Supporting Information

Synthesis of Fluorescent Jasplakinolide Analogs for Live-Cell STED[#] Microscopy of Actin

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[#] STED: Stimulated Emission Depletion

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1. Cell culture and *in vitro* labelling of actin in living U-2 OS and COS-7 cells

The human Osteosarcoma cell line U-2 OS was obtained from the European Collection of Authenticated Cell Cultures (ECACC, Porton Down, Salisbury, UK; Cat no. 92022711, Lot. 17E015). U-2 OS cells were cultivated in McCoy´s medium (Thermo Fisher Scientific, Waltham, MA, USA) supplemented with 10 % (v/v) fetal bovine serum (Thermo Fisher Scientific, Waltham, MA, USA), 1 % (v/v) sodium pyruvate (Sigma Aldrich, St. Louis, MO, USA) and Penicillin-Streptomycin (Sigma Aldrich, St. Louis, MO, USA).

The COS-7 cell line, which is a kidney cell line derived from the African green monkey, was obtained from the European Collection of Authenticated Cell Cultures (ECACC, Porton Down, Salisbury, UK; Cat no. 87021302, Lot. 05G008). COS-7 cells were cultivated in DMEM, high glucose, pyruvate Medium (Thermo Fisher Scientific, Waltham, MA, USA) supplemented with 10 % (v/v) fetal bovine serum (Thermo Fisher Scientific, Waltham, MA, USA) and Penicillin-Streptomycin (Sigma Aldrich, St. Louis, MO, USA).

In vitro labeling of Actin with jasplakilinolide probes was performed in DMEM, high glucose, HEPES, no phenol red Medium (Thermo Fisher Scientific, Waltham, MA, USA) supplemented with Penicillin-Streptomycin (Sigma Aldrich, St. Louis, MO, USA). U-2 OS and COS-7 cells were incubated with *580CP*-jasplakinolide (5 µM for 30 min) or *610CP*-jasplakinolide (1 µM for 60 min), respectively. For a subsequent washing step, the cells were incubated in medium without fluorescent probes for additional 30 min.

2. Live-cell STED microscopy

In vitro STED images were acquired using a quad scanning STED microscope (Abberior Instruments, Göttingen, Germany) equipped with a UPlanSApo 100x/1,40 Oil objective (Olympus, Tokyo, Japan). For all images a pixel size of 20 nm was utilized. 580CP was excited using a 561 nm laser beam, 610CP was excited using a 640 nm laser beam and STED was performed applying a laser beam with an emission wavelength of 775 nm. With the exception of contrast stretching no further image processing was applied.

3. HPLC Traces and ESI-MS data

Figure S1. LC-MS analysis of the reaction mixture **5**-C(CH_3)$_2$$C_6H_5$-H → **5**-H-H (11.2 min) + **5**-H-C(CH_3)$_2$$C_6H_5$ (12.3 min); see Scheme 2 in the main text.

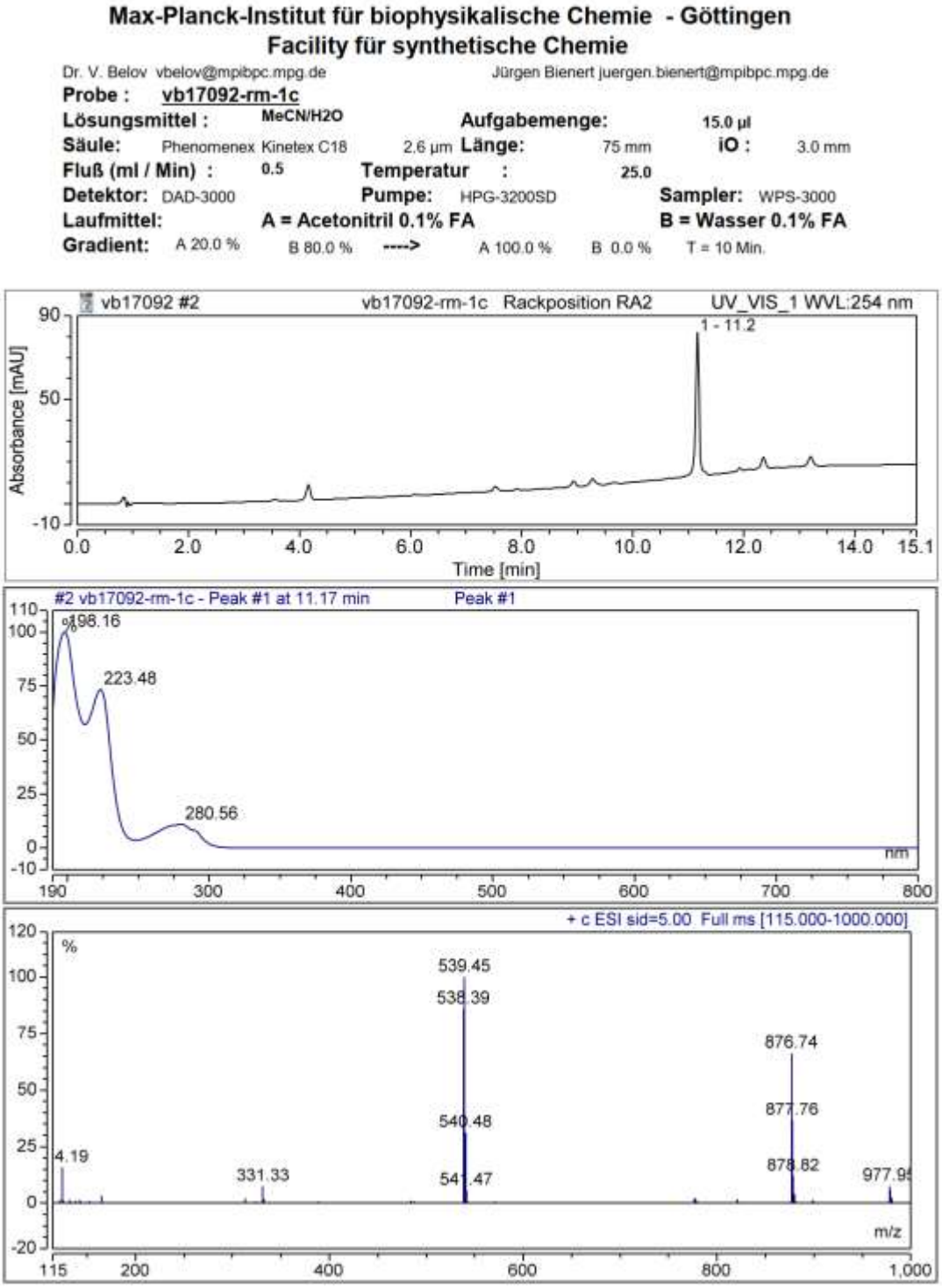

Figure S2a. HPLC trace of amine **9** formed from compound **7**-H (R = Boc) and formic acid according Scheme 4 in the main text.

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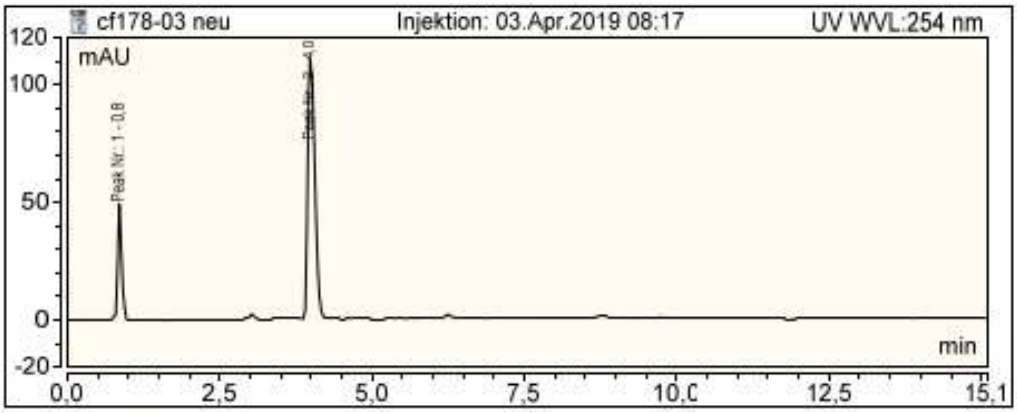
Probe : cf178-03 neu

Lösungsmittel :	MeCN/H2O	**Konzentration :**	? %
Aufgabeart :	Handaufgabe	**Aufgabemenge :**	1 µl
Säule :	Kinetex 2.6 µm C18 100		
Länge :	7.5 cm	**Innendurchmesser :**	4.6 mm
Fluß (ml / Min) :	1,0	**Temperatur :**	25,0
Detektor :	DAD-3000	**Pumpe:**	HPG-3400SD

Laufmittel : A = Acetonitril B = Wasser 0.05% TFA

Gradient : A 20,0 % B 80,0 % ----> A 100,0 % B 0,0 % T = 10 Min.



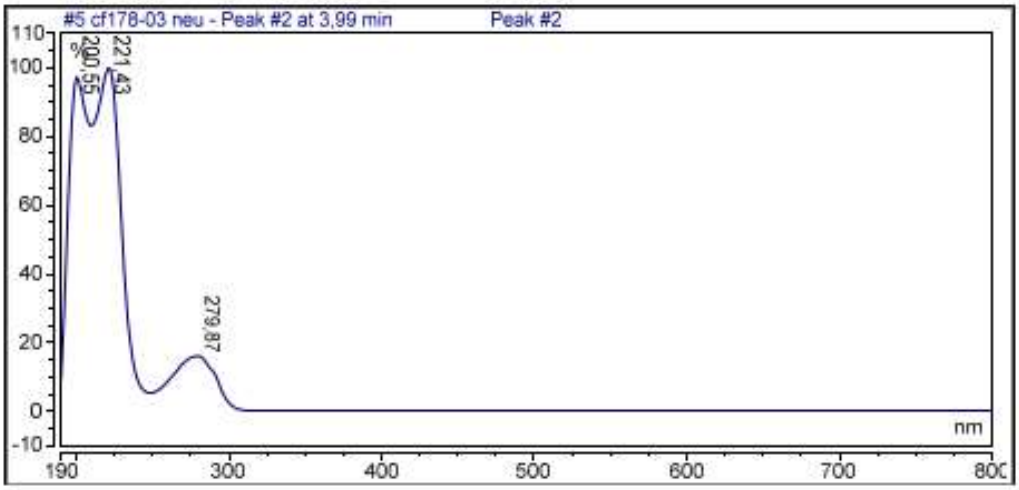


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Figure S2b. ESI-MS (positive mode) of amine **9** ($C_{38}H_{51}N_5O_6$, M = 674.4) formed from compound **7**-H (R = Boc) and HCOOH; see Scheme 4 in the main text.

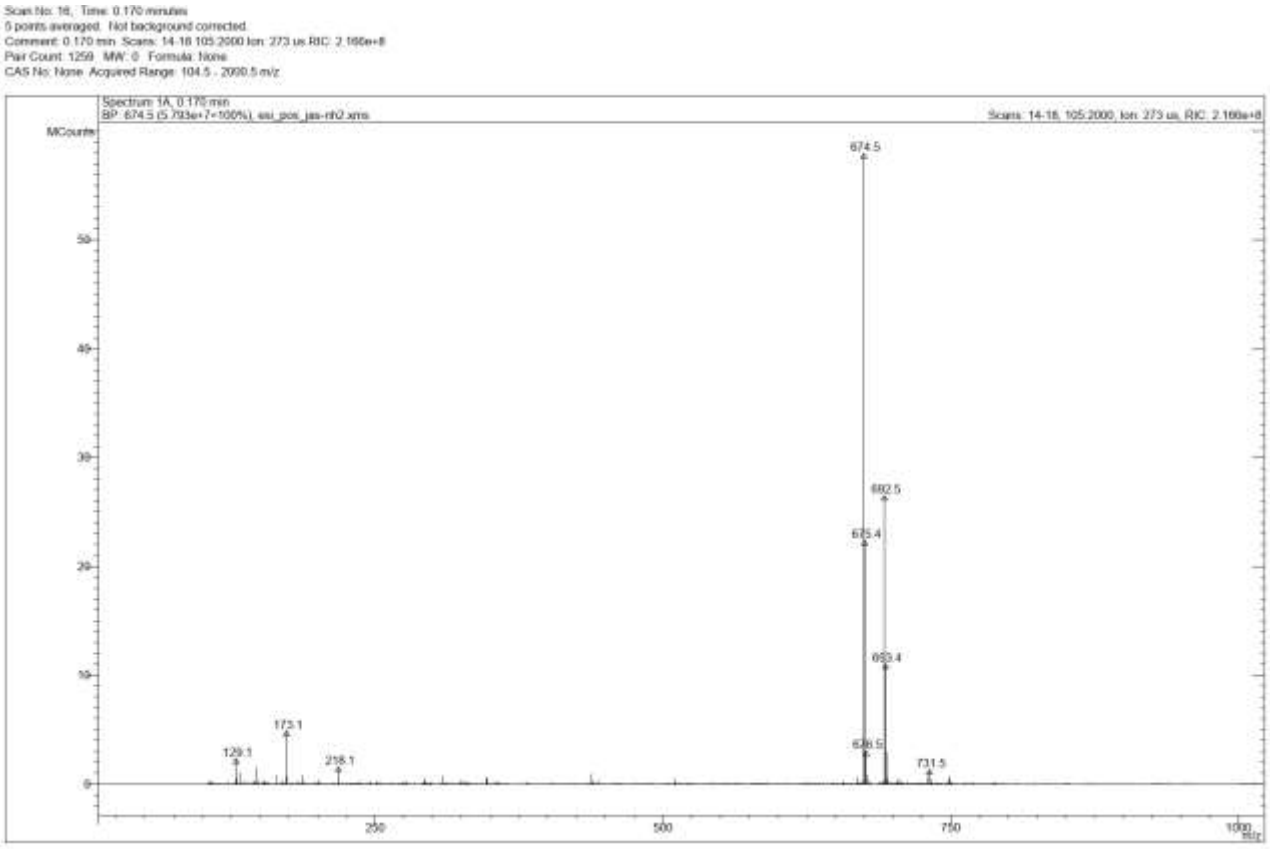

Figure S3a. HPLC trace of *580CP*-jasplakinolide conjugate (see Scheme 4 and TOC graph)

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Probe : cf178-04 Fr 9-12 neu

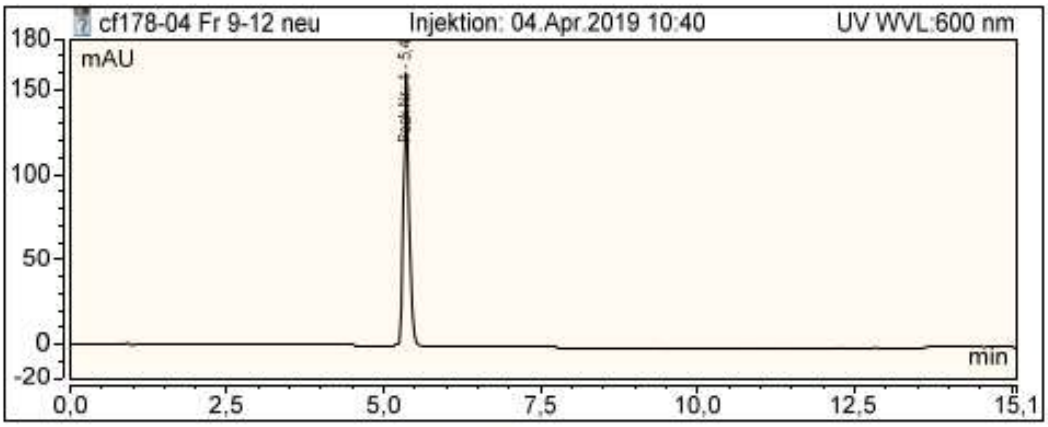
Lösungsmittel : MeCN/H2O **Konzentration :** ? %
Aufgabeart : Handaufgabe **Aufgabemenge :** 1 µl

Säule : Kinetex 2.6 µm C18 100
Länge : 7.5 cm **Innendurchmesser :** 4.6 mm

Fluß (ml / Min) : 1,0 **Temperatur :** 25,0
Detektor : DAD-3000 **Pumpe:** HPG-3400SD

Laufmittel : A = Acetonitril B = Wasser 0.05% TFA

Gradient : A 20,0 % B 80,0 % ----> A 100,0 % B 0,0 % T = 10 Min.



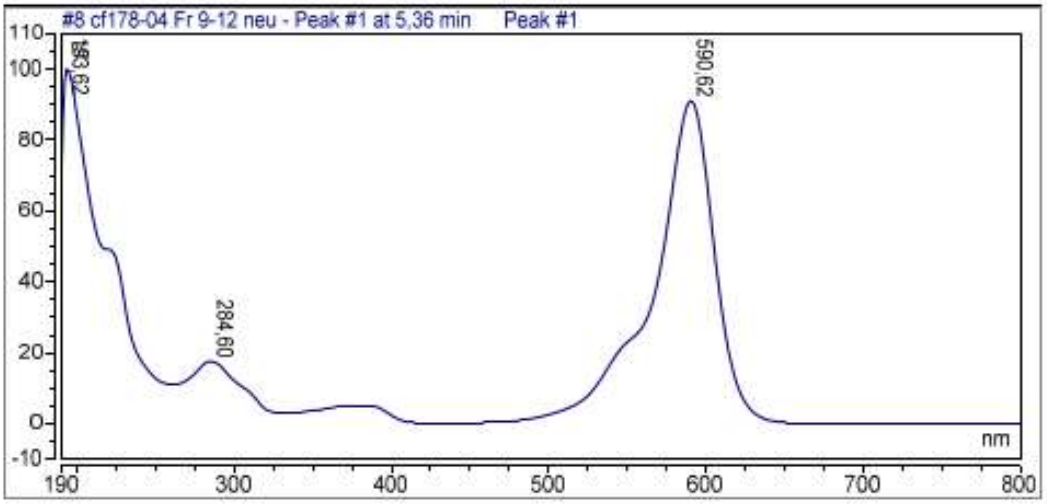


Figure S3b. HPLC trace of *610CP*-jasplakinolide conjugate (see Scheme 4 and TOC graph)

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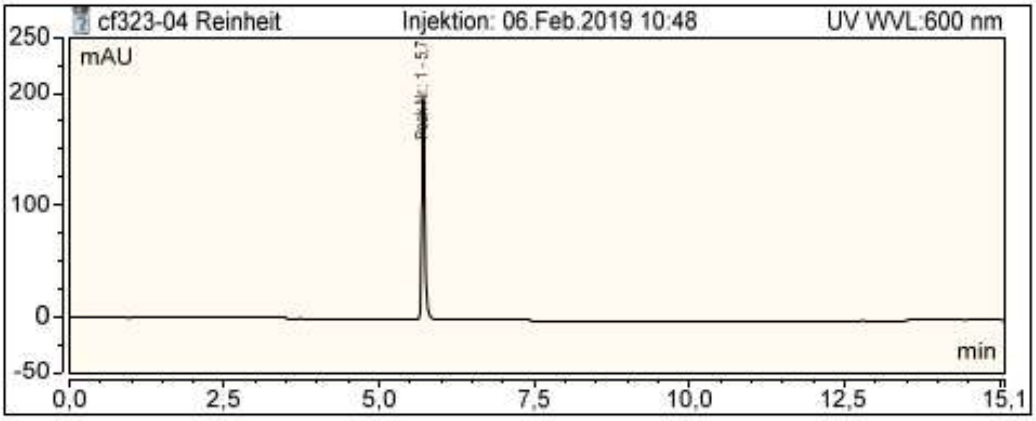
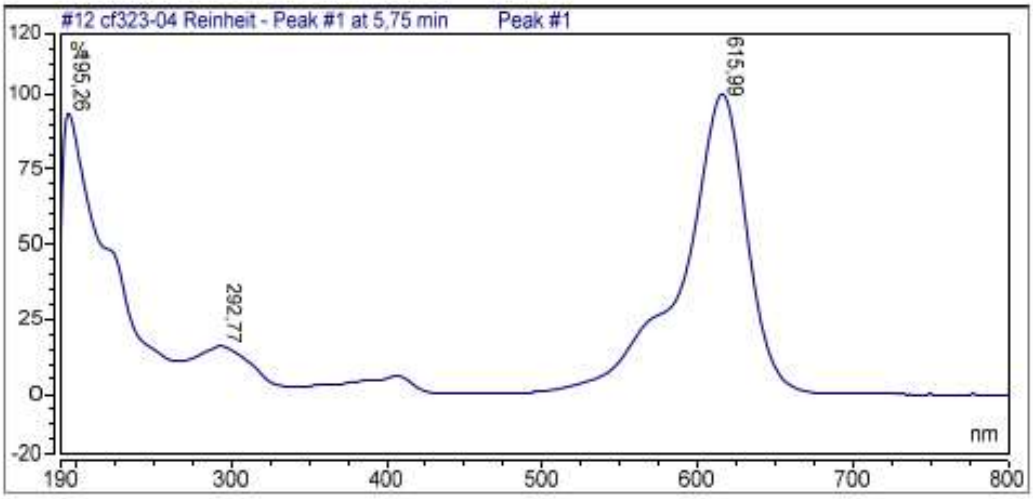
Probe : cf323-04 Reinheit

Lösungsmittel :	MeCN/H2O	**Konzentration :**	? %
Aufgabeart :	Handaufgabe	**Aufgabemenge :**	1 µl
Säule :	Kinetex 2.6 µm C18 100		
Länge :	7.5 cm	**Innendurchmesser :**	4.6 mm
Fluß (ml / Min) :	1,0	**Temperatur :**	25
Detektor :	DAD-3000	**Pumpe:**	HPG-3400SD

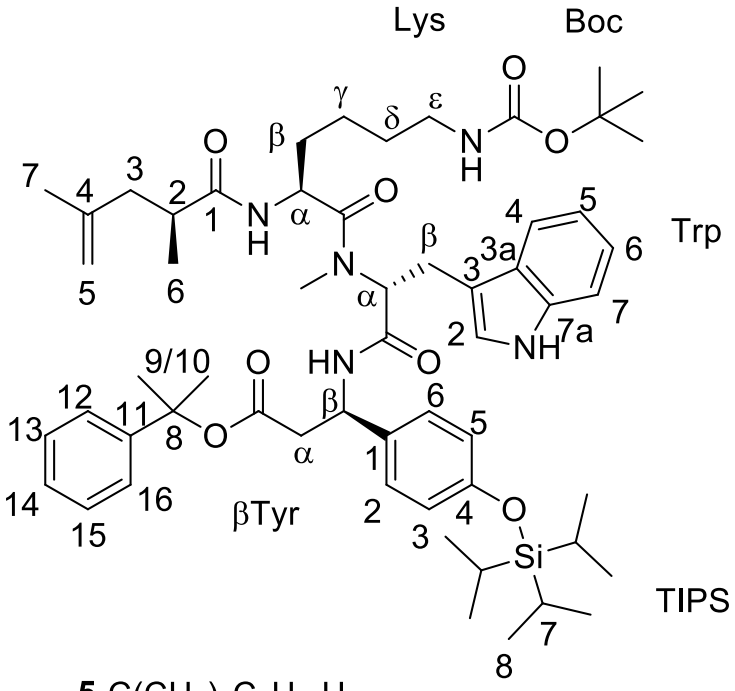
Laufmittel : A = Acetonitril B = Wasser 0.05% TFA

Gradient : A 100,0 % B 0,0 % ----> A 100,0 % B 0,0 % T = 10 Min.





4. NMR Spectra



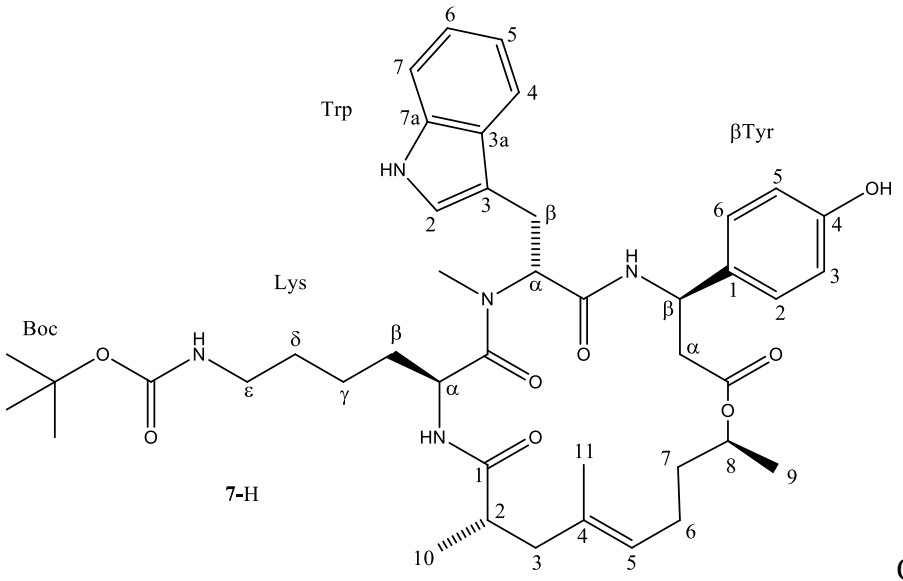
5-$C(CH_3)_2C_6H_5$-H

$CDCl_3$, 600 MHz ^1H

Position	δ(1H) / ppm	δ($^{13}C\{^1H\}$) / ppm	COSY	HMBC	NOESY
Trp α	5,62	56,58	Trp β	Trp β Trp NMe Trp 3 Trp CO Lys CO	Trp NMe Trp β Trp 2 Trp 4
Trp β	3,20 / 3,41	23,07	Trp 2 Trp α	Trp α Trp 3	Trp NMe Trp α Trp 4 Trp 2
Trp NH	9,52	-	Trp 2	-	Trp 2 Trp 7
Trp 2	6,92	121,81	Trp NH	Trp 3	Trp α Trp NH Trp β Trp NMe
Trp 3	-	110,58	-	-	-
Trp 3a	-	127,31	-	-	-
Trp 4	7,56	118,47	Trp 5 Trp 6	Trp 3 Trp 6 Trp 3a Trp 7a	Trp NMe Trp β Trp α Trp 5

Trp 5	7,06	119,04	Trp 4 Trp 6	Trp 7 Trp 3a	Trp 4
Trp 6	7,12	121,69	Trp 5 Trp 7	Trp 4 Trp 7a Trp CO	Trp 7
Trp 7	7,30	111,30	Trp 6	Trp 5 Trp 3a	Trp 6 Boc Me
Trp 7a	-	136,39	-	-	-
Trp NMe	2,70	30,58	-	Trp α Lys CO	Trp α Trp β Trp 2 Trp 4
Trp CO	-	169,10	-	-	-
βTyr NH	7,12	-	βTyr β	-	βTyr β
βTyr α	2,75 / 2,90	41,47	βTyr β	βTyr β βTyr 1 βTyr CO	βTyr β βTyr 2/6
βTyr β	5,35	49,54	βTyr α βTyr 2/6 βTyr NH	βTyr α βTyr 2/6 βTyr 1 βTyr CO	βTyr α βTyr 2/6
βTyr CO	-	169,34	-	-	-
βTyr 1	-	133,18	-	-	-
βTyr 2/6	7,13	127,66	βTyr β βTyr 3/5	βTyr β βTyr 6/2 βTyr 4	βTyr α βTyr β βTyr 3/5
βTyr 3/5	6,79	119,79	βTyr 2/6	βTyr 5/3 βTyr 1 βTyr 4	TIPS 7 TIPS 8 βTyr 2/6
βTyr 4	-	155,38	-	-	-
TIPS 7	1,22	12,65	TIPS 8	TIPS 8	TIPS 8 βTyr 3/5
TIPS 8	1,06 / 1,08	12,65 / 17,92	TIPS 7	TIPS 7 TIPS 8	TIPS 7 TIPS 8
1	-	176,10	-	-	-
2	2,35	38,73	3 7	7 2 5 3	7 1 6 Lys NH
3	1,98 / 2,30	41,82	4 6	6 4 1 7 2 5	7 1 6
4	-	142,82	-	-	-
5	4,66 / 4,73	112,43	1	1	3

			3	3	4 1
6	1,05	17,27	4	4 3 5	3 4
7	1,64	22,25	6	6 2	6 3 4
8	-	81,96	-	-	-
9/10	1,65 / 1,63	28,78 / 28,10	-	10/9 8 11	7,24
11	-	145,51	-	-	-
12/16	7,22	124,41	13/15 14	8 16/12 14	9/10
13/15	7,26	128,19	12/16 14	11 15/13 12/16	-
14	7,19	126,83	13/15 12/16	12/16	-
Lys NH	6,17	-	Lys α	5	7 4 Lys α
Lys CO	-	173,20	-	-	-
Lys α	4,45	49,63	Lys NH	Lys γ Lys β Lys CO	Lys γ Lys β Trp NMe Lys NH
Lys β	1,05 / 1,35	31,01	Lys α	Lys α	Lys δ Lys γ Lys α
Lys γ	0,74 (both)	21,42	Lys β Lys δ	Lys β Lys δ Lys ε	Lys δ Lys β Lys ε Lys α
Lys δ	1,19 (both)	30,01	Lys γ Lys ε	Lys γ Lys ε	Lys ε Lys β Lys γ
Lys ε	2,85 / 2,89	40,29	Lys δ	Lys δ	Lys γ Lys δ
Lys ε/NH	4,62	-	Lys ε	-	Lys ε
Boc CO	-	156,47	-	-	-
Boc C	-	79,75	-	-	-
Boc Me	1,49	28,48	-	Boc C Boc Me	-



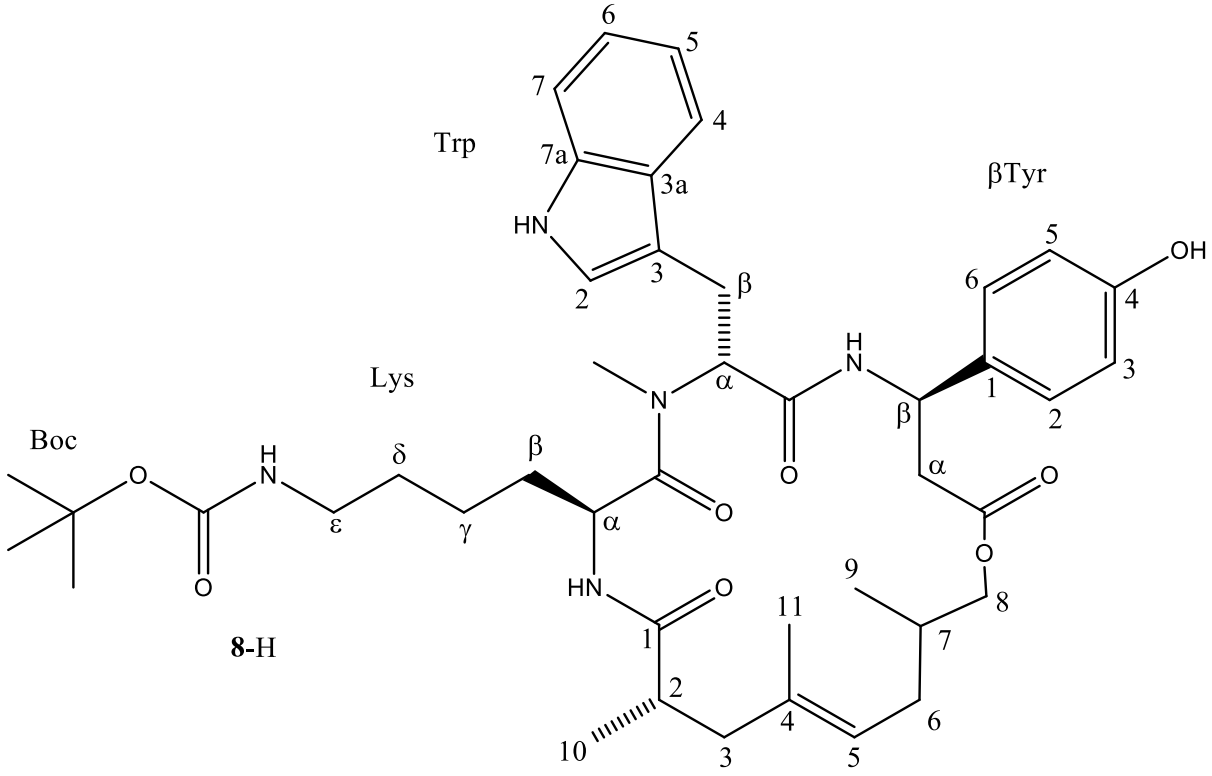
$CDCl_3$, 600 MHz ^1H

Position	δ(^{1}H) / ppm	δ(^{13}C{^{1}H}) / ppm	COSY	HMBC	NOESY
Trp α	5,70	56,38	Trp β	Trp CO Lys CO Trp β Trp NMe	Trp β Trp 2 βTyr NH Trp 4
Trp β	3,31 / 3,35	22,56	Trp α Trp 2	Trp 3 Trp 3a Trp 2 Trp α	Trp NMe Trp α Trp 2 Trp 4
Trp 2	6,95	121,78	Trp β Trp NH	Trp 3 Trp 3a Trp 7a	Lys γ Lys β Trp NMe Trp β Trp α Trp NH
Trp 3	-	110,12	-	Trp β Trp 2 Trp 4	-
Trp 3a	-	127,25	-	Trp 2 Trp 4 Trp 5 Trp 7	-
Trp 4	7,60	118,50	Trp 5 Trp 7	Trp 3 Trp 6 Trp 3a Trp 7a	Trp β Trp α Trp 5 Trp 6
Trp 5	7,10	119,22	Trp 4 Trp 6 Trp 7	Trp 7 Trp 3a	Trp 6 Trp 4

Trp 6	7,16	121,94	Trp 4 Trp 5 Trp 7	Trp 7a Trp 4	Trp 5 Trp 7
Trp 7	7,36	111,64	Trp 4 Trp 5 Trp 6	Trp 3a Trp 5	Trp 6 Trp NH Boc Me
Trp 7a	-	136,68	-	Trp 2 Trp 4 Trp 6	-
Trp NH	9,90	-	Trp 2	-	Boc Me Lys ε/NH Trp 2 Trp 7
Trp CO	-	169,58	-	Trp α	-
Trp NMe	2,91	30,43	-	Trp α Lys CO	Lys β Trp β Lys α Trp 2
βTyr NH	7,44	-	βTyr β	-	βTyr β Trp α βTyr 2/6
βTyr β	5,20	49,37	βTyr NH βTyr α	βTyr 2/6 βTyr 1 Trp CO βTyr CO βTyr α	βTyr α βTyr 2/6 βTyr NH
βTyr α	2,76 / 2,57	39,77	βTyr β	βTyr β βTyr 1 βTyr CO	βTyr α βTyr β βTyr 2/6
βTyr 1	-	132,71	-	βTyr β βTyr α	-
βTyr 2/6	7,13	127,54	βTyr 3/5	βTyr 4 βTyr β βTyr 5/3	11 βTyr α βTyr β βTyr 3/5 βTyr NH
βTyr 3/5	6,77	115,71	βTyr 2/6	βTyr 6/2 βTyr 1 βTyr 4	11 Tyr 2/6
βTyr 4	-	155,40	-	βTyr 2/6 βTyr 3/5	-
βTyr CO	-	170,80	-	βTyr β βTyr α	-
1	-	175,54	-	2 3	-
2	2,47	39,84	10 3	1	10 11

					Lys NH
3	1,88 / 2,43	43,34	2	11 2 5 4 1	5 3 10 11
4	-	133,72	-	3	-
5	4,99	125,08	6 11	11 6 7 3	7 6 3 8
6	1,79 (both)	23,29	5 7	5 7 8 4	5 9 11 7 8
7	1,35 / 1,54	35,59	6 8	9 6 8 5	5 9 7 6 8
8	4,80	69,81	7 9	βTyr CO 7 6 5	9 7 6 5
9	1,10	20,64	8	7 8	7 6 8
10	1,14	20,36	2	2 3 1	3 2
11	1,42	16,12	5 3 6	3 4 5	6 3 2
Lys NH	6,77	-	Lys α	Lys CO 1	2 Lys α
Lys α	4,88	49,98	Lys NH Lys β	Lys γ Lys β Lys CO 1	Lys γ Lys β Trp NMe Lys NH
Lys CO	-	173,94	-	Lys NH Lys α	-
Lys β	1,03 / 1,53	30,99	Lys α Lys γ	Lys α	Lys β Lys α Lys γ
Lys γ	0,64 / 0,98	21,12	Lys β Lys δ	Lys α Lys δ	Lys β Lys α

Lys δ	1,21 / 1,26	30,24	Lys γ Lys ε	-	Lys γ Lys β Lys ε
Lys ε	2,82 / 3,04	40,85	Lys δ	-	Lys δ
Lys ε/NH	4,75	-	-	-	-
Boc CO	-	156,80	-	-	-
Boc C	-	80,05	-	Boc Me	-
Boc Me	1,52	28,65	-	Boc C	-



8-H

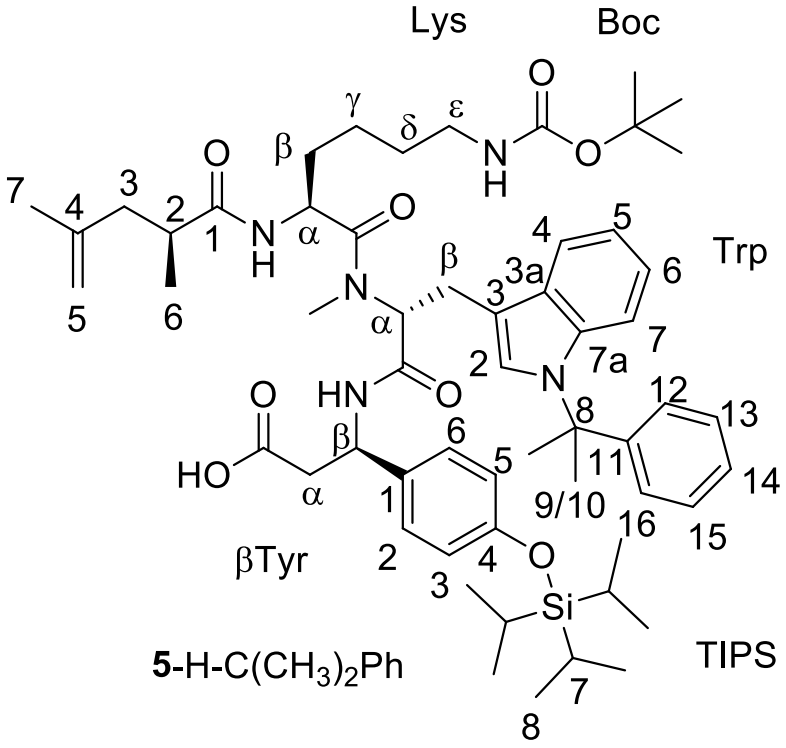
$CDCl_3$, 500 MHz ^1H

Position	δ(^{1}H) / ppm	δ(^{13}C{^{1}H}) / ppm	COSY	HMBC	NOESY
Trp α	5,55	56,28	Trp β	Trp β Trp NMe Trp CO Lys CO	Trp β Trp 2 Trp 5 Trp 4
Trp β	3,18 / 3,40	22,53	Trp β Trp α Trp 2	Trp 3 Trp 2 Trp 3a	Trp NMe Trp α Trp 2 Trp 4
Trp 2	6,92	121,67	Trp β Trp NH	Trp 3 Trp 3a Trp 7a	Lys γ 11 Trp NMe

					Trp α Trp NH
Trp 3	-	109,82	-	Trp 4 Trp 2 Trp β	-
Trp 3a	-	127,08	-	Trp β Trp 2 Trp 5 Trp 7 Trp 4	-
Trp 4	7,58	118,34	Trp 5 Trp 6 Trp 7	Trp 3a Trp 3 Trp 7a Trp 6	Trp NMe Trp β Trp α Trp 5
Trp 5	7,08	119,09	Trp 7 Trp 4 Trp 6	Trp 3a Trp 7 Trp 4	βTyr α βTyr β Trp α Trp 4
Trp 6	7,13	121,80	Trp 5 Trp 7 Trp 4	Trp 4 Trp 7a	βTyr α Trp 7
Trp 7	7,32	111,50	Trp 4 Trp 5 Trp 6	Trp 5 Trp 3a	Lys β Boc Trp 6 Trp NH
Trp 7a	-	136,52	-	Trp 6 Trp 4 Trp 2	-
Trp NH	9,87	-	Trp 2	-	Trp 7 Trp 2 Lys ε Boc
Trp CO	-	169,50	-	Trp α βTyr β	-
Trp NMe	2,92	30,44	-	Trp α Lys CO	Trp 4 Trp 2 Trp β
βTyr NH	7,08	-	βTyr β	-	
βTyr β	5,33	48,75	βTyr NH βTyr α	βTyr α βTyr 1 βTyr 2/6 βTyr CO	βTyr α βTyr 2/6
βTyr α	2,59 / 2,76	39,89	βTyr β	βTyr β βTyr 1 βTyr CO	βTyr β βTyr 2/6
βTyr 1	-	132,75	-	βTyr β βTyr α	-

βTyr 2/6	7,14	127,48	βTyr 3/5	βTyr β βTyr 2/6 βTyr 4	βTyr α βTyr β βTyr 3/5
βTyr 3/5	6,78	115,58	βTyr 2/6	βTyr 3/5 βTyr 1 βTyr 4	βTyr 2/6
βTyr 4	-	155,23	-	βTyr 2/6 βTyr 3/5	-
βTyr CO	-	170,82	-	βTyr β βTyr α	-
1	-	175,24	-	10 3 2 Lys NH	-
2	2,45	40,01	10 3	10 1	10 11 3 5 Lys NH
3	1,88 / 2,41	43,46	2	2 1 4 5	10 11
4	-	133,94	-	11 3	-
5	5,06	124,36	11 6	11 6	9 6 7 3 8
6	1,73 / 1,90	31,16	5 7 11	8 4 5	9 5
7	1,65	33,04	9 8	9 6 8	9 6 8 5
8	3,70 / 3,97	67,05	7	9 6 7 βTyr CO	9 7 5 Lys α
9	0,84	17,47	7	6 7 8	6 7 8
10	1,11	20,01	3 2	2 3 1	3 2

11	1,49	15,82	-	3 5 4	Lys β 3 2
Lys NH	6,65	-	Lys α	Lys CO 1	10 Lys β 11 3 Lys α
Lys α	4,74	49,80	Lys NH Lys β	Lys γ Lys β Lys CO	Lys γ Lys β 11 Trp NMe 8 Lys NH
Lys CO	-	173,54	-	Lys α Trp NMe Trp α Lys NH	-
Lys β	0,94 / 1,50	30,74	Lys α Lys γ	Lys α	Lys γ 11 Trp NMe Lys α Lys NH
Lys γ	0,59 / 0,93	20,91	Lys β Lys δ	Lys α	Lys δ Trp 2
Lys δ	1,16 / 1,22	30,06	Lys γ Lys ε	-	Lys ε Lys γ
Lys ε	2,78 / 3,01	40,68	Lys δ	-	Lys δ
Lys ε/NH	4,73	-	-	-	-
Boc CO	-	156,69	-	-	-
Boc C	-	79,91	-	-	-
Boc Me	1,50	28,50	-	-	-

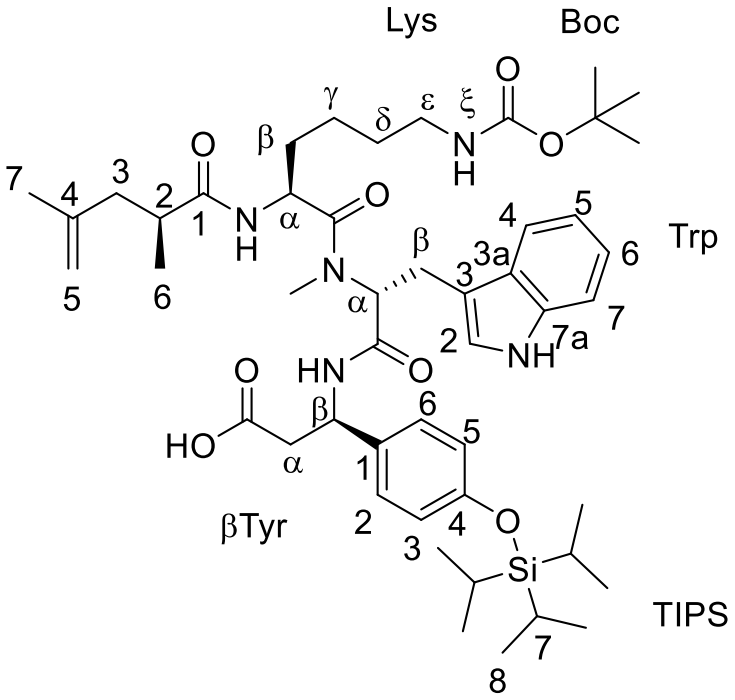


$CDCl_3$, 600 MHz ^1H

Position	δ(^{1}H) / ppm	δ(^{13}C{^{1}H}) / ppm	COSY	HMBC	NOESY
Trp α	5,56	57,31	Trp β	Trp β Trp NMe	
Trp β	3,24 / 3,47	23,09	Trp α	Trp α Trp 2 Trp 3 Trp 3a	Trp α Trp 4 Trp NMe
Trp 2	7,27	123,80	-	Trp β Trp 3 Trp 3a Trp 7a 8	9/10
Trp 3	-	109,53	-	-	-
Trp 3a	-	129,55	-	-	-
Trp 4	7,54	118,75	Trp 5 Trp 6	Trp 3 Trp 6 Trp 3a Trp 7a	Trp 5
Trp 5	6,97	118,94	Trp 4 Trp 6 Trp 7	Trp 7 Trp 3a	Trp 4 Trp 6
Trp 6	6,84	121,02	Trp 4 Trp 5 Trp 7	Trp 4 Trp 7a	Trp 5 Trp 7

Trp 7	6,56	113,77	Trp 5 Trp 6	Trp 5 Trp 3a	9/10 Trp 6 12/16
Trp 7a	-	135,48	-	-	-
Trp NMe	3,00	31,13	-	Lys CO Trp α	Lys α Lys NH
Trp CO	-	169,22	-	-	-
βTyr NH	7,10	-	βTyr β		
βTyr α	2,83 / 2,78	40,92	βTyr β	βTyr β βTyr 1 βTyr CO	βTyr 2/6
βTyr β	5,37	49,63	βTyr α βTyr NH	βTyr α βTyr 2/6 βTyr 1 βTyr CO	βTyr 2/6
βTyr CO	-	172,6	-	-	-
βTyr 1	-	133,42	-	-	-
βTyr 2/6	7,13	127,40	βTyr 3/5	βTyr β βTyr 2/6 βTyr 4	βTyr β βTyr 3/5 βTyr α
βTyr 3/5	6,77	119,96	βTyr 2/6	βTyr 3/5 βTyr 1 βTyr 4	βTyr α βTyr β βTyr 2/6 TIPS 7 TIPS 8
βTyr 4	-	155,43	-	-	-
TIPS 7	1,21	12,80	TIPS 8	TIPS 8	TIPS 8 βTyr 3/5
TIPS 8	1,07	18,07	TIPS 7	TIPS 7 TIPS 8	TIPS 7
1	-	178,17	-		-
2	2,55	38,97	3 7	5 3 7	3 1 7 6 5
3	2,05 / 2,40	41,81	4 6	4 6 2 5 1	3 7
4	-	142,84	-		-
5	4,71 / 4,76	112,69	1 3	1 3	6 1 3 4
6	1,12	17,49	4	4	3

				3 5	4 Lys NH
7	1,69	22,42	6	3 6 2	3 4
8	-	60,43	-	Trp 2	-
9/10	1,87 / 1,88	30,41 / 30,33	-	10/9 8 11	Trp 2 Trp 7 12/16
11	-	146,86	-	-	-
12/16	7,10	125,24	13/15 14	8 16/12 14	9/10 Trp 7
13/15	7,25	128,75	12/16 14	15/13 11 12/16	12/16 14
14	7,22	127,08	12/16 13/15	12/16	13/15 14
Lys NH	6,71	-	Lys α	-	Trp NMe 7
Lys CO	-	173,28	-	-	-
Lys α	4,65	49,93	Lys β Lys NH	-	Trp NMe
Lys β	1,33 / 1,29	31,12	Lys α Lys γ	-	-
Lys γ	1,17	22,49	Lys β	-	-
Lys δ	1,30 / 1,17	29,68	Lys ε	Lys ε	Lys ε
Lys ε	2,99 / 2,91	39,61	Lys δ Lys ε/NH	-	-
Lys ε/NH	4,51	-	Lys ε	-	-
Boc CO	-	156,48	-	-	-
Boc C	-	79,48	-	-	-
Boc Me	1,43	28,57	-	Boc Me Boc C	-



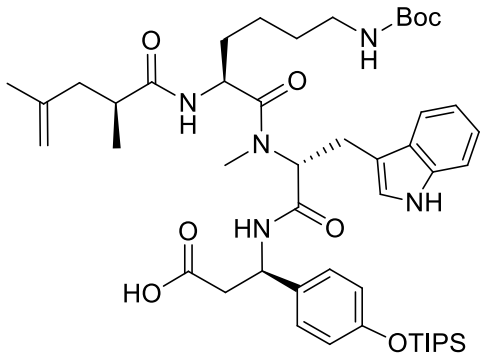
5-H-H = **1**-H-TIPS $CDCl_3$, 600 MHz ^1H

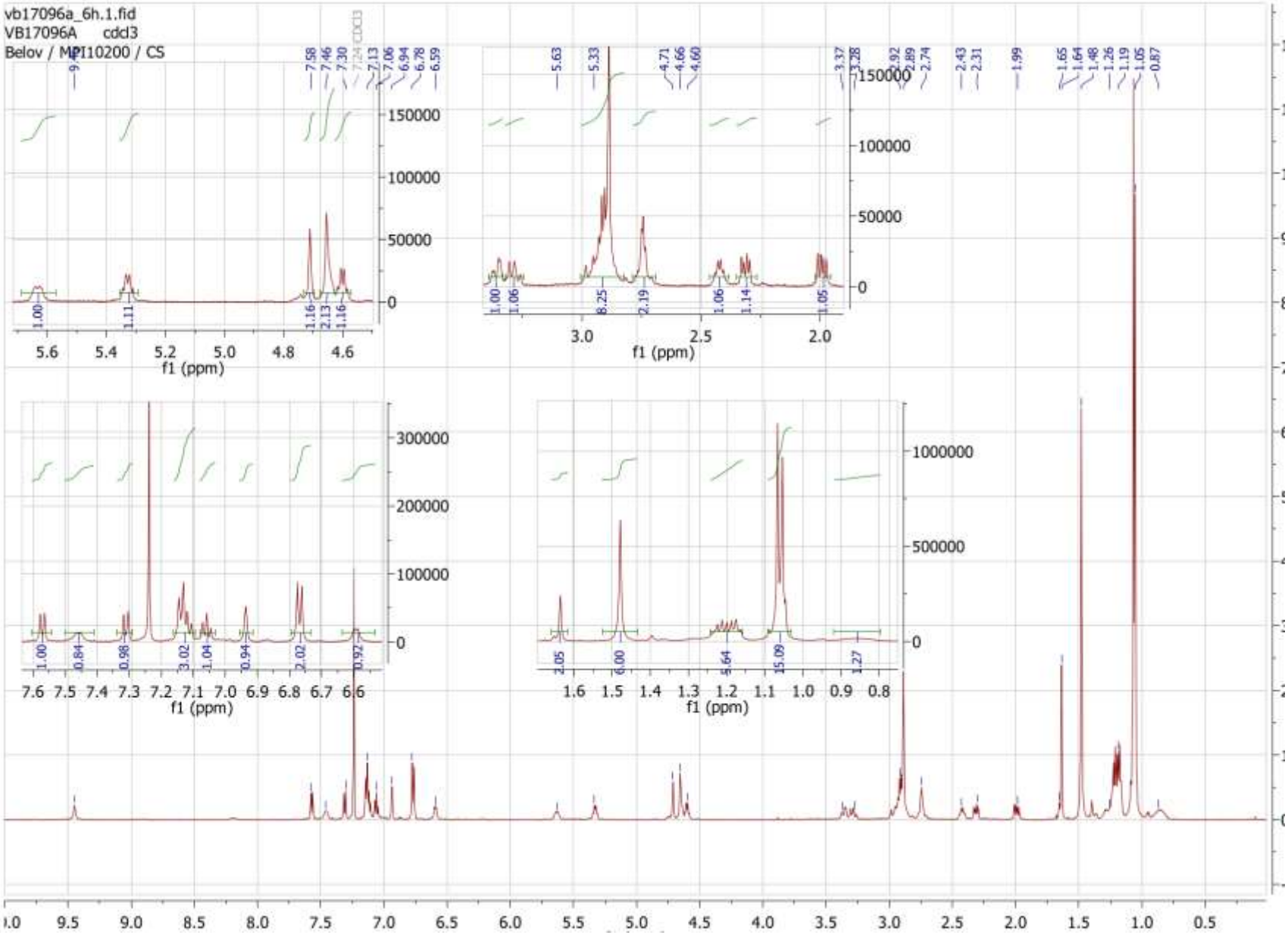
Position	δ(^{1}H) / ppm	δ(^{13}C{^{1}H}) / ppm	COSY	HMBC	NOESY
Trp α	5,59	56,26	Trp β	-	Trp β Trp NMe βTyr NH
Trp β	3,25 3,32	22,54	Trp α	Trp 3 Trp 2 Trp 3a	Trp α
Trp NH	9,41	-	Trp 2	-	Trp 2
Trp 2	6,90	121,63	Trp NH	Trp 3 Trp 3a Trp 7a	Trp NH
Trp 3	-	110,22	-	-	-
Trp 3a	-	126,98	-	-	-
Trp 4	7,53	118,19	Trp 5	Trp 3 Trp 6 Trp 3a Trp 7a	Trp 5
Trp 5	7,02	118,77	Trp 4 Trp 6	Trp 7 Trp 3a	Trp 4 Trp 6
Trp 6	7,08	121,41	Trp 5 Trp 7	Trp 4 Trp 7a	Trp 7 Trp 5
Trp 7	7,27	110,98	Trp 6	Trp 5 Trp 3a	Trp 6

Trp 7a	-	136,06	-	-	-
Trp NMe	2,85	30,25	-	Trp α Lys CO	Trp α Lys α βTyr NH
Trp CO	-	168,89	-	-	-
βTyr NH	7,42	-	βTyr β	-	βTyr β Trp α βTyr α Trp NMe
βTyr α	2,71	40,78	βTyr β	βTyr β βTyr 1 βTyr CO	βTyr β βTyr 2/6 βTyr NH
βTyr β	5,29	49,10	βTyr NH βTyr α	βTyr α βTyr 2/6 βTyr 1 Trp CO βTyr CO	βTyr 2/6 βTyr NH βTyr α
βTyr CO	-	173,35	-	-	-
βTyr 1	-	133,16	-	-	-
βTyr 2/6	7,10	127,02	βTyr 3/5	βTyr 4 βTyr β βTyr 6/2	βTyr α βTyr β βTyr 3/5
βTyr 3/5	6,73	119,38	βTyr 2/6	βTyr 4 βTyr 5/3 βTyr 1	βTyr 2/6 TIPS 8 TIPS 7
βTyr 4	-	154,86	-	-	-
TIPS 7	1,17	12,32	TIPS 8	TIPS 8	βTyr 3/5
TIPS 8	1,02	17,60	TIPS 7	TIPS 8 TIPS 7	βTyr 3/5
1	-	176,79	-	-	-
2	2,38	38,56	3 7	7 5	3 1 6 7
3	1,95 2,27	41,35	4 6	1 4 6 2 5 7	4 6 1
4	-	142,41	-	-	-
5	4,62 4,67	112,16	1 3	1 3	1 3 4
6	1,01	17,04	4	4 3 5	4 Lys NH

7	1,60	21,92	6	3 6 2	3 4 6
Lys NH	6,55	-	Lys α	5	7 3 Lys α
Lys CO	-	172,66	-	-	-
Lys α	4,56	49,31	Lys β Lys NH	Lys γ Lys β Lys CO 5	Lys β Trp NMe Lys NH
Lys β	1,07 1,24	30,61	Lys α Lys γ	-	-
Lys γ	0,82	21,43	Lys β Lys δ	-	-
Lys δ	1,18	29,60	Lys γ Lys ε	-	-
Lys ε	2,84 2,91	39,86	Lys δ Lys ξ	Boc CO	-
Lys ξ	4,61	-	Lys ε	-	-
Boc CO	-	156,20	-	-	-
Boc C	-	79,43	-	-	-
Boc Me	1,44	28,16	-	Boc Me Boc C	-

Figures S4a-e. NMR spectra of compound **1**-H-TIPS (**5**-H-H) in $CDCl_3$: ^{1}H (600 MHz), $^{13}C\{^{1}H\}$ (151 MHz), APT (CH/CH_3 +, C_q/CH_2 –), ^{1}H-^{1}H, and ^{1}H-^{13}C (HSQC) COSY.

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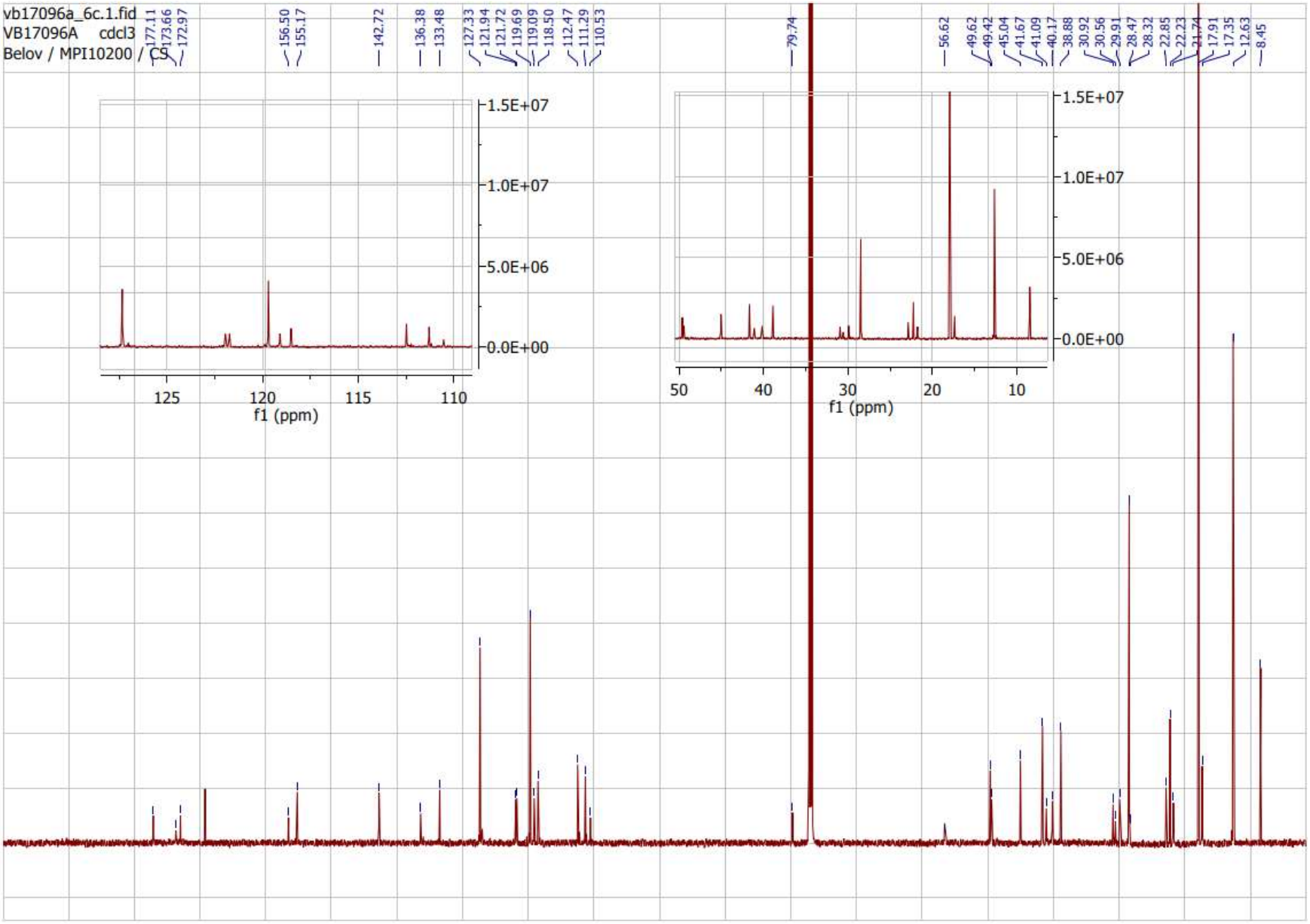
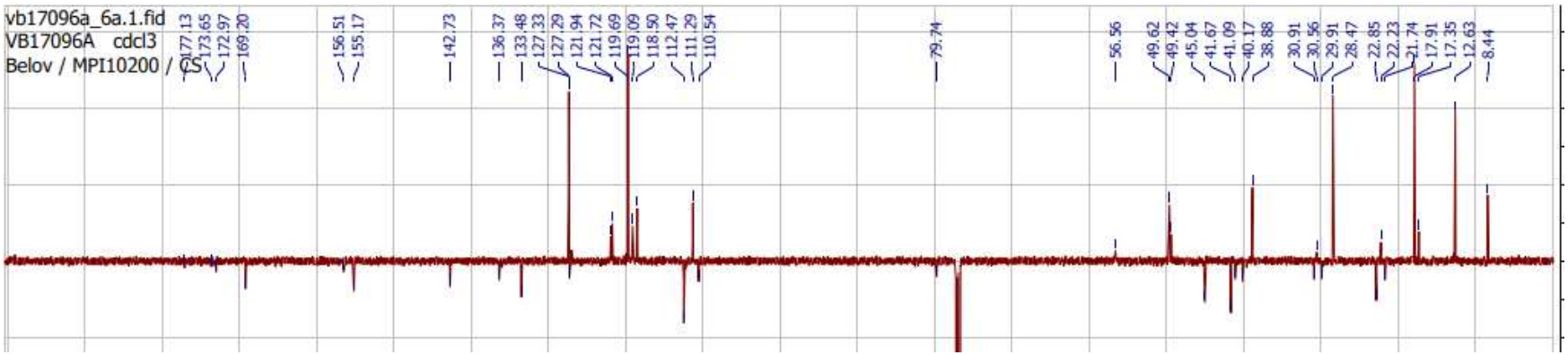
VB17096A cdcl3
Belov / MPI10200 / CS
f1 (ppm)


vb17096a_6c.1.fid
VB17096A cdcl3
Belov / MPI10200 / CS
177.11
173.66
172.97
156.50
155.17
142.72
136.38
133.48
127.33
121.94
121.72
119.69
119.09
118.50
112.47
111.29
110.53
79.74
56.62
49.62
49.42
45.04
41.67
41.09
40.17
38.88
30.92
30.56
29.91
28.47
28.32
22.85
22.23
21.74
17.91
17.35
12.63
8.45
1.5E+07
1.0E+07
5.0E+06
0.0E+00
125
120
115
110
f1 (ppm)
50
40
30
20
10


vb17096a_6a.1.fid
VB17096A cdcl3
Belov / MPI10200 / CS
177.13
173.65
172.97
169.20
156.51
155.17
142.73
136.37
133.48
127.33
127.29
121.94
121.72
119.69
119.09
118.50
112.47
111.29
110.54
79.74
56.56
49.62
49.42
45.04
41.67
41.09
40.17
38.88
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30.56
29.91
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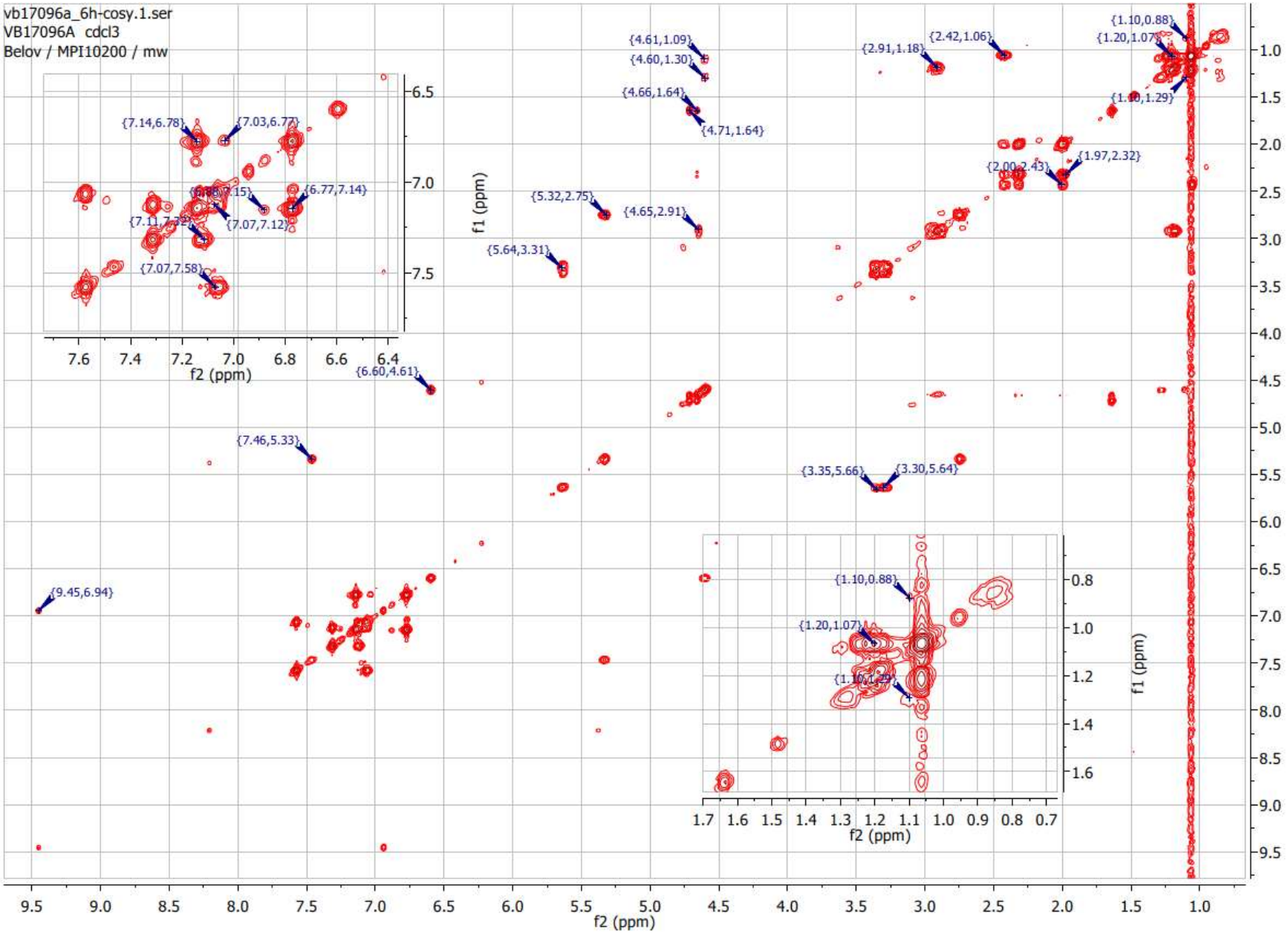
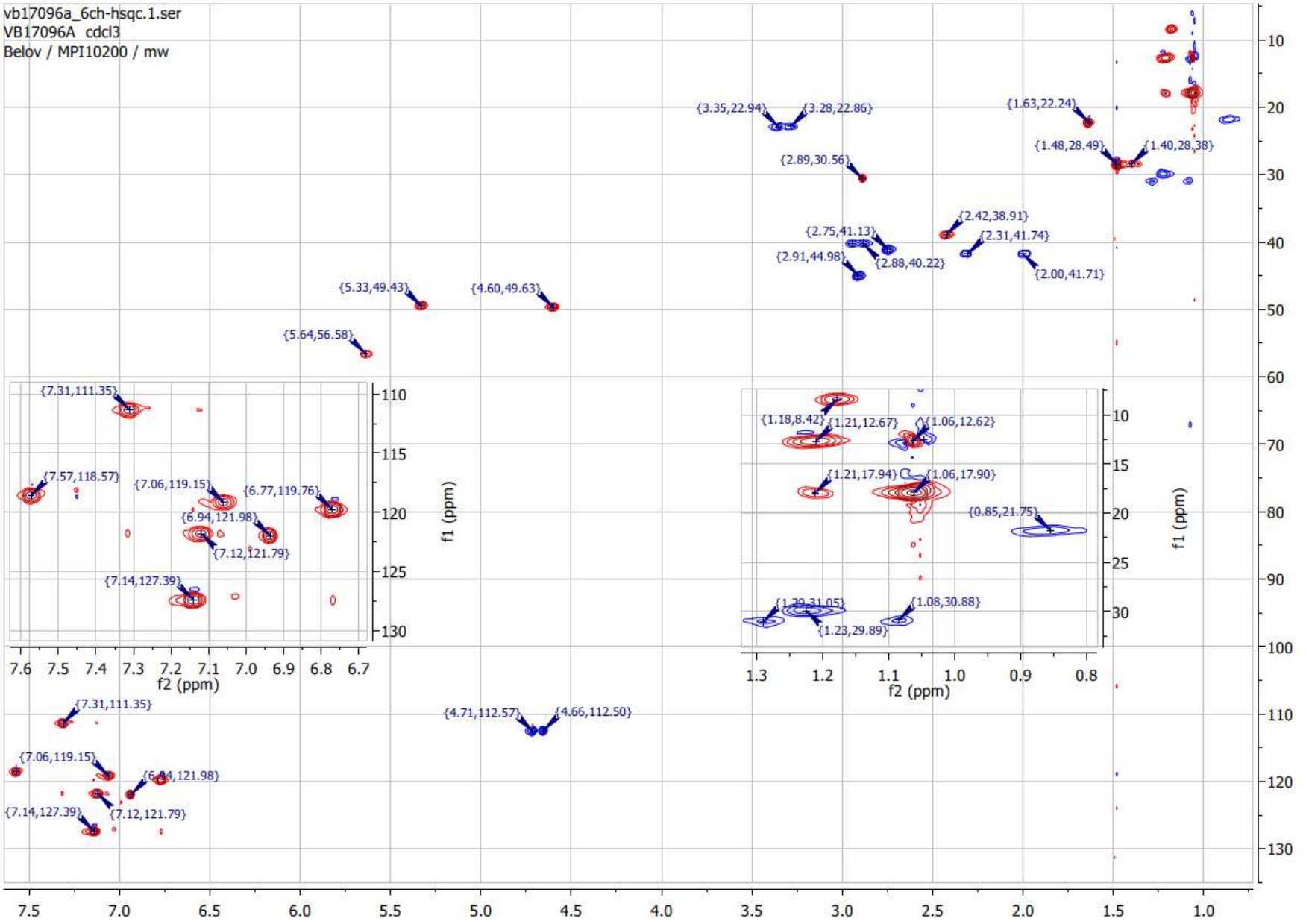
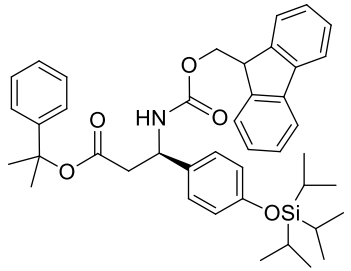
22.85
22.23
21.74
17.91
17.35
12.63
8.44

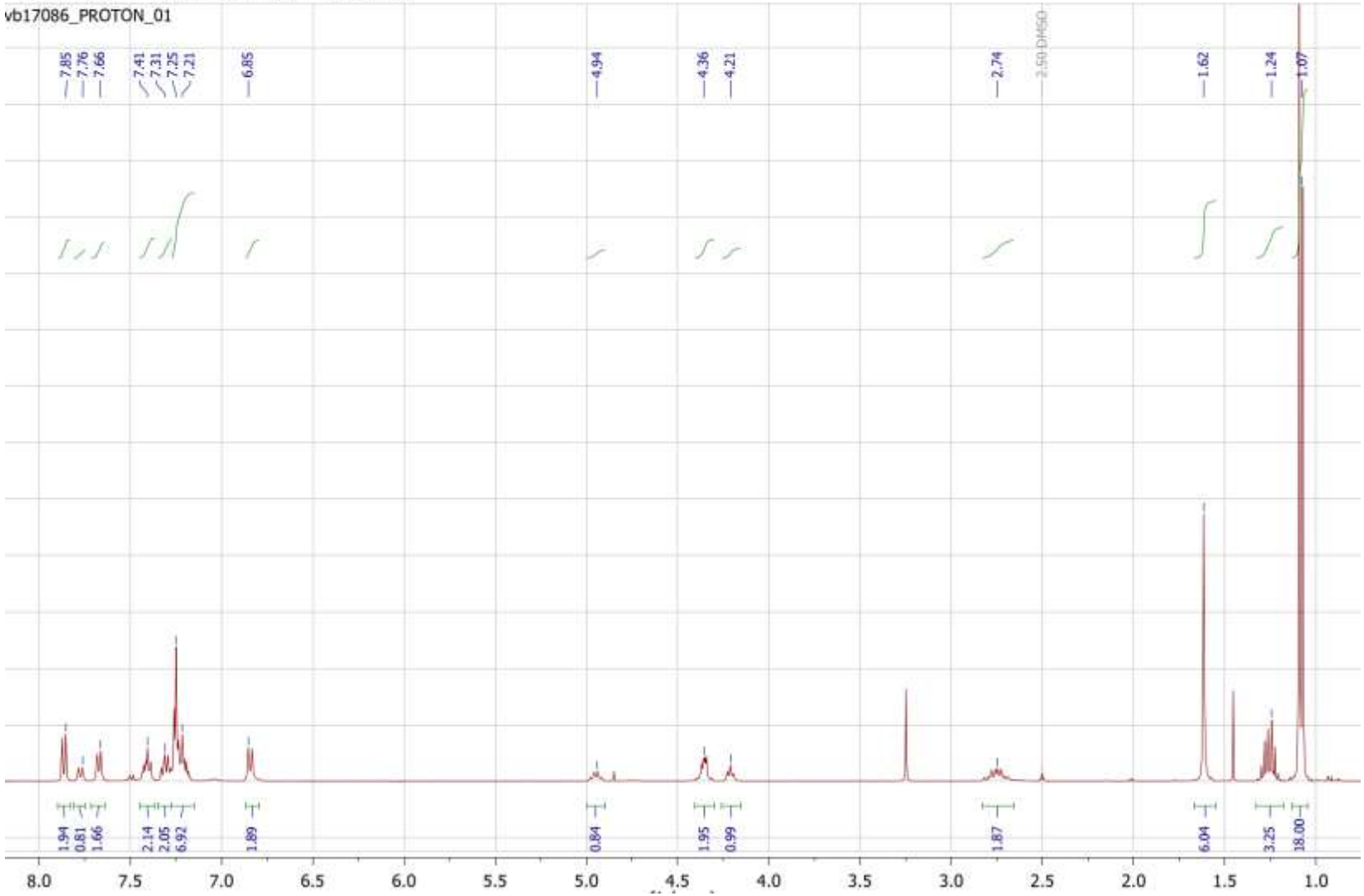

vb17096a_6h-cosy.1.ser
VB17096A cdcl3
Belov / MPI10200 / mw
f1 (ppm)
f2 (ppm)
{4.61,1.09}
{4.60,1.30}
{4.66,1.64}
{4.71,1.64}
{2.91,1.18}
{2.42,1.06}
{1.10,0.88}
{1.20,1.07}
{1.10,1.29}
{1.97,2.32}
{2.00,2.43}
{5.32,2.75}
{4.65,2.91}
{5.64,3.31}
{6.60,4.61}
{7.46,5.33}
{3.35,5.66}
{3.30,5.64}
{9.45,6.94}
{7.14,6.78}
{7.03,6.77}
{6.77,7.14}
{7.07,7.12}
{7.07,7.58}

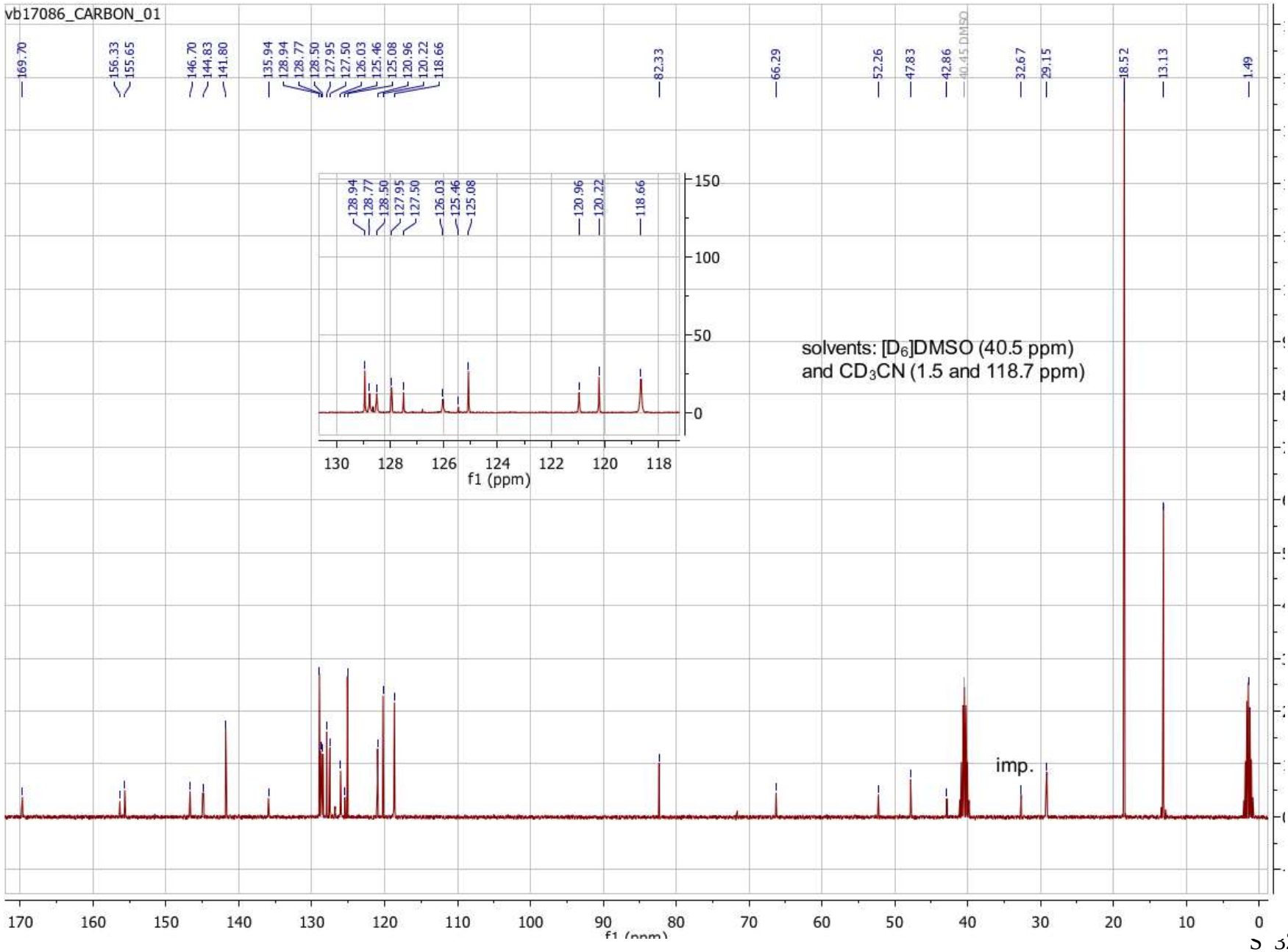

vb17096a_6ch-hsqc.1.ser
VB17096A cdcl3
Belov / MPI10200 / mw
{3.35,22.94}
{3.28,22.86}
{1.63,22.24}
{1.48,28.49}
{1.40,28.38}
{2.89,30.56}
{2.42,38.91}
{2.75,41.13}
{2.31,41.74}
{2.91,44.98}
{2.88,40.22}
{2.00,41.71}
{5.33,49.43}
{4.60,49.63}
{5.64,56.58}
{7.31,111.35}
{7.57,118.57}
{7.06,119.15}
{6.77,119.76}
{6.94,121.98}
{7.12,121.79}
{7.14,127.39}
{1.18,8.42}
{1.21,12.67}
{1.06,12.62}
{1.21,17.94}
{1.06,17.90}
{0.85,21.75}
{1.29,31.05}
{1.08,30.88}
{1.23,29.89}
{4.71,112.57}
{4.66,112.50}
f1 (ppm)
f2 (ppm)

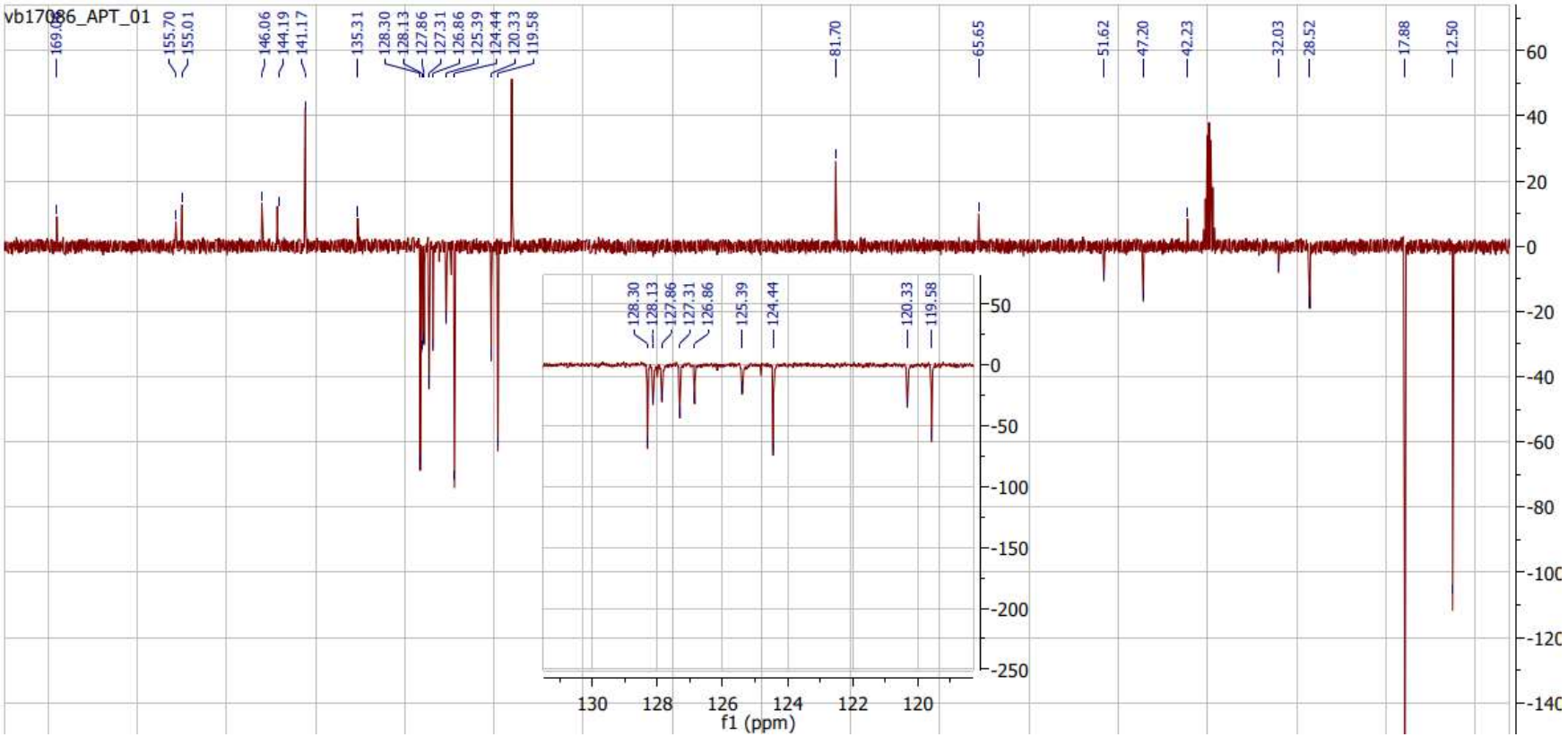
Figures S5a-c. NMR spectra of compound **2** in [D_6]DMSO: ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz) and APT (CH/CH_3 +, C_q/CH_2 –).



^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 (dt, J = 7.7, 0.9 Hz, 2H), 7.75 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 7.5 Hz, 2H), 7.38 (dtd, J = 7.5, 4.3, 3.8, 1.7 Hz, 2H), 7.32 – 7.13 (m, 9H), 6.86 – 6.75 (m, 2H), 4.92 (q, J = 8.1 Hz, 1H), 4.33 (dt, J = 6.4, 3.3 Hz, 2H), 4.19 (t, J = 6.8 Hz, 1H), 2.73 (qd, J = 15.1, 7.8 Hz, 2H), 1.59 (s, 6H), 1.31 – 1.15 (m, 3H), 1.06 (d, J = 7.4 Hz, 18H).

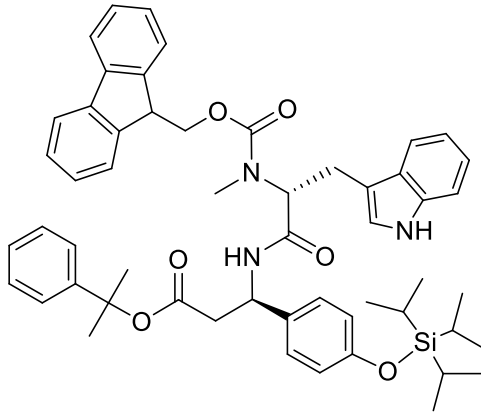



vb17086_CARBON_01
169.70
156.33
155.65
146.70
144.83
141.80
135.94
128.94
128.77
128.50
127.95
127.50
126.03
125.46
125.08
120.96
120.22
118.66
82.33
66.29
52.26
47.83
42.86
40.45 DMSO
32.67
29.15
18.52
13.13
1.49
solvents: [D6]DMSO (40.5 ppm)
and CD3CN (1.5 and 118.7 ppm)
imp.
f1 (ppm)

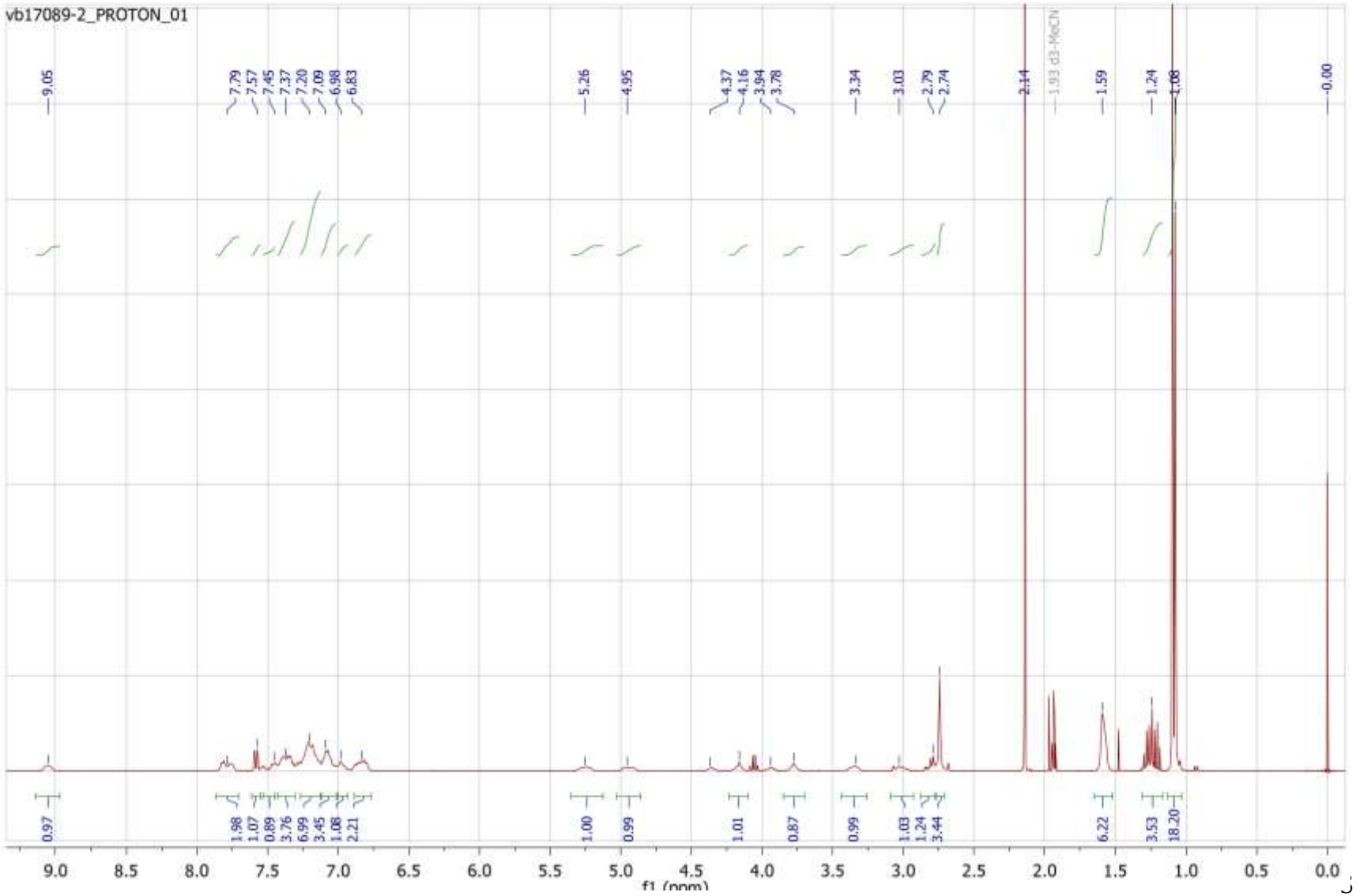


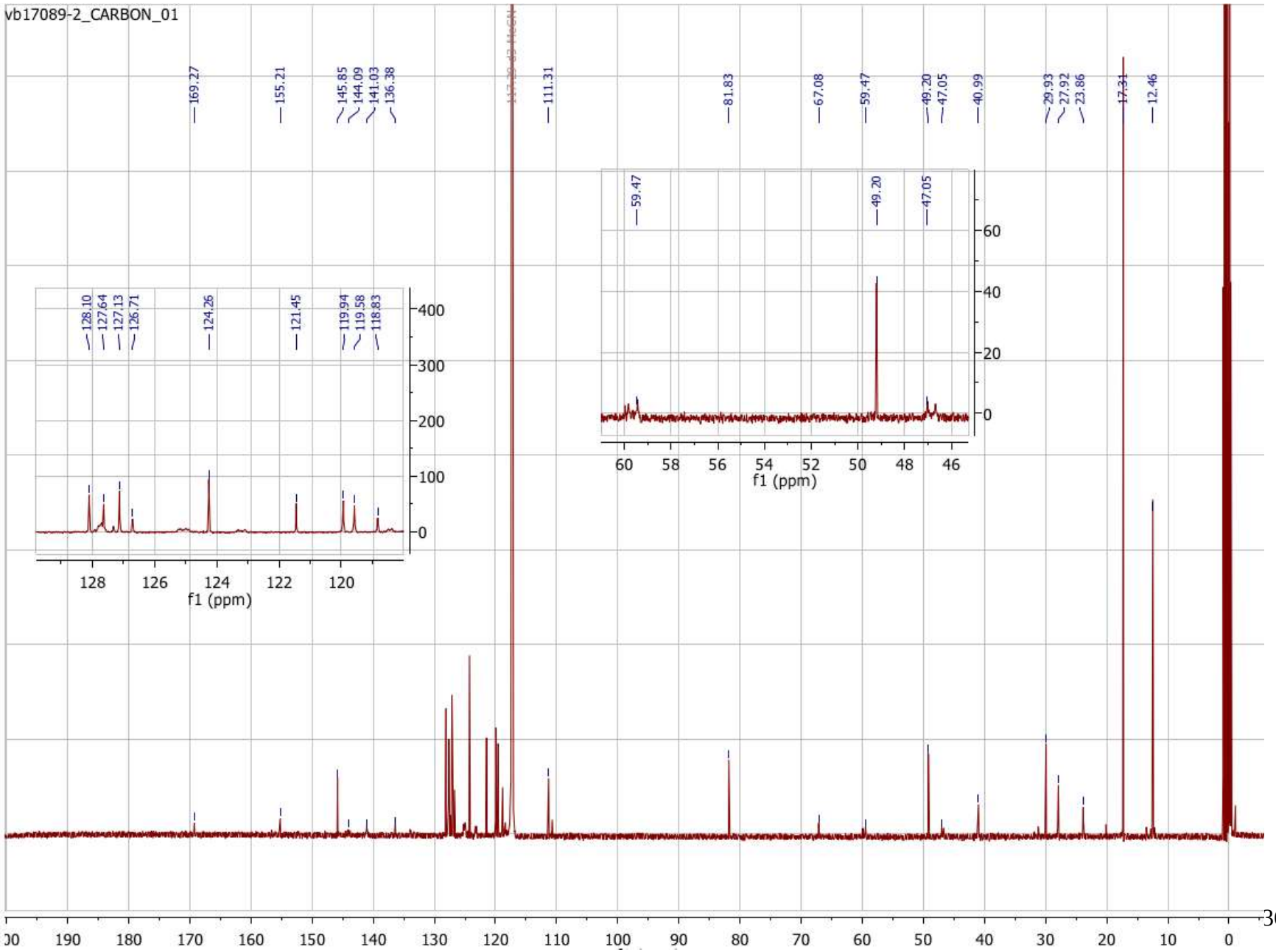
[D_6]DMSO (40.5 ppm); ^{13}C-NMR and APT (101 MHz)

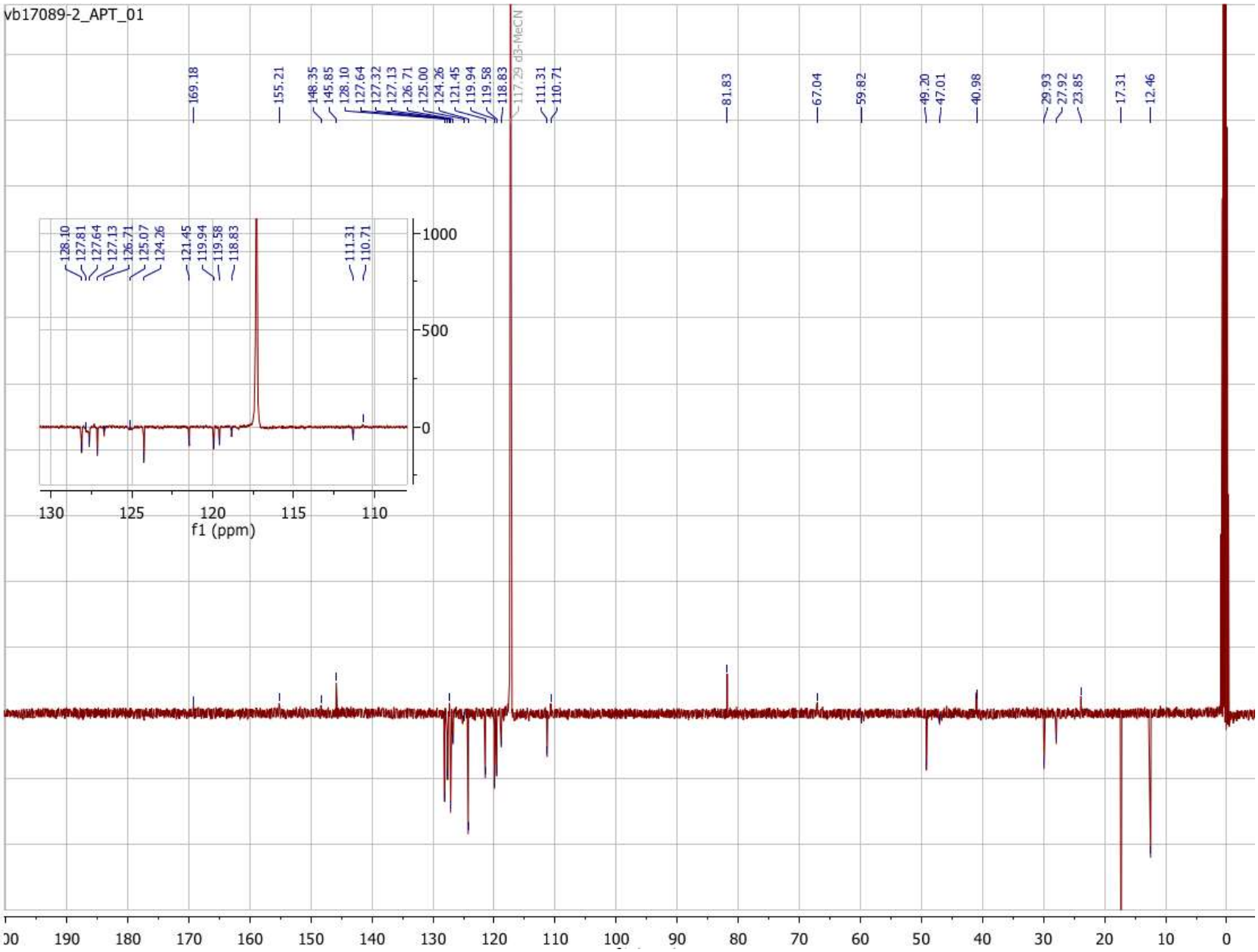
Figures S6a-e. NMR spectra of compound **3** in [D_3]MeCN: ^{1}H (400 MHz), ^{13}C{^{1}H} (101 MHz), APT (CH/CH_3 +, C_q/CH_2 –), ^{1}H-^{1}H-, and ^{1}H-^{13}C-(HSQC) COSY.

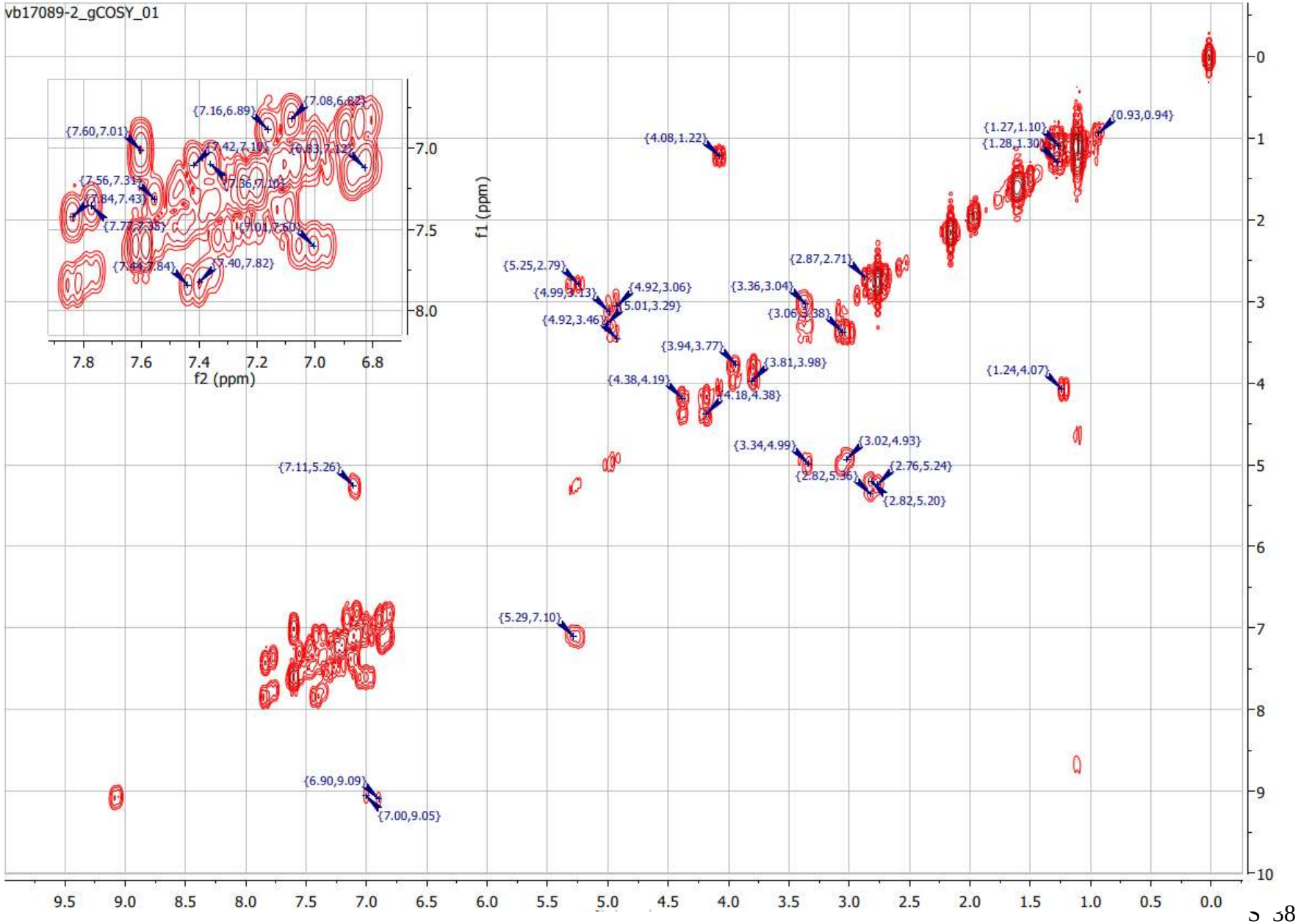


^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 9.05 (d, J = 10.6 Hz, 1H), 7.79 (dd, J = 24.1, 7.9 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.54 – 6.76 (m, 18H), 5.30 – 5.16 (m, 1H), 5.02 – 4.85 (m, 1H), 4.36 (s, 1H), 4.17 (d, J = 8.2 Hz, 1H), 3.93 (d, J = 12.1 Hz, 0H), 3.78 (s, 1H), 3.34 (d, J = 11.8 Hz, 1H), 3.09 – 2.94 (m, 1H), 2.84 – 2.76 (m, 1H), 2.74 (s, 3H), 1.65 – 1.50 (m, 6H), 1.31 – 1.15 (m, 3H), 1.09 (d, J = 7.3 Hz, 16H).




vb17089-2_CARBON_01
169.27
155.21
145.85
144.09
141.03
136.38
111.31
81.83
67.08
59.47
49.20
47.05
40.99
29.93
27.92
23.86
17.31
12.46
128.10
127.64
127.13
126.71
124.26
121.45
119.94
119.58
118.83
f1 (ppm)
f1 (ppm)


vb17089-2_APT_01
169.18
155.21
148.35
145.85
128.10
127.64
127.32
127.13
126.71
125.00
124.26
121.45
119.94
119.58
118.83
117.29 d3-MeCN
111.31
110.71
81.83
67.04
59.82
49.20
47.01
40.98
29.93
27.92
23.85
17.31
12.46
f1 (ppm)


vb17089-2_gCOSY_01
f1 (ppm)
f2 (ppm)
{7.60,7.01}
{7.16,6.89}
{7.08,6.82}
{7.42,7.10}
{7.83,7.12}
{7.56,7.31}
{7.84,7.43}
{7.36,7.10}
{7.77,7.35}
{7.01,7.60}
{7.44,7.84}
{7.40,7.82}
{4.08,1.22}
{1.27,1.10}
{1.28,1.30}
{0.93,0.94}
{5.25,2.79}
{4.99,3.13}
{4.92,3.06}
{5.01,3.29}
{4.92,3.46}
{2.87,2.71}
{3.36,3.04}
{3.06,3.38}
{3.94,3.77}
{3.81,3.98}
{4.38,4.19}
{4.18,4.38}
{1.24,4.07}
{3.34,4.99}
{3.02,4.93}
{2.82,5.36}
{2.76,5.24}
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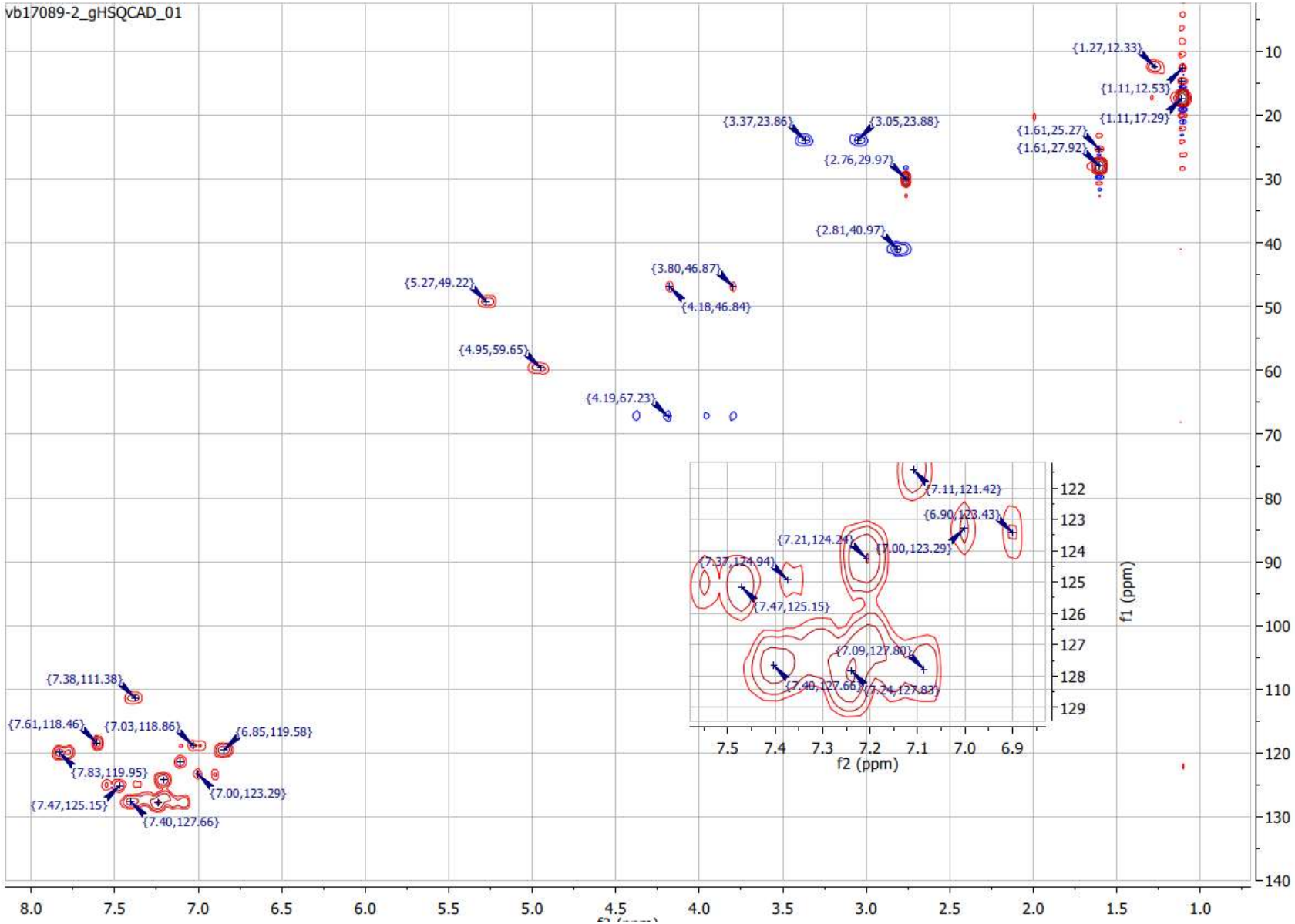
{7.11,5.26}
{5.29,7.10}
{6.90,9.09}
{7.00,9.05}


vb17089-2_gHSQCAD_01
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{1.11,17.29}
{1.61,25.27}
{1.61,27.92}
{3.37,23.86}
{3.05,23.88}
{2.76,29.97}
{2.81,40.97}
{3.80,46.87}
{4.18,46.84}
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{4.95,59.65}
{4.19,67.23}
{7.11,121.42}
{6.90,123.43}
{7.21,124.24}
{7.00,123.29}
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{7.47,125.15}
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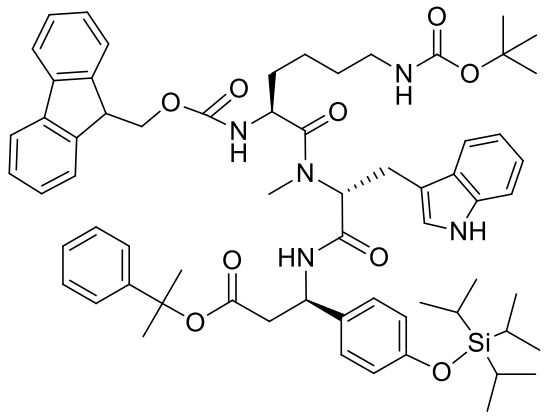
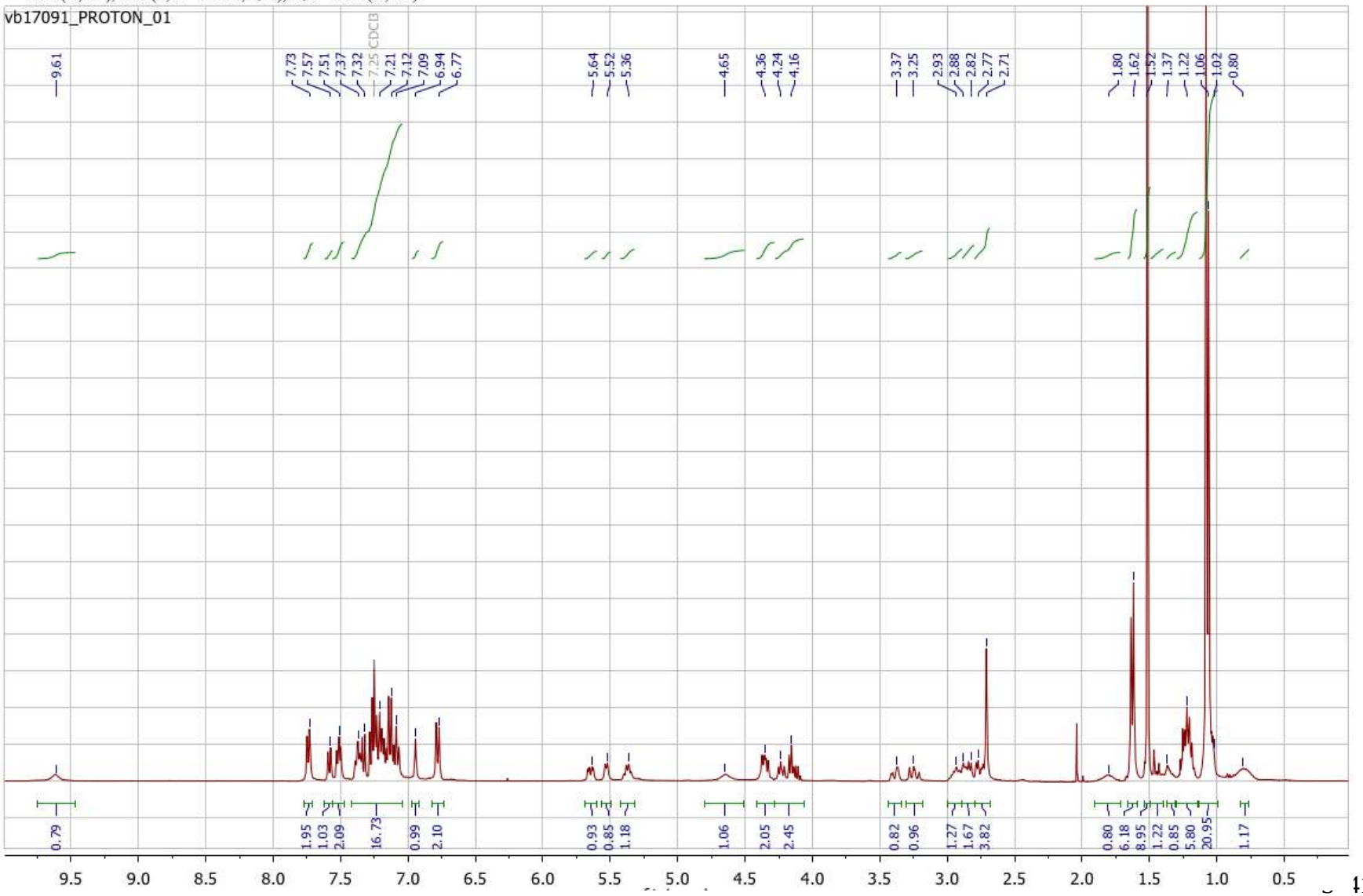
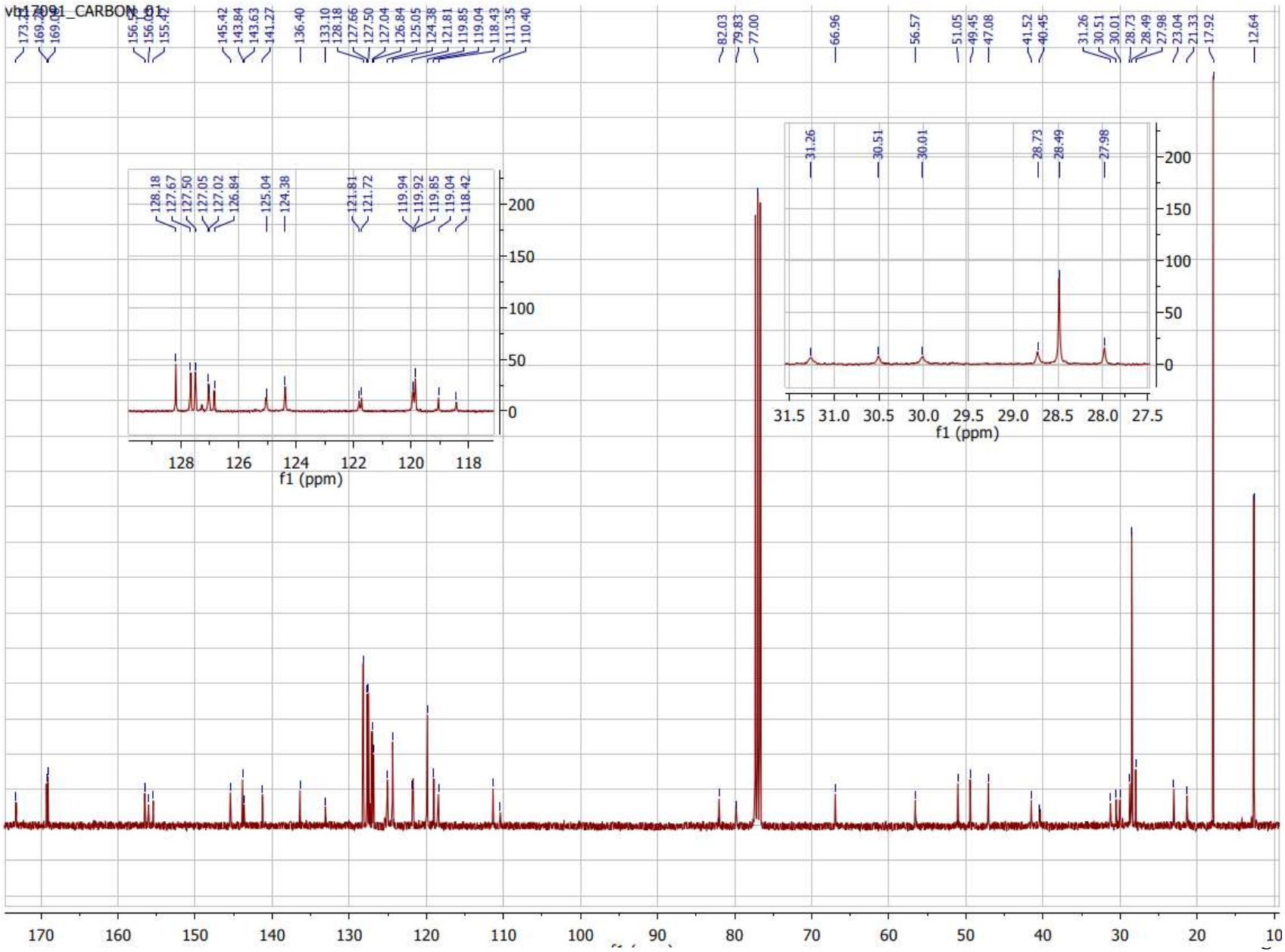
{7.40,127.66}
{7.24,127.83}
{7.38,111.38}
{7.61,118.46}
{7.03,118.86}
{6.85,119.58}
{7.83,119.95}
{7.00,123.29}
{7.47,125.15}
{7.40,127.66}
f1 (ppm)
f2 (ppm)

Figures S7a-e. NMR spectra of compound **4** in $CDCl_3$: ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz), APT (CH/CH_3 +, C_q/CH_2 –), ^{1}H-^{1}H-, and ^{1}H-^{13}C- (HSQC) COSY.



^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.62 (s, 1H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.51 (dd, *J* = 7.5, 5.2 Hz, 2H), 7.36 (ddd, *J* = 19.7, 9.8, 5.3 Hz, 3H), 7.30 – 7.02 (m, 12H), 6.94 (s, 1H), 6.83 – 6.70 (m, 2H), 5.65 (dd, *J* = 12.2, 4.6 Hz, 1H), 5.53 (d, *J* = 6.6 Hz, 1H), 5.37 (q, *J* = 7.4 Hz, 1H), 4.64 (s, 1H), 4.35 (dd, *J* = 11.0, 7.1 Hz, 2H), 4.23 (dd, *J* = 10.5, 6.9 Hz, 1H), 4.19 – 4.09 (m, 1H), 3.3 (dd, *J* = 16.2, 4.6 Hz, 1H), 3.24 (dd, *J* = 16.1, 12.3 Hz, 1H), 3.00 – 2.85 (m, 1H), 2.81 (dd, *J* = 21.6, 6.8 Hz, 1H), 2.71 (s, 3H), 1.81 (s, 1H), 1.64 (s, 3H), 1.62 (s, 4H), 1.52 (s, 9H), 1.47 – 1.32 (m, 1H), 1.3 1.15 (m, 5H), 1.07 (d, *J* = 7.3 Hz, 19H), 0.95 – 0.70 (m, 2H).

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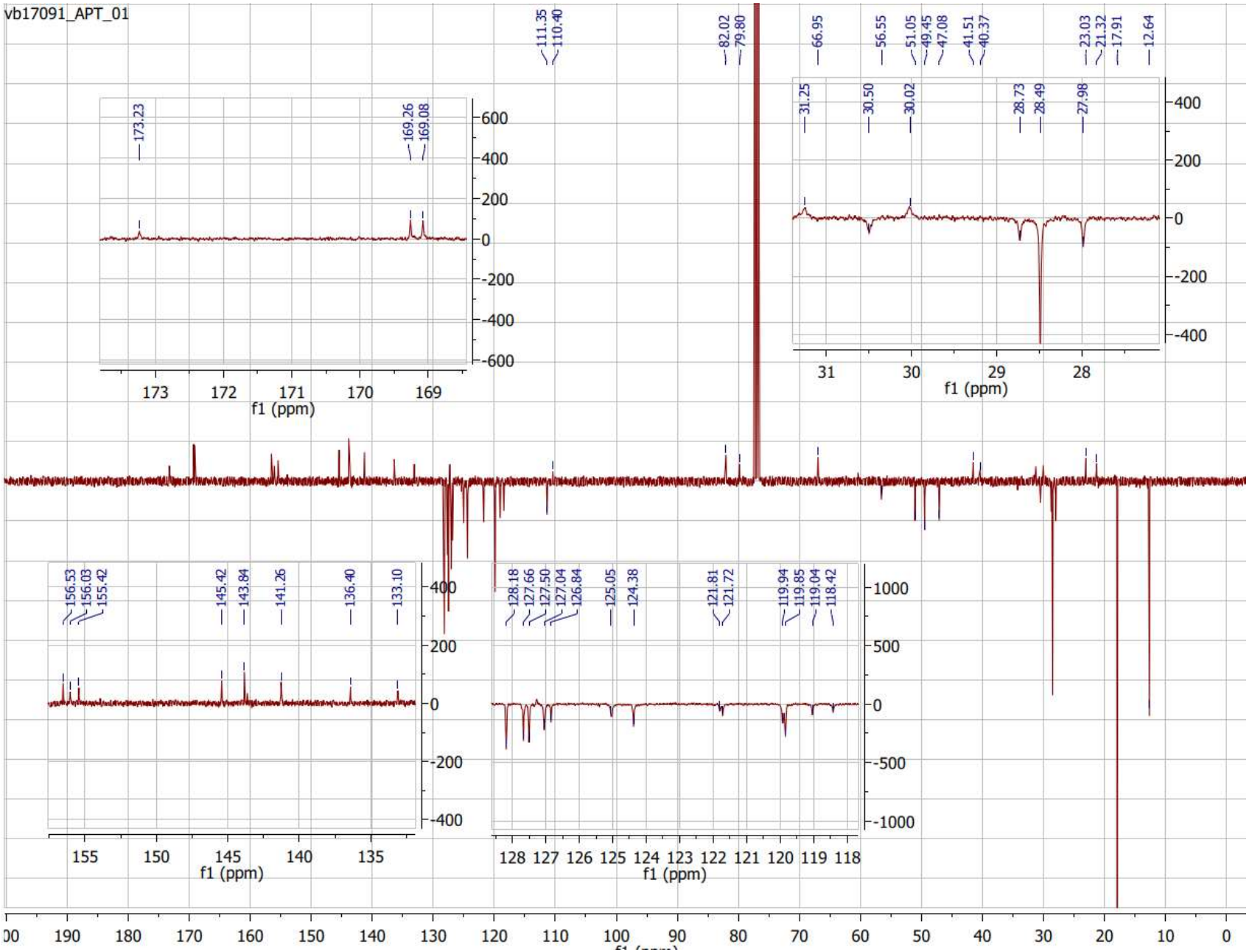
f1 (ppm)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82.02
79.80
66.95
56.55
51.05
49.45
47.08
41.51
40.37
23.03
21.32
17.91
12.64
173.23
169.26
169.08
f1 (ppm)
31.25
30.50
30.02
28.73
28.49
27.98
f1 (ppm)
156.53
156.03
155.42
145.42
143.84
141.26
136.40
133.10
f1 (ppm)
128.18
127.66
127.50
127.04
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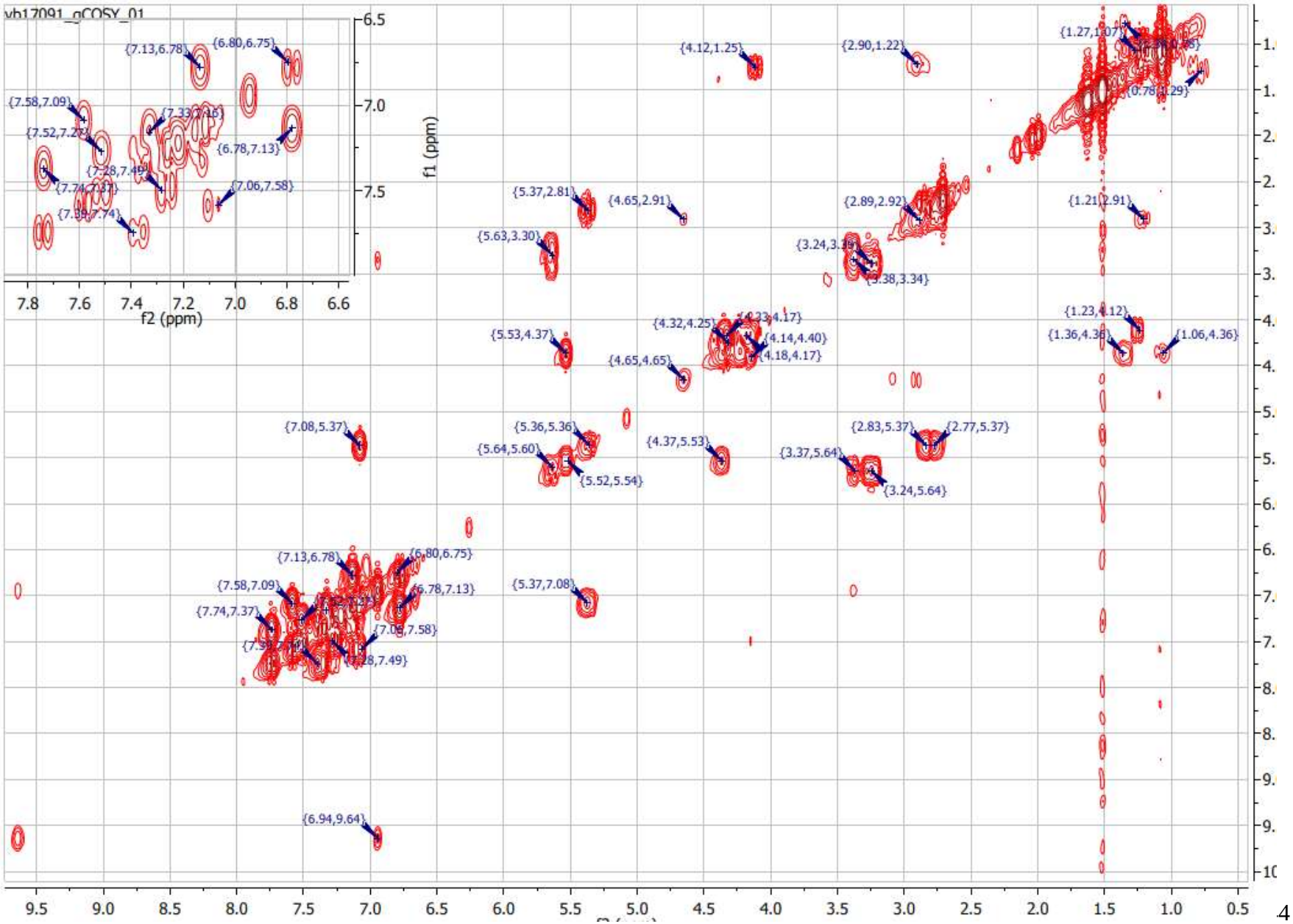
125.05
124.38
121.81
121.72
119.94
119.85
119.04
118.42
f1 (ppm)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f2 (ppm)
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{7.28,7.49}
{7.06,7.58}
{4.12,1.25}
{2.90,1.22}
{5.37,2.81}
{4.65,2.91}
{2.89,2.92}
{5.63,3.30}
{3.38,3.34}
{5.53,4.37}
{4.32,4.25}
{4.14,4.40}
{4.18,4.17}
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{1.06,4.36}
{7.08,5.37}
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{5.64,5.60}
{5.52,5.54}
{4.37,5.53}
{2.83,5.37}
{2.77,5.37}
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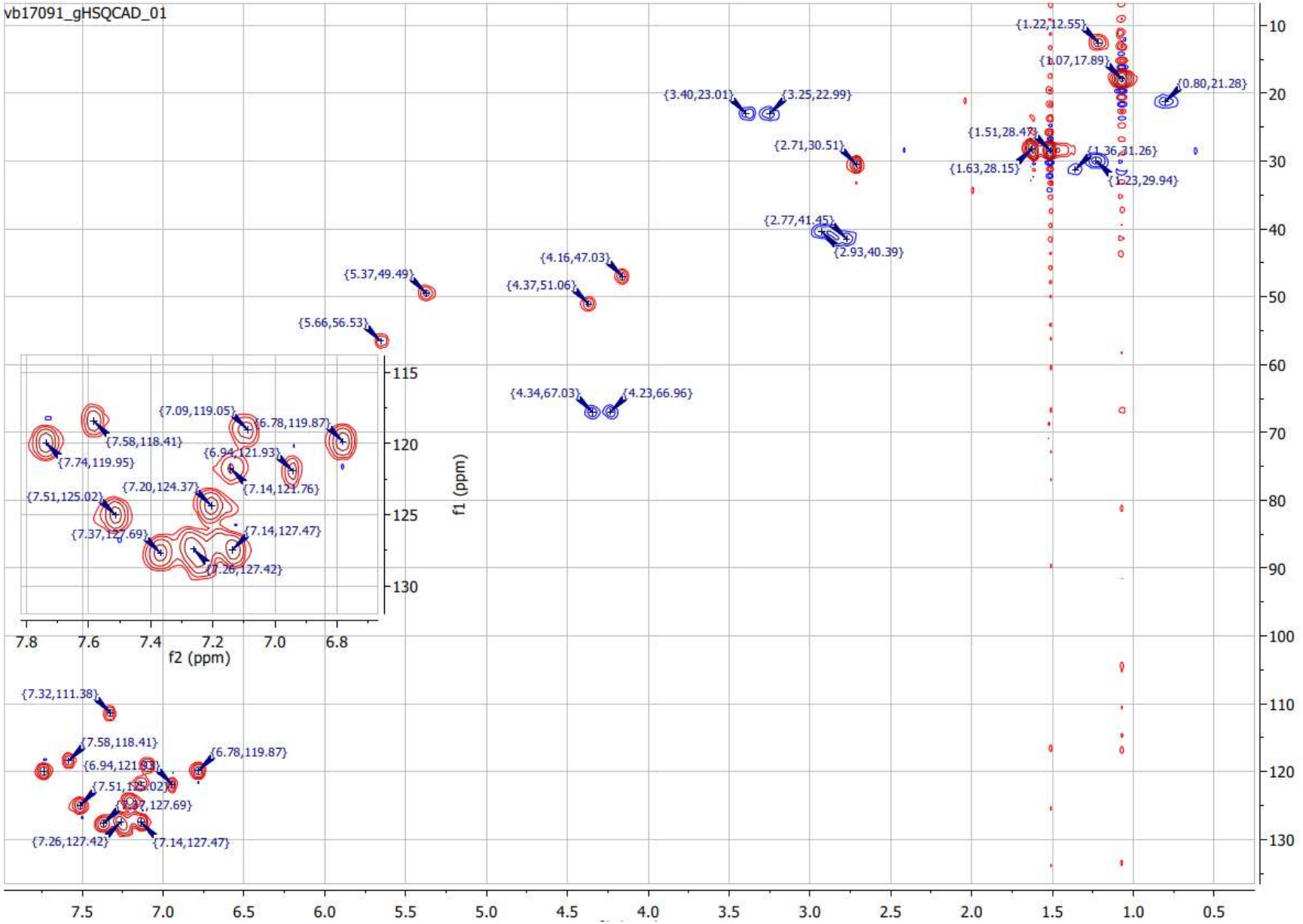
{5.37,7.08}
{6.94,9.64}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{7.58,118.41}
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{6.94,121.93}
{7.14,121.76}
{7.20,124.37}
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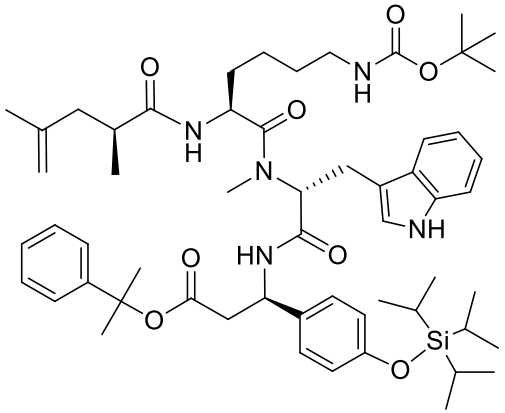
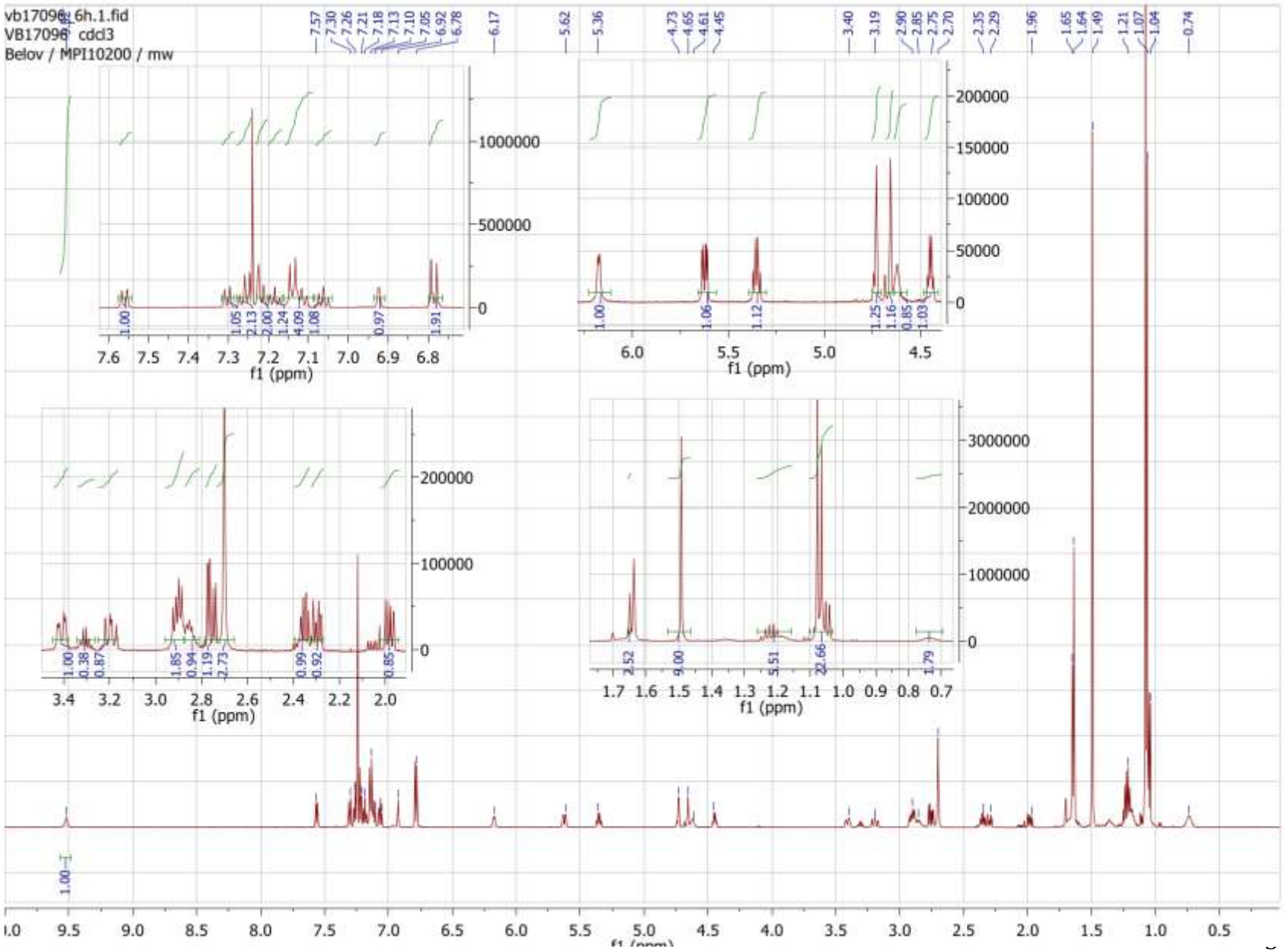
{7.37,127.69}
{7.14,127.47}
{7.26,127.42}
{7.32,111.38}
f1 (ppm)
f2 (ppm)

Figures S8a-e. NMR spectra of compound **5**-$C(CH_3)_2C_6H_5$-H in $CDCl_3$: ^1H (600 MHz), $^{13}C\{^1H\}$ (126 MHz), APT (CH/CH_3 +, C_q/CH_2 –), ^1H-^1H-, and ^1H-^{13}C- (HSQC) COSY.

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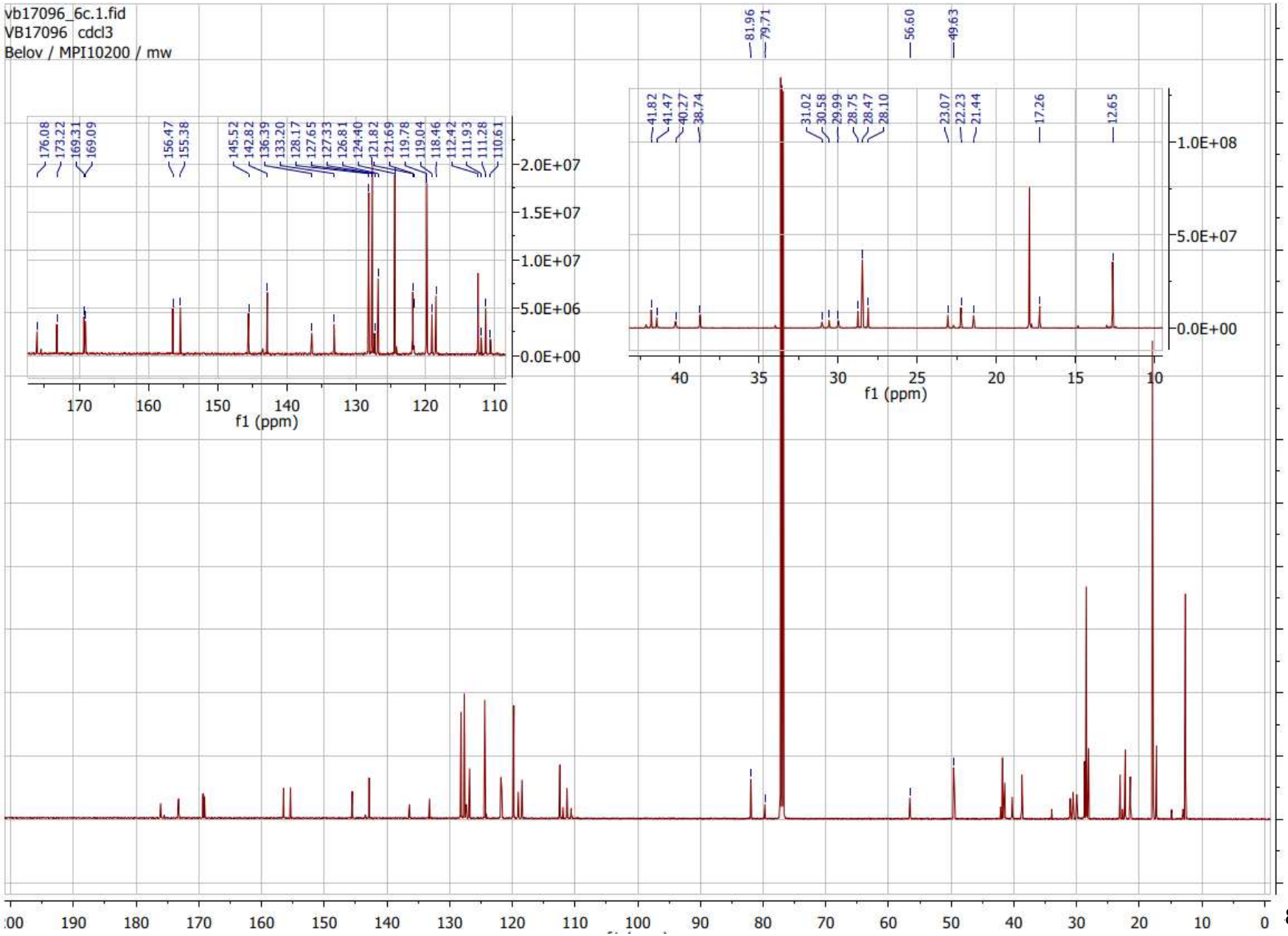
VB17096 cdd3
Belov / MPI10200 / mw
f1 (ppm)


vb17096_6c.1.fid
VB17096 cdcl3
Belov / MPI10200 / mw
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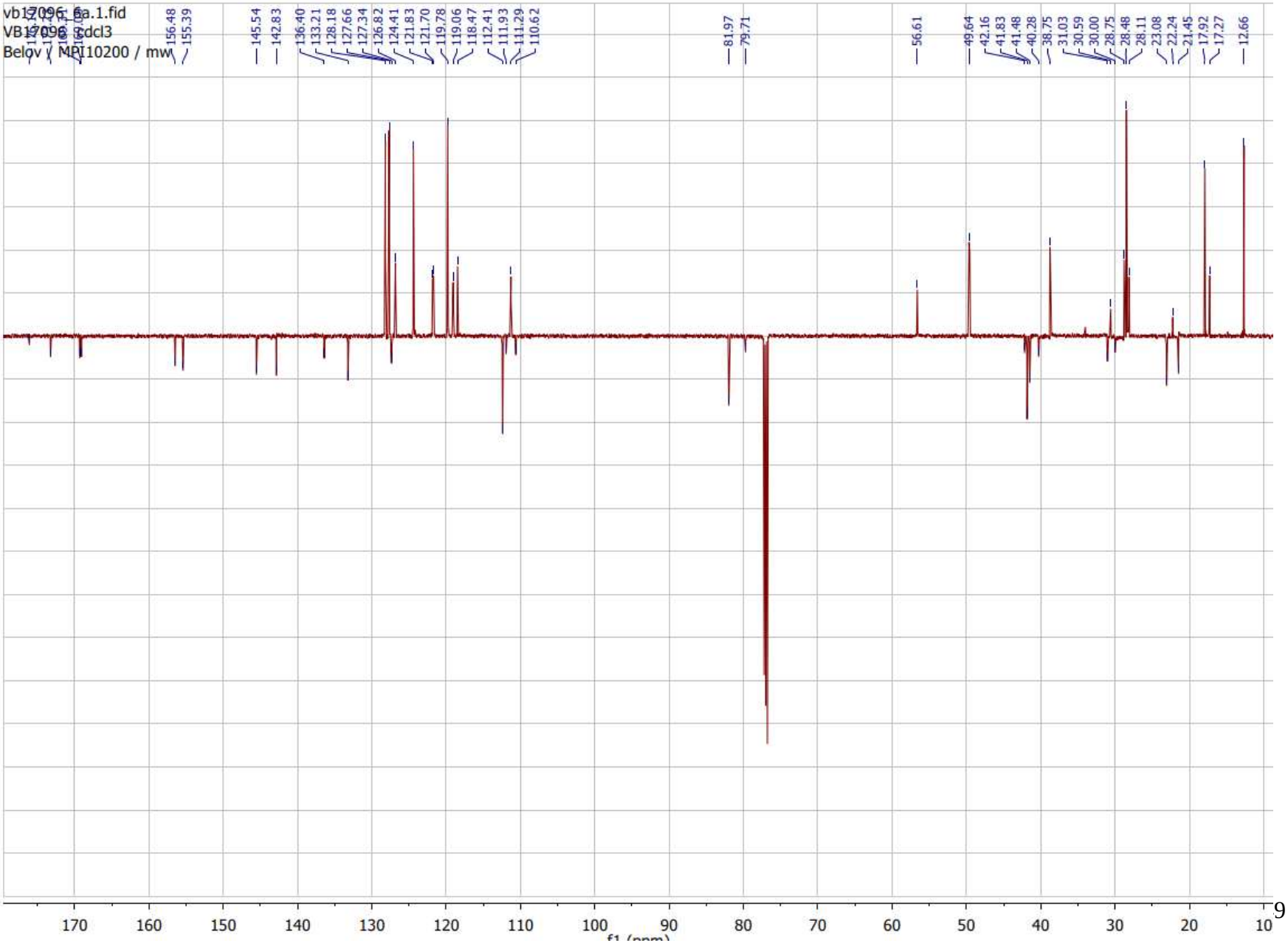
173.22
169.31
169.09
156.47
155.38
145.52
142.82
136.39
133.20
128.17
127.65
127.33
126.81
124.40
121.82
121.69
119.78
119.04
118.46
112.42
111.93
111.28
110.61
81.96
79.71
56.60
49.63
41.82
41.47
40.27
38.74
31.02
30.58
29.99
28.75
28.47
28.10
23.07
22.23
21.44
17.26
12.65
f1 (ppm)
f1 (ppm)


vb17096_6a.1.fid
VB17096 cdcl3
Belov / MPI10200 / mw
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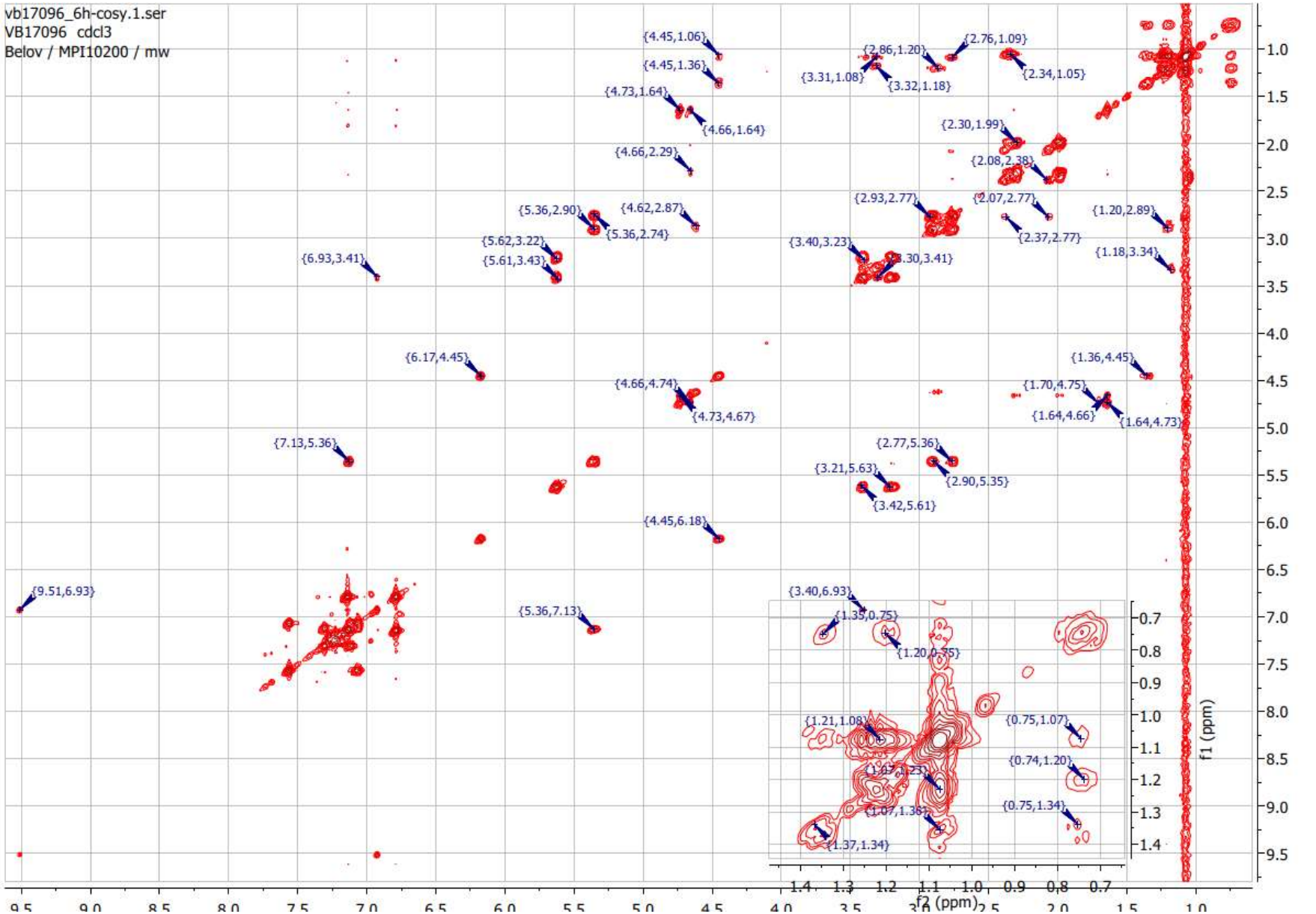
155.39
145.54
142.83
136.40
133.21
128.18
127.66
127.34
126.82
124.41
121.83
121.70
119.78
119.06
118.47
112.41
111.93
111.29
110.62
81.97
79.71
56.61
49.64
42.16
41.83
41.48
40.28
38.75
31.03
30.59
30.00
28.75
28.48
28.11
23.08
22.24
21.45
17.92
17.27
12.66
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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VB17096 cdcl3
Belov / MPI10200 / mw
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{5.36,2.90}
{4.62,2.87}
{5.36,2.74}
{5.62,3.22}
{5.61,3.43}
{6.93,3.41}
{6.17,4.45}
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{4.73,4.67}
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{4.45,6.18}
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{2.34,1.05}
{2.30,1.99}
{2.08,2.38}
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{2.37,2.77}
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{3.30,3.41}
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{1.70,4.75}
{1.64,4.66}
{1.64,4.73}
{2.77,5.36}
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{2.90,5.35}
{3.42,5.61}
{3.40,6.93}
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{1.20,0.75}
{1.21,1.08}
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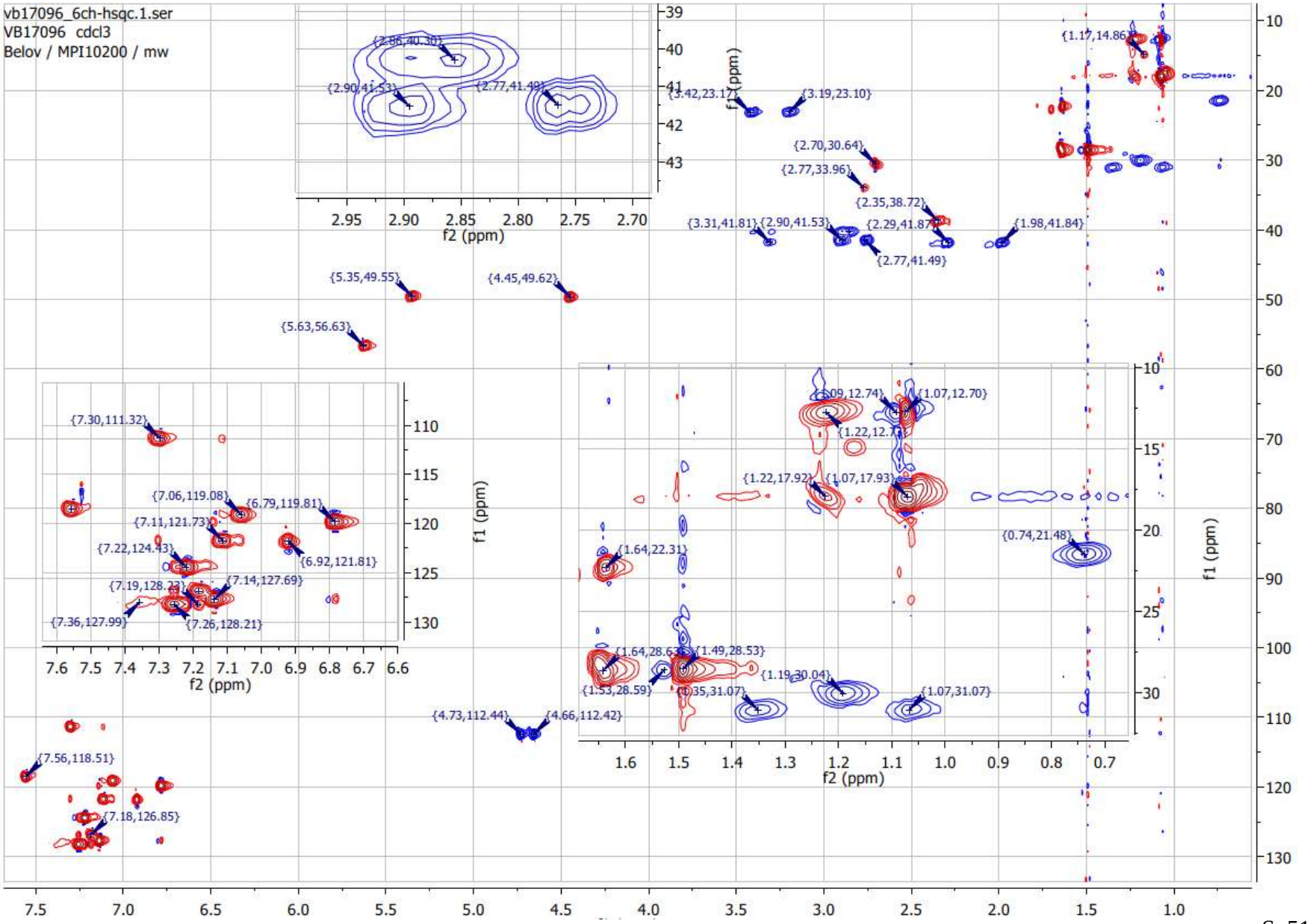
{0.74,1.20}
{0.75,1.34}
{1.37,1.34}
f2 (ppm)
f1 (ppm)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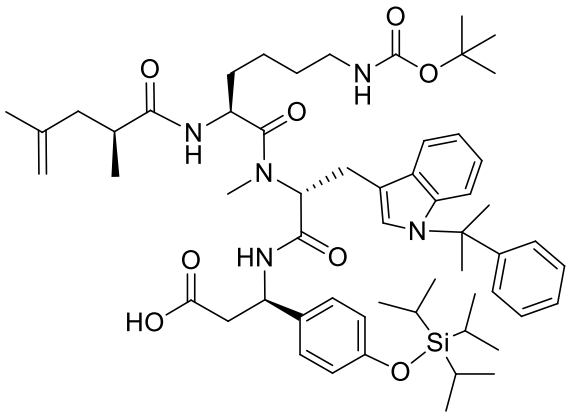
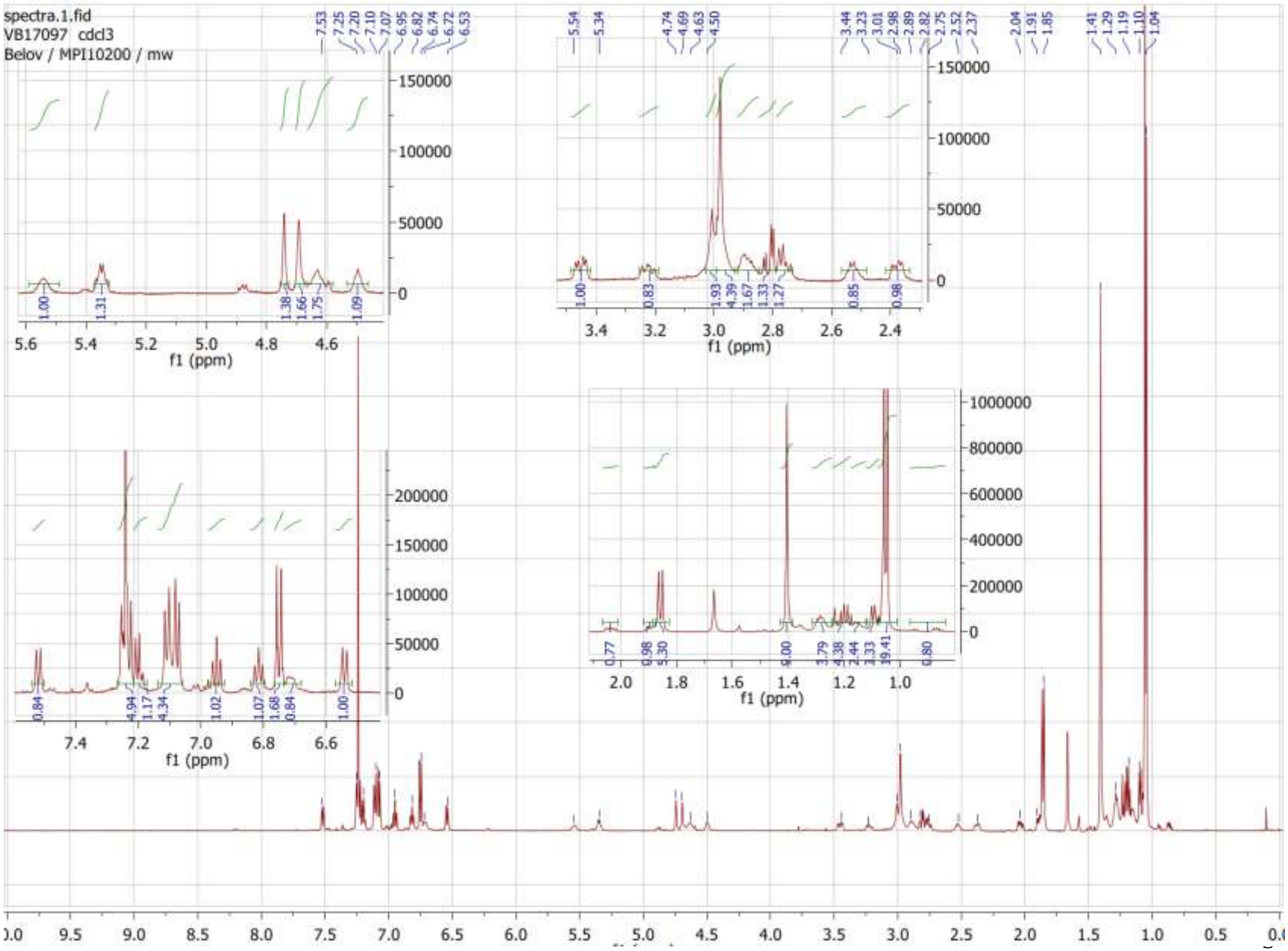
VB17096 cdcl3
Belov / MPI10200 / mw
f2 (ppm)
f1 (ppm)



Figures S9a-e. NMR spectra of compound **5**-H-$C(CH_3)_2C_6H_5$ in $CDCl_3$: ^{1}H (600 MHz), $^{13}C\{^{1}H\}$ (126 MHz), APT CH/CH_3 +, C_q/CH_2 –), ^{1}H-^{1}H-, and ^{1}H-^{13}C- (HSQC) COSY.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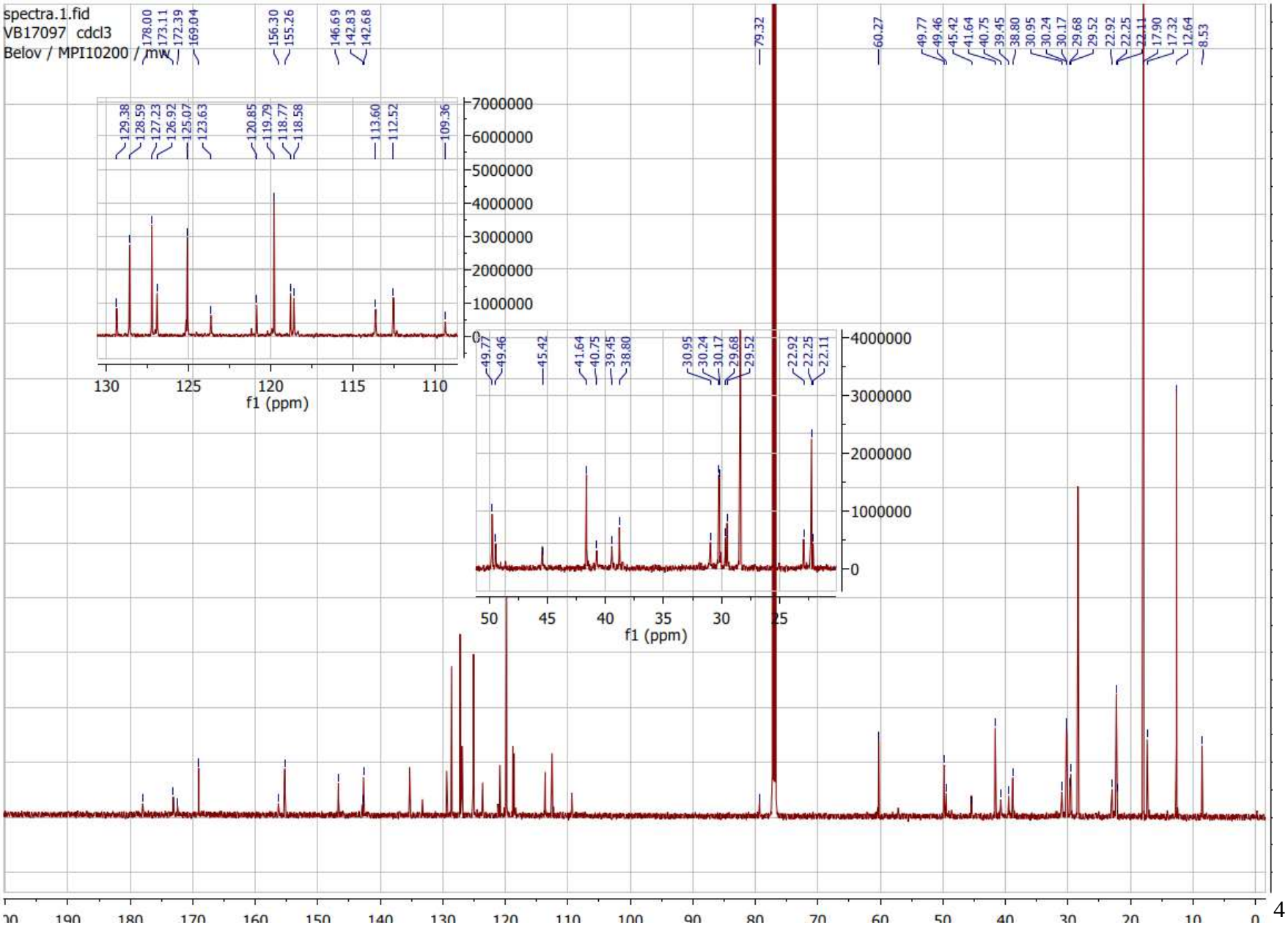
VB17097 cdcl3
Belov / MPI10200 / mw
f1 (ppm)


spectra.1.fid
VB17097 cdcl3
Belov / MPI10200 / mw
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173.11
172.39
169.04
156.30
155.26
146.69
142.83
142.68
79.32
60.27
49.77
49.46
45.42
41.64
40.75
39.45
38.80
30.95
30.24
30.17
29.68
29.52
22.92
22.25
22.11
17.90
17.32
12.64
8.53
129.38
128.59
127.23
126.92
125.07
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119.79
118.77
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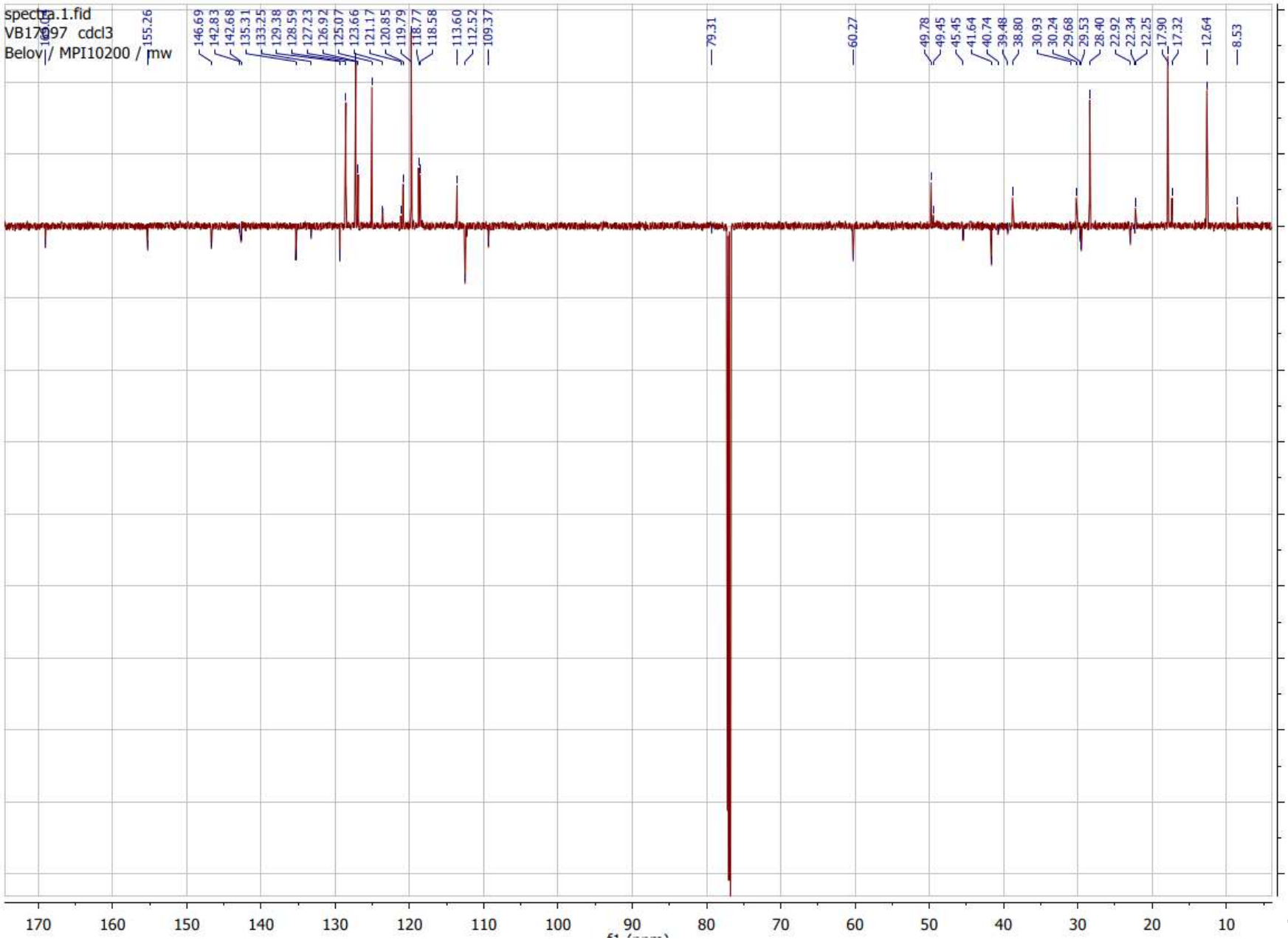
113.60
112.52
109.36
f1 (ppm)
f1 (ppm)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VB17097 cdcl3
Below // MPI10200 / mw
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146.69
142.83
142.68
135.31
133.25
129.38
128.59
127.23
126.92
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123.66
121.17
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119.79
118.77
118.58
113.60
112.52
109.37
79.31
60.27
49.78
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45.45
41.64
40.74
39.48
38.80
30.93
30.24
29.68
29.53
28.40
22.92
22.34
22.25
17.90
17.32
12.64
8.53
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150
140
130
120
110
100
90
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40
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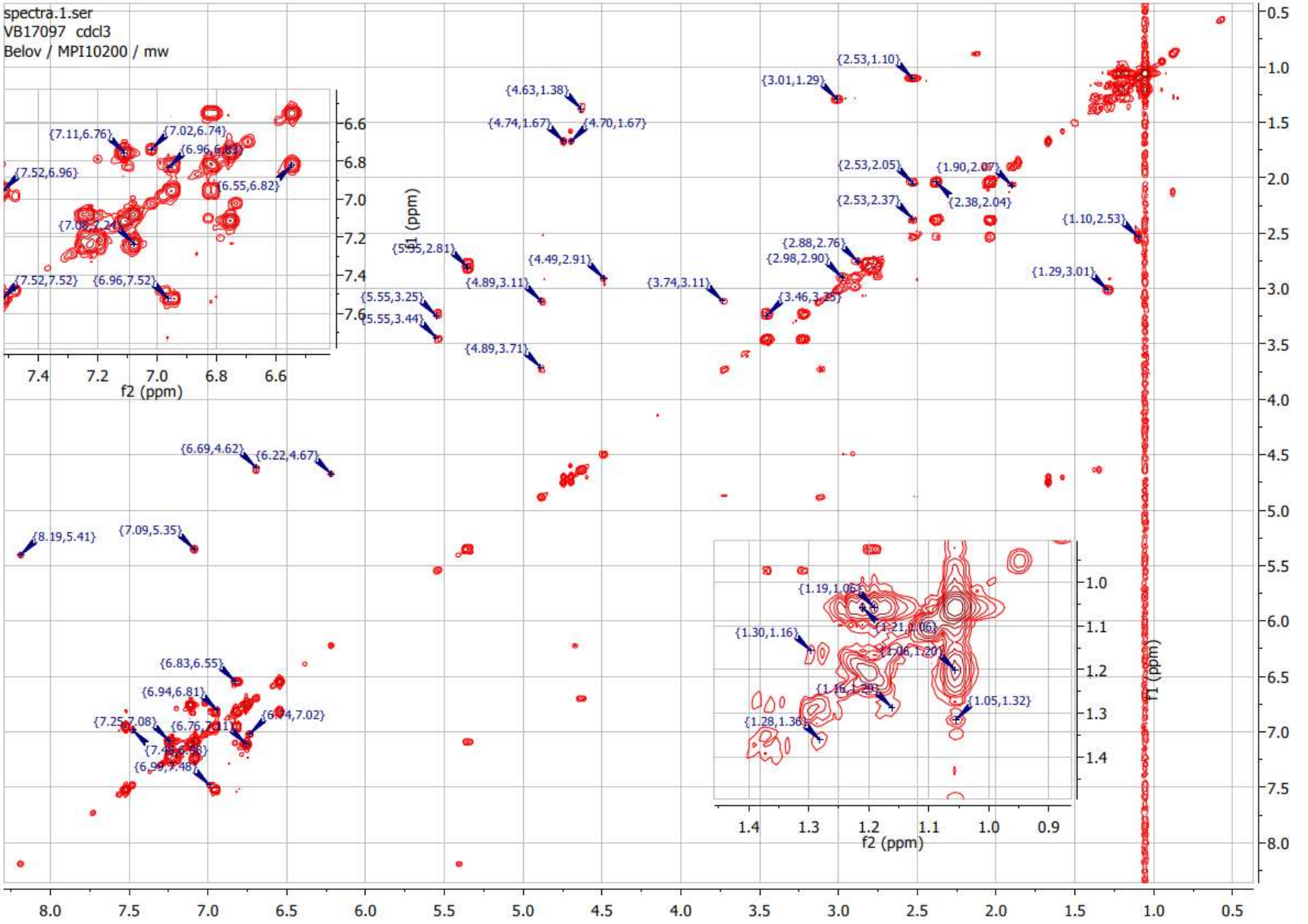
20
10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VB17097 cdcl3
Belov / MPI10200 / mw
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{2.53,2.05}
{1.90,2.07}
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{1.10,2.53}
{2.88,2.76}
{2.98,2.90}
{1.29,3.01}
{3.74,3.11}
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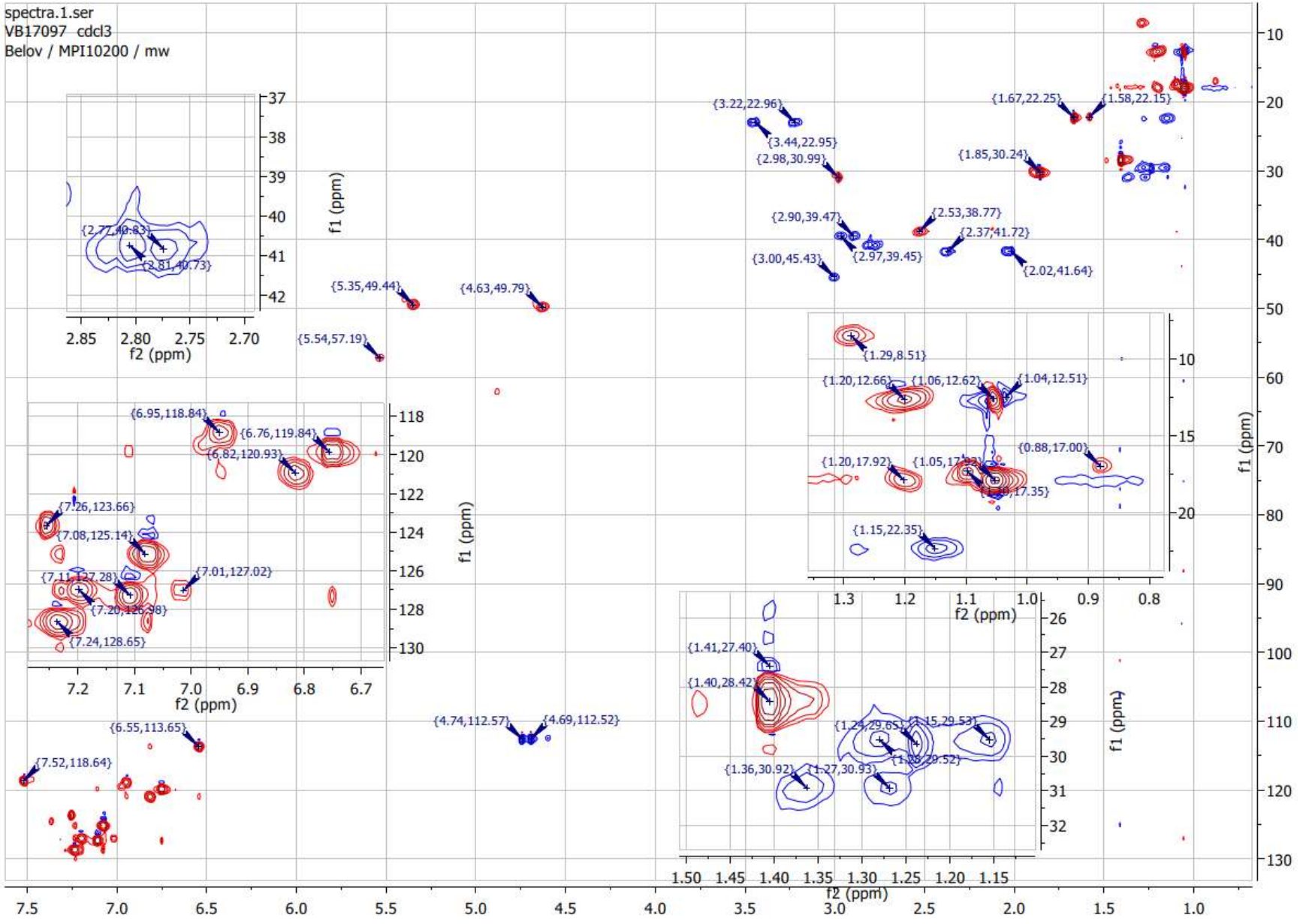
{6.96,7.52}
f1 (ppm)
f2 (ppm)


spectra.1.ser
VB17097 cdcl3
Belov / MPI10200 / mw
f1 (ppm)
f2 (ppm)
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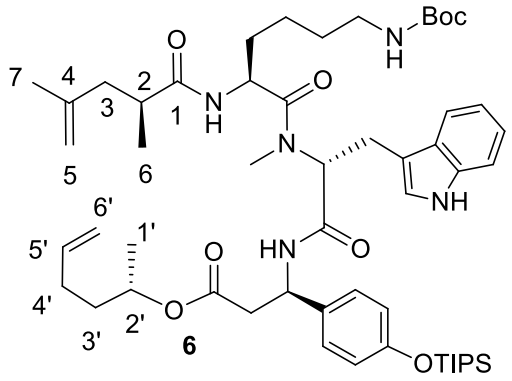
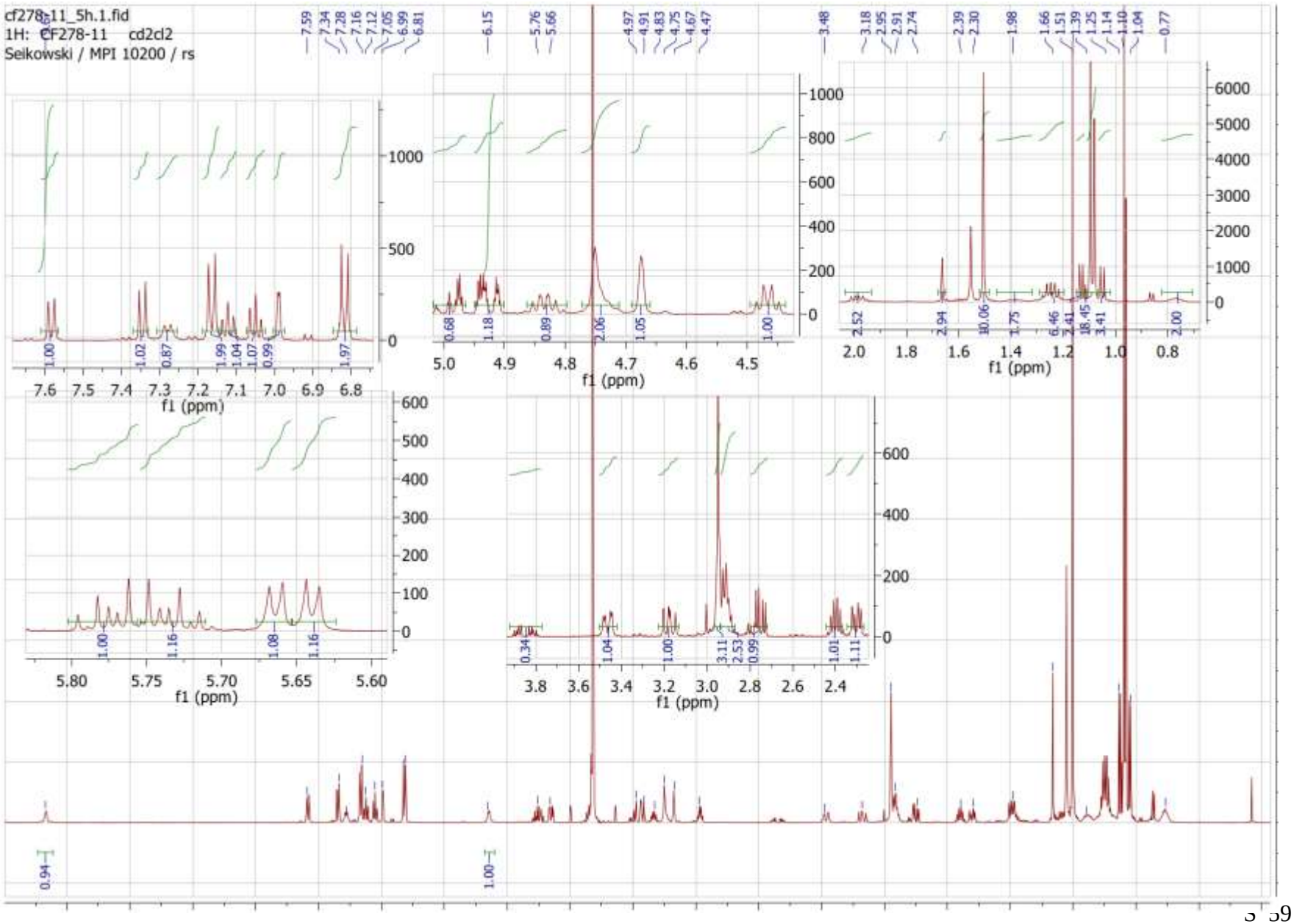
{1.20,29.52}
{1.36,30.92}
{1.27,30.93}

Figures S10a-d. NMR spectra of compound **6** in CD_2Cl_2: ^1H (500 MHz), $^{13}C\{^1H\}$ (126 MHz), ^1H-^1H, and ^1H-^{13}C COSY.

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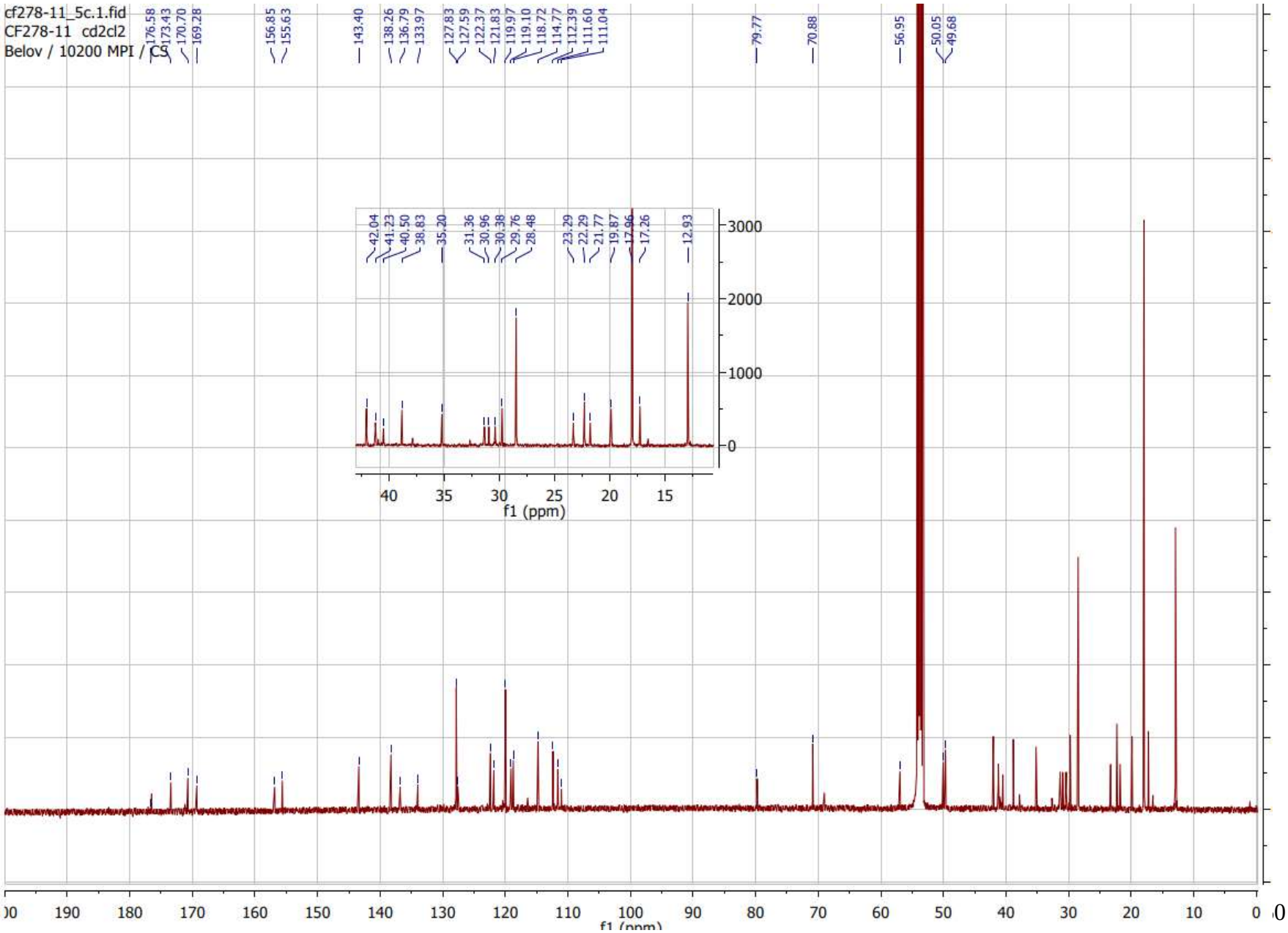
1H: CF278-11 cd2cl2
Selkowski / MPI 10200 / rs
f1 (ppm)


cf278-11_5c.1.fid
CF278-11 cd2cl2
Belov / 10200 MPI / CS
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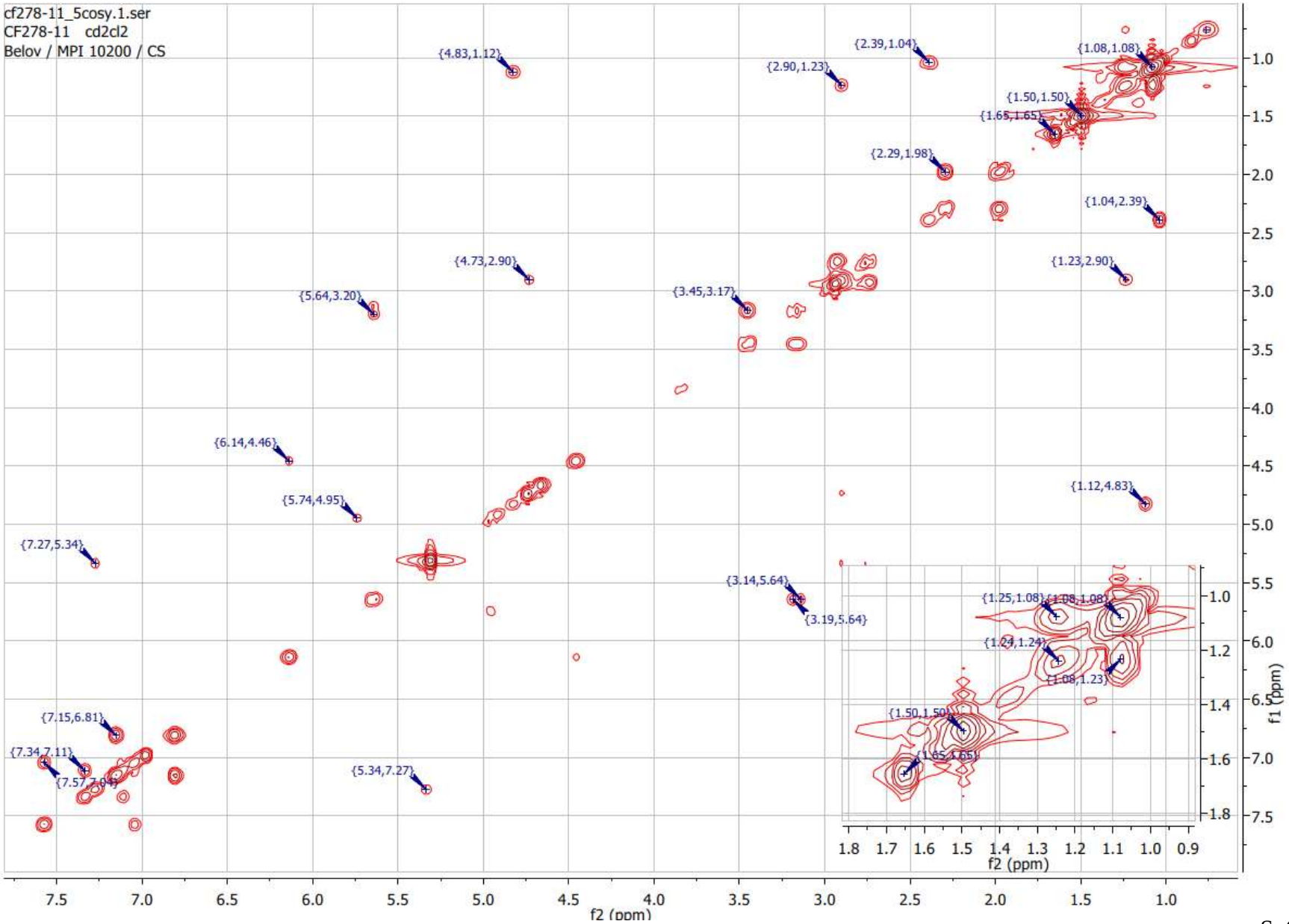
170.70
169.28
156.85
155.63
143.40
138.26
136.79
133.97
127.83
127.59
122.37
121.83
119.97
119.10
118.72
114.77
112.39
111.60
111.04
79.77
70.88
56.95
50.05
49.68
42.04
41.23
40.50
38.83
35.20
31.36
30.96
30.38
29.76
28.48
23.29
22.29
21.77
19.87
17.96
17.26
12.93
3000
2000
1000
0
40
35
30
25
20
15
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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CF278-11 cd2cl2
Belov / MPI 10200 / CS
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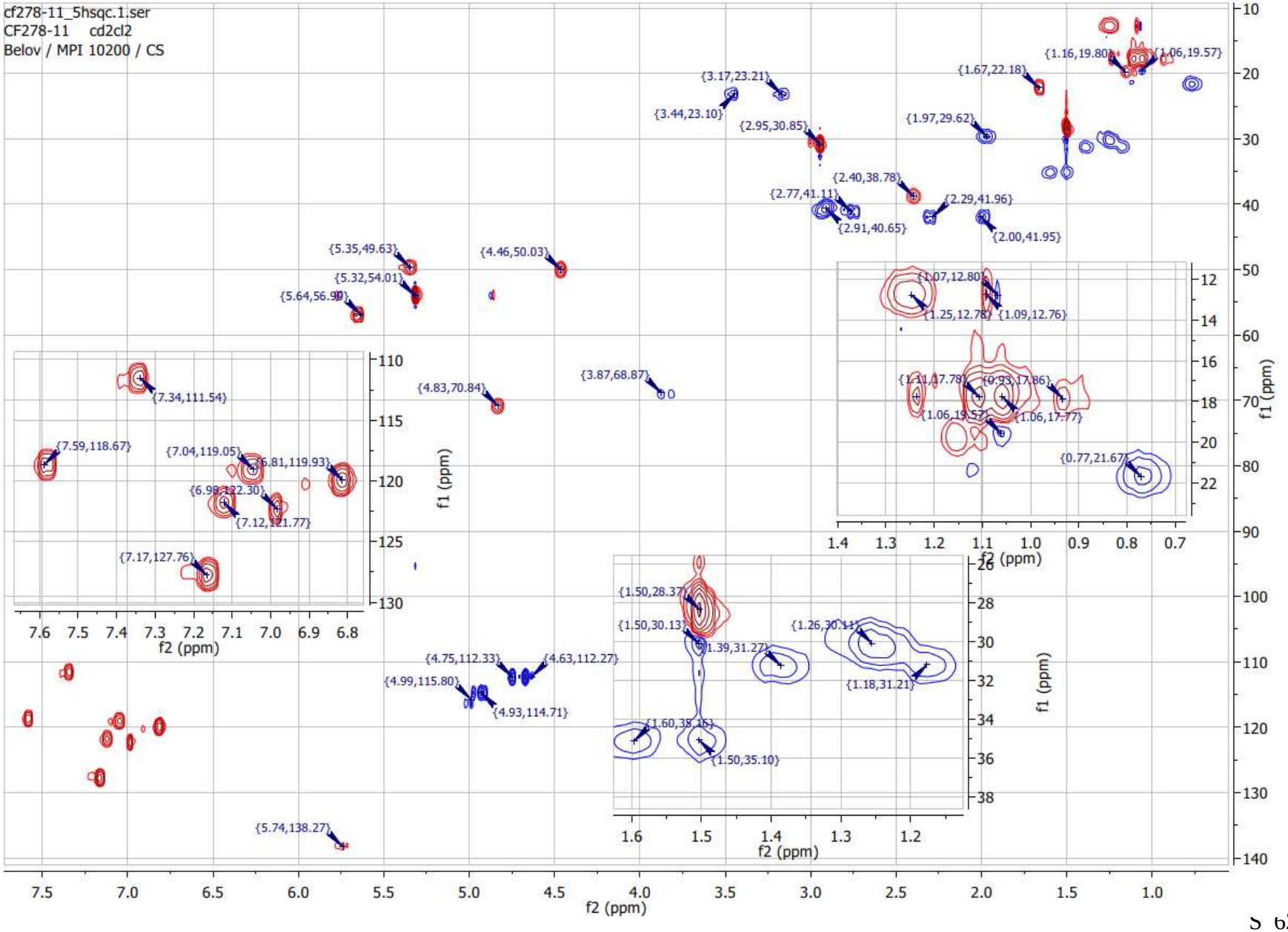
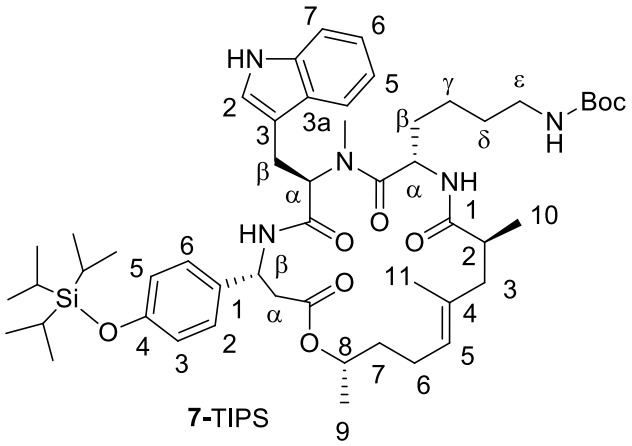
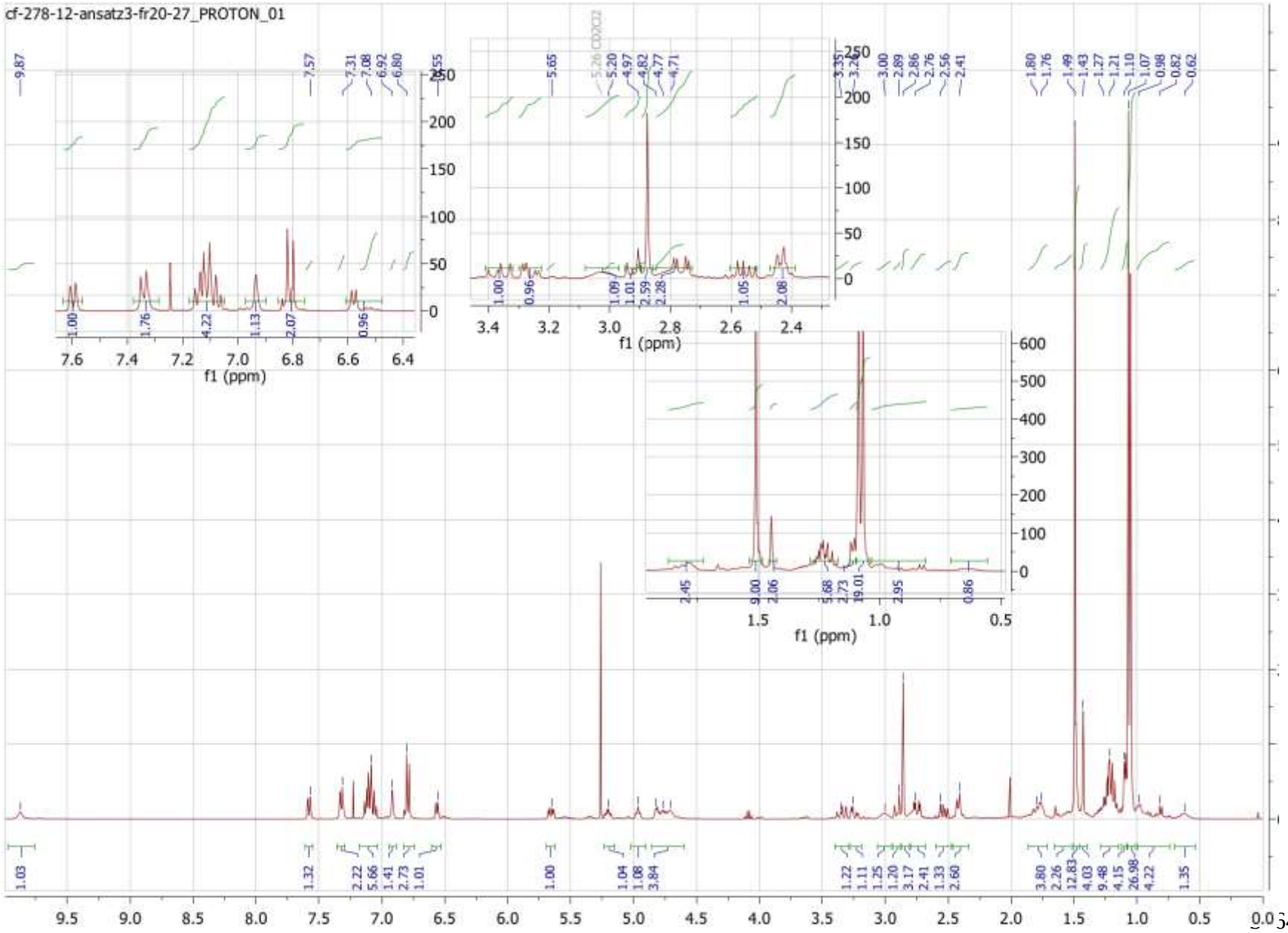
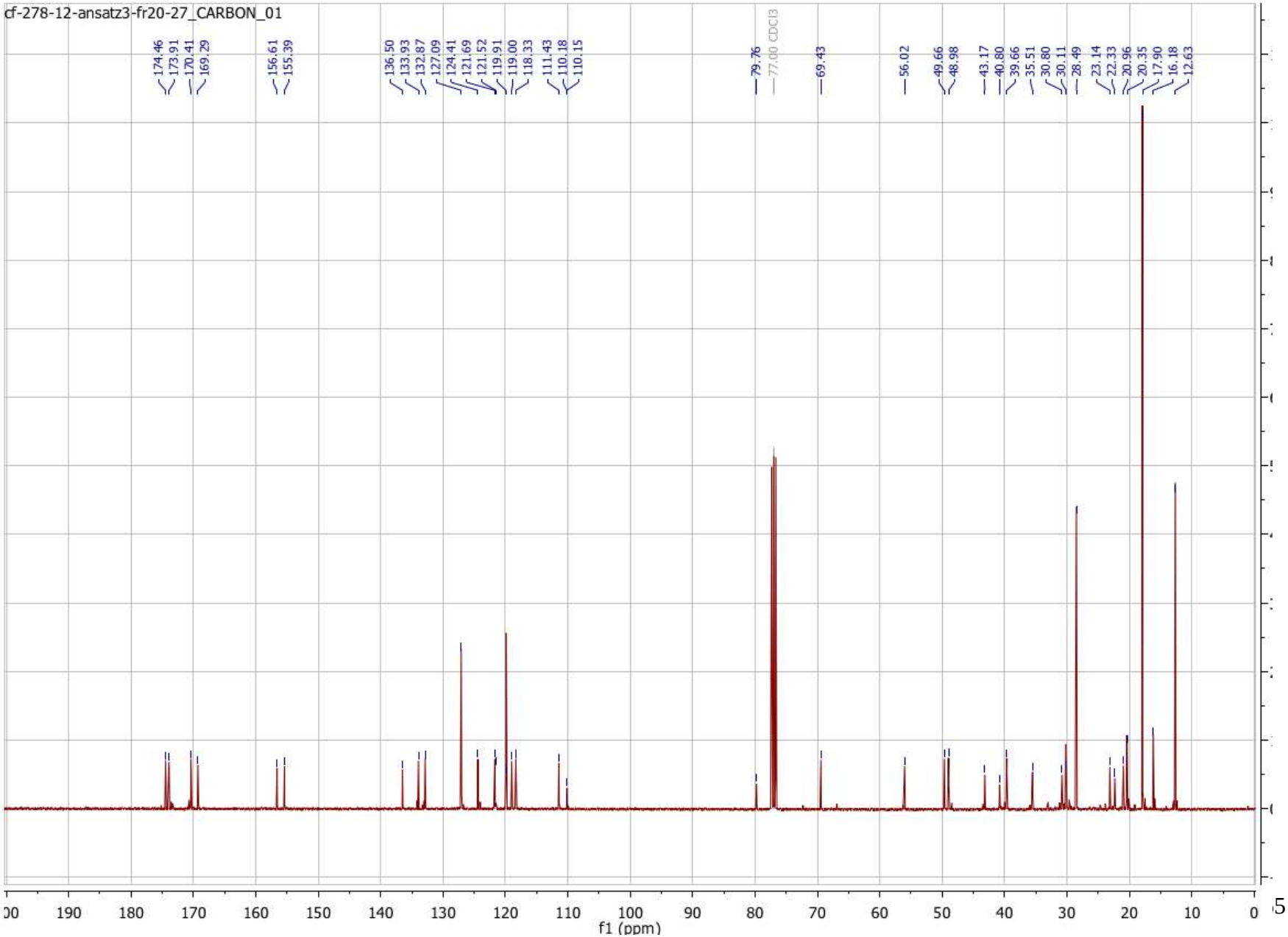
{3.19,5.64}
{1.25,1.08}
{1.24,1.24}
{1.08,1.23}
{7.15,6.81}
{7.34,7.11}
{7.57,7.04}
{5.34,7.27}
f2 (ppm)
f1 (ppm)

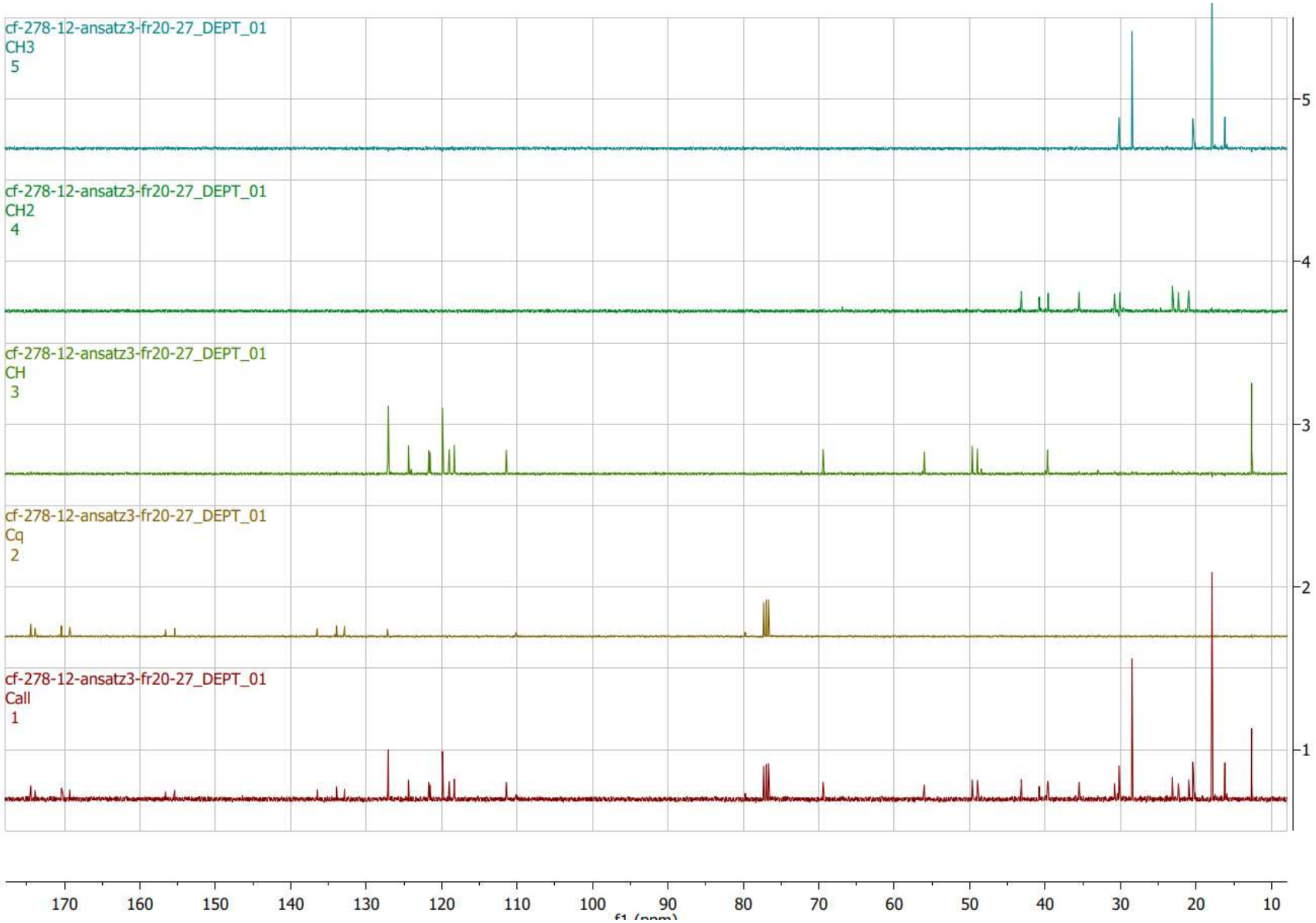

cf278-11_5hsqc.1.ser
CF278-11 cd2cl2
Belov / MPI 10200 / CS
{1.16,19.80}
{1.06,19.57}
{1.67,22.18}
{3.17,23.21}
{3.44,23.10}
{2.95,30.85}
{1.97,29.62}
{2.40,38.78}
{2.77,41.11}
{2.29,41.96}
{2.91,40.65}
{2.00,41.95}
{5.35,49.63}
{4.46,50.03}
{5.32,54.01}
{5.64,56.90}
{1.07,12.80}
{1.25,12.78}
{1.09,12.76}
{1.11,17.78}
{0.93,17.86}
{1.06,19.57}
{1.06,17.77}
{0.77,21.67}
{7.34,111.54}
{3.87,68.87}
{4.83,70.84}
{7.59,118.67}
{7.04,119.05}
{6.81,119.93}
{6.98,122.30}
{7.12,121.77}
{7.17,127.76}
{1.50,28.37}
{1.50,30.13}
{1.39,31.27}
{1.26,30.11}
{1.18,31.21}
{1.60,35.16}
{1.50,35.10}
{4.75,112.33}
{4.63,112.27}
{4.99,115.80}
{4.93,114.71}
{5.74,138.27}
f1 (ppm)
f2 (ppm)

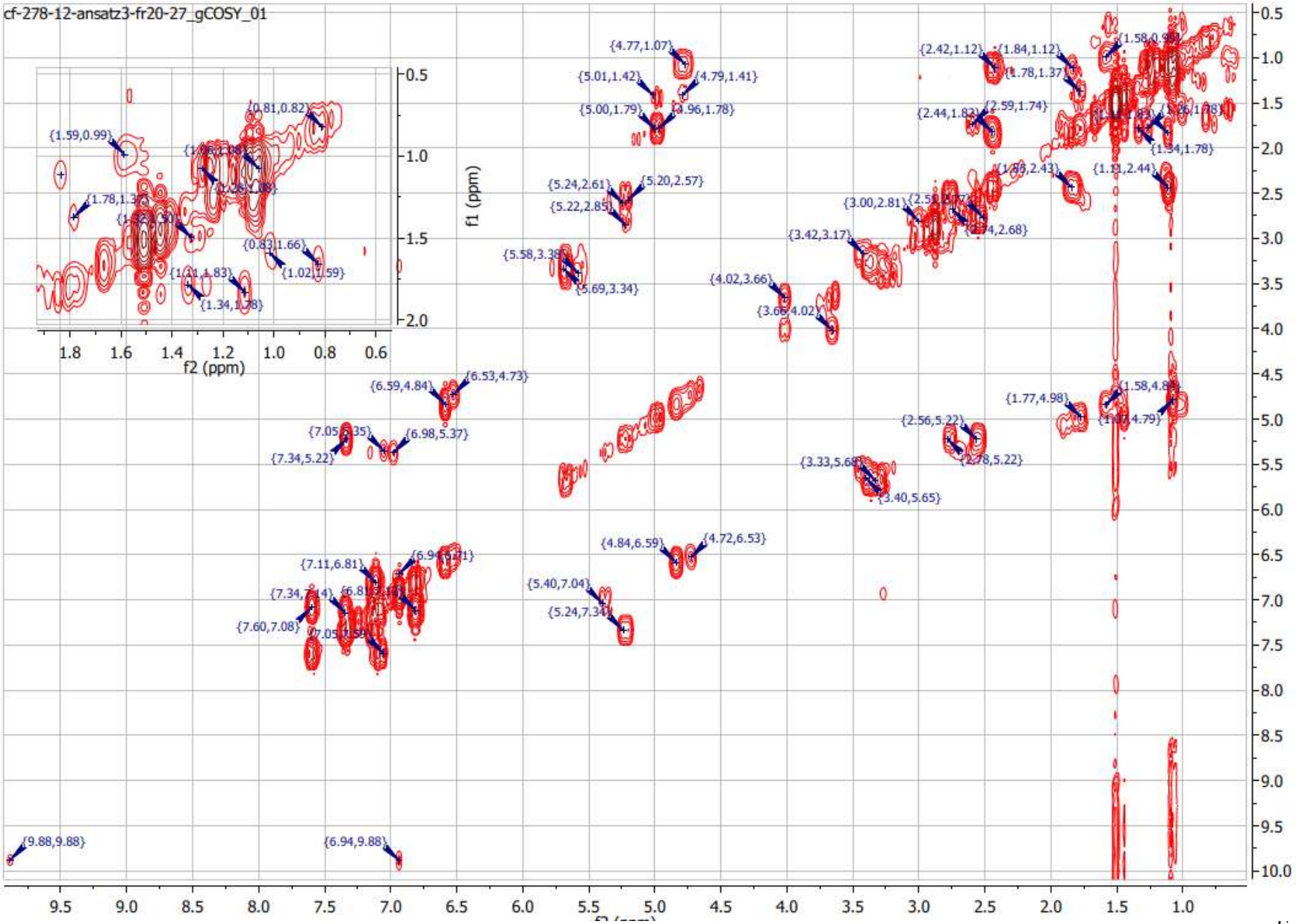
Figures S11a-e. NMR spectra of compound **7**-TIPS in $CDCl_3$: ^1H (400 MHz), $^{13}C\{^1H\}$ (101 MHz), DEPT, ^1H-^1H, and ^1H-^{13}C (HSQC) COSY.

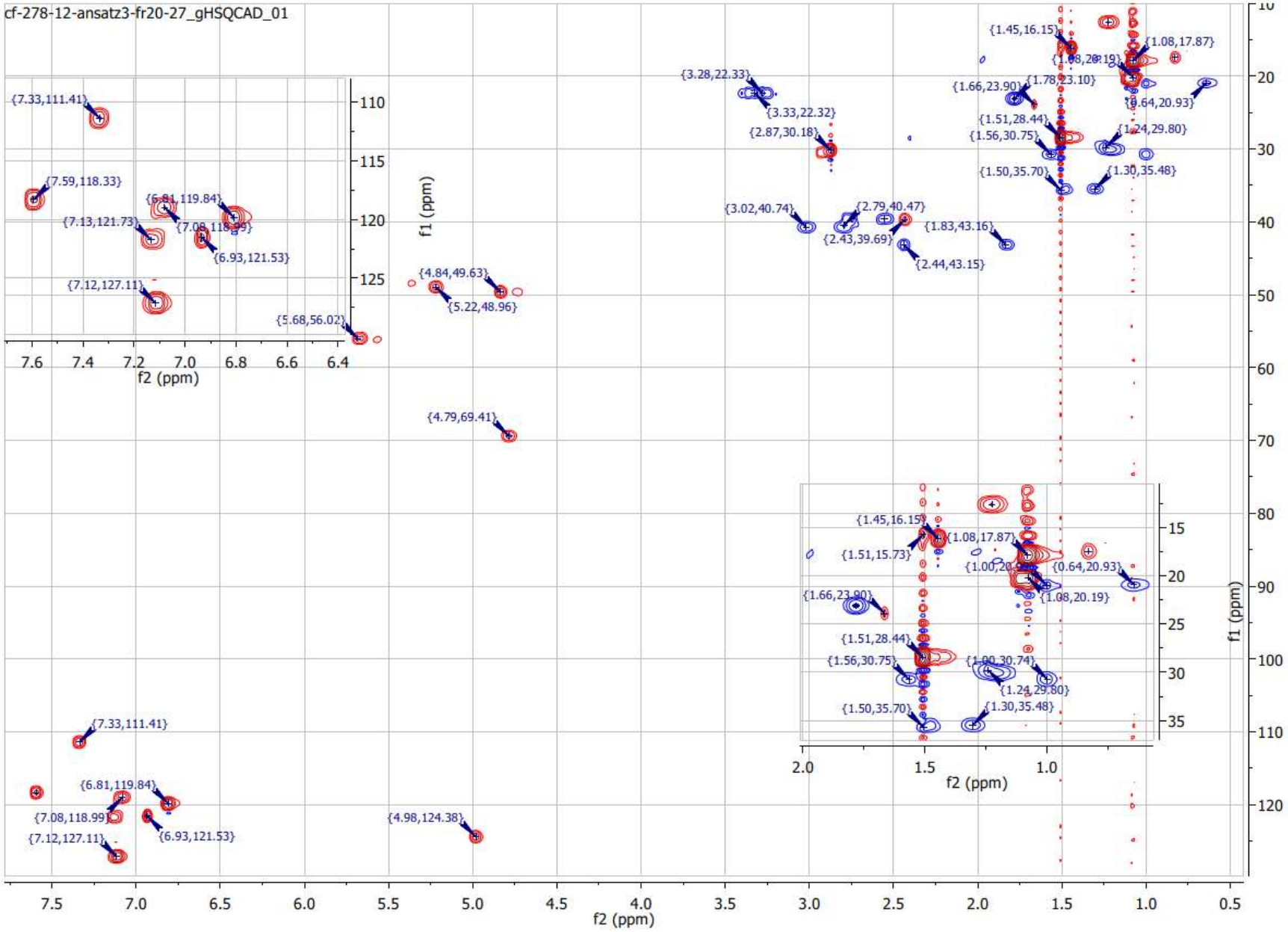



cf-278-12-ansatz3-fr20-27_PROTON_01
f1 (ppm)
f1 (ppm)
f1 (ppm)

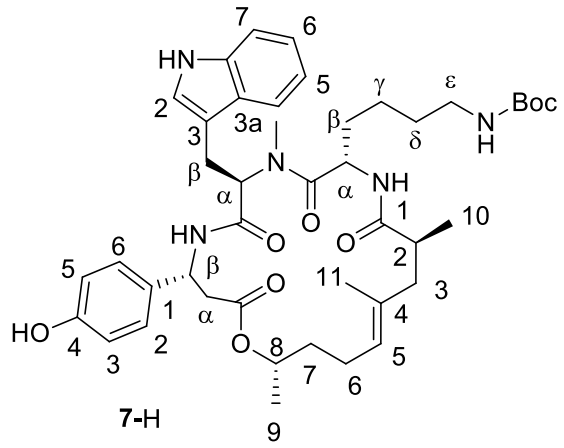

cf-278-12-ansatz3-fr20-27_CARBON_01
174.46
173.91
170.41
169.29
156.61
155.39
136.50
133.93
132.87
127.09
124.41
121.69
121.52
119.91
119.00
118.33
111.43
110.18
110.15
79.76
77.00 CDCl3
69.43
56.02
49.66
48.98
43.17
40.80
39.66
35.51
30.80
30.11
28.49
23.14
22.33
20.96
20.35
17.90
16.18
12.63
f1 (ppm)


cf-278-12-ansatz3-fr20-27_DEPT_01
CH3
5
cf-278-12-ansatz3-fr20-27_DEPT_01
CH2
4
cf-278-12-ansatz3-fr20-27_DEPT_01
CH
3
cf-278-12-ansatz3-fr20-27_DEPT_01
Cq
2
cf-278-12-ansatz3-fr20-27_DEPT_01
Call
1
5
4
3
2
1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

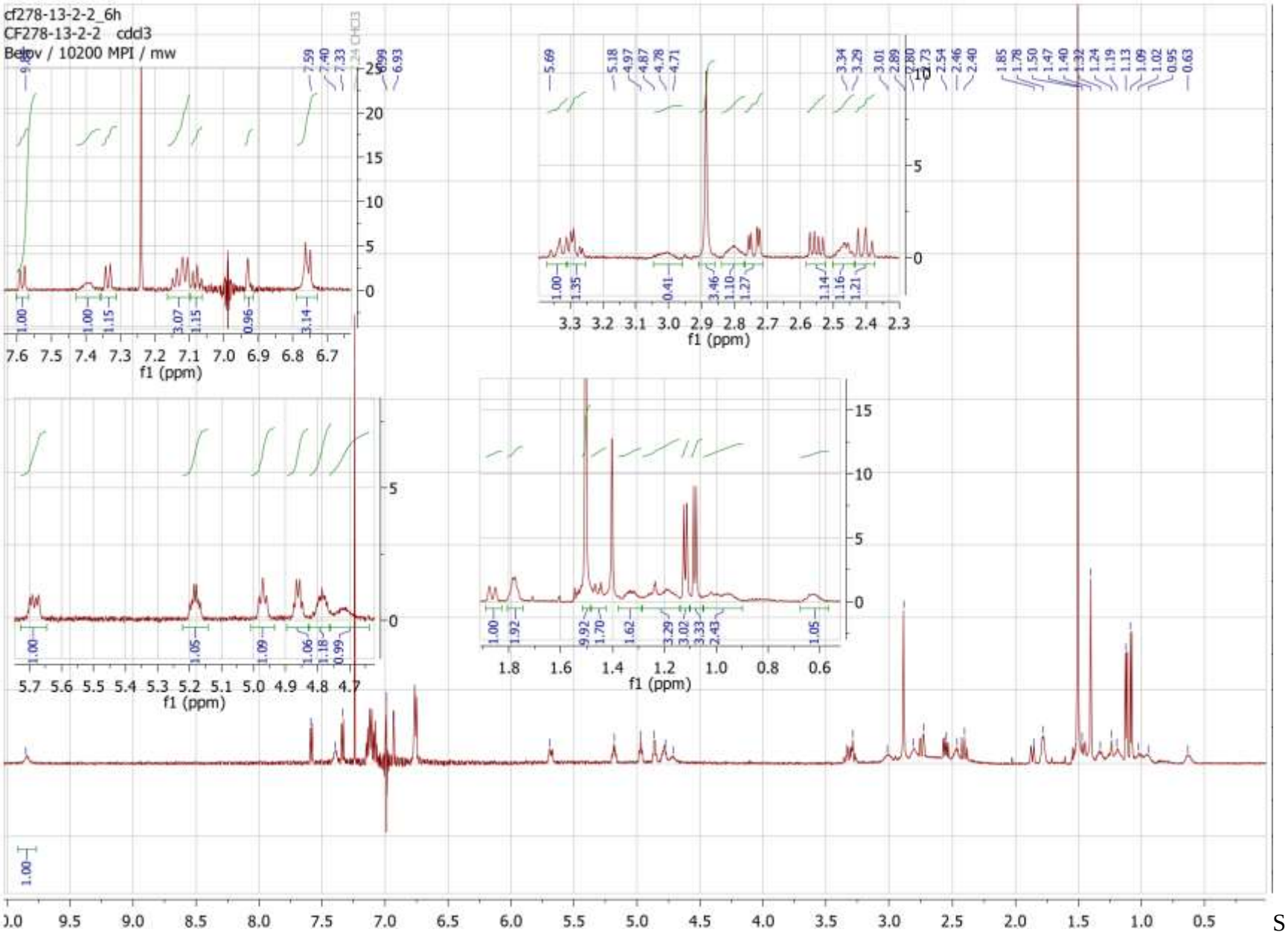

cf-278-12-ansatz3-fr20-27_gCOSY_01
f1 (ppm)
f2 (ppm)
{9.88,9.88}
{6.94,9.88}
{6.59,4.84}
{6.53,4.73}
{7.34,5.22}
{6.98,5.37}
{7.11,6.81}
{7.60,7.08}
{4.77,1.07}
{5.01,1.42}
{4.79,1.41}
{5.00,1.79}
{4.96,1.78}
{5.24,2.61}
{5.20,2.57}
{5.22,2.85}
{5.58,3.38}
{5.69,3.34}
{4.84,6.59}
{4.72,6.53}
{5.40,7.04}
{5.24,7.34}
{4.02,3.66}
{3.66,4.02}
{3.42,3.17}
{3.00,2.81}
{2.42,1.12}
{1.84,1.12}
{1.78,1.37}
{2.44,1.82}
{2.59,1.74}
{1.86,2.43}
{1.91,2.44}
{1.34,1.78}
{1.77,4.98}
{1.58,4.85}
{1.37,4.79}
{2.56,5.22}
{2.78,5.22}
{3.33,5.68}
{3.40,5.65}
{1.59,0.99}
{0.81,0.82}
{1.78,1.37}
{0.83,1.66}
{1.02,1.59}
{1.11,1.83}
{1.34,1.78}

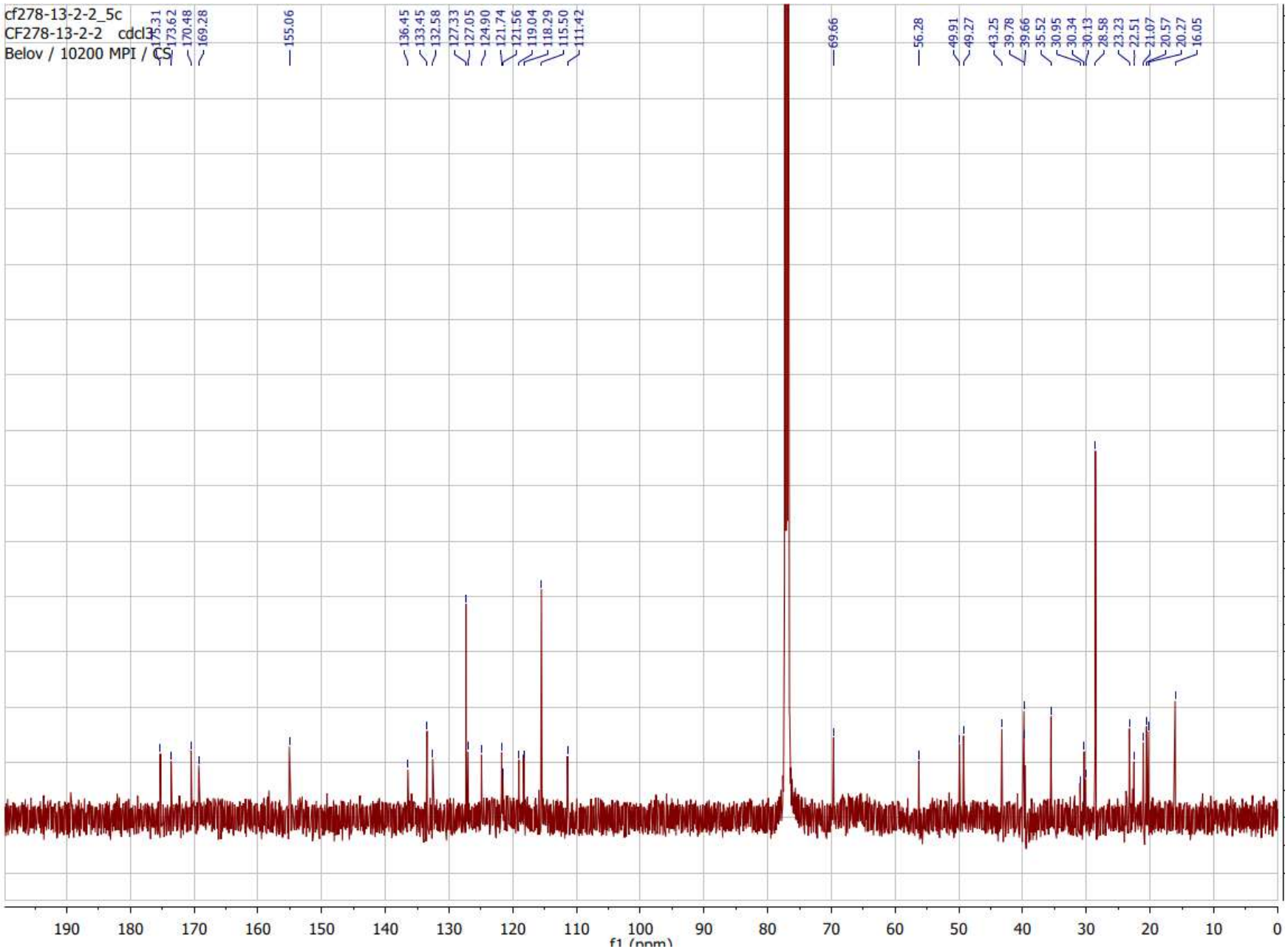

cf-278-12-ansatz3-fr20-27_gHSQCAD_01
f2 (ppm)
f1 (ppm)
{7.33,111.41}
{7.59,118.33}
{6.81,119.84}
{7.13,121.73}
{7.08,118.99}
{6.93,121.53}
{7.12,127.11}
{5.68,56.02}
{4.84,49.63}
{5.22,48.96}
{4.79,69.41}
{4.98,124.38}
{3.28,22.33}
{3.33,22.32}
{2.87,30.18}
{3.02,40.74}
{2.79,40.47}
{2.43,39.69}
{2.44,43.15}
{1.83,43.16}
{1.45,16.15}
{1.08,17.87}
{1.08,20.19}
{1.66,23.90}
{1.78,23.10}
{0.64,20.93}
{1.51,28.44}
{1.56,30.75}
{1.24,29.80}
{1.50,35.70}
{1.30,35.48}
{1.51,15.73}
{1.00,20.74}
{1.00,30.74}

Figures S12a,b. ^{1}H (600 MHz) and $^{13}C\{^{1}H\}$ NMR (125 MHz) spectra of compound **7**-H in $CDCl_3$.

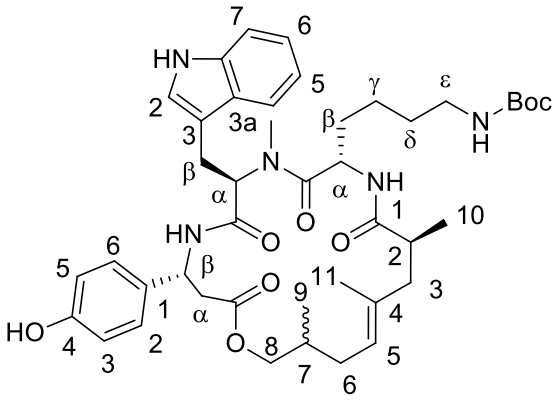


7-H

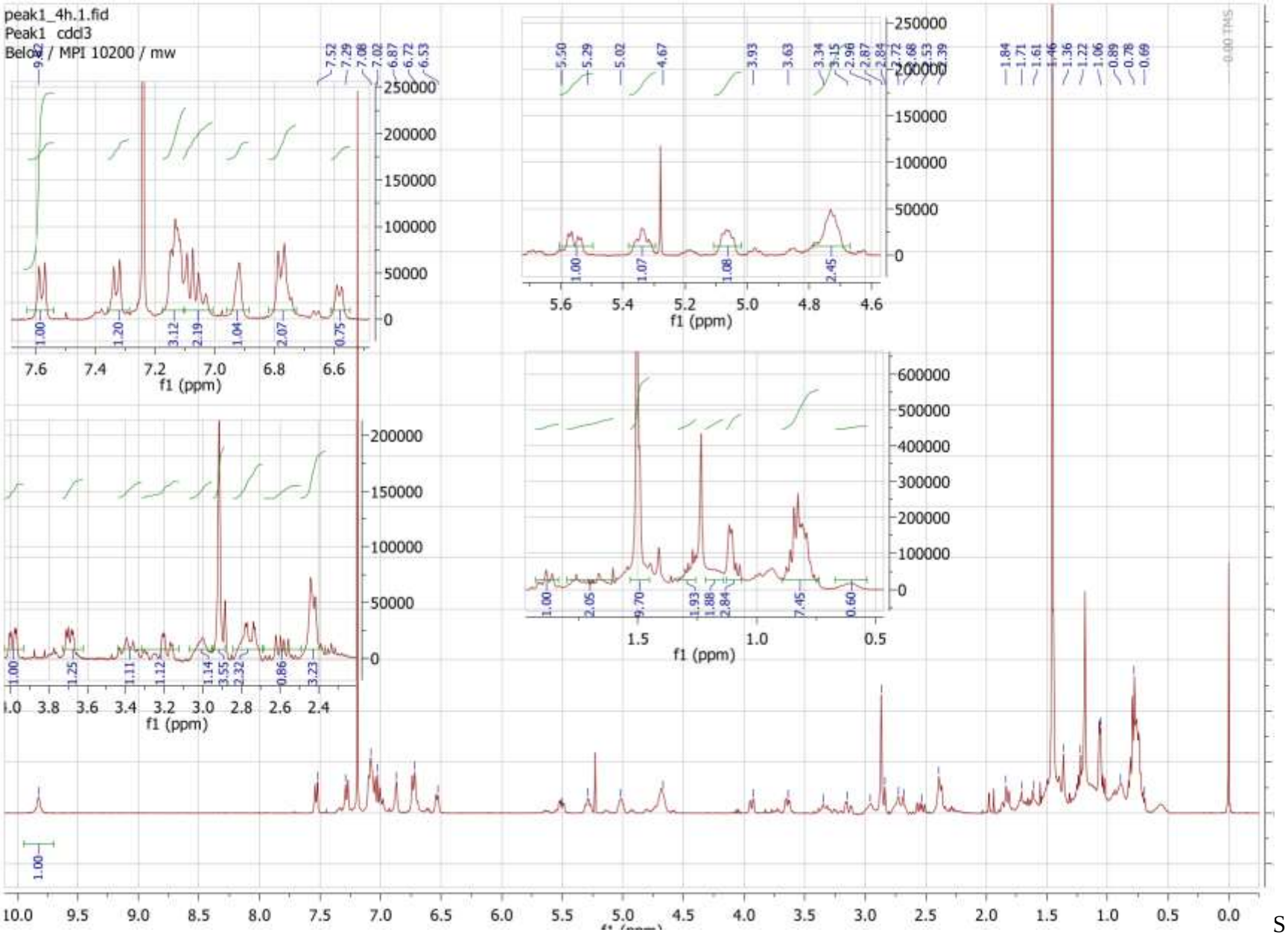

cf278-13-2-2_6h
CF278-13-2-2 cdcl3
Belov / 10200 MPI / mw
f1 (ppm)


cf278-13-2-2_5c
CF278-13-2-2 cdcl3
Belov / 10200 MPI / CS
175.31
173.62
170.48
169.28
155.06
136.45
133.45
132.58
127.33
127.05
124.90
121.74
121.56
119.04
118.29
115.50
111.42
69.66
56.28
49.91
49.27
43.25
39.78
39.66
35.52
30.95
30.34
30.13
28.58
23.23
22.51
21.07
20.57
20.27
16.05
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

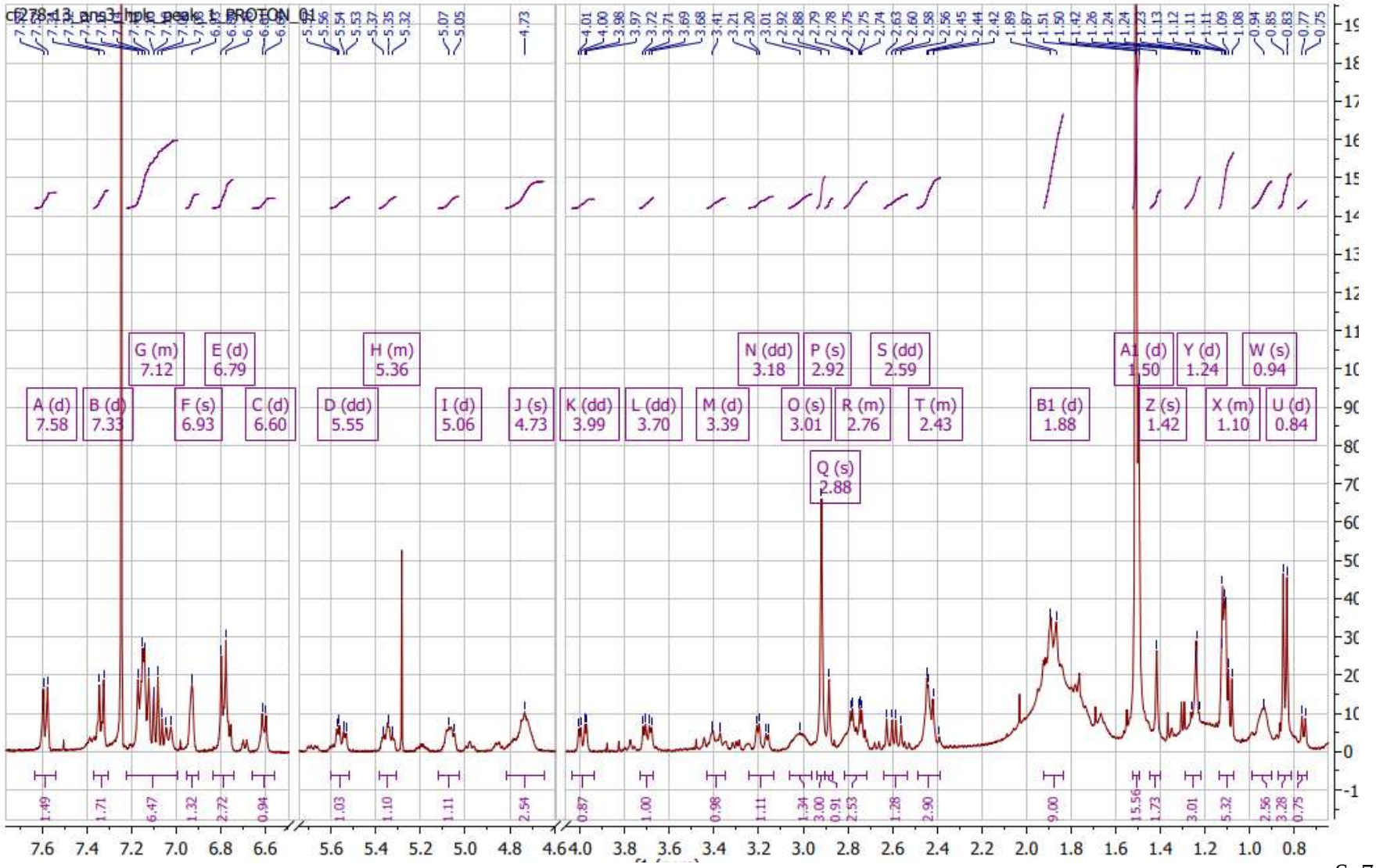
Figures S13a-d. ^{1}H (400 MHz), ^{13}C{^{1}H} NMR (101 MHz), APT (101 MHz), ^{1}H-^{1}H (600 MHz) and ^{1}H-^{13}C- (HSQC, 400 MHz) spectra of compound **8**-H in $CDCl_3$.

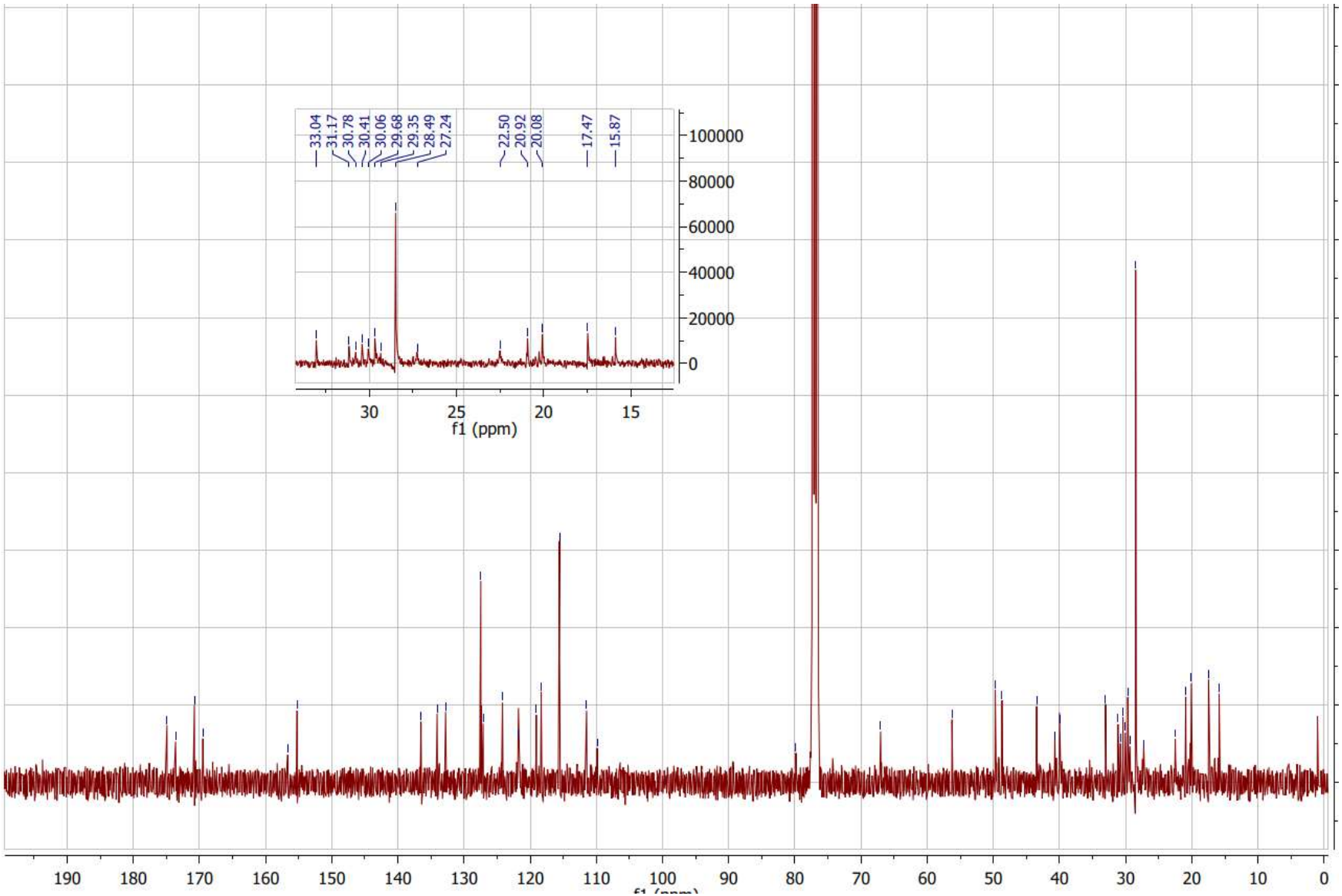


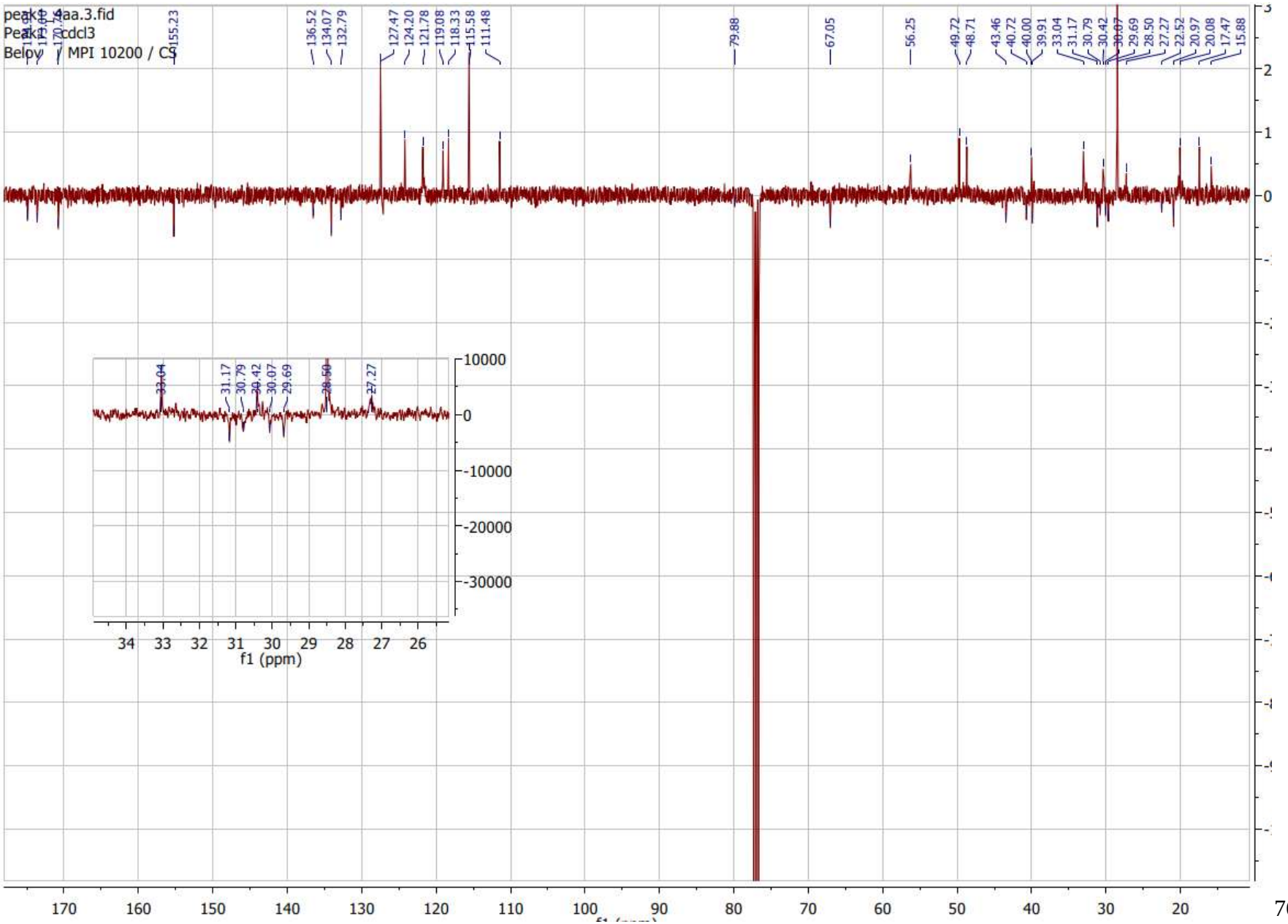
8-H

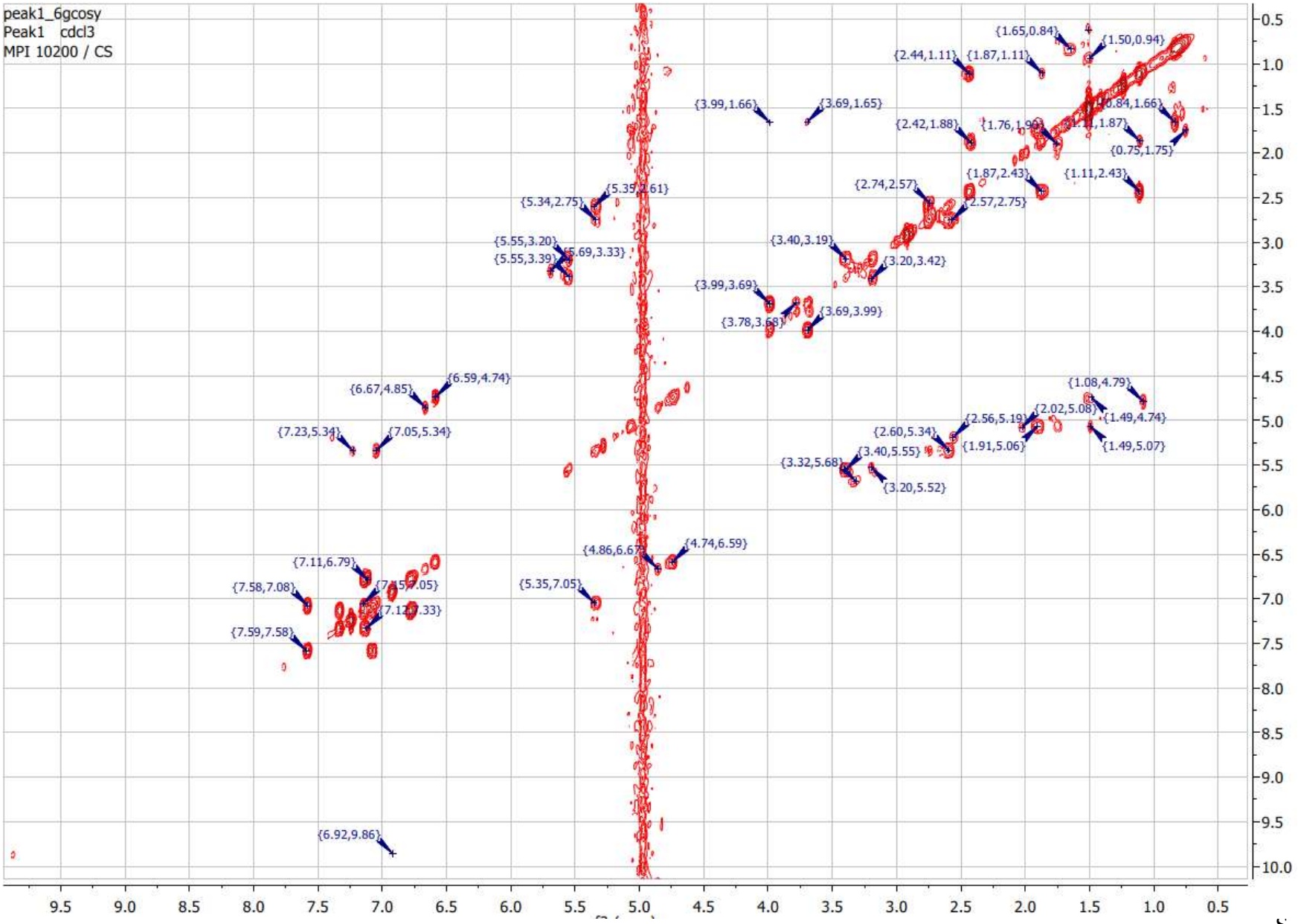

peak1_4h.1.fid
Peak1 cdcl3
Belo / MPI 10200 / mw
f1 (ppm)

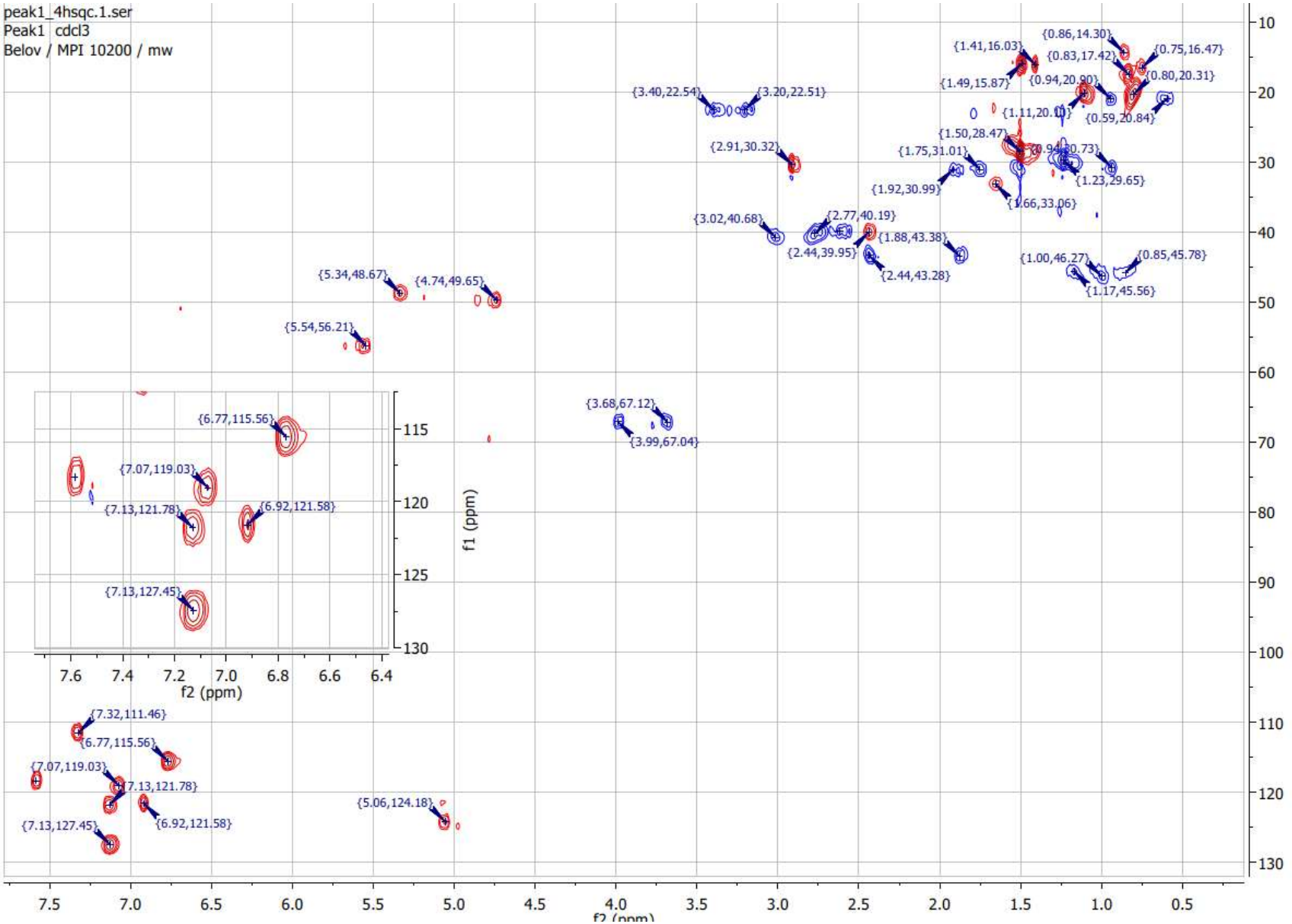
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.22 – 6.99 (m, 6H), 6.93 (s, 1H), 6.79 (d, *J* = 8.4 Hz, 3H), 6.60 (d, *J* = 6.7 Hz, 1H), 5.55 (dd, *J* = 12.2, 4.4 Hz, 1H), 5.38 – 5.31 (m, 1H), 5.06 (d, *J* = 9.5 Hz, 1H), 4.73 (s, 3H), 3.99 (dd, *J* = 10.6, 3.5 Hz, 1H), 3.70 (dd, *J* = 10.6, 4.2 Hz, 1H), 3.39 (d, *J* = 13.6 Hz, 1H), 3.18 (dd, *J* = 16.4, 4.5 Hz, 1H), 3.01 (s, 1H), 2.92 (s, 3H), 2.88 (s, 1H), 2.82 – 2.71 (m, 3H), 2.59 (dd, *J* = 16.3, 9.5 Hz, 1H), 2.49 – 2.39 (m, 3H), 1.88 (d, *J* = 10.0 Hz, 9H), 1.50 (d, *J* = 5.1 Hz, 16H), 1.42 (s, 2H), 1.24 (d, *J* = 2.2 Hz, 3H), 1.13 – 1.07 (m, 5H), 0.94 (s, 3H), 0.84 (d, *J* = 6.7 Hz, 3H), 0.76 (d, *J* = 6.2 Hz, 1H).




33.04
31.17
30.78
30.41
30.06
29.68
29.35
28.49
27.24
22.50
20.92
20.08
17.47
15.87
100000
80000
60000
40000
20000
0
30
25
20
15
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


peak6_4aa.3.fid
Peak1_ccdcl3
Belpy / MPI 10200 / C
155.23
136.52
134.07
132.79
127.47
124.20
121.78
119.08
118.33
115.58
111.48
79.88
67.05
56.25
49.72
48.71
43.46
40.72
40.00
39.91
33.04
31.17
30.79
30.42
30.07
29.69
28.50
27.27
22.52
20.97
20.08
17.47
15.88
10000
0
-10000
-20000
-30000
34 33 32 31 30 29 28 27 26
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20


peak1_6gcosy
Peak1 cdcl3
MPI 10200 / CS
{1.65,0.84}
{1.50,0.94}
{2.44,1.11}
{1.87,1.11}
{3.99,1.66}
{3.69,1.65}
{2.42,1.88}
{0.84,1.66}
{0.75,1.75}
{1.87,2.43}
{1.11,2.43}
{2.74,2.57}
{2.57,2.75}
{5.34,2.75}
{5.55,3.20}
{5.69,3.33}
{5.55,3.39}
{3.40,3.19}
{3.20,3.42}
{3.99,3.69}
{3.78,3.68}
{3.69,3.99}
{6.67,4.85}
{6.59,4.74}
{7.23,5.34}
{7.05,5.34}
{1.08,4.79}
{2.02,5.08}
{1.49,4.74}
{2.56,5.19}
{2.60,5.34}
{1.91,5.06}
{1.49,5.07}
{3.40,5.55}
{3.32,5.68}
{3.20,5.52}
{4.86,6.67}
{4.74,6.59}
{7.11,6.79}
{7.58,7.08}
{5.35,7.05}
{7.59,7.58}
{6.92,9.86}


peak1_4hsqc.1.ser
Peak1 cdcl3
Belov / MPI 10200 / mw
{0.86,14.30}
{1.41,16.03}
{0.75,16.47}
{0.83,17.42}
{1.49,15.87}
{0.94,20.90}
{0.80,20.31}
{3.40,22.54}
{3.20,22.51}
{1.11,20.01}
{0.59,20.84}
{1.50,28.47}
{2.91,30.32}
{1.75,31.01}
{1.23,29.65}
{1.92,30.99}
{1.66,33.06}
{3.02,40.68}
{2.77,40.19}
{1.88,43.38}
{2.44,39.95}
{2.44,43.28}
{1.00,46.27}
{0.85,45.78}
{1.17,45.56}
{5.34,48.67}
{4.74,49.65}
{5.54,56.21}
{3.68,67.12}
{3.99,67.04}
{6.77,115.56}
{7.07,119.03}
{7.13,121.78}
{6.92,121.58}
{7.13,127.45}
f1 (ppm)
f2 (ppm)
{7.32,111.46}
{6.77,115.56}
{7.07,119.03}
{7.13,121.78}
{5.06,124.18}
{7.13,127.45}
{6.92,121.58}
f2 (ppm)