Concise Total Synthesis and Structural Revision of (+)-Pestalazine B

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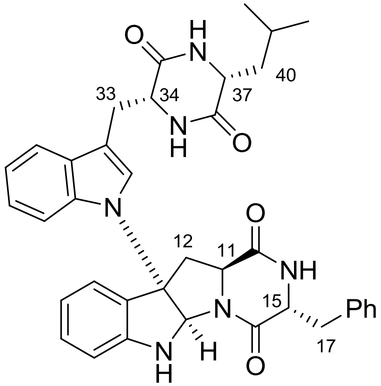
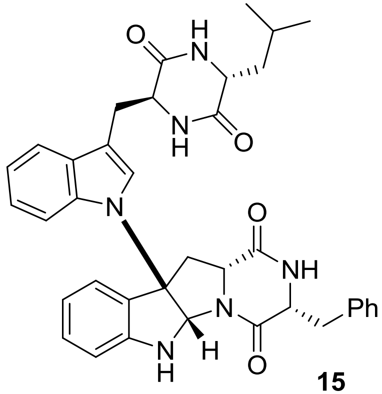
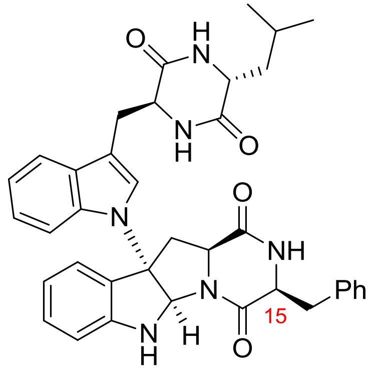
Contents

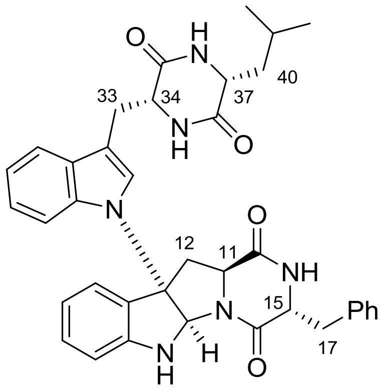
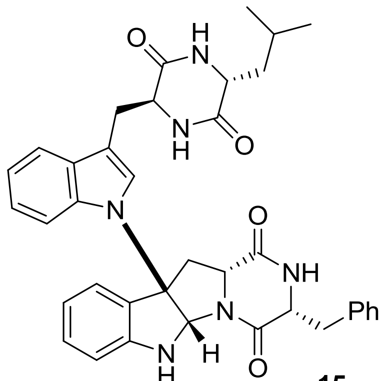
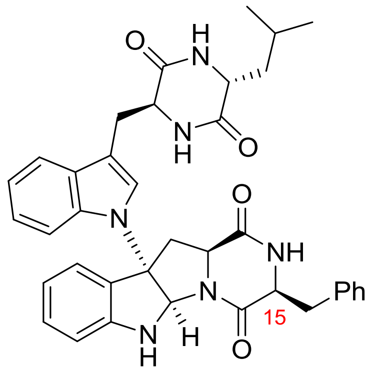
1. General synthetic methods.

Solvents were dried according to published methods and distilled before use. All reagents were commercial compounds of the highest purity available. Reactions were carried out under an argon atmosphere, unless indicated otherwise. Analytical TLC was performed on aluminum plates with Merck Kieselgel $60F_{254}$ and visualised by UV irradiation (254 nm) or by staining with a ethanolic solution of phosphomolibdic acid. Flash-column chromatography was carried out using Merck Kieselgel 60 (230-400 mesh) under pressure. IR spectra were obtained on a JASCO IR 4200 spectrophotometer from a thin film deposited onto NaCl glass. Specific rotations were obtained on a JASCO P-1020 polarimeter. Mass spectra and HRMS (ESI^+) were taken on a Apex III FT ICR MS (Bruker Daltonics) and (FAB^+) on a Micromass AutoSpec apparatus. ^{1}H-NMR spectra were recorded in $CDCl_3$, CD_3OD, $(CD_3)_2CO$ or DMSO-d_6 at ambient temperature or the indicated temperature on a Bruker AMX-400 spectrometer at 400 MHz with residual protic solvent as the internal reference $CDCl_3$ (δ_H= 7.24 ppm), CD_3OD (δ_H= 3.31 ppm), $(CD_3)_2CO$ (δ_H= 2.05 ppm). Chemical shifts (δ) are given in parts per million (ppm) and coupling constants (J) are given in Hertz (Hz). The proton spectra are reported as follows: δ (multiplicity, coupling constant J, number of protons, assignment). ^{13}C-NMR spectra were recorded in $CDCl_3$, CD_3OD or $(CD_3)_2CO$ at ambient temperature otherwise indicated on the same spectrometer at 100 MHz, with the central peak of $CDCl_3$ (δ_C= 77.23 ppm), CD_3OD (δ_C= 49.15 ppm), $(CD_3)_2CO$ (δ_C= 29.92 ppm) as the internal reference. DEPT135 and bi-dimensional (COSY, HSQCed, HMBC) sequences were used where appropriate to aid in the assignment of signals. CD spectra were recorded on a JASCO J-815 spectropolarimeter, using CH_3OH as a solvent.

Assignment	**Che´s Report** **Acetone –d_6-600 MHz** **Pestalazine B** $[\alpha]_D$ +199º (c 0.1 MeOH)	***Epi*-C34** **Acetone –d_6-400 MHz**  **11** $[\alpha]_D$ +122º (c 0.1 MeOH)	**Acetone –d_6-400 MHz**  **15** $[\alpha]_D$ -79º (c 0.09 MeOH)	***Epi*-C15** **Acetone –d_6-400 MHz**  **16** $[\alpha]_D$ +166º (c 0.1 MeOH)
N1	6.83 (d, *J* = 3.0 Hz)	6.67 overlapped	6.54 (d, *J* = 3.9 Hz)	6.61 (d, *J* = 3.7 Hz)
C2	6.03 (d, *J* = 3.0 Hz)	6.07 (d, *J* = 4.0 Hz)	5.92 (d, *J* = 3.9 Hz)	6.06 (d, *J* = 3.4 Hz)
C3	-	-	-	-
C4	-	-	-	-
C5	6.90 (d, *J* = 7.2 Hz)	6.86 overlapped	7.20 overlapped	6.92 (d, *J* = 7.2 Hz)
C6	6.62 (t, *J* = 7.2 Hz)	6.64	6.68	6.65 (t, *J* = 7.4 Hz)
C7	7.14 m	7.19 (d, *J* = 7.7 Hz)	6.98	7.19 (m)
C8	6.83 (d, *J* = 7.8 Hz)	6.86 overlapped	6.64	6.86 (d, *J* = 8.0 Hz)
C9	-		-	
C11	4.82 (dd, *J* = 12.0, 6.0 Hz)	4.76 (dd, *J* = 12.1, 5.7 Hz)	4.97 (dd, *J* = 11.7, 6.2 Hz)	4.84 (dd, *J* = 11.6, 6.0 Hz)

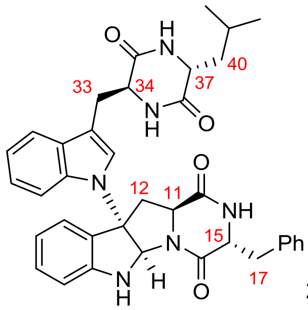
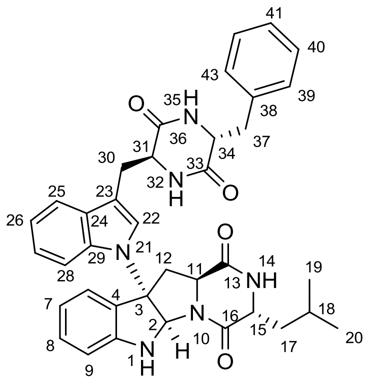
C12	3.68 (dd, *J* = 14.0, 6.0 Hz) 2.42 (dd, *J* = 14.0, 12.0 Hz)	3.65 overlapped 2.38 (dd, *J* = 14.7, 12.2 Hz)	3.56 overlapped 2.45 (dd, *J* = 14.8, 11.8 Hz)	3.68 (dd, *J* = 14.6, 6.1 Hz) 2.41 (dd, *J* = 14.6, 11.7 Hz)
C13	-	-	-	
N14	7.32 br s	7.38 (d, *J* = 4.3 Hz)	7.4-7.3	6.85 br s
C15	3.47 (br t, *J* = 4.8 Hz)	4.12 (dt, *J* = 11.4, 4.0, 4.0 Hz)	4.76 (dd, *J* = 7.5, 4.8 Hz)	4.53 (dd, *J* = 6.7, 5.2 Hz)
C16	-	-	-	
C17	3.06 (dd, *J* = 14.5, 4.8 Hz) 2.88 overlapped	3.55 overlapped 3.05 (dd, *J* = 13.6, 3.9Hz)	3.41 (dd, *J* = 14.4, 4.7 Hz) 3.00 (dd, *J* = 14.8, 7.6 Hz)	3.68 (dd, *J* = 14.6, 6.1 Hz) 3.02 (dd, *J* = 14.6, 7.6 Hz)
C18	-	-	-	
C19, C23	7.14 m	7.33 (dd, *J* = 7.8, 1.4 Hz)	7.3-7.2 m	7.38 (d, *J* = 7.4 Hz)
C20, C22	7.20 m	7.25 overlapped	7.4-7.3 m	7.27 (d, *J* = 7.6 Hz)
C21	7.20 m	7.25 overlapped	7.4-7.3 m	7.20 (m)
	DKP	DKP	DKP	
C24	6.75 (d, *J* = 7.8 Hz)	6.68 overlapped	6.63 m	6.80 (d, *J* = 8.3 Hz)
C25	6.95 (t, *J* = 7.8 Hz)	6.93 (t, *J* = 7.0 Hz)	6.92 m	6.92 (m)
C26	6.98 (t, *J* = 7.8 Hz)	6.99 (t, *J* = 7.0 Hz)	6.98 m	7.00 (m)
C27	7.53 (d, *J* = 7.8 Hz)	7.61 (t, *J* = 7.6 Hz)	7.61 (d, *J* = 7.8 Hz)	7.62 (d, *J* = 7.9 Hz)
C28	-	-	-	-
C29	-	-	-	-
N30	-	-	-	-
C31	7.64 s	7.71 s	7.66 (s)	7.69 (s)
C32	-	-	-	
C33	3.21 (dd, *J* = 14.0, 5.4 Hz) 3.15 (dd, *J* = 14.0, 4.8 Hz)	3.64 overlapped 3.23 (dd, *J* = 14.4, 5.4 Hz)	3.55 overlapped 3.15 (dd, *J* = 14.4, 5.0 Hz)	3.27 (m) 3.27 (m)

C34	3.62 (dd, *J* = 5.2, 4.8 Hz)	4.35 m	4.3-4.2 (m)	4.22 (m)
N35	7.38 br s	7.55 (t, *J* = 1.6 Hz)	7.11 s	7.17 br s
C36	-	-	-	
C37	3.85 (m)	3.60 overlapped	2.13 (dd, *J* = 8.5, 4.2 Hz)	2.98 m
N38	8.05	7.09 (d, *J* = 1.9 Hz)	6.84	6.99 (m)
C39	-	-	-	-
C40	1.73 (m) 1.50 (m)	0.96 (ddd, *J* = 13.3, 11.0, 2.6Hz) -0.49 (ddd, *J* = 13.3, 11.0, 2.6Hz)	1.39 (ddd, *J* = 13.5, 9.0, 4.3 Hz) 1.27 (ddd, *J* = 13.5, 8.4, 5.7 Hz)	1.56 (ddd, *J* = 13.5, 8.8, 4.5 Hz) 1.43 (m)
C41	1.80 m	1.2-1.1 (m)	1.6-1.5 (m)	1.69 (m)
C42	0.95 (d, *J* = 6.6 Hz)	0.60 (dd, *J* = 6.5Hz)	0.68 (d, *J* = 6.5 Hz)	0.78 (d, *J* = 6.6 Hz)
C43	0.90 (d, *J* = 6.0 Hz)	0.34 (dd, *J* = 6.5 Hz)	0.39 (d, *J* = 6.5 Hz)	0.59 (d, *J* = 6.5 Hz)

Assignment	**Che´s Report** **Acetone –d_6-600 MHz** **Pestalazine B** $[\alpha]_D$ +199º (c 0.1 MeOH)	***Epi*-C34** **Acetone –d_6-100 MHz**  **11** $[\alpha]_D$ +122º (c 0.1 MeOH)	**Acetone –d_6-100 MHz**  **15** $[\alpha]_D$ -79º (c 0.09 MeOH)	***Epi*-C15** **Acetone –d_6-100 MHz**  **16** $[\alpha]_D$ +166º (c 0.1 MeOH)
N1				
C2	83.4 CH	84.1 CH	83.6 CH	83.1 CH
C3	74.2 qC	74.3 qC	75.2 qC	74.9 qC
C4	129.8 qC	129.6 qC	129.5 qC	129.8 qC
C5	123.3 CH	123.5 CH	130.8 CH	123.7 CH
C6	119.4 CH	119.8 CH	119.8 CH	119.8 CH
C7	130.5 CH	130.8 CH	120.7 CH	130.8 CH
C8	110.9 CH	111.1 CH	111.3 CH	111.1 CH
C9	148.9 qC	148.9 qC	148.9 qC	148.9 qC
C11	57.2 CH	57.5 CH	58.7 CH	58.6CH
C12	41.2 CH_2	41.6 CH_2	40.2 CH_2	40.6 CH_2

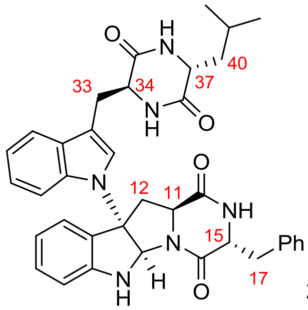
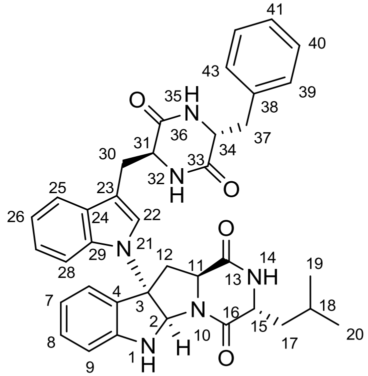
C13	168.8 qC	169.0 qC	170.5 qC	168.8 qC
N14	-	-		-
C15	56.1 CH	60.1 CH	57.0 CH	57.2 CH
C16	168.4 qC	170.2 qC	168.7 qC	168.2 qC
C17	38.9 CH_2	39.9 CH_2	35.7 CH_2	36.2 CH_2
C18	137.1 qC	138.2 qC	138.5 qC	138.1 qC
C19, C23	130.9 CH	130.8 CH	130.3 CH	130.5 CH
C20, C22	130.9 CH	129.3 CH	129.4 CH	129.4 CH
C21	127.4 CH	129.3 CH	127.5 CH	127.6 CH
	DKP	DKP	DKP	
C24	112.8 qC	113.1 qC	113.2 CH	113.0 CH
C25	122.2 CH	122.4 CH	122.6 CH	122.5 CH
C26	120.3 CH	120.7 CH	123.5 CH	120.7 CH
C27	120.3 CH	120.9 CH	120.8 CH	120.4 CH
C28	130.8 qC	131.3 qC	130.7 qC	130.9 qC
C29	136.3 qC	136.2 qC	136.7 qC	136.9 qC
N30	-	-	-	-
C31	126.4 CH	127.6 CH	127.8	126.8 CH
C32	109.9 qC	109.6 qC	109.9 qC	110.1 qC
C33	30.2 CH_2	30.7 CH_2	30.8 CH_2	30.4 CH_2
C34	55.8 CH	55.6 CH	56.9 CH	56.7 CH
N35	-	-	-	
C36	168.9 qC	167.9 qC	171.0 qC	169.9 qC
C37	56.7 CH	54.0 CH	52.7 CH	53.3 CH

N38	-	-	-	
C39	168.6 qC	167.9 qC	169.6 qC	169.6 qC
C40	42.8 CH_2	44.1 CH_2	41.4 CH_2	42.4 CH_2
C41	24.9 CH	24.1 CH	24.3 CH	24.7 CH
C42	23. 2 CH_3	23.9 CH_3	23.4 CH_3	23. 4 CH_3
C43	21.7 CH_3	21.0 CH_3	21.2 CH_3	21.9 CH_3

Assignment Pestalazine A numbering	**Che´s Report Acetone –d_6-600 MHz** **Pestalazine B** $[\alpha]_D$ +199º (c 0.1 MeOH)	**Acetone –d_6-400 MHz**  **2** $[\alpha]_D$ +87º (c 0.1 MeOH)	**Acetone –d_6-600 MHz**  **21** $[\alpha]_D$ +194º (c 0.1 MeOH)	**Assignment Revised numbering**
N1	6.83 (d, J = 3.0 Hz)	6.59 (d, J = 3.6 Hz)	6.65 (d, J = 3.0 Hz)	N1
C2	6.03 (d, J = 3.0 Hz)	5.86 (d, J = 3.6 Hz)	6.05 (d, J = 3.3 Hz)	C2
C3	-	-	-	C3
C4	-	-	-	C4
C5	6.90 (d, J = 7.2 Hz)	6.86 (d, J = 7.9 Hz)	6.93 (m)	C5
C6	6.62 (t, J = 7.2 Hz)	6.60 (t, J = 7.2 Hz)	6.64 (t, J = 7.2 Hz)	C6
C7	7.14 m	7.13 (t, J = 7.2 Hz)	7.17 (m)	C7
C8	6.83 (d, J = 7.8 Hz)	6.79 overlapped	6.85 (d, J = 7.8 Hz)	C8
C9	-	-		C9
C11	4.82 (dd, J = 12.0, 6.0 Hz)	3.33 overlapped	4.84 (dd, J = 11.7, 6.0 Hz)	C11

C12	3.68 (dd, *J* = 14.0, 6.0 Hz) 2.42 (dd, *J* = 14.0, 12.0 Hz)	3.35 overlapped 2.19 (dd, *J* = 15.8, 13.3 Hz)	3.69 (dd, *J* = 14.8, 6.0 Hz) 2.41 (dd, *J* = 14.6, 11.7 Hz)	C12
C13	-	-	-	C13
N14	7.32 br s	7.48 (d, *J* = 4.0 Hz)	6.98 (m)	N14
C15	3.47 (br t, *J* = 4.8 Hz)	4.21 (dt, *J* = 5.7, 4.4, 4.4 Hz)	3.50 (br t, *J* = 4.7 Hz)	C34
C16	-	-		C16
C17	3.06 (dd, *J* = 14.5, 4.8 Hz) 2.88 overlapped	3.14 (dd, *J* = 13.6, 6.1 Hz) 2.99(dd, *J* = 13.6, 6.1 Hz)	3.06 (dd, *J* = 13.9, 5.4 Hz) 2.96 (dd, *J* = 13.9, 4.6 Hz)	C37
C18	-	-		C38
C19, C23	7.14 m	7.12 overlapped	7.12 (m)	C39, C43
C20, C22	7.20 m	7.10 overlapped	7.20 (m)	C40, C42
C21	7.20 m	7.22 (t, *J* = 7.3 Hz)	7.20 (m)	C41
		DKP		
C24	6.75 (d, *J* = 7.8 Hz)	6.66 (d, *J* = 8.0 Hz)	6.78 (d, *J* = 8.2 Hz)	C28
C25	6.95 (t, *J* = 7.8 Hz)	6.89 (t, *J* = 7.8 Hz)	6.94 (m)	C27
C26	6.98 (t, *J* = 7.8 Hz)	6.98 (t, *J* = 7.8 Hz)	6.98 (m)	C26
C27	7.53 (d, *J* = 7.8 Hz)	7.62 (d, *J* = 7.8 Hz)	7.52 (d, *J* = 7.8 Hz)	C25
C28	-	-	-	C24
C29	-	-	-	C29
N30	-	-	-	N30
C31	7.64 (s)	7.29 s	7.66 (s)	C22
C32	-	-		C23
C33	3.21 (dd, *J* = 14.0, 5.4 Hz)	3.50 (dd, *J* = 14.5, 5.1 Hz)	3.21 (m)	C30

	3.15 (dd, *J* = 14.0, 4.8 Hz)	3.36 overlapped	3.21 (m)	
C34	3.62 (dd, *J* = 5.2, 4.8 Hz)	4.30 (dd, *J* = 4.8, 2.3 Hz)	3.66 (m)	C31
N35	7.38 br s	7.14 br s	7.11 (m)	N32
C36	-	-		C33
C37	3.85 (m)	2.82 overlapped	3.89 (dt, *J* = 9.6, 4.8 Hz)	C15
N38	8.05	6.79 overlapped	7.81 (d, *J* = 4.3 Hz)	N35
C39	-	-	-	C36
C40	1.73 (m) 1.50 (m)	1.57 (m) 1.42 (m)	1.75 (m) 1.52 (ddd, *J* = 13.6, 8.5, 5.3 Hz)	C17
C41	1.80 (m)	1.69 m	1.80 (m)	C18
C42	0.95 (d, *J* = 6.6 Hz)	0.76 (d, *J* = 6.5 Hz)	0.95 (d, *J* = 6.5 Hz)	C19
C43	0.90 (d, *J* = 6.0 Hz)	0.52 (d, *J* = 6.5 Hz)	0.90 (d, *J* = 6.5 Hz)	C20

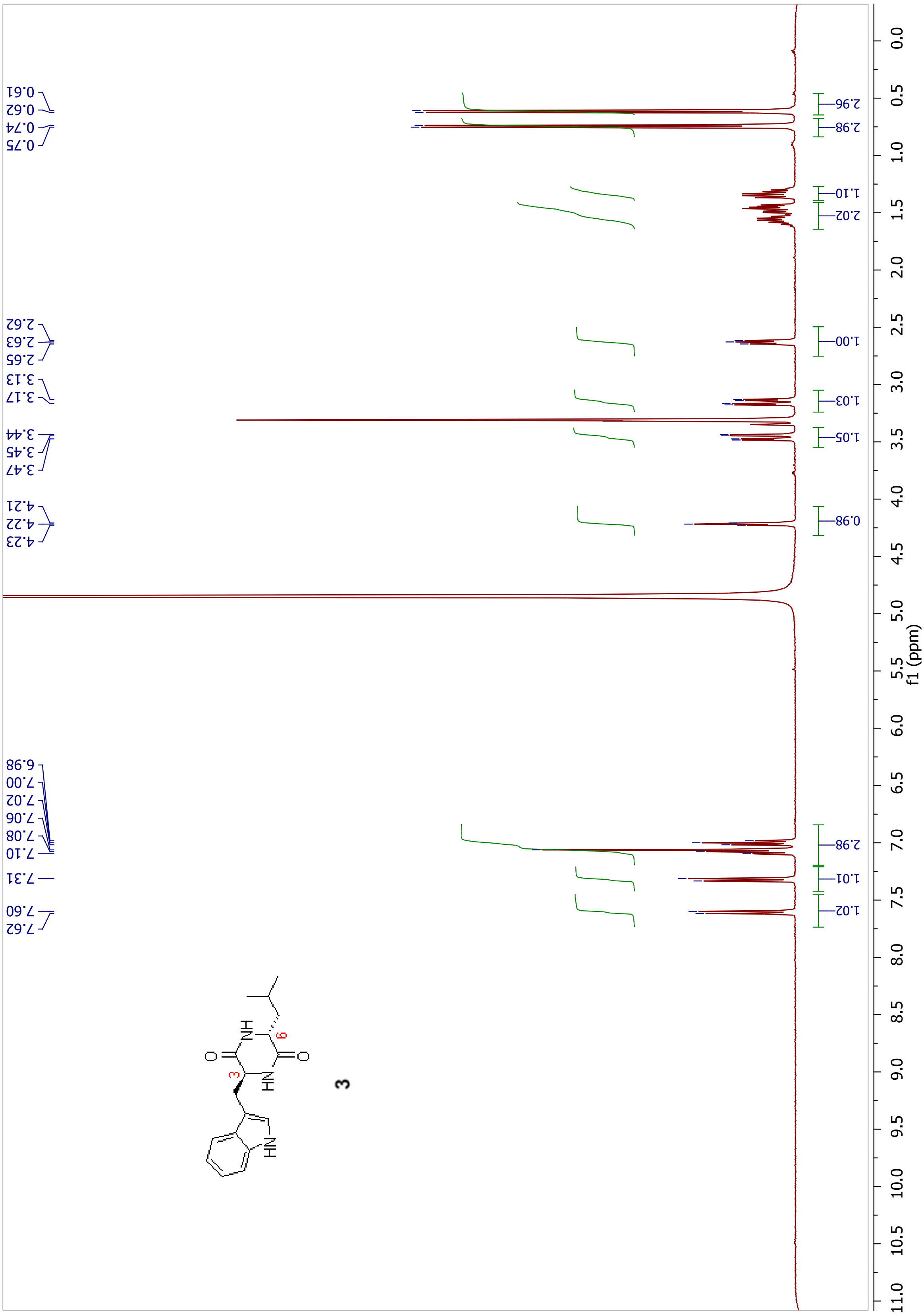
Assignment Pestalazine A numbering	**Che´s Report Acetone –d_6-150 MHz** **Pestalazine B** $[\alpha]_D$ +199º (c 0.1 MeOH)	**Acetone –d_6-100 MHz**  **2** $[\alpha]_D$ +87º (c 0.1 MeOH)	**Acetone –d_6-100 MHz**  **21** $[\alpha]_D$ +194º (c 0.1 MeOH)	**Assignment Revised numbering**
N1				N1
C2	83.4 CH	83.2 CH	83.5 CH	C2
C3	74.2 qC	74.1 qC	74.4 qC	C3
C4	129.8 qC	129.6 qC	129.9 qC	C4
C5	123.3 CH	122.5 CH	123.6 CH	C5
C6	119.4 CH	119.7 CH	119.7 CH	C6
C7	130.5 CH	128.0 CH	130.8 CH	C7
C8	110.9 CH	111.0 CH	111.0 CH	C8
C9	148.9 qC	148.9 qC	148.9 qC	C9
C11	57.2 CH	56.8 CH	57.3 CH	C11
C12	41.2 CH_2	41.2 CH_2	41.3 CH_2	C12

C13	168.8 qC	168.8 qC	169.0 qC	C13
N14	-	-	-	N14
C15	56.1 CH	59.8 CH	56.3 CH	C34
C16	168.4 qC	167.7 qC	168.6 qC	C16
C17	38.9 CH_2	40.5 CH_2	39.1 CH_2	C37
C18	137.1 qC	137.0 qC	137.1 qC	C38
C19, C23	130.9 CH	130.8 CH	131.0 CH	C39, C43
C20, C22	130.9 CH	129.4 CH	129.1 CH	C40, C42
C21	127.4 CH	123.8 CH	127. 7 CH	C41
	DKP	DKP	DKP	
C24	112.8 CH	112.8 qC	113.0 CH	C28
C25	122.2 CH	122.5 CH	122.4 CH	C27
C26	120.3 CH	120.5 CH	120.5 CH	C26
C27	120.3 CH	120.6CH	120.4 CH	C25
C28	130.8 qC	130.7 qC	130.8 qC	C24
C29	136.3 qC	136.5 qC	136.6 qC	C29
N30	-	-	-	N30
C31	126.4 CH	126.9 CH	126.6 CH	C22
C32	109.9 qC	109.8 qC	110.0 qC	C23
C33	30.2 CH_2	30.4 CH_2	30.3 CH_2	C30
C34	55.8 CH	56.5 CH	55.8 CH	C31
N35	-	-		N32
C36	168.9 qC	171.5 qC	169.0 qC	C33
C37	56.7 CH	53.2 CH	56.9 CH	C15

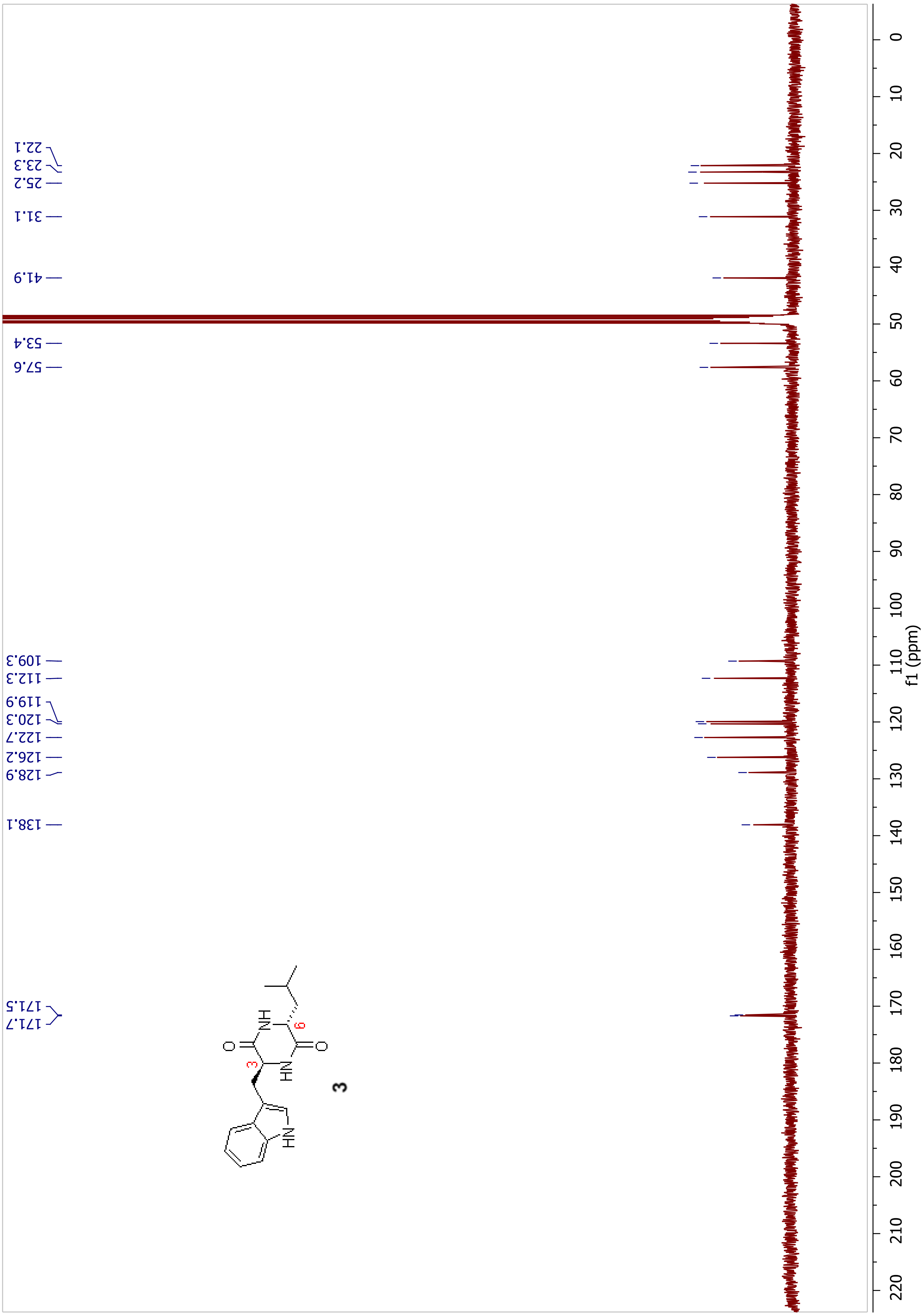
N38	-	-	-	N35
C39	168.6 qC	169.7 qC	168.6 qC	C36
C40	42.8 CH_2	42.3 CH_2	42.9 CH_2	C17
C41	24.9 CH	24.5 CH	25.1 CH	C18
C42	23. 2 CH_3	23.4 CH_3	23.3 CH_3	C19
C43	21.7 CH_3	21.7 CH_3	21.8 CH_3	C20

3. ^{1}H NMR, ^{13}C NMR Spectral Data.

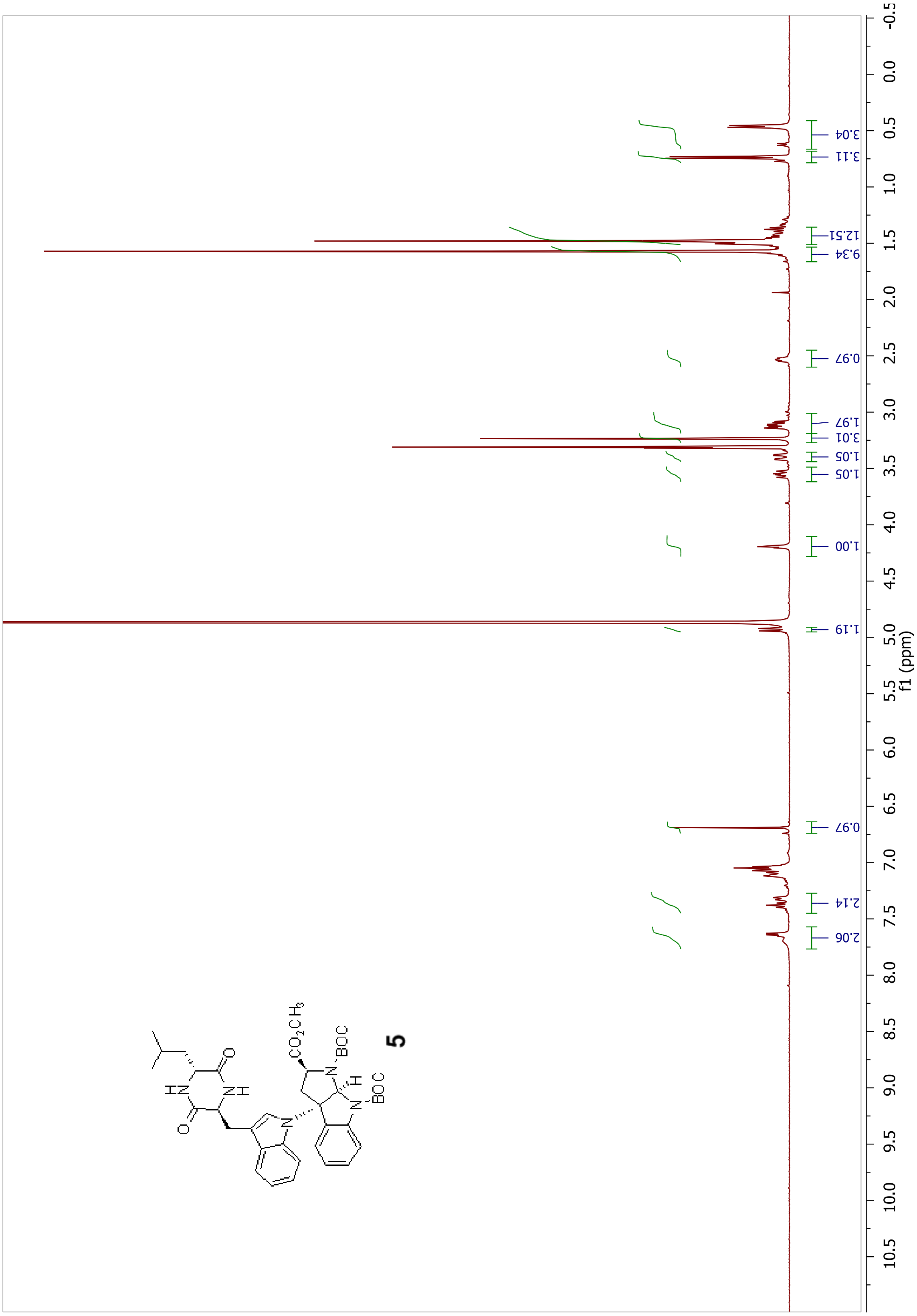
^{1}H NMR (400 MHz, CD_3OD)



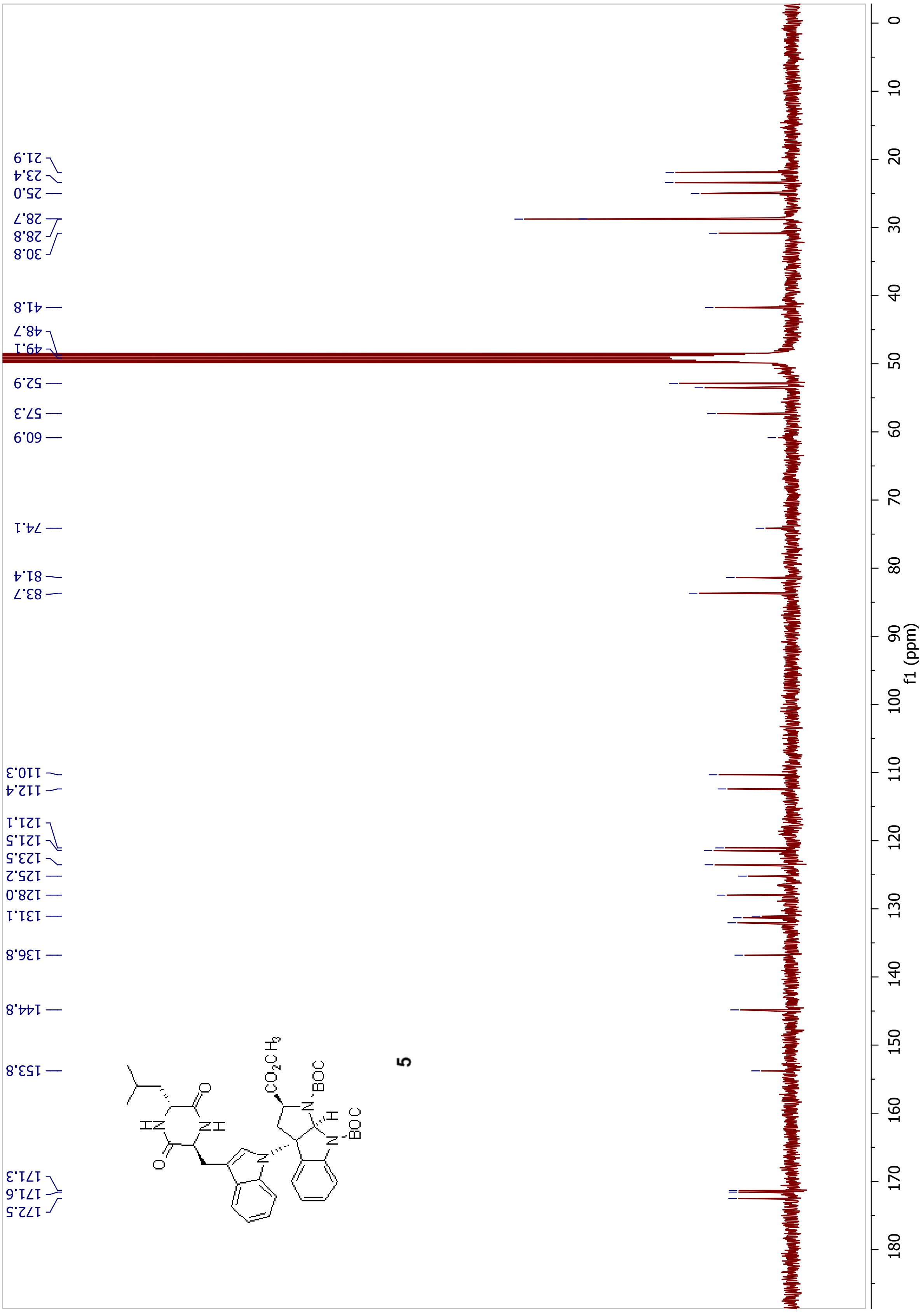
^{13}C NMR (100 MHz, CD_3OD)



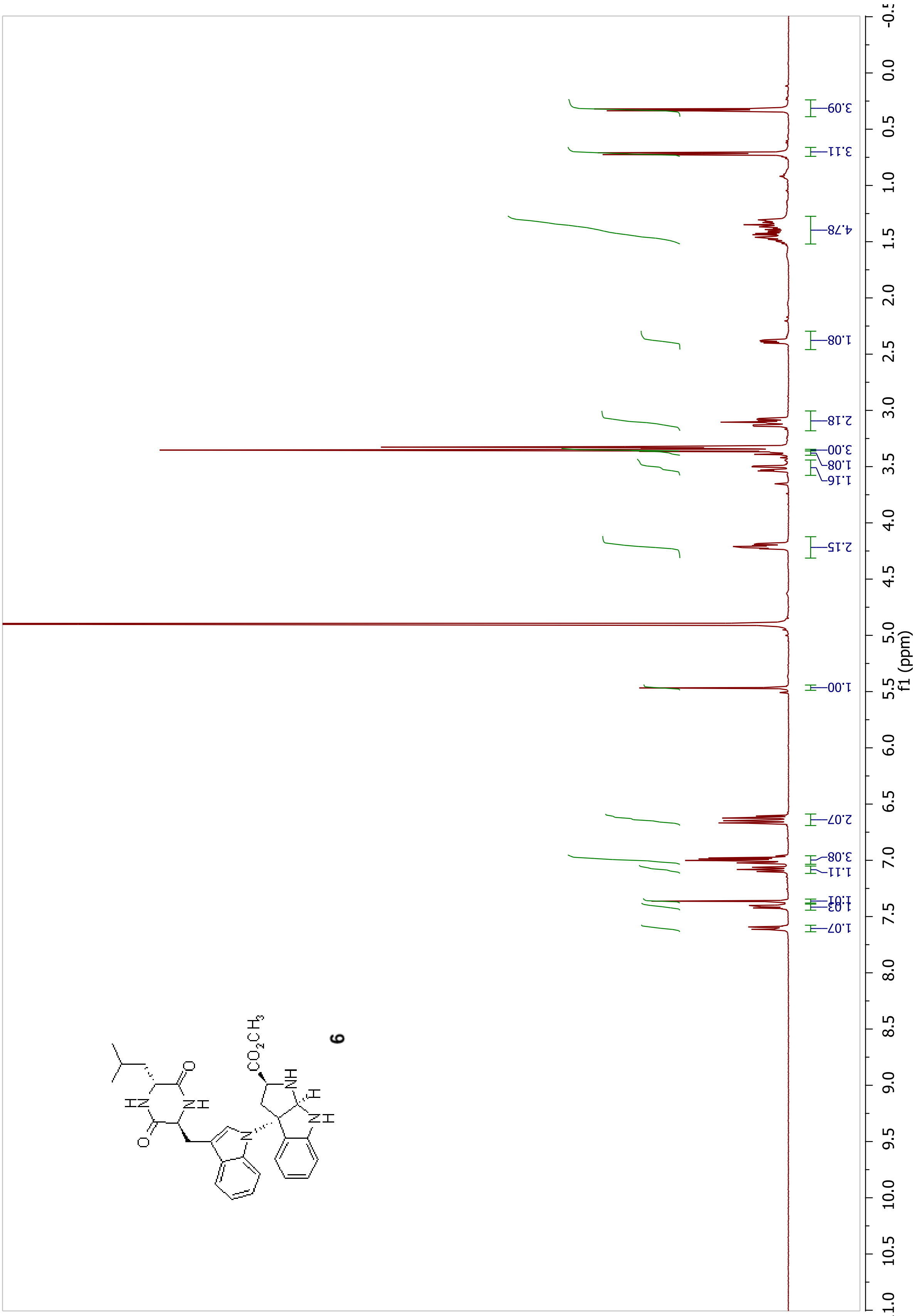
^{13}C NMR (400 MHz, CD_3OD)



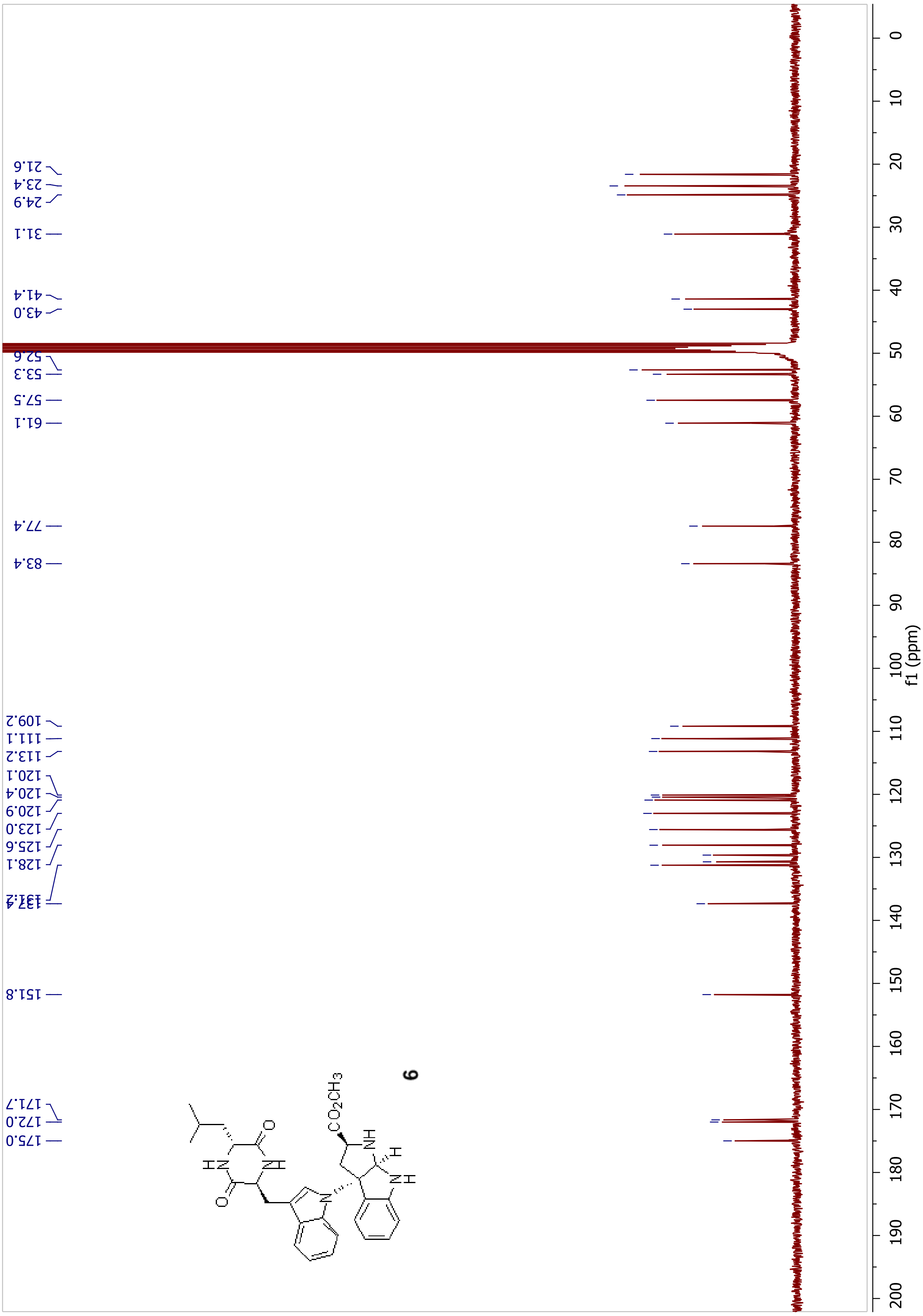
^{13}C NMR (100 MHz, CD_3OD)



^{13}C NMR (400 MHz, CD_3OD)

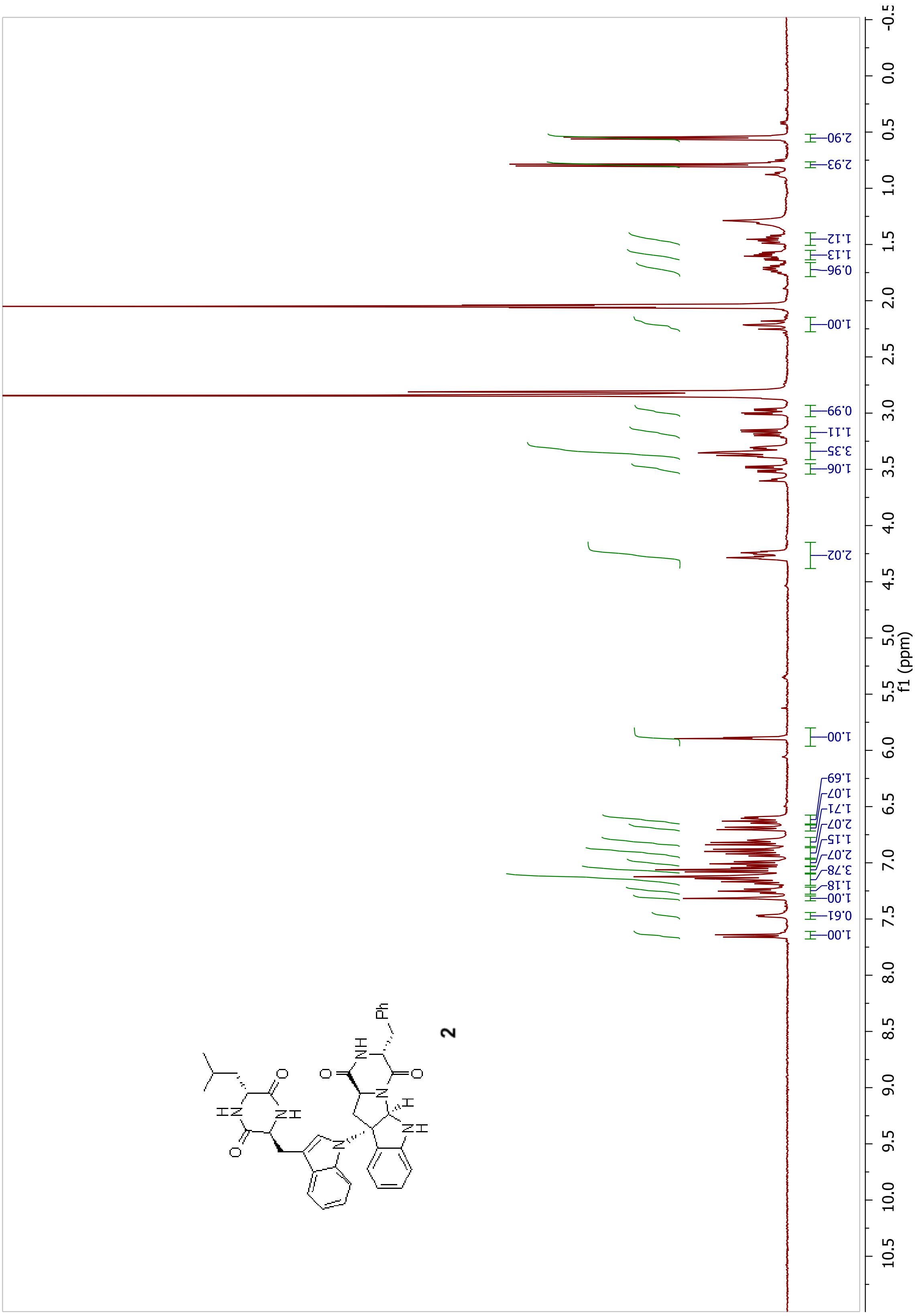


^{13}C NMR (100 MHz, CD_3OD)

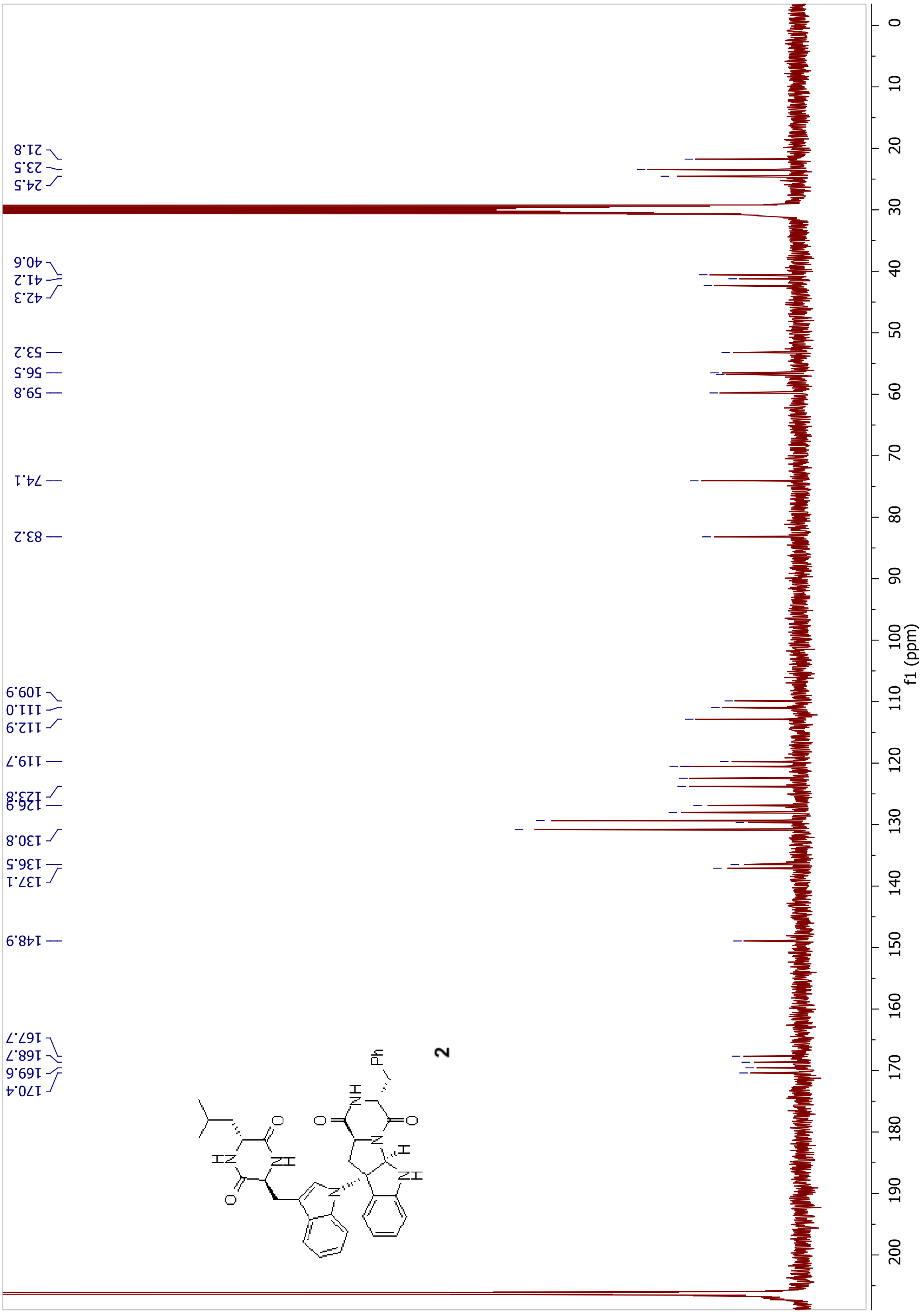


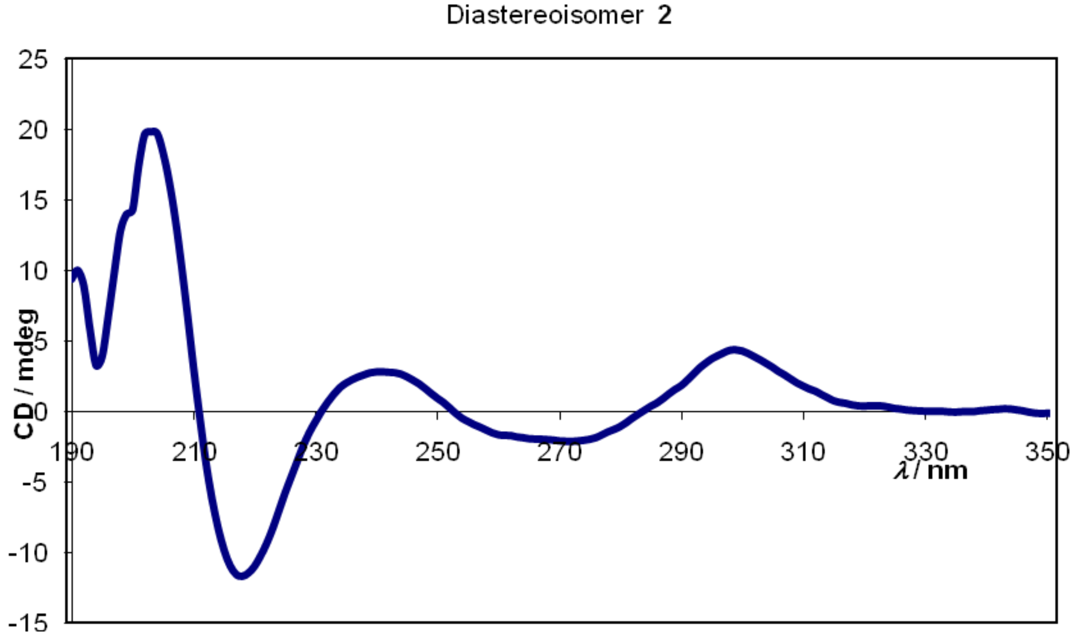
6

^{1}H NMR (400 MHz, $(CD_3)_2CO$)

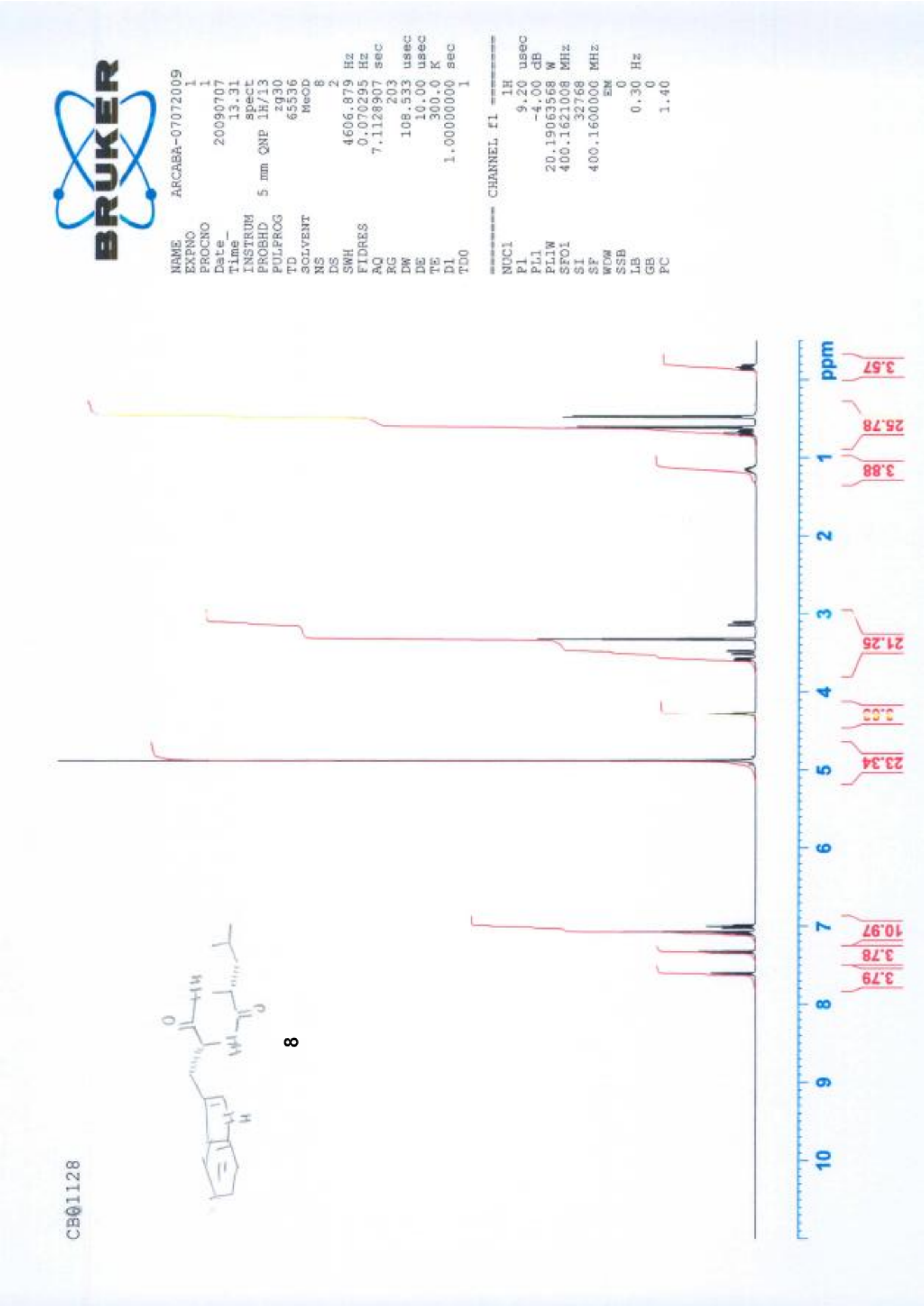


^{1}H NMR (100 MHz, $(CD_3)_2CO$)

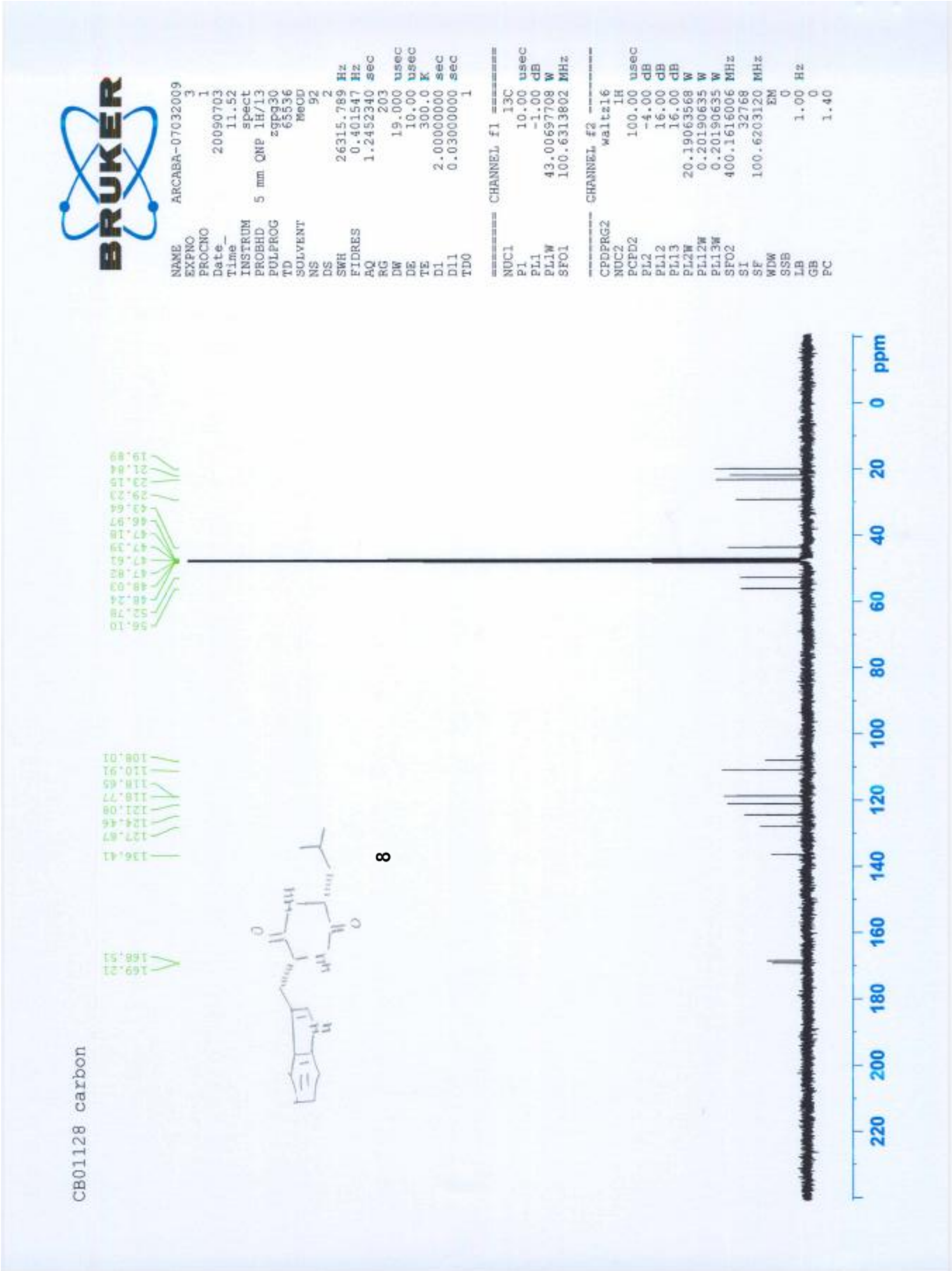



Diastereoisomer 2
25
20
15
10
5
0
-5
-10
-15
CD / mdeg
190
210
230
250
270
290
310
330
350
λ / nm

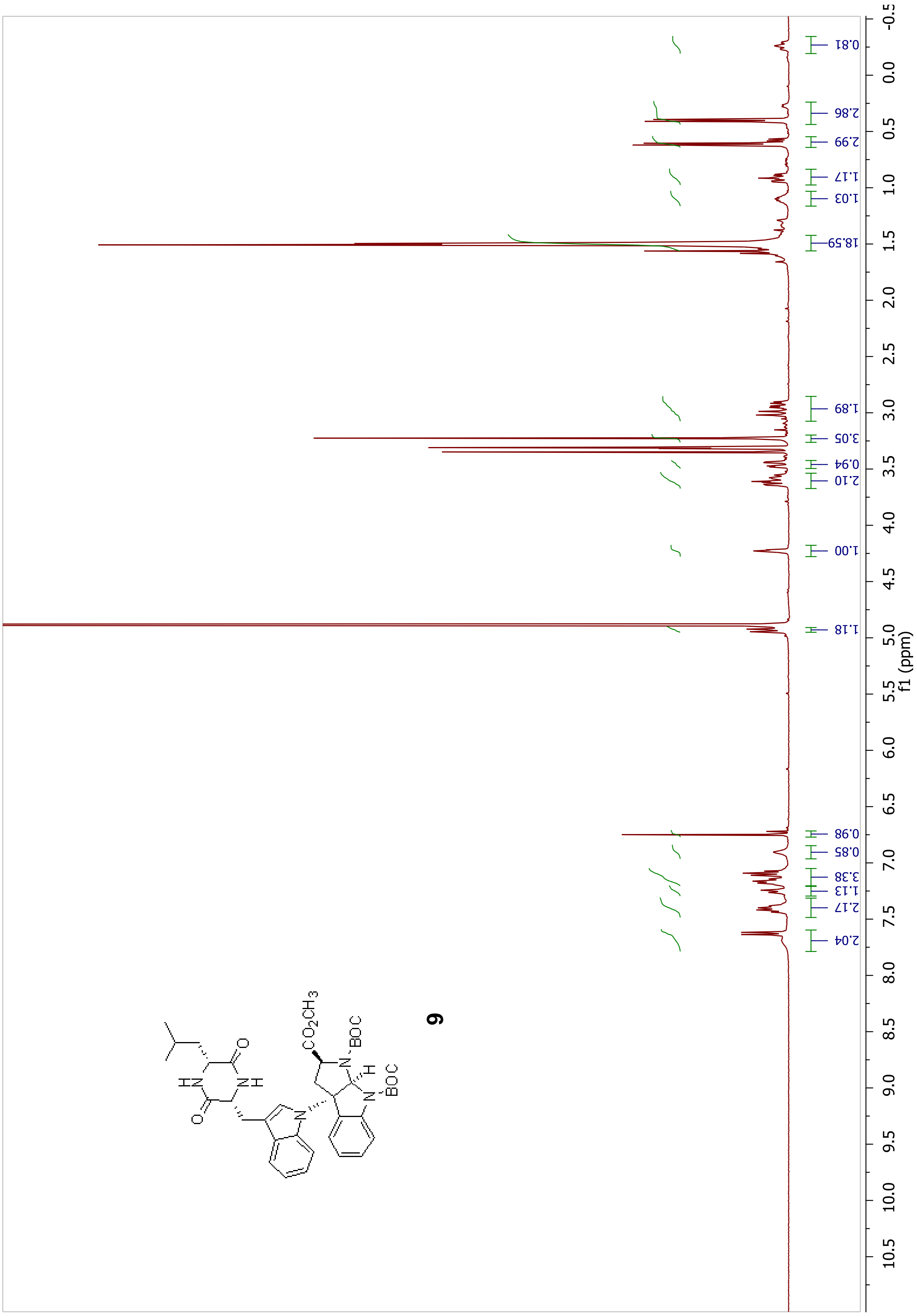
^{1}H NMR (400 MHz, CD_3OD)



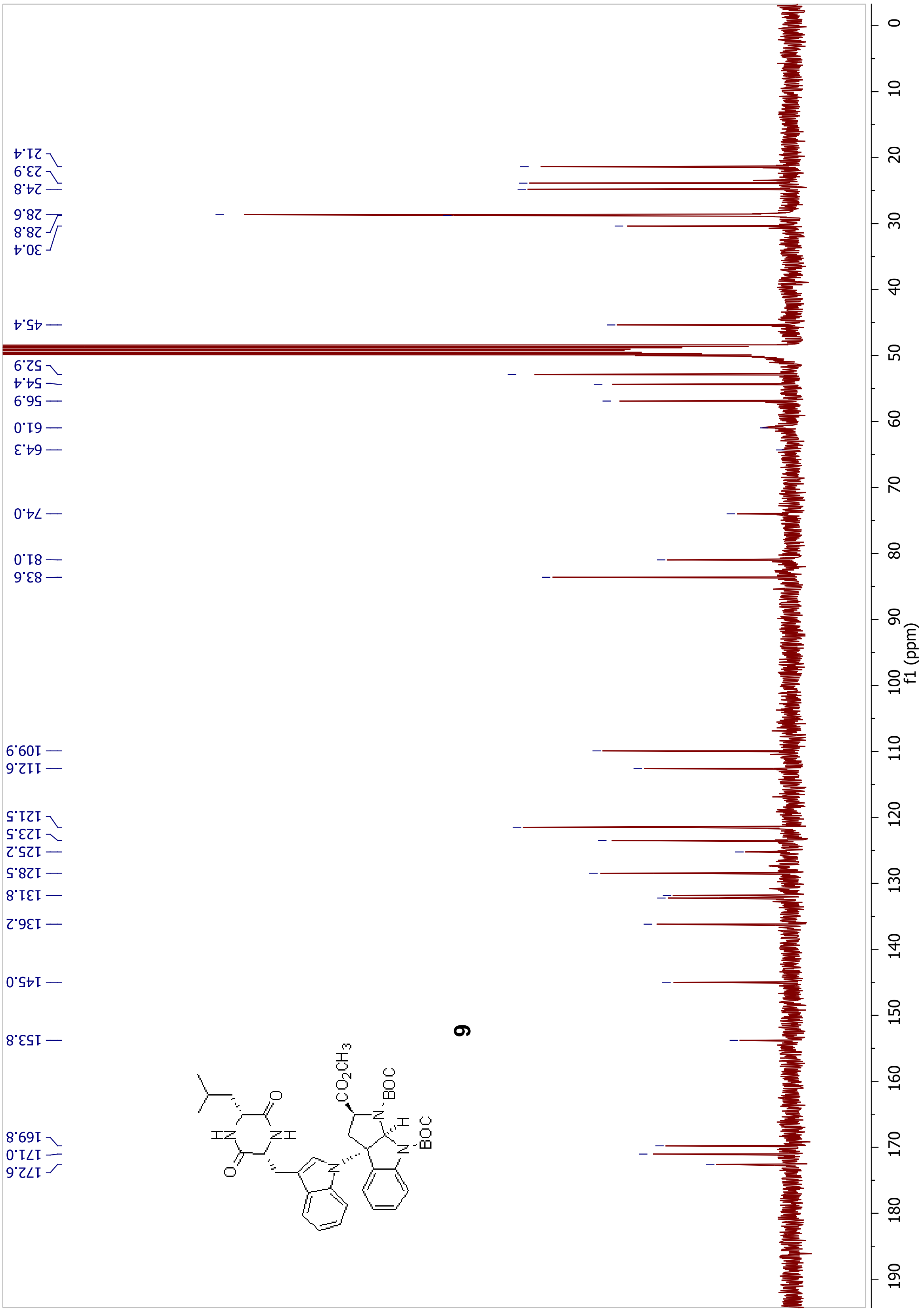
^{1}H NMR (100 MHz, CD_3OD)



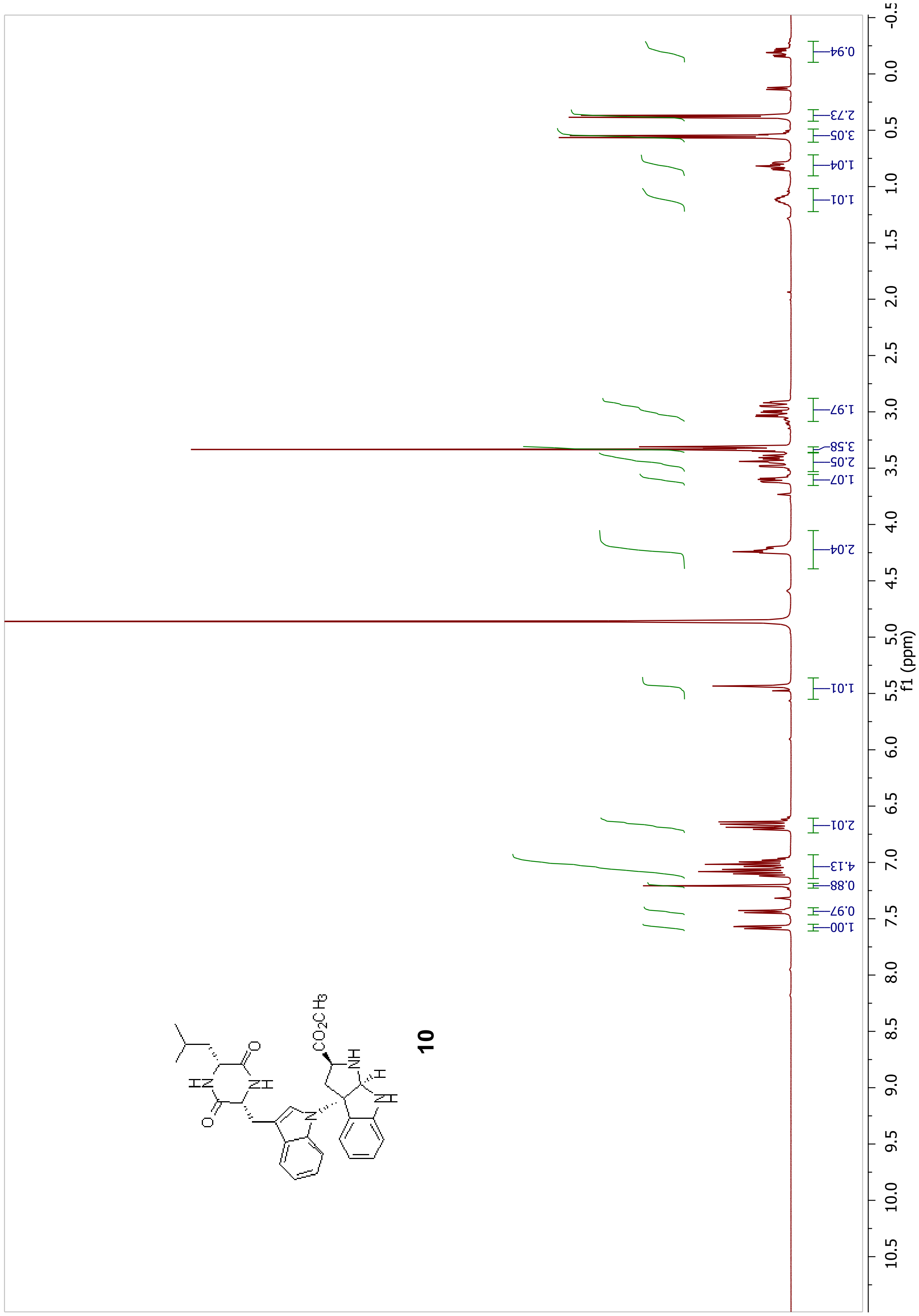
^{1}H NMR (400 MHz, CD_3OD)



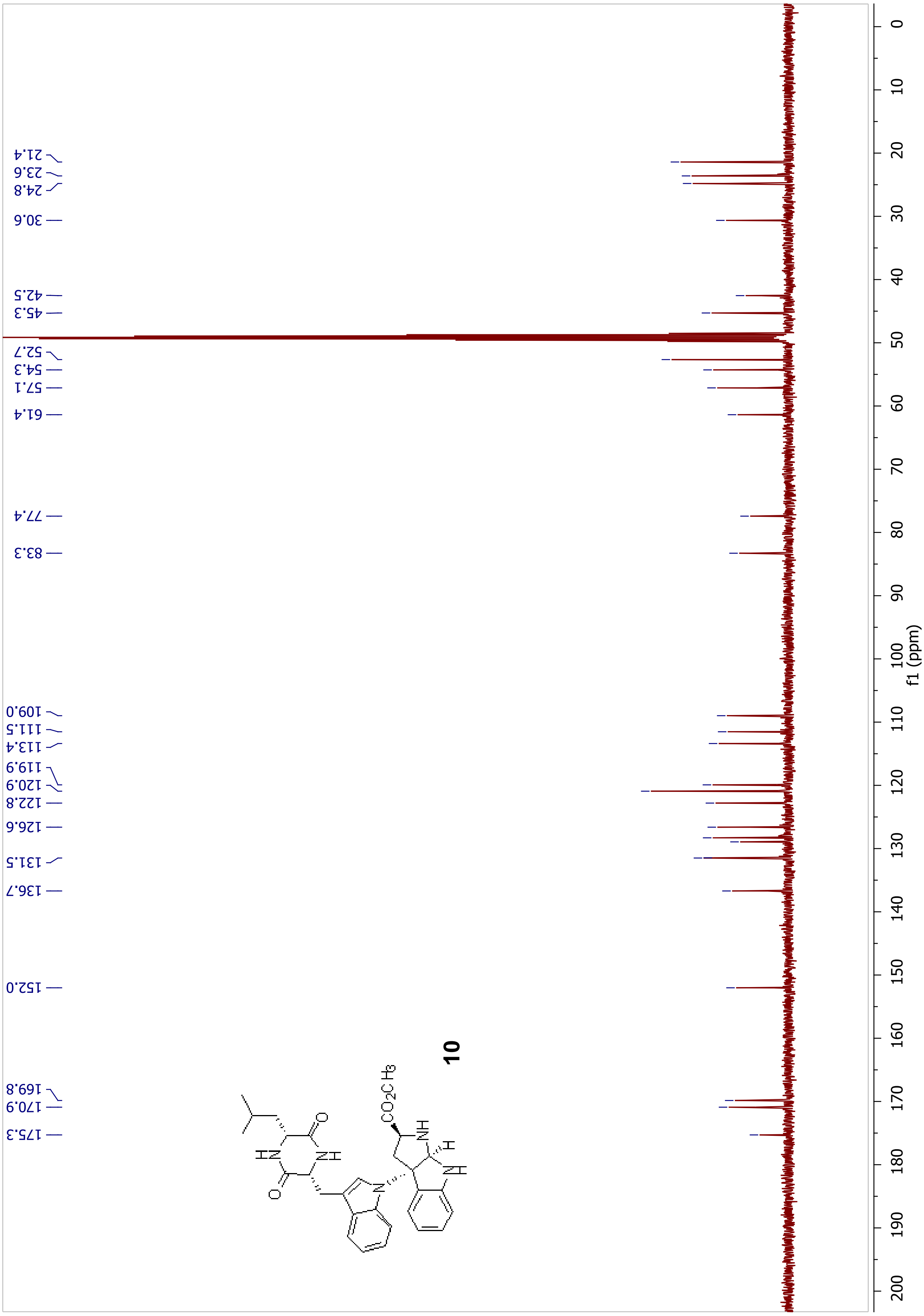
^{13}C NMR (100 MHz, CD_3OD)



^{1}H NMR (400 MHz, CD_3OD)



^{13}C NMR (100 MHz, CD_3OD)



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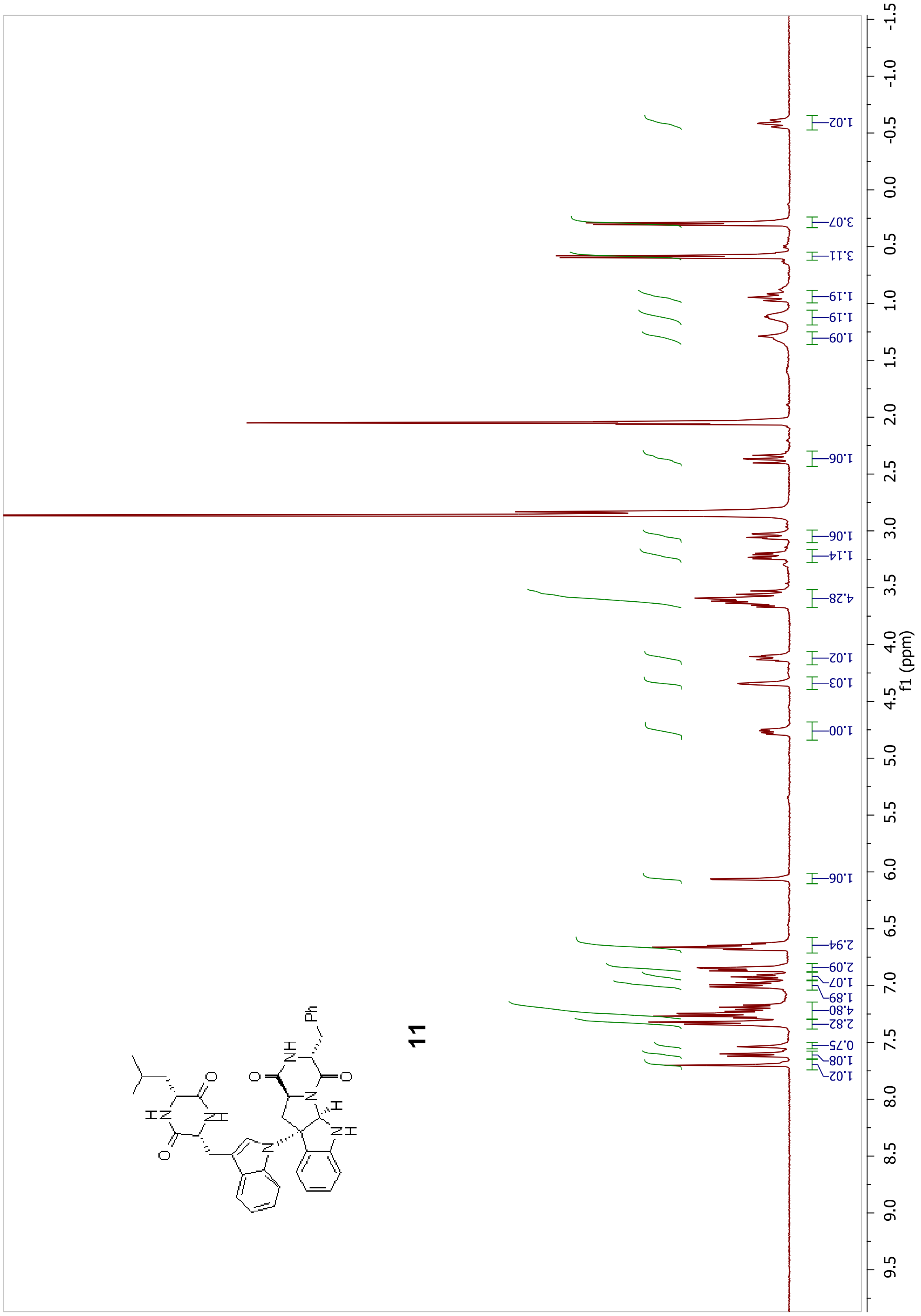
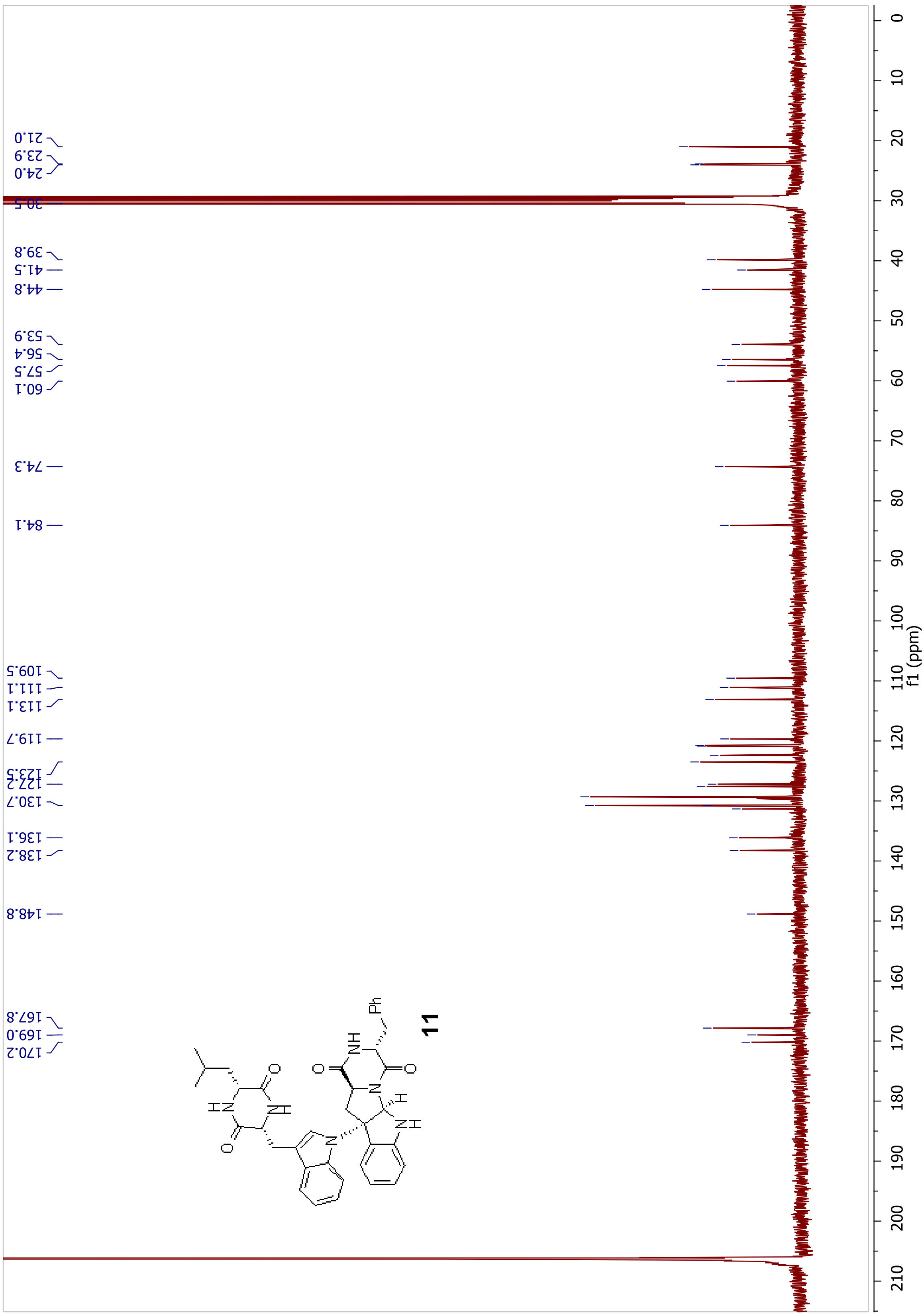
Supplementary Material (ESI) for Organic & Biomolecular Chemistry

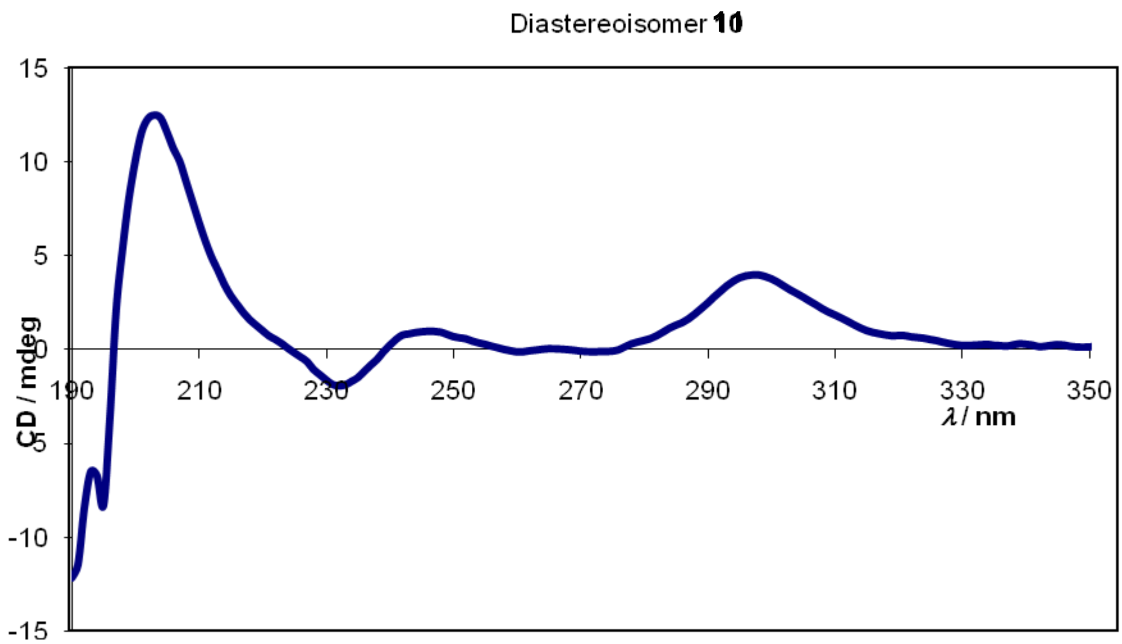
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



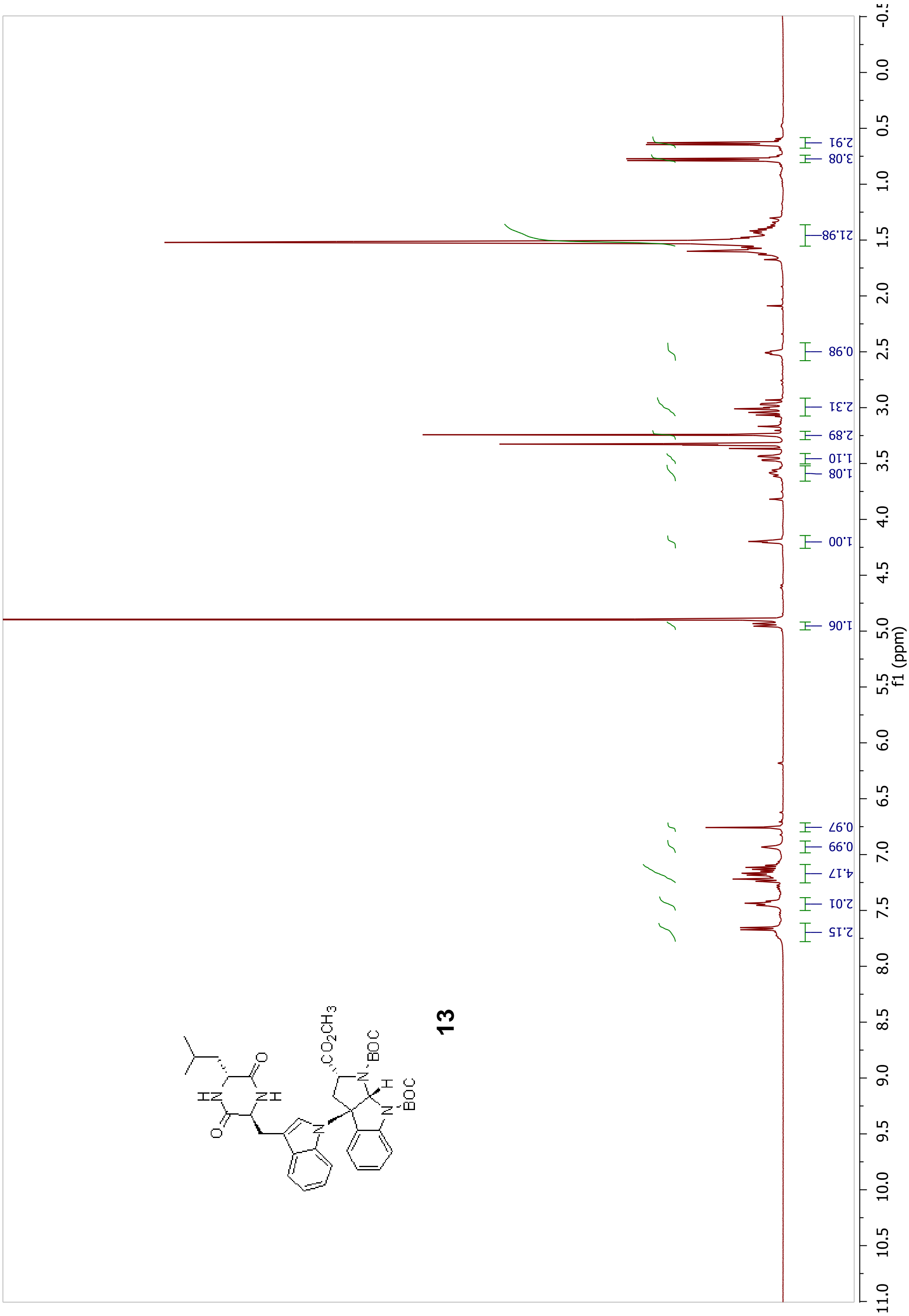
11

^{1}H NMR (100 MHz, $(CD_3)_2CO$)

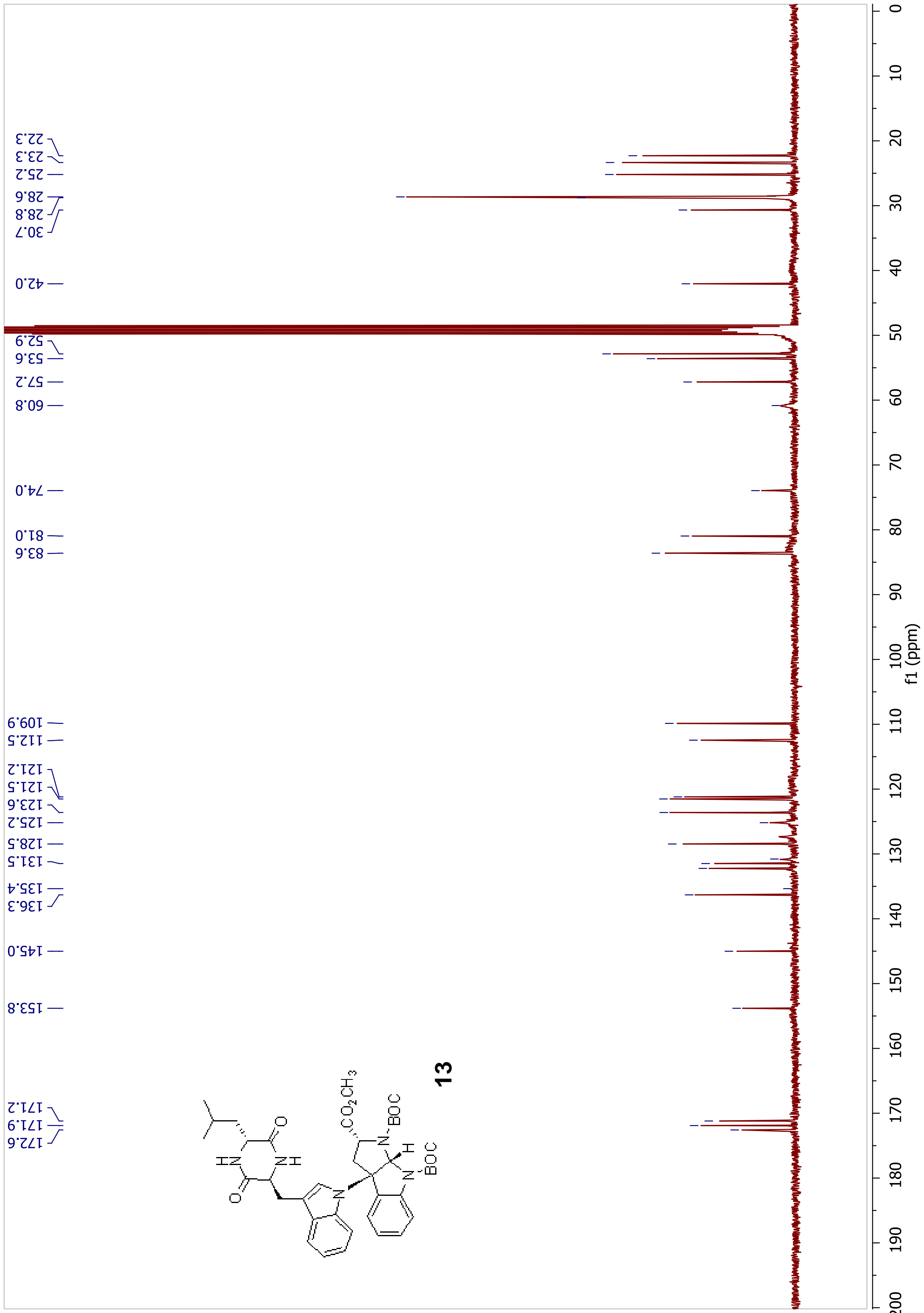



Diastereoisomer 10
15
10
5
0
-5
-10
-15
CD / mdeg
190
210
230
250
270
290
310
330
350
λ / nm

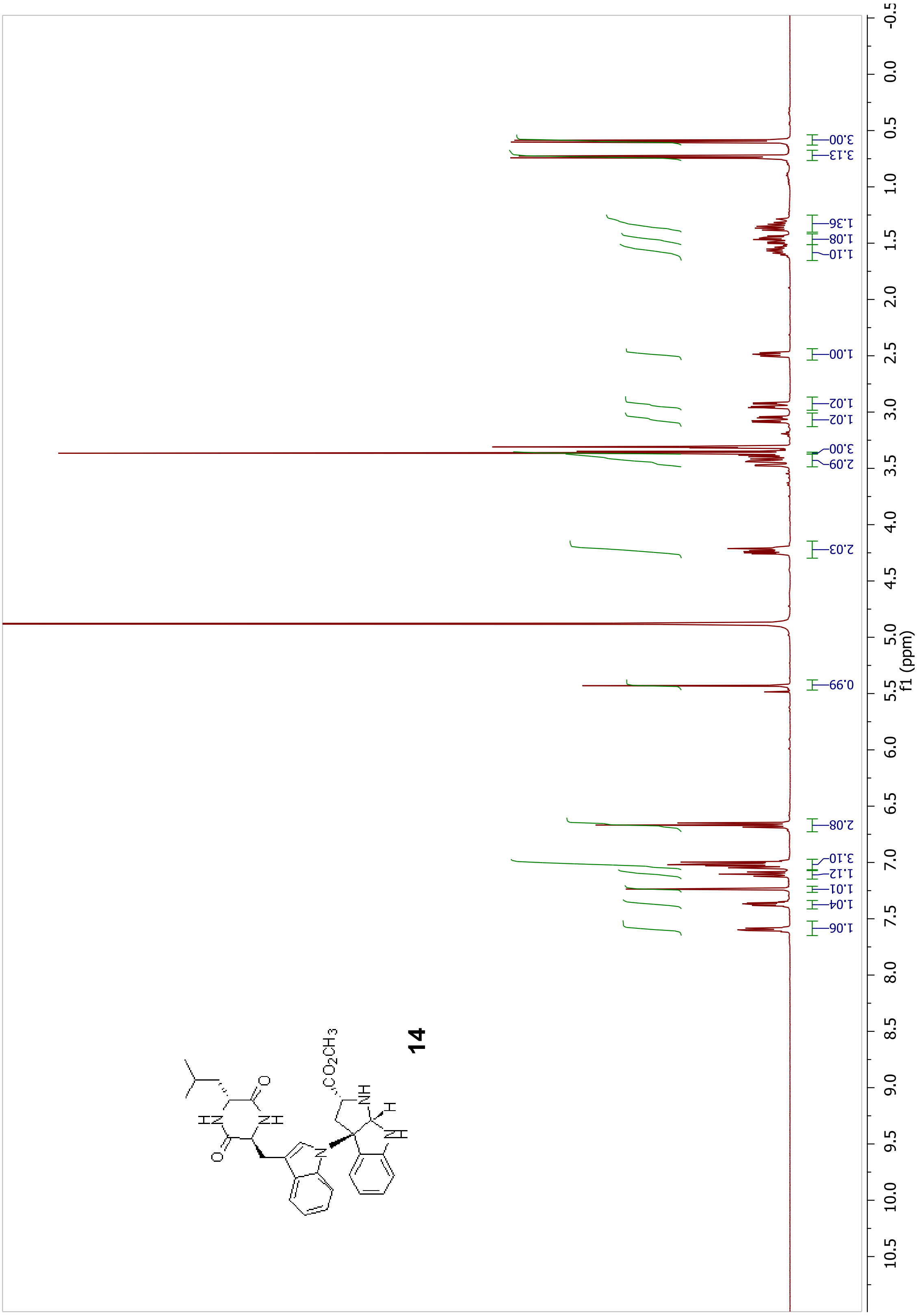
^{1}H NMR (400 MHz, CD_3OD)



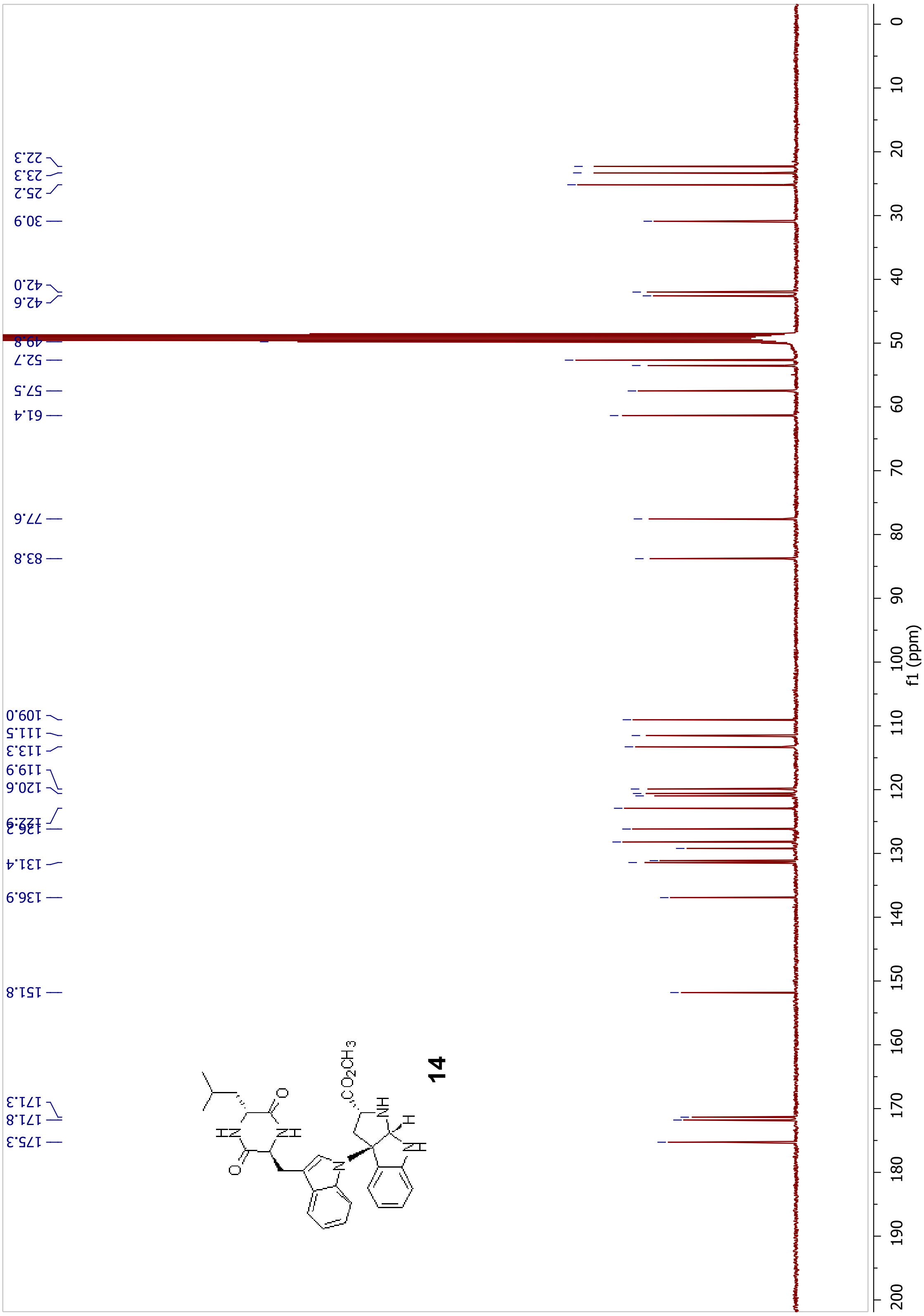
^{13}C NMR (100 MHz, CD_3OD)



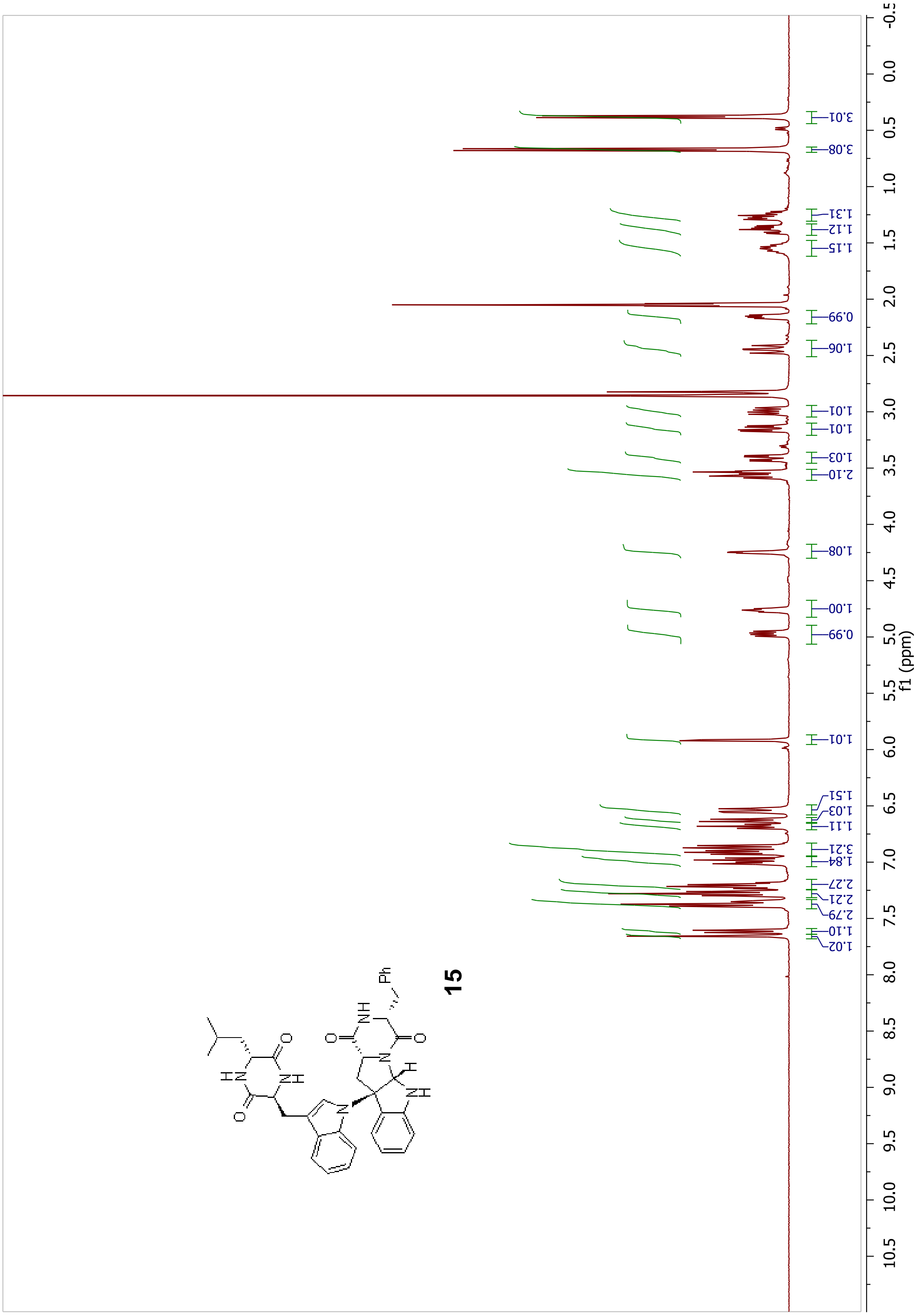
^{1}H NMR (400 MHz, CD_3OD)



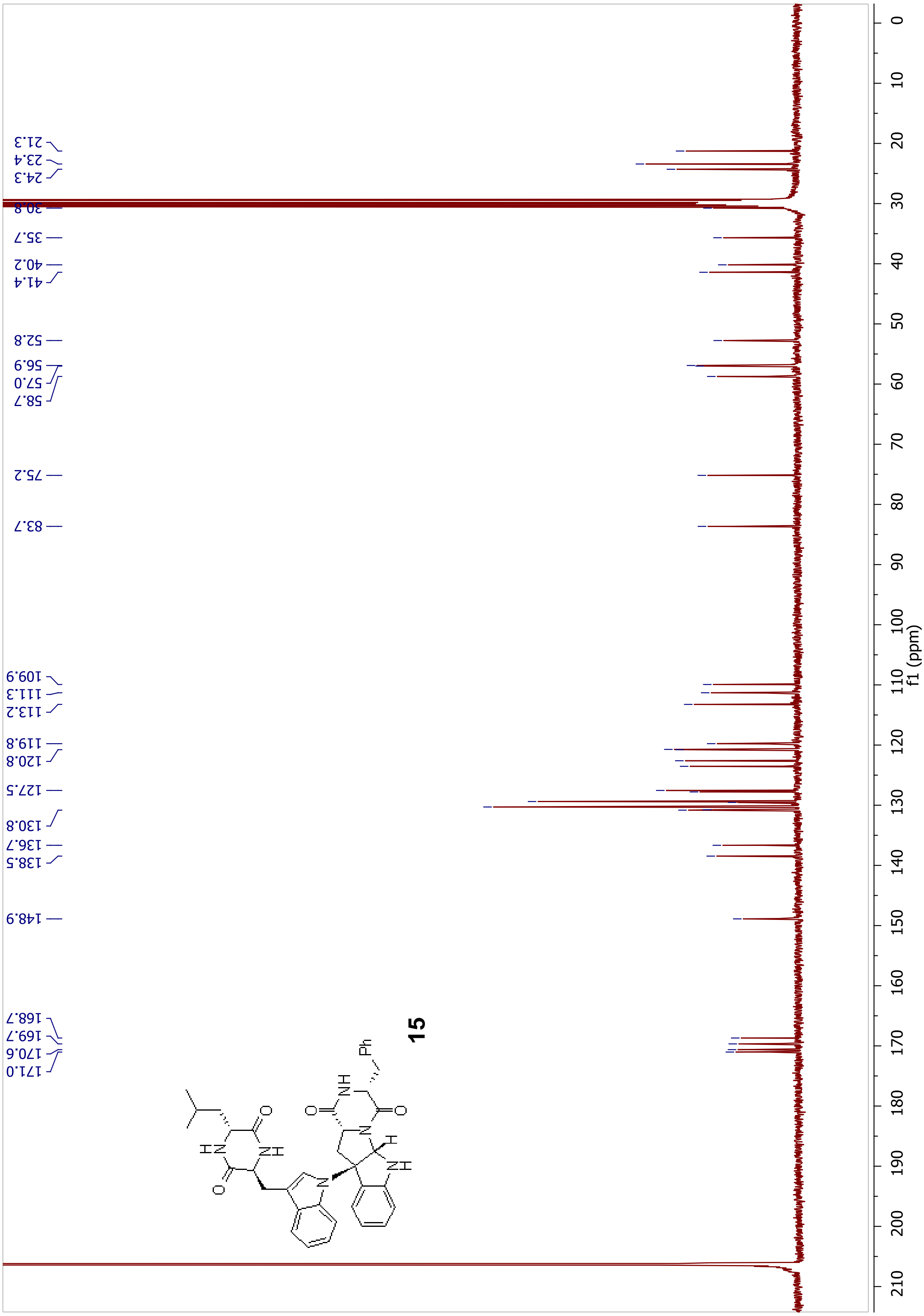
^{13}C NMR (100 MHz, CD_3OD)

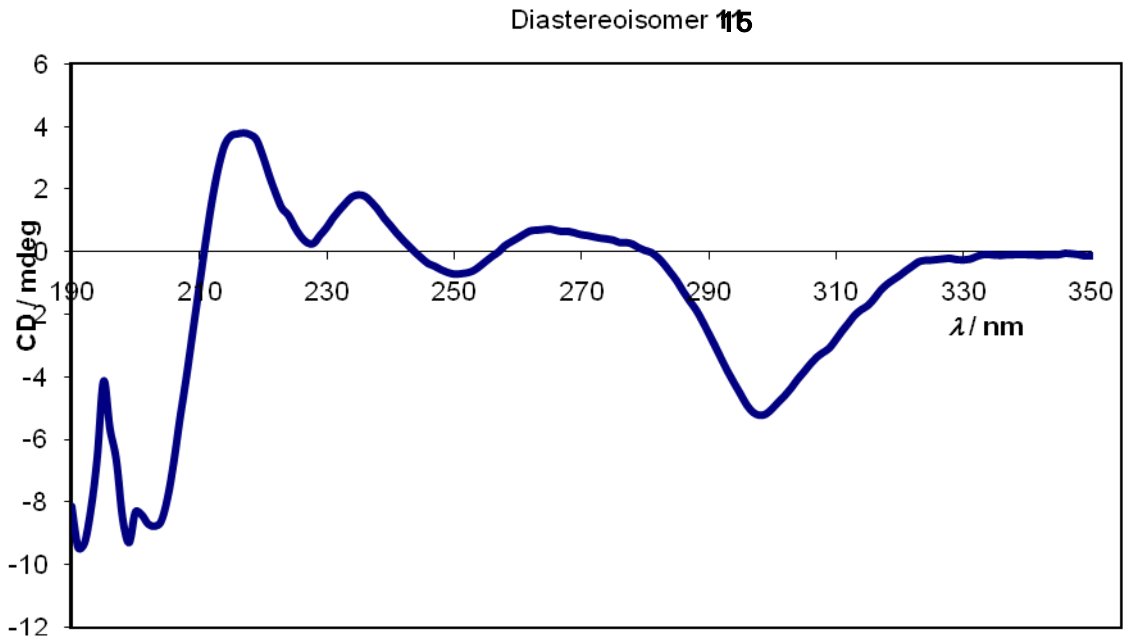


^{1}H NMR (400 MHz, $(CD_3)_2CO$)

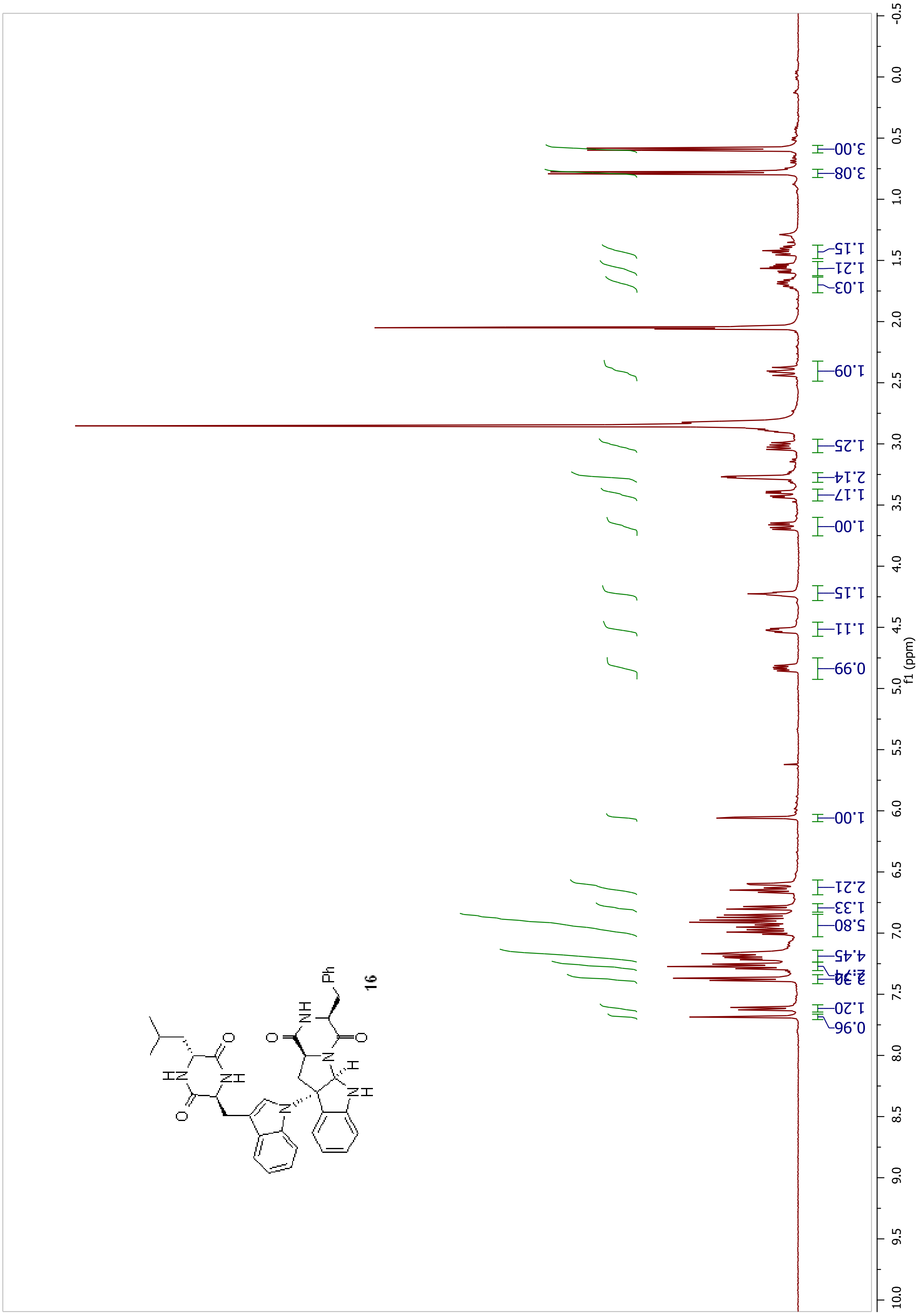


^{1}H NMR (100 MHz, $(CD_3)_2CO$)

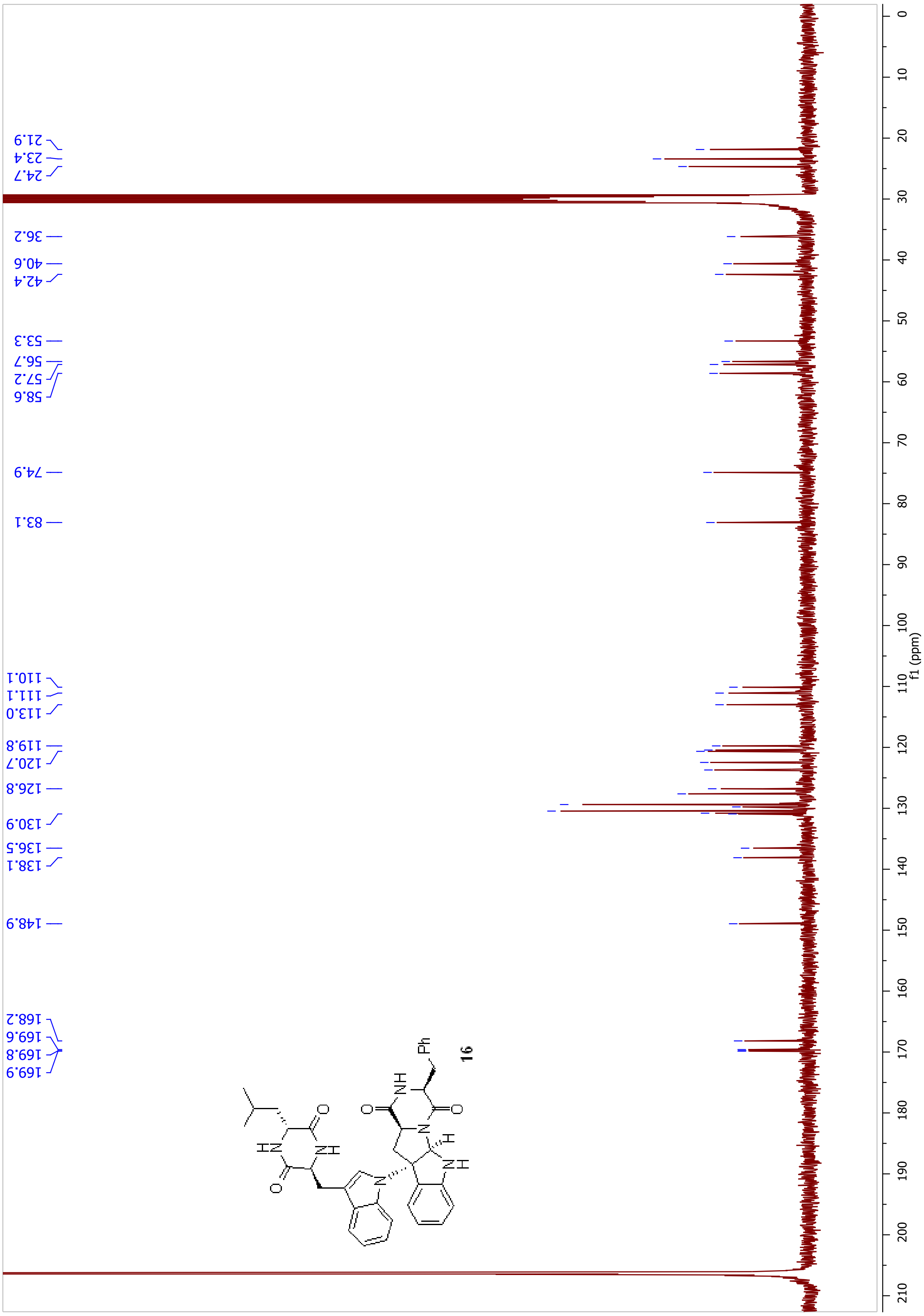



Diastereoisomer 115
CD / mdeg
λ / nm
6
4
2
0
-2
-4
-6
-8
-10
-12
190
210
230
250
270
290
310
330
350

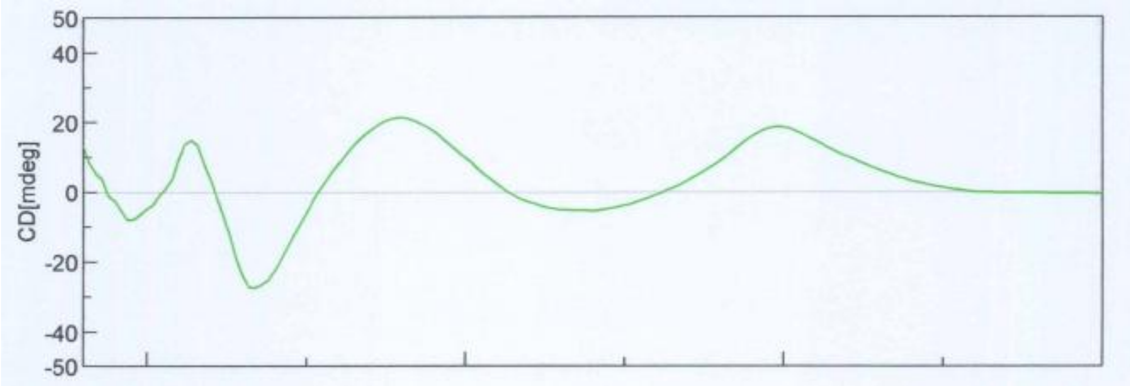
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



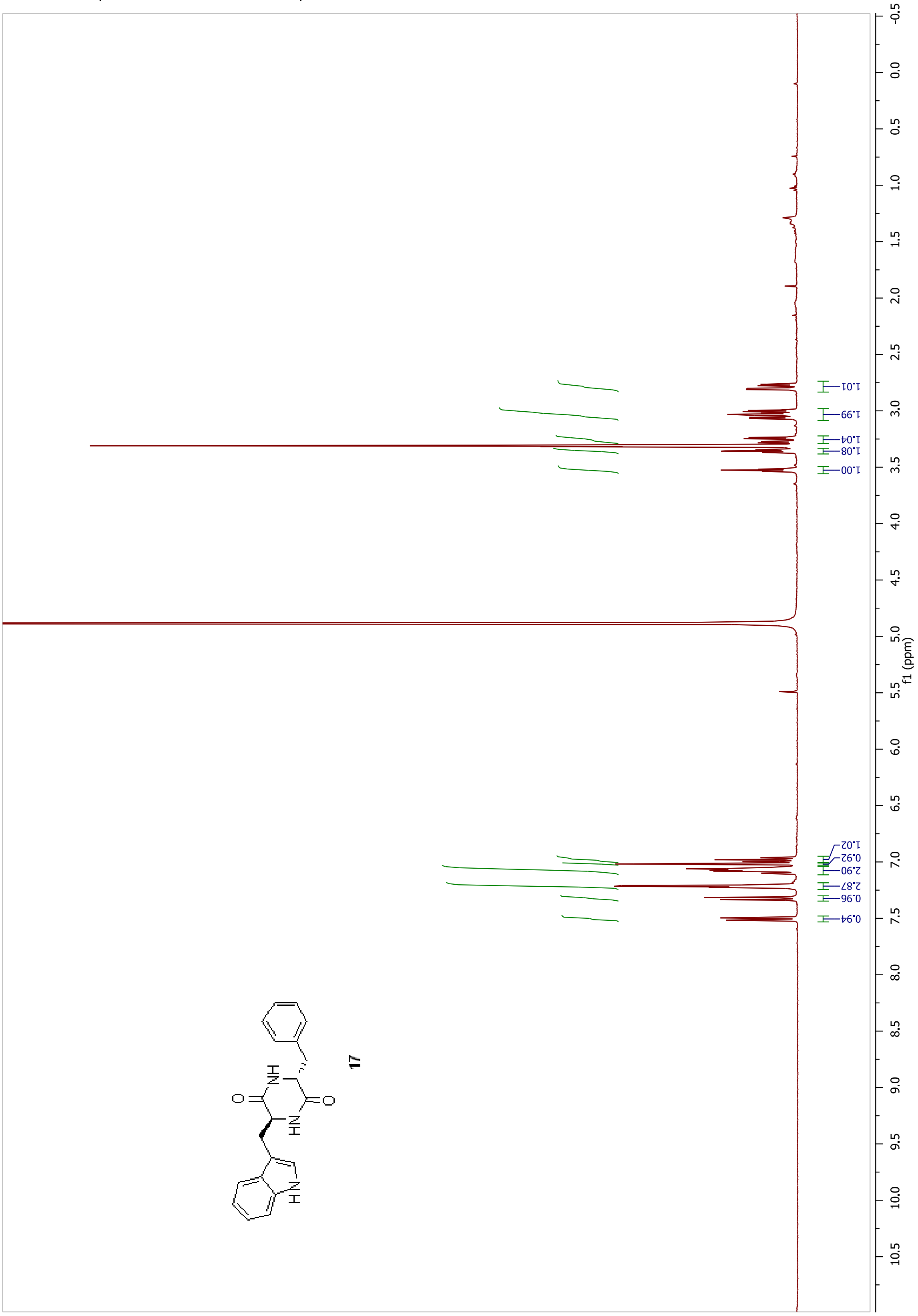
^{1}H NMR (100 MHz, $(CD_3)_2CO$)



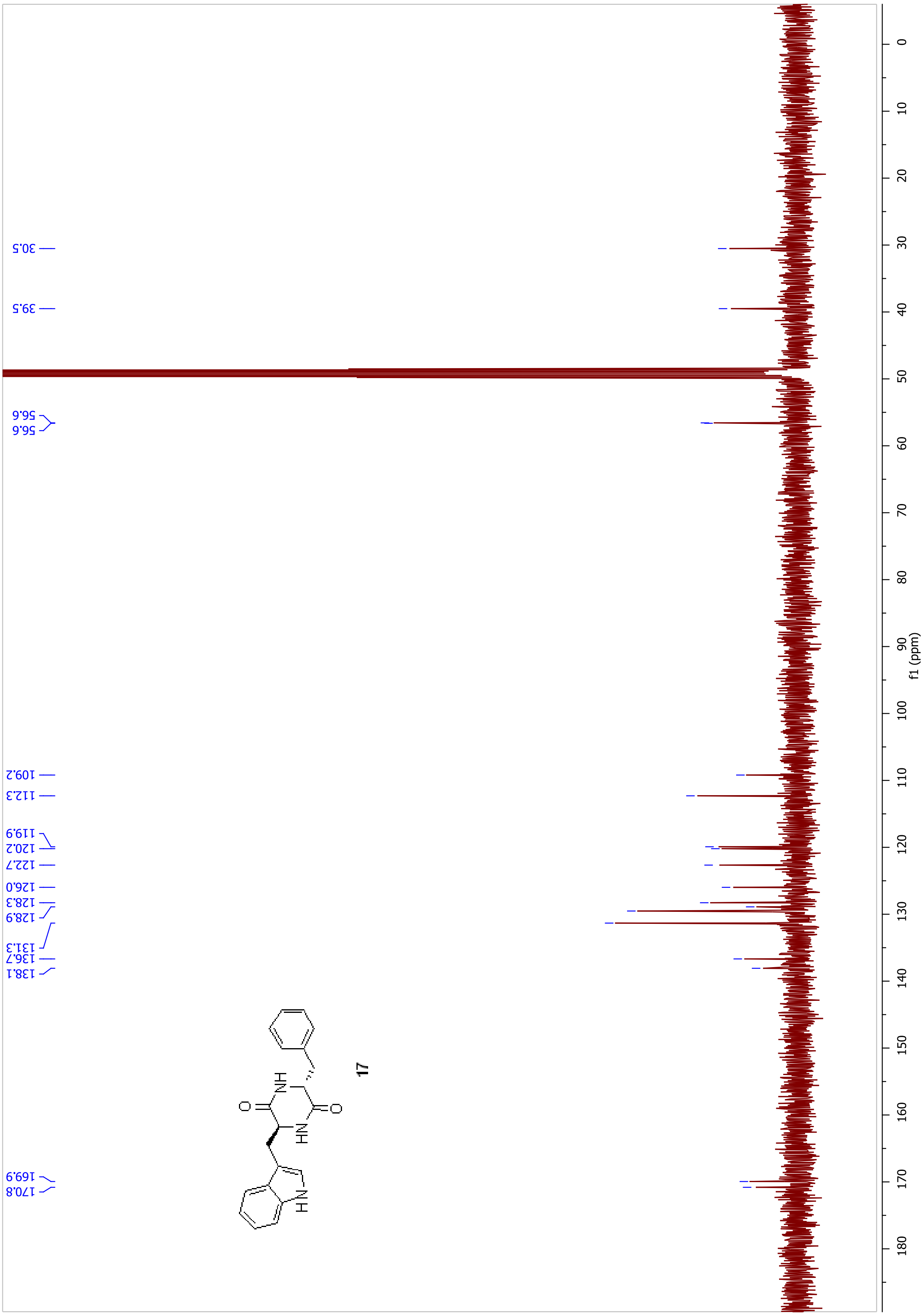
Diastereoisomer 16



^{1}H NMR (400 MHz, CD_3OD)

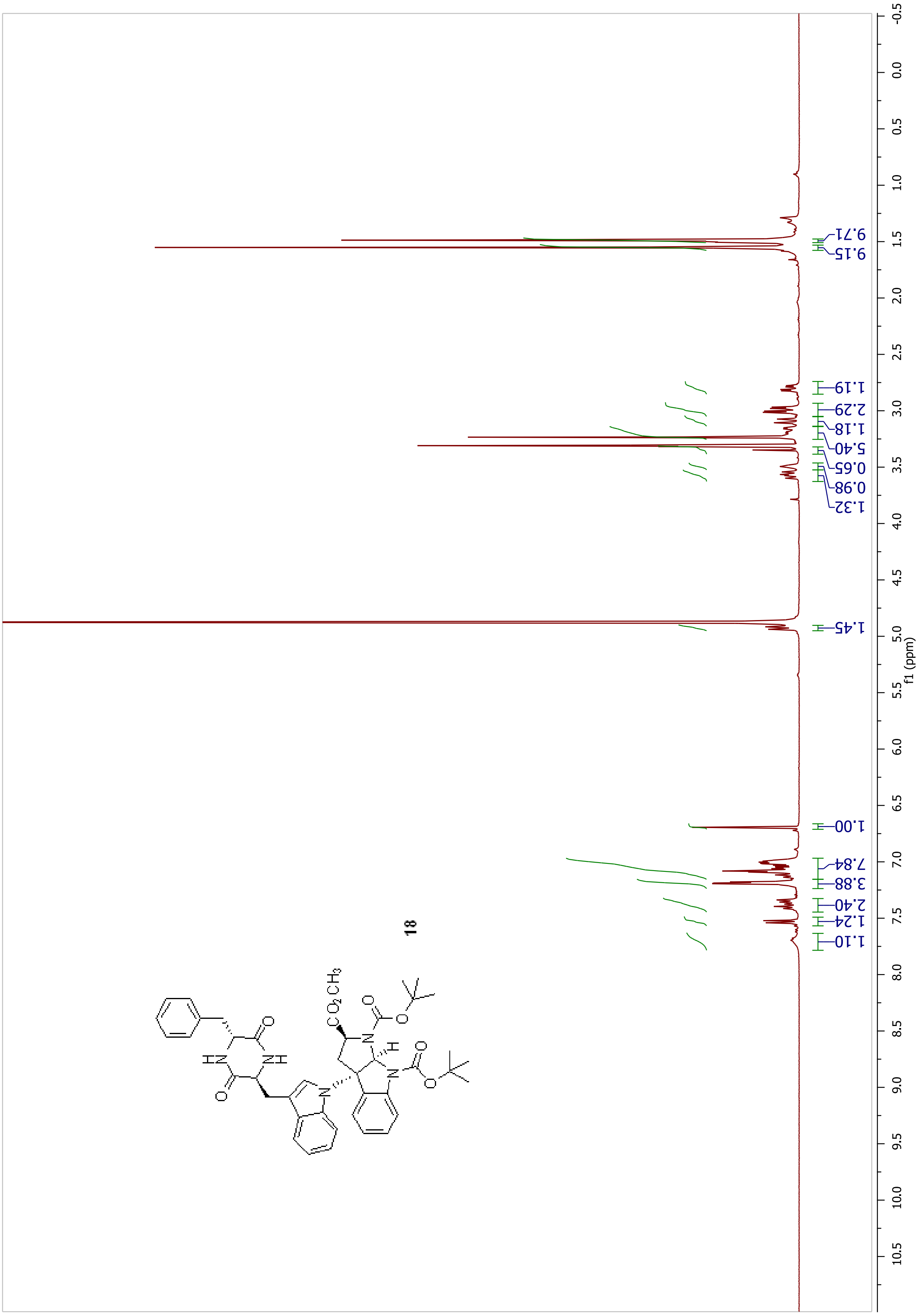


^{1}H NMR (100 MHz, CD_3OD)

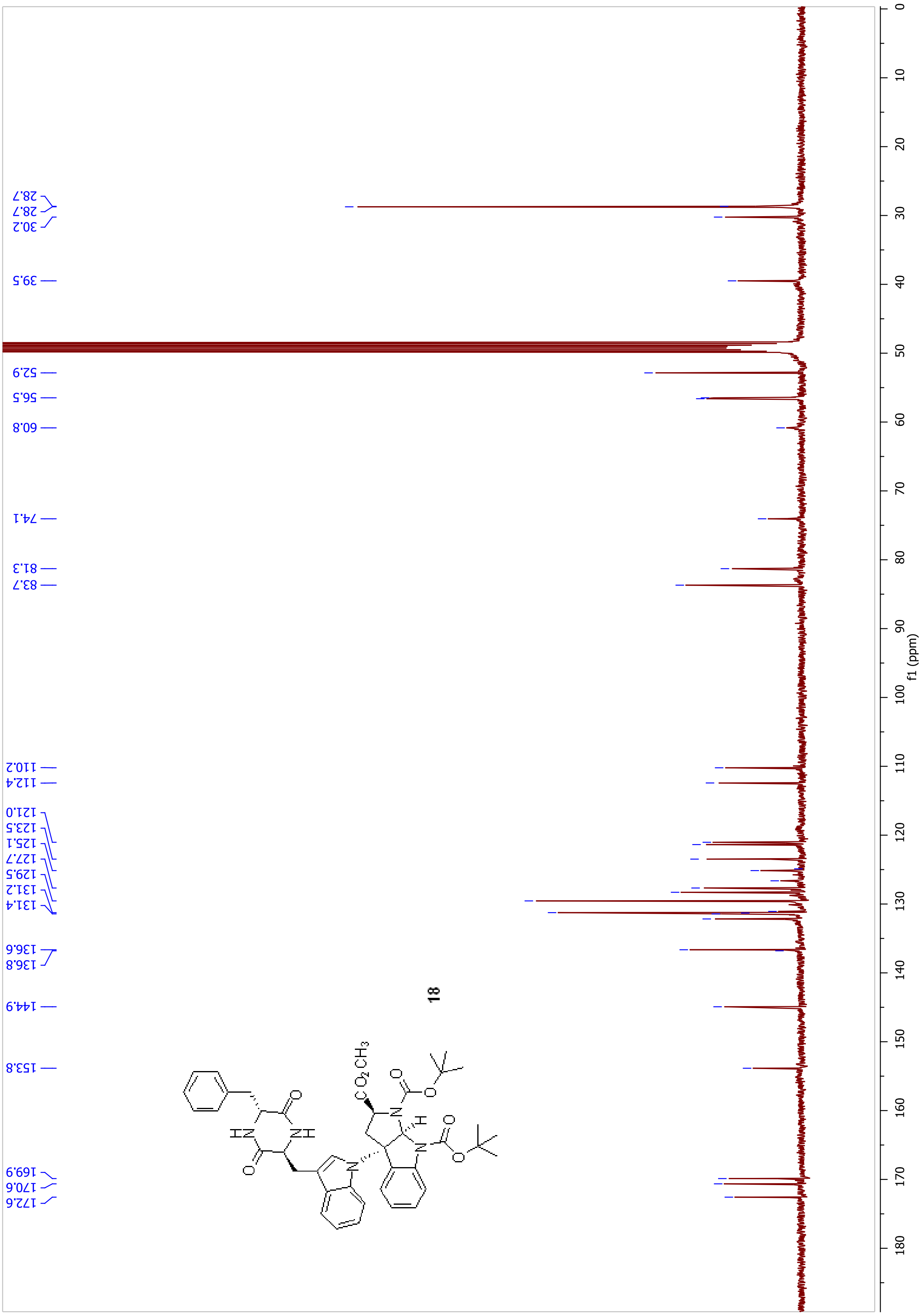


Supplementary Material (ESI) for Organic & Biomolecular Chemistry

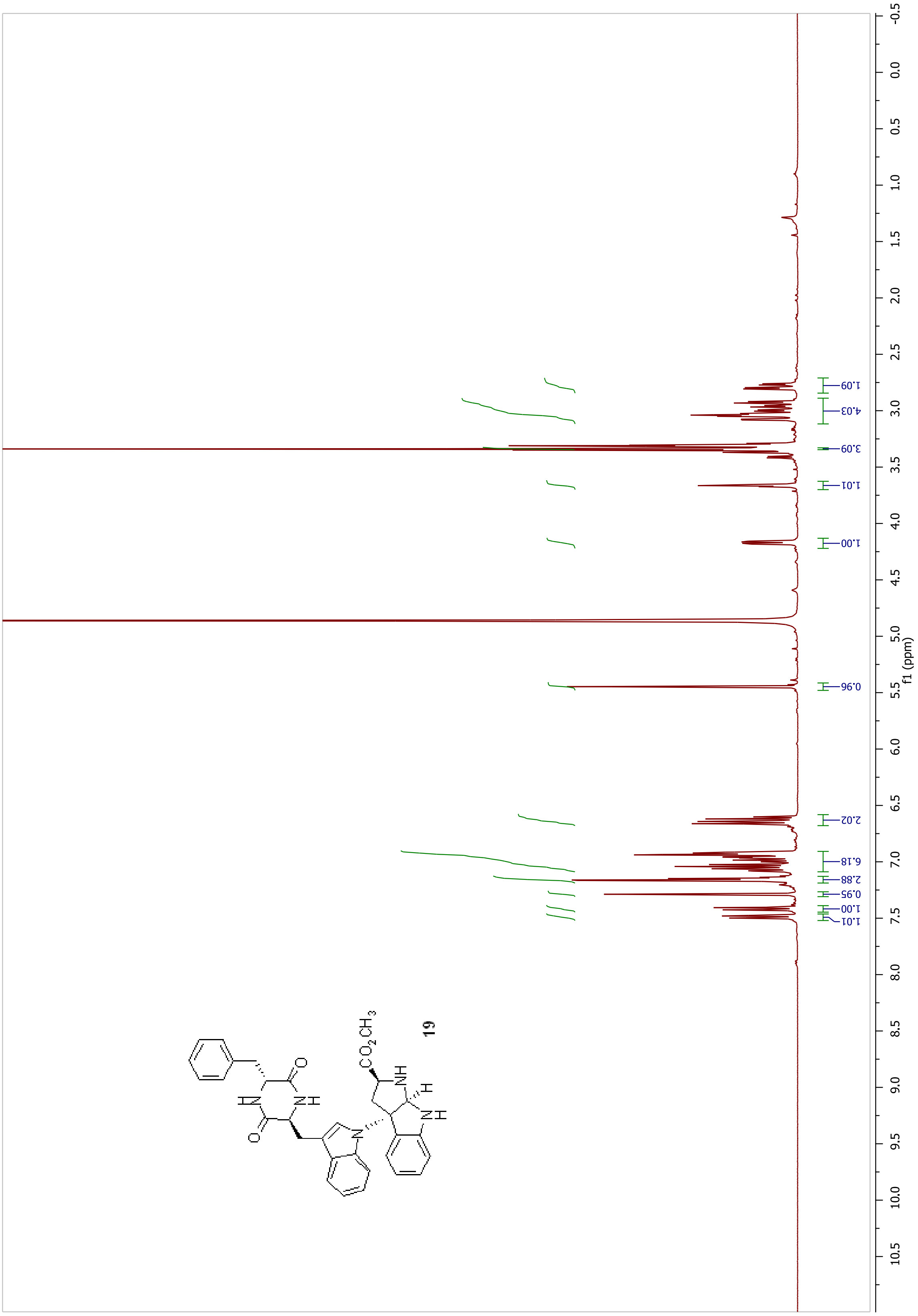
^{1}H NMR (400 MHz, CD_3OD)



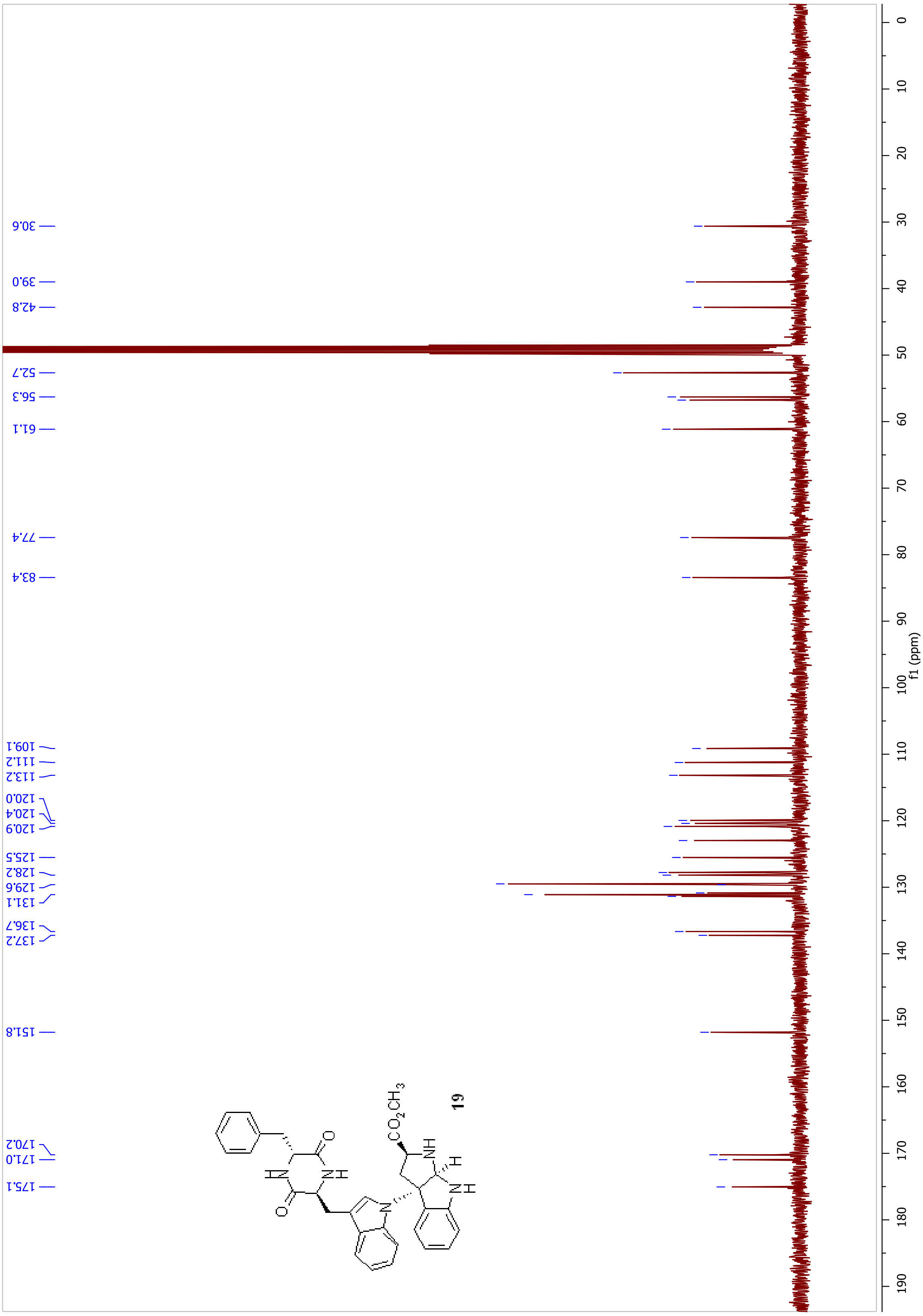
^{1}H NMR (100 MHz, CD_3OD)



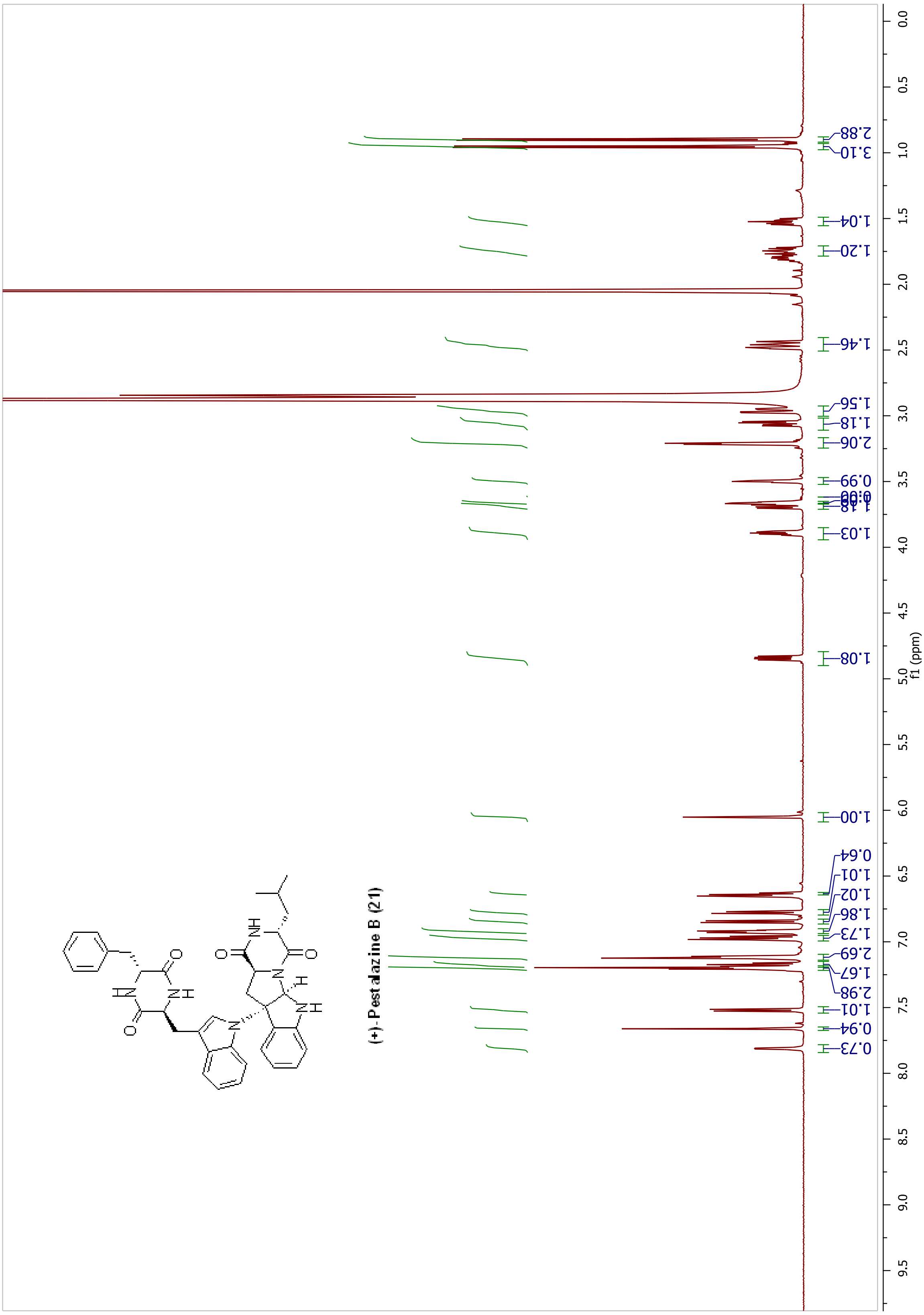
^{1}H NMR (400 MHz, CD_3OD)



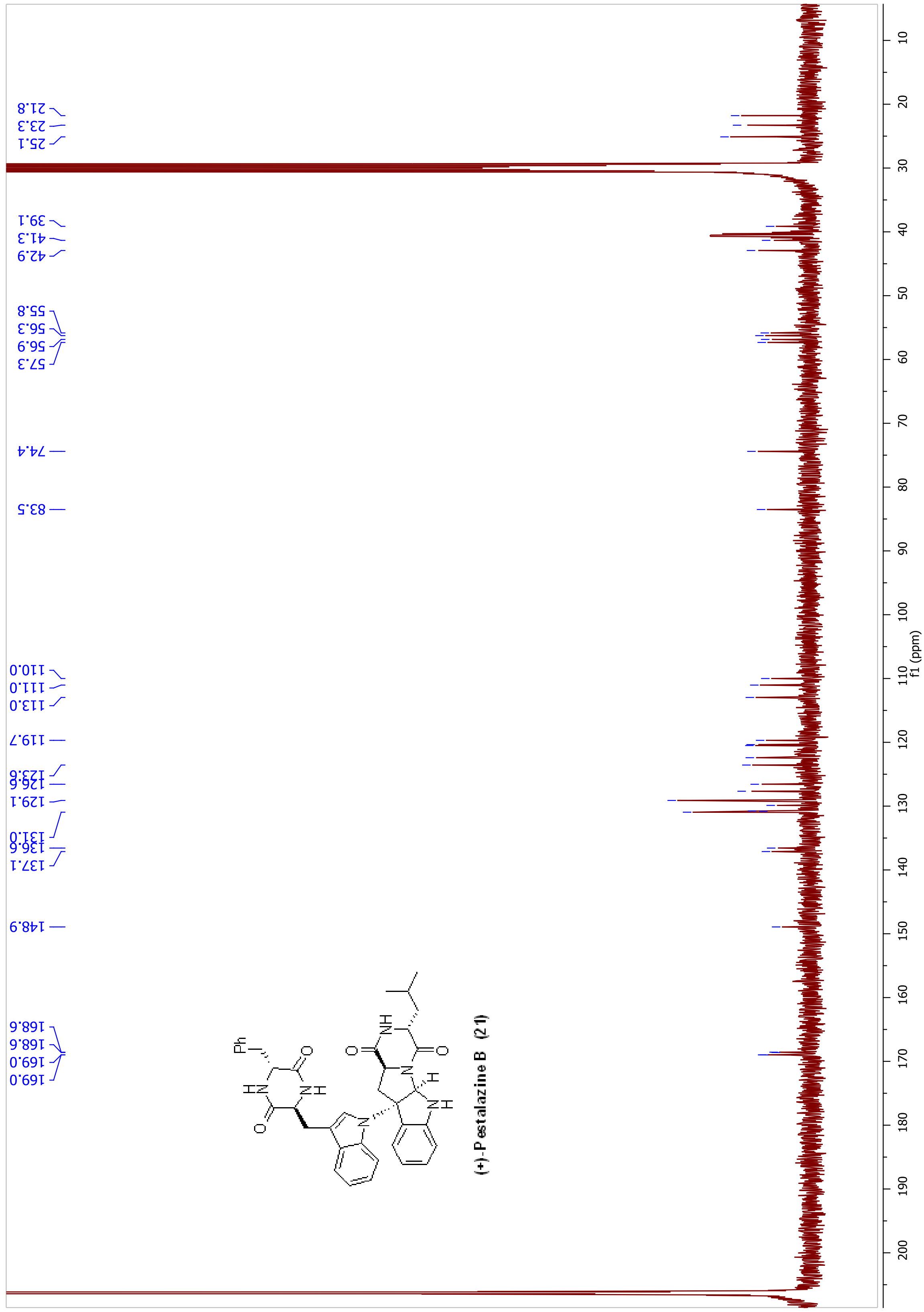
^{1}H NMR (100 MHz, CD_3OD)



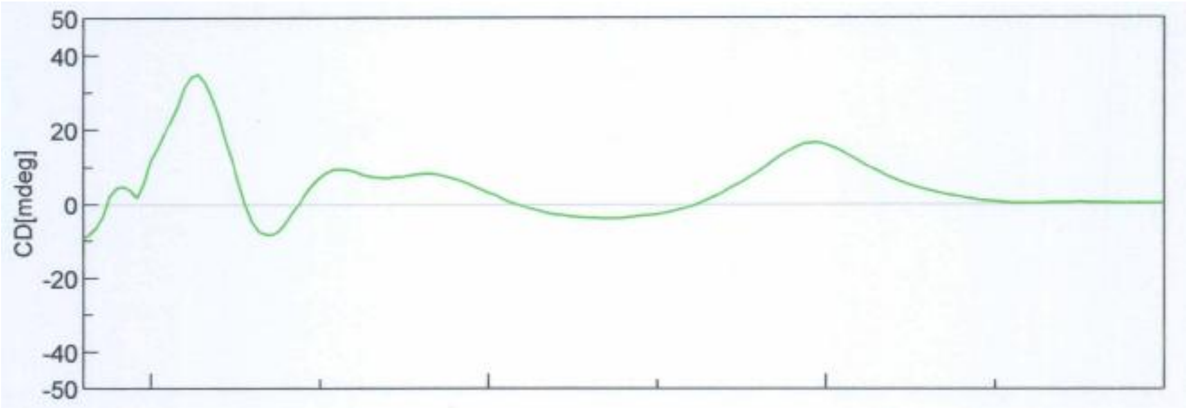
^{1}H NMR (600 MHz, $(CD_3)_2CO$)



^{1}H NMR (100 MHz, $(CD_3)_2CO$)



Pestalazine B (21)



4. X-Ray Details

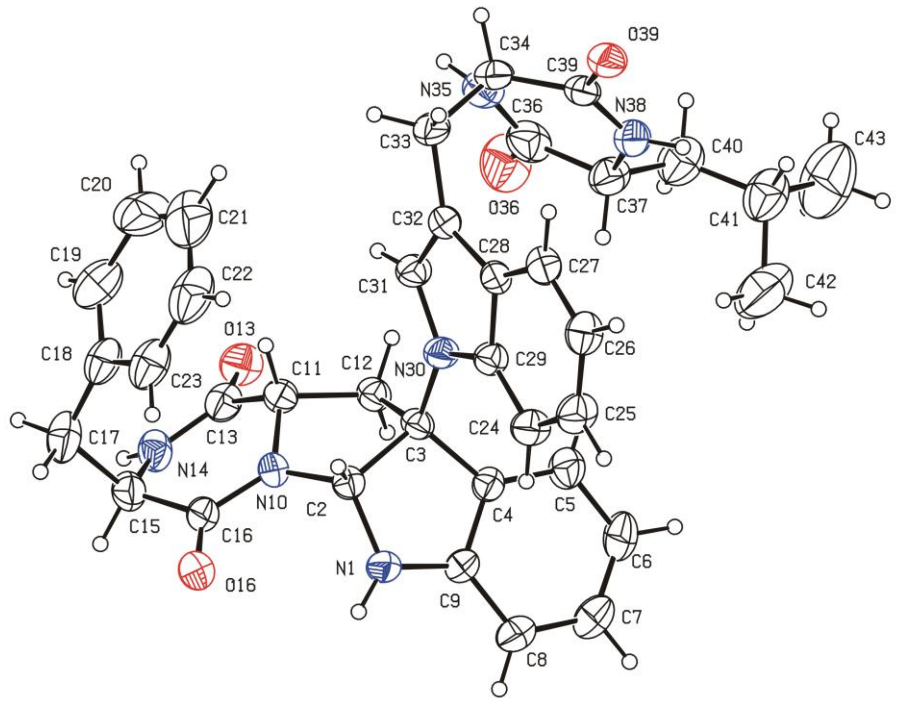


Table 1. Crystal data and structure refinement for ar1658s.

Identification code	ar1658s	
Empirical formula	C37 H38 N6 O7	
Formula weight	678.73	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4(3)	
Unit cell dimensions	a = 12.0209(8) Å	α= 90°.
	b = 12.0209(8) Å	β= 90°.
	c = 25.881(3) Å	γ = 90°.
Volume	3739.8(6) $Å^3$	
Z	4	
Density (calculated)	1.205 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	1432	
Crystal size	0.50 x 0.35 x 0.35 mm^3	
Theta range for data collection	1.69 to 25.05°.	
Index ranges	-9<=h<=14, -14<=k<=13, -29<=l<=30	
Reflections collected	19786	
Independent reflections	6553 [R(int) = 0.0570]	
Completeness to theta = 25.05°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.808	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6553 / 1 / 501	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0613, wR2 = 0.1525	
R indices (all data)	R1 = 0.1265, wR2 = 0.1936	
Absolute structure parameter	4(2)	
Extinction coefficient	0.0070(12)	
Largest diff. peak and hole	0.572 and -0.209 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ar1658s. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	3173(3)	8323(3)	682(2)	59(1)
C(2)	3995(3)	9122(3)	513(2)	48(1)
C(3)	4949(3)	8395(3)	266(2)	46(1)
C(4)	4560(4)	7226(3)	366(2)	49(1)
C(5)	5076(5)	6235(4)	253(2)	67(1)
C(6)	4520(5)	5251(4)	366(2)	80(2)
C(7)	3467(6)	5285(4)	566(2)	80(2)
C(8)	2942(5)	6262(4)	680(2)	65(1)
C(9)	3505(4)	7256(3)	580(2)	52(1)
N(10)	3624(3)	9841(3)	98(1)	51(1)
C(11)	4397(4)	9847(4)	-336(2)	52(1)
C(12)	4858(4)	8684(4)	-320(2)	51(1)
C(13)	3830(4)	10166(4)	-835(2)	60(1)
O(13)	4207(3)	9847(3)	-1251(1)	74(1)
N(14)	2924(3)	10800(3)	-786(2)	64(1)
C(15)	2502(4)	11257(4)	-312(2)	67(1)
C(16)	2756(4)	10523(4)	144(2)	59(1)
O(16)	2193(3)	10579(3)	542(2)	75(1)
C(17)	2930(6)	12466(4)	-204(3)	85(2)
C(18)	4125(5)	12495(4)	-76(2)	73(2)
C(19)	4899(7)	12706(5)	-469(3)	98(2)
C(20)	6040(8)	12625(7)	-359(6)	129(3)
C(21)	6398(9)	12353(7)	119(6)	137(4)
C(22)	5626(9)	12177(5)	508(4)	113(3)
C(23)	4520(7)	12248(4)	415(2)	83(2)
C(24)	5909(4)	7742(4)	1352(2)	61(1)
C(25)	6504(5)	7568(5)	1805(2)	70(1)
C(26)	7573(5)	7976(4)	1866(2)	67(1)
C(27)	8068(4)	8585(4)	1479(2)	57(1)
C(28)	7496(3)	8791(4)	1025(2)	48(1)
C(29)	6419(4)	8347(4)	961(2)	50(1)
N(30)	6047(3)	8647(3)	472(1)	51(1)
C(31)	6856(4)	9304(4)	254(2)	53(1)

C(32)	7750(4)	9414(4)	568(2)	54(1)
C(33)	8816(4)	10021(4)	449(2)	62(1)
C(34)	9649(4)	9302(4)	138(2)	68(1)
N(35)	9197(3)	8990(4)	-360(2)	74(1)
C(36)	8704(5)	8037(6)	-464(2)	80(2)
O(36)	8148(5)	7915(4)	-861(2)	119(2)
C(37)	8809(5)	7097(4)	-84(2)	71(1)
N(38)	9581(3)	7332(4)	336(2)	64(1)
C(39)	9999(4)	8322(4)	451(2)	60(1)
O(39)	10662(3)	8454(3)	822(1)	69(1)
C(40)	9202(6)	6060(5)	-377(3)	96(2)
C(41)	9309(7)	5016(6)	-59(3)	104(2)
C(42)	8220(9)	4725(10)	236(5)	155(4)
C(43)	9630(18)	4058(9)	-415(6)	193(5)
O(1W)	1026(5)	209(7)	1585(2)	156(2)
O(2WA)	-186(10)	3176(9)	1312(5)	174(5)
O(2WB)	1794(12)	2264(12)	1218(6)	142(5)
O(3W)	6240(18)	3870(20)	1590(11)	550(20)

Table 3. Bond lengths [Å] and angles [°] for ar1658s.

N(1)-C(9)	1.369(6)
N(1)-C(2)	1.446(6)
C(2)-N(10)	1.449(5)
C(2)-C(3)	1.577(6)
C(3)-N(30)	1.456(5)
C(3)-C(4)	1.504(6)
C(3)-C(12)	1.558(6)
C(4)-C(5)	1.374(6)
C(4)-C(9)	1.384(6)
C(5)-C(6)	1.389(8)
C(6)-C(7)	1.369(8)
C(7)-C(8)	1.366(8)
C(8)-C(9)	1.398(6)
N(10)-C(16)	1.332(6)
N(10)-C(11)	1.456(6)
C(11)-C(12)	1.505(6)
C(11)-C(13)	1.512(7)
C(13)-O(13)	1.229(6)
C(13)-N(14)	1.335(7)
N(14)-C(15)	1.436(7)
C(15)-C(16)	1.504(8)
C(15)-C(17)	1.567(7)
C(16)-O(16)	1.235(6)
C(17)-C(18)	1.474(9)
C(18)-C(23)	1.388(8)
C(18)-C(19)	1.402(9)
C(19)-C(20)	1.403(12)
C(20)-C(21)	1.350(13)
C(21)-C(22)	1.385(14)
C(22)-C(23)	1.353(10)
C(24)-C(25)	1.388(7)
C(24)-C(29)	1.389(7)
C(25)-C(26)	1.385(7)
C(26)-C(27)	1.376(7)
C(27)-C(28)	1.384(7)
C(28)-C(29)	1.410(6)

C(28)-C(32)	1.433(6)
C(29)-N(30)	1.390(6)
N(30)-C(31)	1.374(5)
C(31)-C(32)	1.354(6)
C(32)-C(33)	1.506(6)
C(33)-C(34)	1.550(7)
C(34)-N(35)	1.449(7)
C(34)-C(39)	1.490(7)
N(35)-C(36)	1.318(8)
C(36)-O(36)	1.234(7)
C(36)-C(37)	1.503(8)
C(37)-N(38)	1.457(7)
C(37)-C(40)	1.534(9)
N(38)-C(39)	1.326(6)
C(39)-O(39)	1.257(6)
C(40)-C(41)	1.506(9)
C(41)-C(43)	1.524(13)
C(41)-C(42)	1.554(13)
C(9)-N(1)-C(2)	111.4(3)
N(1)-C(2)-N(10)	114.2(3)
N(1)-C(2)-C(3)	104.6(3)
N(10)-C(2)-C(3)	104.7(3)
N(30)-C(3)-C(4)	114.4(3)
N(30)-C(3)-C(12)	111.9(3)
C(4)-C(3)-C(12)	110.8(3)
N(30)-C(3)-C(2)	113.2(3)
C(4)-C(3)-C(2)	102.8(3)
C(12)-C(3)-C(2)	102.7(3)
C(5)-C(4)-C(9)	121.4(4)
C(5)-C(4)-C(3)	129.3(4)
C(9)-C(4)-C(3)	109.2(4)
C(4)-C(5)-C(6)	118.4(5)
C(7)-C(6)-C(5)	120.0(5)
C(8)-C(7)-C(6)	122.3(5)
C(7)-C(8)-C(9)	118.1(5)
N(1)-C(9)-C(4)	111.6(4)
N(1)-C(9)-C(8)	128.6(4)

C(4)-C(9)-C(8)	119.8(4)
C(16)-N(10)-C(2)	122.8(4)
C(16)-N(10)-C(11)	124.5(4)
C(2)-N(10)-C(11)	112.1(3)
N(10)-C(11)-C(12)	102.1(3)
N(10)-C(11)-C(13)	111.9(4)
C(12)-C(11)-C(13)	115.2(4)
C(11)-C(12)-C(3)	105.0(4)
O(13)-C(13)-N(14)	124.3(5)
O(13)-C(13)-C(11)	120.2(5)
N(14)-C(13)-C(11)	115.5(5)
C(13)-N(14)-C(15)	126.1(4)
N(14)-C(15)-C(16)	111.9(4)
N(14)-C(15)-C(17)	113.0(5)
C(16)-C(15)-C(17)	109.7(4)
O(16)-C(16)-N(10)	122.6(5)
O(16)-C(16)-C(15)	120.7(4)
N(10)-C(16)-C(15)	116.7(5)
C(18)-C(17)-C(15)	112.5(4)
C(23)-C(18)-C(19)	118.3(7)
C(23)-C(18)-C(17)	122.3(6)
C(19)-C(18)-C(17)	119.2(6)
C(18)-C(19)-C(20)	119.3(8)
C(21)-C(20)-C(19)	120.9(10)
C(20)-C(21)-C(22)	119.3(9)
C(23)-C(22)-C(21)	121.2(8)
C(22)-C(23)-C(18)	120.9(8)
C(25)-C(24)-C(29)	117.8(5)
C(26)-C(25)-C(24)	121.4(5)
C(27)-C(26)-C(25)	120.4(5)
C(26)-C(27)-C(28)	119.9(5)
C(27)-C(28)-C(29)	119.3(4)
C(27)-C(28)-C(32)	133.5(4)
C(29)-C(28)-C(32)	107.2(4)
C(24)-C(29)-N(30)	131.1(4)
C(24)-C(29)-C(28)	121.1(4)
N(30)-C(29)-C(28)	107.7(4)
C(31)-N(30)-C(29)	107.2(3)

C(31)-N(30)-C(3)	127.7(4)
C(29)-N(30)-C(3)	124.9(3)
C(32)-C(31)-N(30)	111.8(4)
C(31)-C(32)-C(28)	106.0(4)
C(31)-C(32)-C(33)	126.9(4)
C(28)-C(32)-C(33)	127.1(4)
C(32)-C(33)-C(34)	112.7(4)
N(35)-C(34)-C(39)	112.7(5)
N(35)-C(34)-C(33)	111.4(4)
C(39)-C(34)-C(33)	109.9(4)
C(36)-N(35)-C(34)	125.2(5)
O(36)-C(36)-N(35)	121.1(6)
O(36)-C(36)-C(37)	120.1(6)
N(35)-C(36)-C(37)	118.8(5)
N(38)-C(37)-C(36)	113.3(5)
N(38)-C(37)-C(40)	109.3(5)
C(36)-C(37)-C(40)	108.2(5)
C(39)-N(38)-C(37)	125.7(4)
O(39)-C(39)-N(38)	121.6(4)
O(39)-C(39)-C(34)	119.7(5)
N(38)-C(39)-C(34)	118.7(5)
C(41)-C(40)-C(37)	115.7(6)
C(40)-C(41)-C(43)	108.7(8)
C(40)-C(41)-C(42)	112.6(7)
C(43)-C(41)-C(42)	109.9(10)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for ar1658s. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	51(2)	49(2)	77(3)	4(2)	19(2)	0(2)
C(2)	49(2)	47(2)	50(2)	0(2)	1(2)	2(2)
C(3)	37(2)	48(2)	52(2)	-5(2)	-2(2)	0(2)
C(4)	52(3)	44(2)	51(2)	1(2)	-4(2)	-1(2)
C(5)	76(3)	52(3)	74(3)	-8(2)	5(3)	5(3)
C(6)	106(5)	43(3)	92(4)	-8(3)	1(4)	11(3)
C(7)	99(5)	53(3)	87(4)	0(3)	1(3)	-16(3)
C(8)	67(3)	59(3)	71(3)	5(2)	2(3)	-15(3)
C(9)	55(3)	44(3)	56(3)	1(2)	1(2)	-7(2)
N(10)	49(2)	43(2)	60(2)	0(2)	3(2)	6(2)
C(11)	47(3)	53(3)	56(3)	2(2)	-6(2)	-2(2)
C(12)	46(3)	52(3)	56(3)	-4(2)	-2(2)	1(2)
C(13)	65(3)	55(3)	59(3)	3(2)	-14(3)	-9(2)
O(13)	78(2)	88(3)	55(2)	10(2)	-2(2)	-1(2)
N(14)	63(3)	54(2)	75(3)	2(2)	-24(2)	2(2)
C(15)	58(3)	49(3)	94(4)	-2(3)	-11(3)	3(2)
C(16)	51(3)	41(3)	85(4)	0(2)	0(3)	0(2)
O(16)	66(2)	60(2)	99(3)	4(2)	15(2)	10(2)
C(17)	109(5)	49(3)	98(5)	2(3)	-21(4)	8(3)
C(18)	101(5)	38(3)	79(4)	-11(2)	-11(3)	-12(3)
C(19)	129(7)	70(4)	94(5)	-11(3)	-7(5)	-33(4)
C(20)	102(7)	94(6)	192(10)	-25(6)	12(8)	-41(5)
C(21)	115(8)	75(5)	222(12)	-8(6)	-70(9)	-23(4)
C(22)	140(8)	65(4)	135(7)	4(4)	-55(7)	-28(4)
C(23)	116(5)	59(3)	73(4)	0(3)	-24(4)	-14(3)
C(24)	57(3)	74(3)	52(3)	7(2)	-3(2)	-4(3)
C(25)	79(4)	80(4)	52(3)	17(3)	-2(3)	-4(3)
C(26)	78(4)	67(3)	54(3)	4(2)	-11(3)	4(3)
C(27)	56(3)	52(3)	63(3)	-7(2)	-10(2)	2(2)
C(28)	43(3)	44(2)	58(3)	-1(2)	-2(2)	4(2)
C(29)	48(3)	54(3)	49(3)	1(2)	0(2)	0(2)
N(30)	43(2)	58(2)	51(2)	8(2)	-2(2)	-4(2)
C(31)	46(3)	59(3)	53(3)	8(2)	-5(2)	-5(2)

C(32)	45(3)	52(2)	65(3)	10(2)	-3(2)	1(2)
C(33)	47(3)	57(3)	82(3)	11(3)	-11(3)	-12(2)
C(34)	42(3)	73(3)	89(4)	22(3)	4(3)	-10(2)
N(35)	60(3)	95(4)	67(3)	22(3)	5(2)	5(2)
C(36)	64(4)	106(5)	72(4)	10(3)	-11(3)	4(3)
O(36)	132(4)	130(4)	94(3)	13(3)	-36(3)	5(3)
C(37)	68(4)	72(4)	73(3)	8(3)	-6(3)	-11(3)
N(38)	57(2)	66(3)	69(2)	14(2)	-3(2)	0(2)
C(39)	38(2)	71(3)	70(3)	19(3)	4(2)	0(2)
O(39)	49(2)	75(2)	83(2)	14(2)	-4(2)	-5(2)
C(40)	111(5)	83(4)	95(4)	-1(4)	-11(5)	-13(4)
C(41)	124(6)	79(4)	111(5)	3(4)	-26(5)	-16(4)
C(42)	167(9)	118(8)	180(9)	42(8)	-18(8)	-53(7)
C(43)	286(18)	87(7)	206(11)	-35(8)	7(17)	-3(8)
O(1W)	122(4)	224(7)	122(4)	-22(4)	31(4)	-7(4)
O(2WA)	202(11)	117(7)	202(11)	-16(7)	63(9)	-16(7)
O(2WB)	134(11)	124(10)	169(13)	-69(10)	29(10)	-4(9)
O(3W)	450(30)	660(40)	540(30)	-410(30)	170(30)	-160(30)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for ar1658s.

	x	y	z	U(eq)
H(1)	2554	8496	828	100(20)
H(2)	4277	9558	804	37(10)
H(5)	5781	6224	105	84(18)
H(6)	4864	4571	305	66(14)
H(7)	3095	4619	626	110(20)
H(8)	2230	6266	821	48(12)
H(11)	4997	10377	-264	50(11)
H(12A)	5583	8653	-484	66(14)
H(12B)	4364	8169	-494	76(15)
H(14)	2560	10949	-1063	80(18)
H(15)	1690	11296	-344	120(20)
H(17A)	2798	12922	-507	80(17)
H(17B)	2510	12781	81	130(30)
H(19)	4660	12898	-799	110(20)
H(20)	6556	12761	-619	150(30)
H(21)	7155	12285	187	150(30)
H(22)	5872	12006	839	130(30)
H(23)	4019	12130	683	90(20)
H(24)	5193	7462	1312	55(13)
H(25)	6177	7168	2073	85(17)
H(26)	7960	7837	2171	74(14)
H(27)	8785	8859	1523	70(15)
H(31)	6797	9632	-70	43(11)
H(33A)	9162	10249	771	52(12)
H(33B)	8644	10688	254	48(11)
H(34)	10313	9757	75	75(14)
H(35)	9255	9464	-608	86(19)
H(37)	8074	6945	64	77(16)
H(38)	9784	6781	526	79(18)
H(40A)	8684	5918	-657	100(20)
H(40B)	9920	6221	-531	100(20)
H(41)	9906	5123	194	110(20)

H(42A)	8012	5340	452	220(60)
H(42B)	8341	4078	446	280(70)
H(42C)	7637	4579	-8	300(90)
H(43A)	10321	4227	-583	110(30)
H(43B)	9060	3955	-671	240(80)
H(43C)	9710	3389	-216	240(60)

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DATE: OCTOBER 19TH 2009
CACTI'S CODE: AR1658
USER'S CODE: CB61122

EXPERIMENTAL REPORT_CB61122(AR1658)

A single crystal of **CB61122** was analysed by X-ray diffraction and a summary of the crystallographic data and the structure refinement parameters is reported in Table 1. Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) at 20 ºC using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), and were corrected for Lorentz and polarisation effects. The software SMART[1] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT[2] for integration of intensity of reflections and scaling, and SADABS[3] for empirical absorption correction. The structure (Figure 1) was solved by direct methods using the program SHELXS97.[4] All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using the program SHELXL97.[5] Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters except for the hydrogen atoms of crystallisation water molecules since due to the disorder these hydrogen atoms could not be located. One water molecule (O2w) is disordered ever two sites. Site occupations factors were refined with a sum constrained to 1, converging to 0.60 for atom O2wA and to 0.40 for atom O2wB.

[1] SMART Version 5.054, *Instrument control and data collection software,* Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA, 1997.
[2] SAINT Version 6.01, *Data Integration software package.* Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA, 1997.
[3] Sheldrick, G. M., SADABS. *A Computer Program for Absorption Corrections.* University of Göttingen, Germany, 1996.
[4] Sheldrick, G. M.. SHELXS97. *A Computer Program for the Solution of Crystal Structures from X-ray Data.* University of Göttingen, Germany, 1997
[5] Sheldrick, G. M. SHELXL97. *A Computer Program for the Refinement of Crystal Structures from X-ray Data.* University of Göttingen, Germany, 1997

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Table 1. Crystal data and structure refinement for CB61122.

Empirical formula	C37 H38 N6 O7	
Formula weight	678.73	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4(3)	
Unit cell dimensions	a = 12.0209(8) Å	a= 90°.
	b = 12.0209(8) Å	b= 90°.
	c = 25.881(3) Å	g = 90°.
Volume	3739.8(6) $Å^3$	
Z	4	
Density (calculated)	1.205 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	1432	
Crystal size	0.50 x 0.35 x 0.35 mm^3	
Theta range for data collection	1.69 to 25.05°.	
Index ranges	-9<=h<=14, -14<=k<=13, -29<=l<=30	
Reflections collected	19786	
Independent reflections	6553 [R(int) = 0.0570]	
Completeness to theta = 25.05°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.808	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6553 / 1 / 501	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0613, wR2 = 0.1527	
R indices (all data)	R1 = 0.1265, wR2 = 0.1939	
Absolute structure parameter	4(2)	
Extinction coefficient	0.0070(12)	
Largest diff. peak and hole	0.572 and -0.209 e.$Å^{-3}$	

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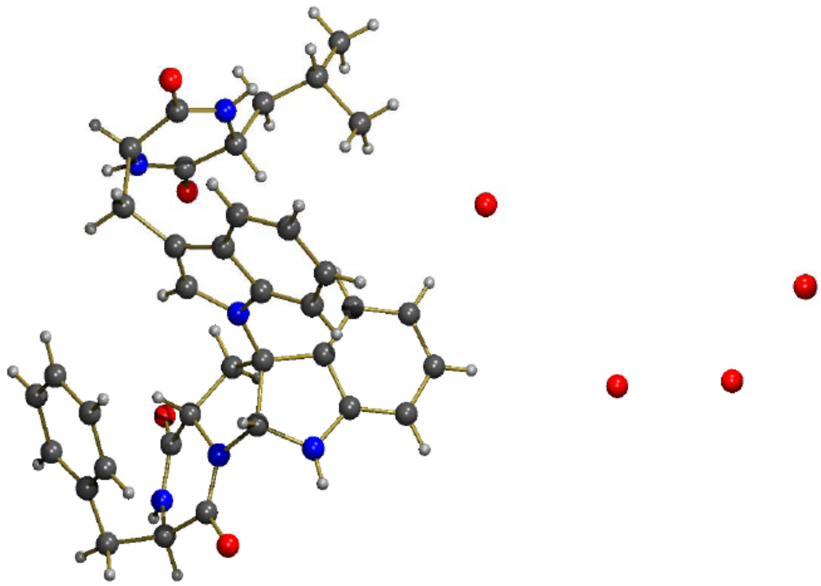

Figure 1. Molecular structure of CB61122.

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