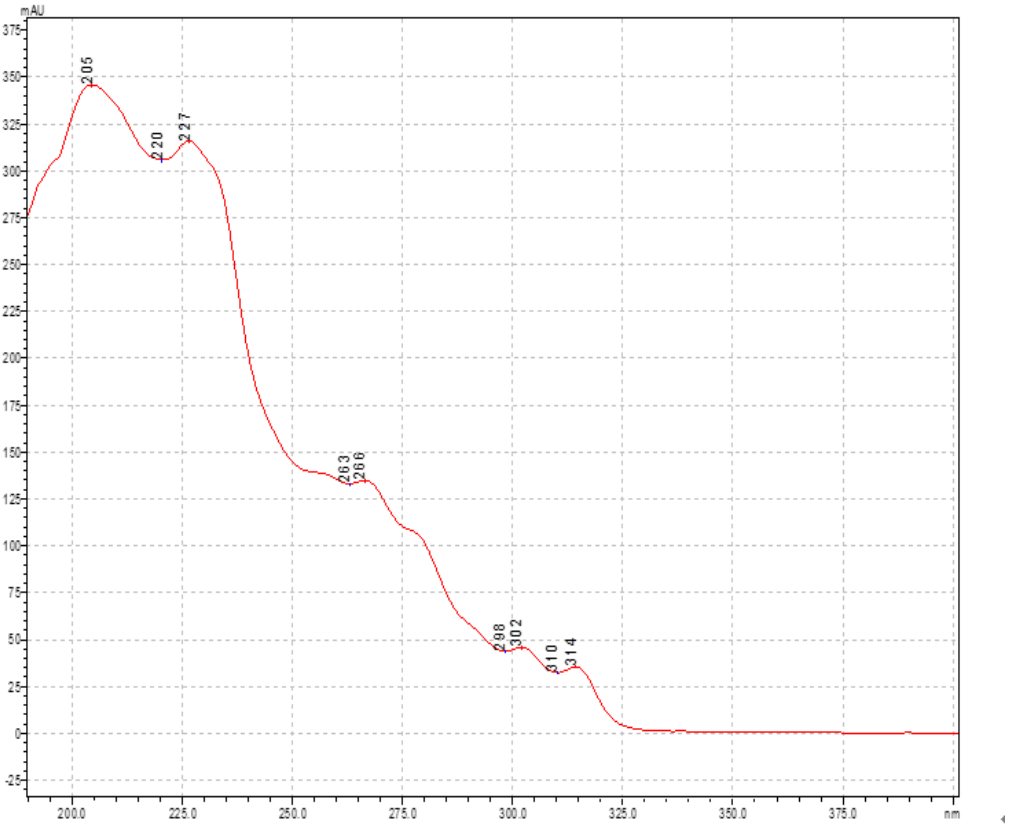
Electronic Supplementary Material (ESI) for RSC Advances.

Versiquinazolines L–Q, new polycyclic alkaloids from the marine-derived fungus *Aspergillus versicolor*

Supporting Information

Figure S1 UV spectrum of **1**



UV spectrum of compound **1**

Figure S2 IR Spectrum of **1**

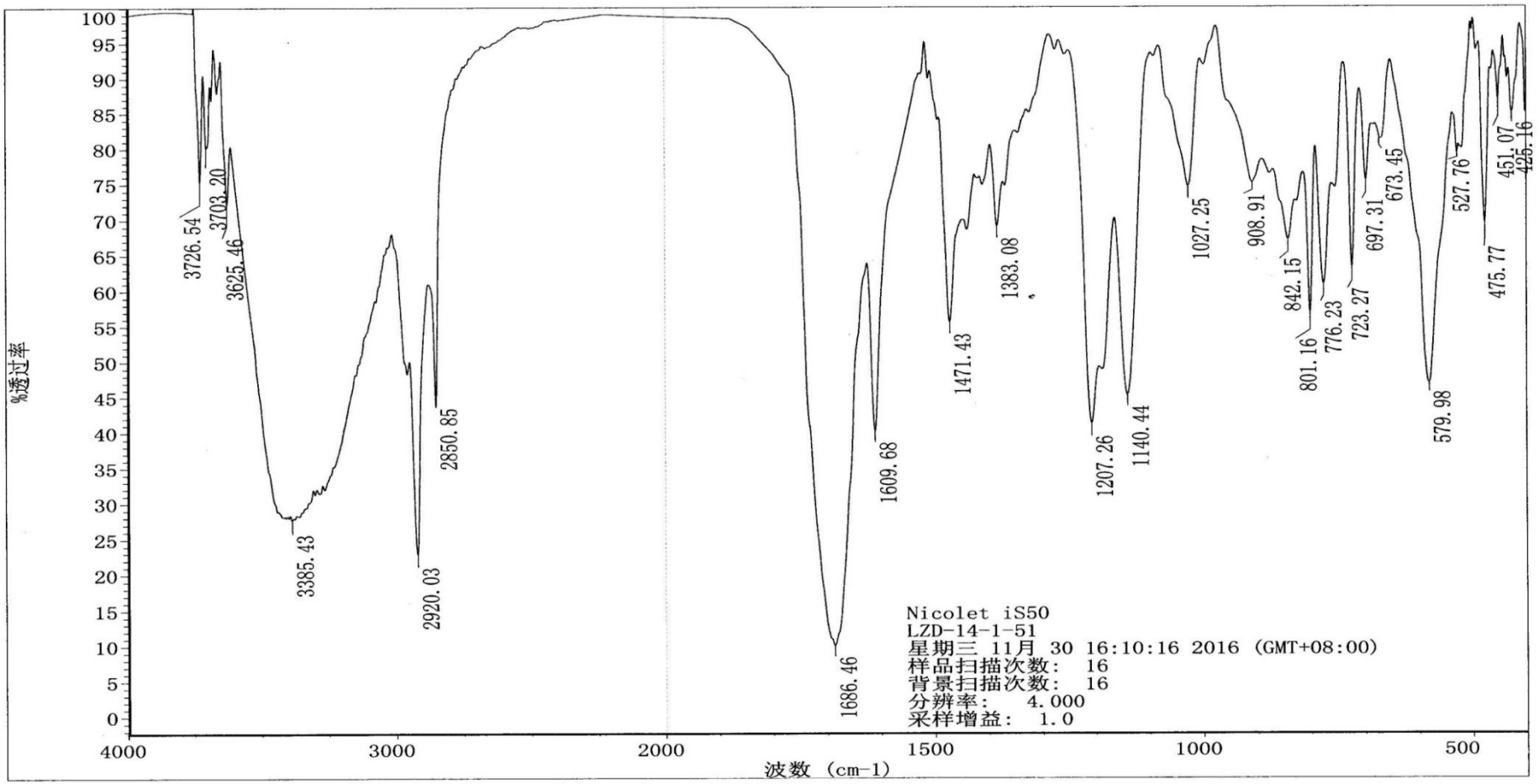


Figure S3 ^{1}H NMR Spectrum of **1** in DMSO-d_6

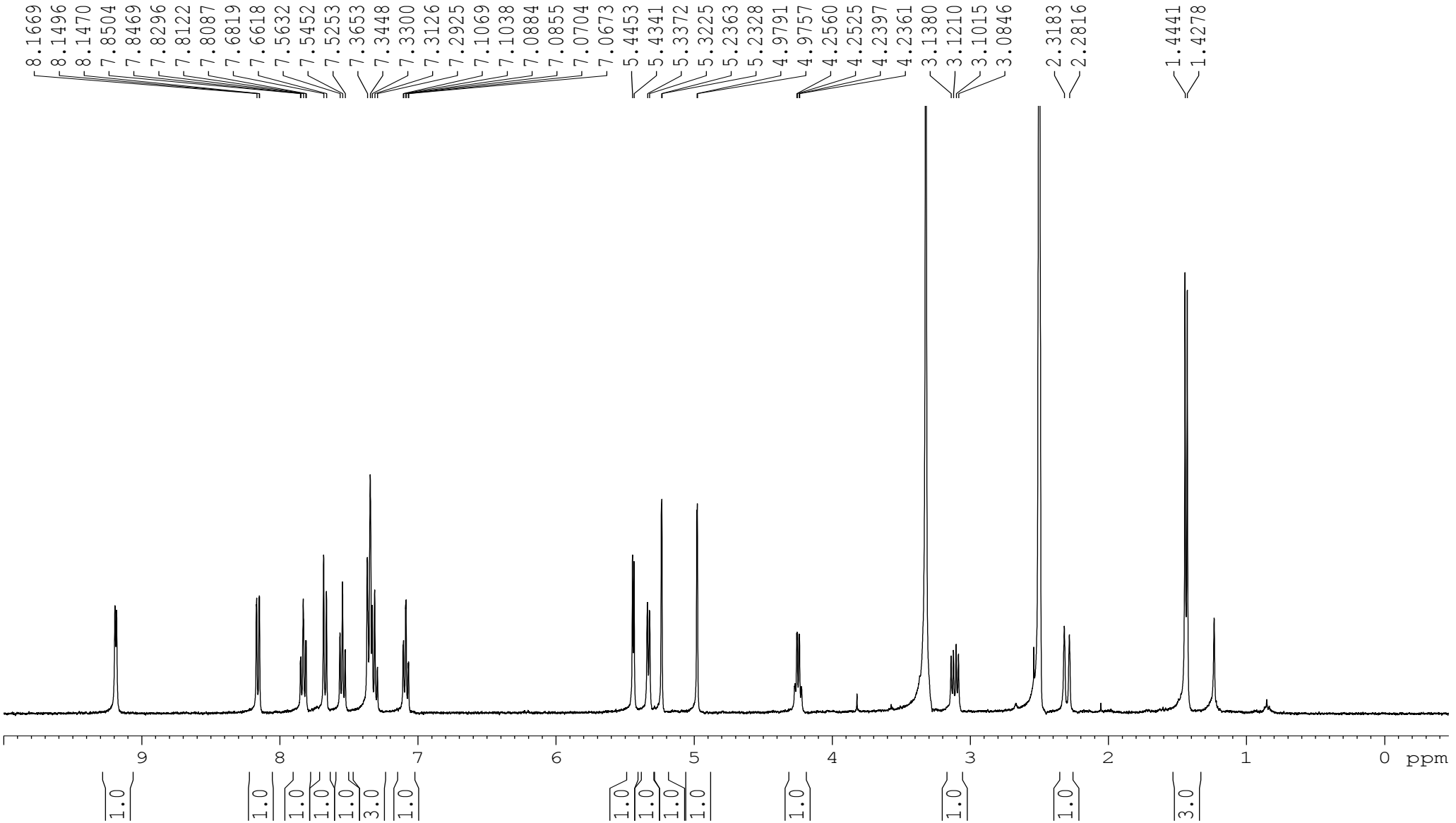


Figure S4 DEPTQ Spectrum of **1** in DMSO-d_6

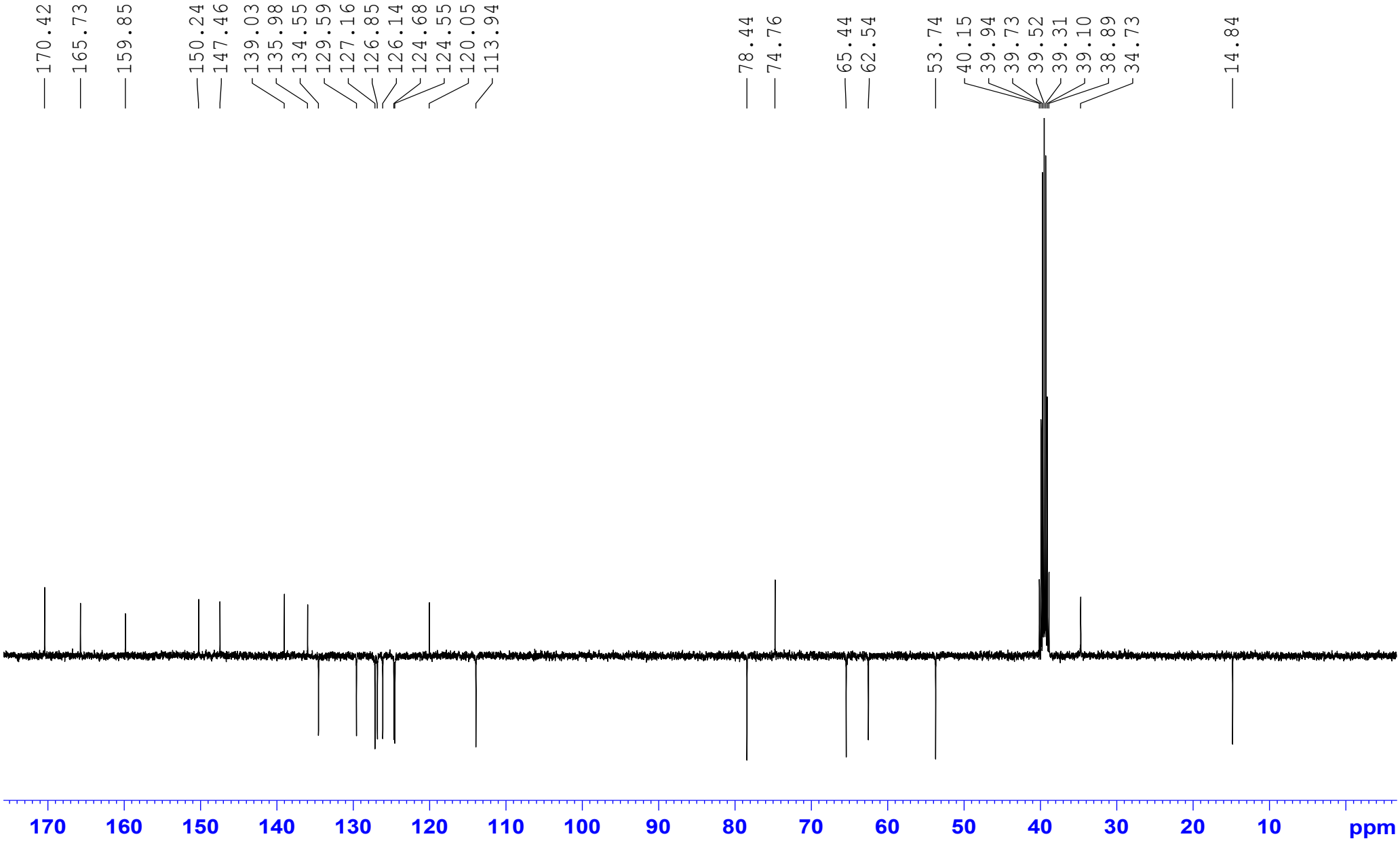


Figure S5 HSQC Spectrum of **1** in DMSO-d_6

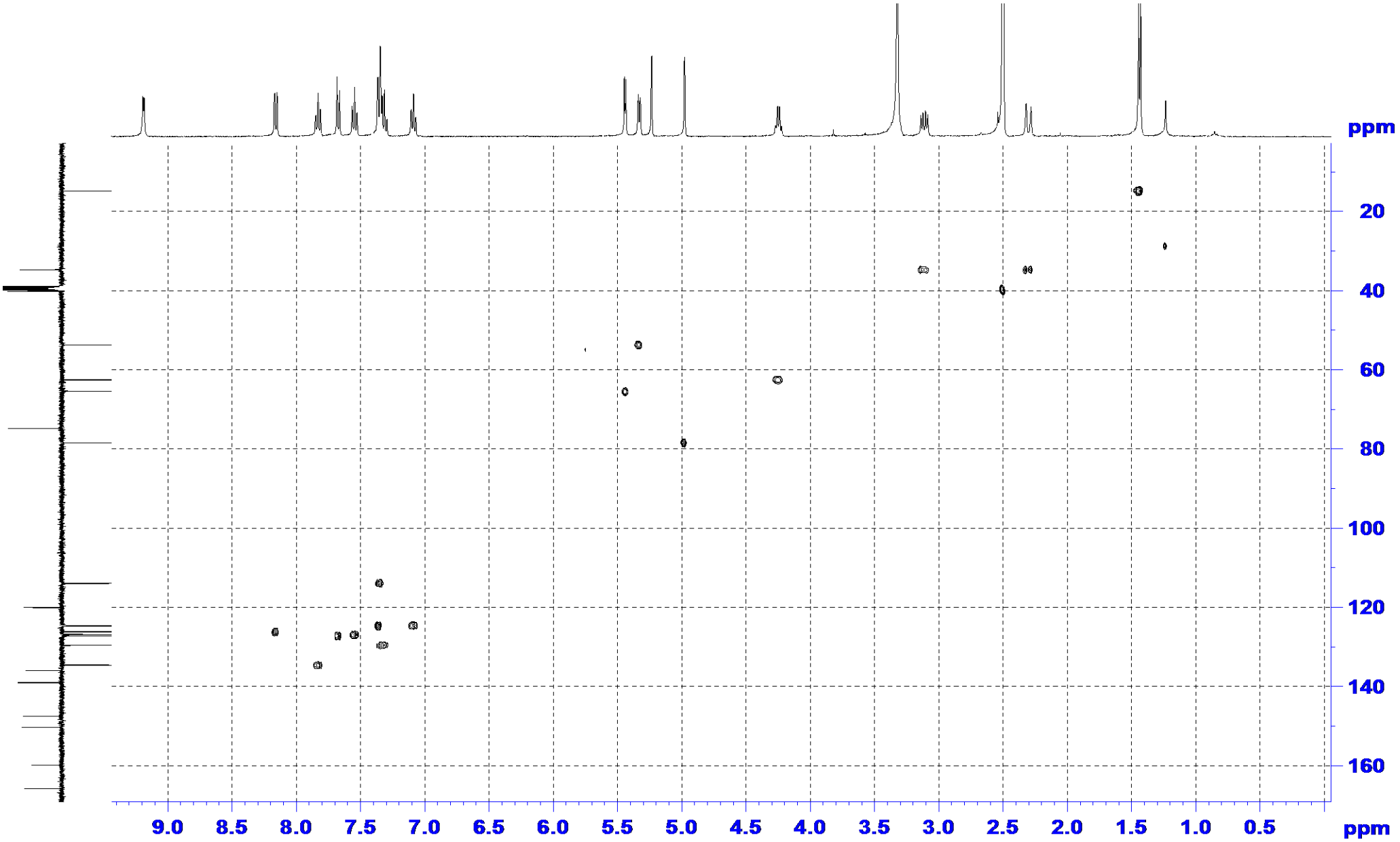


Figure S6 ^{1}H-^{1}H COSY Spectrum of **1** in DMSO-d_6

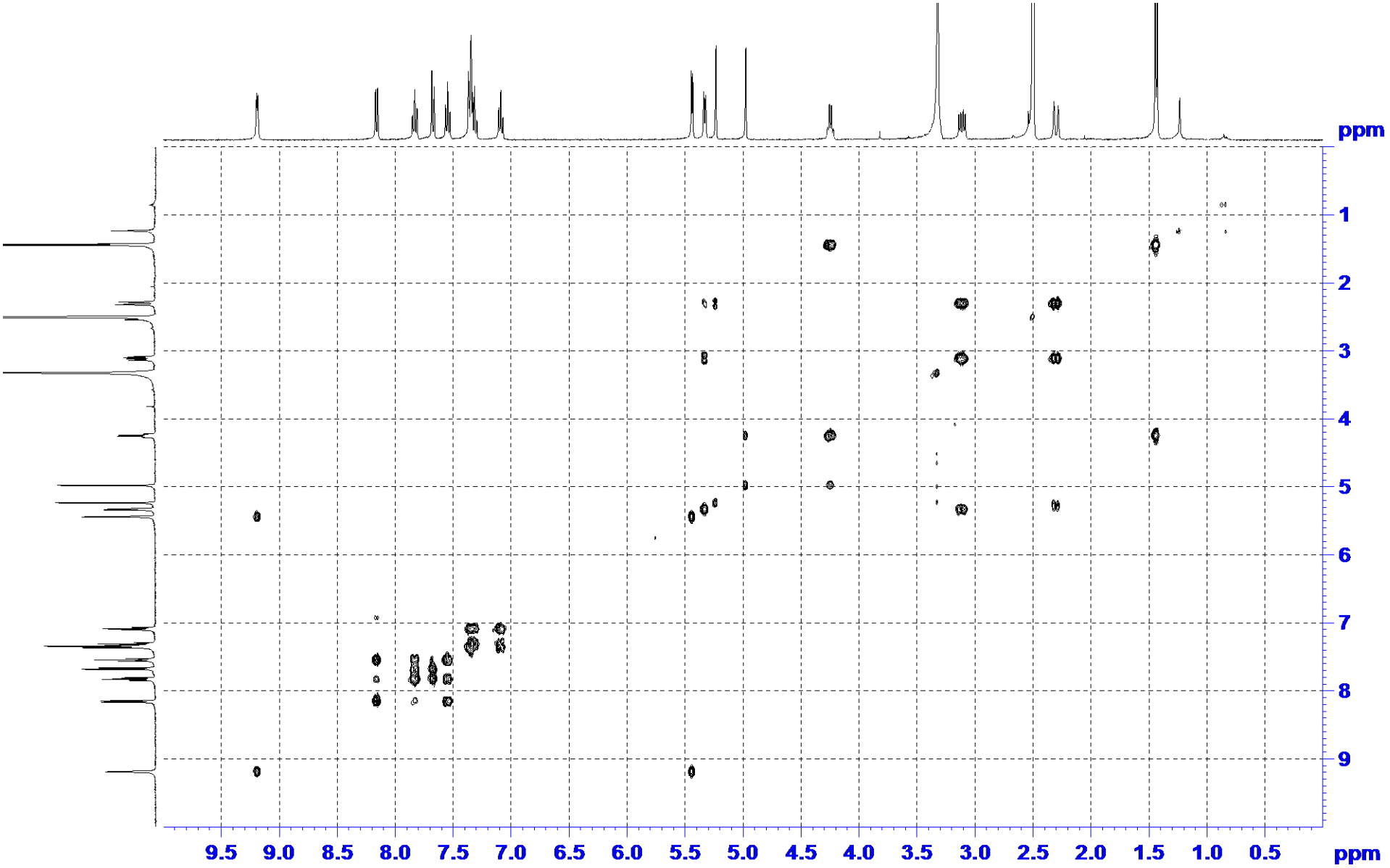


Figure S7 HMBC Spectrum of **1** in DMSO-d_6

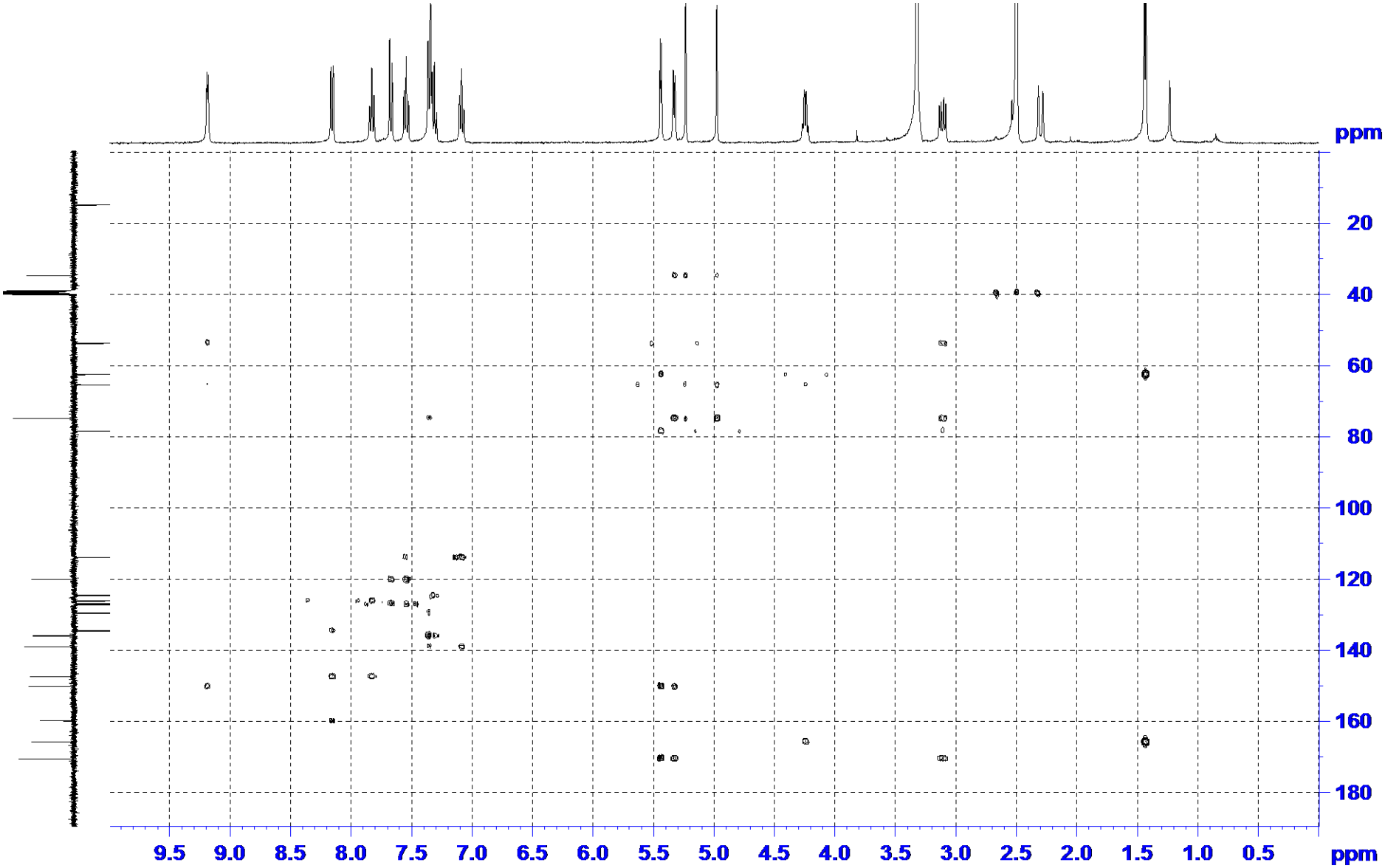


Figure S8 NOESY Spectrum of **1** in DMSO-d_6

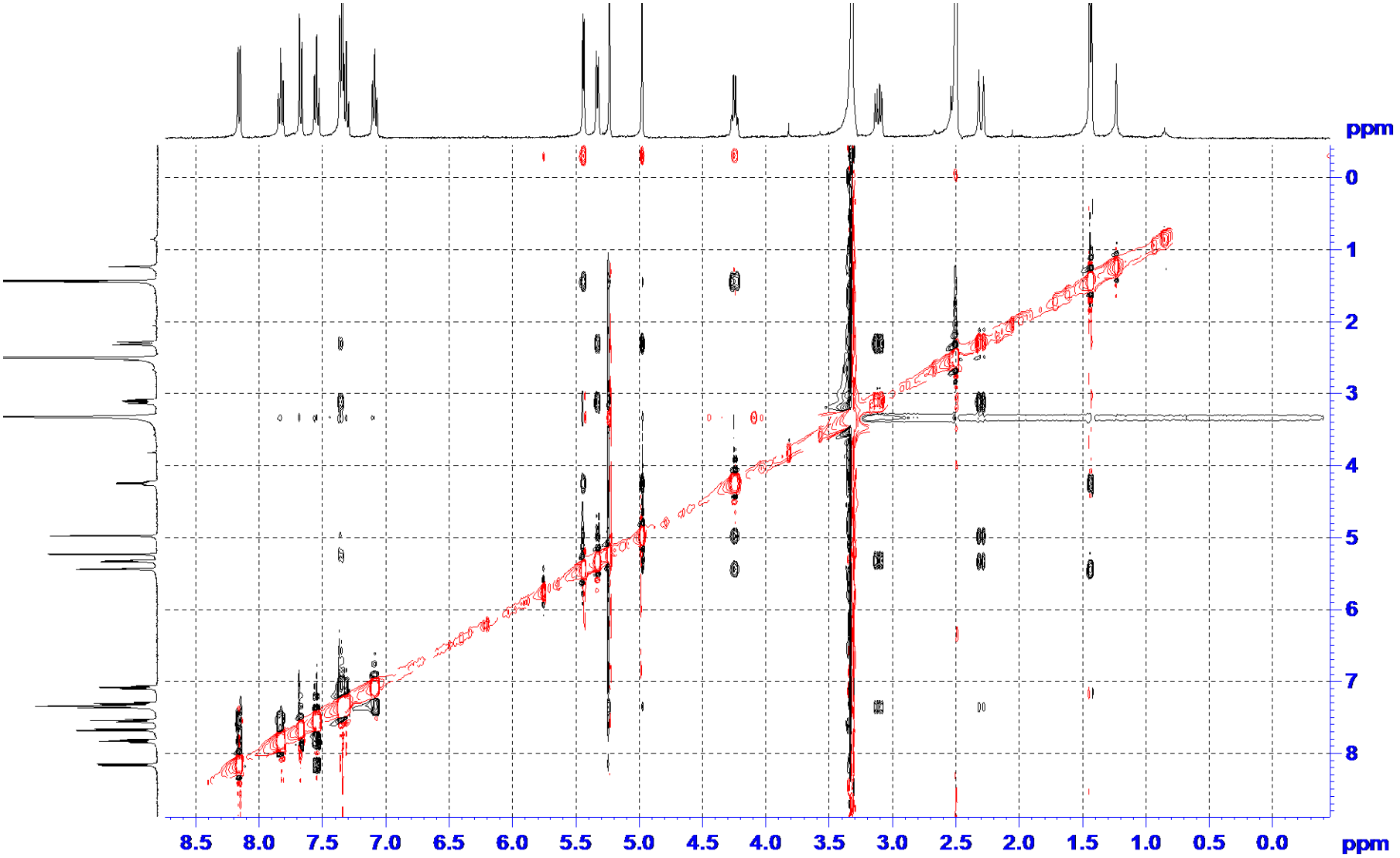


Figure S9 HRESIMS Data of **1**

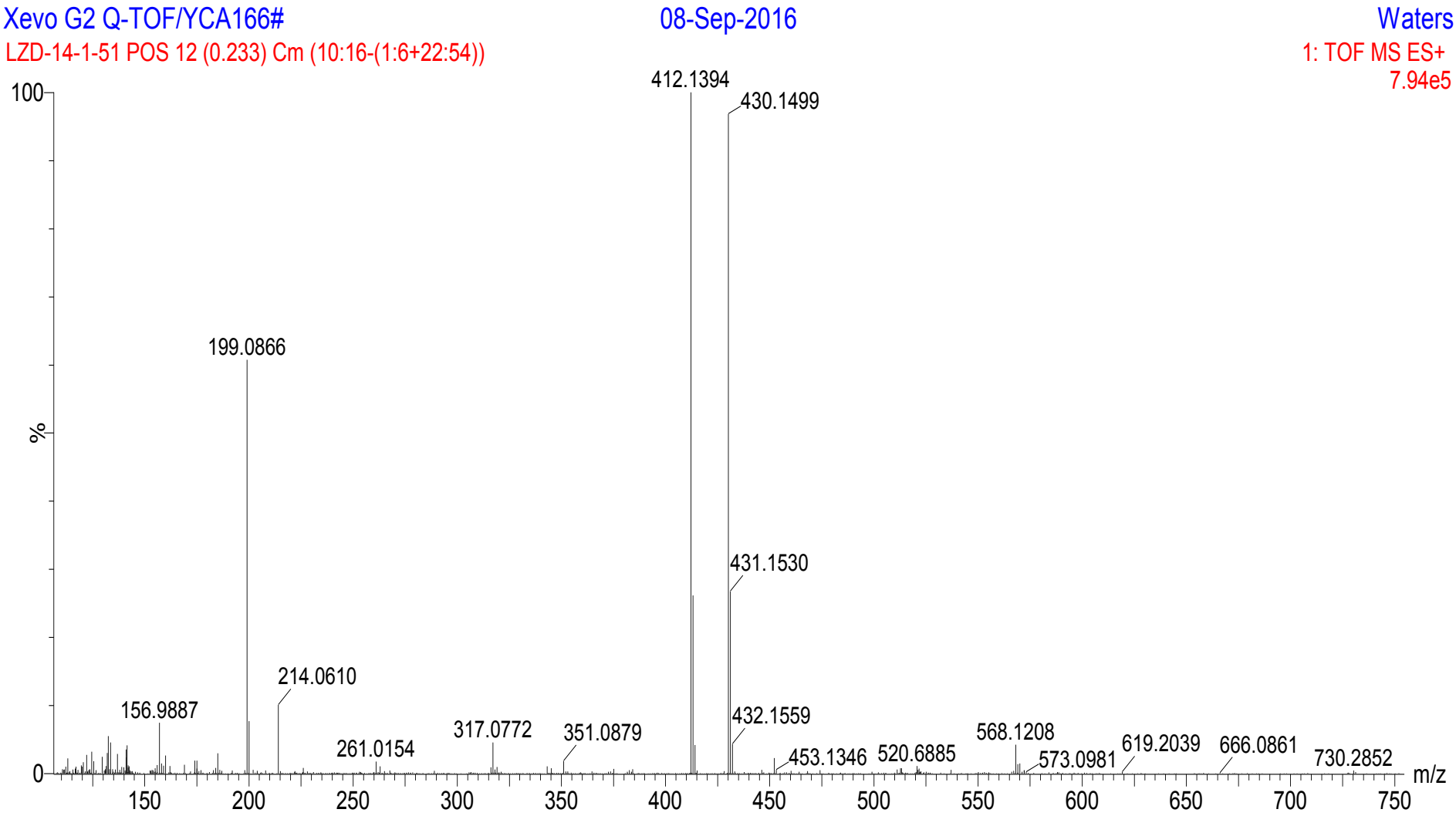
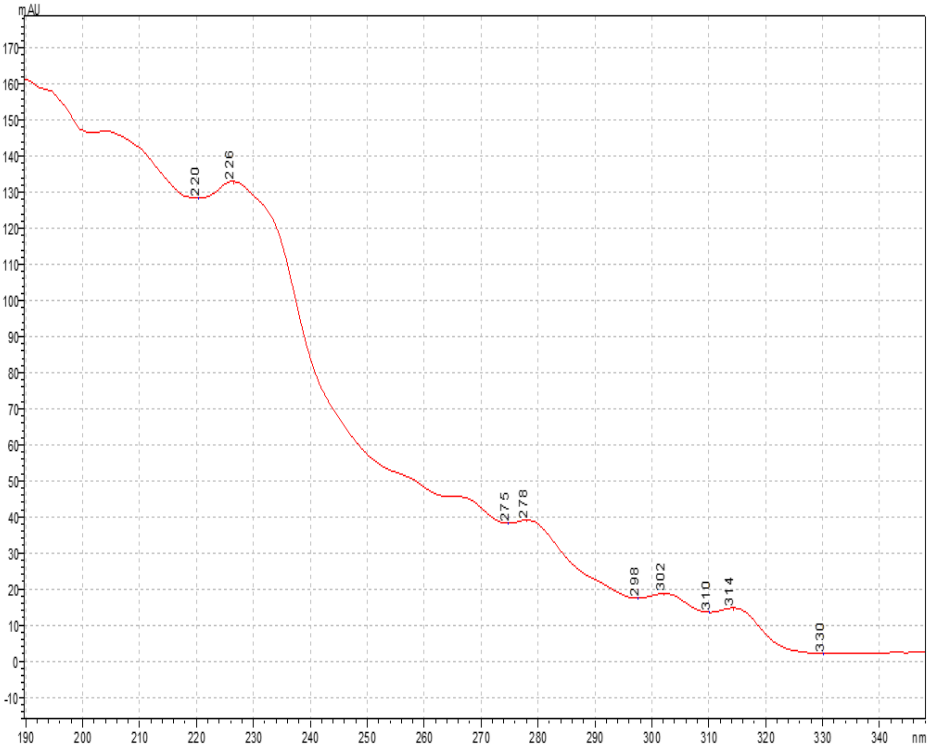


Figure S10 UV spectrum of **2**



UV spectrum of compound **2**

Figure S11 IR Spectrum of **2**

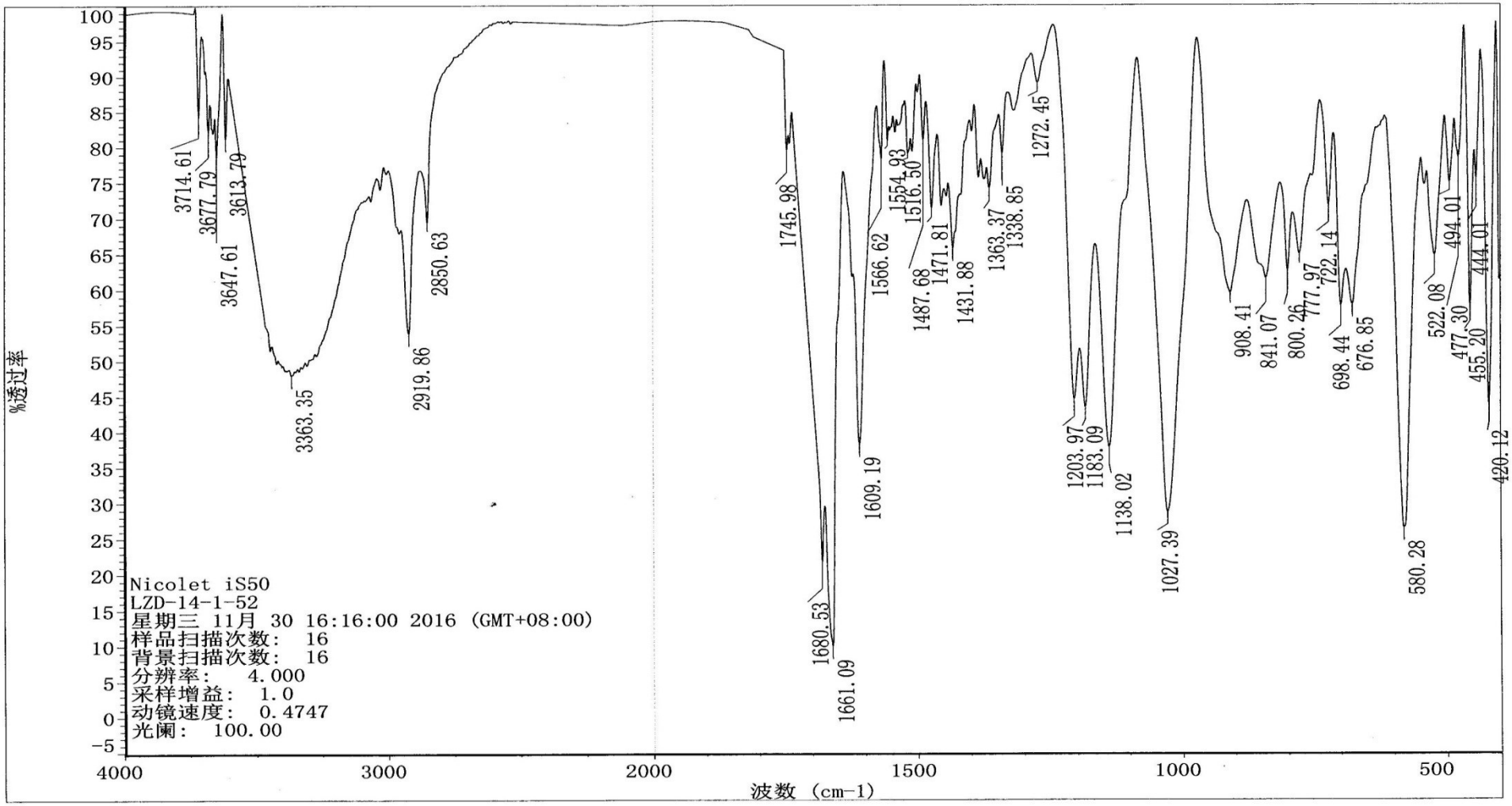


Figure S12 ^{1}H NMR Spectrum of **2** in DMSO-d_6

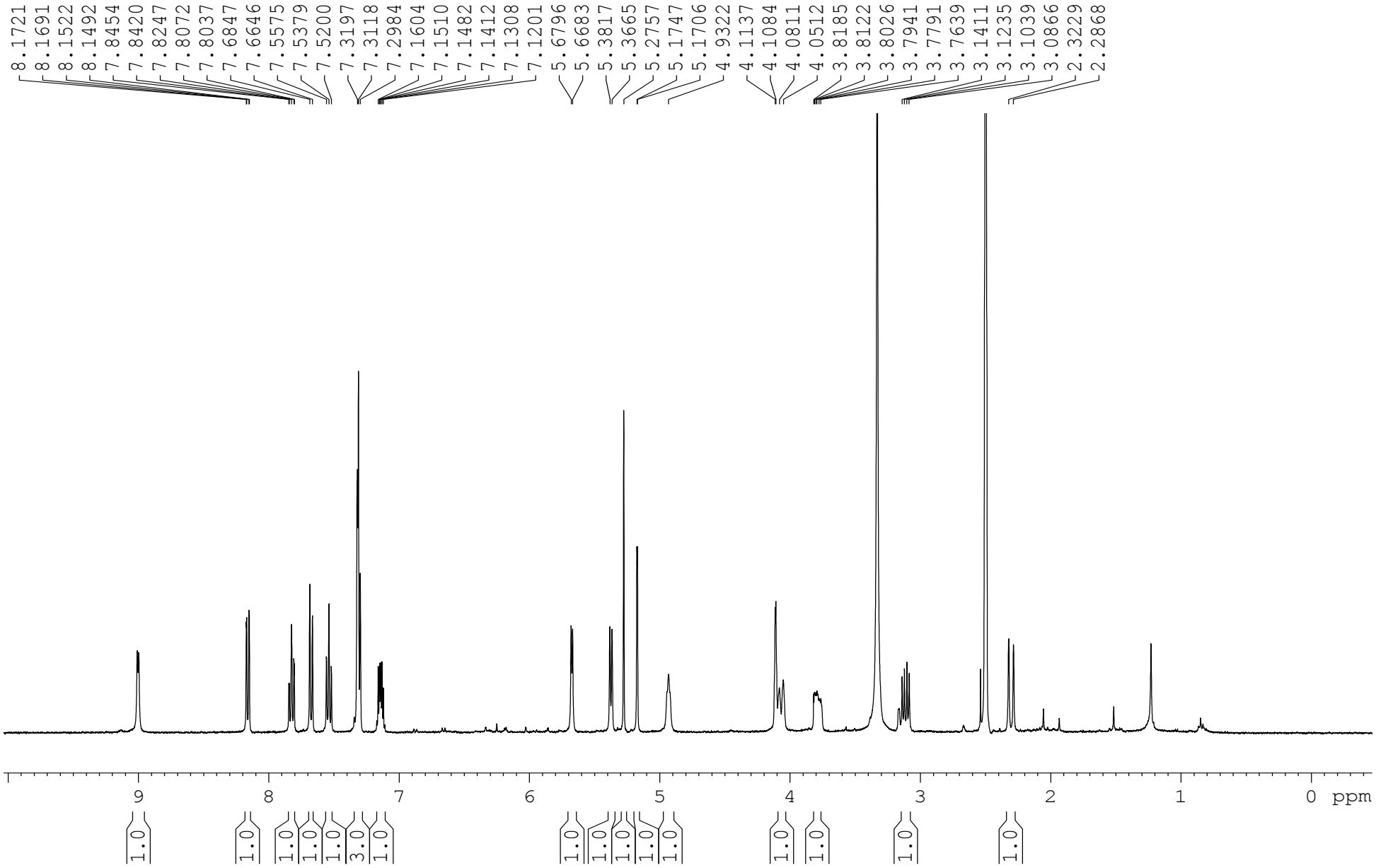


Figure S13 DEPTQ Spectrum of **2** in DMSO-d_6

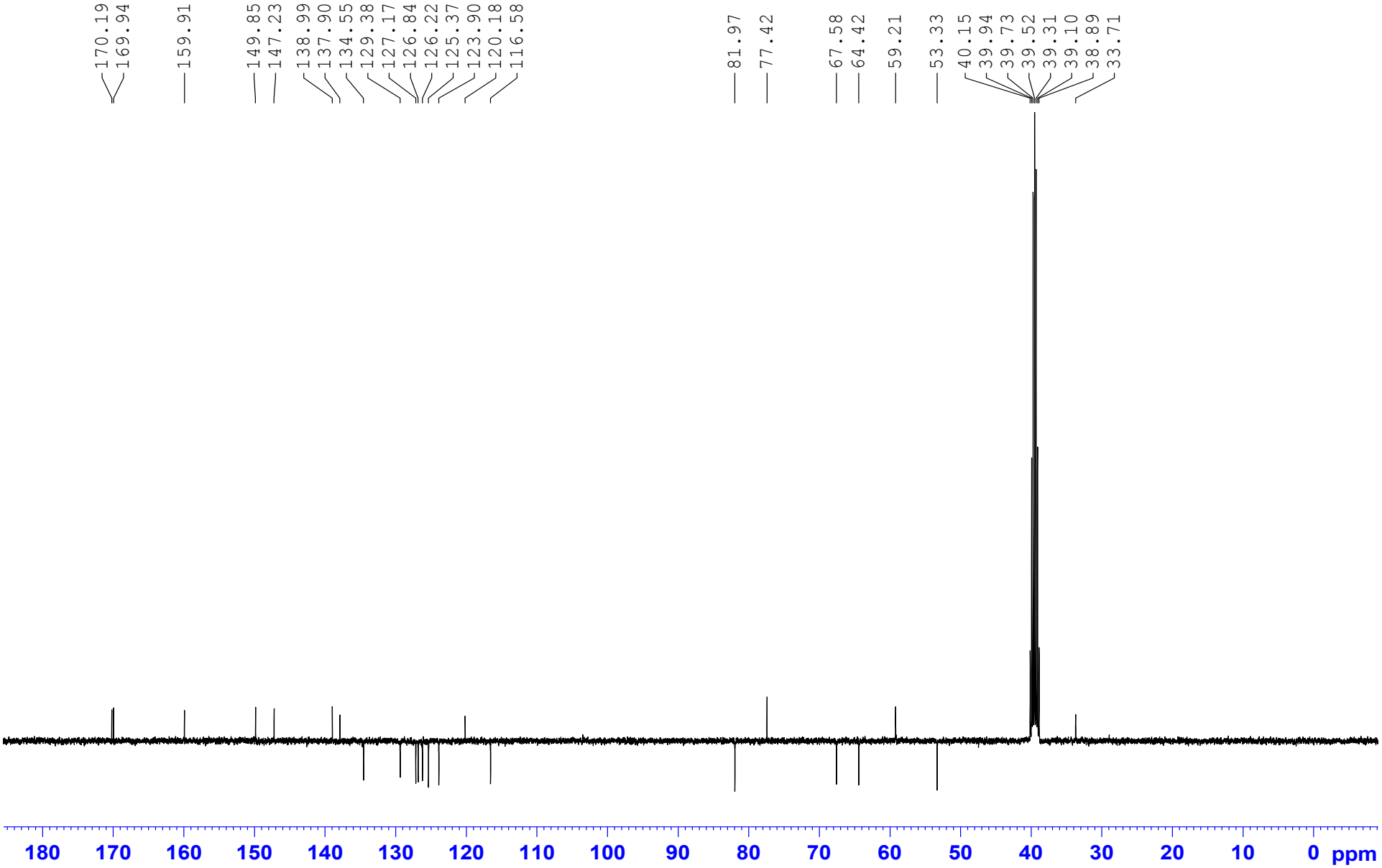


Figure S14 HSQC Spectrum of **2** in DMSO-d_6

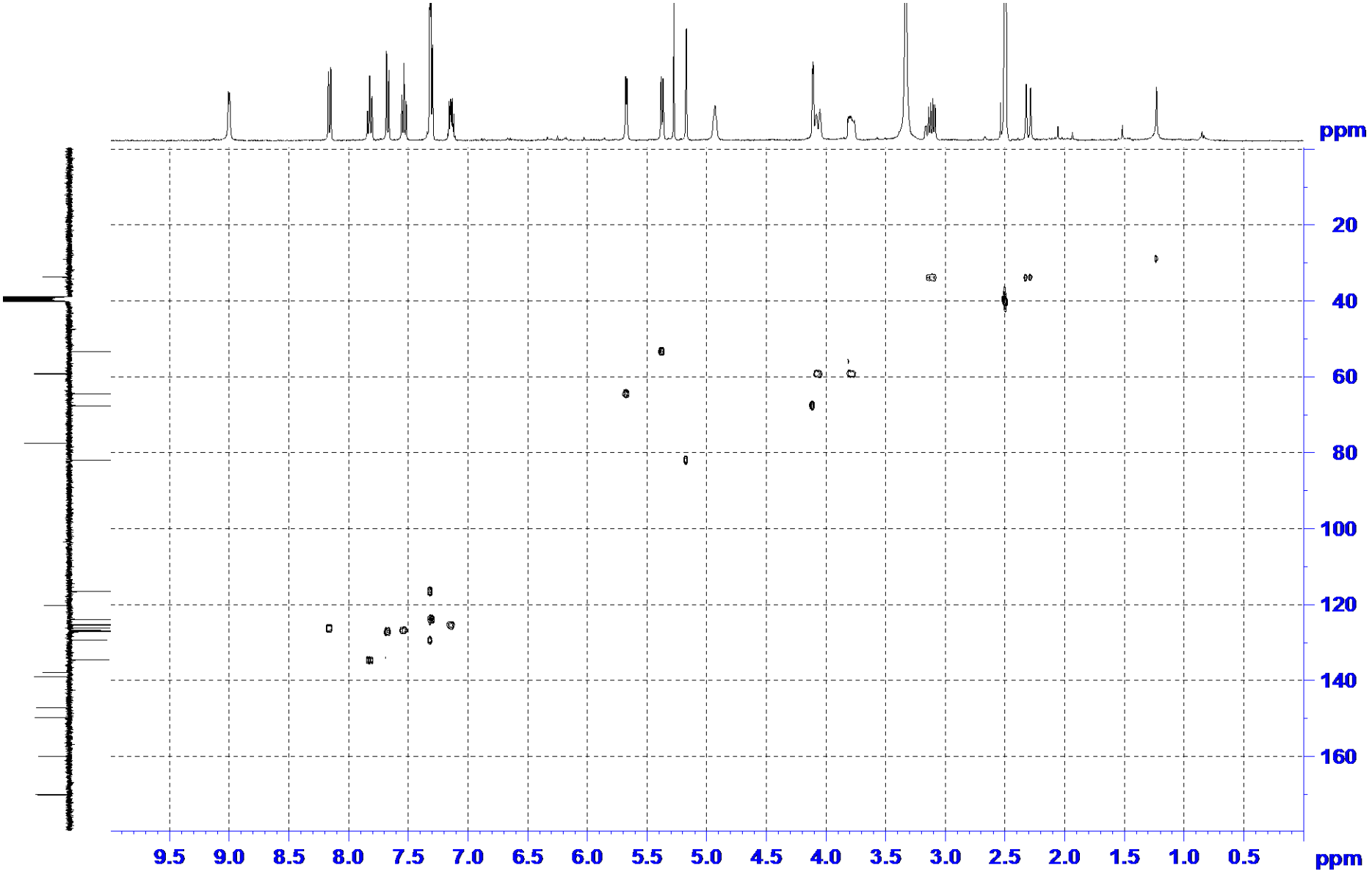


Figure S15 ^{1}H-^{1}H COSY Spectrum of **2** in DMSO-d_6

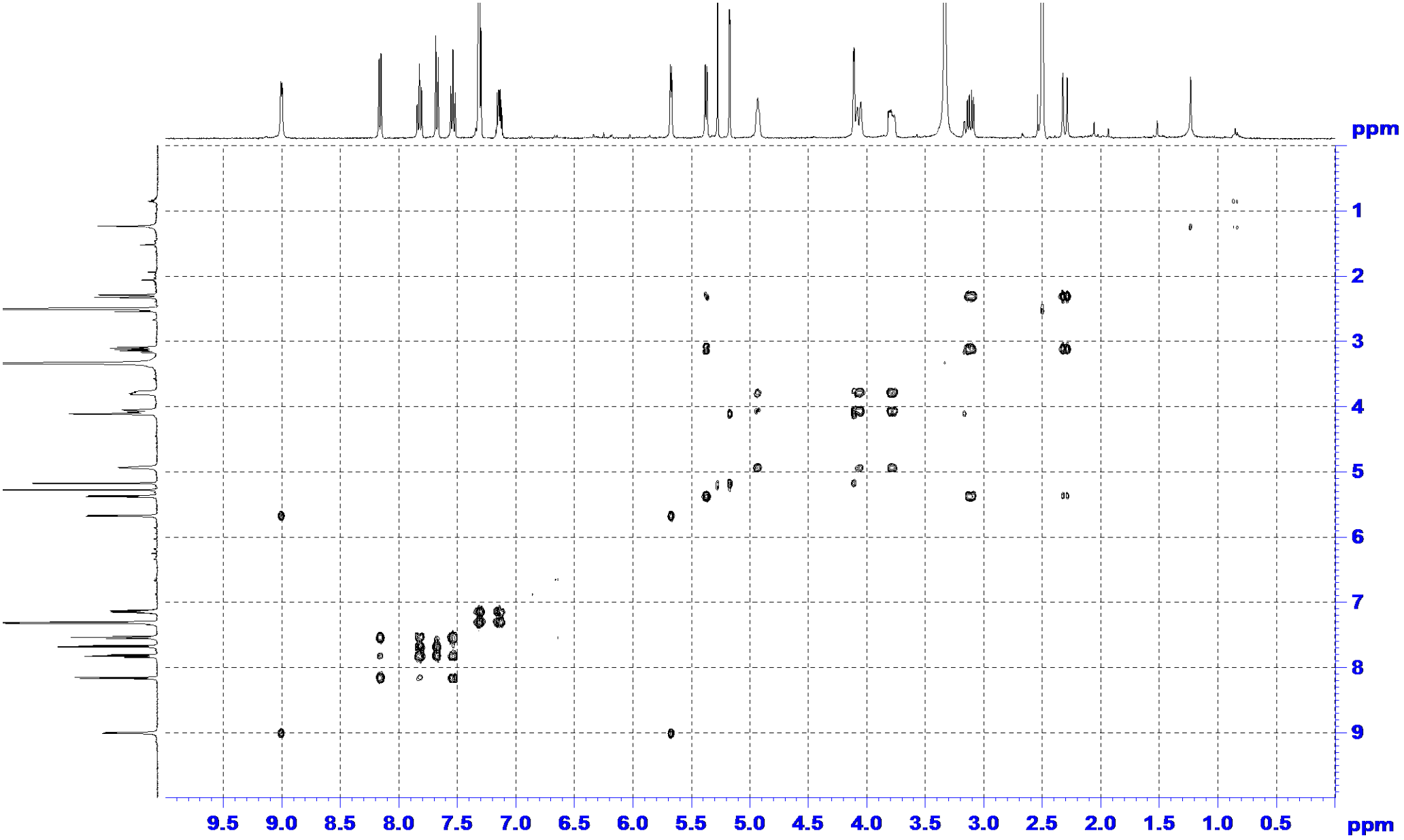


Figure S16 HMBC Spectrum of **2** in DMSO-d_6

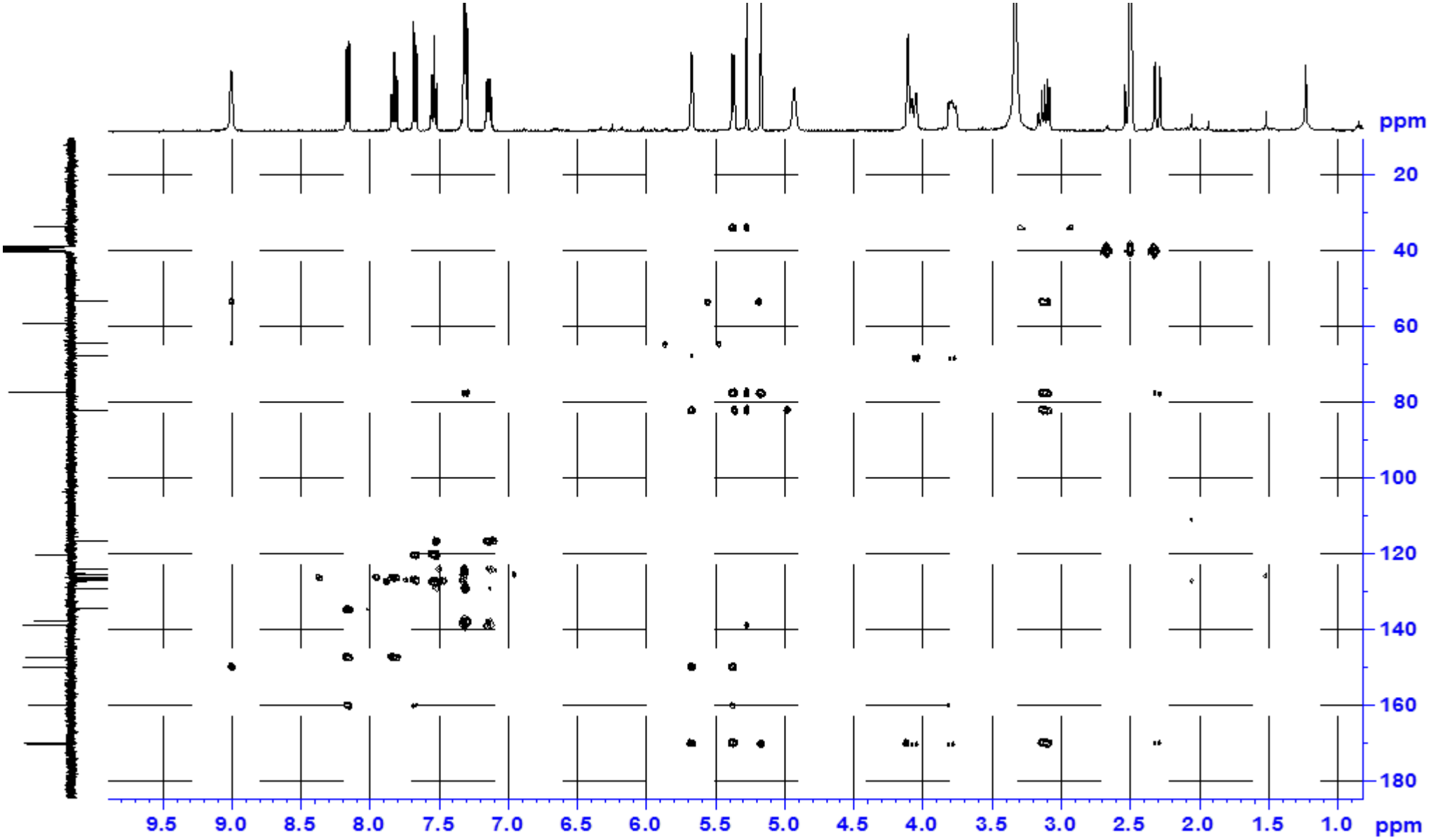


Figure S17 NOESY Spectrum of **2** in DMSO-d_6

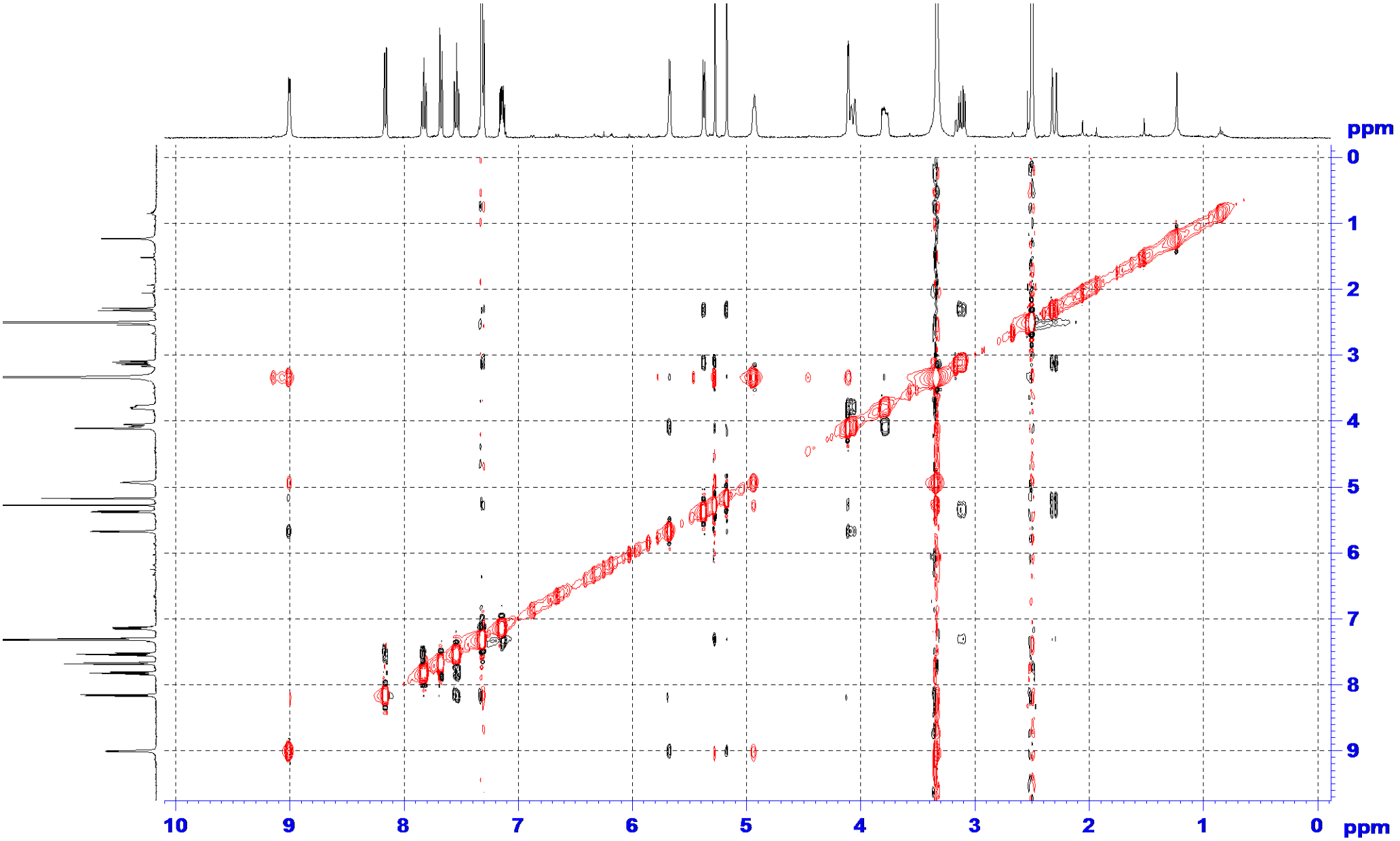


Figure S18 HRESIMS Data of **2**

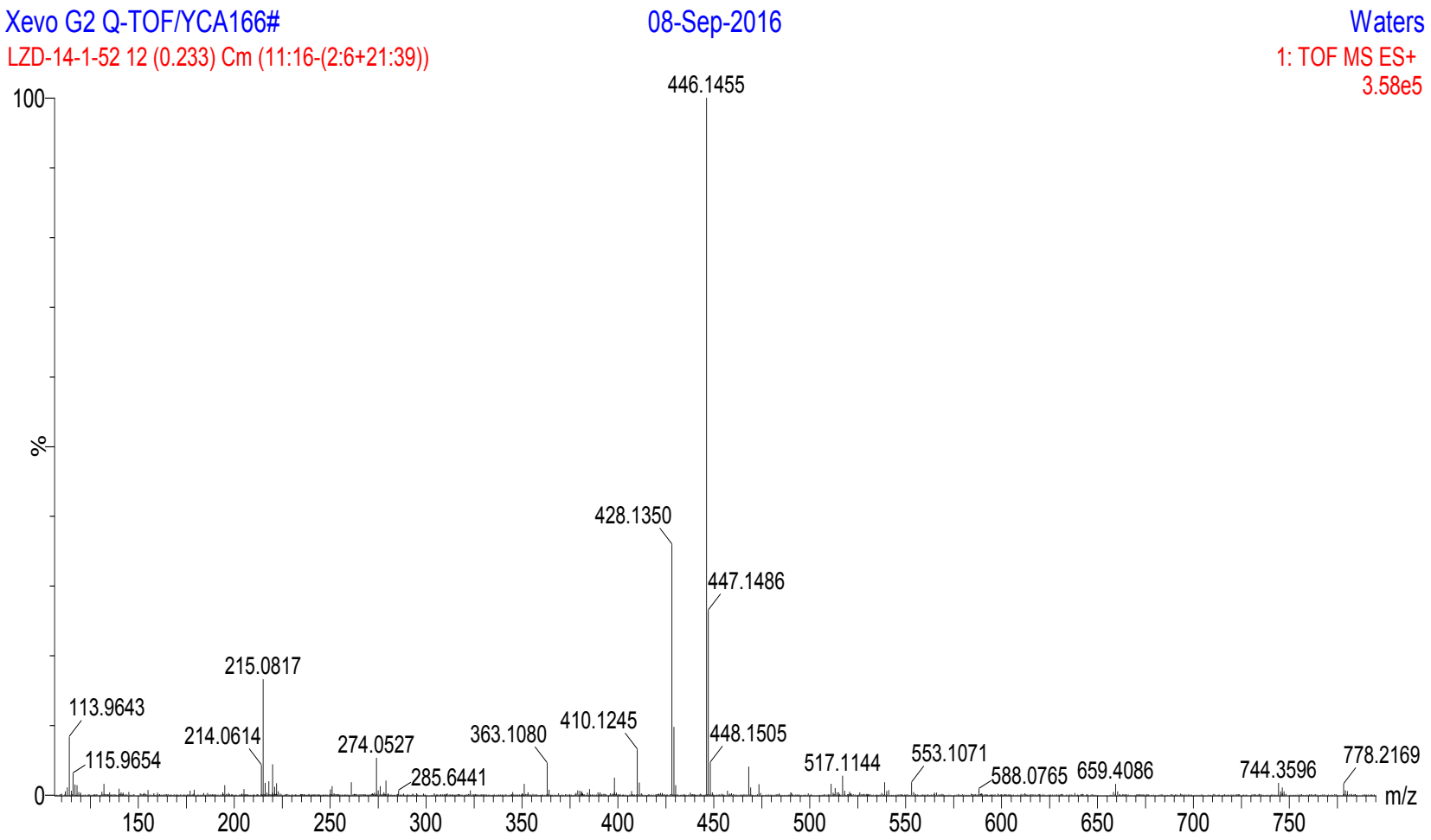
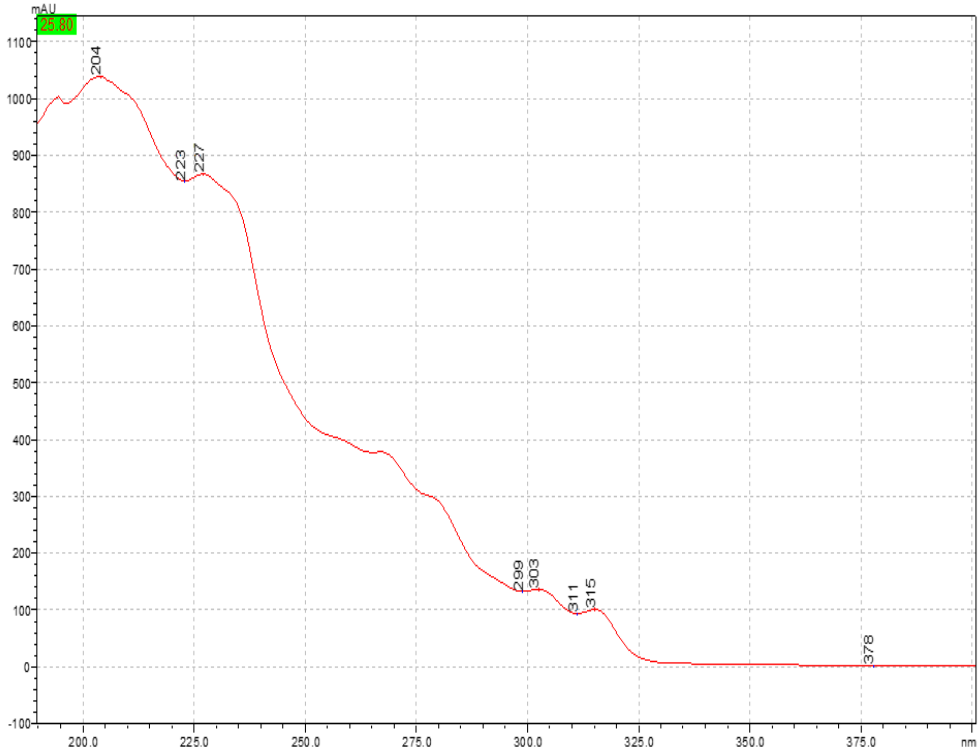


Figure S19 UV spectrum of **3**



UV spectrum of compound **3**

Figure S20 IR Spectrum of **3**

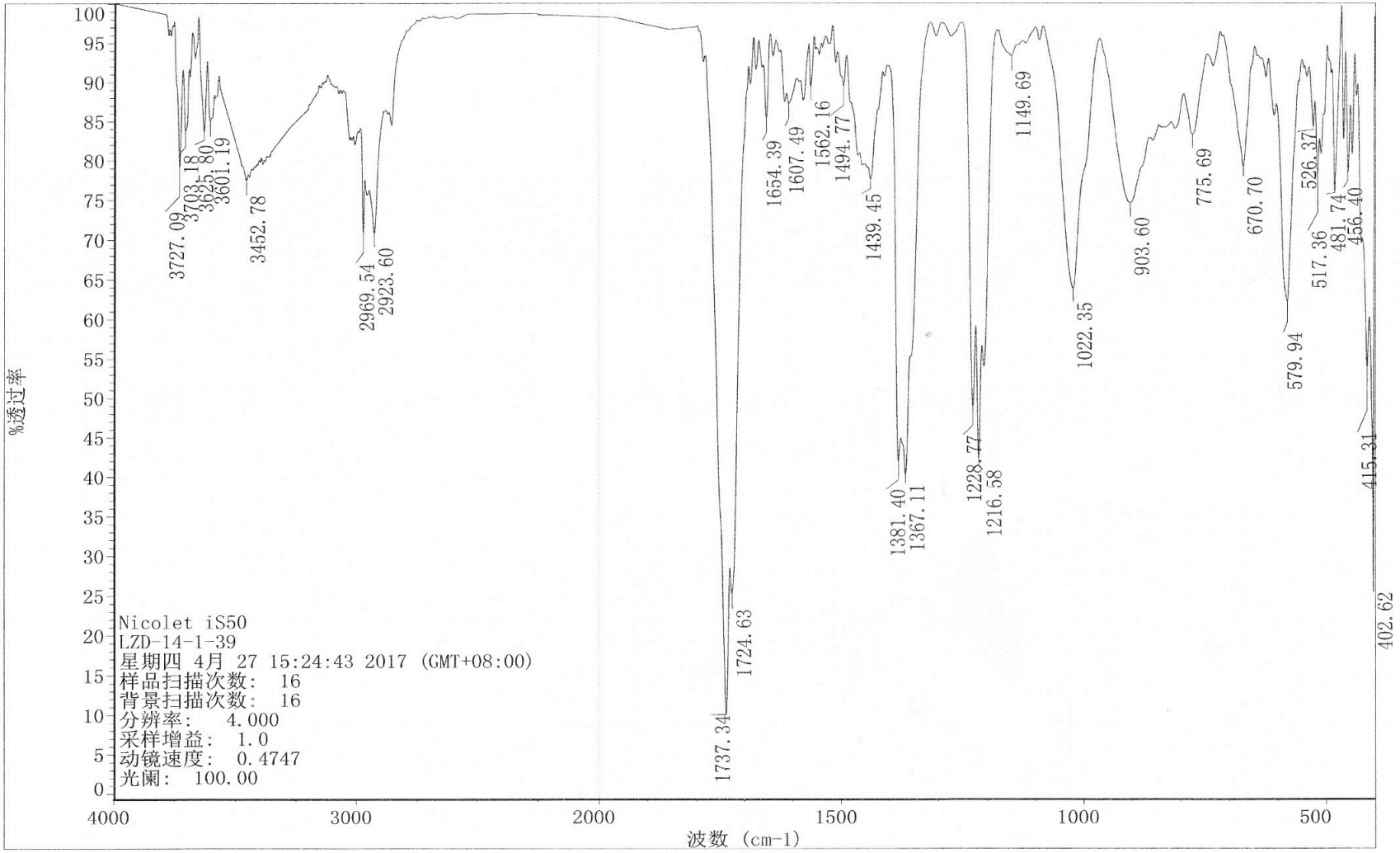


Figure S21 ^{1}H NMR Spectrum of **3** in DMSO-d_6

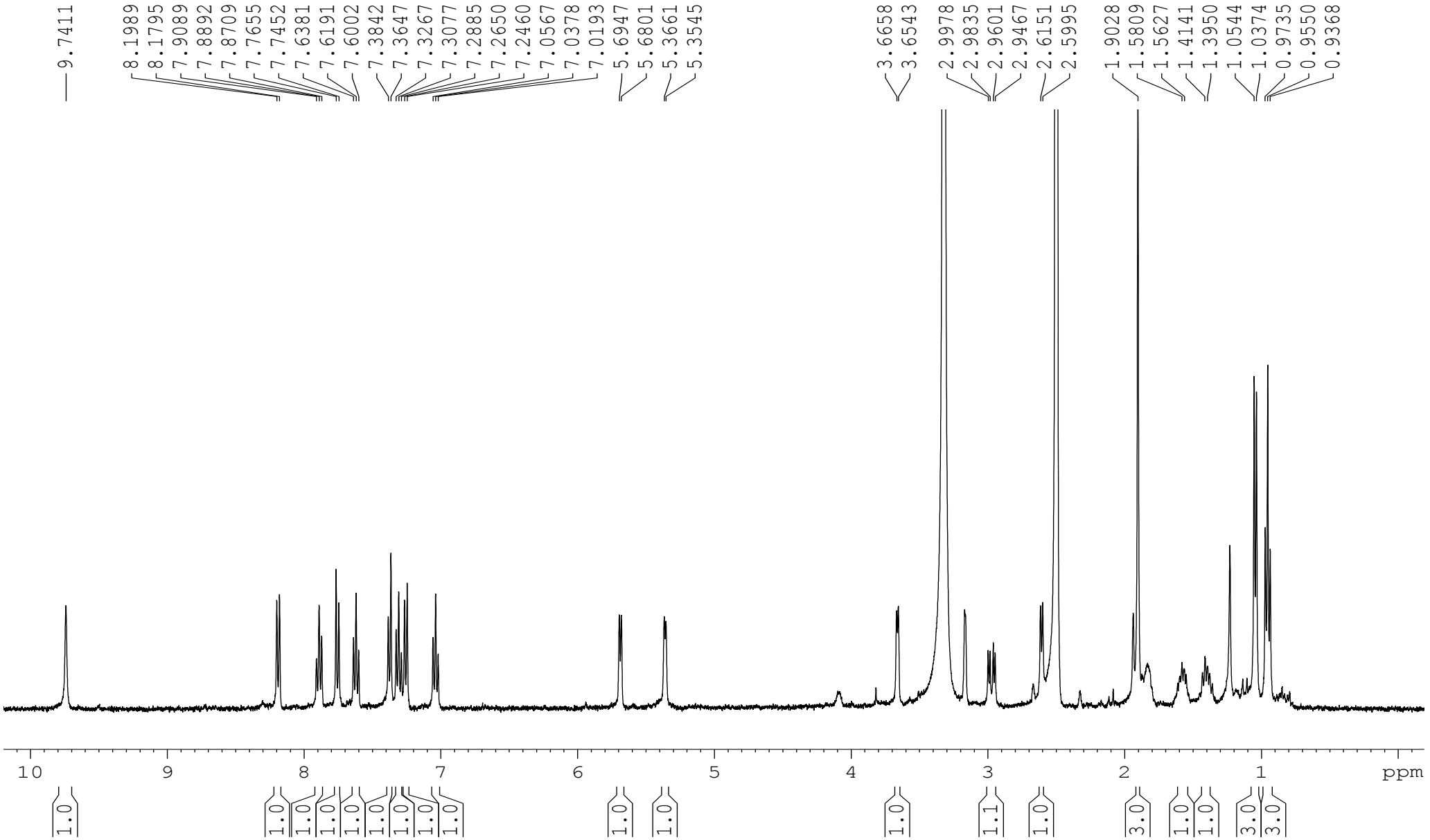


Figure S22 DEPTQ Spectrum of **3** in DMSO-d_6

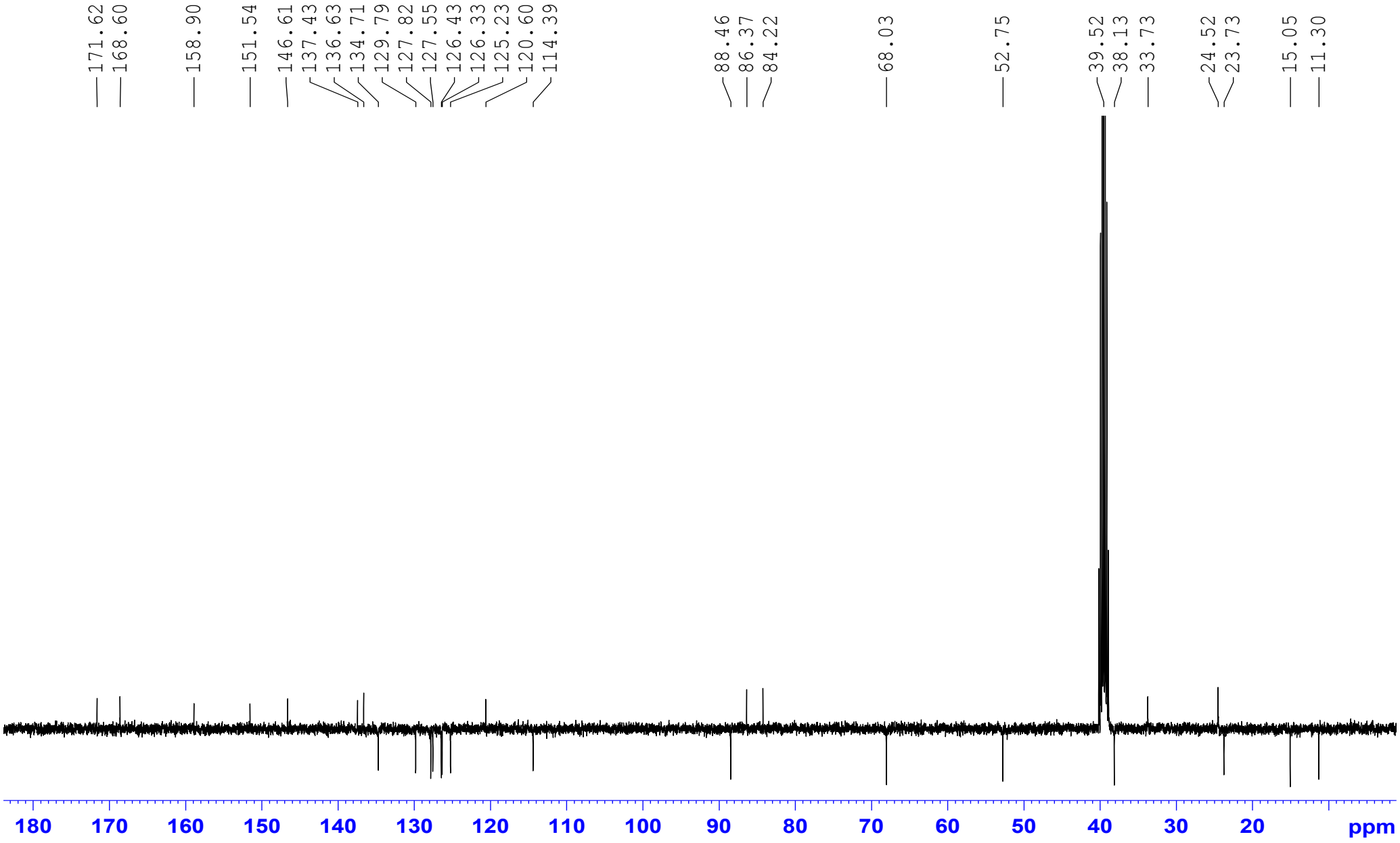


Figure S23 HSQC Spectrum of **3** in DMSO-d_6

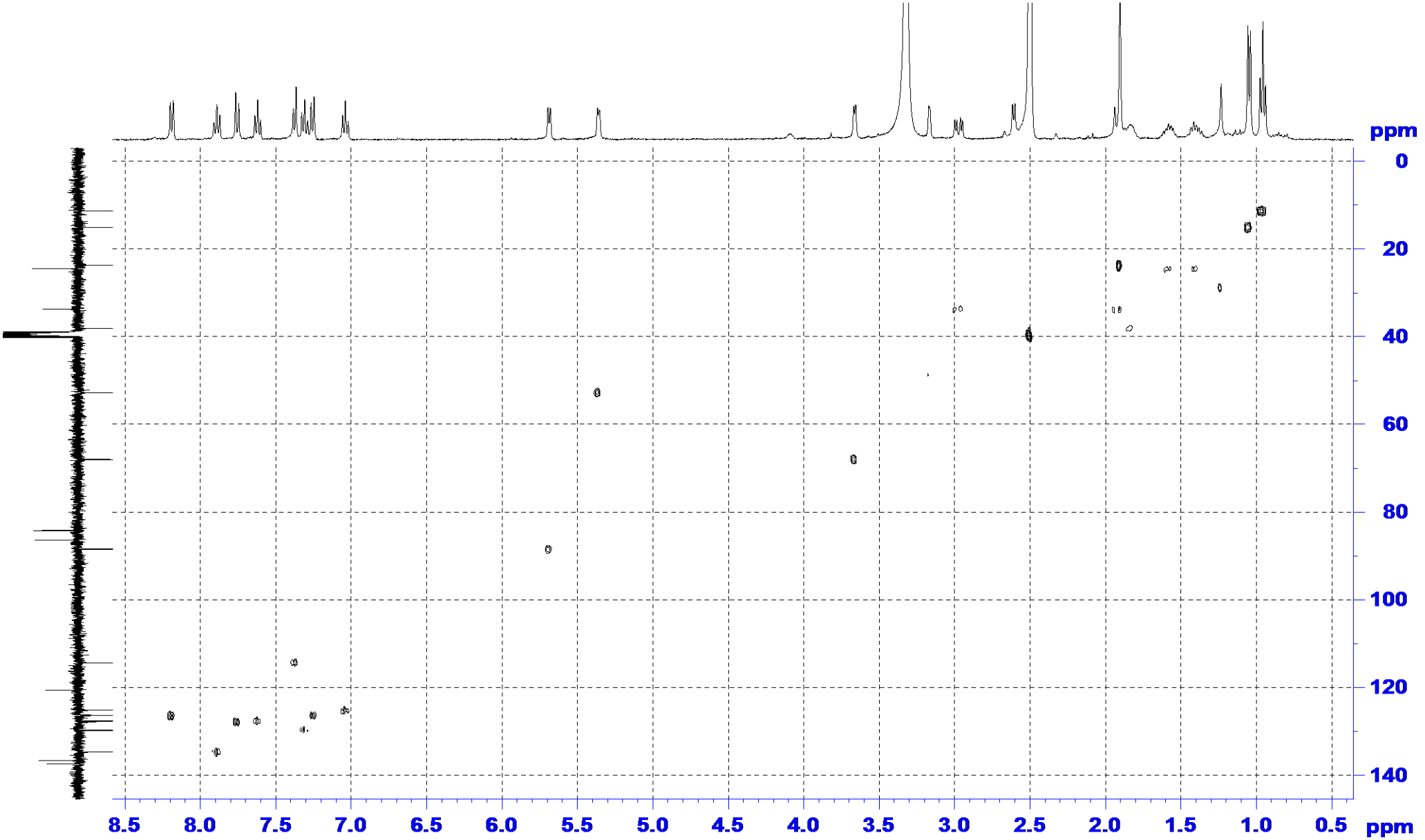


Figure S24 ^{1}H-^{1}H COSY Spectrum of **3** in DMSO-d_6

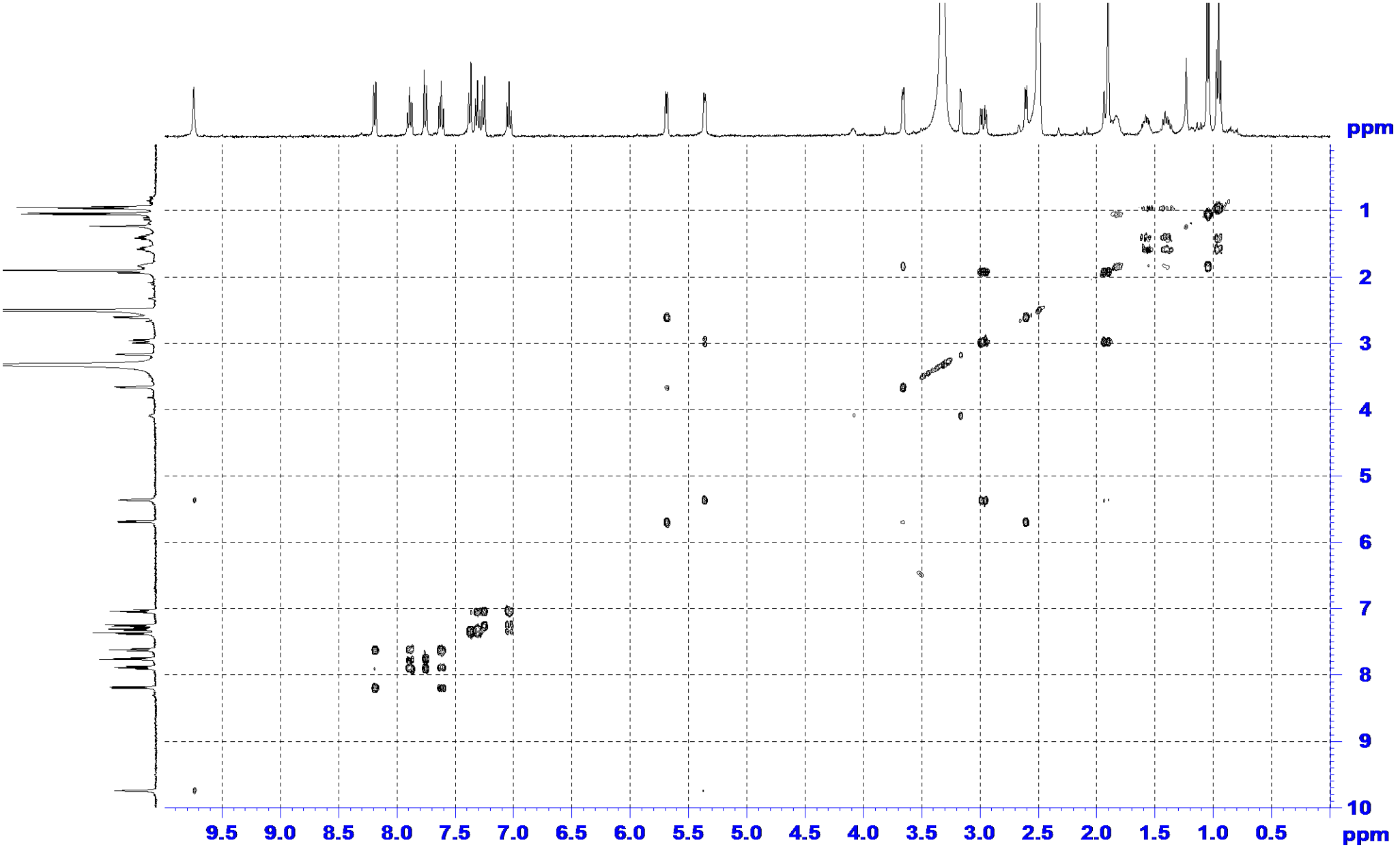


Figure S25 HMBC Spectrum of **3** in DMSO-d_6

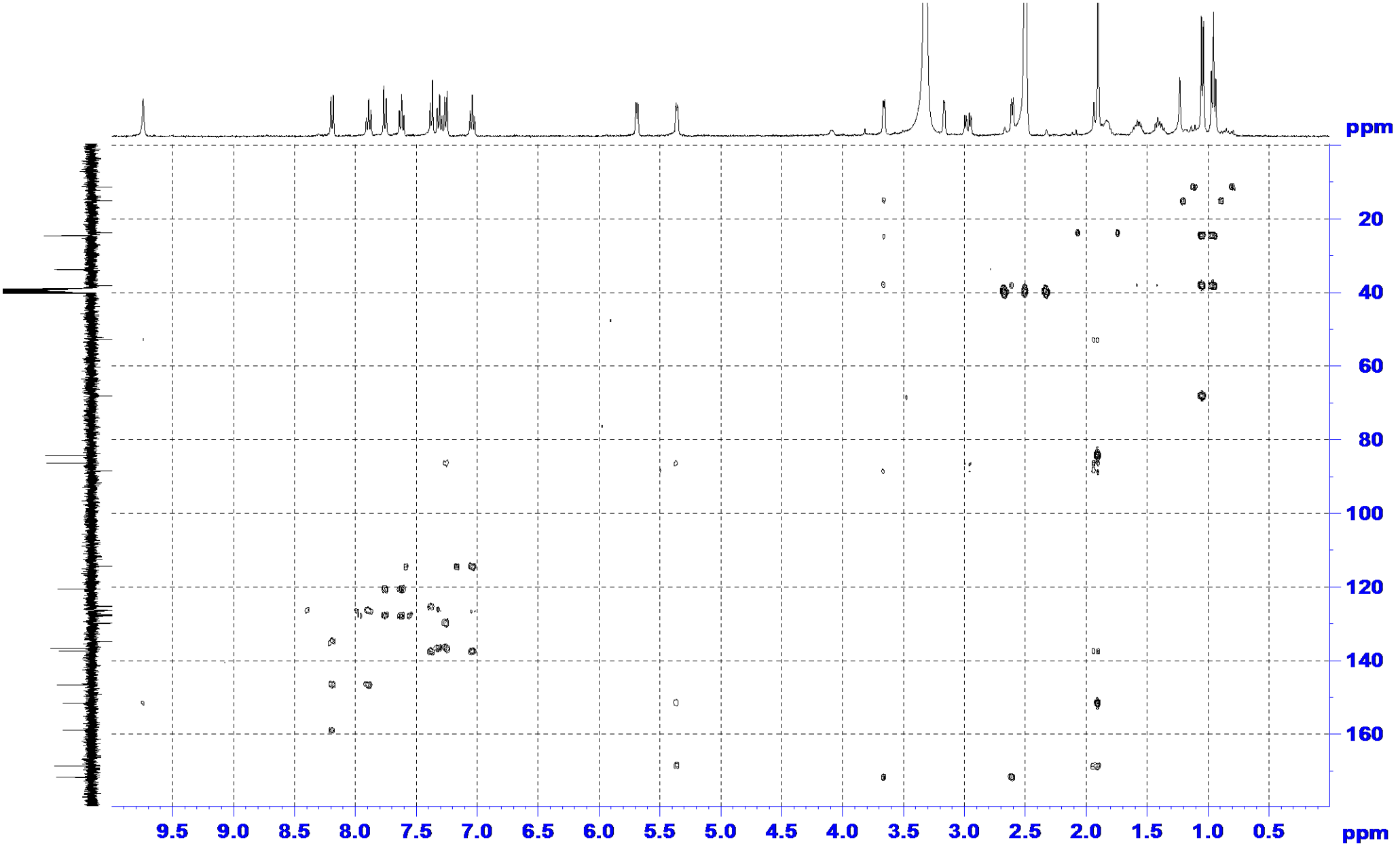


Figure S26 NOESY Spectrum of **3** in DMSO-d_6

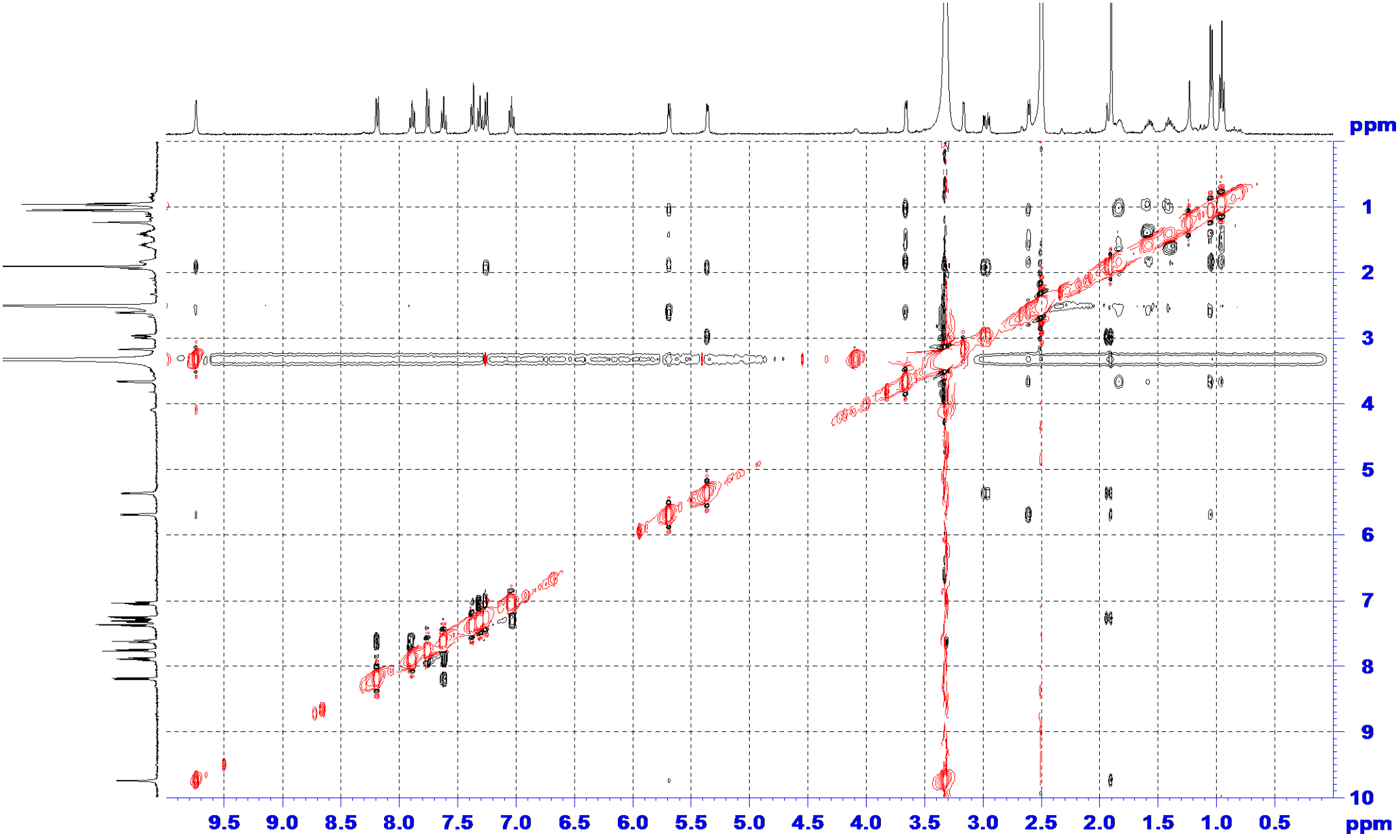


Figure S27 HRESIMS Data of **3**

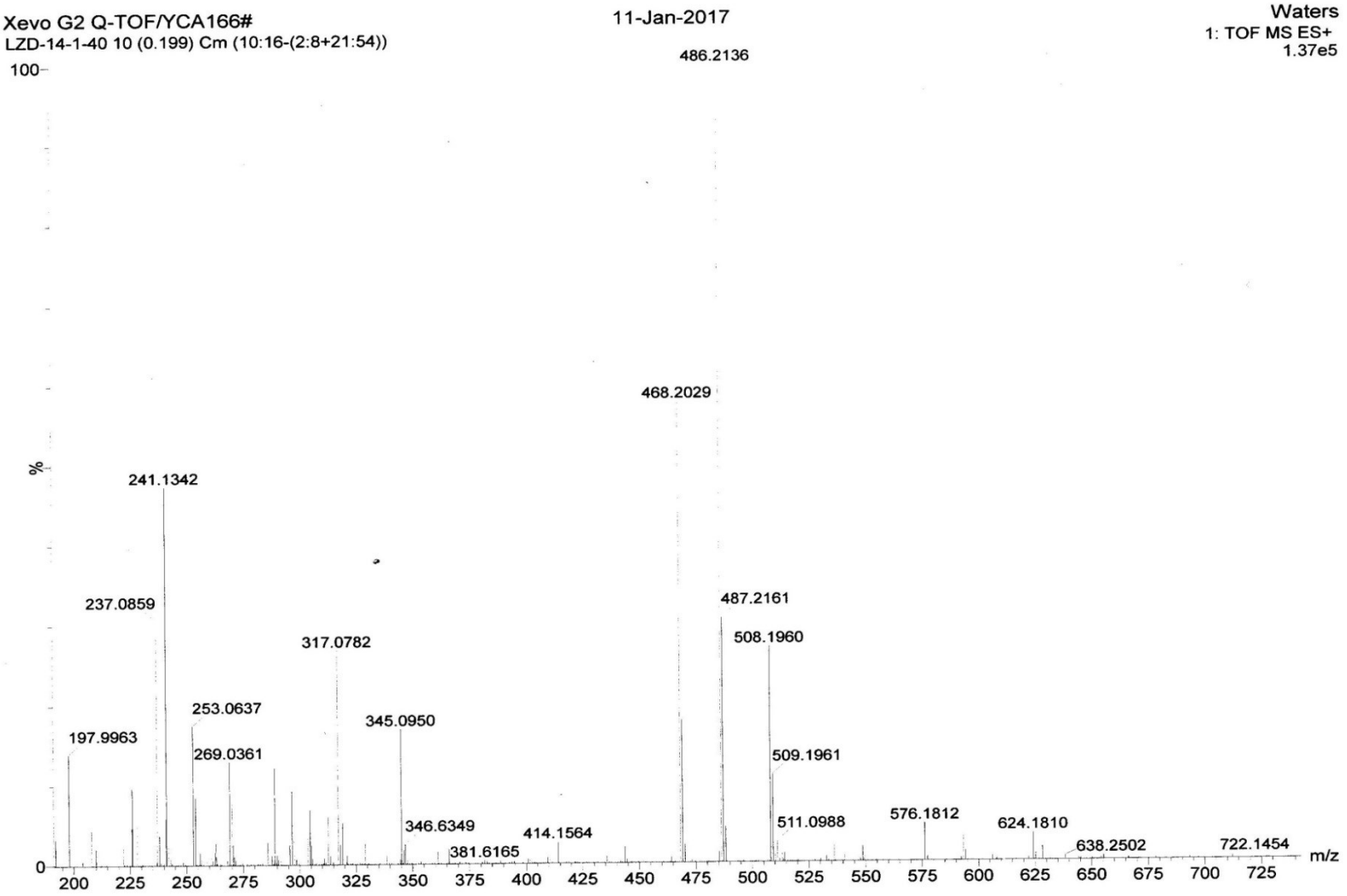
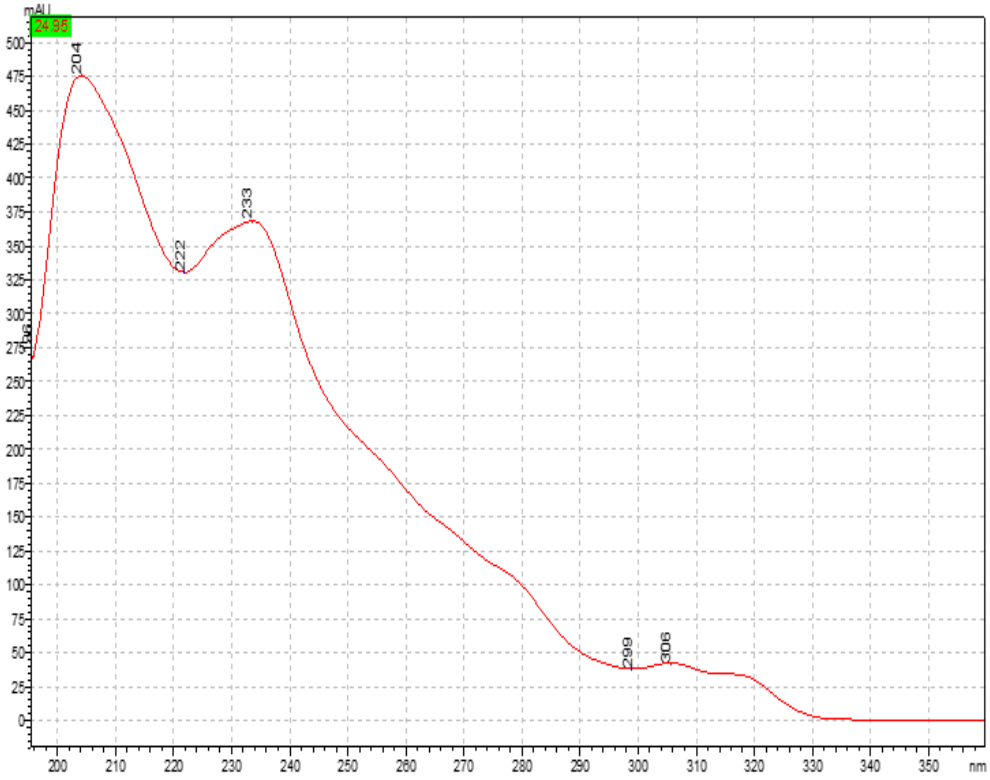


Figure S28 UV spectrum of **4**



UV spectrum of compound **4**

Figure S29 IR Spectrum of **4**

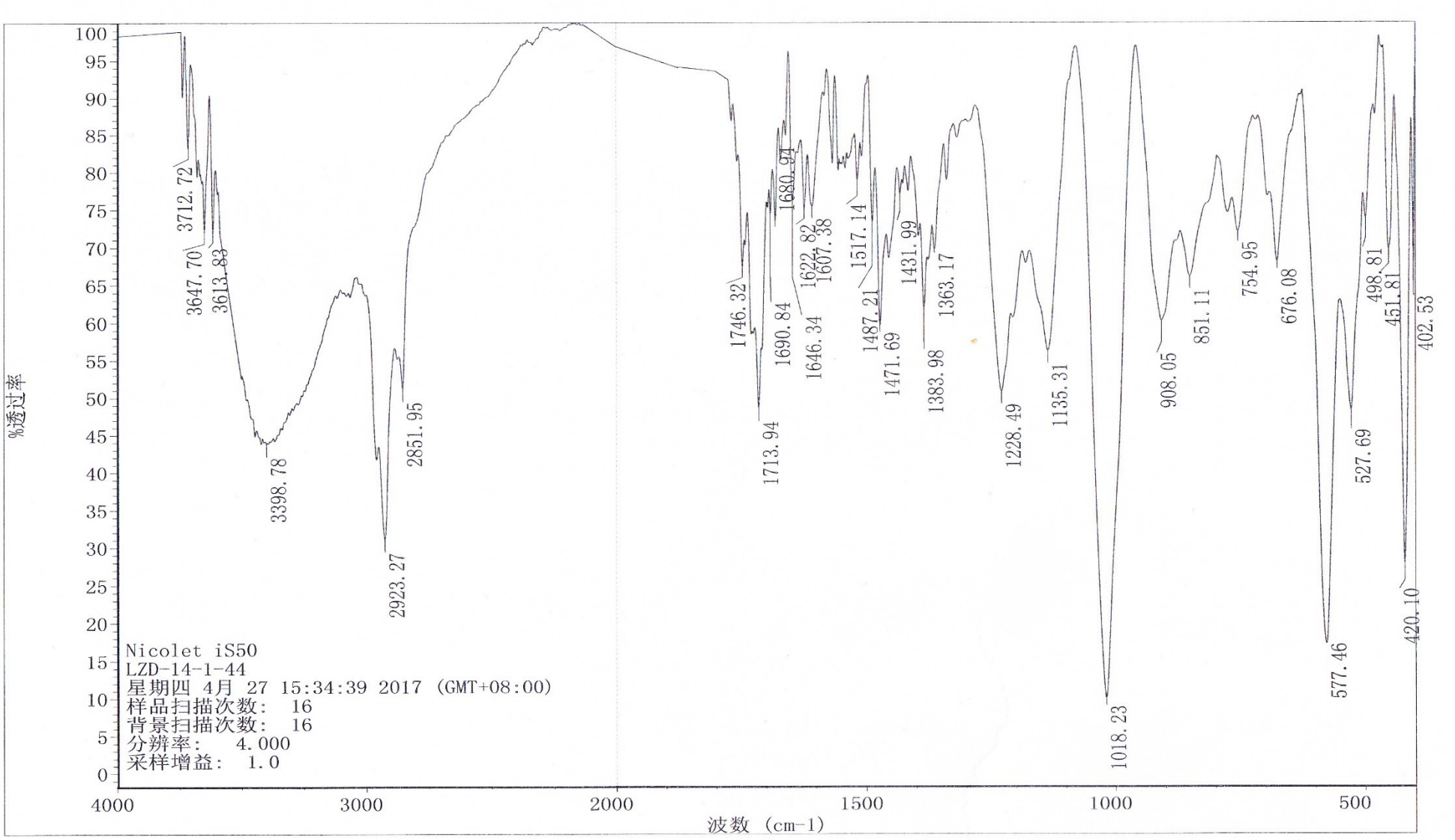


Figure S30 ^{1}H NMR Spectrum of **4** in DMSO-d_6

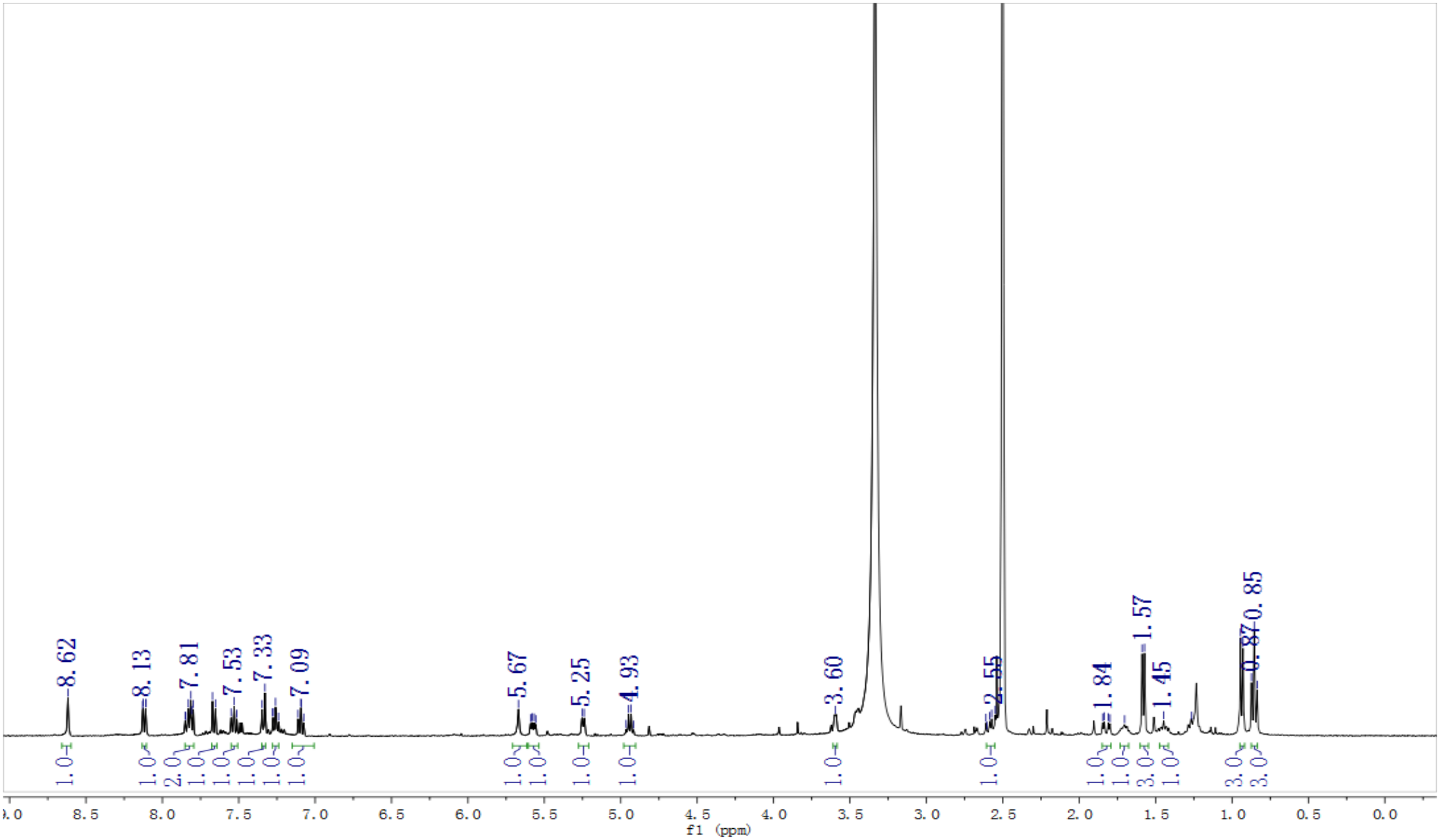


Figure S31 ^{13}C NMR Spectrum of **4** in DMSO-d_6

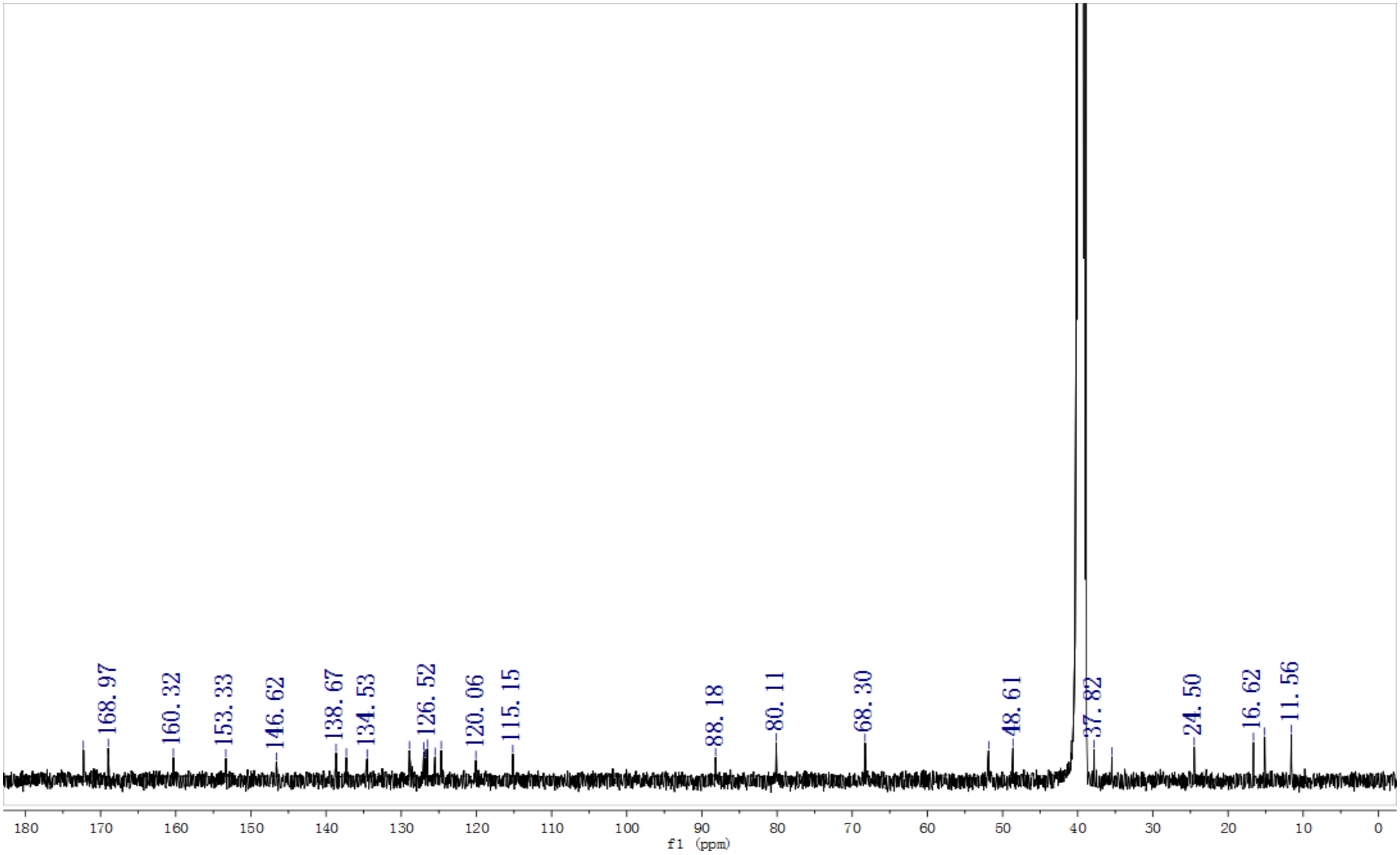


Figure S32 HSQC Spectrum of **4** in DMSO-d_6

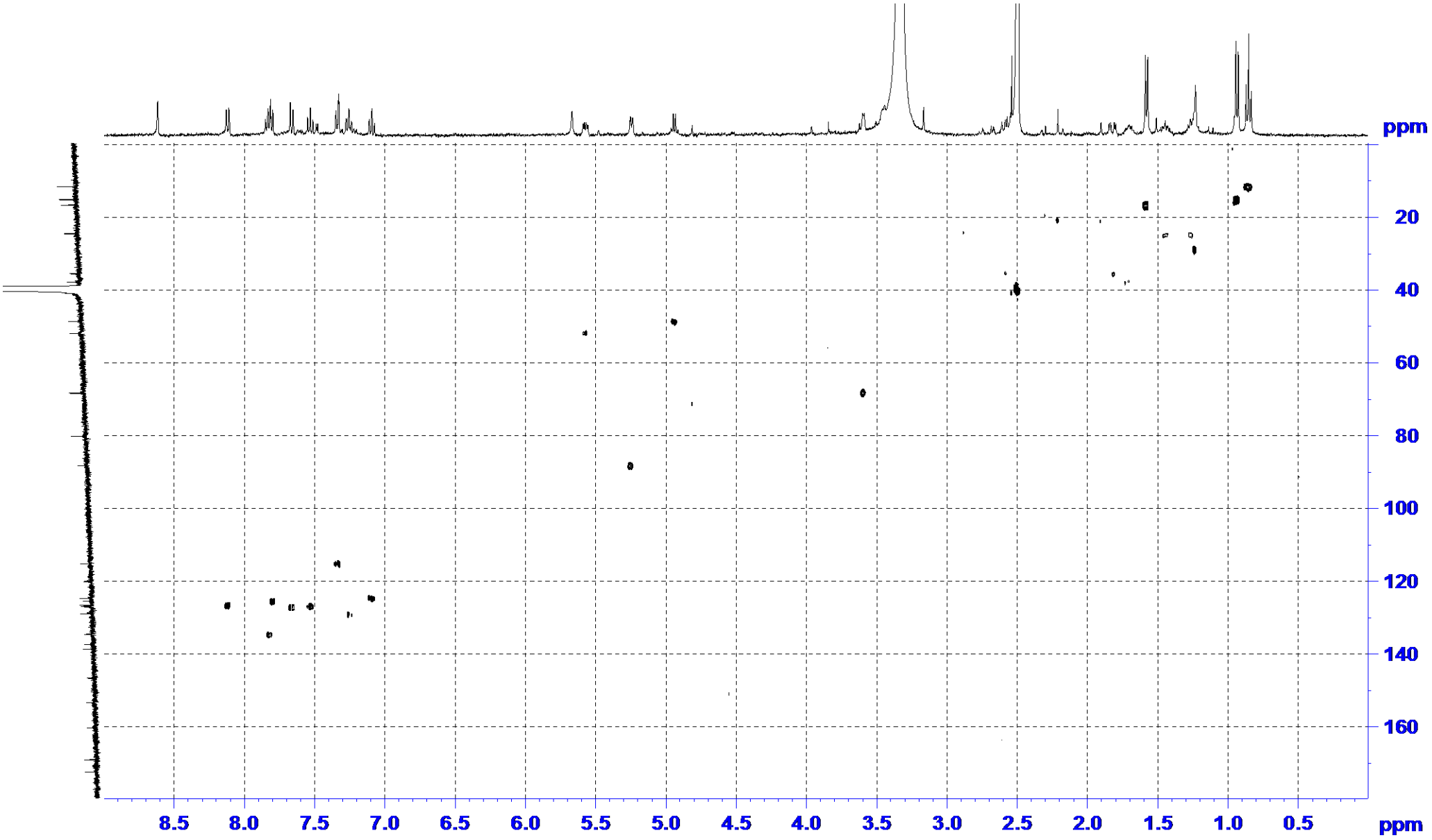


Figure S33 ^{1}H-^{1}H COSY Spectrum of **4** in DMSO-d_6

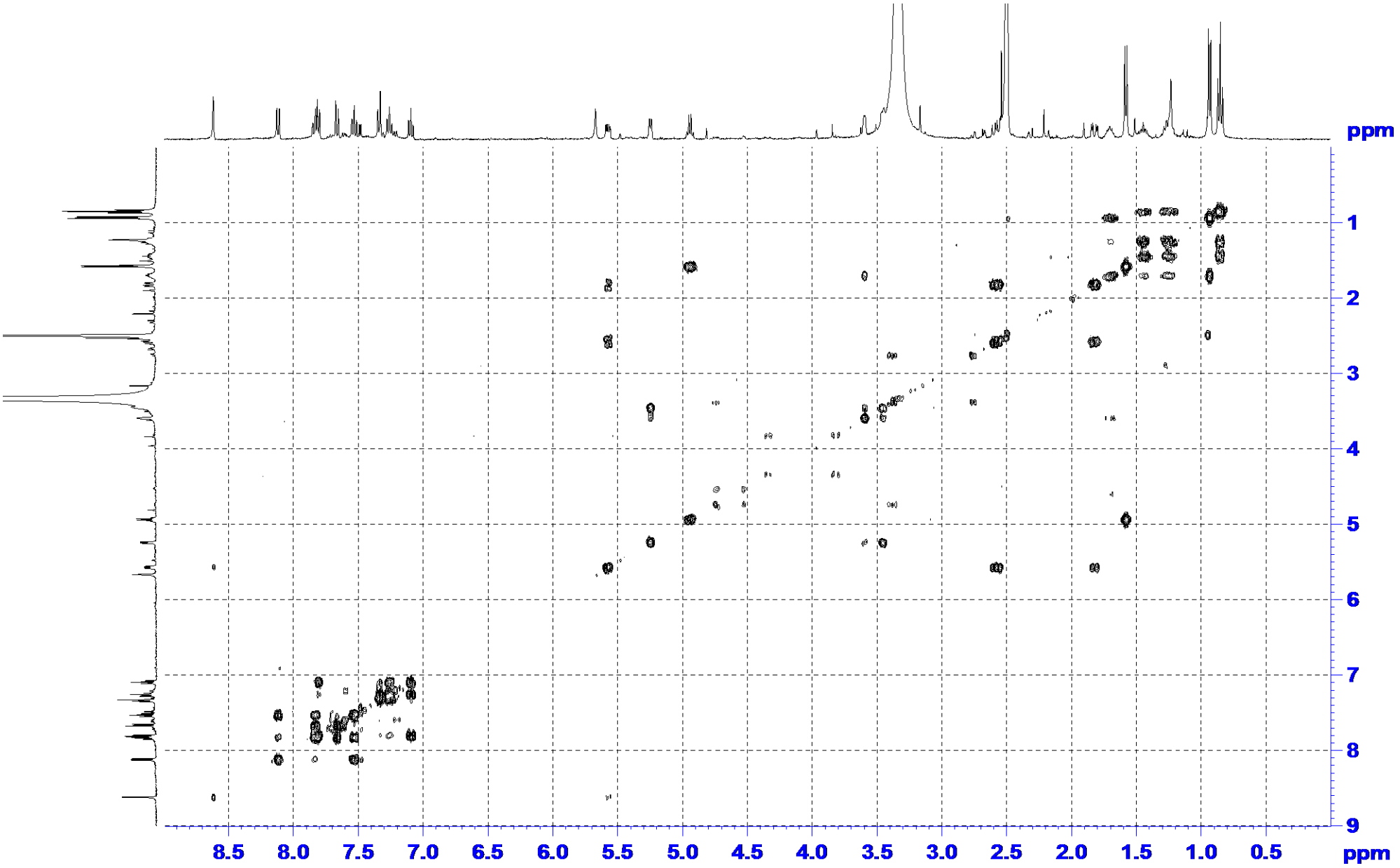


Figure S34 HMBC Spectrum of **4** in DMSO-d_6

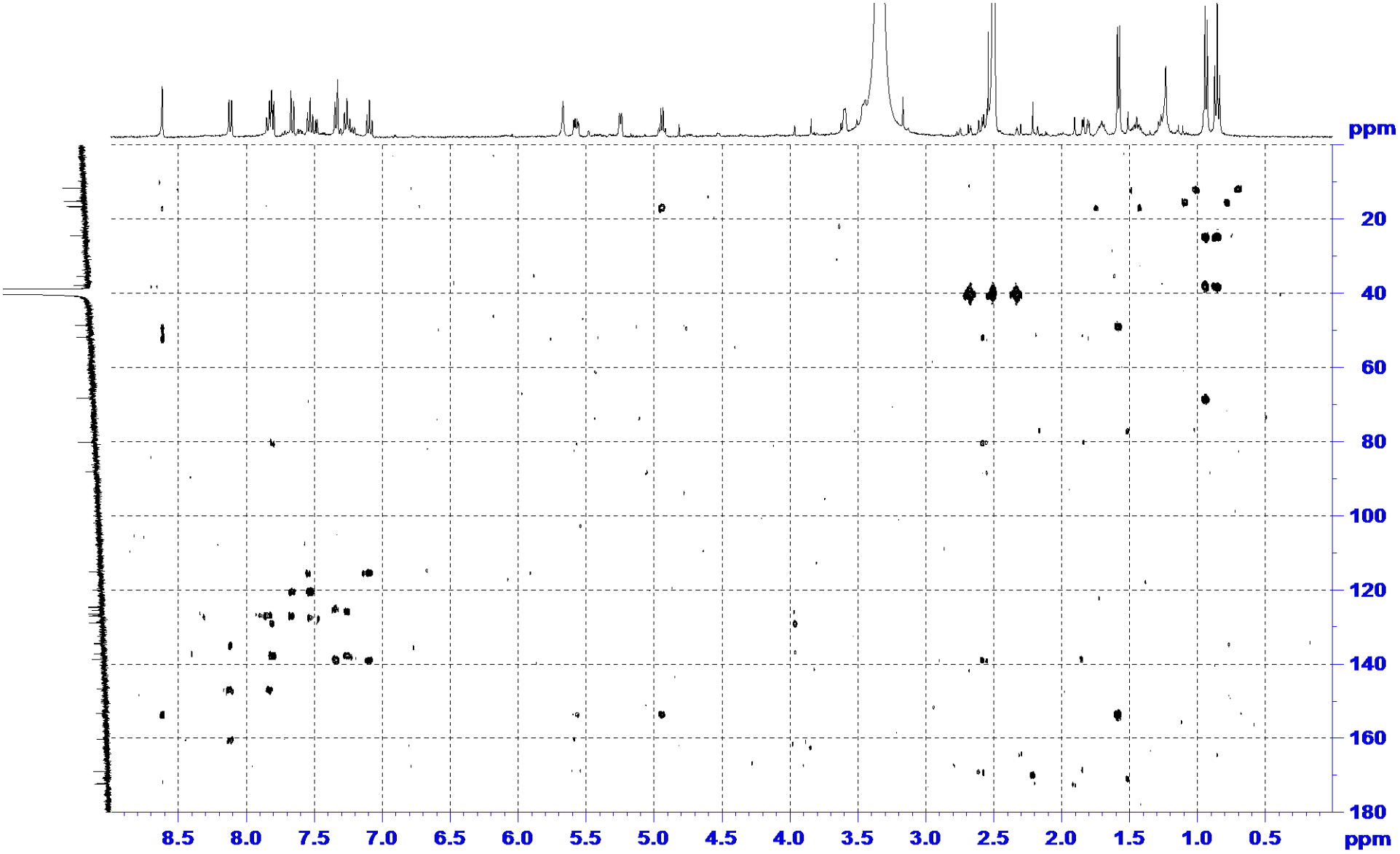


Figure S35 NOESY Spectrum of **4** in DMSO-d_6

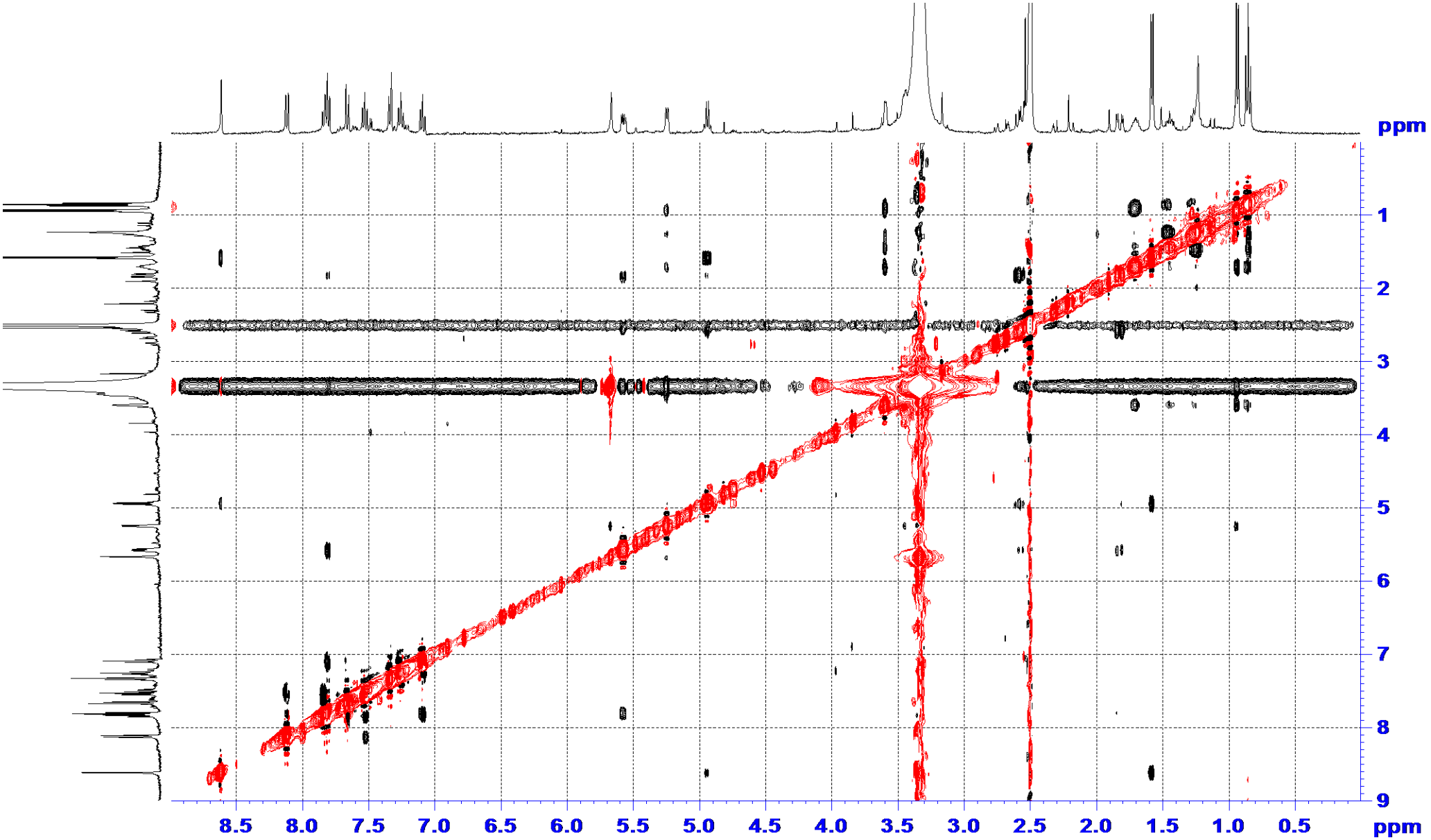


Figure S36 HRESIMS Data of **4**

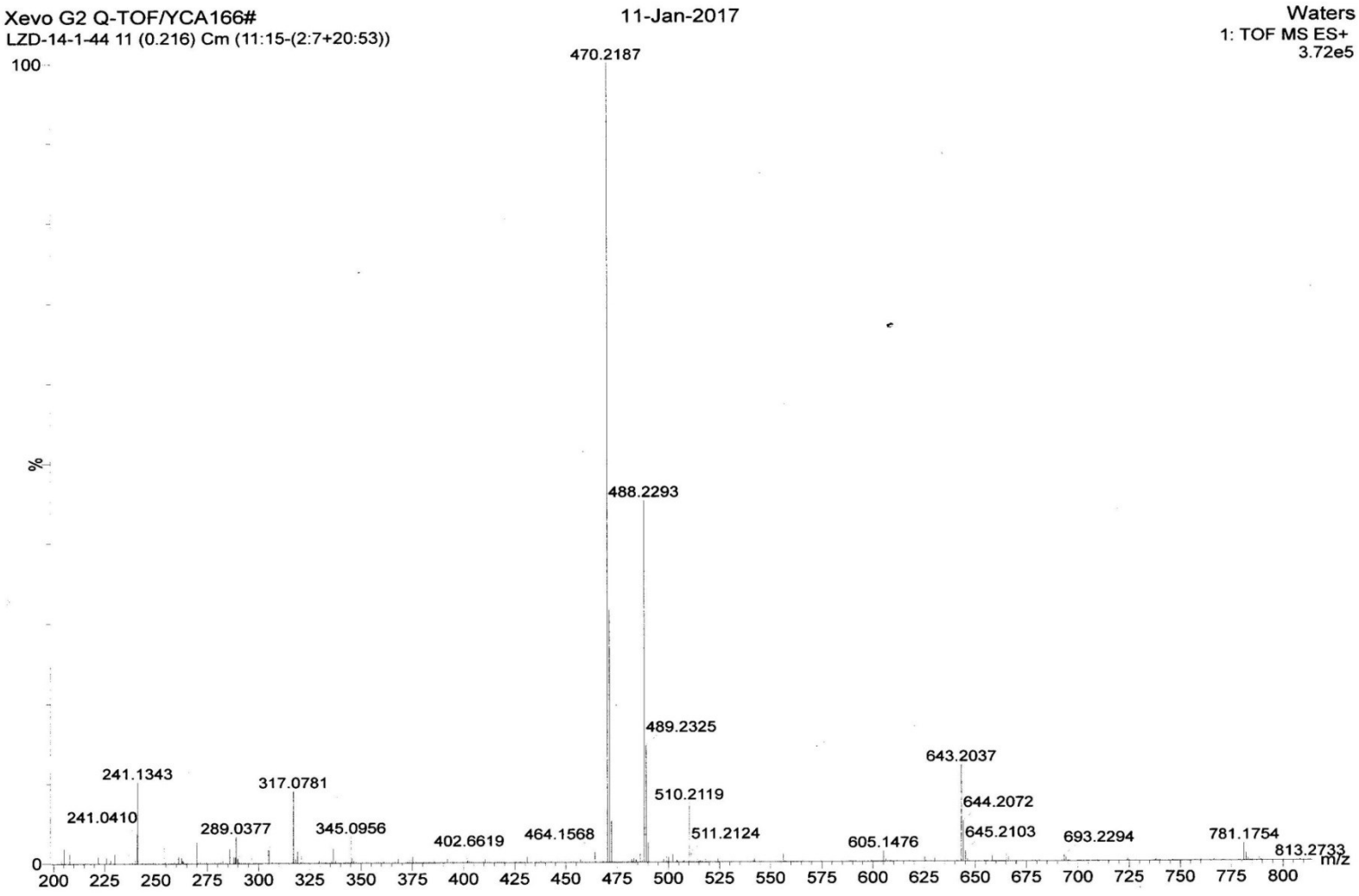
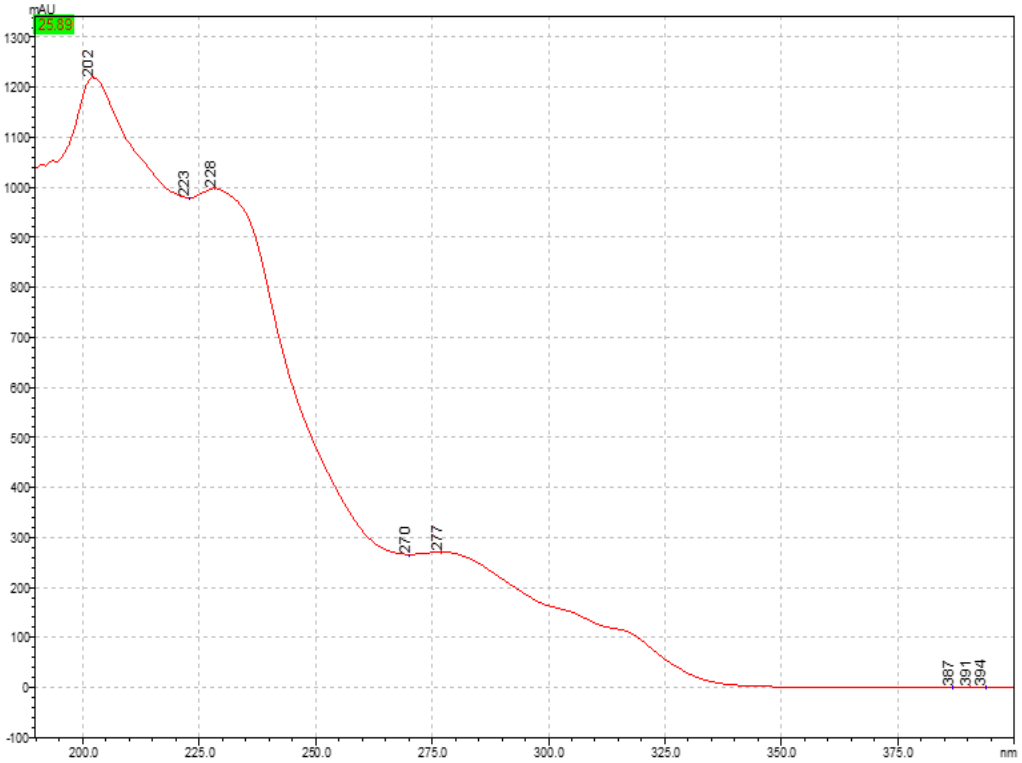


Figure S37 UV spectrum of **5**



UV spectrum of compound **5**

Figure S38 IR Spectrum of **5**

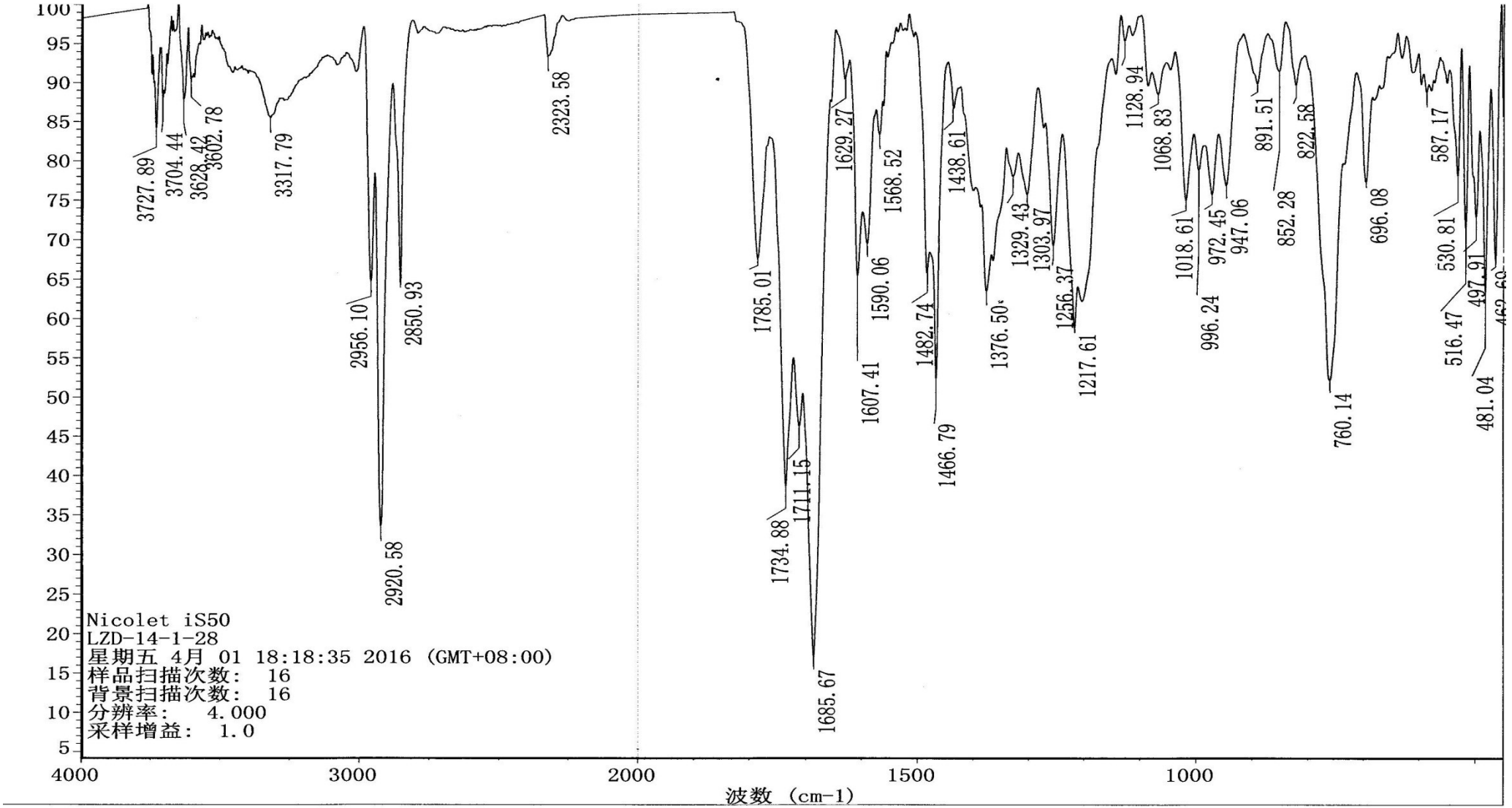


Figure S39 ^{1}H NMR Spectrum of **5** in DMSO-d_6

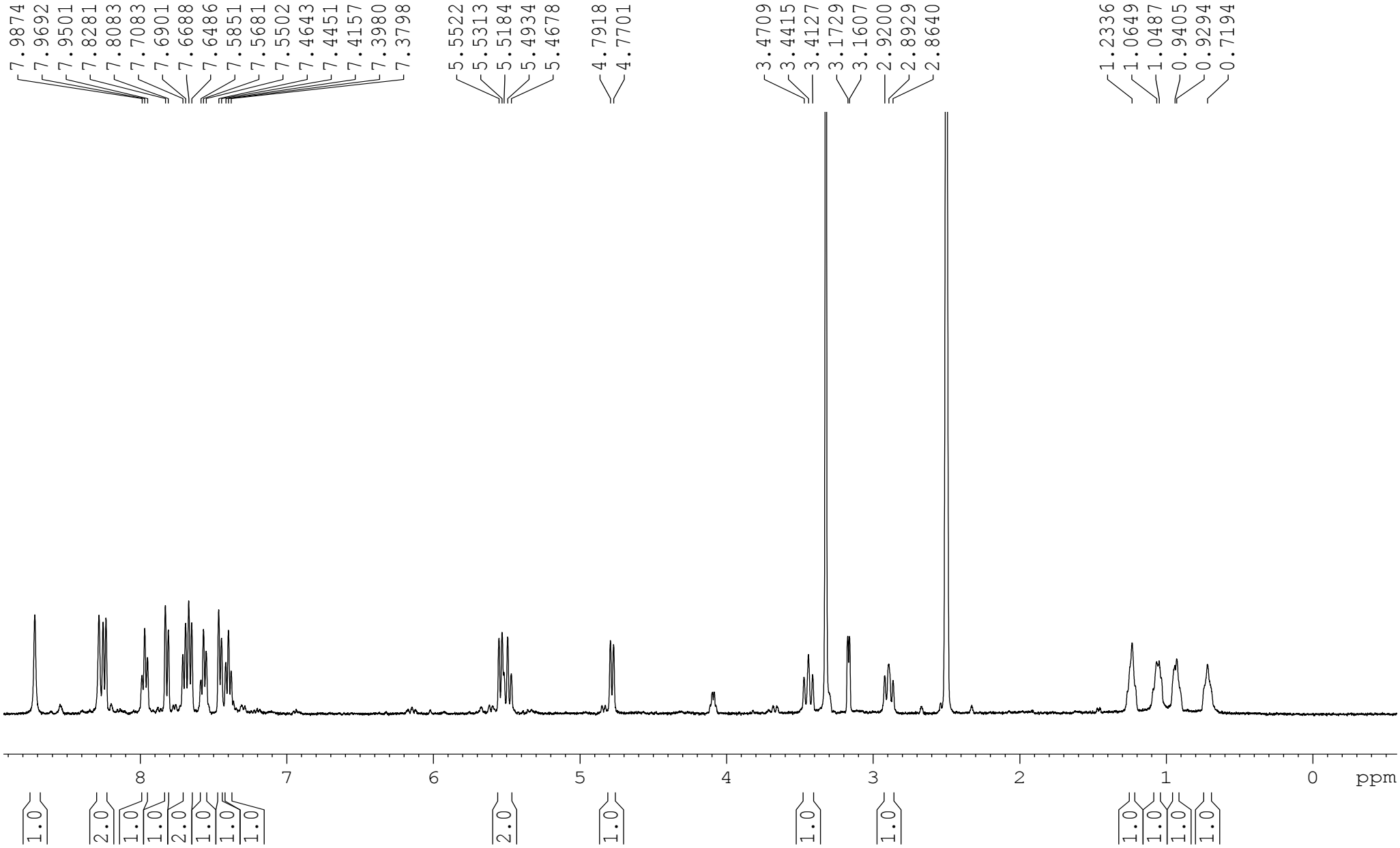


Figure S40 ^{13}C NMR Spectrum of **5** in DMSO-d_6

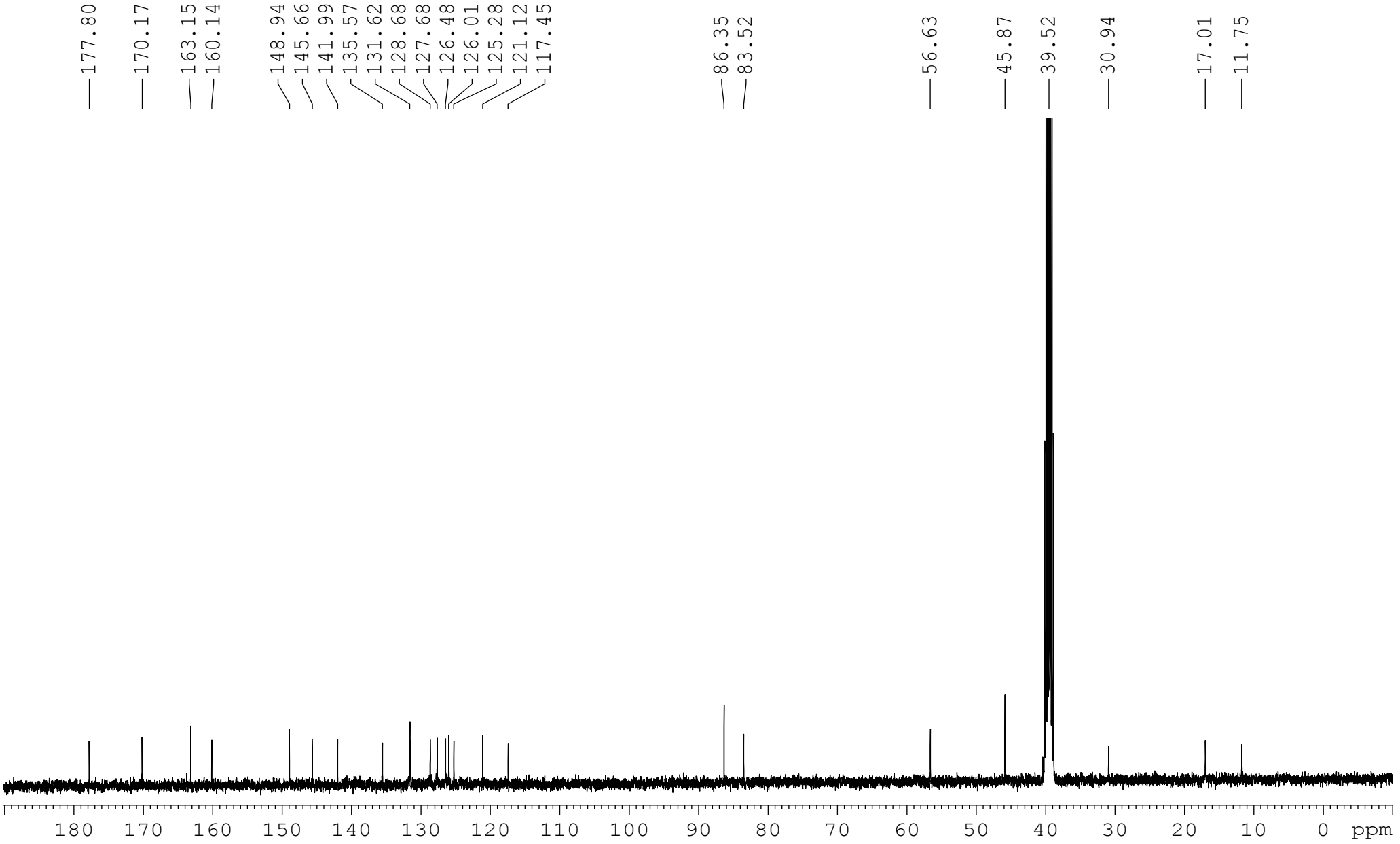


Figure S41 HSQC Spectrum of **5** in DMSO-d_6

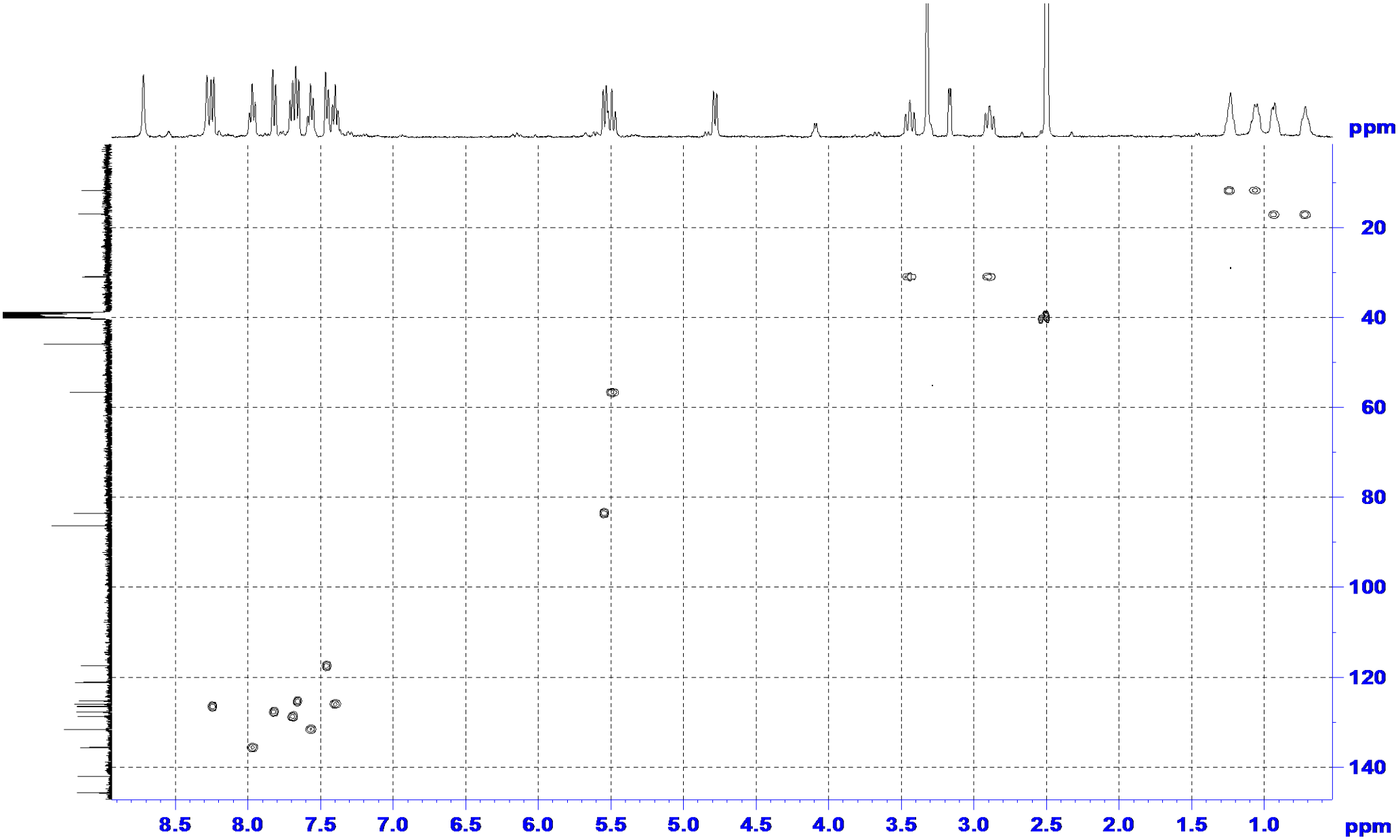


Figure S42 ^{1}H-^{1}H COSY Spectrum of **5** in DMSO-d_6

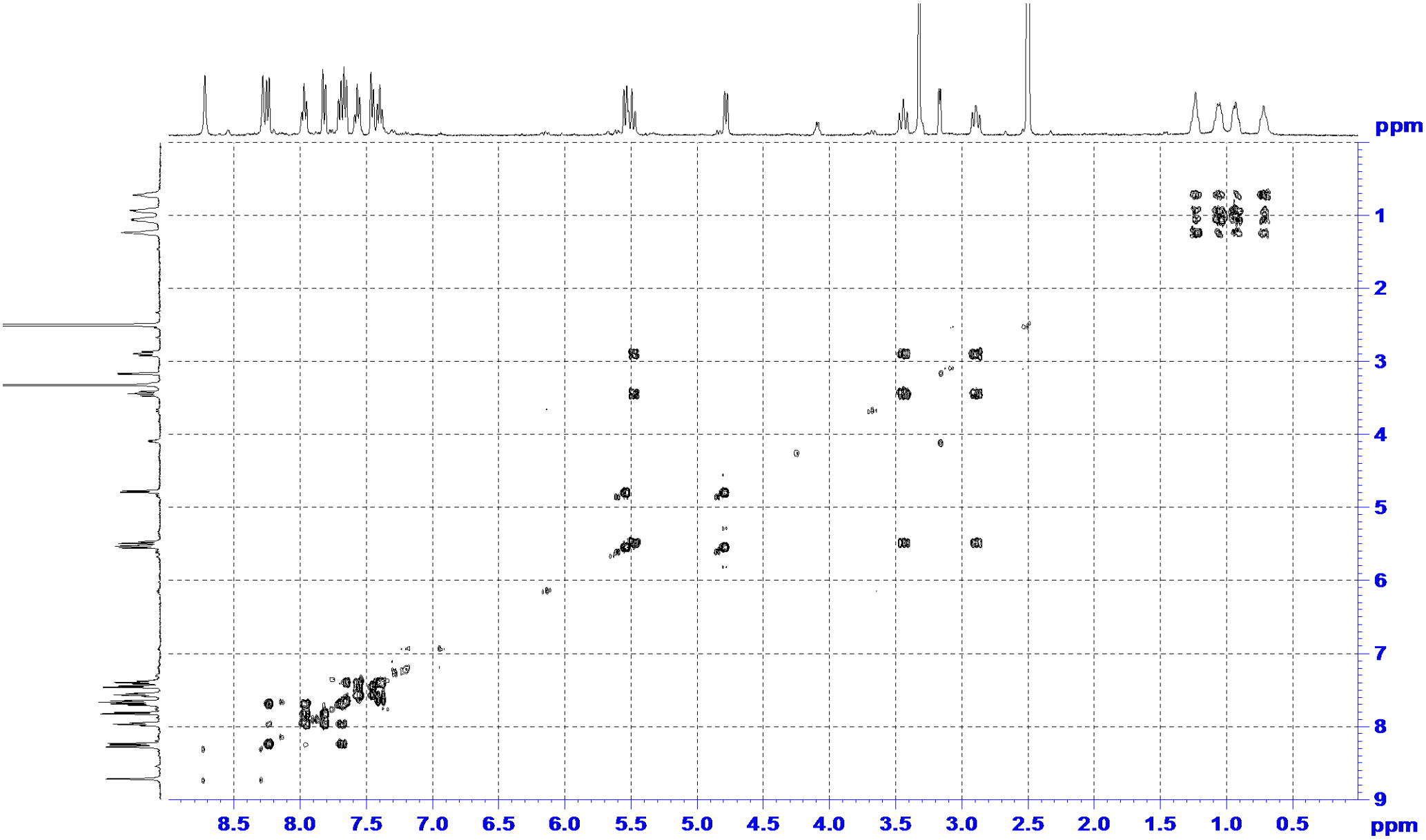


Figure S43 HMBC Spectrum of **5** in DMSO-d_6

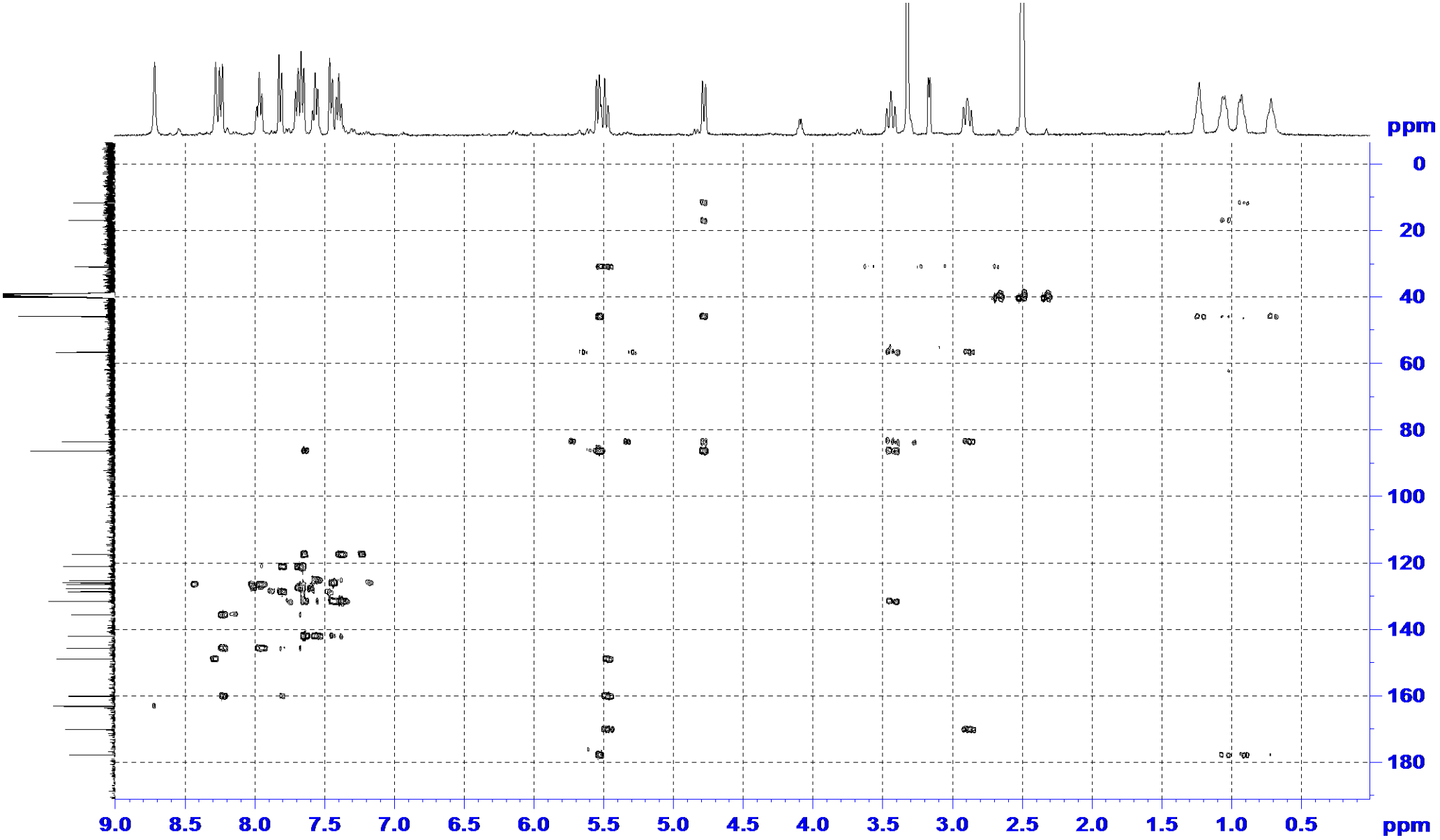


Figure S44 NOESY Spectrum of **5** in DMSO-d_6

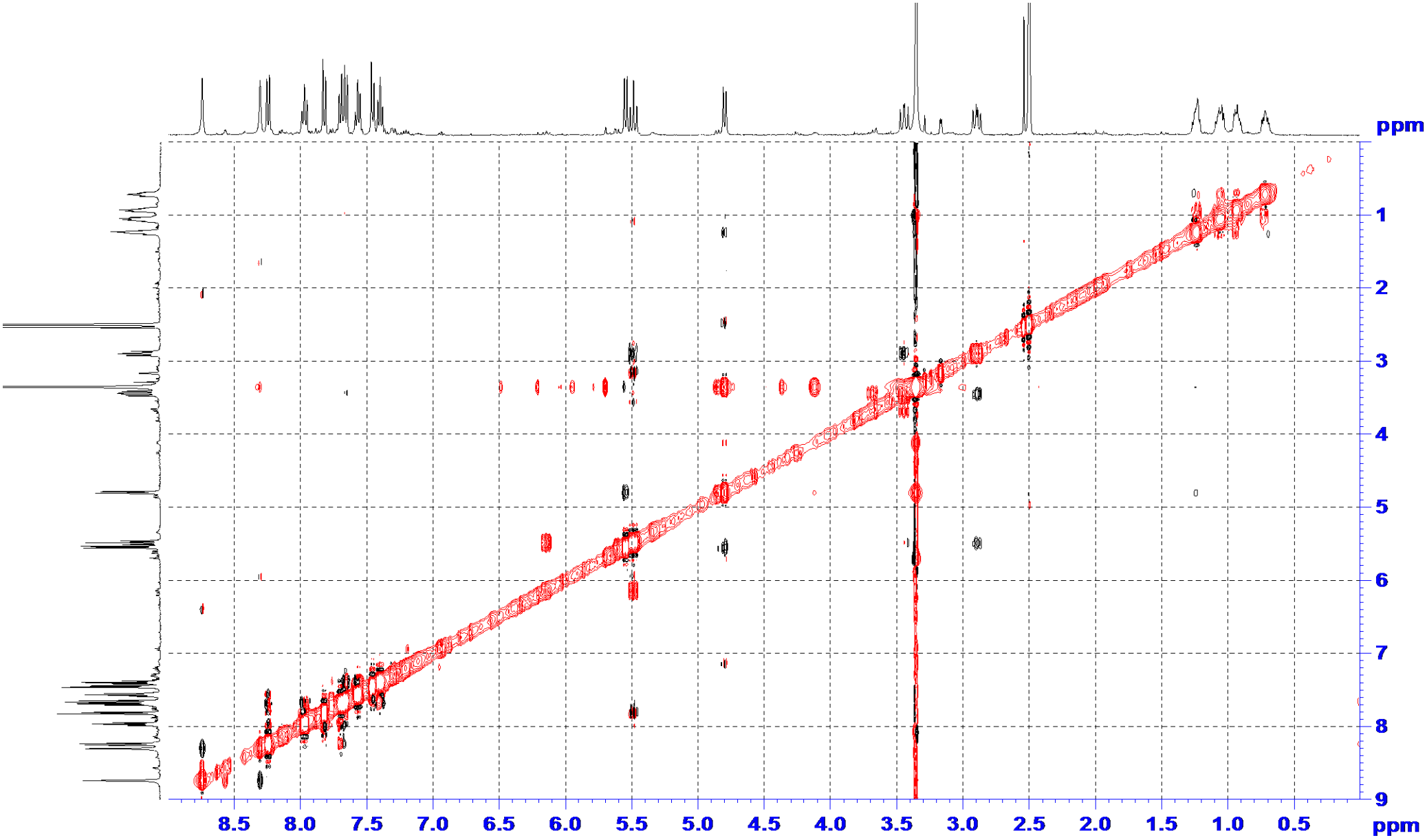


Figure S45 HRESIMS Data of **5**

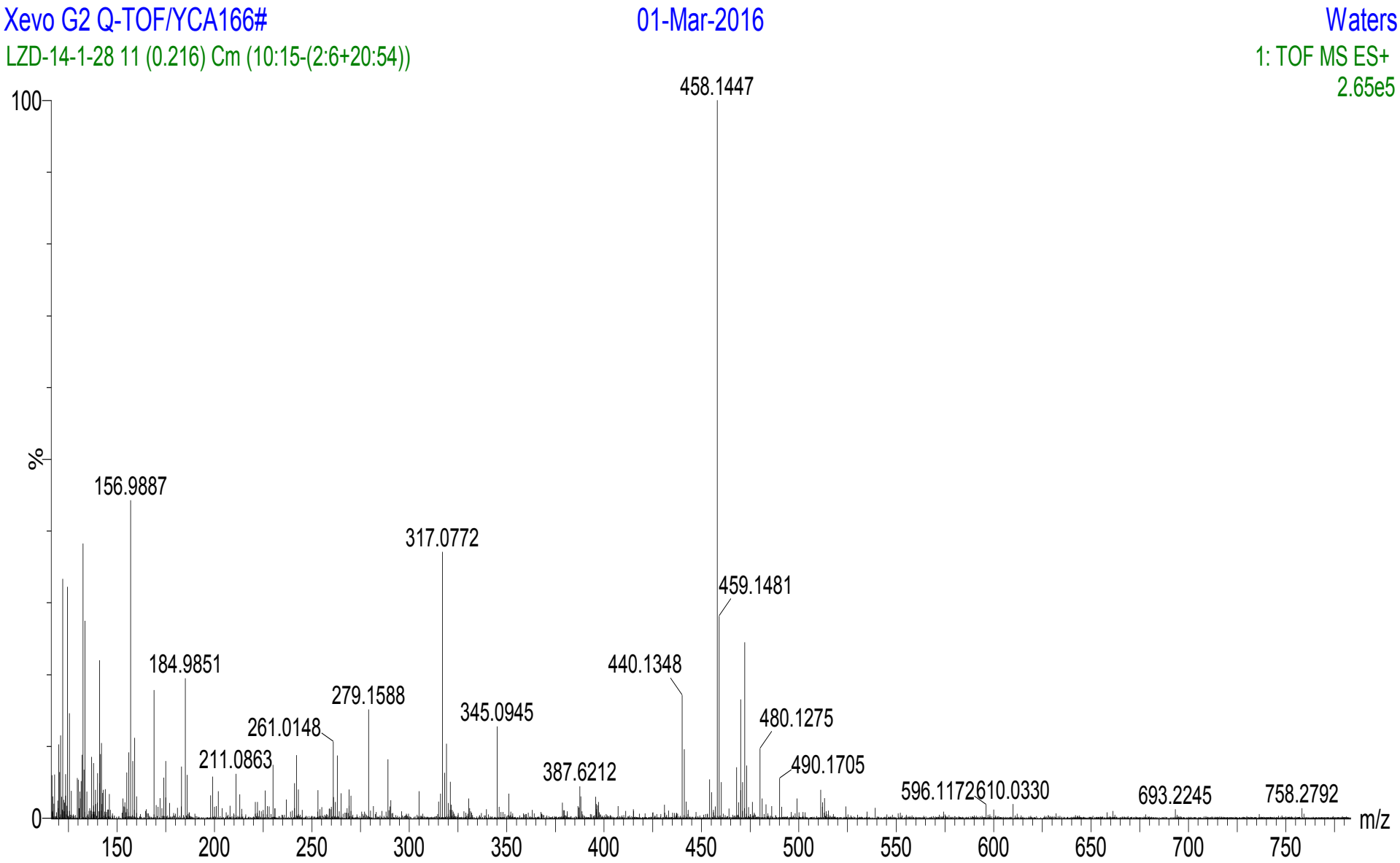
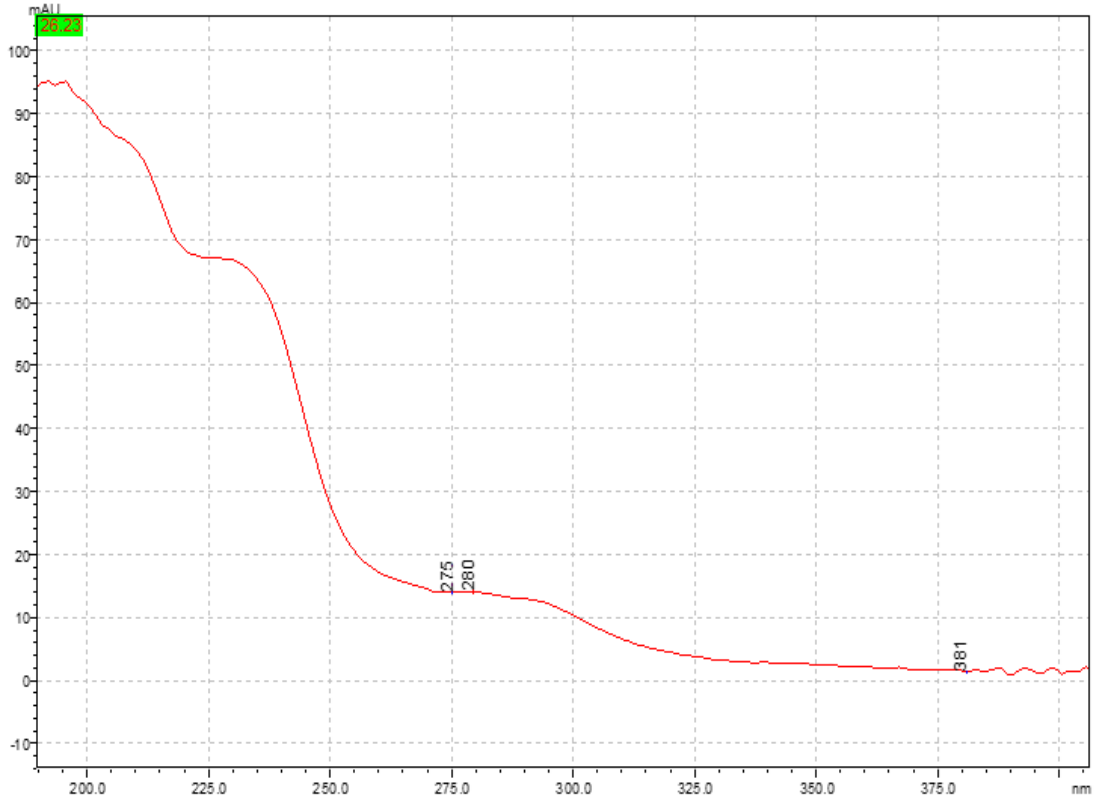


Figure S46 UV spectrum of **6**



UV spectra of compound **6**

Figure S47 IR Spectrum of **6**

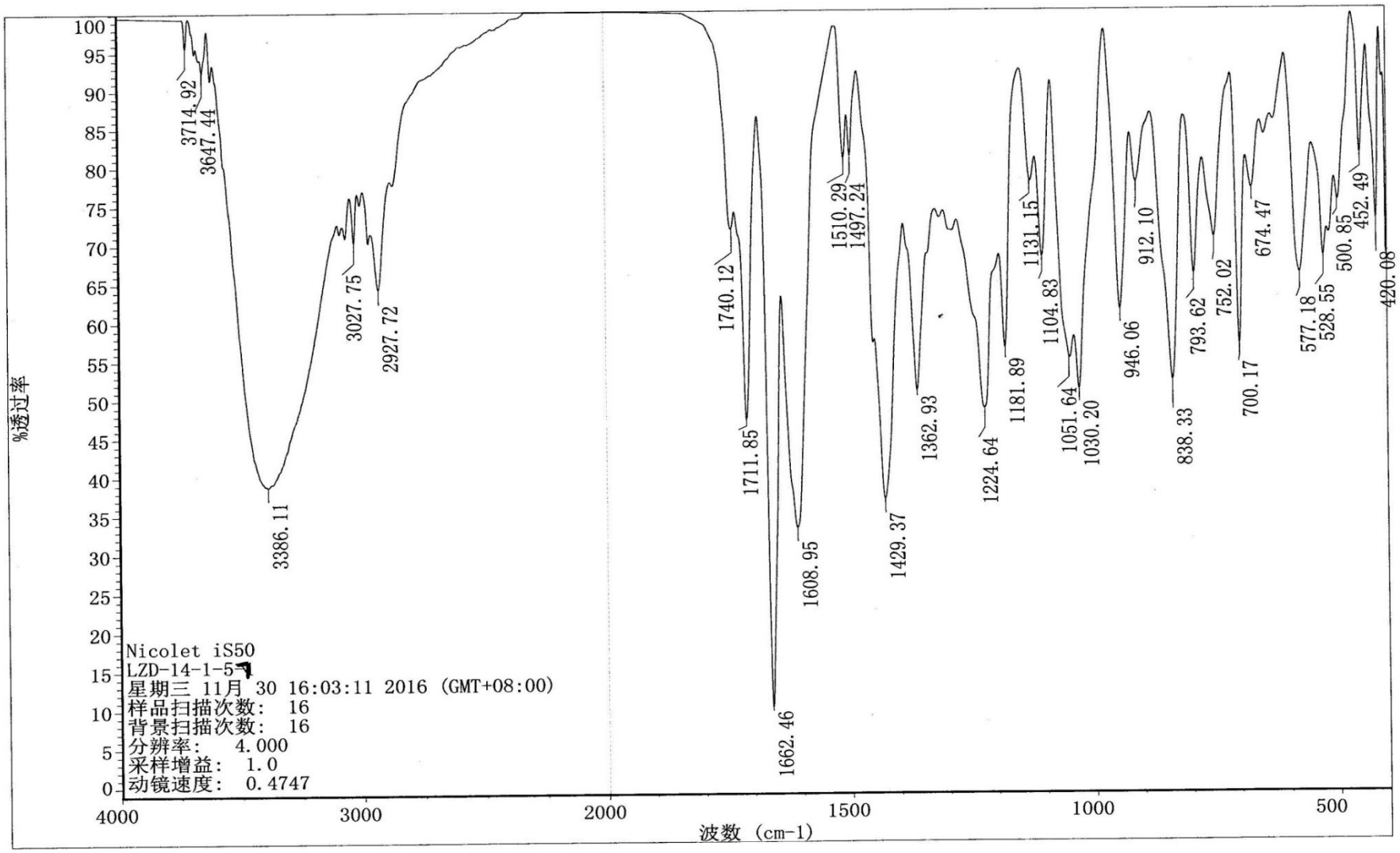


Figure S48 ^{1}H NMR Spectrum of **6** in DMSO-d_6

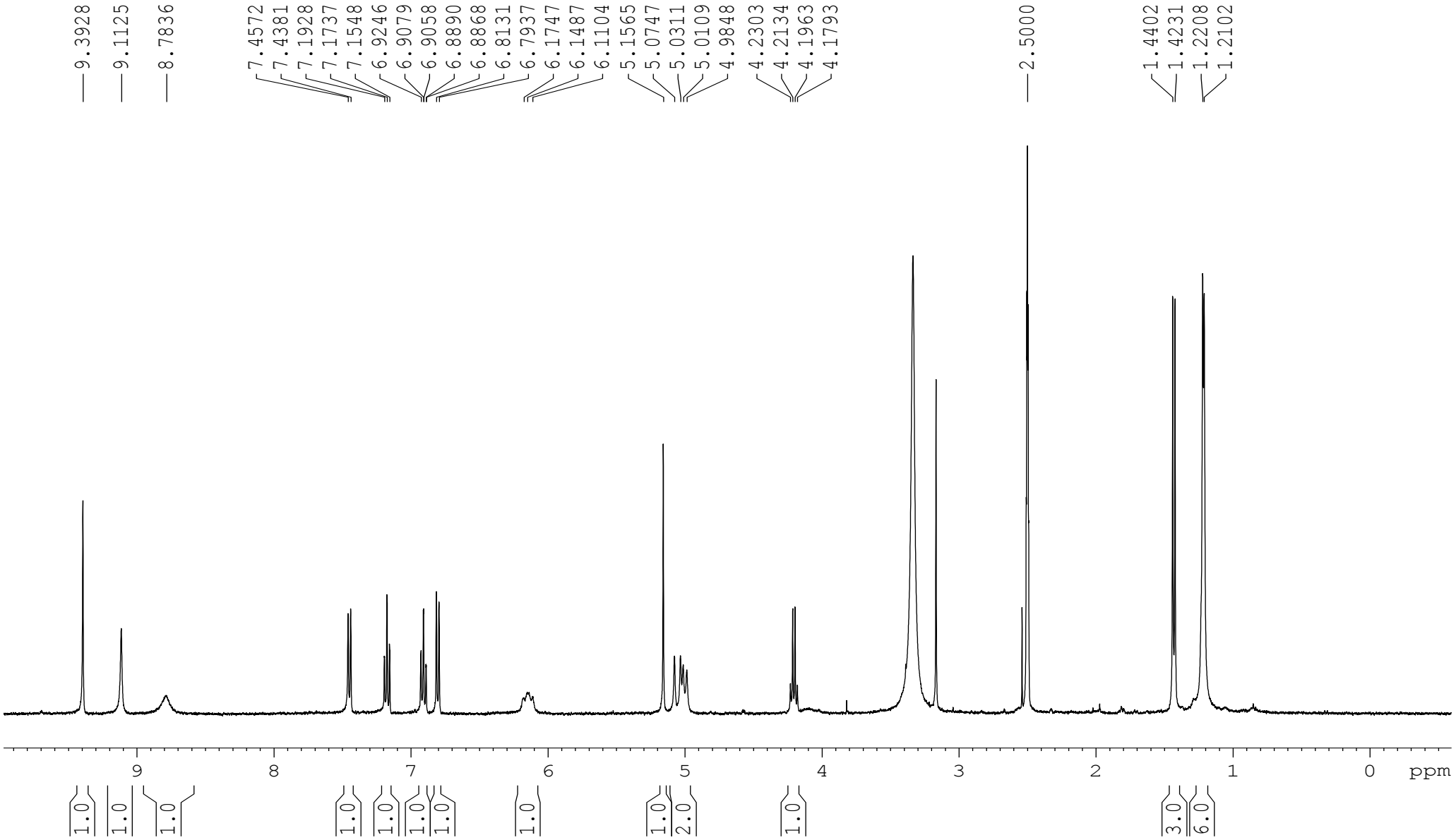


Figure S49 DEPTQ Spectrum of **6** in DMSO-d_6

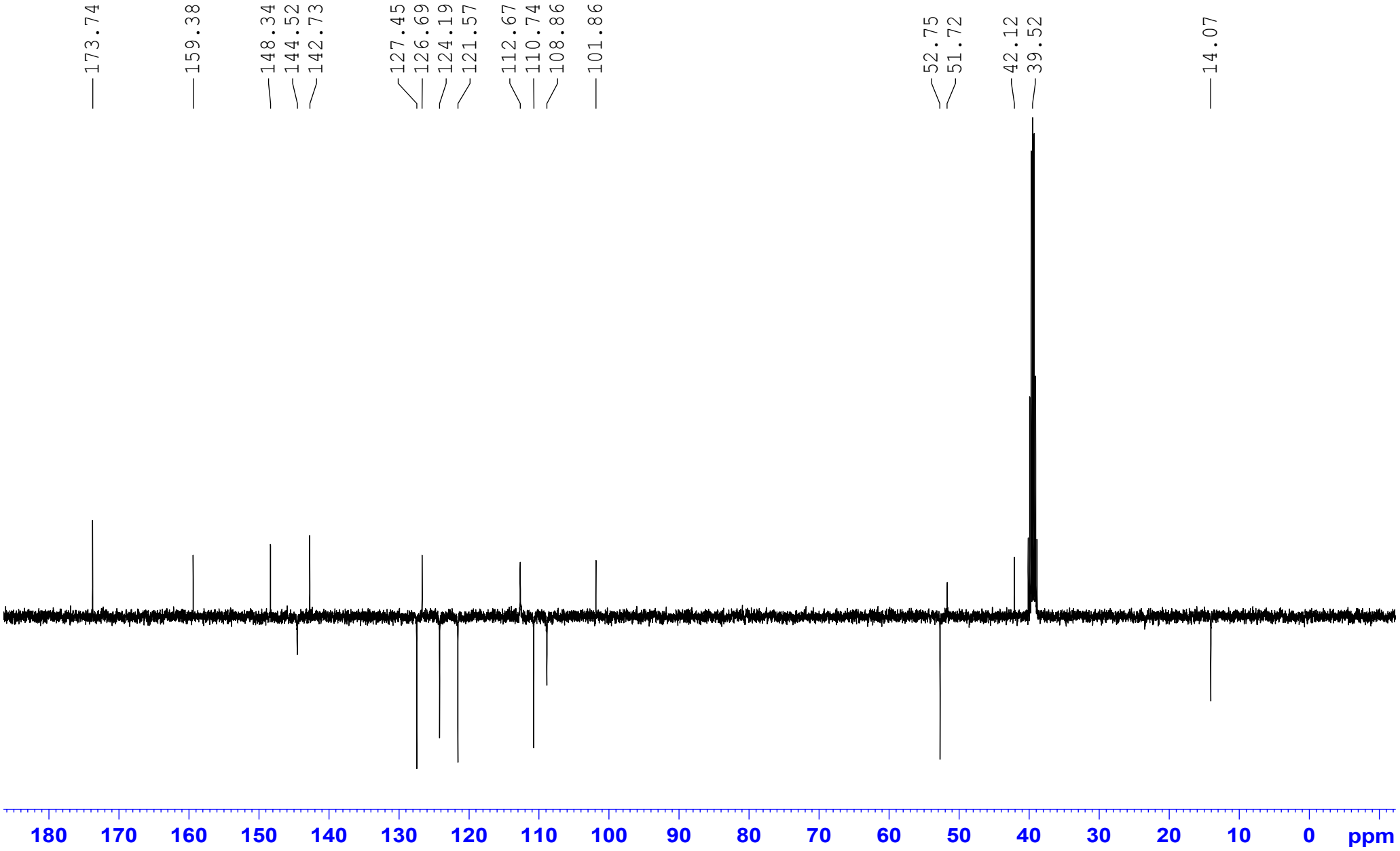


Figure S50 HSQC Spectrum of **6** in DMSO-d_6

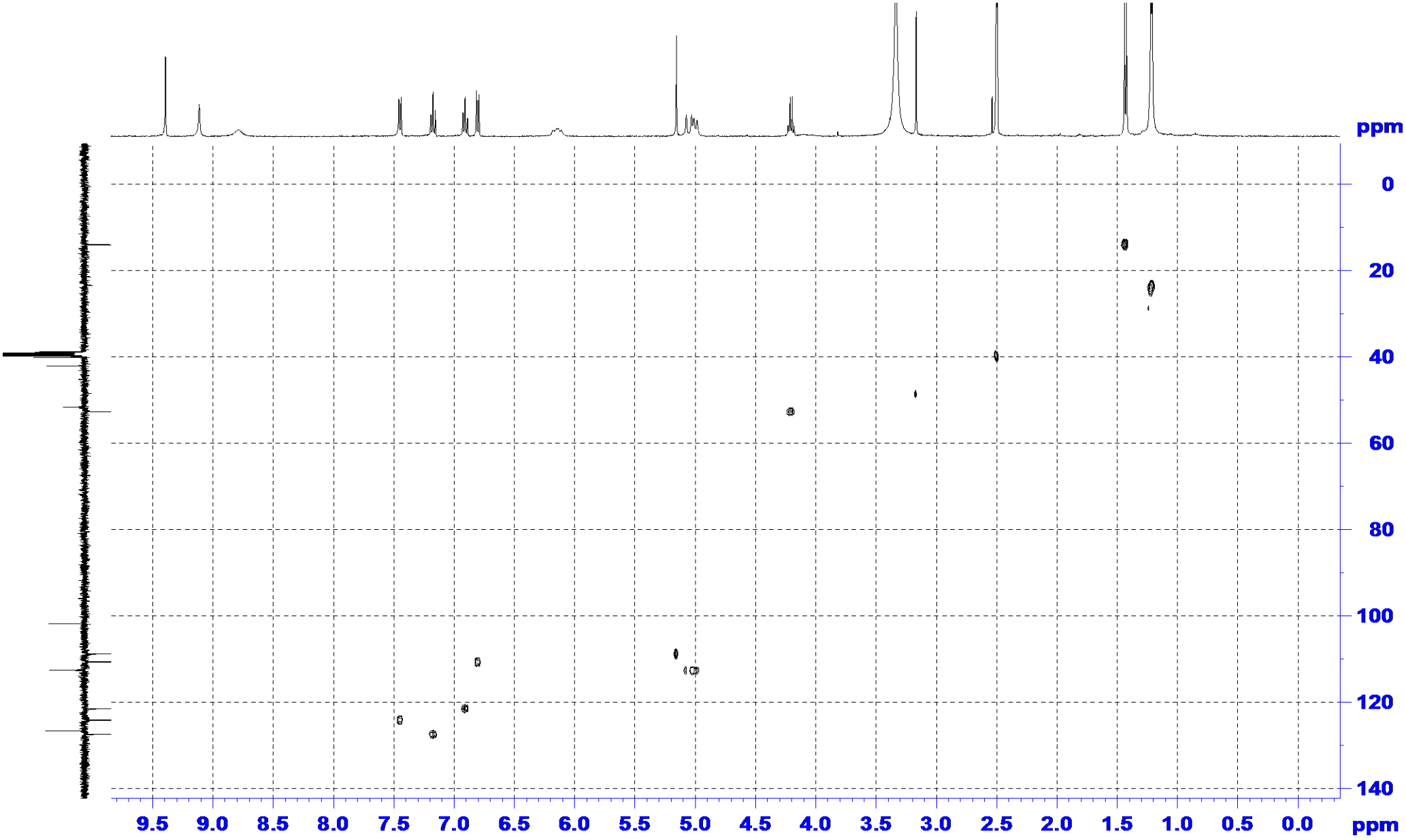


Figure S51 ^{1}H-^{1}H COSY Spectrum of **6** in DMSO-d_6

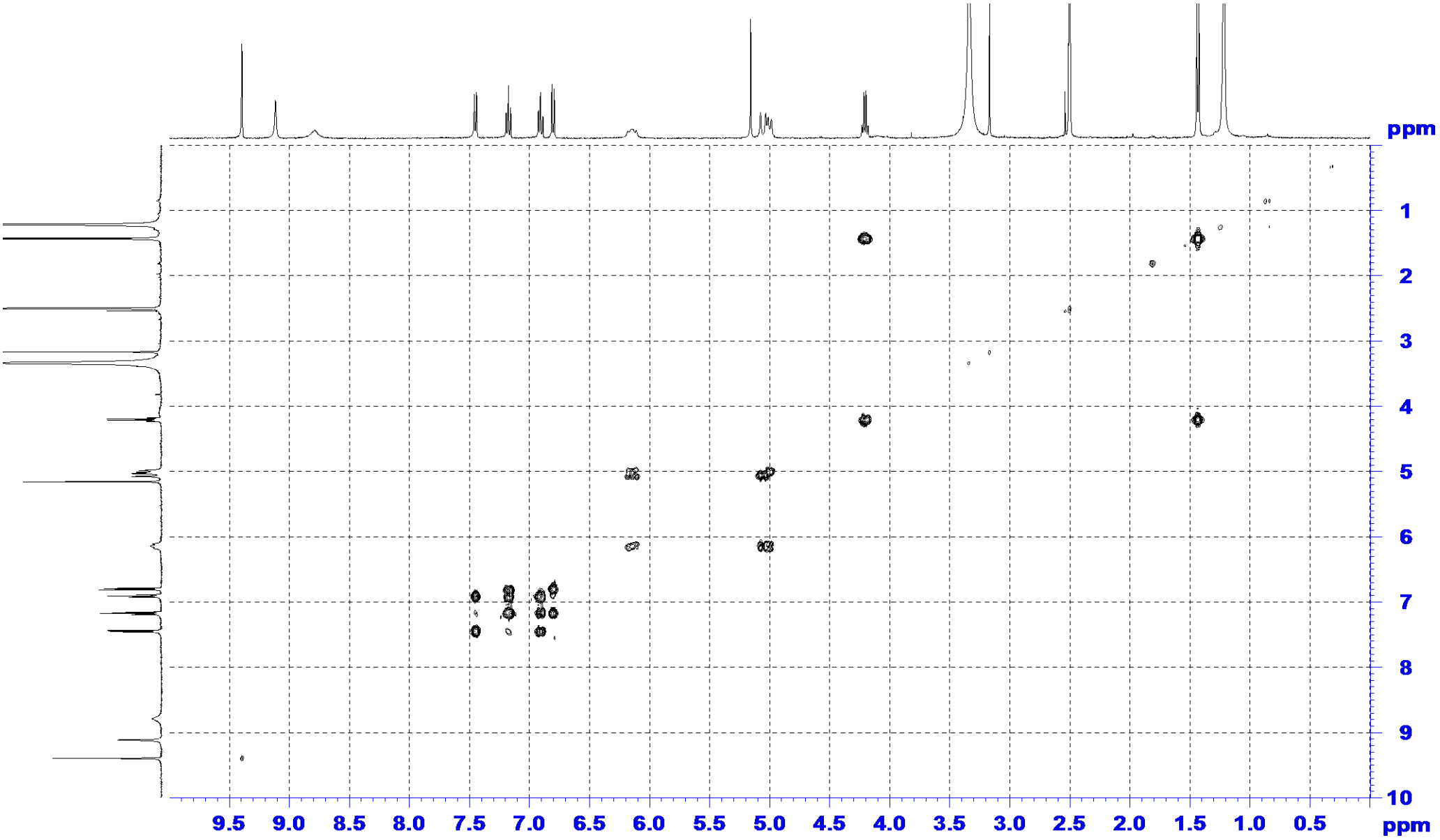


Figure S52 HMBC Spectrum of **6** in DMSO-d_6

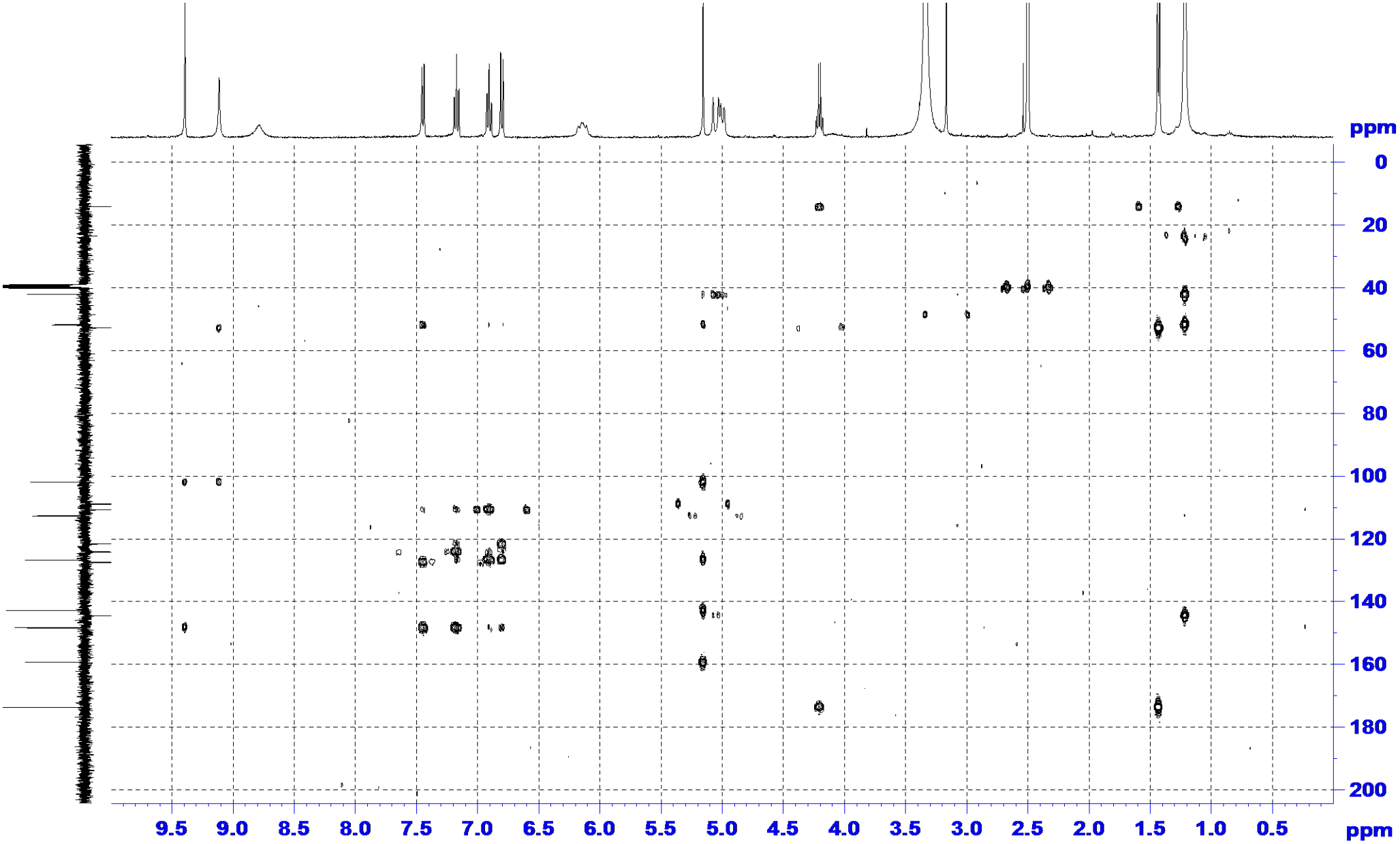


Figure S53 NOESY Spectrum of **6** in DMSO-d_6

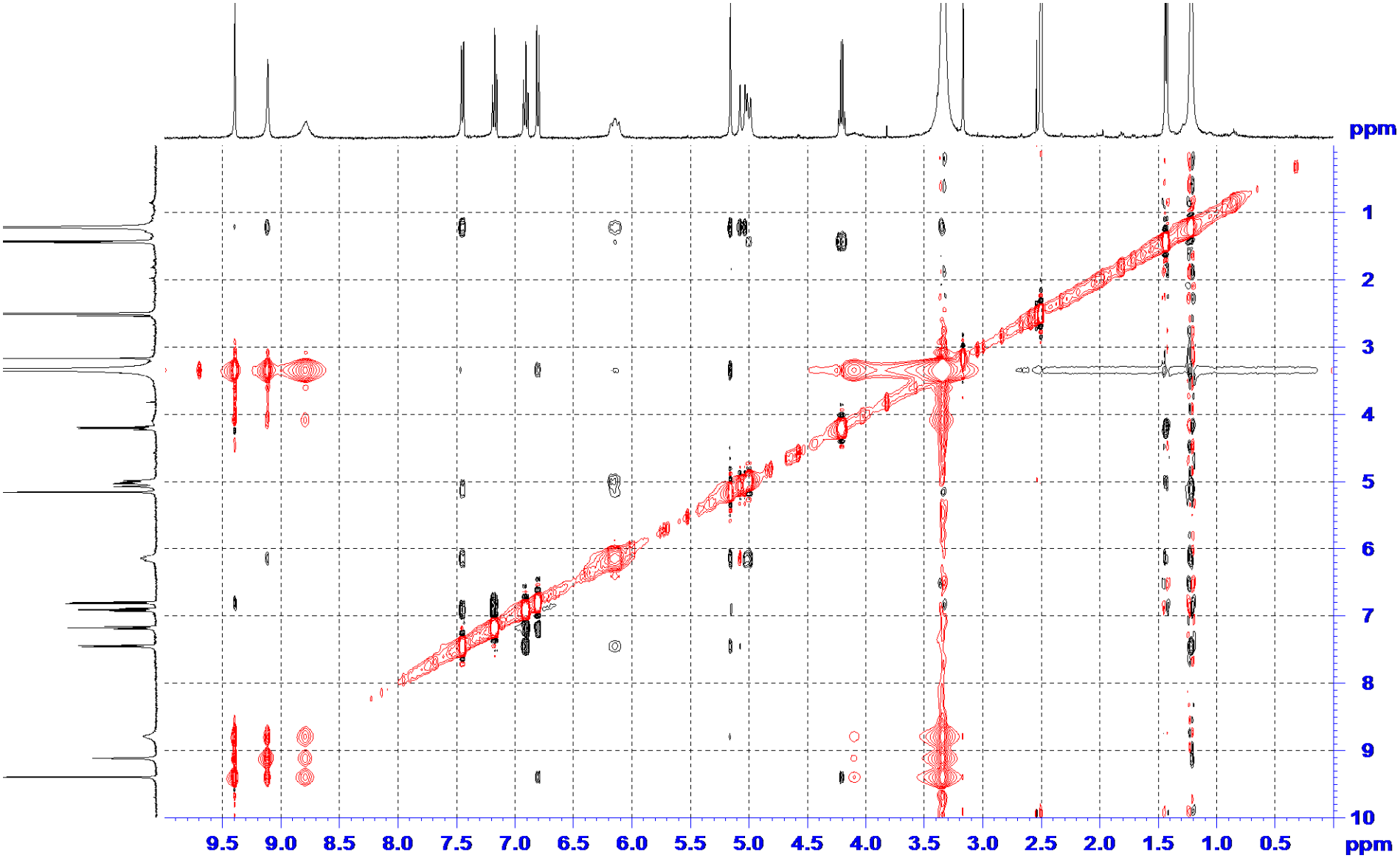


Figure S54 HRESIMS Data of **6**

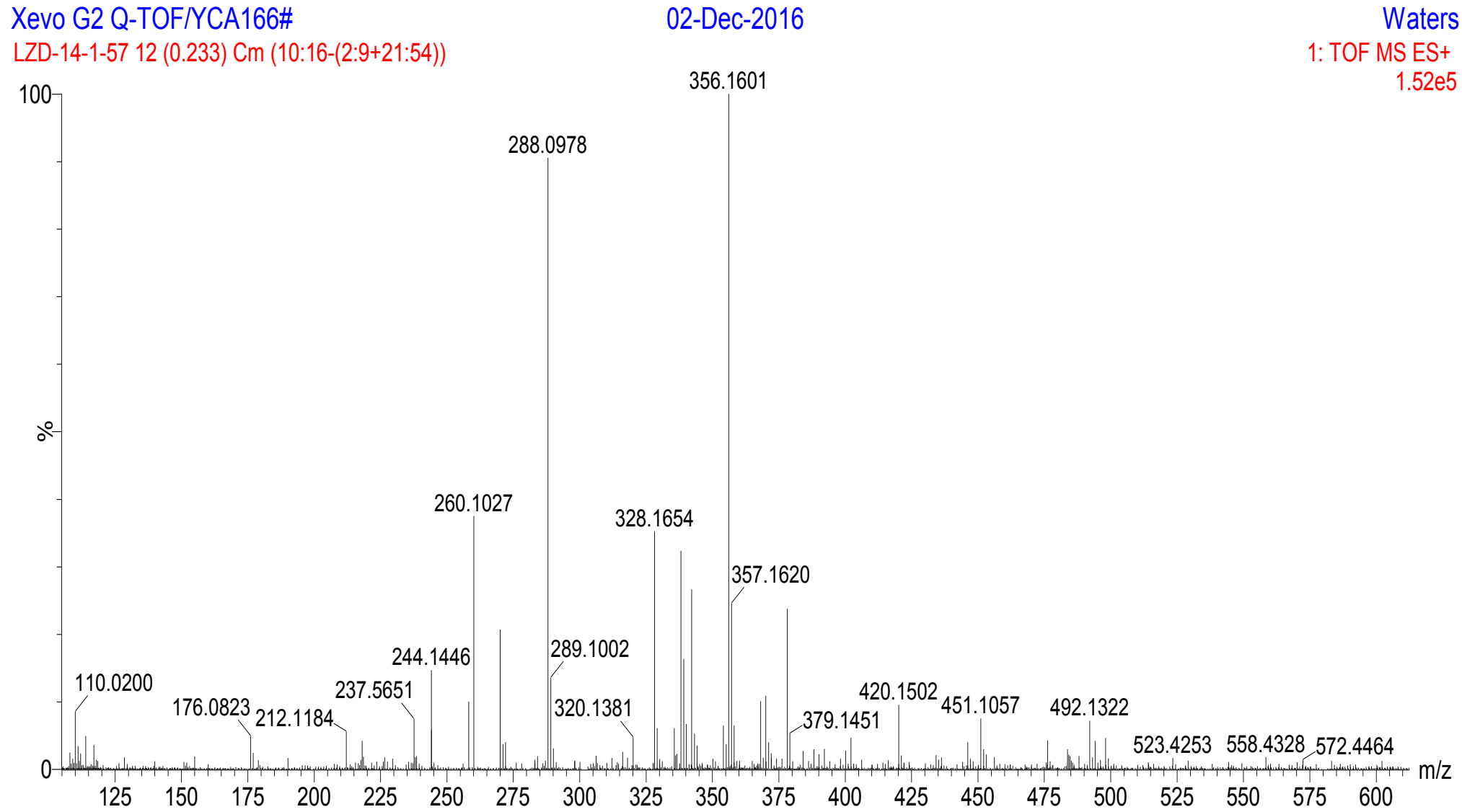


Table S1. Crystal data and structure refinement for 1.

Identification code	**1**
Empirical formula	$C_{23}H_{19}N_5O_4$
Formula weight	429.43
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.44940(7)
b/Å	13.81570(14)
c/Å	18.11204(16)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1864.07(3)
Z	4
ρ_{calc}g/cm^3	1.530
μ/mm^{-1}	0.893
F(000)	896.0
Crystal size/mm^3	0.58 × 0.5 × 0.3
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.048 to 137.254
Index ranges	$-8 \le h \le 8$, $-16 \le k \le 15$, $-21 \le l \le 21$
Reflections collected	15719
Independent reflections	3344 [R_{int} = 0.0239, R_{sigma} = 0.0129]
Data/restraints/parameters	3344/0/292
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0245, wR_2 = 0.0623
Final R indexes [all data]	R_1 = 0.0252, wR_2 = 0.0626
Largest diff. peak/hole / e Å^{-3}	0.18/-0.13
Flack parameter	0.07(5)

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O3	8938.4(16)	4048.9(9)	5185.4(7)	17.4(3)
O2	11408.7(17)	5815.9(10)	6345.5(7)	20.8(3)
O1	6741.0(19)	7509.2(9)	5068.1(8)	23.9(3)
O4	3493.1(18)	2783.7(9)	4116.4(8)	24.7(3)
N13	8423(2)	5563.1(10)	6161.3(8)	16.0(3)
N2	5218(2)	6273.3(11)	5610.2(9)	19.9(3)
N25	5246(2)	4535.0(11)	5297.3(8)	18.4(3)
N18	5583(2)	4019.8(11)	4116.7(8)	18.1(3)
N5	6684(2)	4489.6(11)	6887.6(8)	20.1(3)
C12	10028(2)	5403.1(13)	6534.8(10)	17.1(4)
C1	6726(2)	6719.9(13)	5374.8(9)	17.4(4)
C24	8559(3)	4251.0(12)	3870.0(9)	17.3(4)
C17	6186(2)	4767.2(12)	4625.8(10)	16.3(4)
C27	4165(2)	3504.0(13)	4387.2(10)	18.8(4)
C16	8259(2)	4687.3(12)	4637.0(9)	15.8(4)
C14	8491(2)	6188.1(12)	5499.1(9)	15.9(4)
C11	9878(3)	4717.3(13)	7147.2(10)	19.4(4)
C19	6986(3)	3810.6(13)	3620.4(10)	18.3(4)
C21	8533(3)	3145.9(14)	2599.6(10)	24.4(4)
C15	9140(2)	5663.6(13)	4787.7(9)	15.5(4)
C20	6929(3)	3252.6(14)	2984.3(10)	21.7(4)
C10	11378(3)	4493.9(14)	7583.4(10)	23.0(4)
C23	10135(3)	4137.4(13)	3476.6(10)	20.1(4)
C22	10110(3)	3583.2(14)	2834.1(10)	23.8(4)
C9	11205(3)	3844.7(15)	8160.4(10)	27.3(5)
C4	6867(2)	5095.4(13)	6353.7(9)	17.2(4)
C26	3590(2)	4013.5(13)	5103(1)	19.5(4)
C3	5238(2)	5271.0(13)	5873.3(10)	18.8(4)
C28	3010(3)	3310.2(14)	5692.3(11)	25.1(4)
C6	8215(3)	4279.5(13)	7290.1(10)	20.0(4)
C7	8077(3)	3599.1(14)	7867.4(10)	25.2(4)
C8	9562(3)	3390.4(14)	8293.6(11)	28.5(5)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O3	18.0(7)	15.8(6)	18.4(6)	3.7(5)	-1.2(5)	-0.5(5)
O2	15.0(6)	24.7(7)	22.7(6)	1.1(5)	-1.6(5)	0.8(5)
O1	24.7(7)	16.2(6)	30.9(7)	2.0(5)	-5.2(6)	3.3(5)
O4	22.6(7)	17.2(6)	34.3(7)	-2.0(6)	-5.2(6)	-3.1(6)
N13	16.1(7)	16.2(7)	15.6(7)	-0.1(6)	0.9(6)	1.8(6)
N2	14.3(8)	19.5(8)	25.9(8)	-3.5(7)	-1.3(6)	3.6(6)
N25	15.2(8)	19.8(8)	20.1(7)	-0.8(6)	0.9(6)	-2.7(6)
N18	18.0(7)	16.4(8)	19.8(7)	-1.2(6)	-4.2(6)	-0.7(6)
N5	21.1(8)	20.8(8)	18.5(7)	-1.7(6)	3.0(6)	-1.3(7)
C12	17.5(9)	17.6(8)	16.3(8)	-4.6(7)	0.3(7)	3.6(7)
C1	18.6(9)	16.5(9)	17.2(8)	-3.8(7)	-3.0(7)	2.1(7)
C24	22.3(9)	12.8(8)	16.9(8)	1.7(7)	-1.8(7)	1.5(7)
C17	18.8(9)	13.1(8)	17.2(8)	0.0(7)	-1.9(7)	0.0(7)
C27	16.2(9)	15.4(9)	25.0(9)	2.7(7)	-6.5(7)	1.5(7)
C16	17.1(9)	14.4(8)	15.8(8)	1.9(7)	-0.3(7)	0.8(7)
C14	16.0(9)	14.8(8)	16.8(8)	0.2(7)	-0.4(7)	0.4(7)
C11	23.9(9)	18.3(9)	16.0(8)	-3.2(7)	0.2(7)	4.3(8)
C19	22.8(9)	15.1(8)	16.9(8)	3.7(7)	-1.8(7)	0.6(7)
C21	37.8(11)	18.3(9)	16.9(9)	0.0(7)	0.0(8)	3.6(9)
C15	15.7(9)	15.7(9)	15.1(8)	1.1(7)	-0.4(6)	-0.2(7)
C20	28.4(10)	17.1(9)	19.6(9)	0.9(7)	-6.3(8)	-0.3(8)
C10	28.9(10)	21.7(9)	18.5(9)	-3.8(7)	-2.3(8)	6.2(8)
C23	23.4(9)	18.4(9)	18.6(8)	2.5(7)	-0.1(7)	0.5(8)
C22	29.4(10)	22.4(10)	19.7(9)	1.8(8)	4.0(8)	3.5(8)
C9	38.7(12)	25.1(10)	18.0(9)	-3.7(8)	-4.7(9)	12.6(9)
C4	16.5(9)	16.9(8)	18.2(9)	-4.1(7)	3.0(7)	-0.1(7)
C26	14.5(9)	17.3(9)	26.7(9)	1.0(7)	-3.2(7)	-0.5(7)
C3	14.7(9)	20.1(9)	21.5(9)	-1.2(7)	2.1(7)	-0.5(7)
C28	22.9(10)	21.7(9)	30.7(10)	1.7(8)	2.4(8)	-3.1(8)
C6	26.8(10)	17.8(9)	15.5(8)	-4.4(7)	2.1(7)	1.9(8)
C7	36.6(11)	19.7(9)	19.5(9)	-2.0(7)	5.9(8)	0.2(8)
C8	50.3(13)	18.5(10)	16.6(9)	1.1(8)	2.4(9)	8.9(9)

Table S4. Bond Lengths for 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O3	C16	1.422(2)	C24	C16	1.531(2)
O2	C12	1.225(2)	C24	C19	1.396(3)
O1	C1	1.224(2)	C24	C23	1.382(3)
O4	C27	1.217(2)	C17	C16	1.548(2)
N13	C12	1.391(2)	C27	C26	1.536(3)
N13	C14	1.479(2)	C16	C15	1.525(2)
N13	C4	1.372(2)	C14	C15	1.555(2)
N2	C1	1.351(2)	C11	C10	1.403(3)
N2	C3	1.465(3)	C11	C6	1.402(3)
N25	C17	1.440(2)	C19	C20	1.387(3)
N25	C26	1.471(2)	C21	C20	1.391(3)
N25	C3	1.457(2)	C21	C22	1.388(3)
N18	C17	1.455(2)	C10	C9	1.383(3)
N18	C27	1.365(2)	C23	C22	1.393(3)
N18	C19	1.408(2)	C9	C8	1.397(3)
N5	C4	1.286(2)	C4	C3	1.513(2)
N5	C6	1.384(3)	C26	C28	1.507(3)
C12	C11	1.463(3)	C6	C7	1.410(3)
C1	C14	1.523(2)	C7	C8	1.379(3)

Table S5 Bond Angles for 1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	N13	C14	117.24(15)	C15	C16	C17	111.64(14)
C4	N13	C12	121.85(14)	N13	C14	C1	111.84(14)
C4	N13	C14	120.65(14)	N13	C14	C15	114.24(13)
C1	N2	C3	121.74(15)	C1	C14	C15	111.75(14)
C17	N25	C26	108.35(14)	C10	C11	C12	120.56(18)
C17	N25	C3	116.84(14)	C6	C11	C12	119.12(17)
C3	N25	C26	120.65(14)	C6	C11	C10	120.32(17)
C27	N18	C17	112.43(15)	C24	C19	N18	109.08(15)
C27	N18	C19	134.11(15)	C20	C19	N18	128.43(17)
C19	N18	C17	108.74(14)	C20	C19	C24	122.49(18)
C4	N5	C6	116.44(16)	C22	C21	C20	121.87(17)
O2	C12	N13	120.76(16)	C16	C15	C14	115.27(14)
O2	C12	C11	125.29(17)	C19	C20	C21	116.65(18)
N13	C12	C11	113.94(16)	C9	C10	C11	119.6(2)
O1	C1	N2	123.92(17)	C24	C23	C22	118.80(18)
O1	C1	C14	119.26(16)	C21	C22	C23	120.41(18)
N2	C1	C14	116.81(15)	C10	C9	C8	120.22(19)
C19	C24	C16	110.05(16)	N13	C4	C3	117.14(15)
C23	C24	C16	129.55(17)	N5	C4	N13	125.92(17)
C23	C24	C19	119.78(16)	N5	C4	C3	116.87(17)
N25	C17	N18	103.14(14)	N25	C26	C27	101.09(14)
N25	C17	C16	117.26(15)	N25	C26	C28	112.74(15)
N18	C17	C16	105.39(14)	C28	C26	C27	112.47(15)
O4	C27	N18	126.90(18)	N2	C3	C4	110.30(15)
O4	C27	C26	126.86(18)	N25	C3	N2	115.29(15)
N18	C27	C26	106.23(15)	N25	C3	C4	107.26(14)
O3	C16	C24	109.73(13)	N5	C6	C11	122.69(16)
O3	C16	C17	114.12(14)	N5	C6	C7	118.07(18)
O3	C16	C15	105.70(14)	C11	C6	C7	119.25(18)
C24	C16	C17	99.32(14)	C8	C7	C6	119.75(19)
C15	C16	C24	116.61(15)	C7	C8	C9	120.81(18)

Table S6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1.

Atom	*x*	*y*	*z*	U(eq)
H3	8243.32	3573.78	5230.55	26
H2	4196.06	6593.12	5605.5	24
H17	5813.14	5420.13	4443.32	20
H14	9406.83	6698.43	5606.32	19
H21	8549.27	2762.88	2164.08	29
H15A	8914.07	6092.75	4359.95	19
H15B	10453.44	5565.92	4823.36	19
H20	5848.44	2957.92	2819.57	26
H10	12505.74	4786.69	7482.92	28
H23	11215.58	4431.88	3641.41	24
H22	11179.54	3504.24	2554.71	29
H9	12208.04	3707.4	8467.15	33
H26	2602.78	4484.45	4998.32	23
H3A	4143.91	5169.1	6183.7	23
H28A	4003.96	2869.94	5806.42	38
H28B	1979.25	2935.82	5515.39	38
H28C	2671.34	3667.37	6138.52	38
H7	6966.19	3285.49	7962.42	30
H8	9465.47	2932	8682.55	34

Computational Details.

In general, conformational analyses were carried out via random searching in the Sybyl-X 2.0 using the MMFF94S force field with an energy cutoff of 2.5 kcal/mol.[1] The results showed one lowest energy conformer for 3*R*, 14*R*, 16*R*, 17*R*, 26*S*, 28*S*-**3** and two for 3*R*, 14*R*, 16*R*, 17*R*, 26*S*, 28*S*-**4**, one for 14*S*, 16*S*, and 17*R*-**5**.

ECD calculation: Subsequently, the conformers were re-optimized using DFT at the b3lyp/6-31+g(d) level in gas phase by the GAUSSIAN 09 program.[2] The energies, oscillator strengths, and rotational strengths (velocity) of the first 60 electronic excitations were calculated using the TDDFT methodology at the b3lyp/6-311++g(d,p) level in vacuum. The ECD spectra were simulated by the overlapping Gaussian function (half the bandwidth at 1/e peak height, σ =0.25 for **3** and **5**, 0.3 for **4**).[3] To get the final spectra, the simulated spectra of the conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy (ΔG). Theoretical ECD spectrum of the corresponding enantiomer was obtained by directly inverse of the ECD spectrum of the calculated model molecule, respectively. By comparing the experiment spectrum with the calculated ECD spectra, the absolute configuration of **3–5** was resolved.

^{13}C NMR calculation: The conformers were re-optimized using DFT at the B3LYP/6-31G* level in gas phase by the GAUSSIAN 09 program. The ^{13}C NMR shielding constants of **1** and **5** were calculated with the GIAO method at MPW1PW91/6-31G(d,p) level in gas phase. The computational ^{13}C NMR were finally obtained by linear regression analysis method.[4]

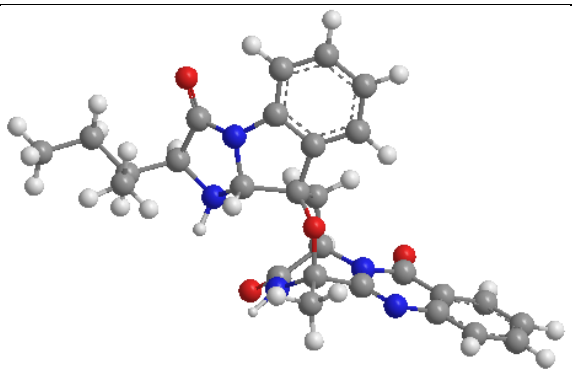
1. Sybyl Software, version X 2.0; Tripos Associates Inc.: St. Louis, MO, 2013.

2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Rev. C 01; Gaussian, Inc., Wallingford CT, 2009.

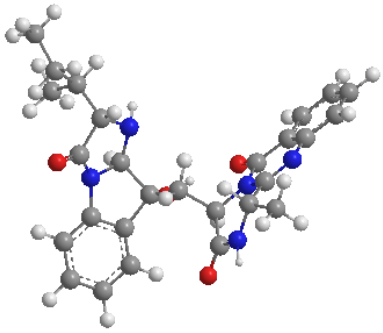
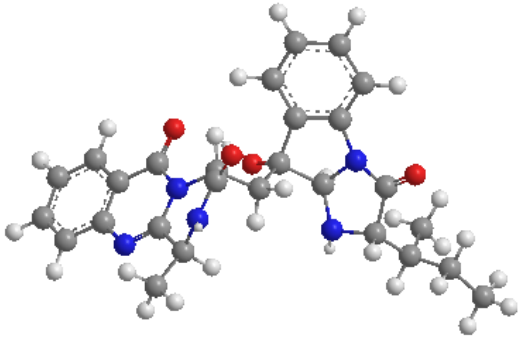
3. Stephens, P. J.; Harada, N. ECD cotton effect approximated by the Gaussian curve and other methods. *Chirality* **2010**, *22*, 229–233.

4. Lodewyk MW, Siebert MR, Tantillo DJ. Computational prediction of ^{1}H and ^{13}C chemical shifts: a useful tool for natural product, mechanistic, and synthetic organic chemistry. Chem Rev 2012;112:1839-1862.

1. The optimized conformers of 3*R*, 14*R*, 16*R*, 17*R*, 26*S*, 28*S*-**3**.

C1

E(RB3LYP) -1620.32031938

2. The optimized conformers of 3*R*, 14*R*, 16*R*, 17*R*, 26*S*, 28*S*-**4**.

C1	C2
	

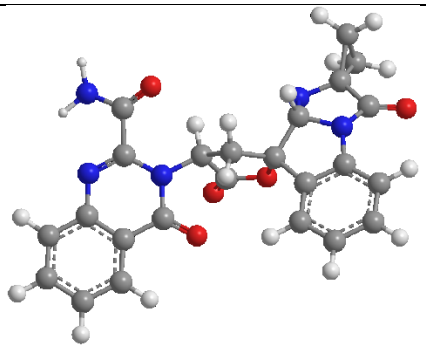
3. B3LYP-calculated relative energies (Kcal/mol) and conformational population (%) for the most stable conformers of 3*R*, 14*R*, 16*R*, 17*R*, 26*S*, 28*S*-**4**

Comound	conformer	ΔE (kcal/mol) [a]	Population (%)
4	C1	0	94.16
	C2	0.002624	5.84

[a]Relative to conformer C1 with E6-31+G(d) = -1621.545237 Kcal/mol. [b]Calculated using free energy values from Gaussian 03W according to ΔG = -RT In K.

4. The optimized conformers of 3*R*, 14*R*, 16*R*, 17*R*, 26*S*, 28*S*-**5**.

C1



E(RB3LYP) -1575.62296994