

Supplementary Material

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

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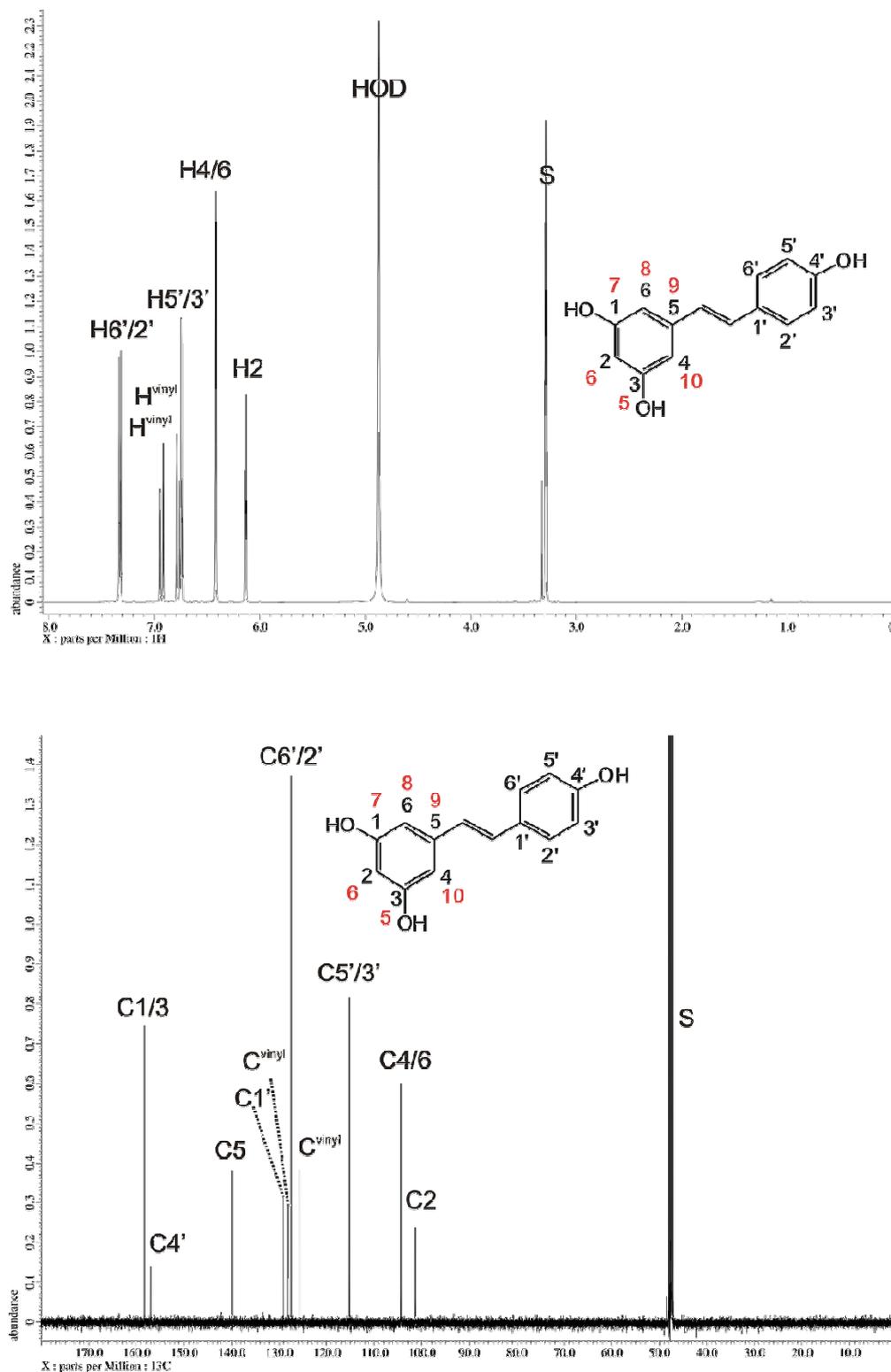


Figure 1S. Top: $^1\text{H-NMR}$ spectrum; bottom: $^{13}\text{C-NMR}$ spectrum of resveratrol (1) in MeOD.

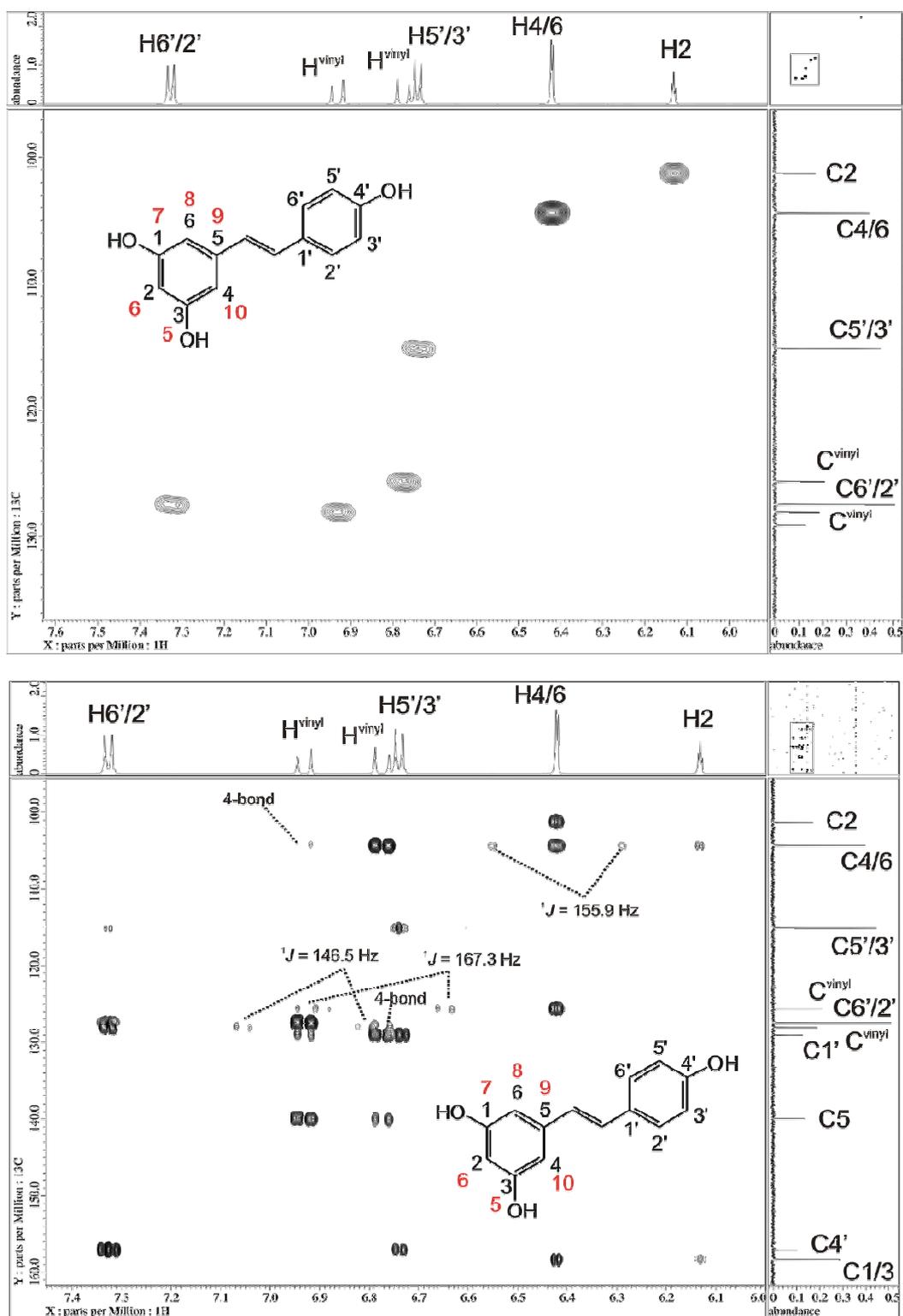


Figure 2S. Top: $^1\text{H}/^{13}\text{C}$ -HMQC; bottom: $^1\text{H}/^{13}\text{C}$ -HMBC of resveratrol (1) in MeOD.

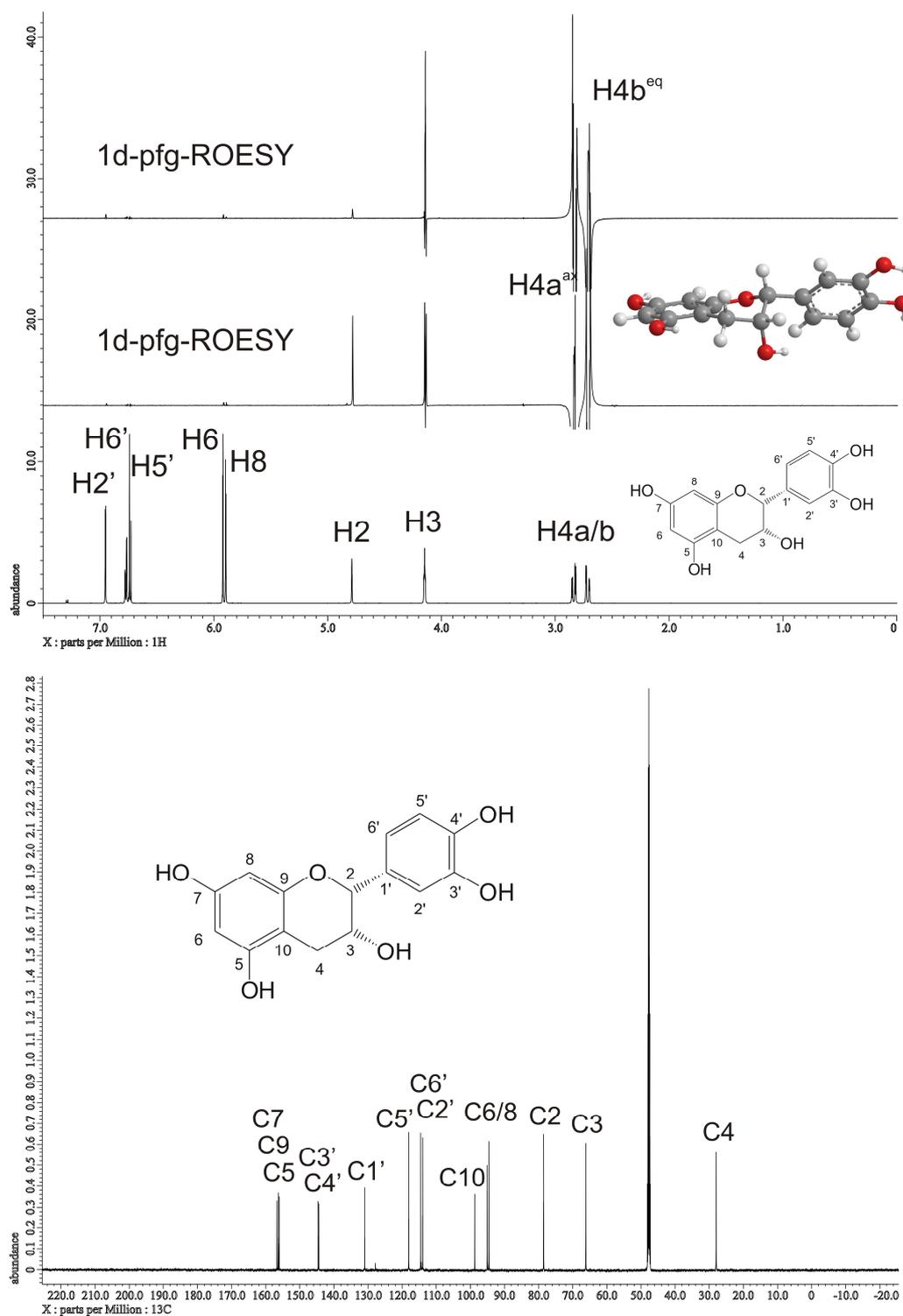


Figure 3S. Top: ¹H-NMR spectrum and AM1-minimized molecular model; inset: 1D-pfg-ROESY spectra with irradiation at H4^e and H4^a; bottom: ¹³C-NMR spectrum of (-)-epicatechin (2) in MeOD.

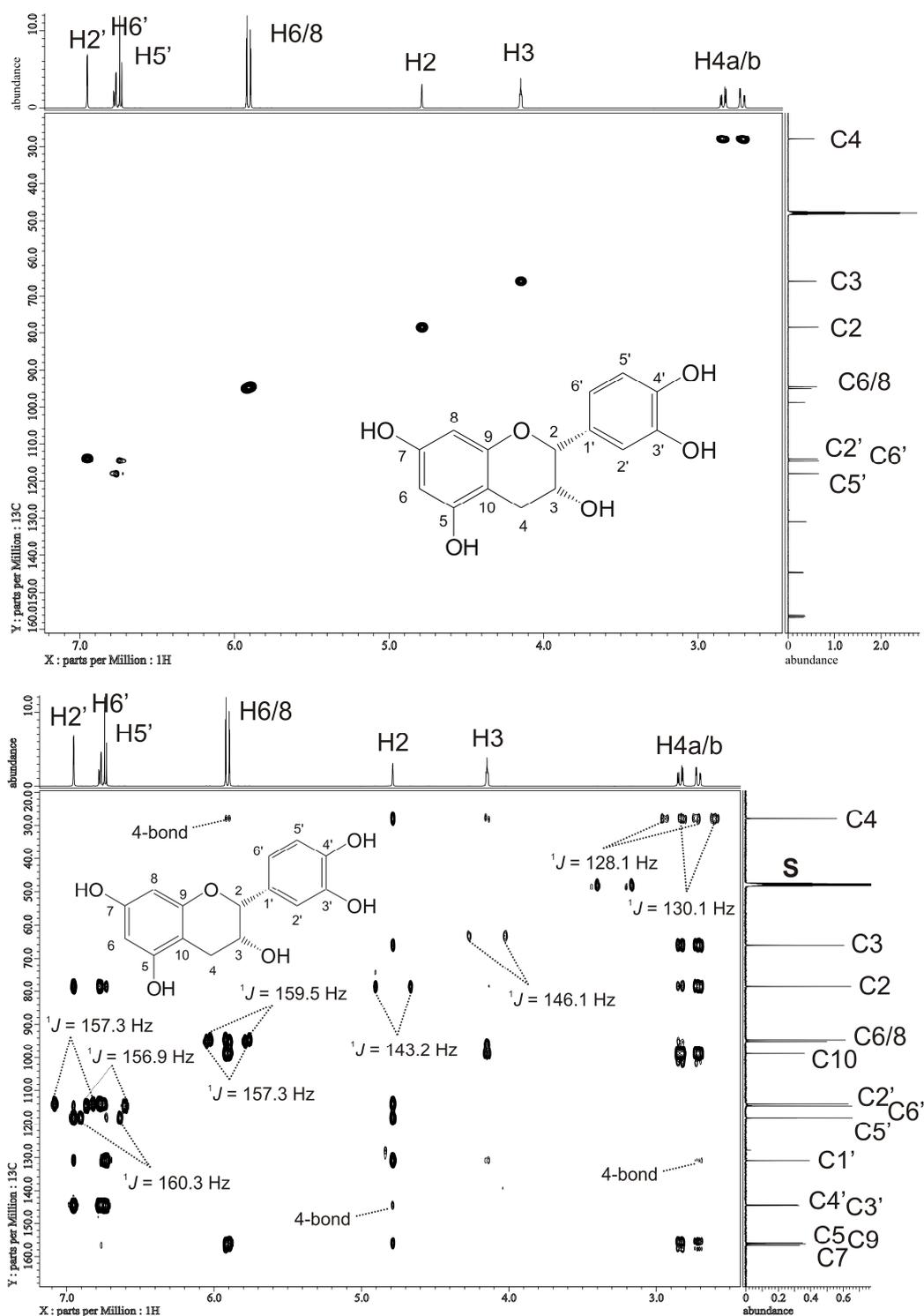


Figure 4S. Top: $^1\text{H}/^{13}\text{C}$ -HMQC; bottom: $^1\text{H}/^{13}\text{C}$ -HMBC of (-)-epicatechin (2) in MeOD.

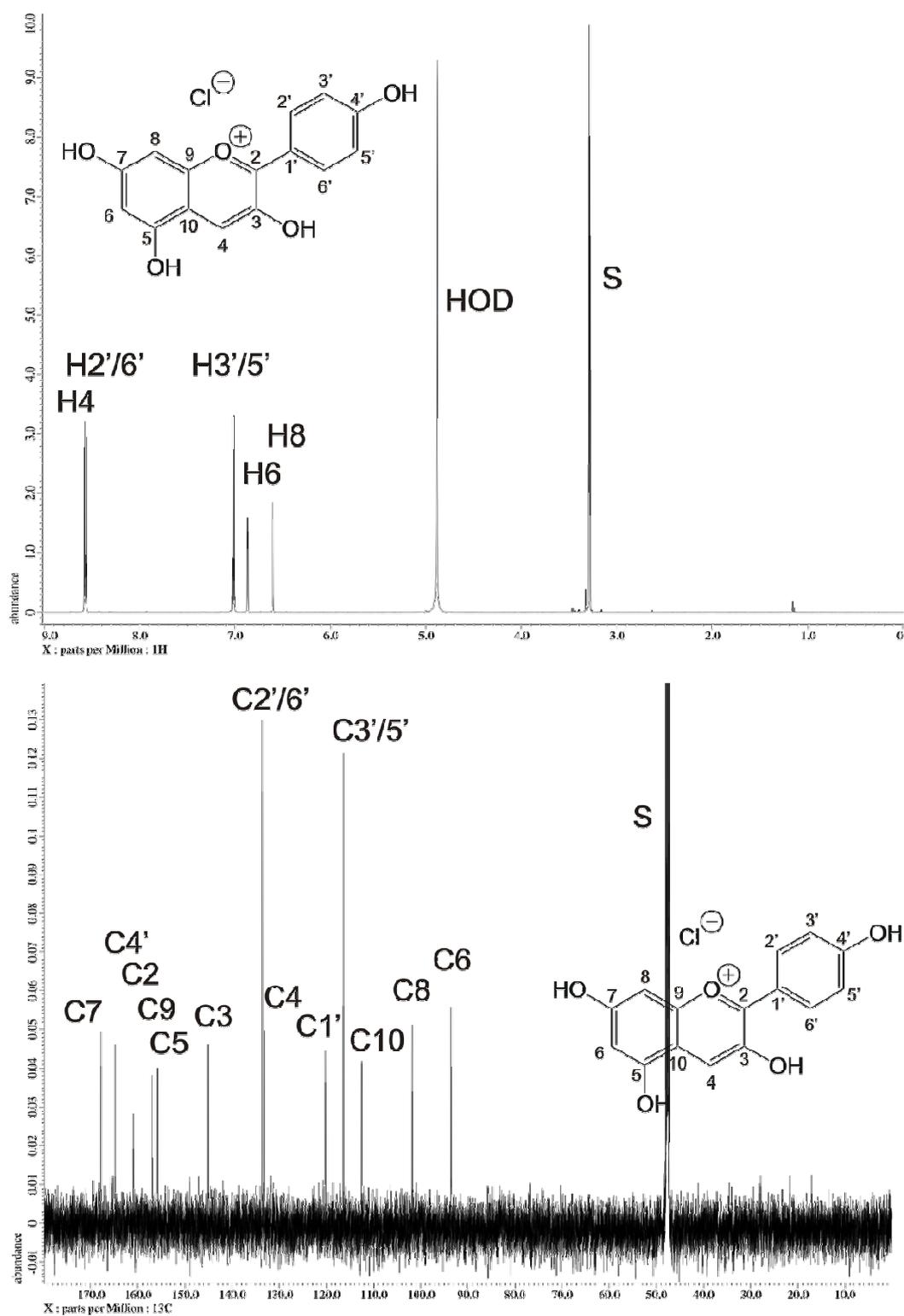


Figure 5S. Top: ¹H-NMR spectrum; bottom: ¹³C-NMR spectrum of pelargonidin chloride in MeOD.

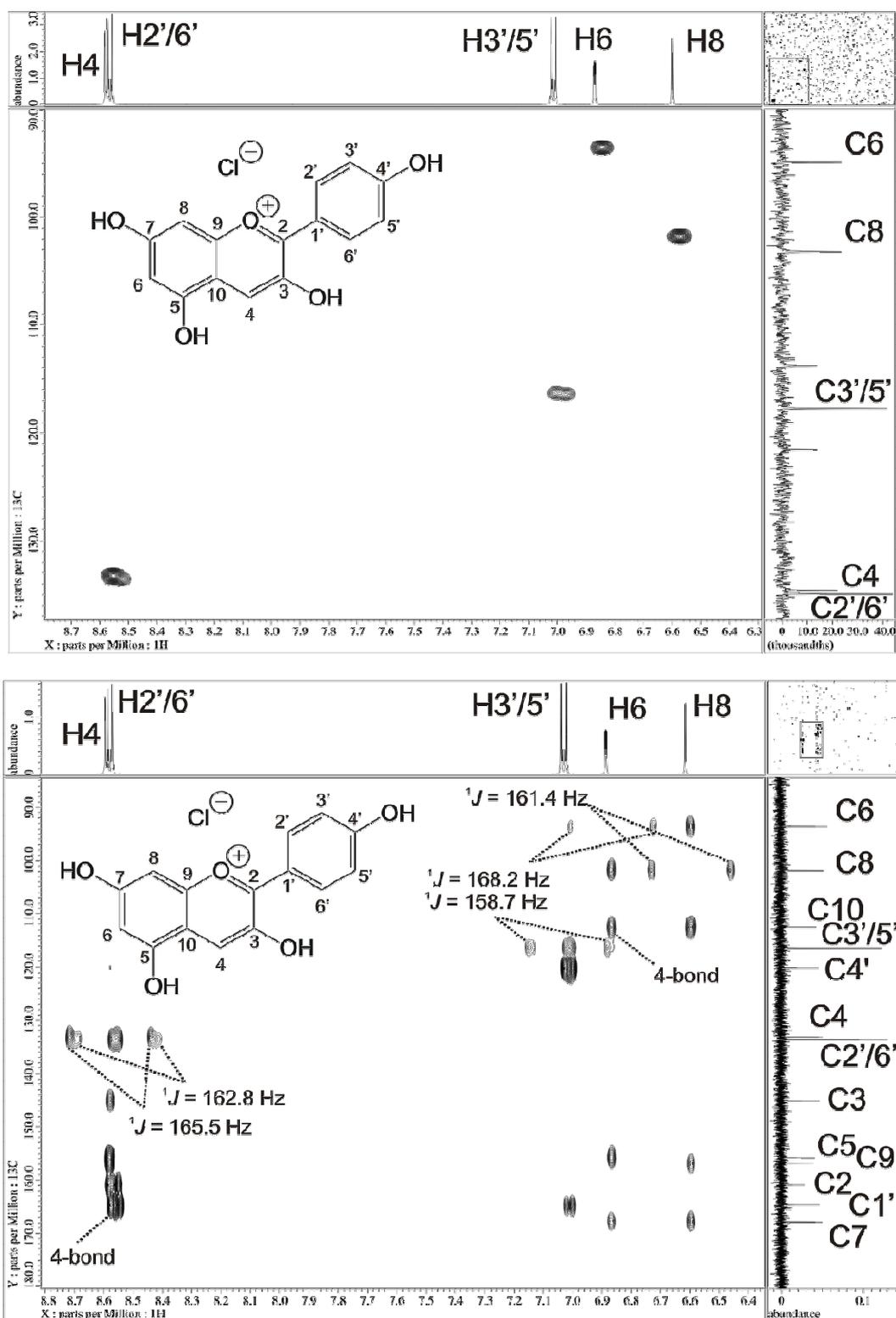


Figure 6S. Top: $^1\text{H}/^{13}\text{C}$ -HMQC; bottom: $^1\text{H}/^{13}\text{C}$ -HMBC of pelargonidin chloride in MeOD.

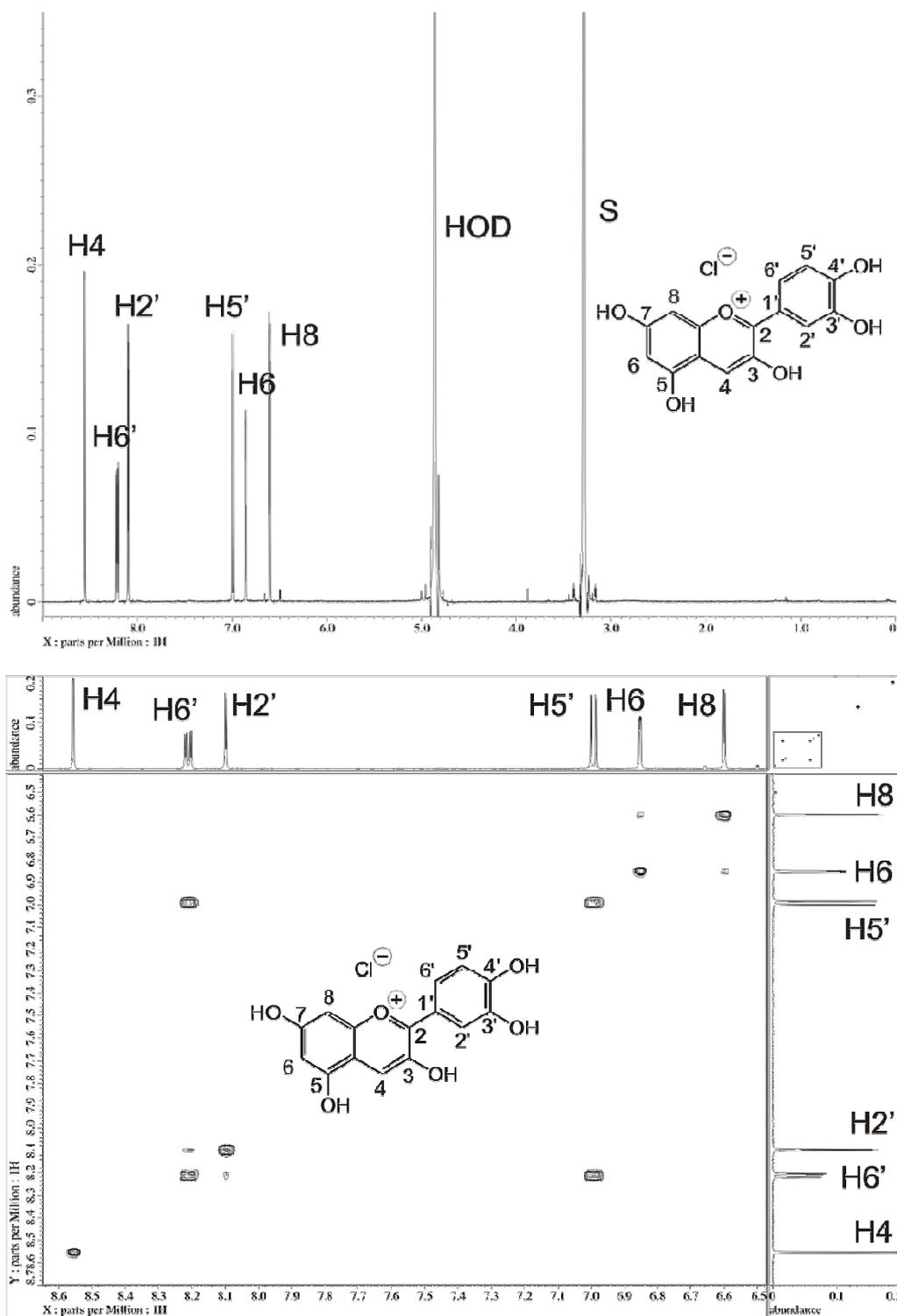


Figure 7S. Top: ^1H -NMR spectrum; bottom: ^1H - ^1H -COSY-NMR spectrum of cyanidin chloride in MeOD.

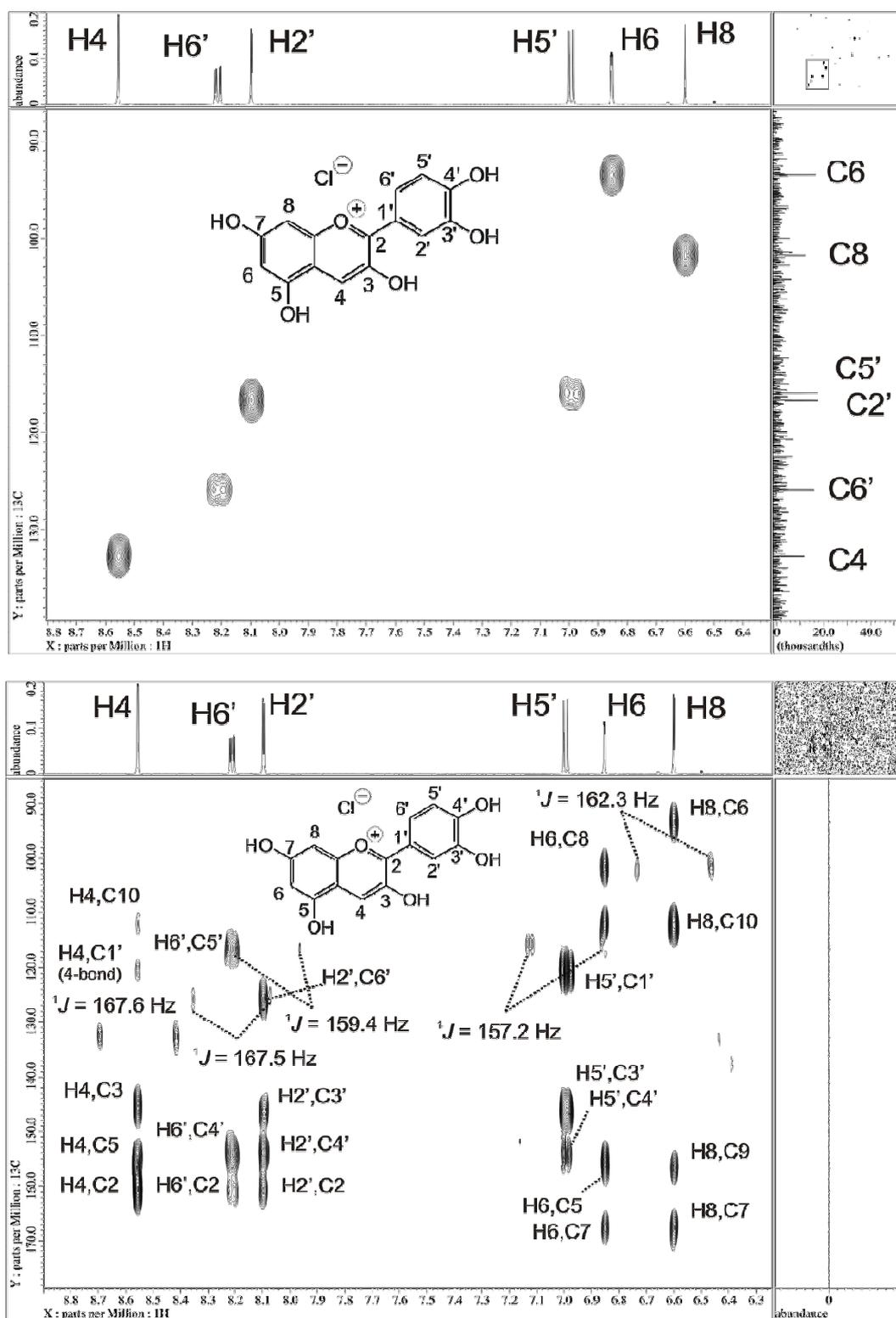


Figure 8S. Top: $^1\text{H}/^{13}\text{C}$ -HMQC; bottom: $^1\text{H}/^{13}\text{C}$ -HMBC of cyanidin chloride in MeOD.

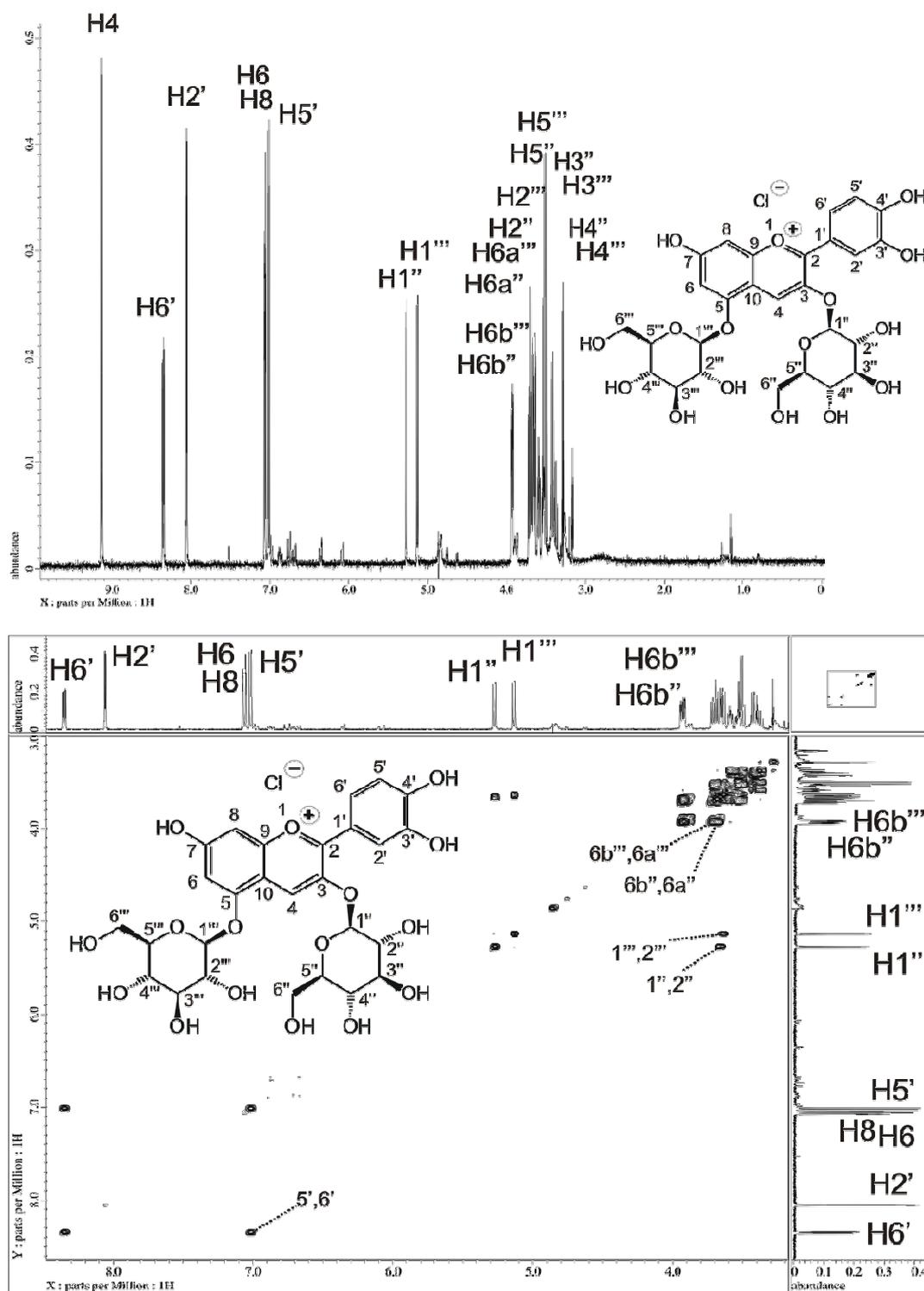


Figure 9S. Top: ^1H -NMR spectrum; bottom: ^1H - ^1H -COSY NMR spectrum of cyanin chloride in MeOD.

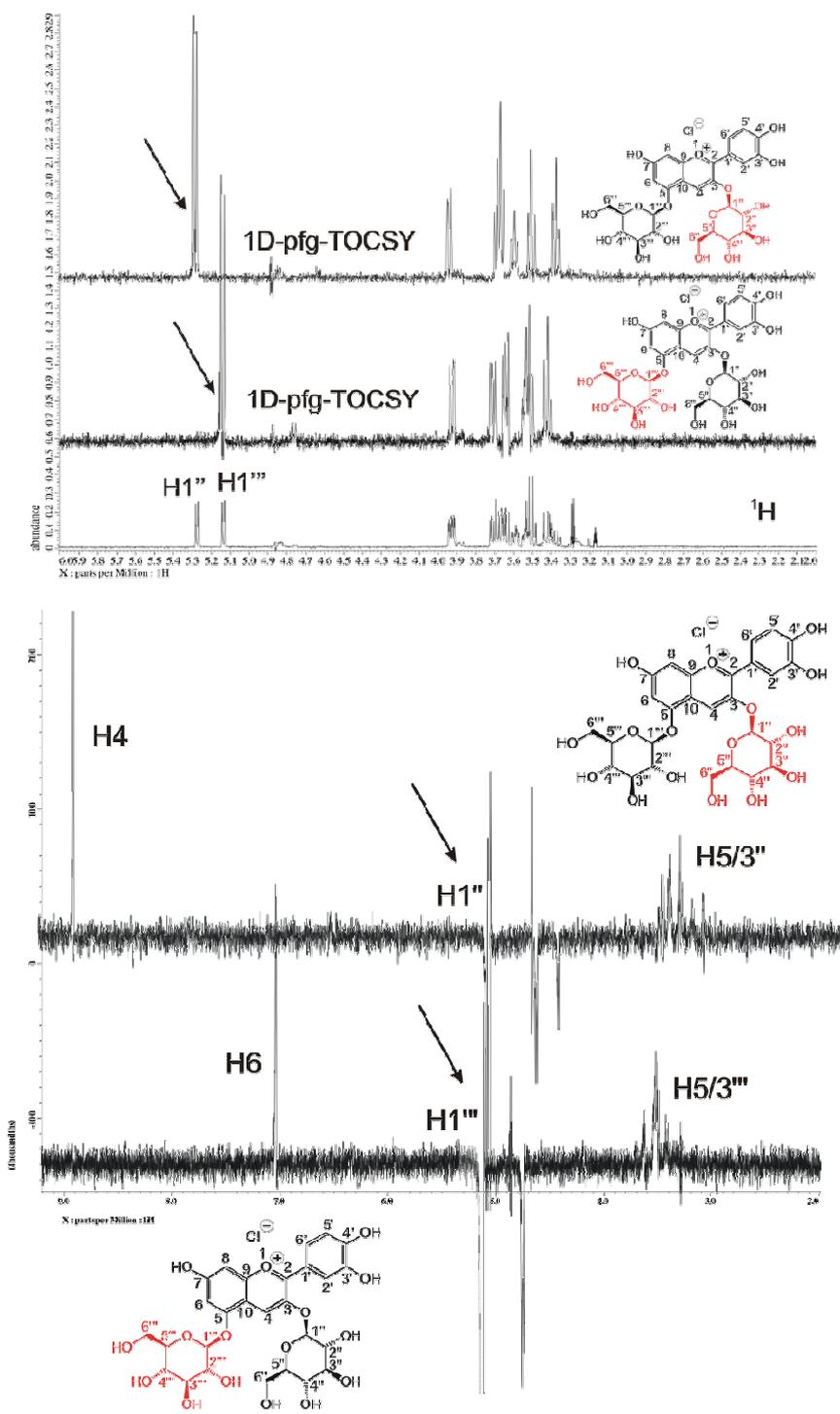


Figure 10S. Top: ^1H -pfg-TOCSY of cyanin chloride in MeOD; bottom: ^1H -pfg-rOe of cyanin chloride in MeOD. The enhancements on H4 and H6 are clearly visible.

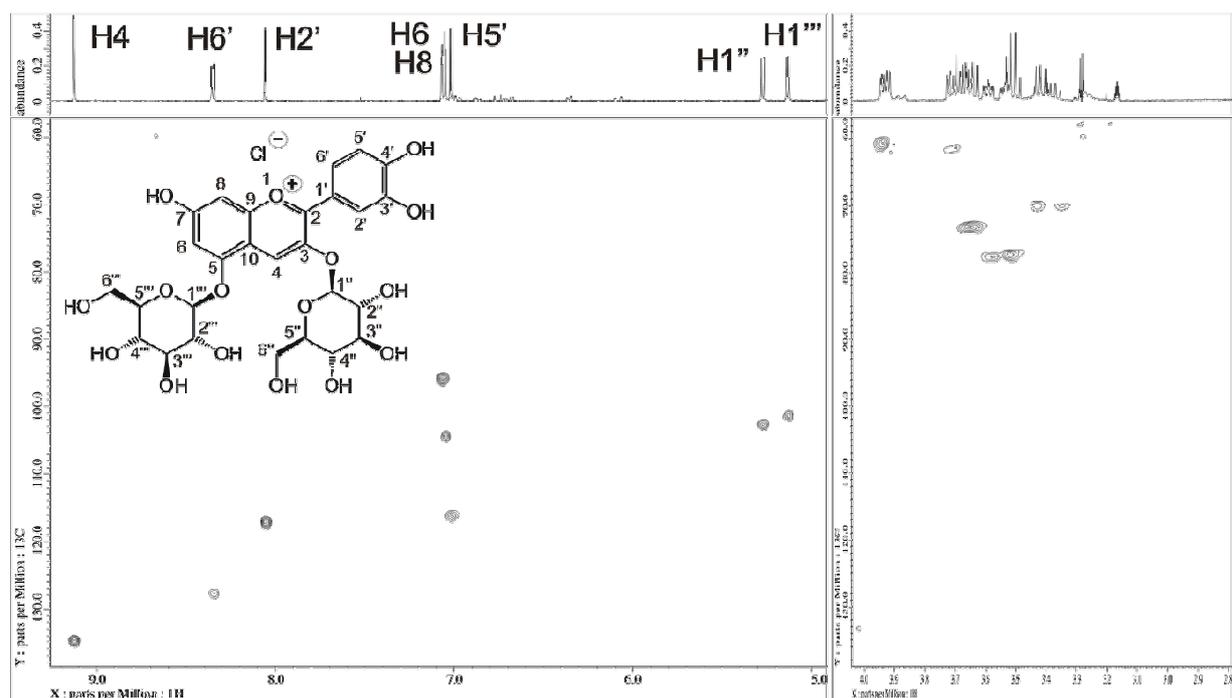


Figure 11S. $^1\text{H}/^{13}\text{C}$ -HMOC of cyanin chloride in MeOD.

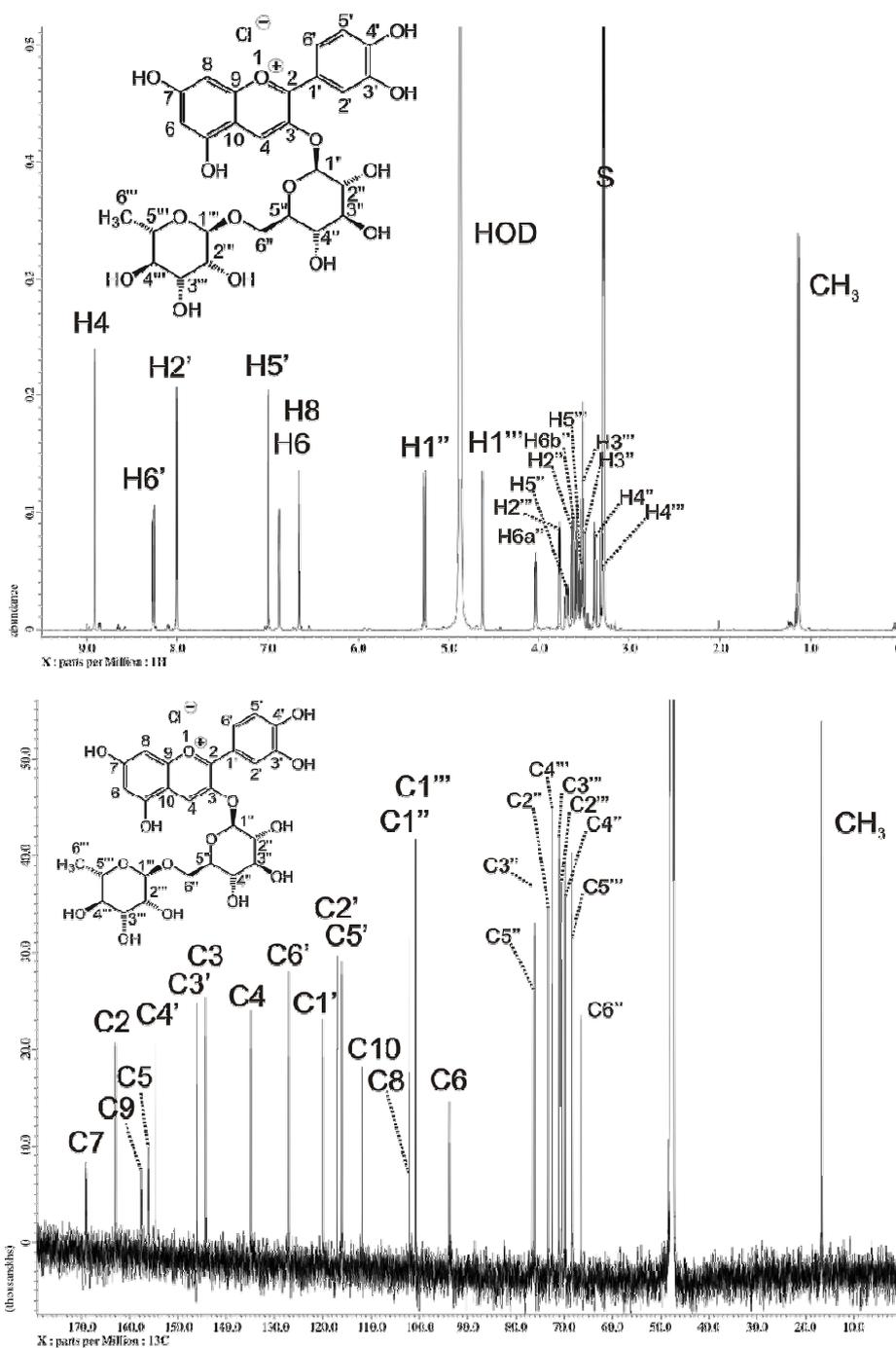


Figure 12S. Top: ¹H-NMR spectrum; bottom: ¹³C-NMR spectrum of keracyanin chloride in MeOD.

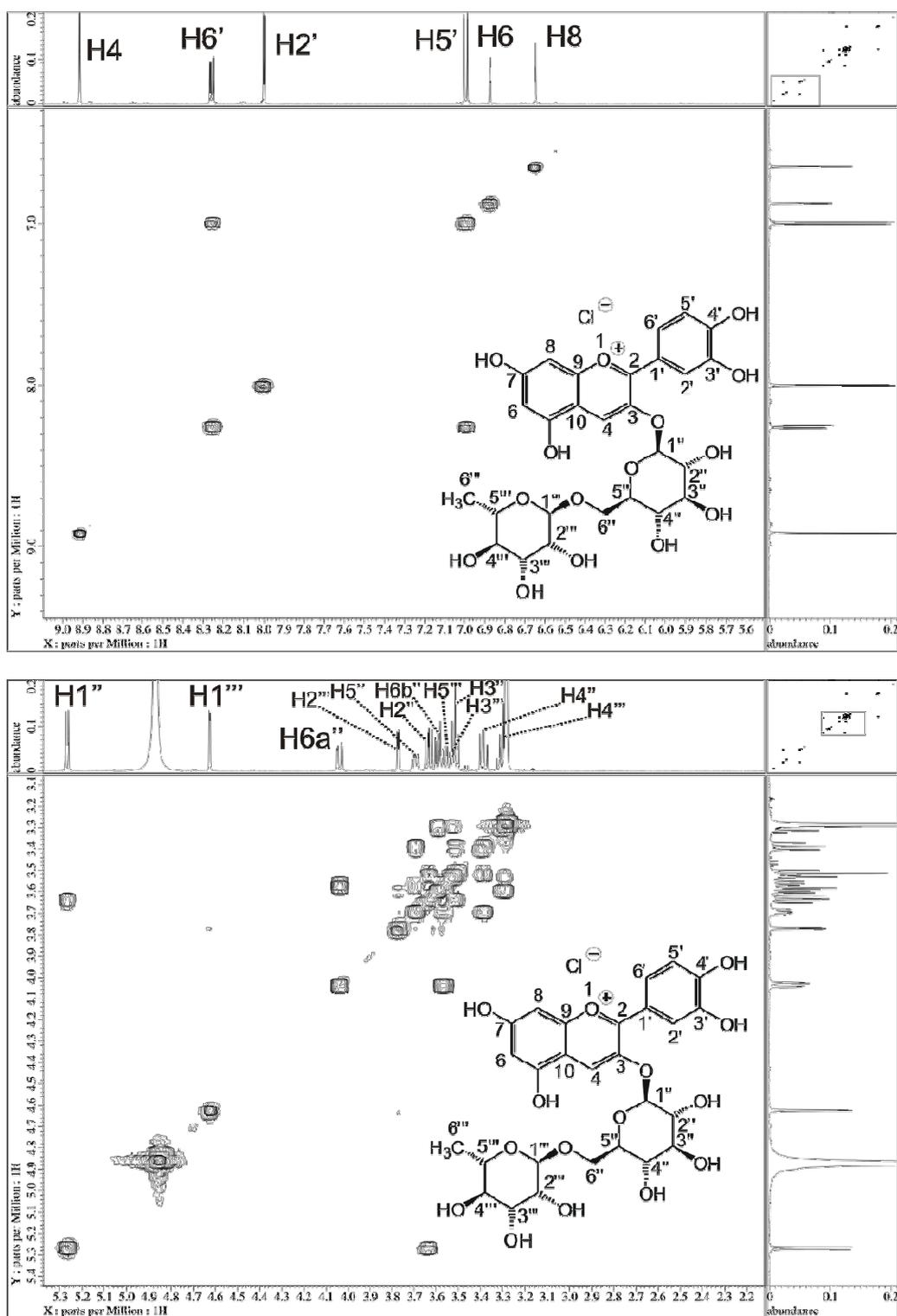


Figure 13S. ^1H - ^1H -COSY NMR spectrum of keracyanin chloride in MeOD.

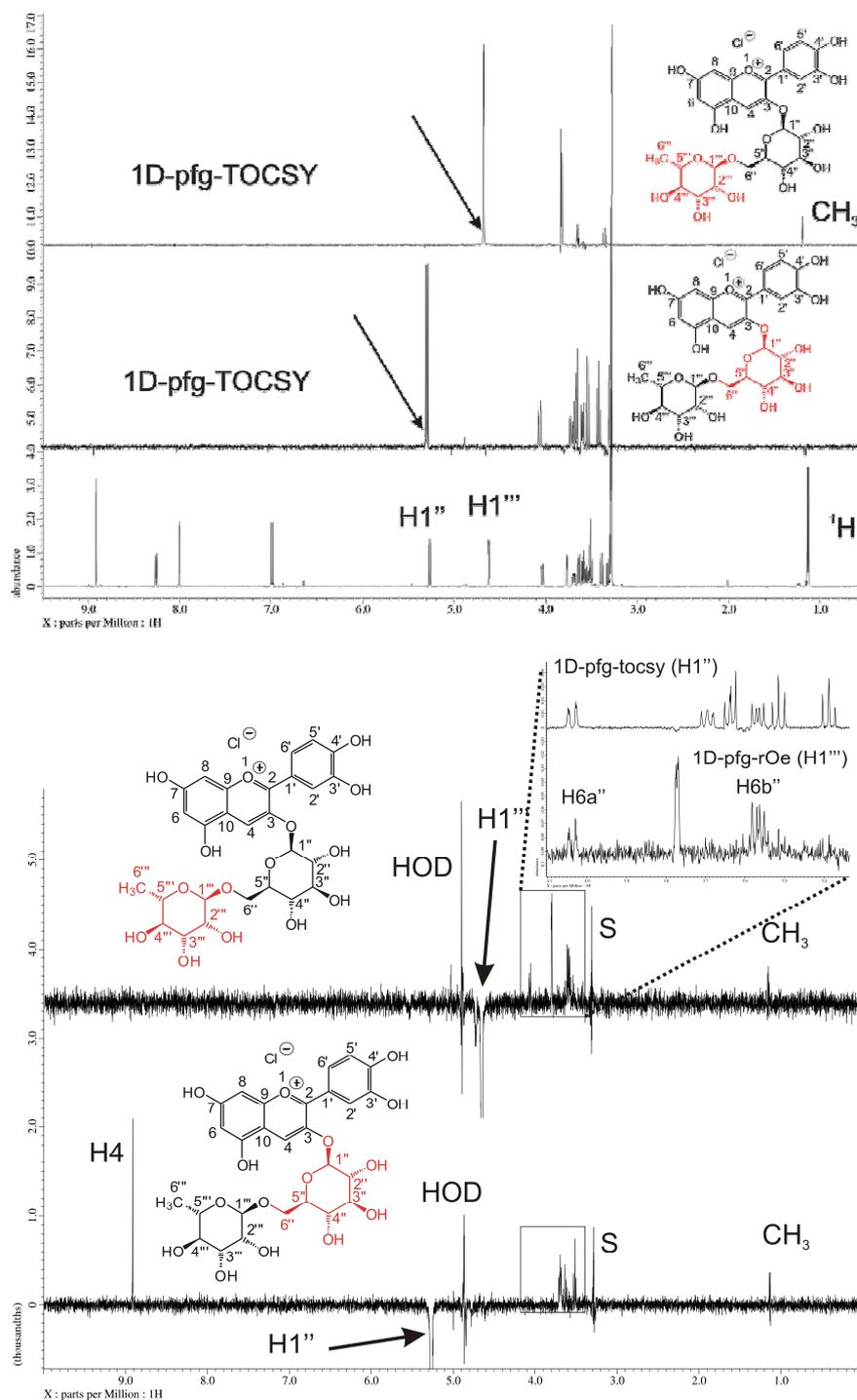


Figure 14S. Top: ^1H -pfg-TOCSY of keracyanin chloride in MeOD; bottom: ^1H -pfg-rOe of keracyanin chloride in MeOD. The enhancements on H4 and H6 are clearly visible.

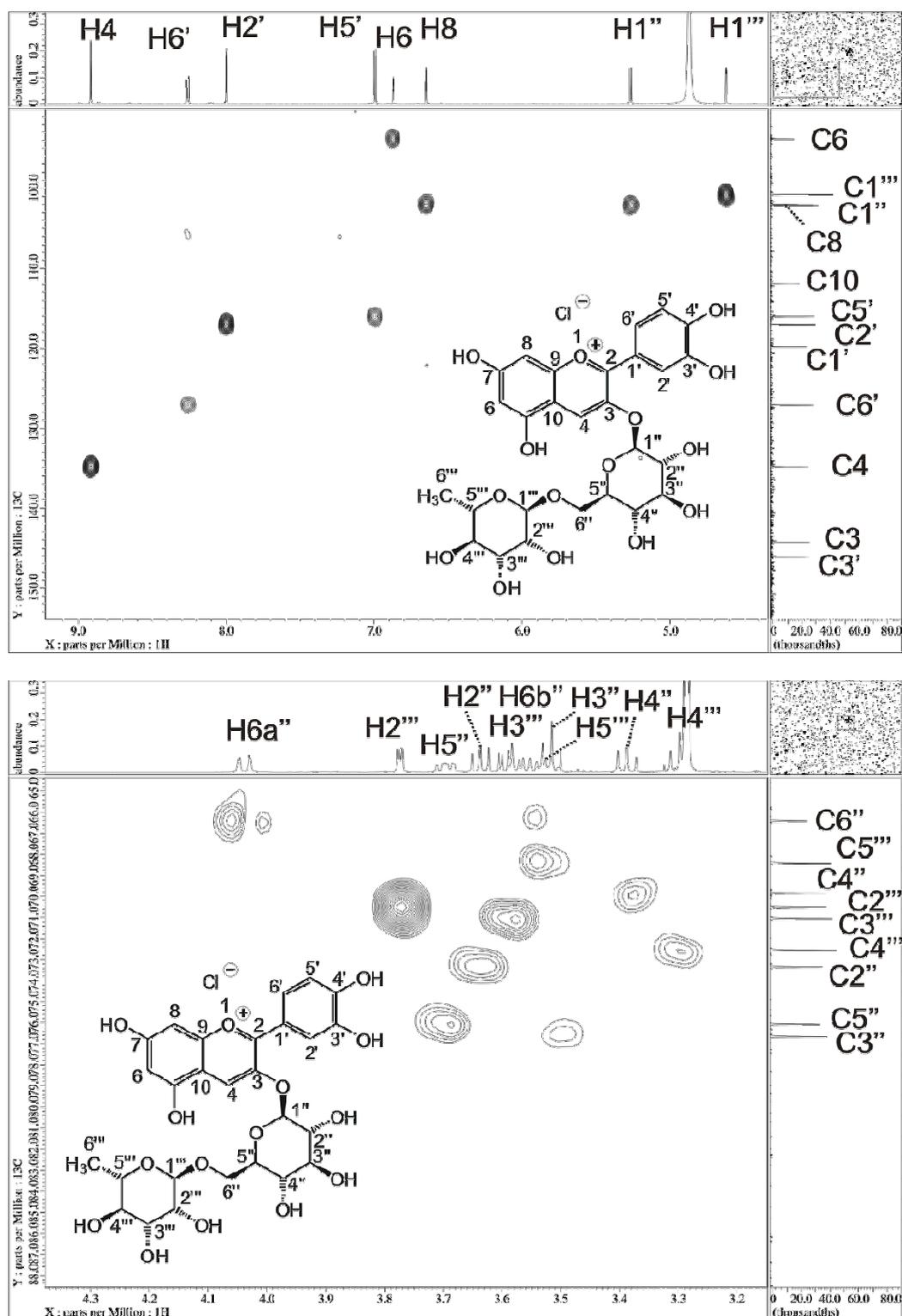


Figure 15S. ^1H - ^{13}C -HMQC NMR spectrum of keracyanin chloride in MeOD.

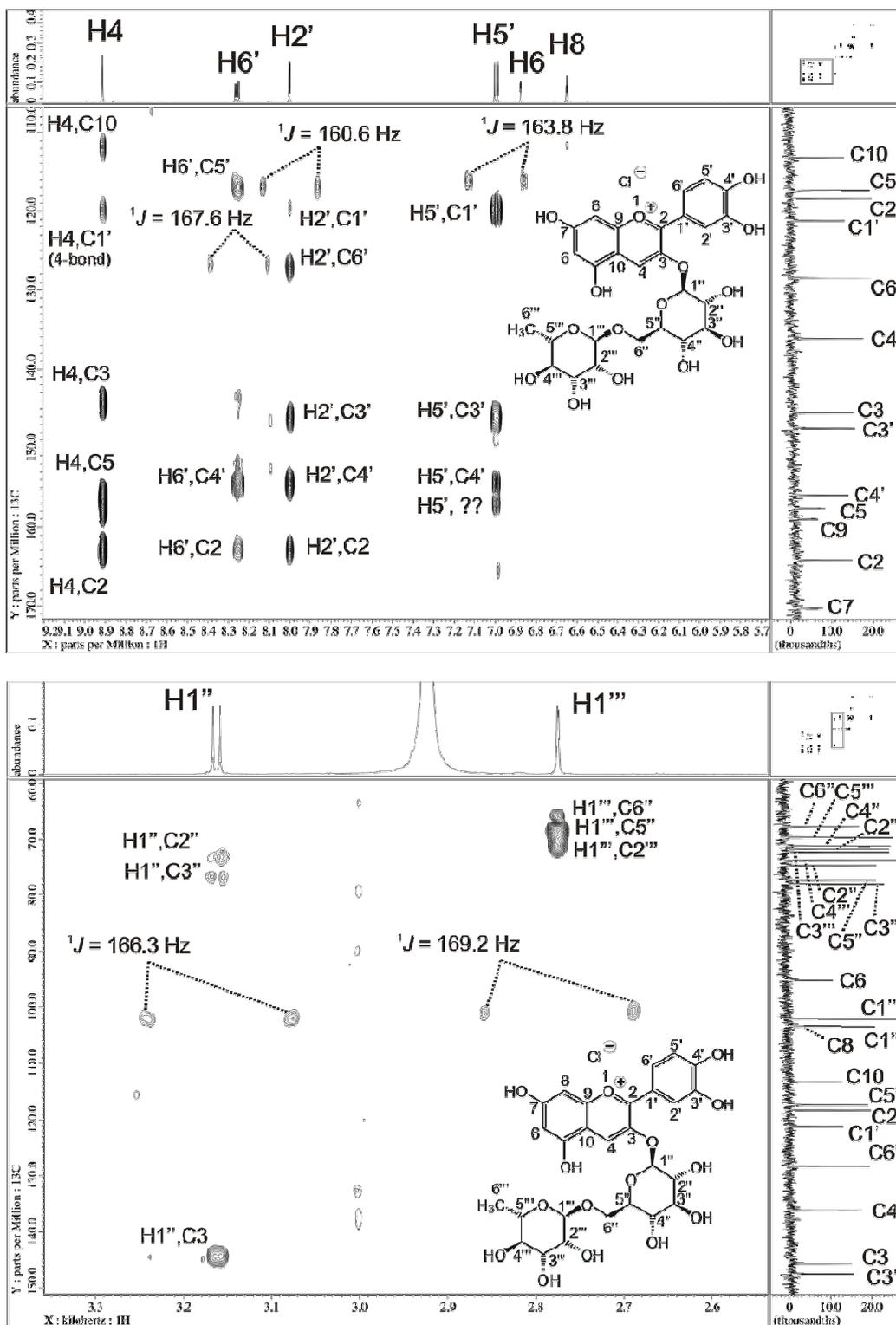


Figure 16S. ^1H - ^{13}C -HMBC NMR spectrum of keracyanin chloride in MeOD.

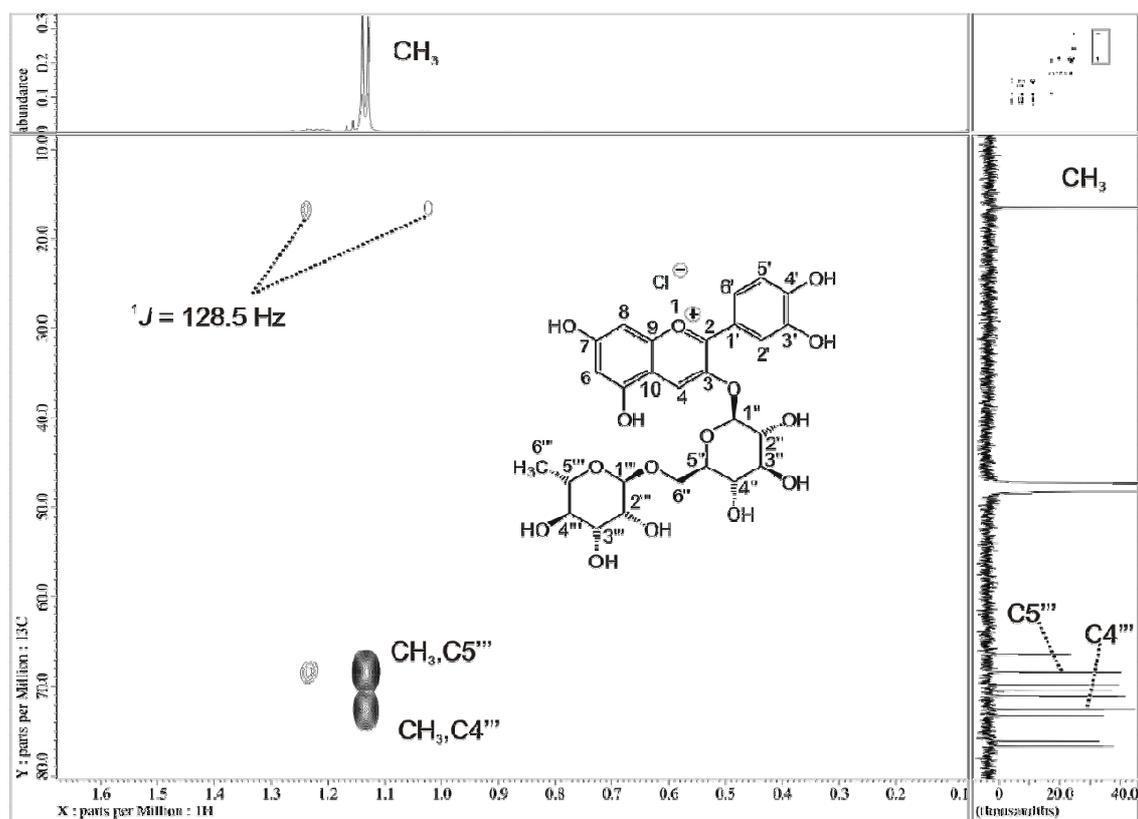


Figure 16S cont'd. ^1H - ^{13}C -HMBC NMR spectrum of keracyanin chloride in MeOD.

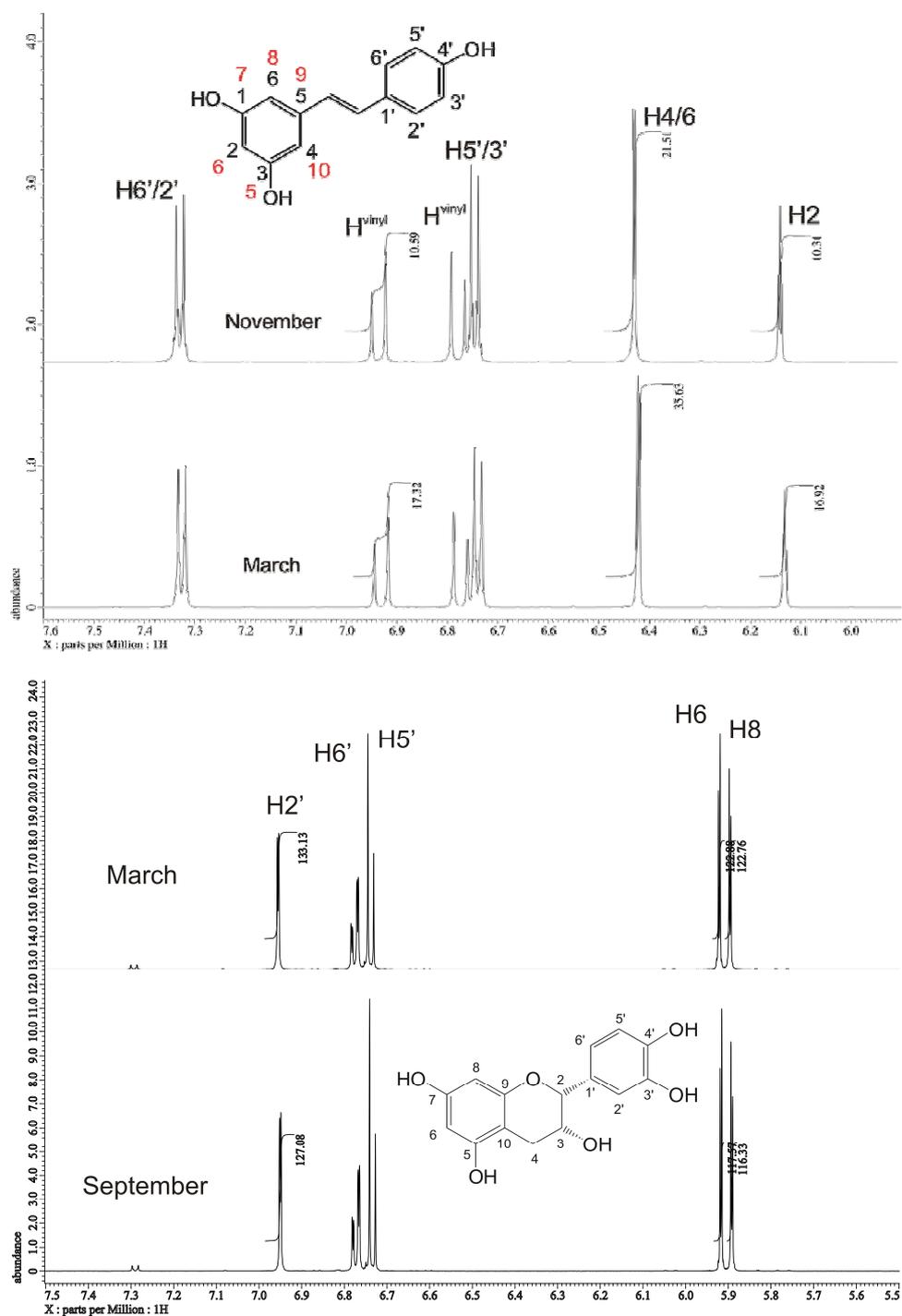


Figure 18S. Absence of H/D-exchange for resveratrol (1, top) and for (-)-epicatechin (2, bottom) in the NMR tube (MeOD).

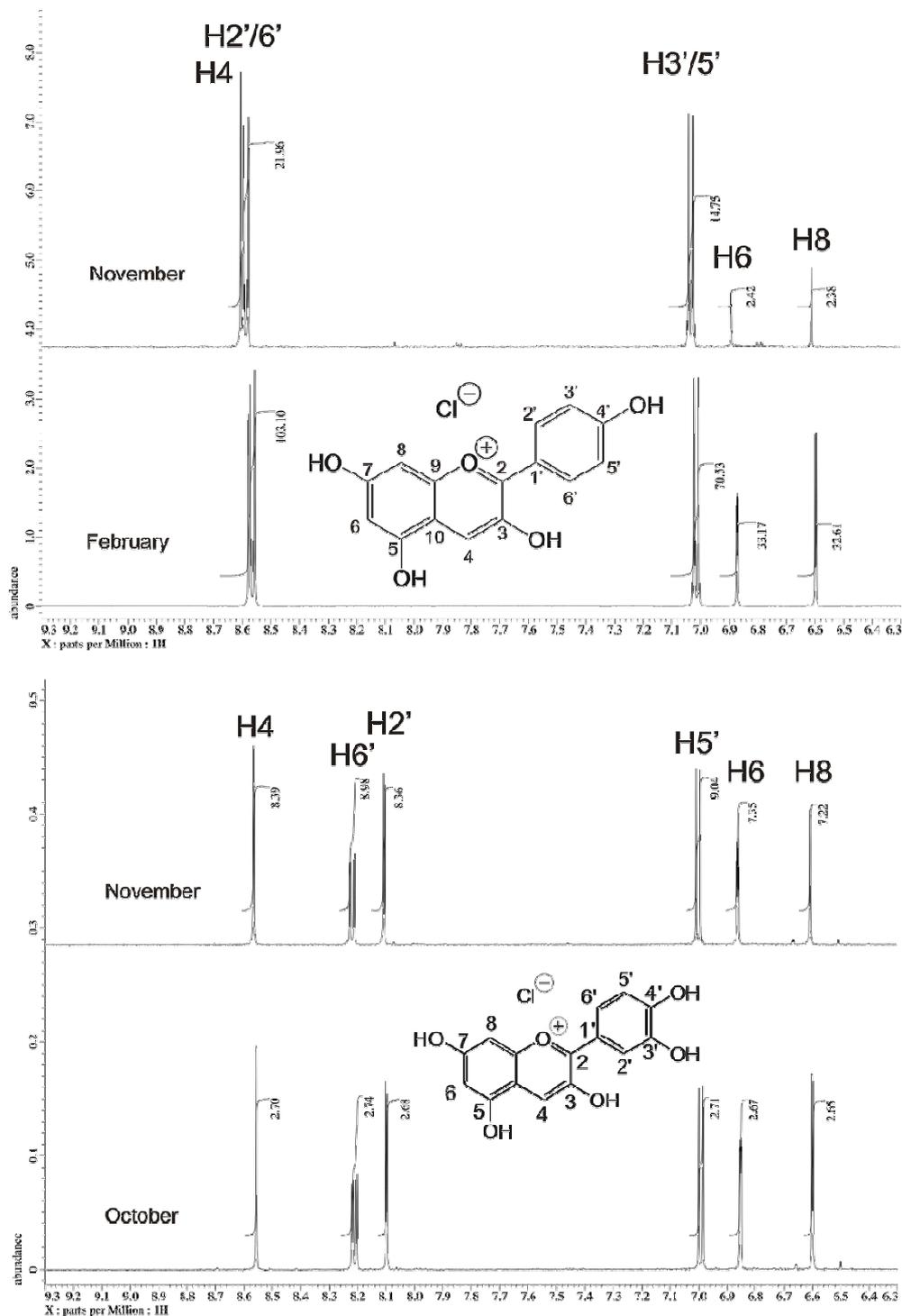


Figure 19S. Top: H/D-exchange for pelargonidin chloride (**3**) in the NMR tube (MeOD). Significant exchange was observed after about 8 months; bottom: H/D-exchange for cyanidin chloride (**4**) in the NMR tube (MeOD). Significant exchange was observed for both H6 and H8 after less than one month.

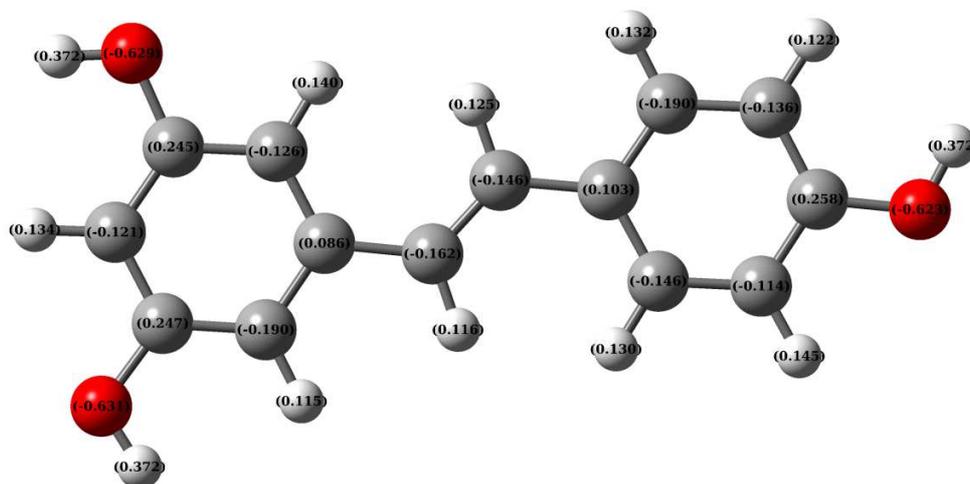
Table 1S. ¹H-NMR chemical shifts in ppm (ref. TMS) and coupling constants in Hz for the aromatic core of polyphenol standards **1-6** in MeOD at rt (¹H/¹³C IUPAC assignment in parentheses; see Figure 1), ^as, ^bd, ^ct, ^ddd, ^eddd, ^fdq, ^gAB-mixing, ^hn. det., ⁱbroad.

	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 J _{149.1}	-	-	-	-	-	-	-	-	-	-
2	6.94 ^b (H ^{vinyl}) ³ J _{2,1} 16.3	128.0 (C ^{vinyl}) ¹ J _{146.4}	4.79 ^{a1}	78.5 ¹ J _{143.2}	-	160.9	-	161.0	-	164.2	-	162.9
3	-	-	4.15 ^c ³ J _{3,2} 1.5 ³ J _{3,4a} 3.0 ³ J _{3,4c} 4.6	66.2 ¹ J _{146.1} ¹ J _{143.2}	-	145.1	-	146.0	-	145.7	-	144.3
4	-	-	2.71 ^d /2.84 ^d ³ J _{4a,3} 3.0 ³ J _{4a,4c} 16.8 ³ J _{4c,3} 4.6 ³ J _{4c,4a} 16.6	27.9 ¹ J _{130.1}	8.59 ^b ⁵ J _{4,6} 0.8	133.2 ¹ J _{168.2}	8.56 ^b ⁵ J _{4,6} 0.6	132.9 ¹ J _{167.9}	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 J _{157.3}	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 J _{162.1}	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 J _{153.7}	5.90 ^{b,g} ⁴ J _{8,6} 2.4	94.6 ¹ J _{159.5}	6.61 ^b ³ J _{8,6} 2.0	101.8 ¹ J _{159.9}	6.61 ^b ³ J _{8,6} 2.0	102.0 ¹ J _{162.5}	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 J _{153.8}	-	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 J _{155.1}	6.95 ^b ⁴ J _{2',2'0.4} ³ J _{2',6'} 1.9	114.0 ¹ J _{157.3}	8.57 ^{b,g} ³ J _{2',3'} 9.1	133.6 ¹ J _{167.0}	8.11 ^b ³ J _{2',6'} 2.3	117.4 ¹ J _{159.0}	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 J _{161.3}
3'	6.75 ^b ³ J _{3',2'} 8.6	115.1 ¹ J _{162.0}	-	144.6	7.03 ^{b,g} ³ J _{3',2'} 9.1	116.4 ¹ J _{161.3}	-	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 J _{162.0}	6.74 ^b ³ J _{5',5'} 8.1	118.1 ¹ J _{156.9}	7.03 ^{b,g} ³ J _{5',6'} 9.1	116.4 ¹ J _{161.3}	7.00 ^b ³ J _{5',6'} 8.7	116.4 ¹ J _{157.8}	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 J _{162.7}
6'	7.34 ^b ³ J _{6',5'} 8.6	127.5 ¹ J _{155.1}	6.77 ^c ⁴ J _{6',2'0.4} ³ J _{6',2'} 1.9 ³ J _{6',5'} 8.2	114.6 ¹ J _{160.3}	8.57 ^{b,g} ³ J _{6',5'} 9.1	133.6 ¹ J _{167.0}	8.22 ^d ³ J _{6',5'} 8.7 ³ J _{6',2'} 2.3	126.4 ¹ J _{167.9}	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 J _{168.6}

Table 2S. ^1H -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 ($^1\text{H}/^{13}\text{C}$ IUPAC assignment in parentheses; see Figure 1), ^as, ^bd, ^ct, ^ddd, ^eddd, ^fdq, ^gAB-mixing, ^hn. det., ⁱbroad.

	5		6	
	^1H	^{13}C	^1H	^{13}C
1''	5.28 ^b $^3J_{1'',2''}$ 7.9	102.7 $^1J_{157.8}$	5.27 ^b $^3J_{1'',2''}$ 7.7	102.1 $^1J_{164.0}$
2''	3.67 ^d $^3J_{2'',3''}$ 9.5 $^3J_{2'',1''}$ 7.9	73.3 $^1J^h$	3.64 ^d $^3J_{2'',3''}$ 9.2 $^3J_{2'',1''}$ 7.8	73.3 $^1J^h$
3''	3.51 ^c $^3J_{3'',4''}$ 9.3 $^3J_{3'',2''}$ 9.3	77.5 $^1J^h$	3.52 ^c $^3J_{3'',4''}$ 9.2 $^3J_{3'',2''}$ 9.2	68.3 $^1J^h$
4''	3.38 ^d $^3J_{4'',5''}$ 9.4 $^3J_{4'',3''}$ 9.2	70.1 $^1J^h$	3.39 ^d $^3J_{4'',5''}$ 9.8 $^3J_{4'',3''}$ 9.1	69.9 $^1J^h$
5''	3.60 ^e $^3J_{5'',6a''}$ 2.1 $^3J_{5'',6b''}$ 6.9 $^3J_{5'',4''}$ 9.5	77.7 $^1J^h$	3.70 ^e $^3J_{5'',6a2''}$ 6.6 $^3J_{5'',6b''}$ 1.7 $^3J_{5'',4''}$ 9.7	76.1 $^1J_{116.8}$
6_S''	3.68 ^d $^3J_{6S'',6R''}$ 11.9 $^3J_{6S'',5''}$ 6.9	61.3 $^1J^h$	3.57 ^d $^3J_{6S'',6R''}$ 11.2 $^3J_{6S'',5''}$ 6.6	66.3 $^1J_{136.8}$
6_R''	3.95 ^d $^3J_{6R'',5''}$ 2.2 $^3J_{6R'',6S''}$ 12.0	61.3 $^1J^h$	4.04 ^d $^3J_{6R'',5''}$ 1.7 $^3J_{6R'',6S''}$ 11.2	66.3 $^1J_{136.8}$
1'''	5.14 ^b $^3J_{1''',2'''}7.8$	101.4 $^1J^h$	4.62 ^b $^3J_{1''',2'''}1.5$	100.8 $^1J_{169.7}$
2'''	3.65 ^d $^3J_{2''',3'''}9.3$ $^3J_{2''',1'''}7.8$	73.0 $^1J^h$	3.77 ^d $^3J_{2''',3'''}3.5$ $^3J_{2''',1'''}1.6$	70.6 $^1J^h$
3'''	3.52 ^c $^3J_{3''',4'''}9.2$ $^3J_{3''',2'''}9.2$	77.1 $^1J^h$	3.60 ^d $^3J_{3''',4'''}9.5$ $^3J_{3''',2'''}3.5$	71.1 $^1J^h$
4'''	3.43 ^d $^3J_{4''',5'''}9.4$ $^3J_{4''',3'''}9.3$	70.0 $^1J^h$	3.30 ^c $^3J_{4''',5'''}9.6$ $^3J_{4''',3'''}9.6$	72.6 $^1J^h$
5'''	3.55 ^e $^3J_{5''',6a'''}2.5$ $^3J_{5''',6b'''}5.8$ $^3J_{5''',4'''}9.8$	77.4 $^1J^h$	3.53 ^f $^3J_{5''',\text{CH}_3}$ 6.1 $^3J_{5''',4'''}9.3$	66.3 $^1J^h$
6_S'''	3.72 ^d $^3J_{6S''',6R'''}12.1$ $^3J_{6S''',5'''}5.8$	61.1 $^1J^h$	-	-
6_R'''	3.93 ^d $^3J_{6R''',5'''}2.2$ $^3J_{6R''',6S'''}12.1$	-	-	-
CH₃	-	-	1.15 ^b $^3J_{\text{CH}_3,5'''}6.2$	16.5 $^1J_{129.1}$

a)



b)

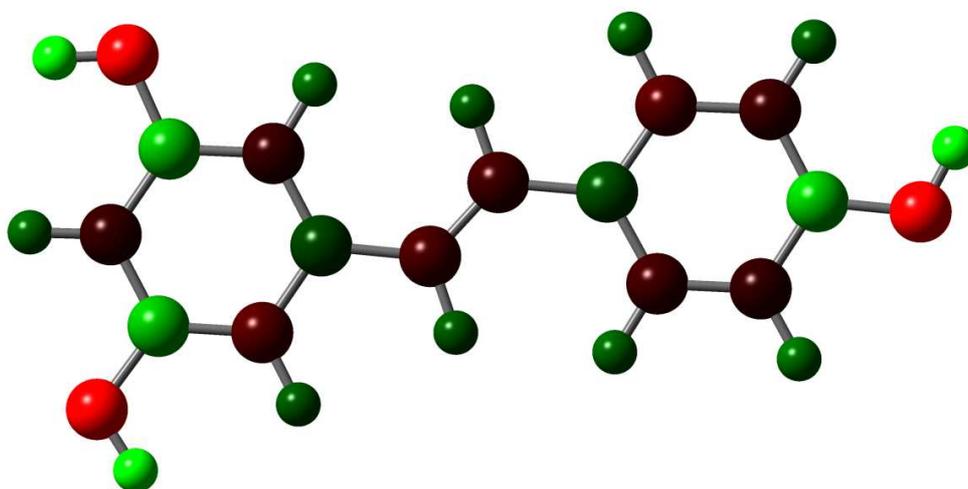
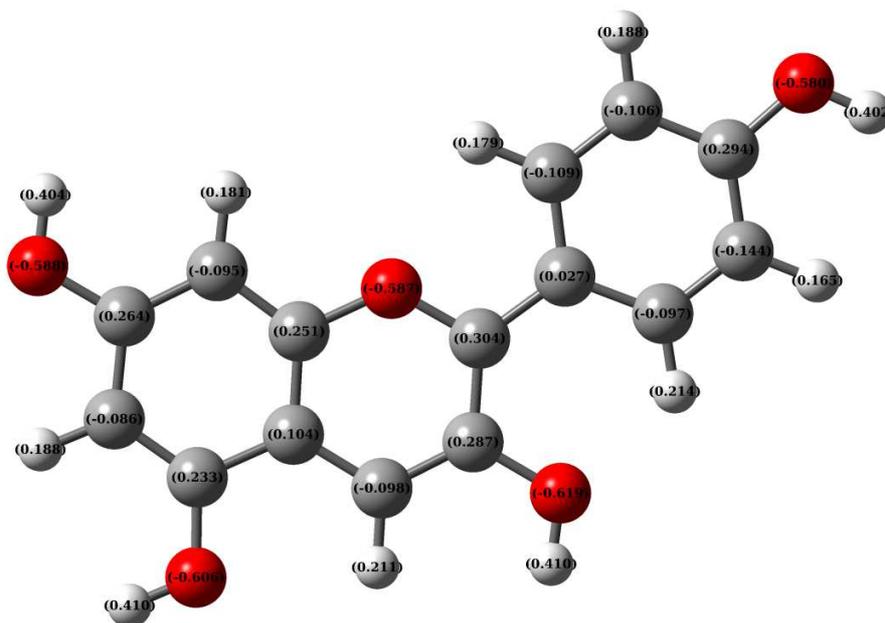


Figure 20S. a) Resveratrol (**1**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown; b) Resveratrol (**1**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown in color-gradients; red: negative, black: neutral, green: positive).

a)



b)

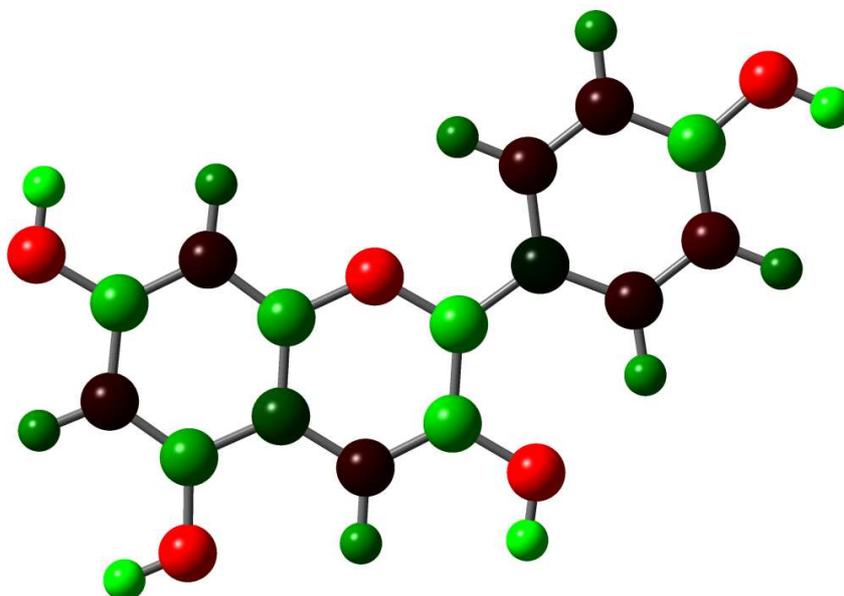
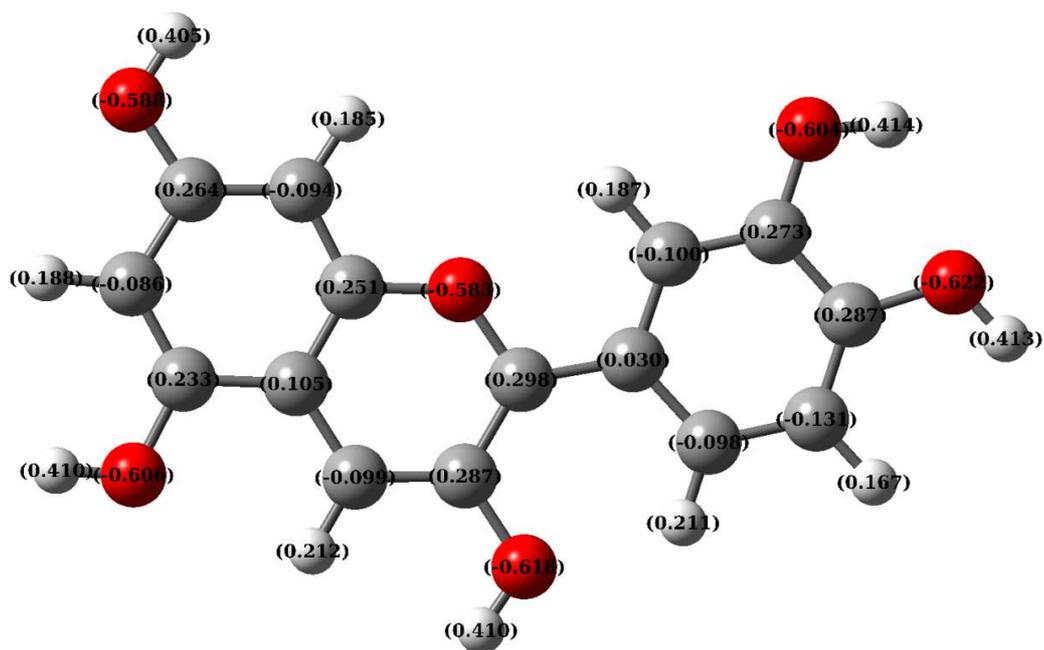


Figure 21S. a) Pelargonidin cation (**3**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown; b) Pelargonidin cation (**3**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown in color-gradients; red: negative, black: neutral, green: positive).

a)



b)

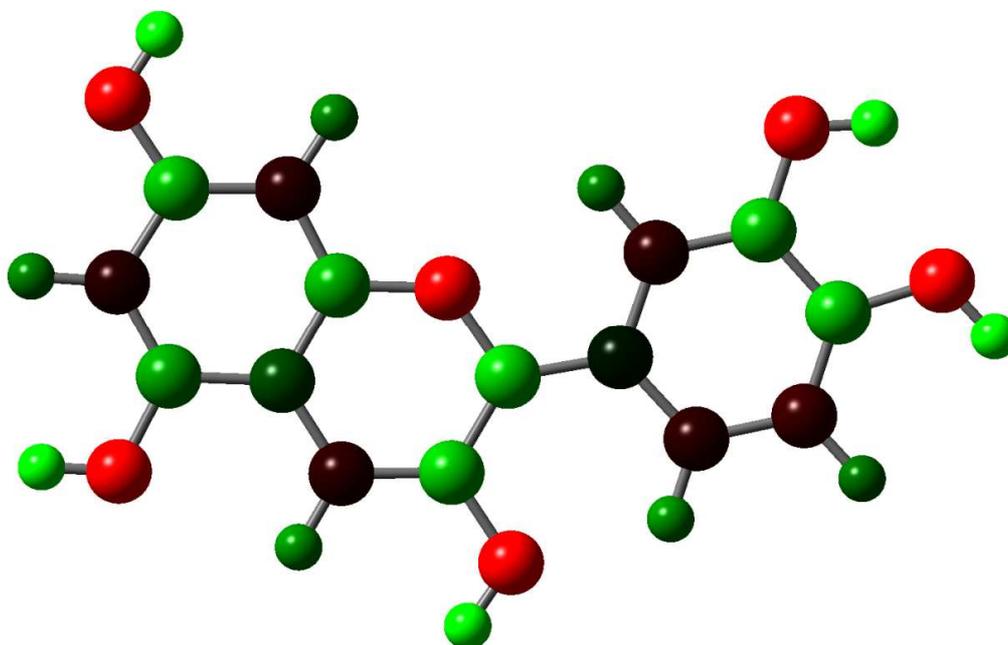
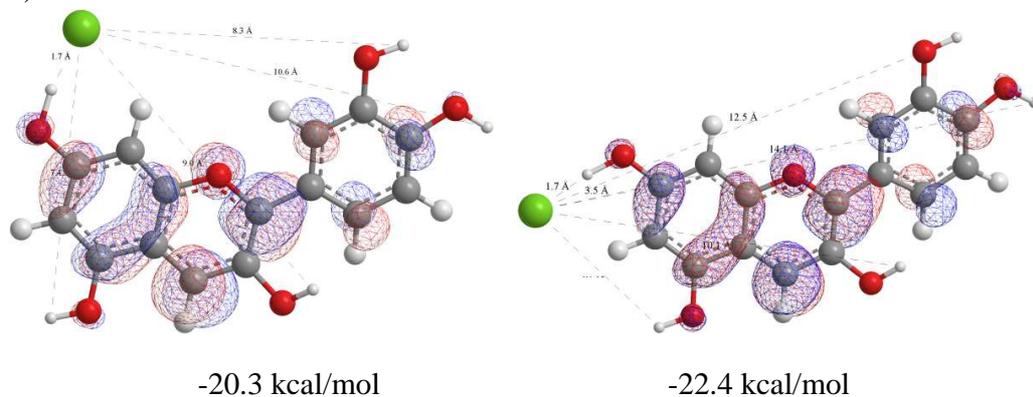
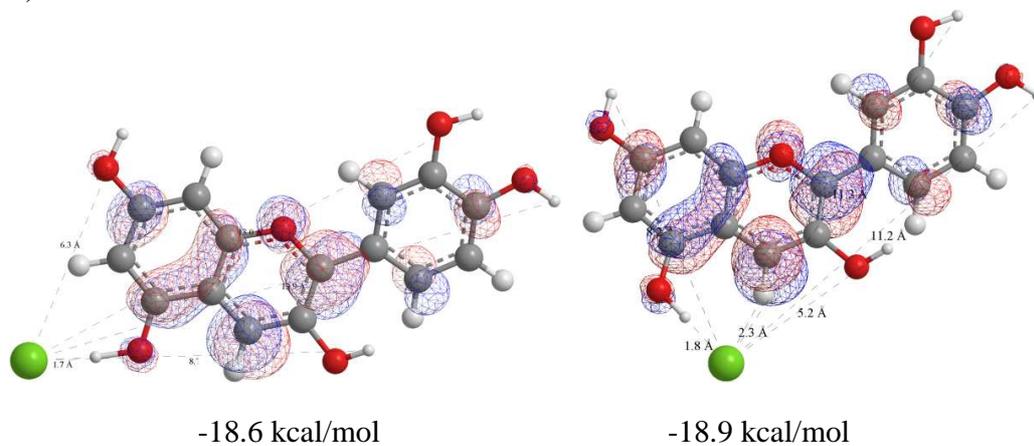


Figure 22S. a) Cyanidin cation (**4**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown; b) Cyanidin cation (**4**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown in color-gradients; red: negative, black: neutral, green: positive).

a)



b)



c)

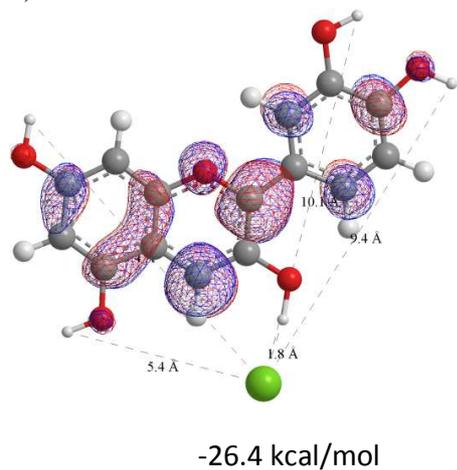
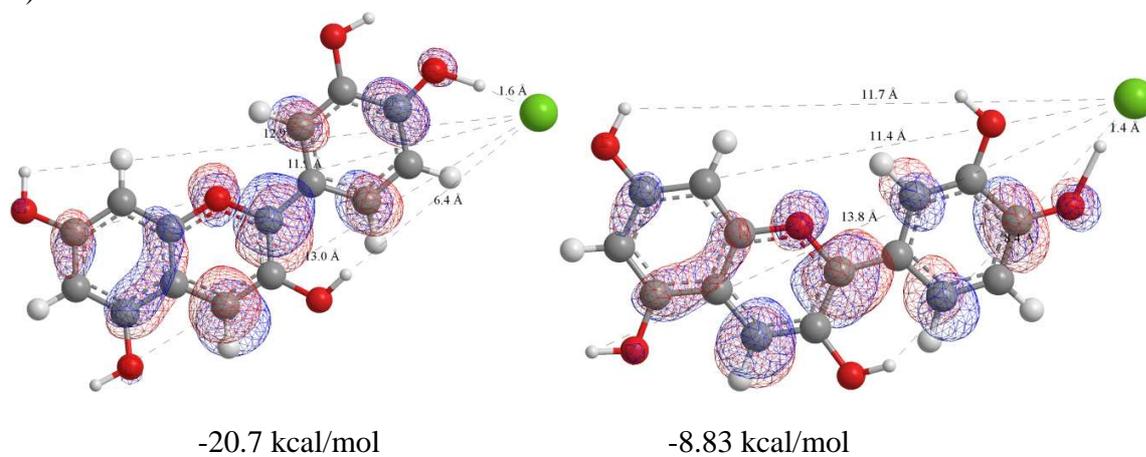


Figure 23S. Cyanidin chloride (**4**) (ChemBio3D Ultra, DFT-B3LYP-6-31G, 0 K). The LUMO is shown. The right structure is more stable relative to structure by a) left: -20.3 kcal/mol; right: -22.4 kcal/mol; b) left: -18.6 kcal/mol; right: -18.9 kcal/mol; c) -26.4 kcal/mol.

d)



e)

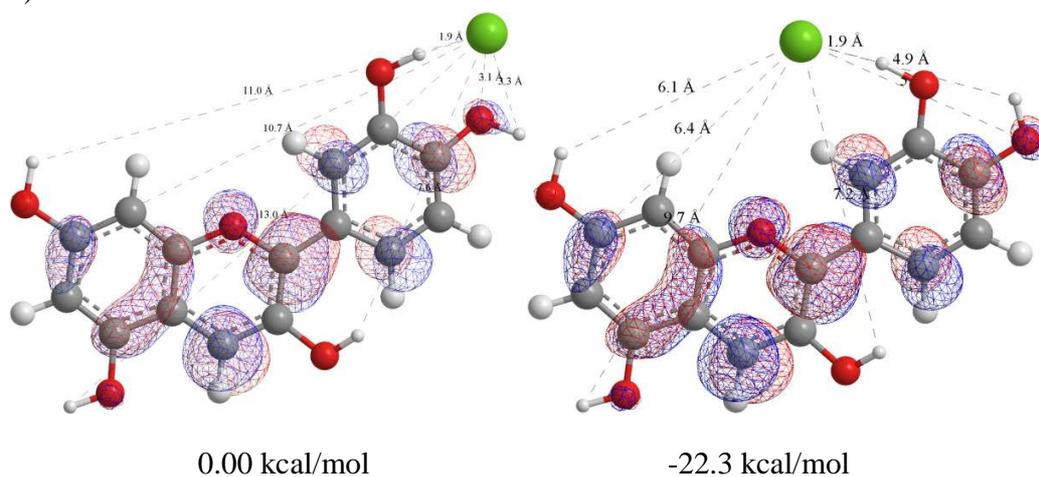
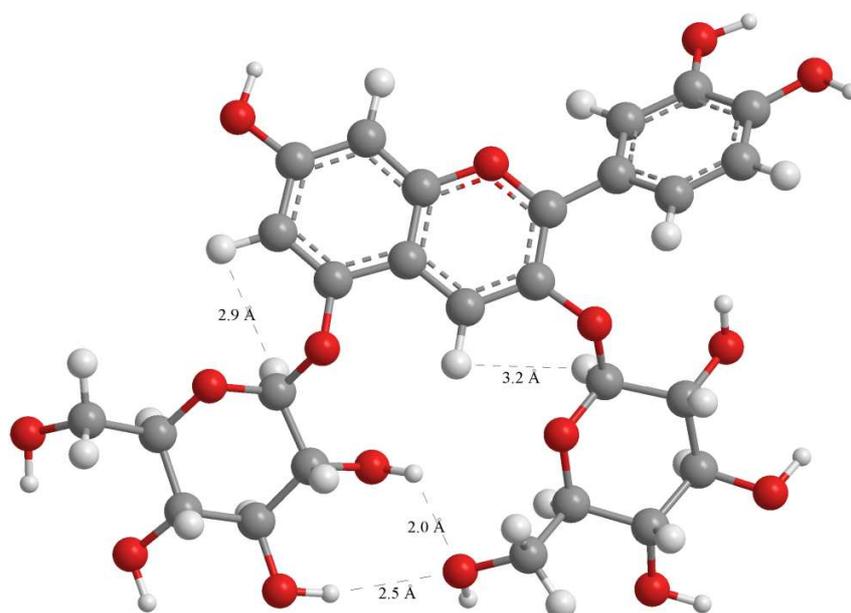


Figure 23S cont'd. Cyanidin chloride (**4**) (ChemBio3D Ultra, DFT-B3LYP-6-31G, 0 K). The LUMO is shown. The right structure is more stable by d) left: -20.7 kcal/mol; right: -8.83 kcal/mol; e) left: 0.00 kcal/mol; right: -22.3 kcal/mol.

a)



b)

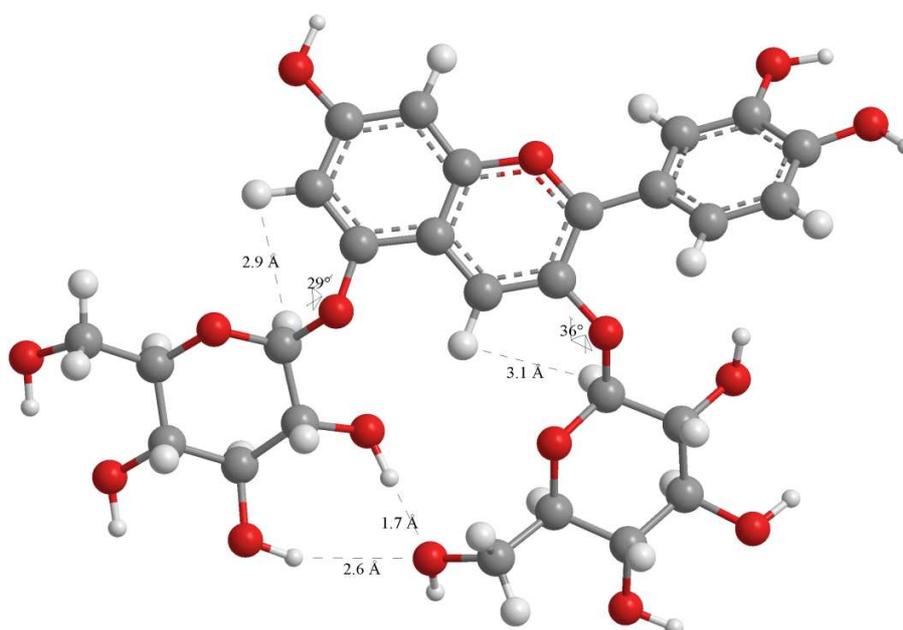
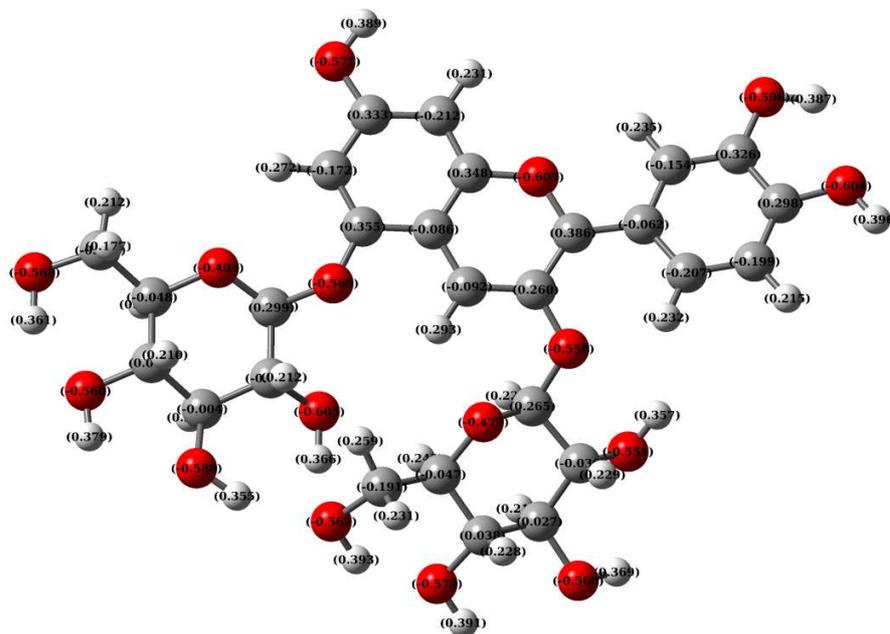


Figure 24S. a) Cyanin cation (**5**) (ChemBio3D Ultra, AM1, 0 K, vacuum, $\phi'' = -86^\circ$, $\psi'' = -108^\circ$ and $\phi''' = 59^\circ$, $\psi''' = -97^\circ$; glycosidic dihedrals $H1''C''OC3 = +33^\circ$ and $H1'''C1'''OC5 = +22^\circ$); b) Cyanin cation (**5**) (ChemBio3D Ultra, DFT-B3LYP-6-31G,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

a)



b)

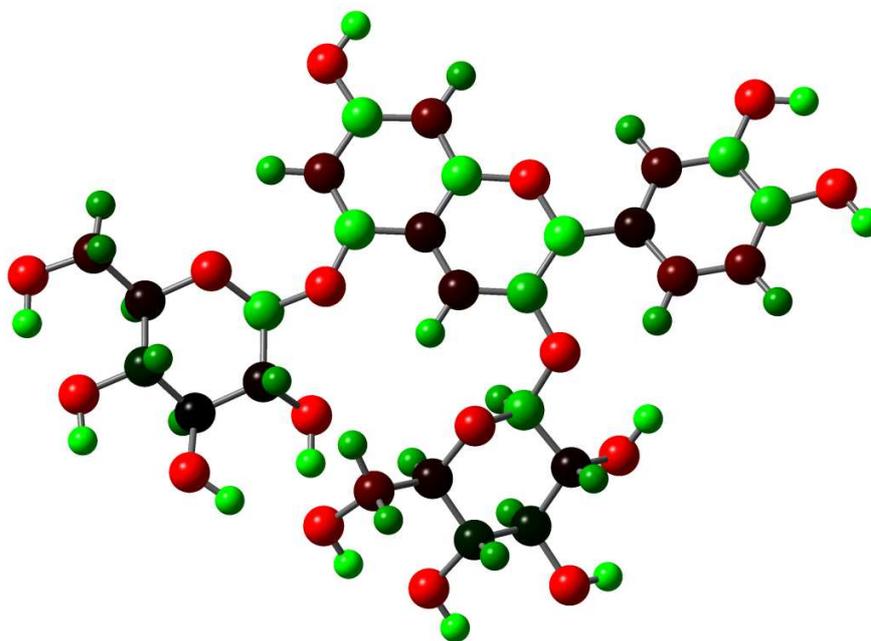
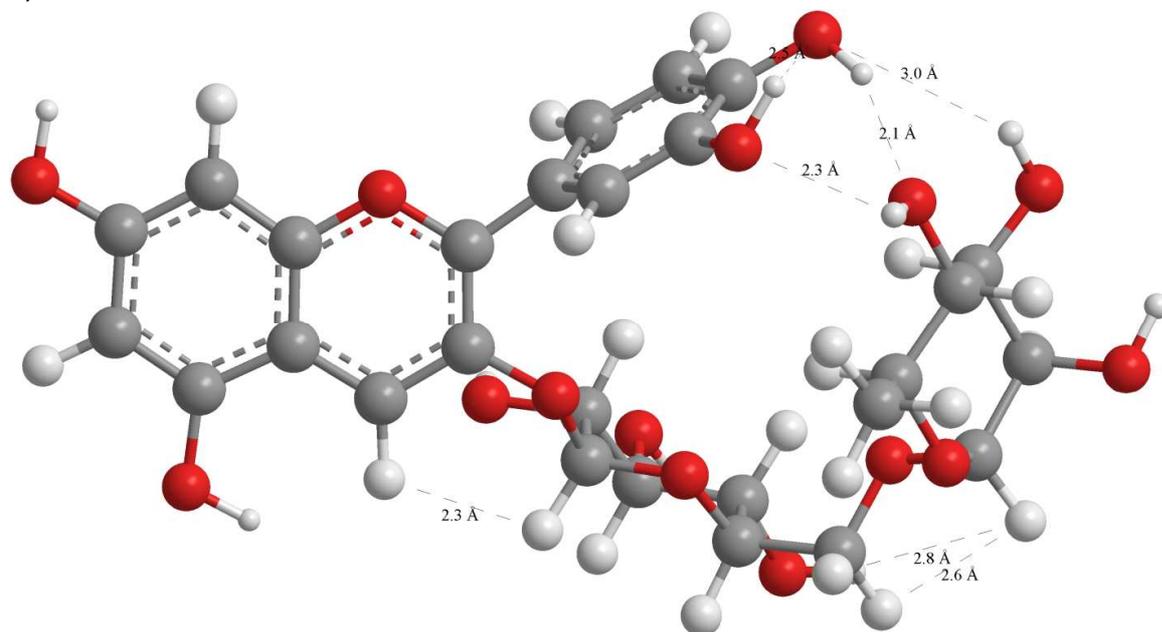


Figure 25S. a) Cyanin cation (**5**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown; b) Cyanin cation (**5**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown in color-gradients; red: negative, black: neutral, green: positive).

a)



b)

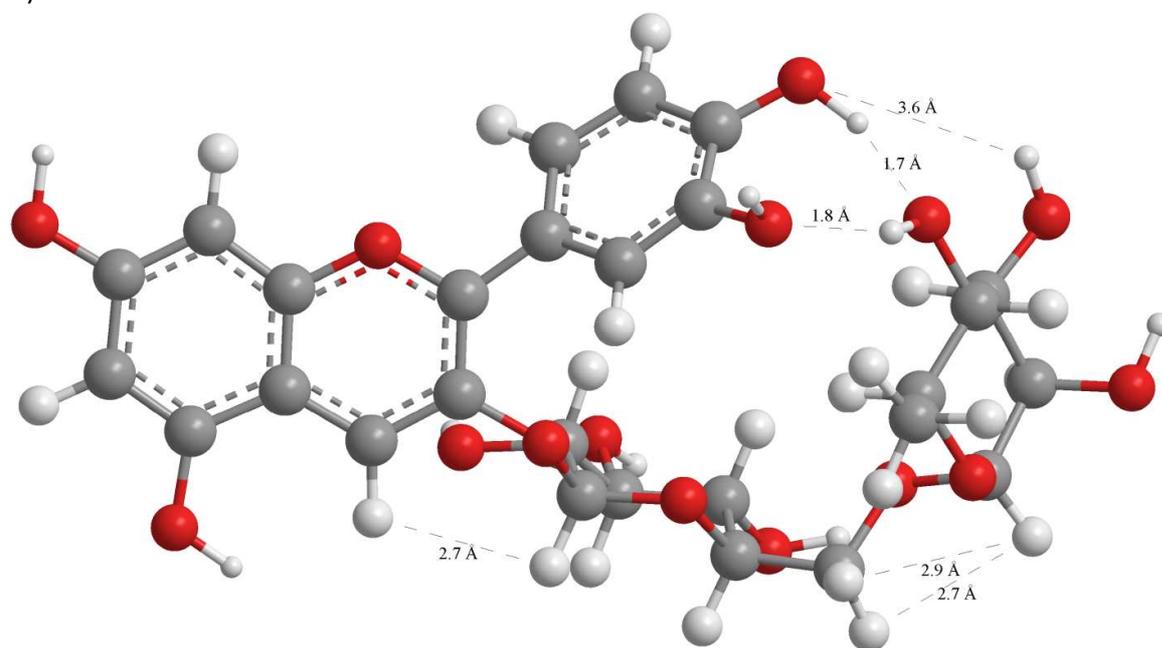
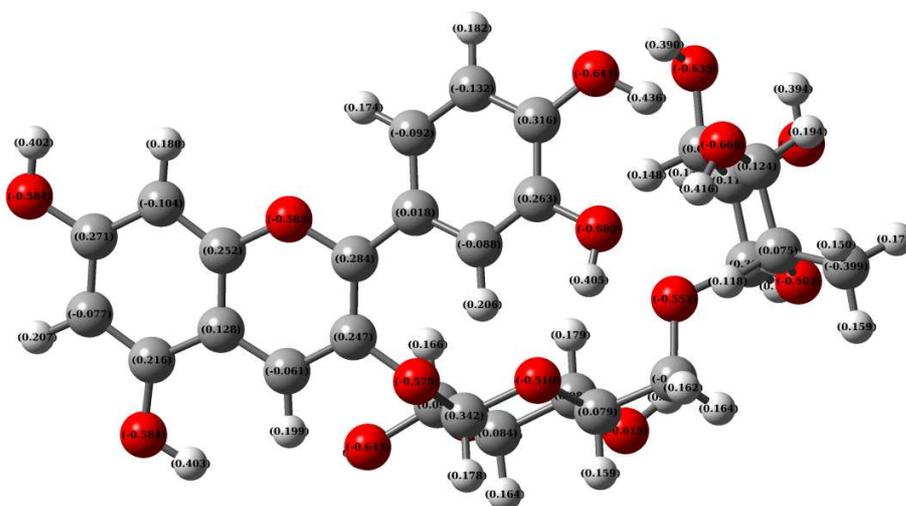


Figure 26S. a) Keracyanin cation (**6**) (ChemBio3D Ultra, **AM1**, 0 K, vacuum, $\phi'' = +57^\circ$, $\psi'' = +167^\circ$ and $\phi''' = -64^\circ$, $\psi''' = +167^\circ$; glycosidic dihedrals $H1''C''OC3 = -76^\circ$ and $H1'''C1'''OC6'' = +50^\circ$); b) Keracyanin cation (**6**) (ChemBio3D Ultra,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

a)



b)

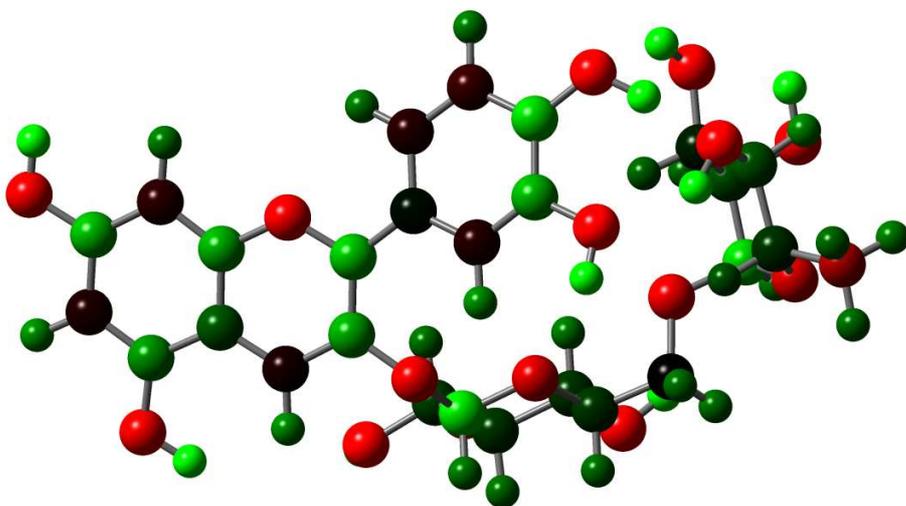


Figure 27S. a) Keracyanin cation (**6**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown; b) Keracyanin cation (**6**) (Gaussian09, DFT-B3LYP-6-31G, 0 K). Mulliken charge densities are shown in color-gradients; red: negative, black: neutral, green: positive).

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 blossoms³
Plant infection by bacteria and fungi^{2,4}
Relief of oxidative stress by polyphenols⁴
Polyphenol applications as antioxidants^{2,5,6}
Polyphenols as antiangiogenic/anti-cancer agents⁶
Isolation of polyphenols by ion exchange chromatography⁷⁻¹⁰
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 IR¹⁷
Polyphenol content in berries¹⁸⁻²¹
Total synthesis of polyphenols²²
Semi-synthetic modifications of natural products²²
Carbohydrate ring geometry by NMR^{23,24}
Karplus relation²⁵⁻²⁷
Carbohydrate nomenclature^{28,29}
Conformations of oligosaccharides³⁰⁻³⁷
J-HMBC techniques³⁸
Coupling, conformational averaging, electron-withdrawing features^{39,40}
H/D-Exchange through transition metal catalysis⁴¹⁻⁴⁸
H/D-Exchange under harsh reaction condotions⁴⁹
H/D-Exchange on aromatic heterocycles⁴⁶
H/D-Exchange on phenols^{49,50}
Isotope effects in NMR chemical shifts⁵¹⁻⁵⁵
Isotope effects in H-bonded systems⁵⁶⁻⁷⁰
Isotope effects in the structure determination of small proteins^{71,72}
Reviews of isotope effects in NMR^{58,73-76}

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