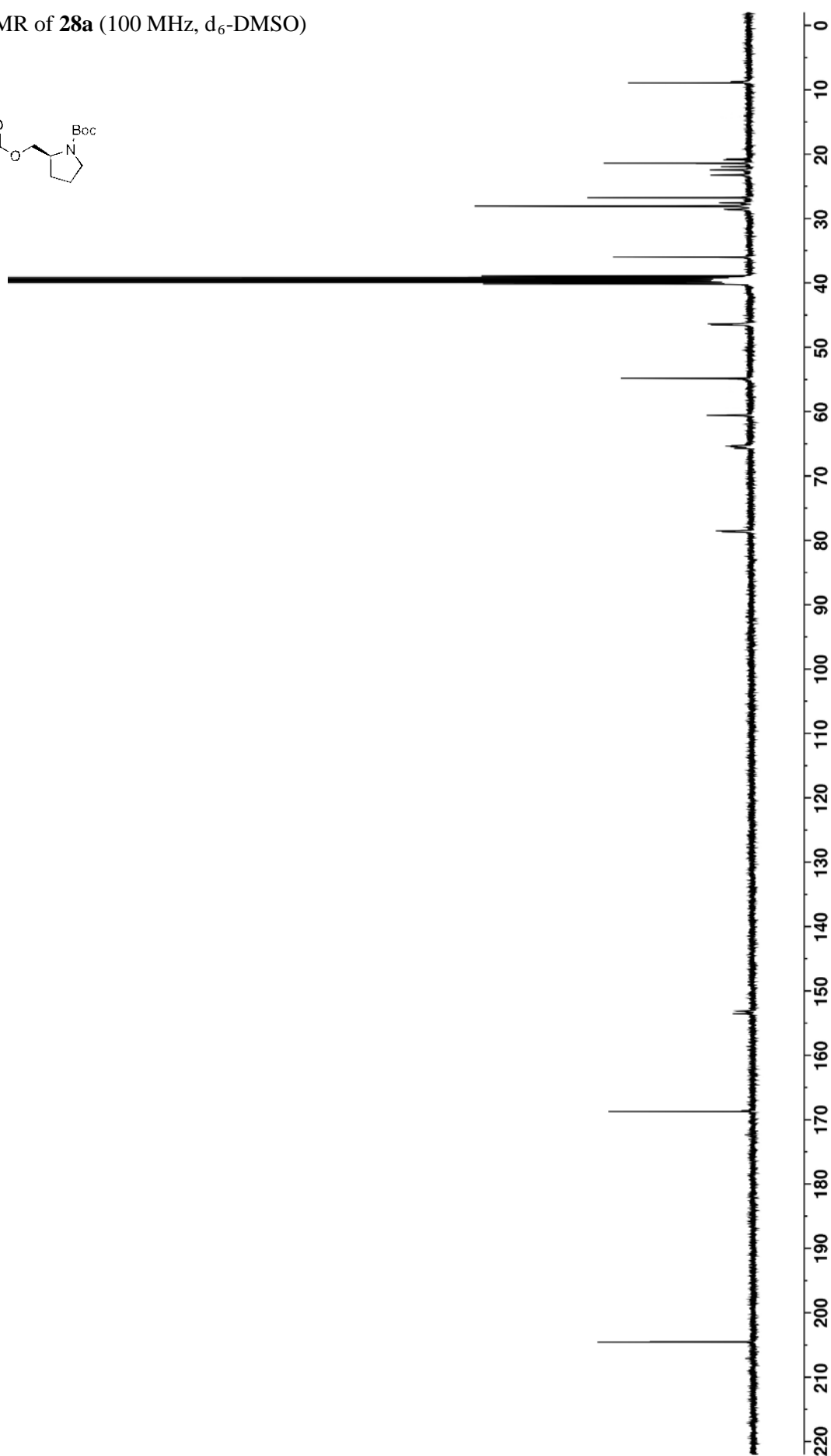
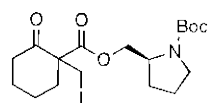
^1H -NMR of **30a** (400 MHz, CDCl_3)



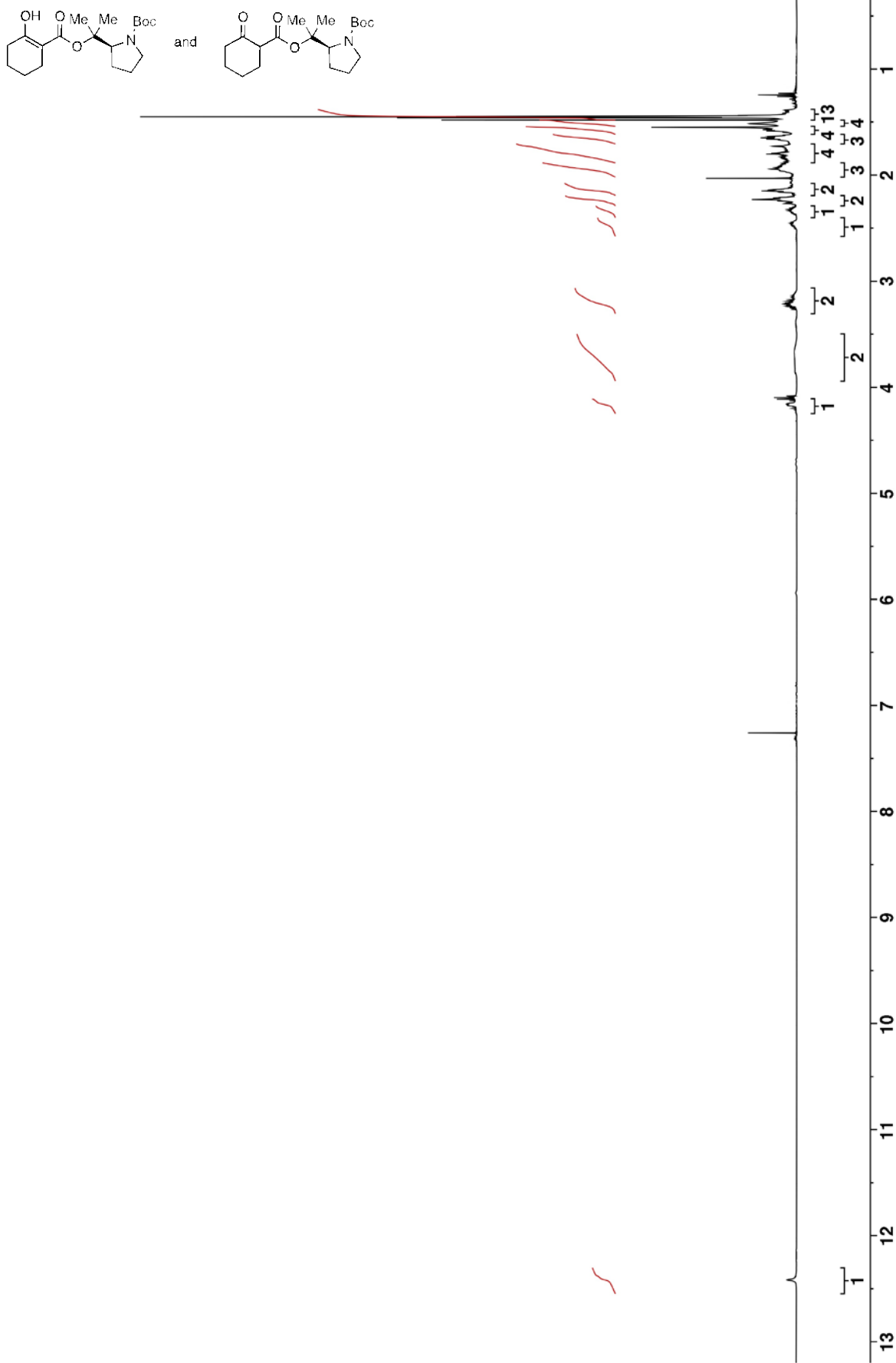
^{13}C -NMR of **30a** (100 MHz, d_6 -DMSO)



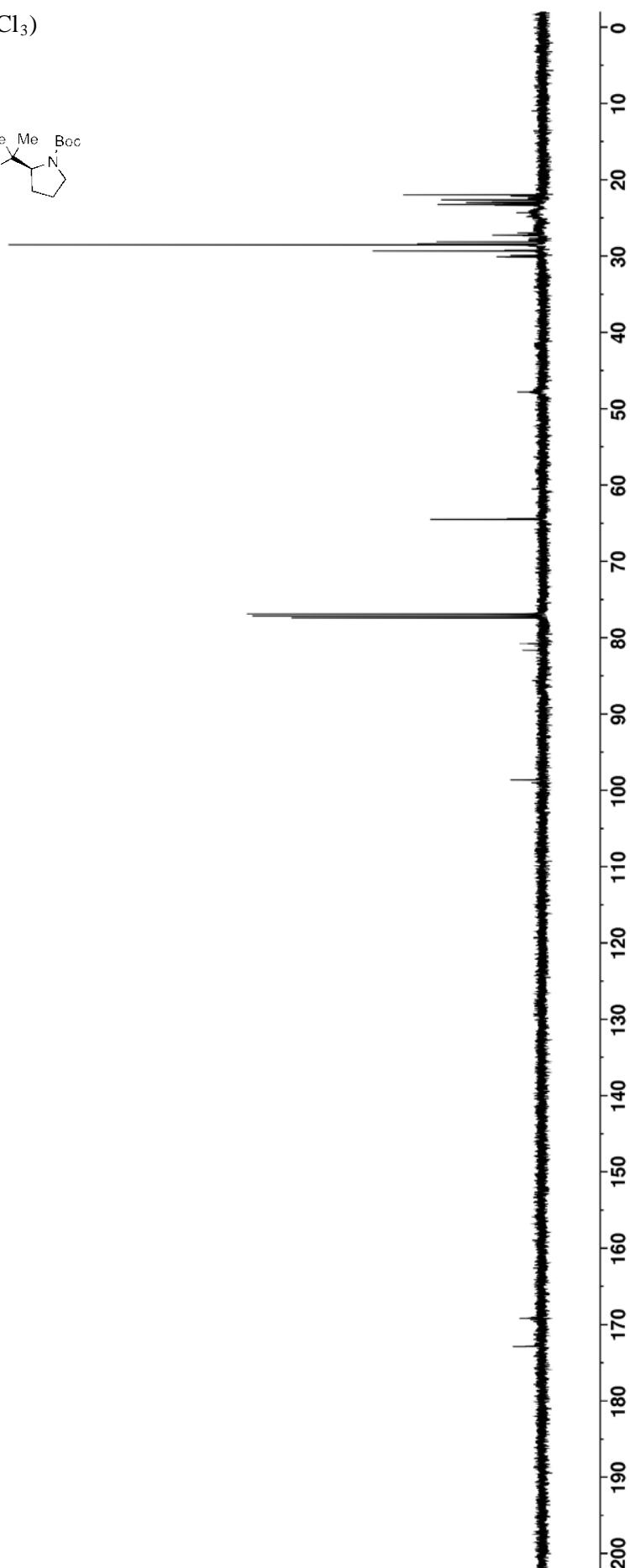
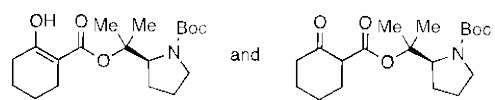
^{13}C -NMR of **28a** (100 MHz, d_6 -DMSO)



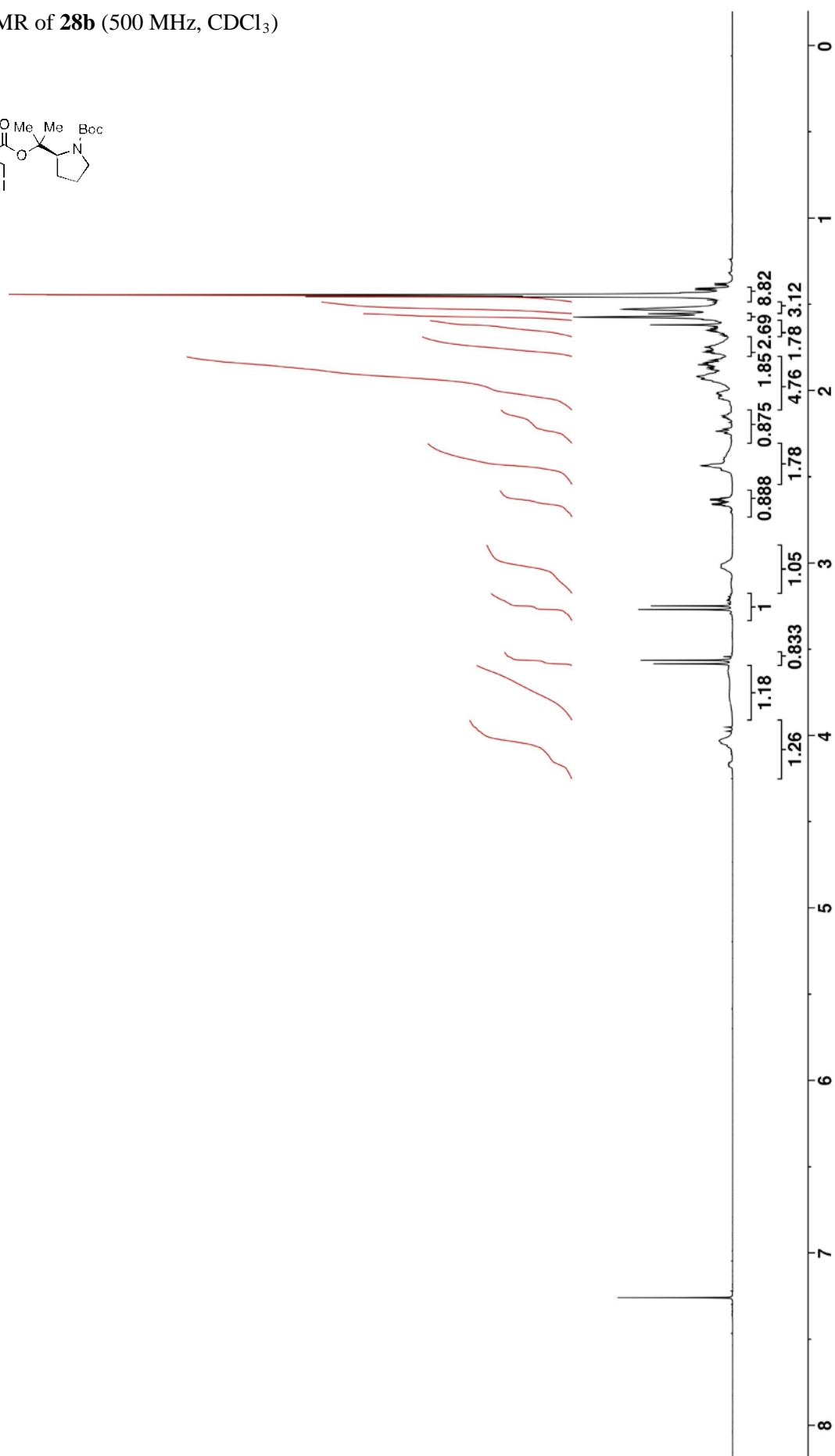
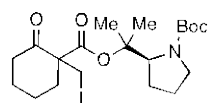
¹H-NMR of **30b** (500 MHz, CDCl₃)



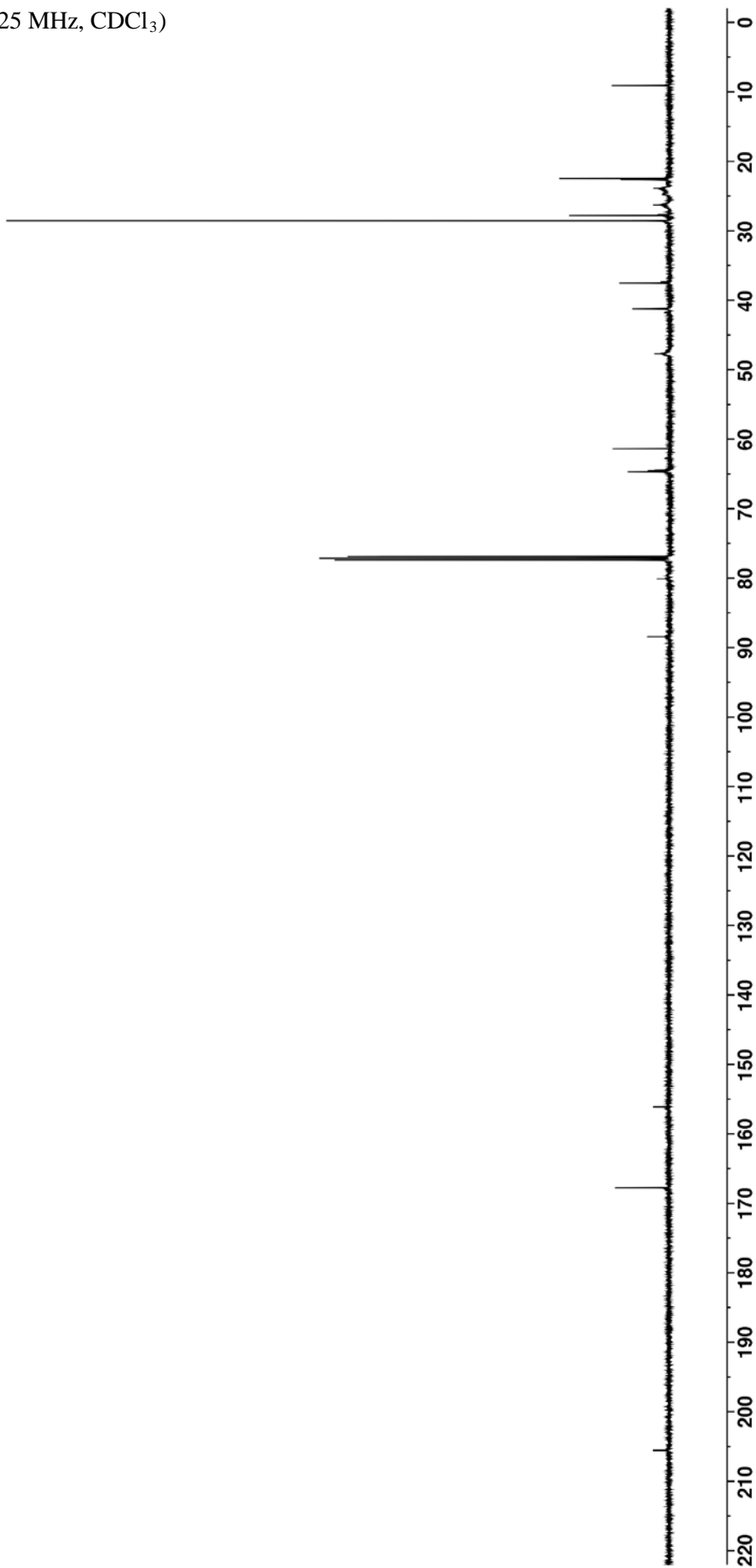
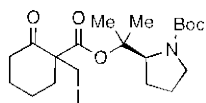
^{13}C -NMR of **30b** (125 MHz, CDCl_3)



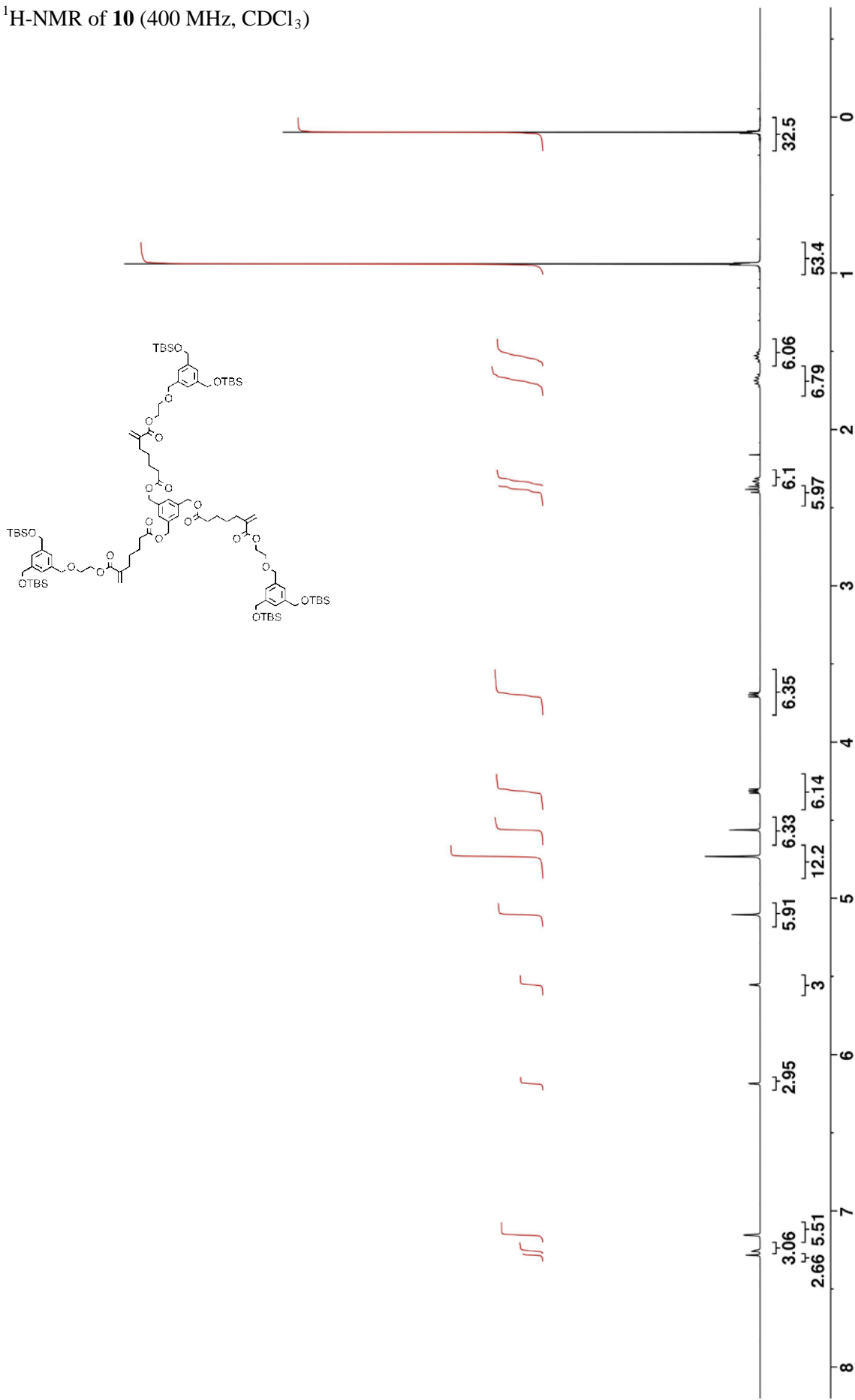
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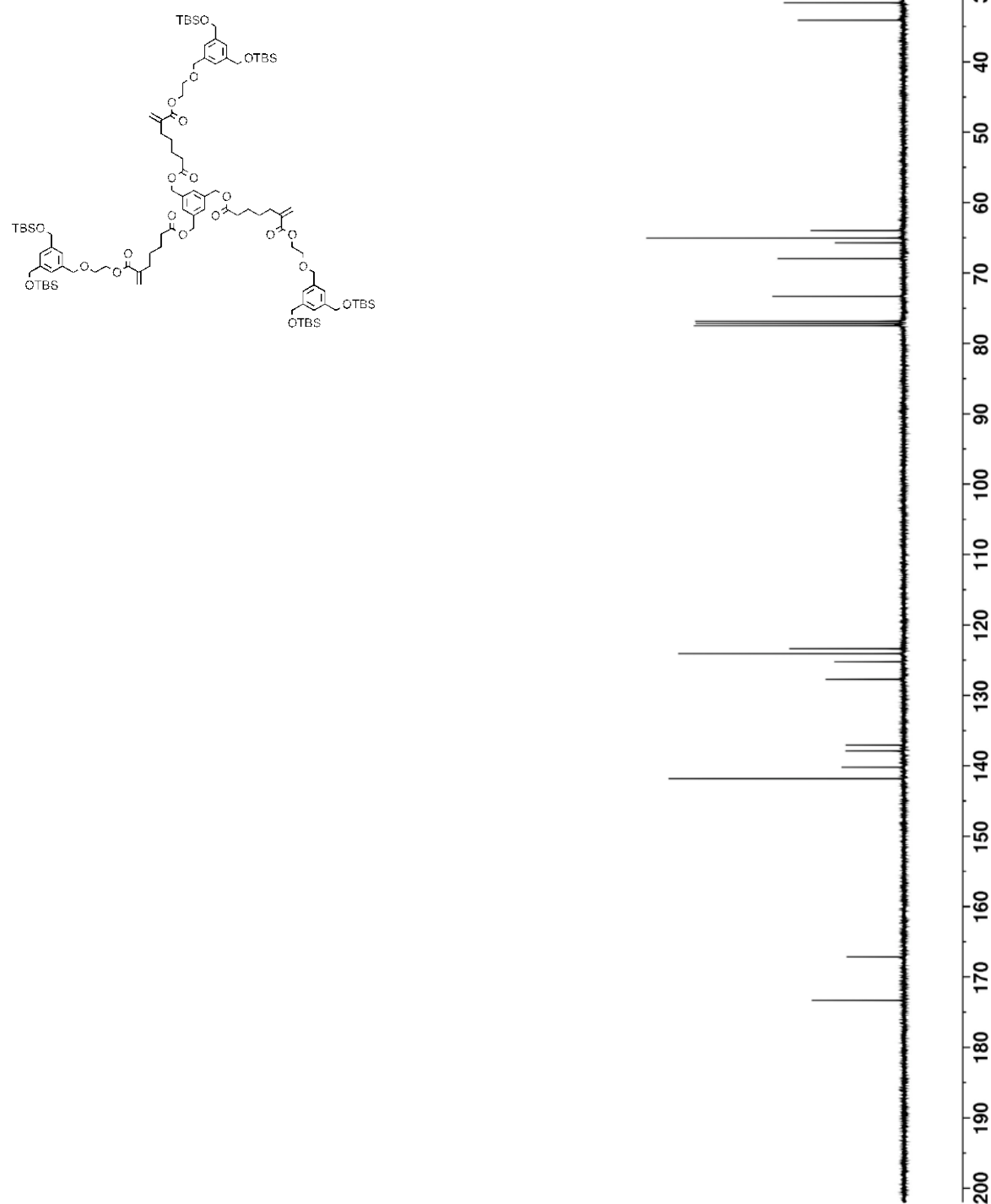
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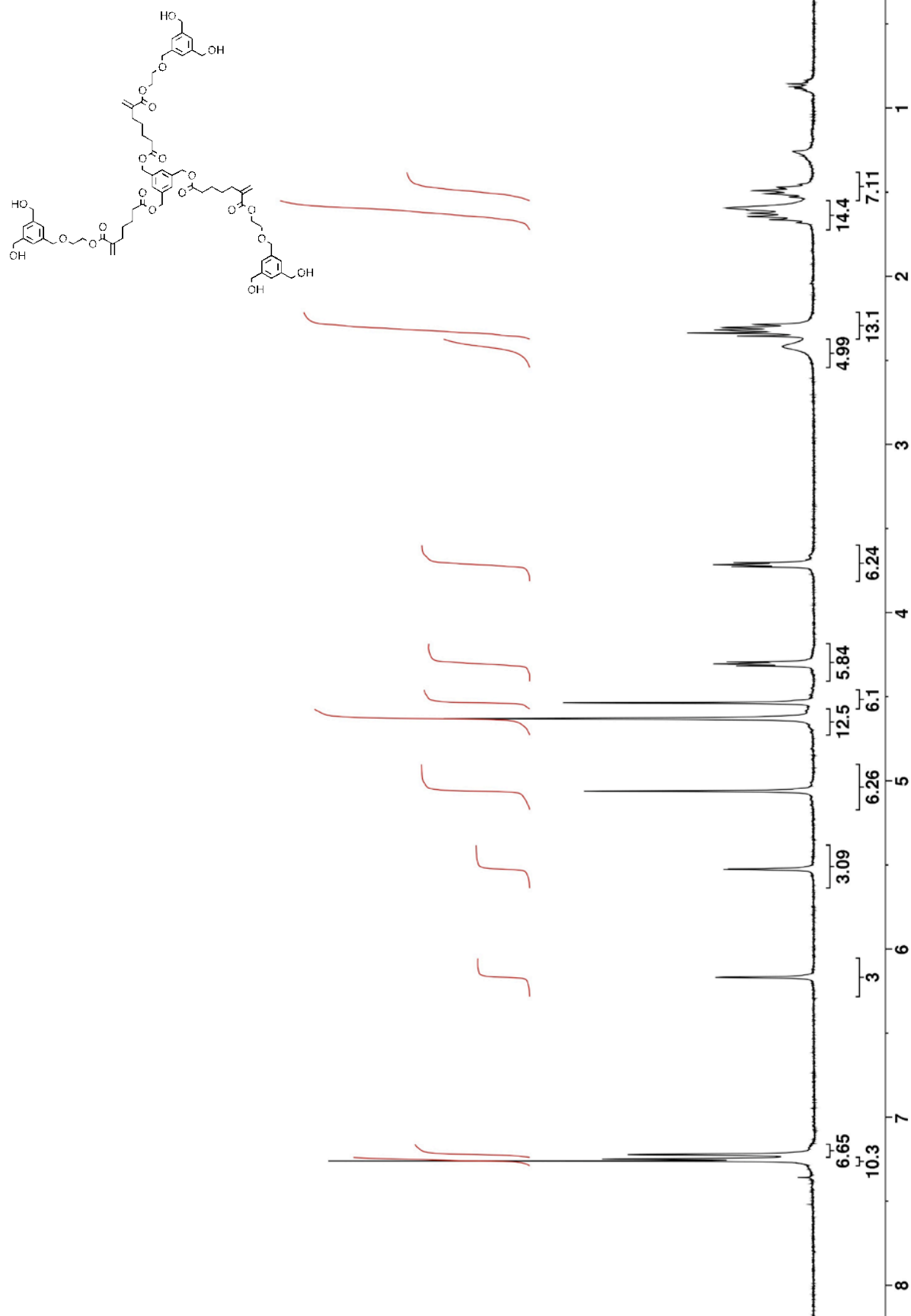
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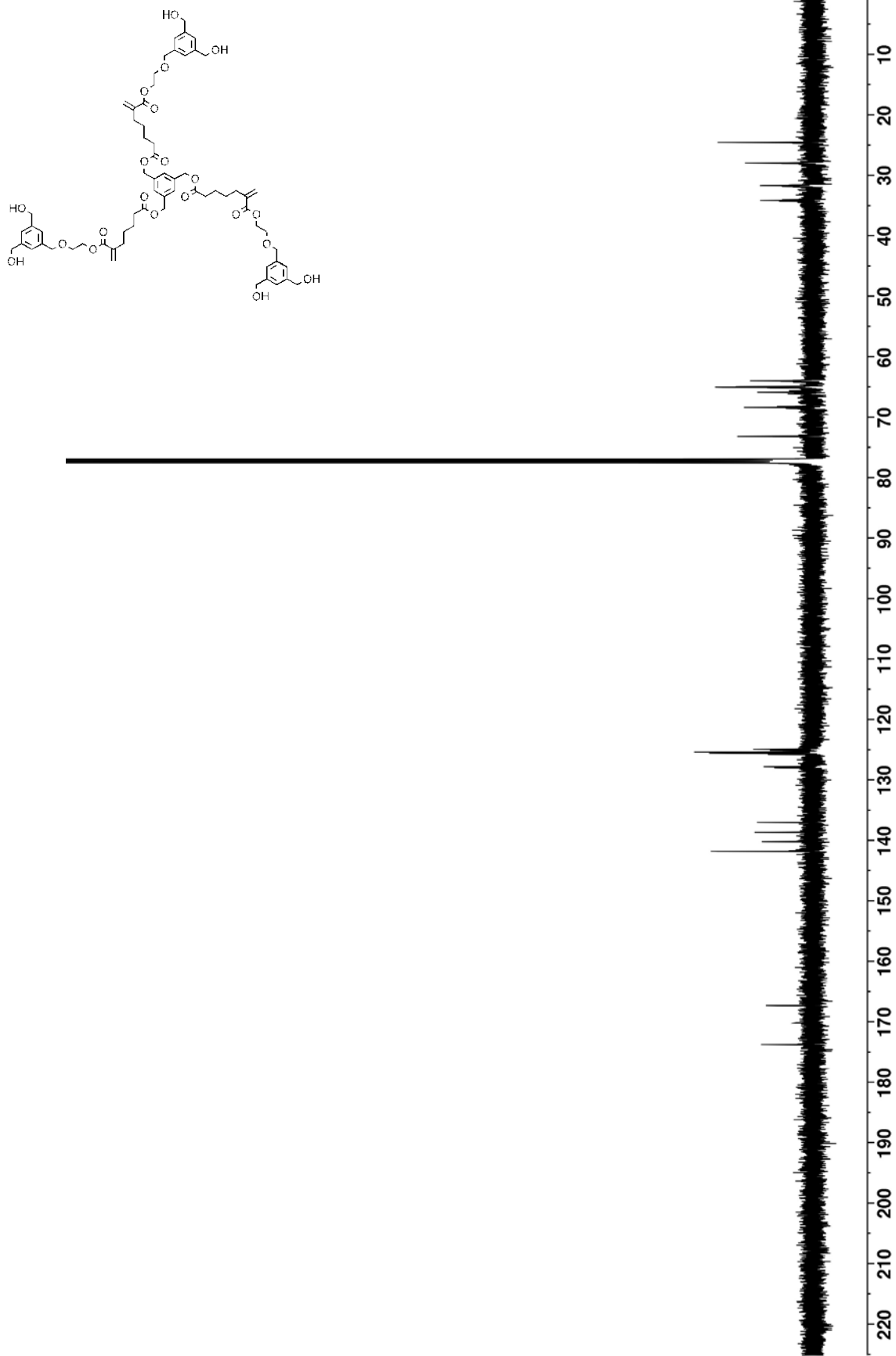
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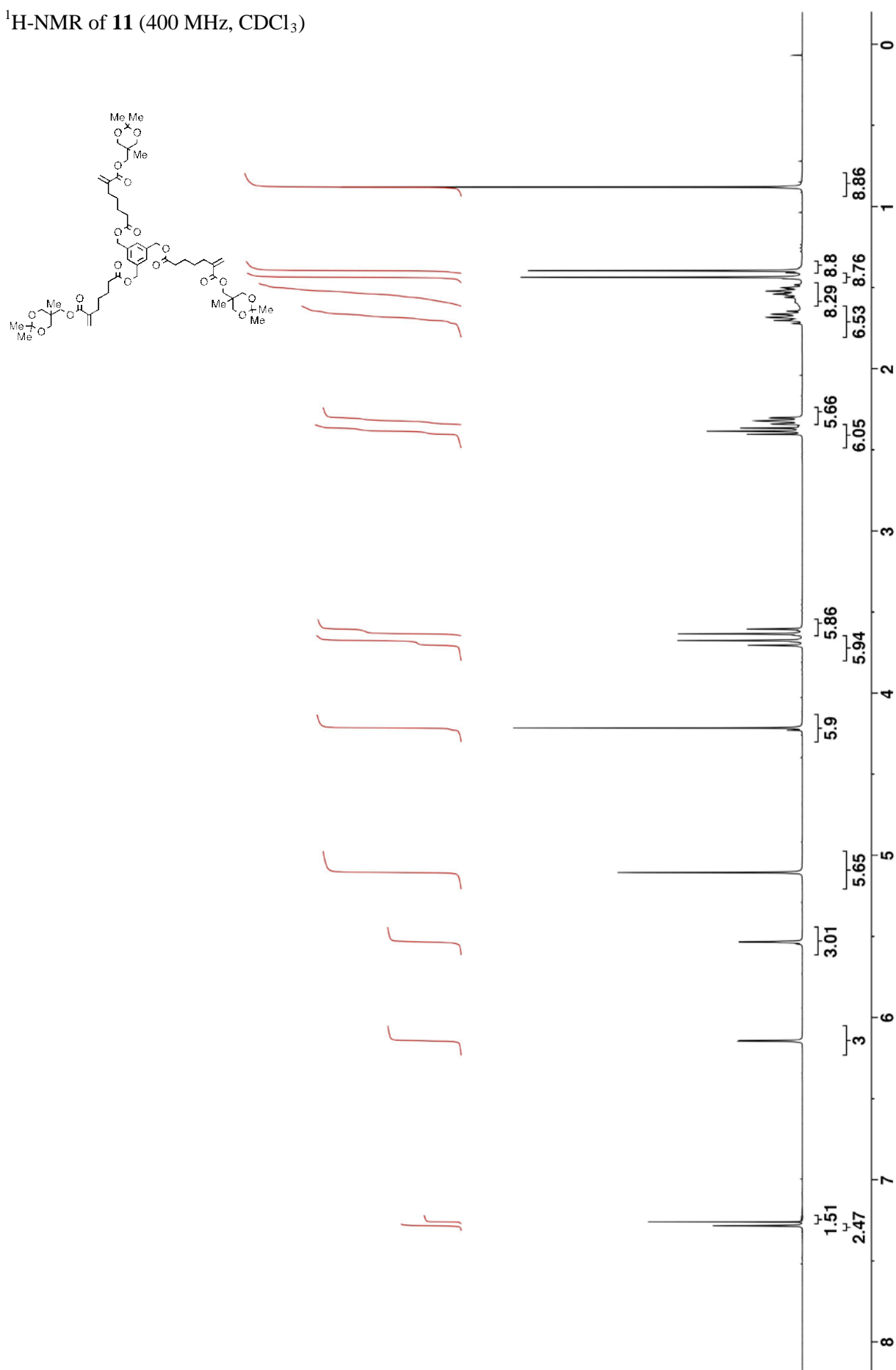
^1H -NMR of **12** (400 MHz, CDCl_3)



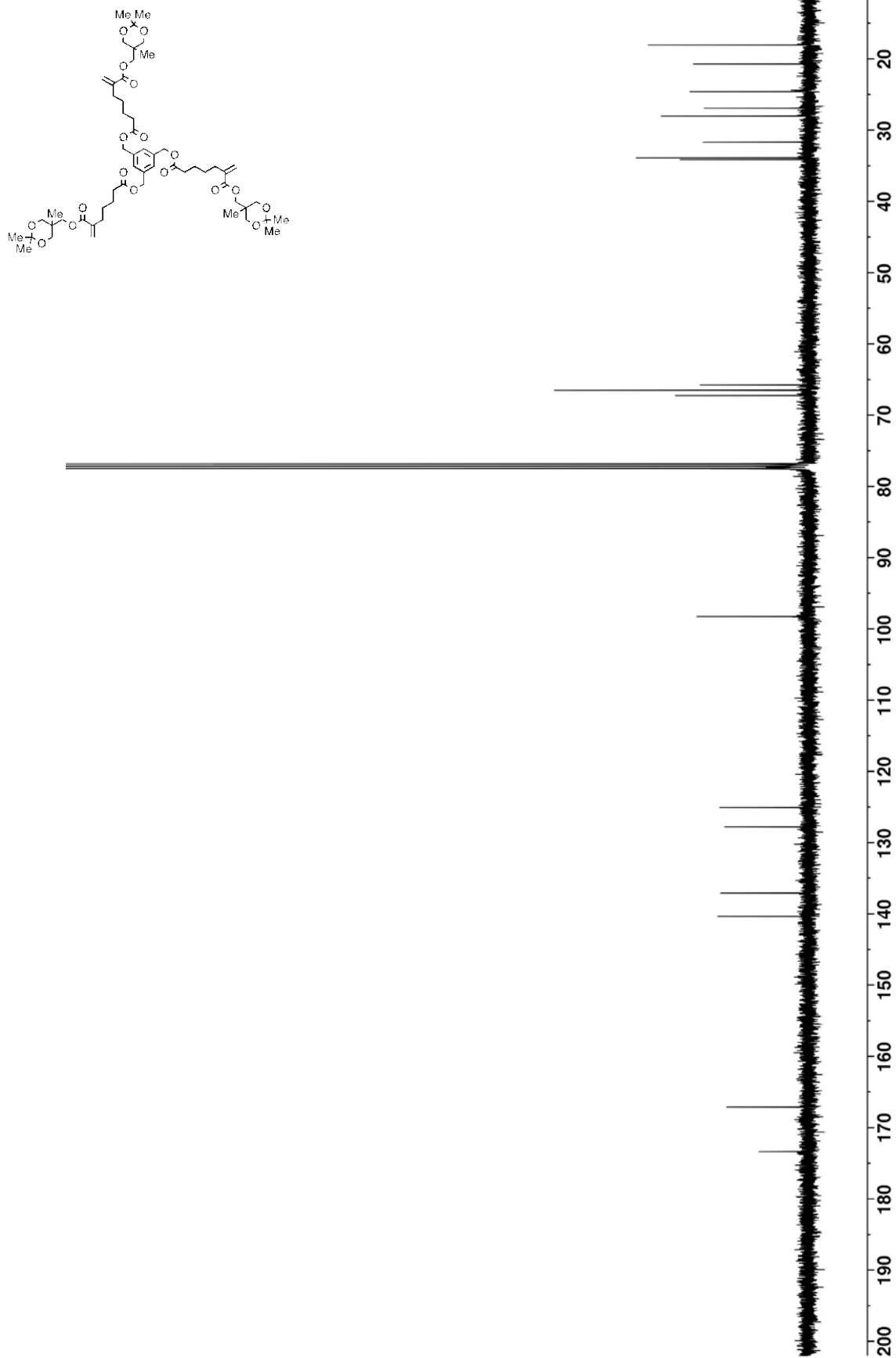
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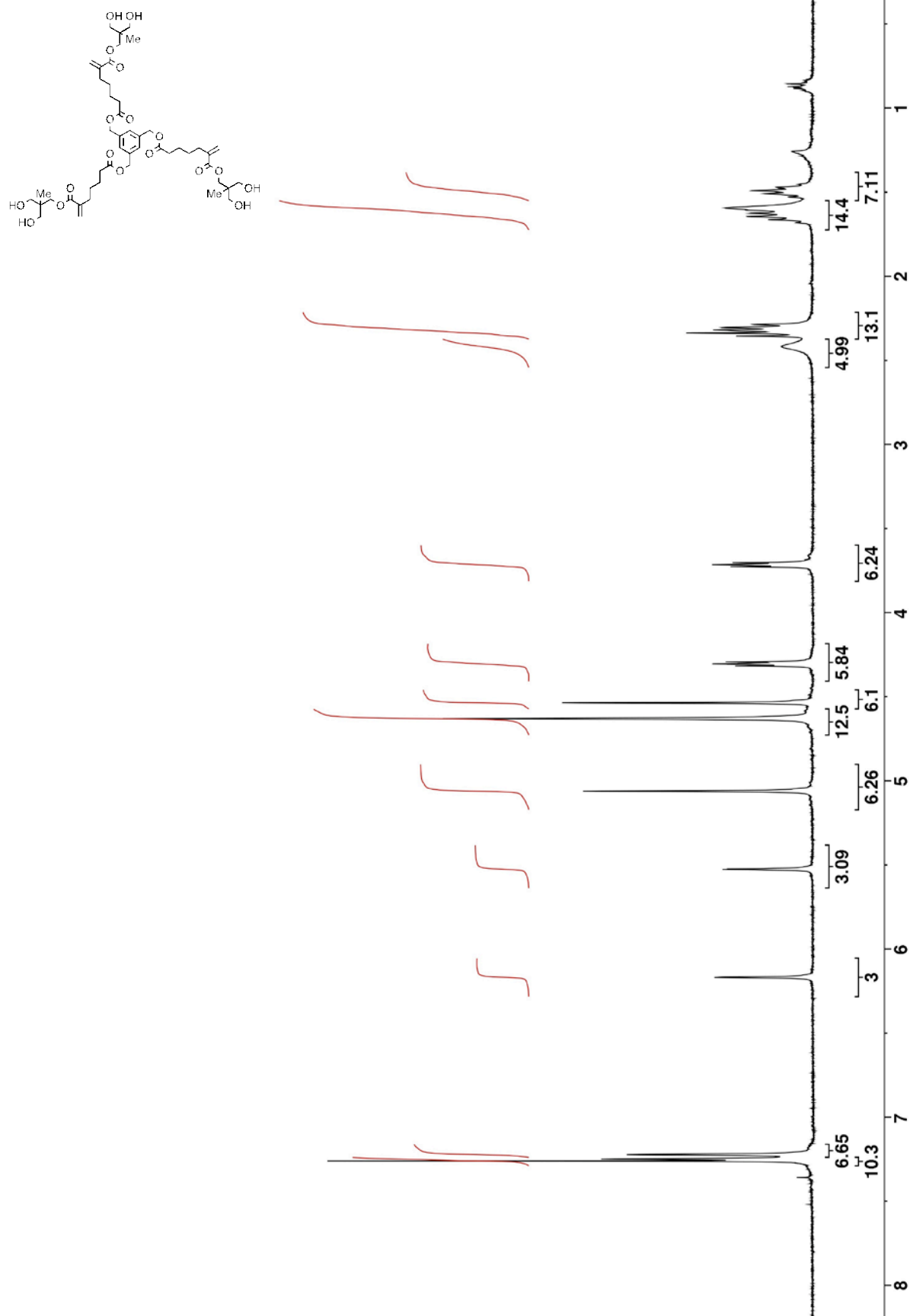
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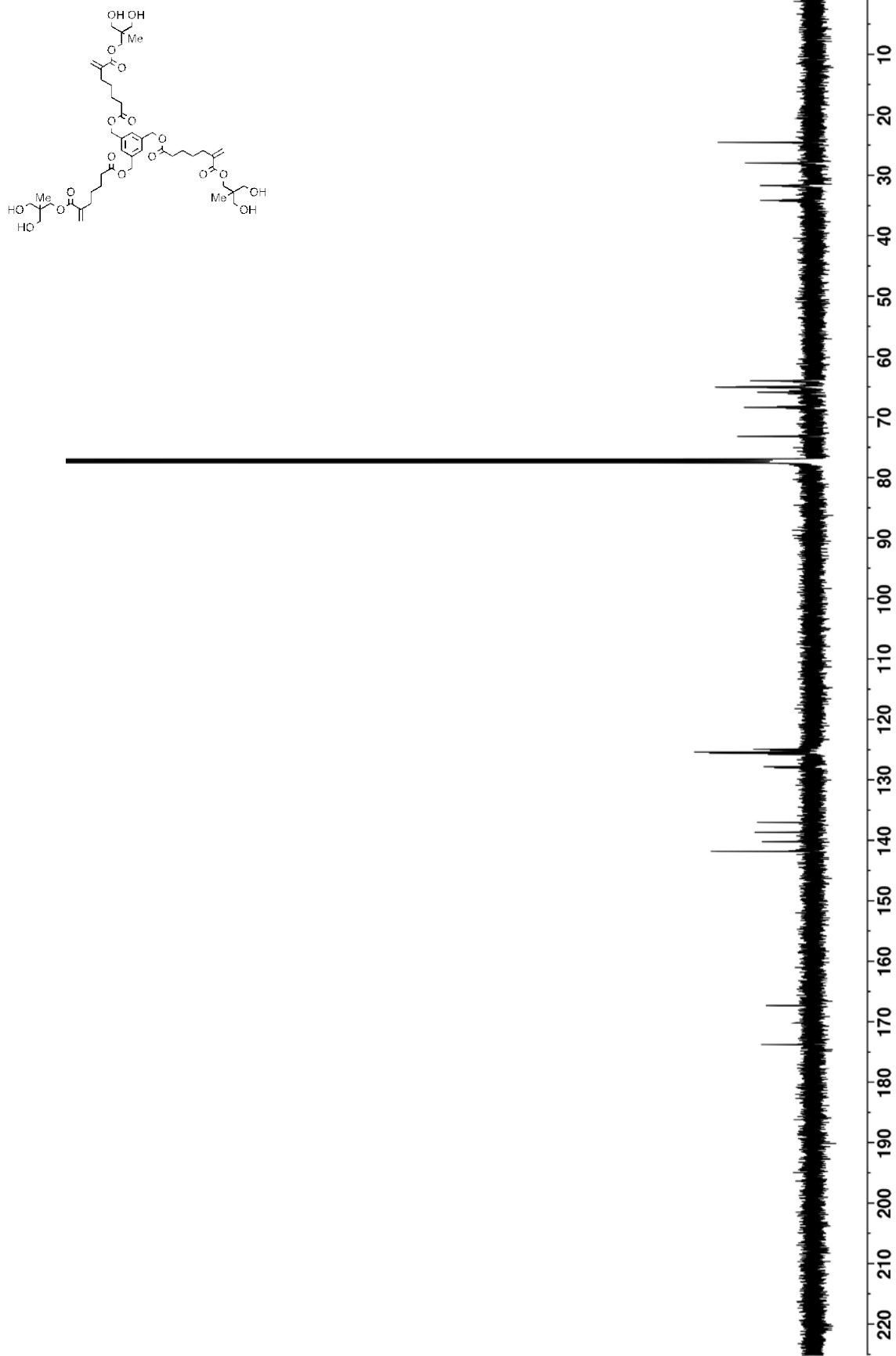
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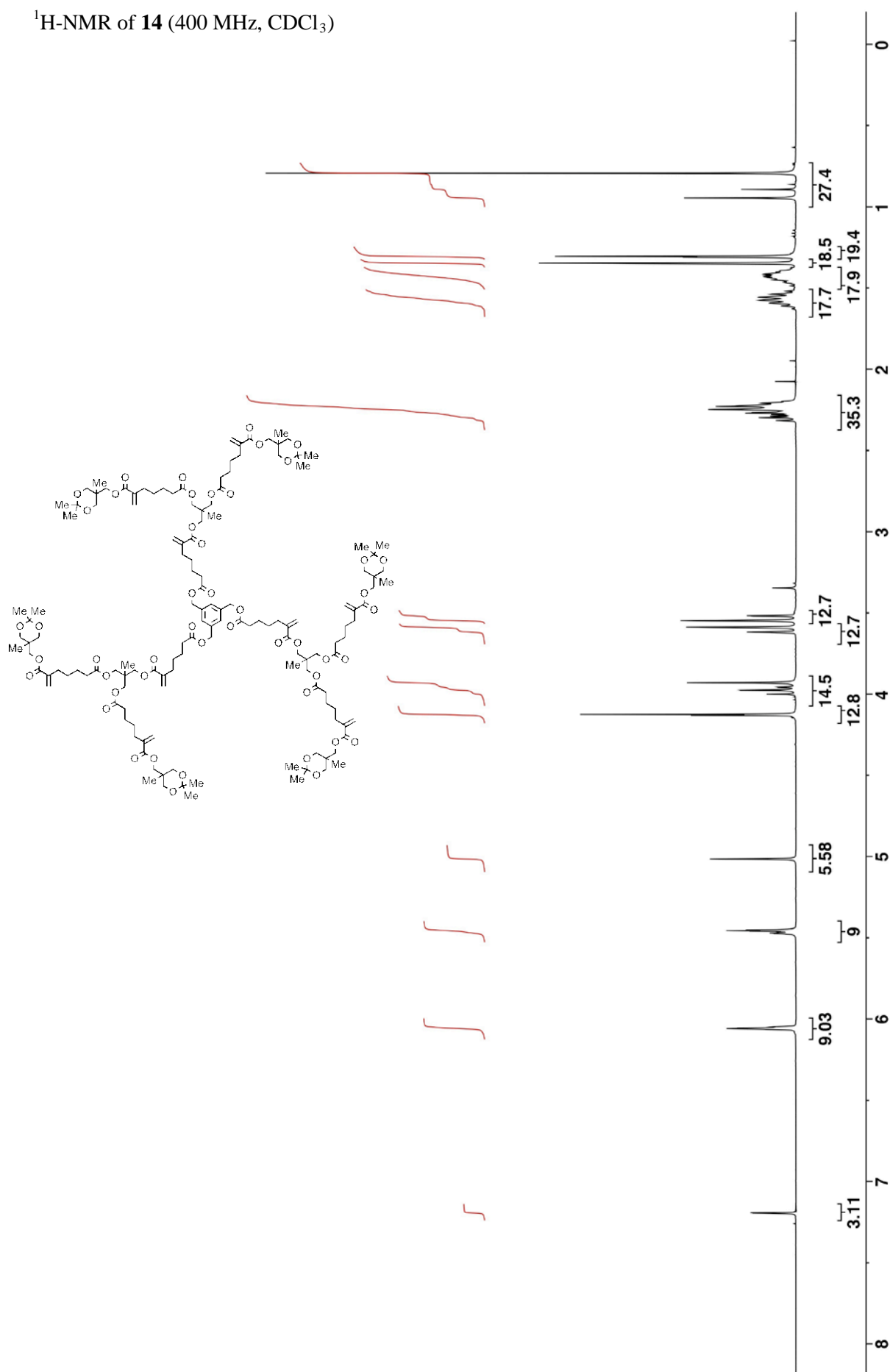
^1H -NMR of **13** (400 MHz, CDCl_3)



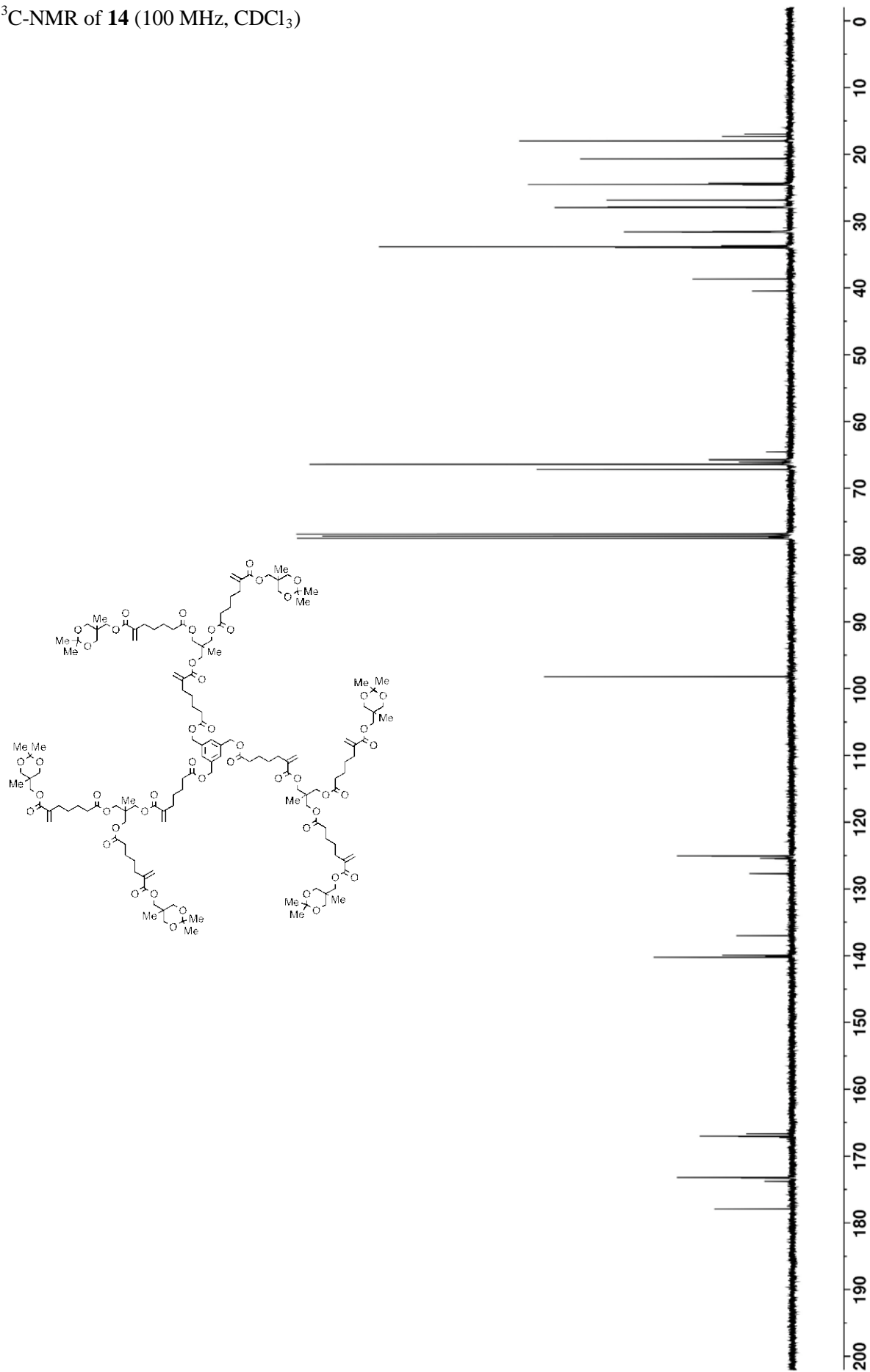
¹³C-NMR of **13** (75 MHz, CDCl₃)



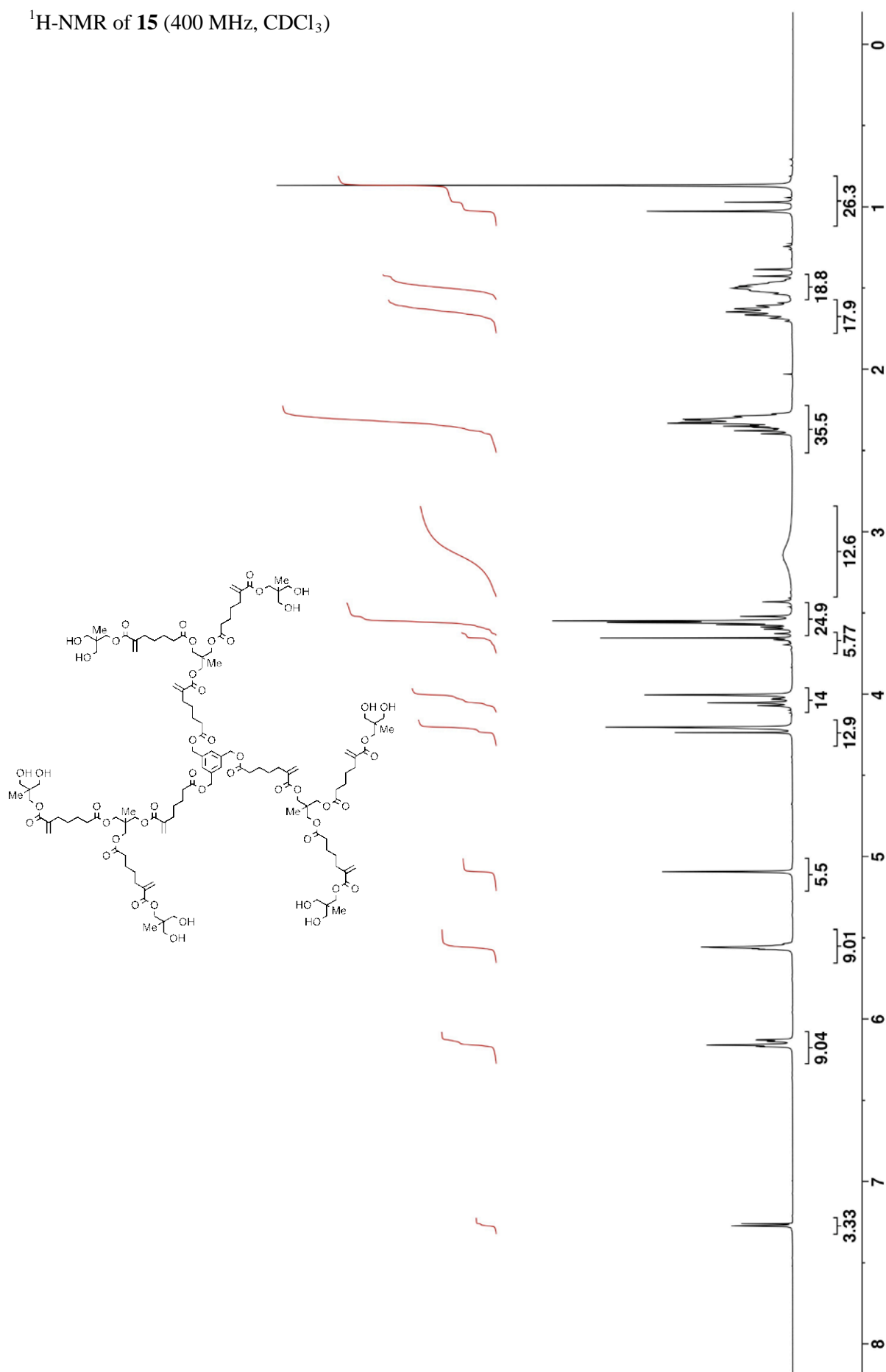
$^1\text{H-NMR}$ of **14** (400 MHz, CDCl_3)



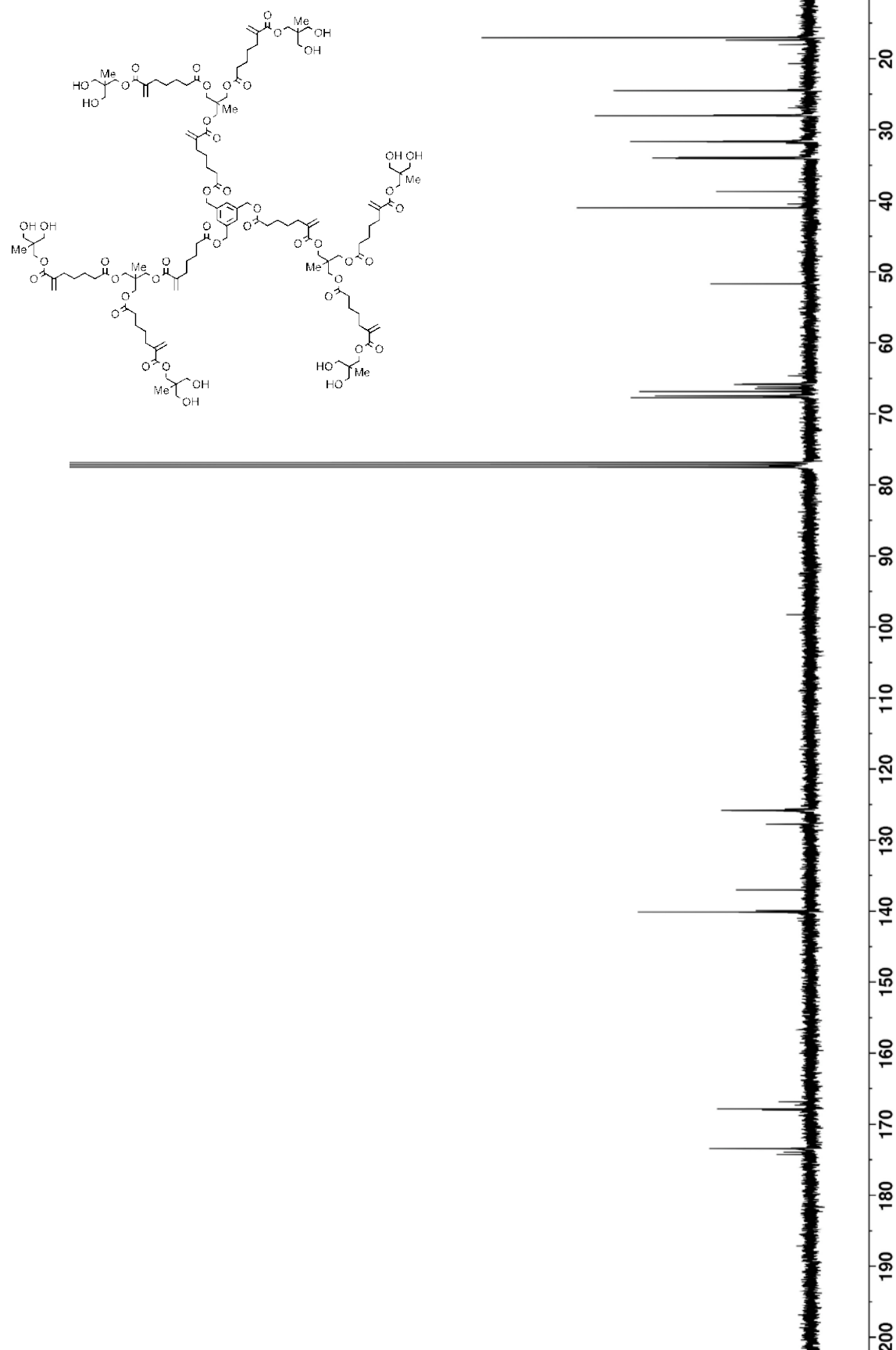
¹³C-NMR of **14** (100 MHz, CDCl₃)



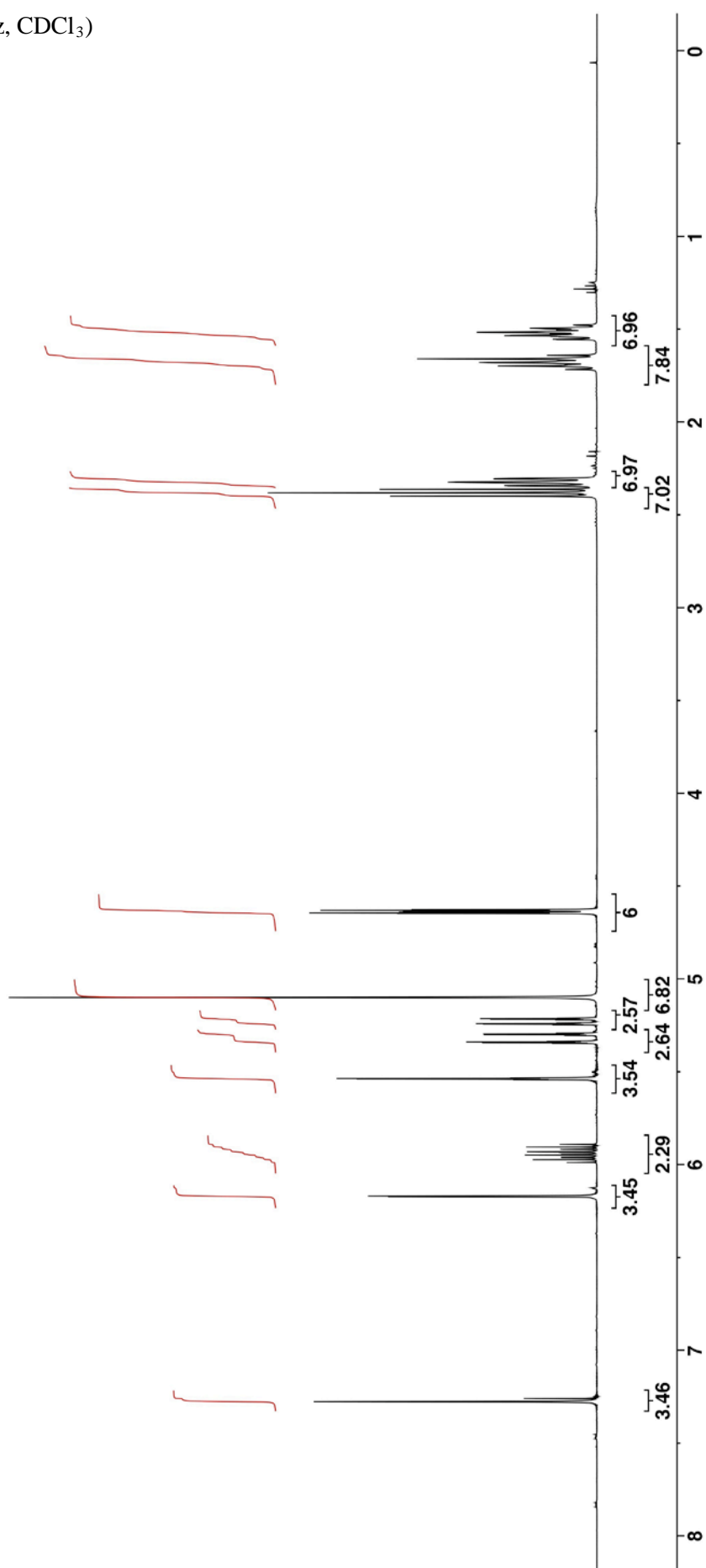
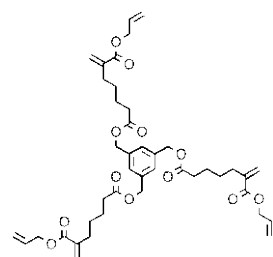
^1H -NMR of **15** (400 MHz, CDCl_3)



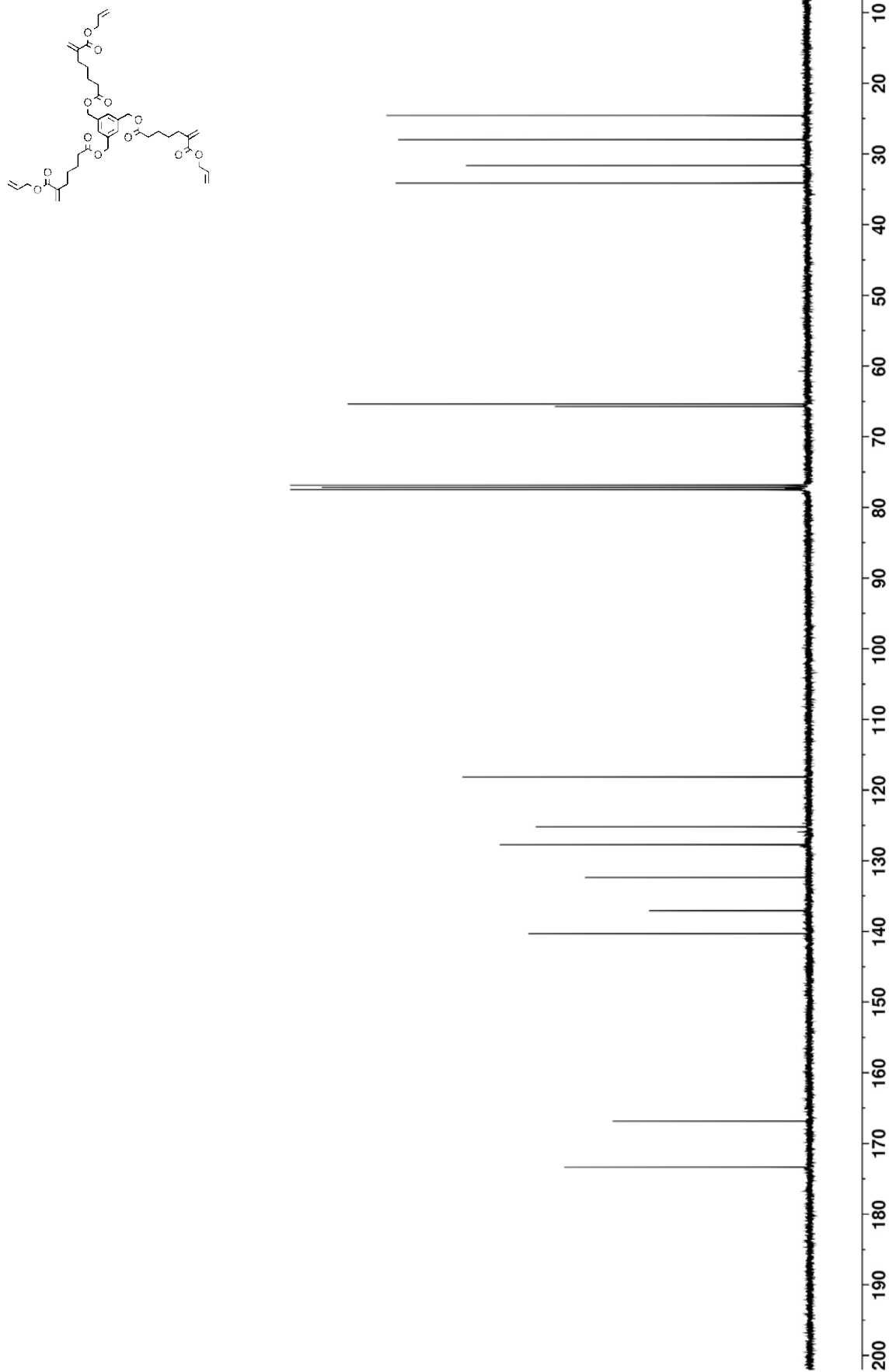
^{13}C -NMR of **15** (100 MHz, CDCl_3)



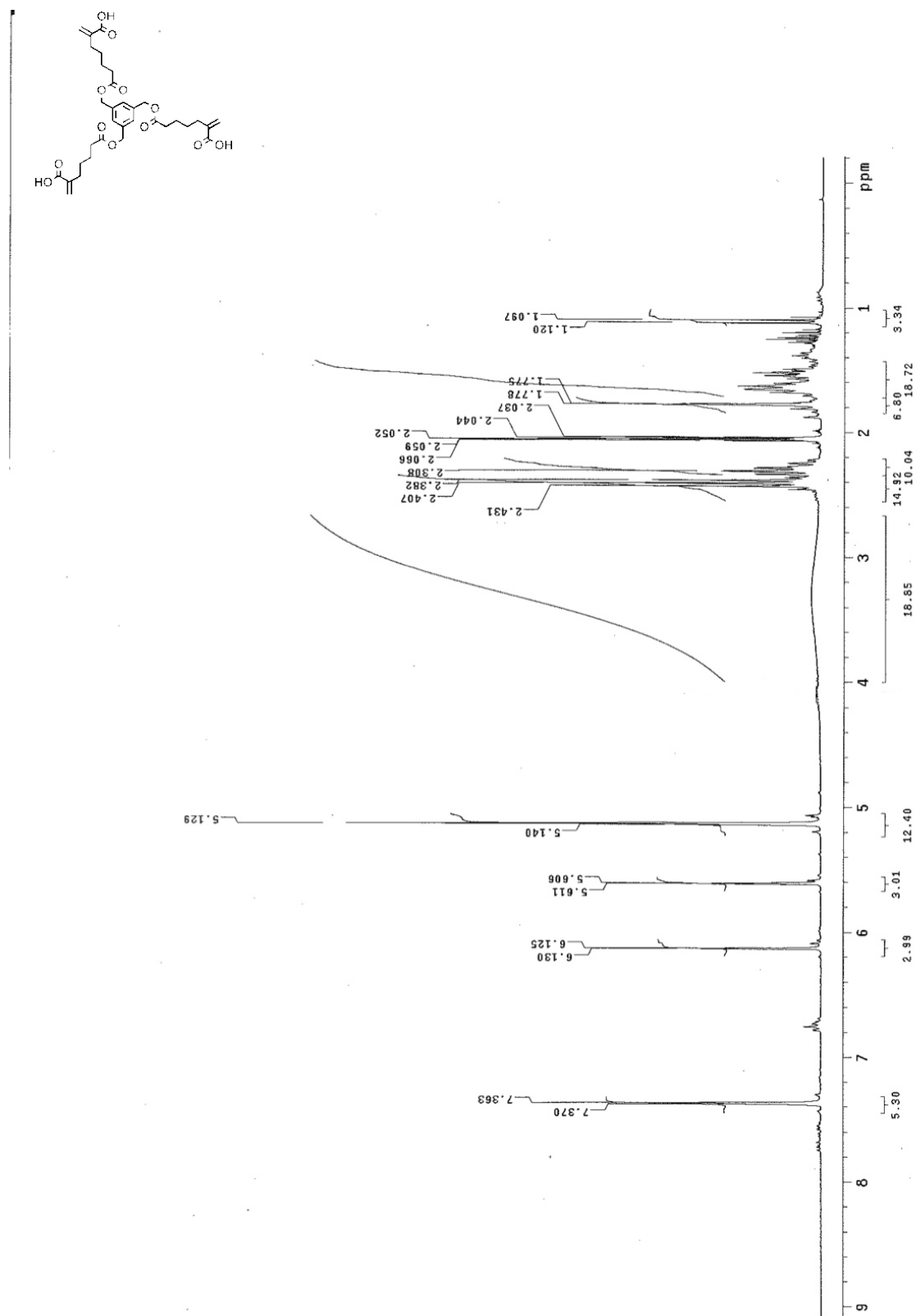
^1H -NMR of **21** (400 MHz, CDCl_3)



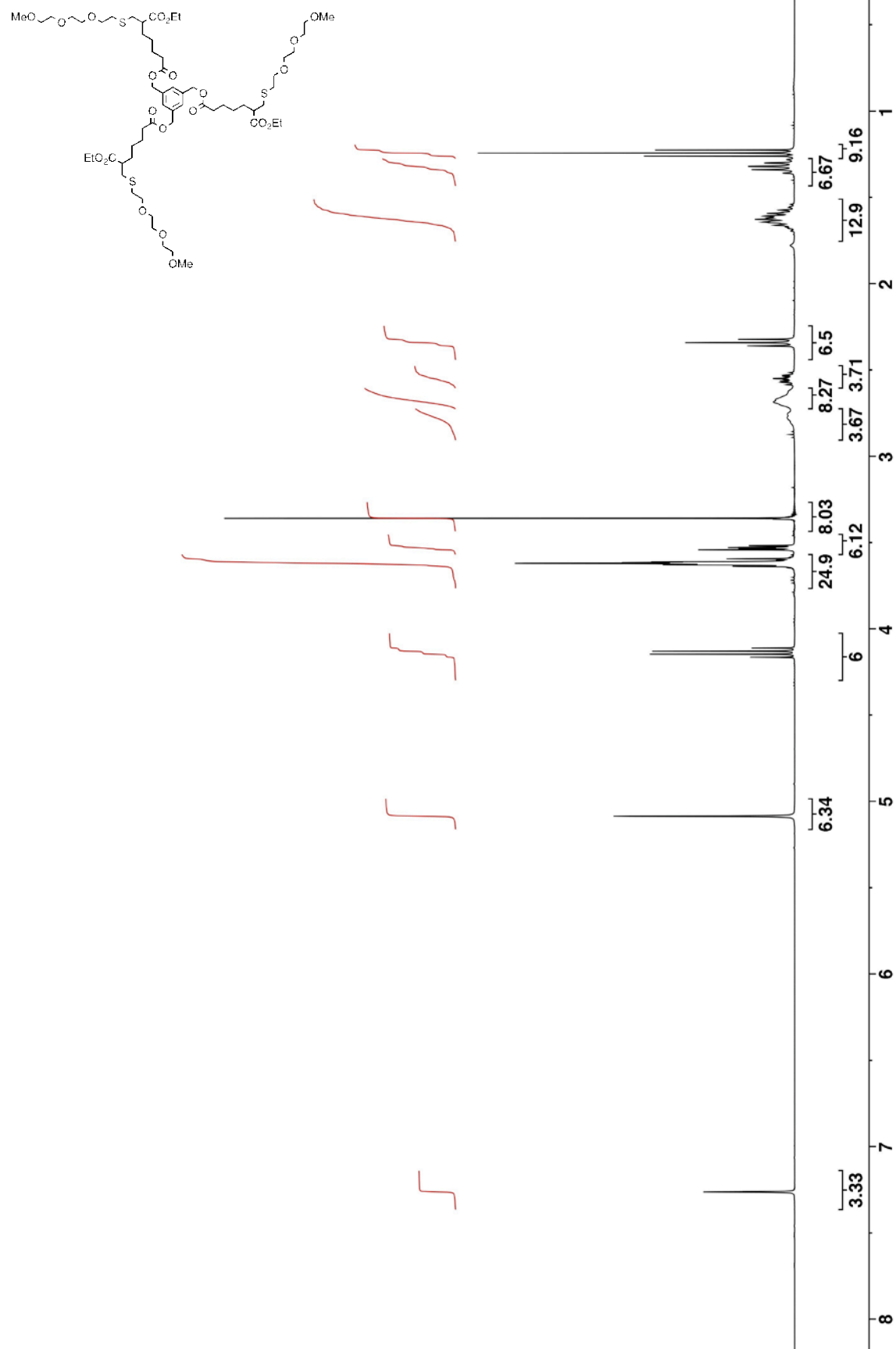
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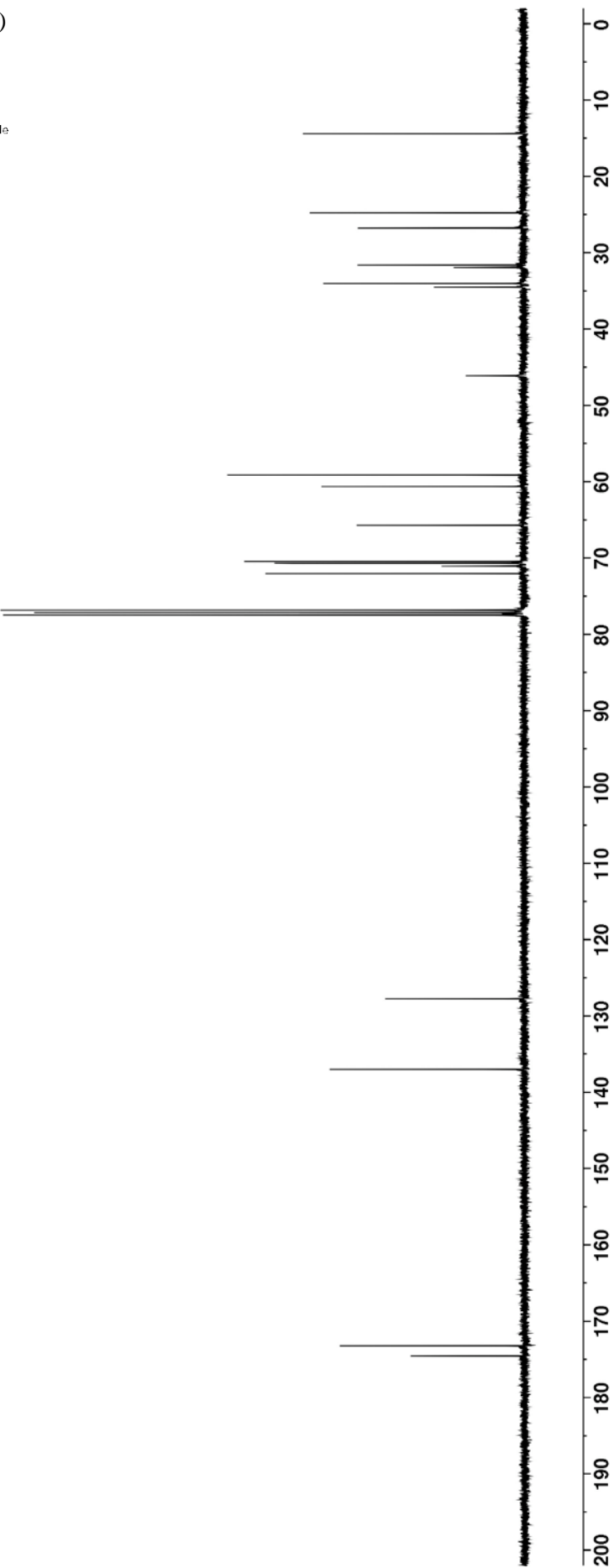
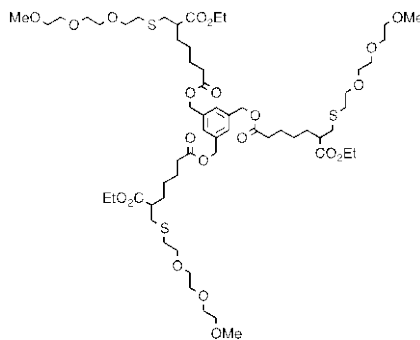
^1H -NMR of **22** (500 MHz, d_6 -acetone)



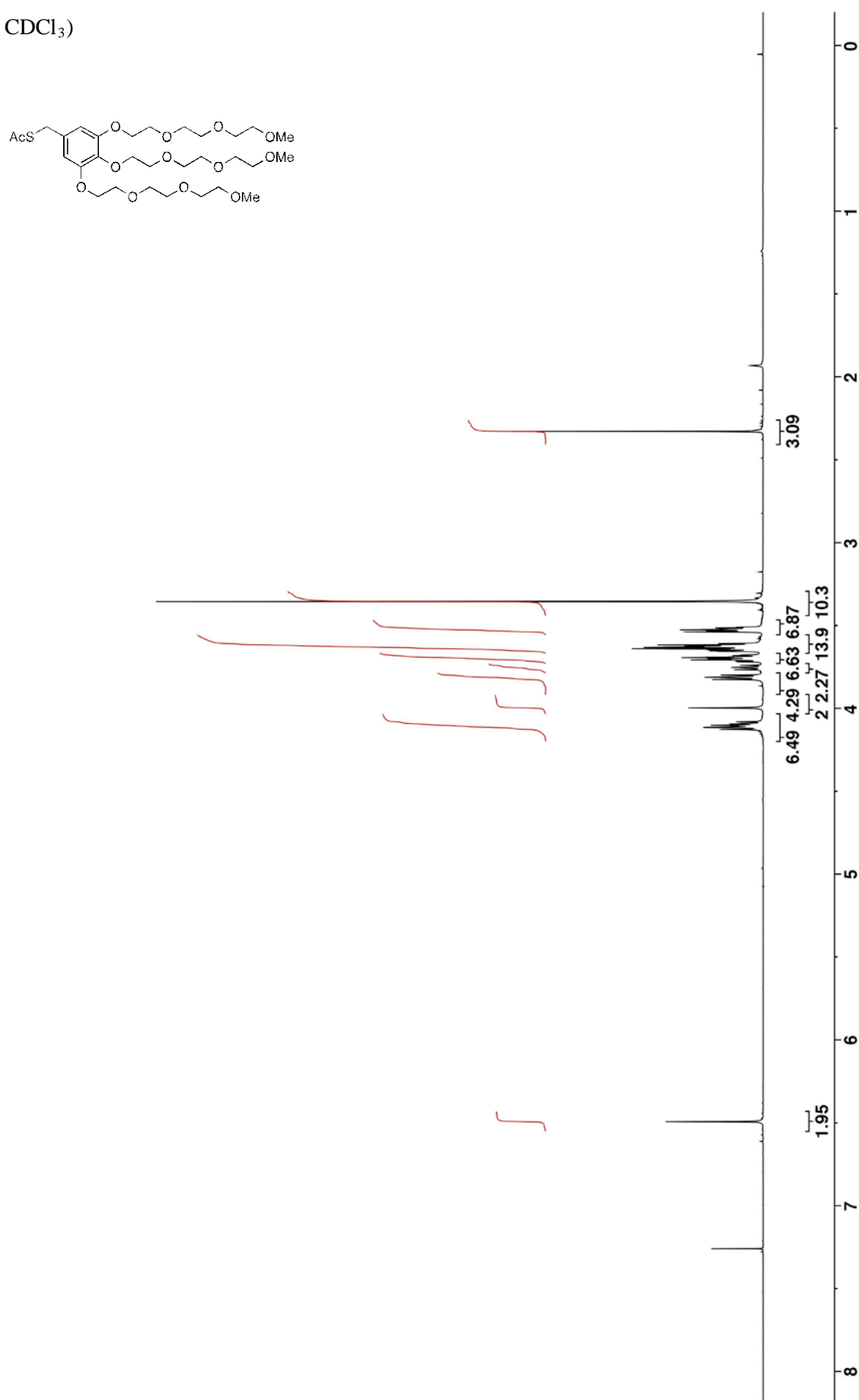
^1H -NMR of **26** (400 MHz, CDCl_3)



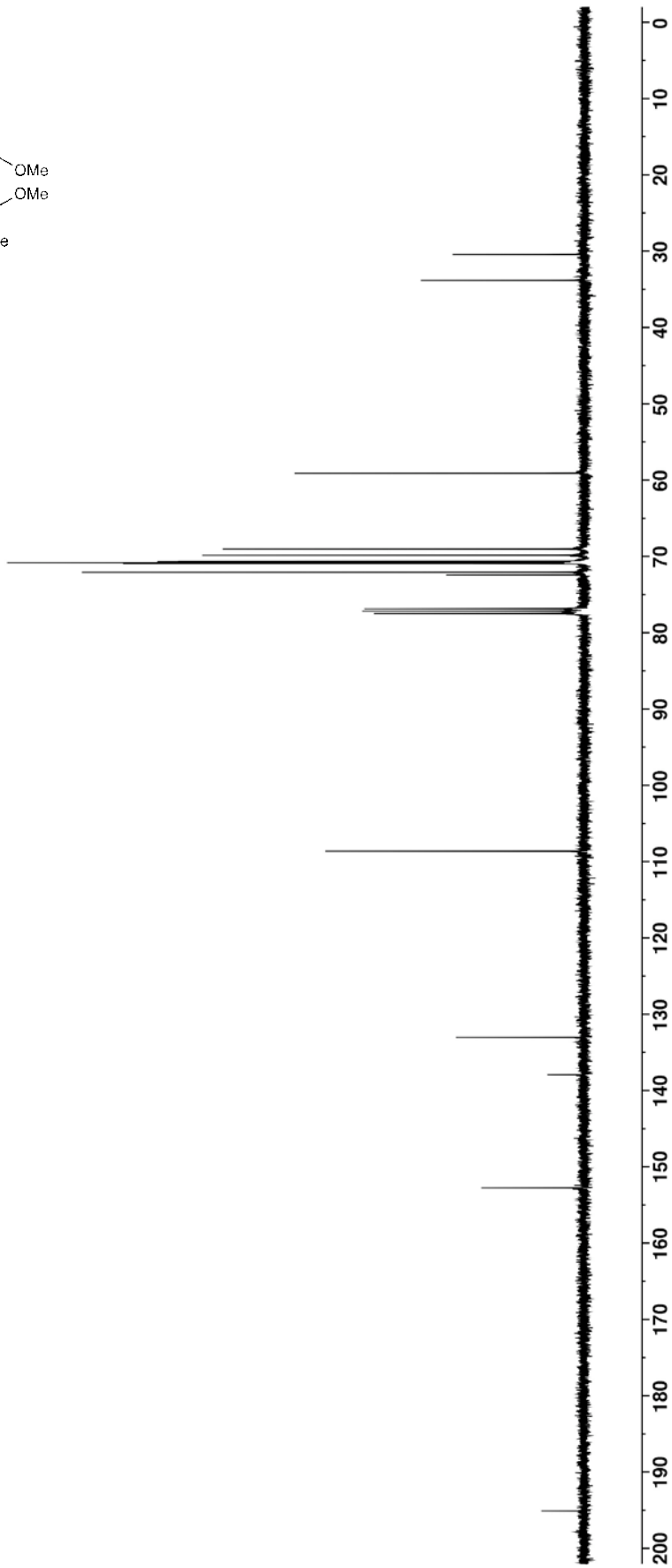
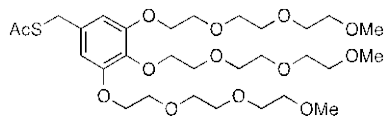
¹³C-NMR of **26** (100 MHz, CDCl₃)



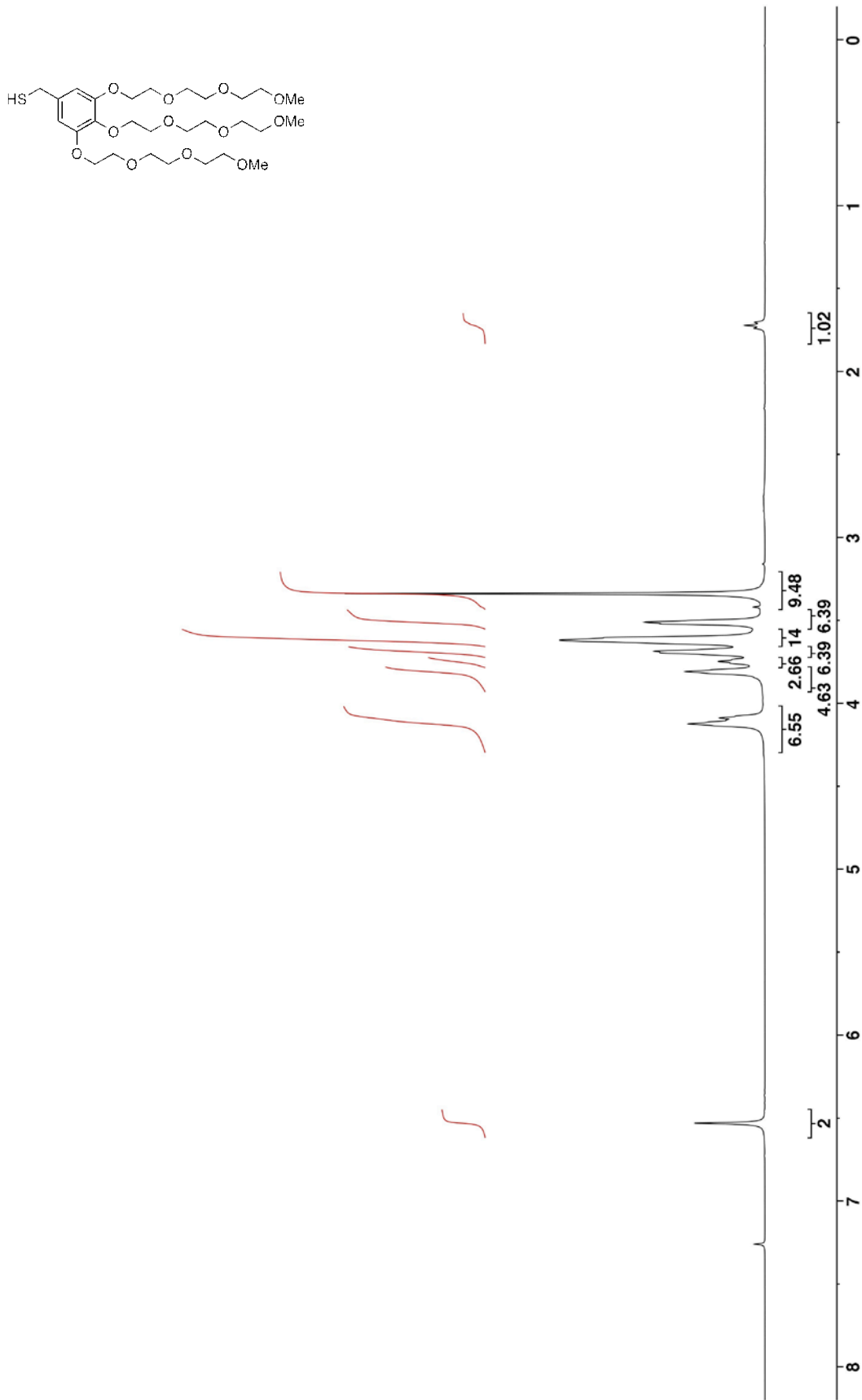
$^1\text{H-NMR}$ of *S*-3,4,5-tris(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)benzylethane-thioate (400 MHz, CDCl_3)



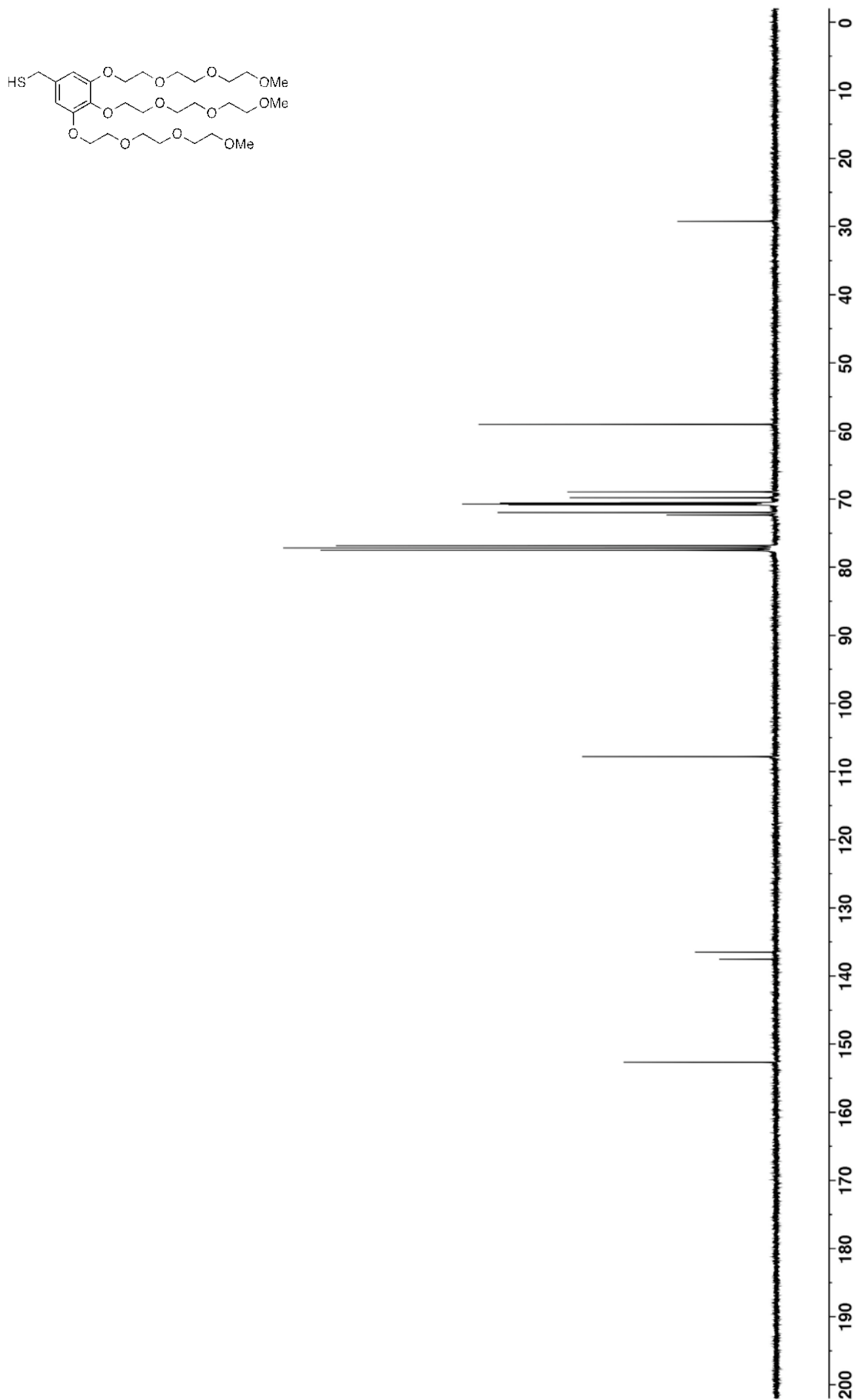
¹³C-NMR of *S*-3,4,5-tris(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)benzylethane-thioate (100 MHz, CDCl₃)



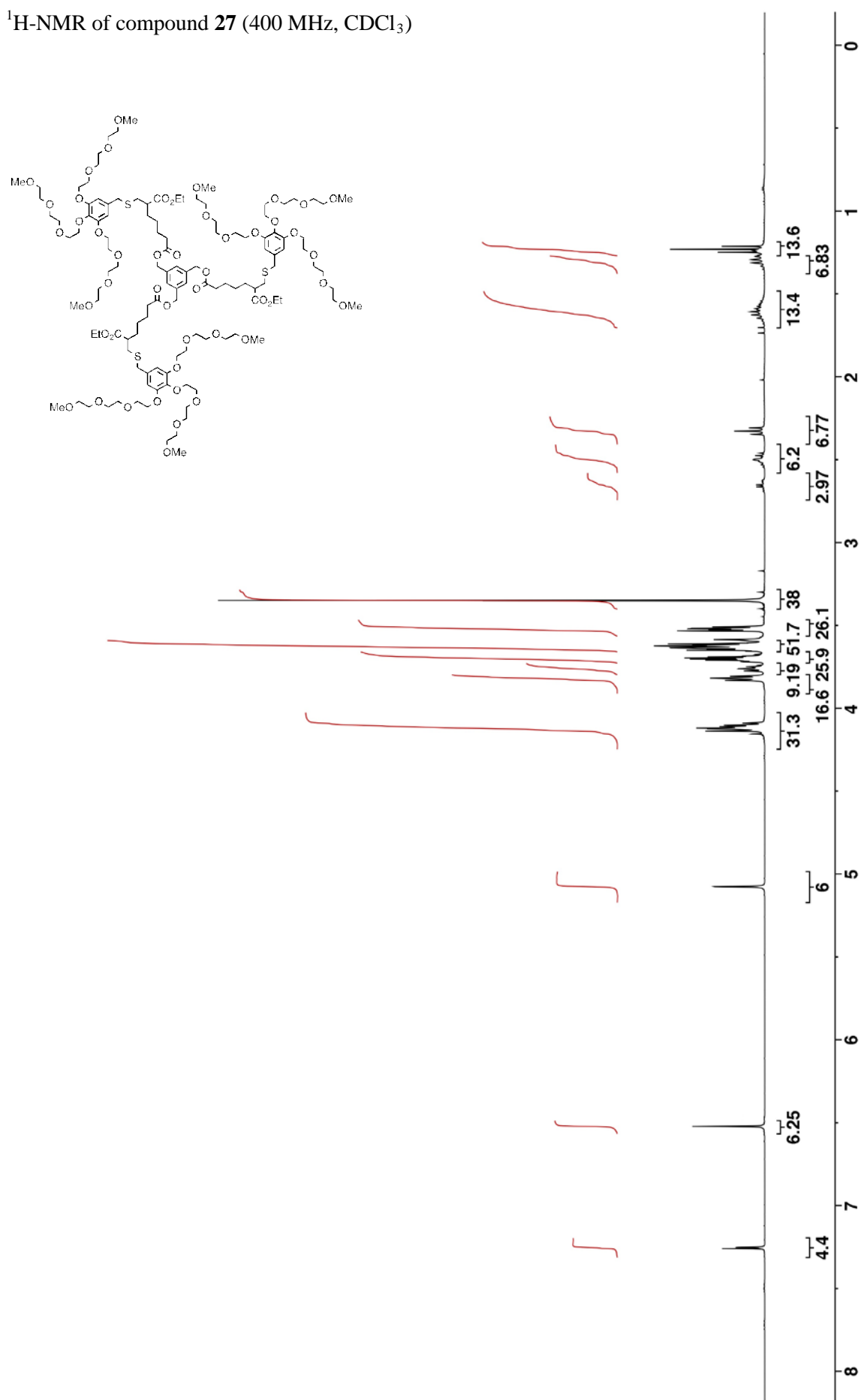
¹H-NMR of **24** (400 MHz, CDCl₃)



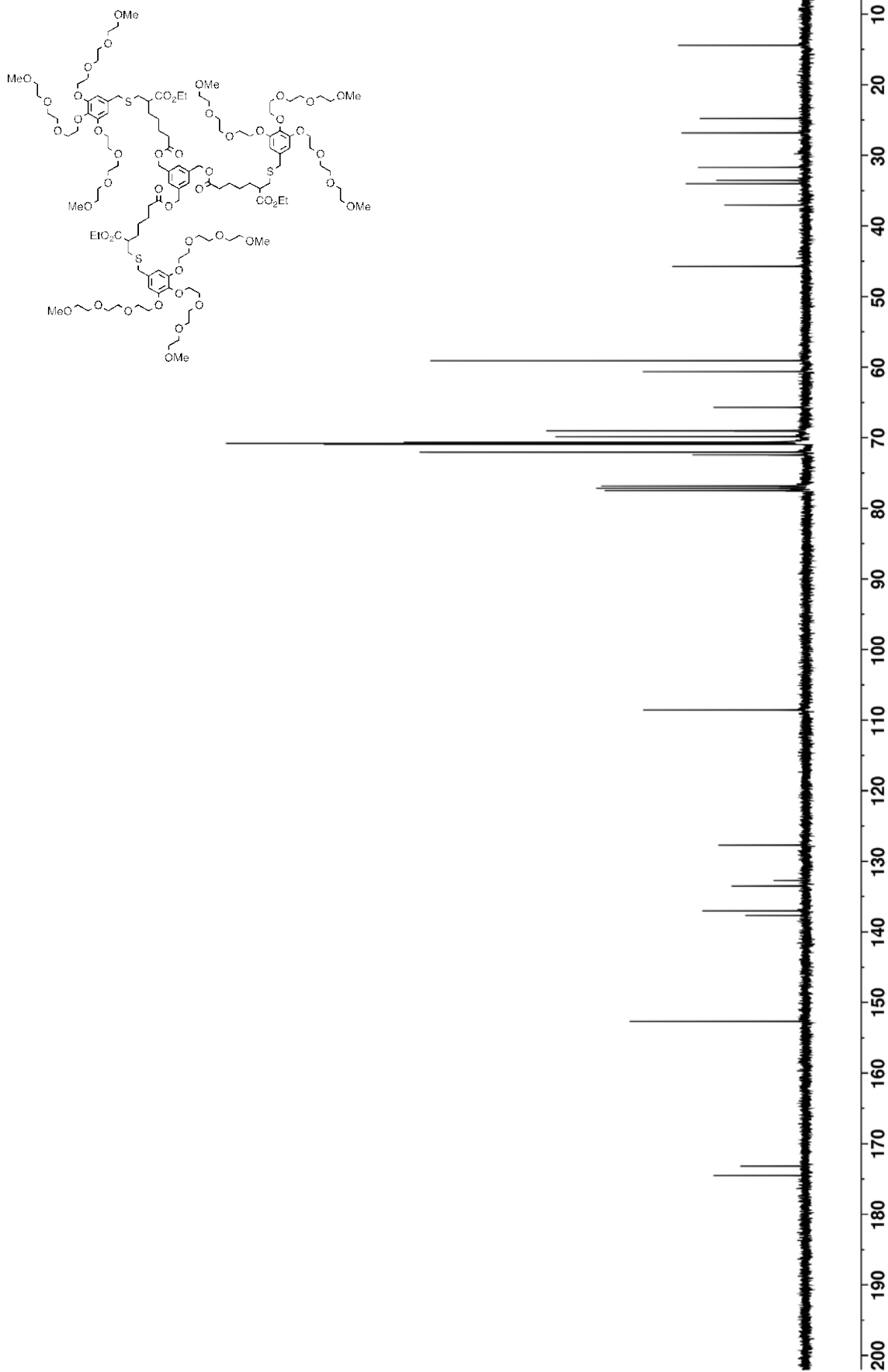
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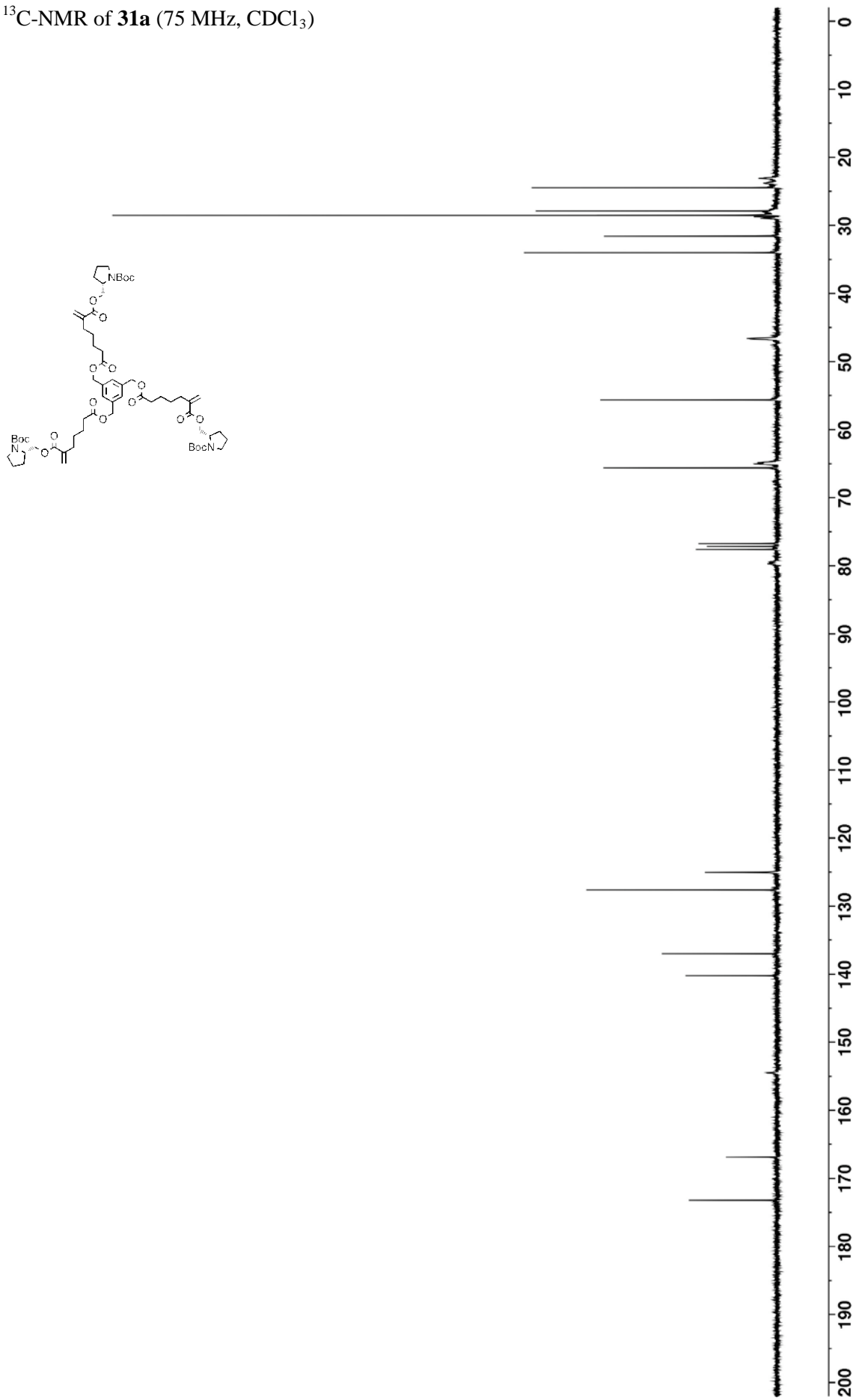
^1H -NMR of compound **27** (400 MHz, CDCl_3)



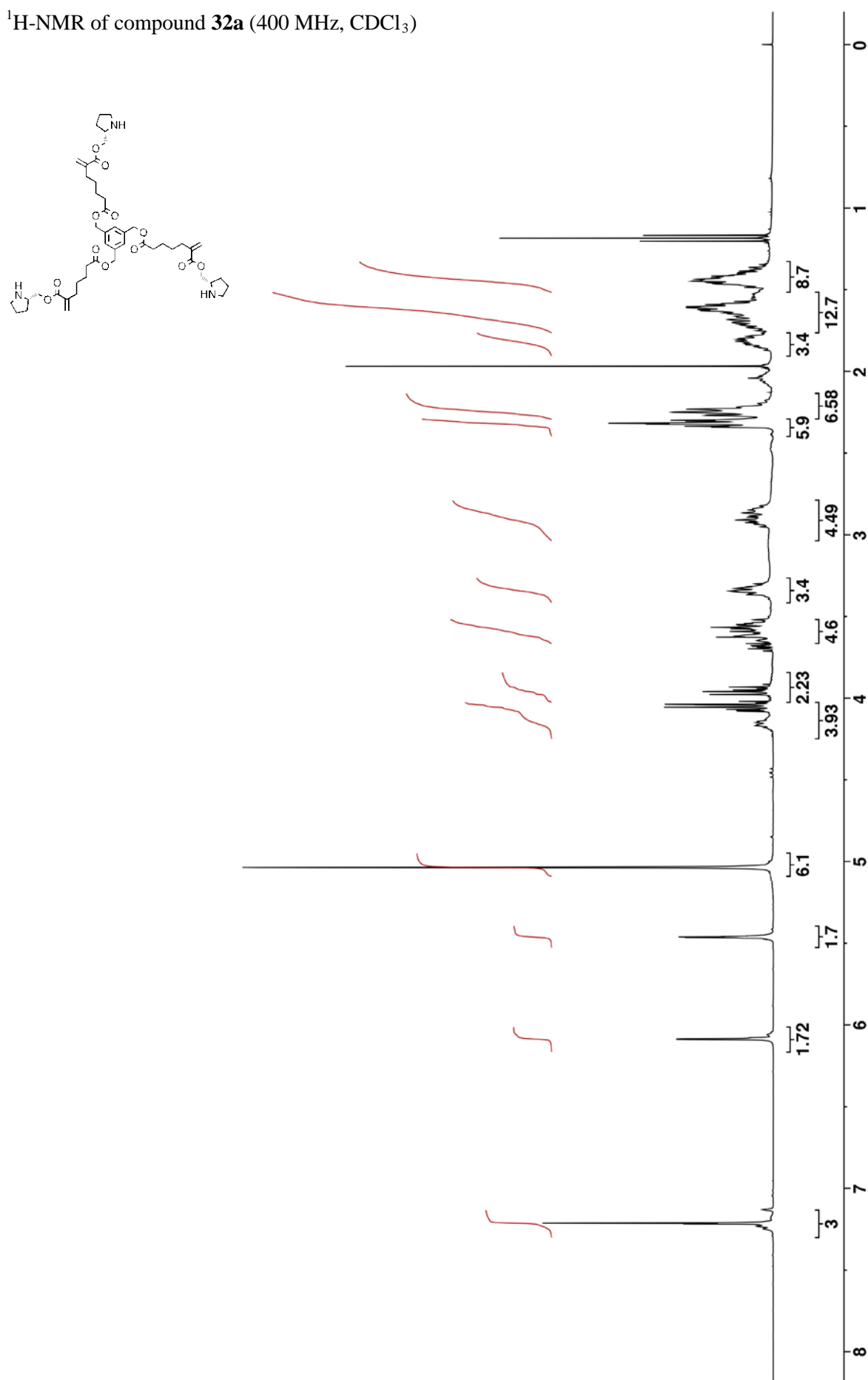
¹³C-NMR of compound **27** (100 MHz, CDCl₃)



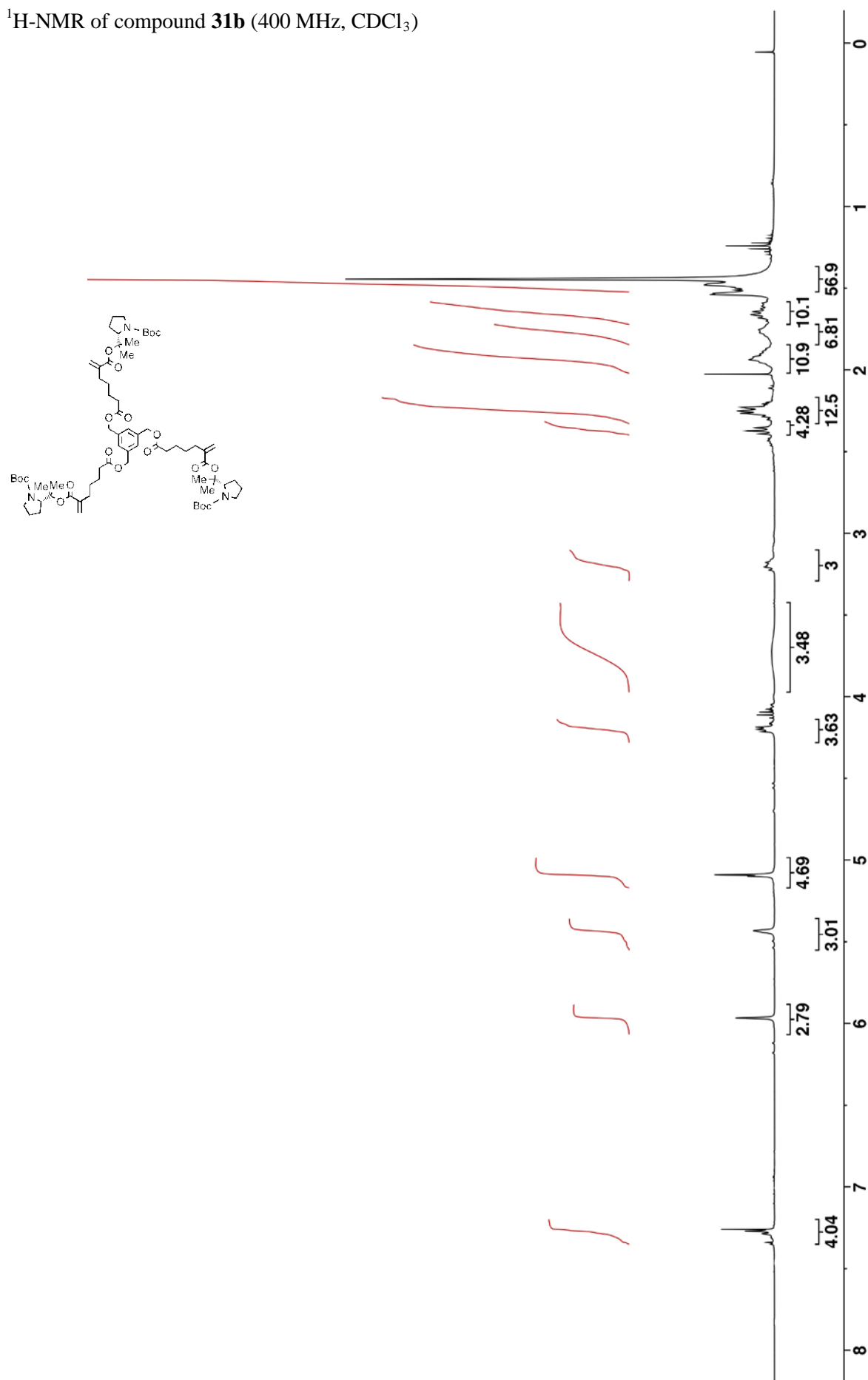
^{13}C -NMR of **31a** (75 MHz, CDCl_3)



^1H -NMR of compound **32a** (400 MHz, CDCl_3)



^1H -NMR of compound **31b** (400 MHz, CDCl_3)



^1H -NMR of compound **32b** (400 MHz, CDCl_3)

