Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 115–117

New reactions of 2,3-diaminonaphthaline with carbonyl electrophiles

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1D and 2D NMR spectra were recorded at 20 °C on a Bruker AVANCE 600 (600 MHz) using $CDCl_3$ and DMSO-d_6 as solvents. Chemical shifts of nuclei ^1H (δ , ppm) and ^{13}C were measured relatively to the residual signals of the deuteron solvents (δ = 2.49 ppm for protons and 39.5 ppm for carbon nuclei). Mass spectrum of compound **3** was recorded on a Finnigan MAT INCOS 50 spectrometer at direct introduction of the sample (EI, ionization energy 70 eV). Electrospray-ionization high resolution mass spectra (ESI-HRMS) of compounds **6**,**7** and were obtained on a Bruker maxis Q-TOF mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany). Mass spectrum of compound **9** was recorded on an Agilent 6470 Triple Quadrupole Jetstream LC/MS spectrometer. IR spectra were recorded on a FT/IR-6800 FTIR spectrometer (JASCO). All of the solvents were of analytical grade. 2,3-Diaminonaphtalene (97%) and alloxan monohydrate (98%) were obtained from Alfa Aesar.

Experimental

3-[(3-Amino-2-naphthyl)amino]-5,5-dimethyl-cyclohex-2-en-1-one 3.
A mixture of 2,3-diaminonaphthalene (0.8 g, 5 mmol) and dimedone (0.9 g, 6.4 mmol) in MeCN (15 ml) was heated until dissolve. Iodine (30 mg) was added, and the mixture was refluxed with stirring at 60 °C for 1 h. The mixture darkens rapidly and a light precipitate begins to form. After cooling with cold water, the precipitate was filtered off, washed with cold MeCN, diethyl ether, and petroleum ether. Light-beige compound, mp 250–255°C (MeCN). Yield 1.23 g (83%). IR (Nujol, ν/cm^{-1}): 3439m, 3323m, 3203m (NH), 1643w (CO), 1604m, 1589m, 1558s, 1523s, 1495s (CH arom.). ^1H NMR (600 MHz, DMSO-d_6) δ: 1.02 (s, 6H, CH_3), 2.00 (s, 2H, C^6H_2), 2.42

(s, 2H, C^4H_2), 4.75 (s, 1H, C^2H), 5.16 (s, 2H, NH_2), 7.02 (s, 1H, $C^{4'}H$), 7.09 (t, 1H, $C^{6'}H$, J = 7.5 Hz), 7.26 (t, 1H, C^7H, J = 7.5 Hz), 7.48 (s, 1H, $C^{1'}H$), 7.51 (d, 1H, $C^{8'}H$, J = 8.0 Hz), 7.63 (d, 1H, $C^{5'}H$, J = 8.3 Hz), 8.36 (s, 1H, $N^{9'}H$). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 28.05 (C^7, C^8), 32.30 (C^5), 41.53 (C^4), 50.28 (C^6), 96.37 (C^2), 108.00 ($C^{4'}$), 121.54 ($C^{6'}$), 124.76 ($C^{8'}$), 125.22 ($C^{1'}$), 125.78 ($C^{7'}$), 126.21 ($C^{2'}$), 126.37 ($C^{4'a}$), 127.12 ($C^{5'}$), 133.33 ($C^{8'a}$), 142.55 ($C^{3'}$), 162.16 (C^3), 194.76 (C^1). MS (El, 70 eV), m/z (%): 280 (18) [M^+], 265 (14), 223 (37), 182 (100), 143 (6), 130 (15), 115 (26).

5-[2-[(3-Amino-2-naphthyl)amino]-4,4-dimethyl-6-oxocyclohexen-1-yl]-5-hydroxy-hexahydropyrimidine-2,4,6-trione 6.

A solution of compound **3 (**0.28 g, 1 mmol) and alloxan **4** (0.18 g, 1.1 mmol) in EtOH (5 ml) with CF_3COOH (2 drops) was refluxed for 2 min. The solution was cooled to room temperature and kept on ice for 30 min, triturating with a stick. The precipitate was filtered off, washed with cold EtOH, diethyl ether and petroleum ether. Colourless compound, mp> 200 °C, changes colour and decomposes above 210°C (MeCN). Yield 0.28 g (69%). IR (Nujol, ν/cm^{-1}): 3531w, 3458w, 3397w, 3279m, 3188w, 3060m (NH, OH), 2968m, 2868m (CH aliph.), 1747m, 1718s, 1701vs (CO), 1637m, 1604m, 1535vs, 1514s (CH arom.). ^1H NMR (600 MHz, DMSO-d_6) δ:0.87 (s, 6H, CH_3), 1.99 (s, 2H, $C^{6'}H_2$), 2.22 (s, 2H, $C^{4'}H_2$), 5.35 (s, 2H, NH_2), 7.02 (s, 1H, $C^{4''}H$), 7.13 (td, 1H, $C^{7''}H$, ^3J = 7.5 Hz, ^4J = 1.0 Hz), 7.29 (td, 1H, $C^{6'}H$, ^3J = 7.5 Hz, ^4J = 1.0 Hz), 7.53 (d, 1H, $C^{5''}H$, J = 8.3 Hz), 7.56 (s, 1H, $C^{1''}H$), 7.66 (d, 1H, $C^{8''}H$, J = 8.1 Hz), 8.03 (s, 1H, OH), 9.41 (s, 1H, NH), 11.14 (s, 2H, N^1H, N^3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 27.50 ($2CH_3$, 32.13 ($C^{5'}$), 40.19 ($C^{4'}$), 48.97 ($C^{6'}$), 74.71 (C^5), 106.70 ($C^{2'}$), 107.56 ($C^{4''}$), 121.74 ($C^{7''}$), 124.90 ($C^{5''}$), 125.82 ($C^{3''}$), 126.06 ($C^{2''}$), 126.16 ($C^{6''}$), 126.35 ($C^{1''}$), 127.45 ($C^{8''}$), 133.72 ($C^{4''a}$), 143.44 ($C^{8''a}$), 150.34 (C^2), 164.69 ($C^{3'}$), 171.10 (C^4, C^6), 193.27 ($C^{1'}$). ESI-HRMS: found m/z 423.1663$[M+H]^+$; calculated for $C_{22}H_{22}N_4O_5+H^+$ 423.1663.

3,3-Dimethylspiro[2,4,5,12-tetrahydronaphtho[2,3-*b*][1,4]benzodiazepine-13,5'-hexahydropyrimidine]-1,2',4',6'-tetraone 7.

a) A mixture of compound **6** (0.11 g 0.25 mmol) and CF_3COOH (0.2 ml, 2.7 mmol) was heated under reflux at 100 °C for 5 min. The resulting dark red solution with precipitate was brought to ambient temperature and ether (3 ml) was added. The precipitate was filtered off, boiled with ethyl acetate (4 ml), cooled, filtered off and recrystallized from MeOH (4 ml). Colourless compound, mp 350–360 °C (decomp.). Yield 0.02 g (23%).

b) A mixture of compound **3** (0.07 g 0.25 mmol) and alloxan **4** (0.05 g 0.3 mmol) was ground in an agate mortar, transferred to a 25 ml round-bottom flask, CF_3COOH (0.4 ml, 5.4 mmol) was added, and this was boiled for 1 min. The resulting dark mass was cooled to room temperature, ether (5 ml) was added, and the precipitate was filtered off. The resulting brown substance (0.124 g) was boiled with ethyl acetate (5 ml) for 2–3 min, filtered off, and added to boiling MeOH (5 ml), triturating with a stick. After cooling to room temperature, the precipitate was filtered off, washed with ethyl acetate and petroleum ether. Colourless compound, mp 350–360 °C (decomp.). Yield 0.058 g (57%). IR (ν/cm^{-1}): 3322m, 3303m, 3225m, 3106w (NH), 1754m, 1720s, 1687vs (CO), 1647w, 1625w, 1578w, 1552m, 1526s, 1494s (CH arom.). ^1H NMR (600 MHz, DMSO-d_6) δ:1.09 (s, 6H, CH_3), 2.02 (s, 2H, C^2H_2), 2.63 (s, 2H, $C^{4'}H_2$), 6.60 (s, 1H, $N^{12}H$), 7.28 (m, 2H, C^8H, C^9H), 7.37 (s, 1H, $C^{11}H$), 7.52 (s, 1H, C^6H), 7.60 (m, 1H, C^7H),

7.68 (m, 1H, $C^{10}H$), 9.30 (s, 1H, $N^{5}H$), 11.06 (s, 2H, $N^{1'}H$, $N^{3'}H$). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 27.49 ($C^{14}H$, $C^{15}H$), 31.36 (C^{3}), 44.37 (C^{4}), 48.69 (C^{2}), 66.28 (C^{13}), 106.82 (C^{13a}), 116.28 (C^{6}), 117.13 (C^{11}), 124.20 (C^{9}), 124.58 (C^{8}), 125.80 (C^{7}), 126.37 (C^{10}), 129.20 (C^{6a}), 130.33 (C^{10a}), 134.76 (C^{5a}), 136.23 (C^{4}), 150.41 (C^{2a}), 155.58 (C^{4a}), 169.32 ($C^{4'}$, $C^{6'}$), 194.99 (C^{1}). ESI-HRMS: found m/z 405.1557$[M+H]^+$; calculated for $C_{22}H_{20}N_4O_4+H^+$ 405.1558.

12a-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-3,3-dimethyl-4,12-dihydro-2*H*-benzo[*i*]phenazin-1-one 9.

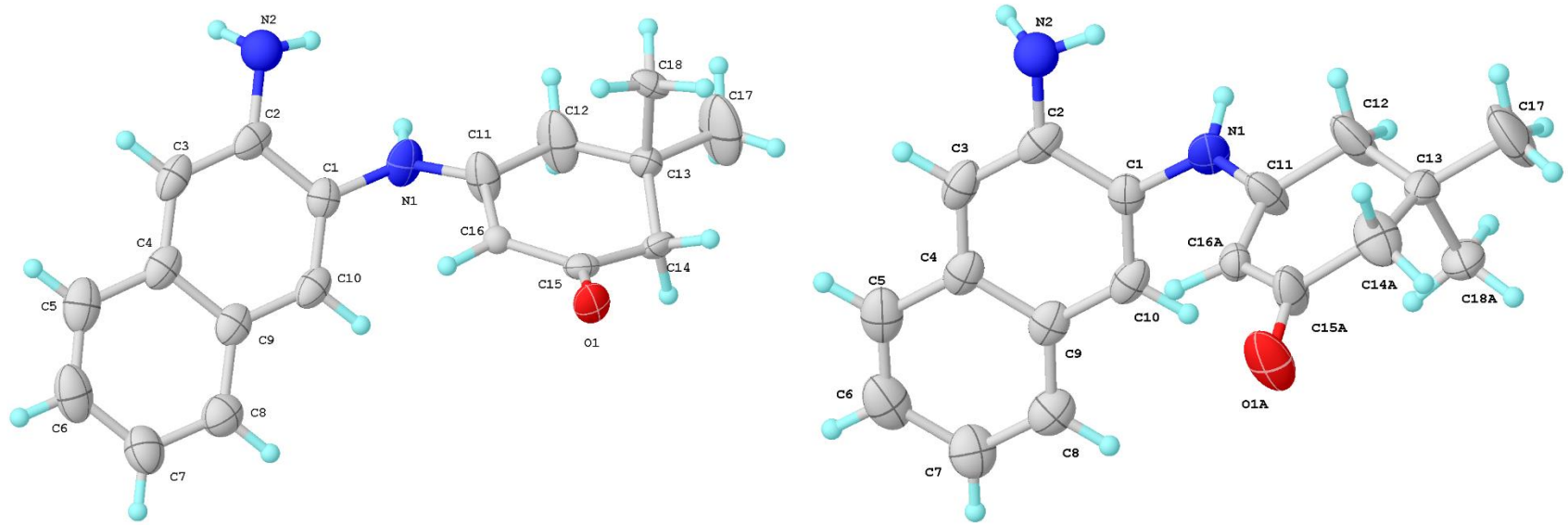
A solution of compound **3** (0.14 g 0.5 mmol), 3,5-di-*tert*-butyl-1,4-benzoquinone **8** (0.11 g, 0.5 mmol) in EtOH (10 ml) was heated until complete dissolution of the reagents. Then CF_3COOH (1 drop) was added, and this was left for a day. The precipitate that formed was filtered off, washed with cold EtOH and petroleum ether. Yellow crystals, mp 111 °C (decomp.). Yield 0.1 g (41%). Another crop (46 mg) of the substance was isolated from the filtrate. Total yield 0.146 g (60%). IR (ν/cm^{-1}): 3613m (OH), 3367s (NH), 2949s (t-Bu), 2869m (CH aliph), 1712vs (CO), 1634s (C=N), 1605m, 1516w, (CH arom.). ^1H NMR (600 MHz, $CDCl_3$) δ: 1.01 (s, 3H, $C^{15}H_3$), 1.13 (s, 3H, $C^{14}H_3$), 1.29 (s, 18H, $2C(CH_3)_3$), 2.40 (dd, 1H, $C^{2}H_2$, ^2J = 13.8 Hz, ^4J = 2.9 Hz), 2.65 (d, 1H, $C^{2}H_2$, ^2J = 13.9 Hz), 2.74 (dd, 1H, $C^{4}H_2$, ^2J = 14.7 Hz, ^4J = 2.9 Hz), 2.87 (d, 1H, $C^{4}H_2$, ^2J = 14.6 Hz), 5.18 (s, 1H, $N^{12}H$), 5.21 (s, 1H, OH), 6.76 (s, 1H, $C^{11}H$), 6.86 (s, 2H, $C^{2'}H$), 7.15 (m, 1H, $C^{9}H$), 7.26 (m, 1H, $C^{8}H$), 7.46 (d, 1H, $C^{7}H$, J = 8.3 Hz), 7.67 (d, 1H, $C^{10}H$, J = 8.2 Hz), 7.72 (s, 1H, $C^{6}H$). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 26.02 (C^{15}), 30.11 ($C^{8'}$), 30.52 (C^{14}), 32.50 (C^{3}), 34.45 ($C^{7'}$), 49.14 (C^{4}), 51.70 (C^{2}), 68.34 (C^{13}), 107.94 (C^{11}), 122.37 (C^{9}), 122.55 ($C^{2'}$, $C^{6'}$), 125.28 (C^{7}), 125.78 (C^{6}), 126.32 (C^{8}), 128.31 (C^{10}), 129.17 ($C^{1'}$), 132.61 (C^{5a}), 134.33 (C^{11a}), 134.45 (C^{6a}), 136.91 ($C^{3'}$, $C^{5'}$) 154.05 ($C^{4'}$), 165.29 (C^{4a}), 205.03 (C^{1}). MS: found m/z 483.300 $[M+H]^+$; calculated for $C_{32}H_{38}N_2O_2+H^+$ 483.3006.

Cartesian coordinates of structure 6 calculated by B3LYP/6-311+G**

O	-1.529601000	-2.280267000	-0.952055000
O	-6.039721000	-1.908317000	-0.731380000
O	-3.641373000	0.329944000	2.414725000
O	-1.603876000	-1.402651000	1.747467000
H	-1.726229000	-0.871980000	2.549892000
O	-3.643789000	1.379614000	-0.481120000
N	-3.766537000	-1.978048000	-0.866773000
H	-3.868696000	-2.580522000	-1.675234000
N	-4.828808000	-0.864502000	0.896359000
H	-5.693269000	-0.563971000	1.329891000
N	0.621100000	-0.407841000	0.517739000
H	0.164864000	-1.190890000	0.975607000
N	1.338584000	-1.450176000	-1.984183000
H	0.440206000	-1.712585000	-1.592280000
H	1.616946000	-2.042998000	-2.751871000
C	-2.484907000	-1.742024000	-0.427159000
C	-4.969814000	-1.587492000	-0.272843000
C	-3.664316000	-0.308296000	1.384894000
C	-2.329295000	-0.718416000	0.714699000
C	-1.583412000	0.499401000	0.159916000
C	-2.416928000	1.519393000	-0.435087000
C	-1.775325000	2.742596000	-1.062277000
H	-2.457582000	3.583752000	-0.912900000
H	-1.747588000	2.554913000	-2.144083000
C	-0.359388000	3.055825000	-0.553888000
C	0.458393000	1.749750000	-0.608797000
H	0.638886000	1.472162000	-1.655557000
H	1.443417000	1.905119000	-0.163025000
C	-0.202576000	0.565231000	0.057446000
C	-0.409166000	3.607564000	0.884877000
H	-0.976254000	4.542322000	0.914089000
H	0.599645000	3.818650000	1.252617000
H	-0.884235000	2.910348000	1.578637000
C	0.305240000	4.099877000	-1.466194000
H	0.366667000	3.745435000	-2.499539000
H	1.320377000	4.329082000	-1.127432000
H	-0.264882000	5.033501000	-1.464372000
C	2.006639000	-0.556083000	0.180764000
C	2.348404000	-1.126317000	-1.089374000
C	3.690099000	-1.282134000	-1.396155000
H	3.969641000	-1.709418000	-2.354563000
C	4.712121000	-0.912223000	-0.492083000
C	6.091861000	-1.069835000	-0.797941000
H	6.370709000	-1.480708000	-1.762651000
C	7.060383000	-0.711075000	0.108540000
H	8.107765000	-0.838553000	-0.141734000
C	6.705767000	-0.175728000	1.370193000
H	7.481618000	0.101636000	2.074300000
C	5.381141000	-0.010742000	1.697833000
H	5.100956000	0.398149000	2.663315000
C	4.357474000	-0.370492000	0.784191000
C	2.982170000	-0.210284000	1.082288000
H	2.686156000	0.202959000	2.040748000

X-Ray diffracton study.

3.

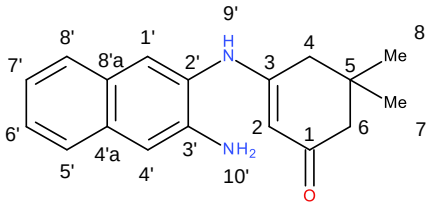


3a **3b**

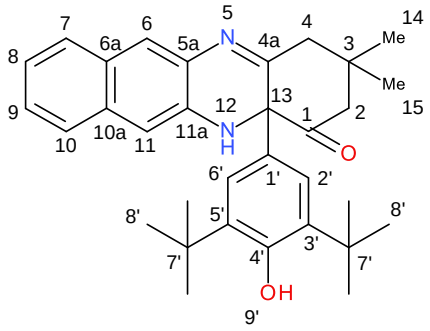
Figure S1 Molecular structures of conformational isomers **3a** and **3c** in the crystal of compound

Spectral data for compounds 3,6,7 and 9.

Table S1. Chemical shifts ^{1}H, ^{13}C, ^{15}N of compounds **3** in DMSO-d_6 and **9** in $CDCl_3$.



3

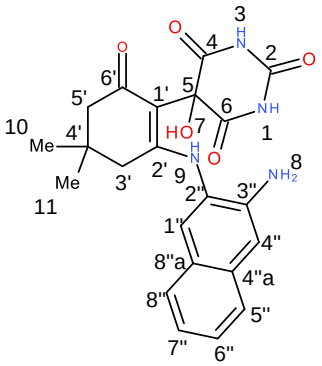


9

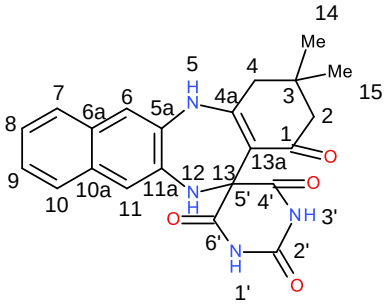
Comp.	Nucleus	1	2	3	4	5	6	7	8	1’	2’	3’	4’	4a’	5’	6’	7’	8’	8a’	9’(^{15}N)	10’(^{15}N
3	^{1}H	-	4.75	-	2.42	-	2.00	1.01	1.01	7.48	-	-	7.02	-	7.63	7.09	7.26	7.51	-	8.36	5.16
	^{13}C	194.76	96.37	162.16	41.53	32.30	50.28	28.05	28.05	125.22	126.21	142.55	108.00	126.37	127.12	121.54	125.78	124.76	133.33	106.13	57.42

Comp.	Nucleus	1	2	3	4	4a	5(^{15}N)	5a	6	6a	7	8	9	10	10a
9	^{1}H	-	2.65, 2.40	-	2.87, 2.74	-	-	-	7.72	-	7.46	7.26	7.15	7.67	-
	$^{13}C/^{15}N$	205.03	51.70	32.50	49.14	165.29	315.57	132.61	125.28	134.45	125.28	126.32	122.37	128.31	128.31
	Nucleus	11	11a	12(^{15}N)	13	14	15	1’	2’, 6’	3’, 5’	4’	7’	8’	9’	
	^{1}H	6.76	-	5.18	-	1.13	1.01	-	6.86	-	-	-	1.29	5.23	
	$^{13}C/^{15}N$	107.94	134.33	81.36	68.34	30.52	26.02	129.17	122.55	136.91	154.05	34.45	30.11	-	

Table S2. Chemical shifts ^{1}H, ^{13}C, ^{15}N of compounds **6** and **7** in DMSO-d_6.



6



7

Comp.	Nucleus	1(^{15}N)	2	3(^{15}N)	4	5	6	7	8(^{15}N)	9(^{15}N)	10	11	1’	2’	3’
6	^{1}H	11.14	-	11.14	-	-	-	8.03	5.35	9.41	0.87	0.87	-	-	2.22
	$^{13}C/^{15}N$	147.59	150.34	147.59	171.10	74.71	171.10	-	56.68	105.83	27.50	27.50	106.70	164.69	40.18
	Ядро	4’	5’	6’	1’’	2’’	3’’	4’’	4a’’	5’’	6’’	7’’	8’’	8a’’	
	^{1}H	-	1.99	-	7.56	-	-	7.02	-	-	7.29	7.13	7.66	-	
	$^{13}C/^{15}N$	74.71	48.97	193.27	126.35	126.06	125.82	107.57	133.72	124.90	126.17	121.74	127.45	143.44	

Comp.	Nucleus	1	2	3	4	4a	5(^{15}N)	5a	6	6a	7	8	9	10	10a
7	^{1}H	-	2.02	-	2.63	-	9.30	-	-	-	7.60	7.28	7.28	7.68	-
	$^{13}C/^{15}N$	194.99	48.69	31.36	44.37	155.58	118.37	134.76	116.28	129.20	125.80	124.58	124.20	126.37	130.33
	Nucleus	11	11a	12(^{15}N)	13	13a	14	15	1’(^{15}N)	2’	3’(^{15}N)	4’	5’	6’	
	^{1}H	7.37	-	6.60	-	-	1.09	1.09	11.06	-	11.06	-	-	-	
	$^{13}C/^{15}N$	117.13	136.23	72.21	66.28	106.82	27.49	27.49	147.92	150.41	147.92	169.31	66.28	169.32	

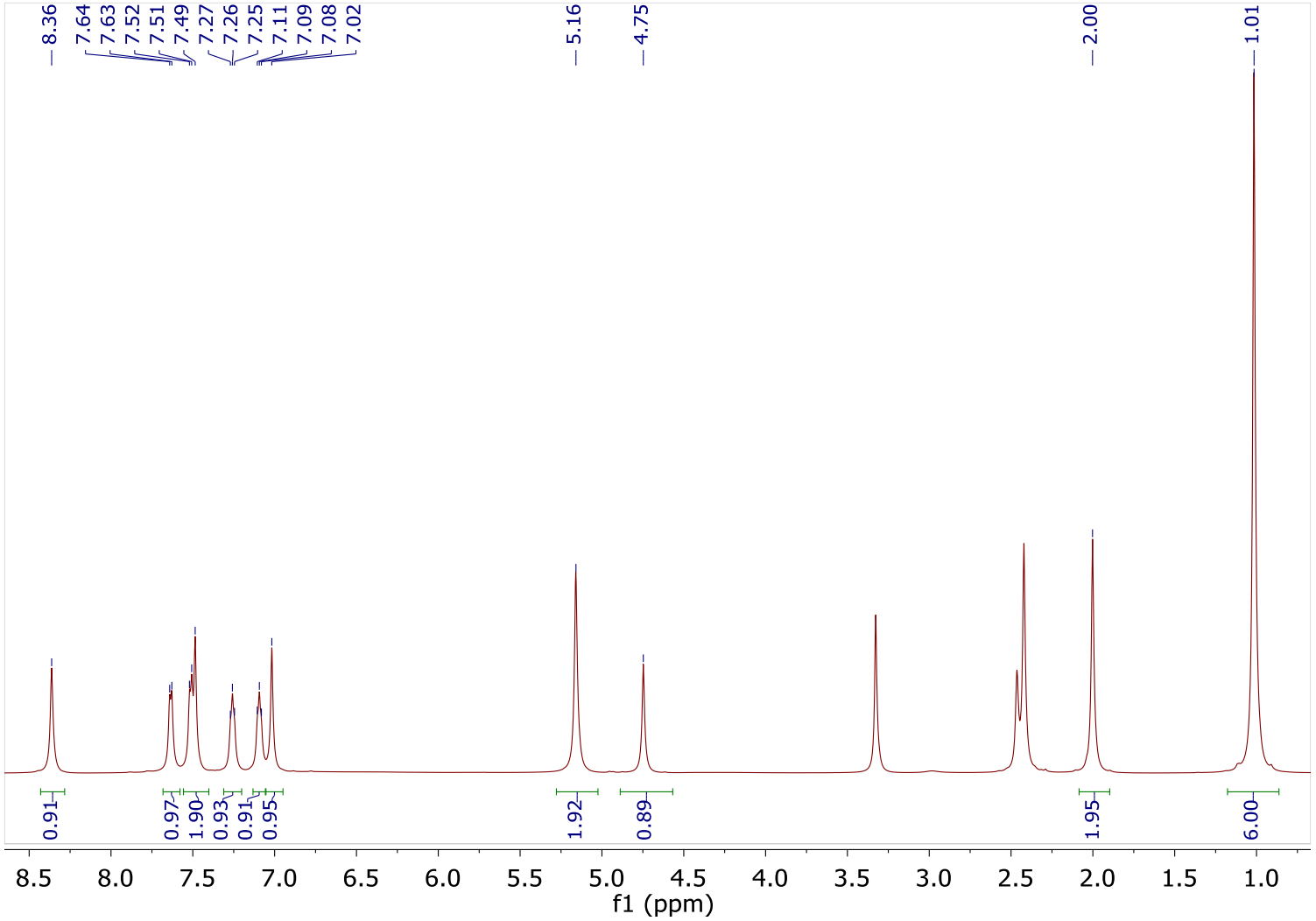


Figure S2 ^{1}H NMR spectrum of compound **3** recorded at 600 MHz in DMSO-d_6.

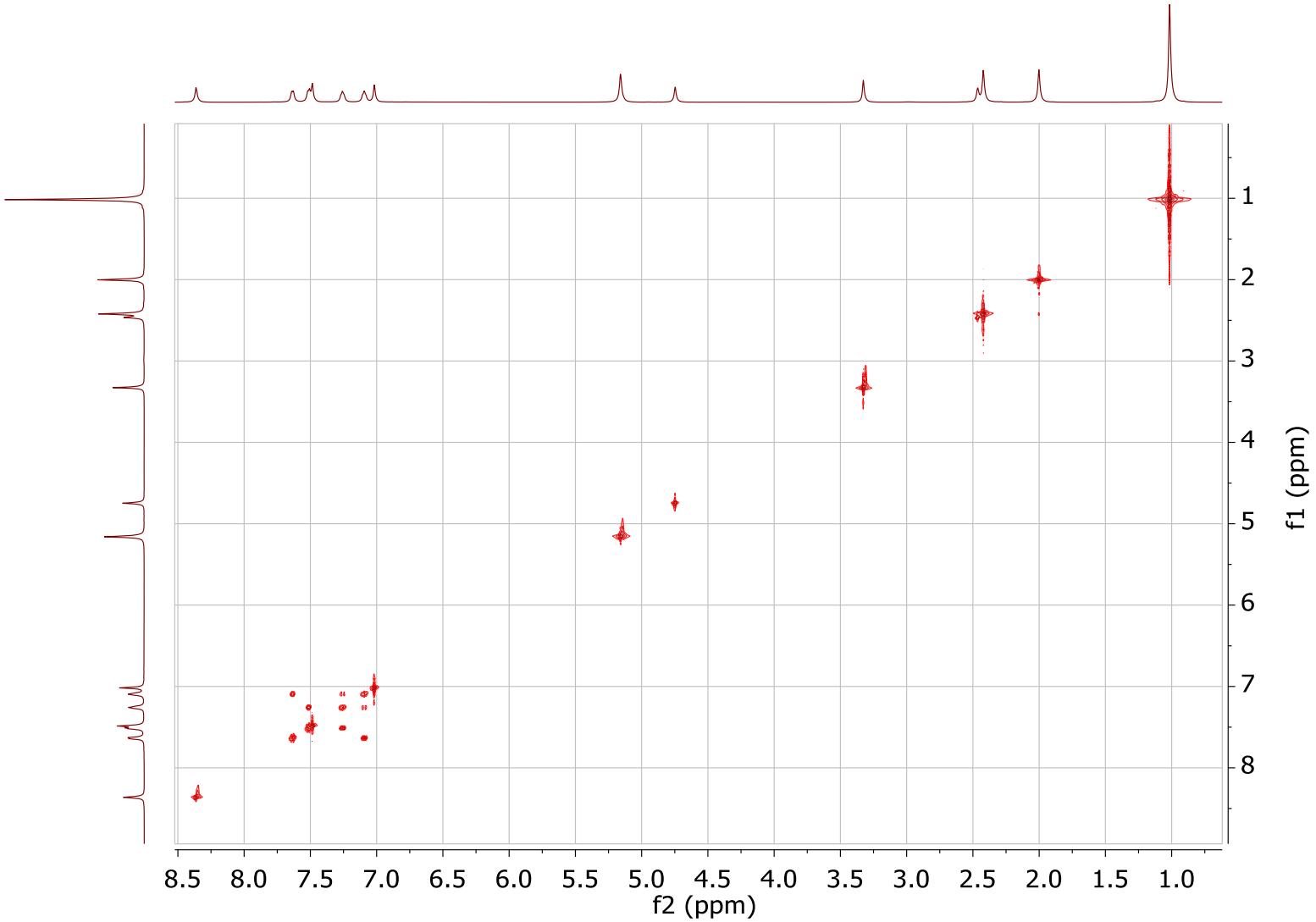


Figure S3 COSY spectrum of compound **3** recorded at 600, 600 MHz in DMSO-d_6.

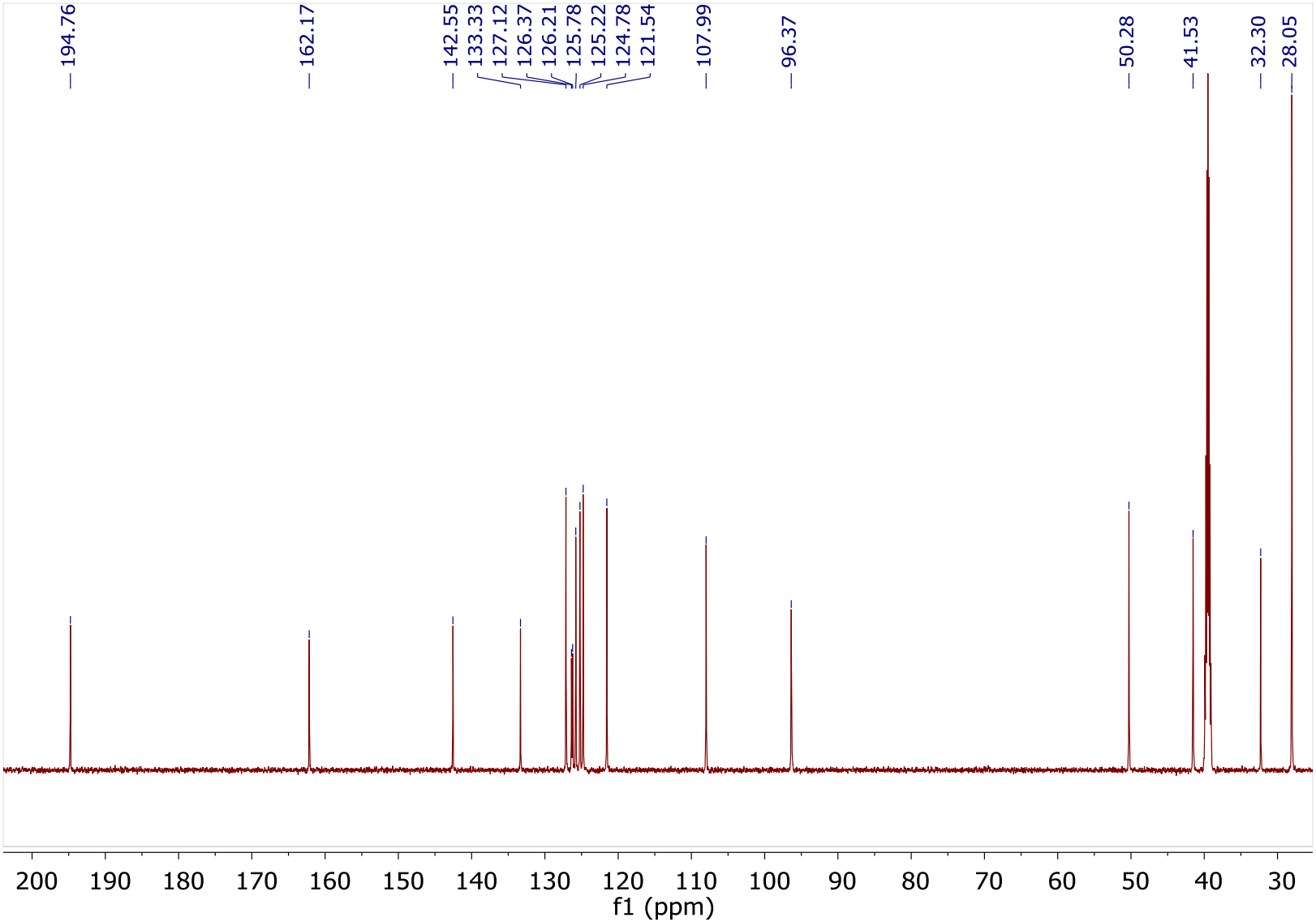


Figure S4 ^{13}C NMR spectrum of compound **3** recorded at 150 MHz in DMSO-d_6.

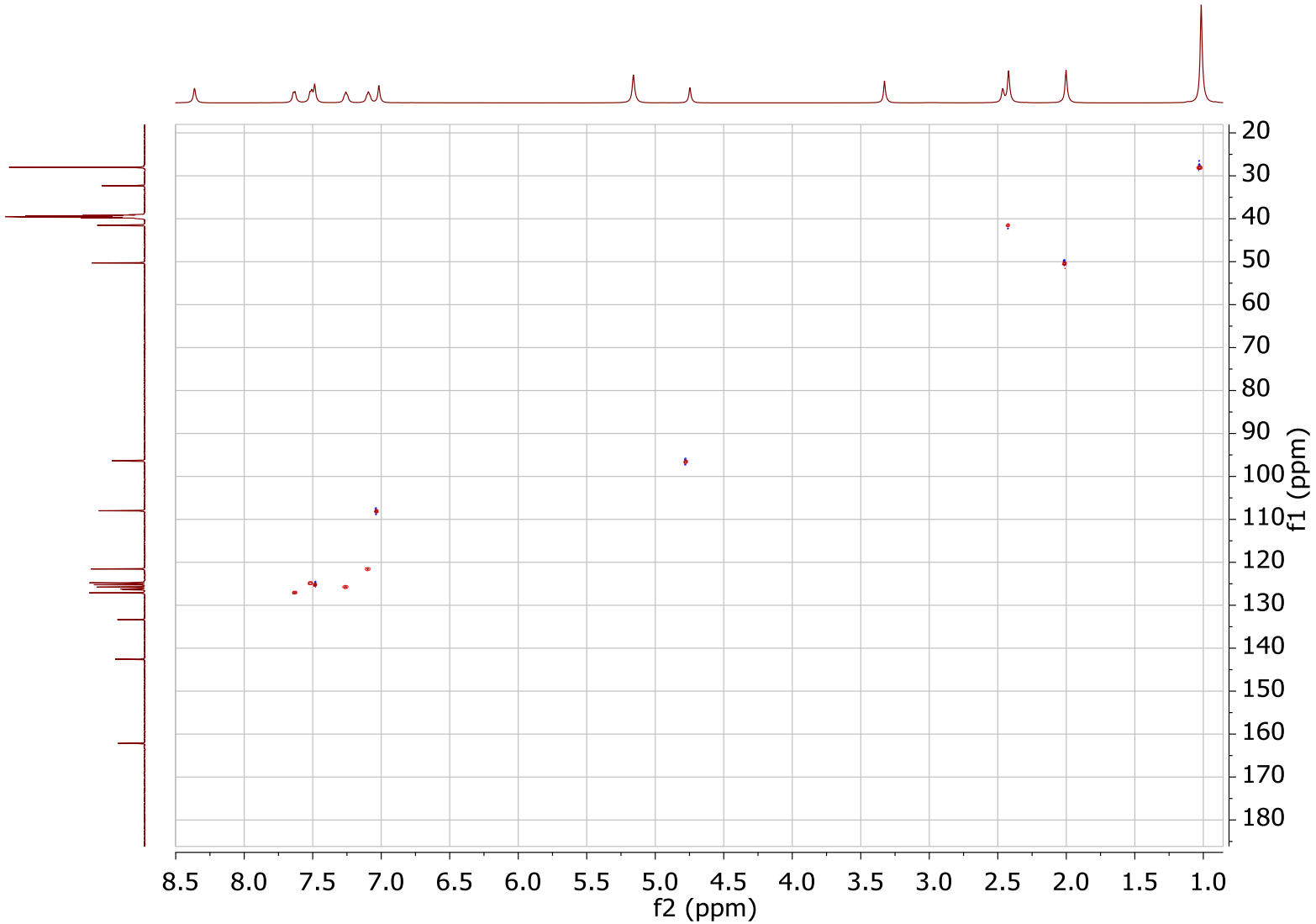


Figure S5 ^{1}H – ^{13}C HSQC spectrum of compound **3** recorded at 600, 150 MHz in DMSO-d_6.

Figure S6 ^{1}H – ^{13}C HMBC spectrum of compound **3** recorded at 600, 150 MHz in DMSO-d_6.

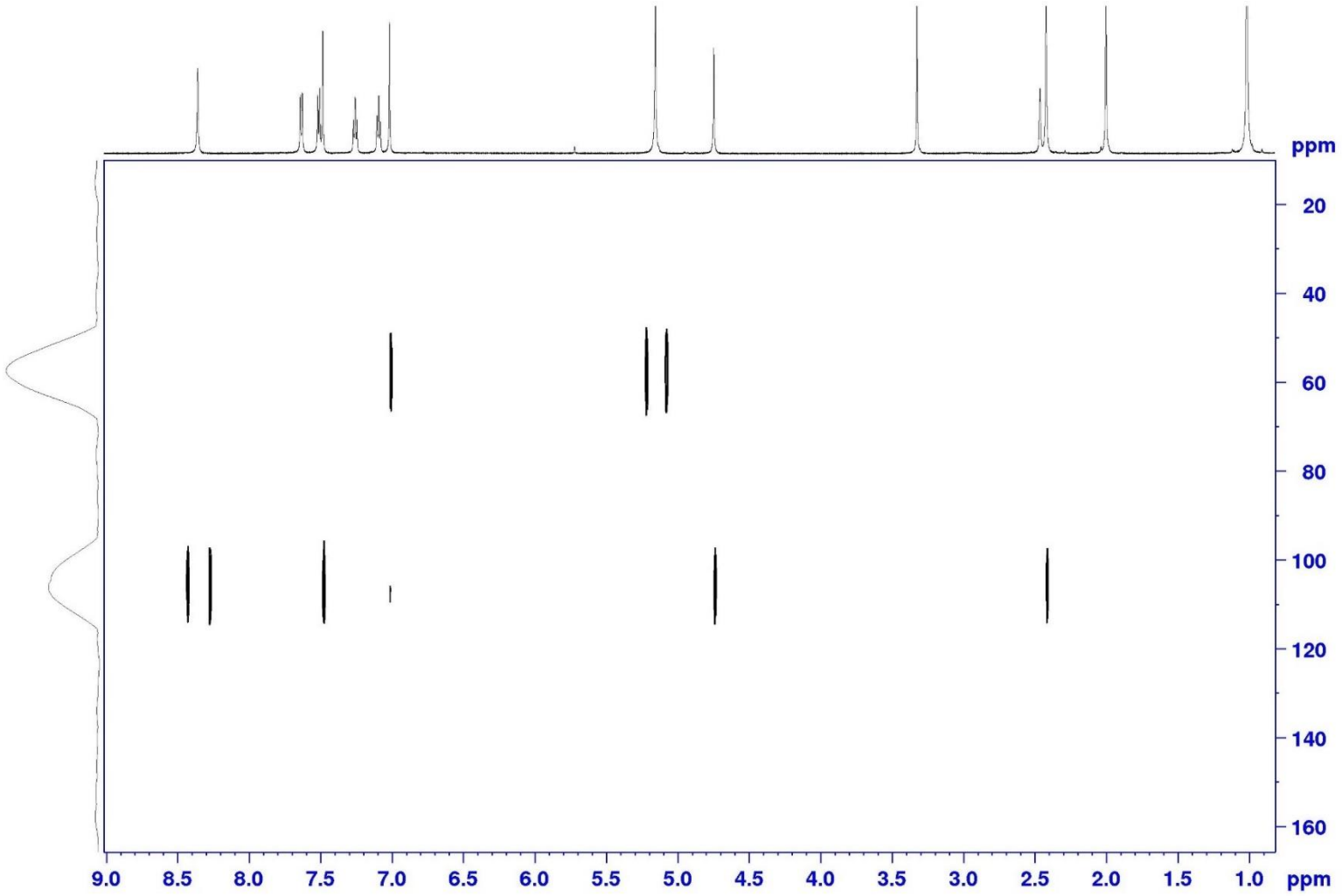


Figure S7 ^{1}H – ^{15}N HMBC spectrum of compound **3** recorded at 600, 60MHz in DMSO-d_6.

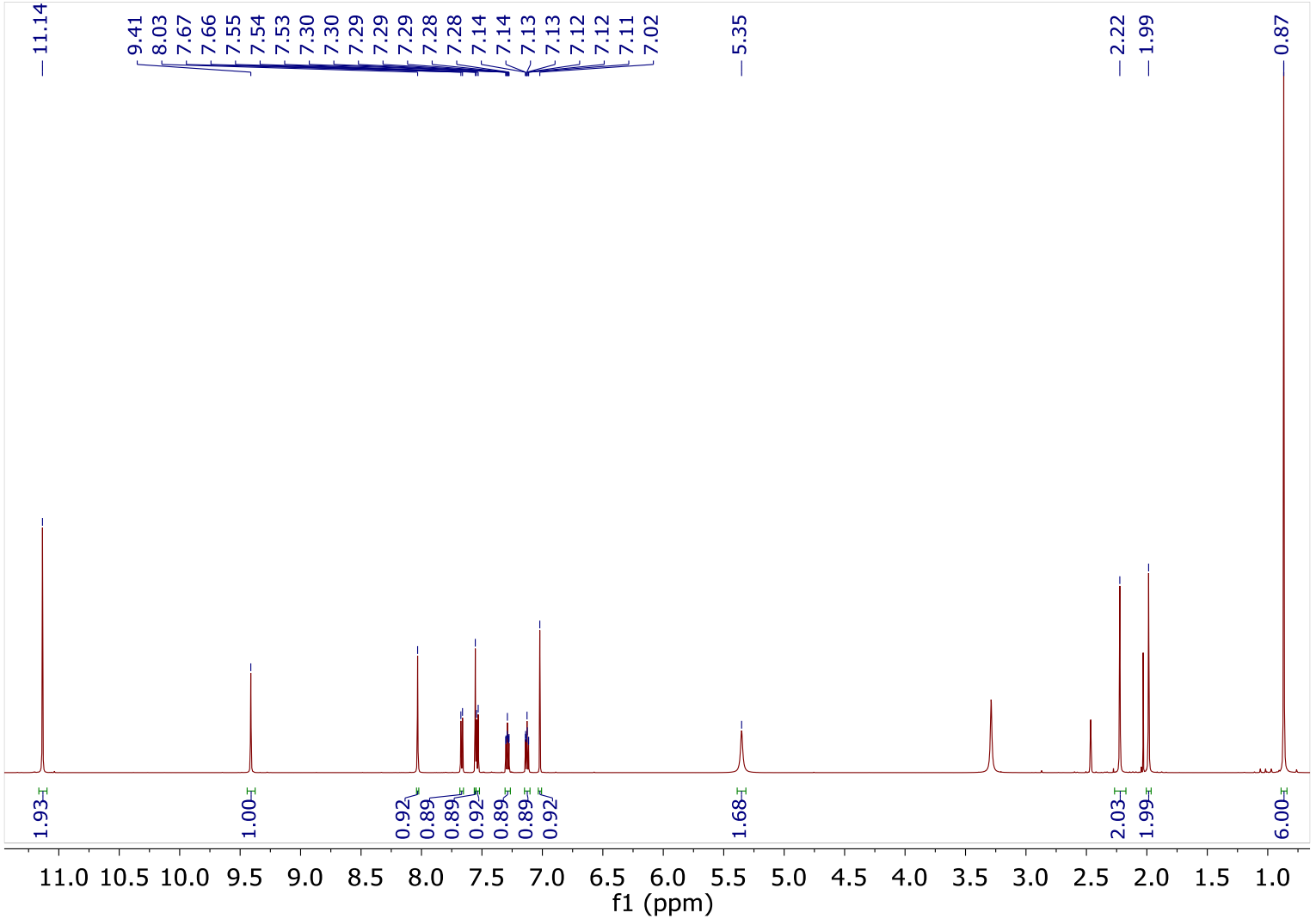


Figure S8 ^{1}H NMR spectrum of compound **6** recorded at 600 MHz in DMSO-d_6.

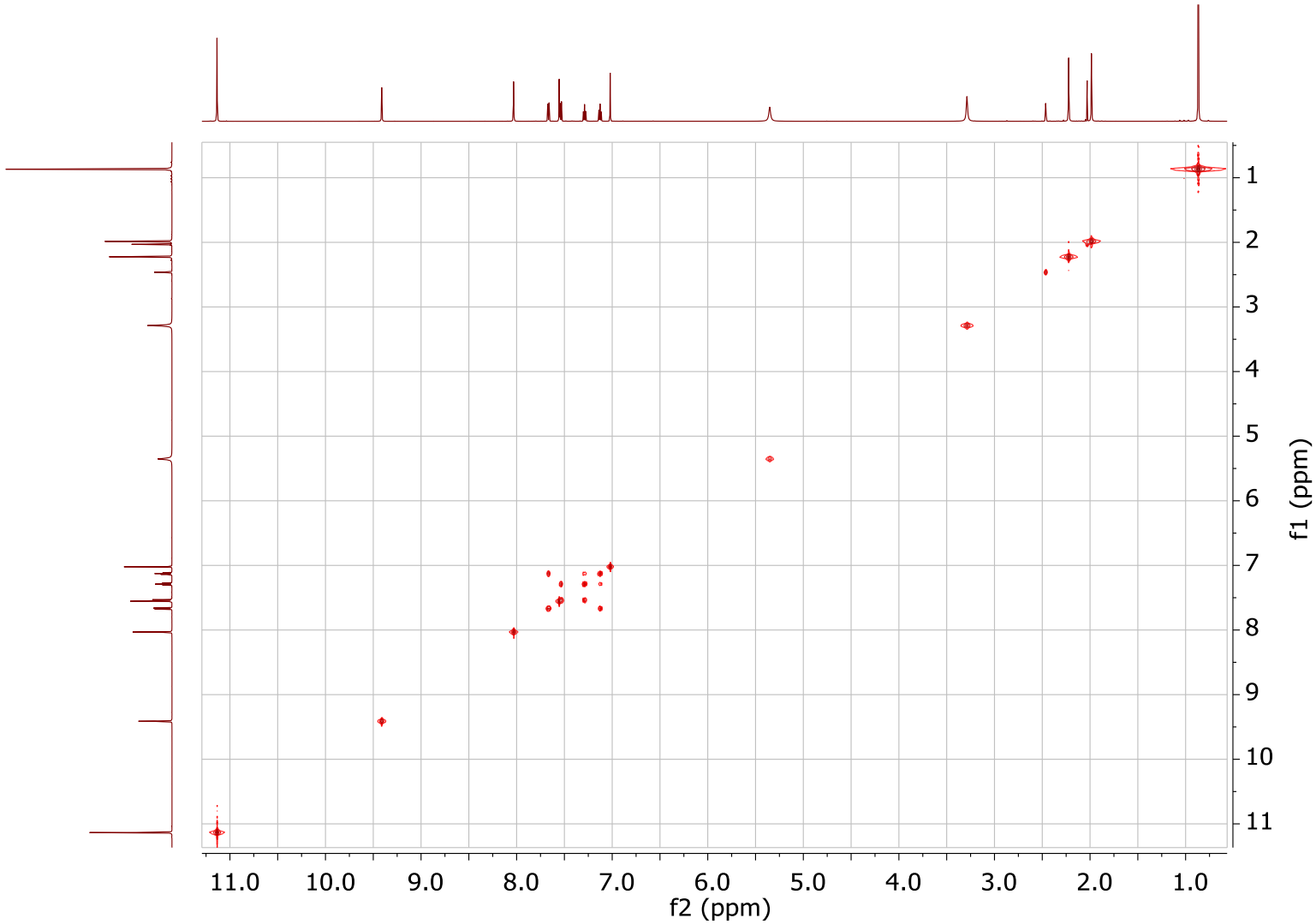


Figure S9 COSY spectrum of compound **6** recorded at 600, 600 MHz in DMSO-d_6.

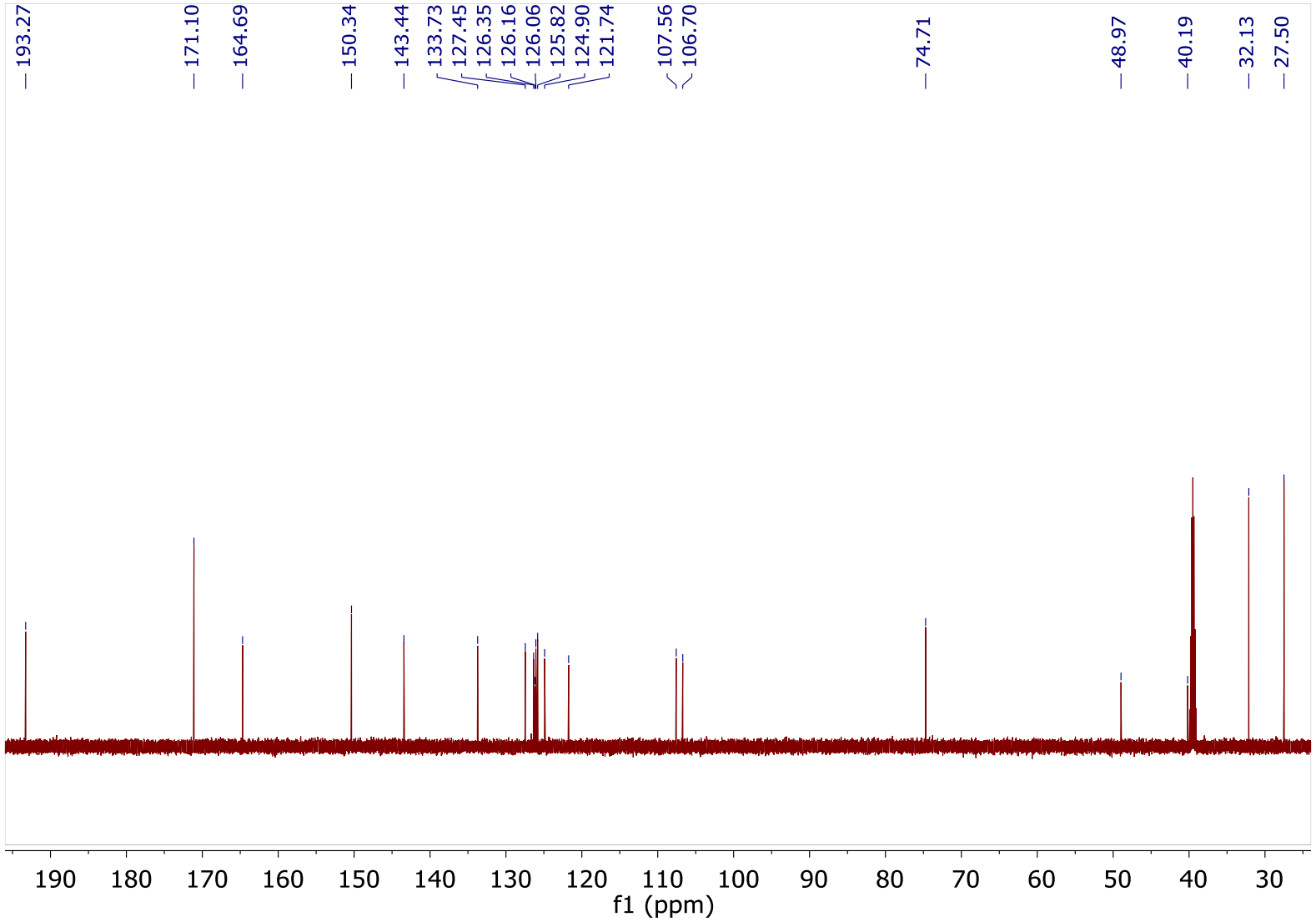


Figure S10 ^{13}C NMR spectrum of compound **6** recorded at 150 MHz in DMSO-d_6.

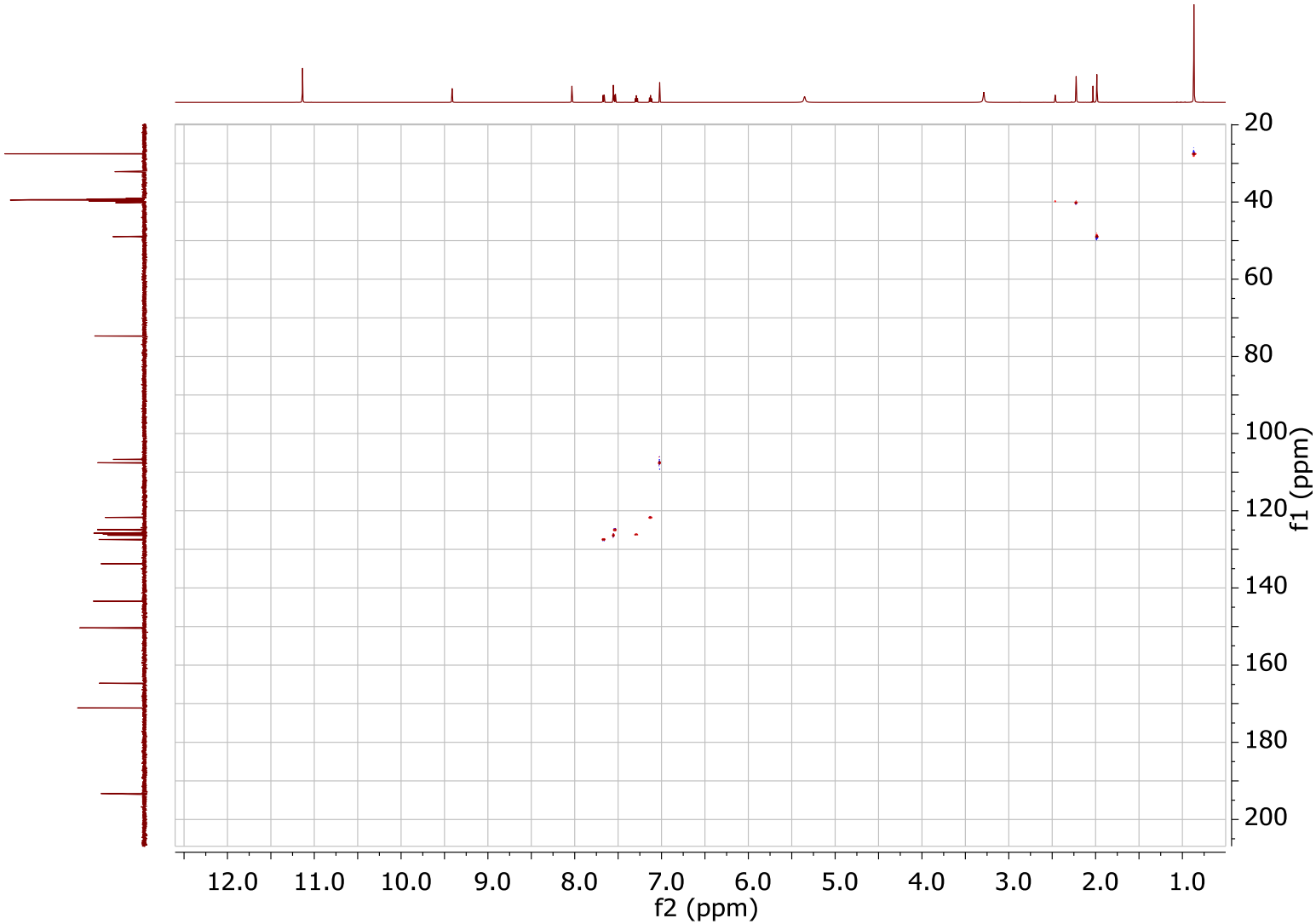


Figure S11 ^{1}H – ^{13}C HSQC spectrum of compound **6** recorded at 600, 150 MHz in DMSO-d_6.

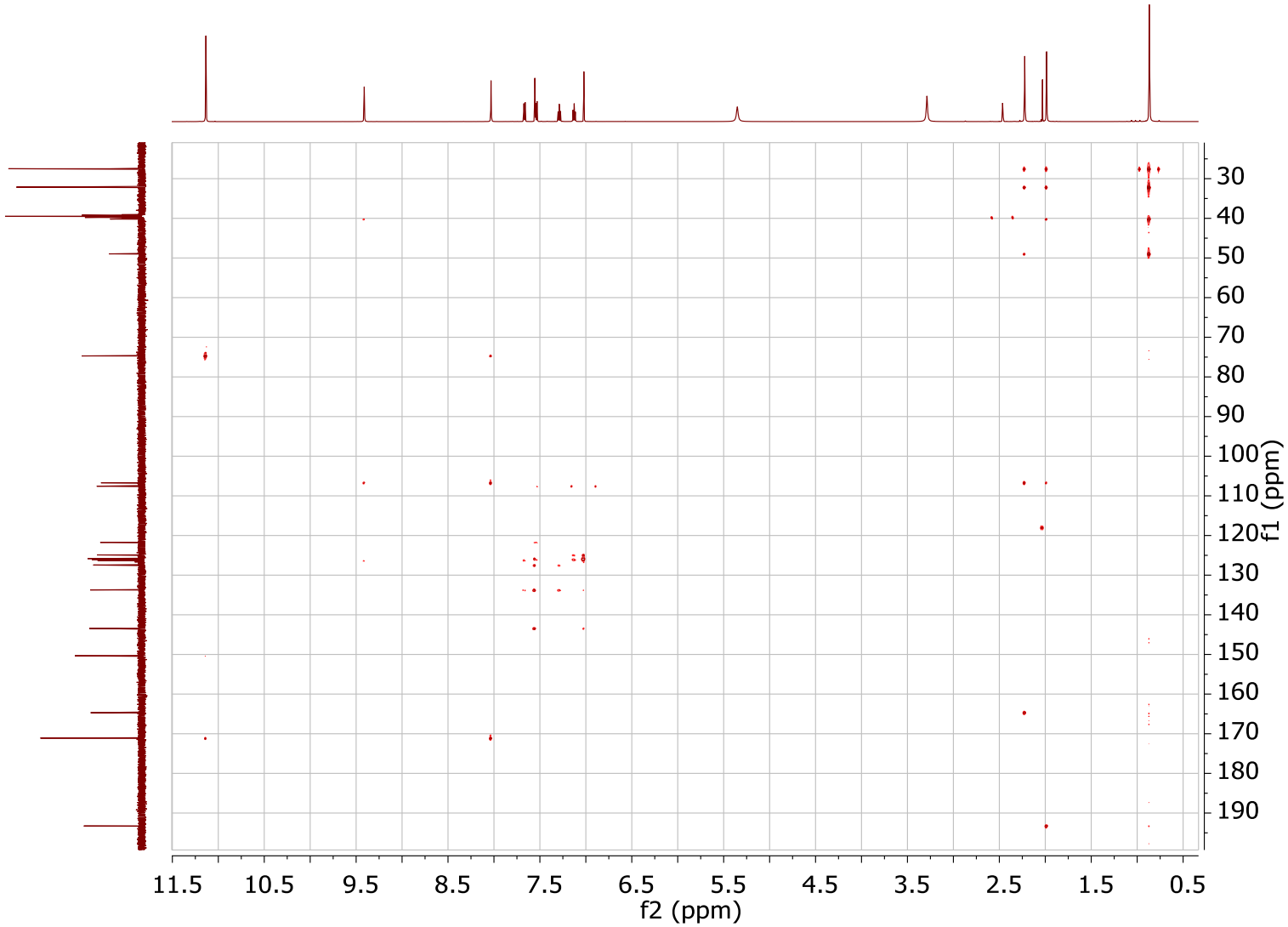


Figure S12 ^{1}H – ^{13}C HMBC spectrum of compound **6** recorded at 600, 150 MHz in DMSO-d_6.

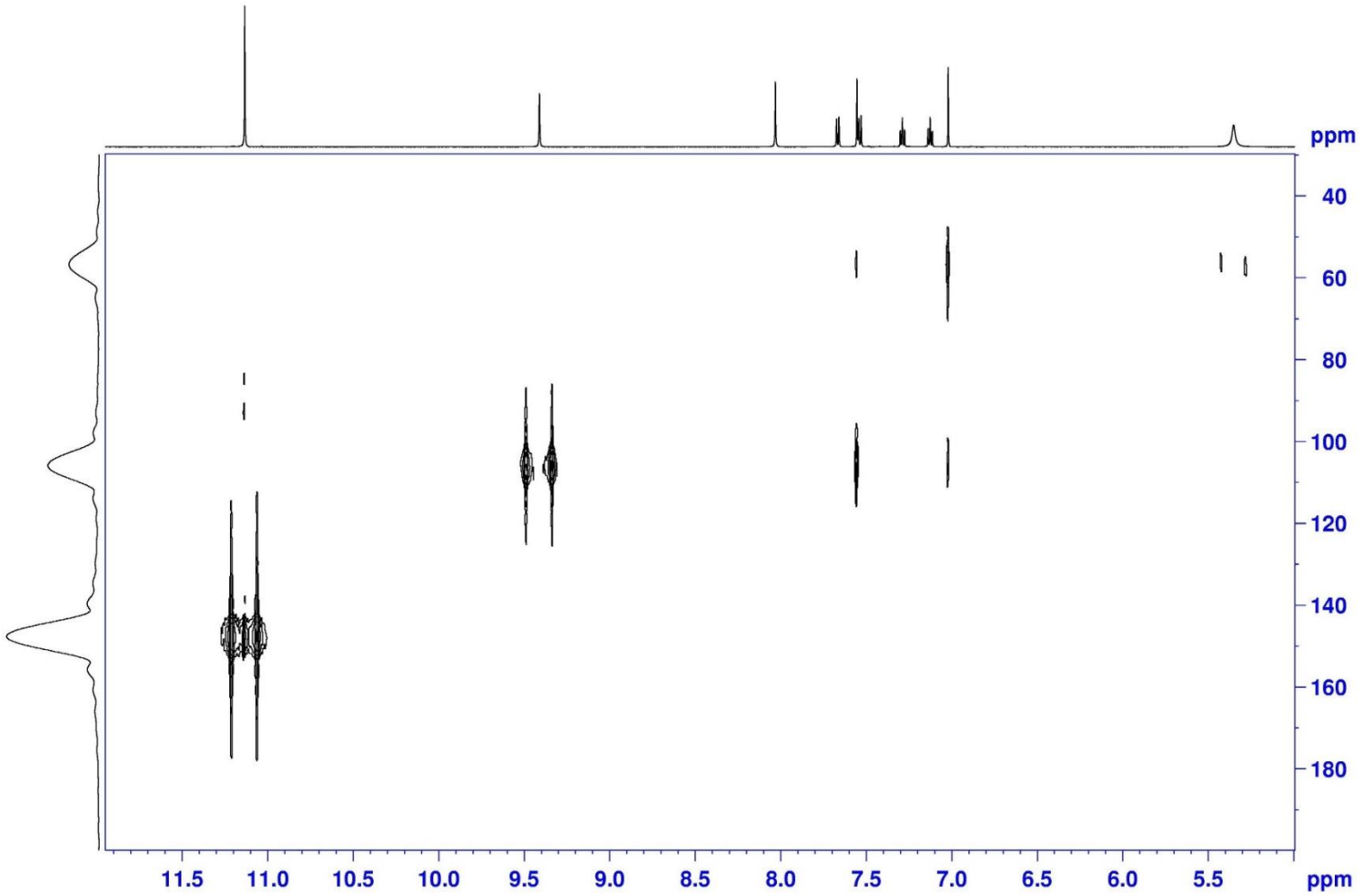


Figure S13 ^{1}H – ^{15}N HMBC spectrum of compound **6** recorded at 600, 60 MHz in DMSO-d_6.

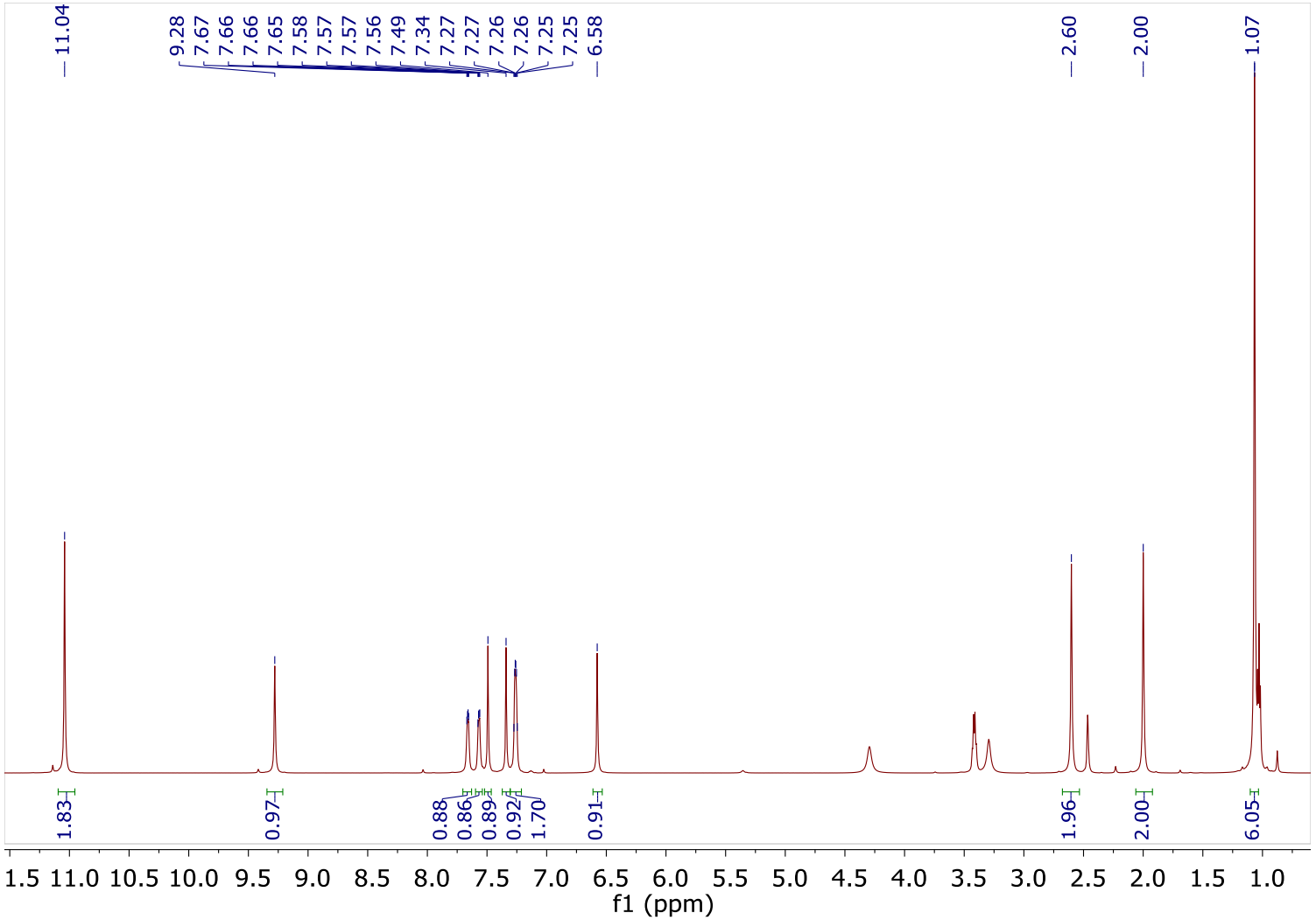


Figure S14 ^{1}H NMR spectrum of compound **7** recorded at 600 MHz in DMSO-d_6.

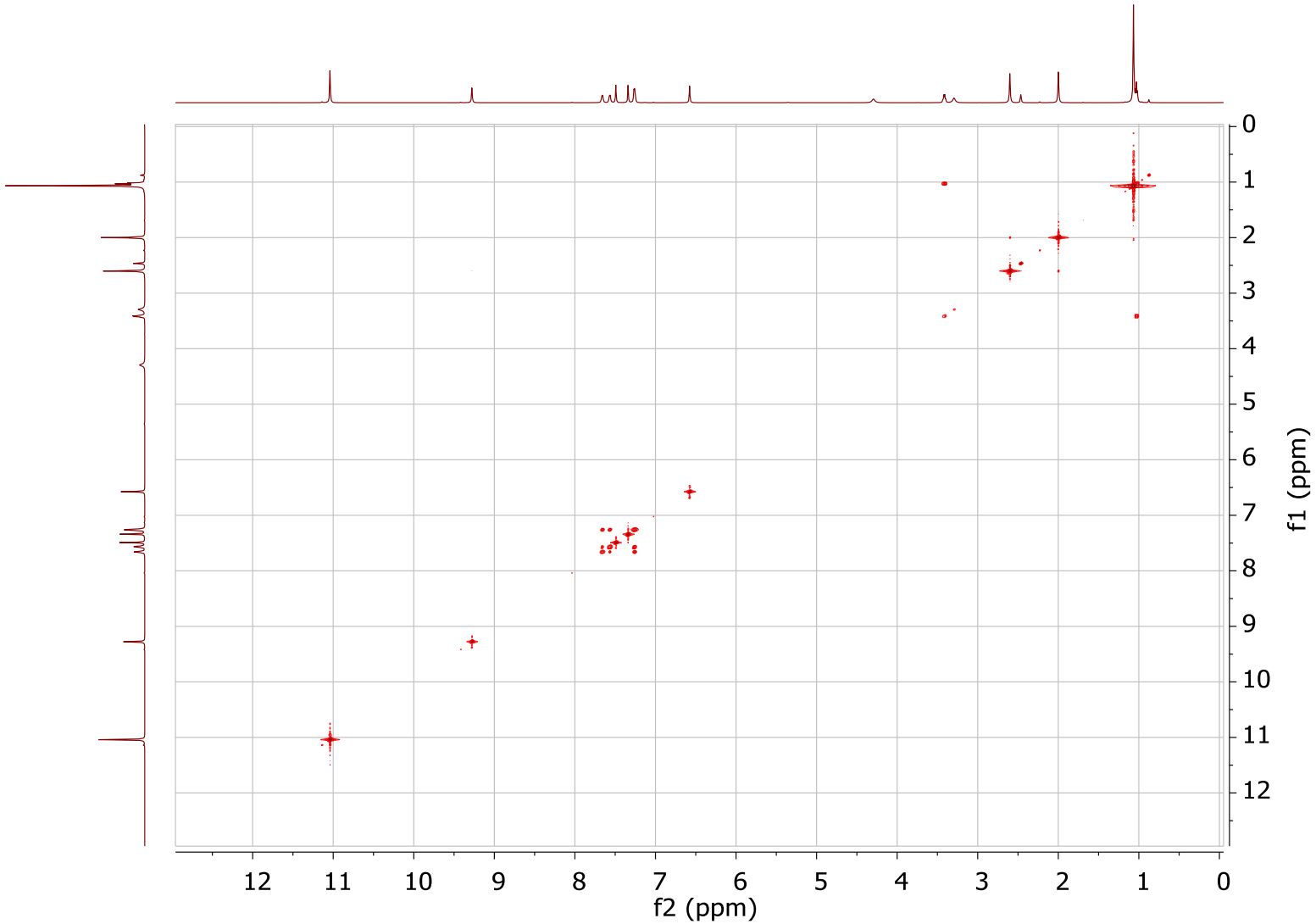


Figure S15 COSY spectrum of compound **7** recorded at 600, 600 MHz in DMSO-d_6.

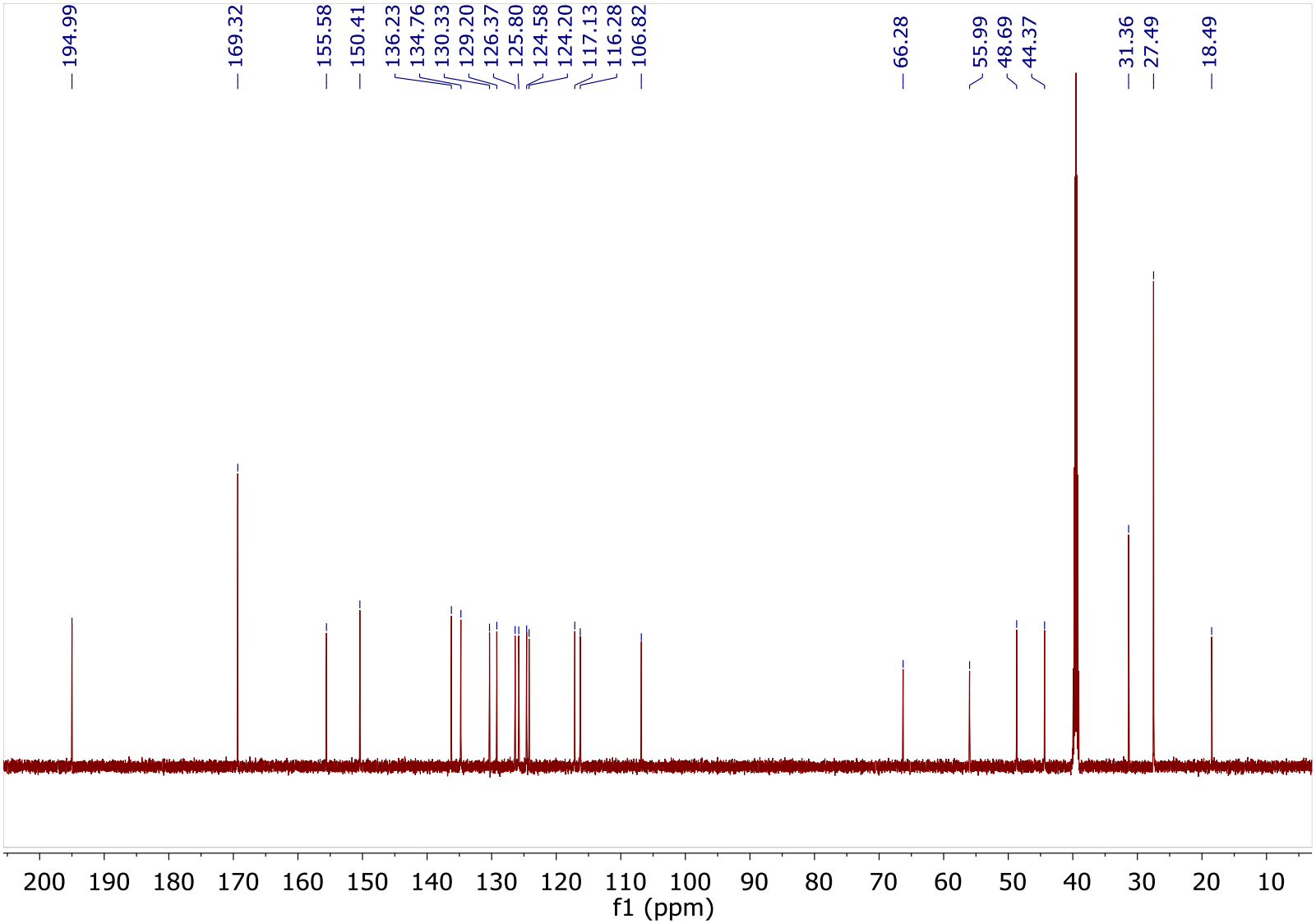


Figure S16 ^{13}C NMR spectrum of compound **7** recorded at 150 MHz in DMSO-d_6.

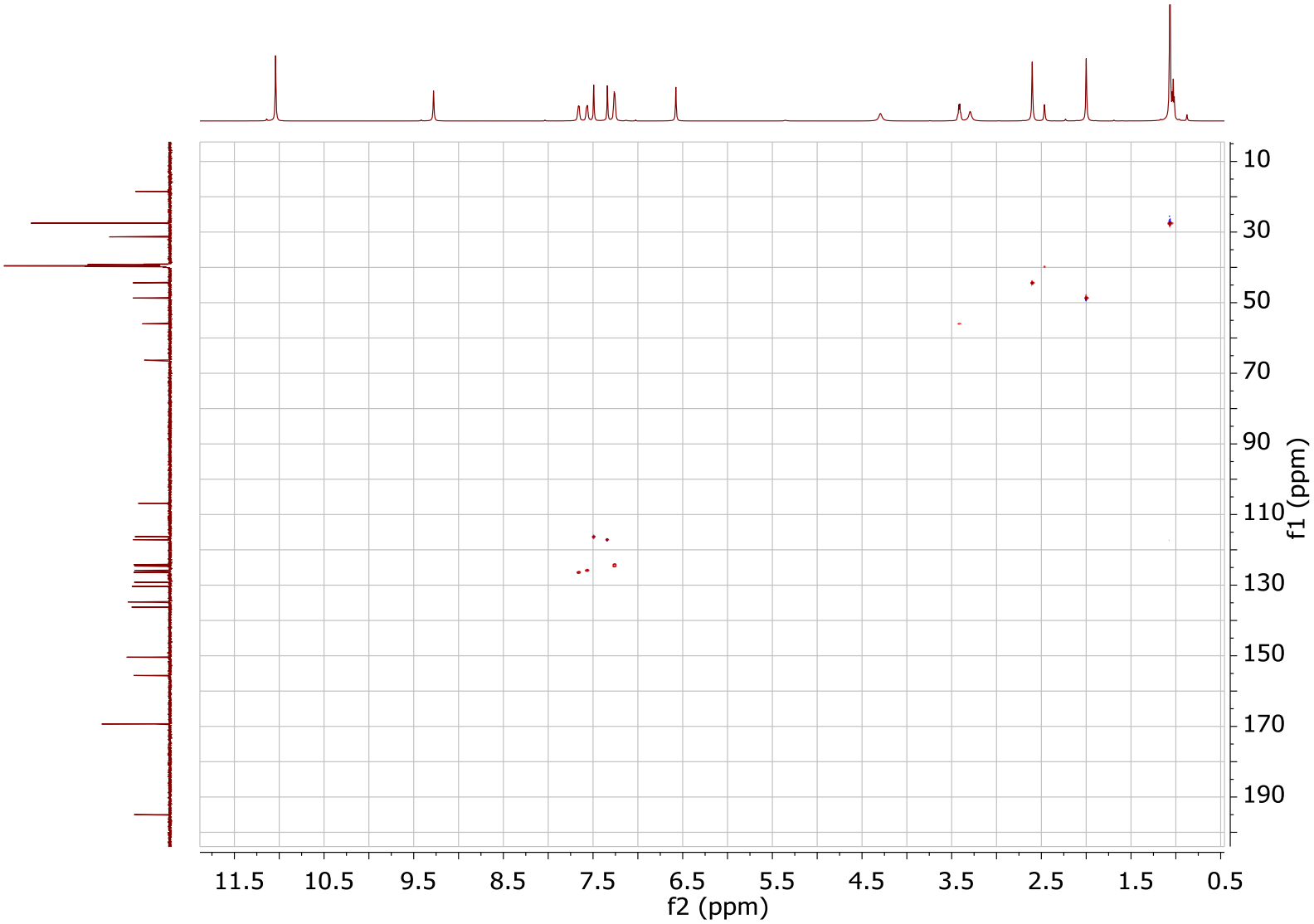


Figure S17 ^{1}H – ^{13}C HSQC spectrum of compound **7** recorded at 600, 150 MHz in DMSO-d_6.

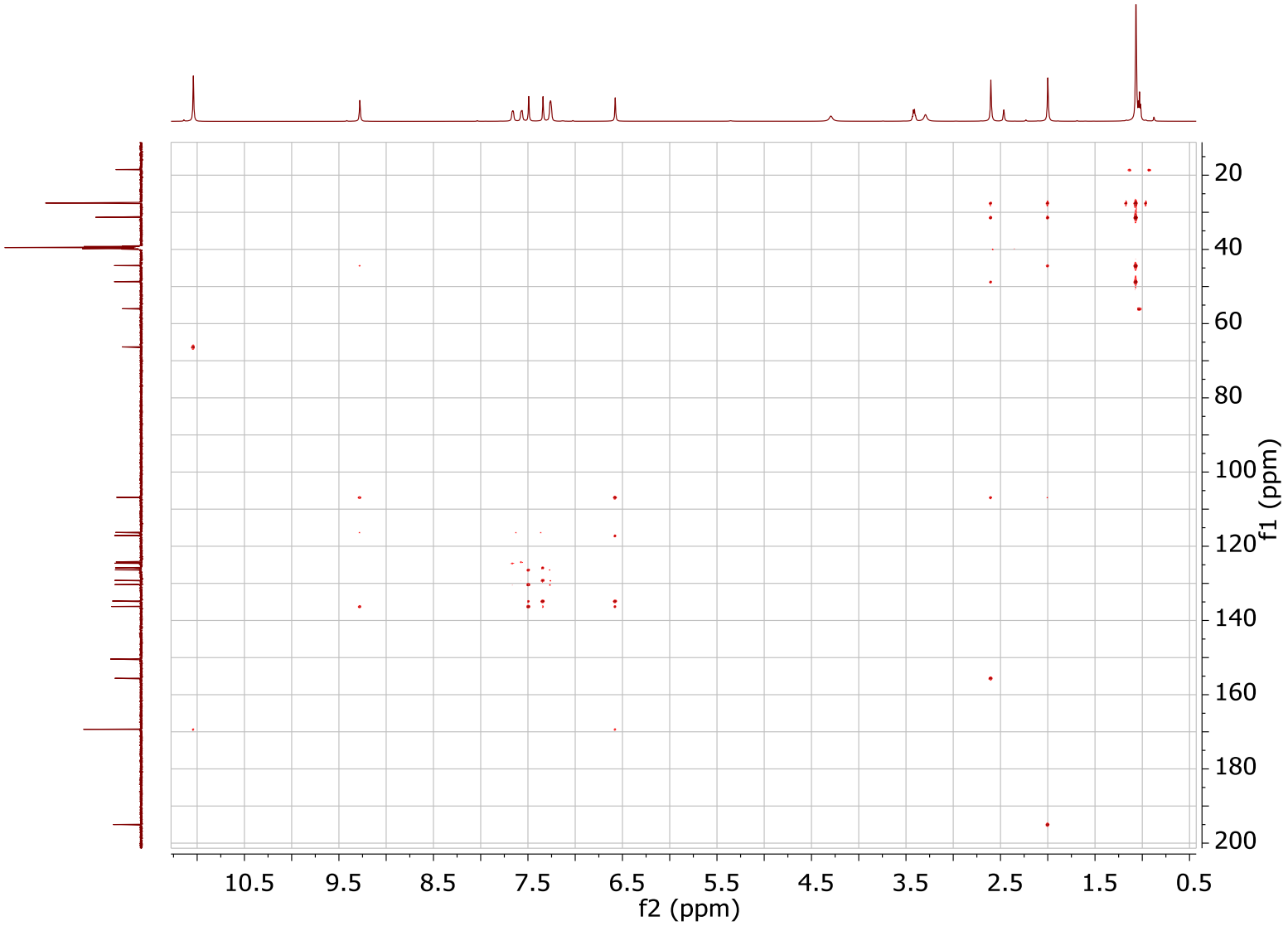


Figure S18 ^{1}H – ^{13}C HMBC spectrum of compound **7** recorded at 600, 150 MHz in DMSO-d_6.

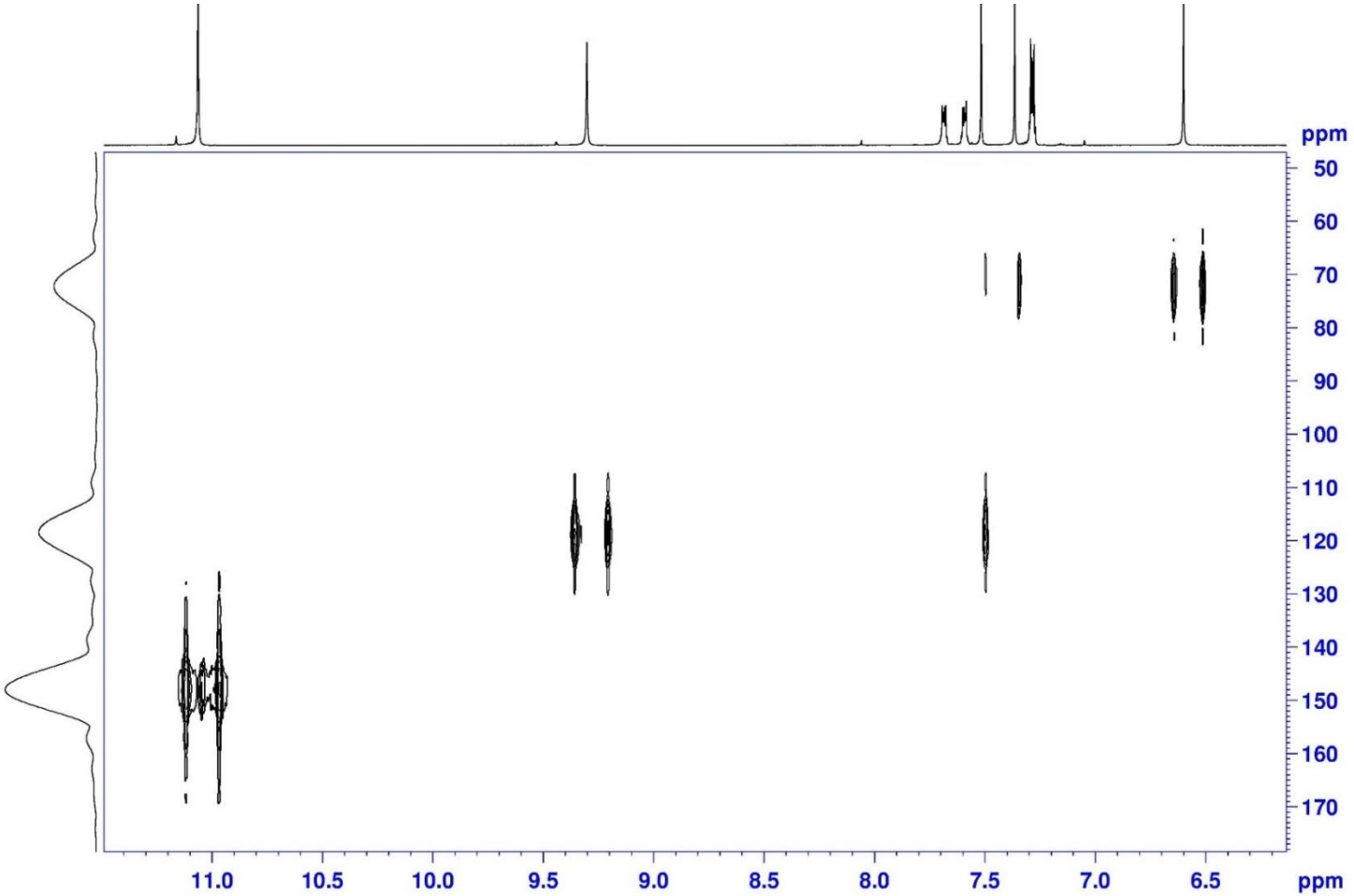


Figure S19 ^{1}H – ^{15}N HMBC spectrum of compound **7** recorded at 600, 60MHz in DMSO-d_6.

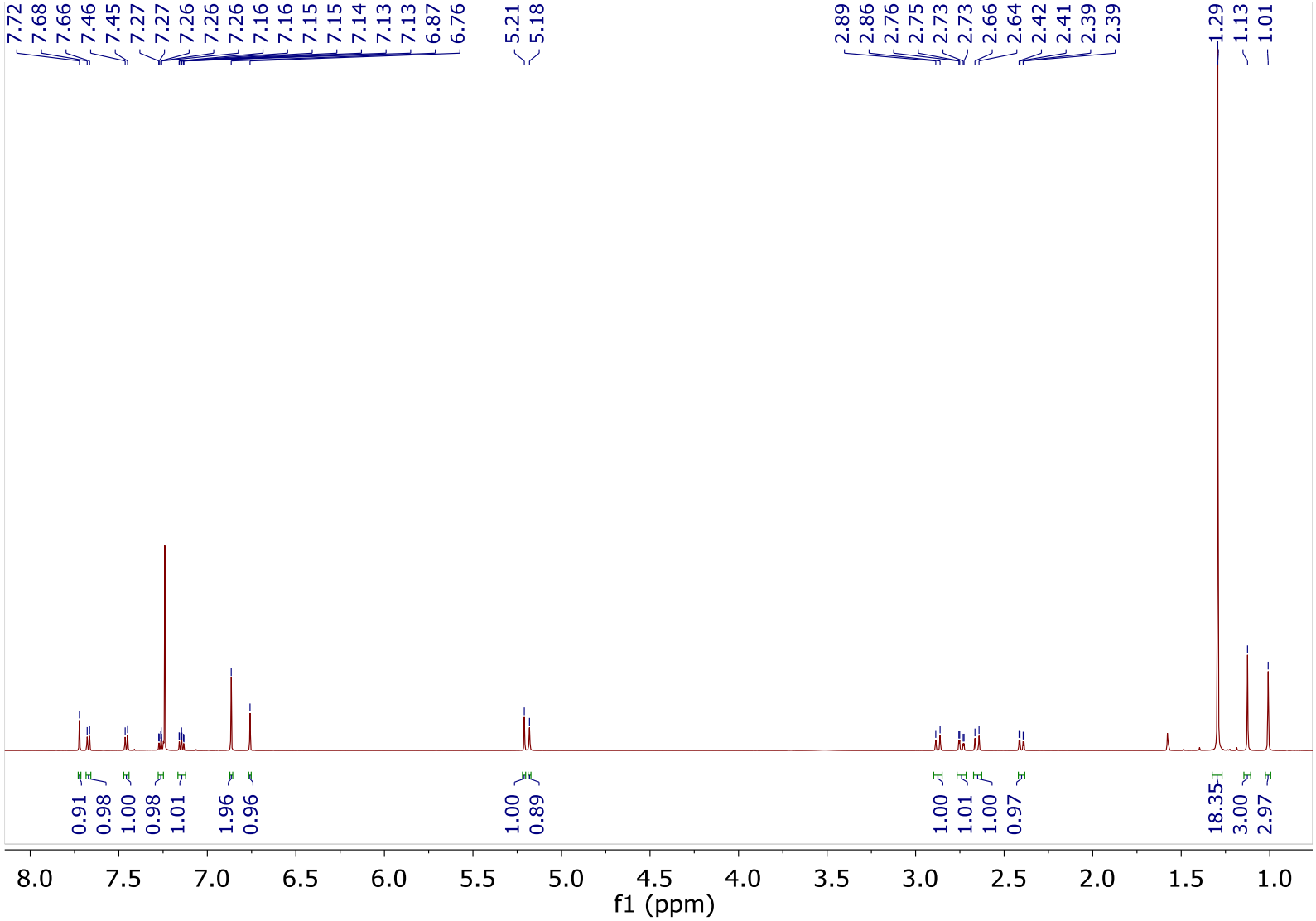


Figure S20 ^{1}H NMR spectrum of compound **9** recorded at 600 MHz in $CDCl_3$.

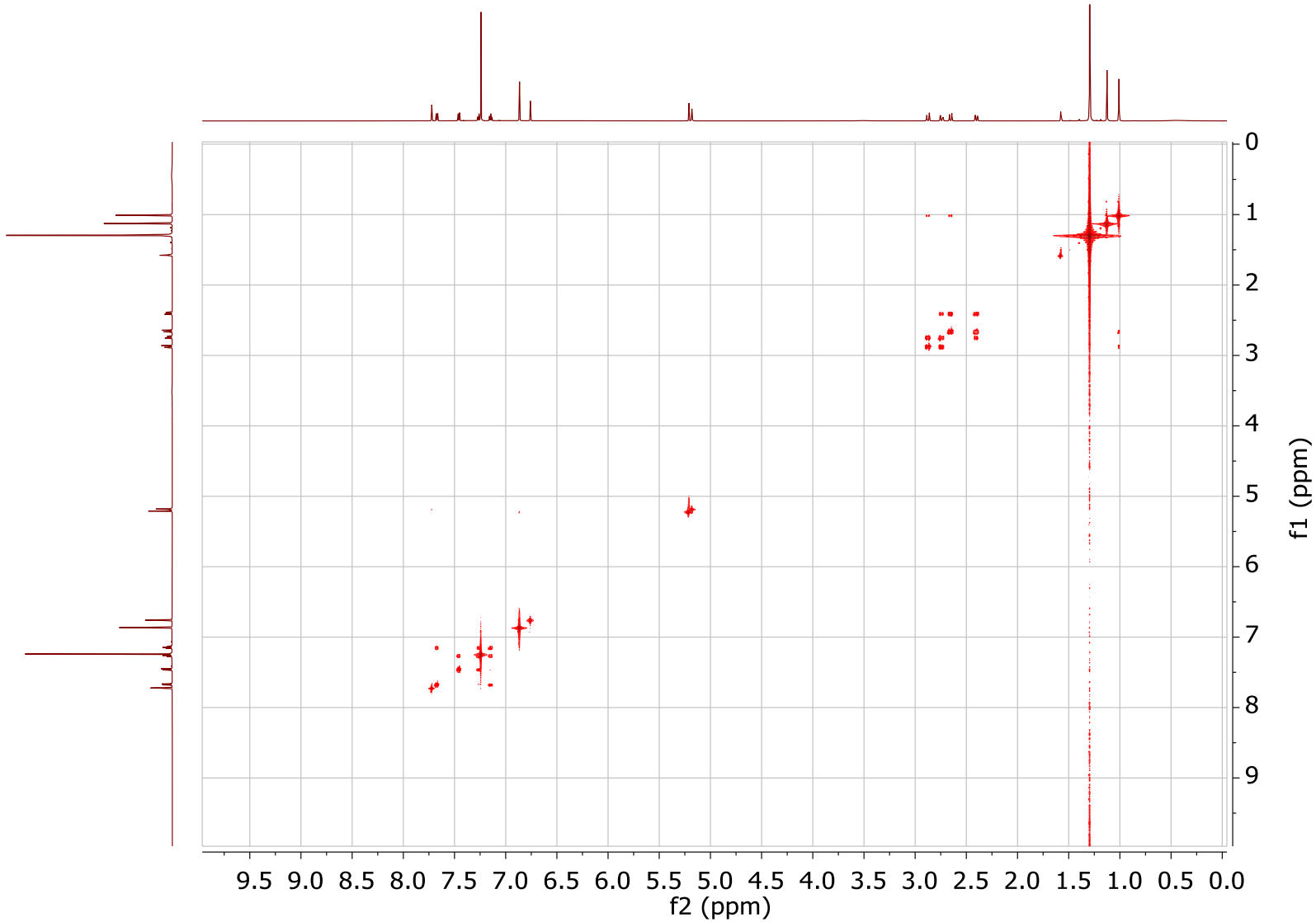


Figure S21 COSY spectrum of compound **9** recorded at 600, 600 MHz in $CDCl_3$.

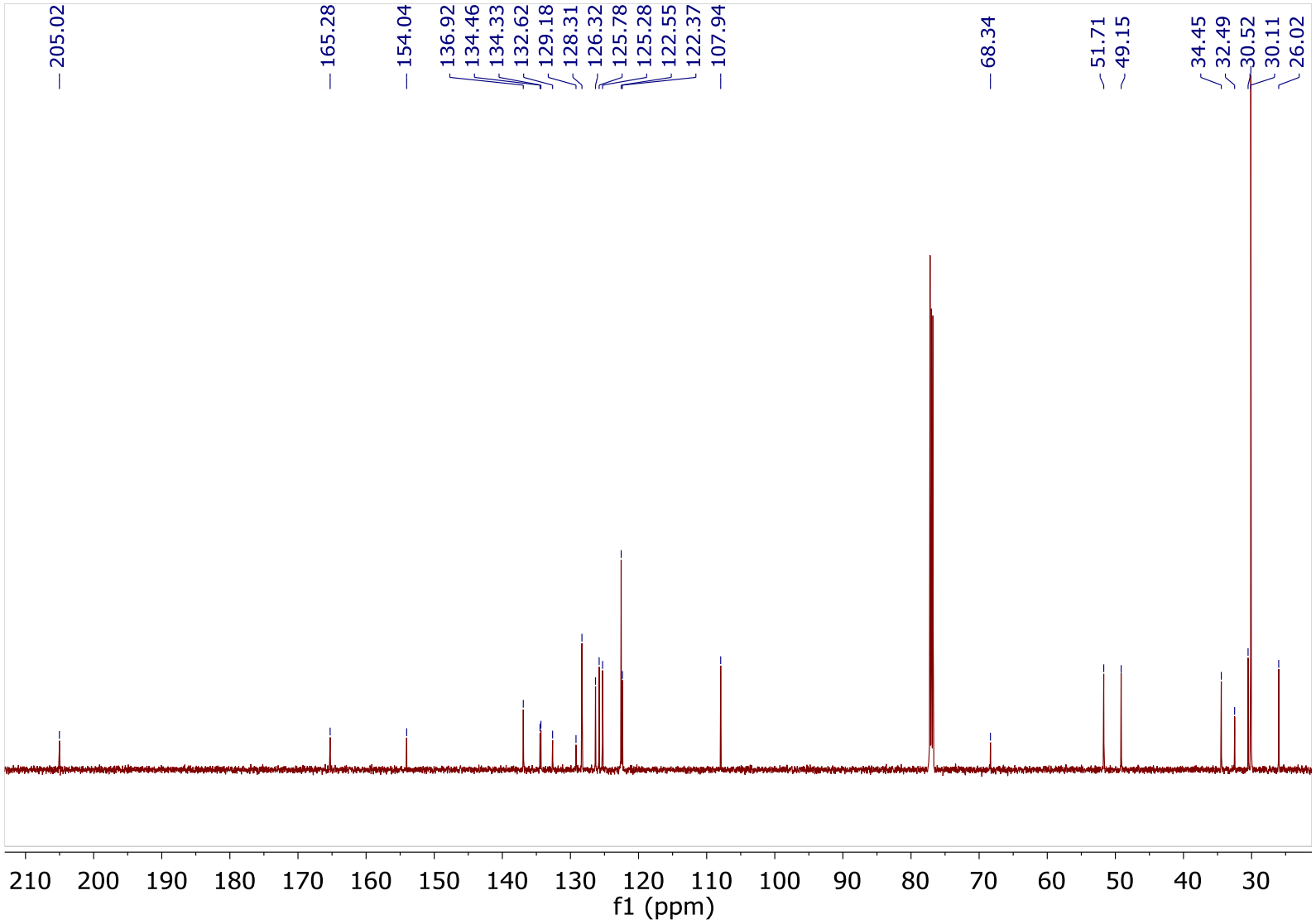


Figure S22 ^{13}C NMR spectrum of compound **9** recorded at 150 MHz in $CDCl_3$.

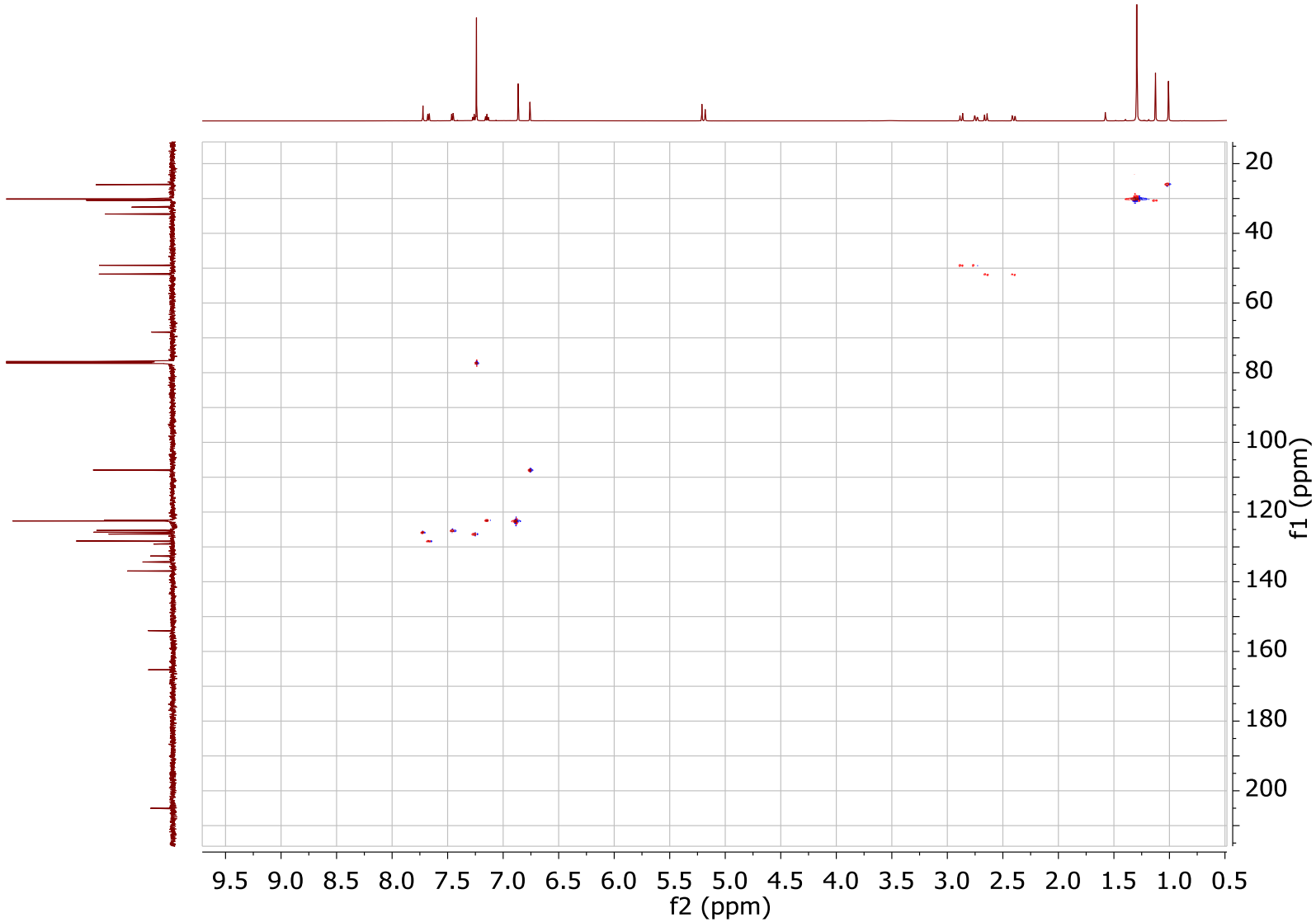


Figure S23 ^{1}H – ^{13}C HSQC spectrum of compound **9** recorded at 600, 150 MHz in $CDCl_3$.

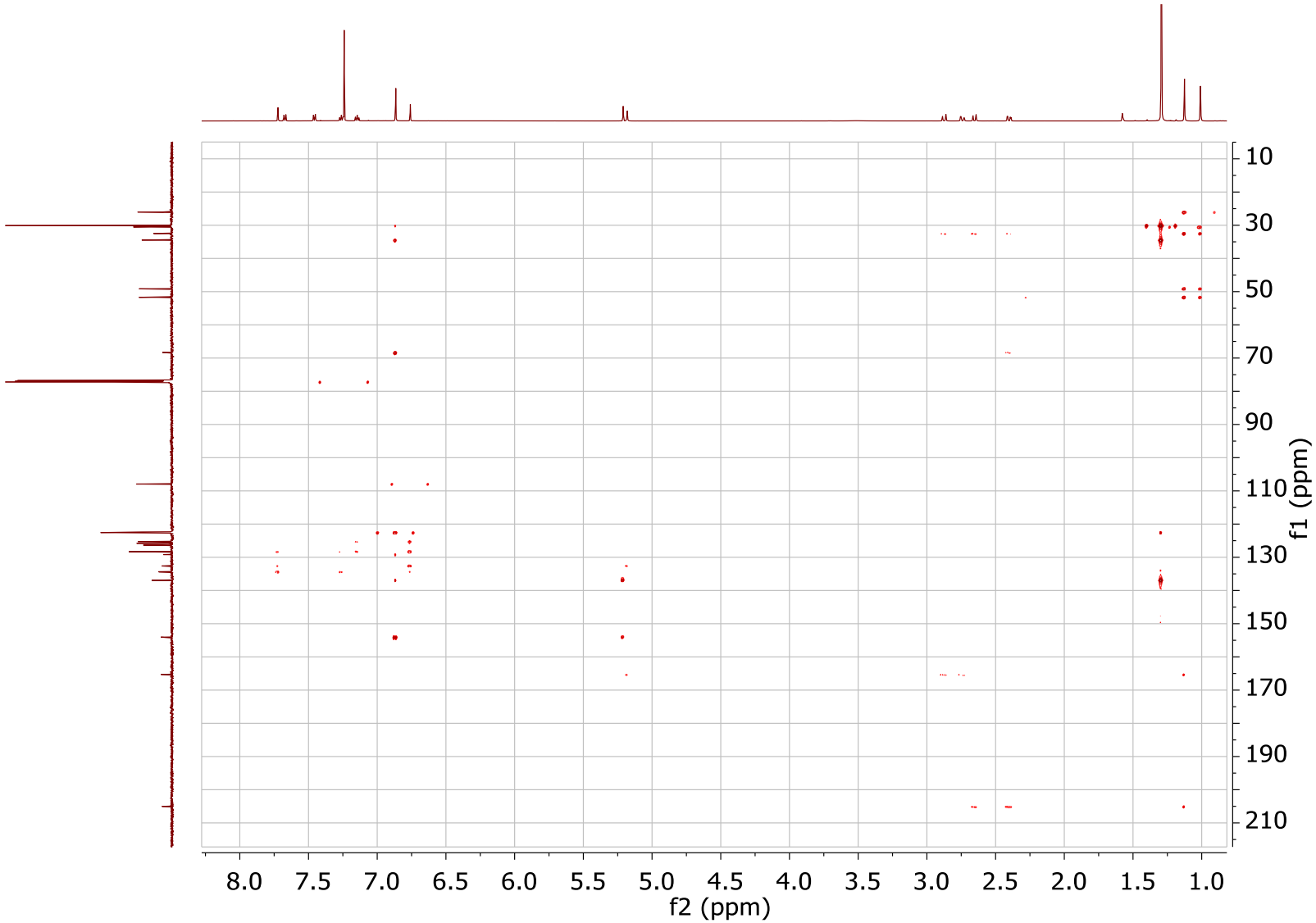


Figure S24 ^{1}H – ^{13}C HMBC spectrum of compound **9** recorded at 600, 150 MHz in $CDCl_3$.

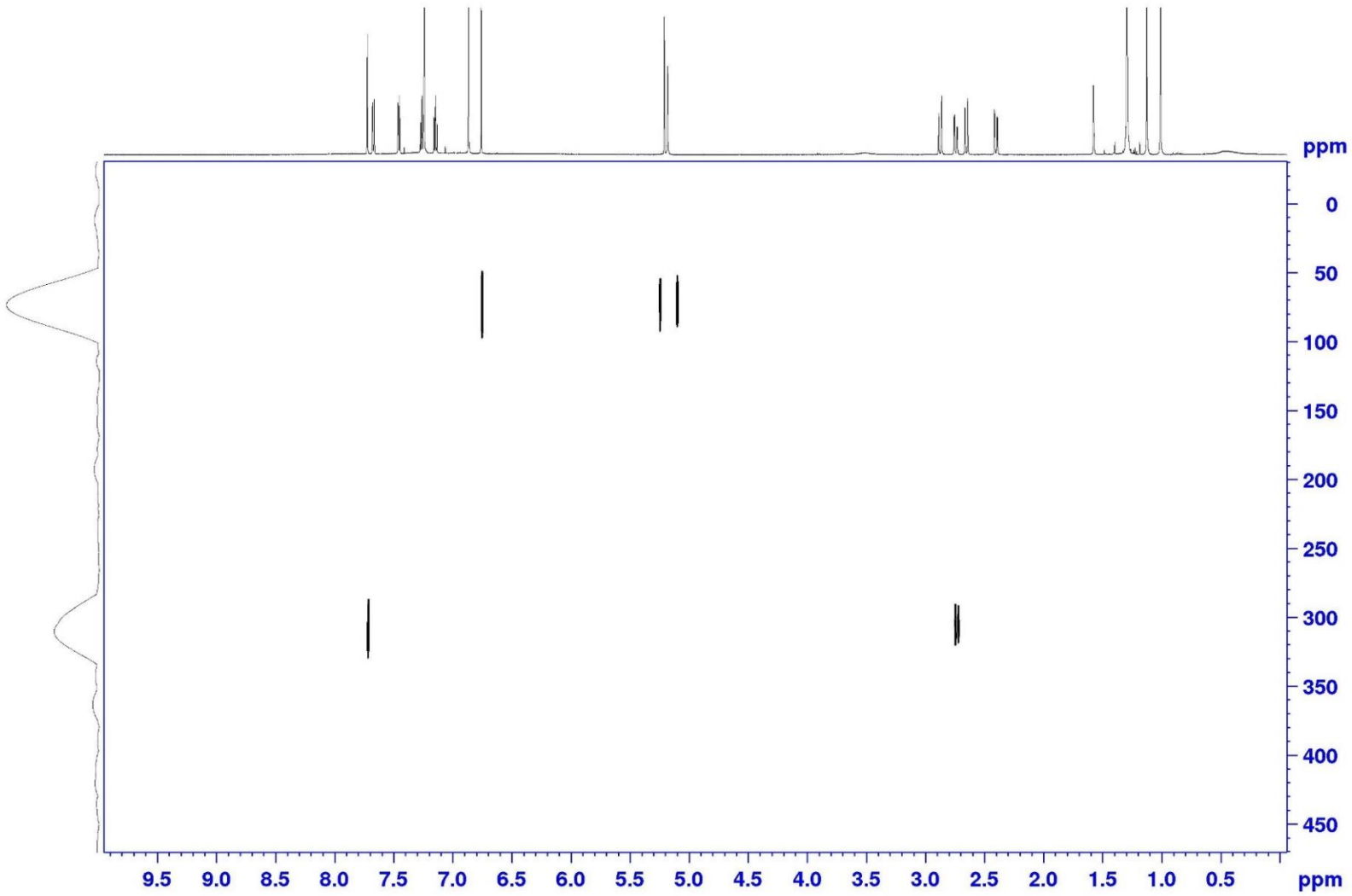


Figure S25 ^{1}H – ^{15}N HMBC spectrum of compound **3** recorded at 600, 60 MHz in $CDCl_3$.