Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information

Targeted solid phase fermentation of the soil dwelling fungus *Gymnascella dankaliensis* yields new brominated tyrosine-derived alkaloids

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Contents

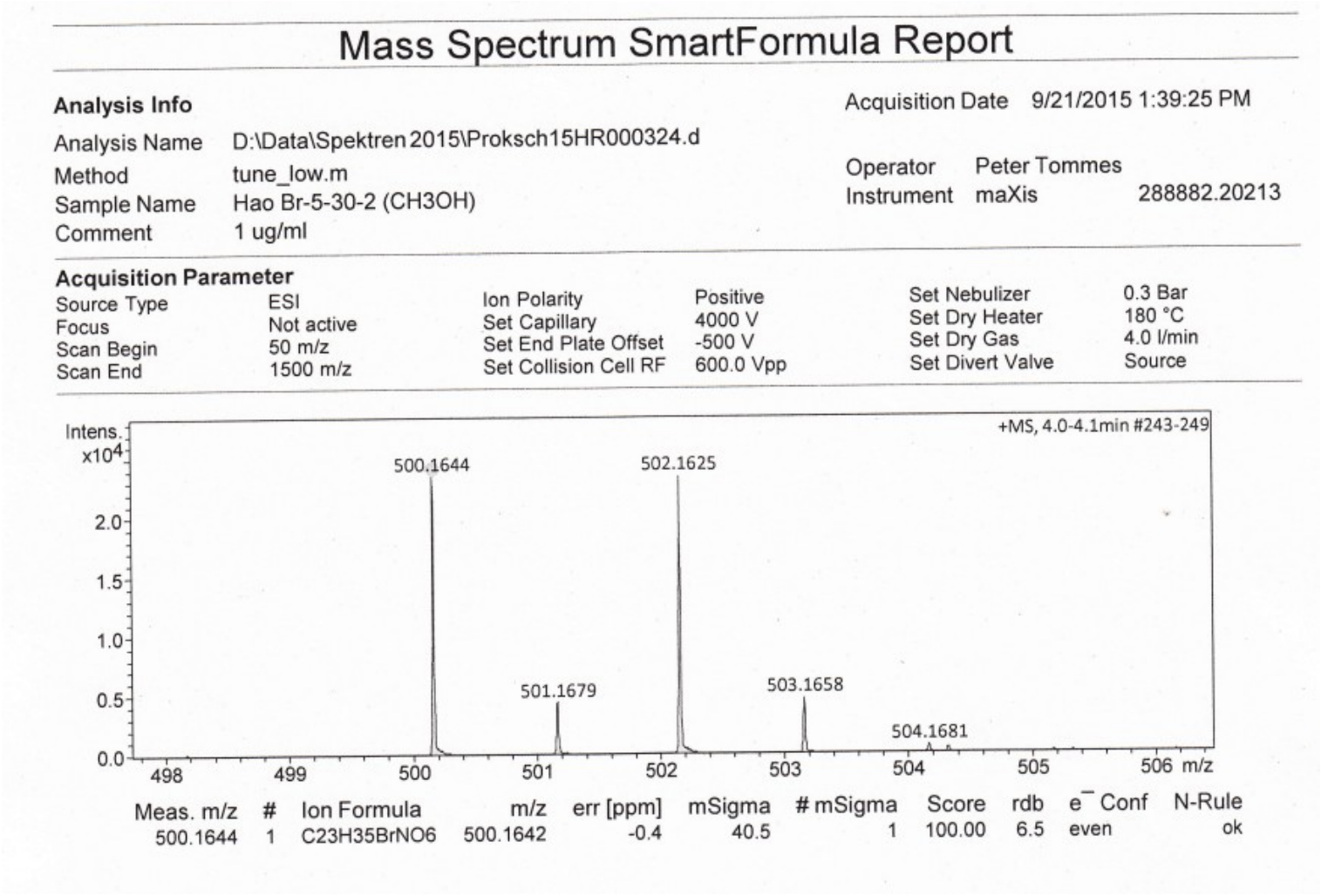

Figure S1. HRESIMS of compound **1**.

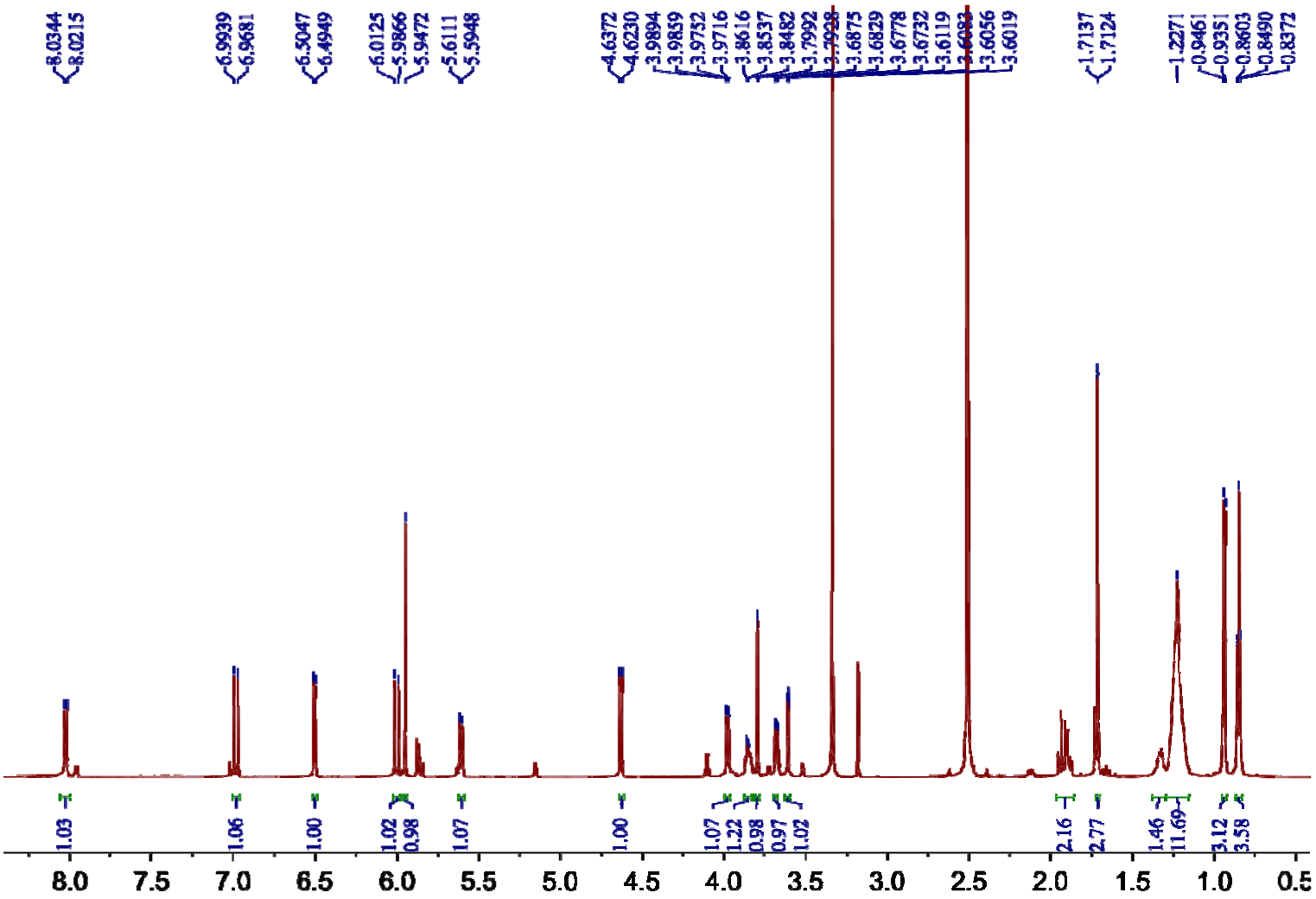

Figure S2. ^{1}H NMR (600MHz, DMSO-d_6) spectrum of compound **1**.

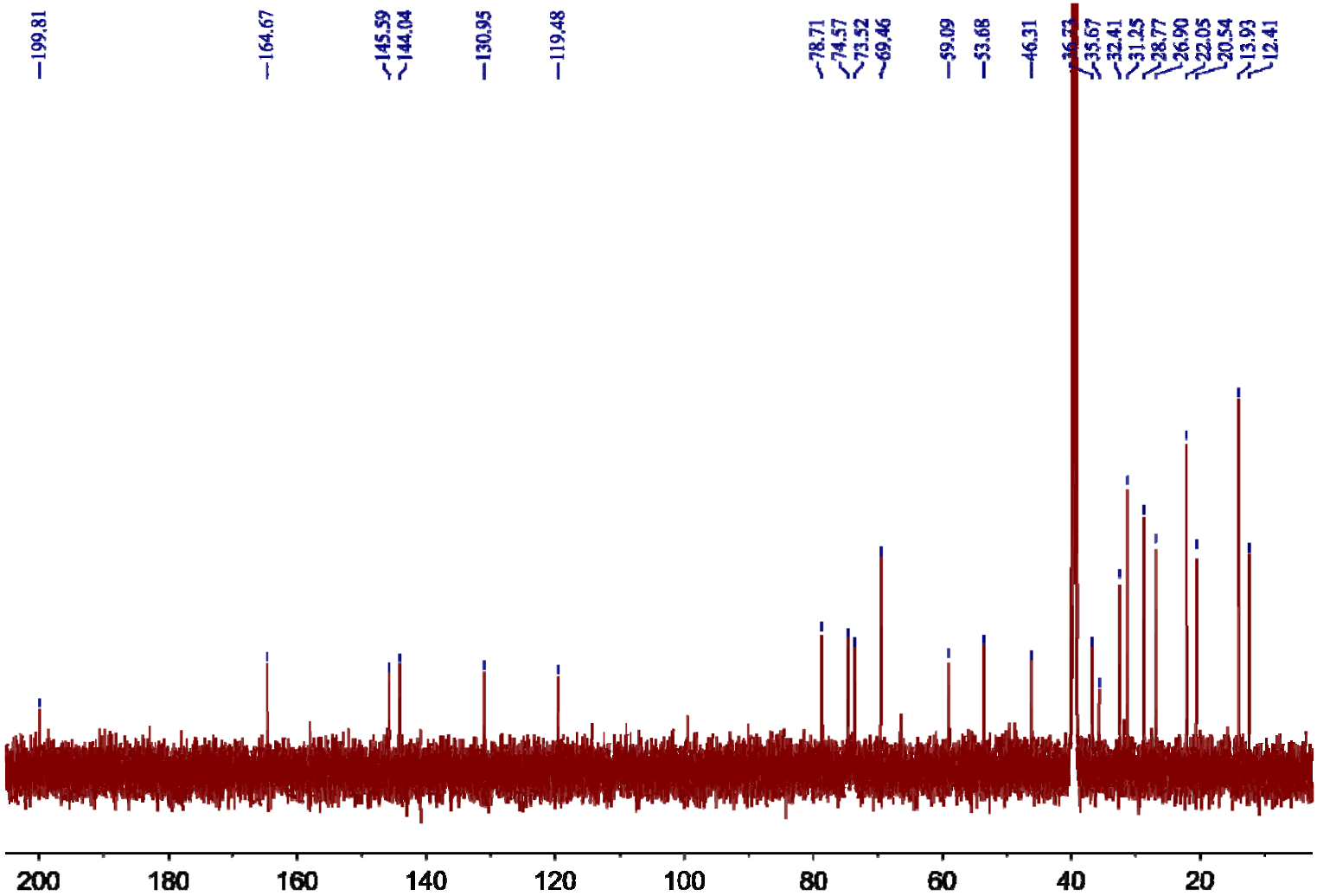

Figure S3. ^{13}C NMR (150MHz, DMSO-d_6) spectrum of compound **1**.

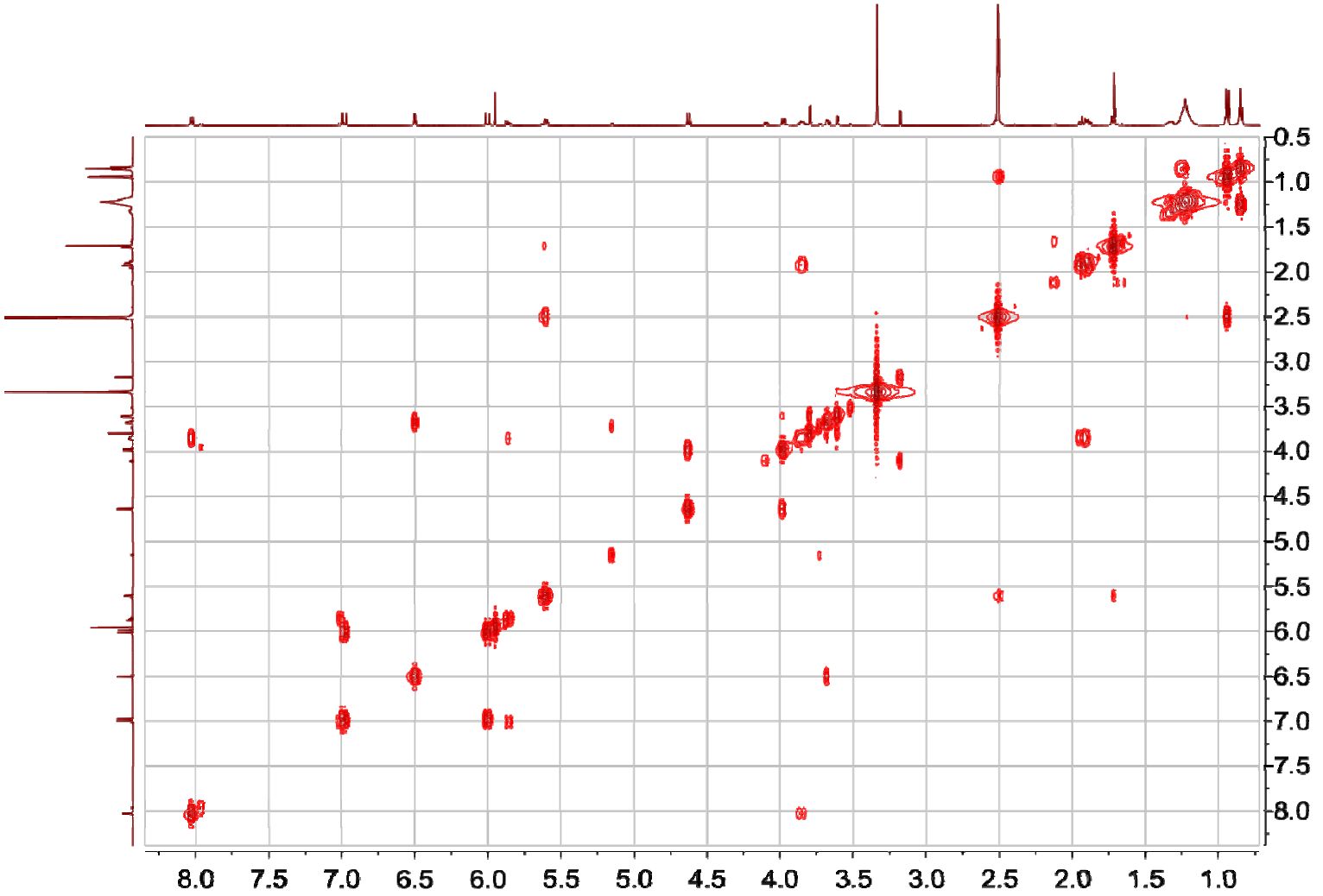

Figure S4. ^{1}H-^{1}H COSY (600MHz, DMSO-d_6)spectrum of compound **1**.

Figure S5. HSQC (600MHz, 150MHz, DMSO-d_6) spectrum of compound **1**.

Figure S6. HMBC (600MHz, 150MHz, DMSO-d_6) spectrum of compound **1**.

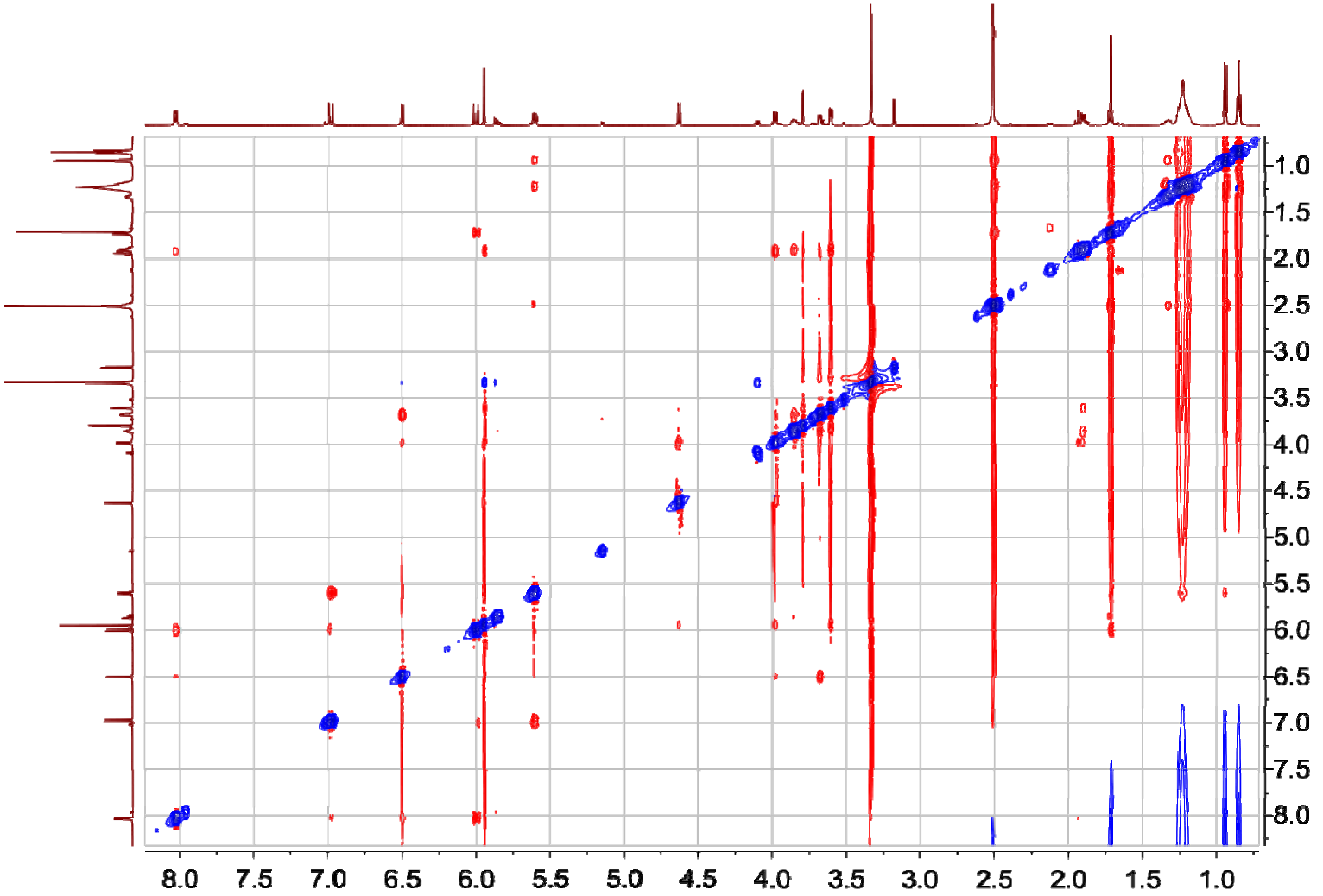

Figure S7. ROESY (600MHz, DMSO-d_6) spectrum of compound **1**.

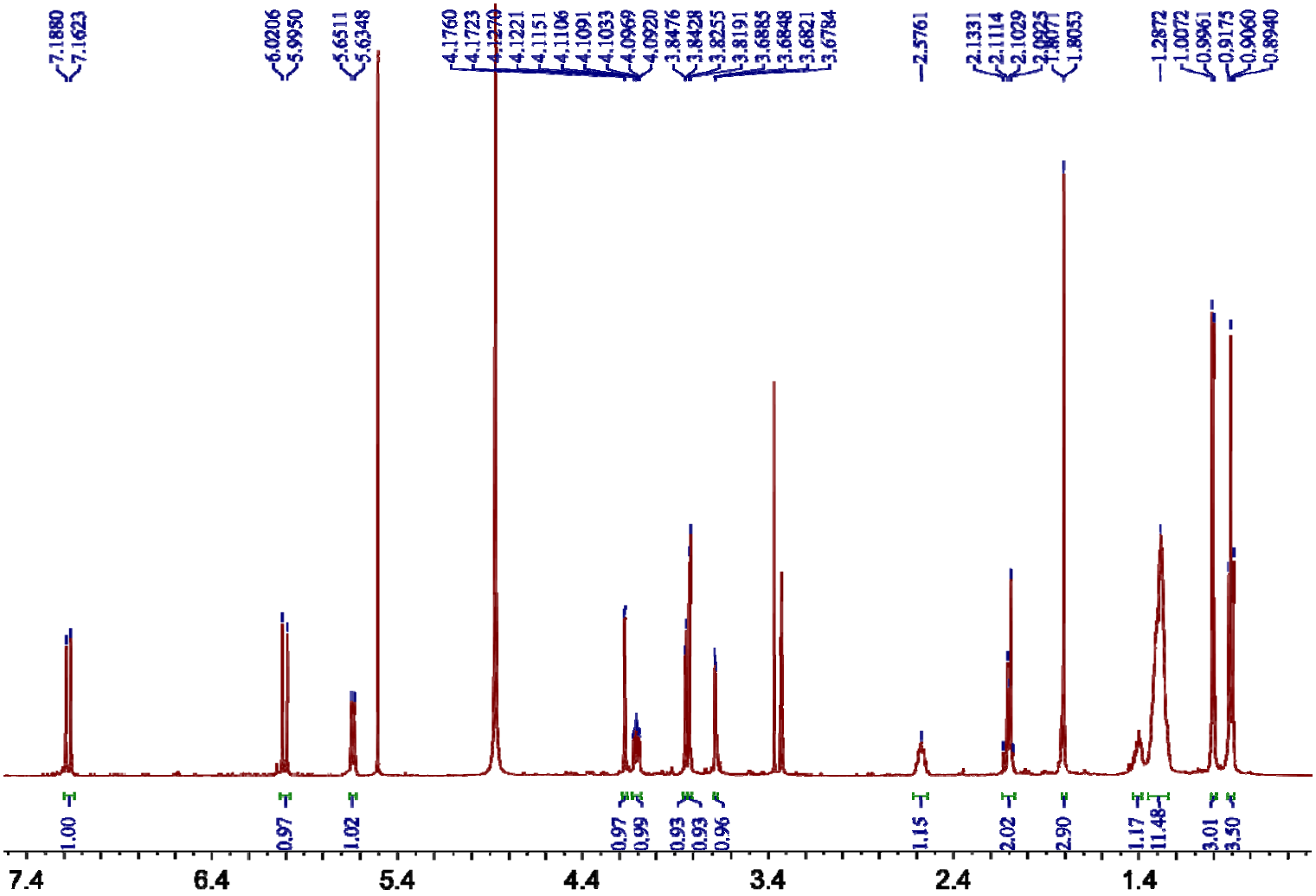

Figure S8. ^{1}H NMR (600MHz, methanol-d_4) spectrum of compound **1**.

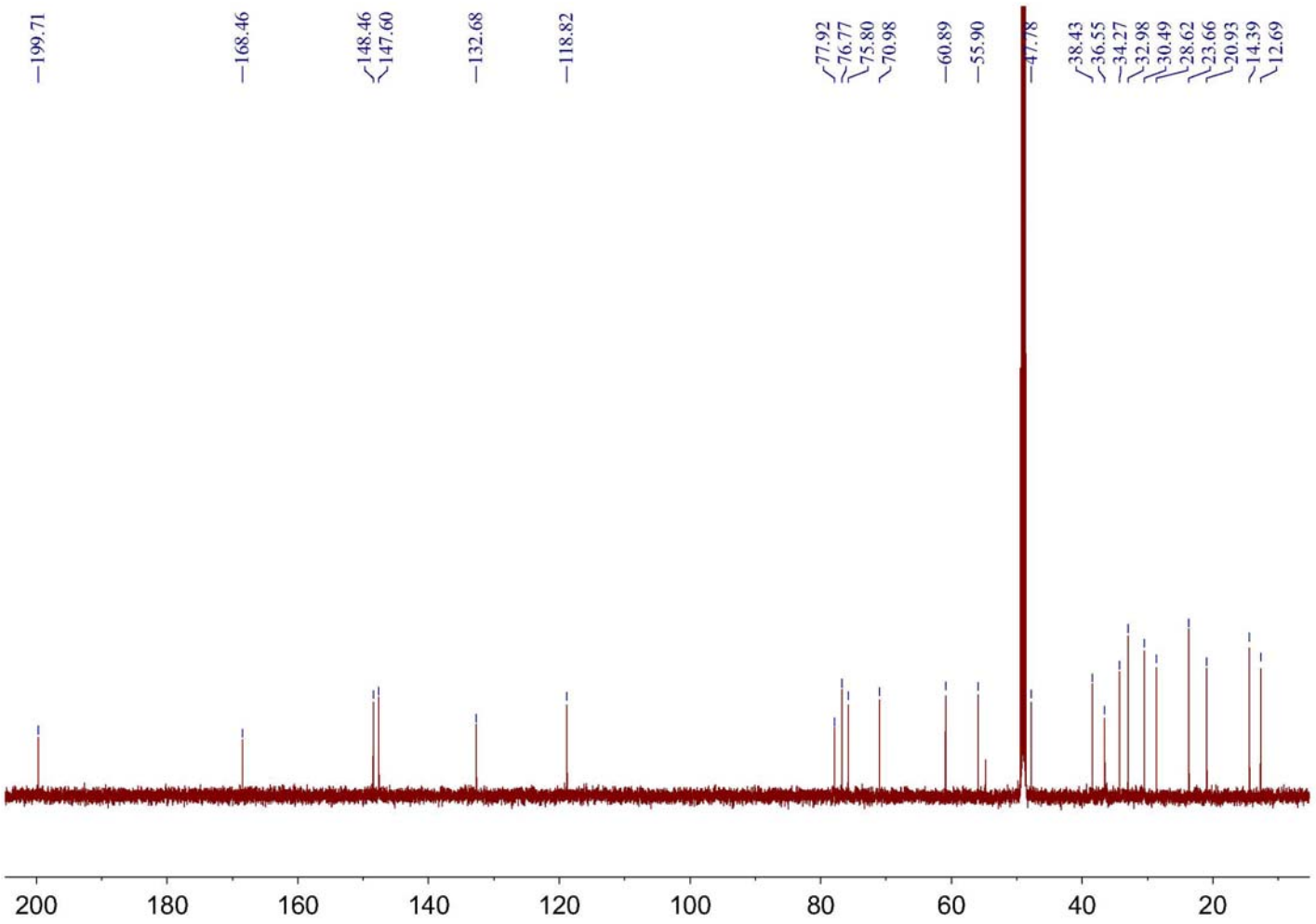

Figure S9. ^{13}C NMR (150MHz, methanol-d_4) spectrum of compound **1**.

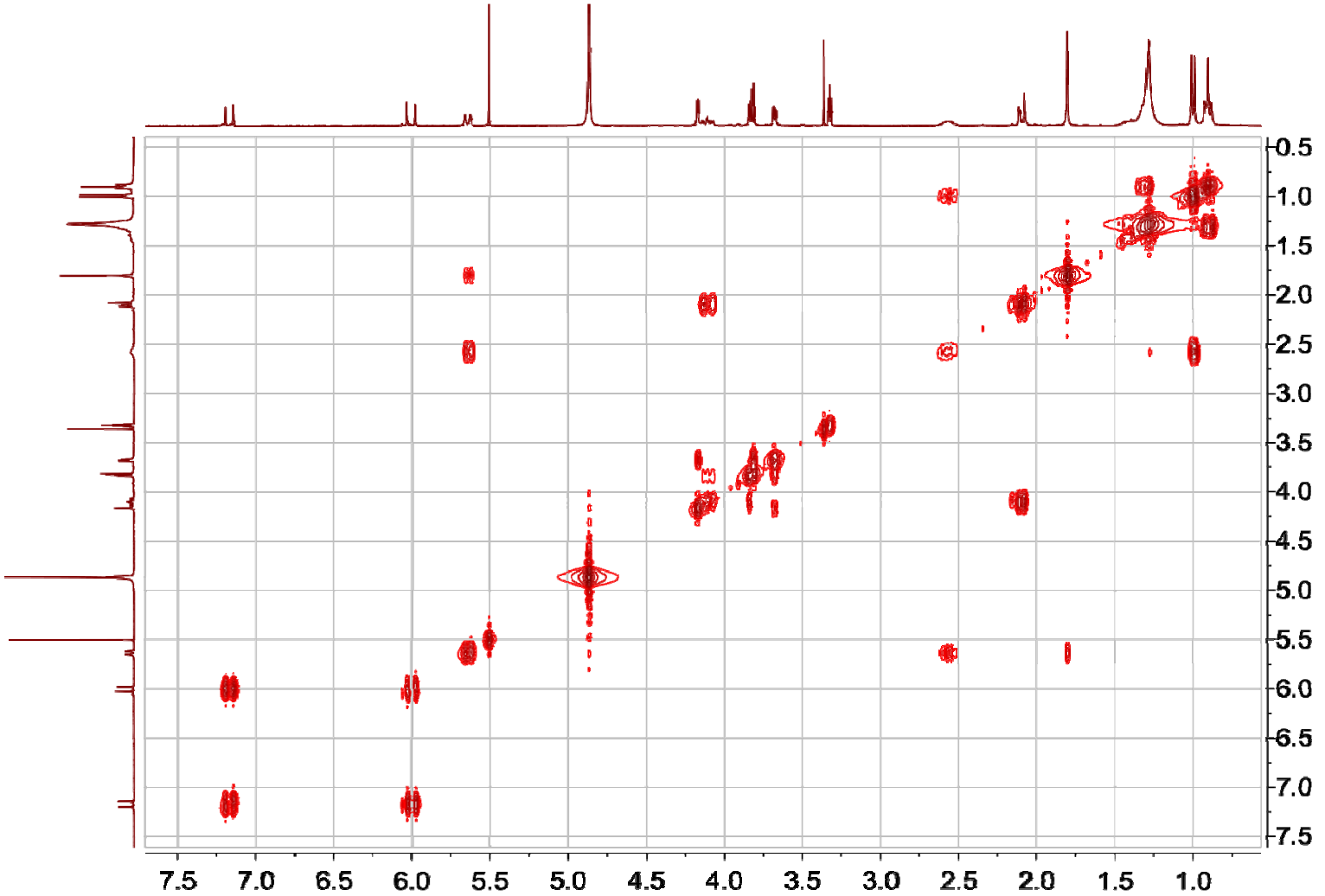

Figure S10. ^{1}H-^{1}H COSY (600MHz, methanol-d_4) spectrum of compound **1**.

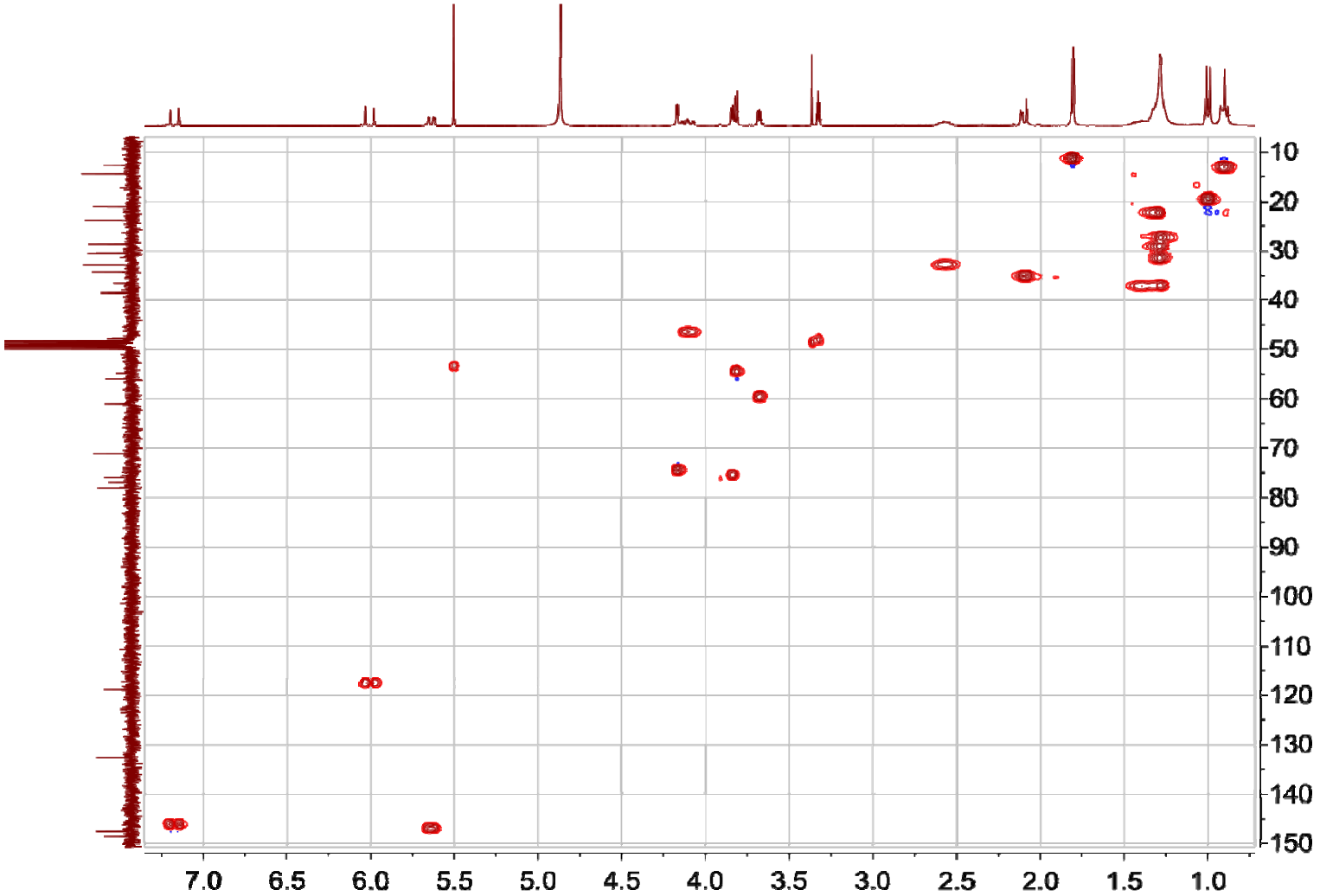

Figure S11. HSQC (600 MHz, 150 MHz, methanol-d_4) spectrum of compound **1**.

Figure S12. HMBC (600MHz, 150MHz, methanol-d_4)spectrum of compound **1**.

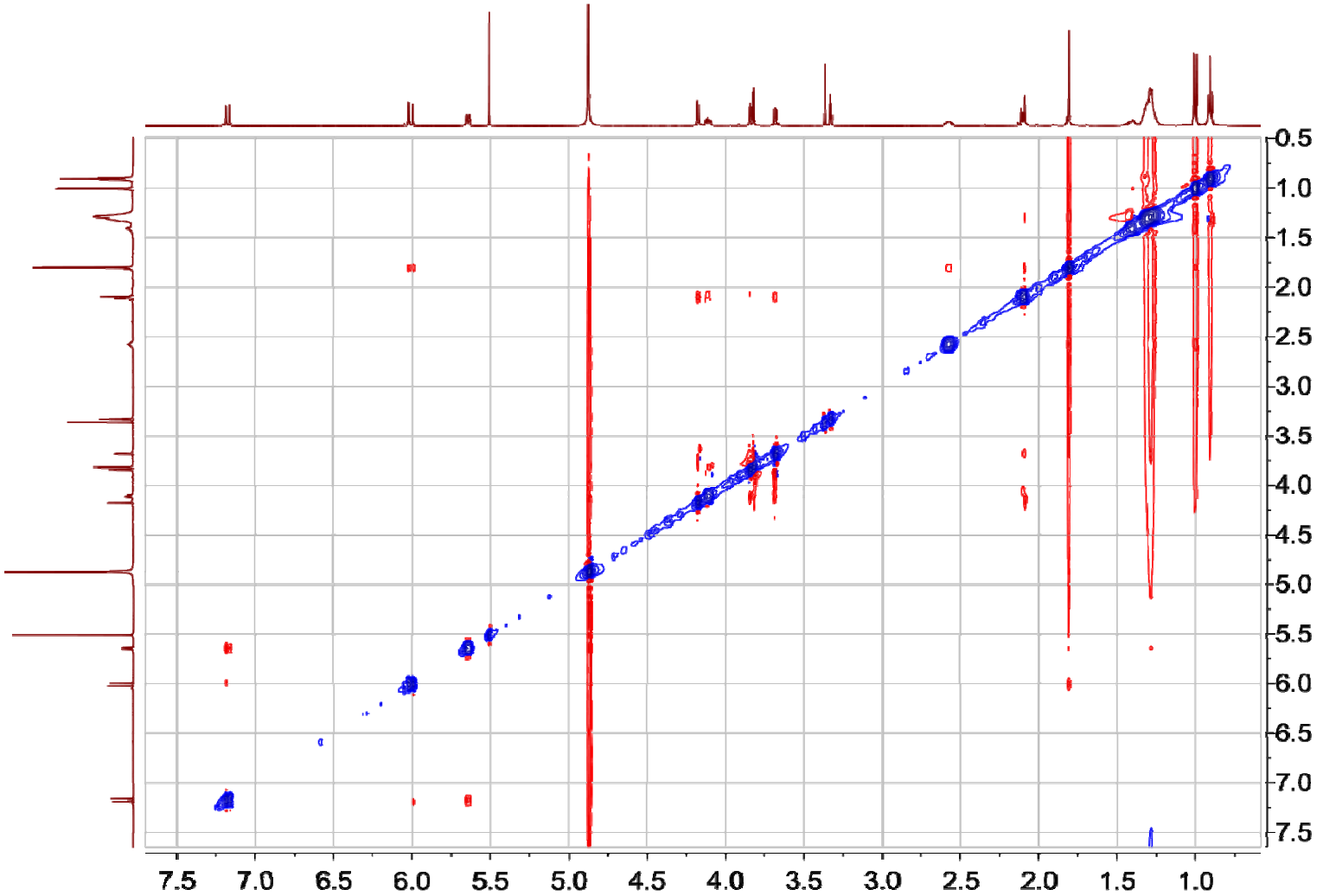

Figure S13. ROESY (600MHz, methanol-d_4)spectrum of compound **1**.

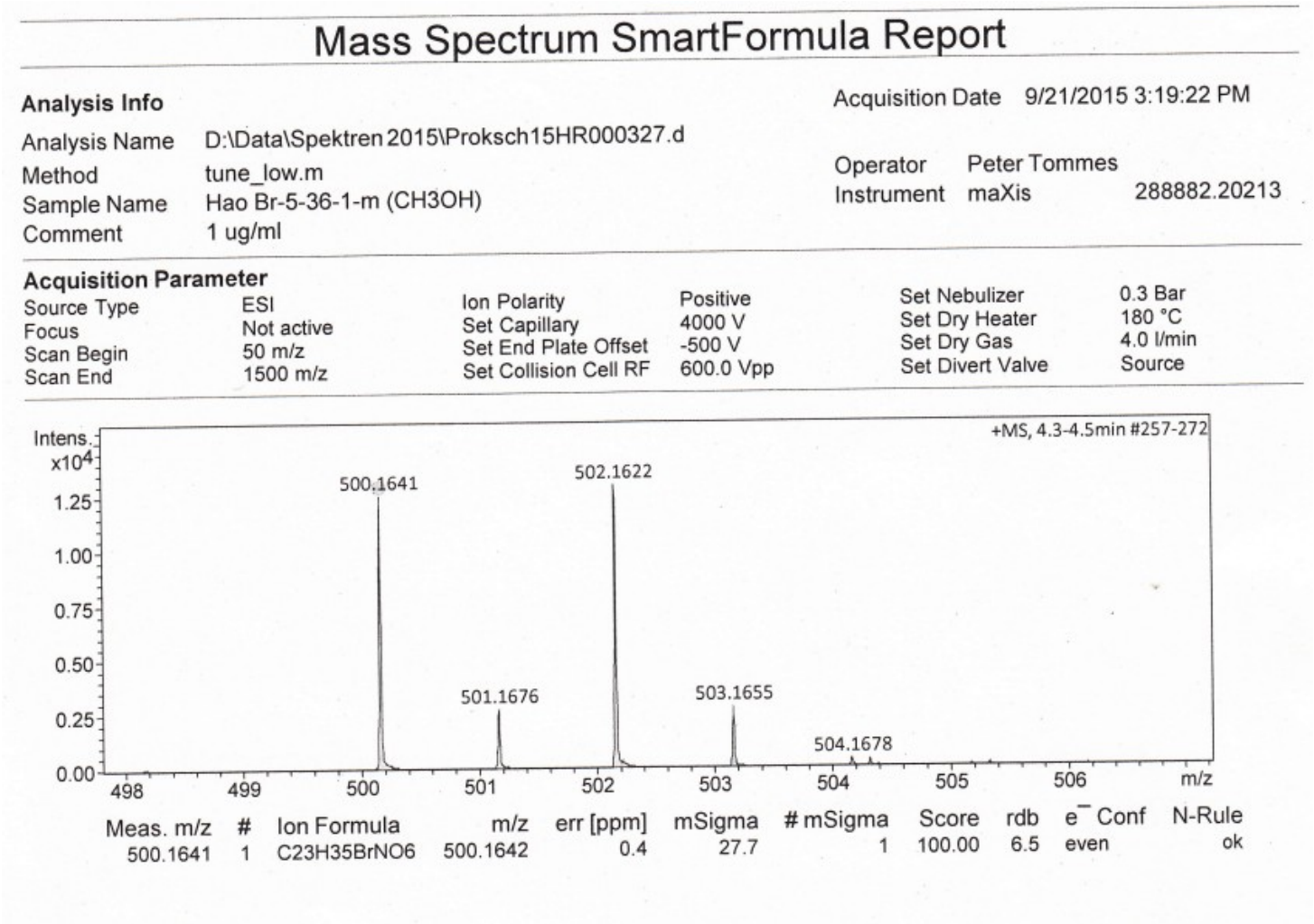

Figure S14. HRESIMS of compound **2**.

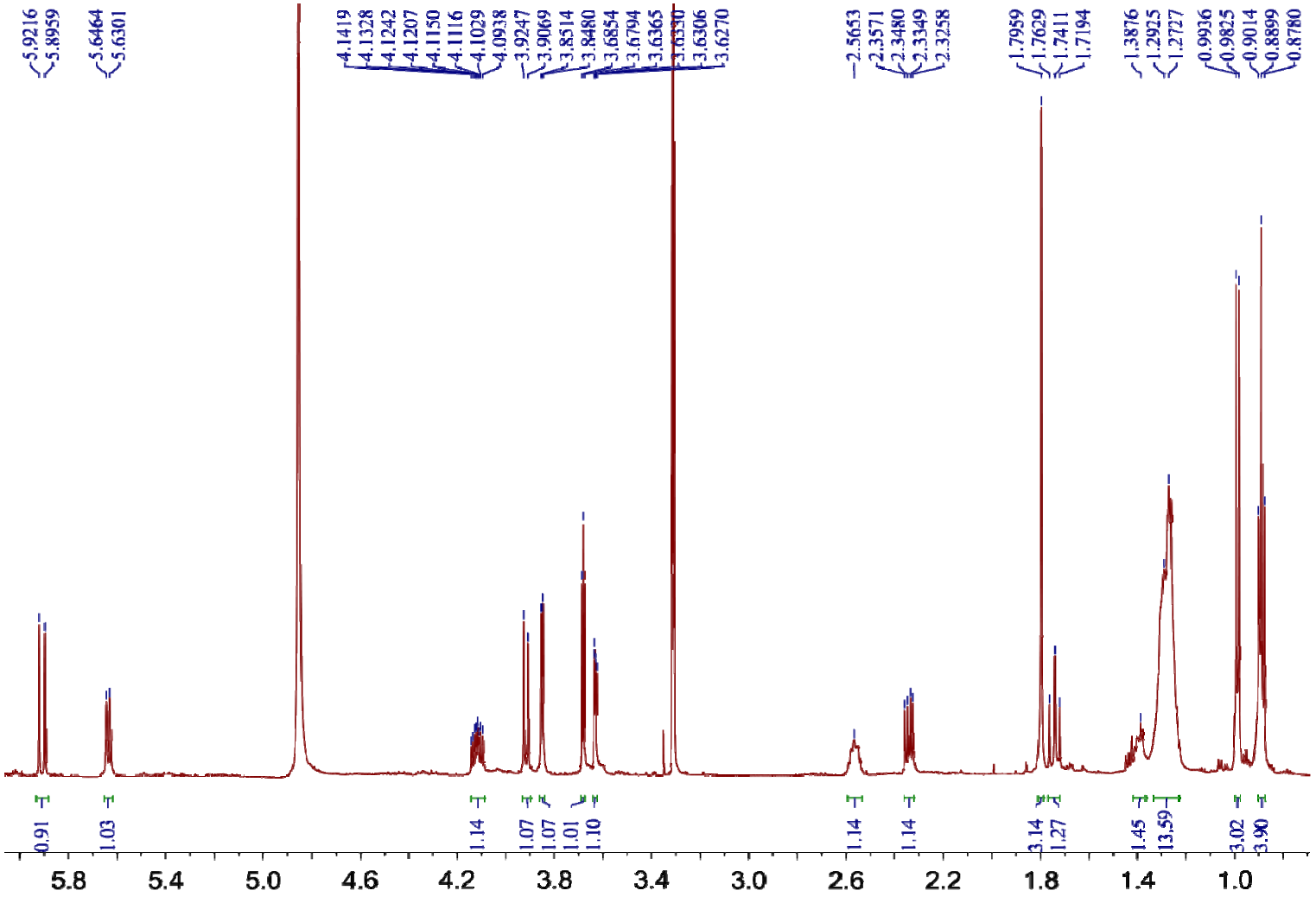

Figure S15. ^{1}H NMR (600MHz, methanol-d_4) spectrum of compound **2**.

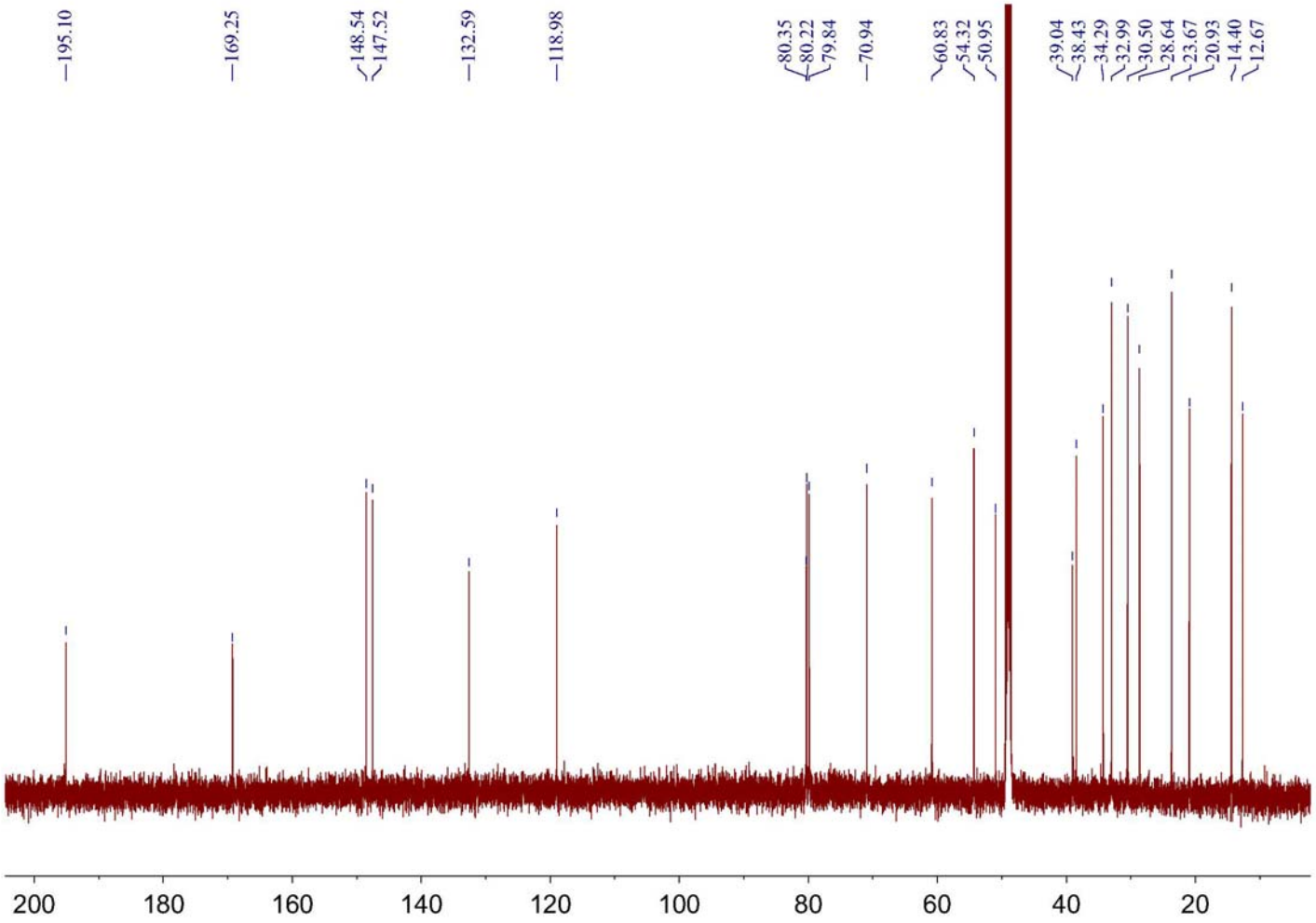

Figure S16. ^{13}C NMR (150MHz, methanol-d_4) spectrum of compound **2**.

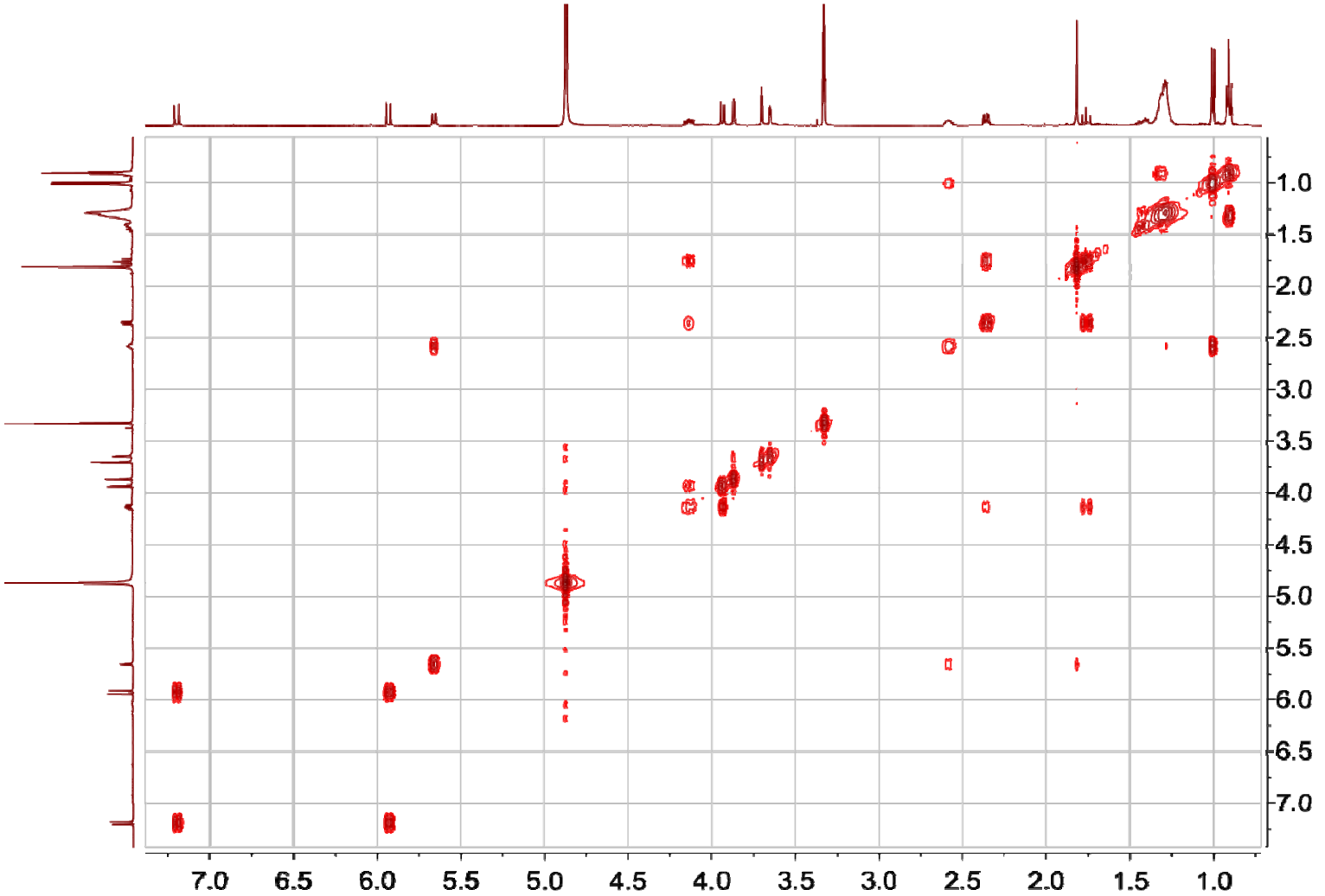

Figure S17. ^{1}H-^{1}H COSY (600MHz, methanol-d_4) spectrum of compound **2**.

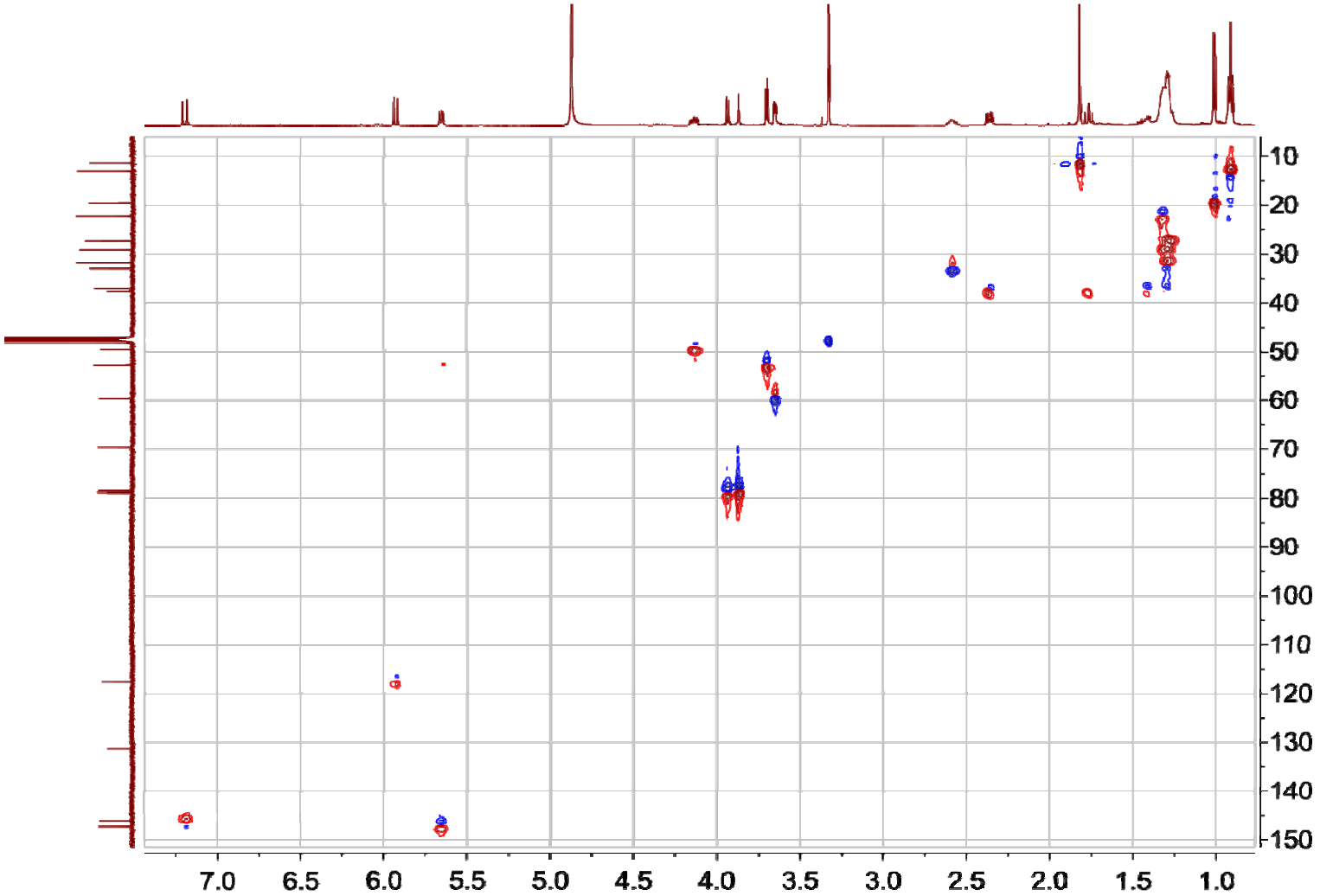

Figure S18. HSQC (600MHz, 150MHz, methanol-d_4) spectrum of compound **2**.

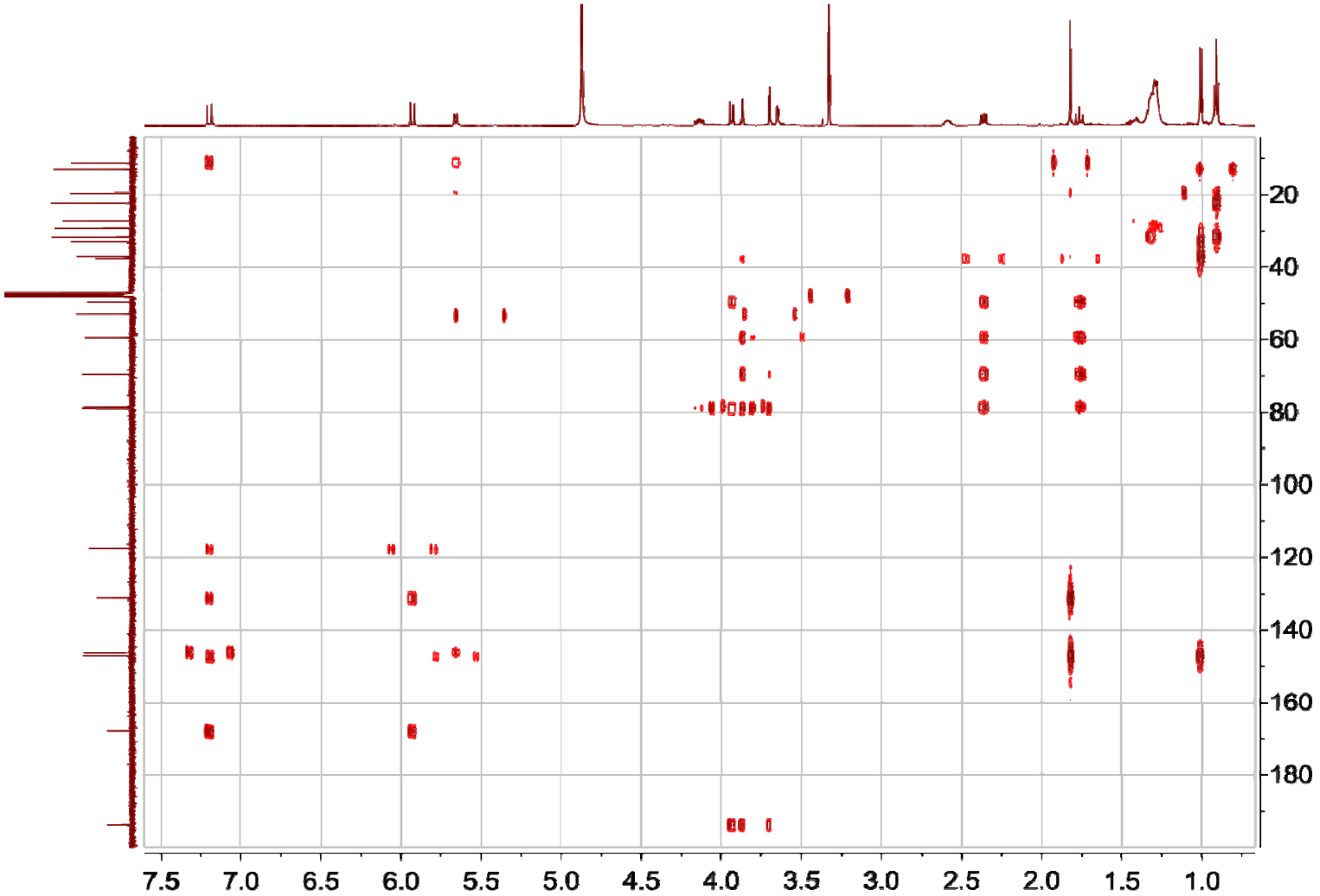

Figure S19. HMBC (600MHz, 150MHz, methanol-d_4) spectrum of compound **2**.

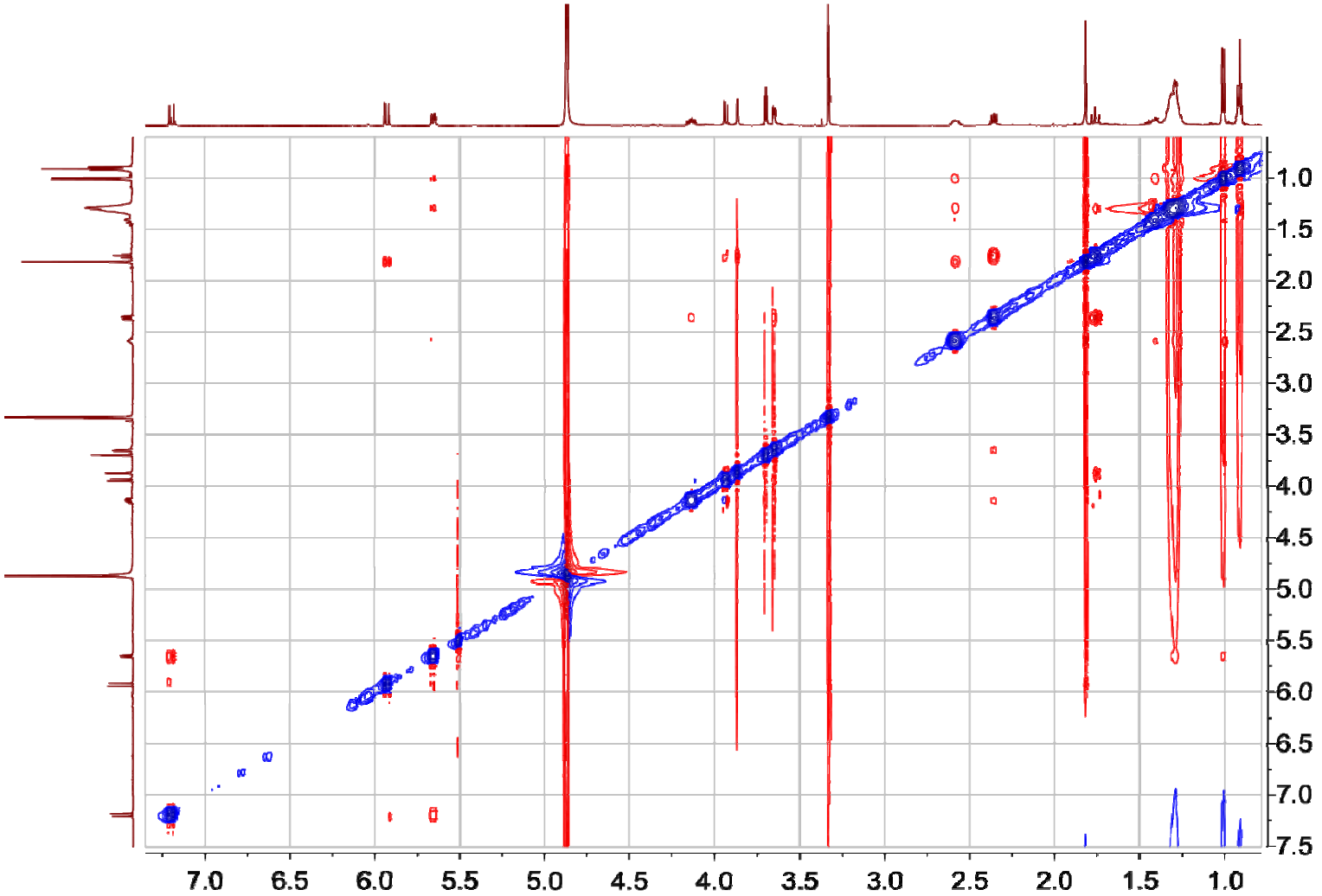

Figure S20. ROESY (600MHz, methanol-d_4) spectrum of compound **2**.

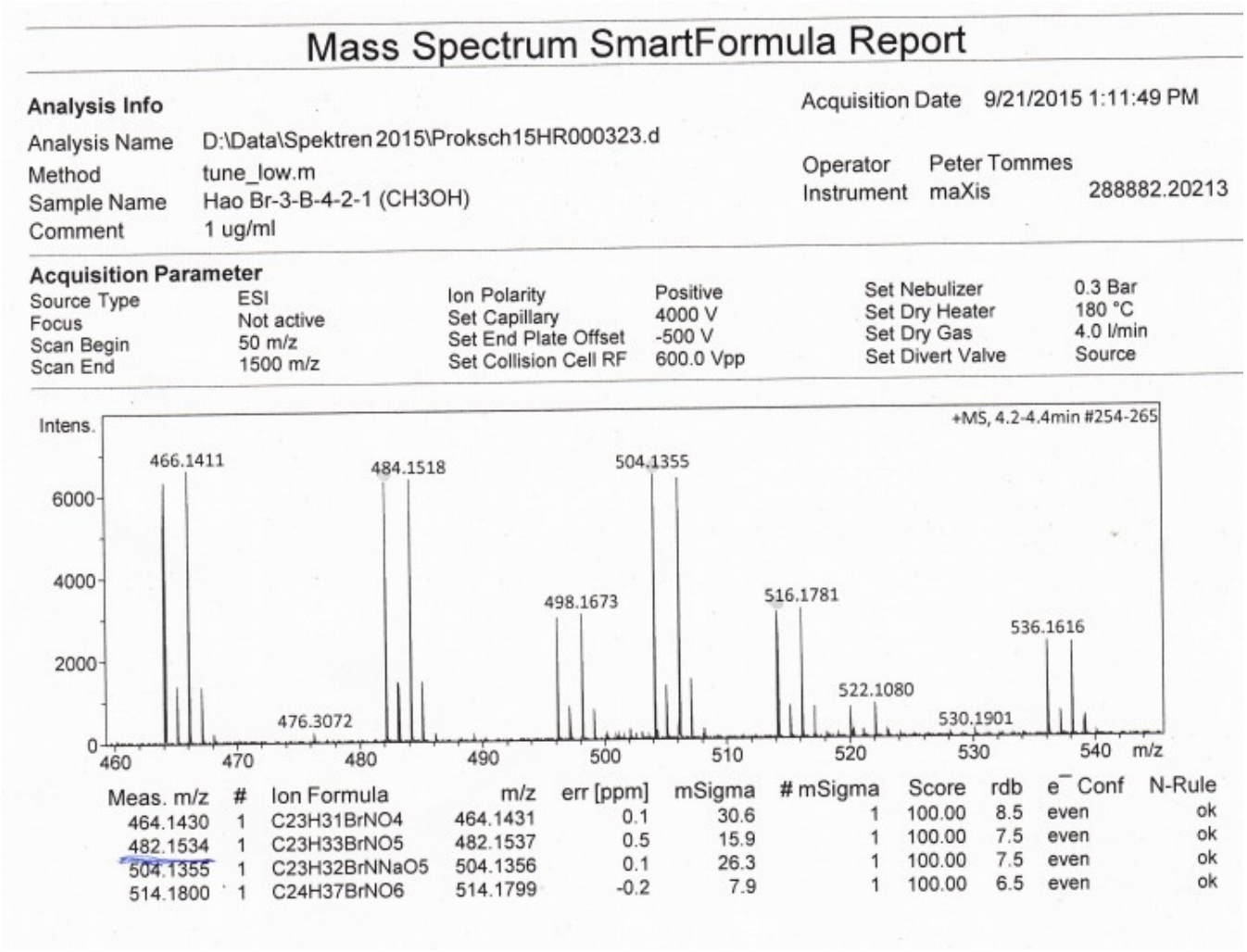

Figure S21. HRESIMS of compound **3**.

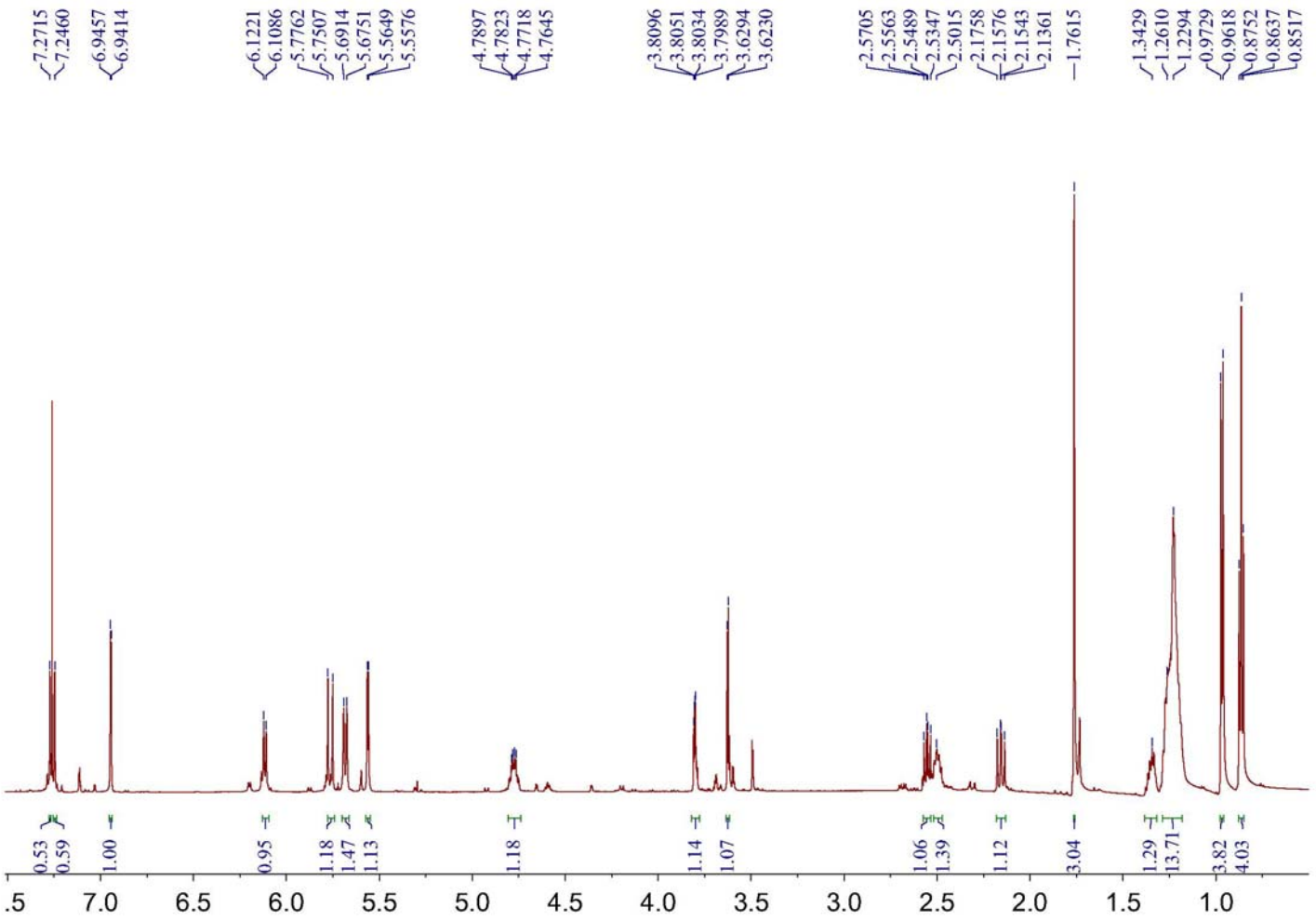

Figure S22. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of compound **3**.

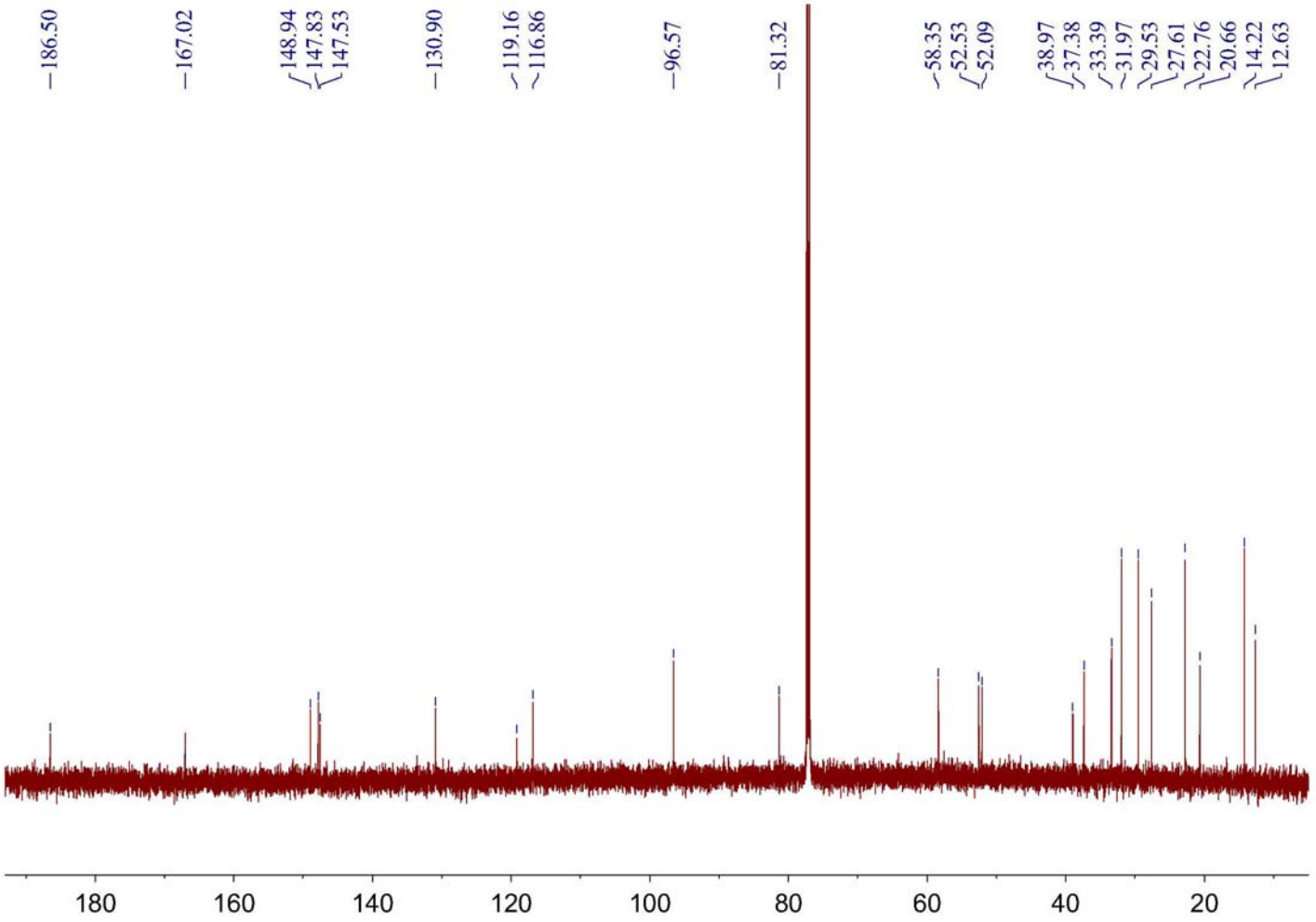

Figure S23. ^{13}C NMR (150MHz, $CDCl_3$) spectrum of compound **3**.

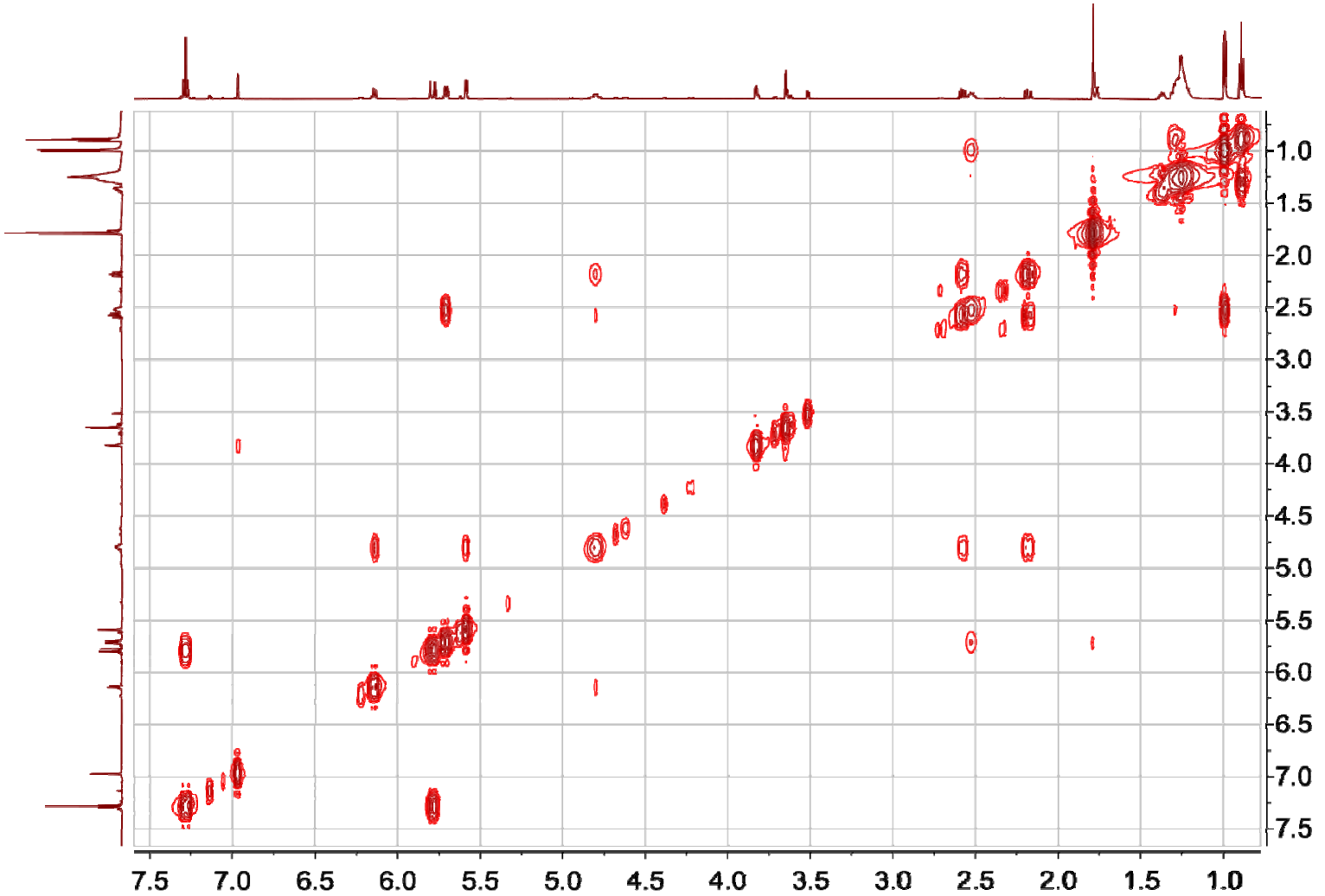

Figure S24. ^{1}H-^{1}H COSY (600MHz, $CDCl_3$) spectrum of compound **3**.

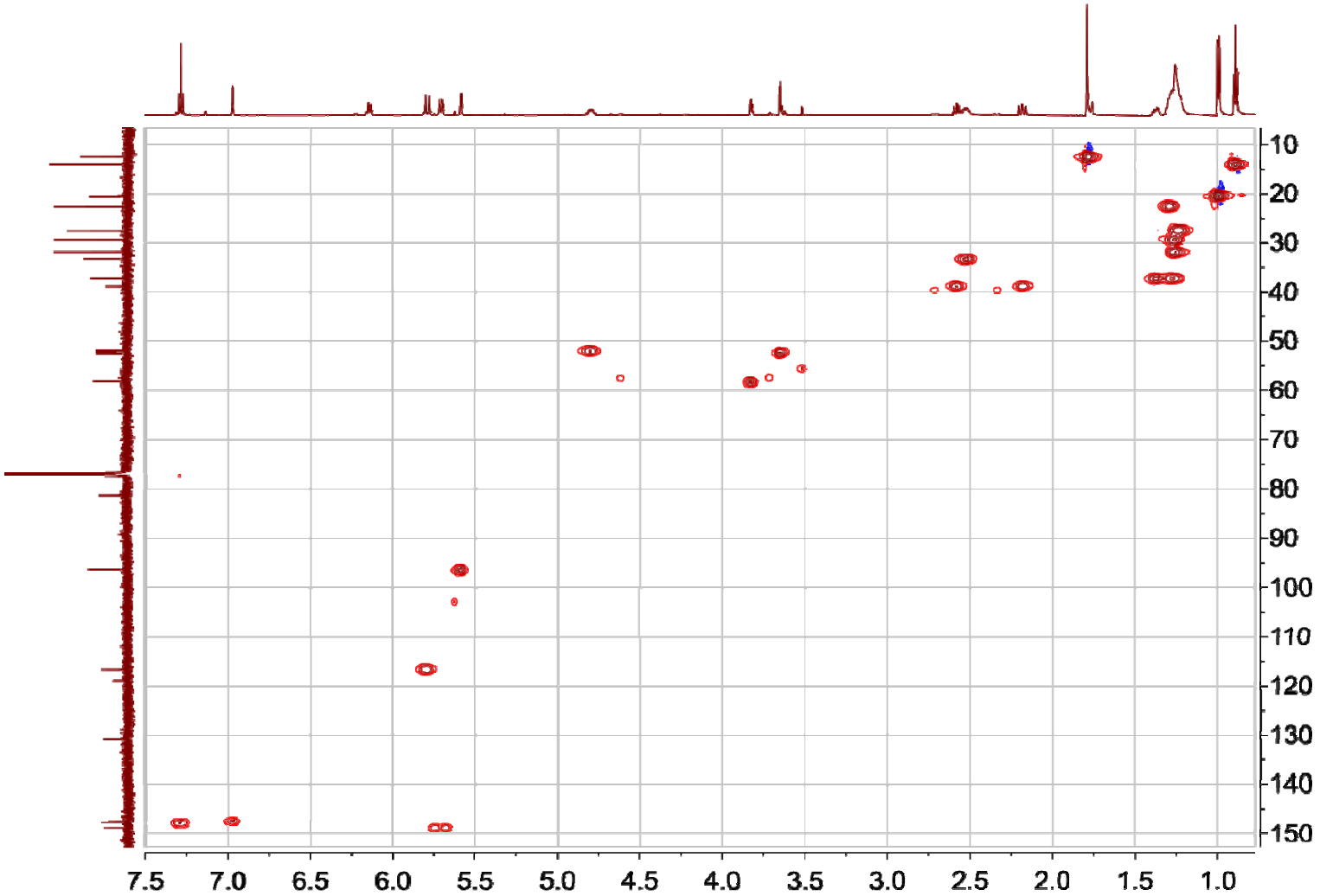

Figure S25. HSQC (600MHz, 150MHz, $CDCl_3$) spectrum of compound **3**.

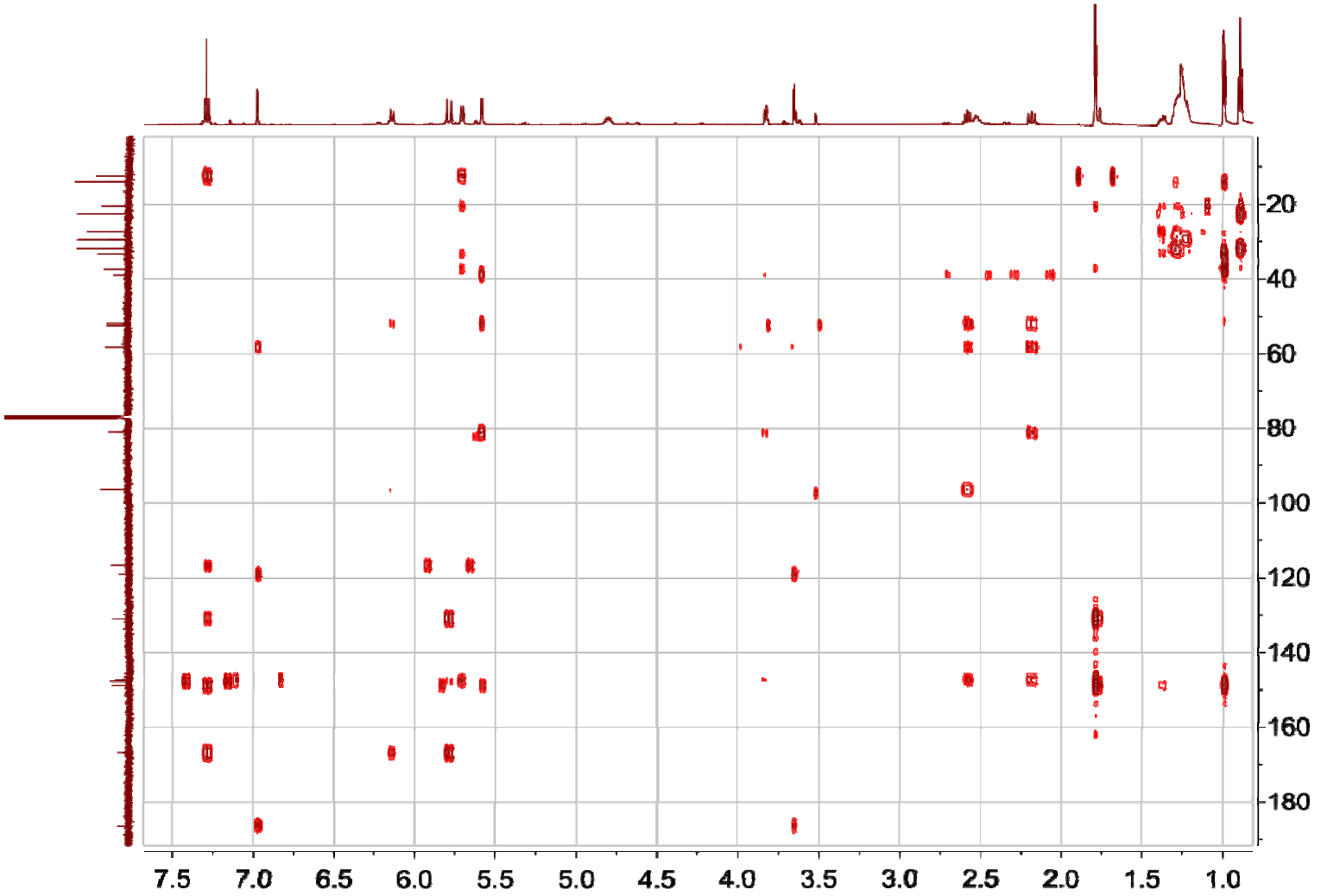

Figure S26. HMBC (600MHz, 150MHz, $CDCl_3$) spectrum of compound **3**.

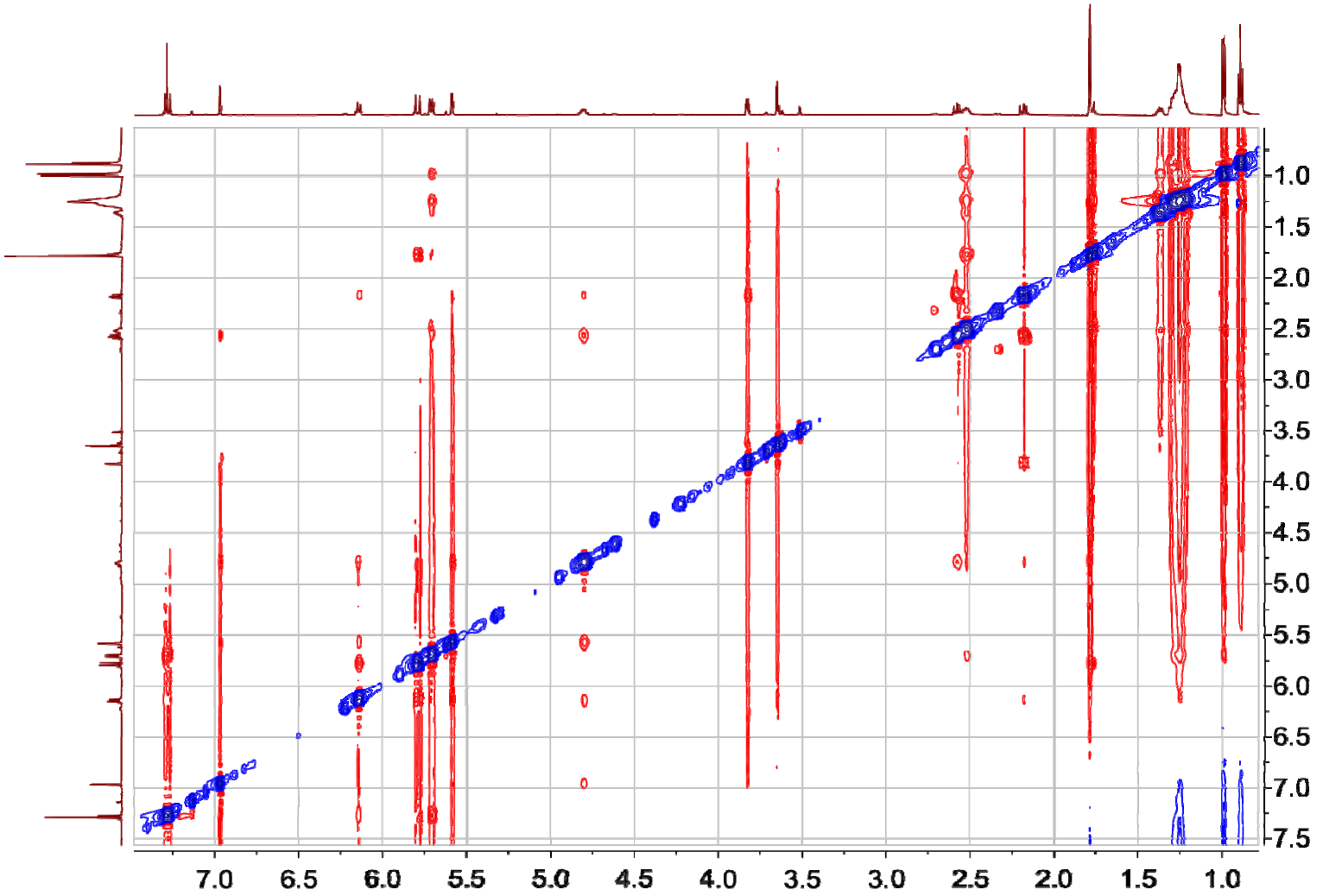

Figure S27. ROESY (600MHz, $CDCl_3$) spectrum of compound **3**.

Mass Spectrum SmartFormula Report

Analysis Info

Acquisition Date 9/21/2015 1:59:46 PM

Analysis Name	D:\Data\Spektren 2015\Proksch15HR000325.d
Method	tune_low.m
Sample Name	Hao Br-3-B-4-4 (CH3OH)
Comment	1 ug/ml

Operator	Peter Tommes				
Instrument	maXis	288882.20213			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	180 °C
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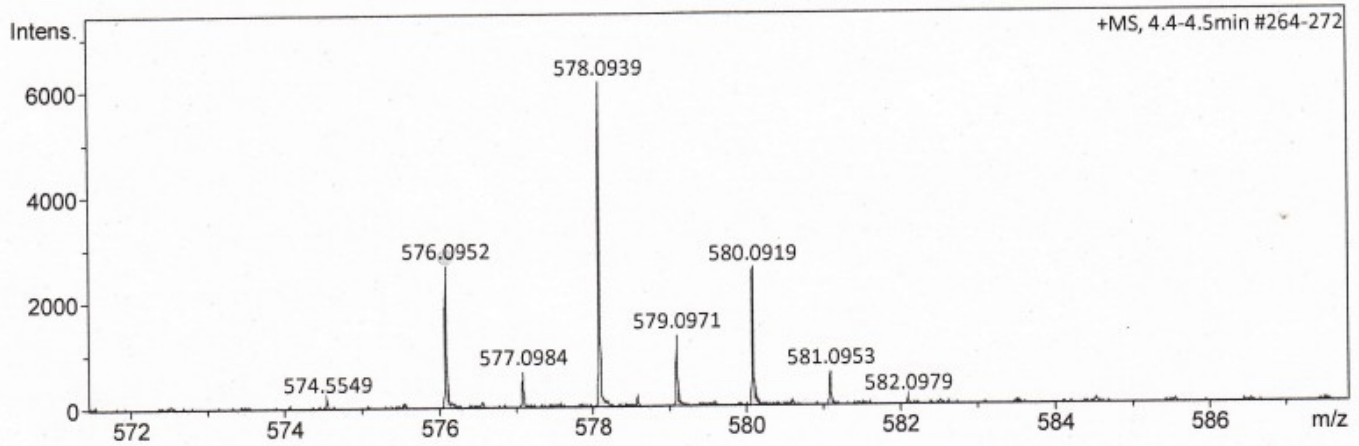
Scan End	1500 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
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Figure S28. HRESIMS of compound **4**.

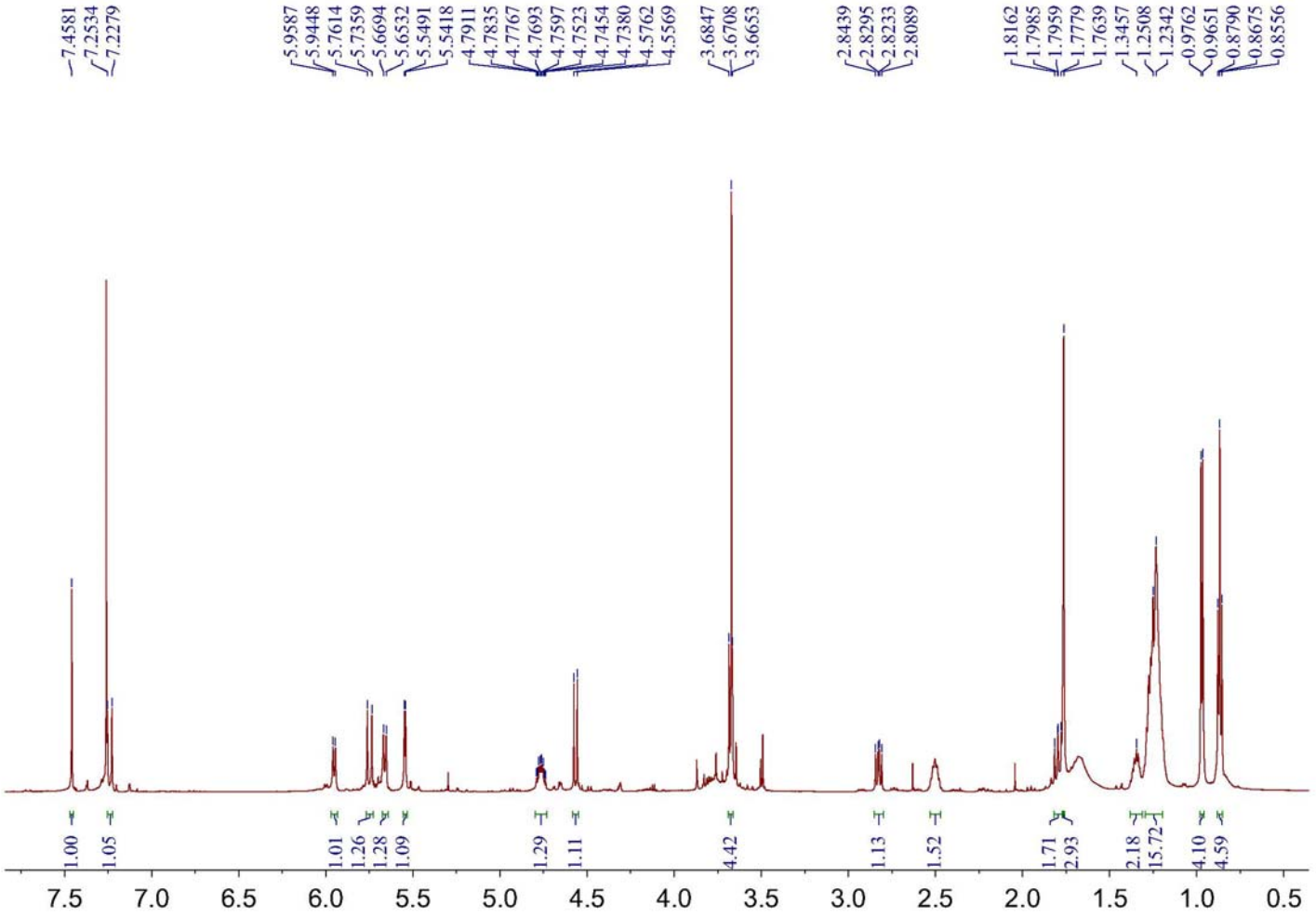

Figure S29. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of compound **4**.

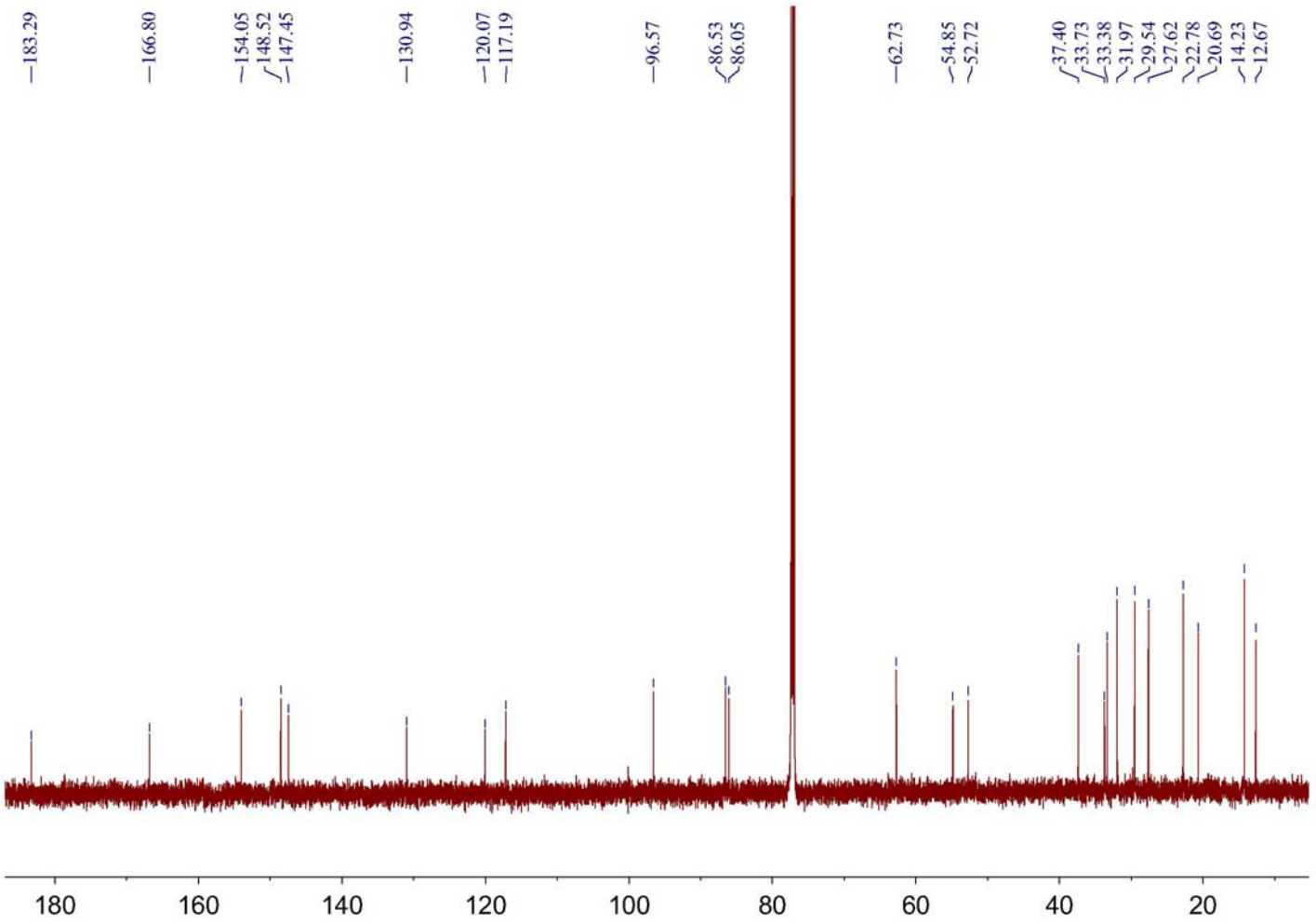

Figure S30. ^{13}C NMR (150MHz, $CDCl_3$) spectrum of compound **4**.

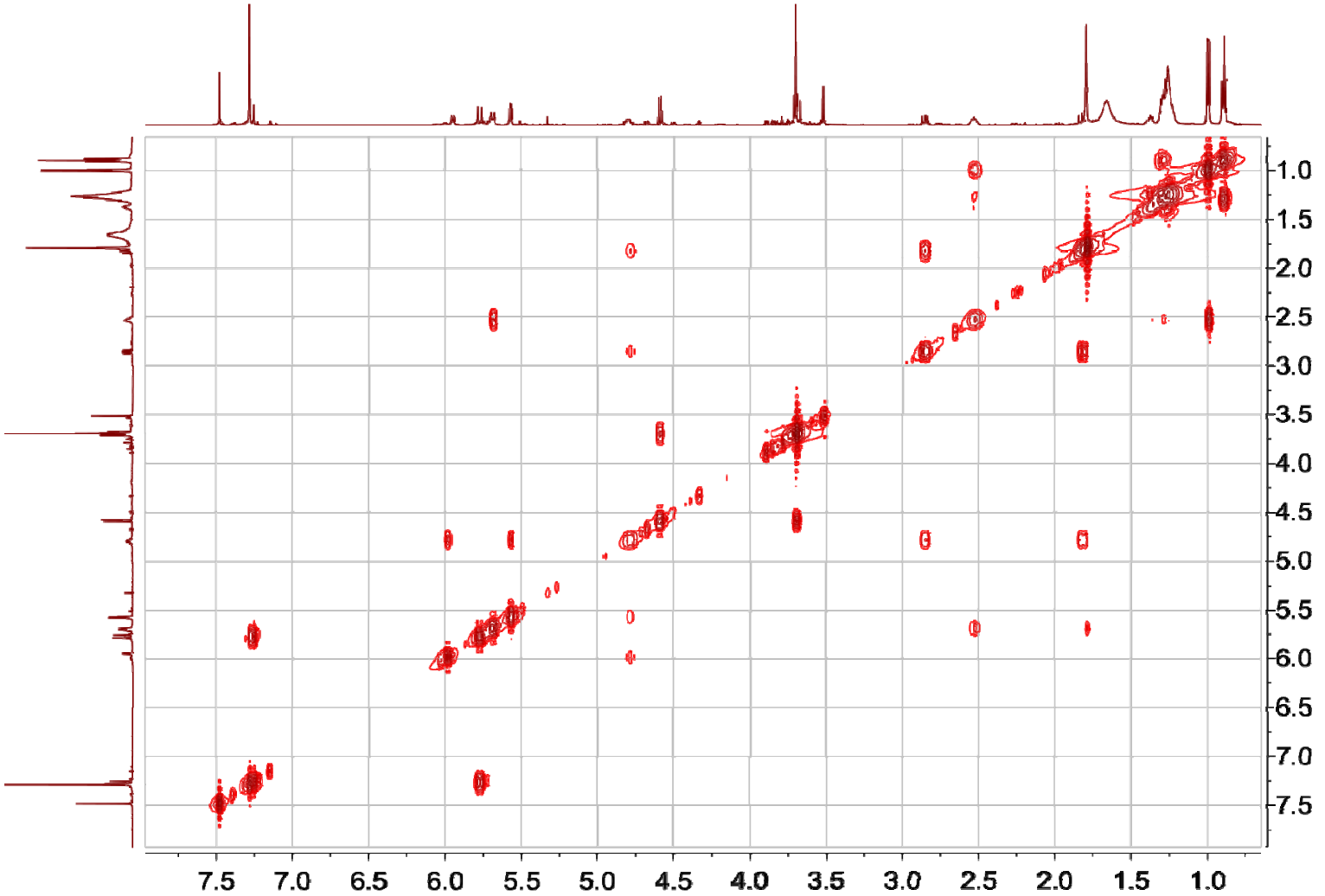

Figure S31. ^{1}H-^{1}H COSY (600MHz, $CDCl_3$) spectrum of compound **4**.

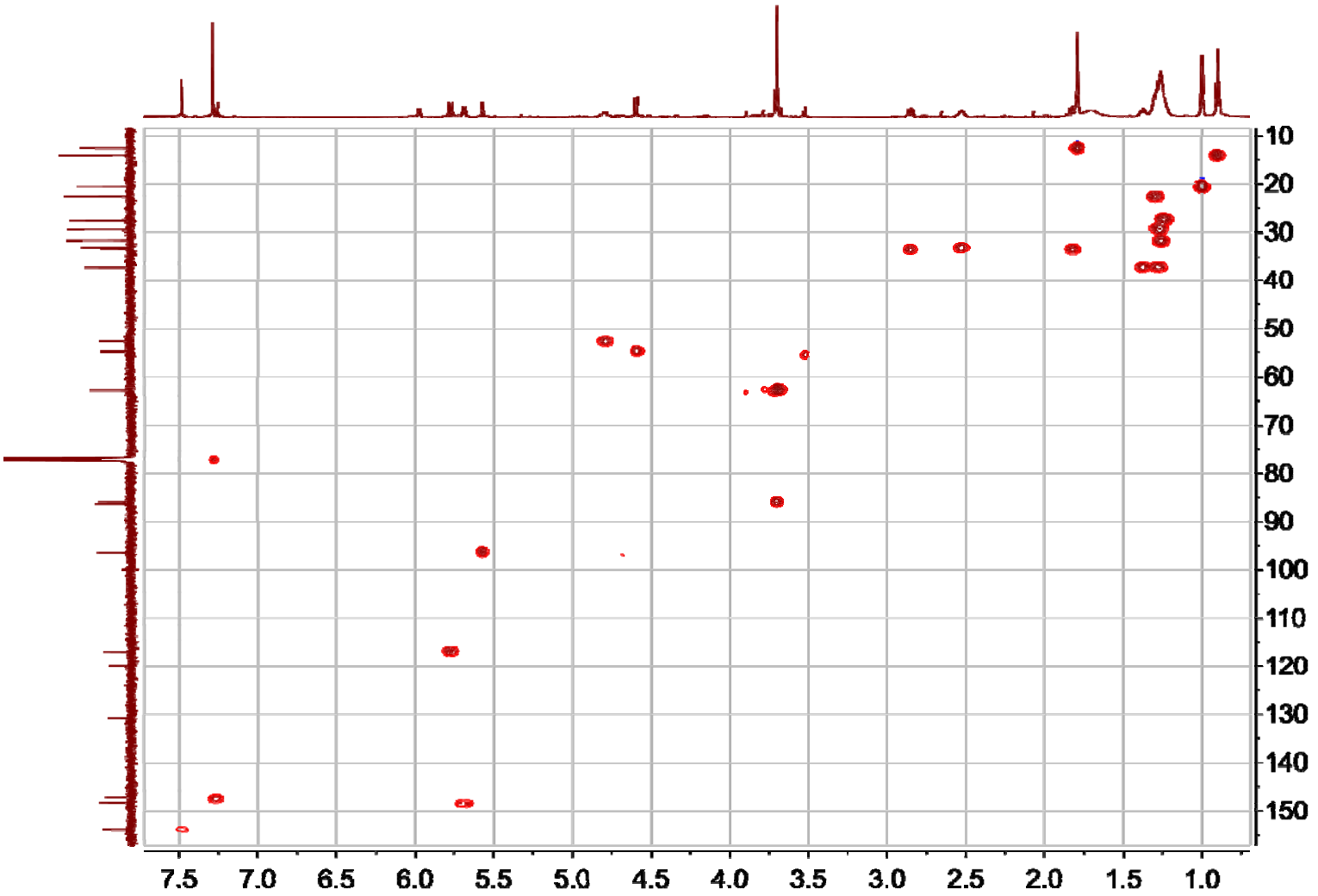

Figure S32. HSQC (600MHz, 150MHz, $CDCl_3$) spectrum of compound **4**.

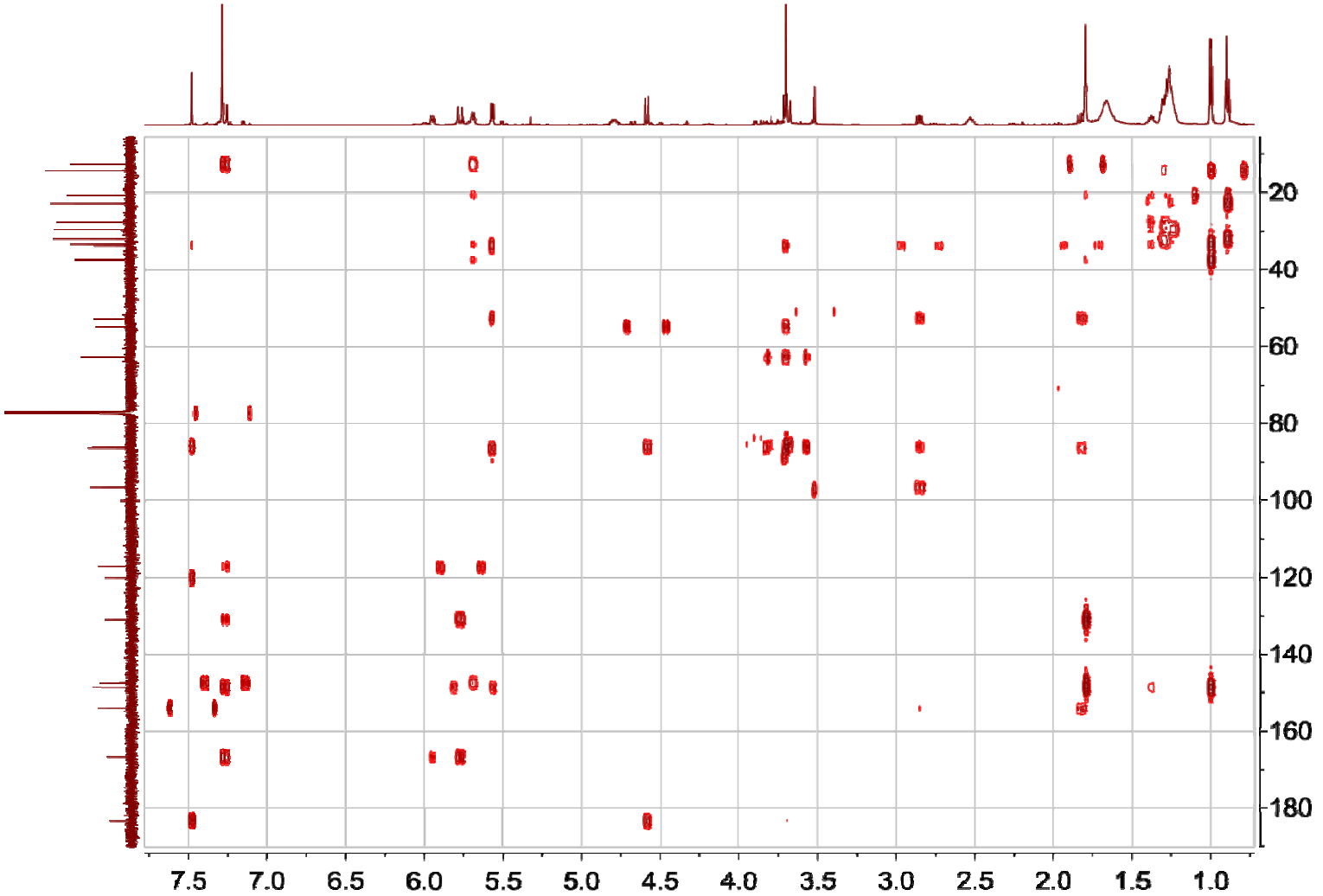

Figure S33. HMBC (600MHz, 150MHz, $CDCl_3$) spectrum of compound **4**.

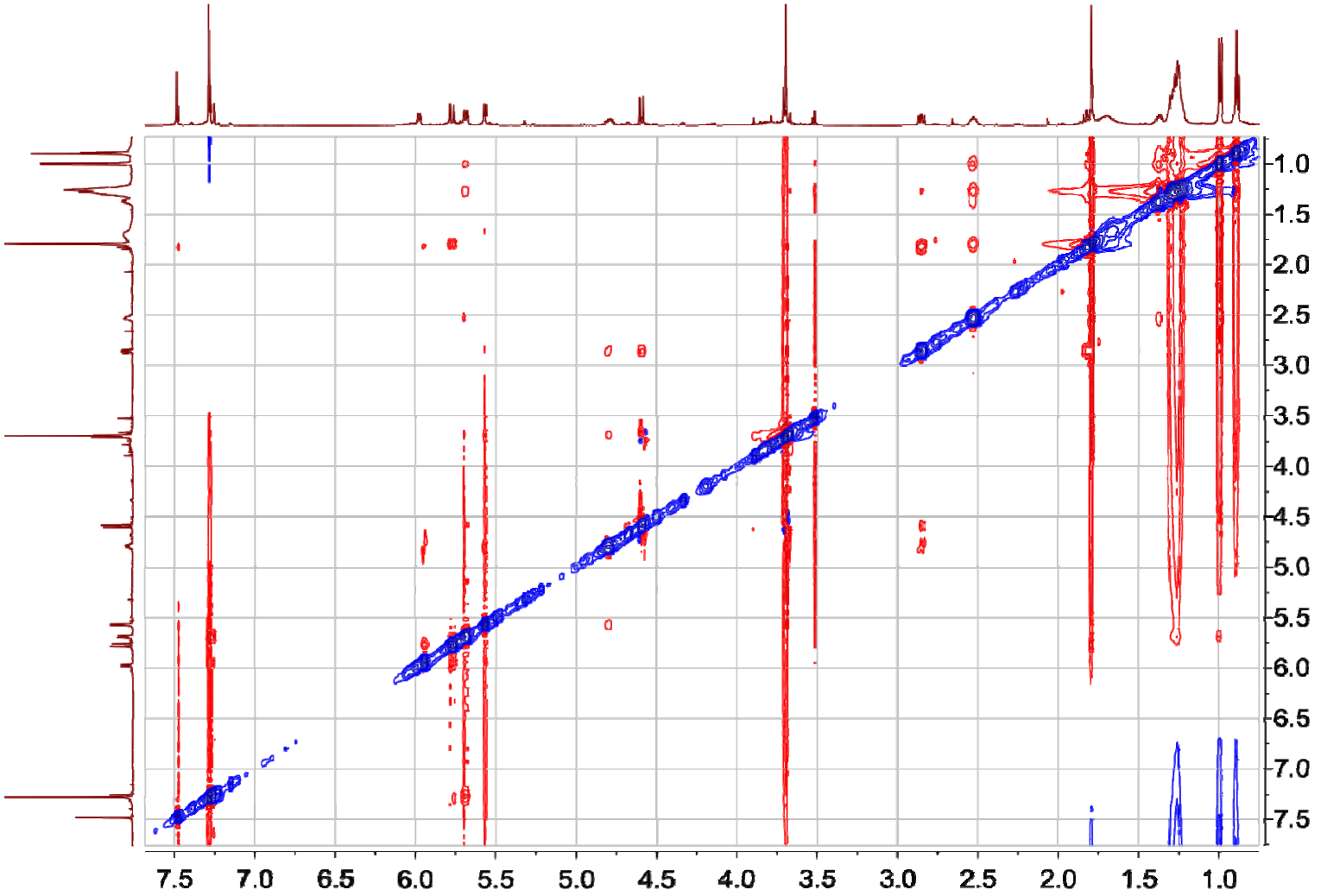

Figure S34. ROESY (600MHz, $CDCl_3$) spectrum of compound **4**.

Mass Spectrum SmartFormula Report

Analysis Info

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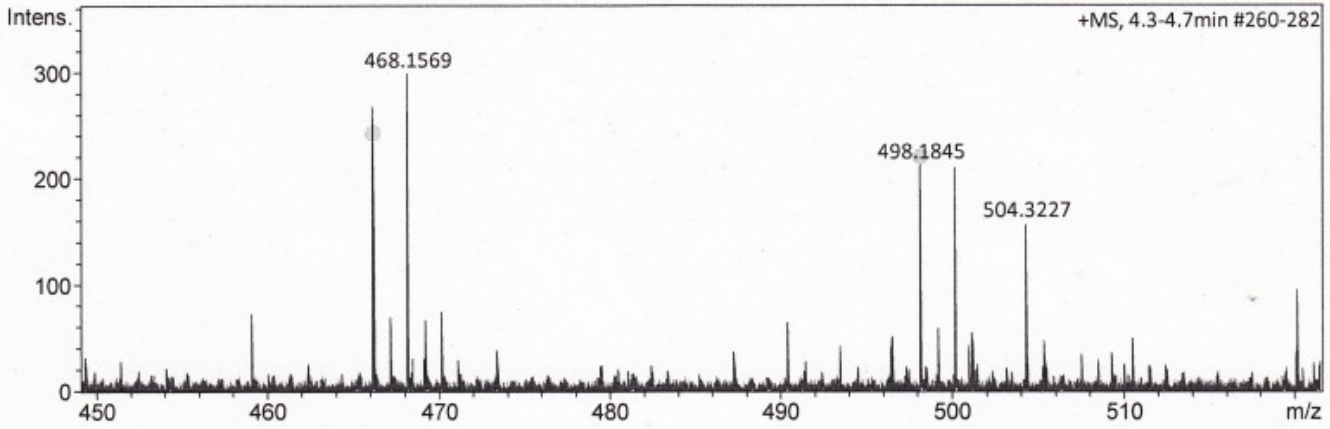
Method	tune_low.m	Operator	Peter Tommes
Sample Name	Hao Br-5-50-2-4 (CH3OH)	Instrument	maXis 288882.20213
Comment	3 ul in 1000 ul		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
466.1584	1	C23H33BrNO4	466.1587	0.7	184.9	1	100.00	7.5	even	ok
498.1845	1	C24H37BrNO5	498.1850	1.0	168.2	1	100.00	6.5	even	ok

Figure S35. HRESIMS of compound **5**.

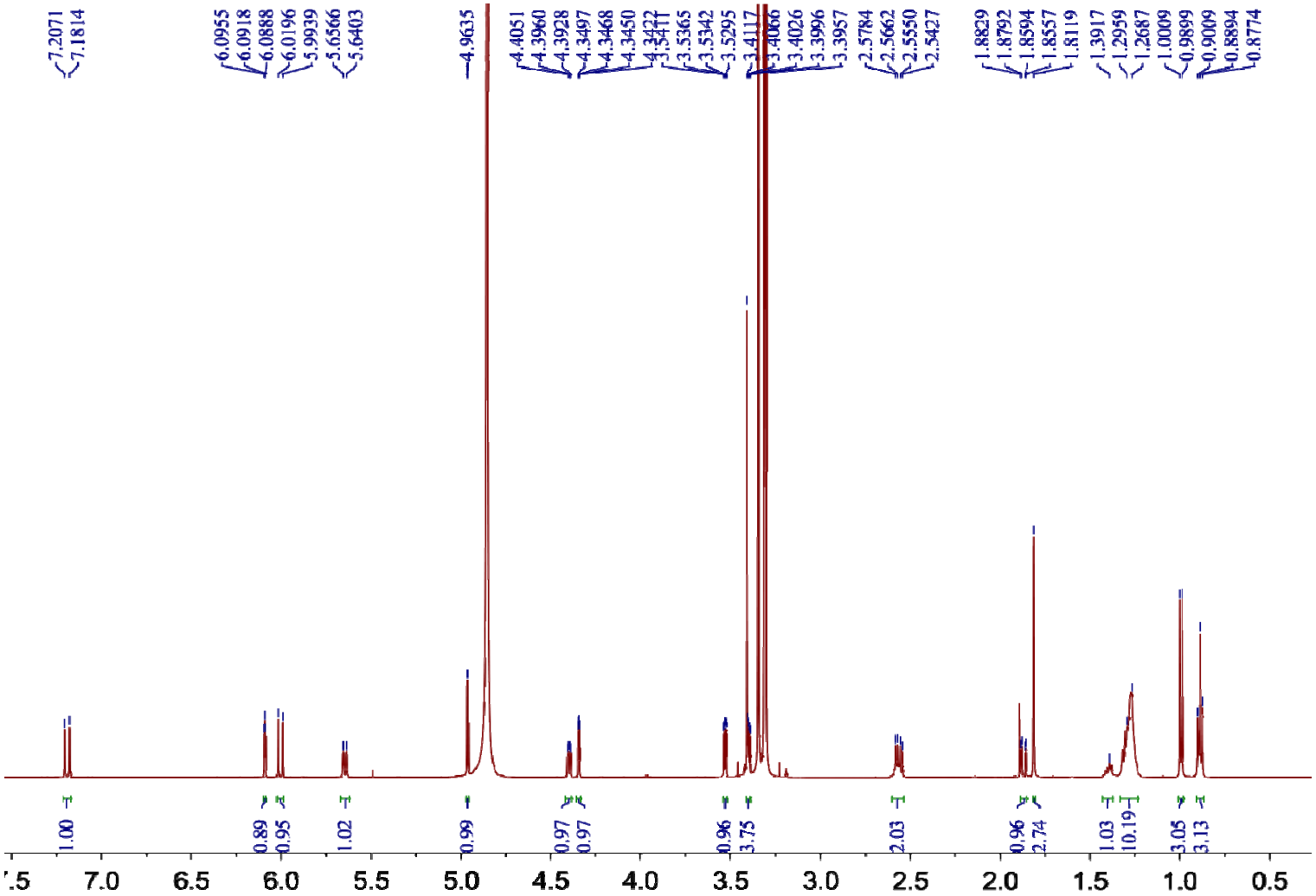


Figure S36. ^{1}H NMR (600MHz, methanol-d_4) spectrum of compound **5**.

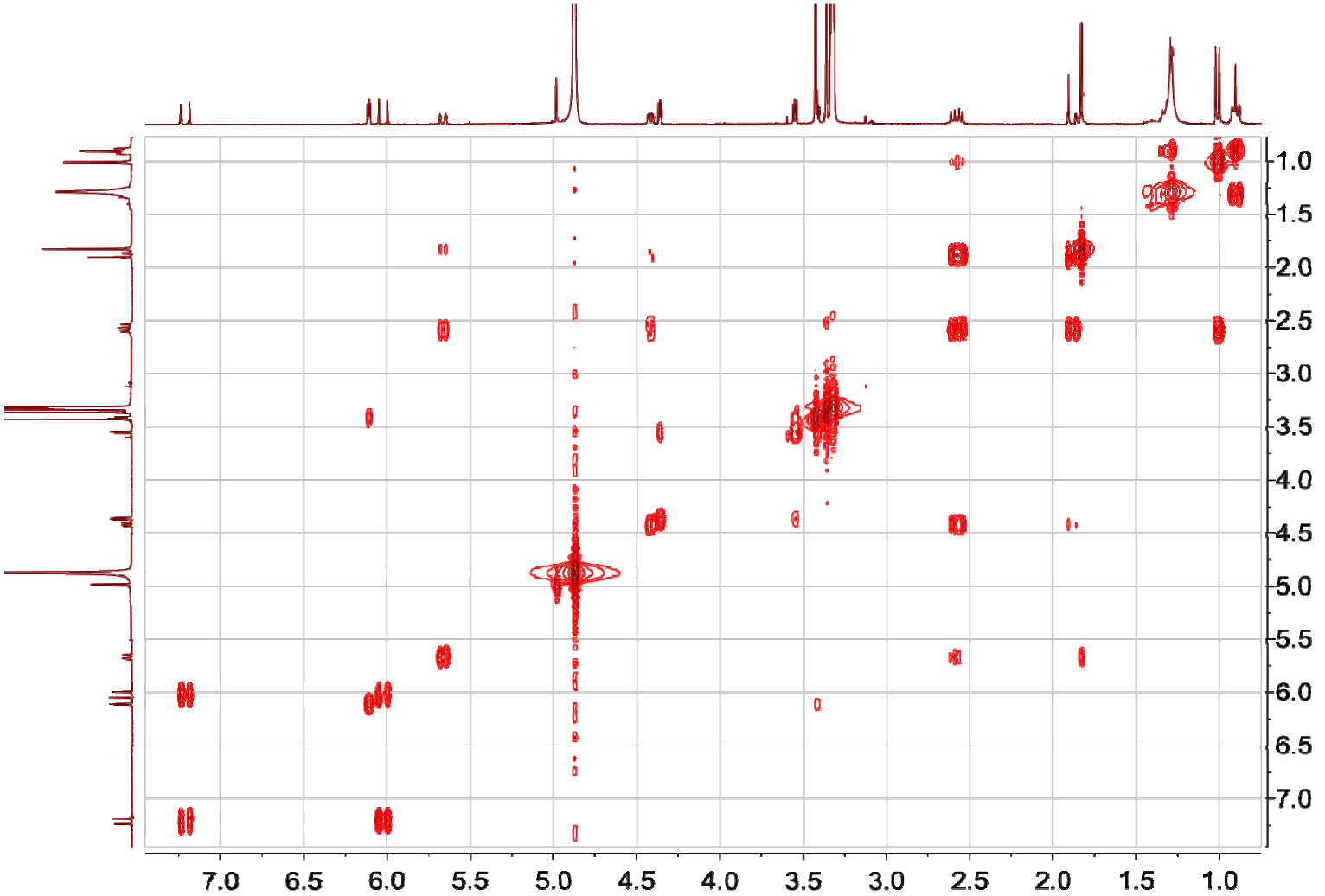


Figure S37. ^{1}H-^{1}H COSY (300MHz, methanol-d_4) spectrum of compound **5**.

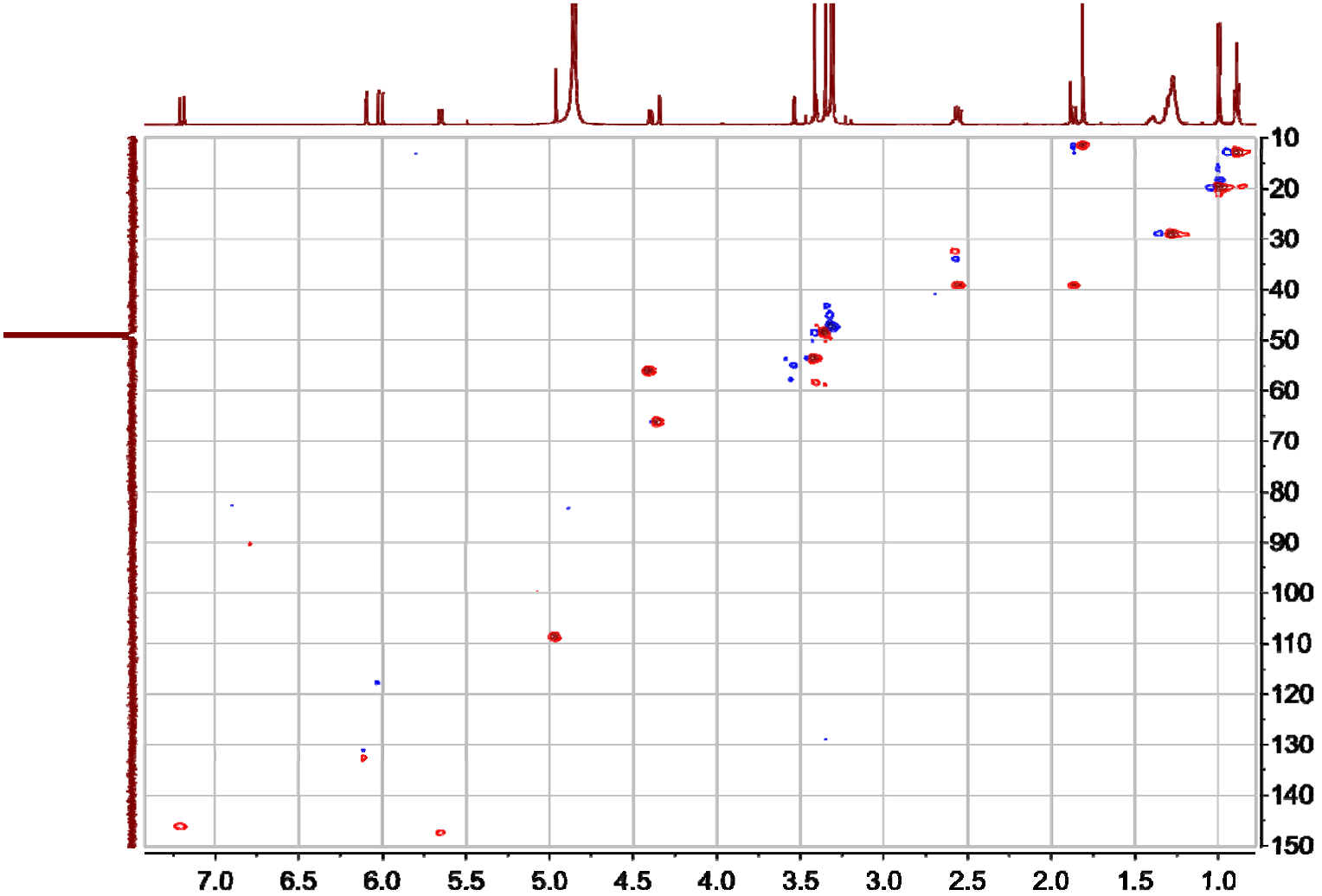


Figure S38. HSQC (600MHz, 150MHz, methanol-d_4) spectrum of compound **5**.

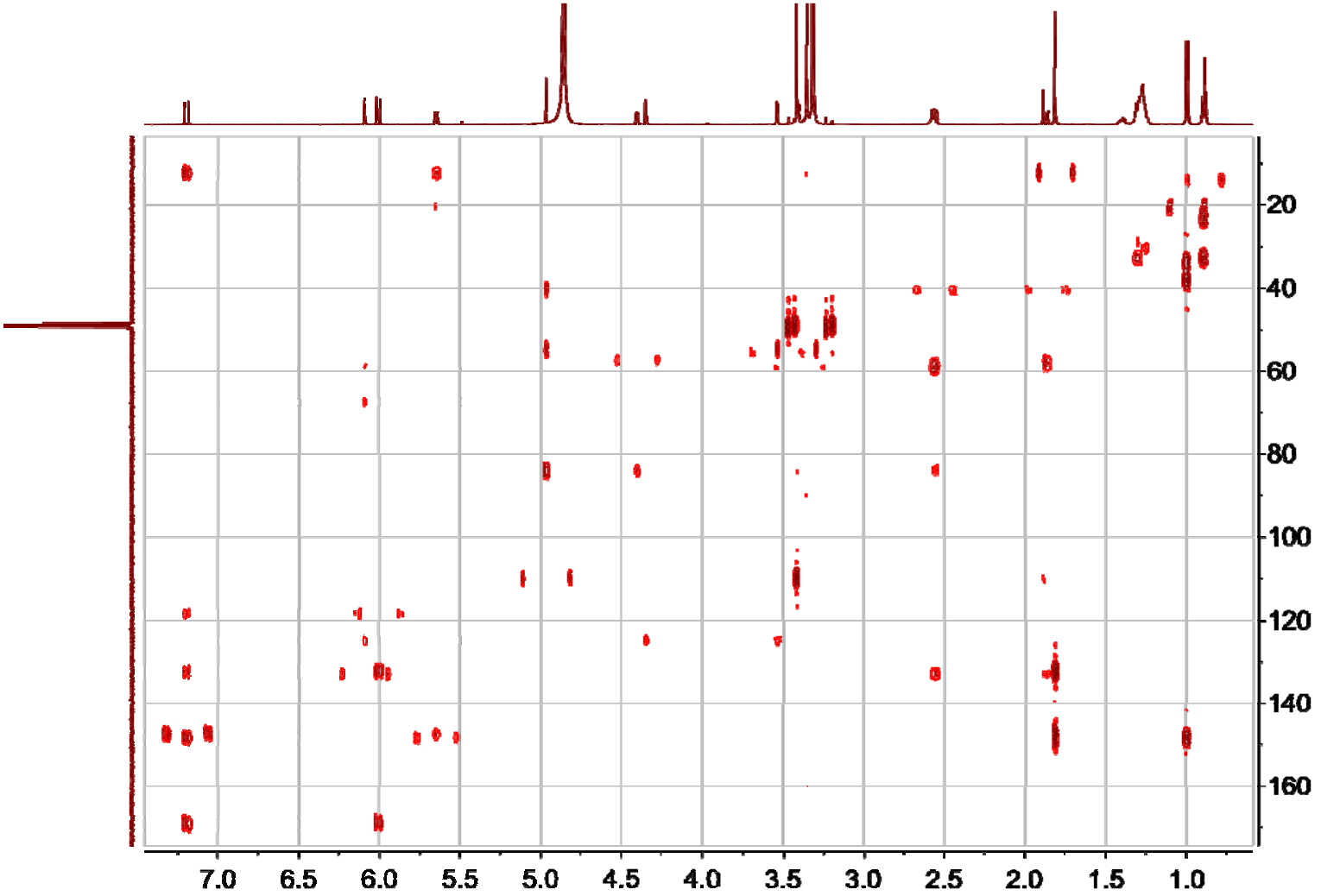


Figure S39. HMBC (600MHz, 150MHz, methanol-d_4) spectrum of compound **5**.

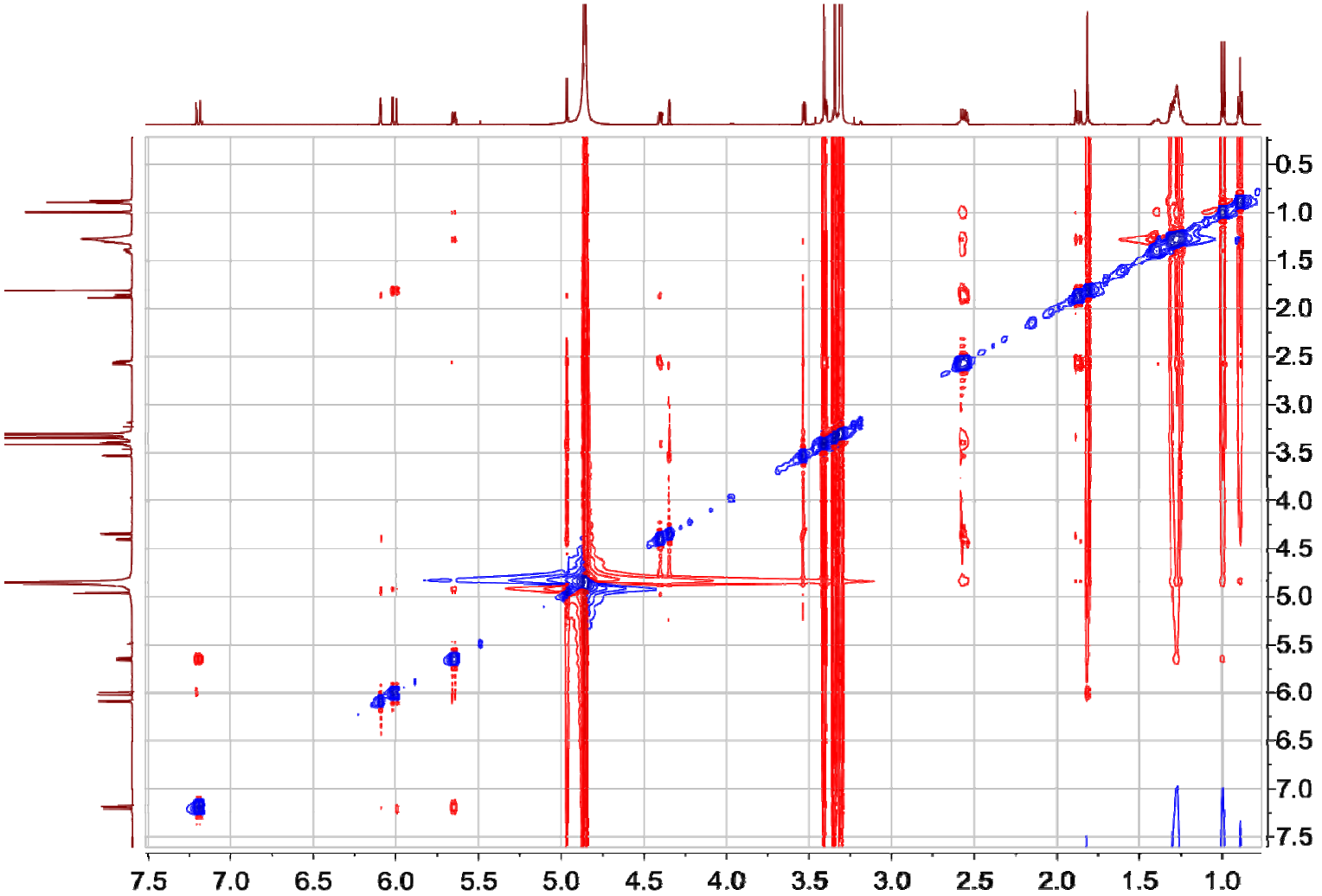


Figure S40. ROESY (600MHz, methanol-d_4) spectrum of compound **5**.

Mass Spectrum SmartFormula Report

Analysis Info

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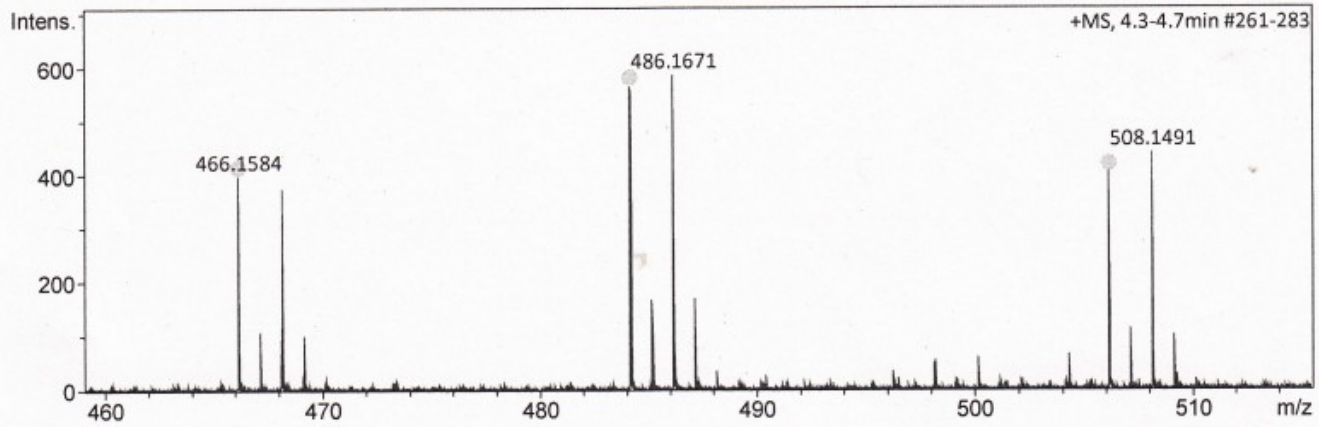
Method	tune_low.m	Operator	Peter Tommes
Sample Name	Hao Br-5-50-2-1 (CH3OH)	Instrument	maXis 288882.20213
Comment	10 ul in 1000 ul		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
466.1584	1	C23H33BrNO4	466.1587	0.7	33.0	1	100.00	7.5	even	ok
484.1689	1	C23H35BrNO5	484.1693	0.9	30.0	1	100.00	6.5	even	ok
506.1510	1	C23H34BrNNaO5	506.1513	0.4	35.5	1	100.00	6.5	even	ok

Figure S41. HRESIMS of compound **6**.

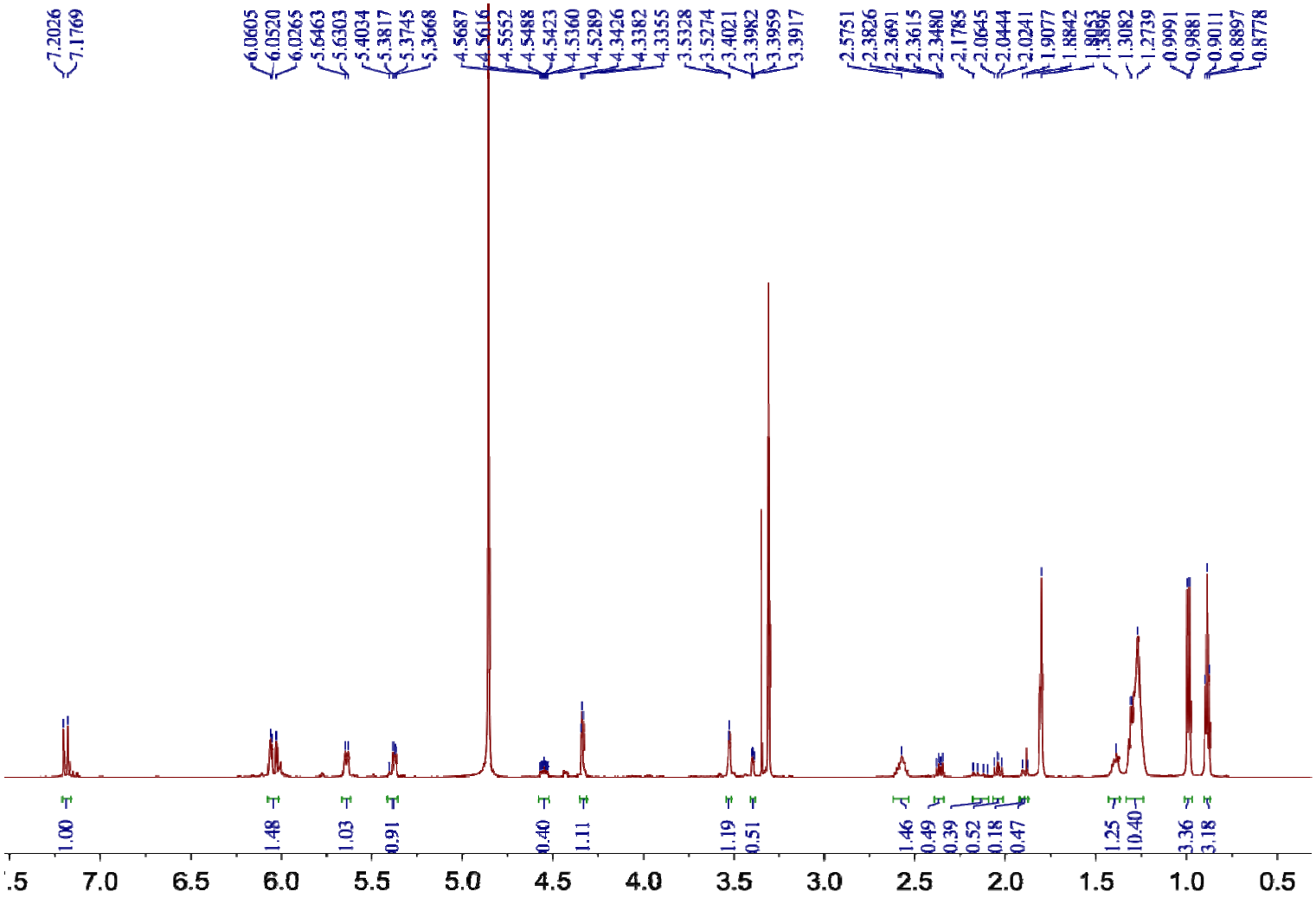


Figure S42. ^{1}H NMR (600MHz, methanol-d_4) spectrum of compound **6**.

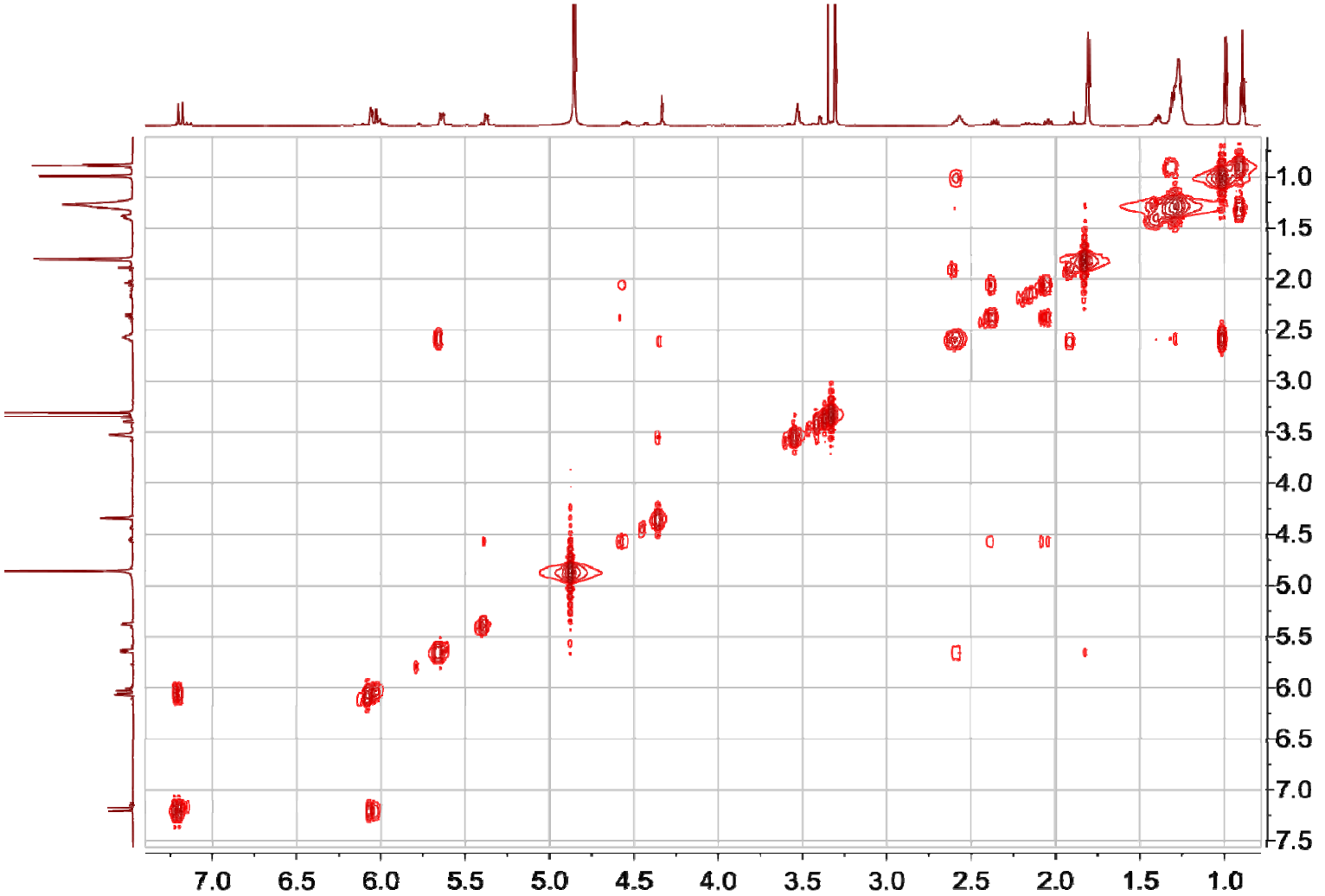


Figure S43. ^{1}H-^{1}H COSY (600MHz, methanol-d_4) spectrum of compound **6**.

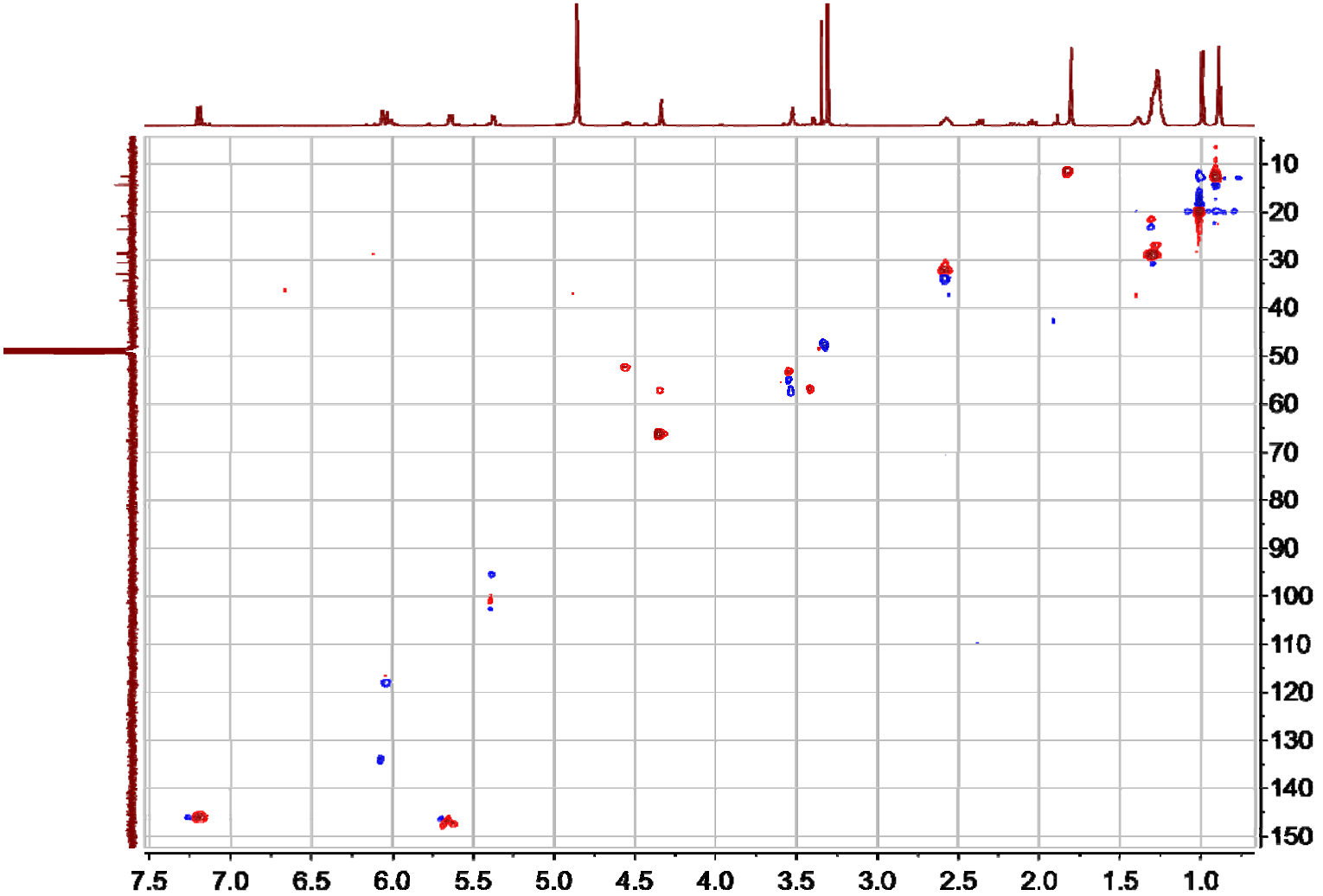


Figure S44. HSQC (600MHz, 150MHz, methanol-d_4) spectrum of compound **6**.

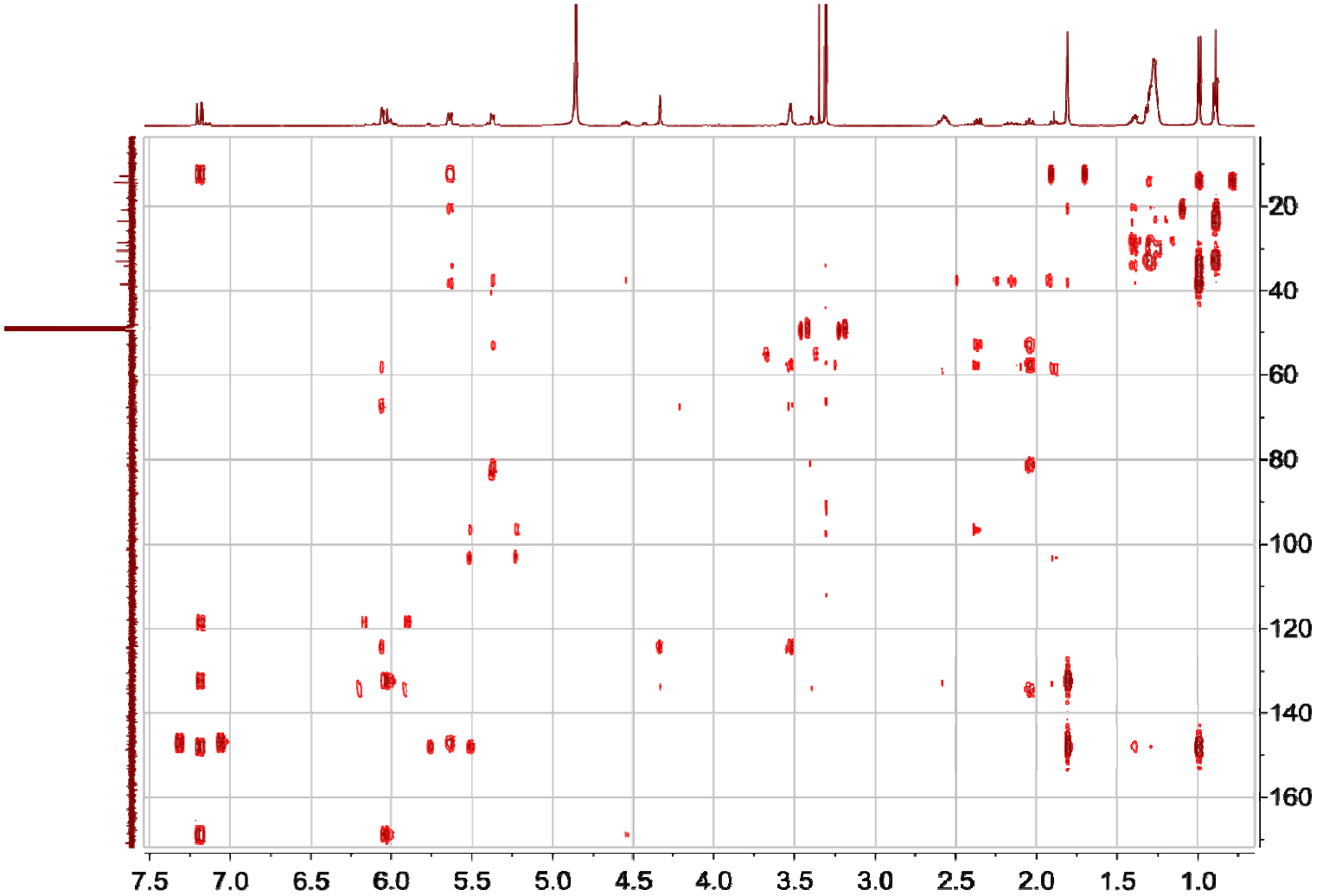


Figure S45. HMBC (600MHz, 150MHz, methanol-d_4) spectrum of compound **6**.

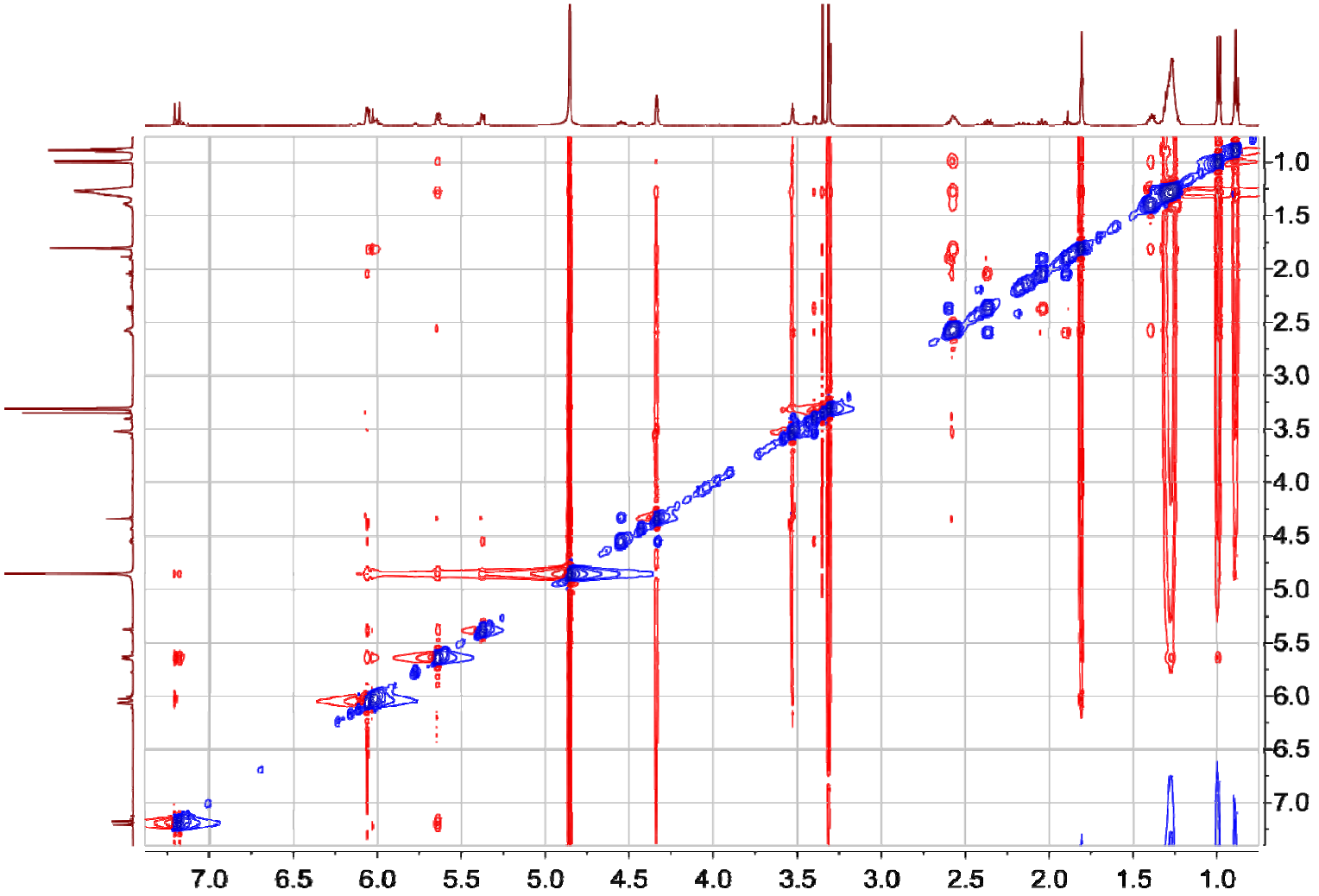


Figure S46. ROESY (600MHz, methanol-d_4) spectrum of compound **6**.

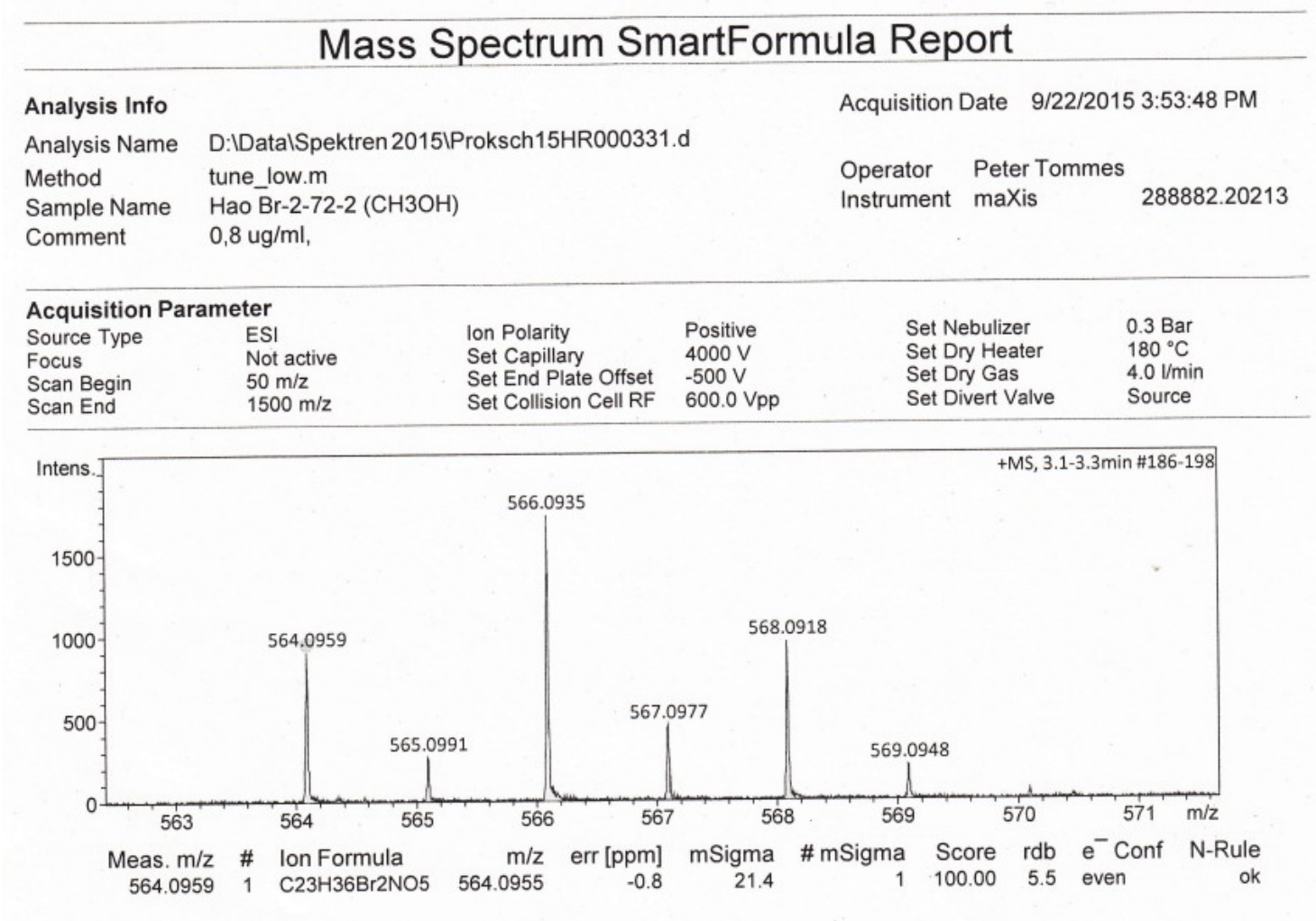


Figure S47. HRESIMS of compound **7**.

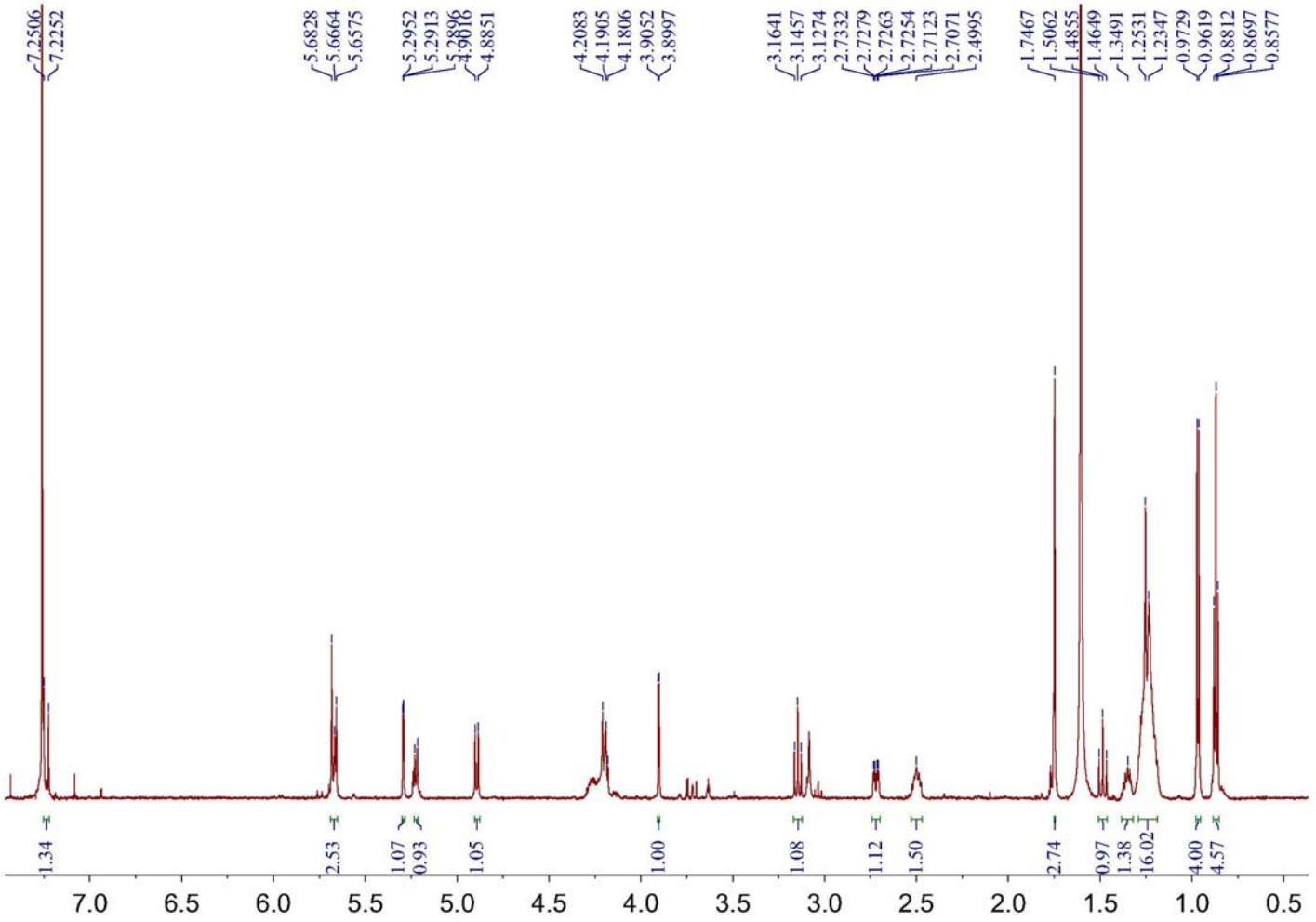


Figure S48. ^{1}H NMR (600MHz, $CDCl_3$) spectrum of compound **7**.

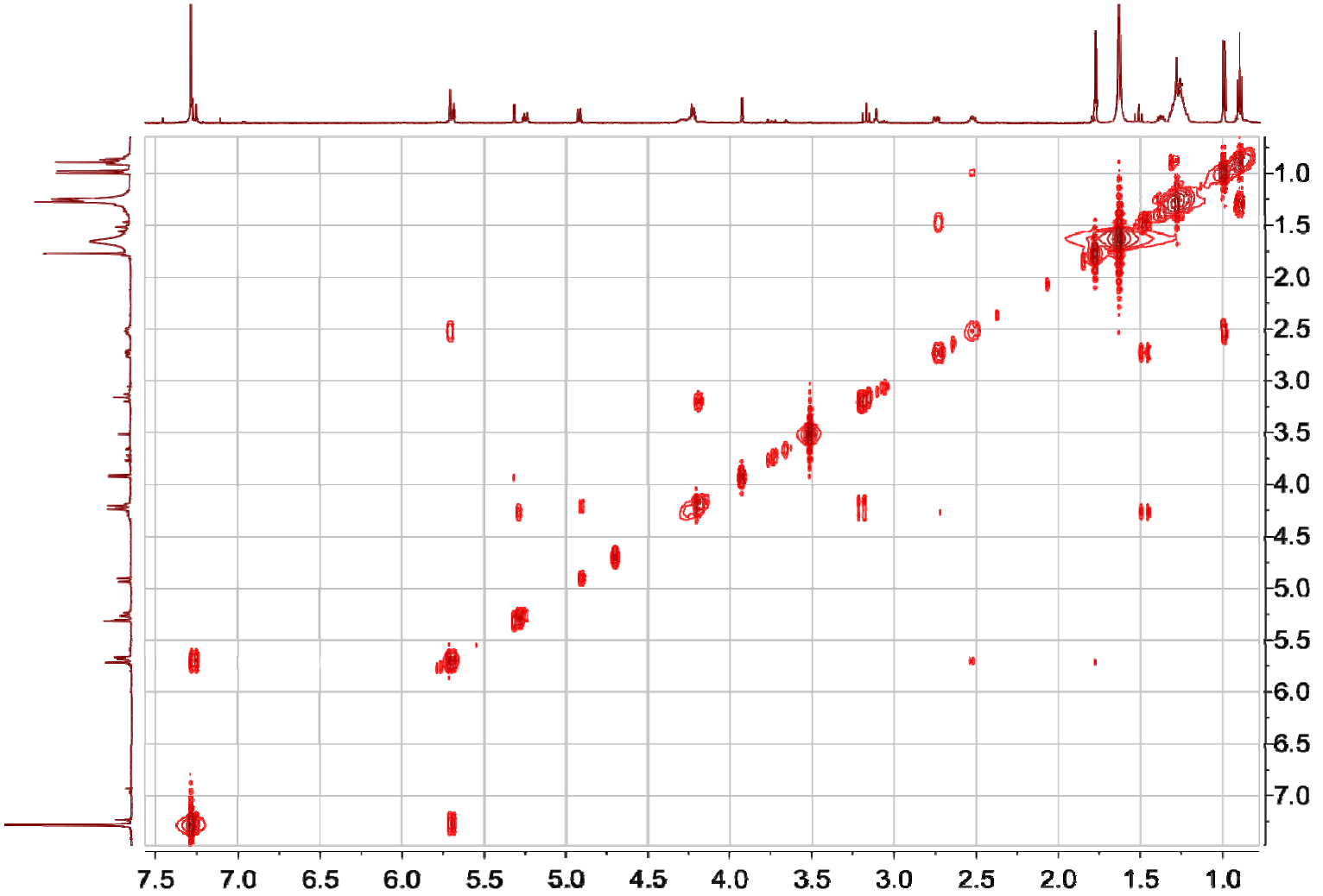


Figure S49. ^{1}H-^{1}H COSY (600MHz, $CDCl_3$) spectrum of compound **7**.

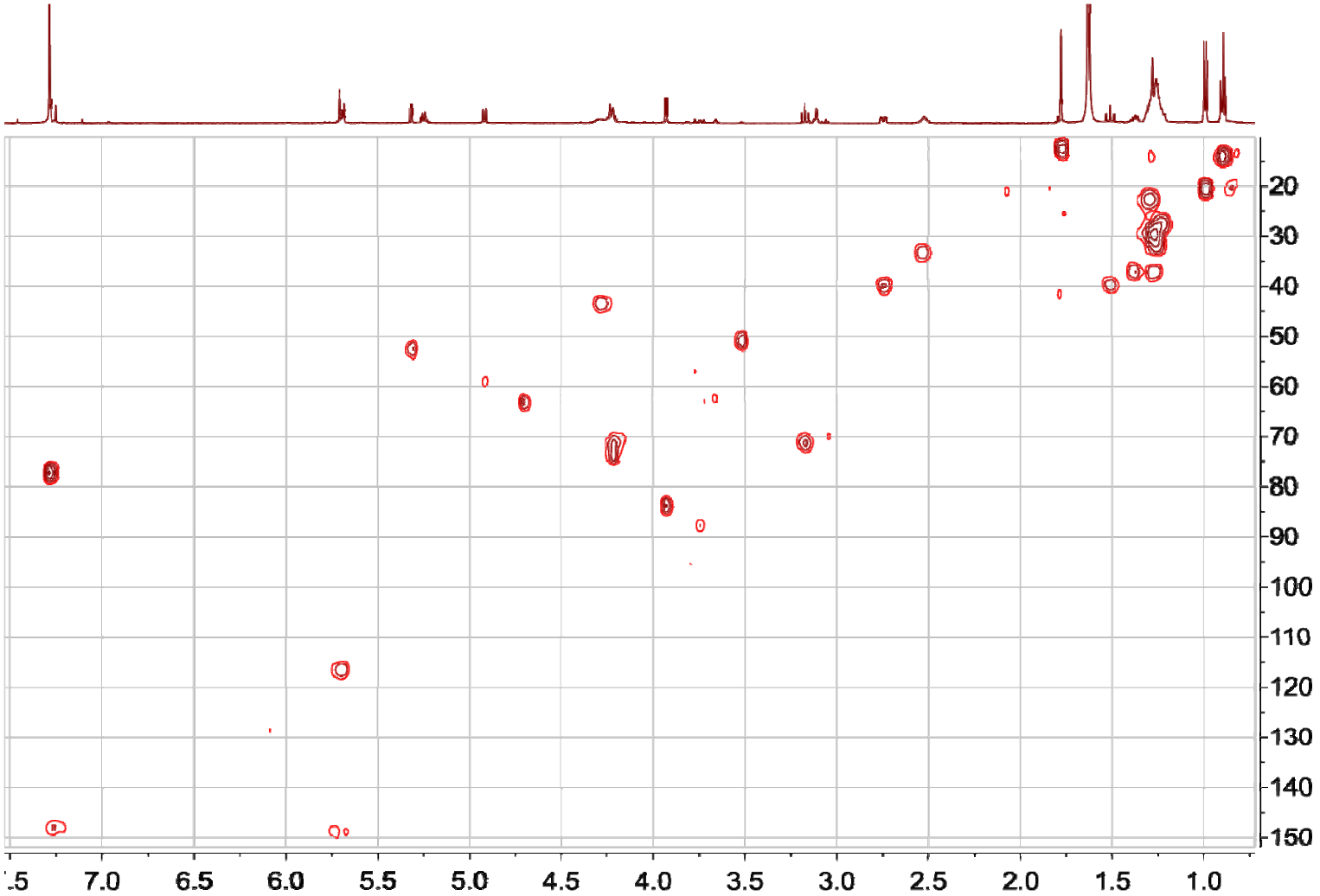


Figure S50. HSQC (600MHz, 150MHz, $CDCl_3$) spectrum of compound **7**.

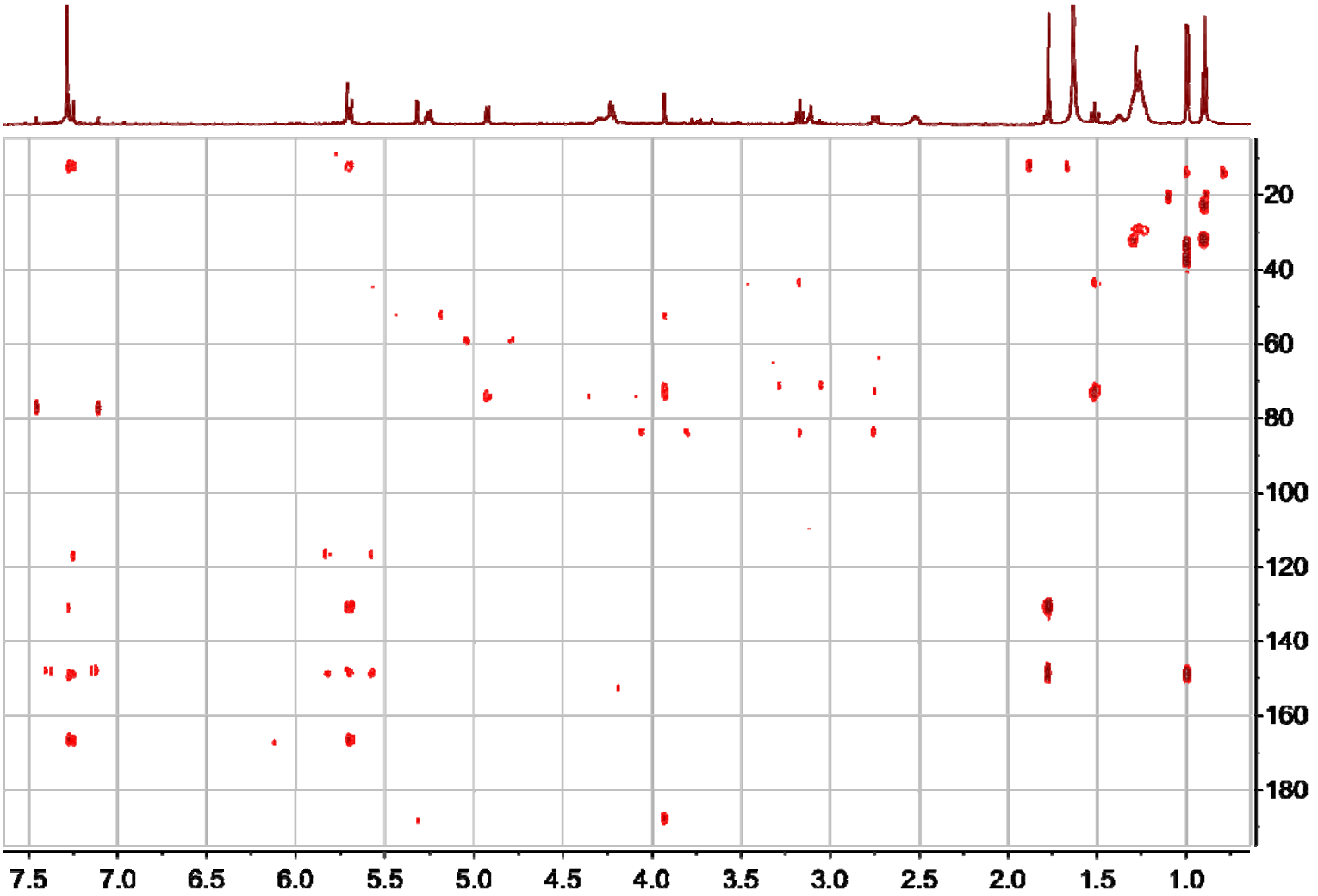


Figure S51. HMBC (600MHz, 150MHz, $CDCl_3$) spectrum of compound **7**.

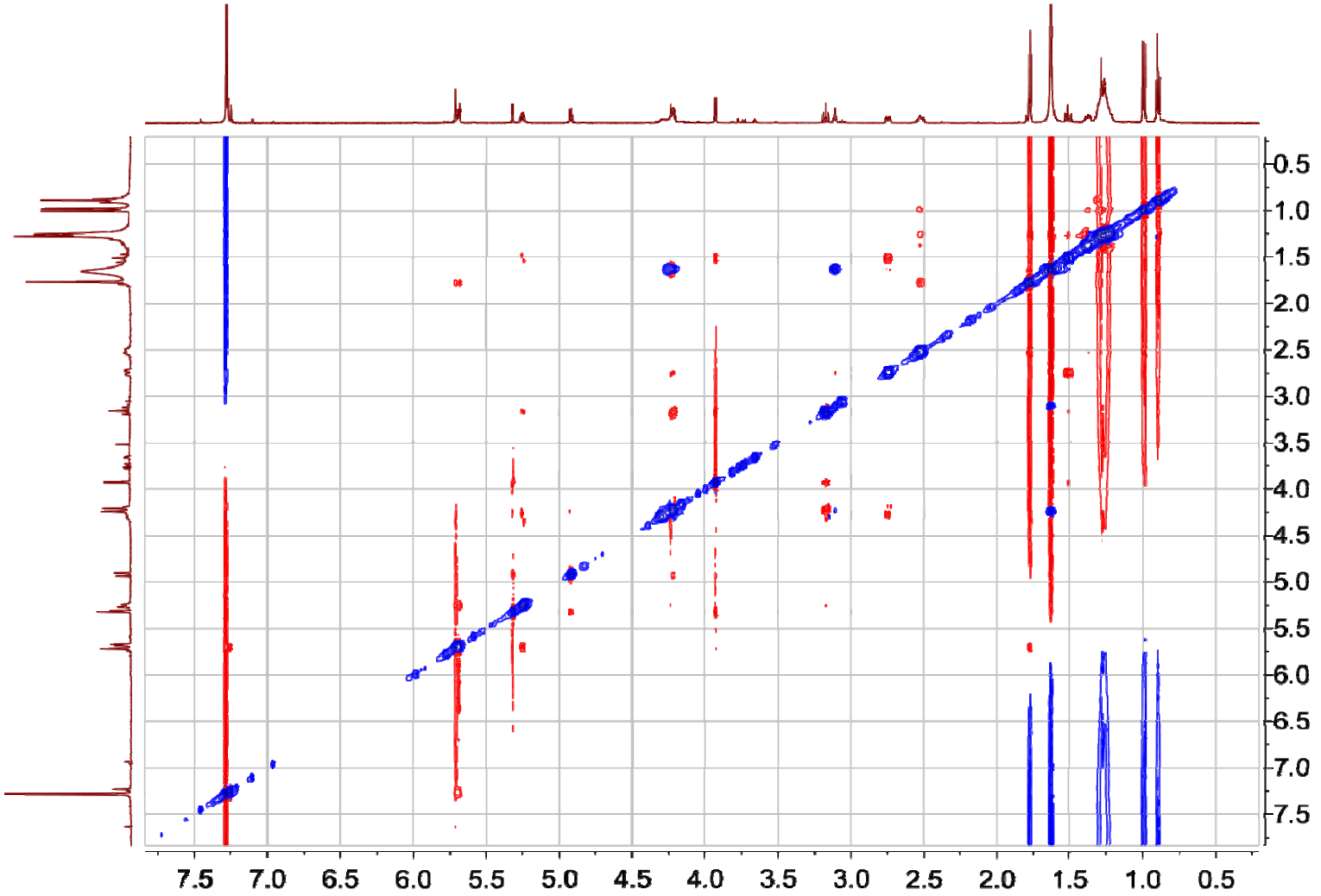


Figure S52. ROESY (600MHz, $CDCl_3$) spectrum of compound **7**.

X-ray crystallographic parameters of compound 1 (CCDC 1481781)

Crystallization conditions: X-ray quality crystal of **1** was obtained by slow evaporation from MeOH solution. A suitable single crystal was carefully selected under a polarizing microscope. *Data collection*: Bruker Kappa APEX2 CCD diffractometer (with microfocus tube), Mo-Kα radiation (λ = 0.71073 Å), multilayer mirror, ω- and ϕ-scan; data collection with APEX2, cell refinement and data reduction with SAINT,[1] experimental absorption correction with SADABS.[2] *Structure Analysis and Refinement*: The structure was solved by direct methods using SHELXS-97; refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite.[3] All non-hydrogen positions were refined with anisotropic displacement parameters. Hydrogen atoms were positioned geometrically (with C-H = 0.95 Å for aromatic/olefinic CH, 1.00 Å for tertiary CH, 0.99 Å for CH_2 and 0.98 Å for CH_3) and refined using riding models (AFIX 43, 13, 23 and 133 or 137, respectively), with U_{iso}(H) = -1.2U_{eq}(CH, CH_2) and -1.5U_{eq}(CH_3). The hydrogen atoms on the hydroxyl groups with O1 and O7 (methanol solvent molecule) were found and refined with U_{iso}(H) = 1.5U_{eq}(O). The N-H hydrogen atom has been found and refined with U_{iso}(H) = 1.5U_{eq}(N). The H atoms on O2 and O5 had to be calculated and refined with AFIX 83 to avoid their wrong intramolecular positioning (O2-H towards O5 and O5-H towards O3) which would lead to C-O-H angles < 92°. The apparent disorder due higher thermal motion and less constrained crystal packing of the bent alkyl chain and the methyl group of the methanol solvent molecules leads to short intermolecular H···H contacts and short C-C bonds as artefacts which are noted as Alert level A and B in the Checkcif file.

The gymnastatin T molecule (**1**) crystallizes in the non-centrosymmetric orthorhombic

space group $P\ 2_12_12_1$. A methanol solvent molecule of crystallization is embedded in the crystal lattice per formula unit (**Figure S53**). The O-H and N-H group are part of a hydrogen-bonding network (**Figure S54**, **Table S5**). The larger thermal ellipsoids of the carbon atoms of the bent alkyl chain indicate their higher thermal motion and less constrained crystal packing compared to the more rigid hydrogen-bonded part, the OH-functionalized bicyclo[3.3.1]nonane ring of the molecule. The unit cell packing can be seen as a separation of the hydrophilic hydrogen-bonding part, the OH-substituted bicyclo[3.3.1]nonane ring of the molecule (in layers parallel to the *ab* plane) and the hydrophobic branched alkyl chain (sandwiched between the hydrophilic layers) (**Figure S55**).[4] The bent alkyl chains from adjacent molecules interdigitate (interlock) along the *c* direction.[5]

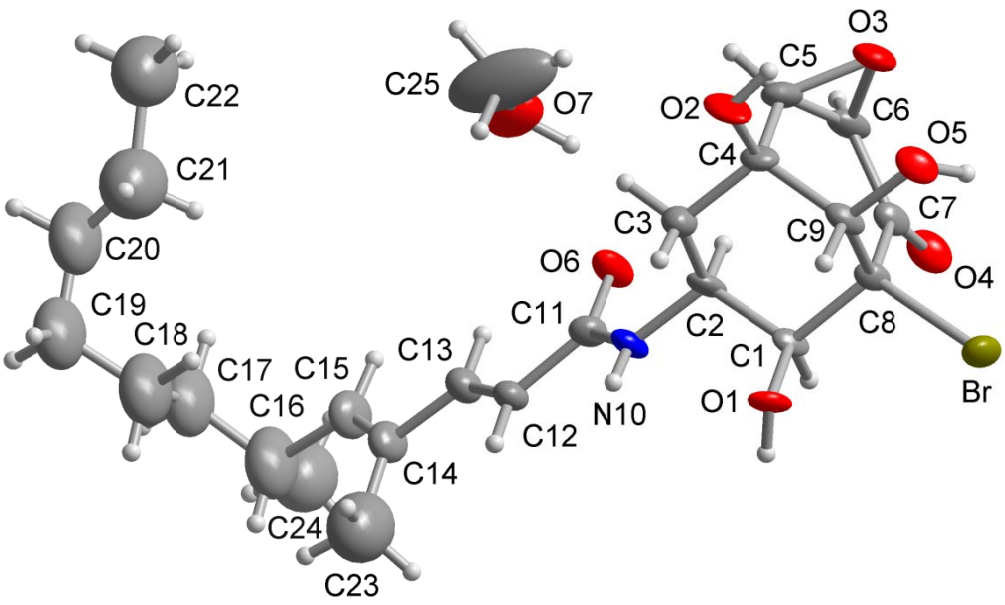


Figure S53. Molecular structure of **1** from single-crystal X-ray diffractometry (50% thermal ellipsoids, 20% for C25, H atoms of arbitrary radii).

Table S1. Crystal data and structure refinement for **1**

Compound	**1**
Data set	Br_5_30_2
CCDC number	1481781
Empirical formula	$C_{23}H_{34}BrNO_6 \cdot CH_3OH$
M/g mol^{-1}	532.46
Crystal size/mm^3	0.40 × 0.05 × 0.01
Temperature/K	150
θ range/° (completeness)	2.5–25.3° (0.99)
h; k; l range	-8/9, 14/14, -41/42
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	7.0251(3)
b/Å	11.3852(5)
c/Å	32.3080(15)
α/°	90
β/°	90
γ/°	90
V/Å^3	2584.1(2)
Z	4
D_{calc}/g cm^{-3}	1.369
μ (Mo Kα)/mm^{-1}	1.63
F(000)	1120
Max./min. transmission	0.674, 0.746
Reflections collected	39194
Independent reflect. (R_{int})	6086 (0.0445)
Data/restraints/parameters	6088/5/275
Max./min. Δρ/e Å^{-3} [a]	1.469/-0.977
R_1/wR_2 [I>2σ(I)] [b]	0.0626/0.1579
R_1/wR_2 (all data) [b]	0.0747/0.1637
Goodness-of-fit on F^2 [c]	1.092
Flack parameter [d]	0.043(4)

[a] Largest difference peak and hole; [b] $R_1 = [\sum(||F_o| - |F_c||)/\sum|F_o|]$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; [c] Goodness-of-fit = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$; [d] Absolute structure parameter.[6]

Table S2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **1**.

	x	*y*	*z*	U_{iso}*/U_{eq}
Br	0.94426 (9)	1.08655 (6)	0.19418 (2)	0.0331 (2)
C1	0.8297 (8)	0.9768 (5)	0.2698 (2)	0.0202 (12)
H1A	0.8167	0.9026	0.2535	0.024*
O1	1.0197 (6)	0.9889 (4)	0.28372 (16)	0.0254 (10)
H1	1.064 (12)	0.922 (5)	0.279 (2)	0.038*
C2	0.6985 (8)	0.9727 (5)	0.3068 (2)	0.0254 (13)
H2A	0.5659	0.9626	0.2961	0.030*
C3	0.7037 (10)	1.0866 (6)	0.3311 (2)	0.0302 (13)
H3A	0.8320	1.0969	0.3432	0.036*
H3B	0.6109	1.0822	0.3541	0.036*
C4	0.6570 (9)	1.1935 (5)	0.3039 (2)	0.0275 (13)
O2	0.6805 (9)	1.2931 (4)	0.32925 (18)	0.0448 (15)
H2	0.6520	1.3538	0.3158	0.067*
C5	0.4558 (11)	1.1811 (6)	0.2891 (2)	0.0343 (16)
H5A	0.3559	1.1797	0.3111	0.041*
O3	0.4054 (7)	1.2410 (4)	0.25144 (16)	0.0322 (11)
O5	0.7751 (6)	1.3017 (4)	0.24330 (16)	0.0283 (10)
H5	0.7530	1.2839	0.2185	0.042*
C6	0.4112 (9)	1.1138 (6)	0.2507 (2)	0.0306 (15)
H6A	0.2859	1.0722	0.2499	0.037*
C7	0.5720 (9)	1.0579 (5)	0.2273 (2)	0.0249 (13)
O4	0.5394 (8)	0.9852 (4)	0.20181 (16)	0.0357 (11)
C8	0.7758 (7)	1.0839 (6)	0.24217 (19)	0.0213 (11)
C9	0.7976 (9)	1.1982 (5)	0.2668 (2)	0.0252 (14)
H9	0.9294	1.1992	0.2785	0.030*
N10	0.7407 (8)	0.8721 (5)	0.33274 (19)	0.0263 (12)
H10	0.864 (9)	0.879 (7)	0.343 (2)	0.039*
C11	0.6062 (8)	0.7934 (6)	0.3423 (2)	0.0258 (14)

O6	0.4378 (7)	0.8024 (4)	0.32919 (16)	0.0358 (11)
C12	0.6652 (10)	0.6938 (6)	0.3689 (2)	0.0275 (14)
H12	0.7938	0.6869	0.3776	0.033*
C13	0.5372 (11)	0.6140 (6)	0.3806 (2)	0.0331 (15)
H13	0.4106	0.6271	0.3714	0.040*
C15	0.4129 (13)	0.4462 (7)	0.4146 (3)	0.047 (2)
H15	0.2948	0.4750	0.4045	0.056*
C16	0.407 (3)	0.3322 (11)	0.4394 (4)	0.094 (2)
H16	0.5385	0.3039	0.4457	0.113*
C17	0.296 (3)	0.3515 (12)	0.4784 (4)	0.094 (2)
H17A	0.2717	0.2749	0.4919	0.113*
H17B	0.1712	0.3870	0.4715	0.113*
C14	0.5664 (13)	0.5091 (6)	0.4058 (2)	0.0389 (16)
C18	0.400 (3)	0.4306 (11)	0.5081 (4)	0.094 (2)
H18A	0.5280	0.3969	0.5131	0.113*
H18B	0.4183	0.5078	0.4946	0.113*
C19	0.307 (3)	0.4500 (12)	0.5485 (4)	0.094 (2)
H19A	0.2852	0.3732	0.5620	0.113*
H19B	0.3936	0.4962	0.5664	0.113*
C20	0.130 (2)	0.5107 (12)	0.5447 (4)	0.094 (2)
H20A	0.0428	0.4550	0.5306	0.113*
H20B	0.0811	0.5194	0.5732	0.113*
C21	0.102 (3)	0.6087 (14)	0.5274 (6)	0.116 (3)
H21A	0.1329	0.5957	0.4979	0.139*
H21B	0.2038	0.6605	0.5383	0.139*
C22	-0.091 (3)	0.6901 (14)	0.5273 (5)	0.116 (3)
H22A	-0.0559	0.7726	0.5233	0.173*
H22B	-0.1576	0.6812	0.5538	0.173*
H22C	-0.1748	0.6649	0.5047	0.173*
C23	0.771 (3)	0.4818 (15)	0.4187 (6)	0.116 (3)
H23A	0.8468	0.4636	0.3942	0.173*
H23B	0.7712	0.4142	0.4375	0.173*

H23C	0.8251	0.5501	0.4329	0.173*
C24	0.297 (3)	0.2407 (15)	0.4134 (5)	0.116 (3)
H24A	0.1806	0.2764	0.4025	0.173*
H24B	0.2640	0.1734	0.4309	0.173*
H24C	0.3772	0.2142	0.3904	0.173*
C25	0.173 (4)	0.944 (4)	0.3908 (14)	0.34 (3)
H25A	0.0883	0.9704	0.4131	0.503*
H25B	0.1786	1.0047	0.3692	0.503*
H25C	0.3012	0.9314	0.4020	0.503*
O7	0.1023 (9)	0.8365 (8)	0.3735 (2)	0.066 (2)
H7	0.148 (19)	0.826 (13)	0.347 (2)	0.099*

Table S3. Atomic displacement parameters (Å^2) for **1**.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0232 (3)	0.0367 (3)	0.0396 (3)	0.0050 (3)	0.0103 (3)	0.0075 (3)
C1	0.016 (3)	0.009 (3)	0.036 (4)	-0.003 (2)	-0.001 (2)	0.007 (2)
O1	0.0088 (19)	0.019 (2)	0.048 (3)	0.0035 (15)	0.0011 (17)	0.002 (2)
C2	0.012 (2)	0.021 (3)	0.043 (4)	0.004 (2)	-0.001 (3)	0.010 (3)
C3	0.031 (3)	0.026 (3)	0.033 (3)	0.007 (3)	0.004 (3)	0.005 (3)
C4	0.029 (3)	0.019 (3)	0.035 (4)	0.009 (2)	0.001 (3)	-0.004 (3)
O2	0.065 (4)	0.023 (2)	0.047 (3)	0.027 (3)	-0.012 (3)	-0.011 (2)
C5	0.025 (3)	0.032 (4)	0.046 (4)	0.012 (3)	0.011 (3)	0.008 (3)
O3	0.025 (3)	0.022 (2)	0.049 (3)	0.0080 (19)	-0.003 (2)	0.007 (2)
O5	0.025 (2)	0.015 (2)	0.044 (3)	-0.0085 (18)	-0.008 (2)	0.004 (2)
C6	0.014 (3)	0.026 (3)	0.052 (4)	0.001 (2)	0.001 (3)	0.013 (3)
C7	0.019 (3)	0.018 (3)	0.038 (3)	-0.005 (2)	-0.001 (3)	0.010 (2)
O4	0.035 (3)	0.024 (2)	0.048 (3)	-0.009 (2)	-0.011 (2)	0.004 (2)
C8	0.014 (2)	0.016 (3)	0.034 (3)	-0.003 (2)	0.000 (2)	0.005 (3)
C9	0.018 (3)	0.016 (3)	0.041 (4)	-0.003 (2)	-0.006 (3)	0.009 (3)
N10	0.018 (2)	0.023 (3)	0.038 (3)	0.004 (2)	-0.004 (2)	0.011 (2)
C11	0.016 (3)	0.024 (3)	0.038 (4)	-0.002 (2)	0.001 (2)	0.003 (3)

O6	0.016 (2)	0.040 (3)	0.051 (3)	-0.002 (2)	-0.002 (2)	0.019 (2)
C12	0.025 (3)	0.026 (3)	0.032 (4)	0.006 (3)	0.001 (3)	0.006 (3)
C13	0.033 (3)	0.030 (4)	0.037 (4)	0.004 (3)	0.001 (3)	0.009 (3)
C15	0.051 (5)	0.034 (4)	0.054 (5)	-0.009 (4)	0.010 (4)	0.016 (3)
C16	0.134 (6)	0.069 (4)	0.078 (4)	-0.011 (4)	0.014 (4)	0.023 (3)
C17	0.134 (6)	0.069 (4)	0.078 (4)	-0.011 (4)	0.014 (4)	0.023 (3)
C14	0.046 (4)	0.027 (3)	0.044 (4)	-0.001 (4)	0.007 (4)	0.012 (3)
C18	0.134 (6)	0.069 (4)	0.078 (4)	-0.011 (4)	0.014 (4)	0.023 (3)
C19	0.134 (6)	0.069 (4)	0.078 (4)	-0.011 (4)	0.014 (4)	0.023 (3)
C20	0.134 (6)	0.069 (4)	0.078 (4)	-0.011 (4)	0.014 (4)	0.023 (3)
C21	0.139 (8)	0.090 (6)	0.118 (6)	0.003 (5)	0.024 (6)	0.016 (5)
C22	0.139 (8)	0.090 (6)	0.118 (6)	0.003 (5)	0.024 (6)	0.016 (5)
C23	0.139 (8)	0.090 (6)	0.118 (6)	0.003 (5)	0.024 (6)	0.016 (5)
C24	0.139 (8)	0.090 (6)	0.118 (6)	0.003 (5)	0.024 (6)	0.016 (5)
C25	0.13 (2)	0.41 (6)	0.47 (7)	-0.01 (3)	-0.03 (3)	-0.28 (6)
O7	0.036 (3)	0.096 (6)	0.066 (4)	0.012 (3)	0.000 (3)	-0.013 (4)

Table S4. Geometric parameters (Å, º) for **1**.

Br—C8	1.951 (6)	C15—C14	1.326 (12)
C1—O1	1.415 (7)	C15—C16	1.525 (14)
C1—C2	1.509 (10)	C15—H15	0.9500
C1—C8	1.559 (8)	C16—C17	1.500 (19)
C1—H1A	1.0000	C16—C24	1.54 (2)
O1—H1	0.84 (5)	C16—H16	1.0000
C2—N10	1.450 (8)	C17—C18	1.51 (2)
C2—C3	1.516 (10)	C17—H17A	0.9900
C2—H2A	1.0000	C17—H17B	0.9900
C3—C4	1.536 (9)	C14—C23	1.53 (2)
C3—H3A	0.9900	C18—C19	1.476 (19)
C3—H3B	0.9900	C18—H18A	0.9900
C4—O2	1.410 (8)	C18—H18B	0.9900

C4—C5	1.499 (10)	C19—C20	1.43 (2)
C4—C9	1.553 (10)	C19—H19A	0.9900
O2—H2	0.8400	C19—H19B	0.9900
C5—O3	1.438 (8)	C20—C21	1.262 (18)
C5—C6	1.491 (11)	C20—H20A	0.9900
C5—H5A	1.0000	C20—H20B	0.9900
O3—C6	1.449 (8)	C21—C22	1.64 (2)
O5—C9	1.410 (8)	C21—H21A	0.9900
O5—H5	0.8400	C21—H21B	0.9900
C6—C7	1.500 (9)	C22—H22A	0.9800
C6—H6A	1.0000	C22—H22B	0.9800
C7—O4	1.190 (8)	C22—H22C	0.9800
C7—C8	1.539 (8)	C23—H23A	0.9800
C8—C9	1.534 (9)	C23—H23B	0.9800
C9—H9	1.0000	C23—H23C	0.9800
N10—C11	1.338 (8)	C24—H24A	0.9800
N10—H10	0.93 (6)	C24—H24B	0.9800
C11—O6	1.261 (8)	C24—H24C	0.9800
C11—C12	1.482 (9)	C25—O7	1.44 (3)
C12—C13	1.333 (10)	C25—H25A	0.9800
C12—H12	0.9500	C25—H25B	0.9800
C13—C14	1.459 (9)	C25—H25C	0.9800
C13—H13	0.9500	O7—H7	0.91 (6)
O1—C1—C2	109.2 (5)	C14—C15—C16	126.5 (10)
O1—C1—C8	109.5 (5)	C14—C15—H15	116.7
C2—C1—C8	109.2 (5)	C16—C15—H15	116.7
O1—C1—H1A	109.6	C17—C16—C15	109.3 (11)
C2—C1—H1A	109.6	C17—C16—C24	107.2 (14)
C8—C1—H1A	109.6	C15—C16—C24	107.6 (11)
C1—O1—H1	102 (6)	C17—C16—H16	110.9
N10—C2—C1	110.9 (5)	C15—C16—H16	110.9

N10—C2—C3	111.9 (6)	C24—C16—H16	110.9
C1—C2—C3	111.6 (5)	C16—C17—C18	111.7 (13)
N10—C2—H2A	107.4	C16—C17—H17A	109.3
C1—C2—H2A	107.4	C18—C17—H17A	109.3
C3—C2—H2A	107.4	C16—C17—H17B	109.3
C2—C3—C4	112.1 (5)	C18—C17—H17B	109.3
C2—C3—H3A	109.2	H17A—C17—H17B	107.9
C4—C3—H3A	109.2	C15—C14—C13	116.6 (8)
C2—C3—H3B	109.2	C15—C14—C23	126.5 (9)
C4—C3—H3B	109.2	C13—C14—C23	116.8 (9)
H3A—C3—H3B	107.9	C19—C18—C17	115.9 (14)
O2—C4—C5	111.8 (5)	C19—C18—H18A	108.3
O2—C4—C3	106.2 (6)	C17—C18—H18A	108.3
C5—C4—C3	108.1 (6)	C19—C18—H18B	108.3
O2—C4—C9	110.2 (6)	C17—C18—H18B	108.3
C5—C4—C9	111.0 (6)	H18A—C18—H18B	107.4
C3—C4—C9	109.4 (5)	C20—C19—C18	112.4 (13)
C4—O2—H2	109.5	C20—C19—H19A	109.1
O3—C5—C6	59.3 (4)	C18—C19—H19A	109.1
O3—C5—C4	117.2 (6)	C20—C19—H19B	109.1
C6—C5—C4	120.7 (6)	C18—C19—H19B	109.1
O3—C5—H5A	115.9	H19A—C19—H19B	107.9
C6—C5—H5A	115.9	C21—C20—C19	126.8 (16)
C4—C5—H5A	115.9	C21—C20—H20A	105.6
C5—O3—C6	62.2 (5)	C19—C20—H20A	105.6
C9—O5—H5	109.5	C21—C20—H20B	105.6
O3—C6—C5	58.6 (4)	C19—C20—H20B	105.6
O3—C6—C7	117.0 (5)	H20A—C20—H20B	106.1
C5—C6—C7	118.6 (6)	C20—C21—C22	128.8 (16)
O3—C6—H6A	116.7	C20—C21—H21A	105.1
C5—C6—H6A	116.7	C22—C21—H21A	105.1
C7—C6—H6A	116.7	C20—C21—H21B	105.1

O4—C7—C6	119.9 (6)	C22—C21—H21B	105.1
O4—C7—C8	121.9 (6)	H21A—C21—H21B	105.9
C6—C7—C8	117.5 (6)	C21—C22—H22A	109.5
C9—C8—C7	114.7 (5)	C21—C22—H22B	109.5
C9—C8—C1	110.0 (5)	H22A—C22—H22B	109.5
C7—C8—C1	104.8 (5)	C21—C22—H22C	109.5
C9—C8—Br	109.8 (4)	H22A—C22—H22C	109.5
C7—C8—Br	108.6 (4)	H22B—C22—H22C	109.5
C1—C8—Br	108.7 (4)	C14—C23—H23A	109.5
O5—C9—C8	114.7 (6)	C14—C23—H23B	109.5
O5—C9—C4	111.9 (5)	H23A—C23—H23B	109.5
C8—C9—C4	107.9 (5)	C14—C23—H23C	109.5
O5—C9—H9	107.4	H23A—C23—H23C	109.5
C8—C9—H9	107.4	H23B—C23—H23C	109.5
C4—C9—H9	107.4	C16—C24—H24A	109.5
C11—N10—C2	121.2 (5)	C16—C24—H24B	109.5
C11—N10—H10	130 (5)	H24A—C24—H24B	109.5
C2—N10—H10	109 (5)	C16—C24—H24C	109.5
O6—C11—N10	122.1 (6)	H24A—C24—H24C	109.5
O6—C11—C12	121.3 (6)	H24B—C24—H24C	109.5
N10—C11—C12	116.7 (5)	O7—C25—H25A	109.5
C13—C12—C11	119.8 (6)	O7—C25—H25B	109.5
C13—C12—H12	120.1	H25A—C25—H25B	109.5
C11—C12—H12	120.1	O7—C25—H25C	109.5
C12—C13—C14	128.4 (7)	H25A—C25—H25C	109.5
C12—C13—H13	115.8	H25B—C25—H25C	109.5
C14—C13—H13	115.8	C25—O7—H7	110 (10)
O1—C1—C2—N10	-61.9 (7)	O1—C1—C8—Br	61.3 (6)
C8—C1—C2—N10	178.3 (5)	C2—C1—C8—Br	-179.2 (4)
O1—C1—C2—C3	63.6 (6)	C7—C8—C9—O5	-69.6 (7)
C8—C1—C2—C3	-56.2 (7)	C1—C8—C9—O5	172.6 (5)

N10—C2—C3—C4	-179.4 (5)	Br—C8—C9—O5	53.0 (6)
C1—C2—C3—C4	55.7 (7)	C7—C8—C9—C4	55.8 (7)
C2—C3—C4—O2	-175.8 (6)	C1—C8—C9—C4	-62.0 (6)
C2—C3—C4—C5	64.1 (7)	Br—C8—C9—C4	178.4 (4)
C2—C3—C4—C9	-56.8 (7)	O2—C4—C9—O5	-57.0 (7)
O2—C4—C5—O3	87.9 (7)	C5—C4—C9—O5	67.4 (7)
C3—C4—C5—O3	-155.6 (6)	C3—C4—C9—O5	-173.5 (5)
C9—C4—C5—O3	-35.6 (8)	O2—C4—C9—C8	176.0 (5)
O2—C4—C5—C6	156.6 (6)	C5—C4—C9—C8	-59.6 (7)
C3—C4—C5—C6	-86.9 (8)	C3—C4—C9—C8	59.5 (7)
C9—C4—C5—C6	33.1 (8)	C1—C2—N10—C11	-124.2 (7)
C4—C5—O3—C6	111.3 (7)	C3—C2—N10—C11	110.5 (7)
C5—O3—C6—C7	-108.6 (7)	C2—N10—C11—O6	0.4 (11)
C4—C5—C6—O3	-105.4 (7)	C2—N10—C11—C12	179.9 (6)
O3—C5—C6—C7	105.8 (6)	O6—C11—C12—C13	-2.4 (11)
C4—C5—C6—C7	0.4 (9)	N10—C11—C12—C13	178.1 (7)
O3—C6—C7—O4	-128.0 (6)	C11—C12—C13—C14	178.6 (7)
C5—C6—C7—O4	164.9 (6)	C14—C15—C16—C17	115.7 (14)
O3—C6—C7—C8	61.2 (8)	C14—C15—C16—C24	-128.2 (13)
C5—C6—C7—C8	-5.9 (8)	C15—C16—C17—C18	-69.2 (16)
O4—C7—C8—C9	166.0 (6)	C24—C16—C17—C18	174.4 (12)
C6—C7—C8—C9	-23.4 (7)	C16—C15—C14—C13	178.5 (9)
O4—C7—C8—C1	-73.3 (7)	C16—C15—C14—C23	-0.6 (17)
C6—C7—C8—C1	97.3 (6)	C12—C13—C14—C15	177.1 (8)
O4—C7—C8—Br	42.7 (7)	C12—C13—C14—C23	-3.7 (14)
C6—C7—C8—Br	-146.7 (4)	C16—C17—C18—C19	-176.8 (13)
O1—C1—C8—C9	-59.0 (6)	C17—C18—C19—C20	-64.6 (17)
C2—C1—C8—C9	60.5 (6)	C18—C19—C20—C21	-56 (2)
O1—C1—C8—C7	177.2 (5)	C19—C20—C21—C22	-171.3 (17)
C2—C1—C8—C7	-63.2 (6)		

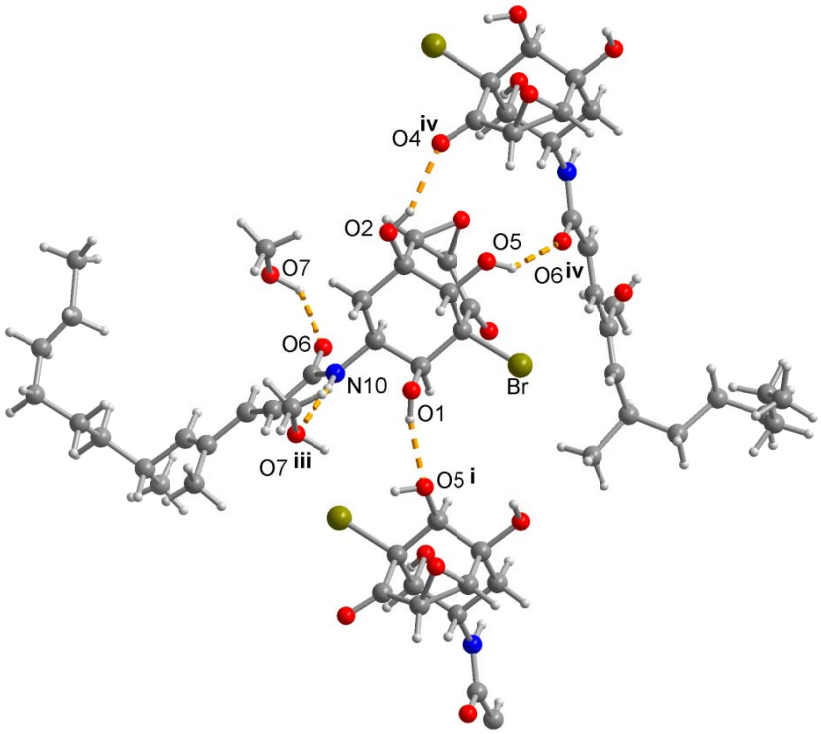


Figure S54. Hydrogen-bonding network in **1** indicated as dashed orange lines. See Table X for details. Symmetry codes: (i) -*x*+2, *y*-1/2, -*z*+1/2; (iii) *x*+1, *y*, *z*; (iv) -*x*+1, *y*+1/2, -*z*+1/2.

Table S5. Hydrogen-bond geometry (Å, º) for **1**.[a]

D—H···A	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)
O1—H1···O5^{i}	0.84(5)	1.91(6)	2.717(6)	160(8)
C1—H1*A*···O3^{ii}	1.00	2.42	3.225(7)	137
N10—H10···O7^{iii}	0.93(6)	2.00(6)	2.889(9)	158(7)
O2—H2···O4^{iv}	0.84	2.09	2.859(7)	152
O5—H5···O6^{iv}	0.84	2.05	2.779(7)	144
C6—H6*A*···Br^{v}	1.00	3.00	3.767(7)	134
C6—H6*A*···O1^{v}	1.00	2.36	3.276(7)	151
O7—H7···O6	0.91(6)	2.14(12)	2.784(8)	128(12)

[a] Standard deviations for refined atom contacts are given in parentheses. Symmetry codes: (i) -*x*+2, *y*-1/2, -*z*+1/2; (ii) -*x*+1, *y*-1/2, -*z*+1/2; (iii) *x*+1, *y*, *z*; (iv) -*x*+1, *y*+1/2, -*z*+1/2; (v) *x*-1, *y*, *z*.

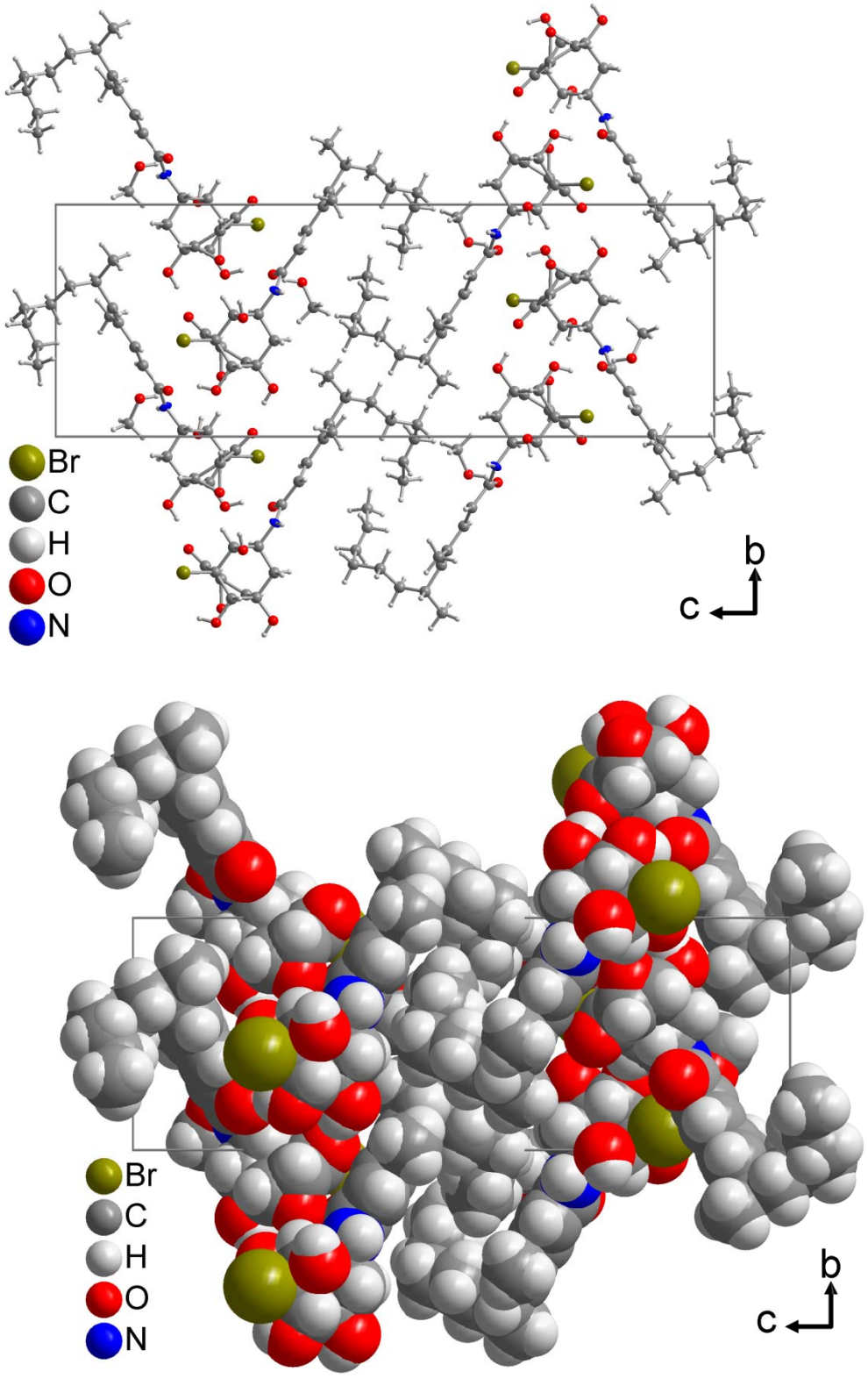


Figure S55. Unit cell packing diagram of **1** projected onto the *bc* plane – in ball-and-stick and in space-filling mode – showing the separation of the hydrophilic hydrogen-bonding part of the molecule (in layers parallel to the *ab* plane) and the interdigitated (interlocking) hydrophobic branched alkyl chain (sandwiched between the hydrophilic layers).

Notes and references

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