# Microginins from a *Microcystis* sp. bloom material collected from the Kishon Reservoir, Israel

**Anat Lodin-Friedman and Shmuel Carmeli ***

Raymond and Beverly Sackler School of Chemistry and Faculty of Exact Sciences, Tel Aviv University, Ramat-Aviv Tel- Aviv 69978, Israel; anatlodin@gmail.com (ALF), carmeli@post.tau.ac.il (SC)

## Supplementary Material

# Table of content

S4. **Table S1**. Isolated Microginins.

| Name | Residue 1[a] | 2 | 3 | 4 | 5 | 6 | Activity |
|---|---|---|---|---|---|---|---|
| Microginin[1] | (2*S*,3*R*)-Ahda | L-Ala | L-Val | *N*Me-L-Tyr | L-Tyr | - | ACE |
| Microginin 299-A[2] | Cl-(2*S*,3*S*)-Ahda | L-Val | *N*Me-L-Val | *N*Me-L-Tyr | L-Pro | L-Tyr | APM (5.2 uM), ACE-ni |
| Microginin 299-B[2] | $Cl_2$-(2*S*,3*S*)-Ahda | L-Val | *N*Me-L-Val | *N*Me-L-Tyr | L-Pro | L-Tyr | APM (7.1 uM), ACE-ni |
| Microginin FR1[3] | (2*S*,3*R*)-Ahda | L-Ala | L-Leu | *N*Me-L-Tyr | L-Tyr | | ACE (16 uM), cAPM (1.3 uM), mAPM (6 nM) |
| Microginin 299-C[4] | (2*S*,3*S*)-Ahda | L-Val | *N*Me-L-Val | *N*Me-L-Tyr | L-Pro | L-Tyr | APM (2.3 uM), ACE-ni |
| Microginin 299-D[4] | $Cl_2$-(2*S*,3*S*)-Ahda | L-Val | *N*Me-L-Val | *N*Me-L-Tyr | L-Pro | | APM (8.5 uM), ACE-ni |
| Microginin 99-A[4] | Cl-(3*R*)-Ada | L-Tyr | L-Leu | *N*Me-L-Tyr | L-Pro | | APM, ACE-ni |
| Microginin 99-B[4] | $Cl_2$-(3*R*)-Ada | L-Tyr | L-Leu | *N*Me-L-Tyr | L-Pro | | APM, ACE-ni |
| Microginin T1[5] | Cl-Ahda | L-Ala | L-Pro | L-Tyr | L-Tyr | | ACE (6.8 uM), AMP (2.7 uM) |
| Microginin T2[5] | Ahda | L-Ala | L-Pro | L-Tyr | L-Tyr | | ACE (10 uM), AMP (2.9 uM) |
| Microginin 478[6] | *N*Me-(2*S*,3*S*)-Ahda | L-Val | *N*Me-L-Val | *N*Me-L-Tyr | L-Tyr | | APM (132 uM), ACE (13.2 uM) |
| Microginin 51-A[6] | (2*S*,3*S*)-Ahda | L-Tyr | *N*Me-L-Val | *N*Me-L-Tyr | L-Pro | L-Tyr | APM (4.9 uM), ACE-ni |
| Microginin 51-B[6] | *N*Me-(2*S*,3*S*)-Ahda | L-Tyr | *N*Me-L-Val | *N*Me-L-Tyr | L-Pro | L-Tyr | APM, ACE-ni |
| Microginin 91-A[6] | (2*R*,3*R*)-Ahda | L-Ile | *N*Me-L-Leu | L-Pro | | | APM, ACE-ni |
| Microginin 91-B[6] | Cl-(2*R*,3*R*)-Ahda | L-Ile | *N*Me-L-Leu | L-Pro | | | APM, ACE-ni |
| Microginin 91-C[6] | (2*R*,3*R*)-Ahda | L-Ile | *N*Me-L-Leu | L-Pro | L-Tyr | | APM (71.1 uM), ACE-ni |
| Microginin 91-D[6] | Cl-(2*R*,3*R*)-Ahda | L-Ile | *N*Me-L-Leu | L-Pro | L-Tyr | | APM (43.4 uM), ACE-ni |
| Microginin 91-E[6] | $Cl_2$-(2*R*,3*R*)-Ahda | L-Ile | *N*Me-L-Leu | L-Pro | L-Tyr | | APM (19.5 uM), ACE-ni |
| Microginin SD755[7] | *N*Me-Ahoa | L-Val | *N*Me-L-Ile | *N*Me-L-Tyr | L-Tyr | | APN (18.5 uM) |
| Nostoginin BN741[8] | (2*S*,3*S*)-Ahoa | L-Val | *N*Me-L-Ile | *N*Me-L-Tyr | L-Tyr | | APN (1.3 uM) |
| Nostoginin BN578[8] | (2*S*,3*S*)-Ahoa | L-Val | *N*Me-L-Ile | *N*Me-L-Tyr | - | | ND |
| Cyanostatin A[9] | (2*S*,3*R*)-Ahda | L-Ala | L-Val | *N*Me-L-Tyr | L-Hty | | APM (55 uM), ACE (150 uM) |
| Cyanostatin B[9] | (2*S*,3*R*)-Ahda | L-Tyr | *N*Me-L-Leu | L-Pro | L-Tyr | | APM (16 uM), ACE (170 uM) |
| Microginin AL584[10] | Cl-(2*S*,3*S*)-Ahda | L-Ala | *N*Me-L-Val | L-Tyr | | | APN-ni |
| Microginin HG787[11] | Cl-Ahda | L-Tyr | *N*Me-L-Ile | L-Pro | L-Tyr | | APN (7.7 uM) |
| Microginin 680[12] | (*2S*,3R**)-$Cl_2$-Ahoa | L-Tyr | *N*Me-L-Tyr | L-Pro | | | |
| Microginin 646[12] | (*2S*,3R**)-Cl-Ahoa | L-Tyr | *N*Me-L-Tyr | L-Pro | | | |
| Microginin 612[12] | (*2S*,3R**)-Ahoa | L-Tyr | *N*Me-L-Tyr | L-Pro | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Microginin 565[13] | Ahda | Ala | *N*Me-Leu | Tyr | | | |
| Microginin KR767[14] | (2*R*,3*R*)-*N*Me-Ahda | L-Tyr | *N*Me-L-Leu | L-Pro | L-Tyr | | APM (0.5 nM) |
| Microginin KR801[14] | (2*R*,3*R*)-*N*Me-Cl-Ahda | L-Tyr | *N*Me-L-Leu | L-Pro | L-Tyr | | APM (0.1 nM) |
| Microginin KR835[14] | (2*R*,3*R*)-*N*Me-$Cl_2$-Ahda | L-Tyr | *N*Me-L-Leu | L-Pro | L-Tyr | | APM (0.4 nM) |
| Microginin KR604[14] | (2*R*,3*R*)-*N*Me-Ahda | L-Tyr | *N*Me-L-Leu | L-Pro | | | APM (7.5 nM) |
| Microginin KR638[14] | (2*R*,3*R*)-*N*Me-Cl-Ahda | L-Tyr | *N*Me-L-Leu | L-Pro | | | APM (3.8 nM) |
| Microginin KR815[14] | (2*R*,3*R*)-*N*Me-Cl-Ahda | L-Tyr | *N*Me-L-Leu | L-Pro | L-Tyr-OMe | | APM (72.0 nM) esterification product |
| Microginin KR781[14] | (2*R*,3*R*)-*N*Me-Ahda | L-Tyr | *N*Me-L-Leu | L-Pro | L-Tyr-OMe | | APM (? nM) esterification product |
| Microginin KR787[14] | (2*R*,3*R*)-Cl-Ahda | L-Tyr | *N*Me-L-Leu | L-Pro | L-Tyr | | APM (5.7 nM) |
| Microginin FR3[14] | (2*S*,3*R*)-Ahda | L-Thr | L-Pro | L-Tyr | L-Tyr | | APM (6.2 nM) |
| Microginin FR4[14] | (2*S*,3*R*)-*N*Me-Ahda | L-Thr | L-Pro | L-Tyr | L-Tyr | | APM (1.8 nM) |
| Microginin 674[15] | (2*S*,3*S*)-Ahda | *N*Me-L-Met | L-Tyr | L-Tyr | | | ACE inhibitor |
| Microginin 690[16] | (2*S*,3*S*)-Ahda | *N*Me-L-Met(O) | L-Tyr | L-Tyr | | | ACE inhibitor oxidation product of 674 |

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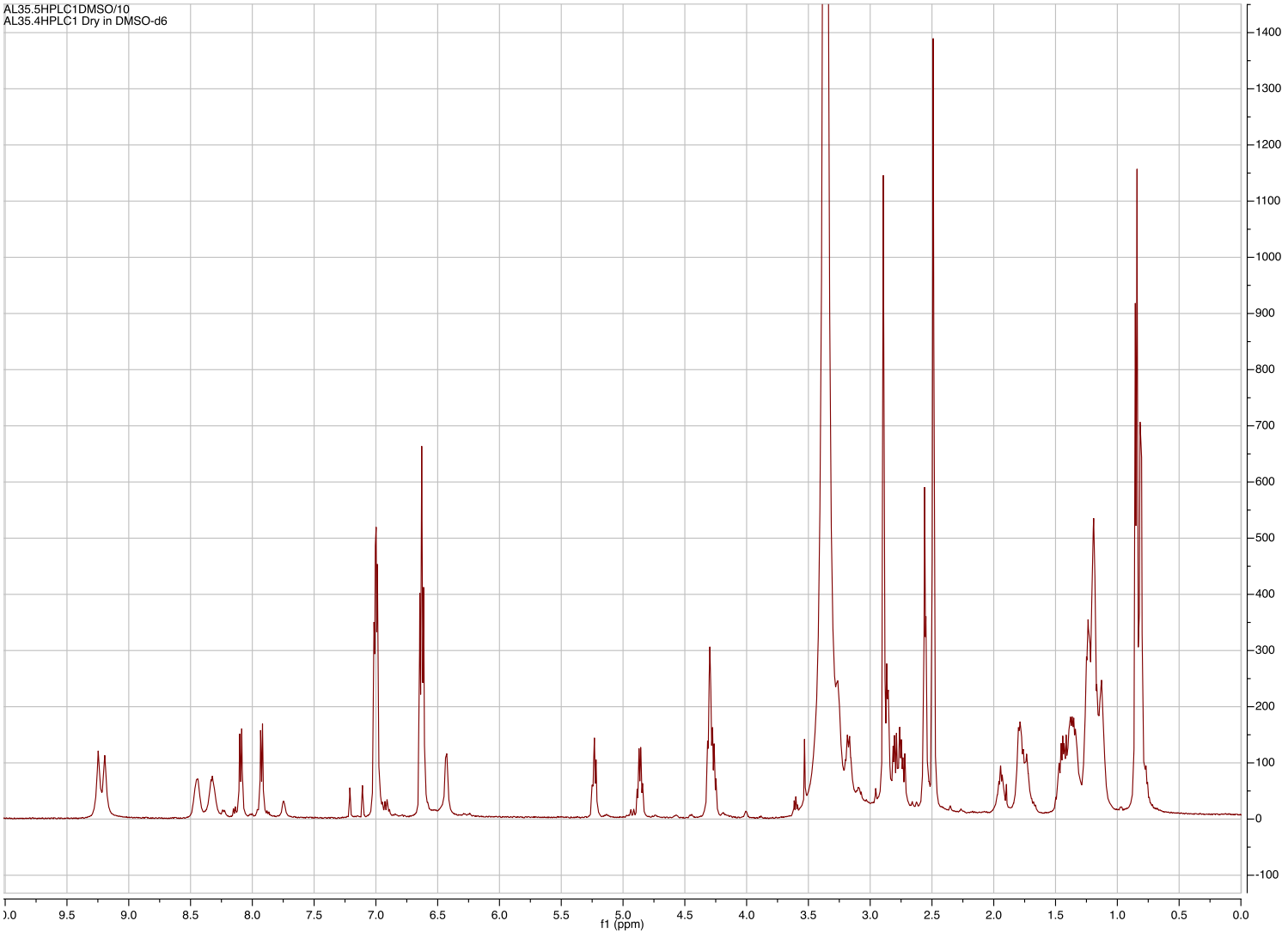
15. Product of LKT Laboratories, Inc.
16. Product of Santa Cruz Biotechnology.

S6. **Table S2**. NMR Data (500/125 MHz) of Microginin KR767 (**1**) in DMSO-$d_6$.

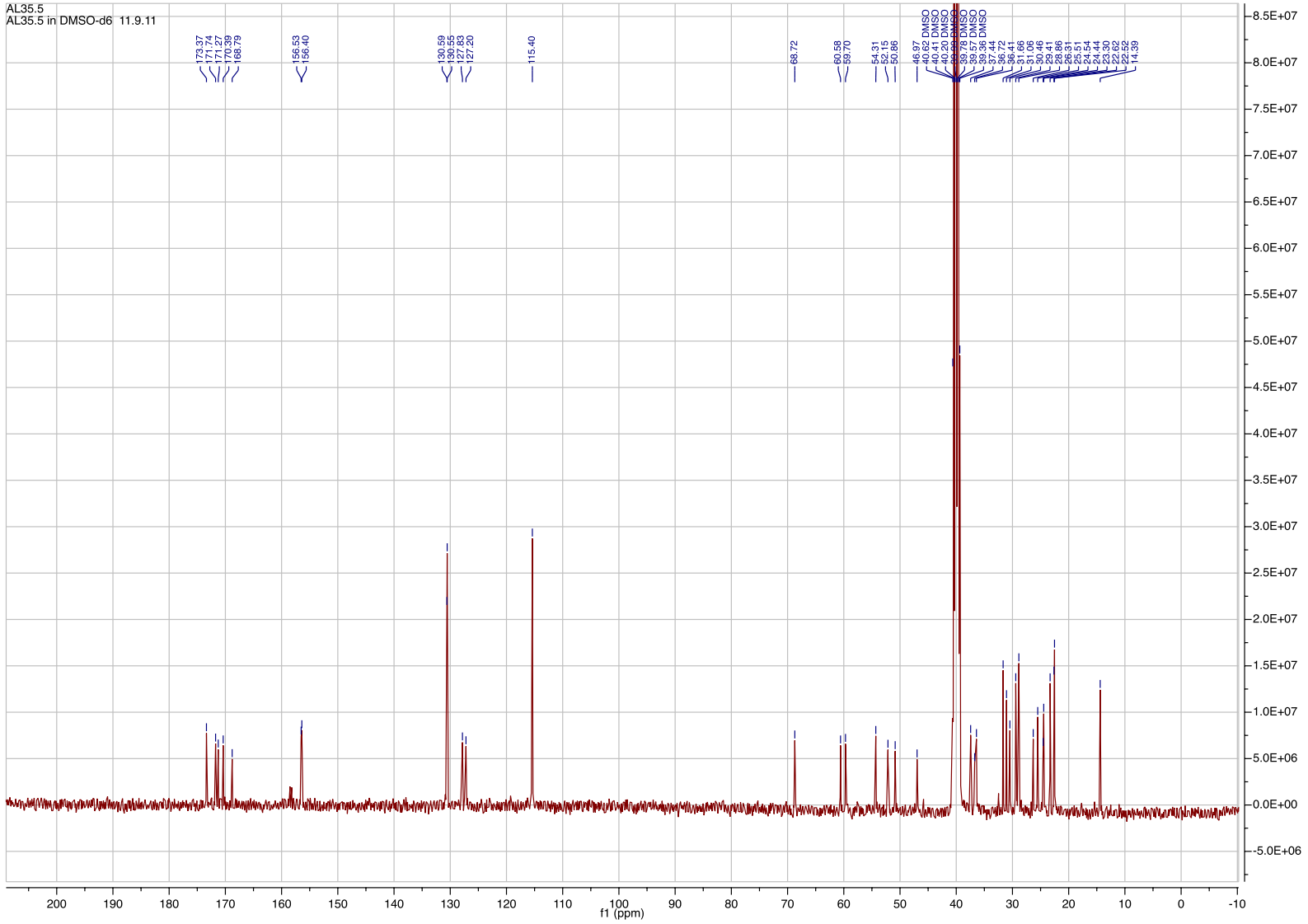
| Position | $\delta_C$ | $\delta_H$ Multiplicity, *J* (Hz) | HMBC correlations | COSY correlations | NOESY correlations |
|---|---|---|---|---|---|
| Ahda 1 | 170.1 C | | Ahda-2,2-OH, $^1$Tyr-2,NH | | |
| 2 | 68.5 CH | 4.30 brs | Ahda-2-OH | Ahda-2-OH,3 | Ahda-2-OH,3,3-$NH_2$, *N*$CH_3$,4,4',5',5', $^1$Tyr-NH |
| 2-OH | | 6.47 d, 6.1 | | Ahda-2 | Ahda-2,3,3-*N*$CH_3$,4,6, $^1$Tyr-NH |
| 3 | 60.3 CH | 3.27 brm | Ahda-2,2-OH,3-*N*$CH_3$ | Ahda-2,3-$NH_2$,4,4' | Ahda-2,2-OH,3-$NH_2$, *N*$CH_3$,4,4',5',5', $^1$Tyr-NH |
| 3-$NH_2$ | | 8.35 brs | | Ahda-3,3-NH',3-*N*$CH_3$ | Ahda-2,3,3-*N*$CH_3$ |
| | | 8.49 brs | | Ahda-3,3-NH',3-*N*$CH_3$ | Ahda-2,3,3-*N*$CH_3$ |
| 3-*N*$CH_3$ | 30.8 $CH_3$ | 2.56 brt, 4.7 | | Ahda-3-$NH_2$ | Ahda-2,2-OH,3,3-$NH_2$, 4,4' |
| 4 | 26.1 $CH_2$ | 1.39 m | Ahda-2 | Ahda-3,4',5,5' | Adha-2,3 |
| | | 1.33 m | | Ahda-3,4,5,5' | Adha-2,3 |
| 5 | 25.2 $CH_2$ | 1.25 m | Ahda-4,4' | Ahda-4,4',5',6 | Adha-2,3 |
| | | 1.13 m | | Ahda-4,4',5,6 | Adha-2,3 |
| 6 | 29.2 $CH_2$ | 1.18 m | Ahda-7,8 | | |
| | | 1.13 m | | Ahda-7 | |
| 7 | 28.6 $CH_2$ | 1.19 m | Ahda-5,5',6,6' | Ahda-6' | |
| 8 | 31.4 $CH_2$ | 1.20 m | Ahda-9,10 | Ahda-9 | |
| 9 | 22.2 $CH_2$ | 1.24 m | Ahda-8,10 | Ahda-8,10 | |
| 10 | 14.1 $CH_3$ | 0.84 t, 7.3 | Ahda-9 | Ahda-9 | |
| $^1$Tyr 1 | 171.0 C | | $^1$Tyr-2,3,3', *N*MeLeu-2, *N*$CH_3$ | | |
| 2 | 50.6 CH | 4.86 ddd, 8.2,7.7,6.3 | $^1$Tyr-3,3',NH | $^1$Tyr-2-NH,3,3' | $^1$Tyr-2-NH,3,3',5,5', *N*MeLeu-*N*Me |
| 2-NH | | 8.10 d, 8.2 | | $^1$Tyr-2 | $^1$Tyr-2,3,3',5,5', Ahda-2,2-OH,3 |
| 3 | 36.4 $CH_2$ | 2.86 m | $^1$Tyr-2,5,5' | $^1$Tyr-2,3' | $^1$Tyr-2,3',5,5' |
| | | 2.74 m | | $^1$Tyr-2,3 | $^1$Tyr-2,3,5,5' |
| 4 | 126.1 C | | $^1$Tyr-2,3,3',6,6' | | |
| 5,5' | 130.2 CH | 7.00 d, 8.4 | $^1$Tyr-3,3',5',5,6,6' | $^1$Tyr-6,6' | $^1$Tyr-2,3,3',6,6' |

| | | | | | |
|---|---|---|---|---|---|
| 6,6’ | 115.1 CH | 6.62 d, 8.4 | $^{1}$Tyr-5,5’,6’,6,7-OH | $^{1}$Tyr-5,5’ | $^{1}$Tyr-5,5’,7-OH |
| 7 | 156.2 C | | $^{1}$Tyr-5,5’,6,6’,7-OH | | |
| 7-OH | | 9.25 s | | | $^{1}$Tyr-6,6’ |
| *N*MeLeu 1 | 168.5 C | | *N*MeLeu-2,3,3’ | | |
| 2 | 51.9 CH | 5.23 dd, 8.1,6.6 | *N*MeLeu-3,3’,*N*Me | *N*MeLeu-3,3’ | *N*MeLeu-3,3’,5,6,*N*Me, Pro-5,5’ |
| 2-*N*$CH_3$ | 30.2 $CH_3$ | 2.89 s | *N*MeLeu-2 | | *N*MeLeu-2,3,3’ |
| 3 | 37.2 $CH_2$ | 1.48 m | *N*MeLeu-2,4,5,6 | *N*MeLeu-2,3’,4 | *N*MeLeu-2,5,6,*N*Me Pro-5,5’ |
| | | 1.42 m | | *N*MeLeu-2,3,4 | *N*MeLeu-2,5,6,*N*Me, Pro-5,5’ |
| 4 | 24.2 CH | 1.37 m | *N*MeLeu-2,3,3’,5,6 | *N*MeLeu-3,3’,5,6 | *N*MeLeu-*N*Me |
| 5 | 22.4 $CH_3$ | 0.81 d, 6.6 | *N*MeLeu-3,3’,4,6 | *N*MeLeu-4 | *N*MeLeu-2,3,3’ |
| 6 | 23.0 $CH_3$ | 0.85 d, 6.6 | *N*MeLeu-3,3’,4,5 | *N*MeLeu-4 | *N*MeLeu-2,3,3’ |
| Pro 1 | 171.4 C | | Pro-2,3’, $^{2}$Tyr-NH | | |
| 2 | 59.4 CH | 4.31 m | Pro-4’ | Pro-3,3’ | Pro-3,4,5’ |
| 3 | 29.1 $CH_2$ | 1.94 m | Pro-2,4,4’,5’ | Pro-2,3’,4,4’ | Pro-2,4’ |
| | | 1.79 m | | Pro-2,3,4,4’ | |
| 4 | 24.3 $CH_2$ | 1.80 m | Pro-2,3,5’ | Pro-3,3’,5,5’ | Pro-2 |
| | | 1.73 m | | Pro-3,3’,5,5’ | Pro-3 |
| 5 | 46.7 $CH_2$ | 3.40 m | Pro-2 | Pro-4,4’,5’ | Pro-4,4’,5’, *N*MeLeu-2,3,3’ |
| | | 3.18 dt, 9.0, 7.3 | | Pro-4,4’,5 | Pro-2,3,4,4’,5, *N*MeLeu-2,3,3’ |
| $^{2}$Tyr 1 | 173.1 C | | $^{2}$Tyr-2,3,3’ | | |
| 2 | 54.0 CH | 4.27 td, 7.6,5.6 | $^{2}$Tyr-3,3’,NH | $^{2}$Tyr-3,3’,NH | $^{2}$Tyr-3,3’,5,5’,NH |
| 2-NH | | 7.92 d, 7.6 | | $^{2}$Tyr-2 | $^{2}$Tyr-2,3,3’,5,5’, Pro-3’ |
| 3 | 36.1 $CH_2$ | 2.86 m | $^{2}$Tyr-2,NH,5,5’ | $^{2}$Tyr-2,3’ | $^{2}$Tyr-2,3’,5,5’,NH |
| | | 2.79 m | | $^{2}$Tyr-2,3 | $^{2}$Tyr-2,3,5,5’,NH |
| 4 | 127.5 C | | $^{2}$Tyr-2,3,3’,6,6’ | | |
| 5,5’ | 130.3 CH | 7.01d, 8.4 | $^{2}$Tyr-3,3’,5’,5,6,6’ | $^{2}$Tyr-6,6’ | $^{2}$Tyr-2,3,3’,6,6’,NH |
| 6,6’ | 115.1 CH | 6.64 d, 8.4 | $^{2}$Tyr-5,5’,6’,6,7-OH | $^{2}$Tyr-5,5’ | $^{2}$Tyr-5,5’,7-OH |
| 7 | 156.1 C | | $^{2}$Tyr-5,5’,6,6’,7-OH | | |
| 7-OH | | 9.20 s | | | $^{2}$Tyr-6,6’ |

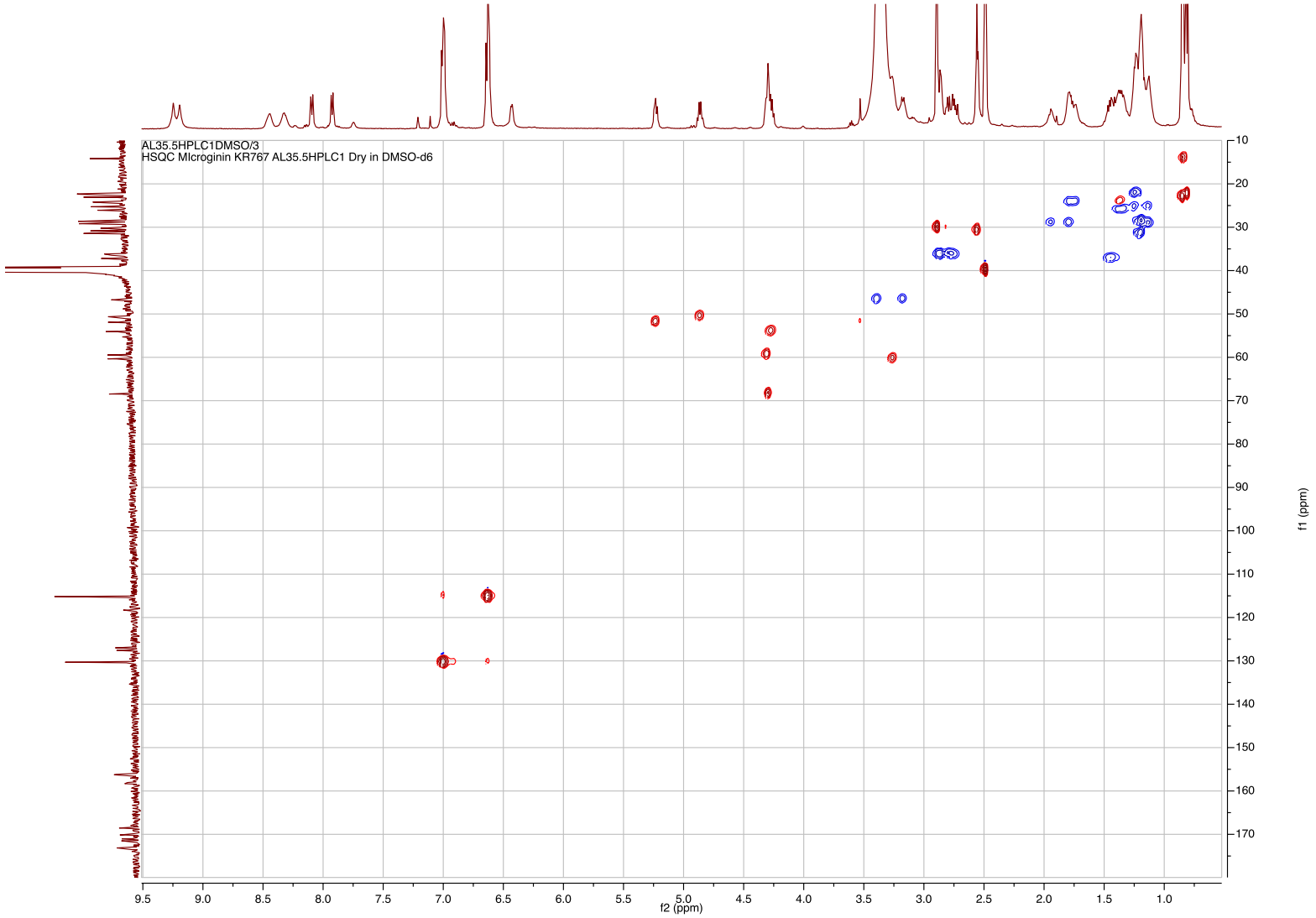
S8. $^{1}$H NMR Spectrum of Microginin KR767 (**1**) in DMSO-$d_6$



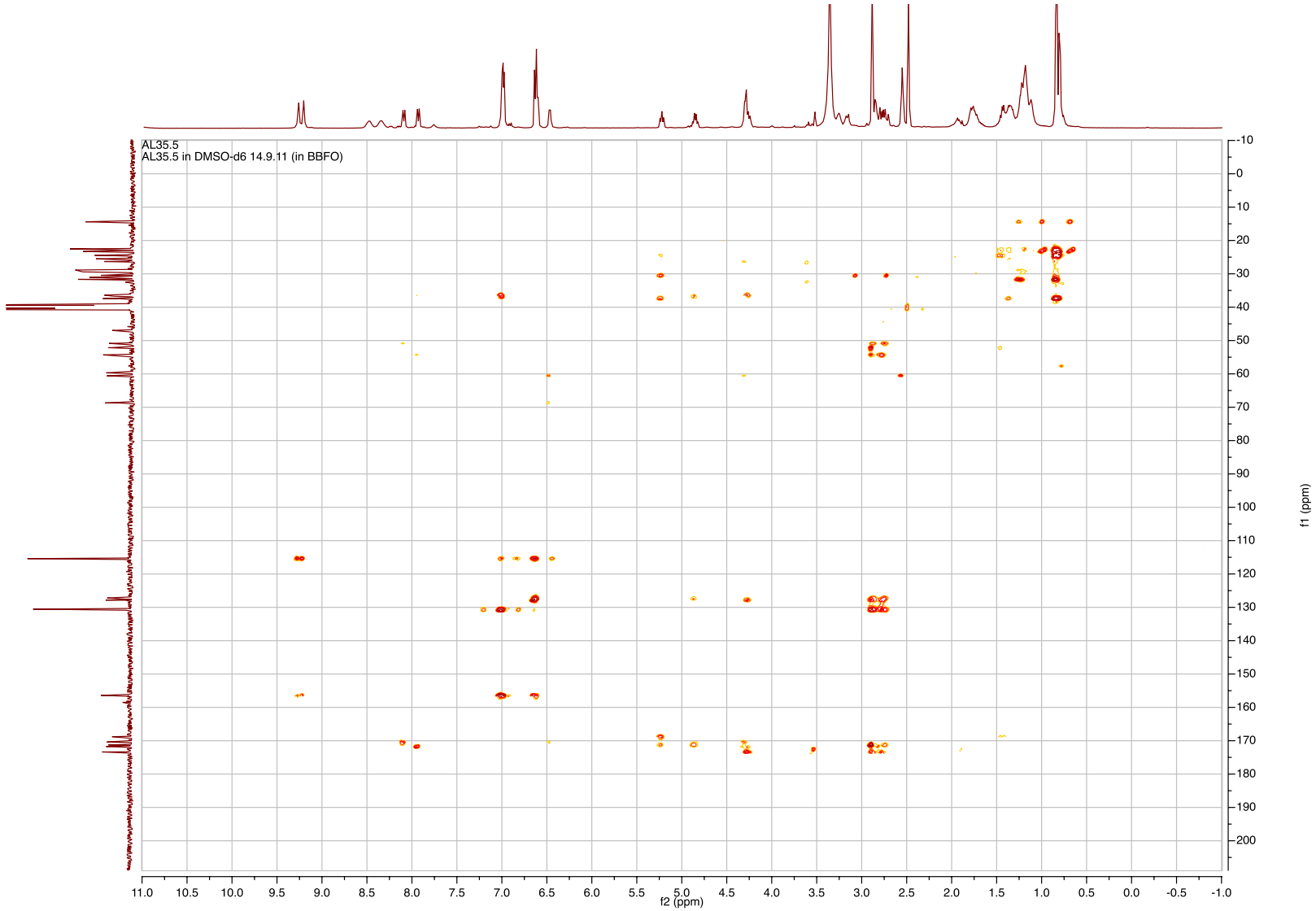
S9. $^{13}$C NMR Spectrum of Microginin KR767 (**1**) in DMSO-$d_6$



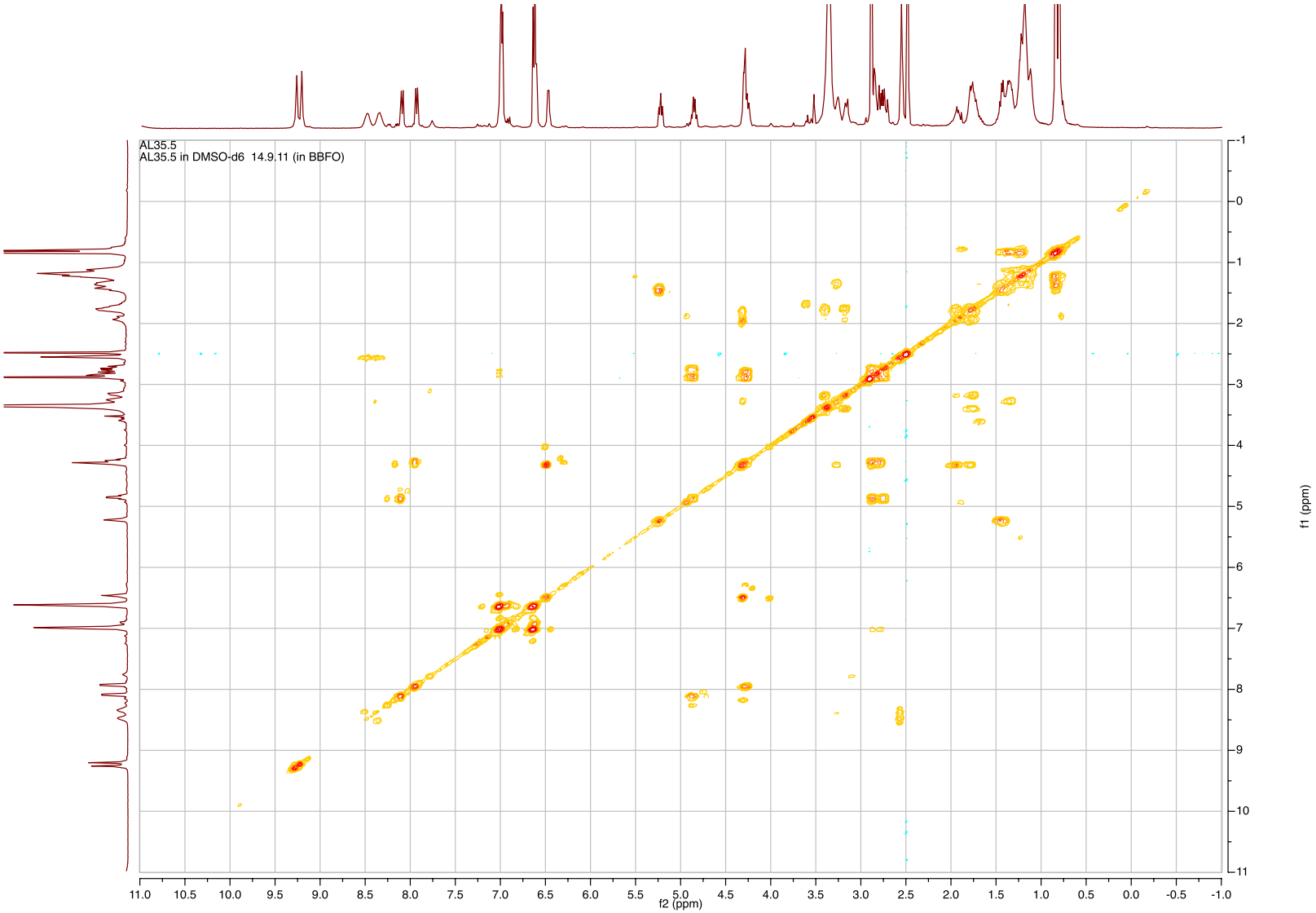
S10. HSQC Spectrum Microginin KR767 (**1**) in DMSO-$d_6$



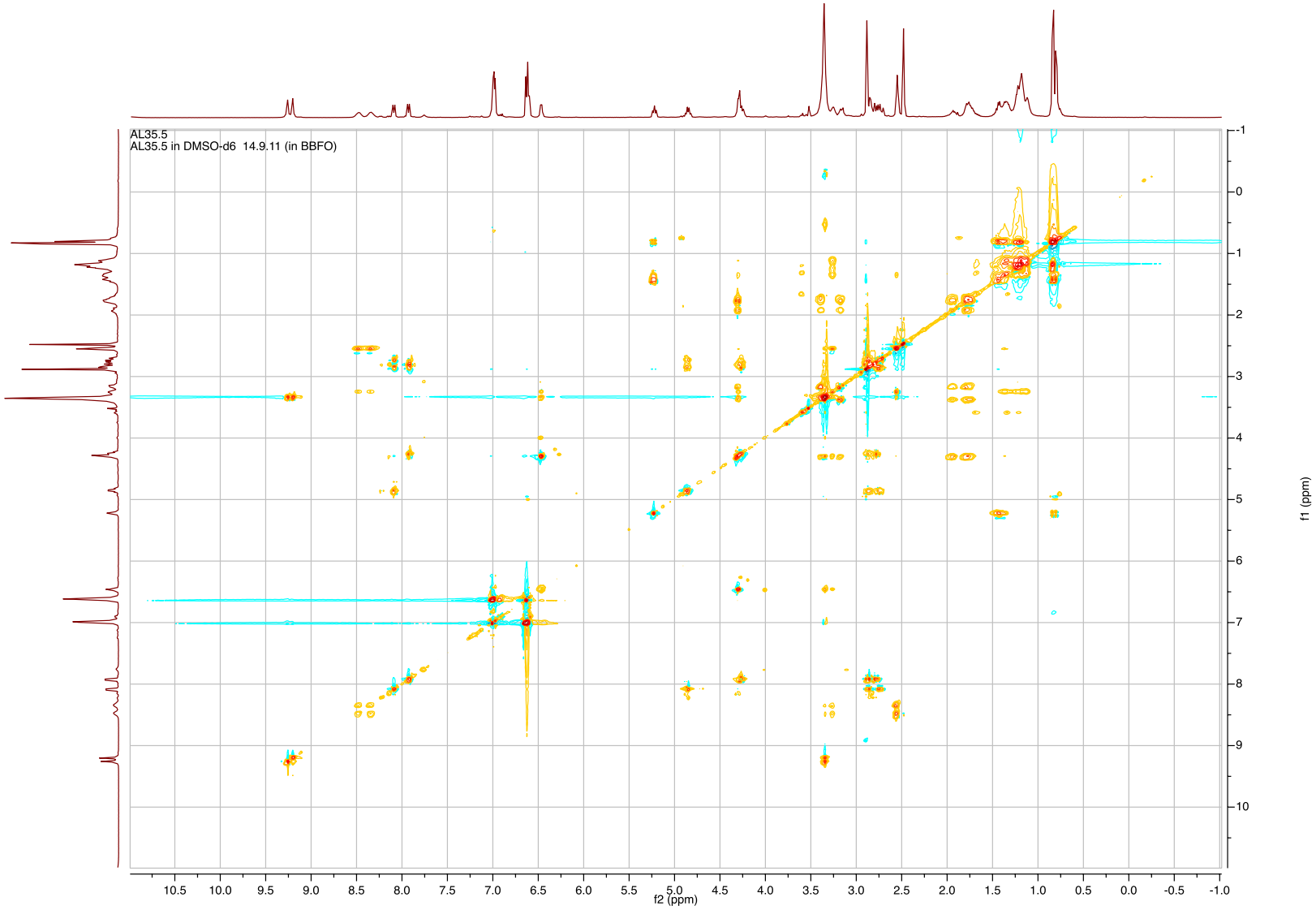
S11. HMBC Spectrum of Microginin KR767 (**1**) in DMSO-$d_6$



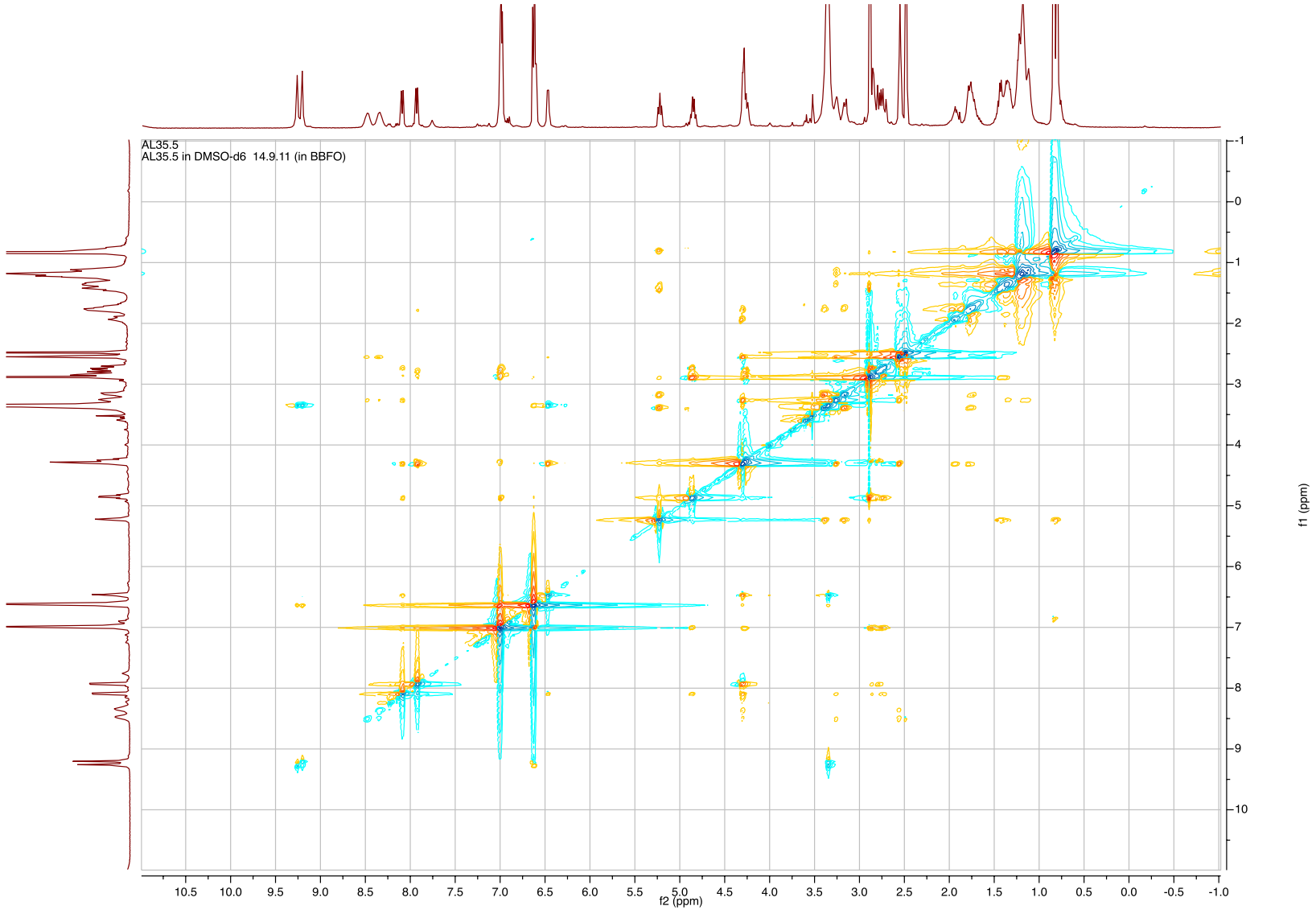
S12. COSY Spectrum of Microginin KR767 (**1**) in DMSO-$d_6$



S13. TOCSY Spectrum of Microginin KR767 (**1**) in DMSO-$d_6$



S14. ROESY Spectrum of Microginin KR767 (**1**) in DMSO-$d_6$



S15. HR ESI MS data of Microginin KR767 (**1**)

**Elemental Composition Report** 

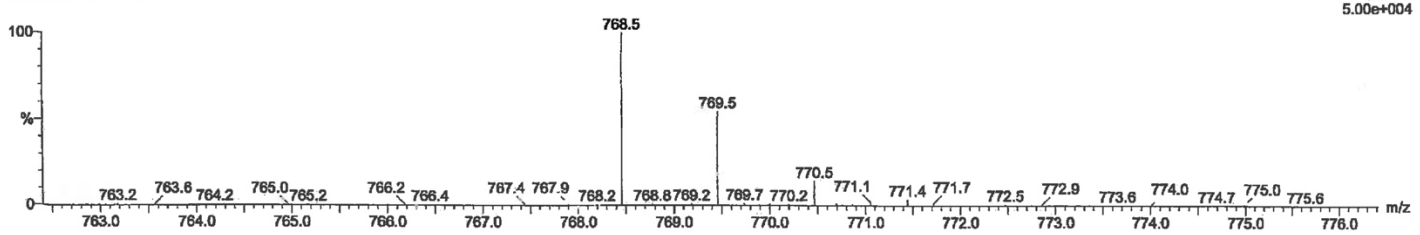
**Single Mass Analysis**
Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
309 formula(e) evaluated with 3 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 35-45 H: 55-65 N: 0-10 O: 5-15 Cl: 0-3

AL35.5
carmeli684 40 (1.770)

Anat Iodin

1: TOF MS ES+
5.00e+004



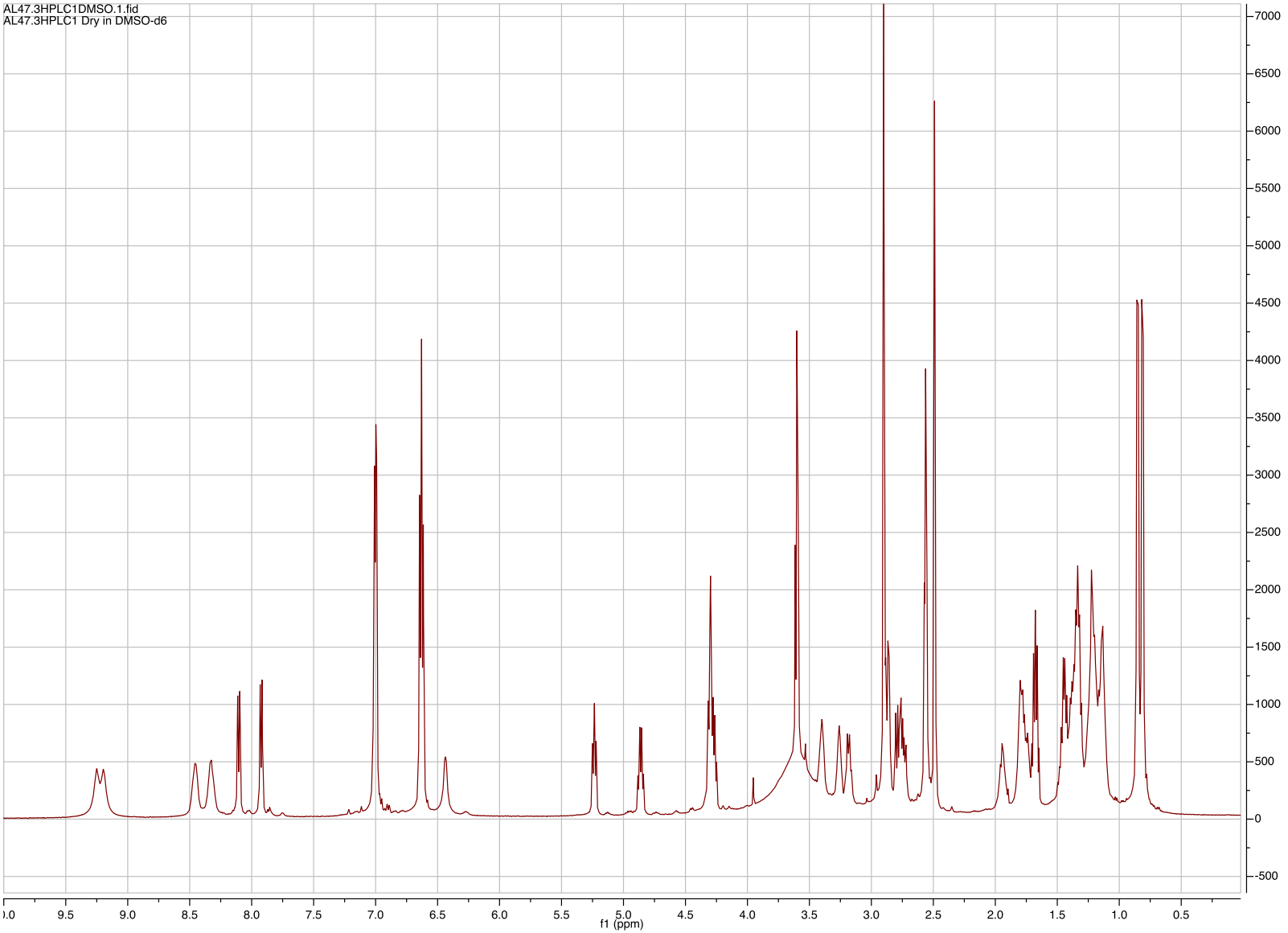

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | |
| Maximum: | | 10.0 | 2.0 | 50.0 | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
| 768.4551 | 768.4548 | 0.3 | 0.4 | 13.5 | 62.0 | 1.2 | C41 H62 N5 O9 ← |
| | 768.4561 | -1.0 | -1.3 | 18.5 | 61.2 | 0.4 | C42 H58 N9 O5 |
| | 768.4539 | 1.2 | 1.6 | 9.5 | 64.4 | 3.6 | C36 H63 N9 O7 Cl |

S16. **Table S3**. NMR Data (500/125 MHz) of Microginin KR801 (**2**) in DMSO-$d_6$.

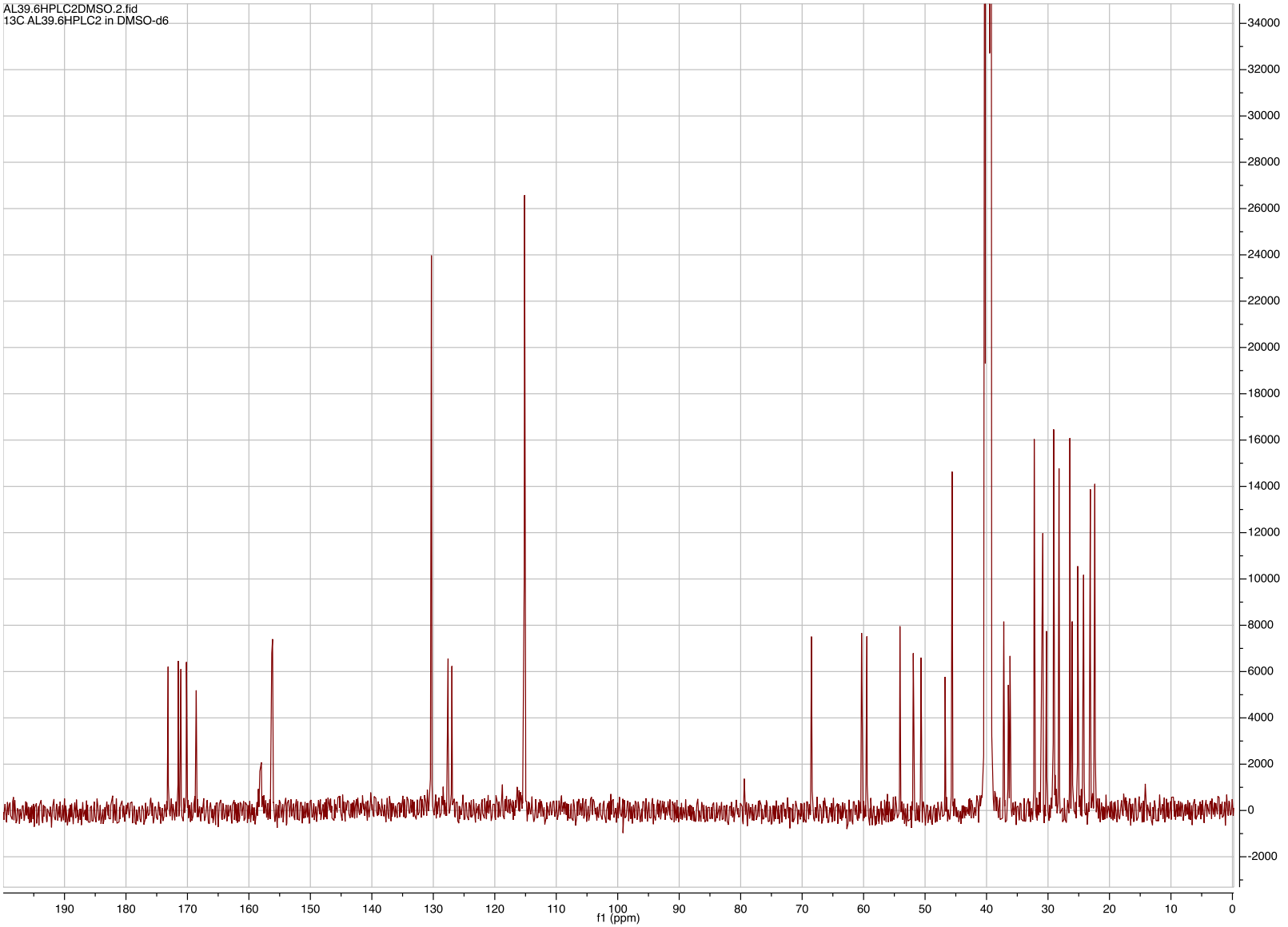
| Position | $\delta_C$ | $\delta_H$ Multiplicity, *J* (Hz) | HMBC correlations | COSY correlations | NOESY correlations |
|---|---|---|---|---|---|
| Ahda 1 | 170.1 C | | Ahda-2, $^1$Tyr-2,NH | | |
| 2 | 68.4 CH | 4.30 brs | Ahda-2-OH | Ahda-2-OH,3 | Ahda-2-OH,3,3-$NH_2$,$NCH_3$,4,4',5',5', $^1$Tyr-NH |
| 2-OH | | 6.47 d, 5.6 | | Ahda-2 | Ahda-2,3,3-$NCH_3$,4,4'5, $^1$Tyr-NH |
| 3 | 60.3 CH | 3.27 brm | Ahda-2,4',3-$NCH_3$ | Ahda-2,3-$NH_2$,4,4' | Ahda-2,2-OH,3-$NH_2$,$NCH_3$,4,4',5',5', $^1$Tyr-NH |
| 3-$NH_2$ | | 8.36 brs | | Ahda-3,3-NH',3-$NCH_3$ | Ahda-2,3,3-$NCH_3$ |
| | | 8.49 brs | | Ahda-3,3-NH',3-$NCH_3$ | Ahda-2,3,3-$NCH_3$ |
| 3-$NCH_3$ | 30.8 $CH_3$ | 2.56 brt, 4.8 | | Ahda-3-$NH_2$ | Ahda-2,2-OH,3,3-$NH_2$, 4,4' |
| 4 | 26.0 $CH_2$ | 1.39 m | | Ahda-3,4',5,5' | Adha-2,3,2-OH |
| | | 1.32 m | | Ahda-3,4,5,5' | Adha-2,3,2-OH |
| 5 | 25.1 $CH_2$ | 1.23 m | Ahda-4,4',6,7 | Ahda-4,4',5',6 | Adha-2,3,2-OH |
| | | 1.11 m | | Ahda-4,4',5,6 | Adha-2,3 |
| 6 | 29.0 $CH_2$ | 1.13 m | Ahda-5,8 | Ahda-7 | |
| 7 | 28.2 $CH_2$ | 1.18 m | Ahda-8,9 | Ahda-6,8 | |
| 8 | 26.3 $CH_2$ | 1.33 m | Ahda-7,9,10 | Ahda-7,9 | |
| 9 | 32.2 $CH_2$ | 1.68 tt, 7.3,6.6 | Ahda-8,10 | Ahda-8,10 | |
| 10 | 45.4 $CH_2$ | 3.60 t, 6.6 | Ahda-8,9 | Ahda-9 | |
| $^1$Tyr 1 | 171.0 C | | $^1$Tyr-2,3,3', *N*MeLeu-2, $NCH_3$ | | |
| 2 | 50.6 CH | 4.86 ddd, 8.5,7.7,6.2 | $^1$Tyr-3,3',NH | $^1$Tyr-2-NH,3,3' | $^1$Tyr-2-NH,3,3',5,5', *N*MeLeu-*N*Me |
| 2-NH | | 8.09 d, 8.5 | | $^1$Tyr-2 | $^1$Tyr-2,3,3',5,5', Ahda-2,2-OH,3 |
| 3 | 36.4 $CH_2$ | 2.86 m | $^1$Tyr-2,5,5',NH | $^1$Tyr-2,3' | $^1$Tyr-2,3',5,5',NH |
| | | 2.74 m | | $^1$Tyr-2,3 | $^1$Tyr-2,3,5,5',NH |
| 4 | 126.9 C | | $^1$Tyr-2,3,3',6,6' | | |
| 5,5' | 130.3 CH | 7.00 d, 8.1 | $^1$Tyr-3,3',5',5,6,6' | $^1$Tyr-6,6' | $^1$Tyr-2,3,3',6,6' |
| 6,6' | 115.1 CH | 6.62 d, 8.1 | $^1$Tyr-5,5',6',6 | $^1$Tyr-5,5' | $^1$Tyr-5,5',7-OH |

| | | | | | |
|---|---|---|---|---|---|
| 7 | 156.2 C | | $^{1}$Tyr-5,5',6,6' | | |
| 7-OH | | 9.26 s | | | $^{1}$Tyr-6,6' |
| *N*MeLeu 1 | 168.5 C | | *N*MeLeu-2,3,3' | | |
| 2 | 51.9 CH | 5.23 dd, 8.0,6.4 | *N*MeLeu-3,3',4,*N*Me | *N*MeLeu-3,3' | *N*MeLeu-3,3',4,5,6,*N*Me, Pro-5,5' |
| 2-*N*$CH_3$ | 30.2 $CH_3$ | 2.90 s | *N*MeLeu-2 | | *N*MeLeu-2,3,3',4 |
| 3 | 37.1 $CH_2$ | 1.45 m | *N*MeLeu-2,4,5,6 | *N*MeLeu-2,3',4 | *N*MeLeu-2,5,6,*N*Me Pro-5 |
| | | 1.42 m | | *N*MeLeu-2,3,4 | *N*MeLeu-2,5,6,*N*Me, Pro-5 |
| 4 | 24.3 CH | 1.35 m | *N*MeLeu-2,3,3',5,6 | *N*MeLeu-3,3',5,6 | *N*MeLeu-*N*Me |
| 5 | 22.3 $CH_3$ | 0.81 d, 6.3 | *N*MeLeu-3,3',4,6 | *N*MeLeu-4 | *N*MeLeu-2,3,3' |
| 6 | 23.1 $CH_3$ | 0.85 d, 6.4 | *N*MeLeu-3,3',4,5 | *N*MeLeu-4 | *N*MeLeu-2,3,3' |
| Pro 1 | 171.5 C | | Pro-2,3,3', $^{2}$Tyr-NH | | |
| 2 | 59.4 CH | 4.31 m | Pro-3,3',4,4' | Pro-3,3' | Pro-3,3' |
| 3 | 29.1 $CH_2$ | 1.95 m | Pro-2,4,5' | Pro-2,3',4,4',5,5' | Pro-2,4' |
| | | 1.79 m | | Pro-2,3,4,4' | Pro-2 |
| 4 | 24.2 $CH_2$ | 1.76 m | Pro-2,3,3',5' | Pro-3,3',5,5' | Pro-2 |
| | | 1.73 m | | Pro-3,3',5,5' | Pro-3 |
| 5 | 46.7 $CH_2$ | 3.40 m | Pro-2,3',4,4' | Pro-3,4,4',5' | Pro-3,5', *N*MeLeu-2,3,3' |
| | | 3.18 dt, 9.0, 7.8 | | Pro-3,4,4',5 | Pro-3,4,4',5, *N*MeLeu-2,*N*Me |
| $^{2}$Tyr 1 | 173.1 C | | $^{2}$Tyr-2,3,3' | | |
| 2 | 54.0 CH | 4.27 td, 7.6,5.6 | $^{2}$Tyr-3,3',NH | $^{2}$Tyr-3,3',NH | $^{2}$Tyr-3,3',5,5',NH |
| 2-NH | | 7.92 d, 7.6 | | $^{2}$Tyr-2 | $^{2}$Tyr-2,3,3', Pro-2,3' |
| 3 | 36.1 $CH_2$ | 2.86 m | $^{2}$Tyr-2,5,5',NH | $^{2}$Tyr-2,3' | $^{2}$Tyr-2,3',5,5',NH |
| | | 2.78 m | | $^{2}$Tyr-2,3 | $^{2}$Tyr-2,3,5,5',NH |
| 4 | 127.5 C | | $^{2}$Tyr-2,3,3',6,6' | | |
| 5,5' | 130.3 CH | 7.01 d, 8.3 | $^{2}$Tyr-3,3',5',5,6,6' | $^{2}$Tyr-6,6' | $^{2}$Tyr-2,3,3',6,6',NH |
| 6,6' | 115.1 CH | 6.64 d, 8.3 | $^{2}$Tyr-5,5',6',6 | $^{2}$Tyr-5,5' | $^{2}$Tyr-5,5',7-OH |
| 7 | 156.1 C | | $^{2}$Tyr-5,5',6,6' | | |
| 7-OH | | 9.21 s | | | $^{2}$Tyr-6,6' |

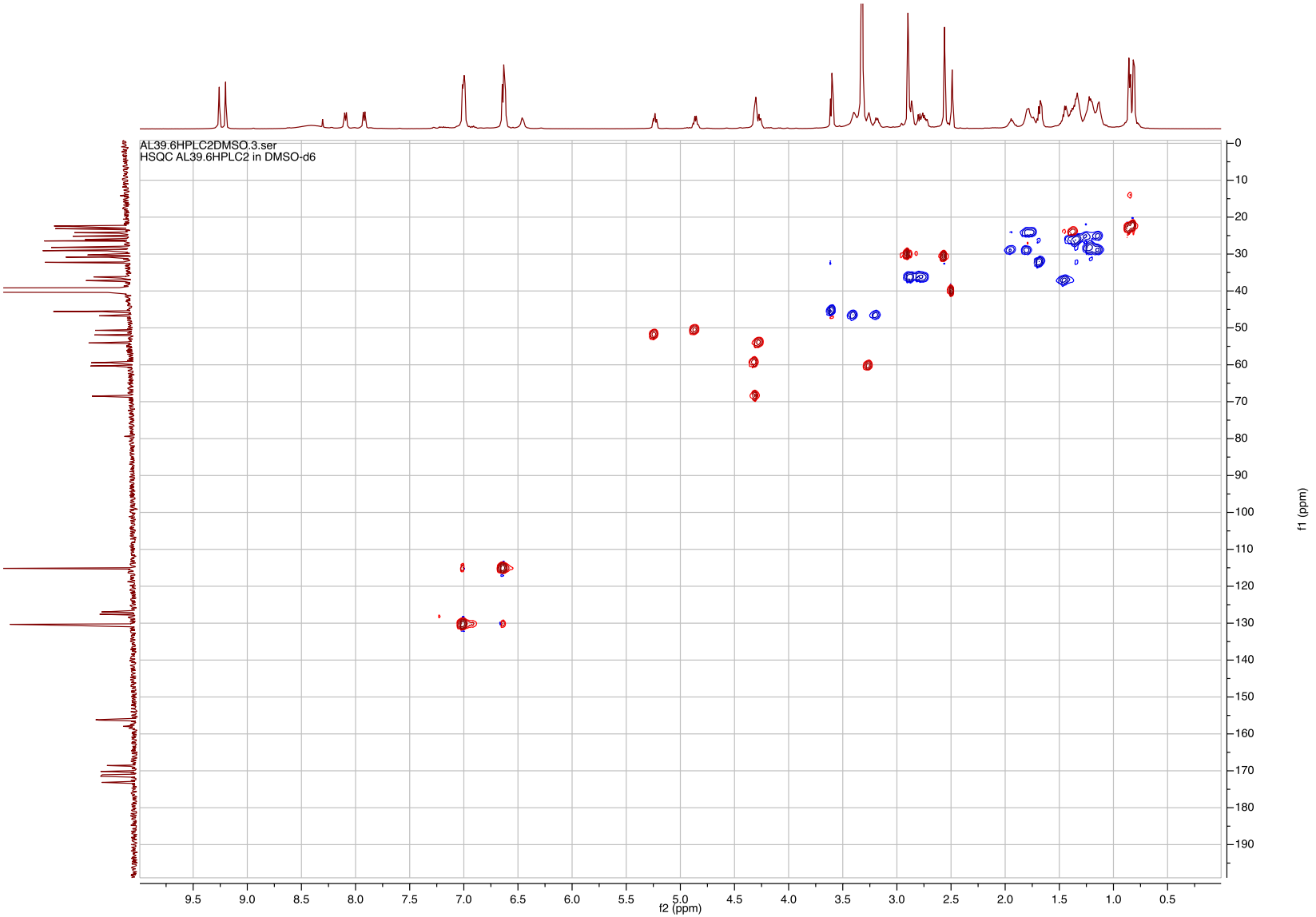
S18. $^{1}$H NMR Spectrum of Microginin KR801 (**2**) in DMSO-$d_6$



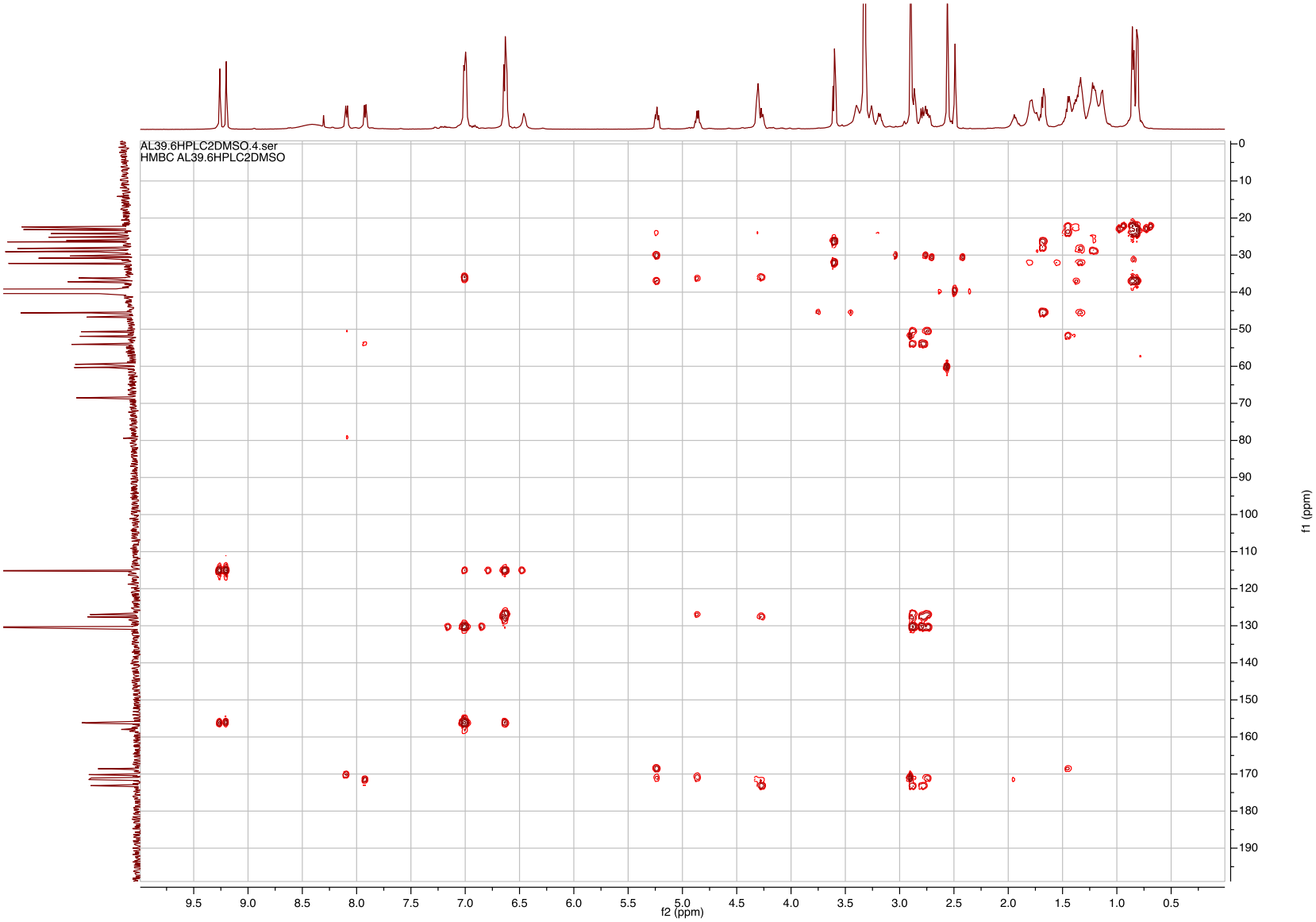
S19. $^{13}C$ NMR Spectrum of Microginin KR801 (**2**) in DMSO-$d_6$



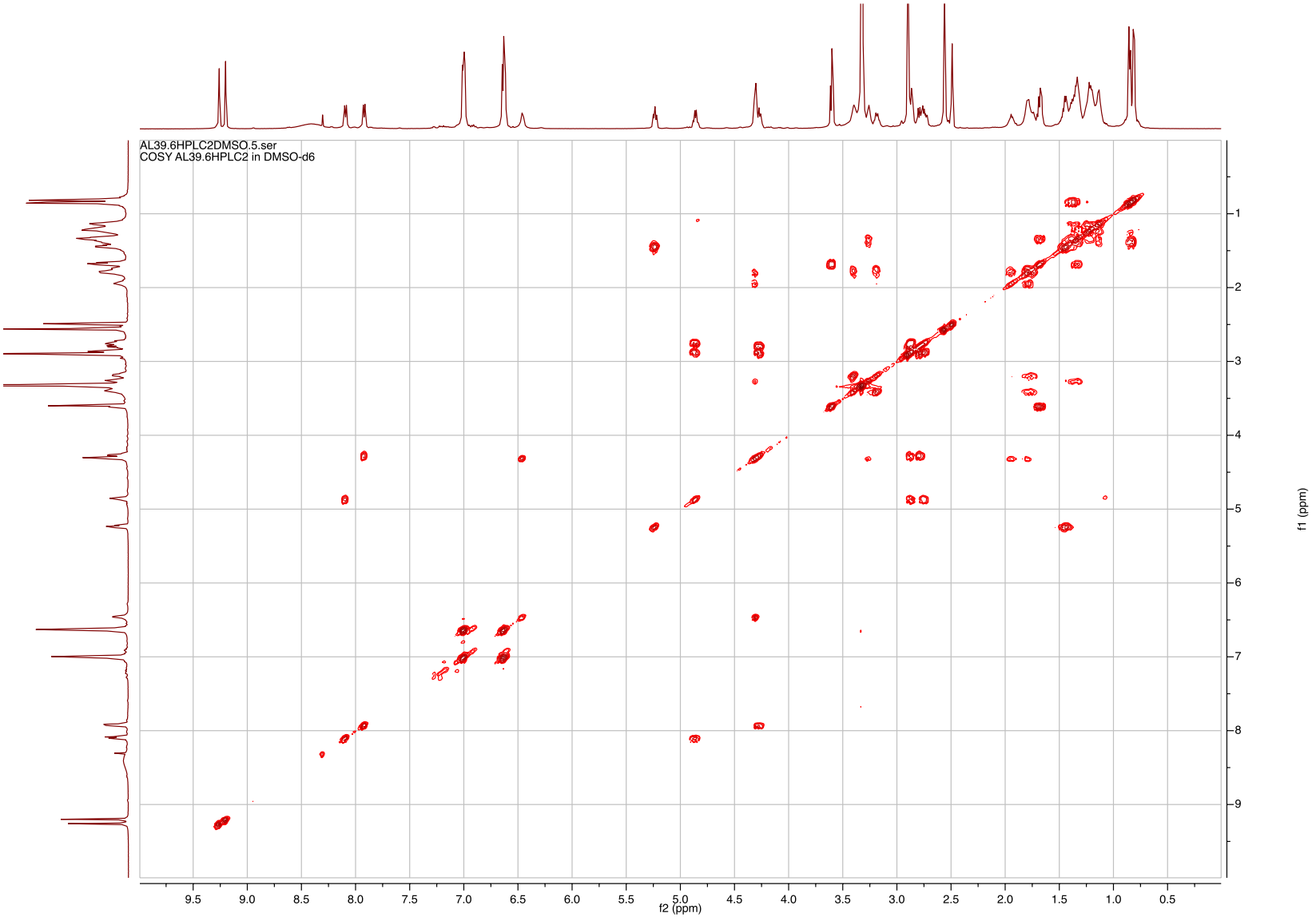
S20. HSQC Spectrum Microginin KR801 (**2**) in DMSO-$d_6$



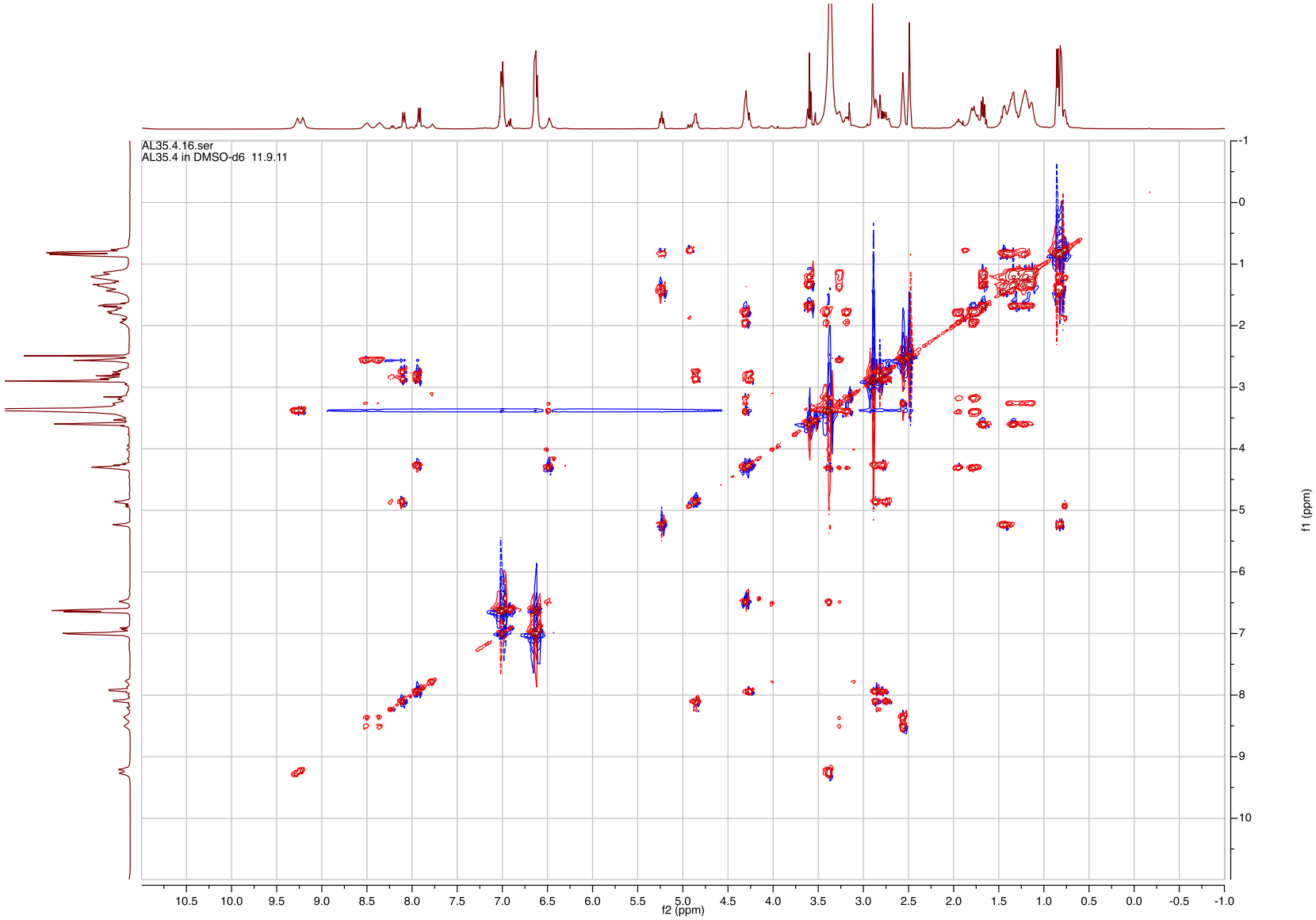
S21. HMBC Spectrum of Microginin KR801 (**2**) in DMSO-$d_6$



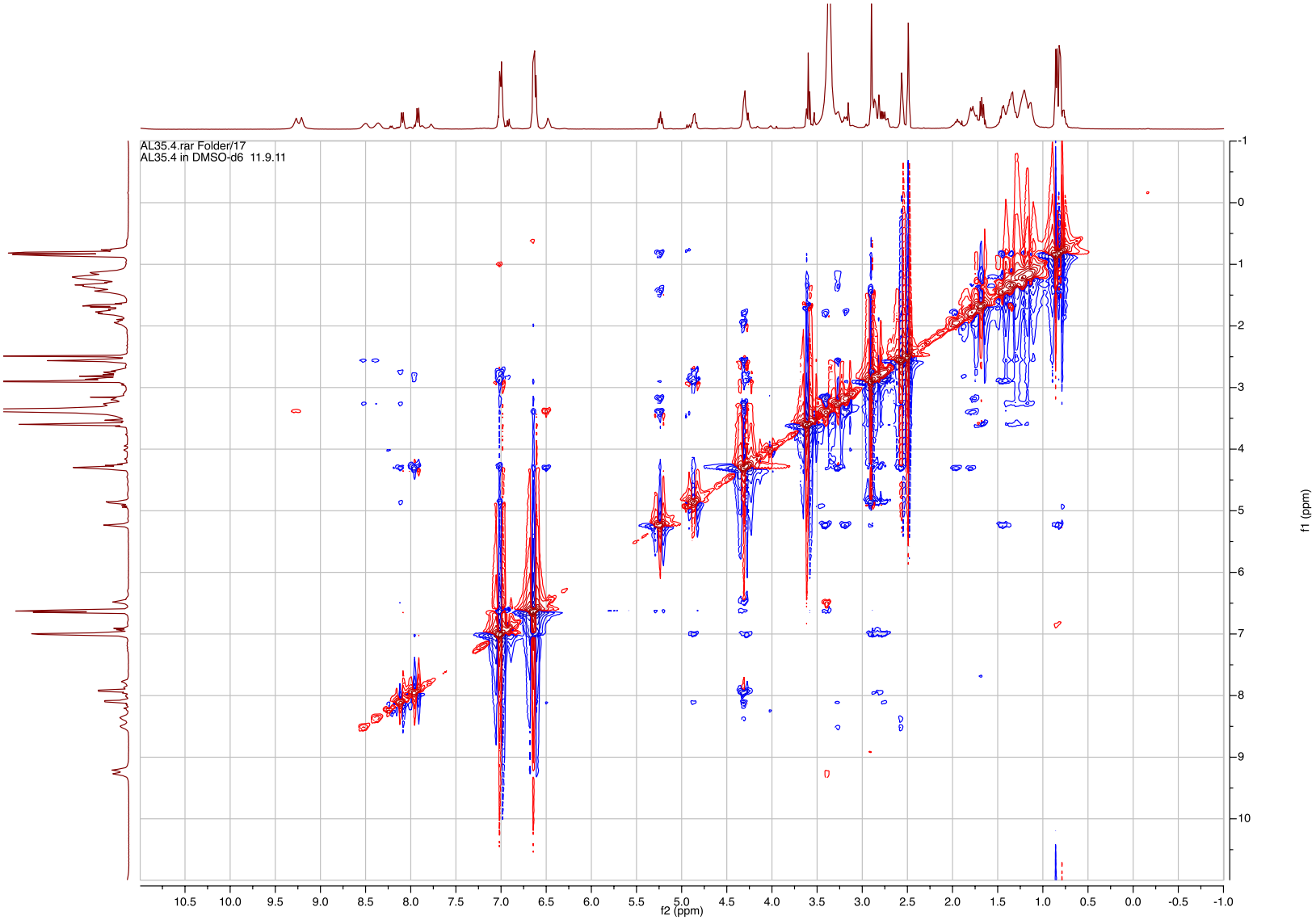
S22. COSY Spectrum of Microginin KR801 (**2**) in DMSO-$d_6$



S23. TOCSY Spectrum of Microginin KR801 (**2**) in DMSO-$d_6$



S24. ROESY Spectrum of Microginin KR801 (**2**) in DMSO-$d_6$



S25. HR ESI MS data of Microginin KR801 (**2**)

**Elemental Composition Report** Page 1

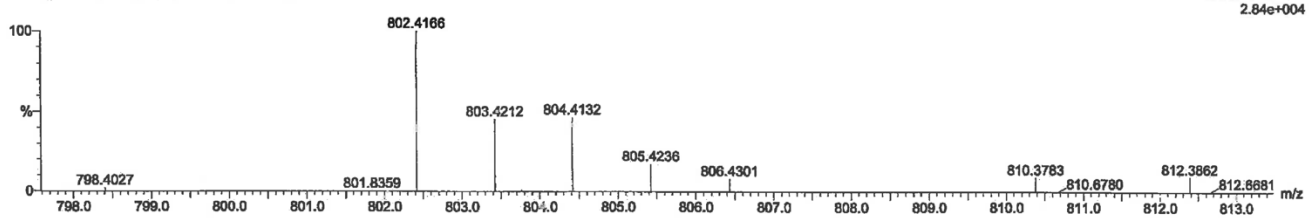
**Single Mass Analysis**
Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
299 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 35-45 H: 55-65 N: 0-10 O: 5-15 Cl: 0-3

AL35.4
carmeli683 39 (1.736) Cm (38:39-5:21x10.000)

Anat Iodin

1: TOF MS ES+
2.84e+004



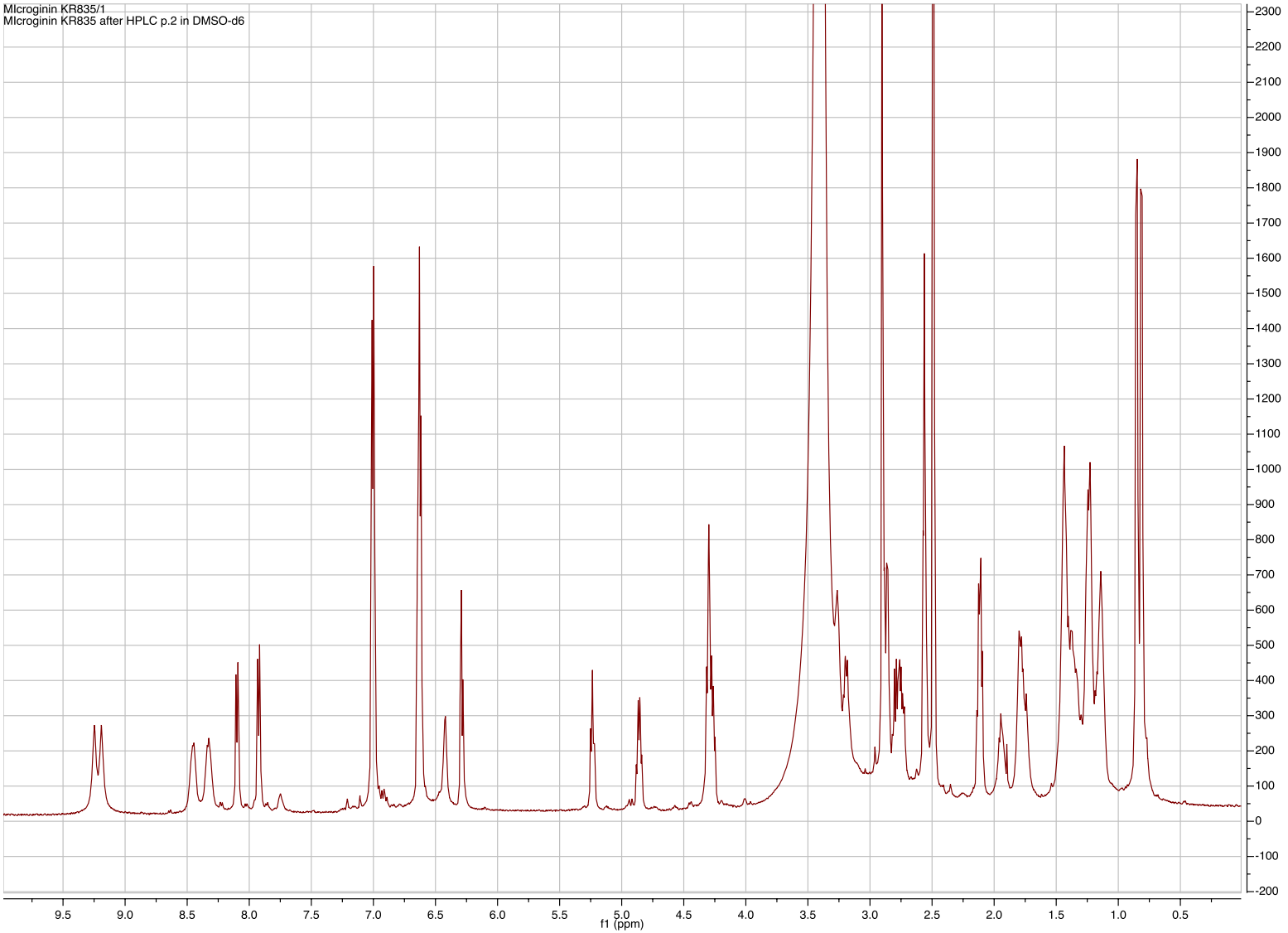

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | |
| Maximum: | | 10.0 | 2.0 | 50.0 | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
| 802.4166 | 802.4171 | -0.5 | -0.6 | 18.5 | 35.8 | 1.1 | C42 H57 N9 O5 Cl |
| | 802.4158 | 0.8 | 1.0 | 13.5 | 35.1 | 0.4 | C41 H61 N5 O9 Cl |

S26. **Table S4**. NMR Data (500/125 MHz) of Microginin KR835 (**3**) in DMSO-$d_6$

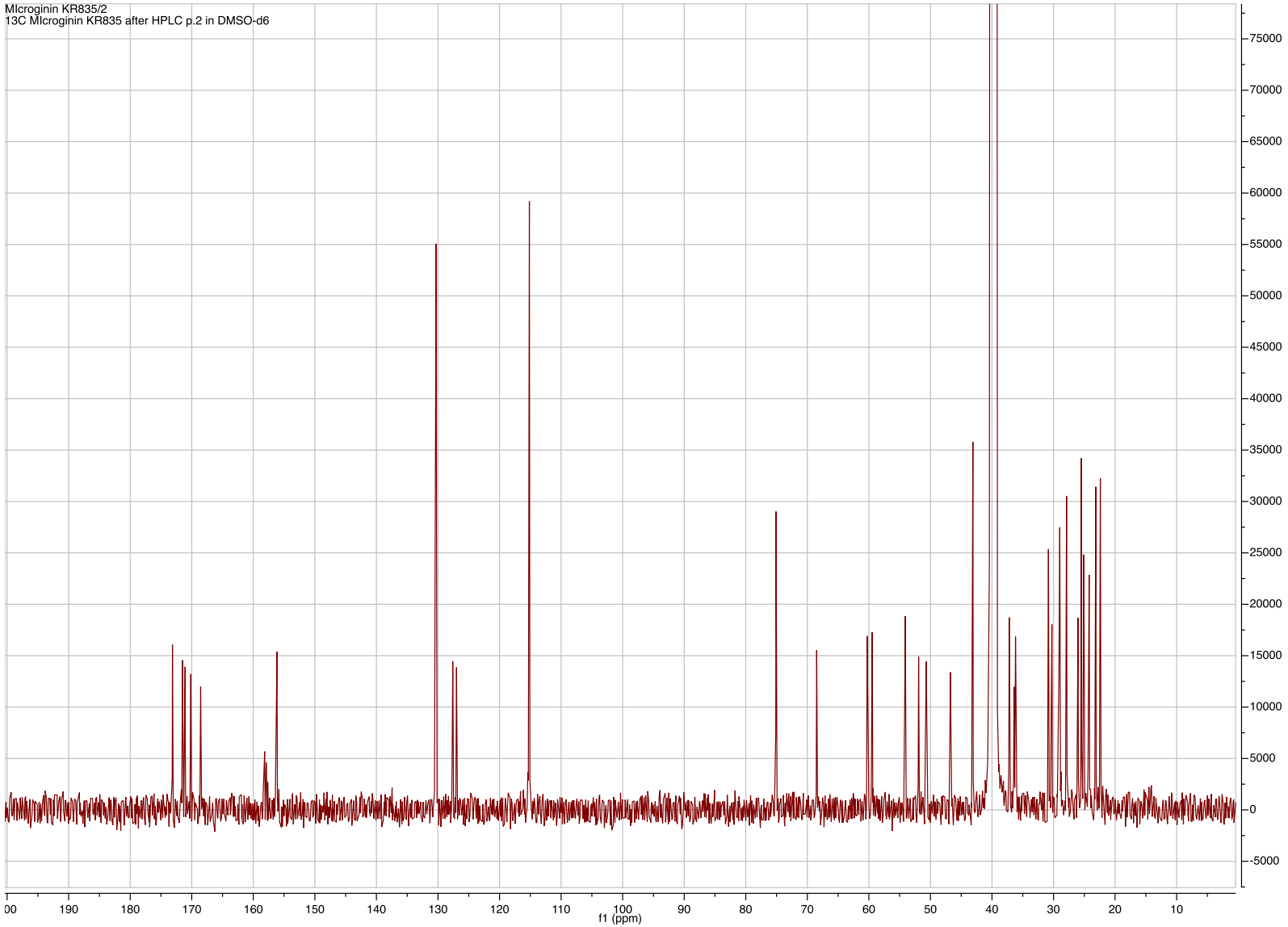
| Position | $\delta_C$ | $\delta_H$ Multiplicity, *J* (Hz) | HMBC correlations | COSY correlations | NOESY correlations |
|---|---|---|---|---|---|
| Ahda 1 | 170.1 C | | Ahda-2,2-OH, $^1$Tyr-2,NH | | |
| 2 | 68.5 CH | 4.30 brd, 5.6 | Ahda-2-OH | Ahda-2-OH,3 | Ahda-2-OH,3,3-$NH_2$, *N*$CH_3$,4,4',5',5', $^1$Tyr-NH |
| 2-OH | | 6.46 d, 6.0 | | Ahda-2 | Ahda-2,3,3-*N*$CH_3$,4,6, $^1$Tyr-NH |
| 3 | 60.2 CH | 3.27 brm | Ahda-2,2-OH,3-*N*$CH_3$ | Ahda-2,3-$NH_2$,4,4' | Ahda-2,2-OH,3-$NH_2$, *N*$CH_3$,4,4',5',5' |
| 3-$NH_2$ | | 8.35 brs | | Ahda-3,3-NH',3-*N*$CH_3$ | Ahda-2,3,3-*N*$CH_3$ |
| | | 8.48 brs | | Ahda-3,3-NH',3-*N*$CH_3$ | Ahda-2,3,3-*N*$CH_3$ |
| 3-*N*$CH_3$ | 30.8 $CH_3$ | 2.56 brt, 4.7 | | Ahda-3-$NH_2$ | Ahda-2,2-OH,3,3-$NH_2$, 4,4' |
| 4 | 26.0 $CH_2$ | 1.40 m | Ahda-2 | Ahda-3,4',5,5' | Adha-2,3 |
| | | 1.33 m | | Ahda-3,4,5,5' | Adha-2,3 |
| 5 | 25.0 $CH_2$ | 1.24 m | Ahda-4,4',6,6' | Ahda-4,4',5',6,6' | Adha-2,3 |
| | | 1.14 m | | Ahda-4,4',5,6,6' | Adha-2,3 |
| 6 | 28.9 $CH_2$ | 1.22 m | Ahda-5,7,8 | | |
| | | 1.15 m | | | |
| 7 | 27.8 $CH_2$ | 1.24 m | Ahda-8,9 | | |
| 8 | 25.4 $CH_2$ | 1.43 m | Ahda-9,10 | Ahda-7,9 | |
| 9 | 43.0 $CH_2$ | 2.12 td, 7.3,5.9 | Ahda-7,8,10 | Ahda-8,10 | |
| 10 | 75.0 CH | 6.29 t, 5.9 | Ahda-8,9 | Ahda-9 | |
| $^1$Tyr 1 | 171.0 C | | $^1$Tyr-2,3,3', *N*MeLeu-2, *N*$CH_3$ | | |
| 2 | 50.6 CH | 4.86 ddd, 8.0,7.7,6.4 | $^1$Tyr-3,3',NH | $^1$Tyr-2-NH,3,3' | $^1$Tyr-2-NH,3,3',5,5' |
| 2-NH | | 8.09 d, 8.0 | | $^1$Tyr-2 | $^1$Tyr-2,3,3', Ahda-2,2-OH,3 |
| 3 | 36.4 $CH_2$ | 2.86 m | $^1$Tyr-2,5,5',NH | $^1$Tyr-2,3' | $^1$Tyr-2,3',5,5',NH |
| | | 2.74 m | | $^1$Tyr-2,3 | $^1$Tyr-2,3,5,5',NH |
| 4 | 126.9 C | | $^1$Tyr-2,3,3',6,6' | | |
| 5,5' | 130.3 CH | 7.00 d, 8.3 | $^1$Tyr-3,3',5',5,6,6' | $^1$Tyr-6,6' | $^1$Tyr-2,3,3',6,6' |
| 6,6' | 115.1 CH | 6.62 d, 8.3 | $^1$Tyr-5,5',6',6,7-OH | $^1$Tyr-5,5' | $^1$Tyr-5,5',7-OH |

| | | | | | |
|---|---|---|---|---|---|
| 7 | 156.2 C | | $^{1}$Tyr-5,5',6,6',7-OH | | |
| 7-OH | | 9.26 s | | | $^{1}$Tyr-6,6' |
| *N*MeLeu 1 | 168.5 C | | *N*MeLeu-2,3,3' | | |
| 2 | 51.9 CH | 5.23 dd, 8.2,6.6 | *N*MeLeu-3,3',4,*N*Me | *N*MeLeu-3,3' | *N*MeLeu-3,3',5,6,*N*Me, Pro-5 |
| 2-*N*$CH_3$ | 30.2 $CH_3$ | 2.90 s | *N*MeLeu-2 | | *N*MeLeu-2,3,3', $^{2}$Tyr-2,3 |
| 3 | 37.2 $CH_2$ | 1.46 m | *N*MeLeu-2,4,5,6 | *N*MeLeu-2,3',4 | *N*MeLeu-2,5,6,*N*Me |
| | | 1.42 m | | *N*MeLeu-2,3,4 | *N*MeLeu-2,5,6,*N*Me |
| 4 | 24.2 CH | 1.37 m | *N*MeLeu-2,3,3',5,6 | *N*MeLeu-3,3',5,6 | *N*MeLeu-5,6 |
| 5 | 22.4 $CH_3$ | 0.81 d, 6.2 | *N*MeLeu-3,3',4,6 | *N*MeLeu-4 | *N*MeLeu-2,3,3',4,6 |
| 6 | 23.1 $CH_3$ | 0.85 d, 6.3 | *N*MeLeu-3,3',4,5 | *N*MeLeu-4 | *N*MeLeu-2,3,3',4,5 |
| Pro 1 | 171.5 C | | Pro-2,3,3', $^{2}$Tyr-NH | | |
| 2 | 59.4 CH | 4.32 dd, 8.5,5.0 | Pro-4' | Pro-3,3' | Pro-3', $^{2}$Tyr-NH |
| 3 | 29.1 $CH_2$ | 1.94 m | Pro-2,4,5' | Pro-2,3',4,4',5' | Pro-2,3',4 |
| | | 1.79 m | | Pro-2,3,4,4' | Pro-2,3,4' |
| 4 | 24.3 $CH_2$ | 1.80 m | Pro-2,3,3',5,5' | Pro-3,3',5,5' | Pro-3,5' |
| | | 1.73 m | | Pro-3,3',5,5' | Pro-3' |
| 5 | 46.7 $CH_2$ | 3.40 m | Pro-2 | Pro-4,4',5' | Pro-4, *N*MeLeu-2, $^{2}$Tyr-7-OH |
| | | 3.19 dt, 9.3,7.3 | | Pro-3,4,4',5 | Pro-2,4,5, *N*MeLeu-2 |
| $^{2}$Tyr 1 | 173.1 C | | $^{2}$Tyr-2,3,3',NH | | |
| 2 | 54.0 CH | 4.26 td, 7.7,5.7 | $^{2}$Tyr-3,3',NH | $^{2}$Tyr-3,3',NH | $^{2}$Tyr-3,5,5',NH |
| 2-NH | | 7.92 d, 7.7 | | $^{2}$Tyr-2 | $^{2}$Tyr-2,3', Pro-2 |
| 3 | 36.1 $CH_2$ | 2.87 m | $^{2}$Tyr-2,5,5',NH | $^{2}$Tyr-2,3' | $^{2}$Tyr-2,3',5,5' |
| | | 2.78 m | | $^{2}$Tyr-2,3 | $^{2}$Tyr-2,3,5,5',NH |
| 4 | 127.6 C | | $^{2}$Tyr-2,3,3',6,6' | | |
| 5,5' | 130.3 CH | 7.01d, 8.0 | $^{2}$Tyr-3,3',5',5,6,6' | $^{2}$Tyr-6,6' | $^{2}$Tyr-2,3,6,6' |
| 6,6' | 115.1 CH | 6.64 d, 8.0 | $^{2}$Tyr-5,5',6',6,7-OH | $^{2}$Tyr-5,5' | $^{2}$Tyr-5,5',7-OH |
| 7 | 156.1 C | | $^{2}$Tyr-5,5',6,6',7-OH | | |
| 7-OH | | 9.20 s | | | $^{2}$Tyr-6,6' |

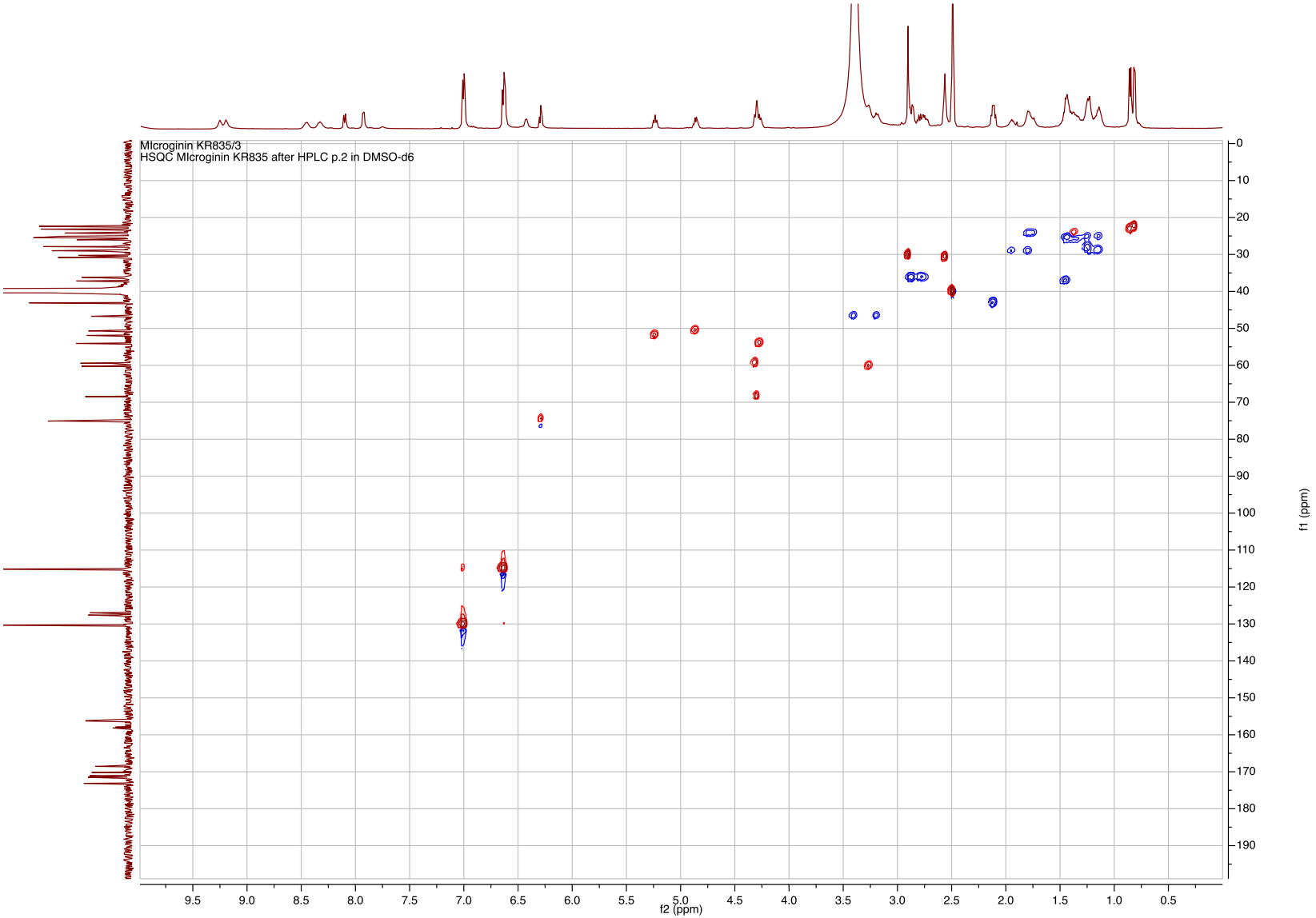
S28. $^{1}$H NMR Spectrum of Microginin KR835 (**3**) in DMSO-$d_6$



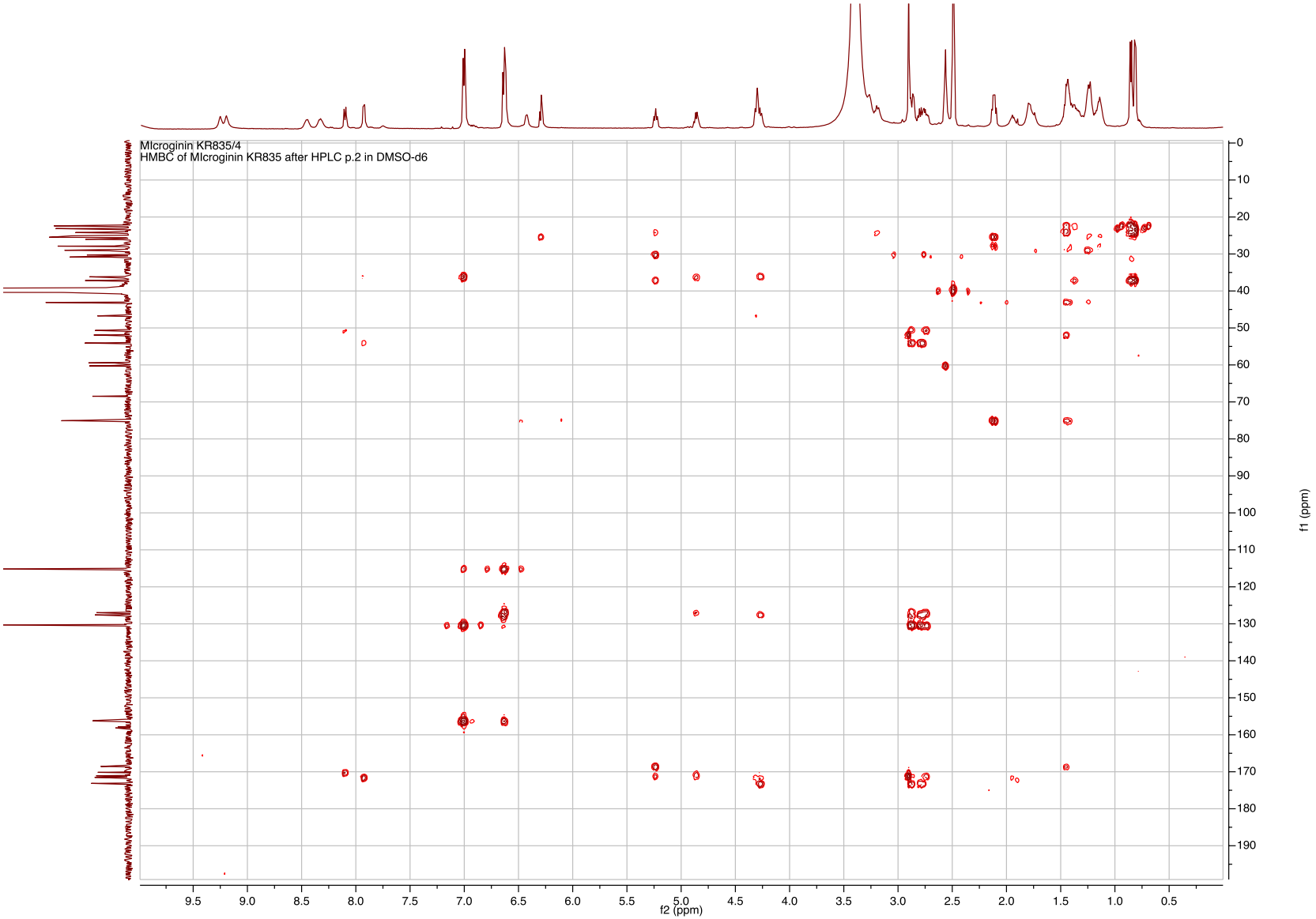
S29. $^{13}$C NMR Spectrum of Microginin KR835 (**3**) in DMSO-$d_6$



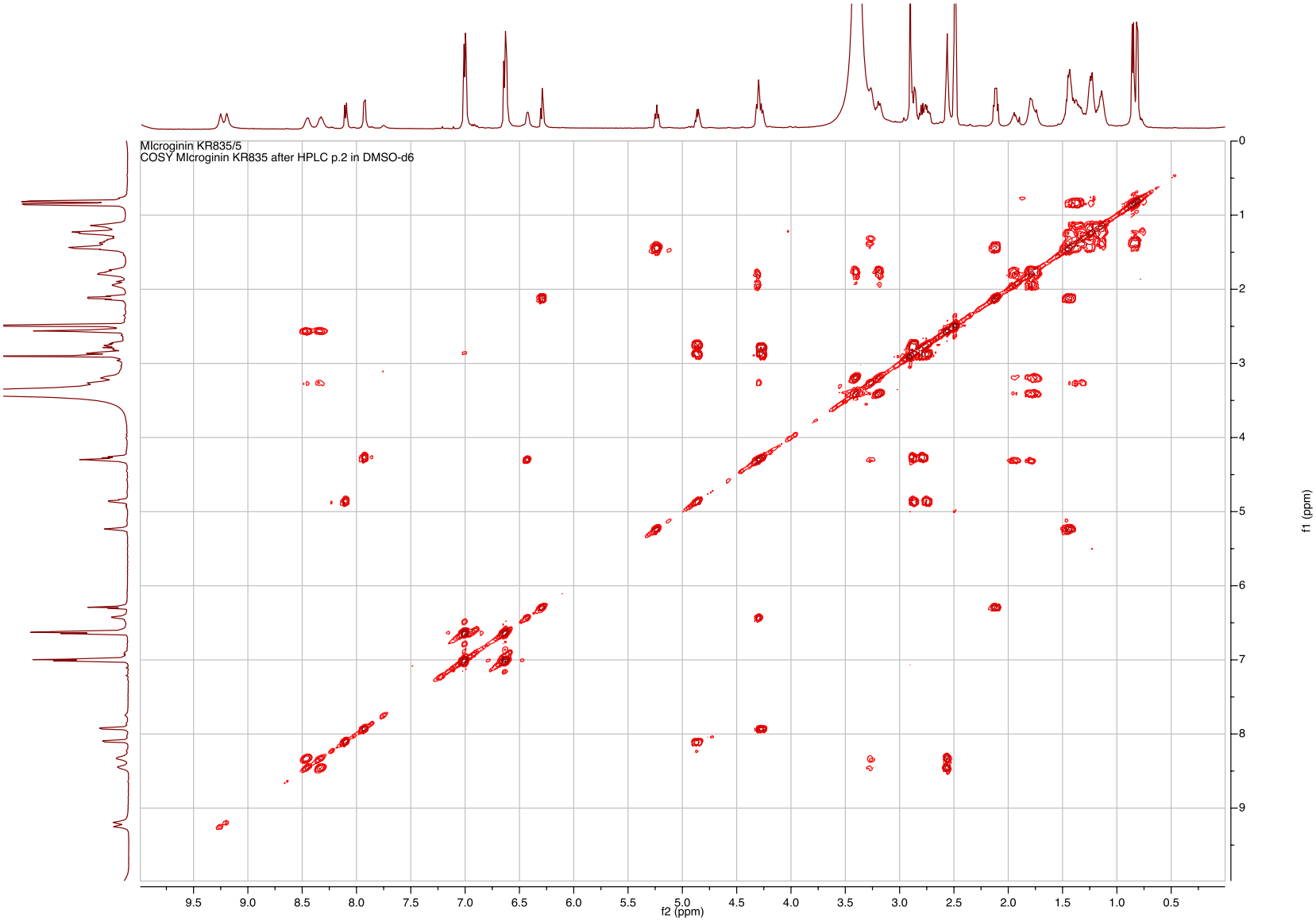
S30. HSQC Spectrum Microginin KR835 (**3**) in DMSO-$d_6$



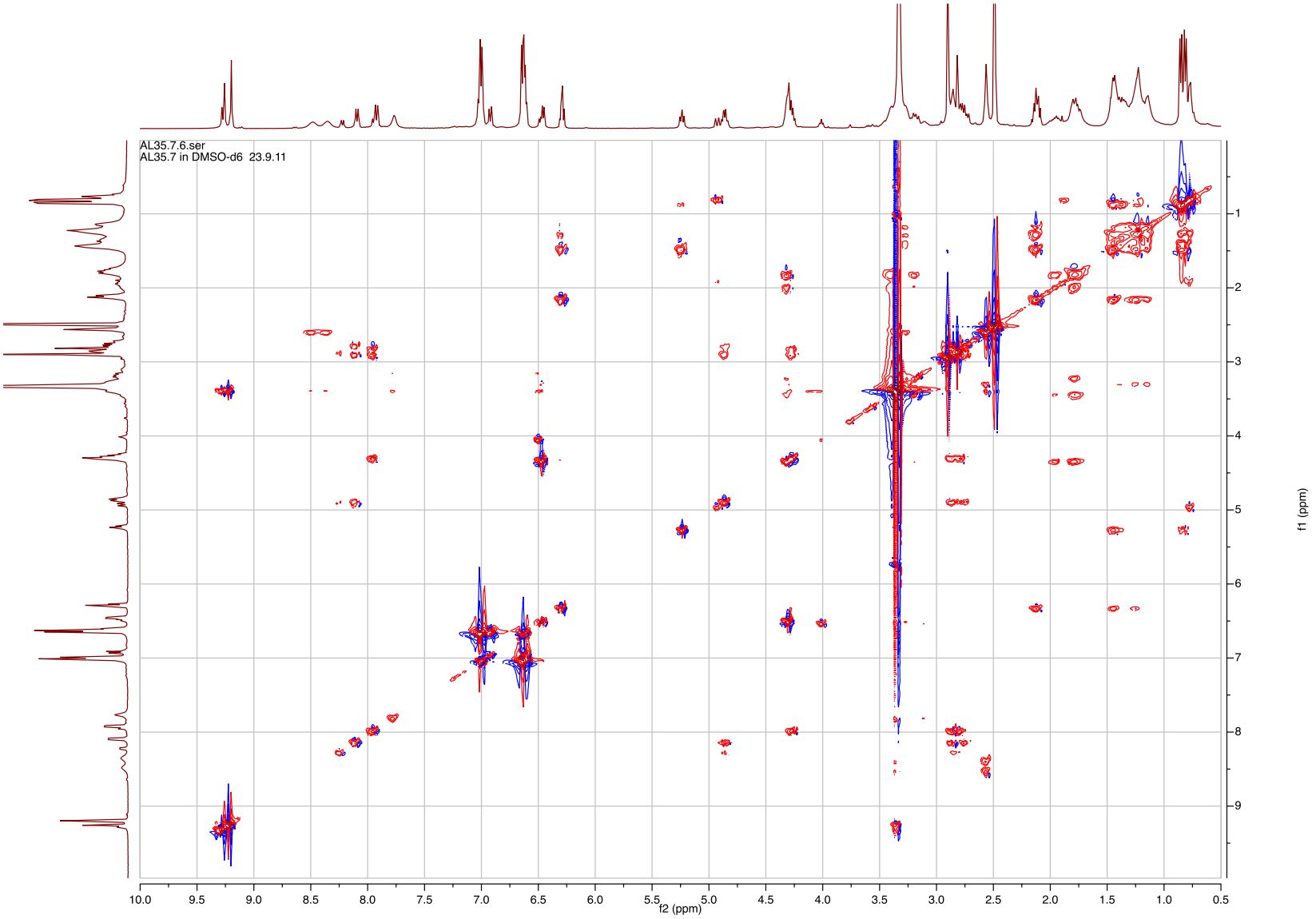
S31. HMBC Spectrum of Microginin KR835 (**3**) in DMSO-$d_6$



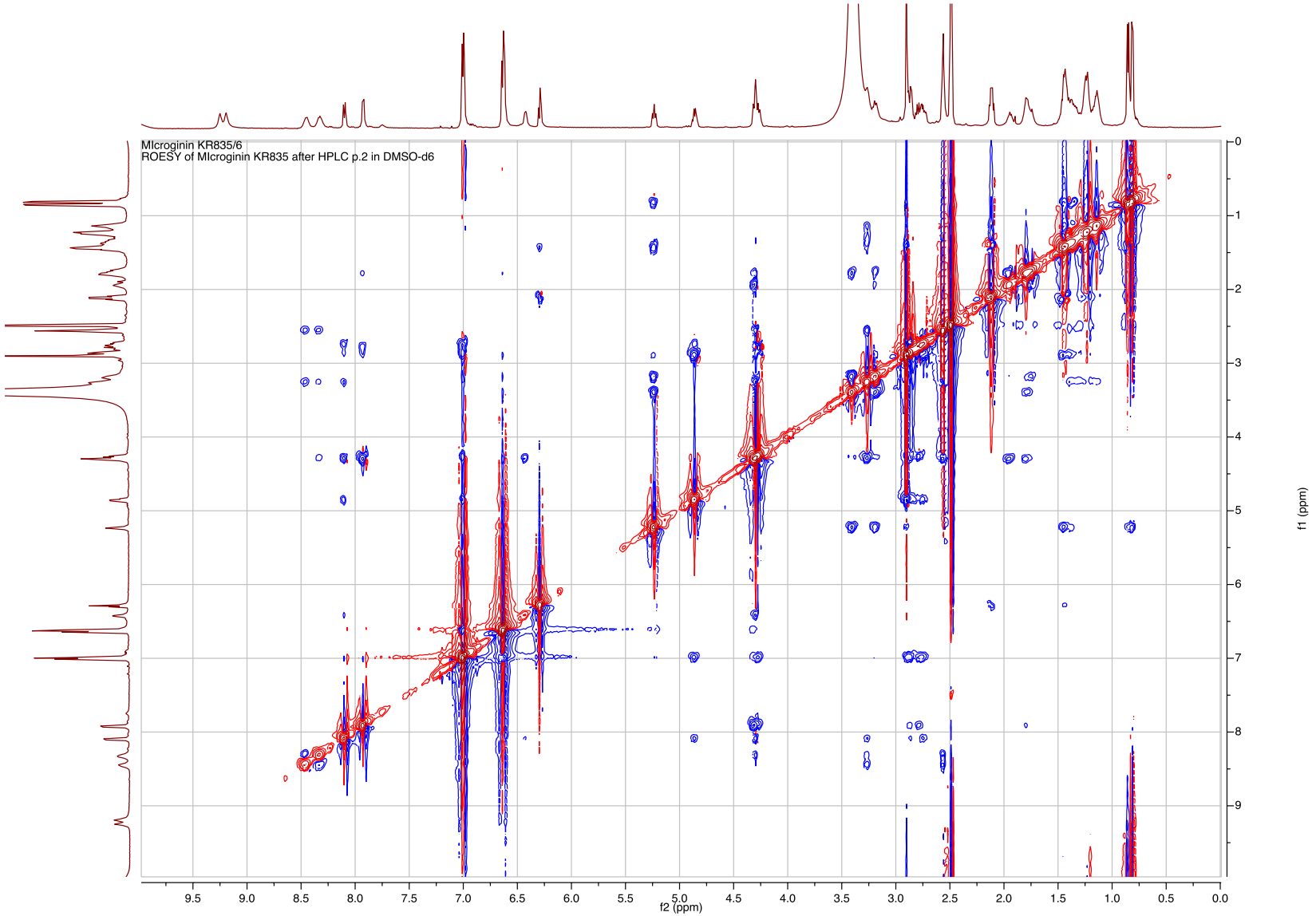
S32. COSY Spectrum of Microginin KR835 (**3**) in DMSO-$d_6$



S33. TOCSY Spectrum of Microginin KR835 (**3**) in DMSO-$d_6$



S34. ROESY Spectrum of Microginin KR835 (**3**) in DMSO-$d_6$



S35. HR ESI MS data of Microginin KR835 (**3**)

**Elemental Composition Report**



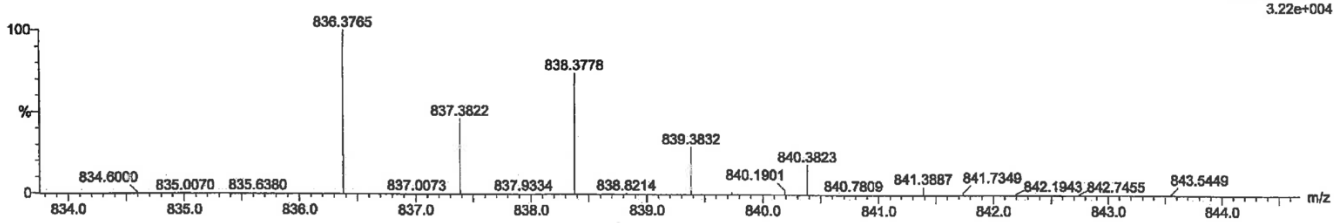
**Single Mass Analysis**
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
446 formula(e) evaluated with 7 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 35-45 H: 55-65 N: 0-10 O: 5-15 Cl: 0-5

AL35.7
carmell682 39 (1.736) Cm (39:52-(70:72+69:72)x10.000)

Anat Iodin

1: TOF MS ES+
3.22e+004



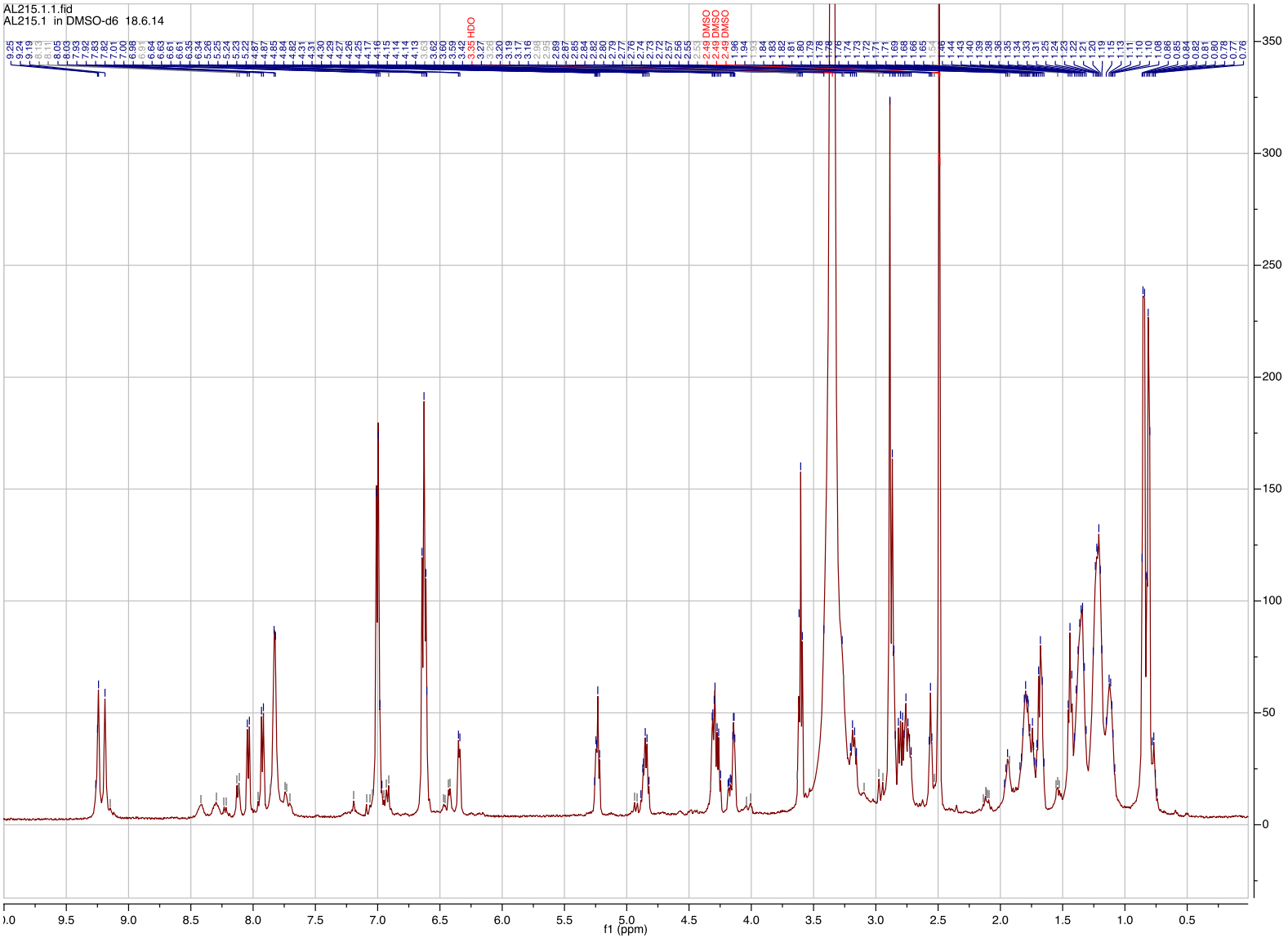

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | |
| Maximum: | | 10.0 | 3.0 | 50.0 | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
| 836.3765 | 836.3768 | -0.3 | -0.4 | 13.5 | 76.8 | 3.8 | C41 H60 N5 O9 Cl2 ← |
| | 836.3760 | 0.5 | 0.6 | 9.5 | 76.6 | 3.6 | C36 H61 N9 O7 Cl3 |
| | 836.3755 | 1.0 | 1.2 | 8.5 | 73.8 | 0.8 | C40 H64 N O13 Cl2 |
| | 836.3750 | 1.5 | 1.8 | 18.5 | 79.6 | 6.6 | C42 H55 N7 O9 Cl |
| | 836.3781 | -1.6 | -1.9 | 18.5 | 78.8 | 5.8 | C42 H56 N9 O5 Cl2 |
| | 836.3746 | 1.9 | 2.3 | 4.5 | 79.9 | 6.9 | C35 H65 N5 O11 Cl3 |
| | 836.3786 | -2.1 | -2.5 | 8.5 | 73.8 | 0.7 | C40 H65 N3 O9 Cl3 |

S36. **Table S5**. NMR Data (500/125 MHz) of Microginin KR787 (**4**) in DMSO-$d_6$

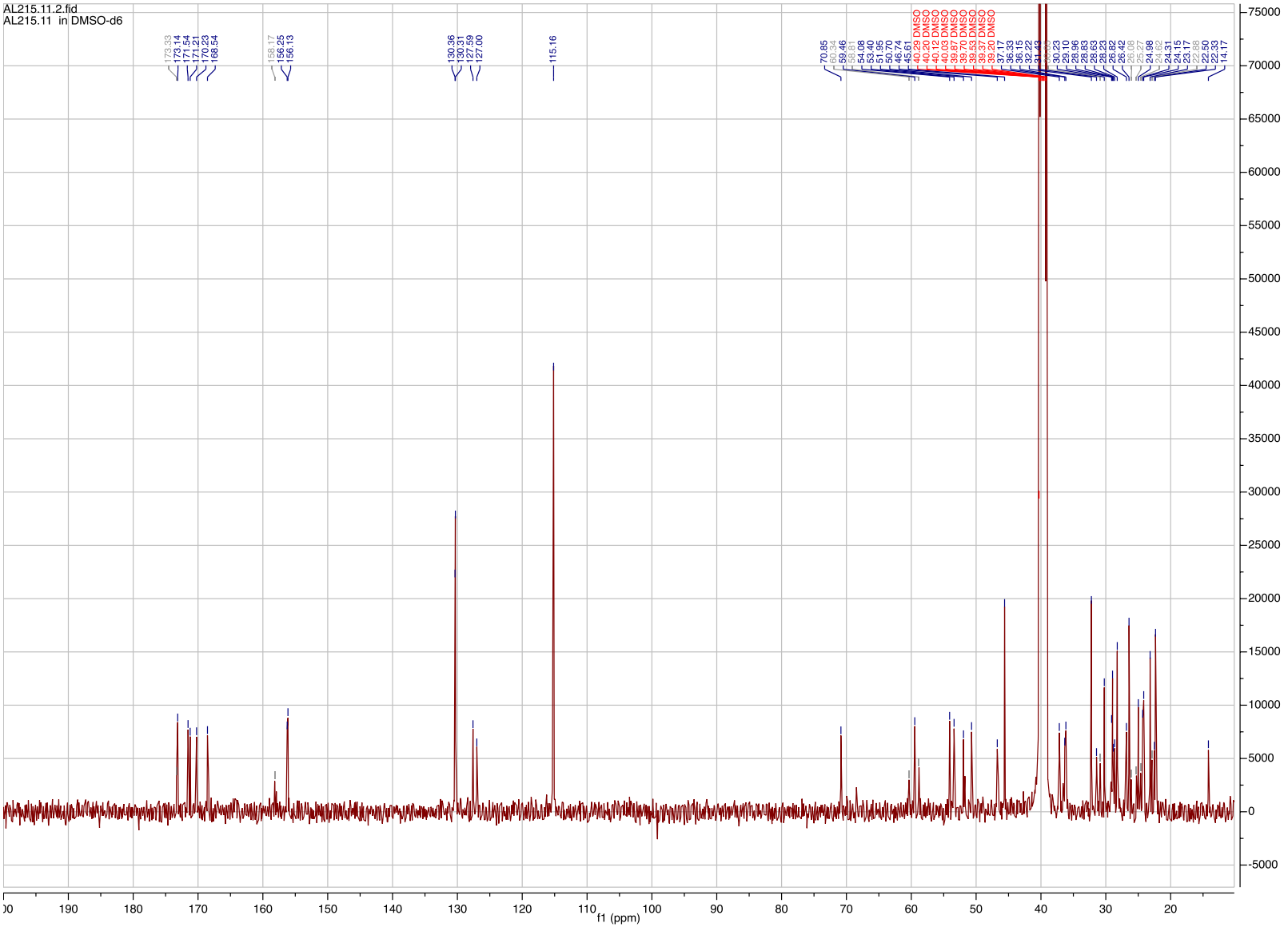
| Position | $\delta_C$ | $\delta_H$ Multiplicity, *J* (Hz) | HMBC correlations | COSY correlations | NOESY correlations |
|---|---|---|---|---|---|
| Ahda 1 | 170.2 C | | $^1$Tyr-NH | | |
| 2 | 70.9 CH | 4.14 dd, 5.4,2.5 | | Ahda-2-OH,3 | Ahda-2-OH,3,3-$NH_2$,4,4',5',5', $^1$Tyr-NH |
| 2-OH | | 6.35 d, 5.4 | | Ahda-2 | Ahda-2, $^1$Tyr-NH |
| 3 | 53.4 CH | 3.27 brm | Ahda-2,$NH_2$ | Ahda-2,3-$NH_2$,4,4' | Ahda-2,3-$NH_2$,4',5,5', $^1$Tyr-NH |
| 3-$NH_2$ | | 7.83 brd, 2.6 | | Ahda-3 | Ahda-2,3 |
| 4 | 26.8 $CH_2$ | 1.37 m | | Ahda-3,4',5,5' | Adha-3 |
| | | 1.22 m | | Ahda-3,4,5,5' | Adha-2,3 |
| 5 | 25.0 $CH_2$ | 1.26 m | | Ahda-4,4',5',6 | Adha-2,3 |
| | | 1.12 m | | Ahda-4,4',5,6 | Adha-2,3 |
| 6 | 29.0 $CH_2$ | 1.13 m | Ahda-5,8 | Ahda-7 | |
| 7 | 28.2 $CH_2$ | 1.22 m | Ahda-9 | Ahda-6,8 | |
| 8 | 26.4 $CH_2$ | 1.34 m | Ahda-9,10 | Ahda-7,9 | |
| 9 | 32.2 $CH_2$ | 1.68 tt, 7.6,6.7 | Ahda-8,10 | Ahda-8,10 | Ahda-10 |
| 10 | 45.6 $CH_2$ | 3.60 t, 6.7 | Ahda-8,9 | Ahda-9 | Ahda-7,8,9 |
| $^1$Tyr 1 | 171.2 C | | $^1$Tyr-2,3,3', *N*MeLeu-2, *N*$CH_3$ | | |
| 2 | 50.7 CH | 4.84 ddd, 8.2,7.4,6.2 | $^1$Tyr-3,3' | $^1$Tyr-2-NH,3,3' | $^1$Tyr-2-NH,3,3',5,5', *N*MeLeu-*N*Me |
| 2-NH | | 8.04 d, 8.2 | | $^1$Tyr-2 | $^1$Tyr-2,3,3',5,5', Ahda-2,2-OH,3 |
| 3 | 36.3 $CH_2$ | 2.88 m | $^1$Tyr-2,5,5' | $^1$Tyr-2,3' | $^1$Tyr-2,3',5,5',NH |
| | | 2.74 dd, 13.6,7.9 | | $^1$Tyr-2,3 | $^1$Tyr-2,3,5,5',NH |
| 4 | 127.0 C | | $^1$Tyr-2,3,3',6,6' | | |
| 5,5' | 130.4 CH | 7.00 d, 8.1 | $^1$Tyr-3,3',5',5,6,6' | $^1$Tyr-6,6' | $^1$Tyr-2,3,3',6,6',NH |
| 6,6' | 115.2 CH | 6.62 d, 8.1 | $^1$Tyr-5,5',6',6,7-OH | $^1$Tyr-5,5' | $^1$Tyr-5,5',7-OH |
| 7 | 156.2 C | | $^1$Tyr-5,5',6,6',7-OH | | |
| 7-OH | | 9.24 s | | | $^1$Tyr-6,6' |
| *N*MeLeu 1 | 168.5 C | | *N*MeLeu-2,3,3' | | |
| 2 | 52.0 CH | 5.23 dd, 8.1,6.9 | *N*MeLeu-3,3',4,*N*Me | *N*MeLeu-3,3' | *N*MeLeu-3,3',4,5,6,*N*Me, Pro-5,5' |

| | | | | | |
|---|---|---|---|---|---|
| 2-*N*$CH_3$ | 30.2 $CH_3$ | 2.89 s | *N*MeLeu-2 | | *N*MeLeu-2,3,3’,4, Pro-5’ |
| 3 | 37.2 $CH_2$ | 1.45 m | *N*MeLeu-2,4,5,6 | *N*MeLeu-2,3’,4 | *N*MeLeu-2,5,6,*N*Me |
| | | 1.42 m | | *N*MeLeu-2,3,4 | *N*MeLeu-2,5,6,*N*Me |
| 4 | 24.3 CH | 1.37 m | *N*MeLeu-2,3,3’,5,6 | *N*MeLeu-3,3’,5,6 | *N*MeLeu-*N*Me |
| 5 | 22.3 $CH_3$ | 0.80 d, 6.1 | *N*MeLeu-3,3’,4,6 | *N*MeLeu-4 | *N*MeLeu-2,3,3’ |
| 6 | 23.2 $CH_3$ | 0.85 d, 6.2 | *N*MeLeu-3,3’,4,5 | *N*MeLeu-4 | *N*MeLeu-2,3,3’ |
| Pro 1 | 171.5 C | | Pro-2, $^2$Tyr-NH | | |
| 2 | 59.4 CH | 4.30 m | | Pro-3,3’ | Pro-3,3’, $^2$Tyr-NH |
| 3 | 29.1 $CH_2$ | 1.94 m | Pro-5’ | Pro-2,3’,4,4’,5,5’ | Pro-2,3’ |
| | | 1.81 m | | Pro-2,3,4,4’ | Pro-2,3, $^2$Tyr-NH |
| 4 | 24.1 $CH_2$ | 1.81 m | Pro-2 | Pro-3,3’,5,5’ | Pro-2 |
| | | 1.76 m | | Pro-3,3’,5,5’ | |
| 5 | 46.7 $CH_2$ | 3.40 m | | Pro-3,4,4’,5’ | Pro-3,5, *N*MeLeu-2, |
| | | 3.18 dt, 9.0,7.2 | | Pro-3,4,4’,5 | Pro-3,4,4’, *N*MeLeu-2,*N*Me |
| $^2$Tyr 1 | 173.1 C | | $^2$Tyr-2,3,3’ | | |
| 2 | 54.1 CH | 4.27 td, 7.6,5.9 | $^2$Tyr-3,3’,NH | $^2$Tyr-3,3’,NH | $^2$Tyr-3,3’,5,5’,NH |
| 2-NH | | 7.93 d, 7.6 | | $^2$Tyr-2 | $^2$Tyr-2,3,3’,5,5 Pro-2,3’ |
| 3 | 36.2 $CH_2$ | 2.88 m | $^2$Tyr-2,5,5’ | $^2$Tyr-2,3’ | $^2$Tyr-2,3’,5,5’,NH |
| | | 2.78 dd, 16.7,8.5 | | $^2$Tyr-2,3 | $^2$Tyr-2,3,5,5’,NH |
| 4 | 127.6 C | | $^2$Tyr-2,3,3’,6,6’ | | |
| 5,5’ | 130.3 CH | 7.00 d, 8.3 | $^2$Tyr-3,3’,5’,5,6,6’ | $^2$Tyr-6,6’ | $^2$Tyr-2,3,3’,6,6’,NH |
| 6,6’ | 115.2 CH | 6.64 d, 8.3 | $^2$Tyr-5,5’,6’,6,7-OH | $^2$Tyr-5,5’ | $^2$Tyr-5,5’,7-OH |
| 7 | 156.1 C | | $^2$Tyr-5,5’,6,6’ | | |
| 7-OH | | 9.19 s | | | $^2$Tyr-6,6’ |

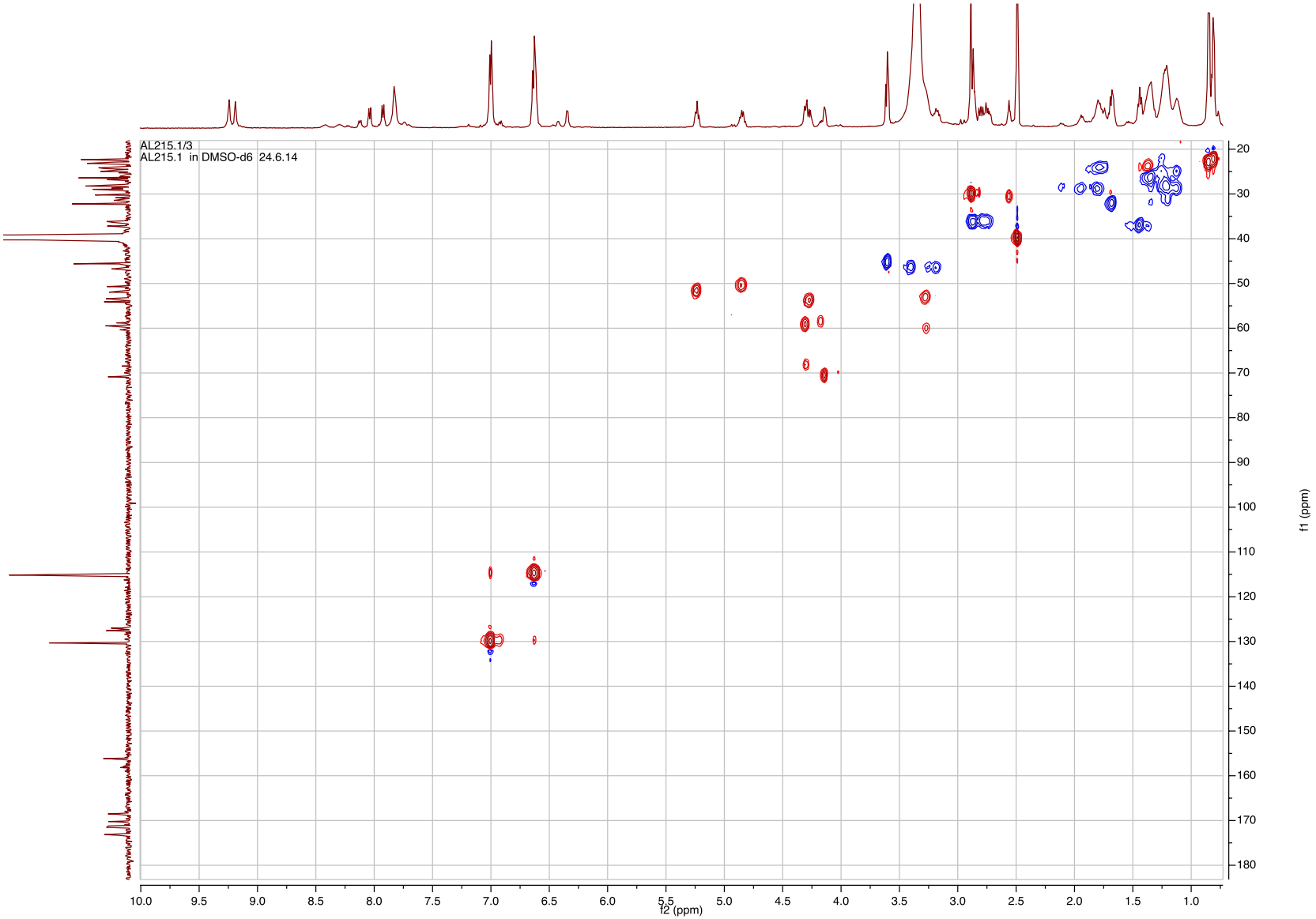
S38. $^{1}$H NMR Spectrum of Microginin KR787 (**4**) in DMSO-$d_6$



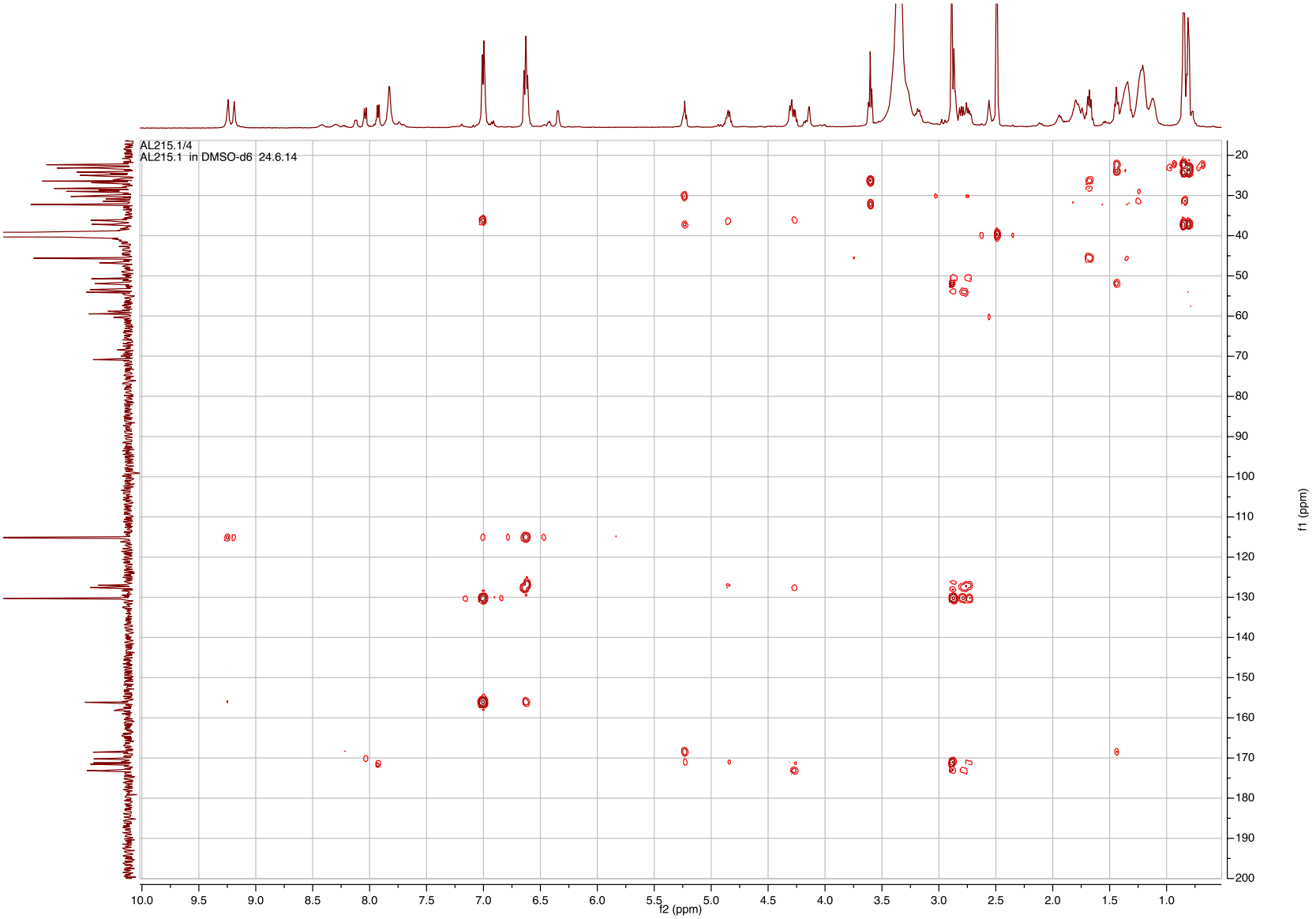
S39. $^{13}$C NMR Spectrum of Microginin KR787 (**4**) in DMSO-$d_6$



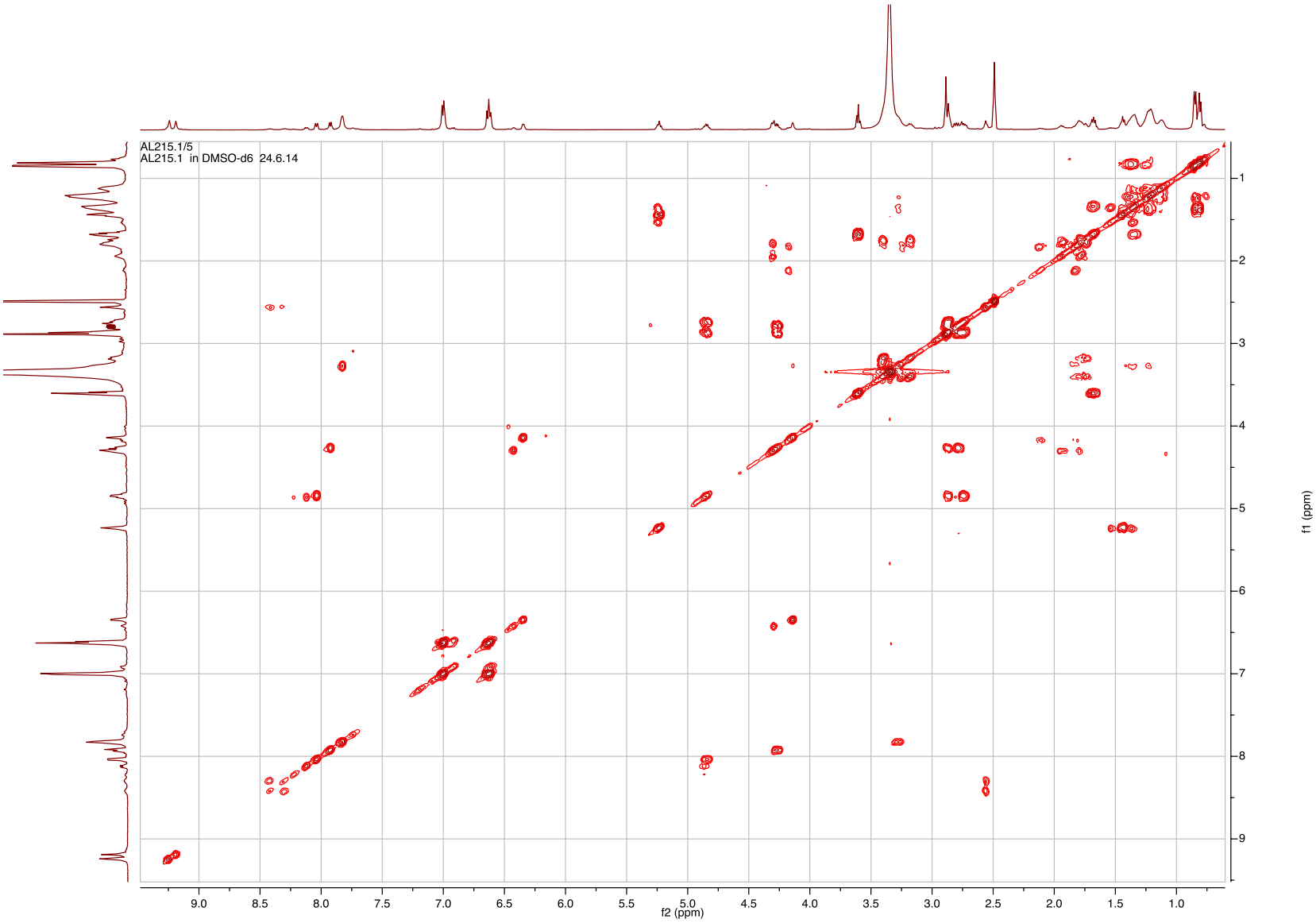
S40. HSQC Spectrum Microginin KR787 (**4**) in DMSO-$d_6$



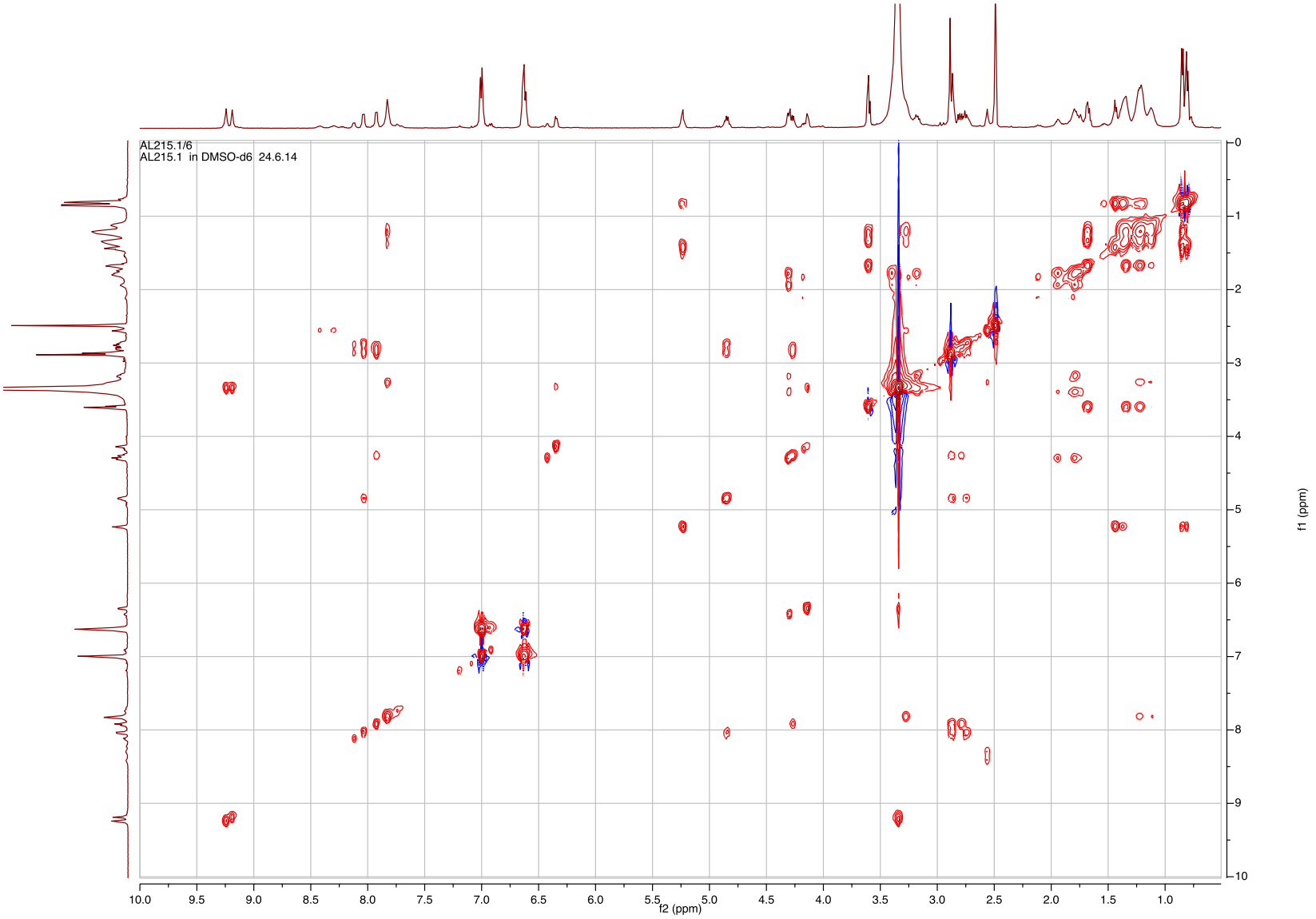
S41. HMBC Spectrum of Microginin KR787 (**4**) in DMSO-$d_6$



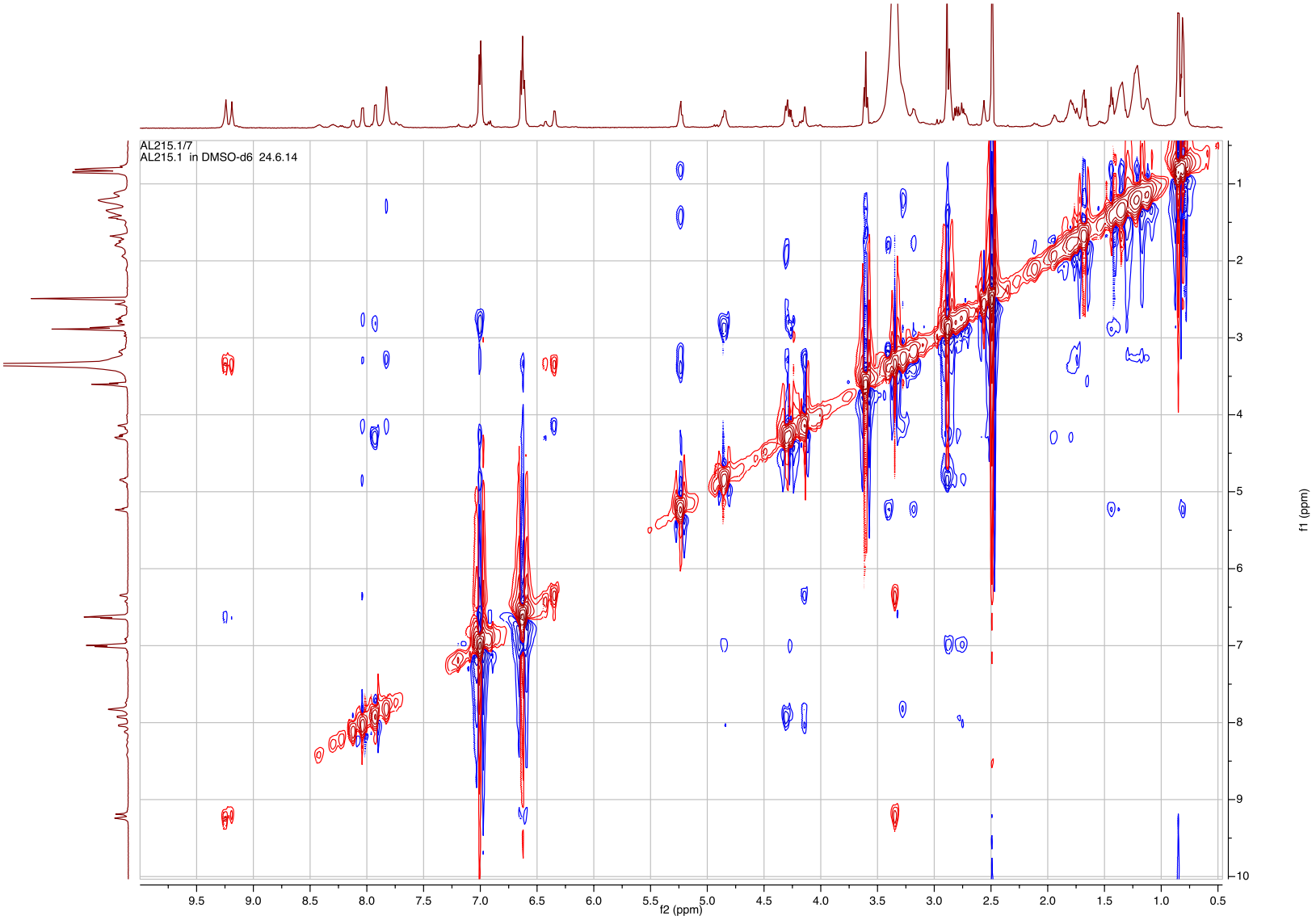
S42. COSY Spectrum of Microginin KR787 (**4**) in DMSO-$d_6$



S43. TOCSY Spectrum of Microginin KR787 (**4**) in DMSO-$d_6$



S44. ROESY Spectrum of Microginin KR787 (**4**) in DMSO-$d_6$



S45. HR ESI MS data of Microginin KR787 (**4**)

**Elemental Composition Report** Page 1

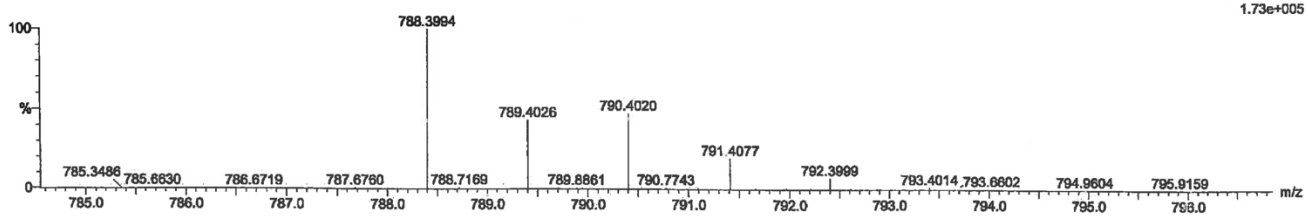
**Single Mass Analysis**
Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
98 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 38-45 H: 55-65 N: 0-10 O: 0-15 Cl: 1-1

AL129.1
carmeli688b 27 (1.210) Cm (27:30)

Anat Iodin

1: TOF MS ES+
1.73e+005



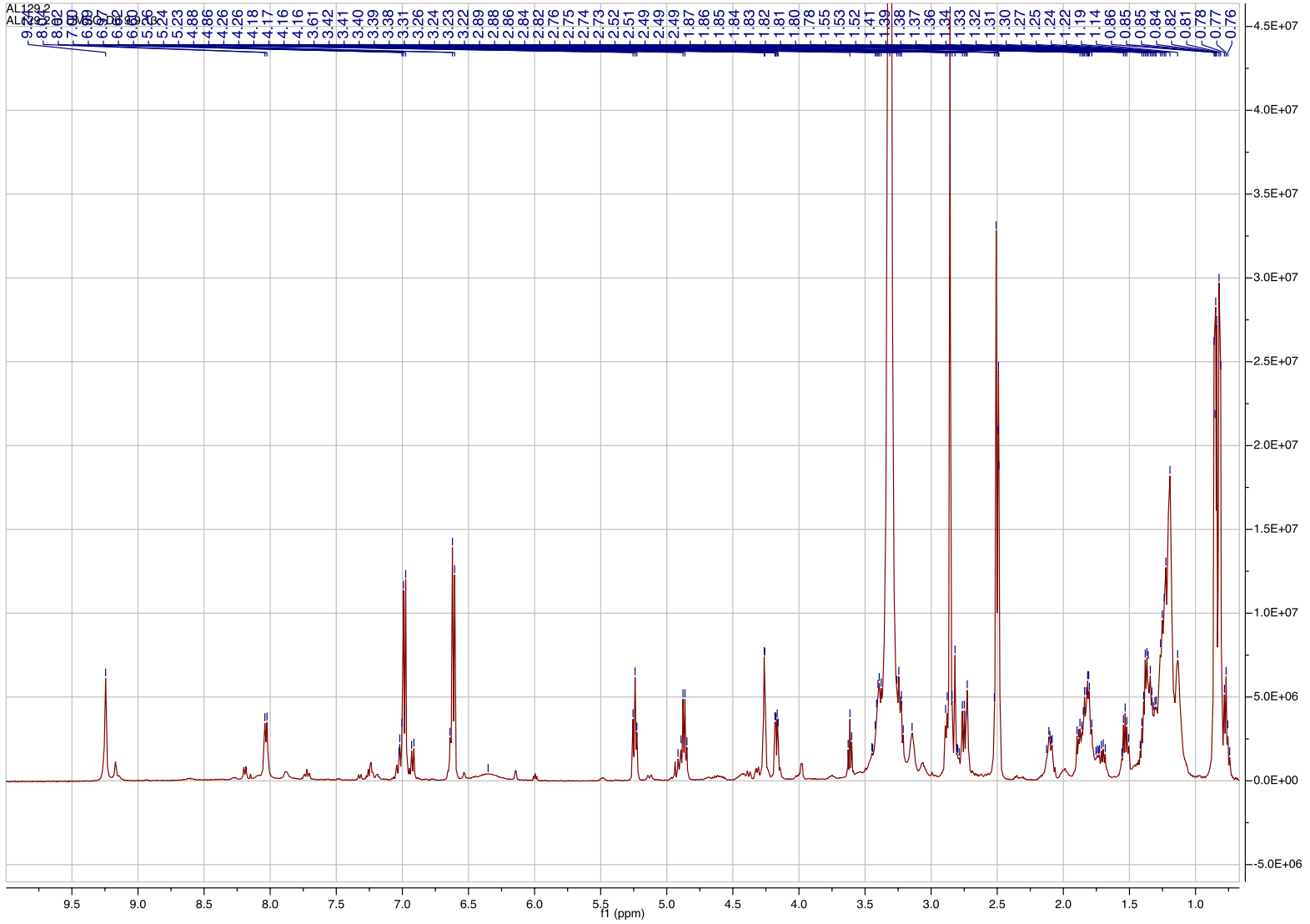

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | |
| Maximum: | | 5.0 | 2.0 | 50.0 | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
| 788.3994 | 788.3988 | 0.6 | 0.8 | 8.5 | 237.4 | 0.4 | C39 H63 N O13 Cl |
| | 788.4001 | -0.7 | -0.9 | 13.5 | 238.2 | 1.1 | C40 H59 N5 O9 Cl |

S46. **Table S6**. NMR Data (500/125 MHz) of Microginin KR604 (**5**) in DMSO-$d_6$

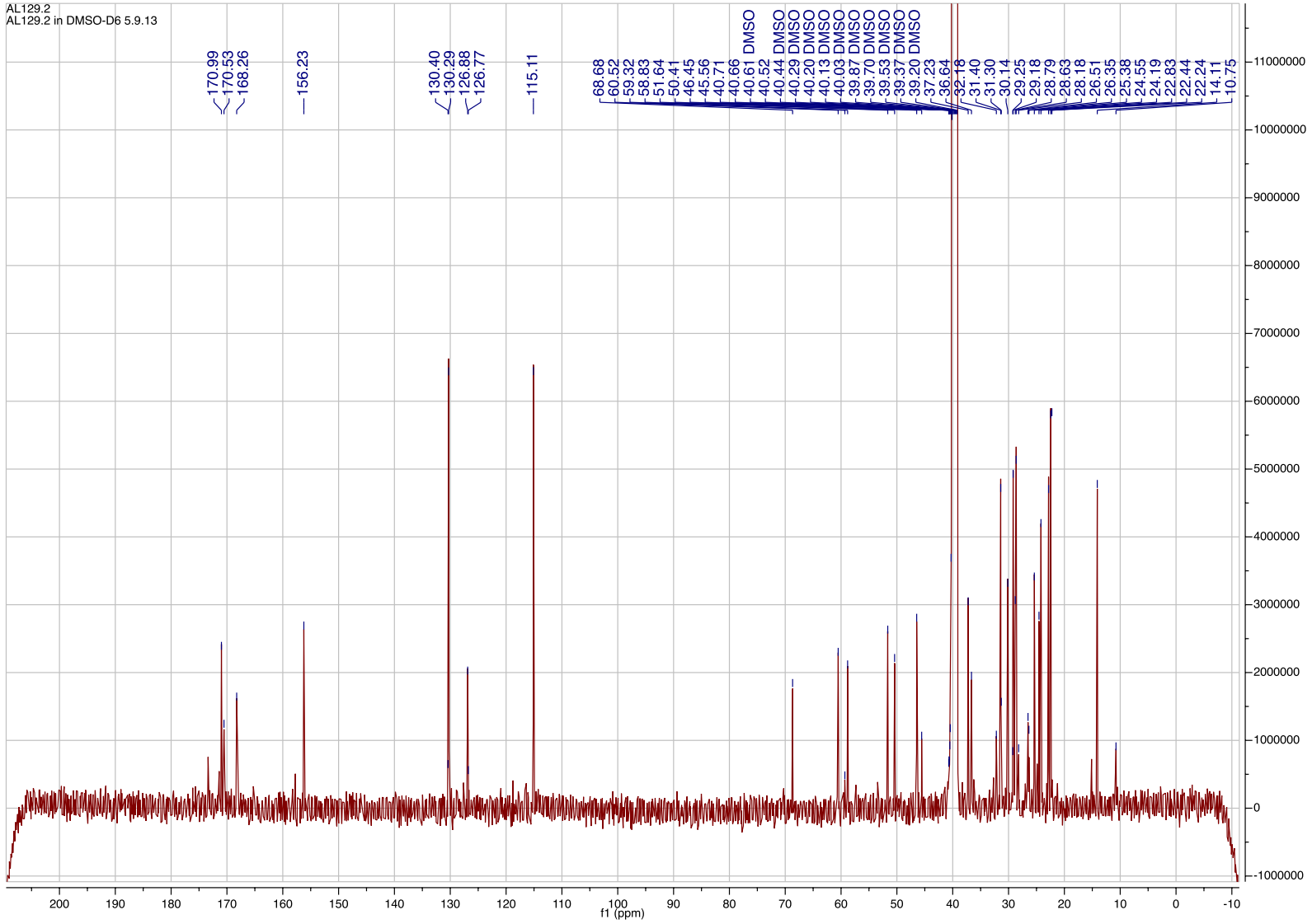
| Position | $\delta_C$ | $\delta_H$ Multiplicity, *J* (Hz) | HMBC correlations | COSY correlations | NOESY correlations |
|---|---|---|---|---|---|
| Ahda 1 | 170.5 C | | Ahda-2, $^1$Tyr-NH | | |
| 2 | 68.7 CH | 4.26 brd, 2.0 | | Ahda-3 | Ahda-3,3-*N*$CH_3$, $^1$Tyr-NH |
| 2-OH | | 6.35 brs | | | |
| 3 | 60.5 CH | 3.14 brs | Ahda-2,3-*N*$CH_3$ | Ahda-2,4,4’ | Ahda-2,3-*N*$CH_3$ |
| 3-NH | | 8.00 brs | | | |
| 3-*N*$CH_3$ | 31.4 $CH_3$ | 2.51 brs | | | Ahda-2,3 |
| 4 | 25.4 $CH_2$ | 1.34 m | | Ahda-3,4’,5,5’ | |
| | | 1.28 m | | Ahda-3,4,5,5’ | |
| 5 | 24.2 $CH_2$ | 1.27 m | Ahda-4 | Ahda-4,4’,5’,6 | |
| | | 1.13 m | | Ahda-4,4’,5,6 | |
| 6 | 28.6 $CH_2$ | 1.14 m | Ahda-5 | Ahda-6 | |
| 7 | 29.2 $CH_2$ | 1.19 m | Ahda-8 | | |
| 8 | 31.3 $CH_2$ | 1.20 m | Ahda-9,10 | | |
| 9 | 22.2 $CH_2$ | 1.26 m | Ahda-8,10 | Ahda-8,10 | |
| 10 | 14.1 $CH_3$ | 0.84 t, 6.6 | Ahda-9 | Ahda-9 | |
| $^1$Tyr 1 | 171.0 C | | $^1$Tyr-2,3,3’, *N*MeLeu-2, *N*$CH_3$ | | |
| 2 | 50.4 CH | 4.87 dt, 8.1,7.4 | $^1$Tyr-3,3’ | $^1$Tyr-2-NH,3,3’ | $^1$Tyr-2-NH,3,3’, *N*MeLeu-*N*Me |
| 2-NH | | 8.03 d, 8.1 | | $^1$Tyr-2 | $^1$Tyr-2,3,3’, Ahda-2 |
| 3 | 36.6 $CH_2$ | 2.87 dd, 13.8,6.4 | $^1$Tyr-2,5,5’ | $^1$Tyr-2,3’ | $^1$Tyr-2,3’,5,5’ |
| | | 2.74 dd, 13.8,7.6 | | $^1$Tyr-2,3 | $^1$Tyr-2,3,5,5’ |
| 4 | 126.9 C | | $^1$Tyr-2,3,3’,6,6’ | | |
| 5,5’ | 130.3 CH | 6.98 d, 8.3 | $^1$Tyr-3,3’,5’,5,6,6’ | $^1$Tyr-6,6’ | $^1$Tyr-2,3,3’,6,6’, *N*MeLeu-*N*Me |
| 6,6’ | 115.1 CH | 6.61 d, 8.3 | $^1$Tyr-5,5’,6’,6,7-OH | $^1$Tyr-5,5’ | $^1$Tyr-5,5’,7-OH, *N*MeLeu-*N*Me |
| 7 | 156.2 C | | $^1$Tyr-5,5’,6,6’,7-OH | | |
| 7-OH | | 9.24 s | | | $^1$Tyr-6,6’ |
| *N*MeLeu 1 | 168.3 C | | *N*MeLeu-2,3,3’ | | |

| | | | | | |
|---|---|---|---|---|---|
| 2 | 51.6 CH | 5.24 dd, 7.8,6.6 | *N*MeLeu-3,3',*N*Me | *N*MeLeu-3,3' | *N*MeLeu-3,3',5,6,*N*Me, Pro-5,5' |
| 2-*N*$CH_3$ | 30.1 $CH_3$ | 2.86 s | *N*MeLeu-2 | | *N*MeLeu-2,3',4 |
| 3 | 37.2 $CH_2$ | 1.53 dt, 6.6,6.0 | *N*MeLeu-2,4,5,6 | *N*MeLeu-2,3',4 | *N*MeLeu-2,5,6 |
| | | 1.36 m | | *N*MeLeu-2,3,4 | *N*MeLeu-2,5,6,*N*Me |
| 4 | 24.2 CH | 1.39 m | *N*MeLeu-2,3,3',5,6 | *N*MeLeu-3,3',5,6 | *N*MeLeu-*N*Me |
| 5 | 22.4 $CH_3$ | 0.82 d, 6.2 | *N*MeLeu-3,3',4,6 | *N*MeLeu-4 | *N*MeLeu-2,3,3' |
| 6 | 22.8 $CH_3$ | 0.85 d, 6.2 | *N*MeLeu-3,3',4,5 | *N*MeLeu-4 | *N*MeLeu-2,3,3' |
| Pro 1 | 173.4 C | | Pro-2,3,3' | | |
| 2 | 58.8 CH | 4.17 dd, 8.9,3.8 | Pro-3,4,4' | Pro-3,3' | Pro-3,4' |
| 3 | 28.8 $CH_2$ | 2.10 m | Pro-2,4,4',5,5' | Pro-2,3',4,4' | Pro-2,3',4' |
| | | 1.82 m | | Pro-2,3,4,4' | Pro-3 |
| 4 | 24.6 $CH_2$ | 1.86 m | Pro-2,3,3',5,5' | Pro-3,3',5,5' | Pro-3,4' |
| | | 1.81 m | | Pro-3,3',5,5' | Pro-2,4 |
| 5 | 46.5 $CH_2$ | 3.40 dt, 9.9,5.2 | | Pro-4,4',5' | Pro-4,4',5' |
| | | 3.24 dt, 9.9,6.9 | | Pro-4,4',5 | Pro-4,4',5 |

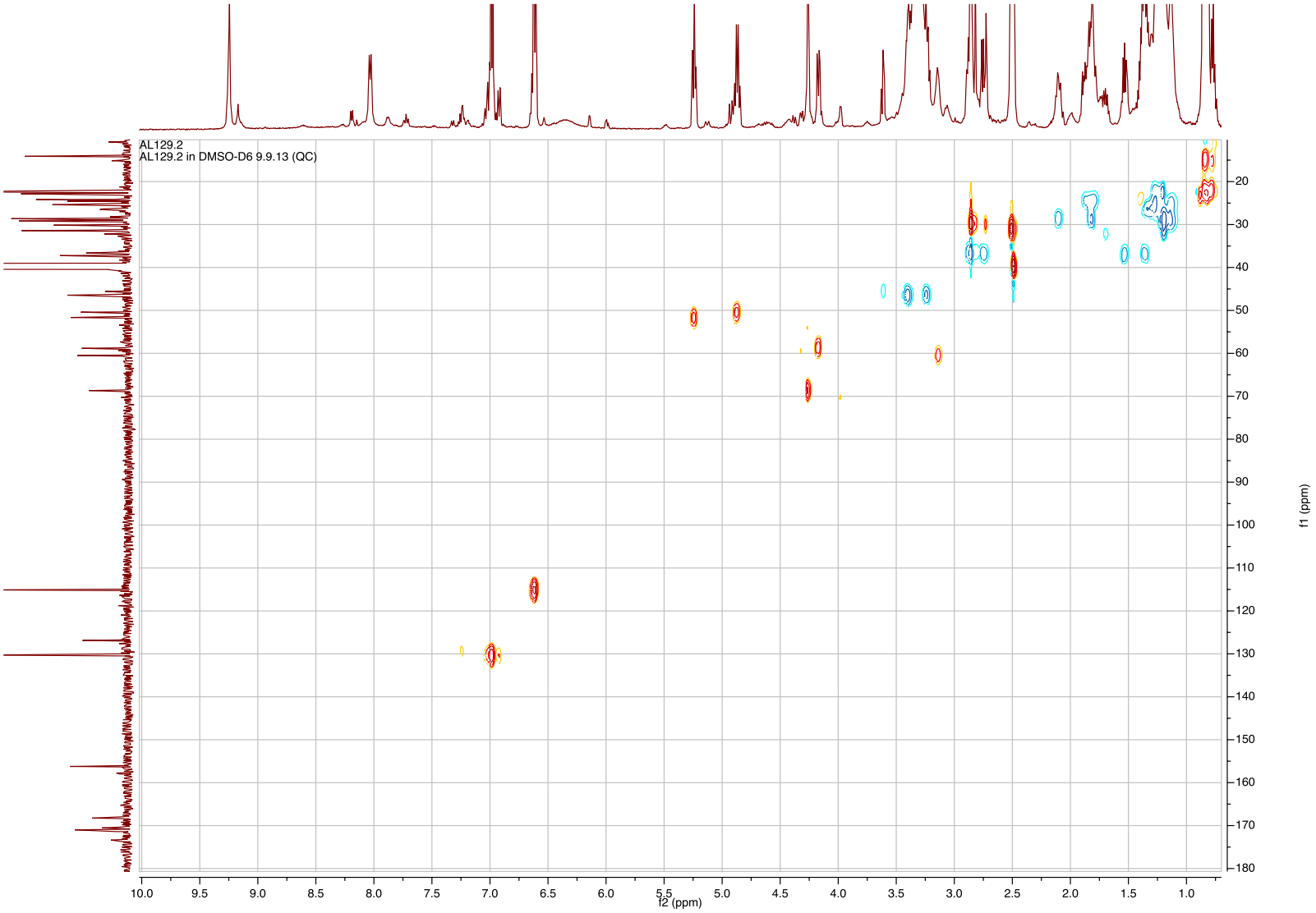
S48. $^{1}$H NMR Spectrum of Microginin KR604 (**5**) in DMSO-$d_6$



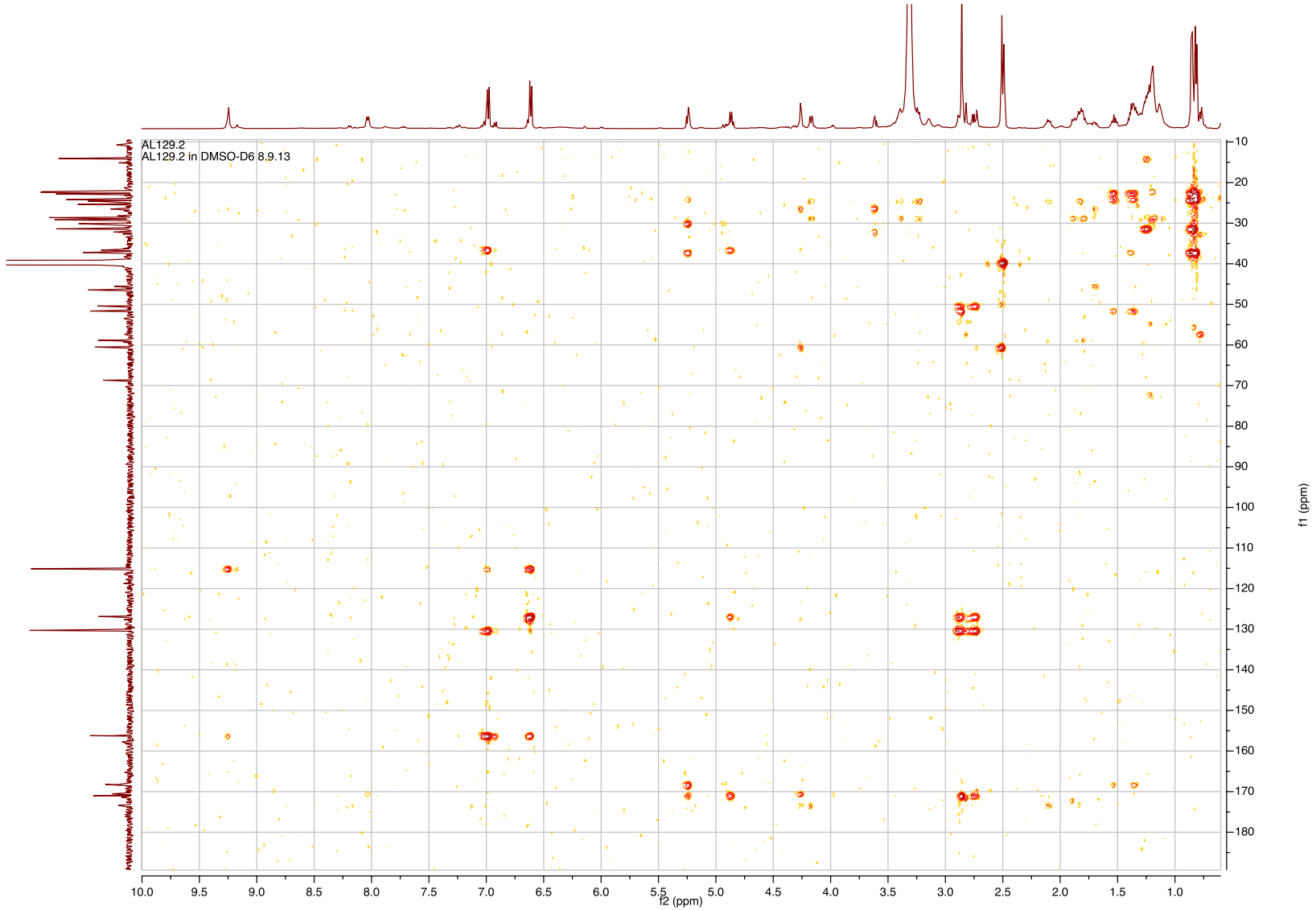
S49. $^{13}$C NMR Spectrum of Microginin KR604 (**5**) in DMSO-$d_6$



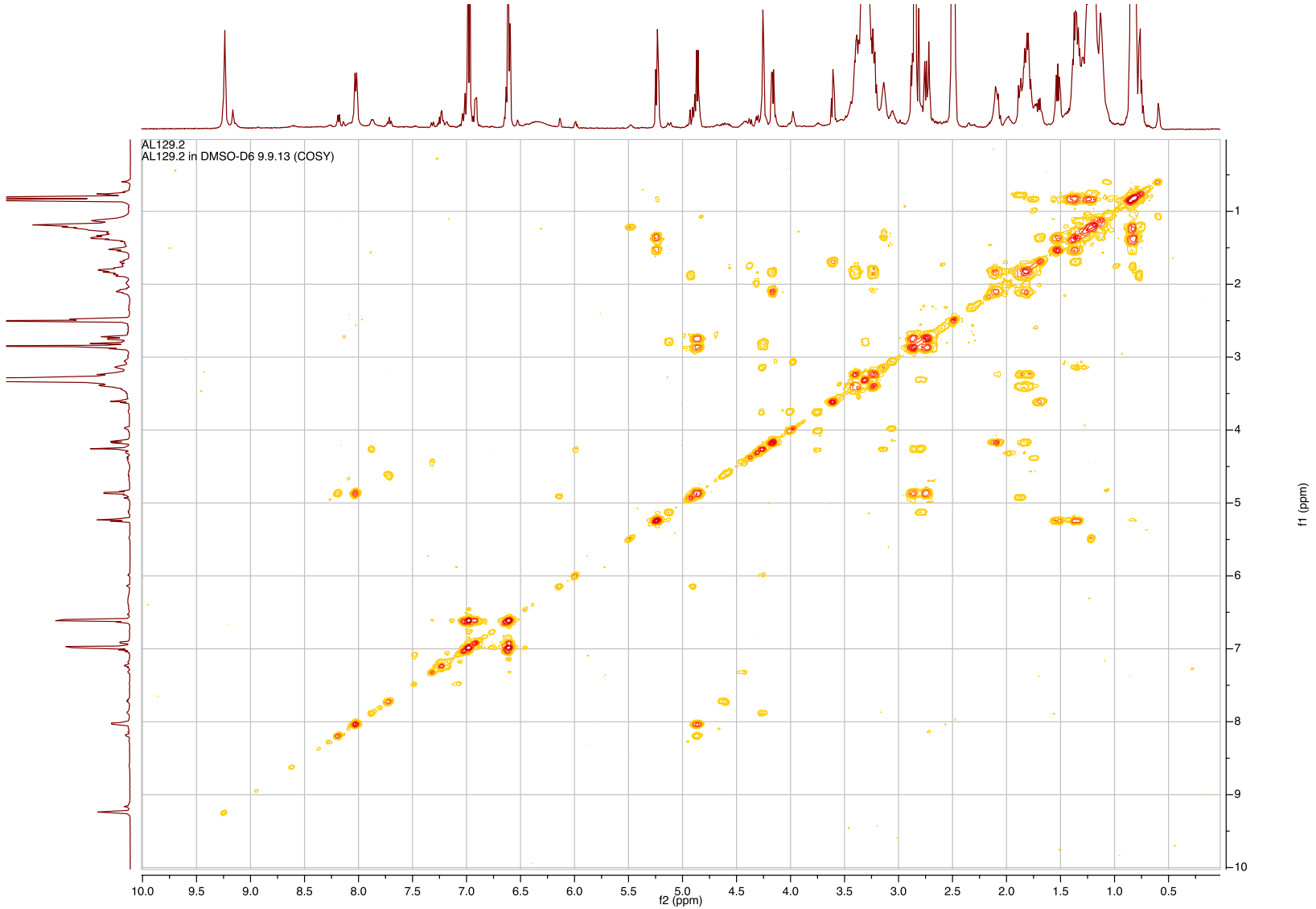
S50. HSQC Spectrum Microginin KR604 (**5**) in DMSO-$d_6$



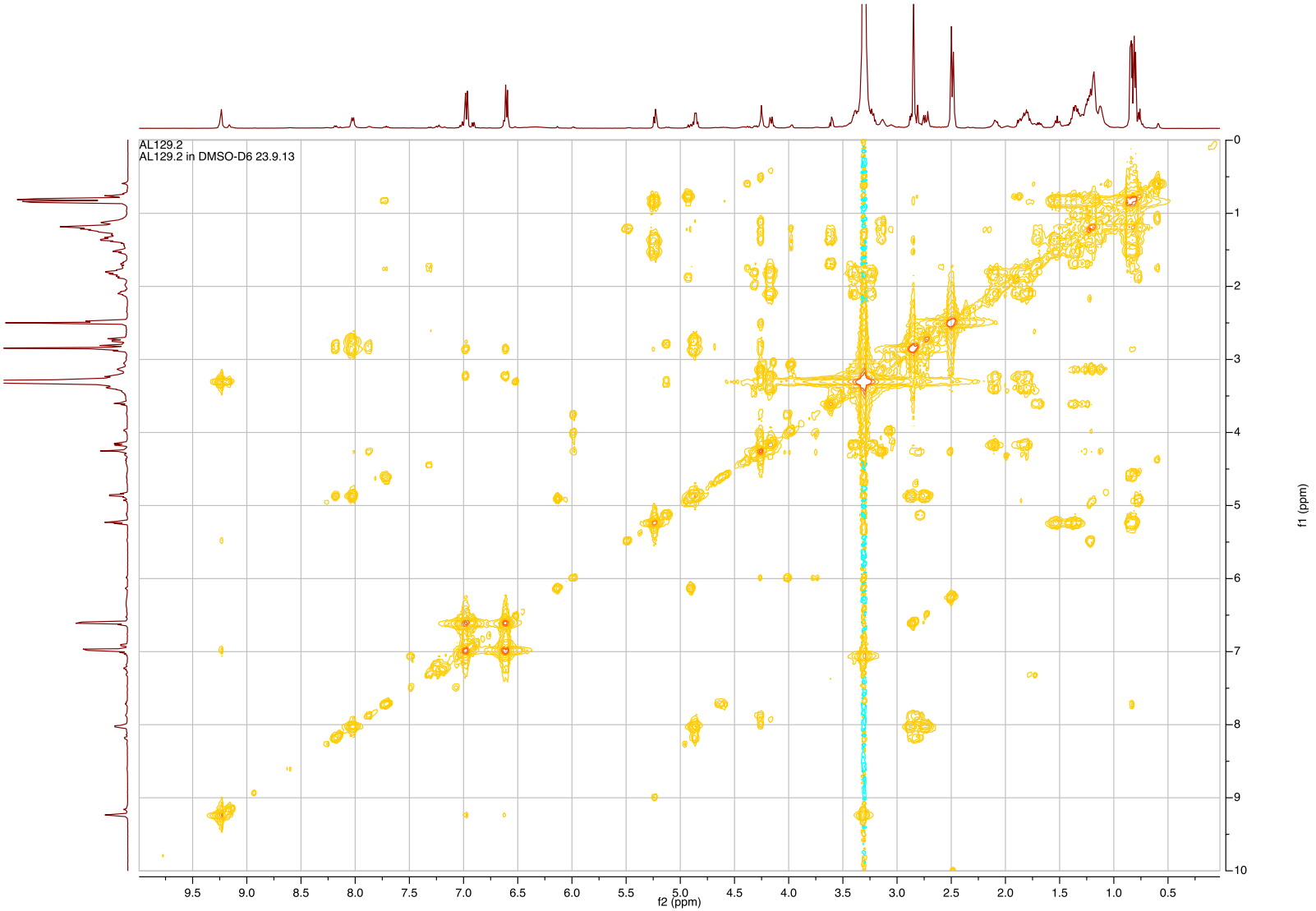
S51. HMBC Spectrum of Microginin KR604 (**5**) in DMSO-$d_6$



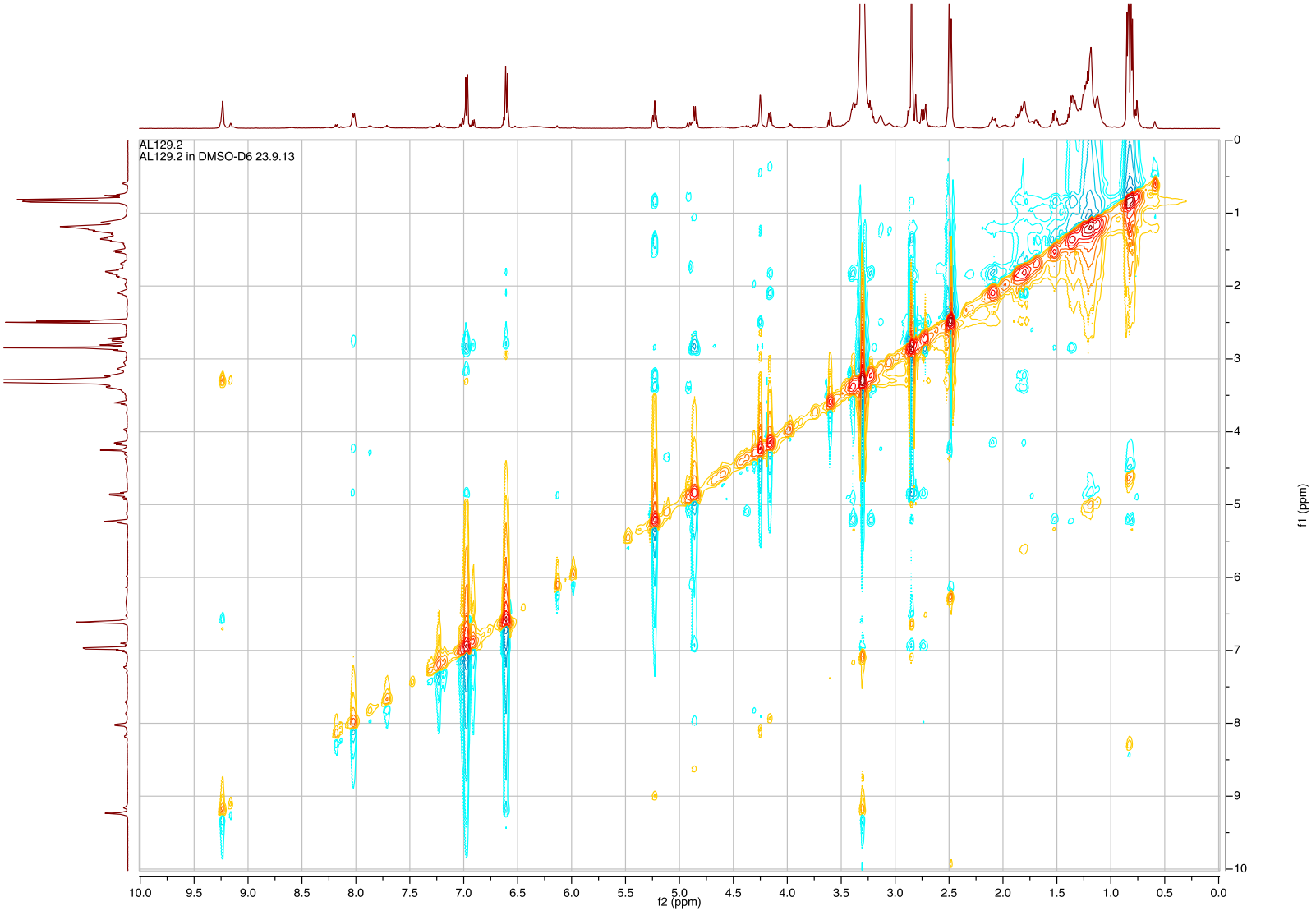
S52. COSY Spectrum of Microginin KR604 (**5**) in DMSO-$d_6$



S53. TOCSY Spectrum of Microginin KR604 (**5**) in DMSO-$d_6$



S54. ROESY Spectrum of Microginin KR604 (**5**) in DMSO-$d_6$



S55. HR ESI MS data of Microginin KR604 (**5**)

**Elemental Composition Report** Page 1

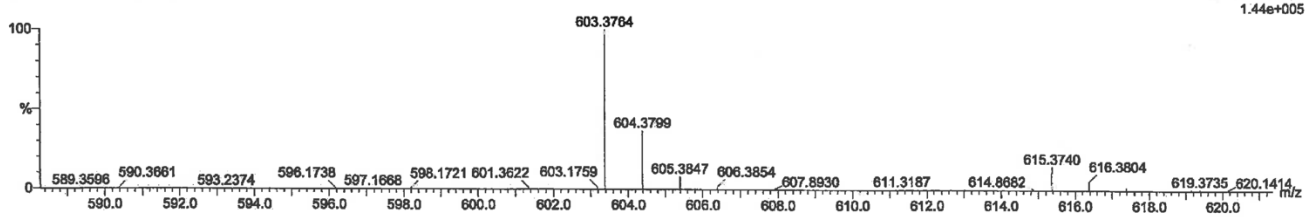
**Single Mass Analysis**
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
302 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 28-38 H: 45-60 N: 0-10 O: 0-15 23Na: 0-1

AL129.2
carmeli687 50 (1.913) Cm (50:55)

Anat Iodin

1: TOF MS ES-
1.44e+005



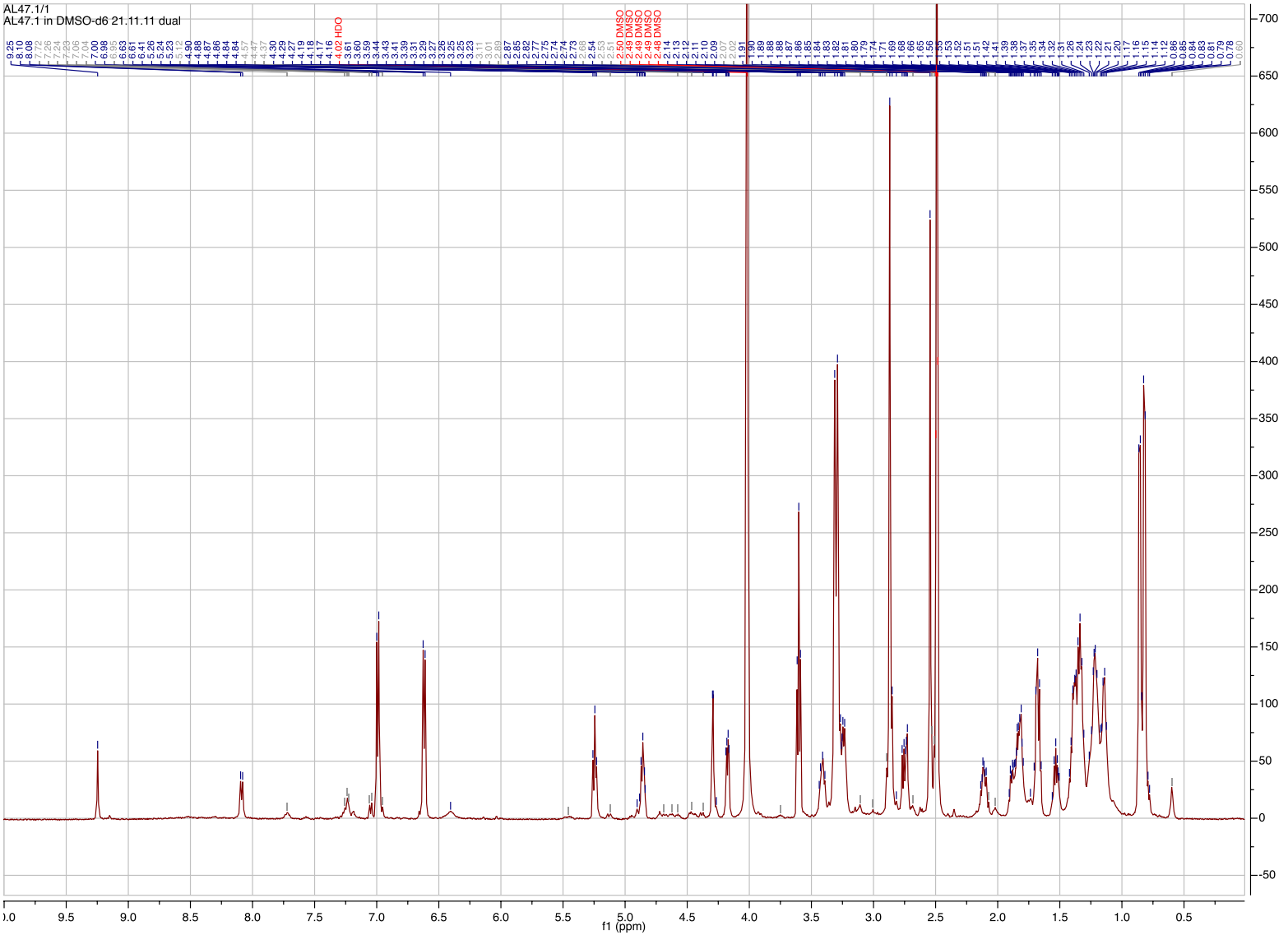

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | | | | |
| Maximum: | | 10.0 | 3.0 | 50.0 | | | | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula | | | | |
| 603.3764 | 603.3758 | 0.6 | 1.0 | 9.5 | 126.9 | 0.1 | C32 | H51 | N4 | O7 | |
| | 603.3771 | -0.7 | -1.2 | 14.5 | 130.1 | 3.3 | C33 | H47 | N8 | O3 | |
| | 603.3774 | -1.0 | -1.7 | 10.5 | 130.5 | 3.8 | C35 | H52 | N2 | O5 | 23Na |
| | 603.3747 | 1.7 | 2.8 | 11.5 | 129.4 | 2.6 | C31 | H48 | N8 | O3 | 23Na |

S56. **Table S7**. NMR Data (500/125 MHz) of Microginin KR638 (**6**) in DMSO-$d_6$

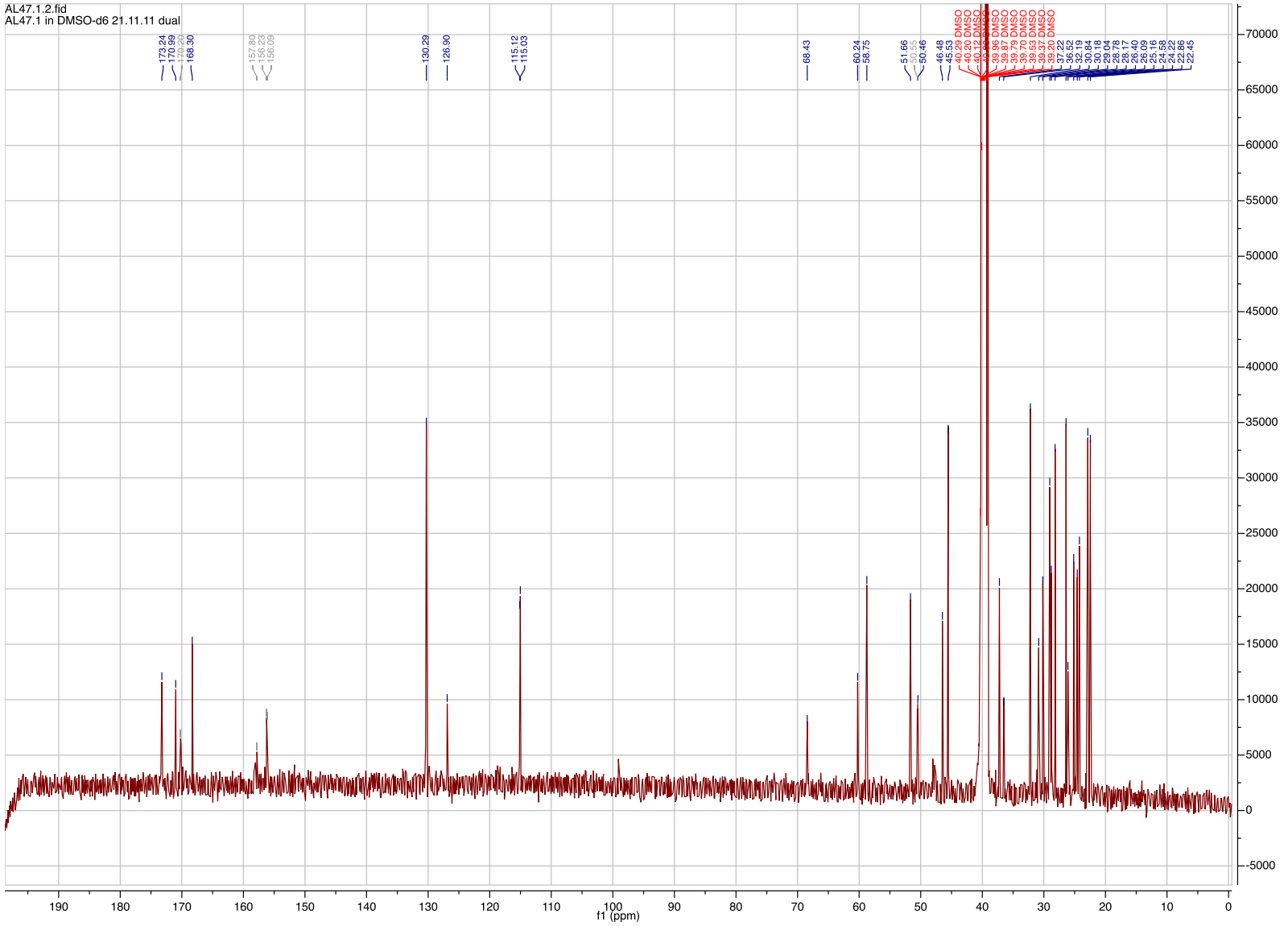
| Position | $\delta_C$ | $\delta_H$ Multiplicity, *J* (Hz) | HMBC correlations | COSY correlations | NOESY correlations |
|---|---|---|---|---|---|
| Ahda 1 | 170.1 C | | Ahda-2, $^1$Tyr-NH | | |
| 2 | 68.4 CH | 4.29 brs | | Ahda-2-OH,3 | Ahda-3,3-*N*$CH_3$,_$^1$Tyr-NH |
| 2-OH | | 6.41 brs | | Ahda-2 | |
| 3 | 60.2 CH | 3.24 m | Ahda-2,3-*N*$CH_3$ | Ahda-2,4,4’ | Ahda-2,5,5’,3-*N*$CH_3$, $^1$Tyr-NH |
| 3-NH | | 7.24 brs | | | |
| 3-*N*$CH_3$ | 30.8 $CH_3$ | 2.55 brs | | | Ahda-2,3 |
| 4 | 26.1 $CH_2$ | 1.41 m | Ahda-2 | Ahda-3,4’,5,5’ | |
| | | 1.33 m | | Ahda-3,4,5,5’ | |
| 5 | 25.2 $CH_2$ | 1.38 m | Ahda-4,4’,6,7 | Ahda-4,4’,5’,6 | Adha-3 |
| | | 1.14 m | | Ahda-4,4’,5,6 | Adha-3 |
| 6 | 29.1 $CH_2$ | 1.15 m | Ahda-7 | Ahda-6 | |
| 7 | 28.2 $CH_2$ | 1.22 m | Ahda-6,8,9 | | |
| 8 | 26.4 $CH_2$ | 1.34 tt. 7.7,7.4 | Ahda-9,10 | Ahda-7’,9 | Ahda-10 |
| 9 | 32.2 $CH_2$ | 1.68 tt, 7.4,6.8 | Ahda-8,10 | Ahda-8,10 | Ahda-10 |
| 10 | 45.5 $CH_2$ | 3.60 t, 6.8 | Ahda-8,9 | Ahda-9 | Ahda-8,9 |
| $^1$Tyr 1 | 171.0 C | | $^1$Tyr-2,3,3’, *N*MeLeu-2, *N*$CH_3$ | | |
| 2 | 50.5 CH | 4.86 ddd, 8.2,7.7,6.3 | $^1$Tyr-3,3’,NH | $^1$Tyr-2-NH,3,3’ | $^1$Tyr-2-NH,3,3’,5,5’, *N*MeLeu-*N*Me |
| 2-NH | | 8.09 d, 8.2 | | $^1$Tyr-2 | $^1$Tyr-2,3,3’, Ahda-2,3 |
| 3 | 36.5 $CH_2$ | 2.87 dd, 14.3,6.3 | $^1$Tyr-2,5,5’ | $^1$Tyr-2,3’ | $^1$Tyr-2,3’,5,5’ |
| | | 2.75 dd, 14.3,7.7 | | $^1$Tyr-2,3 | $^1$Tyr-2,3,5,5’ |
| 4 | 126.9 C | | $^1$Tyr-3,3’,6,6’ | | |
| 5,5’ | 130.3 CH | 6.99 d, 8.2 | $^1$Tyr-3,3’,5’,5 | $^1$Tyr-6,6’ | $^1$Tyr-2,3,3’,6,6, *N*MeLeu-*N*Me |
| 6,6’ | 115.0 CH | 6.62 d, 8.2 | $^1$Tyr-5,5’,6’,6,7-OH | $^1$Tyr-5,5’ | $^1$Tyr-5,5’,7-OH, *N*MeLeu-*N*Me |
| 7 | 156.0 C | | $^1$Tyr-5,5’,6,6’,7-OH | | |
| 7-OH | | 9.25 s | | | $^1$Tyr-6,6’ |
| *N*MeLeu 1 | 168.3 C | | *N*MeLeu-2,3,3’ | | |

| | | | | | |
|---|---|---|---|---|---|
| 2 | 51.7 CH | 5.24 dd, 7.6,6.8 | *N*MeLeu-3,3',*N*Me | *N*MeLeu-3,3' | *N*MeLeu-3,3',5,6,*N*Me, Pro-5,5' |
| 2-*N*$CH_3$ | 30.2 $CH_3$ | 2.87 s | *N*MeLeu-2 | | *N*MeLeu-2,3,3' |
| 3 | 37.2 $CH_2$ | 1.53 m | *N*MeLeu-2,4,5,6 | *N*MeLeu-2,3',4 | *N*MeLeu-2,5,6,*N*Me |
| | | 1.38 m | | *N*MeLeu-2,3,4 | *N*MeLeu-2,5,6,*N*Me |
| 4 | 24.2 CH | 1.39 m | *N*MeLeu-2,3,3',5,6 | *N*MeLeu-3,3',5,6 | *N*MeLeu-*N*Me |
| 5 | 22.5 $CH_3$ | 0.82 d, 6.2 | *N*MeLeu-3,3',4,6 | *N*MeLeu-4 | *N*MeLeu-2,3,3' |
| 6 | 22.9 $CH_3$ | 0.86 d, 6.2 | *N*MeLeu-3,3',4,5 | *N*MeLeu-4 | *N*MeLeu-2,3,3' |
| Pro 1 | 173.2 C | | Pro-2,3,3' | | |
| 2 | 58.8 CH | 4.18 dd, 8.9,3.8 | Pro-3,4,4',5' | Pro-3,3' | Pro-3,4' |
| 3 | 28.8 $CH_2$ | 2.11 m | Pro-2,4,4',5,5' | Pro-2,3',4,4' | Pro-2,3',4' |
| | | 1.82 m | | Pro-2,3,4,4' | Pro-3 |
| 4 | 24.6 $CH_2$ | 1.86 m | Pro-2,3,3',5,5' | Pro-3,3',5,5' | Pro-2 |
| | | 1.81 m | | Pro-3,3',5,5' | Pro-3 |
| 5 | 46.5 $CH_2$ | 3.41 m | Pro-2,3' | Pro-4,4',5' | Pro-4,4',5' |
| | | 3.26 m | | Pro-4,4',5 | Pro-2,3,4,4',5 |

S58. $^{1}$H NMR Spectrum of Microginin KR638 (**6**) in DMSO-$d_6$

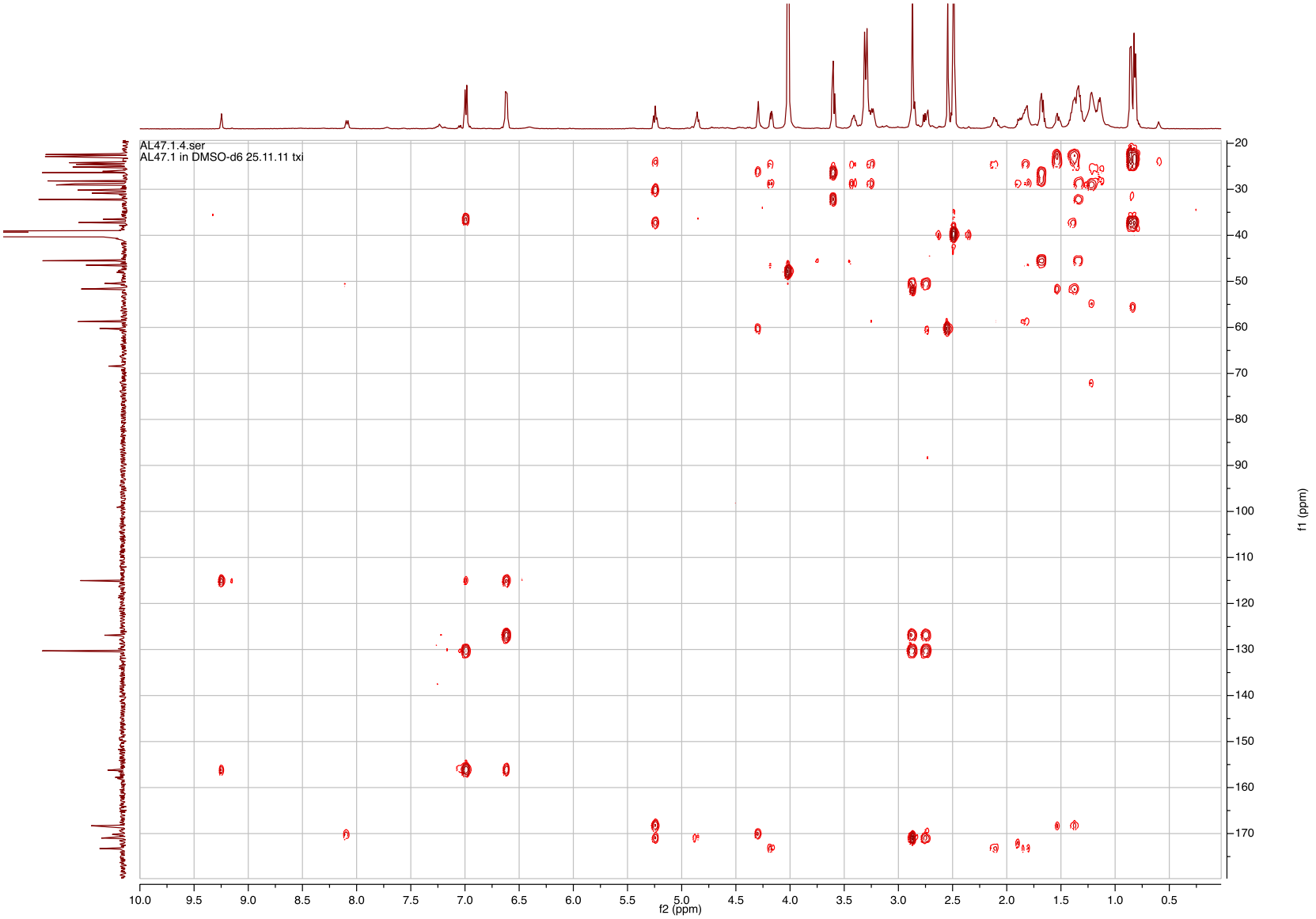


S59. $^{13}$C NMR Spectrum of Microginin KR638 (**6**) in DMSO-$d_6$

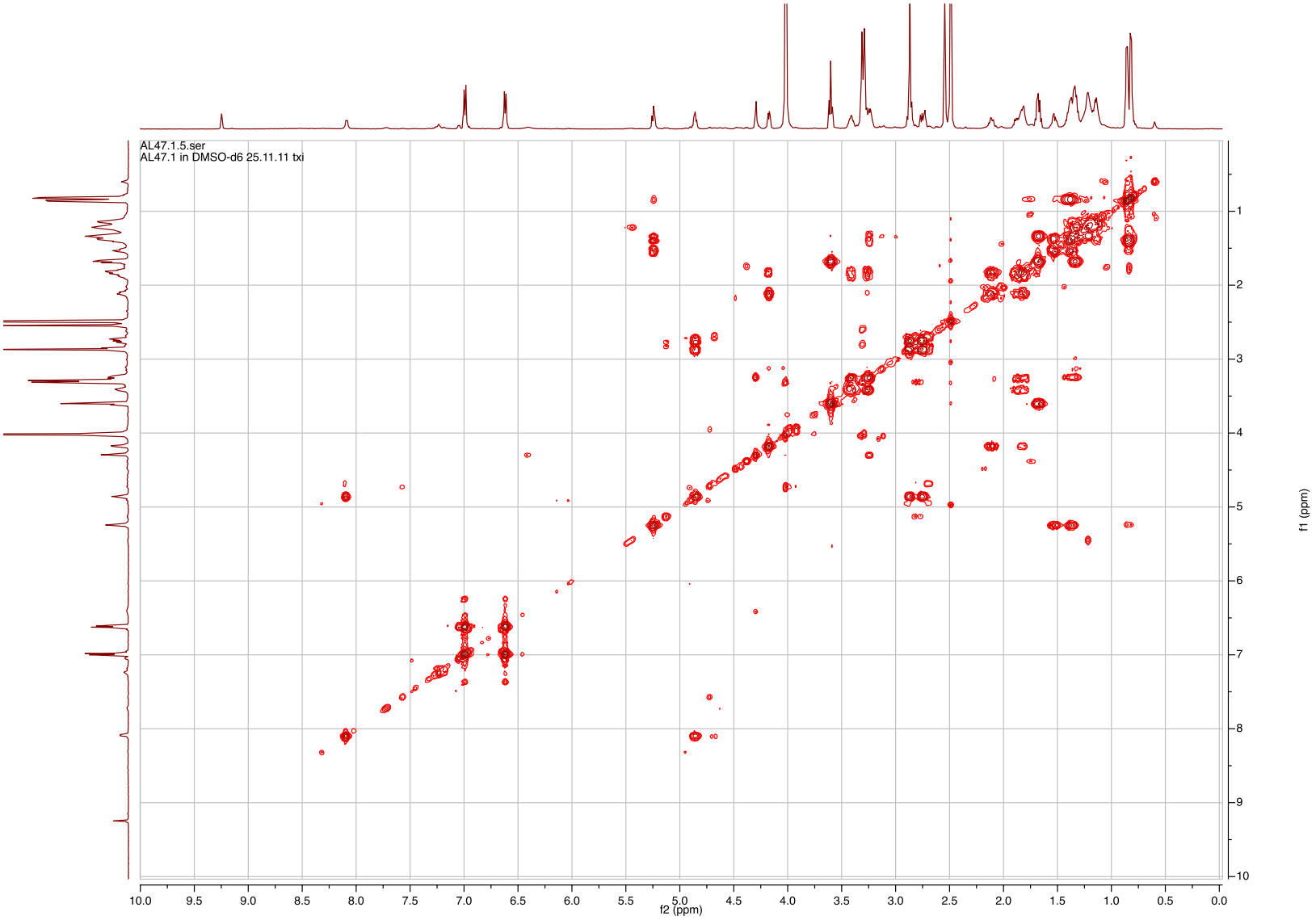


S60. HSQC Spectrum Microginin KR638 (**6**) in DMSO-$d_6$

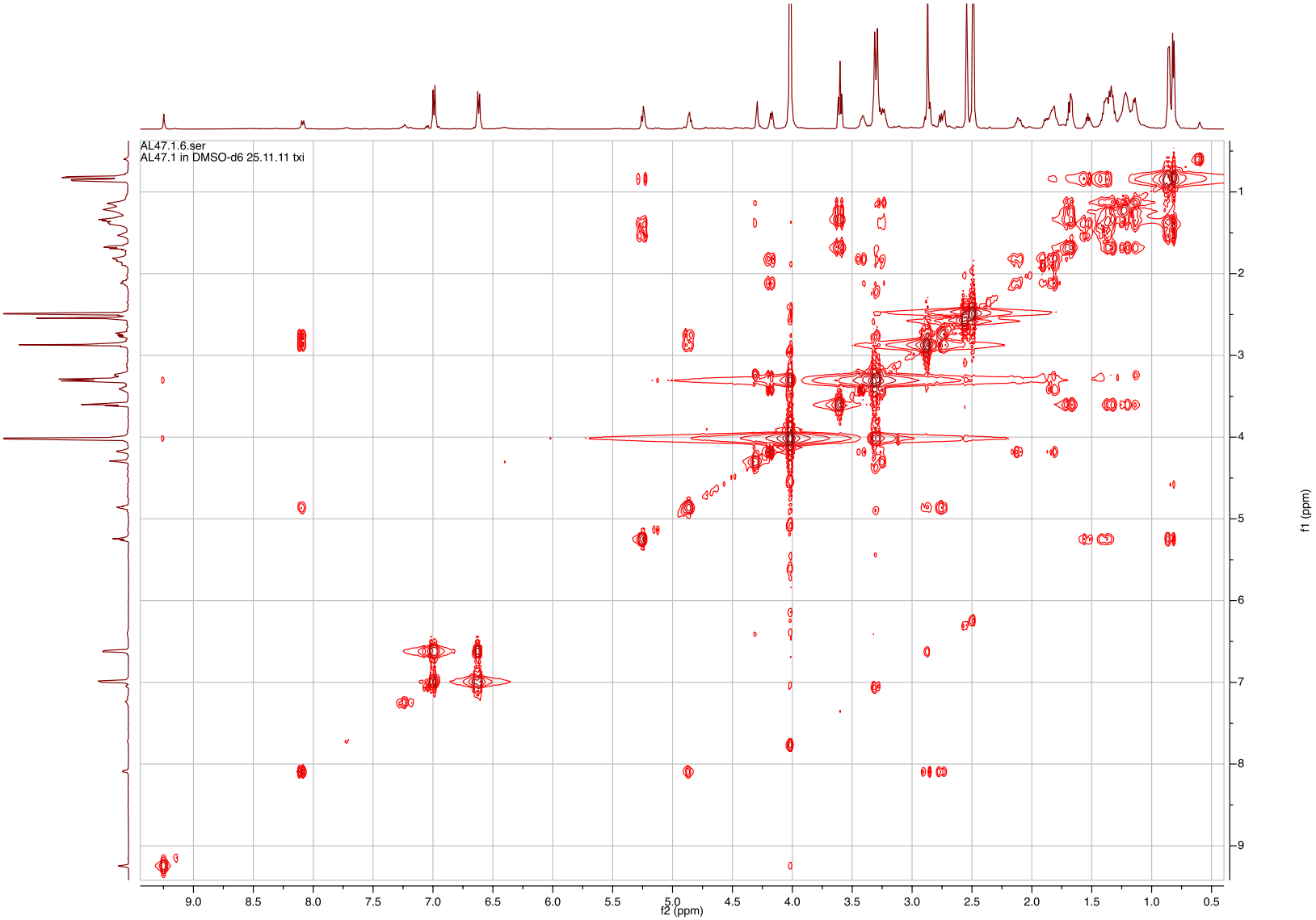
S61. HMBC Spectrum of Microginin KR638 (**6**) in DMSO-$d_6$



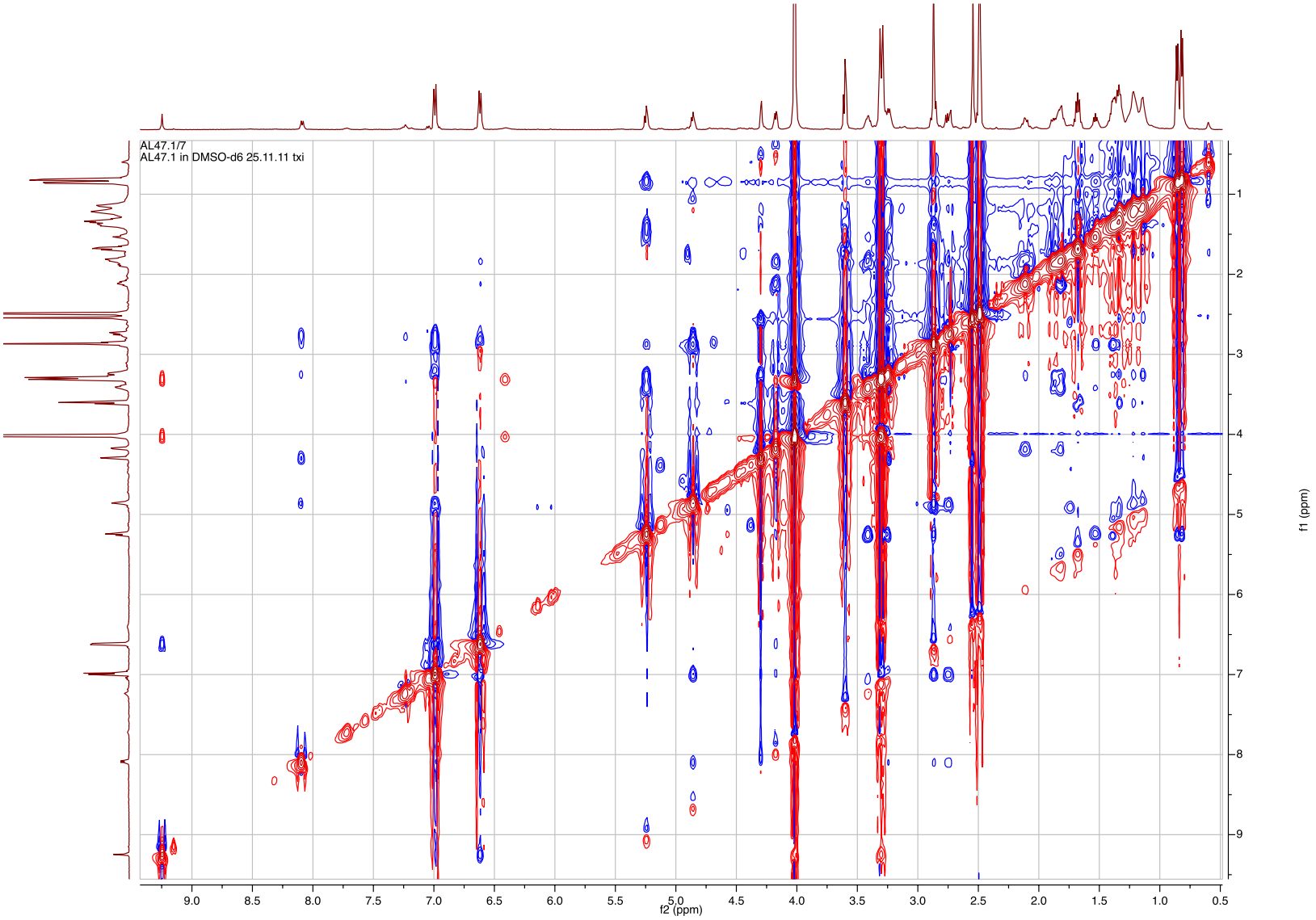
S62. COSY Spectrum of Microginin KR638 (**6**) in DMSO-$d_6$



S63. TOCSY Spectrum of Microginin KR638 (**6**) in DMSO-$d_6$



S64. ROESY Spectrum of Microginin KR638 (**6**) in DMSO-$d_6$



S65. HR ESI MS data of Microginin KR638 (**6**)

**Elemental Composition Report**



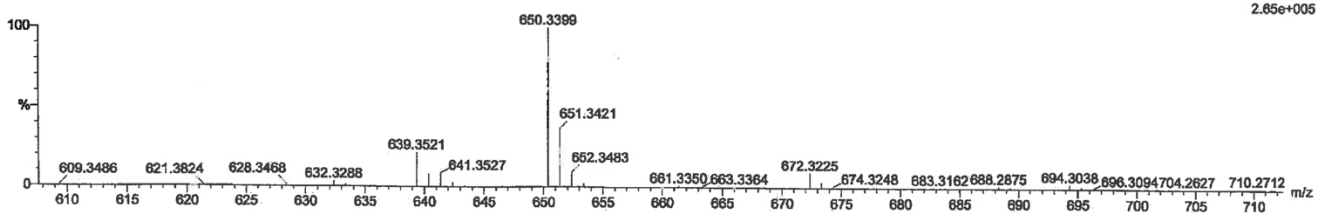
**Single Mass Analysis**
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
283 formula(e) evaluated with 31 results within limits (up to 5 closest results for each mass)
Elements Used:
C: 28-35 H: 48-58 N: 0-10 O: 0-10 Na: 0-1 S: 0-1 Cl: 1-1

Al47.1
carmeli404d 166 (7.294) Cm (159:166)

Anat Iodin

1: TOF MS ES+
2.65e+005



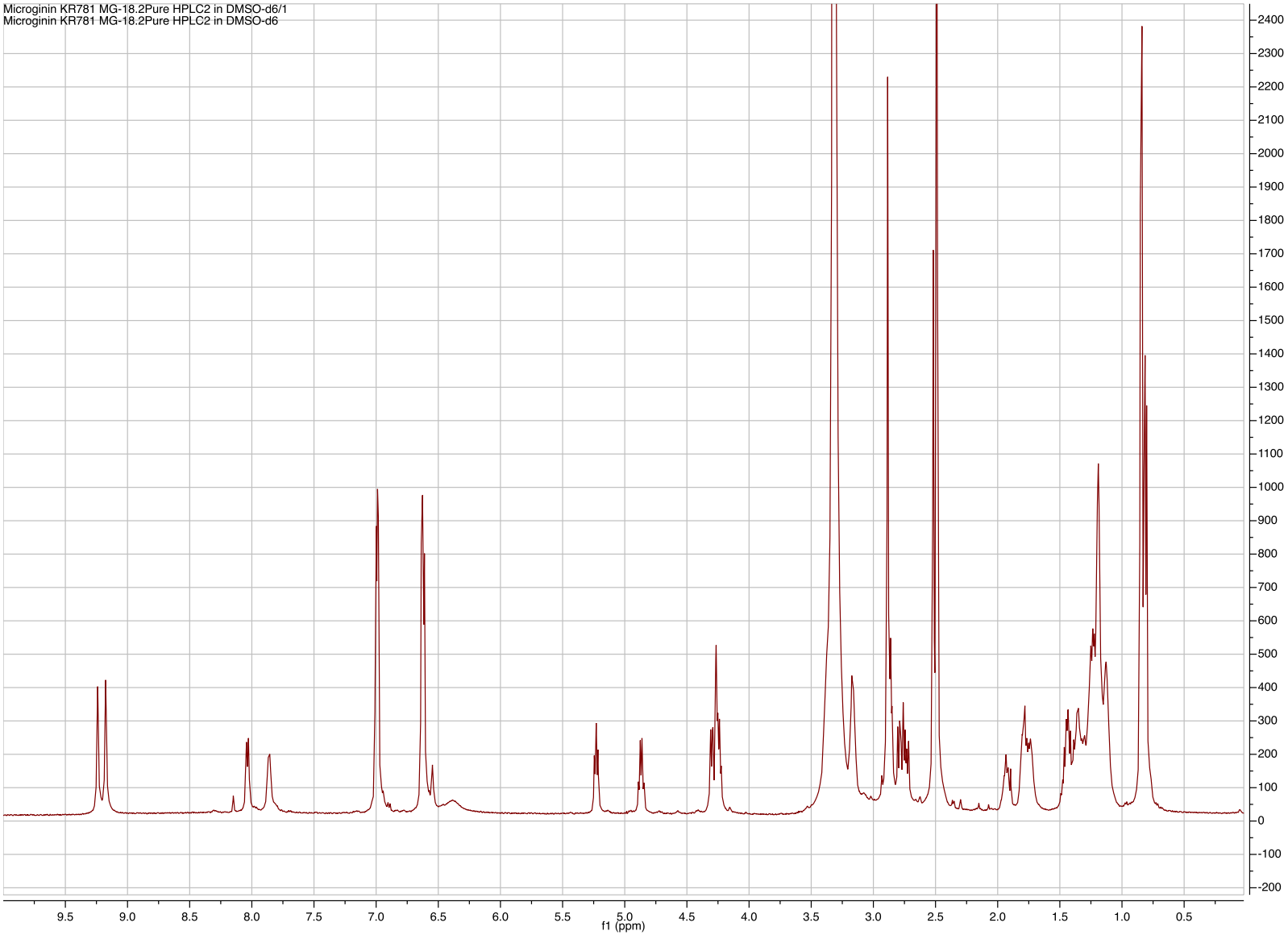

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | | | | | | |
| Maximum: | | 5.0 | 20.0 | 50.0 | | | | | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula | | | | | |
| 639.3521 | 639.3525 | -0.4 | -0.6 | 8.5 | 276.9 | 3.9 | C32 | H52 | N4 | O7 | Cl | ✓ |
| | 639.3514 | 0.7 | 1.1 | 10.5 | 277.7 | 4.7 | C31 | H49 | N8 | O3 | Na | Cl |
| | 639.3538 | -1.7 | -2.7 | 13.5 | 280.5 | 7.5 | C33 | H48 | N8 | O3 | Cl | |
| | 639.3541 | -2.0 | -3.1 | 9.5 | 280.1 | 7.1 | C35 | H53 | N2 | O5 | Na | Cl |
| | 639.3500 | 2.1 | 3.3 | 5.5 | 273.0 | 0.0 | C30 | H53 | N4 | O7 | Na | Cl |

S66. **Table S8**. NMR Data (500/125 MHz) of Microginin KR781 (**7**) in DMSO-$d_6$

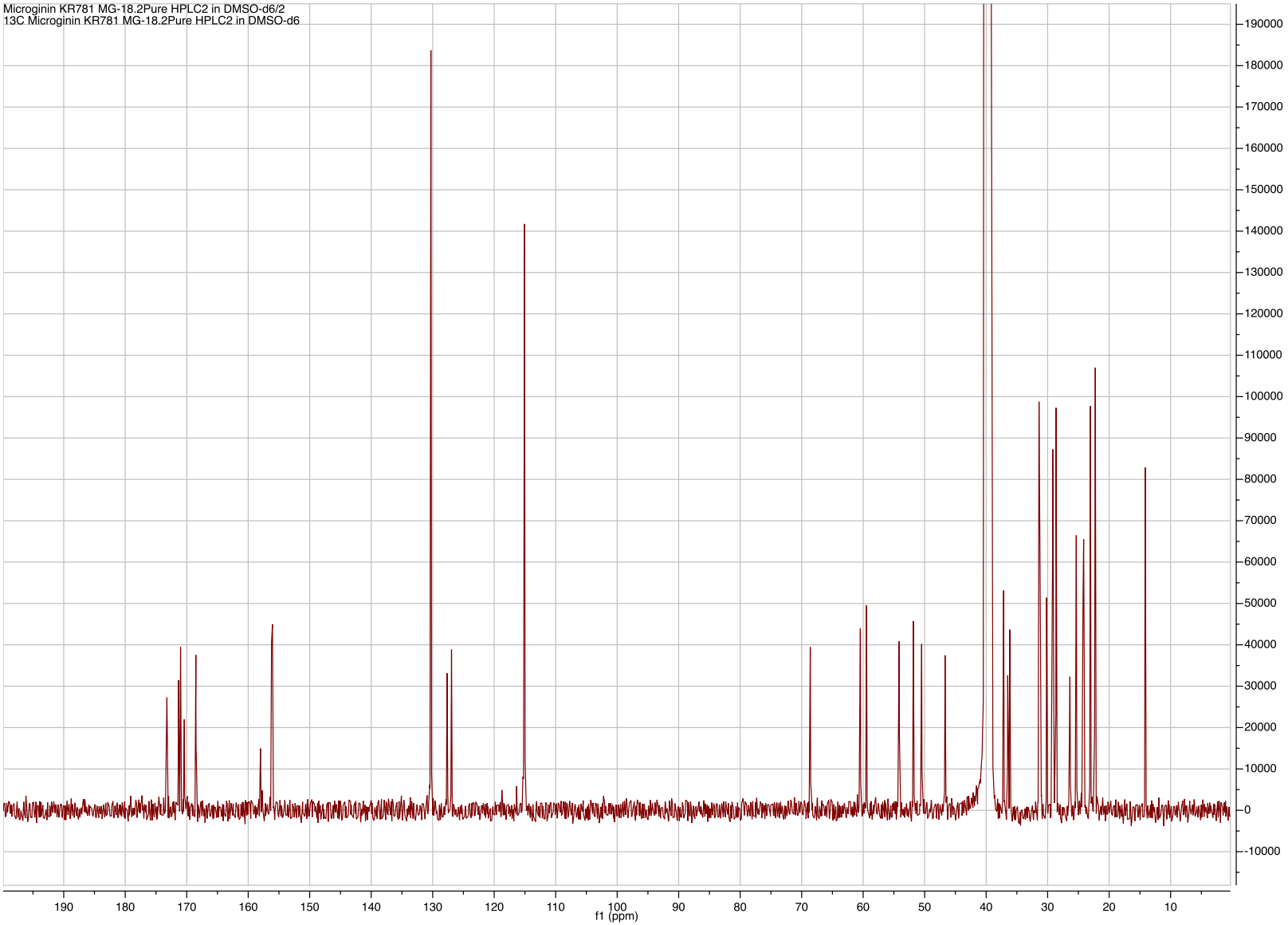
| Position | $\delta_C$ | $\delta_H$ Multiplicity, *J* (Hz) | HMBC correlations | COSY correlations | NOESY correlations |
|---|---|---|---|---|---|
| Ahda 1 | 170.2 C | | Ahda-2, $^1$Tyr-2,NH | | |
| 2 | 68.5 CH | 4.30 brs | | Ahda-2-OH | Ahda-2-OH,3,3-*N*$CH_3$, $^1$Tyr-NH |
| 2-OH | | 6.35 brm | | Ahda-2 | Ahda-2,3 |
| 3 | 60.3 CH | 3.22 brm | Ahda-2,3-*N*$CH_3$ | Ahda-4, | Ahda-2,2-OH |
| 3-NH | | 8.43 brm | | 3-*N*$CH_3$(TOCSY) | Ahda-3-*N*$CH_3$ |
| 3-*N*$CH_3$ | 30.8 $CH_3$ | 2.53 brs | | Ahda-3-NH(TOCSY) | Ahda-2,2-OH,3,3-NH |
| 4 | 26.1 $CH_2$ | 1.36 m | Ahda-2 | Ahda-3,4',5,5' | |
| | | 1.32 m | | Ahda-4,5,5' | |
| 5 | 25.3 $CH_2$ | 1.24 m | | Ahda-4,4',5',6 | |
| | | 1.13 m | | Ahda-4,4',5,6 | |
| 6 | 29.2 $CH_2$ | 1.17 m | Ahda-5,5',7,7' | Ahda-6 | |
| | | 1.13 m | | | |
| 7 | 28.6 $CH_2$ | 1.20 m | Ahda-6,6',8 | | |
| 8 | 31.4 $CH_2$ | 1.20 m | Ahda-9,10 | Ahda-9 | |
| 9 | 22.3 $CH_2$ | 1.25 m | Ahda-8,10 | Ahda-8,10 | |
| 10 | 14.1 $CH_3$ | 0.84 t, 7.4 | Ahda-9 | Ahda-9 | |
| $^1$Tyr 1 | 171.0 C | | $^1$Tyr-2,3,3', *N*MeLeu-2, *N*$CH_3$ | | |
| 2 | 50.6 CH | 4.86 ddd, 7.7,7.4,6.5 | $^1$Tyr-3,3' | $^1$Tyr-2-NH,3,3' | $^1$Tyr-2-NH,3,3',5,5', *N*MeLeu-*N*Me |
| 2-NH | | 8.05 d, 7.4 | | $^1$Tyr-2 | $^1$Tyr-2,3,3', Ahda-2 |
| 3 | 36.4 $CH_2$ | 2.87 m | $^1$Tyr-2,5,5' | $^1$Tyr-2,3' | $^1$Tyr-2,2-NH,3',5,5' |
| | | 2.74 dd, 13.8,8.0 | | $^1$Tyr-2,3 | $^1$Tyr-2,2-NH,3,5,5' |
| 4 | 126.9 C | | $^1$Tyr-2,3,3',6,6' | | |
| 5,5' | 130.3 CH | 6.99 d, 8.3 | $^1$Tyr-3,3',5',5 | $^1$Tyr-6,6' | $^1$Tyr-2,3,3',6,6' |
| 6,6' | 115.2 CH | 6.62 d, 8.3 | $^1$Tyr-5,5',6',6,7-OH | $^1$Tyr-5,5' | $^1$Tyr-5,5',7-OH |
| 7 | 156.2 C | | $^1$Tyr-5,5',6,6',7-OH | | |
| 7-OH | | 9.25 s | | | $^1$Tyr-6,6' |

| | | | | | |
|---|---|---|---|---|---|
| *N*MeLeu 1 | 168.4 C | | *N*MeLeu-2,3,3’ | | |
| 2 | 51.9 CH | 5.23 dd, 8.0,6.5 | *N*MeLeu-3,3’,*N*Me | *N*MeLeu-3,3’ | *N*MeLeu-3,3’,5,6,*N*Me, Pro-5,5’ |
| 2-*N*$CH_3$ | 30.2 $CH_3$ | 2.88 s | *N*MeLeu-2 | | *N*MeLeu-2, $^{1}$Tyr-2 |
| 3 | 37.2 $CH_2$ | 1.47 m | *N*MeLeu-2,4,5,6 | *N*MeLeu-2,3’,4 | *N*MeLeu-2,5,6 |
| | | 1.42 m | | *N*MeLeu-2,3,4 | *N*MeLeu-2,5,6 |
| 4 | 24.3 CH | 1.38 m | *N*MeLeu-2,3,3’,5,6 | *N*MeLeu-3,3’,5,6 | *N*MeLeu-2 |
| 5 | 22.4 $CH_3$ | 0.81 d, 6.6 | *N*MeLeu-3,3’,4,6 | *N*MeLeu-4 | *N*MeLeu-2,3,3’ |
| 6 | 23.0 $CH_3$ | 0.85 d, 6.6 | *N*MeLeu-3,3’,4,5 | *N*MeLeu-4 | *N*MeLeu-2,3,3’ |
| Pro 1 | 171.7 C | | Pro-2, $^{2}$Tyr-NH | | |
| 2 | 59.3 CH | 4.29 m | | Pro-3,3’ | Pro-3,3’,5’ |
| 3 | 29.2 $CH_2$ | 1.95 m | Pro-4,4’ | Pro-2,3’,4,4’ | Pro-2 |
| | | 1.73 m | | Pro-2,3,4,4’ | Pro-2 |
| 4 | 24.2 $CH_2$ | 1.80 m | Pro-3,5’ | Pro-3,3’,5,5’ | |
| | | 1.75 m | | Pro-3,3’,5,5’ | |
| 5 | 46.7 $CH_2$ | 3.39 m | | Pro-4,4’,5’ | Pro-5’, *N*MeLeu-2 |
| | | 3.17 m | | Pro-4,4’,5 | Pro-2,5, *N*MeLeu-2 |
| $^{2}$Tyr 1 | 172.2 C | | $^{2}$Tyr-2,3,3’, $OCH_3$ | | |
| 2 | 54.3 CH | 4.31 m | $^{2}$Tyr-3,3’ | $^{2}$Tyr-3,3’,NH | $^{2}$Tyr-3,3’,5,5’,NH |
| 2-NH | | 8.15 d, 7.3 | | $^{2}$Tyr-2 | $^{2}$Tyr-2,3,3’ |
| 3 | 36.1 $CH_2$ | 2.86 m | $^{2}$Tyr-2,5,5’ | $^{2}$Tyr-2,3’ | $^{2}$Tyr-2,3’,5,5’,NH |
| | | 2.82 m | | $^{2}$Tyr-2,3 | $^{2}$Tyr-2,3,5,5’,NH |
| 4 | 127.2 C | | $^{2}$Tyr-2,3,3’,6,6’ | | |
| 5,5’ | 130.2 CH | 7.00 d, 8.4 | $^{2}$Tyr-3,3’,5’,5 | $^{2}$Tyr-6,6’ | $^{2}$Tyr-2,3,3’,6,6’ |
| 6,6’ | 115.2 CH | 6.64 d, 8.4 | $^{2}$Tyr-5,5’,6’,6,7-OH | $^{2}$Tyr-5,5’ | $^{2}$Tyr-5,5’,7-OH |
| 7 | 156.2 C | | $^{2}$Tyr-5,5’,6,6’,7-OH | | |
| 7-OH | | 9.23 s | | | $^{2}$Tyr-6,6’ |
| $OCH_3$ | 51.9 $CH_3$ | 3.53 s | | | |

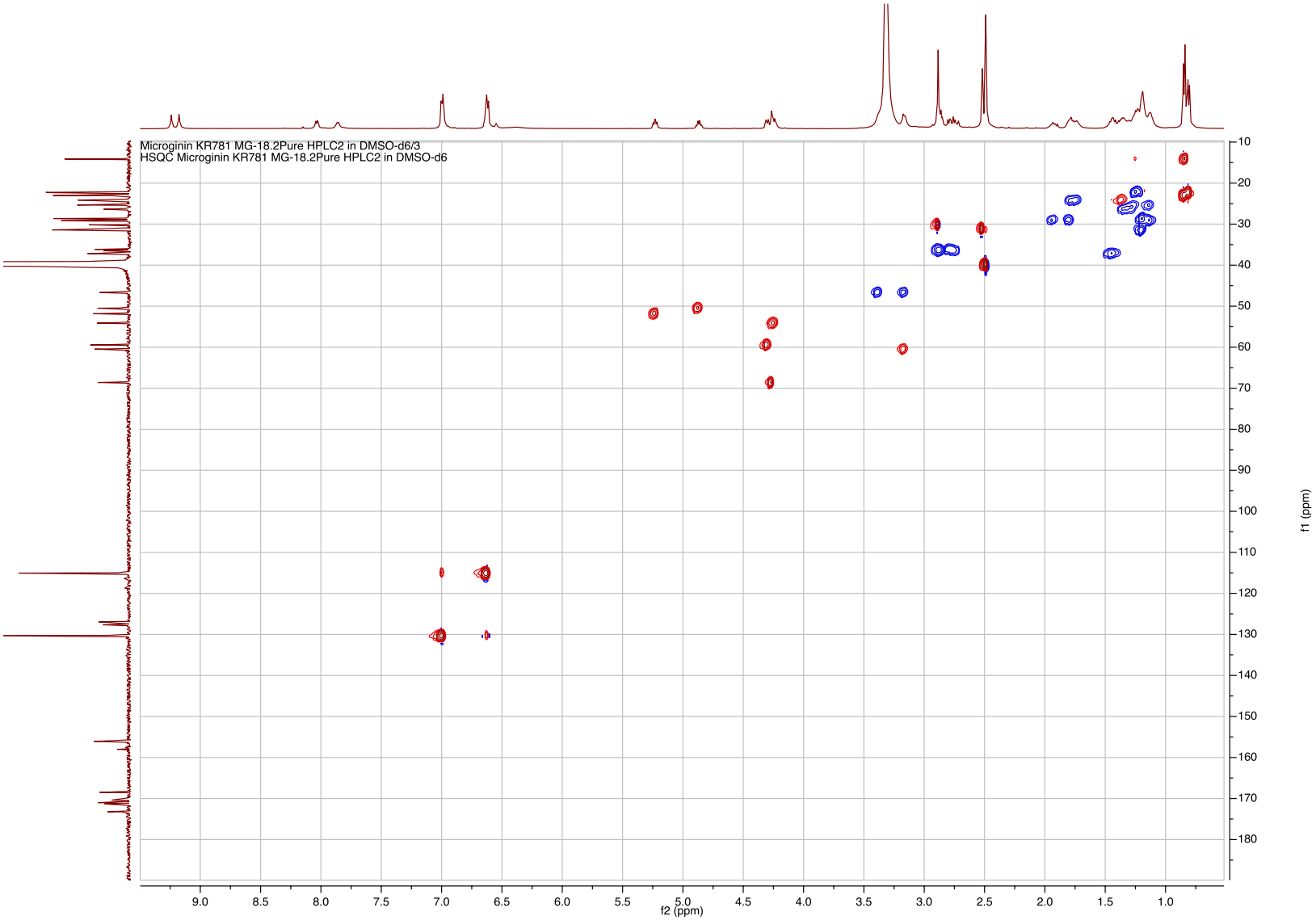
S68. $^{1}$H NMR Spectrum of Microginin KR781 (**7**) in DMSO-$d_6$



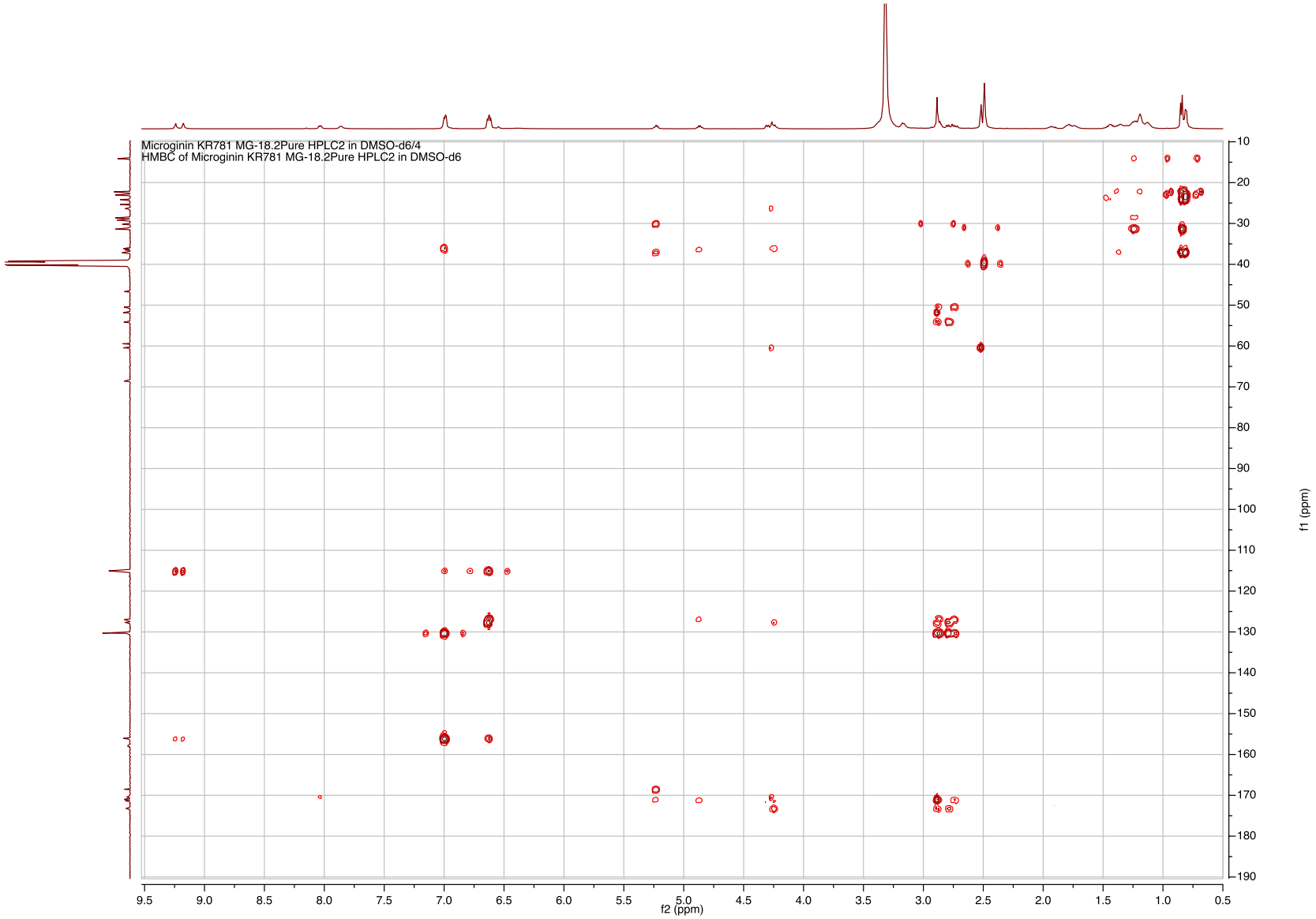
S69. $^{13}$C NMR Spectrum of Microginin KR781 (**7**) in DMSO-$d_6$



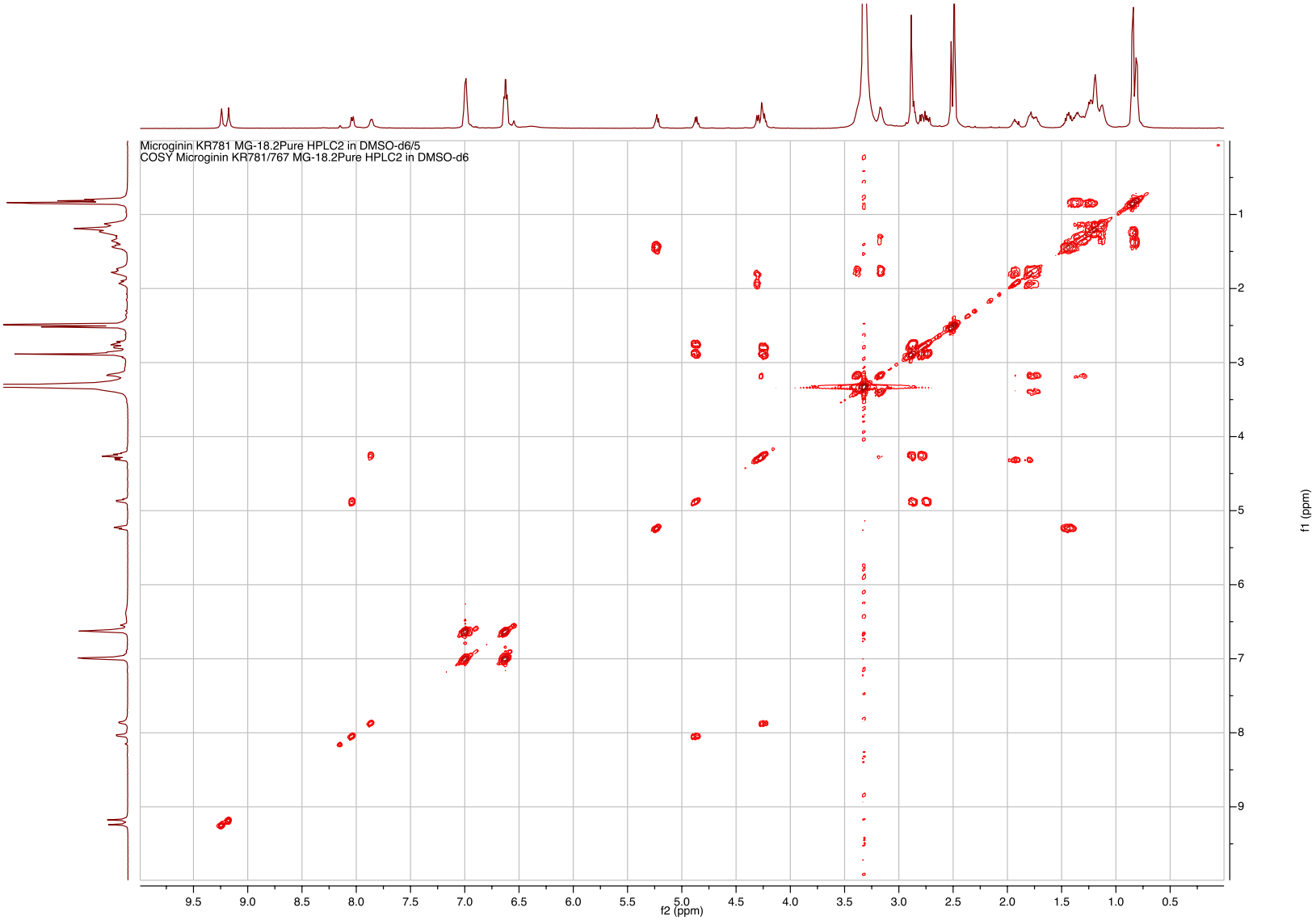
S70. HSQC Spectrum Microginin KR781 (**7**) in DMSO-$d_6$



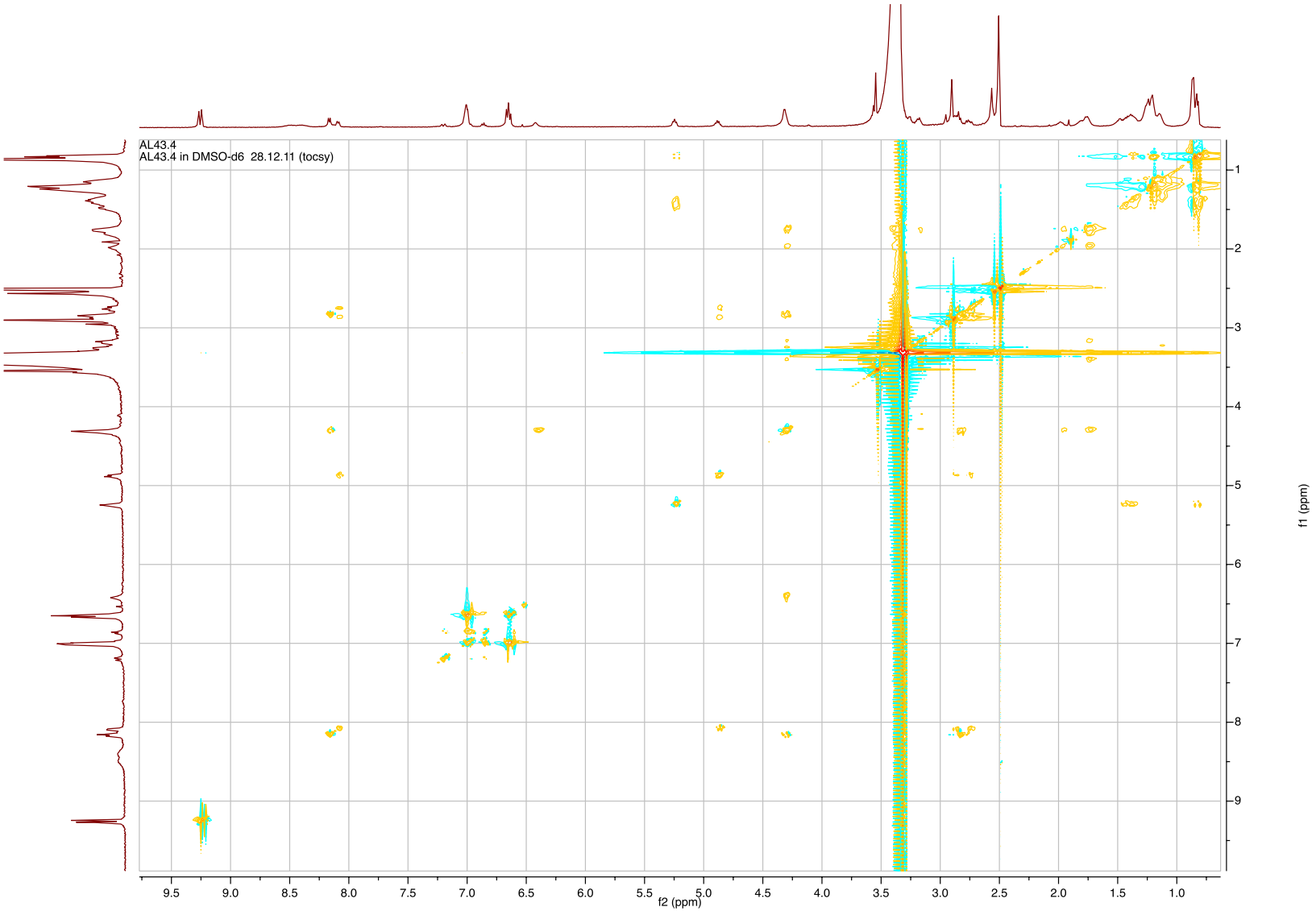
S71. HMBC Spectrum of Microginin KR781 (**7**) in DMSO-$d_6$



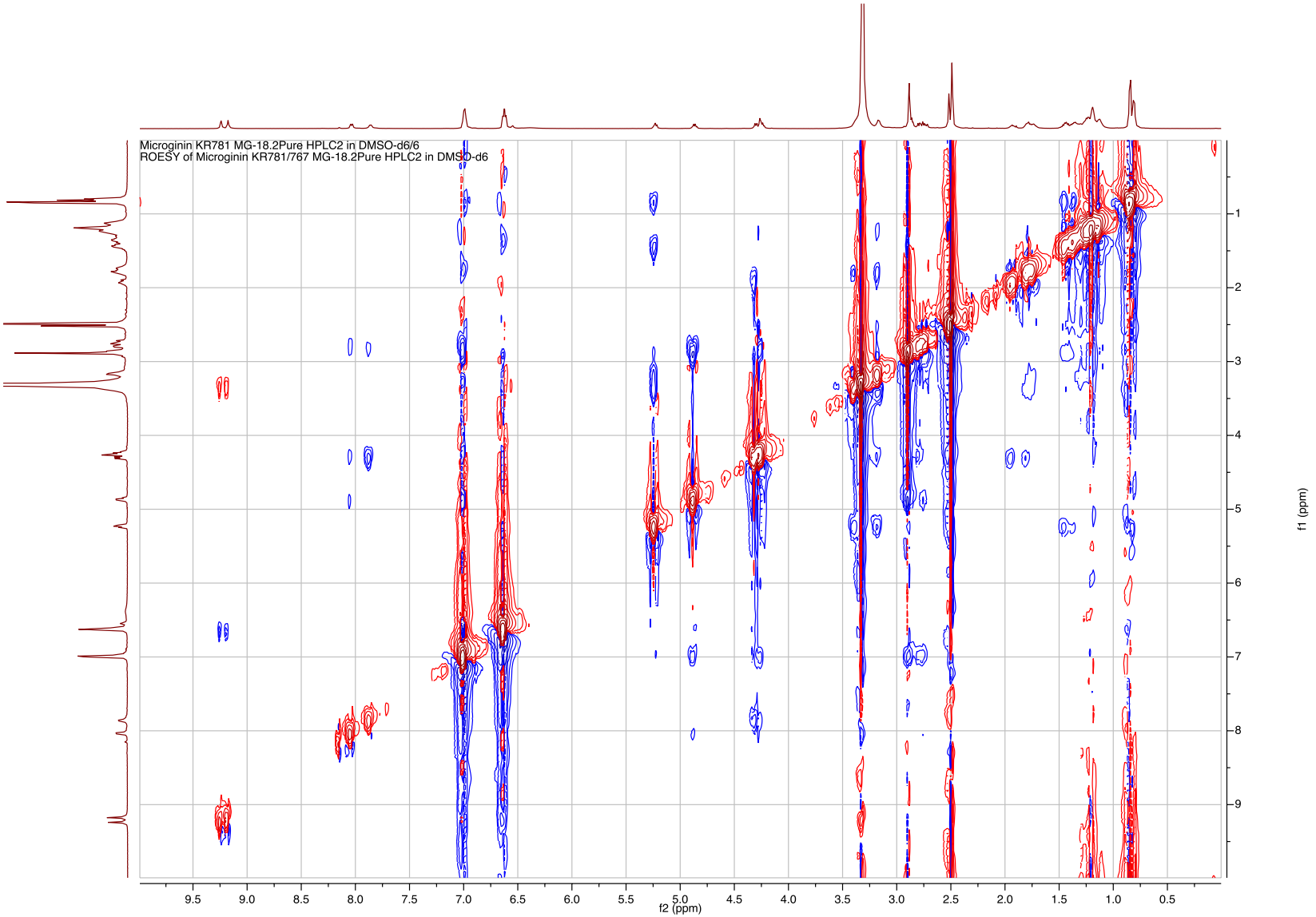
S72. COSY Spectrum of Microginin KR781 (**7**) in DMSO-$d_6$



S73. TOCSY Spectrum of Microginin KR781 (**7**) in DMSO-$d_6$



S74. ROESY Spectrum of Microginin KR781 (**7**) in DMSO-$d_6$



S75. HR ESI MS data of Microginin KR781 (**7**)

**Elemental Composition Report**

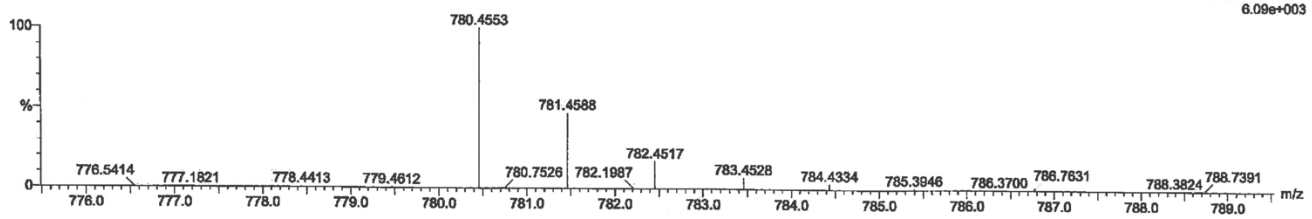


**Single Mass Analysis**
Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
65 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 40-45 H: 60-65 N: 0-10 O: 0-15
AL43.4
Carmell411b 62 (2.380) Cm (62)

Anat Lodin

1: TOF MS ES-
6.09e+003



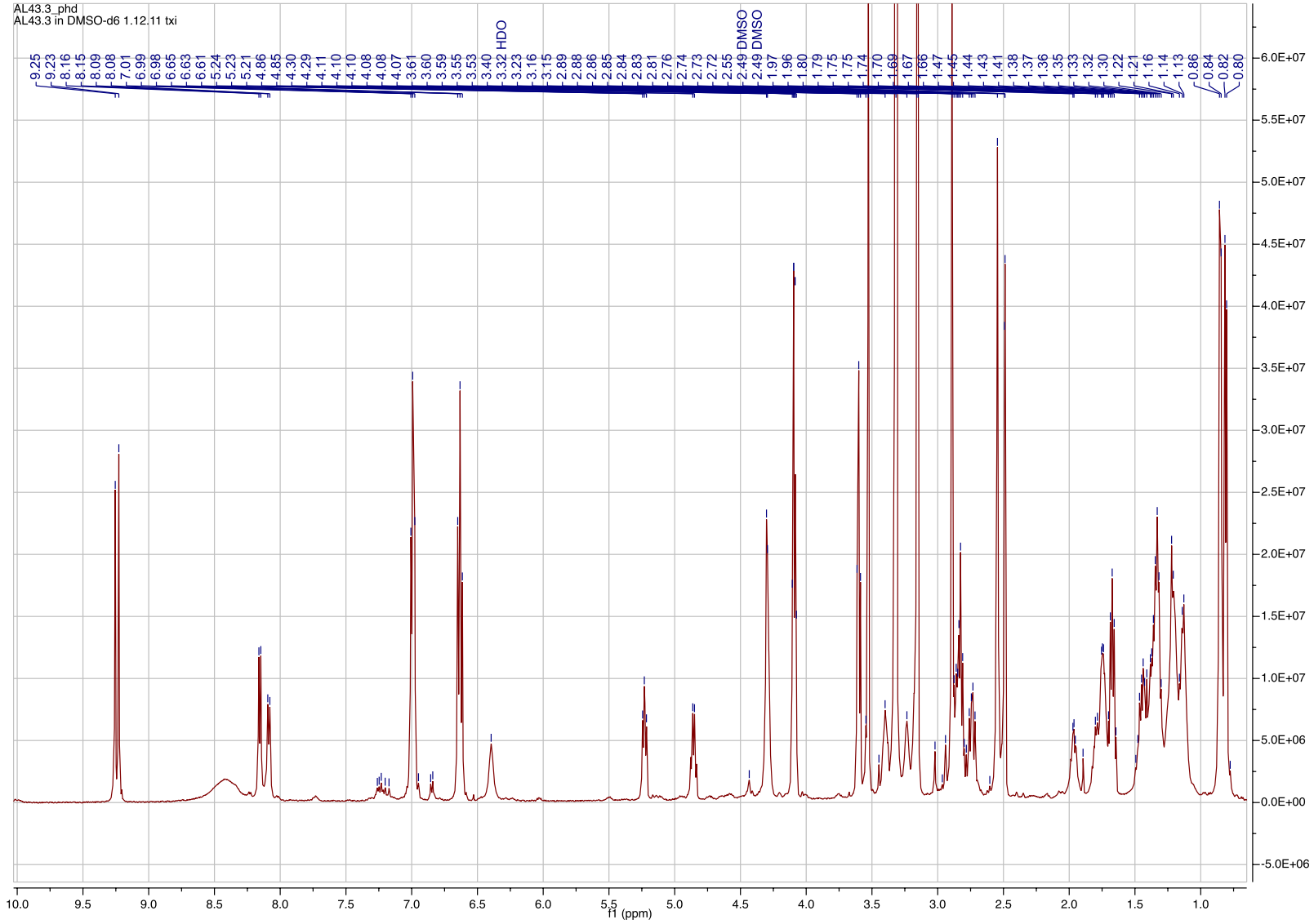

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | |
| Maximum: | | 5.0 | 2.0 | 50.0 | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
| 780.4553 | 780.4548 | 0.5 | 0.6 | 14.5 | 59.8 | 0.0 | C42 H62 N5 O9 |

S76. **Table S9**. NMR Data (500/125 MHz) of Microginin KR815 (**8**) in DMSO-$d_6$

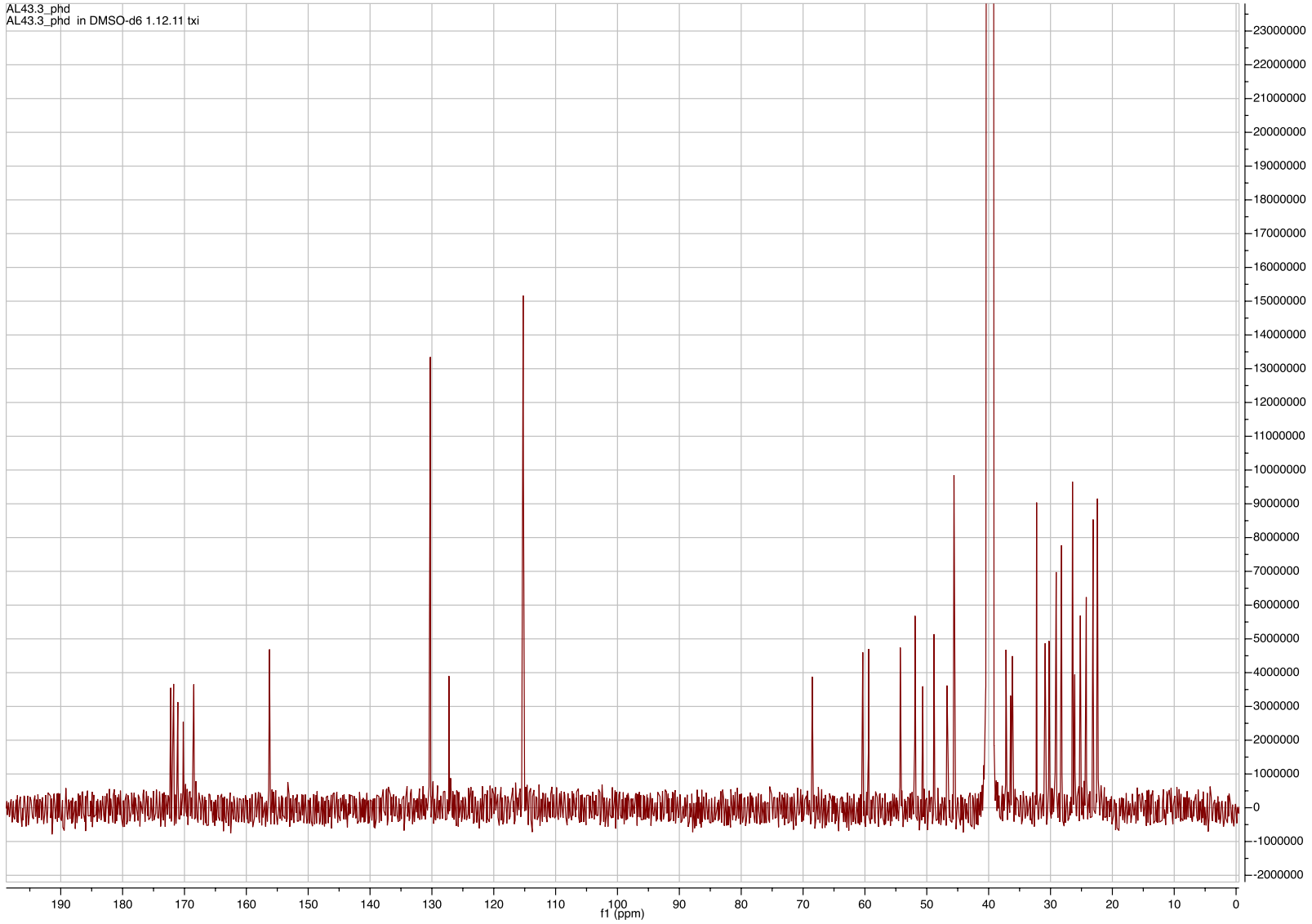
| Position | $\delta_C$ | $\delta_H$ Multiplicity, *J* (Hz) | HMBC correlations | COSY correlations | NOESY correlations |
|---|---|---|---|---|---|
| Ahda 1 | 170.1 C | | Ahda-2, $^1$Tyr-2,NH | | |
| 2 | 68.4 CH | 4.30 brs | | Ahda-2-OH,3 | Ahda-2-OH,3,3-*N*$CH_3$, $^1$Tyr-NH |
| 2-OH | | 6.40 brm | | Ahda-2 | Ahda-2,3 |
| 3 | 60.3 CH | 3.24 brm | Ahda-2,3-*N*$CH_3$ | Ahda-2,4,4’ | Ahda-2,2-OH |
| 3-NH | | 8.42 brm | | 3-*N*$CH_3$ | Ahda-3-*N*$CH_3$ |
| 3-*N*$CH_3$ | 30.8 $CH_3$ | 2.55 brs | | Ahda-3-NH | Ahda-2,2-OH,3,3-NH |
| 4 | 26.0 $CH_2$ | 1.39 m | Ahda-2,5,5’ | Ahda-3,4’,5,5’ | |
| | | 1.31 m | | Ahda-3,4,5,5’ | |
| 5 | 25.1 $CH_2$ | 1.24 m | Ahda-4,4’,6 | Ahda-4,4’,5’,6 | |
| | | 1.13 m | | Ahda-4,4’,5,6 | |
| 6 | 29.0 $CH_2$ | 1.13 m | Ahda-4,5,7,8 | Ahda-7 | |
| 7 | 28.2 $CH_2$ | 1.22 m | Ahda-5,5’6,8 | Ahda-8 | |
| 8 | 26.4 $CH_2$ | 1.33 tt, 7.6,7.1 | Ahda-6’7,9,10 | Ahda-7,9 | |
| 9 | 32.2 $CH_2$ | 1.67 tt, 7.6,6.6 | Ahda-8,10 | Ahda-8,10 | |
| 10 | 45.5 $CH_2$ | 3.60 t, 6.6 | Ahda-9,8 | Ahda-9 | |
| $^1$Tyr 1 | 171.0 C | | $^1$Tyr-2,3,3’, *N*MeLeu-2, *N*$CH_3$ | | |
| 2 | 50.6 CH | 4.86 ddd, 8.0,6.6,6.0 | $^1$Tyr-3,3’ | $^1$Tyr-2-NH,3,3’ | $^1$Tyr-2-NH,3,3’,5,5’, *N*MeLeu-*N*Me |
| 2-NH | | 8.09 d, 8.0 | | $^1$Tyr-2 | $^1$Tyr-2,3,3’, Ahda-2 |
| 3 | 36.4 $CH_2$ | 2.85 m | $^1$Tyr-2,5,5’ | $^1$Tyr-2,3’ | $^1$Tyr-2,2-NH,3’,5,5’ |
| | | 2.74 dd, 13.9,8.0 | | $^1$Tyr-2,3 | $^1$Tyr-2,2-NH,3,5,5’ |
| 4 | 126.9 C | | $^1$Tyr-2,3,3’,6,6’ | | |
| 5,5’ | 130.3 CH | 6.99 d, 8.4 | $^1$Tyr-3,3’,5’,5 | $^1$Tyr-6,6’ | $^1$Tyr-2,3,3’,6,6’ |
| 6,6’ | 115.2 CH | 6.62 d, 8.4 | $^1$Tyr-5,5’,6’,6,7-OH | $^1$Tyr-5,5’ | $^1$Tyr-5,5’,7-OH |
| 7 | 156.2 C | | $^1$Tyr-5,5’,6,6’,7-OH | | |
| 7-OH | | 9.25 s | | | $^1$Tyr-6,6’ |
| *N*MeLeu 1 | 168.4 C | | *N*MeLeu-2,3,3’ | | |

| | | | | | |
|---|---|---|---|---|---|
| 2 | 51.9 CH | 5.23 dd, 8.0,6.5 | *N*MeLeu-3,3',*N*Me | *N*MeLeu-3,3' | *N*MeLeu-3,3',5,6,*N*Me, Pro-5,5' |
| 2-*N*$CH_3$ | 30.2 $CH_3$ | 2.89 s | *N*MeLeu-2 | | *N*MeLeu-2, $^{1}$Tyr-2 |
| 3 | 37.1 $CH_2$ | 1.47 m | *N*MeLeu-2,4,5,6 | *N*MeLeu-2,3',4 | *N*MeLeu-2,5,6 |
| | | 1.41 m | | *N*MeLeu-2,3,4 | *N*MeLeu-2,5,6 |
| 4 | 24.2 CH | 1.38 m | *N*MeLeu-2,3,3',5,6 | *N*MeLeu-3,3',5,6 | *N*MeLeu-2 |
| 5 | 22.4 $CH_3$ | 0.81 d, 6.5 | *N*MeLeu-3,3',4,6 | *N*MeLeu-4 | *N*MeLeu-2,3,3' |
| 6 | 23.0 $CH_3$ | 0.85 d, 6.5 | *N*MeLeu-3,3',4,5 | *N*MeLeu-4 | *N*MeLeu-2,3,3' |
| Pro 1 | 171.7 C | | Pro-2,3, $^{2}$Tyr-NH | | |
| 2 | 59.3 CH | 4.29 m | | Pro-3,3' | Pro-3,3',5' |
| 3 | 29.1 $CH_2$ | 1.97 m | Pro-2,4,4',5,5' | Pro-2,3',4,4' | Pro-2 |
| | | 1.74 m | | Pro-2,3,4,4',5' | Pro-2 |
| 4 | 24.3 $CH_2$ | 1.78 m | Pro-2,3,3'5,5' | Pro-3,3',5,5' | |
| | | 1.73 m | | Pro-3,3',5,5' | |
| 5 | 46.7 $CH_2$ | 3.40 m | Pro-2 | Pro-4,4',5' | Pro-5', *N*MeLeu-2 |
| | | 3.18 m | | Pro-3,4,4',5 | Pro-2,5, *N*MeLeu-2 |
| $^{2}$Tyr 1 | 172.2 C | | $^{2}$Tyr-2,3,3',$OCH_3$ | | |
| 2 | 54.2 CH | 4.30 m | $^{2}$Tyr-2-NH,3,3' | $^{2}$Tyr-2-NH,3,3' | $^{2}$Tyr-3,3',5,5',NH |
| 2-NH | | 8.15 d, 7.6 | | $^{2}$Tyr-2 | $^{2}$Tyr-2,3,3' |
| 3 | 36.1 $CH_2$ | 2.86 m | $^{2}$Tyr-2,2-NH,5,5' | $^{2}$Tyr-2,3' | $^{2}$Tyr-2,3',5,5',NH |
| | | 2.82 m | | $^{2}$Tyr-2,3 | $^{2}$Tyr-2,3,5,5',NH |
| 4 | 127.2 C | | $^{2}$Tyr-2,3,3',6,6' | | |
| 5,5' | 130.2 CH | 7.00 d, 8.4 | $^{2}$Tyr-3,3',5',5 | $^{2}$Tyr-6,6' | $^{2}$Tyr-2,3,3',6,6' |
| 6,6' | 115.1 CH | 6.64 d, 8.4 | $^{2}$Tyr-5,5',6',6,7-OH | $^{2}$Tyr-5,5' | $^{2}$Tyr-5,5',7-OH |
| 7 | 156.2 C | | $^{2}$Tyr-5,5',6,6',7-OH | | |
| 7-OH | | 9.23 s | | | $^{2}$Tyr-6,6' |
| $OCH_3$ | 51.8 $CH_3$ | 3.53 s | | | |

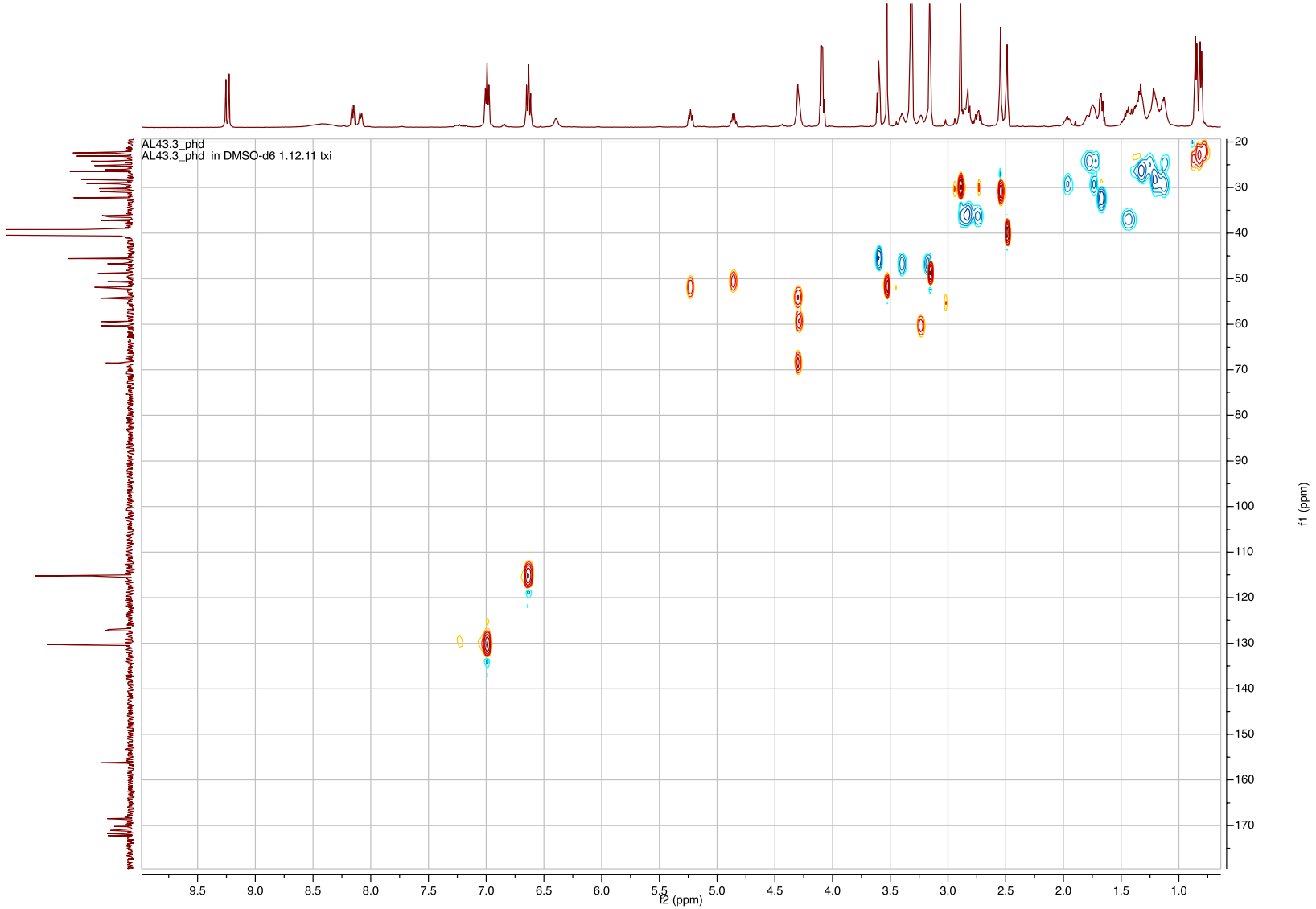
S78. $^{1}$H NMR Spectrum of Microginin KR815 (**8**) in DMSO-$d_6$



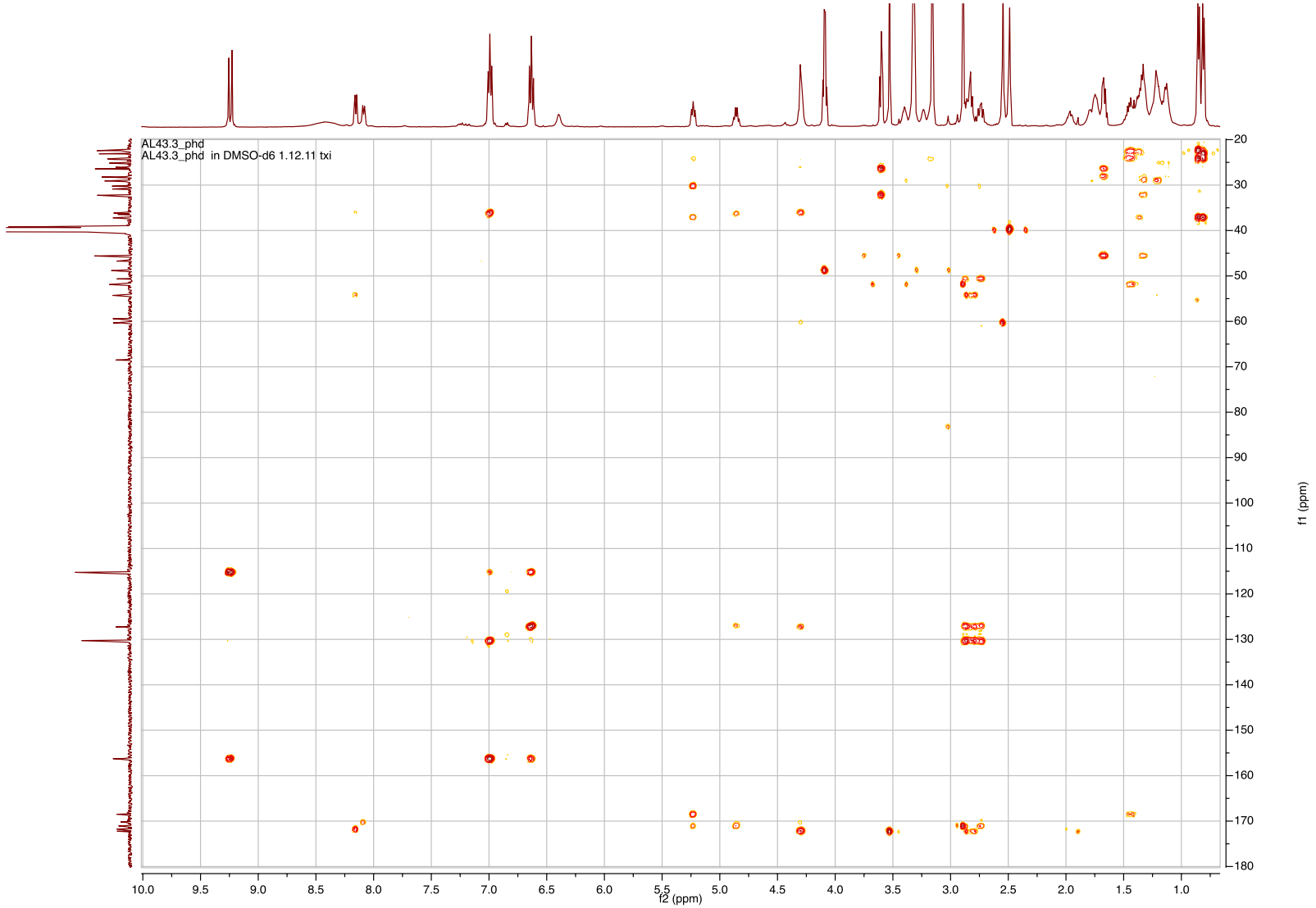
S79. $^{13}$C NMR Spectrum of Microginin KR815 (**8**) in DMSO-$d_6$



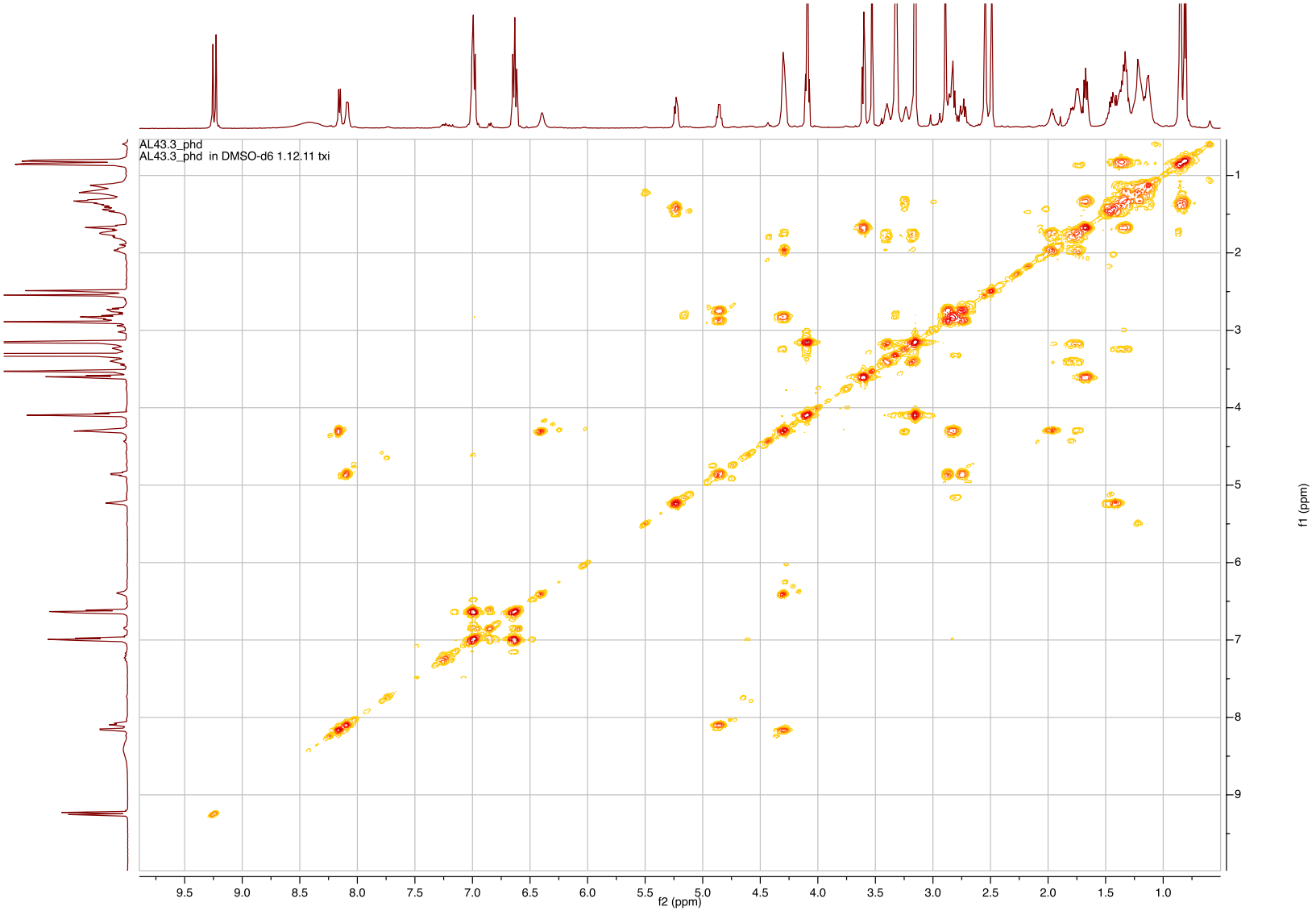
S80. HSQC Spectrum Microginin KR815 (**8**) in DMSO-$d_6$



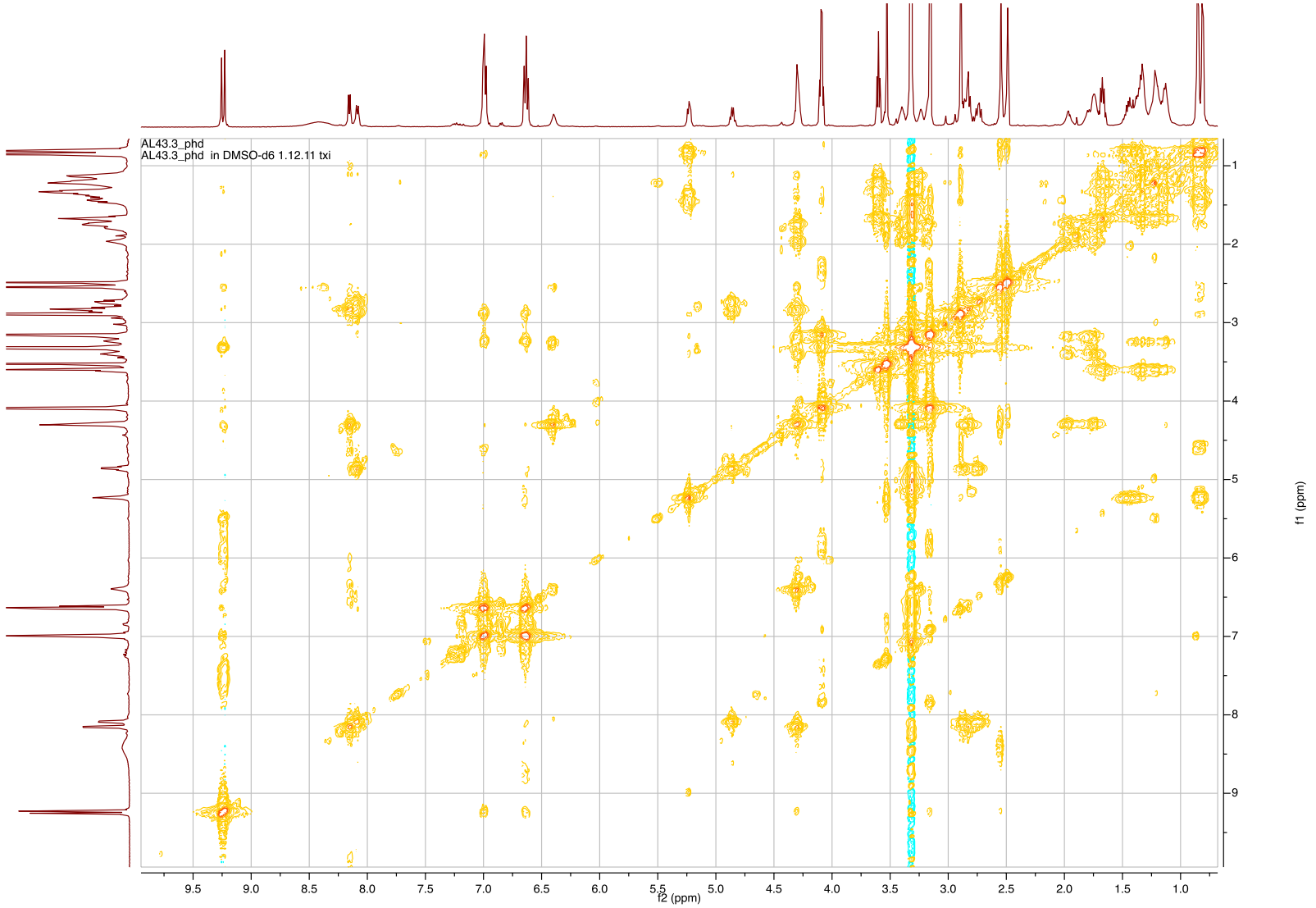
S81. HMBC Spectrum of Microginin KR815 (**8**) in DMSO-$d_6$



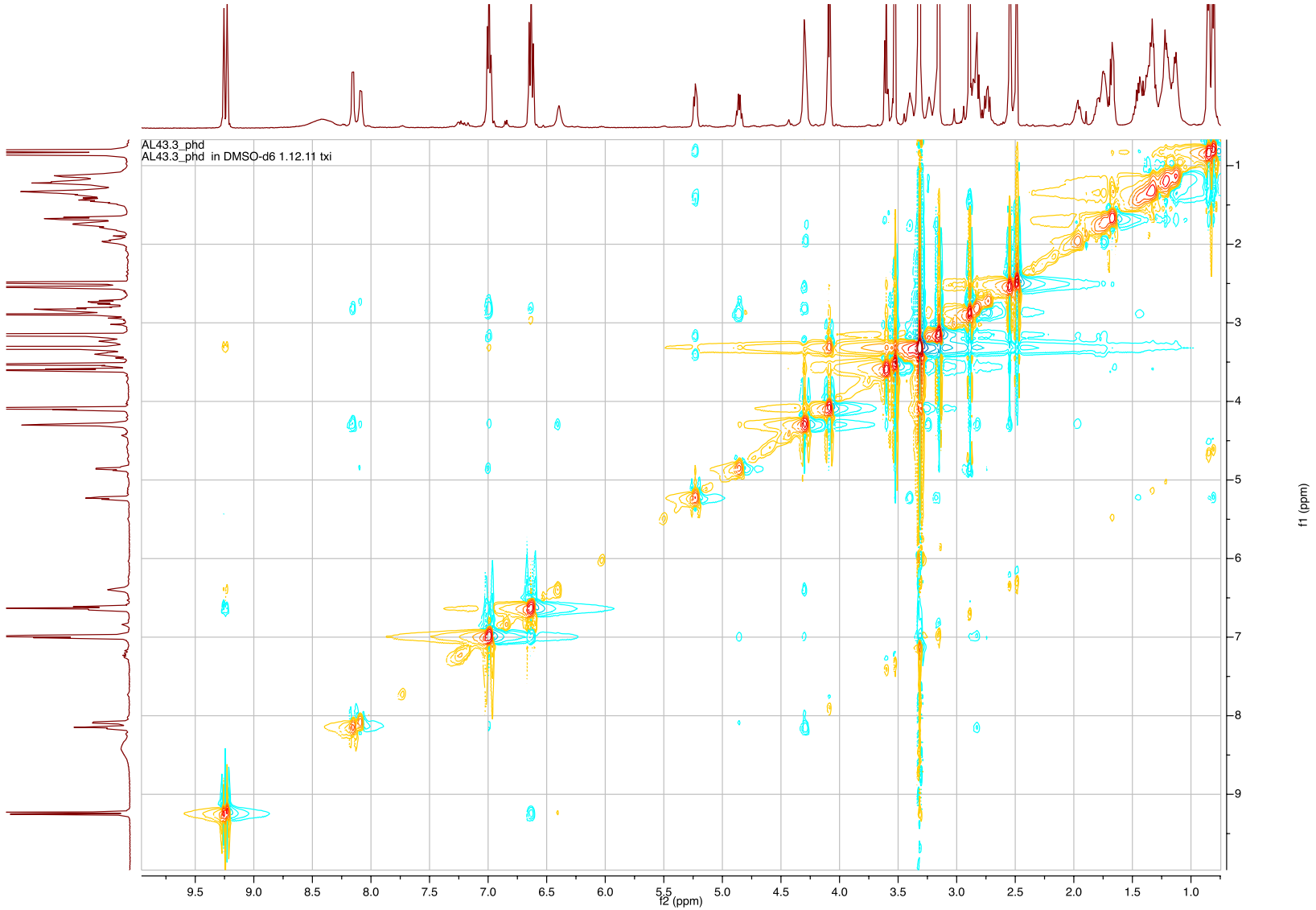
S82. COSY Spectrum of Microginin KR815 (**8**) in DMSO-$d_6$



S83. TOCSY Spectrum of Microginin KR815 (**8**) in DMSO-$d_6$



S84. ROESY Spectrum of Microginin KR815 (**8**) in DMSO-$d_6$



S85. HR ESI MS data of Microginin KR815 (**8**)

**Elemental Composition Report**



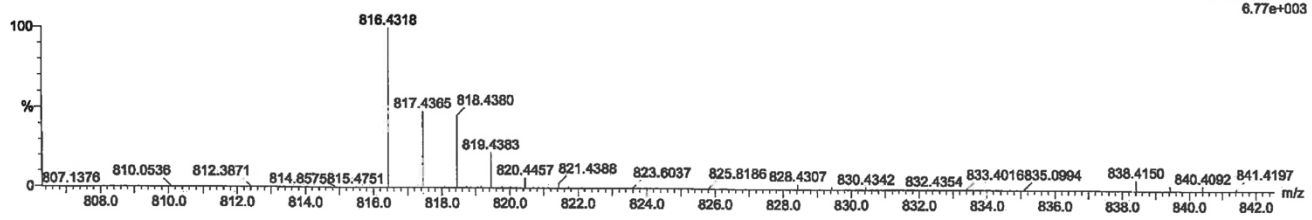
**Single Mass Analysis**
Tolerance = 1.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
447 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 38-50 H: 55-70 N: 0-10 O: 0-15 Cl: 0-2

AL43.3
carmeli407 132 (5.803) Cm (132)

Anat Lodin

1: TOF MS ES+
6.77e+003



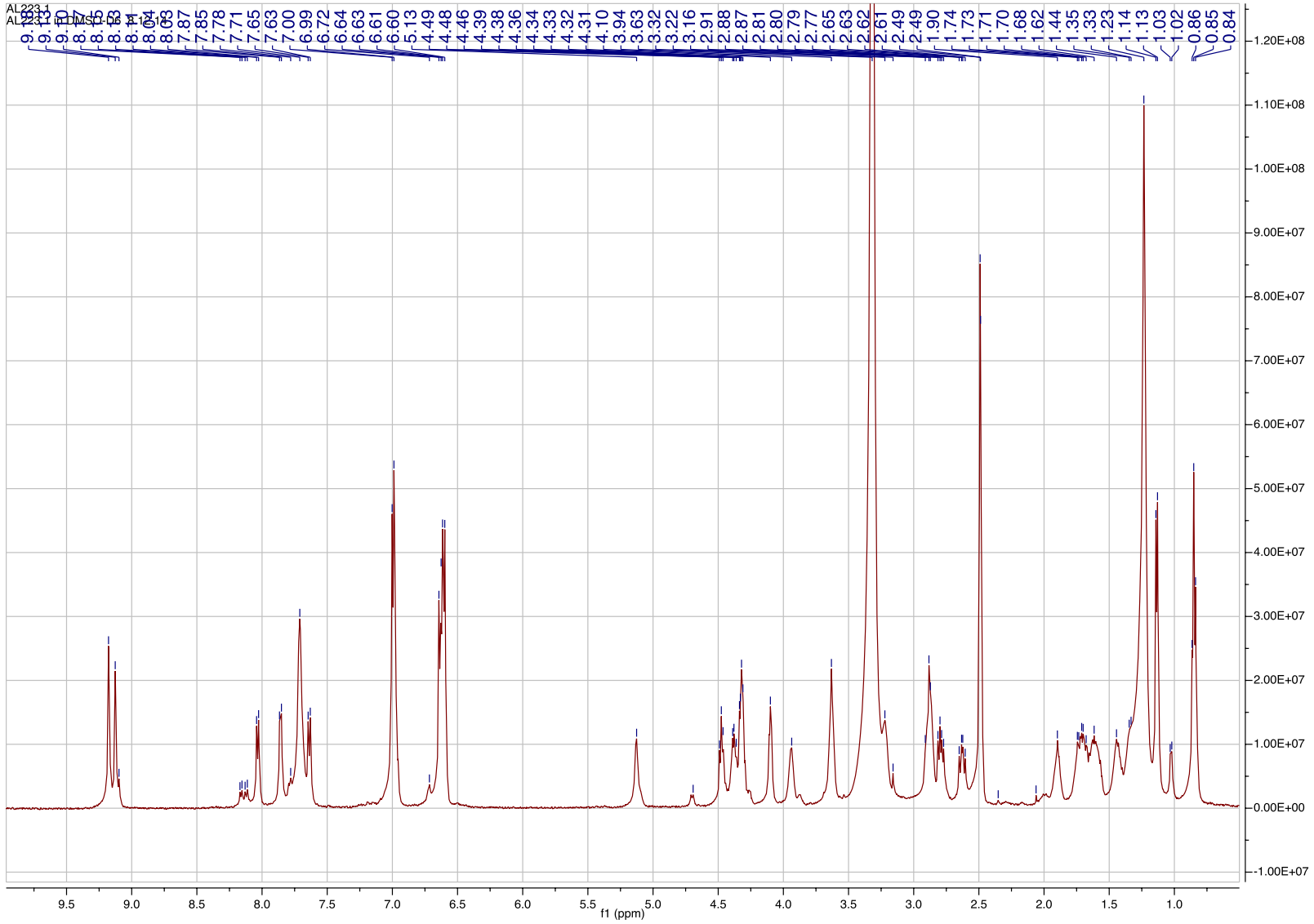

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | |
| Maximum: | | 5.0 | 1.0 | 50.0 | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
| 816.4318 | 816.4314 | 0.4 | 0.5 | 13.5 | 76.4 | 0.0 | C42 H63 N5 O9 Cl |
| | 816.4323 | -0.5 | -0.6 | 17.5 | 82.9 | 6.5 | C47 H62 N O11 |

S86. **Table S10**. NMR Data (500/125 MHz) of Microginin FR3 (**9**) in DMSO-$d_6$

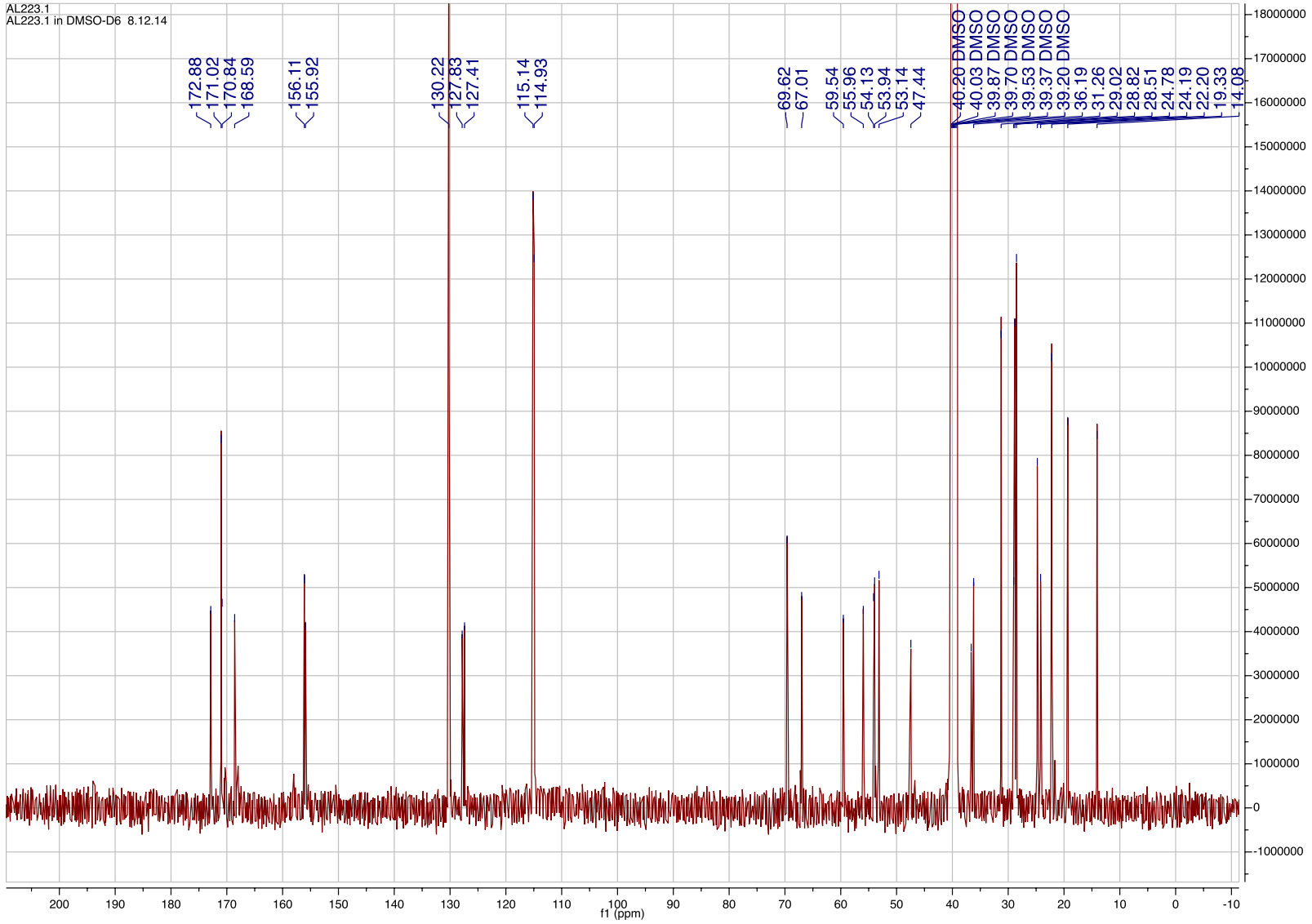
| Position | $\delta_C$ | $\delta_H$ Multiplicity, *J* (Hz) | HMBC correlations | COSY correlations | NOESY correlations |
|---|---|---|---|---|---|
| Ahda 1 | 170.8 C | | Ahda-2,2-OH, Thr-2,NH | | |
| 2 | 69.6 CH | 4.10 t, 4.6 | Ahda-2-OH | Ahda-2-OH,3 | Ahda-2-OH,3,3-$NH_3$,4,4',5',5', Thr-2-NH |
| 2-OH | | 6.61 m | | Ahda-2 | Ahda-2,3,4 |
| 3 | 53.1 CH | 3.22 m | Ahda-2-OH | Ahda-3-$NH_3$,4,4' | Ahda-2,2-OH,3-$NH_3$,4,4'5,5', Thr-2-NH |
| 3-$NH_3$ | | 7.71 m | | Ahda-3 | Ahda-2,3, ,4,4'5,5' |
| 4 | 28.8 $CH_2$ | 1.59 m | Ahda-2,5,5',6 | Ahda-3,4',5,5' | Ahda-2,2-OH,3,3-$NH_3$,4',5',5' |
| | | 1.44 m | | Ahda-3,4,5,5' | Ahda-2,3,3-$NH_3$,4,5,5' |
| 5 | 24.8 $CH_2$ | 1.34 m | Ahda-6,7 | Ahda-4,4',5',6 | Ahda-2,3,3-$NH_3$,4,4',5' |
| | | 1.29 m | | Ahda-4,4',5,6 | Ahda-2,3,3-$NH_3$,4,4',5 |
| 6 | 28.5 $CH_2$ | 1.23 m | Ahda-5,5',7,8 | Ahda-5,5' | |
| 7 | 28.9 $CH_2$ | 1.23 m | | | |
| 8 | 31.3 $CH_2$ | 1.23 m | Ahda-7,9,10 | | |
| 9 | 22.2 $CH_2$ | 1.24 m | Ahda-8,10 | Ahda-10 | Ahda-10 |
| 10 | 14.1 $CH_3$ | 0.85 t, 6.8 | Ahda-8,9 | Ahda-9 | Ahda-9 |
| Thr 1 | 168.6 C | | Thr-2 | | |
| 2 | 56.0 CH | 4.48 dd, 7.2,6.6 | Thr-2-OH,4 | Thr-2-NH,3 | Thr-2-NH,3,4, Pro-5 |
| 2-NH | | 7.86 d, 7.2 | | Thr-2 | Thr-2,3,4, Ahda-2,3 |
| 3 | 67.0 CH | 3.94 brdq, 6.6,6.6 | Thr-2,3-OH,4 | Thr-2,3-OH,4 | Thr-2,2-NH,3-OH,4 |
| 3-OH | | 5.13 d, 3.6 | | Thr-3 | Thr-3,4 |
| 4 | 19.3 $CH_3$ | 1.14 d. 6.6 | Thr-2 | Thr-3 | Thr-2,2-NH,3,3-OH, $^2$Tyr-6,6' |
| Pro 1 | 171.0 C | | Pro-2,3, $^1$Tyr-NH | | |
| 2 | 59.5 CH | 4.32 dd, 7.8,3.2 | | Pro-3,3' | Pro-3,3' |
| 3 | 29.0 $CH_2$ | 1.90 m | Pro-4,4',5 | Pro-2,3',4,4' | Pro-2,3',5 |
| | | 1.69 m | | Pro-2,3,4,4' | Pro-2,3, $^1$Tyr-2-NH,5,5' |
| 4 | 24.2 $CH_2$ | 1.74 m | Pro-3,5 | Pro-3,3',4',5 | Pro-5 |
| | | 1.62 m | | Pro-3,3',4,5 | Pro-5, $^1$Tyr-5,5' |

| | | | | | |
|---|---|---|---|---|---|
| 5 | 47.4 $CH_2$ | 3.63 m | | Pro-4,4’ | Pro-3,4,4’, $^{1}$Tyr-5,5’, Thr-2 |
| $^{1}$Tyr 1 | 171.0 C | | $^{1}$Tyr-2,3,3’, $^{2}$Tyr-NH | | |
| 2 | 54.1 CH | 4.38 ddd, 9.5,8.2,4.8 | $^{1}$Tyr-2-NH,3,3’ | $^{1}$Tyr-2-NH,3,3’ | $^{1}$Tyr-2-NH,3,3’5,5’ $^{2}$Tyr-2-NH |
| 2-NH | | 7.64 d, 8.2 | | $^{1}$Tyr-2 | $^{1}$Tyr-2,3,3’, $^{2}$Tyr-2, Pro-3’,5 |
| 3 | 36.6 $CH_2$ | 2.87 dd, 13.8,4.8 | $^{1}$Tyr-2,2-NH,5,5’ | $^{1}$Tyr-2,3’ | $^{1}$Tyr-2,2-NH,5,5’ |
| | | 2.63 dd, 13.8,9.5 | | $^{1}$Tyr-2,3 | $^{1}$Tyr-2,2-NH,5,5’ |
| 4 | 127.8 C | | $^{1}$Tyr-3,3’,5,5’ | | |
| 5,5’ | 130.2 CH | 7.00 d, 8.5 | $^{1}$Tyr-3,3’,5’,5 | $^{1}$Tyr-6,6’ | $^{1}$Tyr-2,3,3’,6,6’, Pro-3’,4’,5, Thr-3,4 |
| 6,6’ | 114.9 CH | 6.61 d, 8.5 | $^{1}$Tyr-5,5’,6’,6,7-OH | $^{1}$Tyr-5,5’ | $^{1}$Tyr-5,5’,7-OH |
| 7 | 155.9 C | | $^{1}$Tyr-5,5’,6,6’,7-OH | | |
| 7-OH | | 9.13 s | | | $^{1}$Tyr-6,6’ |
| $^{2}$Tyr 1 | 172.9 C | | $^{2}$Tyr-2,3,3’ | | |
| 2 | 53.9 CH | 4.31 m | $^{2}$Tyr-2-NH,3,3’ | $^{2}$Tyr-2-NH,3,3’ | $^{2}$Tyr-2-NH,3,3’ |
| 2-NH | | 8.03 d, 7.6 | | $^{2}$Tyr-2 | $^{2}$Tyr-2,3,3’, $^{1}$Tyr-2 |
| 3 | 36.2 $CH_2$ | 2.89 dd, 14.1,5.9 | $^{2}$Tyr-2,5,5’ | $^{2}$Tyr-2,3’ | $^{2}$Tyr-2,2-NH, |
| | | 2.79 dd, 14.1,7.8 | | $^{2}$Tyr-2,3 | $^{2}$Tyr-2,2-NH, |
| 4 | 127.4 C | | $^{2}$Tyr-2,3,3’,5,5’ | | |
| 5,5’ | 130.2 CH | 7.00 d, 8.1 | $^{2}$Tyr-3,3’,5’,5 | $^{2}$Tyr-6,6’ | $^{2}$Tyr-2,3,3’,6,6’ |
| 6,6’ | 115.1 CH | 6.63 d, 8.1 | $^{2}$Tyr-5,5’,6’,6,7-OH | $^{2}$Tyr-5,5’ | $^{2}$Tyr-5,5’,7-OH, Thr-4 |
| 7 | 156.1 C | | $^{2}$Tyr-5,5’,6,6’7-OH | | |
| 7-OH | | 9.18 s | | | $^{2}$Tyr-6,6’ |

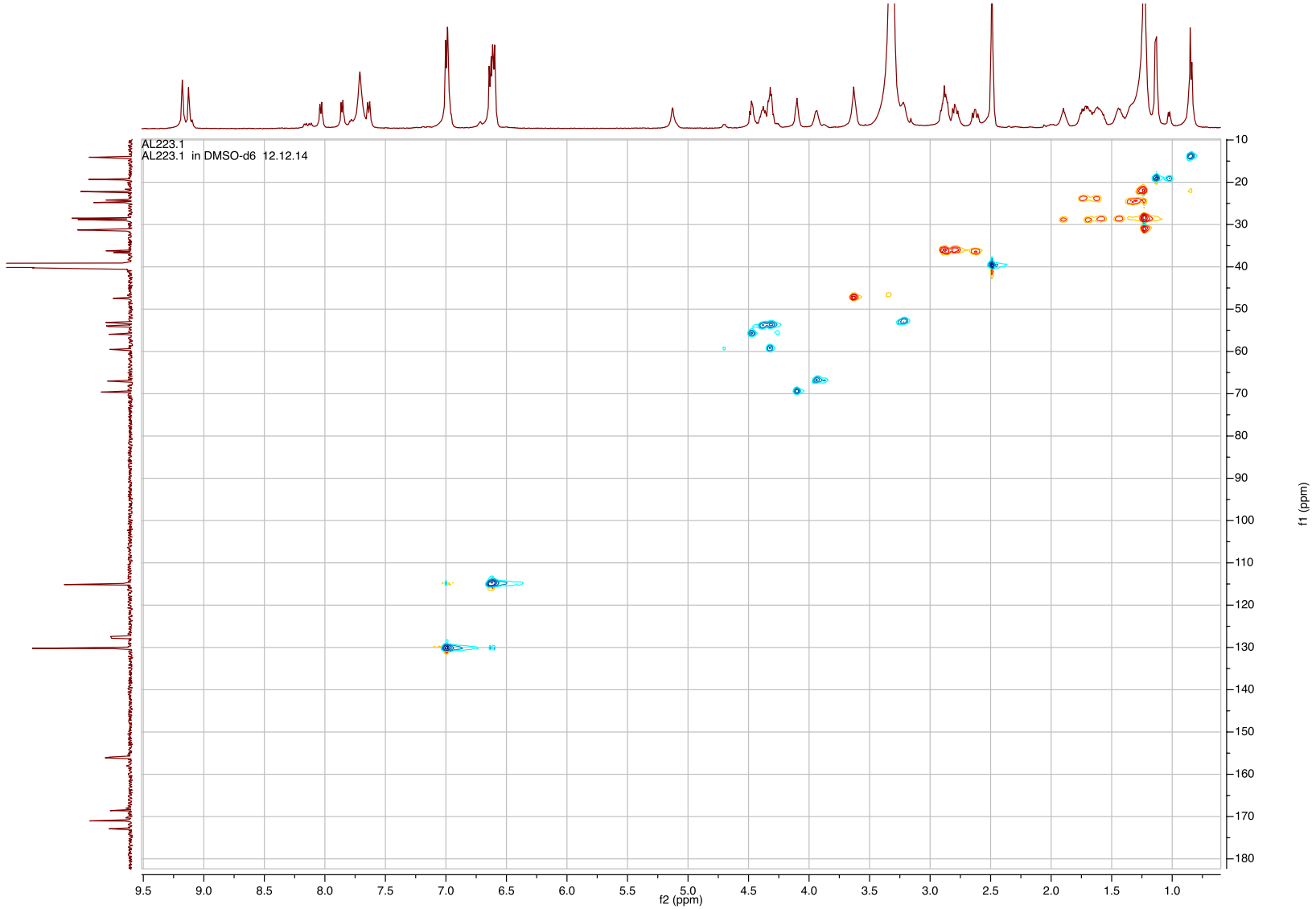
S88. $^{1}$H NMR Spectrum of Microginin FR3 (**9**) in DMSO-$d_6$



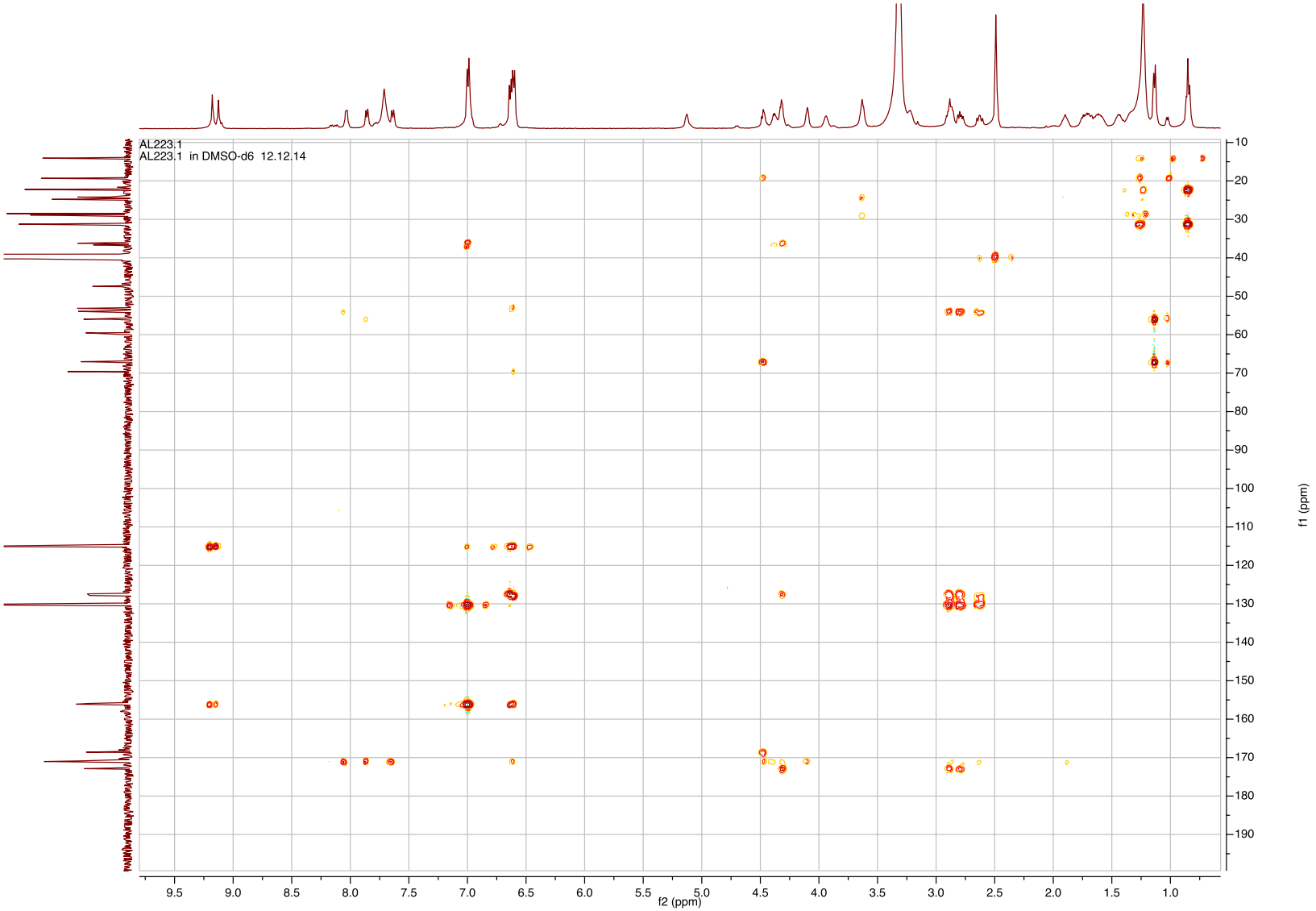
S89. $^{13}$C NMR Spectrum of Microginin FR3 (**9**) in DMSO-$d_6$



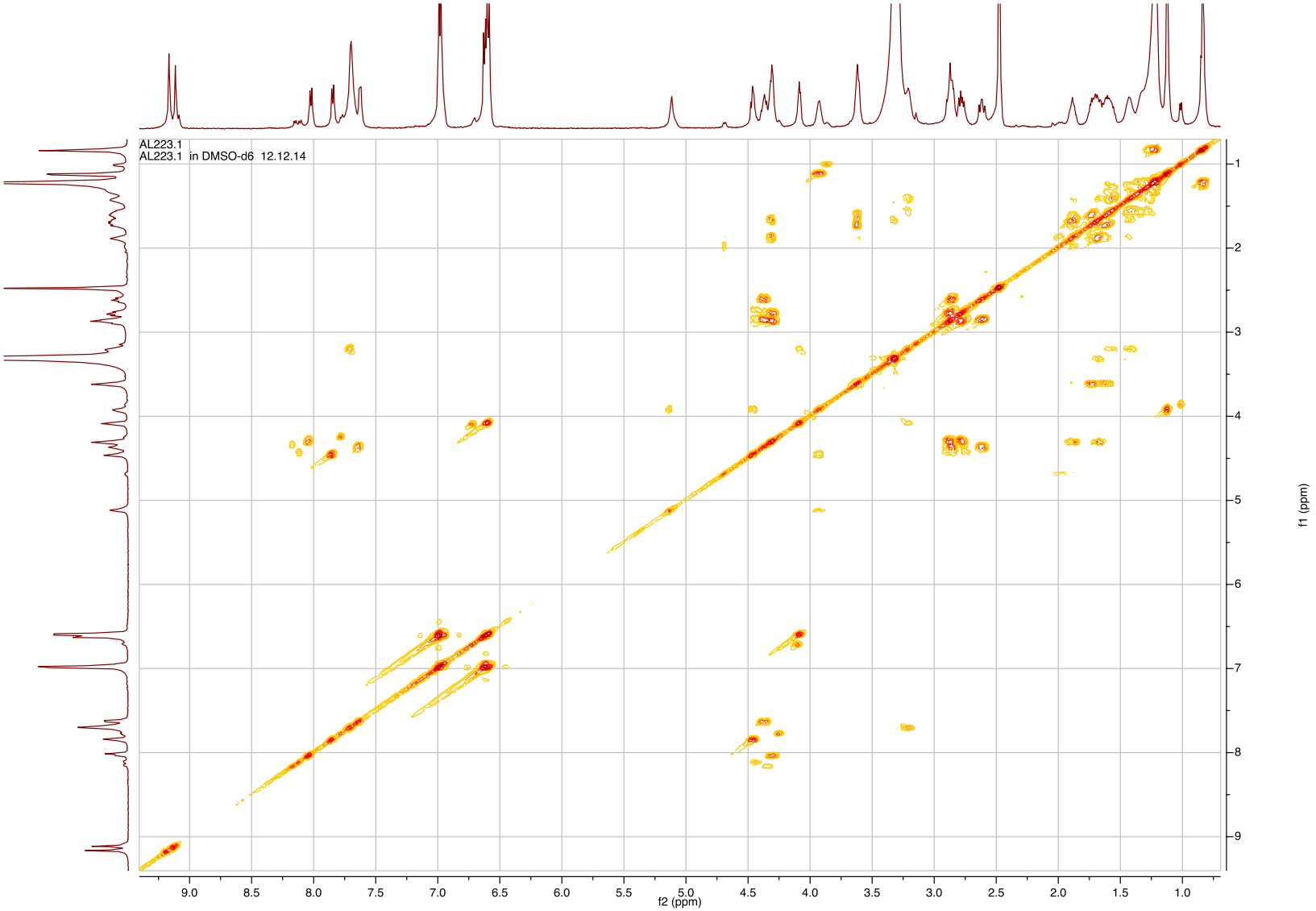
S90. HSQC Spectrum Microginin FR3 (**9**) in DMSO-$d_6$



S91. HMBC Spectrum of Microginin FR3 (**9**) in DMSO-$d_6$

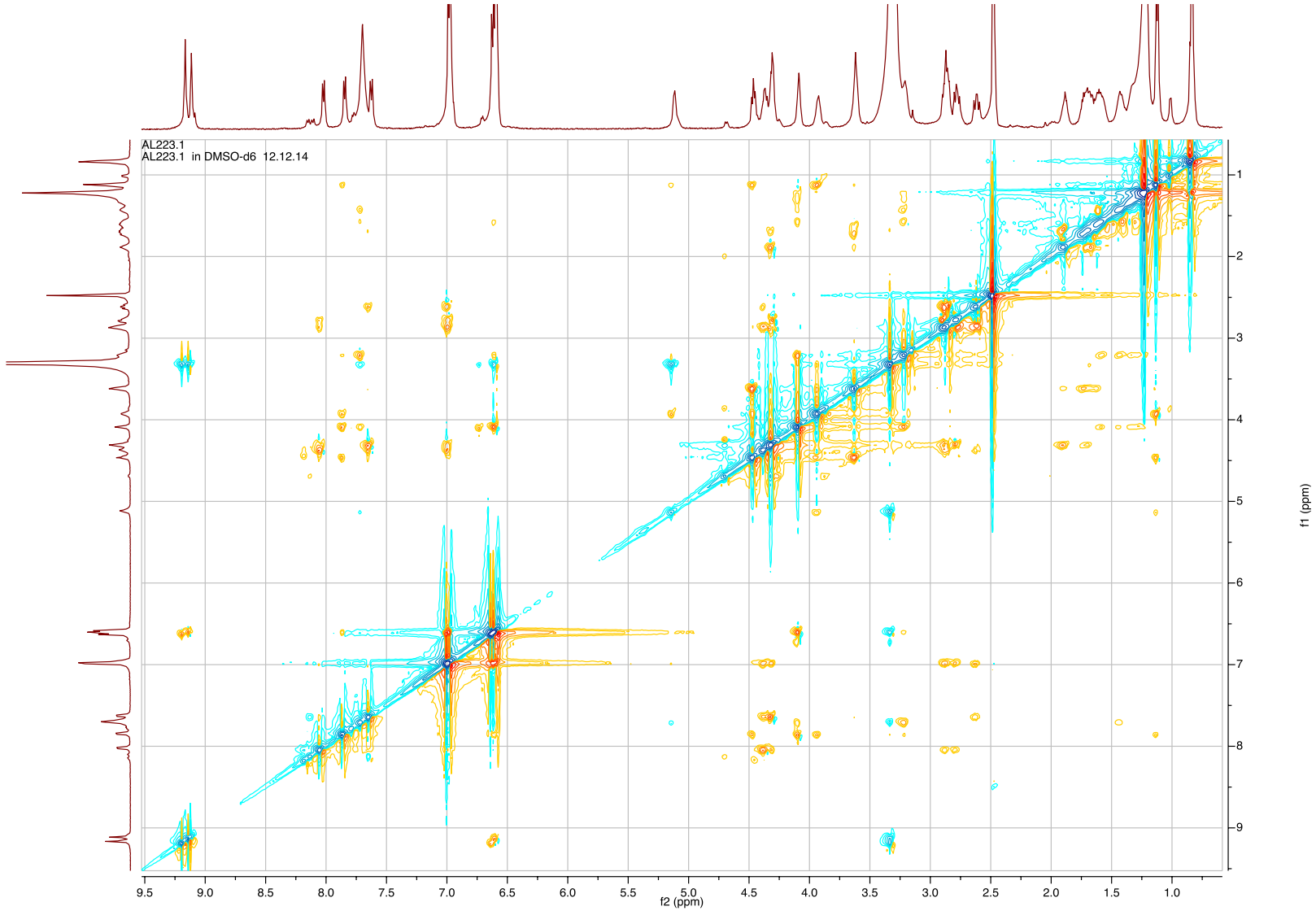


S92. COSY Spectrum of Microginin FR3 (**9**) in DMSO-$d_6$



S93. TOCSY Spectrum of Microginin FR3 (**9**) in DMSO-$d_6$

S94. ROESY Spectrum of Microginin FR3 (**9**) in DMSO-$d_6$



S95. HR ESI MS data of Microginin FR3 (**9**)

**Elemental Composition Report**



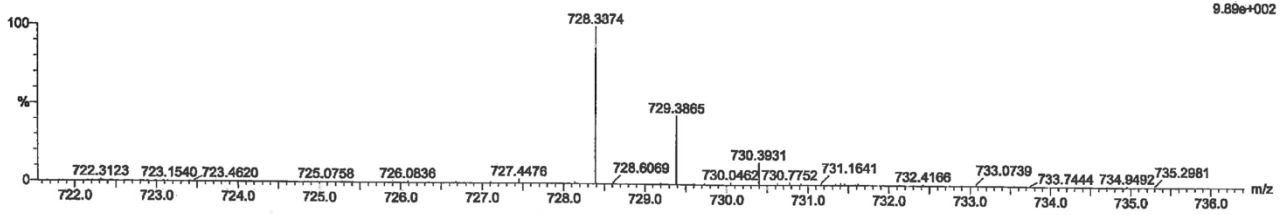
**Single Mass Analysis**
Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
140 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 35-45 H: 50-65 N: 0-10 O: 0-15

AL223.1
carmeli968 46 (2.033) Cm (46:47)

Anat Lodin

1: TOF MS ES+
9.89e+002



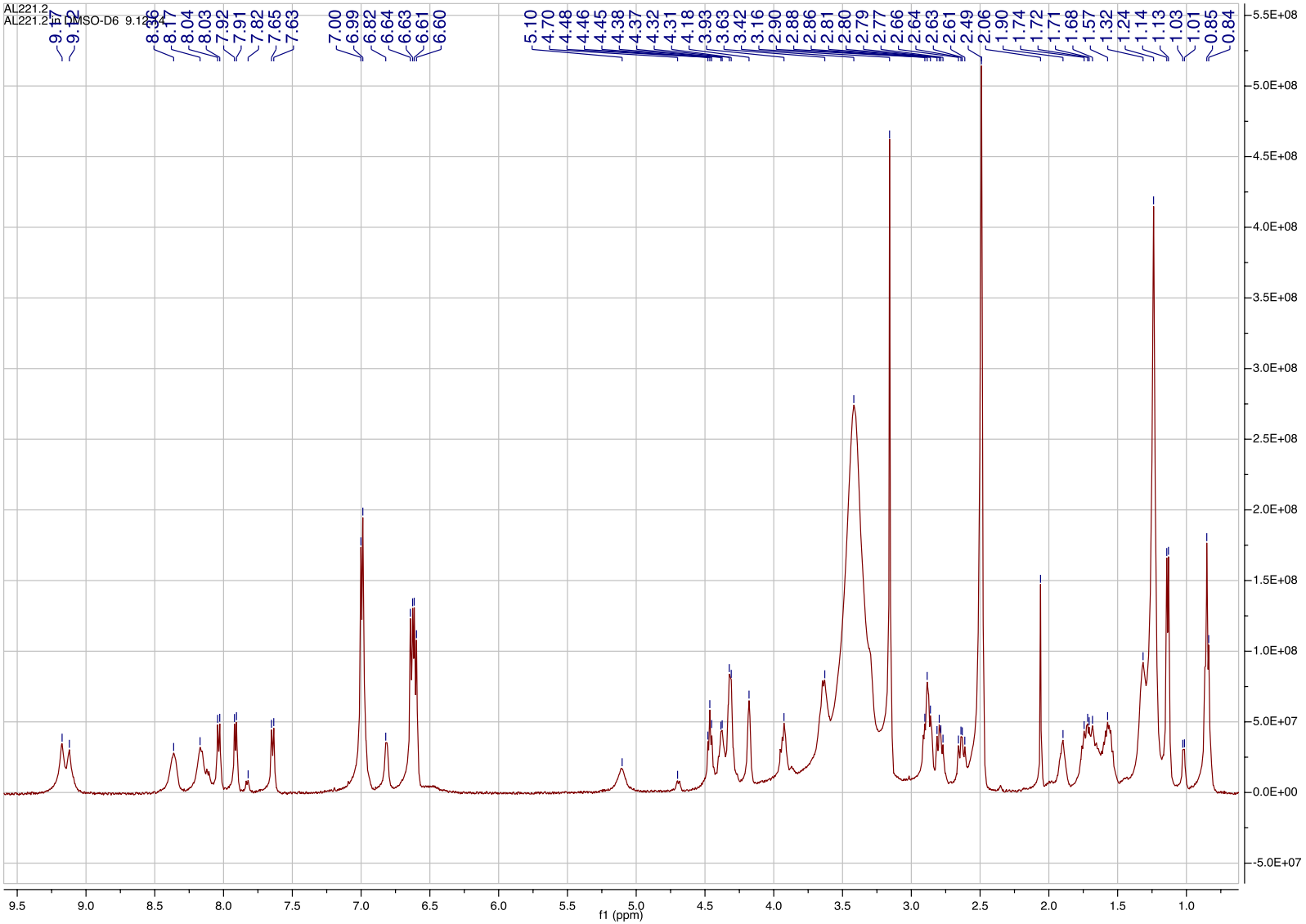

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | |
| Maximum: | | 5.0 | 2.0 | 50.0 | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
| 728.3874 | 728.3871 | 0.3 | 0.4 | 13.5 | 63.0 | 0.3 | C37 H54 N5 O10 ← |
| | 728.3884 | -1.0 | -1.4 | 18.5 | 64.0 | 1.3 | C38 H50 N9 O6 |

S96. **Table S11**. NMR Data (500/125 MHz) of Microginin FR4 (**10**) in DMSO-$d_6$

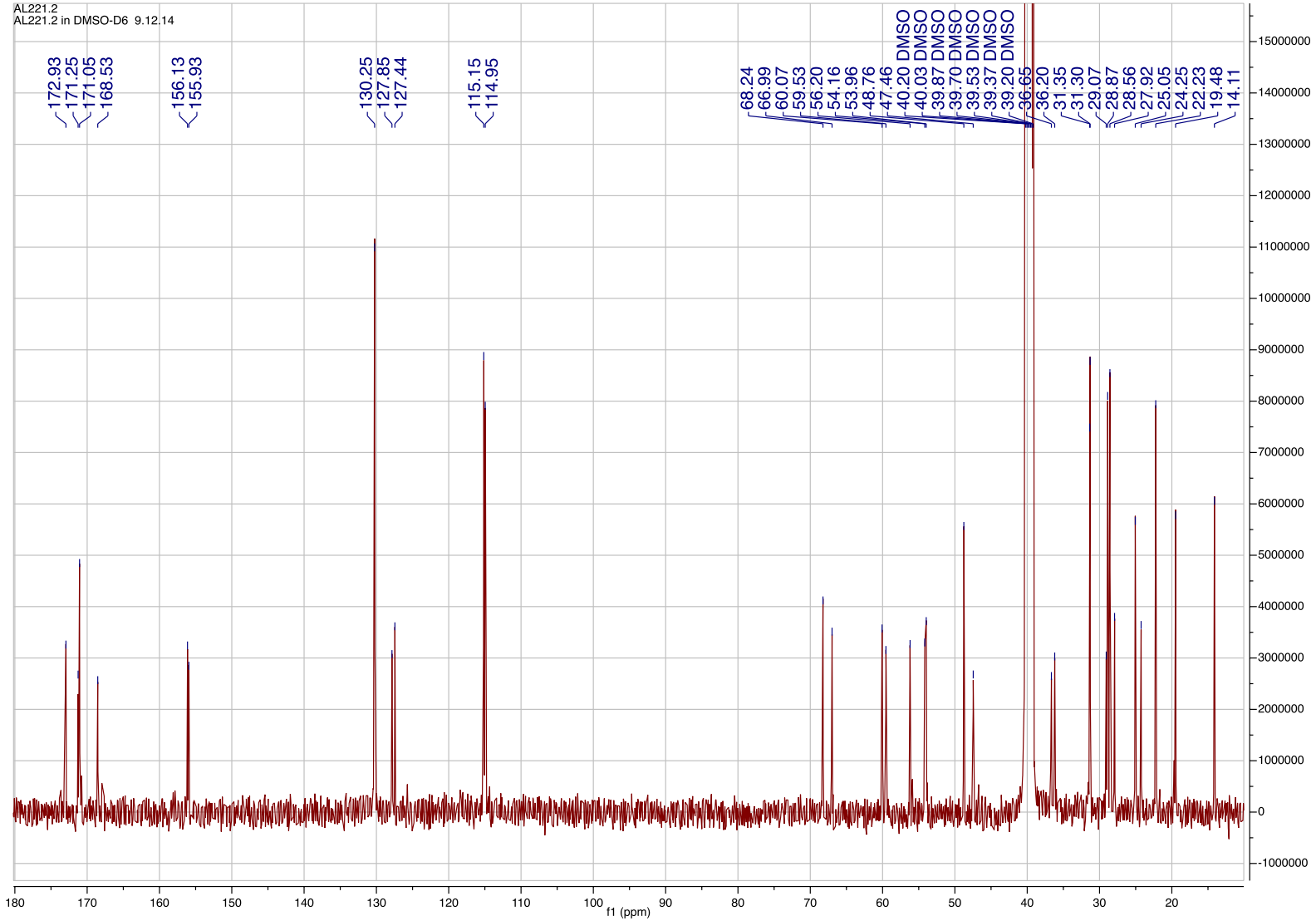
| Position | $\delta_C$ | $\delta_H$ Multiplicity, *J* (Hz) | HMBC correlations | COSY correlations | NOESY correlations |
|---|---|---|---|---|---|
| Ahda 1 | 171.2 C | | Ahda-2-OH, Thr-2,NH | | |
| 2 | 68.2 CH | 4.18 t, 4.4 | Ahda-4’ | Ahda-2-OH,3 | Ahda-2-OH,3,3-$NH_2$,4,4’,5’,5’, Thr-2-NH |
| 2-OH | | 6.82 d, 4.4 | | Ahda-2 | Ahda-2,3,4,5, Thr-2-NH |
| 3 | 60.1 CH | 3.30 m | Ahda-3-$NCH_3$,4,4’ | Ahda-2,3-NH,4,4’ | Ahda-2,2-OH,3-$NH_2$,4, Thr-2-NH |
| 3-$NH_2$ | | 8.36 brs | | Ahda-3,NH’,$NCH_3$ | Ahda-2,3,NH’,4,4’5,5’, Thr-2 |
| | | 8.17 brs | | Ahda-3,NH,$NCH_3$ | Ahda-3-NH, |
| 3-$NCH_3$ | 31.3 $CH_3$ | 2.50 brt, 5.3 | | | Thr-2-NH |
| 4 | 27.9 $CH_2$ | 1.58 m | Ahda-5,5’ | Ahda-3,4’,5,5’ | Ahda-2,2-OH,3,3-$NH_2$, |
| | | 1.55 m | | Ahda-3,4,5,5’ | Ahda-2,3,3-$NH_2$, |
| 5 | 25.1 $CH_2$ | 1.33 m | Ahda-4,4’ | Ahda-4,4’,5’,6 | Ahda-2,3,3-$NH_2$, |
| | | 1.30 m | | Ahda-4,4’,5,6 | Ahda-2 |
| 6 | 28.6 $CH_2$ | 1.23 m | Ahda-7,8 | Ahda-5,5’ | |
| 7 | 28.9 $CH_2$ | 1.23 m | Ahda-5,5’,9 | | |
| 8 | 31.4 $CH_2$ | 1.23 m | Ahda-9,10 | | |
| 9 | 22.2 $CH_2$ | 1.24 m | Ahda-8,10 | Ahda-10 | Ahda-10 |
| 10 | 14.1 $CH_3$ | 0.85 t, 6.8 | Ahda-8,9 | Ahda-9 | Ahda-9 |
| Thr 1 | 168.5 C | | Thr-2 | | |
| 2 | 56.2 CH | 4.47 dd, 7.4,6.0 | Thr-4 | Thr-2-NH,3 | Thr-2-NH,3,4, Pro-5, Ahda-3-NH, $^1$Tyr-5,5’ |
| 2-NH | | 7.91 d, 7.4 | | Thr-2 | Thr-2,3,4, Ahda-2,2-OH,3,3-$NCH_3$ |
| 3 | 67.0 CH | 3.93 brdq, 6.0,6.0 | Thr-2,4 | Thr-2,4 | Thr-2,2-NH,4, $^1$Tyr-2-NH,5,5’ |
| 3-OH | | 5.10 brs | | | |
| 4 | 19.5 $CH_3$ | 1.14 d, 6.0 | Thr-2 | Thr-3 | Thr-2,2-NH,3, $^1$Tyr-2-NH,5,5’ |
| Pro 1 | 171.0 C | | Pro-2, $^1$Tyr-NH | | |
| 2 | 59.5 CH | 4.32 m | | Pro-3,3’ | Pro-3,3’ |
| 3 | 29.1 $CH_2$ | 1.90 m | Pro-4,4’,5 | Pro-2,3’,4,4’,5 | Pro-2,3’4,4’ |
| | | 1.70 m | | Pro-2,3,4,4’ | Pro-2,3, $^1$Tyr-2-NH |
| 4 | 24.2 $CH_2$ | 1.74 m | Pro-3,5 | Pro-3,3’,4’,5 | Pro-3,5 |

| | | | | | |
|---|---|---|---|---|---|
| | | 1.65 m | | Pro-3,3',4,5 | Pro-3,5 |
| 5 | 47.5 $CH_2$ | 3.64 m | | Pro-3,4,4' | Pro-4,4', Thr-2 |
| $^{1}$Tyr 1 | 171.0 C | | $^{1}$Tyr-2,3, $^{2}$Tyr-NH | | |
| 2 | 54.2 CH | 4.38 ddd, 9.0,8.2,4.2 | $^{1}$Tyr-3' | $^{1}$Tyr-2-NH,3,3' | $^{1}$Tyr-2-NH,3,3',5,5' $^{2}$Tyr-2-NH |
| 2-NH | | 7.64 d, 8.2 | | $^{1}$Tyr-2 | $^{1}$Tyr-2,3',6,6', $^{2}$Tyr-2, Pro-3',5, Thr-3,4 |
| 3 | 36.7 $CH_2$ | 2.87 dd, 13.8,4.2 | $^{1}$Tyr-5,5' | $^{1}$Tyr-2,3' | $^{1}$Tyr-2,3',5,5' |
| | | 2.63 dd, 13.8,9.0 | | $^{1}$Tyr-2,3 | $^{1}$Tyr-2,2-NH,3,5,5' |
| 4 | 127.9 C | | $^{1}$Tyr-2,3,3',5,5' | | |
| 5,5' | 130.2 CH | 7.00 d, 8.6 | $^{1}$Tyr-3,3',5',5 | $^{1}$Tyr-6,6' | $^{1}$Tyr-2,3,3',6,6', Pro-3',4',5, Thr-2,3,4 |
| 6,6' | 115.0 CH | 6.60 d, 8.6 | $^{1}$Tyr-5,5',6',6 | $^{1}$Tyr-5,5' | $^{1}$Tyr-2-NH,5,5',7-OH |
| 7 | 155.9 C | | $^{1}$Tyr-5,5',6,6' | | |
| 7-OH | | 9.12 s | | | $^{1}$Tyr-6,6' |
| $^{2}$Tyr 1 | 172.9 C | | $^{2}$Tyr-2,3,3' | | |
| 2 | 54.0 CH | 4.31 m | $^{2}$Tyr-3,3' | $^{2}$Tyr-2-NH,3,3' | $^{2}$Tyr-2-NH,3,3',5,5' |
| 2-NH | | 8.04 d, 7.6 | | $^{2}$Tyr-2 | $^{2}$Tyr-2,3,3',6,6',$^{1}$Tyr-2 |
| 3 | 36.2 $CH_2$ | 2.90 dd, 14.0,5.7 | $^{2}$Tyr-2,5,5' | $^{2}$Tyr-2,3' | $^{2}$Tyr-2,2-NH,3',5,5' |
| | | 2.79 dd, 14.0,7.9 | | $^{2}$Tyr-2,3 | $^{2}$Tyr-2,2-NH,3,5,5' |
| 4 | 127.4 C | | $^{2}$Tyr-2,3,3',5,5' | | |
| 5,5' | 130.3 CH | 7.00 d, 8.1 | $^{2}$Tyr-3,3',5',5 | $^{2}$Tyr-6,6' | $^{2}$Tyr-2,3,3',6,6' |
| 6,6' | 115.1 CH | 6.63 d, 8.1 | $^{2}$Tyr-5,5',6',6 | $^{2}$Tyr-5,5' | $^{2}$Tyr-2-NH,5,5',7-OH |
| 7 | 156.1 C | | $^{2}$Tyr-5,5',6,6' | | |
| 7-OH | | 9.17 s | | | $^{2}$Tyr-6,6' |

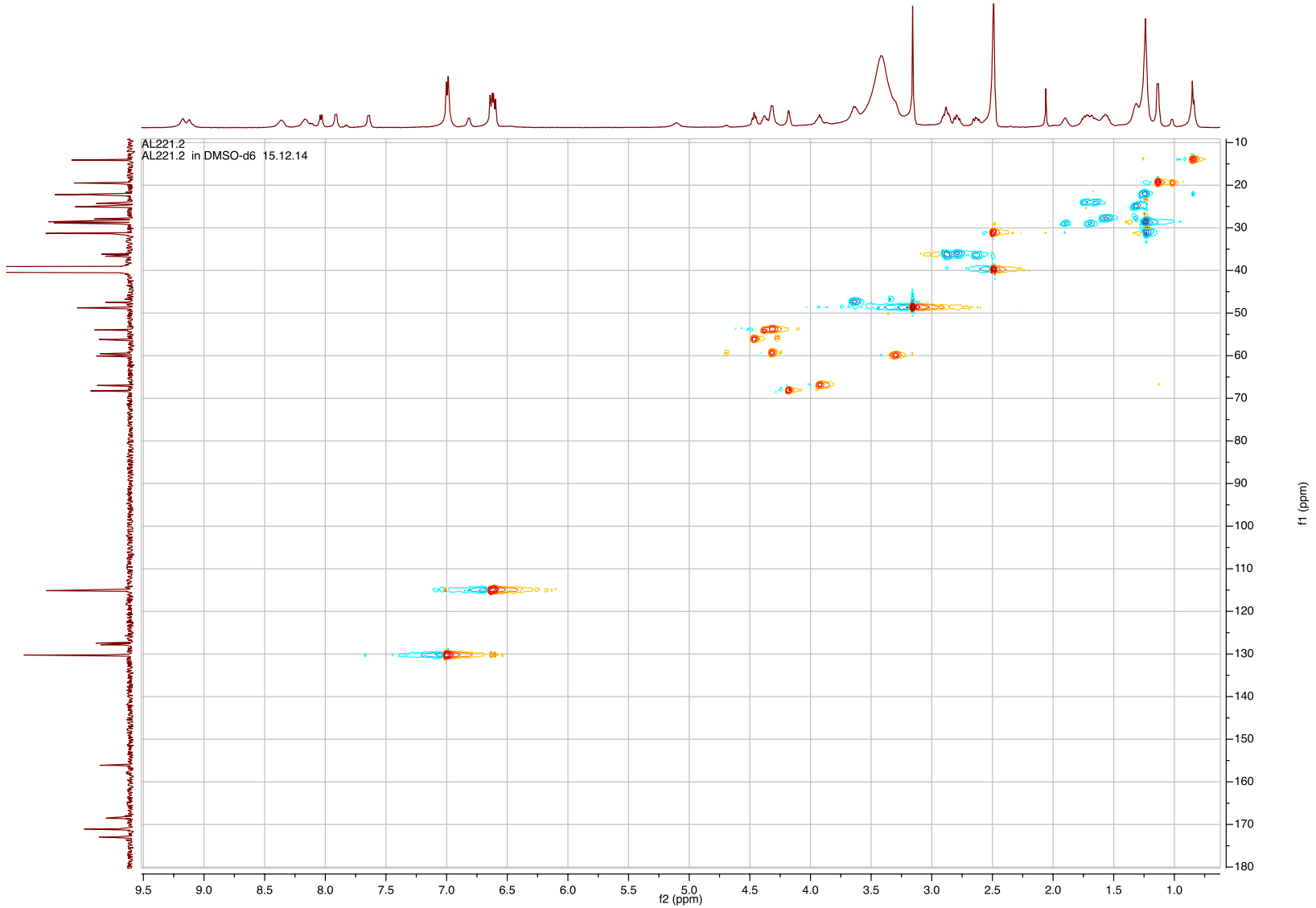
S98. $^{1}$H NMR Spectrum of Microginin FR4 (**10**) in DMSO-$d_6$



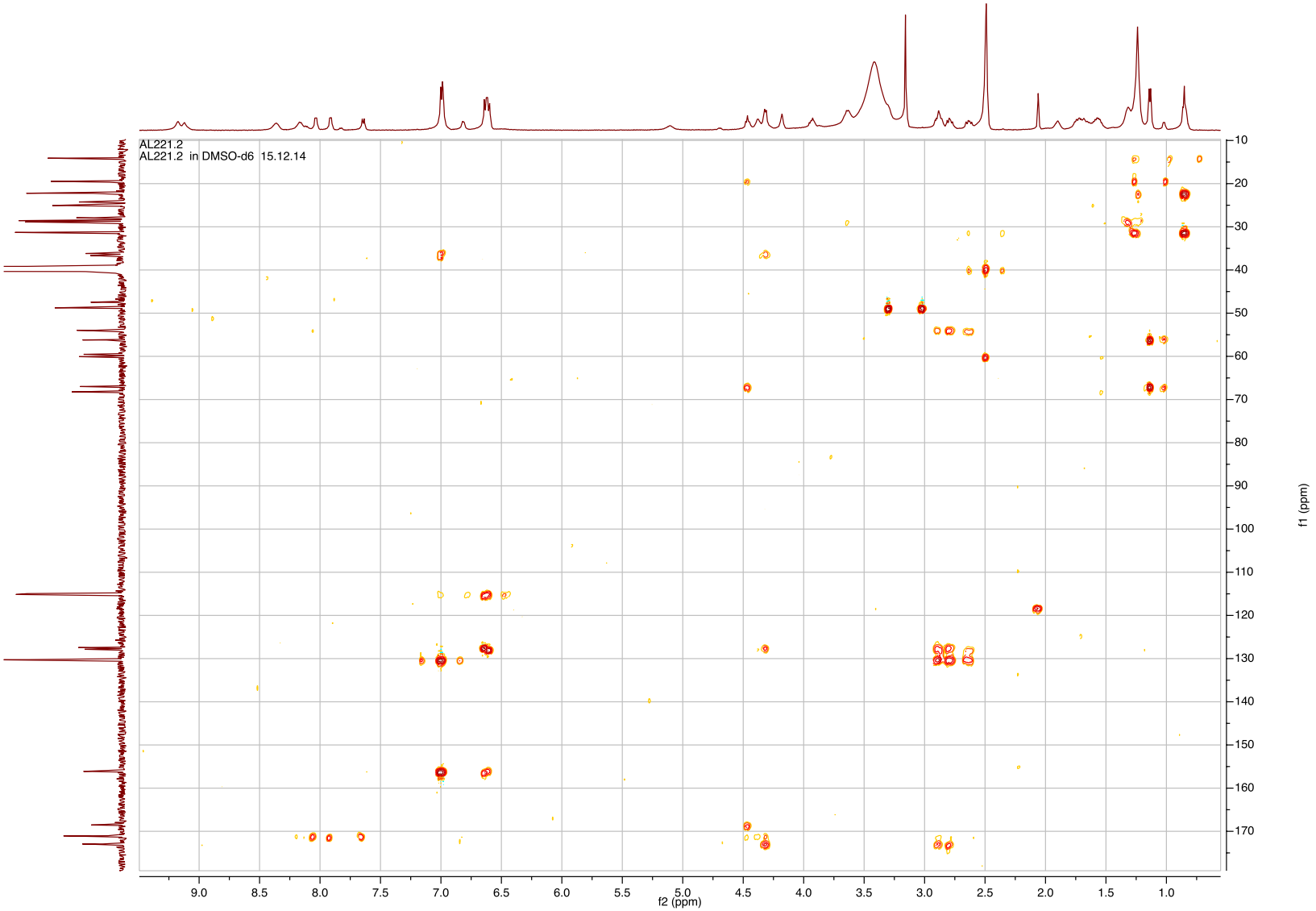
S99. $^{13}$C NMR Spectrum of Microginin FR4 (**10**) in DMSO-$d_6$



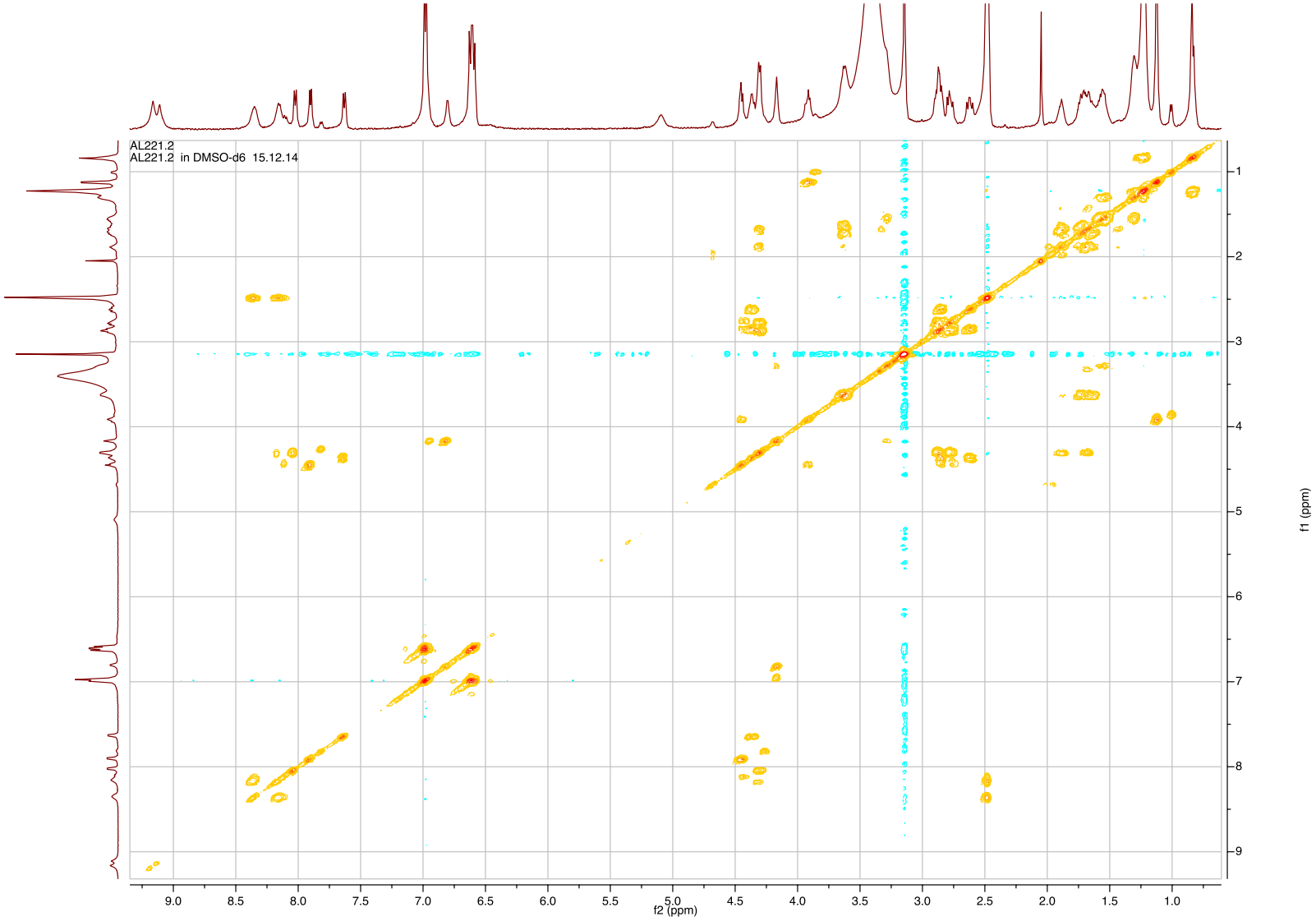
S100. HSQC Spectrum Microginin FR4 (**10**) in DMSO-$d_6$



S101. HMBC Spectrum of Microginin FR4 (**10**) in DMSO-$d_6$

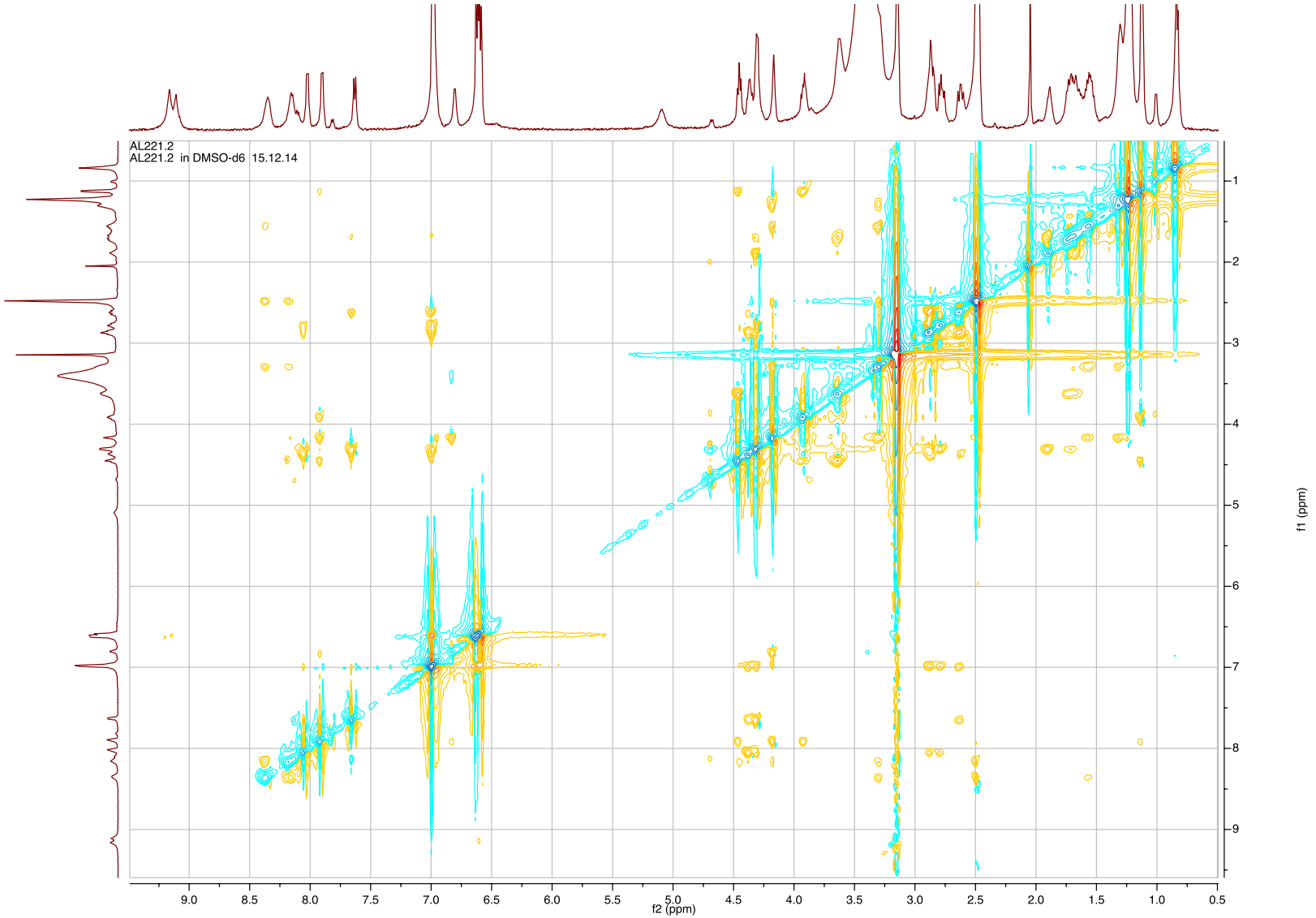


S102. COSY Spectrum of Microginin FR4 (**10**) in DMSO-$d_6$



S103. TOCSY Spectrum of Microginin FR4 (**10**) in DMSO-$d_6$

S104. ROESY Spectrum of Microginin FR4 (**10**) in DMSO-$d_6$



S105. HR ESI MS data of Microginin FR4 (**10**)

**Elemental Composition Report** 

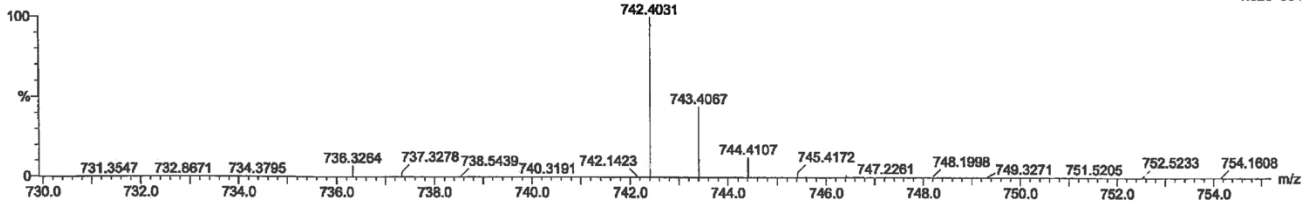
**Single Mass Analysis**
Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
138 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 35-45 H: 50-65 N: 0-10 O: 0-15

AL221.2
carmeli897 48 (2.121) Cm (48:51)

Anat Lodin

1: TOF MS ES+
1.82e+004




| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | |
| Maximum: | | 5.0 | 2.0 | 50.0 | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
| 742.4031 | 742.4027 | 0.4 | 0.5 | 13.5 | 167.2 | 0.0 | C38 H56 N5 O10 |
| | 742.4041 | -1.0 | -1.3 | 18.5 | 170.4 | 3.3 | C39 H52 N9 O6 |