Application of Negishi Cross-Coupling to the Synthesis of the Cyclic Tripeptides OF-4949-III and K-13

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Supporting Information

Comparison of Data for Z-OF4949-III-OMe 3

^{1}H NMR in CD_3OD

Figure 1: Pearson's ^{1}H NMR in CD_3OD for Z-OF4949-III-OMe (300 MHz)

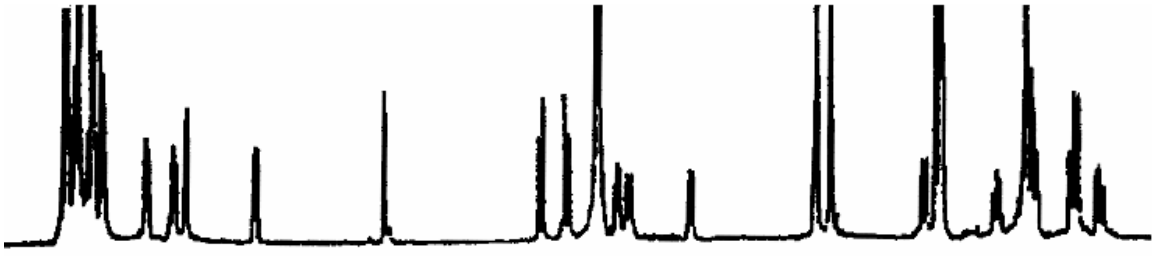


Figure 2: Our ^{1}H NMR in CD_3OD for Z-OF4949-III-OMe (400 MHz)

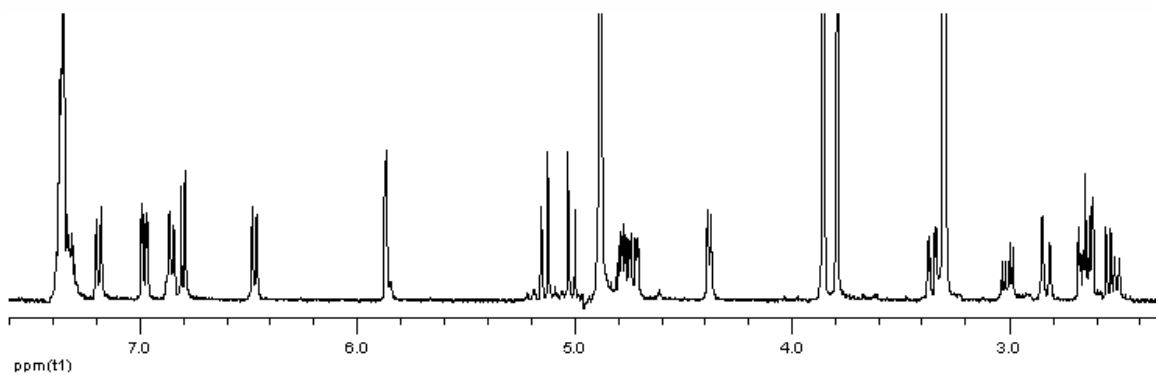


Table 3 compares our ^{1}H chemical shift for Z-OF4949-III-OMe (**3**) in deuterated methanol with both Pearson's[1] and Boger's[2] listed data.

Table 3 (Z-OF4949-III-OMe, ^{1}H, CD_3OD)

Ours (400MHz)			Pearson (300 MHz)		Boger (300MHz)		
Shift	H, mul., Hz	Attr.	Shift	H, mul., Hz	Shift	H, mul., Hz	Attr.
7.43-7.28	6, m	Ar	7.70-7.54	7, m	7.40-7.20	7, m	Ar
7.20	1, dd, 8.5 2.0	Ar	-	-	-	-	-
6.98	1, dd, 8.0 2.5	Ar	7.36	1, dd, 8.0 1.9	6.98	1, dd, 8 2	Ar
6.85	1, dd, 8.0 2.5	Ar	7.23	1, dd, 8.0 1.9	6.93	1, dd, 8 2	Ar
6.80	1, d, 8.0	Ar	7.10	1, dd, 8.0 1.9	6.82	1, dd, 8 2	Ar
6.47	1, dd, 8.0 2.0	Ar	6.75	1, dd, 8.0 1.9	6.69	1, dd, 8 2	Ar
5.87	1, d, 2.0	H_{sh}	6.05	1, s	5.88	1, s	H_{sh}
5.14	1, d, 12.5	Z	5.24	1, d, 12.4	5.08	2, s	Z
5.02	1, d, 12.5	Z	5.12	1, d, 12.4	-	-	-
4.83-4.70	2, m	α	4.90	1, m	4.80	1, m	α
-	-	-	4.81	1, m	4.61	1, m	α
4.42-4.37	1, m	α	4.56	1, m	4.50	1, m	α
3.85	3, s	OMe	3.88	3, s	3.82	3, s	OMe
3.79	3, s	OMe	3.80	3, s	3.66	3, s	OMe
3.35	1, dd, 13.0 3.5	β	3.36	1, dd, 13.5 2.5	3.31	1, dd, 13 4	β
3.01	1, dd, 14.0 6.5	β	2.97	1, dd, 13.5 3.1	3.10	1, dd, 13 6	β
2.83	1, dd, 14.0 1.5	β	2.76	1, dd, 14.0 3.3	2.84	1, dd, 13 6	β
2.69-2.61	2, m	β	2.97 (?)	2, m	2.83	1, dd, 13 5	β
2.53	1, dd, 15.5 8.0	β	2.45	1, dd, 14.0 3.3	-	-	-

Z-OF4949-III-OMe **3** has 34 protons, five of which are NHs that exchange in deuterated methanol, so in total, 29 protons. The symmetrical ring in the macrocycle has no possibility of free rotation and all the protons and carbon atoms are therefore inequivalent. Pearson's spectrum (Fig. 1) and our spectrum (Fig. 2) show the correct number of protons *via* integration; Boger reported 27 protons in total. The tabulated data reported by Boger[2] (Table 3) do not match the spectrum provided in that publication's supporting information, and Boger has acknowledged in a personal communication that the reproduced spectrum for Z-OF4949-III-OMe (compound **129**) in the SI for that paper must be the wrong spectrum. Because of the poor solubility of Z-OF4949-III-OMe **3** in methanol, some experiments were performed by adding a small amount of deuterated chloroform to aid solubility. This resulted in the multiplet at 4.83-4.70 being split into two double doublets: 4.75 (1H, J_{AB} 12.5 Hz, J_{AX} 3.5 Hz) and 4.81 (1H, J_{AB} 8.0 Hz, J_{AX} 5.0 Hz). Some experiments were performed in deuterated chloroform, but without acidic protons. To promote proton/deuterium exchange, the sample of **3** was sonicated in the presence of deuterated methanol (the compound is not soluble in water) and then the solvent was removed by

evaporation. Usually small quantities of methanol were observed in the spectra prepared under these conditions. We observed that changes in the concentration of the sample and the composition of the solvent have dramatic effects on the appearance of the NMR spectra. This may explain the minor differences between the chemical shifts observed in our spectra and those previously reported. Evans noted that the presence of traces of acid in the NMR sample can affect the appearance of the spectrum of OF4949-III itself.[3]

^{13}C NMR experiments

Table 4 shows the chemical shift for the ^{13}C (125 MHz, CD_3OD) from Pearson,[1] our data for a Pendant experiment (100 MHz, mixed solvent 3% *circa* $CDCl_3$ in CD_3OD), for a CPD experiment in CD_3OD, for a CPD experiment performed in CD_3OD in which a catalytic amount of $NaHCO_3$ was added and a ^{13}C in $CDCl_3$.

Table 4: ^{13}C, CD_3OD, Z-OF4949-III-OMe

Pearson (CD_3OD)	Our (mix, Pendant)	Our (CD_3OD, CPD)	Our (CD_3OD+ $NaHCO_3$)	Our ($CDCl_3$)	Assign.
174.4	174.4	173.0	173.0	173.1	C
173.0	172.9	171.5	171.5	171.7	C
171.9	171.9	170.5	170.5	169.7	C
171.3	171.3	169.8	169.8	169.4	C
157.3	157.3	155.9	155.8	155.8	C
155.3	155.3	153.8	153.8	153.7	C
150.6	150.6	149.1	149.1	149.1	C
149.3	149.3	147.8	147.8	147.6	C
138.1	138.2	136.8	136.7	136.3	C
135.2	135.2	133.8	133.8	133.2	C
133.2	133.2	131.7	131.7	132.1	CH
131.6	131.6	130.2	130.2	130.3	CH
130.4?	-	-	-	-	-
130.2?	-	-	-	-	-
129.7	-	-	-	-	-
129.5	129.5	128.1	128.0	128.4 x 2	CH
129.3	129.3 (not real?)	127.9 (not real?)	127.9	128.0	CH
129.1	129.12 (CH+C)	127.7 (CH+C)	127.7	127.8 x 2	CH
127.9	129.08	127.6	127.6	127.1 C	-
124.9	124.9	123.4	123.4	123.5	CH
123.4	123.4	122.0	122.0	122.7	CH
122.9	122.9	121.5	121.5	121.7	CH
117.3	117.3	115.8	115.8	115.6	CH
113.1	113.1	111.6	111.6	111.4	CH
67.6	67.6	66.2	66.2	66.7	CH_2 Z
56.6	56.6	55.1	55.1	55.8	OCH_3 Ar
55.1	55.1	53.7	53.7	53.6	CHα
54.9	54.8	53.4	53.4	53.5	CHα
-	53.0	51.5	-	52.5	OCH_3 Est
-	50.0	48.6	48.6	48.3	CHα
42.1?	-	-	48.4 (CH_3OD)	-	-
40.1	40.1	38.7	38.7	39.2	CH_2β
39.4	39.4	37.9	37.9	38.6	CH_2β
38.2	38.2	36.8	36.8	37.3	CH_2β
35.9?	-	-	-	-	-

Figure 3: ^{13}C in CD_3OD for Z-OF4949-III-OMe (Pearson's, ours)

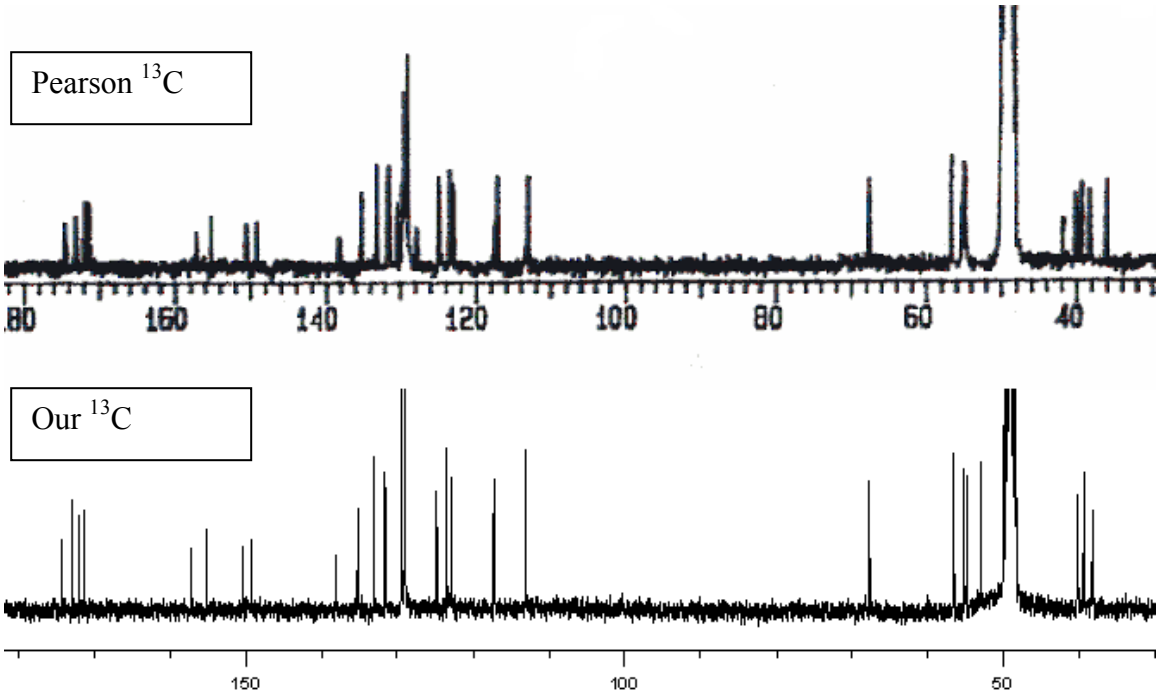
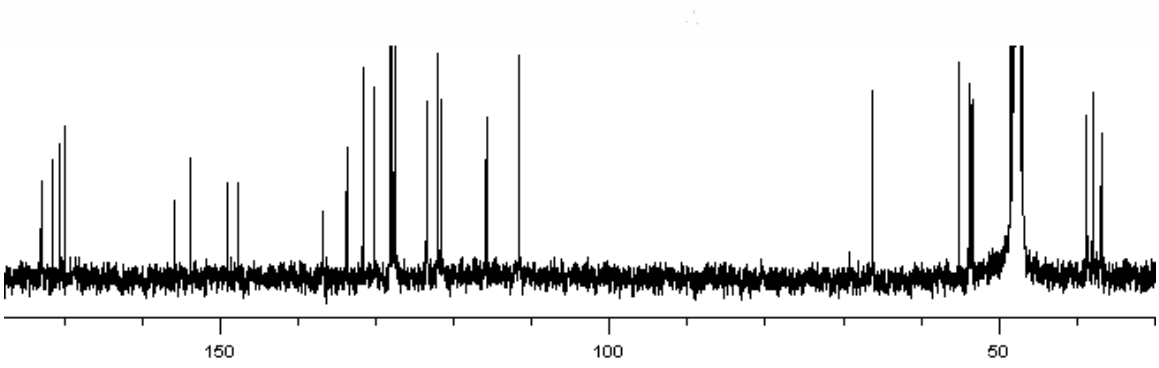


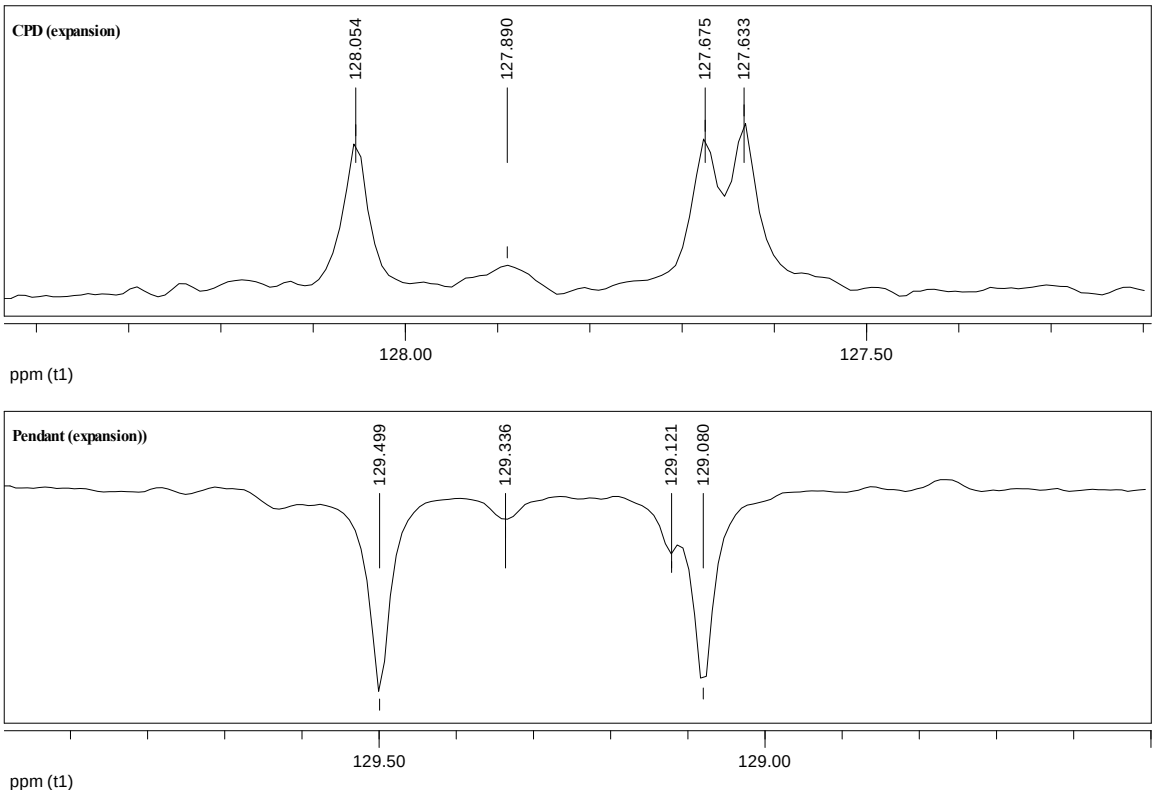
Figure 4: Our ^{13}C in CD_3OD for Z-OF4949-III-OMe + bicarbonate



The signals for the Pendant experiment (3 % $CDCl_3$ in CD_3OD) are slightly shifted from the CPD experiment (in just CD_3OD), but correspond. We suspect the signal at 129.3 (in the Pendant) and 127.9 (CPD) is a signal related to an impurity. The molecule requires 21 signals in the aromatic region: 10 signals for aromatic CH carbons and 11 quaternary carbons. From the pendant experiment we can see one quaternary fewer (10 instead of 11) and one CH more (11 instead of 10). Figure 5 shows the signal at 129.3 (Pendant), which corresponds to the signal at 127.9 (CPD) which is very weak and is on the odd side (together with CH and CH_3). Looking at the pendant experiment we notice the signal at

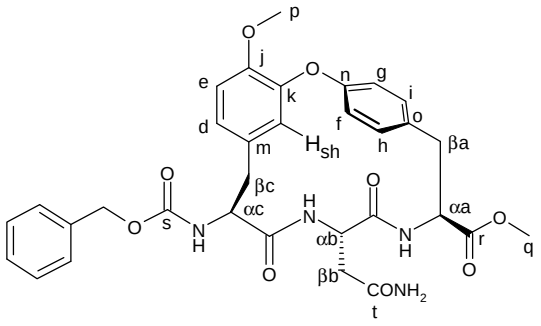
129.12 is much smaller than the nearby signal at 129.08. When we compare the corresponding signals in the CPD experiment, 127.7 is as intense as nearby signal at CH at 127.6. The signal at 129.08 (127.6 in the CPD) is one of the signals for two aromatic CHs from the symmetric Z protecting group. This observation can be rationalized by considering the presence of a quaternary carbon obscured by the signal at 129.12 (Pendant) or 127.7 (CPD), respectively. The quaternary carbon will increase its signal in the CPD and decrease in the pendant, where it would appear on the even side of the spectrum. In this way the number of signals becomes correct. Given the analysis of the data above, it should be mentioned that the same signal at 129.3, which we believe is an impurity, was also reported by Pearson.[1]

Figure 5: expansion of Pendant and CPD



NMR Structure Assignment for Z-OF4949-III-OMe 3 in $CDCl_3$

Figure 6: Z-OF4949-III-OMe (3)



In the ^1H NMR of Z-OF4949-III-OMe, a striking, but expected,[1,2] value for the chemical shift of H_{sh} (Figure 6) was observed, at 5.82 ppm (in deuterated chloroform) and 5.87 ppm (in deuterated methanol). Before attempting the NMR structure determination for **3**, a molecular structure was generated using "Maestro" software and a conformational search using the "Montecarlo" method (MMFF/THCG pair) was performed to find a low energy conformation, which was then validated by calculation of the expected chemical shift of H_{sh}.

The settings chosen were the following:

Solvent	chloroform
Maximum iterations	500
Number of steps	1000
Method	torsional sampling
Energy window for saving structures	50.0 KJ/mol

In most of the minimized structure, a similar motif for the ring was observed with the major changes related only to the external groups (Z-group, OMe, Asn and COOMe). We then compared the lowest energy structure (Figure 7a, sticks and Figure 7b, space filling) for the macrocycle with an arbitrarily chosen minimized open structure, with H_{sh} far away from any source of magnetic perturbation (Figure 8), chosen as zero.

Figure 7a: Z-OF4949-III-OMe (sticks)

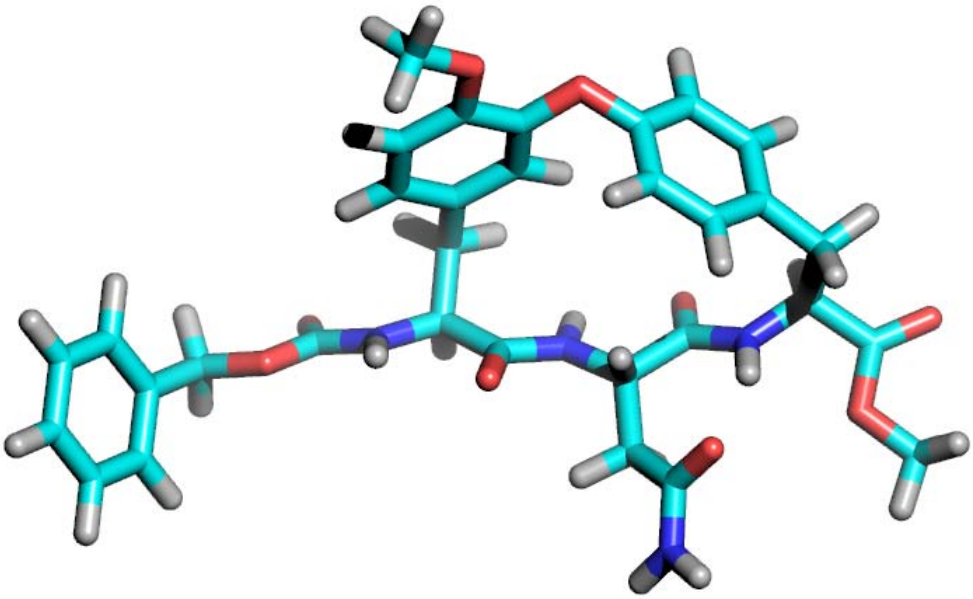


Figure 7b: Z-OF4949-III-OMe (space filling)

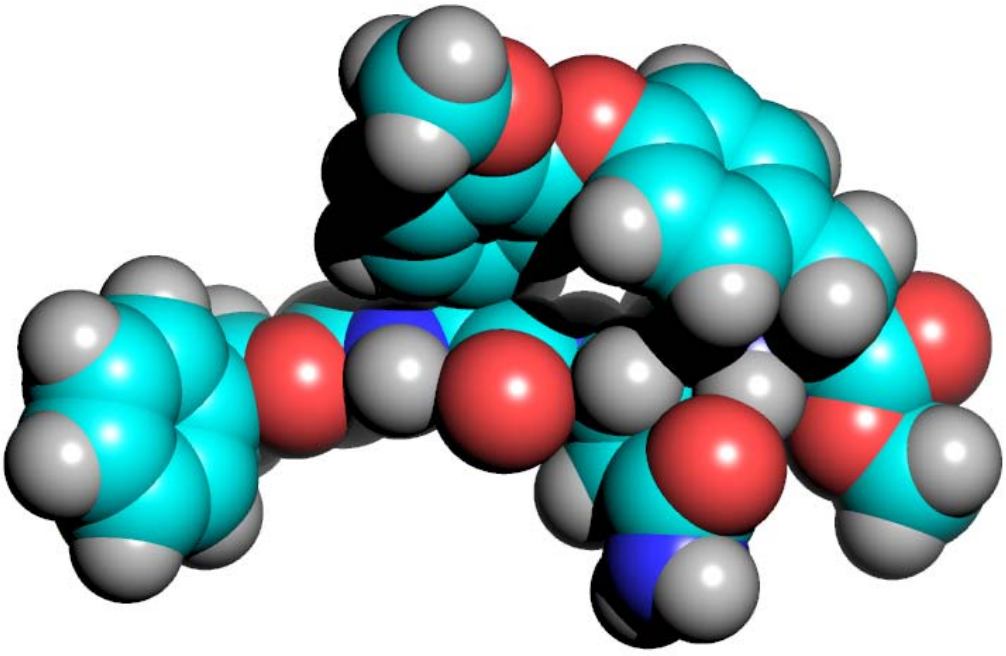
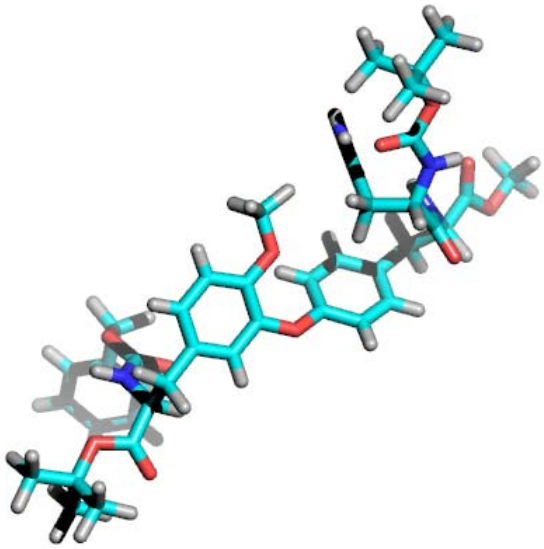


Figure 8: Precursor to Z-OF4949-III-OMe (3.16)

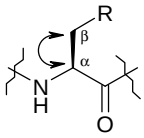


Performing a change-induced in chemical shift calculation for H_{sh}, using Hunter's approach,[4] we found a value of -0.93 ppm, which is in agreement with the experimental data. The calculated distance between H_{sh} and the close sphere of protons, are consistent with the NOE data obtained.

COSY experiment in $CDCl_3$

Due to improved solubility, $CDCl_3$ was chosen as solvent for the initial NMR experiments. The sample for the COSY experiment was prepared dissolving the non recrystallised material (**3**) in deuterated methanol, in order to exchange the acidic NHs, and then evaporation of the solvent and subsequent dissolution of the solid in $CDCl_3$. Traces of methanol had the effect of completely splitting the three sets of signals for the two overlapping α protons. Under these conditions it was possible to clearly identify the α-β proton sets coupled together (see Figure 9).

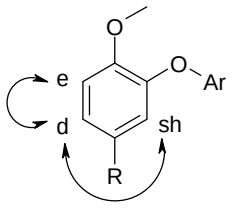
Figure 9: COSY α-β correlation



Irradiated		Coupled with	
signal	ppm	signal	ppm
α_c	4.48	β_c	2.93, 2.73
α_b	4.61	β_b	2.54-2.45, 2.40
α_a	4.78	β_a	2.54-2.45, 3.28

With the COSY experiment it was also possible to identify both the symmetrical and unsymmetrical aromatic system (see Figure 10).

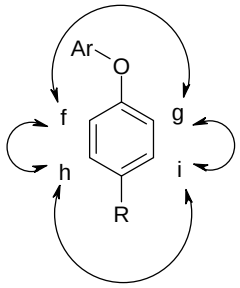
Figure 10: COSY unsymmetrical aromatic system



Irradiated		Couple with	
signal	ppm	signal	ppm
H_{sh}	5.80	H_d	6.47
H_d	6.47	H_e	6.70
		H_{sh}	5.80
H_e	6.70	H_d	6.47

Concerning the symmetrical aromatic system, and basing our assumption on data from literature,[5] it is reasonable to assign the higher field signals as protons H_f and H_g, in the *ortho* position of O-Ar. The H_h and H_i, (*meta* to the O-Ar) are therefore the signals at lower field (see Figure 11).

Figure 11: COSY symmetrical aromatic system



Irradiated		Couple with	
signal	ppm	signal	ppm
H_f	6.82	H_h	7.09
		H_g	6.99
H_g	6.99	H_i	7.24
		H_f	6.82
H_h	7.09	H_f	6.82
		H_i	7.24
H_i	7.24	H_g	6.99
		H_h	7.09

HMQC experiment in $CDCl_3$

The HMQC experiment, run on the same sample used for the COSY experiment, determines the C-H connectivity in the molecule (see Table 5).

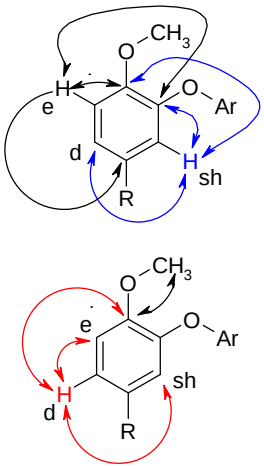
Table 5: HMQC in $CDCl_3$

HMQC ($CDCl_3$ no acidic proton)		
carbon	proton	description
132.1	7.09	H_h
130.3	7.24	Hi
128.4 x 2	7.30	Z 5H
128.1		
127.8 x 2		
123.5	6.47	H_d
122.7	6.99	H_g
121.7	6.82	H_f
115.6	5.80	H_{sh}
111.4	6.70	H_e
66.7	5.10, 4.99	CH_2Z
55.9	3.86	(ArOMe)
53.6	4.48	α_c
53.5	4.78	α_a
52.5	3.74	(CO_2Me)
48.3	4.61	α_b
39.3	2.54-2.45, 2.40	β_b
38.5	2.54-2.45, 3.28	β_a
37.3	2.93, 2.73	β_c

HMBC experiment in $CDCl_3$

In order to try to obtain more information from the HMBC experiment, compound **3** was dissolved in deuterated chloroform only, in order to see all the protons present in the molecule. Figure 12 shows the connectivity between carbons and protons at two bond distance (C-X-H) and three bond distance (C-X-X-H) in the unsymmetrical aromatic system.

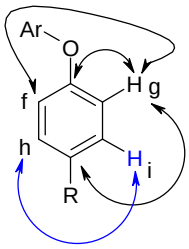
Figure 12: HMBC unsymmetrical aromatic system



Proton		Coupled Carbon	
signal	ppm	signal	ppm
OCH_3	3.88	C_j	147.7
		C_d	123.5
H_{sh}	5.82	COMe	147.7
		COAr	149.1
		C_e	111.4
H_d	6.50	C_{sh}	115.6
		COMe	147.7
		CR	127.1
H_e	6.72	COMe	147.7
		COAr	149.1

Figure 13 shows the C-H long distance correlations in the symmetrical aromatic system.

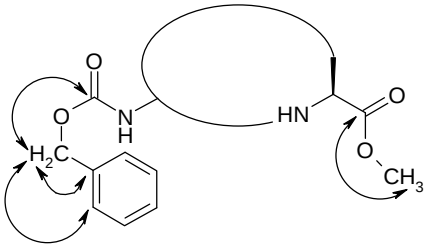
Figure 13: HMBC symmetrical aromatic system



Proton		Coupled Carbon	
signal	ppm	signal	ppm
		C_f	121.8
H_g	7.00	CR	133.2
		COAr	153.7
H_i	7.24	C_h	132.1

Figure 14 shows the C-H long distance relationships in the ester and carbamate protecting group.

Figure 14: HMBC protecting groups



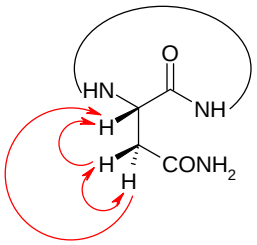
Proton		Coupled Carbon	
signal	ppm	signal	ppm
OCH_3	3.76	-C(O)O	171.8
		o-CHs	127.8
CH_2Z	5.12	*ipso*-C	136.3
		OC(O)N	155.8

Use of pure chloroform as solvent resulted in little change in the chemical shifts observed in the overall spectrum for both carbon and proton. The signals for the protons α_b and α_c collapsed to a broad signal at 4.55 ppm, together with the change in the multiplicity at the α protons, which now couple with the NHs. Unfortunately no C-H long range correlation to the peptide chain was observed. With the information obtained from the HMBC experiment, we were able to determine the quaternary carbons of the aromatic rings and assign some of the carbonyl groups in the structure.

NOESY experiment in $CDCl_3$

Only the most significant signals are reported here. The sample was dissolved in chloroform and no deuterium exchanged was carried out. The multiplet at 2.35-2.60 ppm is generated from the overlapping of 3 protons: two β_b and one of the two β_a. From the spectrum, it is possible to assign the right shoulder (rs) of the signal to the two β_b and the left shoulder (ls) to β_a. This data was also confirmed from the COSY experiment. Irradiation of the multiplet at 2.35-2.60 ppm gave an enhancement to the geminal protons β_b and β_a and to the signal at 4.55 (α_b and α_c). The irradiation of the signal at 4.55 ppm (α_b and α_c) gave enhancement not just to the right shoulder of the multiplet at 2.35-2.60, related to α_b (Figure 15), but also to the protons spatially related to α_c (see Figure 18). The irradiation of the right shoulder had no NOE effect on any of the aromatic signals, so the β_bs must belong to the asparagine, distant from both aromatic rings. For reasons of clarity, the figure below shows the enhancement related only to the α_b β_b system.

Figure 15: NOESY $CDCl_3$ – α_b β_b system (asparagine)

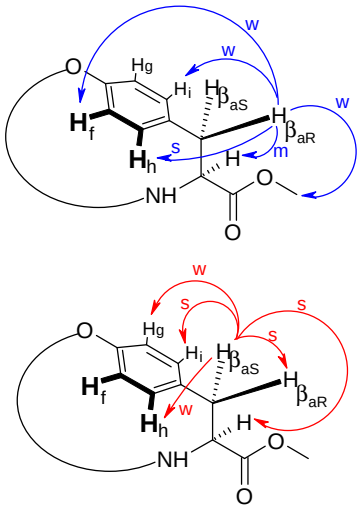


Irradiated	Signal	NOE	Strength	Signal
2.35-2.60(rs)	β_b	2.35-2.60	s	β_b
		4.55	m	α_b
4.55	α_b/ α_c	2.35-2.60	m	β_b

The irradiation of the left shoulder (ls) of the signal at 2.35-2.60 (β_a) gave a NOE enhancement of the methyl ester protecting group. This allowed us to assign the β_a as belonging to the symmetrical tyrosine (the one bearing the methyl ester protecting group). A weak enhancement of H_f and H_i and a strong enhancement of H_h led to the conclusion that β_a at 2.35-2.60 is on the same side as the two aromatics H_h, H_f and opposite to H_i. The observation was confirmed from the irradiation of β_a at 3.27 which enhanced H_i strongly and H_g weakly. Because irradiation of β_a at 2.35-2.60 gave a medium NOE of α_a at 4.79-4.90 and irradiation of β_a at 3.27 ppm gave a strong enhancement to the same proton, it was

possible to define the spatial arrangement of the two β_a and the close aromatic system, given that the amino acid is of *S*-configuration. This identifies β_a at 2.35-2.60 as the prochiral R proton, and so is labelled β_{aR}; β_a at 3.27 is then β_{aS} (see Figure 16).

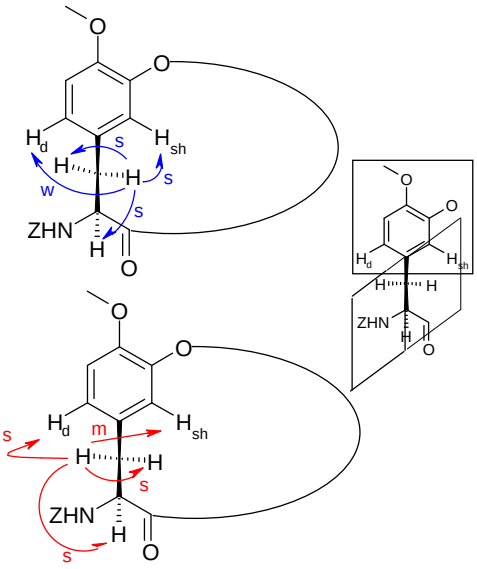
Figure 16: NOESY $CDCl_3$ symmetrical tyrosine



Irradiated	Signal	NOE	Strength	Signal
2.35-2.60 (ls)	β_{aR}	3.27	s	β_{aS}
		4.79-4.90	m	α_a
		6.82	w	H_f
		7.08	m	H_h
		7.24	w	H_i
3.27	β_{aS}	2.35-2.60	s	β_{aR}
		4.79-4.90	s	α_a
		7.00	w	H_g
		7.08	w	H_h
		7.24	s	H_i

Irradiation of β_c at 2.78 (Figure 17) gave a NOE enhancement to the geminal proton β_c (2.96), the α_c (4.55) and also the aromatics H_{sh} and H_d. With H_d in particular, the enhancement was stronger. Irradiation of β_c at 2.96 enhanced the geminal proton β_c (2.78), α_c (4.55), and again the two aromatics H_{sh} and H_d. The relative strength of the enhancements was reversed relative to those observed with β_c at 2.78. This gives the impression that the plane of the aromatic ring is almost orthogonal to the plane that bisects the two protons β_c. The proton H_d is closer to β_c at 2.96 and H_{sh} is closer to β_c at 2.78.

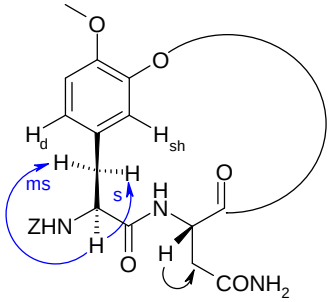
Figure 17: NOESY $CDCl_3$ unsymmetrical tyrosine



Irradiated	Signal	NOE	Strength	Signal
2.78	β_c	2.96	s	β_c
		4.55	s	$\alpha_b\alpha_c$
		5.82	s	H_{sh}
		6.50	w	H_d
2.96	β_c	2.78	s	β_c
		4.55	s	α_c
		5.82	m	H_{sh}
		6.50	s	H_d

With the irradiation of the signal at 4.55 ($\alpha_b\alpha_c$), it was not possible to confirm the spatial arrangement of the protons in the unsymmetrical aromatic system, because only few signals can be assignd with certainty to α_b or to α_c. The NOE effect observed on β_c at 2.78 is just slightly stronger than the one for β_c at 2.96, suggesting that α_c is almost halfway from the two β_c (Figure 18), which is in agreement with the observation made before (Figure 17).

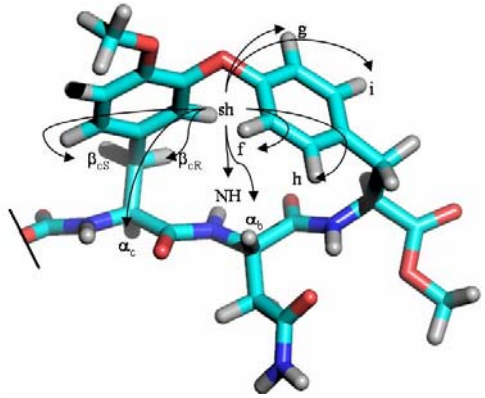
Figure 18: NOESY - irradiation of α_c/α_b



Irradiated	Signal	NOE	Strength	Signal
4.55	α_b α_c	2.35-2.60	m	β_b β_b
		2.78	s	β_c
		2.96	m/s	
		4.79-4.90	w	α_a
		5.68	m	NH
		5.82	m	H_{sh}
		6.50	w	H_d
		6.82	w	H_f
		7.00	vw	H_g
		7.08	w	H_h
		7.26-7.36	m	Ar(Z)

A very weak but interesting enhancement of α_a, which may be rationalized by a long range effect between the two alpha protons α_a and α_c, which point, in our model, in the same direction. Irradiation of the proton H_{sh} (5.82) shows its central position in the molecule very clearly, giving an NOE with almost all the protons facing the cavity of the molecule (see Figure 19).

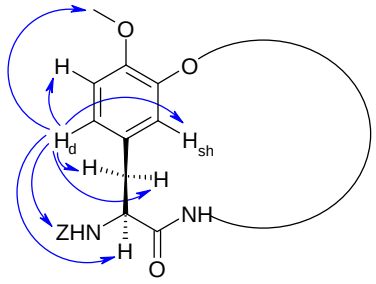
Figure 19: NOESY $CDCl_3$ - irradiation of H_{sh}



Irradiated	Signal	NOE	Strength	Signal
5.82	H_{sh}	2.78	s	β_c
		2.96	m	
		4.55	m	α_b α_c
		5.68	m	NH
		6.50	w	H_d
		6.82	s	H_f
		7.00	m	H_g
		7.08	w	H_h
		7.24	w	H_i
		7.26-7.36	w	Ar(Z)

Irradiation of H_d, at 6.50 ppm, once again gave an indication of the relative position of the two β_c protons, showing a stronger NOE with 2.96 and weaker one with 2.78, in a complementary fashion to H_{sh} (see Figure 20).

Figure 20: NOESY $CDCl_3$ irradiation of H_d

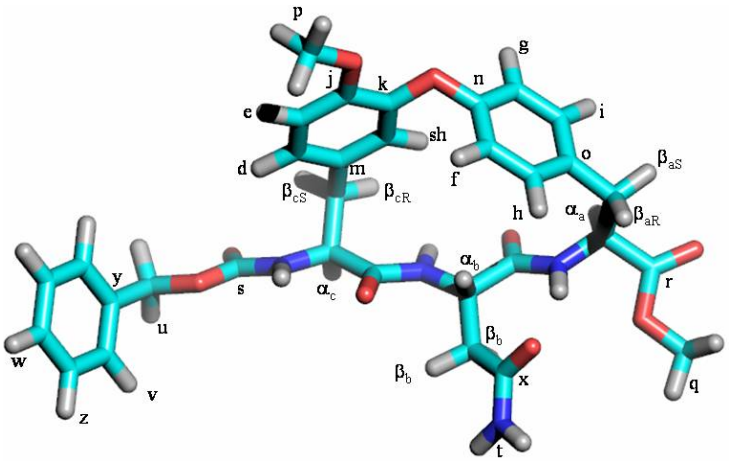


Irradiated	Signal	NOE	Strength	Signal
6.50	H_d	2.78	m	β_c
		2.96	s	
		4.55	w	α_b α_c
		5.68	m	NH
		5.82	w	H_{sh}
		6.72	s	H_e
		7.26-7.36	w	Ph(Z)

The two NH protons at 5.95 and 6.42 ppm gave a NOE effect just between each other; this reasonably identifies them as the $C(O)NH_2$ of the asparagine residue.

With the help of the computer model and the data already in our possession, we analyzed the NOESY spectrum, confirming some of the data and finally achieving what we think is the most complete assignment (Figure 21) for the fully protected precursor of OF4949-III **3**, which is shown below.

Figure 21: $CDCl_3$ assignment



^{1}H	^{13}C	Assign.
7.26-7.36	128.4	z
	128.0	w
	127.8	v
7.24	130.3	i
7.08	132.1	h
7.00	122.7	g
6.82	121.8	f
6.72	111.4	e
6.50	123.5	d
5.82	115.6	H_{sh}
5.12	66.7	u
5.02		
4.79-4.90	53.5	α_a
4.55	53.6	α_c
	48.3	α_b
3.88	55.8	p
3.76	52.5	q
3.27	38.6	β_{aS}
2.96	37.3	β_{cS}
2.78	37.3	β_{cR}
2.35-2.60 ls	38.6	β_{aR}
2.35-2.60 rs	39.2	β_b β_b
-	173.1	x
-	171.7	r
-	169.7	C=O
-	169.4	C=O
-	155.8	s
-	153.7	n
-	149.1	k
-	147.6	j
-	136.3	y
-	133.2	o
	127.1	m

NOESY study in $CDCl_3$ (following H/D exchange)

The sample was dissolved in deuterated methanol, evaporated and dissolved in deuterated chloroform. All the signals for the NH were lost. The signals for α_b and α_c were separated into two different signals at 4.38 (α_c) and 4.55 (α_b). The only important issue was the confirmation of the spatial arrangement in the unsymmetrical tyrosine. The irradiation of 2.93 (β_{cS}) enhanced H_d (6.50) and irradiation of 2.78 (β_{cR}) enhanced H_{sh} (5.81).

NMR Structure Assignment for Z-OF4949-III-OMe 3 in CD_3OD

HMQC experiment in CD_3OD

Table 6 lists the chemical shifts from the HMQC experiment in CD_3OD. In addition to an assignment of the C-H connectivity in the molecule, this experiment allowed us to define the different signals for each of the α and β protons and the corresponding carbons.

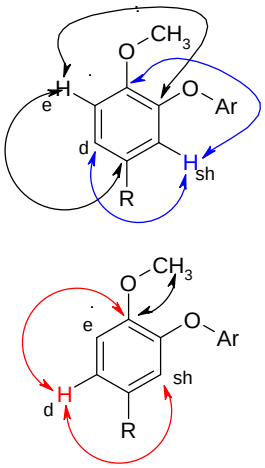
Table 6: HMQC in CD_3OD

HMQC CD_3OD		
carbon	proton	description
131.7	7.19	Ar
130.2	7.43-7.28	Ar
128.1 (x 2)	7.43-7.28	Ar Z
127.7 (CH+C)		
127.6 (x 2)		
123.4	6.47	H_d
122.0	6.98	Ar
121.5	6.85	Ar
115.8	5.87	H_{sh}
111.6	6.80	H_e
66.2	5.14, 5.01	CH_2Z
55.1	3.86	(ArOMe)
53.7	4.70-4.83	α_c
53.4	4.38	α_a
51.5	3.79	(CO_2Me)
48.6	4.70-4.83	α_b
38.7	2.65, 2.52	β_b
37.9	3.35, 2.65	β_a
36.8	3.01, 2.83	β_c

HMBC experiment in CD_3OD

Figure 22 shows the HMBC experiment in deuterated methanol for **3**. As was previously shown before with the experiment in chloroform, the only information we can get is related just to the aromatic system. None of the carbons or protons in the peptide chain gives signals distinguishable from the background noise. Although less information was obtained in this experiment, in comparison with the one performed in chloroform, the data obtained were consistent. Figure 22 shows the connectivity in the unsymmetrical aromatic ring. The experiment allowed us to assign the quaternary carbon in the unsymmetrical aromatic ring.

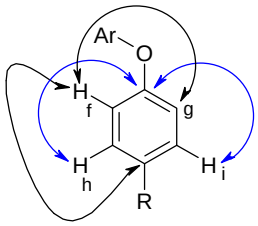
Figure 22: HMBC in CD_3OD - unsymmetrical aromatic system



Proton		Coupled Carbon	
signal	ppm	signal	ppm
OCH_3	3.86	COMe	147.8
H_{sh}	5.87	C_d	123.4
		COMe	147.8
H_d	6.47	C_{sh}	115.8
		COMe	147.8
H_e	6.72	CR	127.7
		COAr	149.1

Figure 23 shows the C-H long distant correlation in the symmetrical aromatic system. Again the information obtained was less than the experiment in chloroform, but still consistent with the latter. As before, the experiment allowed us to assign the quaternary carbon in the symmetrical aromatic ring.

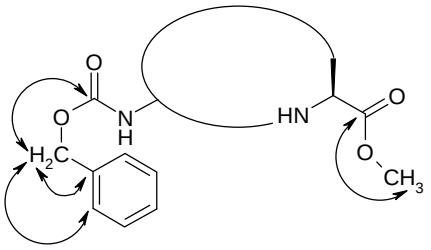
Figure 23: HMBC in CD_3OD - symmetrical aromatic system



Proton		Coupled Carbon	
signal	ppm	signal	ppm
H_f	6.85	CR	133.8
		C_g	122.0
H_h	7.19	COAr	153.8
H_i	7.24	COAr	153.8

Figure 24: shows the C-H long distance relationships in the ester and carbamate protecting group.

Figure 24: HMBC in CD_3OD - protecting groups



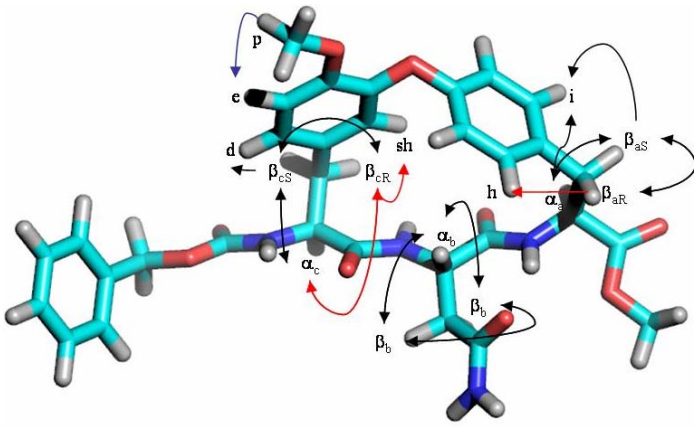
Proton		Coupled Carbon	
signal	ppm	signal	ppm
OCH_3	3.79	-C(O)O	171.5
		o-CHs	127.6
CH_2Z	5.14, 5.01	*ipso*-C	136.8
		OC(O)N	155.9

With this information we were able to assign the quaternary carbons of the aromatic rings and some of the carbonyl groups in the structure.

NOESY experiment in CD_3OD

The figure below shows mainly the results for the irradiation of the alpha and beta protons in the peptide chain. In particular it was possible to assign the spatial arrangement of the cluster a and c.

Figure 25: NOESY CD_3OD – β and α

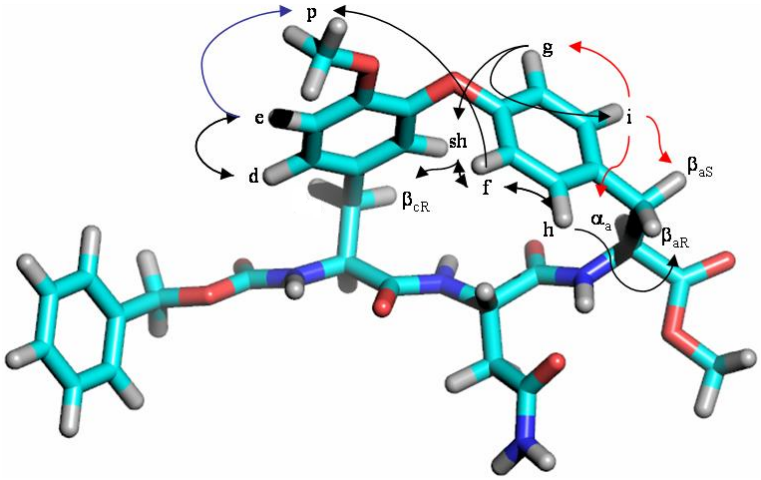


Irradiated	Signal	NOE	Strength	Signal
2.53	β_b	2.69-2.61	s	$\beta_b + \beta_{aR}$
		4.78	w	α_b
2.69-2.61	$\beta_b + \beta_{aR}$	2.53	s	β_b
		3.35	s	β_{aS}
		4.78	w	α_b
		7.19	m	H_h
2.83	β_{cR}	3.01	m	β_{cS}
		4.42-4.37	w	α_c
		5.87	w	H_{sh}
3.01	β_{cS}	2.83	m	β_{cR}
		4.42-4.37	w	α_c
		6.47	w	H_d
3.35	β_{aS}	2.69-2.61	s	$\beta_b + \beta_{aR}$
		4.73	w	α_a
		7.28-7.43	w	H_i
3.38	MeOAr	6.8	m	H_e
4.42-4.37	α_c	2.83	w	β_{cR}
		3.01	w	β_{cS}
4.73	α_a	3.35	w	β_{aS}
		7.28-7.43	w	H_i
4.78	α_b	2.69-2.61	ws	$\beta_b + \beta_{aR}$

Once more, the results obtained were consistent with the computer generated structure, even though the conformational search was performed using chloroform as solvent.

Figure 26 shows the results from the irradiation of the aromatic protons.

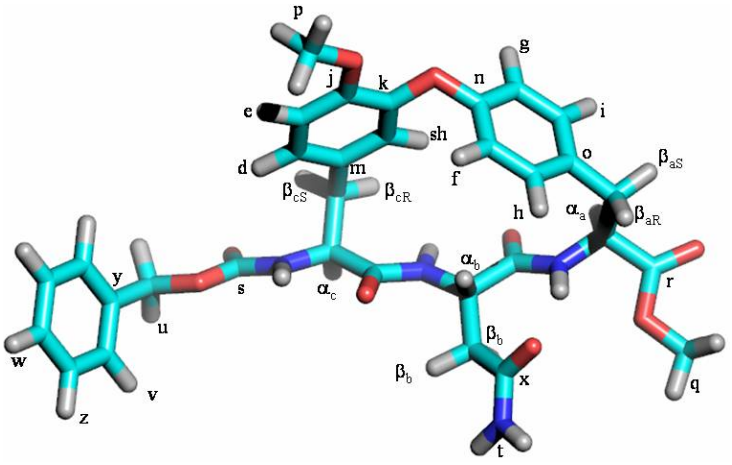
Figure 26: NOESY CD_3OD – aromatic system



Irradiated	Signal	NOE	Strength	Signal
5.87	H_{sh}	6.85	vw	H_f
		2.83	w	β_{cR}
6.47	H_d	6.47	m	H_e
6.80	H_e	6.47	m	H_d
		3.85	m	MeOAr
6.85	H_f	3.85	m	MeOAr
		5.87	w	H_{sh}
		7.20	m	H_h
6.98	H_g	5.87	vw	H_{sh}
		7.28-7.43	m	H_i
7.20	H_h	2.69-2.61	w	$\beta_b + \beta_{aR}$
		6.85	m	H_f
7.28-7.43	H_i	3.35	w	β_{aS}
		4.73	w	α_a
		6.98	m	H_g

Figure 27 shows the assignment in CD_3OD.

Figure 27: CD_3OD assignment



^{1}H	^{13}C	Assign.
7.28-7.43	128.1	z
	127.7	w (m)
	127.6	v
7.28-7.43	130.2	i
7.20	131.7	h
6.98	122.0	g
6.85	121.5	f
6.80	111.6	e
6.47	123.4	d
5.87	115.8	H_{sh}
5.14	66.2	u
5.02		
4.70-4.83 (4.78)	48.6	α_b
4.70-4.83 (4.73)	53.7	α_a
4.37-4.42	53.4	α_c
3.85	55.1	p
3.79	51.5	q
3.35	37.9	β_{aS}
3.01	36.8	β_{cS}
2.83		β_{cR}
2.69-2.61	38.7	β_{aR}
	37.9	β_b
2.53	38.7	β_b
-	173.0	x
-	171.5	r
-	170.5	C=O
-	169.8	C=O
-	155.9	s
-	153.8	n
-	149.1	k
-	147.8	j
-	136.8	y
-	133.8	o
-	127.7	m (w)

Table 7: Comparison of assignments in chloroform and methanol

Assignment in $CDCl_3$			Assignment in CD_3OD		
^{1}H	^{13}C	Assign.	Shift	^{13}C	Assign.
7.26-7.36	128.4	z	7.28-7.43	128.1	z
	128.0	w		127.7	w (m)
	127.8	v		127.6	v
7.24	130.3	i	7.28-7.43	130.2	i
7.08	132.1	h	7.20	131.7	h
7.00	122.7	g	6.98	122.0	g
6.82	121.8	f	6.85	121.5	f
6.72	111.4	e	6.80	111.6	e
6.50	123.5	d	6.47	123.4	d
5.82	115.6	sh	5.87	115.8	sh
5.12	66.7	u	5.14	66.2	u
5.02			5.02		
4.79-4.90	53.5	α_a	4.70-4.83 (4.78)	48.6	α_b
4.55	53.6	α_c	4.70-4.83 (4.73)	53.7	α_a
	48.3	α_b	4.37-4.42	53.4	α_c
3.88	55.8	p	3.85	55.1	p
3.76	52.5	q	3.79	51.5	q
3.27	38.6	β_{aS}	3.35	37.9	β_{aS}
2.96	37.3	β_{cS}	3.01	36.8	β_{cS}
2.78	37.3	β_{cR}	2.83		β_{cR}
2.35-2.60 ls	38.6	β_{aR}	2.69-2.61	38.7	β_{aR}
2.35-2.60 rs	39.2	β_b β_b		37.9	β_b
-	173.1	x	2.53	38.7	β_b
-	171.7	r	-	173.0	x
-	169.7	C=O	-	171.5	r
-	169.4	C=O	-	170.5	C=O
-	155.8	s	-	169.8	C=O
-	153.7	n	-	155.9	s
-	149.1	k	-	153.8	n
-	147.6	j	-	149.1	k
-	136.3	y	-	147.8	j
-	133.2	o	-	136.8	y
	127.1	m	-	133.8	o
			-	127.7	m (w)

Comparison of Data for OF4949-III 1

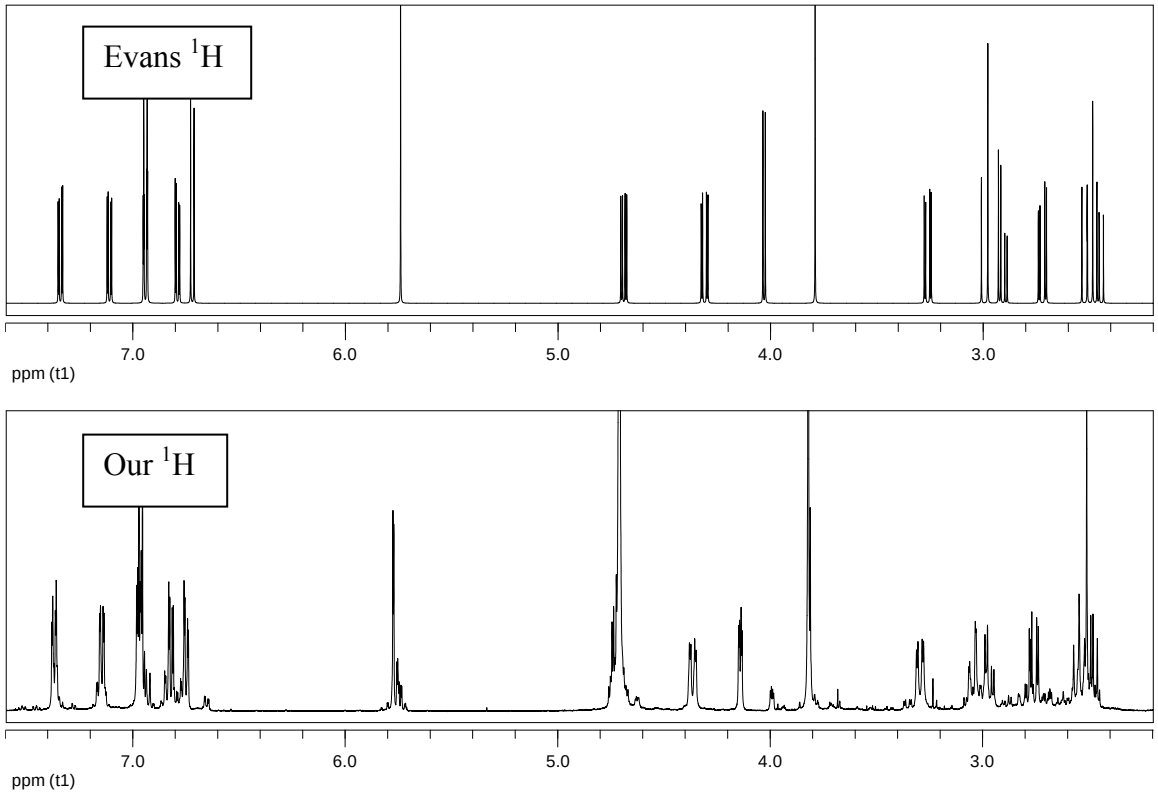
Table 8 shows the ^{1}H NMR data for OF4949-III found by Evans[3] and us.

Table 8: OF4949-III ^{1}H in D_2O

Evans 500 MHz D_2O			Ours 500 MHz		
shift	H, mul, J	Descr.	shift	H, mul., J	Descr.
7.34	1, dd, 8.3, 1.7	Ar	7.37	1, dd, 8.5, 2.0	H_i
			7.14	1, dd, 8.5, 2.0	H_h
7.11	1, dd, 8.3, 1.7	‘’	6.97	1, dd, 8.0, 2.5	H_g
6.94	2, d, 8.2	‘’	6.96	1, d, 8.5	H_e
6.79	1, dd, 8.3, 2.4	‘’	6.82	1, dd, 8.0, 2.5	H_f
6.72	1, d, 8.1	‘’	6.75	1, dd, 8.0, 2.0	H_d
5.74	1, s	sh	5.77	1, d, 2.0	H_{sh}
4.69	1, dd, 10.0, 3.9	Asn α	4.73	1, dd, 10.0, 4.0	α_b
4.31	1, dd, 12.4, 3.4	α	4.36	1, dd, 12.5, 3.5	α_a
4.03	1, d, 3.9	α	4.14	1, dd, 6.0, 2.0	α_c
3.79	3, s	OMe	3.82	3, s	OMe
3.26	1, dd, 13.2, 3.3	β	3.29	1, dd, 13.0, 3.5	β_a
2.99	1, d, 14.9	β	3.05	1, dd, 15.0, 2.0	β_c
2.91	1, dd, 15.0, 5.8	β	2.97	1, dd, 15.5, 6.0	β_c
2.72	1, dd, 15.4, 3.9	Asn β	2.76	1, dd, 15.5, 4.0	β_b
2.51	1, t, 12.8	β	2.55	1, t, 13.0	β_a
2.46	1, dd, 15.3, 10.1	β	2.48	1, dd, 15.5, 10.0	β_b
Tot	19 H	-		19 H	

Figure 28 shows a comparison of our ^{1}H spectrum in D_2O and a simulated spectrum using the data tabulated from Evans fed into the NMR simulation software from MestRe-C (beta 3.9.9.0; Frequency 500 MHz, Number of points 32768, Threshold 0.000001, Line width 0.5).

Figure 28: ^{1}H in D_2O of OF4949-III 1 (Evans' simulated spectrum, and our spectrum)



OF4949-III 1: NMR Assignment

Table 9 shows the results of the HMQC experiment on the final product OF4949-III **1** as a zwitterion in D_2O. Again it was used to assigne the three different αβ systems as well as the C-H connectivity.

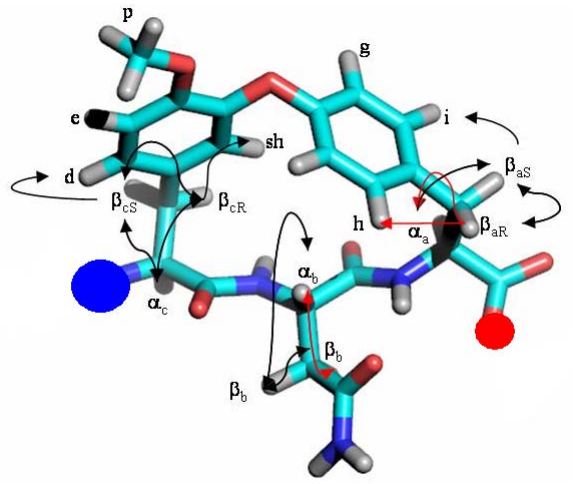
Table 9: OF4949-III HMQC experiment

HMQC		
proton	carbon	description
7.37	130.7	Ar
7.14	131.9	Ar
6.95-6.98	122.2	Ar
	112.3	H_e
6.82	121.4	Ar
6.75	124.3	H_d
5.77	115.1	H_{sh}
4.73	49.1	α_b
4.36	56.8	α_a
4.14	52.4	α_c
3.82	55.8	OMe
3.29	38.8	β_a
3.05	35.2	β_c
2.97	35.2	β_c
2.76	38.7	β_b
2.55	38.8	β_a
2.48	38.7	β_b

OF4949-III NOESY experiment

Figure 29 shows the irradiation of the protons in the peptidic chain and the related enhancement. The picture here used is adapted from that used for the Z-OF4949-III-OMe. It should be only considered as pictorial help; no computer modelling with minimized energy conformations was performed.

Figure 29: NOESY of OF4949-III – peptidic protons



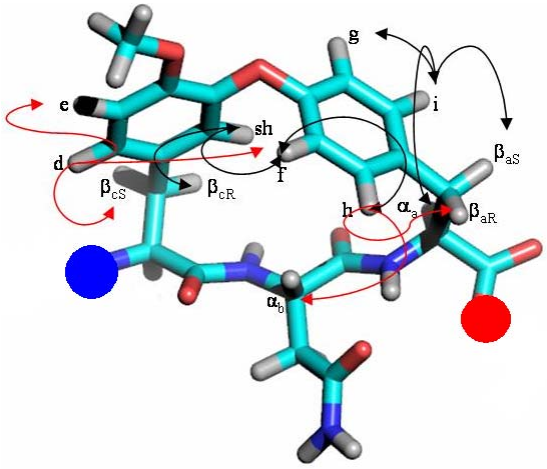
Irradiated	Signal	NOE	Strength	Signal
2.48	β_b	2.76	s	β_b
		4.73	m	α_b
2.55	β_{aR}	3.29	s	β_{aS}
		4.36	w	α_a
		7.14	m	H_h
2.76	β_b	2.48	s	β_b
		4.73	m	α_b
2.97	β_{cS}	3.05	m	β_{cR}
		4.14	m	α_c
		6.75	s	H_d
3.05	β_{cR}	2.97	m	β_{cS}
		4.14	m	α_c
		5.77	s	H_{sh}
3.29	β_{aS}	2.55	s	β_{aR}
		4.36	s	α_a
		7.37	s	H_i
3.82	OMe	6.95-6.98	s	H_g H_e
4.14	α_c	2.97	m	β_{cS}
		3.05	m	β_{cR}
4.36	α_a	3.29	s	β_{aS}
4.73	α_b	2.48	s	β_b
		2.76	s	β_b

The NOE data fit the computer generated structure, despite the fact that the calculations were carried out on the protected derivative, and in chloroform as solvent. In particular we were able to define the spatial arrangement around the stereogenic centers a and c. Irradiation of the methoxy group probably

generates an enhancement of the signal for H_e, but because the signals for the latter overlap with H_g (which could be close enough to generate the NMR response), no further information about the preferred arrangement of the methoxy group could be obtained.

Figure 30 shows the irradiation of the aromatic signals in the molecule and the enhancements generated. The figure is the same used for the Z-OF4949-III-OMe. When a certain assignment was not possible, no arrows were reported in the picture. In particular the signals at 6.95-6.98 were not easy to interpret because of the overlap between H_e and H_g.

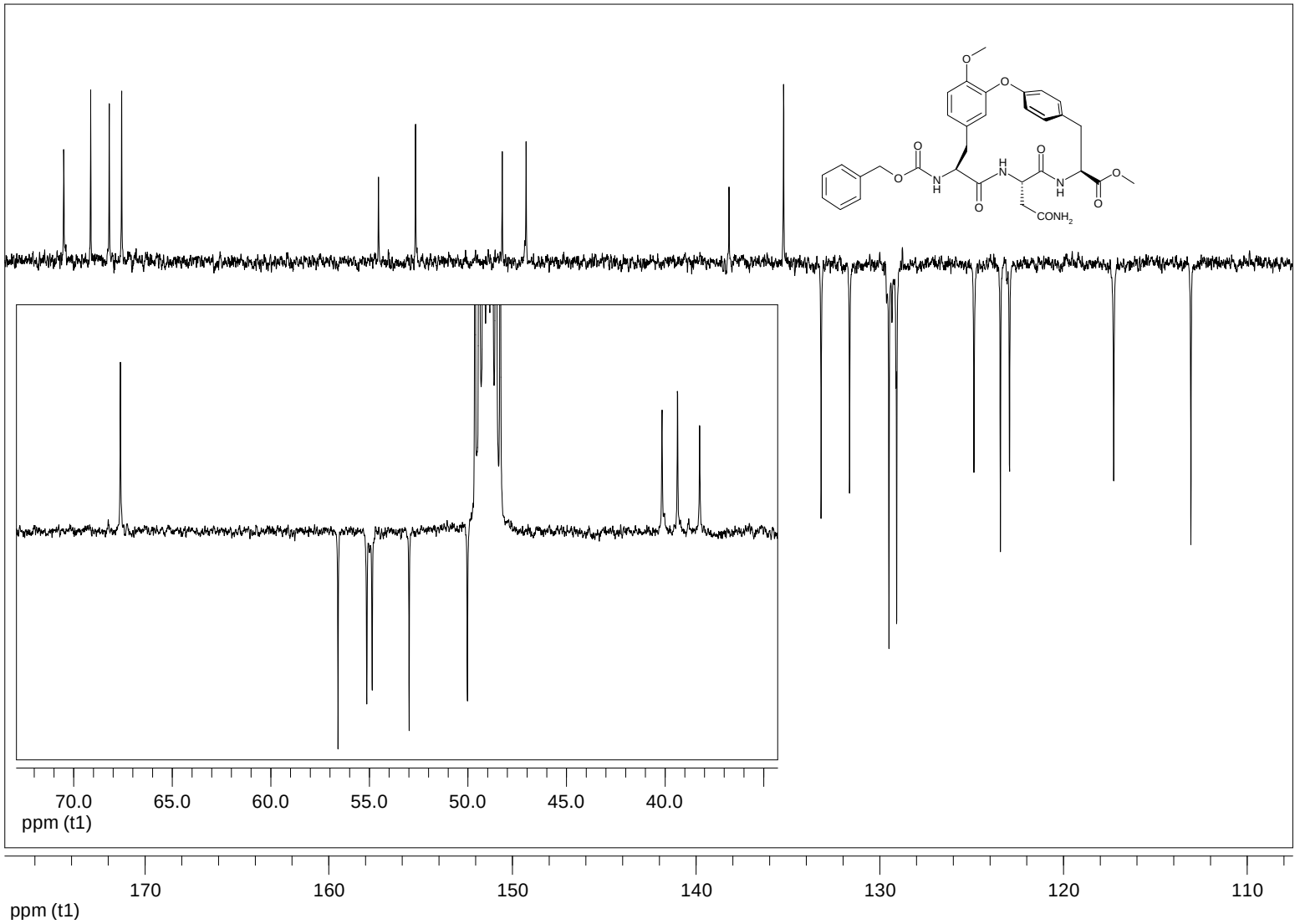
Figure 30: NOESY of OF4949-III – aromatic protons



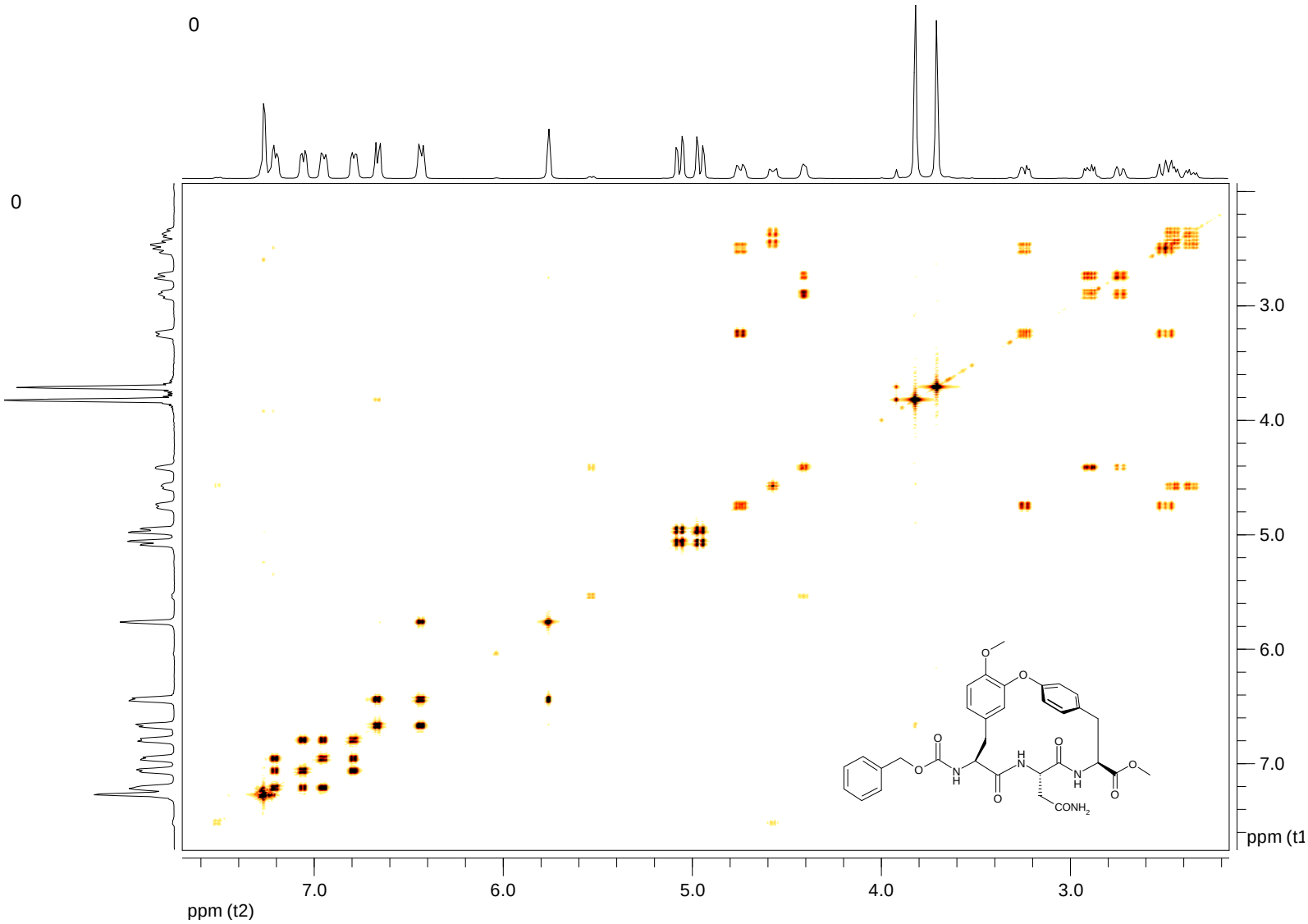
Irradiated	Signal	NOE	Strength	Signal
		3.05	m	β_{cR}
5.77	H_{sh}	6.82	m	H_f
		6.95-6.98	w	H_g H_e
		2.97	m	β_{cS}
6.75	H_d	5.77	w	H_{sh}
		6.95-6.98	s	H_g H_e
		5.77	w	H_{sh}
6.82	H_f	6.95-6.98	w	H_g H_e
		7.14	m	H_h
		3.82	m	OMe
6.95-6.98	H_g H_e	5.77	w	H_{sh}
		7.37	m	H_i
		2.55	m	β_{aR}
7.14	H_h	4.73	m	α_b
		6.82	m	H_f
		7.37	w	H_i
		3.29	m	β_{aS}
7.37	H_i	4.36	m	α_a
		6.95-6.98	s	H_g H_e
		7.14	w	H_h

References

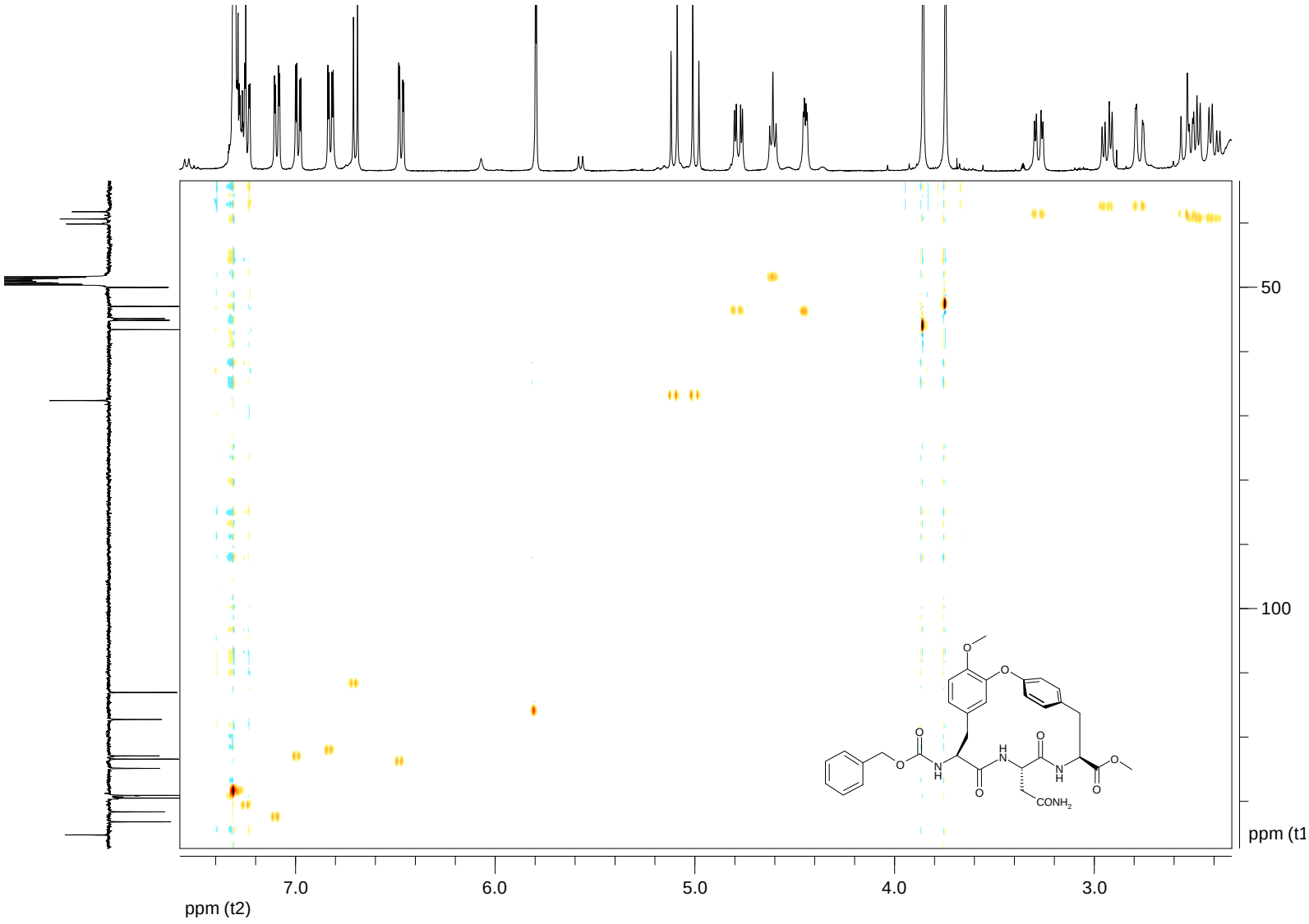
(1) Pearson, A. J.; Zhang, P. L.; Lee, K. *J. Org. Chem.* **1996**, *61*, 6581-6586.
(2) Boger, D. L.; Yohannes, D. *J. Org. Chem.* **1990**, *55*, 6000-6017.
(3) Evans, D. A.; Ellman, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 1063-1072.
(4) Hunter, C. A.; Packer, M. J. *Chemistry-a European Journal* **1999**, *5*, 1891-1897.
(5) Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*; 6th ed.; John Wiley & Sons, Inc.: New York, 1997.



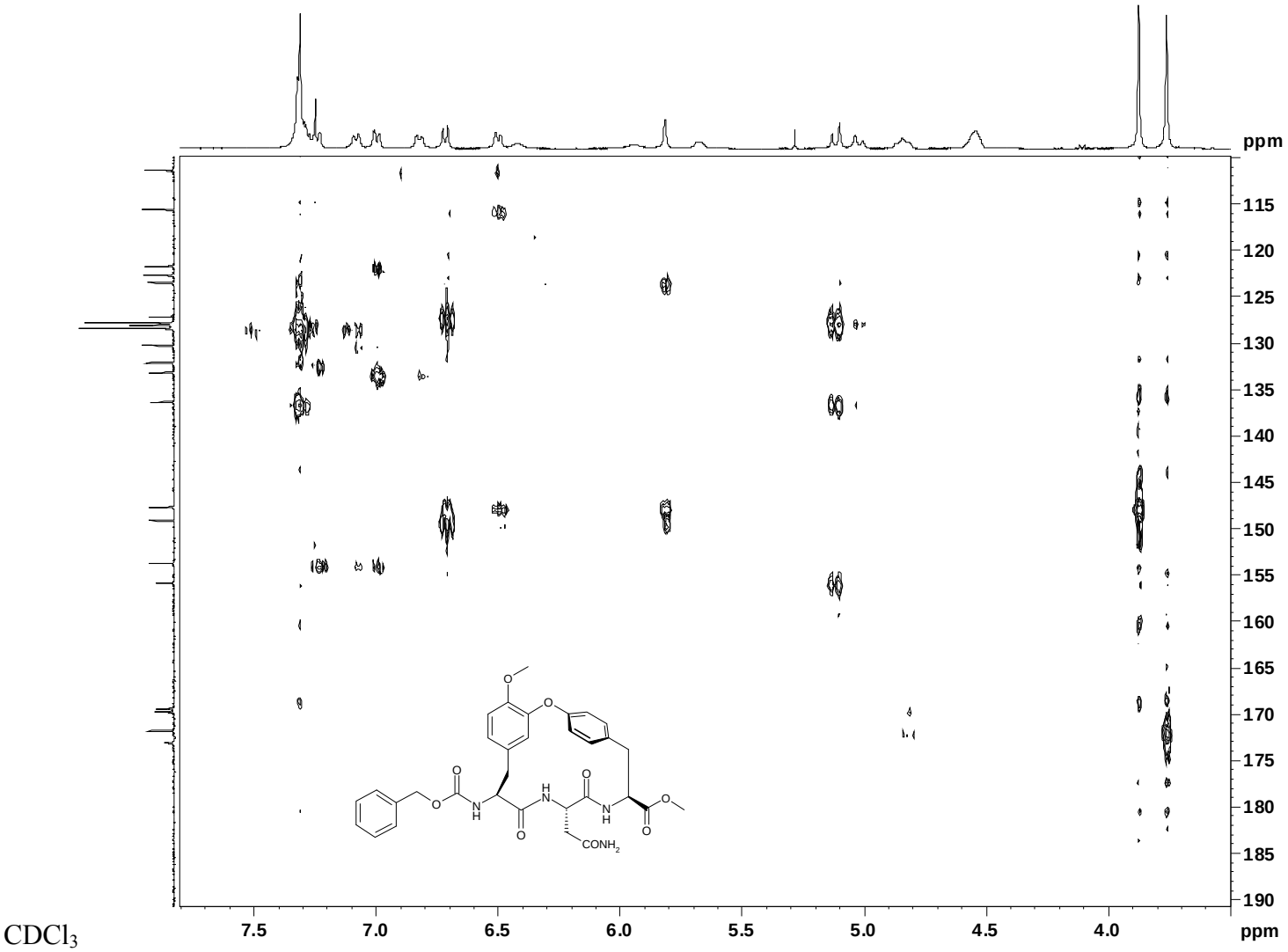
Spectrum 1, **3**, Pendant, 100 MHz, CD_3OD



Spectrum 2, **3**, COSY, 400 MHz, $CDCl_3$

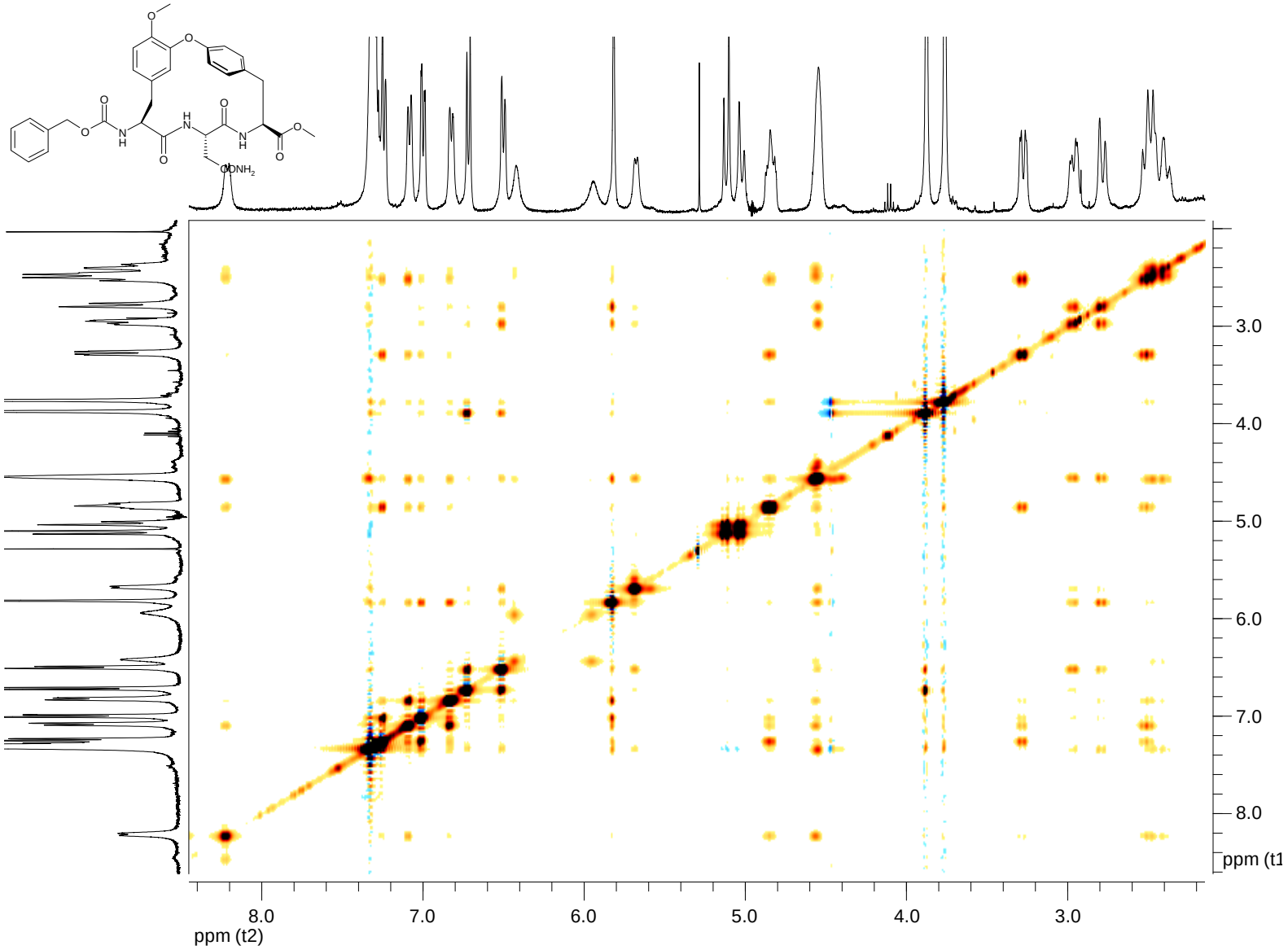


Spectrum 3, **3**, HMQC, $CDCl_3$

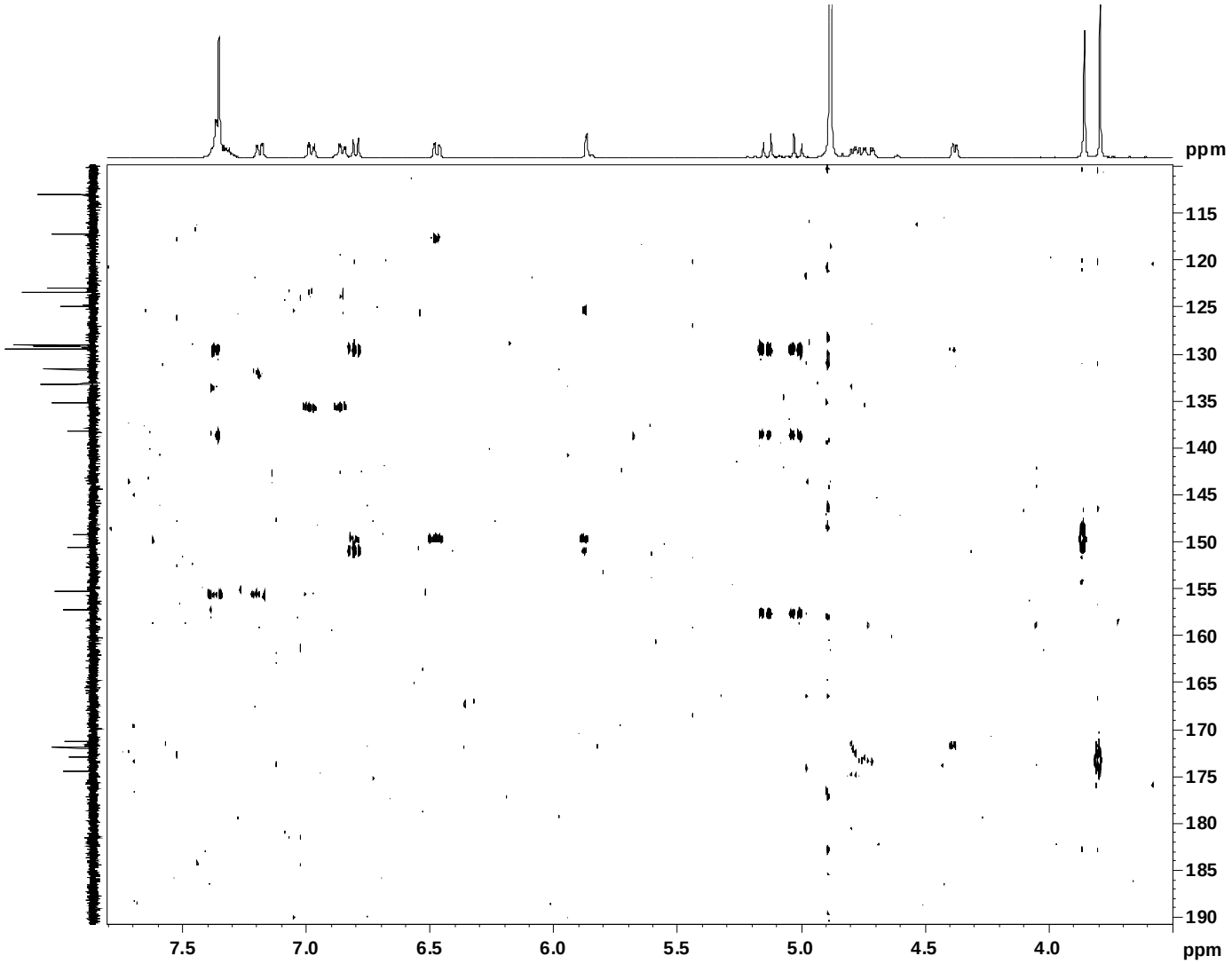


$CDCl_3$

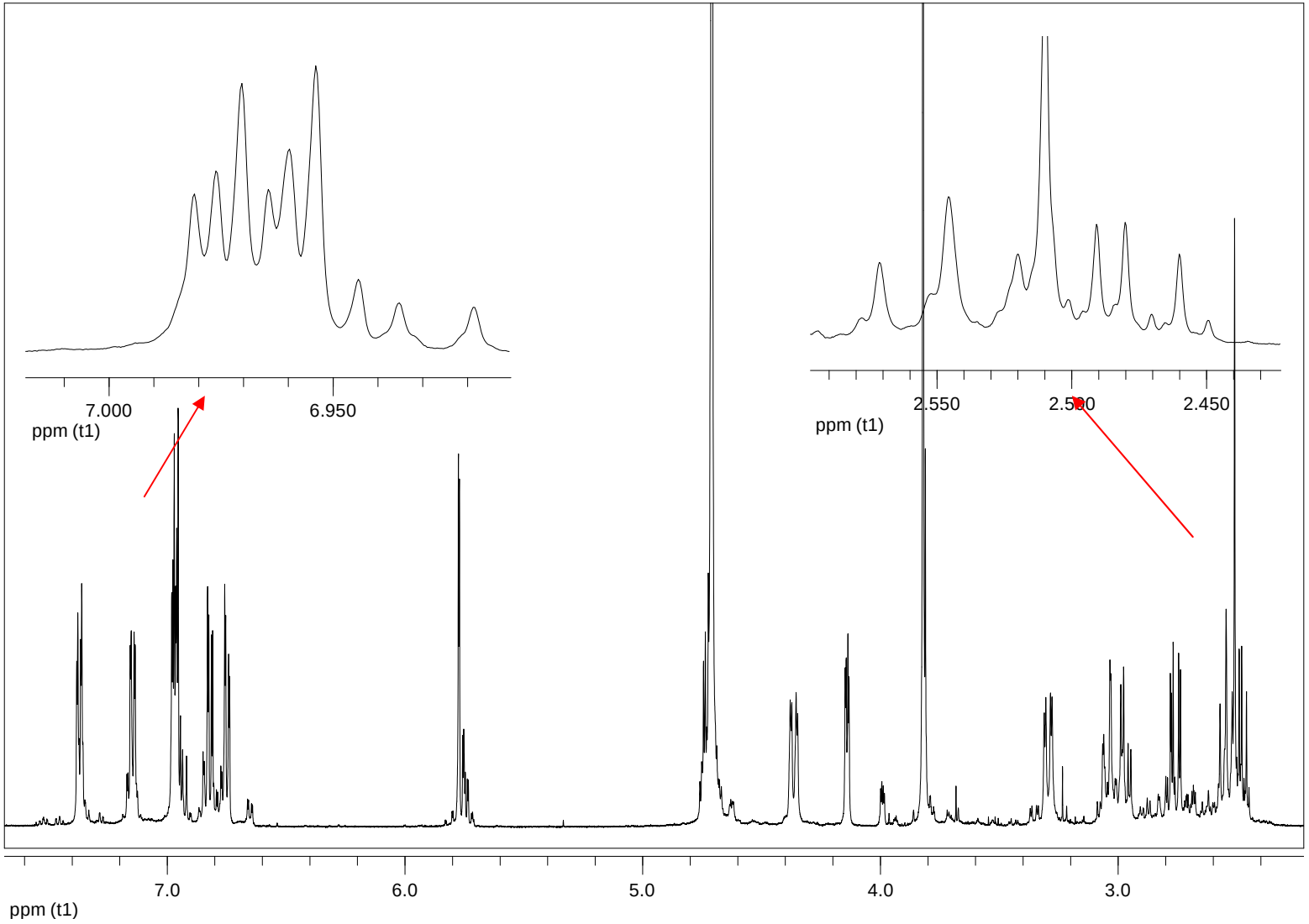
Spectrum 4, **3**, HMBC, $CDCl_3$



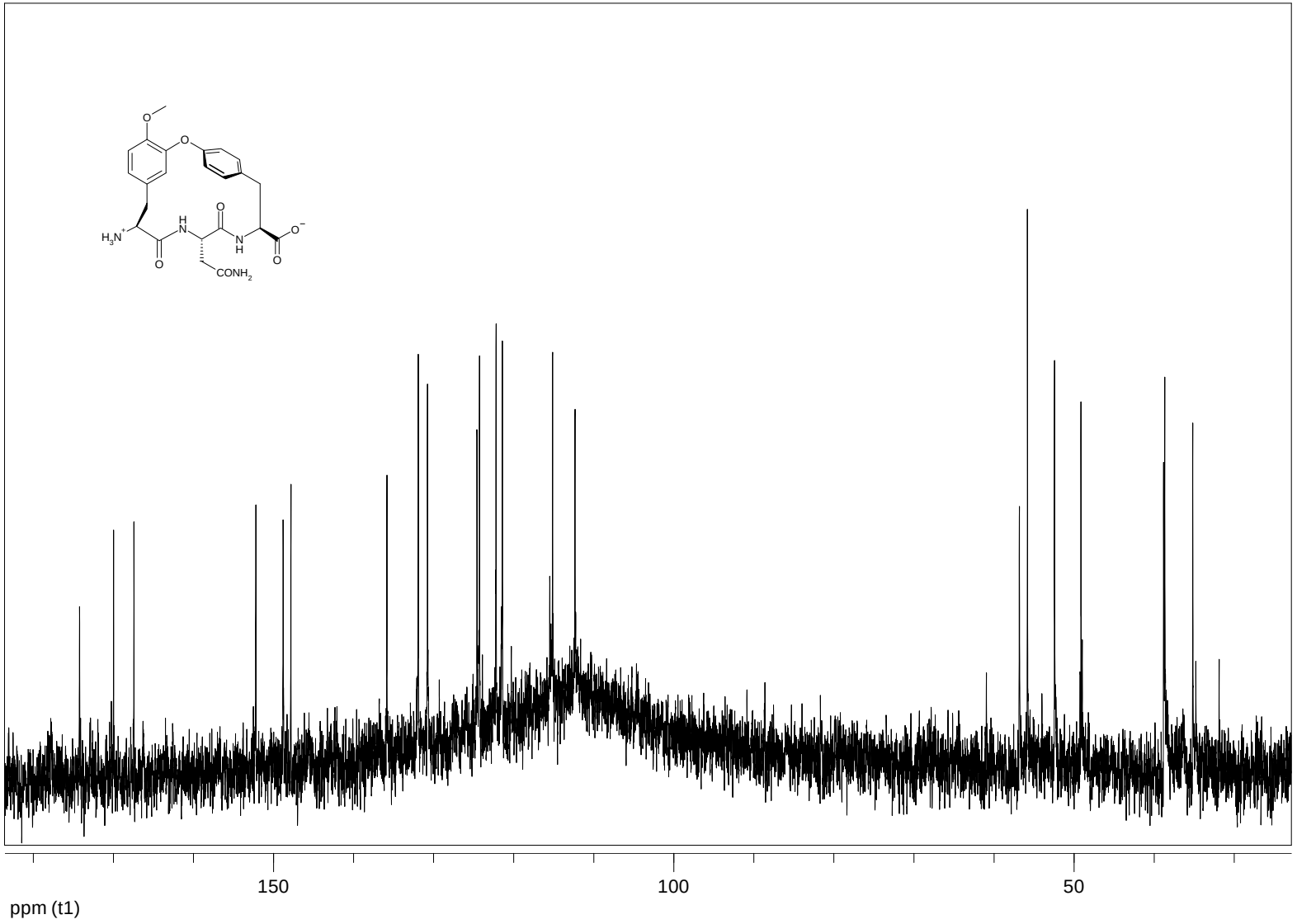
Spectrum 5, **3**, NOESY, 400 MHz, $CDCl_3$



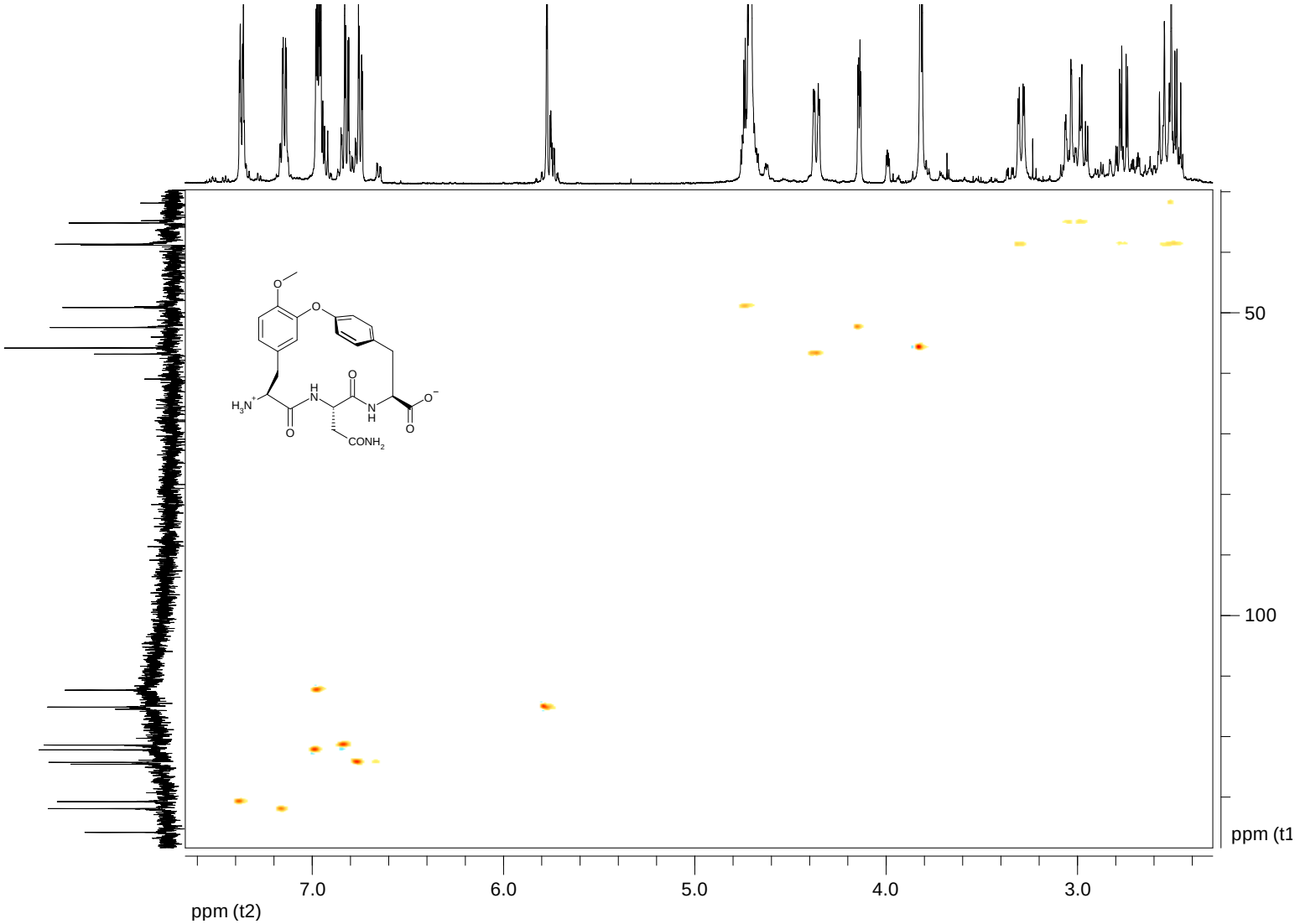
Spectrum 6, **3**, HMBC, CD_3OD



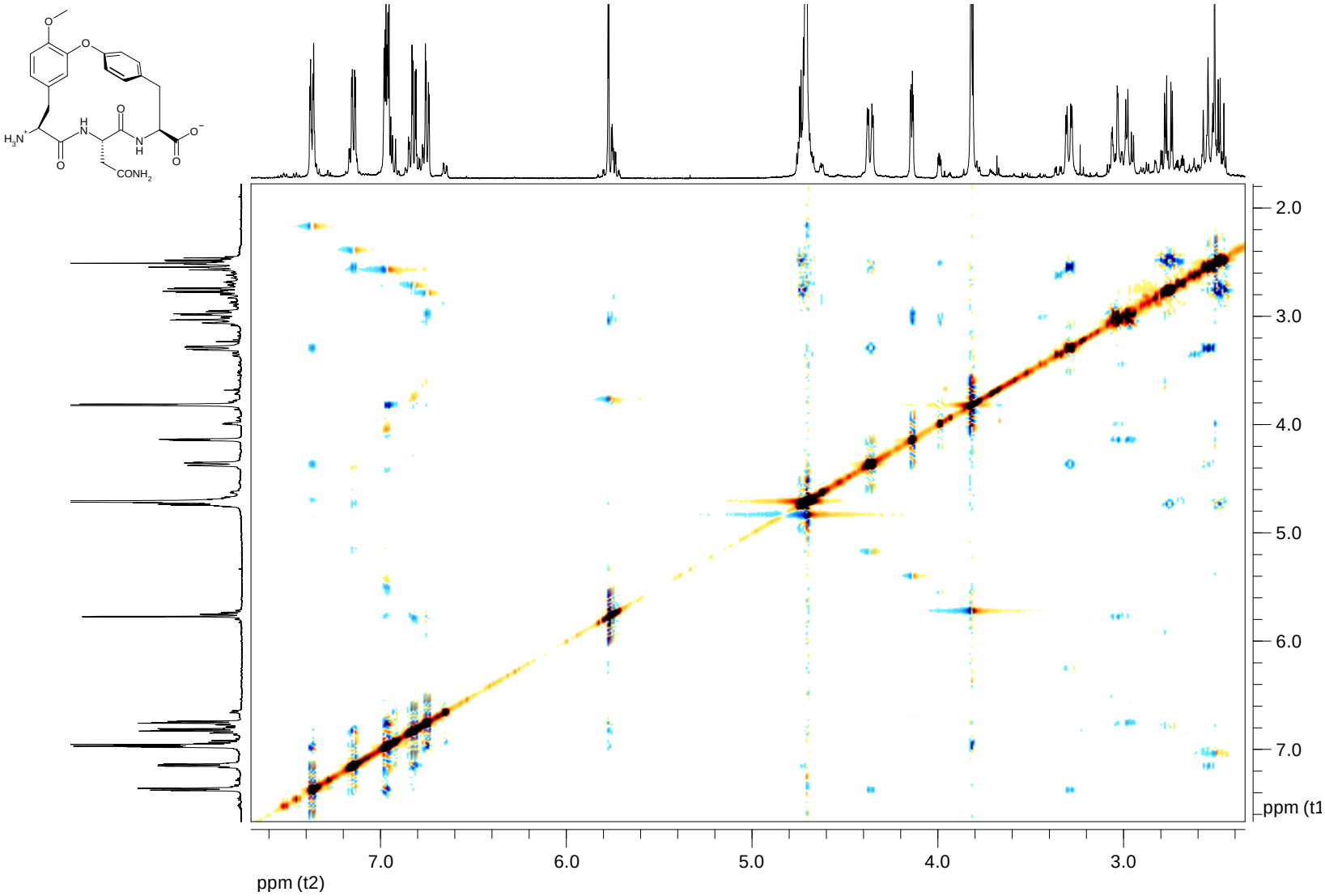
Spectrum 7, OF4949-III **1**, ^{1}H, 500 MHz, D_2O



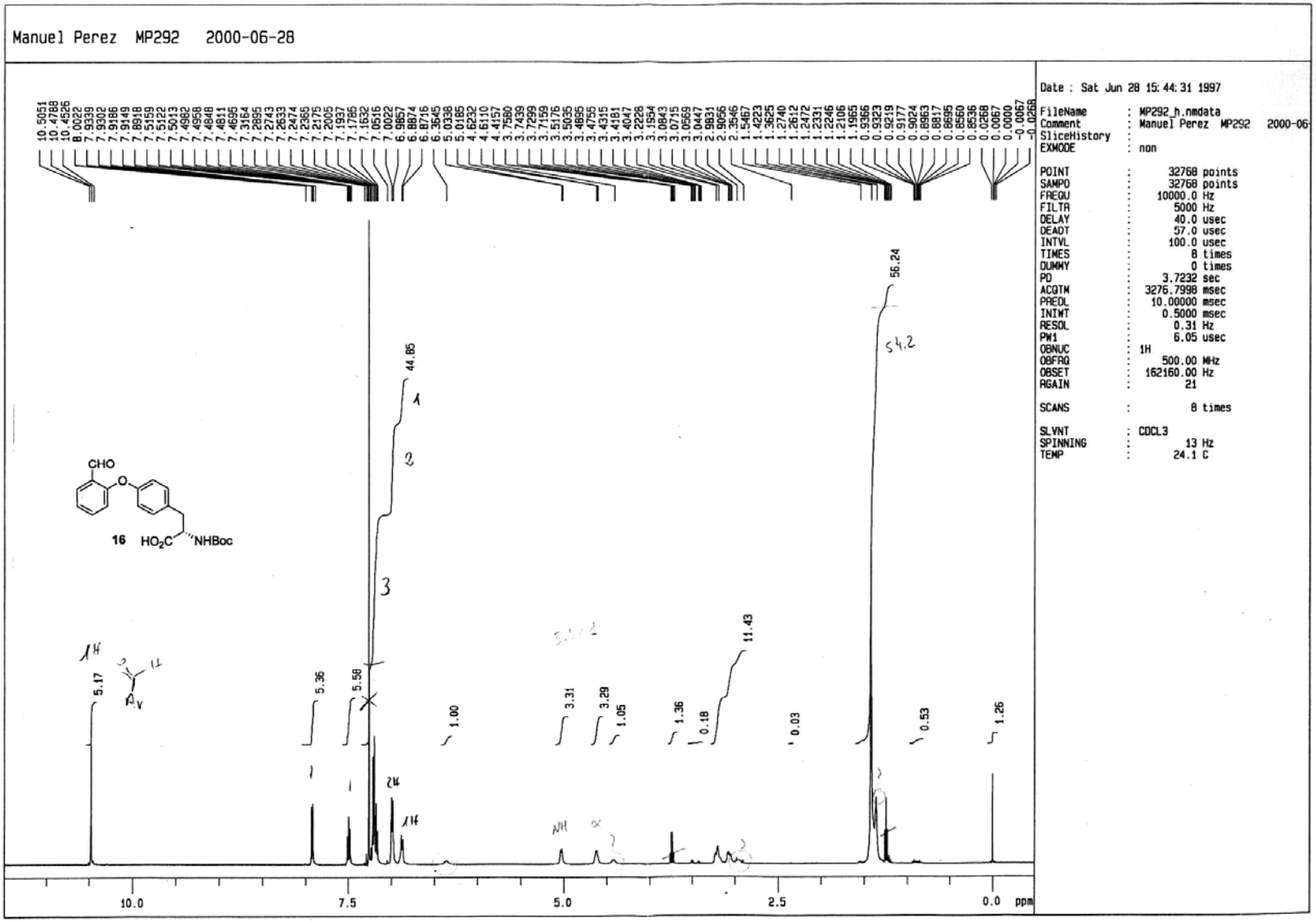
Spectrum 8, OF4949-III **1**, ^{13}C, 125 MHz, D_2O



Spectrum 9, OF4949-III **1**, HMQC, D_2O



Spectrum 10, OF4949-III **1**, NOESY, 500 MHz, D_2O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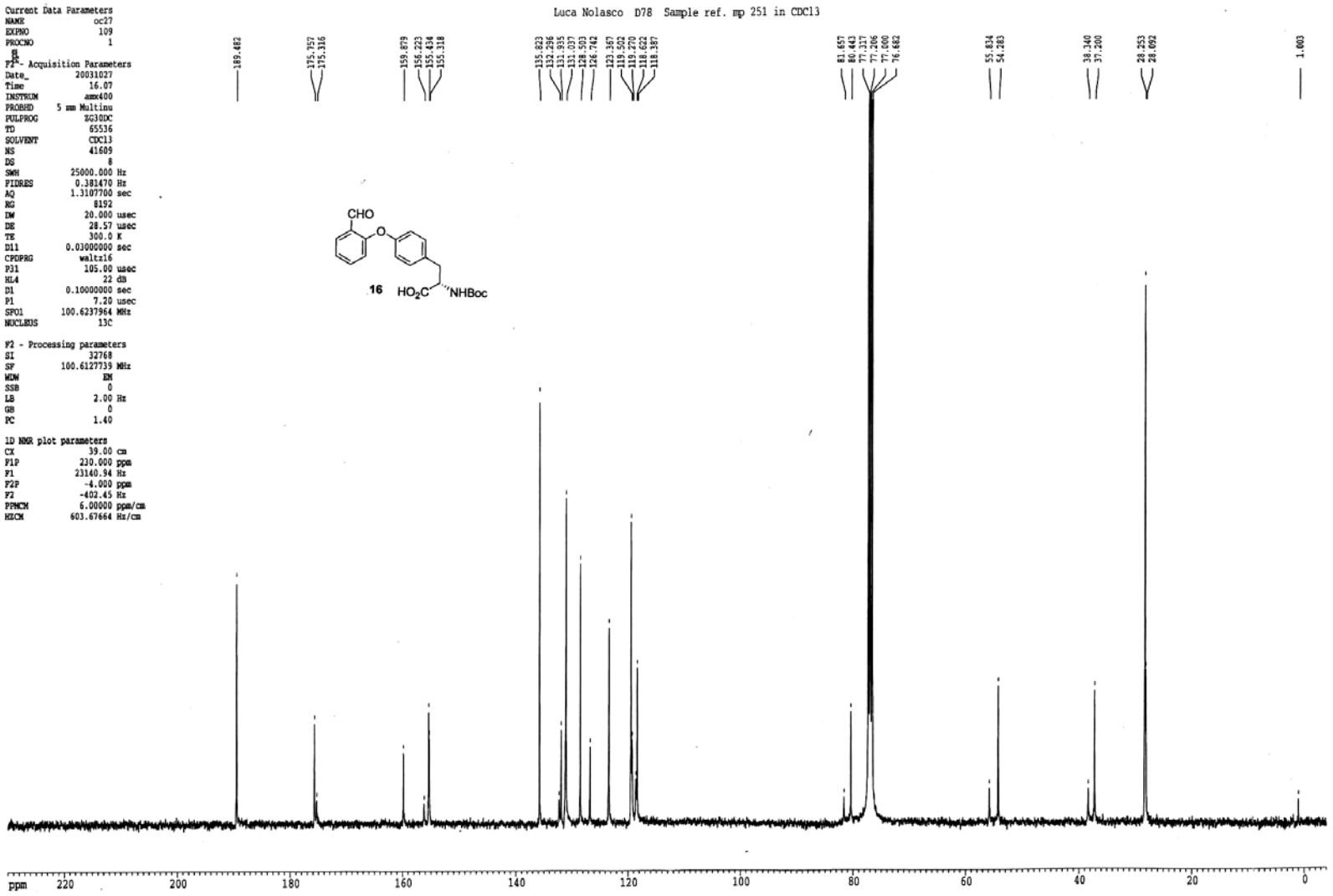
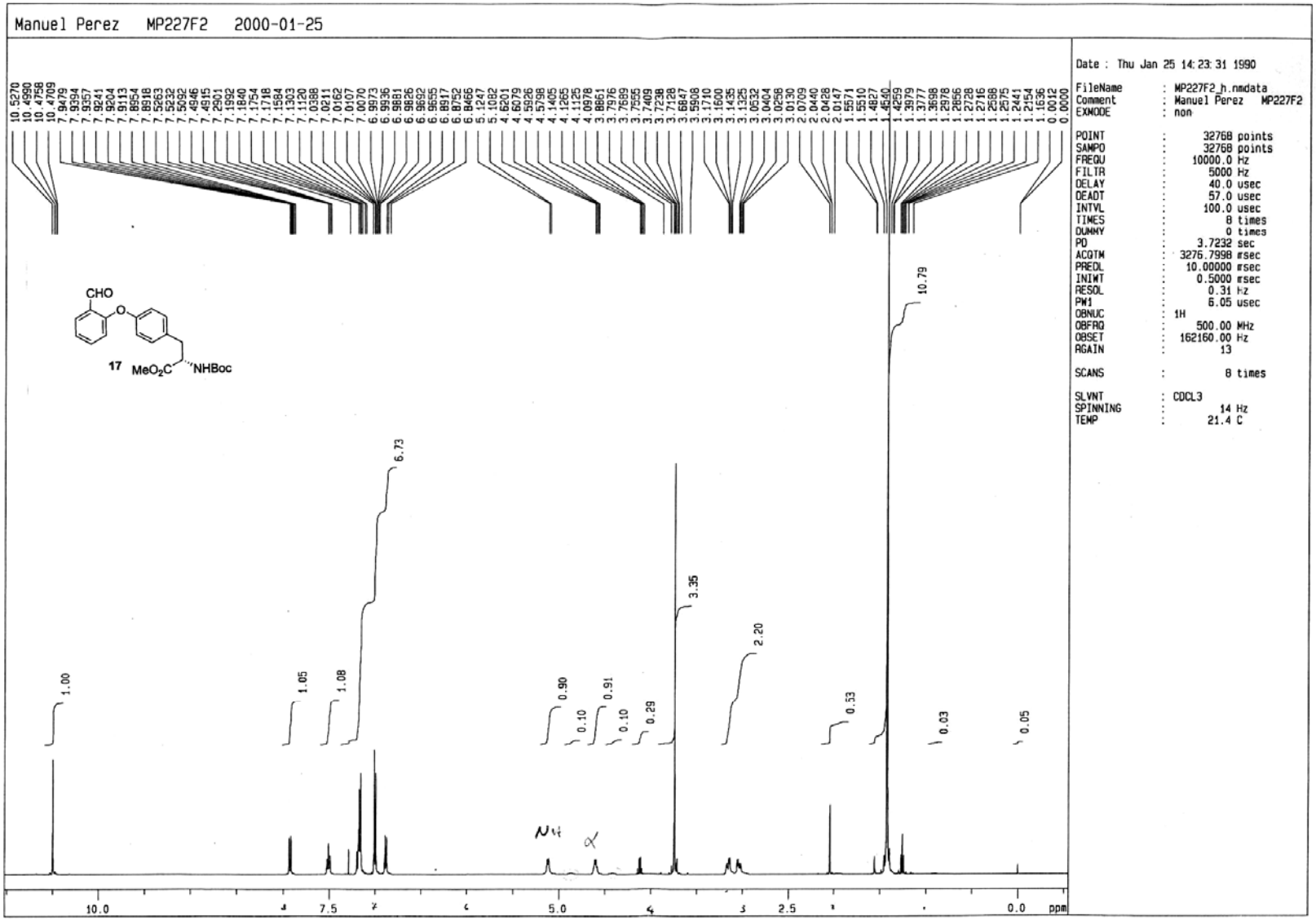
SAMPO : 32768 points
FREQU : 10000.0 Hz
FILTR : 5000 Hz
DELAY : 40.0 usec
DEADT : 57.0 usec
INTVL : 100.0 usec
TIMES : 8 times
DUMMY : 0 times
PD : 3.7232 sec
ACQTM : 3276.7998 msec
PREDL : 10.00000 msec
INIWT : 0.5000 msec
RESOL : 0.31 Hz
PW1 : 6.05 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162160.00 Hz
RGAIN : 21
SCANS : 8 times
SLVNT : CDCL3
SPINNING : 13 Hz
TEMP : 24.1 C
CHO
16 HO2C NHBoc
10.0
7.5
5.0
2.5
0.0 ppm


Luca Nolasco D78 Sample ref. mp 251 in CDCl3
Current Data Parameters
NAME oc27
EXPNO 109
PROCNO 1
F2 - Acquisition Parameters
Date_ 20031027
Time 16.07
INSTRUM amx400
PROBHD 5 mm Multinu
PULPROG zg30dc
TD 65536
SOLVENT CDCl3
NS 41609
DS 8
SWH 25000.000 Hz
FIDRES 0.381470 Hz
AQ 1.3107700 sec
RG 8192
DW 20.000 usec
DE 28.57 usec
TE 300.0 K
D11 0.03000000 sec
CPDPRG waltz16
P31 105.00 usec
HL4 22 dB
D1 0.10000000 sec
P1 7.20 usec
SFO1 100.6237964 MHz
NUCLEUS 13C
F2 - Processing parameters
SI 32768
SF 100.6127739 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 39.00 cm
F1P 230.000 ppm
F1 23140.94 Hz
F2P -4.000 ppm
F2 -402.45 Hz
PPMCM 6.00000 ppm/cm
HZCM 603.67664 Hz/cm
189.482
175.757
175.316
159.879
156.223
155.434
155.318
135.823
132.296
131.935
131.037
128.503
126.742
123.367
119.502
119.270
118.622
118.387
81.657
80.443
77.317
77.206
77.000
76.682
55.834
54.283
38.340
37.200
28.253
28.092
1.003
CHO
O
16 HO2C NHBoc
ppm
220
200
180
160
140
120
100
80
60
40
20
0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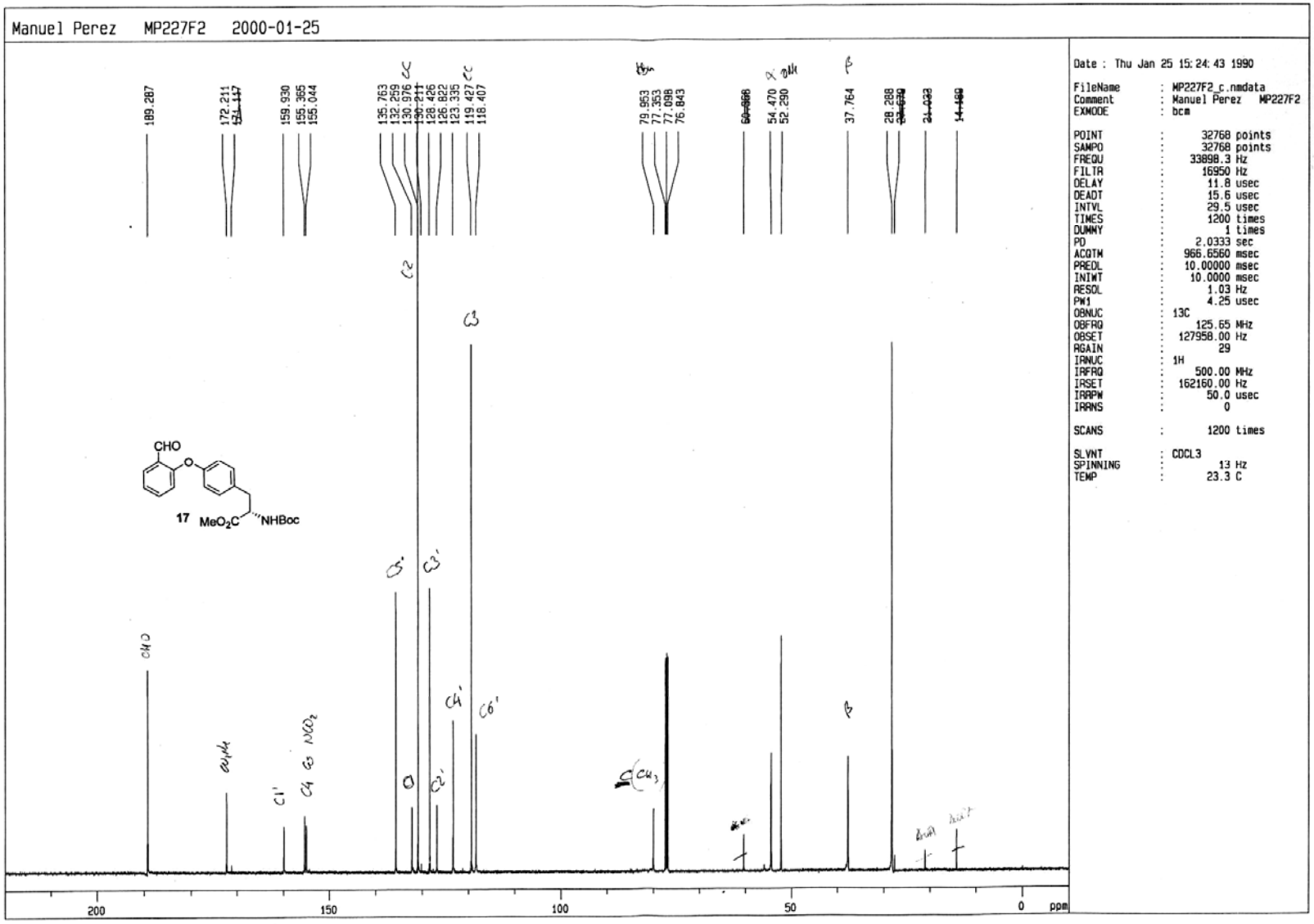
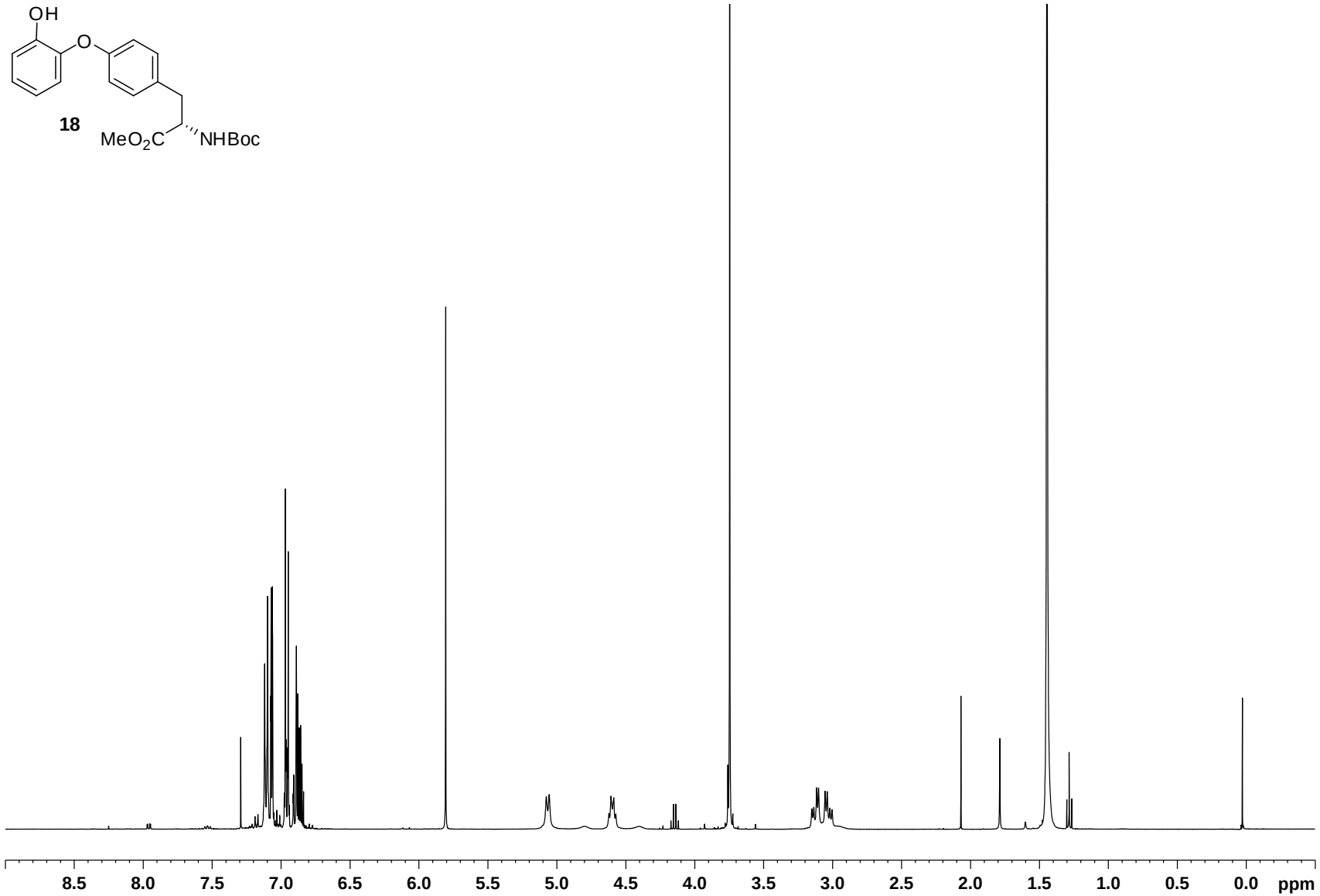
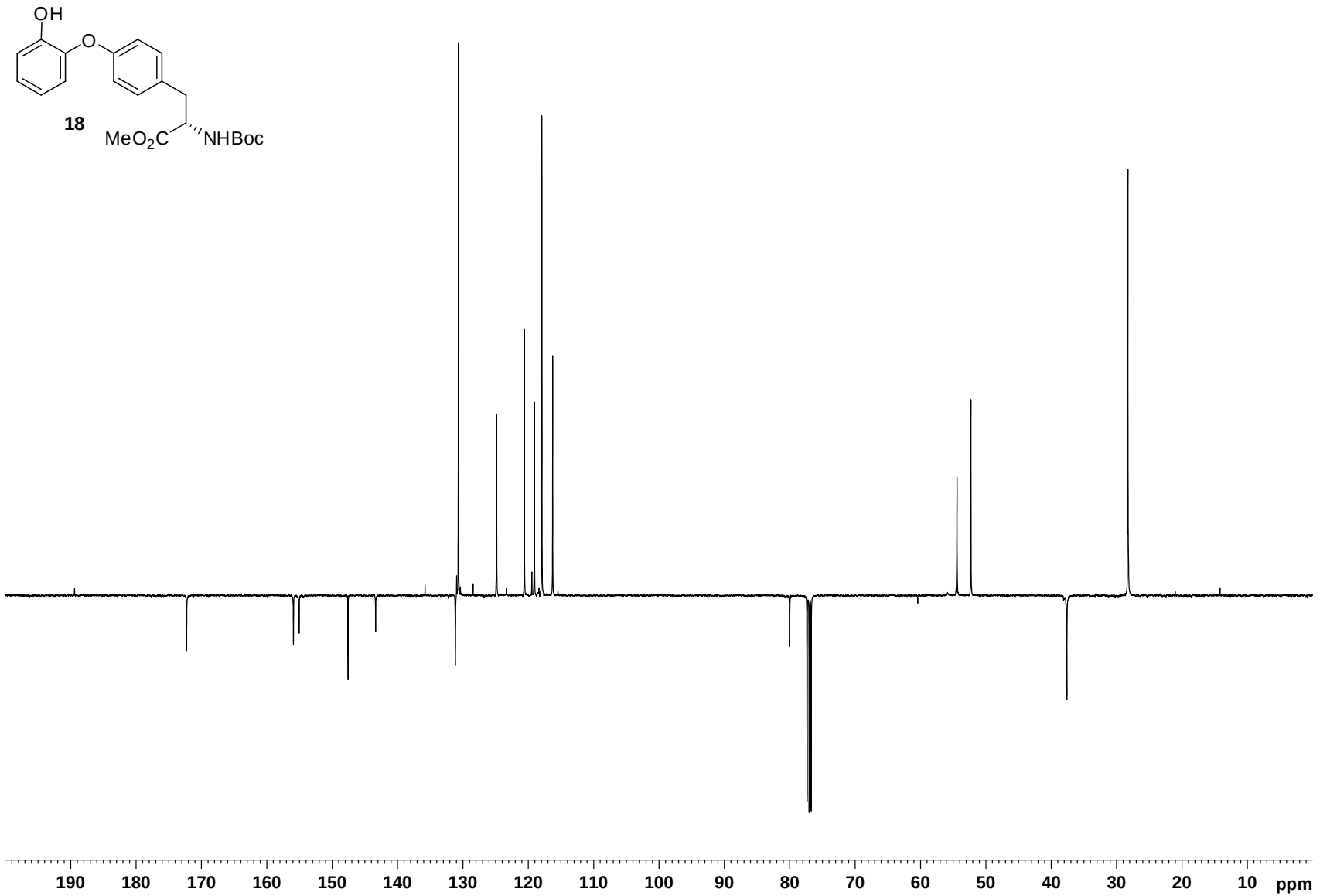
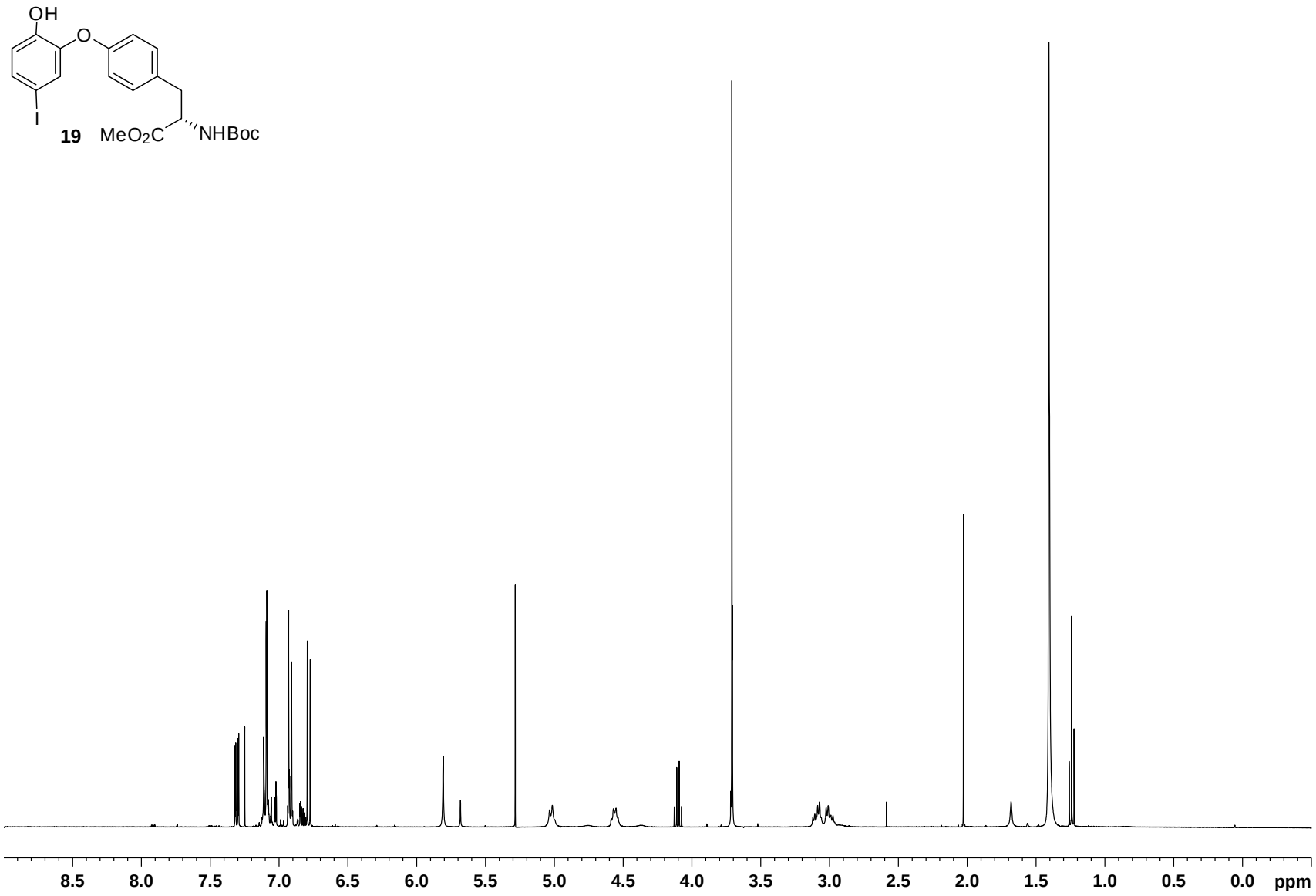
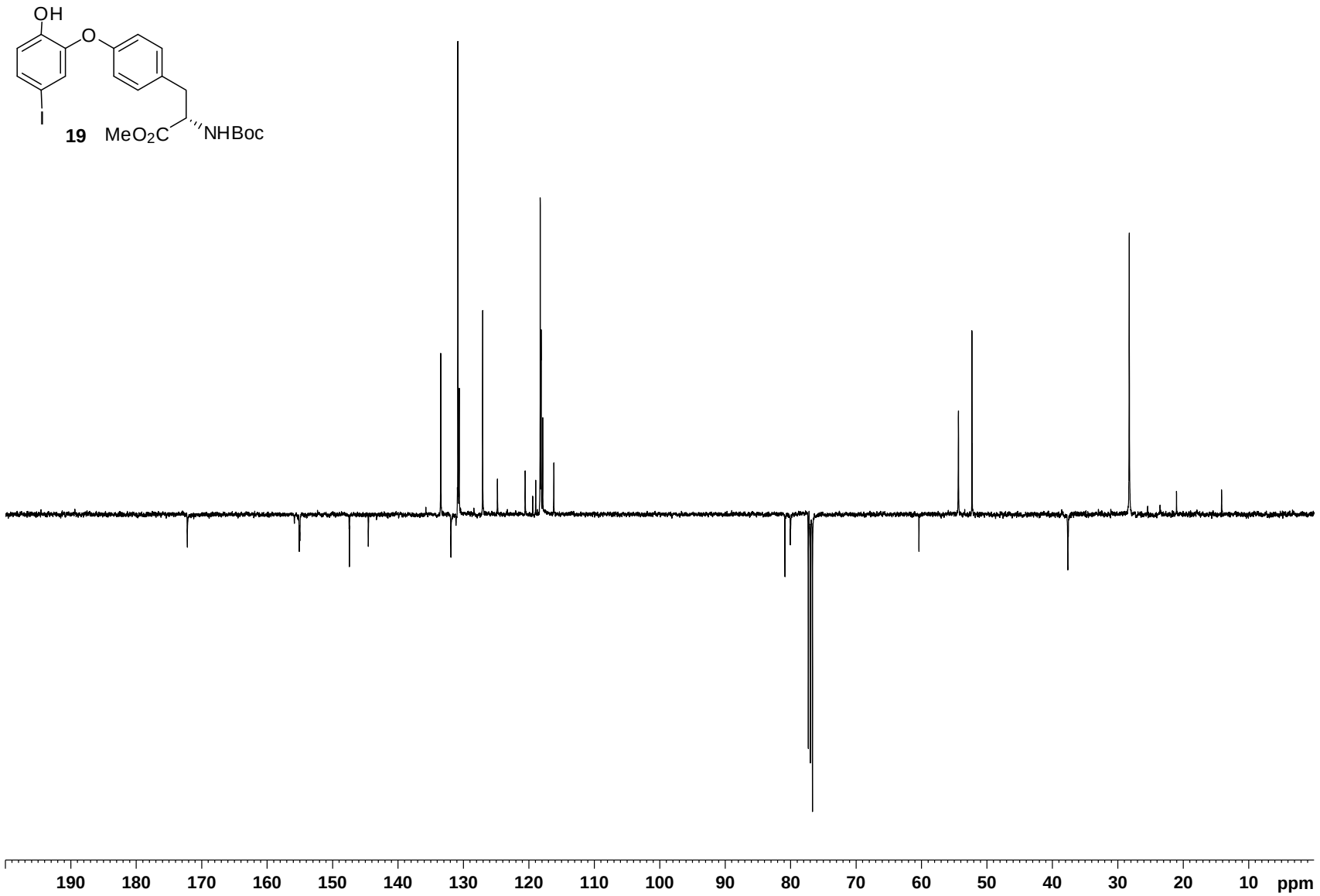
Date : Thu Jan 25 14:23:31 1990
FileName : MP227F2_h.nmdata
Comment : Manuel Perez MP227F2
EXMODE : non
POINT : 32768 points
SAMPO : 32768 points
FREQU : 10000.0 Hz
FILTR : 5000 Hz
DELAY : 40.0 usec
DEADT : 57.0 usec
INTVL : 100.0 usec
TIMES : 8 times
DUMMY : 0 times
PD : 3.7232 sec
ACQTM : 3276.7998 msec
PREDL : 10.00000 msec
INIWT : 0.5000 msec
RESOL : 0.31 Hz
PW1 : 6.05 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162160.00 Hz
AGAIN : 13
SCANS : 8 times
SLVNT : CDCL3
SPINNING : 14 Hz
TEMP : 21.4 C
CHO
17 MeO2C NHBoc
1.00
1.05
1.08
6.73
0.90
0.10
0.91
0.10
0.29
3.35
2.20
0.53
10.79
0.03
0.05
NH
α
10.0
7.5
5.0
2.5
0.0
ppm

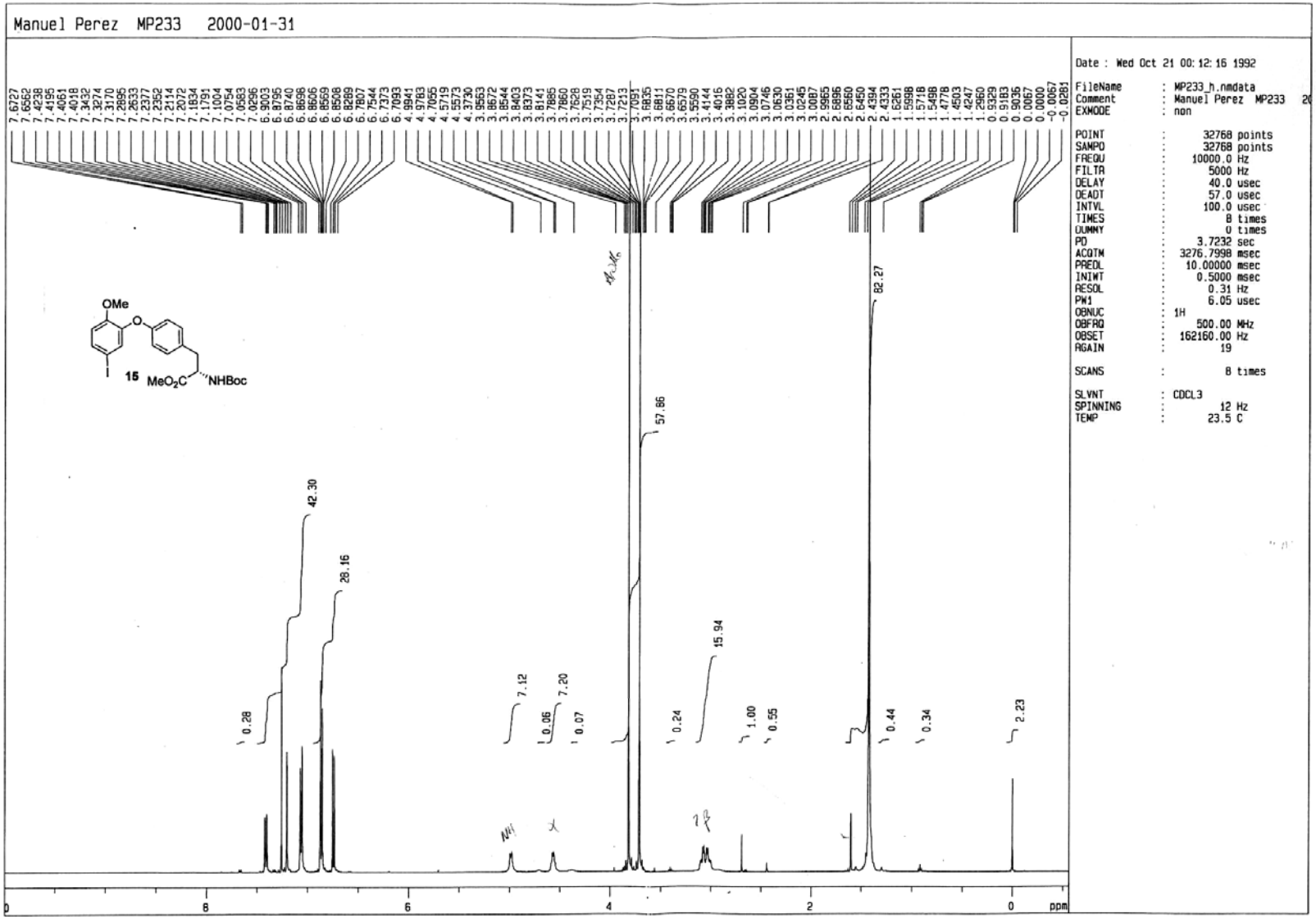

Manuel Perez MP227F2 2000-01-25
189.287
172.211
159.930
155.365
155.044
135.763
132.259
130.976
130.211
128.426
126.822
123.335
119.427
118.407
79.953
77.353
77.098
76.843
54.470
52.290
37.764
28.288
CHO
17 MeO2C NHBoc
C2
C3
C1'
C3'
C4'
C6'
C2'
C4 es NO2
Date : Thu Jan 25 15:24:43 1990
FileName : MP227F2_c.nmdata
Comment : Manuel Perez MP227F2
EXMODE : bcm
POINT : 32768 points
SAMPO : 32768 points
FREQU : 33898.3 Hz
FILTR : 16950 Hz
DELAY : 11.8 usec
DEADT : 15.6 usec
INTVL : 29.5 usec
TIMES : 1200 times
DUMMY : 1 times
PD : 2.0333 sec
ACQTM : 966.6560 msec
PREDL : 10.00000 msec
INIWT : 10.0000 msec
RESOL : 1.03 Hz
PW1 : 4.25 usec
OBNUC : 13C
OBFRQ : 125.65 MHz
OBSET : 127958.00 Hz
RGAIN : 29
IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162160.00 Hz
IRAPW : 50.0 usec
IRANS : 0
SCANS : 1200 times
SLVNT : CDCL3
SPINNING : 13 Hz
TEMP : 23.3 C
200
150
100
50
0
ppm

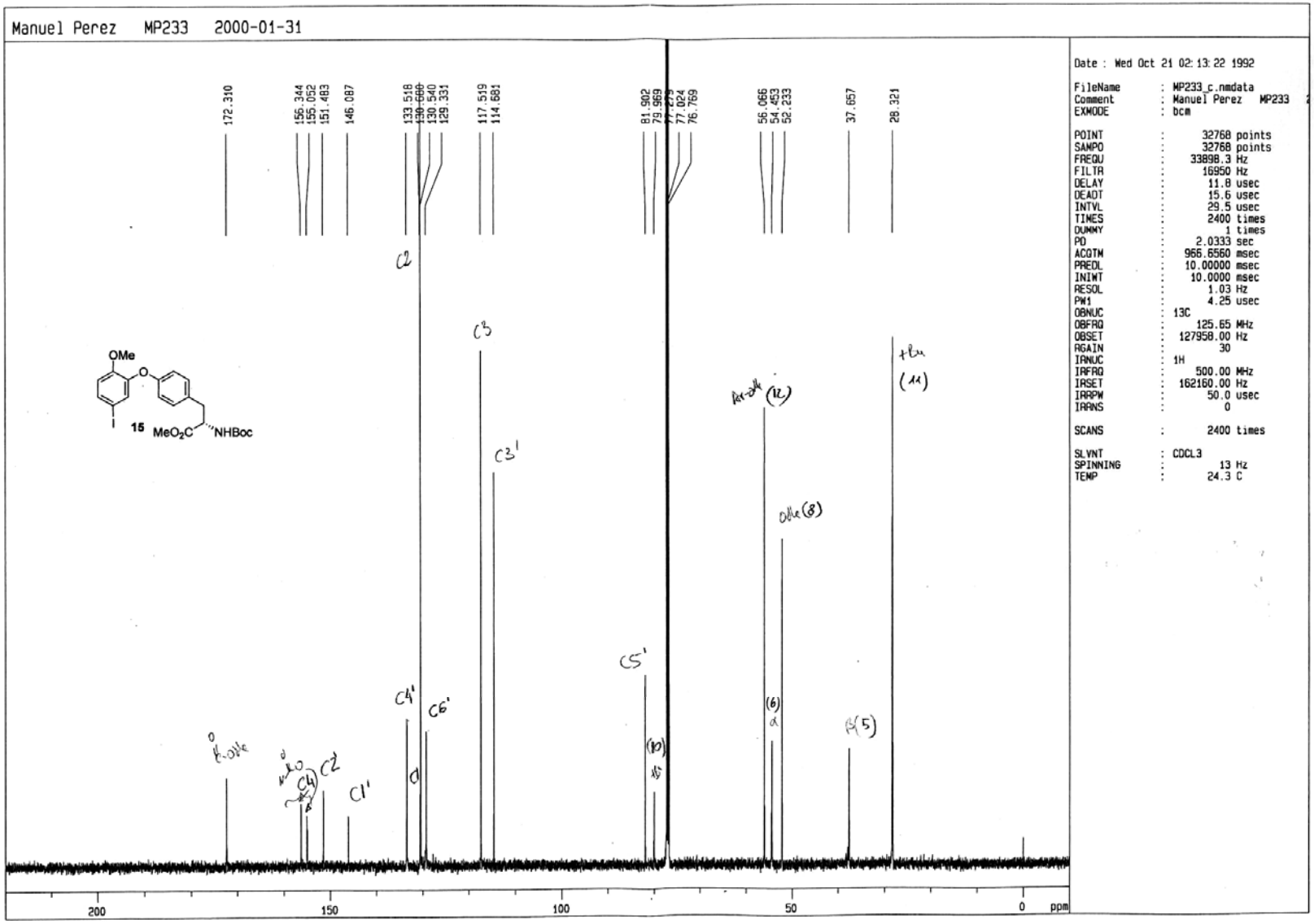

OH
O
18
MeO2C
NHBoc
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

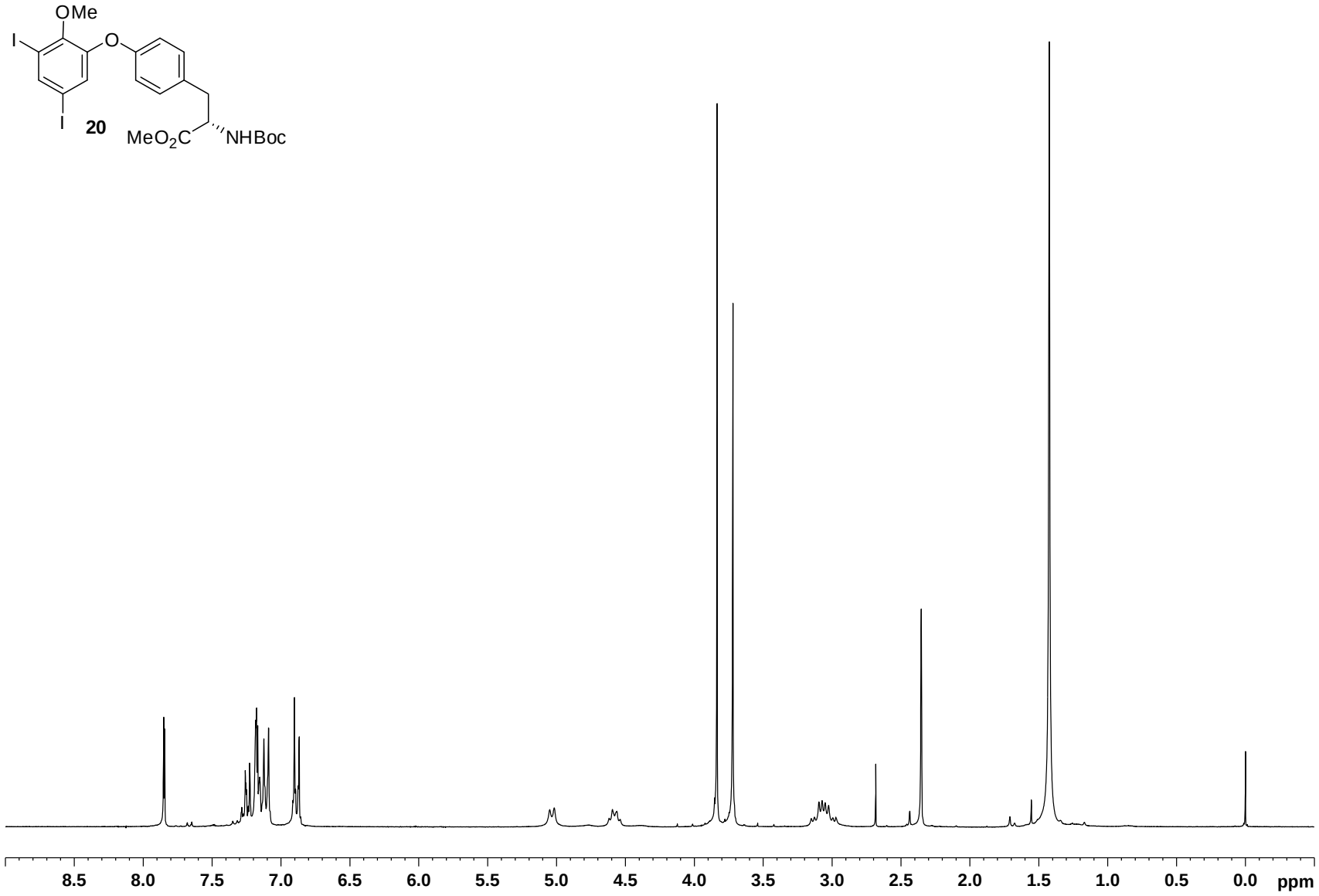

OH
O
18
MeO2C
NHBoc
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

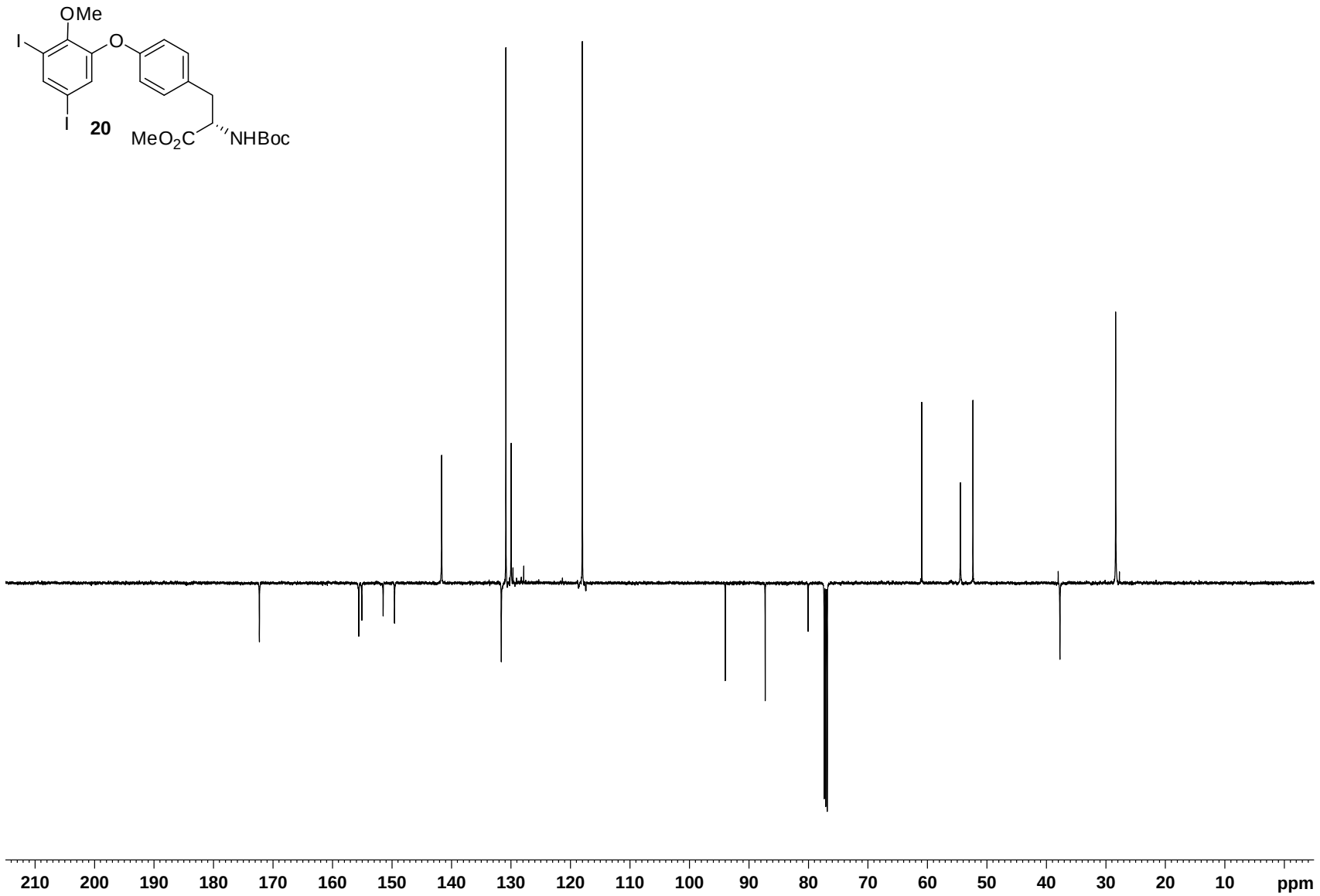

OH
O
I
19
MeO2C
NHBoc
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

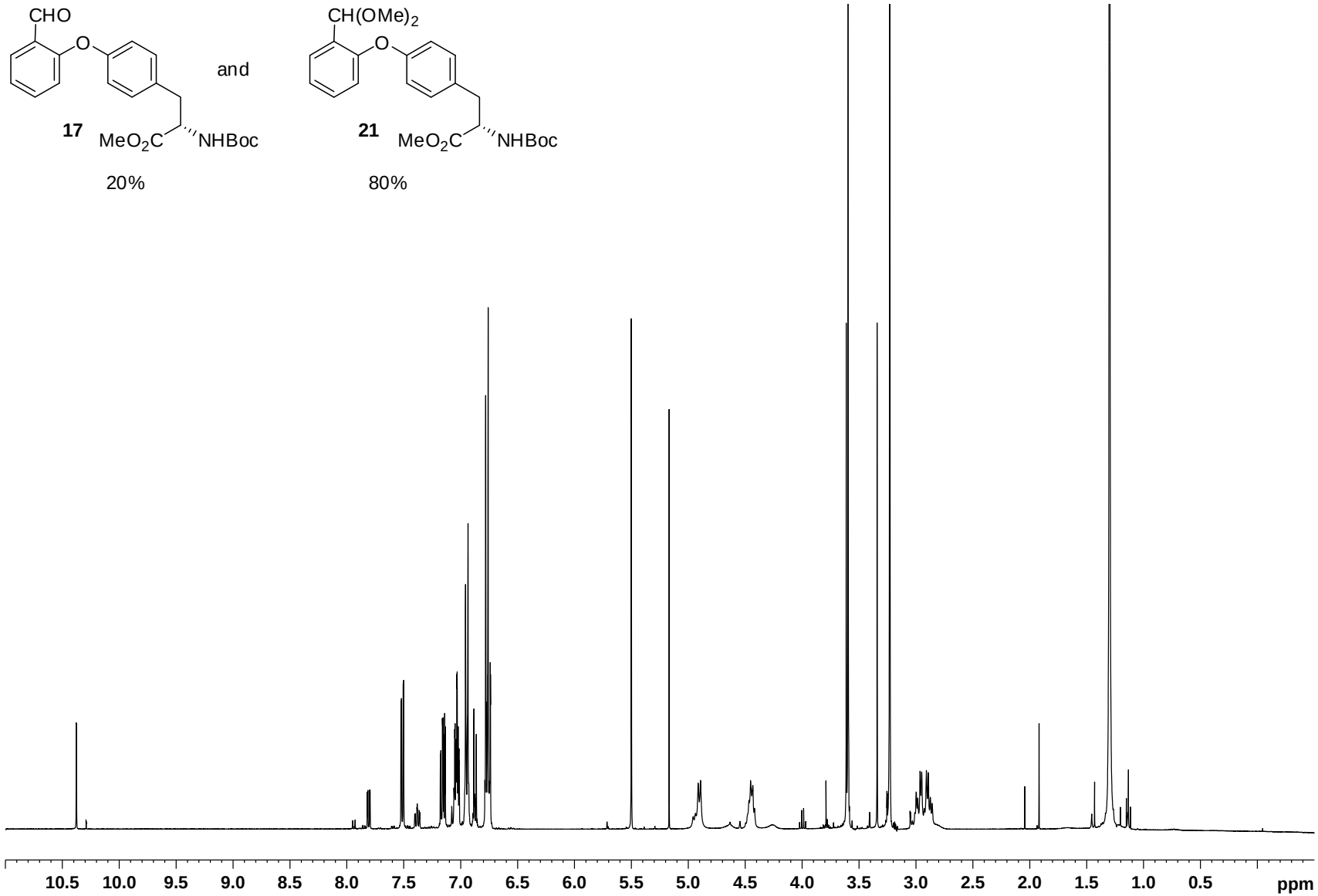

OH
O
I
19 MeO2C
NHBoc
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

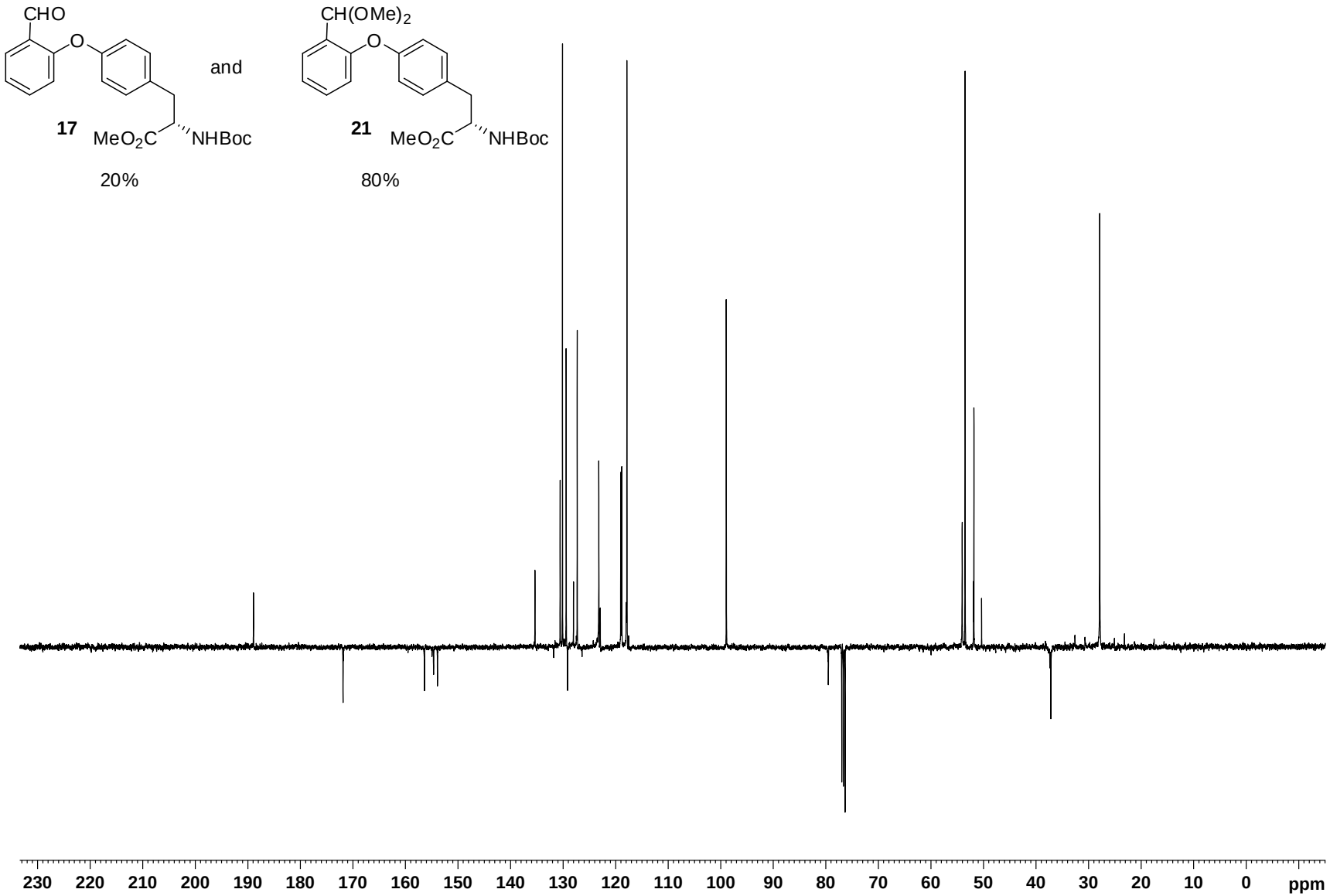

Manuel Perez MP233 2000-01-31
OMe
15 MeO2C NHBoc
Date : Wed Oct 21 00:12:16 1992
FileName : MP233_h.nmdata
Comment : Manuel Perez MP233
EXMODE : non
POINT : 32768 points
SAMPD : 32768 points
FREQU : 10000.0 Hz
FILTR : 5000 Hz
DELAY : 40.0 usec
DEADT : 57.0 usec
INTVL : 100.0 usec
TIMES : 8 times
DUMMY : 0 times
PD : 3.7232 sec
ACQTM : 3276.7998 msec
PREDL : 10.00000 msec
INIWT : 0.5000 msec
RESOL : 0.31 Hz
PW1 : 6.05 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162160.00 Hz
AGAIN : 19
SCANS : 8 times
SLVNT : CDCL3
SPINNING : 12 Hz
TEMP : 23.5 C
42.30
28.16
57.86
82.27
15.94
0.28
7.12
7.20
0.06
0.07
0.24
1.00
0.55
0.44
0.34
2.23
NH
8
6
4
2
0
ppm

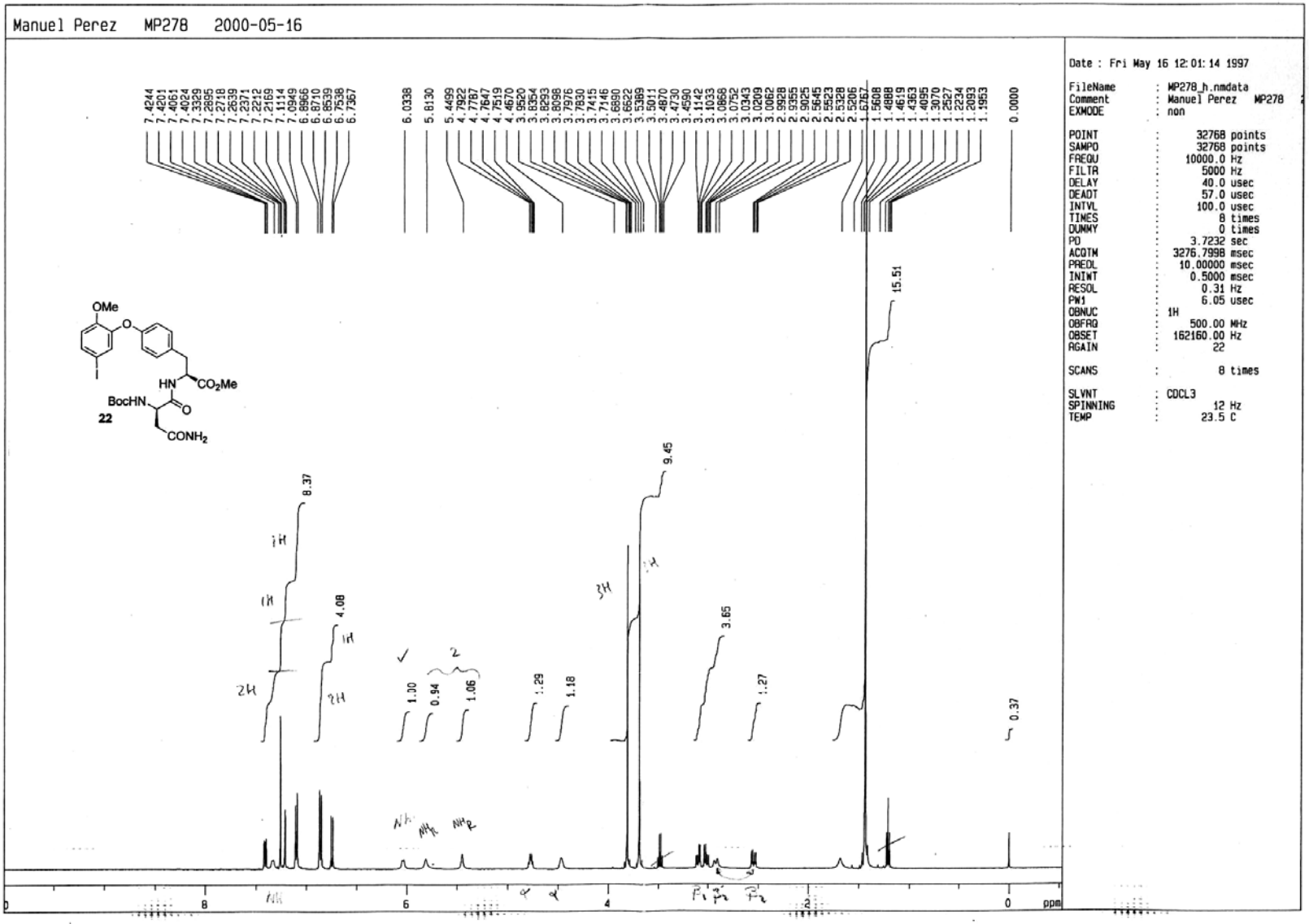

Manuel Perez MP233 2000-01-31
172.310
156.344
155.052
151.483
146.087
133.518
130.660
130.340
129.331
117.519
114.681
81.902
79.969
77.624
76.769
56.066
54.453
52.233
37.657
28.321
OMe
I
15
MeO2C
NHBoc
C2
C3
C3'
C5'
C4'
C6'
C1'
C4
C2'
(12)
(11)
(8)
(6)
(5)
(10)
200
150
100
50
0
ppm
Date : Wed Oct 21 02:13:22 1992
FileName : MP233_c.nmdata
Comment : Manuel Perez MP233
EXMODE : bcm
POINT : 32768 points
SAMPO : 32768 points
FREQU : 33898.3 Hz
FILTR : 16950 Hz
DELAY : 11.8 usec
DEADT : 15.6 usec
INTVL : 29.5 usec
TIMES : 2400 times
DUMMY : 1 times
PD : 2.0333 sec
ACQTM : 966.6560 msec
PREDL : 10.00000 msec
INIWT : 10.0000 msec
RESOL : 1.03 Hz
PW1 : 4.25 usec
OBNUC : 13C
OBFRQ : 125.65 MHz
OBSET : 127958.00 Hz
RGAIN : 30
IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162160.00 Hz
IRPPW : 50.0 usec
IRNS : 0
SCANS : 2400 times
SLVNT : CDCL3
SPINNING : 13 Hz
TEMP : 24.3 C


OMe
I
O
I
20
MeO2C
NHBoc
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


OMe
I
O
I
20
MeO2C
NHBoc
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


CHO
O
MeO2C
NHBoc
17
20%
and
CH(OMe)2
O
MeO2C
NHBoc
21
80%
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


CHO
O
and
17
MeO2C
NHBoc
20%
CH(OMe)2
O
21
MeO2C
NHBoc
80%
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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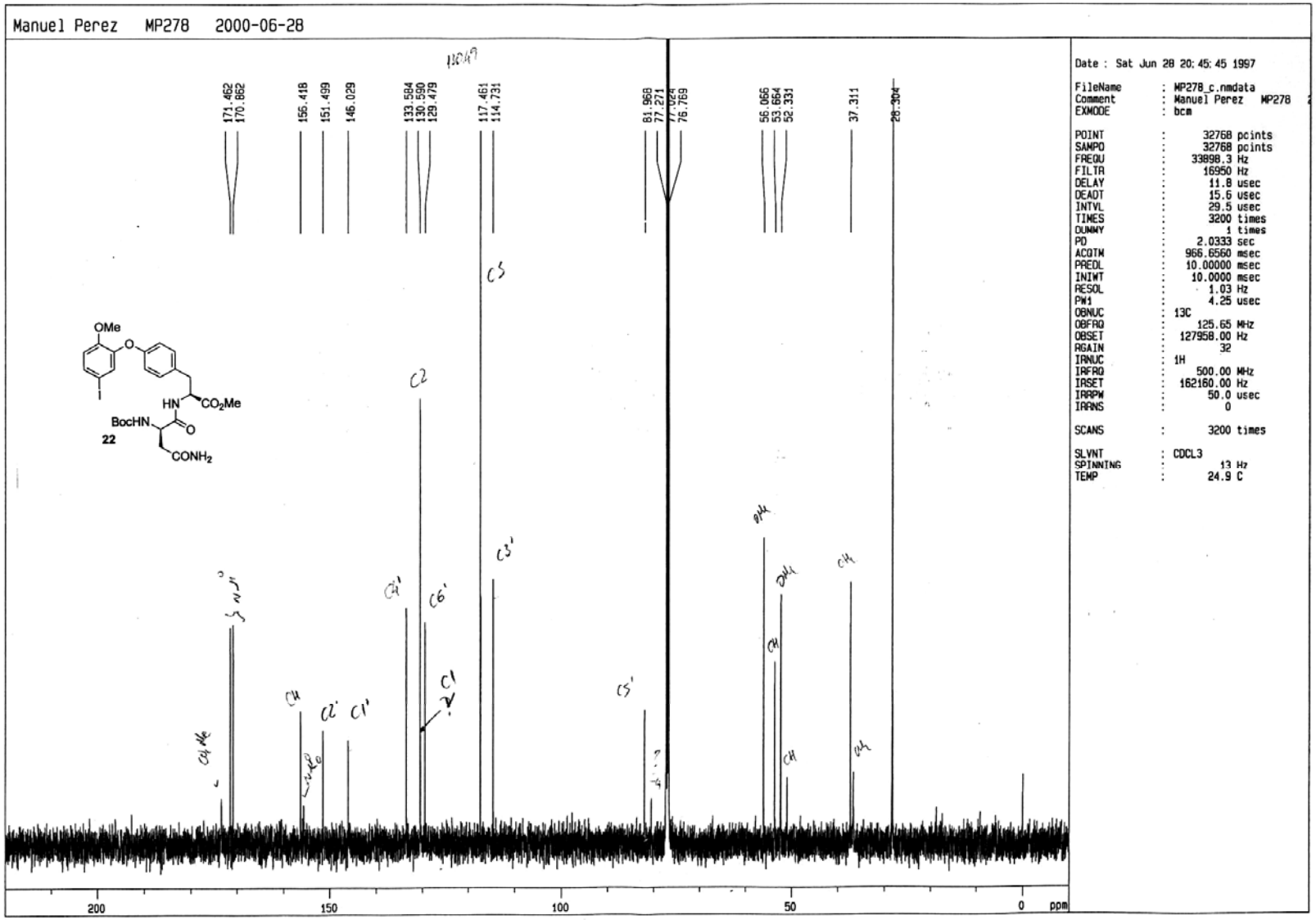
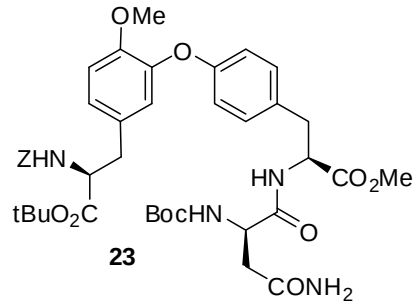
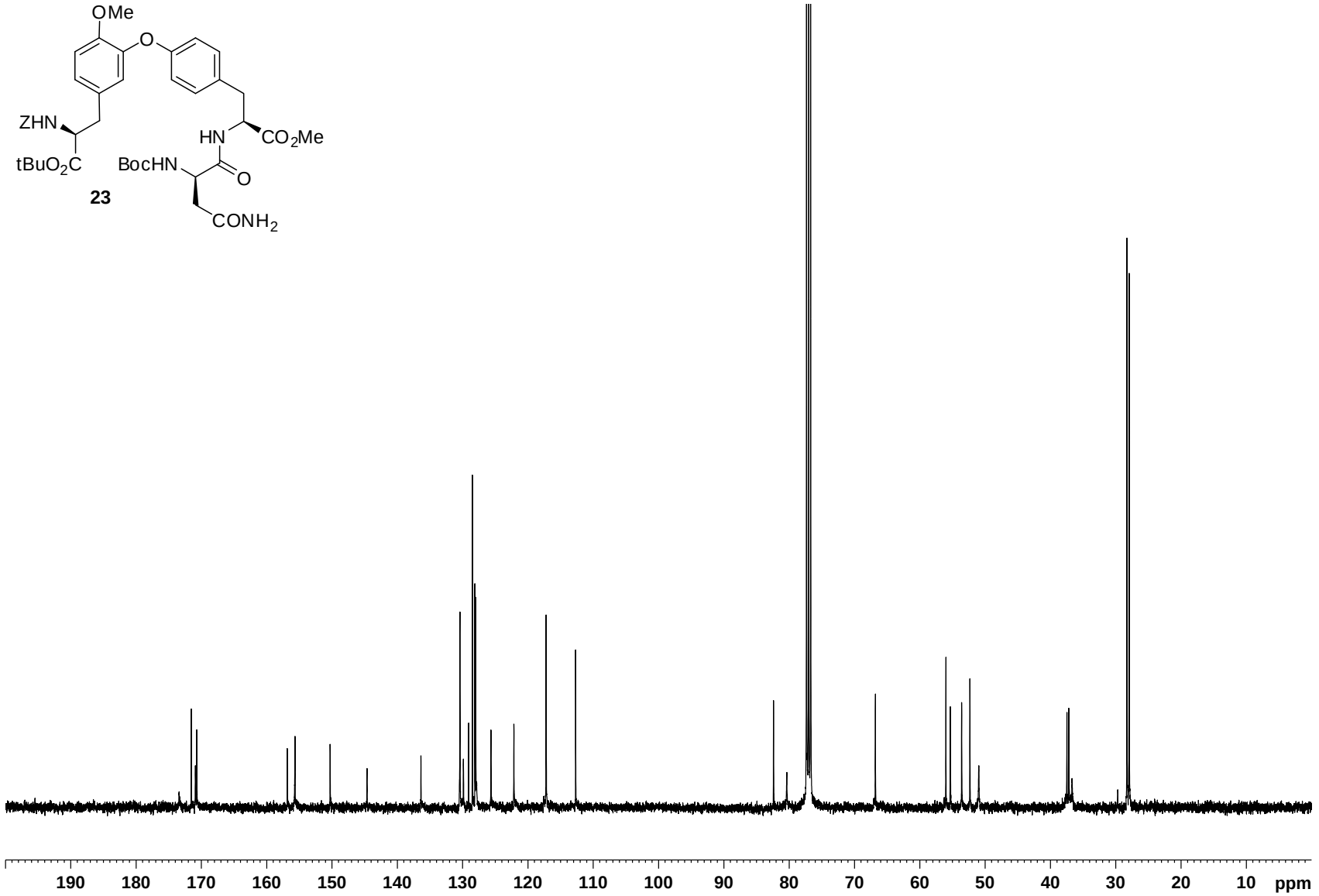
SAMPO : 32768 points
FREQU : 10000.0 Hz
FILTR : 5000 Hz
DELAY : 40.0 usec
DEADT : 57.0 usec
INTVL : 100.0 usec
TIMES : 8 times
DUMMY : 0 times
PD : 3.7232 sec
ACQTM : 3276.7998 msec
PREDL : 10.00000 msec
INIWT : 0.5000 msec
RESOL : 0.31 Hz
PW1 : 6.05 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162160.00 Hz
AGAIN : 22
SCANS : 8 times
SLVNT : CDCL3
SPINNING : 12 Hz
TEMP : 23.5 C
OMe
HN
CO2Me
BocHN
CONH2
22
ppm

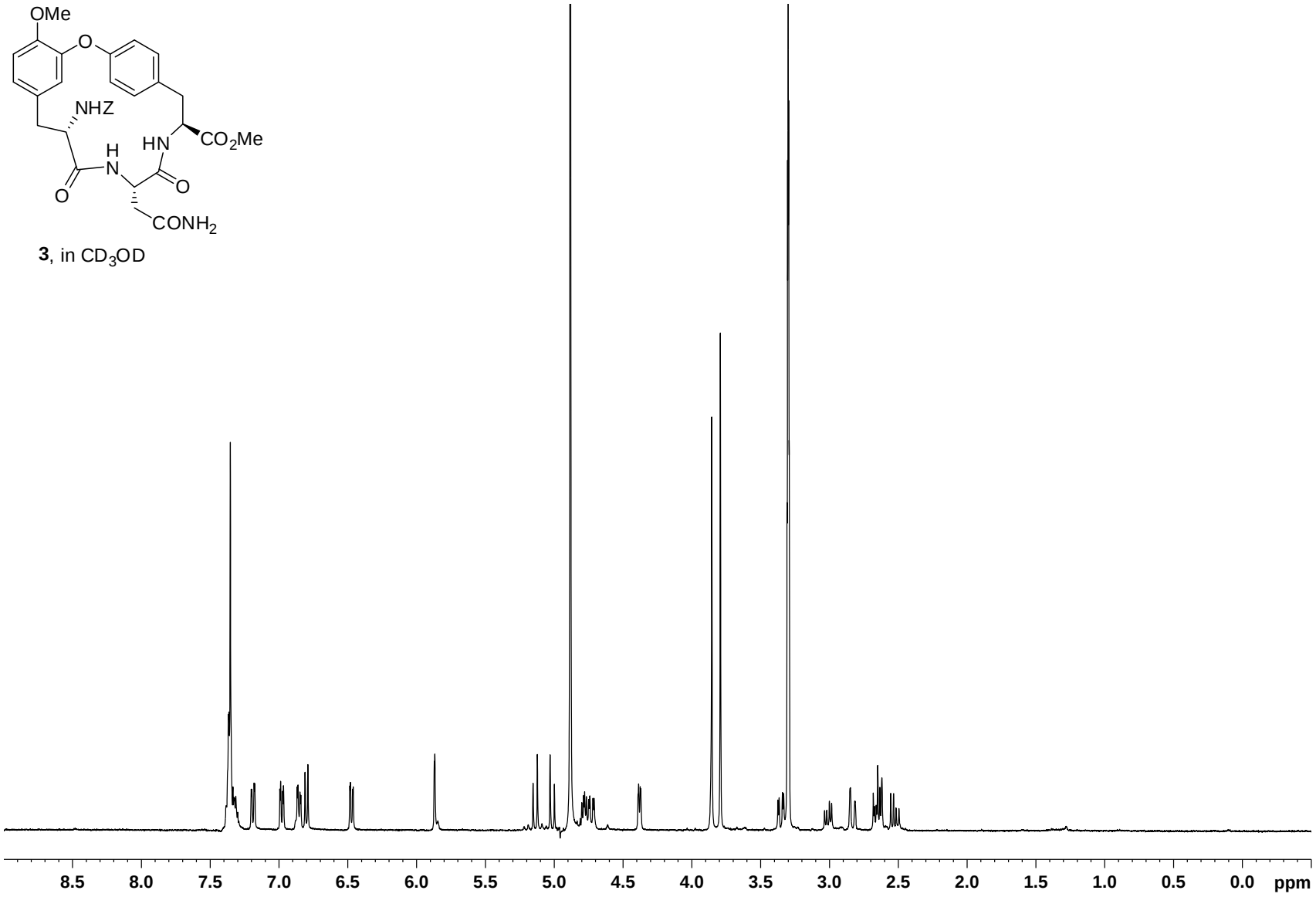

Manuel Perez MP278 2000-06-28
171.462
170.862
156.418
151.499
146.029
133.584
130.590
129.479
117.461
114.731
81.966
77.271
76.769
56.066
53.664
52.331
37.311
28.304
OMe
HN
CO2Me
BocHN
22
CONH2
C3
C2
C3'
C2'
C6'
C1'
C1
C5'
CH
CH2
CH3
200
150
100
50
0
ppm
Date : Sat Jun 28 20:45:45 1997
FileName : MP278_c.nmdata
Comment : Manuel Perez MP278
EXMODE : bcm
POINT : 32768 points
SAMPO : 32768 points
FREQU : 33898.3 Hz
FILTR : 16950 Hz
DELAY : 11.8 usec
DEADT : 15.6 usec
INTVL : 29.5 usec
TIMES : 3200 times
DUMMY : 1 times
PD : 2.0333 sec
ACQTM : 966.6560 msec
PREDL : 10.00000 msec
INIWT : 10.0000 msec
RESOL : 1.03 Hz
PW1 : 4.25 usec
OBNUC : 13C
OBFRQ : 125.65 MHz
OBSET : 127958.00 Hz
RGAIN : 32
IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162160.00 Hz
IRPPM : 50.0 usec
IRNS : 0
SCANS : 3200 times
SLVNT : CDCL3
SPINNING : 13 Hz
TEMP : 24.9 C


OMe
O
ZHN
HN
CO2Me
tBuO2C
BocHN
O
CONH2

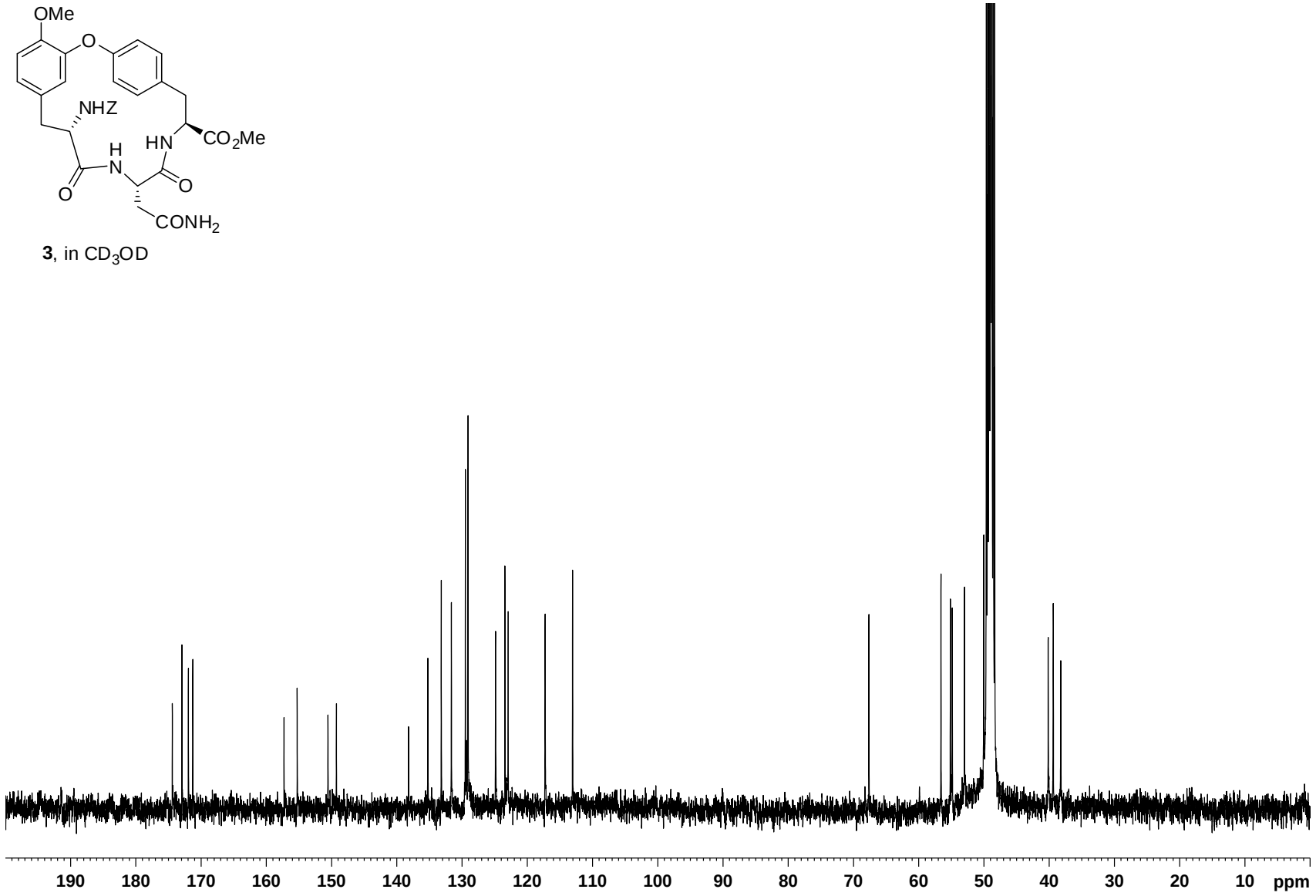
23

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

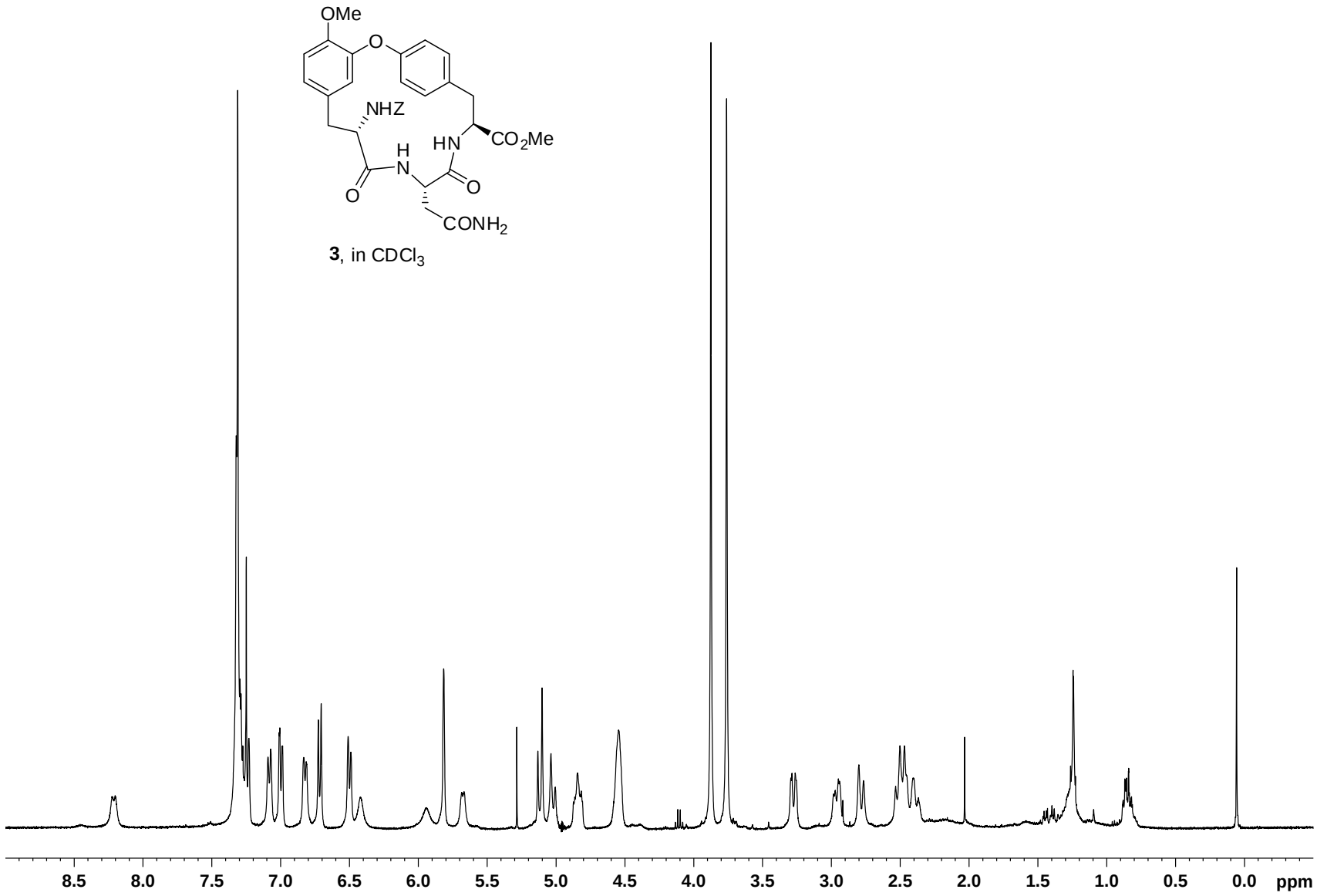

OMe
O
ZHN
tBuO2C
HN
CO2Me
BocHN
O
CONH2
23
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OMe
O
NHZ
HN
CO2Me
H
N
O
O
O
CONH2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

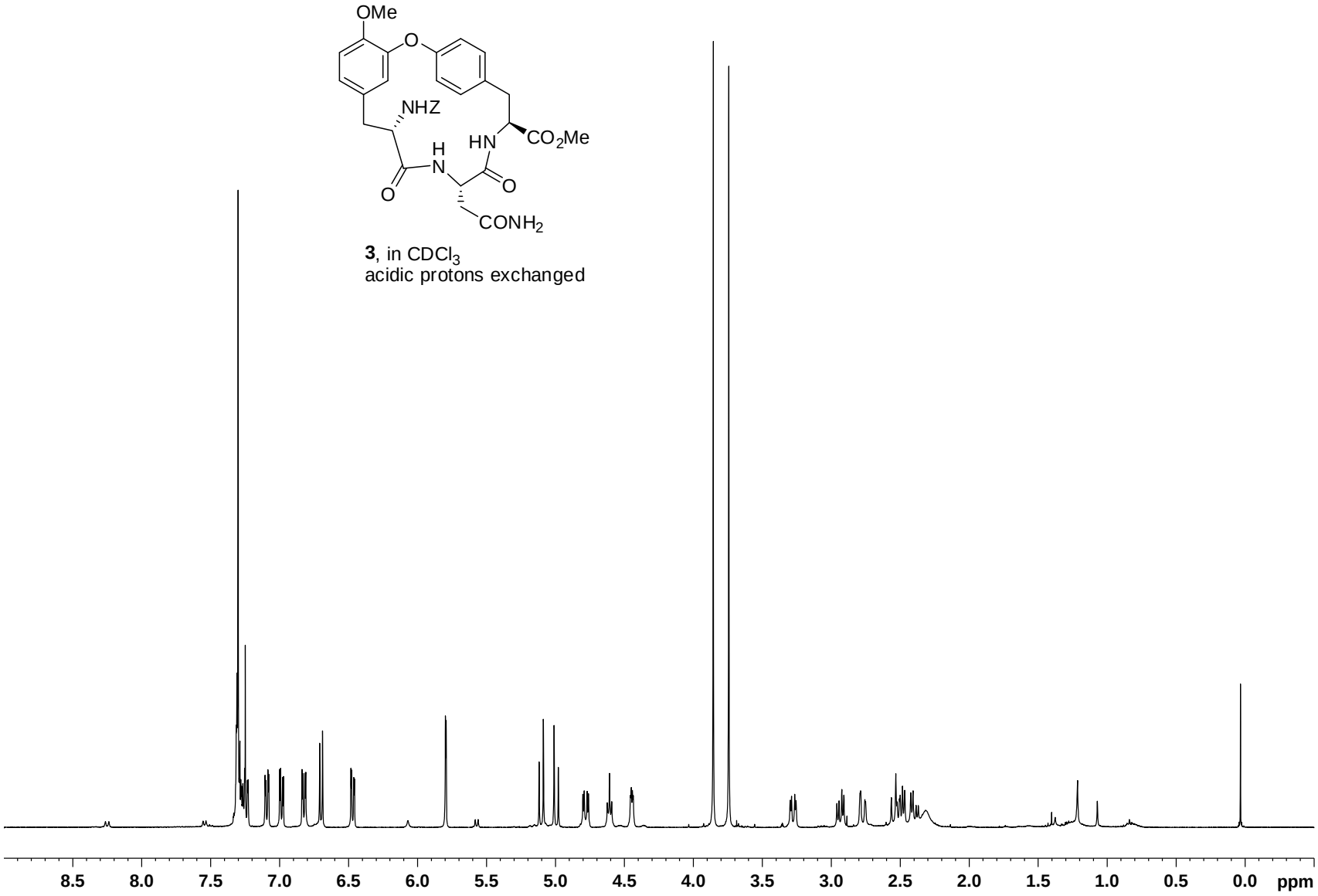
3, in CD_3OD

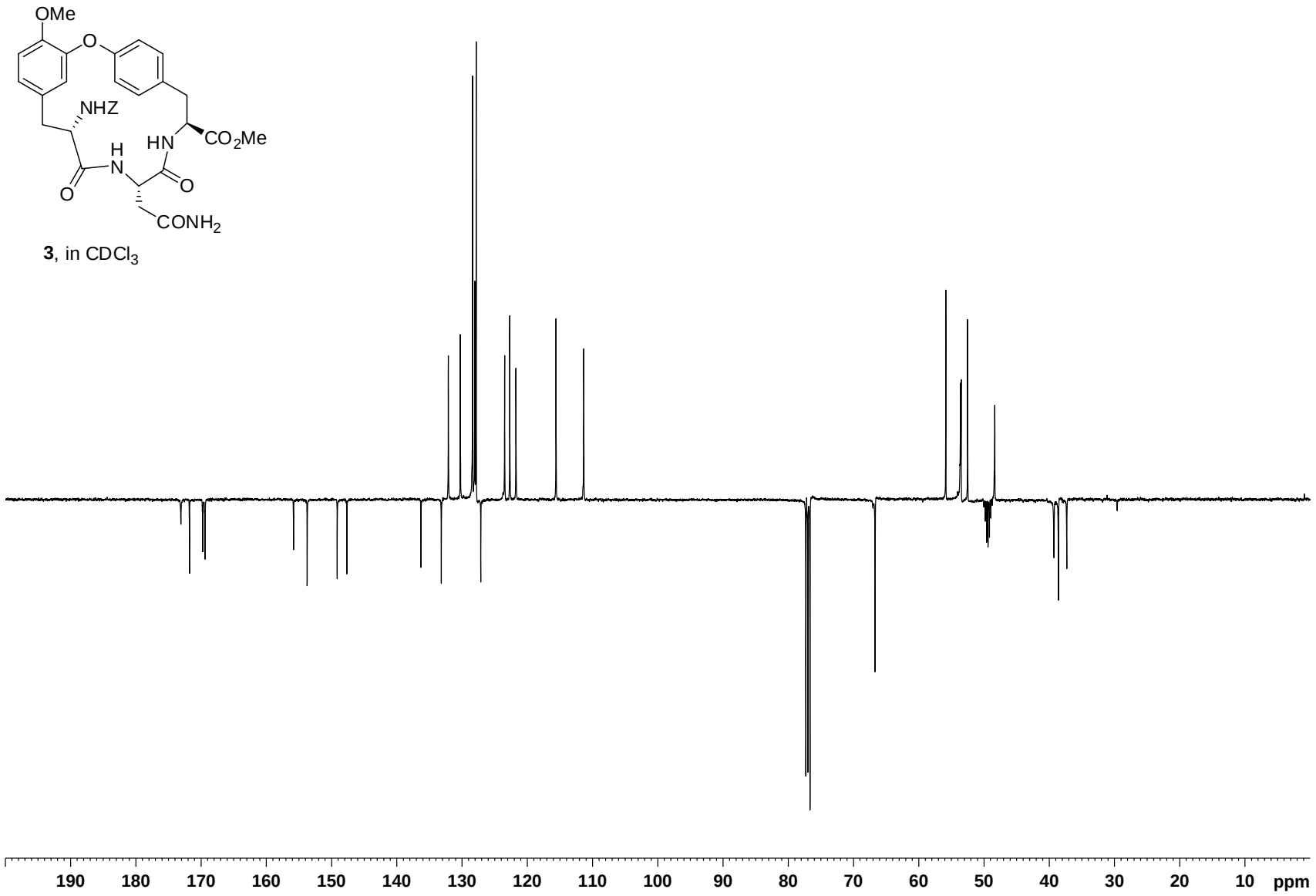

OMe
O
NHZ
HN
CO2Me
H
N
O
O
CONH2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

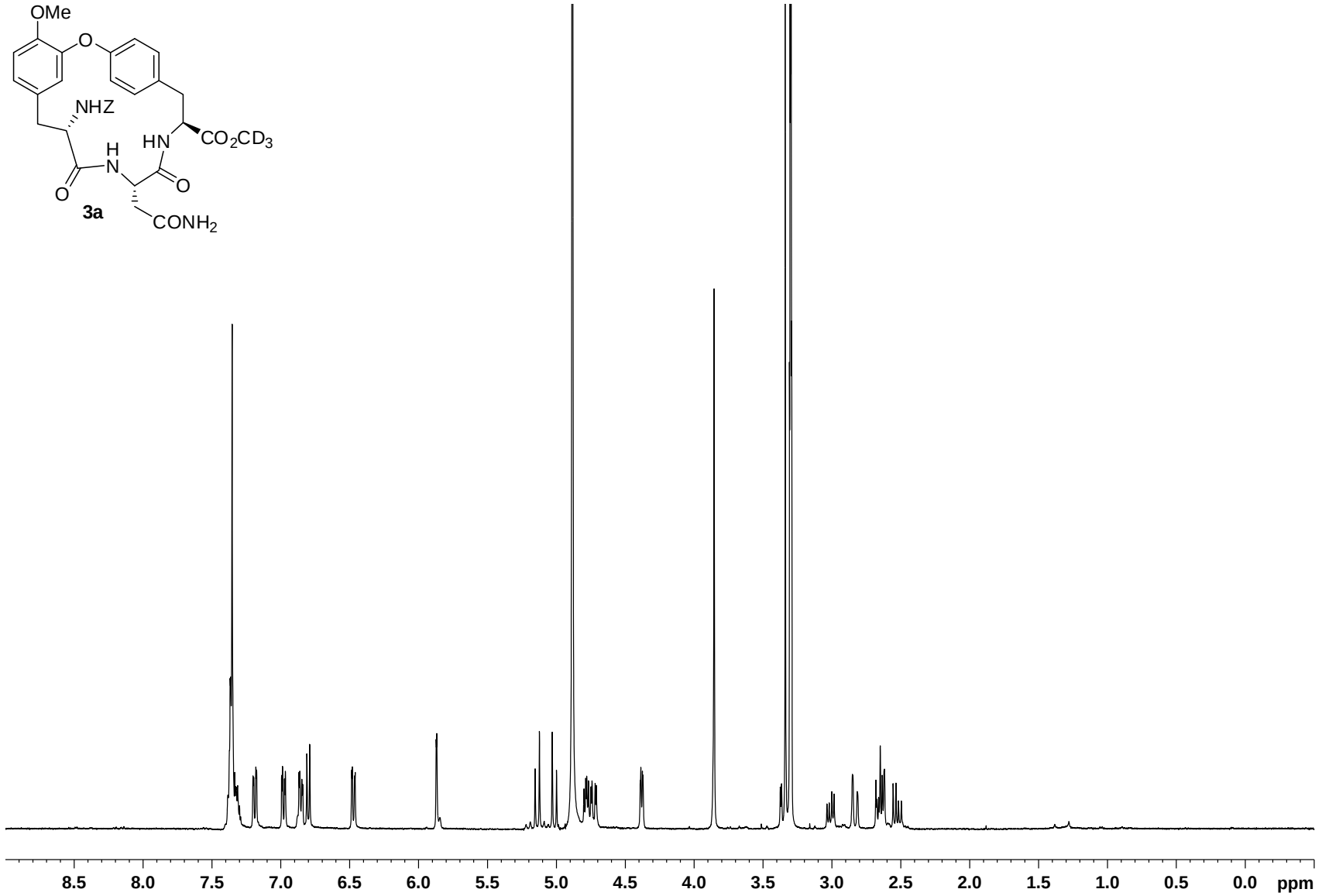
3, in CD_3OD

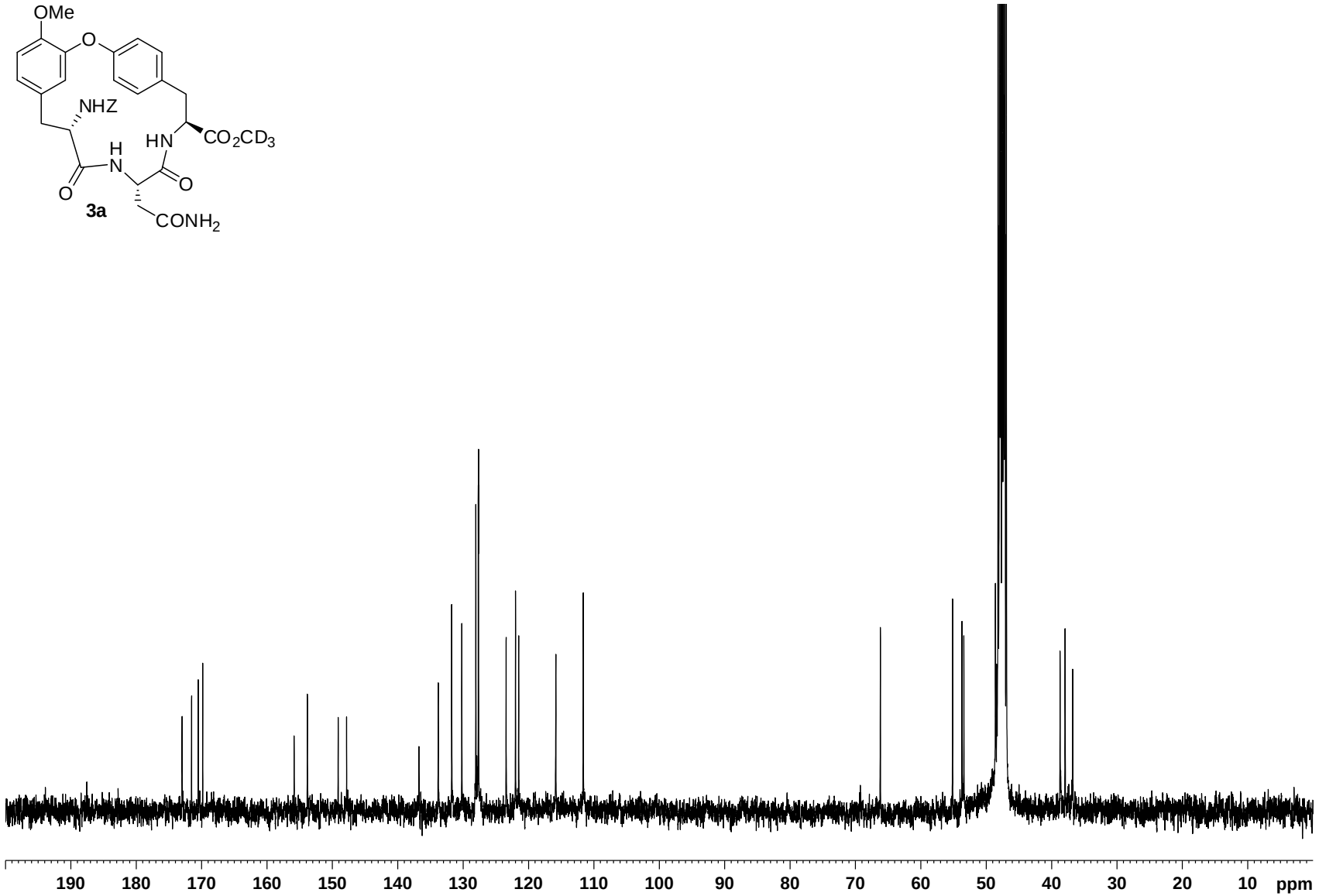

OMe
O
NHZ
HN
CO2Me
H
N
O
O
O
CONH2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

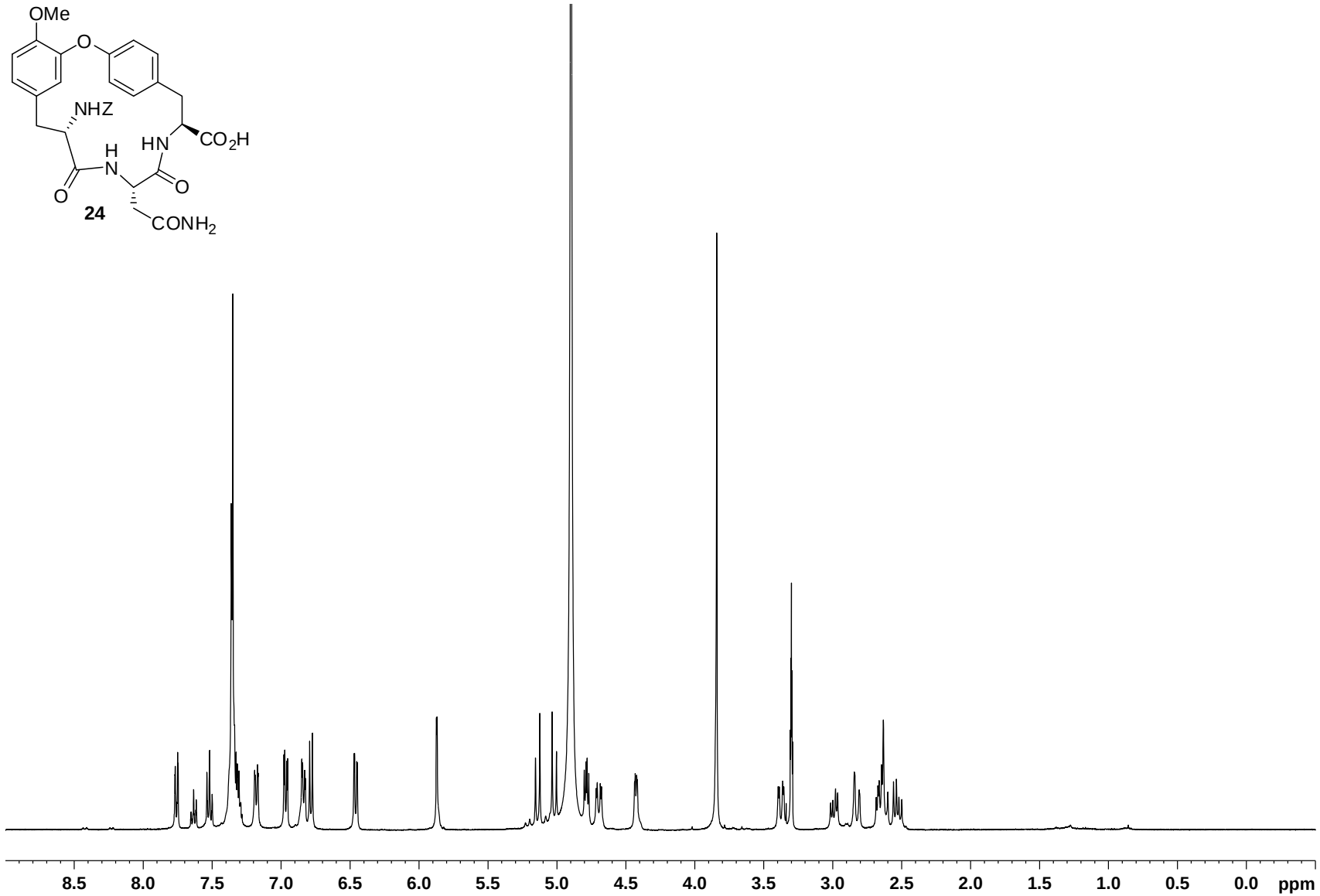
3, in $CDCl_3$

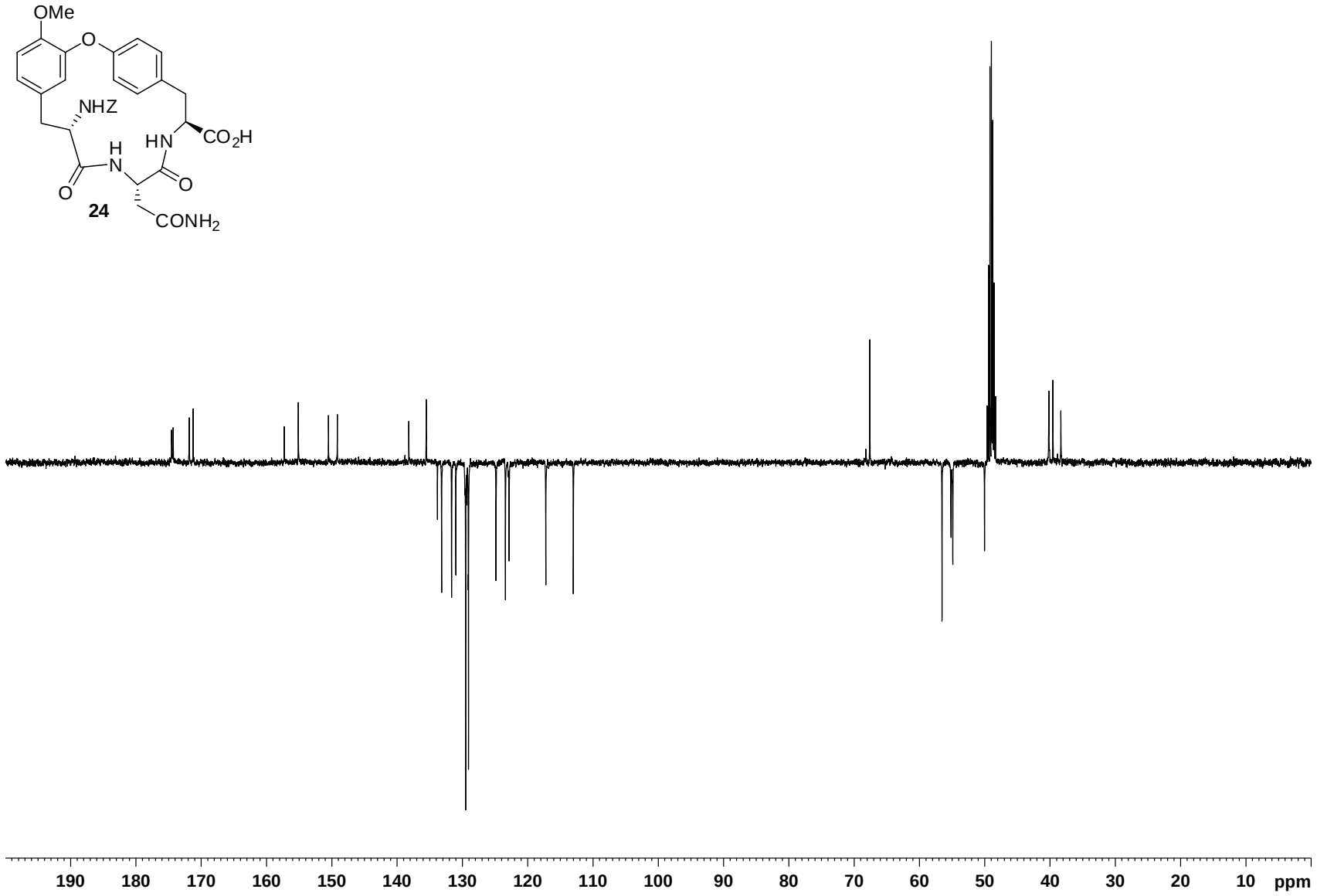

OMe
O
NHZ
HN
CO2Me
H
N
O
O
O
CONH2
3, in CDCl3
acidic protons exchanged
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

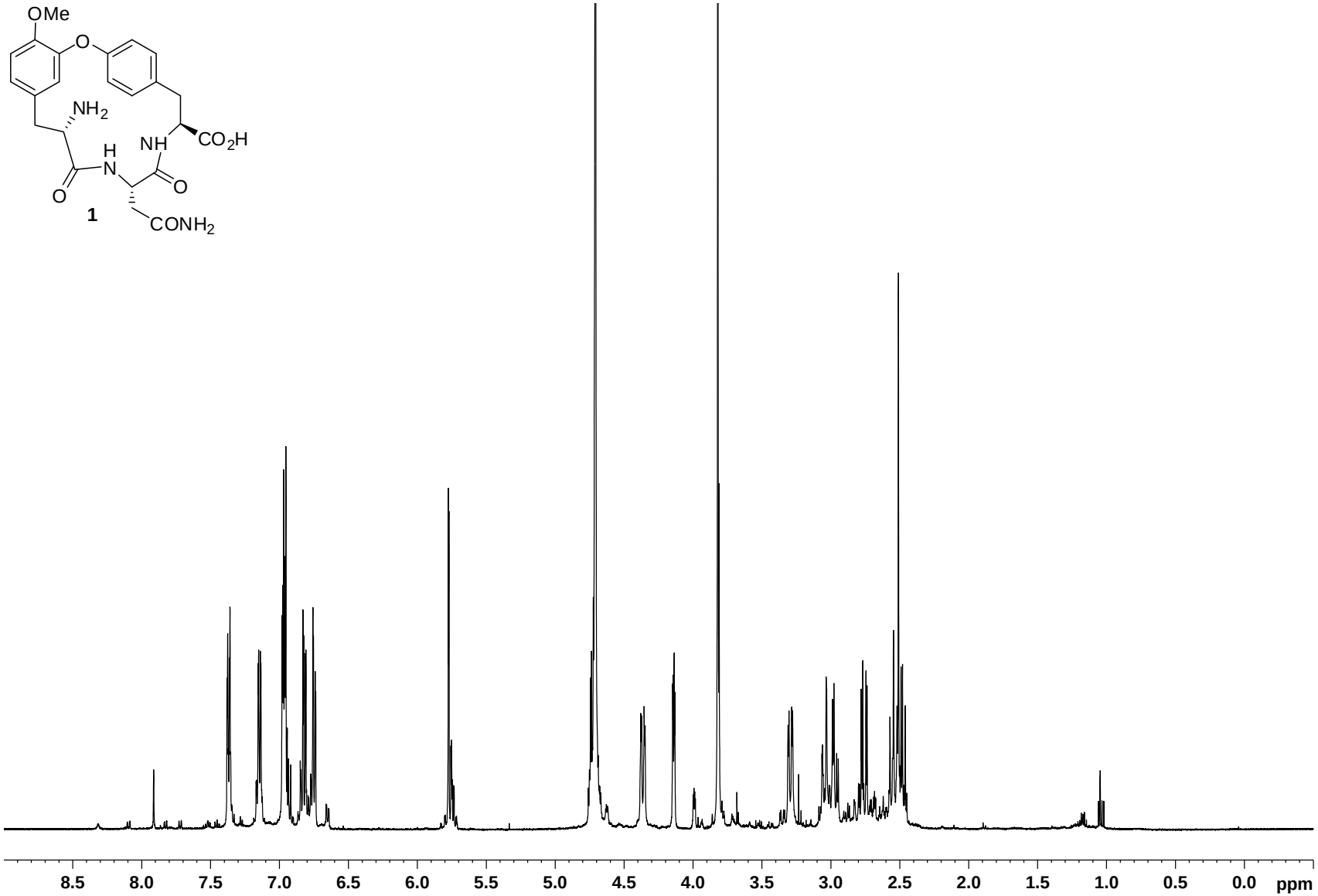

OMe
O
NHZ
HN
CO2Me
H
N
O
O
CONH2
3, in CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

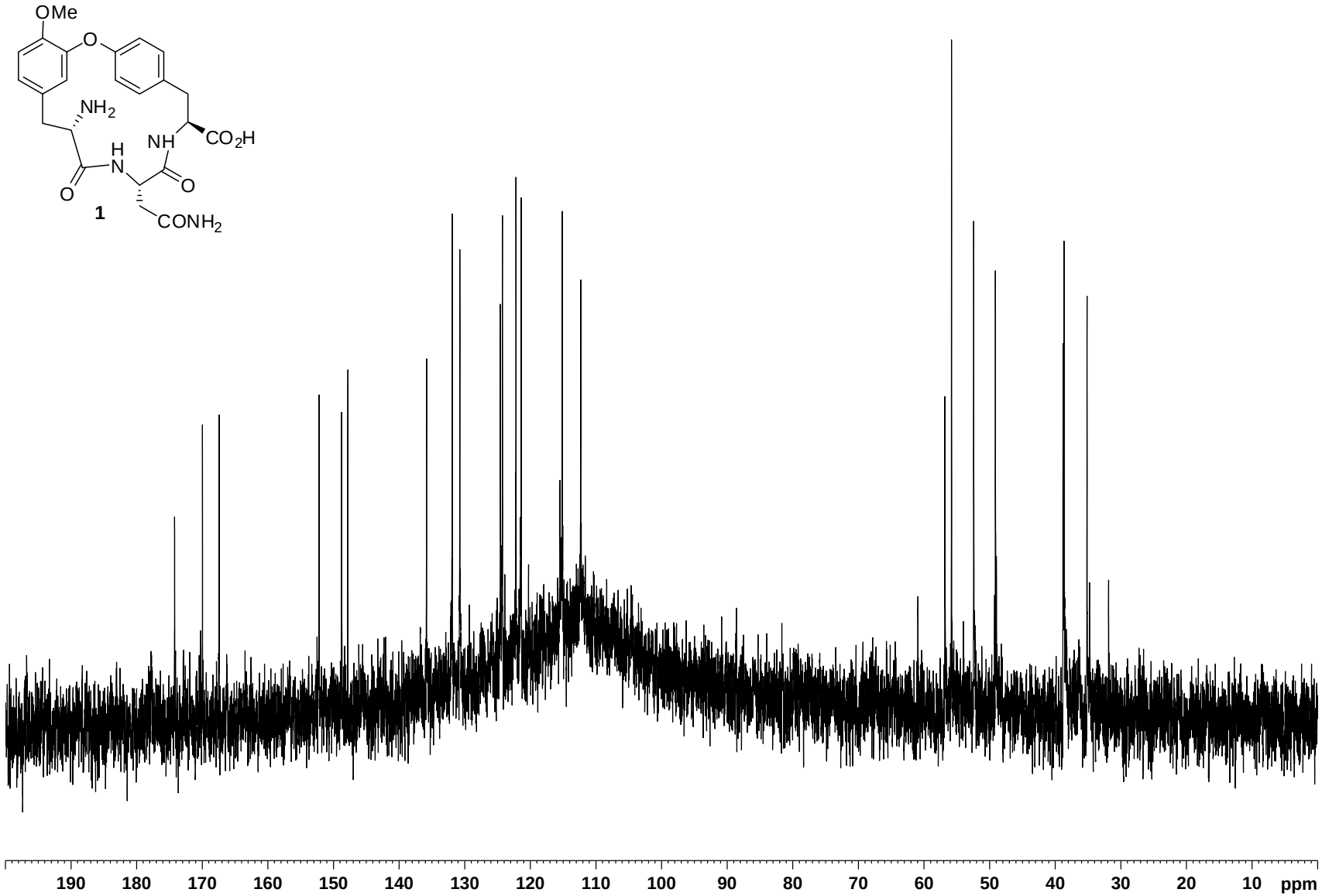

OMe
O
NHZ
HN
CO2CD3
H
N
O
O
O
3a
CONH2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

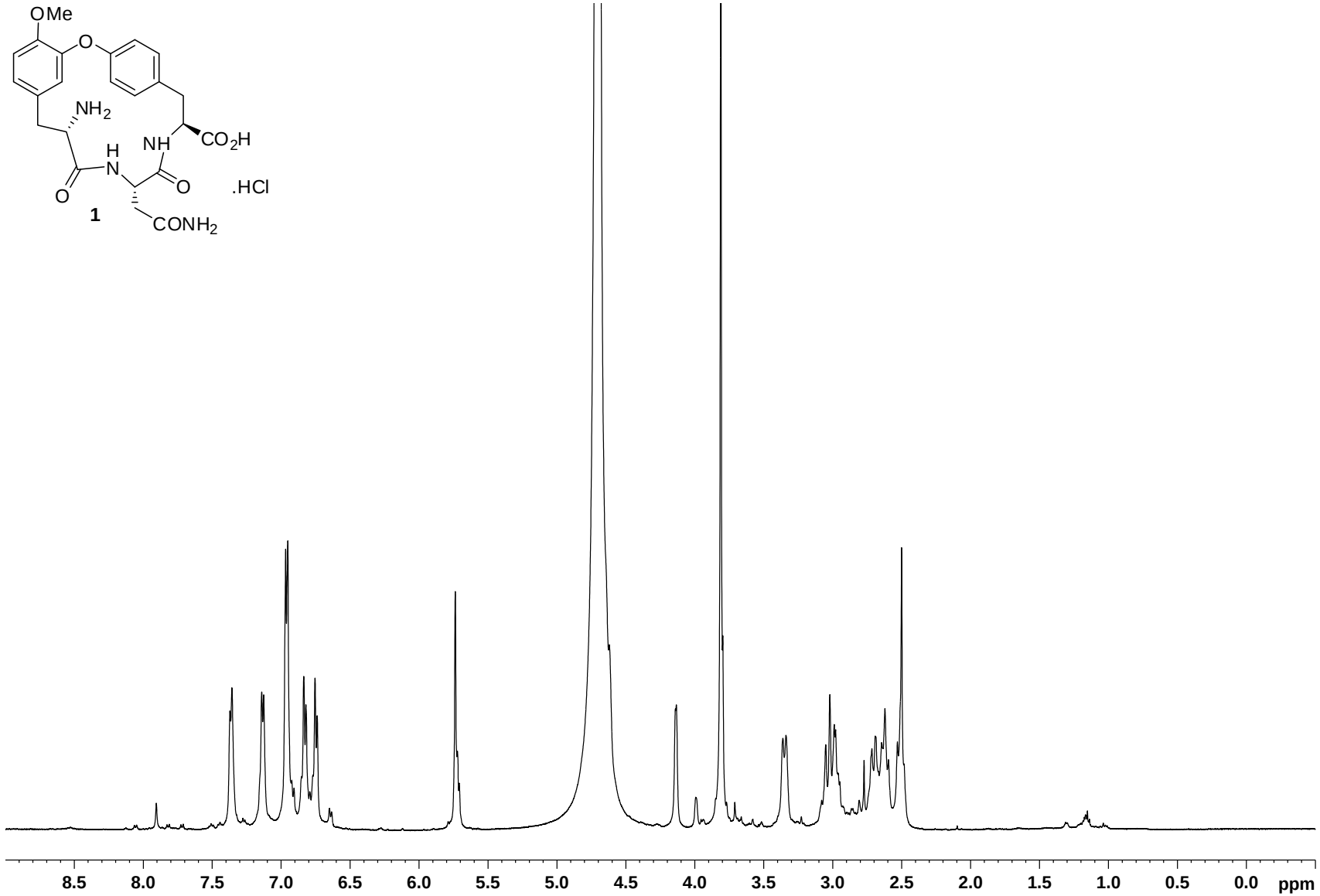

OMe
O
NHZ
HN
CO2CD3
H
N
O
O
O
CONH2
3a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

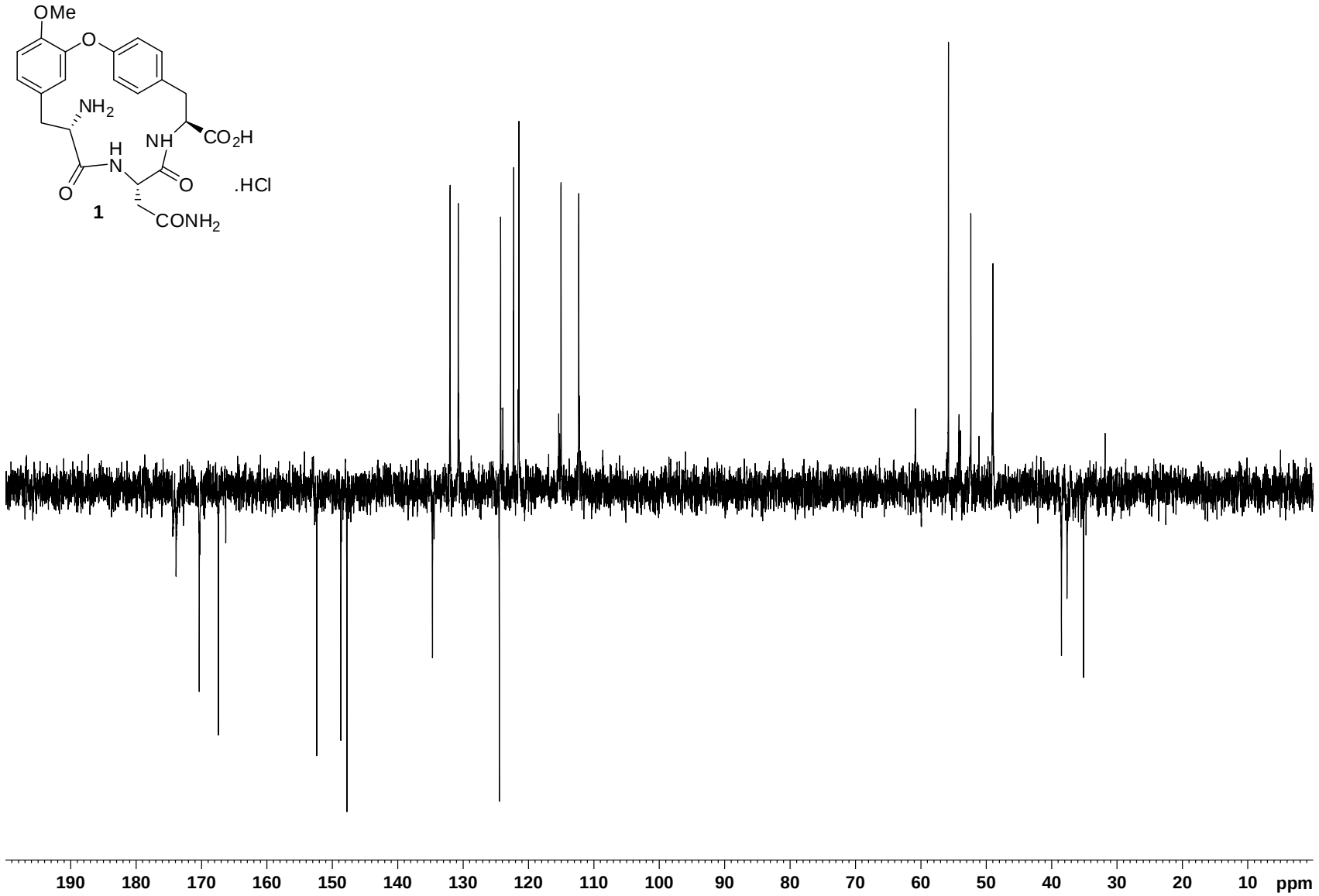

OMe
O
NHZ
HN
CO2H
H
N
O
O
O
24
CONH2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

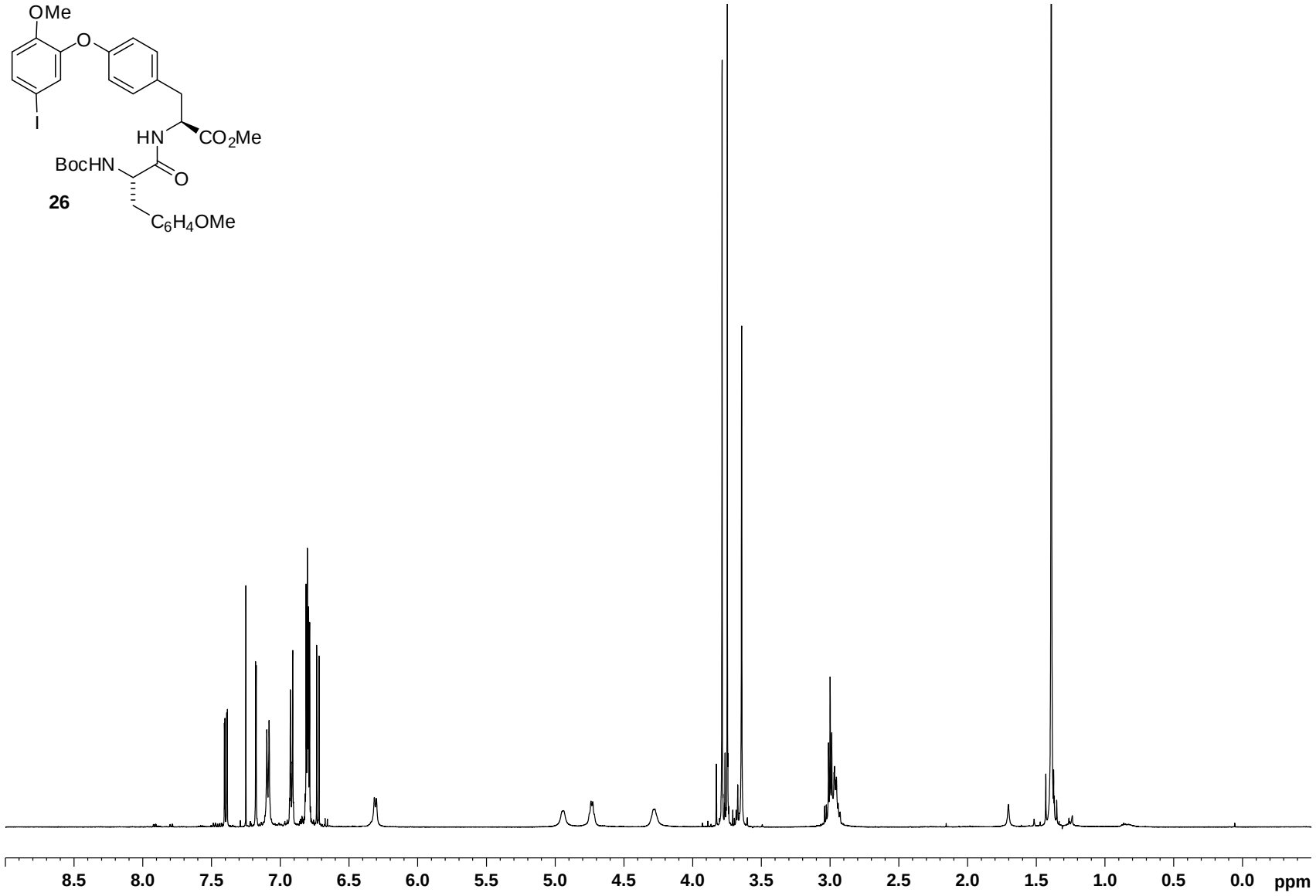

OMe
O
NHZ
HN
CO2H
H
N
O
O
O
CONH2
24
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

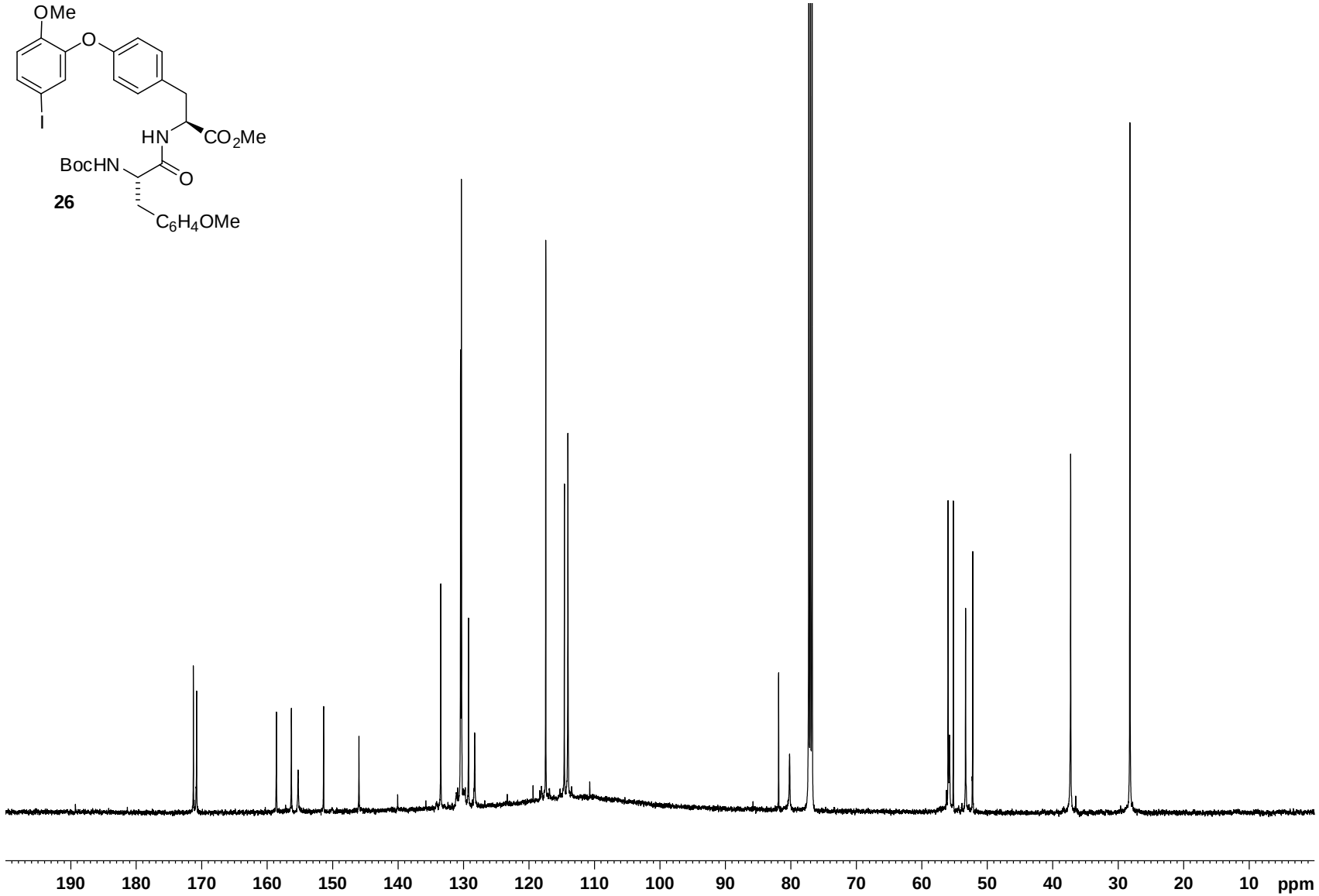

OMe
O
NH2
NH
CO2H
H
N
O
O
O
1
CONH2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

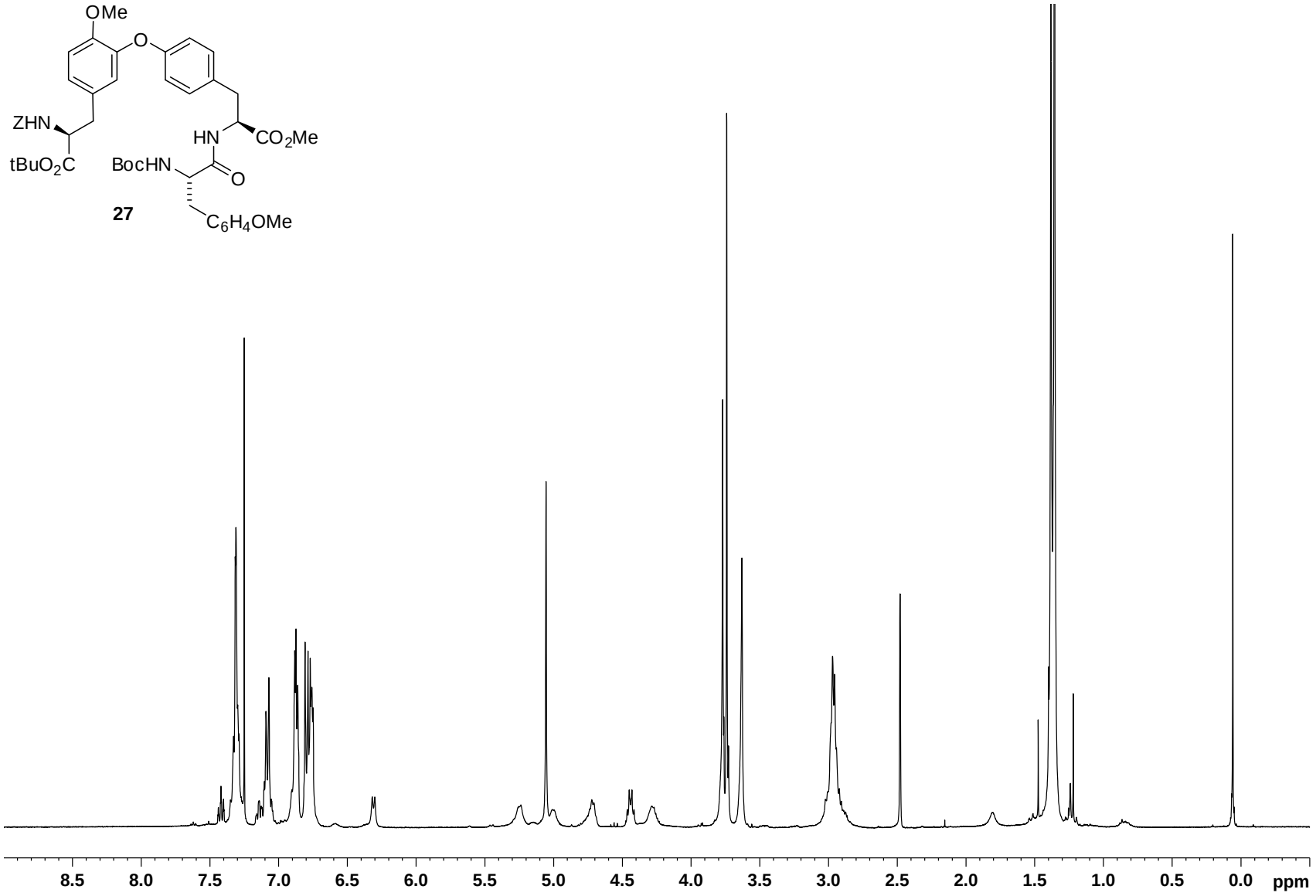

OMe
O
NH2
NH
CO2H
H
N
O
O
O
CONH2
1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

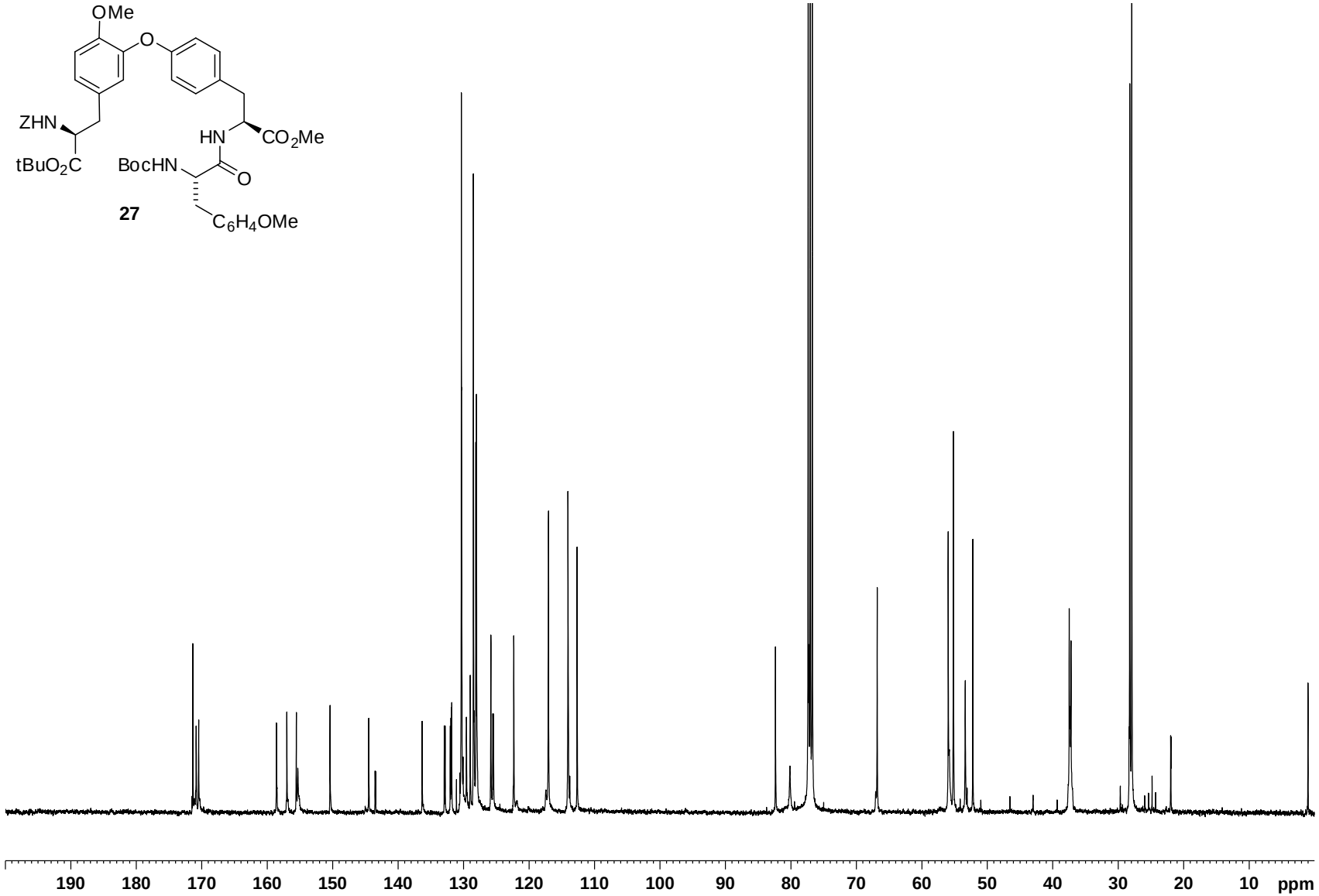

OMe
O
NH2
NH
CO2H
H
N
O
O
.HCl
1
CONH2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

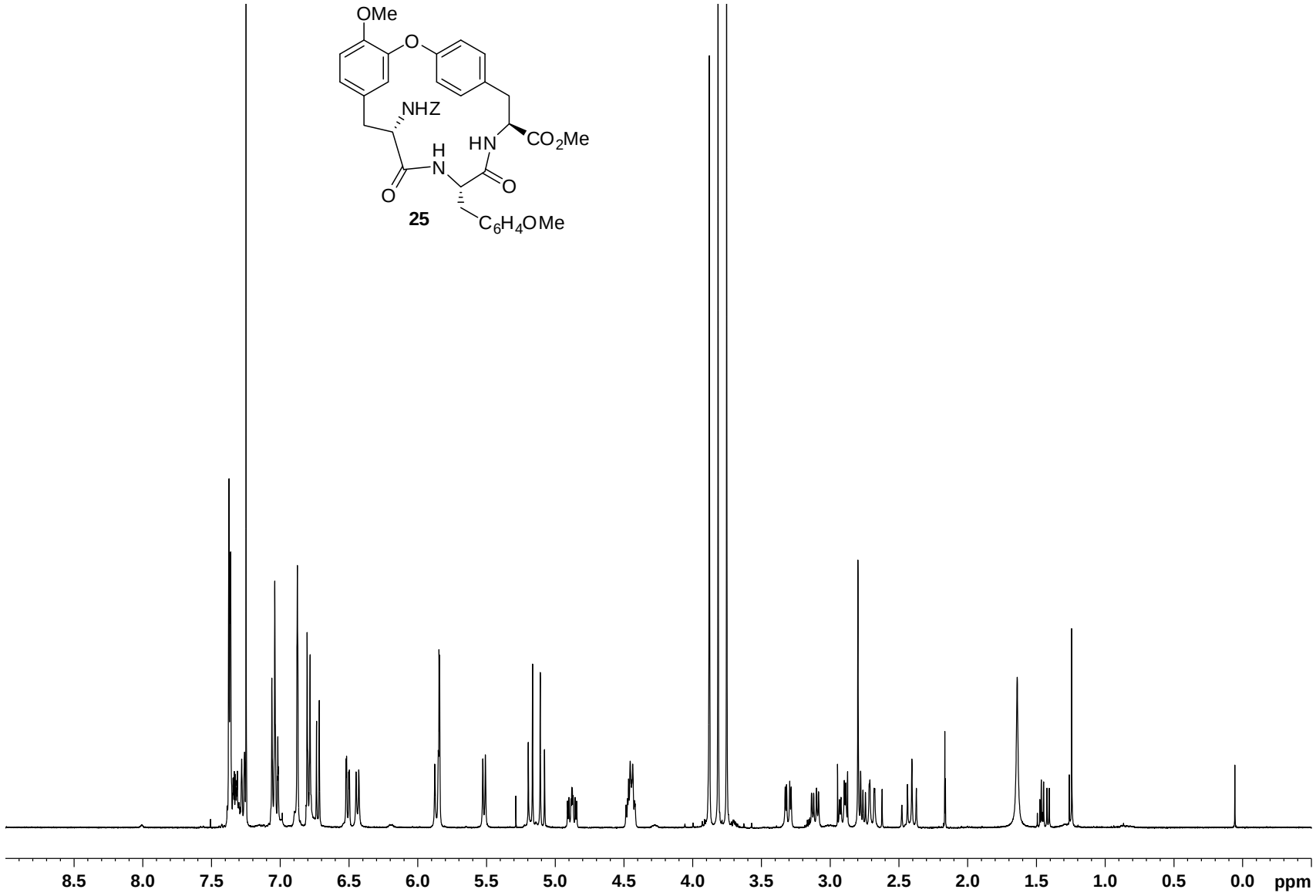

OMe
O
NH2
NH
CO2H
H
N
O
O
.HCl
1
CONH2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

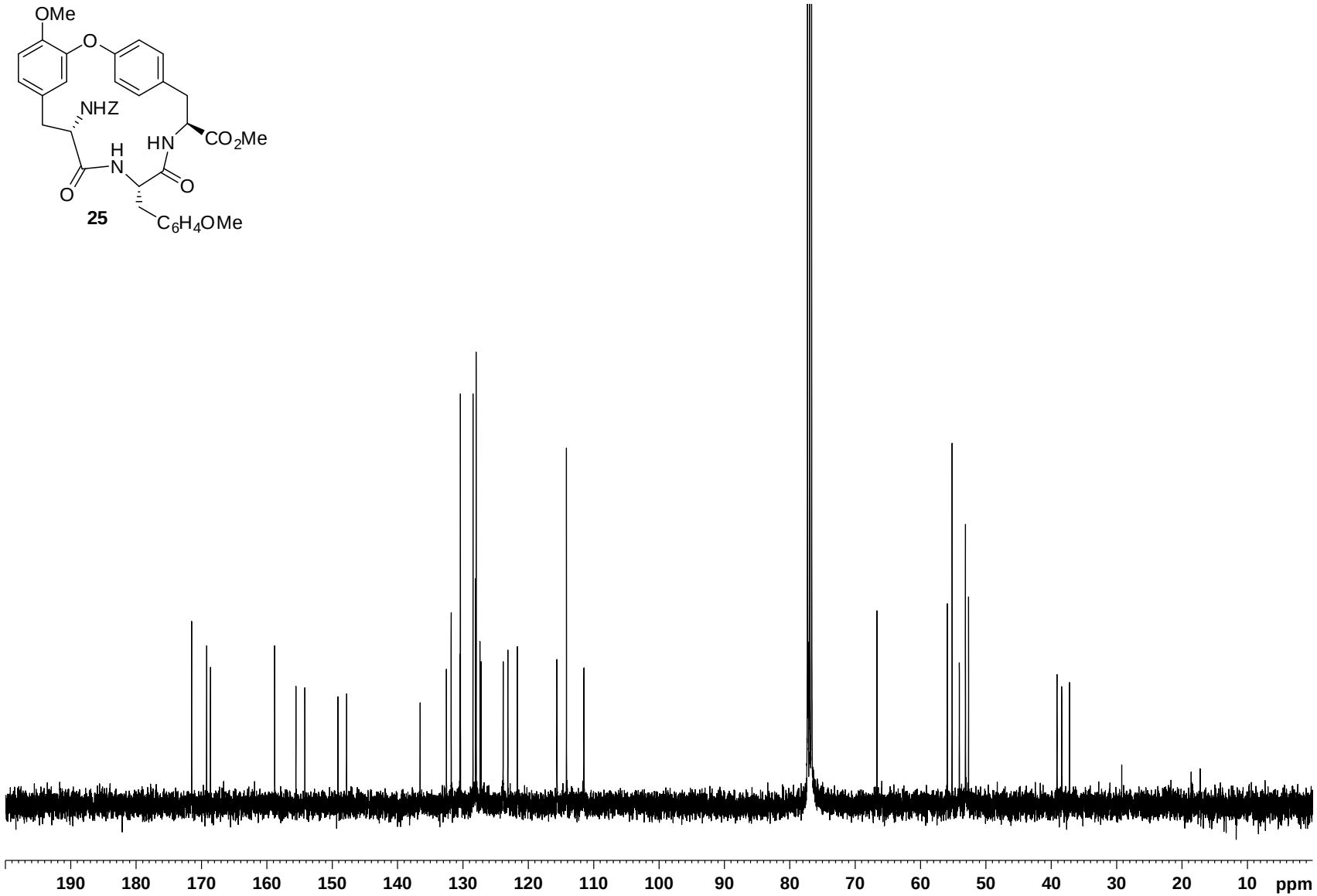

OMe
O
I
HN
CO2Me
BocHN
O
26
C6H4OMe
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

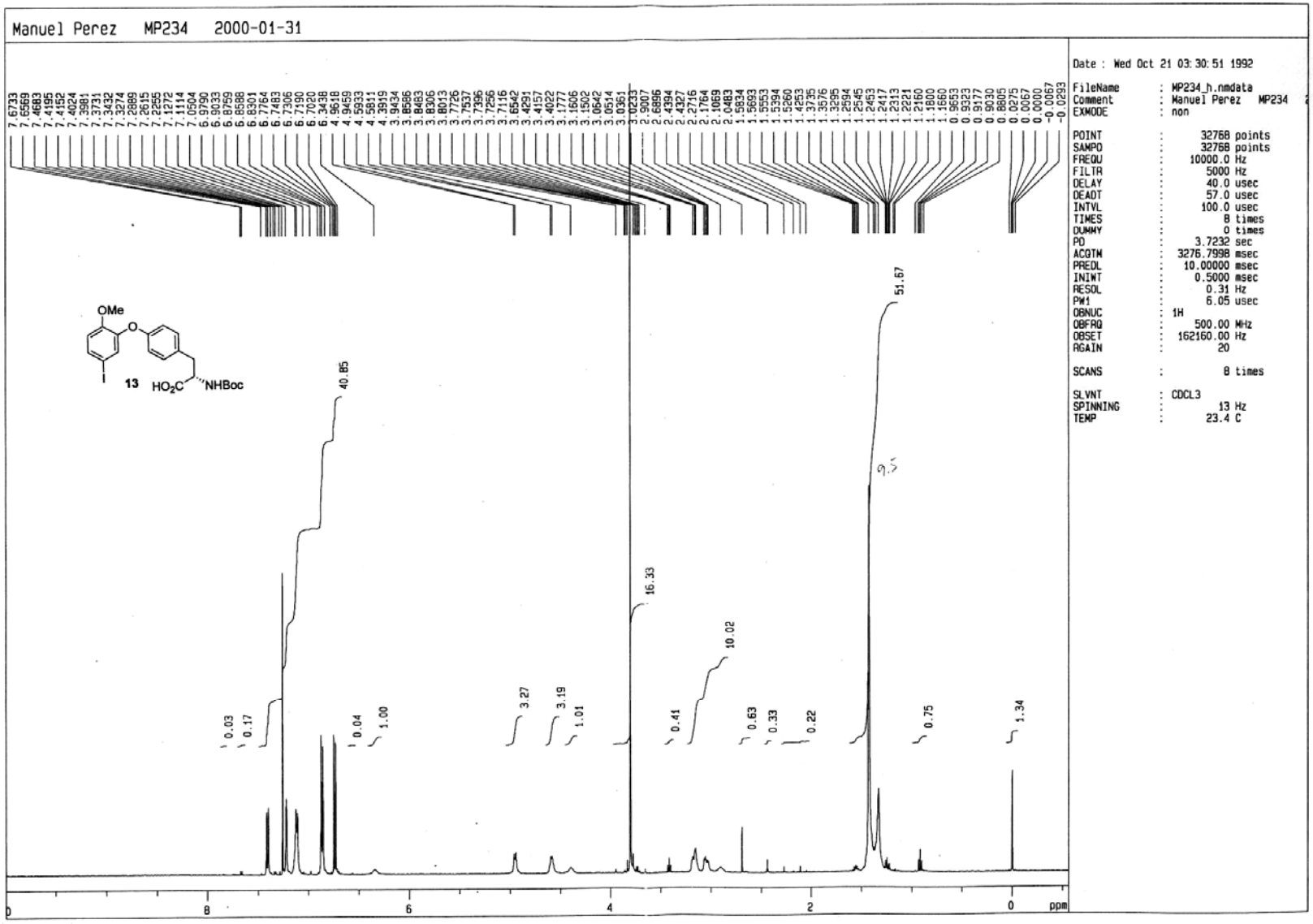

OMe
O
I
HN
CO2Me
BocHN
O
26
C6H4OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

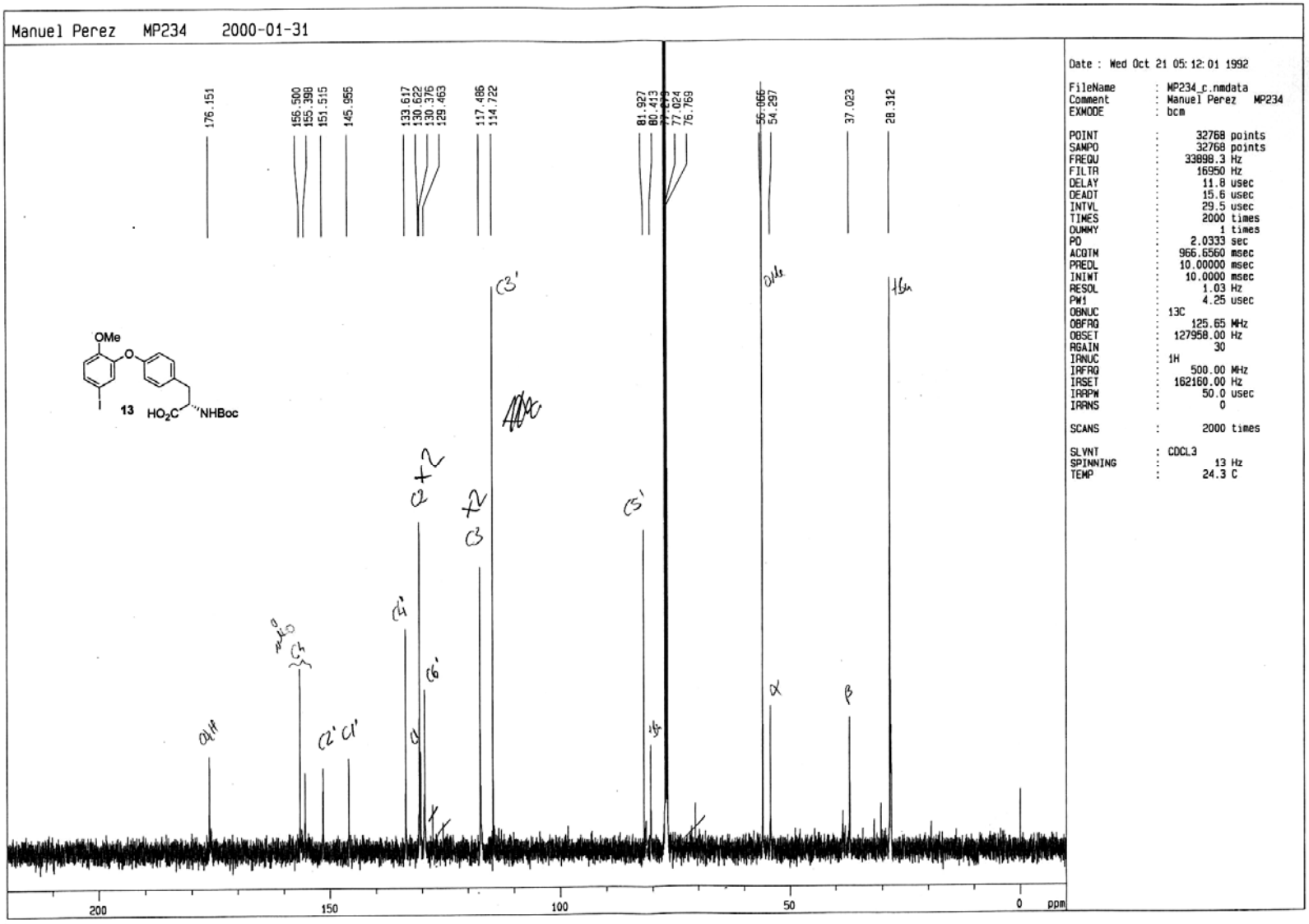

OMe
O
ZHN
HN
CO2Me
tBuO2C
BocHN
O
27
C6H4OMe
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

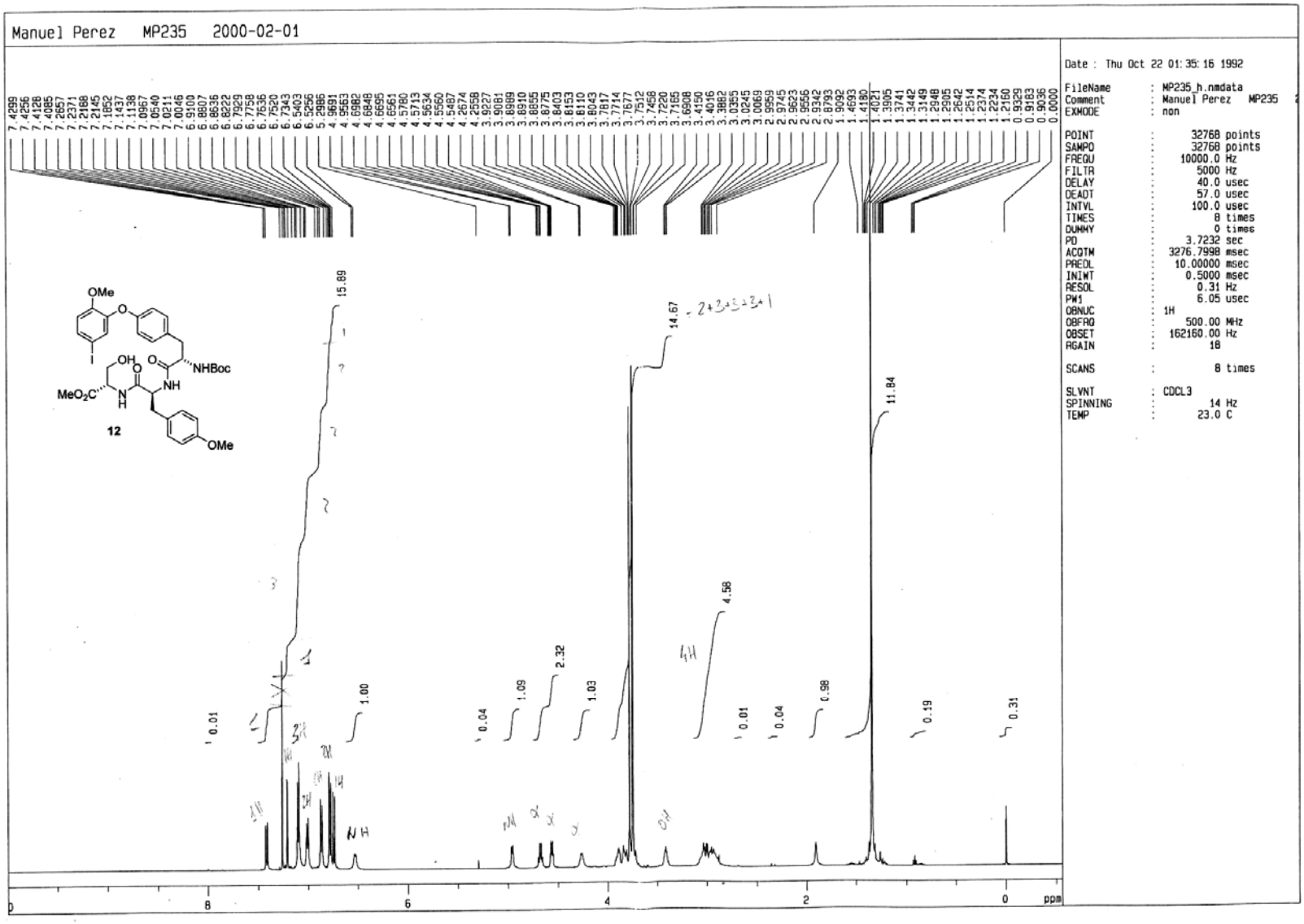

OMe
O
ZHN
tBuO2C
HN
CO2Me
BocHN
O
27
C6H4OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

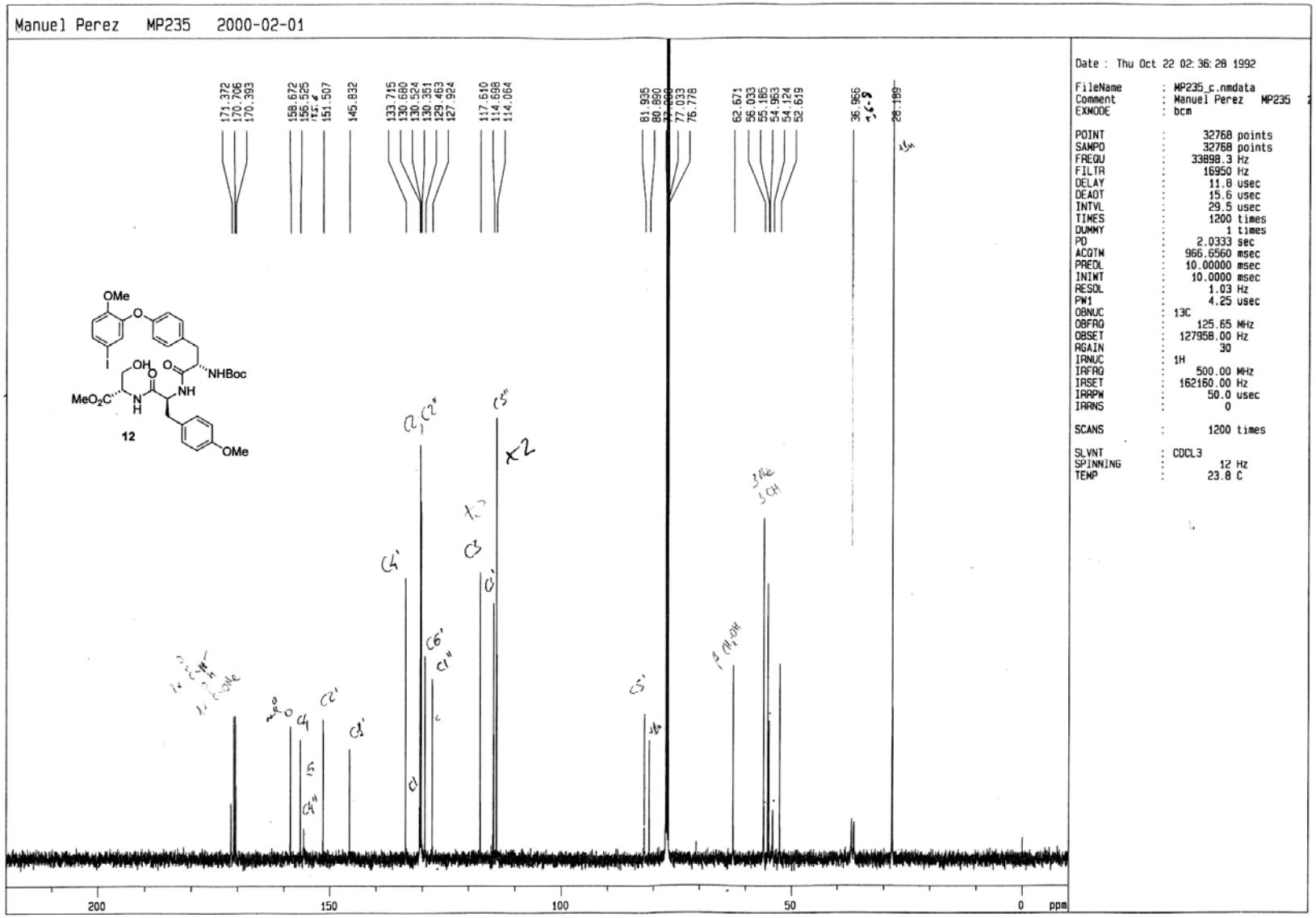

OMe
O
NHZ
HN
CO2Me
H
N
O
O
25
C6H4OMe
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

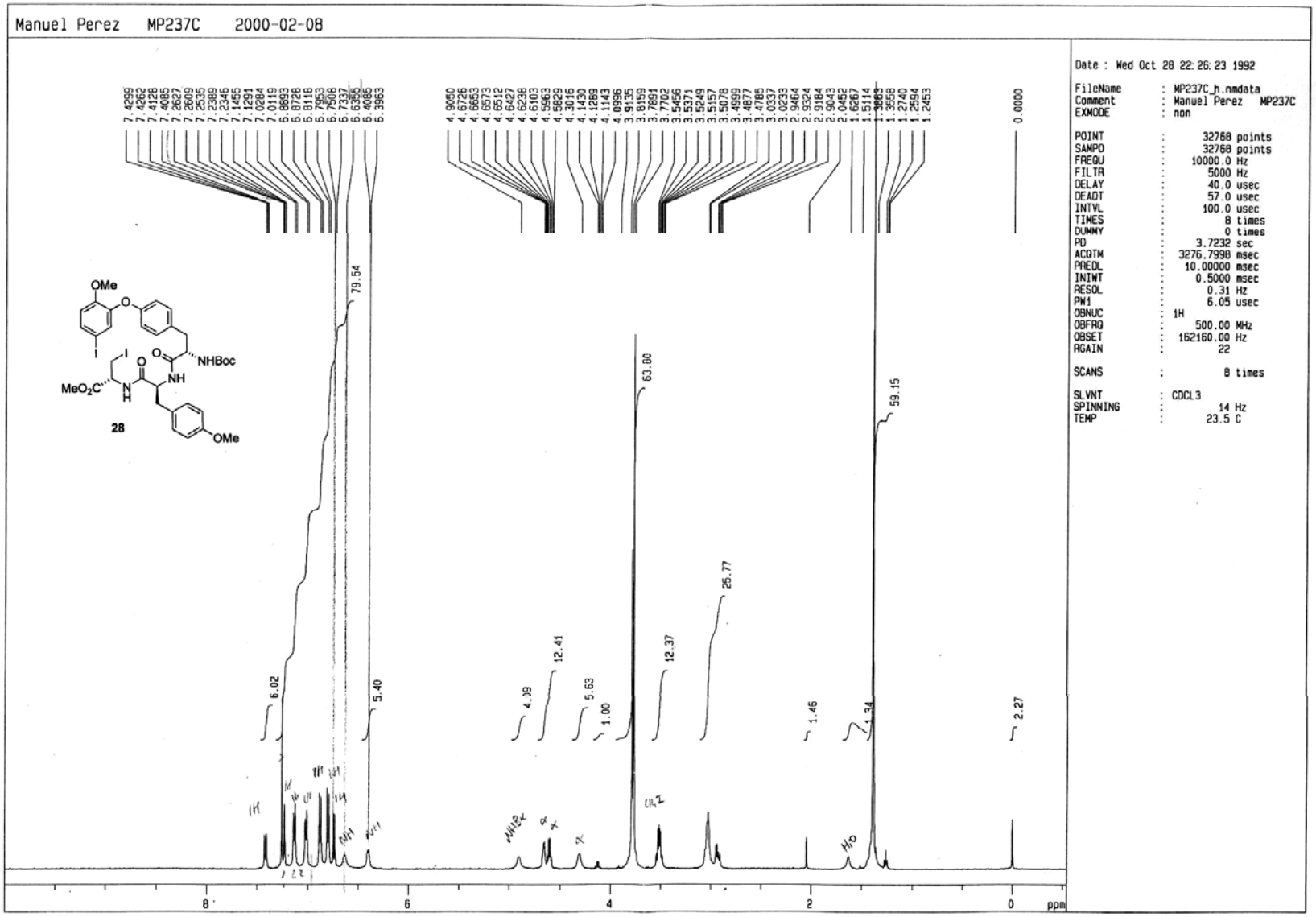

OMe
O
NHZ
HN
CO2Me
H
N
O
O
25
C6H4OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

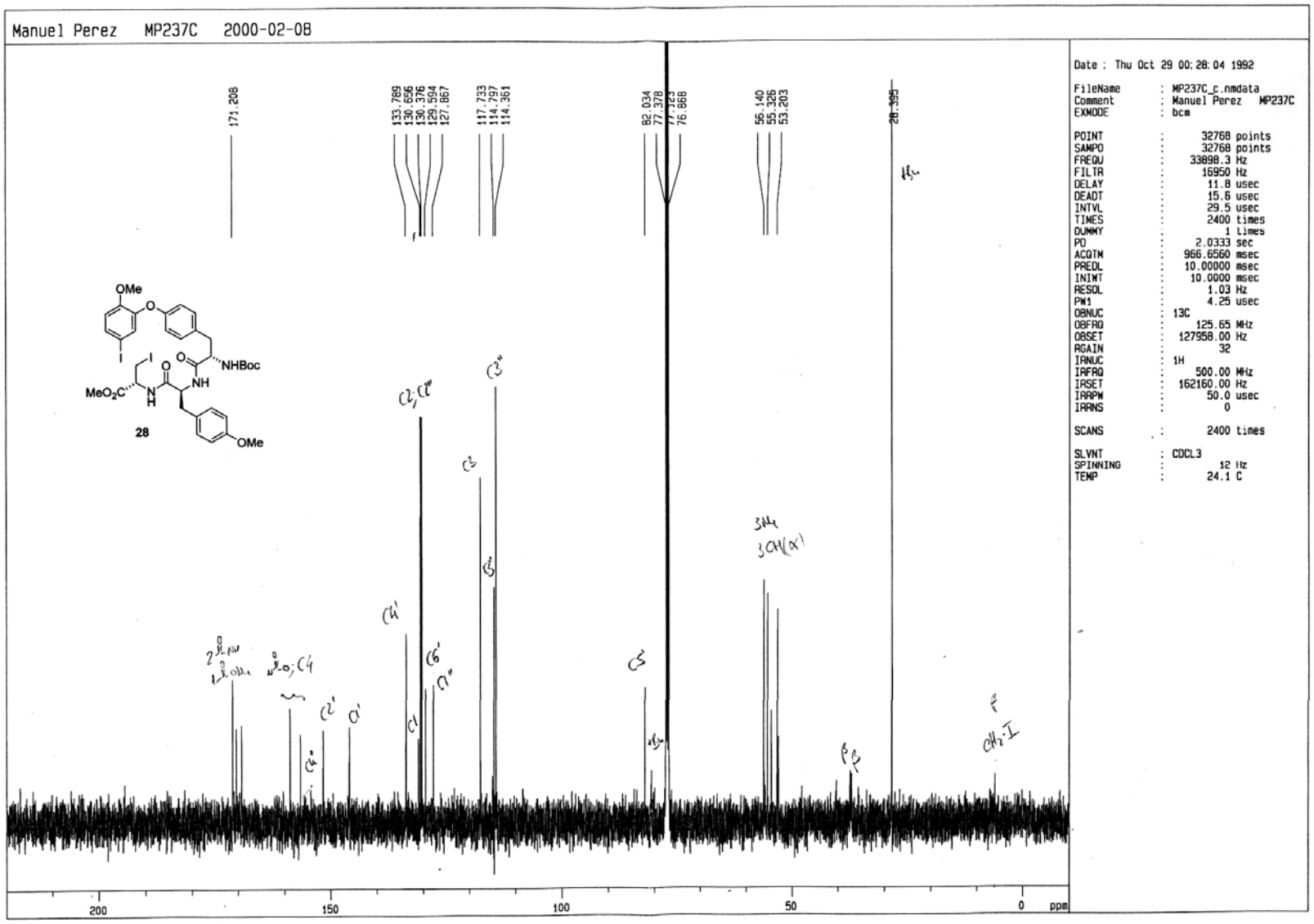

Manuel Perez MP234 2000-01-31
OMe
13 HO2C NHBoc
Date : Wed Oct 21 03:30:51 1992
FileName : MP234_h.nmdata
Comment : Manuel Perez MP234
EXMODE : non
POINT : 32768 points
SAMPO : 32768 points
FREQU : 10000.0 Hz
FILTR : 5000 Hz
DELAY : 40.0 usec
DEADT : 57.0 usec
INTVL : 100.0 usec
TIMES : 8 times
DUMMY : 0 times
PD : 3.7232 sec
ACQTM : 3276.7998 msec
PREDL : 10.00000 msec
ININT : 0.5000 msec
RESOL : 0.31 Hz
PW1 : 6.05 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162160.00 Hz
RGAIN : 20
SCANS : 8 times
SLVNT : CDCL3
SPINNING : 13 Hz
TEMP : 23.4 C
0.03
0.17
40.85
0.04
1.00
3.27
3.19
1.01
16.33
0.41
10.02
0.63
0.33
0.22
51.67
0.75
1.34
8
6
4
2
0
ppm

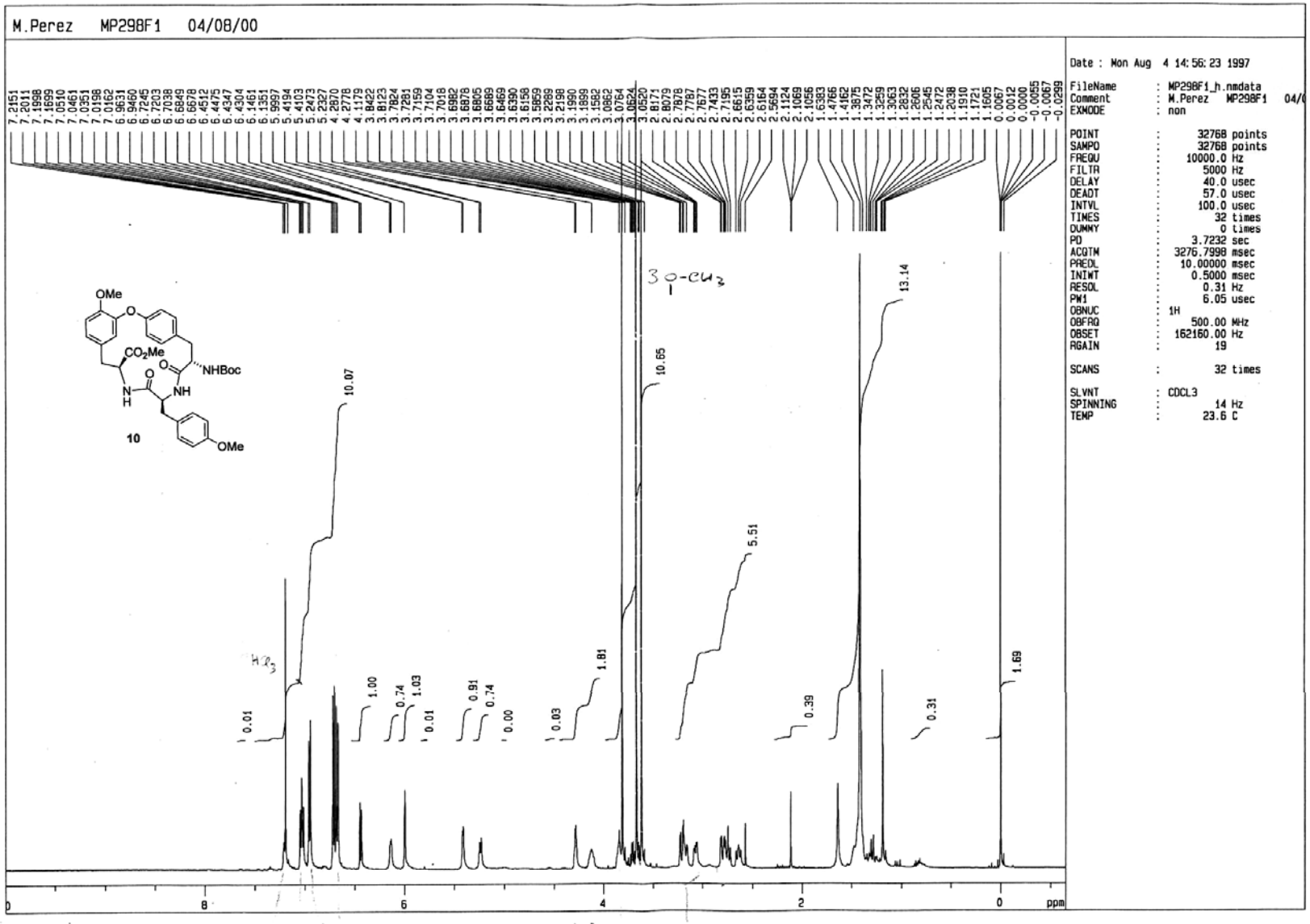

Manuel Perez MP234 2000-01-31
176.151
156.500
155.398
151.515
145.966
133.617
130.622
130.376
129.463
117.486
114.722
81.927
80.413
77.024
76.769
56.066
54.297
37.023
28.312
OMe
13
HO2C
NHBoc
C3'
C2
C3
C5'
C6'
C2' C1'
Date : Wed Oct 21 05:12:01 1992
FileName : MP234_c.nmdata
Comment : Manuel Perez MP234
EXMODE : bcm
POINT : 32768 points
SAMPO : 32768 points
FREQU : 33898.3 Hz
FILTR : 16950 Hz
DELAY : 11.8 usec
DEADT : 15.6 usec
INTVL : 29.5 usec
TIMES : 2000 times
DUMMY : 1 times
PD : 2.0333 sec
ACQTM : 966.6560 msec
PREDL : 10.00000 msec
INIWT : 10.0000 msec
RESOL : 1.03 Hz
PW1 : 4.25 usec
OBNUC : 13C
OBFRQ : 125.65 MHz
OBSET : 127958.00 Hz
RGAIN : 30
IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162160.00 Hz
IRPW : 50.0 usec
IRNS : 0
SCANS : 2000 times
SLVNT : CDCL3
SPINNING : 13 Hz
TEMP : 24.3 C
200
150
100
50
0
ppm

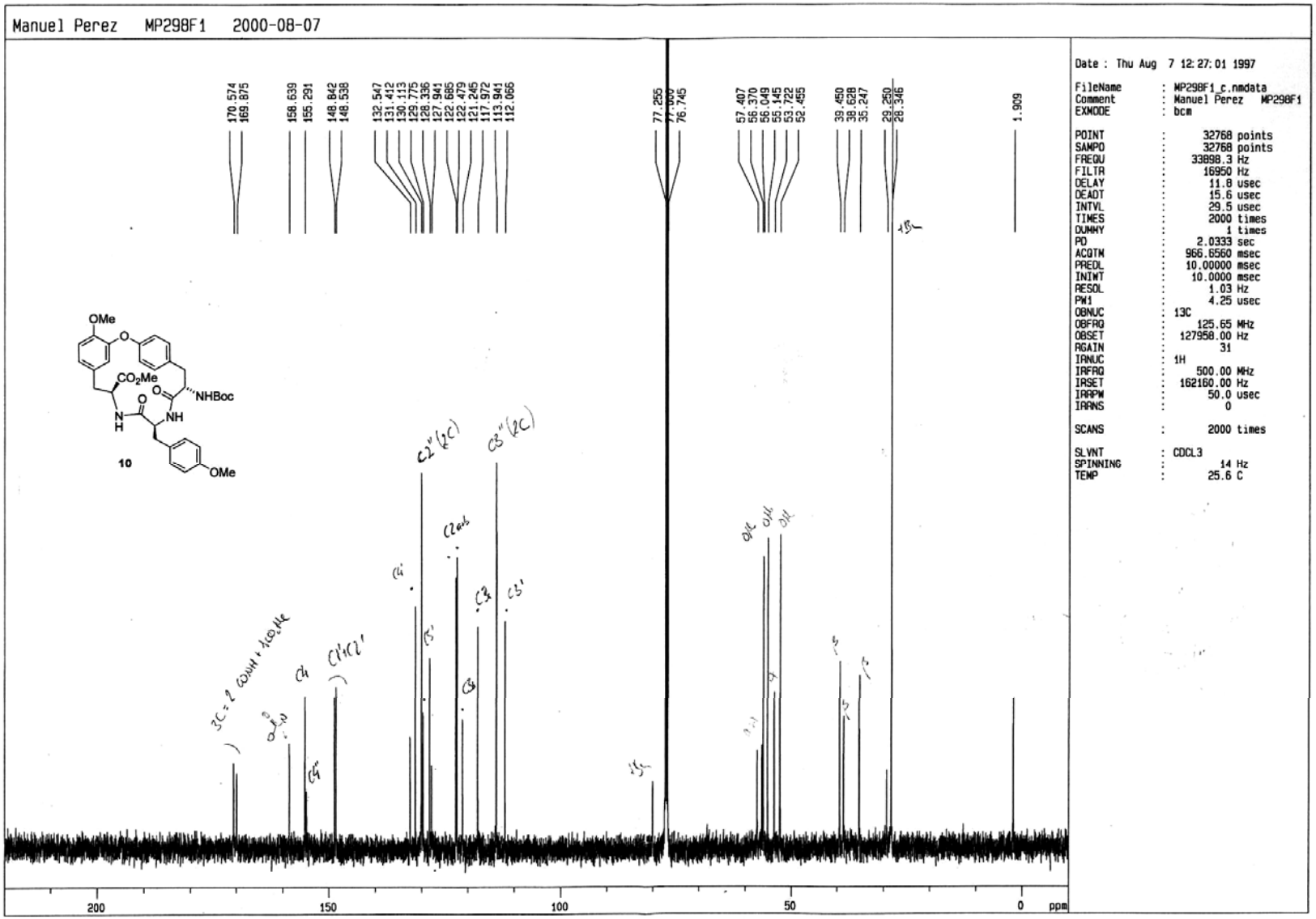

Manuel Perez MP235 2000-02-01
Date : Thu Oct 22 01:35:16 1992
FileName : MP235_h.nmdata
Comment : Manuel Perez MP235
EXMODE : non
POINT : 32768 points
SAMPD : 32768 points
FREQU : 10000.0 Hz
FILTR : 5000 Hz
DELAY : 40.0 usec
DEADT : 57.0 usec
INTVL : 100.0 usec
TIMES : 8 times
DUMMY : 0 times
PD : 3.7232 sec
ACQTM : 3276.7998 msec
PREDL : 10.00000 msec
INIWT : 0.5000 msec
RESOL : 0.31 Hz
PW1 : 6.05 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162160.00 Hz
RGAIN : 18
SCANS : 8 times
SLVNT : CDCL3
SPINNING : 14 Hz
TEMP : 23.0 C
OMe
NHBoc
MeO2C
12
15.89
14.67
11.84
4.58
2.32
1.09
1.03
1.00
0.98
0.31
0.19
0.04
0.01
ppm

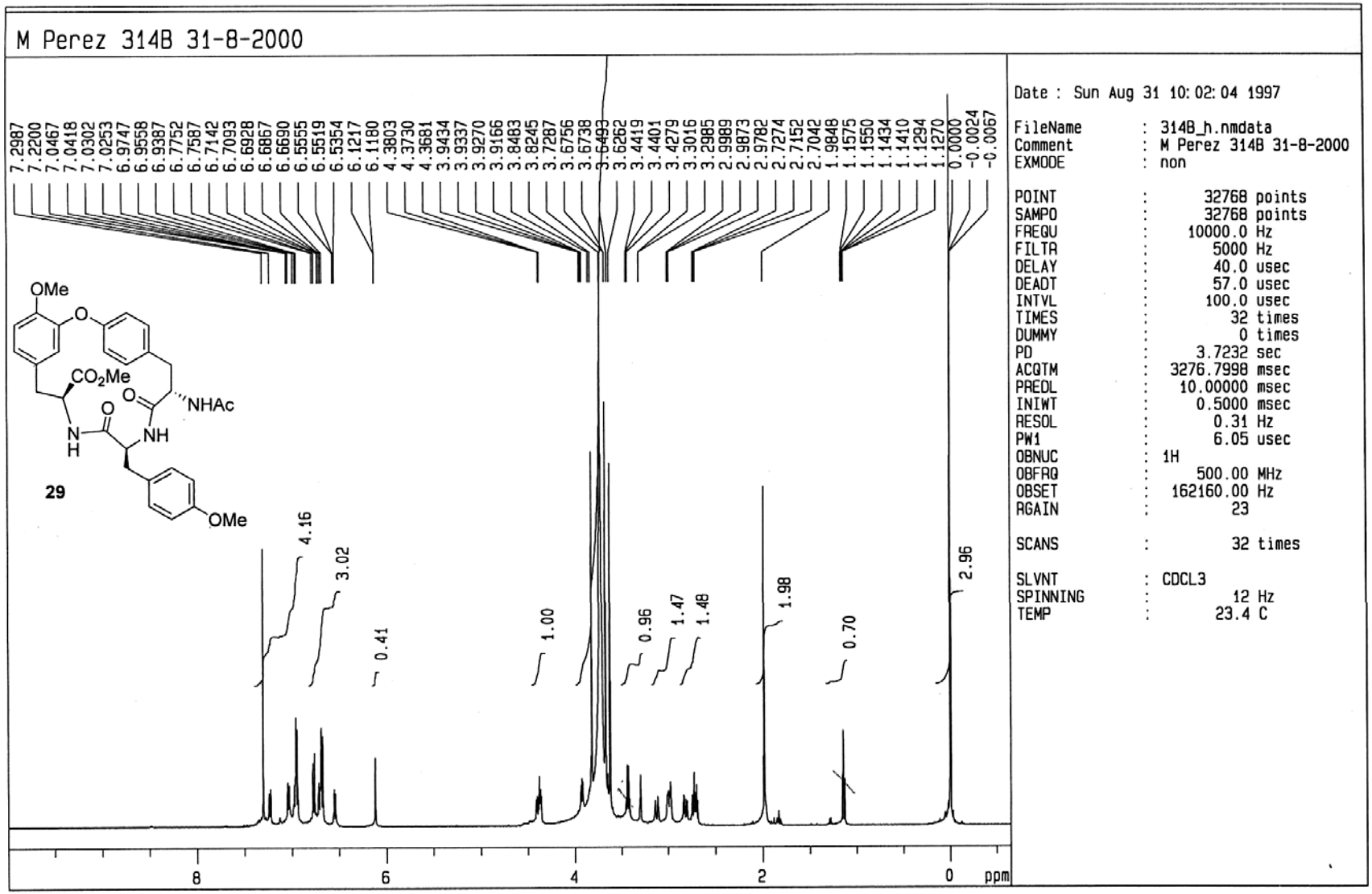

Manuel Perez MP235 2000-02-01
171.372
170.706
170.393
158.672
156.525
151.507
145.832
133.715
130.680
130.524
130.351
129.463
127.924
117.610
114.698
114.064
81.935
80.890
77.033
76.776
62.671
56.033
55.185
54.963
54.124
52.619
36.966
28.189
OMe
NHBoc
MeO2C
12
OMe
x2
200
150
100
50
0
ppm
Date : Thu Oct 22 02:36:28 1992
FileName : MP235_c.nmdata
Comment : Manuel Perez MP235
EXMODE : bcm
POINT : 32768 points
SAMPO : 32768 points
FREQU : 33898.3 Hz
FILTR : 16950 Hz
DELAY : 11.8 usec
DEADT : 15.6 usec
INTVL : 29.5 usec
TIMES : 1200 times
DUMMY : 1 times
PD : 2.0333 sec
ACQTM : 966.6560 msec
PREDL : 10.00000 msec
INIWT : 10.0000 msec
RESOL : 1.03 Hz
PW1 : 4.25 usec
OBNUC : 13C
OBFRQ : 125.65 MHz
OBSET : 127958.00 Hz
RGAIN : 30
IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162160.00 Hz
IRPW : 50.0 usec
IRNS : 0
SCANS : 1200 times
SLVNT : CDCL3
SPINNING : 12 Hz
TEMP : 23.8 C

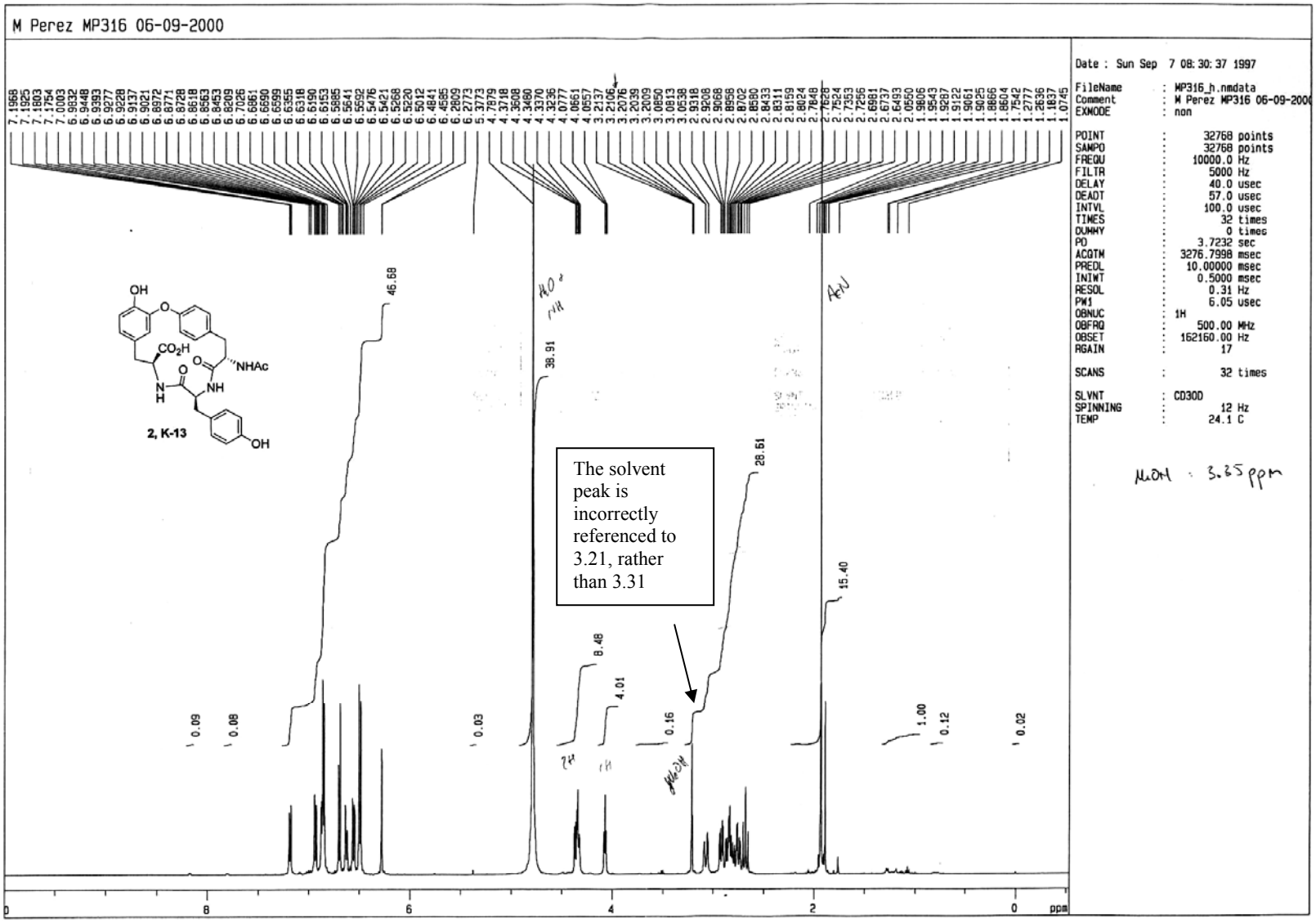

Manuel Perez MP237C 2000-02-08
Date : Wed Oct 28 22:26:23 1992
FileName : MP237C_h.nmdata
Comment : Manuel Perez MP237C
EXMODE : non
POINT : 32768 points
SAMPO : 32768 points
FREQU : 10000.0 Hz
FILTR : 5000 Hz
DELAY : 40.0 usec
DEADT : 57.0 usec
INTVL : 100.0 usec
TIMES : 8 times
DUMMY : 0 times
PD : 3.7232 sec
ACQTM : 3276.7998 msec
PREDL : 10.00000 msec
INIWT : 0.5000 msec
RESOL : 0.31 Hz
PW1 : 6.05 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162160.00 Hz
RGAIN : 22
SCANS : 8 times
SLVNT : CDCL3
SPINNING : 14 Hz
TEMP : 23.5 C
OMe
NHBoc
MeO2C
28
6.02
79.54
5.40
4.09
12.41
5.63
1.00
63.00
12.37
25.77
1.46
1.34
59.15
2.27
8
6
4
2
0
ppm

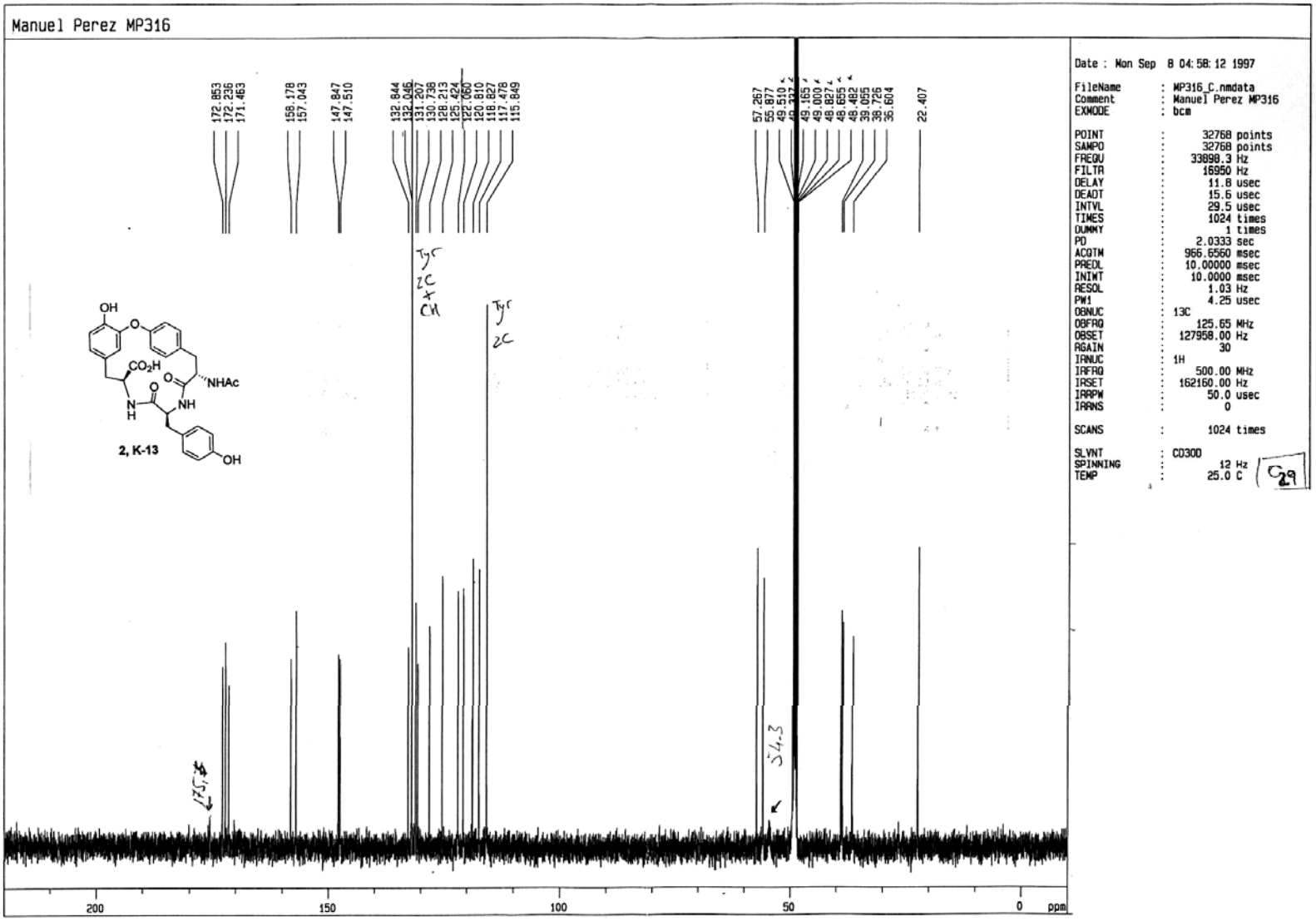

Manuel Perez MP237C 2000-02-08
171.208
133.789
130.656
130.376
129.594
127.867
117.733
114.797
114.361
82.034
77.378
76.868
56.140
55.326
53.203
28.395
OMe
NHBoc
MeO2C
28
OMe
C2;C2"
C3"
C3
C4'
C6'
C1"
C1'
C2'
C6'
C5'
3H
3CH(α)
CH2-I
200
150
100
50
0
ppm
Date : Thu Oct 29 00:28:04 1992
FileName : MP237C_c.nmdata
Comment : Manuel Perez MP237C
EXMODE : bcm
POINT : 32768 points
SAMPO : 32768 points
FREQU : 33898.3 Hz
FILTR : 16950 Hz
DELAY : 11.8 usec
DEADT : 15.6 usec
INTVL : 29.5 usec
TIMES : 2400 times
DUMMY : 1 times
PD : 2.0333 sec
ACQTM : 966.6560 msec
PREDL : 10.00000 msec
INIWT : 10.0000 msec
RESOL : 1.03 Hz
PW1 : 4.25 usec
OBNUC : 13C
OBFRQ : 125.65 MHz
OBSET : 127958.00 Hz
RGAIN : 32
IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162160.00 Hz
IRAPW : 50.0 usec
IRANS : 0
SCANS : 2400 times
SLVNT : CDCL3
SPINNING : 12 Hz
TEMP : 24.1 C

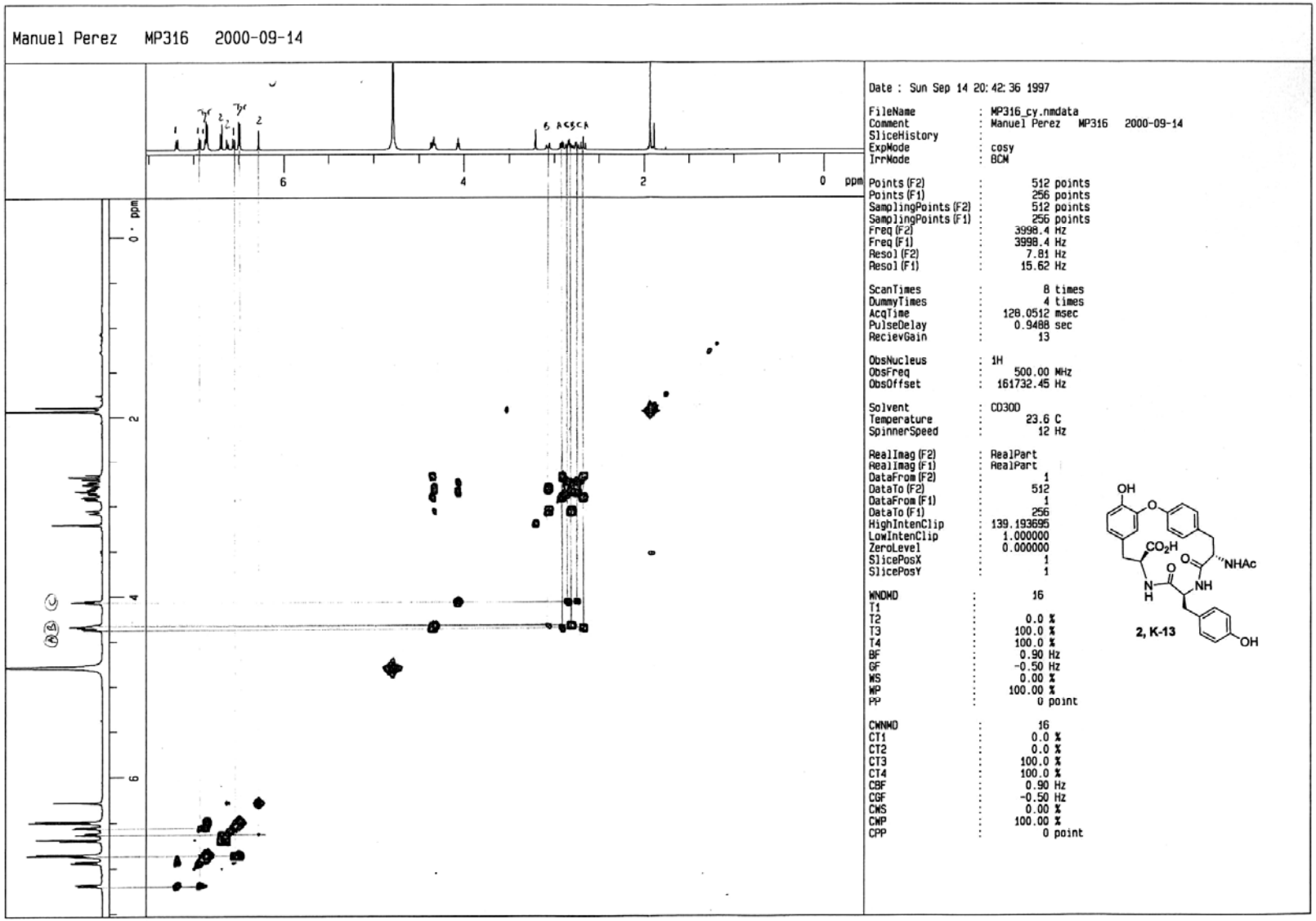

M.Perez MP298F1 04/08/00
Date : Mon Aug 4 14:56:23 1997
FileName : MP298F1_h.nmdata
Comment : M.Perez MP298F1
EXMODE : non
POINT : 32768 points
SAMPD : 32768 points
FREQU : 10000.0 Hz
FILTR : 5000 Hz
DELAY : 40.0 usec
DEADT : 57.0 usec
INTVL : 100.0 usec
TIMES : 32 times
DUMMY : 0 times
PD : 3.7232 sec
ACQTM : 3276.7998 msec
PREDL : 10.00000 msec
INIWT : 0.5000 msec
RESOL : 0.31 Hz
PW1 : 6.05 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162160.00 Hz
RGAIN : 19
SCANS : 32 times
SLVNT : CDCL3
SPINNING : 14 Hz
TEMP : 23.6 C
OMe
CO2Me
NHBoc
NH
10
OMe
10.07
10.65
13.14
5.51
1.81
1.69
1.00
0.74
1.03
0.91
0.74
0.01
0.00
0.03
0.39
0.31
0.01
ppm

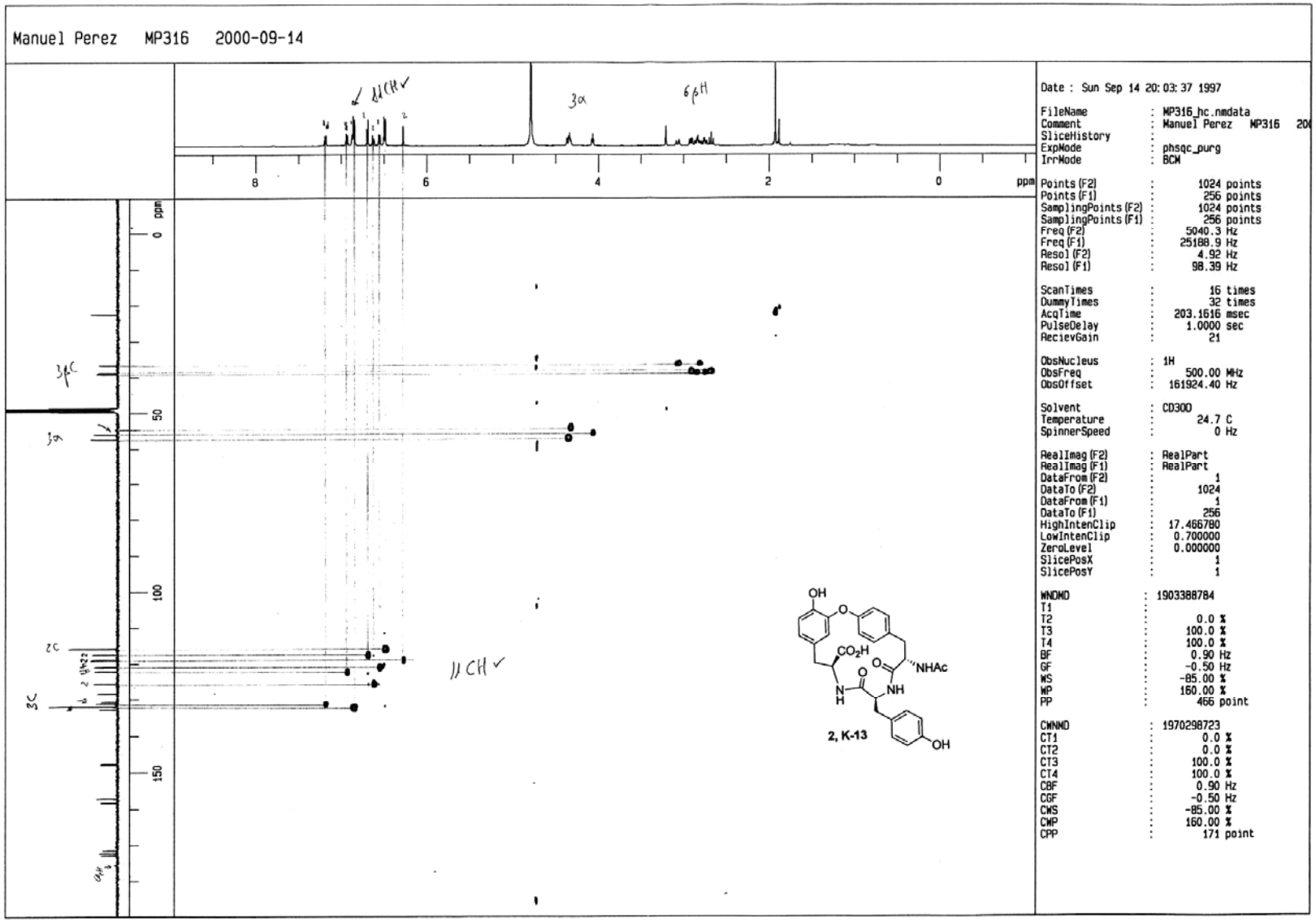

Manuel Perez MP298F1 2000-08-07
170.574
169.875
158.639
155.291
148.842
148.538
132.547
131.412
130.113
129.775
128.336
127.941
122.685
122.479
121.245
117.972
113.941
112.066
77.255
76.745
57.407
56.370
56.049
55.145
53.722
52.455
39.450
38.628
35.247
29.250
28.346
1.909
OMe
CO2Me
NHBoc
NH
10
OMe
200
150
100
50
0
ppm
Date : Thu Aug 7 12:27:01 1997
FileName : MP298F1_c.nmdata
Comment : Manuel Perez MP298F1
EXMODE : bcm
POINT : 32768 points
SAMPD : 32768 points
FREQU : 33898.3 Hz
FILTR : 16950 Hz
DELAY : 11.8 usec
DEADT : 15.6 usec
INTVL : 29.5 usec
TIMES : 2000 times
DUMMY : 1 times
PD : 2.0333 sec
ACQTM : 966.6560 msec
PREDL : 10.00000 msec
ININT : 10.0000 msec
RESOL : 1.03 Hz
PW1 : 4.25 usec
OBNUC : 13C
OBFRQ : 125.65 MHz
OBSET : 127958.00 Hz
RGAIN : 31
IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162160.00 Hz
IRPPW : 50.0 usec
IRANS : 0
SCANS : 2000 times
SLVNT : CDCL3
SPINNING : 14 Hz
TEMP : 25.6 C


M Perez 314B 31-8-2000
7.2987 7.2200 7.0467 7.0418 7.0302 7.0253 6.9747 6.9558 6.9387 6.7752 6.7587 6.7142 6.7093 6.6928 6.6867 6.6690 6.5555 6.5519 6.5354 6.1217 6.1180 4.3803 4.3730 4.3681 3.9434 3.9337 3.9270 3.9166 3.8483 3.8245 3.7287 3.6756 3.6738 3.6493 3.6262 3.4419 3.4401 3.4279 3.3016 3.2985 2.9989 2.9873 2.9782 2.7274 2.7152 2.7042 1.9848 1.1575 1.1550 1.1434 1.1410 1.1294 1.1270 0.0000 -0.0024 -0.0067
OMe
CO2Me
NHAc
NH
29
OMe
4.16
3.02
0.41
1.00
0.96
1.47
1.48
1.98
0.70
2.96
8
6
4
2
0
ppm
Date : Sun Aug 31 10:02:04 1997
FileName : 314B_h.nmdata
Comment : M Perez 314B 31-8-2000
EXMODE : non
POINT : 32768 points
SAMPO : 32768 points
FREQU : 10000.0 Hz
FILTR : 5000 Hz
DELAY : 40.0 usec
DEADT : 57.0 usec
INTVL : 100.0 usec
TIMES : 32 times
DUMMY : 0 times
PD : 3.7232 sec
ACQTM : 3276.7998 msec
PREDL : 10.00000 msec
INIWT : 0.5000 msec
RESOL : 0.31 Hz
PW1 : 6.05 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162160.00 Hz
RGAIN : 23
SCANS : 32 times
SLVNT : CDCL3
SPINNING : 12 Hz
TEMP : 23.4 C


M Perez MP316 06-09-2000
Date : Sun Sep 7 08:30:37 1997
FileName : MP316_h.nmdata
Comment : M Perez MP316 06-09-2000
EXMODE : non
POINT : 32768 points
SAMPO : 32768 points
FREQU : 10000.0 Hz
FILTR : 5000 Hz
DELAY : 40.0 usec
DEADT : 57.0 usec
INTVL : 100.0 usec
TIMES : 32 times
DUMMY : 0 times
PD : 3.7232 sec
ACQTM : 3276.7998 msec
PREDL : 10.00000 msec
INIWT : 0.5000 msec
RESOL : 0.31 Hz
PW1 : 6.05 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162160.00 Hz
RGAIN : 17
SCANS : 32 times
SLVNT : CD3OD
SPINNING : 12 Hz
TEMP : 24.1 C
MeOH : 3.35 ppm
2, K-13
The solvent peak is incorrectly referenced to 3.21, rather than 3.31
46.68
38.91
28.61
15.40
8.48
4.01
0.09
0.08
0.03
0.16
1.00
0.12
0.02
ppm


Manuel Perez MP316
172.853
172.236
171.463
158.178
157.043
147.847
147.510
132.844
132.046
131.207
130.738
128.213
125.424
122.060
120.810
118.827
117.478
115.849
57.267
55.877
49.510
49.165
49.009
48.827
48.655
48.482
39.055
36.726
36.604
22.407
Tyr 2C + CH
Tyr 2C
OH
CO2H
NHAc
NH
N
H
2, K-13
OH
54.3
200
150
100
50
0
ppm
Date : Mon Sep 8 04:58:12 1997
FileName : MP316_C.nmdata
Comment : Manuel Perez MP316
EXMODE : bcm
POINT : 32768 points
SAMPO : 32768 points
FREQU : 33898.3 Hz
FILTR : 16950 Hz
DELAY : 11.8 usec
DEADT : 15.6 usec
INTVL : 29.5 usec
TIMES : 1024 times
DUMMY : 1 times
PD : 2.0333 sec
ACQTM : 966.6560 msec
PREDL : 10.00000 msec
INIWT : 10.0000 msec
RESOL : 1.03 Hz
PW1 : 4.25 usec
OBNUC : 13C
OBFRQ : 125.65 MHz
OBSET : 127958.00 Hz
AGAIN : 30
IRNUC : 1H
IRFRQ : 500.00 MHz
IRSET : 162160.00 Hz
IRPPW : 50.0 usec
IRANS : 0
SCANS : 1024 times
SLVNT : CD3OD
SPINNING : 12 Hz
TEMP : 25.0 C


Manuel Perez MP316 2000-09-14
6 4 2 0 ppm
0 2 4 6 ppm
Date : Sun Sep 14 20:42:36 1997
FileName : MP316_cy.nmdata
Comment : Manuel Perez MP316 2000-09-14
SliceHistory :
ExpMode : cosy
IrrMode : BCM
Points(F2) : 512 points
Points(F1) : 256 points
SamplingPoints(F2) : 512 points
SamplingPoints(F1) : 256 points
Freq(F2) : 3998.4 Hz
Freq(F1) : 3998.4 Hz
Resol(F2) : 7.81 Hz
Resol(F1) : 15.62 Hz
ScanTimes : 8 times
DummyTimes : 4 times
AcqTime : 128.0512 msec
PulseDelay : 0.9488 sec
RecievGain : 13
ObsNucleus : 1H
ObsFreq : 500.00 MHz
ObsOffset : 161732.45 Hz
Solvent : CD3OD
Temperature : 23.6 C
SpinnerSpeed : 12 Hz
RealImag(F2) : RealPart
RealImag(F1) : RealPart
DataFrom(F2) : 1
DataTo(F2) : 512
DataFrom(F1) : 1
DataTo(F1) : 256
HighIntenClip : 139.193695
LowIntenClip : 1.000000
ZeroLevel : 0.000000
SlicePosX : 1
SlicePosY : 1
WNDWD : 16
T1 :
T2 : 0.0 %
T3 : 100.0 %
T4 : 100.0 %
BF : 0.90 Hz
GF : -0.50 Hz
WS : 0.00 %
WP : 100.00 %
PP : 0 point
CWNWD : 16
CT1 : 0.0 %
CT2 : 0.0 %
CT3 : 100.0 %
CT4 : 100.0 %
CBF : 0.90 Hz
CGF : -0.50 Hz
CWS : 0.00 %
CWP : 100.00 %
CPP : 0 point
OH
O
CO2H
NHAc
N
H
O
NH
OH
2, K-13


Manuel Perez MP316 2000-09-14
Date : Sun Sep 14 20:03:37 1997
FileName : MP316_hc.nmdata
Comment : Manuel Perez MP316
SliceHistory :
ExpMode : phsqc_purg
IrrMode : BCM
Points (F2) : 1024 points
Points (F1) : 256 points
SamplingPoints (F2) : 1024 points
SamplingPoints (F1) : 256 points
Freq (F2) : 5040.3 Hz
Freq (F1) : 25188.9 Hz
Resol (F2) : 4.92 Hz
Resol (F1) : 98.39 Hz
ScanTimes : 16 times
DummyTimes : 32 times
AcqTime : 203.1616 msec
PulseDelay : 1.0000 sec
RecievGain : 21
ObsNucleus : 1H
ObsFreq : 500.00 MHz
ObsOffset : 161924.40 Hz
Solvent : CD3OD
Temperature : 24.7 C
SpinnerSpeed : 0 Hz
RealImag (F2) : RealPart
RealImag (F1) : RealPart
DataFrom (F2) : 1
DataTo (F2) : 1024
DataFrom (F1) : 1
DataTo (F1) : 256
HighIntenClip : 17.466780
LowIntenClip : 0.700000
ZeroLevel : 0.000000
SlicePosX : 1
SlicePosY : 1
WNDNO : 1903388784
T1 :
T2 : 0.0 %
T3 : 100.0 %
T4 : 100.0 %
BF : 0.90 Hz
GF : -0.50 Hz
WS : -85.00 %
WP : 160.00 %
PP : 466 point
CWNNO : 1970298723
CT1 : 0.0 %
CT2 : 0.0 %
CT3 : 100.0 %
CT4 : 100.0 %
CBF : 0.90 Hz
CGF : -0.50 Hz
CWS : -85.00 %
CWP : 160.00 %
CPP : 171 point
2, K-13