Metabolite Profiling of *Christia vespertilionis* Leaf Metabolome *via* Molecular Network Approach

Supplementary Materials

Anis Irfan Norazhar [1], Soo Yee Lee [1], Siti Munirah Mohd Faudzi [1,2] and Khozirah Shaari [1,2*]

[1] Natural Medicines and Products Research Laboratory (NaturMeds), Institute of Bioscience, Universiti Putra Malaysia, Serdang 43400, Selangor, Malaysia; anisirfan1512@gmail.com (A.I.N.); leesooyee@upm.edu.my (S.Y.L.); sitimunirah@upm.edu.my (S.M.M.F.); khozirah@upm.edu.my (K.S.)

[2] Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, Serdang 43400, Selangor, Malaysia; sitimunirah@upm.edu.my (S.M.M.F.); khozirah@upm.edu.my (K.S.)

* Correspondence: khozirah@upm.edu.my; Tel.: +60-3-8942148

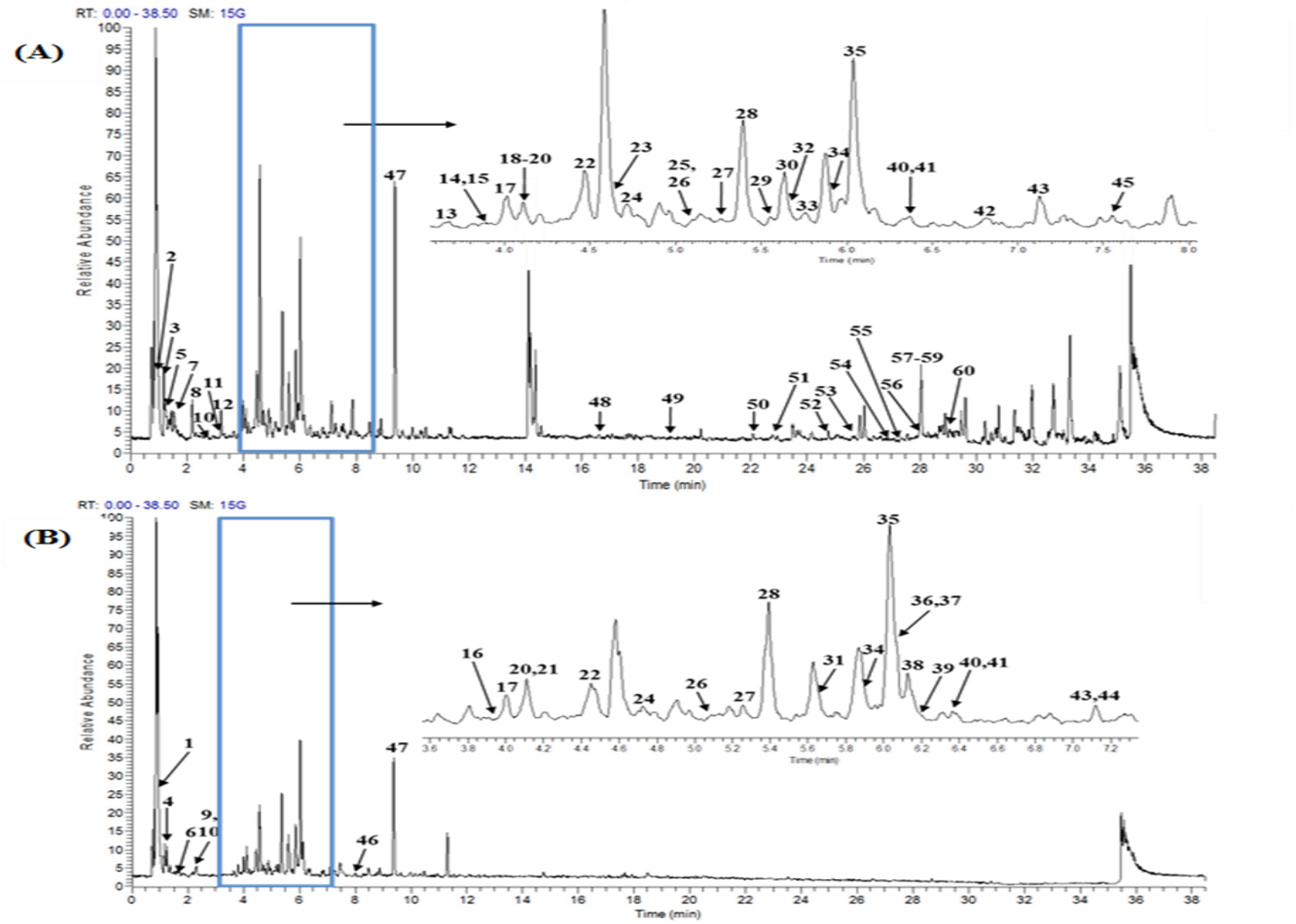

Figure S1a. Total ion chromatograms of the leaf methanolic extract of *Christia vespertilionis* in **(A)** positive and **(B)** negative ion modes. The number above each peak represents the peak numbers, corresponding to the identified metabolites as listed in Table 1.

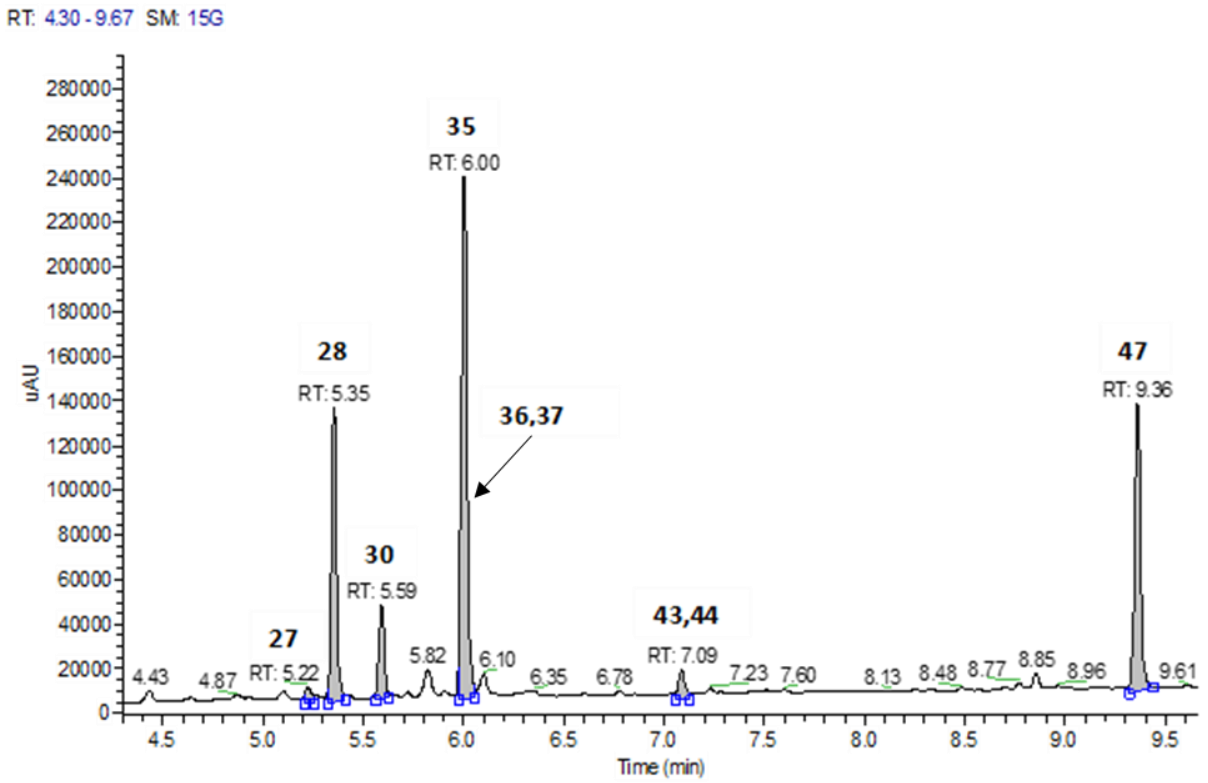

Figure S1b. Photodiode array chromatograms of the methanolic leaf extract of *Christia vespertilionis*. Peaks 28 and 47 were further isolated and elucidated by 1D and 2D NMR experiments. The peak integration and % area for the major metabolites (27, 28, 30, 35, 36, 37, 43, 44, and 47 are given in the Table shown below:

Peak	Apex RT	Start RT	End RT	%Area
27	5.22	5.20	5.25	1.10
28	5.35	5.32	5.41	18.54
30	5.59	5.56	5.62	7.08
35,36,37	6.00	5.97	6.05	42.72
43,44	7.09	7.05	7.13	2.27
47	9.36	9.32	9.43	24.47

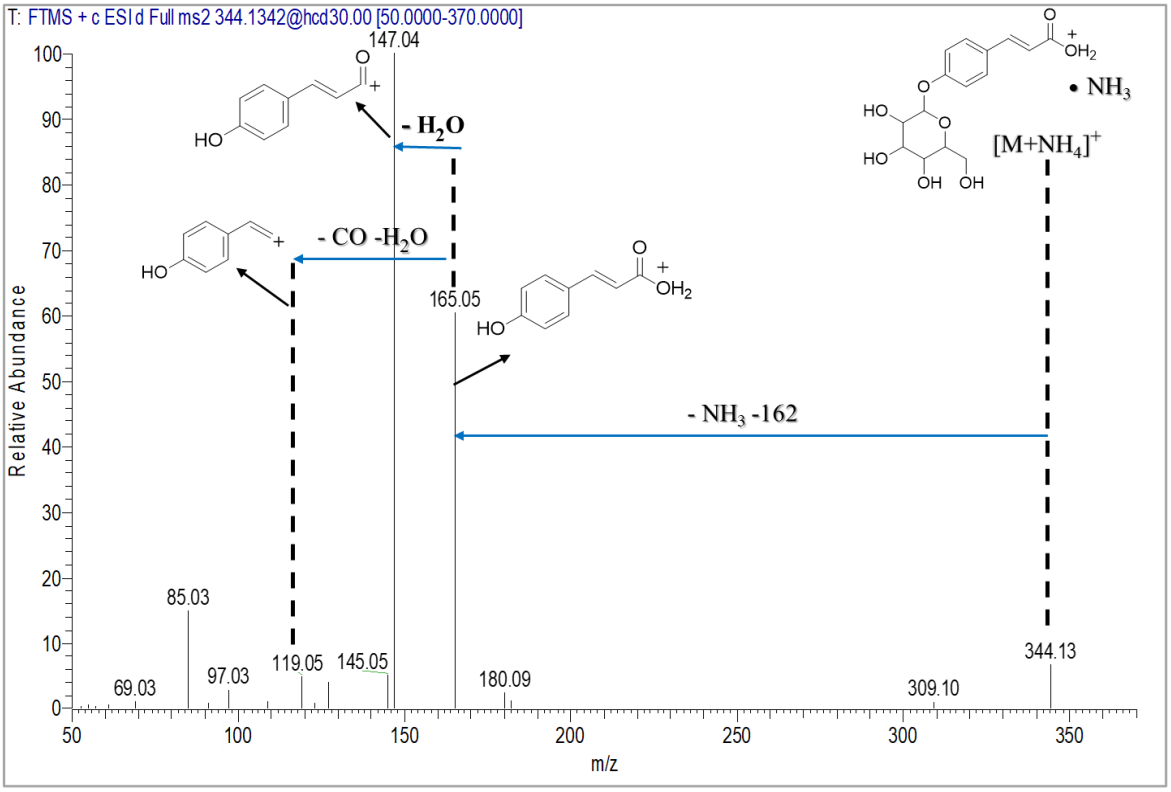

Figure S2. Proposed fragmentation pathway observed in MS/MS spectrum of *p*-coumaric acid 4-*O*-glucoside (**17**).

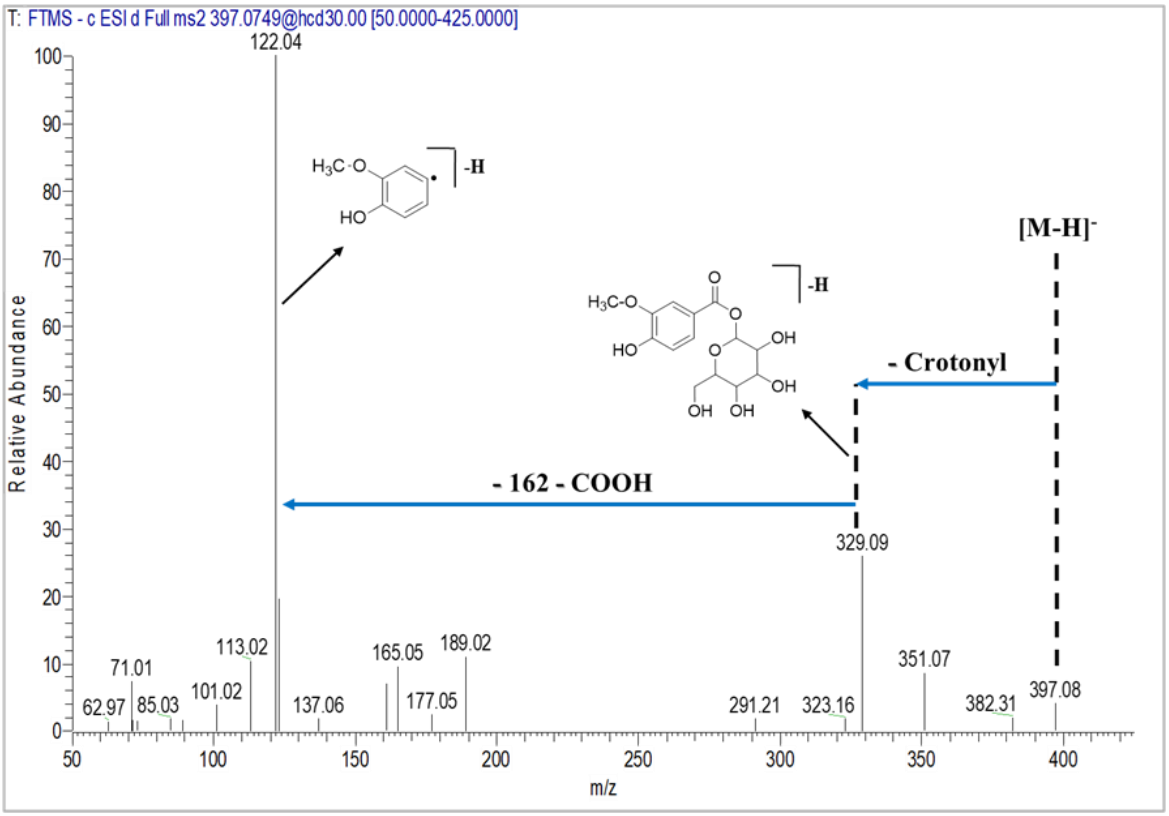

Figure S3. Proposed fragmentation pathway observed in MS/MS spectrum of crotonylated derivative of vanillic acid glucosyl ester (**6**).

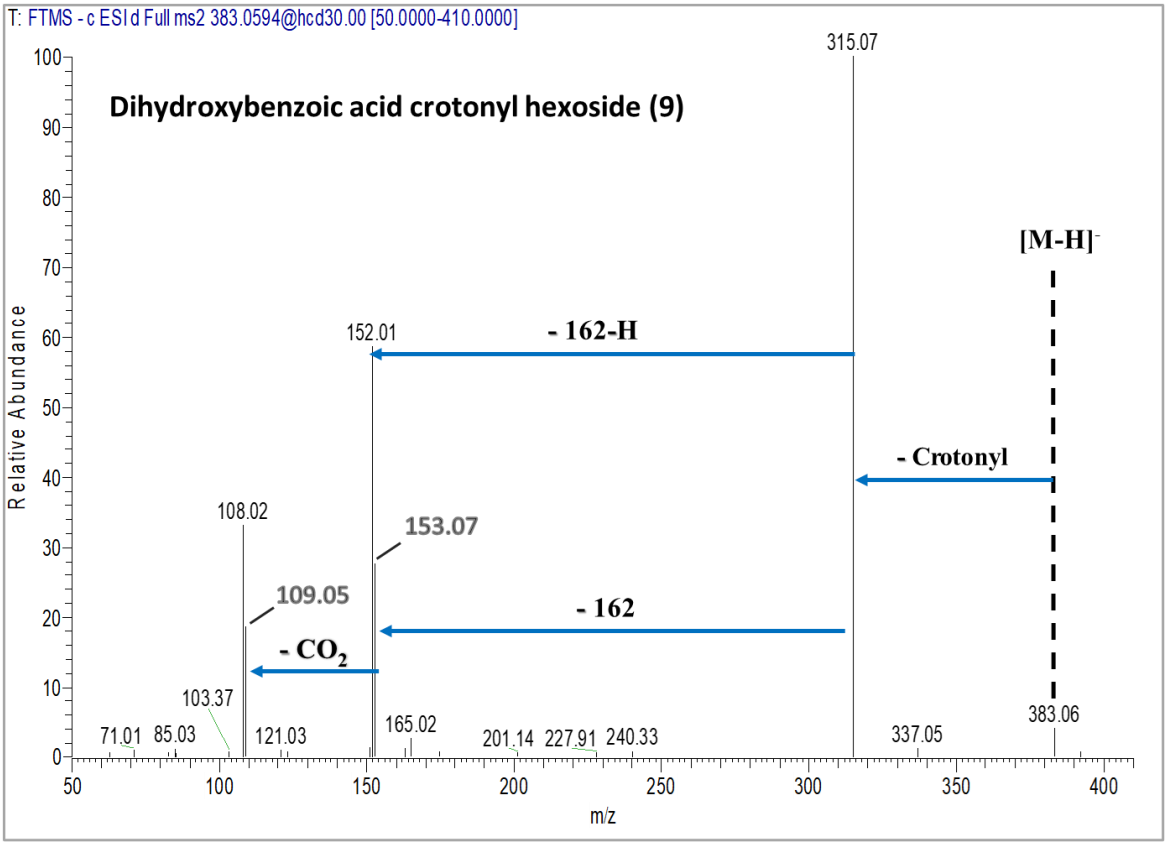

Figure S4. Proposed fragmentation pathway observed in MS/MS spectrum of dihydroxybenzoic acid crotonyl hexoside (**9**).

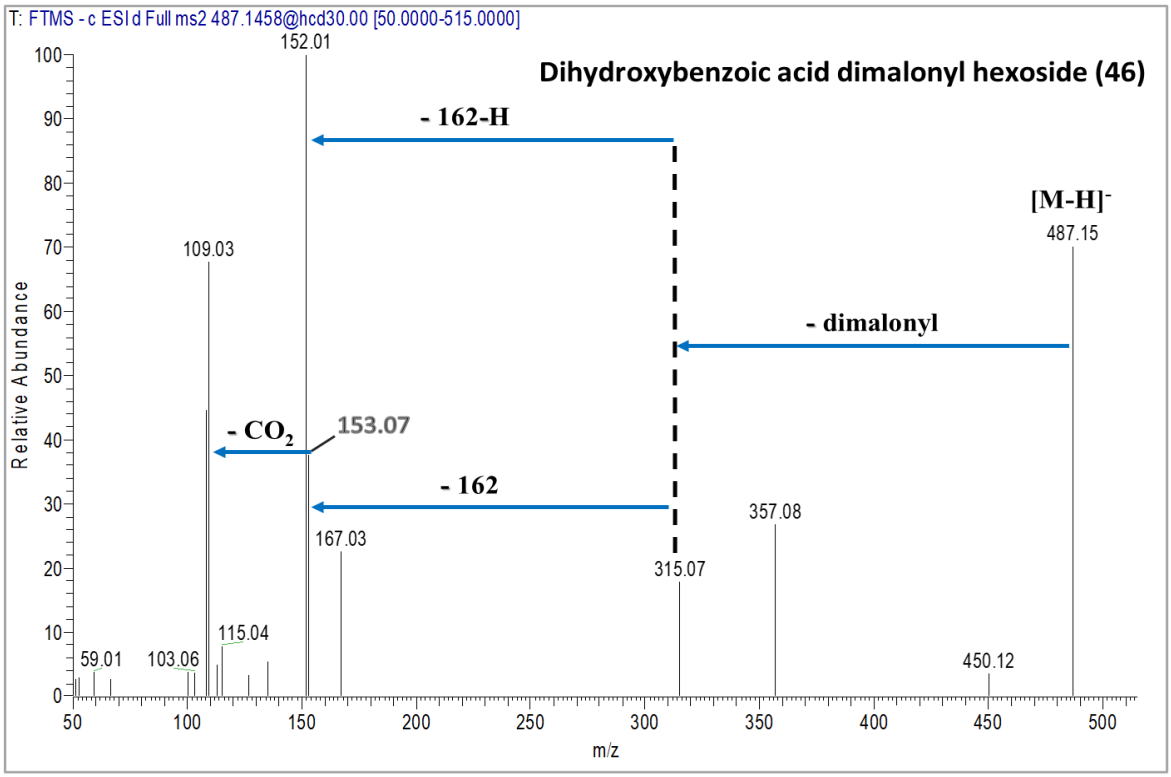

Figure S5. Proposed fragmentation pathway observed in MS/MS spectrum of dihydroxybenzoic acid dimalonyl hexoside (**46**).

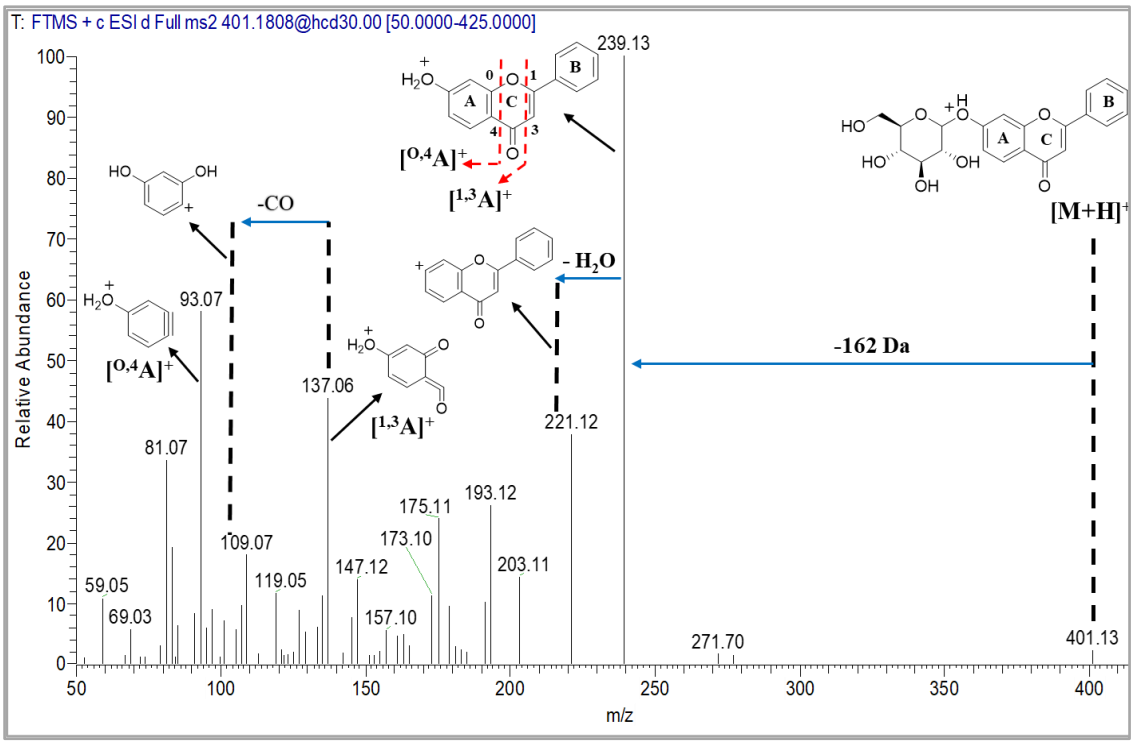

Figure S6. Proposed fragmentation pathway observed in MS/MS spectrum of 7-hydroxyflavone glucoside (**19**).

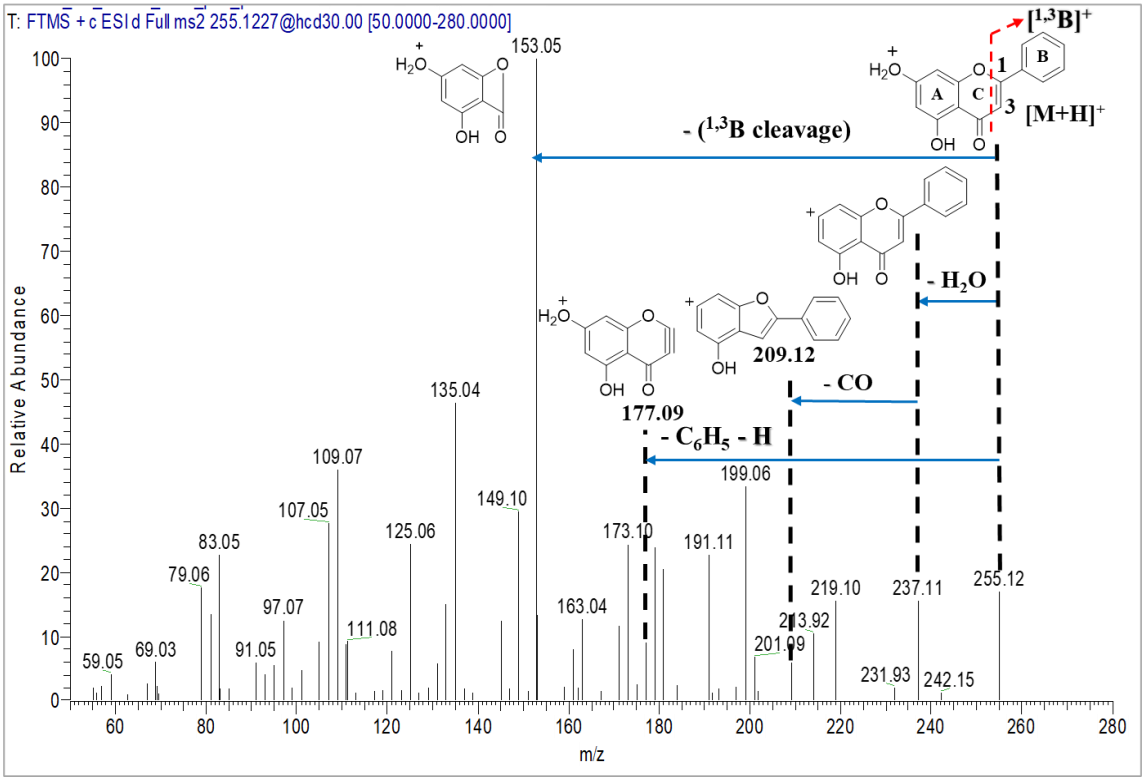

Figure S7. Proposed fragmentation pathway observed in MS/MS spectrum of 5,7-dihydroxyflavone, or known as chrysin (**20**).

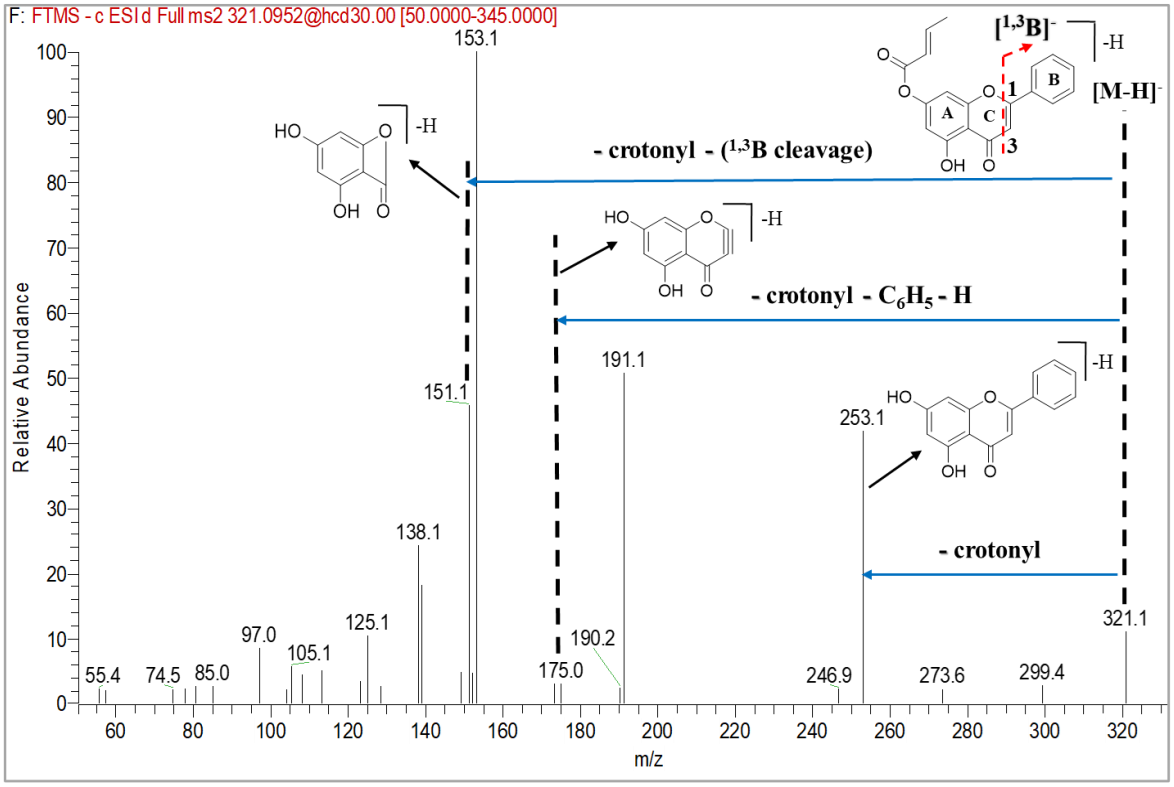

Figure S8. Proposed fragmentation pathway observed in MS/MS spectrum of 7-*O*-crotonylchrysin (**21**).

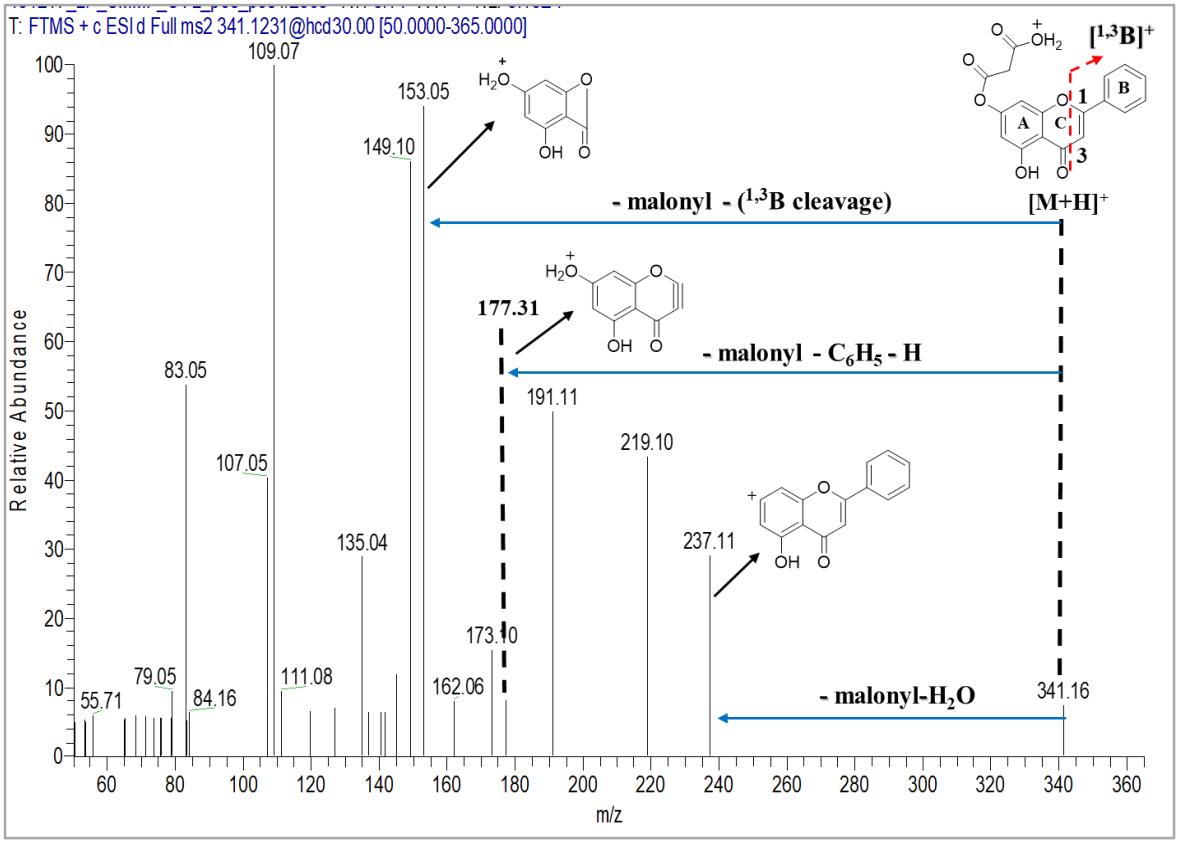

Figure S9. Proposed fragmentation pathway observed in MS/MS spectrum of 7-*O*-malonylchrysin (**25**).

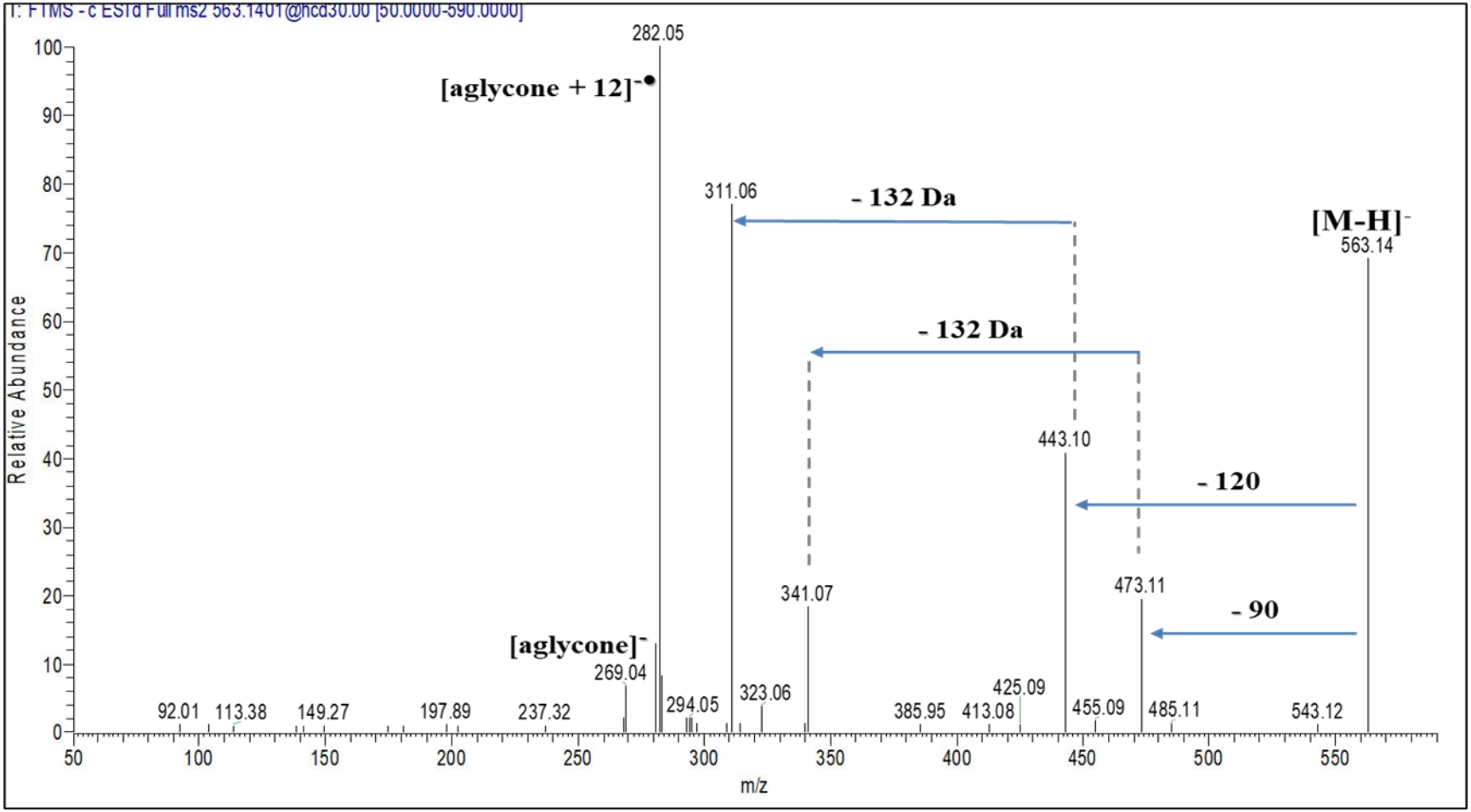

Figure S10. Proposed fragmentation pathway observed in MS/MS spectrum of apigenin-6-*C*-*β*-glucoside 4′-*O*-*α*-apiofuranoside (**28**).

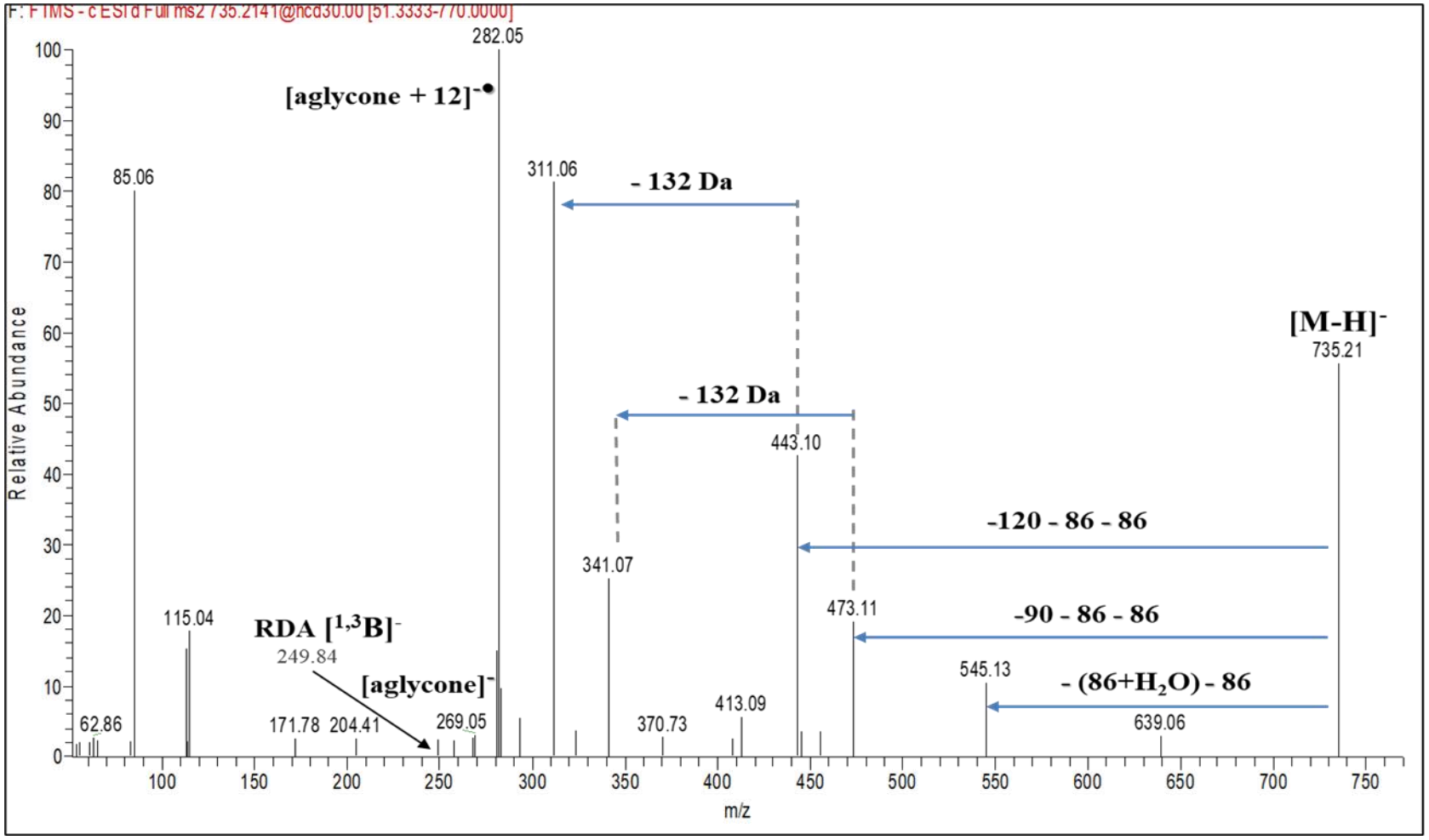

Figure S11. Proposed fragmentation pathway observed in MS/MS spectrum of apigenin-6-*C*-*β*-[(4″,6″-*O*-dimalonyl)-glucoside] 4′-*O*-*α*-apiofuranoside (**47**).

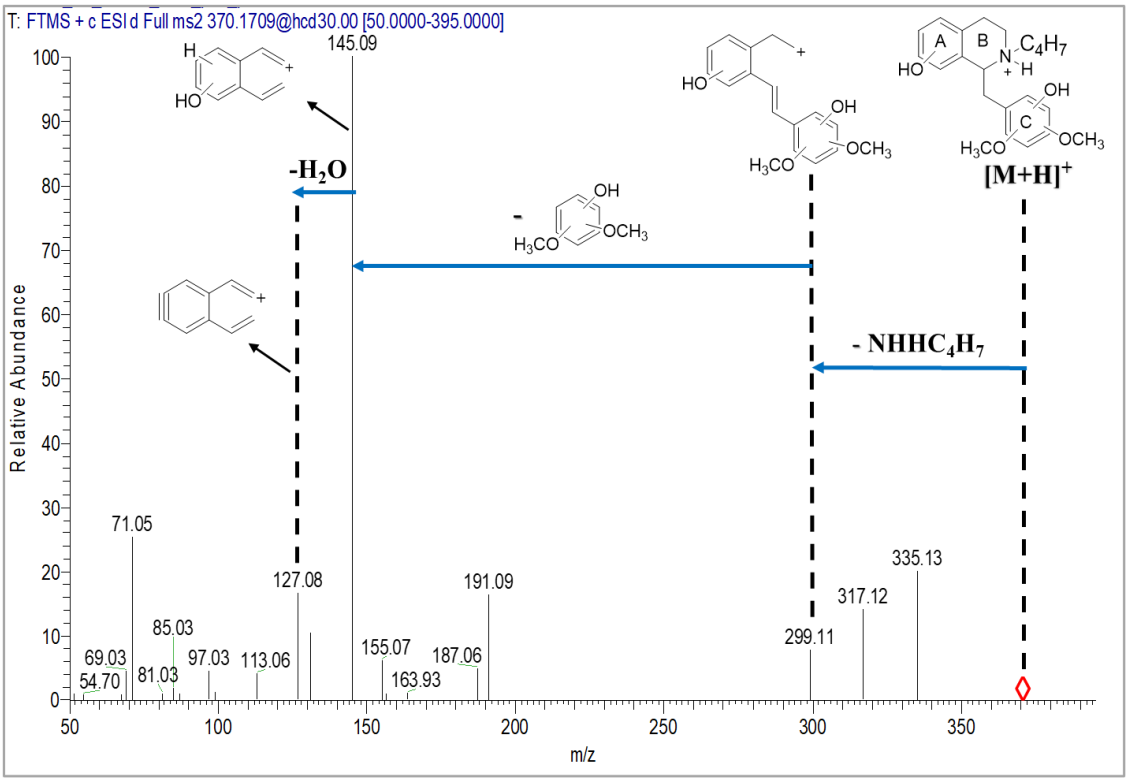

Figure S12. Proposed fragmentation pathway observed in MS/MS spectrum of benzyltetrahydroisoquinoline derivative (**23**).

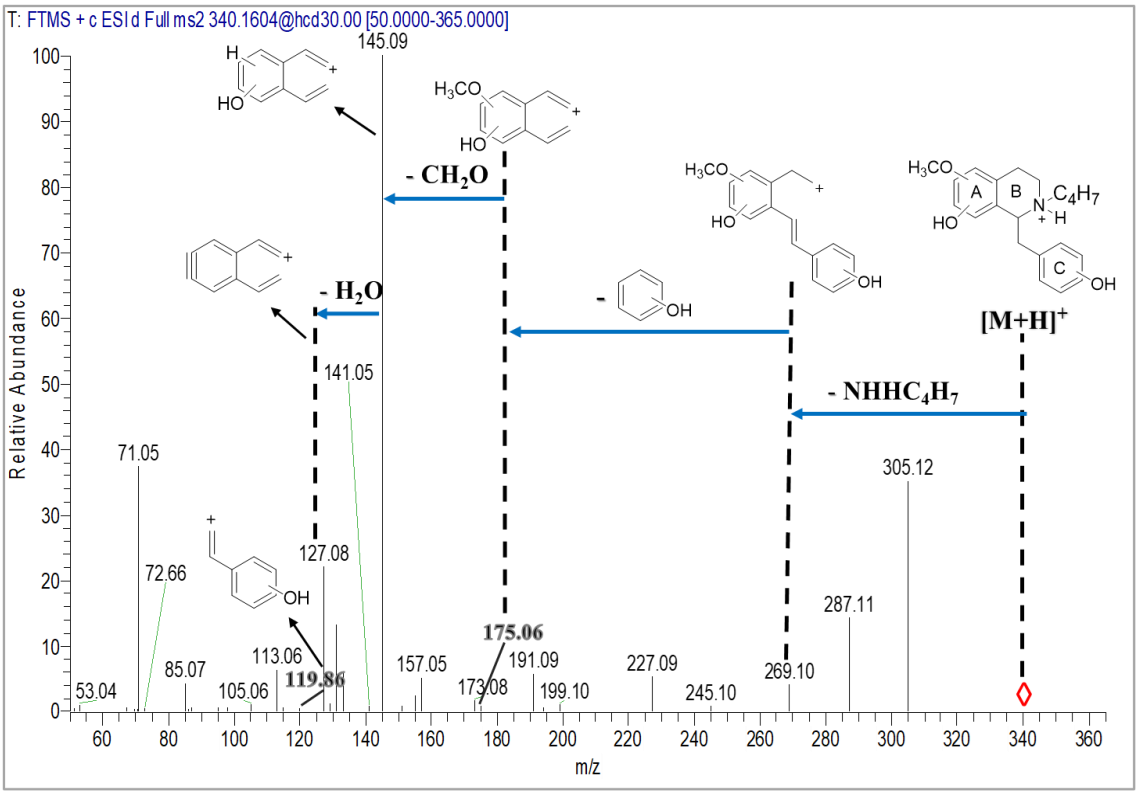

Figure S13. Proposed fragmentation pathway observed in MS/MS spectrum of benzyltetrahydroisoquinoline derivative (**29**).

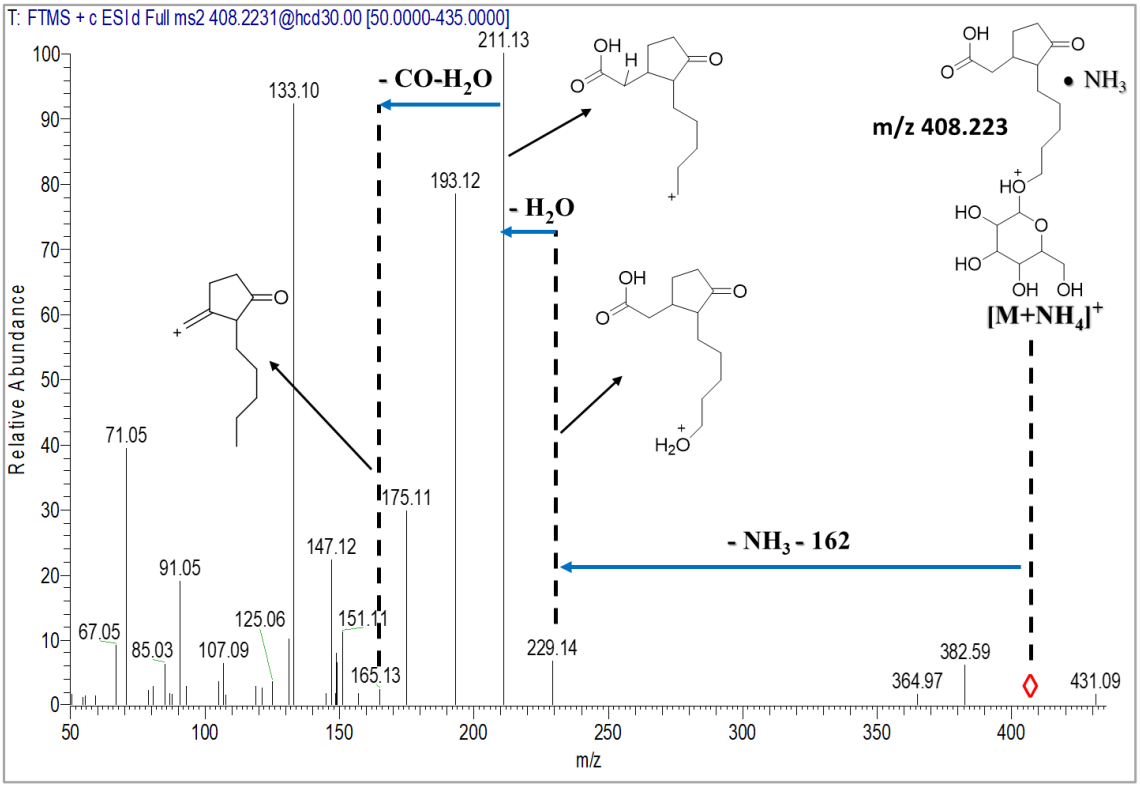

Figure S14. Proposed fragmentation pathway observed in MS/MS spectrum of hydrogenated derivative of tuberonic acid hexoside (**26**).

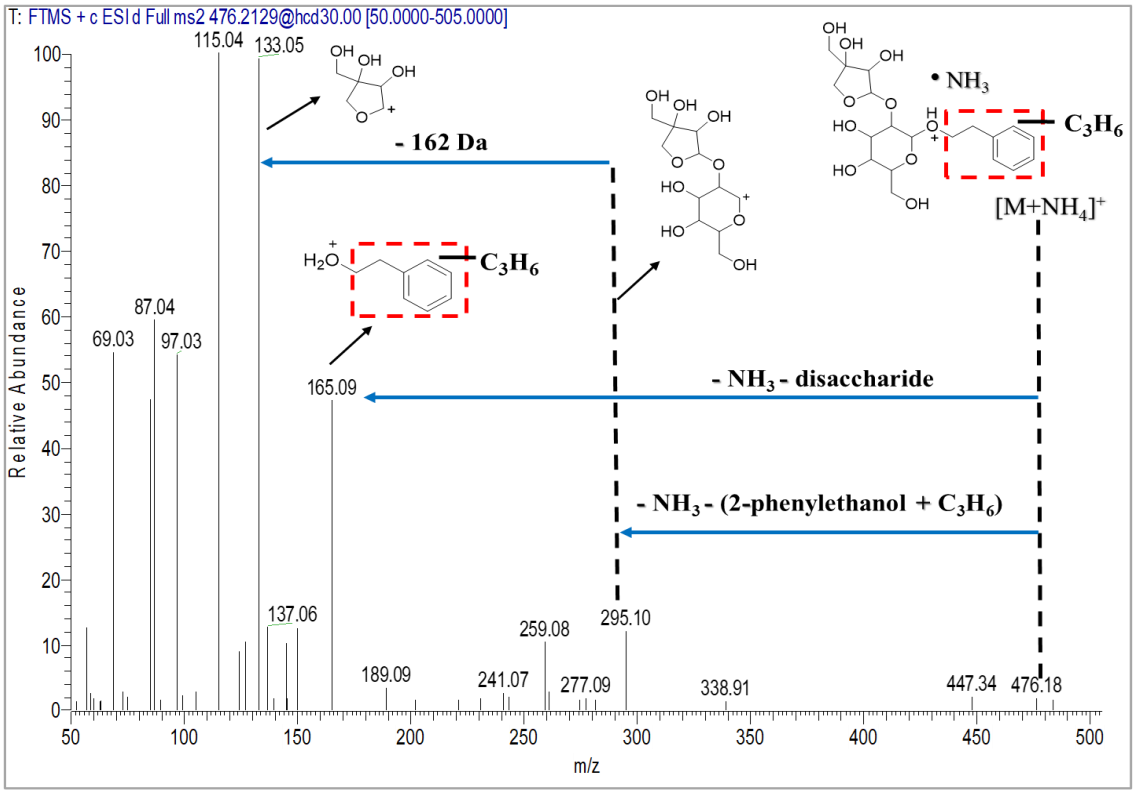

Figure S15. Proposed fragmentation pathway observed in MS/MS spectrum of isopropyl derivative of phenethyl-1-*O*-*β*-D-apiofuranosyl (1→2)-*β*-D-glucopyranoside

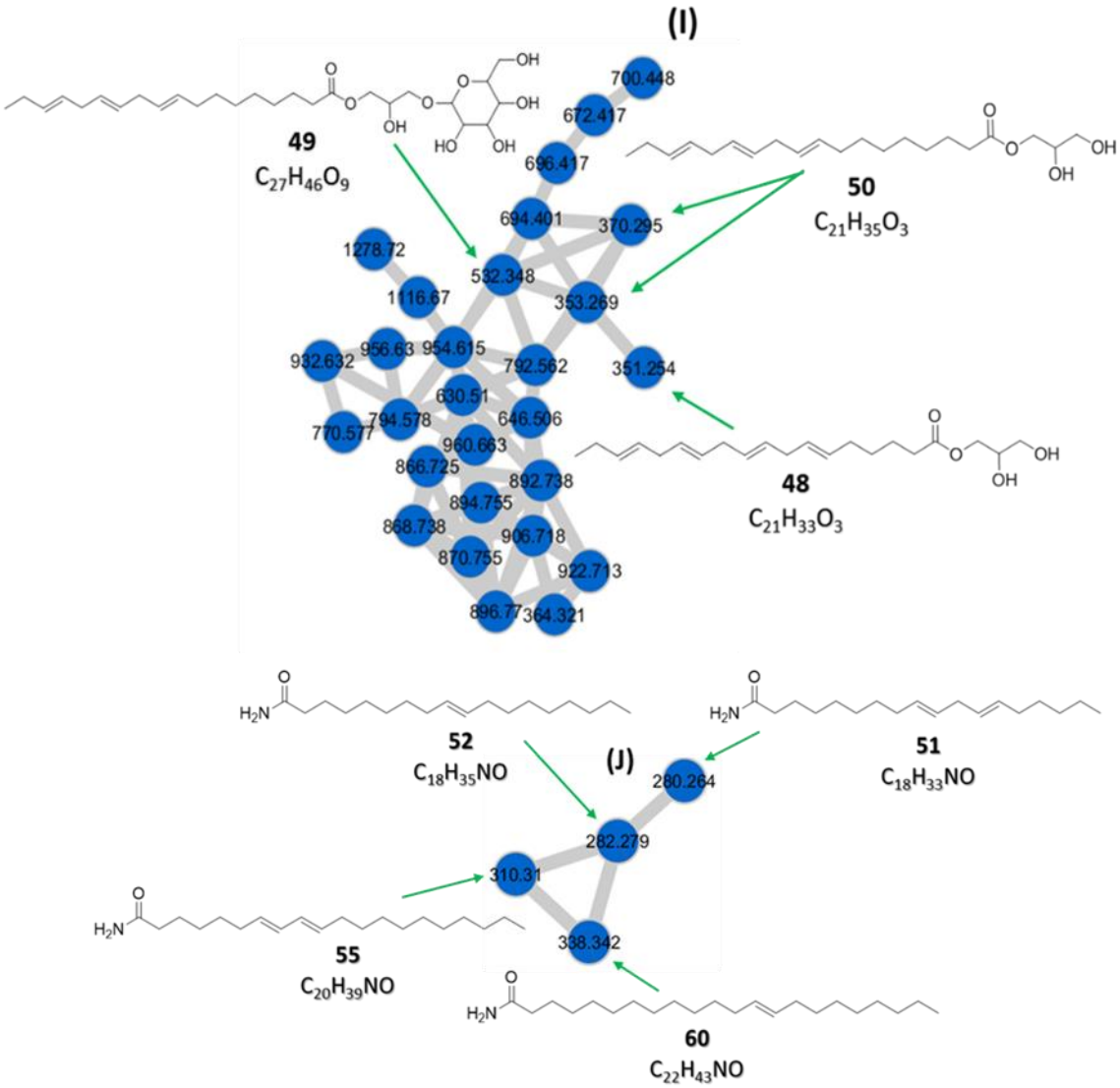

Figure S16. Molecular families of monoacylglycerols (cluster I: positive ion) and fatty acid amides (clusters J: positive ion), extracted from the full MN of *Christia vespertilionis* leaf.

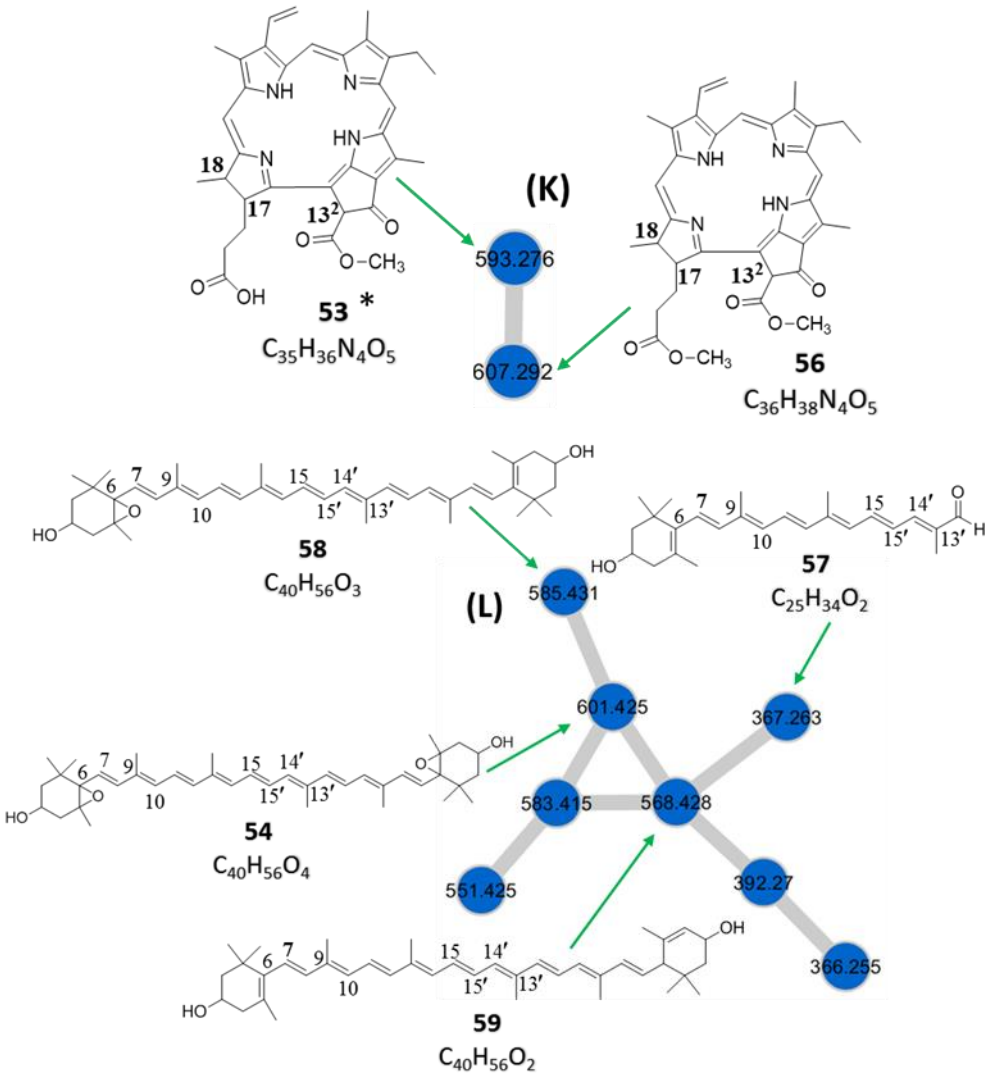

Figure S17. Molecular families of chlorophyll derivatives (cluster K: positive ion) and carotenoids (cluster L: positive ion), extracted from the full MN of *Christia vespertilionis* leaf. * Compound previously reported in *Christia vespertilionis*.

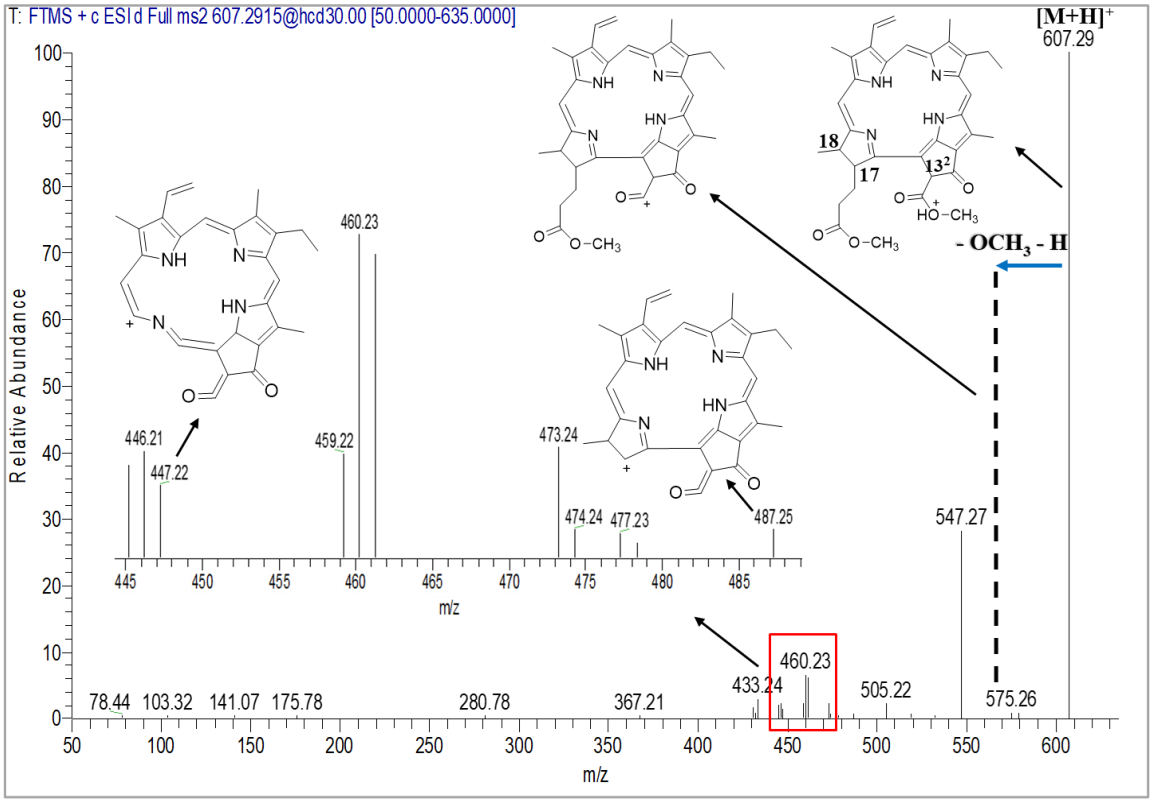

Figure S18. MS/MS spectrum of pheophorbide-a methyl ester (**56**).

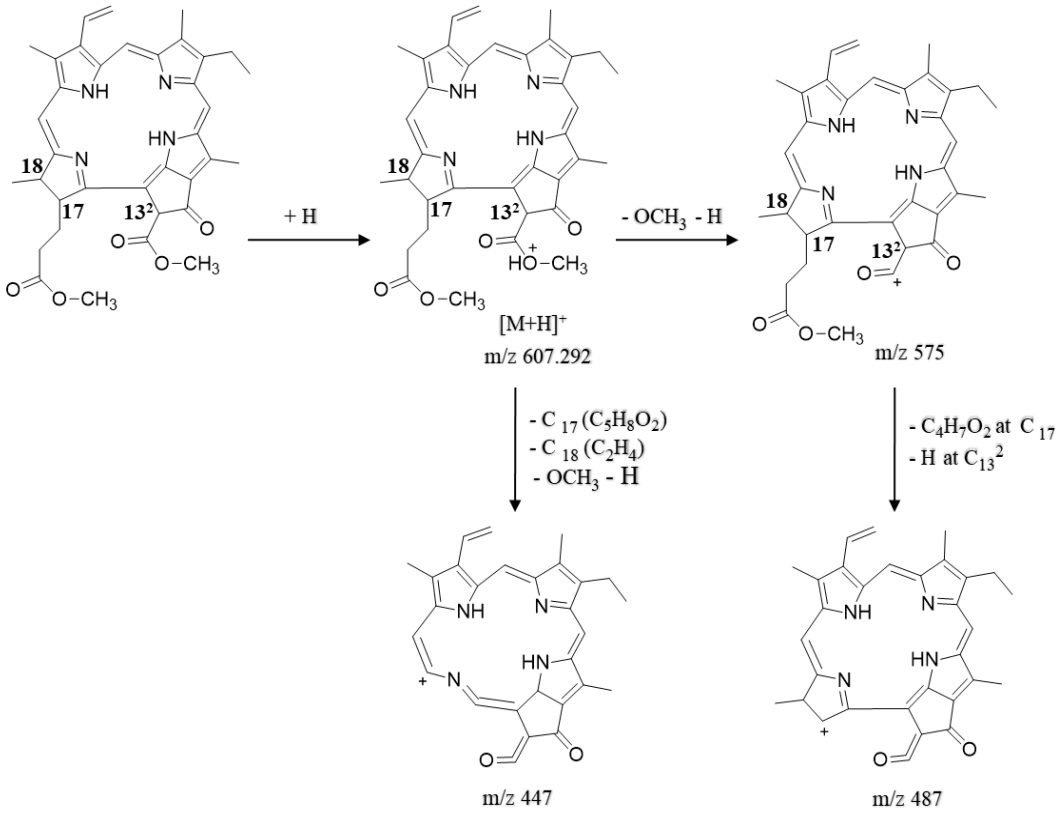

Figure S19. Proposed fragmentation pathway observed in MS/MS spectrum of pheophorbide-a methyl ester (**56**).

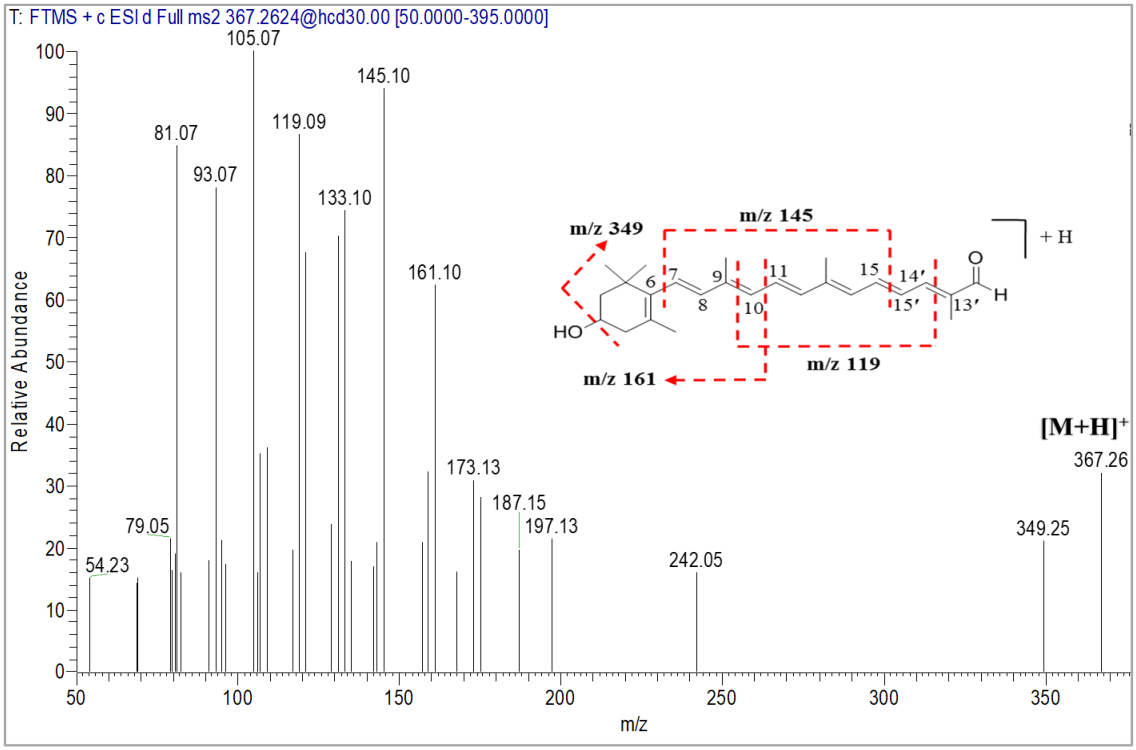

Figure S20. Major fragment ions from the fragmentation of *β*-apo-12′-luteinal (**57**).

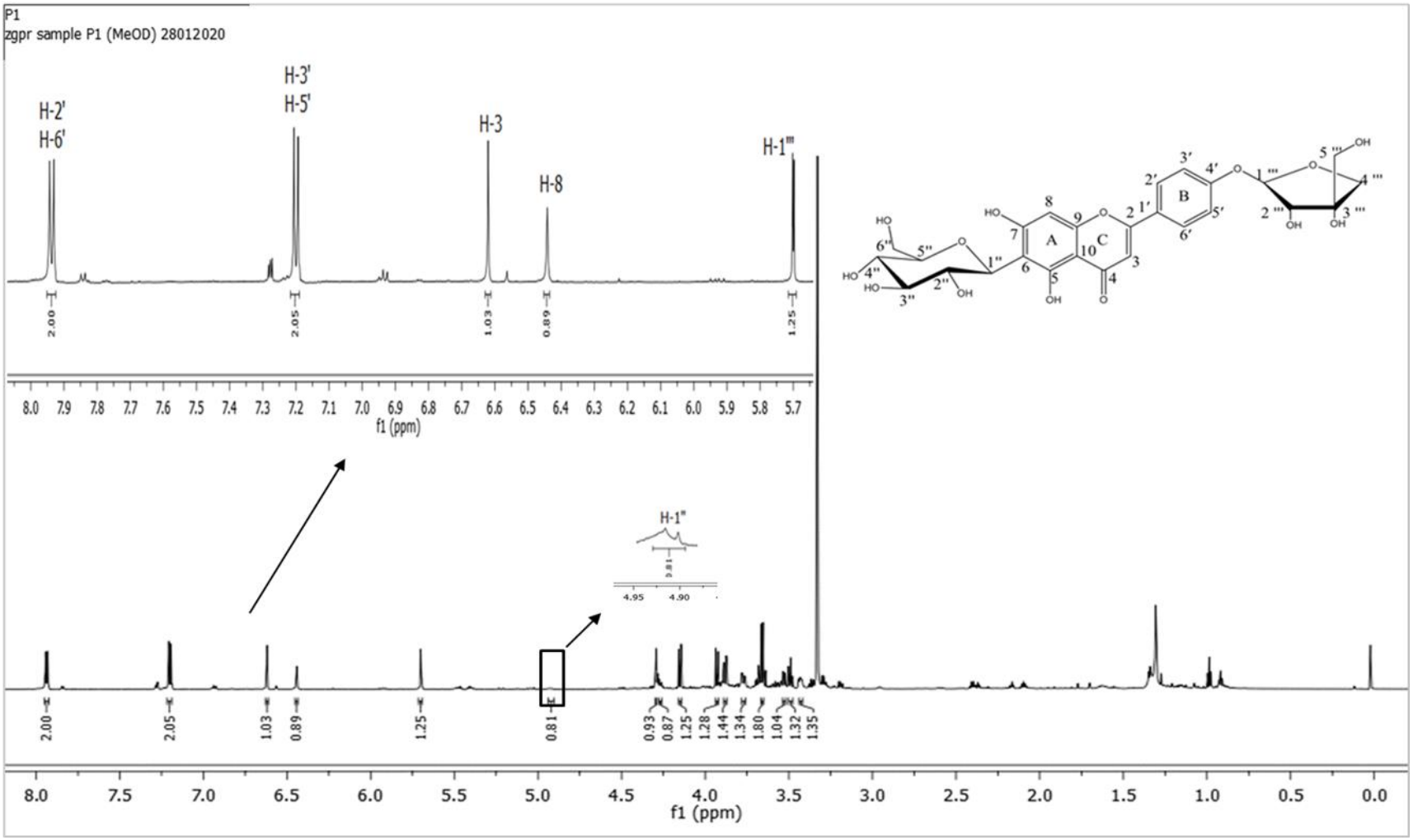

Figure S21. ^{1}H-NMR spectrum of apigenin-6-*C*-*β*-glucoside 4′-*O*-*α*-apiofuranoside (**28**) (700 MHz, in CD_3OD).

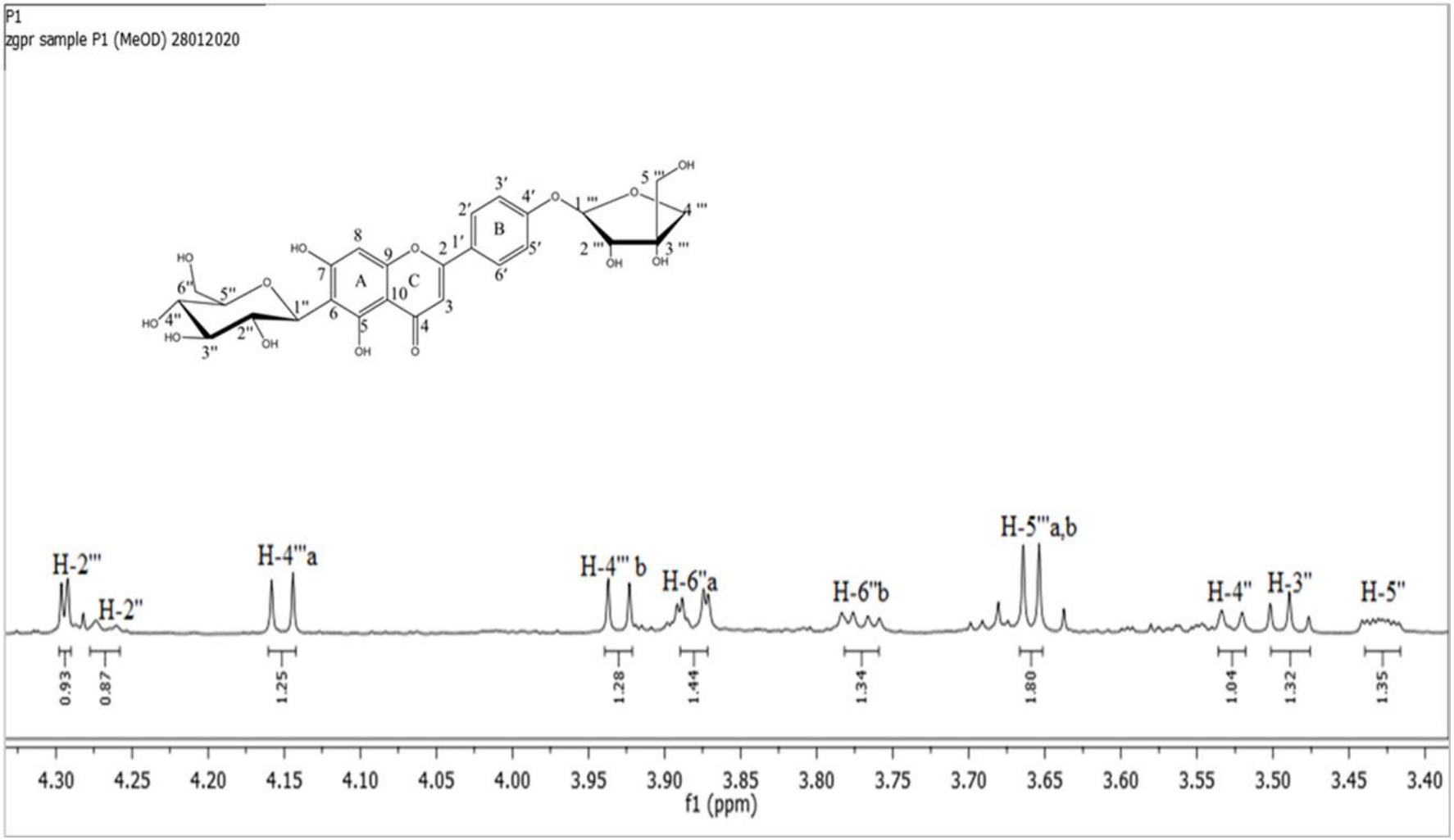

Figure S22. Expanded ^{1}H-NMR spectrum of sugar signals in apigenin-6-*C*-*β*-glucoside 4′-*O*-*α*-apiofuranoside (**28**) (700 MHz, in CD_3OD).

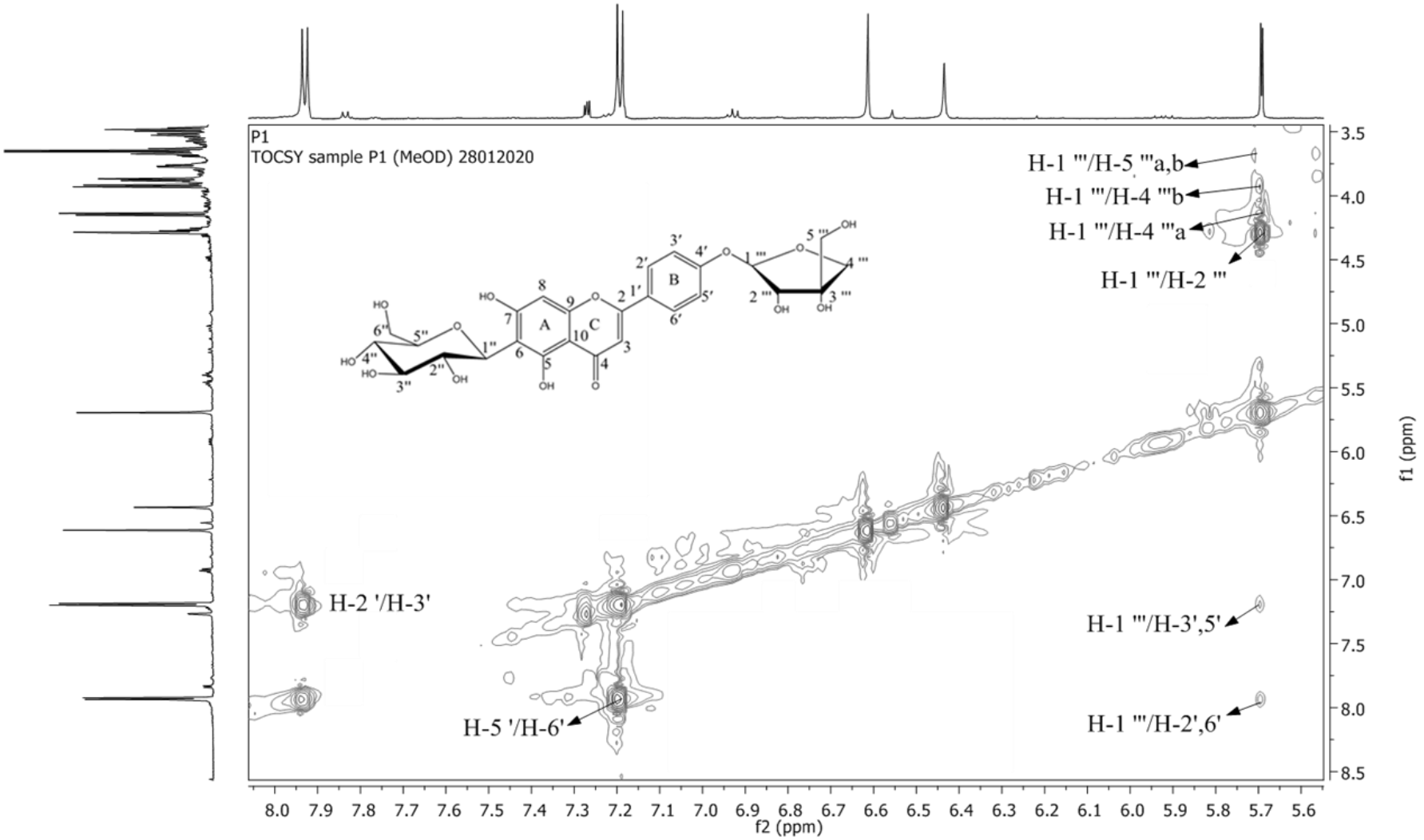

Figure S23. Expanded TOCSY spectrum of apigenin-6-*C*-*β*-glucoside 4′-*O*-*α*-apiofuranoside (**28**) (700 MHz, in CD_3OD).

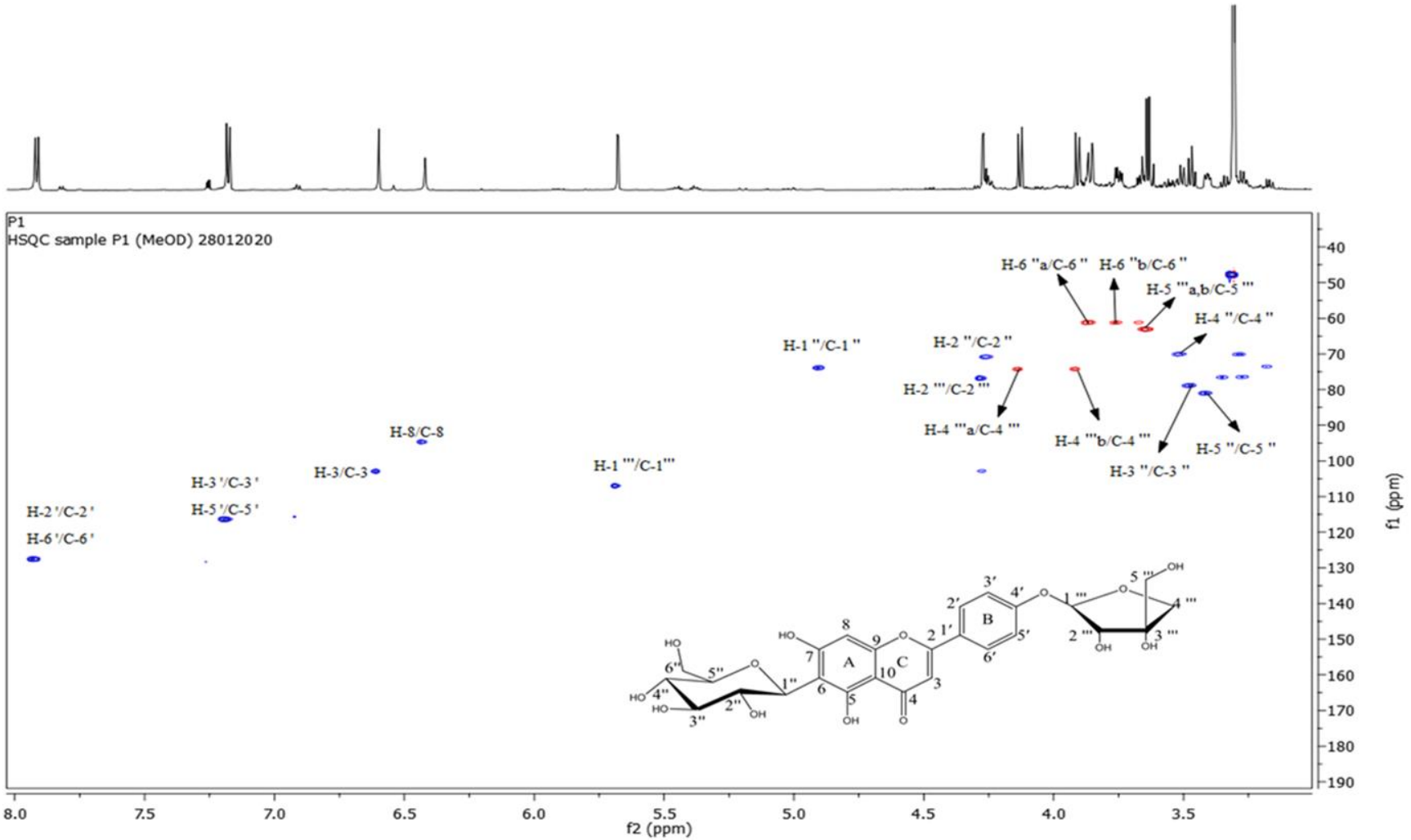

Figure S24. HSQC spectrum of apigenin-6-*C*-*β*-glucoside 4′-*O*-*α*-apiofuranoside (**28**) (700 MHz, in CD_3OD).

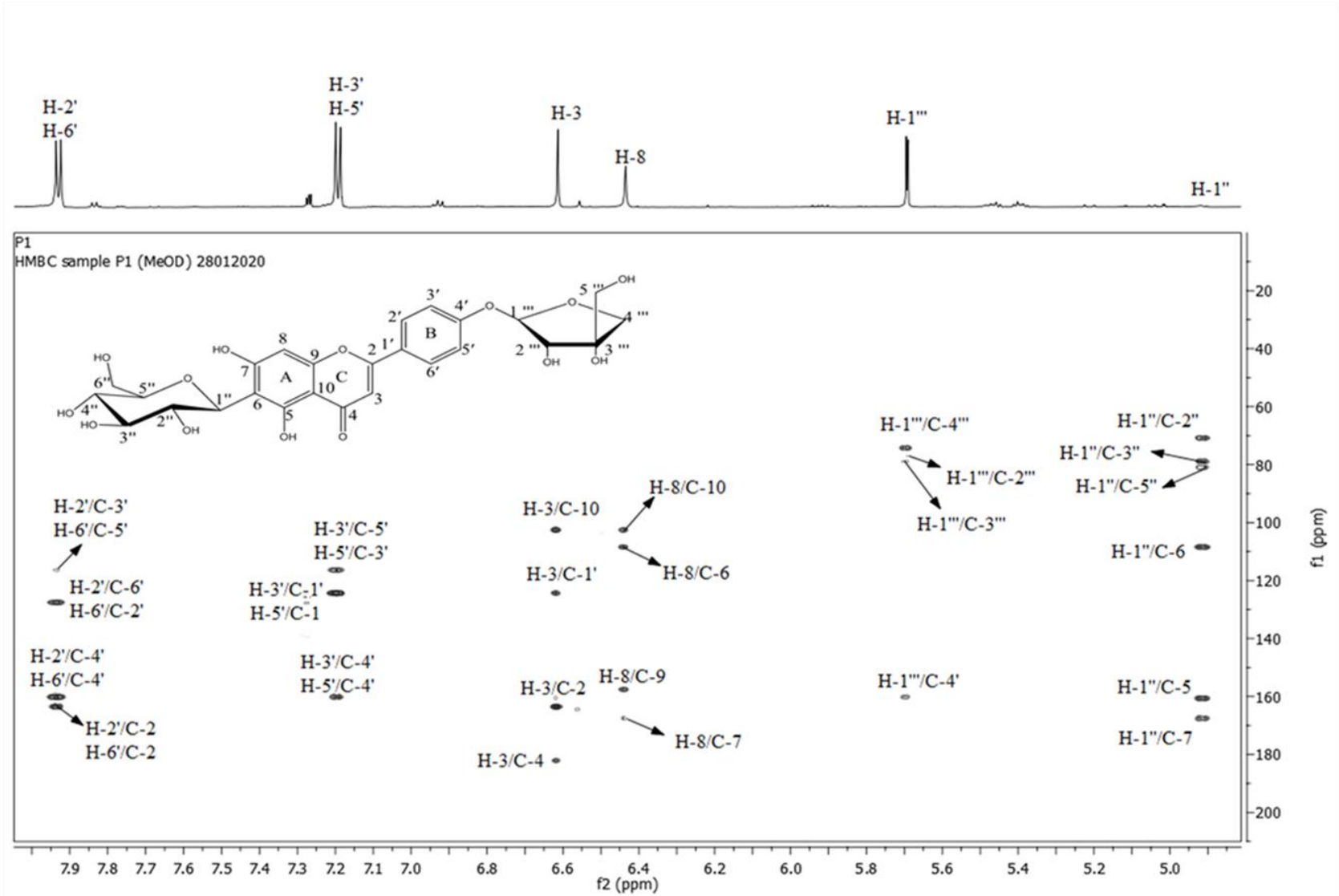

Figure S25. Expanded HMBC spectrum of apigenin-6-*C*-*β*-glucoside 4′-*O*-*α*-apiofuranoside (**28**) (700 MHz, in CD_3OD).

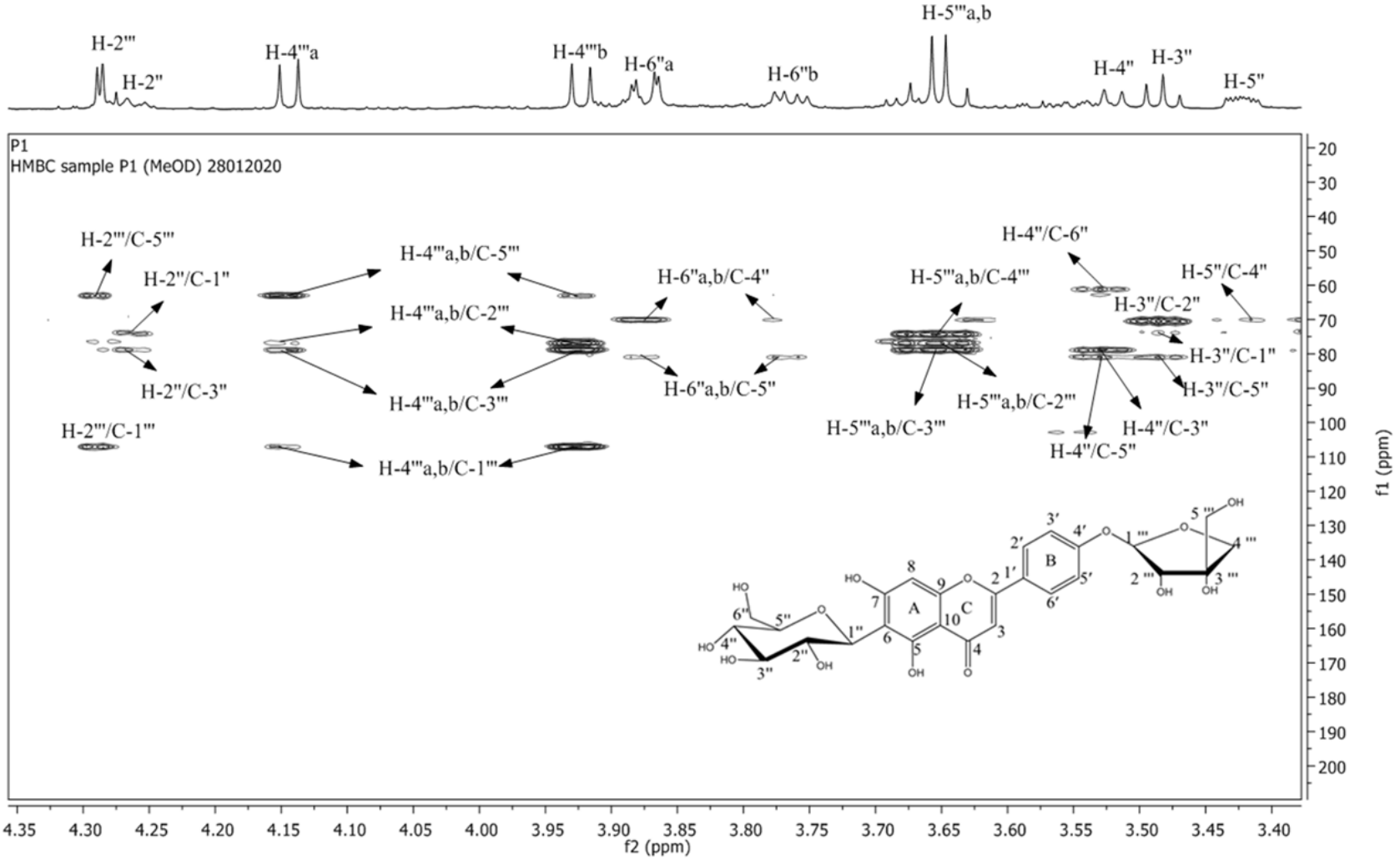

Figure S26. Expanded HMBC spectrum of apigenin-6-*C*-*β*-glucoside 4′-*O*-*α*-apiofuranoside (**28**) (700 MHz, in CD_3OD).

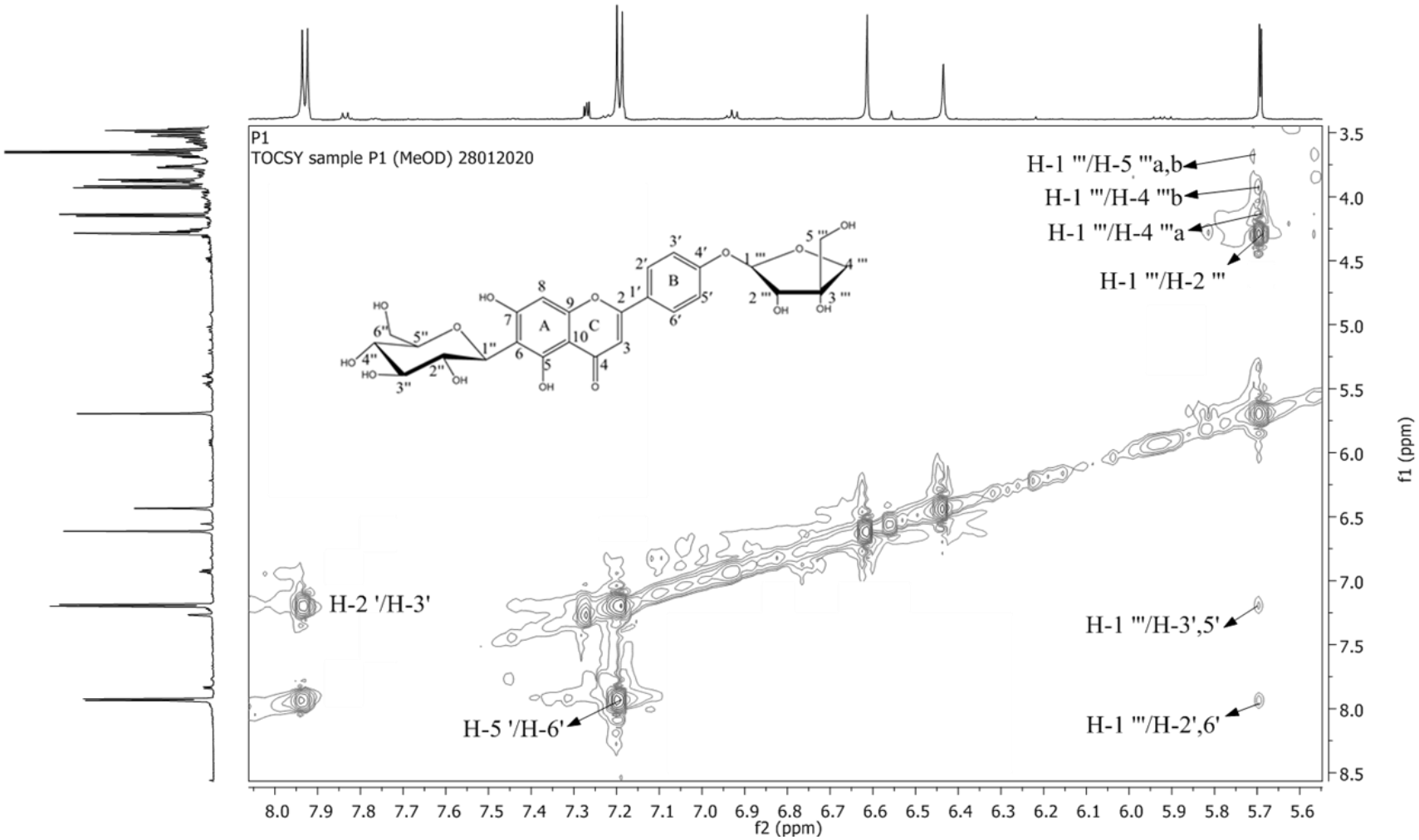

Figure S27. Expanded TOCSY spectrum of apigenin-6-*C*-*β*-glucoside 4′-*O*-*α*-apiofuranoside (**28**) (700 MHz, in CD_3OD).

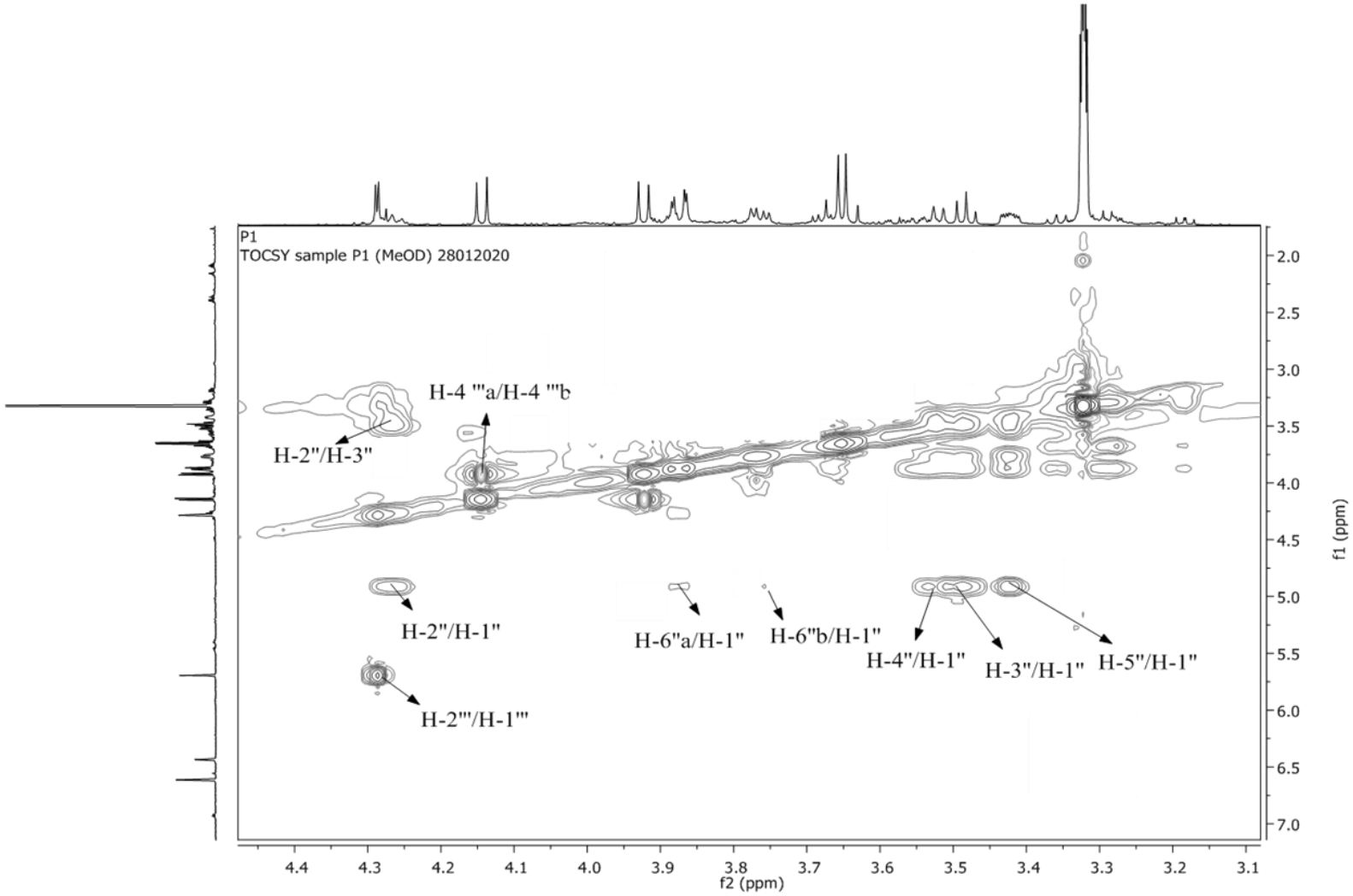

Figure S28. Expanded TOCSY spectrum of apigenin-6-*C*-*β*-glucoside 4′-*O*-*α*-apiofuranoside (**28**) (700 MHz, in CD_3OD).

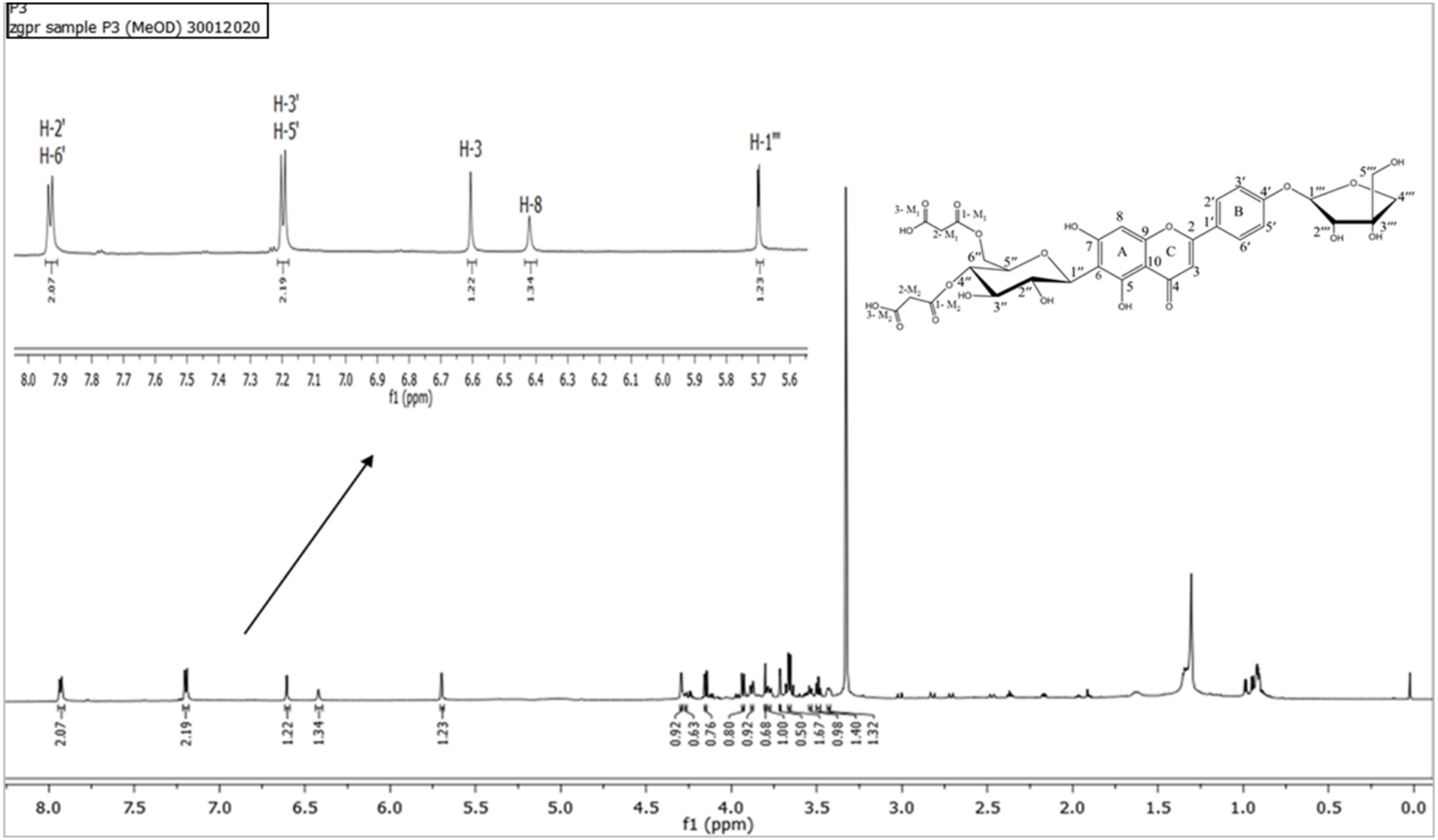

Figure S29. [1]H-NMR spectrum of apigenin-6-*C*-*β*-[(4″,6″-*O*-dimalonyl)-glucoside] 4′-*O*-*α*-apiofuranoside (**47**) (700 MHz, in CD_3OD).

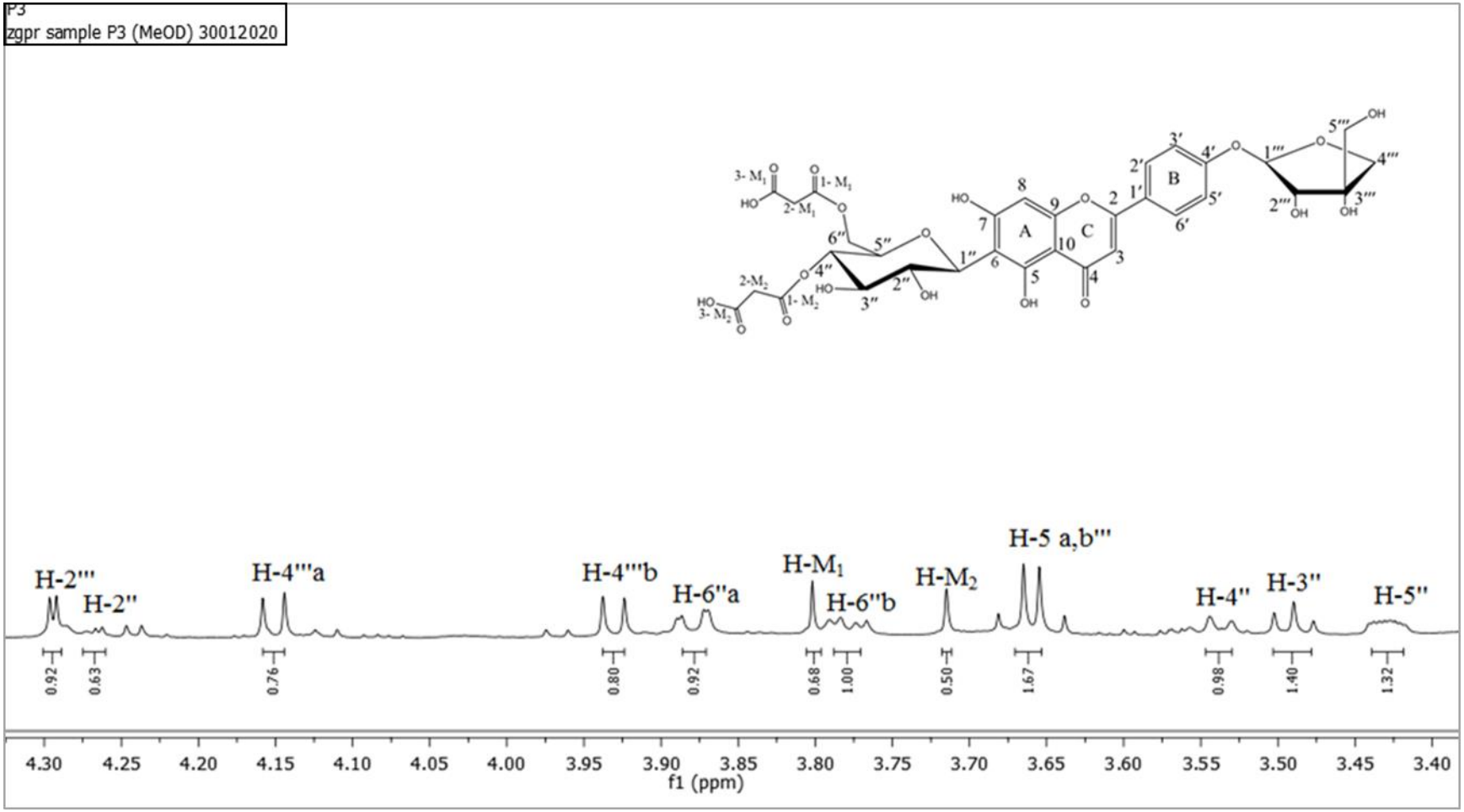

Figure S30. Expanded ^{1}H-NMR spectrum of sugar signals in apigenin-6-*C*-*β*-[(4″,6″-*O*-dimalonyl)-glucoside] 4′-*O*-*α*-apiofuranoside (**47**) (700 MHz, in CD_3OD).

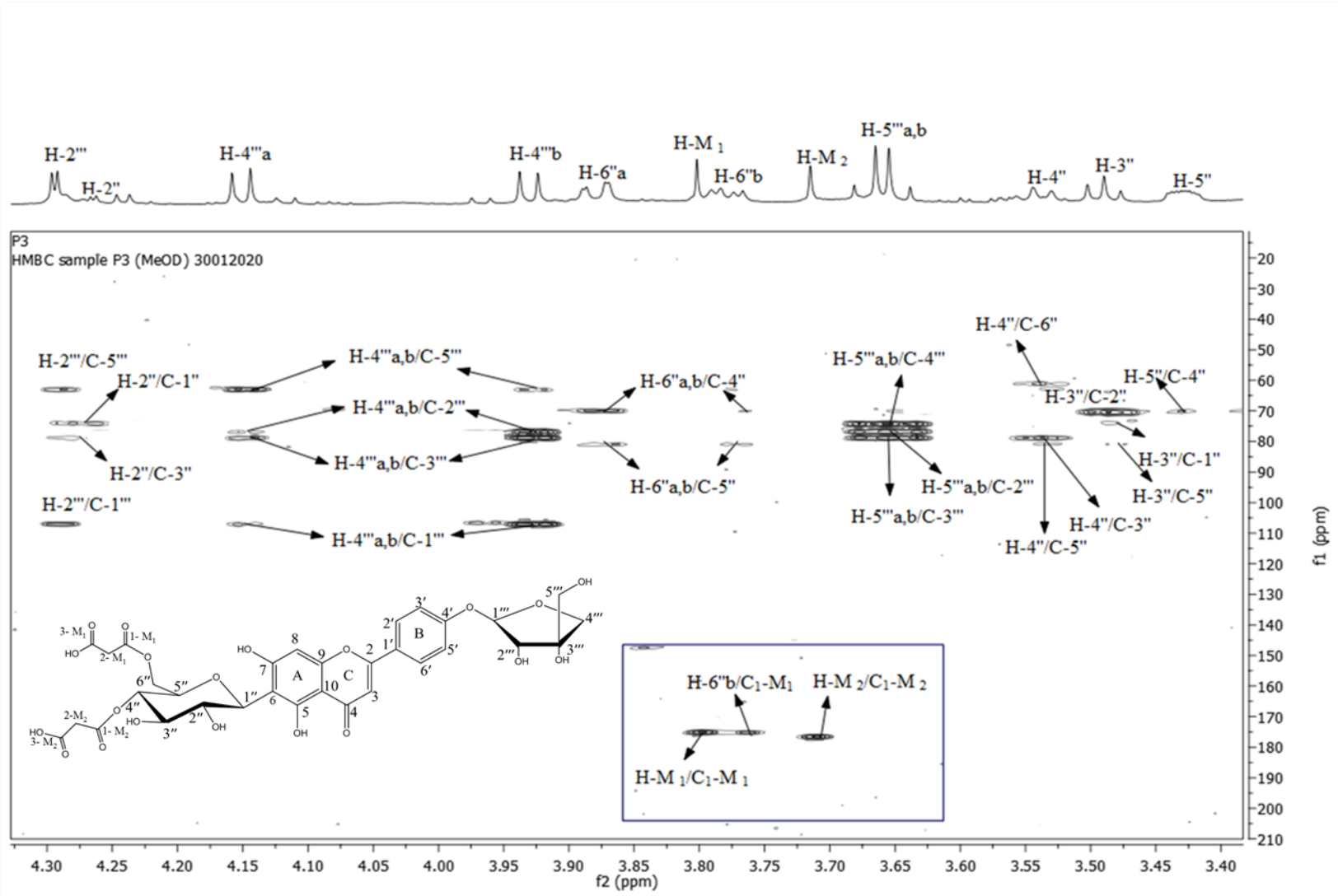

Figure S31. HMBC spectrum of apigenin-6-*C*-*β*-[(4″,6″-*O*-dimalonyl)-glucoside] 4′-*O*-*α*-apiofuranoside (**47**) (700 MHz, in CD_3OD).