

Supporting Information

Sulfonic Acid-Containing Flavonoids from the Roots of *Phyllanthus acidus*

Thuc-Huy Duong^{†,‡}, Mehdi A. Beniddir[§], Van-Kieu Nguyen[‡], Thammarat Aree[‡], Jean-François Gallard[⊥], Dinh-Hung Mac[∇], Huu-Hung Nguyen^{||}, Xuan-Hao Bui[†], Joël Boustie[#], Kim-Phi-Phung Nguyen[□], Warinthorn Chavasiri^{‡,*}, and Pierre Le Pogam^{§,*}

[†] Department of Chemistry, Ho Chi Minh City University of Education, 280 An Duong Vuong Street, District 5, Ho Chi Minh City 748342, Vietnam.

[‡] Center of Excellence in Natural Products Chemistry, Department of Chemistry, Faculty of Science, Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand.

[§] Équipe « Pharmacognosie-Chimie des Substances Naturelles », BioCIS, Univ. Paris-Sud, CNRS, Université Paris-Saclay, 5 Rue J.-B. Clément, 92290 Châtenay-Malabry, France.

[⊥] Institut de Chimie des Substances Naturelles, CNRS, ICSN UPR 2301, Université Paris-Saclay, 21 Avenue de la Terrasse, 91198 Gif-sur-Yvette, France.

[∇] Department of Organic Chemistry, University of Science, Ha Noi National University, 19 Le Thanh Tong Str., Dist. Hoan Kiem, Ha Noi City 748355, Vietnam.

^{||} Faculty of Biotechnology and Environment, Nguyen Tat Thanh University, 300A Nguyen Tat Thanh, District 4. Ho Chi Minh City 748355, Vietnam.

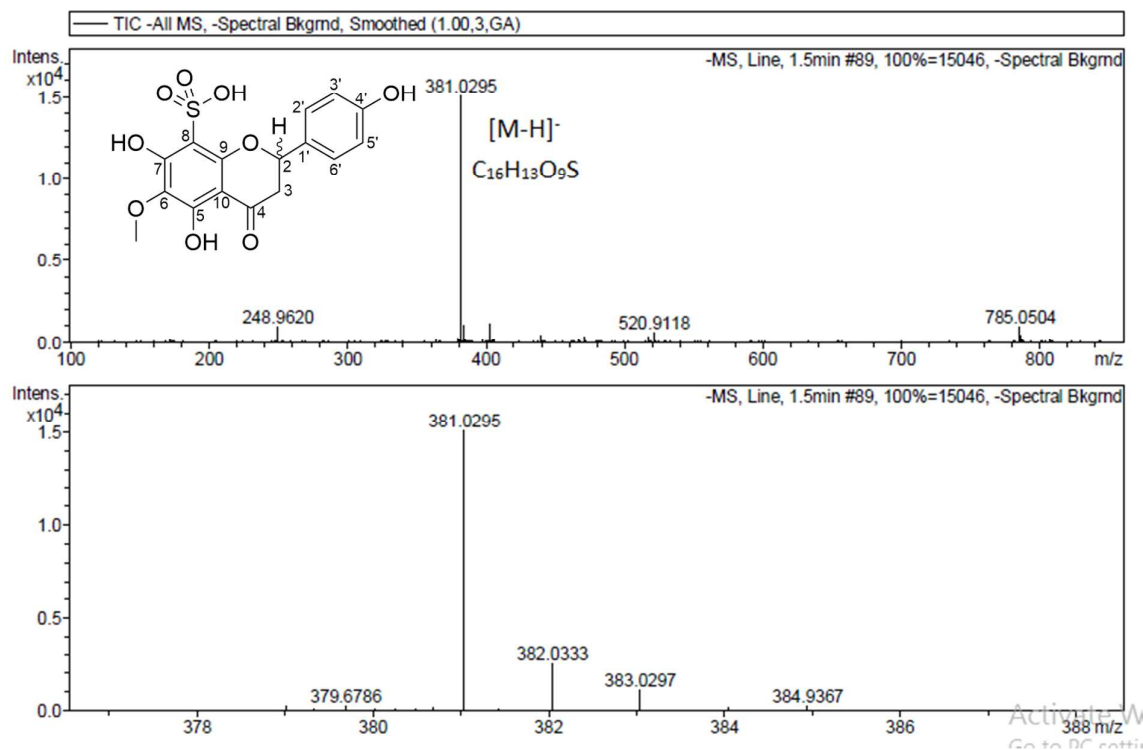
[#] Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France.

[□] Department of Organic Chemistry, University of Science, National University – Ho Chi Minh City, 227 Nguyen Van Cu Str., Dist. 5, Ho Chi Minh City 748355, Vietnam.

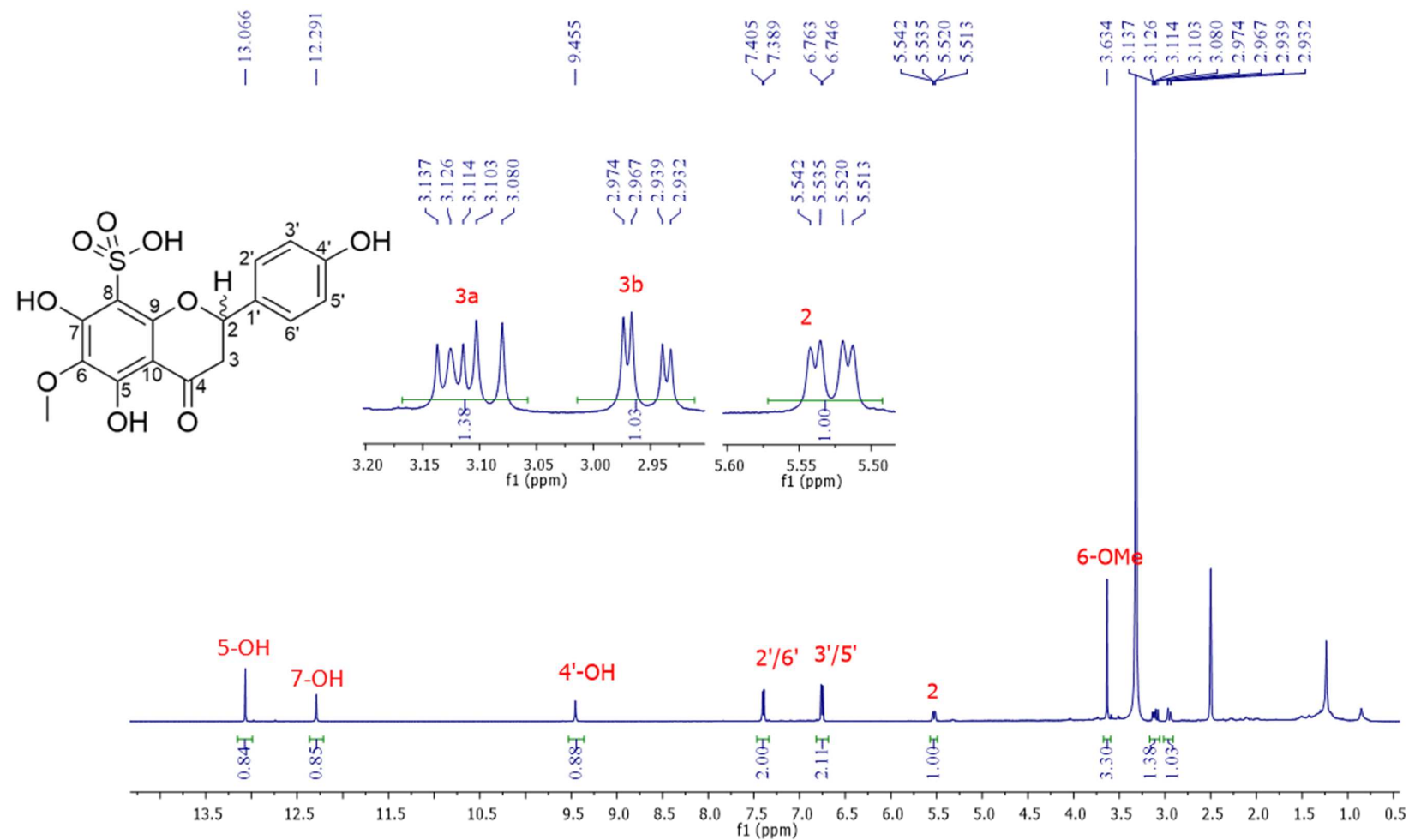
TABLE OF CONTENTS

N°	Content	Page
S1	HRESIMS spectrum of 1	S-3
S2	¹ H NMR (DMSO- <i>d</i> ₆ , 500 MHz) spectrum of 1	S-4
S3	¹³ C NMR (DMSO- <i>d</i> ₆ , 125 MHz) spectrum of 1	S-5
S4	HSQC (DMSO- <i>d</i> ₆ , 500 MHz, 125 MHz) spectrum of 1	S-6
S5	HMBC (DMSO- <i>d</i> ₆ , 500 MHz, 125 MHz) spectrum of 1	S-7
S6	HRESIMS spectrum of 2	S-8
S7	¹ H NMR (DMSO- <i>d</i> ₆ , 500 MHz) spectrum of 2	S-9
S8	JMOD (DMSO- <i>d</i> ₆ , 125 MHz) spectrum of 2	S-10
S9	HSQC (DMSO- <i>d</i> ₆ , 500 MHz, 125 MHz) spectrum of 2	S-11
S10	HMBC (DMSO- <i>d</i> ₆ , 500 MHz, 125 MHz) spectrum of 2	S-12
S11	HRESIMS spectrum of 3	S-13
S12	¹ H NMR (D ₂ O, 500 MHz) spectrum of 3	S-14
S13	¹³ C NMR (D ₂ O, 125 MHz) spectrum of 3	S-15
S14	HSQC (D ₂ O, 500 MHz, 125 MHz) spectrum of 3	S-16
S15	HMBC (D ₂ O, 500 MHz, 125 MHz) spectrum of 3	S-17
S16	HRESIMS spectrum of 4	S-18
S17	¹ H NMR (D ₂ O, 500 MHz) spectrum of 4	S-19
S18	HSQC (D ₂ O, 500 MHz, 125 MHz) spectrum of 4	S-20
S19	HMBC (D ₂ O, 500 MHz, 125 MHz) spectrum of 4	S-21
S20	Zoom into HMBC spectrum of 4 to reveal the ⁴ <i>J</i> correlations of olefinic proton H-10	S-22
S21	HRESIMS spectrum of 5	S-23
S22	¹ H NMR (DMSO- <i>d</i> ₆ , 500 MHz) spectrum of 5	S-24
S23	JMOD (DMSO- <i>d</i> ₆ , 500 MHz) spectrum of 5	S-25
S24	HSQC (DMSO- <i>d</i> ₆ , 500 MHz, 125 MHz) spectrum of 5	S-26
S25	HMBC (DMSO- <i>d</i> ₆ , 500 MHz, 125 MHz) spectrum of 5	S-27
S26	HRESIMS spectrum of 6	S-28
S27	¹ H NMR (DMSO- <i>d</i> ₆ , 600 MHz) spectrum of 6	S-29
S28	¹³ C NMR (DMSO- <i>d</i> ₆ , 150 MHz) spectrum of 6	S-30
S29	HSQC (DMSO- <i>d</i> ₆ , 600 MHz, 150 MHz) spectrum of 6	S-31
S30	HMBC (DMSO- <i>d</i> ₆ , 600 MHz, 150 MHz) spectrum of 6	S-32
S31	Experimental details for X-ray diffraction analyses of 1	S-33

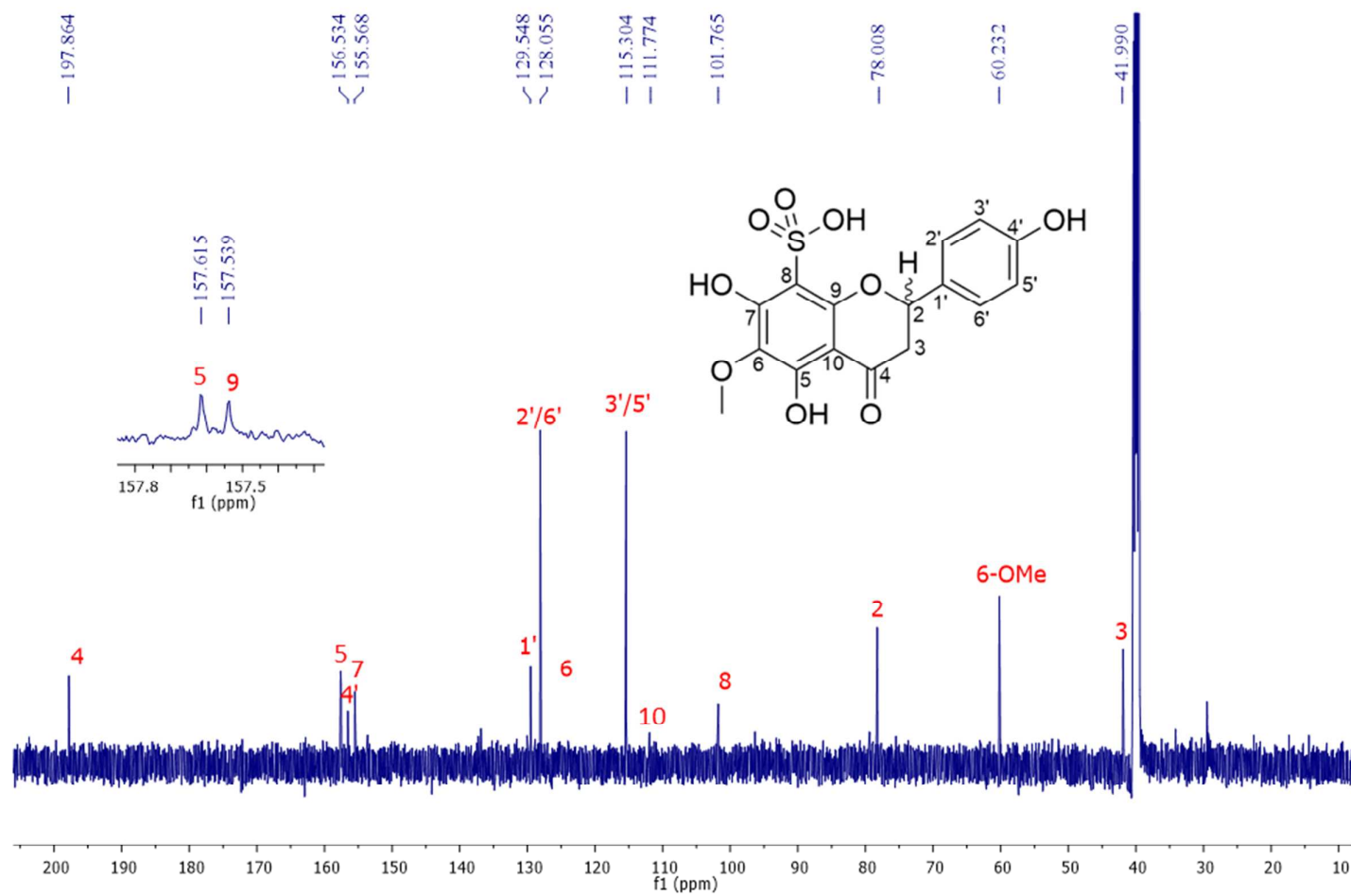
S1. HRESIMS spectrum of **1**



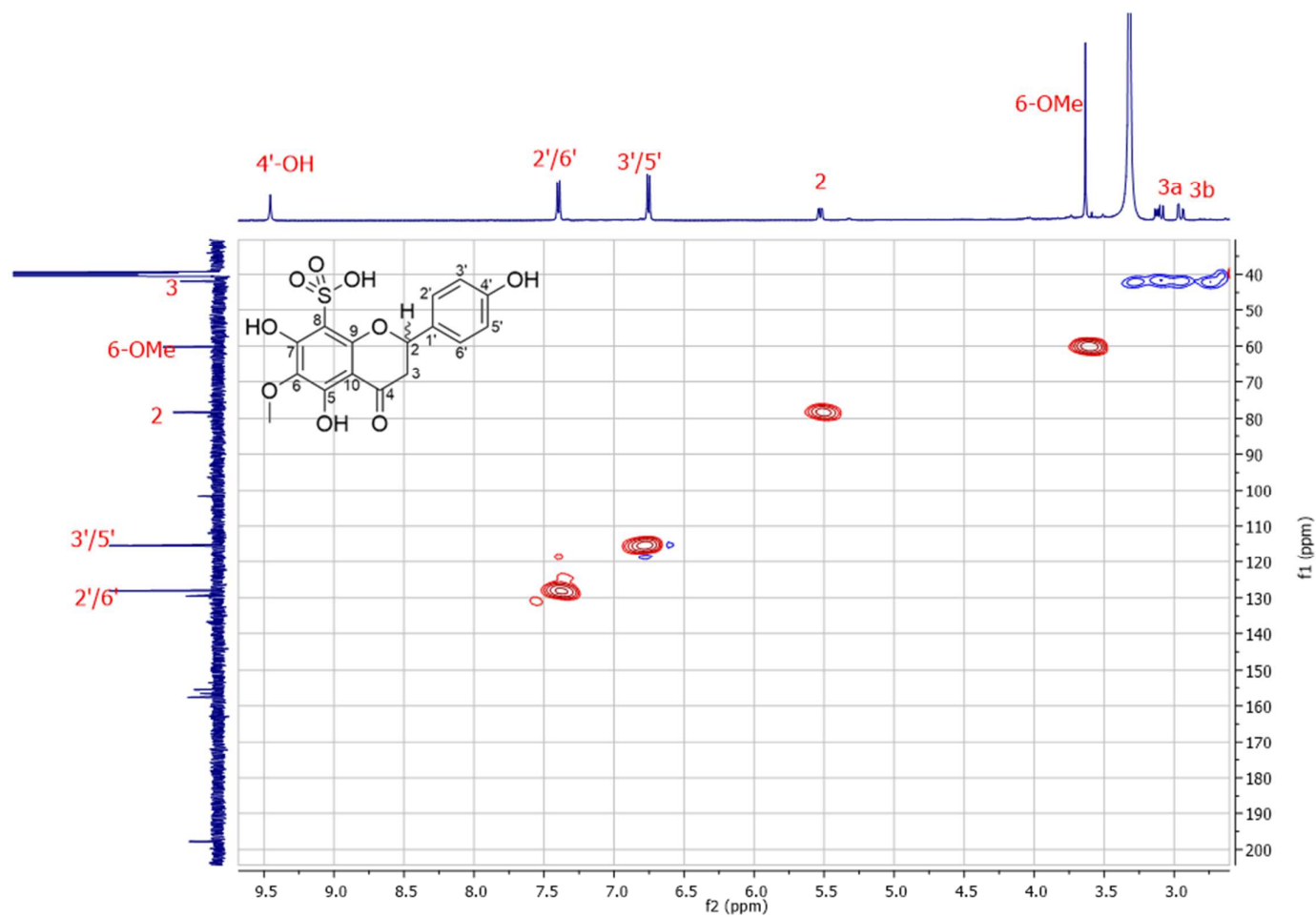
S2. ^1H NMR ($\text{DMSO}-d_6$, 500 MHz) spectrum of **1**



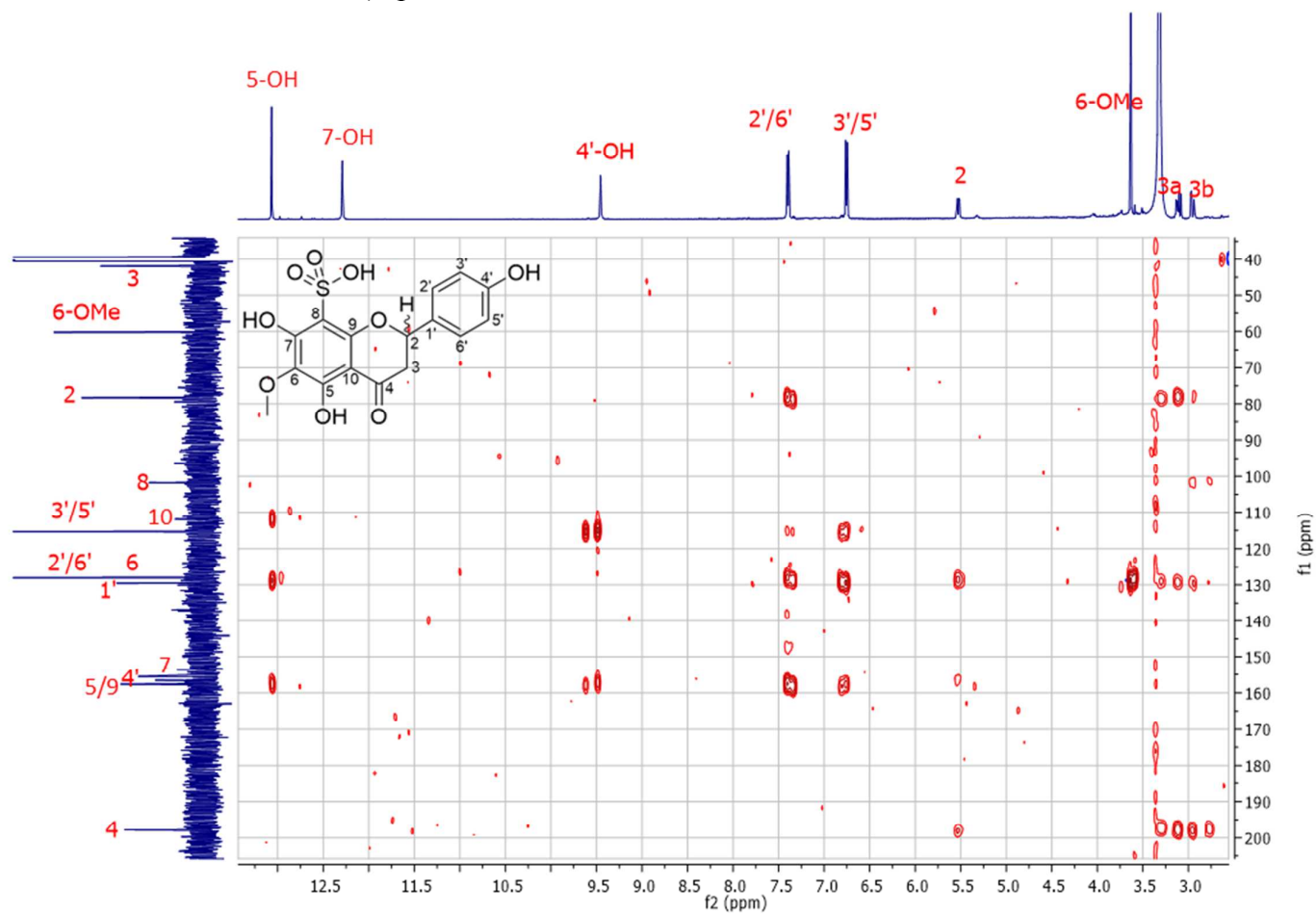
S3. ^{13}C NMR (DMSO- d_6 , 125 MHz) spectrum of **1**



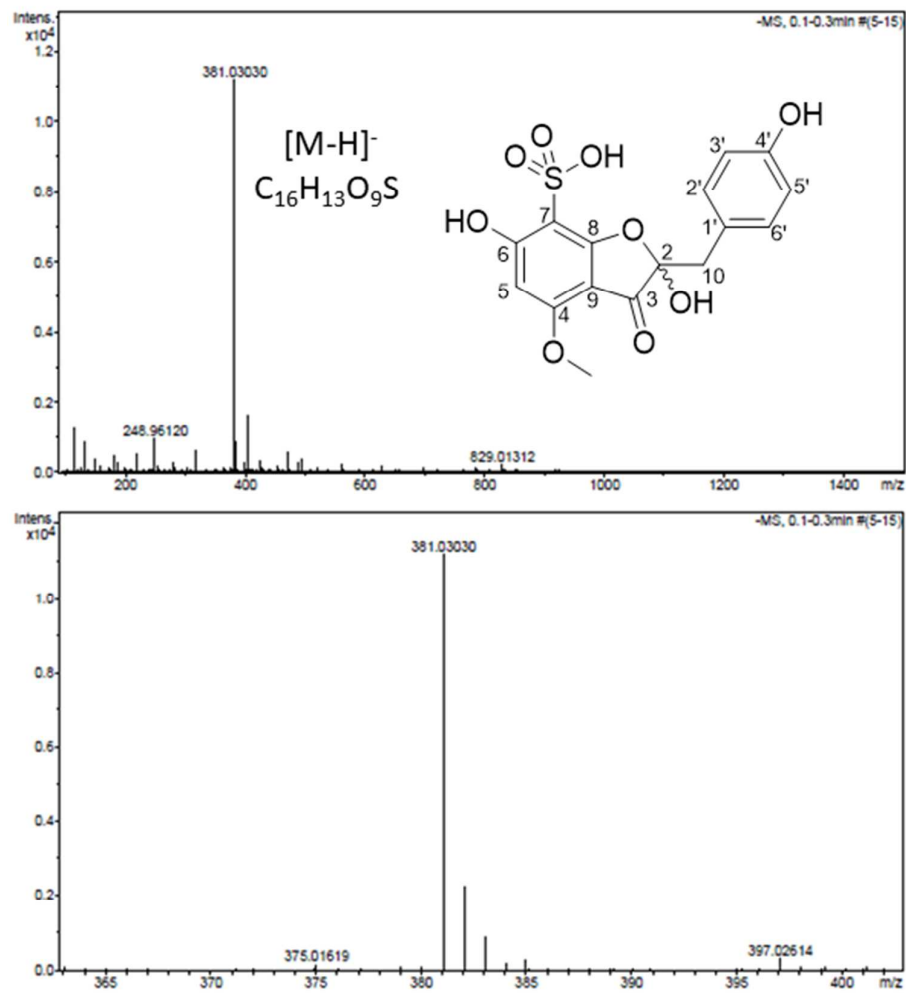
S4. HSQC (DMSO- d_6 , 500 MHz, 125 MHz) spectrum of **1**



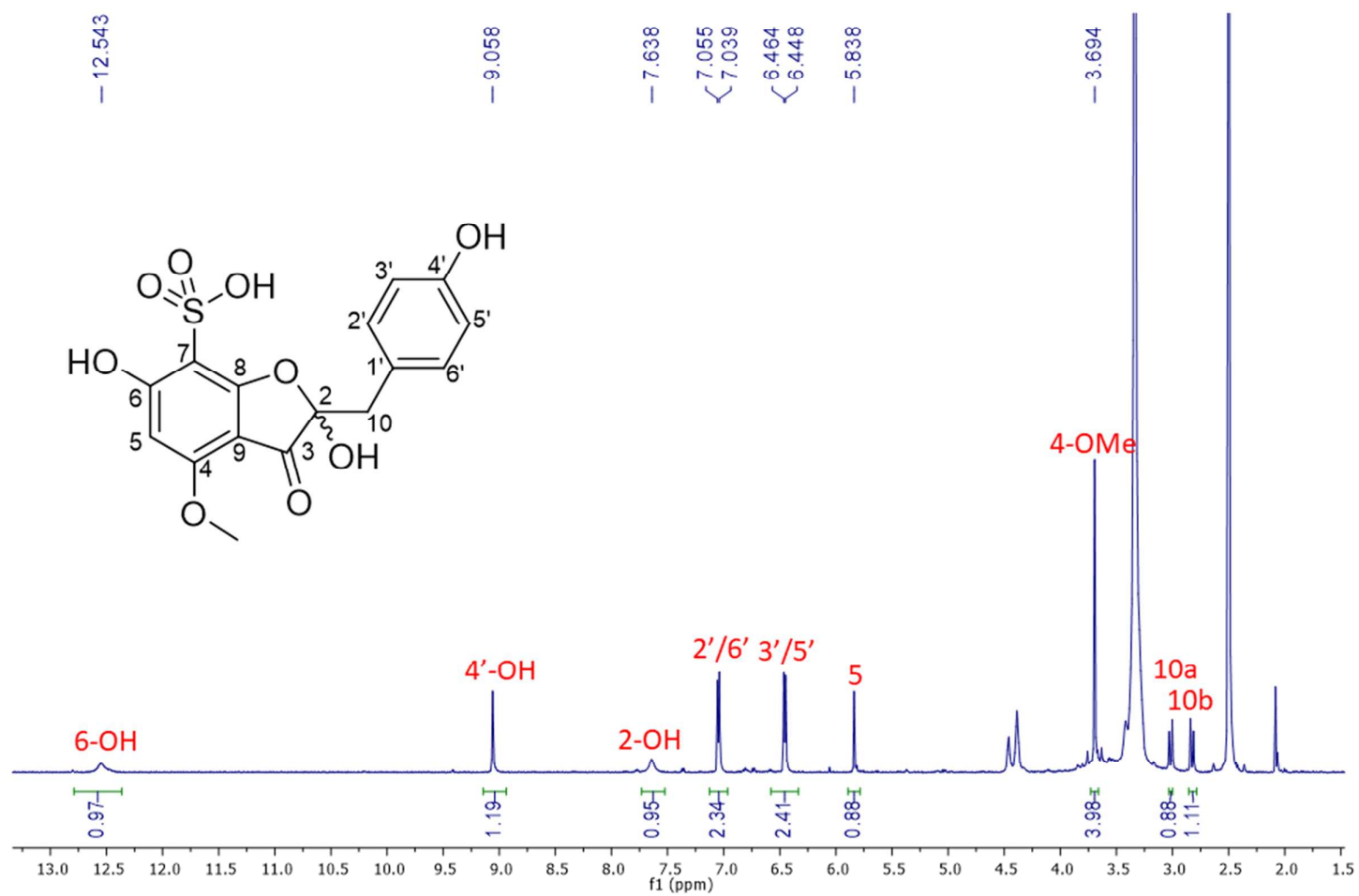
S5. HMBC (DMSO- d_6 , 500 MHz, 125 MHz) spectrum of **1**



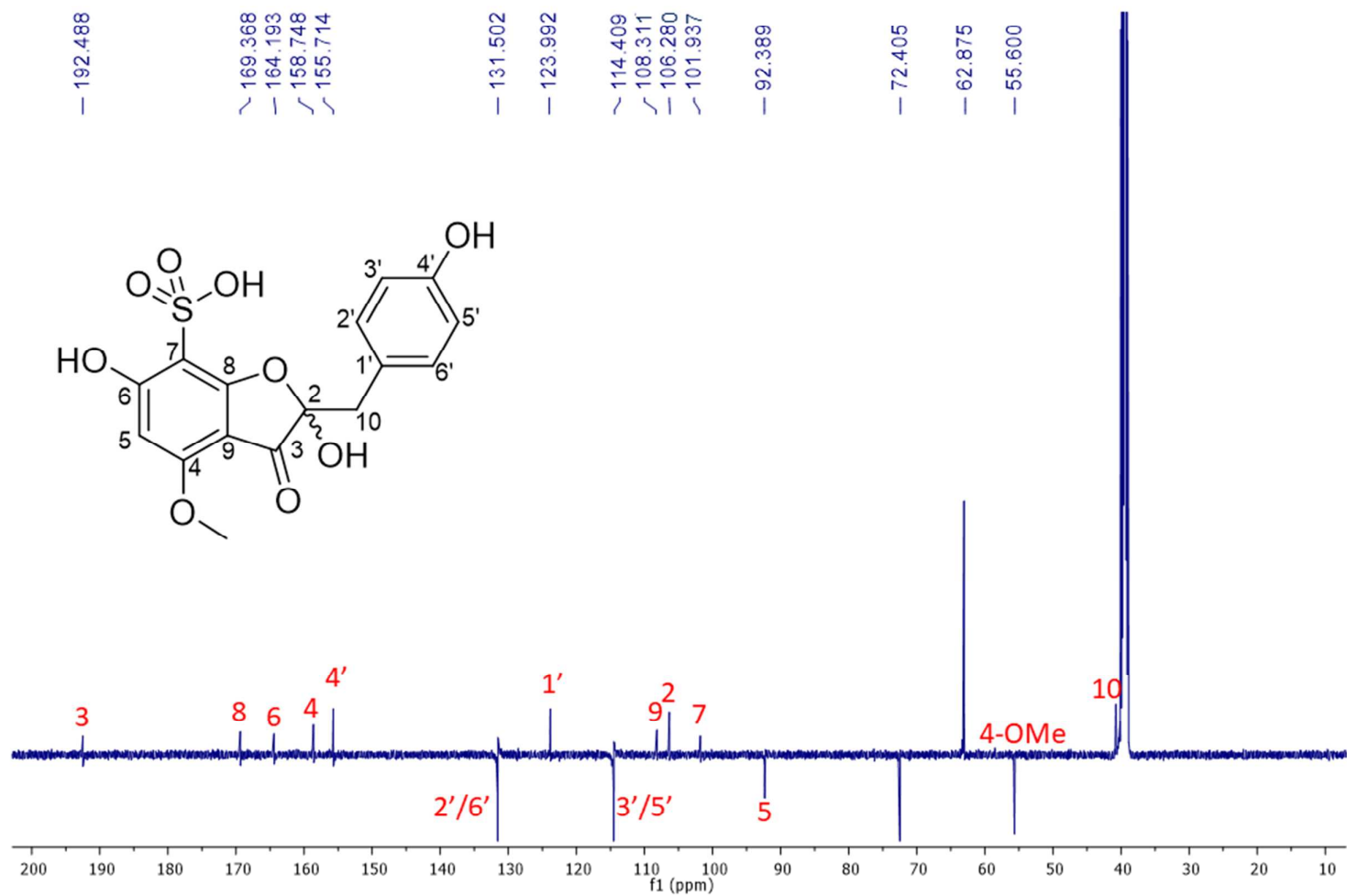
S6. HRESIMS spectrum of **2**



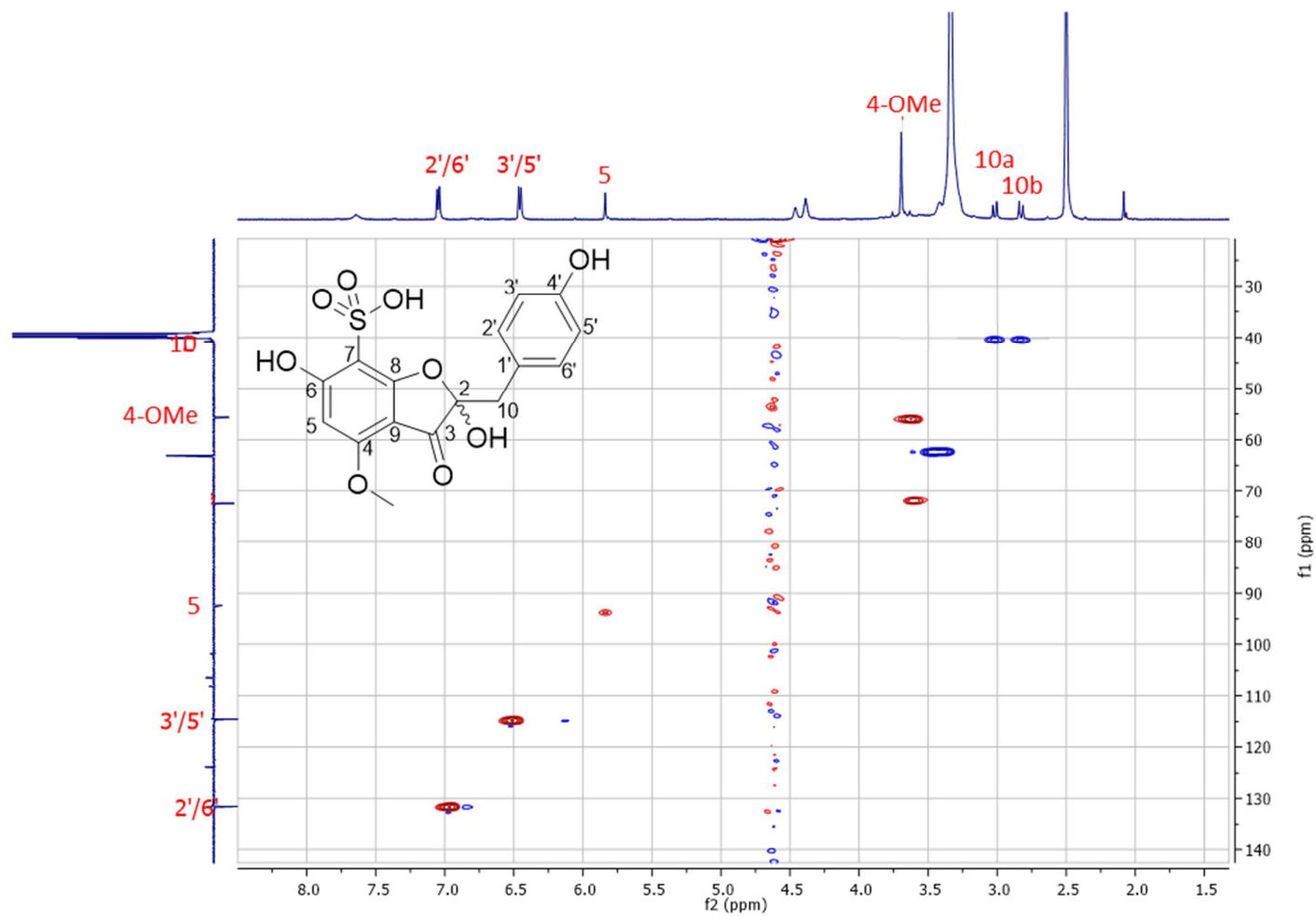
S7. ^1H NMR ($\text{DMSO}-d_6$, 500 MHz) spectrum of **2**



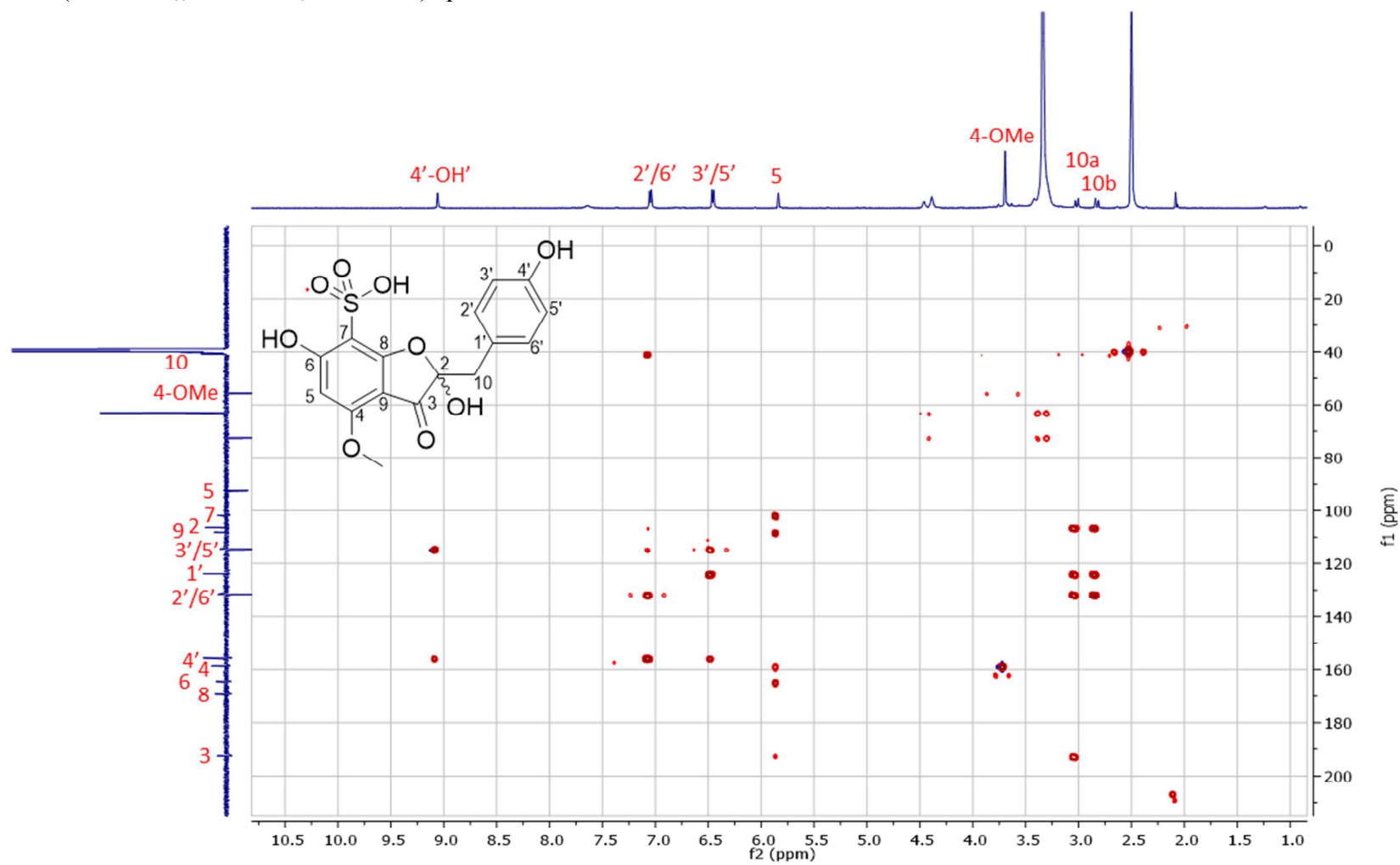
S8. JMOD (DMSO-*d*₆, 125 MHz) spectrum of **2**



S9. HSQC (DMSO- d_6 , 500 MHz, 125 MHz) spectrum of **2**



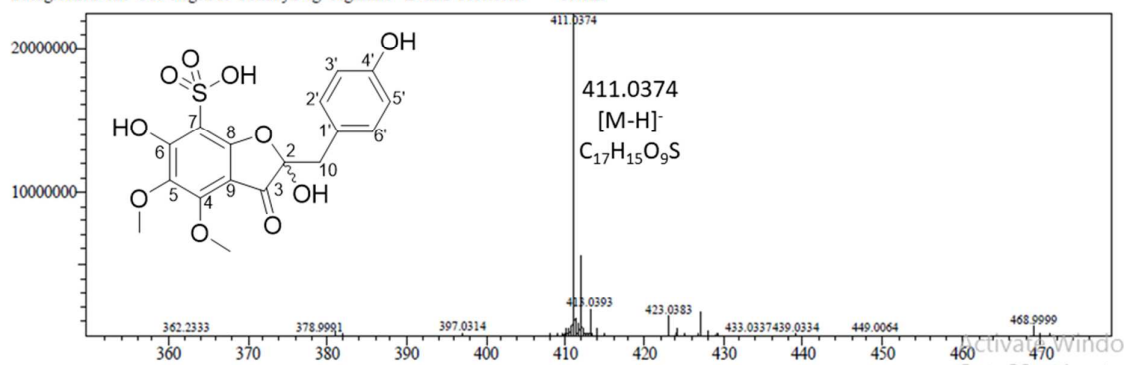
S10. HMBC (DMSO- d_6 , 500 MHz, 125 MHz) spectrum of **2**



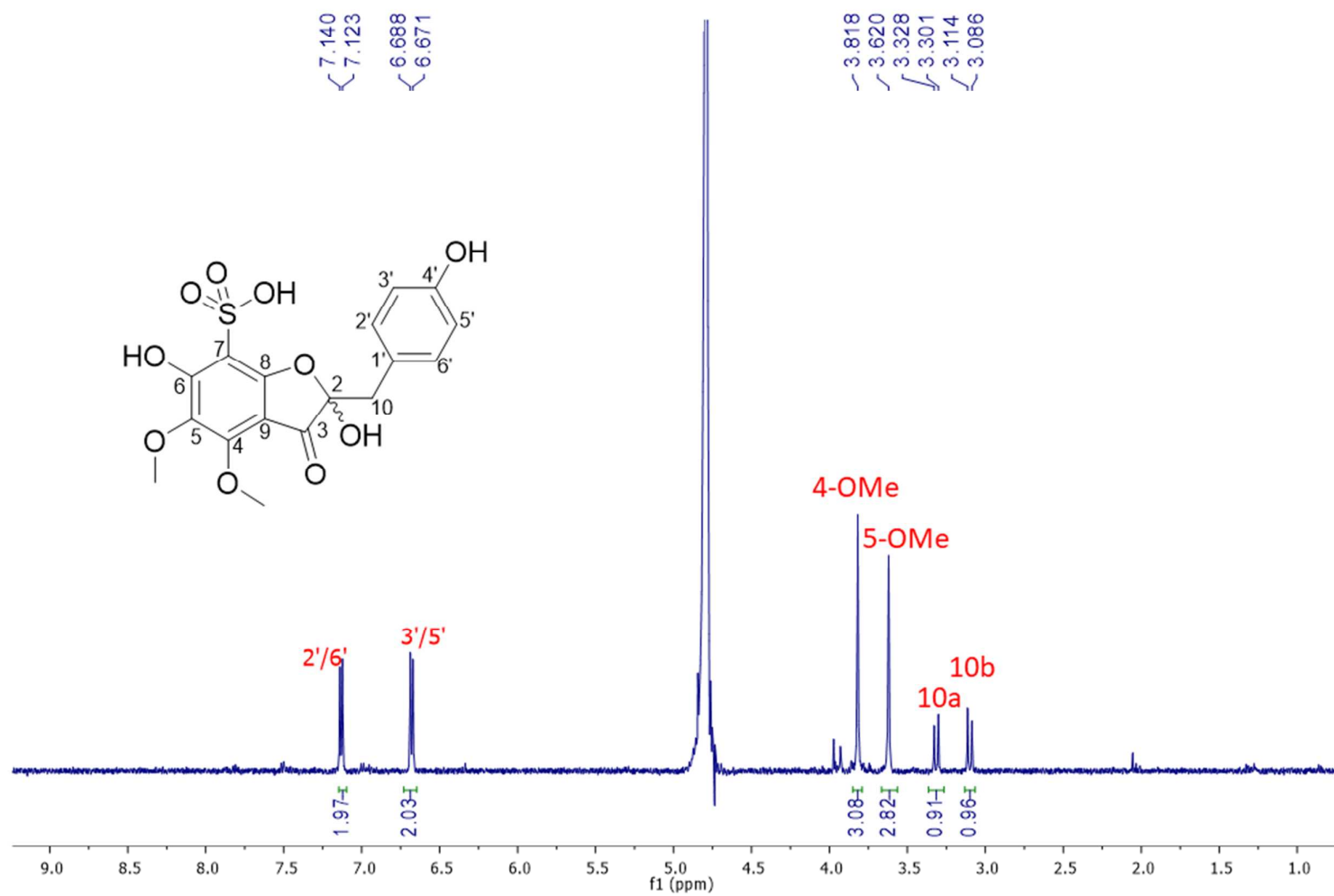
S11. HRESIMS spectrum of **3**

<Spectrum>

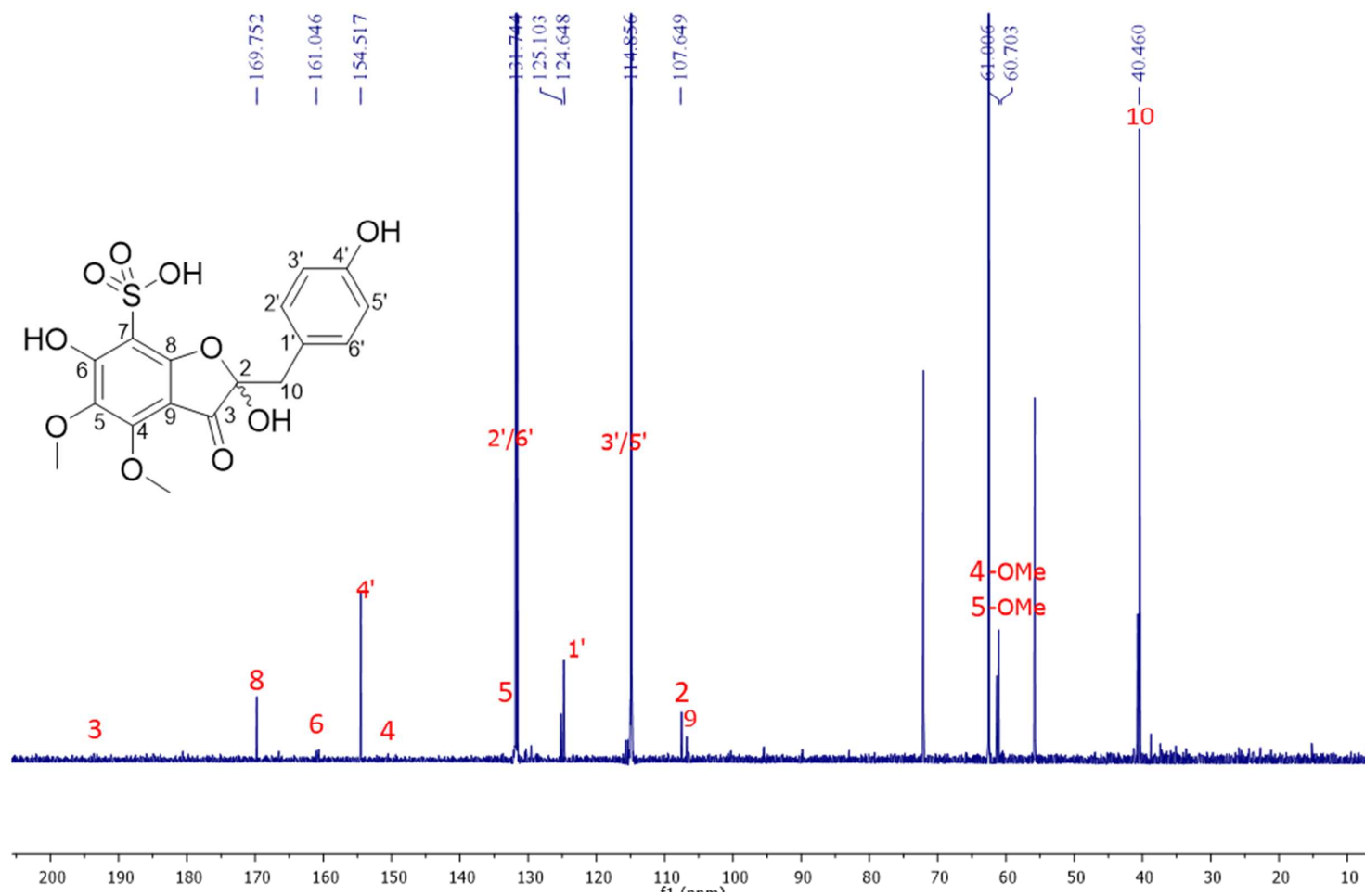
Retention Time: 0.113 (Scan# 36)
 Max Peak: 202 Base Peak: 411.04 (11851426)
 Spectrum: Single 0.113 (36)
 Background: None MS Stage: MS Polarity: Neg Segment 1 - Event 2 Precursor: — Cutoff:



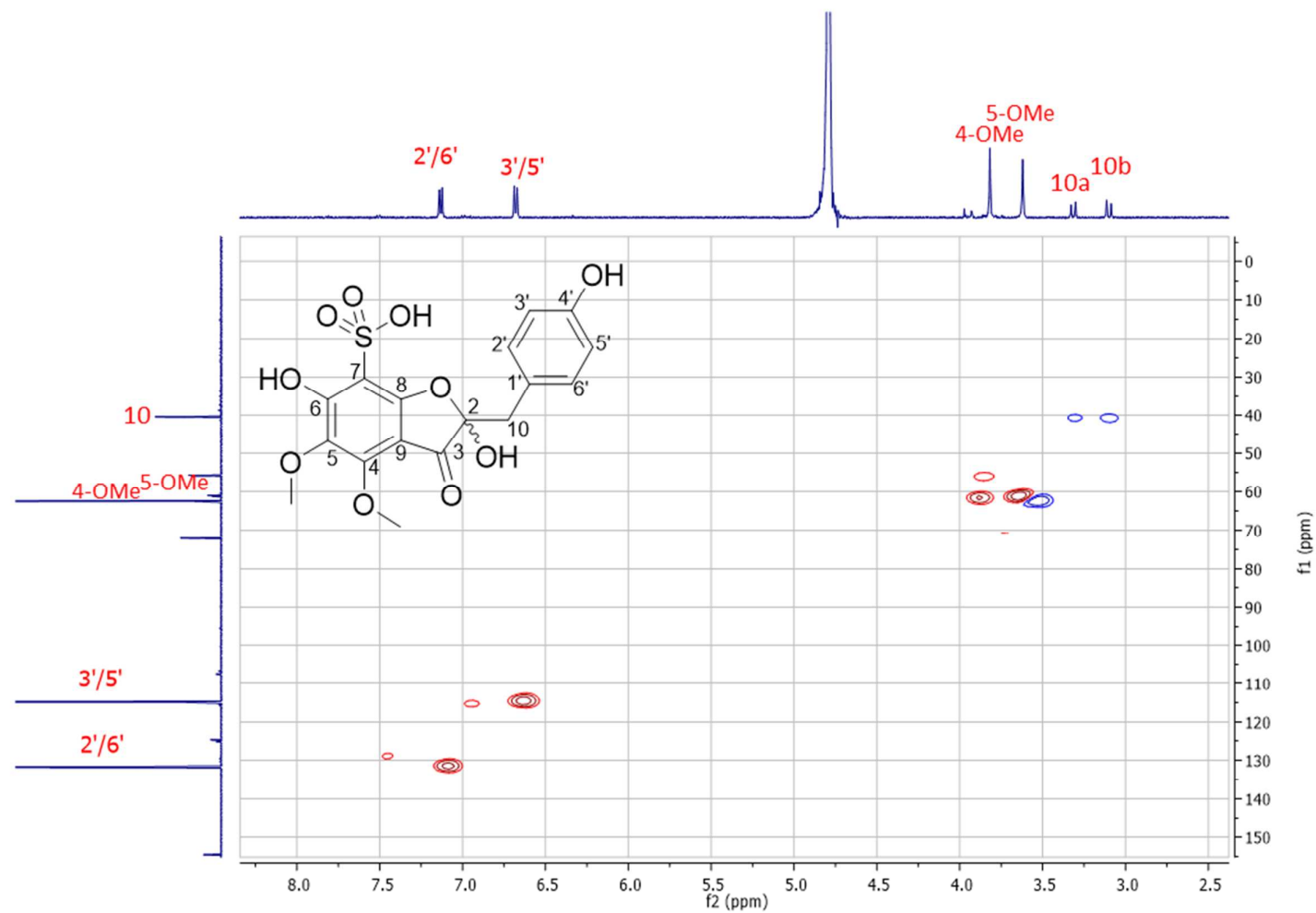
S12. ^1H NMR (D_2O , 500 MHz) spectrum of **3**



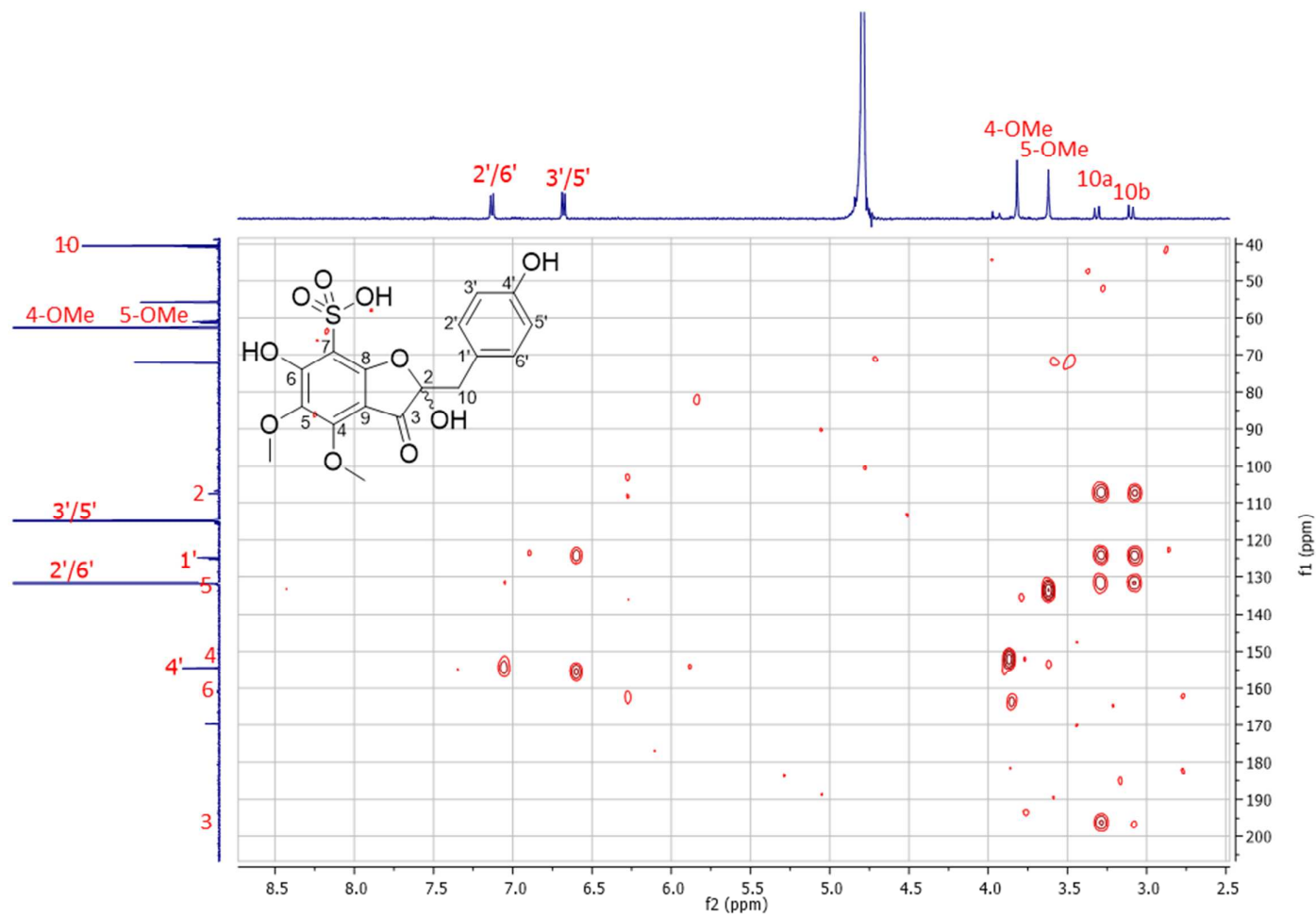
S13. ^{13}C NMR (D_2O , 125 MHz) spectrum of **3**



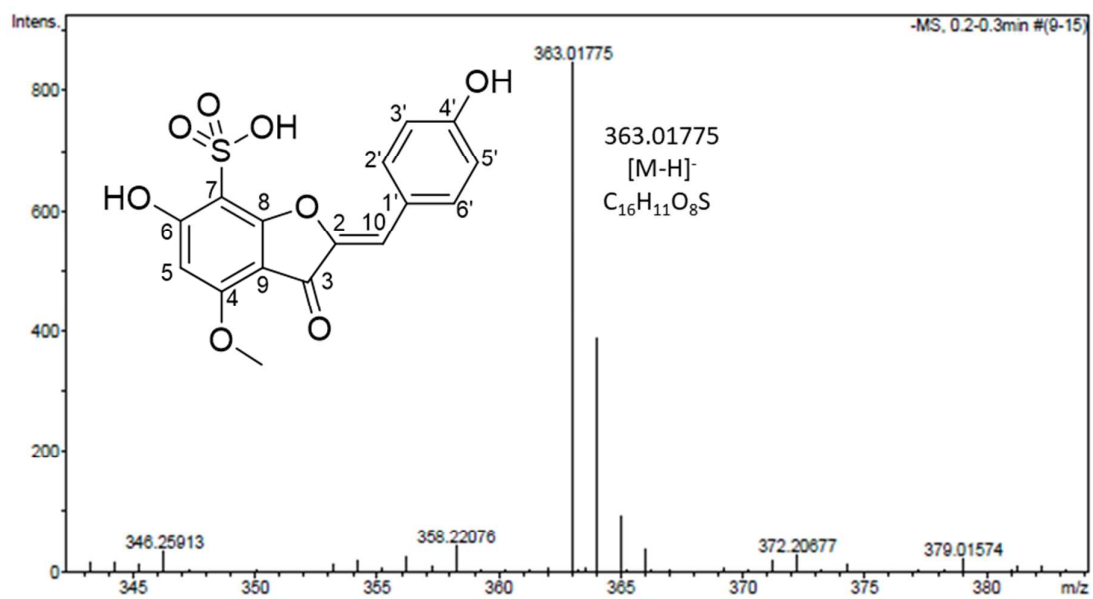
S14. HSQC (D₂O, 500 MHz, 125 MHz) spectrum of **3**



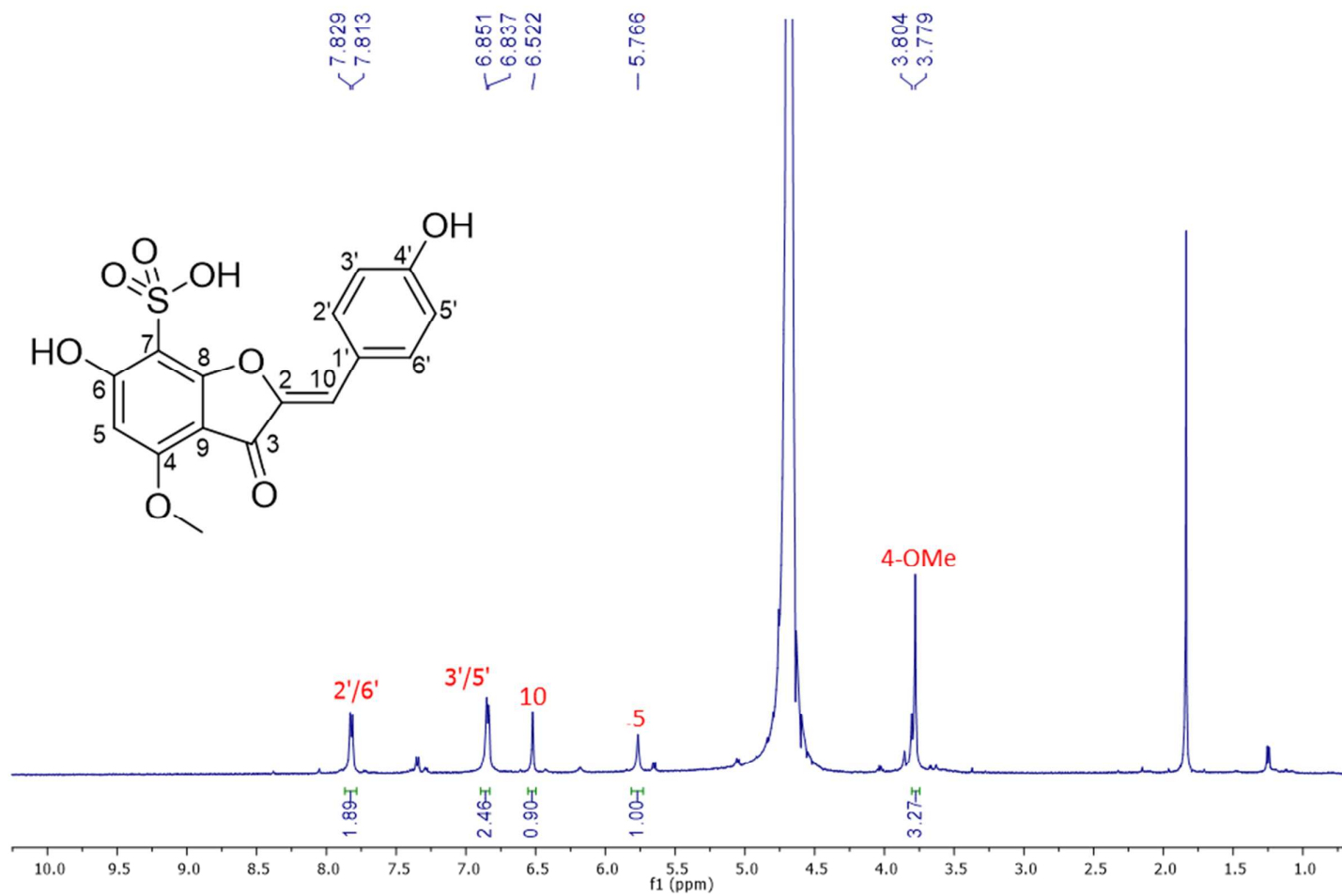
S15. HMBC (D₂O, 500 MHz, 125 MHz) spectrum of **3**



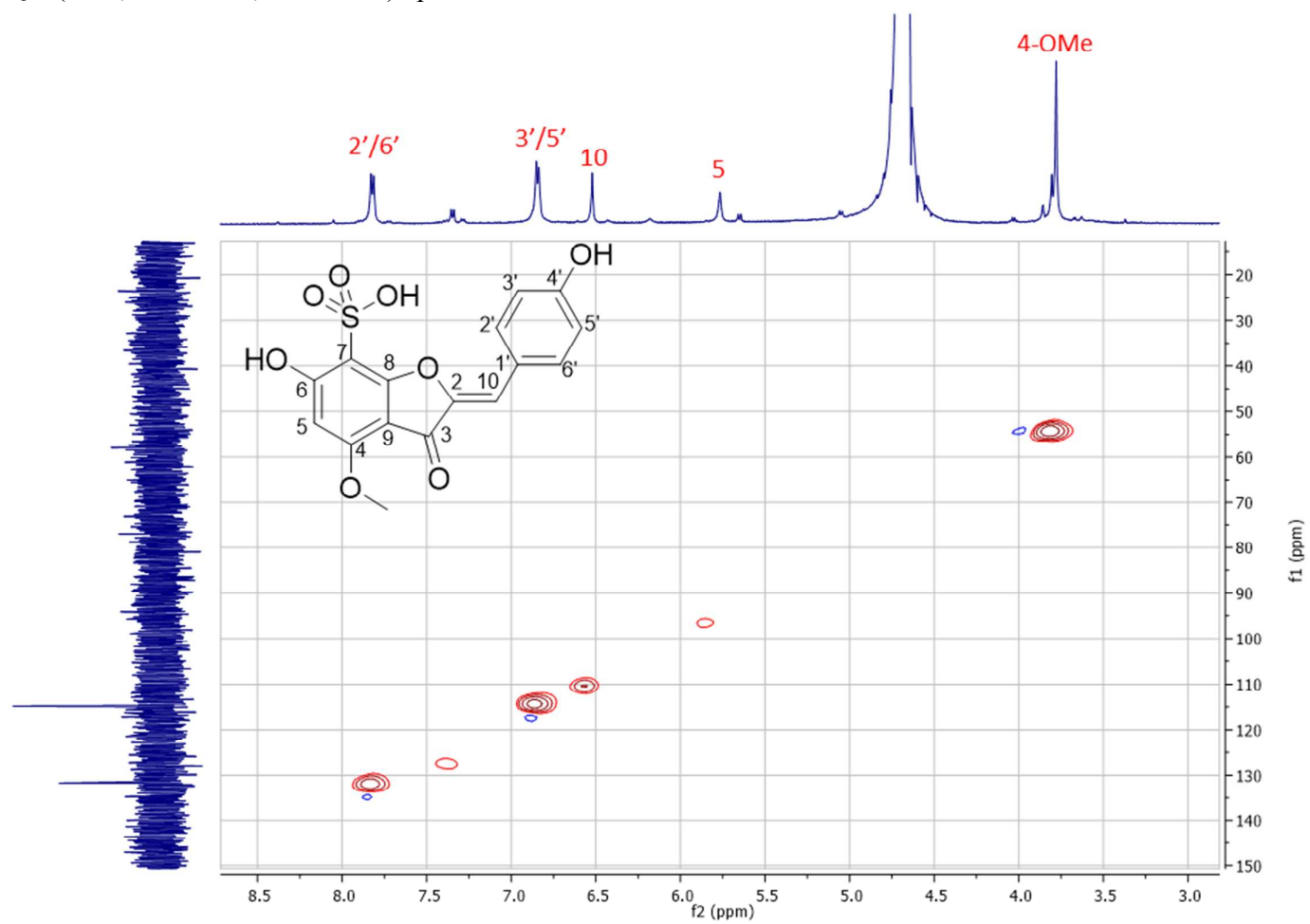
S16. HRESIMS spectrum of **4**



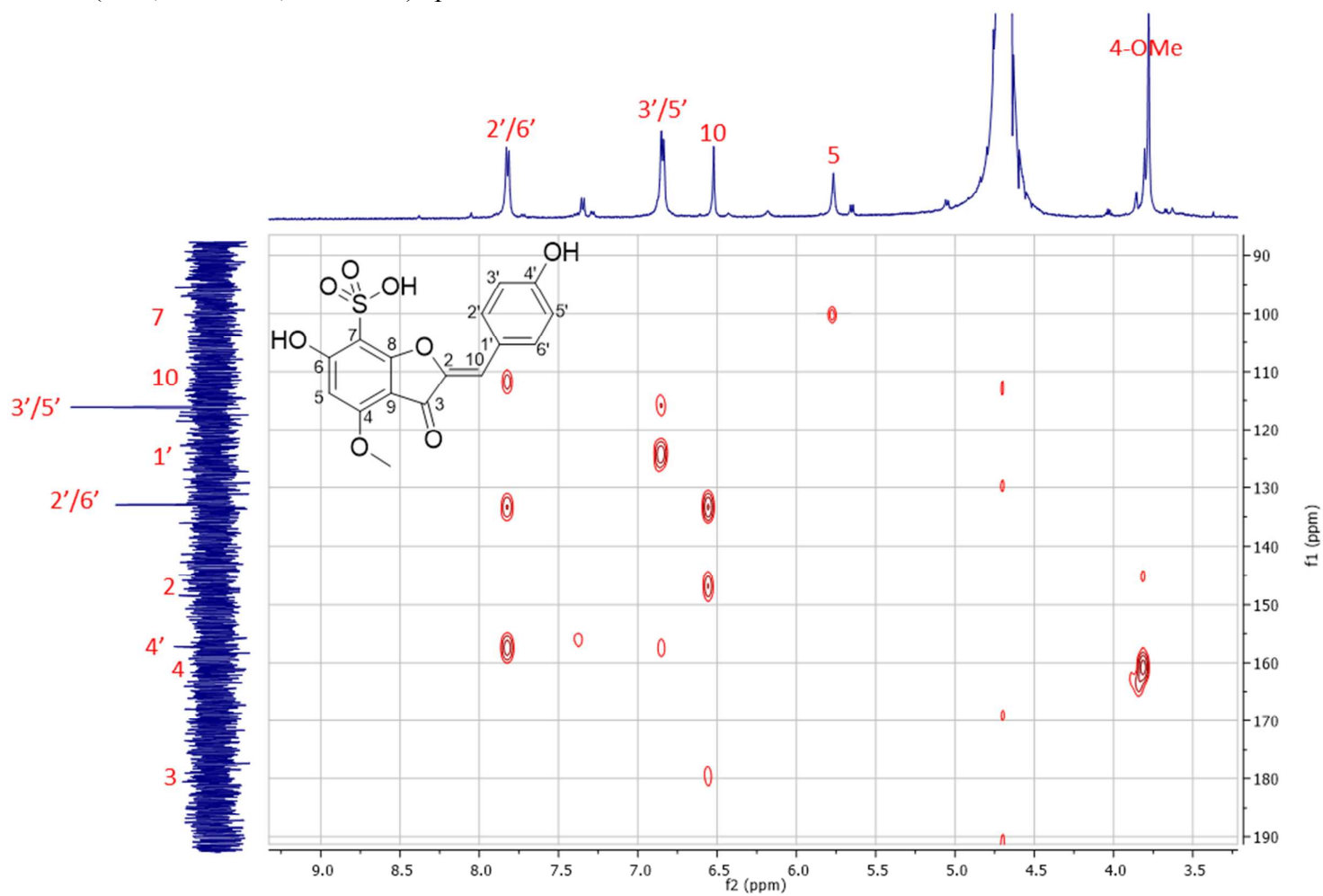
S17. ^1H NMR (D_2O , 500 MHz) spectrum of **4**



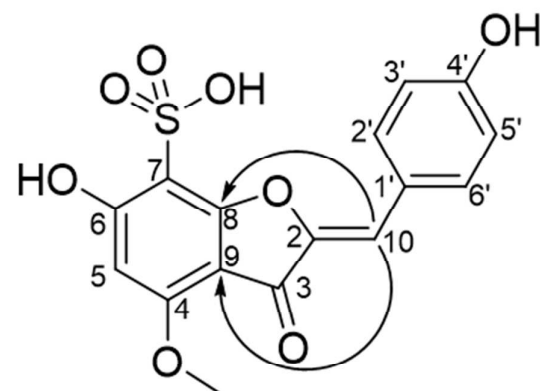
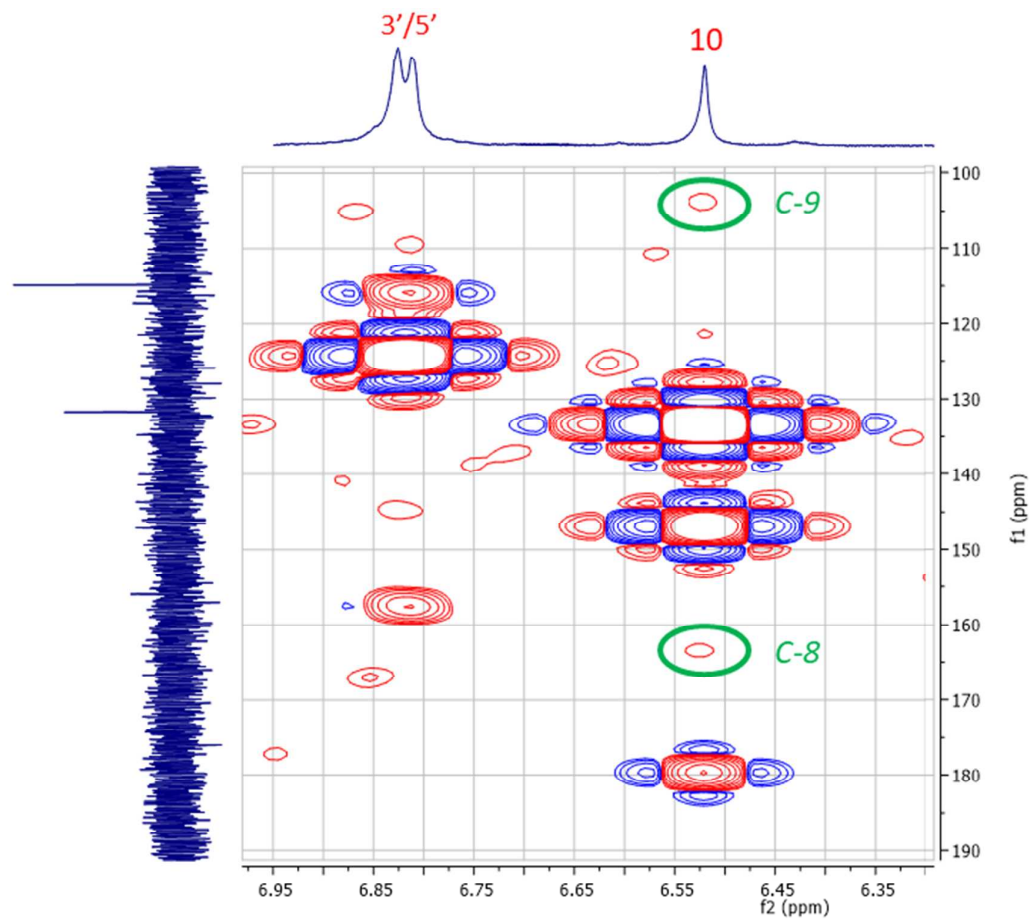
S18. HSQC (D₂O, 500 MHz, 125 MHz) spectrum of **4**



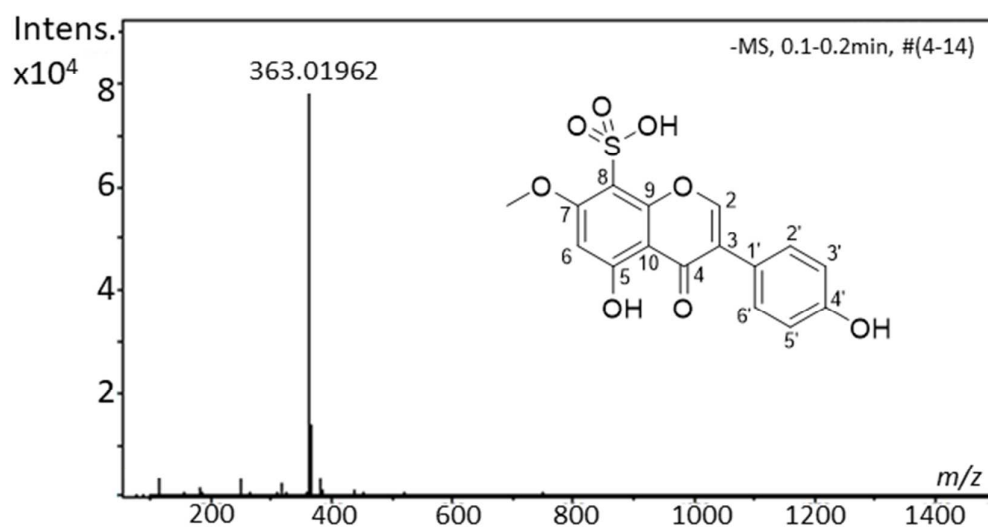
S19. HMBC (D₂O, 500 MHz, 125 MHz) spectrum of **4**



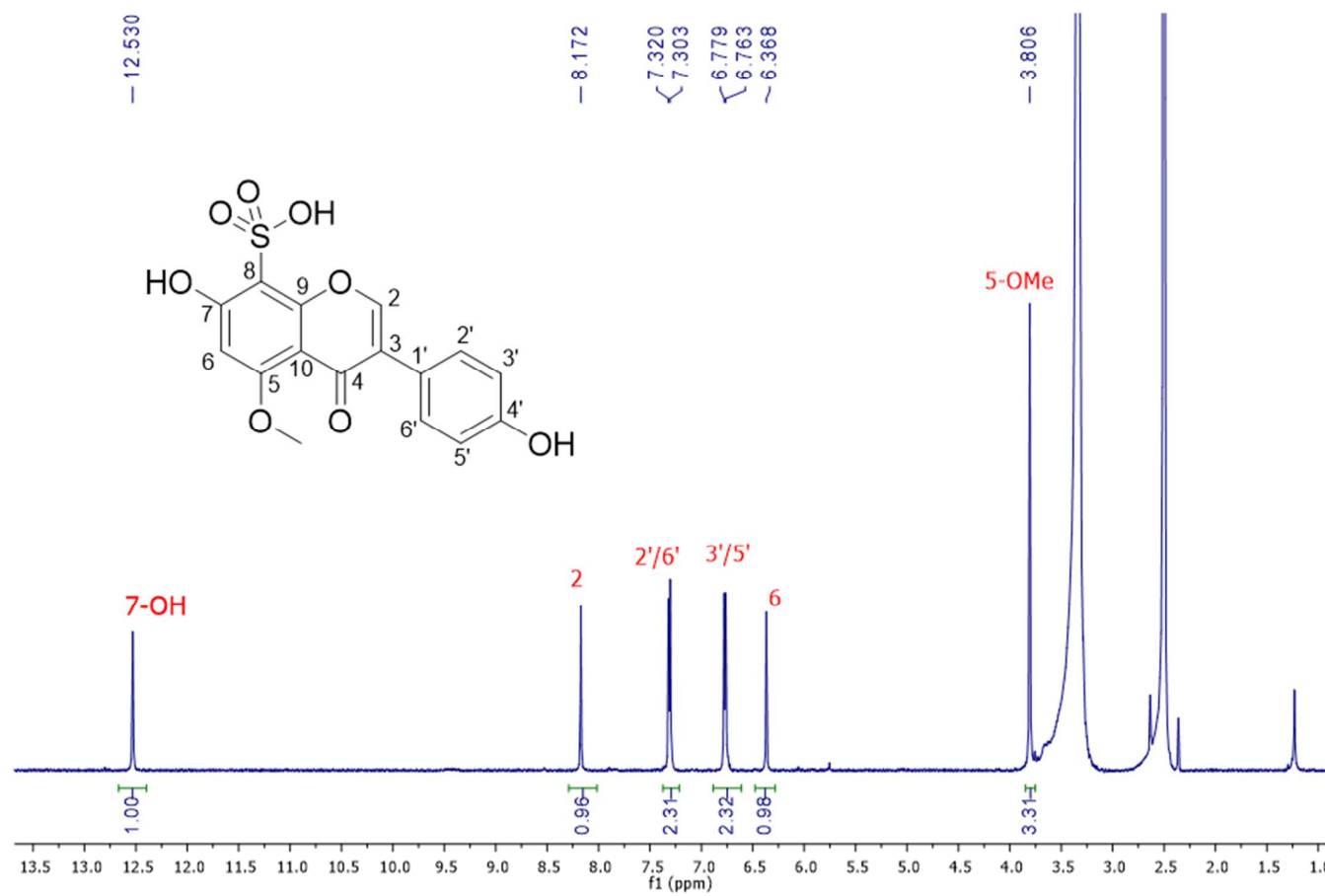
S20. Zoom into HMBC spectrum of **4** to reveal the 4J correlations of olefinic proton H-10.



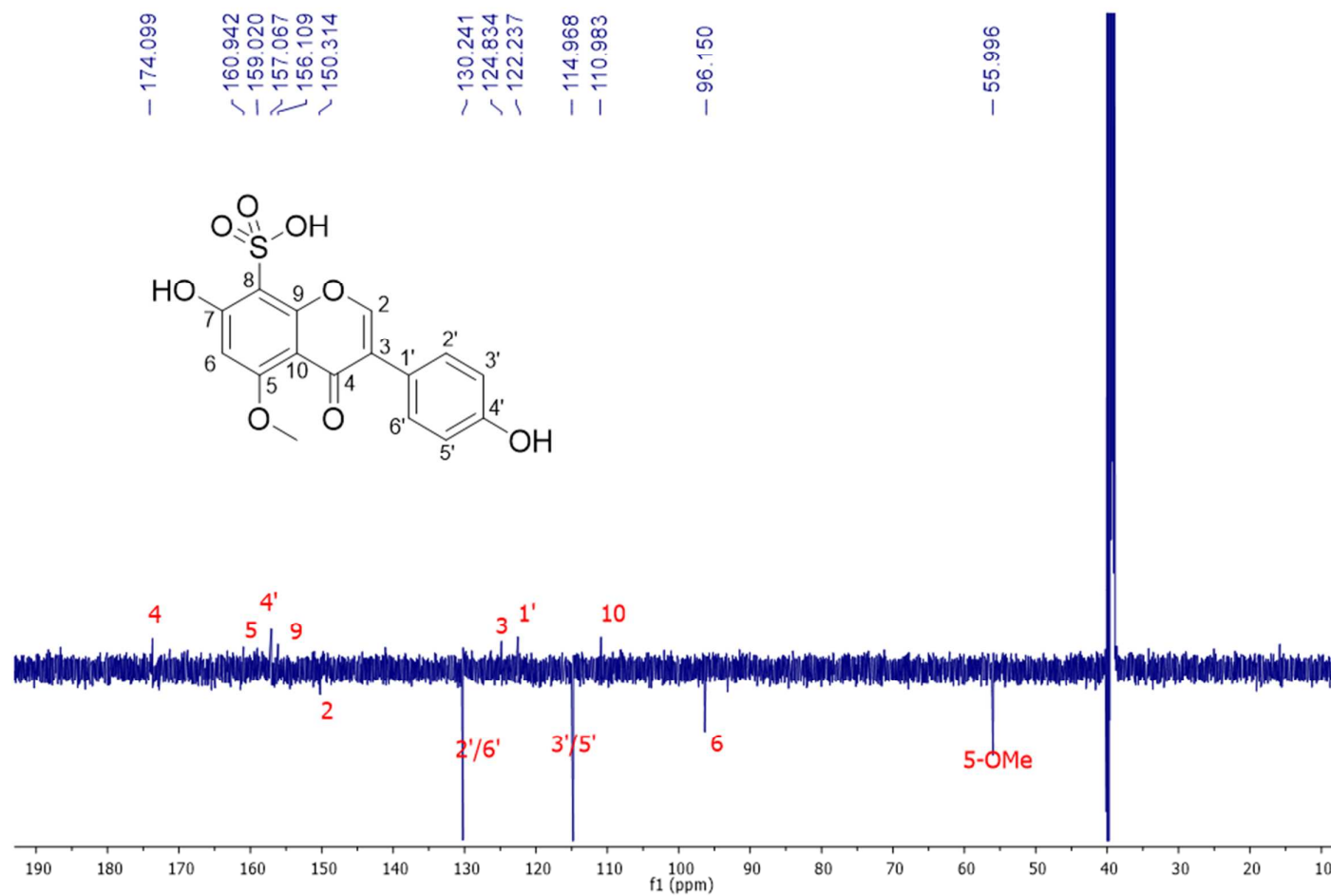
S21. HRESIMS spectrum of **5**



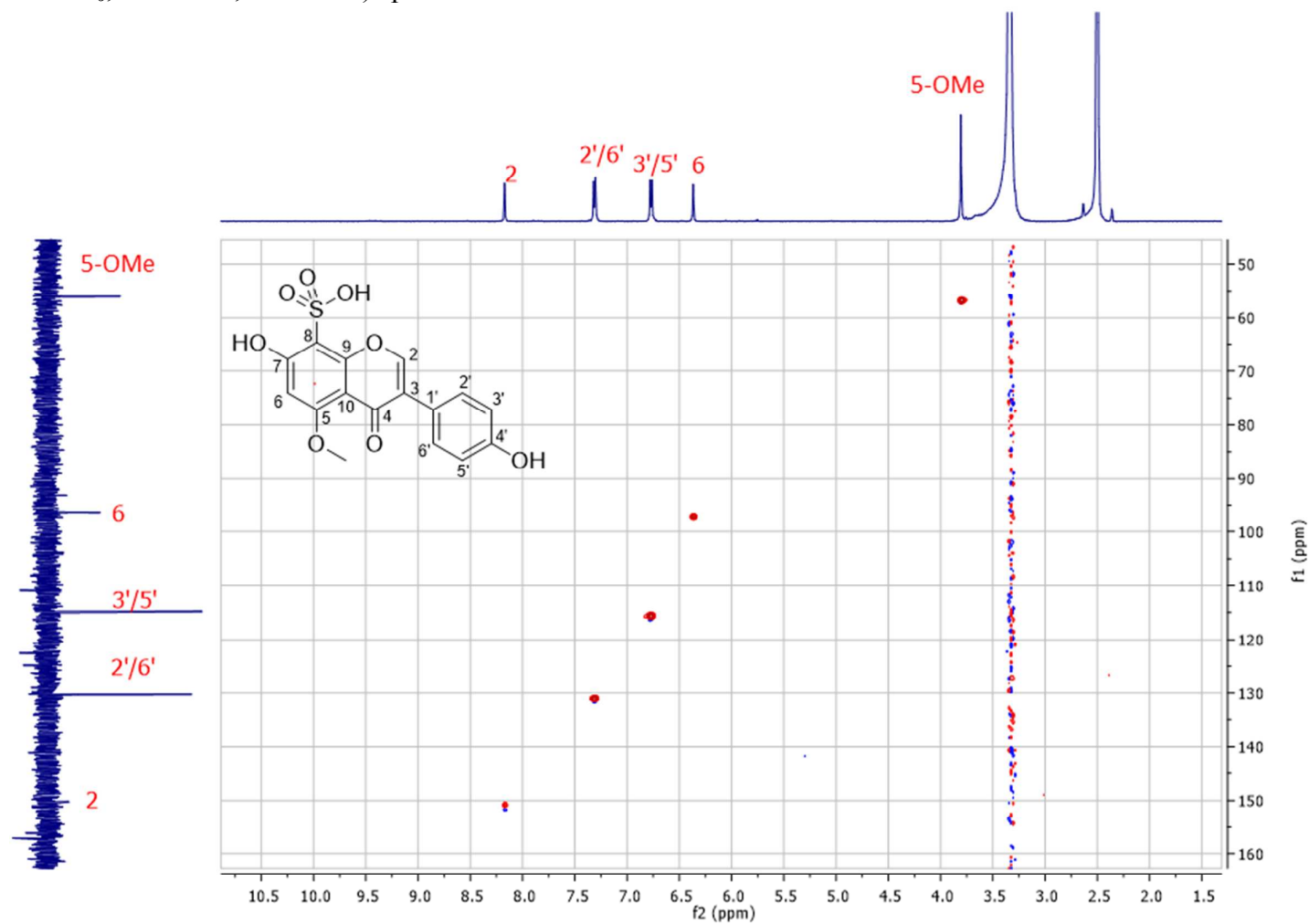
S22. ^1H NMR ($\text{DMSO}-d_6$, 500 MHz) spectrum of **5**



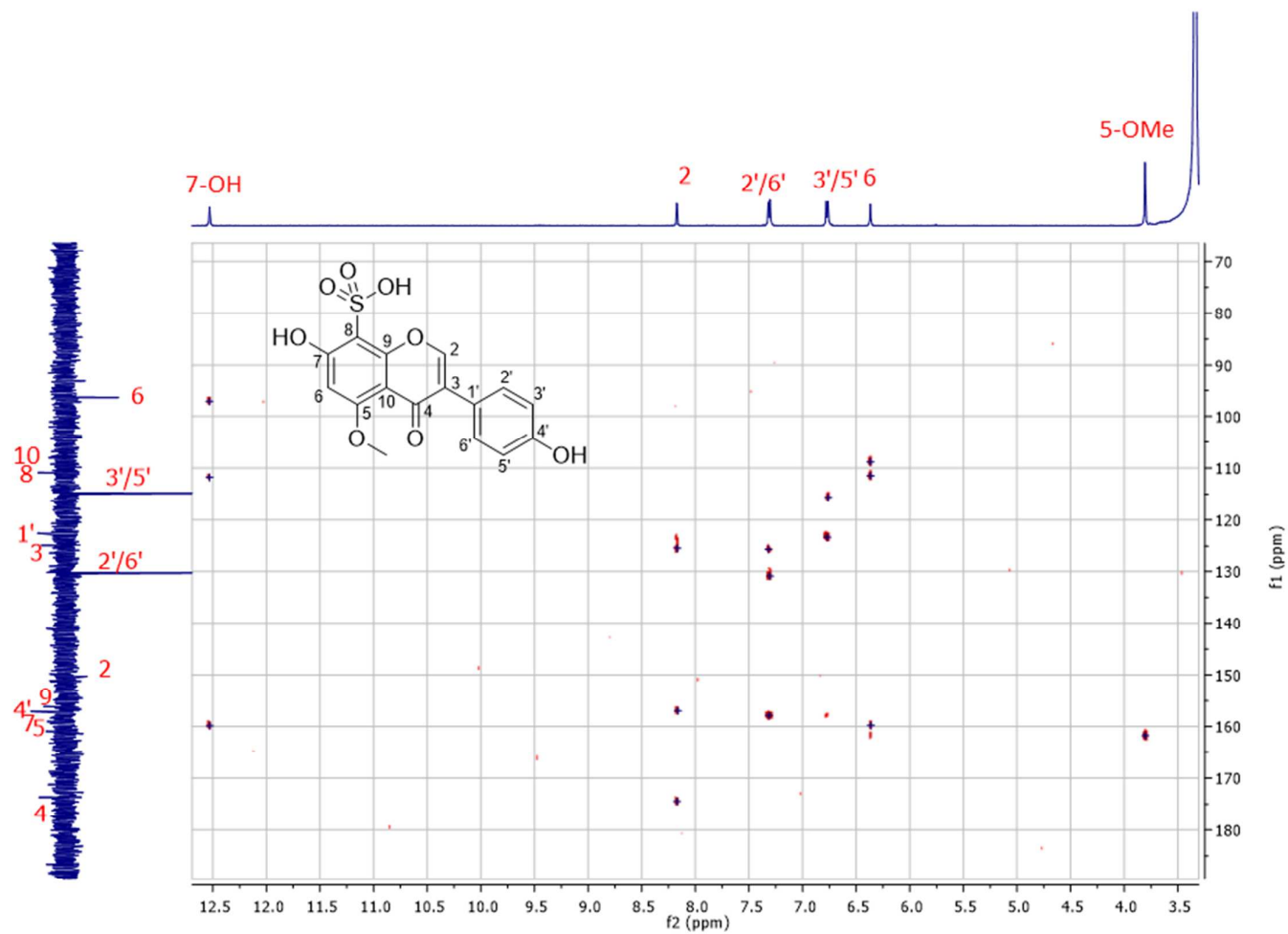
S23. JMOD (DMSO-*d*₆, 500 MHz) spectrum of **5**



S24. HSQC (DMSO-*d*₆, 500 MHz, 125 MHz) spectrum of **5**



S25. HMBC (DMSO-*d*₆, 500 MHz, 125 MHz) spectrum of **5**

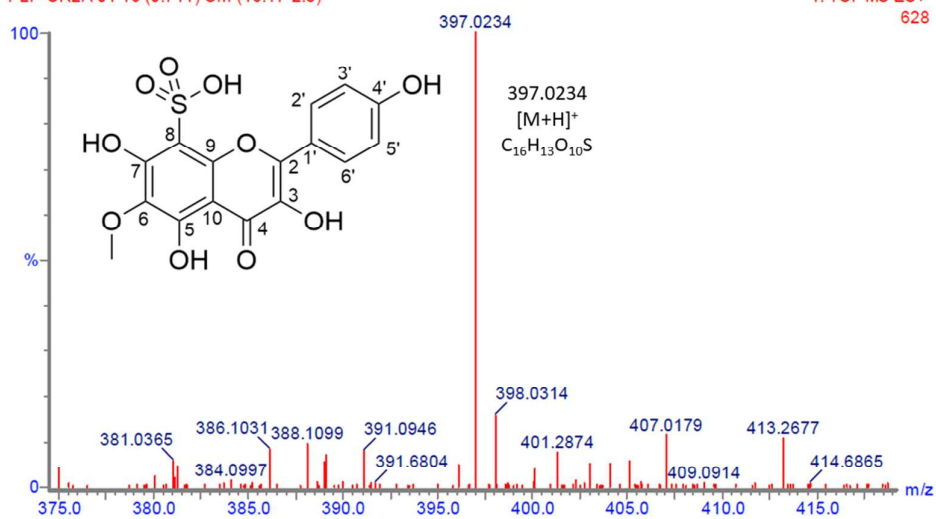


S26. HRESIMS spectrum of **6**

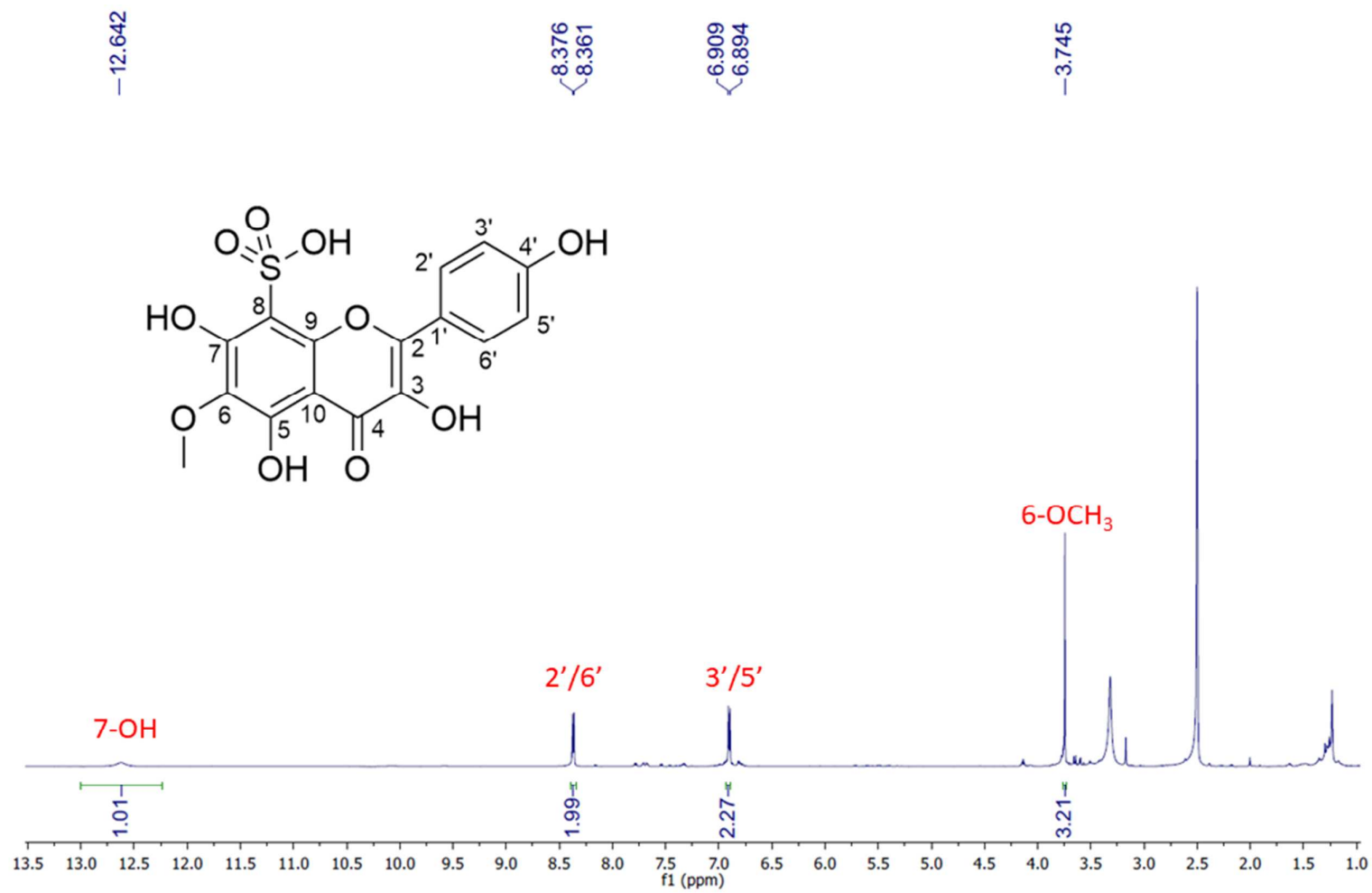
23-Mar-2018

Pierre LE POGAM-ALLUARD - GNOSIE
PLP-CR2A-01 16 (0.711) Cm (16:17-2:8)

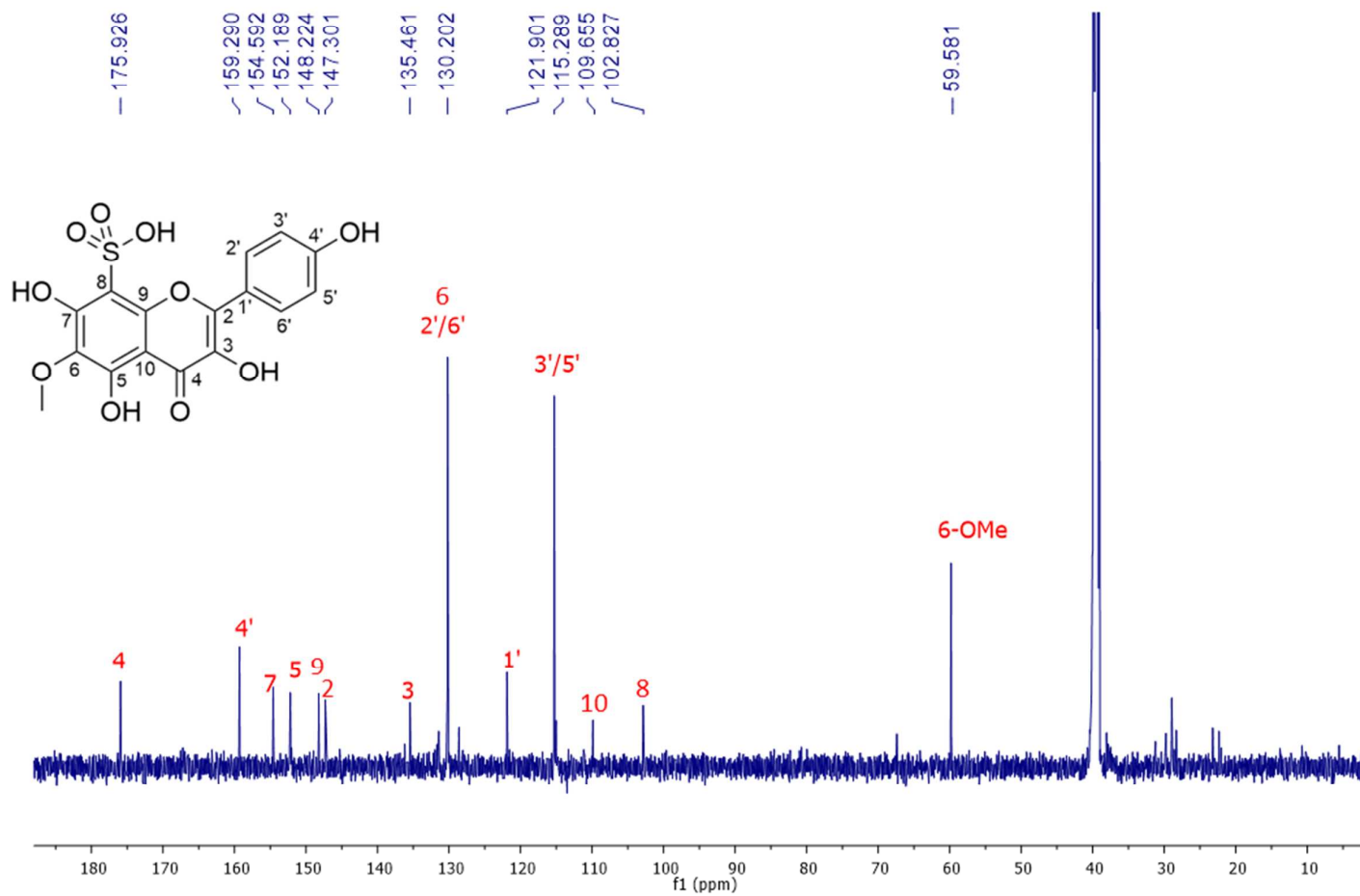
H₂O/MeOH
vial 32
1: TOF MS ES+
628



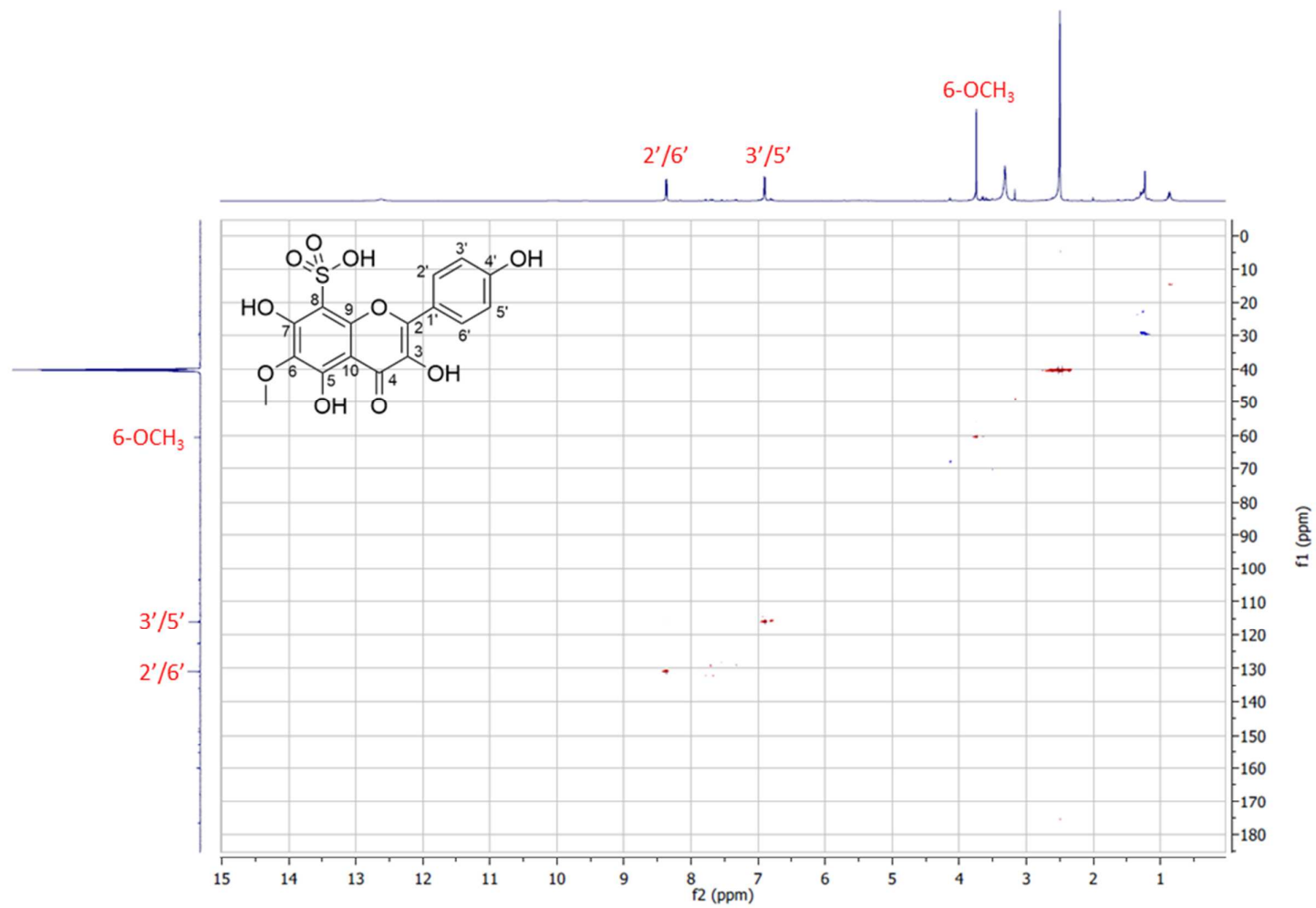
S27. ^1H NMR ($\text{DMSO-}d_6$, 600 MHz) spectrum of **6**



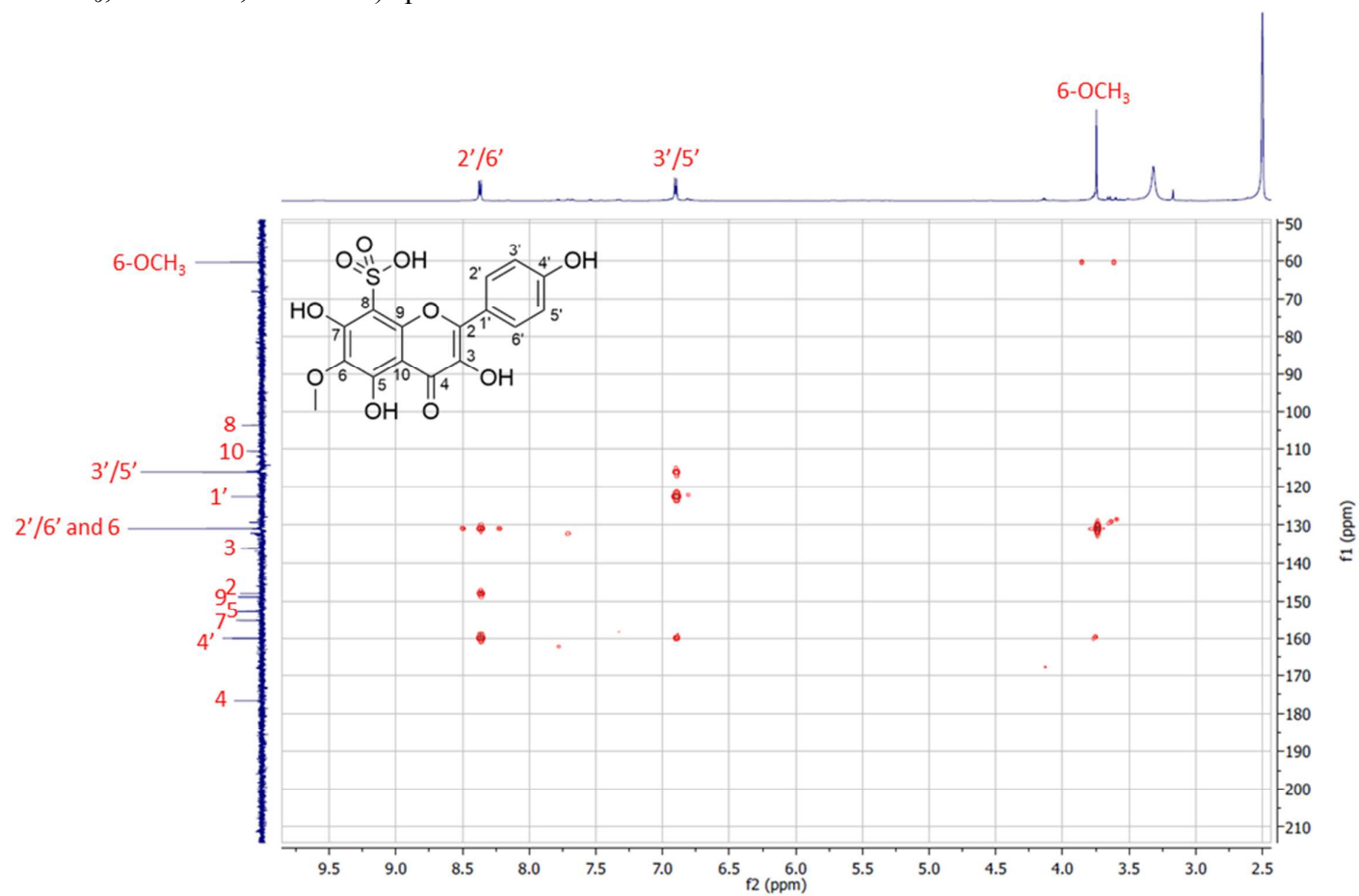
S28. ^{13}C NMR (DMSO- d_6 , 150 MHz) spectrum of **6**



S29. HSQC (DMSO- d_6 , 600 MHz, 150 MHz) spectrum of **6**



S30. HMBC (DMSO- d_6 , 600 MHz, 150 MHz) spectrum of **6**



S31. Experimental details for X-ray diffraction analyses of **1**

(±) Acidoflavanone (**1**) crystallized as $\text{NaC}_{16}\text{H}_{13}\text{O}_9\text{S}$, in the monoclinic system, centrosymmetric space group $P2_1/c$ (no. 14) with unit cell constants $a = 8.9866(4) \text{ \AA}$, $b = 10.5769(5) \text{ \AA}$, $c = 17.8065(8) \text{ \AA}$, $\beta = 101.942(2)^\circ$, $V = 1655.9(1) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.622 \text{ g cm}^{-3}$, $MW = 404.31$. A colorless rod-like single crystal of **1** with dimensions $0.22 \times 0.32 \times 0.36 \text{ mm}$ was mounted on a MiTeGen micromount using epoxy glue. With the help of APEX2 Software Suite, a total of 21,429 reflections were collected at 296(2) K on a Bruker X8 APEXII Kappa CCD area-detector diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data were integrated, reduced by SAINT+, corrected for absorption effects, scaled by SADABS, and merged by XPREP (Bruker AXS Inc.), yielding 5059 unique reflections ($R_{\text{int}} = 0.0338$). The structure was solved by intrinsic phasing method using SHELXTL XT (Bruker AXS Inc.) and refined by full-matrix least squares on F^2 with SHELXTL XLMP (Bruker AXS Inc.); final $R_1 = 0.0486$, $wR_2 = 0.1286$, $\text{Goof} = 1.057$ for 3782 reflections with $F^2 > 2\sigma(F^2)$. Crystallographic data for the structure of **1** have been deposited within the Cambridge Crystallographic Data Center as supplementary publication (CCDC 1836646). Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).