Supplementary Material

Structure assignment and H/D-exchange behavior of several glycosylated polyphenols

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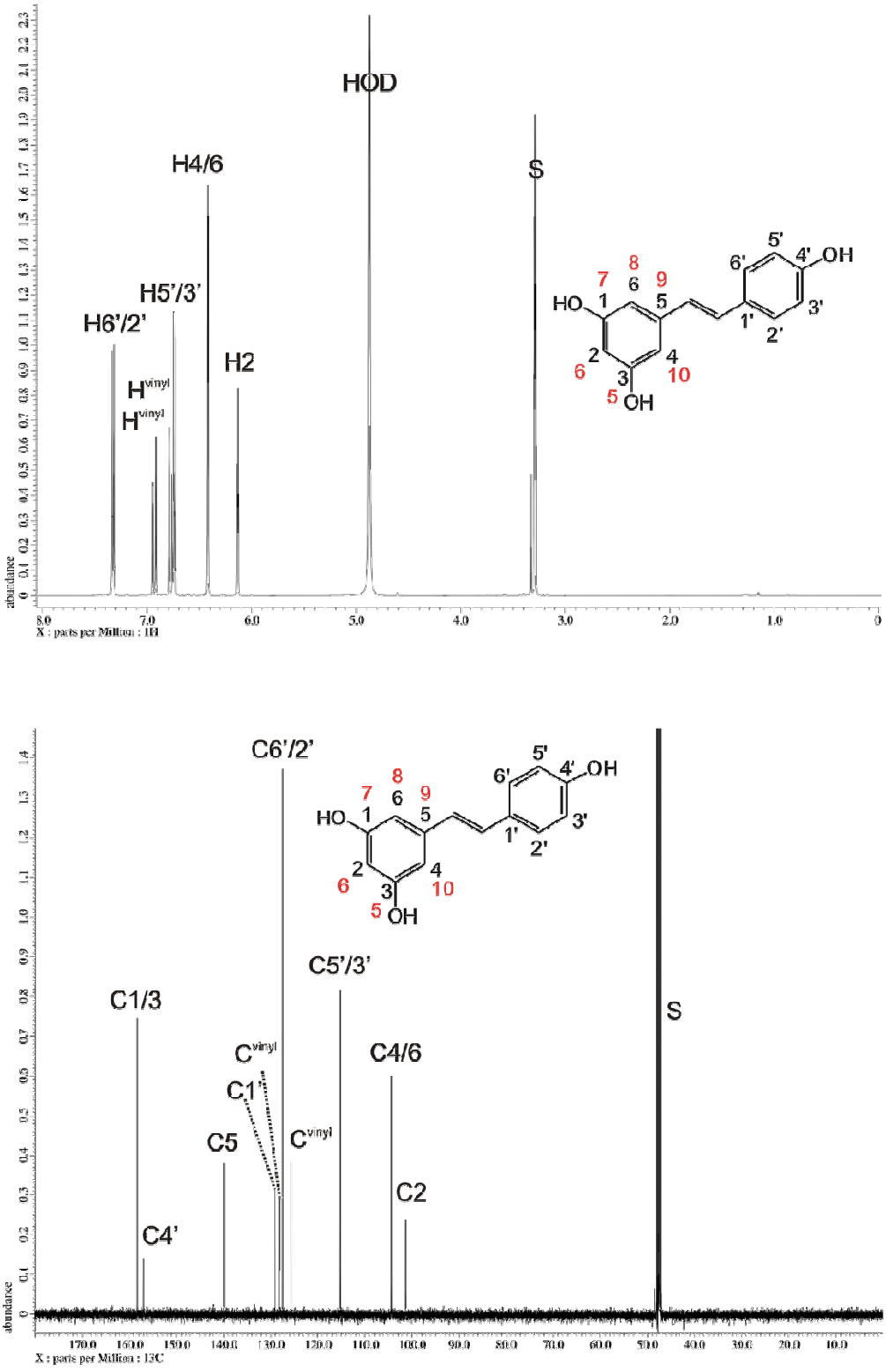


Figure 1S. Top: ^{1}H-NMR spectrum; bottom: ^{13}C-NMR spectrum of resveratrol (**1**) in MeOD.

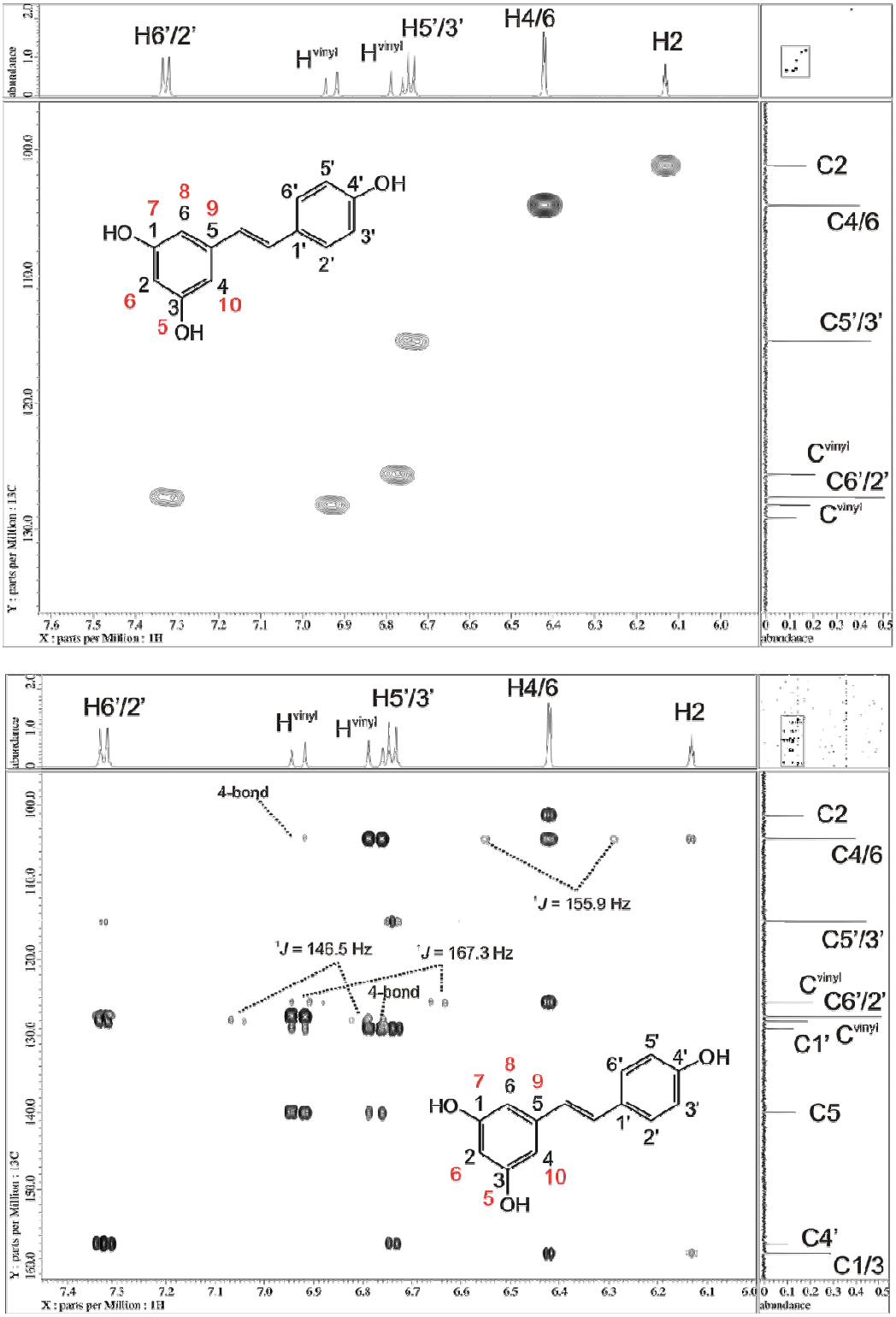


Figure 2S. Top: $^{1}H/^{13}C$-HMQC; bottom: $^{1}H/^{13}C$-HMBC of resveratrol (**1**) in MeOD.

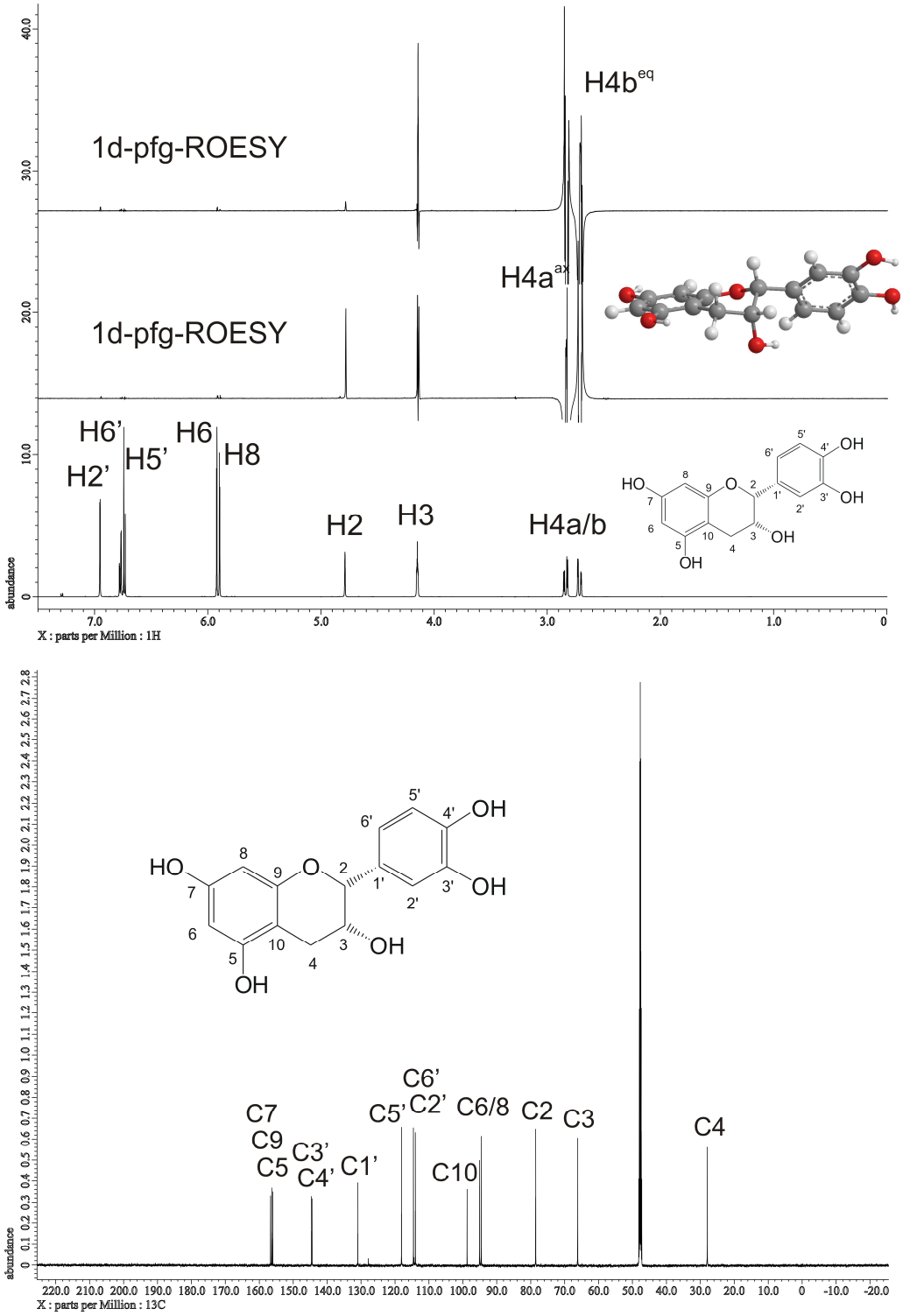


Figure 3S. Top: ^{1}H-NMR spectrum and AM1-minimized molecular model; inset: 1D-pfg-ROESY spectra with irradiation at H4^{e} and H4^{a}; bottom: ^{13}C-NMR spectrum of (-)-epicatechin (**2**) in MeOD.

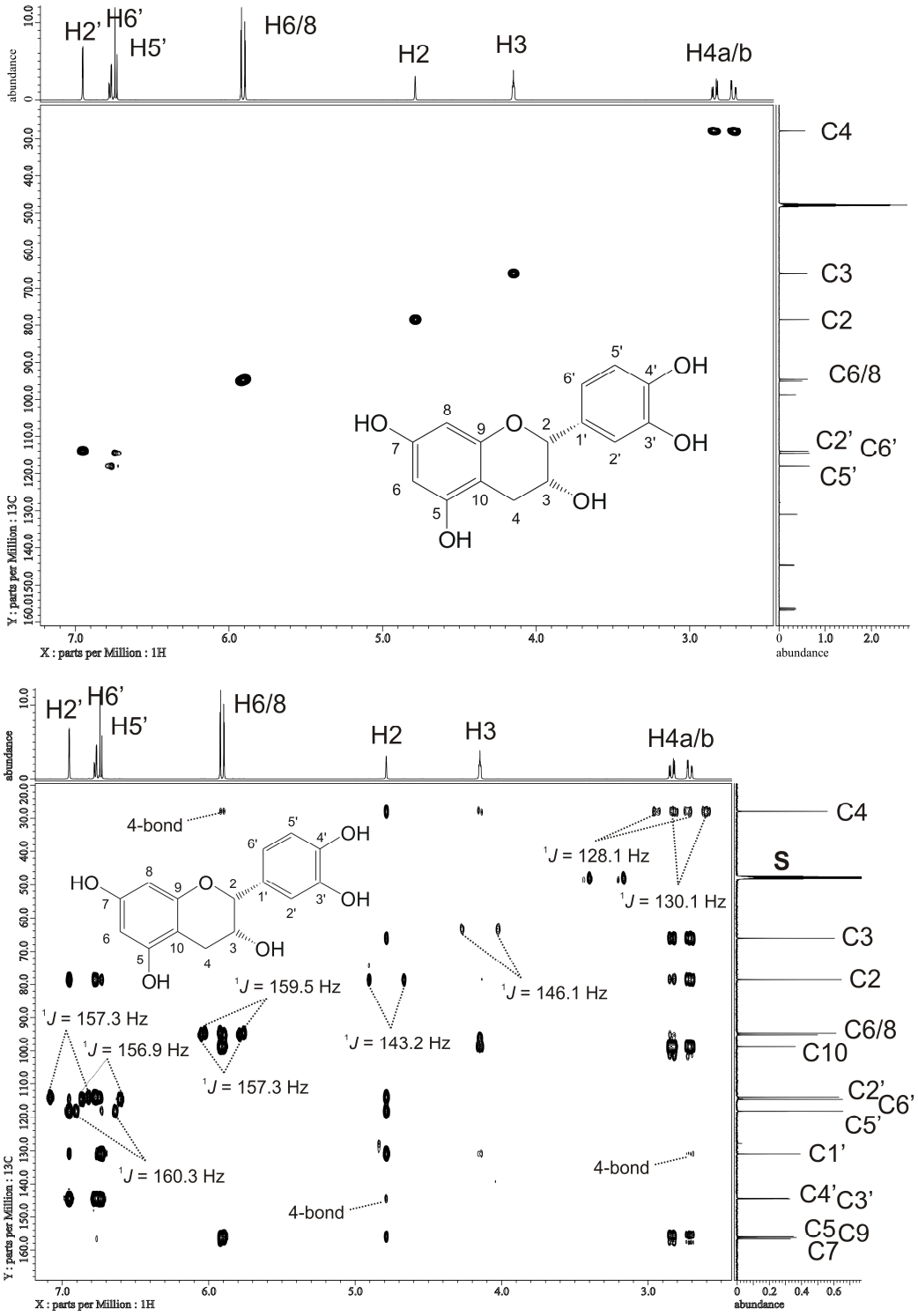


Figure 4S. Top: ^{1}H/^{13}C-HMQC; bottom: ^{1}H/^{13}C-HMBC of (-)-epicatechin (**2**) in MeOD.

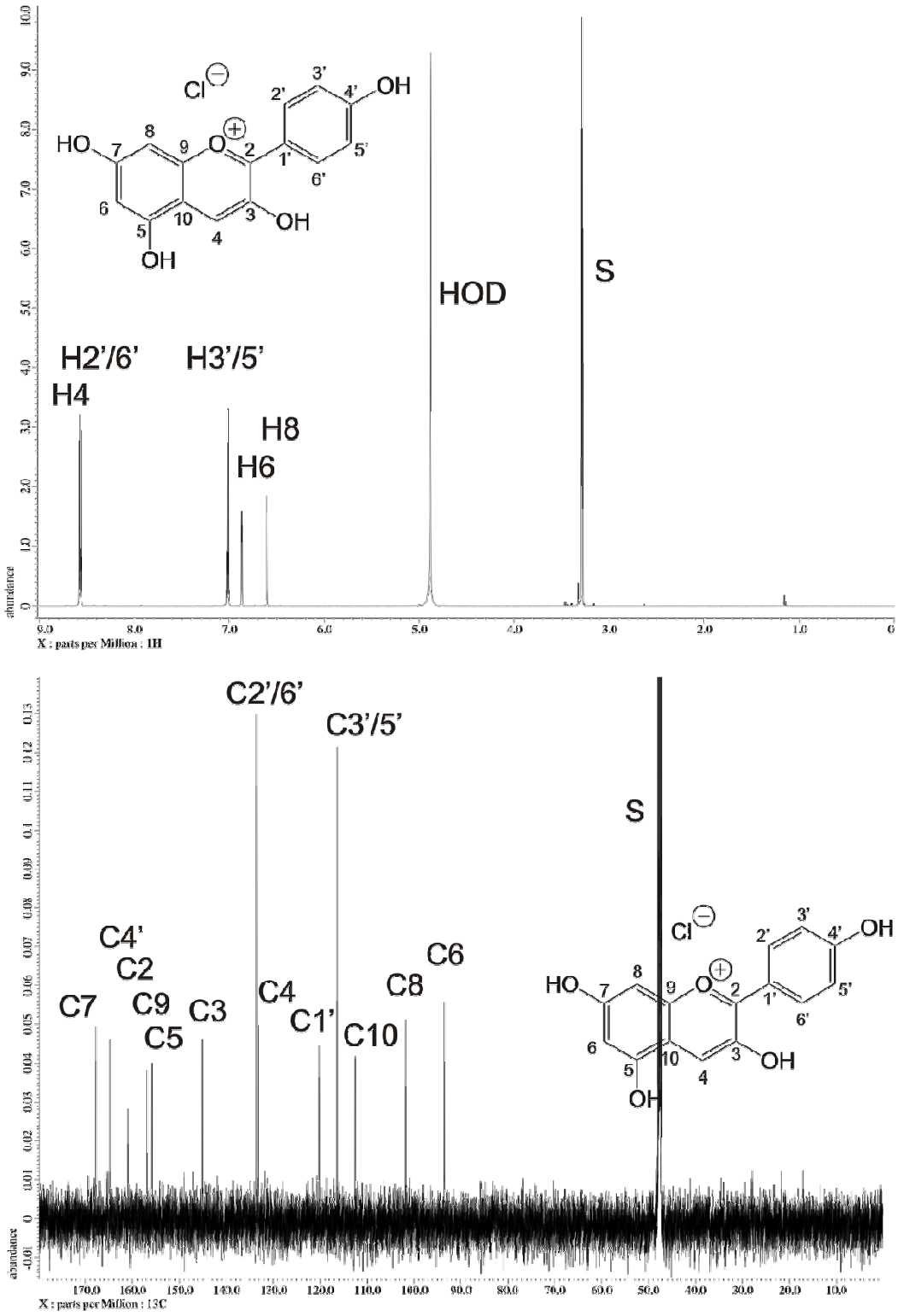


Figure 5S. Top: ^{1}H-NMR spectrum; bottom: ^{13}C-NMR spectrum of pelargonidin chloride in MeOD.

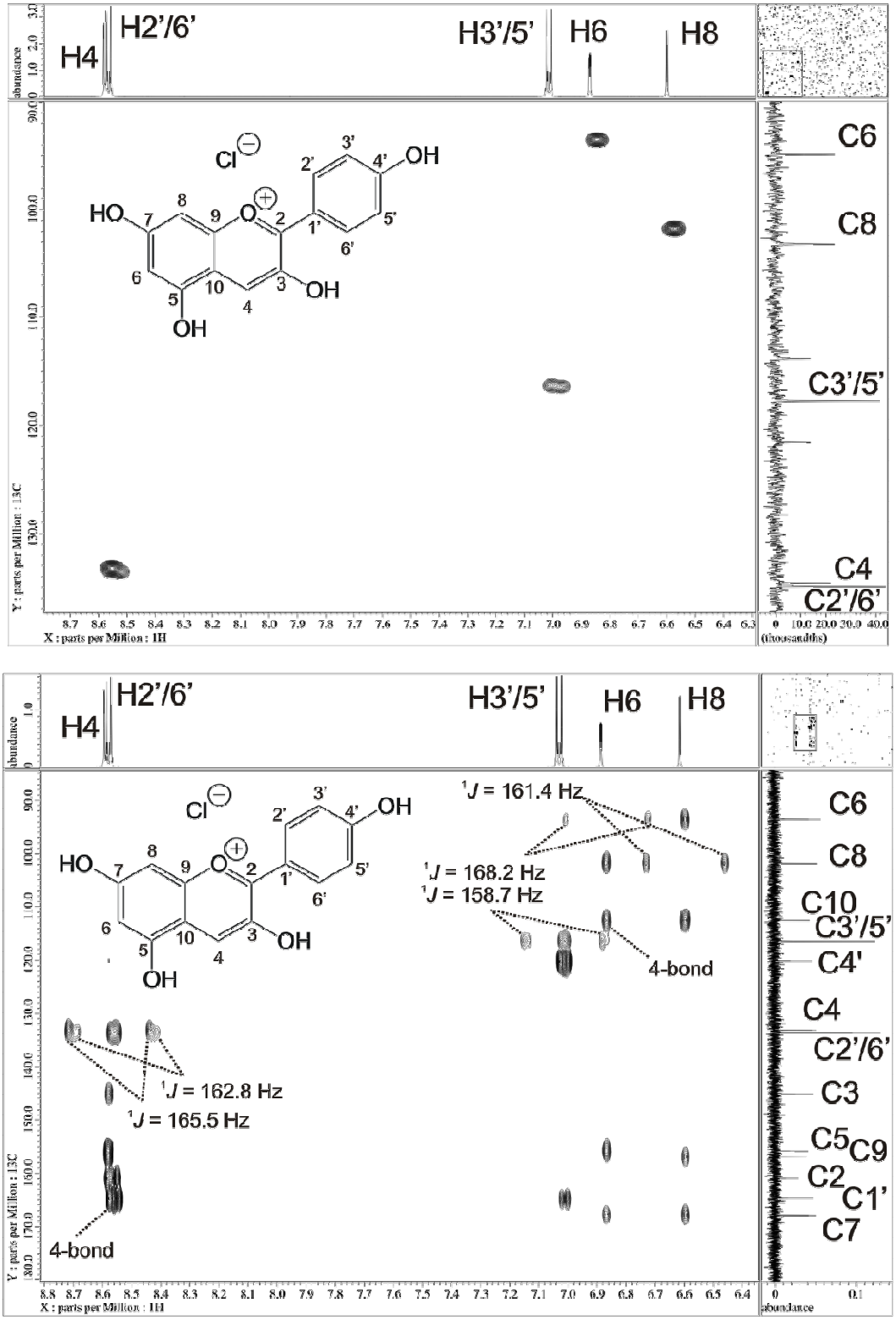


Figure 6S. Top: $^1H/^{13}C$-HMQC; bottom: $^1H/^{13}C$-HMBC of pelargonidin chloride in MeOD.

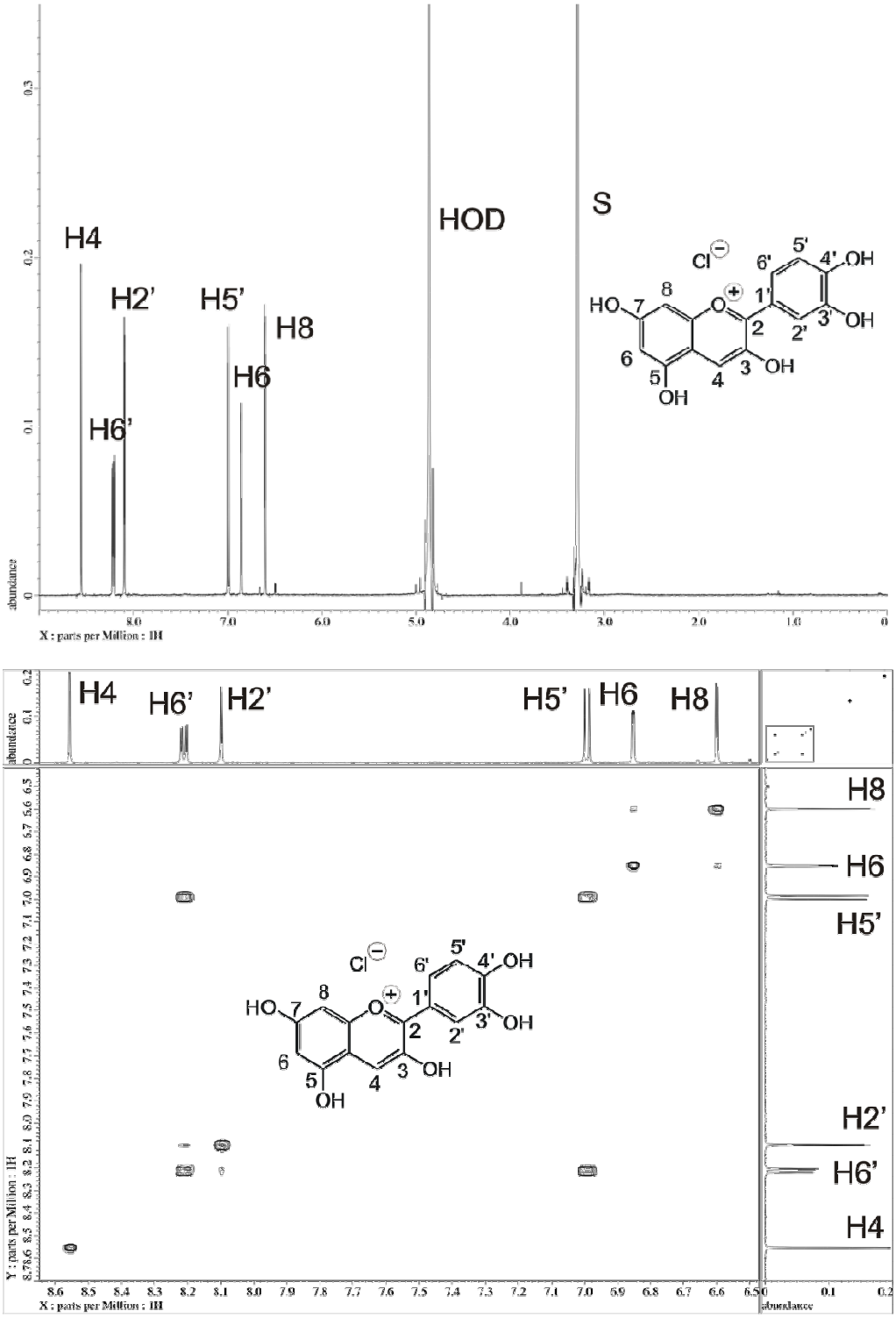


Figure 7S. Top: ^{1}H-NMR spectrum; bottom: ^{1}H-^{1}H-COSY-NMR spectrum of cyanidin chloride in MeOD.

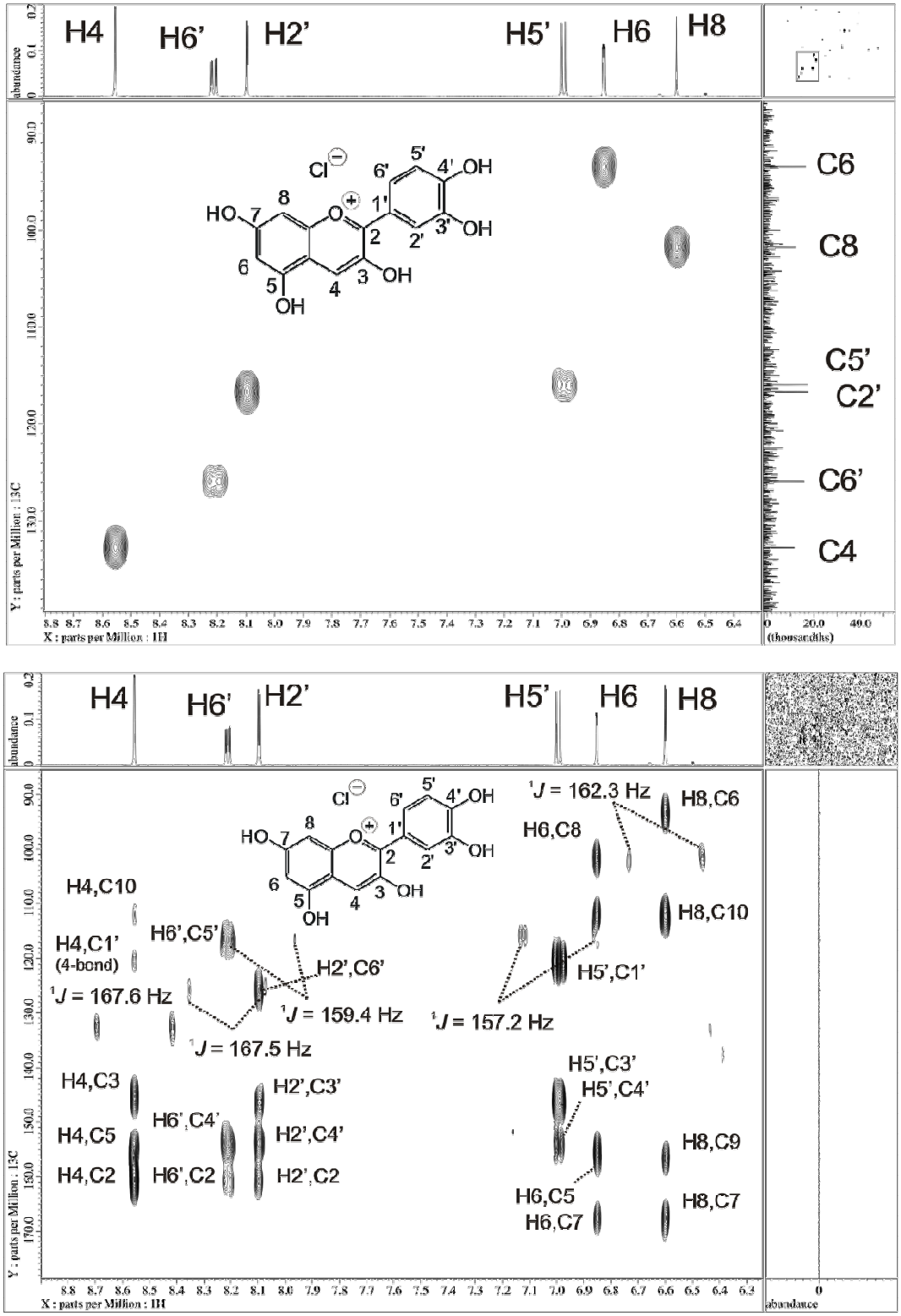


Figure 8S. Top: $^{1}H/^{13}C$-HMQC; bottom: $^{1}H/^{13}C$-HMBC of cyanidin chloride in MeOD.

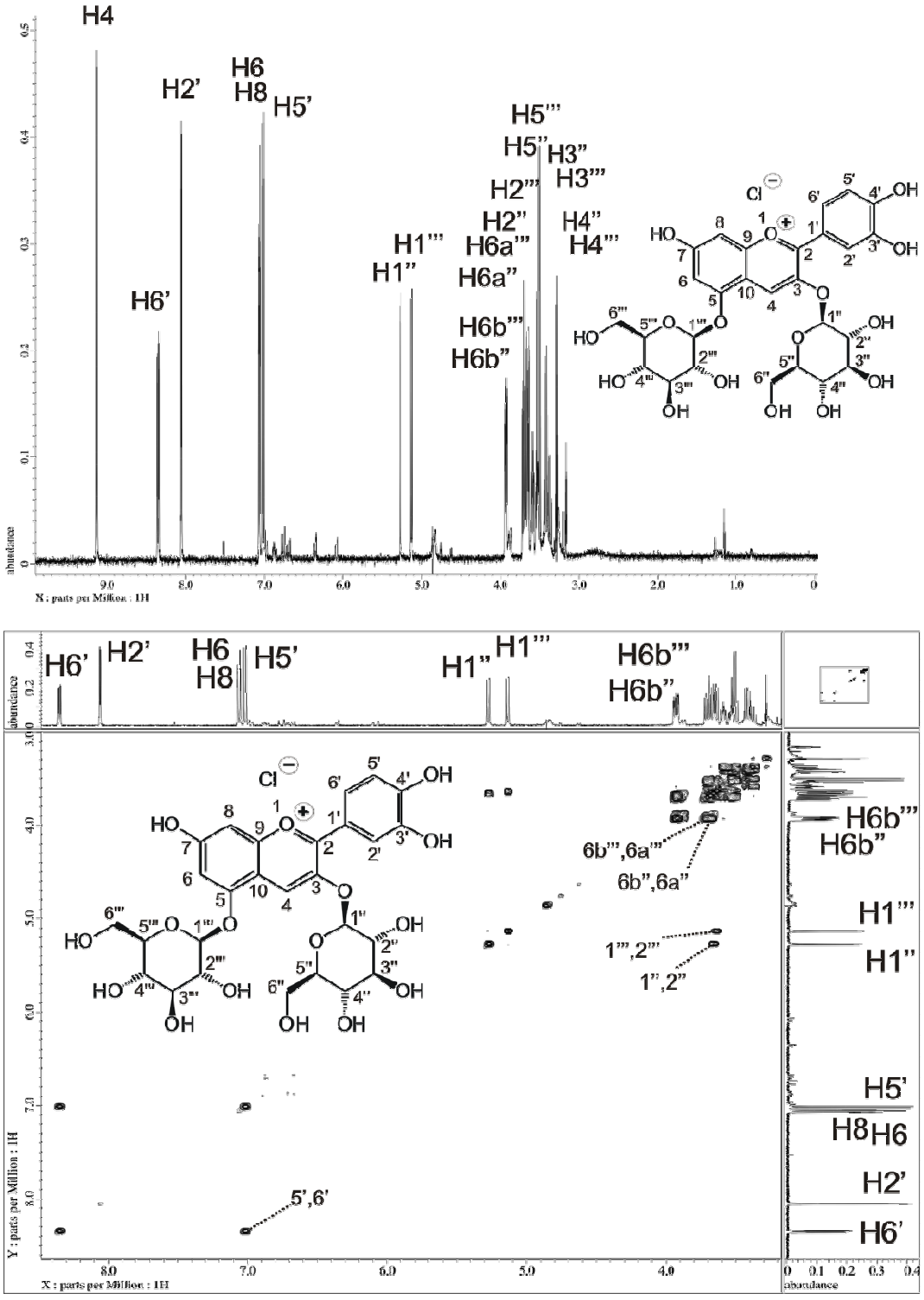


Figure 9S. Top: ^{1}H-NMR spectrum; bottom: ^{1}H-^{1}H-COSY NMR spectrum of cyanin chloride in MeOD.

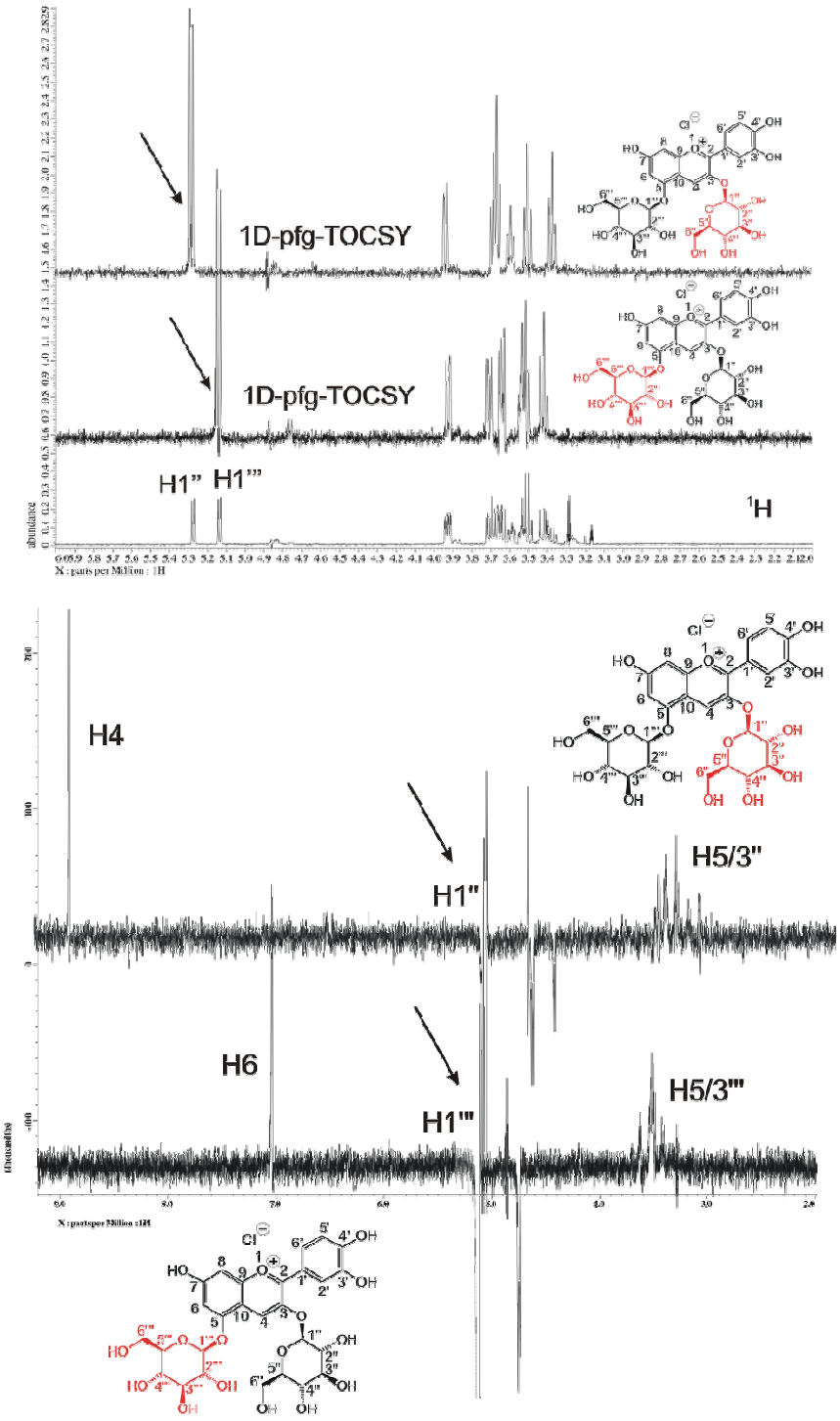


Figure 10S. Top: ^{1}H-pfg-TOCSY of cyanin chloride in MeOD; bottom: ^{1}H-pfg-rOe of cyanin chloride in MeOD. The enhancements on H4 and H6 are clearly visible.

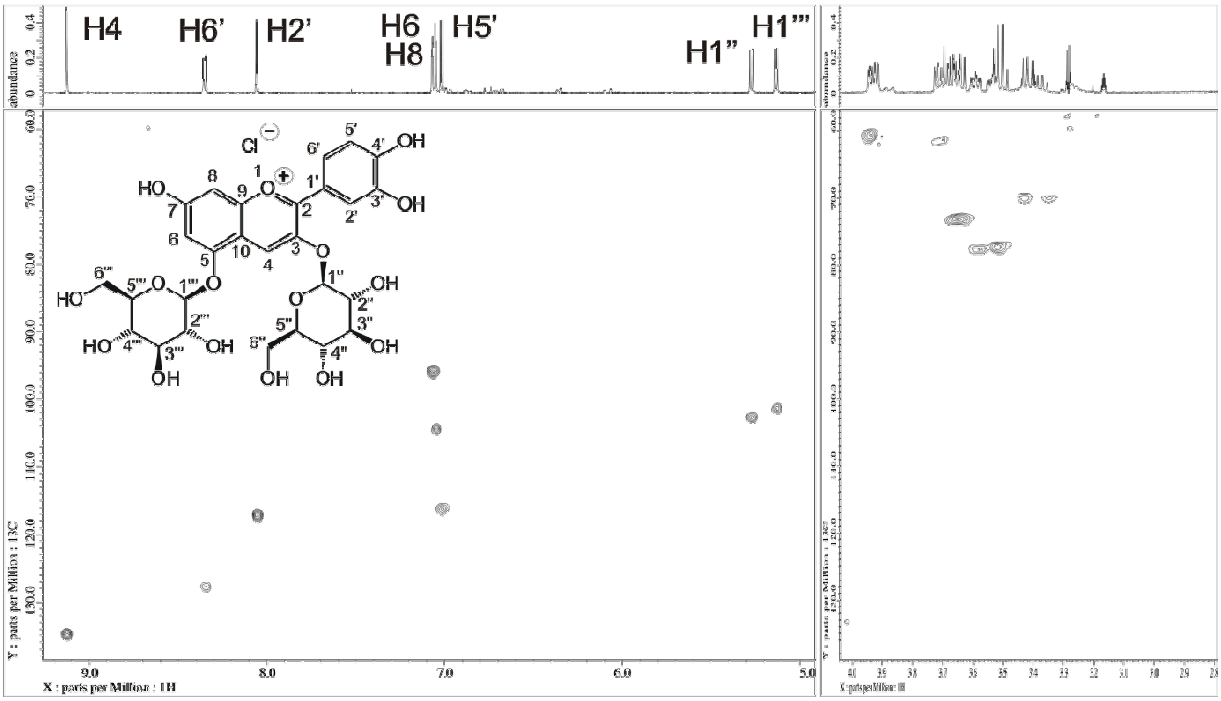


Figure 11S. $^{1}H/^{13}C$-HMQC of cyanin chloride in MeOD.

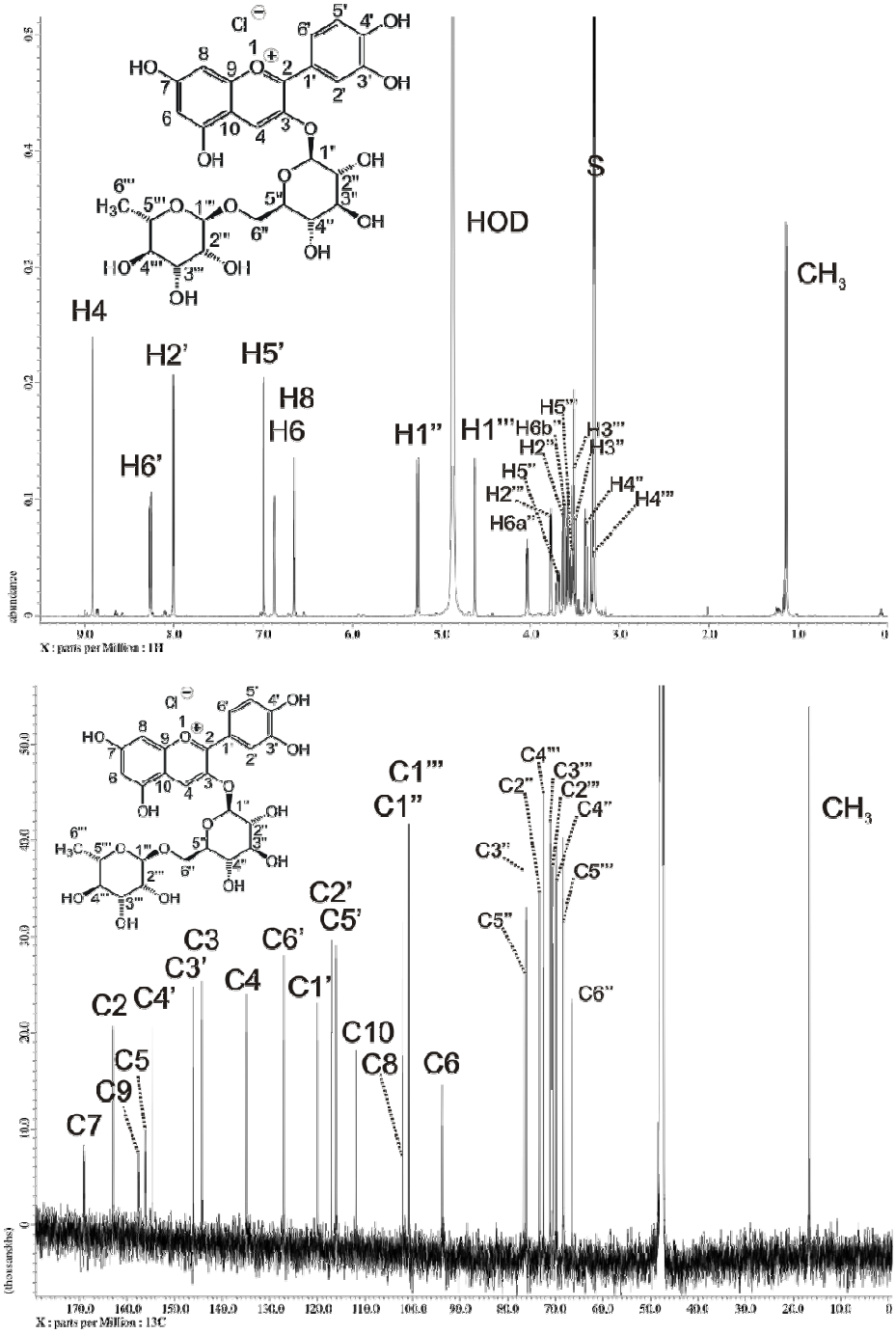


Figure 12S. Top: ^{1}H-NMR spectrum; bottom: ^{13}C-NMR spectrum of keracyanin chloride in MeOD.

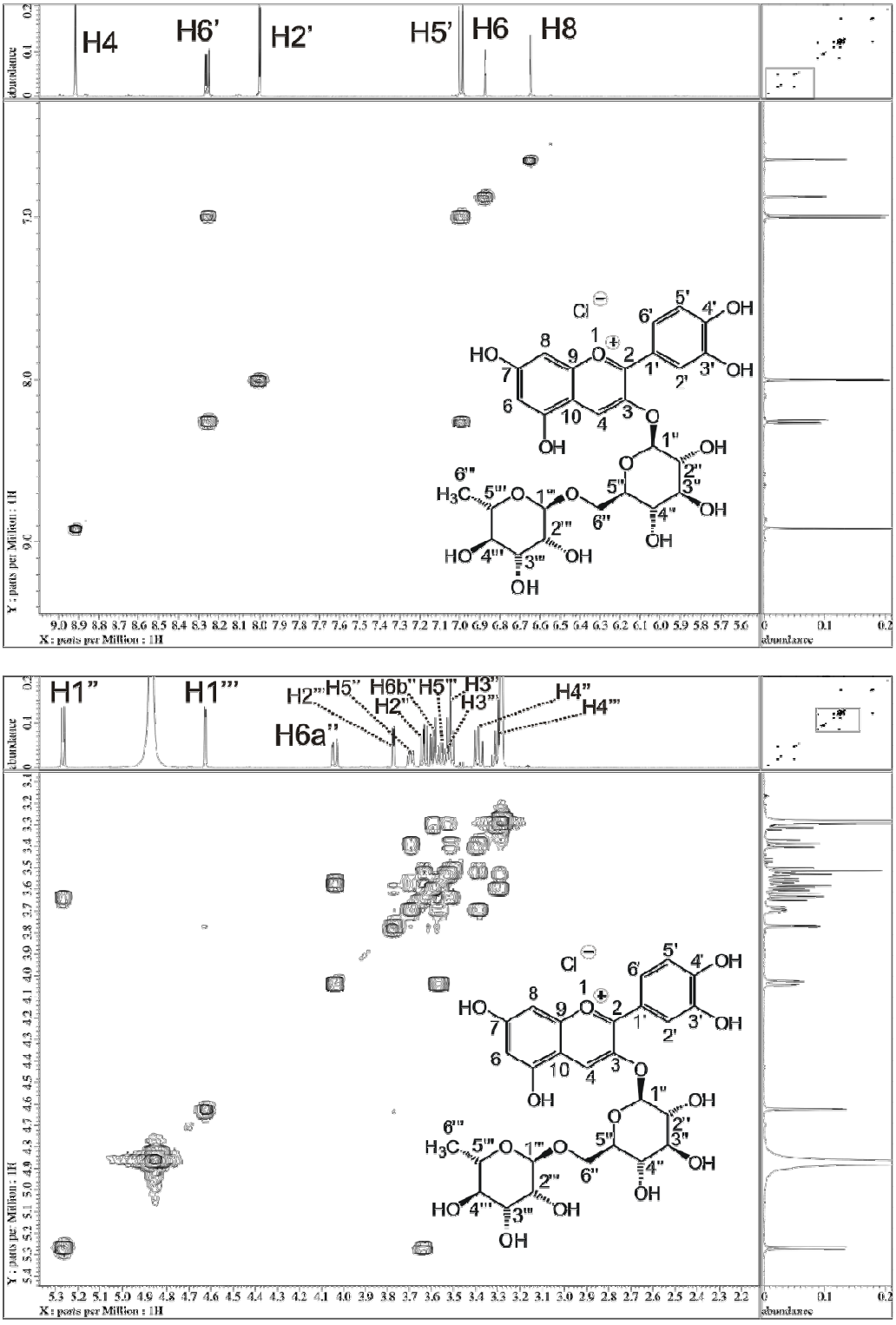


Figure 13S. ^{1}H-^{1}H-COSY NMR spectrum of keracyanin chloride in MeOD.

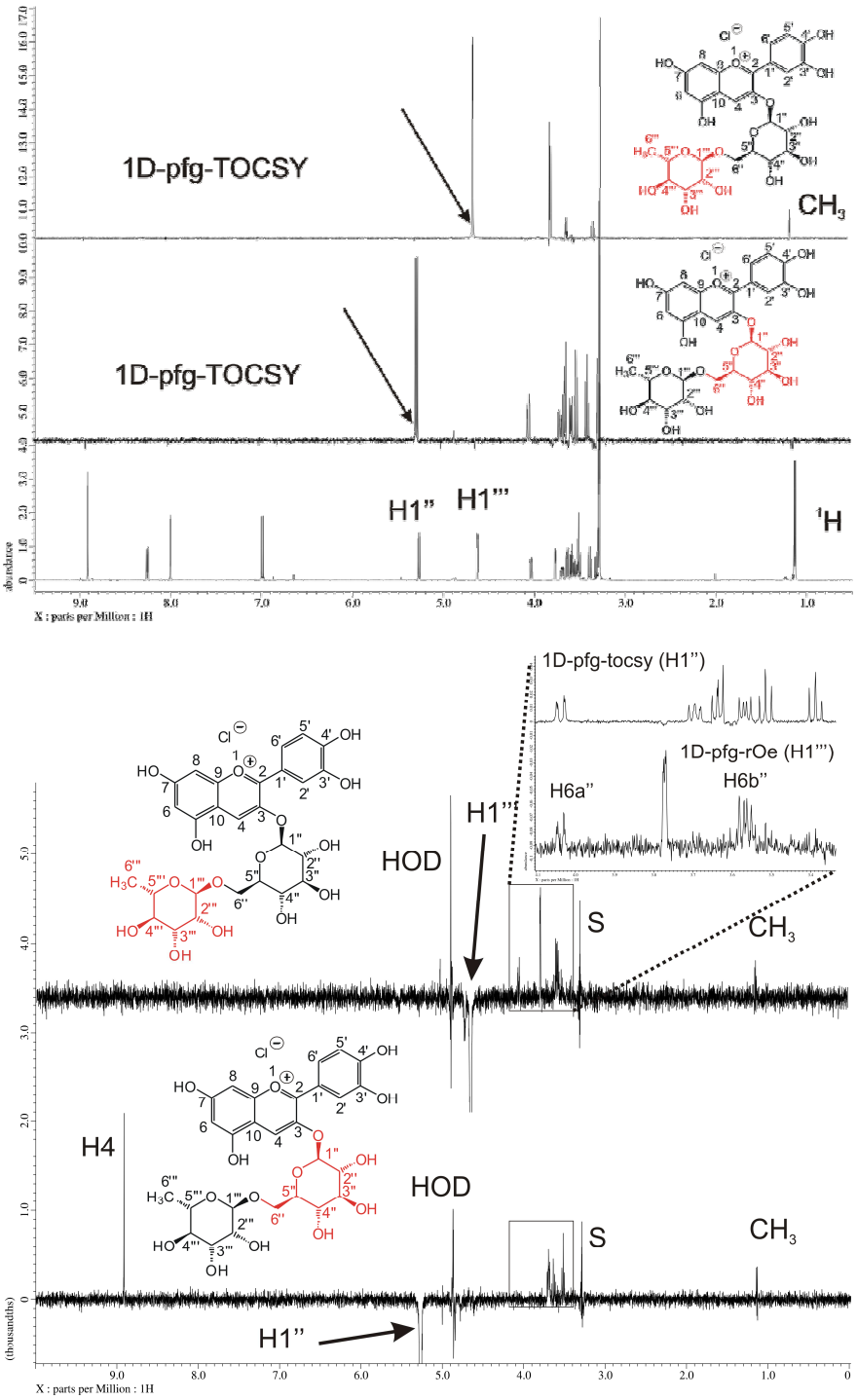


Figure 14S. Top: ^{1}H-pfg-TOCSY of keracyanin chloride in MeOD; bottom: ^{1}H-pfg-rOe of keracyanin chloride in MeOD. The enhancements on H4 and H6 are clearly visible.

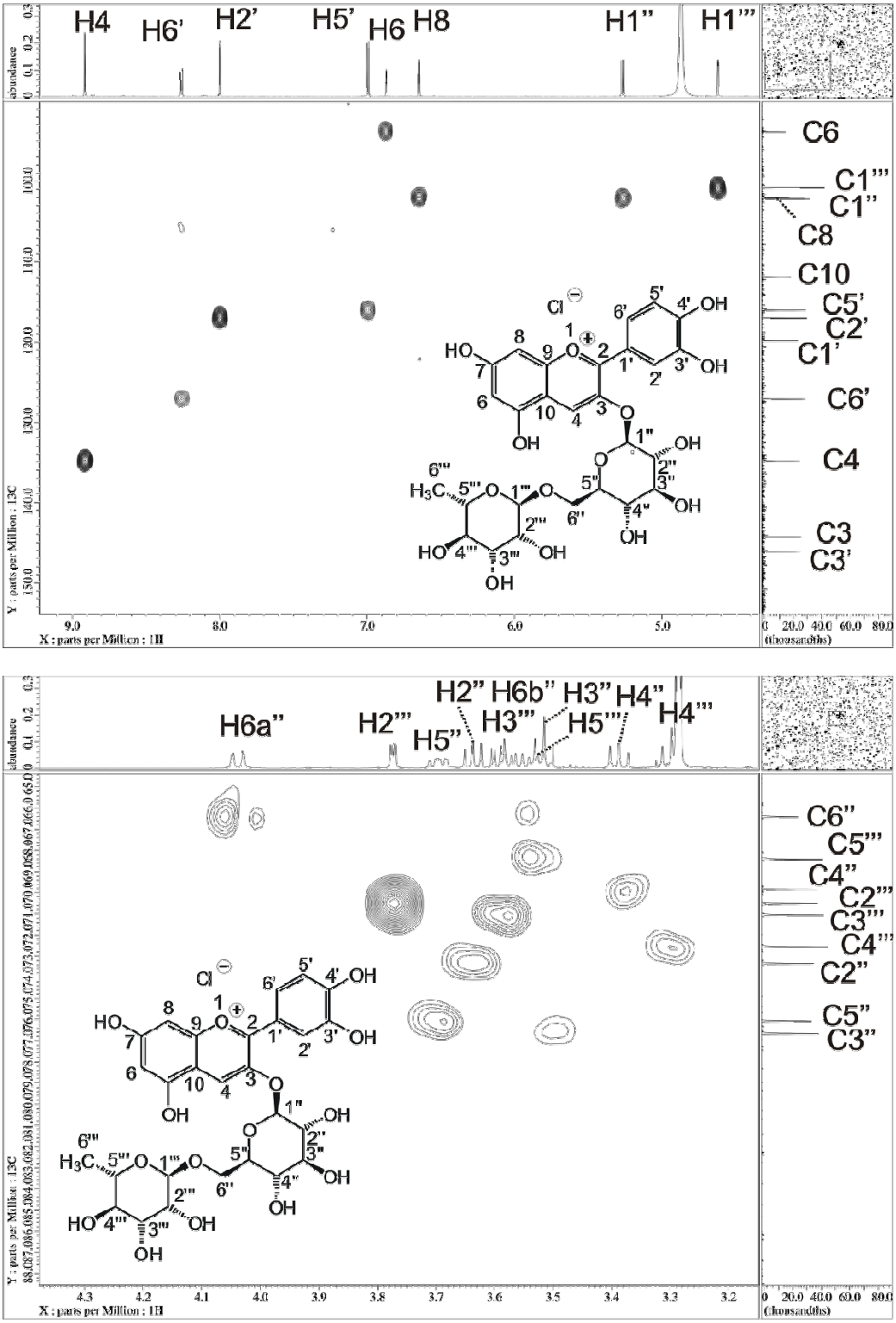


Figure 15S. ^{1}H-^{13}C-HMQC NMR spectrum of keracyanin chloride in MeOD.

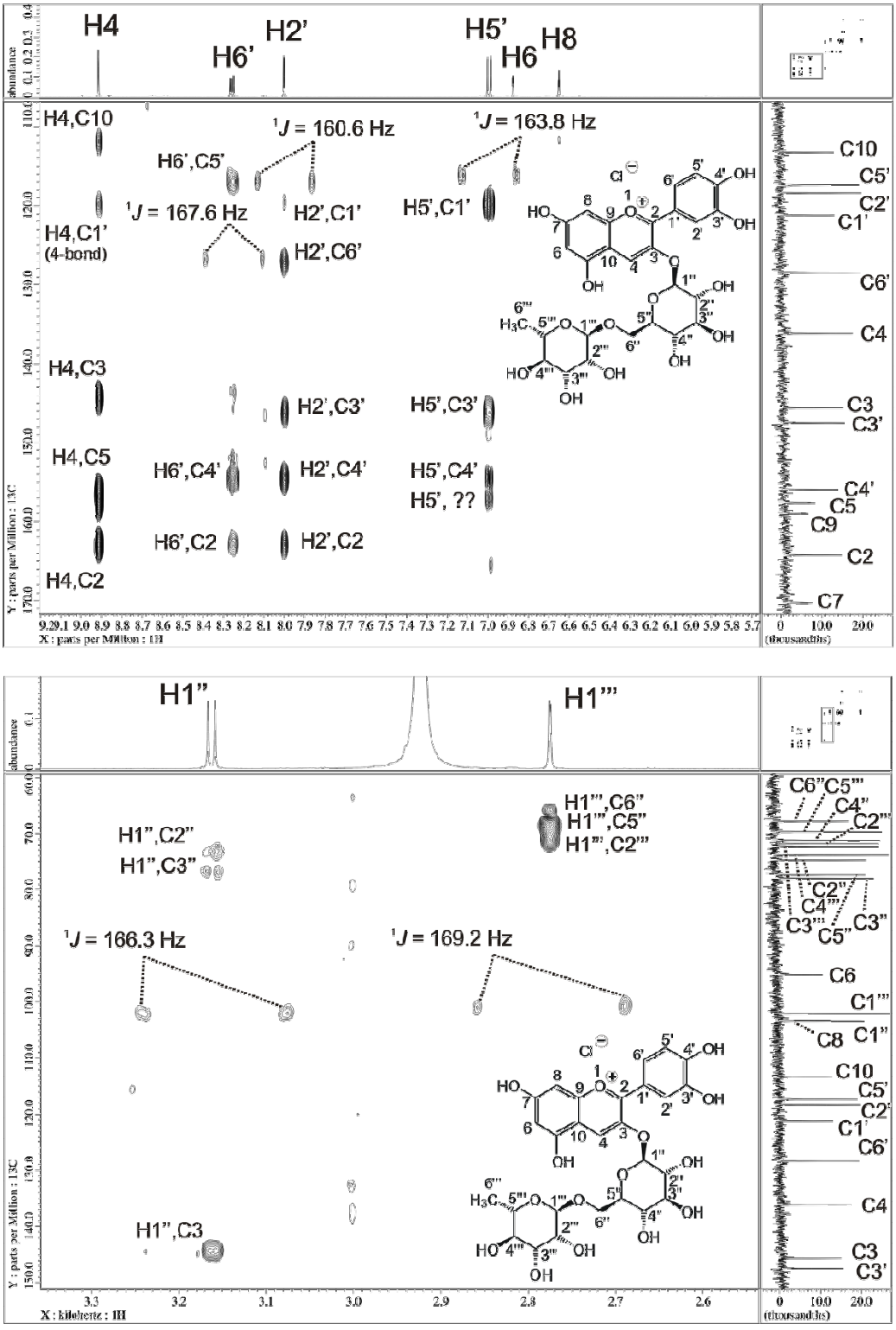


Figure 16S. ^{1}H-^{13}C-HMBC NMR spectrum of keracyanin chloride in MeOD.

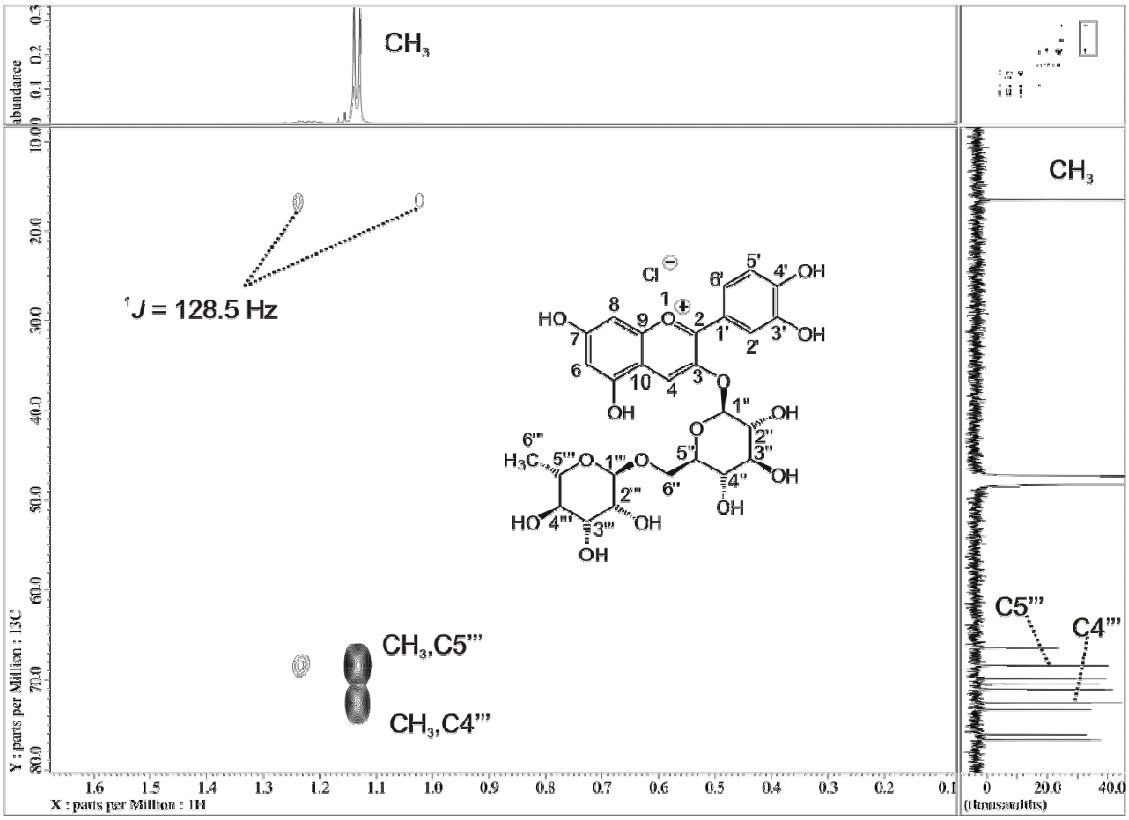


Figure 16S cont'd. ^{1}H-^{13}C-HMBC NMR spectrum of keracyanin chloride in MeOD.

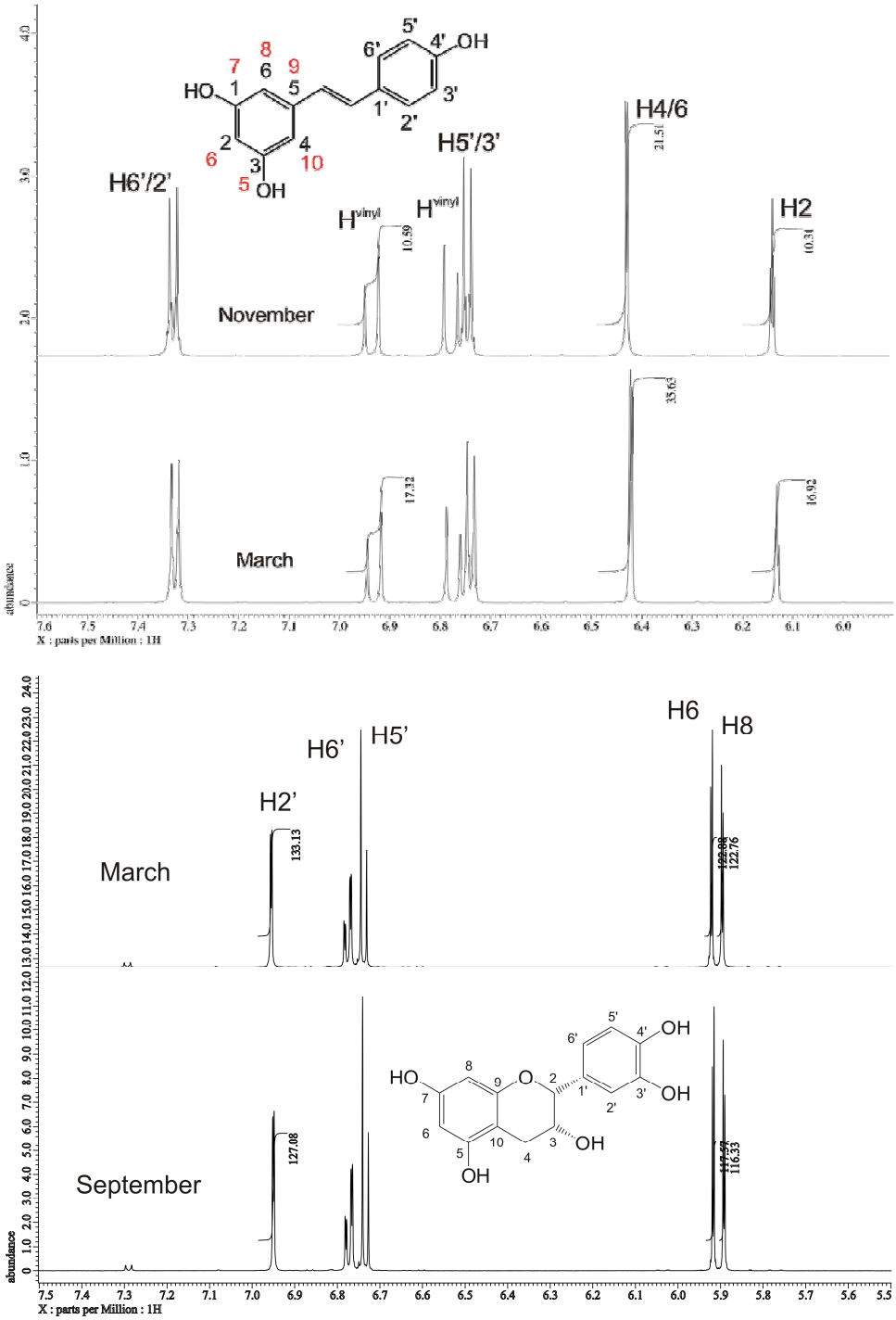


Figure 18S. Absence of H/D-exchange for resveratrol (**1**, top) and for (-)-epicatechin (**2**, bottom) in the NMR tube (MeOD).

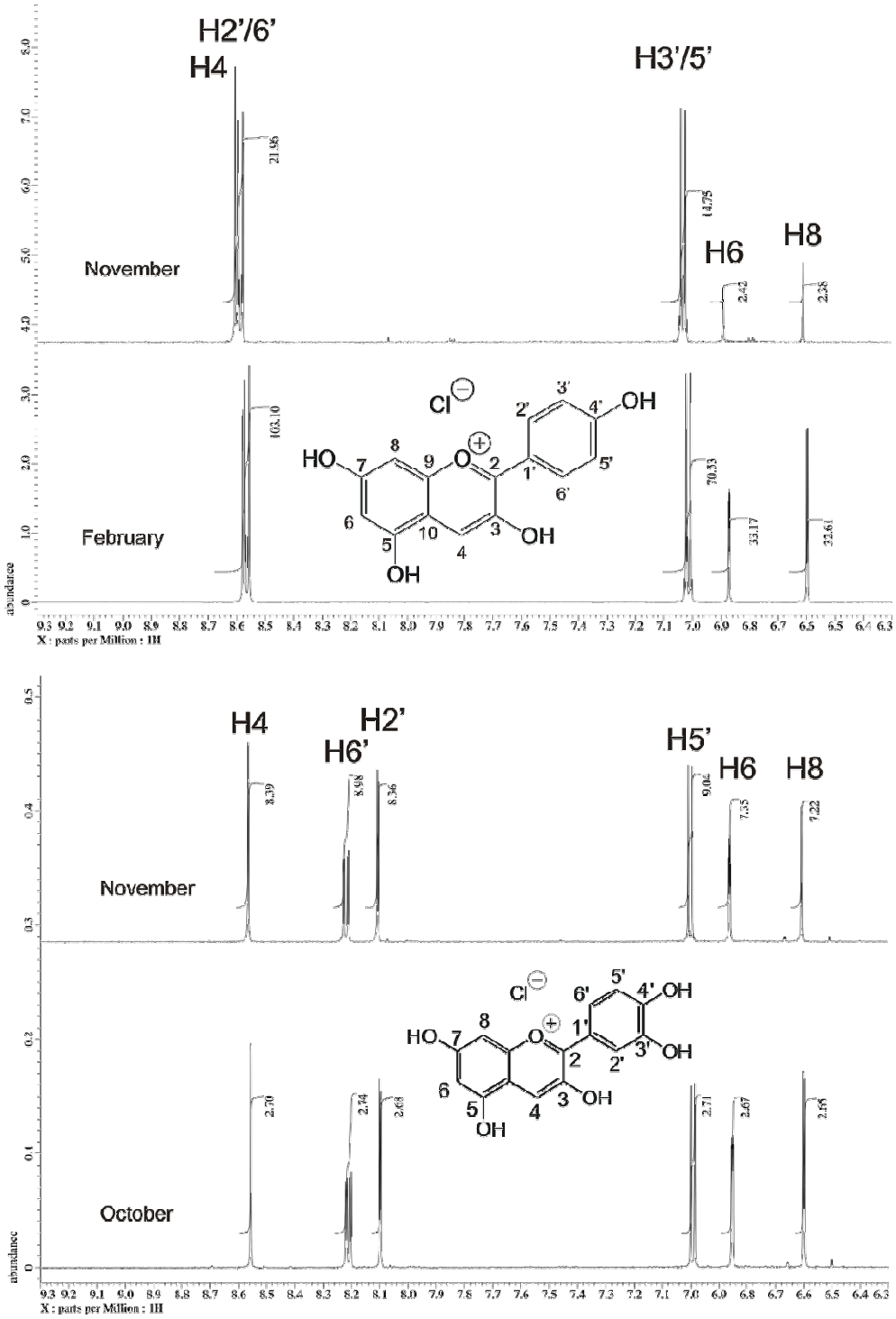


Figure 19S. Top: H/D-exchange for pelargonidin chloride (**3**) in the NMR tube (MeOD). Significant exchange was observed after about 8 months; bottom: H/D-exchange for cyanidin chloride (**4**) in the NMR tube (MeOD). Significant exchange was observed for both H6 and H8 after less than one month.

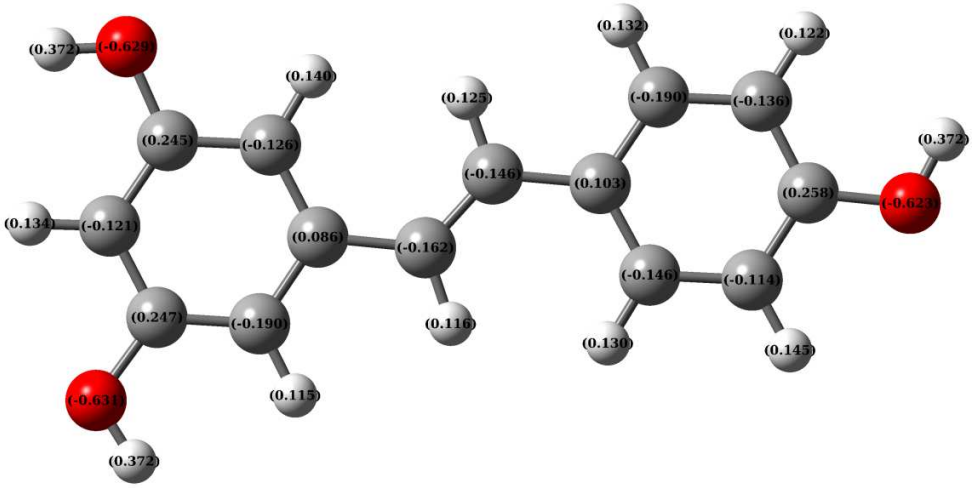
Table 1S. ^{1}H-NMR chemical shifts in ppm (ref. TMS) and coupling constants in Hz for the aromatic core of polyphenol standards **1-6** in MeOD at rt (^{1}H/^{13}C IUPAC assignment in parentheses; see Figure 1), [a]*s*, [b]*d*,[c]*t*, [d]*dd*, [e]*ddd*, [f]*dq*, [g]AB-mixing, [h]n. det., [i]broad.

	1		**2**		**3**		**4**		**5**		**6**	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	6.79[b] (H^{vinyl}) $^{3}J_{1,2}$16.3	125.7 (C^{vinyl}) ^{1}J149.1	-	-	-	-	-	-	-	-	-	-
2	6.94[b] (H^{vinyl}) $^{3}J_{2,1}$16.3	128.0 (C^{vinyl}) ^{1}J146.4	4.79[a,i]	78.5 ^{1}J143.2	-	160.9	-	161.0	-	164.2	-	162.9
3	-	-	4.15[e] $^{3}J_{3,2}$1.5 $^{3}J_{3,4a}$3.0 $^{3}J_{3,4e}$4.6	66.2 ^{1}J146.1 ^{1}J143.2	-	145.1	-	146.0	-	145.7	-	144.3
4	-	-	2.71[d]/2.84[d] $^{3}J_{4a,3}$3.0 $^{3}J_{4a,4e}$16.8 $^{3}J_{4e,3}$4.6 $^{3}J_{4e,4a}$16.6	27.9 ^{1}J130.1	8.59[b] $^{5}J_{4,6}$0.8	133.2 ^{1}J168.2	8.56[b] $^{5}J_{4,6}$0.6	132.9 ^{1}J167.9	9.14[b] $^{5}J_{4,6}$0.5	134.7 ^{1}J [h]	8.92[a] $^{5}J_{4,6}$0.7	134.8 ^{1}J [h]
5	-	158.3(C3) ^{1}J [h]	-	156.0	-	155.8 ^{1}J [h]	-	156.2	-	157.0	-	156.8
6	6.14[c](H2) $^{4}J_{6,8}$2.1 $^{4}J_{6,10}$2.1	101.3(C2) ^{1}J [h]	5.92[b,g] $^{4}J_{6,8}$2.4	95.1 ^{1}J157.3	6.88[d] $^{4}J_{6,8}$2.0 $^{5}J_{6,4}$0.9	93.6 ^{1}J [h]	6.86[d] $^{4}J_{6,8}$1.9 $^{5}J_{6,4}$0.7	93.7 ^{1}J162.1	7.08[d,g] $^{4}J_{6,8}$1.8 $^{5}J_{6,4}$0.6	96.0 ^{1}J [h]	6.87[d] $^{4}J_{6,8}$2.0 $^{5}J_{6,4}$0.8	93.8 ^{1}J [h]
7	-	158.3(C1) ^{1}J [h]	-	156.7	-	167.8 ^{1}J [h]	-	168.3	-	168.5	-	168.4
8	6.43[b](H6) $^{4}J_{8,6}$2.1	104.4(C6) ^{1}J153.7	5.90[b,g] $^{4}J_{8,6}$2.4	94.6 ^{1}J159.5	6.61[b] $^{3}J_{8,6}$2.0	101.8 ^{1}J159.9	6.61[b] $^{3}J_{8,6}$2.0	102.0 ^{1}J162.5	7.06[b,g] $^{3}J_{8,6}$2.0	104.4 ^{1}J [h]	6.65[b] $^{3}J_{8,6}$2.0	102.0 ^{1}J [h]
9	-	140.0(C5) ^{1}J [h]	-	156.3	-	156.8	-	156.2	-	155.9	-	157.3
10	6.43[b](H4) $^{4}J_{10,6}$2.1	104.4(C4) ^{1}J153.8	-	98.7	-	112.5	-	112.9	-	112.3	-	111.9 ^{1}J [h]
1'	-	-	-	131.0	-	120.2	-	121.0	-	120.3	-	119.9 ^{1}J [h]
2'	7.34[b] $^{3}J_{2',3'}$8.6	127.5 ^{1}J155.1	6.95[b] $^{4}J_{2',2}$0.4 $^{3}J_{2',6'}$1.9	114.0 ^{1}J157.3	8.57[b,g] $^{3}J_{2',3'}$9.1	133.6 ^{1}J167.0	8.11[b] $^{3}J_{2',6'}$2.3	117.4 ^{1}J159.0	8.07[b] $^{3}J_{2',6'}$2.4	117.2 ^{1}J [h]	8.00[b] $^{3}J_{2',6'}$2.4	117.0 ^{1}J161.3
3'	6.75[b] $^{3}J_{3',2'}$8.6	115.1 ^{1}J162.0	-	144.6	7.03[b,g] $^{3}J_{3',2'}$9.1	116.4 ^{1}J161.3	-	147.0	-	146.9	-	146.2 ^{1}J [h]
4'	-	157.0 ^{1}J [h]	-	144.4	-	164.8	-	154.5	-	155.5	-	154.6 ^{1}J [h]
5'	6.75[b] $^{3}J_{5',6'}$8.6	115.1 ^{1}J162.0	6.74[b] $^{3}J_{6',5'}$8.1	118.1 ^{1}J156.9	7.03[b,g] $^{3}J_{5',6'}$9.1	116.4 ^{1}J161.3	7.00[b] $^{3}J_{5',6'}$8.7	116.4 ^{1}J157.8	7.03[b] $^{3}J_{5',6'}$8.7	116.2 ^{1}J [h]	6.99[b] $^{3}J_{5',6'}$8.7	116.1 ^{1}J162.7
6'	7.34[b] $^{3}J_{6',5'}$8.6	127.5 ^{1}J155.1	6.77[e] $^{4}J_{6',2}$0.4 $^{3}J_{6',2'}$1.9 $^{3}J_{6',5'}$8.2	114.6 ^{1}J160.3	8.57[b,g] $^{3}J_{6',5'}$9.1	133.6 ^{1}J167.0	8.22[d] $^{3}J_{6',5'}$8.7 $^{3}J_{6',2'}$2.3	126.4 ^{1}J167.9	8.37[d] $^{3}J_{6',5'}$8.8 $^{3}J_{6',2'}$2.4	127.8 ^{1}J [h]	8.26[d] $^{3}J_{6',5'}$8.7 $^{3}J_{6',2'}$2.4	126.9 ^{1}J168.6

Table 2S. ^{1}H-NMR chemical shifts in ppm (ref. TMS) and coupling constants in Hz for the glycosyl substituents of polyphenol standards **5** and **6** in MeOD at rt (^{1}H/^{13}C IUPAC assignment in parentheses; see Figure 1), [a]*s*, [b]*d*, [c]*t*, [d]*dd*, [e]*ddd*, [f]*dq*, [g]AB-mixing, [h]n. det., [i]broad.

	5		**6**	
	^{1}H	^{13}C	^{1}H	^{13}C
1''	5.28[b] $^{3}J_{1'',2''}$7.9	102.7 ^{1}J157.8	5.27[b] $^{3}J_{1'',2''}$7.7	102.1 ^{1}J164.0
2''	3.67[d] $^{3}J_{2'',3''}$9.5 $^{3}J_{2'',1''}$7.9	73.3 ^{1}J [h]	3.64[d] $^{3}J_{2'',3''}$9.2 $^{3}J_{2'',1''}$7.8	73.3 ^{1}J [h]
3''	3.51[c] $^{3}J_{3'',4''}$9.3 $^{3}J_{3'',2''}$9.3	77.5 ^{1}J [h]	3.52[c] $^{3}J_{3'',4''}$9.2 $^{3}J_{3'',2''}$9.2	68.3 ^{1}J [h]
4''	3.38[d] $^{3}J_{4'',5''}$9.4 $^{3}J_{4'',3''}$9.2	70.1 ^{1}J [h]	3.39[d] $^{3}J_{4'',5''}$9.8 $^{3}J_{4'',3''}$9.1	69.9 ^{1}J [h]
5''	3.60[e] $^{3}J_{5'',6a''}$2.1 $^{3}J_{5'',6b''}$6.9 $^{3}J_{5'',4''}$9.5	77.7 ^{1}J [h]	3.70[e] $^{3}J_{5'',6a2''}$6.6 $^{3}J_{5'',6b''}$1.7 $^{3}J_{5'',4''}$9.7	76.1 ^{1}J116.8
6$_S$''	3.68[d] $^{3}J_{6S'',6R''}$11.9 $^{3}J_{6S'',5''}$6.9	61.3 ^{1}J [h]	3.57[d] $^{3}J_{6S'',6R''}$11.2 $^{3}J_{6S'',5''}$6.6	66.3 ^{1}J136.8
6$_R$''	3.95[d] $^{3}J_{6R'',5''}$2.2 $^{3}J_{6R'',6S''}$12.0	61.3 ^{1}J [h]	4.04[d] $^{3}J_{6R'',5''}$1.7 $^{3}J_{6R'',6S''}$11.2	66.3 ^{1}J136.8
1'''	5.14[b] $^{3}J_{1''',2'''}$7.8	101.4 ^{1}J [h]	4.62[b] $^{3}J_{1''',2'''}$1.5	100.8 ^{1}J169.7
2'''	3.65[d] $^{3}J_{2''',3'''}$9.3 $^{3}J_{2''',1'''}$7.8	73.0 ^{1}J [h]	3.77[d] $^{3}J_{2''',3'''}$3.5 $^{3}J_{2''',1'''}$1.6	70.6 ^{1}J [h]
3'''	3.52[c] $^{3}J_{3''',4'''}$9.2 $^{3}J_{3''',2'''}$9.2	77.1 ^{1}J [h]	3.60[d] $^{3}J_{3''',4'''}$9.5 $^{3}J_{3''',2'''}$3.5	71.1 ^{1}J [h]
4'''	3.43[d] $^{3}J_{4''',5'''}$9.4 $^{3}J_{4''',3'''}$9.3	70.0 ^{1}J [h]	3.30[c] $^{3}J_{4''',5'''}$9.6 $^{3}J_{4''',3'''}$9.6	72.6 ^{1}J [h]
5'''	3.55[e] $^{3}J_{5''',6a'''}$2.5 $^{3}J_{5''',6b'''}$5.8 $^{3}J_{5''',4'''}$9.8	77.4 ^{1}J [h]	3.53[f] $^{3}J_{5''',CH3}$6.1 $^{3}J_{5''',4'''}$9.3	66.3 ^{1}J [h]
6$_S$'''	3.72[d] $^{3}J_{6S''',6R'''}$12.1 $^{3}J_{6S''',5'''}$5.8	61.1 ^{1}J [h]	-	-
6$_R$'''	3.93[d] $^{3}J_{6R''',5'''}$2.2 $^{3}J_{6R''',6S'''}$12.1	-	-	-
CH$_3$	-	-	1.15[b] $^{3}J_{CH3,5'''}$6.2	16.5 ^{1}J129.1

a)



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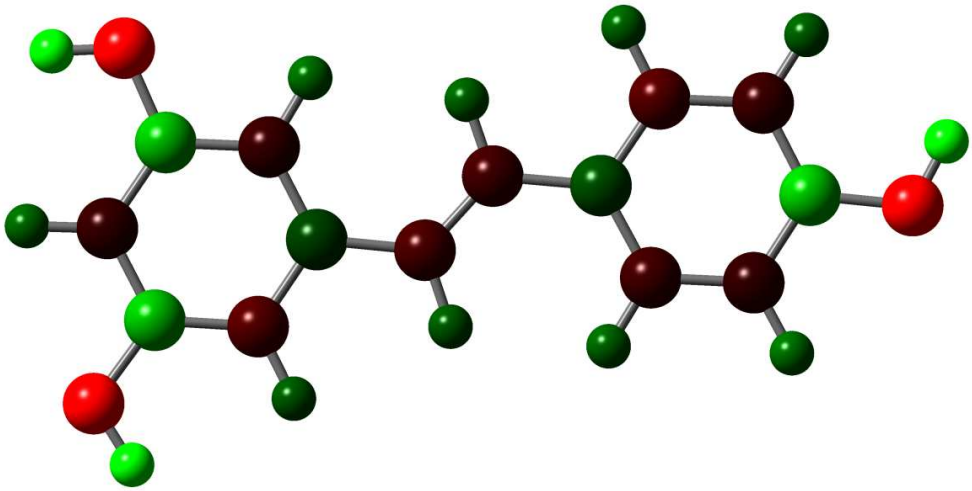
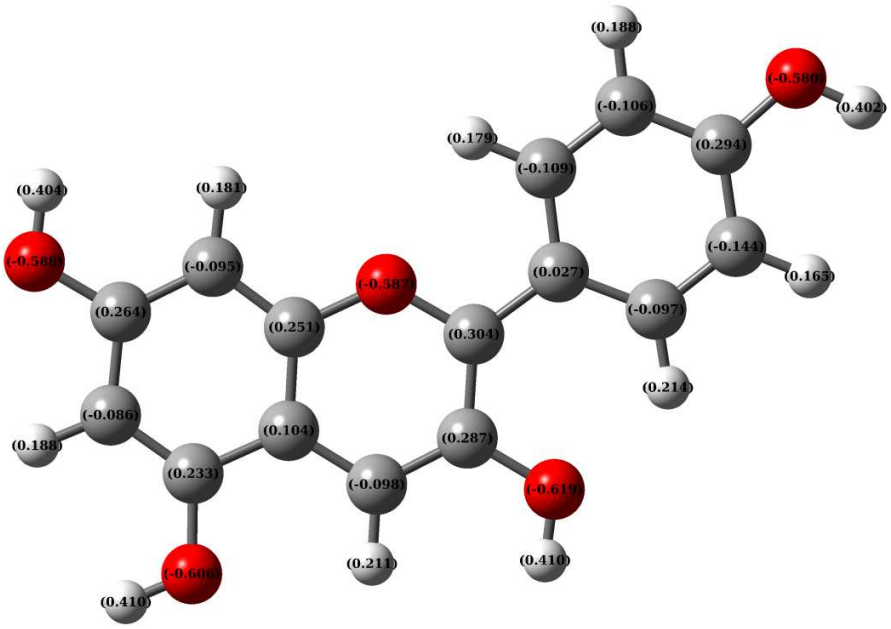


Figure 20S. a) Resveratrol (**1**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown; b) Resveratrol (**1**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown in color-gradients; red: negative, black: neutral, green: positive).

a)



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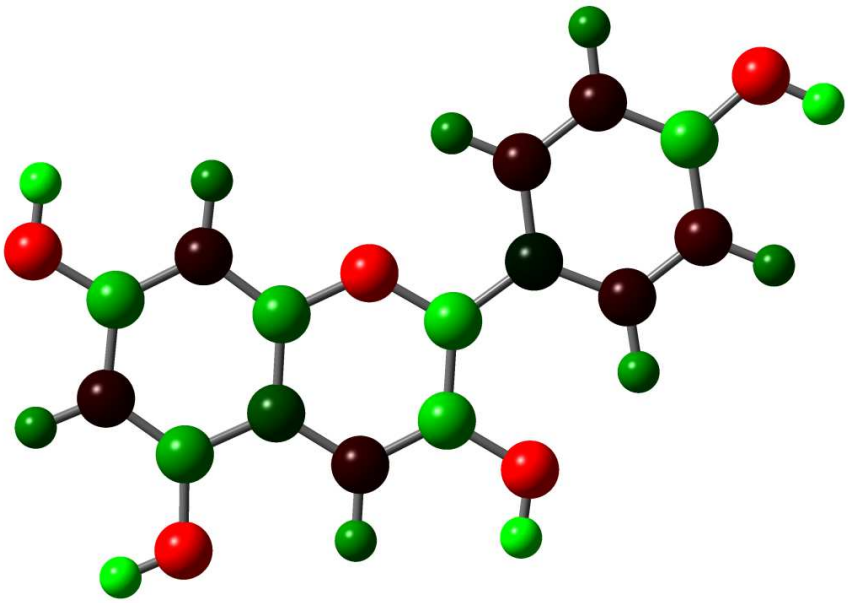
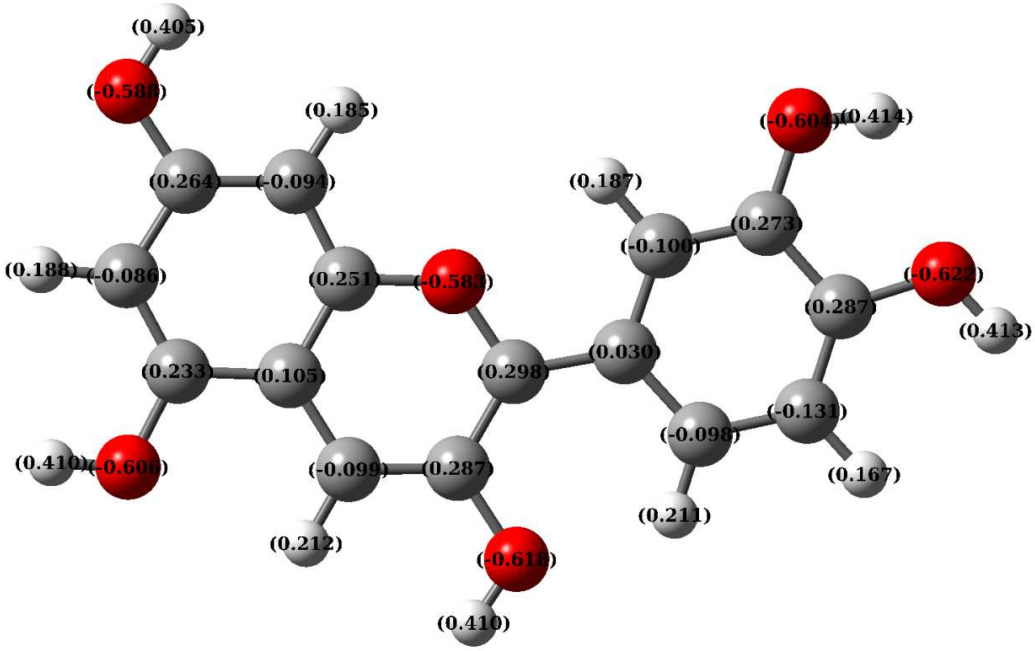


Figure 21S. a) Pelargonidin cation (**3**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown; b) Pelargonidin cation (**3**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown in color-gradients; red: negative, black: neutral, green: positive).

a)



b)

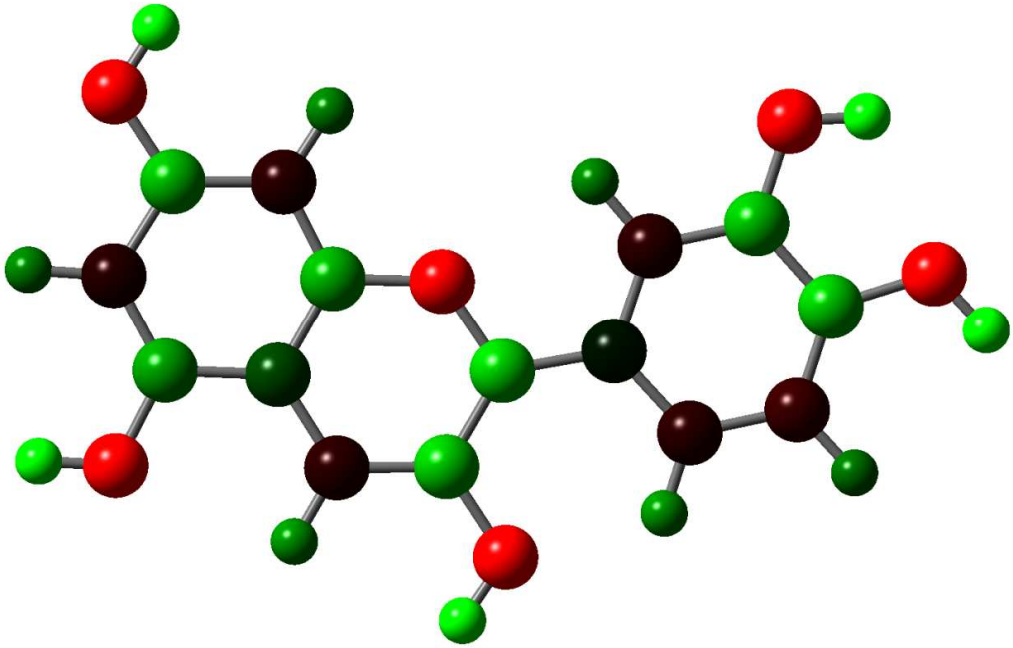
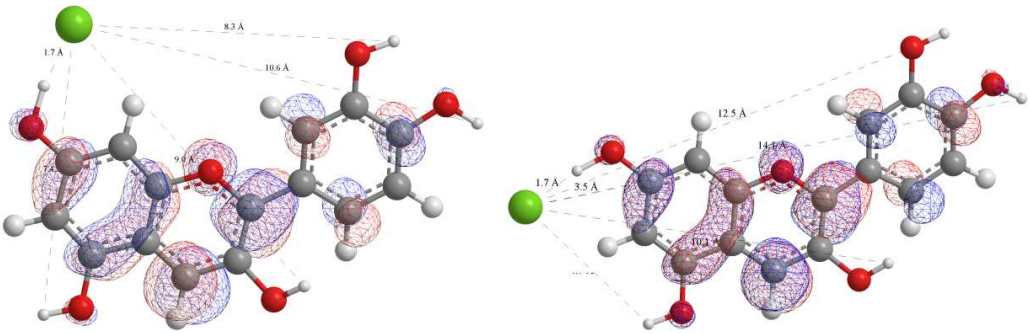


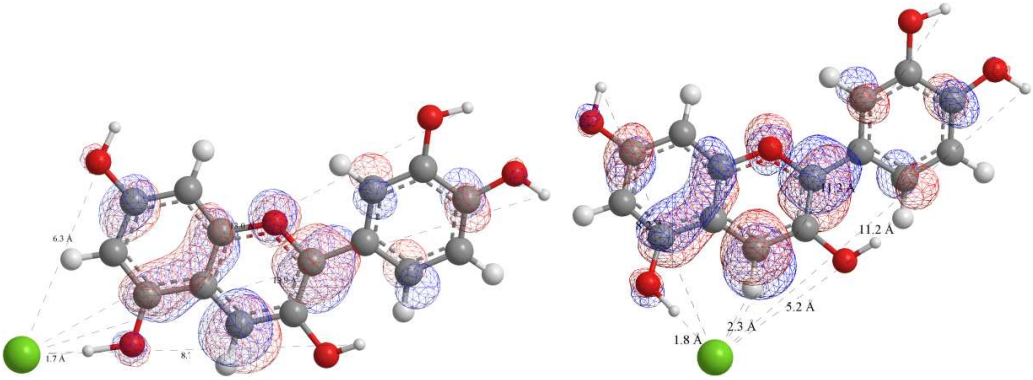
Figure 22S. a) Cyanidin cation (**4**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown; b) Cyanidin cation (**4**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown in color-gradients; red: negative, black: neutral, green: positive).

a)



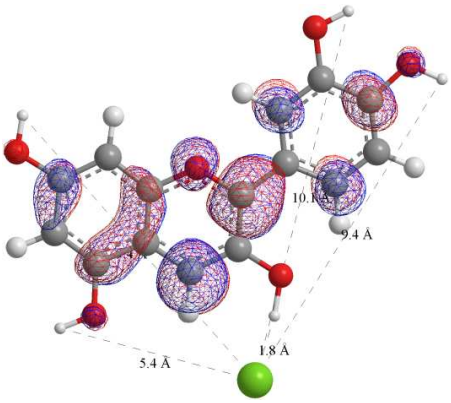
-20.3 kcal/mol -22.4 kcal/mol

b)



-18.6 kcal/mol -18.9 kcal/mol

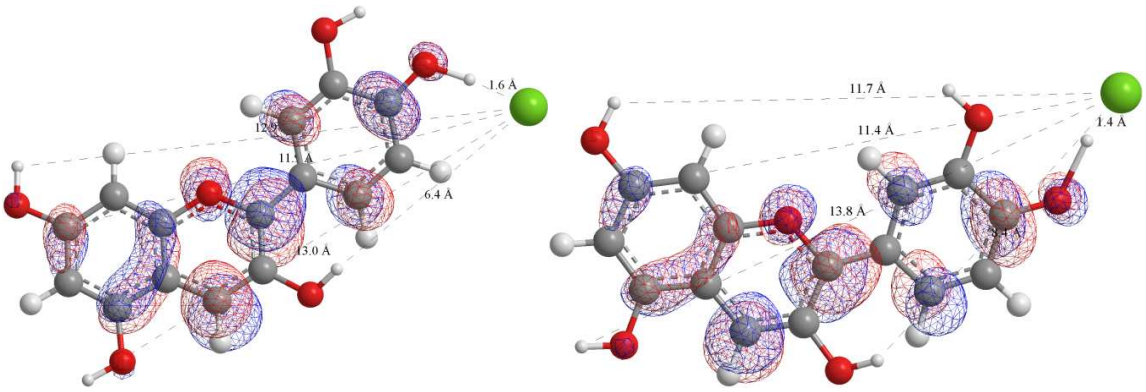
c)



-26.4 kcal/mol

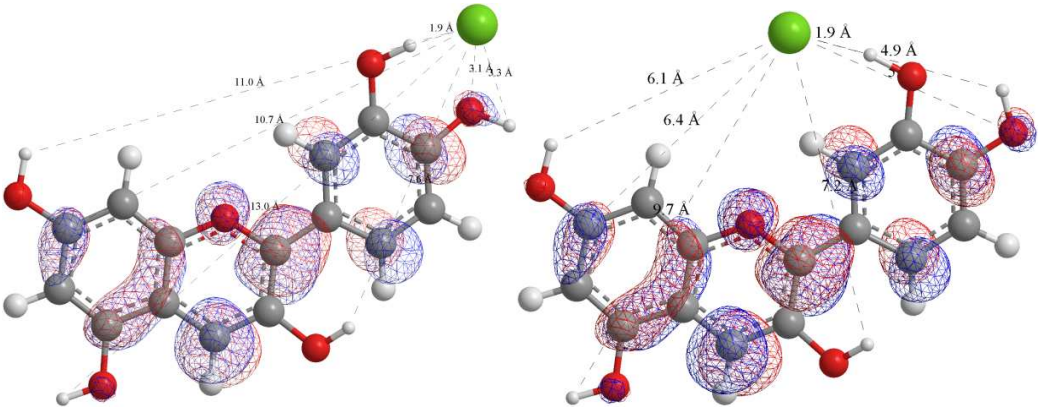
Figure 23S. Cyanidin chloride (**4**) (ChemBio3D Ultra, DFT-B3LYP-6-31G, 0 K). The LUMO is shown. The right structure is more stable relative to structure by a) left: -20.3 kcal/mol; right: -22.4 kcal/mol; b) left: -18.6 kcal/mol; right: -18.9 kcal/mol; c) -26.4 kcal/mol.

d)



-20.7 kcal/mol -8.83 kcal/mol

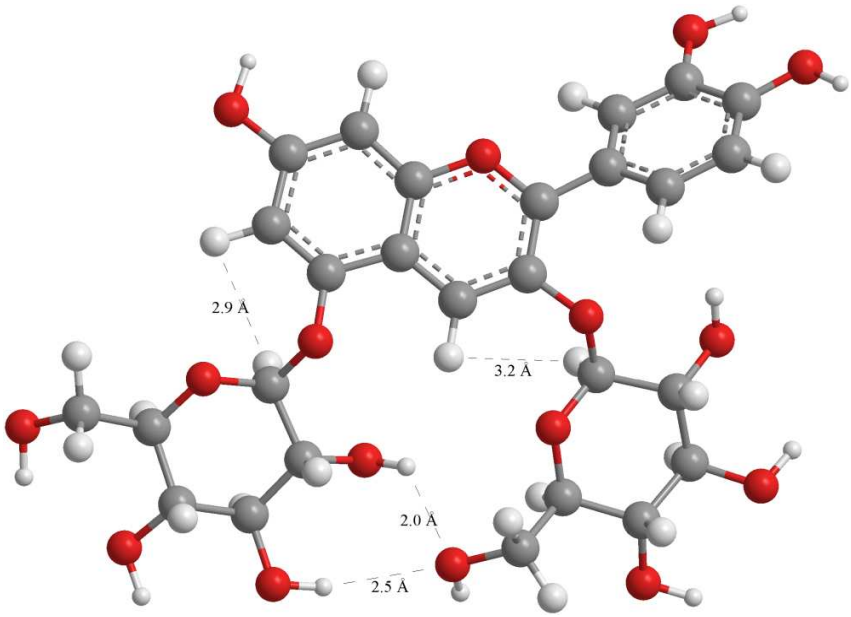
e)



0.00 kcal/mol -22.3 kcal/mol

Figure 23S cont'd. Cyanidin chloride (**4**) (ChemBio3D Ultra, DFT-B3LYP-6-31G, 0 K). The LUMO is shown. The right structure is more stable by d) left: -20.7 kcal/mol; right: -8.83 kcal/mol; e) left: 0.00 kcal/mol; right: -22.3 kcal/mol.

a)



b)

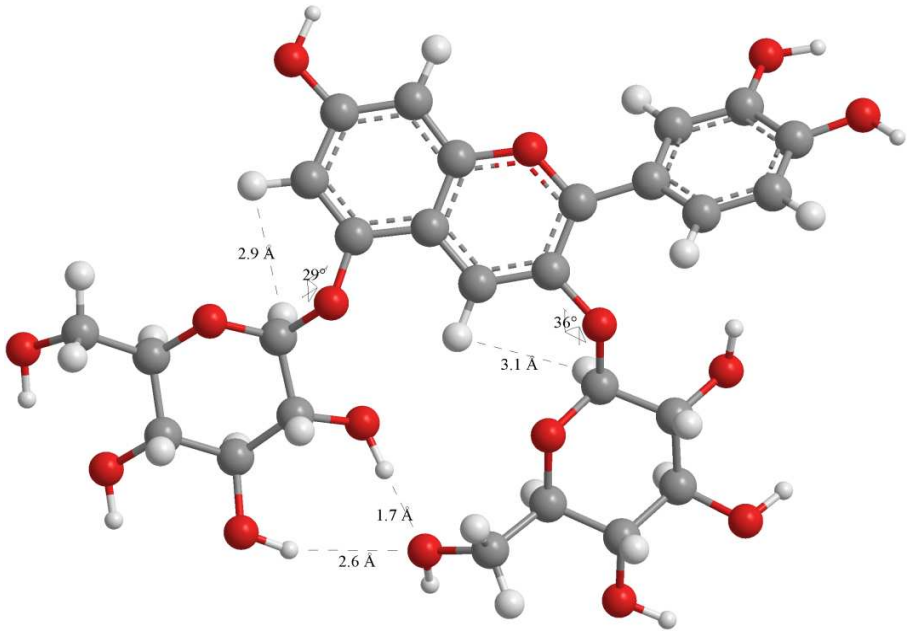
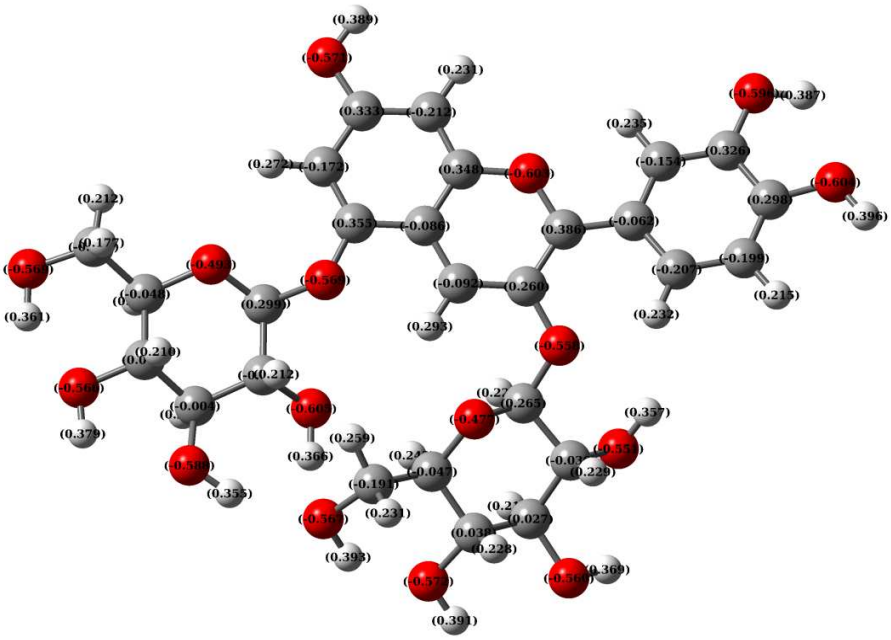


Figure 24S. a) Cyanin cation (**5**) (ChemBio3D Ultra, **AM1**, 0 K, vacuum, ϕ'' = -86 º, ψ'' = -108 º and ϕ''' = 59 º, ψ''' = -97 º; glycosidic dihedrals H1''C''OC3 = +33 º and H1'''C1'''OC5 = +22º); b) Cyanin cation (**5**) (ChemBio3D Ultra, **DFT-B3LYP-6-31G**, 0 K, ϕ'' = -85 º, ψ'' = -124 º and ϕ''' = 50 º, ψ''' = -91 º; glycosidic dihedrals H1''C''OC3 = +36 º and H1'''C1'''OC5 = +29 º).

a)



b)

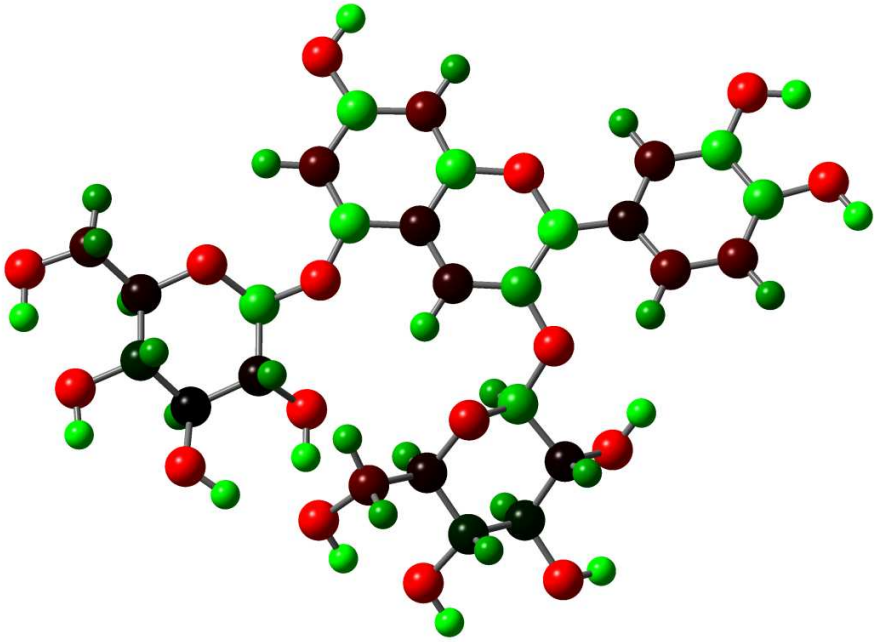
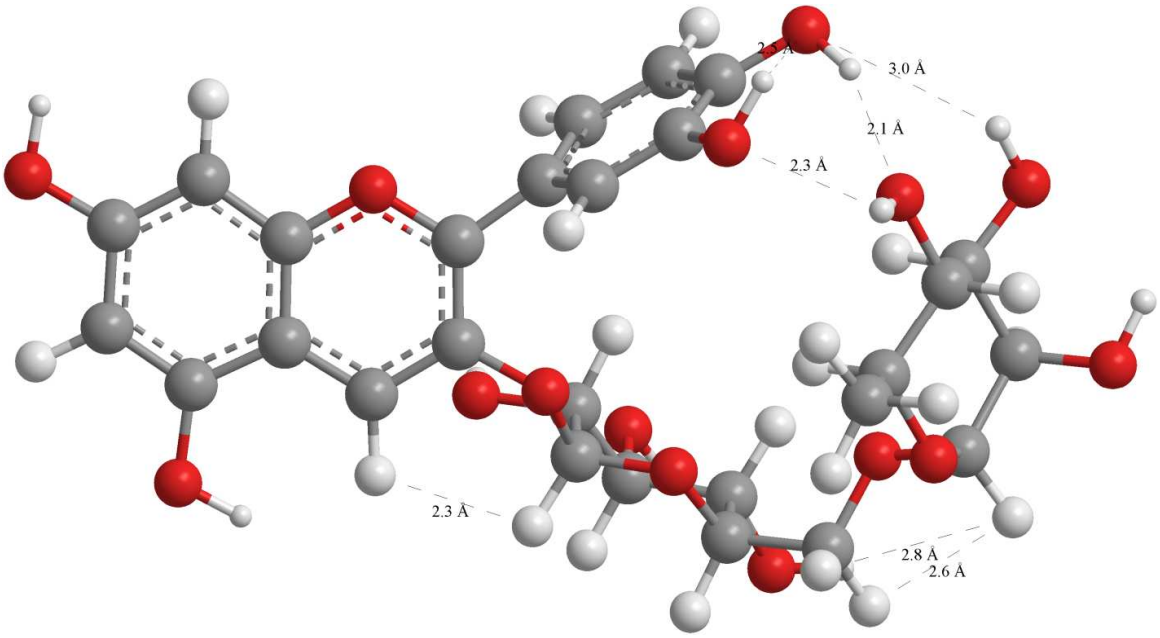


Figure 25S. a) Cyanin cation (**5**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown; b) Cyanin cation (**5**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown in color-gradients; red: negative, black: neutral, green: positive).

a)



b)

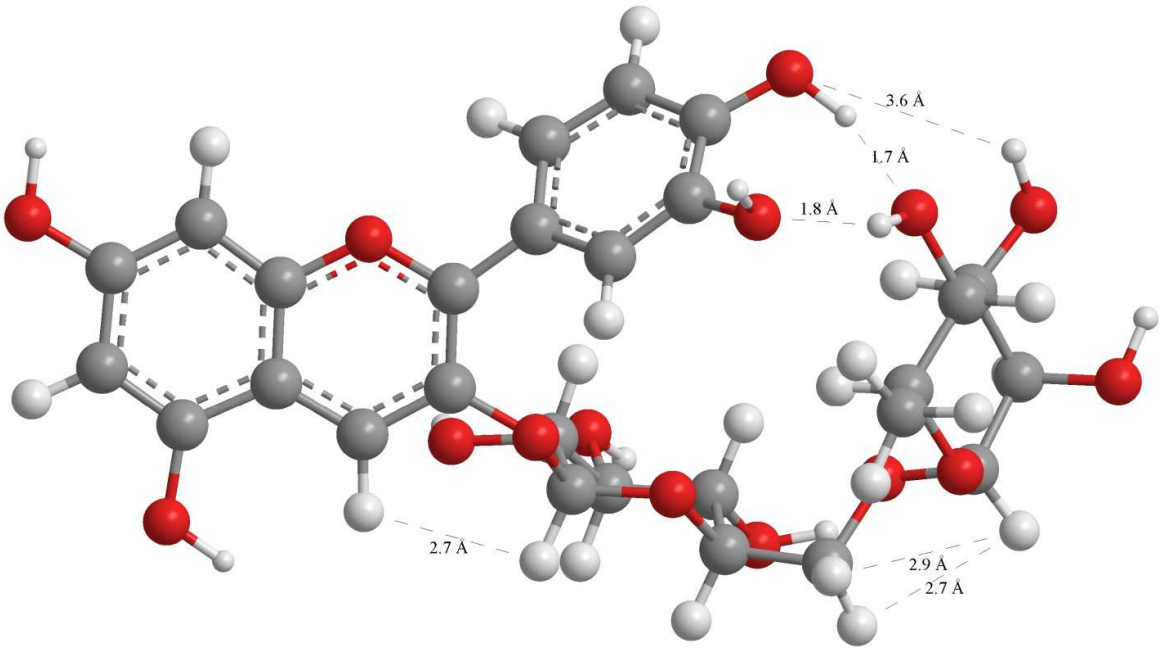
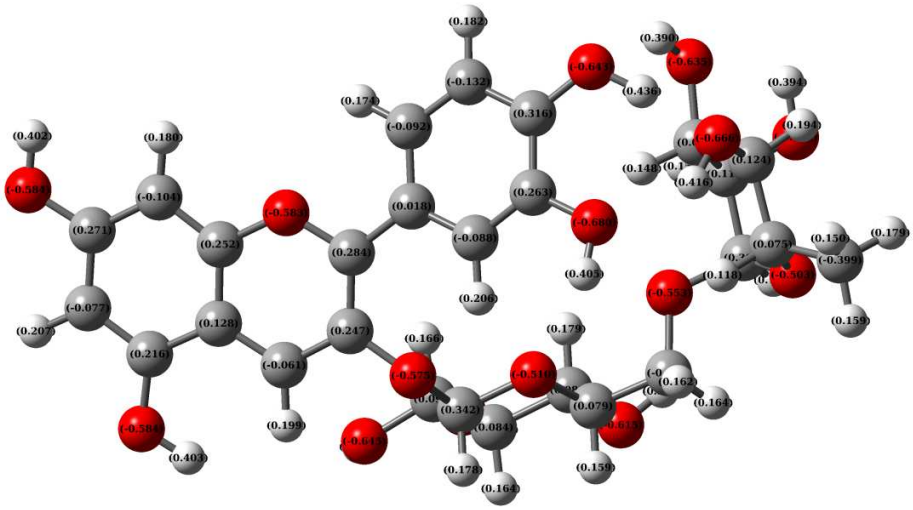


Figure 26S. a) Keracyanin cation (**6**) (ChemBio3D Ultra, **AM1**, 0 K, vacuum, ϕ'' = +57 º, ψ'' = +167 º and ϕ''' = -64 º, ψ''' = +167 º; glycosidic dihedrals H1''C''OC3 = -76 º and H1'''C1'''OC6'' = +50º); b) Keracyanin cation (**6**) (ChemBio3D Ultra, **DFT-B3LYP-6-31G**, 0 K, ϕ''' = +67 º, ψ''' = +156 º and ϕ''' = -56 º, ψ''' = +163 º; glycosidic dihedrals H1''C''OC3 = -86 º and H1'''C1'''OC6'' = +60 º).

a)



b)

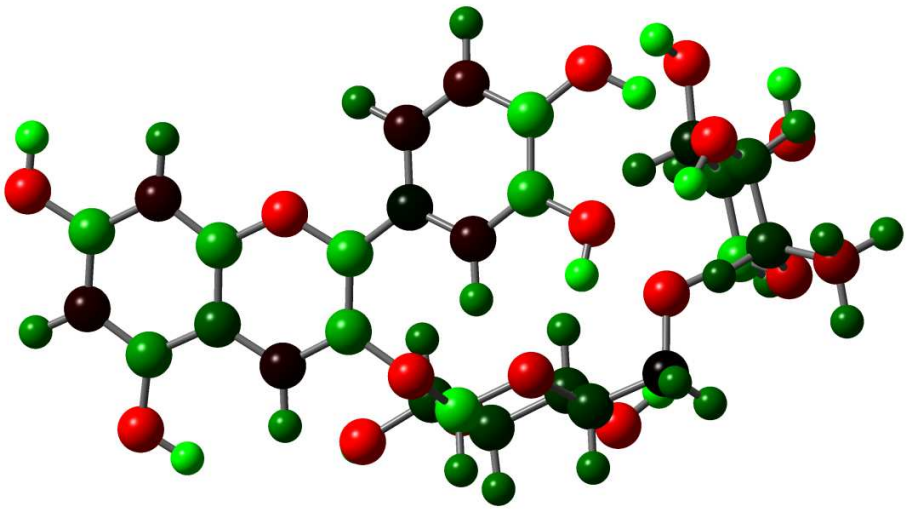


Figure 27S. a) Keracyanin cation (**6**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown; b) Keracyanin cation (**6**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown in color-gradients; red: negative, black: neutral, green: positive).

Table 3S. Mulliken charges (DFT-B3LYP-6-31G) of compounds **3**-**6** with chromelynium core. Substantially higher polarization between the aromatic protons H6 and H8 and their respective carbons C6 and C8 in compound **5** with glycosylation at OH-5 was indicative of higher degree of aromaticity of the ring π-system compared to compounds **3**, **4**, and **6** with free OH-groups at C5 and C7. Higher degree of aromaticity in the π-system led to stronger ring current effect and greater deshielding of H6/H8 and C6/C8 resonances in the spectra of **5** (see Table 1) and lack of H-D-exchange due to enolization (see Scheme 2).

	3	**4**	**5**	**6**
H6/C6	0.181 / -0.095	0.185 / -0.094	0.231 / -0.212	0.180 / -0.104
Δ	0.276	0.279	0.443	0.284
H8/C8	0.188 / -0.086	0.188 / -0.086	0.272 / -0.172	0.207 / -0.077
Δ	0.274	0.274	0.444	0.284
H/D-exchange	+	+	-	+

Additional References:

Classes of polyphenols (reviews)[1,2]
Coloring of blossoms[3]
Plant infection by bacteria and fungi [2,4]
Relief of oxidative stress by polyphenols [4]
Polyphenol applications as antioxidants [2,5,6]
Polyphenols as antiangiogenic/anti-cancer agents[6]
Isolation of polyphenols by ion exchange chromatography[7-10]
Isolation of polyphenols by HPLC[11,12]
Characterization of polyphenols by mass spectrometry[8,10,11,13-16]
Characterization of polyphenols by NMR[10,11,15]
Characterization of polyphenols by UV-VIS[11,17]
Characterization of polyphenols by IR[17]
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Reviews of isotope effects in NMR[58,73-76]

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