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

Electronic Supplementary Information

Molecular Tweezers with a Rotationally Restricted Linker and Freely Rotating Porphyrin Moieties

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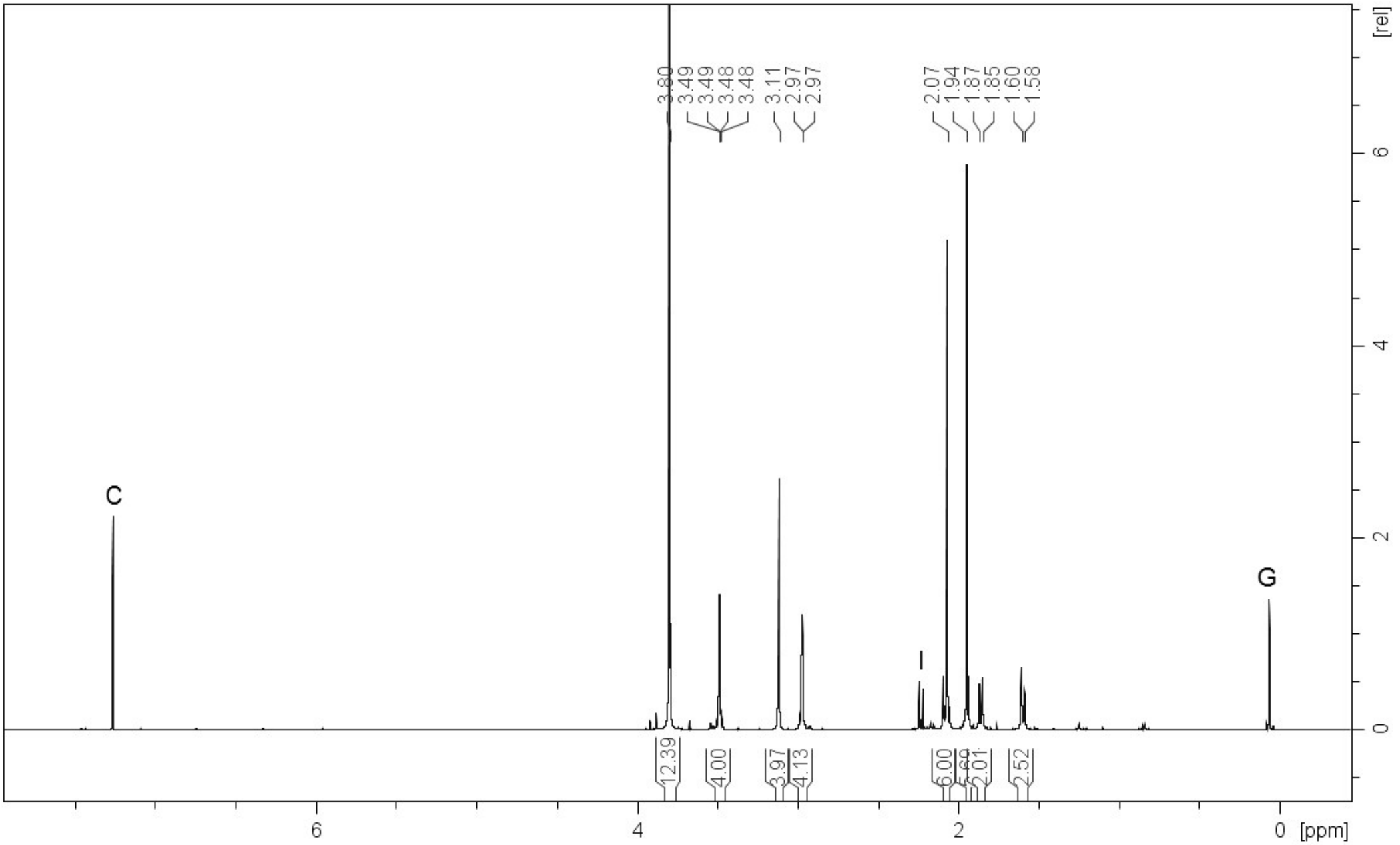
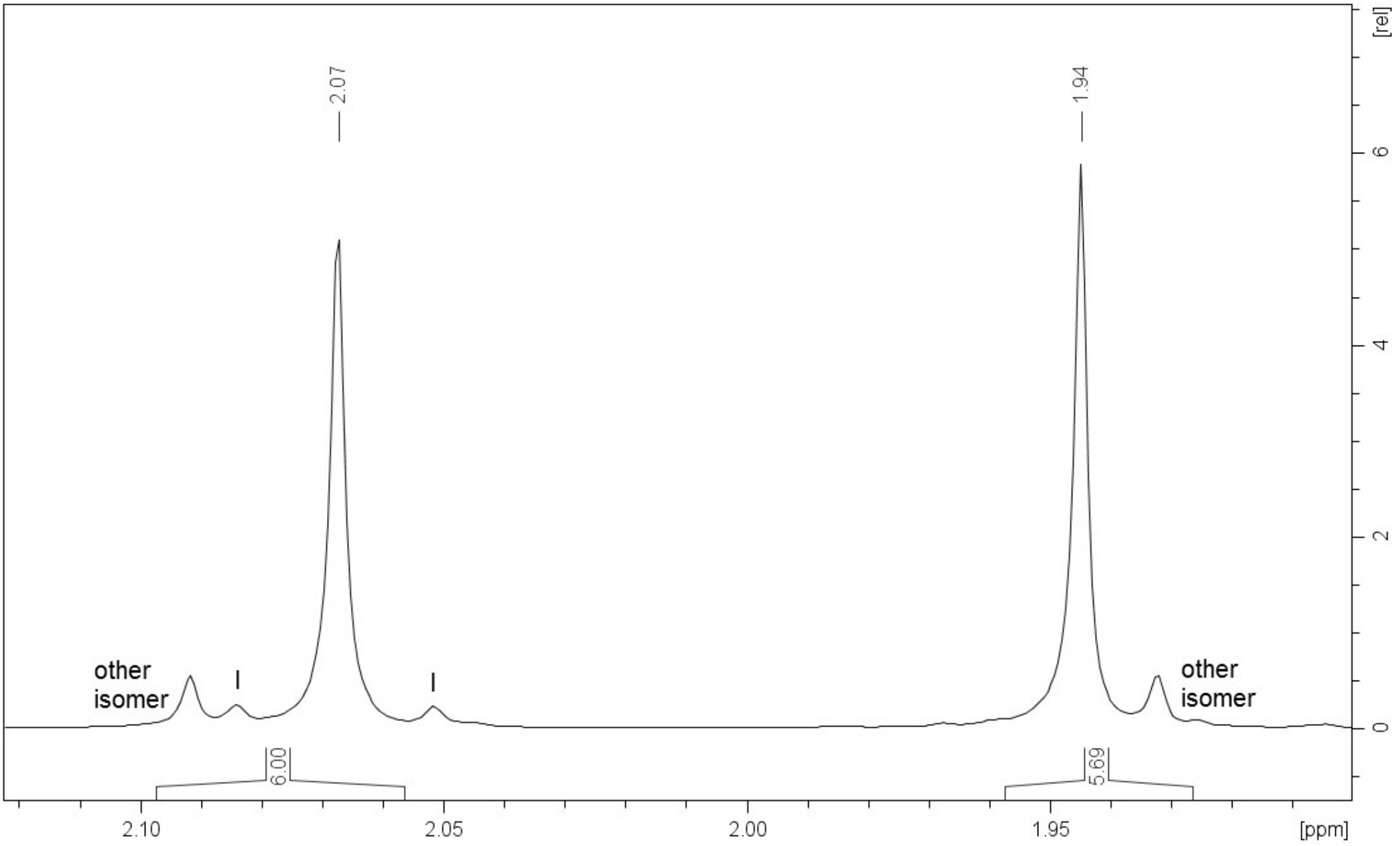
Contents

NMR annotations

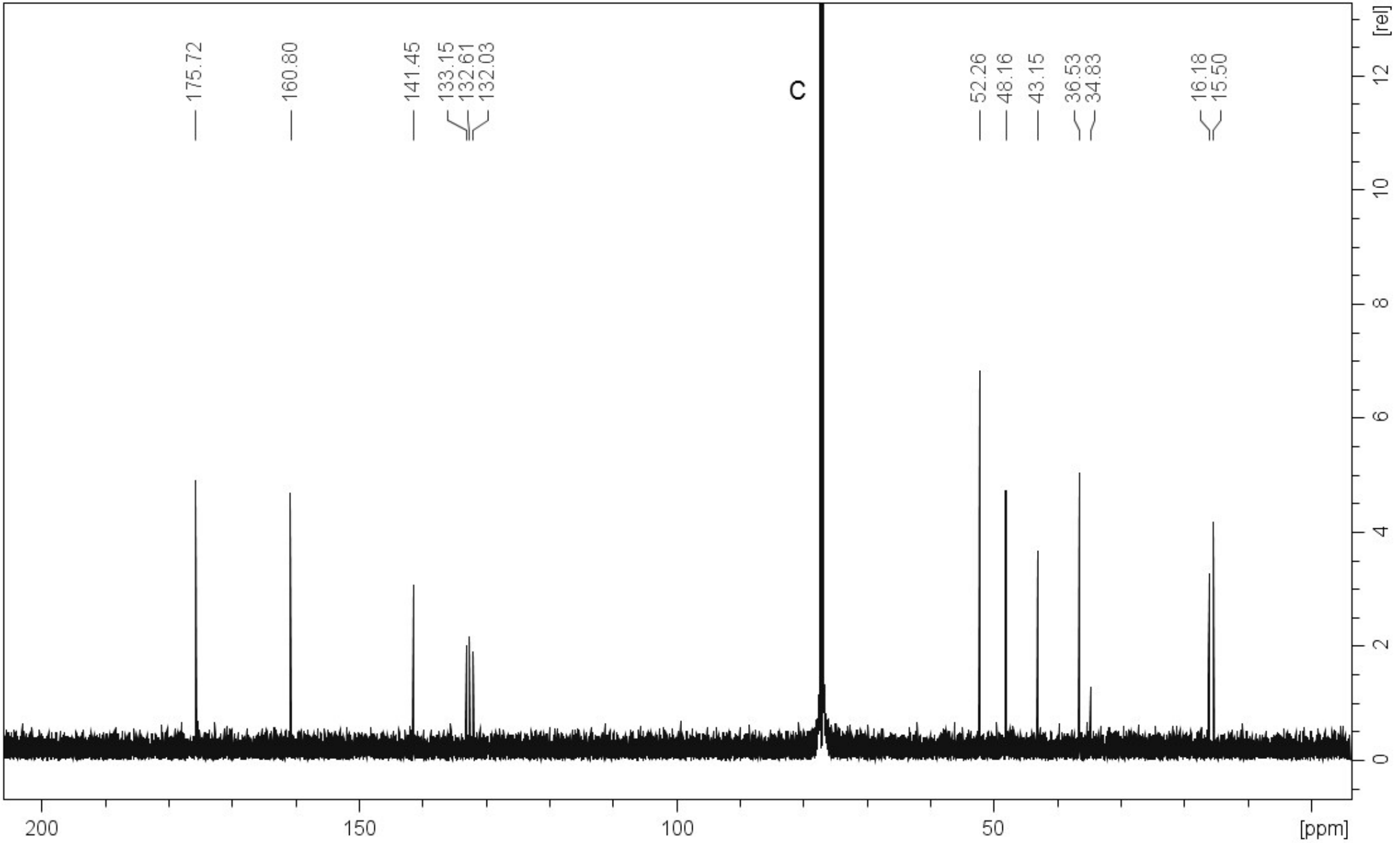
S = solvent	I = impurity	G = grease	SM = starting material
A = acetone	C = $CDCl_3$	W = H_2O	

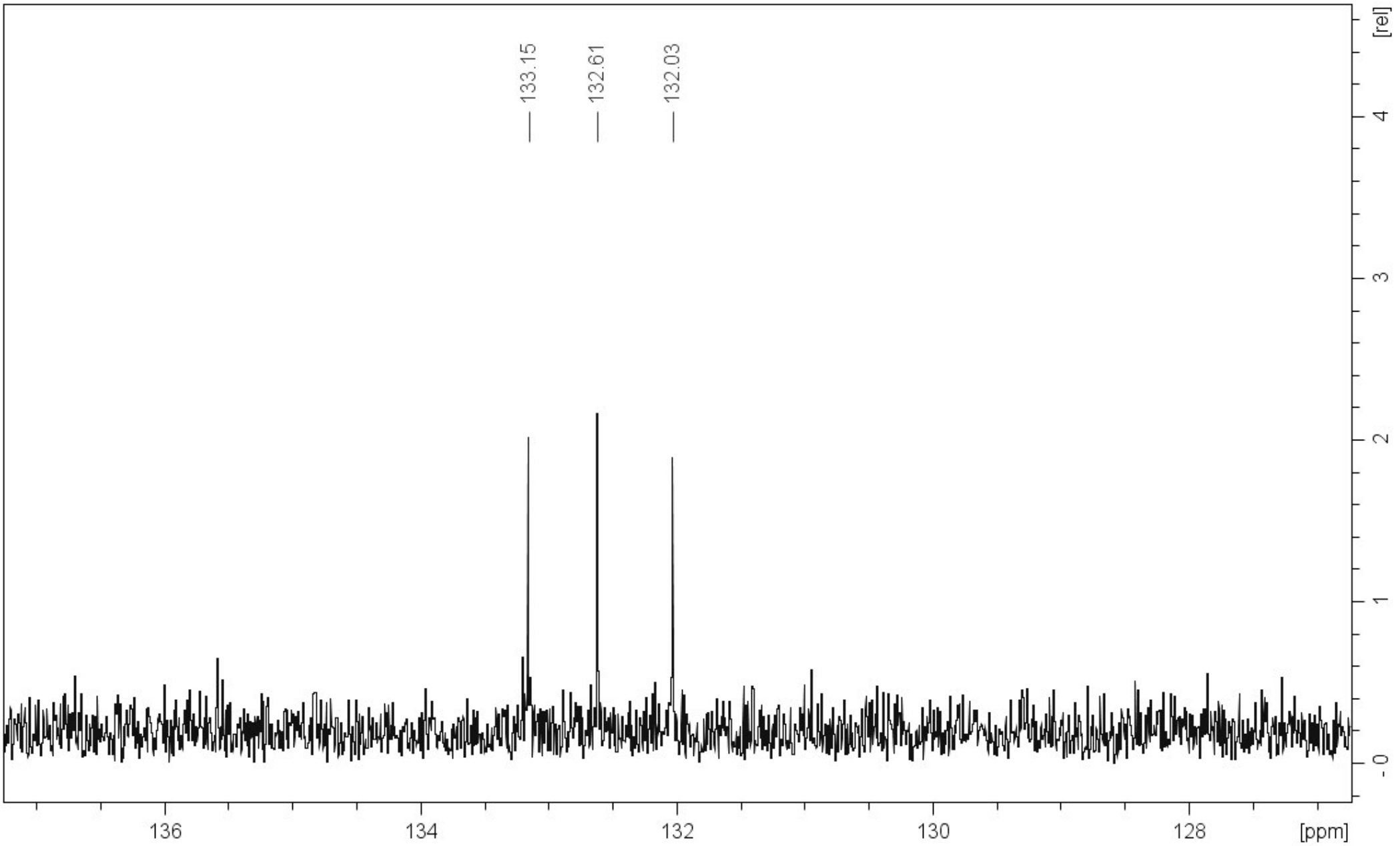
S1: 600 MHz ^{1}H NMR *endo*- linker **6**, inner CH_3 isomer

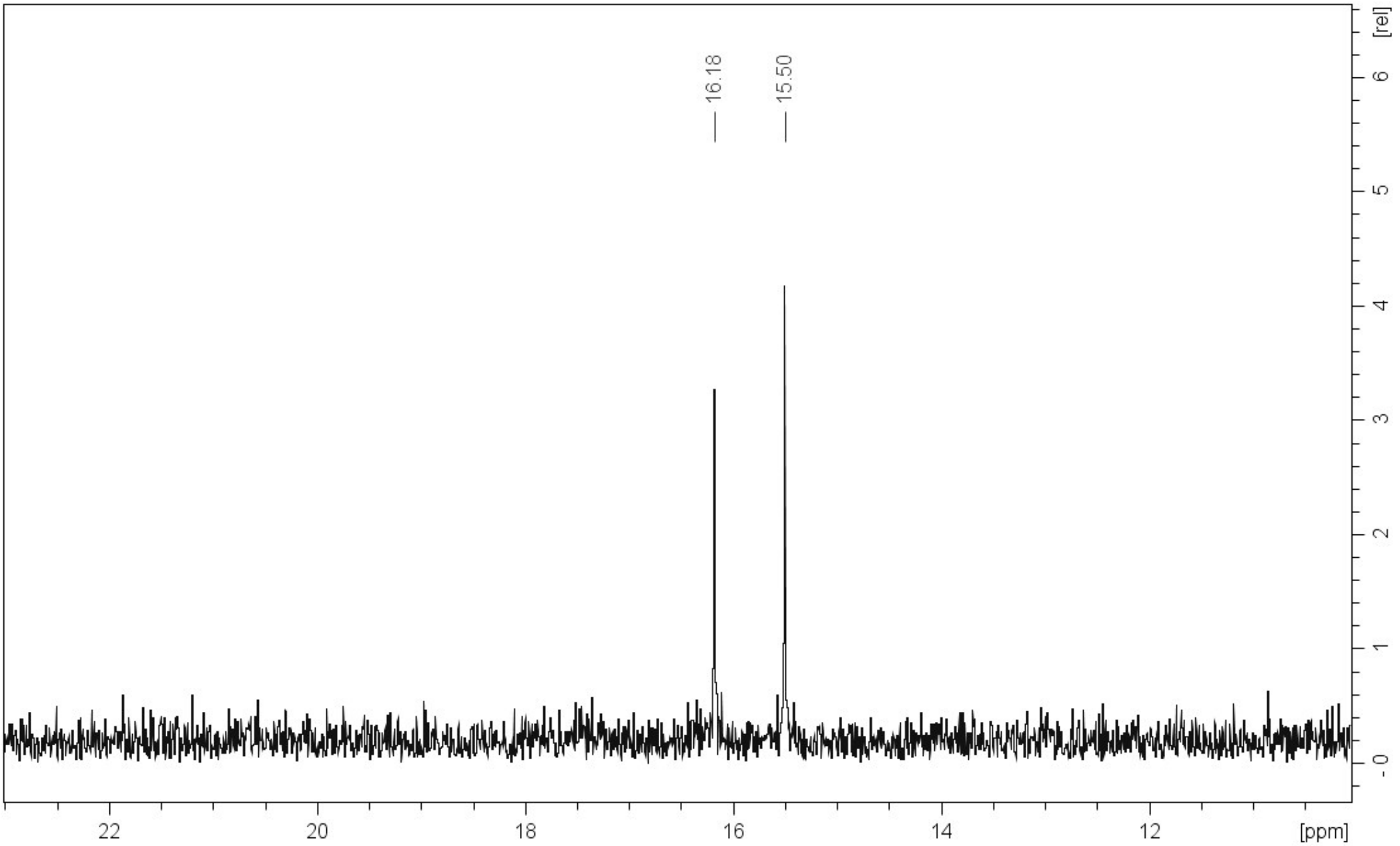



2.07
1.94
other
isomer
other
isomer
6.00
5.69
2.10
2.05
2.00
1.95
[ppm]
[rel]
0
2
4
6

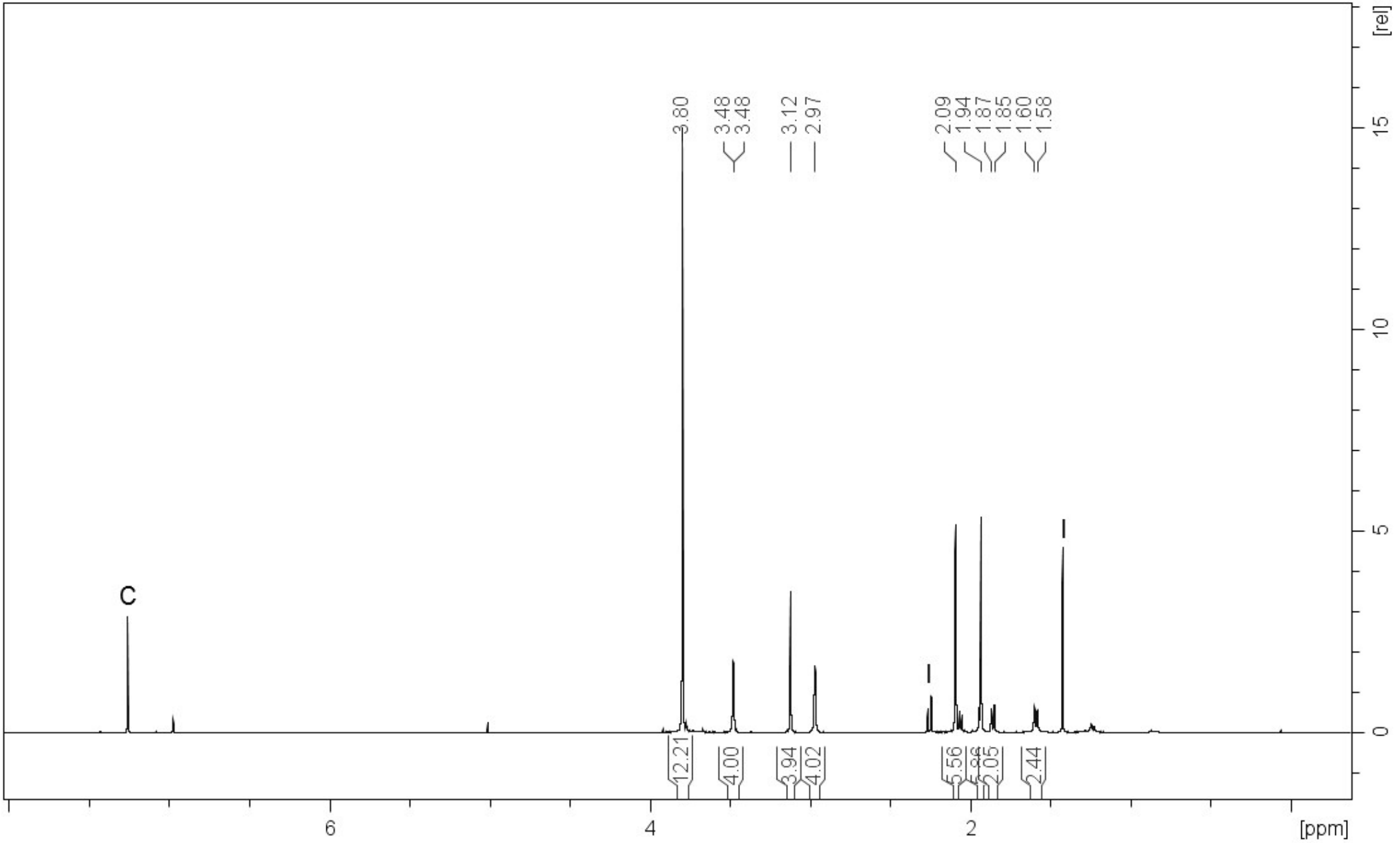
S2: 150 MHz ^{13}C NMR *endo*- linker **6**, inner CH_3 isomer

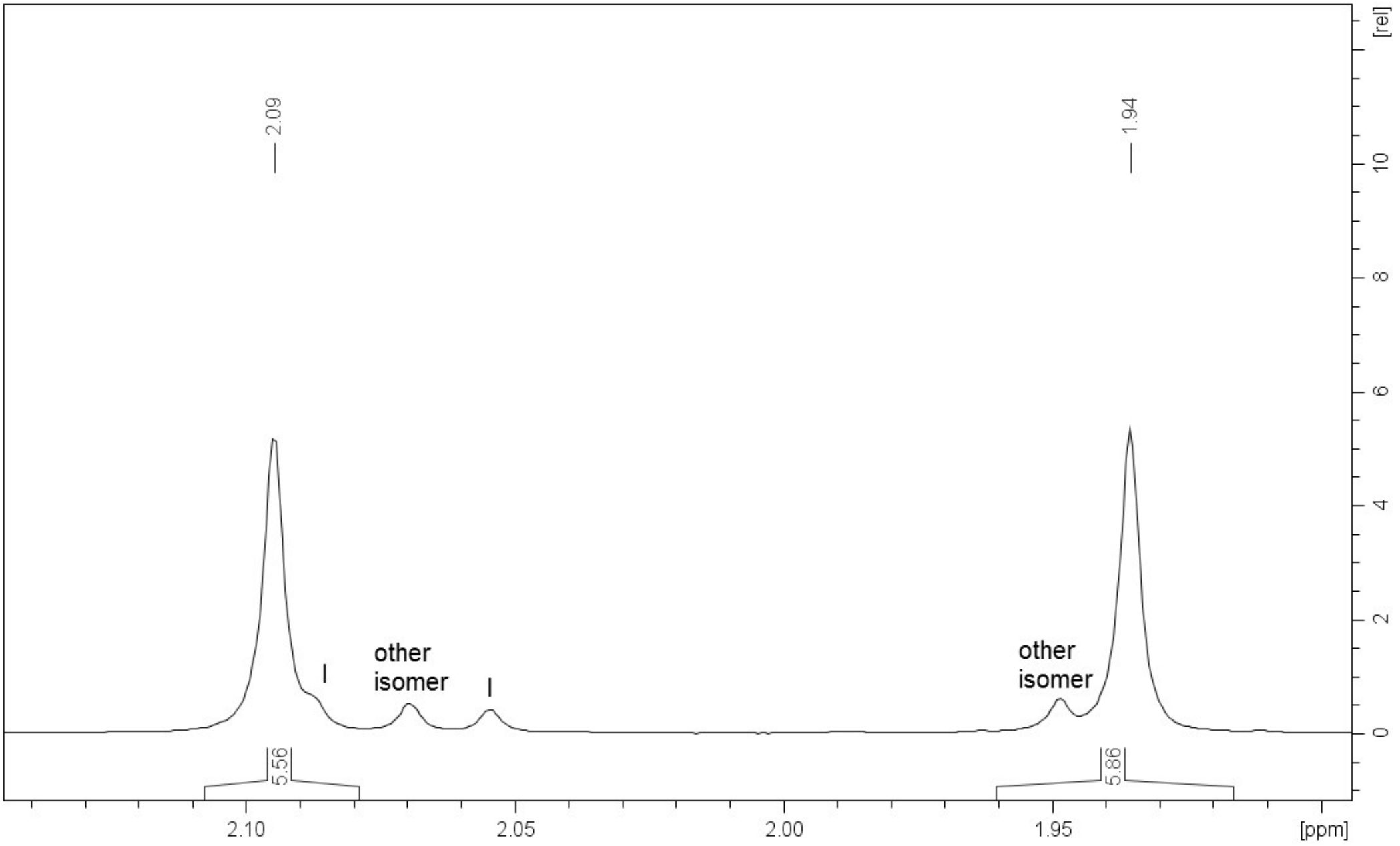



133.15
132.61
132.03
[rel]
4
3
2
1
- 0
136
134
132
130
128
[ppm]

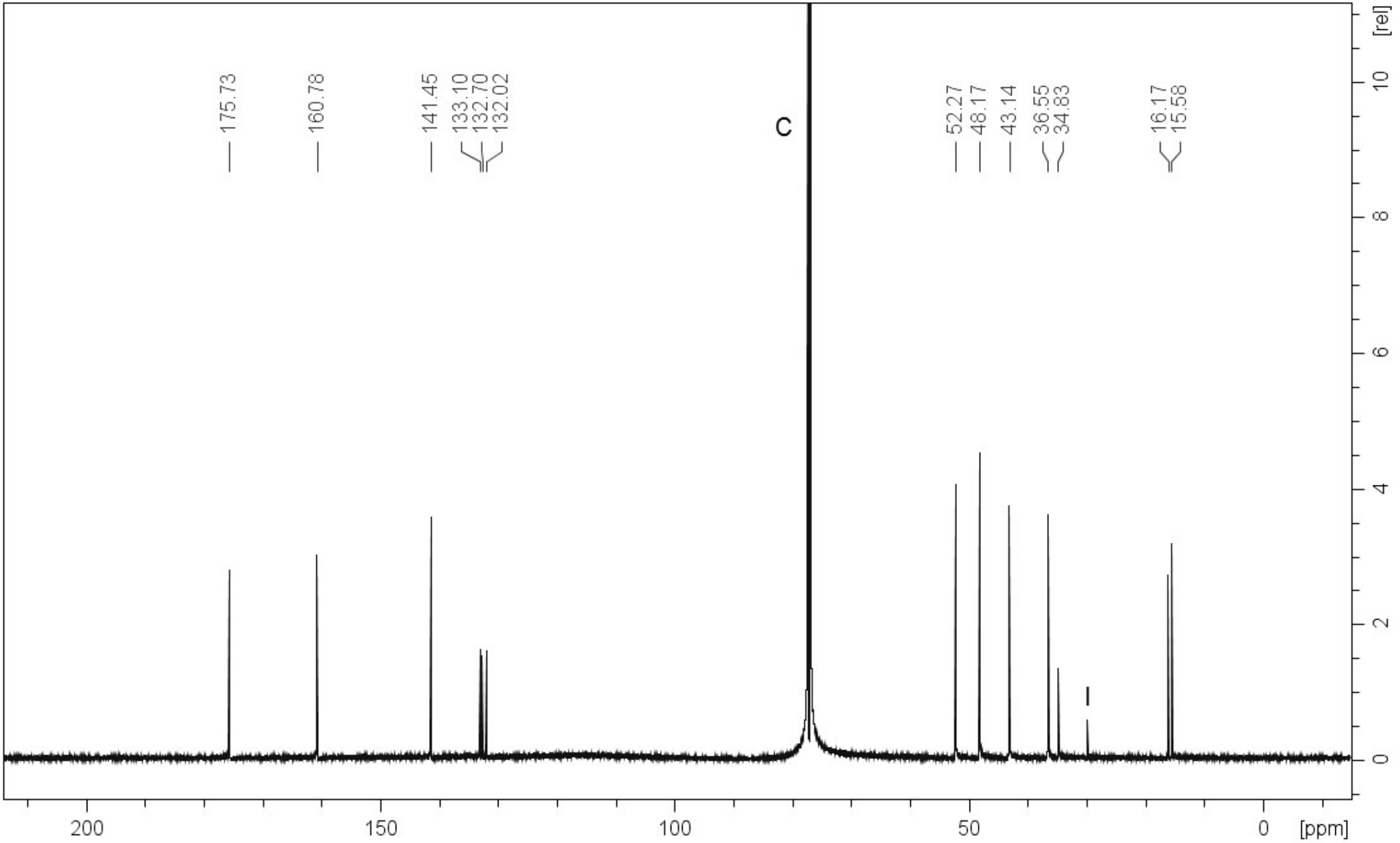

16.18
15.50
[rel]
6
5
4
3
2
1
- 0
22
20
18
16
14
12
[ppm]

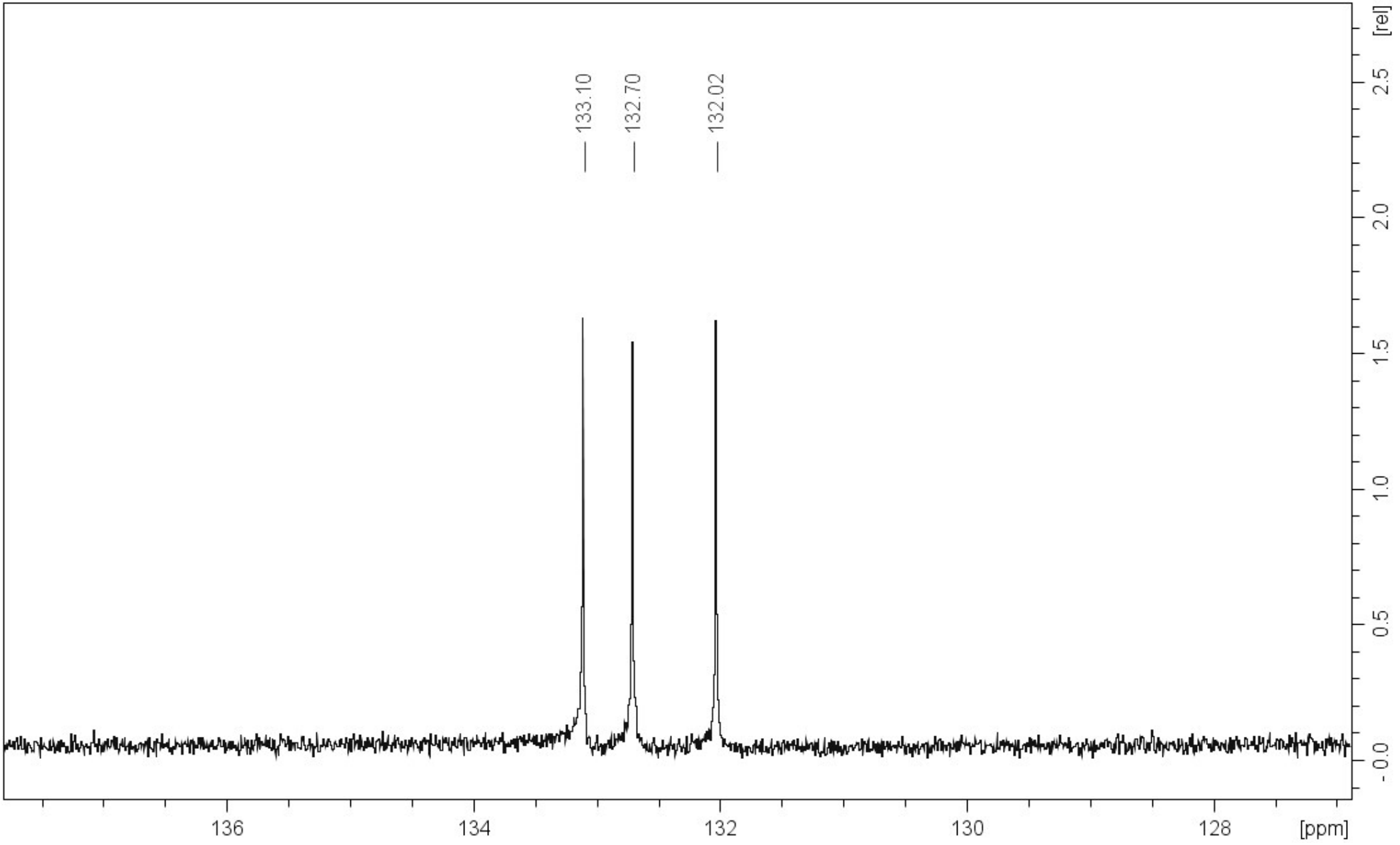
S3: 600 MHz ^{1}H NMR *endo*- linker **6**, outer CH_3 isomer

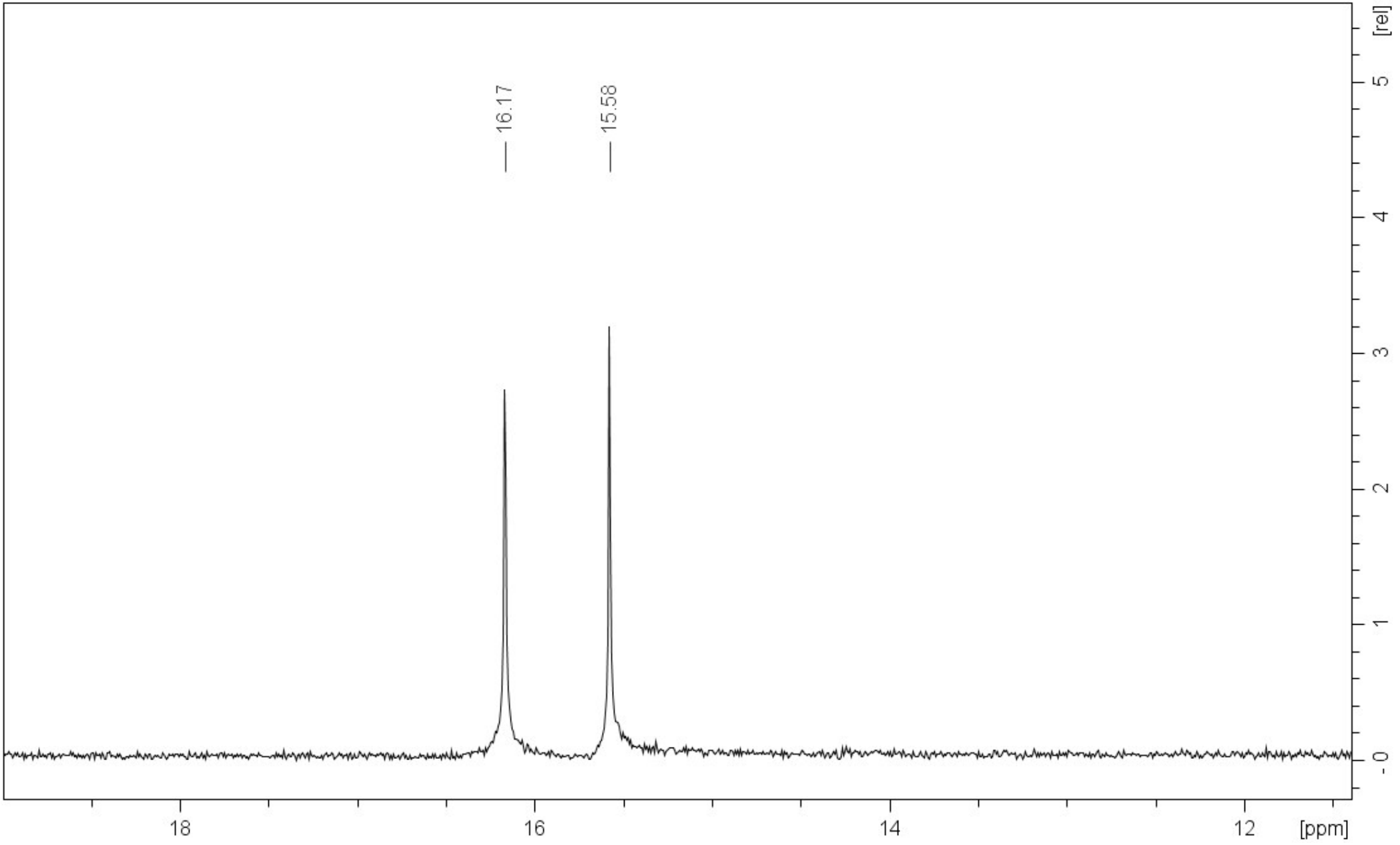



2.09
1.94
other
isomer
other
isomer
5.56
5.86
2.10
2.05
2.00
1.95
[ppm]
[rel]
0
2
4
6
8
10

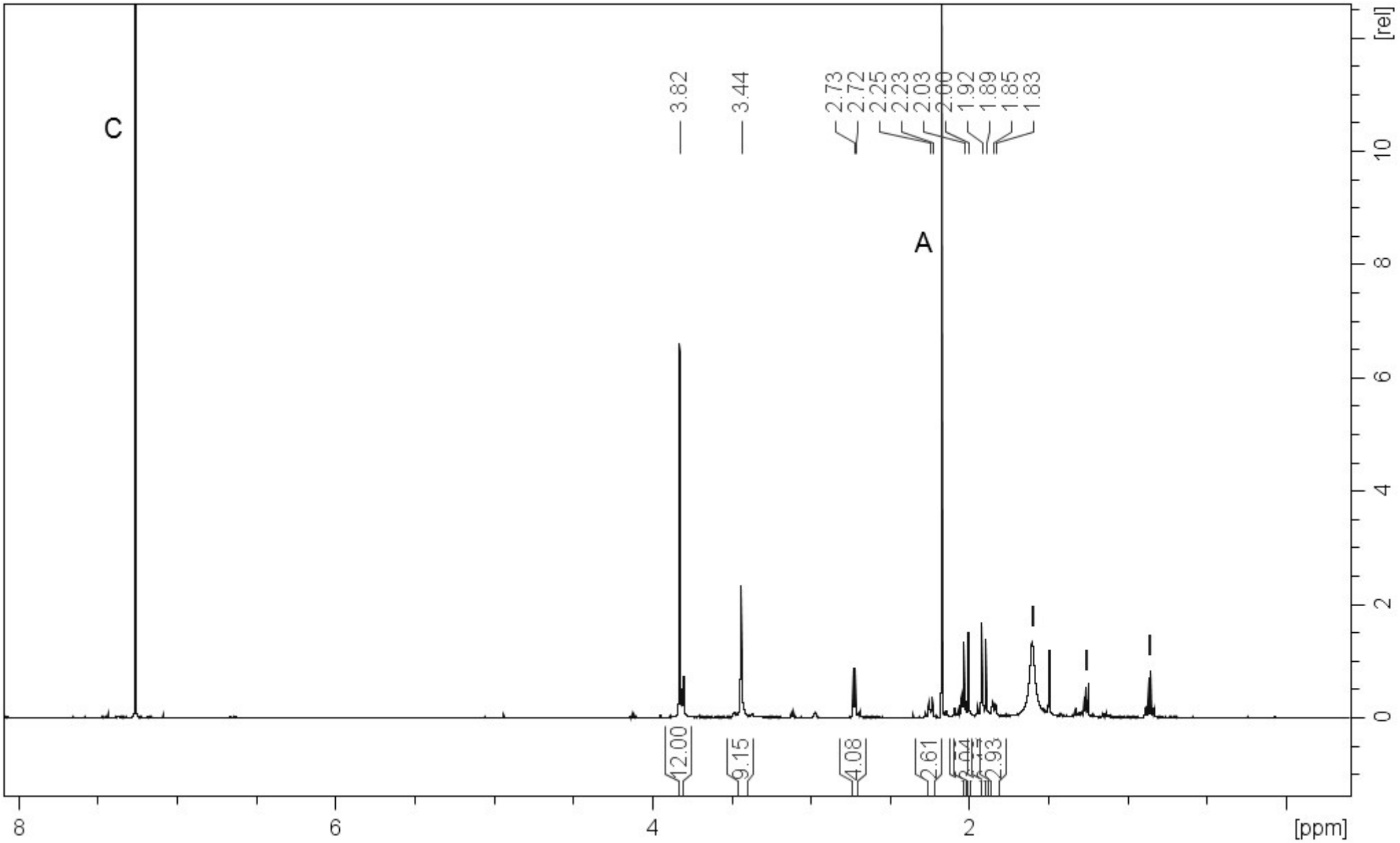
S4: 150 MHz ^{13}C NMR *endo*- linker **6**, outer CH_3 isomer

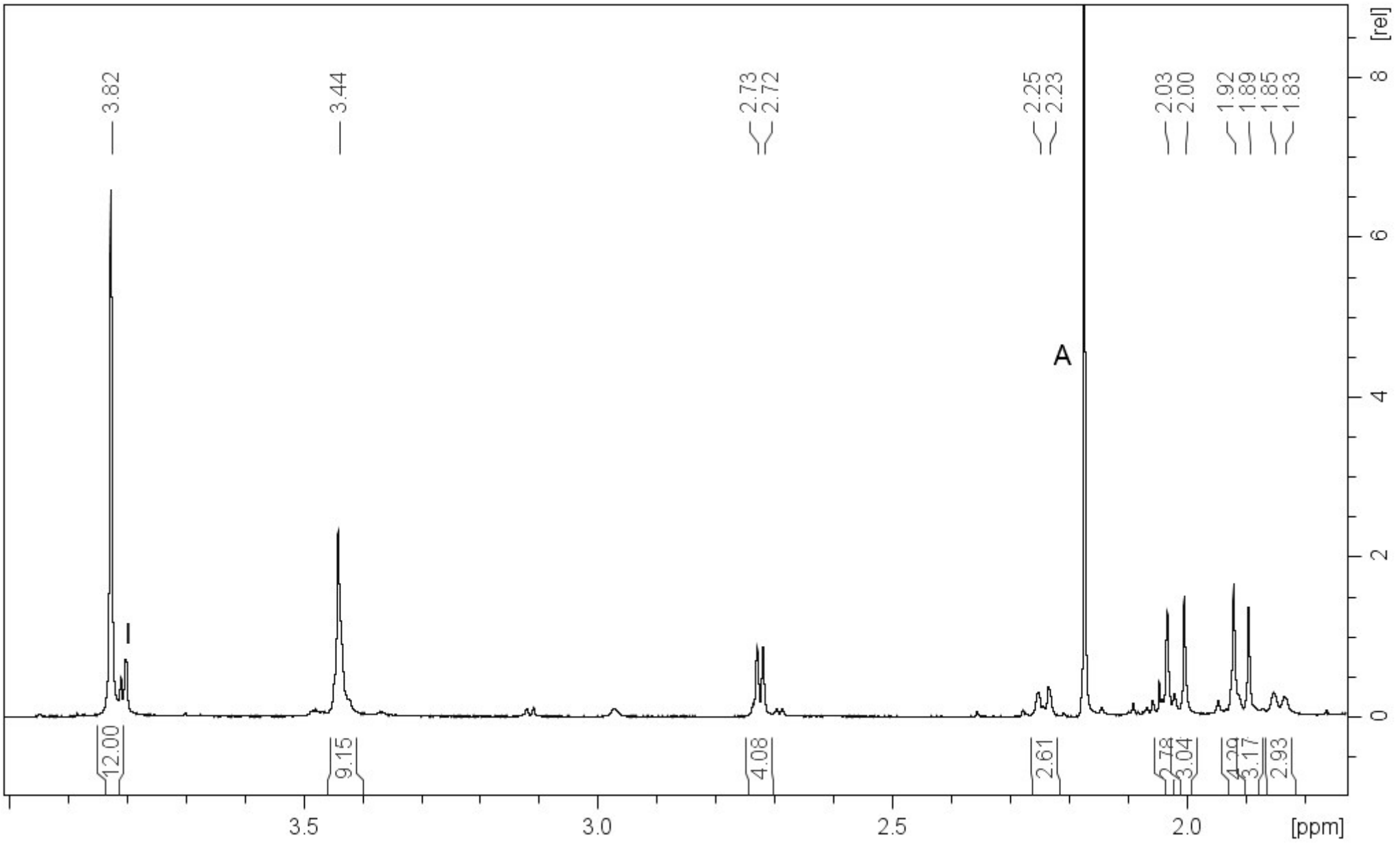


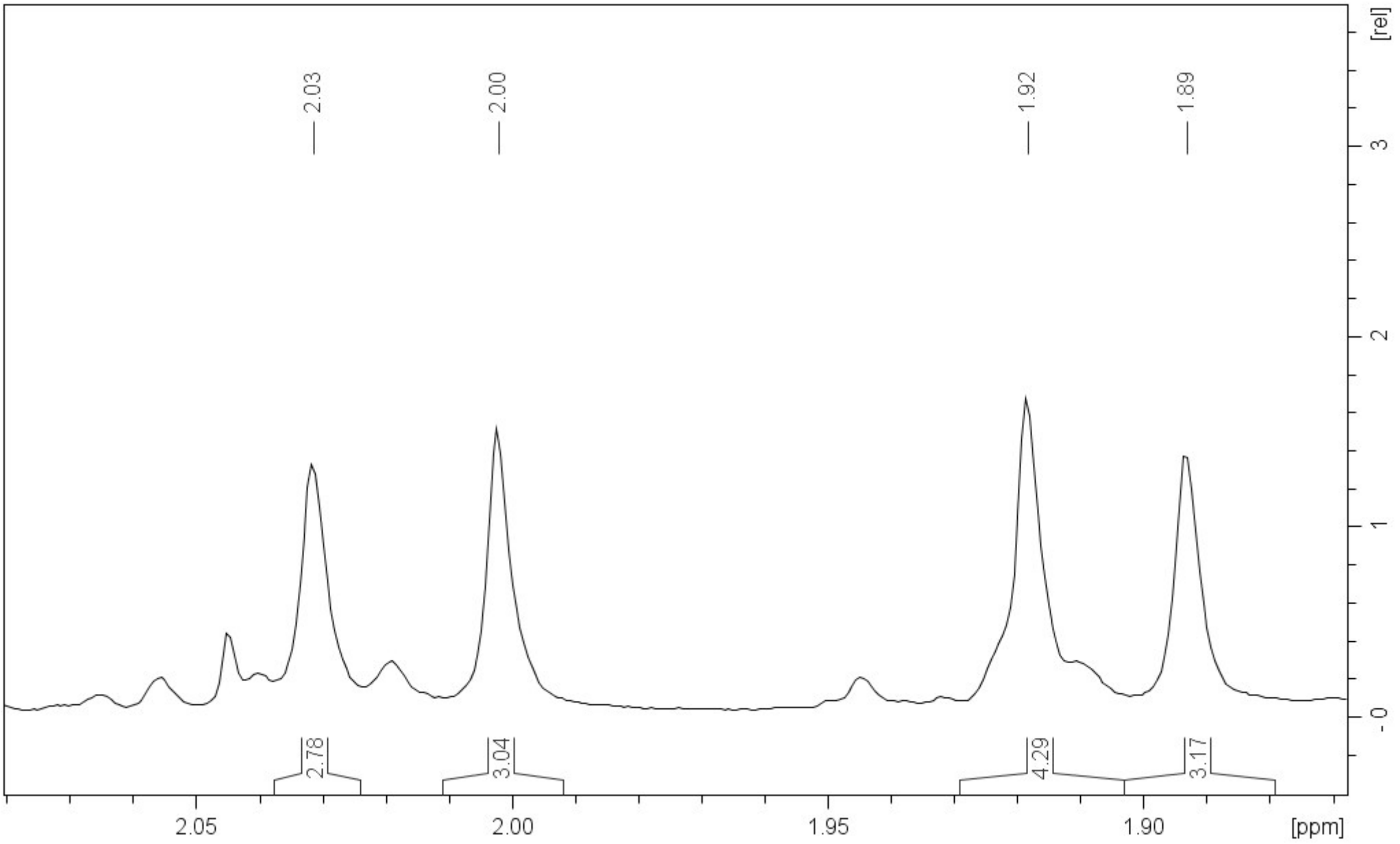

133.10
132.70
132.02
[rel]
2.5
2.0
1.5
1.0
0.5
-0.0
136
134
132
130
128
[ppm]


16.17
15.58
[rel]
5
4
3
2
1
-0
18
16
14
12
[ppm]

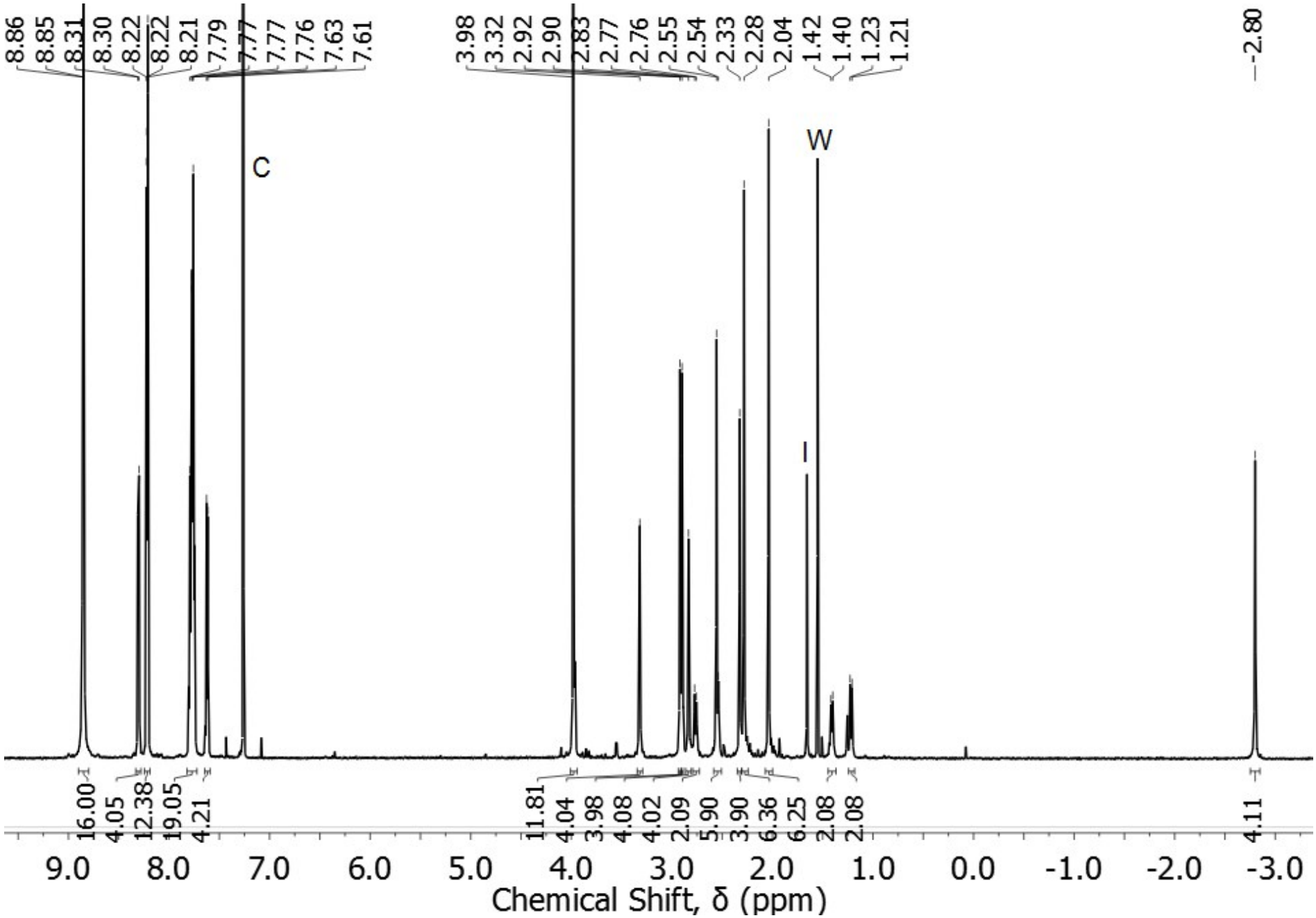
S5: 600 MHz ^{1}H NMR *endo*- bis-epoxide linker **7**, *syn*- + *anti*-

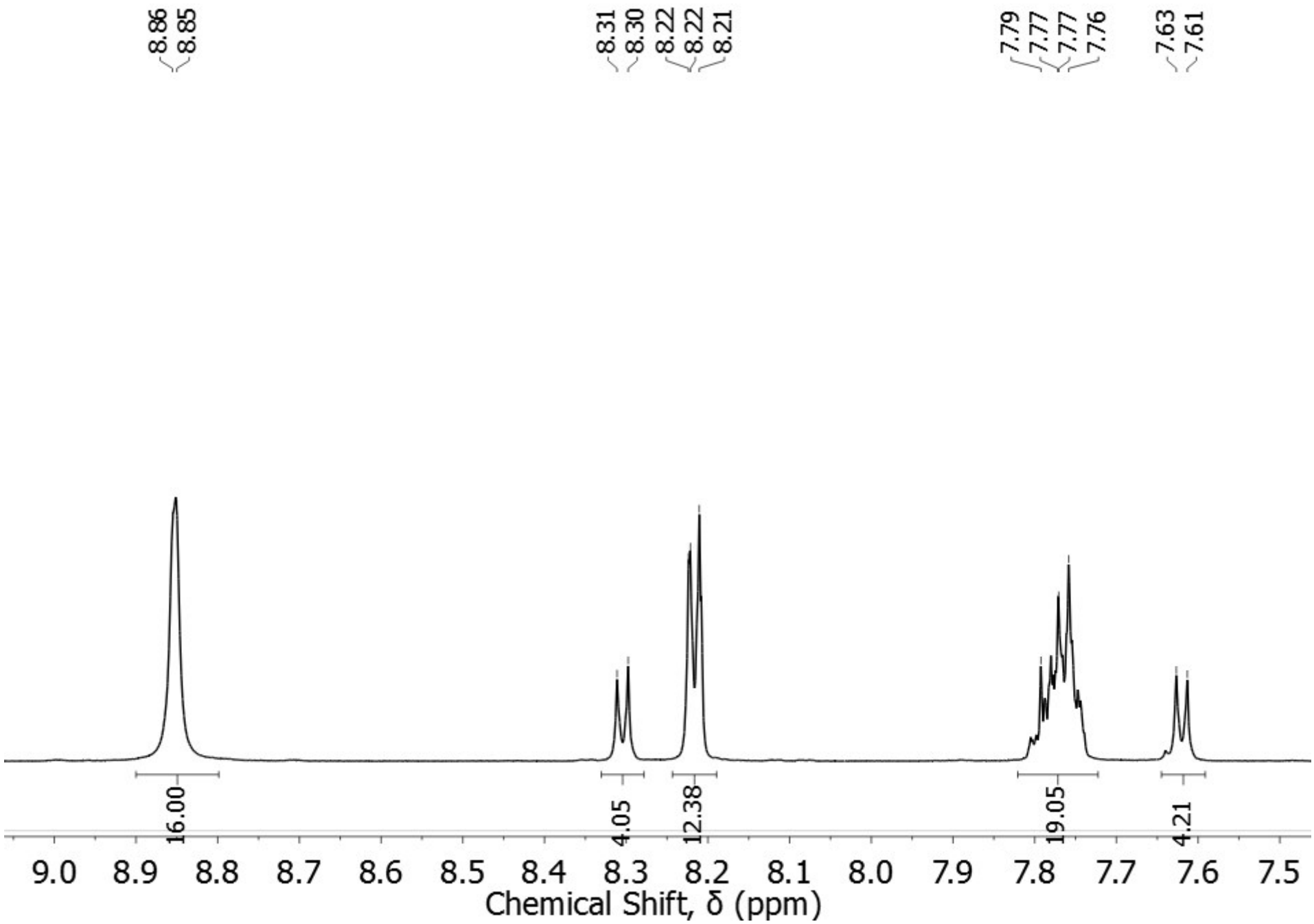


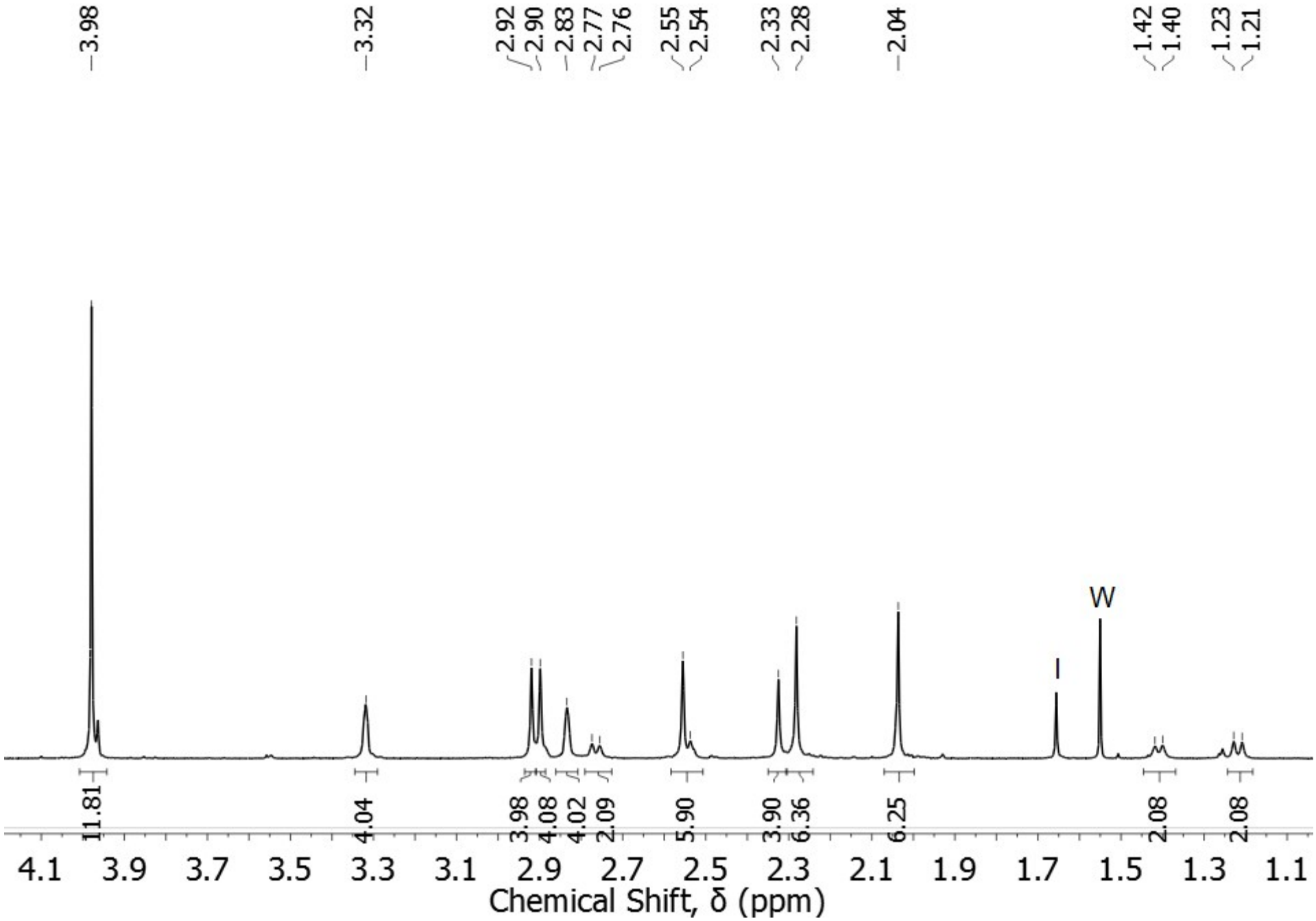

3.82
3.44
2.73
2.72
2.25
2.23
2.03
2.00
1.92
1.89
1.85
1.83
A
I
12.00
9.15
4.08
2.61
2.78
3.04
4.29
3.17
2.93
3.5
3.0
2.5
2.0
[ppm]
[rel]
0
2
4
6
8

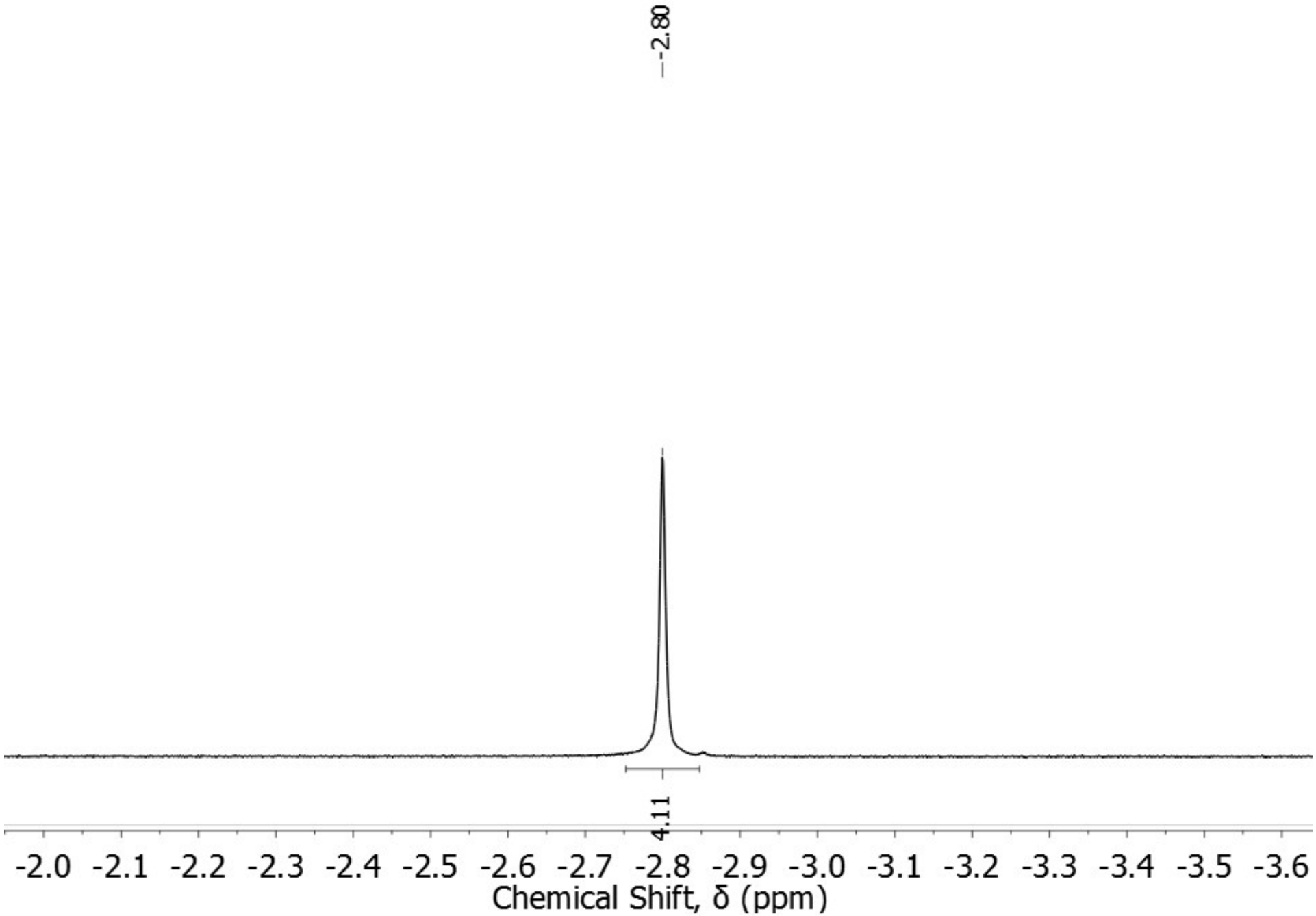

2.03
2.00
1.92
1.89
2.78
3.04
4.29
3.17
2.05
2.00
1.95
1.90
[ppm]
[rel]
3
2
1
- 0

S7: 600 MHz ^{1}H NMR free base tweezer, *anti*- **9b**

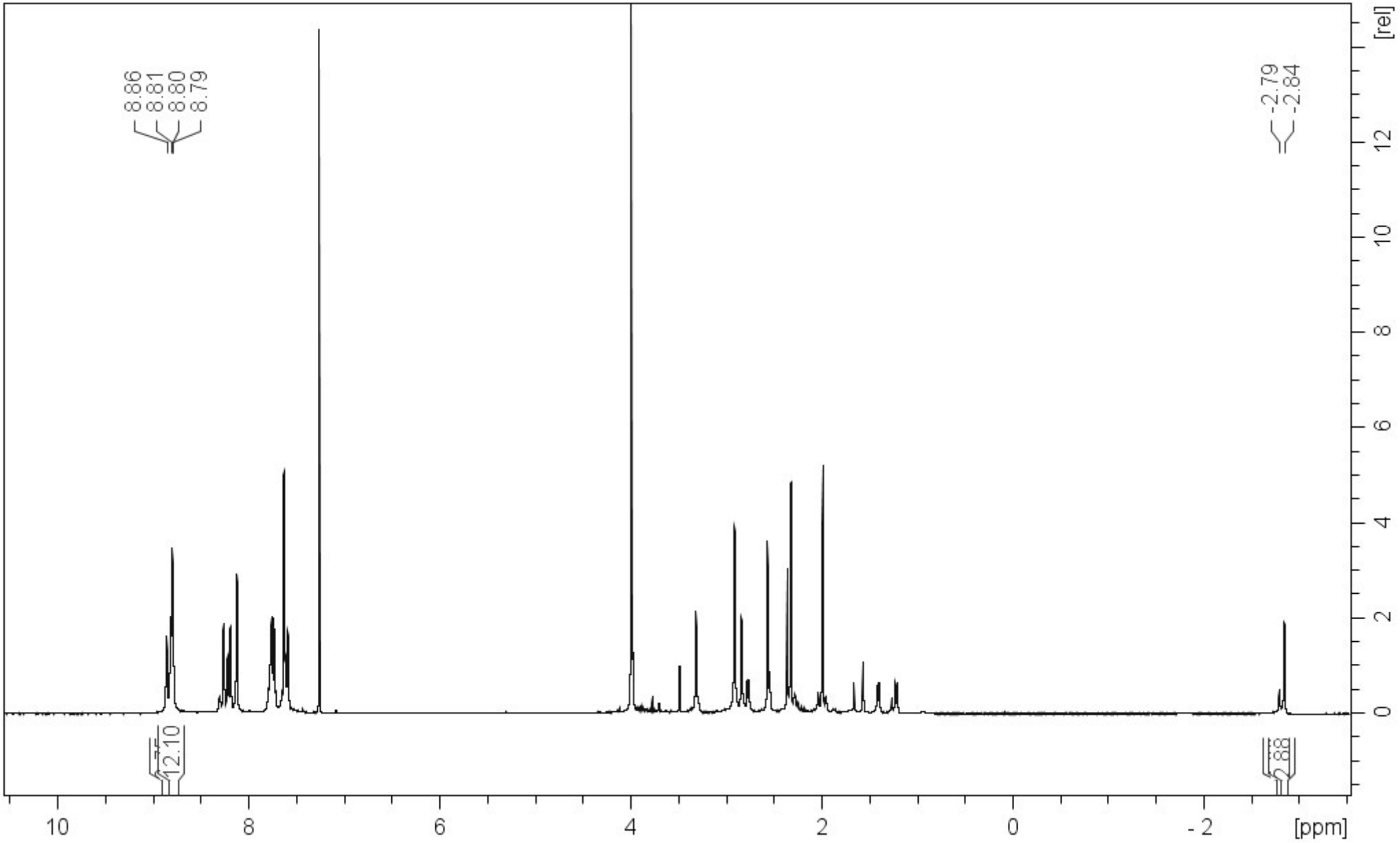


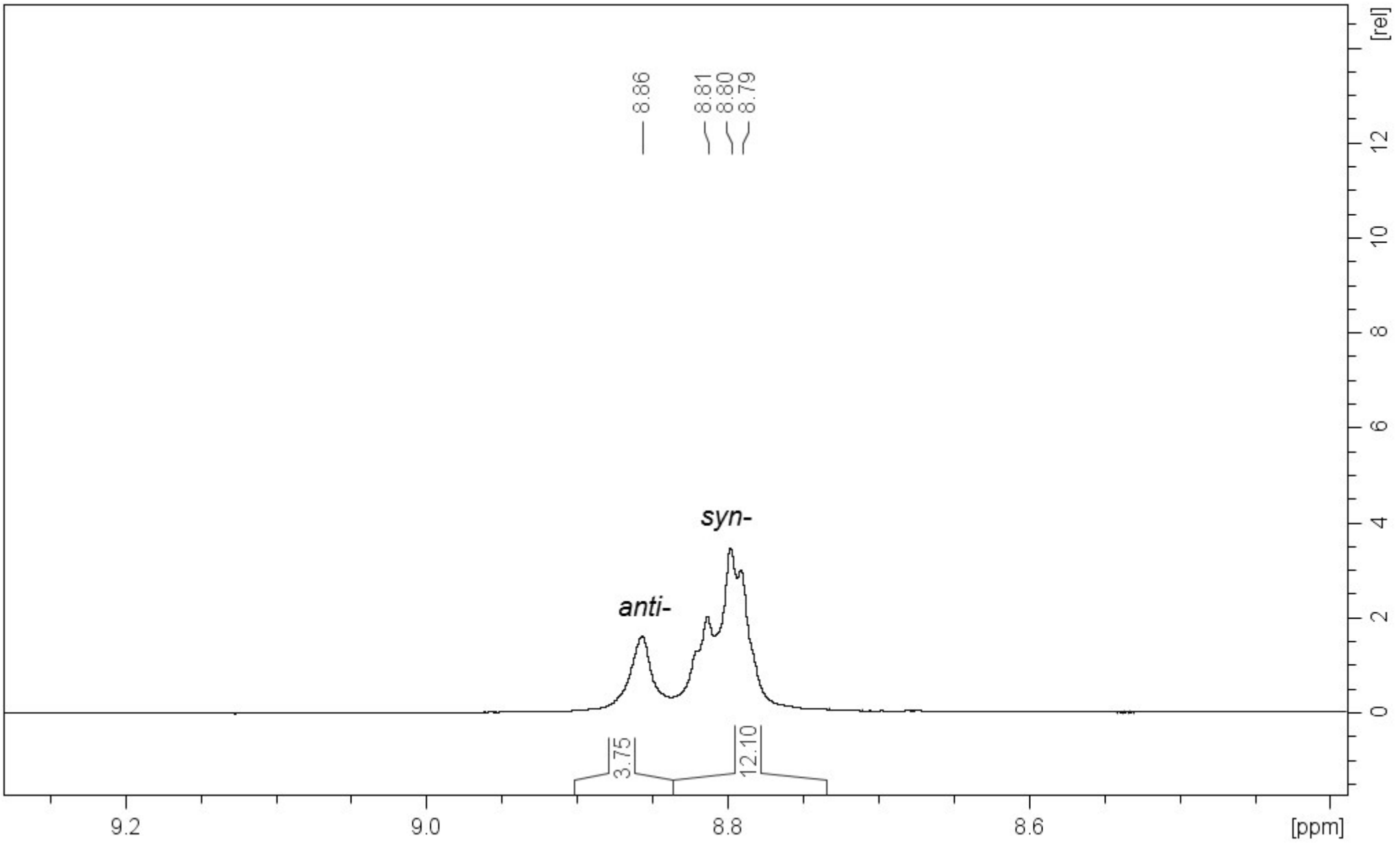

8.86
8.85
8.31
8.30
8.22
8.22
8.21
7.79
7.77
7.77
7.76
7.63
7.61
16.00
4.05
12.38
19.05
4.21
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
Chemical Shift, δ (ppm)

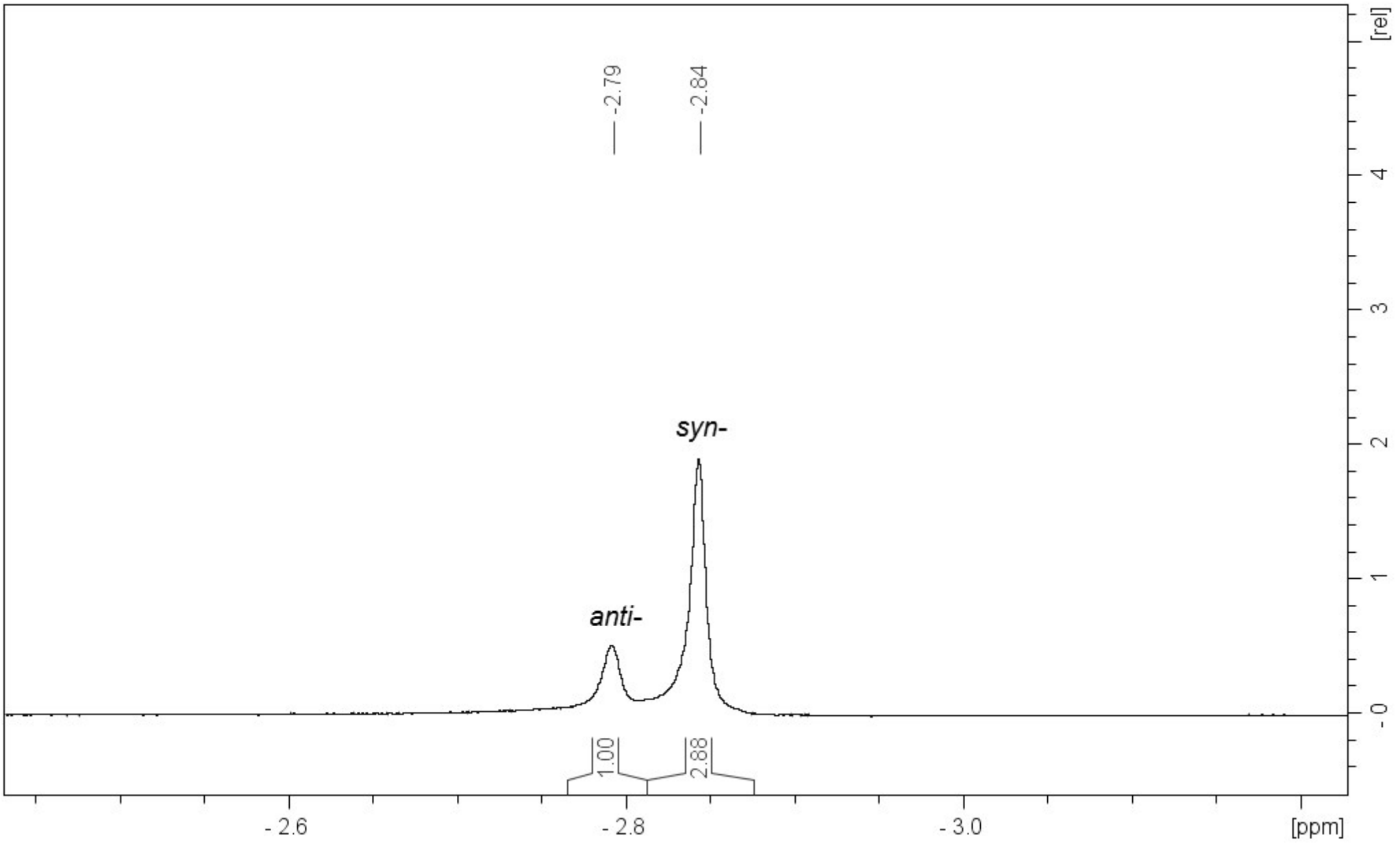

3.98
3.32
2.92
2.90
2.83
2.77
2.76
2.55
2.54
2.33
2.28
2.04
1.42
1.40
1.23
1.21
W
I
11.81
4.04
3.98
4.08
4.02
2.09
5.90
3.90
6.36
6.25
2.08
2.08
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
Chemical Shift, δ (ppm)

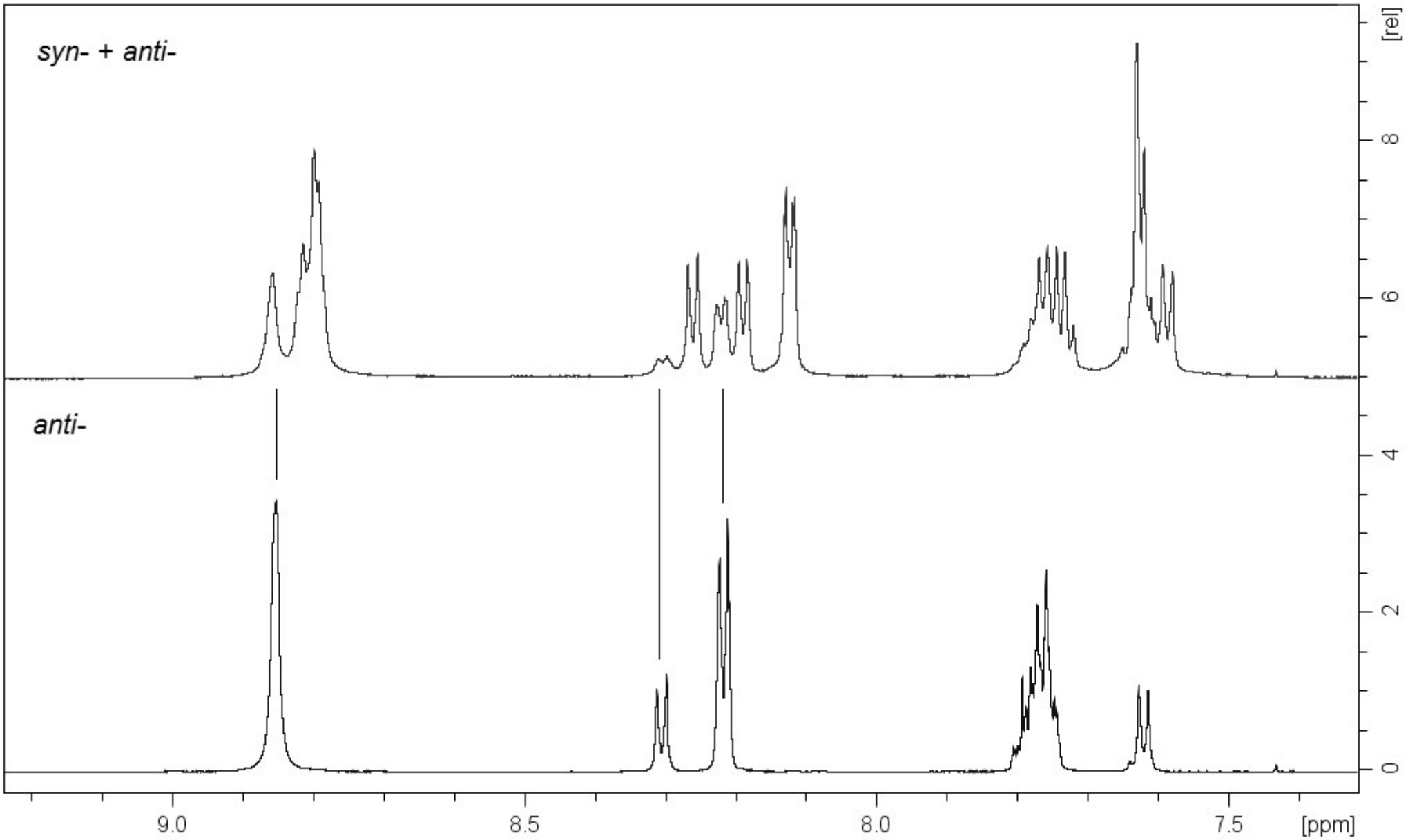

-2.80
4.11
-2.0 -2.1 -2.2 -2.3 -2.4 -2.5 -2.6 -2.7 -2.8 -2.9 -3.0 -3.1 -3.2 -3.3 -3.4 -3.5 -3.6
Chemical Shift, δ (ppm)

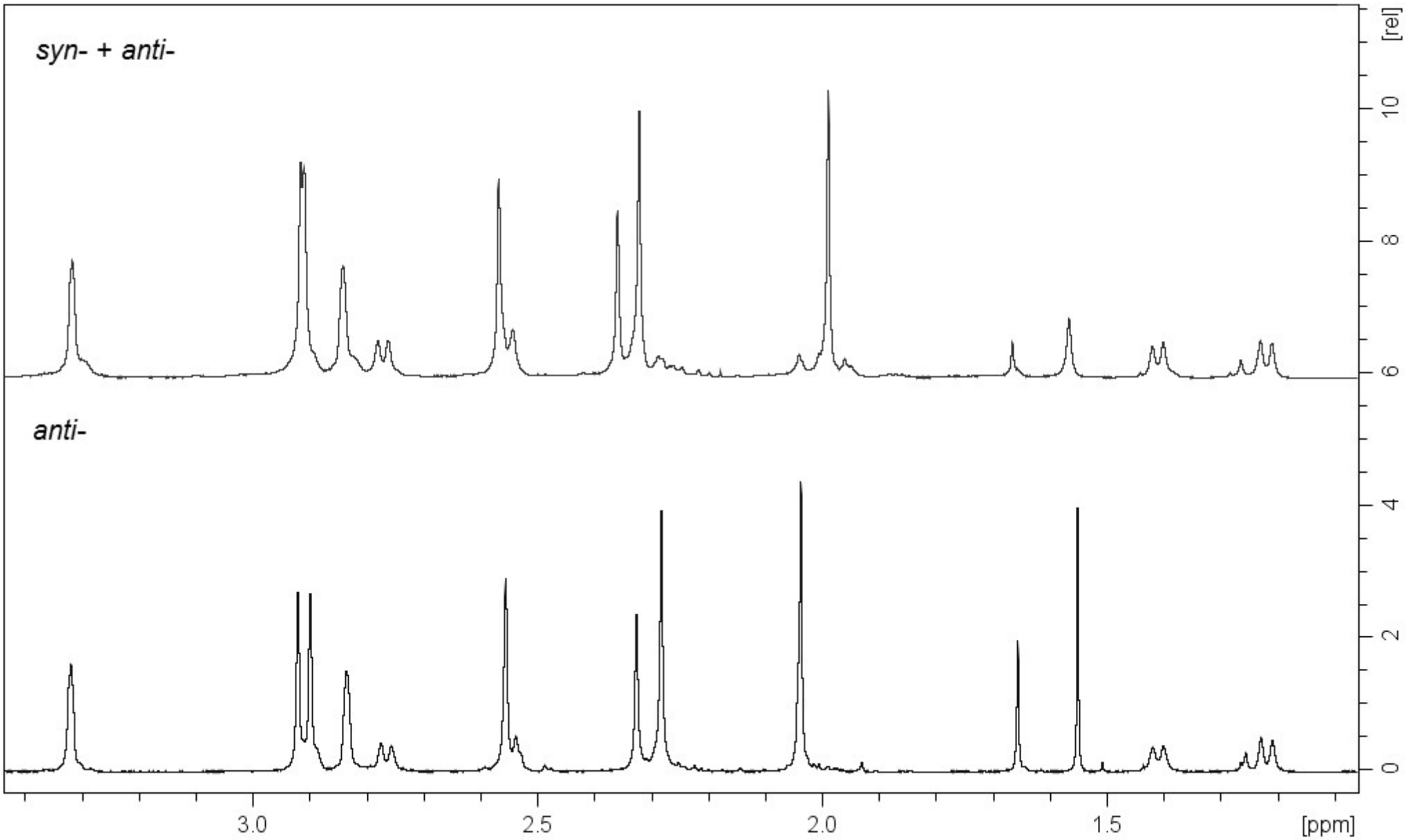
S8: 600 MHz ^{1}H NMR free base tweezer, *syn*- **9a** (as mixture with *anti*- **9b**)

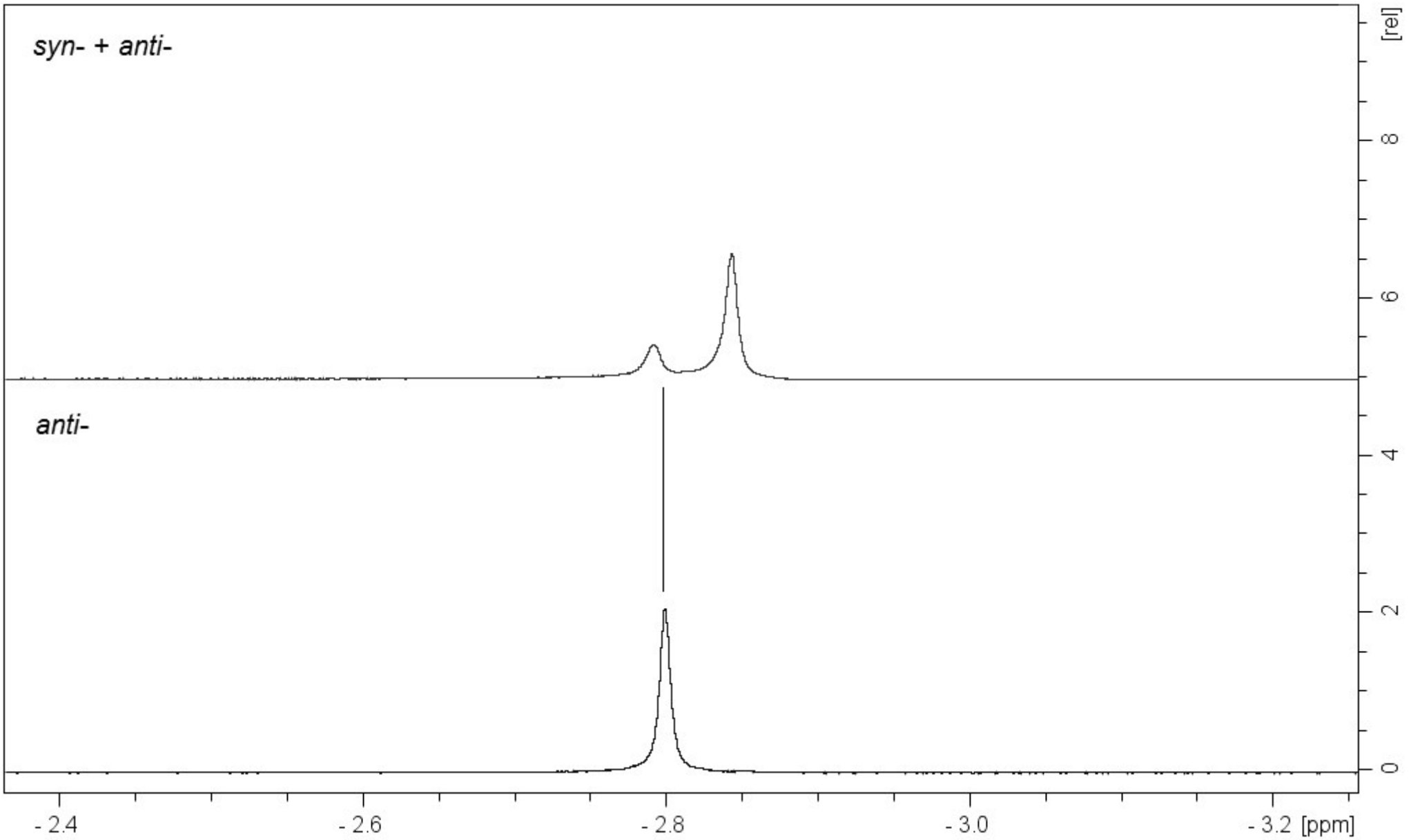



8.86
8.81
8.80
8.79
syn-
anti-
3.75
12.10
[rel]
0
2
4
6
8
10
12
9.2
9.0
8.8
8.6
[ppm]

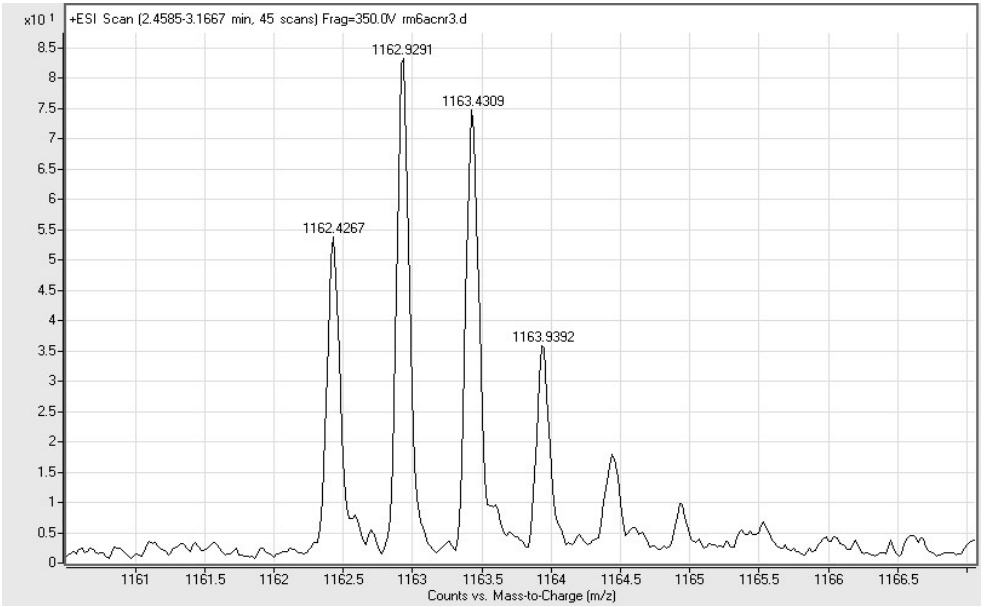

-2.79
-2.84
syn-
anti-
1.00
2.88
- 2.6
- 2.8
- 3.0
[ppm]
[rel]
- 0
1
2
3
4

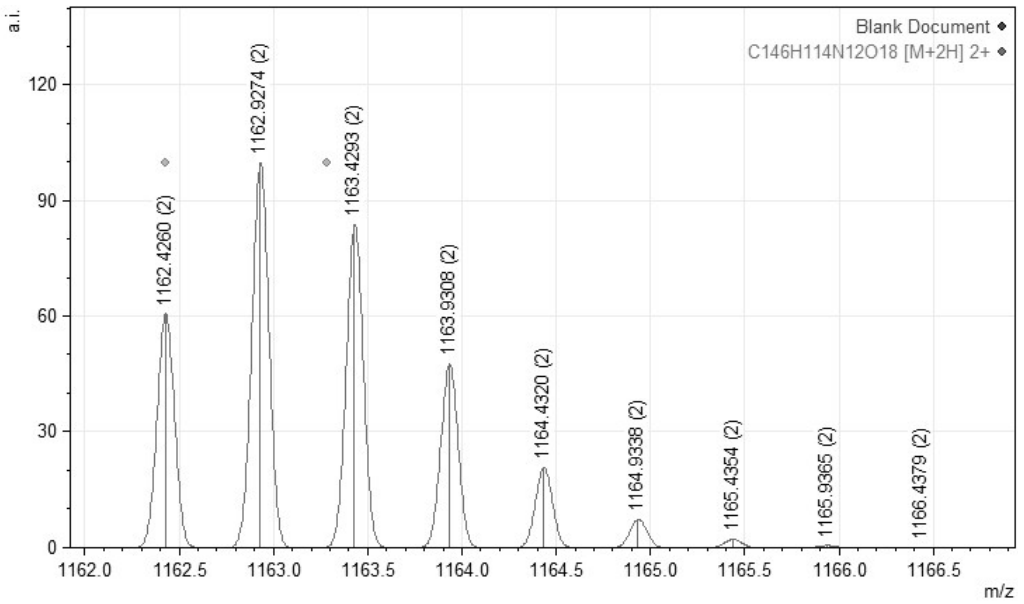

syn- + anti-
anti-
[rel]
8
6
4
2
0
9.0
8.5
8.0
7.5
[ppm]


syn- + anti-
anti-
[rel]
10
8
6
4
2
0
3.0
2.5
2.0
1.5
[ppm]

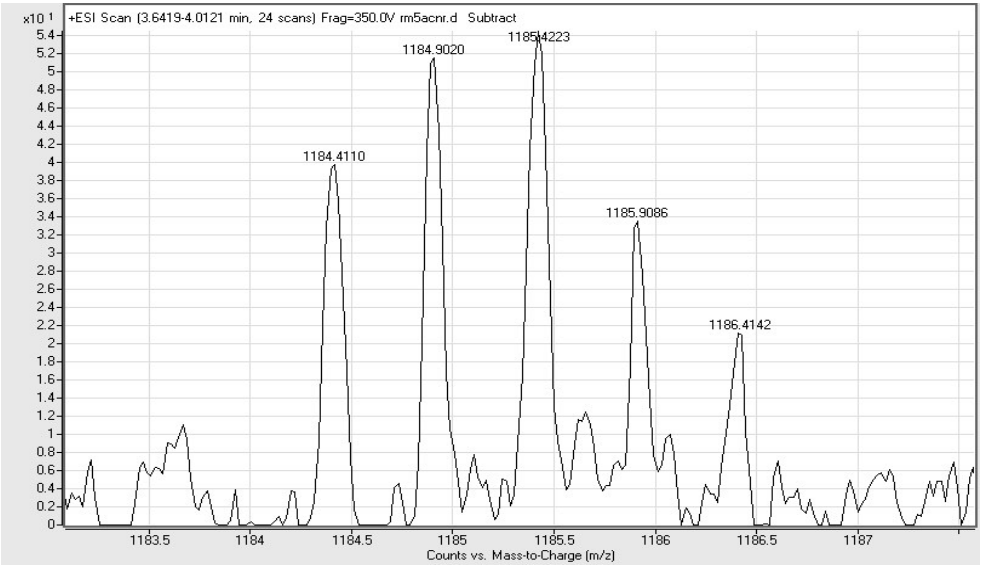

syn- + anti-
anti-
[rel]
8
6
4
2
0
- 2.4
- 2.6
- 2.8
- 3.0
- 3.2 [ppm]

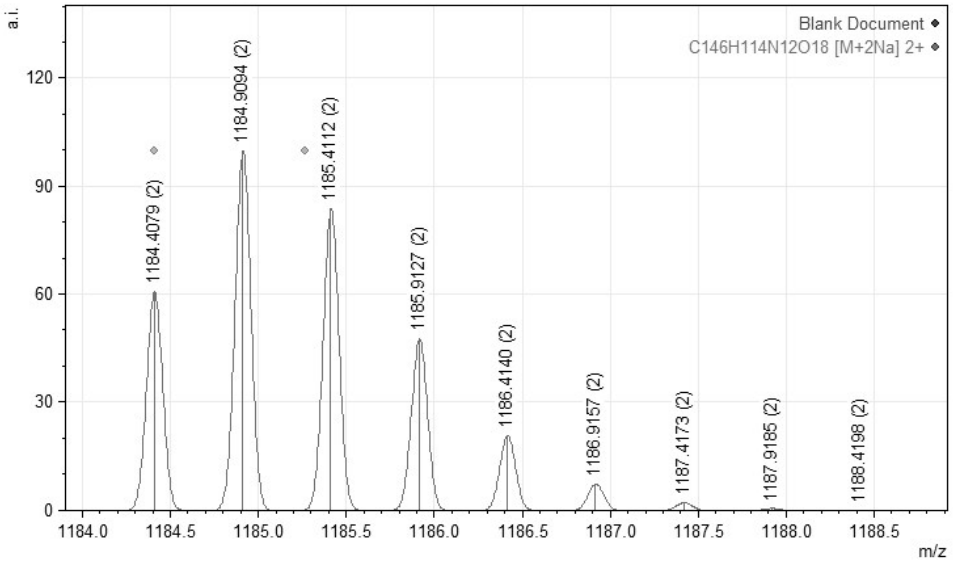
S9: HRMS (ESI-TOF-MS) free base tweezer **9**, two samples containing different ratios of *syn*- **9a**/*anti*- **9b**, experimental and predicted





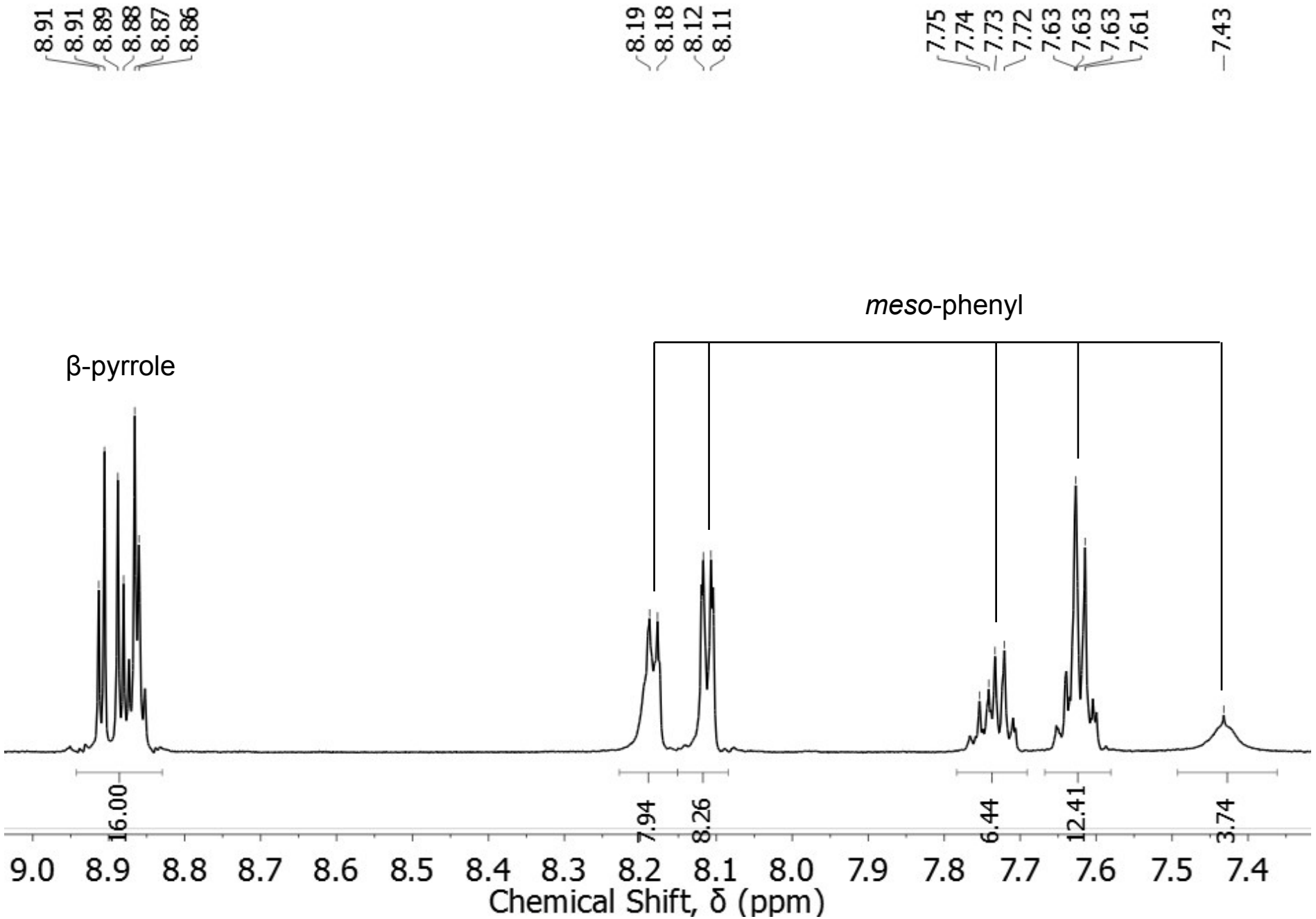
$[C_{146}H_{116}N_{12}O_{18}]^{2+}$ $[M+2H]^{2+}$: Found: 1162.4267. Calc: 1162.4260.

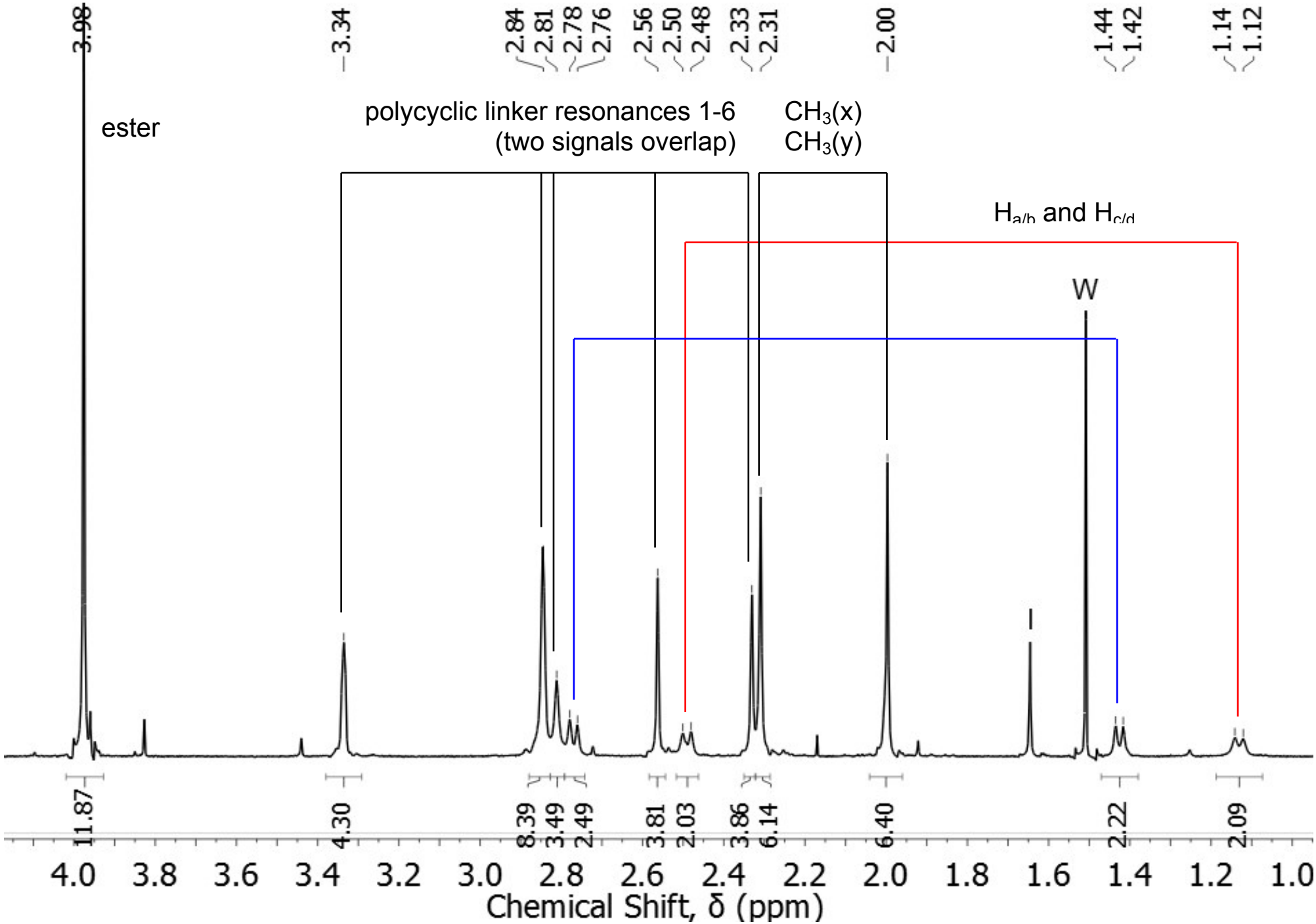




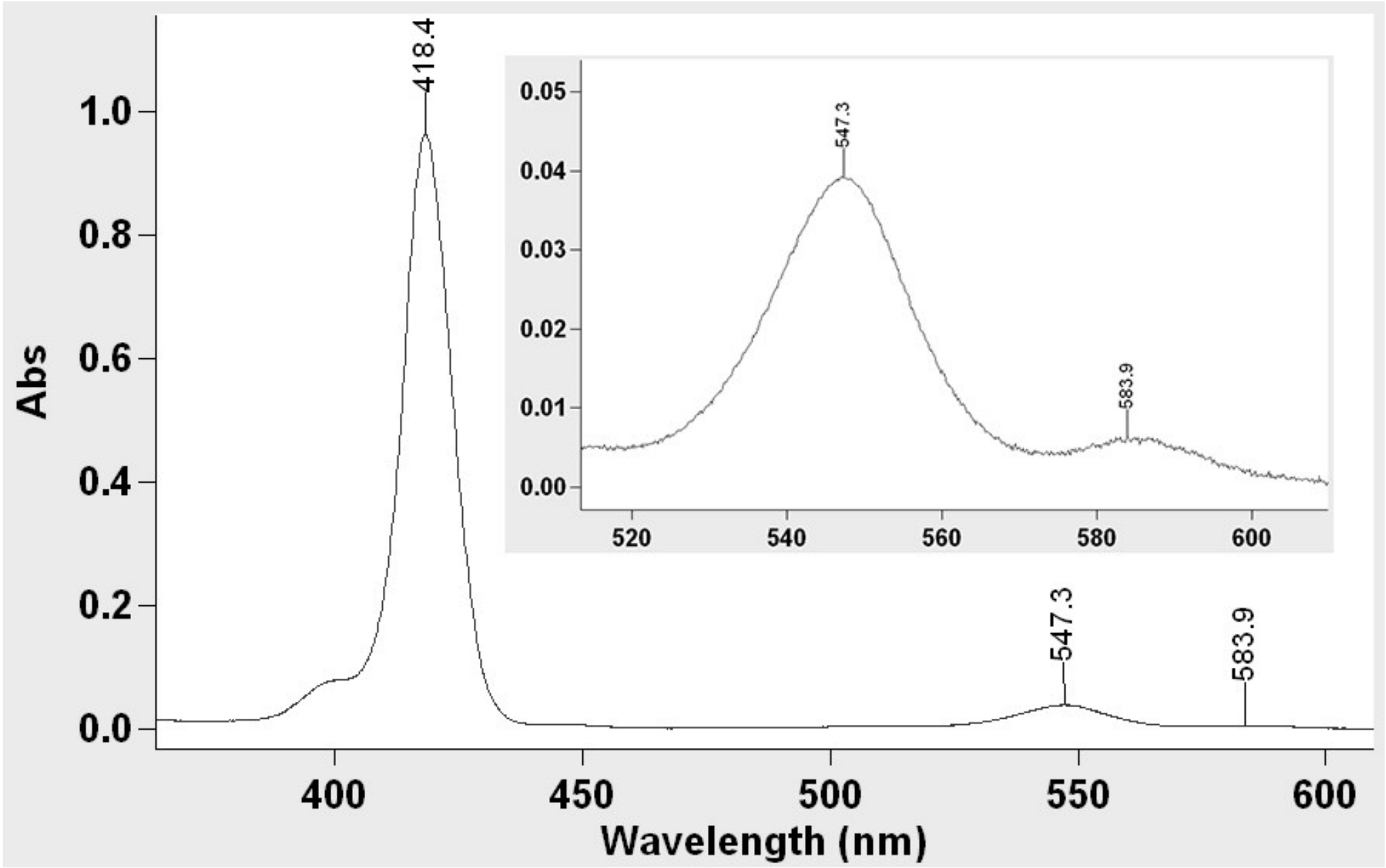
$[C_{146}H_{114}N_{12}O_{18}Na_2]^{2+}$ $[M+2Na]^{2+}$: Found: 1184.4110. Calc: 1184.4079.

S10: 600 MHz ^{1}H NMR *syn*- zinc(II) tweezer **3a**



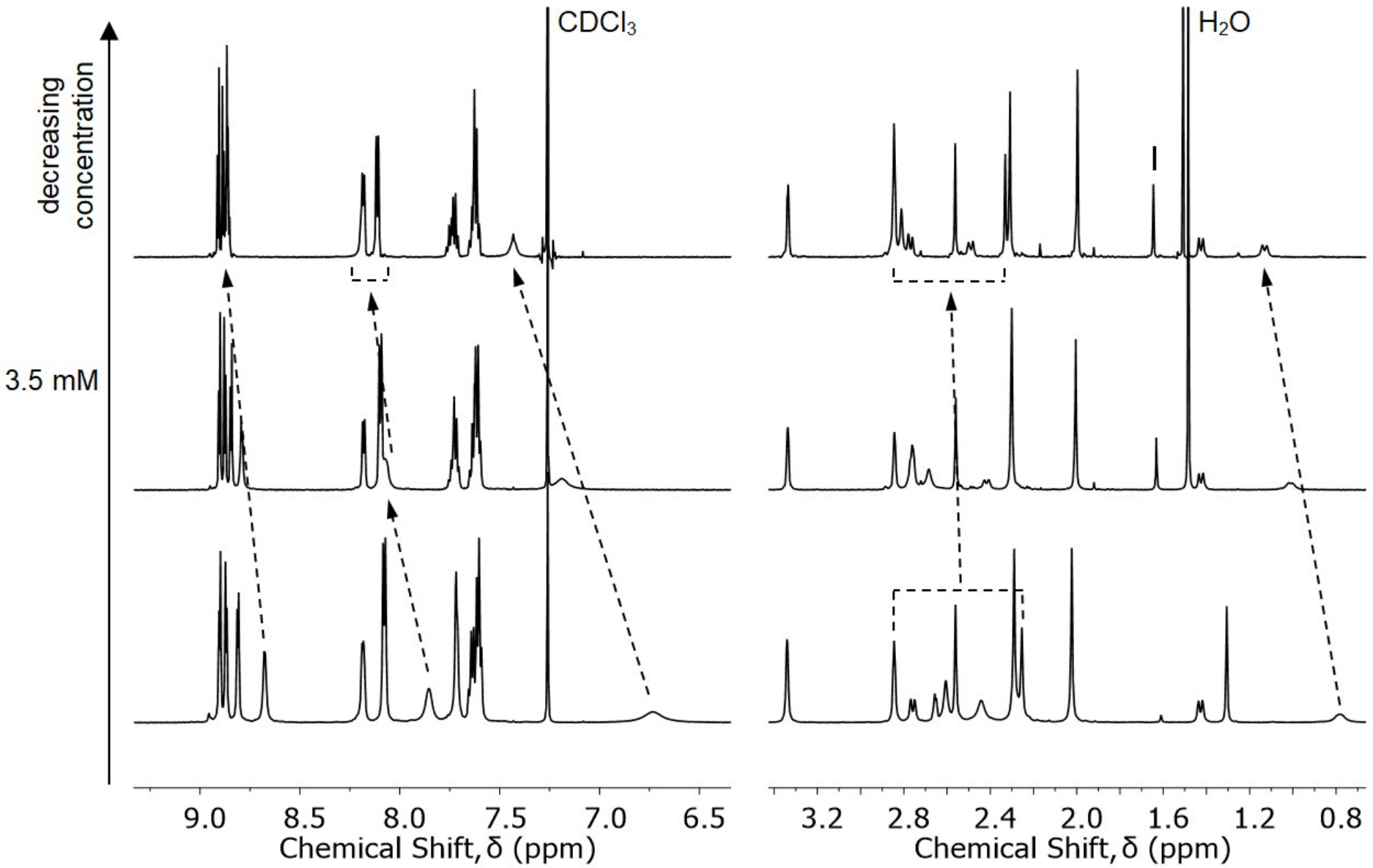

3.98
3.34
2.84
2.81
2.78
2.76
2.56
2.50
2.48
2.33
2.31
2.00
1.44
1.42
1.14
1.12
ester
polycyclic linker resonances 1-6
(two signals overlap)
CH3(x)
CH3(y)
Ha/b and Hc/d
W
11.87
4.30
8.39
3.49
2.49
3.81
2.03
3.86
6.14
6.40
2.22
2.09
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
Chemical Shift, δ (ppm)

S11: UV/Vis *syn*- zinc(II) tweezer **3a**

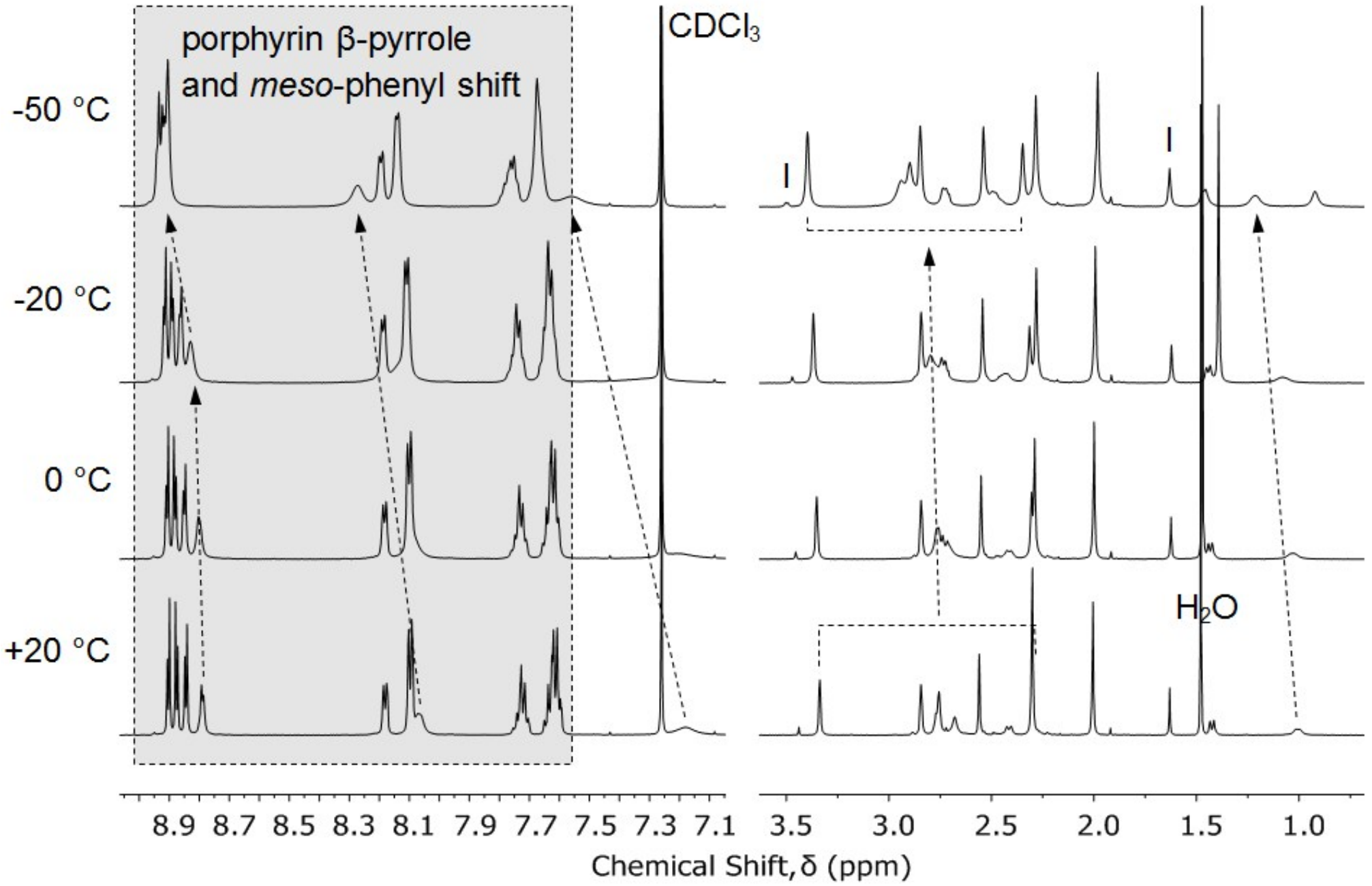


S12: Concentration and Temperature Dependence of ^{1}H NMR of *syn*- zinc(II) tweezer **3a**

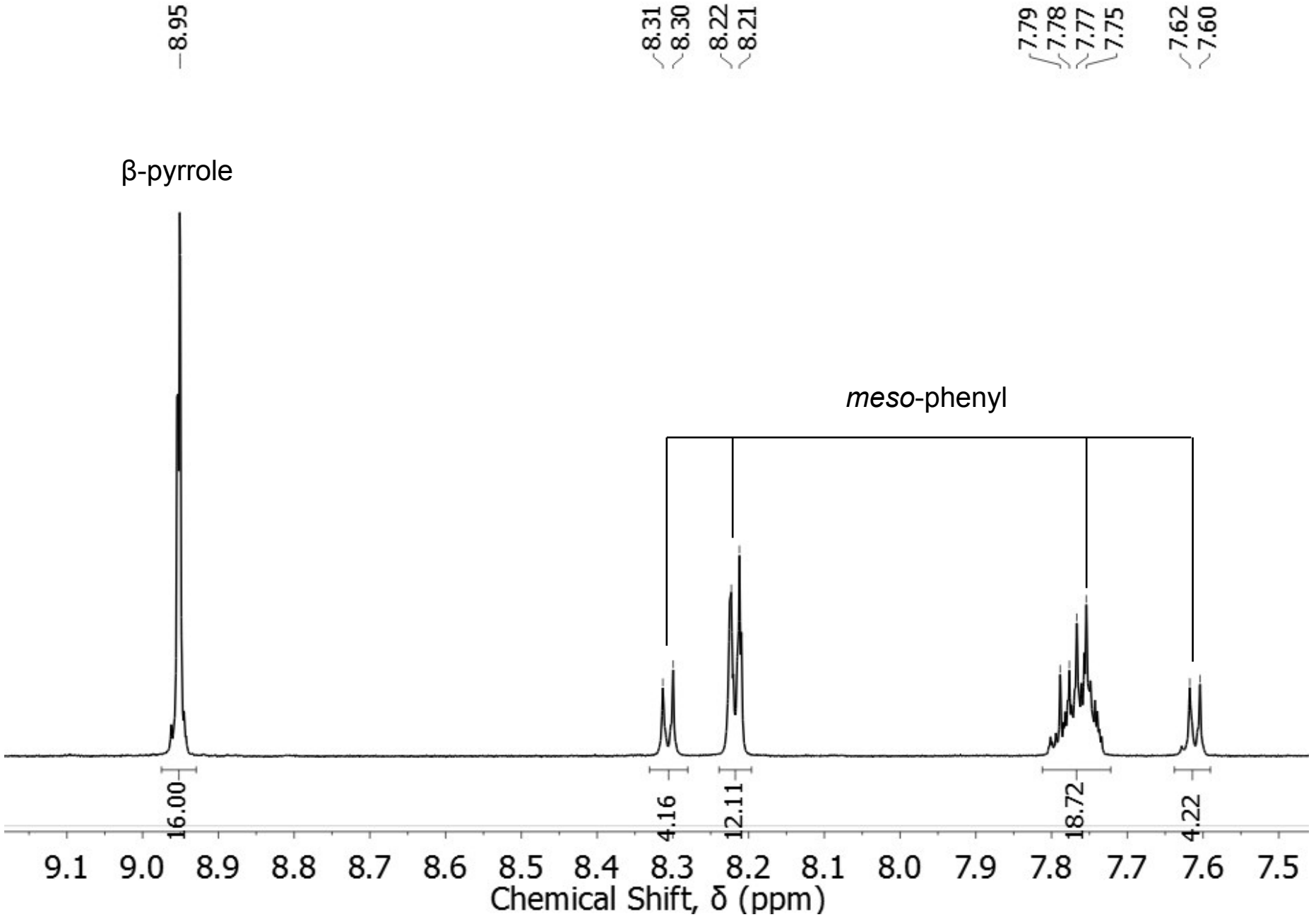
(a)

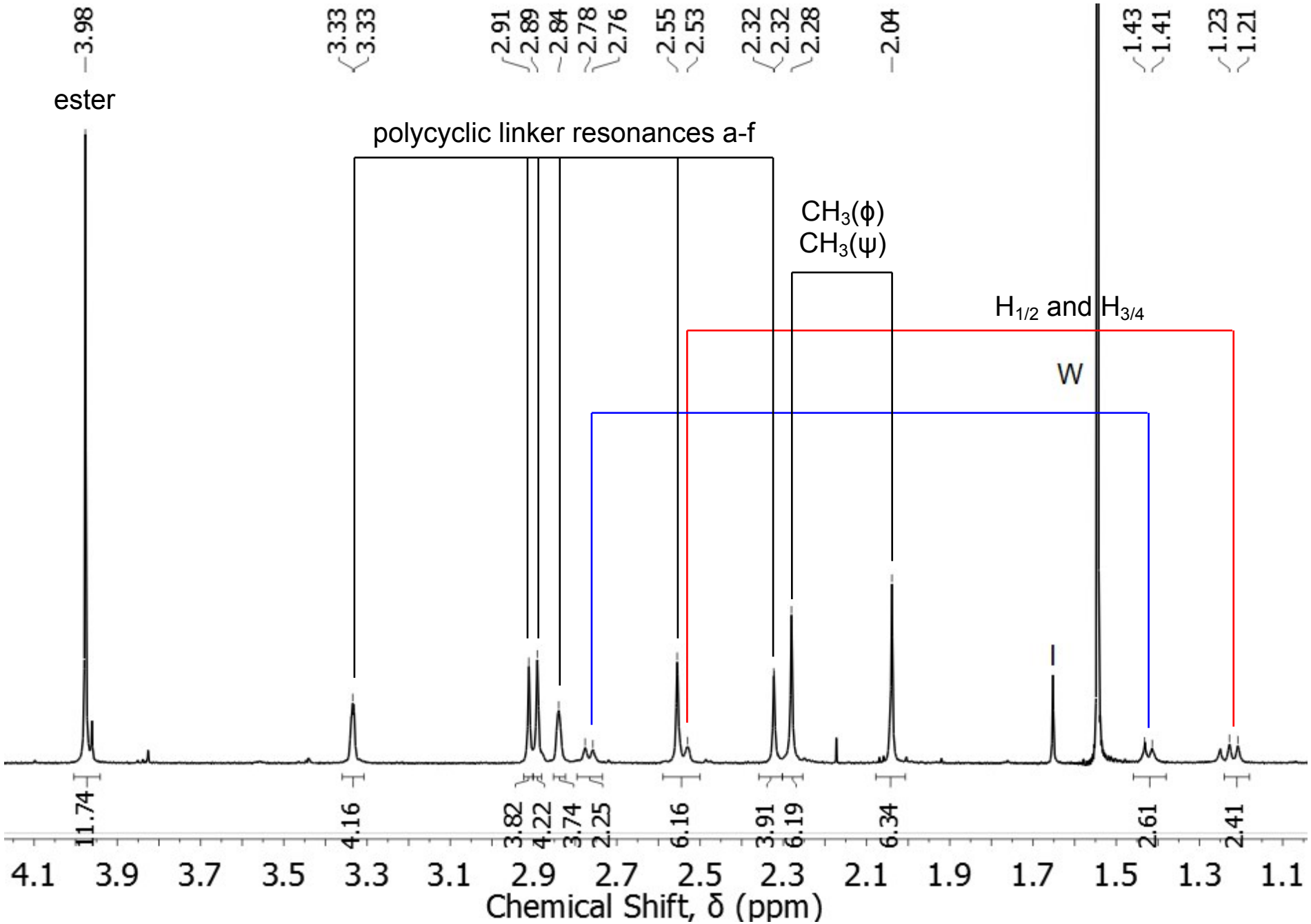


(b)

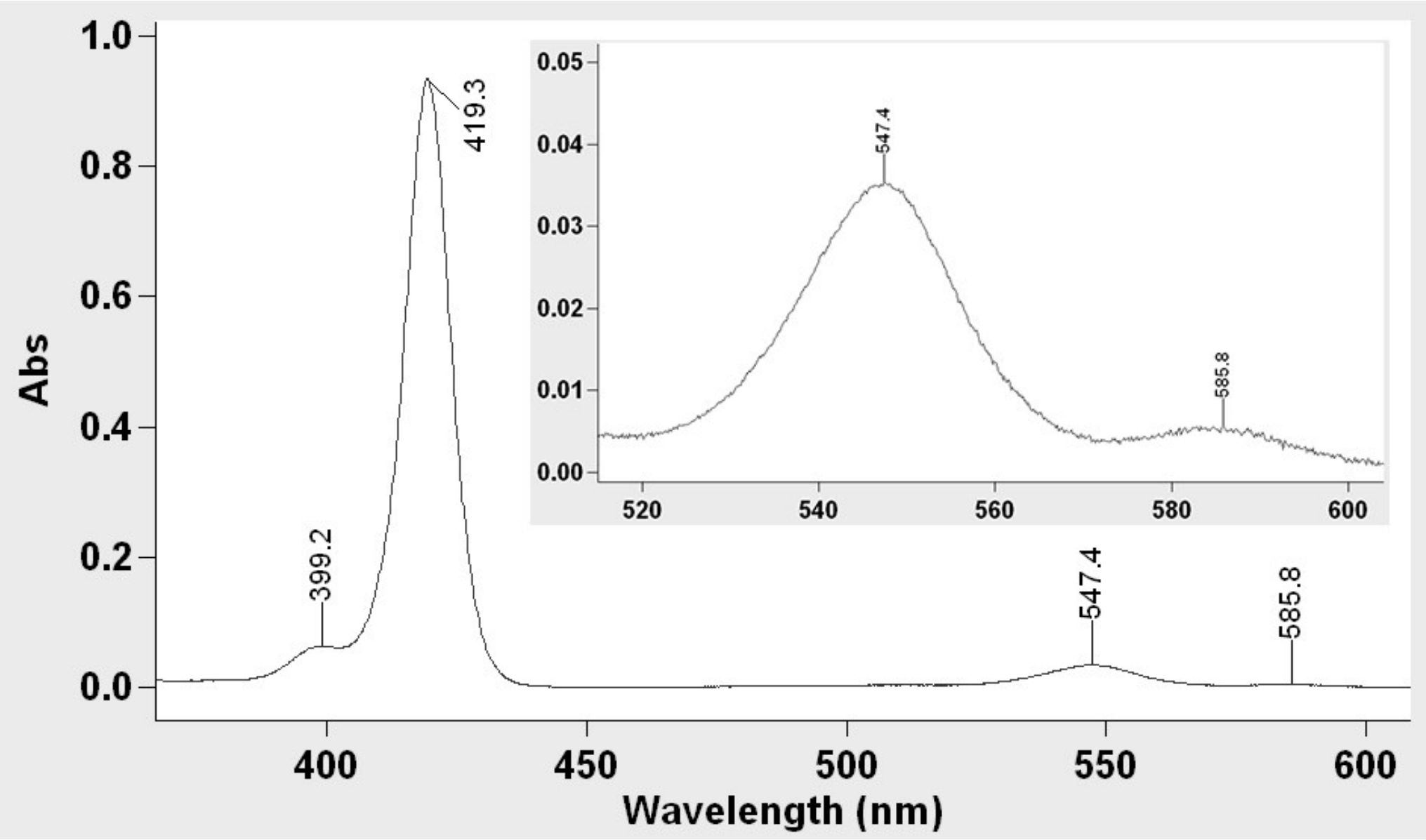

porphyrin β-pyrrole
and *meso*-phenyl shift
CDCl3
-50 °C
-20 °C
0 °C
+20 °C
I
I
H2O
8.9 8.7 8.5 8.3 8.1 7.9 7.7 7.5 7.3 7.1
3.5 3.0 2.5 2.0 1.5 1.0
Chemical Shift, δ (ppm)

S13: 600 MHz ^{1}H NMR *anti*- zinc(II) tweezer **3b**

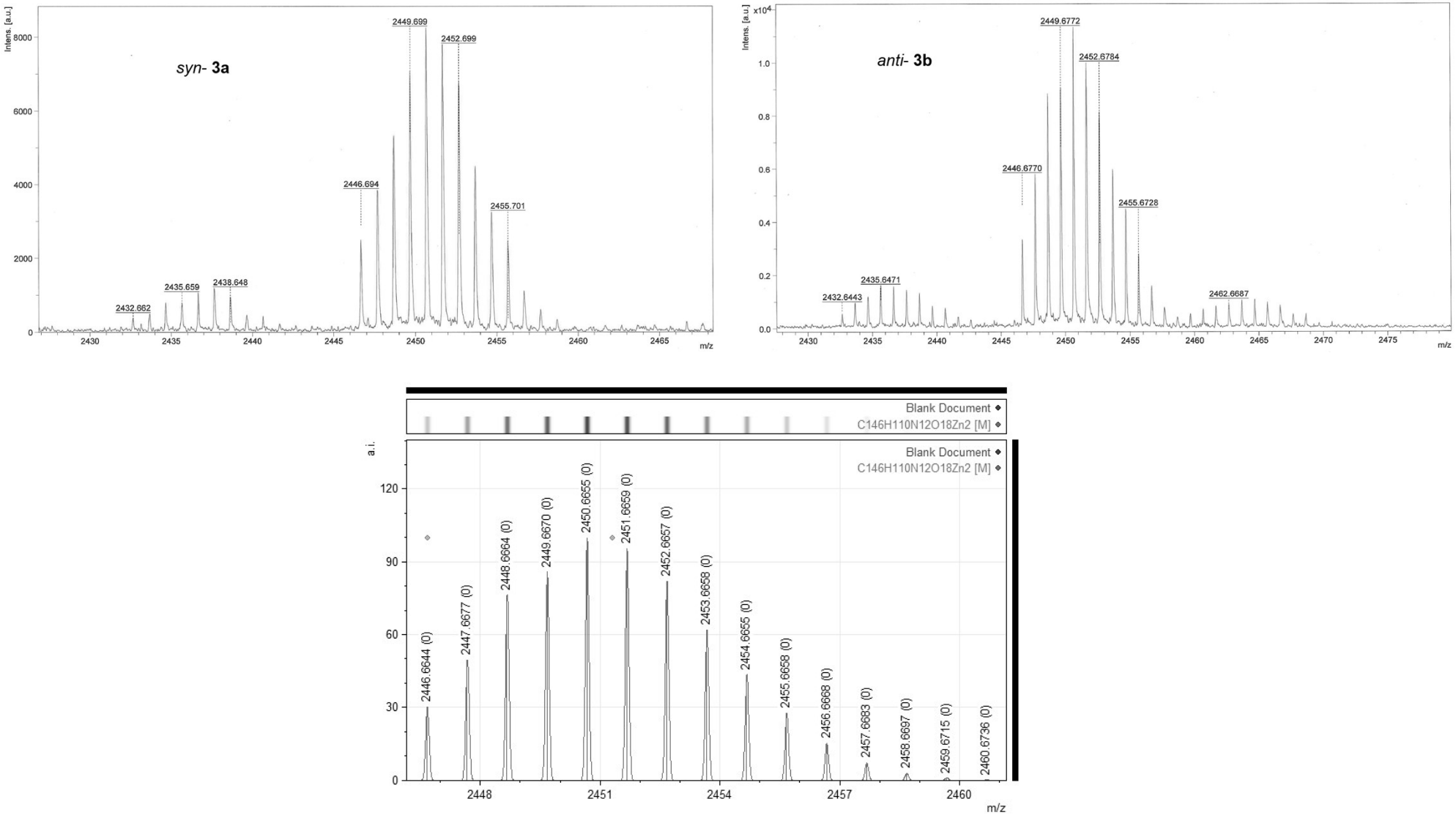



3.98
3.33
3.33
2.91
2.89
2.84
2.78
2.76
2.55
2.53
2.32
2.32
2.28
2.04
1.43
1.41
1.23
1.21
ester
polycyclic linker resonances a-f
CH3(ϕ)
CH3(ψ)
H1/2 and H3/4
W
11.74
4.16
3.82
4.22
3.74
2.25
6.16
3.91
6.19
6.34
2.61
2.41
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
Chemical Shift, δ (ppm)

S14: UV/Vis *anti*- zinc(II) tweezer **3b**

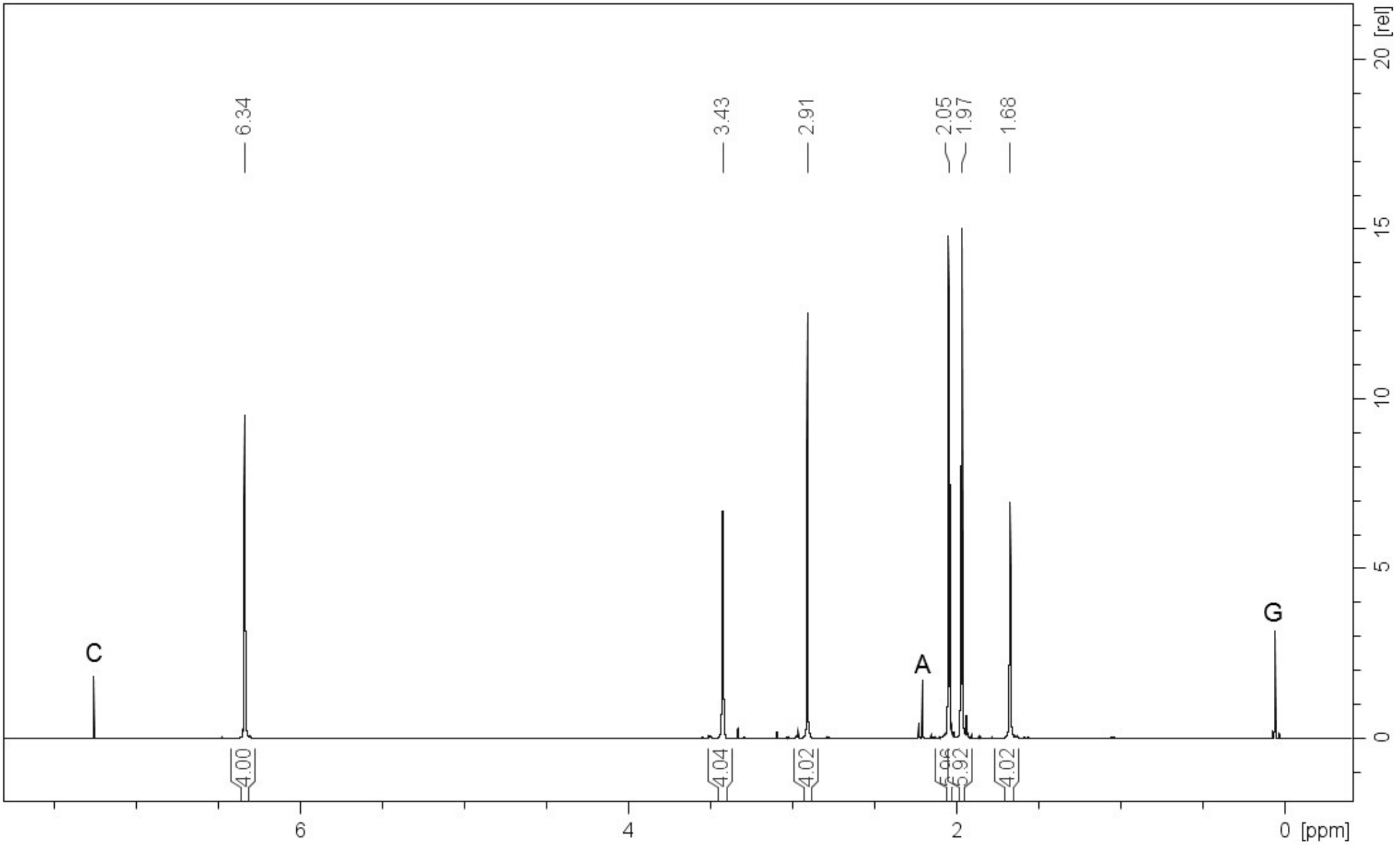


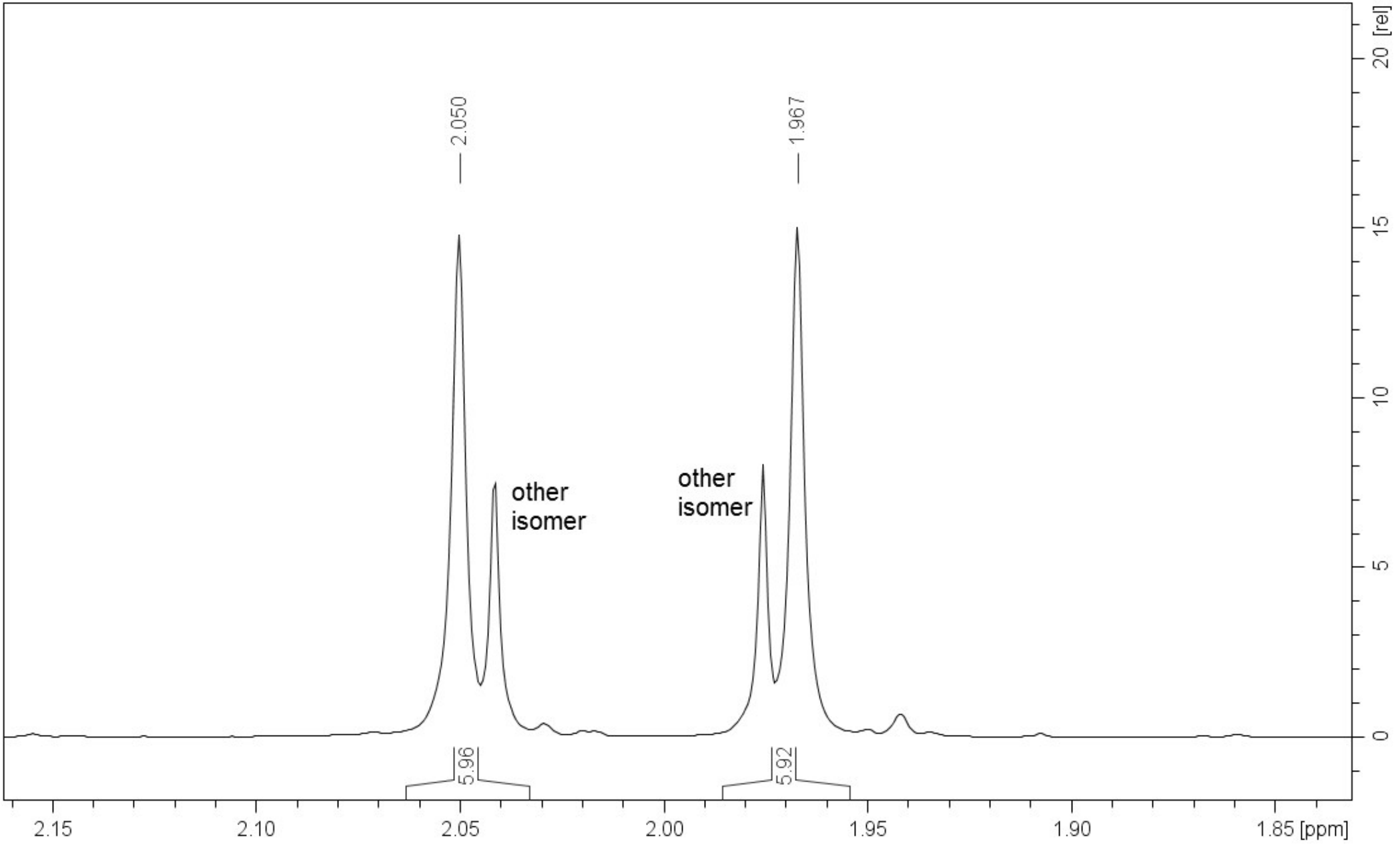
S15: HRMS (MALDI-TOF) *syn*- zinc(II) tweezer **3a** and *anti*- zinc(II) tweezer **3b**, experimental and predicted



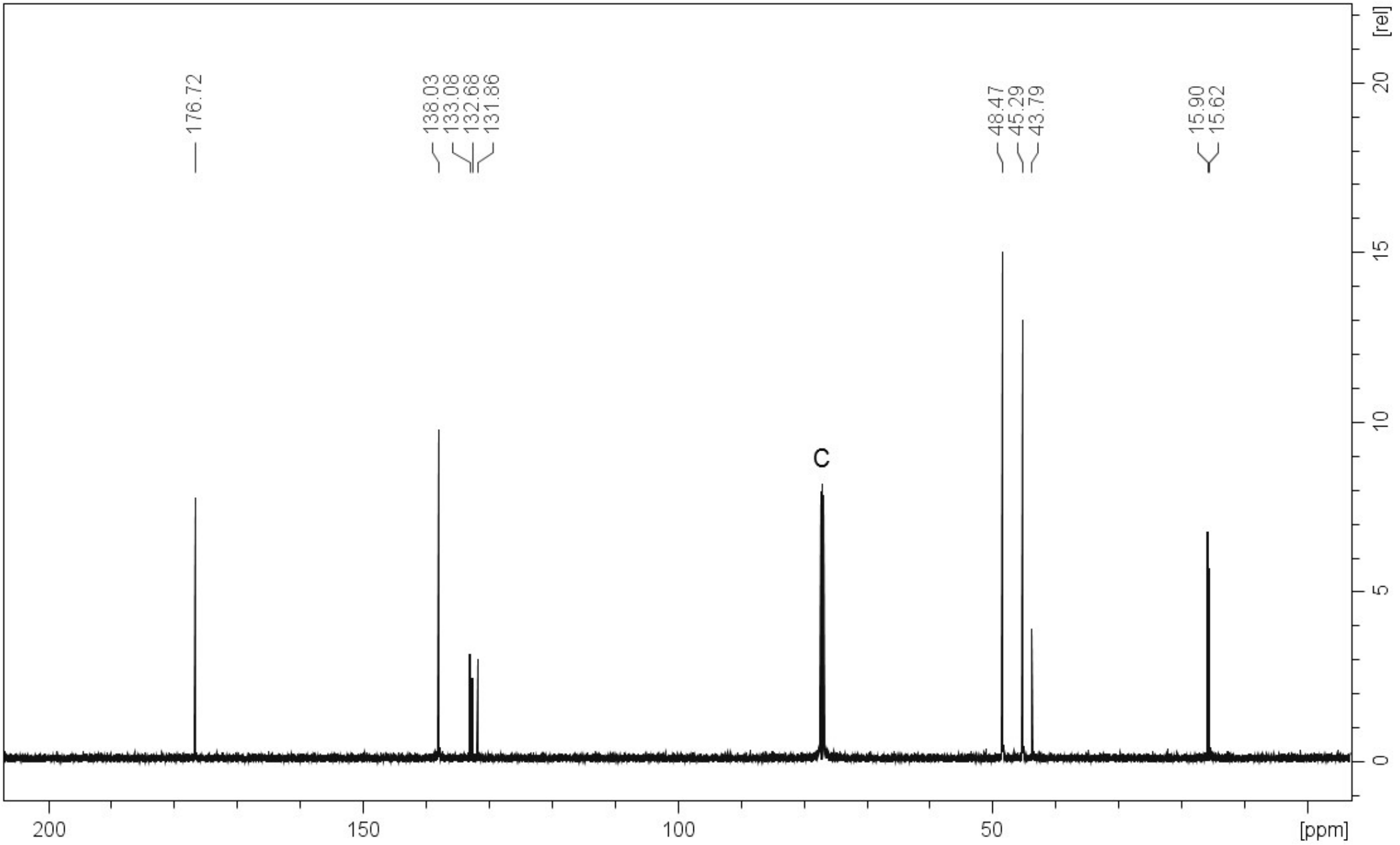
$[C_{146}H_{110}N_{12}O_{18}Zn_2]^{\bullet+}$ $[M]^{\bullet+}$: Calc: 2446.6644 (monoisotopic). Found: 2446.6770 (*syn*- **3a**), 2446.694 (*anti*- **3b**).

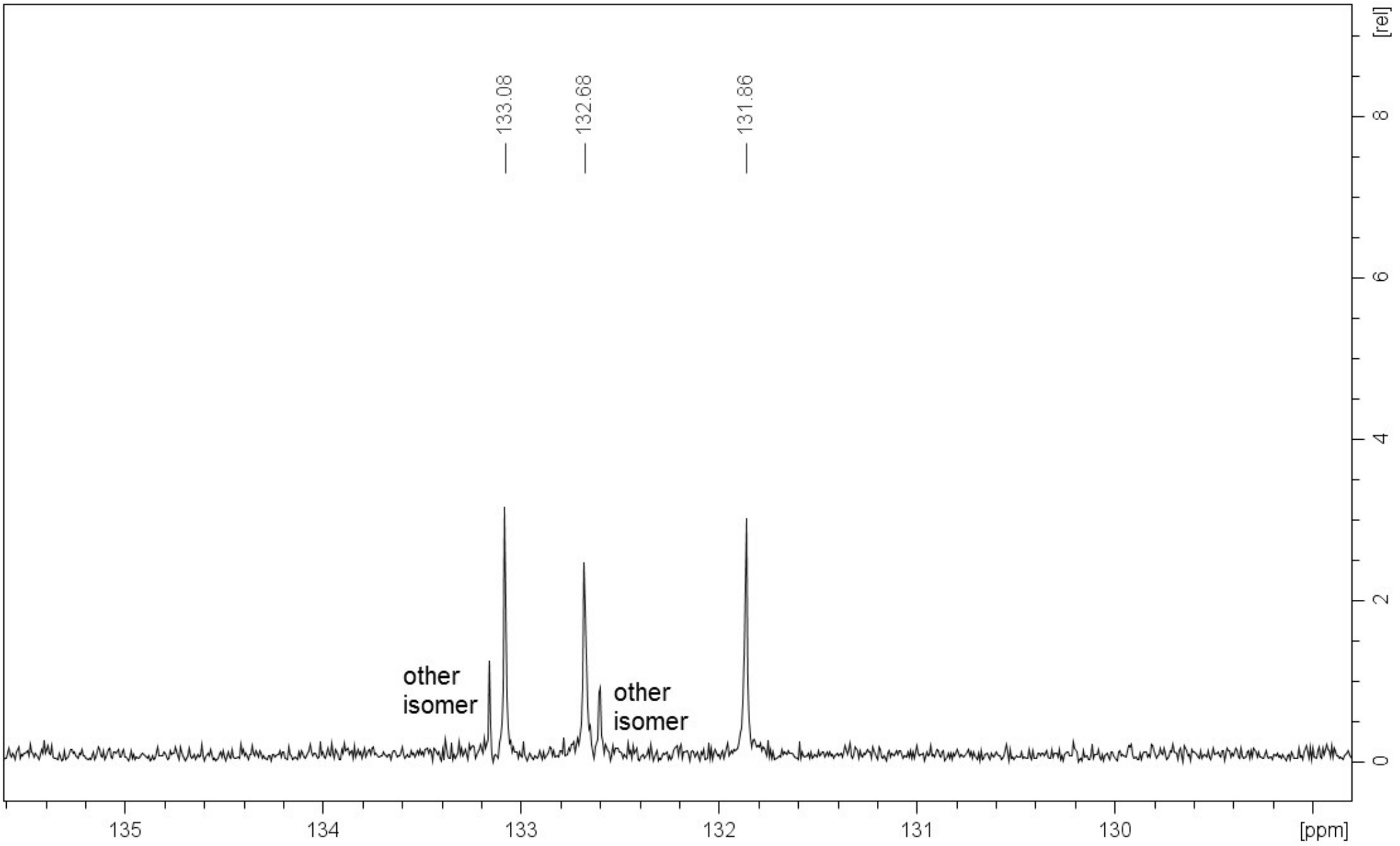
S16: 600 MHz ^{1}H NMR *exo*- linker, *syn*- **11a**

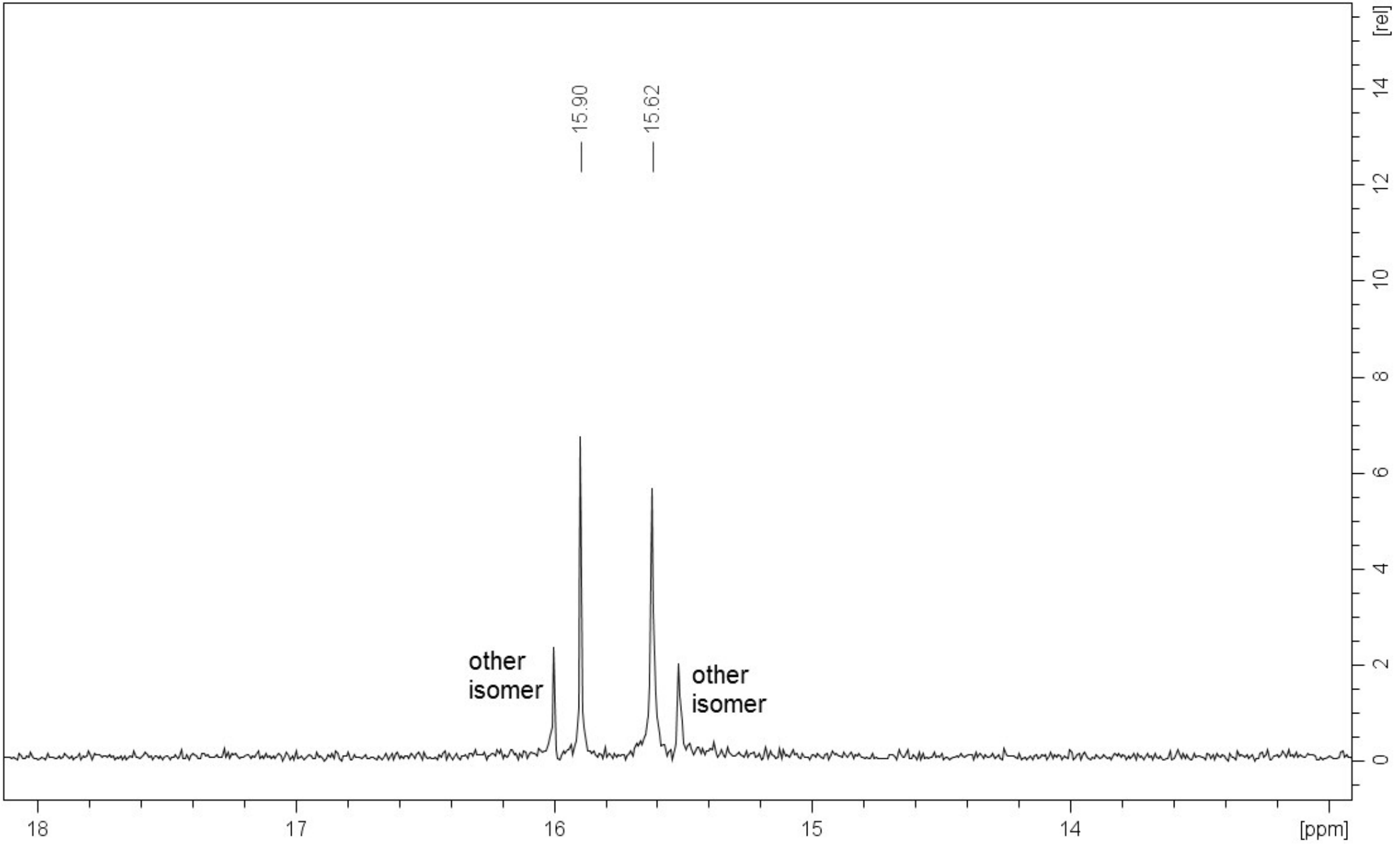



2.050
1.967
other isomer
other isomer
5.96
5.92
2.15
2.10
2.05
2.00
1.95
1.90
1.85 [ppm]
20 [rel]
15
10
5
0

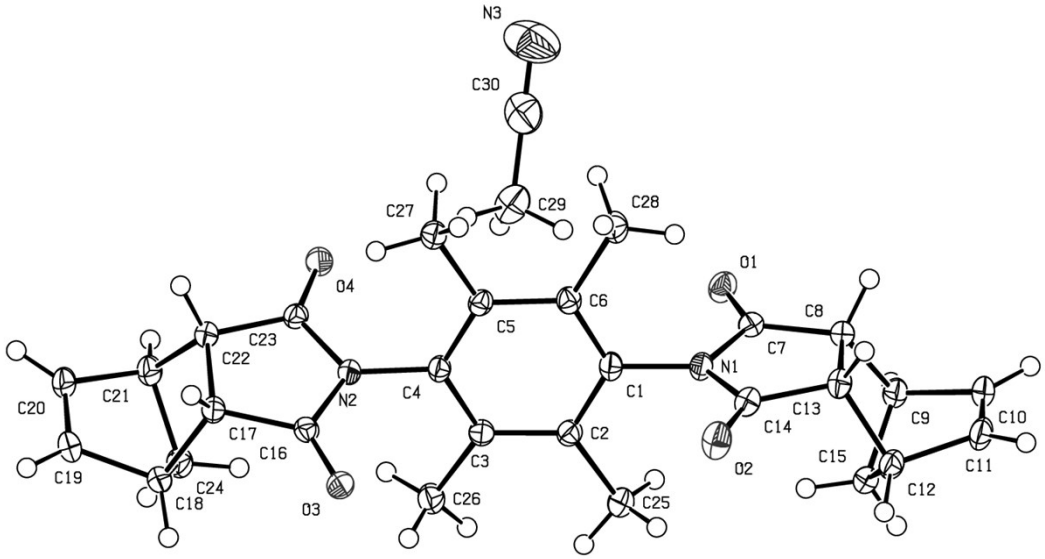
S17: 150 MHz ^{13}C NMR *exo*- linker, *syn*- **11a**

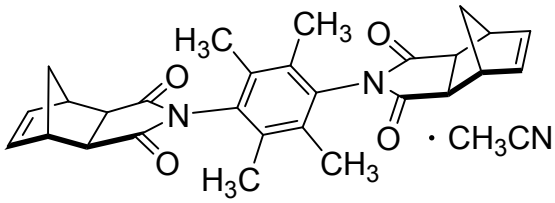



133.08
132.68
131.86
other isomer
other isomer
135
134
133
132
131
130
[ppm]
[rel]
0
2
4
6
8


15.90
15.62
other
isomer
other
isomer
[rel]
0
2
4
6
8
10
12
14
18
17
16
15
14
[ppm]

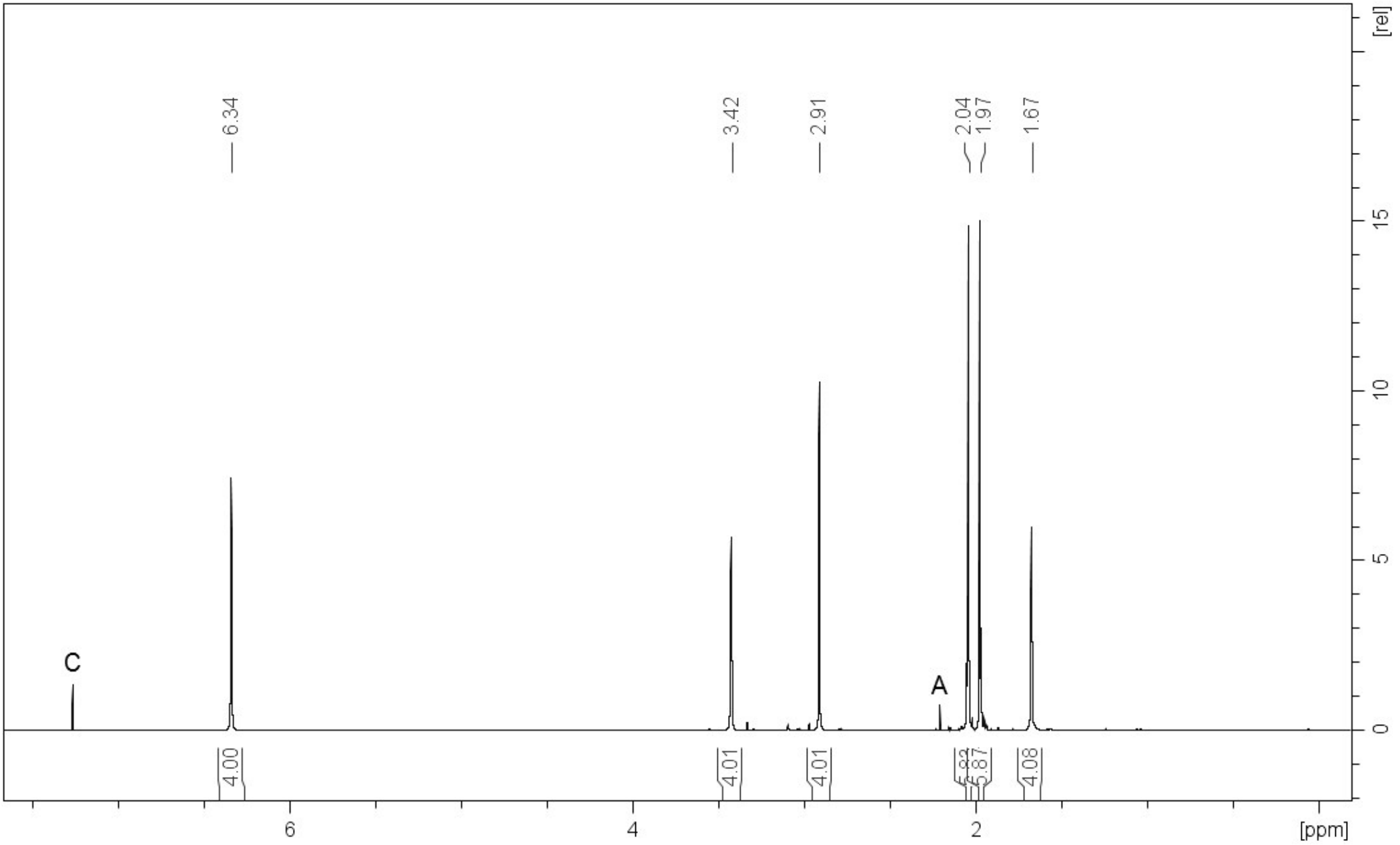
S18: X-Ray Crystal Structure Data and Refinement for *exo*- linker, *syn*- **11a** (CCDC 1526930)

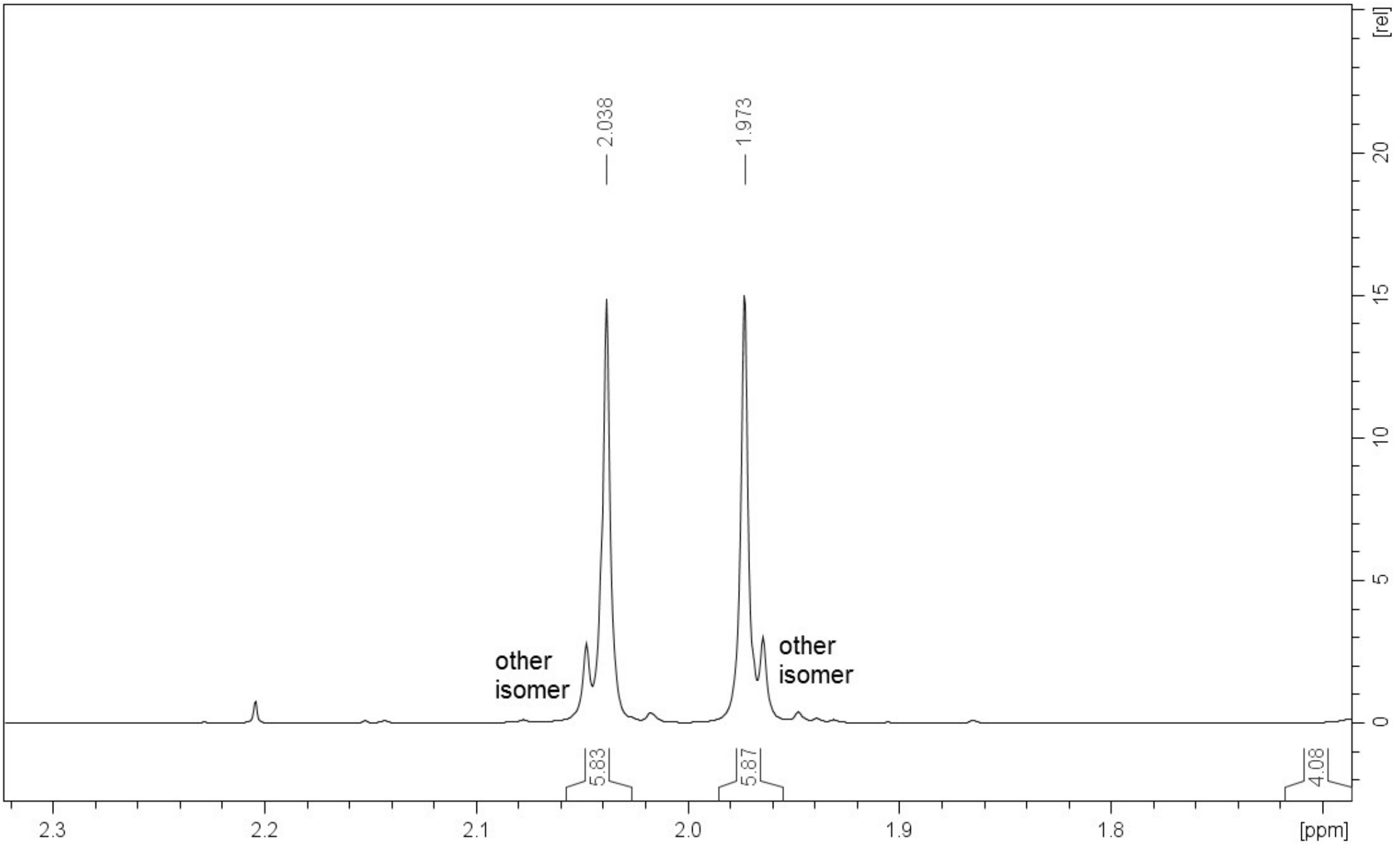




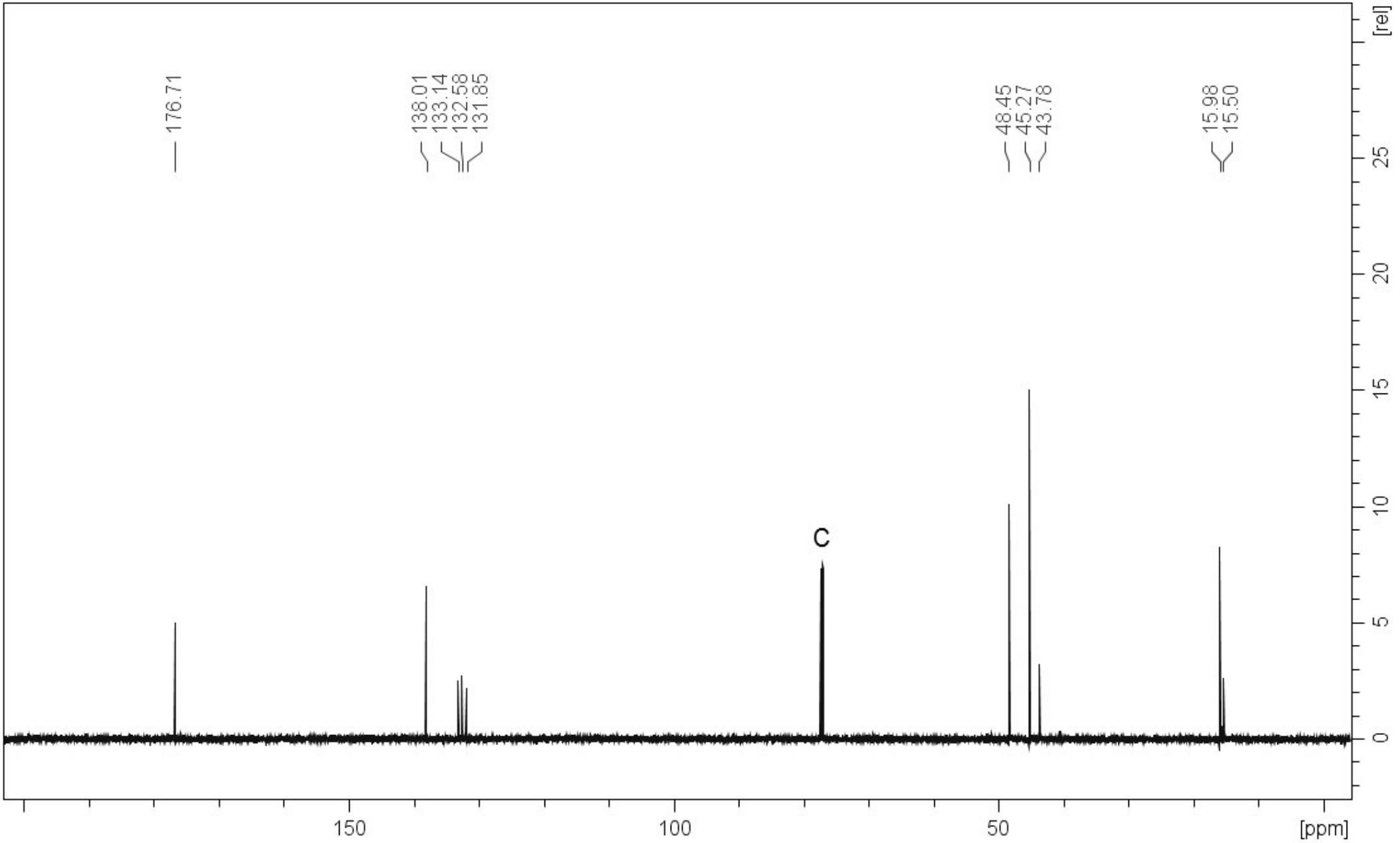
Parameter	***syn*- restricted rotation *exo*- non-Mitsudo linker 11a**
Empirical formula	C30 H31 N3 O4
Formula weight	497.58
Temperature (K)	130.00
Wavelength (Å)	1.5418
Crystal system	Triclinic
Space group	'P-1'
Unit cell dimensions	a = 8.6452(5) b = 11.1356(5) c = 15.0205(6)
Theta max	76.683
Reflections used	5163
Final R indices [I > 2σ(I)]	
R1	0.0407
wR2	0.1054
Data completeness	0.973

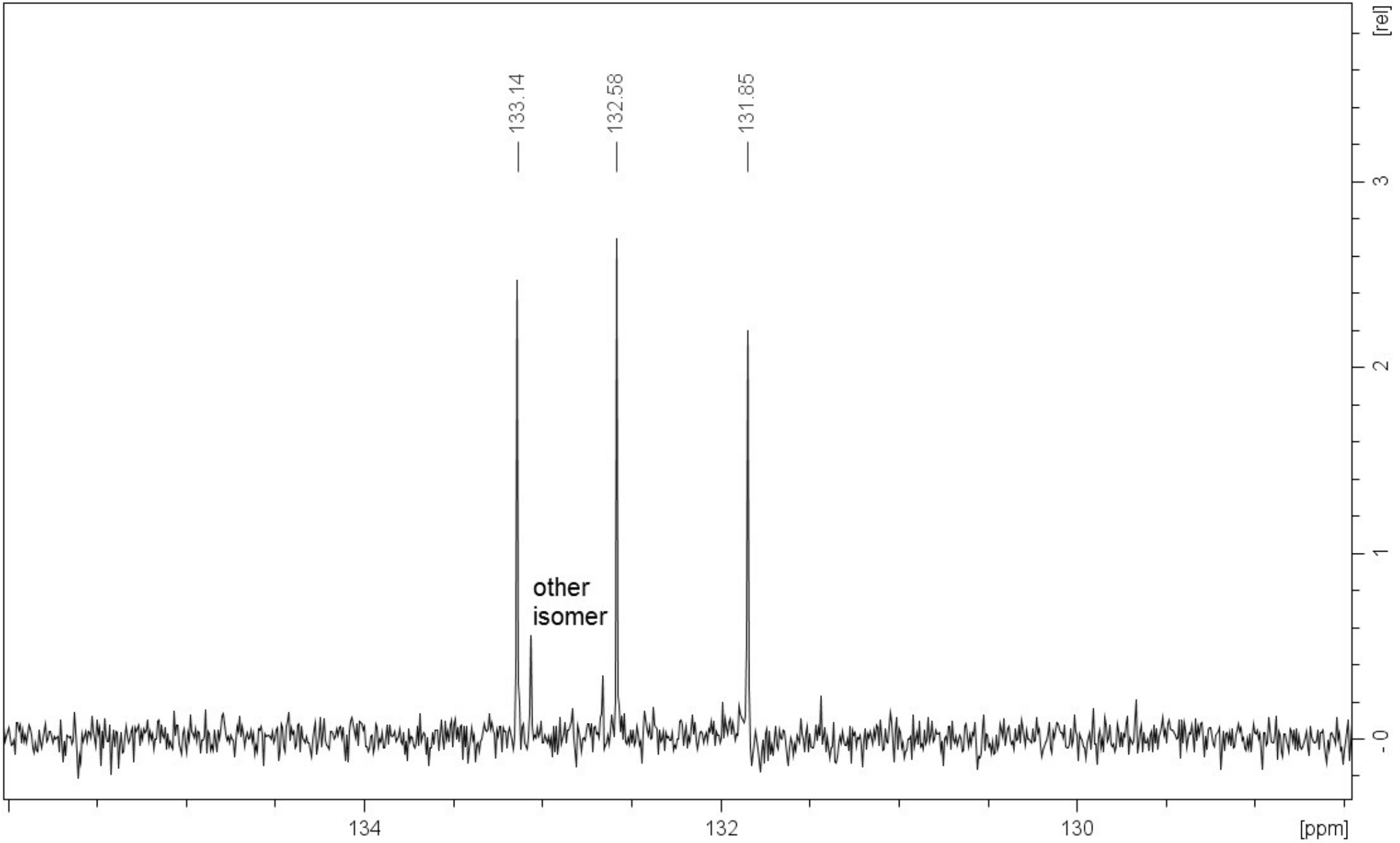
S19: 600 MHz ^{1}H NMR *exo*- linker, *anti*- **11b**

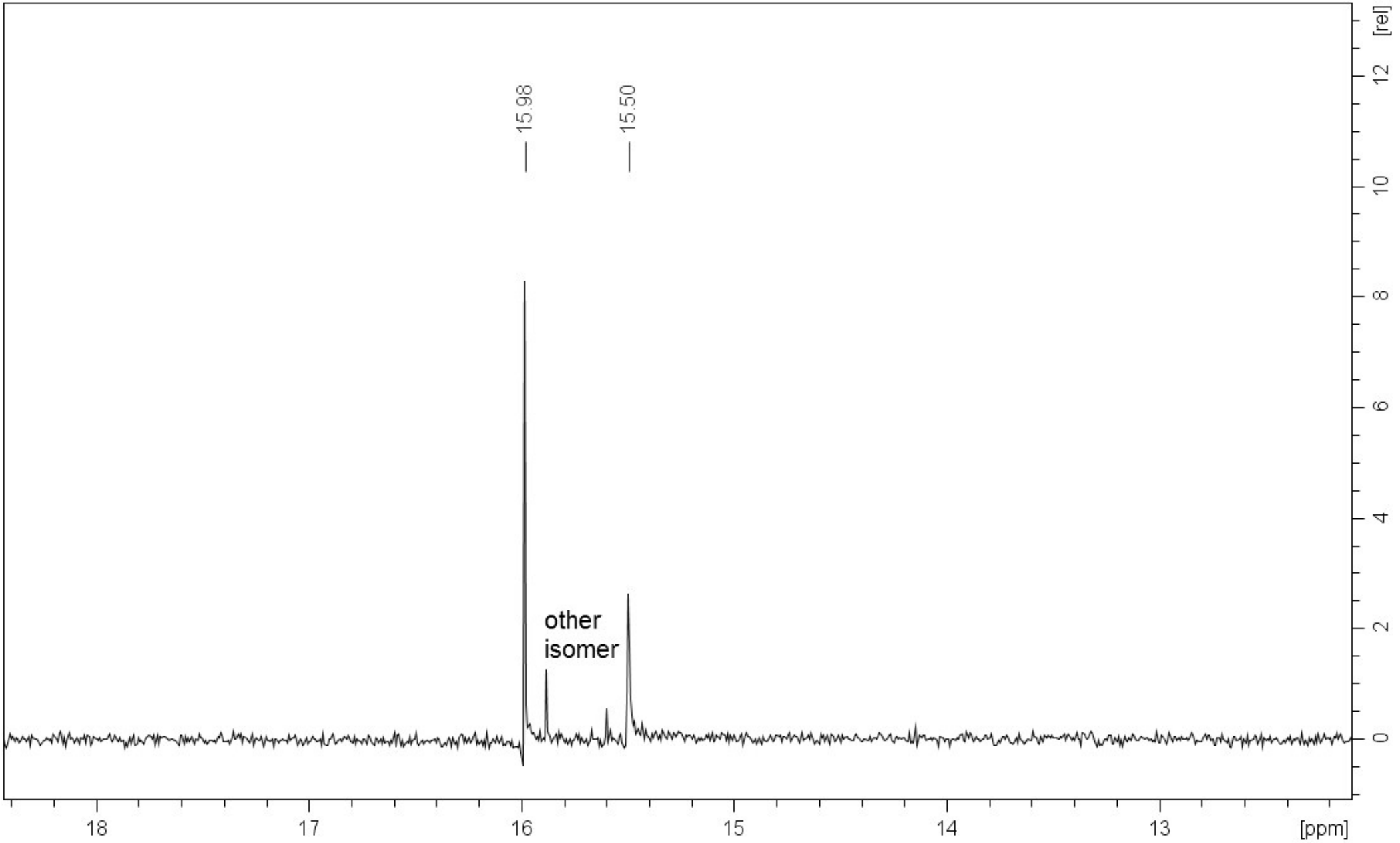



2.038
1.973
other
isomer
other
isomer
5.83
5.87
4.08
2.3
2.2
2.1
2.0
1.9
1.8
[ppm]
[rel]
0
5
10
15
20

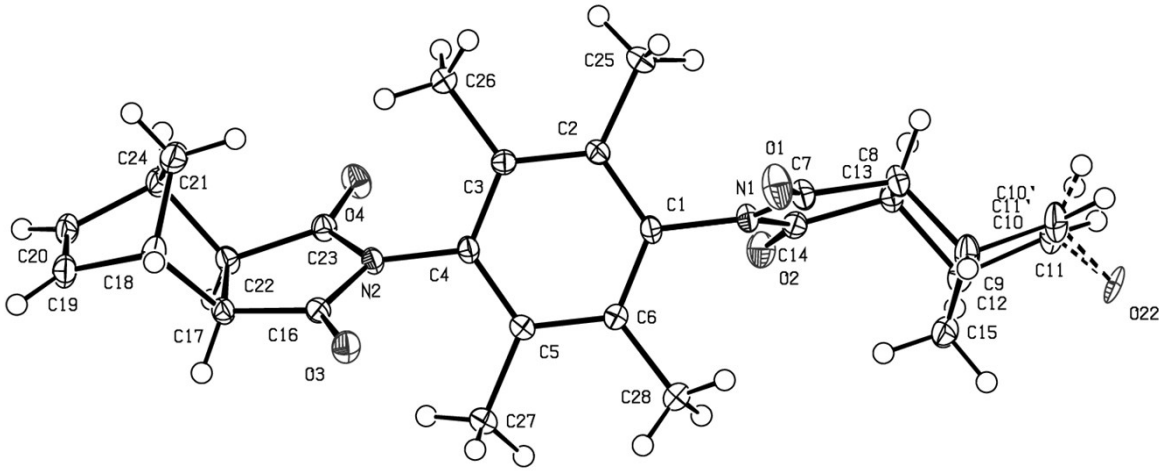
S20: 150 MHz ^{13}C NMR *exo*- linker, *anti*- **11b**

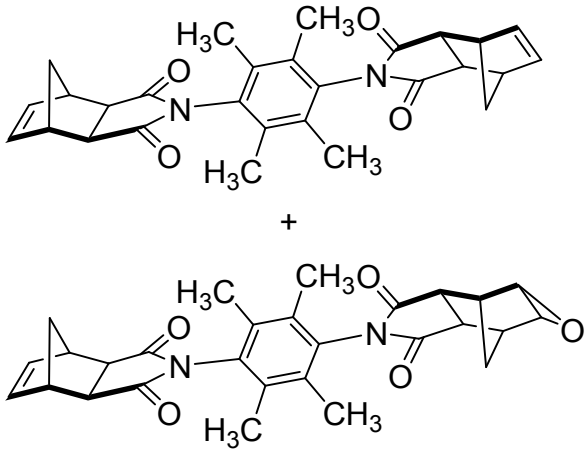



133.14
132.58
131.85
other
isomer
134
132
130
[ppm]
[rel]
3
2
1
-0


15.98
15.50
other
isomer
18
17
16
15
14
13
[ppm]
0
2
4
6
8
10
12
[rel]

S21: X-Ray Crystal Structure Data and Refinement for *exo*- linker, *anti*- **11b** (CCDC 1526931)





Parameter	***anti*- restricted rotation *exo*- non-Mitsudo linker 11b**
Empirical formula	C28 H28 N2 O4.06
Formula weight	457.56
Temperature (K)	130.00
Wavelength (Å)	0.7107
Crystal system	Triclinic
Space group	'P-1'
Unit cell dimensions	a = 10.5365(13) b = 10.7150(9) c = 11.866(2)
Theta max	32.017
Reflections used	6270
Final R indices [I > 2σ(I)]	
R1	0.0486
wR2	0.1311
Data completeness	0.794

S22: Host-Guest Analysis

Examining the fitting results of UV/Vis titration data

The output must be cautiously analysed to determine if the fit is valid (or in circumstances where multiple complexation models can be fitted, which is the best fit). In deciding whether the fit is valid, several considerations are important; (a) visual inspection of the fit; (b) the standard deviation of the association constant(s), and the difference between calculated and observed data points (the residuals); (c) the physical ability of the system to form the species being fitted; (d) whether the calculated UV/Vis spectrum resembles the experimental spectrum (intensity profile), and whether the calculated species assigned to a particular wavelength is experimentally reasonable based on the ratio of components and their known experimental values (e.g. the wavelengths of different porphyrin species [free/uncomplexed, sandwich complexed, and open/mono-complexed] are all experimentally known).

Experimental speciation from NMR titration data

When a system is in slow exchange between two species, free host and complex A, the relative integration of the complexed resonance to the total host resonance (free plus complexed) can be used to determine the population of the species[1-3] (Equation 1).

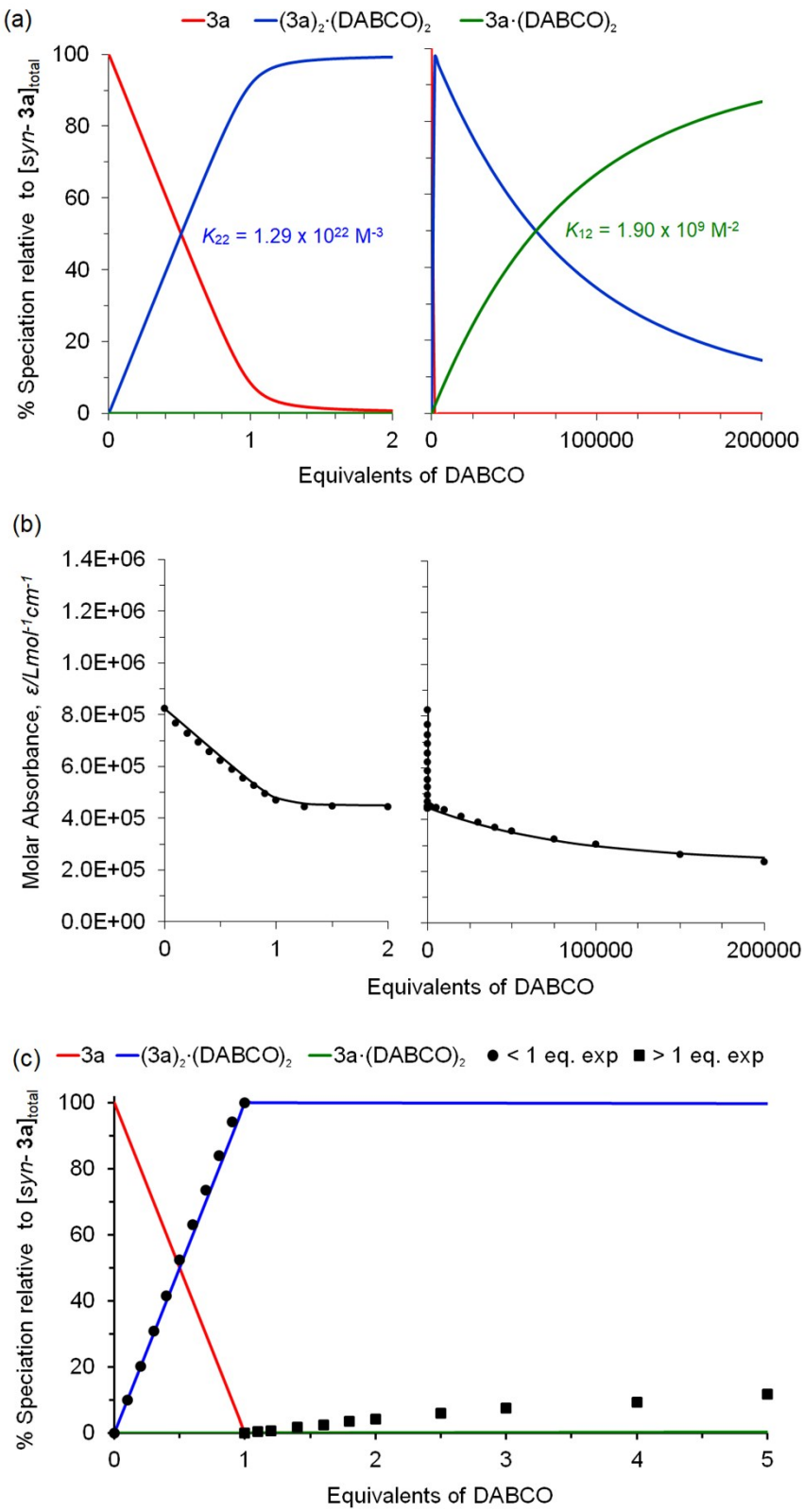
$$\%\ speciation = \left(\frac{\int_{complexed\ resonance\ only}}{\int_{total\ host\ resonance\ (free + complexed)}} \right) \times 100$$ …… Equation 1

Subsequently, when a system moves into fast exchange between two different species, complexes A and B, the average chemical shift can be used to determine the population of the species[1-3], by considering the position of the averaged chemical shift along a continuum between each pure complex A and B, provided these chemical shifts are both known (Equation 2).

$$\%\ speciation\ = abs\left(\frac{\delta_{average} - \delta_{complex\ A}}{\delta_{complex\ B} - \delta_{complex\ A}} \right) \times 100$$ …… Equation 2[2]

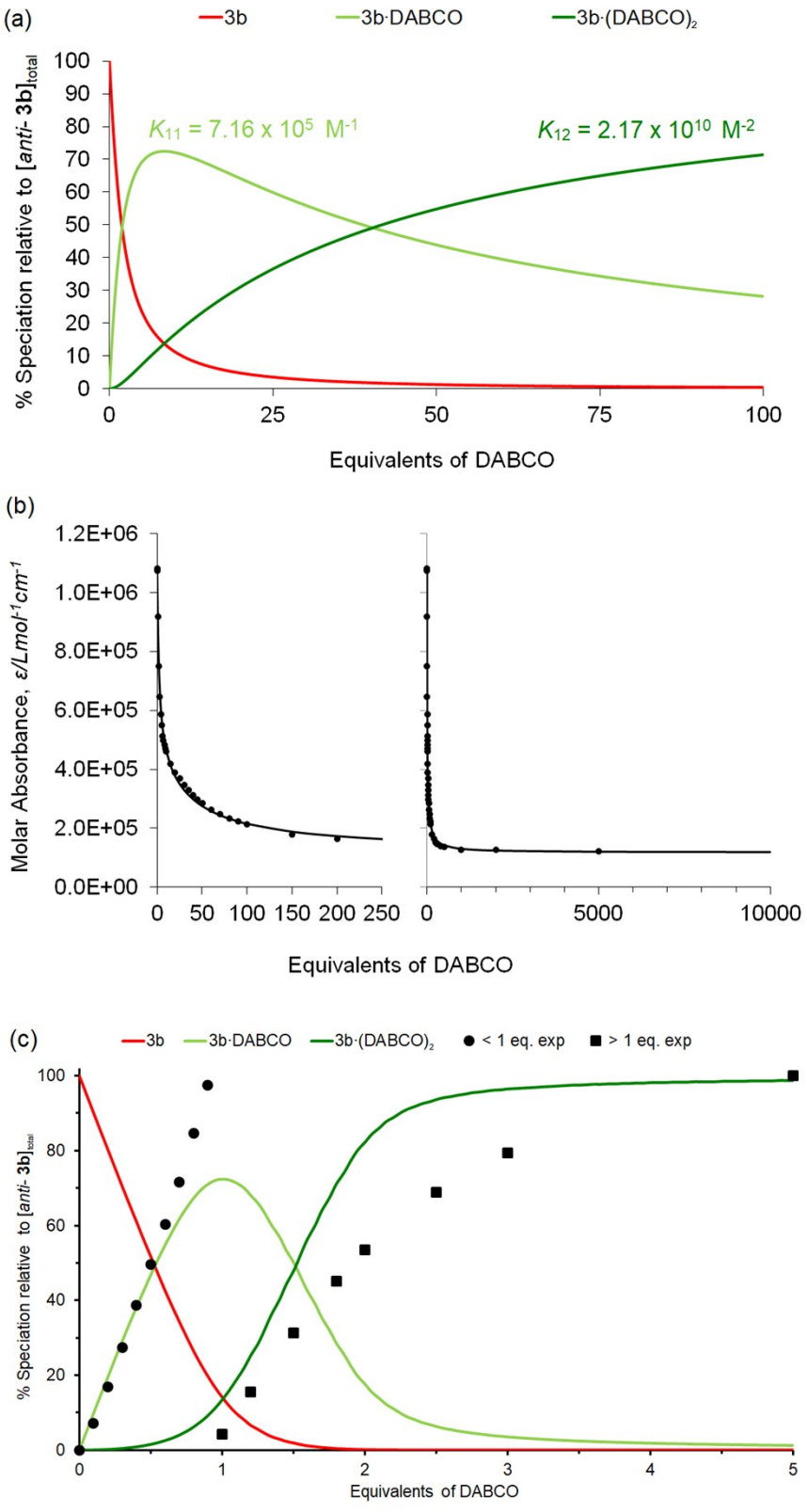
Equations 1 and 2 assume that each stage (slow and fast exchange respectively) only involve two species each; that free host is fully converted to complex A by a given number of equivalents of guest, after which complex B begins to form from complex A.

S23: Alternative complexation model for *syn*- **3a**/DABCO; (**3a**)$_2$·(DABCO)$_2$ and **3a**·(DABCO)$_2$.



(a) derived speciation plot for formation of (**3a**)$_2$·(DABCO)$_2$ (blue line) and **3a**·(DABCO)$_2$ (green line) in the 0-2 and 0-200,000 equivalent ranges of added DABCO in $CHCl_3$ at 20 °C; (b) the corresponding best fits of an algorithm for the formation of (**3a**)$_2$·(DABCO)$_2$ and **3a**·(DABCO)$_2$ (black lines) for the UV/Vis absorbance data obtained at 419 nm (black circles); (c) simulated NMR speciation diagram generated from UV/Vis determined association constants K_{22} and K_{12} for *syn*- **3a**/DABCO, experimental NMR speciation has been overlayed for both the slow and fast exchange regions of the titration, and does not match the simulation for the later.

S24: Alternative complexation model for *anti*- **3b**/DABCO; **3b**·DABCO and **3b**·$(DABCO)_2$.



(a) derived speciation plot for formation of **3b**·DABCO (light green line) and **3b**·$(DABCO)_2$ (dark green line) in the 0-100 equivalent range of added DABCO in $CHCl_3$ at 20 °C; (b) the corresponding best fits of an algorithm for the formation of **3b**·DABCO and **3b**·$(DABCO)_2$ (black lines) for the UV/Vis absorbance data obtained at 419 nm (black circles); (c) simulated NMR speciation diagram generated from UV/Vis determined association constants K_{11} and K_{12} for *anti*- **3b**/DABCO, experimental NMR speciation has been overlayed for both the slow and fast exchange regions of the titration, and does not match the simulaiton.

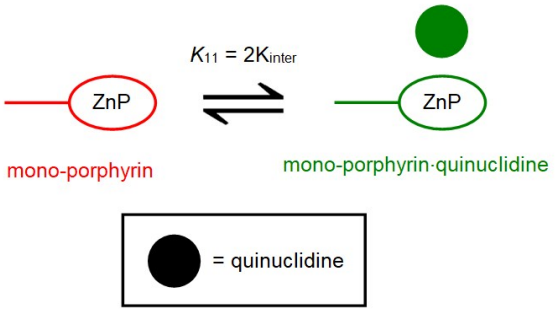
S25: Statistical Analysis of Association Constants and Calculation of Microscopic Effective Molarity (*EM*).

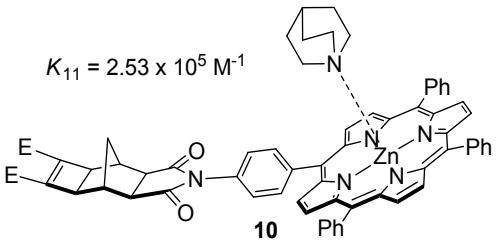
Tables of parameters, diagrams and formulae[4] supporting the statistical analysis of the association constants and calculation of microscopic effective molarity[4, 5] (*EM*).

Symmetry-related parameters

Species	**Point Group**	σ_{ext}	σ_{int}	$\sigma_{species}$	K_σ
Quinuclidine	C_{3v}	3	1	3	-
DABCO	D_{3h}	6	1	6	-
mono-porphyrin **10**	C_s	1	2	2	-
syn- **3a**	C_{2h}	2	4	8	-
freely rotating **1**	C_{2h}	2	4	8	-
anti- **3b**	C_{2h}	2	4	8	-
mono-por·quin	C_s	1	3	3	2
3a·DABCO	C_{2h}	2	3	6	8
1·DABCO	C_{2h}	2	3	6	8
$(\mathbf{3b})_2$·$(DABCO)_2$	C_{2h}	2	9	18	128

Calculating reference K_{inter}





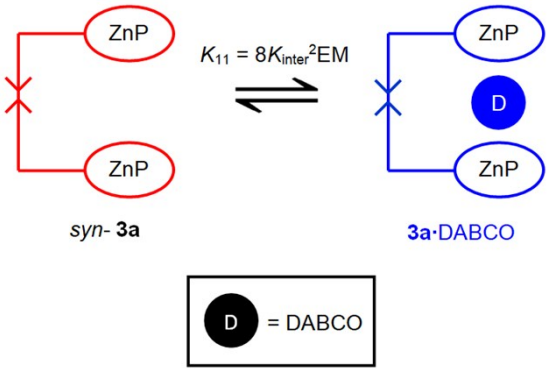
$$K_\sigma = \frac{\sigma_{quin}{}^{1}\sigma_{mono-por}{}^{1}}{\sigma_{mono-por\cdot quin}{}^{1}} = \frac{3 \times 2}{3} = 2$$

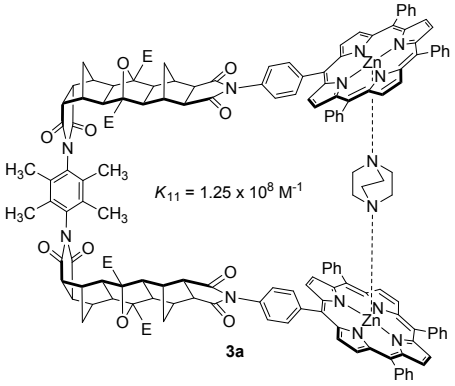
$K_{exp} = \alpha\gamma K_\sigma K_{inter}{}^{b} EM^{c}$ [4] ; $\alpha = 1, \gamma = 1, K_\sigma = 2, b = 1, c = 0$

$K_{11} = 2K_{inter} = 2.53 \times 10^5\, M^{-1}$ (experimentally determined[6])

$$K_{inter} = \frac{K_{11}}{2} = \frac{2.53 \times 10^5\, M^{-1}}{2} = 1.265 \times 10^5\, M^{-1}$$

Calculating Microscopic EM



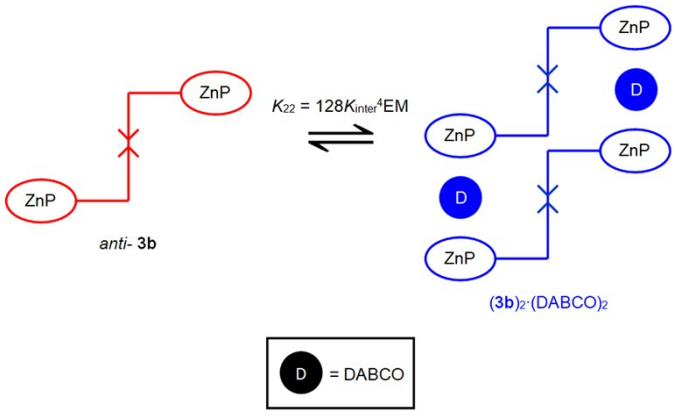


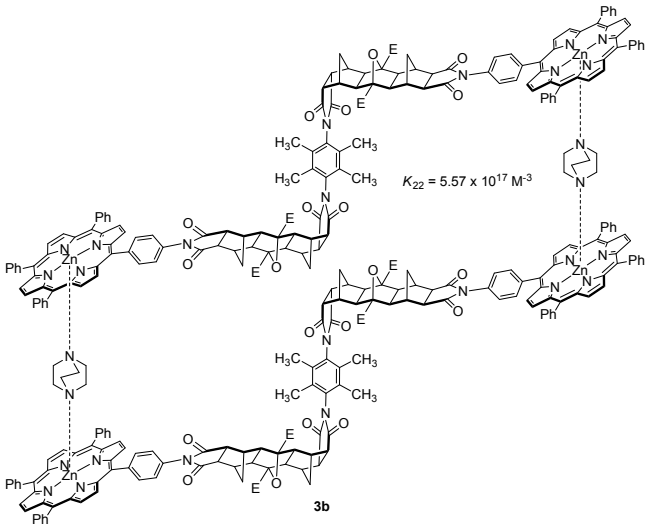
$$K_\sigma = \frac{\sigma_{DABCO}{}^{1}\sigma_{syn}{}^{1}}{\sigma_{syn\cdot DABCO}{}^{1}} = \frac{6\times 8}{6} = 8$$

$K_{exp} = \alpha\gamma K_\sigma K_{inter}^{\ b} EM^c$ [4] ; α = 1 (assumed), γ = 1, K_σ = 8, b = 2, c = 1

$K_{11} = 8K_{inter}^{\ 2}EM = 1.25 \times 10^8\, M^{-1}$ (experimentally determined)

$$EM = \frac{K_{11}}{8K_{inter}^{\ 2}} = \frac{1.25 \times 10^8\, M^{-1}}{8(1.265 \times 10^5\, M^{-1})^2} = 9.76 \times 10^{-4}\, M$$



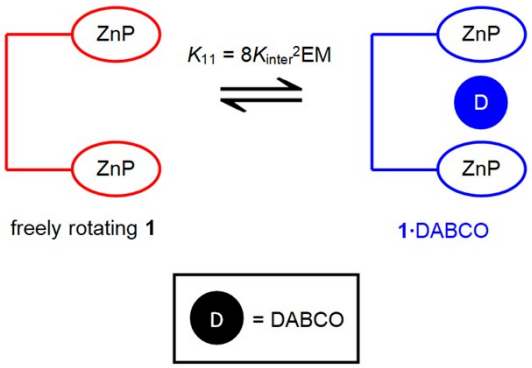


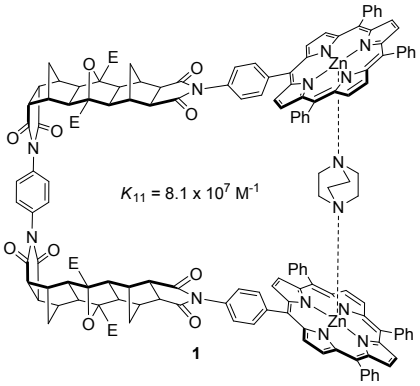
$$K_\sigma = \frac{\sigma_{DABCO}{}^{2}\sigma_{anti}{}^{2}}{\sigma_{anti\cdot DABCO}{}^{1}} = \frac{6^2\times 8^2}{18} = 128$$

$K_{exp} = \alpha\gamma K_\sigma K_{inter}^{\ b} EM^c$ [4] ; α = 1 (assumed), γ = 1, K_σ = 128, b = 4, c = 1

$K_{22} = 128K_{inter}^{4}EM = 5.57 \times 10^{17} M^{-3}$ (experimentally determined)

$$EM = \frac{K_{22}}{128K_{inter}^{4}} = \frac{5.57 \times 10^{17} M^{-3}}{128(1.265 \times 10^{5} M^{-1})^{4}} = 1.70 \times 10^{-5} M$$





$$K_\sigma = \frac{\sigma_{DABCO}{}^{1}\sigma_{freely\,rotating}{}^{1}}{\sigma_{freely\,rotating\cdot DABCO}{}^{1}} = \frac{6\times 8}{6} = 8$$

$K_{exp} = \alpha\gamma K_\sigma K_{inter}^{\,b} EM^c$ [4] ; α = 1 (assumed), γ = 1, K_σ = 8, b = 2, c = 1

$K_{11} = 8K_{inter}^{\,2} EM = 8.1 \times 10^7\, M^{-1}$ (experimentally determined[6])

$$EM = \frac{K_{11}}{8K_{inter}^{\,2}} = \frac{8.1 \times 10^7\, M^{-1}}{8(1.265 \times 10^5\, M^{-1})^2} = 6.33 \times 10^{-4}\, M$$

S26. References for Electronic Supplementary Information

1. P. Ballester, A. I. Oliva, A. Costa, P. M. Deyà, A. Frontera, R. M. Gomila and C. A. Hunter, *J. Am. Chem. Soc.*, 2006, **128**, 5560-5569.
2. P. Ballester, A. Costa, A. M. Castilla, P. M. Deyá, A. Frontera, R. M. Gomilla and C. A. Hunter, *Chem. - Eur. J.*, 2005, **11**, 2196-2206.
3. L. Baldini, P. Ballester, A. Casnati, R. M. Gomila, C. A. Hunter, F. Sansone and R. Ungaro, *J. Am. Chem. Soc.*, 2003, **125**, 14181-14189.
4. G. Ercolani and L. Schiaffino, *Angew. Chem. Int. Ed.*, 2011, **50**, 1762-1768.
5. C. A. Hunter and H. L. Anderson, *Angew. Chem. Int. Ed.*, 2009, **48**, 7488-7499.
6. R. B. Murphy, D.-T. Pham, S. F. Lincoln and M. R. Johnston, *Eur. J. Org. Chem.*, 2013, **2013**, 2985-2993.