

Supplementary Material for:

**Structure Elucidation of Prenyl- and Geranyl Substituted Coumarin Derivatives
in *Gerbera piloselloides* by NMR Spectroscopy, Electronic Circular Dichroism
Calculations, and Single Crystal X-ray Crystallography**

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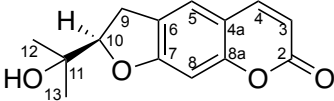
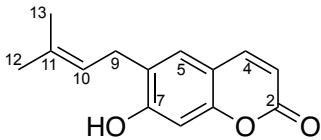
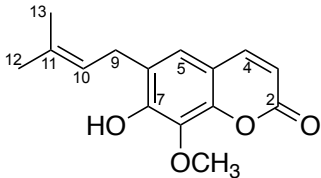
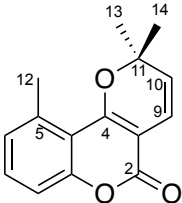
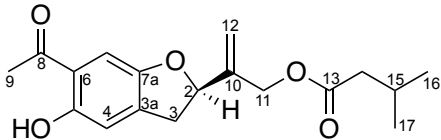
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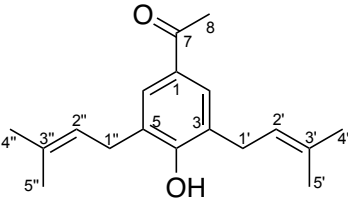
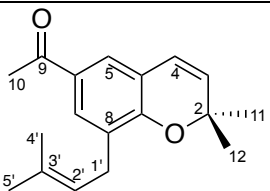
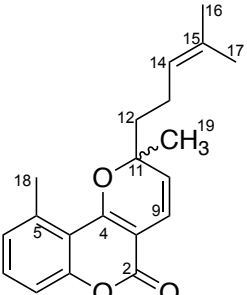
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Table S1. Retention time, name, structure, (+)HRESIMS, and ¹H NMR data of compounds **1**, **3**, **4** and **7-9**, **12** and **16**.

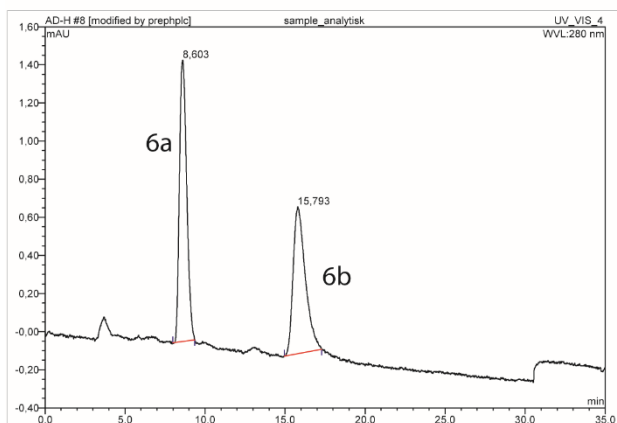
No.	RT (min)	Name	Structure	<i>m/z</i> (MF, ppm)	¹ H NMR (nH, m, <i>J</i> (in Hz)) ^{a,b}
1	18.6	Marmesin		255.1016 [M + H] ⁺ (C ₁₆ H ₁₅ O ₃ ⁺ , ΔM -0.1)	7.84 (1H, d, 9.4 Hz, H-4); 7.39 (1H, s, H-5); 6.71 (1H, s, H-8); 6.18 (1H, d, 9.4 Hz, H-3); 4.75 (1H, t, 9.3 Hz, H-10); 3.23-3.25 (2H, m, H-9); 1.28 (3H, s, H-12); 1.22 (3H, s, H-13)
3	28.4	7-Demethyl-suberosin		231.1021 [M + H] ⁺ (C ₁₄ H ₁₅ O ₃ ⁺ , ΔM -2.3)	7.82 (1H, d, 9.4 Hz, H-4); 7.28 (1H, s, H-5); 6.70 (1H, s, H-8); 6.16 (1H, d, 9.4 Hz, H-3); 5.33 (1H, t, 7.4 Hz, H-10); 3.32 (2H, overlapping, H-9); 1.75 (3H, s, H-12); 1.71 (3H, s, H-13)
4	29.6	Apigravin		261.1118 [M + H] ⁺ (C ₁₅ H ₁₇ O ₄ ⁺ , ΔM 1.3) 283.094 [M + Na] ⁺ (C ₁₅ H ₁₆ O ₄ Na ⁺ , ΔM 0.3)	7.84 (1H, d, 9.5 Hz, H-4); 6.90 (1H, s, H-5); 6.28 (1H, d, 9.5 Hz, H-3); 5.27 (1H, t, 7.2 Hz, H-10); 3.89 (3H, s, 8-OCH ₃); 3.37 (2H, m, H-9); 1.74 (3H, s, H-12); 1.74 (3H, s, H-13)
7	34.1	Bothrioclinin		243.1018 [M + H] ⁺ (C ₁₅ H ₁₅ O ₃ ⁺ , ΔM -0.9) 265.0826 [M + Na] ⁺ (C ₁₅ H ₁₄ O ₃ Na ⁺ , ΔM 3.4)	7.36 (1H, dd, 8.3, 7.6 Hz, H-7); 7.17 (1H, d, 8.3 Hz, H-6); 7.03 (1H, d, 7.6 Hz, H-8); 6.56 (1H, d, 10.0 Hz, H-9); 5.49 (1H, d, 10.0 Hz, H-10); 2.74 (3H, s, H-12); 1.60 (6H, s, H-13, H-14)
8	34.7	(+) 2-[(2 <i>R</i>)-6-acetyl-2,3-Dihydro-5-hydroxy-benzofuran-2-yl]prop-2-enyl 15-methylbutanoate		319.1535 [M + H] ⁺ (C ₁₈ H ₂₃ O ₅ ⁺ , ΔM 1.6) 341.1355 [M + Na] ⁺ (C ₁₈ H ₂₂ O ₅ Na ⁺ , ΔM 1.3)	7.16 (1H, s, H-7); 6.79 (1H, s, H-4); 5.33 (1H, br s, H-12); 5.29 (1H, t, 8.5 Hz, H-2), 5.24 (1H, br s, H-12); 4.72 (1H, d, 13.3 Hz, H-11), 4.63 (1H, d, 13.3 Hz, H-11), 3.45 (1H, dd, 16.9, 8.5 Hz, H-3); 3.17 (1H, dd, 16.9, 8.5, H-3); 2.56 (3H, s, H-9); 2.14 (2H, m, H-14), 2.00 (1H, m, H-15), 0.91 (3H, d, 5.2 Hz, H-17), 0.90 (3H, d, 5.2 Hz, H-16)

9	35.7	3,5-Bis-(isopent-2-en-1-yl)-4-hydroxyacetophenone		273.1849 [M + H] ⁺ (C ₁₈ H ₂₅ O ₂ ⁺ , ΔM 0) 295.1652 [M + Na] ⁺ (C ₁₈ H ₂₄ O ₂ Na ⁺ , ΔM 5.6)	7.60 (2H, s, H-2, H-6); 5.33 (2H, t, 7.3 Hz, H-2', H-2''); 3.35 (2H, br s, H-1', H-1''); 3.34 (2H, br s, H-1', H-1''); 2.49 (3H, s, H-8); 1.76 (6H, s, H-4', H-4''); 1.73 (6H, s, H-5', H-5'')
12	38.5	6-Acetyl-2,2-dimethyl-8-(3'-methyl-2'-butenyl)-2H-chromen		271.1701 [M + H] ⁺ (C ₁₈ H ₂₃ O ₂ ⁺ , ΔM -3.1) 293.1515 [M + Na] ⁺ (C ₁₈ H ₂₂ O ₂ Na ⁺ , ΔM -1.0)	7.64 (1H, d, 2.1 Hz, H-7); 7.53 (1H, d, 2.1 Hz, H-5); 6.42 (1H, d, 9.9 Hz, H-4); 5.75 (1H, d, 9.9 Hz, H-3); 5.25 (1H, tsep, 7.4, 1.4 Hz, H-2'); 3.28 (2H, d, 7.4 Hz, H-1'); 2.51 (3H, s, H-10); 1.74 (3H, s, H-4'); 1.73 (3H, s, H-5'); 1.44 (6H, s, H-11, H-12)
16	43.2	Mutisicoumarin B		311.1629 [M + H] ⁺ (C ₂₀ H ₂₃ O ₃ ⁺ , ΔM 4.1) 333.1469 [M + Na] ⁺ (C ₂₀ H ₂₂ O ₃ Na ⁺ , ΔM -2.4)	7.44 (1H, dd, 8.3, 7.5 Hz, H-7); 7.17 (1H, dd, 8.3, 1.3 Hz, H-8); 7.12 (1H, dd, 7.5, 1.3 Hz, H-6); 6.50 (1H, d, 10.1 Hz, H-9); 5.56 (1H, d, 10.1 Hz, H-10); 5.13 (1H, tq, 7.2, 1.4 Hz, H-14); 2.20 (2H, m, H-13); 1.88 (2H, m, H- 12); 2.75 (3H, s, H-18); 1.57 (3H, s, H-19); 1.54 (3H, d, 1.43 Hz, H-16); 1.52 (3H, br s, H-17)

^a NMR data obtained at 600 MHz with samples in methanol-*d*₄. ^b Multiplicities reported as apparent splittings: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, br = broad.

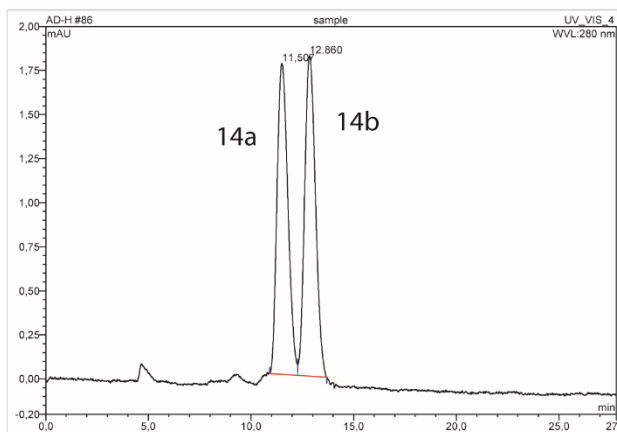
Figure S1. Chiral separation of 6, 11, 14 and 15.

8 sample_analytisk			
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Control Program:	35min-1,0mL_min_20A_80B	Bandwidth:	4
Quantif. Method:	Default1_do not change	Dilution Factor:	1,0000
Recording Time:	29-10-2018 12:34	Sample Weight:	1,0000
Run Time (min):	35,00	Sample Amount:	1,0000



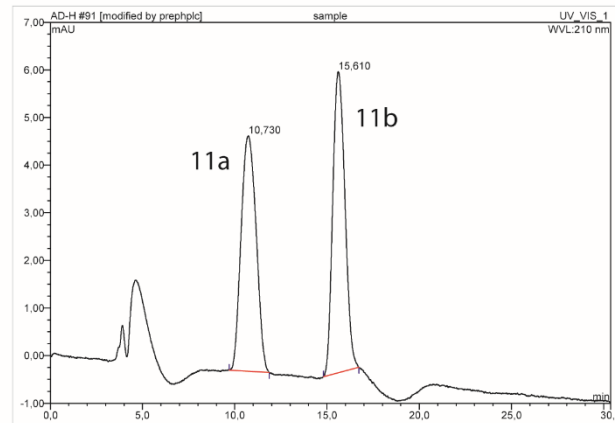
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,60	n.a.	1,476	0,776	53,35	n.a.	BMB*
2	15,79	n.a.	0,770	0,679	46,65	n.a.	BMB*
Total:			2,246	1,455	100,00	0,000	

86 sample			
Sample Name:	sample	Injection Volume:	20,0
Vial Number:	81	Channel:	UV_VIS_4
Sample Type:	unknown	Wavelength:	280,0
Control Program:	45min-0,8mL_min_2A_98B	Bandwidth:	4
Quantif. Method:	Default1_do not change	Dilution Factor:	1,0000
Recording Time:	20-12-2018 13:32	Sample Weight:	1,0000
Run Time (min):	27,78	Sample Amount:	1,0000



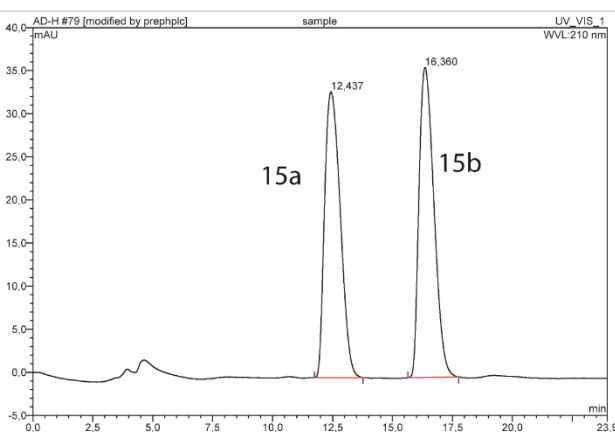
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11,51	n.a.	1,764	1,080	49,37	n.a.	BM
2	12,86	n.a.	1,817	1,108	50,63	n.a.	MB
Total:			3,581	2,188	100,00	0,000	

91 sample			
Sample Name:	sample	Injection Volume:	20,0
Vial Number:	86	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	210,0
Control Program:	45min-1,0mL_min_1A_99B	Bandwidth:	4
Quantif. Method:	Default1_do not change	Dilution Factor:	1,0000
Recording Time:	28-12-2018 20:36	Sample Weight:	1,0000
Run Time (min):	30,36	Sample Amount:	1,0000



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10,73	n.a.	4,947	4,676	49,16	n.a.	BMB
2	15,61	n.a.	6,322	4,835	50,84	n.a.	BMB
Total:			11,270	9,511	100,00	0,000	

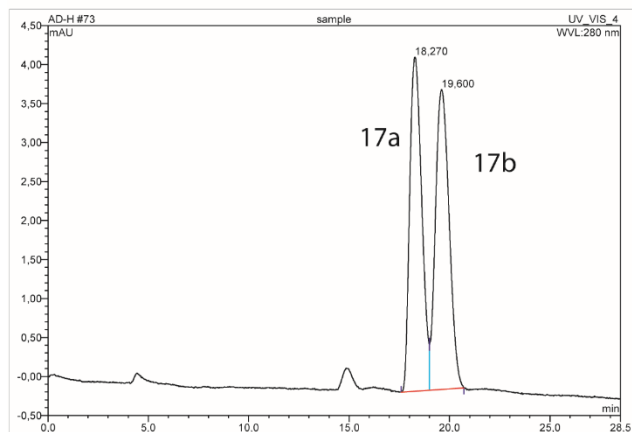
79 sample			
Sample Name:	sample	Injection Volume:	20,0
Vial Number:	74	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	210,0
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Quantif. Method:	Default1_do not change	Dilution Factor:	1,0000
Recording Time:	19-12-2018 17:07	Sample Weight:	1,0000
Run Time (min):	23,95	Sample Amount:	1,0000



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12,44	n.a.	33,178	25,175	49,22	n.a.	BMB
2	16,36	n.a.	35,995	25,971	50,78	n.a.	BMB
Total:			69,172	51,146	100,00	0,000	

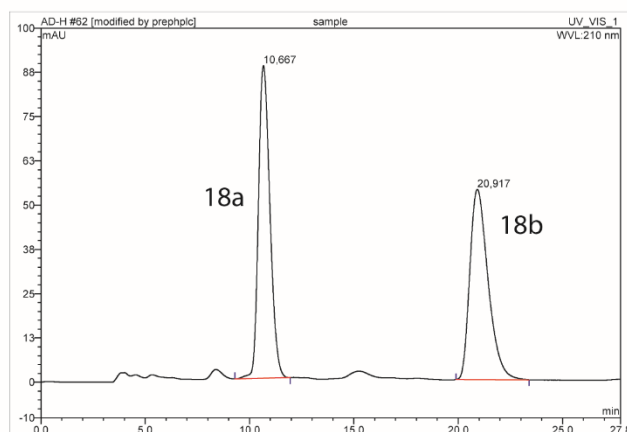
Figure S2. Chiral separation of 17, 18, 19 and 23.

73 sample			
Sample Name:	sample	Injection Volume:	20,0
Vial Number:	68	Channel:	UV_VIS_4
Sample Type:	unknown	Wavelength:	280.0
Control Program:	45min-1,0mL_min_1A_99B	Bandwidth:	4
Quantif. Method:	Default1_do not change	Dilution Factor:	1,0000
Recording Time:	19-12-2018 12:33	Sample Weight:	1,0000
Run Time (min):	28,50	Sample Amount:	1,0000



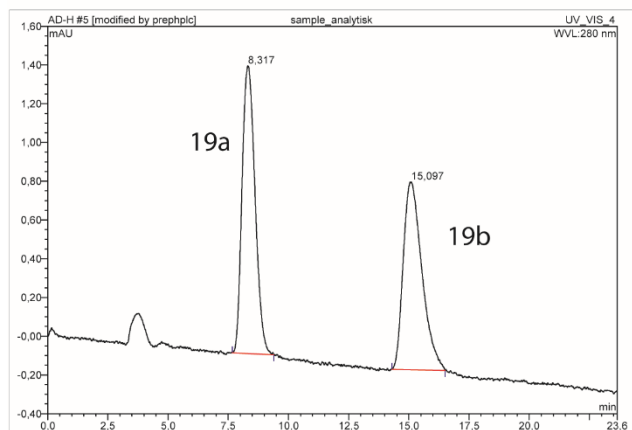
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18,27	n.a.	4,288	2,978	49,39	n.a.	BM
2	19,60	n.a.	3,849	3,051	50,61	n.a.	MB
Total:			8,137	6,030	100,00	0,000	

62 sample			
Sample Name:	sample	Injection Volume:	20,0
Vial Number:	57	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	210.0
Control Program:	35min-1,0mL_min_10A_90B	Bandwidth:	4
Quantif. Method:	Default1_do not change	Dilution Factor:	1,0000
Recording Time:	16-12-2018 17:52	Sample Weight:	1,0000
Run Time (min):	27,77	Sample Amount:	1,0000



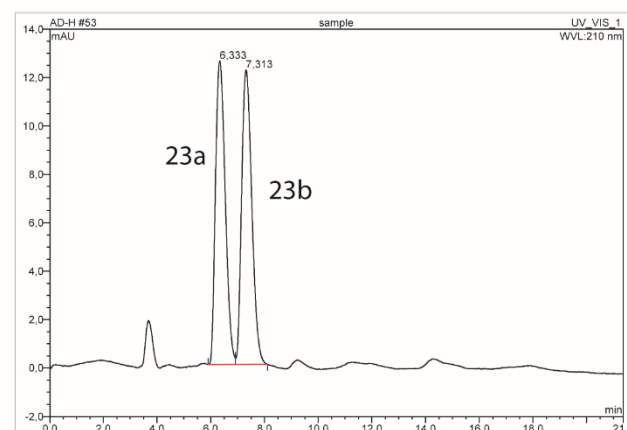
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10,67	n.a.	88,237	56,270	50,78	n.a.	BMB
2	20,92	n.a.	53,716	54,550	49,22	n.a.	BMB
Total:			141,953	110,820	100,00	0,000	

5 sample_analytisk			
Sample Name:	sample_analytisk	Injection Volume:	20,0
Vial Number:	3	Channel:	UV_VIS_4
Sample Type:	unknown	Wavelength:	280.0
Control Program:	25min-1,0mL_min_10A_90B	Bandwidth:	4
Quantif. Method:	Default1_do not change	Dilution Factor:	1,0000
Recording Time:	23-10-2018 12:09	Sample Weight:	1,0000
Run Time (min):	23,65	Sample Amount:	1,0000



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8,32	n.a.	1,486	0,929	51,56	n.a.	BMB*
2	15,10	n.a.	0,969	0,872	48,44	n.a.	BMB*
Total:			2,456	1,801	100,00	0,000	

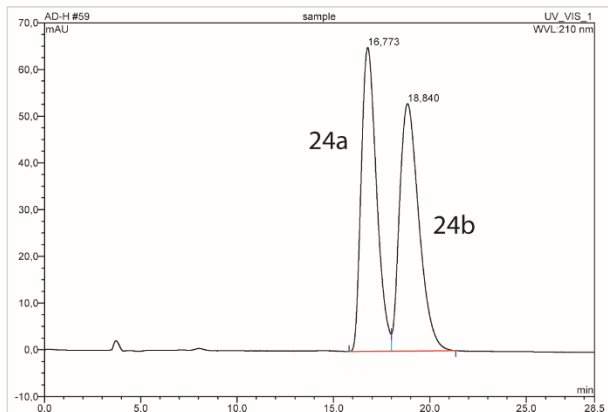
53 sample			
Sample Name:	sample	Injection Volume:	20,0
Vial Number:	48	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	210.0
Control Program:	35min-1,0mL_min_5A_95B	Bandwidth:	4
Quantif. Method:	Default1_do not change	Dilution Factor:	1,0000
Recording Time:	15-12-2018 20:12	Sample Weight:	1,0000
Run Time (min):	21,36	Sample Amount:	1,0000



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6,33	n.a.	12,536	5,297	49,80	n.a.	BM
2	7,31	n.a.	12,162	5,339	50,20	n.a.	MB
Total:			24,697	10,636	100,00	0,000	

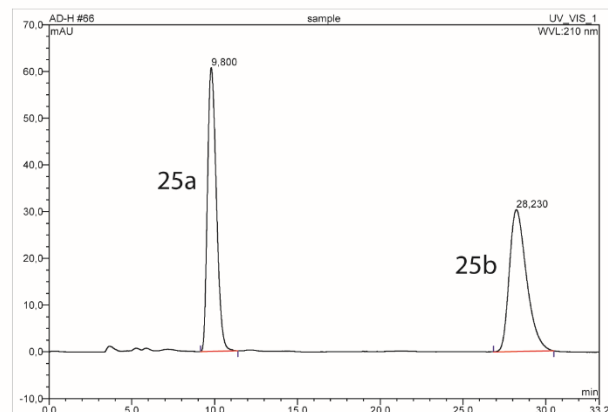
Figure S3. Chiral separation of 24 and 25.

59 sample			
Sample Name:	sample	Injection Volume:	20,0
Vial Number:	54	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	210.0
Control Program:	35min-1,0mL_min_5A_95B	Bandwidth:	4
Quantif. Method:	Default1_do not change	Dilution Factor:	1,0000
Recording Time:	16-12-2018 13:39	Sample Weight:	1,0000
Run Time (min):	28,53	Sample Amount:	1,0000



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16,77	n.a.	65,027	59,787	49,29	n.a.	BM
2	18,84	n.a.	52,915	61,513	50,71	n.a.	MB
Total:			117,942	121,300	100,00	0,000	

66 sample			
Sample Name:	sample	Injection Volume:	20,0
Vial Number:	61	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	210.0
Control Program:	35min-1,0mL_min_10A_90B	Bandwidth:	4
Quantif. Method:	Default1_do not change	Dilution Factor:	1,0000
Recording Time:	16-12-2018 20:54	Sample Weight:	1,0000
Run Time (min):	33,22	Sample Amount:	1,0000



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9,80	n.a.	60,731	37,733	50,77	n.a.	BMB
2	28,23	n.a.	30,335	36,586	49,23	n.a.	BMB
Total:			91,066	74,319	100,00	0,000	

Scheme 1. Possible biosynthesis of **11**, **14**, **15** and **17** via a [4+2] cycloaddition.

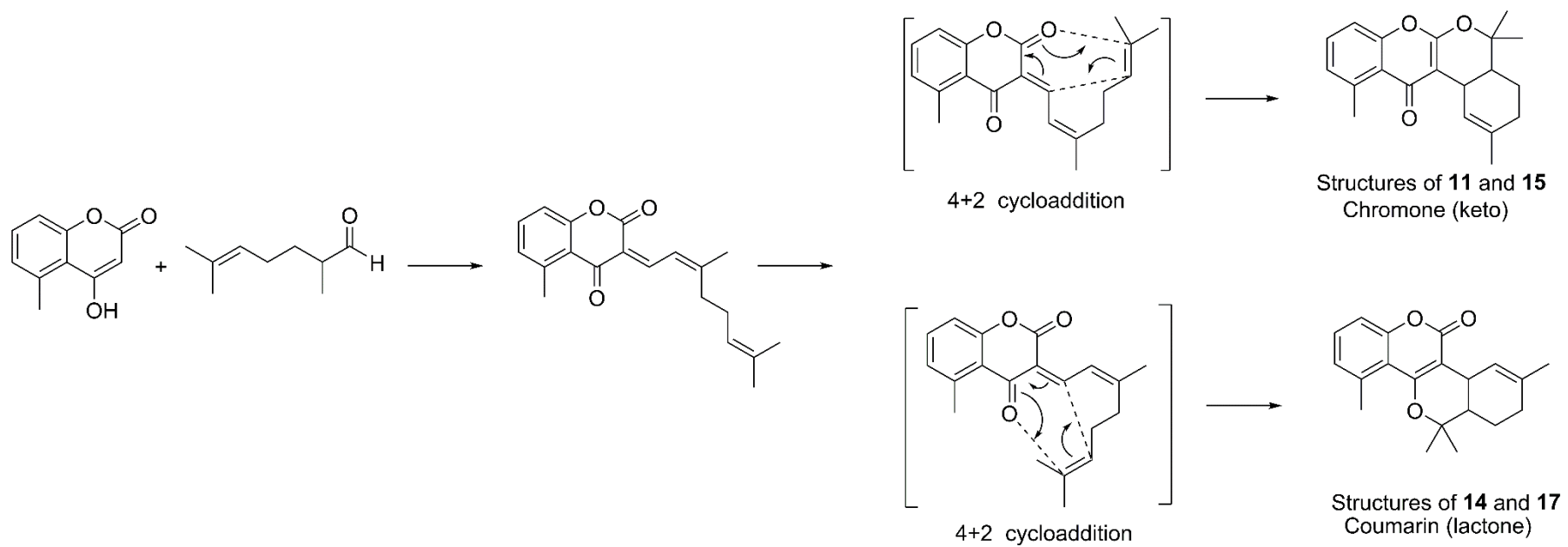


Figure S4. Optimized geometries of the predominant conformers of **6a** at the B3LYP/6-31G(d,p) level in CH₃CN (PCM).

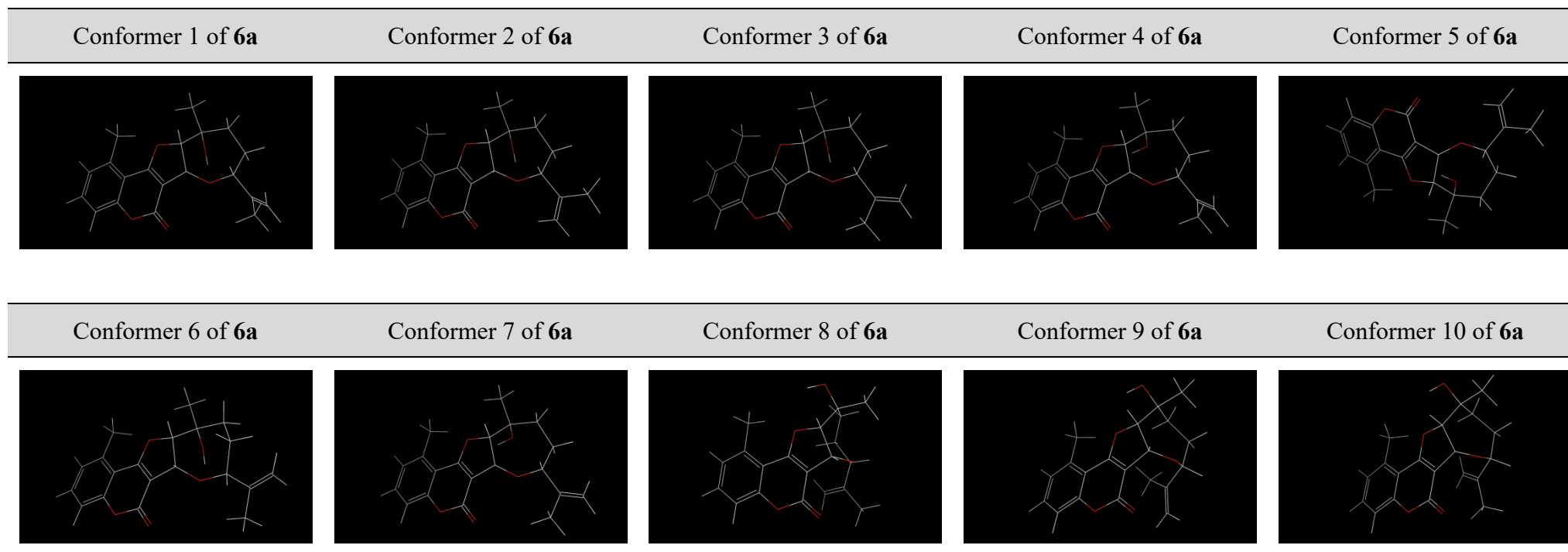


Table S2. Conformational analysis of **6a** at 298K

Conformation	Gibbs Free Energies (in Hartree)	Boltzmann Percentage Weights (%) Population Fractions
6a -Conf-1	-1151.194235	20.16%
6a -Conf-2	-1151.194780	35.93%
6a -Conf-3	-1151.194255	20.59%
6a -Conf-4	-1151.190931	0.61%
6a -Conf-5	-1151.191999	1.88%
6a -Conf-6	-1151.190891	0.58%
6a -Conf-7	-1151.177568	0.00%
6a -Conf-8	-1151.180052	0.00%
6a -Conf-9	-1151.188758	0.06%
6a -Conf-10	-1151.194236	20.18%

Table S3. Cartesian coordinates of optimized **6a** conformers. B3LYP/6-31G(d,p) in CH₃CN (PCM)

6a-Conf-1				6a-Conf-2			
C	4.964225	0.499828	0.568809	C	4.968104	0.475198	0.575713
C	5.269251	-0.86568	0.643671	C	5.278107	-0.89071	0.611968
C	4.297894	-1.82409	0.393086	C	4.312306	-1.8449	0.326131
C	3.009282	-1.40041	0.064366	C	3.023986	-1.41709	0.001317
C	2.683996	-0.02613	-0.01856	C	2.693784	-0.04194	-0.04209
C	3.686203	0.9478	0.241324	C	3.690318	0.927565	0.253163
O	2.096262	-2.39261	-0.1726	O	2.117555	-2.40561	-0.27287
C	0.757841	-2.15419	-0.50864	C	0.779135	-2.16248	-0.61044
C	0.406699	-0.77345	-0.59815	C	0.423394	-0.78038	-0.65511
C	1.310799	0.227874	-0.37358	C	1.321115	0.217453	-0.39593
C	-0.93728	-0.18177	-0.88961	C	-0.92369	-0.18801	-0.92847
C	-0.59486	1.341521	-0.95023	C	-0.58714	1.337962	-0.94989
O	0.812097	1.459236	-0.53156	O	0.816335	1.450865	-0.51821
C	3.407395	2.430052	0.178523	C	3.405703	2.409932	0.232174
O	0.056394	-3.13268	-0.6955	O	0.081662	-3.13364	-0.83687
O	-1.85978	-0.52574	0.153442	O	-1.84363	-0.56616	0.104837
C	-3.26675	-0.38366	-0.194	C	-3.24586	-0.4239	-0.24752
C	-3.75146	1.016743	0.174617	C	-3.74351	0.972958	0.146541
C	-2.95151	2.159574	-0.46979	C	-2.94928	2.137551	-0.46483
C	-1.45374	2.264295	-0.05502	C	-1.45417	2.239549	-0.0413
C	-3.99045	-1.54949	0.459707	C	-4.01102	-1.54685	0.427621
C	-3.59365	-2.90715	-0.06577	C	-3.77544	-1.76168	1.901523
C	-4.91279	-1.39329	1.414328	C	-4.86546	-2.2913	-0.28133
H	-0.62371	1.694742	-1.98474	H	-0.60974	1.713474	-1.97676
H	-1.35611	-0.52118	-1.84395	H	-1.34131	-0.50372	-1.89143
H	-3.34893	-0.51139	-1.28516	H	-3.33845	-0.54215	-1.33535
O	-1.25935	1.924577	1.318805	O	-1.26485	1.873817	1.32665
C	-0.97981	3.712862	-0.20462	C	-0.9851	3.692632	-0.15974
H	5.740581	1.231015	0.77051	H	5.740127	1.203107	0.804163
H	6.276386	-1.17801	0.901089	H	6.284755	-1.20677	0.866773
H	4.508512	-2.88605	0.445198	H	4.527125	-2.90709	0.347638
H	2.627746	2.721637	0.888235	H	3.0624	2.739578	-0.75253
H	4.31408	2.992305	0.41202	H	4.308405	2.968763	0.488241
H	3.058643	2.732073	-0.81308	H	2.620056	2.67752	0.944696
H	-4.80058	1.114085	-0.12494	H	-4.79133	1.059542	-0.16189
H	-3.72106	1.13717	1.262455	H	-3.72937	1.069503	1.237257
H	-3.01916	2.104052	-1.56442	H	-3.01208	2.10828	-1.56077
H	-3.43658	3.099036	-0.18426	H	-3.44149	3.066632	-0.15799
H	-2.50719	-3.03664	-0.03412	H	-4.03047	-0.87092	2.487715
H	-4.0663	-3.71086	0.504557	H	-2.71896	-1.97538	2.0949
H	-3.8923	-3.01542	-1.11714	H	-4.37285	-2.59625	2.276376
H	-5.41176	-2.25333	1.852307	H	-5.45273	-3.07879	0.182941
H	-5.21089	-0.42101	1.790791	H	-5.0134	-2.13539	-1.3466
H	-1.45671	0.974394	1.388798	H	-1.45186	0.920701	1.377011
H	-1.16169	4.080299	-1.21898	H	-1.16413	4.079813	-1.16721
H	-1.53219	4.344846	0.496223	H	-1.5428	4.308324	0.551318
H	0.086376	3.79841	0.015102	H	0.079808	3.777626	0.066245

	6a-Conf-3				6a-Conf-4		
C	4.996574	0.48926	0.553066	C	4.919849	0.528807	0.673249
C	5.311432	-0.87573	0.580842	C	5.258502	-0.83082	0.672358
C	4.346048	-1.83201	0.300621	C	4.316171	-1.79555	0.346912
C	3.053267	-1.4071	-0.00986	C	3.022454	-1.38434	0.022514
C	2.718054	-0.03297	-0.04461	C	2.661807	-0.01623	0.020211
C	3.714226	0.938692	0.244797	C	3.635954	0.964486	0.352124
O	2.147361	-2.39748	-0.27905	O	2.140309	-2.38182	-0.29454
C	0.804995	-2.15759	-0.60196	C	0.801156	-2.15763	-0.63701
C	0.443789	-0.77659	-0.63766	C	0.415121	-0.78198	-0.65205
C	1.341182	0.223199	-0.38413	C	1.287354	0.221309	-0.34019
C	-0.9073	-0.18662	-0.89728	C	-0.95371	-0.21171	-0.88902
C	-0.57506	1.339574	-0.91644	C	-0.62404	1.312022	-0.94402
O	0.831734	1.45545	-0.49754	O	0.748893	1.450917	-0.41442
C	3.424513	2.420151	0.232707	C	3.324622	2.441684	0.36686
O	0.10859	-3.1307	-0.82423	O	0.128246	-3.14004	-0.89254
O	-1.81633	-0.56419	0.145896	O	-1.81993	-0.62417	0.156632
C	-3.21358	-0.44707	-0.18769	C	-3.2291	-0.45865	-0.11221
C	-3.72187	0.950745	0.202419	C	-3.69256	0.939769	0.289778
C	-2.93591	2.121334	-0.40738	C	-3.00812	2.089754	-0.46478
C	-1.43846	2.232426	0.00413	C	-1.50938	2.31692	-0.17135
C	-3.99117	-1.56775	0.481766	C	-3.9314	-1.6211	0.57491
C	-5.46716	-1.61618	0.166058	C	-3.57719	-2.98042	0.023614
C	-3.40403	-2.462	1.281859	C	-4.7968	-1.46394	1.581318
H	-0.60872	1.719608	-1.9413	H	-0.56086	1.6149	-1.99388
H	-1.33427	-0.50192	-1.85607	H	-1.38157	-0.52325	-1.85123
H	-3.31821	-0.56725	-1.27842	H	-3.3826	-0.58095	-1.19885
O	-1.23505	1.864264	1.369121	O	-1.32012	2.163463	1.234983
C	-0.97963	3.688762	-0.11429	C	-1.1116	3.744584	-0.59043
H	5.768398	1.218799	0.776938	H	5.674834	1.265469	0.928953
H	6.321548	-1.18943	0.824586	H	6.269227	-1.13316	0.92753
H	4.564495	-2.89356	0.315831	H	4.553169	-2.85317	0.336743
H	2.644984	2.682148	0.953984	H	2.547614	2.68232	1.098588
H	4.327813	2.980928	0.482288	H	4.221072	3.010964	0.621746
H	3.070496	2.75267	-0.74722	H	2.96029	2.786258	-0.60486
H	-4.76835	1.047085	-0.10364	H	-4.77085	1.011467	0.107002
H	-3.70608	1.033089	1.295204	H	-3.53276	1.076192	1.362581
H	-3.00763	2.097813	-1.50295	H	-3.13629	1.968773	-1.54852
H	-3.43164	3.045716	-0.09198	H	-3.53027	3.016206	-0.20174
H	-5.64387	-1.58763	-0.91646	H	-2.49215	-3.12268	0.006531
H	-5.91894	-2.52917	0.561183	H	-4.03335	-3.78287	0.609074
H	-6.00573	-0.76309	0.594929	H	-3.92244	-3.07789	-1.01444
H	-3.97995	-3.26079	1.740414	H	-5.27803	-2.32235	2.042141
H	-2.34165	-2.4273	1.489969	H	-5.06265	-0.49132	1.980648
H	-1.42493	0.911715	1.420306	H	-0.37086	2.25732	1.401636
H	-1.16913	4.077454	-1.11926	H	-1.34922	3.933368	-1.64235
H	-1.5352	4.299204	0.602926	H	-1.65693	4.465452	0.024315
H	0.086578	3.779705	0.103272	H	-0.0392	3.910297	-0.44912

	6a-Conf-5				6a-Conf-6		
C	4.915189	0.516165	0.69252	C	4.955379	0.511552	0.649991
C	5.267037	-0.83911	0.641476	C	5.299628	-0.84605	0.610552
C	4.336715	-1.79923	0.270917	C	4.359609	-1.80563	0.263809
C	3.041562	-1.38832	-0.04838	C	3.062455	-1.39172	-0.04318
C	2.667759	-0.02435	-3.5E-05	C	2.696286	-0.02539	-0.00639
C	3.629569	0.951716	0.37809	C	3.667929	0.950047	0.347319
O	2.172657	-2.38114	-0.41281	O	2.183396	-2.38431	-0.3831
C	0.832919	-2.15672	-0.75703	C	0.840776	-2.15664	-0.71286
C	0.434386	-0.78484	-0.71838	C	0.450459	-0.78212	-0.6886
C	1.293646	0.214104	-0.3615	C	1.318723	0.216135	-0.35269
C	-0.94025	-0.22087	-0.93565	C	-0.92324	-0.21381	-0.90016
C	-0.62177	1.305834	-0.94646	C	-0.60283	1.312812	-0.91202
O	0.742059	1.440294	-0.39293	O	0.772975	1.444509	-0.38828
C	3.303333	2.424106	0.448711	C	3.350208	2.424898	0.404036
O	0.170453	-3.13139	-1.05961	O	0.168119	-3.13188	-0.99062
O	-1.79989	-0.67405	0.09839	O	-1.77983	-0.65972	0.138729
C	-3.20731	-0.51884	-0.17067	C	-3.17968	-0.51495	-0.11966
C	-3.69345	0.877683	0.240441	C	-3.66079	0.877411	0.319452
C	-3.01723	2.04947	-0.48662	C	-2.98751	2.058928	-0.39411
C	-1.52578	2.286685	-0.16581	C	-1.48909	2.286879	-0.10218
C	-3.93515	-1.63108	0.564221	C	-3.9367	-1.64066	0.568574
C	-3.622	-1.81188	2.028176	C	-5.42637	-1.67988	0.322532
C	-4.82101	-2.39604	-0.08154	C	-3.31901	-2.55219	1.325284
H	-0.54474	1.63291	-1.98826	H	-0.54966	1.647836	-1.95258
H	-1.36691	-0.50735	-1.9061	H	-1.35505	-0.50107	-1.86797
H	-3.37494	-0.64855	-1.25073	H	-3.35174	-0.61569	-1.20639
O	-1.35543	2.104456	1.239675	O	-1.29043	2.089978	1.297377
C	-1.13556	3.726403	-0.54842	C	-1.10341	3.729651	-0.47836
H	5.66088	1.249413	0.98299	H	5.708557	1.244289	0.92182
H	6.278617	-1.14166	0.893017	H	6.31288	-1.15092	0.852372
H	4.584294	-2.85332	0.221422	H	4.601083	-2.86154	0.223871
H	2.521413	2.628405	1.186327	H	2.577227	2.642083	1.147298
H	4.193029	2.991897	0.729283	H	4.245878	2.991167	0.668184
H	2.939103	2.802634	-0.51028	H	2.977728	2.793945	-0.55553
H	-4.77105	0.926619	0.04351	H	-4.73803	0.952212	0.137179
H	-3.55489	1.003681	1.317321	H	-3.50737	0.967906	1.398849
H	-3.12818	1.944114	-1.5739	H	-3.12246	1.976095	-1.48064
H	-3.55554	2.964494	-0.2159	H	-3.51501	2.971177	-0.09416
H	-3.86926	-0.91476	2.607967	H	-5.65473	-1.62139	-0.74912
H	-4.17918	-2.65243	2.449283	H	-5.86086	-2.60317	0.713487
H	-2.55191	-1.99347	2.171637	H	-5.94346	-0.83912	0.799597
H	-5.37662	-3.1775	0.42992	H	-3.8771	-3.35652	1.79643
H	-5.02686	-2.26411	-1.14048	H	-2.24772	-2.52523	1.483227
H	-0.40845	2.195146	1.420636	H	-0.34125	2.188635	1.461947
H	-1.36057	3.935742	-1.59921	H	-1.34829	3.949623	-1.5225
H	-1.69594	4.428848	0.074049	H	-1.65007	4.427135	0.161654
H	-0.06677	3.898486	-0.38872	H	-0.03137	3.898208	-0.33793

	6a-Conf-7				6a-Conf-8		
C	-3.94187	-1.85823	0.672708	C	-4.16098	-1.51527	0.706216
C	-4.77487	-0.76272	0.408485	C	-4.8278	-0.30876	0.455063
C	-4.26153	0.401355	-0.14498	C	-4.15453	0.771562	-0.09677
C	-2.89669	0.460457	-0.43087	C	-2.79812	0.632875	-0.39448
C	-2.04058	-0.6355	-0.17087	C	-2.10776	-0.5768	-0.14581
C	-2.57744	-1.8249	0.393132	C	-2.80801	-1.67897	0.416561
O	-2.45106	1.630137	-0.98517	O	-2.19215	1.72841	-0.94825
C	-1.11193	1.873737	-1.31401	C	-0.83863	1.773099	-1.29976
C	-0.22257	0.793045	-1.03313	C	-0.10809	0.577464	-1.01739
C	-0.66837	-0.3994	-0.53556	C	-0.71556	-0.5384	-0.51266
C	1.271349	0.729762	-1.24876	C	1.356207	0.303598	-1.24989
C	1.474684	-0.80869	-1.15212	C	1.387464	-1.23807	-1.0281
O	0.292626	-1.33286	-0.43729	O	0.107886	-1.59422	-0.38003
C	-1.72232	-3.0314	0.697214	C	-2.13719	-2.99982	0.708475
O	-0.85344	2.960921	-1.80029	O	-0.43664	2.802927	-1.8106
O	2.07819	1.600423	-0.45054	O	2.312486	1.059129	-0.50836
C	2.241751	1.477871	0.987283	C	2.217609	1.198073	0.931492
C	3.20414	0.341813	1.367313	C	1.869863	-0.10093	1.656959
C	2.863356	-1.10294	0.980872	C	2.697979	-1.3209	1.227612
C	2.733495	-1.41668	-0.52091	C	2.550955	-1.85249	-0.2351
C	0.948988	1.629024	1.78109	C	1.384811	2.419205	1.308936
C	0.257425	2.959511	1.588406	C	1.769606	3.691882	0.595033
C	0.517155	0.744334	2.686579	C	0.426839	2.396561	2.242364
H	1.384307	-1.21482	-2.16511	H	1.348062	-1.73749	-2.00062
H	1.538119	1.047049	-2.25997	H	1.643138	0.517641	-2.2827
H	2.799187	2.400814	1.199481	H	3.257033	1.446595	1.191002
O	2.633679	-2.84361	-0.67505	O	2.342564	-3.27609	-0.21314
C	3.962188	-1.00664	-1.33431	C	3.844838	-1.65768	-1.0323
H	-4.36685	-2.75822	1.105736	H	-4.70934	-2.34702	1.136976
H	-5.83376	-0.82511	0.638509	H	-5.88281	-0.21808	0.693305
H	-4.88518	1.261205	-0.3607	H	-4.64785	1.714294	-0.30347
H	-0.92289	-2.78955	1.403693	H	-1.32024	-2.88588	1.427246
H	-2.33426	-3.82551	1.130299	H	-2.86151	-3.70436	1.122777
H	-1.24033	-3.41959	-0.20465	H	-1.7045	-3.43964	-0.19449
H	4.175476	0.598296	0.931449	H	2.056709	0.068671	2.723005
H	3.345315	0.38574	2.453145	H	0.804292	-0.32159	1.57447
H	3.66189	-1.75099	1.35828	H	3.758811	-1.11829	1.414766
H	1.941079	-1.43158	1.469768	H	2.433742	-2.15033	1.890936
H	-0.74021	2.962844	2.034981	H	2.842555	3.894084	0.706214
H	0.843126	3.756224	2.066633	H	1.563973	3.60843	-0.47569
H	0.172974	3.226497	0.532806	H	1.216083	4.54831	0.988875
H	-0.37669	0.940865	3.272712	H	-0.10537	3.303607	2.516005
H	1.029783	-0.18724	2.89481	H	0.136751	1.493558	2.768281
H	1.861064	-3.13408	-0.16813	H	1.498307	-3.43565	0.233847
H	3.864062	-1.36199	-2.3642	H	4.115758	-0.60148	-1.07305
H	4.857331	-1.46111	-0.90048	H	4.64958	-2.21259	-0.54201
H	4.088217	0.07724	-1.34778	H	3.73668	-2.04146	-2.05132

	6a-Conf-9				6a-Conf-10		
C	4.924798	0.757228	0.610139	C	4.964185	0.499908	0.568777
C	5.324729	-0.58398	0.674402	C	5.269331	-0.86558	0.643413
C	4.42874	-1.60493	0.392211	C	4.297984	-1.82403	0.392888
C	3.119583	-1.26955	0.043091	C	3.009286	-1.4004	0.064397
C	2.697996	0.079421	-0.02642	C	2.683932	-0.02615	-0.01842
C	3.624104	1.117806	0.264197	C	3.686092	0.947825	0.241502
O	2.286297	-2.32129	-0.22813	O	2.096246	-2.39262	-0.17243
C	0.942904	-2.17301	-0.59775	C	0.757886	-2.15425	-0.50852
C	0.492233	-0.81986	-0.65554	C	0.40668	-0.77354	-0.59806
C	1.315266	0.240709	-0.40034	C	1.310744	0.227825	-0.37354
C	-0.87704	-0.3264	-1.0009	C	-0.93732	-0.1819	-0.8896
C	-0.67208	1.229265	-0.94445	C	-0.59487	1.341402	-0.95038
O	0.732531	1.435634	-0.55306	O	0.812095	1.459146	-0.53183
C	3.242829	2.577537	0.214301	C	3.407139	2.430055	0.178877
O	0.318679	-3.19102	-0.83381	O	0.056427	-3.13275	-0.69539
O	-1.83475	-0.7996	-0.04393	O	-1.85979	-0.52571	0.153474
C	-3.21223	-0.7455	-0.50224	C	-3.2668	-0.38358	-0.19393
C	-3.53639	0.625949	-1.11245	C	-3.75138	1.016796	0.174876
C	-3.07436	1.86879	-0.32911	C	-2.95146	2.159577	-0.46967
C	-1.57179	1.968334	0.075303	C	-1.45366	2.264277	-0.05515
C	-4.05585	-1.2202	0.669527	C	-3.99051	-1.54949	0.459673
C	-3.62408	-2.53709	1.26914	C	-3.59366	-2.90707	-0.06595
C	-5.13259	-0.5638	1.112839	C	-4.91277	-1.39332	1.41436
H	-0.7687	1.674742	-1.93813	H	-0.62378	1.694536	-1.98492
H	-1.1949	-0.64919	-1.99909	H	-1.3561	-0.52142	-1.84391
H	-3.31368	-1.49963	-1.30076	H	-3.34899	-0.51116	-1.28509
O	-1.34429	1.427358	1.380155	O	-1.25915	1.924687	1.318704
C	-1.17414	3.4444	0.174313	C	-0.97975	3.712832	-0.20495
H	5.643471	1.538912	0.834931	H	5.740493	1.23113	0.770547
H	6.346594	-0.82775	0.947356	H	6.276528	-1.17786	0.900649
H	4.713508	-2.64993	0.433812	H	4.508661	-2.88598	0.444896
H	2.445667	2.807633	0.927345	H	4.313309	2.992358	0.414232
H	4.108056	3.199437	0.453894	H	3.060274	2.732393	-0.81333
H	2.873083	2.863967	-0.77411	H	2.626061	2.721233	0.887133
H	-3.09656	0.657783	-2.11564	H	-4.80056	1.114274	-0.12447
H	-4.61603	0.686571	-1.28163	H	-3.72077	1.137159	1.262714
H	-3.32812	2.739517	-0.94332	H	-3.01929	2.104012	-1.56429
H	-3.63474	1.972725	0.604894	H	-3.43645	3.099067	-0.1841
H	-2.61546	-2.4685	1.687922	H	-3.89211	-3.01518	-1.11738
H	-3.59026	-3.32138	0.502313	H	-2.5072	-3.03657	-0.03406
H	-4.30986	-2.85588	2.057733	H	-4.06641	-3.71086	0.504193
H	-5.7313	-0.96531	1.925431	H	-5.41174	-2.25337	1.852336
H	-5.46666	0.377664	0.691375	H	-5.21083	-0.42104	1.79087
H	-1.58376	0.486101	1.315359	H	-1.4569	0.974626	1.388892
H	-1.23476	3.937055	-0.80033	H	-1.53196	4.34486	0.495984
H	-1.85311	3.955729	0.863003	H	0.086495	3.798385	0.01447
H	-0.1561	3.540344	0.556338	H	-1.16188	4.080197	-1.21929

Figure S5. Optimized geometries of the predominant conformers of **11b** at the B3LYP/6-31G(d,p) level in CH₃CN (PCM).

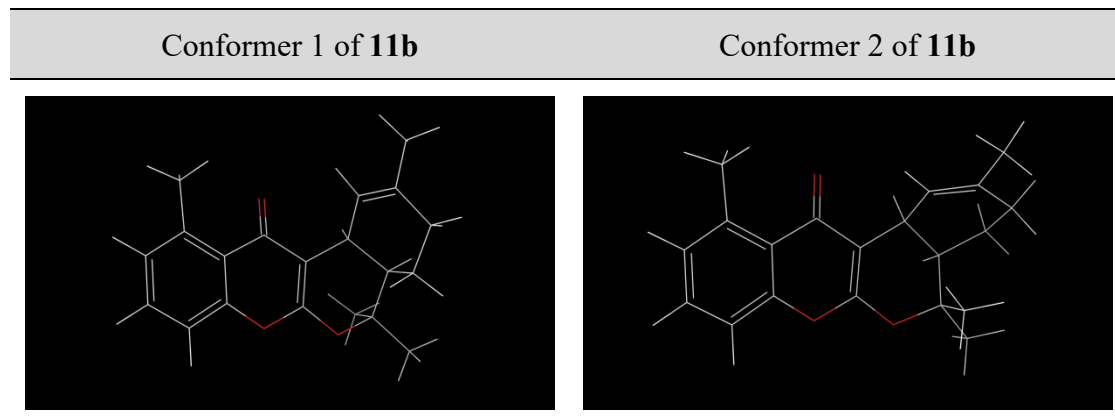


Table S4. Conformational analysis of **11b** at 298K

Conformation	Gibbs Free Energies (in Hartree)	Boltzmann Percentage Weights (%) Population Fractions
11b -Conf-1	-1000.768682	88.93%
11b -Conf-2	-1000.766881	11.07%

Table S5. Cartesian coordinates of optimized **11b** conformers. B3LYP/6-31G(d,p) in CH₃CN (PCM)

	11b-Conf-1				11b-Conf-2		
C	4.755122	0.300156	-0.39365	C	-4.97094	0.345207	0.236045
C	4.685218	-0.95137	-1.01741	C	-4.96177	-1.02605	0.518499
C	3.479657	-1.63254	-1.08209	C	-3.77087	-1.73522	0.497549
C	2.355878	-1.03386	-0.51234	C	-2.59886	-1.04399	0.189707
C	2.388114	0.219629	0.1212	C	-2.57096	0.330548	-0.10362
C	3.635598	0.903932	0.181058	C	-3.80355	1.043004	-0.077
O	1.197403	-1.77258	-0.59258	O	-1.45452	-1.81068	0.196454
C	0.042477	-1.24886	-0.13772	C	-0.26675	-1.23622	-0.07559
C	-0.0828	-0.00437	0.403487	C	-0.1046	0.082484	-0.37183
C	1.122592	0.762154	0.68417	C	-1.26431	0.953579	-0.4408
O	1.093042	1.806071	1.356498	O	-1.15516	2.144807	-0.77876
C	3.797919	2.257026	0.831878	C	-3.89968	2.52139	-0.36988
O	-0.92544	-2.14663	-0.30417	O	0.679263	-2.16694	-0.02824
C	-2.16791	-1.9232	0.471001	C	2.092618	-1.70977	0.034108
C	-2.5816	-0.44226	0.306756	C	2.250998	-0.56214	-1.00056
C	-1.46217	0.502221	0.823919	C	1.262103	0.604399	-0.76784
C	-2.97781	-0.06986	-1.13415	C	3.677177	-0.00276	-1.18438
C	-3.50805	1.364856	-1.21008	C	4.165371	0.928489	-0.06205
C	-2.63287	2.34882	-0.47241	C	3.087046	1.829293	0.494843
C	-1.70995	1.942733	0.408611	C	1.795424	1.663426	0.181577
C	-1.88373	-2.29562	1.931332	C	2.873146	-2.95582	-0.38155
C	-3.15845	-2.91572	-0.13459	C	2.356417	-1.37077	1.503777
C	-2.86339	3.80771	-0.77195	C	3.550191	2.913904	1.433194
H	-1.48496	0.497074	1.923754	H	1.116371	1.099262	-1.7408
H	-3.46146	-0.29354	0.945695	H	1.971379	-1.029	-1.95363
H	5.707463	0.820318	-0.35407	H	-5.91255	0.885443	0.260117
H	5.577607	-1.39064	-1.45197	H	-5.88973	-1.53636	0.756502
H	3.385608	-2.60413	-1.55387	H	-3.72313	-2.79672	0.712796
H	4.825653	2.608158	0.706273	H	-4.93389	2.856394	-0.25414
H	3.115865	2.994826	0.402527	H	-3.26079	3.105649	0.296908
H	3.565485	2.218331	1.899122	H	-3.56455	2.751102	-1.38436
H	-2.10597	-0.17219	-1.79146	H	4.395489	-0.81333	-1.34096
H	-3.74199	-0.75311	-1.51288	H	3.660852	0.5685	-2.12006
H	-4.52945	1.411937	-0.80136	H	4.987406	1.547163	-0.44787
H	-3.60222	1.670273	-2.26076	H	4.613135	0.356738	0.762807
H	-1.08318	2.675011	0.906169	H	1.052229	2.344592	0.588003
H	-2.79492	-2.17645	2.524729	H	2.66177	-3.22324	-1.42061
H	-1.56615	-3.33971	1.995466	H	3.94724	-2.78785	-0.27583
H	-1.10472	-1.6728	2.375167	H	2.598013	-3.79881	0.258076
H	-3.24217	-2.79477	-1.2156	H	3.413458	-1.15157	1.664772
H	-2.83321	-3.93945	0.069178	H	1.774392	-0.5095	1.834674
H	-4.14708	-2.77458	0.311143	H	2.093481	-2.23396	2.12174
H	-2.68459	4.026445	-1.8329	H	4.087479	2.489765	2.291907
H	-3.90501	4.090864	-0.56979	H	4.252734	3.594621	0.9347
H	-2.21379	4.453631	-0.17469	H	2.713316	3.505787	1.814352

Figure S6. Optimized geometries of the predominant conformers of **14b** at the B3LYP/6-31G(d,p) level in CH₃CN (PCM).

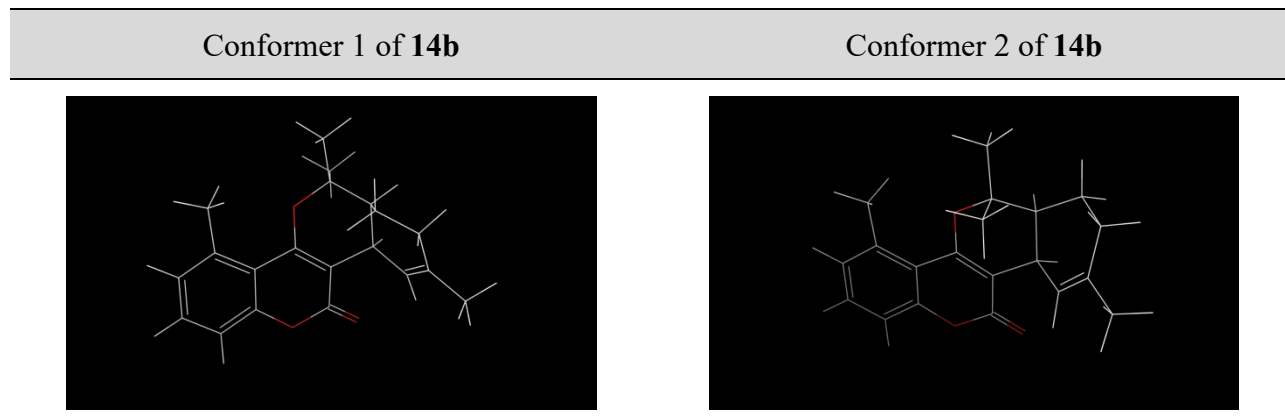


Table S6. Conformational analysis of **14b** at 298K

Conformation	Gibbs Free Energies (in Hartree)	Boltzmann Percentage Weights (%) Population Fractions
14b -Conf-1	-1001.338791	8.57%
14b -Conf-2	-1001.340836	91.43%

Table S7. Cartesian coordinates of the optimized **14b** conformers. B3LYP/6-31G(d,p) in CH₃CN (PCM)

	14b-Conf-1				14b-Conf-2		
C	4.50405	0.826642	0.42911	C	3.67115	-1.91252	-0.21664
C	4.963438	-0.49471	0.411895	C	2.40256	-1.41496	0.07289
C	4.075702	-1.53487	0.189376	C	2.04851	-0.07039	-0.13834
C	2.728936	-1.23117	-0.01401	C	3.03294	0.81	-0.67381
C	2.235434	0.089688	0.003998	C	4.29477	0.29188	-0.95897
C	3.160936	1.151735	0.231822	C	4.61829	-1.04847	-0.73539
O	1.915159	-2.30823	-0.23315	O	1.52293	-2.31643	0.59869
C	0.55832	-2.18306	-0.48325	C	0.20632	-2.00116	0.90147
C	-0.00782	-0.8591	-0.43403	C	-0.24003	-0.66353	0.59931
C	0.796064	0.231404	-0.20843	C	0.67498	0.28324	0.2097
C	-1.47979	-0.72216	-0.77252	C	-1.70954	-0.32015	0.83457
C	-1.84015	0.753887	-1.04373	C	-2.01802	1.11771	0.3513
C	-1.12992	1.723312	-0.06524	C	-0.87042	2.06687	0.74945
O	0.325293	1.48618	-0.18485	O	0.37168	1.58386	0.11478
O	-0.04599	-3.21693	-0.72818	C	-2.65744	-1.33328	0.2138
C	2.779369	2.614759	0.2705	C	-3.50153	-1.08569	-0.79135
C	-2.39771	-1.38808	0.239264	C	-3.55013	0.25912	-1.47158
C	-3.61165	-0.9377	0.581564	C	-2.32992	1.12617	-1.15526
C	-4.18546	0.333328	-0.00065	C	2.79235	2.27296	-0.96845
C	-3.37027	0.900326	-1.17473	O	-0.44553	-2.88676	1.41878
C	-1.45679	1.579191	1.425013	C	-1.03283	3.48784	0.21539
C	-1.28289	3.178475	-0.50897	C	-0.64207	2.10785	2.26553
C	-4.47908	-1.65828	1.581335	C	-4.46522	-2.12639	-1.29828
H	5.212278	1.63098	0.601782	H	-1.88458	-0.36622	1.91736
H	6.016345	-0.70488	0.57094	H	-2.91232	1.46188	0.88266
H	4.390413	-2.57198	0.16522	H	3.88073	-2.95744	-0.02751
H	-1.61386	-1.26406	-1.72197	H	5.04665	0.95526	-1.37017
H	-1.41556	1.01086	-2.02263	H	5.61184	-1.4119	-0.96997
H	2.313257	2.938465	-0.66316	H	-2.6406	-2.31719	0.66644
H	2.061609	2.826329	1.066979	H	-4.47138	0.77889	-1.17227
H	3.672065	3.22152	0.44013	H	-3.63403	0.11774	-2.55553
H	-2.03004	-2.31657	0.668726	H	-1.46435	0.75247	-1.7122
H	-5.21224	0.141427	-0.34148	H	-2.51552	2.1435	-1.50303
H	-4.29466	1.075004	0.802981	H	1.95609	2.41628	-1.6543
H	-3.65159	0.353224	-2.08241	H	2.55378	2.83343	-0.06321
H	-3.64592	1.943581	-1.35649	H	3.6873	2.70543	-1.41814
H	-1.30193	0.559677	1.78065	H	-1.97869	3.9094	0.56331
H	-0.81281	2.253368	1.996959	H	-0.22059	4.11884	0.58153
H	-2.49367	1.85652	1.623313	H	-1.01888	3.51338	-0.87358
H	-2.31298	3.515371	-0.37138	H	-1.541	2.48238	2.76109
H	-0.63395	3.822845	0.090011	H	-0.4094	1.12649	2.6792
H	-1.01509	3.297422	-1.56272	H	0.18465	2.78189	2.49823
H	-5.43265	-1.96258	1.130335	H	-4.27997	-2.34996	-2.35534
H	-3.9875	-2.55158	1.976648	H	-4.39201	-3.05696	-0.73185
H	-4.73154	-1.00478	2.426971	H	-5.49861	-1.76563	-1.23283

Table S8. Cartesian coordinates of the optimized **15b**. B3LYP/6-31G(d,p) in CH₃CN (PCM)

C	4.899619	0.469312	-0.23382
C	4.933224	-0.84784	-0.70724
C	3.766098	-1.59196	-0.78392
C	2.575285	-0.98881	-0.37905
C	2.503588	0.328764	0.102361
C	3.712426	1.077588	0.176934
O	1.458164	-1.78859	-0.46457
C	0.247376	-1.27722	-0.16962
C	0.030069	0.014317	0.215714
C	1.175108	0.86412	0.503917
O	1.046923	1.971908	1.052349
C	3.763783	2.502866	0.673345
O	-0.65805	-2.24041	-0.31504
C	-2.0205	-2.00205	0.227646
C	-2.38901	-0.5506	-0.1285
C	-1.39795	0.462757	0.481133
C	-3.81929	-0.11136	0.212959
C	-4.12458	1.234518	-0.46782
C	-2.95955	2.202682	-0.45837
C	-1.73539	1.850192	-0.04089
C	-2.87311	-3.02625	-0.51705
C	-1.97537	-2.30417	1.726759
C	-3.25853	3.591075	-0.96388
H	-1.54103	0.479492	1.57442
H	-2.27769	-0.48688	-1.22073
H	5.823038	1.038362	-0.18331
H	5.875883	-1.28865	-1.01587
H	3.751427	-2.61478	-1.14306
H	3.449401	2.573813	1.717601
H	4.781919	2.890911	0.583326
H	3.086306	3.149892	0.110942
H	-4.55422	-0.85583	-0.10741
H	-3.92132	-0.01011	1.300419
H	-4.99517	1.704925	0.008845
H	-4.42622	1.063104	-1.5125
H	-0.93409	2.580917	-0.03278
H	-2.44604	-4.02515	-0.39352
H	-2.91876	-2.79554	-1.58509
H	-3.88997	-3.04143	-0.11864
H	-1.26273	-1.66264	2.25039
H	-2.96316	-2.15052	2.170159
H	-1.68535	-3.34543	1.890913
H	-2.36738	4.224795	-0.96031
H	-3.65282	3.56126	-1.9884
H	-4.02814	4.078597	-0.35107

Table S9. Cartesian coordinates of the optimized **17b**. B3LYP/6-31G(d,p) in CH₃CN (PCM)

C	-4.5013	-2.183	-3.6711
C	-4.4555	-3.5145	-3.265
C	-5.1064	-3.8933	-2.1022
C	-5.7955	-2.9315	-1.3611
C	-5.865	-1.5852	-1.7315
C	-5.1952	-1.2071	-2.921
O	-6.4445	-3.4147	-0.2131
C	-7.2256	-2.5962	0.5798
C	-7.1684	-1.1407	0.3162
C	-6.6122	-0.6885	-0.8245
C	-7.8752	-0.211	1.2796
C	-7.5271	1.2605	0.9423
C	-7.6317	1.5019	-0.5728
O	-6.7099	0.6196	-1.2461
C	-7.5932	-0.4312	2.7562
C	-7.6399	0.554	3.6749
C	-7.9597	1.9851	3.3129
C	-8.3528	2.1878	1.8428
O	-7.9409	-3.0783	1.4515
C	-7.1543	2.917	-0.9399
C	-9.0365	1.3021	-1.1606
H	-6.4656	1.4181	1.2016
H	-8.9531	-0.3813	1.1461
C	-5.1691	0.2038	-3.4497
C	-7.3794	0.2936	5.1315
H	-3.9837	-1.9029	-4.5874
H	-3.9154	-4.2492	-3.856
H	-5.0858	-4.9283	-1.7728
H	-7.4021	-1.4458	3.0988
H	-8.7692	2.3614	3.9494
H	-7.0731	2.5958	3.5267
H	-9.423	1.9804	1.719
H	-8.2025	3.2414	1.5872
H	-7.0666	3.0265	-2.0277
H	-7.8345	3.6932	-0.5773
H	-6.1548	3.1097	-0.5333
H	-9.401	0.2792	-1.026
H	-9.7632	1.9886	-0.7154
H	-9.0259	1.4717	-2.244
H	-4.7014	0.8781	-2.7254
H	-4.5819	0.2776	-4.372
H	-6.1811	0.5421	-3.693
H	-7.1467	-0.7582	5.3282
H	-6.531	0.8929	5.4774
H	-8.2589	0.558	5.7274

Table S10. Cartesian coordinates of the optimized **18b**. B3LYP/6-31G(d,p) in CH₃CN (PCM)

C	6.53727	0.34714	-0.75713
C	6.76473	-0.97659	-1.14931
C	5.71659	-1.88241	-1.17786
C	4.44501	-1.44189	-0.80885
C	4.18478	-0.11449	-0.41368
C	5.27263	0.80847	-0.38824
O	3.45653	-2.38342	-0.87437
C	2.1454	-2.12893	-0.50291
C	1.84299	-0.81206	0.00379
C	2.79902	0.17748	-0.05533
C	0.43918	-0.52524	0.50363
C	0.3816	0.87961	1.13245
C	1.1185	1.91411	0.25686
O	2.52946	1.46314	0.21397
O	1.35816	-3.05114	-0.65724
C	5.14454	2.25657	0.02806
C	-0.0634	-1.5646	1.53333
C	-1.4225	-1.19356	2.14934
C	-1.39714	0.21079	2.7476
C	-1.06015	1.21018	1.62655
C	-2.16824	1.0851	0.60187
O	-2.43337	-1.23751	1.06551
C	-2.79534	-0.12634	0.41013
C	-3.90356	-0.27316	-0.52807
C	-4.32658	0.91543	-1.15851
O	-3.73717	2.12356	-0.90493
C	-2.66333	2.27002	-0.04458
C	-4.57737	-1.48819	-0.85305
C	-5.6235	-1.43516	-1.77515
C	-6.02469	-0.23967	-2.38166
C	-5.37636	0.94637	-2.07706
O	-2.22922	3.40713	0.08954
C	-4.22191	-2.83489	-0.2646
C	-1.89021	-2.25087	3.14281
C	1.19879	3.28692	0.91856
C	0.64517	2.03747	-1.19389
H	0.98691	0.84465	2.05009
H	-0.24397	-0.5621	-0.35546
H	-1.07629	2.2277	2.02257
H	7.36979	1.04339	-0.73588
H	7.7638	-1.29454	-1.43013
H	5.85001	-2.91613	-1.47586
H	6.12878	2.73067	0.01299
H	4.4826	2.81323	-0.64008
H	4.72784	2.35595	1.03322
H	0.66127	-1.64451	2.35342
H	-0.13464	-2.54647	1.06434
H	-2.3677	0.44848	3.19523
H	-0.64701	0.24171	3.54371
H	-6.13917	-2.35617	-2.02826
H	-6.84384	-0.24182	-3.09369
H	-5.65522	1.89269	-2.5263
H	-3.17773	-3.09704	-0.45165

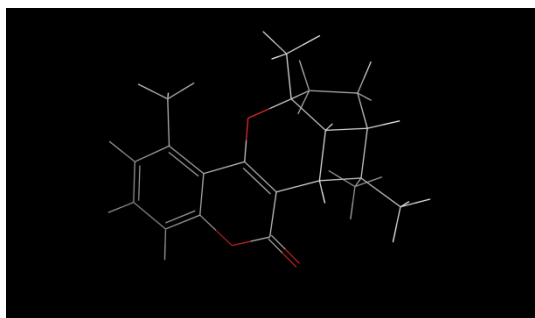
H	-4.35879	-2.85279	0.81953
H	-4.85693	-3.60675	-0.70568
H	-1.18377	-2.3188	3.9747
H	-2.87456	-1.99339	3.54339
H	-1.95207	-3.23107	2.66211
H	1.54594	3.20539	1.9529
H	1.89516	3.9255	0.36815
H	0.21455	3.75926	0.90678
H	-0.34285	2.49738	-1.22514
H	1.33687	2.68342	-1.74215
H	0.6044	1.0724	-1.70335

Table S11. Cartesian coordinates of the optimized **19a**. B3LYP/6-31G(d,p) in CH₃CN (PCM)

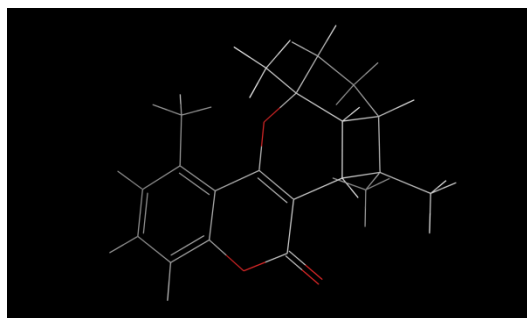
C	-6.61388	-1.35549	-1.08761
C	-5.98186	-2.51813	-0.63047
C	-4.64882	-2.52113	-0.21748
C	-3.91974	-1.2988	-0.26285
C	-4.58765	-0.15095	-0.72315
C	-5.91931	-0.15687	-1.13822
C	-2.49251	-1.17431	0.130948
C	-1.92758	0.163995	0.073721
C	-2.68124	1.193826	-0.40187
O	-3.96332	1.075057	-0.79424
C	-0.46682	0.384472	0.39339
C	0.003037	1.772744	-0.11528
C	-1.04425	2.908067	0.066847
O	-2.29567	2.451779	-0.58836
O	-1.80412	-2.15054	0.474373
C	-4.04178	-3.81763	0.262787
C	-0.12149	0.085233	1.872992
C	1.321263	0.445056	2.262431
C	1.618531	1.898348	1.907241
C	1.445491	2.080435	0.392001
C	-1.44504	3.301382	1.491864
C	-0.66827	4.152018	-0.73907
O	2.245888	-0.43695	1.514189
C	2.764536	-0.05286	0.338266
C	2.423496	1.132371	-0.26756
C	2.968802	1.492721	-1.54793
O	3.875387	0.613697	-2.1177
C	4.240223	-0.56311	-1.52181
C	3.718611	-0.97167	-0.27565
C	5.161811	-1.32938	-2.23637
C	5.578705	-2.53703	-1.69995
C	5.077081	-2.9677	-0.4669
C	4.1546	-2.21795	0.264302
O	2.707728	2.502155	-2.1859
C	1.601748	0.122406	3.725725
C	3.677391	-2.77829	1.585198
H	0.08197	-0.3616	-0.19385
H	0.086561	1.684892	-1.2051
H	1.720765	3.095868	0.098192
H	-7.65203	-1.39132	-1.40233
H	-6.54241	-3.44738	-0.59467
H	-6.37451	0.764255	-1.48411
H	-3.19576	-4.11859	-0.35991
H	-4.79509	-4.60967	0.244467
H	-3.64952	-3.72533	1.278584
H	-0.78386	0.637402	2.547738

H	-0.2966	-0.97744	2.055222
H	2.643861	2.1549	2.194481
H	0.952197	2.54025	2.485294
H	-2.26535	4.02258	1.441174
H	-0.61492	3.781214	2.013647
H	-1.78267	2.446642	2.080553
H	-0.38951	3.889645	-1.7628
H	0.170755	4.672941	-0.27229
H	-1.51635	4.841019	-0.77186
H	5.525462	-0.96115	-3.18891
H	6.295033	-3.15012	-2.23758
H	5.412932	-3.91663	-0.0606
H	1.421903	-0.93725	3.927614
H	2.639684	0.356303	3.978508
H	0.94592	0.71237	4.37199
H	2.59425	-2.92235	1.59712
H	4.15693	-3.74261	1.769
H	3.91263	-2.1111	2.41818

Figure S7. Optimized geometries of the predominant conformers of **23b** at the B3LYP/6-31G(d,p) level in CH₃CN solvent as described by PCM.



Conformer 1 of **23b**



Conformer 2 of **23b**

Table S12. Conformational analysis of **23b** at 298K

Conformation	Gibbs Free Energies (in Hartree)	Boltzmann Percentage Weights (%) Population Fractions
23b -Conf-1	-1000.765921	60.87
23b -Conf-2	-1000.765539	39.13

Table S13. Cartesian coordinates of the optimized **23b** conformers. B3LYP/6-31G(d,p) in CH₃CN (PCM).

23b-Conf-1				23b-Conf-2			
C	4.36793	0.800757	0.2986	C	4.129357	-1.05003	-0.59345
C	4.788291	-0.52969	0.401356	C	4.716074	0.208761	-0.4233
C	3.871251	-1.55938	0.264871	C	3.934283	1.297261	-0.07074
C	2.535348	-1.23639	0.024054	C	2.563971	1.105294	0.10918
C	2.081267	0.094995	-0.08129	C	1.945766	-0.15367	-0.04803
C	3.036333	1.145716	0.061407	C	2.761769	-1.26467	-0.41563
O	1.690931	-2.30577	-0.10128	O	1.858506	2.226074	0.454245
C	0.338908	-2.16446	-0.36518	C	0.484137	2.223136	0.63011
C	-0.18593	-0.82434	-0.44957	C	-0.19213	0.956533	0.50559
C	0.650175	0.258819	-0.32482	C	0.505931	-0.181	0.189013
C	-1.62685	-0.67658	-0.83489	C	-1.67578	0.932135	0.669603
C	-2.12505	0.784984	-0.94766	C	-2.27509	-0.46918	0.950056
C	-1.20676	1.831042	-0.28542	C	-1.35244	-1.68946	0.774774
O	0.218191	1.525672	-0.44034	O	-0.10769	-1.36698	0.037888
C	-2.80092	-1.00973	0.176566	C	-2.6017	1.053545	-0.62538
C	-3.27777	0.489692	0.064393	C	-3.16563	-0.38799	-0.32321
C	-1.57542	1.817478	1.218184	C	-2.14146	-2.58922	-0.18775
C	-3.06492	1.438072	1.258678	C	-2.78988	-1.61358	-1.18988
H	-4.29268	0.571877	-0.33465	H	-4.24051	-0.3727	-0.12046
H	-2.40688	1.088069	-1.95827	H	-2.80128	-0.54514	1.90441
H	-1.77728	-1.23174	-1.76707	H	-1.95848	1.678192	1.415387
C	-3.81416	-1.96885	-0.45812	C	-3.67374	2.131519	-0.43647
C	-2.41283	-1.52614	1.562107	C	-1.88236	1.262879	-1.95563
C	-1.3663	3.211457	-0.91233	C	-0.91829	-2.35083	2.078845
C	2.696732	2.616908	-0.02861	C	2.233963	-2.66544	-0.63107
O	-0.29883	-3.1967	-0.5109	O	-0.03748	3.299614	0.87847
H	5.09832	1.596452	0.407138	H	4.754473	-1.89201	-0.87398
H	5.833545	-0.75536	0.587332	H	5.784241	0.333358	-0.57014
H	4.155236	-2.60317	0.336573	H	4.349139	2.289266	0.067521
H	-0.96878	1.060982	1.725031	H	-1.50431	-3.34932	-0.6498
H	-1.35877	2.777681	1.69542	H	-2.91436	-3.10774	0.391764
H	-3.68316	2.332496	1.119554	H	-3.65655	-2.05231	-1.69209
H	-3.3582	0.997523	2.216606	H	-2.0669	-1.35256	-1.96768
H	-4.71242	-2.05491	0.164687	H	-4.41313	2.090561	-1.24508
H	-3.37801	-2.96704	-0.57257	H	-3.22643	3.131923	-0.43515
H	-4.12773	-1.62168	-1.44904	H	-4.20822	2.001799	0.511186
H	-1.65702	-0.9097	2.055099	H	-1.06904	0.550789	-2.11658
H	-3.29113	-1.56432	2.216544	H	-2.58507	1.164355	-2.79112
H	-2.00858	-2.53948	1.481857	H	-1.45021	2.268902	-1.99952
H	-2.40177	3.54896	-0.81008	H	-1.79562	-2.66762	2.650006
H	-0.71655	3.938758	-0.41731	H	-0.29886	-3.23	1.880258
H	-1.11857	3.183466	-1.97725	H	-0.34429	-1.65314	2.696586
H	1.972309	2.913865	0.733847	H	3.051263	-3.32122	-0.94086
H	2.256125	2.874707	-0.99467	H	1.456876	-2.69433	-1.39838
H	3.603733	3.210838	0.107356	H	1.789894	-3.07676	0.279048

Table S14. Cartesian coordinates of the optimized **24a**. B3LYP/6-31G(d,p) in CH₃CN (PCM).

C	6.654666	-0.1966	-2.11318
C	6.630926	-1.31228	-1.26781
C	5.58222	-1.54285	-0.37599
C	4.506121	-0.61104	-0.33697
C	4.563388	0.495477	-1.2003
C	5.616351	0.721579	-2.08642
C	3.329251	-0.74817	0.562059
C	2.257986	0.216411	0.362327
C	2.479757	1.291474	-0.44805
O	3.575153	1.454505	-1.21268
C	0.957518	0.141342	1.136819
C	-0.06911	1.145933	0.569905
C	0.561017	2.535444	0.328724
O	1.684411	2.34036	-0.62286
O	3.26253	-1.6332	1.431673
C	-0.36065	3.483422	-0.43072
C	1.137245	3.194233	1.583943
C	-1.3953	1.154168	1.427389
C	0.317856	-1.26546	1.145374
C	-1.09549	-1.27597	1.787539
C	-1.37171	0.045011	2.49844
O	-2.09221	-1.46371	0.69537
C	-2.86081	-0.46061	0.250922
C	-2.60371	0.852215	0.571563
C	-4.81713	0.236641	-1.00018
C	-3.98213	-0.83011	-0.60571
O	-4.59974	1.523548	-0.58998
C	-3.52494	1.891614	0.204777
O	-3.46972	3.070168	0.528298
C	-4.29276	-2.14178	-1.07155
C	-5.40826	-2.30247	-1.89447
C	-6.22057	-1.22614	-2.26866
C	-5.92934	0.05318	-1.82284
C	-3.47805	-3.36978	-0.73357
C	-1.30184	-2.49426	2.680548
C	5.633736	-2.77286	0.4987
H	1.181988	0.402143	2.17952
H	-0.3323	0.781429	-0.43128
H	-1.53887	2.126363	1.902774
H	7.488248	-0.0493	-2.79255
H	7.451397	-2.02254	-1.30441
H	5.599055	1.598422	-2.72372
H	0.174367	4.406489	-0.67114
H	-1.24251	3.72919	0.162531
H	-0.69451	3.023194	-1.36521
H	1.898591	2.570922	2.058886
H	1.591022	4.154479	1.325558

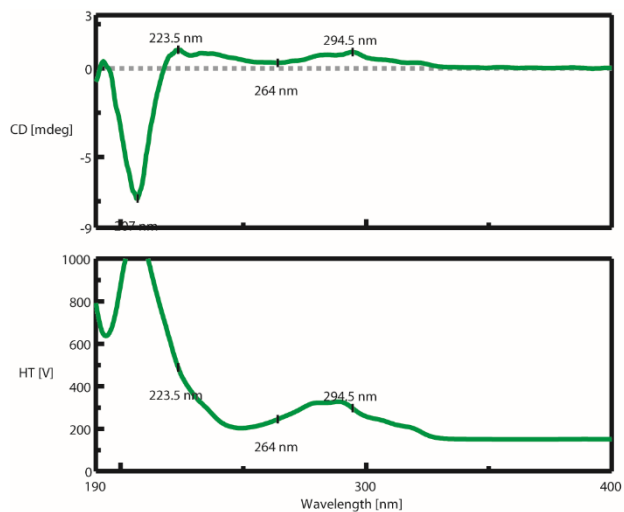
H	0.344236	3.37988	2.313661
H	0.235575	-1.64653	0.121818
H	0.974744	-1.9454	1.687555
H	-0.60171	0.209871	3.255881
H	-2.33369	0.013821	3.01857
H	-5.64866	-3.29785	-2.25473
H	-7.07992	-1.39356	-2.91018
H	-6.53409	0.912413	-2.08969
H	-2.43378	-3.26072	-1.03633
H	-3.47187	-3.56904	0.341037
H	-3.89716	-4.24033	-1.24367
H	-1.11301	-3.41566	2.122058
H	-0.60582	-2.4561	3.523357
H	-2.32287	-2.52237	3.071146
H	5.667927	-2.50894	1.558672
H	4.743864	-3.39421	0.372399
H	6.518761	-3.3659	0.253227

Table S15. Cartesian coordinates of the optimized **25b**. B3LYP/6-31G(d,p) in CH₃CN (PCM).

C	-5.86526	-1.40462	-1.92256
C	-6.496	-0.16969	-2.10916
C	-5.92893	0.984509	-1.59349
C	-4.72676	0.880357	-0.89273
C	-4.0695	-0.34891	-0.68711
C	-4.66404	-1.5304	-1.22286
O	-4.23319	2.05488	-0.3986
C	-3.0351	2.139629	0.293173
C	-2.26781	0.926369	0.442699
C	-2.8165	-0.27733	0.061239
C	-0.91981	0.990897	1.132582
C	-0.18267	-0.35512	0.993835
C	-1.12293	-1.53847	1.295672
O	-2.24463	-1.45685	0.336712
O	-2.74857	3.245589	0.727786
C	-4.06767	-2.91383	-1.09198
C	0.003425	2.11414	0.605405
C	1.435875	2.037071	1.199883
C	1.481886	1.051736	2.363227
C	1.176858	-0.34961	1.79707
C	2.34571	-0.67578	0.896574
O	2.35298	1.569469	0.122831
C	2.849728	0.325254	0.099153
C	3.947978	0.080378	-0.82895
C	4.497972	-1.21821	-0.78335
O	4.044613	-2.17249	0.085817
C	2.987458	-1.95962	0.957364
C	4.493052	1.014836	-1.75829
C	5.543608	0.595765	-2.57564
C	6.070897	-0.69872	-2.50804
C	5.550088	-1.61598	-1.60935
O	2.708059	-2.88626	1.705471
C	3.993486	2.432962	-1.91722
C	1.972361	3.41816	1.559534
C	-1.72219	-1.52443	2.705013
C	-0.49464	-2.89073	0.972175
H	1.146117	-1.07971	2.608033
H	0.068543	-0.46088	-0.06927
H	-1.10477	1.194877	2.19548
H	-6.32077	-2.29918	-2.33549
H	-7.43021	-0.11596	-2.65907
H	-6.38532	1.960363	-1.71421
H	-3.05754	-2.96215	-1.50579
H	-3.99192	-3.22578	-0.04739

H	-4.69379	-3.63444	-1.62342
H	-0.43959	3.080365	0.845269
H	0.078368	2.056457	-0.48576
H	0.761241	1.363427	3.123114
H	2.468518	1.052838	2.83593
H	5.961189	1.30146	-3.28697
H	6.888959	-0.98517	-3.16132
H	5.931279	-2.62739	-1.52599
H	4.547245	2.929602	-2.71746
H	2.928995	2.464121	-2.16217
H	4.119344	3.01243	-0.99913
H	1.359139	3.858044	2.351185
H	3.005518	3.35421	1.912079
H	1.93733	4.081628	0.690573
H	-2.3904	-2.38002	2.832924
H	-0.93078	-1.59795	3.456242
H	-2.29252	-0.61281	2.89792
H	0.357275	-3.0919	1.623371
H	-1.23503	-3.68503	1.1018
H	-0.14403	-2.90981	-0.06393

Figure S8. ECD spectra of 2 and 8.



[Comments]
Sample name Peak 2
Comment
User
Division
Company SUND, CPH

[Detailed Information]
Creation date 12/10/2018 20:42
Date modified 12/10/2018 20:43

Data array type Linear data array * 2
Horizontal axis Wavelength [nm]
Vertical axis(1) CD [mdeg]
Vertical axis(2) HT [V]
Start 400 nm
End 190 nm
Data interval 0.5 nm
Data points 421

[Measurement Information]
Instrument name J-1500
Model name J-1500
Serial No. A037661638

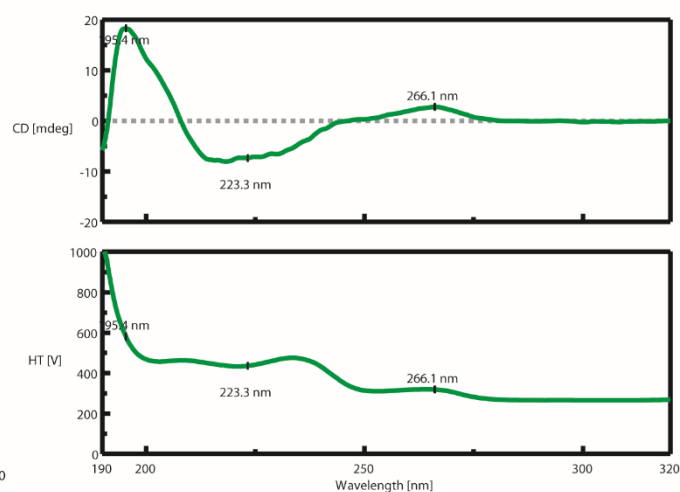
Detector PM-539
Detector S/N A037661638
Lock-in amp. X mode
HT volt Auto

Accessory PTC-510
Accessory S/N C008961763
Temperature 24.98 C
Control sensor Holder
Monitor sensor Holder
Start Mode Keep target temperature +/-0.10 deg C w hile 5 seconds

Measurement date 12/10/2018 20:22

CD Overload detect 354
Photometric mode CD, HT
Measure range 400 - 190 nm
Data pitch 0.5 nm
CD scale 200 mdeg/1.0 dOD
FL scale 200 mdeg/1.0 dOD

Bandwidth 5.00 nm
Start mode Immediately
Scanning speed 50 nm/min
Baseline correction Baseline
Shutter control Auto
Accumulations 3
Concentration 2 (w/v)%
Solvent CH3CN



[Comments]
Sample name Peak 8 G8-2
Comment no dtt
User
Division
Company SUND, CPH

[Detailed Information]
Creation date 25/09/2018 18:41
Date modified 25/09/2018 18:41

Data array type Linear data array * 2
Horizontal axis Wavelength [nm]
Vertical axis(1) CD [mdeg]
Vertical axis(2) HT [V]
Start 360 nm
End 190 nm
Data interval 0.1 nm
Data points 1701

[Measurement Information]
Instrument name J-1500
Model name J-1500
Serial No. A037661638

Detector PM-539
Detector S/N A037661638
Lock-in amp. X mode
HT volt Auto

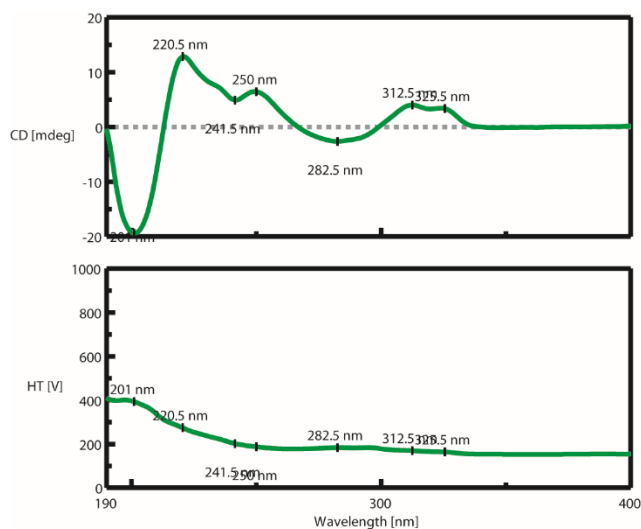
Accessory PTC-510
Accessory S/N C008961763
Temperature 20.01 C
Control sensor Holder
Monitor sensor Holder
Start Mode Keep target temperature +/-0.10 deg C w hile 5 seconds

Measurement date 25/09/2018 18:40

CD Overload detect 1630
Photometric mode CD, HT
Measure range 360 - 190 nm
Data pitch 0.1 nm
CD scale 200 mdeg/1.0 dOD
FL scale 200 mdeg/1.0 dOD

Bandwidth 5.00 nm
Start mode Immediately
Scanning speed 50 nm/min
Baseline correction Baseline
Shutter control Auto
Accumulations 3
Concentration 2 (w/v)%
Solvent CH3CN

Figure S9. ECD spectra of 6a and 6b.

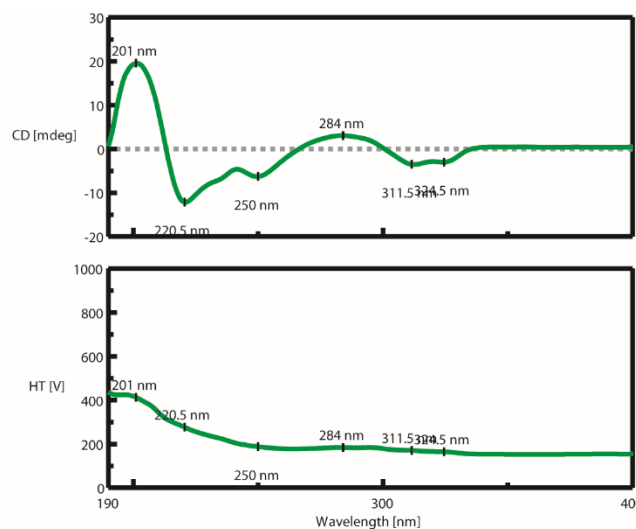


[Comments]
Sample name Peak 6-3a
Comment TL
User
Division
Company SUND, CPH

[Detailed Information]
Creation date 10/12/2018 12.54
Date modified 10/12/2018 12.55

Data array type Linear data array * 2
Horizontal axis Wavelength [nm]
Vertical axis(1) CD [mdeg]
Vertical axis(2) HT [V]
Start 400 nm
End 190 nm
Data interval 0.5 nm
Data points 421

[Measurement Information]
Instrument name J-1500
Model name J-1500
Serial No. A037661638
Detector PM-539
Detector S/N A037661638
Lock-in amp. X mode
HT volt Auto
Accessory PTC-510
Accessory S/N C008961763
Temperature 25.03 C
Control sensor Holder
Monitor sensor Holder
Start Mode Keep target temperature +/-0.10 deg C w hile 5 seconds
Measurement date 10/12/2018 12.51
Photometric mode CD, HT
Measure range 400 - 190 nm
Data pitch 0.5 nm
CD scale 200 mdeg/1.0 dOD
FL scale 200 mdeg/1.0 dOD
D.I.T. 4 sec
Bandwidth 5.00 nm
Start mode Immediately
Scanning speed 50 nm/min
Baseline correction Baseline
Shutter control Auto
Accumulations 3
Concentration 2 (w/v)%
Solvent CH3CN



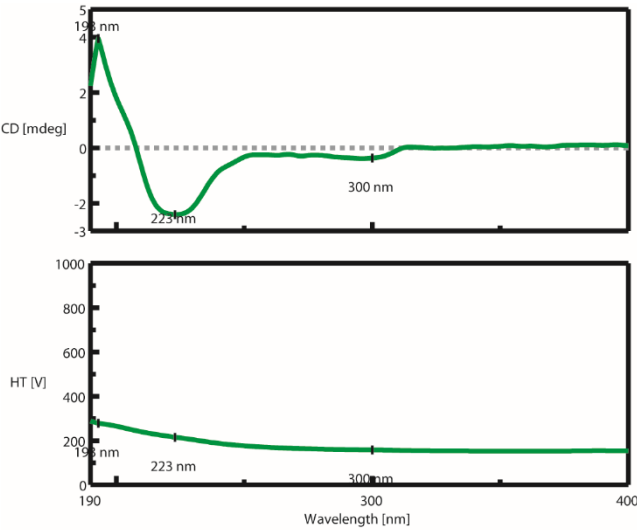
[Comments]
Sample name Peak 6-3b
Comment TL
User
Division
Company SUND, CPH

[Detailed Information]
Creation date 10/12/2018 13.2
Date modified 10/12/2018 13.2

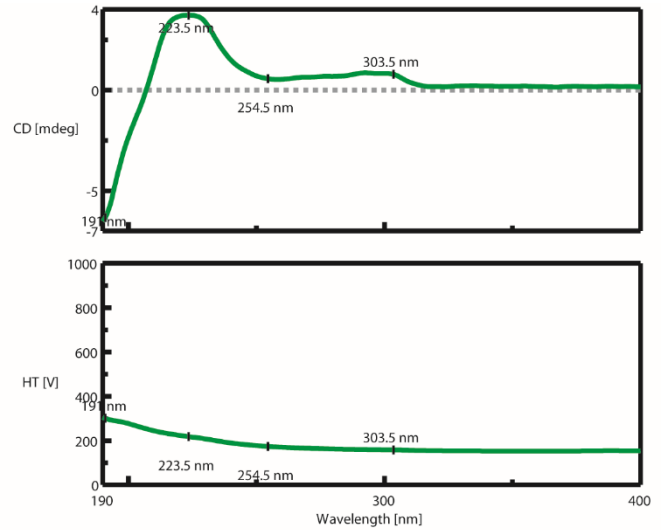
Data array type Linear data array
Horizontal axis Wavelength [nm]
Vertical axis(1) CD [mdeg]
Vertical axis(2) HT [V]
Start 400 nm
End 190 nm
Data interval 0.5 nm
Data points 421

[Measurement Information]
Instrument name J-1500
Model name J-1500
Serial No. A037661638
Detector PM-539
Detector S/N A037661638
Lock-in amp. X mode
HT volt Auto
Accessory PTC-510
Accessory S/N C008961763
Temperature 24.99 C
Control sensor Holder
Monitor sensor Holder
Start Mode Keep target temperature +/-0.10 deg C w hile 5 seconds
Measurement date 10/12/2018 13.24
Photometric mode CD, HT
Measure range 400 - 190 nm
Data pitch 0.5 nm
CD scale 200 mdeg/1.0 dOD
FL scale 200 mdeg/1.0 dOD
D.I.T. 4 sec
Bandwidth 5.00 nm
Start mode Immediately
Scanning speed 50 nm/min
Baseline correction Baseline
Shutter control Auto
Accumulations 3
Concentration 2 (w/v)%
Solvent CH3CN

Figure S10. ECD spectra of 11a and 11b.



[Comments]		Memory-29
Sample name	11a	
Comment		
User		[Detailed Information]
Division		Creation date 28/12/2018 22:56
Company	SUND, CPH	Date modified 28/12/2018 22:56
		Data array type Linear data array * 2
		Horizontal axis Wavelength [nm]
		Vertical axis(1) CD [mdeg]
		Vertical axis(2) HT [V]
		Start 400 nm
		End 190 nm
		Data interval 0.5 nm
		Data points 421
[Measurement Information]		
Instrument name	J-1500	
Model name	J-1500	
Serial No.	A037661638	
Detector	PM-539	
Detector S/N	A037661638	
Lock-in amp.	X mode	
HT volt	Auto	
Accessory	PTC-510	
Accessory S/N	C008961763	
Temperature	24.92 C	
Control sensor	Holder	
Monitor sensor	Holder	
Start Mode	Keep target temperature +/-0.10 deg C w	hile 5 seconds
Measurement date	28/12/2018 22:27	
Photometric mode	CD, HT	
Measure range	400 - 190 nm	
Data pitch	0.5 nm	
CD scale	200 mdeg/1.0 dOD	
FL scale	200 mdeg/1.0 dOD	
D.I.T.	4 sec	
Bandwidth	5.00 nm	
Start mode	Immediately	
Scanning speed	50 nm/min	
Baseline correction	Baseline	
Shutter control	Auto	
Accumulations	3	
Concentration	2 (w/v)%	
Solvent	CH3CN	



[Comments]		Memory-31
Sample name	11b	
Comment		
User		[Detailed Information]
Division		Creation date 28/12/2018 22:57
Company	SUND, CPH	Date modified 28/12/2018 22:58
		Data array type Linear data array * 2
		Horizontal axis Wavelength [nm]
		Vertical axis(1) CD [mdeg]
		Vertical axis(2) HT [V]
		Start 400 nm
		End 190 nm
		Data interval 0.5 nm
		Data points 421
[Measurement Information]		
Instrument name	J-1500	
Model name	J-1500	
Serial No.	A037661638	
Detector	PM-539	
Detector S/N	A037661638	
Lock-in amp.	X mode	
HT volt	Auto	
Accessory	PTC-510	
Accessory S/N	C008961763	
Temperature	24.99 C	
Control sensor	Holder	
Monitor sensor	Holder	
Start Mode	Keep target temperature +/-0.10 deg C w	hile 5 seconds
Measurement date	28/12/2018 22:47	
Photometric mode	CD, HT	
Measure range	400 - 190 nm	
Data pitch	0.5 nm	
CD scale	200 mdeg/1.0 dOD	
FL scale	200 mdeg/1.0 dOD	
D.I.T.	4 sec	
Bandwidth	5.00 nm	
Start mode	Immediately	
Scanning speed	50 nm/min	
Baseline correction	Baseline	
Shutter control	Auto	
Accumulations	3	
Concentration	2 (w/v)%	
Solvent	CH3CN	

Figure S11. ECD spectra of 14a and 14b.

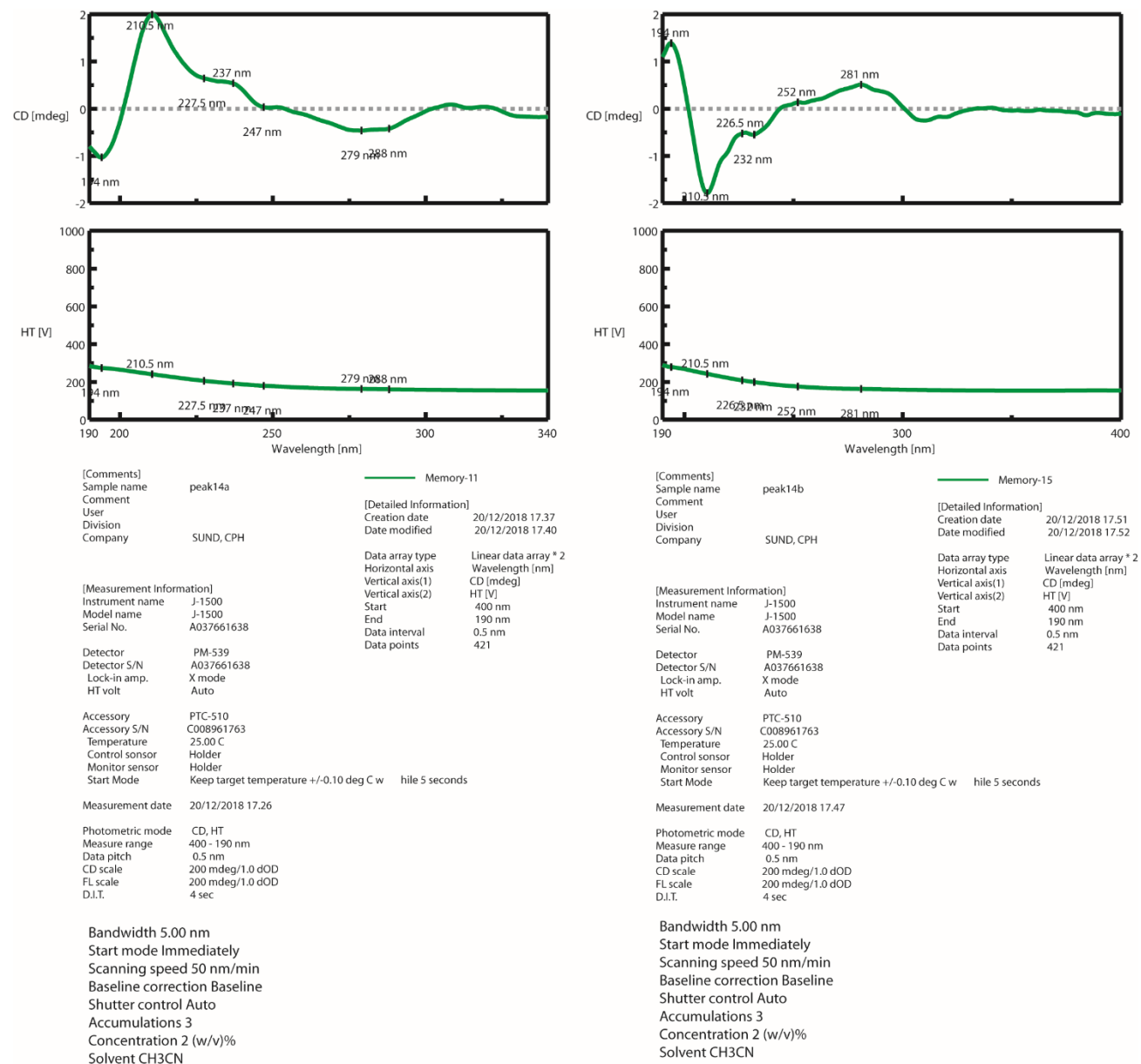


Figure S12. ECD spectra of 15a and 15b.

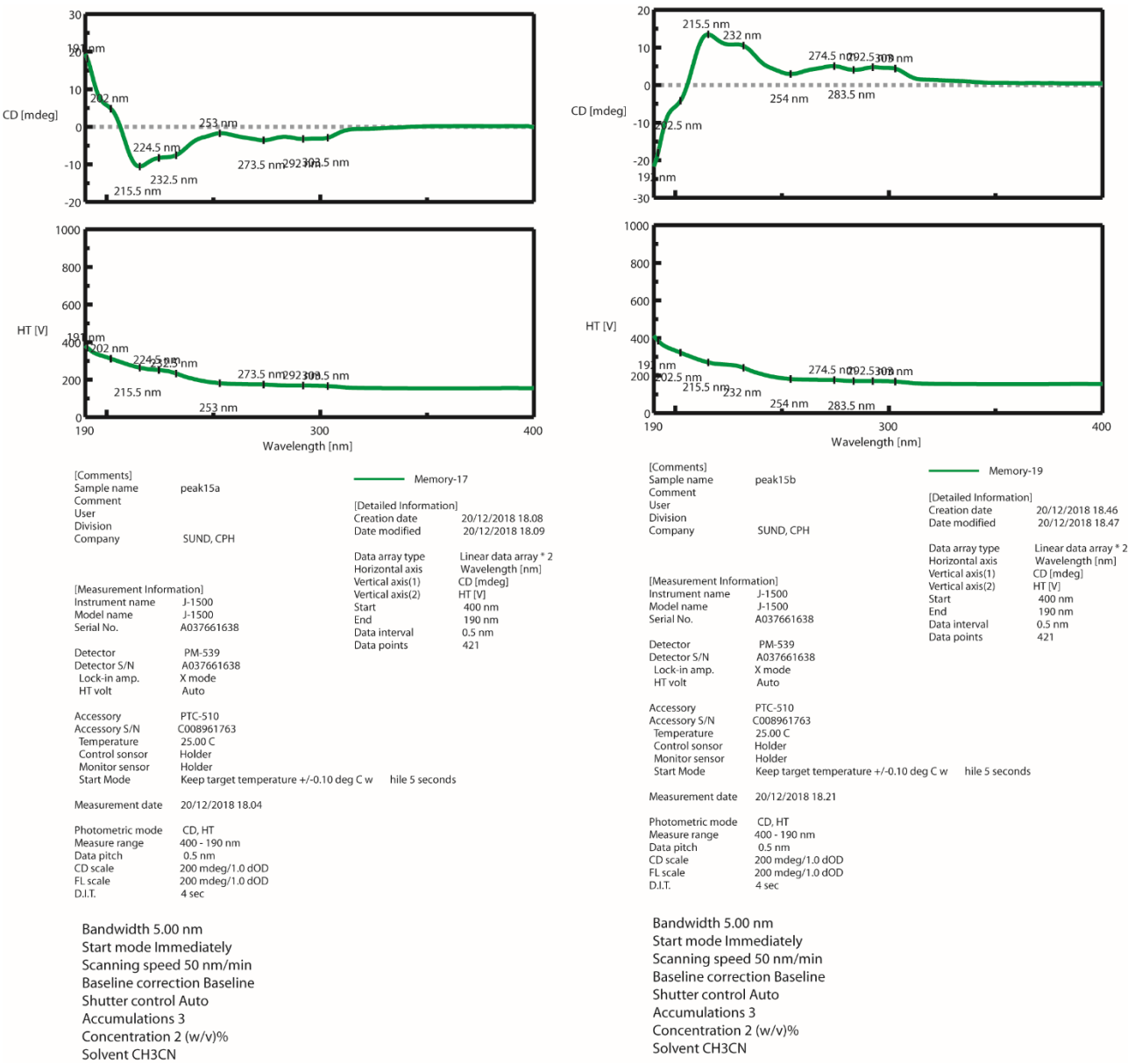
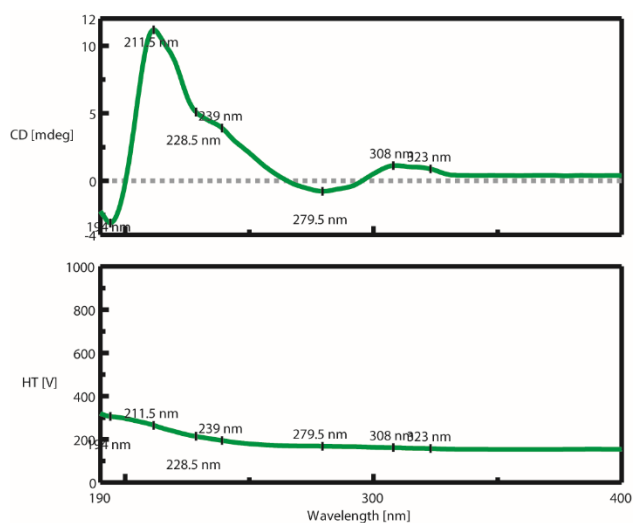
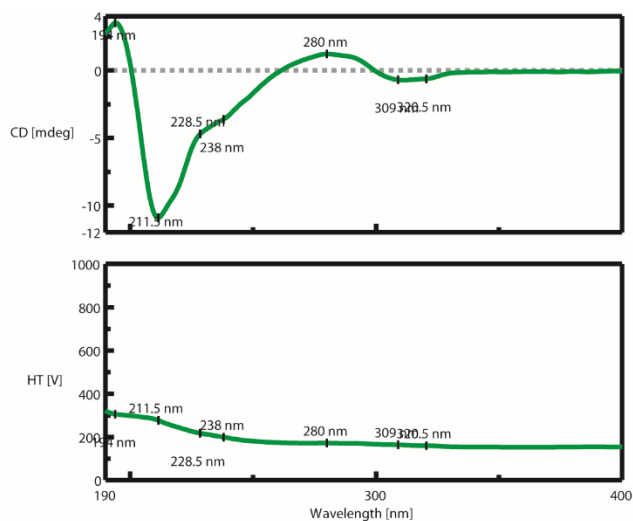


Figure S13. ECD spectra of 17a and 17b.



[Comments]		Memory-2	
Sample name	peak17a		
Comment		[Detailed Information]	
User		Creation date	19/12/2018 16:46
Division		Date modified	19/12/2018 16:47
Company	SUND, CPH	Data array type	Linear data array * 2
		Horizontal axis	Wavelength [nm]
		Vertical axis(1)	CD [mdeg]
		Vertical axis(2)	HT [V]
[Measurement Information]		Start	400 nm
Instrument name	J-1500	End	190 nm
Model name	J-1500	Data interval	0.5 nm
Serial No.	A037661638	Data points	421
Detector	PM-539		
Detector S/N	A037661638		
Lock-in amp.	X mode		
HT volt	Auto		
Accessory	PTC-510		
Accessory S/N	C008961763		
Temperature	25.00 C		
Control sensor	Holder		
Monitor sensor	Holder		
Start Mode	Keep target temperature +/-0.10 deg C w	hile 5 seconds	
Measurement date	19/12/2018 16:42		
Photometric mode	CD, HT		
Measure range	400 - 190 nm		
Data pitch	0.5 nm		
CD scale	200 mdeg/1.0 dOD		
FL scale	200 mdeg/1.0 dOD		
D.I.T.	4 sec		

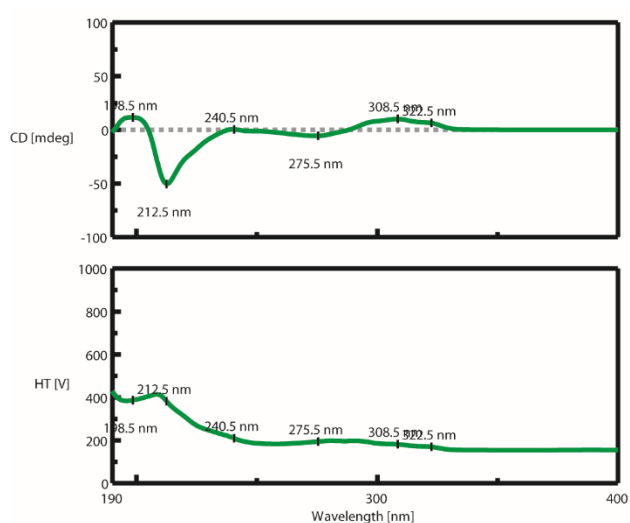
Bandwidth 5.00 nm
 Start mode Immediately
 Scanning speed 50 nm/min
 Baseline correction Baseline
 Shutter control Auto
 Accumulations 3
 Concentration 2 (w/v)%
 Solvent CH3CN



[Comments]		Memory-4	
Sample name	peak17b		
Comment		[Detailed Information]	
User		Creation date	19/12/2018 17:00
Division		Date modified	19/12/2018 17:01
Company	SUND, CPH	Data array type	Linear data array * 2
		Horizontal axis	Wavelength [nm]
		Vertical axis(1)	CD [mdeg]
		Vertical axis(2)	HT [V]
[Measurement Information]		Start	400 nm
Instrument name	J-1500	End	190 nm
Model name	J-1500	Data interval	0.5 nm
Serial No.	A037661638	Data points	421
Detector	PM-539		
Detector S/N	A037661638		
Lock-in amp.	X mode		
HT volt	Auto		
Accessory	PTC-510		
Accessory S/N	C008961763		
Temperature	25.01 C		
Control sensor	Holder		
Monitor sensor	Holder		
Start Mode	Keep target temperature +/-0.10 deg C w	hile 5 seconds	
Measurement date	19/12/2018 16:59		
Photometric mode	CD, HT		
Measure range	400 - 190 nm		
Data pitch	0.5 nm		
CD scale	200 mdeg/1.0 dOD		
FL scale	200 mdeg/1.0 dOD		
D.I.T.	4 sec		

Bandwidth 5.00 nm
 Start mode Immediately
 Scanning speed 50 nm/min
 Baseline correction Baseline
 Shutter control Auto
 Accumulations 3
 Concentration 2 (w/v)%
 Solvent CH3CN

Figure S14. ECD spectra of 18a and 18b.



[Comments]
Sample name peak18a
Comment
User
Division
Company SUND, CPH

[Detailed Information]
Creation date 17/12/2018 20.24
Date modified 17/12/2018 20.25

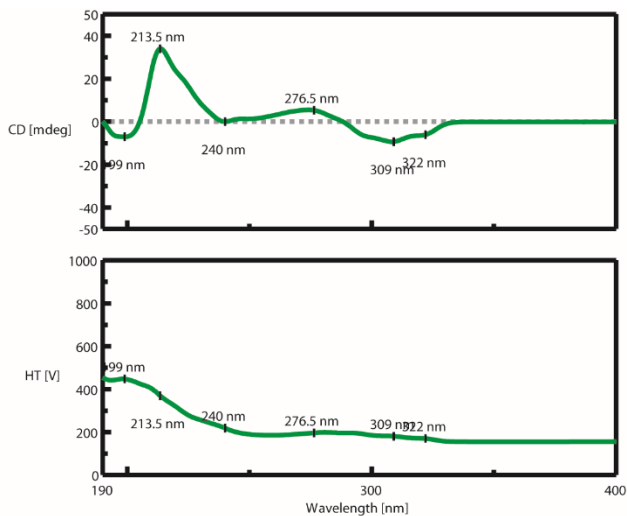
[Measurement Information]
Instrument name J-1500
Model name J-1500
Serial No. A037661638
Detector PM-539
Detector S/N A037661638
Lock-in amp. X mode
HT volt Auto

Accessories
Accessories S/N C008961763
Temperature 24.99 C
Control sensor Holder
Monitor sensor Holder
Start Mode Keep target temperature +/-0.10 deg C w hile 5 seconds

Measurement date 17/12/2018 17.35

Photometric mode CD, HT
Measure range 400 - 190 nm
Data pitch 0.5 nm
CD scale 200 mdeg/1.0 dOD
FL scale 200 mdeg/1.0 dOD
D.I.T. 4 sec

Bandwidth 5.00 nm
Start mode Immediately
Scanning speed 50 nm/min
Baseline correction Baseline
Shutter control Auto
Accumulations 3
Concentration 2 (w/v)%
Solvent CH3CN



[Comments]
Sample name peak18b
Comment
User
Division
Company SUND, CPH

[Detailed Information]
Creation date 17/12/2018 20.26
Date modified 17/12/2018 20.26

[Measurement Information]
Instrument name J-1500
Model name J-1500
Serial No. A037661638
Detector PM-539
Detector S/N A037661638
Lock-in amp. X mode
HT volt Auto

Accessories
Accessories S/N C008961763
Temperature 24.99 C
Control sensor Holder
Monitor sensor Holder
Start Mode Keep target temperature +/-0.10 deg C w hile 5 seconds

Measurement date 17/12/2018 17.53

Photometric mode CD, HT
Measure range 400 - 190 nm
Data pitch 0.5 nm
CD scale 200 mdeg/1.0 dOD
FL scale 200 mdeg/1.0 dOD
D.I.T. 4 sec

Bandwidth 5.00 nm
Start mode Immediately
Scanning speed 50 nm/min
Baseline correction Baseline
Shutter control Auto
Accumulations 3
Concentration 2 (w/v)%
Solvent CH3CN

Figure S15. ECD spectra of 19a and 19b.

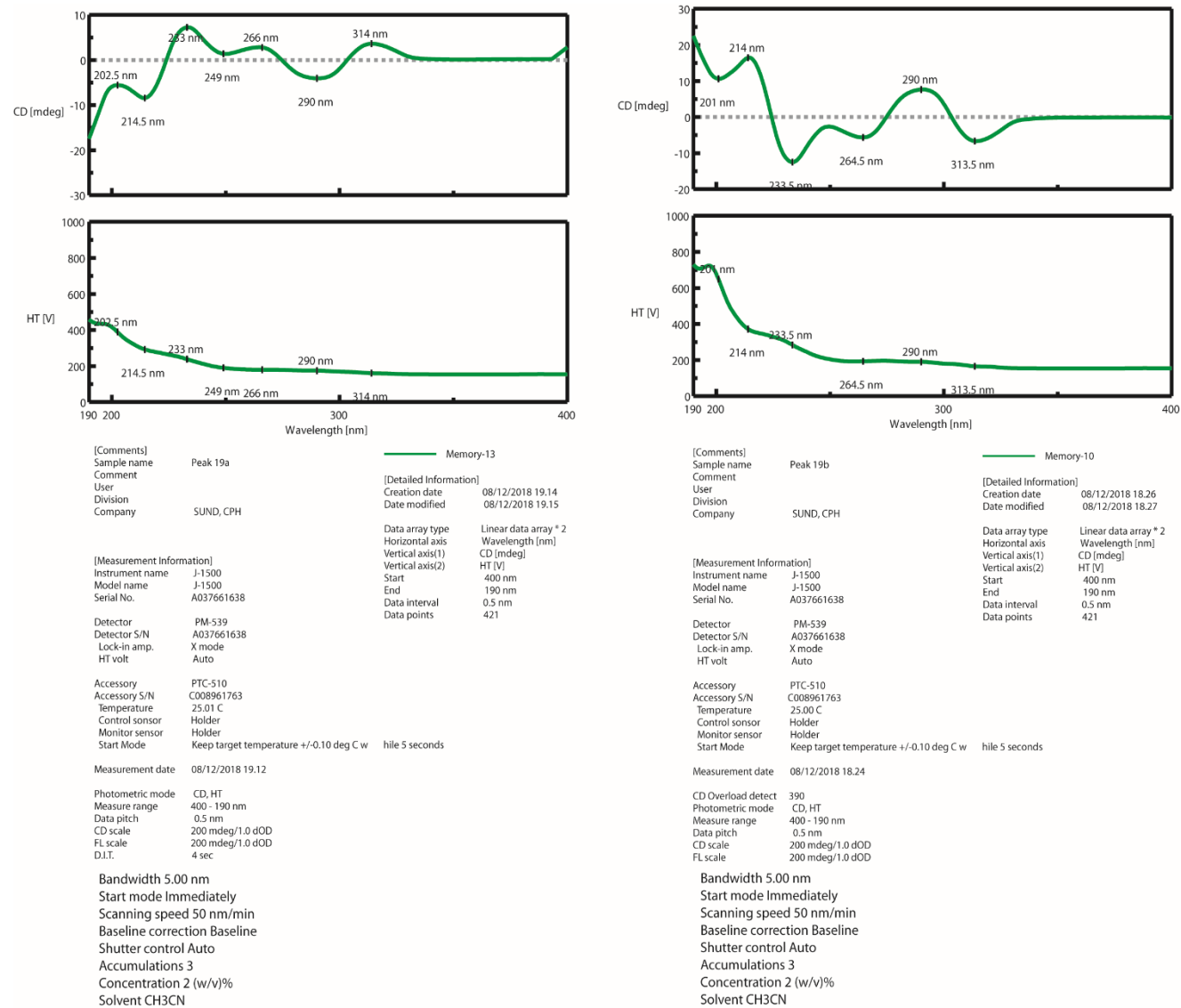
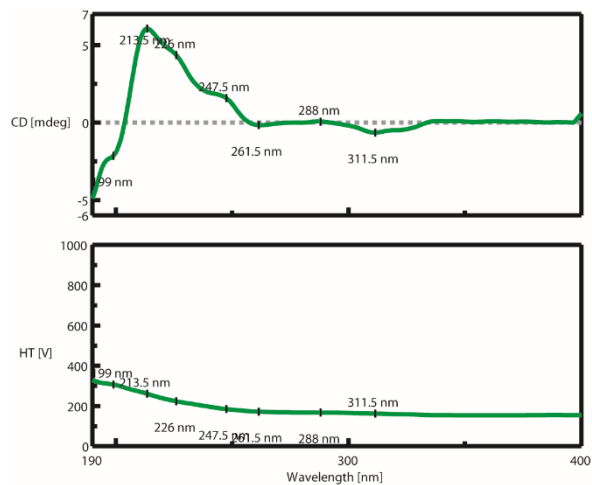


Figure S16. ECD spectra of 23a and 23b.



[Comments]
Sample name peak23-a
User
Division
Company SUND, CPH

[Detailed Information]
Creation date 17/12/2018 20.21
Date modified 17/12/2018 20.22

Data array type Linear data array * 2
Horizontal axis Wavelength [nm]
Vertical axis(1) CD [mdeg]
Vertical axis(2) HT [V]
Start 400 nm
End 190 nm
Data interval 0.5 nm
Data points 421

[Measurement Information]
Instrument name J-1500
Model name J-1500
Serial No. A037661638

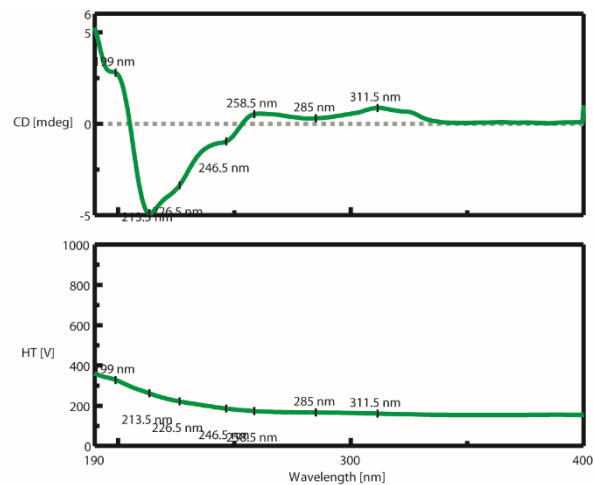
Detector PM-539
Detector S/N A037661638
Lock-in amp. X mode
HT volt Auto

Accessory PTC-510
Accessory S/N C008961763
Temperature 25.00 C
Control sensor Holder
Monitor sensor Holder
Start Mode Keep target temperature +/-0.10 deg C w hile 5 seconds

Measurement date 17/12/2018 16.59

Photometric mode CD, HT
Measure range 400 - 190 nm
Data pitch 0.5 nm
CD scale 200 mdeg/1.0 dOD
FL scale 200 mdeg/1.0 dOD
D.I.T. 4 sec

Bandwidth 5.00 nm
Start mode Immediately
Scanning speed 50 nm/min
Baseline correction Baseline
Shutter control Auto
Accumulations 3
Concentration 2 (w/v)%
Solvent CH3CN



[Comments]
Sample name peak23-b
User
Division
Company SUND, CPH

[Detailed Information]
Creation date 17/12/2018 20.23
Date modified 17/12/2018 20.24

Data array type Linear data array * 2
Horizontal axis Wavelength [nm]
Vertical axis(1) CD [mdeg]
Vertical axis(2) HT [V]
Start 400 nm
End 190 nm
Data interval 0.5 nm
Data points 421

[Measurement Information]
Instrument name J-1500
Model name J-1500
Serial No. A037661638

Detector PM-539
Detector S/N A037661638
Lock-in amp. X mode
HT volt Auto

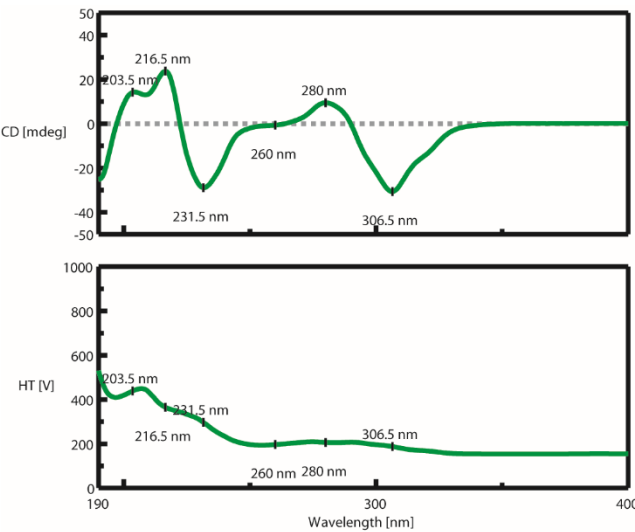
Accessory PTC-510
Accessory S/N C008961763
Temperature 24.99 C
Control sensor Holder
Monitor sensor Holder
Start Mode Keep target temperature +/-0.10 deg C w hile 5 seconds

Measurement date 17/12/2018 17.17

Photometric mode CD, HT
Measure range 400 - 190 nm
Data pitch 0.5 nm
CD scale 200 mdeg/1.0 dOD
FL scale 200 mdeg/1.0 dOD
D.I.T. 4 sec

Bandwidth 5.00 nm
Start mode Immediately
Scanning speed 50 nm/min
Baseline correction Baseline
Shutter control Auto
Accumulations 3
Concentration 2 (w/v)%
Solvent CH3CN

Figure S17. ECD spectra of 24a and 24b.



[Comments]
Sample name 24a
Comment
User
Division
Company SUND, CPH

[Detailed Information]
Creation date 17/12/2018 20.15
Date modified 17/12/2018 20.16

[Measurement Information]
Instrument name J-1500
Model name J-1500
Serial No. A037661638

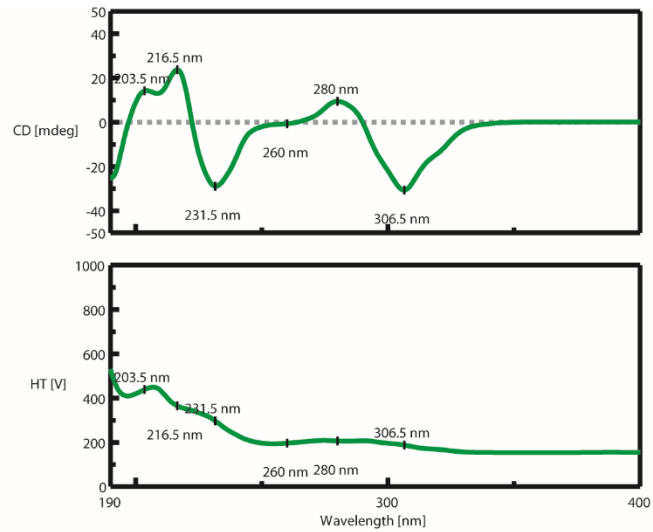
Detector PM-539
Detector S/N A037661638
Lock-in amp. X mode
HT volt Auto

Accessory PTC-510
Accessory S/N C008961763
Temperature 25.01 C
Control sensor Holder
Monitor sensor Holder
Start Mode Keep target temperature +/-0.10 deg C w hile 5 seconds

Measurement date 17/12/2018 19.42

CD Overload detect 419
Photometric mode CD, HT
Measure range 400 - 190 nm
Data pitch 0.5 nm
CD scale 200 mdeg/1.0 dOD
FL scale 200 mdeg/1.0 dOD

Bandwidth 5.00 nm
Start mode Immediately
Scanning speed 50 nm/min
Baseline correction Baseline
Shutter control Auto
Accumulations 3
Concentration 2 (w/v)%
Solvent CH3CN



[Comments]
Sample name 24a
Comment
User
Division
Company SUND, CPH

[Detailed Information]
Creation date 17/12/2018 20.15
Date modified 17/12/2018 20.16

[Measurement Information]
Instrument name J-1500
Model name J-1500
Serial No. A037661638

Detector PM-539
Detector S/N A037661638
Lock-in amp. X mode
HT volt Auto

Accessory PTC-510
Accessory S/N C008961763
Temperature 25.01 C
Control sensor Holder
Monitor sensor Holder
Start Mode Keep target temperature +/-0.10 deg C w hile 5 seconds

Measurement date 17/12/2018 19.42

CD Overload detect 419
Photometric mode CD, HT
Measure range 400 - 190 nm
Data pitch 0.5 nm
CD scale 200 mdeg/1.0 dOD
FL scale 200 mdeg/1.0 dOD

Bandwidth 5.00 nm
Start mode Immediately
Scanning speed 50 nm/min
Baseline correction Baseline
Shutter control Auto
Accumulations 3
Concentration 2 (w/v)%
Solvent CH3CN

Figure S18. ECD spectra of 25a and 25b.

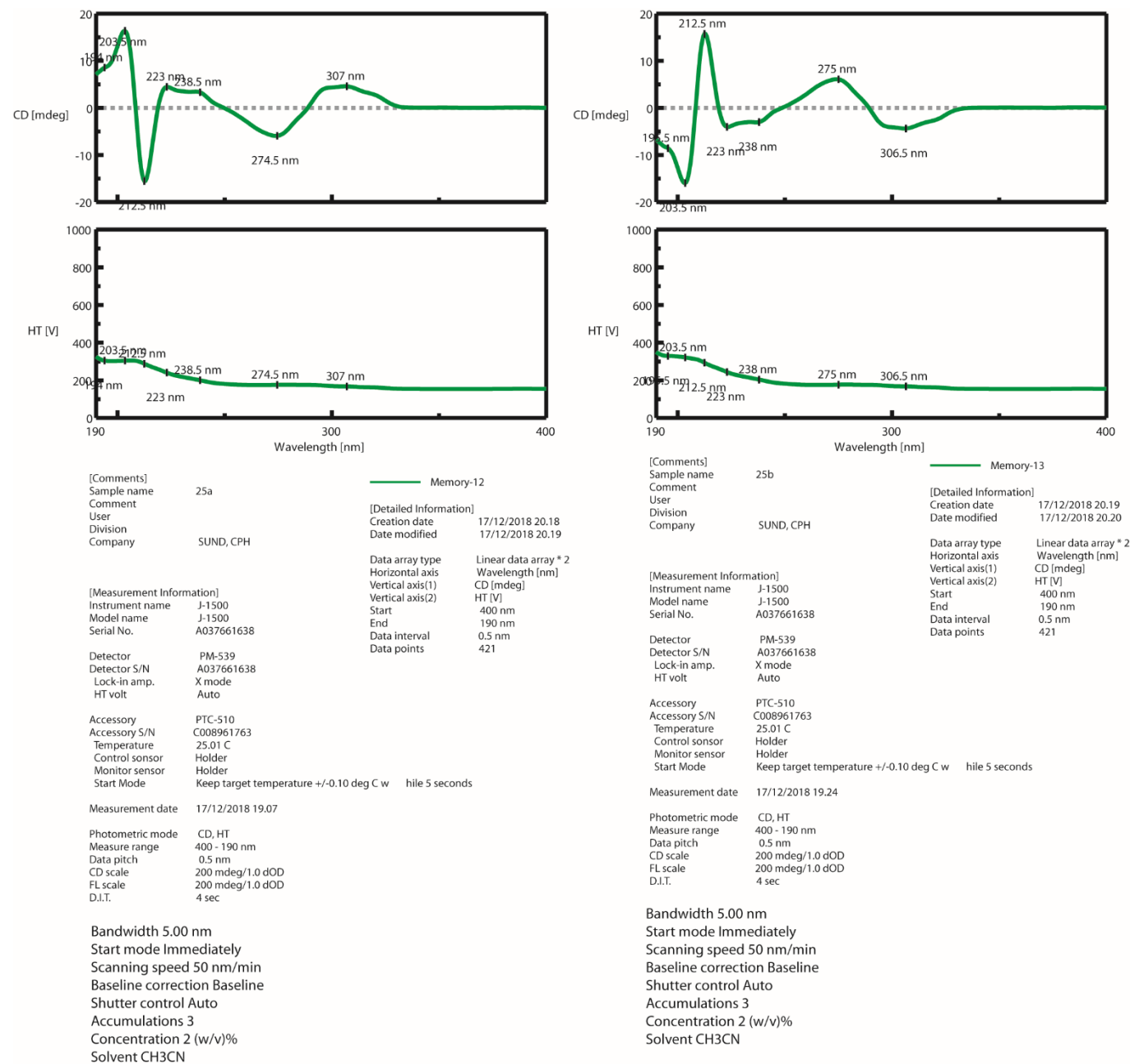
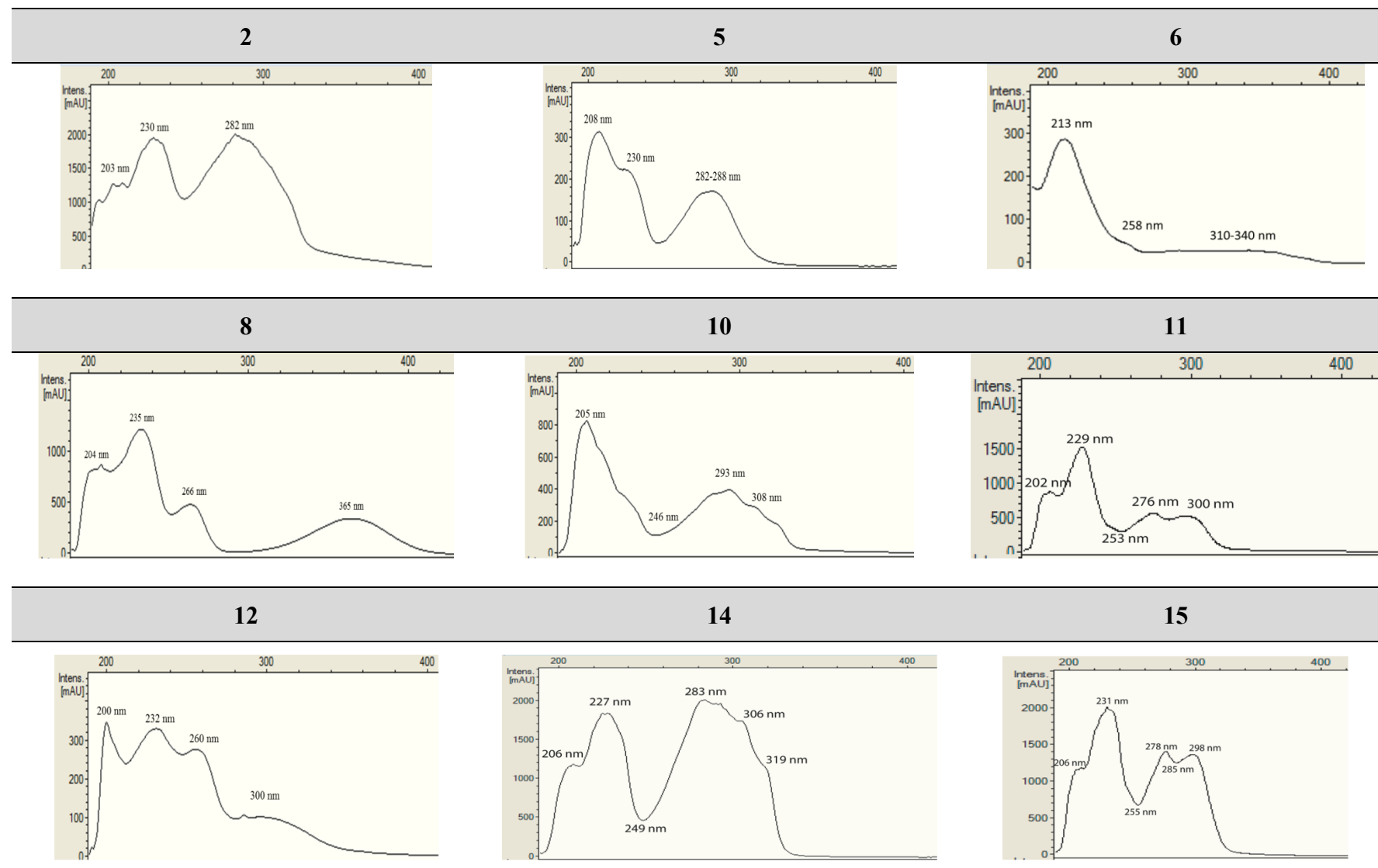


Figure S19. UV spectra obtained from HPLC-PDA-HRMS analysis of new compounds identified in *G. piloselloides*.



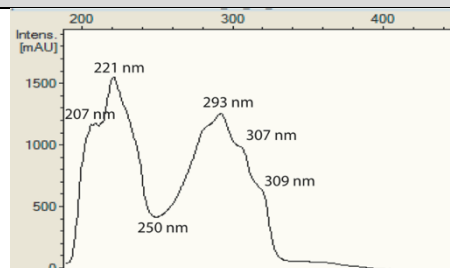
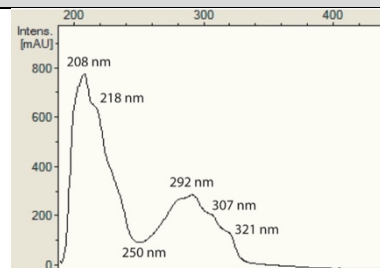
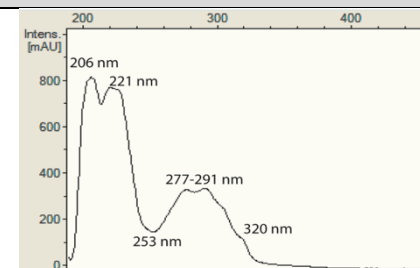
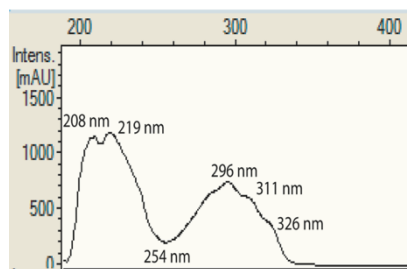
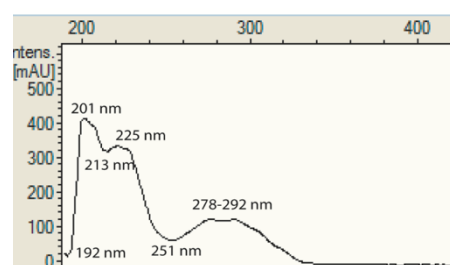
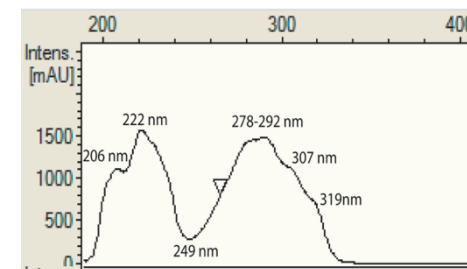
17**18****19****23****24****25**

Figure S20. ^1H NMR spectrum of **1** (600 MHz, methanol- d_4).

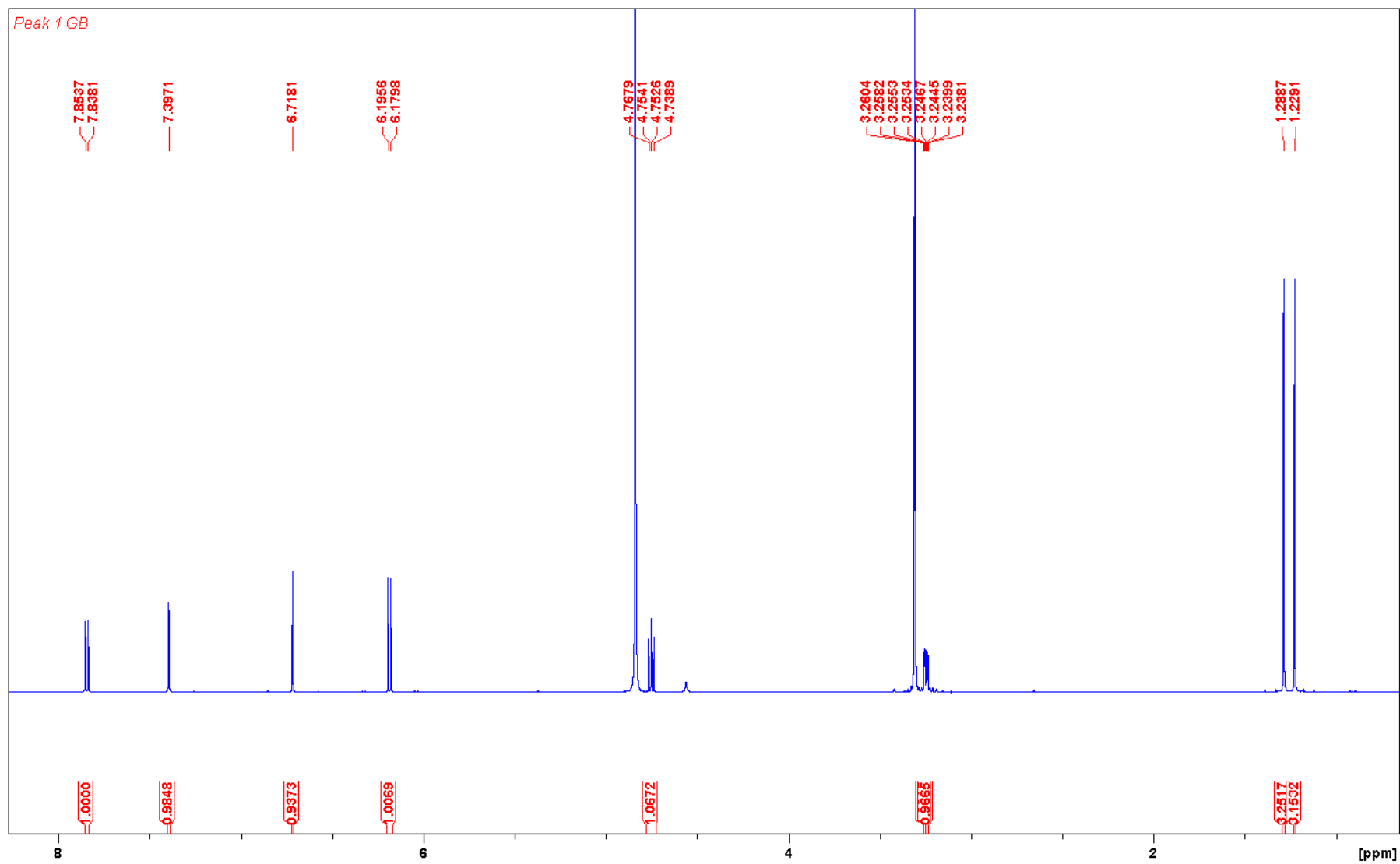


Figure S21. ^1H NMR spectrum of **2** (600 MHz, methanol- d_4).

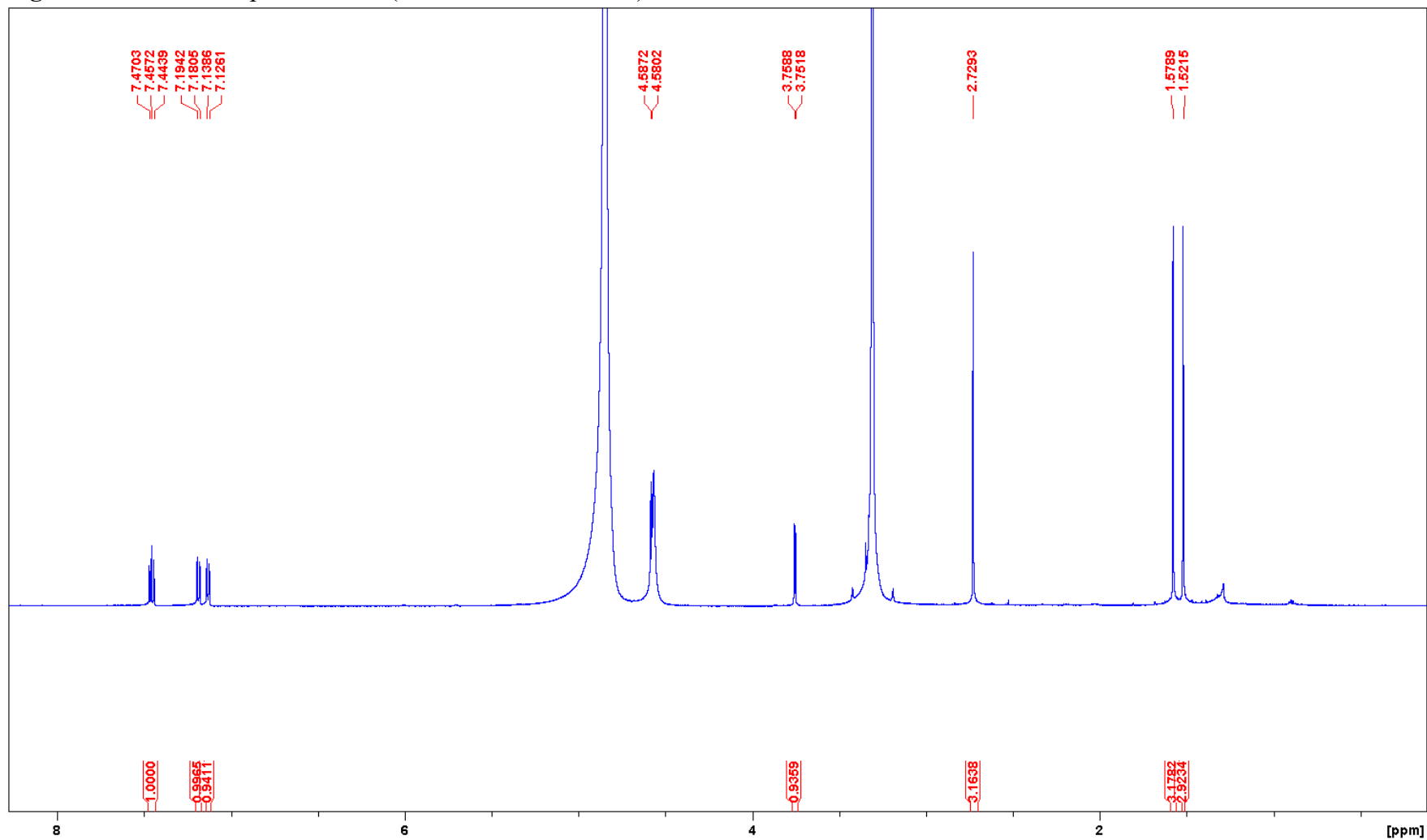


Figure S22. ^{13}C NMR spectrum of **2** (151 MHz, methanol- d_4).

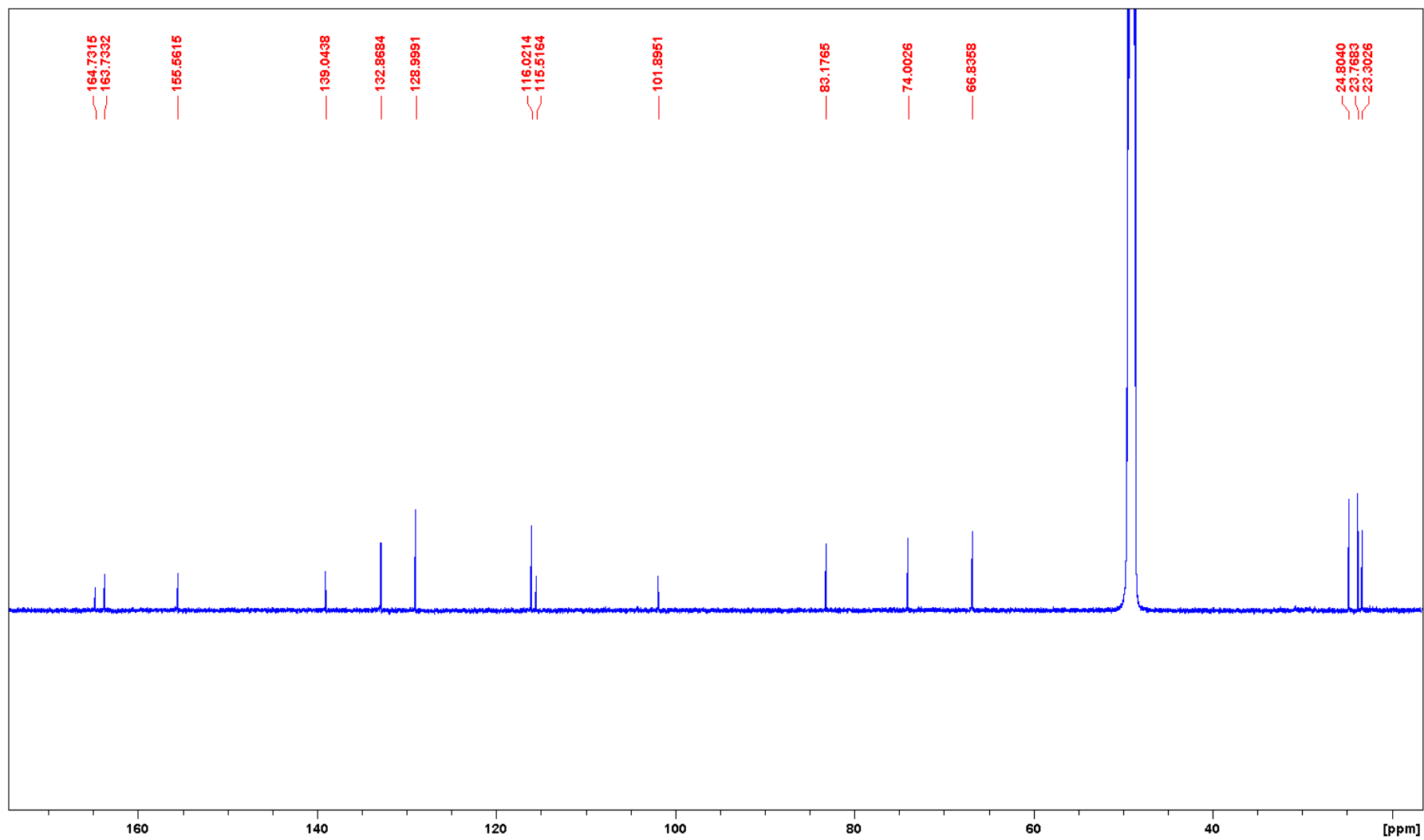


Figure S23. HSQC spectrum of **2** (600 MHz, methanol- d_4).

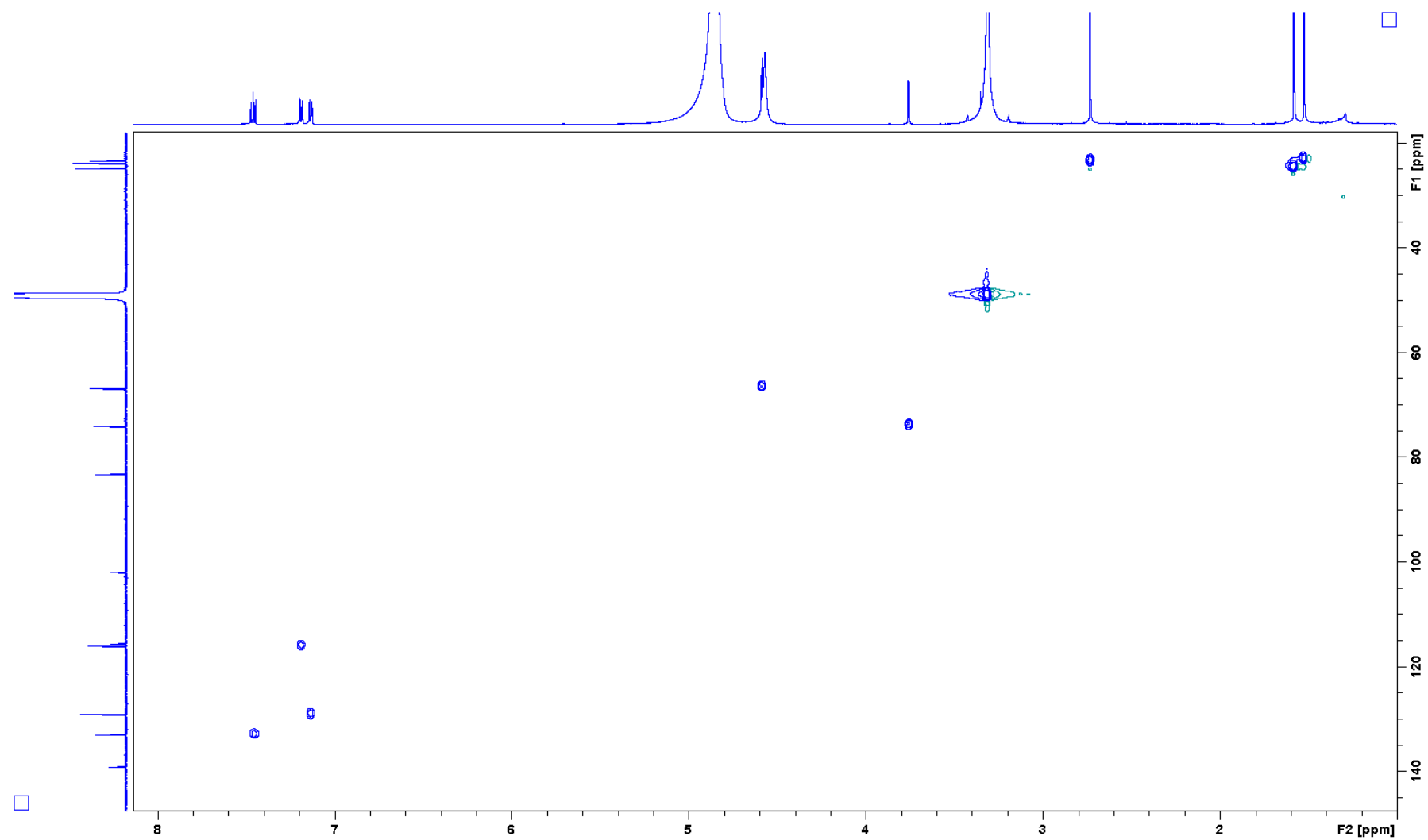


Figure S24. COSY spectrum of **2** (600 MHz, methanol- d_4).

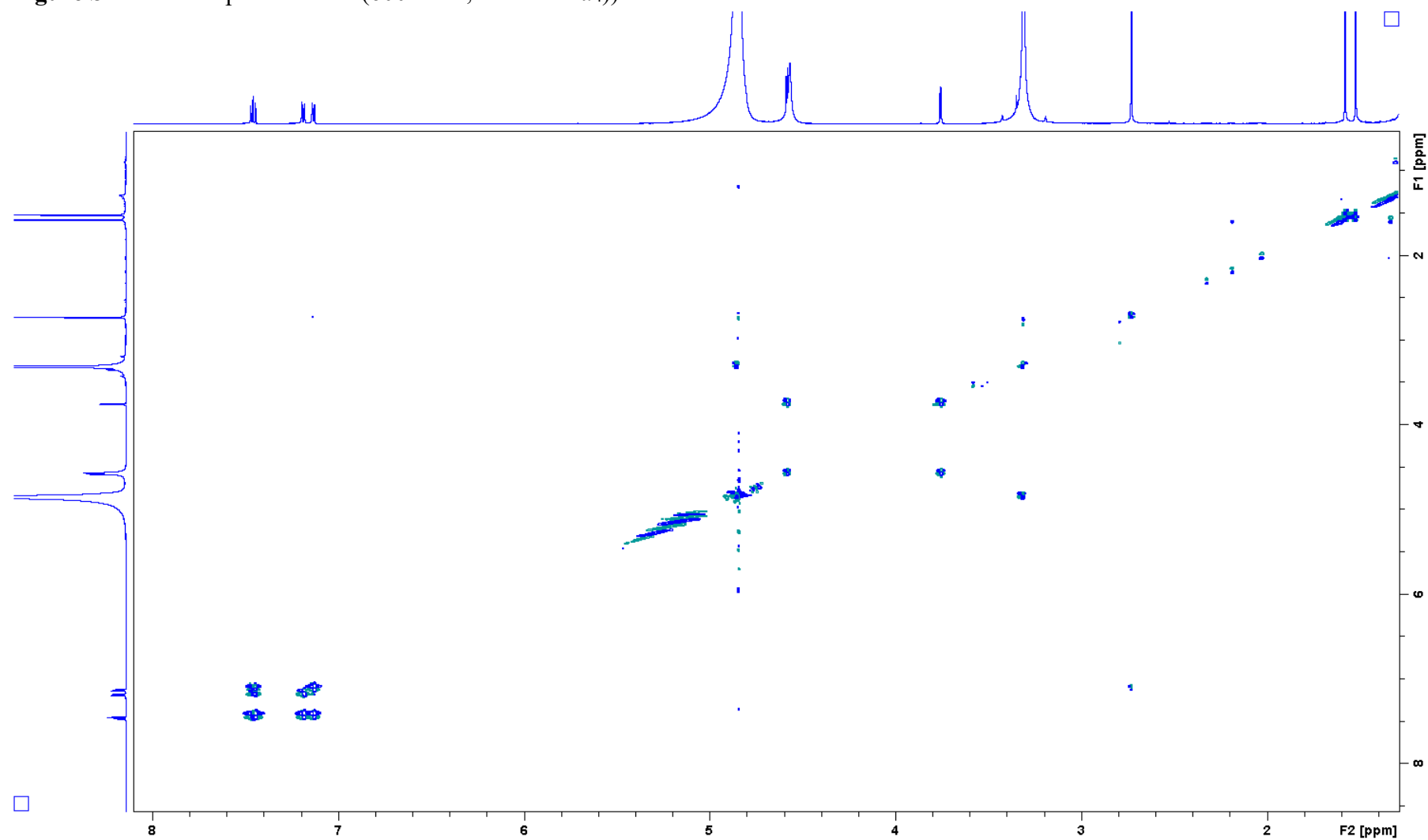


Figure S25. HMBC spectrum of **2** (600 MHz, methanol-*d*₄).

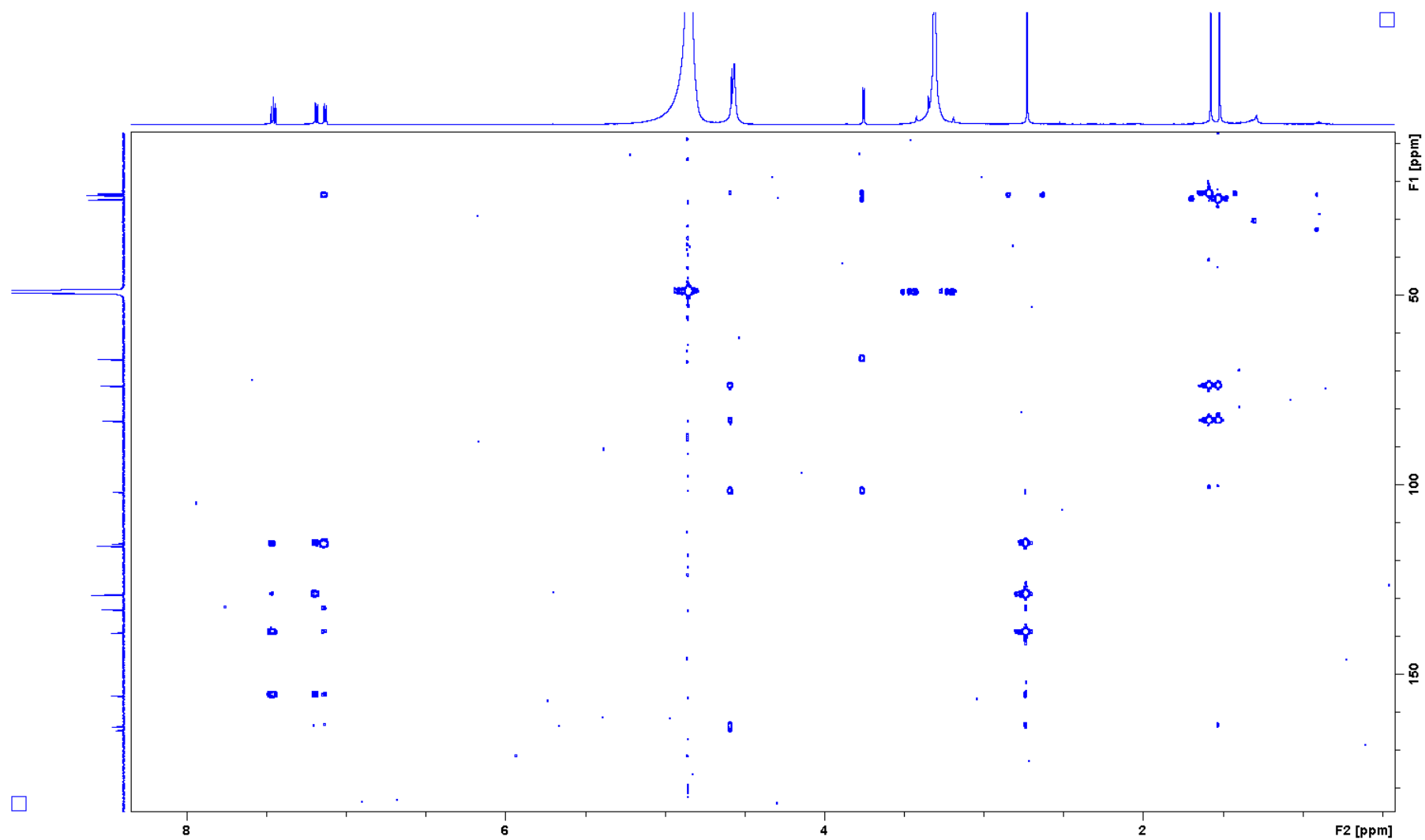


Figure S26. ROESY spectrum of **2** (600 MHz, methanol-*d*₄).

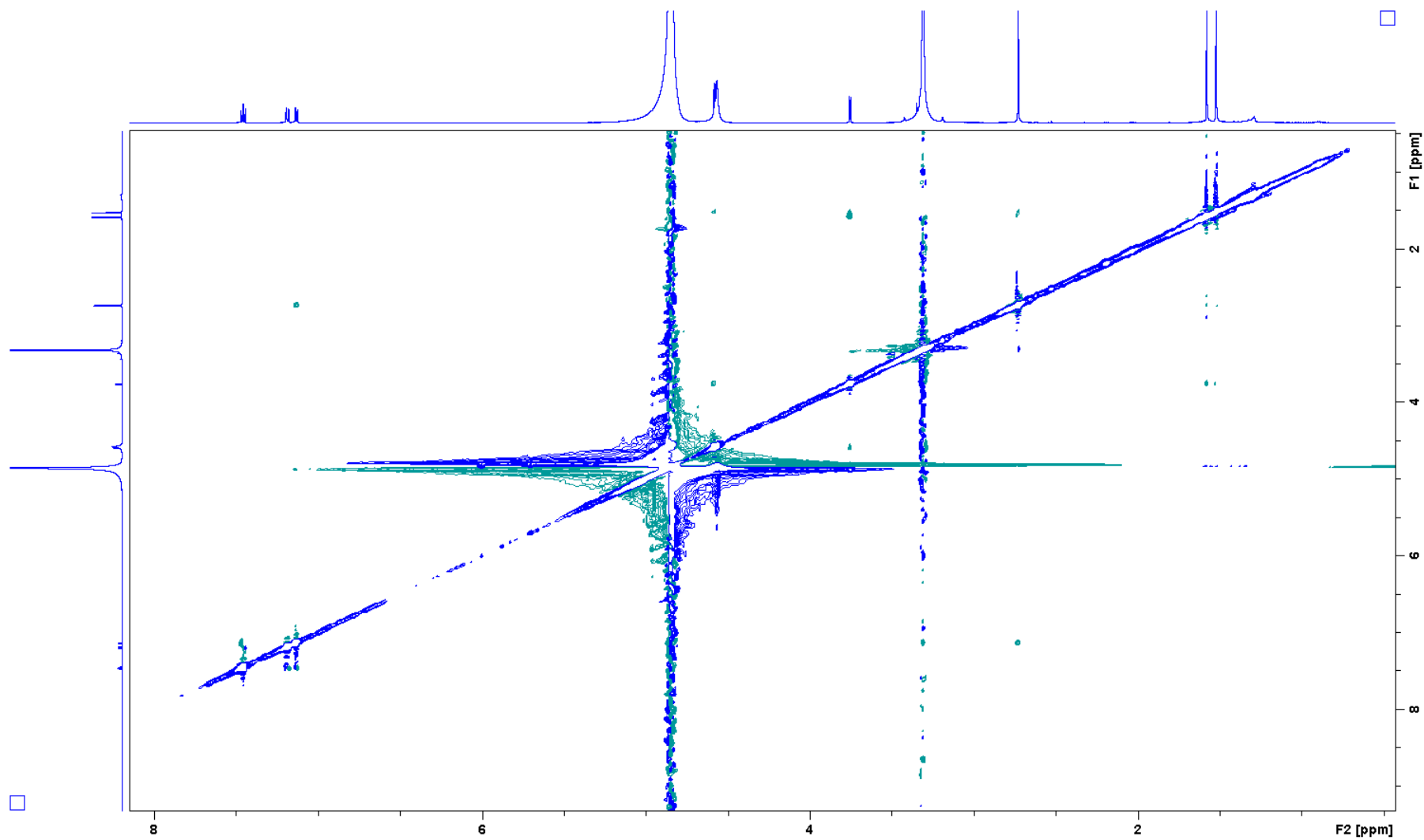


Figure S27. ^1H NMR spectrum of **3** (600 MHz, methanol- d_4).

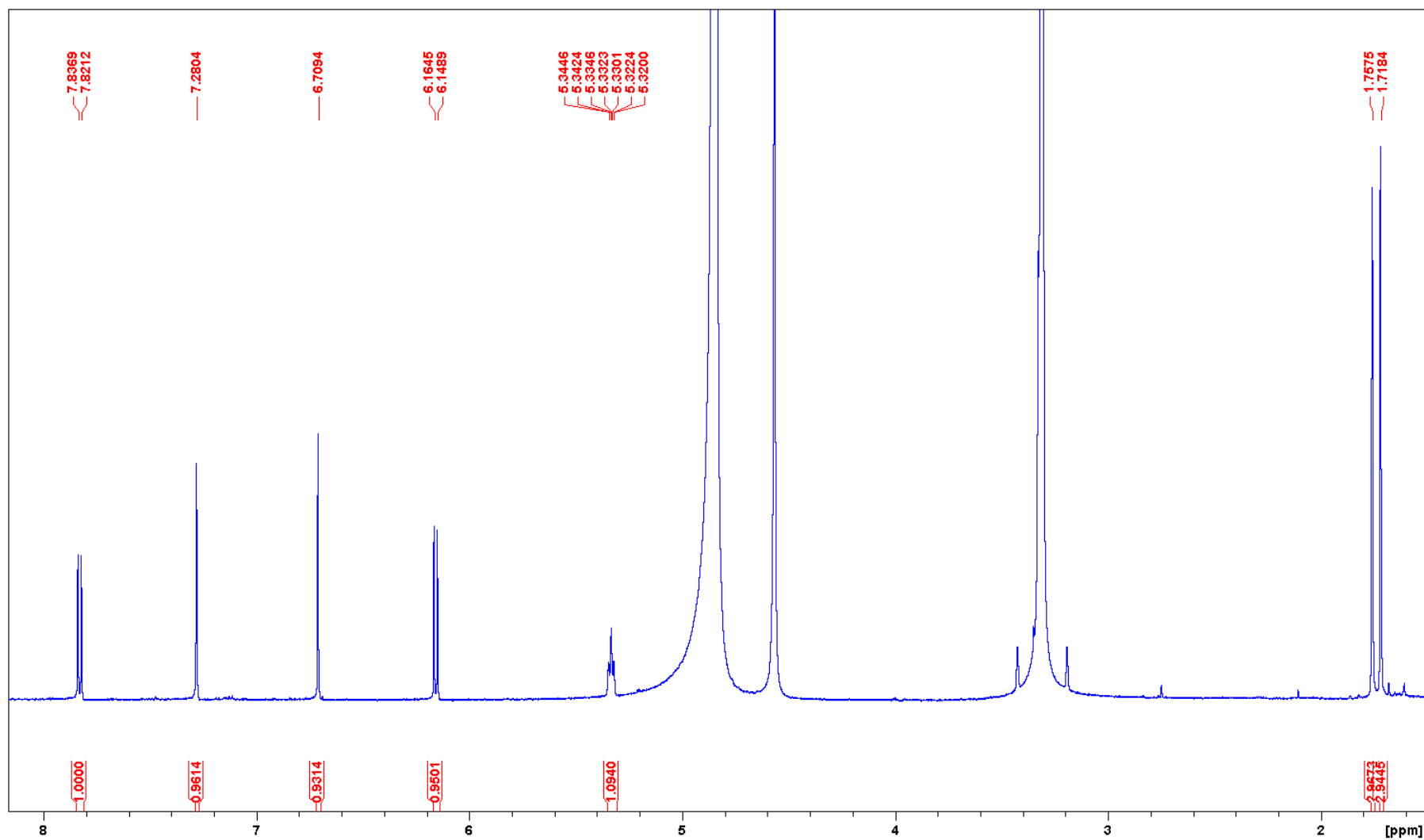


Figure S28. COSY spectrum of **3** (600 MHz, methanol- d_4).

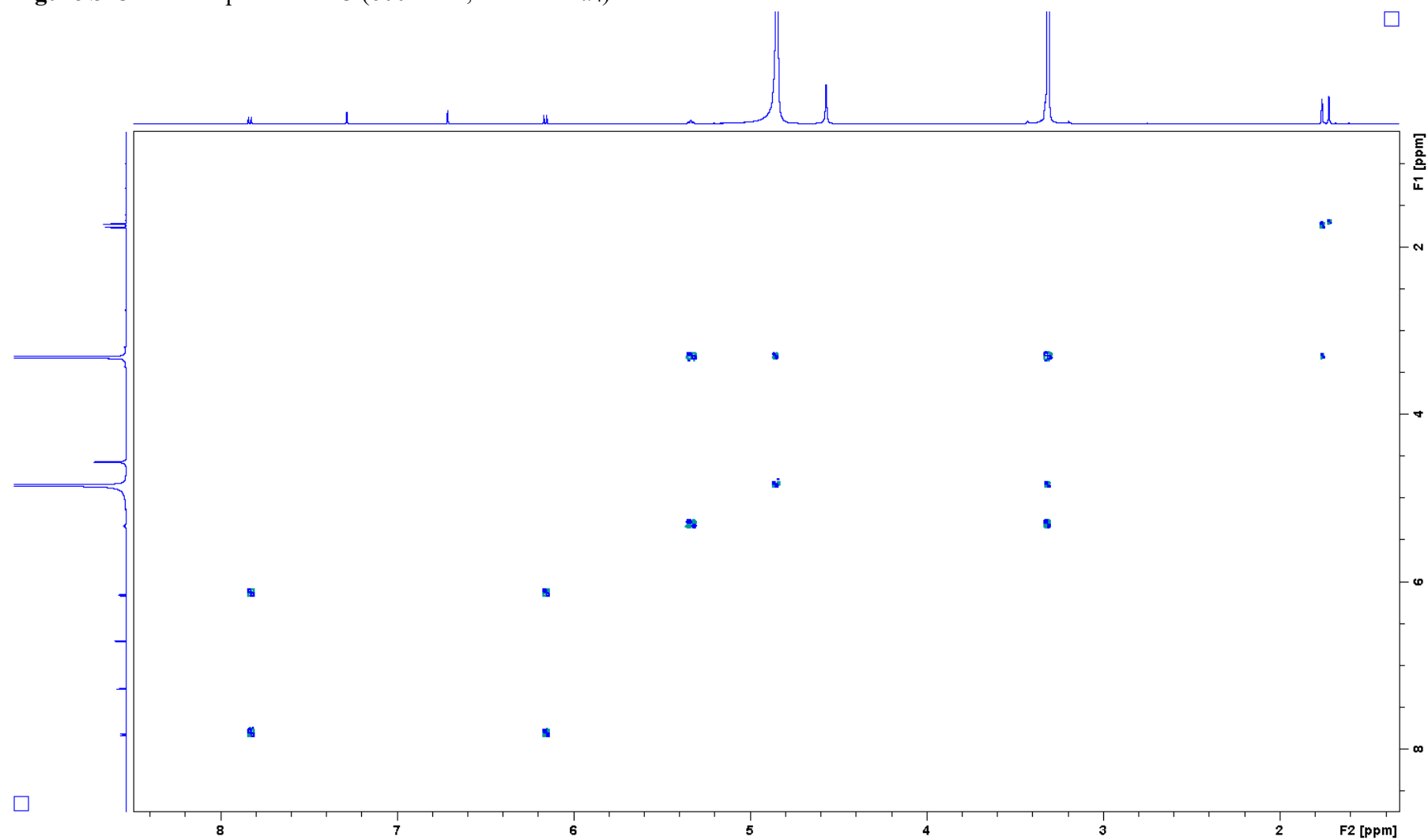


Figure S29. HSQC spectrum of **3** (600 MHz, methanol- d_4).

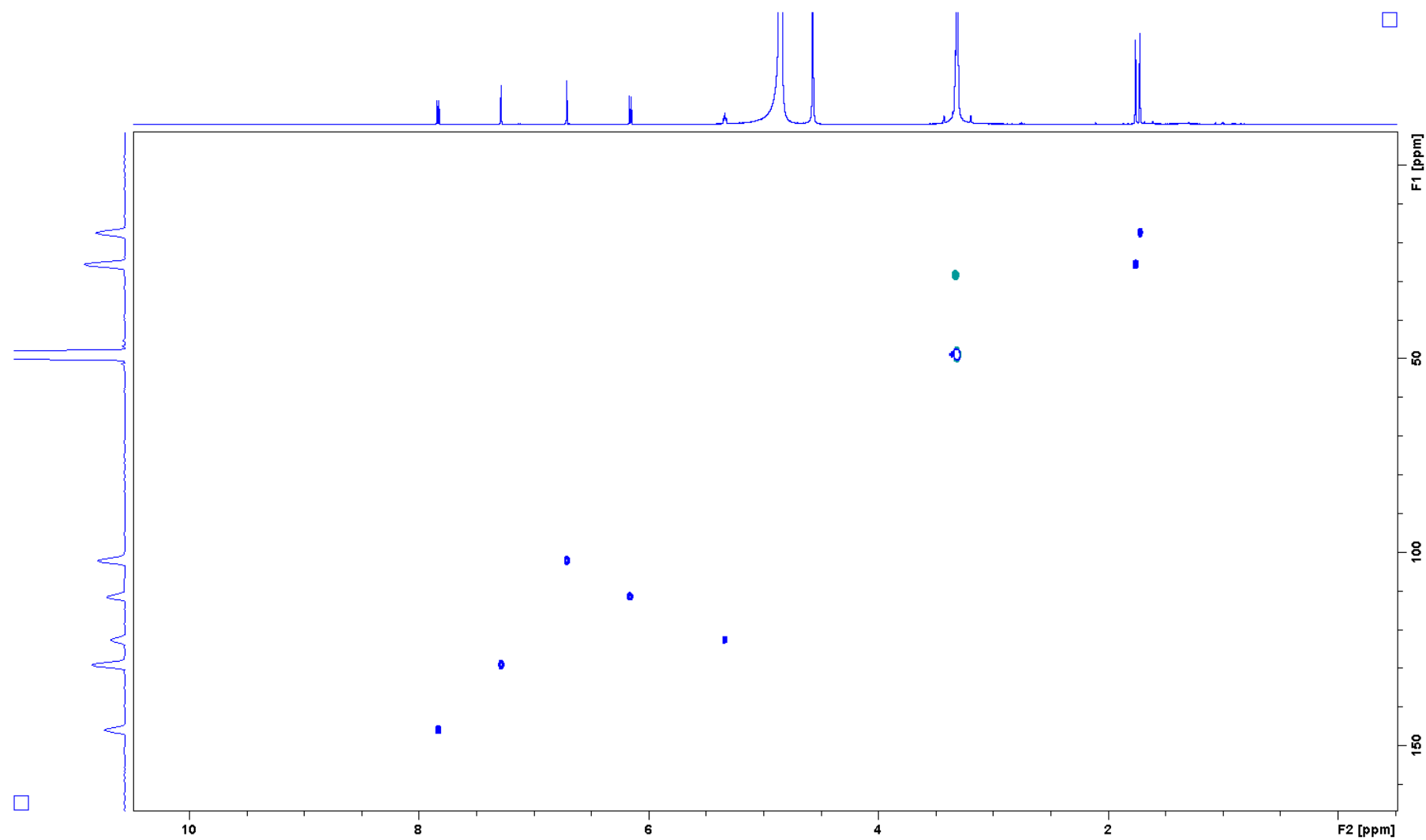


Figure S30. ^1H NMR spectrum of **4** (600 MHz, methanol- d_4).

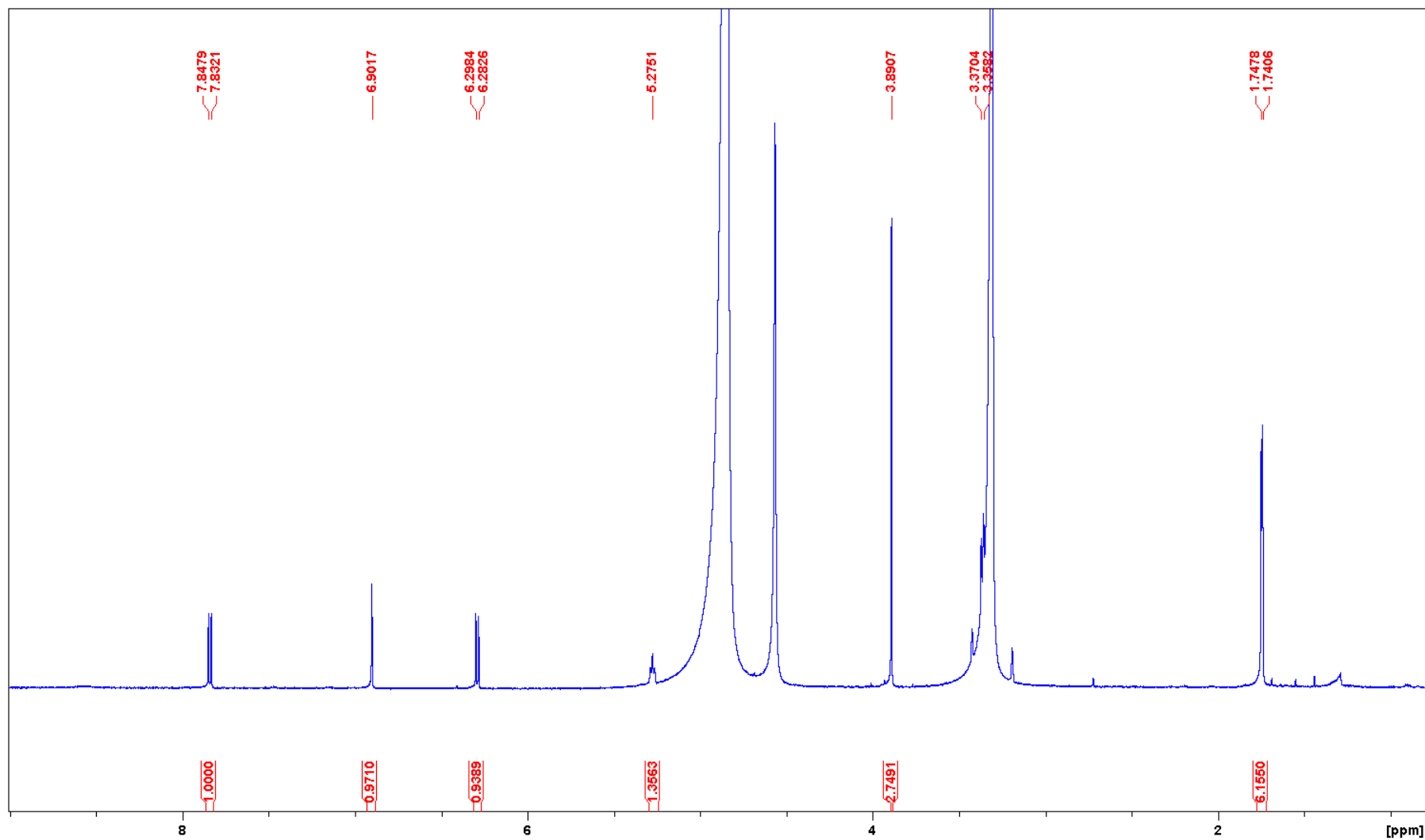


Figure S31. COSY spectrum of **4** (600 MHz, methanol- d_4).

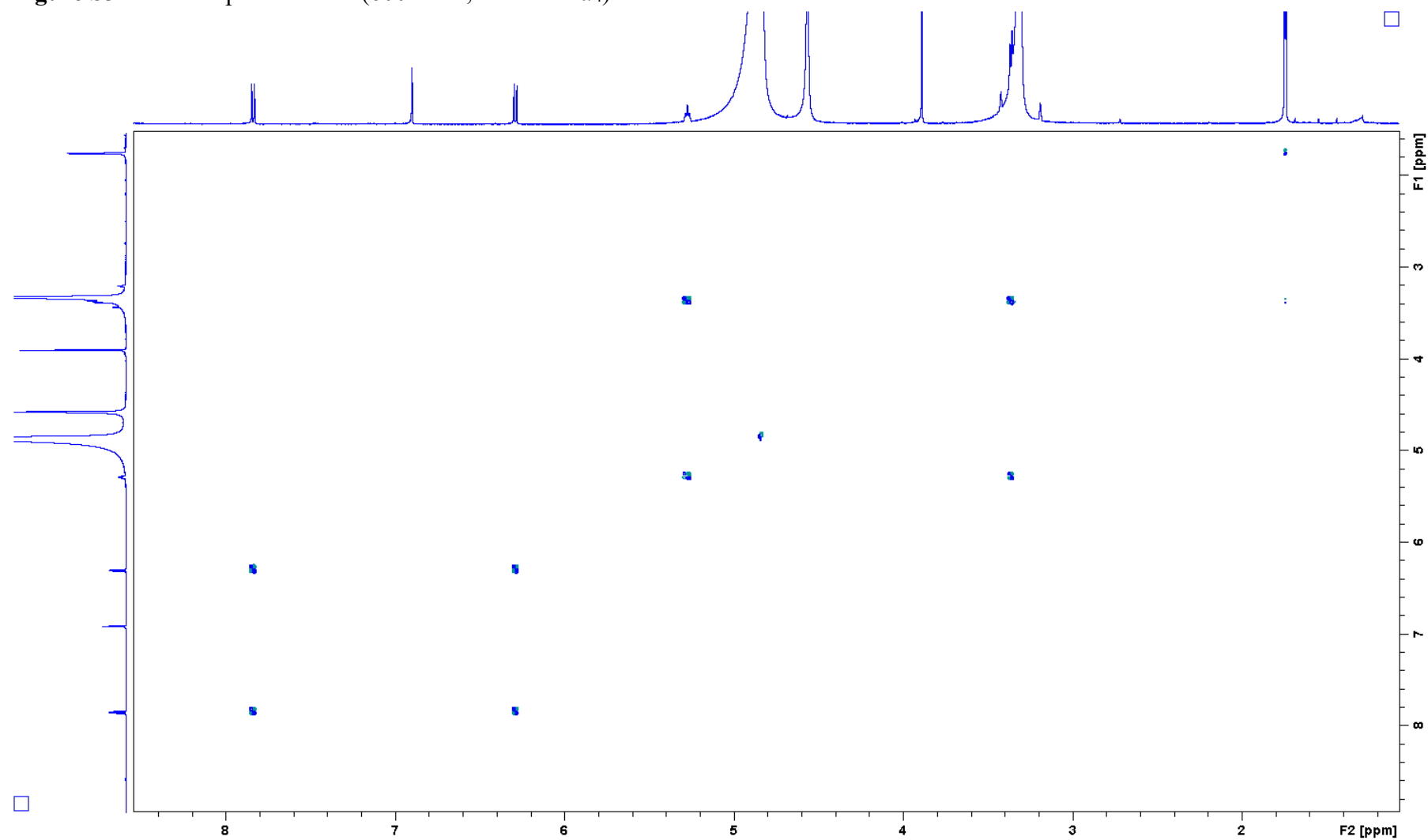


Figure S32. HSQC spectrum of **4** (600 MHz, methanol- d_4).

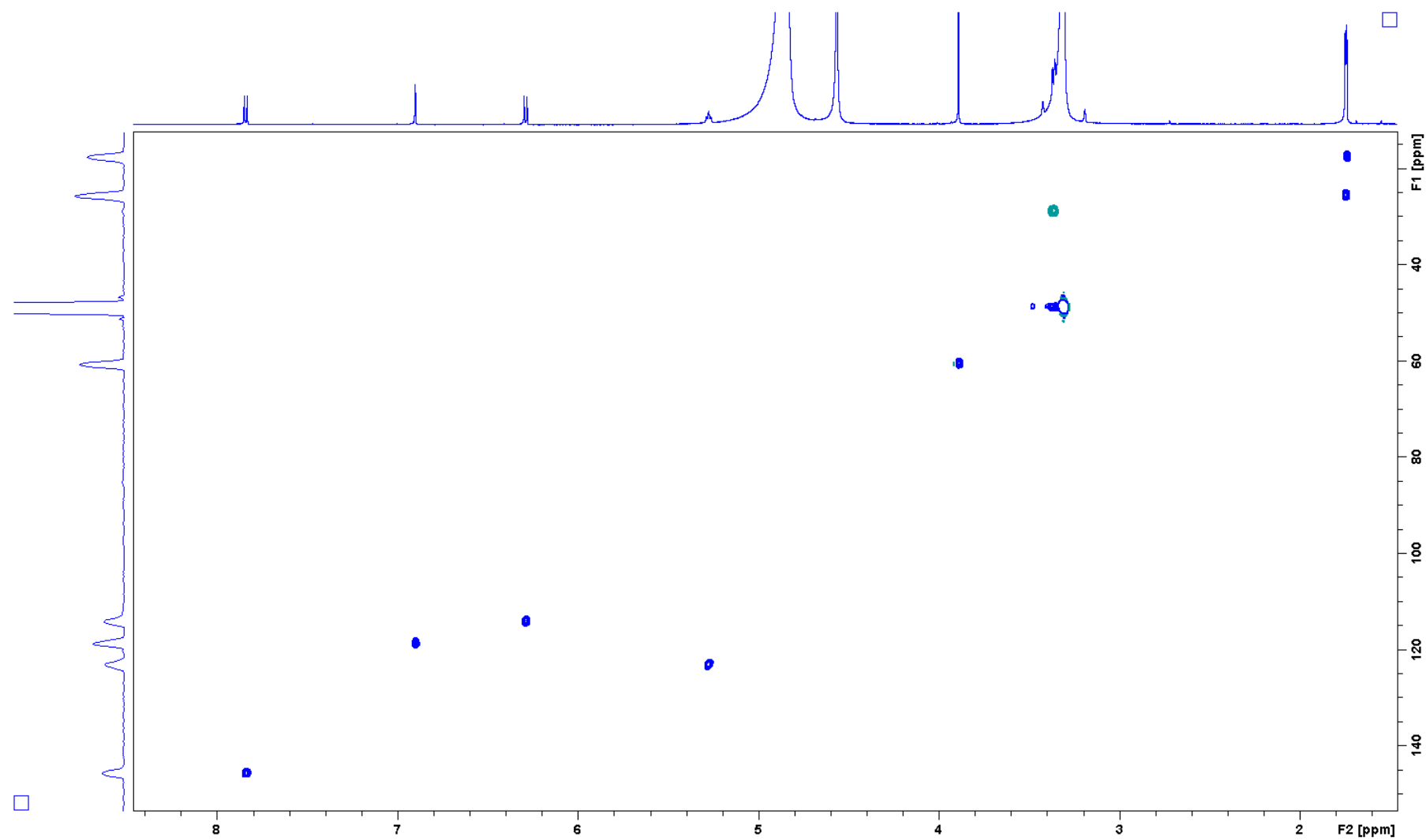


Figure S33. ^1H NMR spectrum of **5** (600 MHz, methanol- d_4).

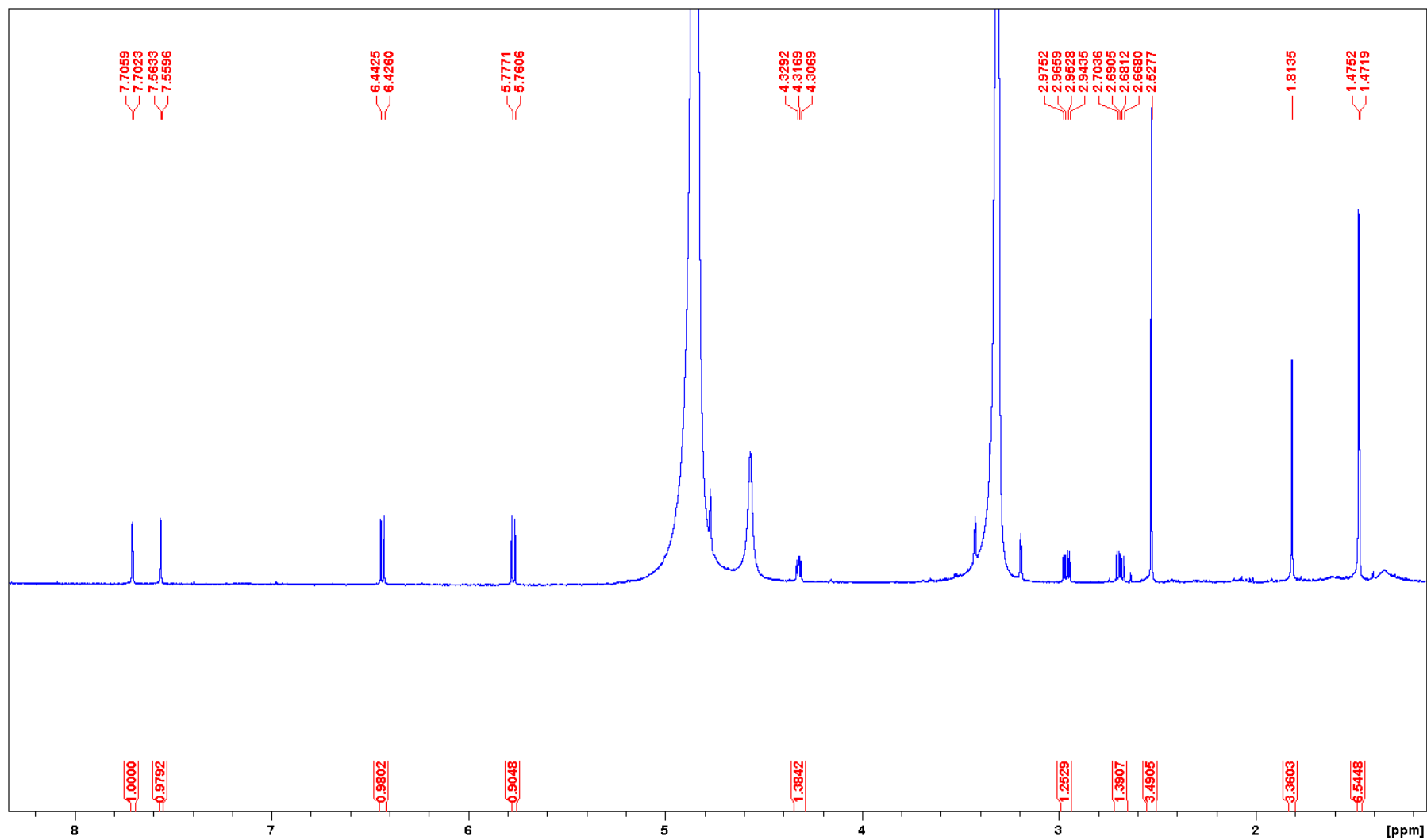


Figure S34. ^{13}C NMR spectrum of **5** (151 MHz, methanol- d_4).

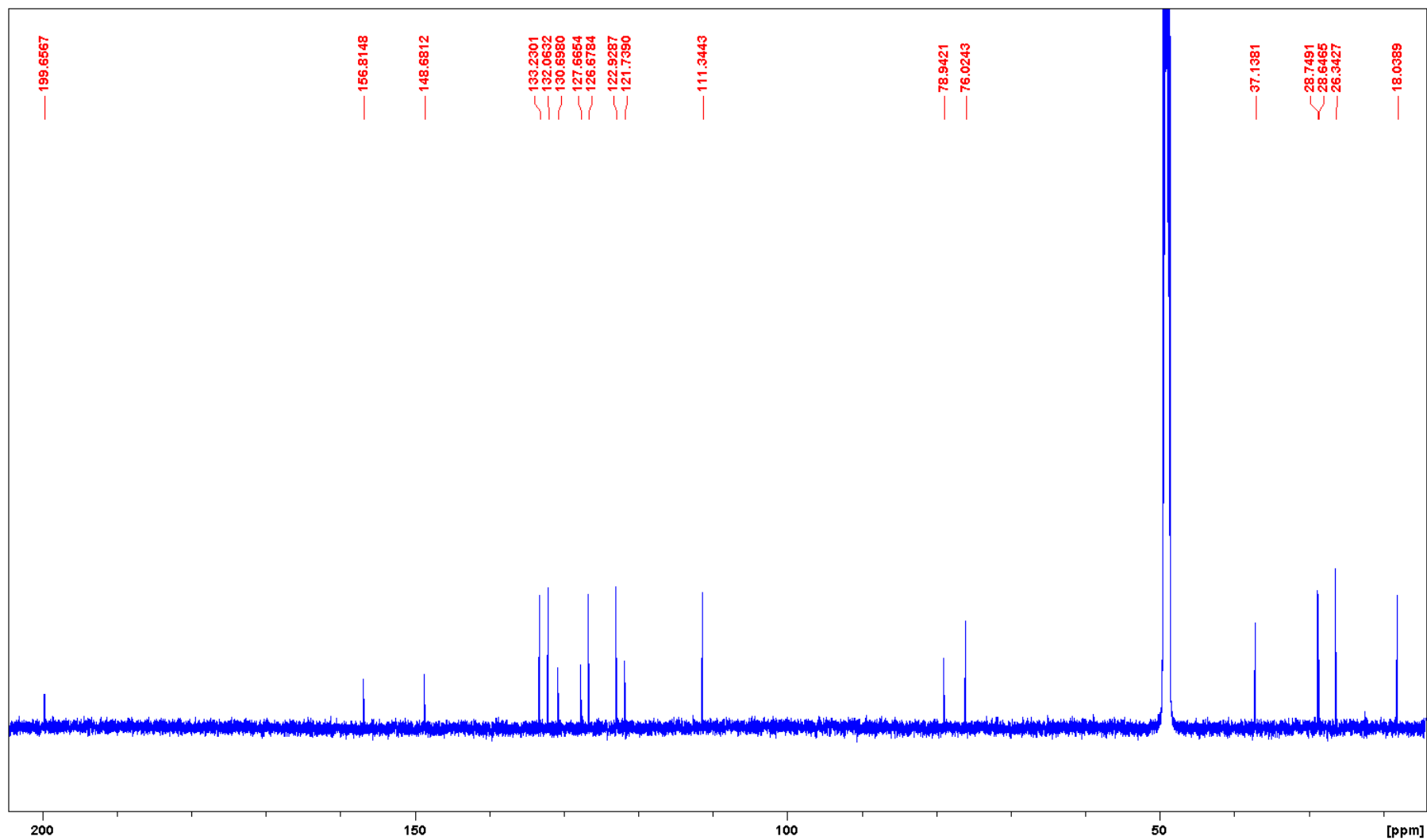


Figure S35. HSQC spectrum of **5** (600 MHz, methanol- d_4).

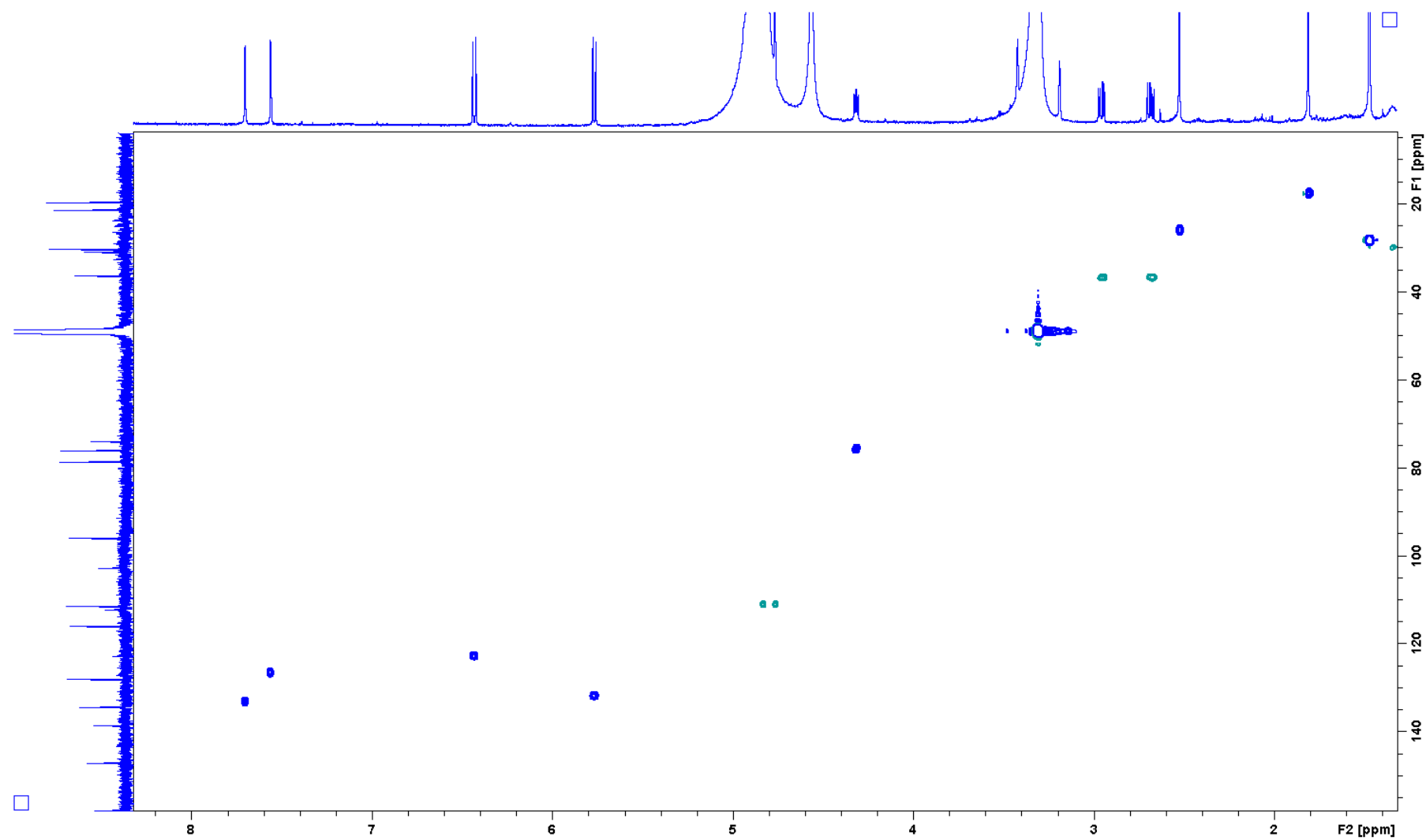


Figure S36. COSY spectrum of **5** (600 MHz, methanol- d_4).

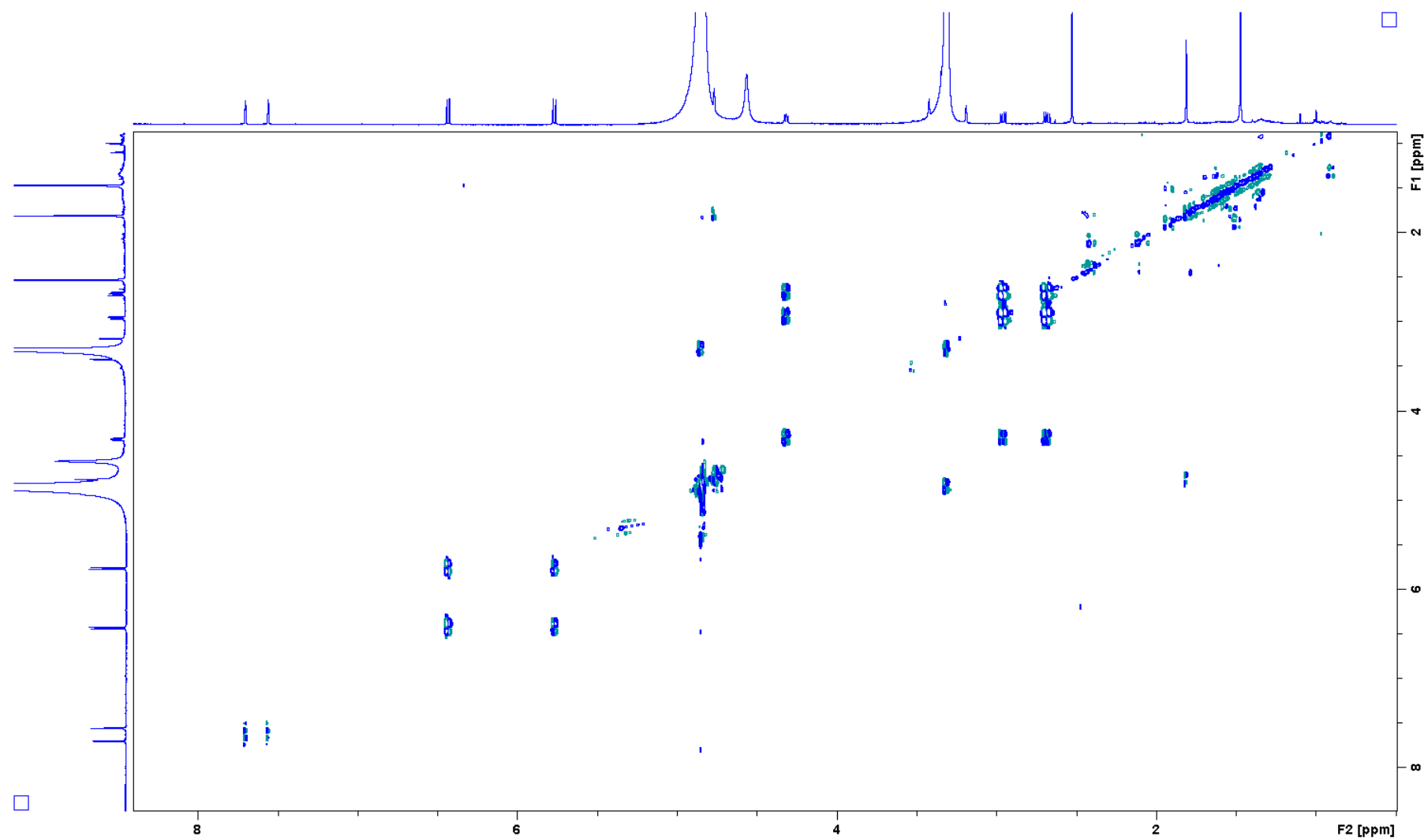


Figure S37. HMBC spectrum of **5** (600 MHz, methanol-*d*₄).

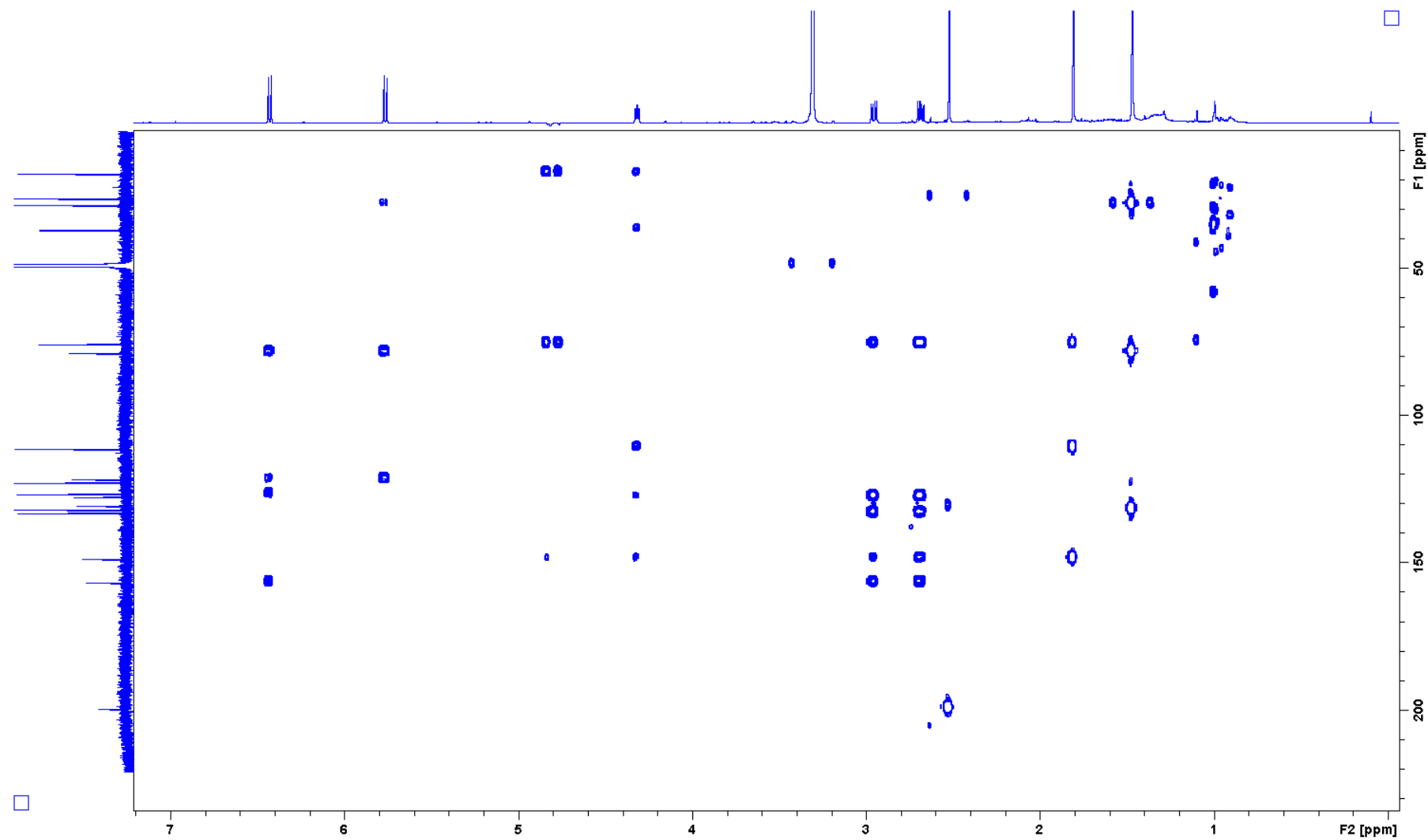


Figure S38. ROESY spectrum of **5** (600 MHz, methanol- d_4).

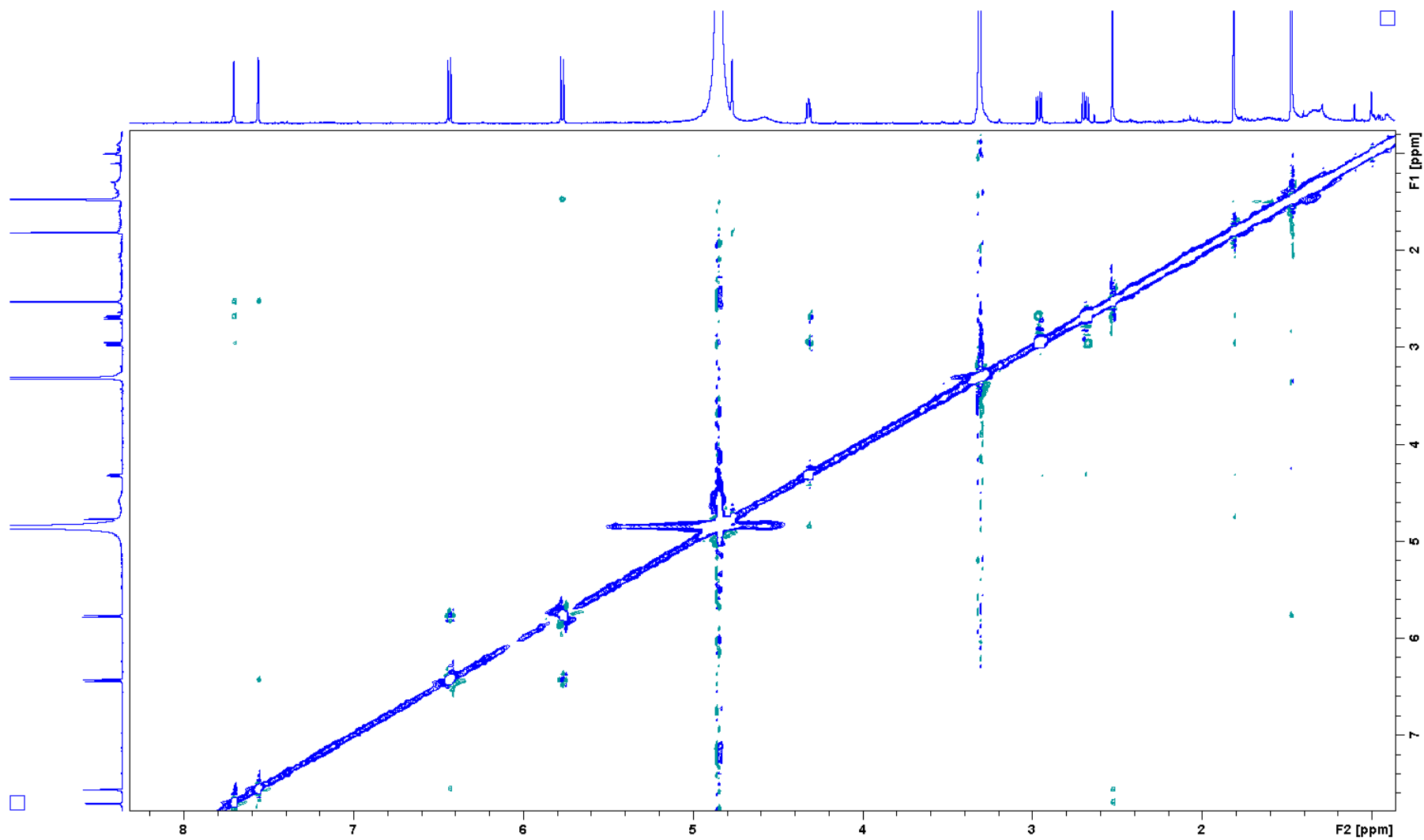


Figure S39. ^1H NMR spectrum of **6** (600 MHz, methanol- d_4).

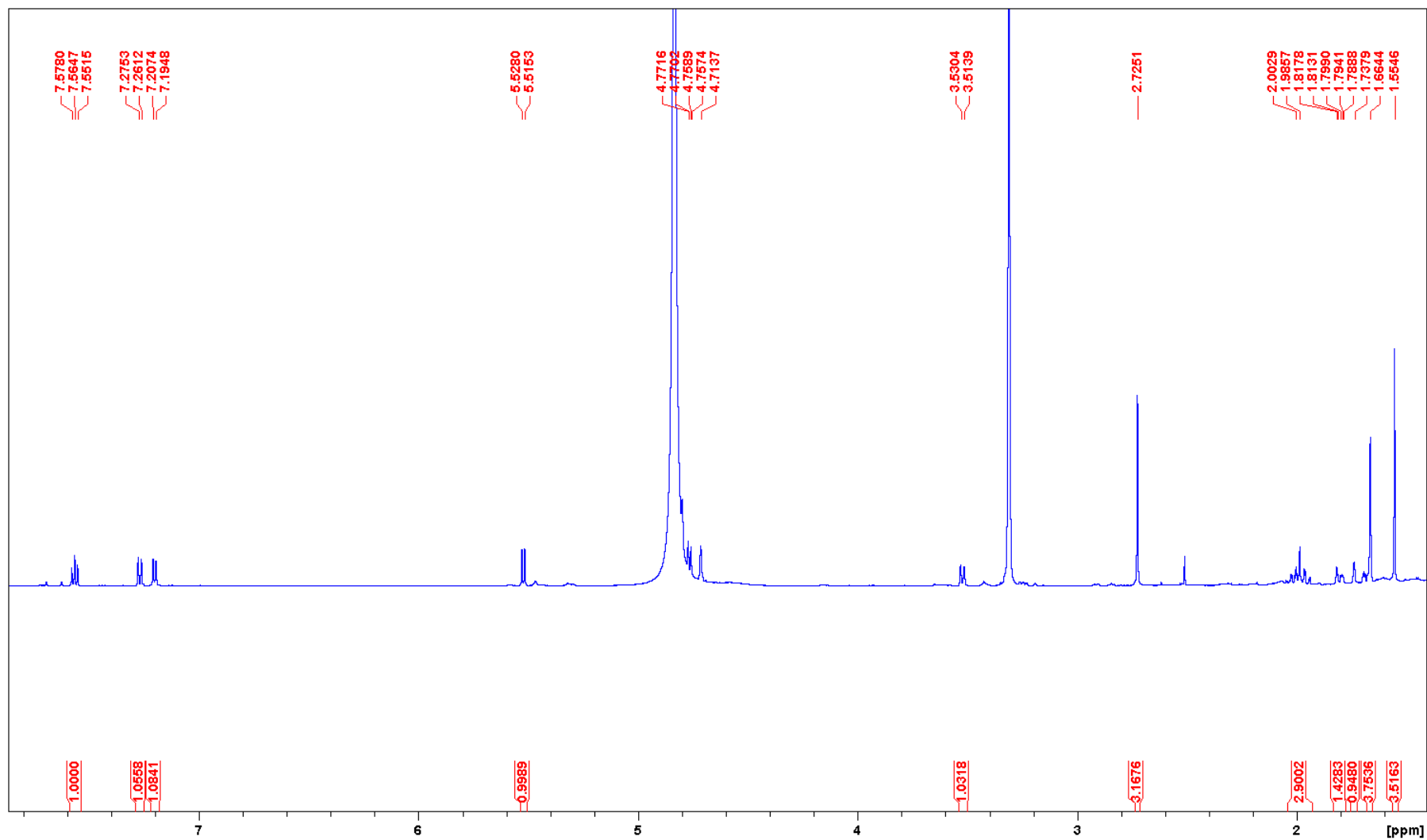


Figure S40. ^{13}C NMR spectrum of **6** (151 MHz, methanol- d_4).

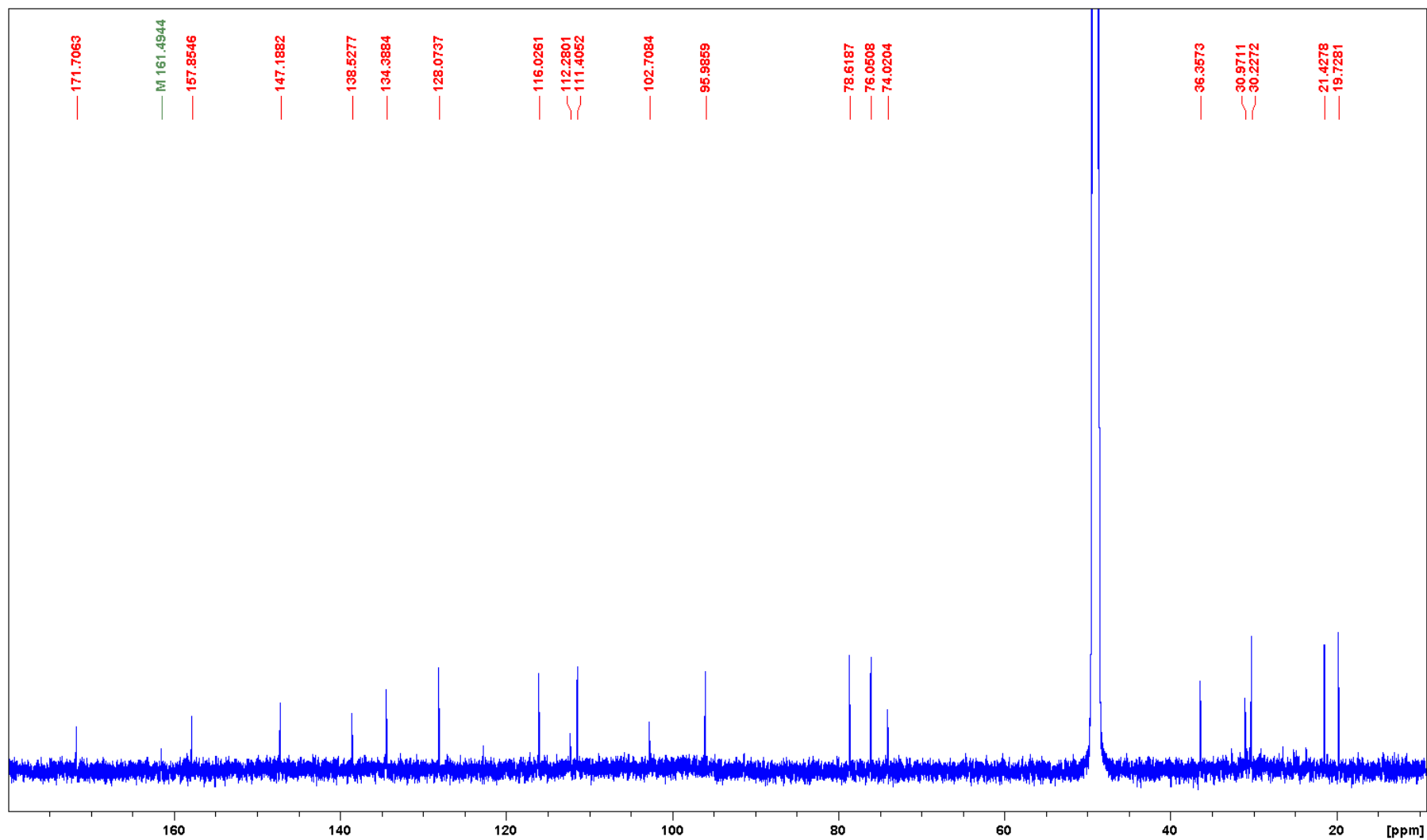


Figure S41. HSQC spectrum of **6** (600 MHz, methanol- d_4).

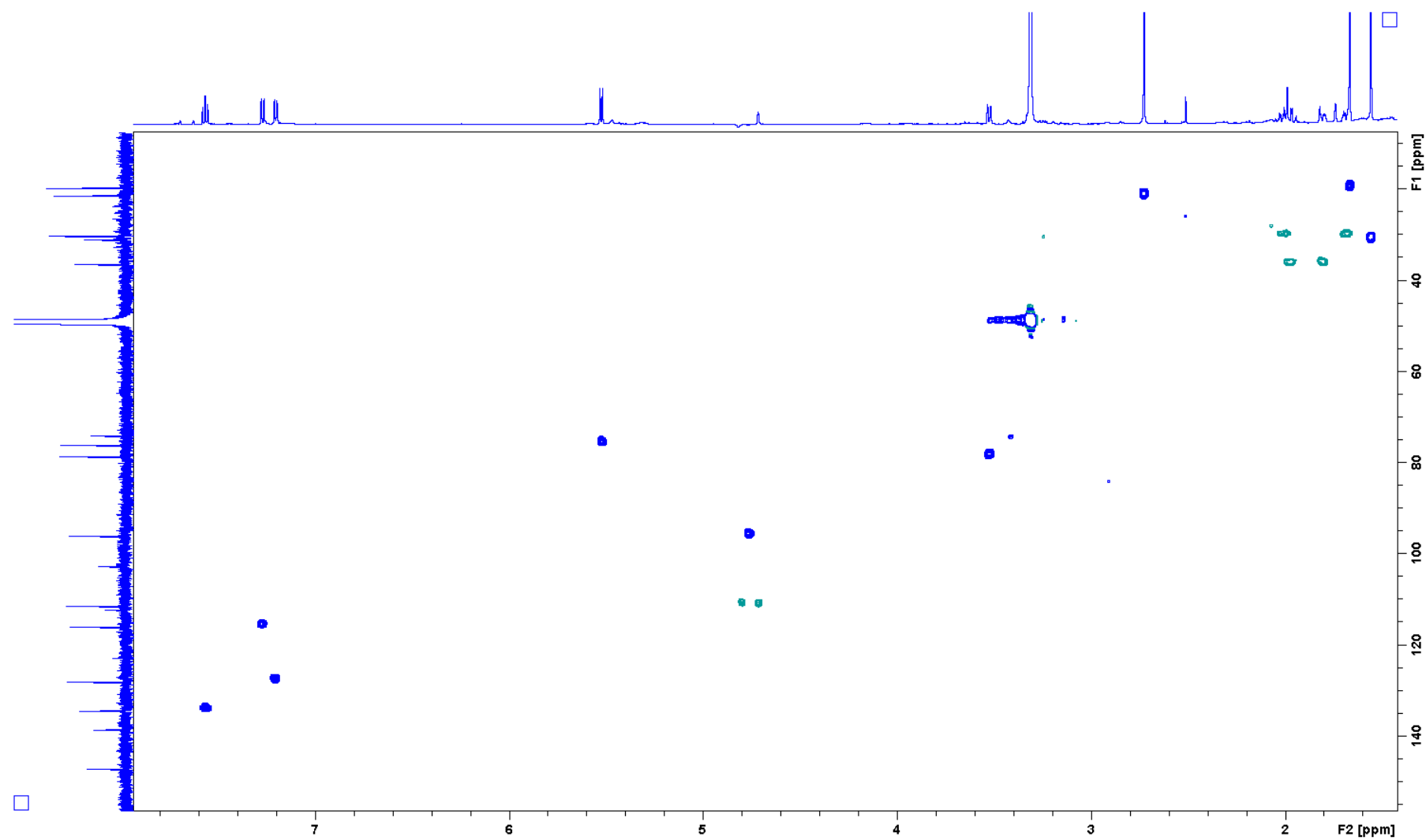


Figure S42. COSY spectrum of **6** (600 MHz, methanol- d_4).

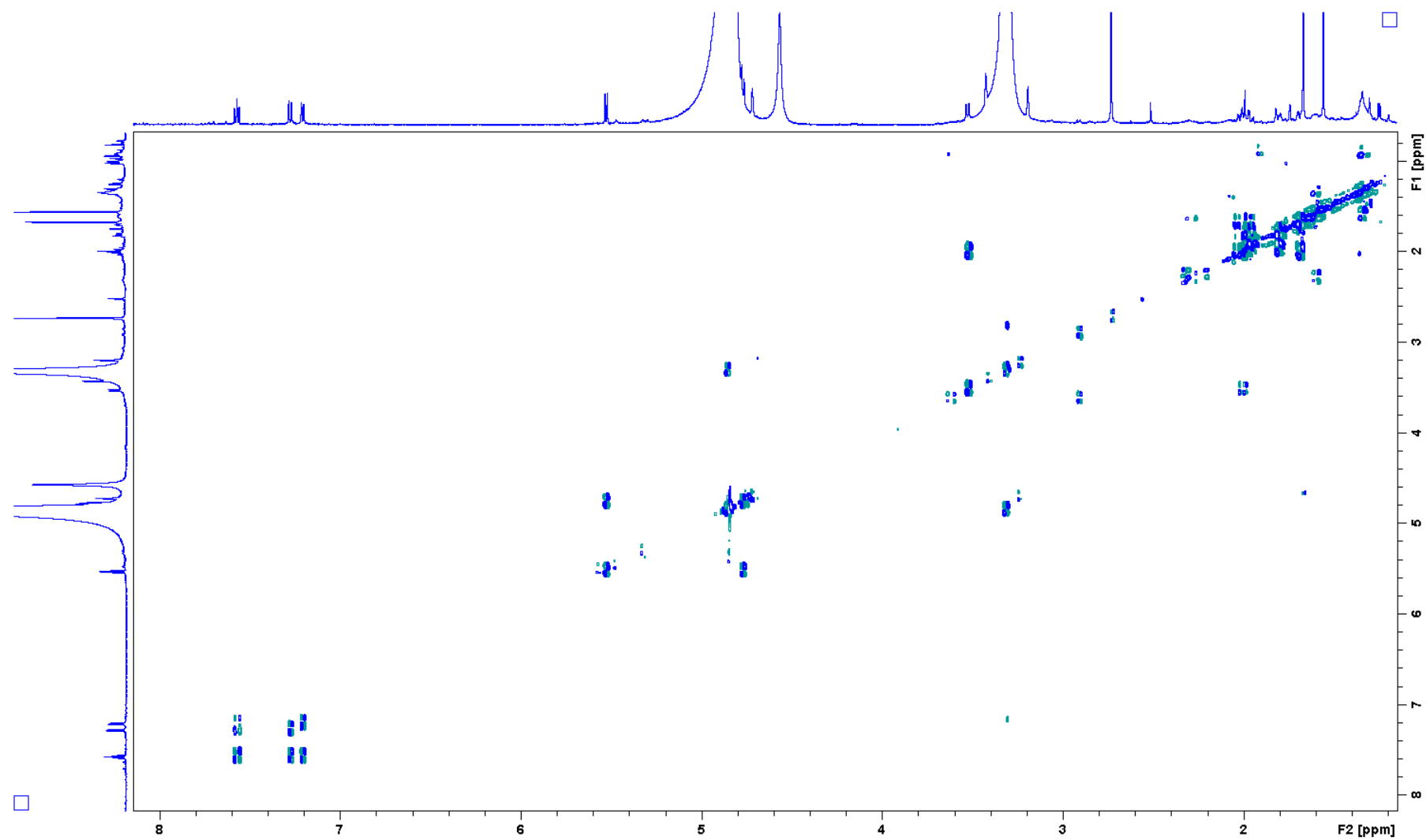


Figure S43. HMBC spectrum of **6** (600 MHz, methanol-*d*₄).

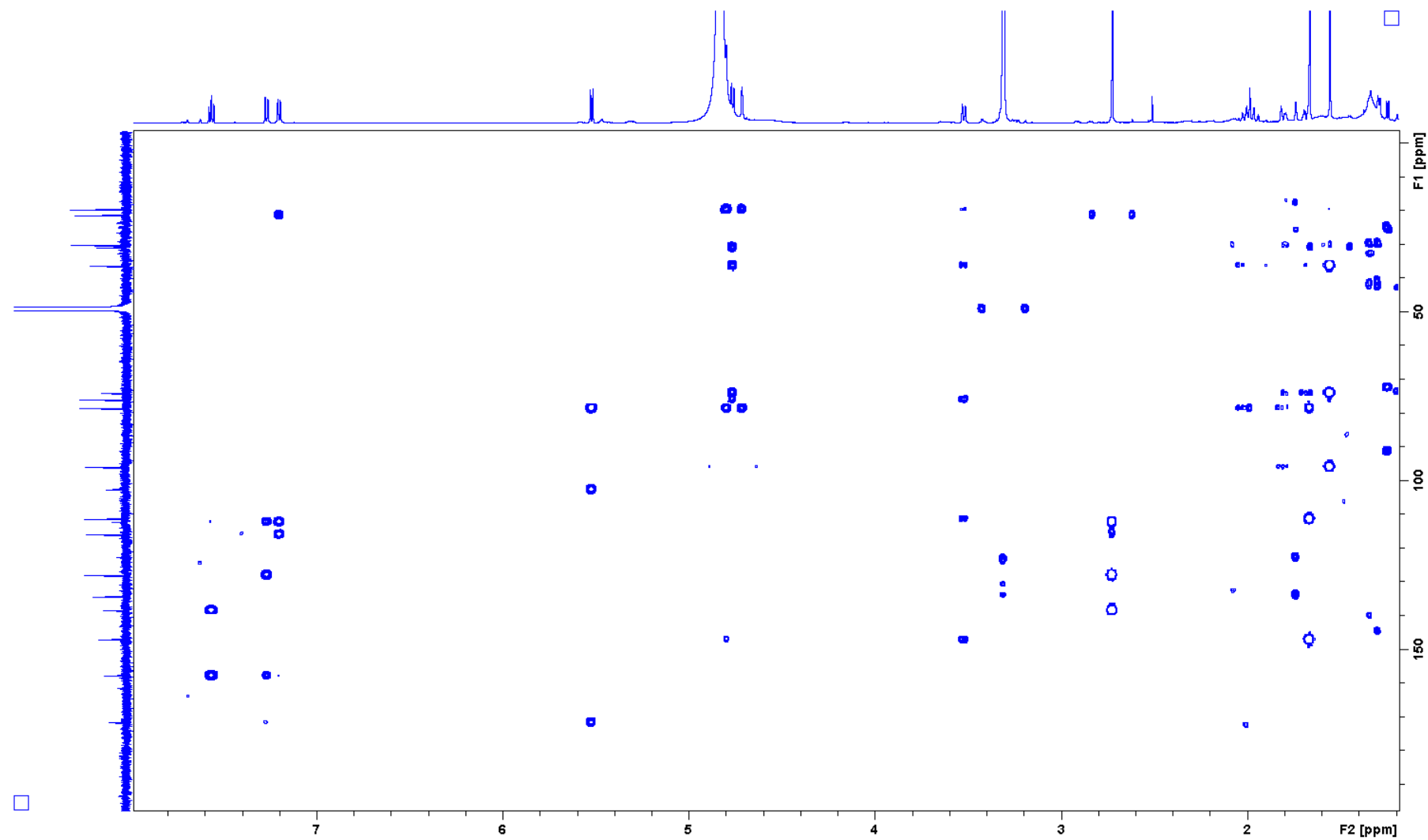


Figure S44. ROESY spectrum of **6** (600 MHz, methanol- d_4).

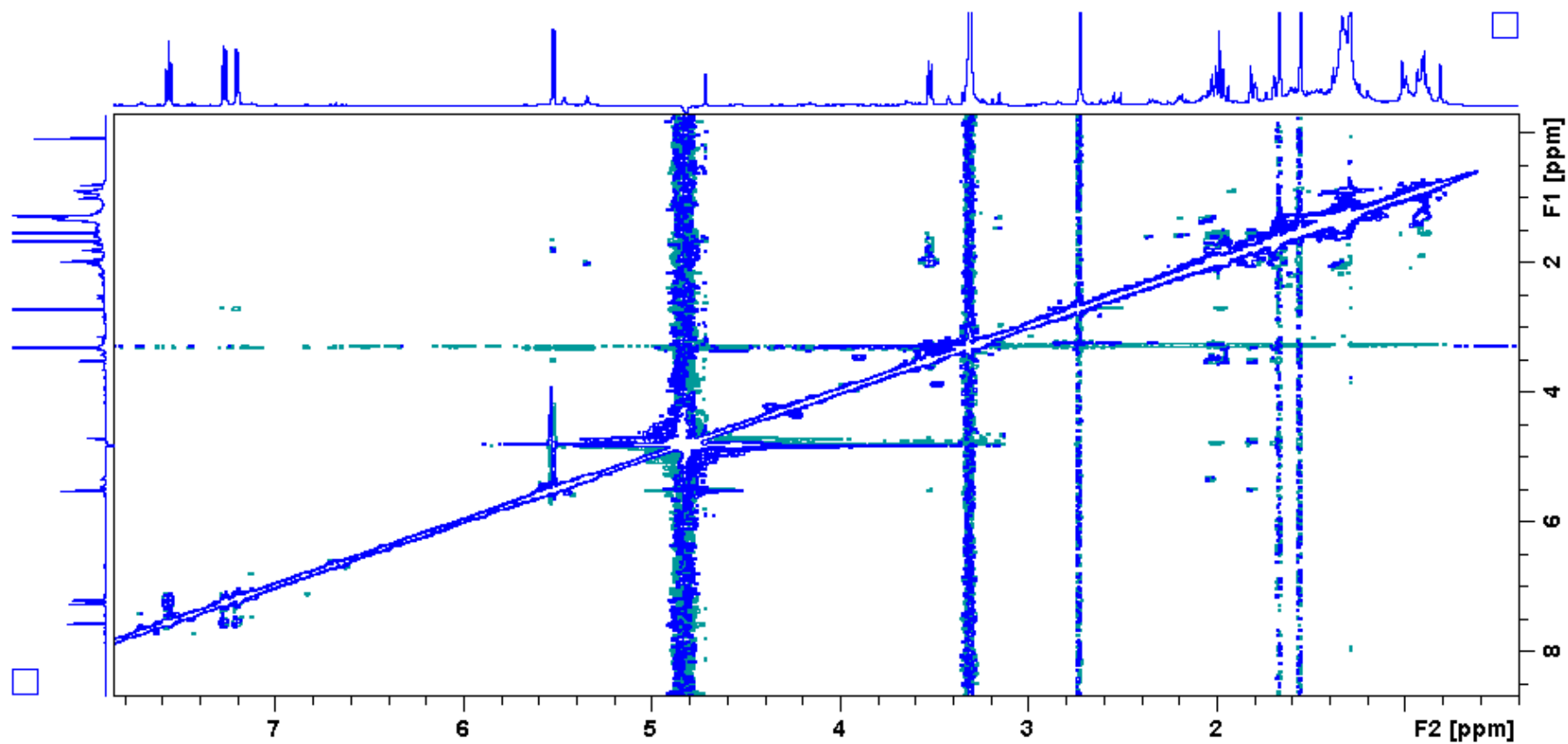


Figure S45. ^1H NMR spectrum of **7** (600 MHz, chloroform-*d*).

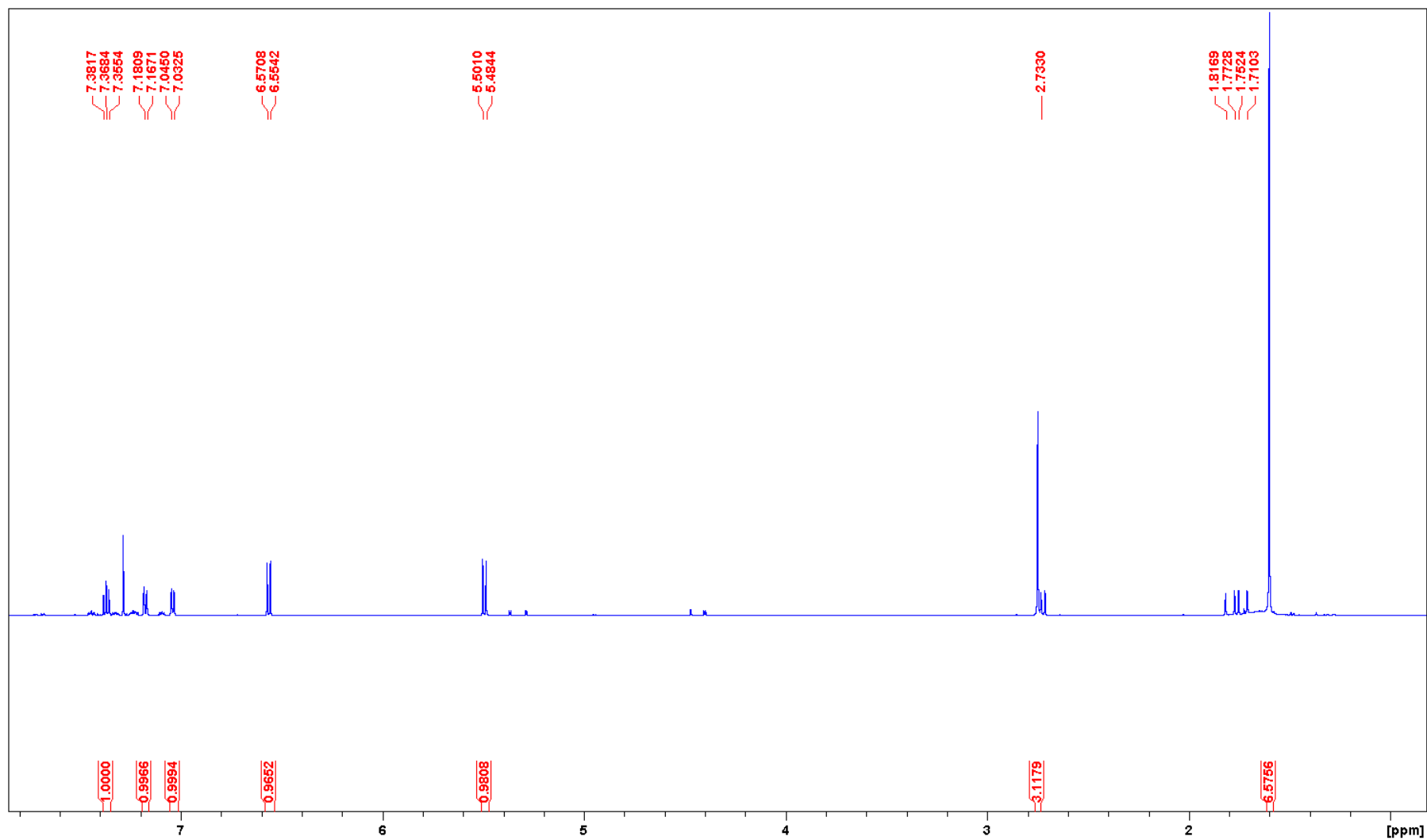


Figure S46. COSY spectrum of **7** (600 MHz, chloroform-*d*).

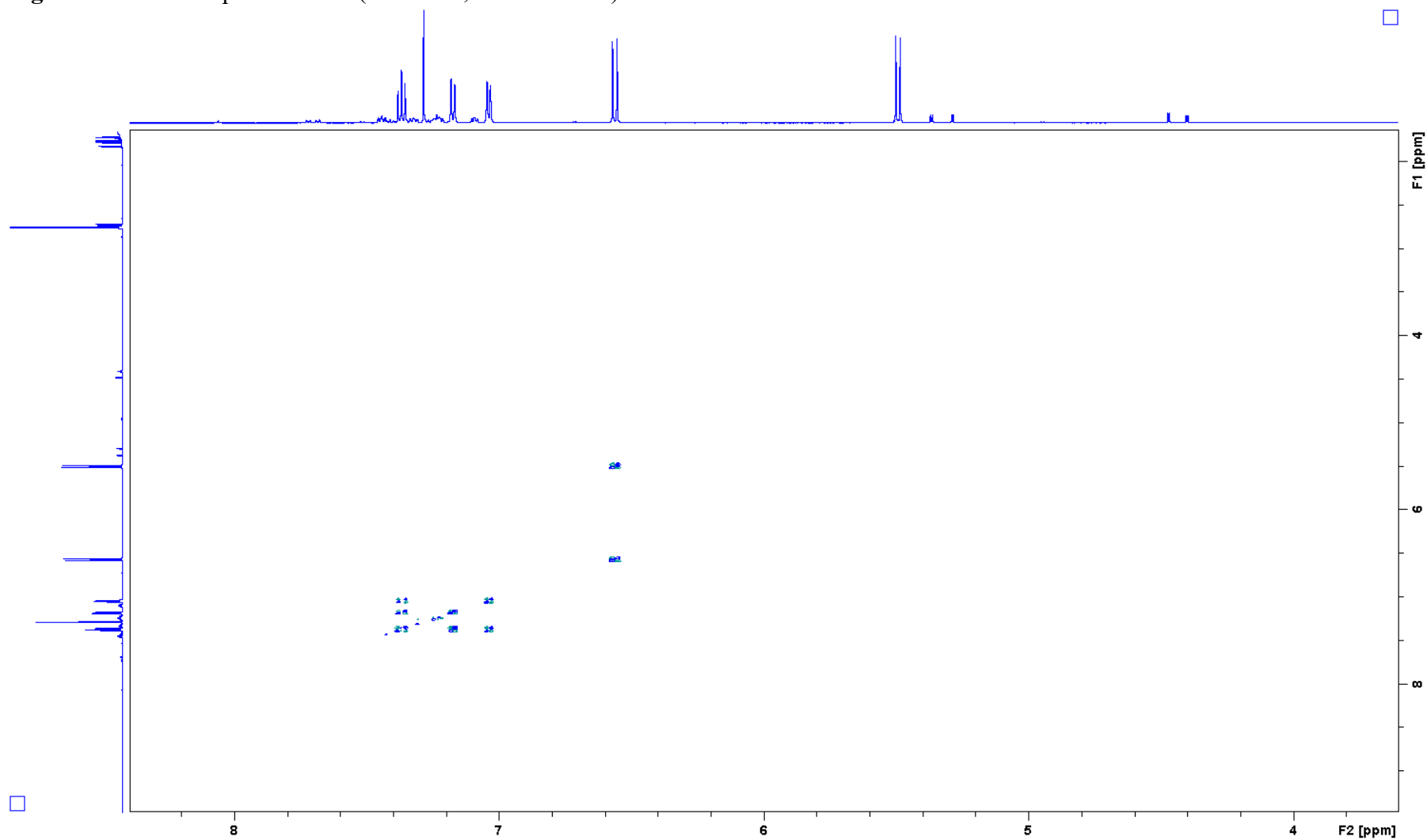


Figure S47. HQSC spectrum of **7** (600 MHz, chloroform-*d*).

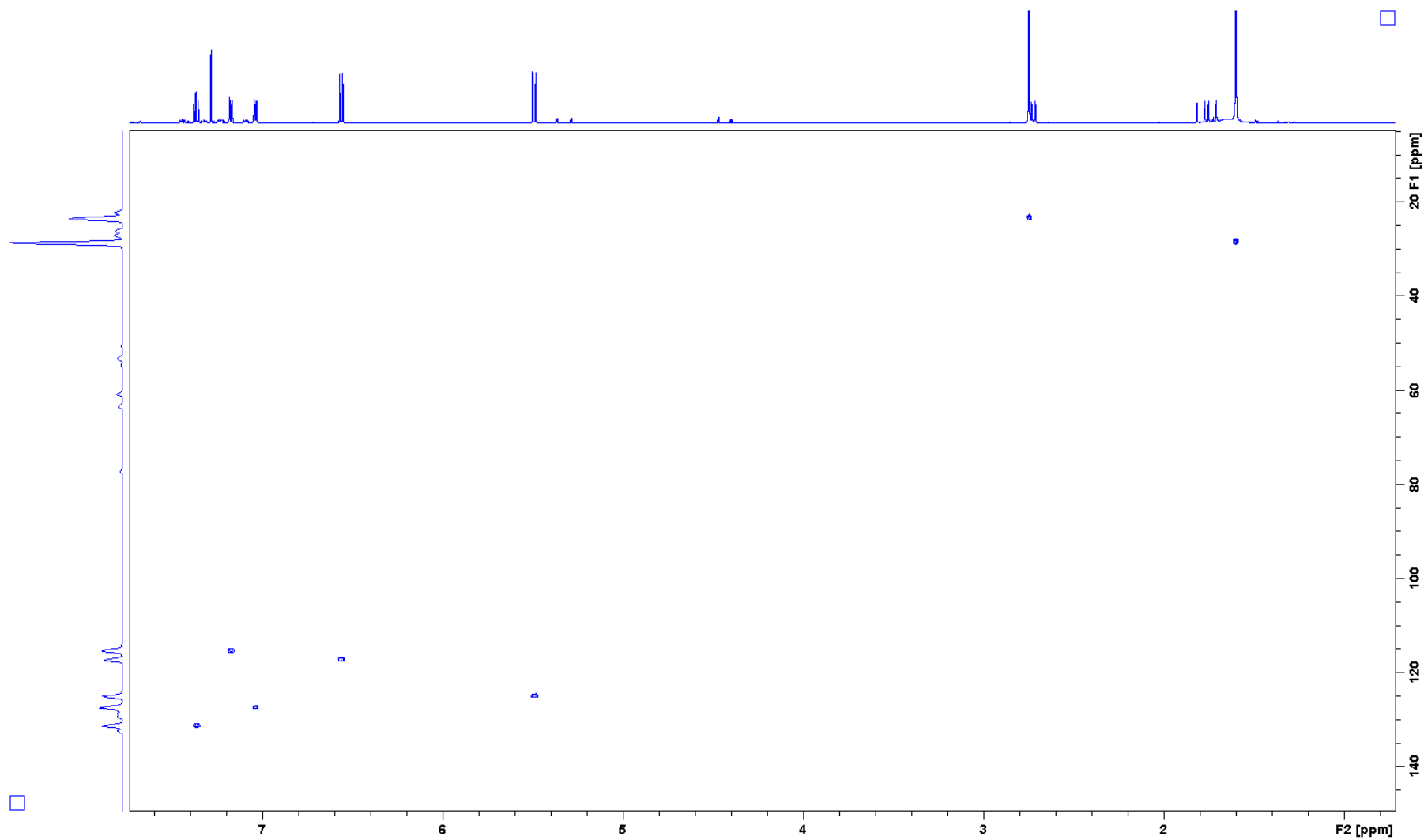


Figure S48. ^1H NMR spectrum of **8** (600 MHz, methanol- d_4).

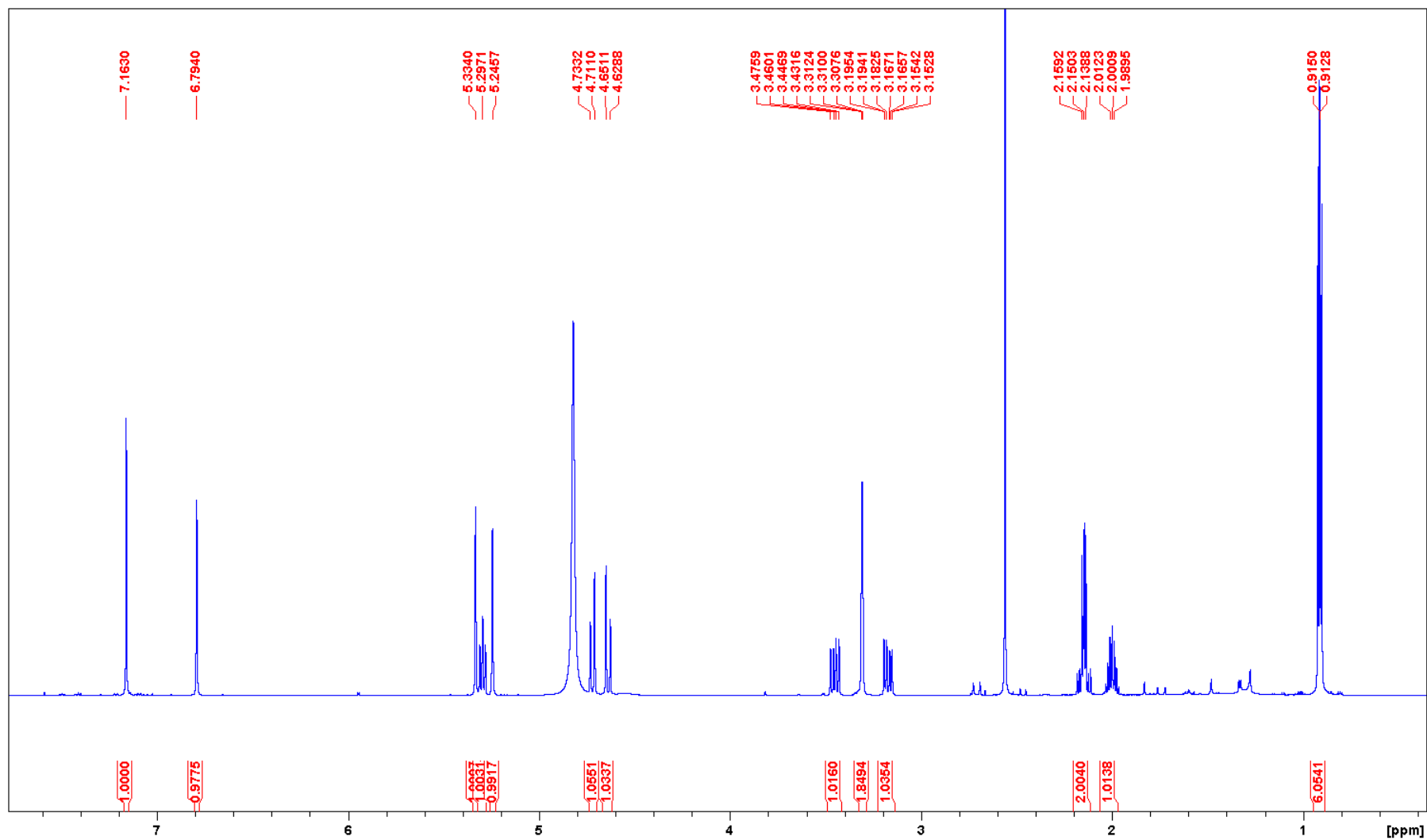


Figure S49. HSQC spectrum of **8** (600 MHz, methanol- d_4).

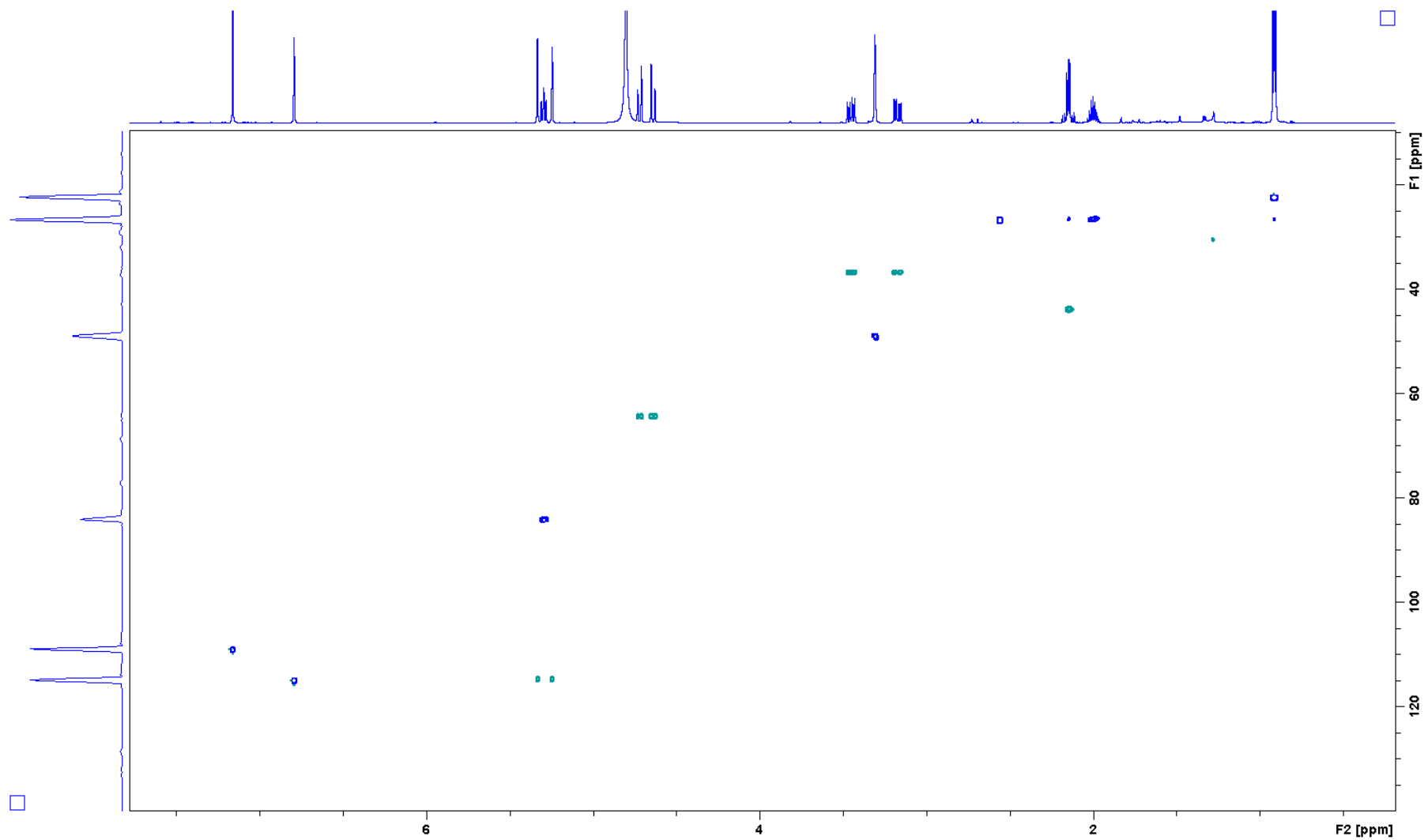


Figure S51. HMBC spectrum of **8** (600 MHz, methanol- d_4).

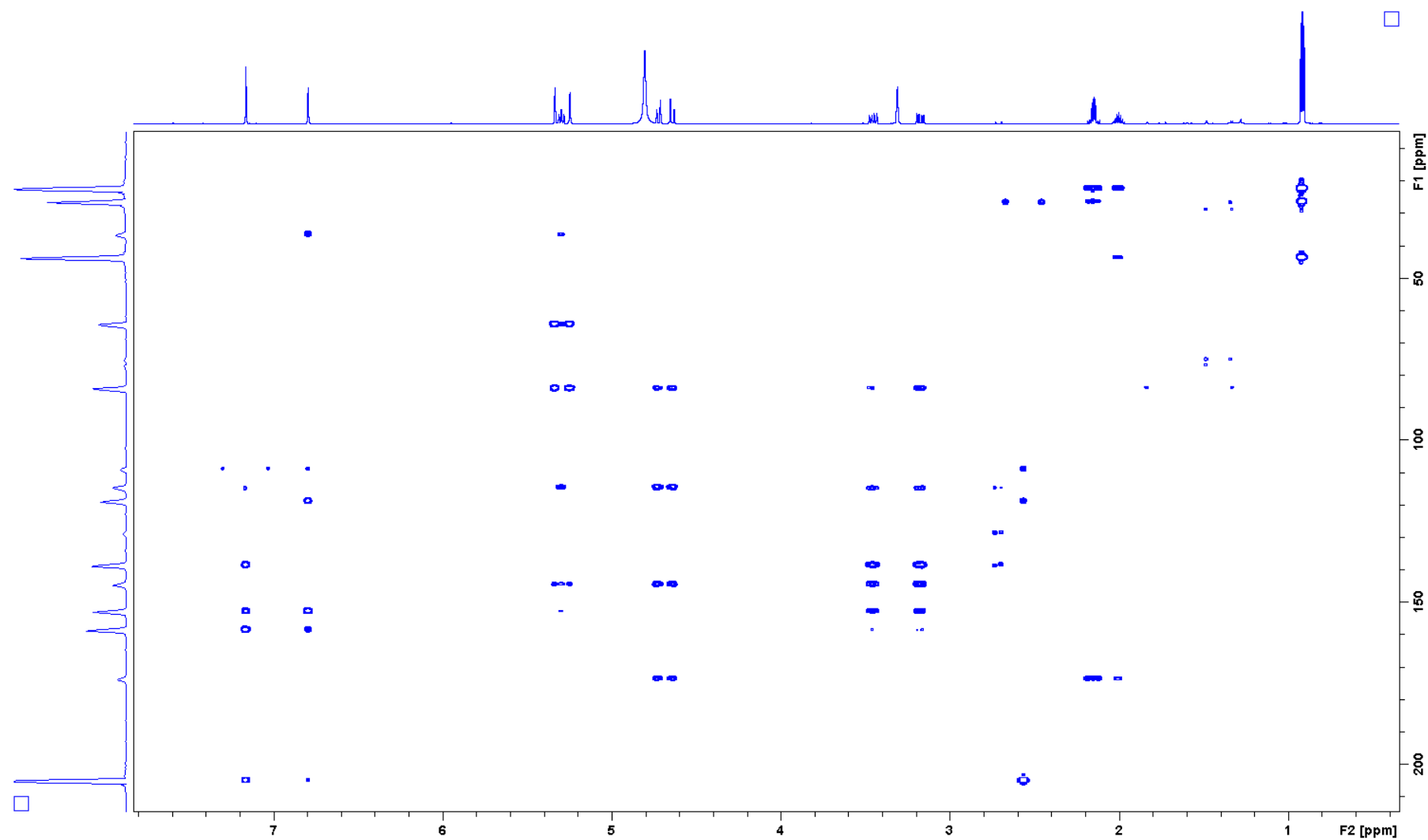


Figure S52. ROESY spectrum of **8** (600 MHz, methanol-*d*₄).

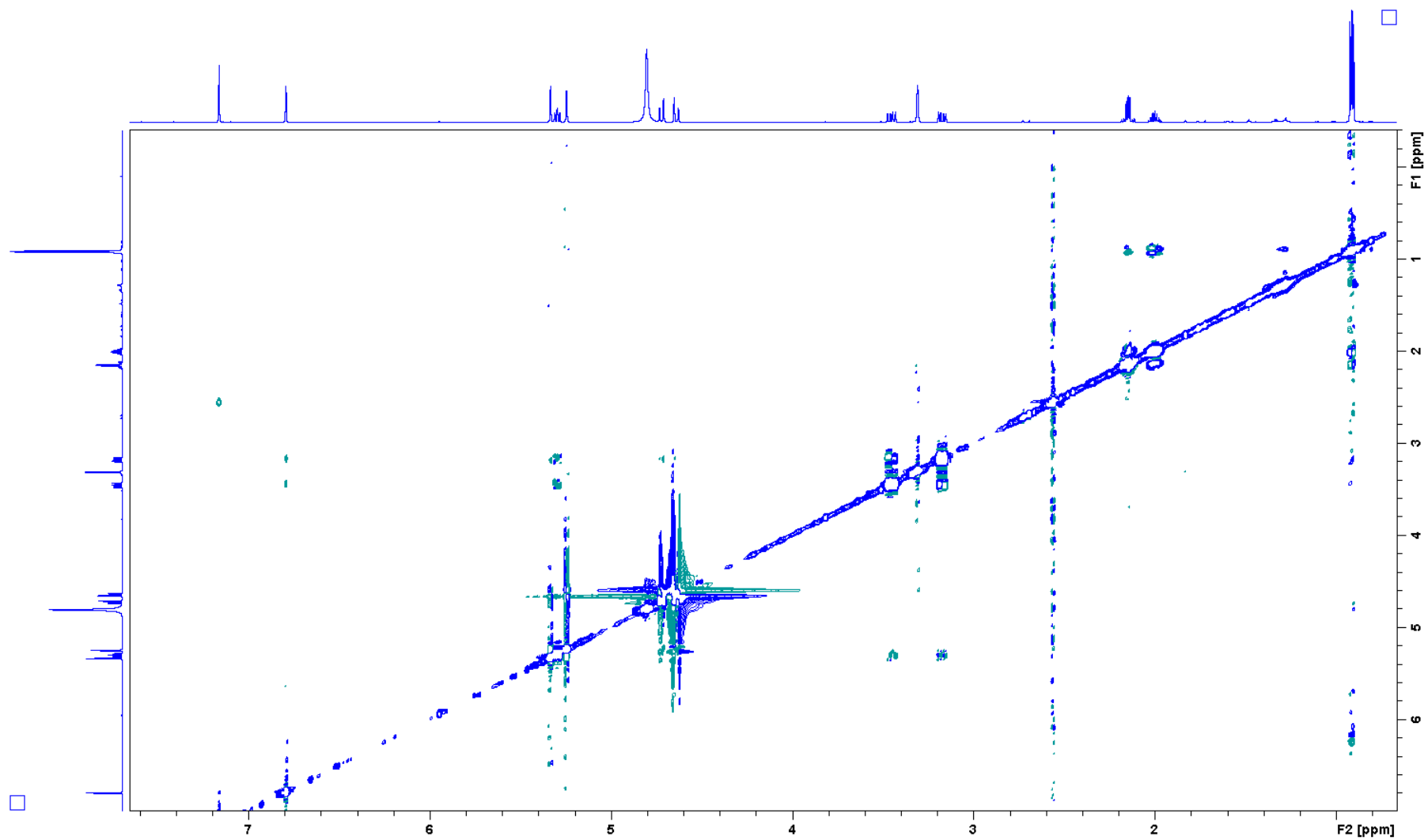


Figure S53. ^1H NMR spectrum of **9** (600 MHz, methanol- d_4).

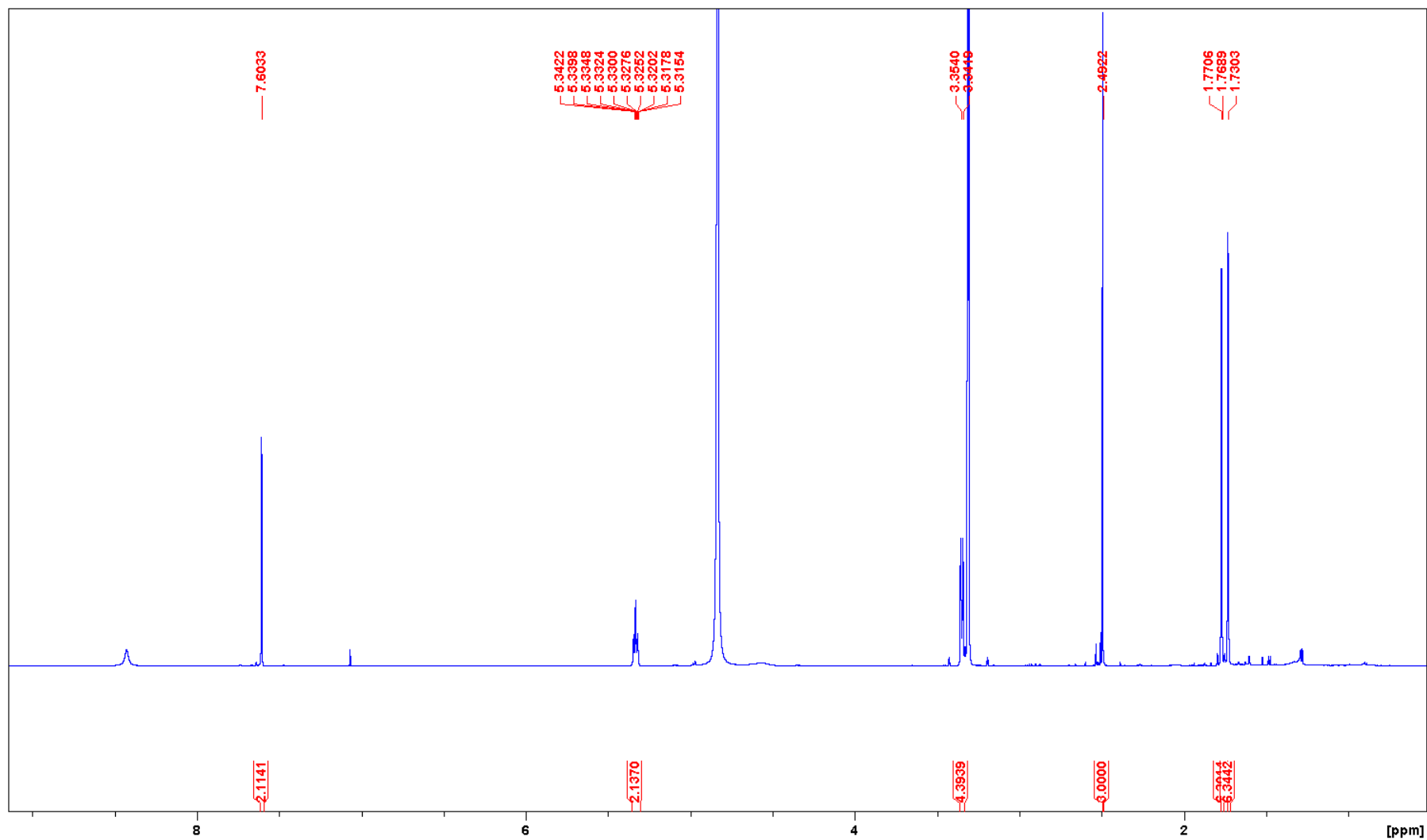


Figure S54. HSQC spectrum of **9** (600 MHz, methanol- d_4).

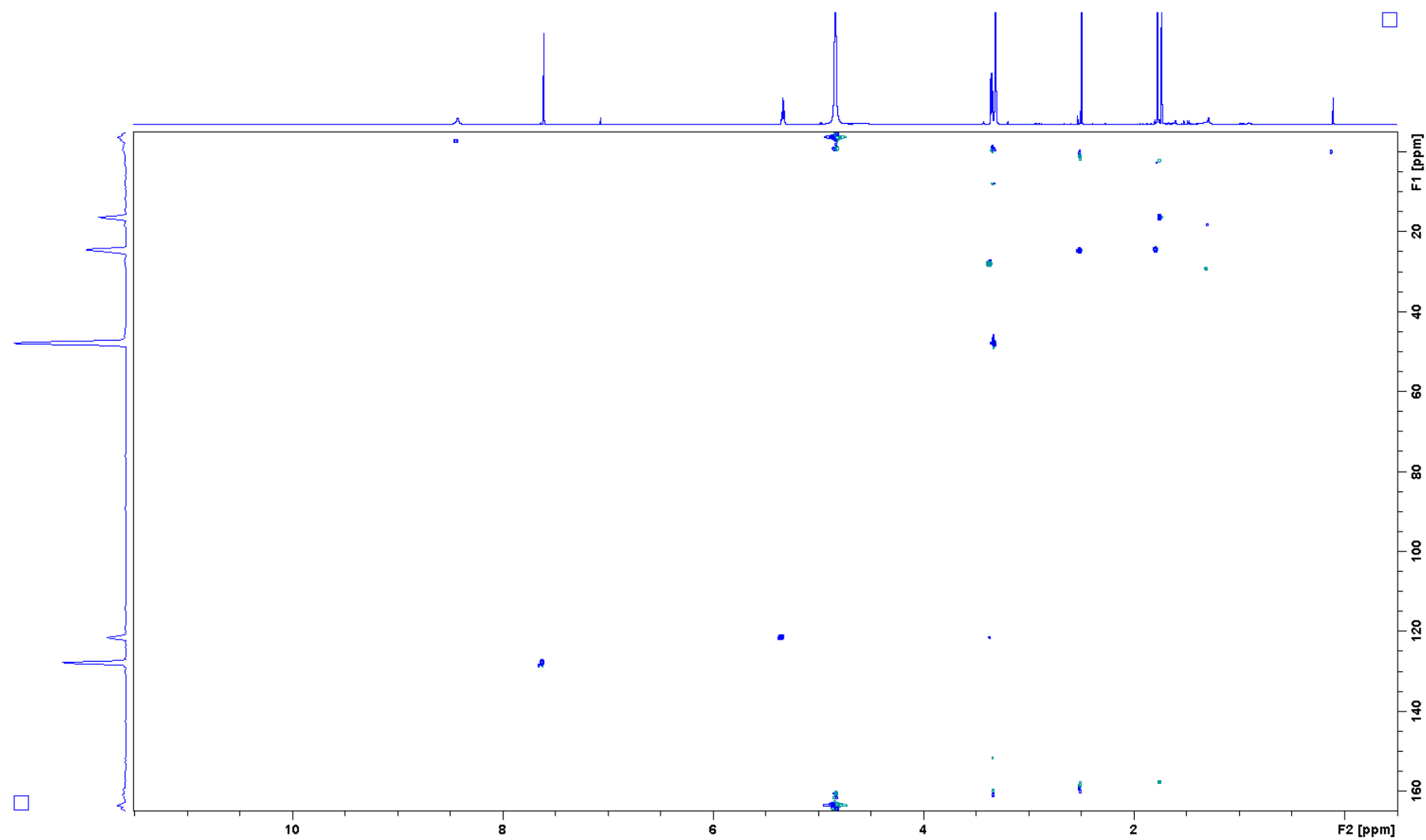


Figure S55. HMBC spectrum of **9** (600 MHz, methanol- d_4).

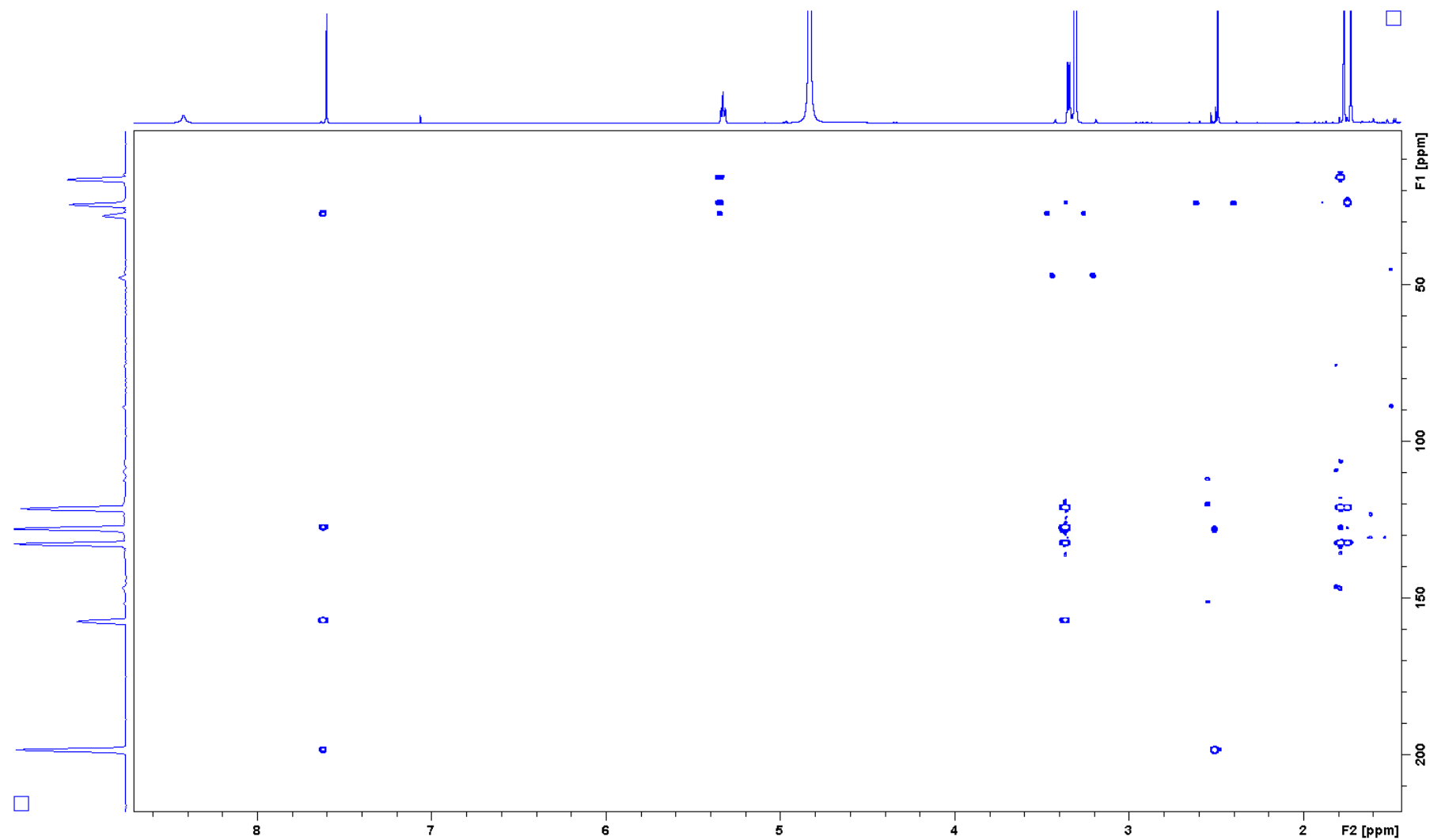


Figure S56. ^1H NMR spectrum of **10** (600 MHz, methanol- d_4).

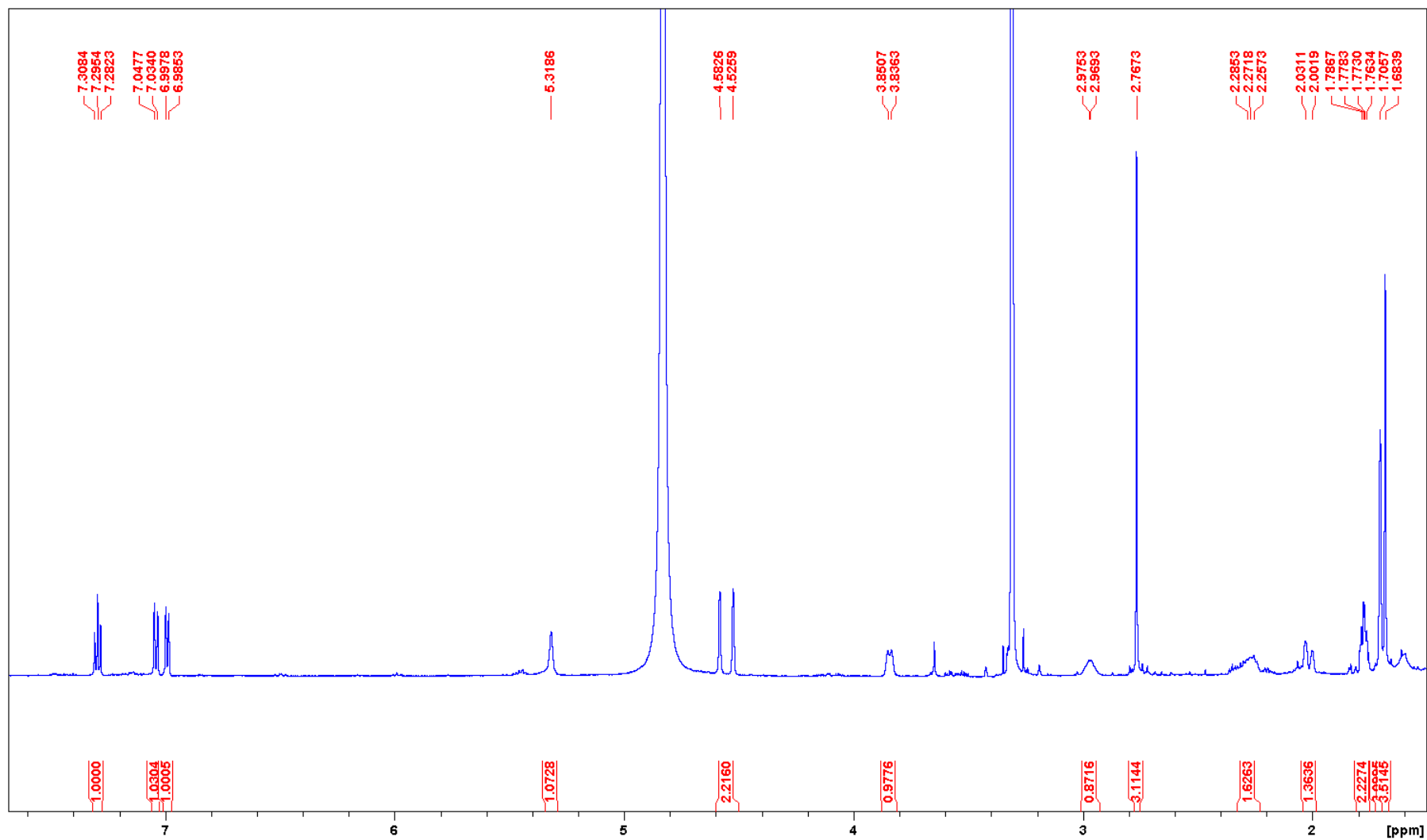


Figure S57. HSQC spectrum of **10** (600 MHz, methanol- d_4).

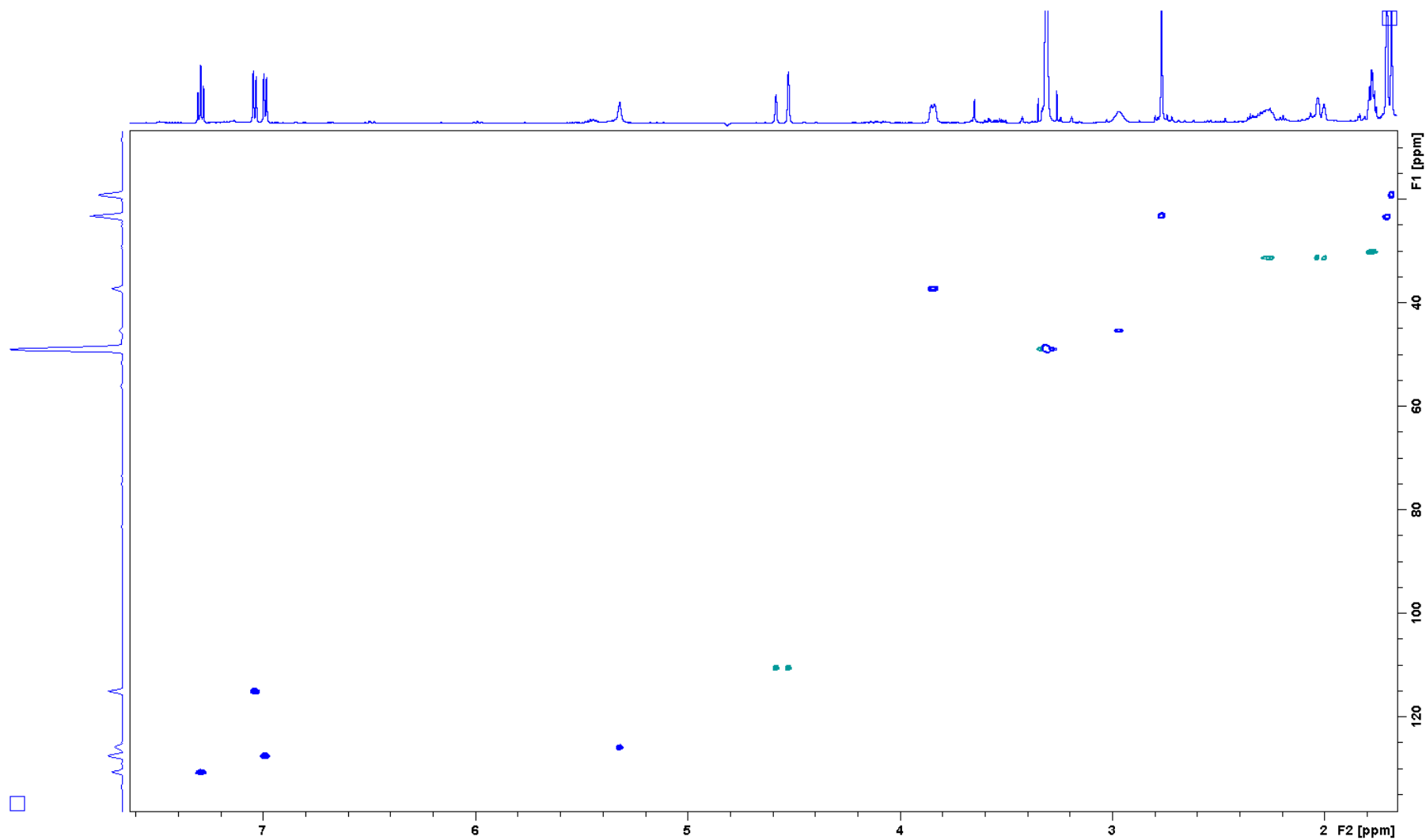


Figure S58. COSY spectrum of **10** (600 MHz, methanol- d_4).

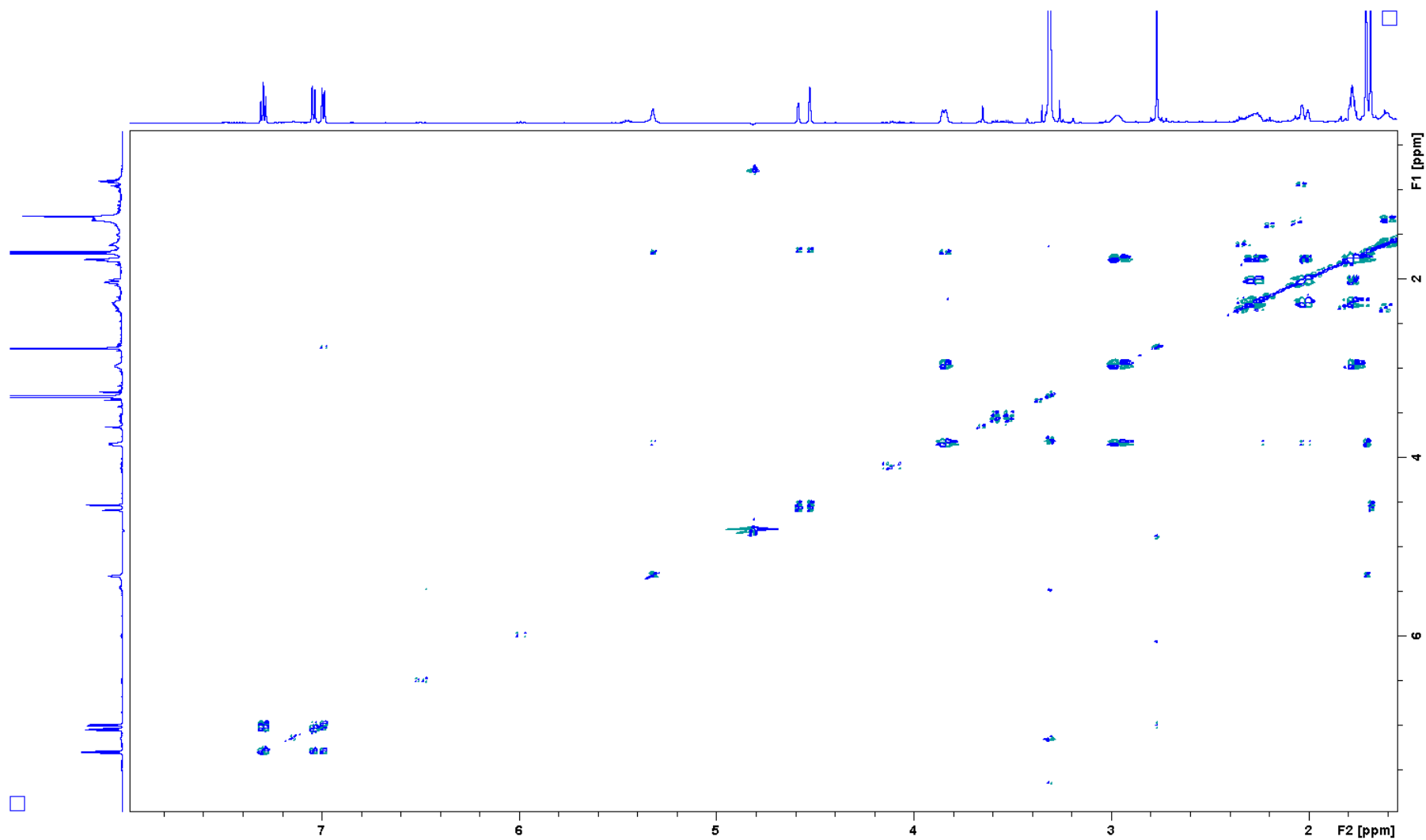


Figure S59. HMBC spectrum of **10** (600 MHz, methanol- d_4).

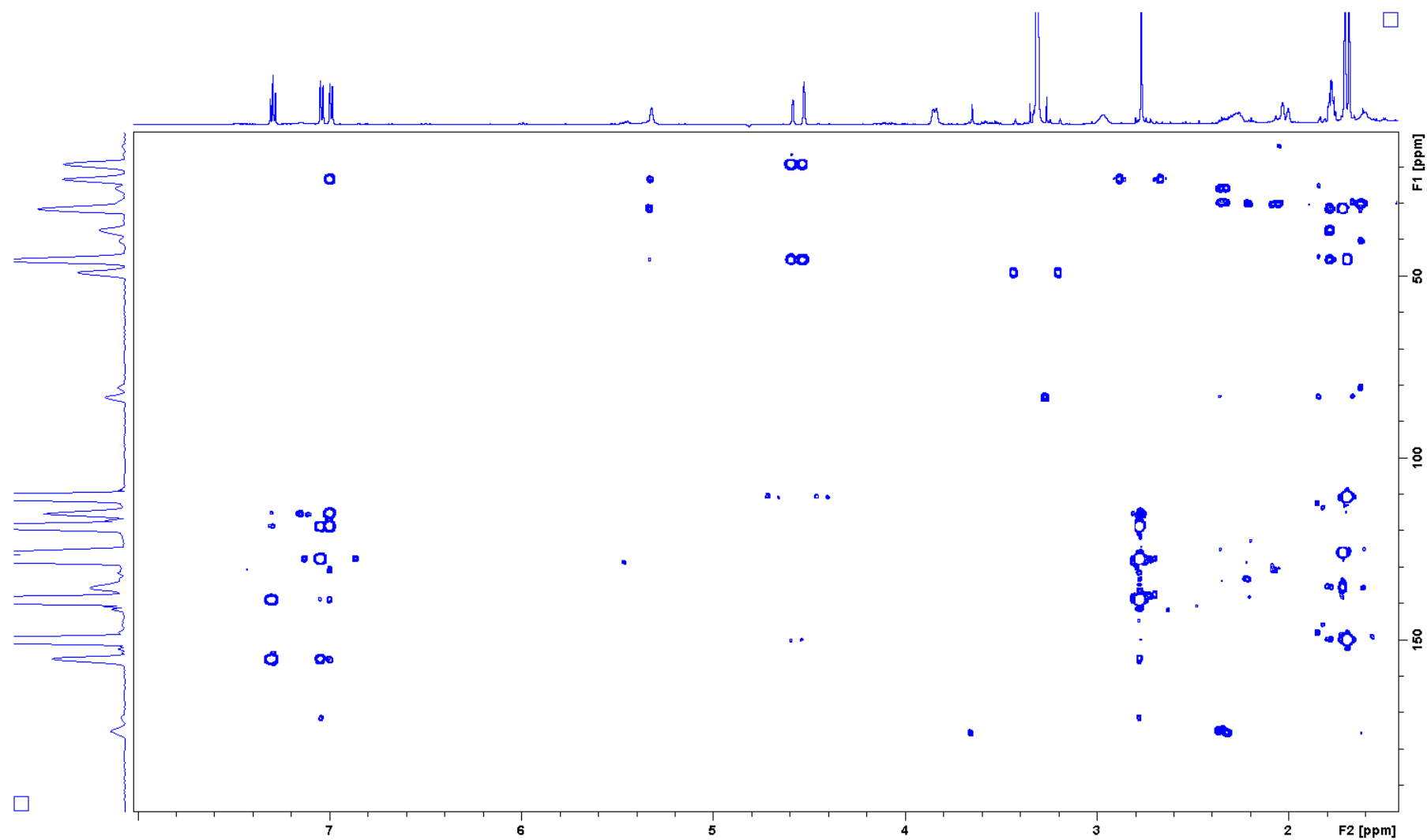


Figure S60. ROESY spectrum of **10** (600 MHz, methanol- d_4).

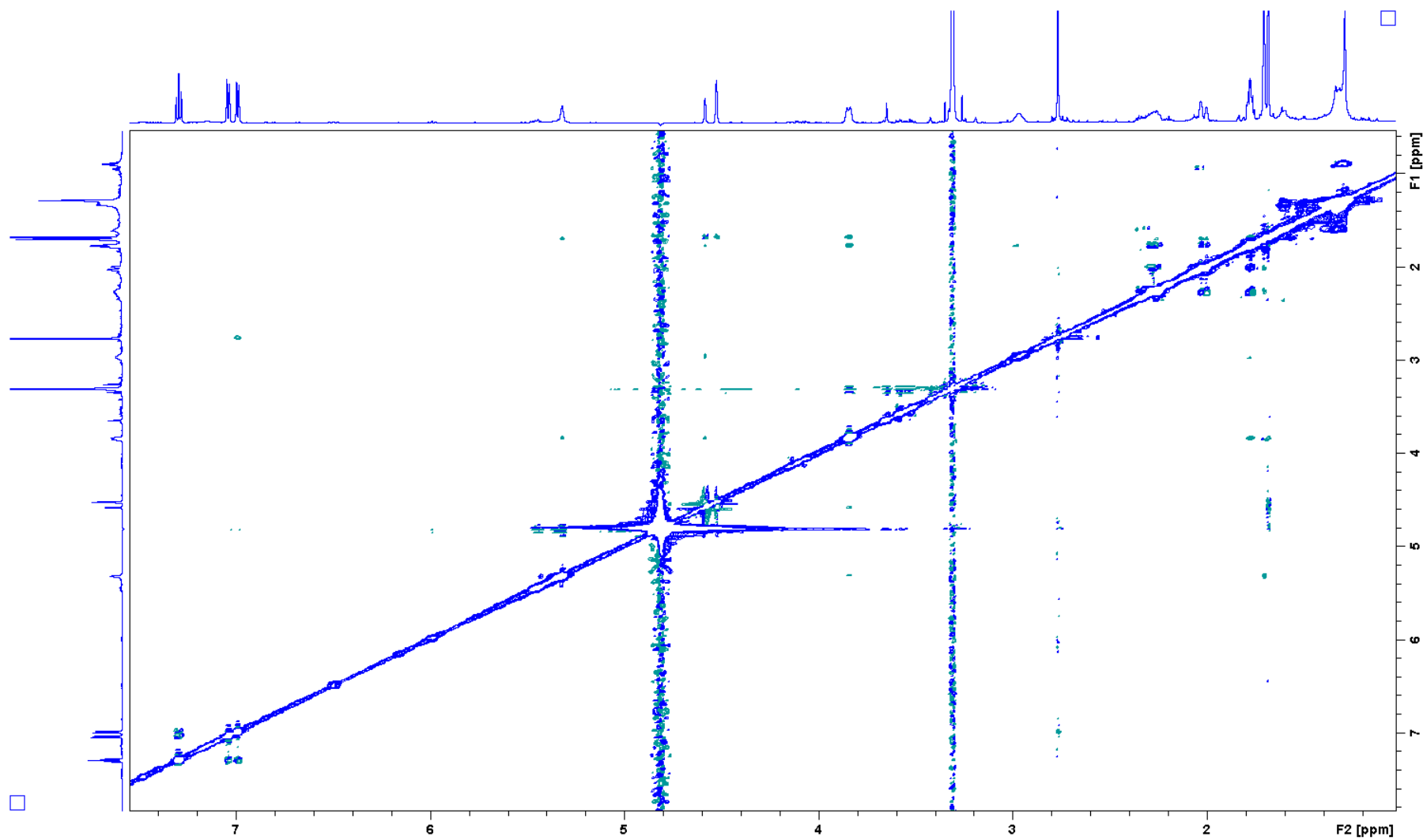


Figure S61. ^1H NMR spectrum of **11** (600 MHz, methanol- d_4).

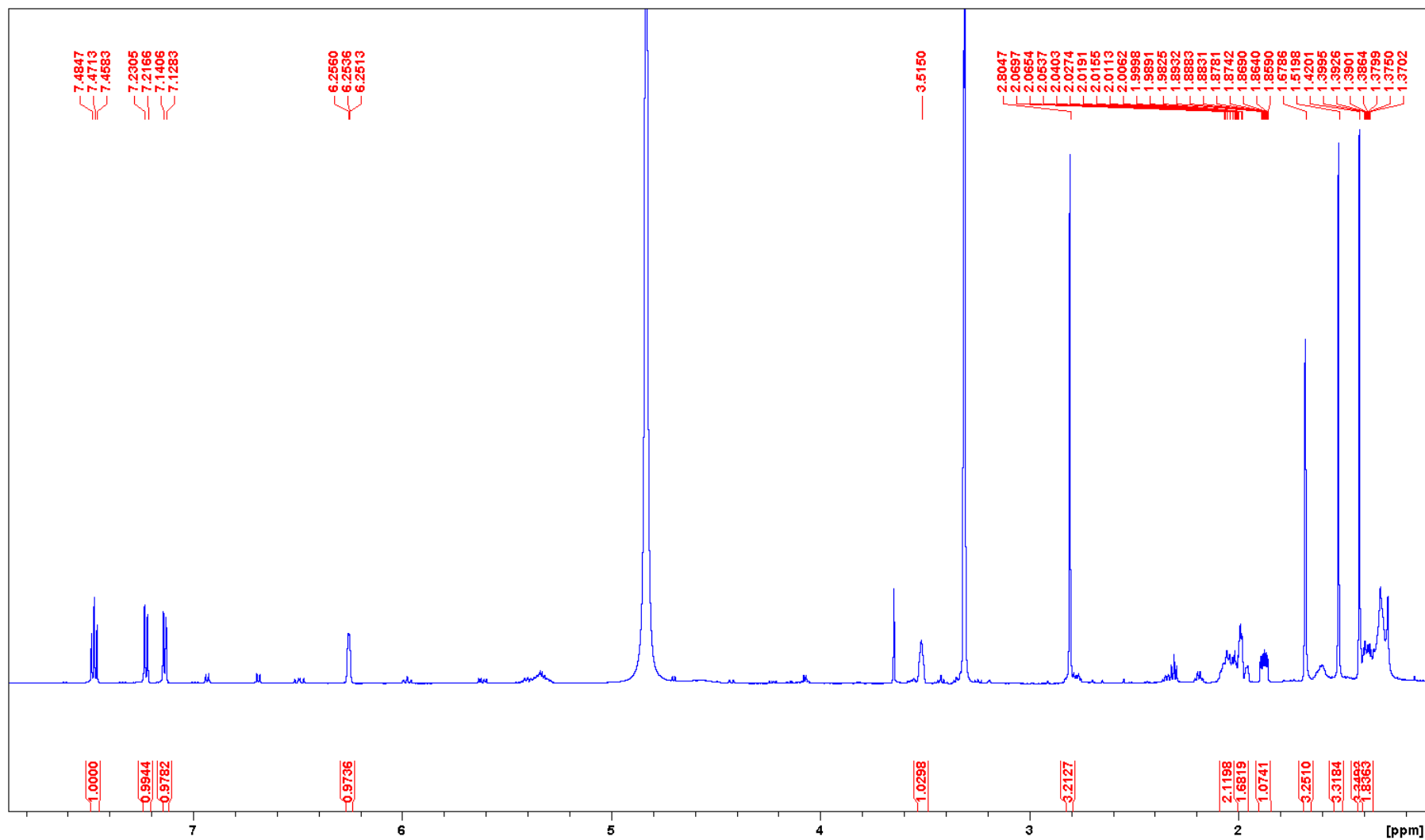


Figure S62. ^{13}C NMR spectrum of **11** (151 MHz, methanol- d_4).

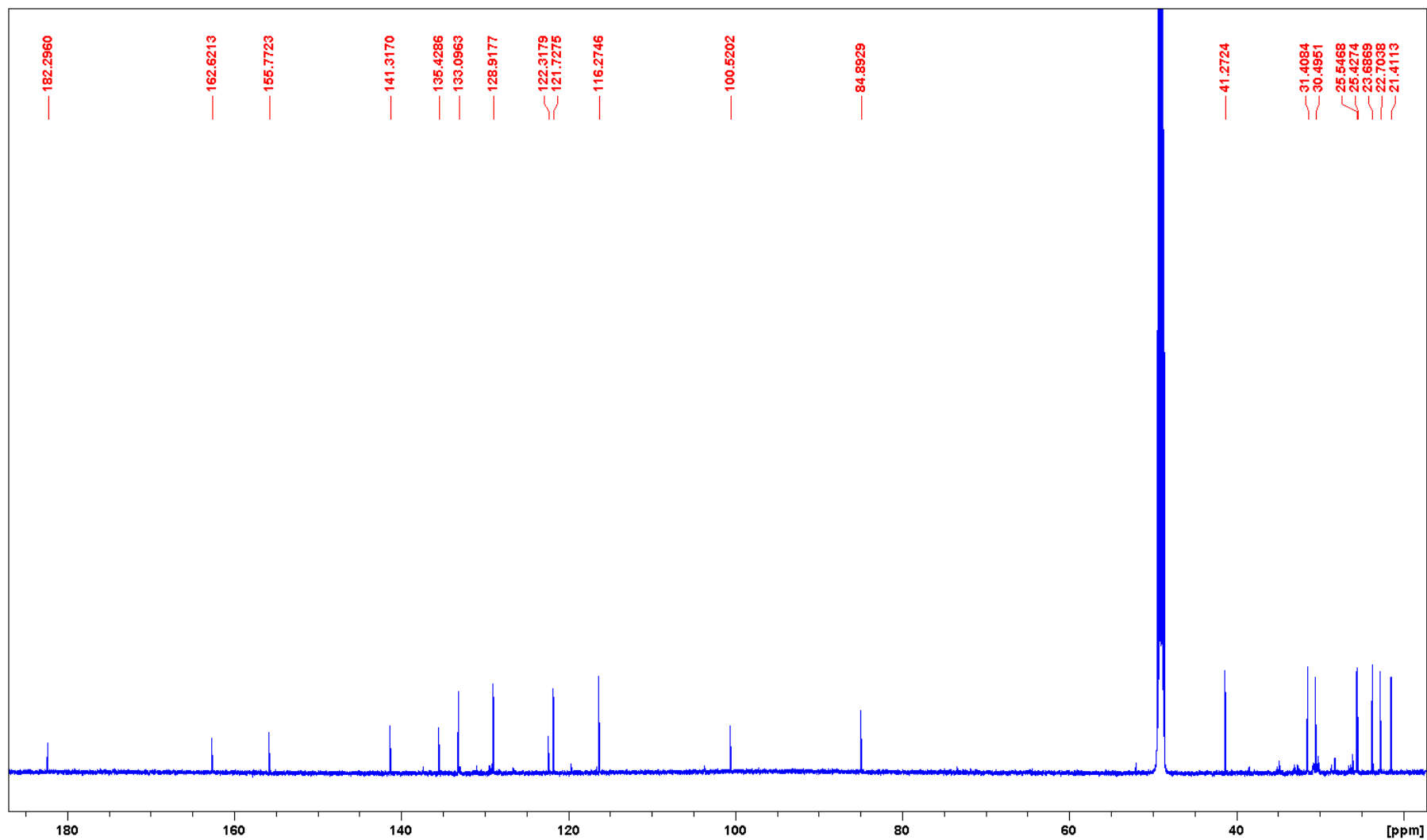


Figure S63. HSQC spectrum of **11** (600 MHz, methanol- d_4).

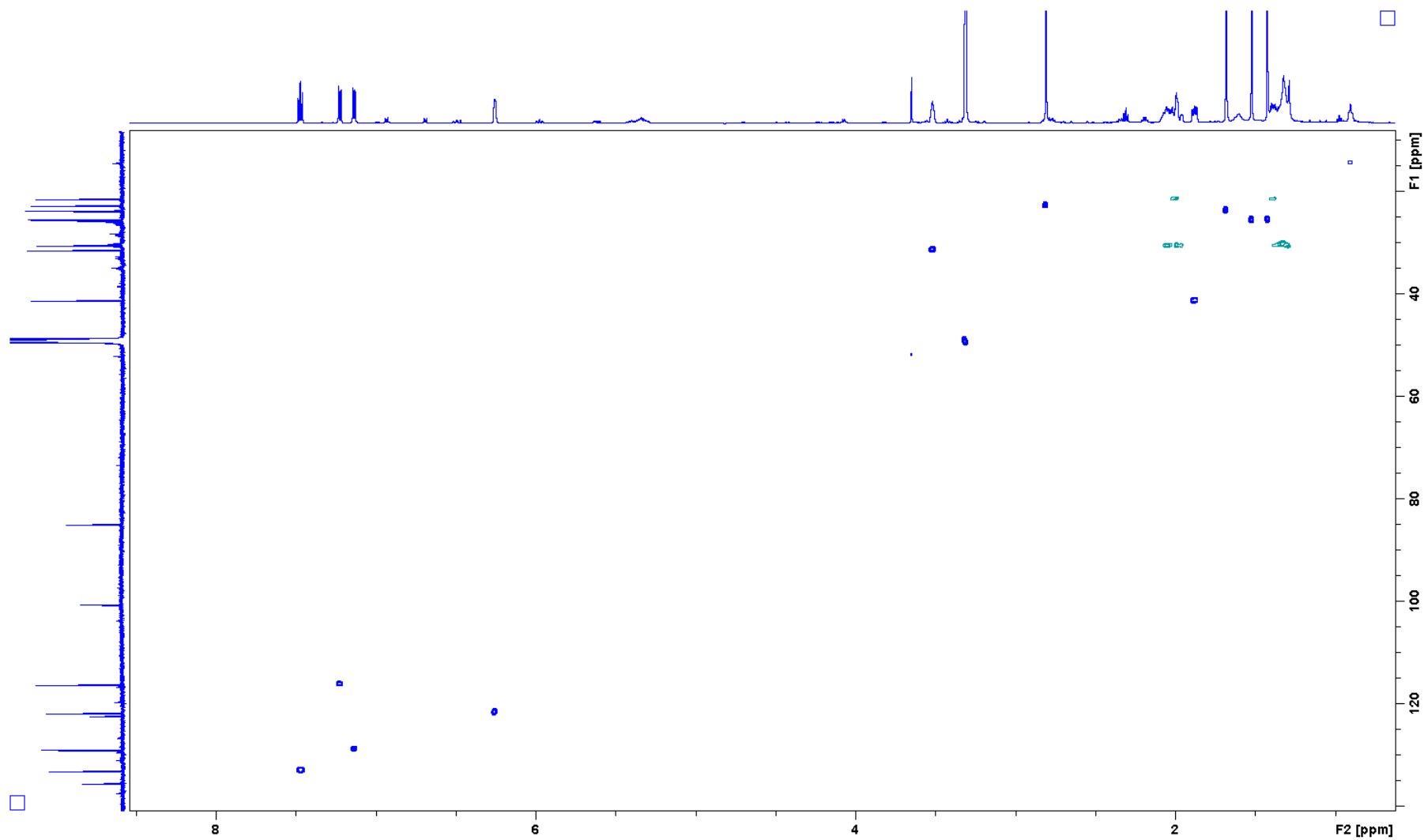


Figure S64. COSY spectrum of **11** (600 MHz, methanol- d_4).

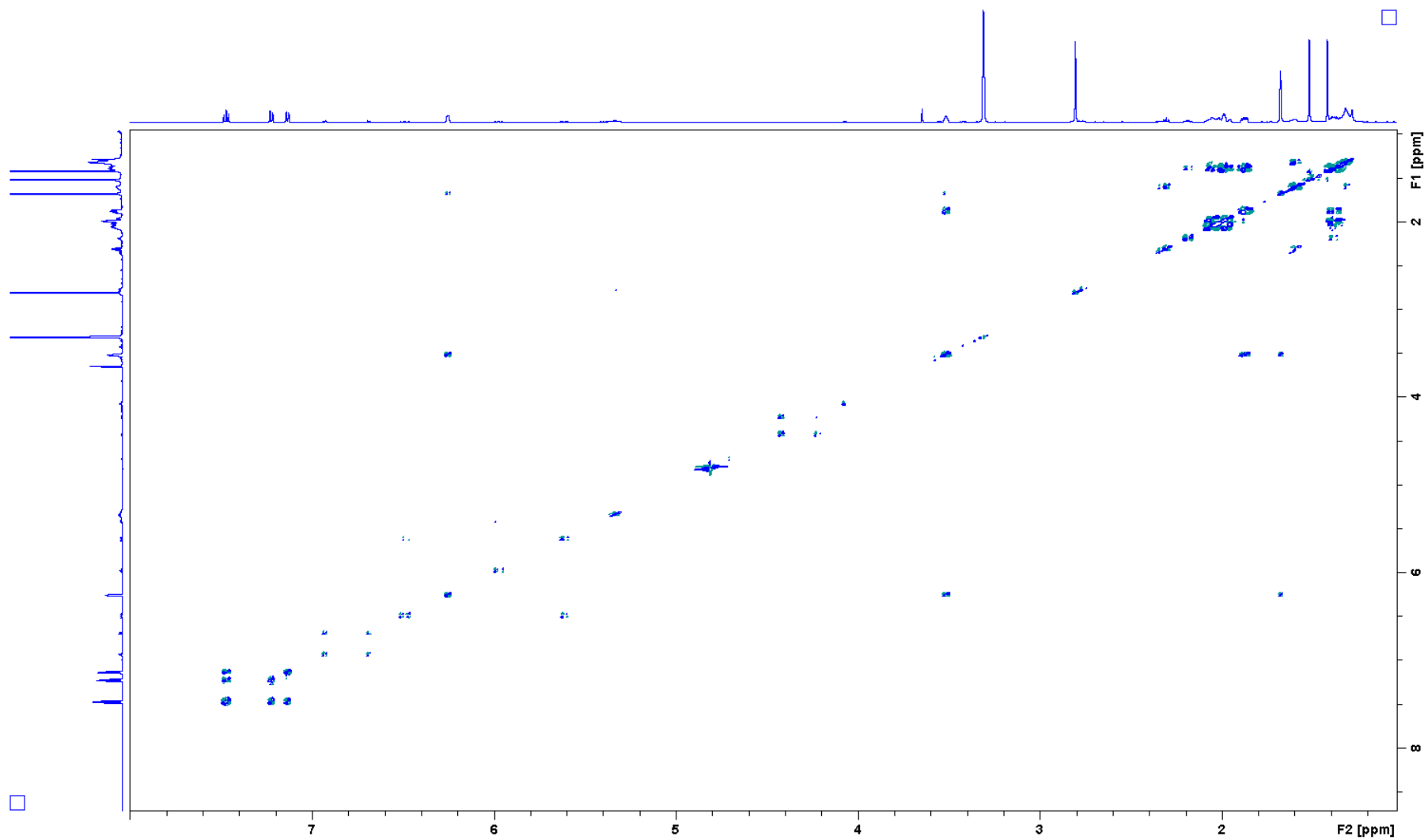


Figure S65. HMBC spectrum of **11** (600 MHz, methanol-*d*₄).

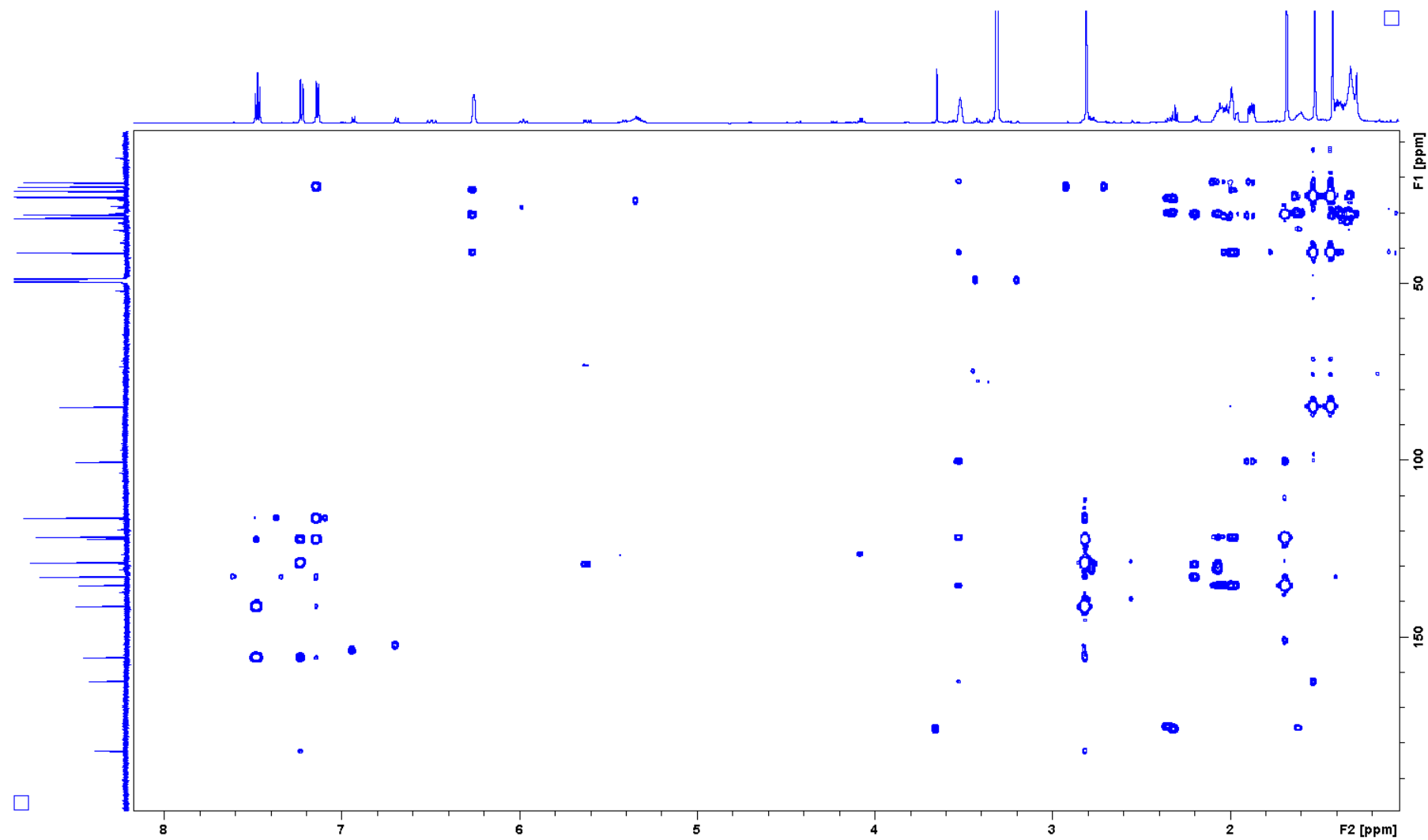


Figure S66. ROESY spectrum of **11** (600 MHz, methanol- d_4).

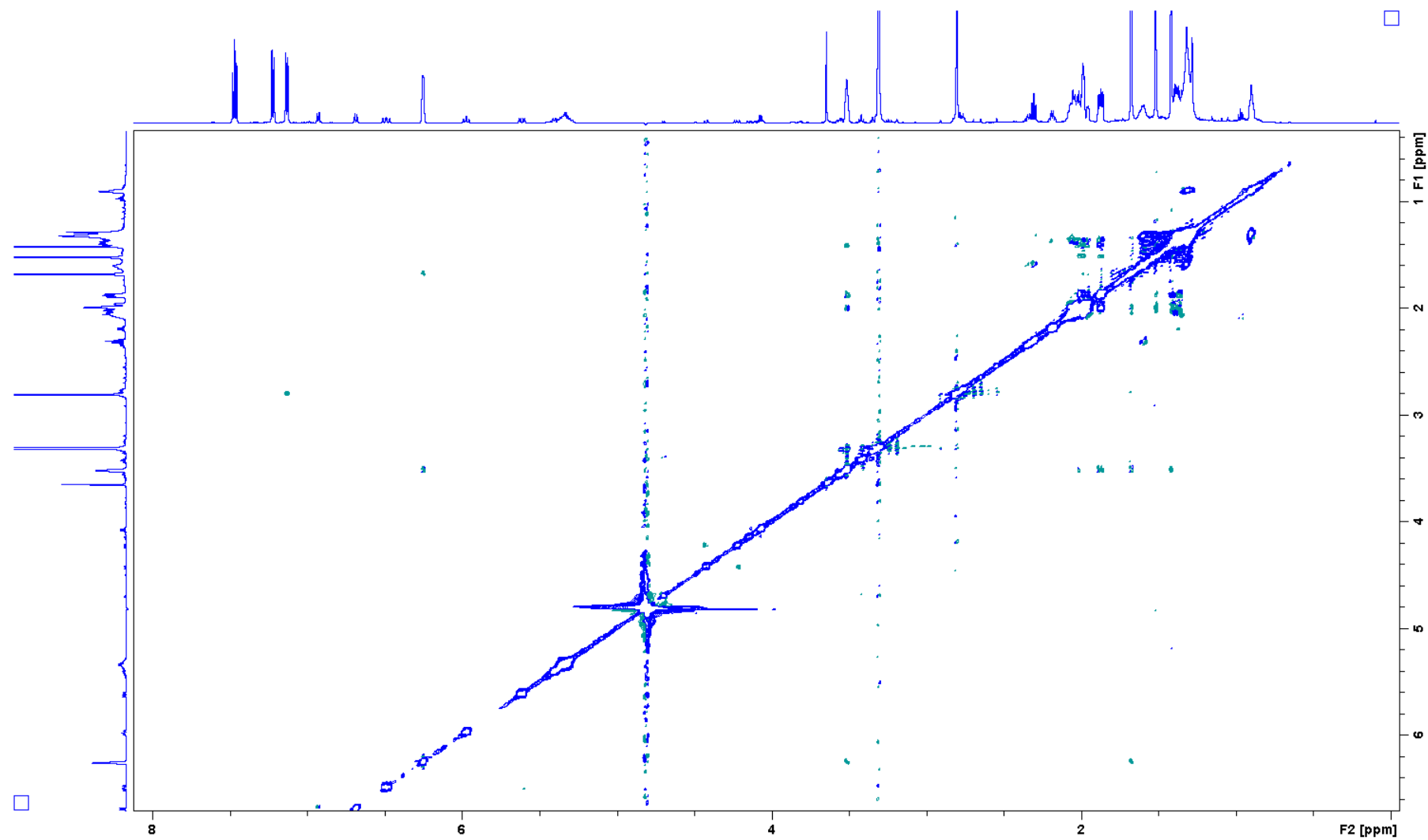


Figure S67. ^1H NMR spectrum of **12** (600 MHz, methanol- d_4).

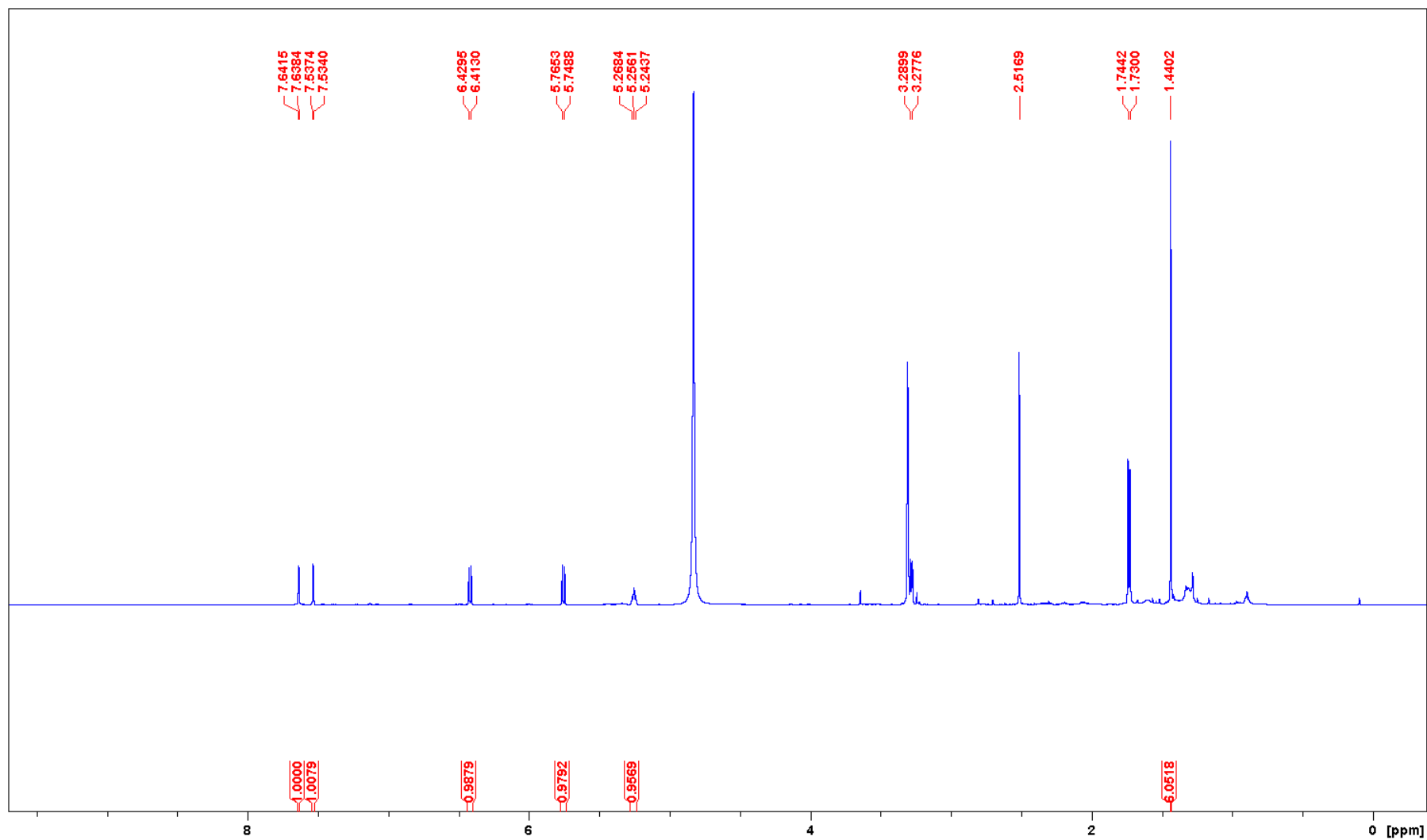


Figure S68. HSQC spectrum of **12** (600 MHz, methanol- d_4).

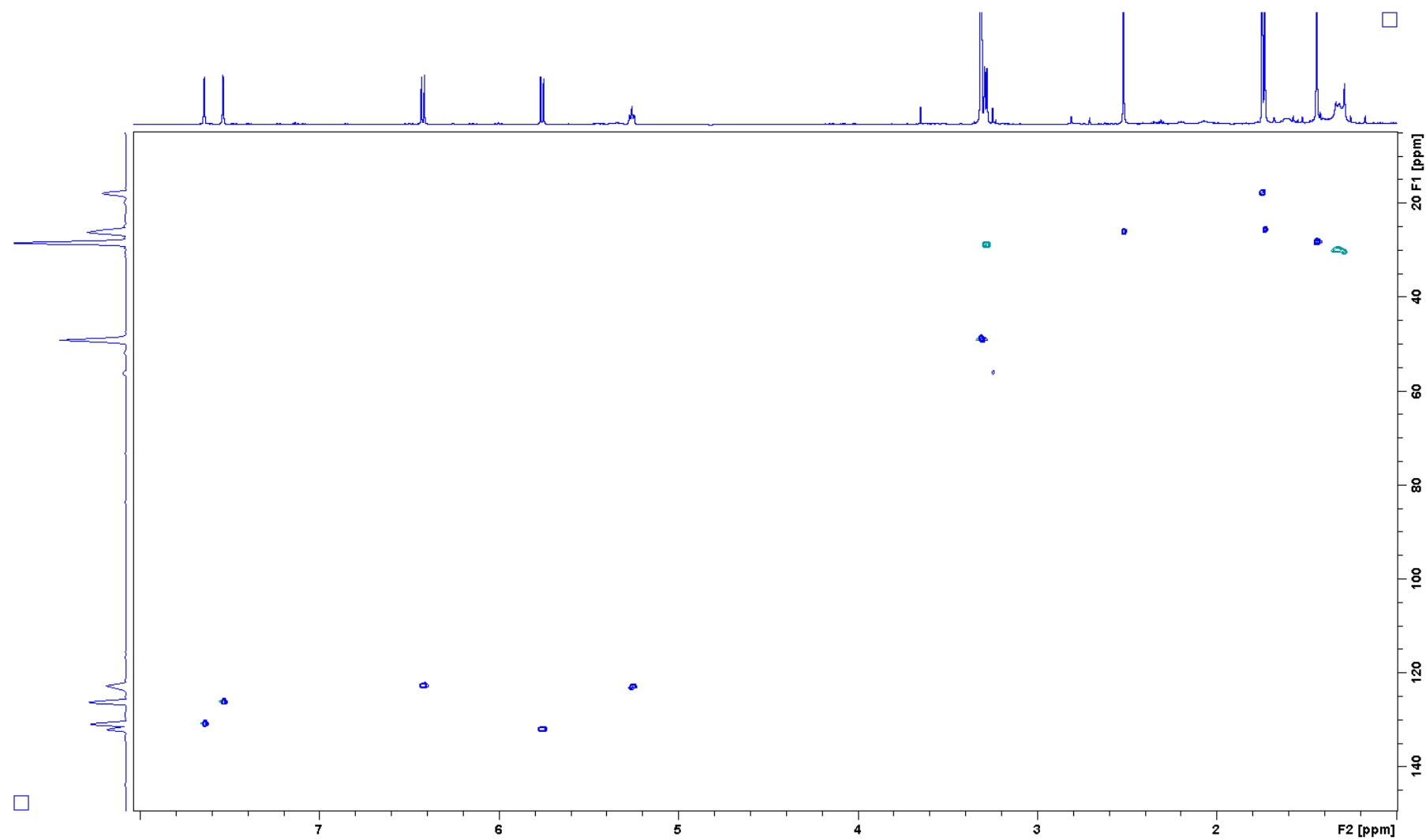


Figure S69. COSY spectrum of **12** (600 MHz, methanol- d_4).

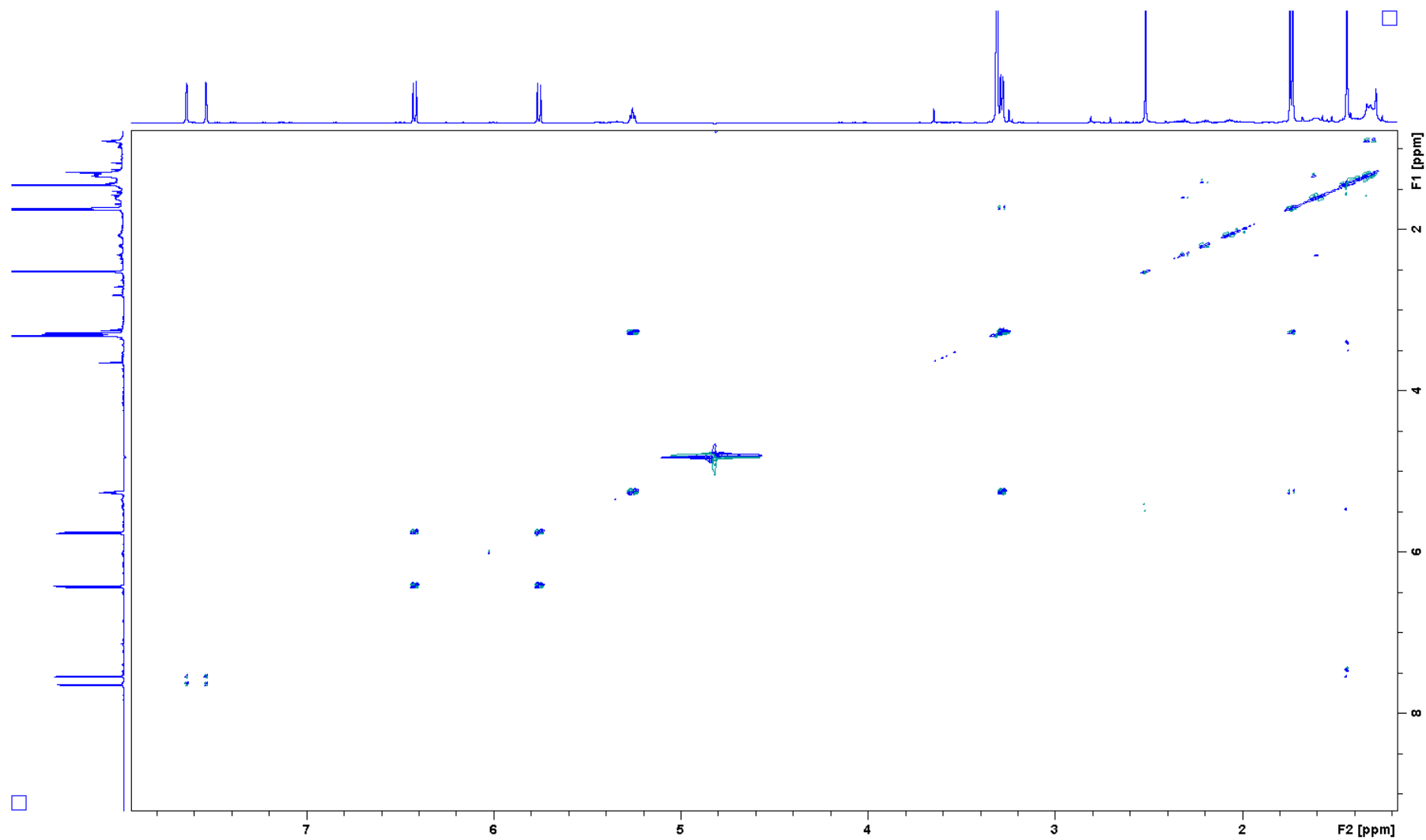


Figure S70. HMBC spectrum of **12** (600 MHz, methanol- d_4).

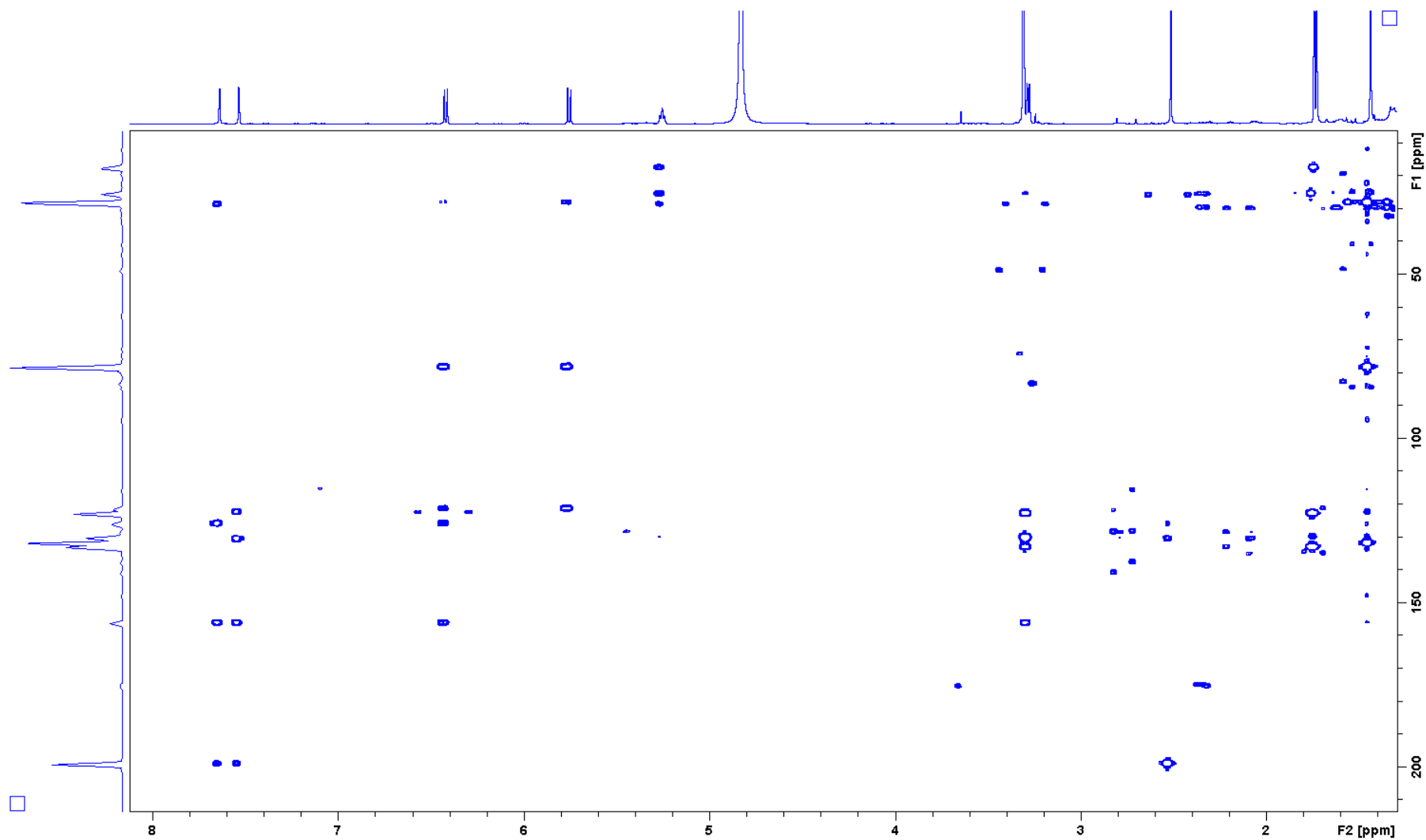


Figure S71. ROESY spectrum of **12** (600 MHz, methanol-*d*₄).

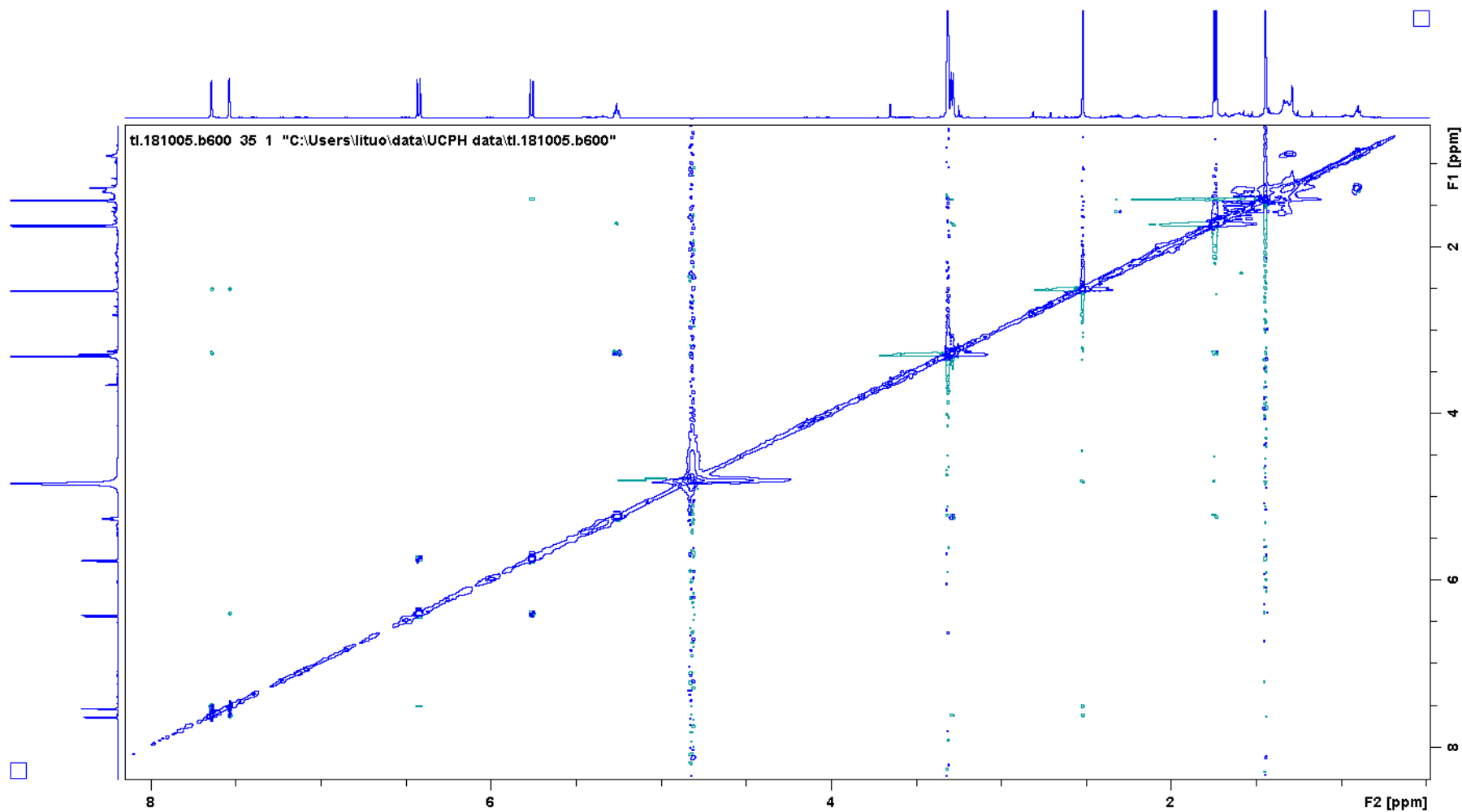


Figure S72. ^1H NMR spectrum of **14** (600 MHz, methanol- d_4).

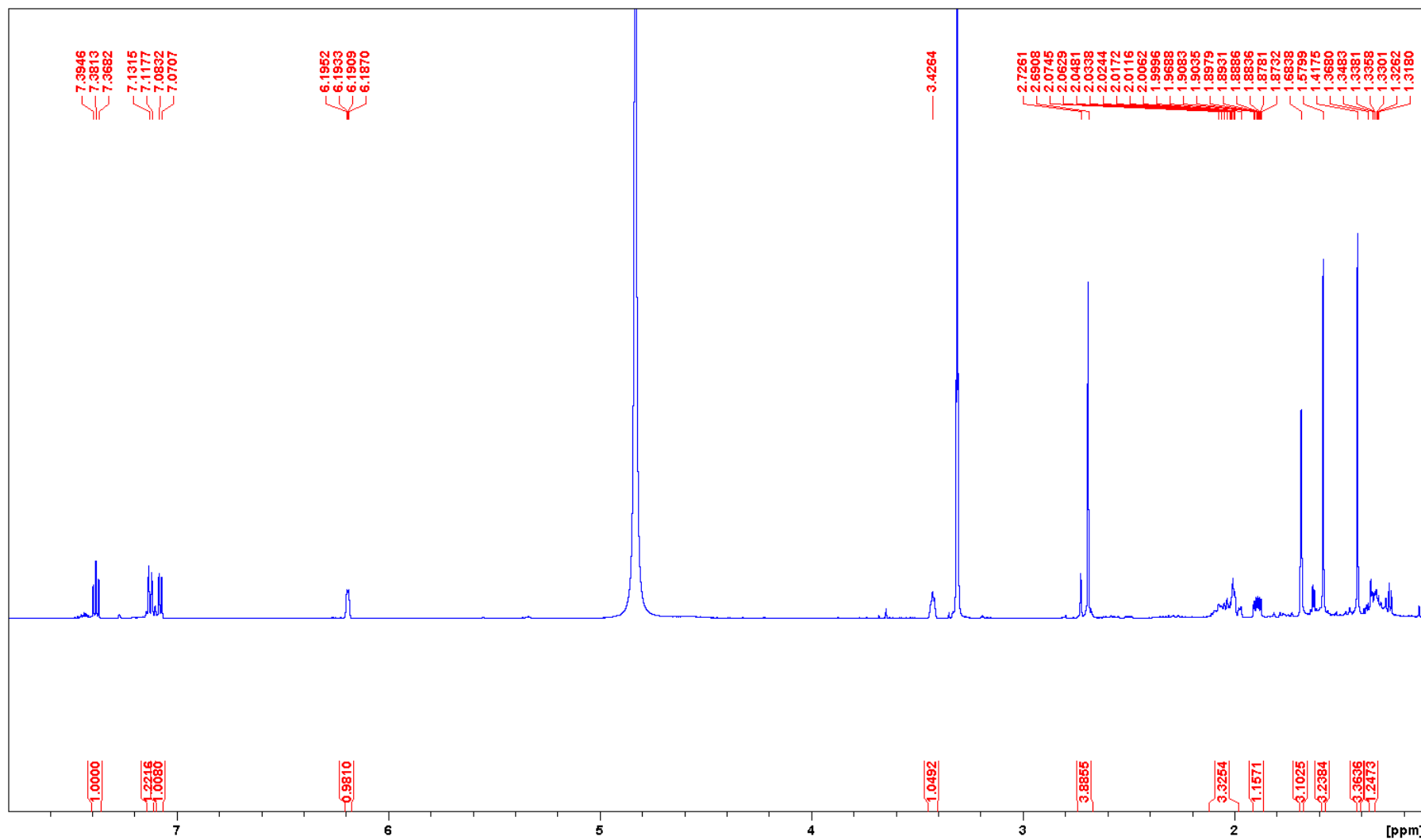


Figure S73. ^{13}C NMR spectrum of **14** (151 MHz, methanol- d_4).

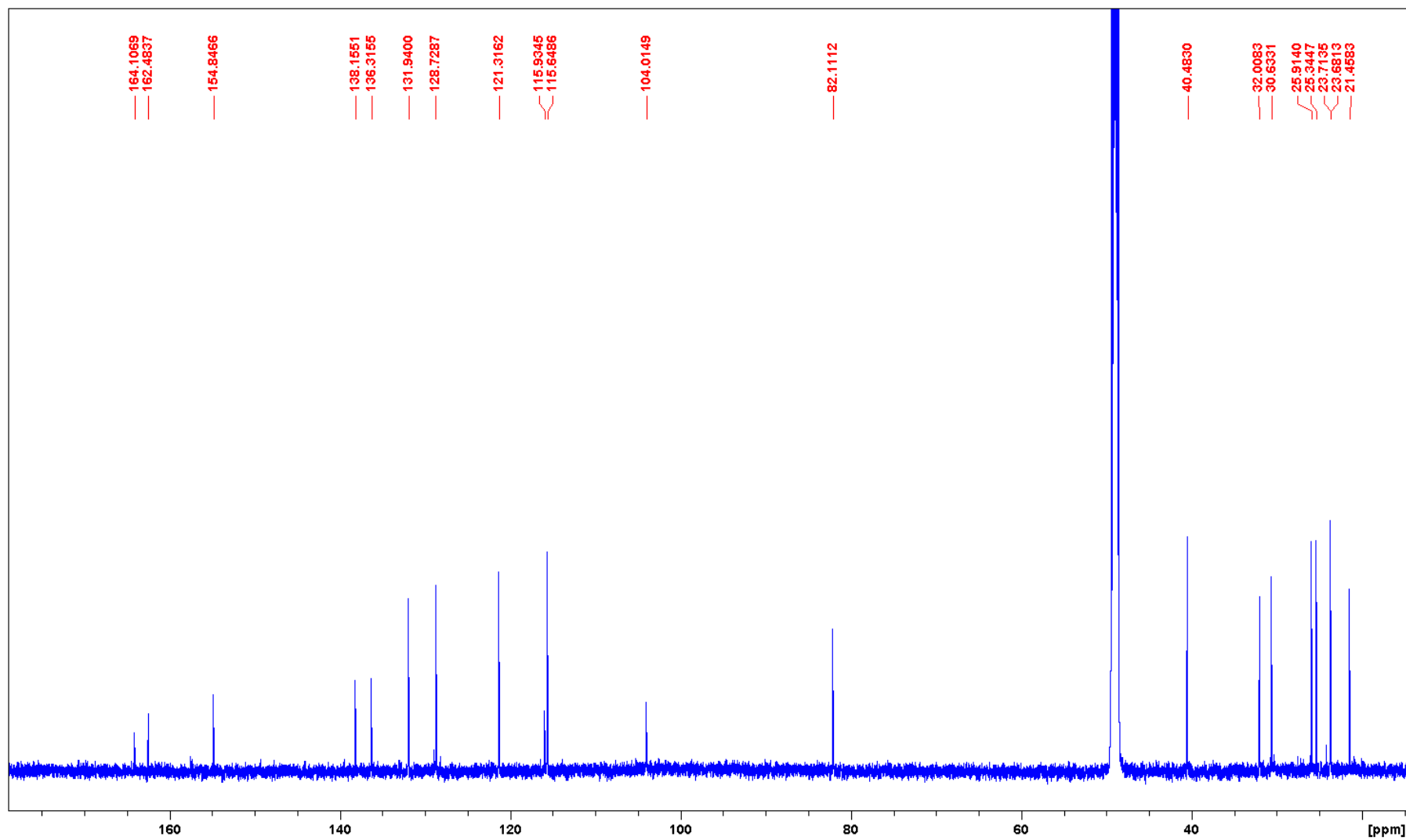


Figure S74. HSQC spectrum of **14** (600 MHz, methanol- d_4).

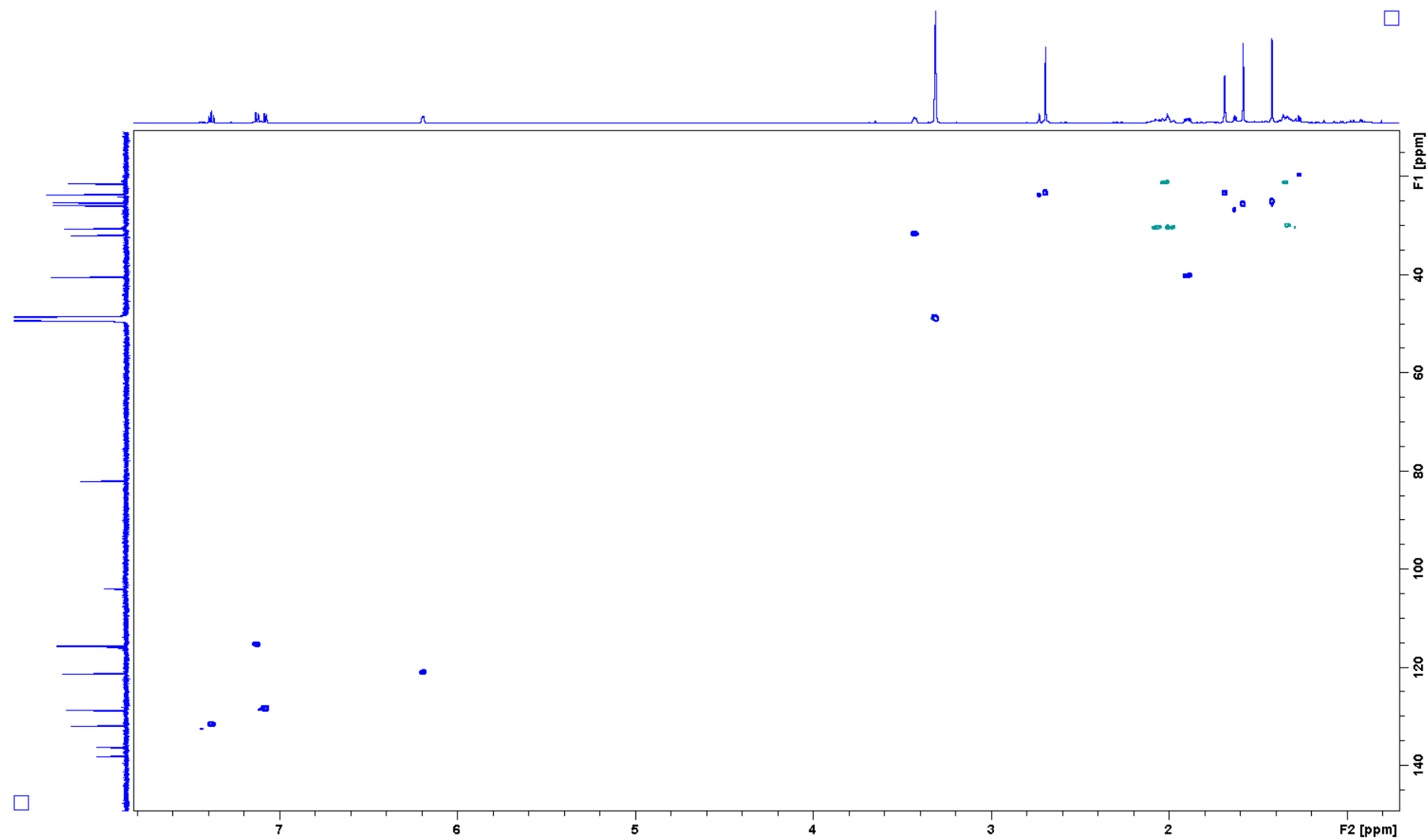


Figure S75. COSY spectrum of **14** (600 MHz, methanol- d_4).

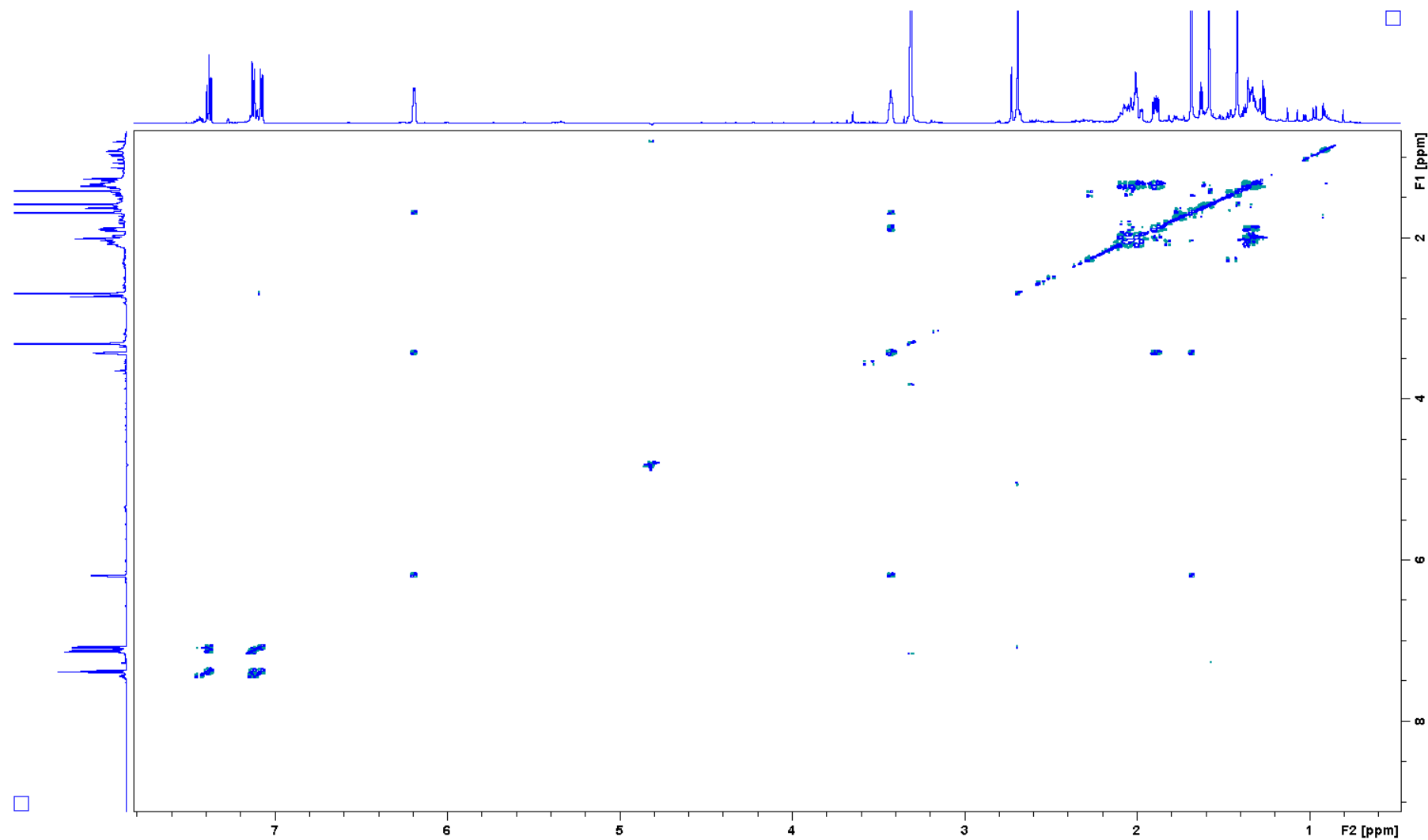


Figure S76. HMBC spectrum of **14** (600 MHz, methanol-*d*₄).

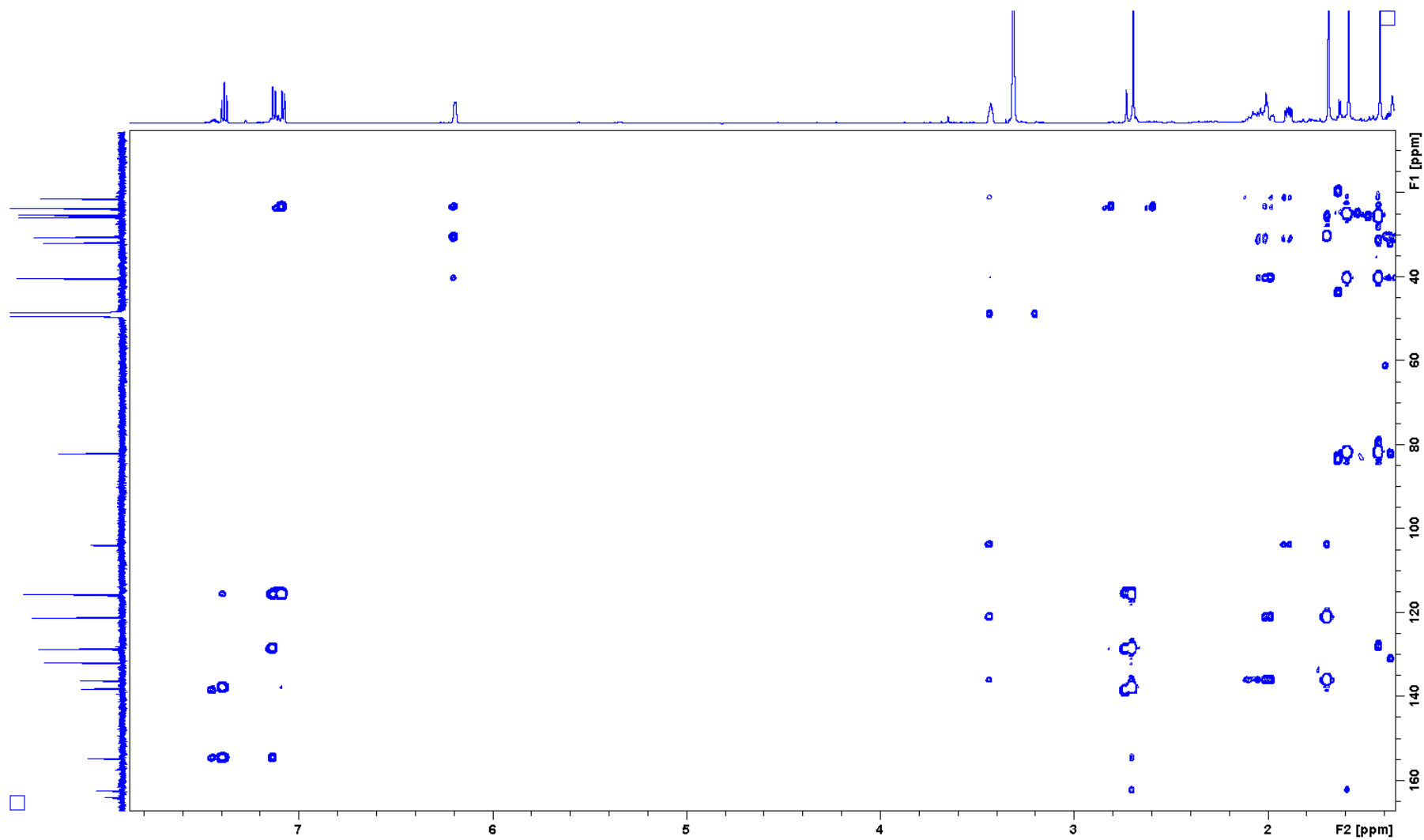


Figure S77. ROESY spectrum of **14** (600 MHz, methanol- d_4).

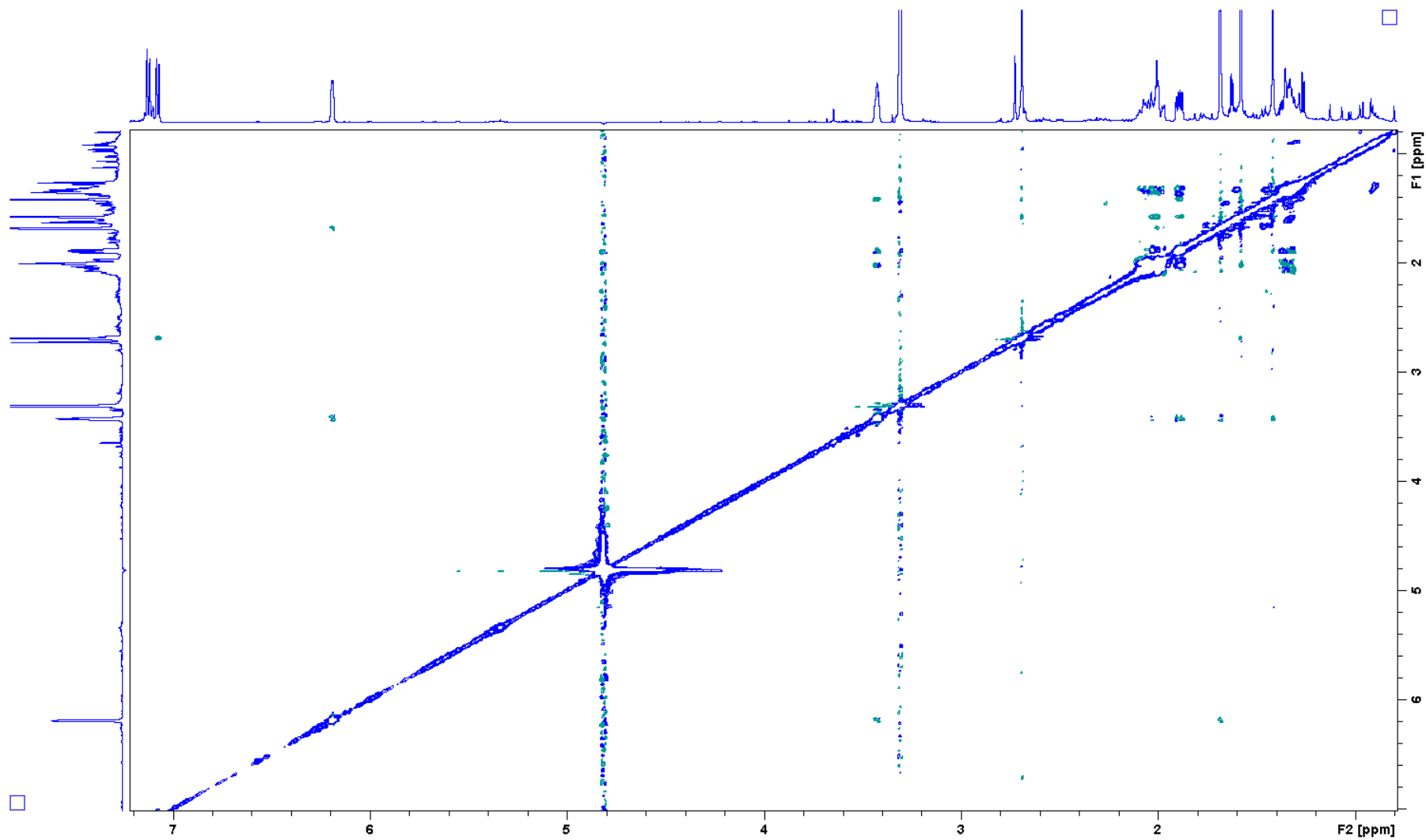


Figure S78. ^1H NMR spectrum of **15** (600 MHz, methanol- d_4).

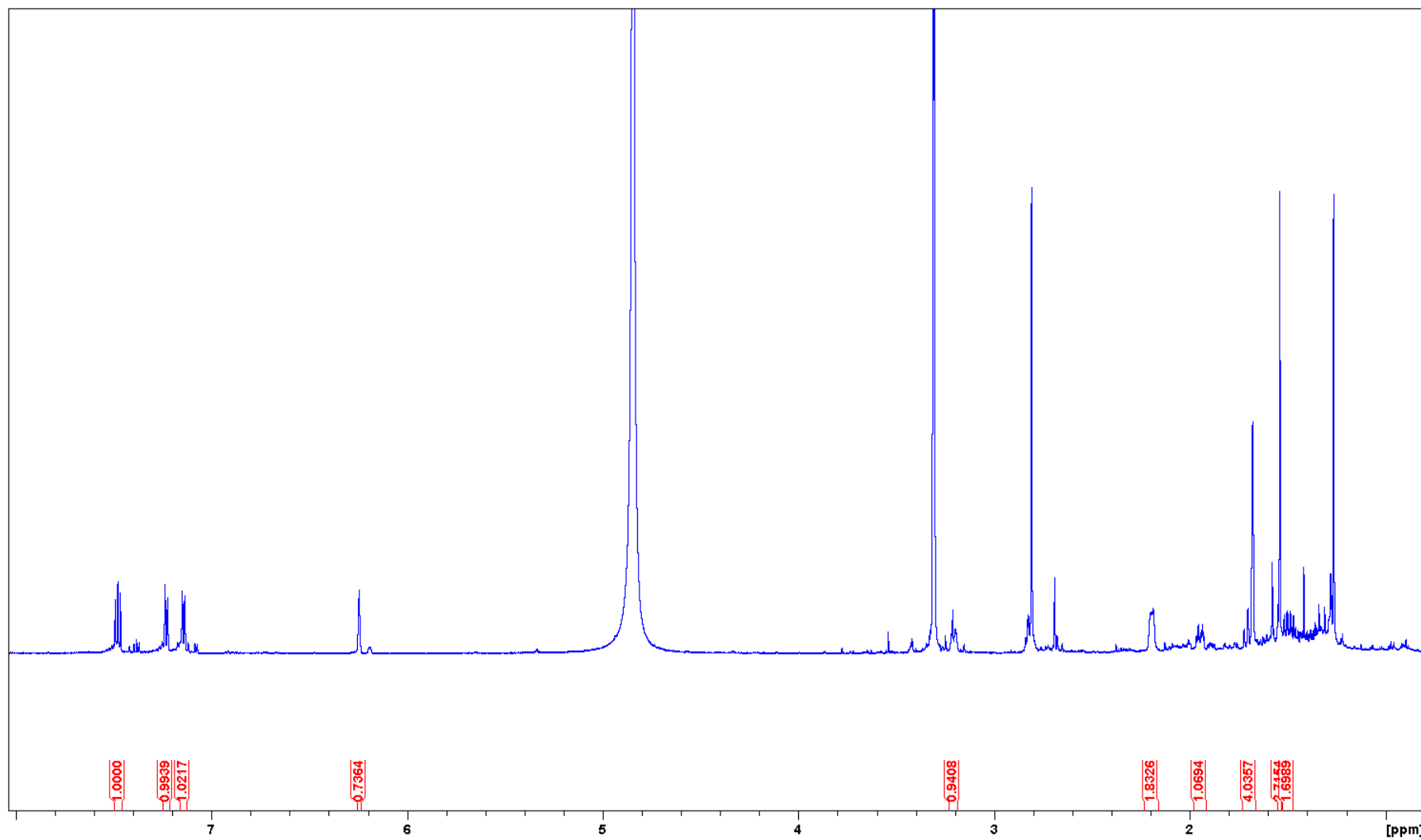


Figure S79. ^{13}C NMR spectrum of **15** (151 MHz, methanol- d_4).

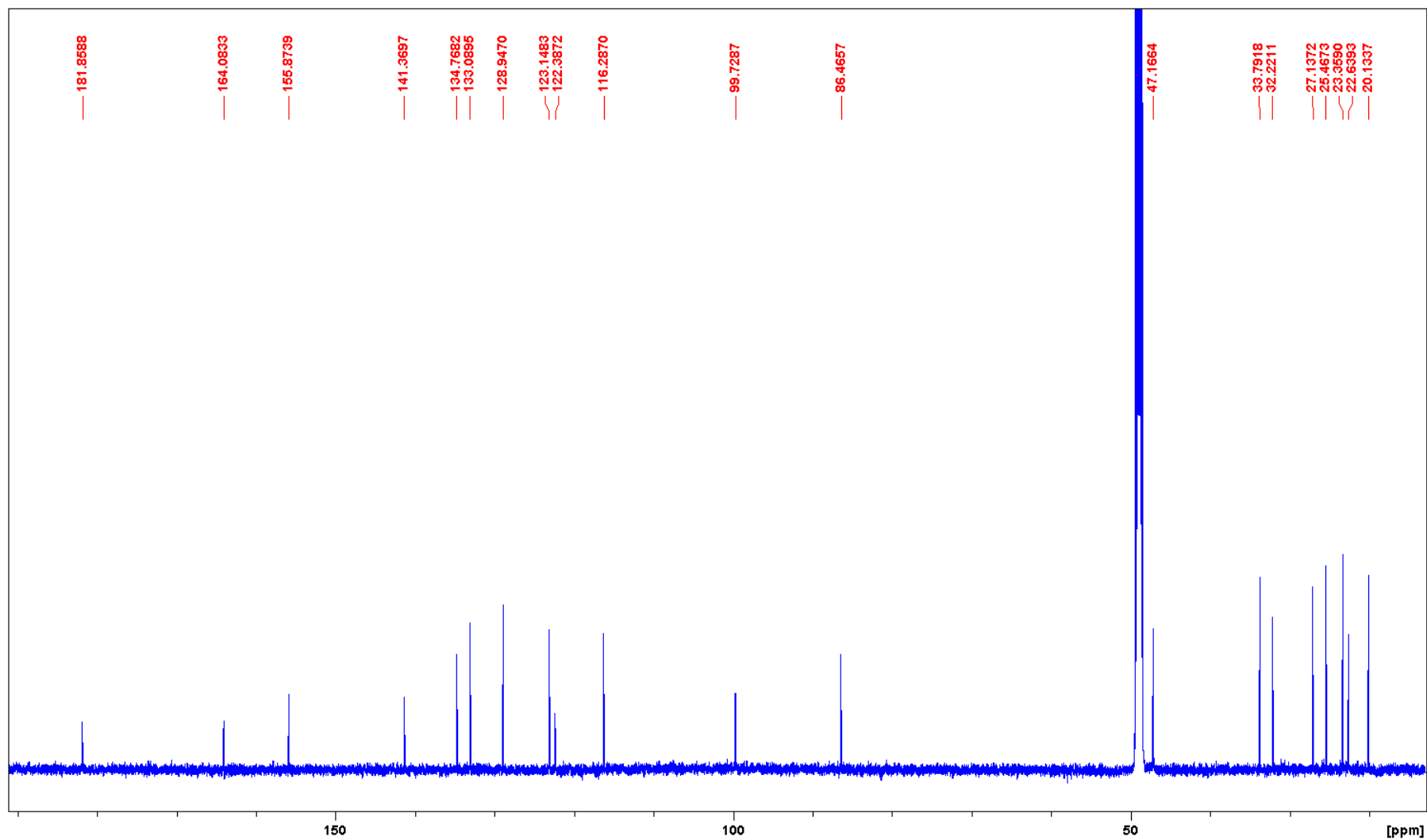


Figure S80. HSQC spectrum of **15** (600 MHz, methanol- d_4).

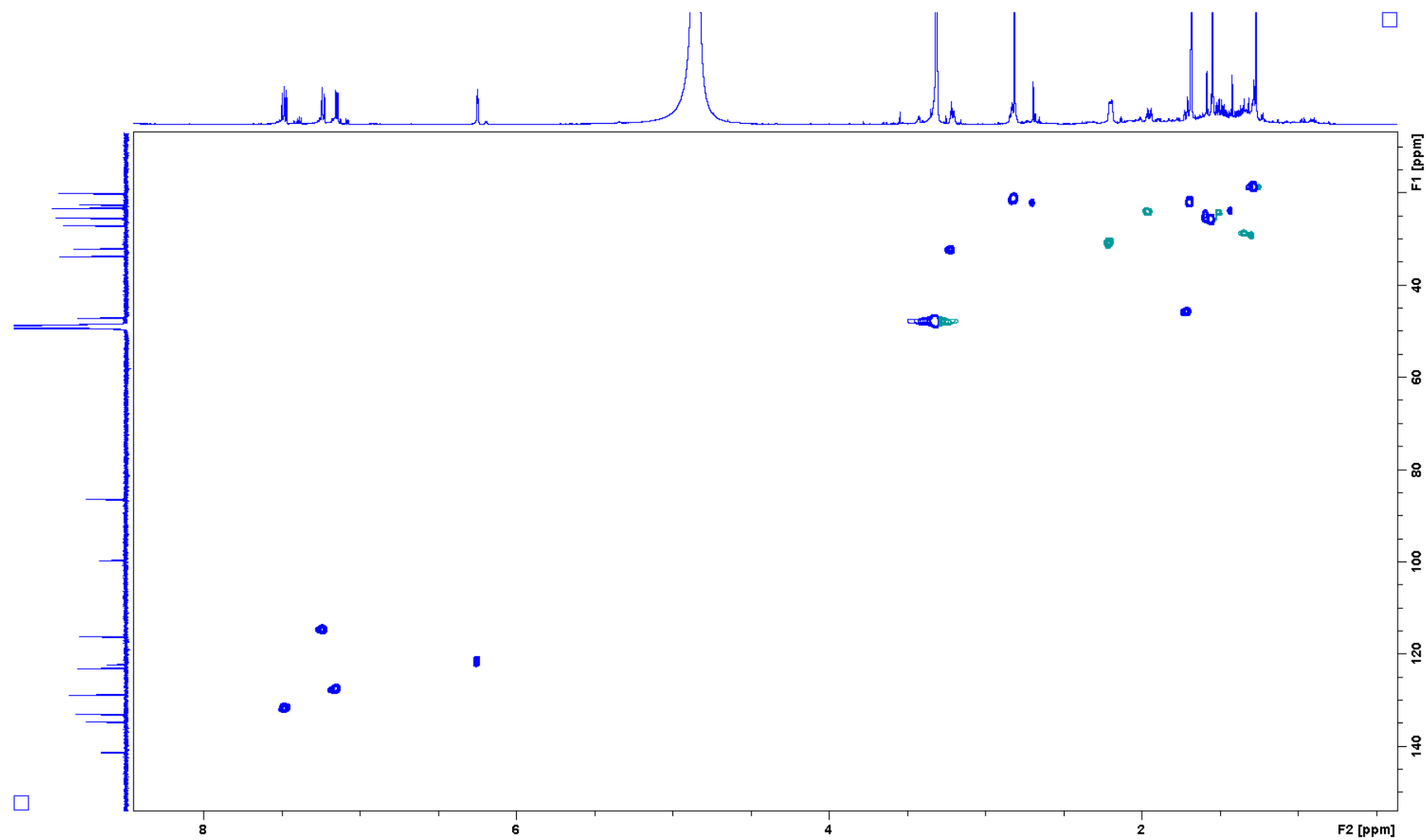


Figure S81. COSY spectrum of **15** (600 MHz, methanol- d_4).

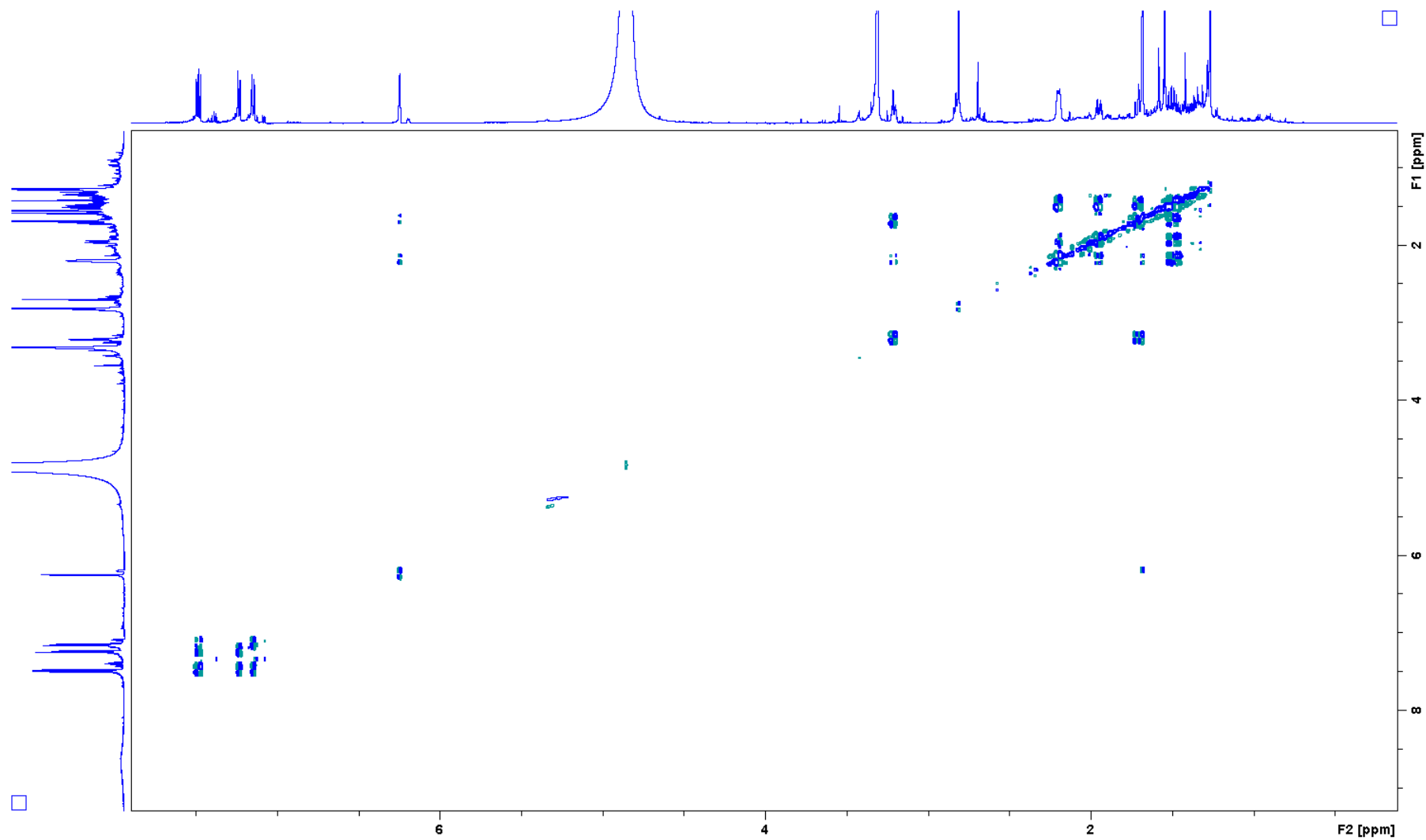


Figure S82. HMBC spectrum of **15** (600 MHz, methanol-*d*₄).

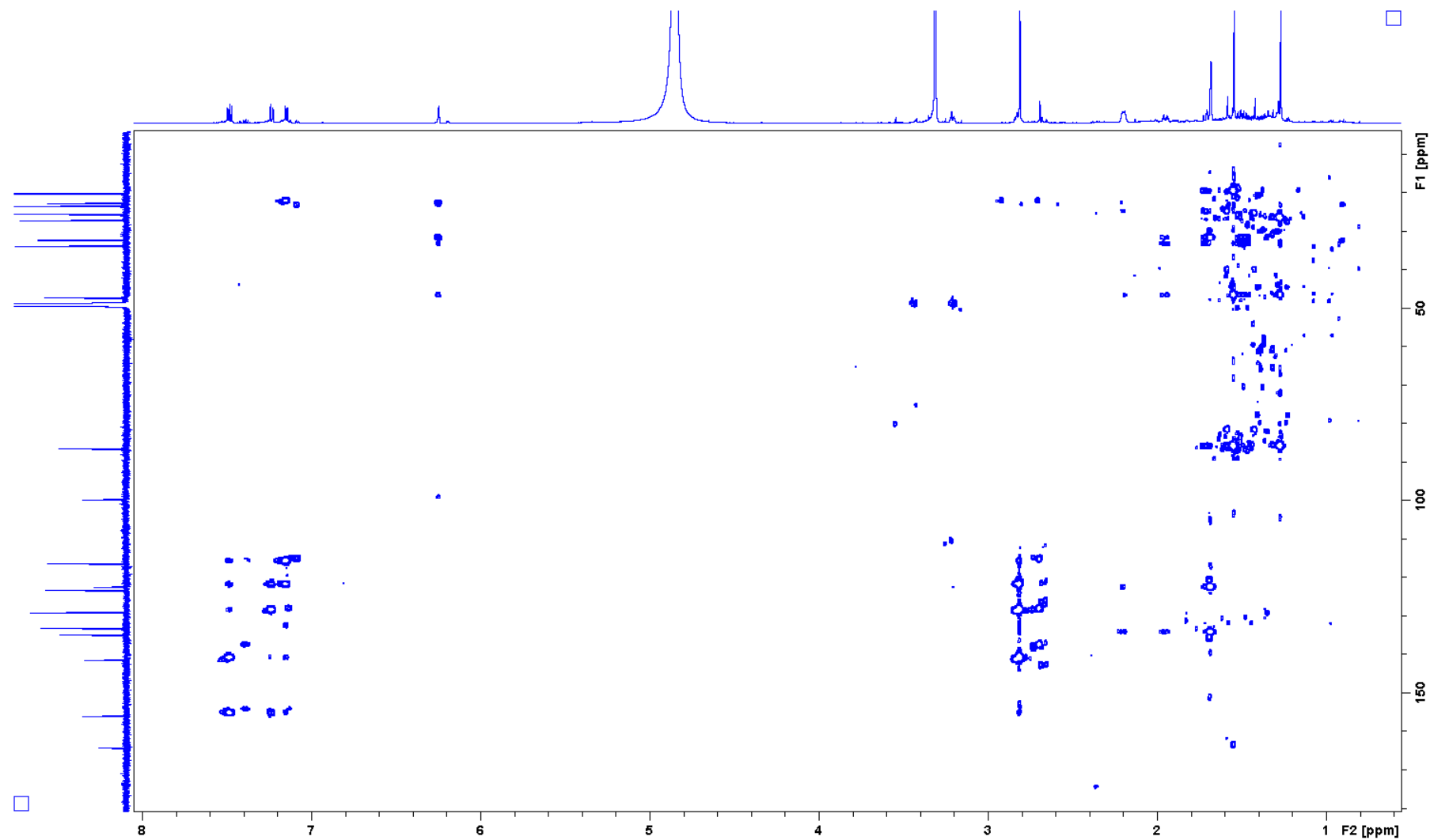


Figure S83. ROESY spectrum of **15** (600 MHz, methanol- d_4).

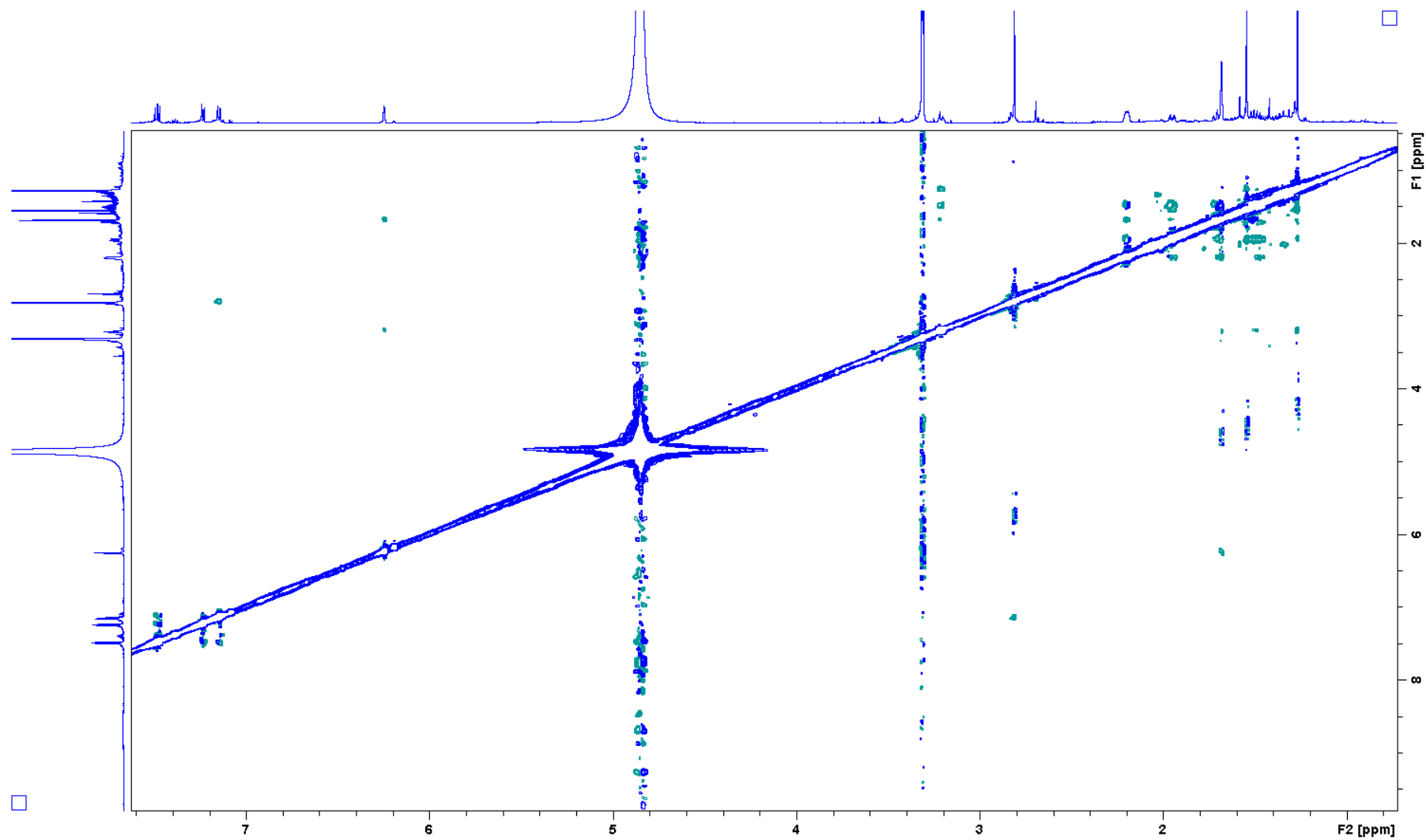


Figure S84. ^1H NMR spectrum of **16** (600 MHz, methanol- d_4).

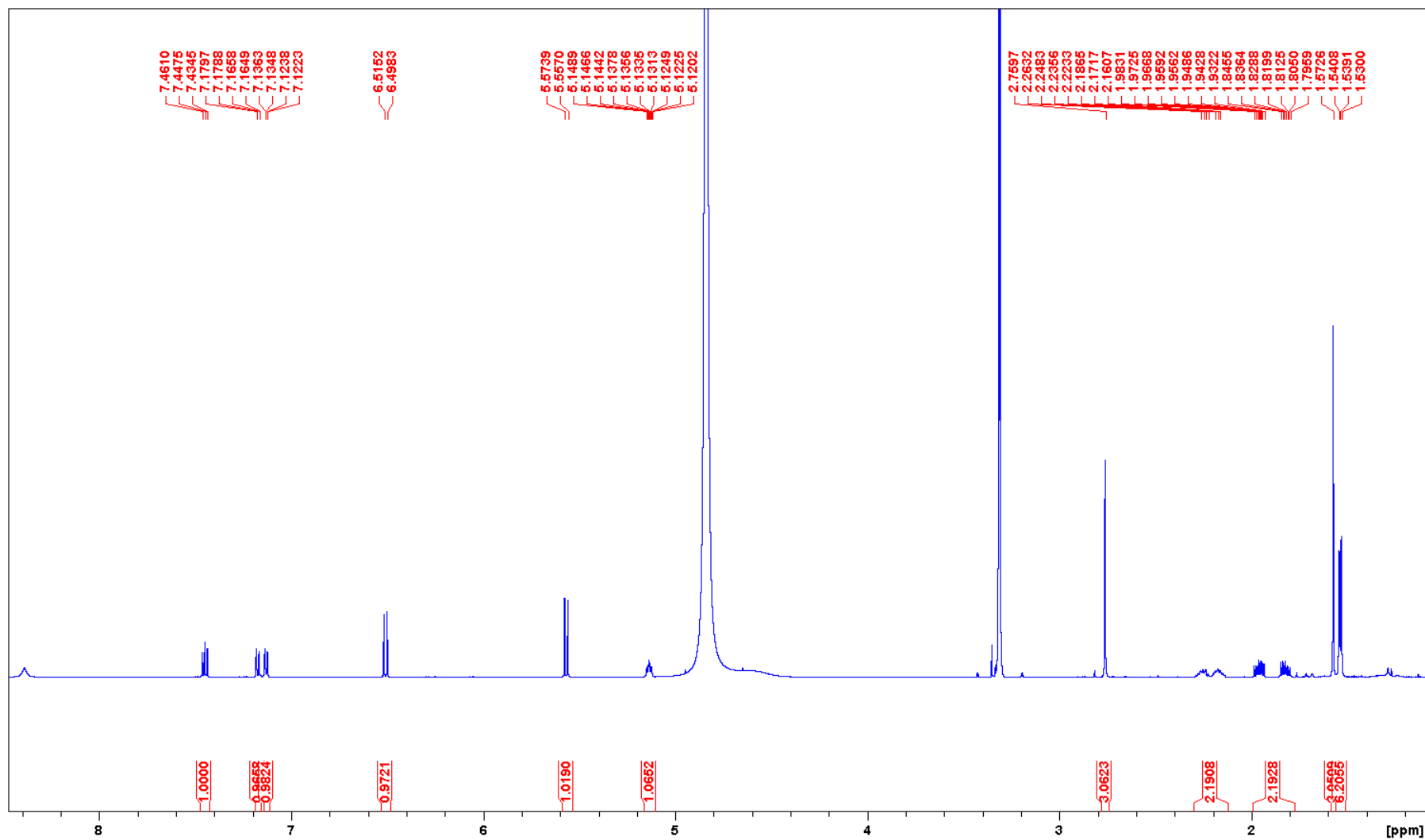


Figure S85. ^{13}C NMR spectrum of **16** (150 MHz, methanol- d_4).

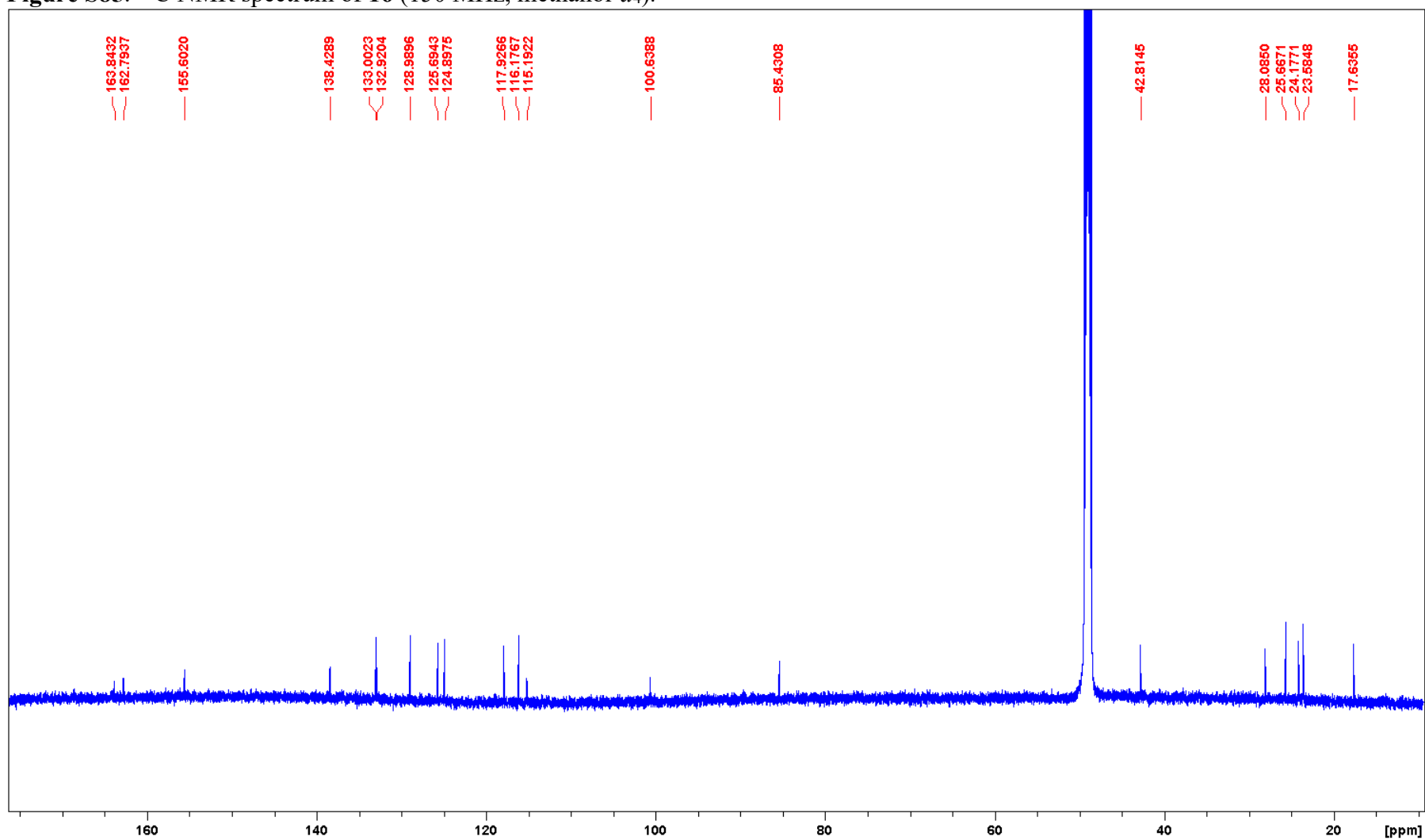


Figure S87. HSQC spectrum of **16** (600 MHz, methanol- d_4).

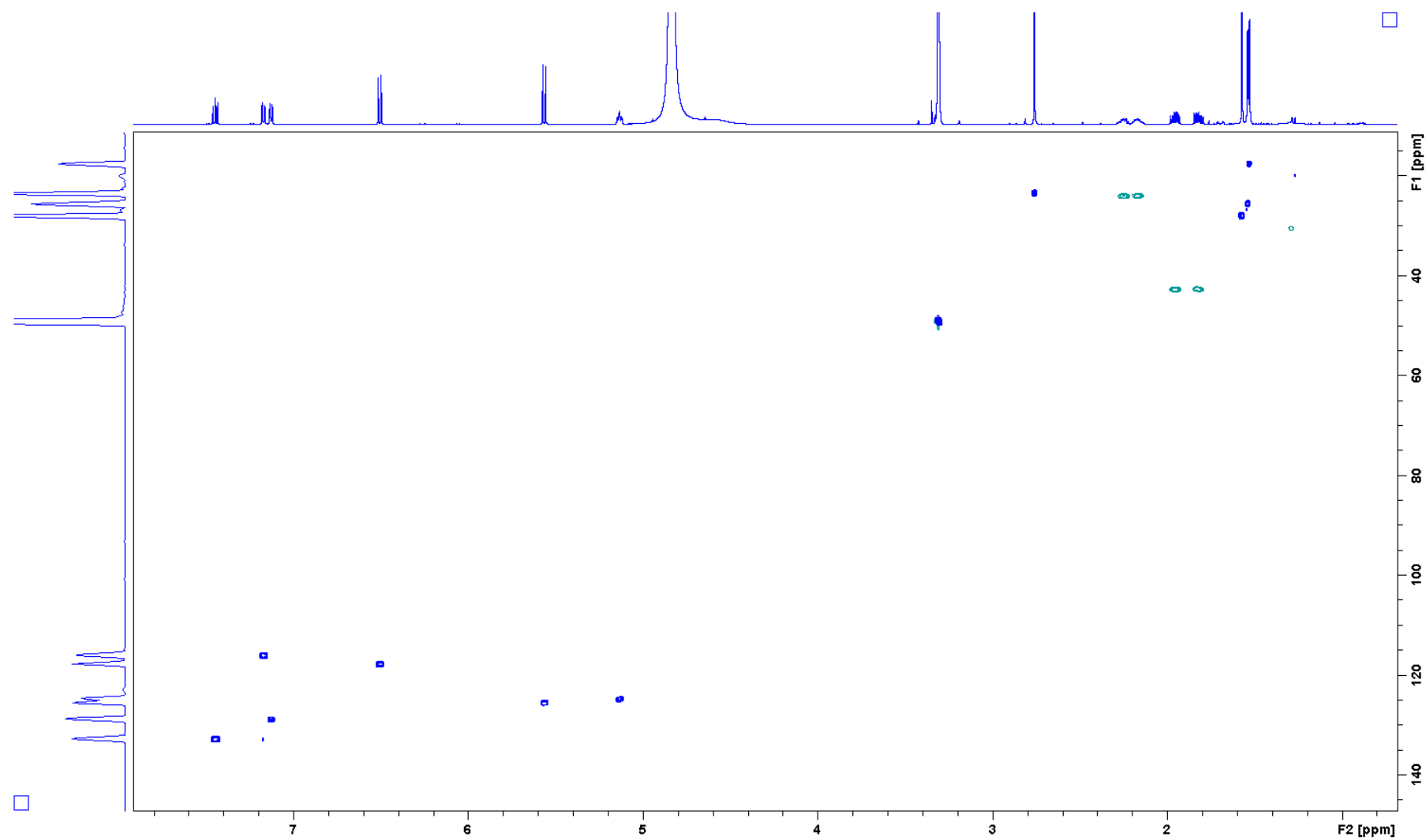


Figure S88. ^1H NMR spectrum of **17** (600 MHz, methanol- d_4).

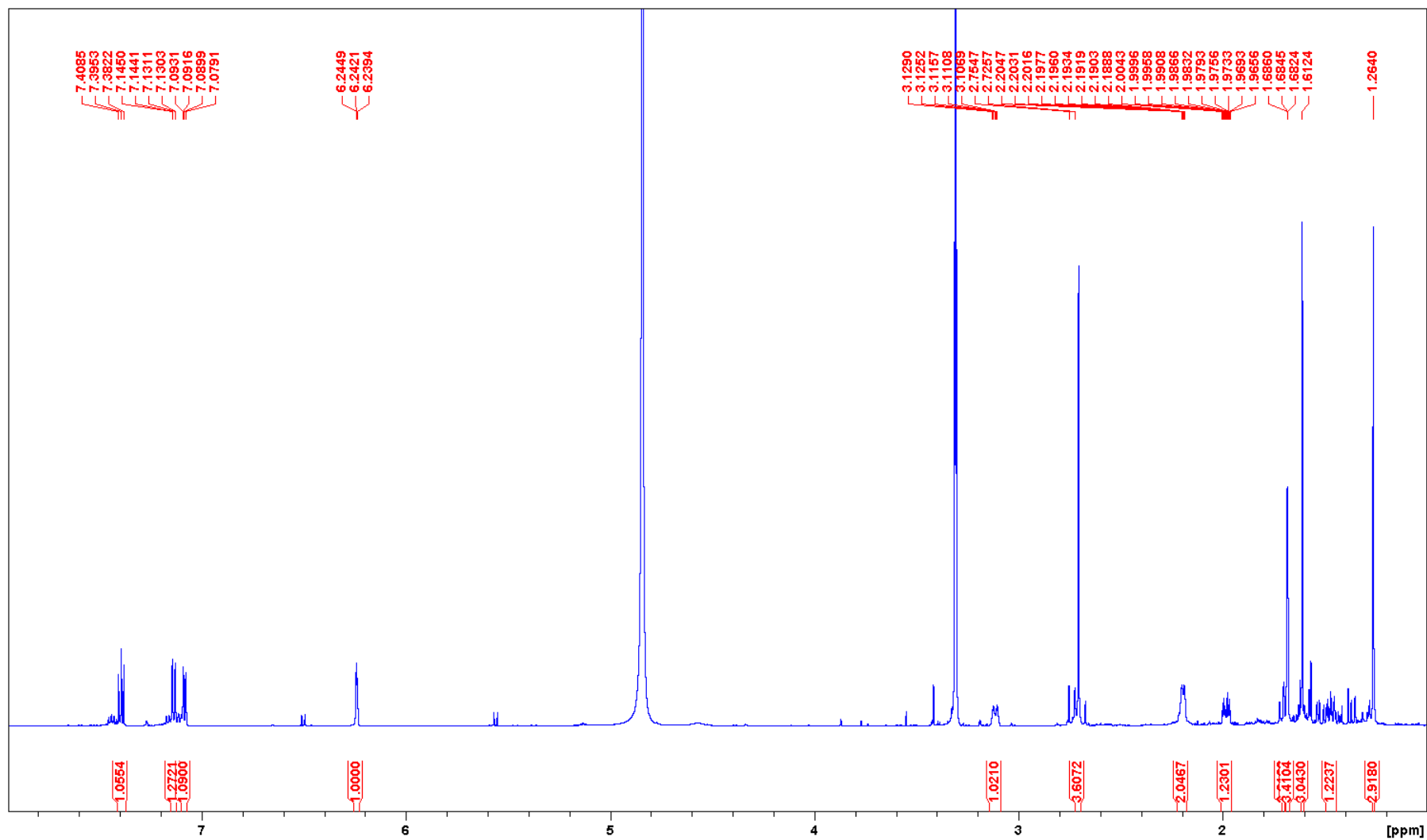


Figure S89. ^{13}C NMR spectrum of **17** (151 MHz, methanol- d_4).

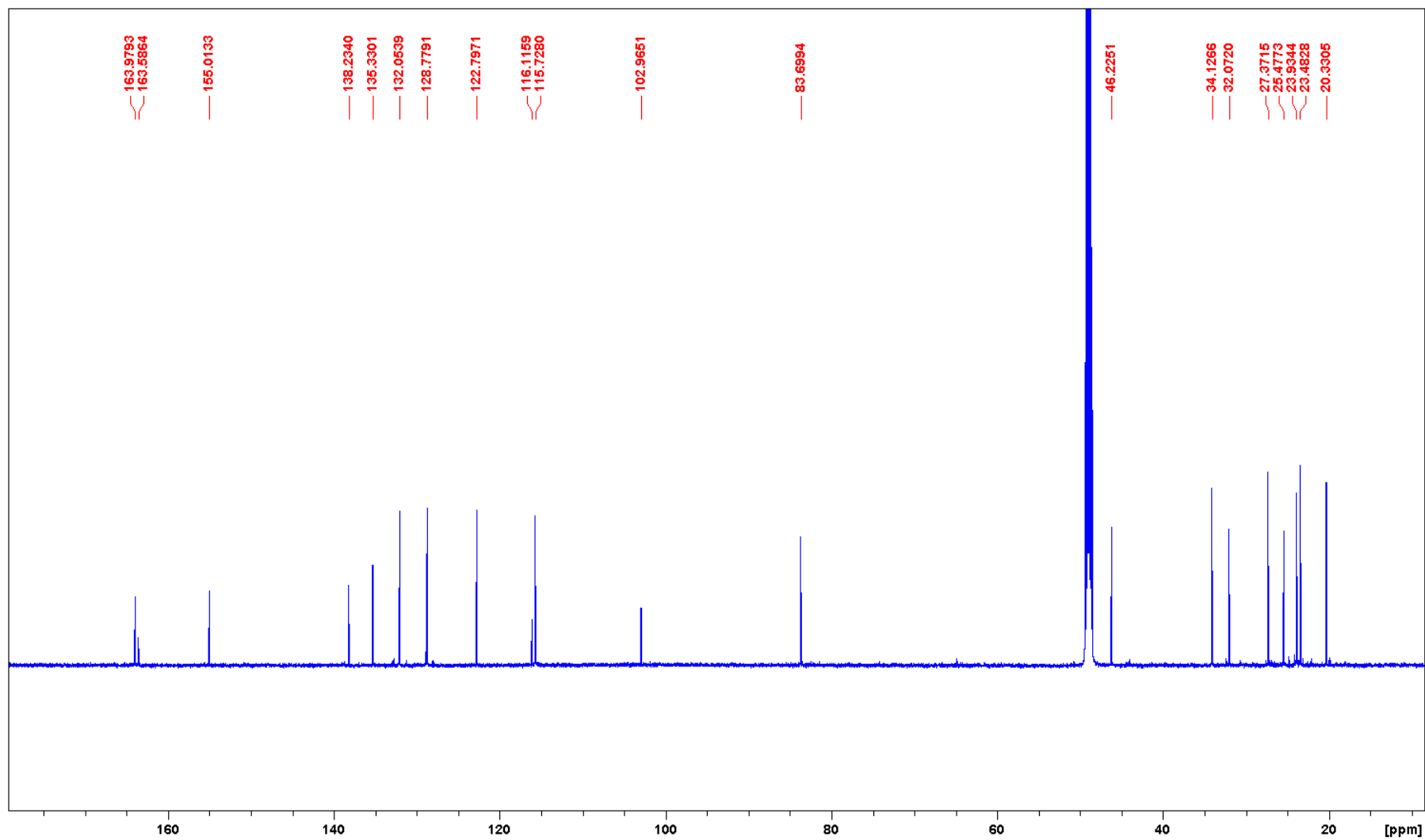


Figure S90. HSQC spectrum of **17** (600 MHz, methanol- d_4).

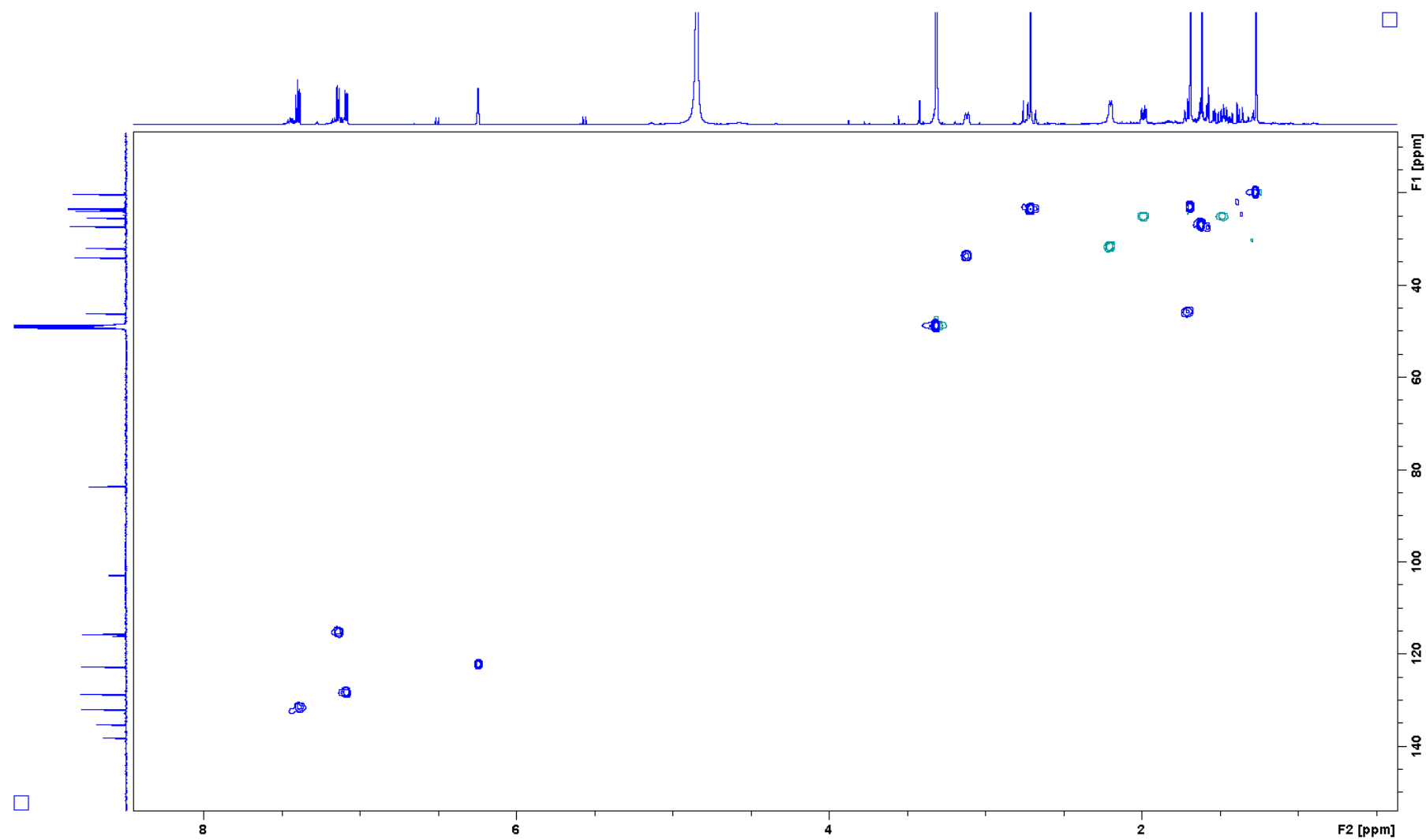


Figure S91. COSY spectrum of **17** (600 MHz, methanol- d_4).

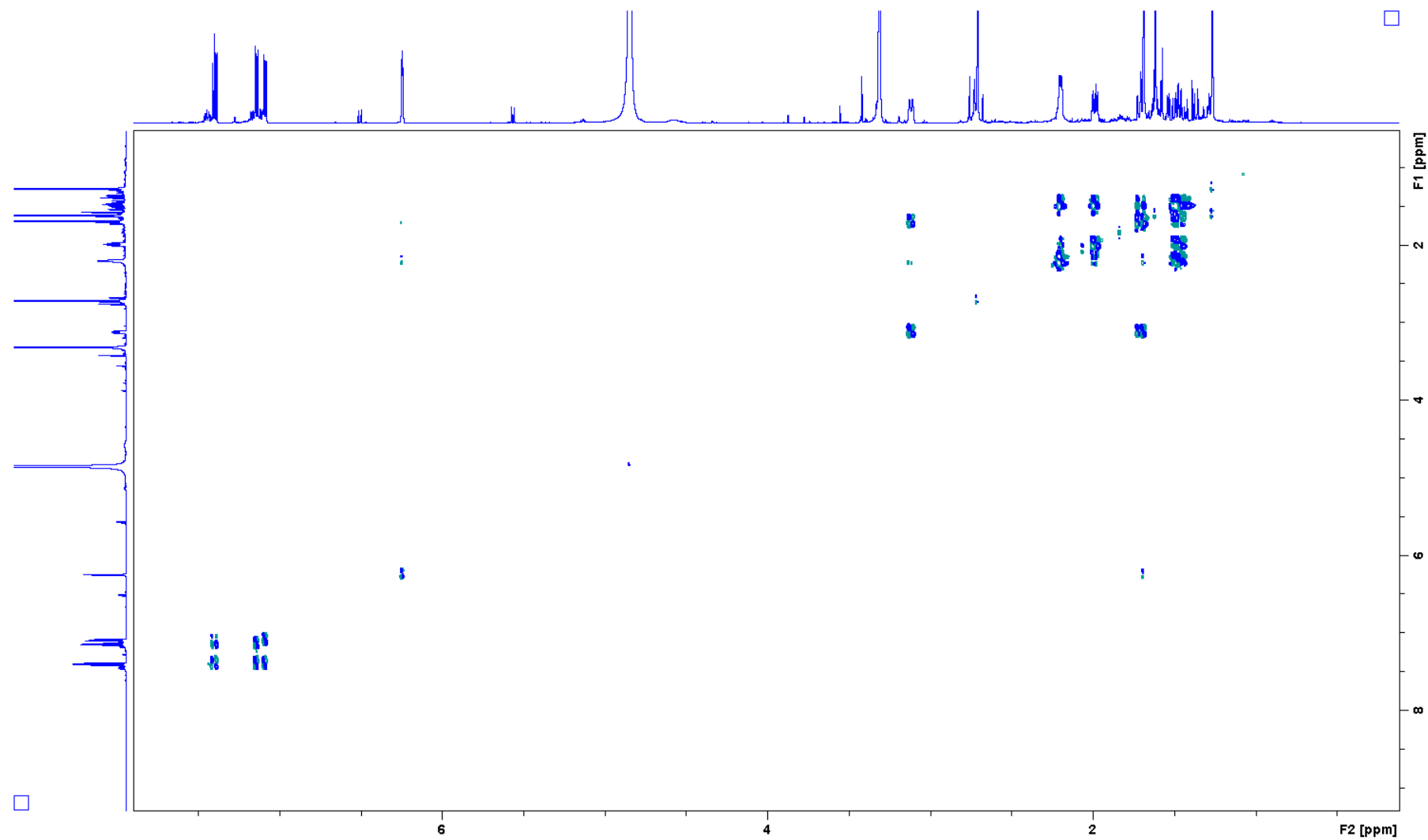


Figure S92. HMBC spectrum of **17** (600 MHz, methanol-*d*₄).

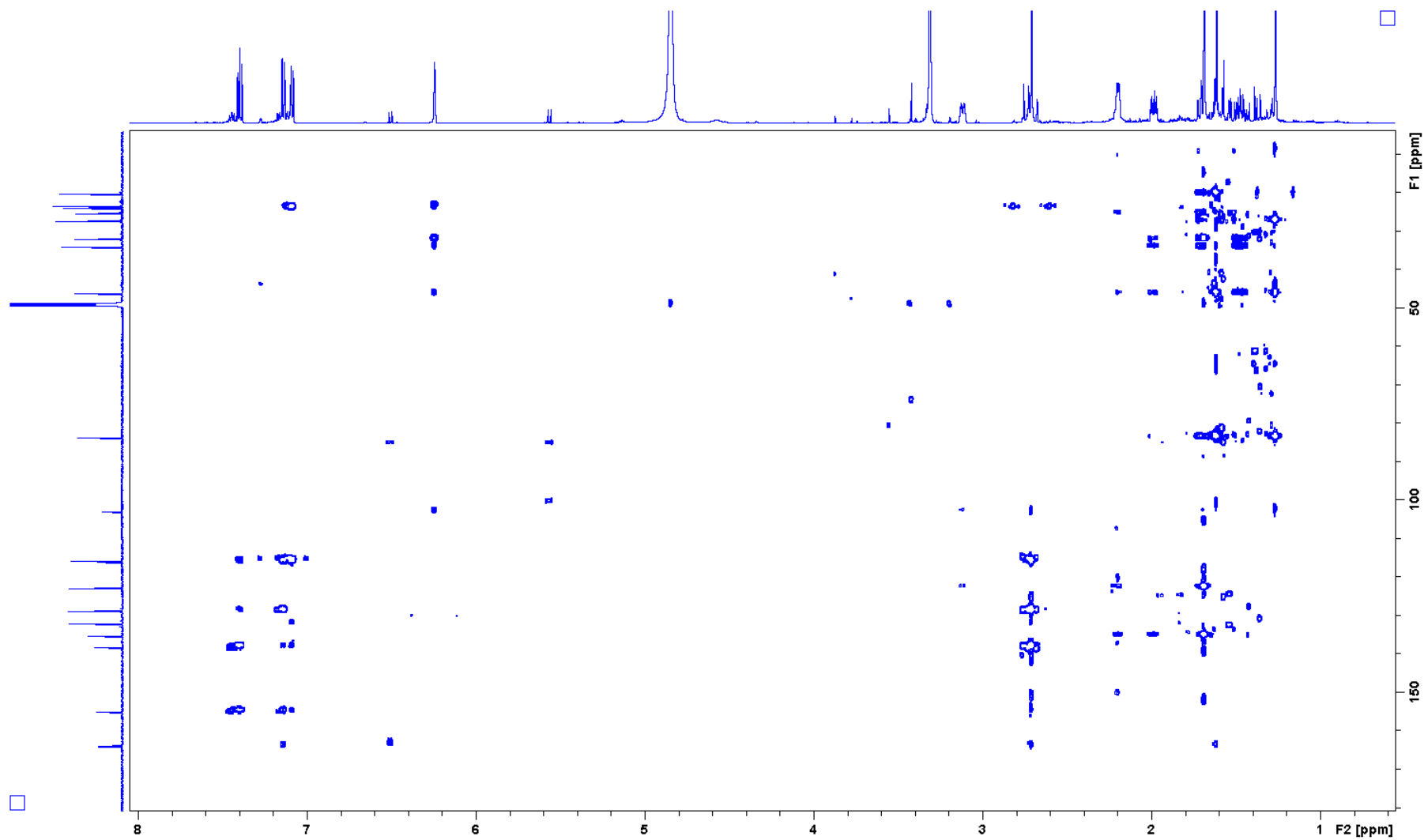


Figure S93. ROESY spectrum of **17** (600 MHz, methanol-*d*₄).

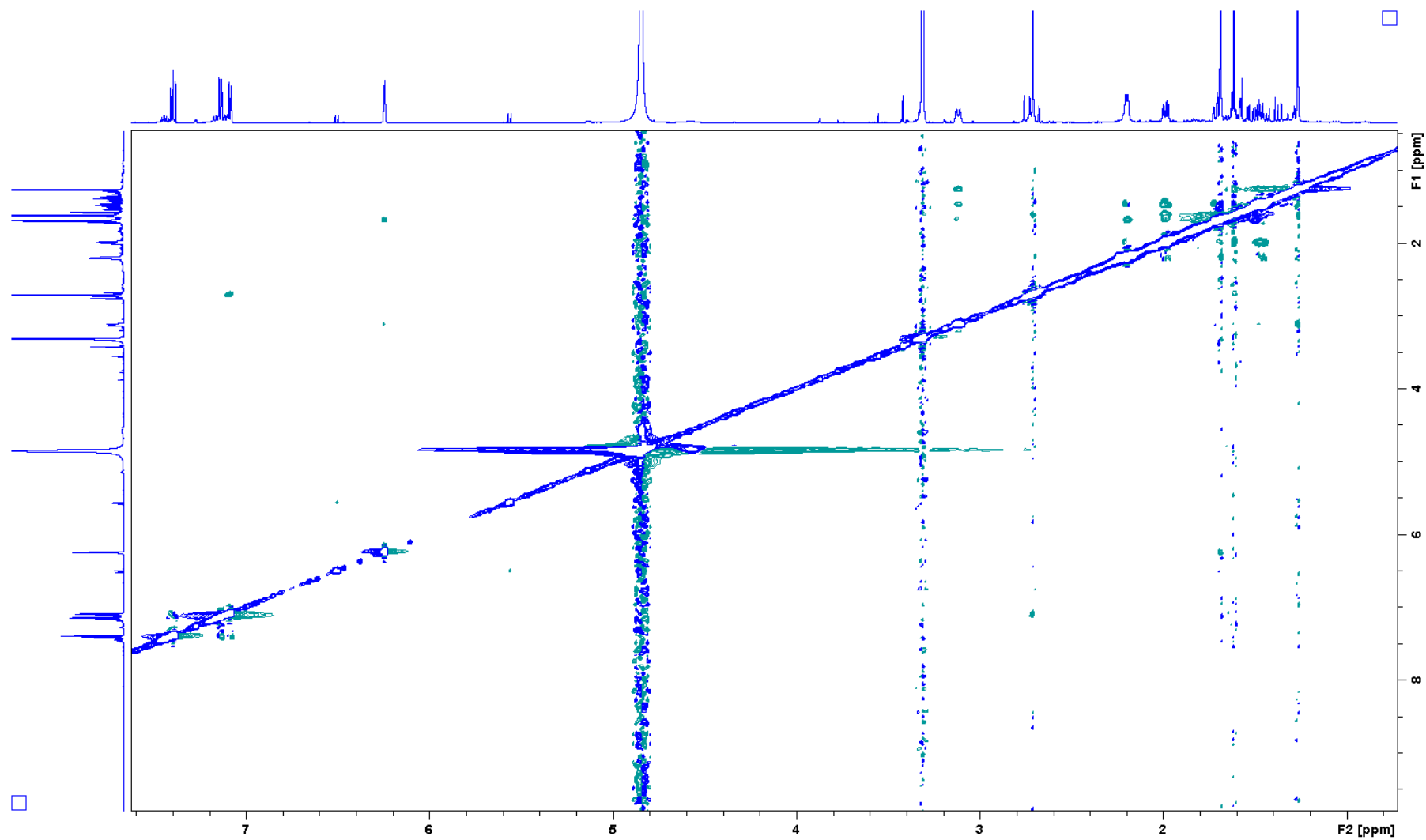


Figure S94. ^1H NMR spectrum of **18** (600 MHz, methanol- d_4).

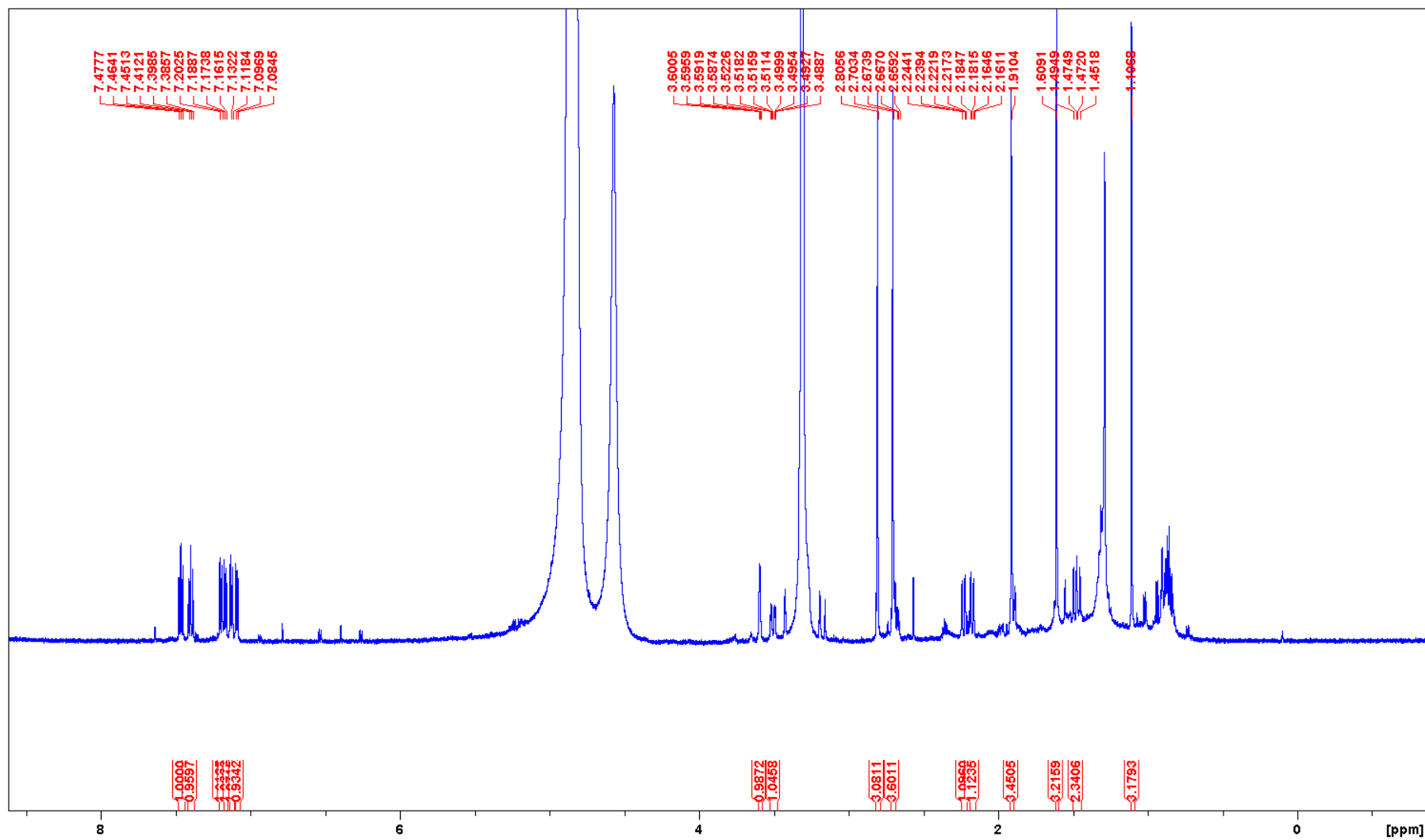


Figure S95. J-MOD NMR spectrum of **18** (600 MHz, methanol-*d*₄).

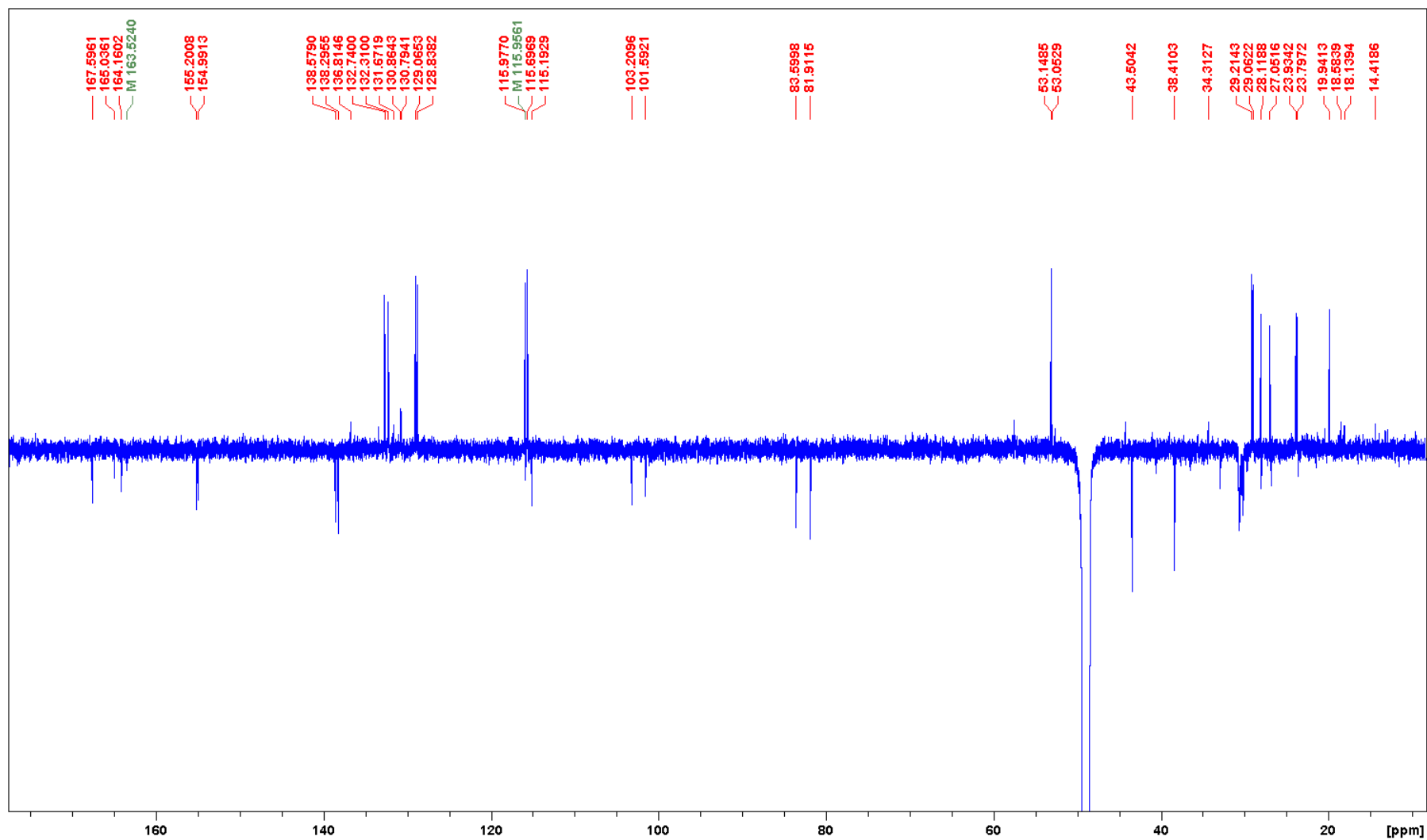


Figure S96. HSQC spectrum of **18** (600 MHz, methanol- d_4).

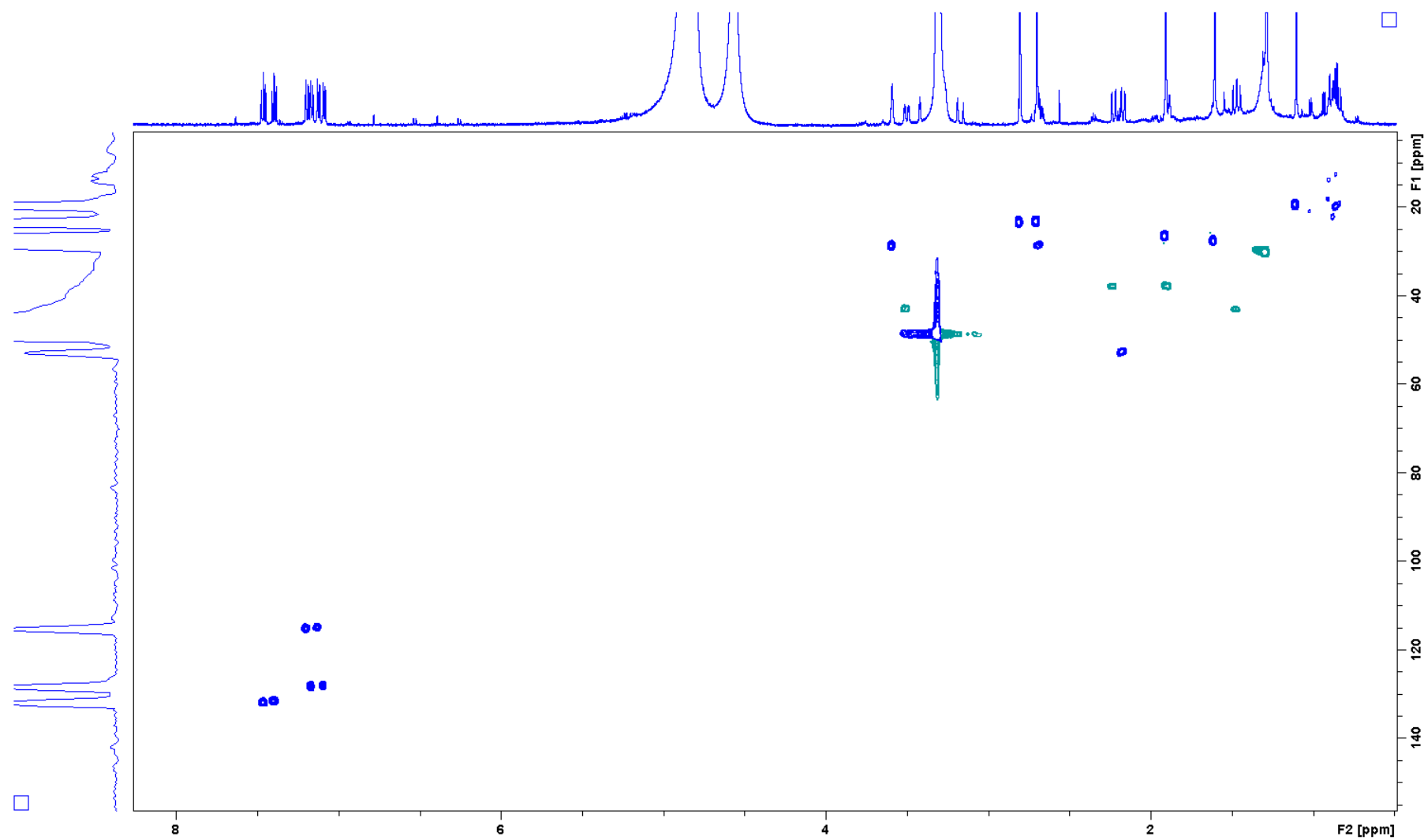


Figure S97. COSY spectrum of **18** (600 MHz, methanol- d_4).

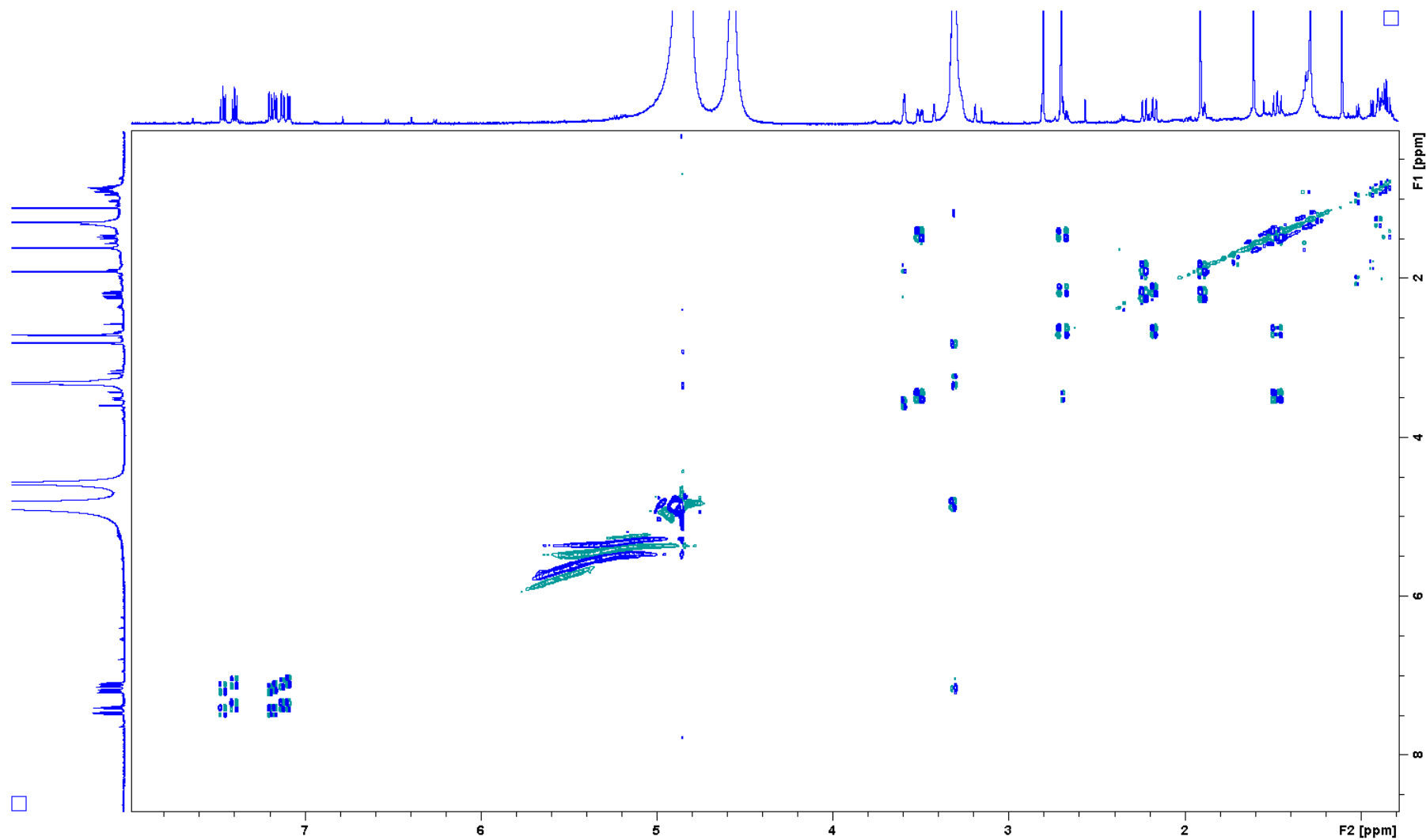


Figure S98. HMBC spectrum of **18** (600 MHz, methanol-*d*₄).

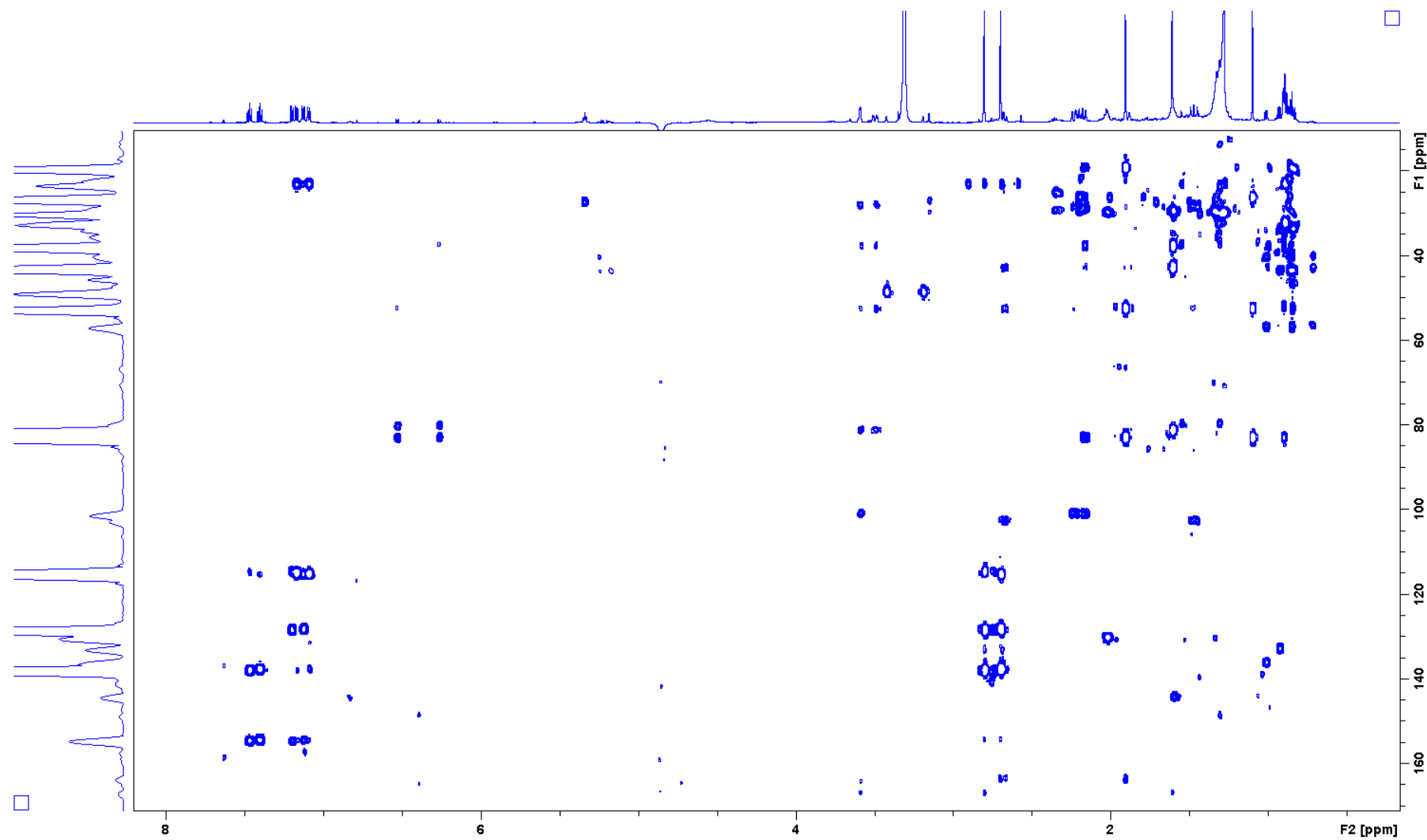


Figure S99. ROESY spectrum of **18** (600 MHz, methanol- d_4).

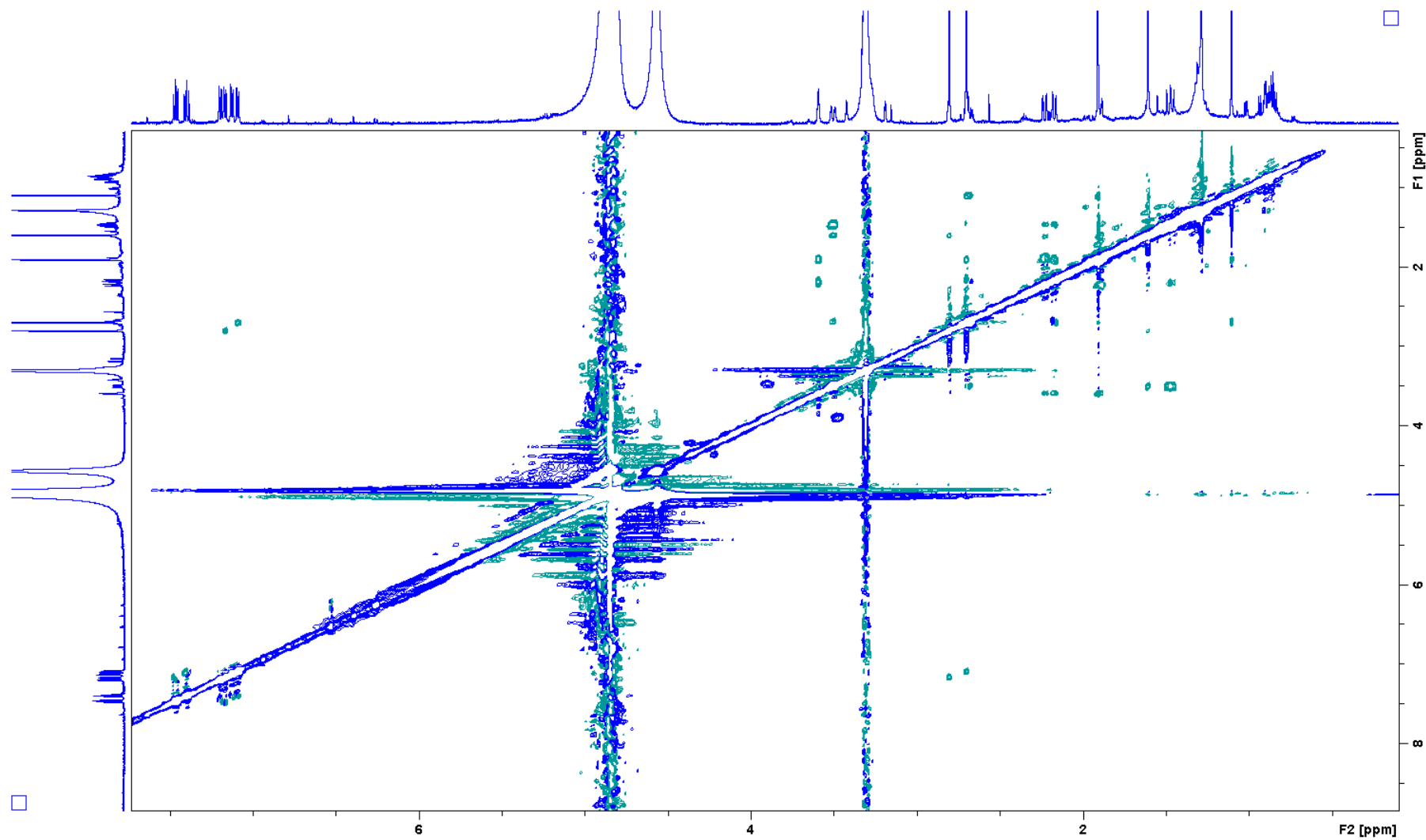


Figure S100. ^1H NMR spectrum of **19** (600 MHz, methanol- d_4).

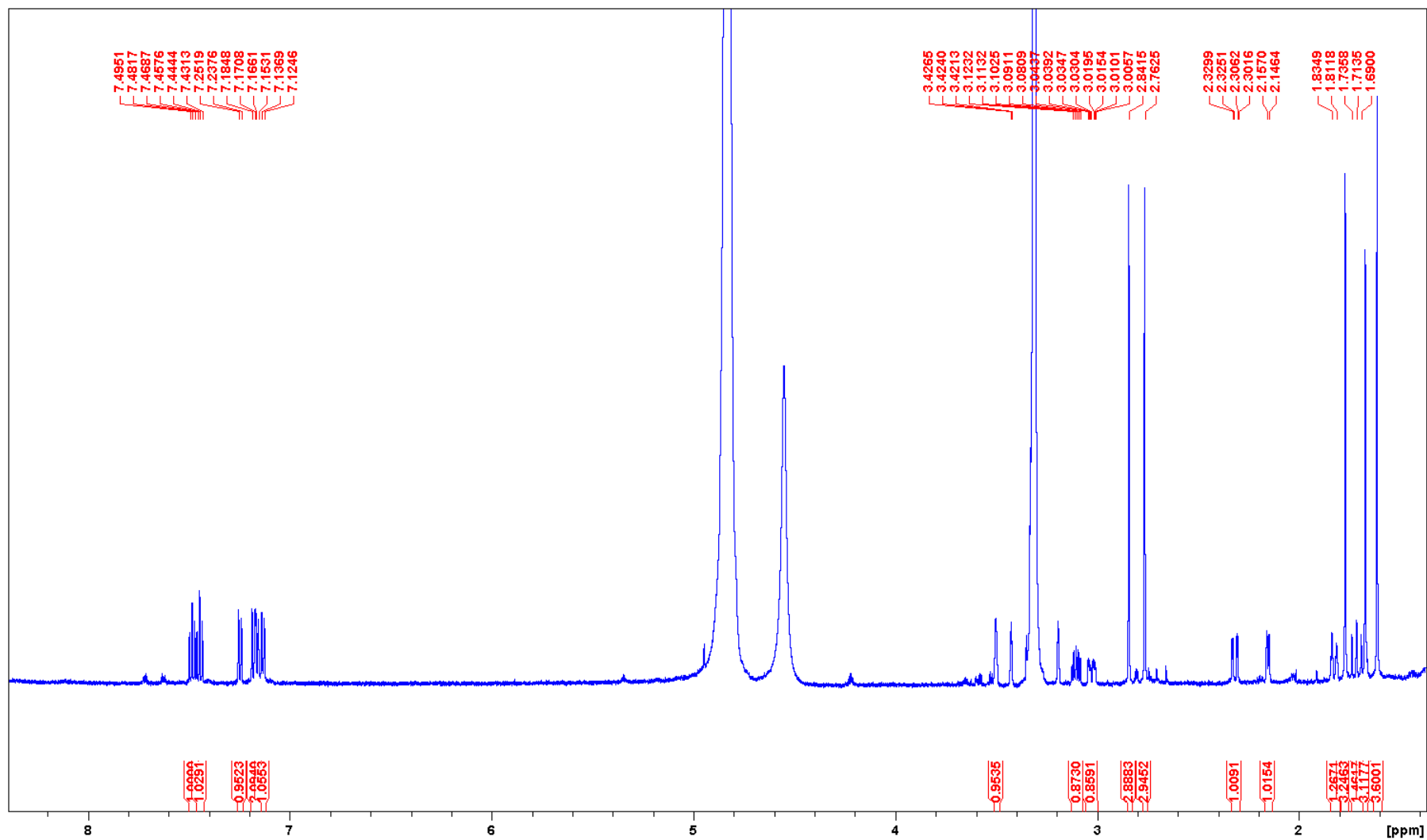


Figure S101. J-MOD NMR spectrum of **19** (151 MHz, methanol-*d*₄).

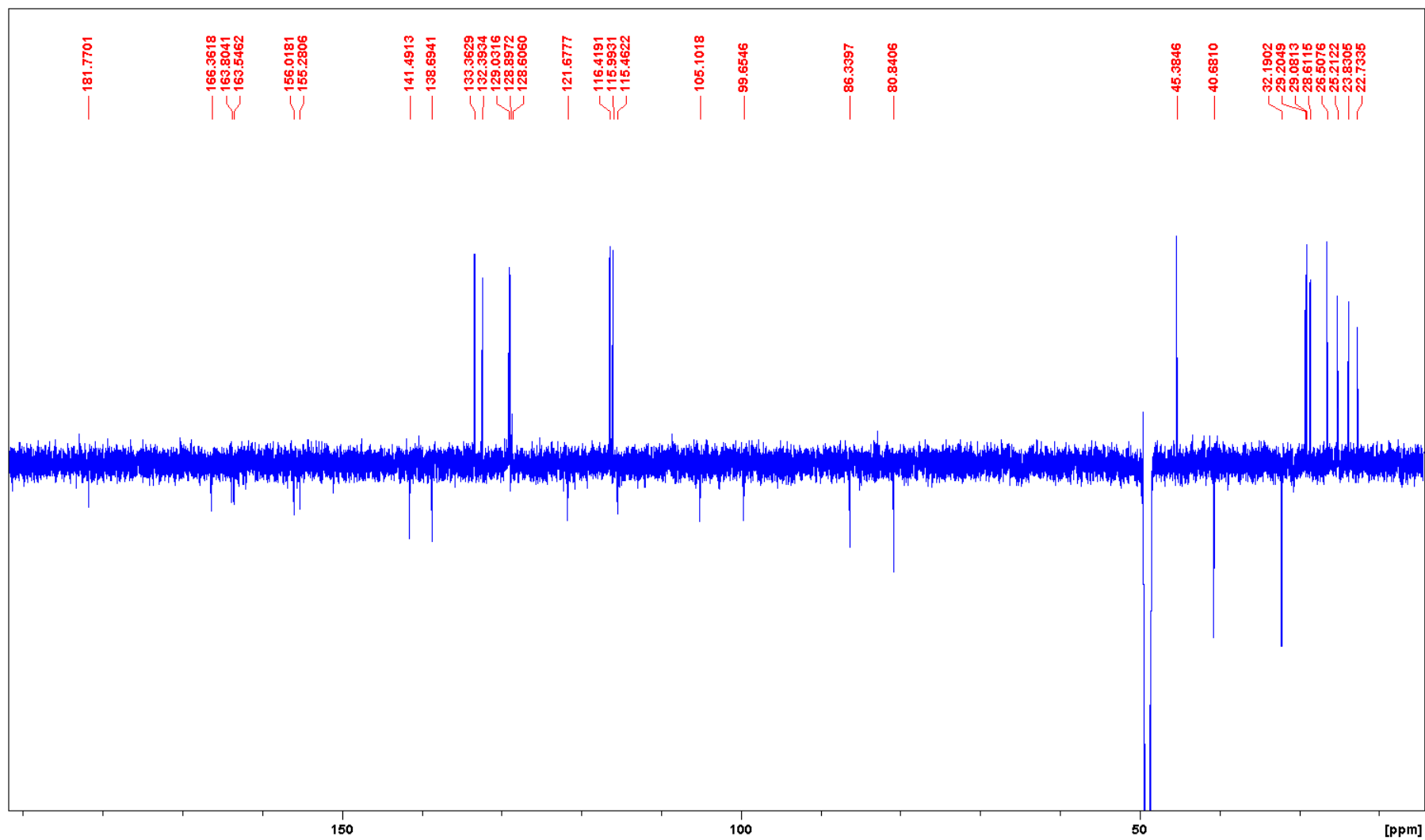


Figure S102. HSQC spectrum of **19** (600 MHz, methanol- d_4).

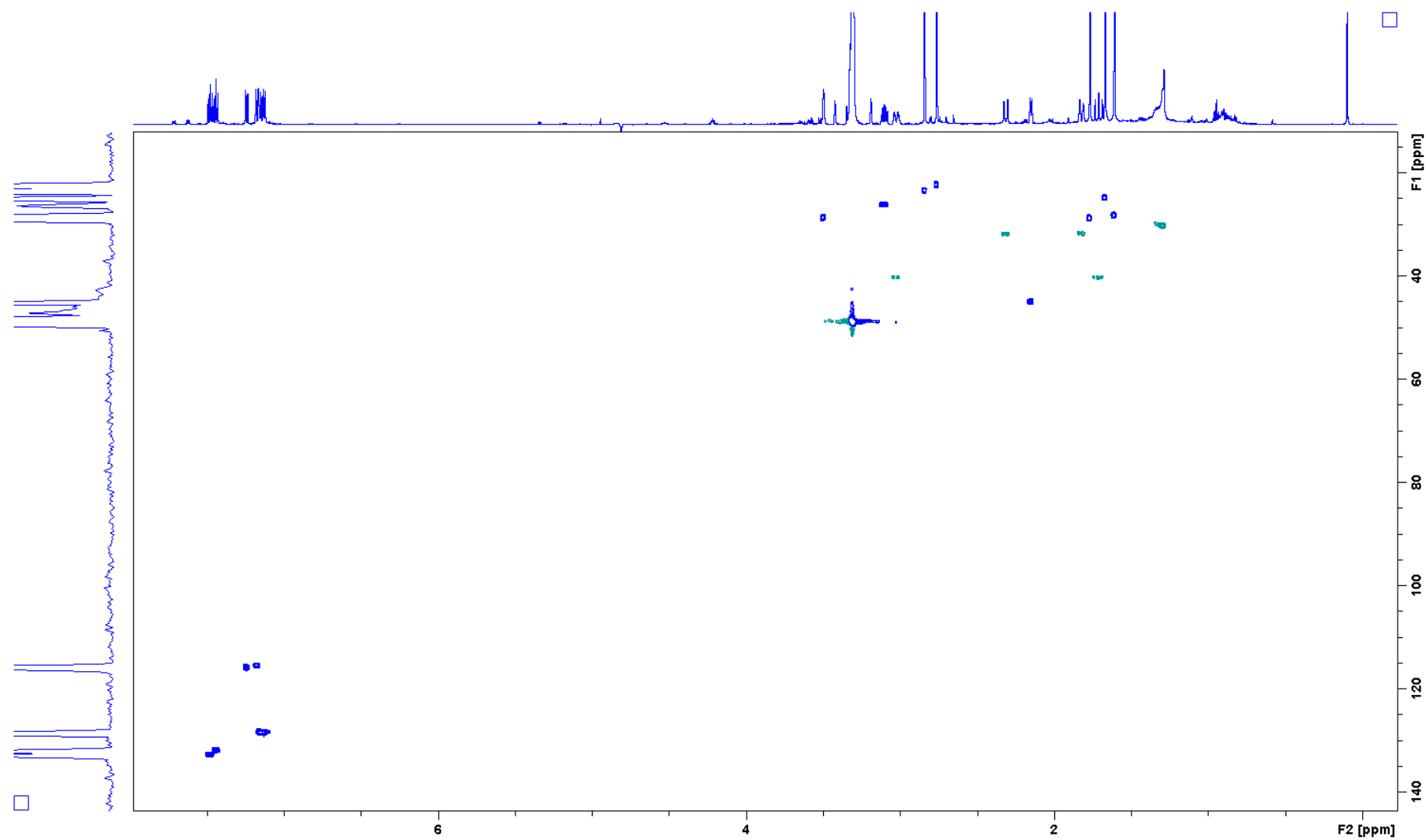


Figure S103. COSY spectrum of **19** (600 MHz, methanol- d_4).

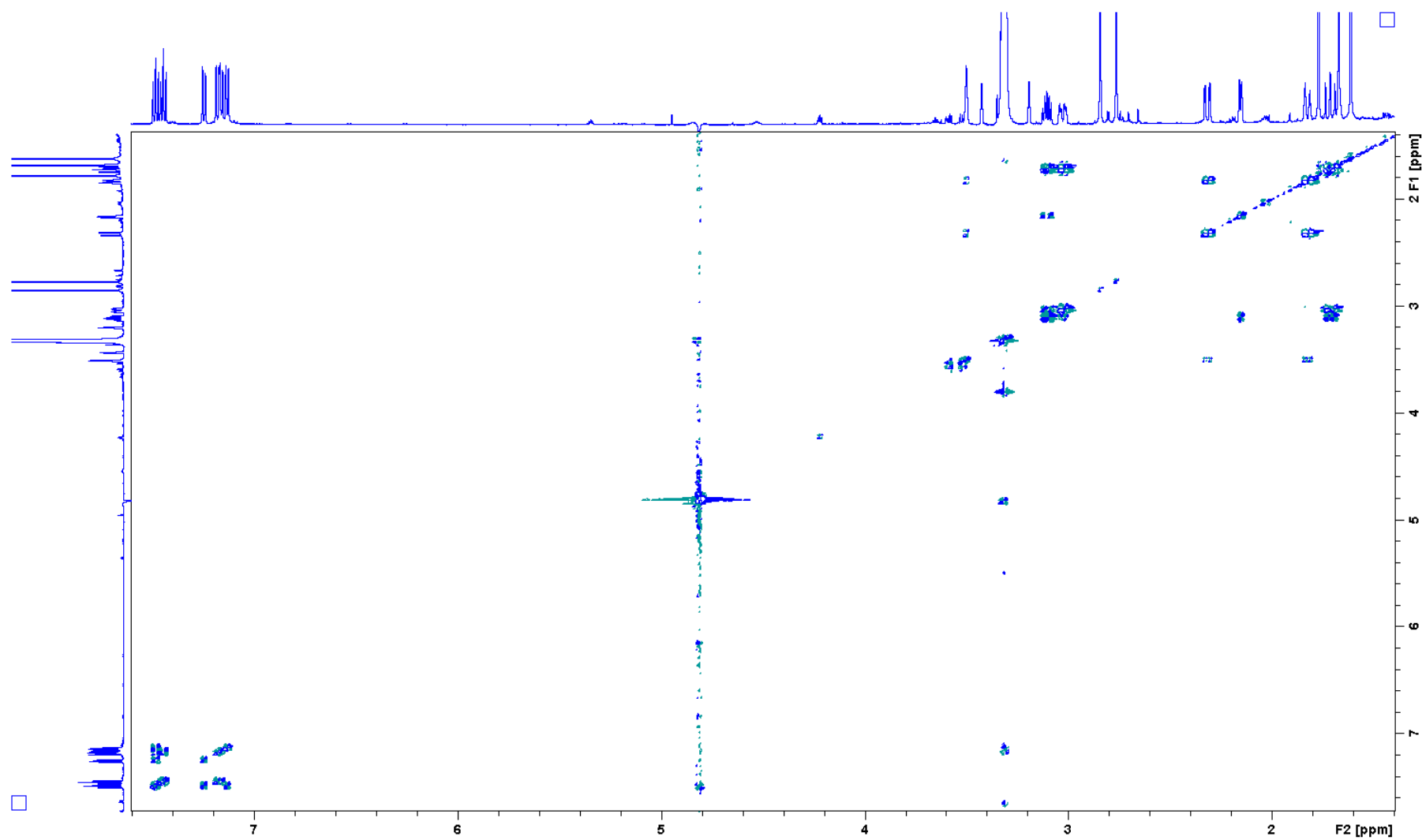


Figure S104. HMBC spectrum of **19** (600 MHz, methanol-*d*₄).

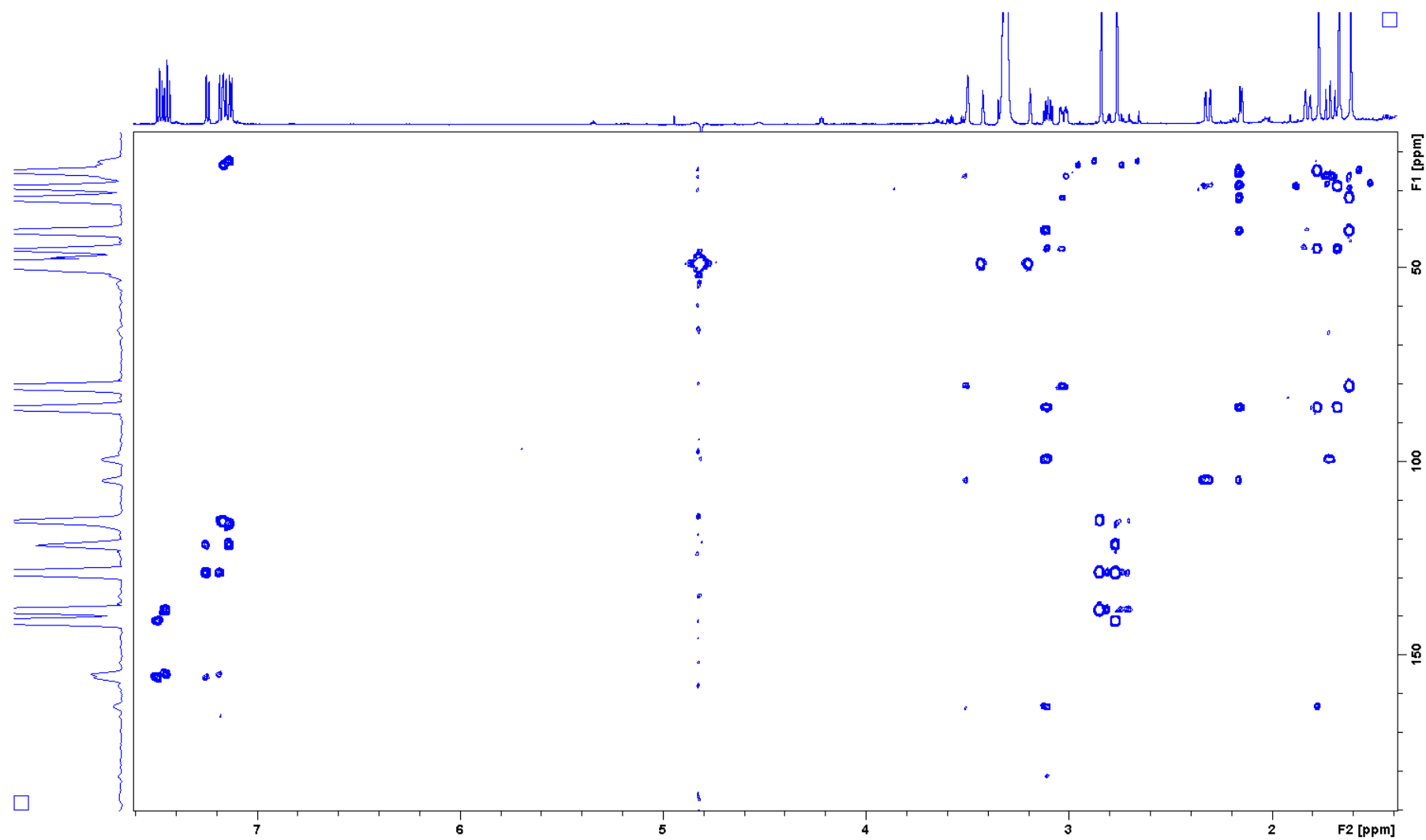


Figure S105. ROESY spectrum of **19** (600 MHz, methanol- d_4).

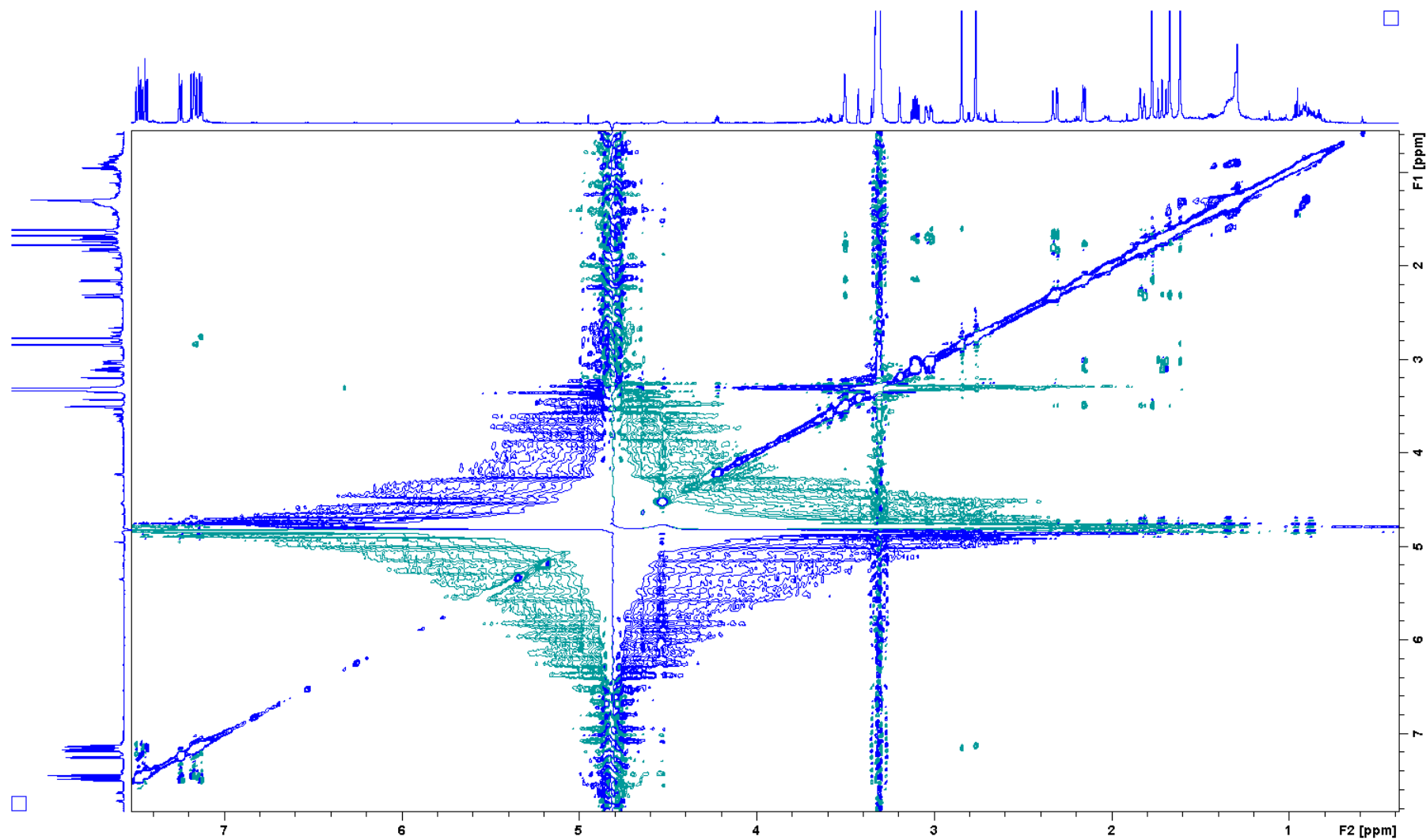


Figure S106. ^1H NMR spectrum of **23** (600 MHz, methanol- d_4).

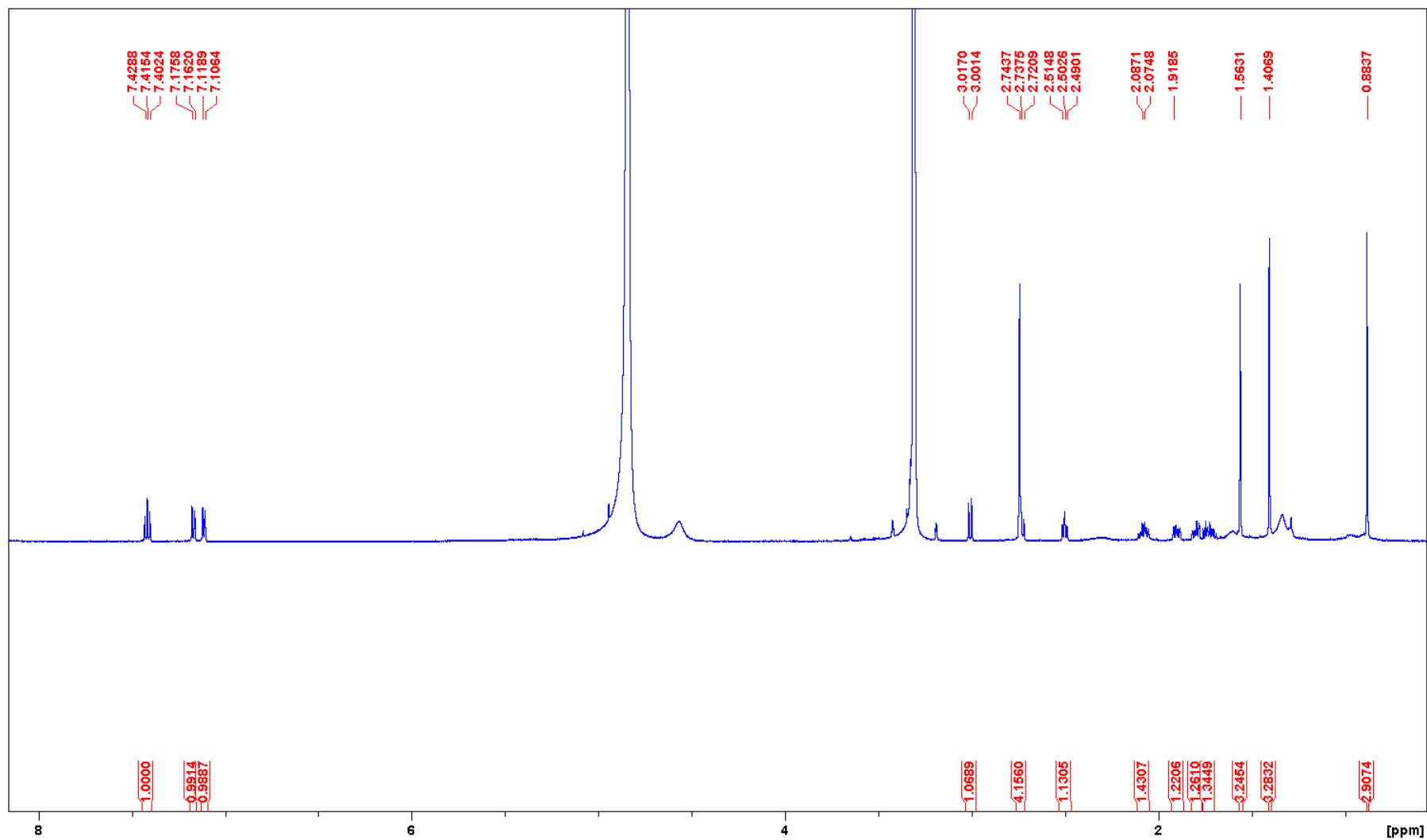


Figure S107. ^{13}C NMR spectrum of **23** (151 MHz, methanol- d_4).

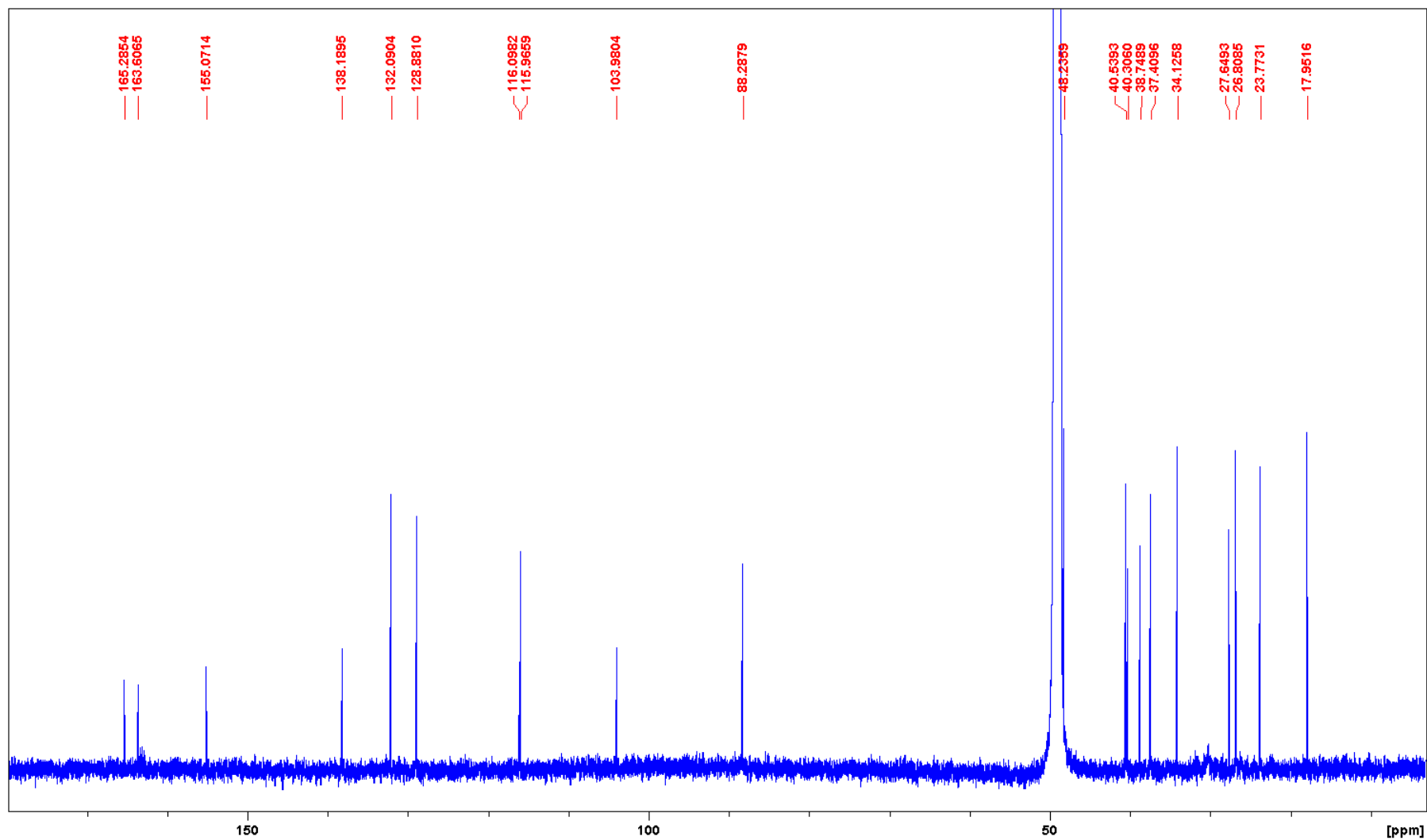


Figure S108. HSQC spectrum of **23** (600 MHz, methanol- d_4).

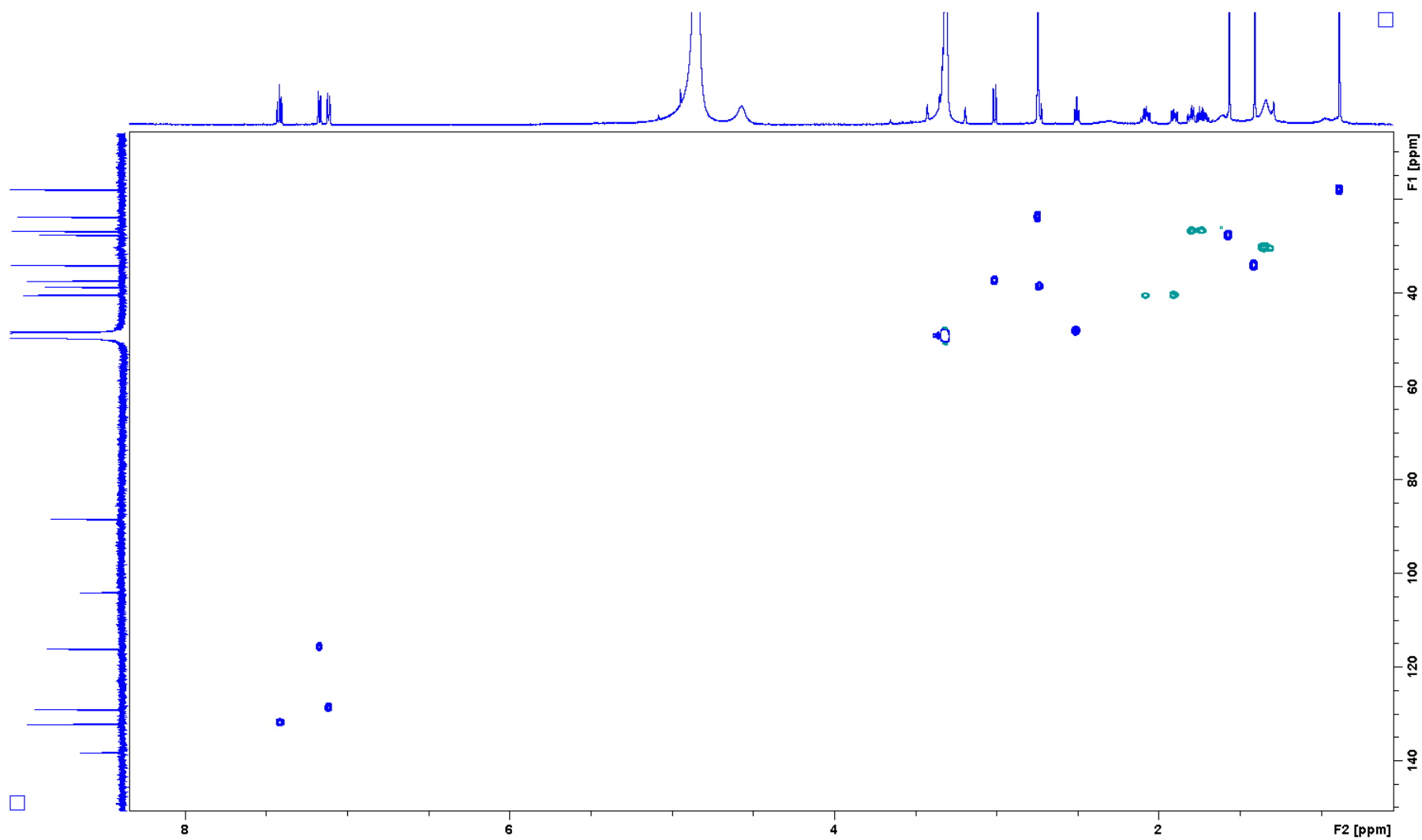


Figure S109. COSY spectrum of **23** (600 MHz, methanol- d_4).

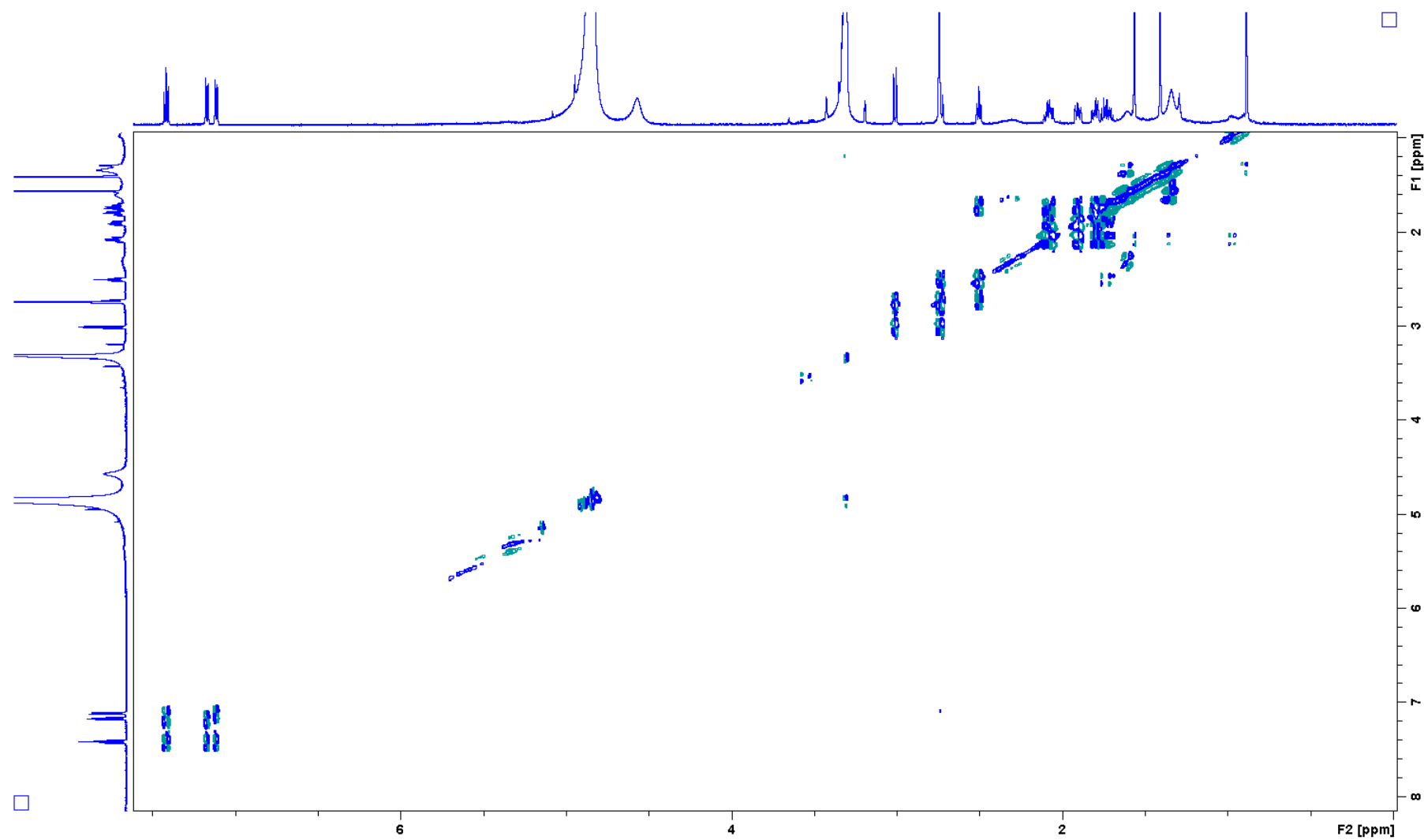


Figure S110. HMBC spectrum of **23** (600 MHz, methanol-*d*₄).

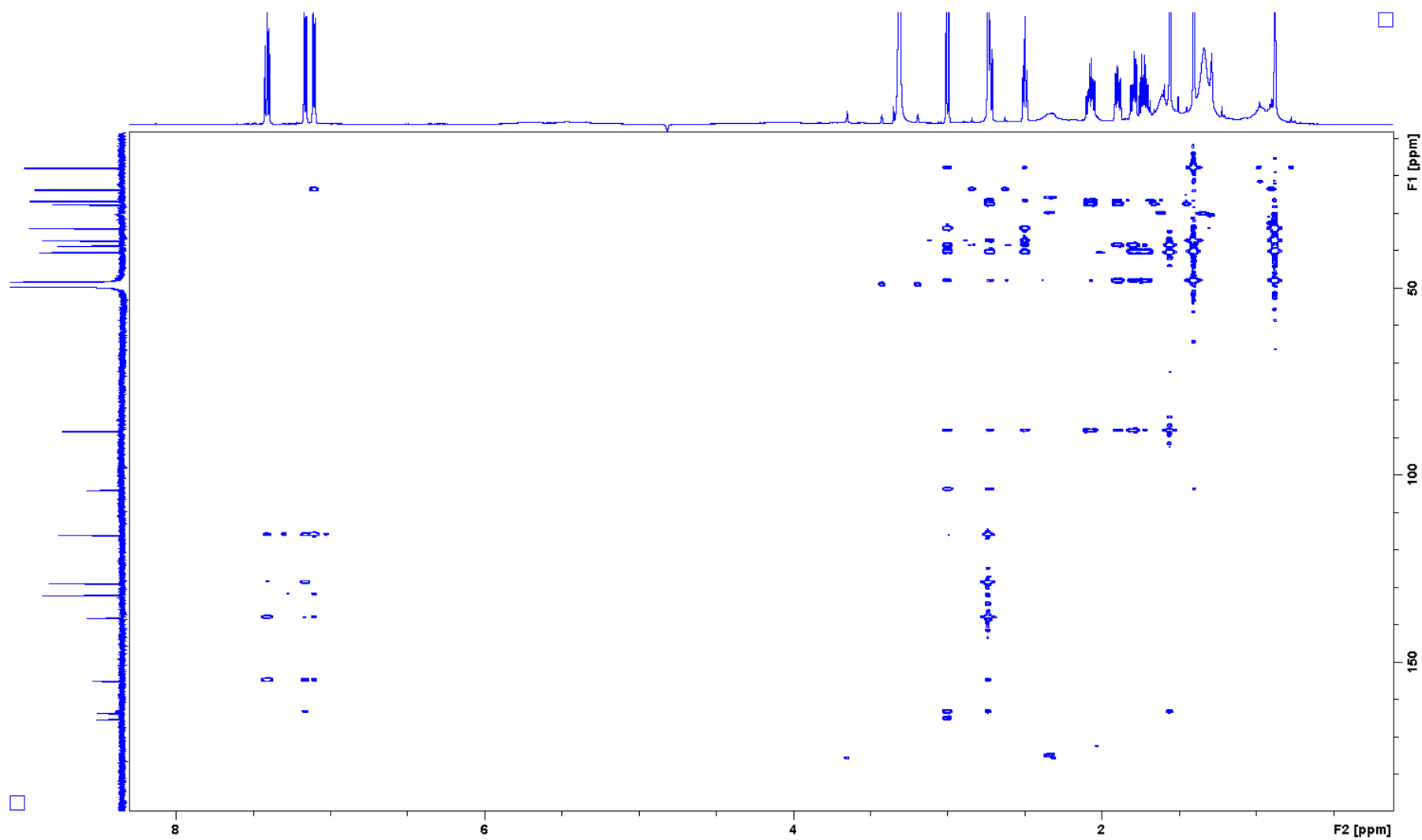


Figure S111. ROESY spectrum of **23** (600 MHz, methanol- d_4).

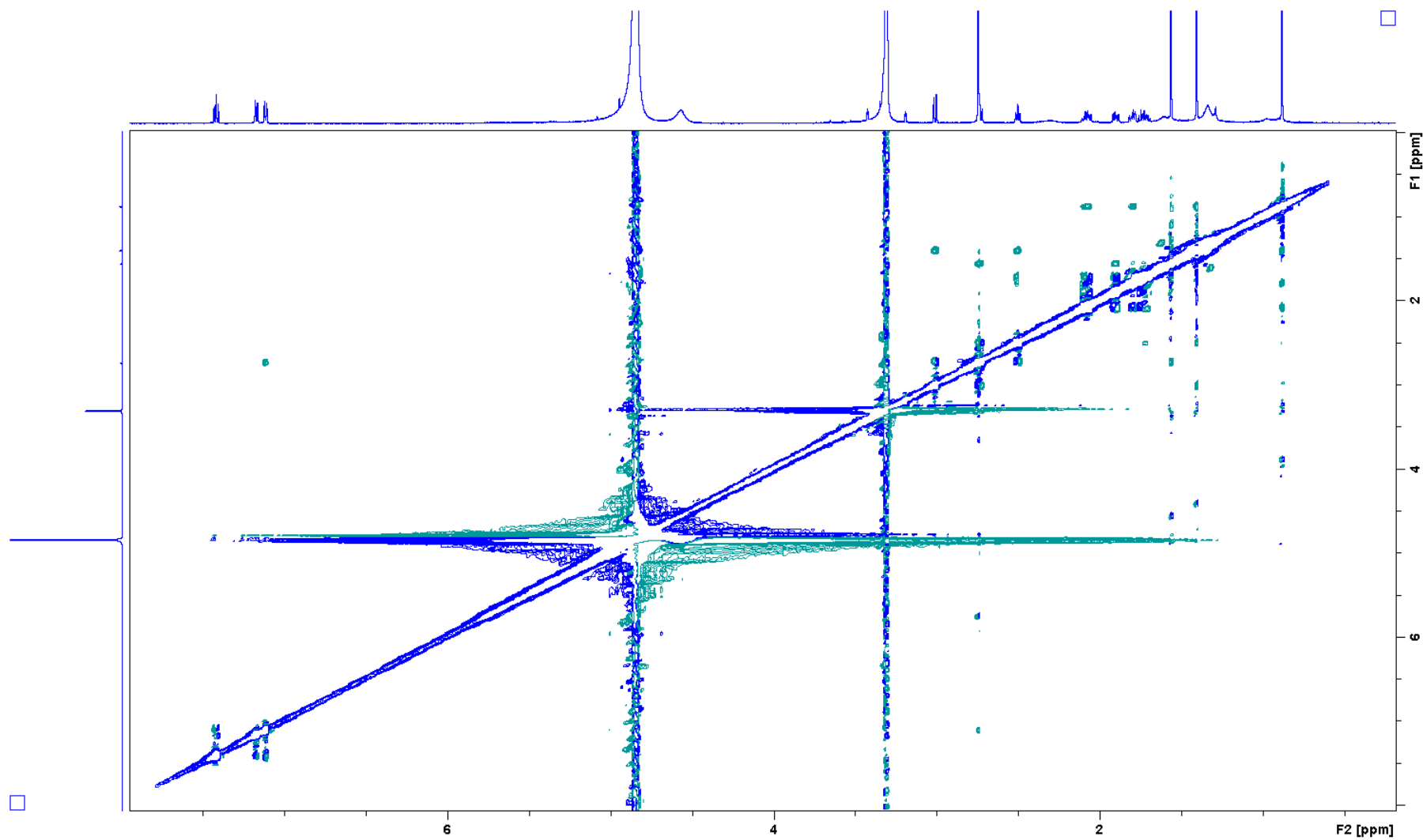


Figure S112. ^1H NMR spectrum of **24** (600 MHz, methanol- d_4).

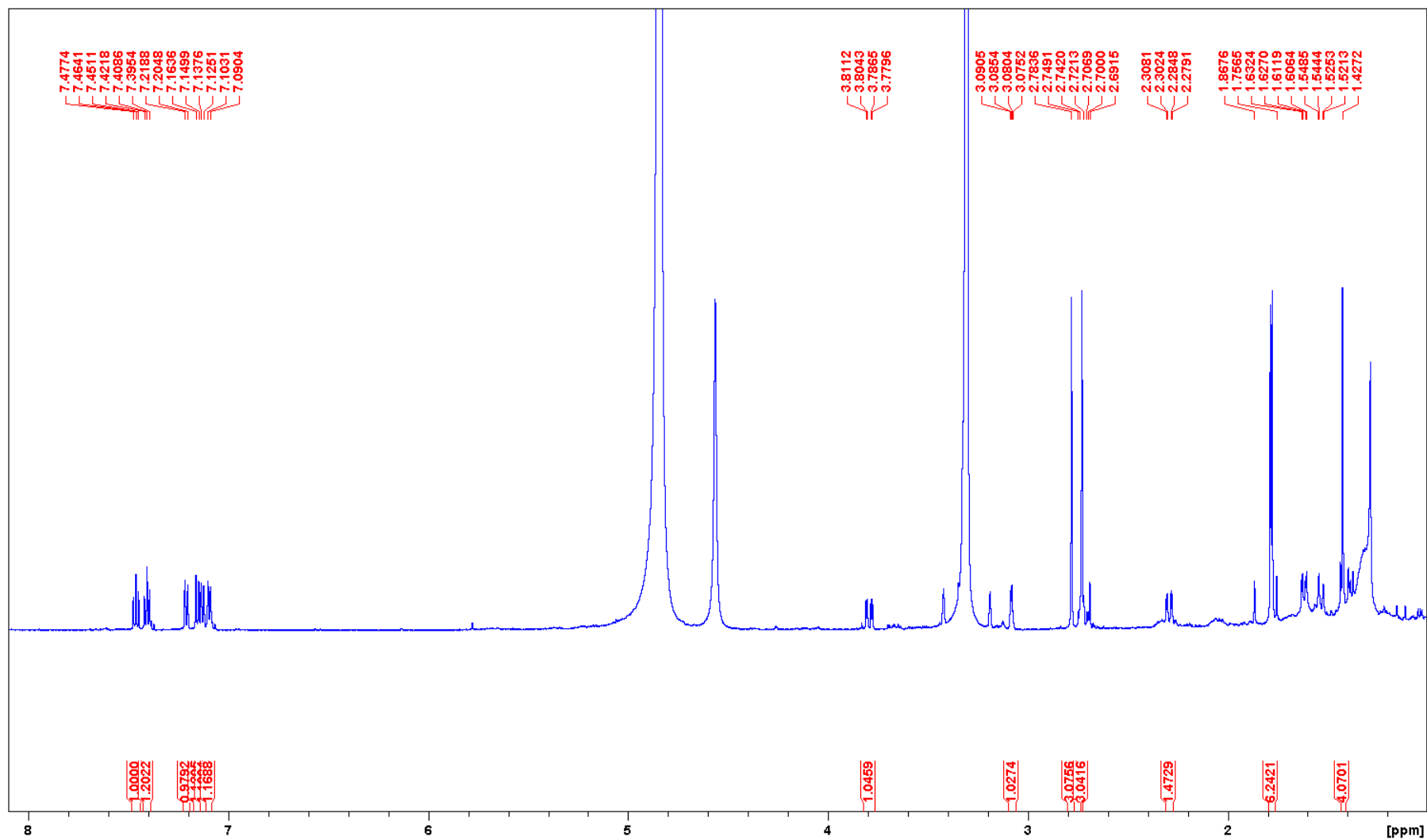


Figure S113. ^{13}C NMR spectrum of **24** (151 MHz, methanol- d_4).

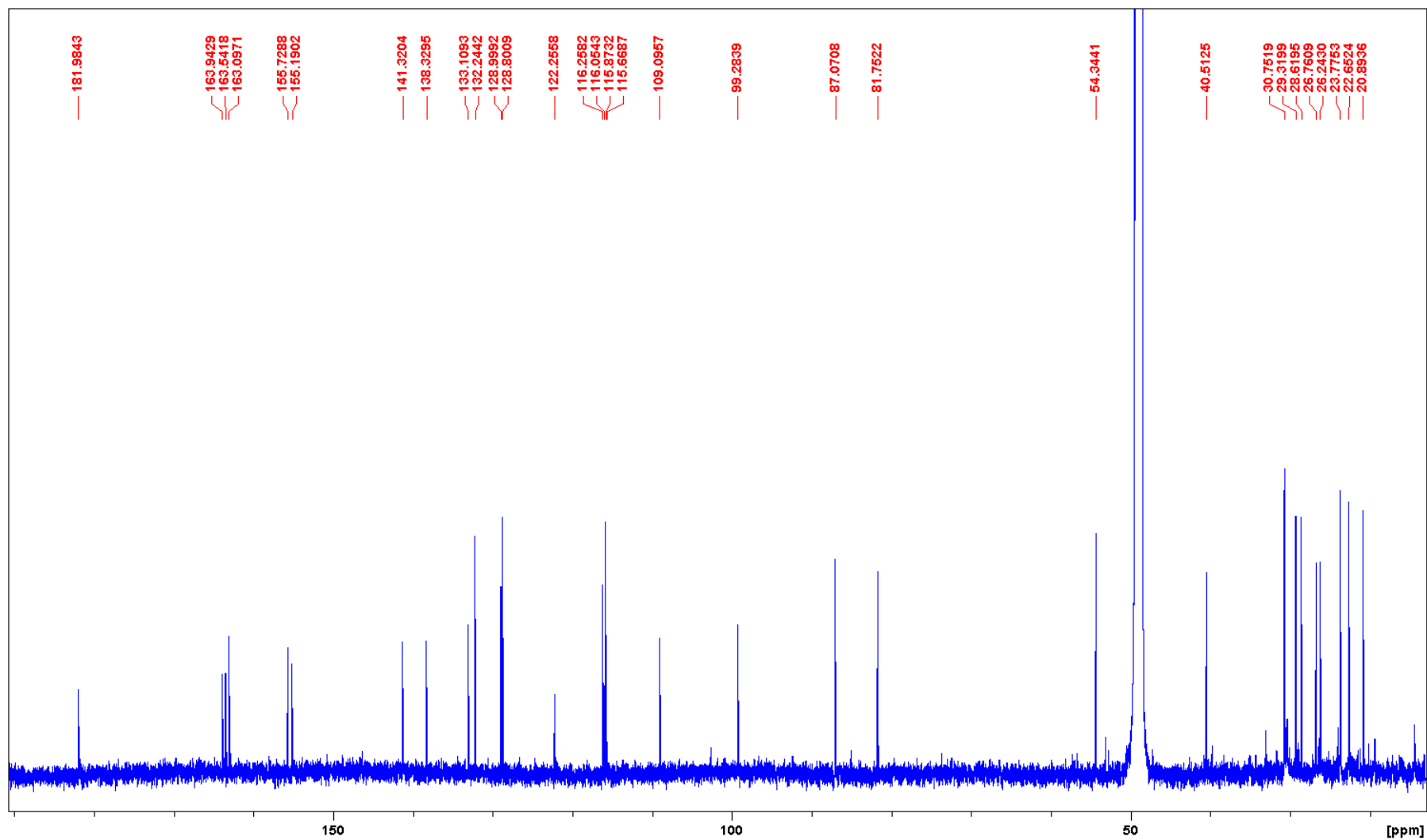


Figure S114. HSQC spectrum of **24** (600 MHz, methanol- d_4).

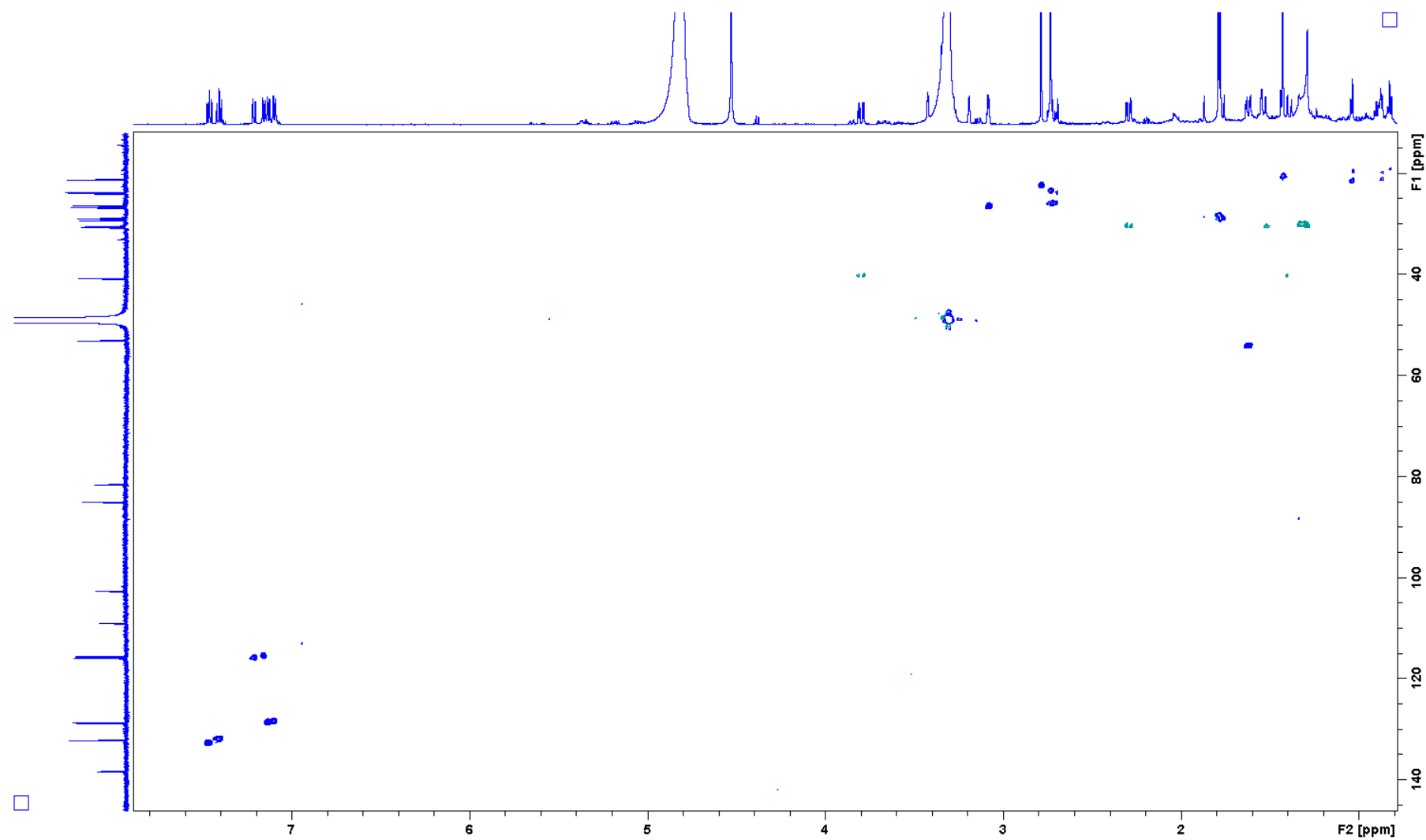


Figure S115. COSY spectrum of **24** (600 MHz, methanol- d_4).

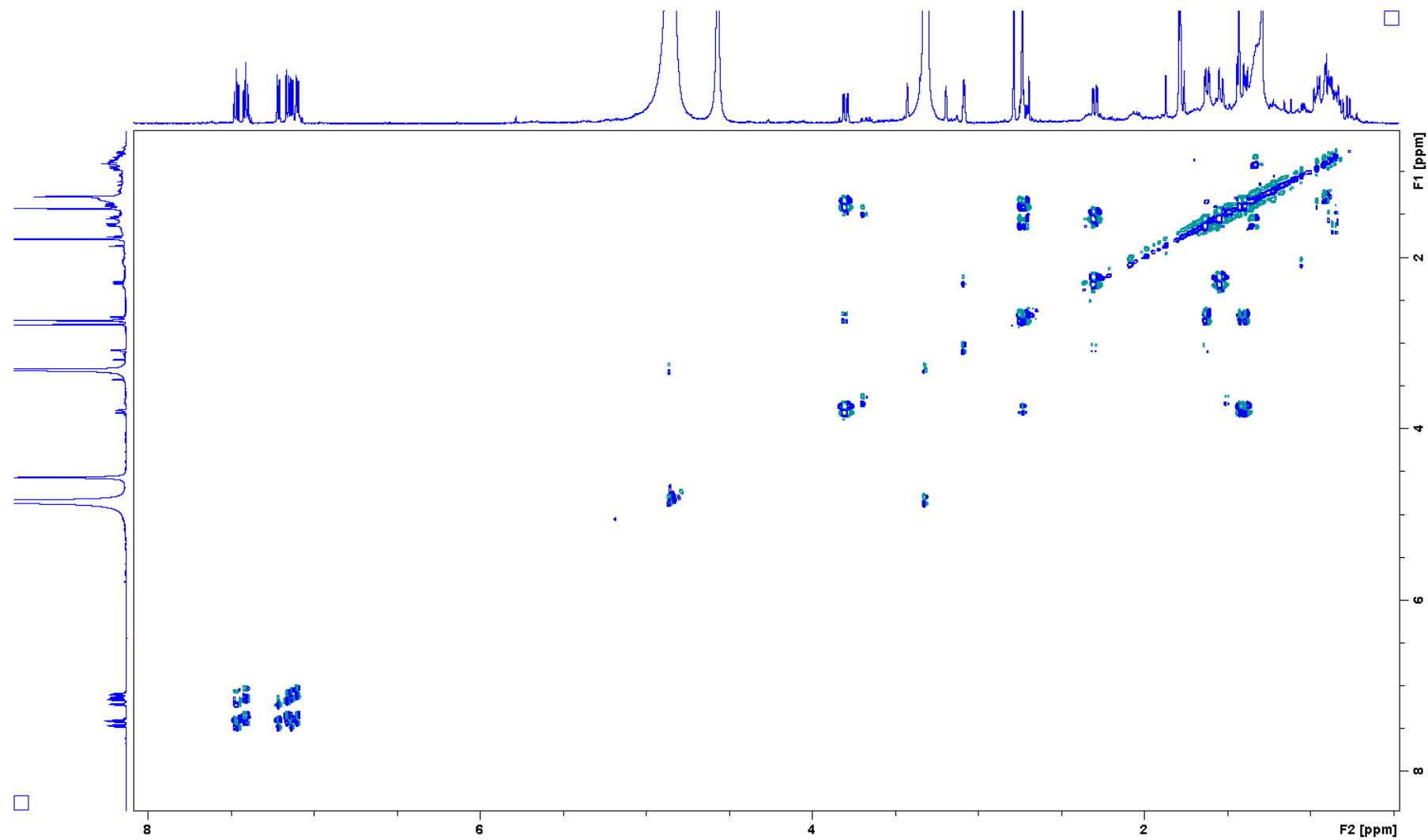


Figure S116. HMBC spectrum of **24** (600 MHz, methanol-*d*₄).

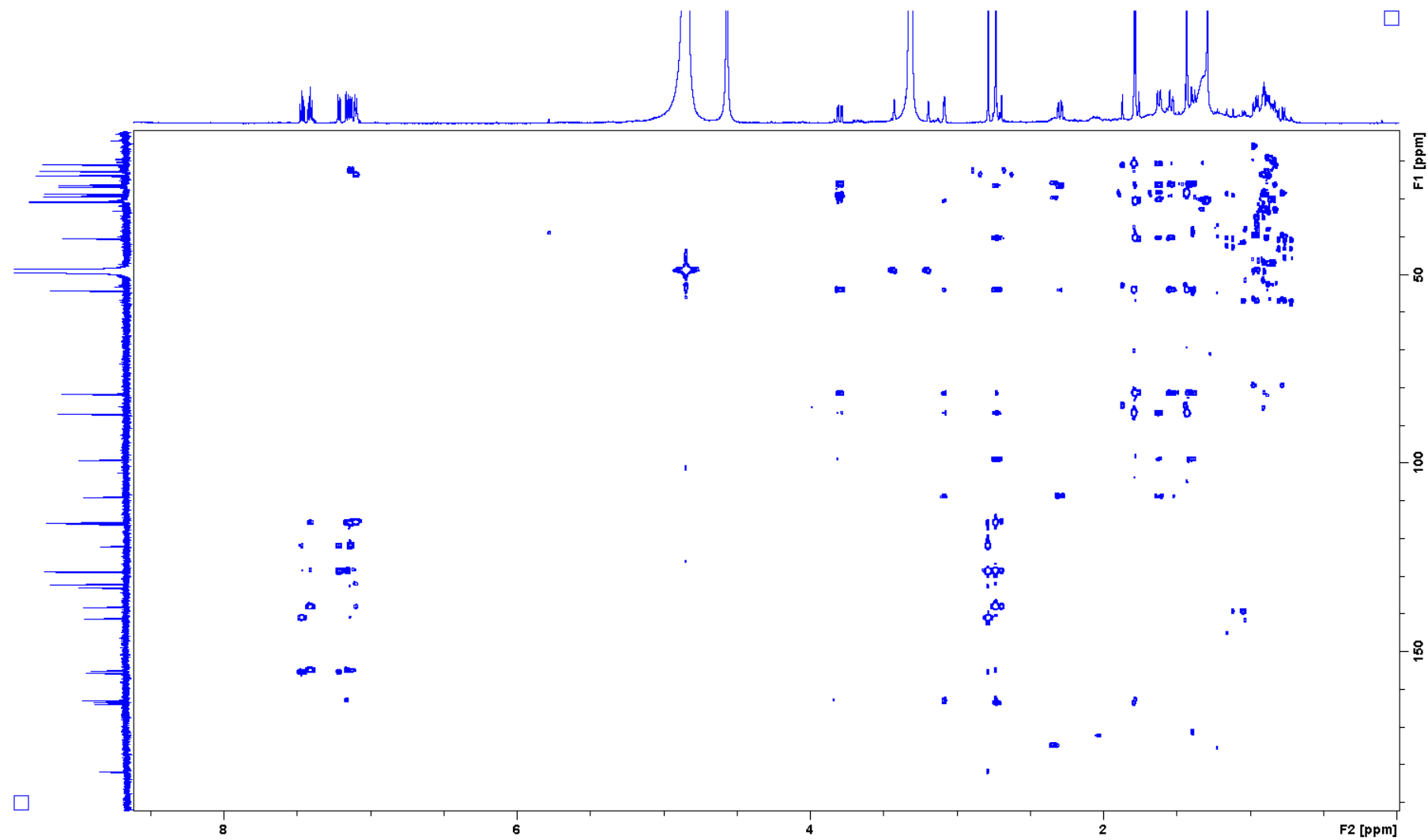


Figure S117. ROESY spectrum of **24** (600 MHz, methanol- d_4).

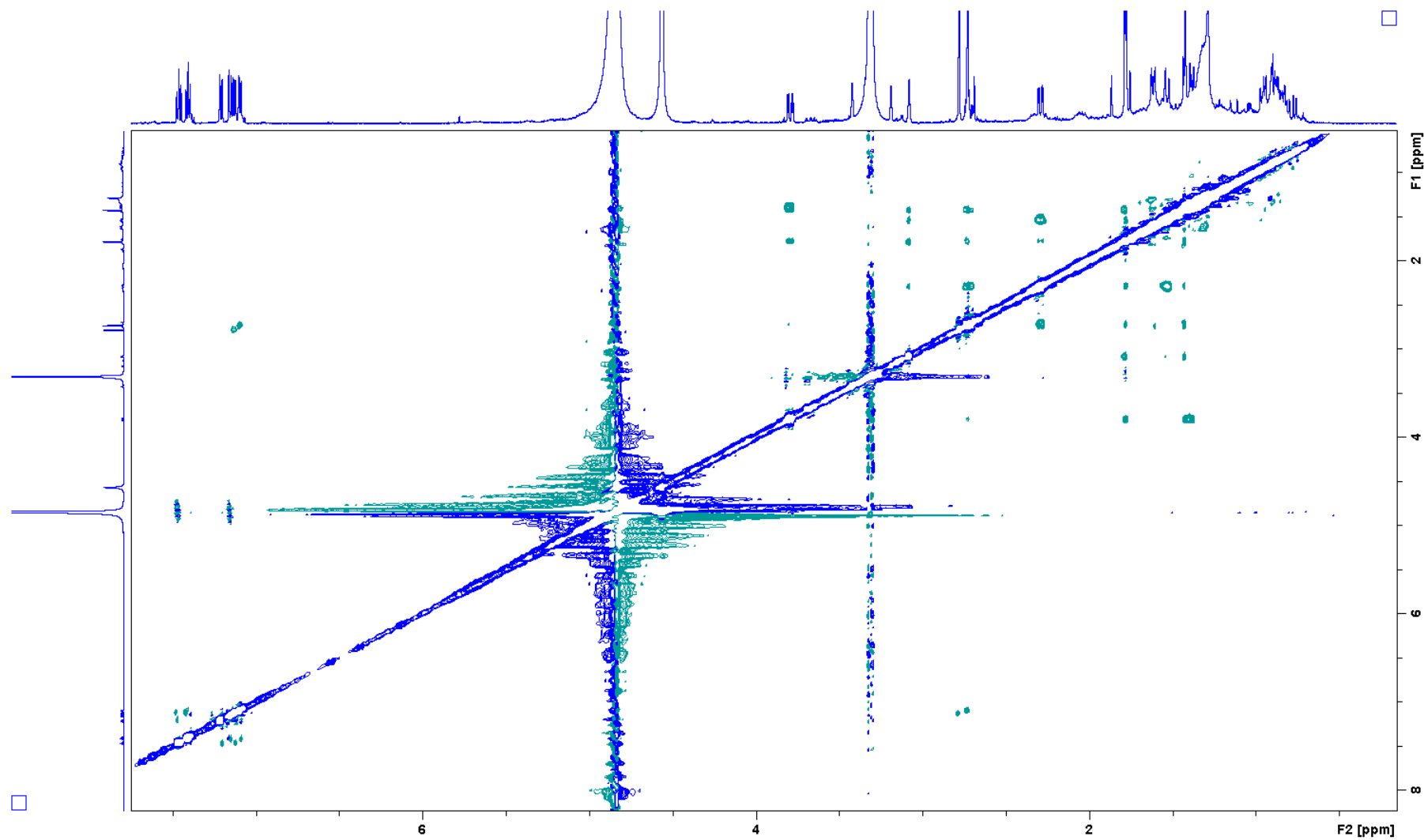


Figure S118. ^1H NMR spectrum of **25** (600 MHz, methanol- d_4).

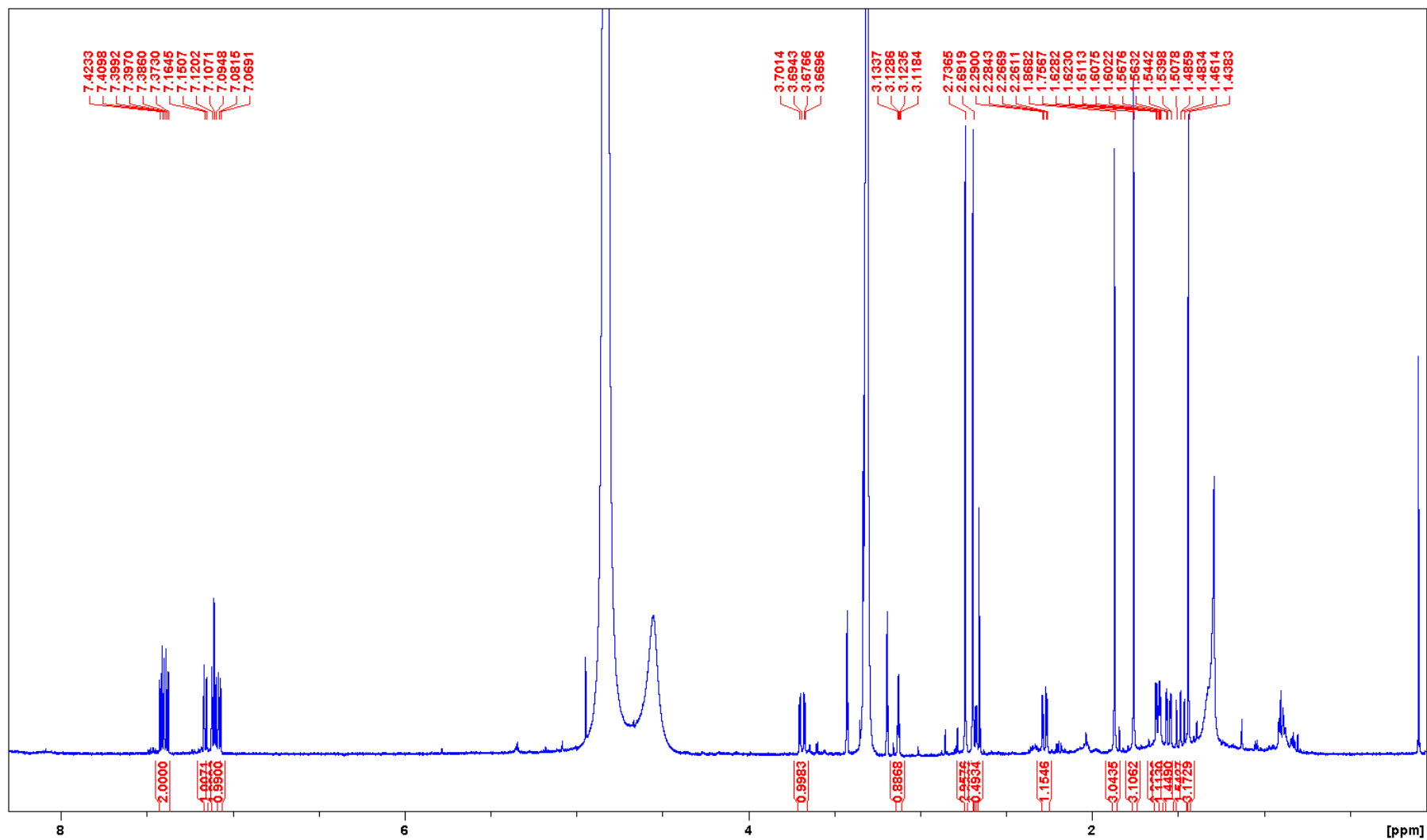


Figure S119. ^{13}C NMR spectrum of **25** (151 MHz, methanol- d_4).

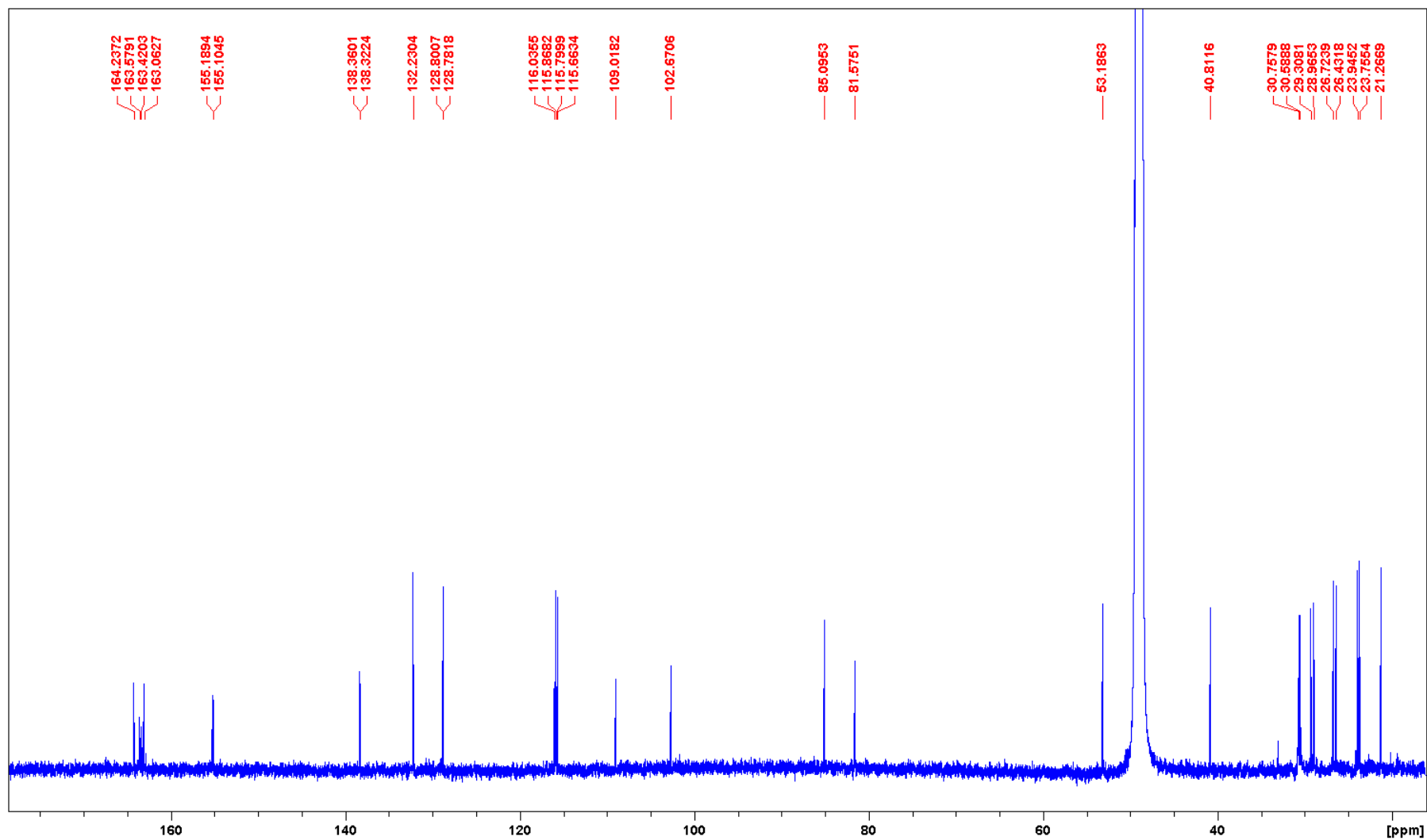


Figure S120. HSQC spectrum of **25** (600 MHz, methanol- d_4).

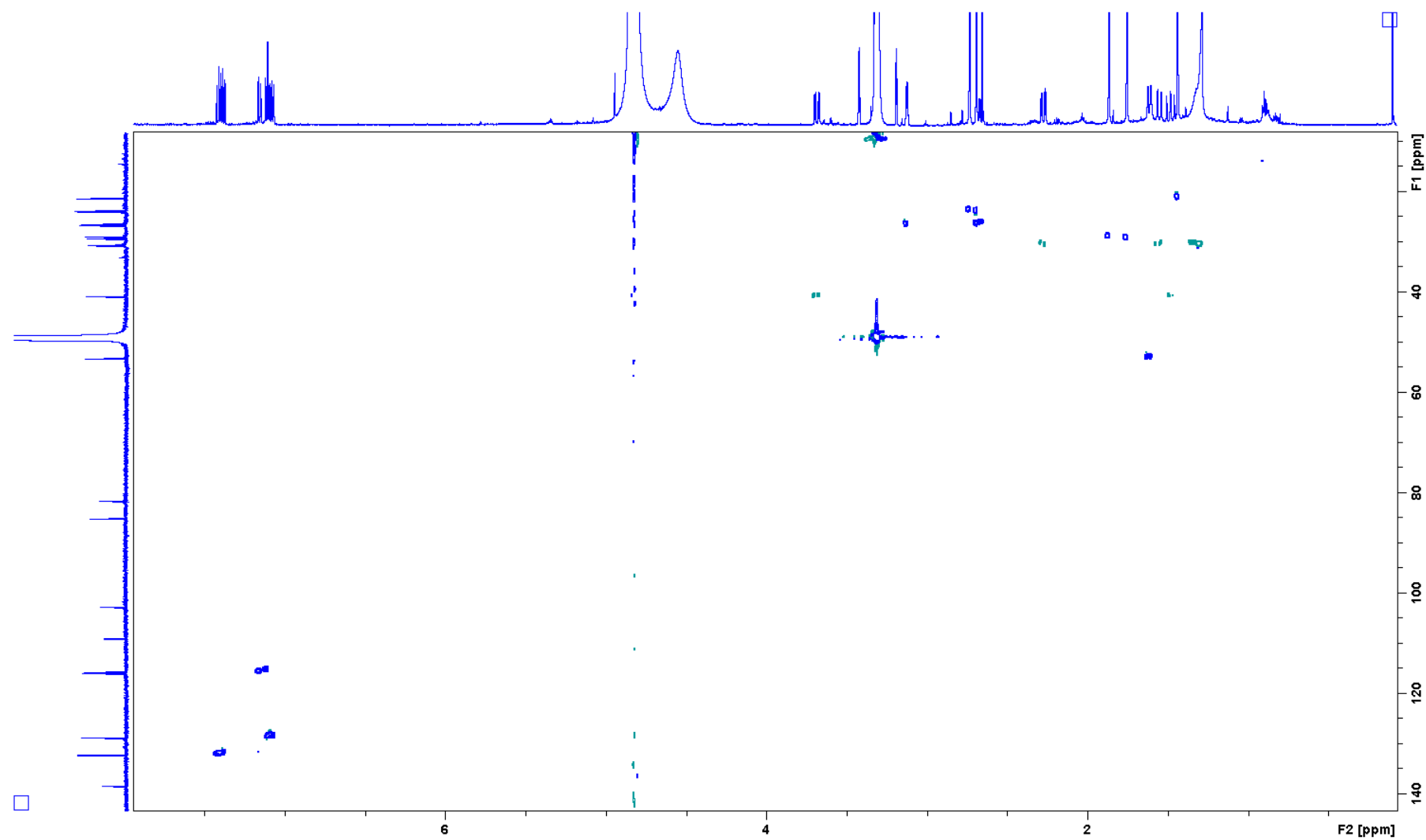


Figure S121. COSY spectrum of **25** (600 MHz, methanol- d_4).

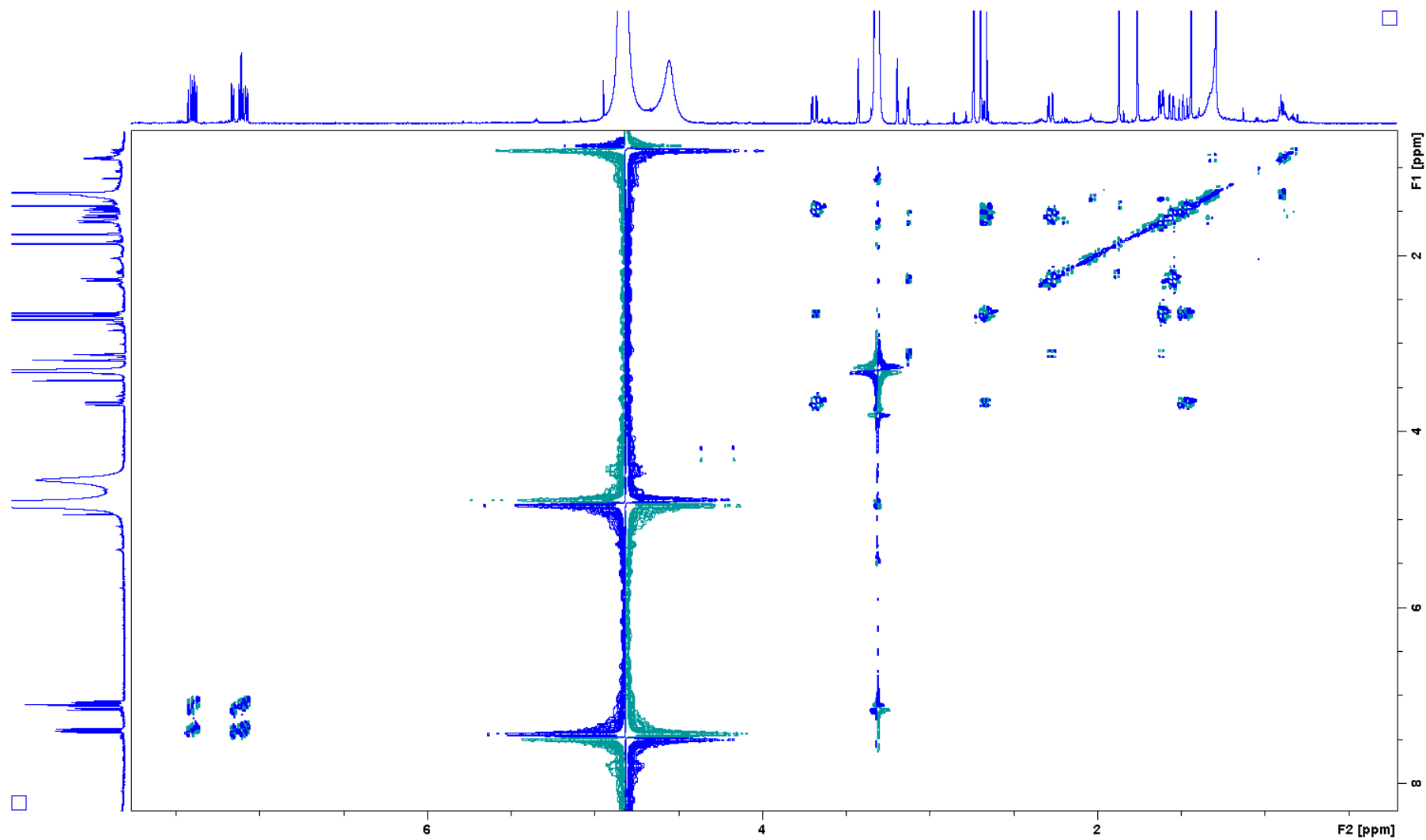


Figure S122. HMBC spectrum of **25** (600 MHz, methanol-*d*₄).

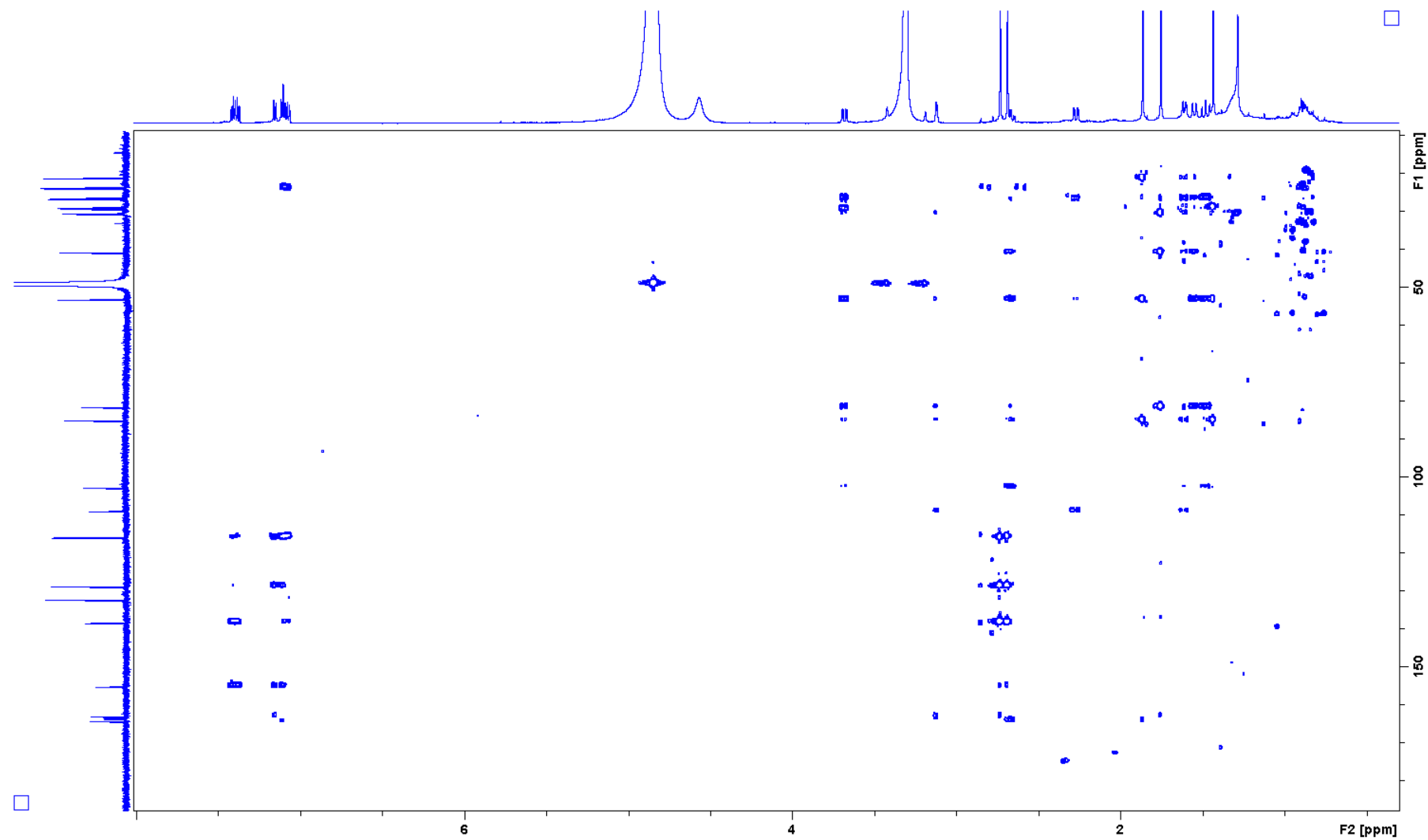


Figure S123. ROESY spectrum of **25** (600 MHz, methanol-*d*₄).

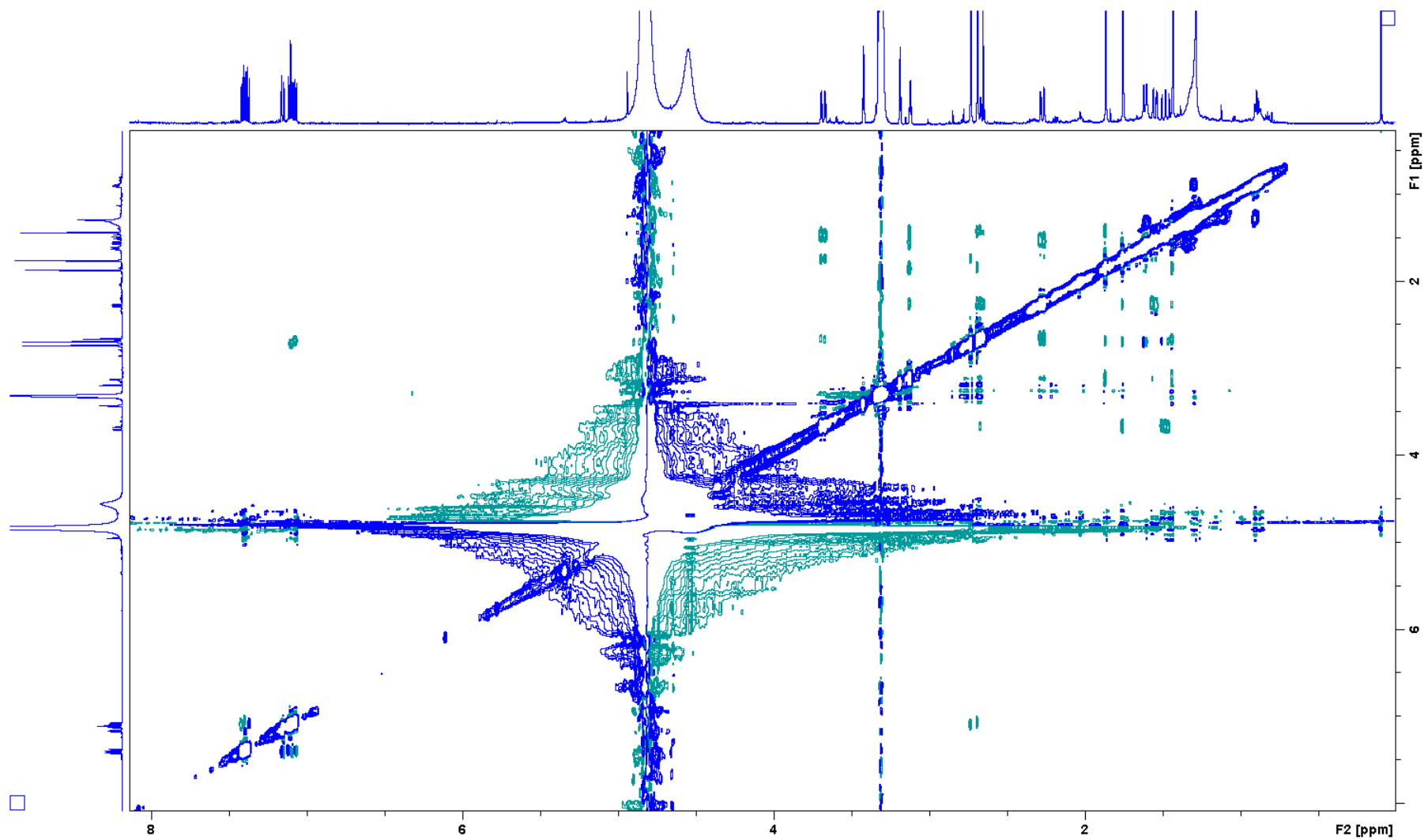


Table S16. Crystal data, data collection and structure refinement data of **19**

Parameter	Value
Formula:	C ₃₀ H ₂₈ O ₆ ; 2 CD ₃ OD
Mw (g/mol)	556.7
Temperature, K	123(2)
Crystal class	monoclinic
Space group	C2/c
Cell parameters	a = 17.720(4) Å
	b = 15.753(3) Å
	c = 20.547(4) Å
	β = 107.81(3)°
V (Å ³), Z	5461(2) / 8
F(000)	2336
d _{calc} (g/cm ³)	1.354
λ	1.54178 Å (CuKα)
θ _{max} (°)	3.84 < θ < 70.17
Reflections total/unique	24636/5191
R _{merge}	0.0302
No. parameters	374
Reflections (I > 2 σ(I))	4591
RI/wR2 (I > 2 σ(I))	0.0357/0.0868
RI/wR2 (all reflections)	0.0416/0.0909
Goodness-of-fit on F ²	1.037
ρ _{max} / ρ _{min} (eÅ ⁻³)	0.35 / -0.33