Supplementary Information

Chemical Composition and Anti-Inflammatory Activity of the Decoction from Leaves of a Cultivated Specimen of *Myracrodruon urundeuva*

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Table S1. Retention time (t_R), UV-Vis wavelength (λ), molecular formula, molecular weight (MW) and MS/MS fragments data of the isolated compounds from the leaf decoction from *M. urundeuva*

	t_R / min	λ / nm	Molecular formula	MW	MS/MS	Name	Reference
1	0.81	212	$C_6H_{11}NO_3$	146.08 $[M + H]^+$	–	*N*-methyl-*trans*-4-hydroxy-L-proline	1
2	0.81	212	$C_7H_{12}O_6$	192.13 $[M + H]^+$	67, 78, 90, 102, 130, 146, 164	quinic acid	2
3	1.31	224, 272	$C_7H_6O_5$	169.01 $[M – H]^–$	125, 97, 69	gallic acid	3
4	1.44	267	$C_6H_6O_3$	125.02 $[M – H]^–$	–	pyrogallol	4
5	3.30	217, 259, 293	$C_7H_6O_4$	153.01 $[M – H]^–$	–	protocatechuic acid	5
6	3.41	218, 274	$C_8H_8O_5$	183.03 $[M – H]^–$	97, 111, 124, 140, 168	*m*-digallic acid	–
7	3.41	218, 274	$C_{14}H_{10}O_9$	321.03 $[M – H]^–$	169, 125	*p*-digallic acid	–
8	3.41	218, 274	$C_{14}H_{10}O_9$	321.03 $[M – H]^–$	169, 125	methyl gallate	6
9	3.97	218, 267	$C_{27}H_{22}O_{18}$	633.07 $[M – H]^–$	169, 249, 275, 300, 329, 419, 463, 559	1-*O*-galloyl-6-*O*-luteoyl-α-glucose	7
10	4.89	228	$C_{19}H_{30}O_8$	387.20 $[M + H]^+$	85, 95, 123, 189, 207, 225, 268, 339	roseoside	8
11	5.07	211, 265, 347	$C_{27}H_{30}O_{15}$	593.15 $[M – H]^–$	67, 151, 227, 255, 284, 327, 387, 440, 519	kaempferol 3-*O*-Rutinoside	–
12	6.04	218, 274	$C_{34}H_{28}O_{22}$	787.10 $[M – H]^–$	169, 277, 295, 313, 405, 447, 465, 617, 635, 684	2,3,4,6-tetra-*O*-galloyl-β-D-glucopyranose	9
13	6.44	211, 254, 369	$C_{15}H_{10}O_7$	301.03 $[M – H]^–$	83, 107, 121, 151, 178, 193, 229, 273	quercetin	–
14	6.52	213, 268, 340	$C_{21}H_{20}O_{10}$	431.10 $[M – H]^–$	269, 311, 341, 413	komovitexin	10
15	6.60	211, 255, 353	$C_{21}H_{18}O_{13}$	477.07 $[M – H]^–$	151, 229, 283, 301, 342, 418	quercetin 3-*O*-β-D-glucoside	11
16	7.25	221, 279	$C_{41}H_{32}O_{26}$	939.11 $[M – H]^–$	169, 295, 465, 617, 769, 878	1,2,3,4,6-penta-*O*-galloyl-β-D-glucopyranose	12
17	7.47	219, 272	$C_{15}H_{12}O_9$	335.89 $[M – H]^–$	184, 243, 261, 289, 307	methyl *m*-digallate	–
18	7.47	219, 272	$C_{15}H_{12}O_9$	335.89 $[M – H]^–$	184, 243, 261, 289, 307	methyl *p*-digallate	–
19	8.14	219, 266, 337	$C_{27}H_{30}O_{14}$	577.16 $[M – H]^–$	71, 161, 229, 269, 311, 399, 457, 531	rhoifolin	13
20	8.35	221, 278	$C_{48}H_{36}O_{30}$	1091.13 $[M – H]^–$	–	3-*O*-(*m*-digalloyl)-1,2,4,6-tetra-*O*-galloyl-β-D-glucopyranose	14
21	8.58	242	$C_{19}H_{32}O_7$	371.90 $[M – H]^–$	67, 103, 145, 223, 235, 279, 327	9-epi-blumenol C	15
22	9.49	212, 266, 352	$C_{27}H_{22}O_{15}$	585.09 $[M – H]^–$	121, 151, 273, 301, 388, 433, 506	quercetin 3-*O*-(2’’-galloyl)-β-D-arabinofuranoside	–
23	9.94	212, 264, 348	$C_{28}H_{24}O_{15}$	599.11 $[M – H]^–$	121, 151, 273, 301, 393, 447, 530	quercetin 3-*O*-(2’’-galloyl)-α-L-rhamnopyranoside	–
24	10.06	212, 265, 348	$C_{28}H_{24}O_{15}$	599.11 $[M – H]^–$	151, 169, 273, 301, 429, 447, 476, 551	quercetin 3-*O*-(3’’-galloyl)-α-L-rhamnopyranoside	16

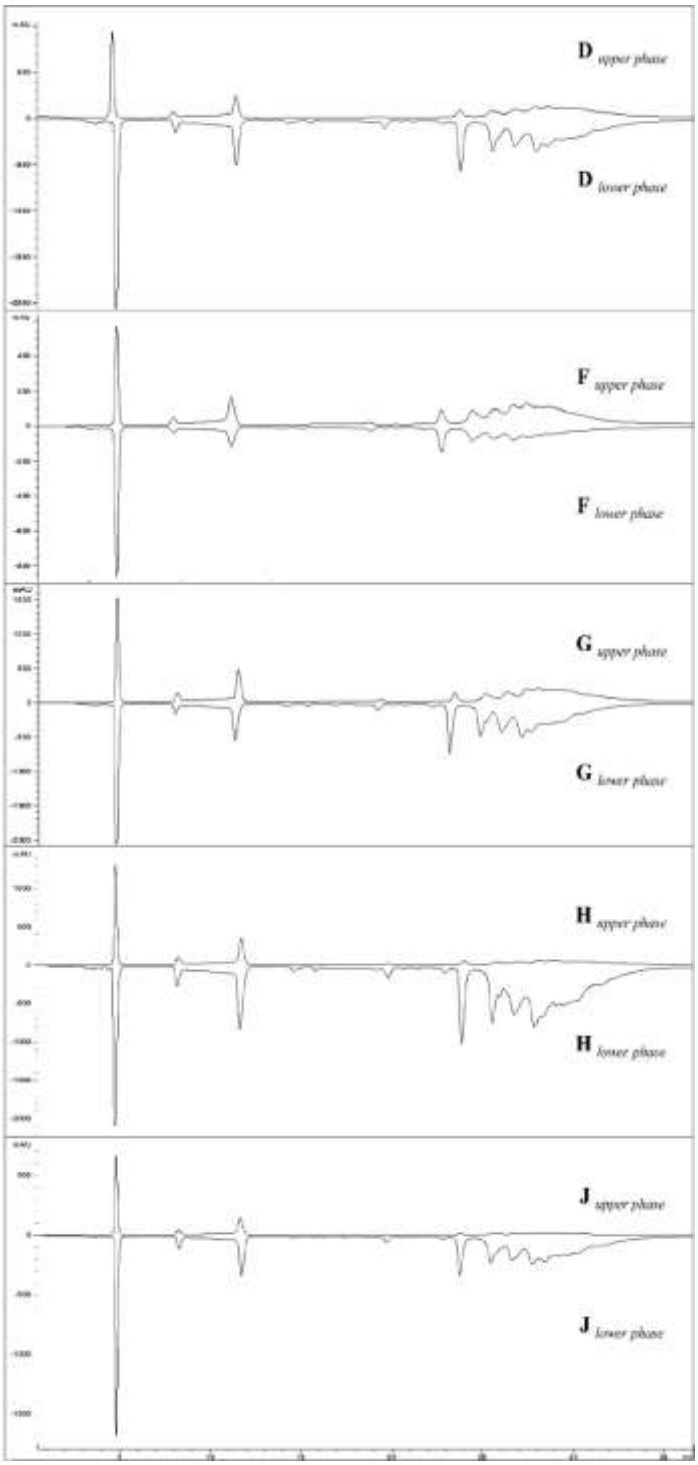


Figure S1. HPLC chromatograms of the upper and lower phases of the crude extract obtained after D, F, G, H and J Arizona solvent systems experiments. HPLC conditions: X-Bridge C-18 column (150 × 4.6 mm i.d., 5 m); mobile phase: MeOH with 0.1% formic acid (eluent A) and H_2O with 0.1% formic acid (eluent B); gradient conditions: 5 to 100% of B in 60 min; flow rate: 1 mL min^{-1}; UV 254 nm.

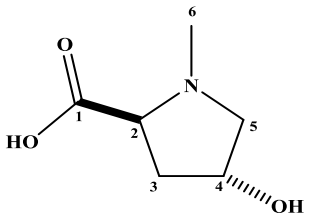


Table S2. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **1**

	HSQC		HMBC		Literature[a] (D_2O)
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	
1	173.0	–	4.05	2.16	170.2
2	72.0	4.05 (dd, 6.7 and 10.5 Hz)	2.16	4.20; 3.83; 3.00	69.7
3	40.4	2.16 (ddd, J 5.0, 10.5 and 13.8 Hz, H_b), 2.44 (ddt, J 2.0, 6.7 and 13.8 Hz, H_a)	4.05	3.07; 3.83	38.7
4	71.0	4.50 (q, J 2.0 and 5.0 Hz)	2.44; 3.83	4.05	69.1
5	64.4	3.07 (dt, 2.0 and 12.5 Hz, H_a), 3.83 (dd, 5.0 and 12.5 Hz, H_b)	–	3.00; 2.16; 2.44	62.4
6	44.1	3.00 (s)	–	3.07; 2.16; 4.05	43.4

[a]Reference 1. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

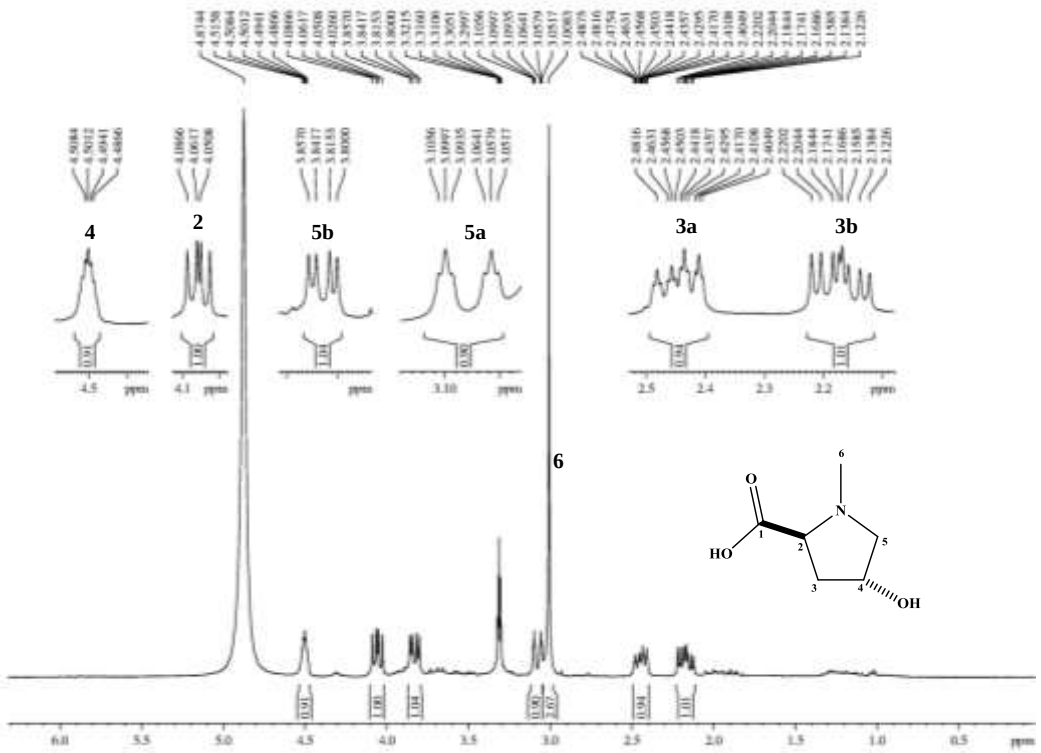


Figure S2. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **1**.

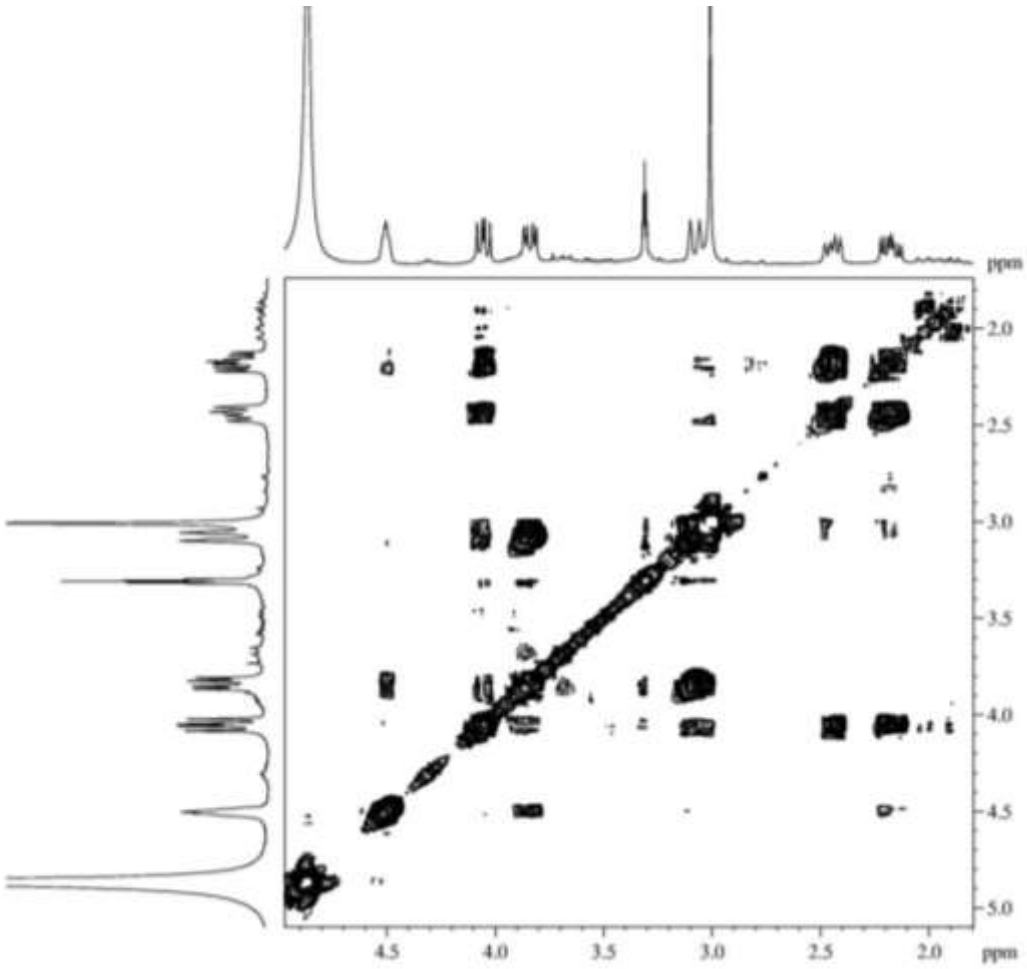


Figure S3. COSY NMR spectrum (500 MHz, CD_3OD) of compound **1**.

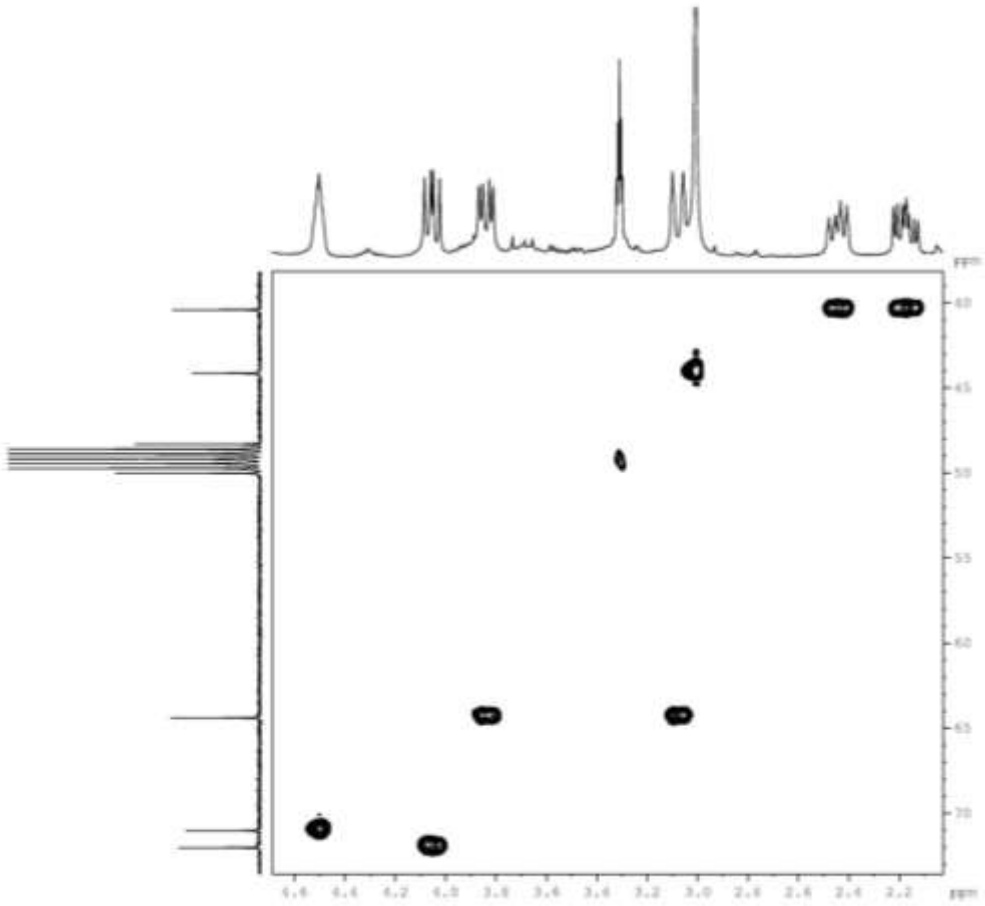


Figure S4. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **1**.

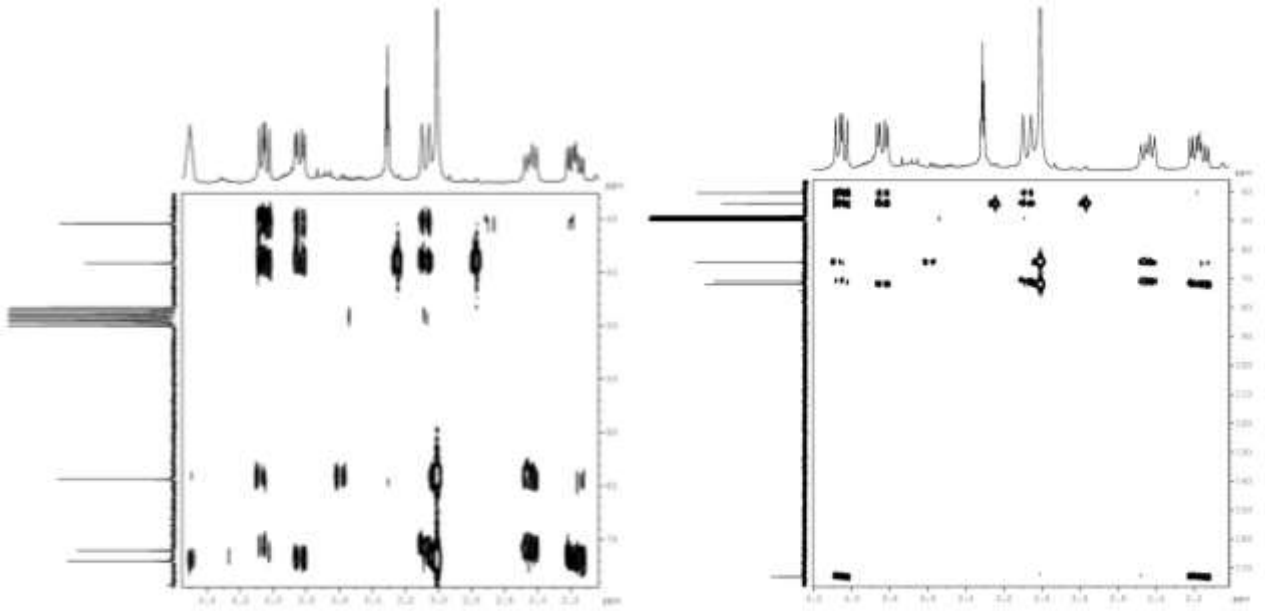


Figure S5. HMBC NMR spectra (500 MHz, CD_3OD) of compound **1**.

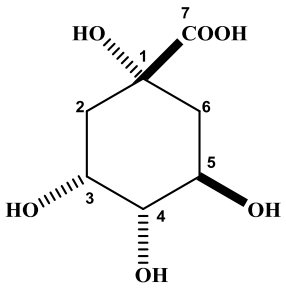


Table S3. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **2**

	HSQC		HMBC		Literature[a] (D_2O)
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	
1	77.0	–	1.93; 2.15; 2.03; 2.10	–	77.0
2	40.6	1.93 (dd, 11.0 and 13.4 Hz, 1H, H_a), 2.15 (m, 1H, H_b)	4.08	2.03; 2.10; 3.61	40.7
3	67.2	4.08 (ddd, 4.0, 9.5 and 11.0 Hz, 1H)	1.93; 2.15; 3.61	4.20	67.1
4	75.2	3.61 (dd, 4.0 and 9.5 Hz, 1H)	4.08	1.93; 2.15	75.2
5	70.4	4.20 (q, 3.9 Hz, 1H)	2.03; 2.10;	4.08	70.5
6	37.4	2.03 (ddd, 2.9, 4.0 and 14.9 Hz, H_a), 2.10 (m, 1H, H_b)	–	1.93; 2.15	37.4
7	181.4	–	–	1.93; 2.15; 2.03; 2.10	181.2

[a]Reference 2. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

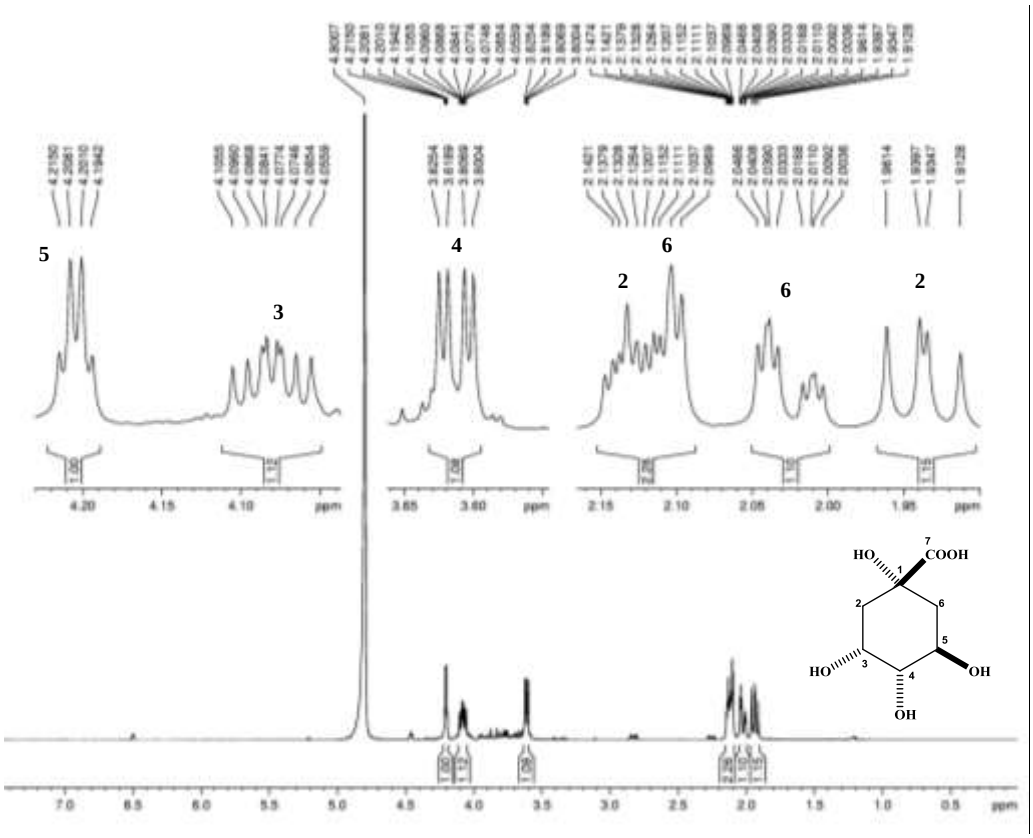


Figure S6. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **2**.

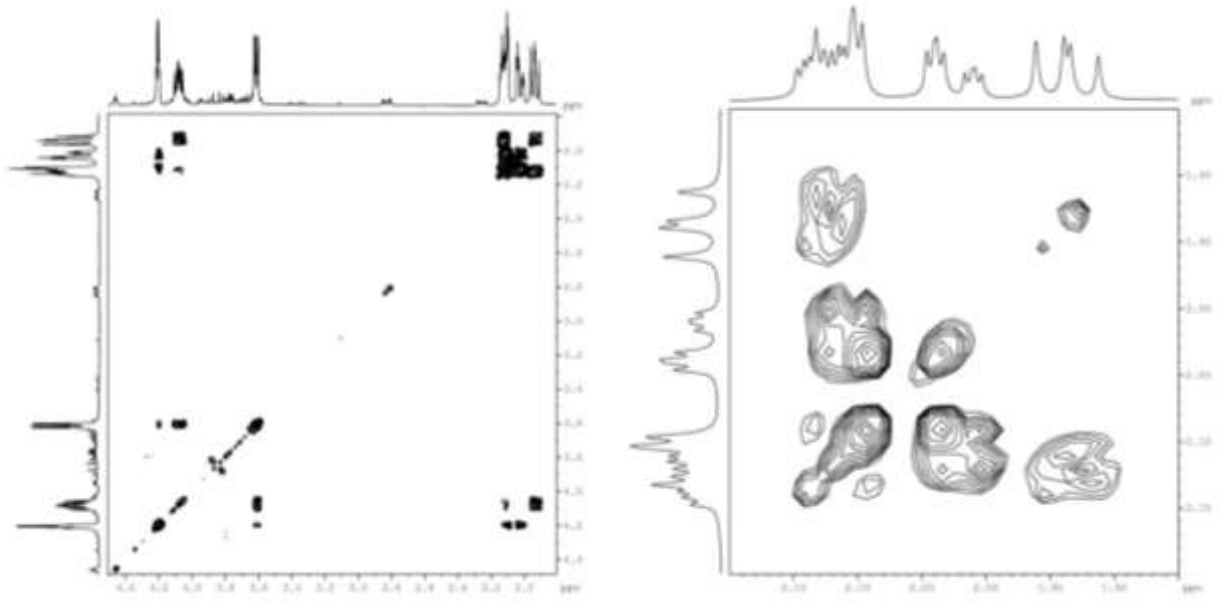


Figure S7. COSY spectra (500 MHz, CD_3OD) of compound **2**.

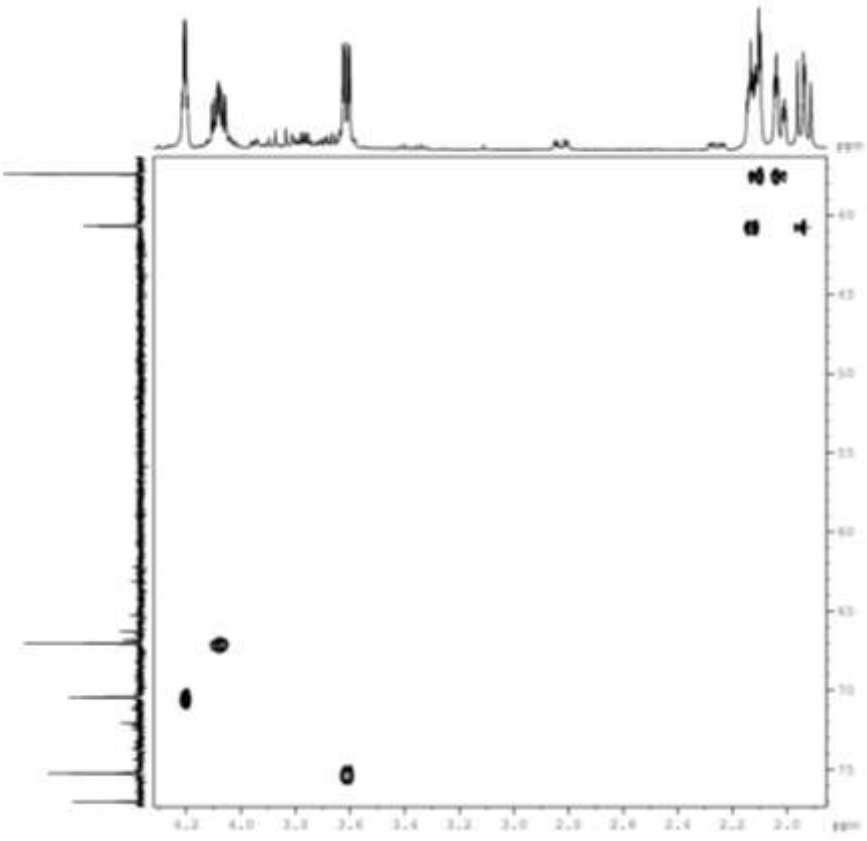


Figure S8. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **2**.

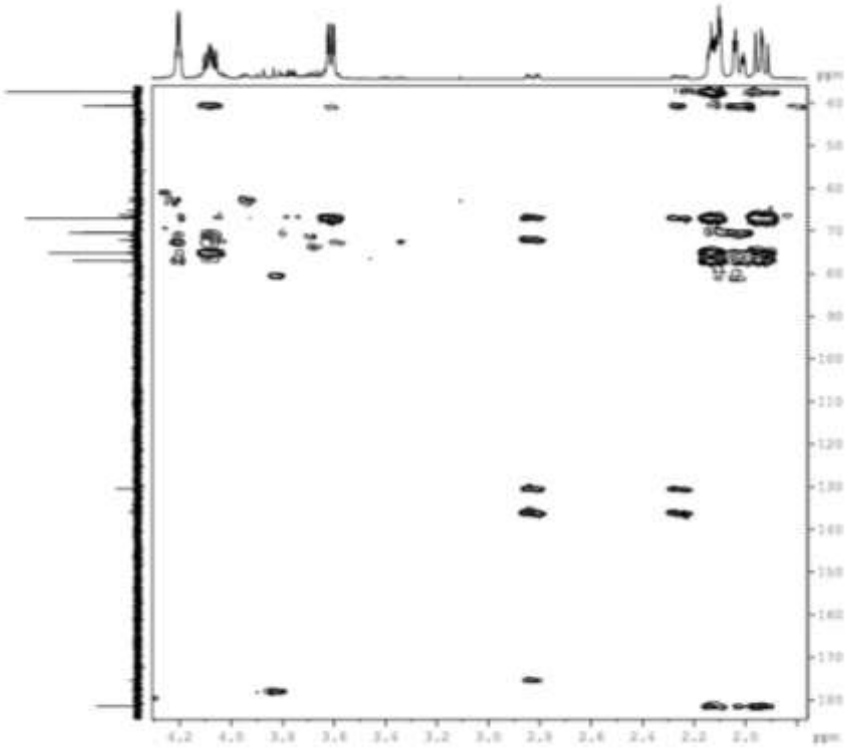


Figure S9. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **2**.

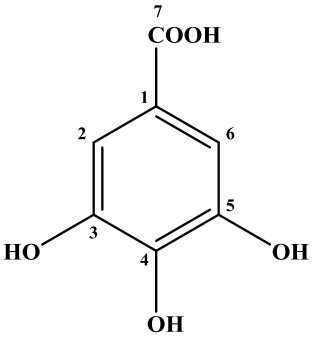


Table S4. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **3**

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(MeOD)
1	125.8	–	7.04	–	121.9
2/6	110.3	7.04 (s, 2H)	–	7.04	110.3
3/5	146.2	–	7.04	–	146.4
4	138.4	–	–	7.04	139.6
7	173.1	–	–	7.04	170.6

[a]Reference 3. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

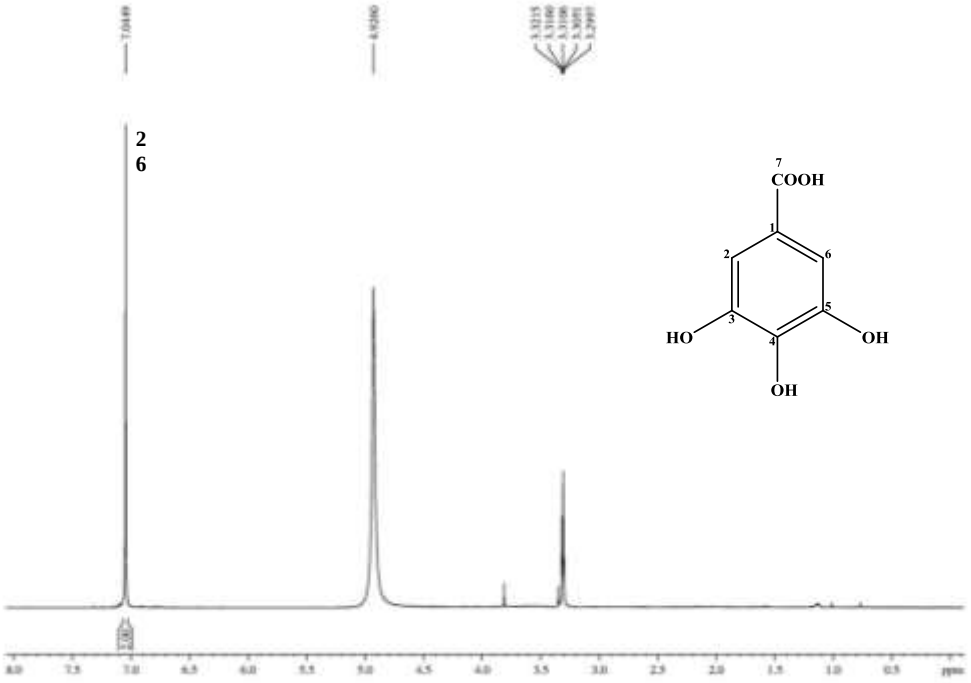


Figure S10. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **3**.

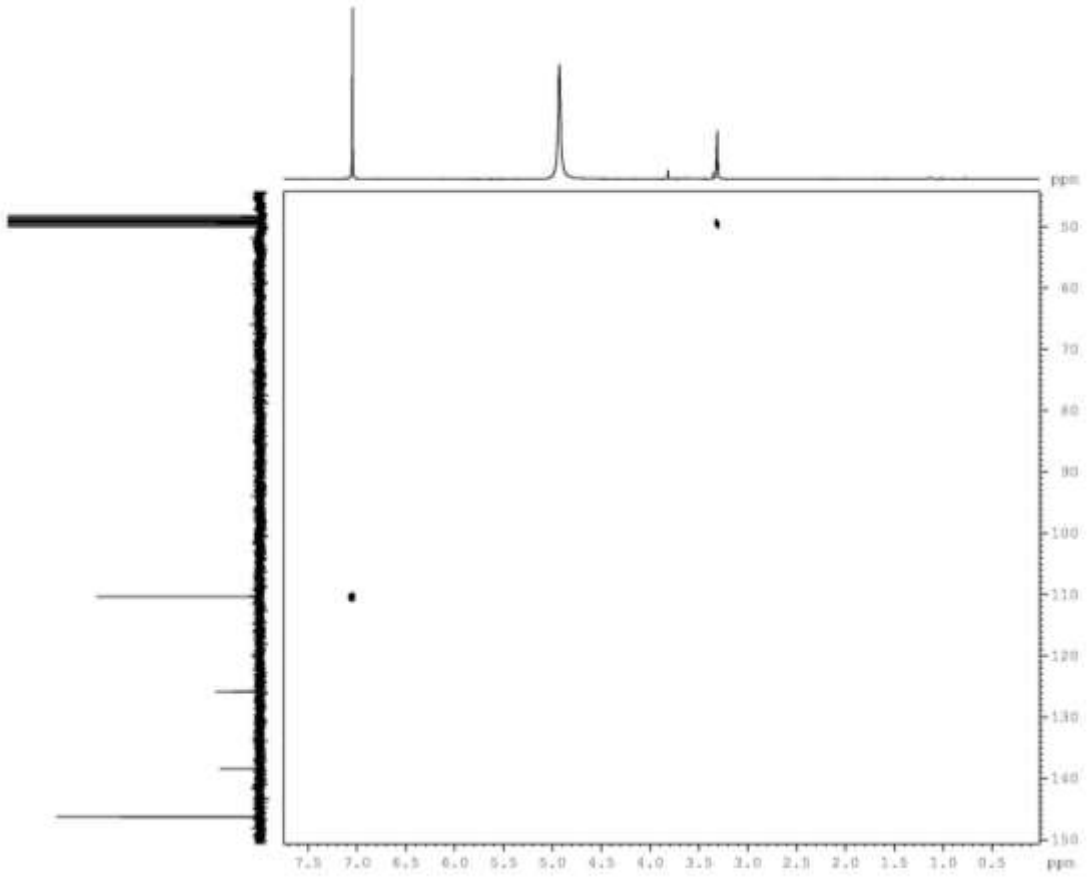


Figure S11. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **3**.

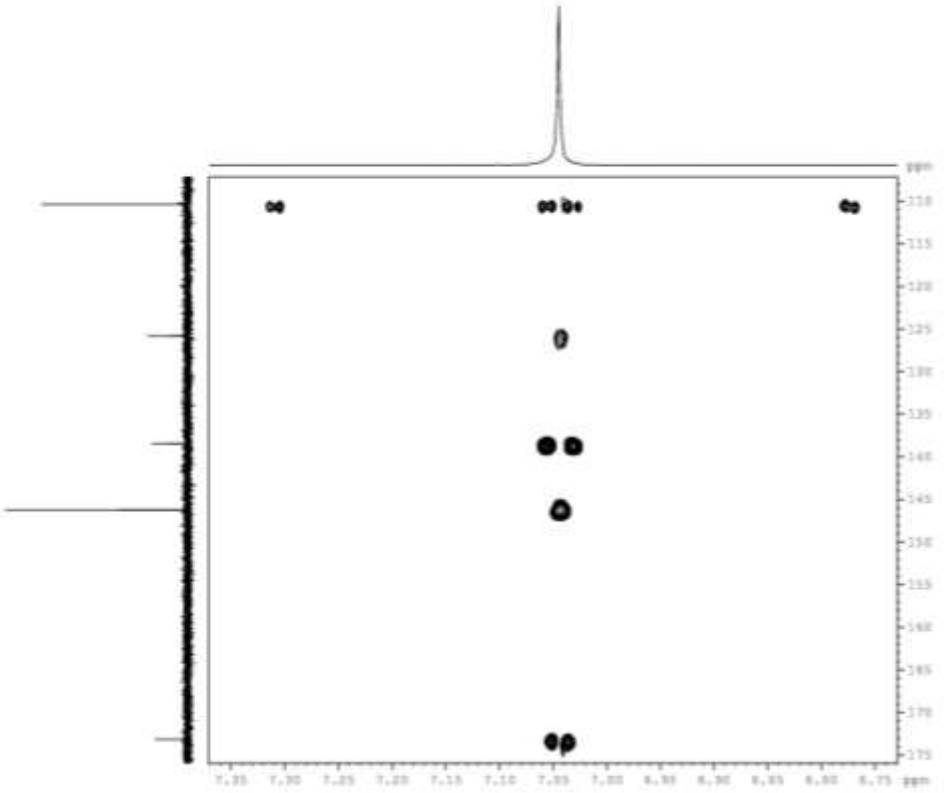


Figure S12. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **3**.

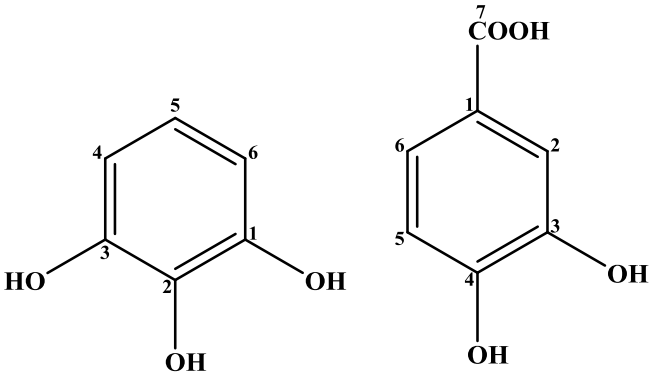


Table S5. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **4**

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(MeOD)
1/3	146.7	–	6.31	6.49	147.7
2	133.8	–	–	6.31	134.9
4/6	107.9	6.31 (d, 8.1 Hz, 2H)	–	–	109.1
5	119.6	6.49 (dd, 8.1 and 8.4 Hz, 1H)	6.31	–	120.9

[a]Reference 4. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

Table S6. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **5**

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(MeOD)
1	124.5	–	–	6.77	122.0
2	117.3	7.43 (d, 2.0 Hz, 1H)	7.41	–	114.6
3	145.5	–	7.43	6.77	144.9
4	150.4	–	–	7.41; 7.43	150.4
5	115.2	6.77 (d, 8.2 Hz, 1H)	–	–	116.6
6	123.3	7.41 (dd, 8.2 and 2.0 Hz, 1H)	–	7.43	122.8
7	171.0	–	–	7.43	169.0

[a]Reference 17. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

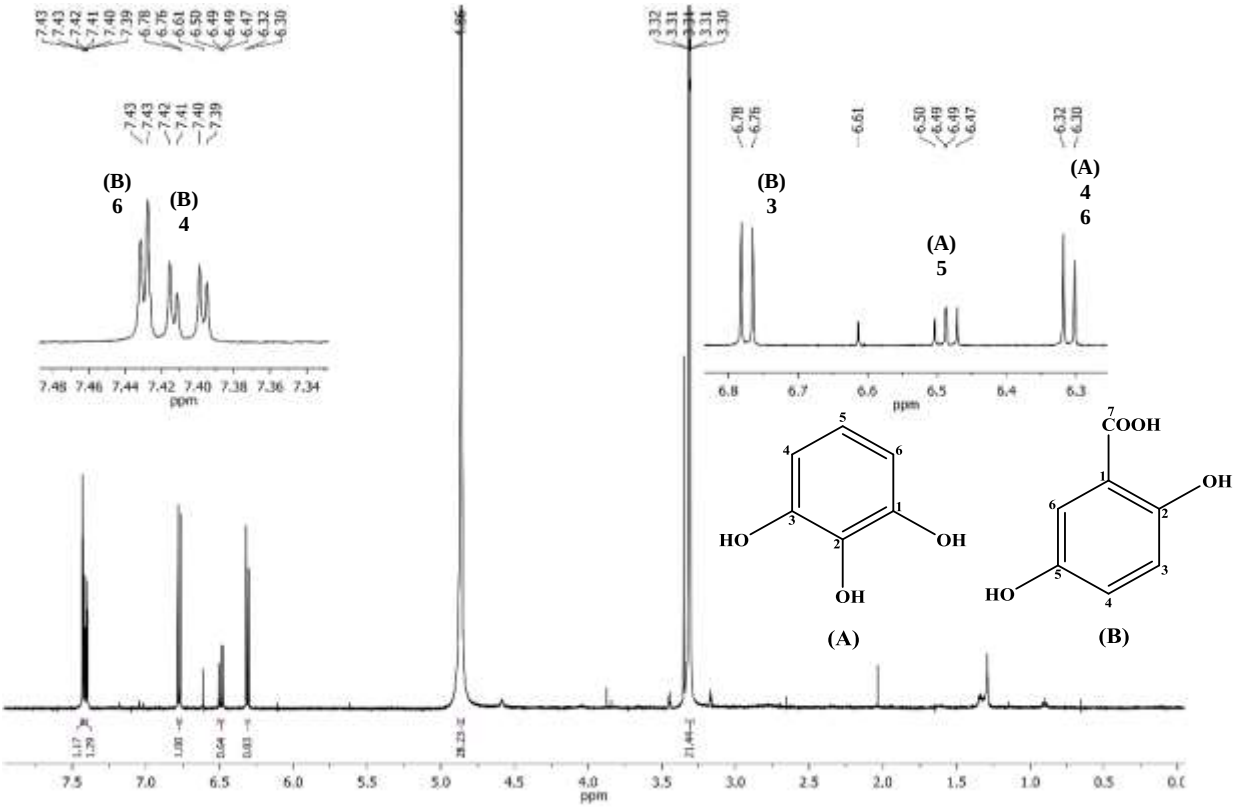


Figure S13. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compounds **4** and **5**.

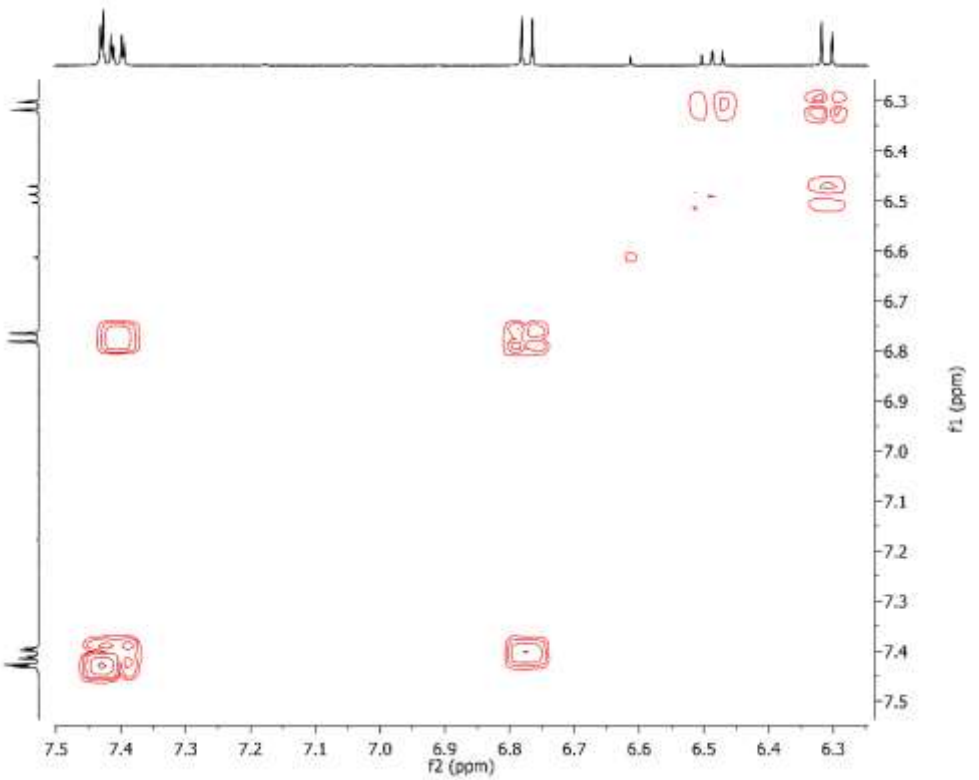


Figure S14. COSY NMR spectrum (500 MHz, CD_3OD) of compounds **4** and **5**.

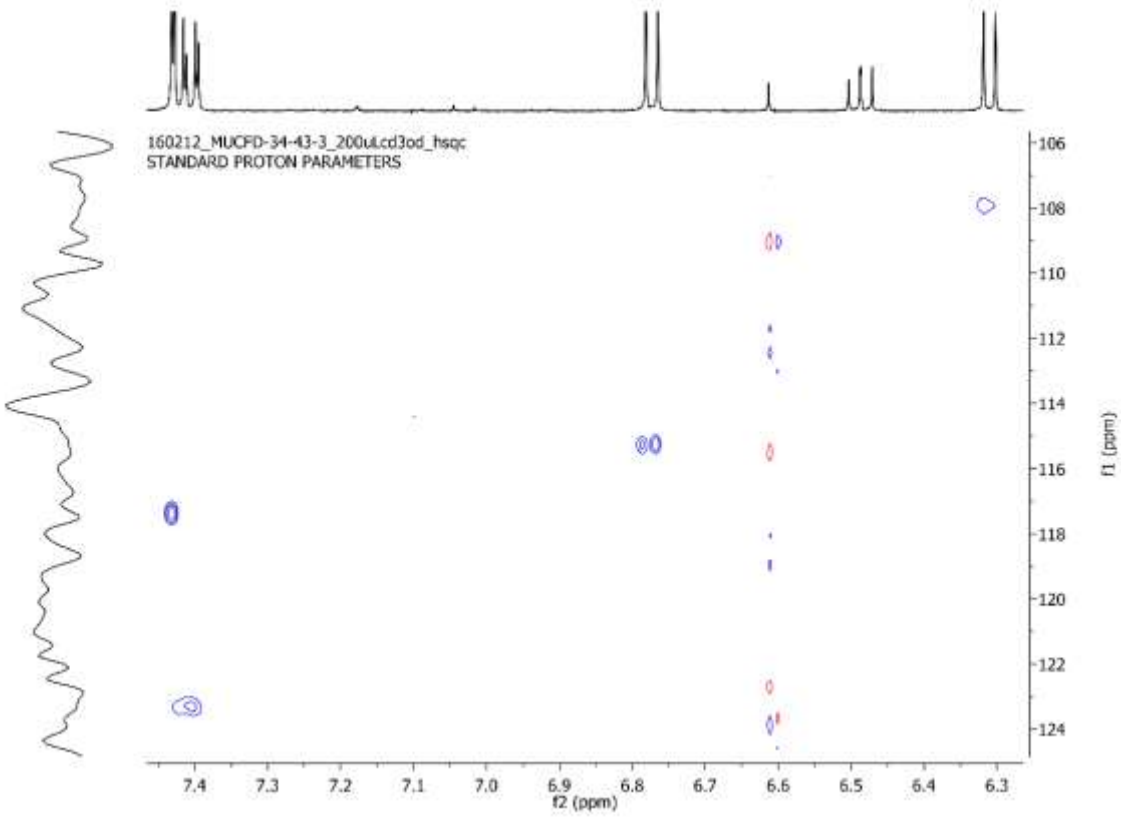


Figure S15. Edited-HSQC NMR spectrum (500 MHz, CD_3OD) of compounds **4** and **5**.

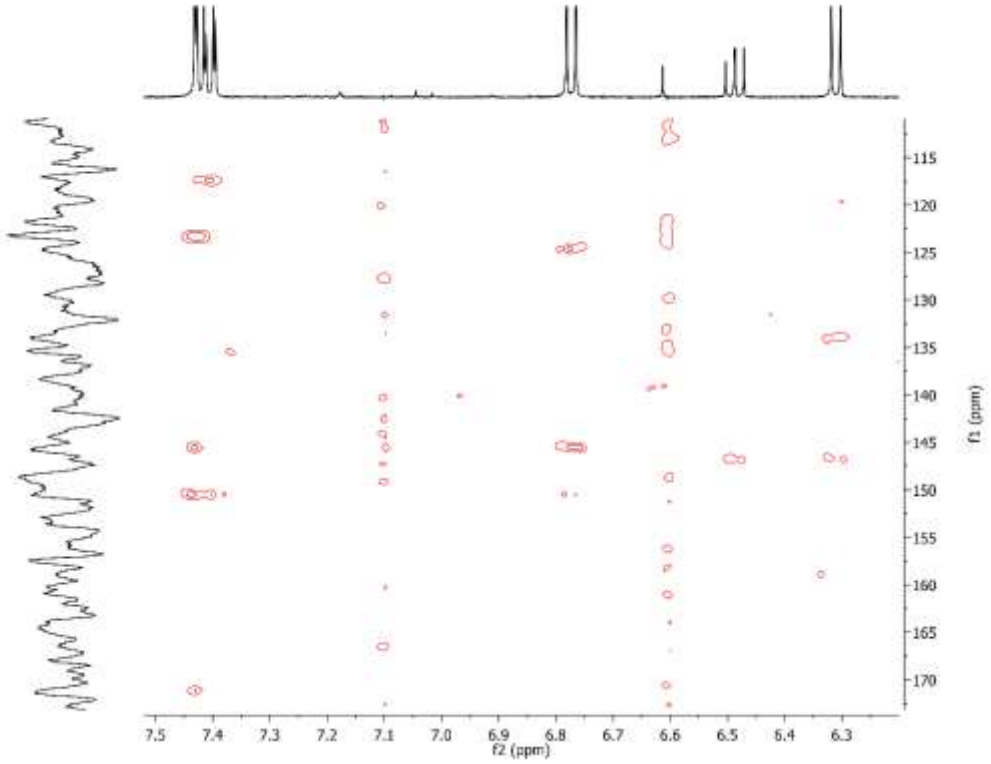


Figure S16. HMBC NMR spectrum (500 MHz, CD_3OD) of compounds **4** and **5**.

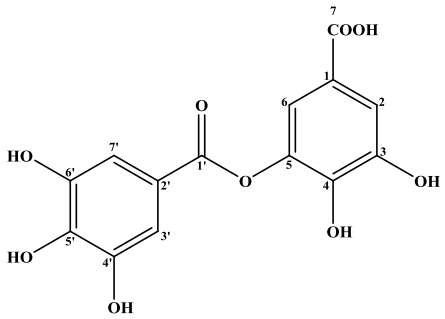
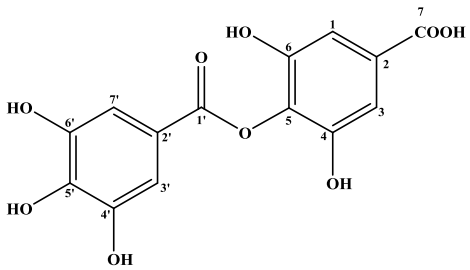



Table S7. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **6**

	HSQC		HMBC	
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$
1	117.2	–	7.41	
2	117.2	7.27 (d, 2.03 Hz, 1H)		7.41
3	147.3	–		
4	143.8	–		7.27; 7.41
5	139.8	–		
6	114.7	7.41 (d, 2.03 Hz, 1H)		7.27
7	169.2	–		7.27; 7.41
1'	166.2	–		7.22
2'	120.2	–	7.22	
3'/7'	110.5	7.22 (s, 2H)		
4'/6'	146.3	–	7.22	
5'	140.2	–		7.22

HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

Table S8. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **7**

	HSQC		HMBC	
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$
1	129.3	–	7.12	–
2/6	109.8	7.12 (s, 1H)	–	–
3/5	151.3	–	7.12	–
4	132.4	–	–	7.12
7	169.3	–	–	7.12
1'	165.9	–	–	7.24
2'	120.4	–	7.24	–
3'/7'	110.5	7.24 (s, 1H)	–	–
4'/6'	146.2	–	7.24	–
5'	140.2	–	–	7.24

HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

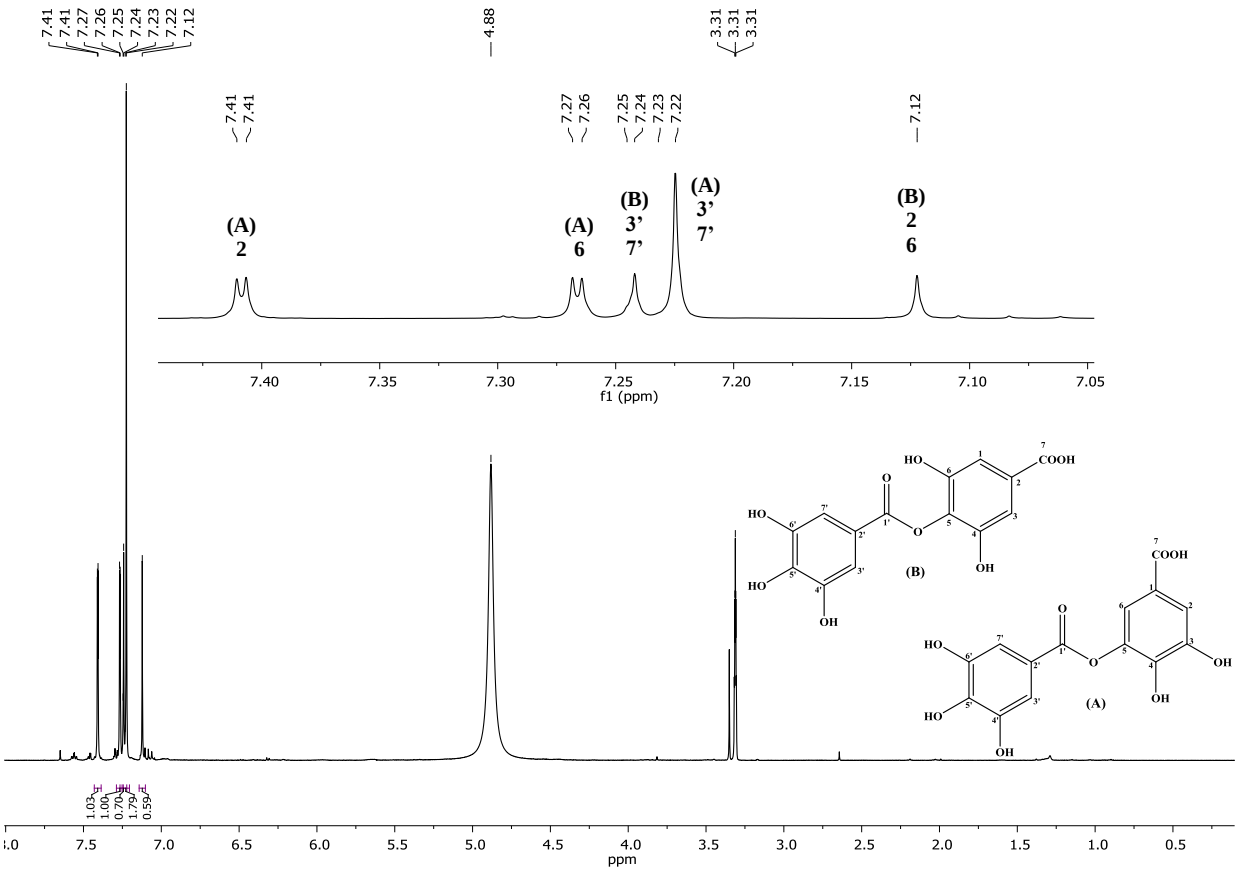


Figure S17. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compounds **6** and **7**.

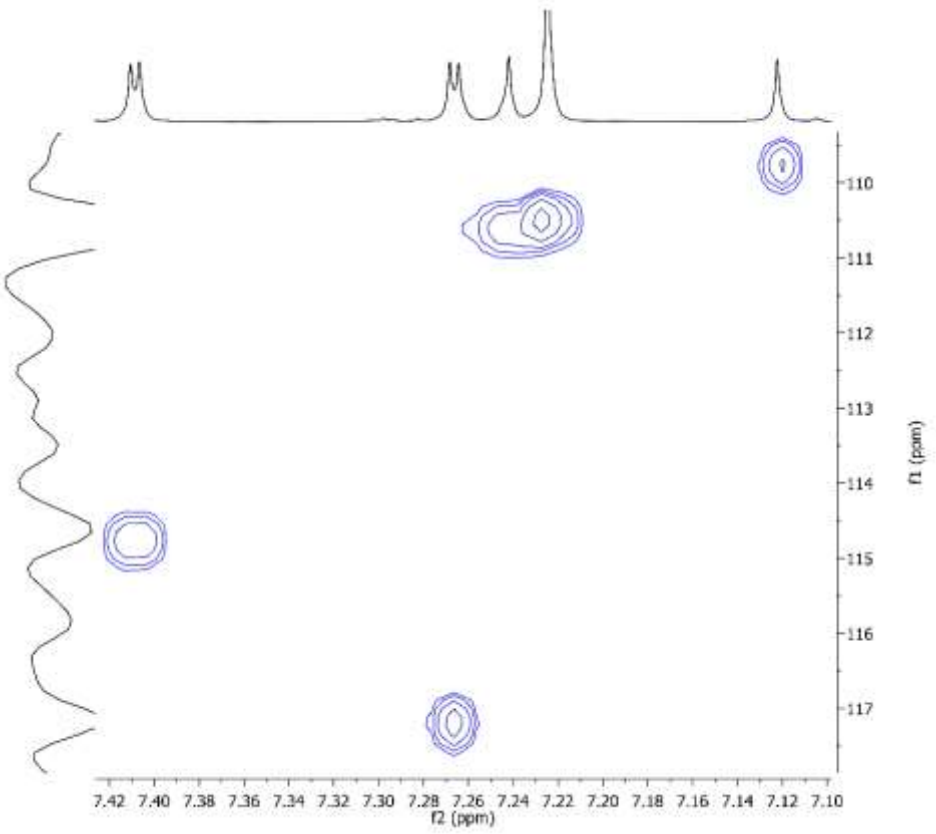


Figure S18. HSQC NMR spectrum (500 MHz, CD_3OD) of compounds **6** and **7**.

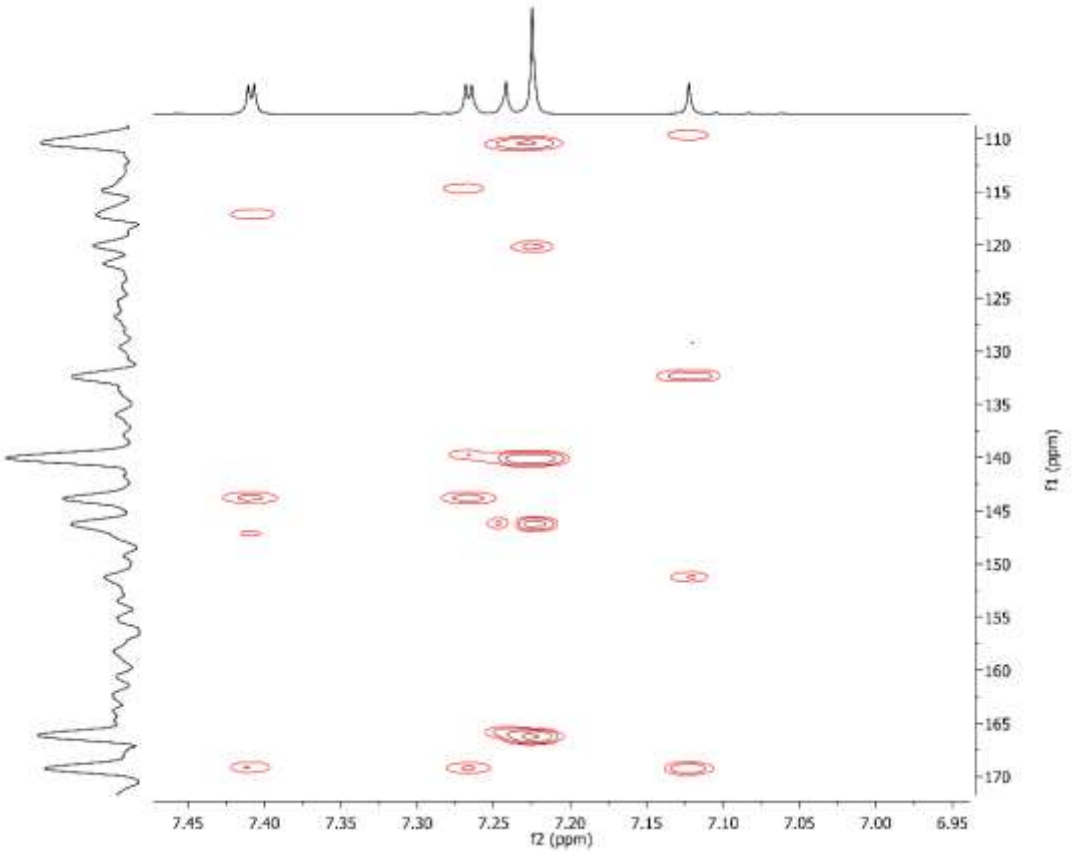


Figure S19. HMBC NMR spectrum (500 MHz, CD_3OD) of compounds **6** and **7**.

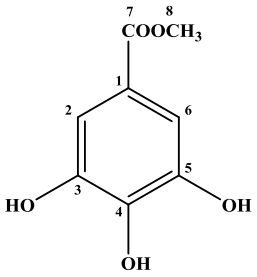


Table S9. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **8**

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(MeOD)
1	121.5		7.04		121.4
2/6	110.1	7.04 (s, 2H)		7.04	110.0
3/5	146.6		7.04		146.5
4	139.8			7.04	139.7
7	169.1			7.04; 3.80	167.5
8	52.4	3.80 (s, 3H)			52.3

[a]Reference 6. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

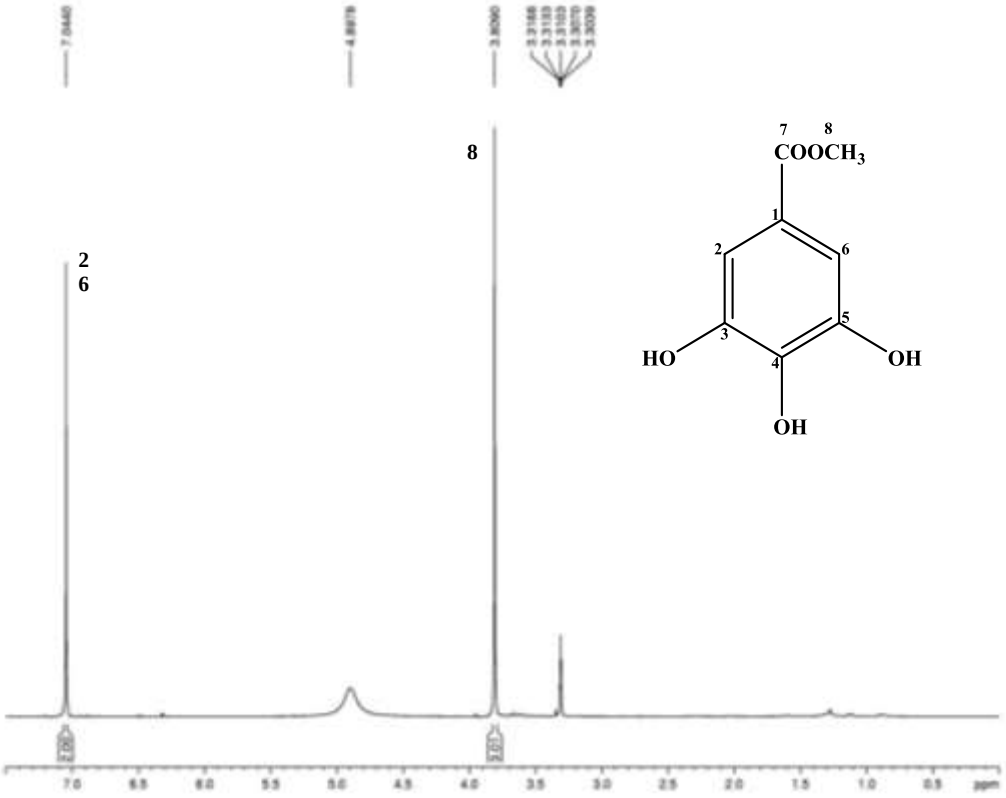


Figure S20. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **8**.

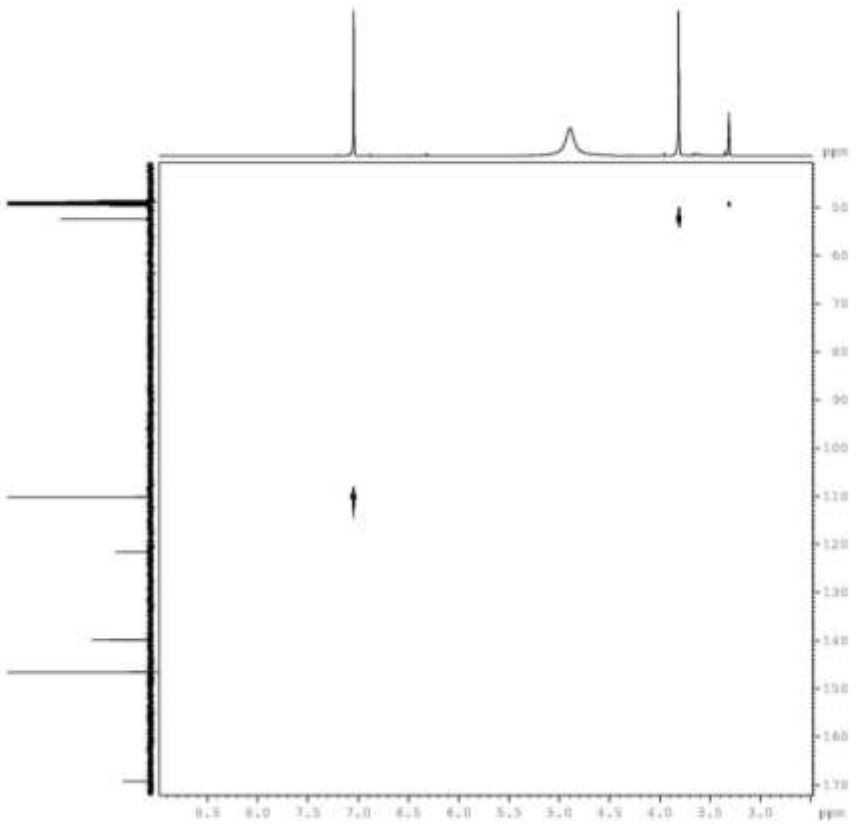


Figure S21. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **8**.

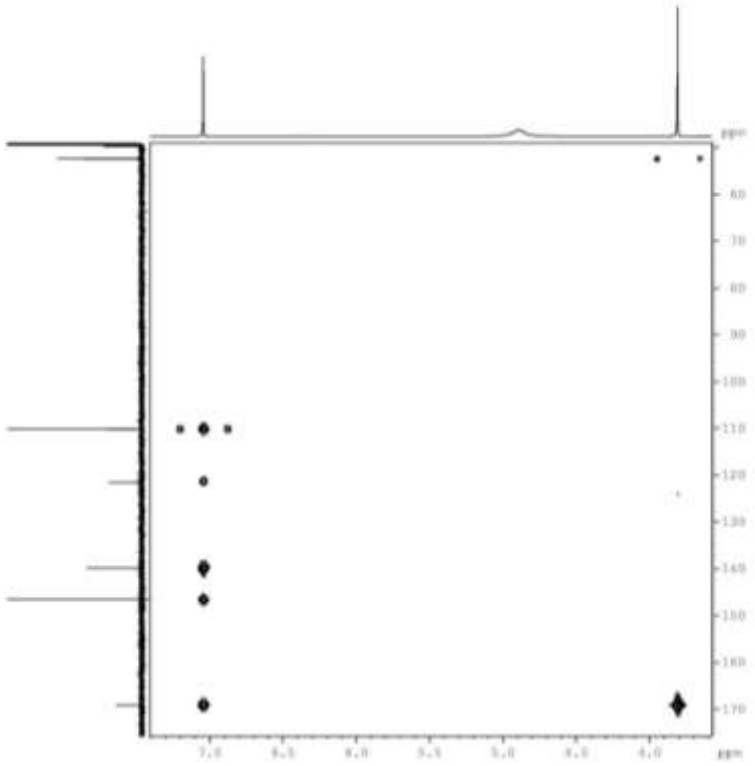


Figure S22. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **8**.

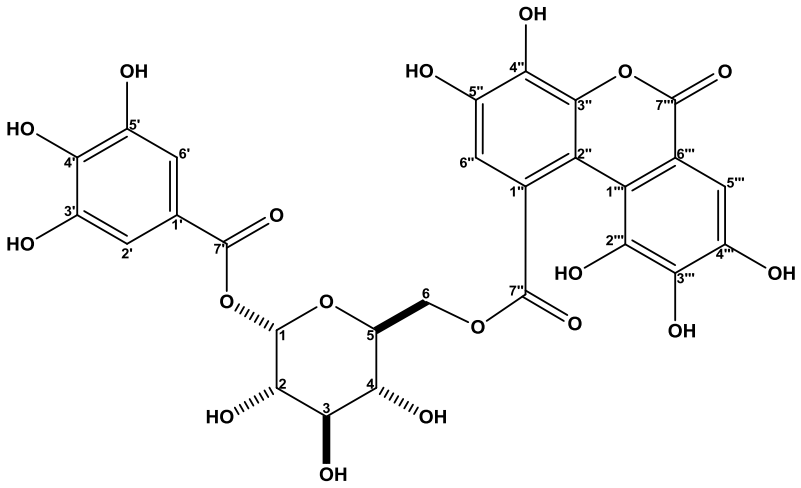


Table S10. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **9**

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(MeOD)
1	94.7	6.36 (d, 1.9 Hz, 1H)			94.9
2	69.2	3.98 (m, 1H)			69.3
3	71.5	4.80 (m, 1H)			71.5
4	62.2	4.46 (m, 1H)			62.4
5	75.9	4.51 (m, 1H)	4.96	6.36	76.1
6	64.7	4.96 (t, 10.8 Hz, 1H), 4.15 (dd, 10.8 and 10.9 Hz, 1H)			64.9
1'	120.3	–	7.05		120.5
2'/6'	110.7	7.05 (s, 2H)		7.05	110.9
3'/5'	146.1	–	7.05		146.3
4'	140.1	–		7.05	140.4
7'	166.4	–		6.36; 7.05	166.7
1''	116.4	–	6.66		116.7
2''	137.4	–		6.66	137.6
3''	n.d.	–			145.3
4''	145.4	–		6.66	145.9
5''	n.d	–			125.4
6''	108.0	6.66 (s, 1H)			108.3
7''	169.9	–		4.96; 6.66	170.1
1'''	137.9	–		6.68	138.2
2'''	n.d.	–			145.4
3'''	145.7	–		6.68	145.5
4'''	n.d.	–			125.3
5'''	109.9	6.68 (s, 1H)			110.9
6'''	116.9	–	6.68		117.2
7'''	168.2	–		6.68	168.5

[a]Reference 7. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy; n.d.: not detected; .

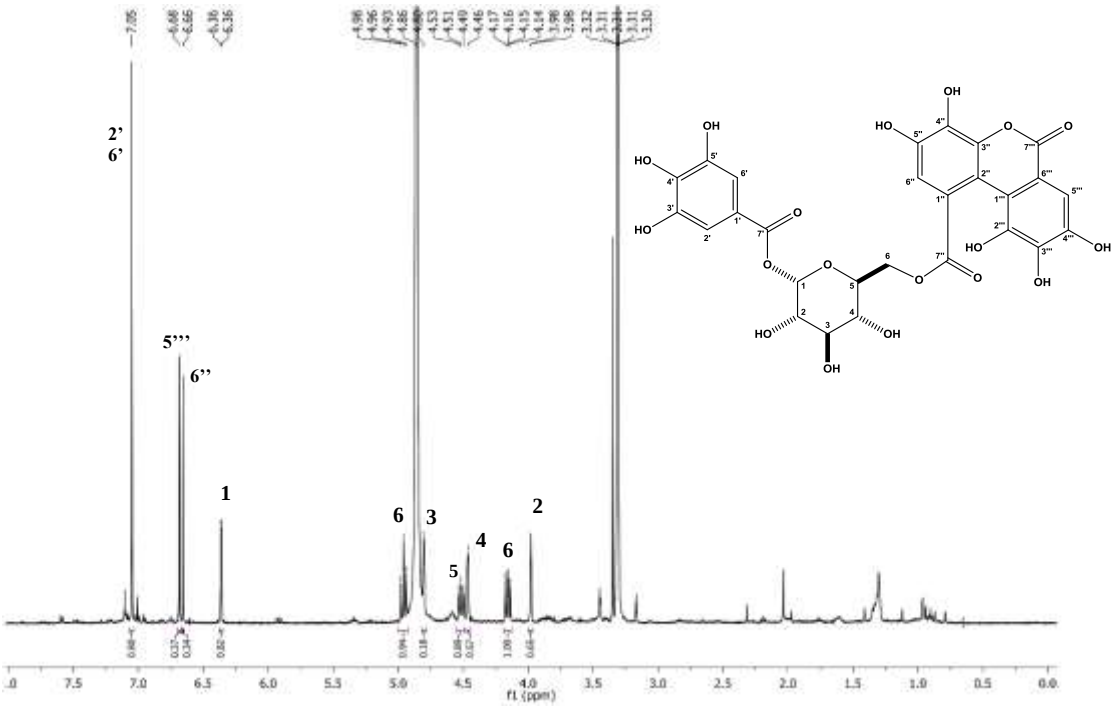


Figure S23. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **9**.

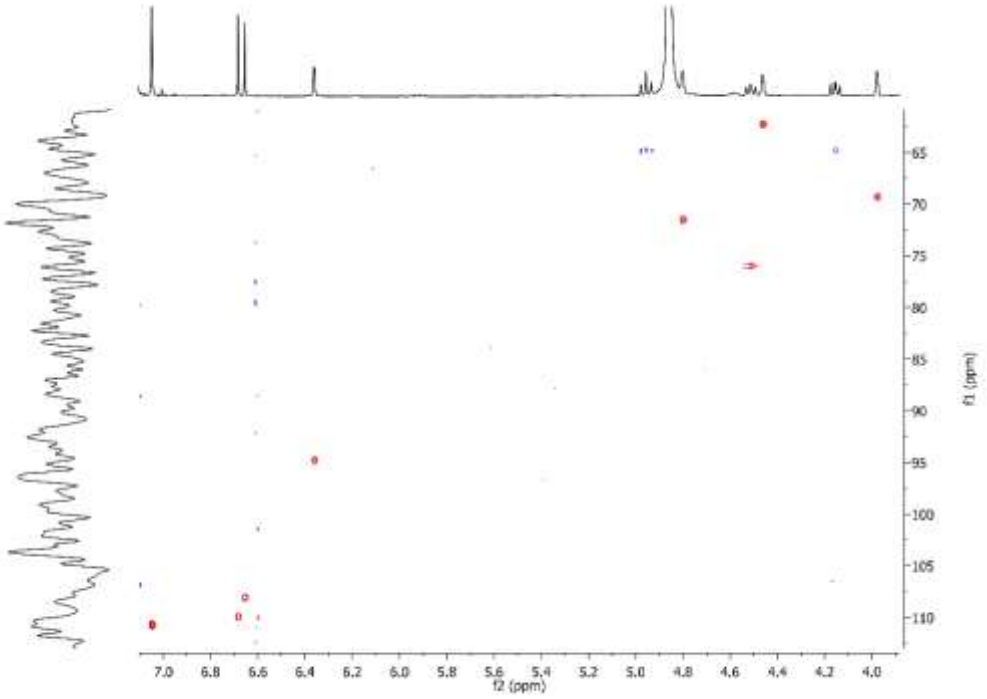


Figure S24. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **9**.

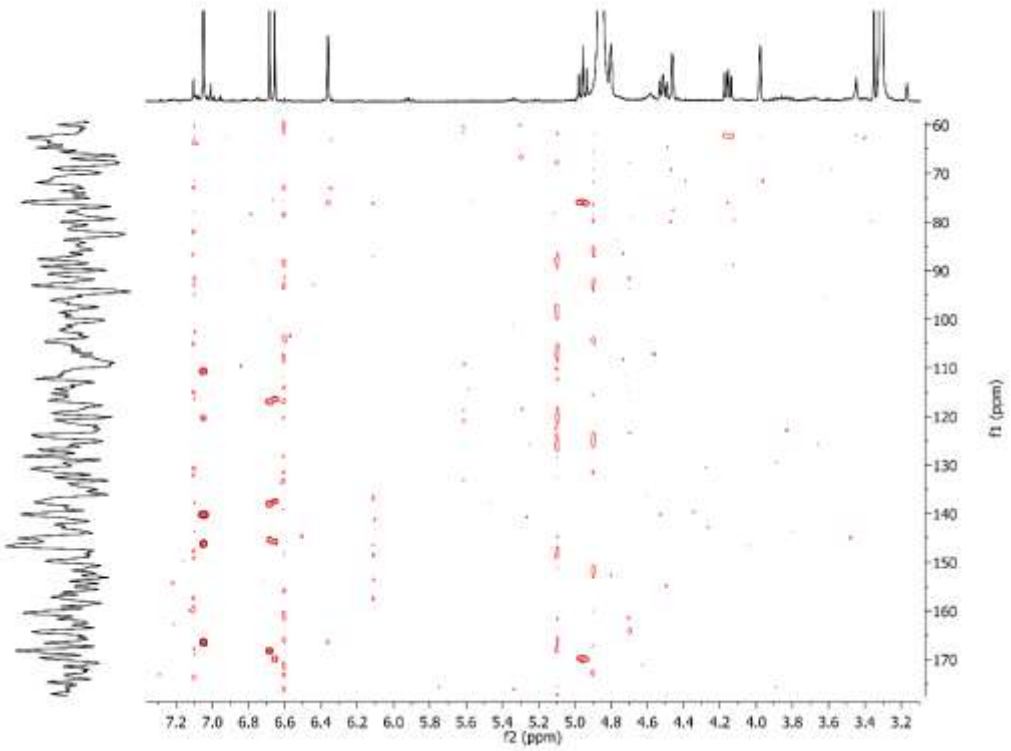


Figure S25. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **9**.

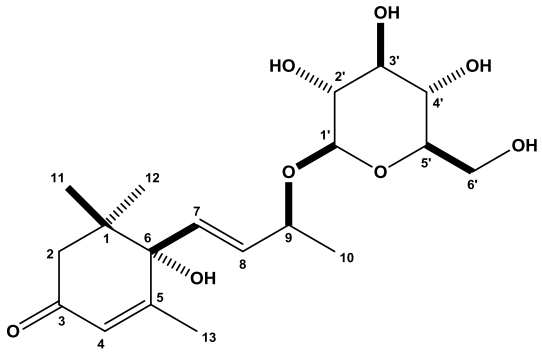


Table S11. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **10**

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(MeOD)
1	42.8	–	1.02; 1.04		42.4
2	50.5	2.17 (d, 16.5 Hz, 1H), 2.61 (d, 16.5 Hz, 1H)		1.02; 1.04	50.8
3	201.7	–	2.17; 2.61		201.1
4	126.8	5.87 (s, 1H)			127.1
5	167.4	–			167.1
6	80.3	–	5.98	1.94; 5.73; 5.87	80.0
7	133.5	5.98 (d, 15.6 Hz, 1H)			133.8
8	133.4	5.73 (dd, 15.6 and 7.2 Hz, 1H)	4.54	1.29	133.7
9	74.4	4.54 (m, 1H)	1.29	4.27; 5.98	74.6
10	21.4	1.29 (d, 6.4 Hz, 3H)			22.2
11	23.2	1.04 (s, 3H)		1.02	23.4
12	24.4	1.02 (s, 3H)		1.04	24.7
13	19.3	1.94 (s, 3H)			19.5
1'	101.0	4.27 (d, 7.8 Hz, 1H)		4.54	101.3
2'	74.8	3.19 (m, 1H)	4.27		75.0
3'	71.4	3.24 (m, 1H)			71.7
4'	78.0	3.16 (m, 1H)	3.24	3.63; 3.19	78.4
5'	77.9	3.14 (m, 1H)			78.2
6'	62.6	3.63 (dd, 11.9 and 6.5 Hz, 1H), 3.85 (dd, 11.9 and 2.2 Hz, 1H)			62.8

[a]Reference 18. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

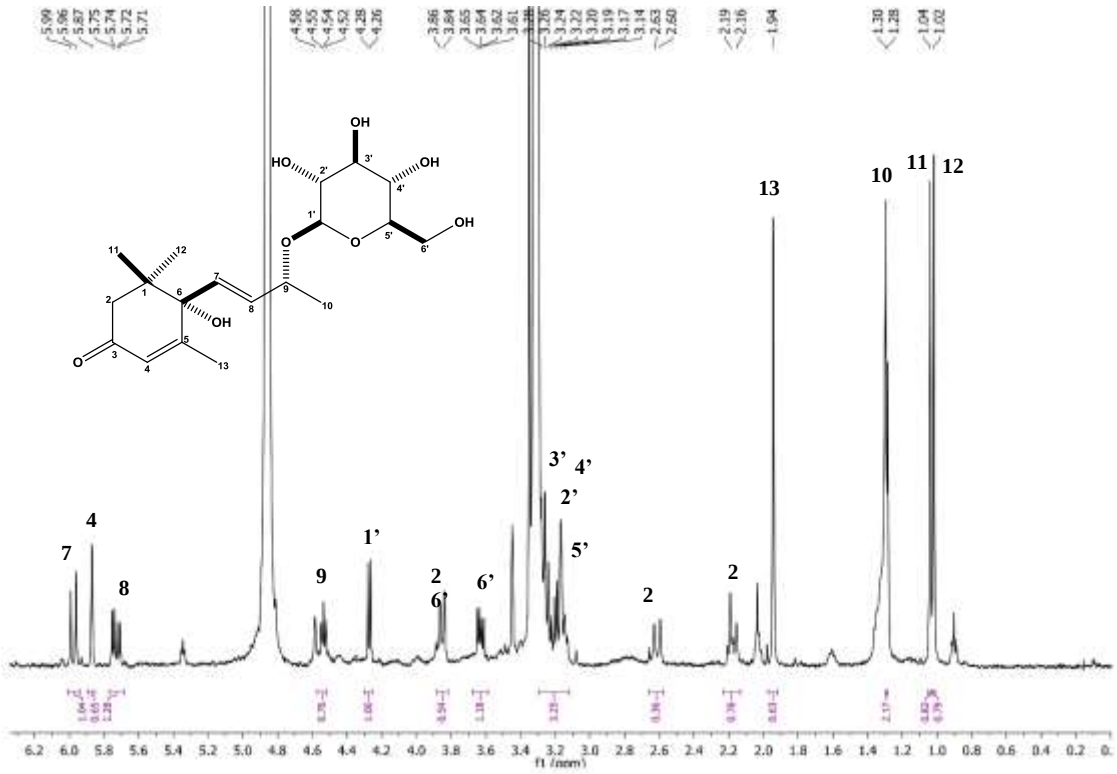


Figure S26. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **10**.

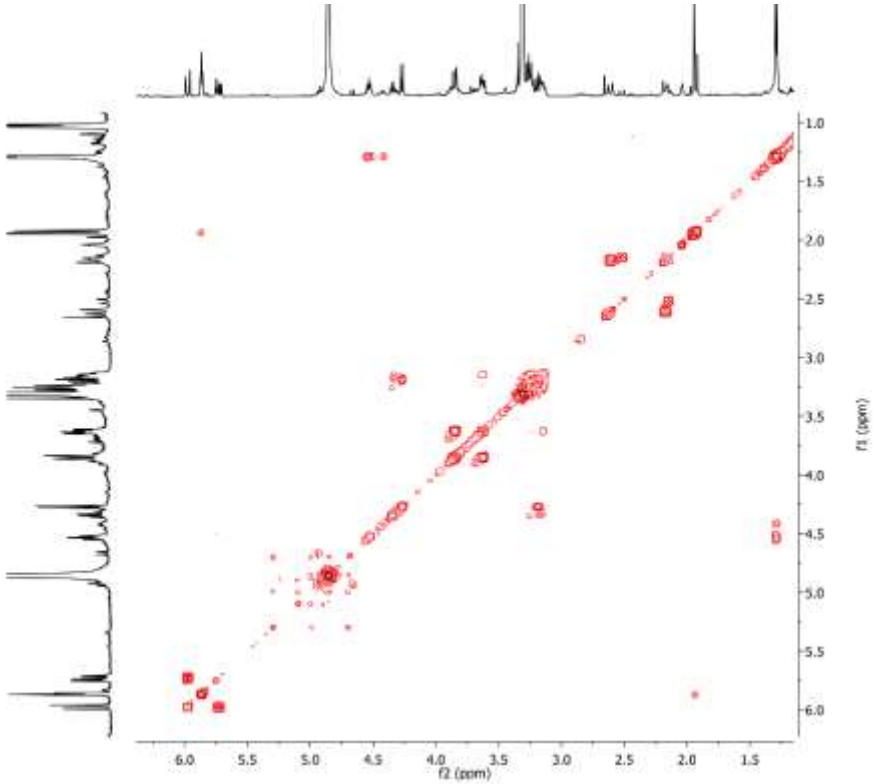


Figure S27. COSY NMR spectrum (500 MHz, CD_3OD) of compound **10**.

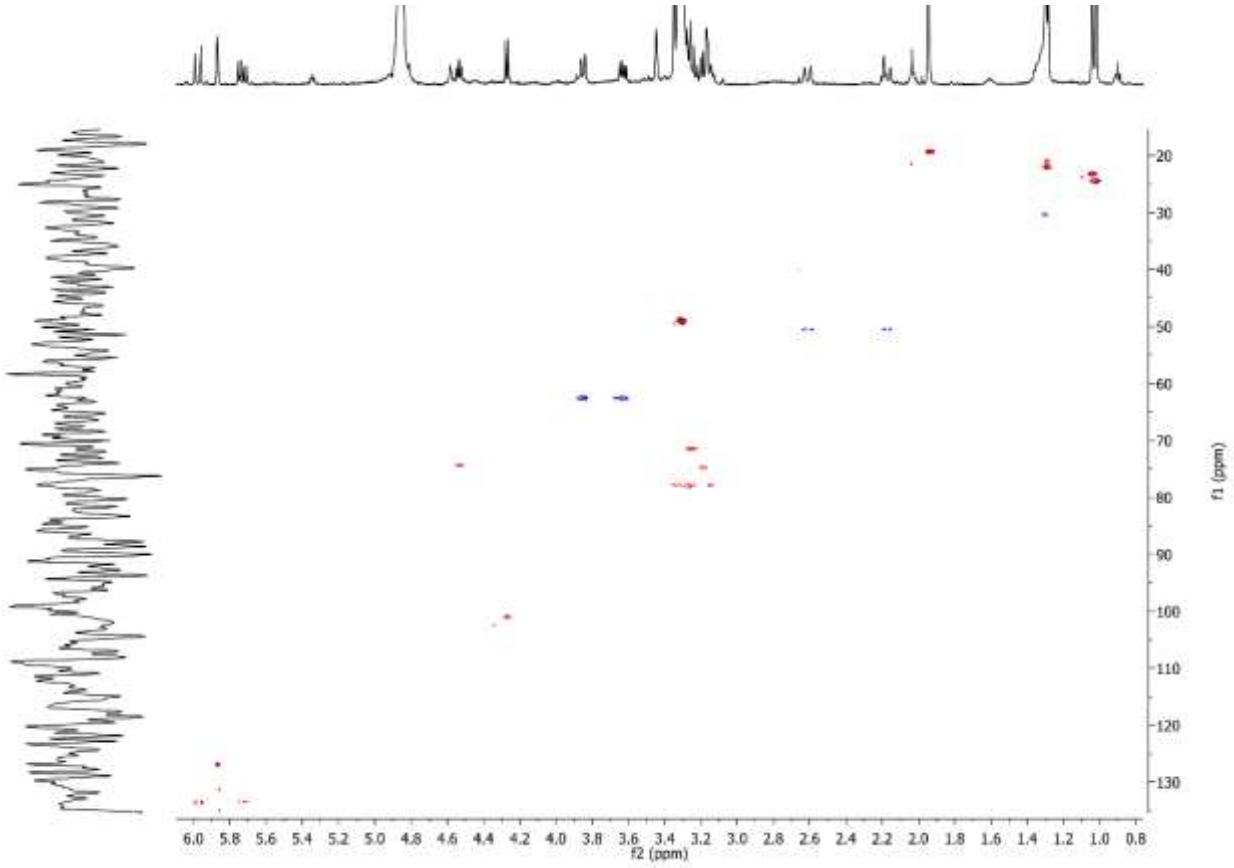


Figure S28. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **10**.

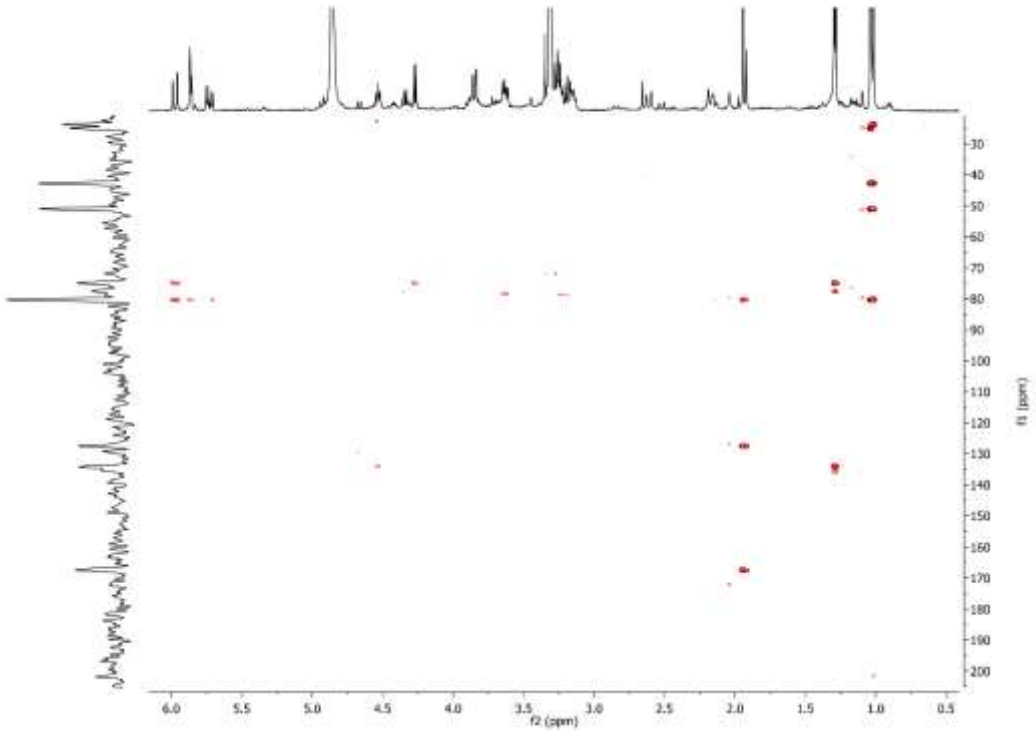


Figure S29. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **10**.

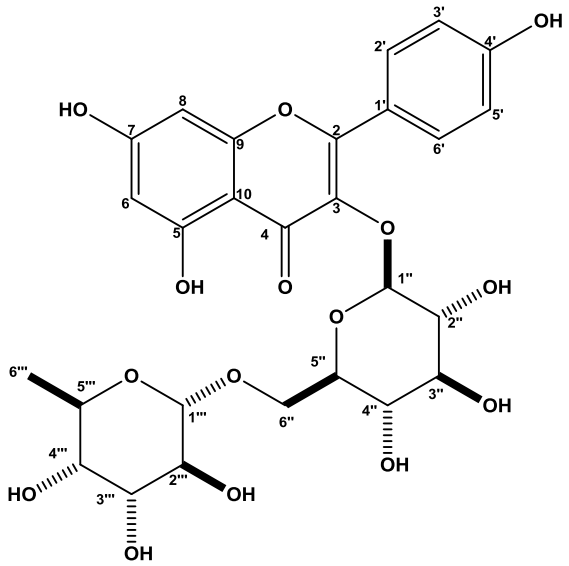


Table S12. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **11**

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(MeOD)
2	158.9	–		8.10	158.7
3	135.2	–		5.05	135.5
4	176.1	–			179.4
5	168.0	–	6.22		163.1
6	99.7	6.22 (d, 2.1 Hz, 1H)		6.42	100.0
7	165.8	–	6.42		166.2
8	94.6	6.42 (d, 2.1 Hz, 1H)		6.22	95.0
9	158.8	–	6.42		159.4
10	105.3	–		6.22; 6.42	105.6
1'	122.4	–		6.89	122.8
2'/6'	132.2	8.10 (d, 8.9 Hz, 1H)		8.10	132.4
3'/5'	115.8	6.89 (d, 8.9 Hz, 1H)			116.2
4'	161.4	–	6.89		161.5
1''	105.2	5.05 (d, 7.7 Hz, 1H)			104.6
2''	72.7	3.79 (m, 1H)			76.8
3''	74.0	3.52 (m, 1H)			78.2
4''	69.8	3.77 (m, 1H)	3.62	3.39	71.5
5''	75.0	3.62 (m, 1H)	3.39		77.2
6''	67.1	3.74 (m, 1H) and 3.39 (m, 1H)	3.62	4.52	68.6
1'''	101.6	4.52 (d, 1.7 Hz, 1H)			102.4
2'''	71.9	3.59 (m, 1H)	4.52	3.28	72.1
3'''	72.0	3.50 (m, 1H)			72.3
4'''	73.5	3.28 (m, 1H)		1.18	74.0
5'''	69.4	3.53 (m, 1H)	1.18; 3.28	4.52	69.7
6'''	17.7	1.18 (d, 6.2 Hz, 1H)			17.9

[a]Reference 16. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

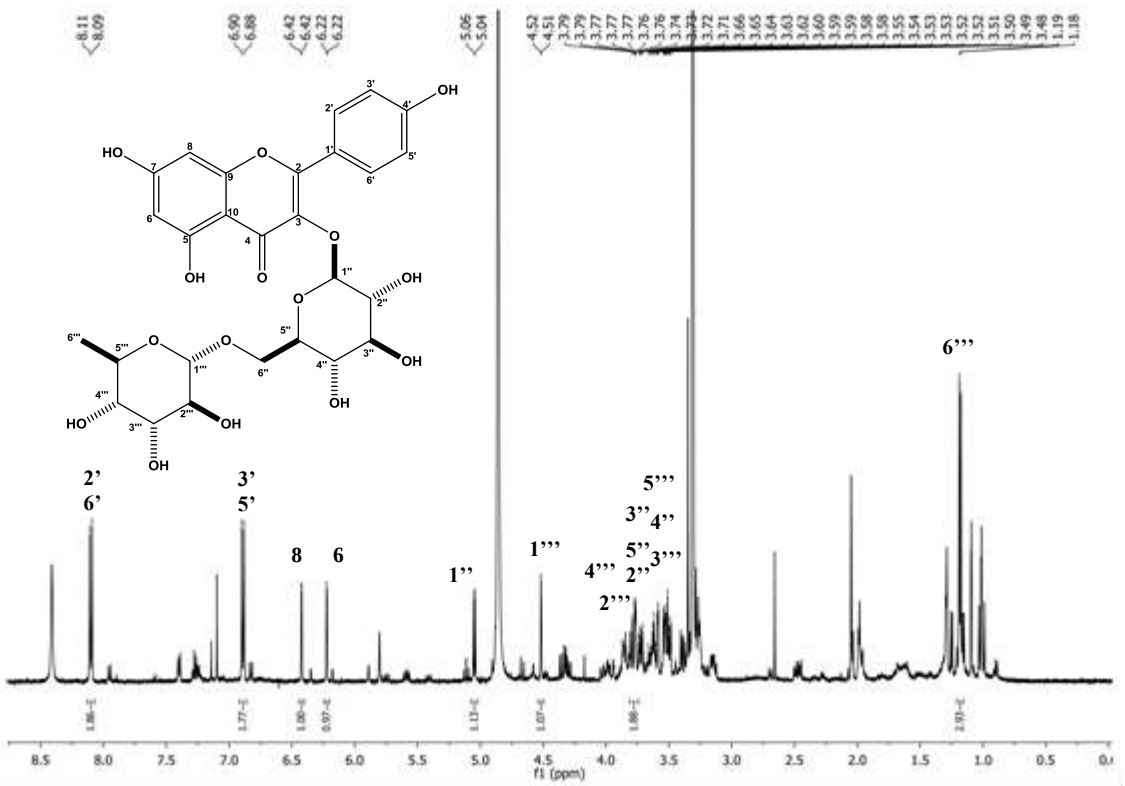


Figure S30. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **11**.

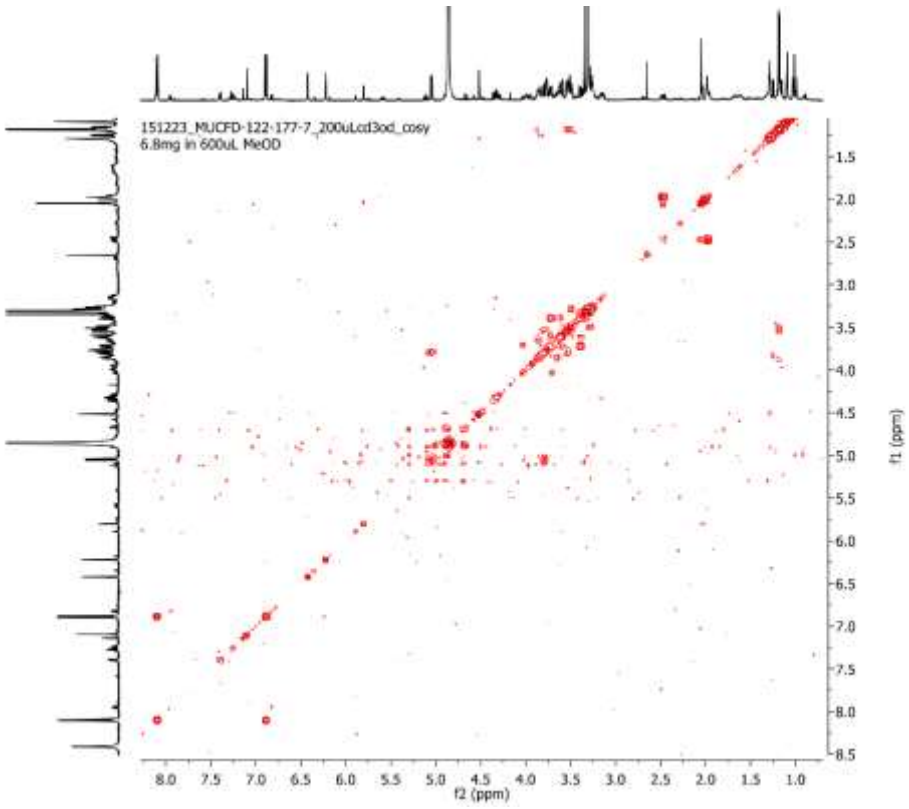


Figure S31. COSY NMR spectrum (500 MHz, CD_3OD) of compound **11**.

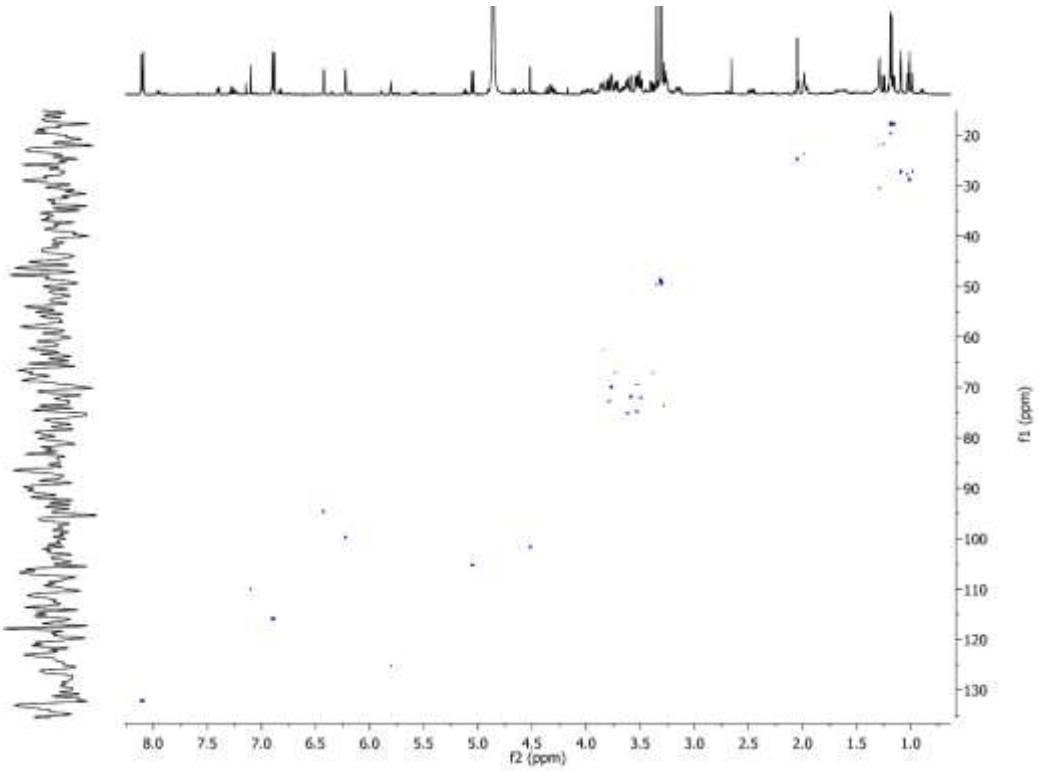


Figure S32. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **11**.

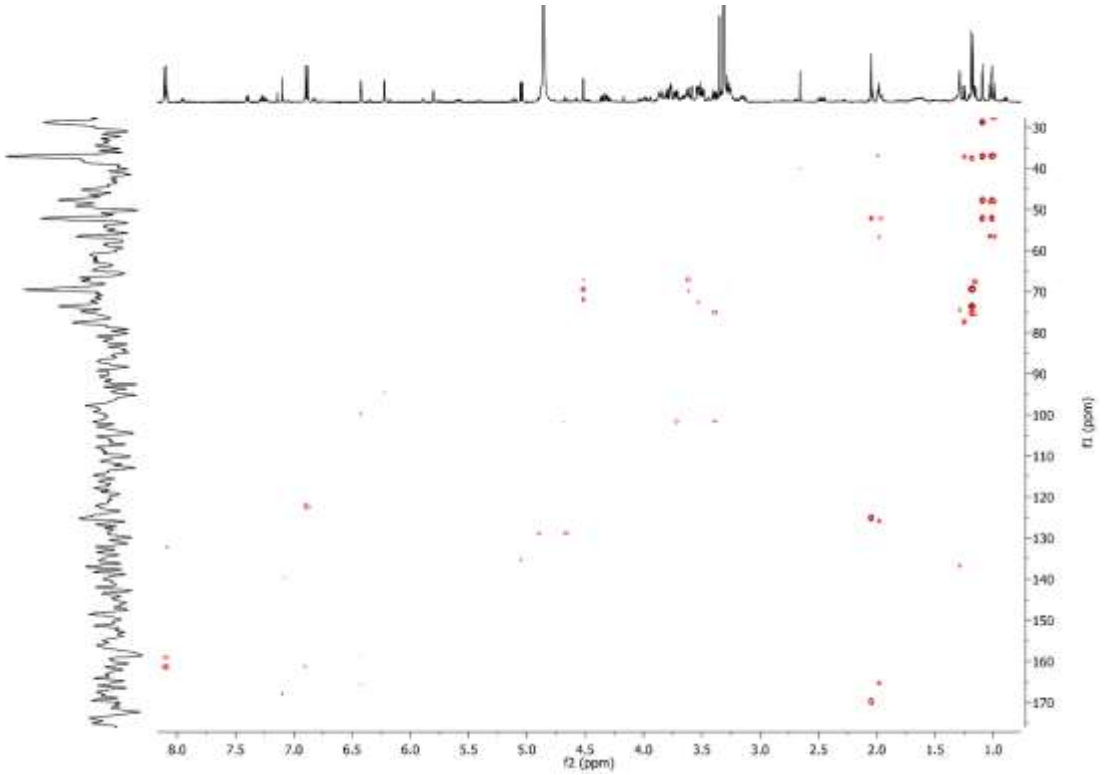


Figure S33. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **11**.

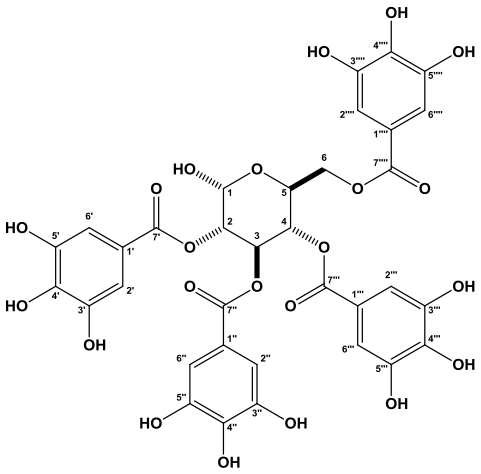


Table S13. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **12**

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(MeOD)
1	91.2	5.52 (d, 3.5 Hz, 1H)			91.5
2	73.1	5.14 (dd, 10.2 and 3.5 Hz, 1H)	6.01		73.4
3	71.4	6.01 (t, 10.2 Hz, 1H)	6.01	5.52	71.4
4	70.2	5.52 (m, 1H)	6.01		70.6
5	68.5	4.56 (m, 1H)	5.52	5.52	68.8
6	63.4	4.33 (dd, 12.1 and 4.6, 1H), 4.43 (dd, 12.5 and 2.5 Hz, 1H)		5.52	63.7
1'	119.4	–	7.02		120.4
2'/6'	110.1	7.02 (s, 2H)		7.02	110.3
3'/5'	145.6	–	7.02		146.3
4'	139.3	–		7.02	139.9
7'	166.7	–		5.14; 7.02	167.1
1''	119.8	–	6.91		120.5
2''/6''	110.0	6.91 (s, 2H)		6.91	110.3
3''/5''	145.4	–	6.91		146.4
4''	139.2	–		6.91	140.0
7''	166.9	–		6.01; 6.91	167.5
1'''	119.5	–	6.98		120.8
2'''/6'''	110.1	6.98 (s, 2H)		6.98	110.4
3'''/5'''	145.6	–	6.98		146.4
4'''	139.4	–		6.98	140.2
7'''	166.3	–		5.52; 6.98	167.7
1''''	120.3	–	7.12		121.2
2''''/6''''	110.9	7.12 (s, 2H)		7.12	110.4
3''''/5''''	145.6	–	7.12		146.5
4''''	139.1	–		7.12	140.3
7''''	167.3	–		4.33; 7.12	168.1

[a]Reference 9. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

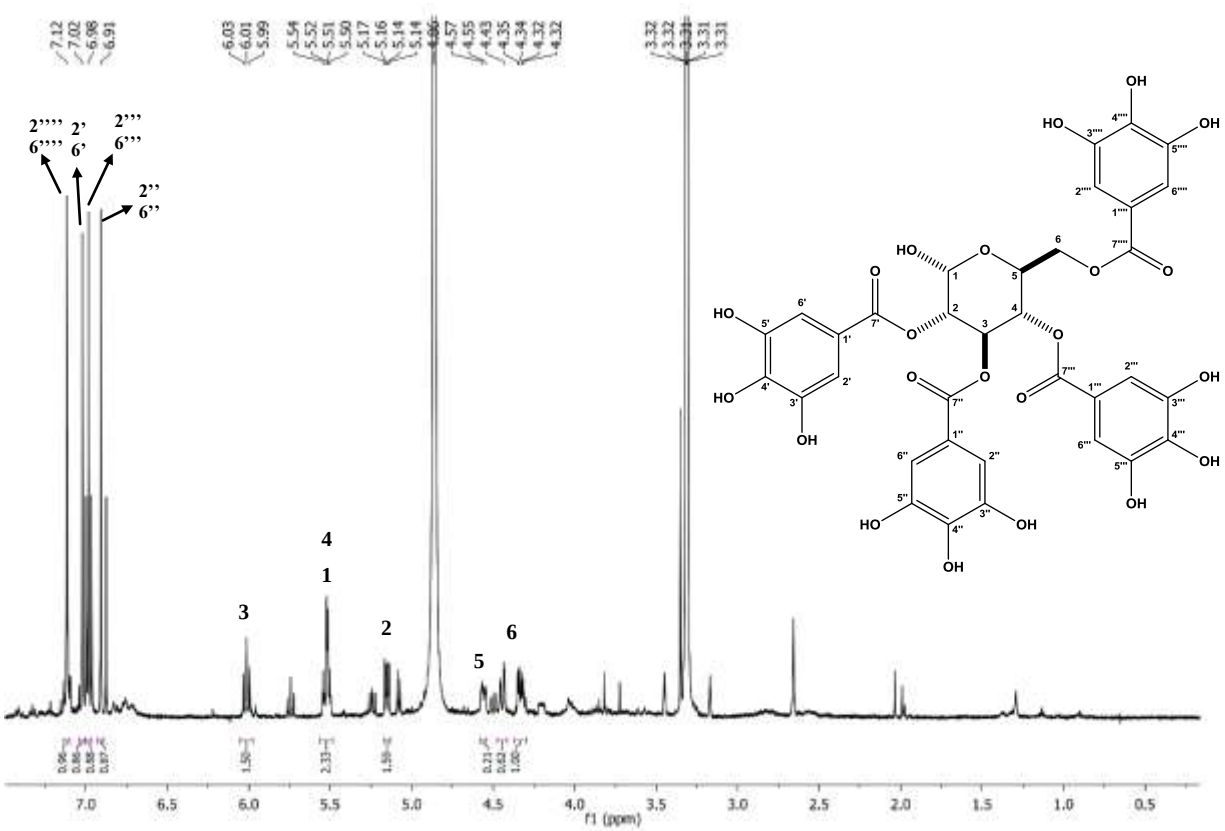


Figure S34. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **12**.

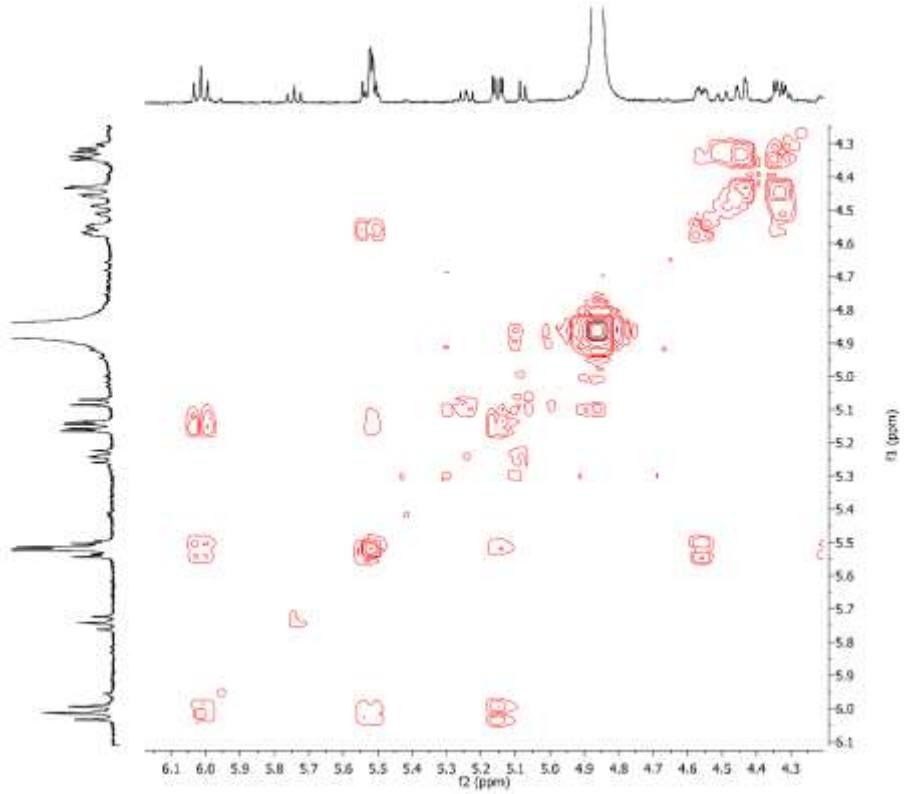


Figure S35. COSY NMR spectrum (500 MHz, CD_3OD) of compound **12**.

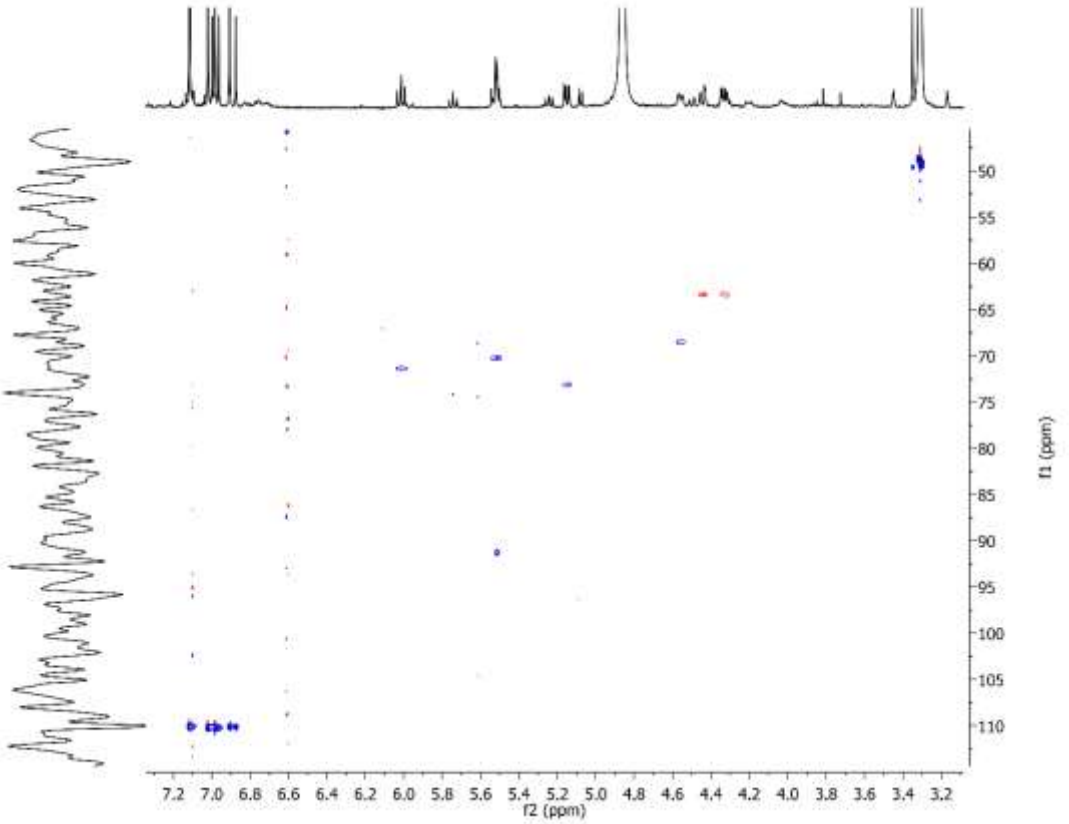


Figure S36. HSQBC NMR spectrum (500 MHz, CD_3OD) of compound **12**.

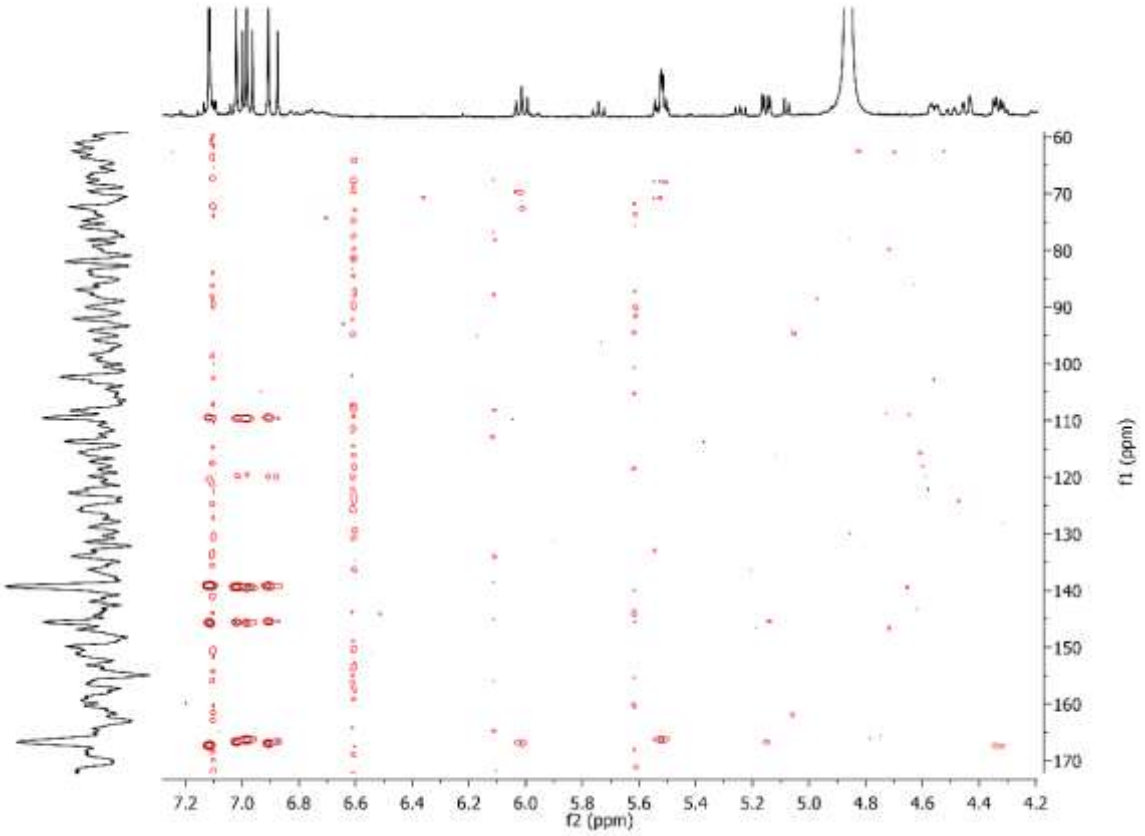


Figure S37. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **12**.

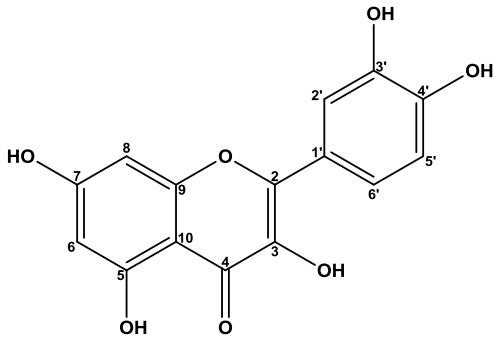


Table S14. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **13**

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(MeOD)
2	146.2	–	–	7.74	146.2
3	n.d.	–	–	–	136.5
4	177.3	–	–	–	176.5
5	162.4	–	6.19	–	161.0
6	99.2	6.19 (d, 1.5 Hz, 1H)	–	6.39	99.5
7	165.5	–	6.39	–	166.0
8	94.4	6.39 (d, 1.5 Hz, 1H)	–	6.19	94.5
9	158.2	–	6.39	–	156.7
10	104.5	–	–	6.19; 6.39	104.0
1'	124.1	–	–	6.89	123.0
2'	115.9	7.74 (s, 1H)	—	–	116.0
3'	148.7	–	7.74	6.89	145.7
4'	148.0	–	6.89	7.64; 7.74	148.1
5'	116.2	6.89 (d, 7.5 Hz, 1H)	7.64	–	116.5
6'	121.6	7.64 (d, 7.5 Hz, 1H)	–	7.74	121.0

[a]Reference 19. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy; n.d.: not detected.

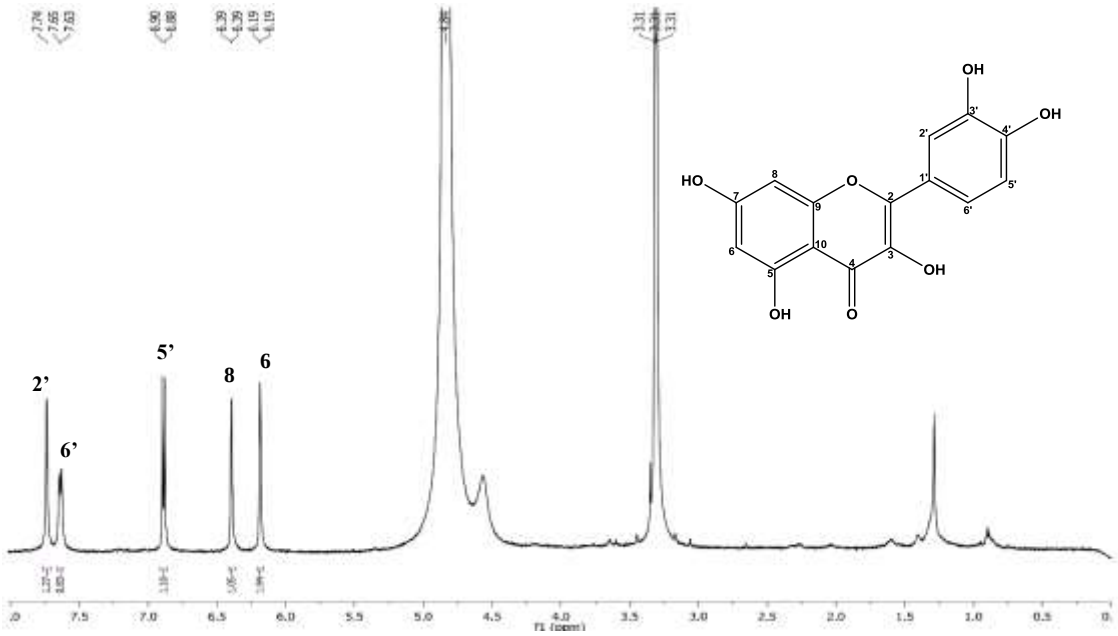


Figure S38. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **13**.

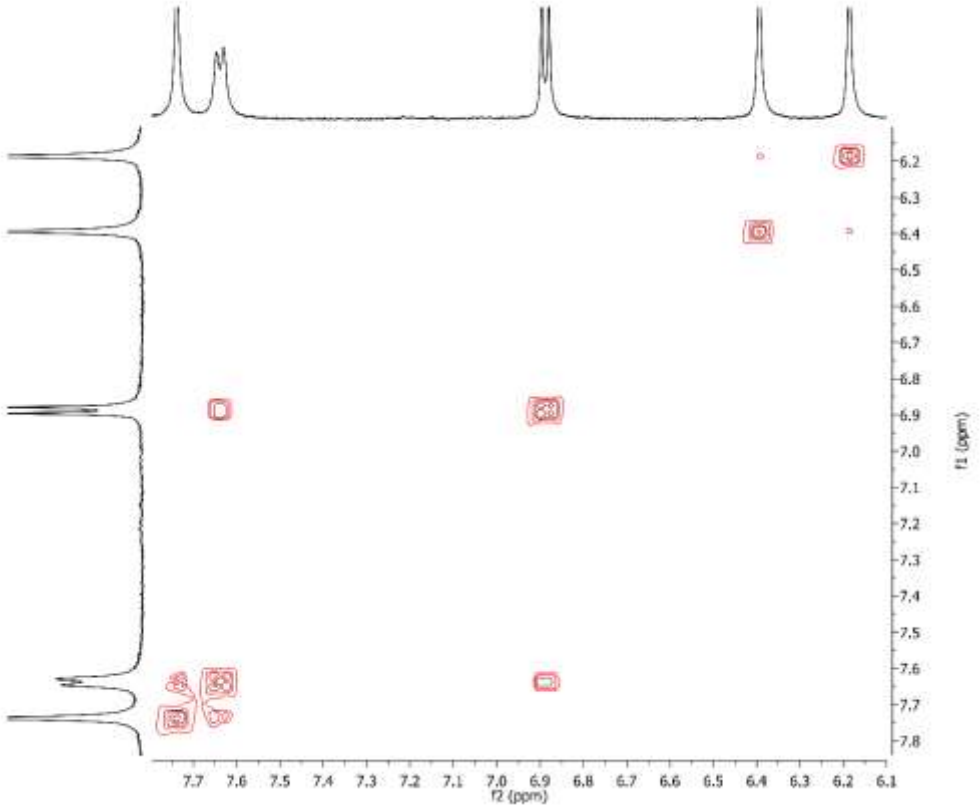


Figure S39. COSY NMR spectrum (500 MHz, CD_3OD) of compound **13**.

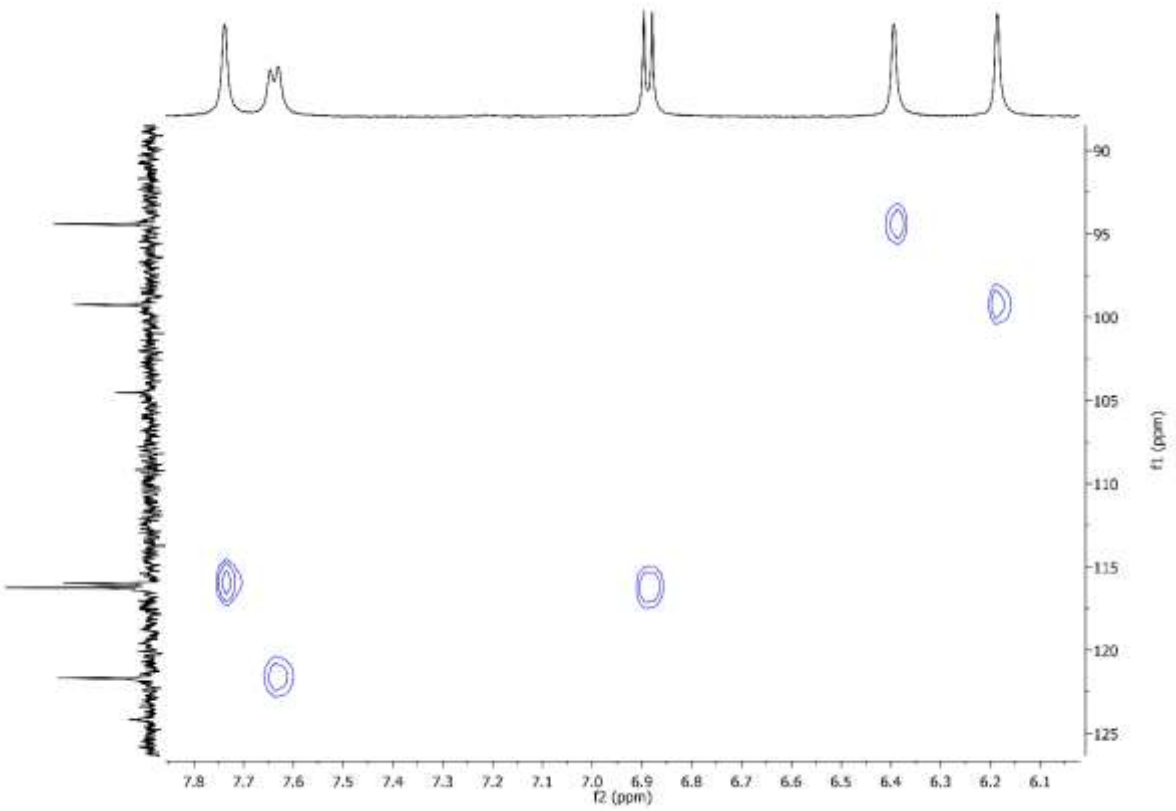


Figure S40. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **13**.

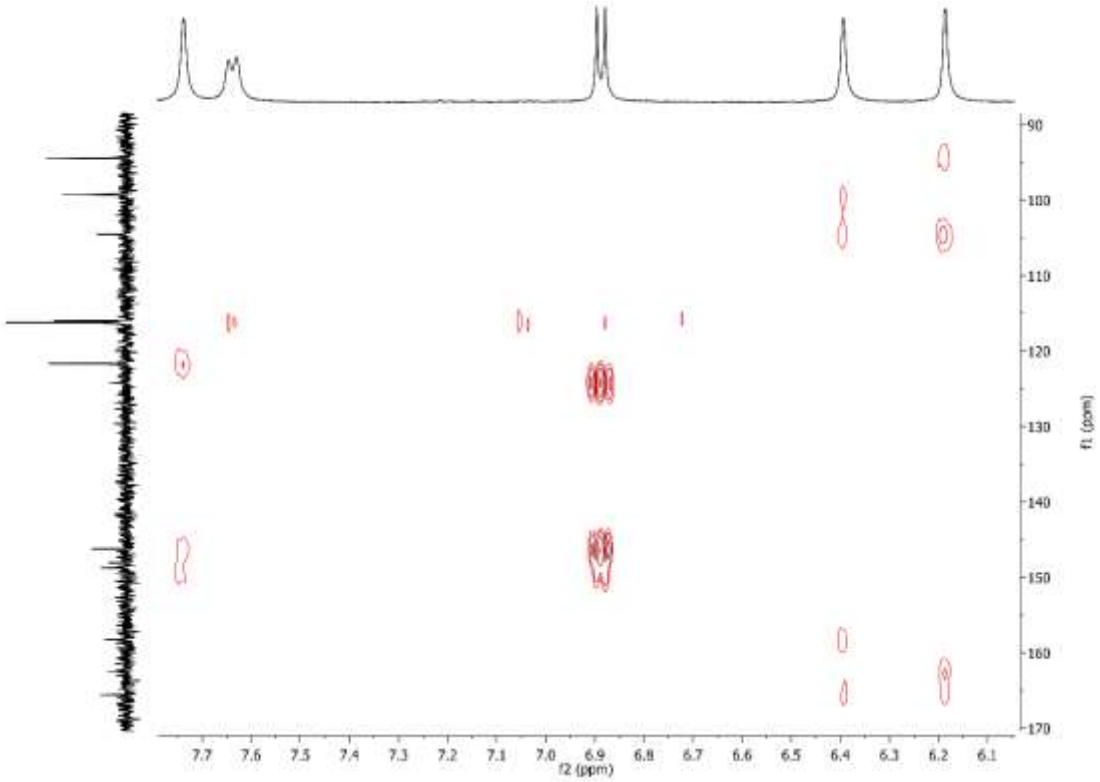


Figure S41. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **13**.

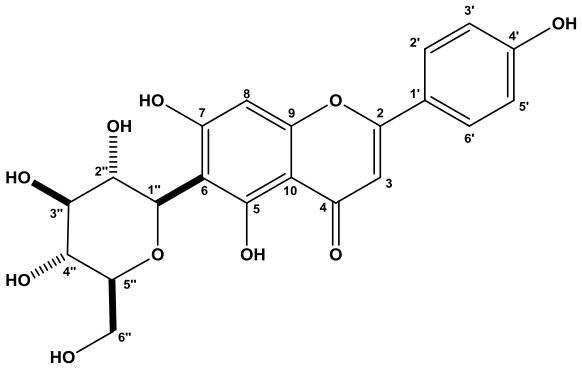


Table S15. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **14**

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(MeOD)
2	166.8	–		7.86	166.2
3	104.5	6.63 (s, 1H)			103.8
4	184.7	–			184.0
5	162.6	–		4.91	162.0
6	109.8	–	4.91	6.53	109.2
7	165.3	–	6.53	4.91	165.3
8	95.6	6.53 (s, 1H)			95.3
9	159.2	–	6.53		158.7
10	105.7	–		6.53; 6.63	104.9
1'	123.6	–		6.64	123.1
2'	129.9	7.86 (d, 8.8 Hz, 2H)			129.4
3'	117.5	6.64 (d, 8.8 Hz, 2H)	7.86		117.5
4'	163.3	–	6.64		162.8
1''	75.3	4.91 (d, 8.9 Hz, 1H)			75.3
2''	73.0	4.16 (t, 8.9 Hz, 1H)	4.91		72.5
3''	80.6	3.49 (m, 1H)	3.48	4.91	80.1
4''	72.3	3.48 (m, 1H)	3.49		71.7
5''	83.1	3.42 (m, 1H)	3.74		82.6
6''	63.3	3.74 (dd, 12.1 and 5.6 Hz, 1H), 3.88 (dd, 12.1 and 2.2 Hz, 1H)			62.8

[a]Reference 20. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

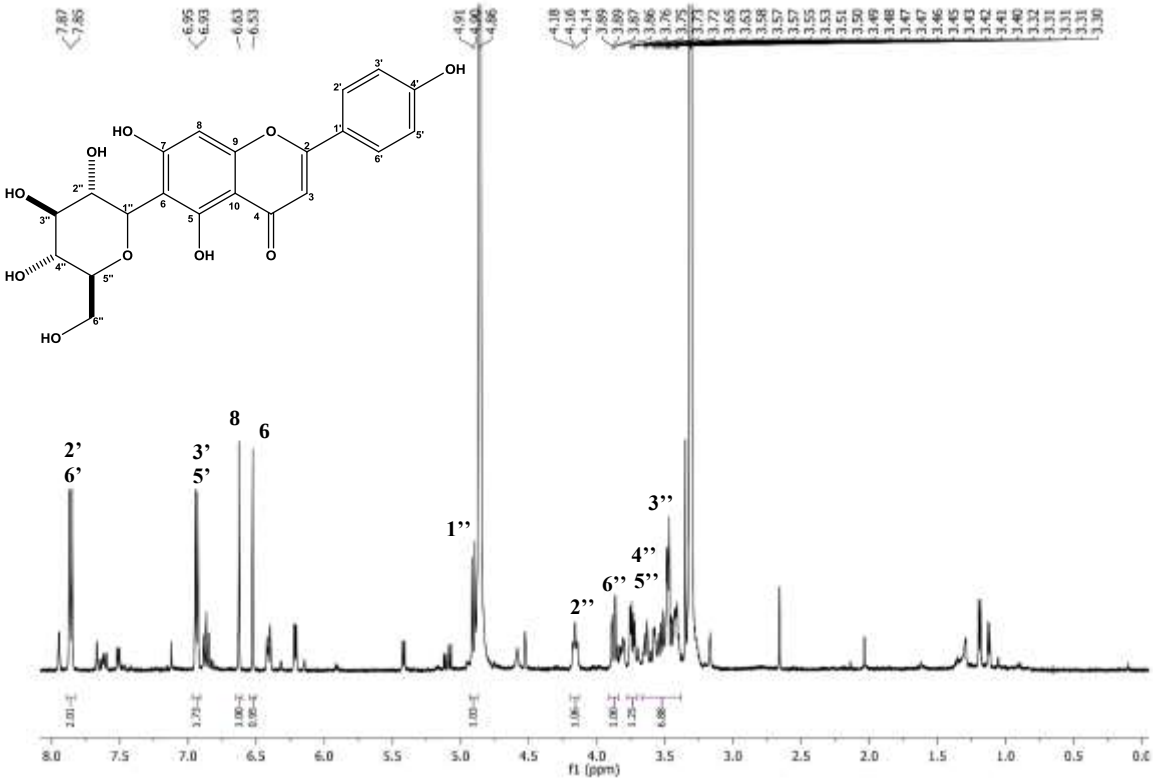


Figure S42. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **14**.

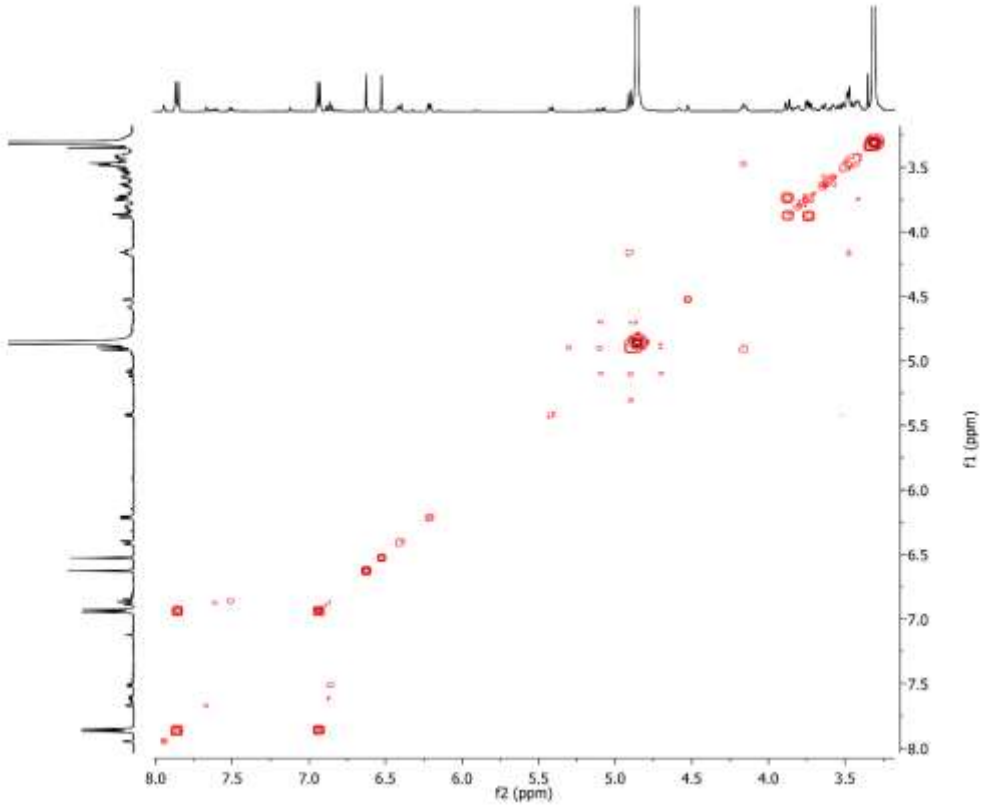


Figure S43. COSY NMR spectrum (500 MHz, CD_3OD) of compound **14**.

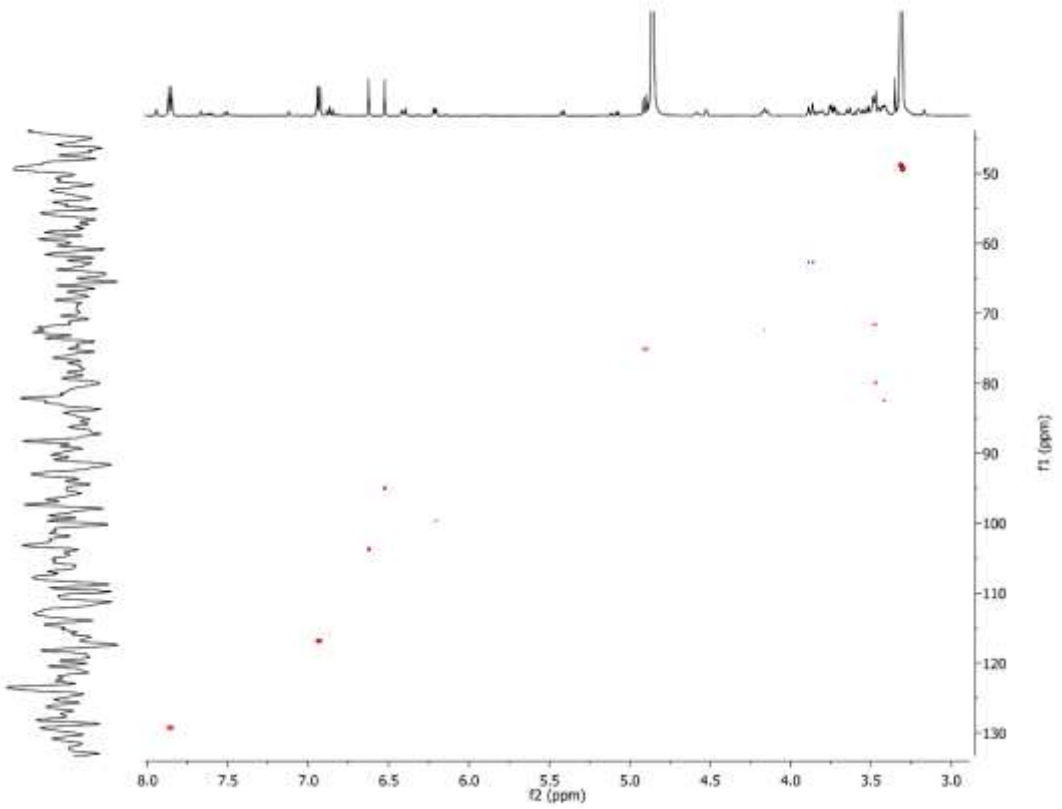


Figure S44. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **14**.

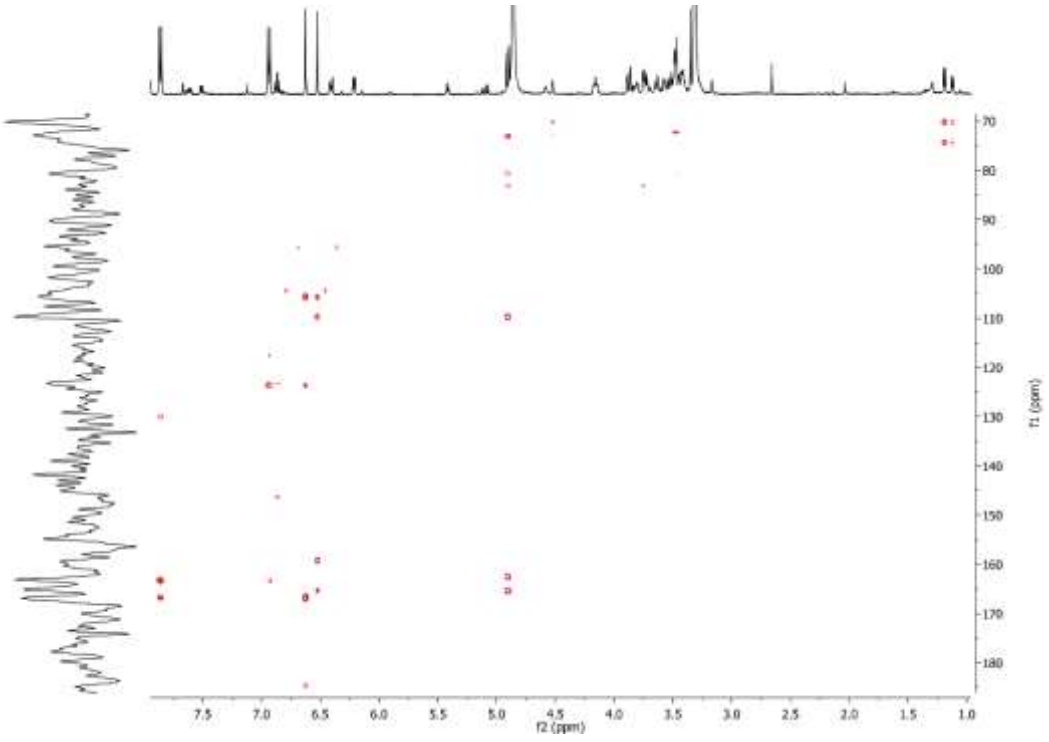


Figure S45. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **14**.

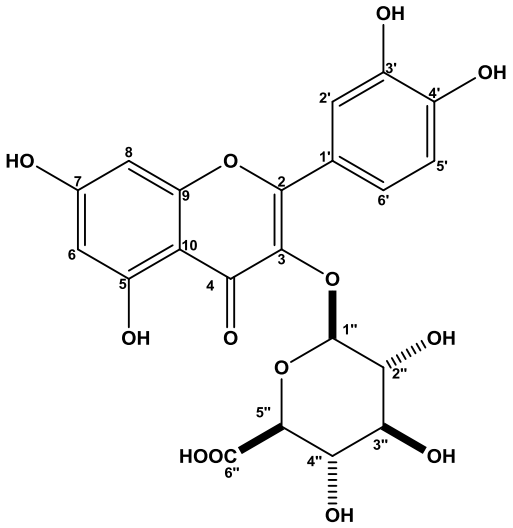


Table S16. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **15**

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(MeOD)
2	157.3	–		7.78	158.5
3	133.8	–		5.37	135.4
4	n.d.	–			166.0
5	161.3	–	6.21		159.1
6	99.6	6.21 (d, 2.1 Hz, 1H)			99.9
7	164.3	–	6.21; 6.40		163.0
8	94.4	6.40 (d, 2.1 Hz, 1H)			94.8
9	156.8	–	6.40		158.5
10	104.6	–		6.21; 6.40	105.7
1'	121.2	–	7.78	6.85	122.9
2'	117.2	7.78 (d, 2.2 Hz, 1H)			117.3
3'	144.2	–	7.78		145.9
4'	148.1	–	6.85	7.57; 7.78	149.9
5'	115.7	6.85 (d, 8.1 Hz, 1H)	7.57		116.1
6'	122.8	7.57 (dd, 8.1 and 2.2 Hz, 1H)			123.5
1''	103.9	5.37 (d, 7.6 Hz, 1H)	3.53		104.3
2''	75.2	3.53 (m, 1H)	3.49	3.58	75.4
3''	77.6	3.49 (m, 1H)			77.1
4''	72.8	3.58 (t, 9.1 Hz, 1H)	3.69		72.9
5''	77.2	3.69 (d, 9.1 Hz, 1H)			77.6
6''	n.d.	–			179.3

[a]Reference 11. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy; n.d.: not detected.

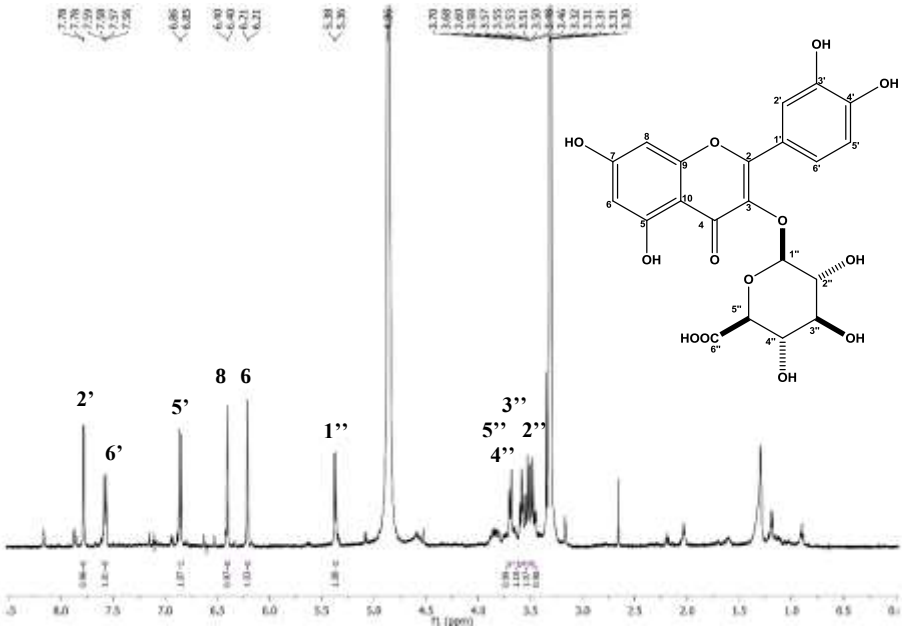


Figure S46. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **15**.

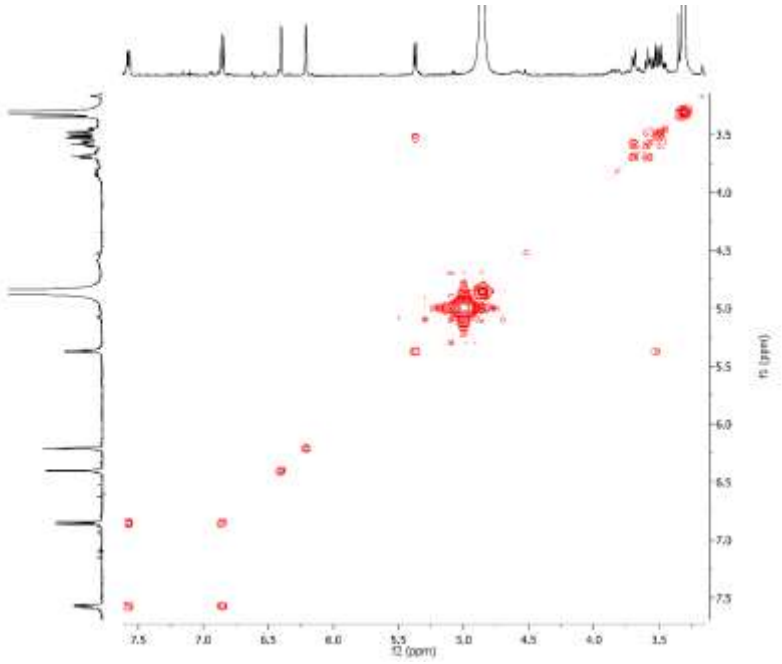


Figure S47. COSY NMR spectrum (500 MHz, CD_3OD) of compound **15**.

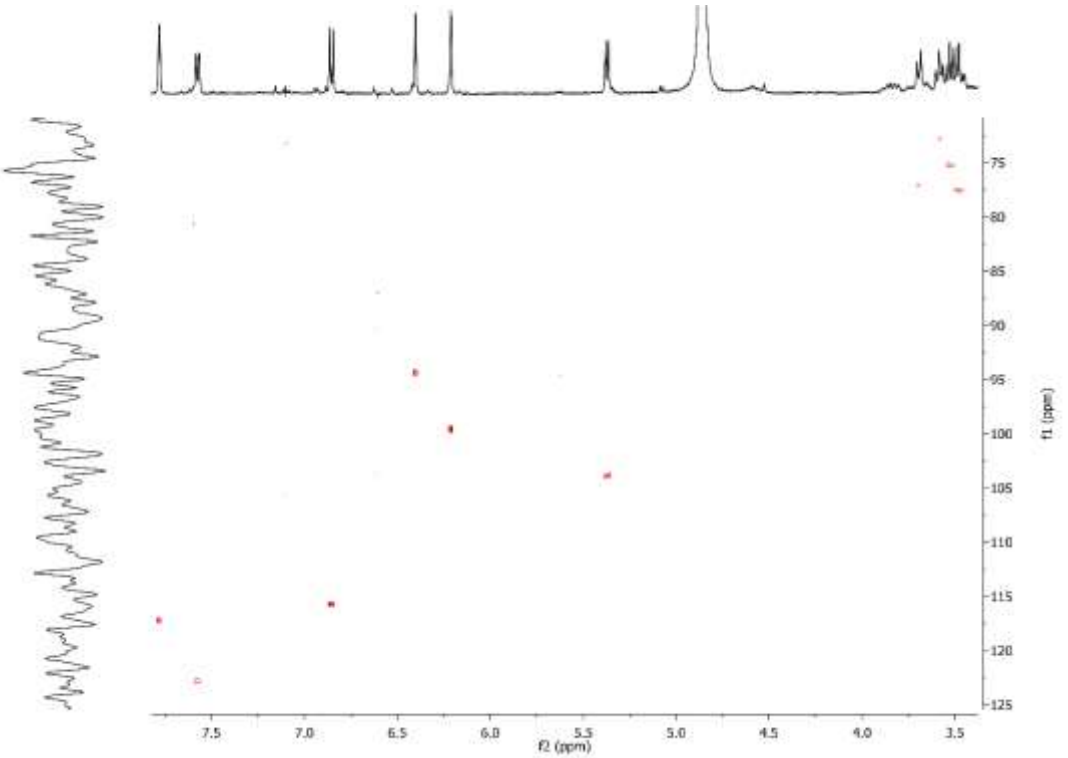


Figure S48. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **15**.

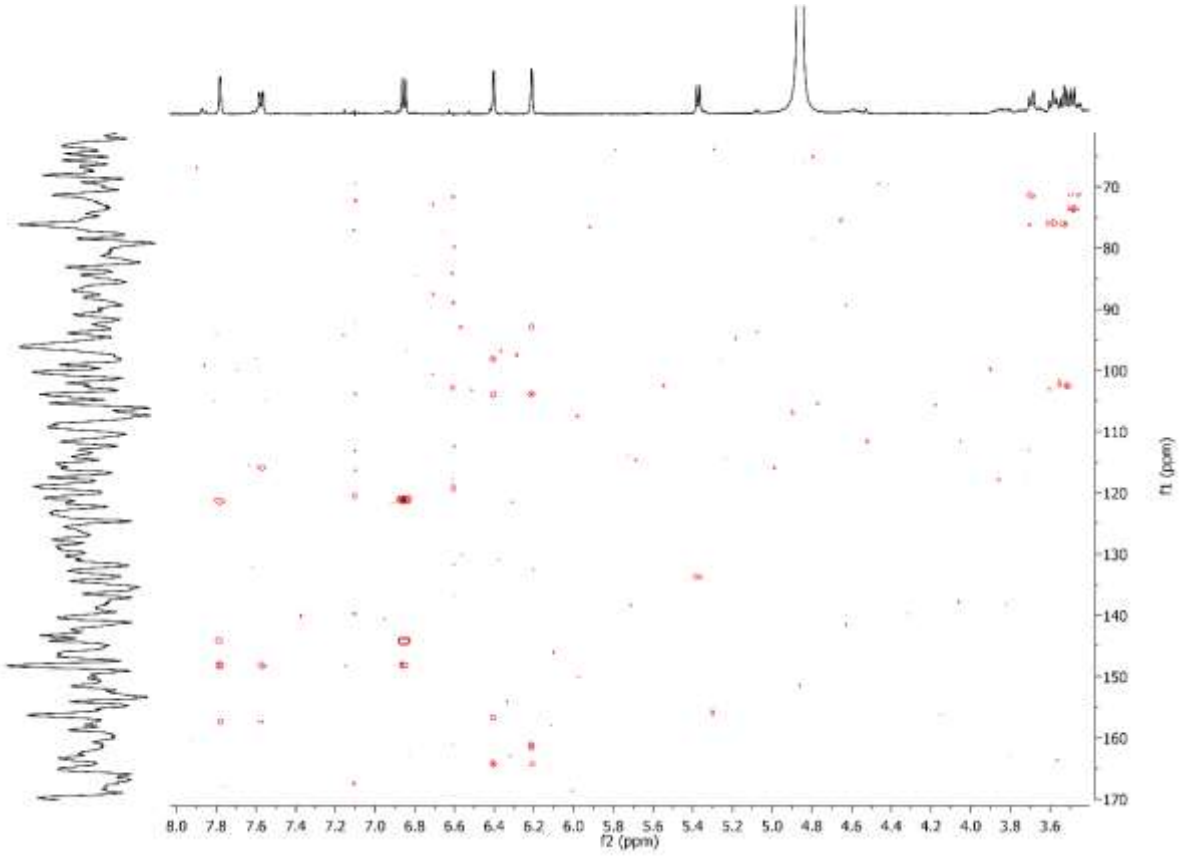


Figure S49. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **15**.

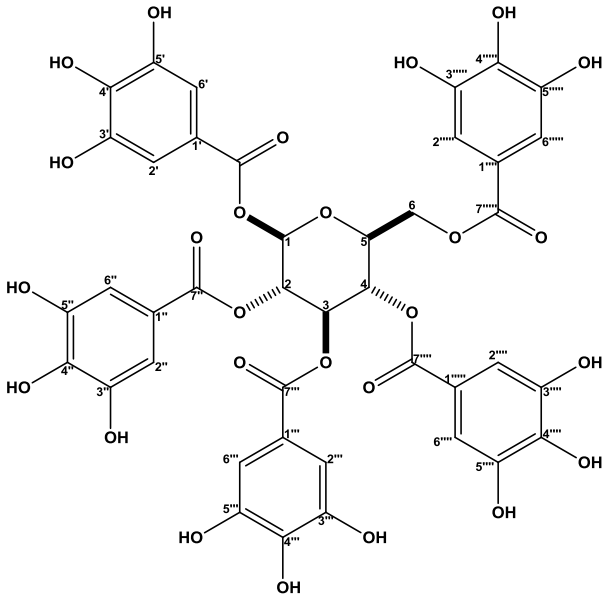


Table S17. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **16**

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(MeOD)
1	94.0	6.23 (d, 9.0 Hz, 1H)		5.90	93.4
2	74.5	4.36 (m, 1H)		5.58	74.5
3	74.2	5.90 (t, 12.0 Hz, 1H)		5.63; 6.23	74.2
4	72.3	5.58 (m, 1H)	5.90		72.4
5	70.0	5.63 (m, 1H)	5.90; 4.52		69.9
6	63.3	4.52 (m, 1H) and 4.35 (m, 1H)	5.63		63.3
1'	120.3		6.90		119.8
2'/6'	110.5	6.90 (s, 2H)		6.90	110.7
3'/5'	146.4		6.90		146.7
4'	140.4			6.90	141.0
7'	167.5			5.90; 6.90	166.4
1''	120.3		6.95		120.3
2''/6''	110.6	6.95 (s, 2H)		6.95	110.5
3''/5''	146.5		6.95		146.5
4''	140.6			6.95	140.5
7''	167.2			5.93; 6.95	167.2
1'''	120.5		6.98		120.5
2'''/6'''	110.6	6.98 (s, 2H)		6.98	110.5
3'''/5'''	146.6		6.98		146.4
4'''	140.5			6.98	140.3
7'''	167.1			5.58; 6.98	167.4
1''''	119.7		7.05		120.3
2''''/6''''	110.8	7.05 (s, 2H)		7.05	110.6
3''''/5''''	146.6		7.05		146.6
4''''	141.1			7.05	140.6

Table S17. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **16** (cont.)

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(MeOD)
7’’’’	166.4			6.23; 7.05	167.1
1’’’’’	121.1		7.11		121.1
2’’’’’/6’’’’’	110.5	7.11 (s, 2H)		7.11	110.4
3’’’’’/5’’’’’	146.7		7.11		146.6
4’’’’’	140.2			7.11	140.2
7’’’’’	168.1		7.11	4.52; 4.35; 7.11	168.1

[a]Reference 12. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

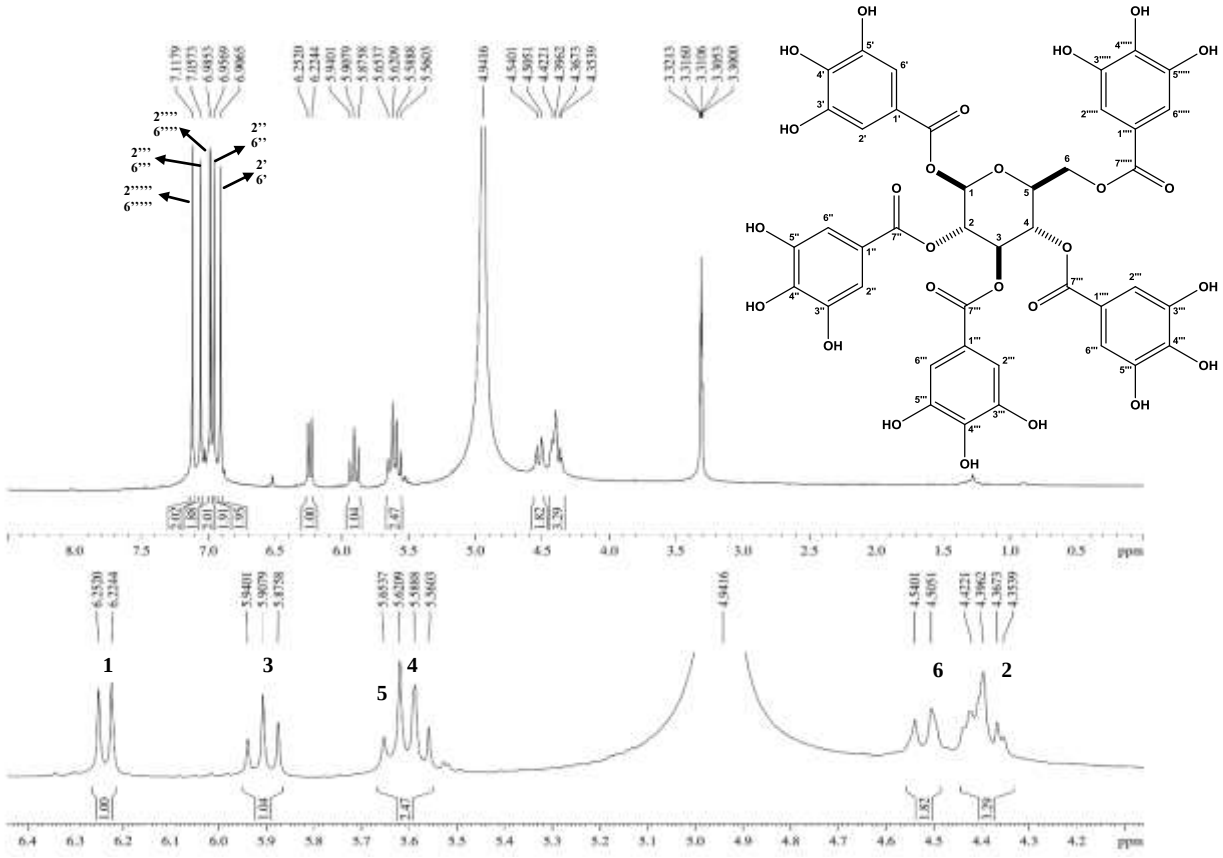


Figure S50. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **16**.

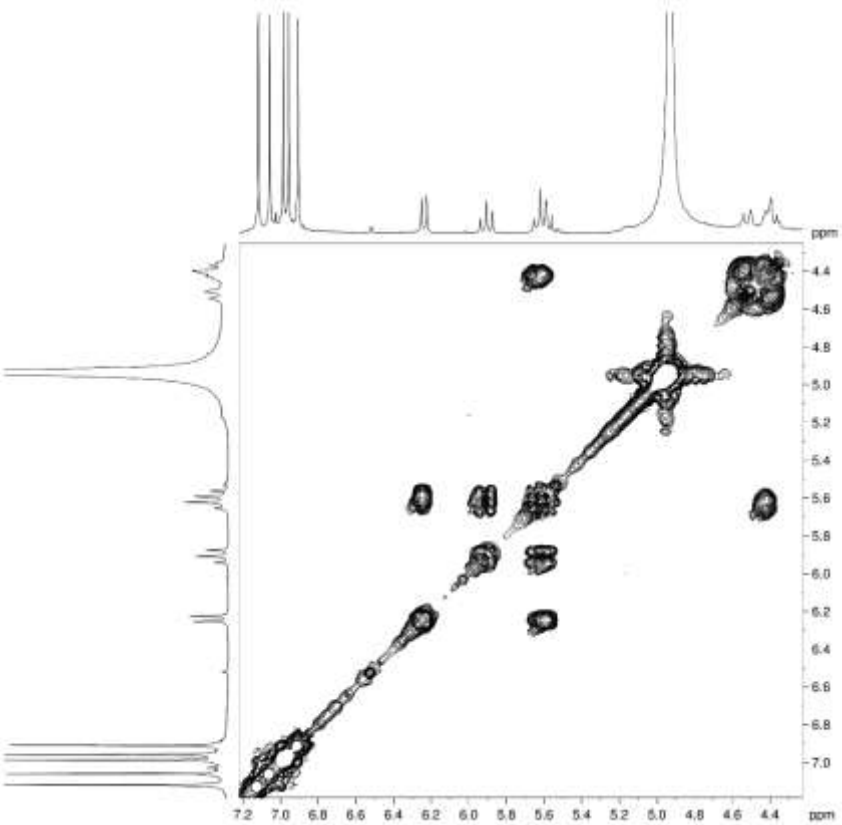


Figure S51. COSY NMR spectrum (500 MHz, CD_3OD) of compound **16**.

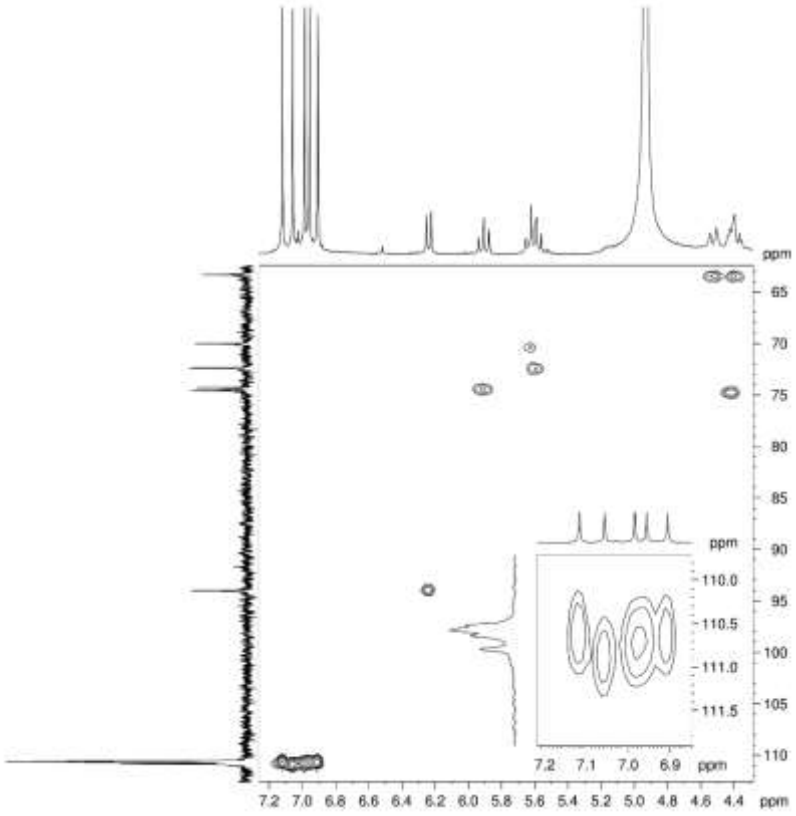


Figure S52. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **16**.

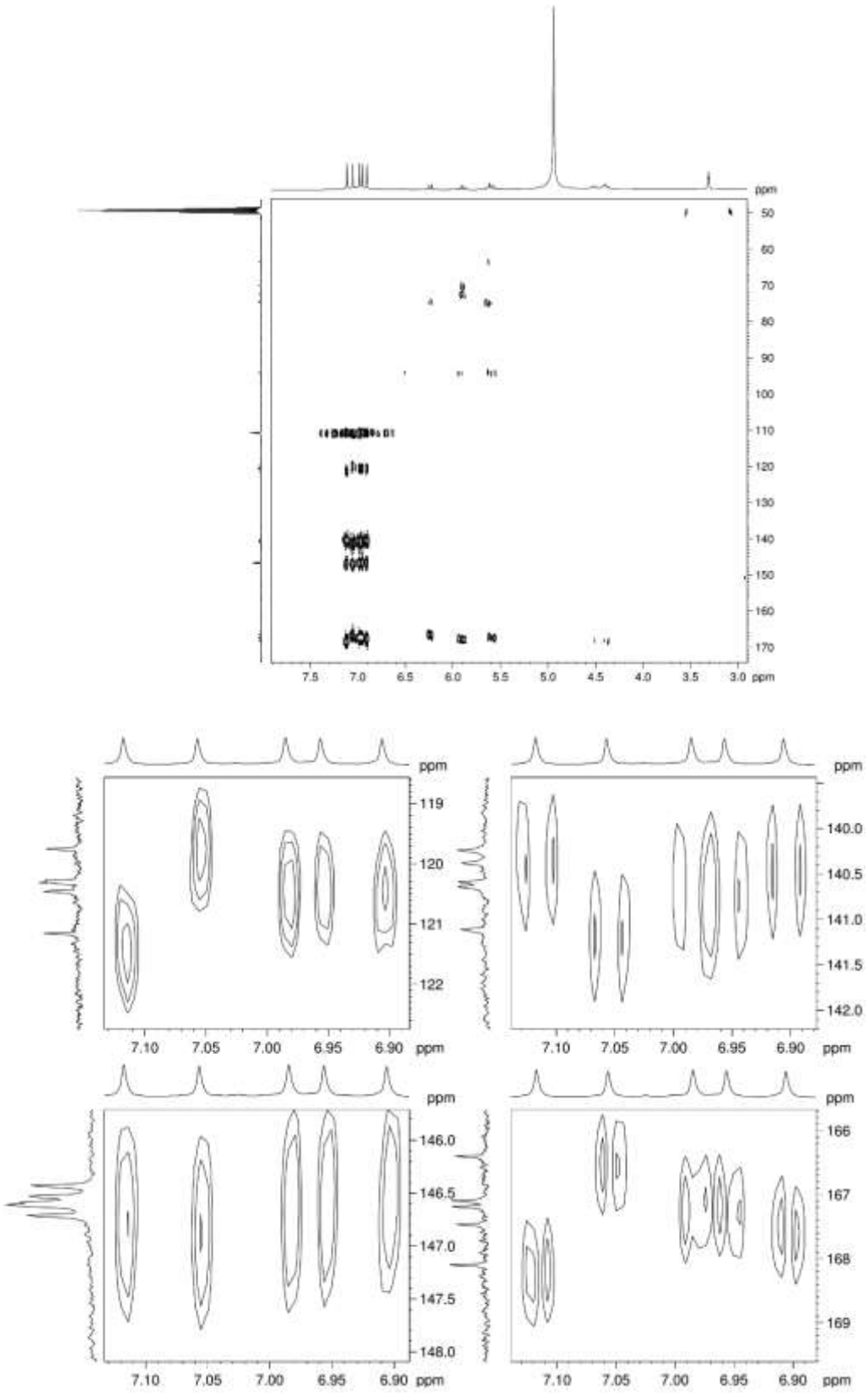
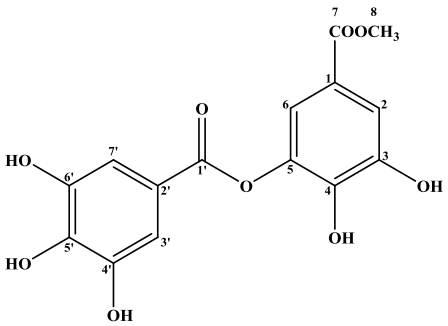


Figure S53. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **16**, with expansions.



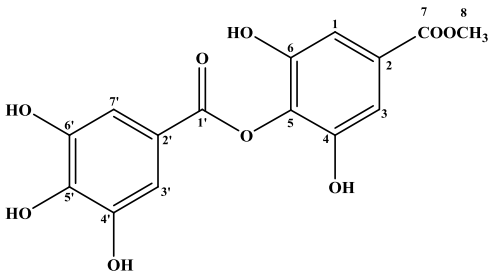


Table S18. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **17**

	HSQC		HMBC	
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$
1	116.5	–	7.39	
2	117.5	7.26 (d, 2.0 Hz, 1H)		
3	139.8	–	7.26	
4	143.9	–		7.26; 7.39
5	147.6	–	7.39	
6	114.4	7.39 (d, 2.0 Hz, 1H)		3.85; 7.26
7	167.8	–		3.85 7.26; 7.39
8	52.3	3.85 (s)		
1'	165.2			7.21
2'	120.0	–	7.21	
3'/7'	110.5	7.21 (s, 2H)		
4'/6'	146.2			
5'	140.1	–		7.21

HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

Table S19. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **18**

	HSQC		HMBC	
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$
1		–	7.04	
2/6	109.5	7.04 (s, 2H)		7.04
3/5	145.3	–	7.04	
4	142.8	–		7.04
7	167.6	–		3.87; 7.04
8	52.3	3.87		
1'	168.5	–		
2'				
3'/7'	109.1	7.10 (s, 2H)	7.10	
4'/6'	145.7			7.10
4'	139.6	–	7.10	

HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

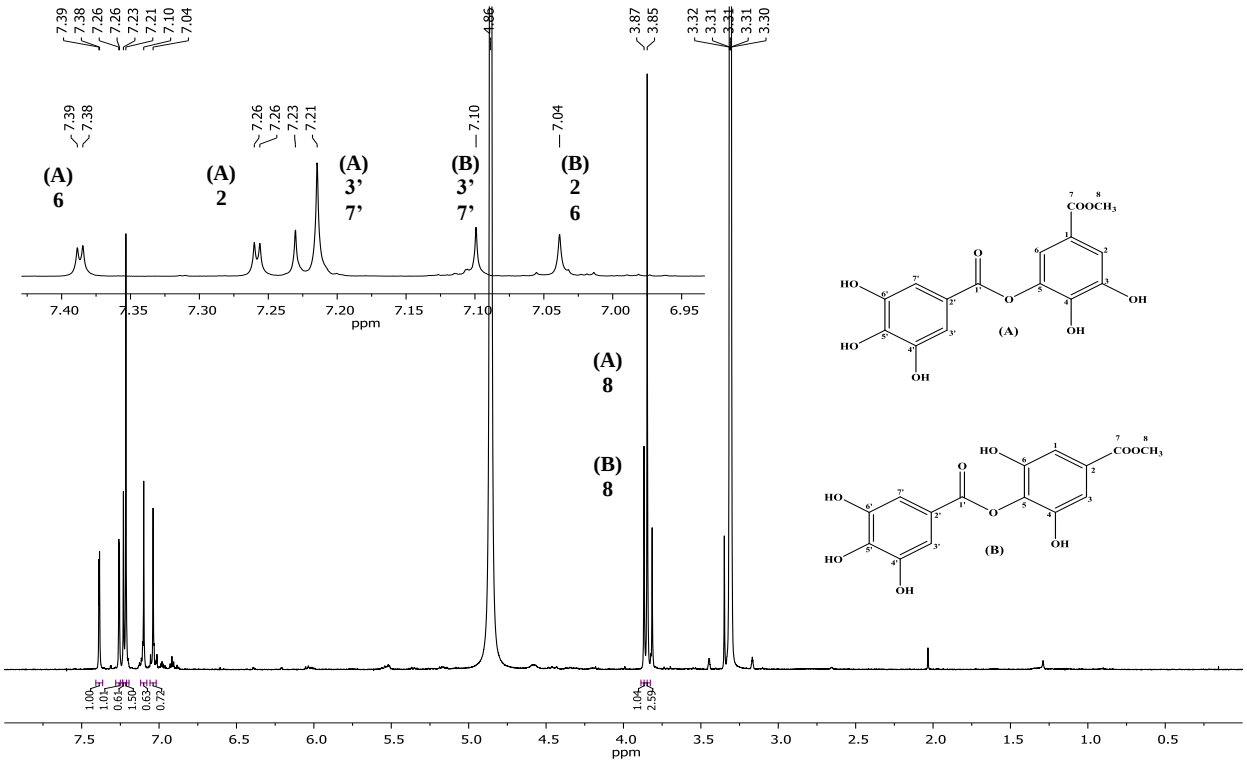


Figure S54. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compounds **17** and **18**.

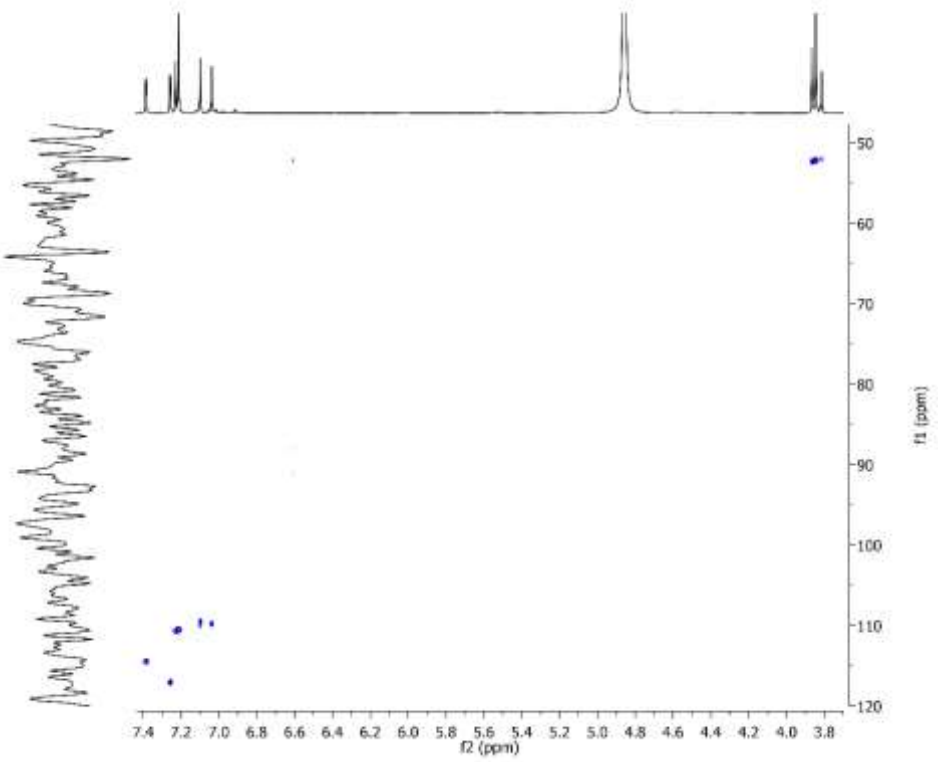


Figure S55. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compounds **17** and **18**.

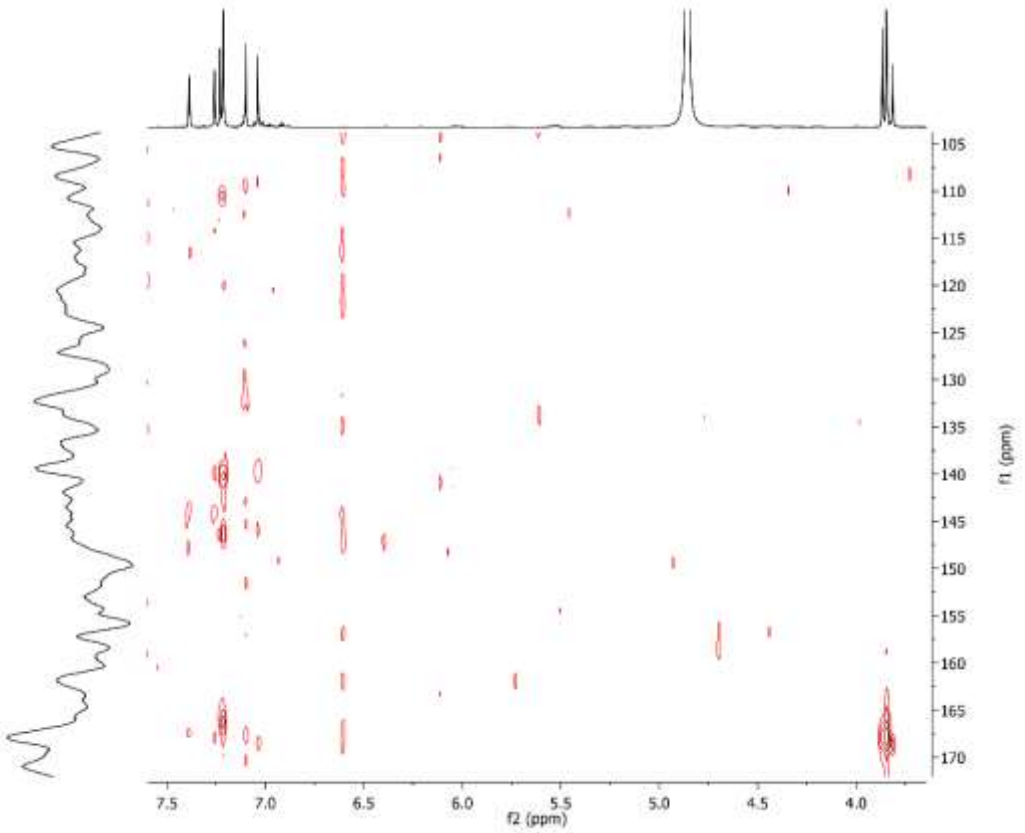


Figure S56. HMBC NMR spectrum (500 MHz, CD_3OD) of compounds **17** and **18**.

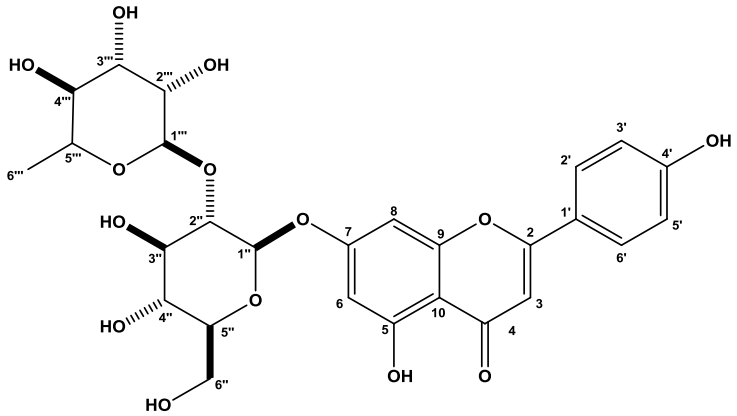


Table S20. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **19**

	HSQC		HMBC	
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$
2	167.9	–	6.67	7.89
3	103.8	6.67 (s, 1H)		
4	185.1	–	6.67	
5	164.1	–	6.43	
6	100.8	6.47 (d, 2.1 Hz, 1H)		
7	165.5	–	6.80	5.21
8	95.7	6.80 (d, 2.1 Hz, 1H)		
9	160.1	–	6.80	
10	108.1	–		6.43; 6.80; 6.94
1'	124.1	–		6.67; 6.94
2'/6	129.8	7.89 (d, 8.7 Hz, 1H)		
3'/5''	116.8	6.94 (d, 8.7 Hz, 1H)		
4'	164.4	–		7.89
1''	99.5	5.21 (d, 7.6 Hz, 1H)		
2''	77.9	3.55 (m, 1H)		5.29
3''	78.8	3.64 (m, 1H)		
4''	69.8	3.93 (m, 1H)		3.71
5''	78.7	3.69 (m, 1H)		
6''	62.1	3.92 (m, 1H) and 3.71 (m, 1H)		
1'''	102.9	5.29 (d, 1.68 Hz, 1H)		
2'''	71.2	3.42 (m, 1H)	5.29	
3'''	71.9	3.60 (m, 1H)	3.42	
4'''	73.6	3.42 (m, 1H)	3.42	1.33; 5.29
5'''	71.9	3.94 (m, 1H)	3.42	1.33
6'''	18.0	1.33 (d, 5.0 Hz, 1H)		

HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

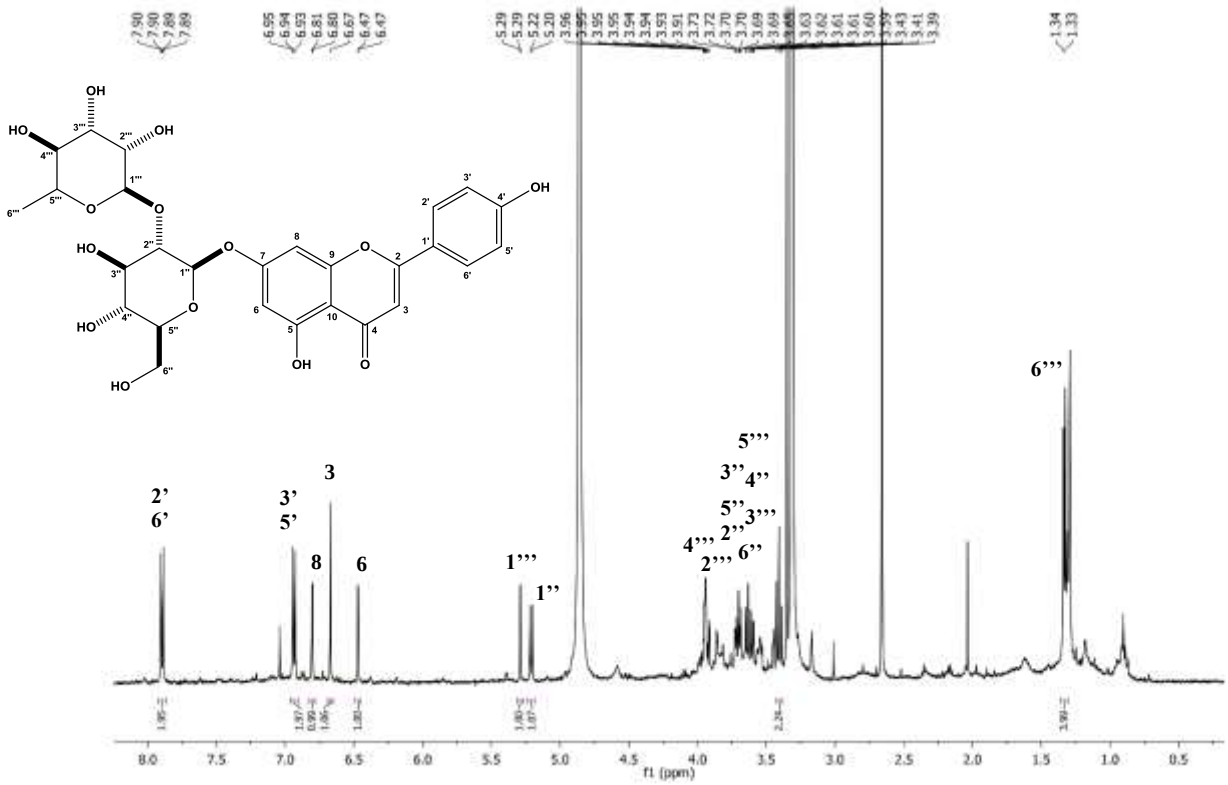


Figure S57. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **19**.

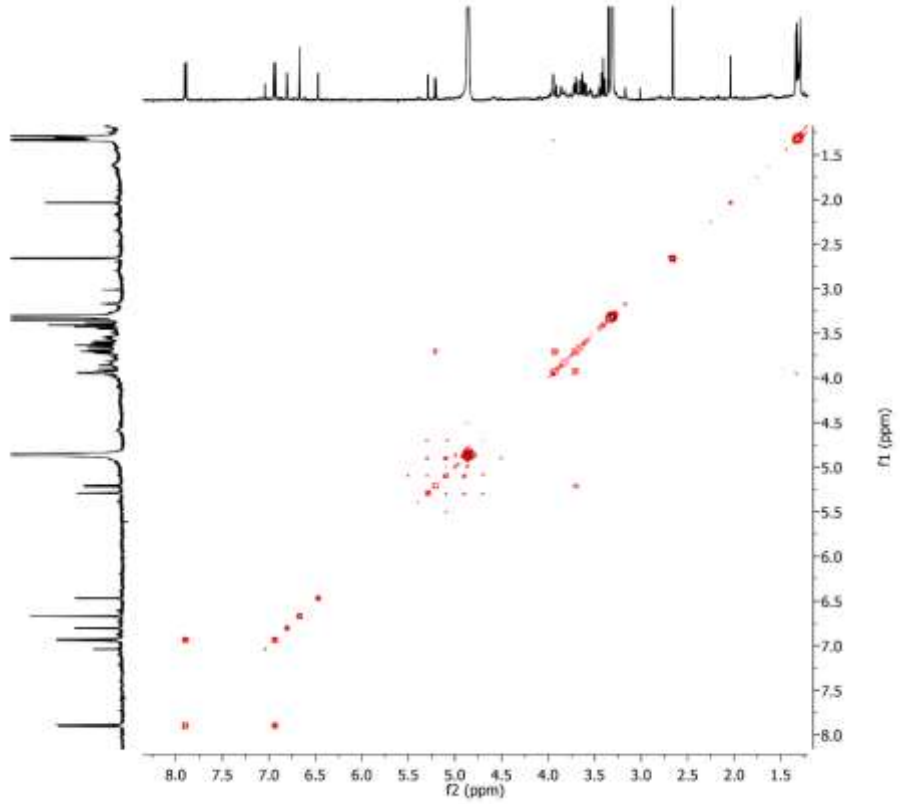


Figure S58. COSY NMR spectrum (500 MHz, CD_3OD) of compound **19**.

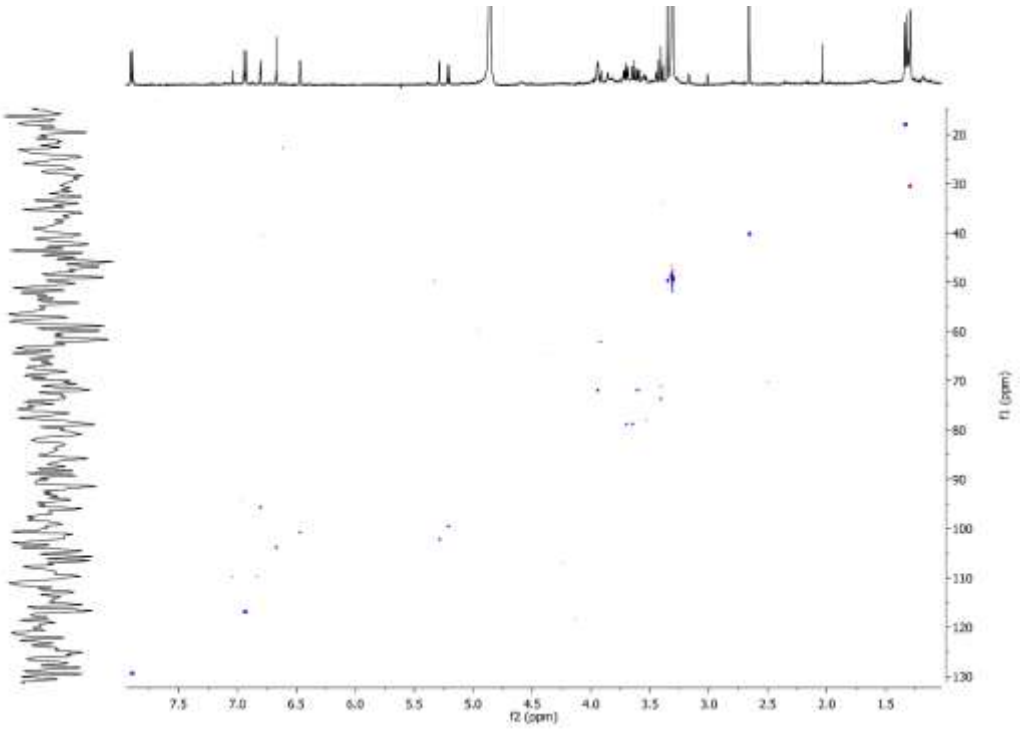


Figure S59. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **19**.

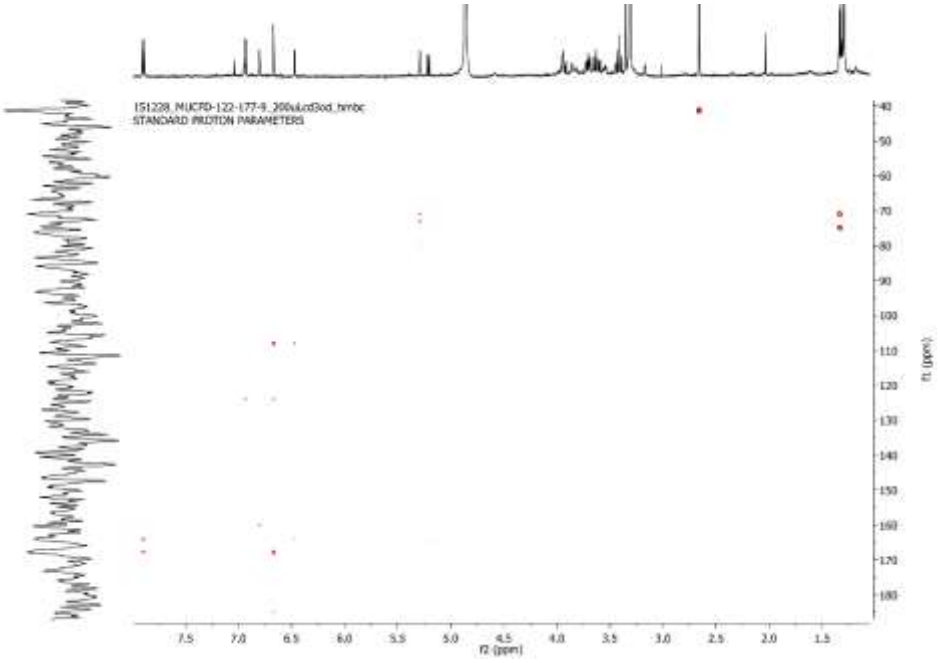


Figure S60. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **19**.

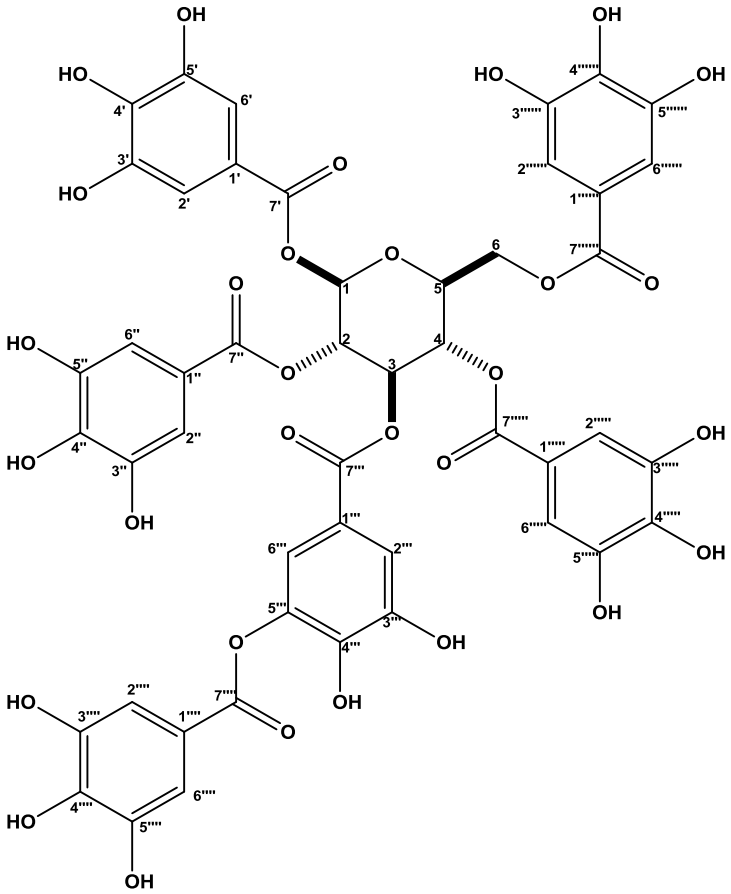


Table S21. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **20**

	HSQC		HMBC	
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$
1	93.5	6.25 (d, 8.6 Hz, 1H)	–	–
2	69.5	5.63 (m. 1H)	5.94	4.37
3	74.1	5.94 (m, 1H)	5.63	–
4	71.9	5.61 (m, 1H)	5.94	–
5	74.1	4.42 (m, 1H)	4.37; 5.63	–
6	62.8	4.52 (m, 1H) and 4.37 (m, 1H)	–	5.63
1'	119.3	–	7.05	–
2'/6'	110.3	7.05 (s, 2H)	–	7.05
3'/5'	146.2	–	7.05	–
4'	140.4	–	–	7.05
7'	164.3	–	–	6.25; 7.05
1''	119.8	–	6.99	–
2''/6''	110.2	6.99 (s, 2H)	–	6.99
3''/5''	146.1	–	6.99	–
4''	134.0	–	–	6.99
7''	165.5	–	–	6.99
1'''	110.5	–	–	5.63; 6.99
2'''	117.2	7.15 (d, 2.0 Hz, 1H)	–	7.26
3'''	139.6	–	7.15	–

Table S21. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **20** (cont.)

	HSQC		HMBC	
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$
4’’’	144.3	–	–	7.15; 7.26
5’’’	147.1	–	7.26	–
6’’’	114.8	7.26 (d, 2.0 Hz, 1H)	–	–
7’’’	165.0	–	–	5.94; 7.15; 7.26
1’’’’	120.0	–	7.20	–
2’’’’/6’’’’	110.6	7.20 (s, 2H)	–	7.20
3’’’’/5’’’’	146.2	–	7.20	–
4’’’’	140.1	–	–	7.20
7’’’’	165.2	–	–	7.20
1’’’’’	119.9	–	6.96	–
2’’’’’/6’’’’’	110.1	6.96 (s, 2H)	–	6.96
3’’’’’/5’’’’’	146.0	–	6.96	–
4’’’’’	140.0	–	–	6.96
7’’’’’	165.6	–	–	5.61; 6.96
1’’’’’’	120.6	–	7.11	–
2’’’’’’/6’’’’’’	110.0	7.11 (s, 2H)	–	7.11
3’’’’’’/5’’’’’’	146.1	–	7.11	–
4’’’’’’	139.6	–	–	7.11
7’’’’’’	166.6	–	–	4.37; 4.52; 7.11

HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

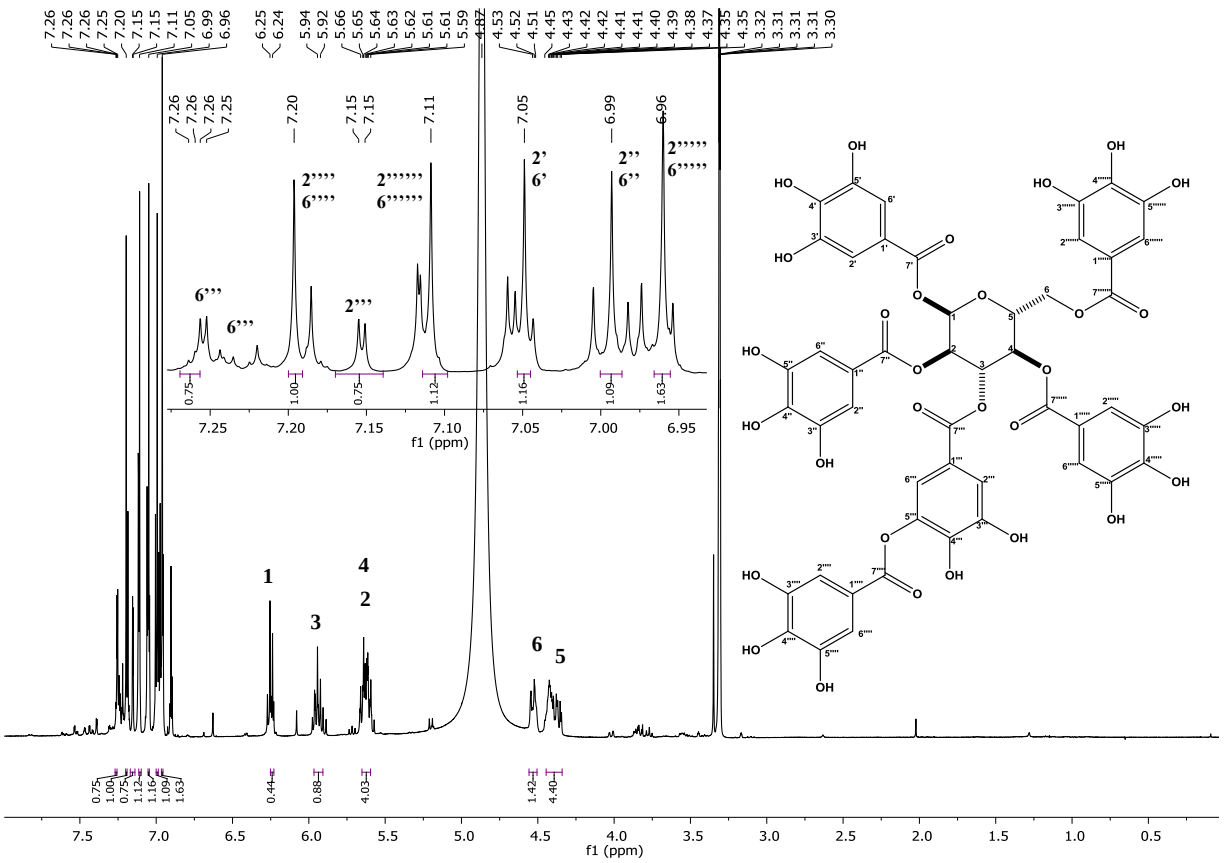


Figure S61. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **20**.

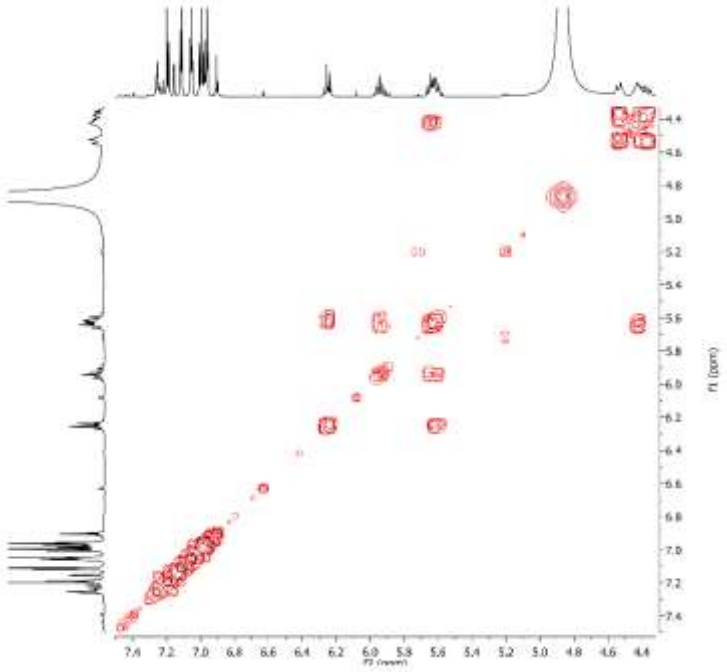


Figure S62. COSY NMR spectrum (500 MHz, CD_3OD) of compound **20**.

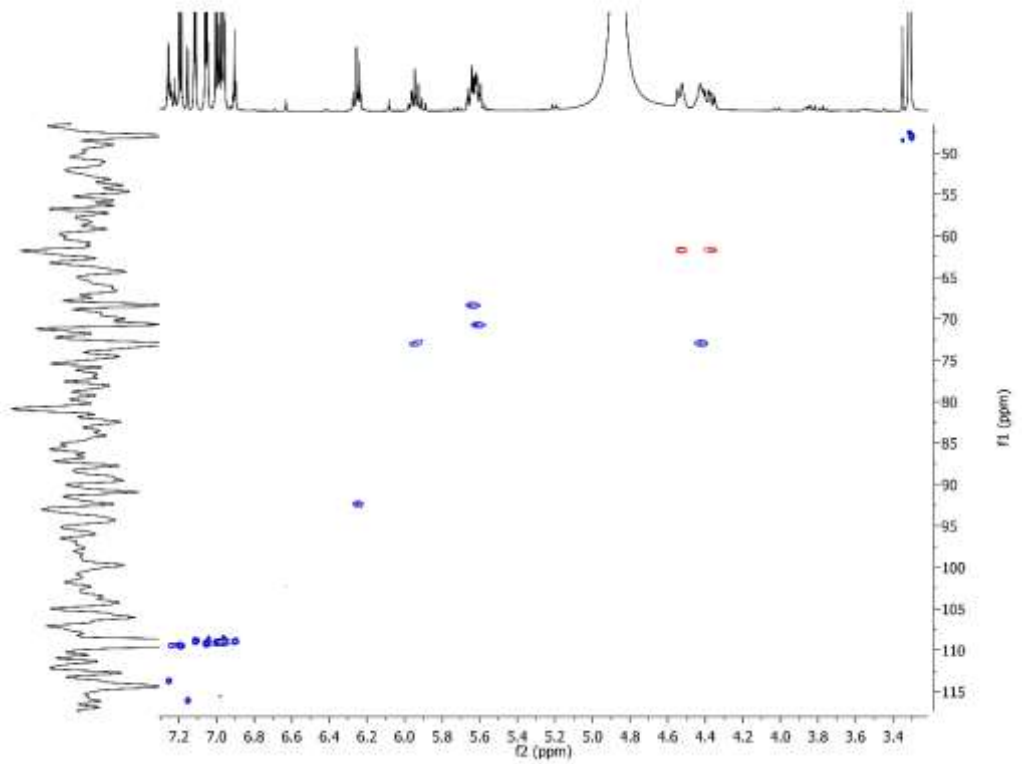


Figure S63. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **20**.

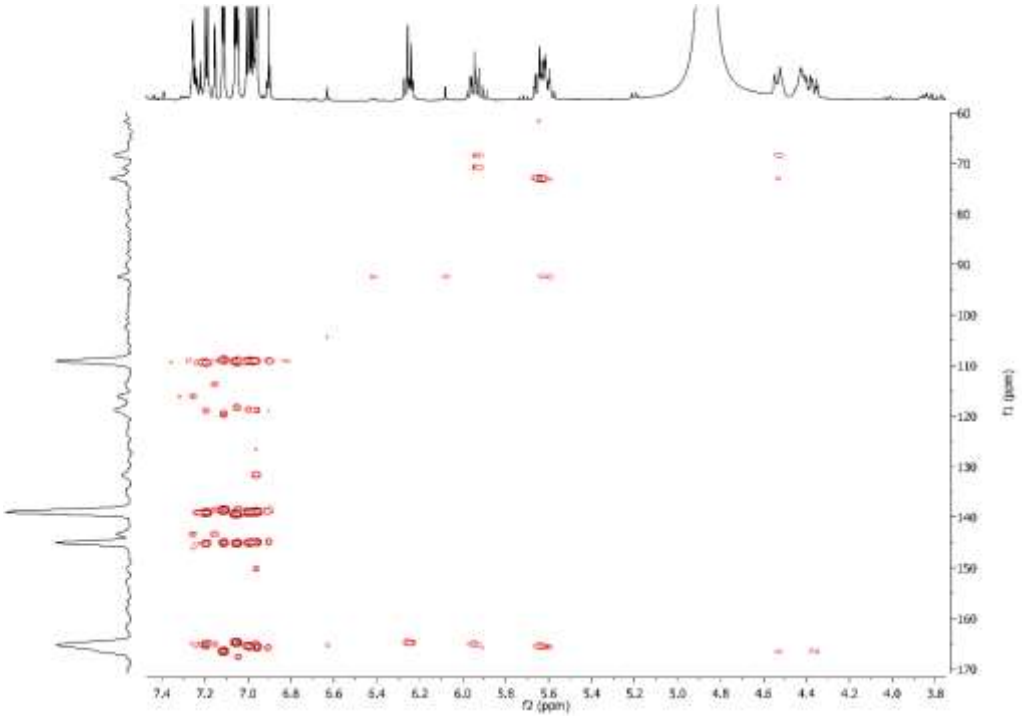


Figure S64. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **20**.

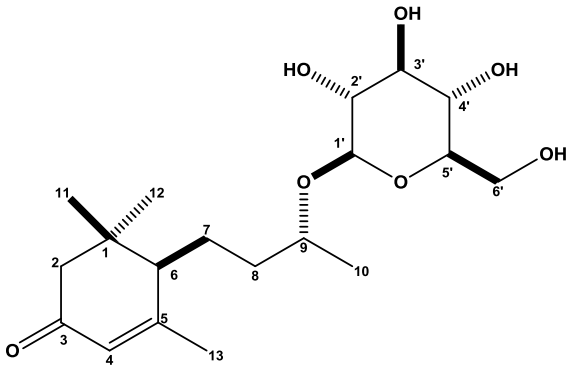


Table S22. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **21**

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(MeOD)
1	37.5	–	1.02; 1.10; 2.47		37.4
2	47.8	1.98 (d, 16.8 Hz, 1H), 2.47 (d, 16.8 Hz, 1H)		1.02; 1.10	48.2
3	202.3	–	2.47		202.5
4	125.2	5.81 (s, 1H)		2.05	125.5
5	169.9	–			170.1
6	52.2	1.97 (m, 1H)		1.02; 1.10; 1.98; 2.05	52.5
7	27.3	1.68 (m, 1H), 1.98 (m, 1H)			26.9
8	37.1	1.63 (m, 1H), 1.66 (m, 1H)	1.98		37.9
9	75.3	3.89 (m, 1H)	1.19	4.32	75.7
10	19.6	1.19 (d, 6.13 Hz, 1H)			19.9
11	28.9	1.02 (s, 3H)		1.10	29.1
12	27.3	1.10 (s, 3H)	1.02	2.47	27.6
13	24.7	2.05 (s, 3H)			25.0
1'	101.9	4.32 (d, 7.8 Hz, 1H)			102.3
2'	74.8	3.15 (m, 1H)			75.3
3'	77.9	3.34 (m, 1H)			78.3
4'	71.5	3.25 (m, 1H)			72.0
5'	77.6	3.25(m, 1H)		3.34	78.0
6'	62.6	3.85 and 3.65 (m, 1H)			63.1

[a]Reference 15. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

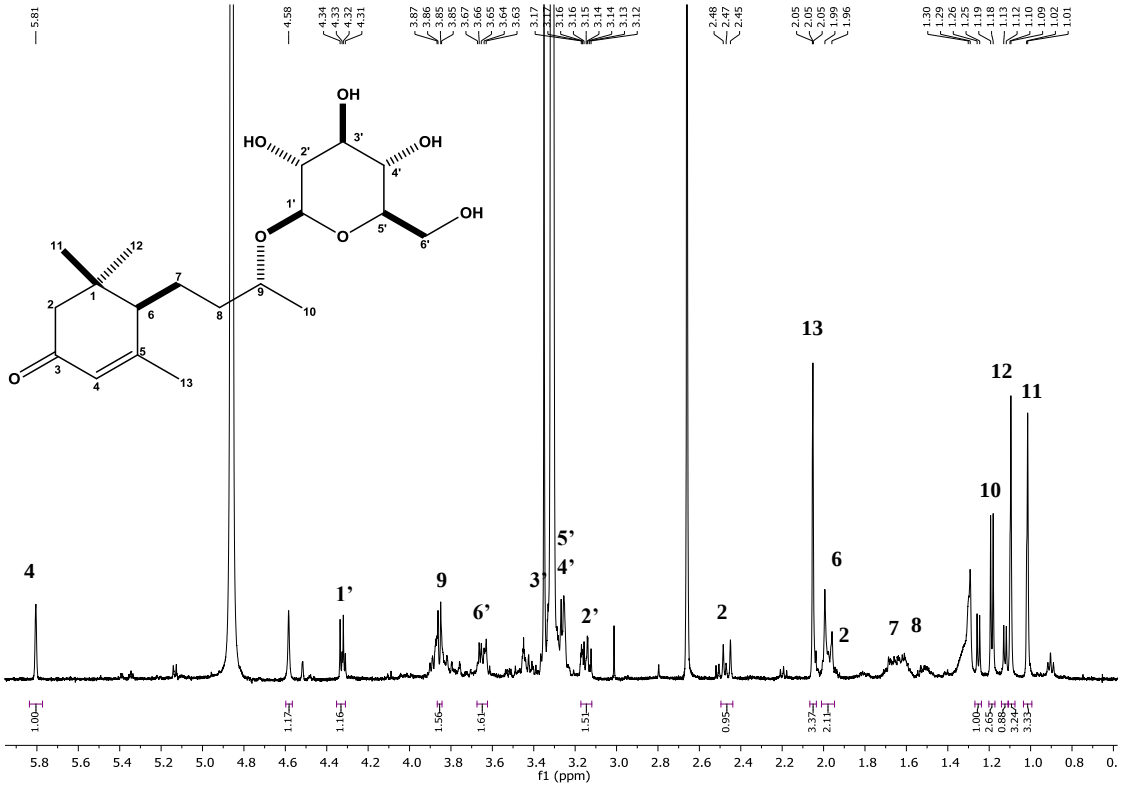


Figure S65. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **21**.

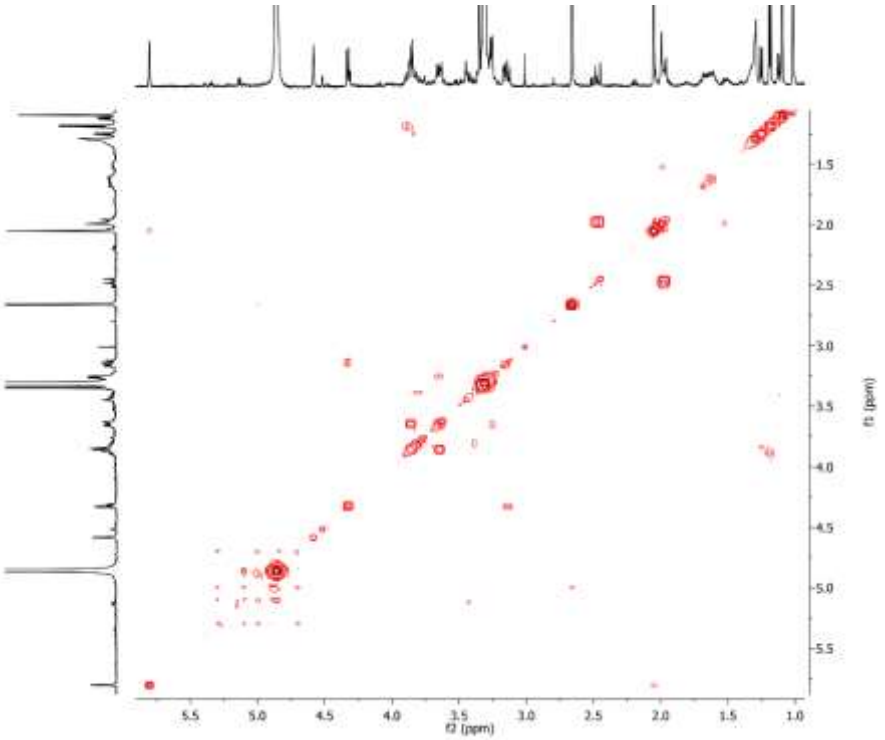


Figure S66. COSY NMR spectrum (500 MHz, CD_3OD) of compound **21**.

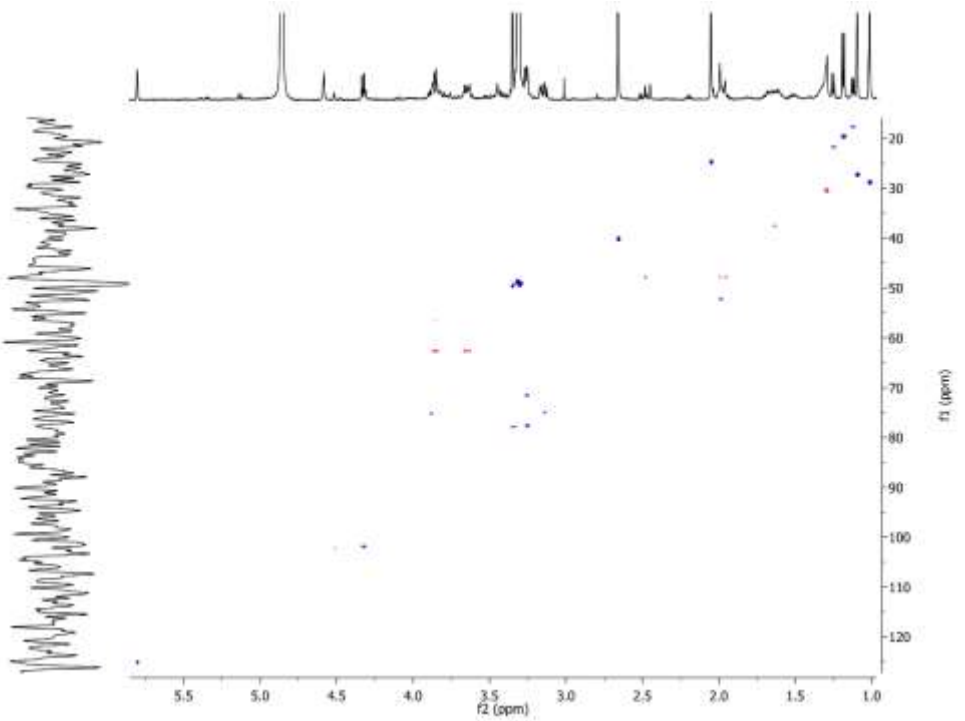


Figure S67. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **21**.

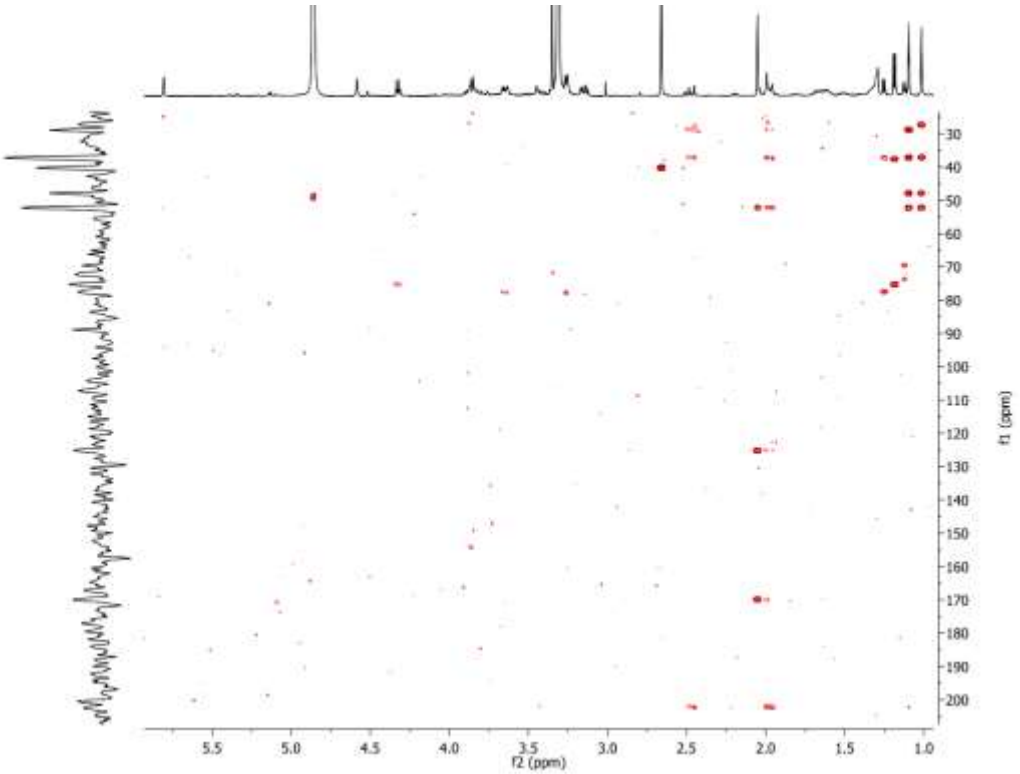


Figure S68. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **21**.

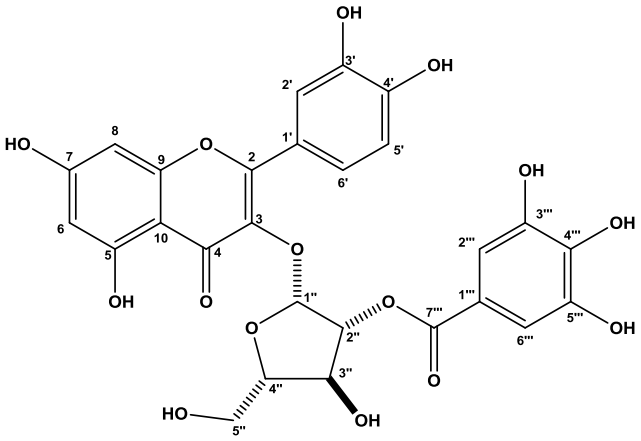


Table S23. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **22**

	HSQC		HMBC	
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$
2	n. d.	–		
3	n. d.	–		
4	n. d.	–		
5	162.8	–	6.21	
6	99.6	6.21 (d, 2.0 Hz, 1H)		6.40
7	165.6	–	6.40	
8	94.4	6.40 (d, 2.0 Hz, 1H)		6.21
9	n. d.	–		
10	105.3	–		6.21; 6.40
1'	122.8	–		
2'	116.2	7.55 (d, 1.9 Hz, 1H)		
3'	146.1	–	7.55	6.90
4'	149.6	–	6.90	7.55
5'	116.4	6.90 (d, 9.5 Hz, 1H)		
6'	122.8	7.54 (dd, 9.5 and 1.9 Hz, 1H)	6.90	7.55
1''	106.9	5.79 (s, 1H)		
2''	85.9	5.49 (dd, 2.7 and 0.7 Hz, 1H)		
3''	76.7	4.15 (dd, 2.7 and 5.8 Hz, 1H)	3.92	3.53
4''	87.6	3.92 (m, 1H)		
5''	61.7	3.53 (d, 3.6 Hz, 1H), 3.56 (d, 5.0 Hz, 1H)		
1'''	120.4	–	7.07	
2'''/6'''	109.9	7.07 (s, 1H)		7.07
3'''	146.2	–	7.07	
4'''	139.9	–		7.07
5'''	146.2	–	7.07	
7'''	166.9	–		5.49; 7.07

HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy; n.d.: not detected.

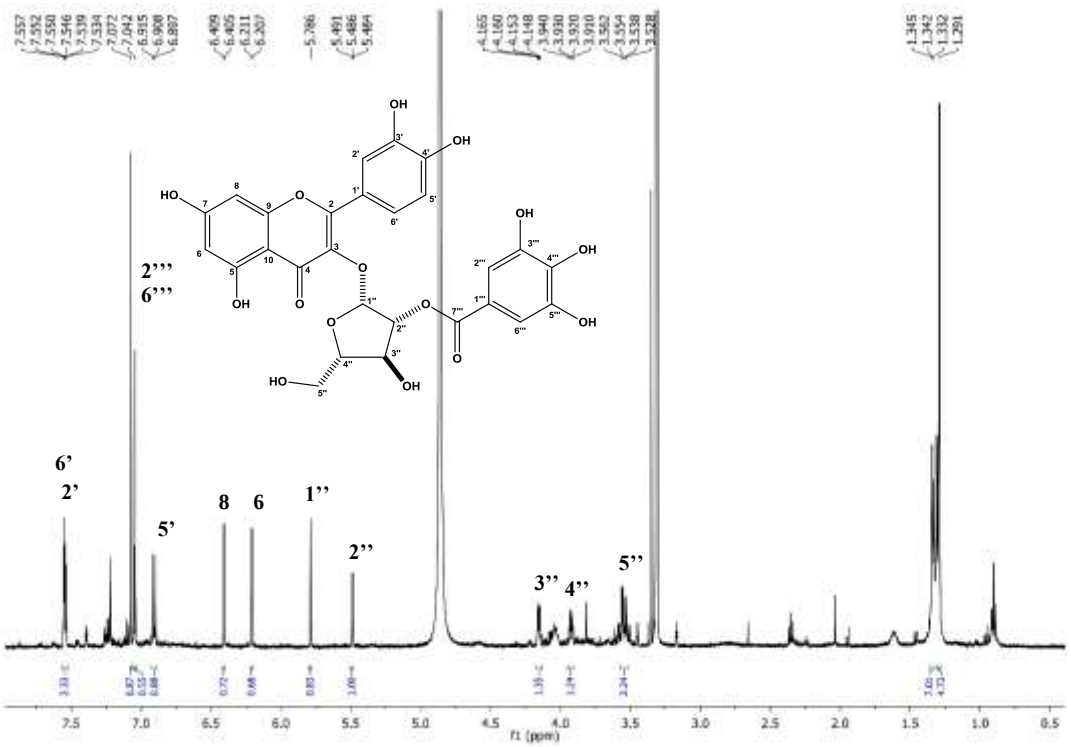


Figure S69. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **22**.

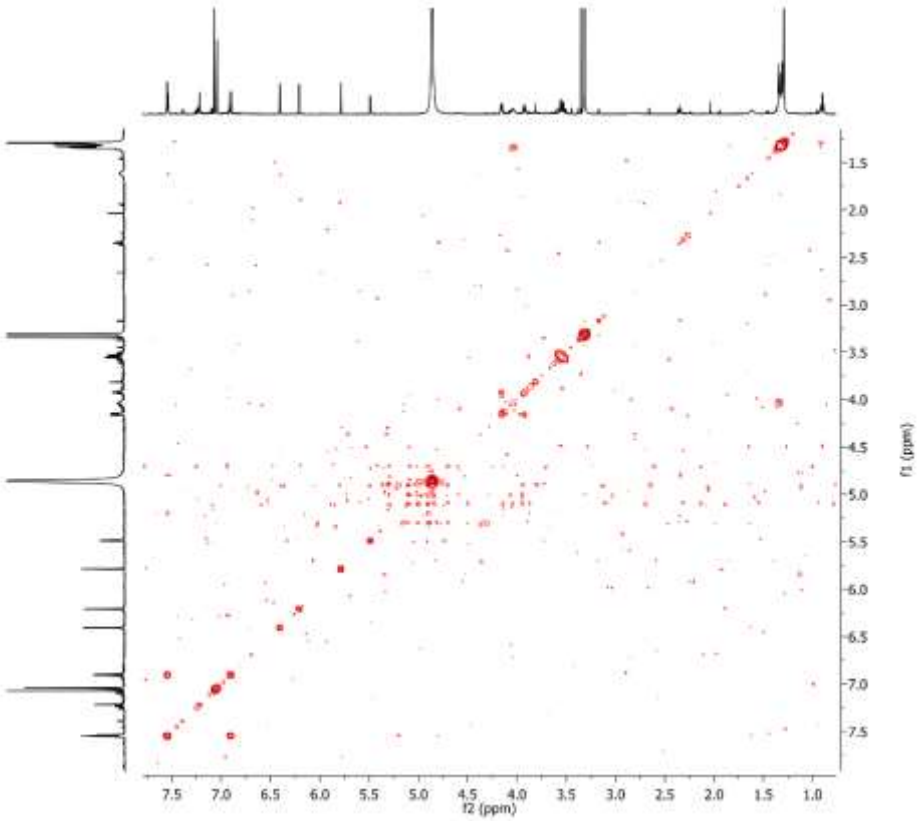


Figure S70. COSY NMR spectrum (500 MHz, CD_3OD) of compound **22**.

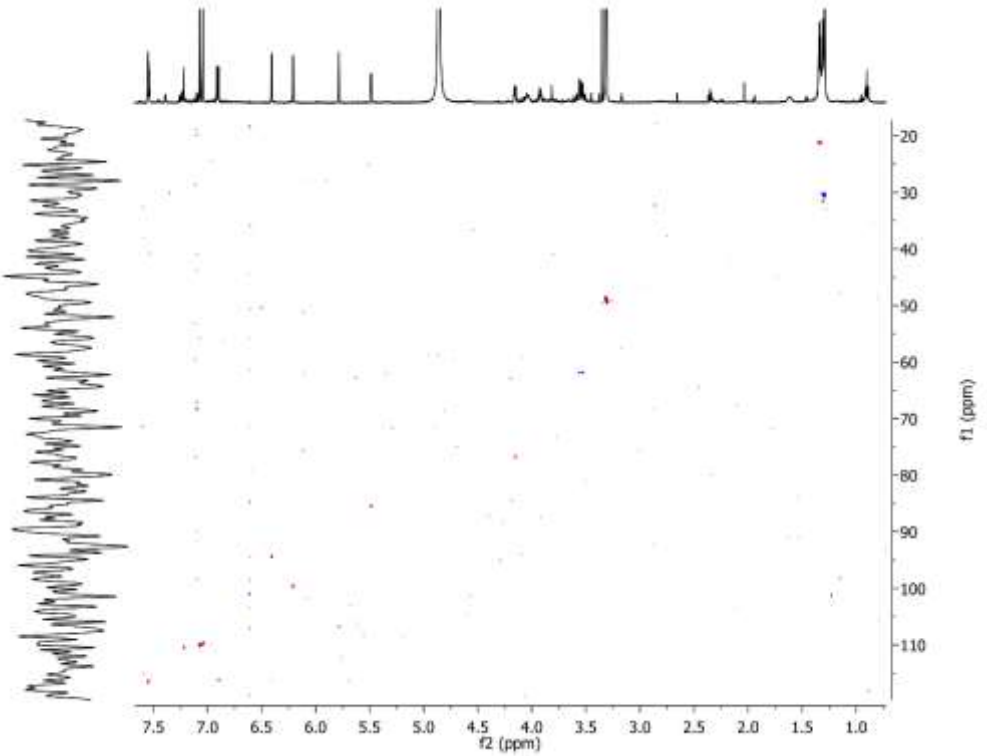


Figure S71. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **22**.

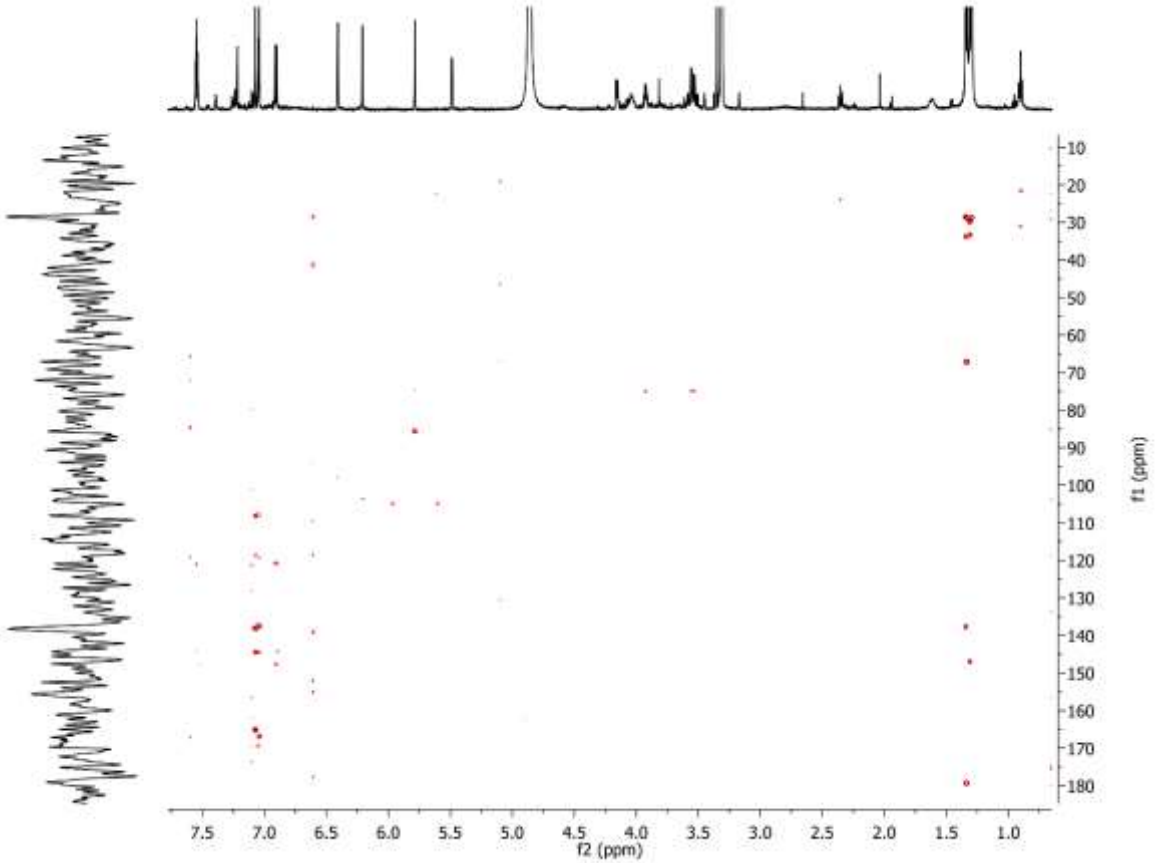


Figure S72. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **22**.

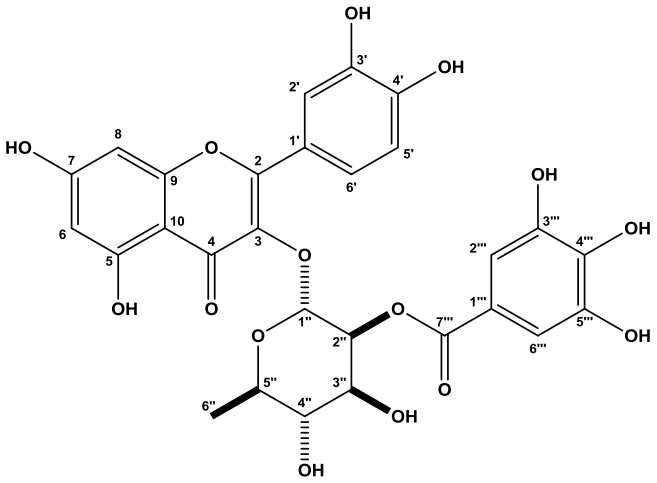


Table S24. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **23**

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(DMSO)
2	159.4	–		7.35	
3	135.8	–		5.50	
4	179.6	–			6.37
5	163.4	–	6.19		
6	100.0	6.19 (d, 2.0 Hz, 1H)		6.37	
7	166.1	–	6.37		
8	94.9	6.37 (d, 2.0 Hz, 1H)			
9	158.7	–	6.37		
10	106.0	–		6.19; 6.37	
1'		–			
2'	117.1	7.36 (d, 2.0 Hz, 1H)		7.35	
3'	146.6	–	7.36	6.94	
4'	150.0	–	6.94	7.35	
5'	116.6	6.94 (d, 8.0 Hz, 1H)			
6'	123.0	7.35 (dd, 8.0 and 2.0 Hz, 1H)	6.94	7.36	
1''	100.7	5.50 (d, 1.5 Hz, 1H)			
2''	73.6	5.62 (m, 1H)			
3''	70.9	4.01 (m, 1H)	5.62	5.50	
4''	73.9	3.47 (m, 1H)	4.01	1.03; 5.62	
5''	72.3	3.47 (m, 1H)	1.03; 3.47	5.50	
6''	18.0	1.03 (d, 5.0 Hz, 3H)		3.47	
1'''	121.4	–	7.07		
2'''/6'''	110.5	7.07 (s, 1H)		7.07	
3'''	146.6	–	7.07		
4'''	140.1	–		7.07	
5'''	146.6	–	7.07		
7'''	167.6	–		5.62; 7.07	

[a]Reference 21. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

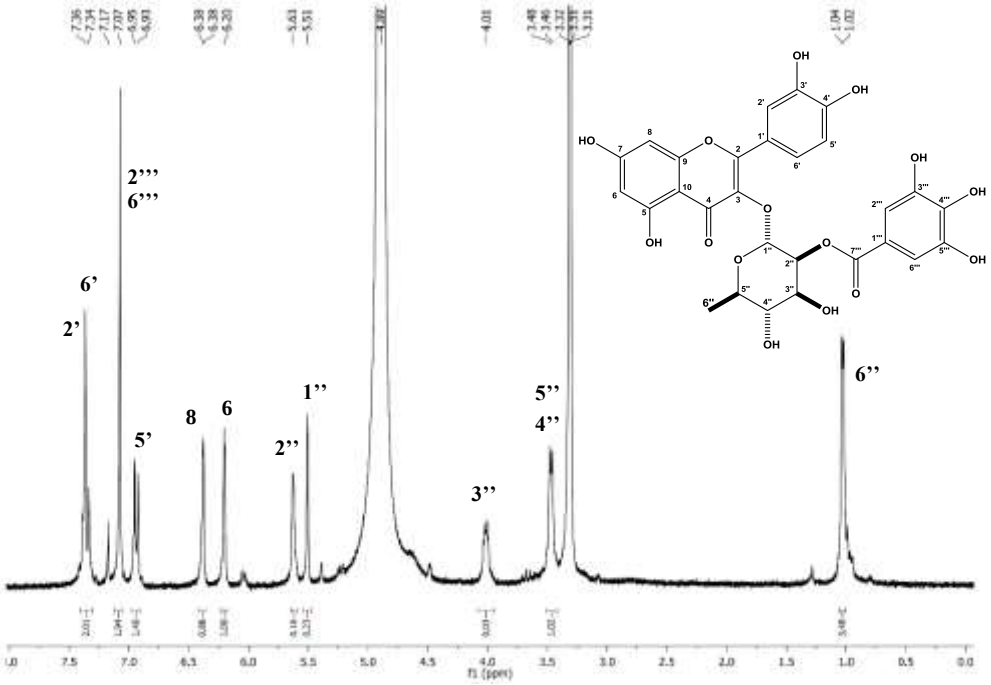


Figure S73. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **23**.

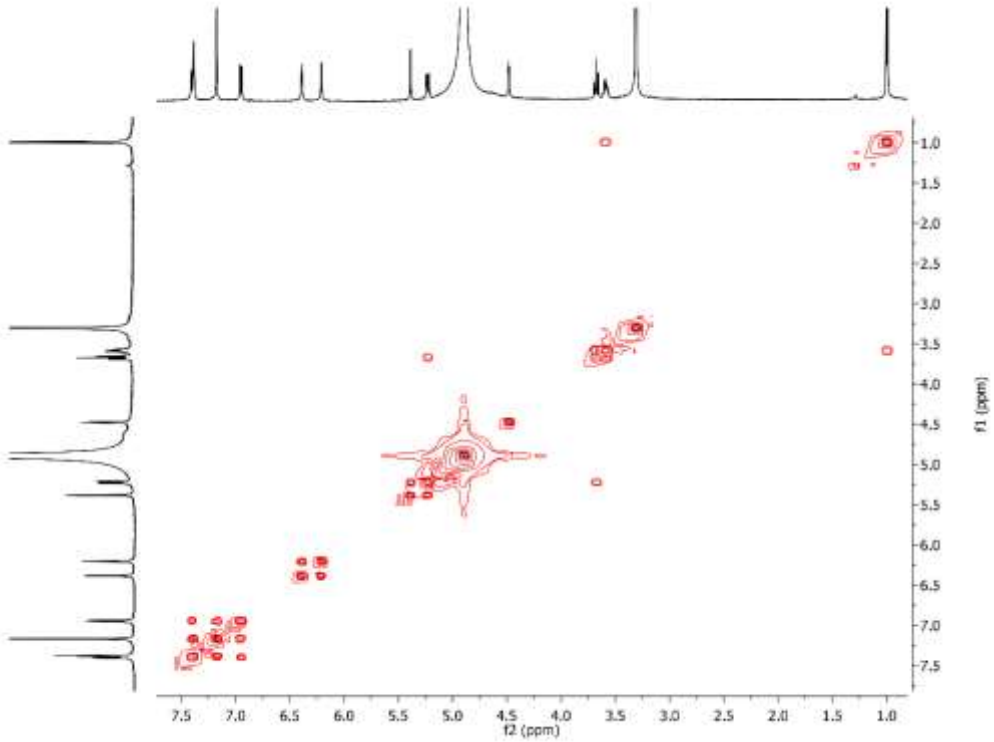


Figure S74. COSY NMR spectrum (500 MHz, CD_3OD) of compound **23**.

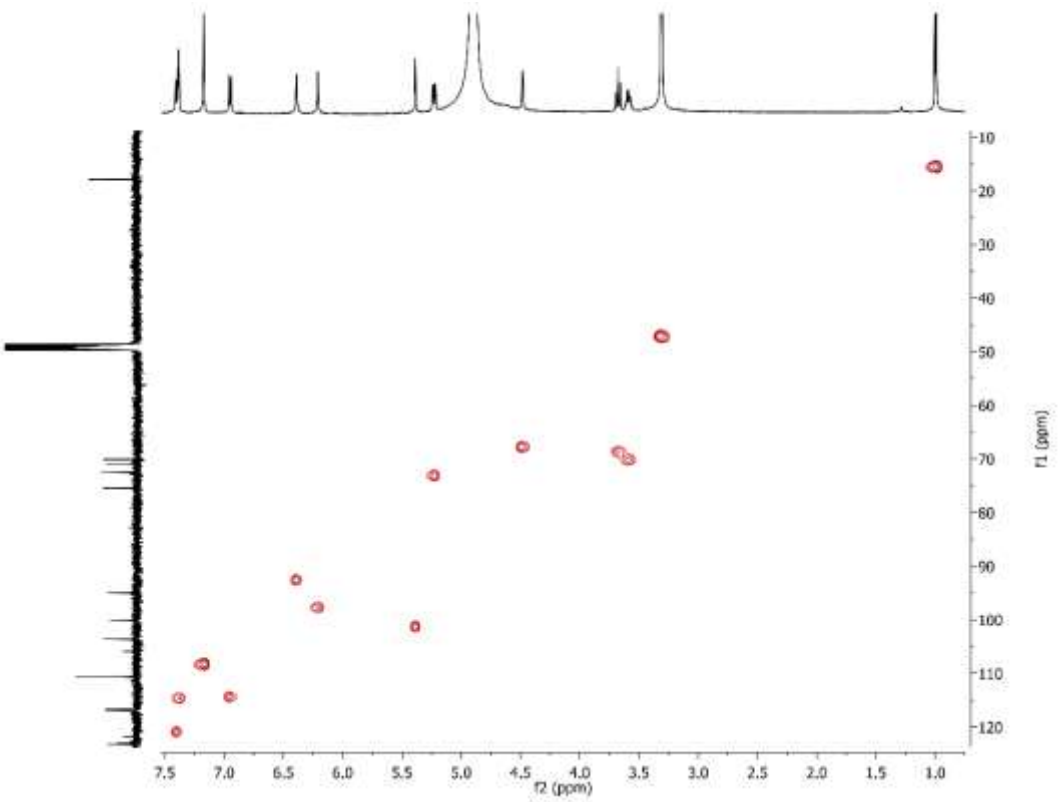


Figure S75. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **23**.

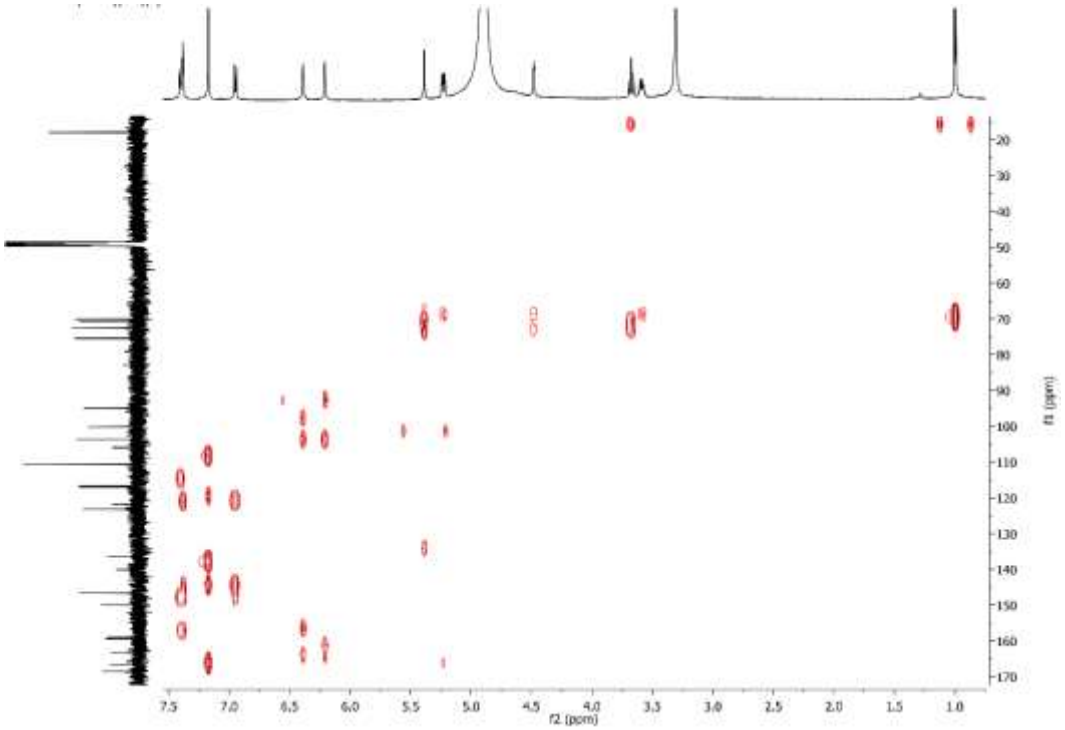


Figure S76. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **23**.

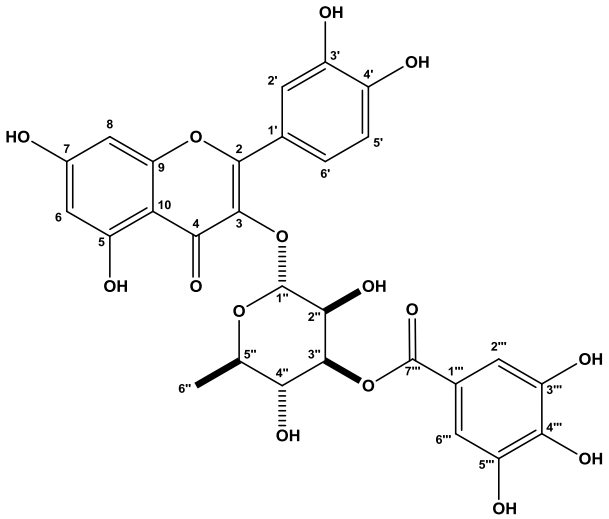


Table S25. ^{1}H and ^{13}C NMR (500 and 125 MHz, MeOD) data assignments (δ in ppm, J in Hz) for compound **24**

	HSQC		HMBC		Literature[a]
	δ_C	δ_H (mult, J, H)	$^{2}J_{CH}$	$^{3}J_{CH}$	(DMSO)
2	159.3	–		7.38; 7.39	
3	136.3	–		5.38	
4	179.6	–			6.38
5	163.3	–		6.20	
6	100.1	6.20 (s, 1H)		6.38	
7	166.5	–	6.20; 6.38		
8	95.0	6.38 (s, 1H)	6.20		
9	158.7	–			
10	105.9	–		6.20; 6.38	
1'	123.1	–	7.38	6.95	
2'	116.9	7.38 (m, 1H)		7.39	
3'	150.0	–	7.38	6.95	
4'	146.6	–	6.95	7.38; 7.39	
5'	116.9	6.95 (d, 8.5 Hz, 1H)	7.39		
6'	123.2	7.39 (m, 1H)			
1''	103.6	5.38 (d, 1.5 Hz, 1H)			
2''	70.1	4.48 (m, 1H)			
3''	75.4	5.22 (dd, 9.5 and 1.5 Hz, 1H)	3.67	3.58	
4''	70.9	3.67 (t, 9.5 Hz, 1H)	3.58; 5.22	1.00	
5''	72.4	3.58 (m, 1H)	1.00; 3.69	5.23	
6''	17.8	1.00 (d, 6.5 Hz, 1H)		3.67	
1'''	121.8		7.17		
2'''/6'''	110.6	7.17 (s, 1H)		7.17	
3'''/5'''	146.5		7.17		
4'''	140.0			7.17	
7'''	168.4			5.22; 7.17	

[a]Reference 22. HSQC: heteronuclear single quantum correlation spectroscopy; HMBC: heteronuclear multiple bond correlation spectroscopy.

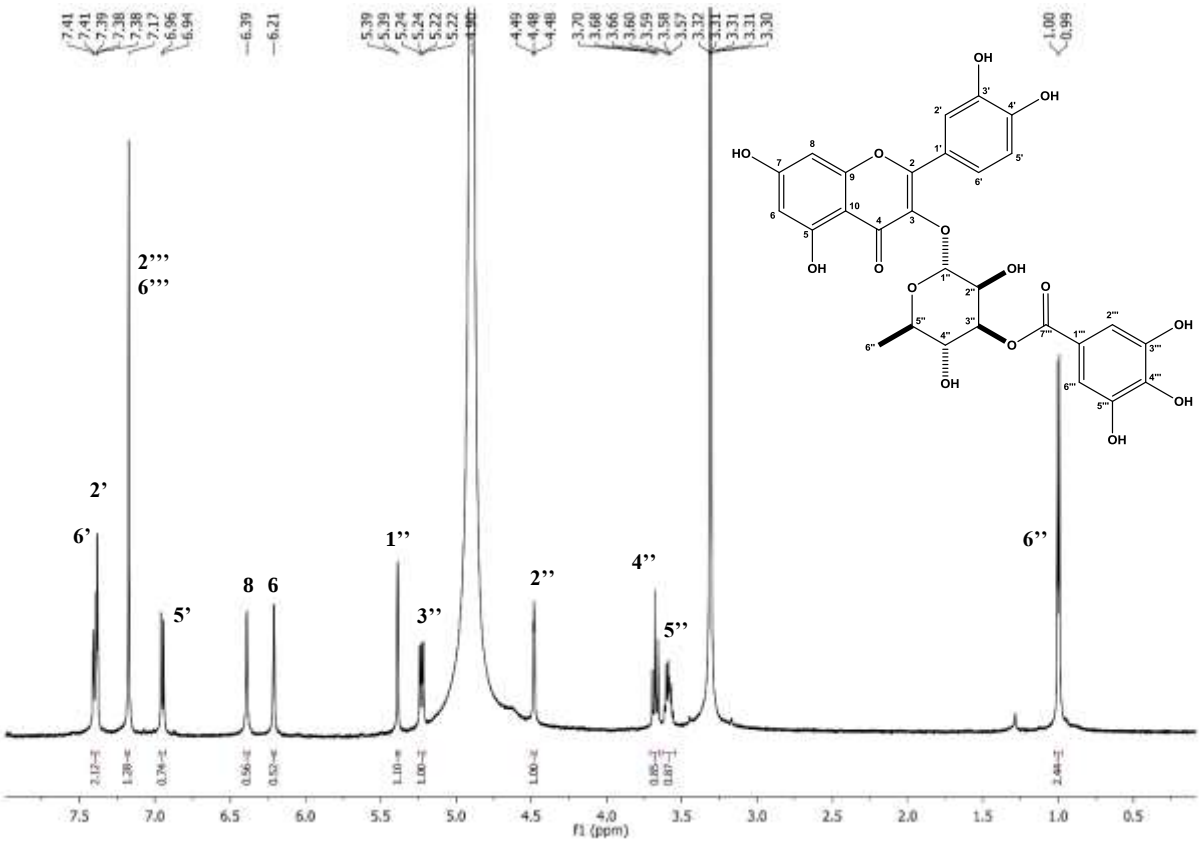


Figure S77. ^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **24**.

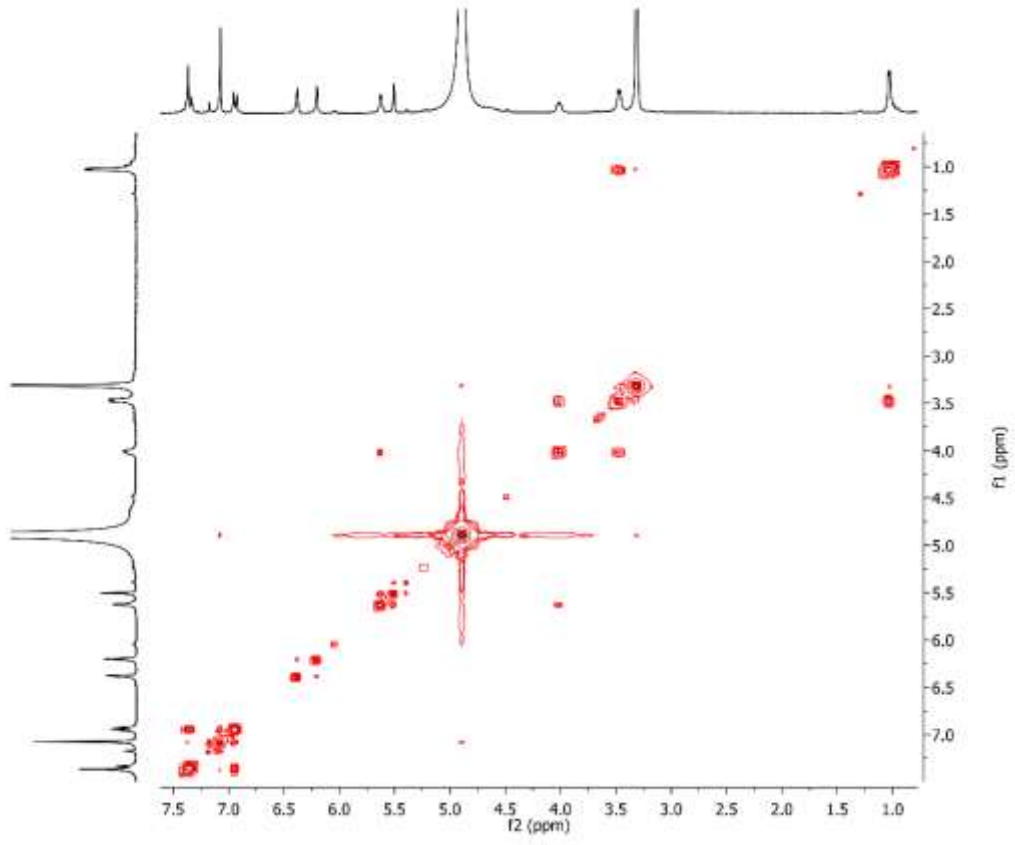


Figure S78. COSY NMR spectrum (500 MHz, CD_3OD) of compound **24**.

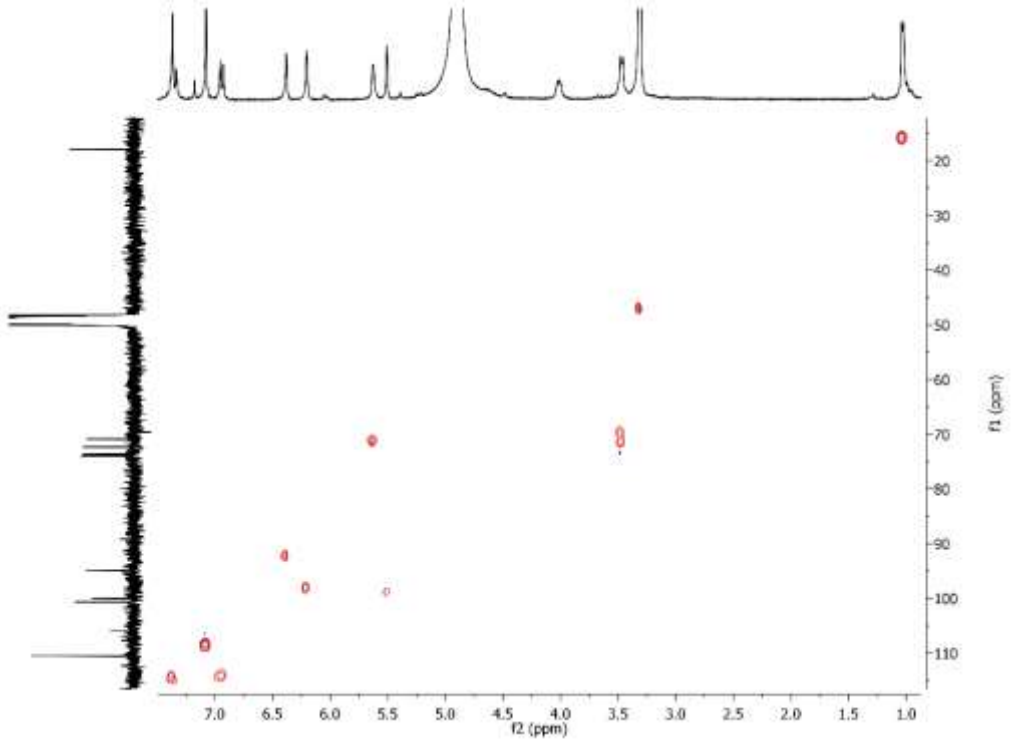


Figure S79. HSQC NMR spectrum (500 MHz, CD_3OD) of compound **24**.

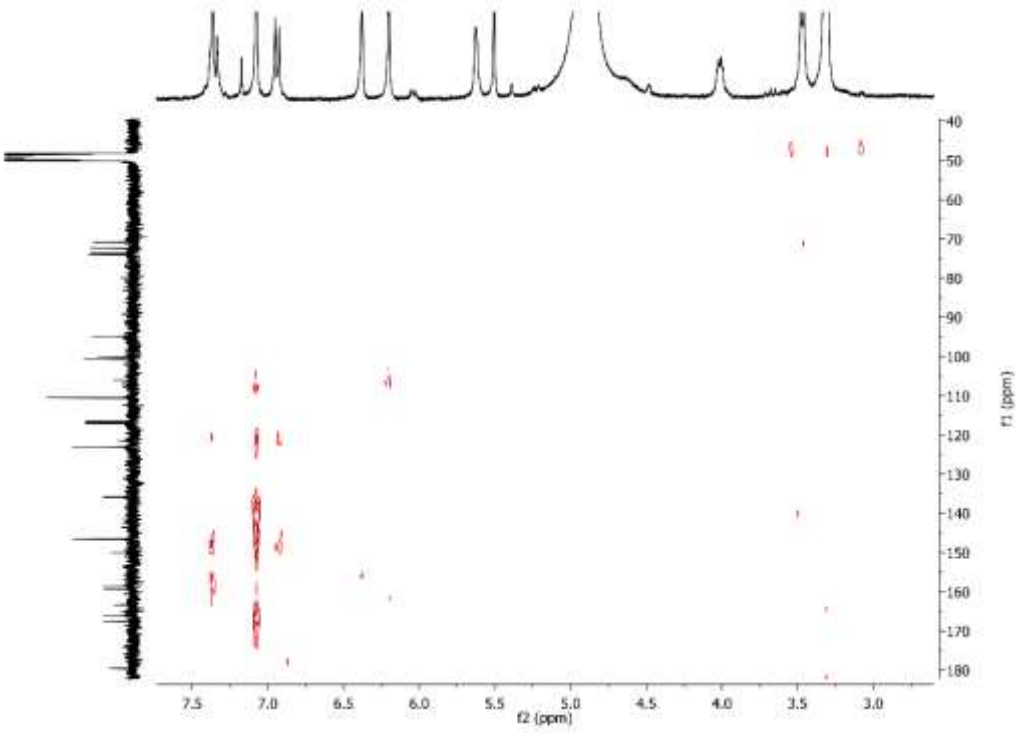


Figure S80. HMBC NMR spectrum (500 MHz, CD_3OD) of compound **24**.

References

1. Winkler, T.; *Magn. Reson. Chem.* **2006**, *44*, 571.
2. Kelley, C. J.; Harruff, R. C.; Carmack, M.; *J. Org. Chem.* **1976**, *41*, 449.
3. Moura, A. C. S.; Vilegas, W.; Santos, L. C.; *Quim. Nova* **2011**, *34*, 1136.
4. Kulkarni, A.; Suzuki, S.; Etoh, H.; *J. Wood Sci.* **2008**, *54*, 153.
5. Takac, M. J.-M.; Topić, D. V.; *Acta Pharm.* **2004**, *54*, 177.
6. Wang, K. J.; Yang, C. R.; Zhang, Y. J.; *Food Chem.* **2006**, *101*, 365.
7. Subeki; Matsuura, H.; Takahashi, K.; Yamasaki, M.; Yamato, O.; Maede, Y.; Katakura, K.; Kobayashi, S.; Trimurningsih; Chairul; Yoshihara, T.; *J. Nat. Prod.* **2005**, *68*, 537.
8. Lopes, E. L.; Andrade Neto, M.; Silveira, E. R.; Pessoa, O. D. L.; Braz-Filho, R.; *Quim. Nova* **2012**, *35*, 2169.
9. Wang, Y.; Yang, J.; Wang, A.; Ma, J.; Tian, J.; Ji, T.; Su, Y.; *Acta Pharm. Sin. B* **2013**, *3*, 46.
10. Piccinelli, A. L.; Mesa, M. G.; Armenteros, D. M.; Alfonso, M. A.; Arevalo, A. C.; Campone, L.; Rastrelli, L. ; *J. Agric. Food Chem.* **2008**, *56*, 1574.
11. Moon, J. H.; Tsushida, T.; Nakahara, K.; Terao, J.; *Free Radic. Biol. Med.* **2001**, *30*, 1274.
12. dos Santos, R. T.; Hiramoto, L. L.; Lago, J. H. G.; Sartorelli, P.; Tempone, A. G.; Pinto, E. G.; Lorenzi, H.; *Quim. Nova* **2012**, *35*, 2229.
13. Mencherini, T.; Campone, L.; Piccinelli, A. L.; García Mesa, M.; Sánchez, D. M.; Aquino, R. P.; Rastrelli, L.; *J. Agric. Food Chem.* **2013**, *61*, 1686.
14. Nishizawa, M.; Yamagishi, T.; Nonaka, G.; Nishioka, I.; Ragan, M. A.; *Phytochemistry* **1985**, *24*, 2411.
15. Matsunami, K.; Hideaki, O.; Takeda, Y.; *Chem. Pharm. Bull.* **2010**, *58*, 438.
16. de Sousa, E. A.; da Silva, A. A. C. A.; Cavalheiro, A. J.; Lago, J. H. G.; Chaves, M. H.; *J. Braz. Chem. Soc.* **2014**, *25*, 704.
17. Chang, S. W.; Kim, K. H.; Lee, I. K.; Choi, S. U.; Ryu, S. Y.; Lee, K. R.; *Nat. Prod. Sci.* **2009**, *15*, 234.
18. Yoshikawa, M.; Shimada, H.; Saka, M.; Yoshizumi, S.; Yamahara, J.; Matsuda, H.; *Chem. Pharm. Bull*. **1997**, *45*, 464.
19. Agrawal, P. K.; *Carbon-13 of Flavonoids*; Elsevier Science: New York, 1989.
20. Ye, M.; Yang, W. Z.; Liu, K. D.; Qiao, X.; Li, B.-J.; Cheng, J.; Feng, J.; Guo, D.-A.; Zho, Y.-Y.; *J. Pharm. Anal.* **2012**, *2*, 35.
21. Estrada, O.; Hasegawa, M.; Gonzalez-Mujíca, F.; Motta, N.; Perdomo, E.; Solorzano, A.; Méndez, J.; Méndez, B.; Zea, E G.; *Phytother. Res.* **2005**, *19*, 859.
22. Moharram, F. A.; Marzouk, M. S. A.; Ibrahim, M. T.; Mabry, T. J.; *Nat. Prod. Res.* **2006**, *20*, 927.