Supporting Information

Nudicaulins, Yellow Flower Pigments of *Papaver nudicaule* – Revised Constitution and Assignment of Absolute Configuration

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S1. General Experimental Procedures.

Preparative HPLC was performed on a Merck-Hitachi LiChrograph chromatography system (L-6200A gradient pump, L-4250 UV/Vis detector) and on a SHIMADZU HPLC (DGU-20A degasser, LC-20AT liquid chromatography pump, SIL-10AP autosampler, CTO-20A column oven, SPD-20A UV detector, FRC-10A fraction collector) using a Purospher STAR RP18ec column (5 µm, 250 × 10 mm). For the isolation of natural nudicaulins (method 1) a linear gradient MeOH–H_2O (0.1% trifluoroacetic acid (TFA)) from 20% to 50% MeOH in 30 min (flow rate 3.5 ml min^{-1}; UV detection 254 nm) was applied. For the identification of dihydronudicaulins and glycosylated nudicaulins (method 2) a linear gradient MeOH–H_2O (0.1% TFA) from 20% to 60% MeOH in 40 min (flow rate 3.5 ml min^{-1}; UV detection 254 nm) was applied. For the isolation of permethylated nudicaulins (method 3) a linear gradient MeOH–H_2O (0.1% TFA) from 50% to 100% MeOH in 30 min (flow rate 3.5 ml min^{-1}; UV detection 254 nm) was applied. Analytical HPLC was performed on an Agilent series HP1100 (binary pump G1312A; auto sampler G1313A; diode array detector G1315B, 200–700 nm) using a Purospher STAR RP18ec column (5 µm, 250 × 4 mm; injection volume 20 µl). For the analytical HPLC (method 4) a linear gradient MeOH–H_2O (0.1% TFA) from 5% to 100% MeOH in 30 min (flow rate 1.0 ml min^{-1}; UV detection 254, 350 and 460 nm) and (method 5) and a linear gradient MeCN–H_2O (0.1% TFA) from 5% to 100% MeCN in 30 min (flow rate 1.0 ml min^{-1}; UV detection 254, 350 and 460 nm) were applied.

NMR spectra (^{1}H NMR, ^{13}C NMR, ^{1}H-^{1}H COSY, ROESY, HSQC, HMBC) were acquired using a Bruker Avance NMR spectrometer, operating at 500.13 MHz for ^{1}H and 125.75 MHz for ^{13}C, equipped with a TCI cryoprobe (5 mm). The residual ^{1}H- and ^{13}C-NMR signals of MeOH-d_4 (δ 3.30 for ^{1}H and δ 48.97 for ^{13}C) and DMSO (δ 2.52 for ^{1}H and δ 40.45 for ^{13}C) were used as an internal standard.

^{1}H,^{13}C-HSQC experiments were acquired with a spectral width 6009Hz in the F_2 (^{1}H) dimension and 22638 in the F_1 (^{13}C) and with an acquisition time 0.09 s. The relaxation delay was 2 s, the data collection matrix was 1024×256, the t_1 dimension was zero-filled to 1k real data points and a π/2

square sine bell window was applied in both dimensions. $^{1}H,^{13}C$-HMBC experiments were acquired with a spectral width 6009 Hz in the F_2 (^{1}H) dimension and 31443 in the F_1 (^{13}C) and with an acquisition time 0.37 s. The long-range delay was optimized for a coupling of 10 Hz. The relaxation delay was 2 s, the data collection matrix was 4048×256, the t_1 dimension was zero-filled to 1k real data points and a π/2 square sine bell window was applied in both dimensions. The data collection matrix in $^{1}H,^{13}C$-HMBC spectrum of nudicaulin I (**3a**) in DMSO-*d*6 was 4048×512. The number of scans was depended on the concentration of the sample$^{1}H,^{15}N$-HMBC experiment was acquired with a spectral width 6009 Hz in the F_2 (^{1}H) dimension and 30410 in the F_1 (^{15}N) and with an acquisition time 0.09 s and 360 scans per increment. The long-range delay was optimized for a coupling of 5 Hz. The relaxation delay was 2.5 s, the data collection matrix was 1024×64, the t_1 dimension was zero-filled to 1k real data points and a π/2 square sine bell window was applied in both dimensions. ROESY spectra were acquired using a spectral width of 6009 Hz, acquisition time of 0.17 s, relaxation delay of 2 s, mixing time of 1000 ms, and 24 transients (4 dummy scans) for each of the 256 increments. The mixing time was optimized using the t1ir1d pulse program.

The LC-MS system consisted of an Ultimate 3000 series RSLC (Dionex, Germaring, Germany) liquid chromatography and an Orbitrap mass spectrometer (Thermo Fisher Scientific, Bremen, Germany). HPLC was performed using Acclaim C18 Column (150 x 2.1 mm, 2.2 μm, Dionex) at a constant flow rate of 300 μL min^{-1} using a binary solvent system: Solvent A, H_2O with 0.1% HCOOH and solvent B, MeCN with 0.1% HCOOH. The HPLC gradient system started with 2% B and linearly increased to 30% B in 10 min, then increased to 90% B in 14 min, held for 4 min and brought back to the 2% B initial condition before being held for 5 min for the column re-equilibration for the next injection. Full scan mass spectra were generated using 30.000 resolving power The mass accuracy was better than 3 ppm for MS experiments. Aliquots from pigment fractions with concentrations of 40 μg ml^{-1} were used for LC/MS analysis of secondary metabolites.

S2. Plant Material.

Seeds of *Papaver nudicaule* L were obtained from the Leibniz Institute of Plant Genetics and Crop Plant Research (Gatersleben, Germany), germinated and grown in soil in the greenhouse facilities of the Max Planck Institute for Chemical Ecology where voucher specimens are lodged. The temperature was 20–24°C during the day and 18–21°C during the night. Relative air humidity was between 60% and 70%. The natural daily photoperiod was supported with 16 h illumination from Phillips Sun-T Agro 400 Na lights.

S3. Extraction and isolation.

Fresh petals of *P. nudicaule*, were harvested, lyophilized, ground and extracted with 90% MeOH (3 × 25 ml) in an ultrasonic bath. The combined extracts were partitioned against n-hexane (3 × 30 ml) and the aqueous phase was used as follows. The aqueous phase remaining after defatting the petal extracts of *P. nudicaule* was loaded on SPE cartridges (LiChrolut C_{18}; 1 g) and eluted with water, 30% MeOH, and MeOH. The 30% MeOH fraction was dried and then reconstituted in phosphate buffer (10 mM, pH 5.60). Nudicaulins were further purified using a strong cationic exchange (SCX) SPE cartridge (1 g). Nudicalins were eluted with a 1:1 (v:v) mixture of a conc. aqueous solution of NH_3 in MeOH (6 ml). Six of eight nudicaulins, which have been identified in flowers of *Papaver nudicaule,* exist in the form of acylated glucosides. In order to simplify the structure diversity and increase the enrichment, the acyl units were removed by basic hydrolysis. As a result of hydrolysis, the compound pattern was simplified to nudicaulin diastereomers I and II. For basic hydrolysis, the fraction was evaporated to dryness and reconstituted in 50% MeOH (4 ml). NaOH (1 M, 600 µl) was added, and stirred for 30 min at room temperature. The hydrolysis was stopped by the addition of glacial acetic acid (100 µl). Nudicaulins I (**3a**) and II (**3b**) were isolated by prep. HPLC (method 1) and fully characterized by NMR and MS.

S4. Hydrogenation, Permethylation and Enzymatic Hydrolysis of Nudicaulins I and II

S4a. Hydrogenation of nudicaulins I (**3a**) and II (**3b**): Nudicaulin I or II (5 mg) was dissolved with stirring in methanol (10 ml) and palladium (1 mg) on carbon was added as a catalyst. The reaction vessel was flushed with argon and sealed with a septum. Hydrogen gas was supplied to the reaction mixture from a balloon connected via a syringe through the septum. After stirring for 12 h at room temperature the catalyst was removed from the reaction mixture by filtration. Hydrogenated nudicaulin was purified by preparative HPLC (method 2).

S4b. Permethylation of nudicaulins I (**3a**) and II (**3b**): To a solution of nudicaulin I or II (5 mg) in dry DMSO small portions of powdered NaOH (30 mg) were added with vigorous stirring. After the base was dissolved, MeI (1 ml) was added to the reaction mixture and stirring continued for 2 h. The reaction mixture was extracted with a small volume of chloroform. The extract was washed twice with water and dried. The permethylated nudicaulins were purified by preparative HPLC (method 3).

S4c. Enzymatic hydrolysis of nudicaulins I (**3a**) and II (**3b**): Nudicaulin I or II (5 mg) was dissolved in 10 ml of acetic acid buffer with pH=5.0. 1 ml of pectinase from *Aspergillus aculeatus* (Sigma Aldrich) was added into solution. The mixture was incubated at 55 C. After 2 h the reaction was stopped by the addition of 500 ml of acetic acid. Partially deglucosylated nudicaulin was purified by preparative HPLC (method 2)

S5. Structures of Nudicaulins.

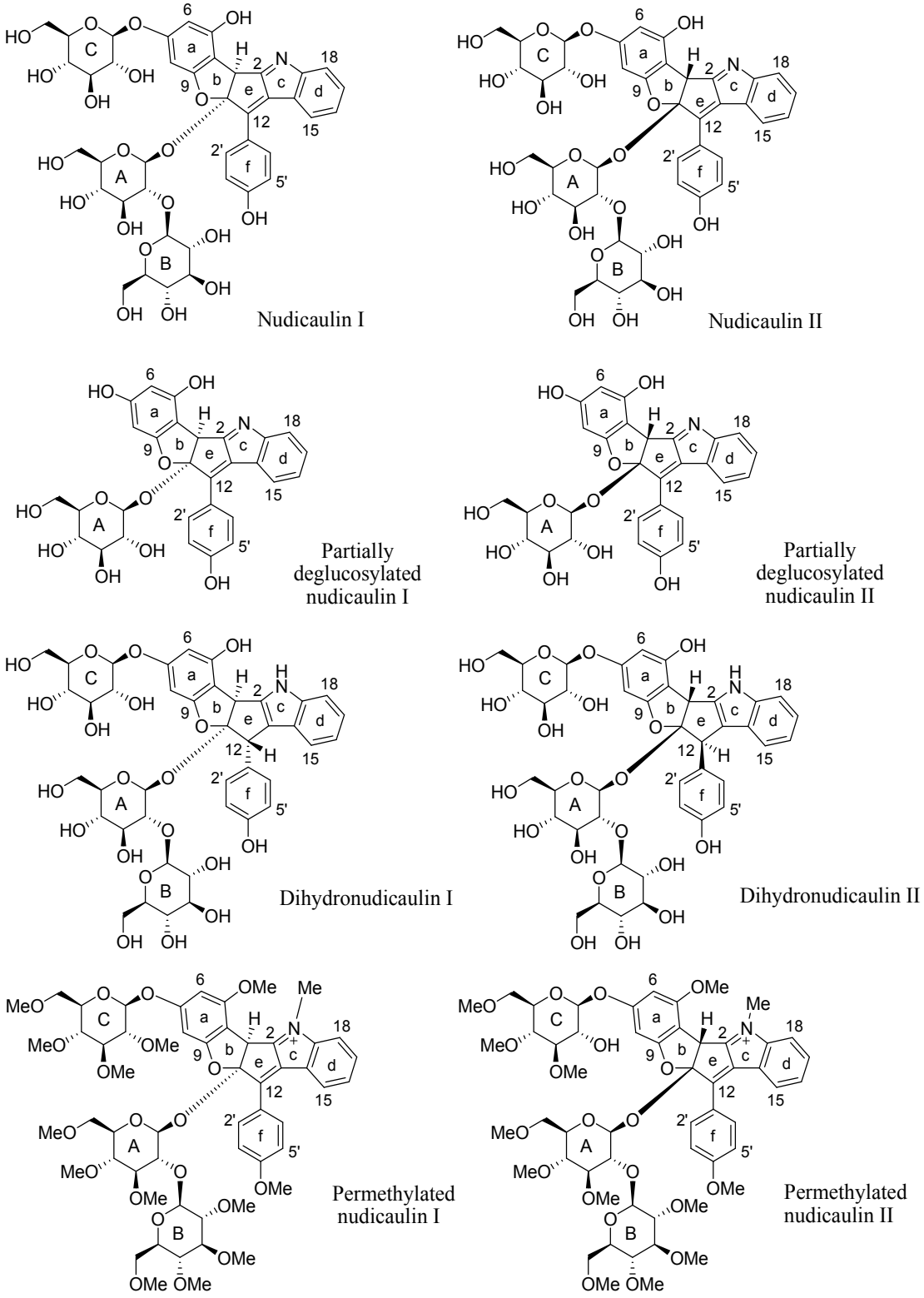

Figure S1. Structures of nudicaulins

S6. NMR Data of Nudicaulins I & II

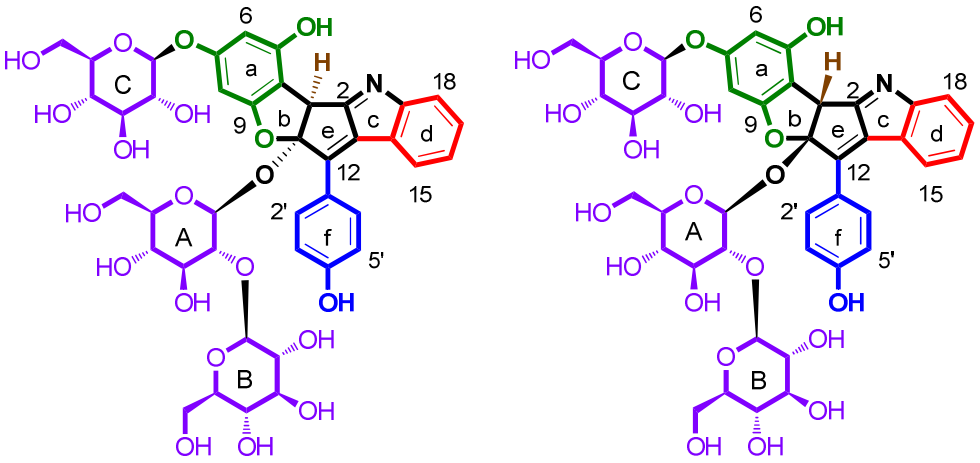

Figure S2. Structures of nudicaulin I (**3a**) and II (**3b**)

Table S1. ^{1}H NMR and ^{13}C NMR spectroscopic data (500 MHz for ^{1}H; 125 MHz for ^{13}C) of nudicaulins I (**3a**) and II (**3b**)

	Nudicaulin I				**Nudicaulin II**	
	MeOH-d_4		DMSO-d_6		MeOH-d_4	
No	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
	δ, mult., *J* (Hz)	δ	δ, mult., *J* (Hz)	δ	δ, mult., *J* (Hz)	δ
Aglycon						
2		177.7		177.1		177.9
3	5.63, *s*	49.8	5.55, s	48.9	5.80, *s*	49.3
4		101.6		101.7		101.7
5		156.3		156.0		156.4
6	6.33, *d*, 2.0	99.2	6.36, d, 2.0	99.0	6.35, *d*, 2.0	99.4
7		162.5		161.6		162.3
8	6.29, *d*, 2.0	92.3	6.15, d, 2.0	91.4	6.27, *d*, 2.0	91.8
9		162.0		160.4		161.3
11		126.7		126.4		125.6
12		168.4		165.0		169.8
13		131.2		130.8		131.5
14		122.7		122.6		122.9
15	8.33, *d*, 7.8	125.3	8.26, d, 7.7	125.5	8.31, *d*, 7.8	125.5
16	7.59, *dd*, 7.8, 7.8	128.5	7.53, dd, 7.7, 7.6	127.8	7.58, *dd*, 7.8, 7.8	128.5
17	7.66, *dd*, 7.8, 7.8	131.4	7.62, dd, 7.6, 7.6	131.2	7.65, *dd*, 7.8, 7.8	131.4
18	7.72, *d*, 7.8	117.0	7.76, d, 7.6	117.9	7.73, *d*, 7.8	117.0
19		148.5		149.5		148.3
1'		122.9		121.6		122.8
2'/6'	8.63, *d*, 9.0	139.2	8.51, d, 8.8	138.2	8.58, *d*, 9.0	139.4
3'/5'	7.16, *d*, 9.0	118.2	7.21, d, 8.8	118.3	7.15, *d*, 9.0	118.2
4'		168.2		166.8		168.1
Glucose A						
1''	4.78, *d*, 7.4	101.2	4.71, d, 7.4	98.4	5.08, *d*, 7.9	97.4
2''	3.56	85.4	3.40	83.6	3.86	78.2
3''	3.55	79.2	3.42	76.8	3.63	78.9
4''	3.39	72.2	3.20	70.0	3.37	70.6
5''	3.33	79.5	3.10	78.4	3.09	78.4
6''A	3.87, *dd*, 12.0, 2.0	62.1	3.61	61.4	3.68, overlap	62.0

6''B	3.67, *dd*, 12.0, 5.9		3.49		3.62, overlap	
Glucose B						
1'''	4.51, *d*, 7.7	107.8	4.40, d, 7.7	105.7	4.96, *d*, 7.5	103.1
2'''	3.24	77.8	3.06	75.4	3.39	77.9
3'''	3.06	79.5	3.15	77.2	3.20	72.1
4'''	3.05	73.4	2.96	71.2	3.34	74.0
5'''	3.39	79.5	3.26	77.7	3.36	78.0
6'''A	3.31, *dd,* 11.8, 1.9	62.4	3.24	62.3	3.71, *dd,* 11.8, 1.9	63.0
6'''B	3.00, *dd,* 11.8, 5.7		2.86		3.24, *dd,* 11.8, 6.0	
Glucose C						
1''''	4.78, *d*, 7.4	103.7	4.72, d, 7.4	101.5	4.81, *d*, 7.3	102.1
2''''	3.38	76.3	3.16	74.0	3.39	75.0
3''''	3.18	80.2	3.20	77.4	3.32	71.1
4''''	3.33	72.9	2.96	77.6	3.38	74.0
5''''	3.31	77.8	3.16	70.5	3.20	78.0
6''''A	3.79, *dd*, 12.1, 2.1	61.9	3.49	61.6	3.85, overlap	62.3
6''''B	3.70, *dd*, 12.1, 5.3		3.67		3.64, overlap	

Some chemical shifts were obtained from 2D NMR spectra (COSY, HSQC, HMBC). ^{1}H NMR signals of H-2 – H-5 of Glc A, Glc B and Glc C partly overlap. Some coupling constants of Glc units were not determined.

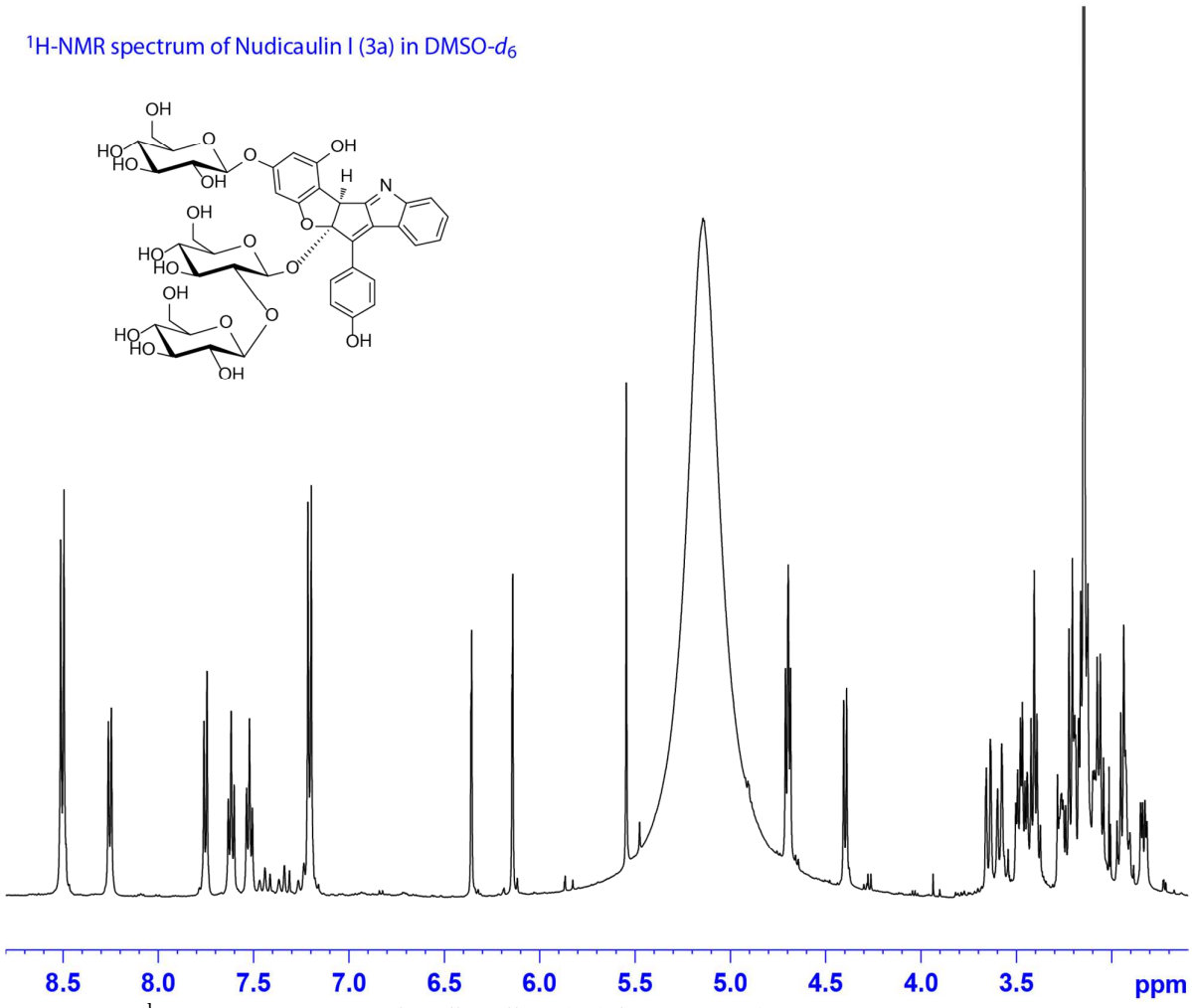

Figure S3. ^{1}H NMR spectrum of nudicaulin I (**3a**) in DMSO-d_6

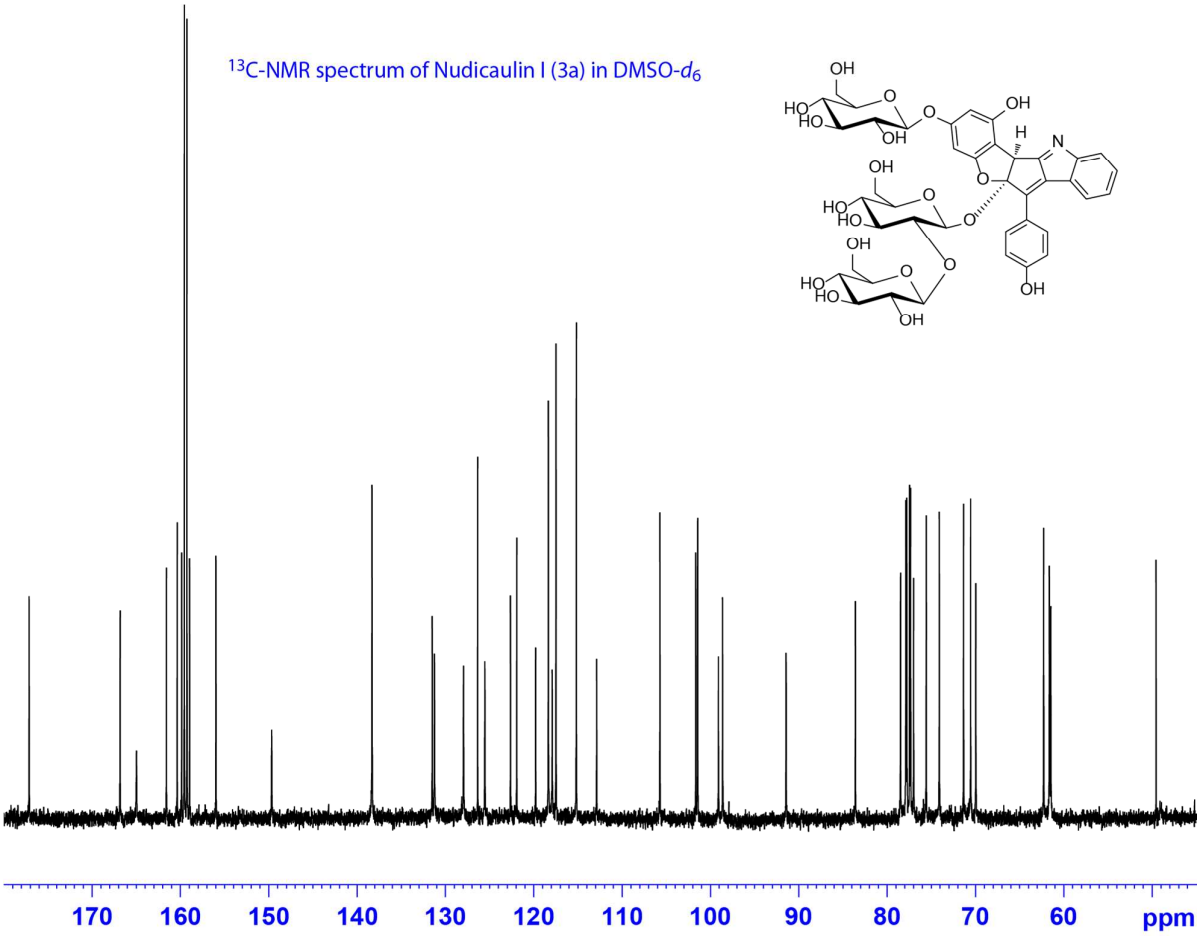

Figure S4. ^{13}C NMR spectrum of nudicaulin I (**3a**) in DMSO-d_6

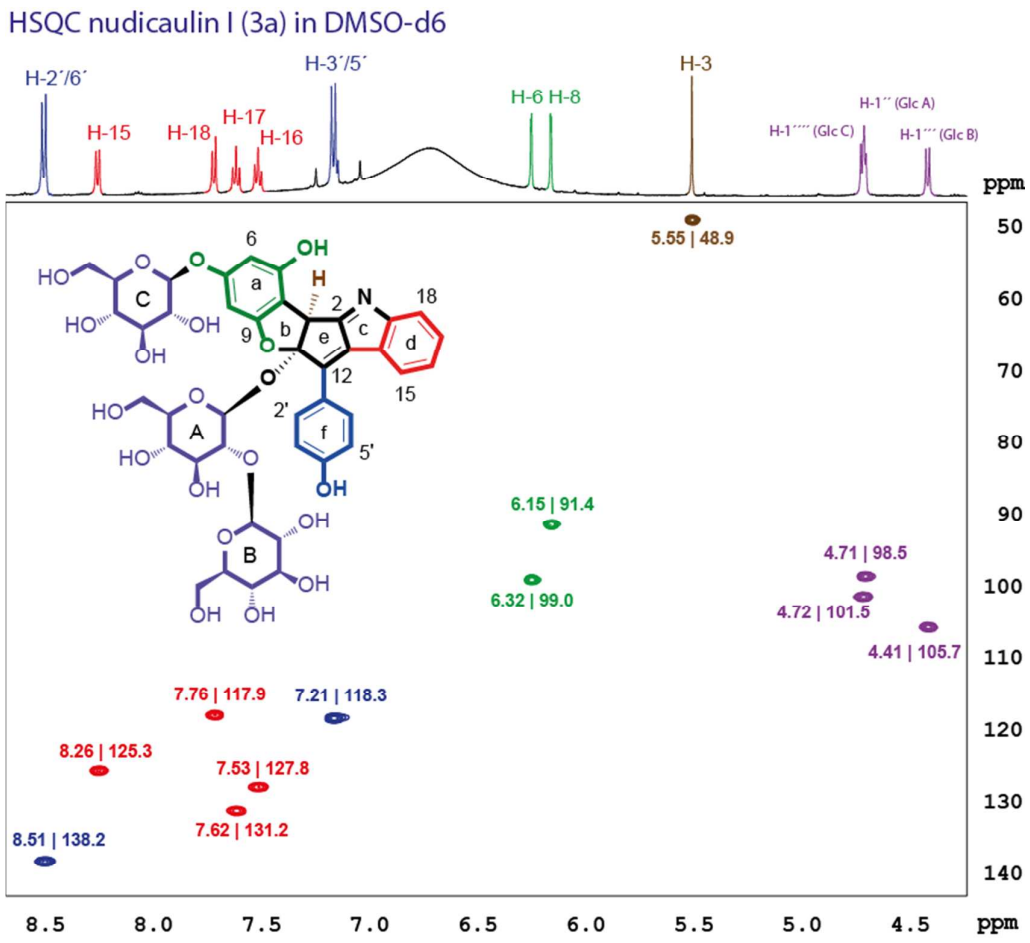

Figure S5. Selected region of the HSQC spectrum of nudicaulin I (**3a**) in DMSO-d_6

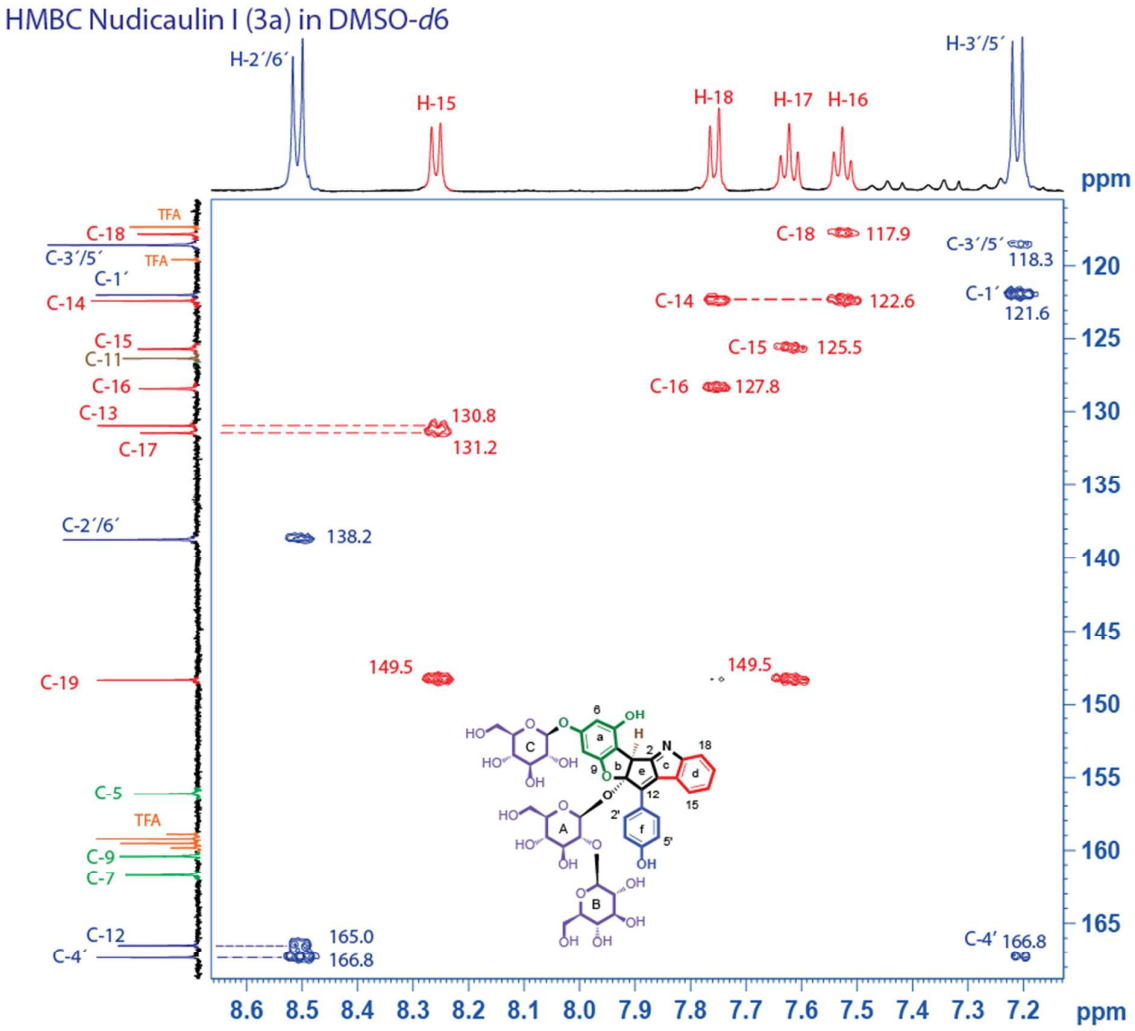

Figure S6. Selected region of the HMBC spectrum of nudicaulin I (**3a**) in DMSO-d_6

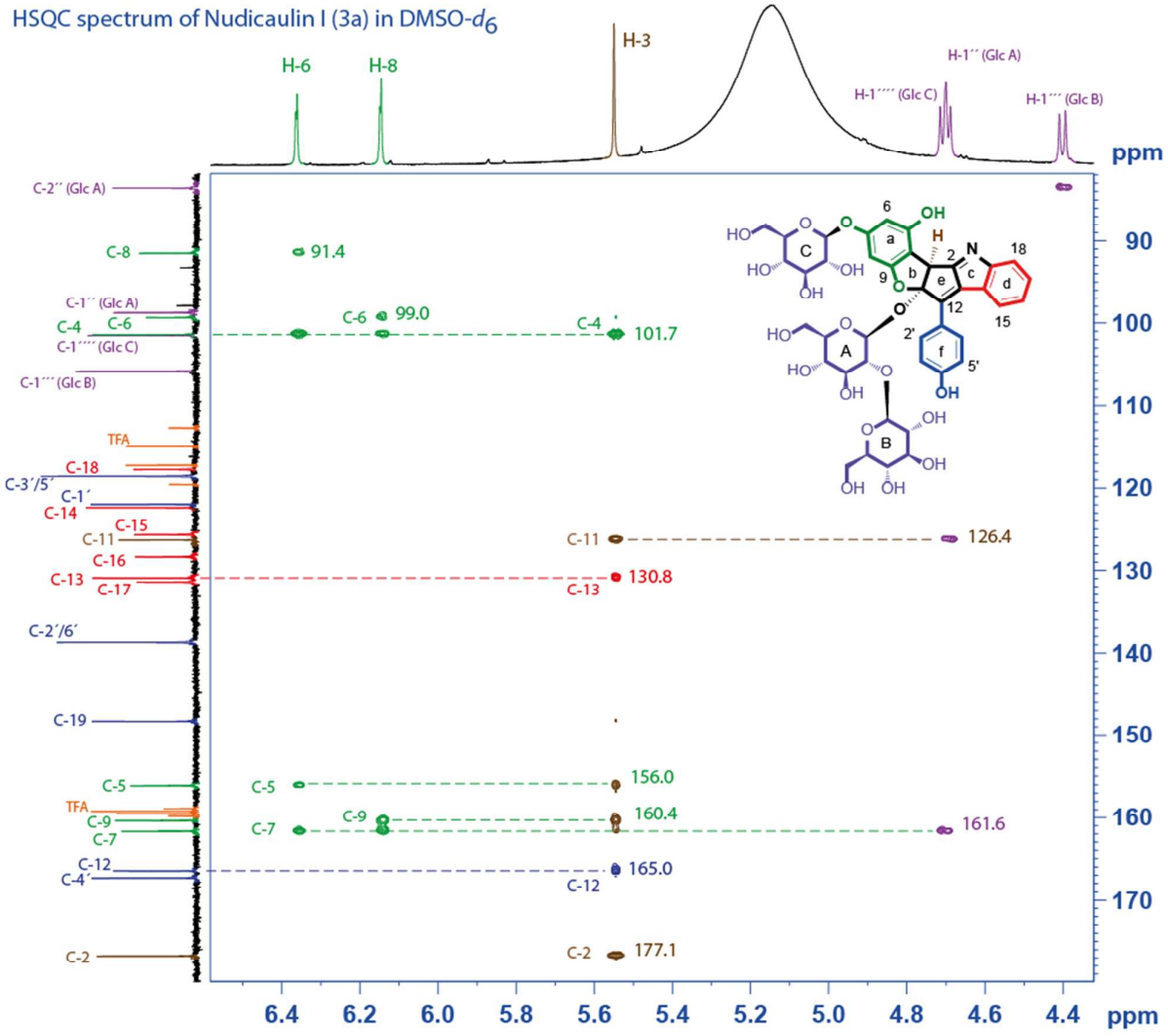

Figure S7. Selected region of the HMBC spectrum of nudicaulin I (**3a**) in DMSO-d_6

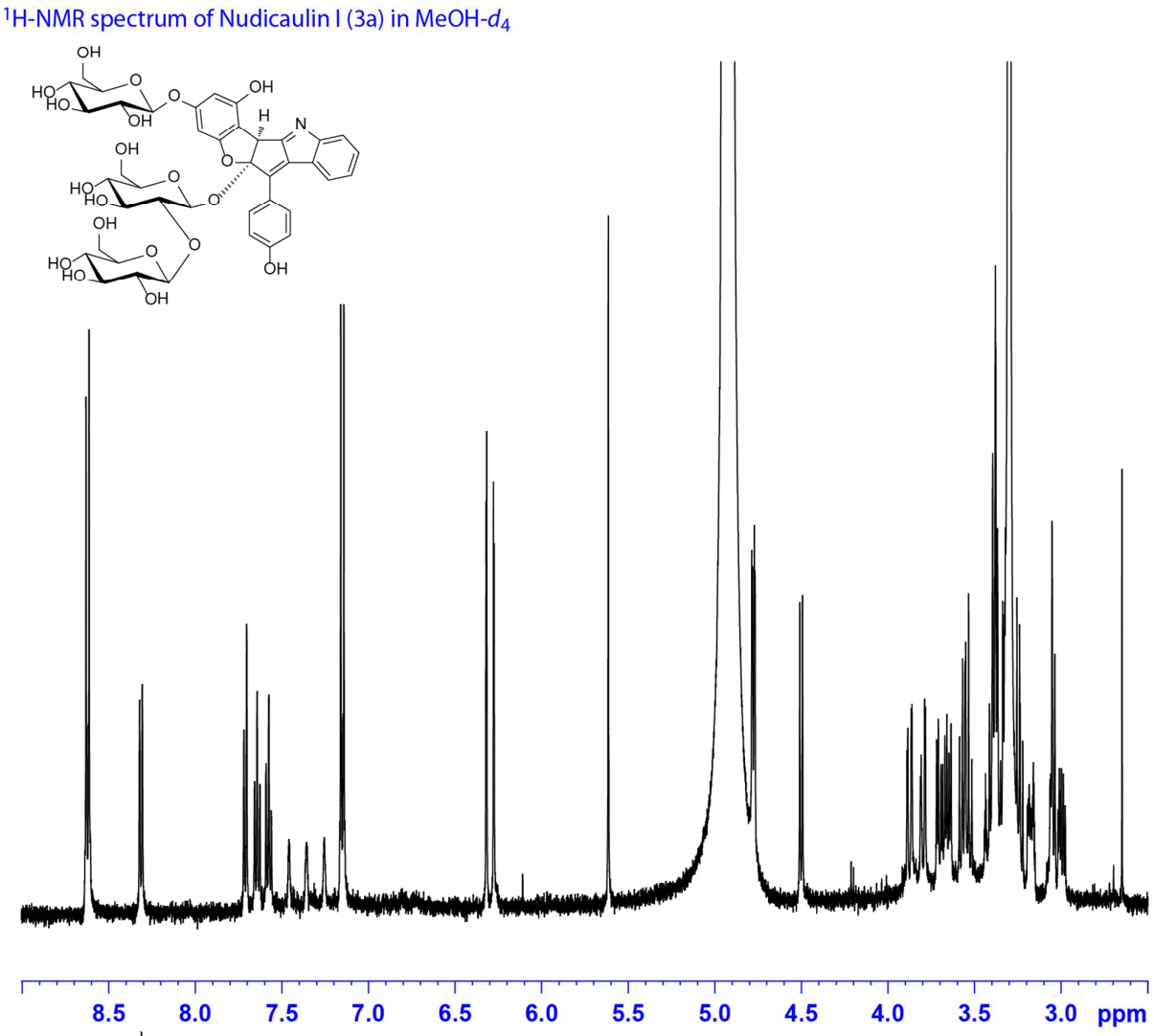

Figure S8. [1]H NMR spectrum of nudicaulin I (**3a**) in MeOH-d_4

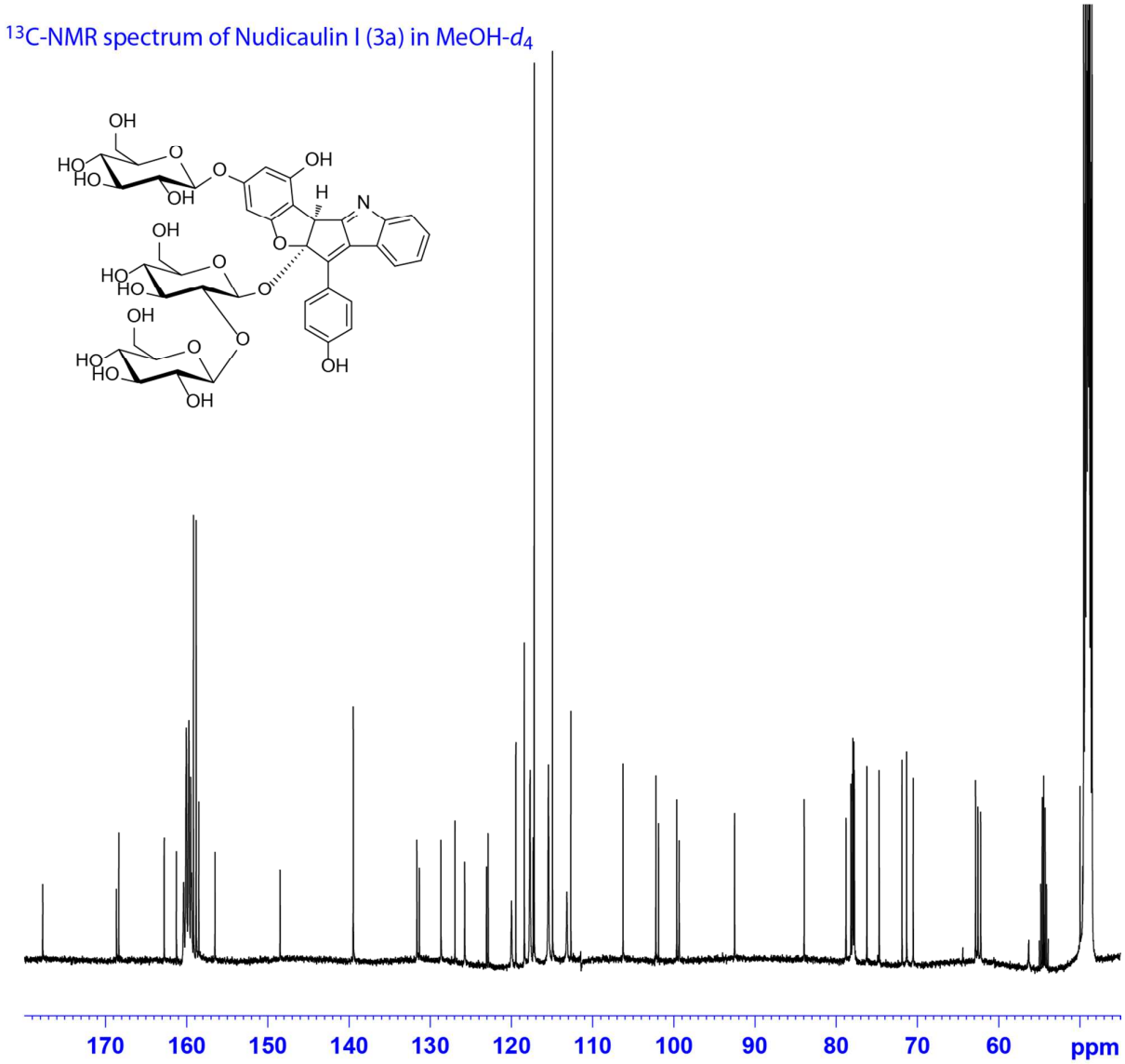

Figure S9. ^{13}C NMR spectrum of nudicaulin I (**3a**) in MeOH-d_4

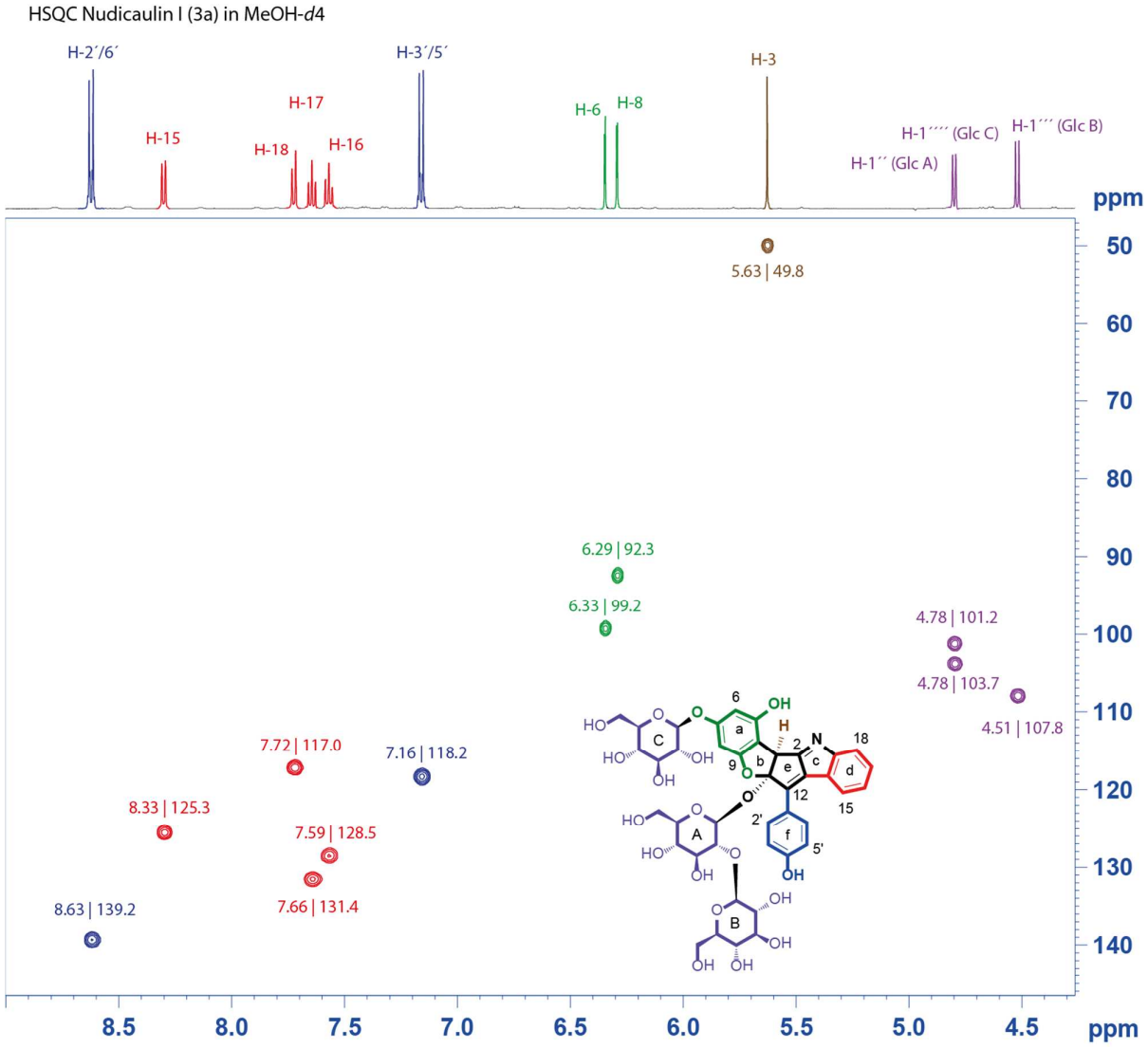

Figure S10. Selected region of the HSQC spectrum of nudicaulin I (**3a**) in MeOH-d_4

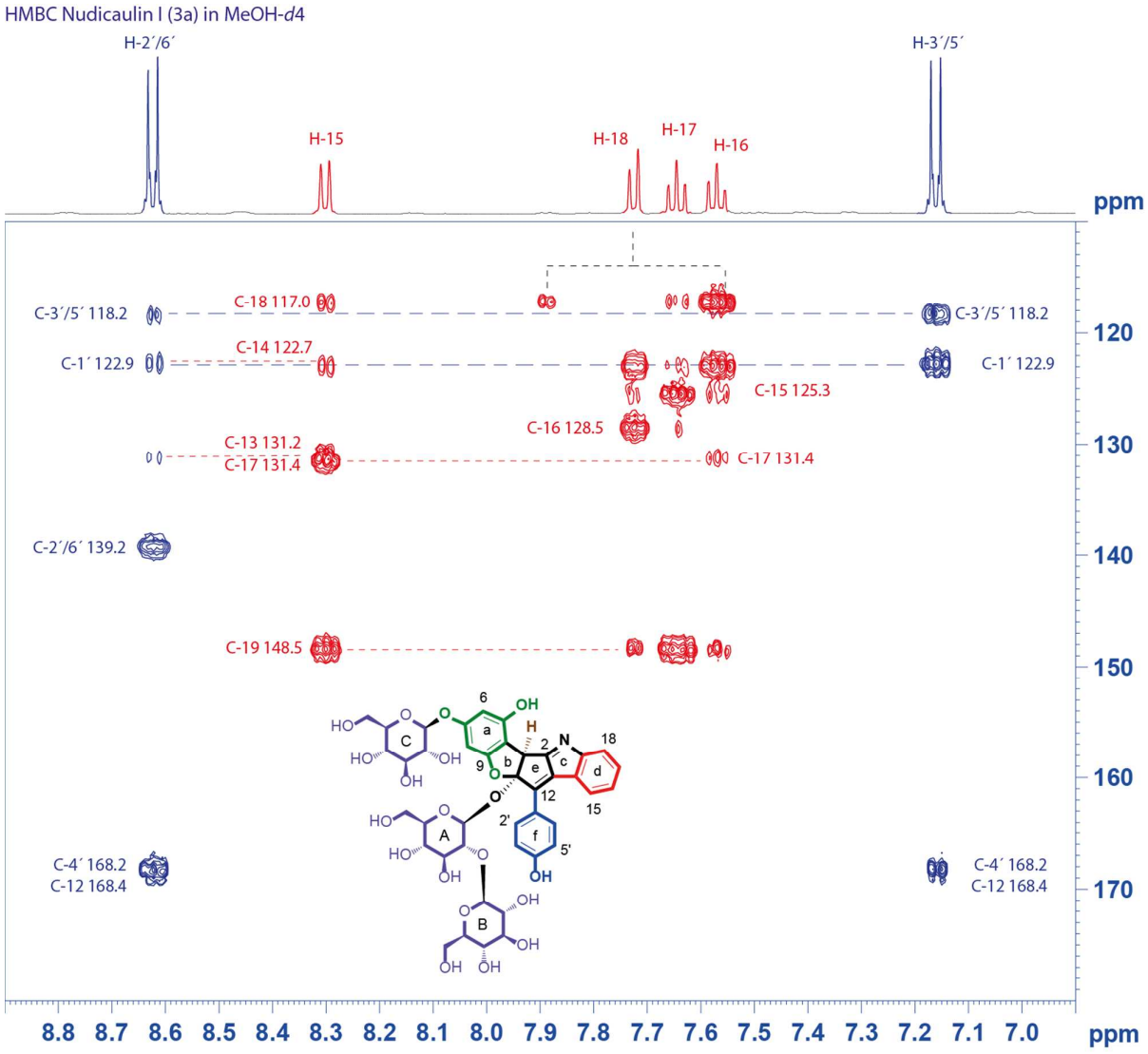

Figure S11. Selected region of the HMBC spectrum of nudicaulin I (**3a**) in MeOH-d_4

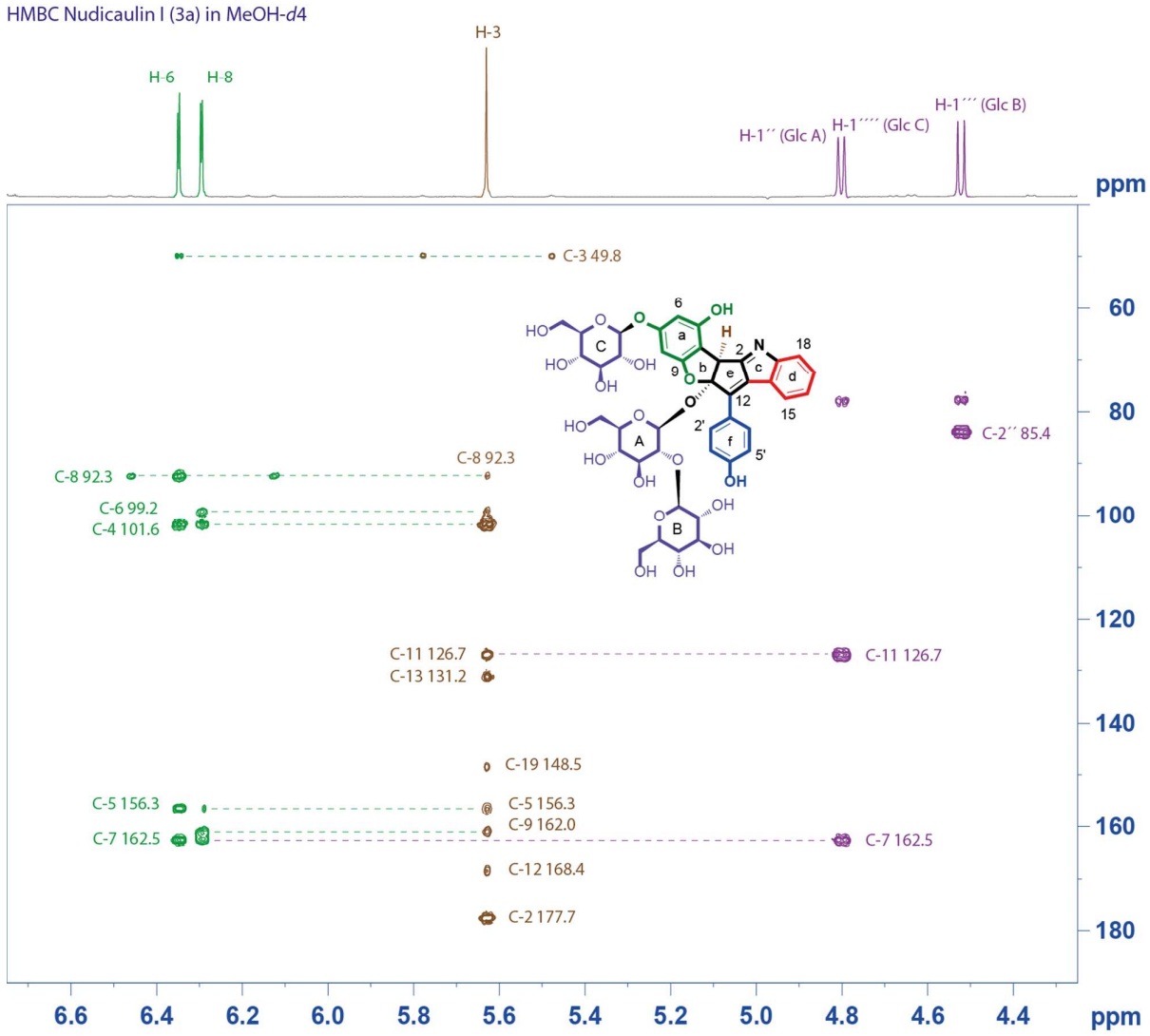

Figure S12. Selected region of the HMBC spectrum of nudicaulin I (**3a**) in MeOH-d_4

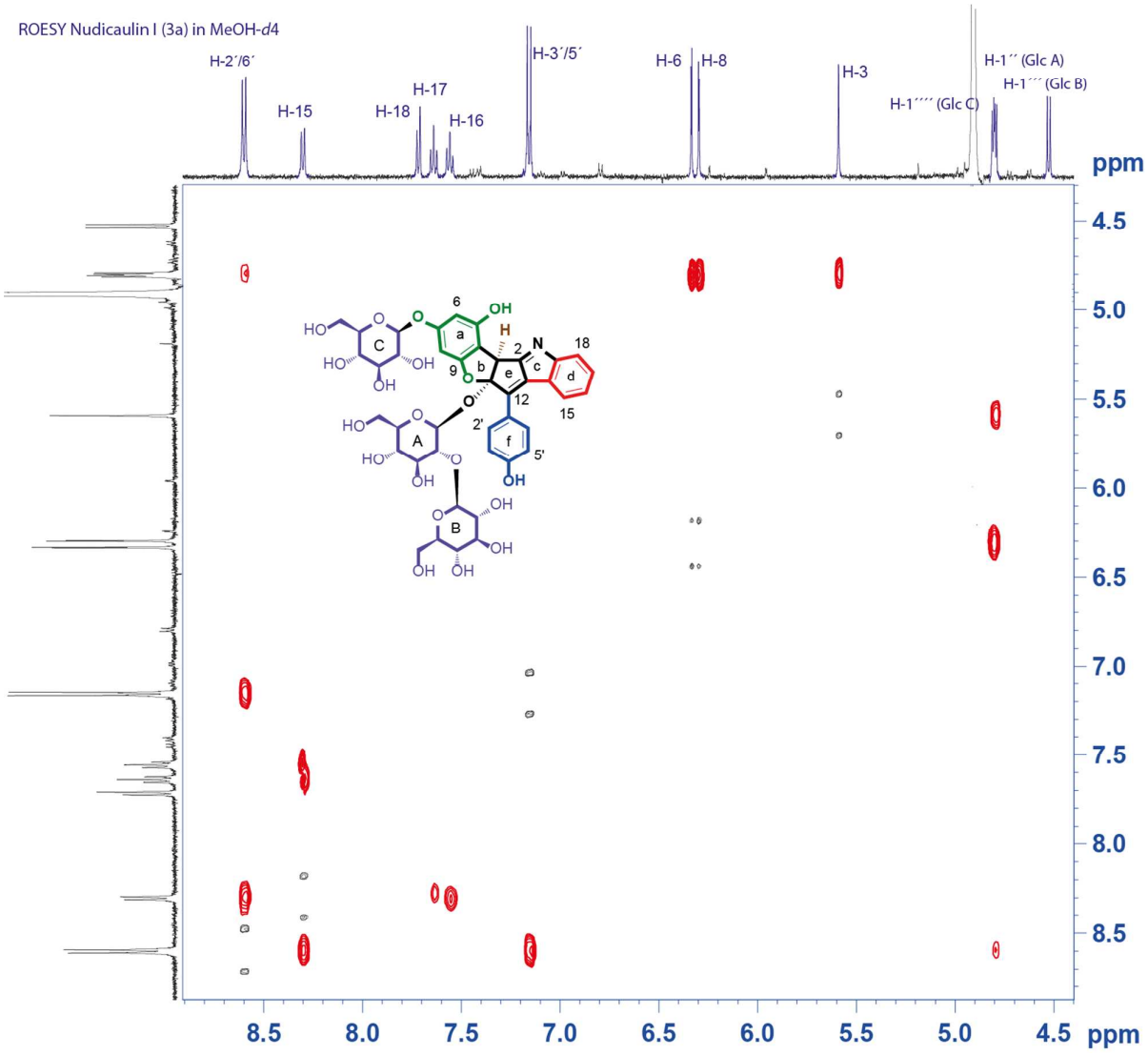

Figure S13. Selected region of the ROESY spectrum of nudicaulin I (**3a**) in MeOH-d_4

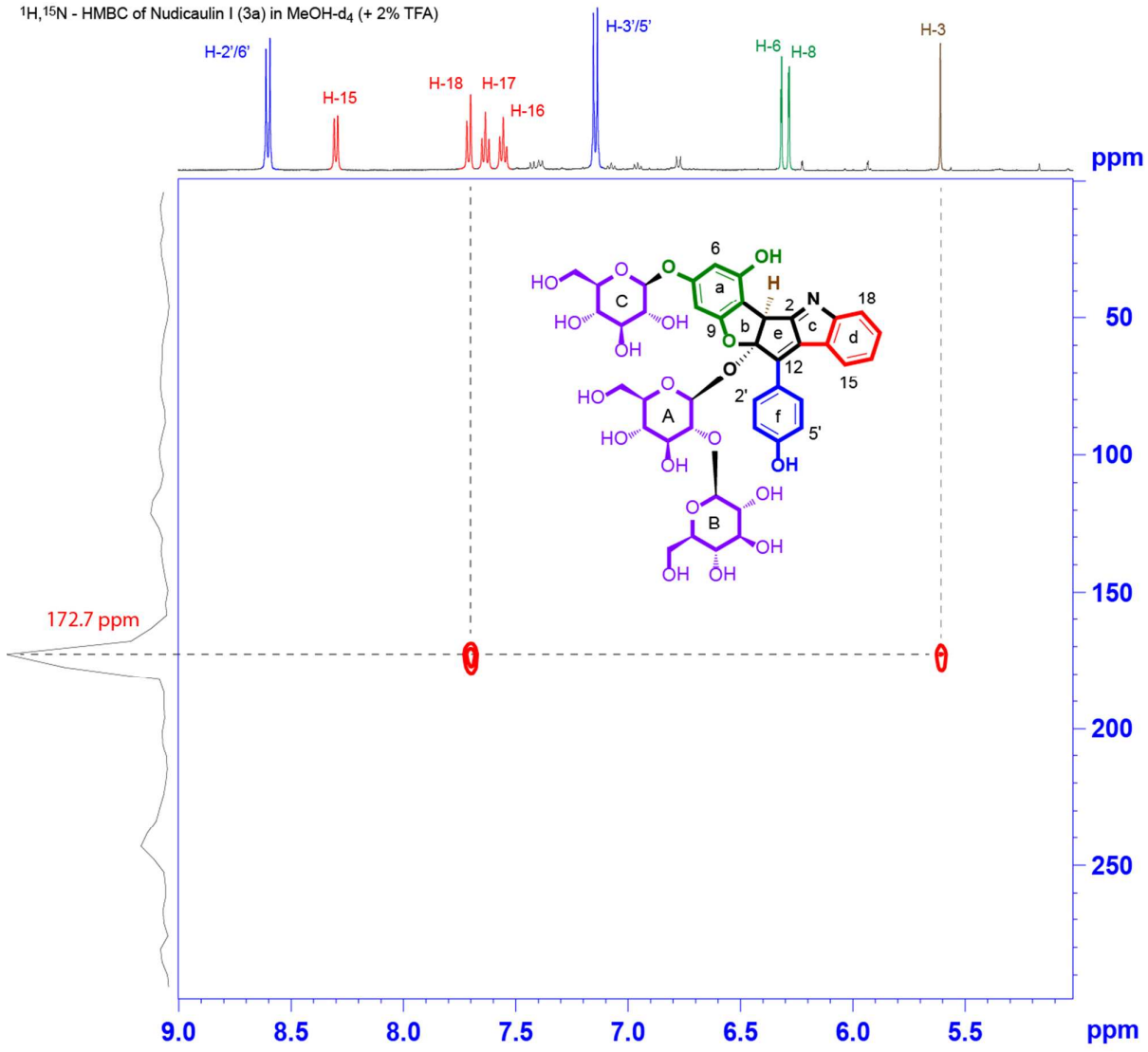

Figure S14. Selected region of the $^{1}H,^{15}N$-HMBC spectrum of nudicaulin I (**3a**) in MeOH-d_4

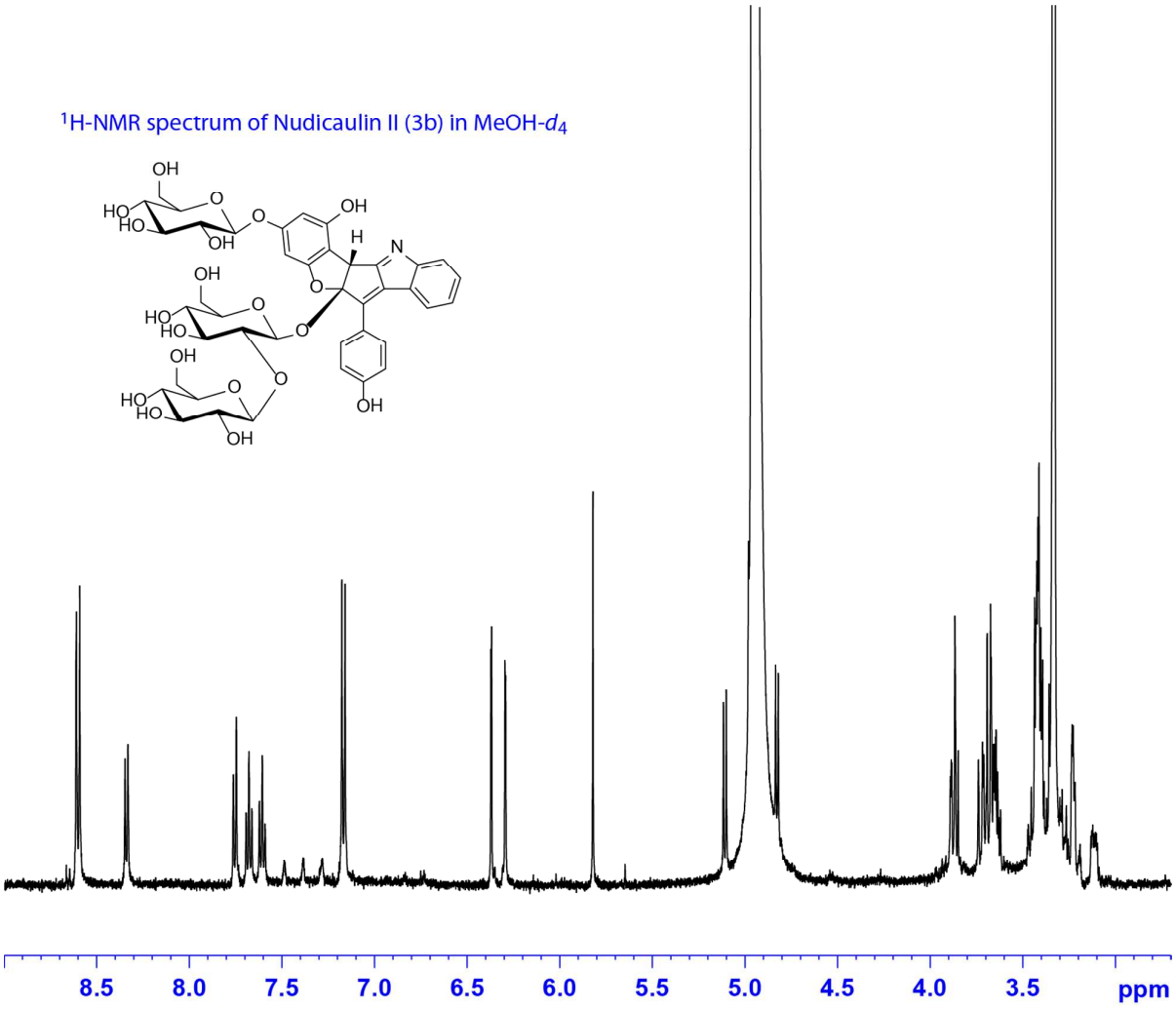

Figure S15. ^{1}H NMR spectrum of nudicaulin II (**3b**) in MeOH-d_4

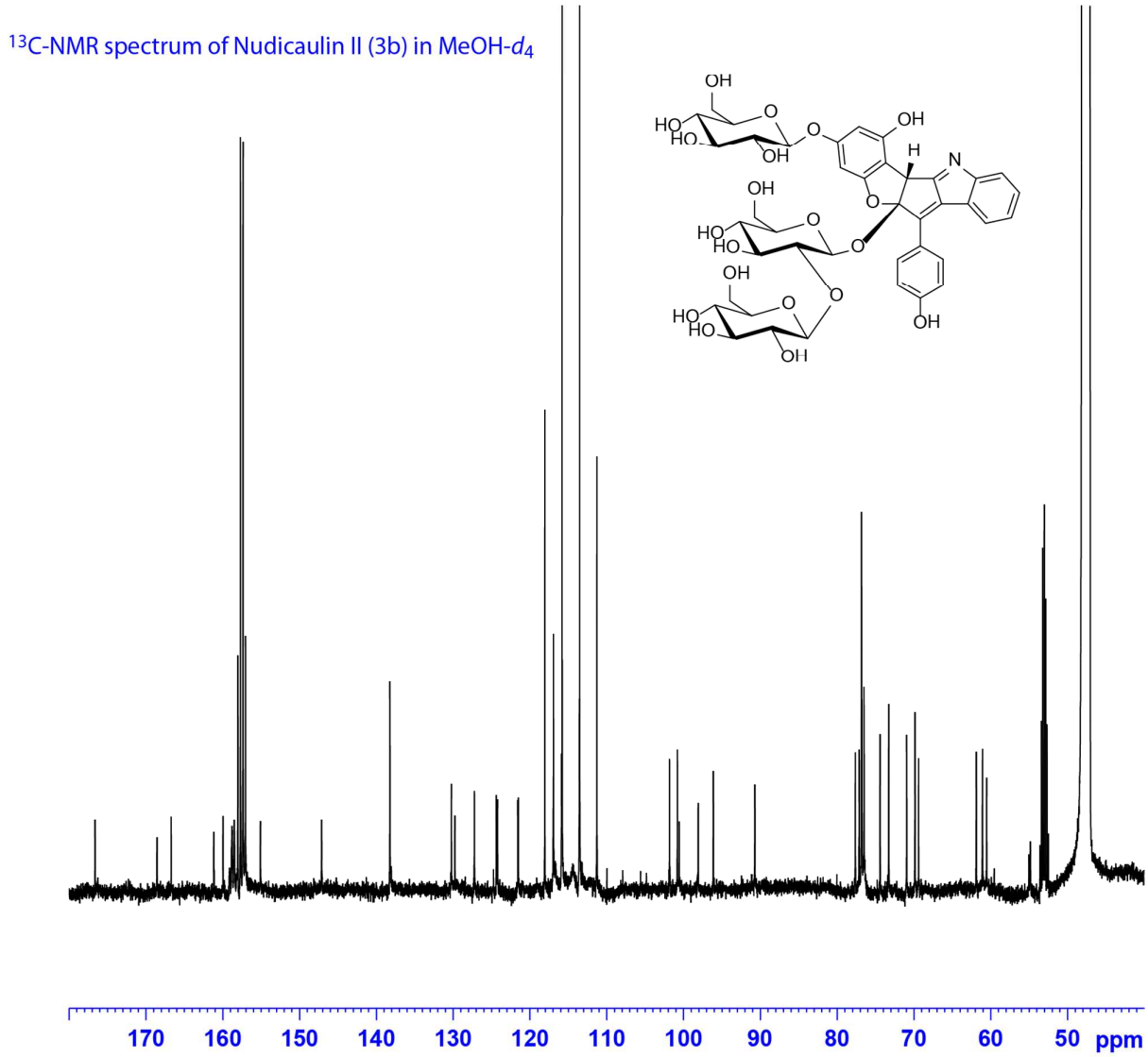

Figure S16. ^{13}C NMR spectrum of nudicaulin II (**3b**) in MeOH-d_4

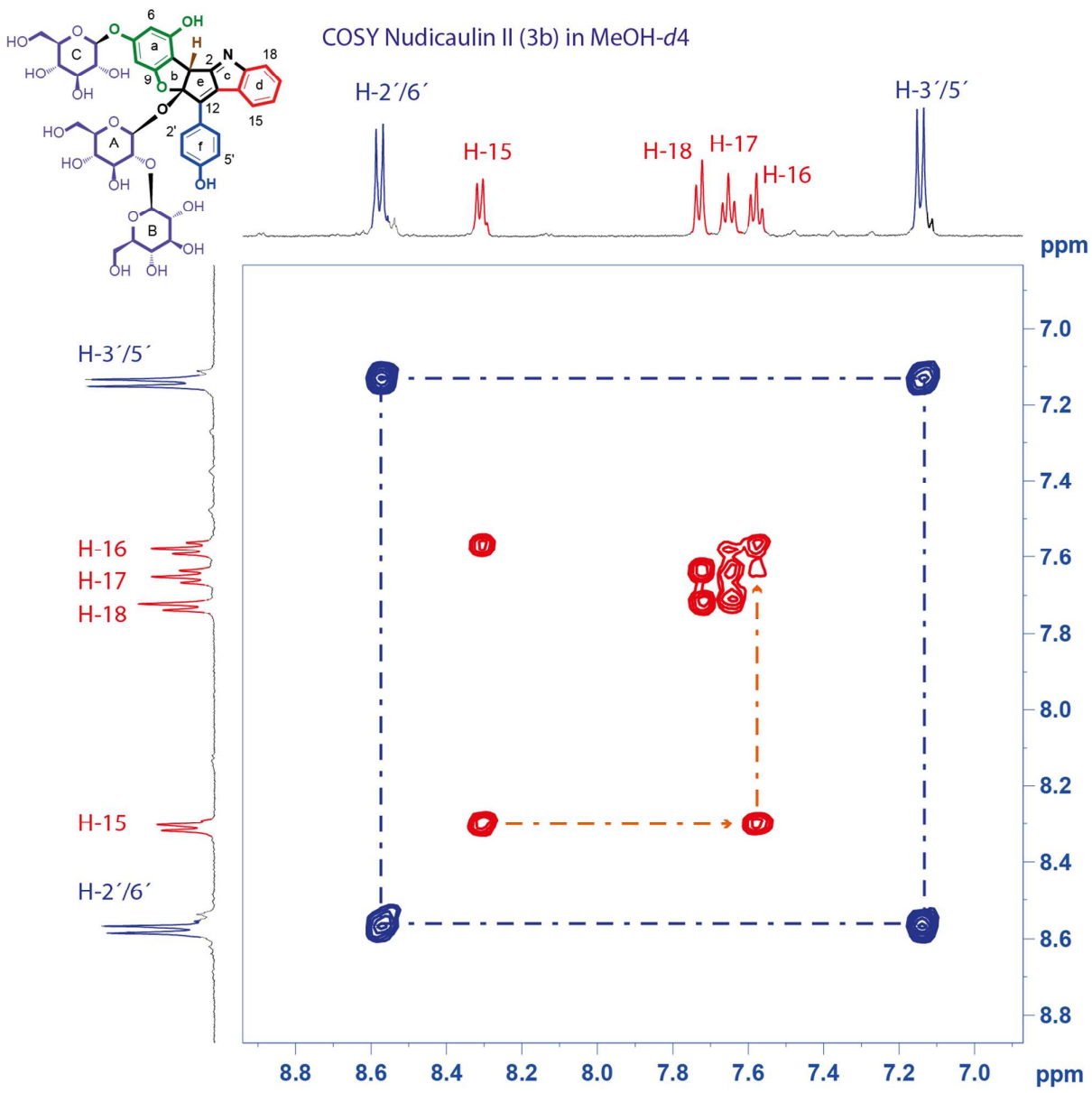

Figure S17. Selected region of the COSY spectrum of nudicaulin II (**3b**) in MeOH-d_4

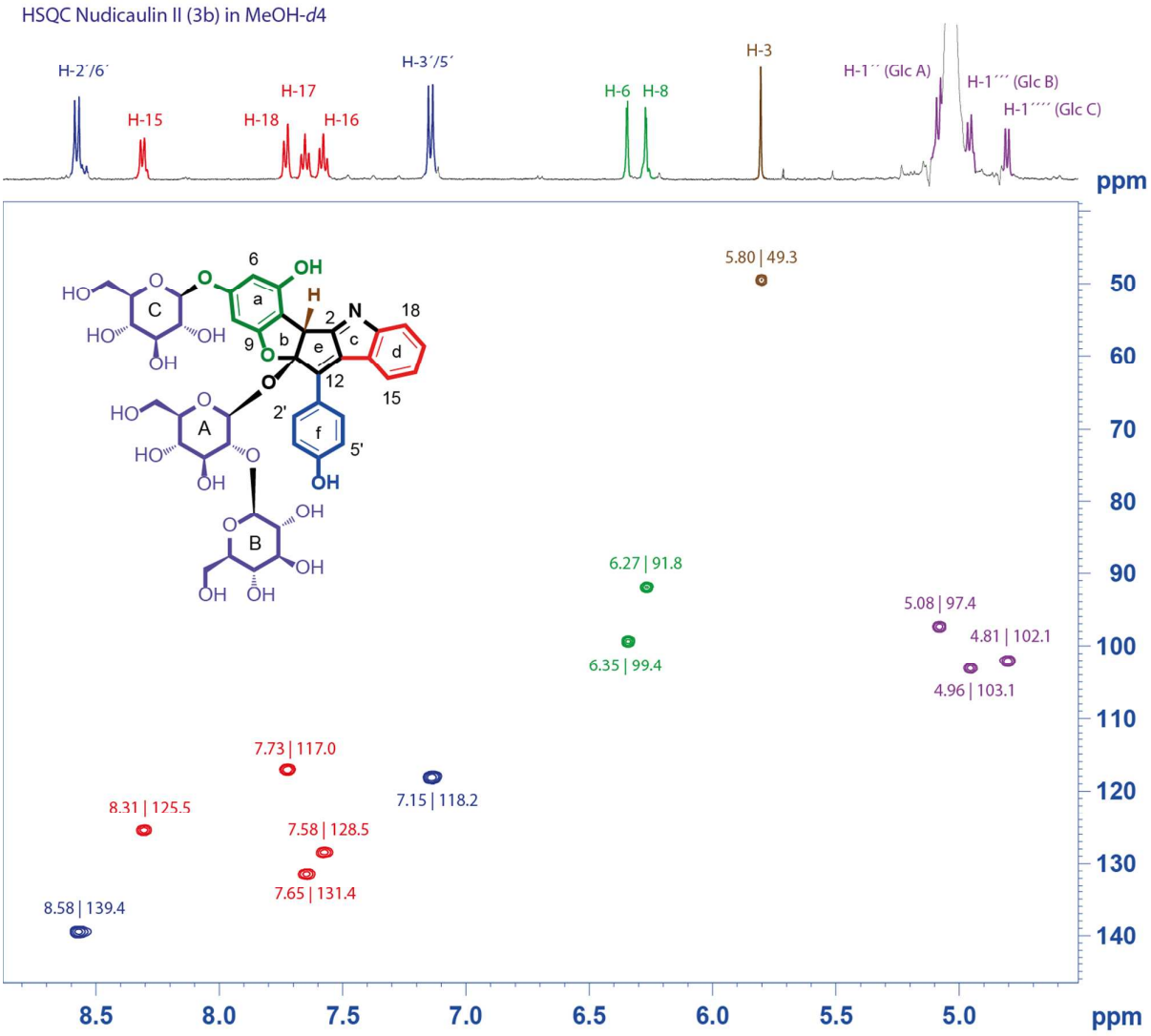

Figure S18. Selected region of the HSQC spectrum of nudicaulin II (**3b**) in MeOH-d_4

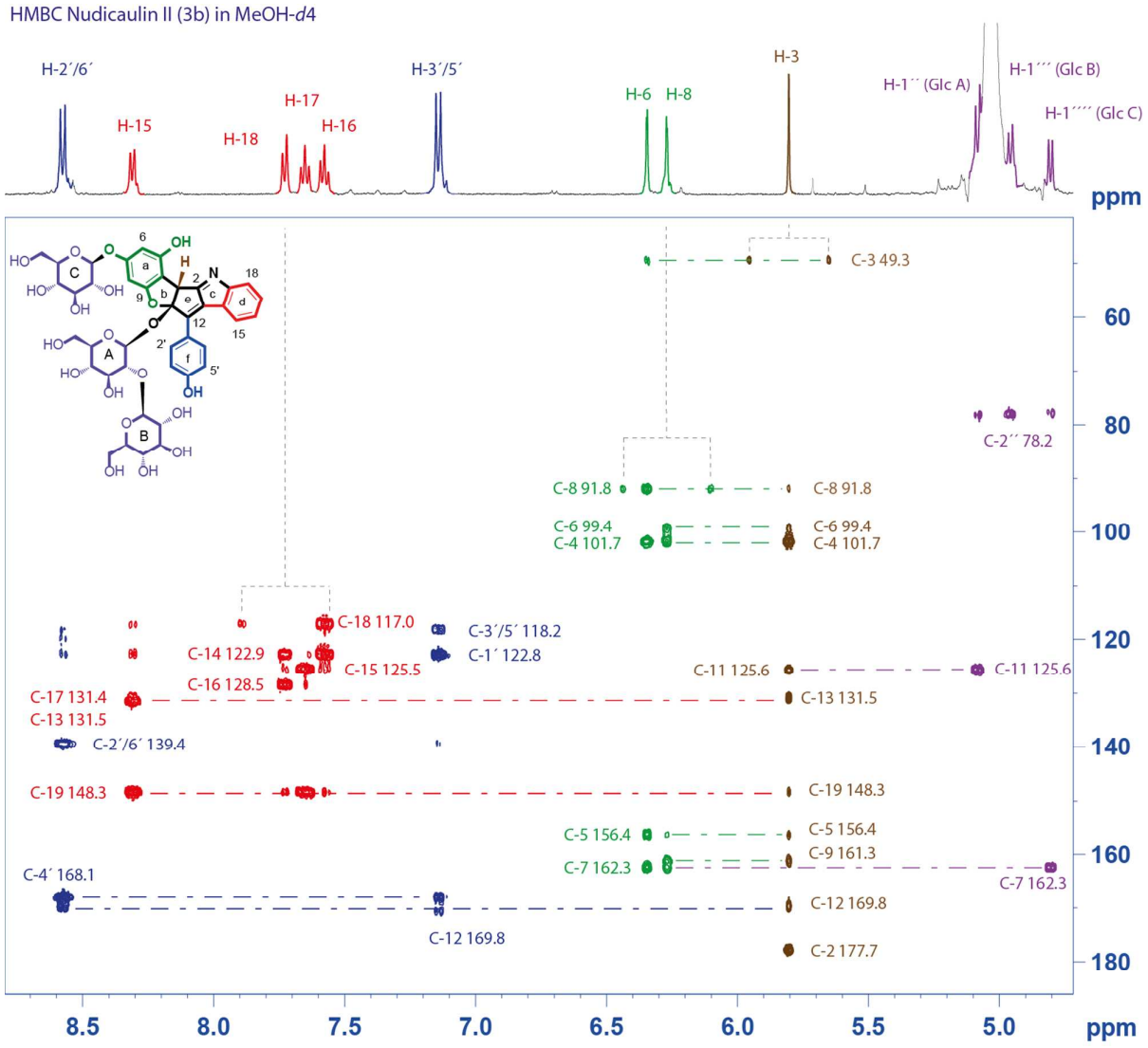

Figure S19. Selected region of the HMBC spectrum of nudicaulin II (**3b**) in MeOH-d_4

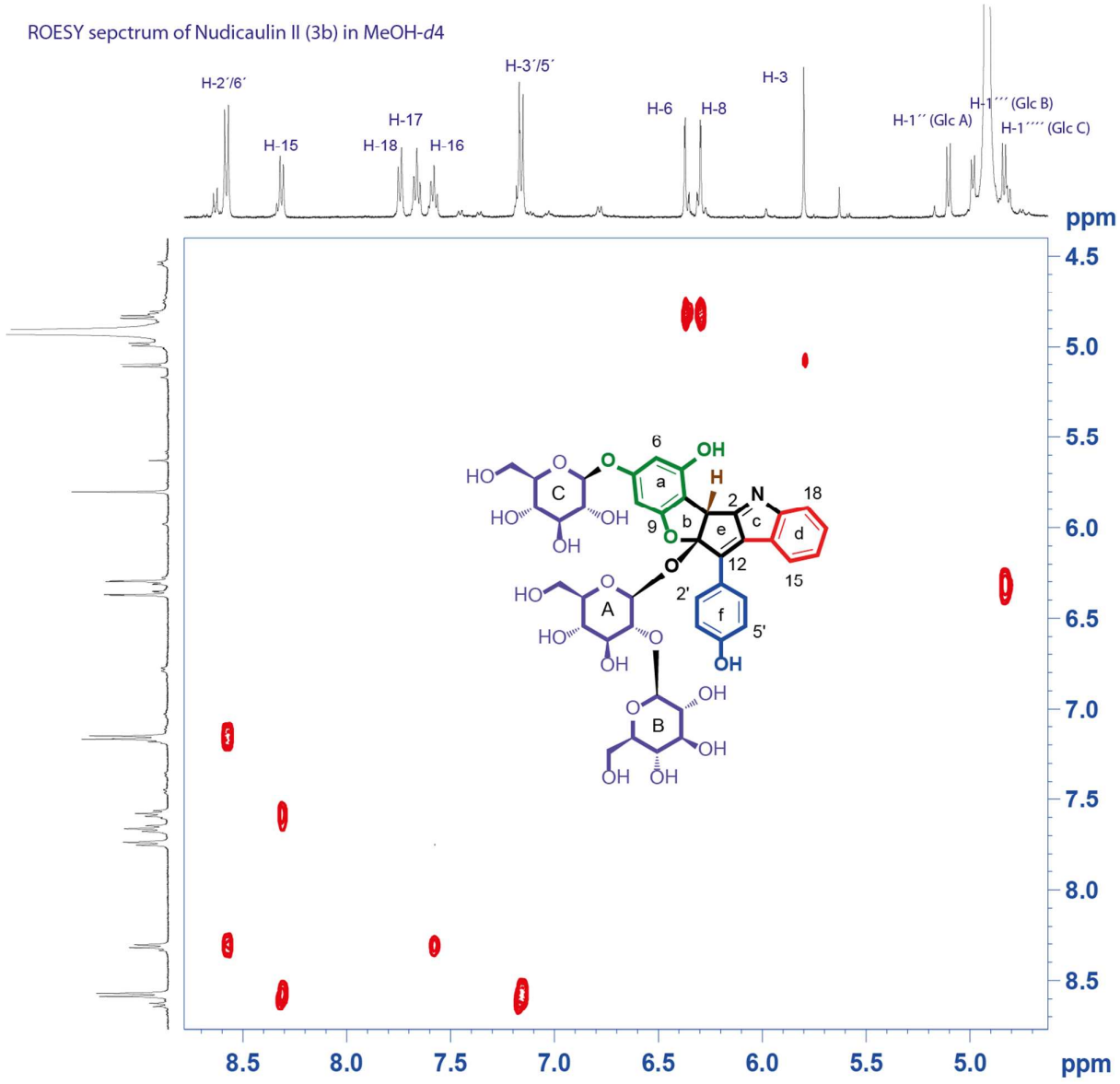

Figure S20. Selected region of the ROESY spectrum of nudicaulin II (**3b**) in MeOH-d_4

S7. NMR data of partially deglucosylated nudicaulins I & II

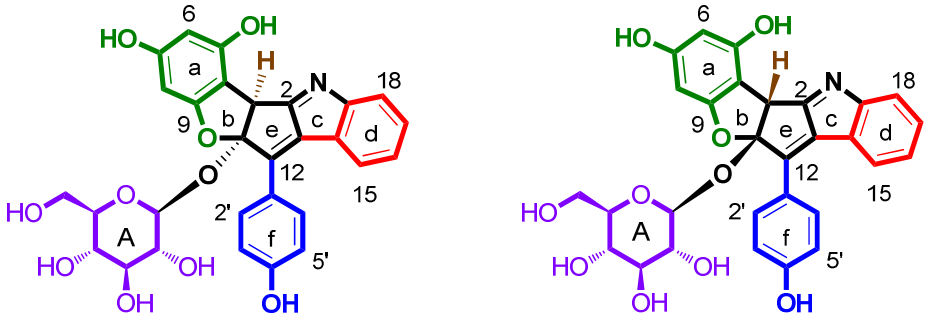

Figure S21. Structures of partially deglucosylated nudicaulins I (**6a**) & II (**6b**)

Table S2. ^{1}H NMR and ^{13}C NMR spectroscopic data (500 MHz for ^{1}H; 125 MHz for ^{13}C) of partially deglucosylated nudicaulins I (**6a**) and II (**6b**) in MeOH-d_4

	Partially Deglucosylated Nudicaulin I		**Partially Deglucosylated Nudicaulin II**	
No	^{1}H δ, mult., *J* (Hz)	^{13}C δ	^{1}H δ, mult., *J* (Hz)	^{13}C δ
Aglycon				
2		179.1		178.3
3	5.34, *s*	50.7	5.63, s	50.0
4		99.7		98.8
5		157.6		155.7
6	6.03 *d*, 2.0	98.4	6.04	98.3
7		163.1		163.1
8	5.91, *d*, 2.0	91.5	5.94	91.3
9		162.3		161.6
11		127.9		125.4
12		166.7		169.9
13		132.6		131.8
14		124.0		122.8
15	8.26, *d*, 7.7	126.1	8.30	126.3
16	7.52, *dd*	128.8	7.54	128.9
17	7.60, *dd*	131.9	7.63	132.1
18	7.68, *d*, 7.8	118.4	7.71	118.2
19		151.4		148.6
1'		123.4		123.0
2'/6'	8.54, *d*, 8.9	139.2	8.57	139.7
3'/5'	7.12, *d*, 8.9	118.8	7.13	118.7
4'		168.1		168.2
Glucose A				
1''	4.61, *d*, 7.5	102.1	4.94	99.6
2''	3.30	75.3	3.30	75.3
3''	3.30	78.2	3.39	78.8
4''	3.34	71.3	3.34	71.5
5''	3.09	79.4	3.11	79.2
6''A	3.75	62.9	3.68	62.6
6''B	3.68		3.63	

Some chemical shifts were obtained from 2D NMR spectra (COSY, HSQC, HMBC). Most coupling constants of Glc units were not determined.

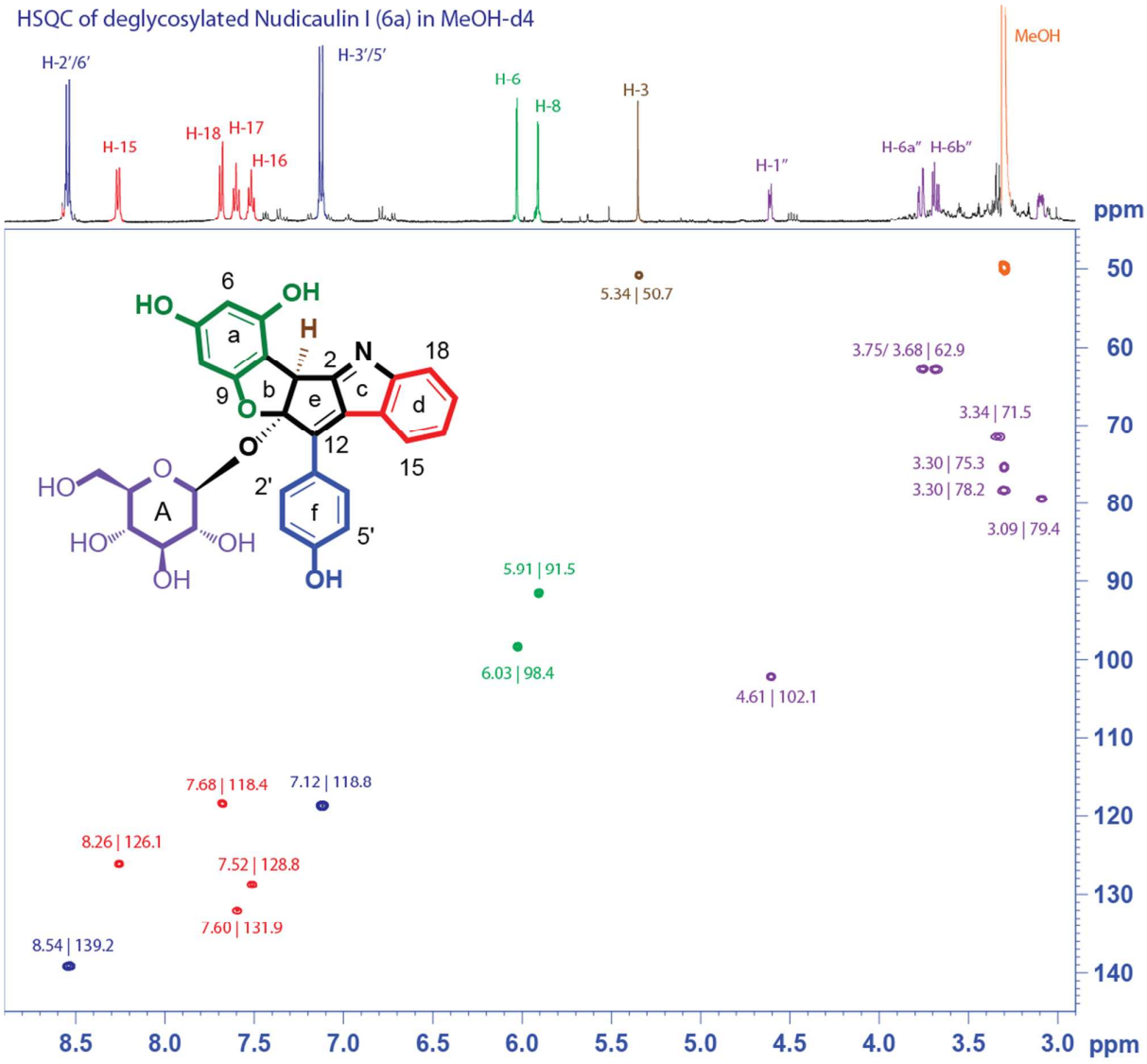

Figure S22. Selected region of the HSQC spectrum of partially deglucosylated nudicaulin I (**6a**) in MeOH-d_4

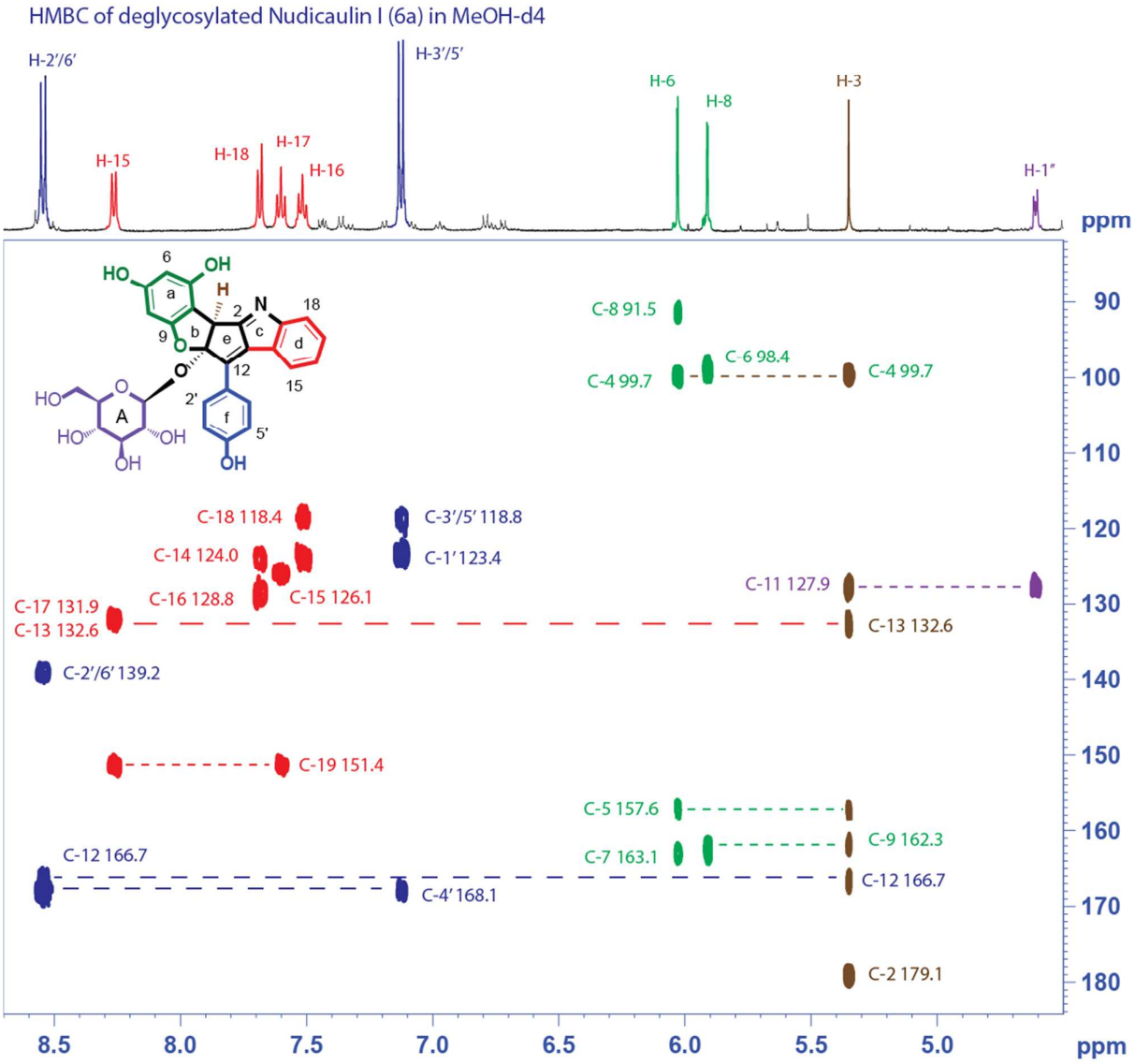

Figure S23. Selected region of the HMBC spectrum of partially deglucosylated nudicaulin I (**6a**) in MeOH-d_4

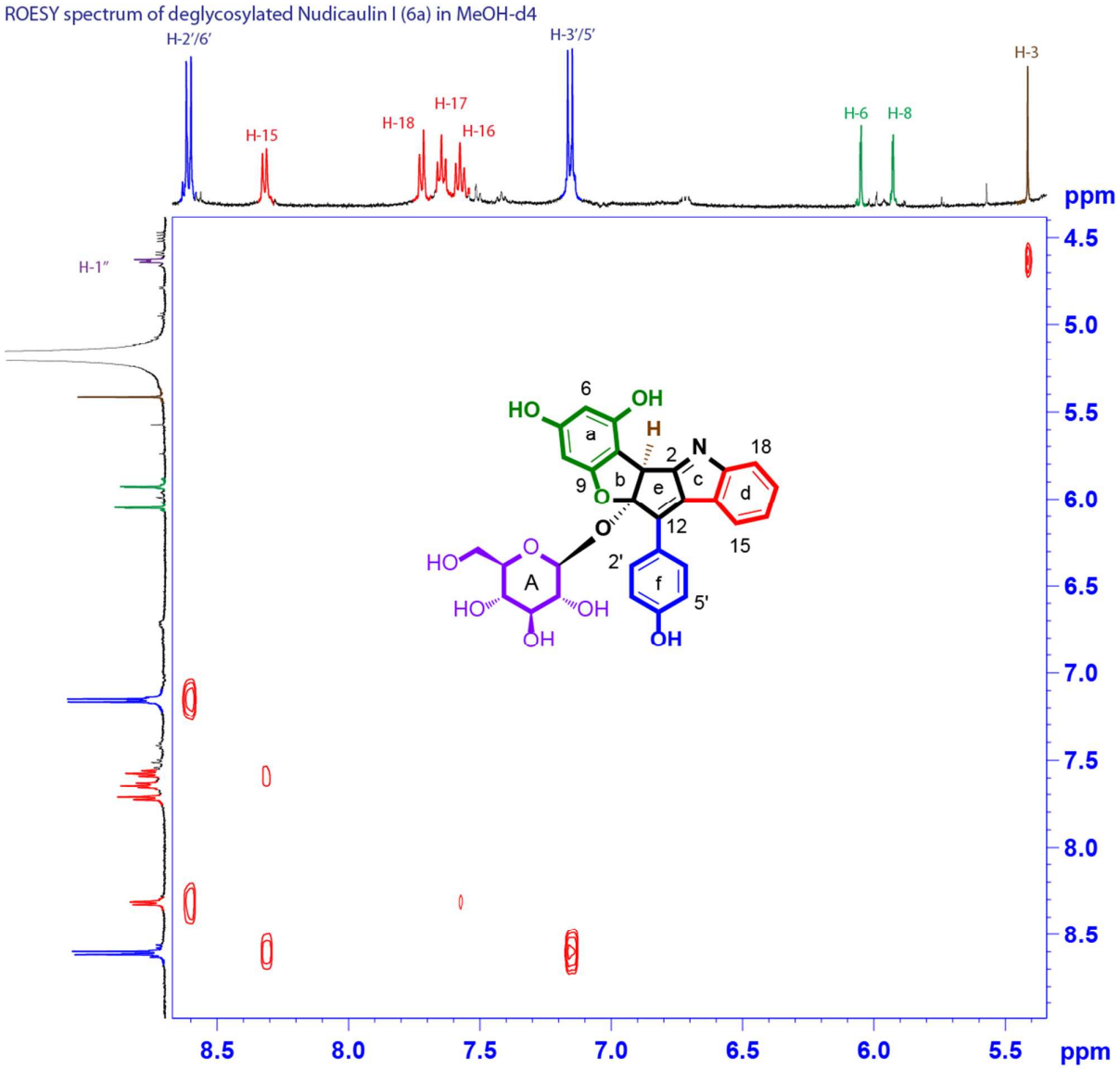

Figure S24. Selected region of the ROESY spectrum of partially deglucosylated nudicaulin I (**6a**) in MeOH-d_4

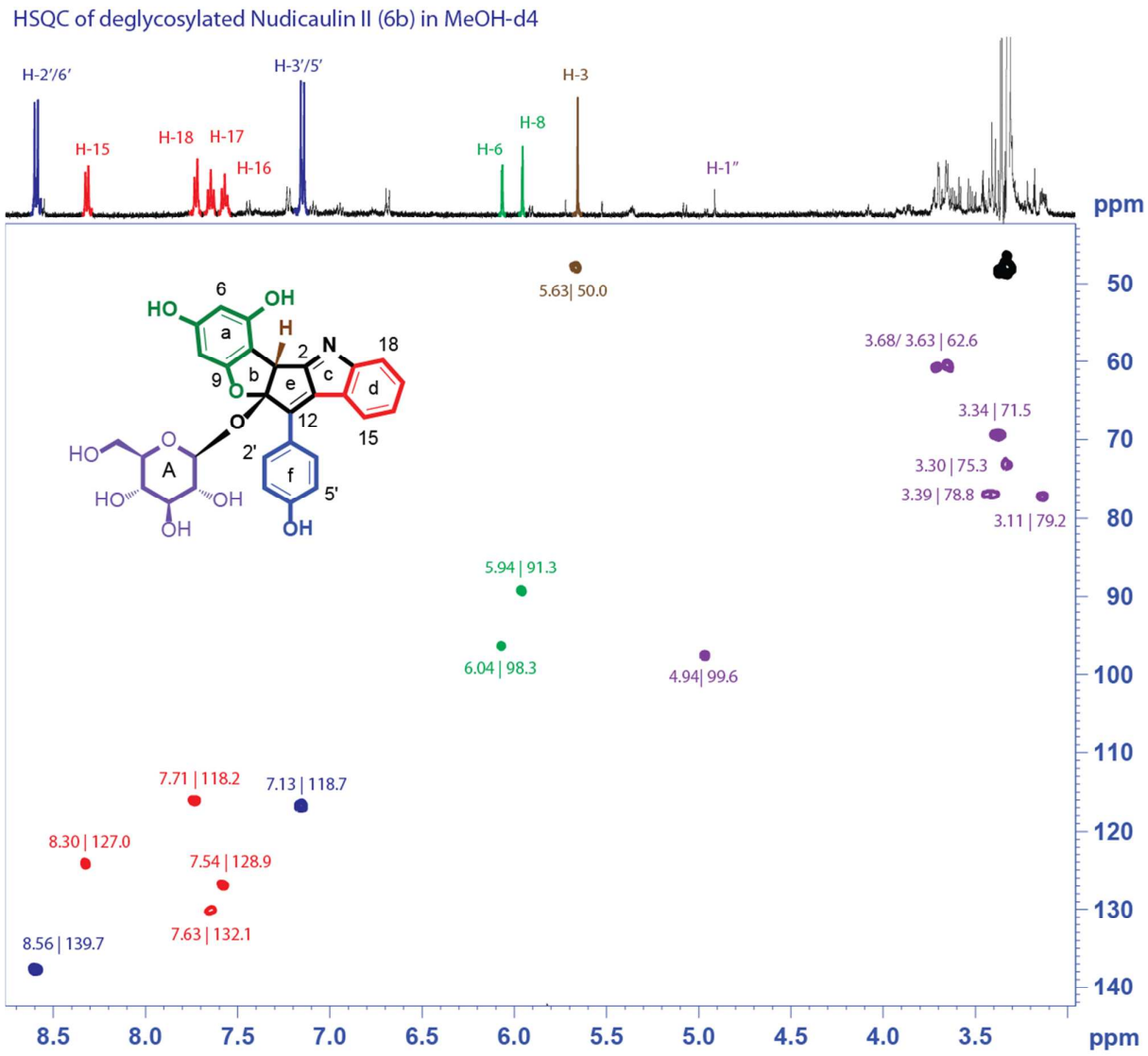

Figure S25. Selected region of the HSQC spectrum of partially deglucosylated nudicaulin II (**6b**) in MeOH-d_4

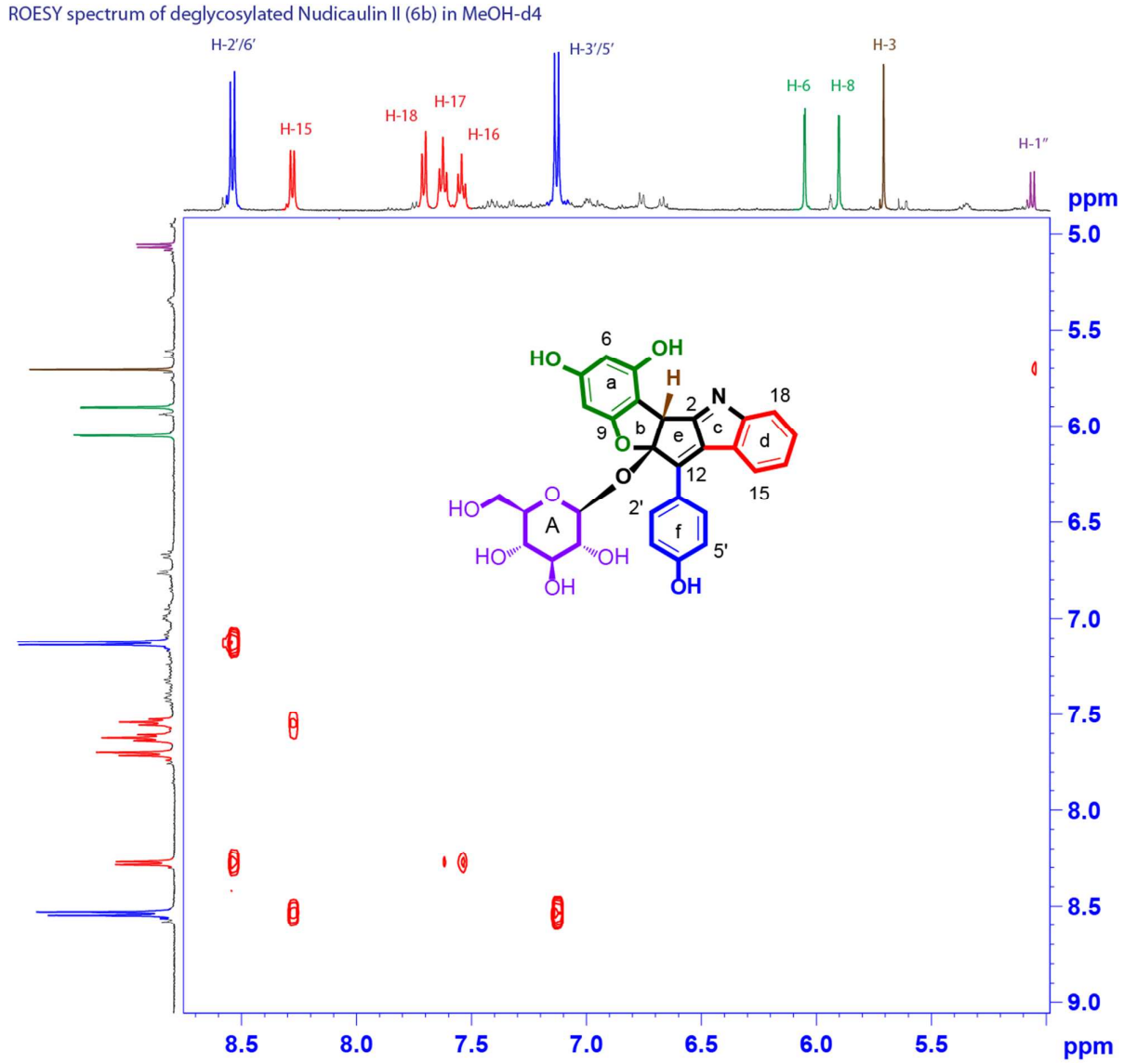

Figure S26. Selected region of the ROESY spectrum of partially deglucosylated nudicaulin II (**6b**) in MeOH-d_4

S8. NMR Data of Dihydronudicaulins I & II

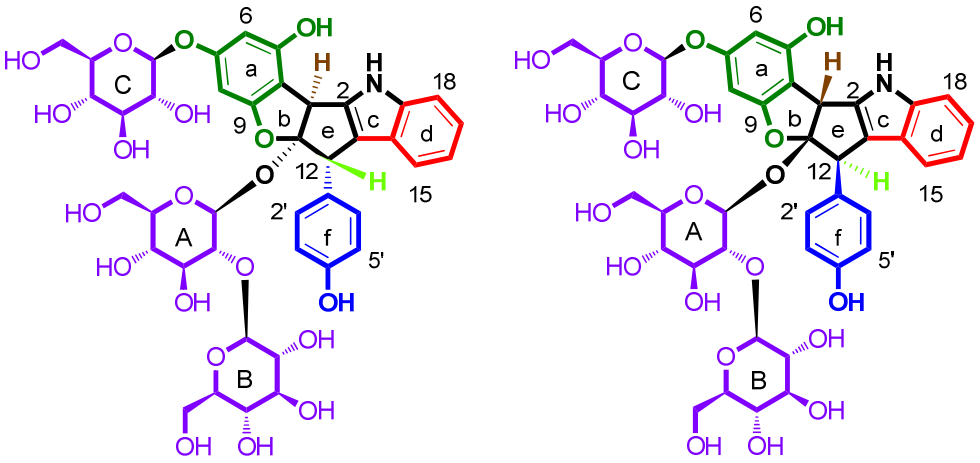

Figure S27. Structures of dihydronudicaulins I (**4a**) & II (**4b**)

Table S3. ^{1}H NMR and ^{13}C NMR spectroscopic data (500 MHz for ^{1}H; 125 MHz for ^{13}C) of dihydronudicaulin I (**4a**) and dihydronudicaulin II (**4b**) in MeOH-d_4

	Dihydronudicaulin I		**Dihydronudicaulin II**	
No	^{1}H δ, mult.	^{13}C δ	^{1}H δ, mult.	^{13}C δ
Aglycon				
2		140.5		141.5
3	5.07, s	51.1	5.15, s	51.3
4		108.3		108.8
5		155.1		155.2
6	6.00, d, 1.9	91.7	6.00, d, 1.9	91.7
7		160.5		160.6
8	6.23, d, 1.9	97.9	6.23, d, 1.9	98.6
9		161.2		161.5
11		126.8		127.4
12	4.99, s	55.0	4.97, s	55.2
13		116.5		116.2
14		124.6		125.4
15	6.80, dd, 3.0/1.2	119.5	6.96, dd, 7.9/1.0	119.9
16	6.80, dd, 5.2/1.2	119.5	6.85, ddd, 7.9/7.0/1.0	120.0
17	6.96, ddd, 8.2/5.2/3.0	121.6	6.99, ddd, 8.2/7.0/1.0	121.8
18	7.36, d, 8.2	113.3	7.36, dd, 8.2/1.0	113.0
19		142.1		142.4
1'		130.4		130.7
2'/6'	7.10, d like, 8.6	132.4	7.23, d like, 8.6	132.0
3'/5'	6.71, d like, 8.6	116.1	6.71, d like, 8.6	115.5
4'		157.1		157.3
Glucose A				
1''	4.70	97.7	4.75	96.5
2''	3.48	81.9	3.67	79.9
3''	3.54	77.7	3.52	78.4
4''	3.39	70.5	3.40	70.4
5''	3.25	77.7	3.24	77.8
6''A **6''B**	3.86 3.65	62.2	3.85 3.65	62.2
Glucose B				
1'''	4.51	104.7	4.73	103.8
2'''	3.10	75.6	3.35	75.7
3'''	2.95	71.3	2.84	77.6
4'''	3.07	71.5	3.38	77.6
5'''	3.38	77.7	3.25	71.8
6'''A **6'''B**	3.78 3.70	62.0	3.76 3.57	62.8
Glucose C				
1''''	4.80	101.9	4.75	102.3
2''''	3.35	74.5	3.36	74.5
3''''	3.11	78.2	3.33	71.0
4''''	3.28	71.0	3.34	77.6
5''''	3.32	70.9	3.33	70.9
6''''A **6''''B**	3.31 3.05	62.4	3.66 3.62	61.8

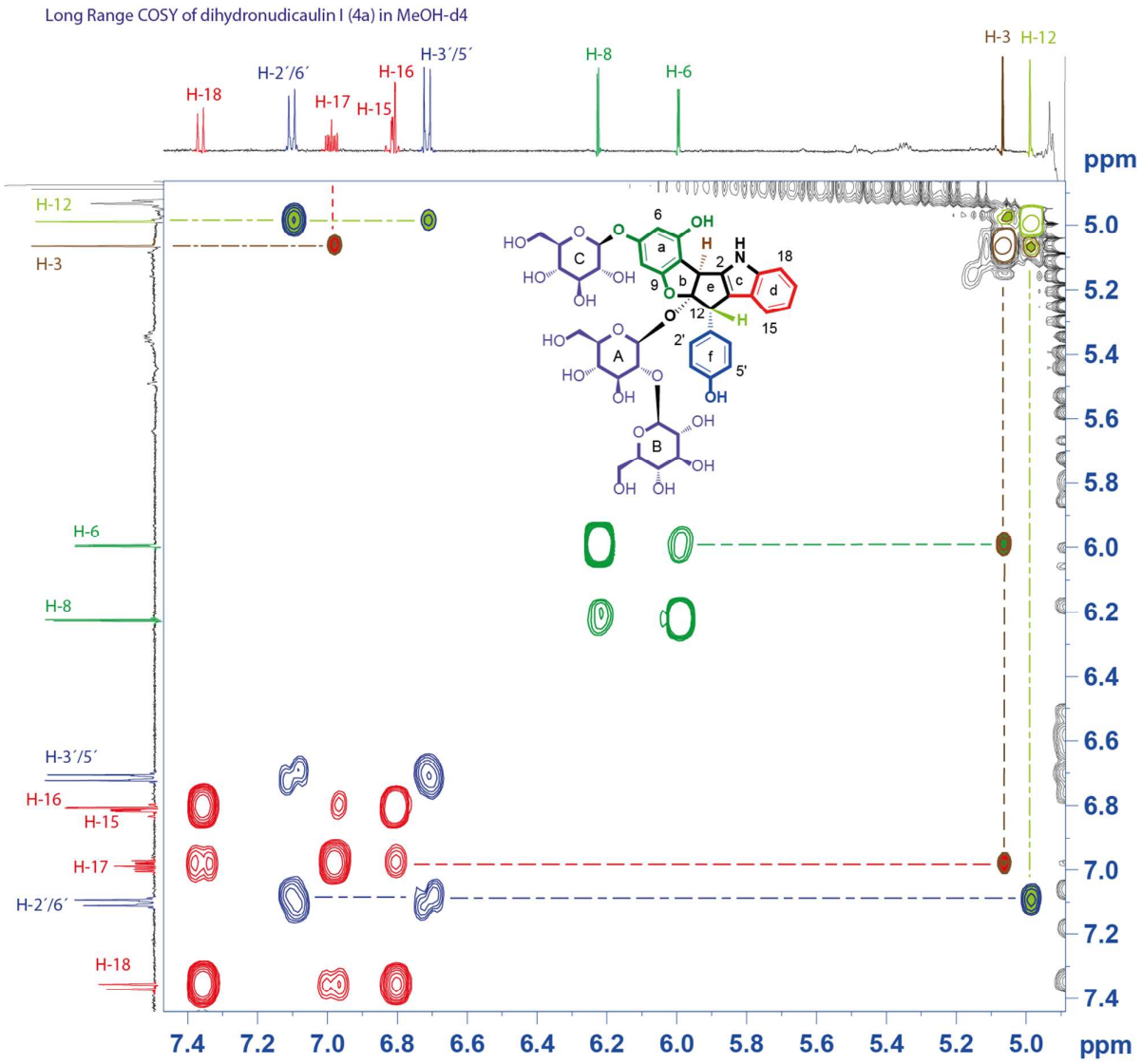

Figure S28. Selected region of the long range COSY spectrum of dihydronudicaulin I (**4a**) in MeOH-d_4

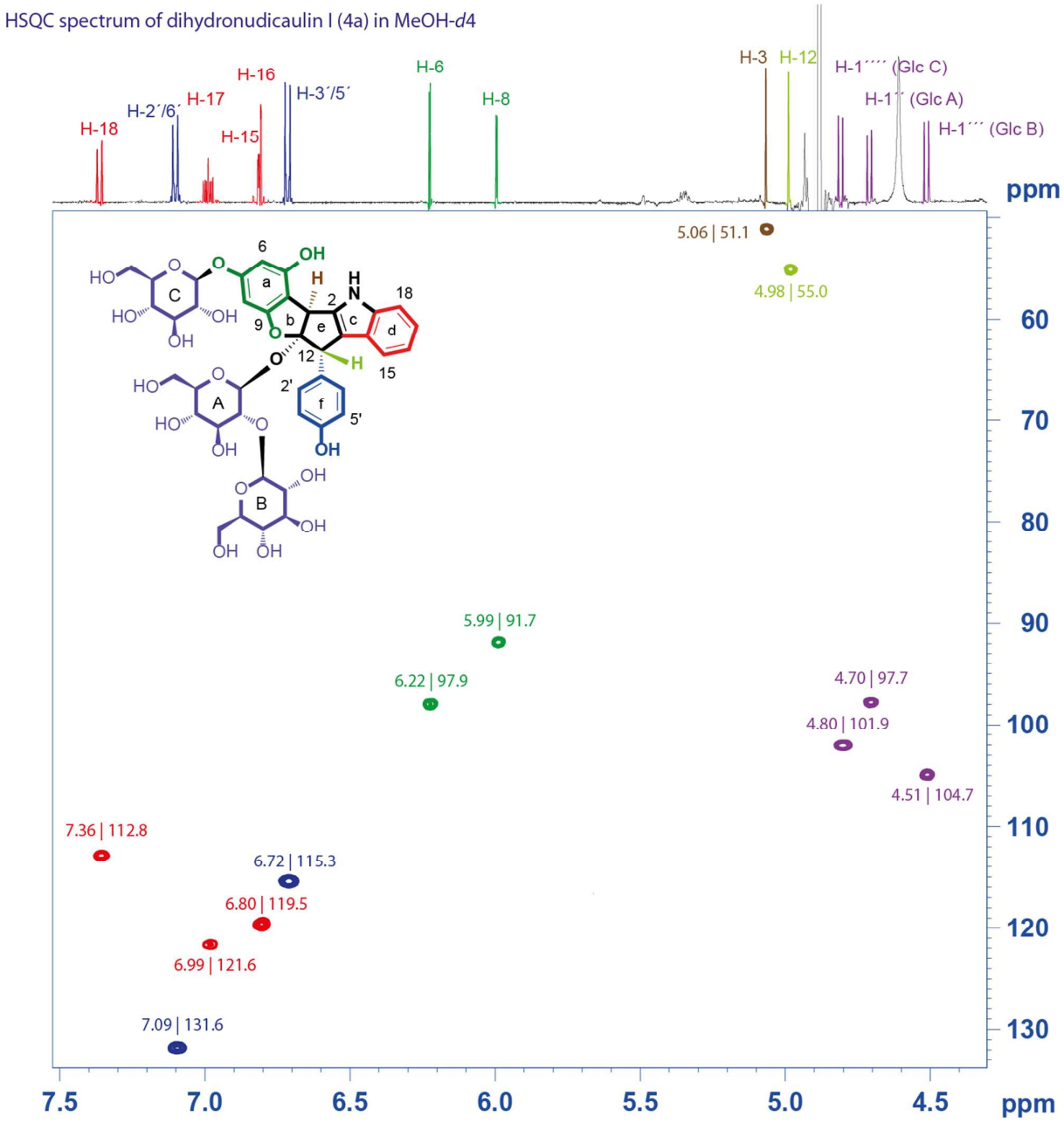

Figure S29. Selected region of the HSQC spectrum of dihydronudicaulin I (**4a**) in MeOH-d_4

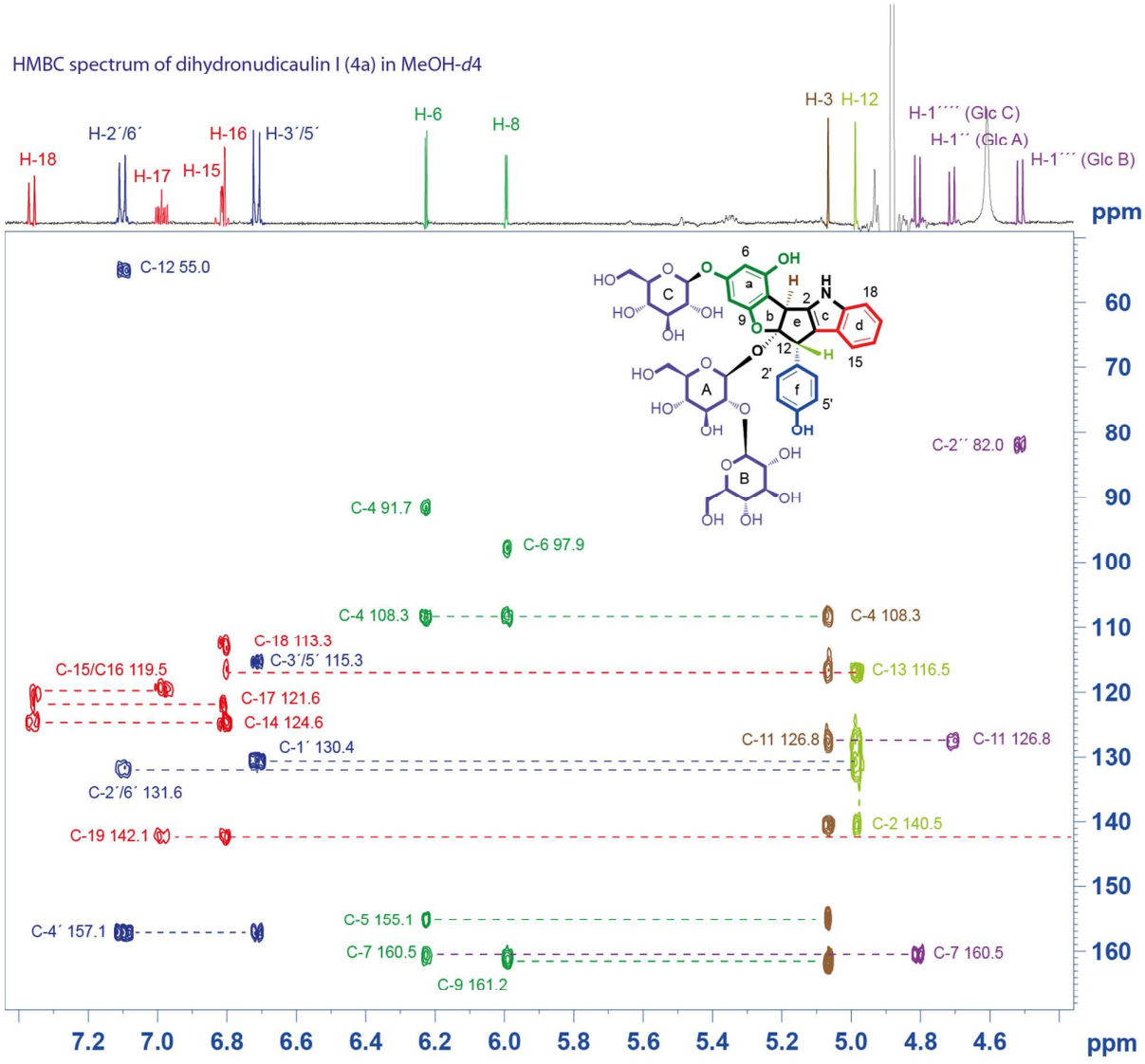

Figure S30. Selected region of the HMBC spectrum of dihydronudicaulin I (**4a**) in MeOH-d_4

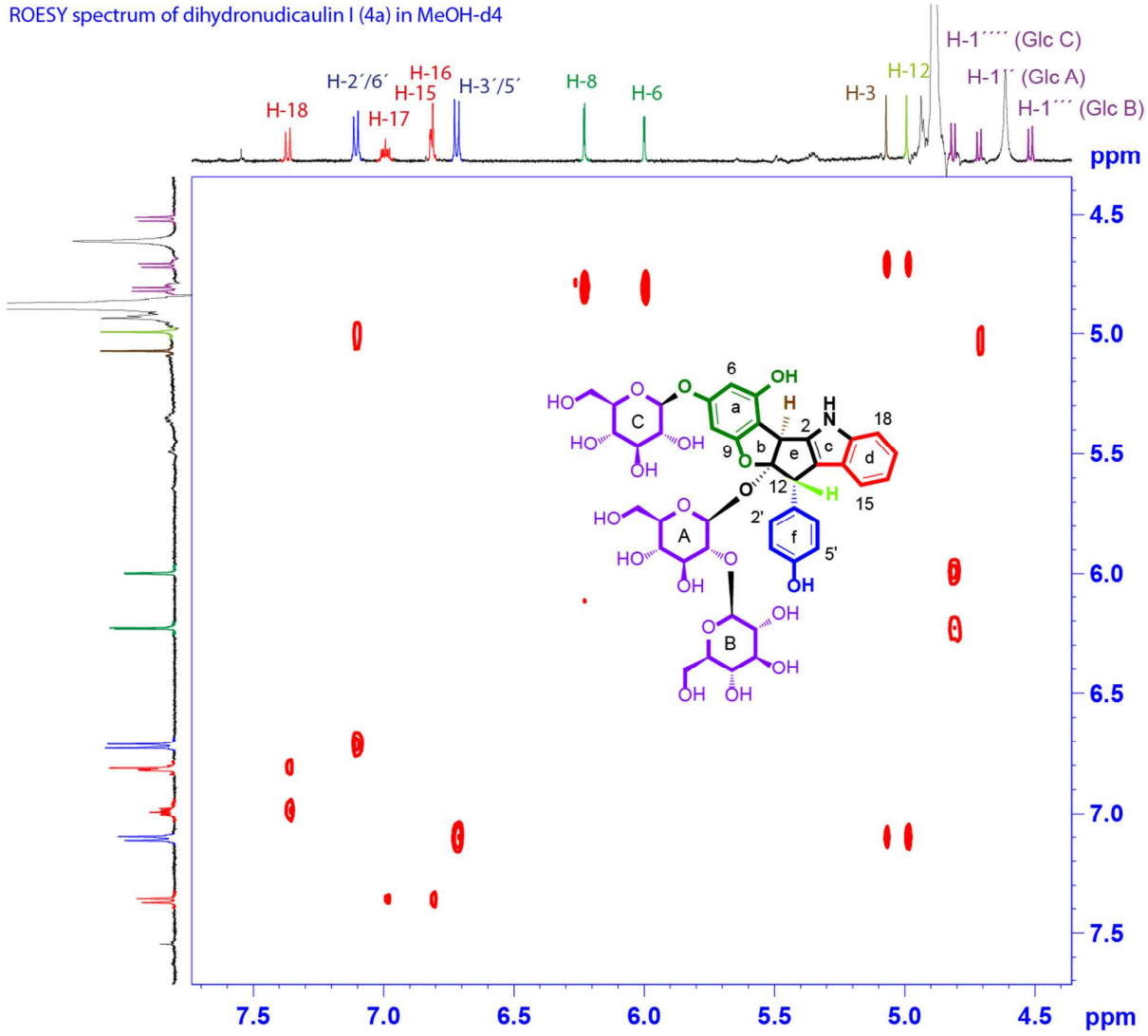

Figure S31. Selected region of the ROESY spectrum of dihydronudicaulin I (**4a**) in MeOH-d_4

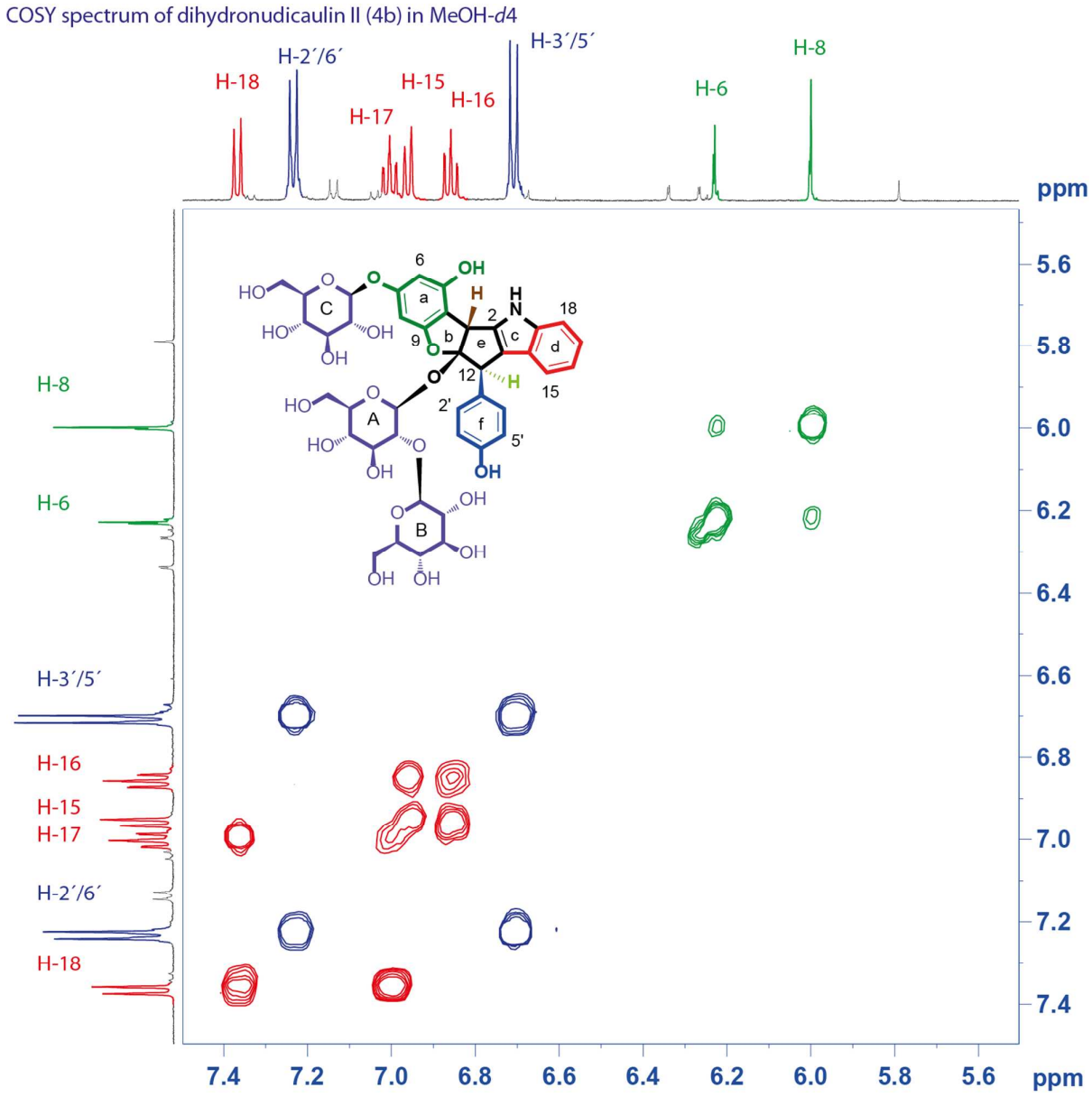

Figure S32. Selected region of the COSY spectrum of dihydronudicaulin II (**4b**) in MeOH-d_4

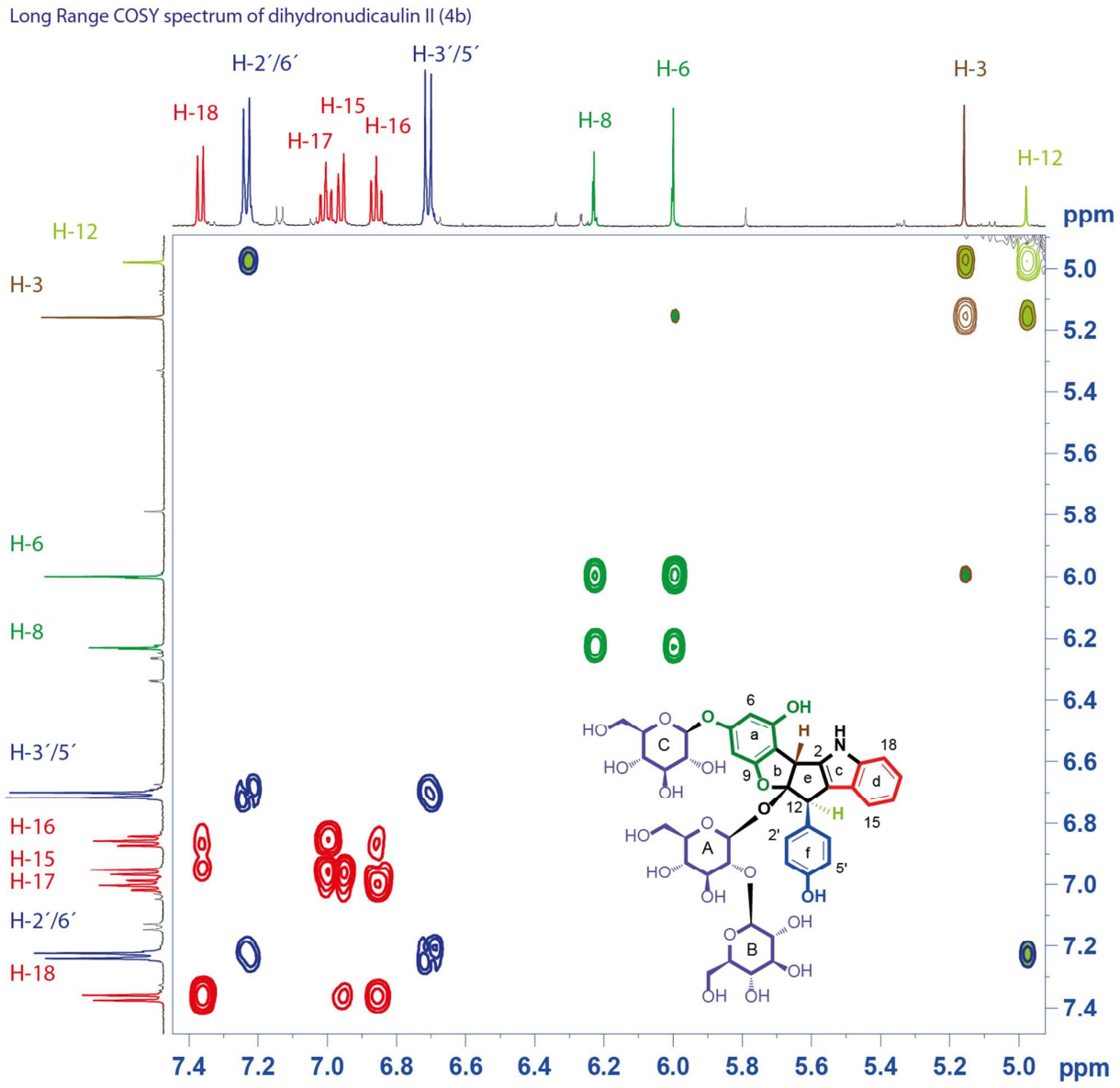

Figure S33. Selected region of the long range COSY spectrum of dihydronudicaulin II (**4b**) in MeOH-d_4

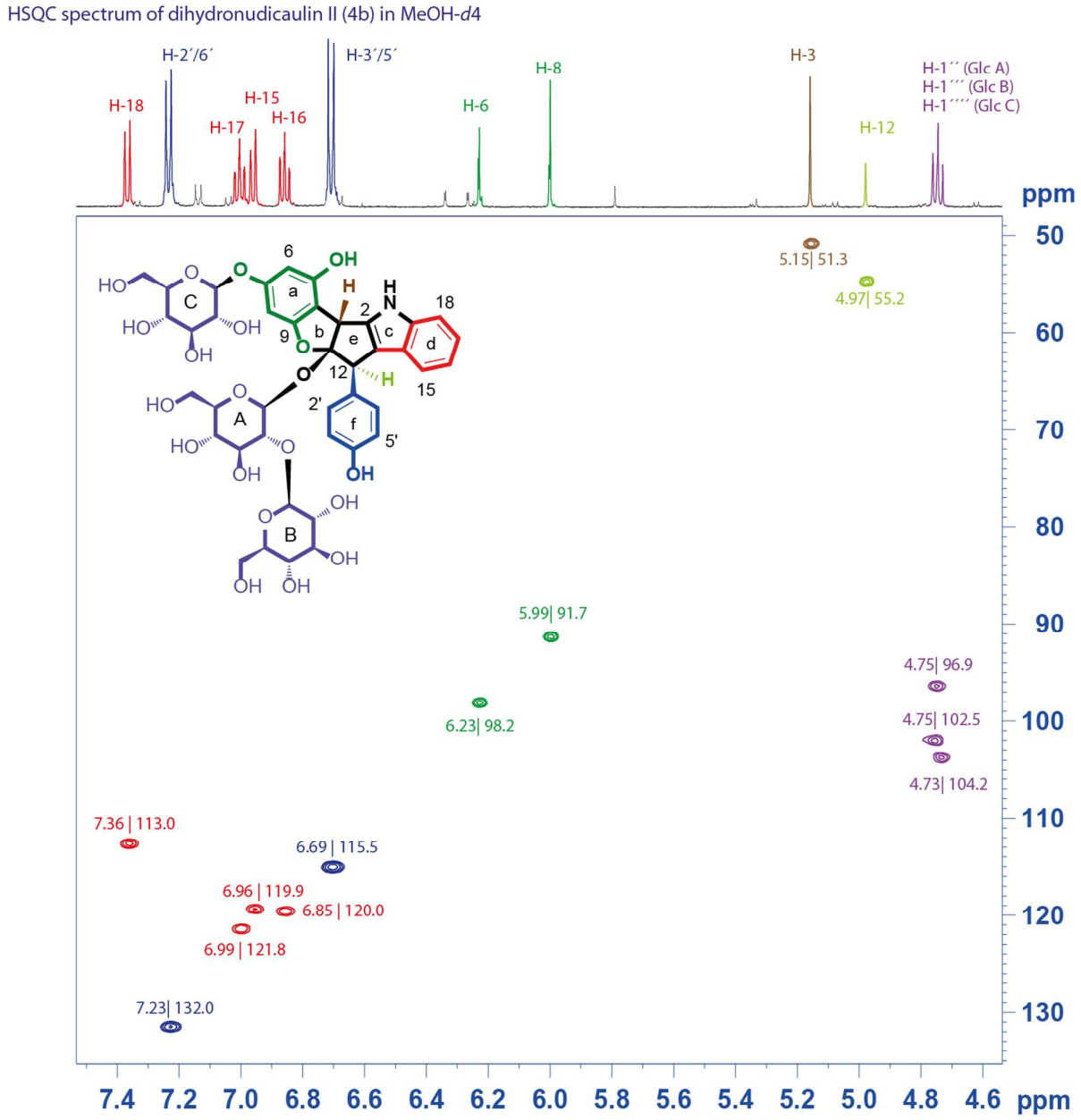

Figure S34. Selected region of the HSQC spectrum of dihydronudicaulin II (**4b**) in MeOH-d_4

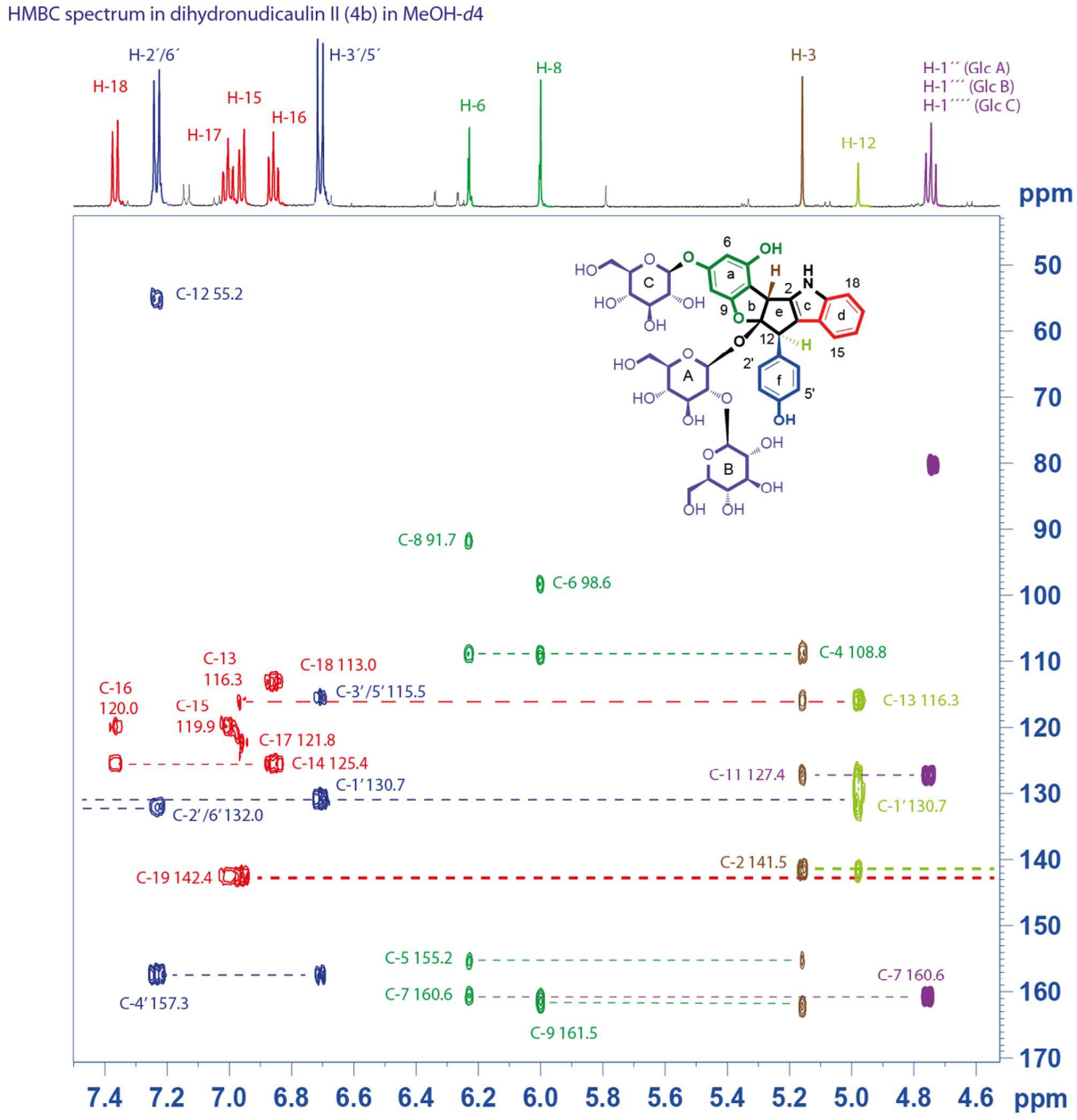

Figure S35. Selected region of the HMBC spectrum of dihydronudicaulin II (**4b**) in MeOH-d_4

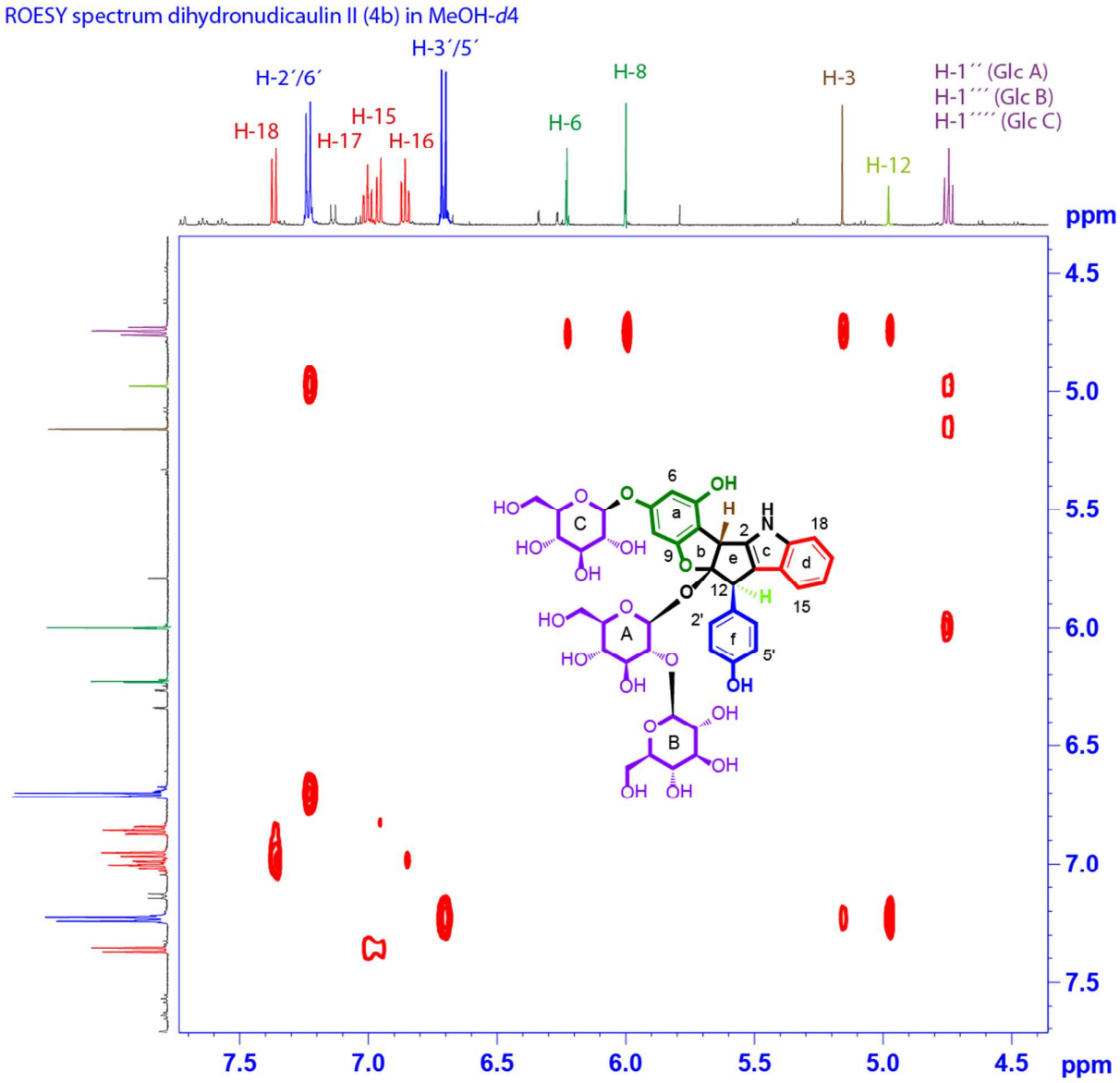

Figure S36. Selected region of the ROESY spectrum of dihydronudicaulin II (**4b**) in MeOH-d_4

S9. NMR Data of Permethylated Nudicaulins I & II

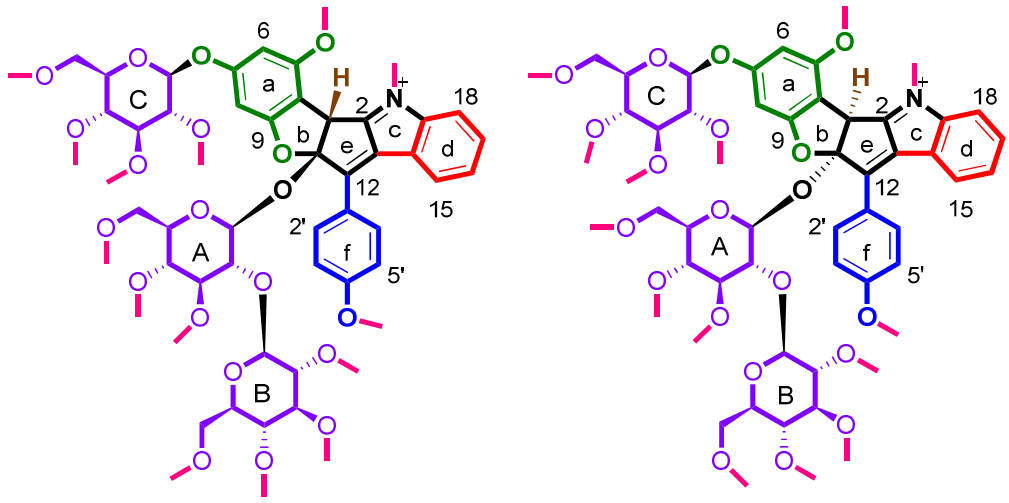

Figure S37. Structures of permethylated nudicaulins I (**5a**) & II (**5b**)

Table S4. ^{1}H NMR and ^{13}C NMR spectroscopic data (500 MHz for ^{1}H; 125 MHz for ^{13}C) of permethylated nudicaulins I (**5a**) and II (**5b**) in MeOH-d_4

	Permethylated Nudicaulin I		**Permethylated Nudicaulin II**	
No	^{1}H	^{13}C	^{1}H	^{13}C
	δ, mult.	δ	δ, mult.	δ
Aglycon				
2		177.6		177.7
3	5.74, *s*	50.1	5.69, *s*	50.0
4		101.9		102.3
5		157.9		157.7
6	6.48, *d* 1.9	96.0	6.50, *d*	95.9
7		162.6		162.5
8	6.37, *d* 1.9	93.2	6.38, *d*	92.9
9		161.5		161.6
11		125.6		124.9
12		166.7		167.4
13		132.0		132.4
14		123.1		122.7
15	8.36, *d* 7.8	125.7	8.30, *d*	125.1
16	7.78, *dd* 7.8/7.8	129.6	7.65, *dd*	129.3
17	7.78, *dd* 7.8/7.8	132.1	7.75, *dd*	131.8
18	7.93, *d*, 7.8	116.1	7.85, *d*	116.3
19		149.6		149.4
1'		123.5		123.6
2'/6'	8.61, *d-like* 9.0	138.2	8.53, *d*	137.9
3'/5'	7.31, *d-like* 9.0	116.6	7.31, *d*	116.3
4'		168.2		167.6
Me-N(1)	4.35, *s*	35.7	4.28, *s*	35.2
Me-O(5)	4.05, *s*	56.6	4.08, *s*	56.5
Me-O(4')	4.01, *s*	56.1	4.01, *s*	56.0
1''	4.81	98.3	5.03, *d* 7.8	96.6
1'''	4.57, *d*, 7.8	103.9	4.66, *d* 7.9	103.1
1''''	4.89	101.6	4.92	101.5

Some chemical shifts were obtained from 2D NMR spectra (COSY, HSQC, HMBC). Most chemical shifts and coupling constants of permethylated Glc units were not determined.

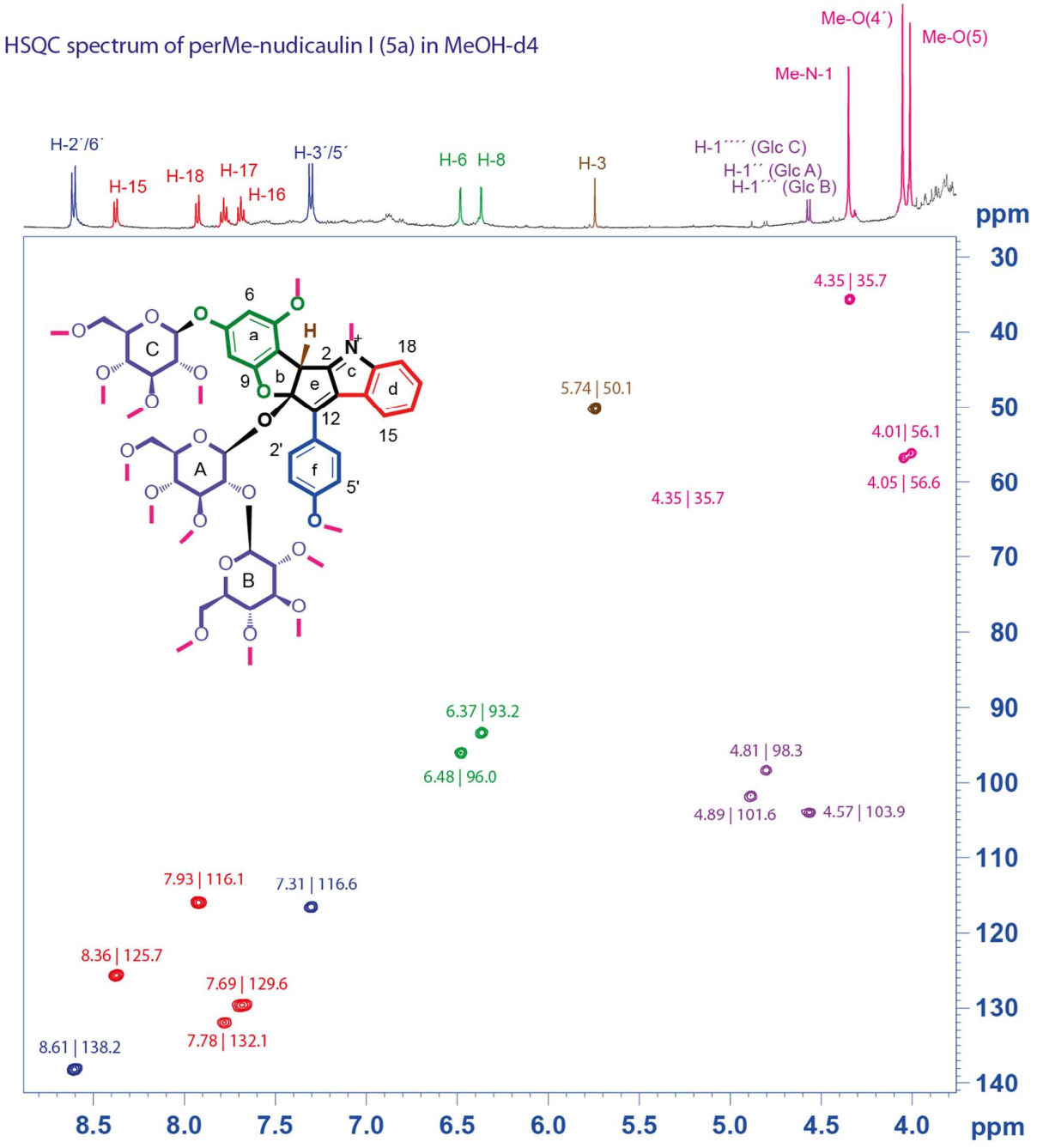

Figure S38. Selected region of the HSQC spectrum of permethylated nudicaulin I (**5a**) in MeOH-d_4

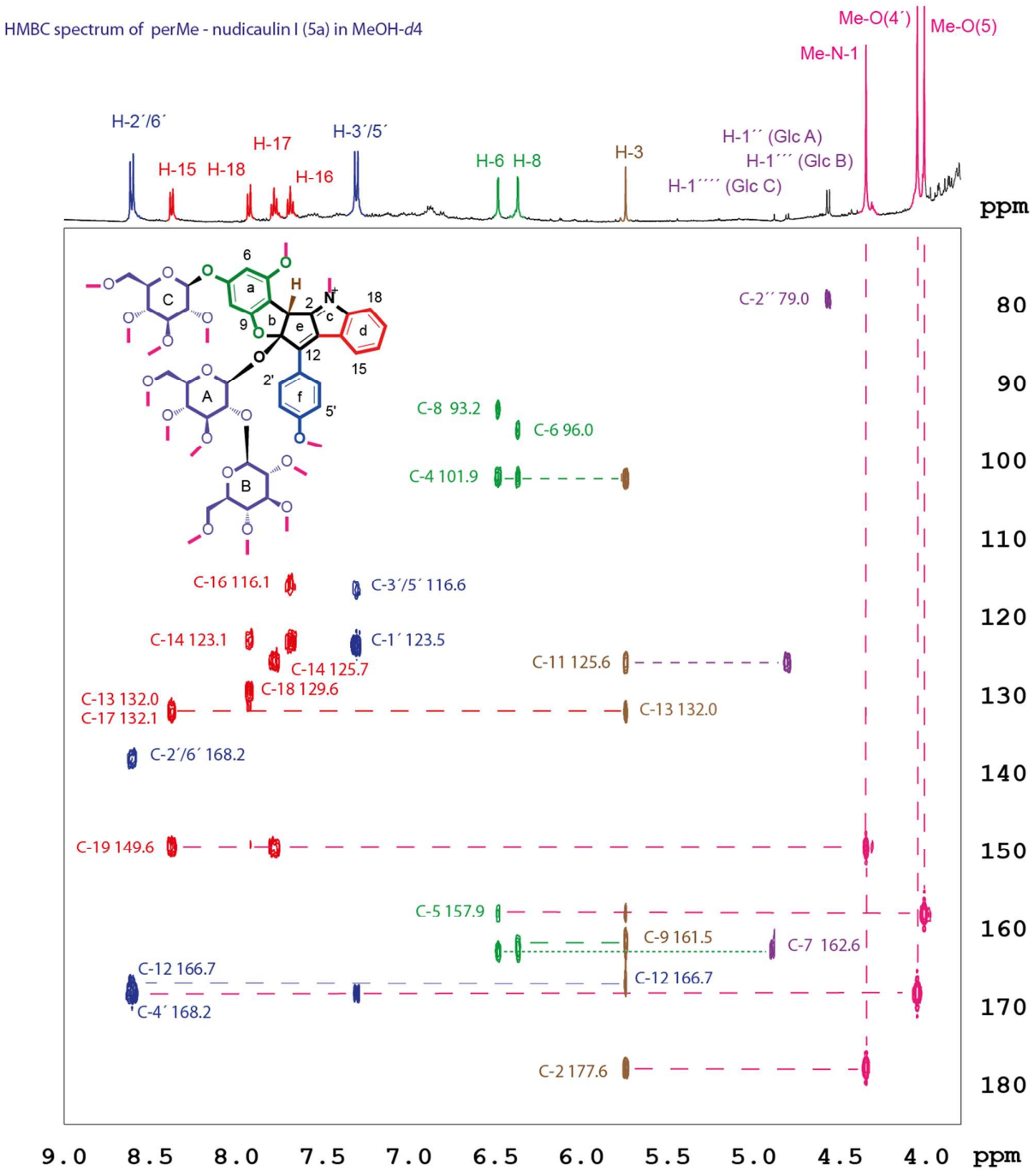

Figure S39. Selected region of the HMBC spectrum of permethylated nudicaulin I (**5a**) in MeOH-d_4

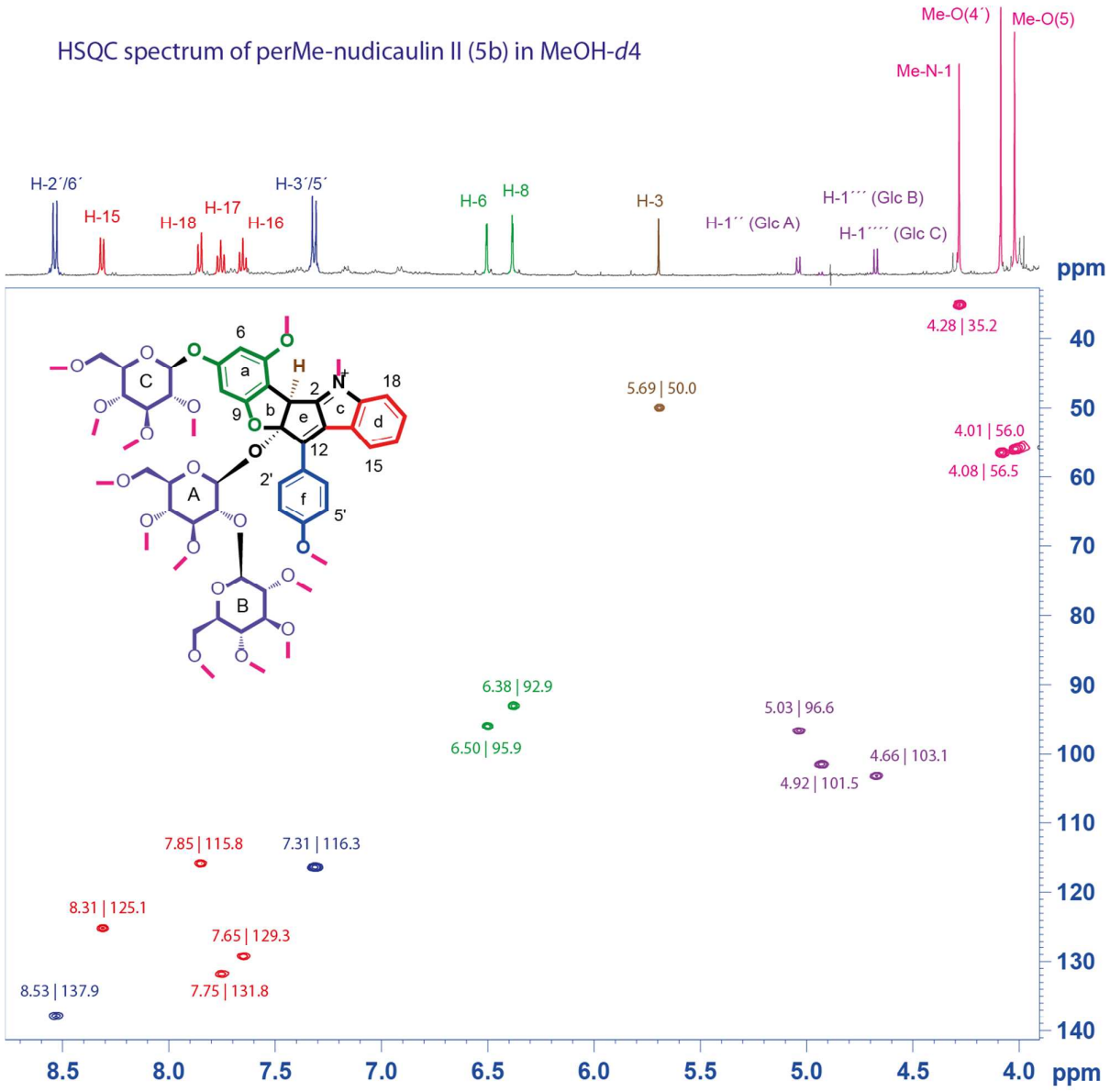

Figure S40. Selected region of the HSQC spectrum of permethylated nudicaulin II (**5b**) in MeOH-d_4

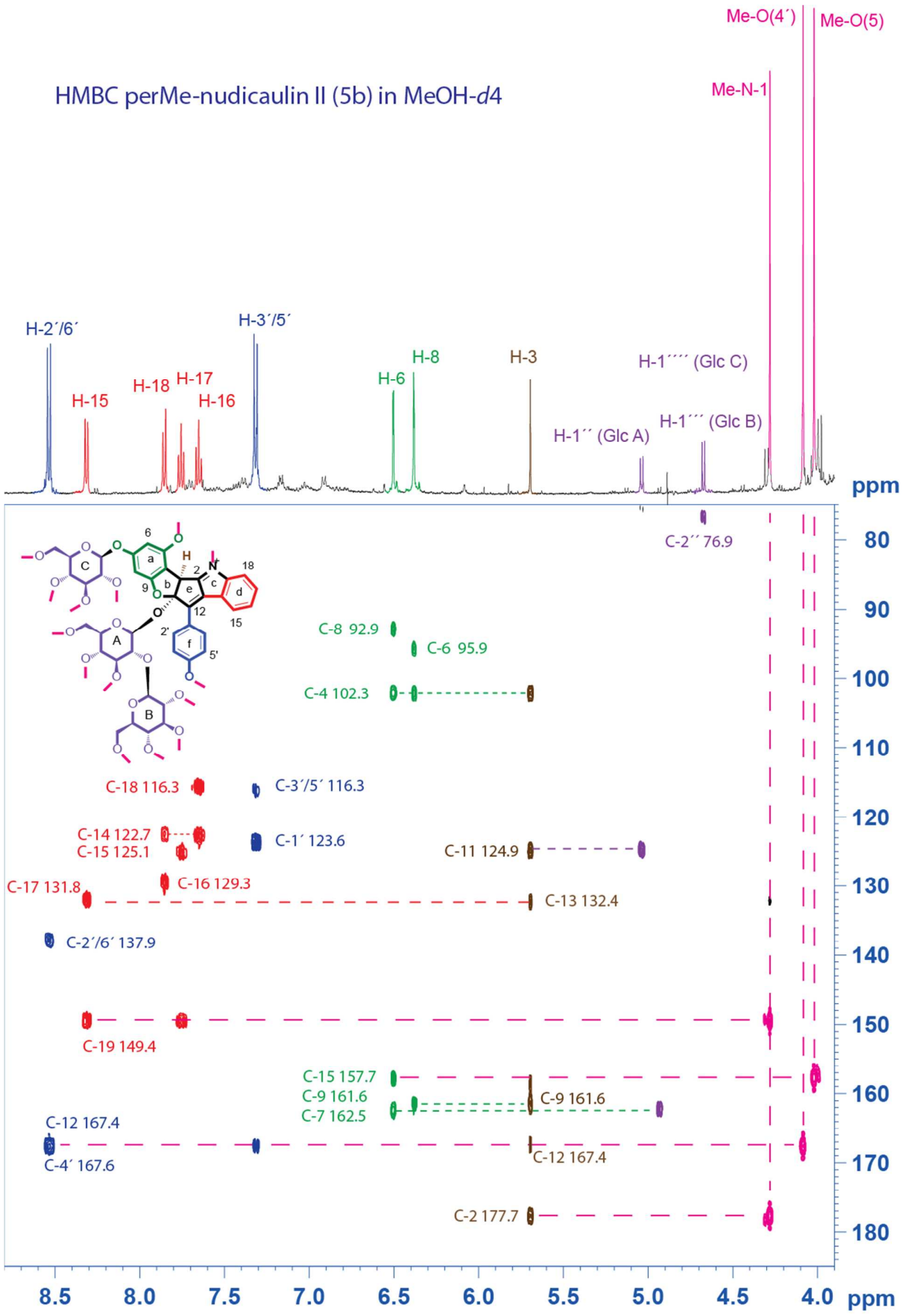

Figure S41. Selected region of the HMBC spectrum of permethylated nudicaulin II (**5b**) in MeOH-d_4

S10. MS and UV/Vis Data of Nudicaulins

1. Nudicaulin I (**3a**)
   HR-ESI-MS: *m/z* 872.26031 ($[M+H]^+$, $C_{41}H_{46}O_{20}N$), calcd *m/z* 872.26079;
   UV/vis: max at 211, 458, 257, 336 nm
2. Nudicaulin II (**3b**)
   HR-ESI-MS: found *m/z* 872.26031 ($[M+H]^+$, $C_{41}H_{46}O_{20}N$), calcd *m/z* 872.26079);
   UV/vis: max at 212, 459, 257, 335 nm
3. Partially deglucosylated nudicaulin I (**6a**)
   HR-ESI-MS: found *m/z* 548.15427 ($[M+H]^+$, $C_{29}H_{26}O_{10}N$), calcd *m/z* 548.15512);
   UV/vis: max at 210, 457, 257, 335 nm
4. Partially deglucosylated nudicaulin II (**6b**)
   HR-ESI-MS: found *m/z* 548.15447 ($[M+H]^+$, $C_{29}H_{26}O_{10}N$), calcd *m/z* 548.15512);
   UV/vis: max at 208, 456, 257, 334 nm
5. Dihydronudicaulin I (**4a**)
   HR-ESI-MS: found *m/z* 874.27482 ($[M+H]^+$, $C_{41}H_{48}NO_{20}$), calcd *m/z* 874.27642);
   UV/vis: max at 255, 211, 277 nm
6. Dihydronudicaulin II (**4b**)
   HR-ESI-MS: found *m/z* 874.27479 ($[M+H]^+$, $C_{41}H_{48}NO_{20}$), calcd *m/z* 874.27642;
   UV/vis: max at 255, 211, 277 nm
7. Permethylated nudicaulin I (**5a**)
   HR-ESI-MS: found *m/z* 1068.47110 ($[M]^+$, $C_{55}H_{74}NO_{20}^+$), calcd *m/z* 1068.47987;
   UV/vis: max at 207, 454, 258, 337 nm
8. Permethylated nudicaulin II (**5b**)
   HR-ESI-MS: found *m/z* 1068.47283 ($[M]^+$, $C_{55}H_{74}NO_{20}^+$), calcd *m/z* 1068.47987;
   UV/vis: max at 207, 454, 258, 337 nm