

Supporting Information

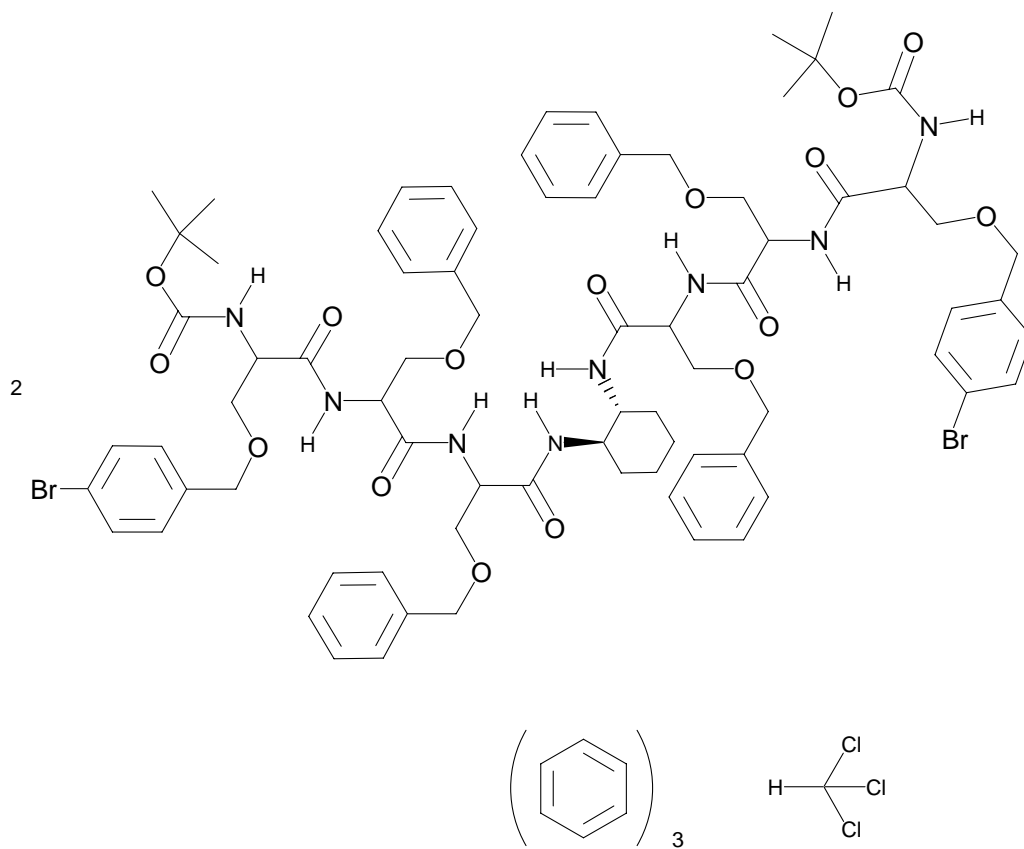
Self-Assembly of Non-cyclic Bis-D,L-tripeptides into Higher Order Tubular Constructs – Design, Synthesis and X-ray Crystal Superstructure

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CRYSTAL AND MOLECULAR STRUCTURE OF COMPOUND 13



X-ray crystallographic data were obtained from a single crystal sample which was mounted on a loop fiber. Data were collected at 100 K on a Bruker three circle platform diffractometer equipped with a 4K Charged-Coupled Device (CCD) Area Detector, a Montel 200 multi-layer optic and a FR591 6KW rotating anode generator ($\text{CuK}\alpha$) loading on a 100 micron focal spot. The crystal-to-detector distance was 5.102 cm, and the data collection was carried out in 512 x 512 pixel mode, utilizing 4 x 4 pixel binning. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 9.0 degree scan in 30 frames over four different parts of the reciprocal space (120 frames total). One complete sphere of data was collected, to better than 0.85 Å resolution. Upon completion of the data collection, the first 101 frames were recollected in order to improve the decay correction analysis.

This sample despite the specimen size did not diffract too much and the data appear truncated at low resolution. The structure was solved using direct methods with SIR2002 (Burla et al., 2003) which found two symmetry-independent molecules in the asymmetric unit. Several full-matrix least squares / difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. Least-square refinements on F^2 were performed using ShelxH (the version of Shelxl-97 suitable for large-scale problem, Sheldrick, 1997). Hydrogen atoms were refined using a riding model with fixed thermal parameters. Some difficulties were experienced in the refinement procedure due to the large size of the molecule. 3866 similarity restraints on distances, geometry and thermal displacement parameter were added to the model to assist in the refinement.

In the course of the refinement, two benzene and one CHCl_3 molecules were located by Fourier difference map and were found no too much disordered in the crystal lattice. A third benzene molecule at the vicinity of a methoxymethyl-benzene arms appeared disordered to such extent that few difference peaks were visible. The data were then treated with the Squeeze/Bypass method (van der Sluis & Spek, 1990) implemented in Platon (Spek, 2000) to subtract the effects of this disordered solvent molecule and to optimize the structural characterization of the ordered part of the structure. Only the 2 benzene and the CHCl_3 molecules were kept in the final refinement, but the structure is reported with formula including the three benzene molecules.

Table S1. Crystal data and structure refinement for compound **13**.

Identification code	Han398
Empirical formula	C ₁₆₅ H ₂₀₁ Br ₄ Cl ₃ N ₁₆ O ₃₂
Formula weight	3346.38
Temperature	100(2)K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	a = 18.146(2) Å $\alpha = 90^\circ$ b = 26.468(3) Å $\beta = 90^\circ$ c = 35.413(3) Å $\gamma = 90^\circ$
Volume	17009(3) Å ³
Z	4
Density (calculated)	1.307 g/cm ³
Absorption coefficient	2.196 mm ⁻¹
F(000)	7000
Crystal size	0.12 x 0.08 x 0.05 mm
Theta range for data collection	2.08 to 68.05°
Index ranges	-21 ≤ h ≤ 21, -31 ≤ k ≤ 31, -42 ≤ l ≤ 42
Reflections collected	167546
Independent reflections	28888 [R _{int} = 0.055]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9000 and 0.7800
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	28888 / 618 / 1886

Goodness-of-fit on F^2	1.107
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0888$, $wR_2 = 0.2119$
R indices (all data)	$R_1 = 0.0937$, $wR_2 = 0.2133$
Absolute structure parameter	-0.10(2) (Flack, 1983)
Largest diff. peak and hole	0.493 and -0.325 e/Å ³

Table S2. Bond lengths [Å] and angles [°] related to the hydrogen bonding for compound **13**.

D-H	..A	d(D-H)	d(H..A)	d(D..A)	<DHA
Molecule A -----					
Intramolecular					
N10-H10	O20	0.88	2.20	2.903(4)	138.4
N11-H11	O24	0.88	2.16	2.935(4)	148.8
N21-H21	O14	0.88	1.99	2.800(4)	168.6
Intermolecular					
N14-H14	O42#1	0.88	2.03	2.869(4)	159.1
N20-H20	O36#2	0.88	2.23	3.065(5)	153.6
N24-H24	O32#2	0.88	2.30	2.998(4)	144.0
N26-H26	O32#2	0.88	2.15	2.950(7)	144.0
Molecule B -----					
Intramolecular					
N30-H30	O40	0.88	2.26	2.991(5)	137.7
N31-H31	O44	0.88	2.06	2.872(5)	155.3
N41-H41	O34	0.88	2.04	2.872(4)	172.9
Intermolecular					
N34-H34	O22#3	0.88	1.96	2.797(5)	171.5
N40-H40	O16#4	0.88	2.24	3.094(5)	169.0
N44-H44	O12#4	0.88	2.23	2.990(4)	144.9
N46-H46	O12#4	0.88	2.13	2.845(5)	145.4

Symmetry transformations used to generate equivalent atoms:

#1 x-1, y-1, z-1	#2 -x+3/2, -y+1, z-1/2
#3 -x+3/2, -y+1, z+1/2	#4 x+1, y+1, z+1

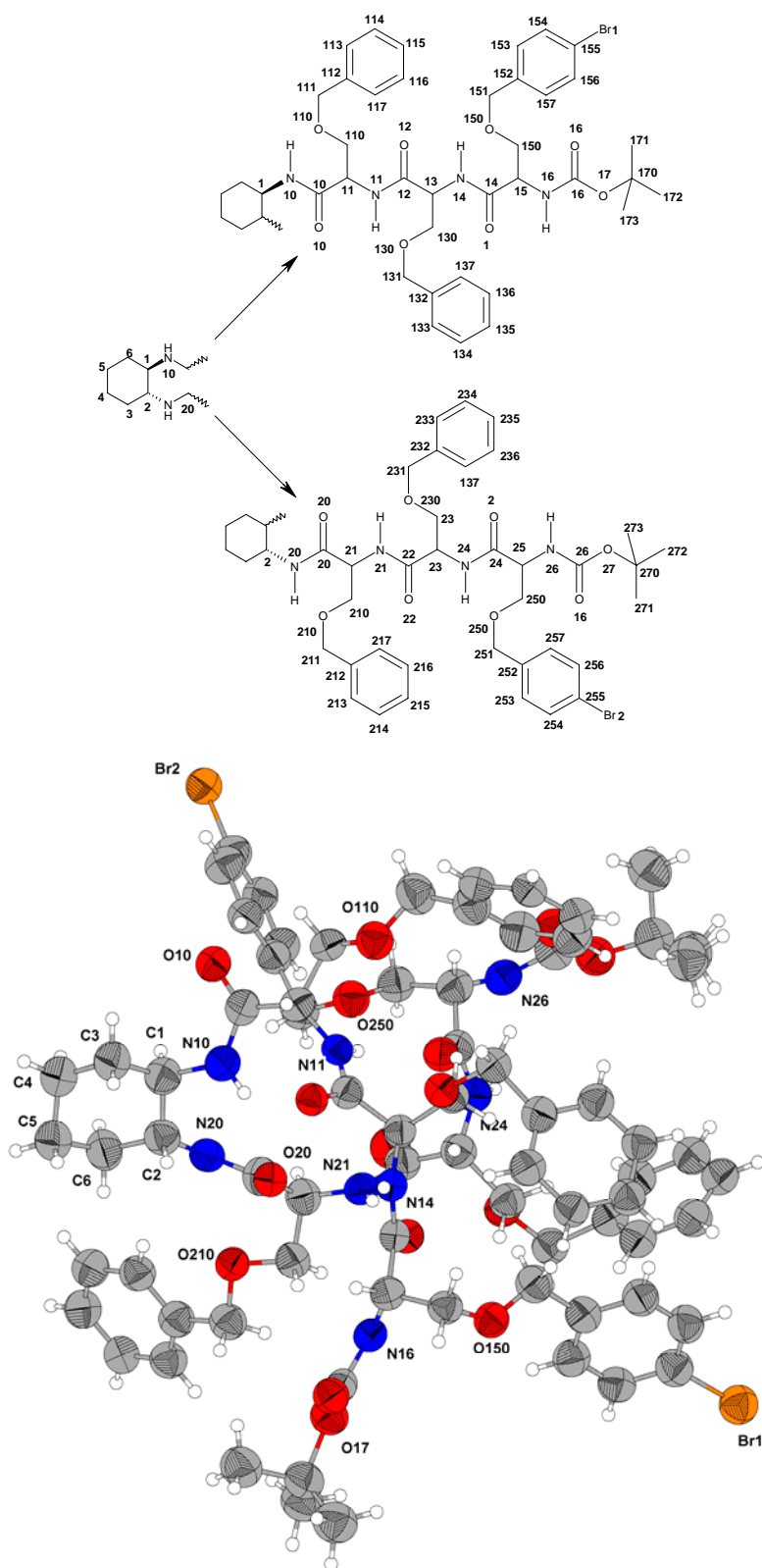


Figure S1. ORTEP view of the first symmetry independent molecule **A** with the numbering scheme adopted. Ellipsoids drawn at 30% probability level. Hydrogen atoms are represented by sphere of arbitrary size.

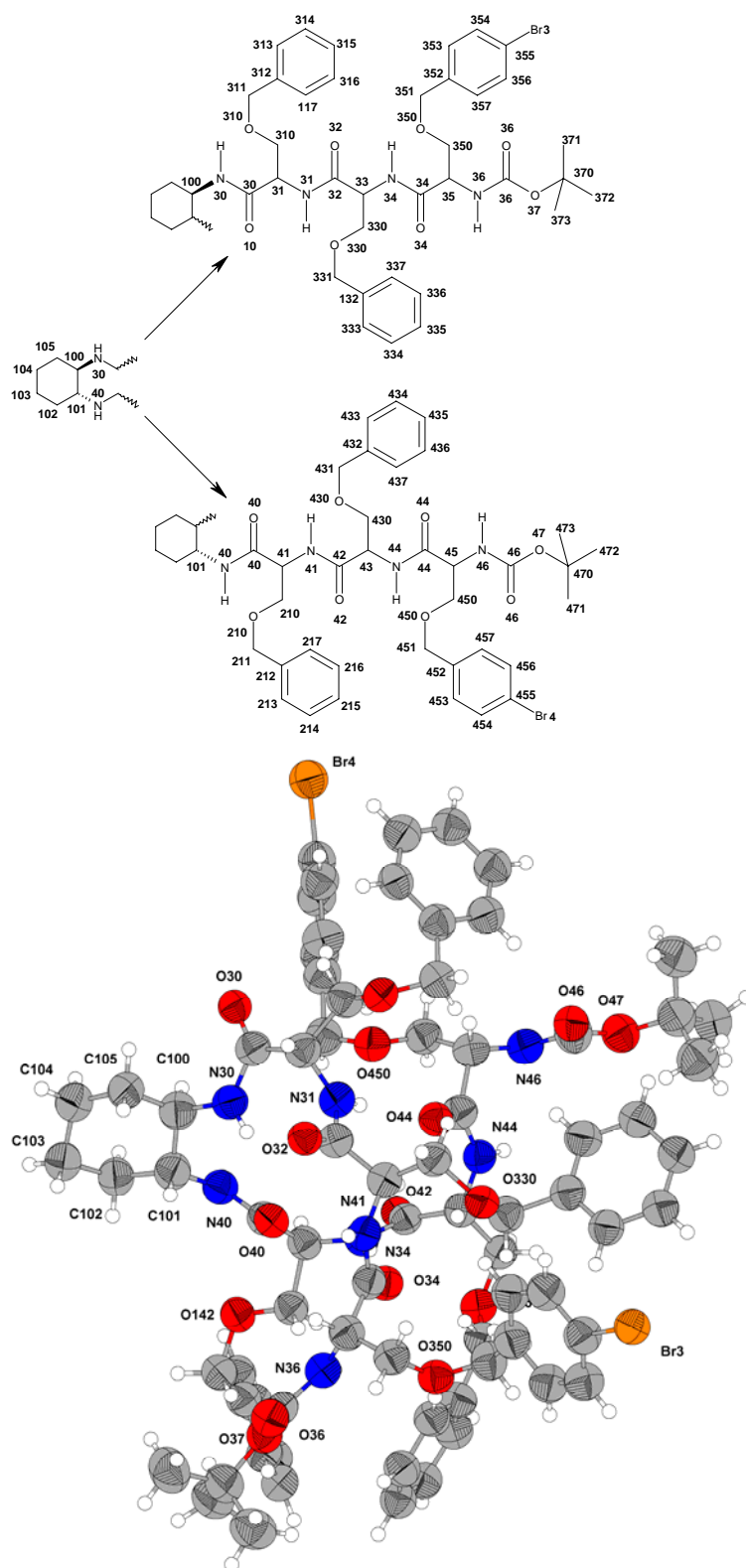


Figure S2. ORTEP view of the second symmetry independent molecule **B** with the numbering scheme adopted. Ellipsoids drawn at 30% probability level. Hydrogen atoms are represented by sphere of arbitrary size.

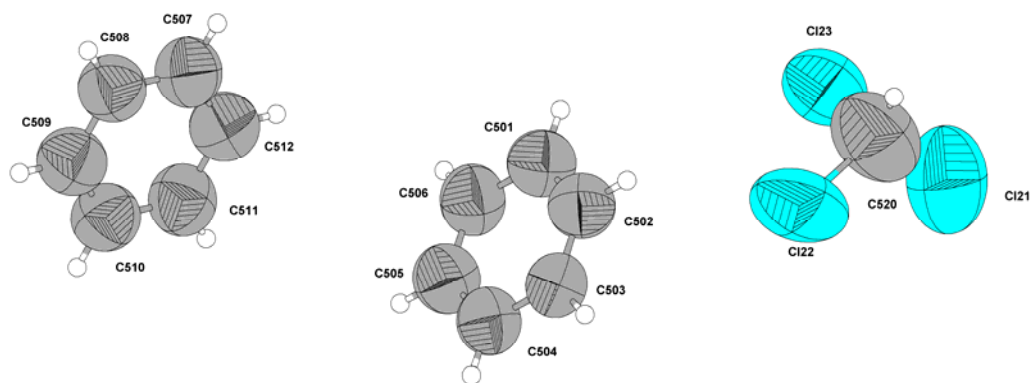


Figure **S3**. ORTEP view of the solvent molecules with the numbering scheme adopted. Ellipsoids drawn at 30% probability level. Hydrogen atoms are represented by sphere of arbitrary size.

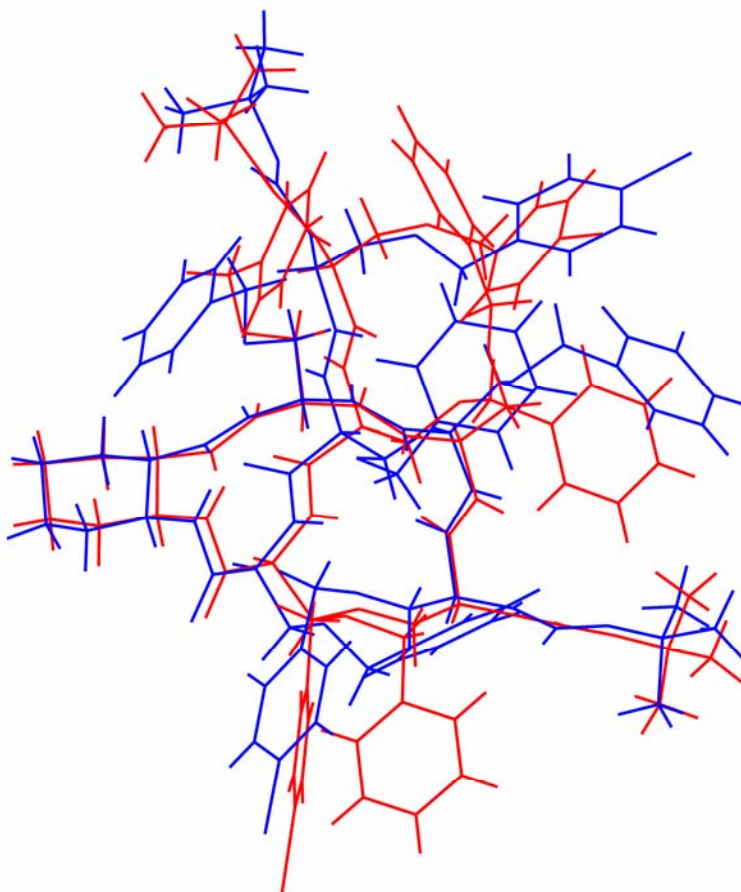


Figure **S4**. Superposition of the two symmetry independent molecules **A** and **B**.

Figure S 5. ^1H NMR dilution experiment in CDCl_3 on compounds **5** (A), **13** (B) and **18** (C).

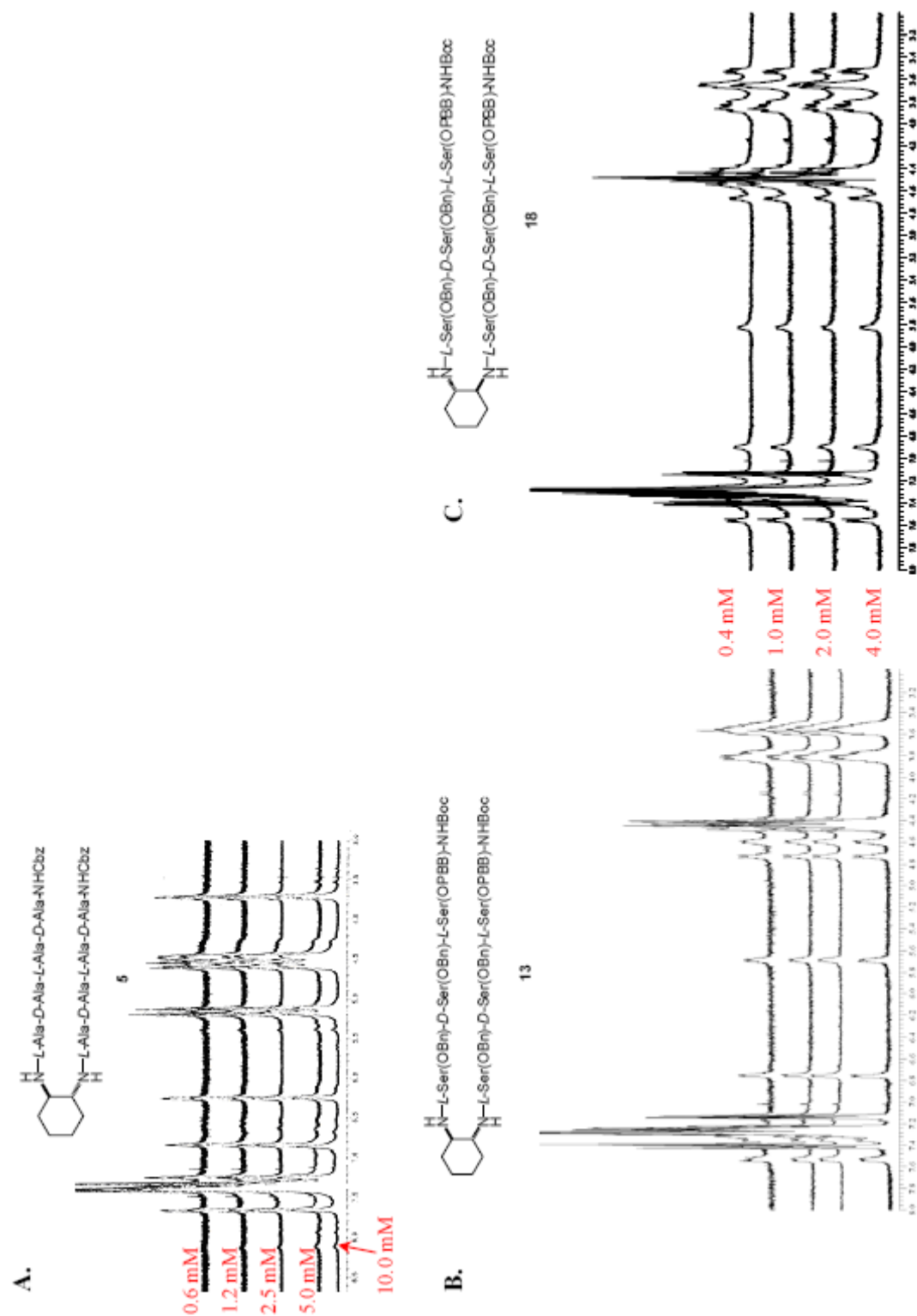


Figure S 6. ^1H NMR DMSO- d_6 titration experiments in CDCl_3 for compounds **5** (A), **11** (B), **13** (C) and **18** (D).

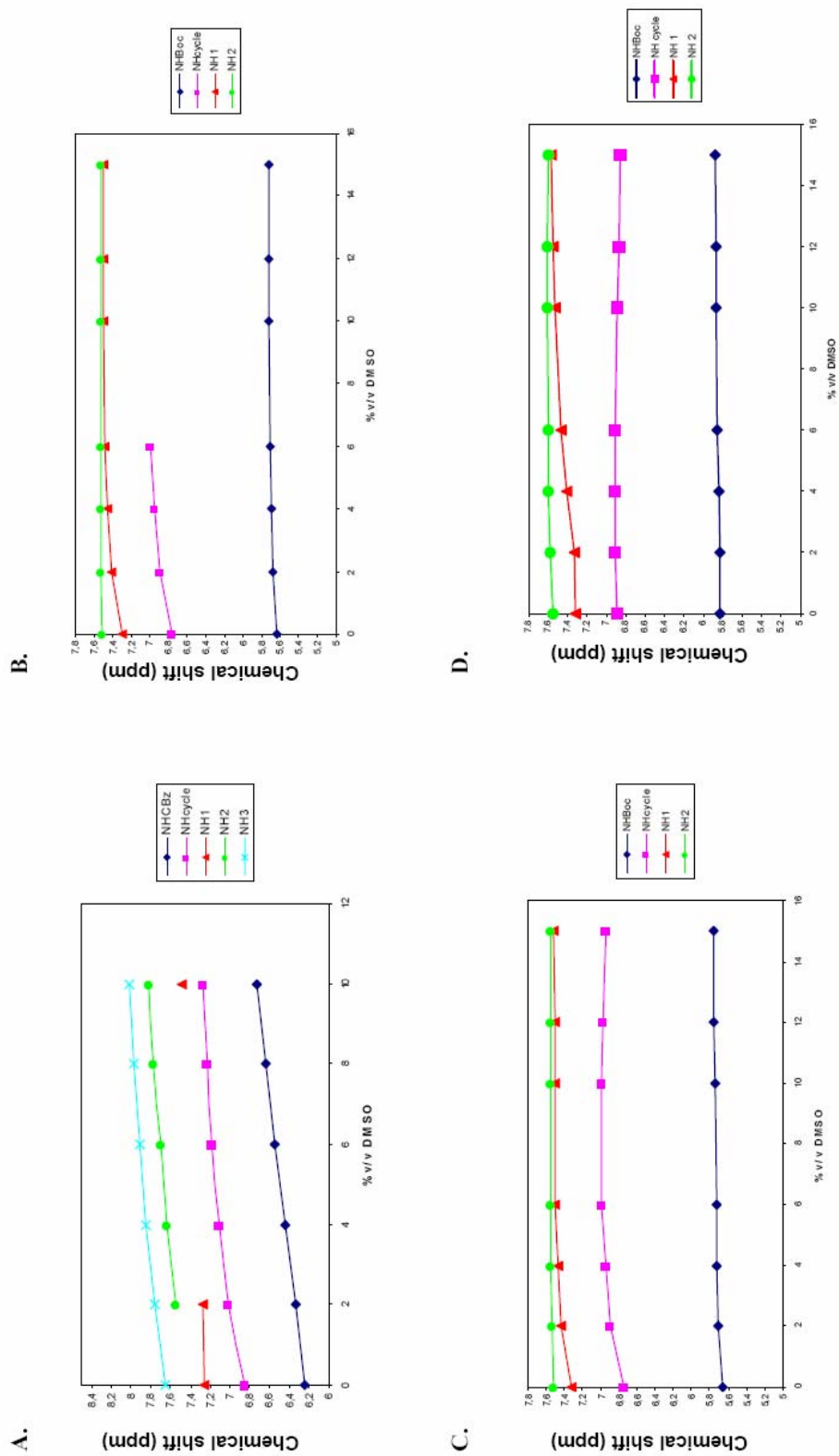
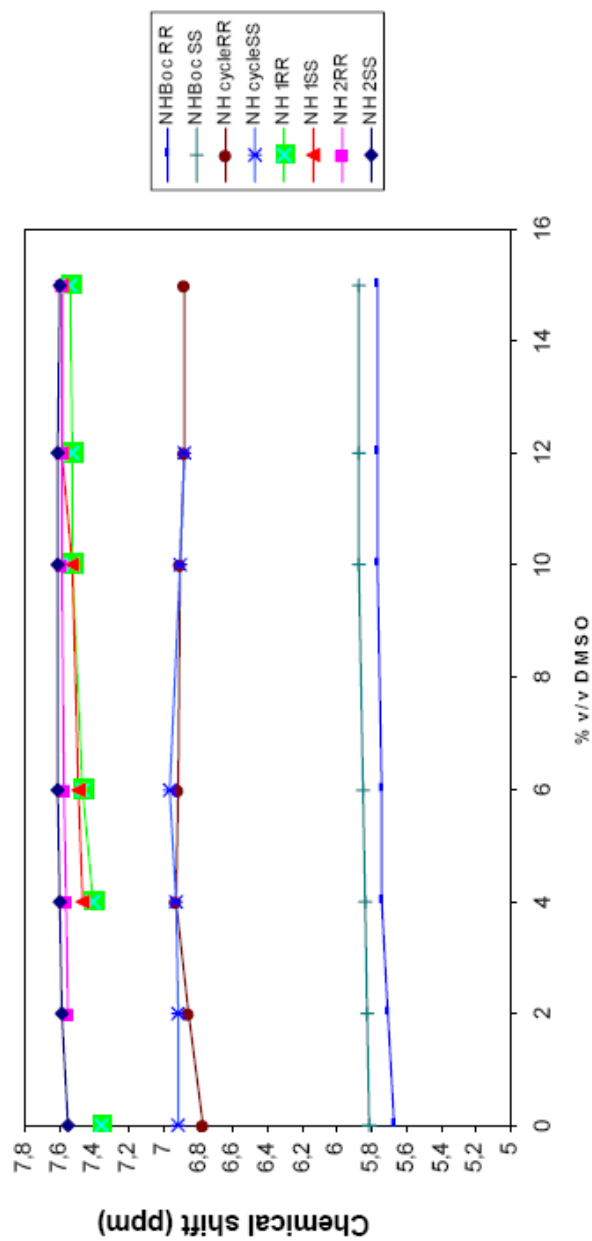


Figure S7. ^1H NMR DMSO- d_6 titration experiment in CDCl_3 on a 1:1 mixture of compounds **13** and **18**.



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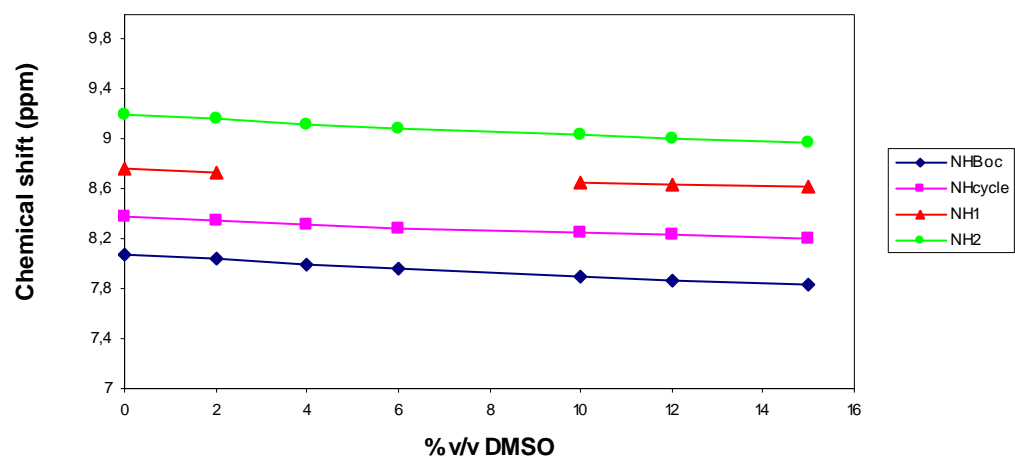
OPBB= p-bromobenzyl ether



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Figure S 8. ^1H NMR DMSO- d_6 titration (**A**) and MeOH d_4 exchange (**B**) experiments in Pyridine- d_5 for compound **14**.

A.



B.

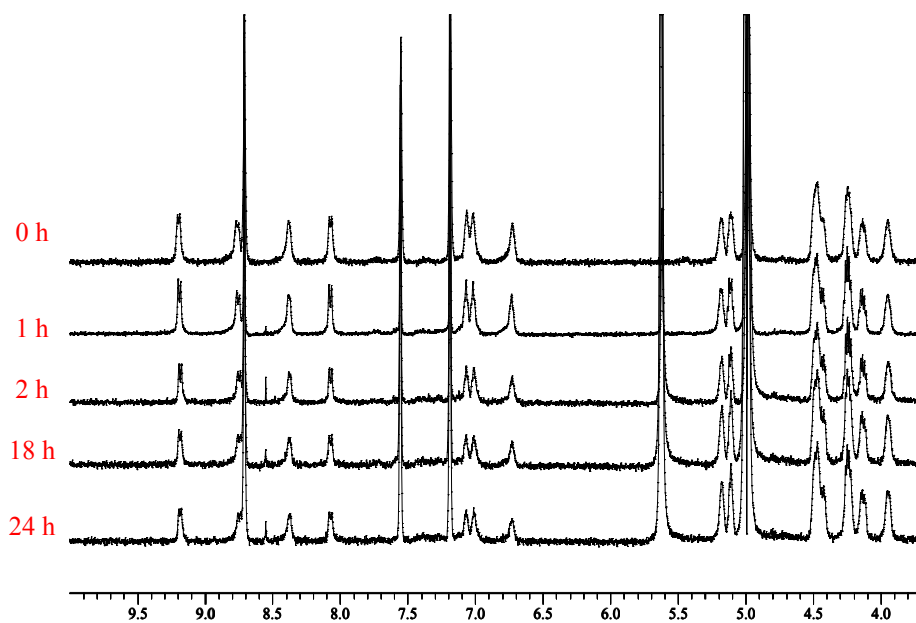
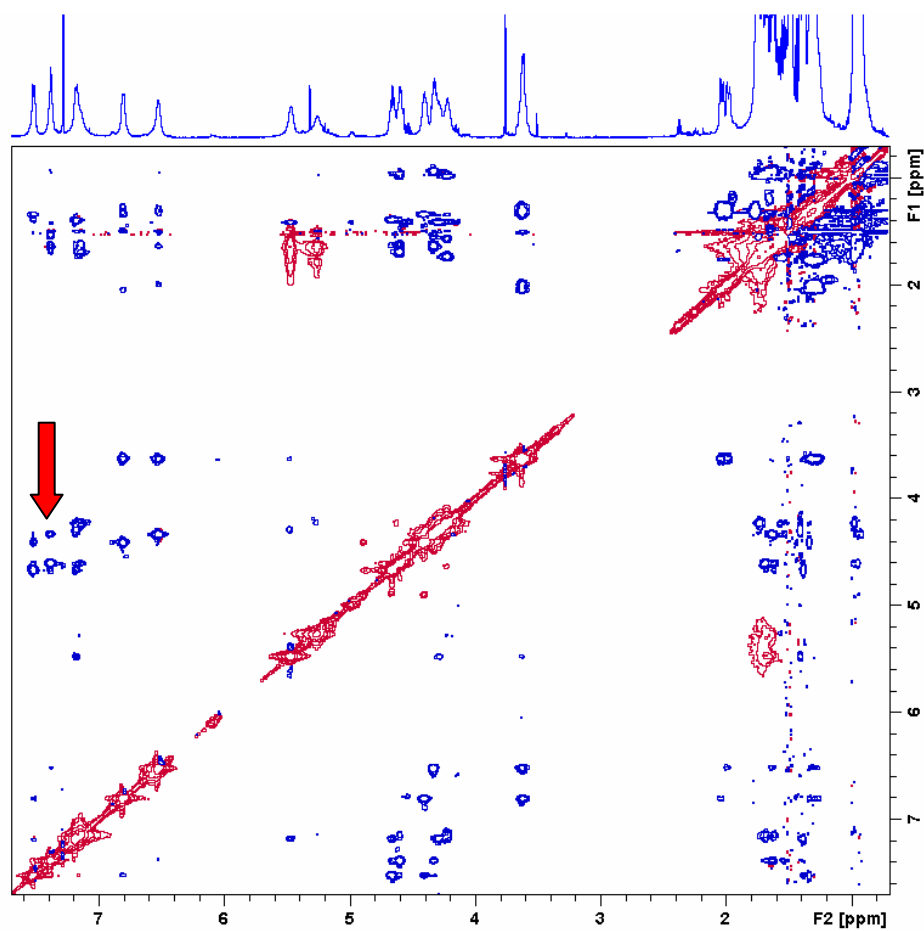


Figure S 9. Noesy spectrum of compound **27** showing the cross-talk between the two strands.



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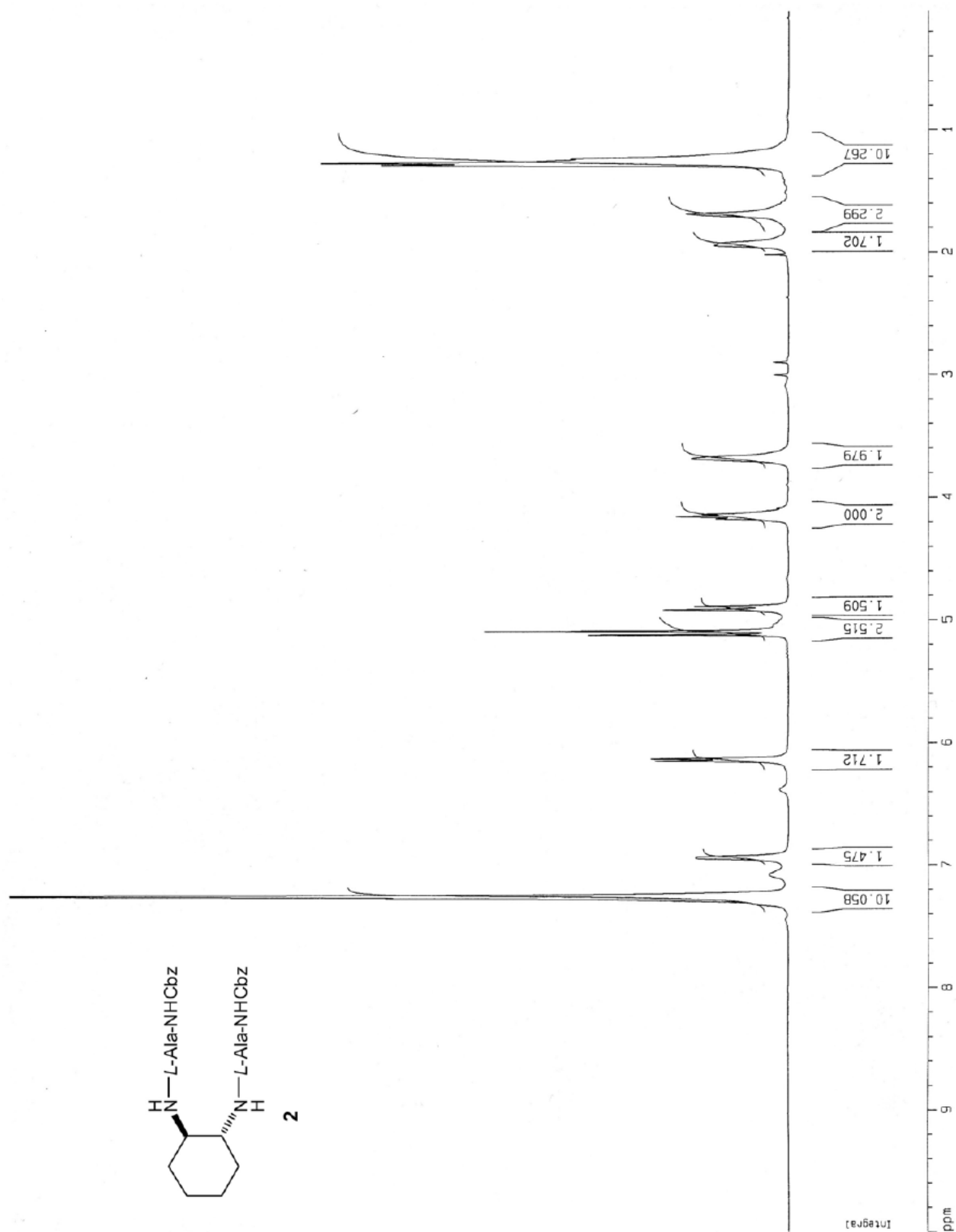
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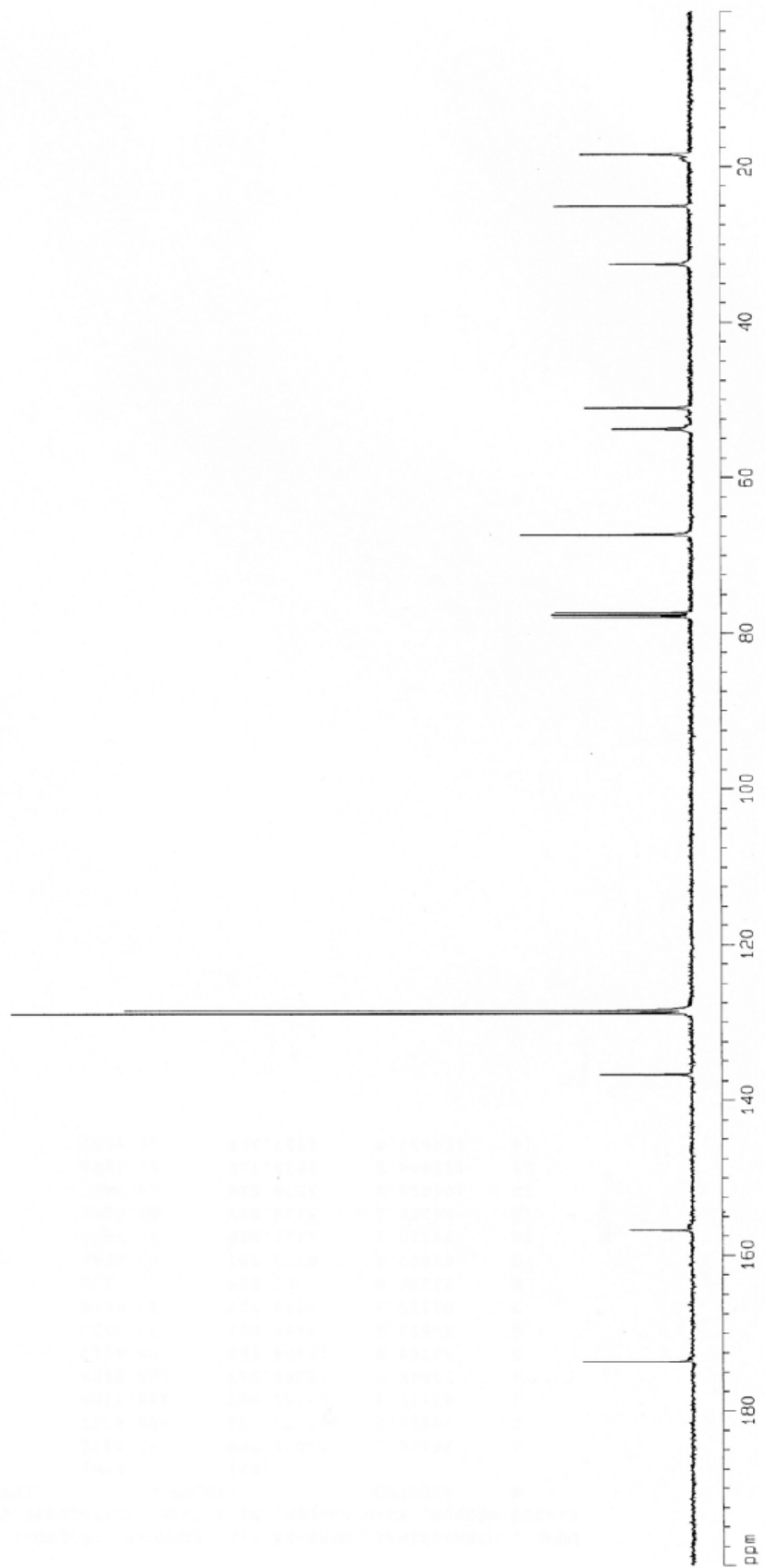
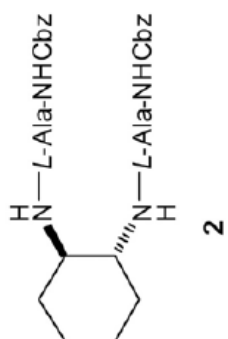
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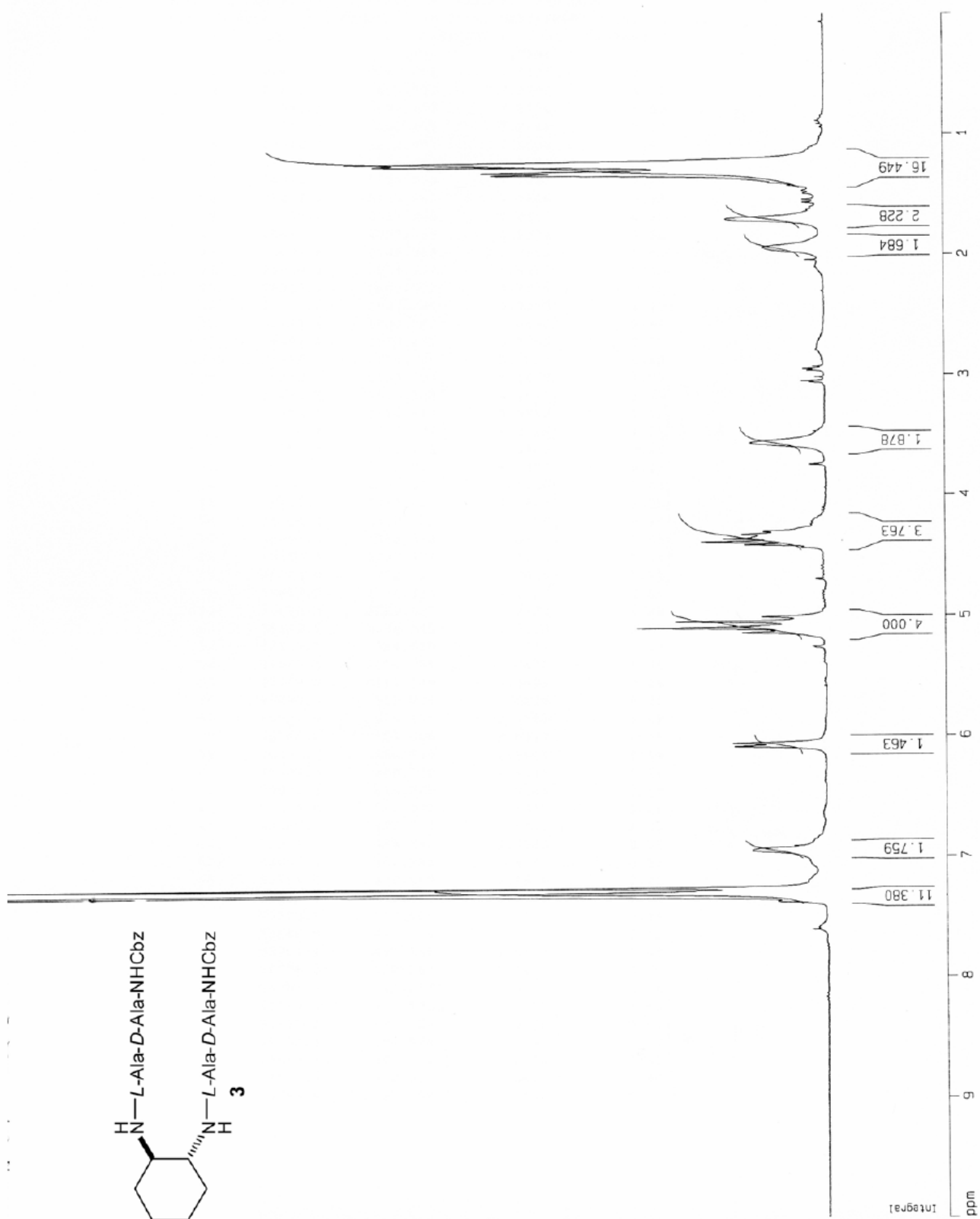
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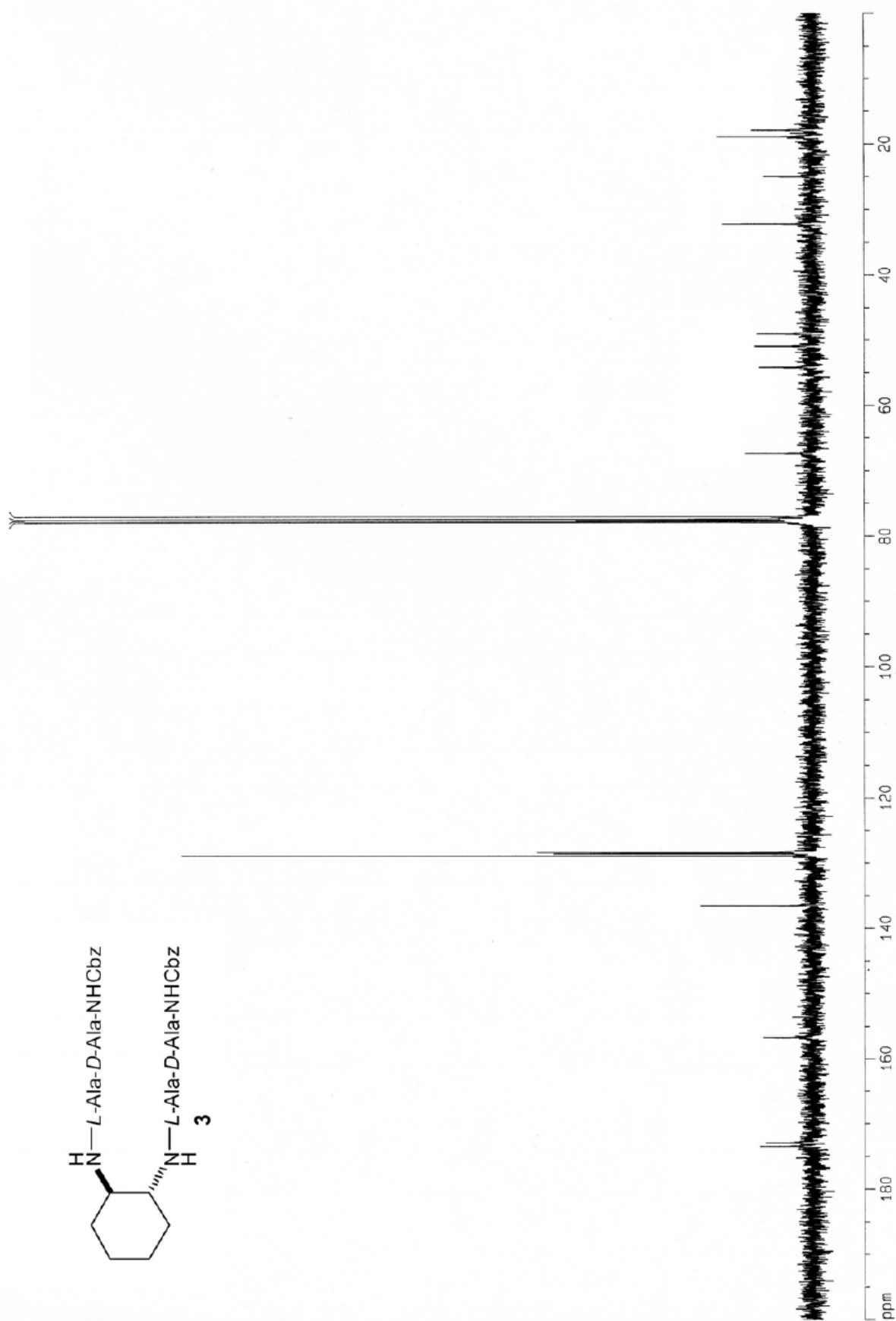
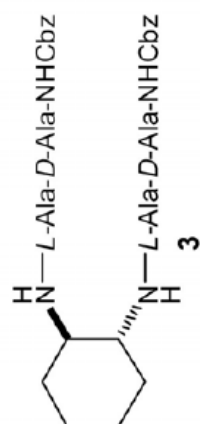
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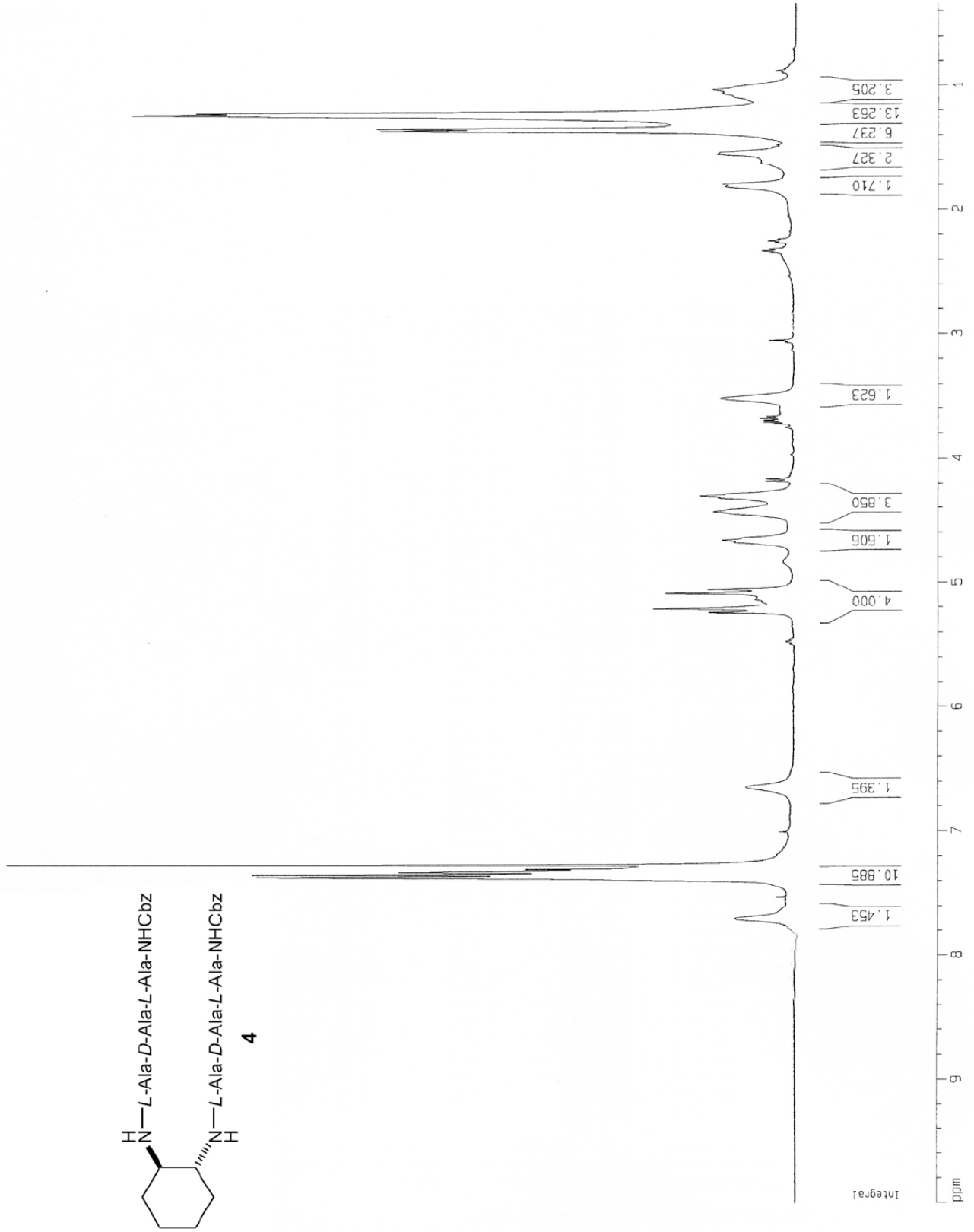
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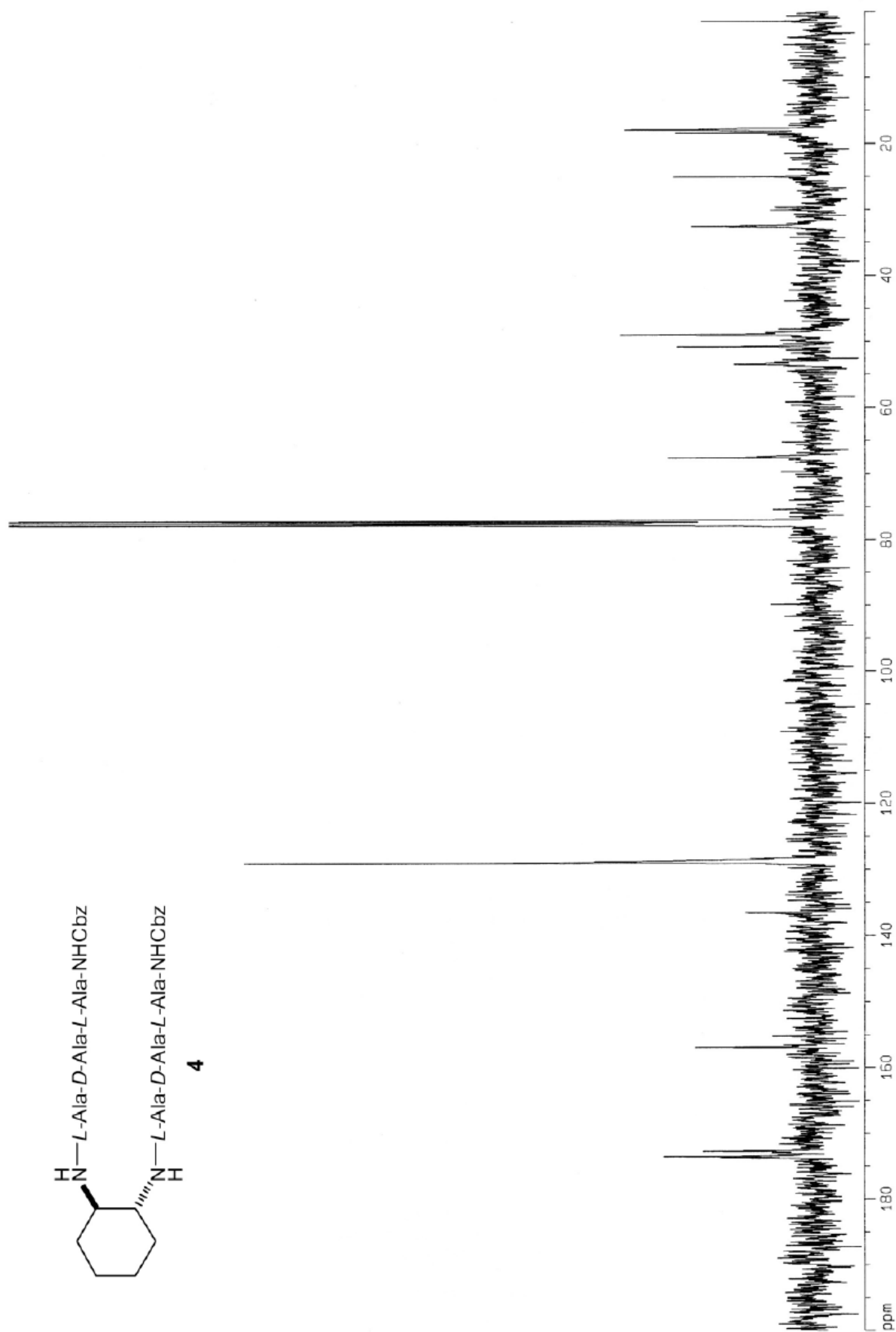
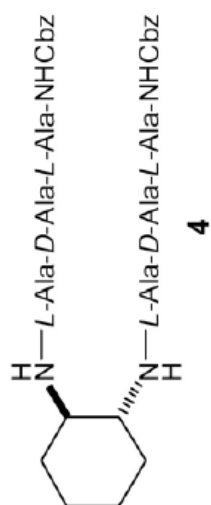


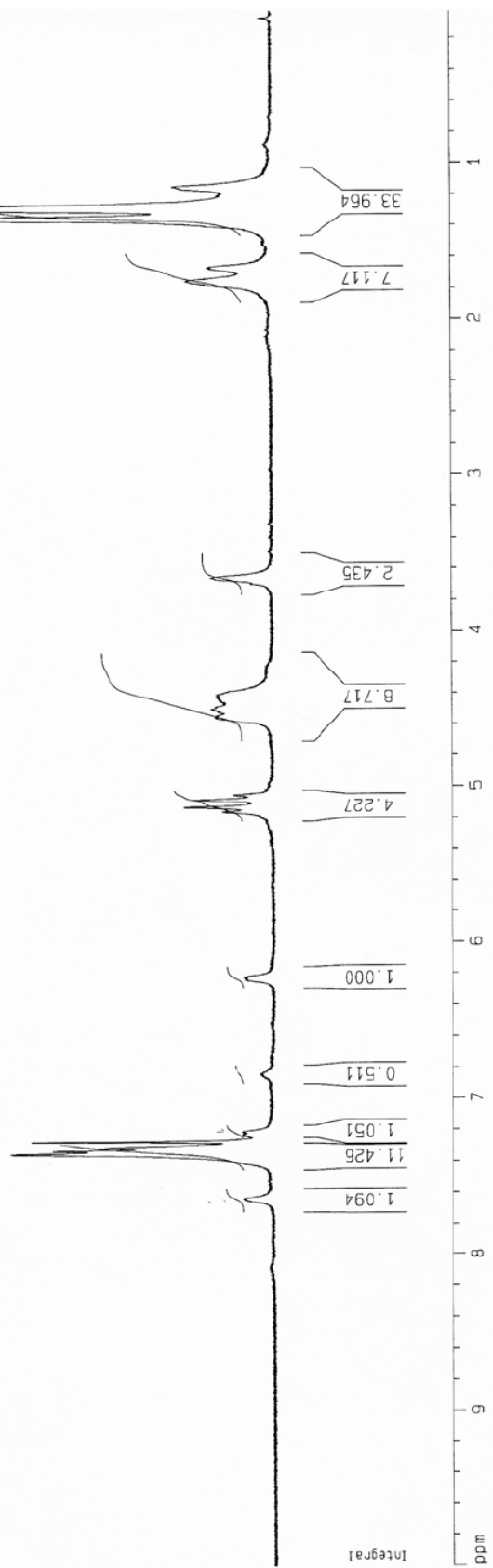
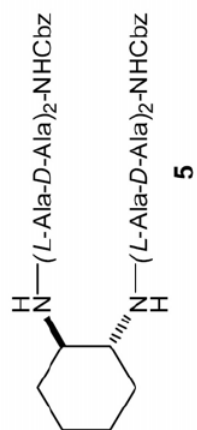


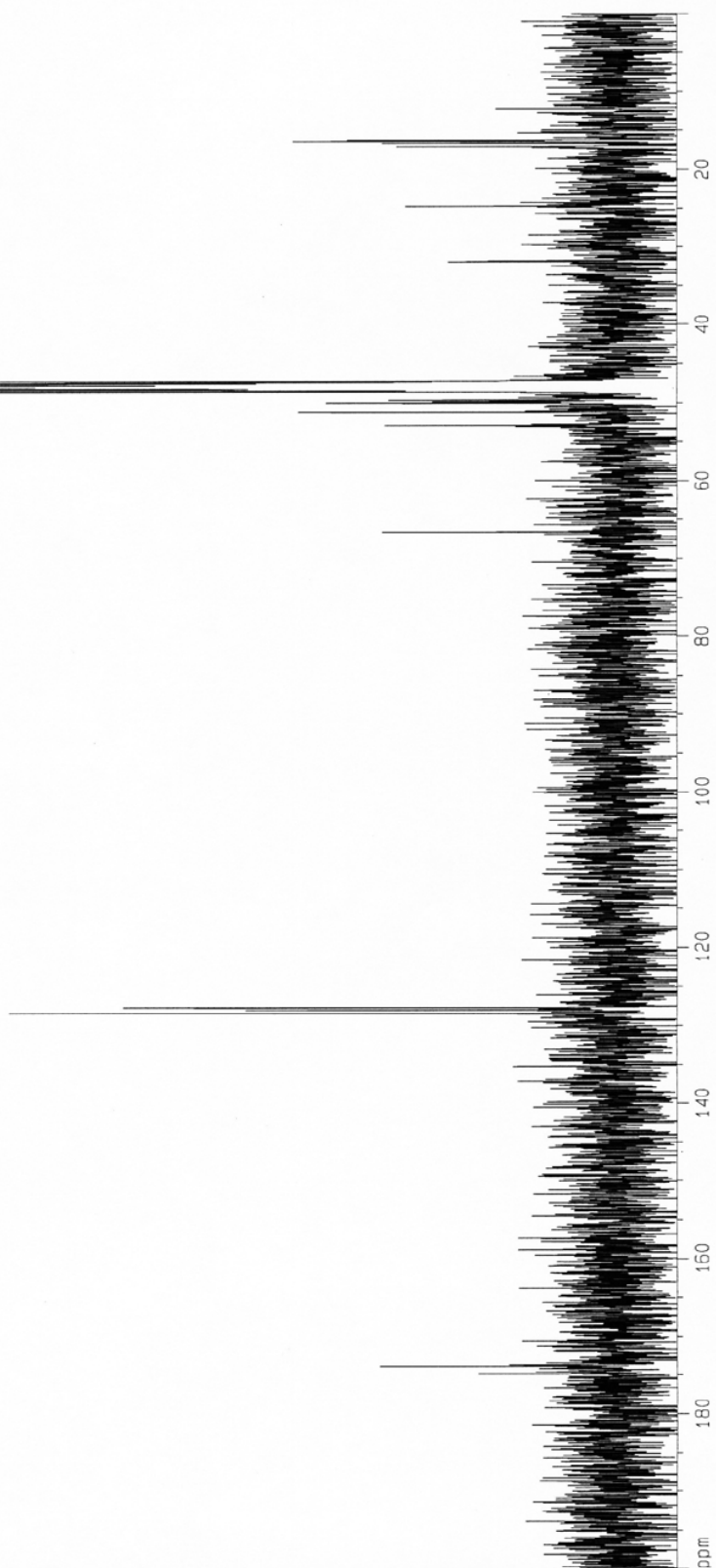


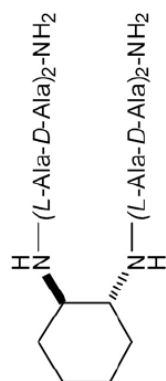




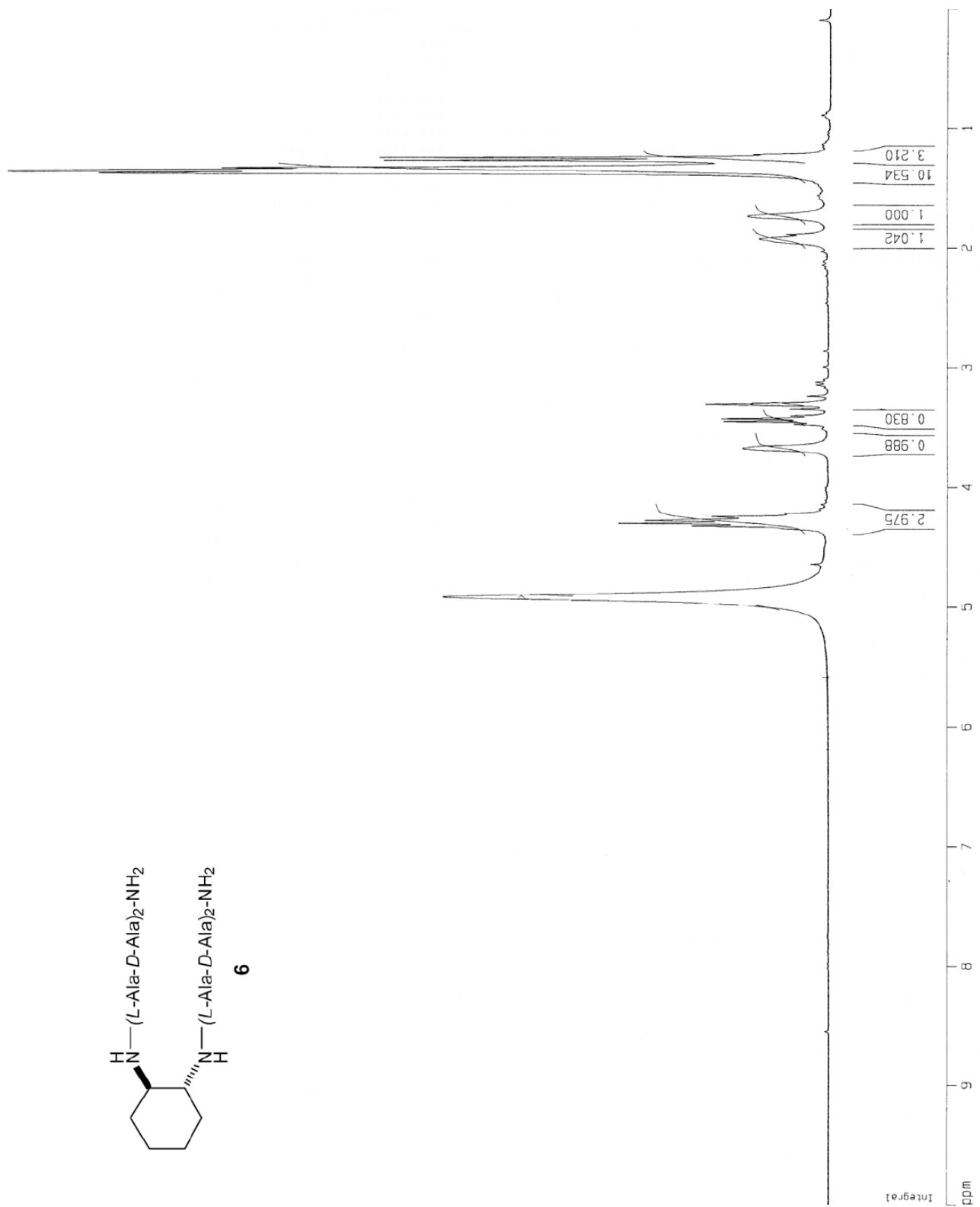


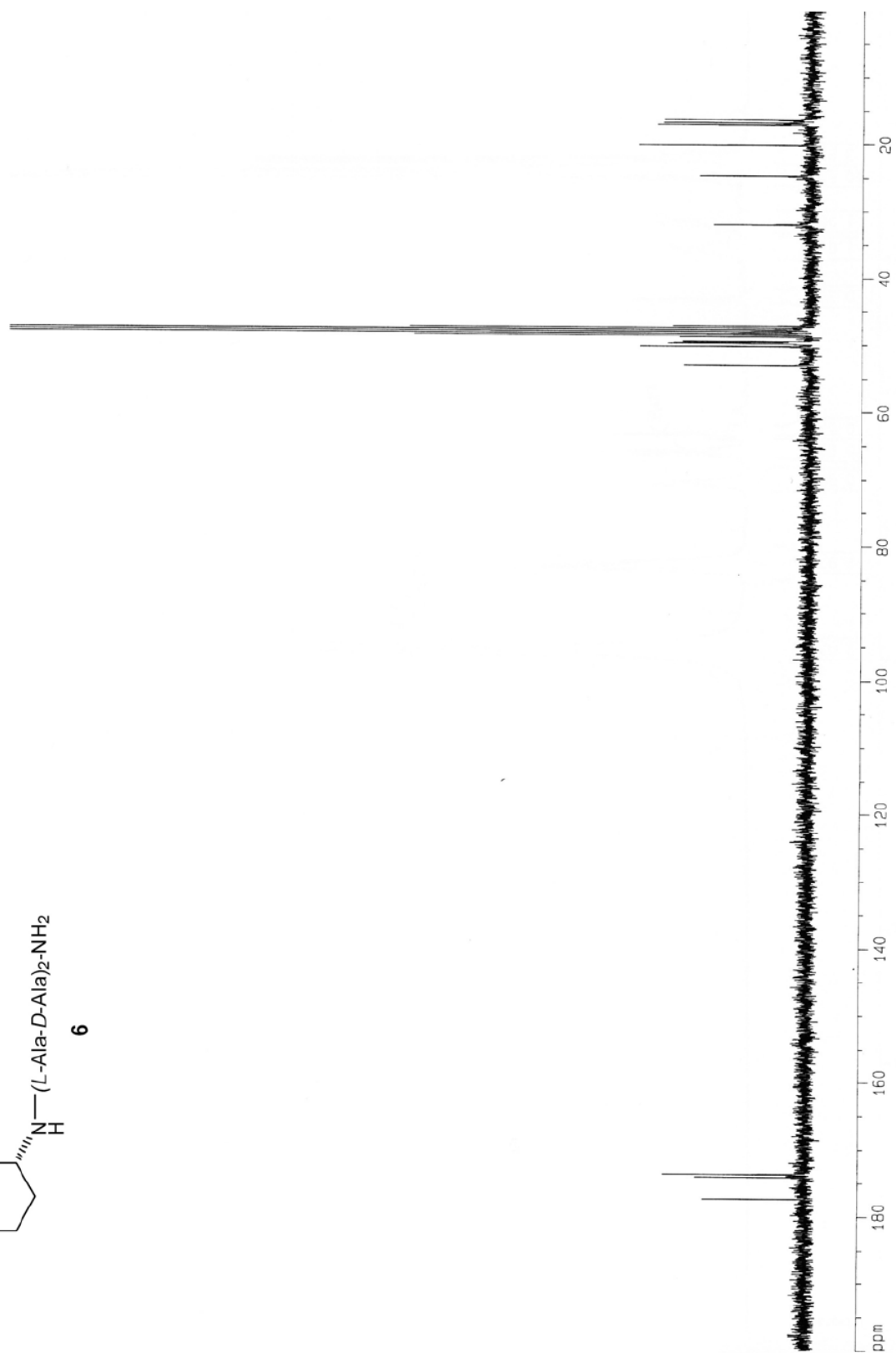
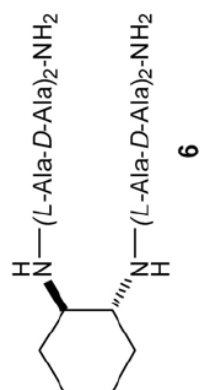


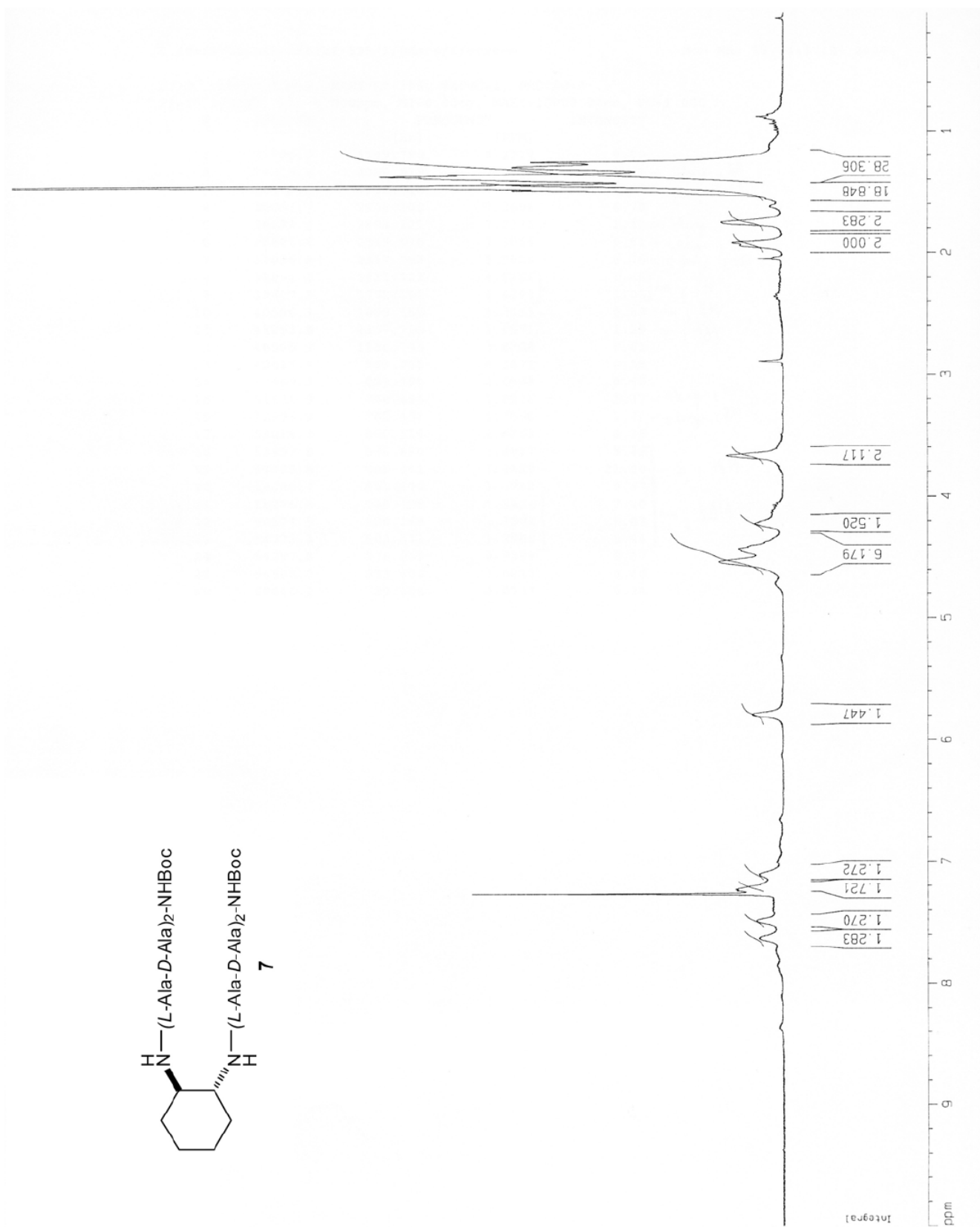


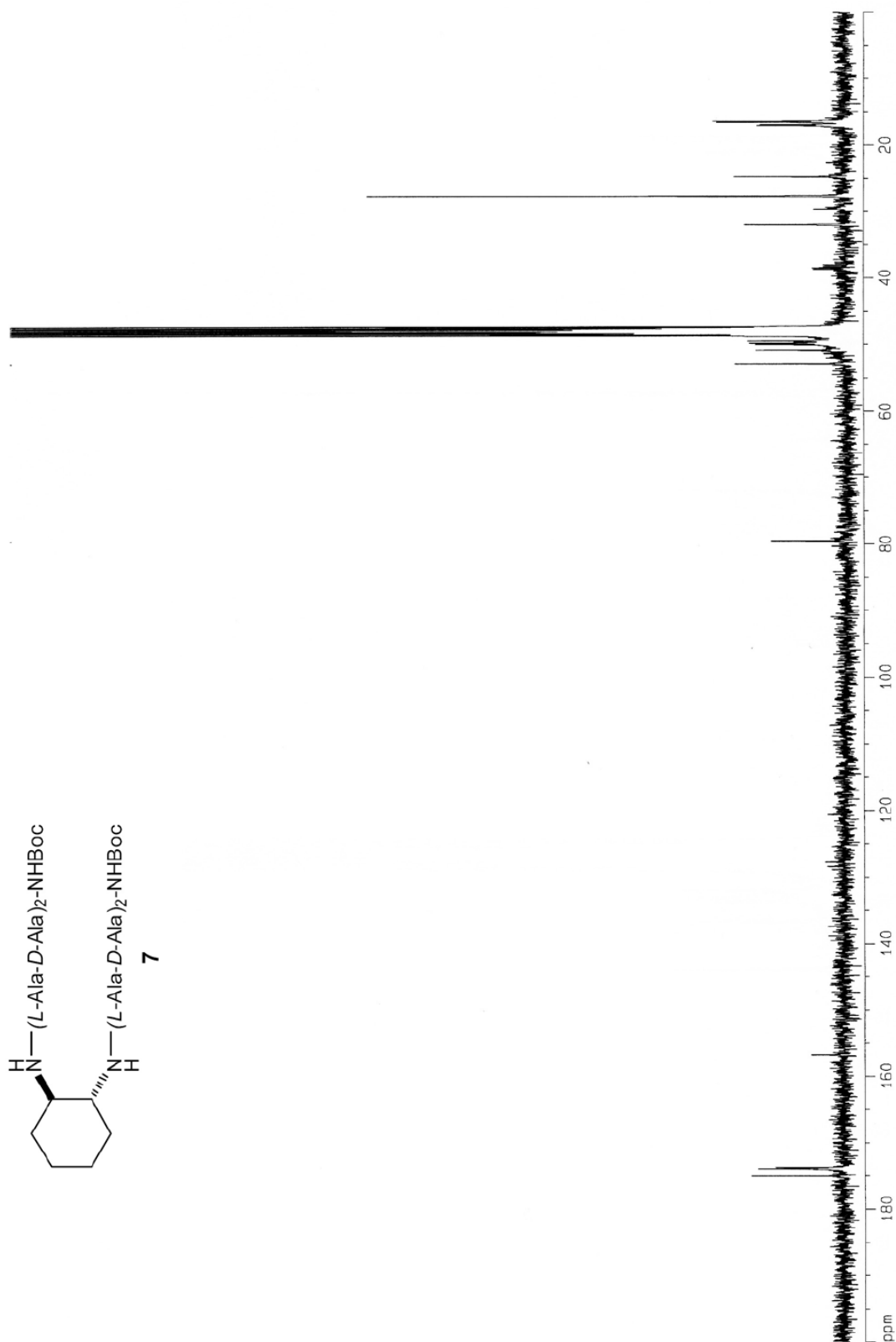
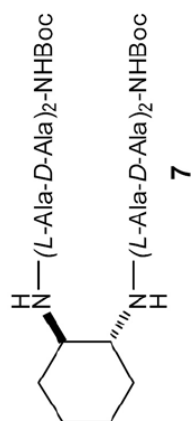


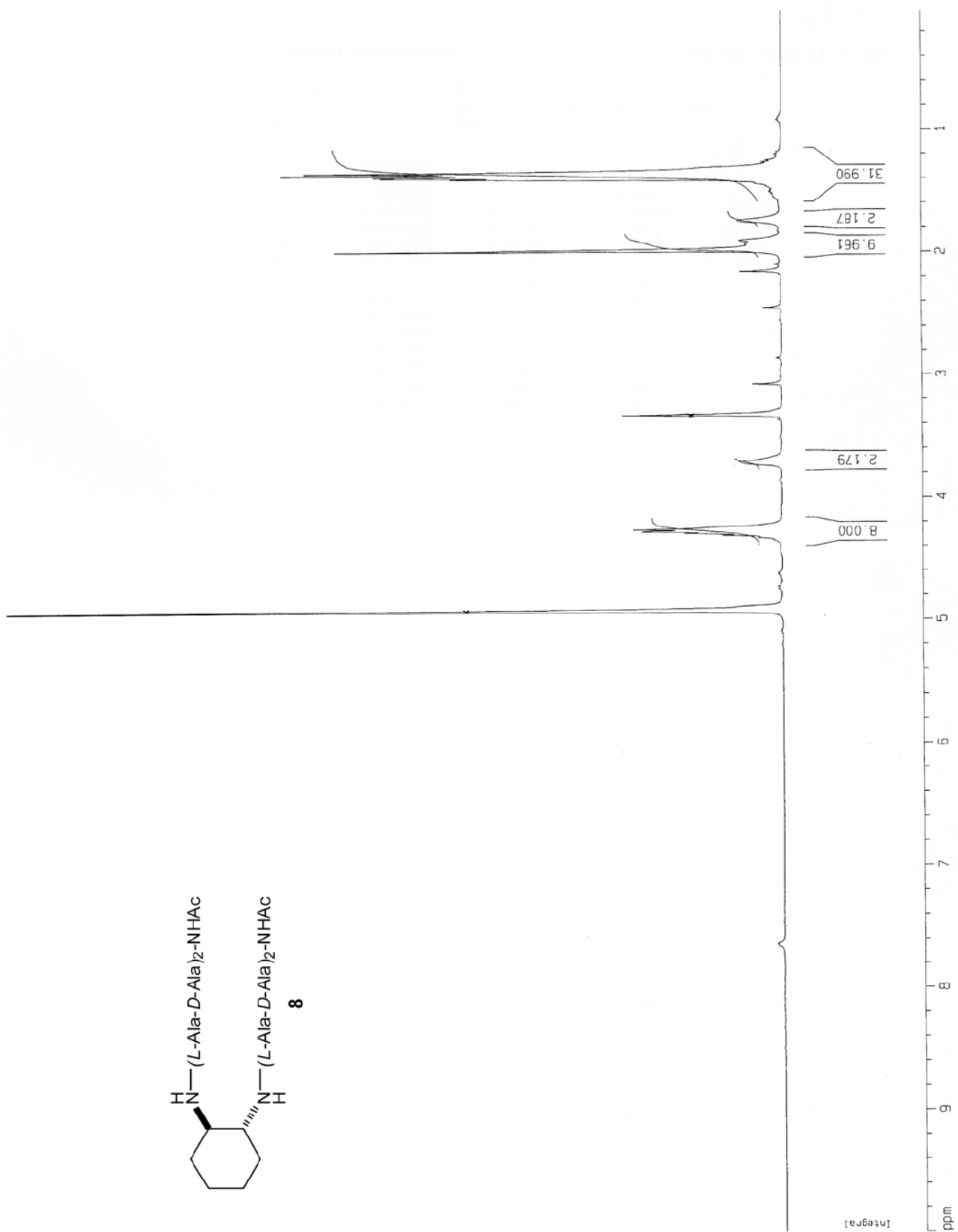
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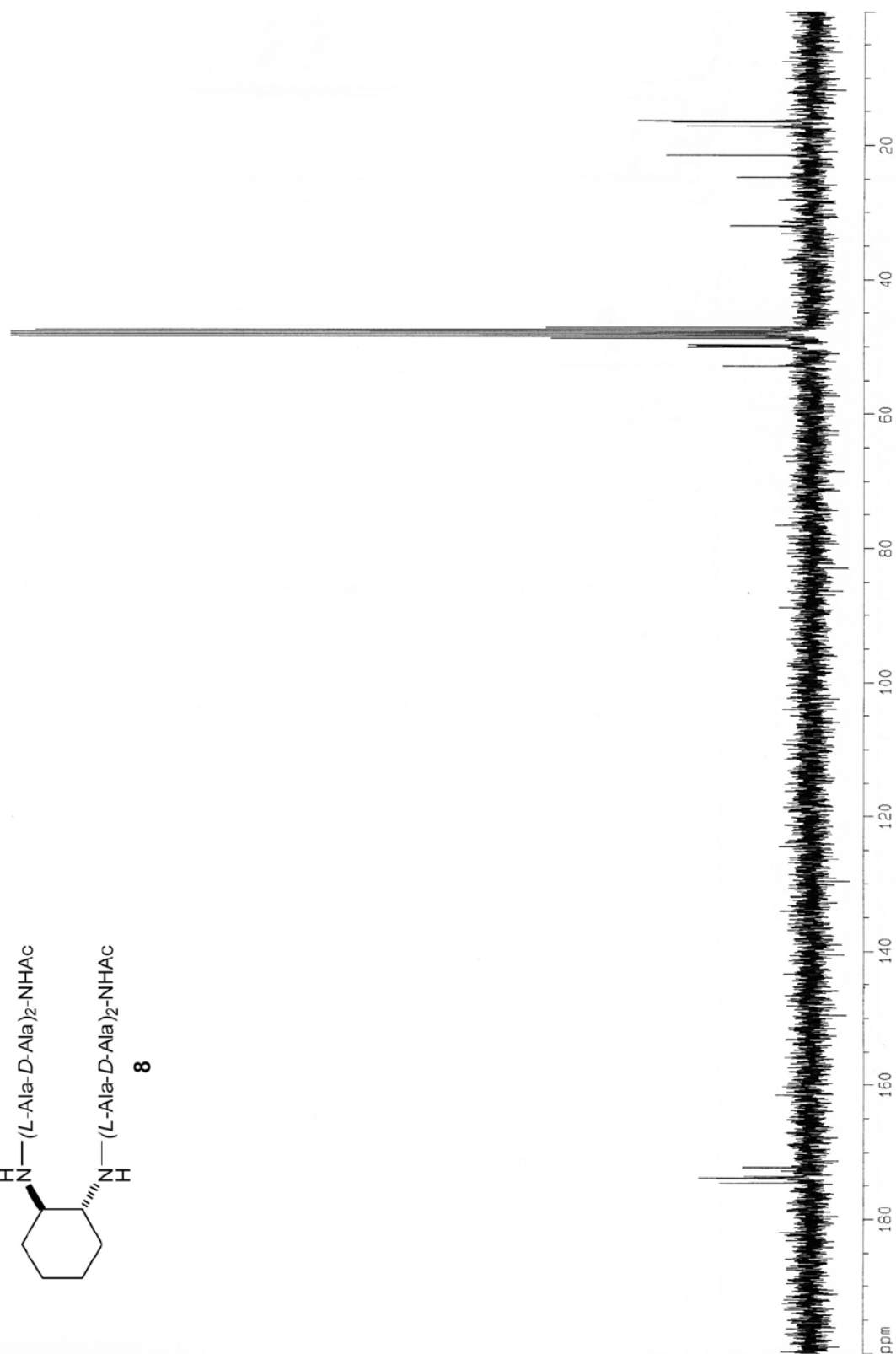
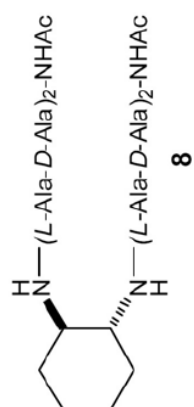


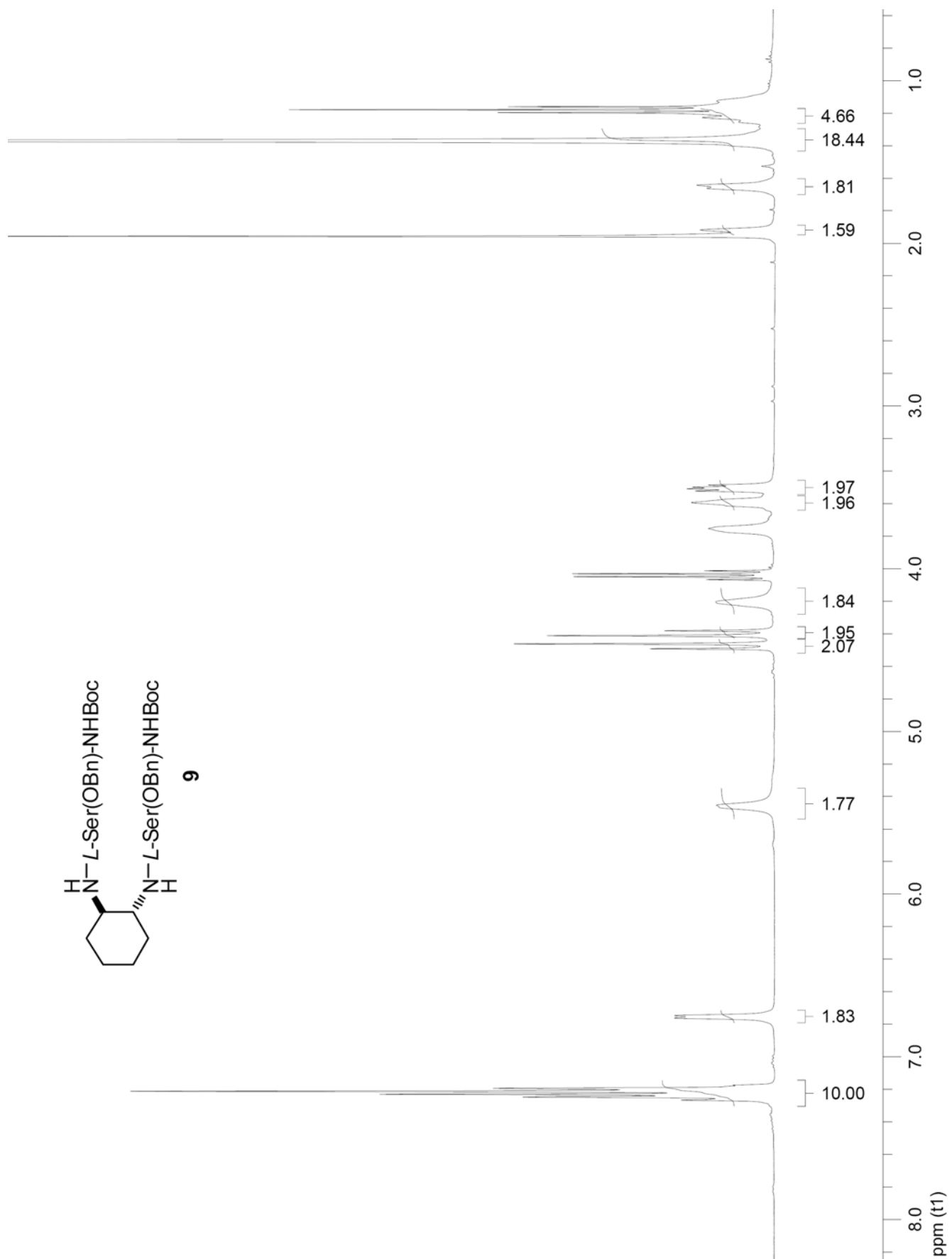


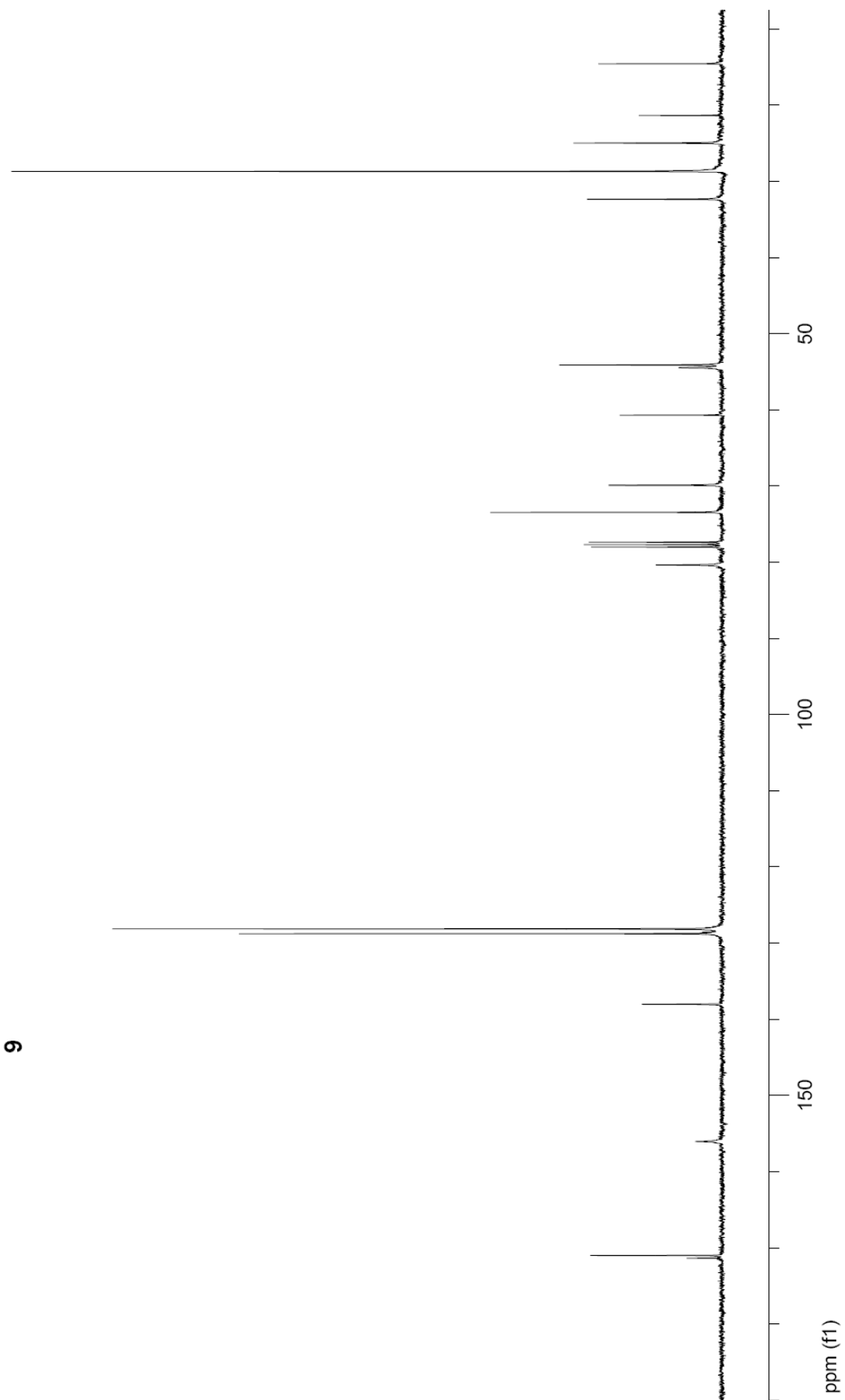
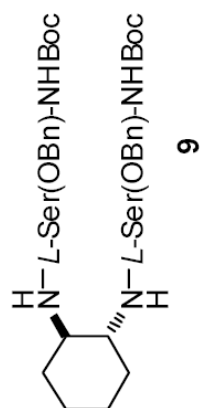


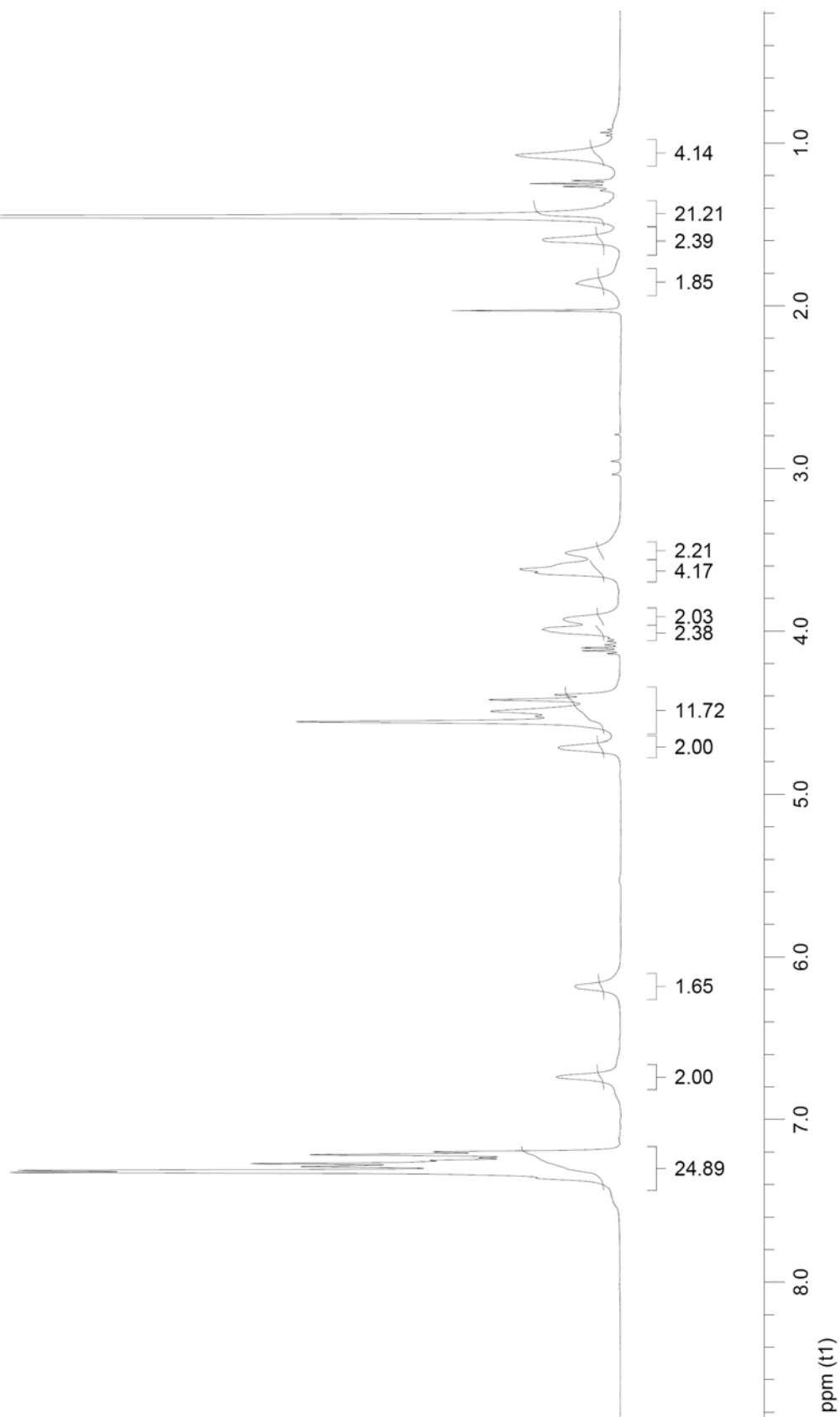
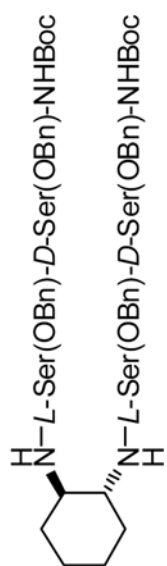


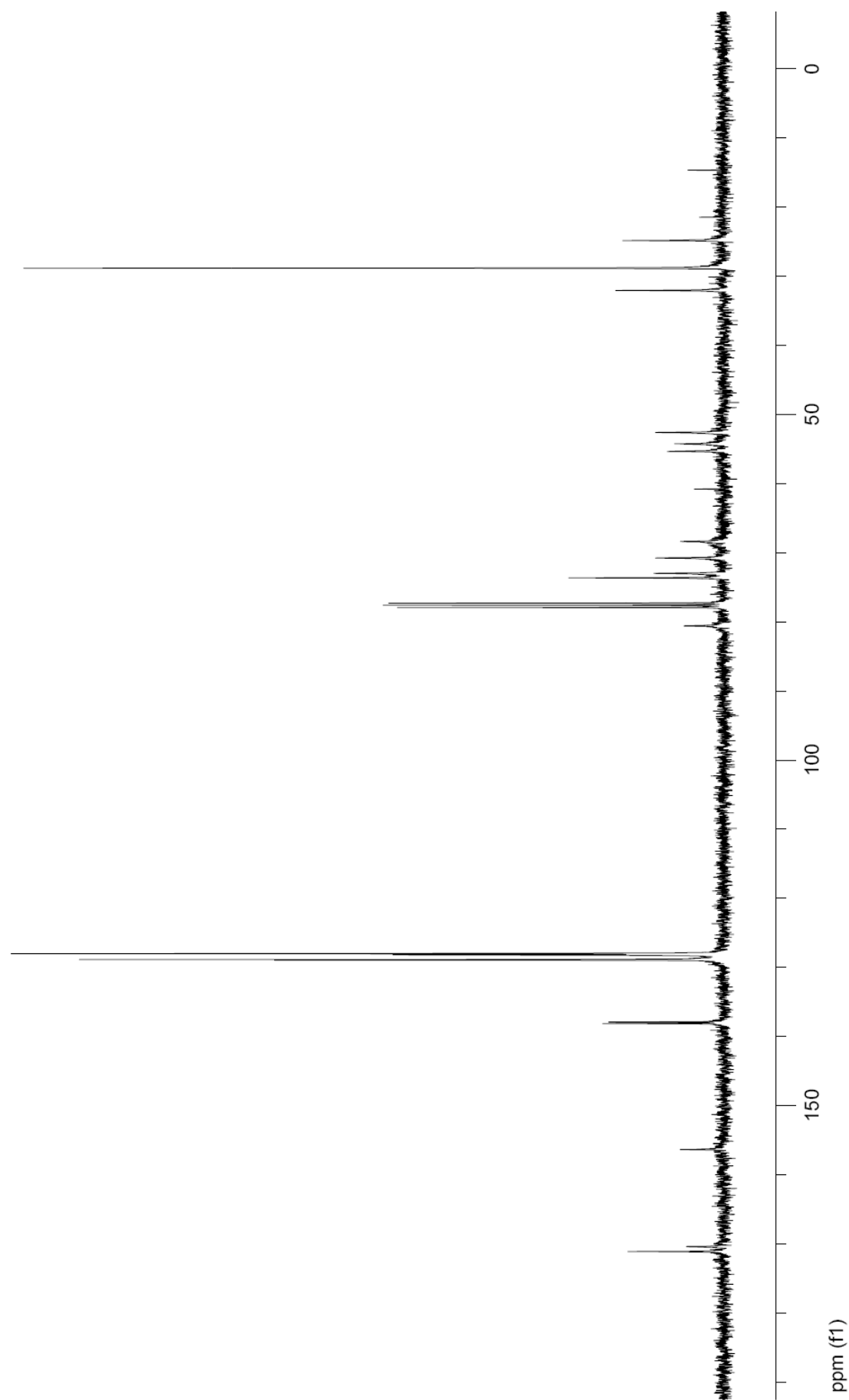
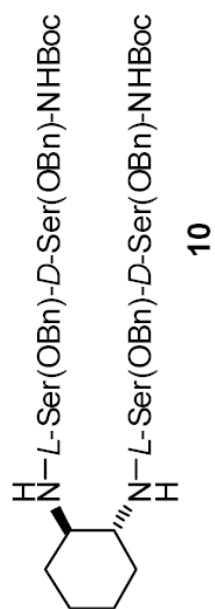


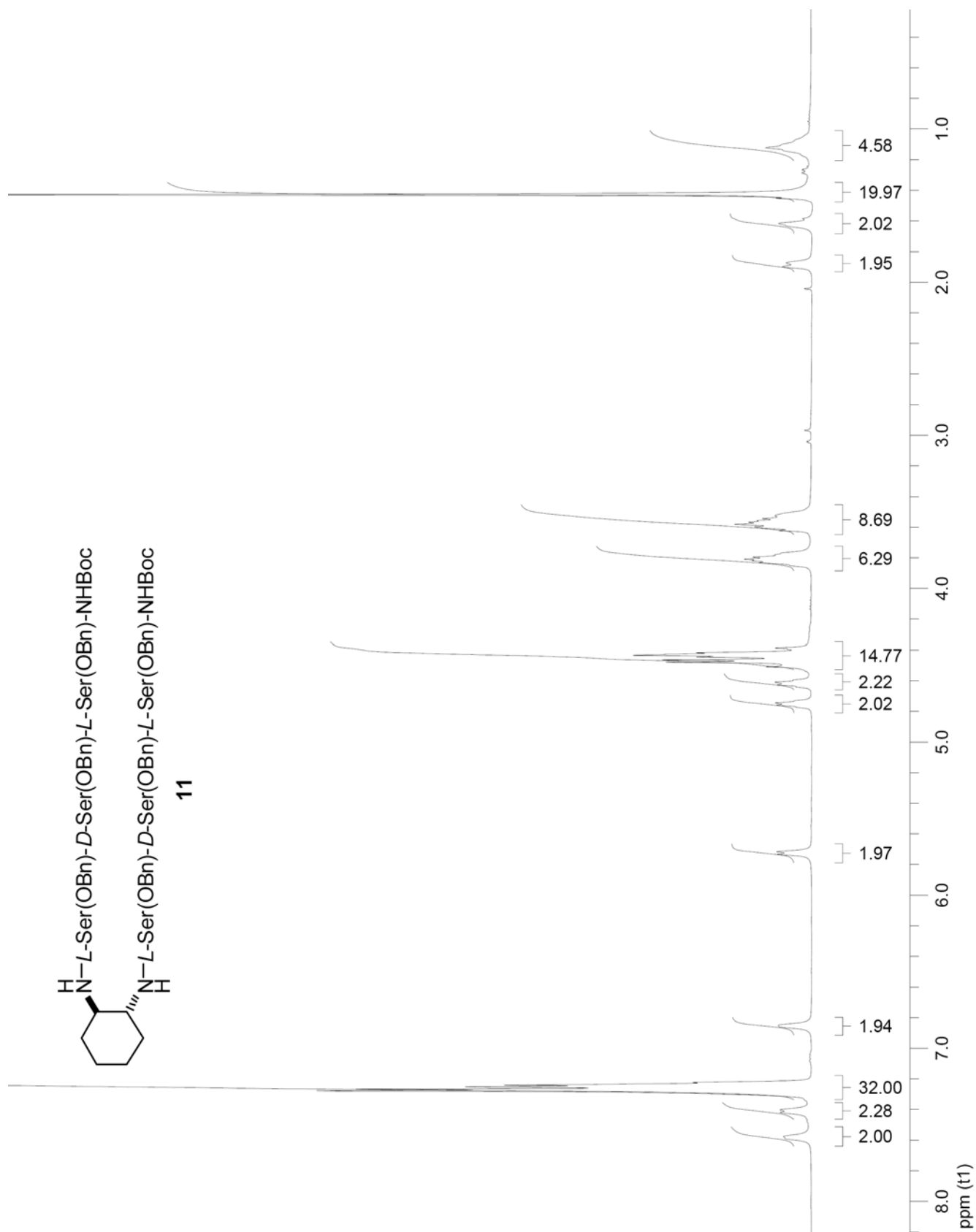


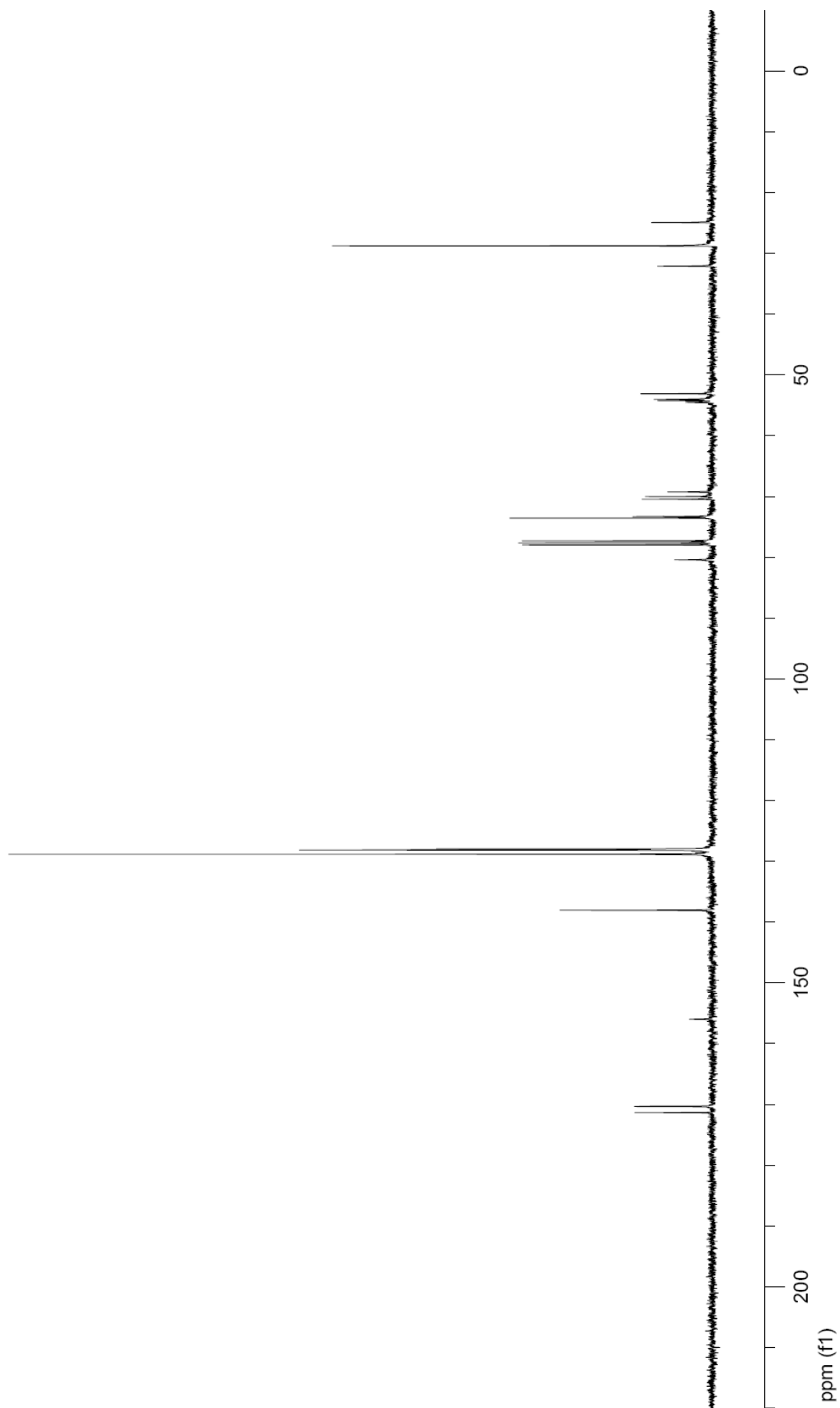
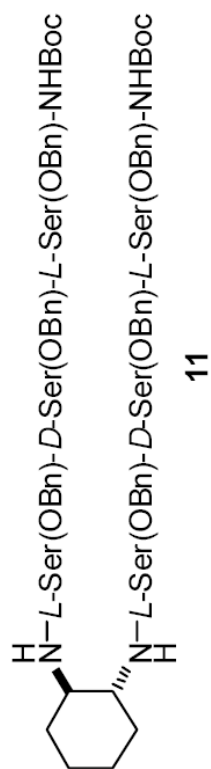


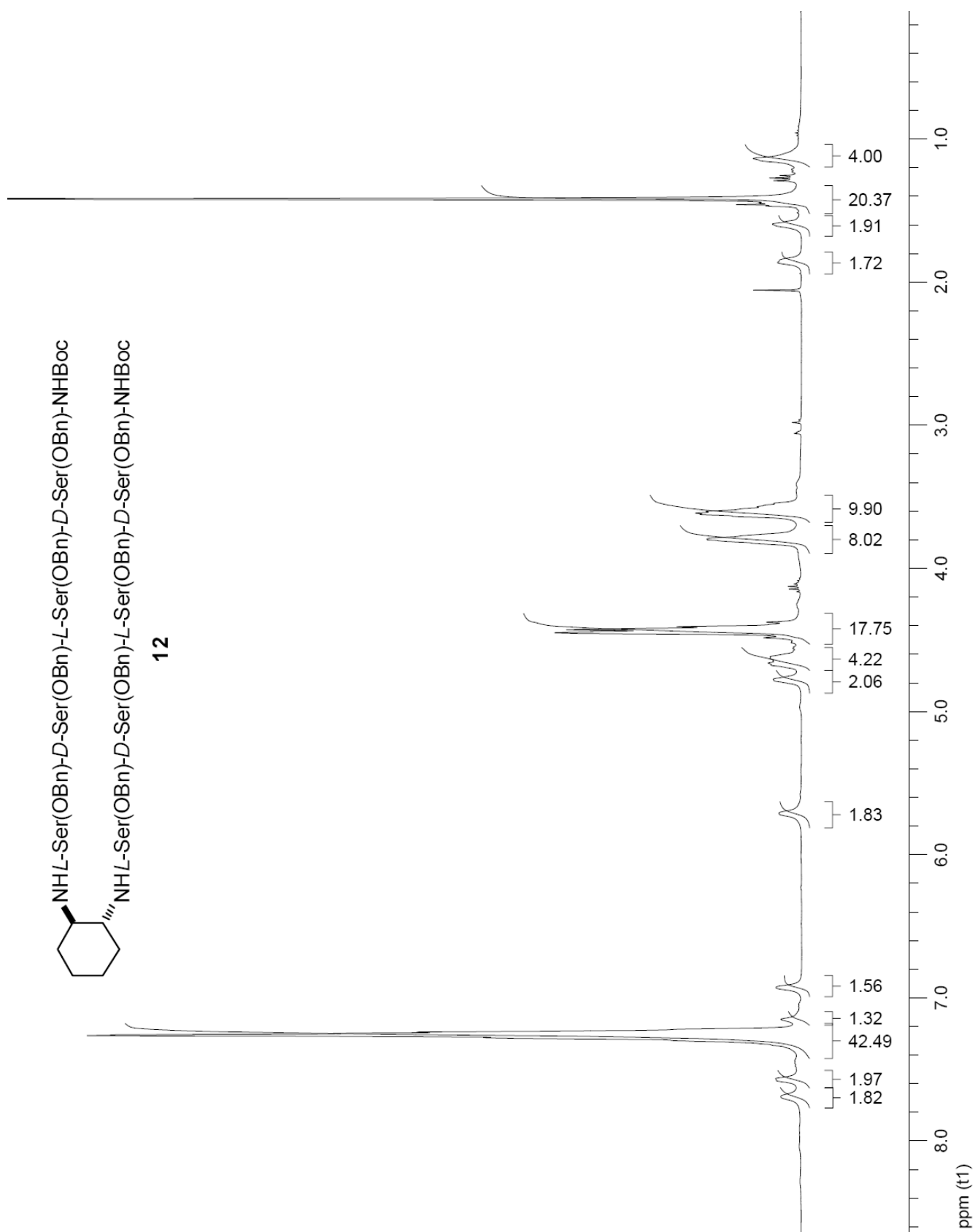






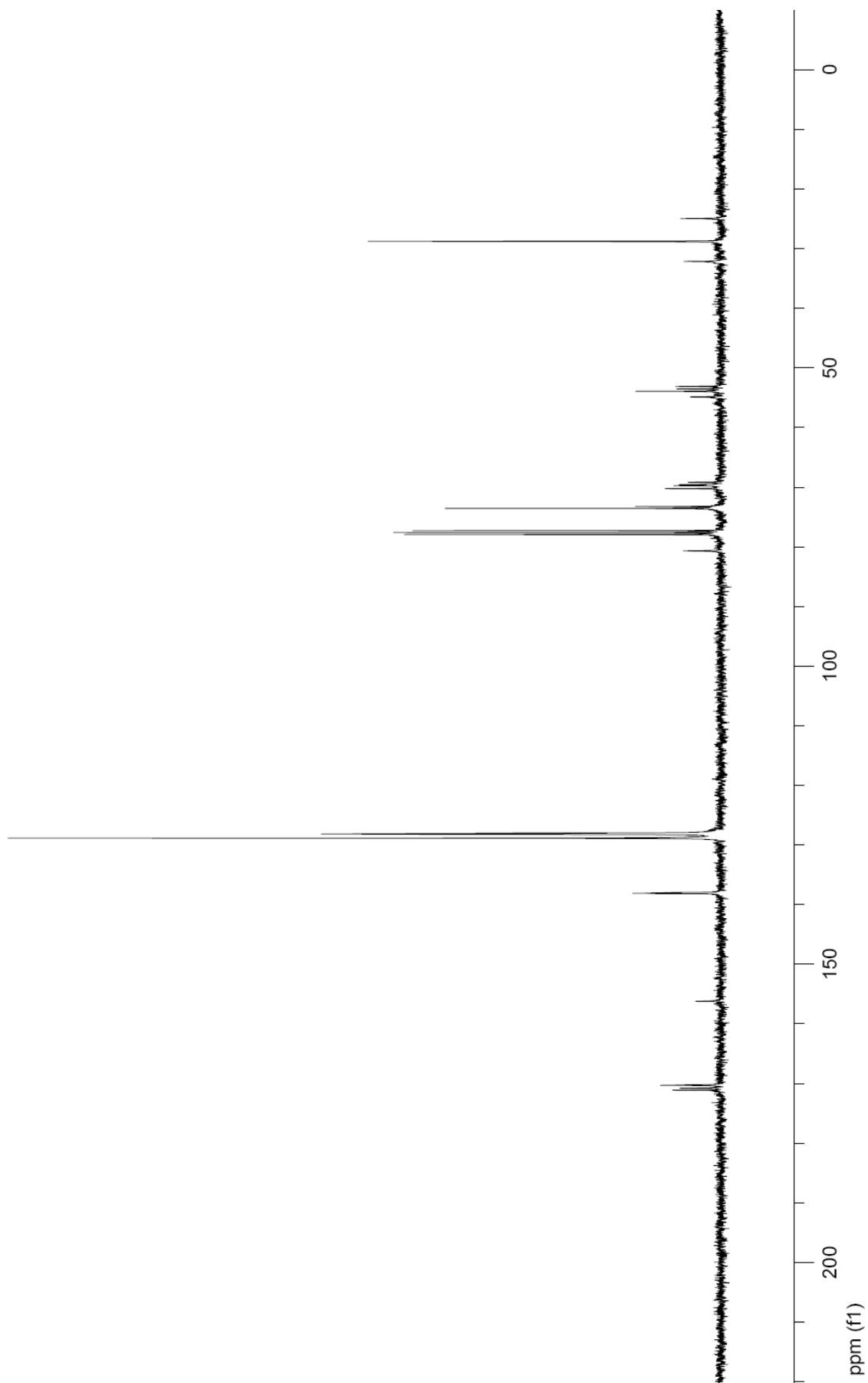


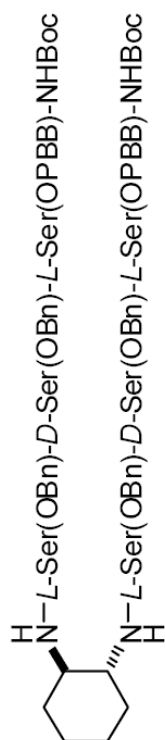




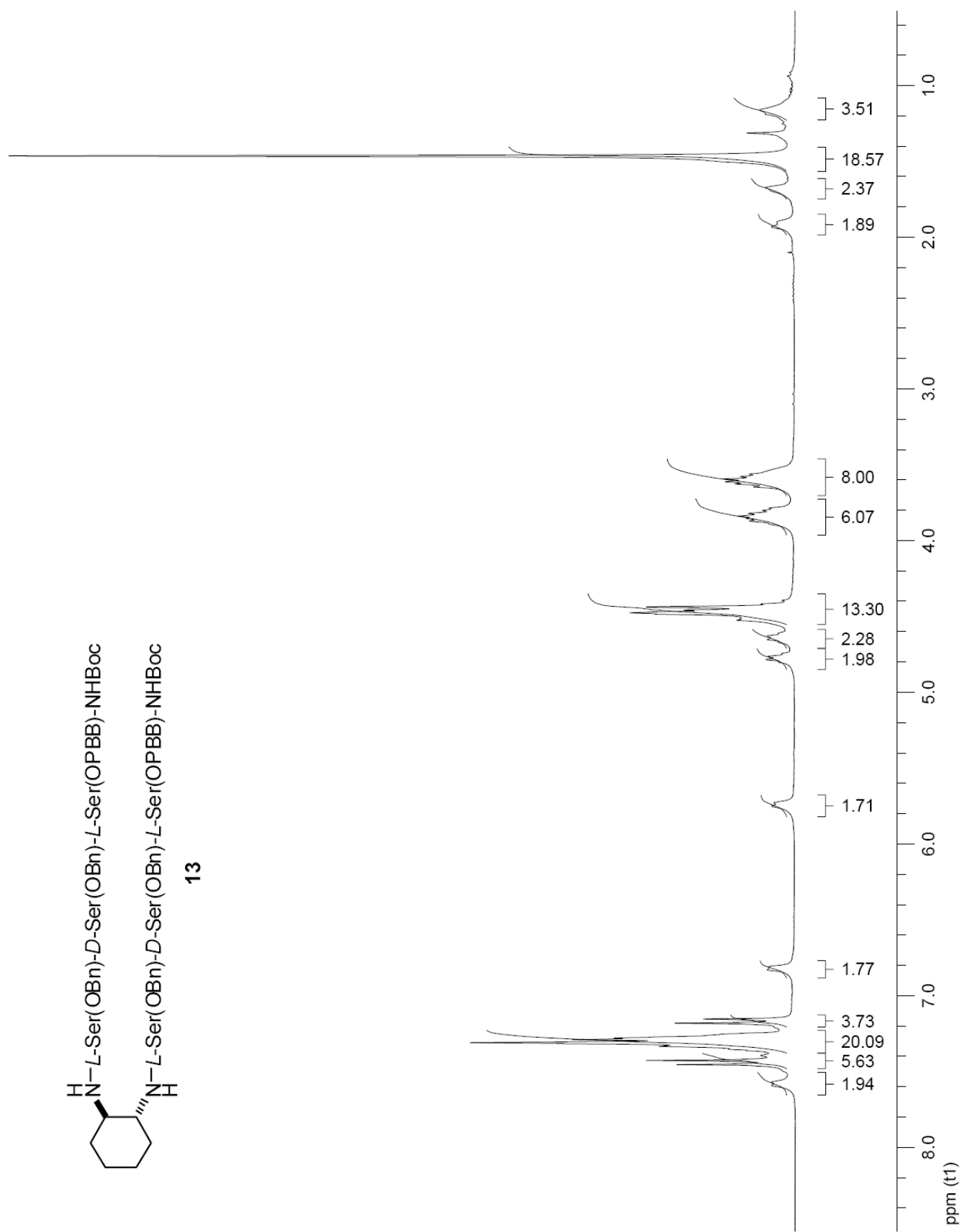


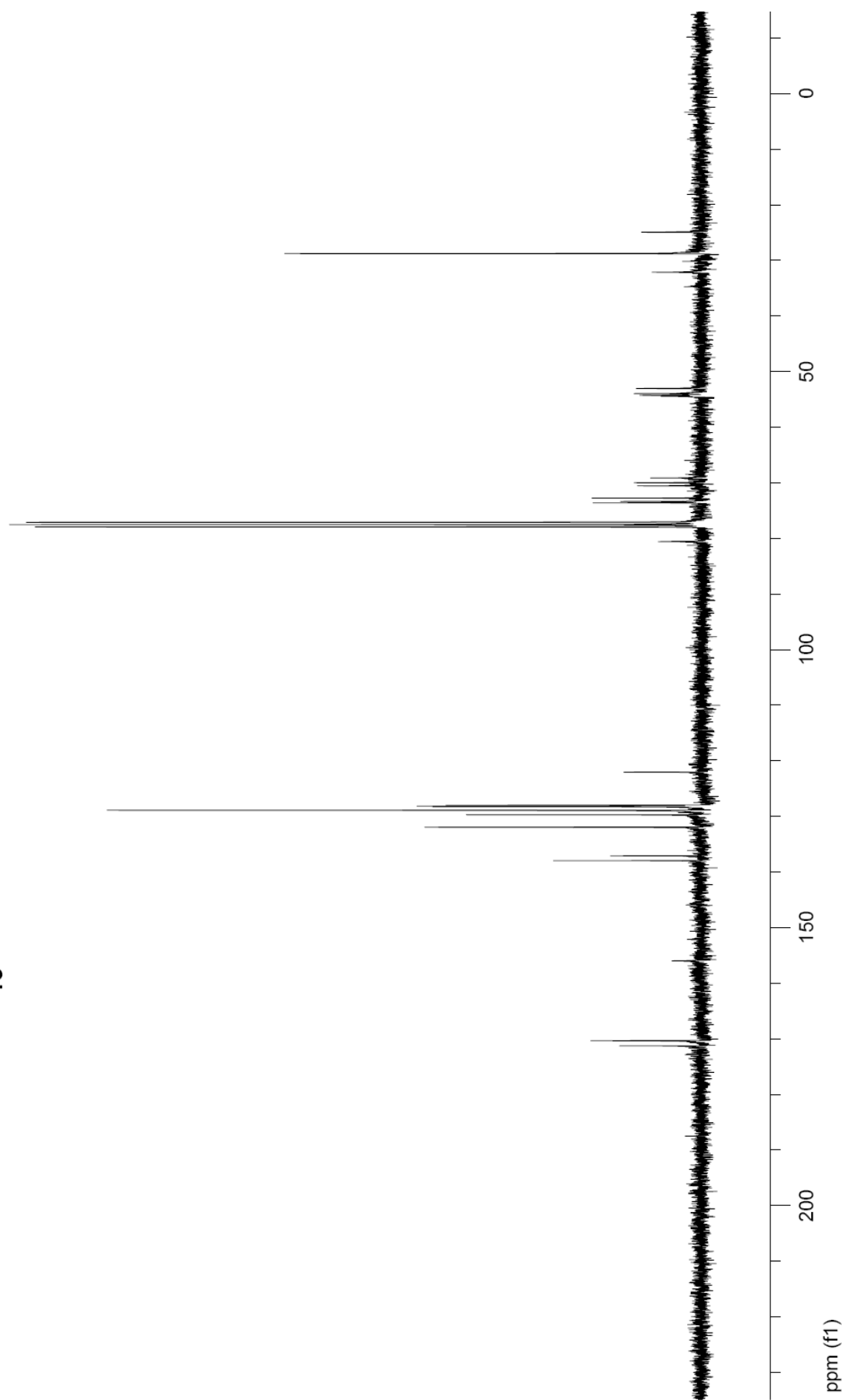
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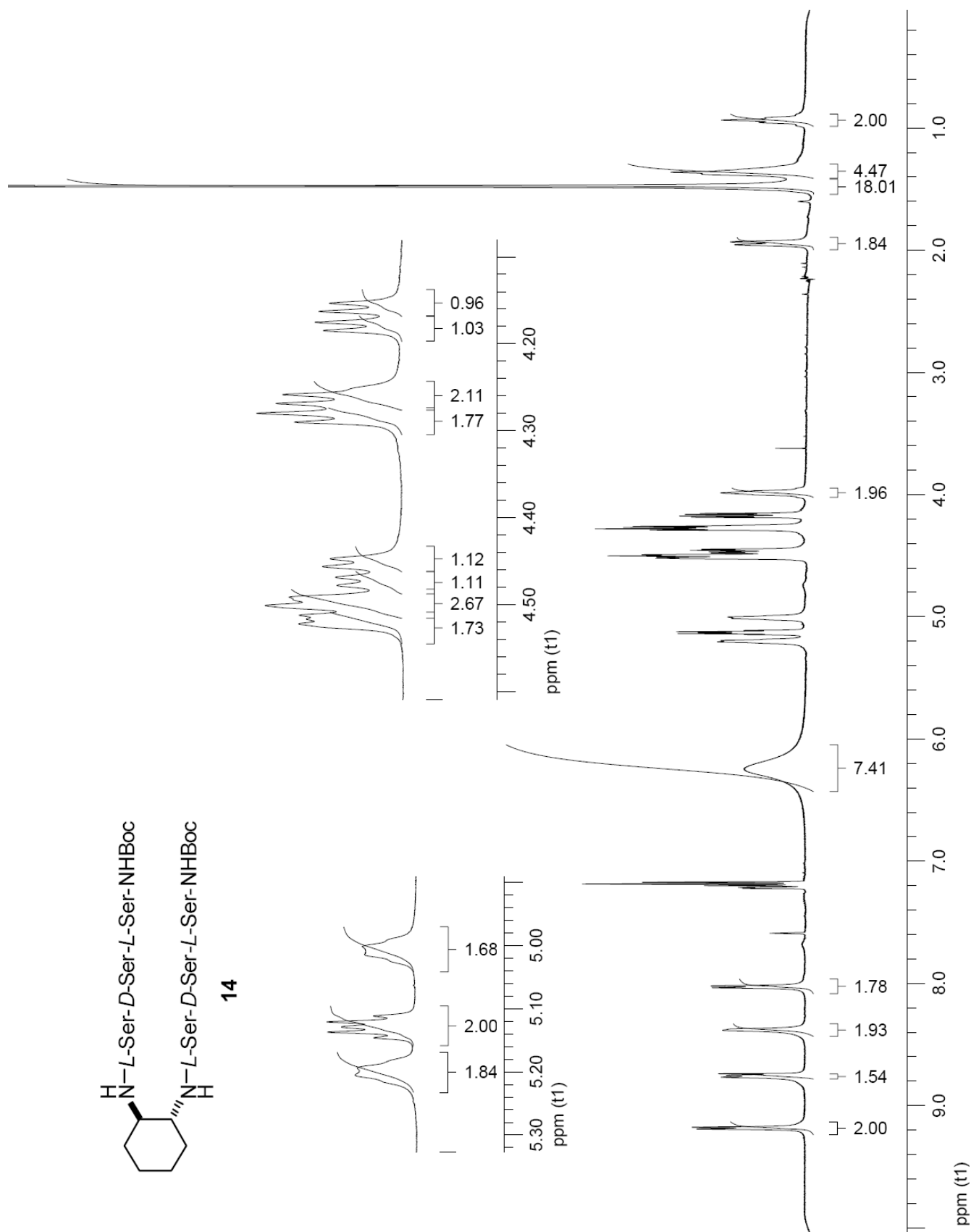


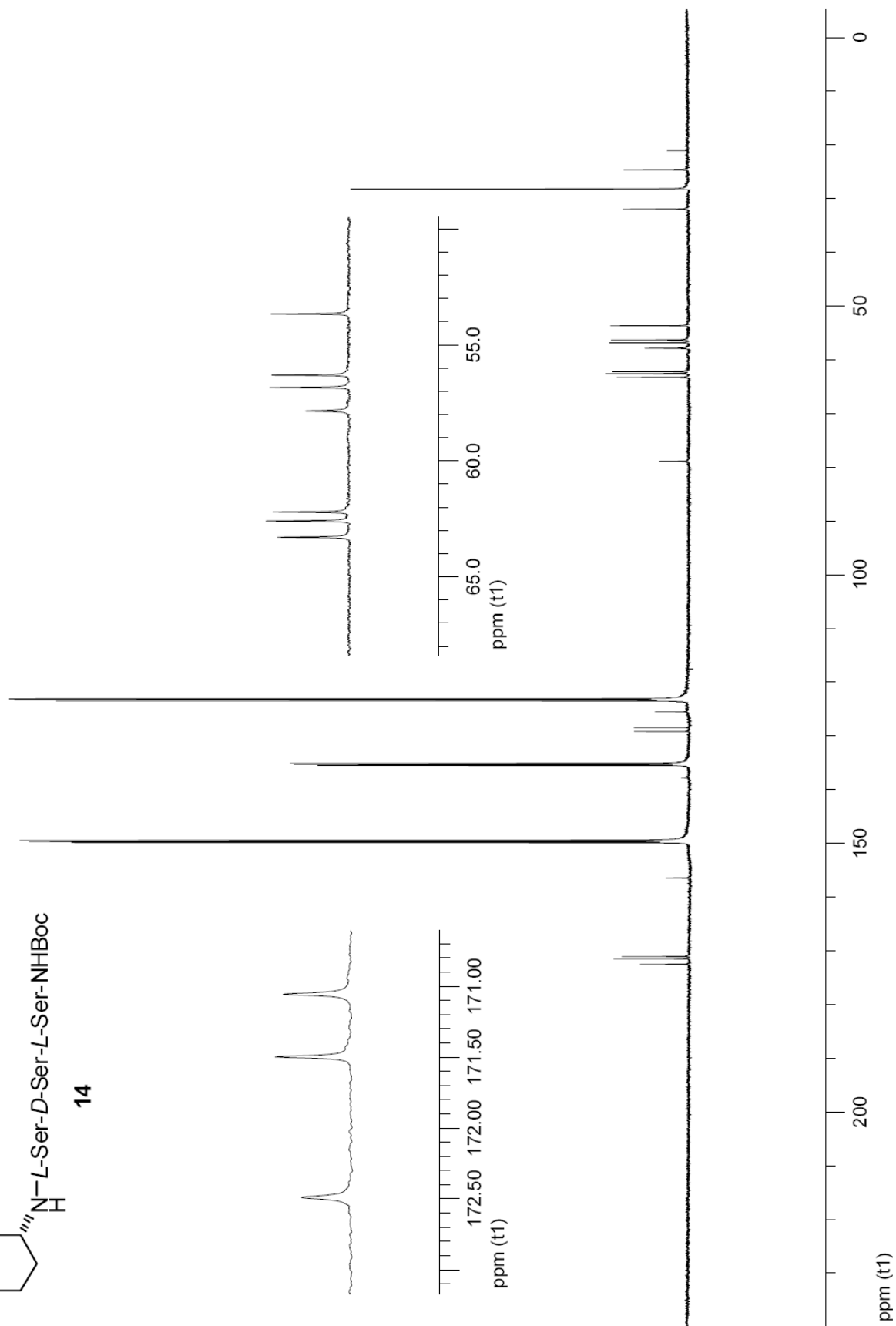
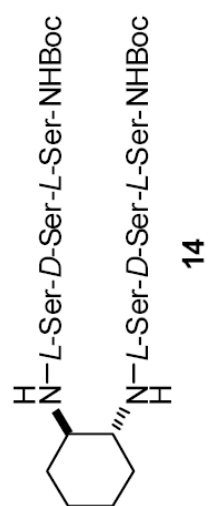


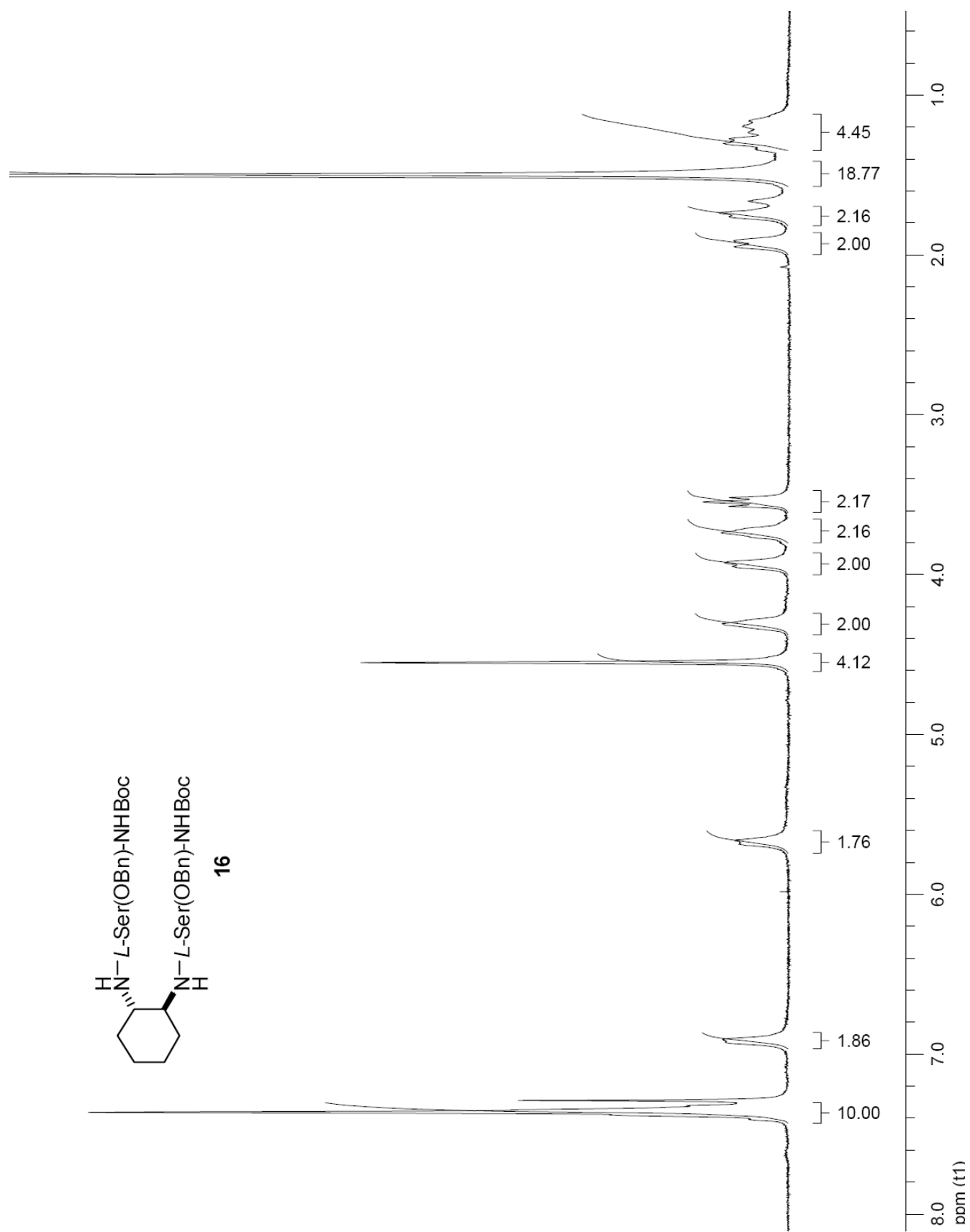
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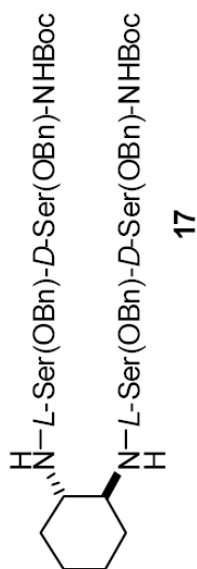


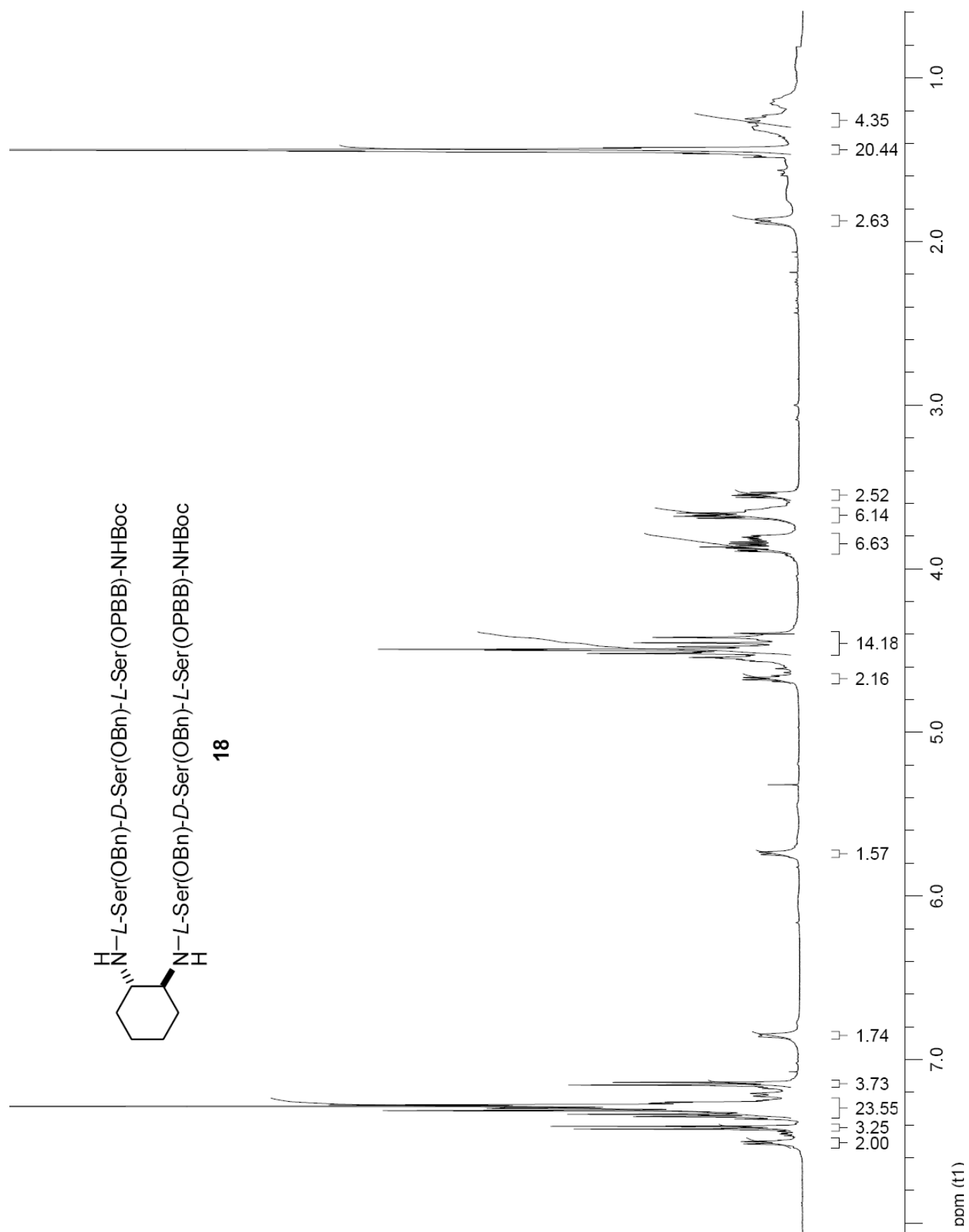
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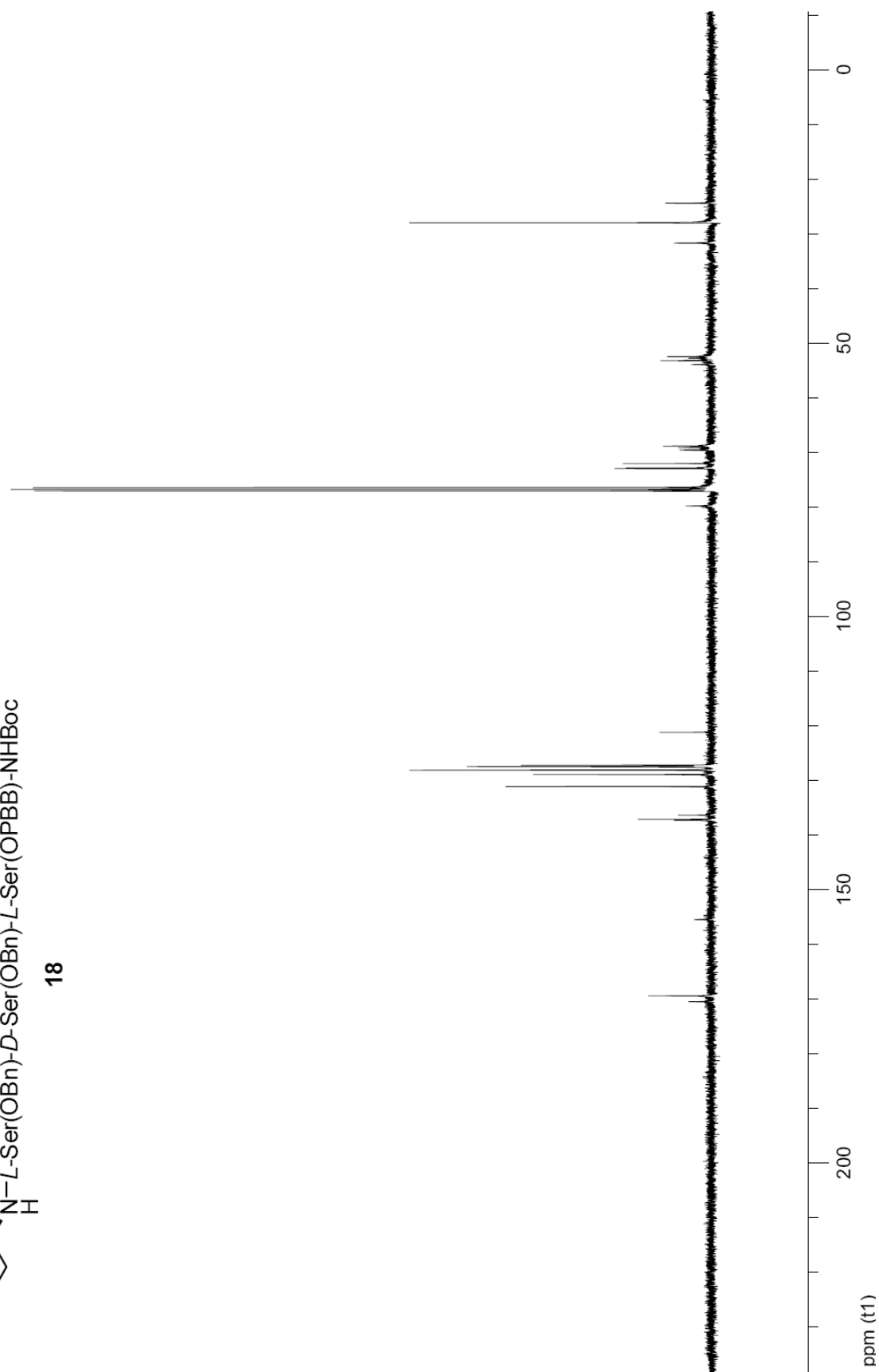
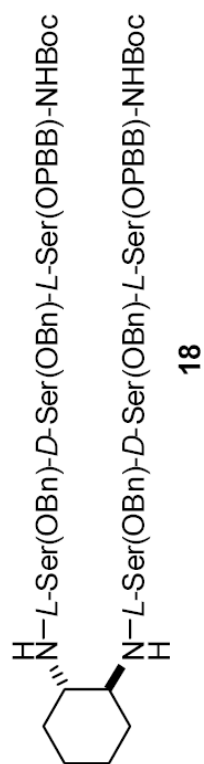
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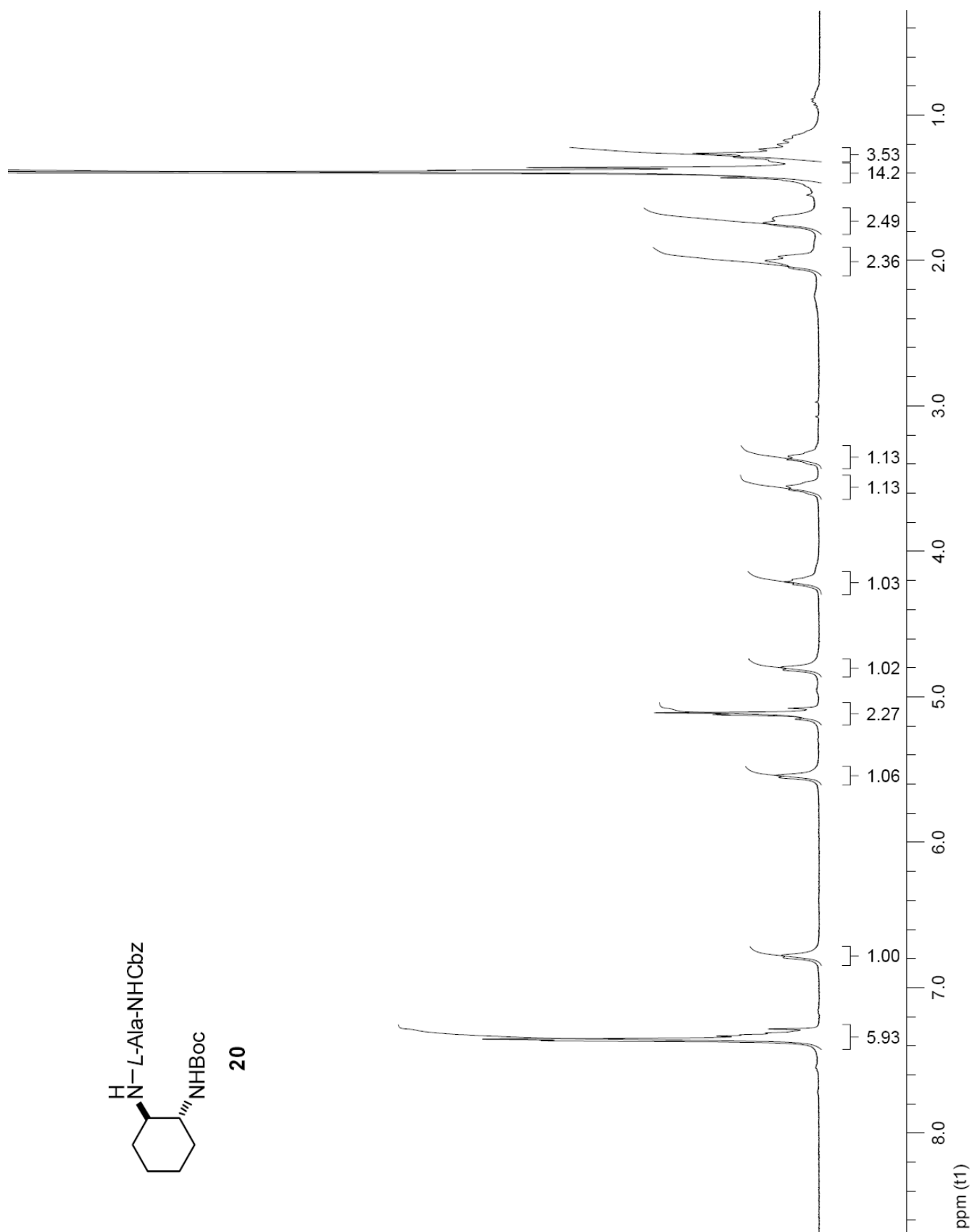


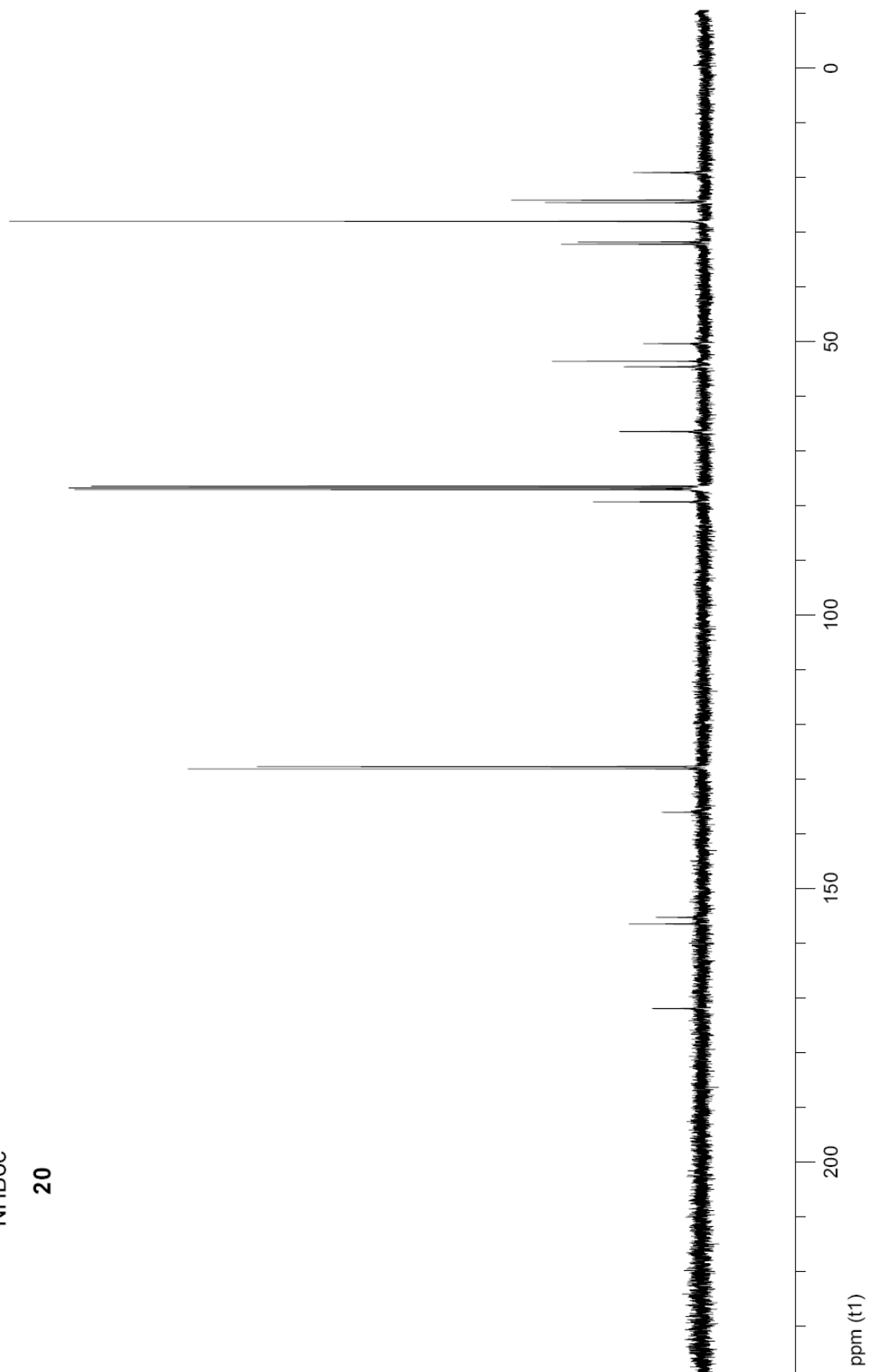
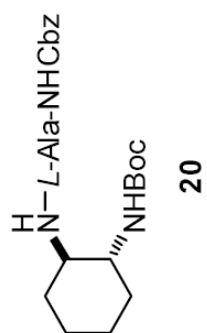


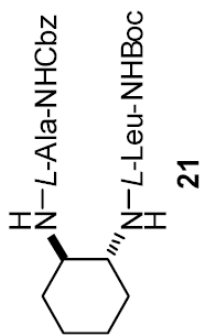


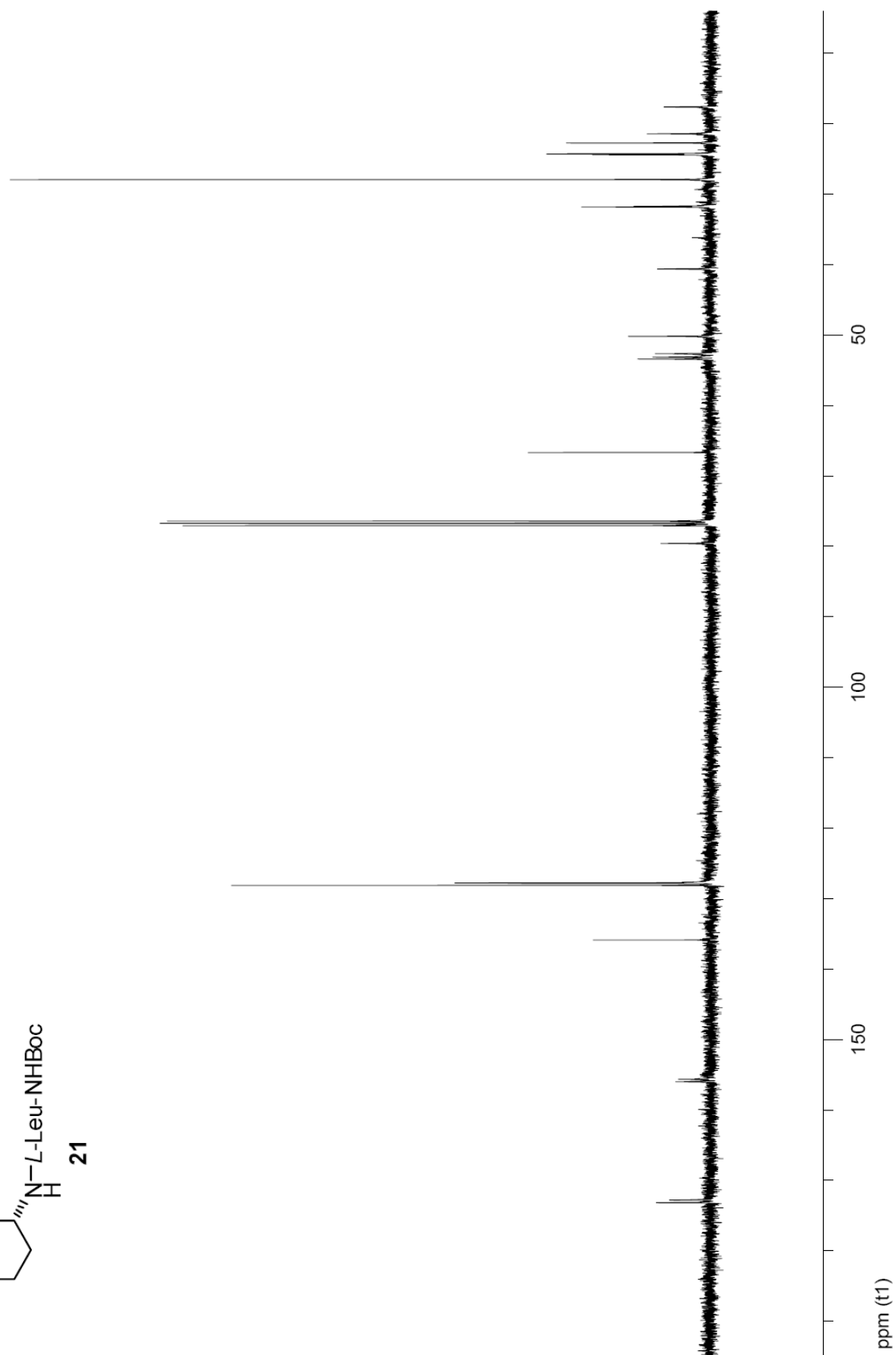
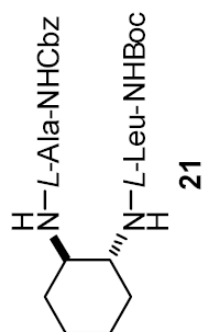


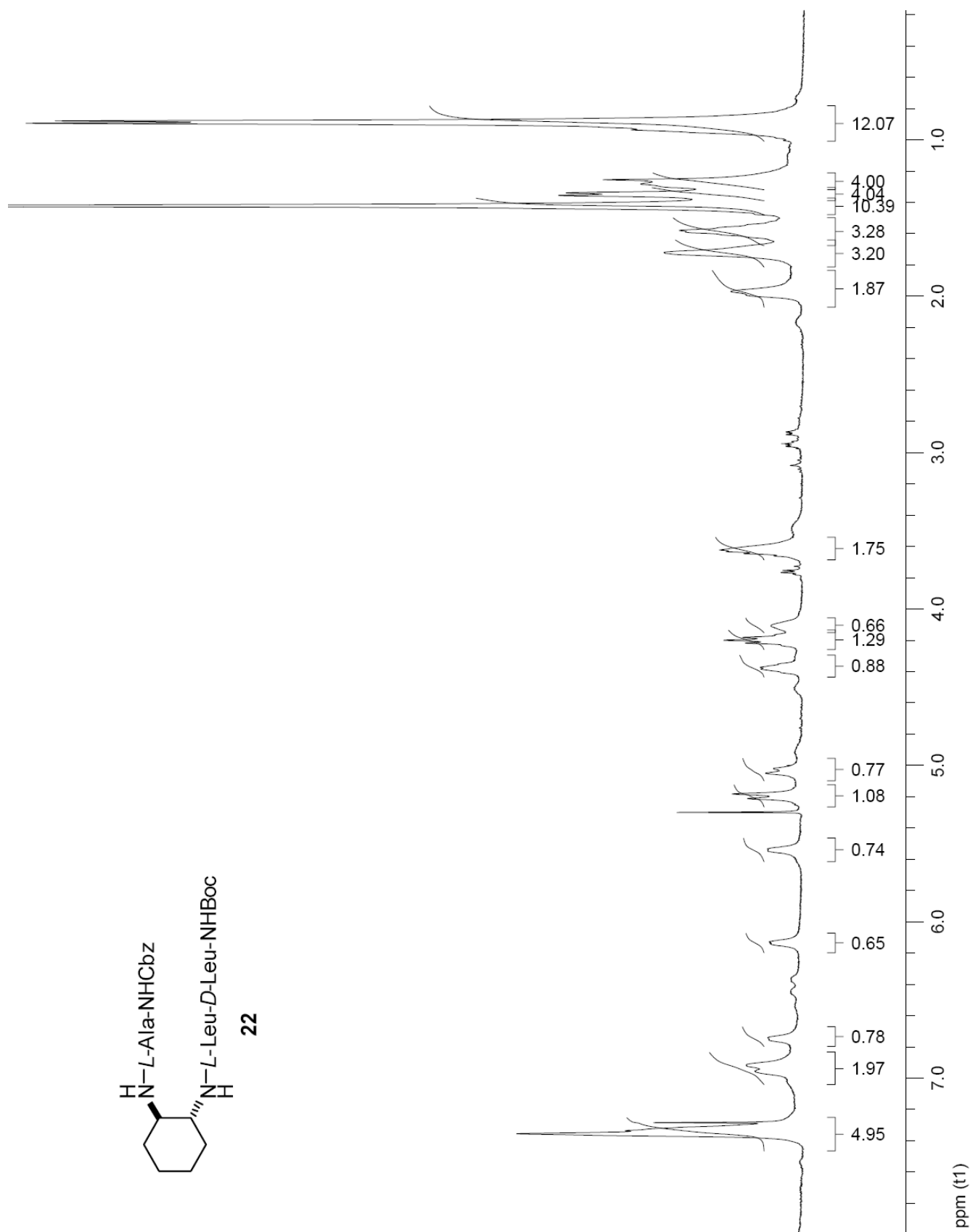


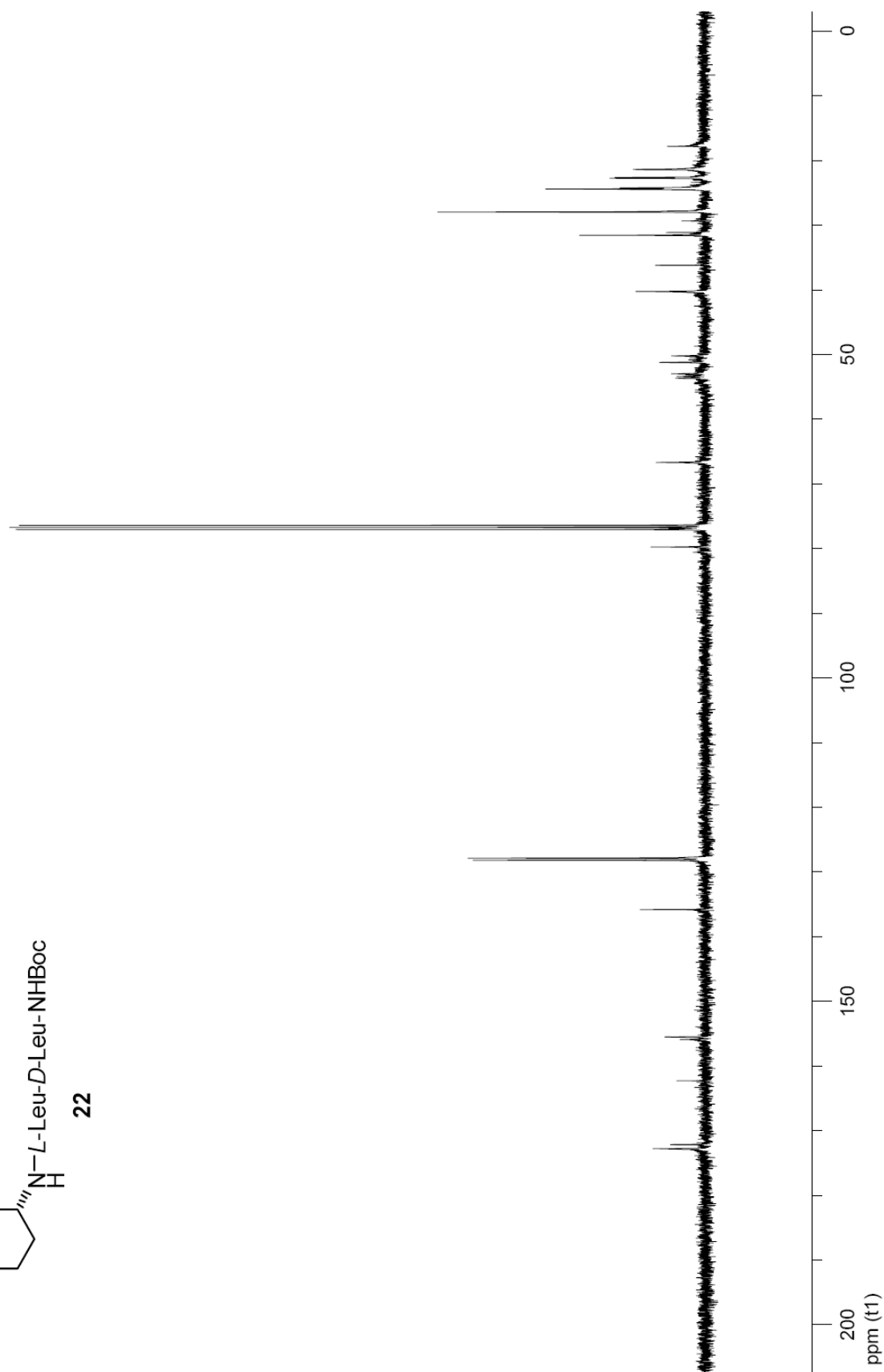
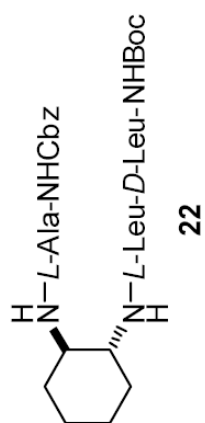
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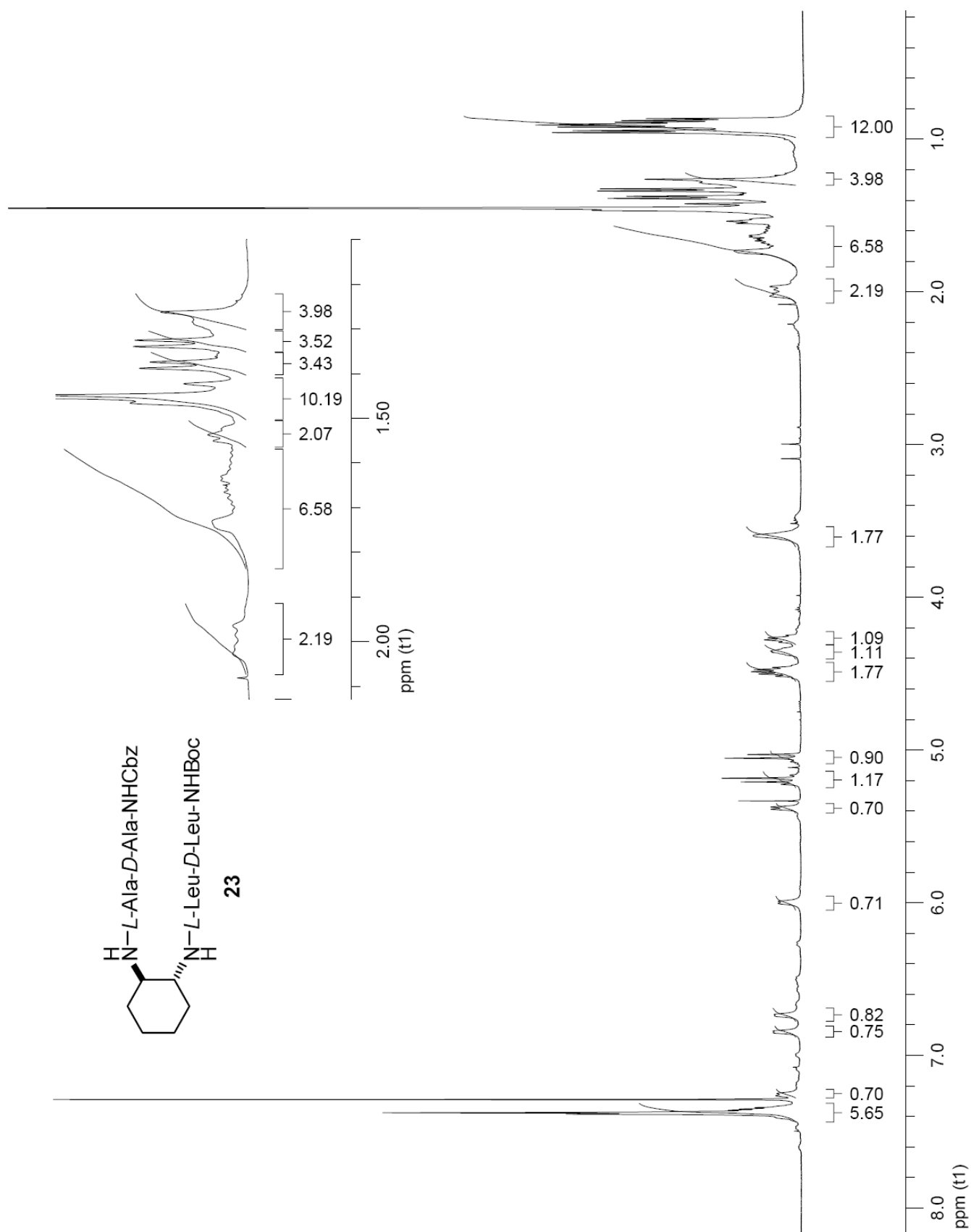


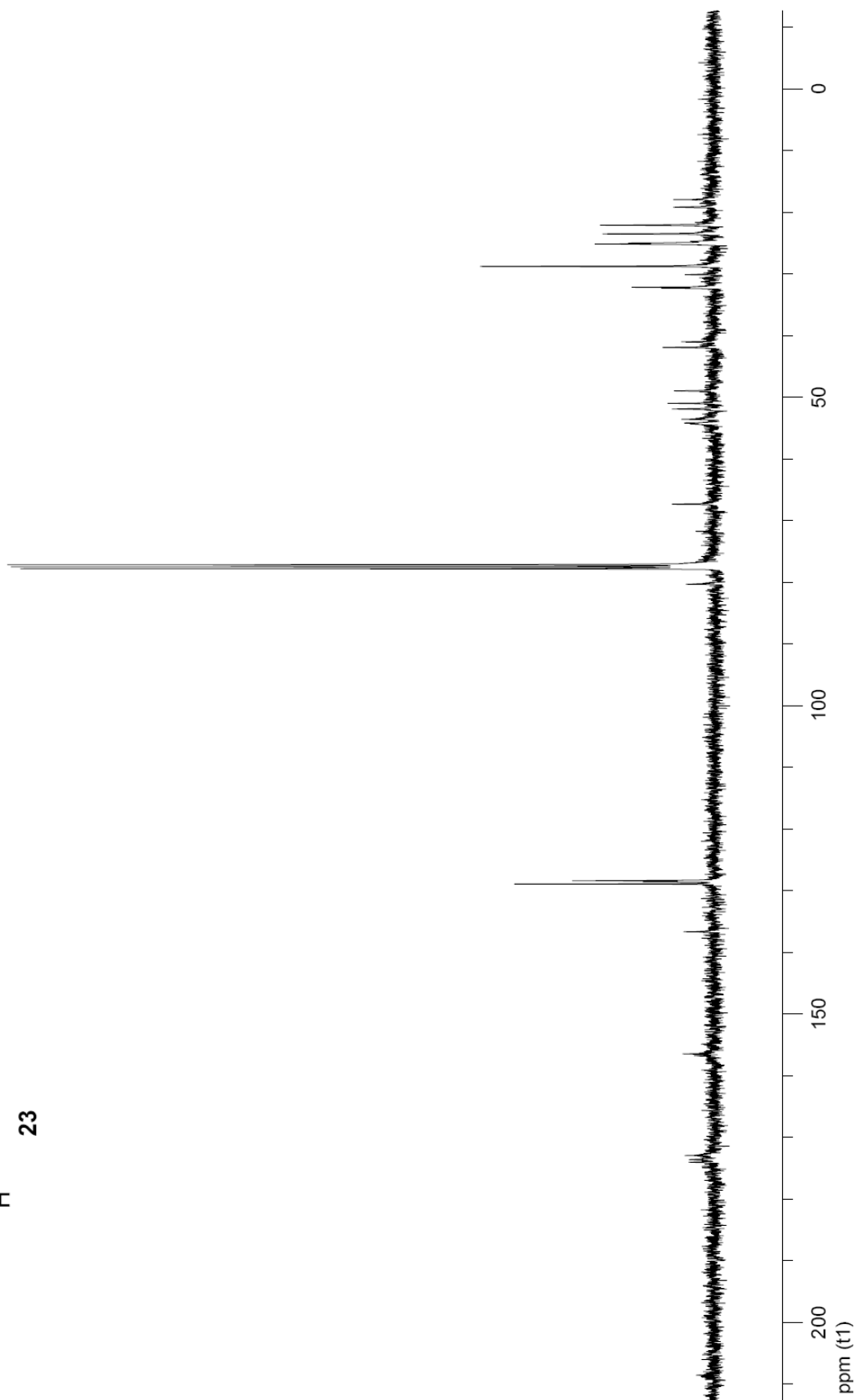
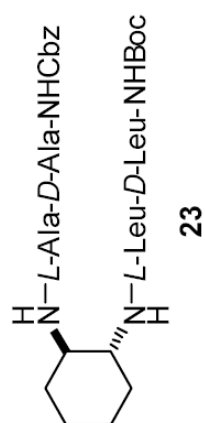


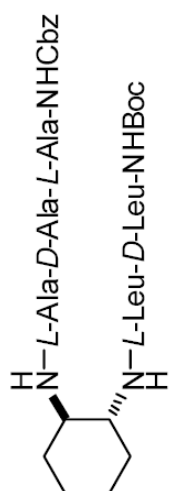
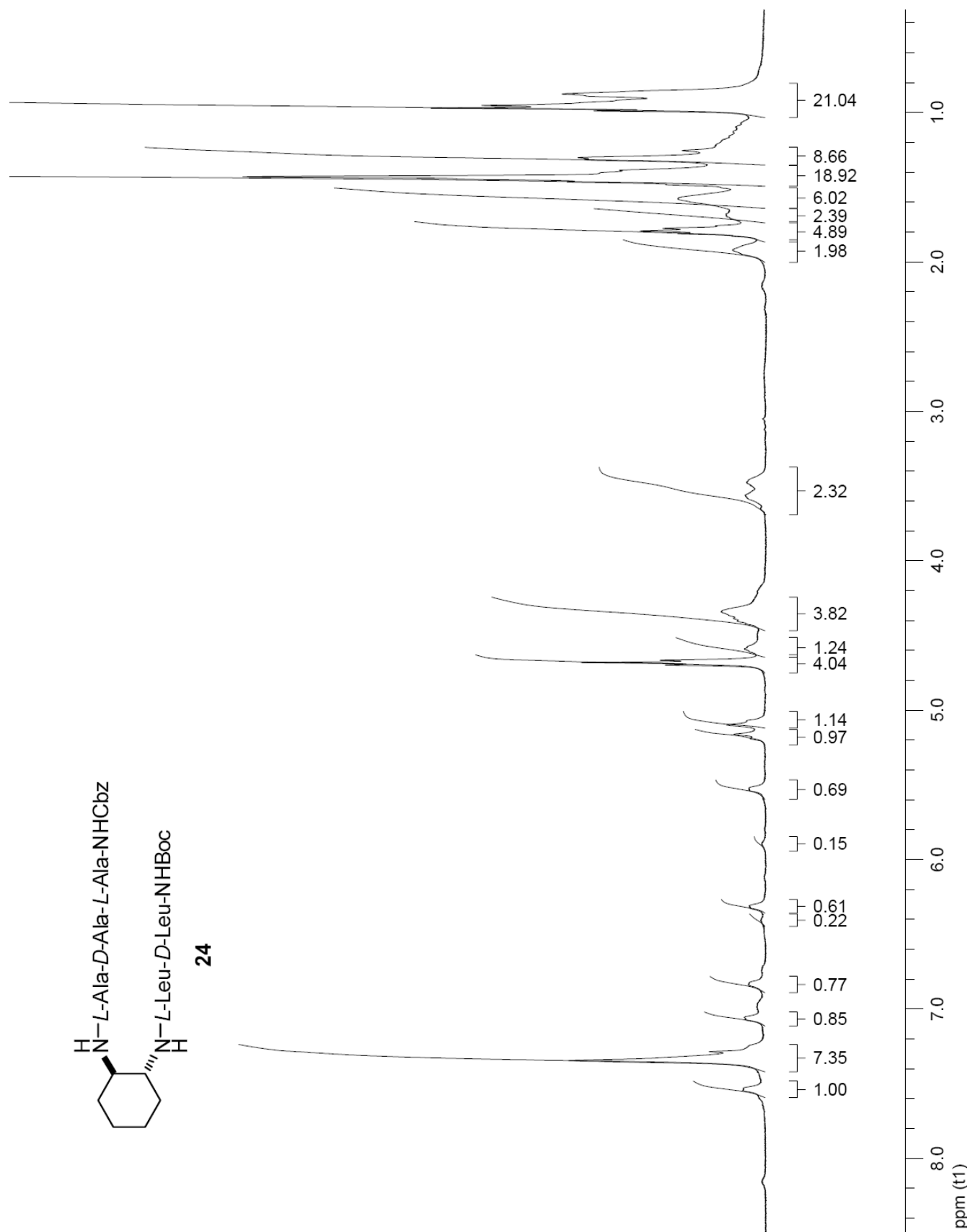


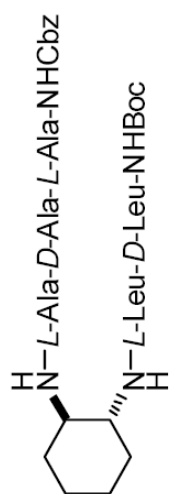
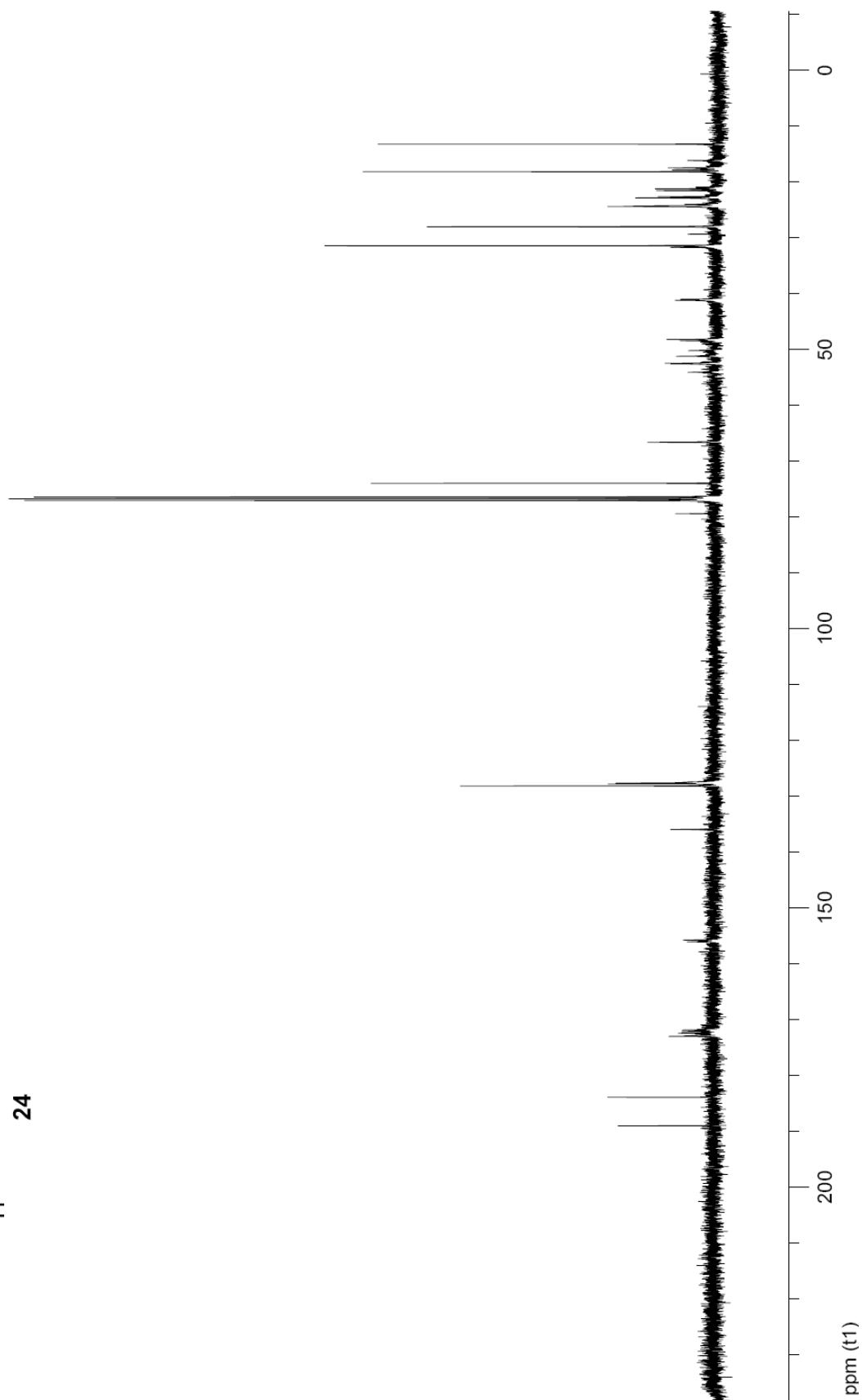






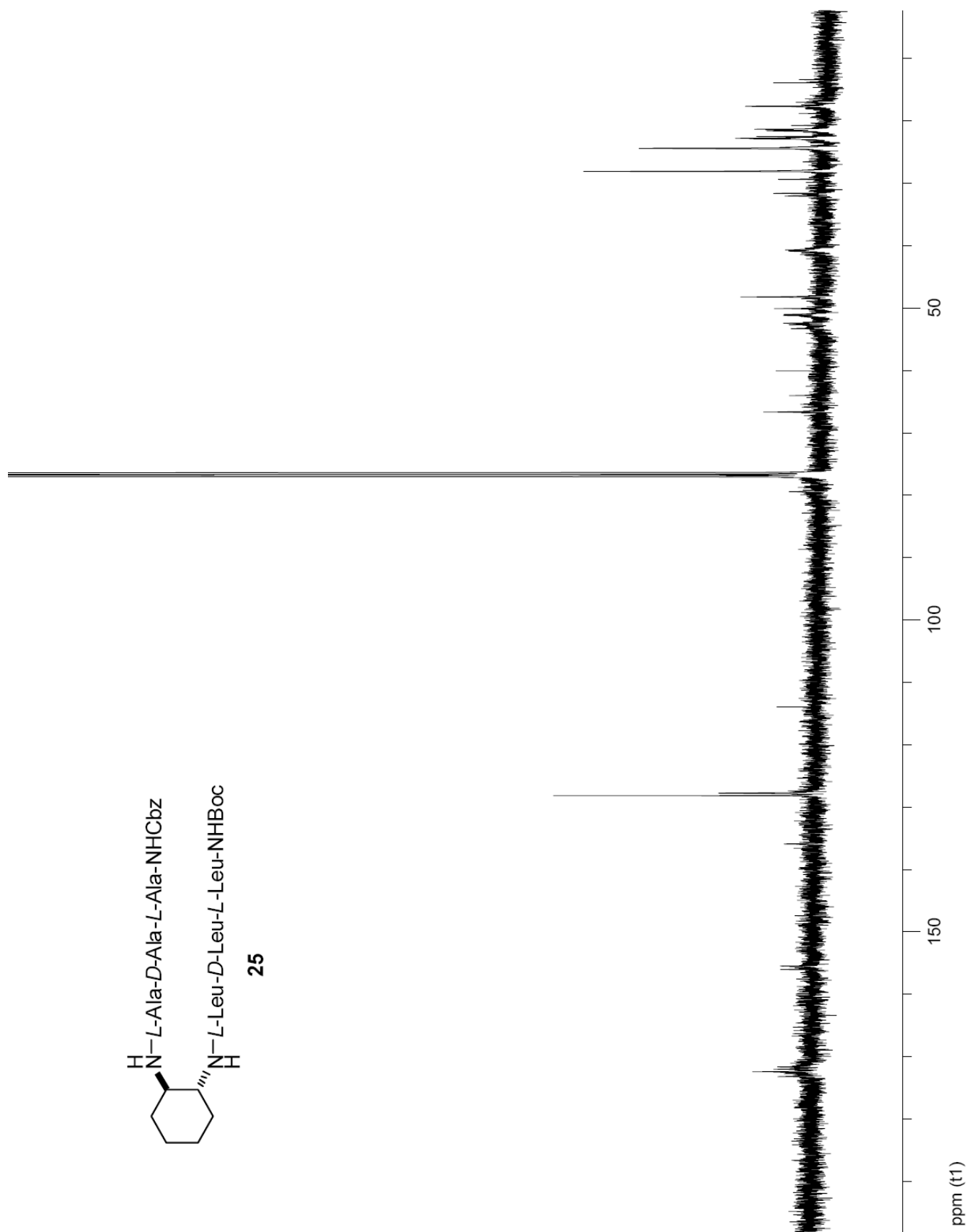


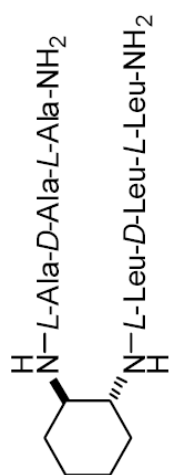
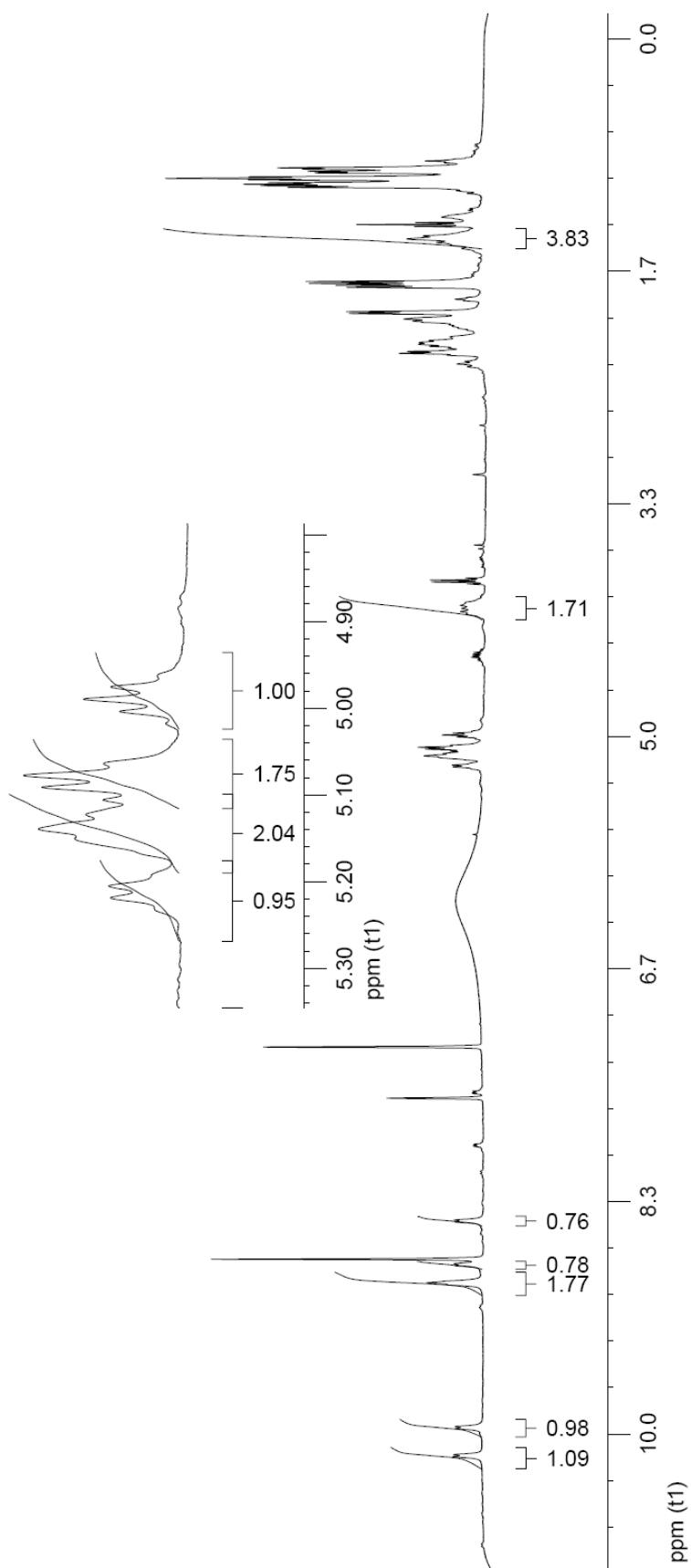
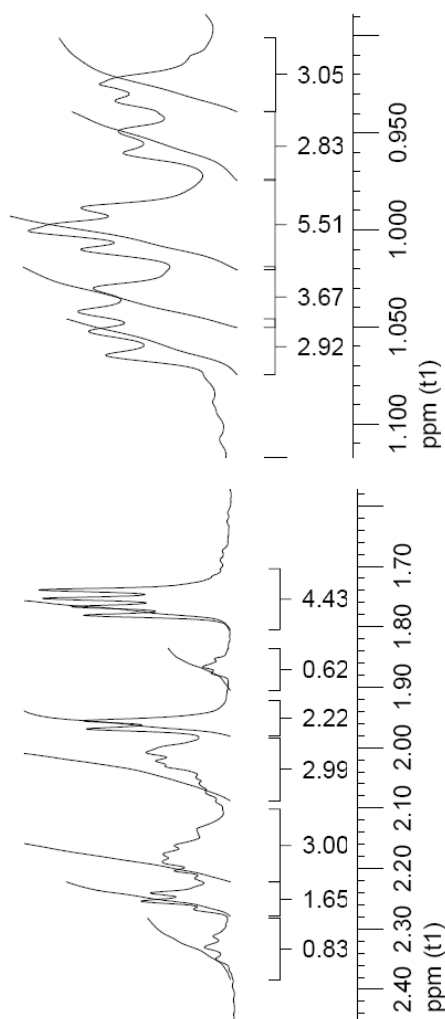
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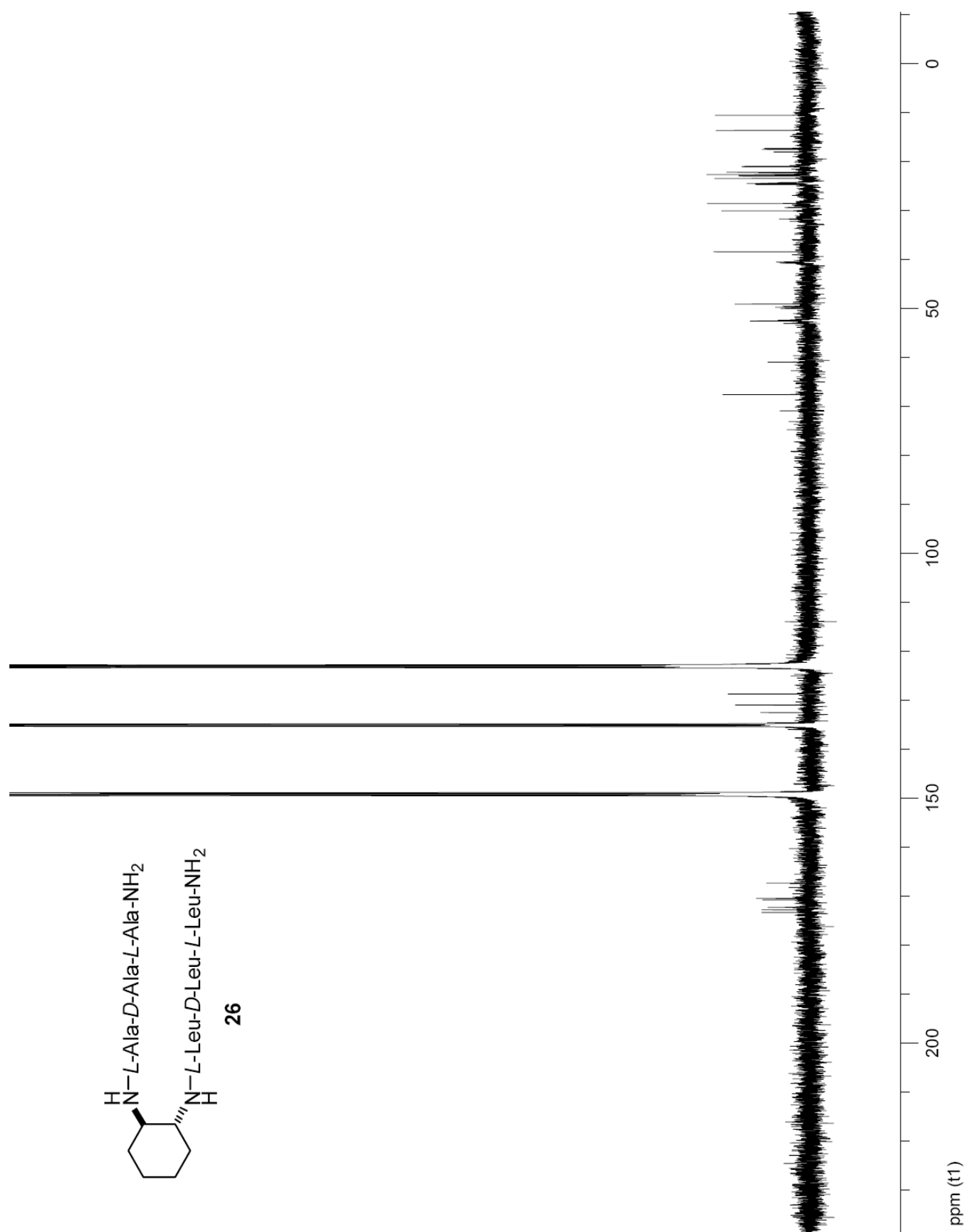
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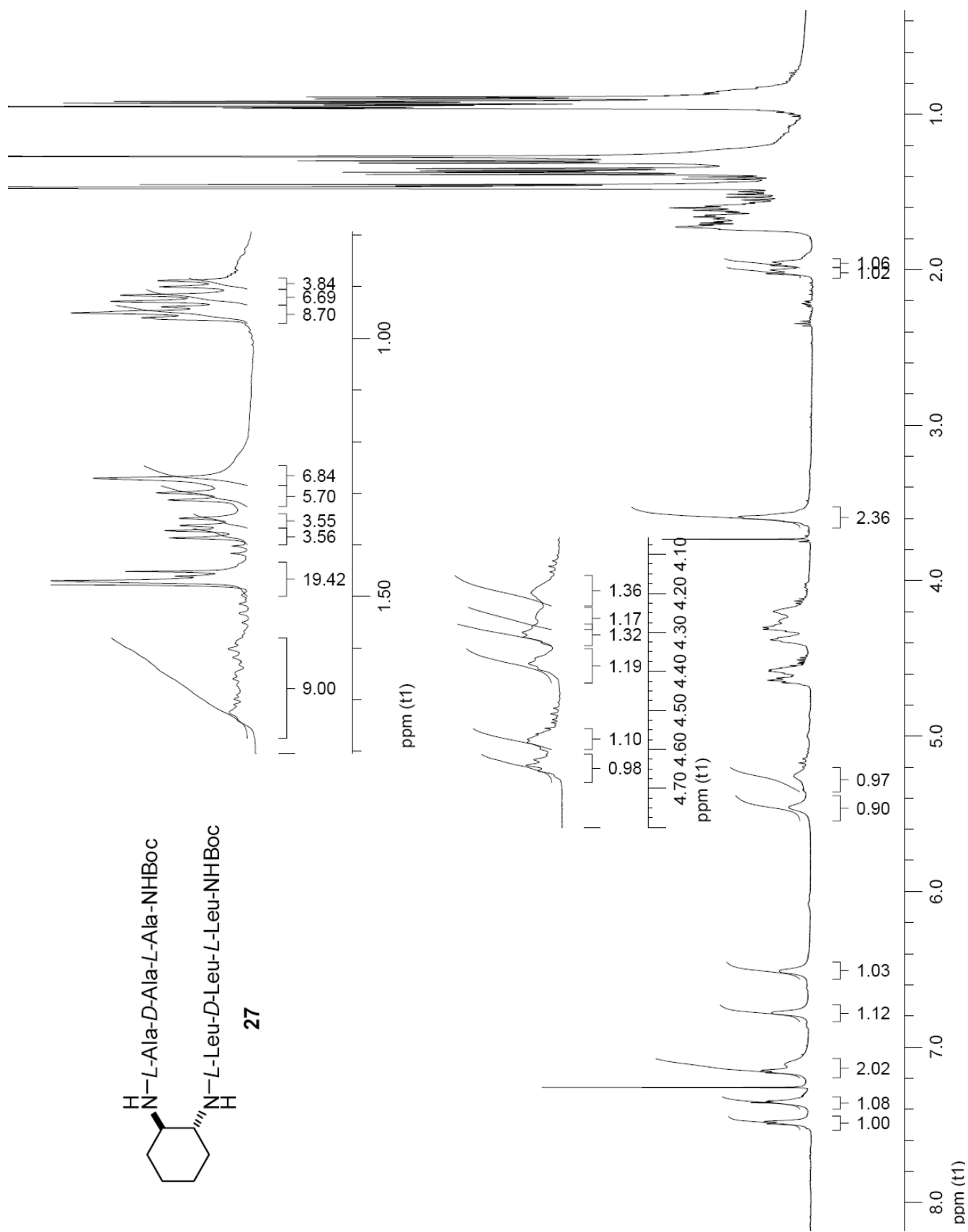


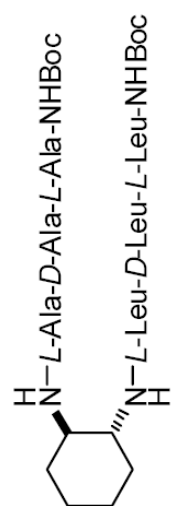
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**26**







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