Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Efficient and selective glucosylation of prenylated phenolic compounds by *Mucor hiemalis*†

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Figure S64	HRESIMS spectrum of **22a**
Figure S65	HRESIMS spectrum of **24a**
Figure S66	^{1}H NMR spectrum of **1a** (600 MHz, DMSO-d_6)
Figure S67	^{13}C NMR spectrum of **1a** (150 MHz, DMSO-d_6)
Figure S68	HSQC spectrum of **1a** (600 MHz, DMSO-d_6)
Figure S69	HMBC spectrum of **1a** (600 MHz, DMSO-d_6)
Figure S70	^{1}H NMR spectrum of **4a** (400 MHz, DMSO-d_6)
Figure S71	^{13}C NMR spectrum of **4a** (100 MHz, DMSO-d_6)
Figure S72	HSQC spectrum of **4a** (400 MHz, DMSO-d_6)
Figure S73	HMBC spectrum of **4a** (400 MHz, DMSO-d_6)
Figure S74	^{1}H NMR spectrum of **7a** (400 MHz, DMSO-d_6)
Figure S75	^{13}C NMR spectrum of **7a** (100 MHz, DMSO-d_6)
Figure S76	HSQC spectrum of **7a** (400 MHz, DMSO-d_6)
Figure S77	HMBC spectrum of **7a** (400 MHz, DMSO-d_6)
Figure S78	^{1}H NMR spectrum of **8a** (400 MHz, DMSO-d_6)
Figure S79	^{13}C NMR spectrum of **8a** (100 MHz, DMSO-d_6)
Figure S80	HSQC spectrum of **8a** (400 MHz, DMSO-d_6)
Figure S81	HMBC spectrum of **8a** (400 MHz, DMSO-d_6)
Figure S82	^{1}H NMR spectrum of **9a** (400 MHz, DMSO-d_6)
Figure S83	^{13}C NMR spectrum of **9a** (100 MHz, DMSO-d_6)
Figure S84	HSQC spectrum of **9a** (400 MHz, DMSO-d_6)
Figure S85	HMBC spectrum of **9a** (400 MHz, DMSO-d_6)
Figure S86	^{1}H NMR spectrum of **10a** (600 MHz, DMSO-d_6)
Figure S87	^{13}C NMR spectrum of **10a** (150 MHz, DMSO-d_6)
Figure S88	HSQC spectrum of **10a** (600 MHz, DMSO-d_6)
Figure S89	HMBC spectrum of **10a** (600 MHz, DMSO-d_6)
Figure S90	^{1}H NMR spectrum of **16a** (400 MHz, DMSO-d_6)
Figure S91	^{13}C NMR spectrum of **16a** (100 MHz, DMSO-d_6)
Figure S92	HSQC spectrum of **16a** (400 MHz, DMSO-d_6)
Figure S93	HMBC spectrum of **16a** (400 MHz, DMSO-d_6)
Figure S94	^{1}H NMR spectrum of **16b** (400 MHz, DMSO-d_6)
Figure S95	^{13}C NMR spectrum of **16b** (100 MHz, DMSO-d_6)
Figure S96	HSQC spectrum of **16b** (400 MHz, DMSO-d_6)
Figure S97	HMBC spectrum of **16b** (400 MHz, DMSO-d_6)
Figure S98	^{1}H NMR spectrum of **16c** (400 MHz, DMSO-d_6)
Figure S99	^{13}C NMR spectrum of **16c** (100 MHz, DMSO-d_6)
Figure S100	HSQC spectrum of **16c** (400 MHz, DMSO-d_6)
Figure S101	HMBC spectrum of **16c** (400 MHz, DMSO-d_6)
Figure S102	^{1}H NMR spectrum of **19a** (400 MHz, DMSO-d_6)
Figure S103	^{13}C NMR spectrum of **19a** (100 MHz, DMSO-d_6)
Figure S104	HSQC spectrum of **19a** (400 MHz, DMSO-d_6)
Figure S105	HMBC spectrum of **19a** (400 MHz, DMSO-d_6)
Figure S106	^{1}H NMR spectrum of **22a** (400 MHz, DMSO-d_6)

Table S1. NMR spectroscopic data for compounds **1**, **10** (DMSO-d_6, 400 MHz), and **1a**, **10a** (DMSO-d_6, 600 MHz).

No.	**1**		**1a**		**10**		**10a**	
	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type
2		159.3, C		159.9, C	8.34 s	154.2, CH	8.38, s	154.5, CH
3		120.4, C		122.0, C		122.1, C		121.9, C
4	7.81 s	136.5, CH	7.87, s	135.9, CH		180.1, C		180.0, C
5		156.1, C		154.7, C		162.0, C		162.0, C
6		118.4, C		120.1, C	6.22 d (1.6)	99.0, CH	6.23, d (2.0)	99.1, CH
7		160.1, C		158.3, C		164.3, C		164.4, C
8	6.61 s	98.0, CH	6.95, s	98.4, CH	6.38 d (1.6)	93.7, CH	6.40, d (2.0)	93.7, CH
9		153.0, C		152.8, C		157.5, C		157.5, C
10		106.3, C		108.1, C		104.4, C		104.4, C
1′		113.5, C		113.2, C		122.7, C		122.6, C
2′		155.3, C		156.1, C	6.73 d (1.6)	117.5, CH	7.01 d (0.8)	121.8, CH
3′	6.37 br s	102.7, CH	6.38, d (2.4)	102.7, CH		145.1, C		145.2, C
4′		158.4, C		158.6, C		140.1, C		142.0, C
5′	6.25 d (8.4)	106.1, CH	6.28, dd (8.4, 2.4)	106.3, CH		121.4, C		120.6, C
6′	7.11 d (8.4)	131.6, CH	7.14, d (8.4)	131.6, CH	6.91 d (1.6)	122.0, CH	7.15 d (0.8)	121.7, CH
1″	3.23 d (6.0)	22.3, CH_2	3.46, m; 3.27, m	22.5, CH_2	6.37 d (9.6)	117.0, CH	6.42, d (10.0)	117.9, CH
2″	5.15 t (6.0)	122.7, CH	5.21, t (7.2)	122.6, CH	5.76 d (9.6)	131.3, CH	5.79, d (10.0)	131.5, CH
3″		130.7, C		130.8, C		76.0, C		76.4, C
4″	1.63 s	25.5, CH_3	1.63, s	25.5, CH_3	1.39 s	27.5, CH_3	1.41, s	27.6, CH_3
5″	1.73 s	17.7, CH_3	1.75, s	17.8, CH_3	1.39 s	27.5, CH_3	1.40,s	27.3, CH_3

1‴			4.98, d (7.8)	100.7, CH	4.83, d (7.2)	100.7, CH
2‴			3.31, d (6.0)	73.4, CH	3.28, d (5.6)	73.2, CH
3‴			3.31, d (6.0)	76.8, CH	3.28, d (5.6)	76.5, CH
4‴			3.18, br s	69.8, CH	3.18, br s	69.7, CH
5‴			3.46, m	77.2, CH	3.33, m	77.1, CH
6‴			3.75, d (10.2); 3.47, m	60.8, CH_2	3.69, d (11.6); 3.50, m	60.7, CH_2
OCH_3	3.76 s	62.8, CH_3	3.79, s	63.0, CH_3		

Table S2. NMR spectroscopic data for compounds **19**, **19a**, **4a**, **24a**, **7** and **7a** (DMSO-d_6, 400 MHz).

No.	**4a**		**24a**		**19**		**19a**		**7**		**7a**	
	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type
2	5.46, s	64.2, CH_2	5.45, m	79.2, CH		146.6, C		147.4, C	8.25, s	155.7, CH	8.48, s	154.7, CH
3		107.4, C	3.16, m; 2.64, br d (16.0)	43.2, CH_2		135.0, C		136.0, C		122.7, C		122.0, C
4		144.2, C		190.6, C		175.9, C		176.1, C		181.4, C		180.9, C
5		152.9, C	7.48, s	126.1, CH		159.1, C		159.4, C		160.9, C		159.8, C
6		117.6, C		124.1, C		110.2, C		111.8, C	6.37, s	98.8, CH	6.62, s	98.2, CH
7		156.3, C		161.4, C		161.7, C		160.6, C		161.6, C		160.5, C
8	6.57, s	100.1, CH	6.68, s	102.4, CH	6.49 s	92.8, CH	6.87, s	93.1, CH		106.7, C		108.2, C
9		152.7, C		161.2, C		154.0, C		154.0, C		153.8, C		154.1, C
10		104.9, C		114.6, C		102.8, C		104.4, C		105.7, C		105.9, C
1′		116.9, C		129.1, C		121.8, C		122.2, C		123.2, C		121.1, C
2′		155.5, C	7.33, d (8.4)	128.4, CH	8.03 d (8.8)	129.5, CH	8.07, d (8.8)	129.6, CH	7.47, d (9.0)	130.6, CH	7.40, d (8.4)	130.2, CH
3′	7.00, d (2.0)	98.0, CH	6.79, d (8.4)	115.1, CH	6.92 d (8.8)	115.4, CH	6.94, d (8.8)	115.5, CH	6.90, d (9.0)	115.4, CH	6.82, d (8.4)	115.1, CH
4′		156.1, C		157.7, C		157.4, C		156.8, C		157.8, C		157.5, C
5′	6.77, dd (8.4, 2.0)	112.4, CH	6.79, d (8.4)	115.1, CH	6.92 d (8.8)	115.4, CH	6.94, d (8.8)	115.5, CH	6.90, d (9.0)	115.4, CH	6.82, d (8.4)	115.1, CH
6′	7.34, d (8.4)	119.2, CH	7.33, d (8.4)	128.4, CH	8.03 d (8.8)	129.5, CH	8.07, d (8.8)	129.6, CH	7.47, d (9.0)	130.6, CH	7.40, d (8.4)	130.2, CH
1″	3.44, m; 3.25, m	22.2, CH_2	3.27, m	27.2, CH_2	3.24 d (7.2)	21.0, CH_2	3.44, m; 3.20, m	21.2, CH_2	3.45, d (6.9)	21.5,CH_2	3.58, m; 3.30, br s	21.3, CH_2
2″	5.21, t (6.4)	123.5, CH	5.32, m	122.2, CH	5.19 t (7.2)	122.3, CH	5.23, t (7.2)	121.6, CH	5.23, t (6.8)	122.5, CH	5.17, br s	122.2, CH
3″		129.9, C		132.1, C		130.6, C		130.7, C		131.5, C		131.2, C
4″	1.63, s	25.5, CH_3	1.67, s	25.6, CH_3	1.65 s	25.5, CH_3	1.62, s	25.5, CH_3	1.66, s	25.3, CH_3	1.62, s	25.5, CH_3

5″	1.75, s	17.7, CH_3	1.71, s	17.6, CH_3	1.76 s	17.7, CH_3	1.75, s	17.8, CH_3	1.81, s	17.4, CH_3	1.78, s	17.8, CH_3
1‴	4.80, d (7.2)	101.0, CH	4.95, m	100.1, CH			5.04, d (6.8)	100.4, CH			5.00, d (6.4)	100.5, CH
2‴	3.28, m	73.4, CH	3.27, m	73.3, CH			3.31, m	73.4, CH			3.30, br s	73.4, CH
3‴	3.27, m	76.7, CH	3.27, m	76.5, CH			3.30, m	76.8, CH			3.30, br s	76.6, CH
4‴	3.14, m	69.7, CH	3.12, br s	69.6, CH			3.17, m	69.7, CH			3.16, d (4.8)	69.7, CH
5‴	3.37, m	77.1, CH	3.36, m	77.0, CH			3.47, m	77.2, CH			3.41, m	77.2, CH
6‴	3.71, d (9.6); 3.45, m	61.7, CH_2	3.67, m; 3.43, m	60.6, CH_2			3.73, m; 3.47, d (7.6)	60.7, CH_2			3.71, m; 3.44, m	60.6, CH_2
OCH_3	3.76, s	58.1, CH_3										

Table S3. NMR spectroscopic data for compounds **8**, **8a**, **9**, **9a**, **22**, **22a** (DMSO-d_6, 400 MHz).

No.	**8**		**8a**		**9**		**9a**		**22**		**22a**	
	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type
2	8.11 s	155.5, CH	8.23, s	156.2, CH	8.08 s	154.9, CH	8.16, s	155.2, CH		146.5, C		155.4, C
3		121.0, C		121.2, C		119.7, C		119.6, C		136.2, C		133.3, C
4		181.0, C		181.4, C		179.9, C		179.9, C		176.7, C		177.8, C
5		158.6, C		157.9, C		161.9, C		161.9, C		158.5, C		158.5, C
6		111.0, C		112.6, C	6.18 br s	99.2, CH	6.23, d (1.8)	99.0, CH	6.30, s	98.2, CH	6.30, s	98.3, CH
7		162.0, C		160.6, C		165.4, C		164.3, C		161.8, C		161.7, C
8	6.44 s	92.8, CH	6.79, s	93.2, CH	6.33 br s	93.8, CH	6.40, d (1.8)	93.8, CH		107.3, C		107.0, C
9		155.5, C		155.5, C		157.7, C		157.6, C		153.9, C		153.6, C
10		104.4, C		106.0, C		103.9, C		104.3, C		103.5, C		104.0, C
1′		109.6, C		109.4, C		109.7, C		107.1, C		124.0, C		122.8, C
2′		154.9, C		154.0, C		151.4, C		151.1, C	8.23, d (9.0)	129.7, CH	8.23, d (9.2)	130.7, CH
3′		115.3, C		115.3, C		109.0, C		112.6, C	7.09, d (9.0)	114.5, CH	7.06, d (9.2)	113.7, CH
4′		156.3, C		156.4, C		153.4, C		153.1, C		160.9, C		161.2, C
5′	6.36 d (8.0)	106.6, CH	6.38, d (8.4)	106.6, CH	6.41 d (8.4)	107.3, CH	6.72, d (8.4)	111.1, CH	7.09, d (9.0)	114.5, CH	7.06, d (9.2)	113.7, CH
6′	6.73 d (8.0)	128.7, CH	6.75, d (8.4)	128.7, CH	6.92 d (8.4)	131.3, CH	7.05, d (8.4)	131.3, CH	8.23, d (9.0)	129.7, CH	8.23, d (9.2)	130.7, CH
1″	3.23 d (7.6)	21.0, CH_2	3.46, m; 3.24 m	21.3, CH_2	6.60 d (10.0)	116.8, CH	6.79, d (9.6)	116.8, CH	2.71, t (8.0)	17.8, CH_2	2.75, t (8.4)	17.4, CH_2
2″	5.18 t (7.6)	122.2, CH	5.20, m	122.1, CH	5.63 d (10.0)	128.5, CH	5.70, d (9.6)	129.6, CH	1.57, t (8.0)	43.3, CH_2	1.56, t (8.4)	42.9, CH_2
3″		130.7, C		130.8, C		75.8, C		76.0, C		68.7, C		68.8, C
4″	1.62 s	25.5, CH_3	1.61, s	25.6, CH_3	1.30 s	27.5, CH_3	1.30, s	27.6, CH_3	1.20, s	29.6, CH_3	1.17, s	29.1, CH_3
5″	1.71 s	17.8, CH_3	1.71, s	18.7, CH_3	1.30 s	27.5, CH_3	1.30, s	27.6, CH_3	1.20, s	29.6, CH_3	1.17, s	29.1, CH_3
1‴	3.25 d (7.6)	22.4, CH_2	3.24, m	22.4, CH_2								

2‴	5.17 t (7.6)	123.5, CH	5.20, m	123.5, CH						
3‴		129.5, C		129.5, C						
4‴	1.62 s	25.5, CH_3	1.61, s	25.6, CH_3						
5‴	1.72 s	17.7, CH_3	1.74, s	17.3, CH_3						
1⁗			5.03, d (6.4)	100.4, CH	4.91, d (7.2)	100.9, CH			5.50, d (7.2)	101.0, CH
2⁗			3.26, m	73.4, CH	3.25, m	73.3, CH			3.22, m	74.2, CH
3⁗			3.26, m	76.7, CH	3.25, m	76.9, CH			3.22, m	76.4, CH
4⁗			3.17, m	69.7, CH	3.16, br s	69.8, CH			3.10, br s	69.9, CH
5⁗			3.46, m	77.3, CH	3.27, m	77.1, CH			3.10, br s	77.5, CH
6⁗			3.72, m; 3.44, m	60.7, CH_2	3.68, d (10.8); 3.45, m	60.7, CH_2			3.57, m; 3.35, br s	60.8, CH_2
OCH_3							3.85, s	55.8, CH_3	3.85, s	55.4, CH_3

Table S4. NMR spectroscopic data for compounds **16**, **16a**, **16b** and **16c** (DMSO-d_6, 400 MHz).

No.	**16**		**16a**		**16b**		**16c**	
	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)	δ_C, type
2	4.08 br d (10.0) 3.85 t (10.0)	69.3, CH_2	4.10, br d (10.0); 3.92, t (10.0)	69.1, CH_2	4.11, br d (10.4); 3.88, t (10.4)	69.4, CH_2	4.23, br d (10.4); 3.73, t (10.4)	69.6, CH_2
3	3.31 m	30.5, CH	3.32, br s	30.5, CH	3.35, br s	30.4, CH	3.63, br s	29.7, CH
4	2.77 dd (4.0, 16.0) 2.61 dd (10.8, 16.0)	26.2, CH_2	2.79, dd (15.6, 4.4); 2.63 m	26.2, CH_2	2.80, m; 2.67, m	26.1, CH_2	2.60, m	27.4, CH_2
5		156.8, C		156.8, C		156.5, C		156.8, C
6		113.1, C		113.1, C		115.4, C		112.9, C
7		154.4, C		154.4, C		154.9, C		154.9, C
8	6.09 s	98.6, CH	6.10, s	98.7, CH	6.39, s	99.3, CH	6.09, s	98.7, CH
9		152.9, C		152.5, C		152.9, C		152.8, C
10		106.8, C		107.0, C		109.8, C		107.0, C
1′		119.7, C		124.2, C		119.5, C		121.4, C
2′		154.4, C		154.9, C		154.5, C		154.3, C
3′		115.9, C		118.7, C		116.0, C		126.5, C
4′		152.9, C		152.9, C		153.1, C		153.0, C
5′	6.33 d (8.4)	107.1, CH	6.62, d (8.4)	106.7, CH	6.34, d (8.4)	107.2, CH	6.62, d (8.4)	111.7, CH
6′	6.73 d (8.4)	123.9, CH	6.87, d (8.4)	123.4, CH	6.74, d (8.4)	124.0, CH	6.87, d (8.4)	124.6, CH
1″	3.14 m	22.3, CH_2	3.14, m	22.3, CH_2	3.18, d (6.4)	22.4, CH_2	3.15, m	22.2, CH_2
2″	5.13 t (6.0)	123.6, CH	5.13, t (6.8)	122.9, CH	5.15, m	123.6, CH	5.13, t (7.2)	124.0, CH
3″		129.2, C		129.2, C		129.3, C		129.1, C
4″	1.62 s	25.5, CH_3	1.61, s	25.5, CH_3	1.61, s	25.5, CH_3	1.62, s	25.4, CH_3
5″	1.69 s	17.7, CH_3	1.69, s	17.7, CH_3	1.71, s	17.7, CH_3	1.69, s	17.6, CH_3

1‴	3.26 d (6.8)	22.5, CH_2	3.52, m; 3.30, br s	22.6, CH_2	3.27, d (6.4)	22.5, CH_2	3.52, m; 3.30, br s	23.0, CH_2
2‴	5.15 t (6.8)	124.2, CH	5.18, t (6.8)	124.2, CH	5.19, m	124.2, CH	5.18, t (7.2)	124.3, CH
3‴		129.5, C		129.7, C		129.6, C		129.5, C
4‴	1.62 s	25.5, CH_3	1.61, s	25.6, CH_3	1.61, s	25.5, C_{H3}	1.62, s	25.5, CH_3
5‴	1.71 s	17.8, CH_3	1.73, s	17.9, CH_3	1.71, s	17.8, CH_3	1.71, s	18.0, CH_3
1⁗			4.71, d (7.6)	101.3, CH	4.71, d (6.8)	101.3, CH	4.46, d (7.6)	104.7, CH
2⁗			3.24, m	73.5, CH	3.17, br s	73.4, CH_2	3.22, m	73.8, CH
3⁗			3.24, m	77.0, CH	3.17, br s	76.9, CH	3.13, m	76.3, CH
4⁗			3.14, m	69.8, CH	3.14 m	69.8, CH	2.99, m	70.1, CH
5⁗			3.32, br s	77.0, CH	3.26, m	77.1, CH	2.97, m	77.4, CH
6⁗			3.69, br d (11.2); 3.46, m	60.0, CH_2	3.70, d (10.0); 3.43, m	60.1, CH_2	3.72, m; 3.35, br s	61.4, CH_2
OCH_3	3.60 s	59.9, CH_3	3.60, s	60.8, CH_3	3.63, s	60.8, CH_3	3.57, s	59.9, CH_3

Table S5. Screening of fungal strains for the glucosylation of glycycoumarin (**1**).

Species	**Conversion (%)**
Absidia coerulea AS 3.3389	0
Alternaria alternata AS 3.4578	100
Alternaria alternata AS 3.577	100
Aspergillus candidus IFFI 2360	0
Aspergillus carbonarius IFFI 2087	70
Aspergillus flavus AS 3.3554	0
Aspergillus niger AS 3.795	95
Botrytis pyramidalis AS 3.193	45
Crebrothecium ashbyii ACCC 2114	0
Cunninghamella blakesleana AS 3.970	0
Cunninghamella elegans AS 3.2028	90
Doratomyces stemonitis AS 3.1411	100
Fusarium oxysporum AS 3.3633	0
Gibberella pulicaris AS 3.4602	0
Mucor circinelloides f. *circinelloides* AS 3.3434	50
Mucor circinelloides f. *circinelloides* AS 3.2489	75
Mucor fragilis AS 3.2215	60
Mucor hiemalis CGMCC 3.14114	100
Mucor rouxianus AS 3.3447	90
Mucor spinosus AS 3.2450	75
Mucor spinosus AS 3.3450	0
Mucor subtilissimus AS 3.2456	90
Penicillium crticae IFFI 4015	0
Penicillium melinii AS 3.4474	0
Phoma pomorum AS 3.2886	0
Rhizopus chinensis IFFI 3043	0

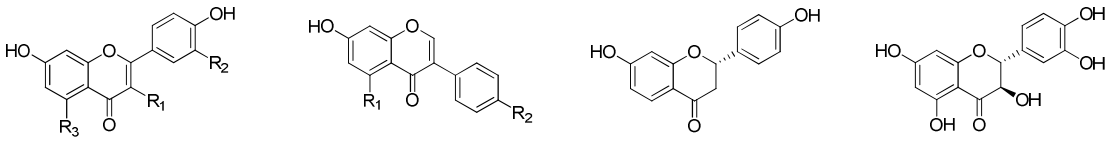
Table S6. Glucosylation of compounds **1**-**35** by *Mucor hiemalis*.

Substrates	Conversion (%)	Major products (%)	Minor products (%)
1*	100%	7-*O*-glucoside (**1a**, 100%)$^{\Delta}$	-
2	100%	*O*-glucoside (100%)	-
3	30	*O*-glucosyl-*O*-sulfate (25%)	*O*-sulfate (5%)
4*	100%	7-*O*-glucoside (**4a**, 93%)$^{\Delta}$	-OH-*O*-glucoside (7%)
5*	94%	7-*O*-glucoside (**5a**, 94%)	-
6*	100%	7-*O*-glucoside (**6a**, 100%)	-
7*	94%	7-*O*-glucoside (**7a**, 94%)$^{\Delta}$	-
8*	95%	7-*O*-glucoside (**8a**, 64%)$^{\Delta}$	di-*O*-glucoside (31%)
9*	97%	4′-*O*-glucoside (**9a**, 97%)$^{\Delta}$	-
10*	100%	3′-*O*-glucoside (**10a**, 100%)$^{\Delta}$	-
11	99%	*O*-glucoside (93%)	*O*-glucoside (6%)
12	100%	*O*-glucoside (100%)	-
13	100%	*O*-glucoside (100%)	-
14	98%	*O*-glucoside (98%)	-
15	100%	*O*-glucoside (65%)	*O*-glucoside (35%)
16*	95%	2′-*O*-glucoside (**16a**, 15%)$^{\Delta}$; 7-*O*-glucoside (**16b**)$^{\Delta}$ and 4′-*O*-glucoside (**16c**)$^{\Delta}$ (72% in total)	di-*O*-glucoside (8%)
17	93%	*O*-glucoside (77%)	*O*-glucoside (16%)
18*	100%	7-*O*-glucoside (**18** 95%)	*O*-glucosyl-*O*-sulfate (5%)
19*	100%	7-*O*-glucoside (**19a**, 100%)$^{\Delta}$	-
20*	100%	7-*O*-glucoside (**20a**, 100%)	-
21	94%	*O*-glucoside (62%)	*O*-glucoside (28%); *O*-sulfate (4%)
22*	72	3-*O*-glucoside (**22a**, 66%)$^{\Delta}$	*O*-glucoside (6%)
23	100%	*O*-glucoside (100%)	-
24*	100%	7-*O*-glucoside (**24a**, 100%)$^{\Delta}$	-
25	94%	*O*-glucoside (94%)	-
26*	100%	7-*O*-glucoside (**26a**, 100%)	-
27	99%	*O*-glucoside (95%)	*O*-glucosyl-*O*-sulfate (4%)
28	95	*O*-glucoside (80%)	*O*-glucoside (15%)
29*	99	3-*O*-glucoside (**29a**, 99%)	-
30*	100	3-*O*-glucoside (**30a**, 100%)	-
31	0	-	-
32	0	-	-
33	0	-	-
34	0	-	-
35	0	-	-

*Glycosylated products were prepared by scaled-up biotransformation, and their structures were determined by MS and NMR spectroscopy. The other products were tentatively characterized by

LC/MS/MS analysis. Conversion rates (%) were calculated according to HPLC peak areas. $^{\Delta}$indicates new compounds.

Substrates: **1**, glycycoumarin; **2**, licoarylcoumarin; **3**, puerarol; **4**, glyurallin A; **5**, wighteone; **6**, luteone; **7**, lupiwighteone; **8**, angustone A; **9**, allolicoisoflavone B; **10**, semilicoisoflavone B; **11**, 6-*C*-prenylorohol; **12**, gancaonin L; **13**, 6,8-diprenylgenistein; **14**, licoisoflavone A; **15**, licoisoflavanone; **16**, licoricidin; **17**, cyclized licoricidin; **18**, licoflavonol; **19**, topazolin; **20**, icaritin; **21**, 5,7,4′-trihydroxy-3′(3-methylbut-2-enyl)-3-methoxy flavone; **22**, wushanicaritin; **23**, licocoumarone; **24**, bavachin; **25**, sophoranone; **26**, corylifolinin; **27**, licochalcone A; **28**, rhodomyrtone; **29**, kaempferol; **30**, quercetin; **31**, kumatakenin B; **32**, formononetin; **33**, genistein; **34**, liquiritigenin; **35**, dihydroquercetin.



Structures of compounds **29**–**35**.

Table S7. Water solubility of **1** and **1a**

1a		**1**	
C/ mg·mL^{-1}	Area	C/ mg·mL^{-1}	Area
0.01	447.3	0.0116	663.9
0.02	931.6	0.0232	1685.8
0.05	2212.9	0.058	4394.9
0.10	4595.9	0.116	9627.6
0.50	22062.5	0.29	23983.9
0.01	447.3	0.0116	663.9
Sample: 0.13	5809.9	Sample: < 0.0116	Not detected

C, concentration; Area, peak area of HPLC chromatograms calculated at λ = 365 nm.

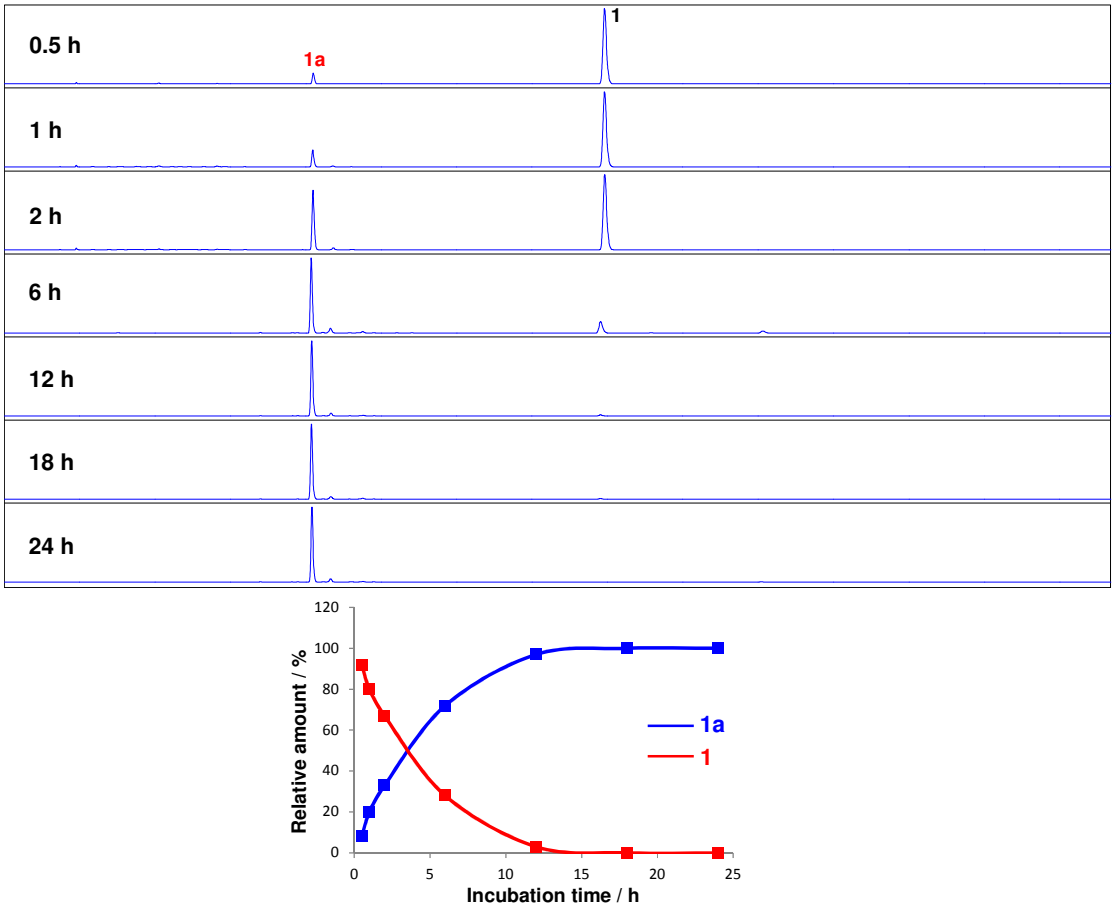


Figure S1. Time-course for glycosylation of **1** by *Mucor hiemalis* (the relative amounts were calculated on the basis of peak areas in the HPLC chromatogram at 365 nm).

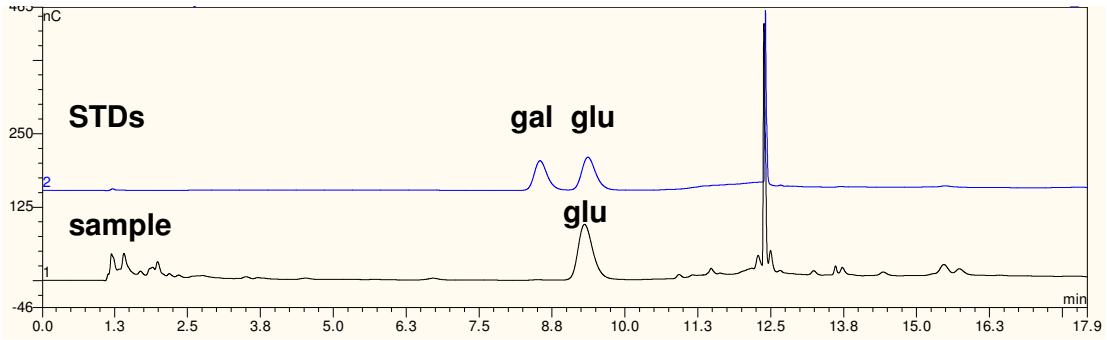


Figure S2. IC-PAD analysis for sugar residue of **1a**. gal, galactose; glu, glucose.

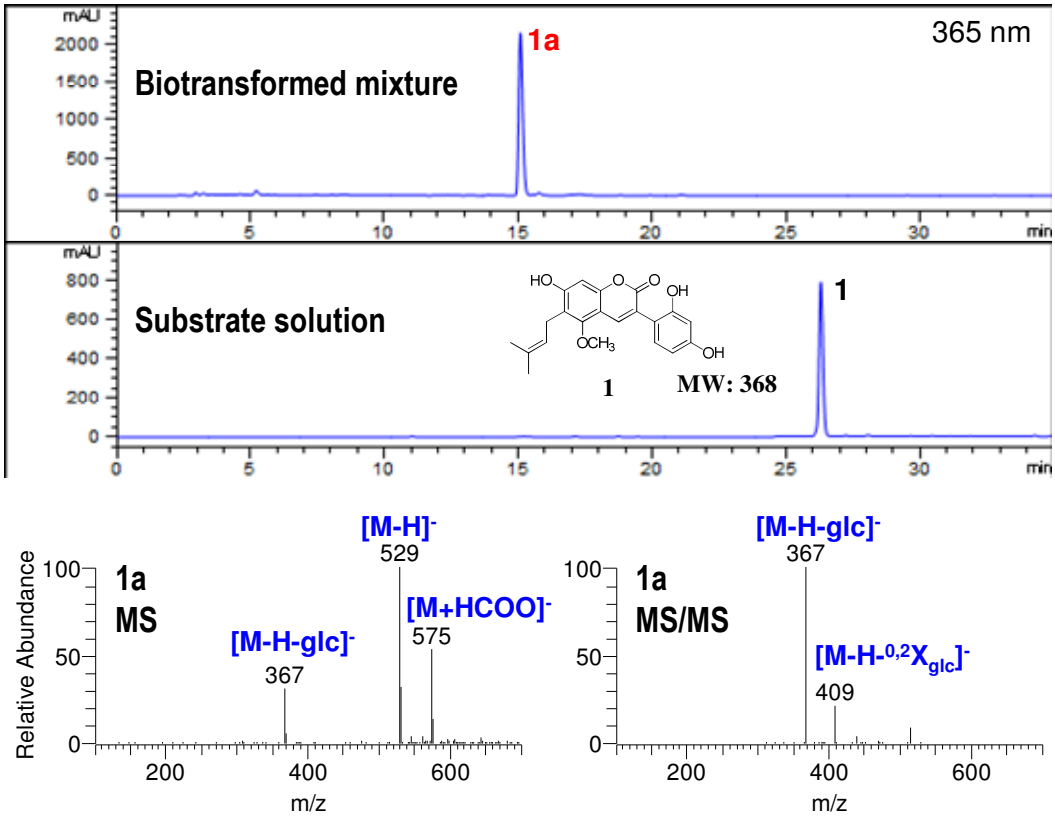


Figure S3. HPLC and ESI-MS/MS analysis for **1** in *M. hiemalis*.

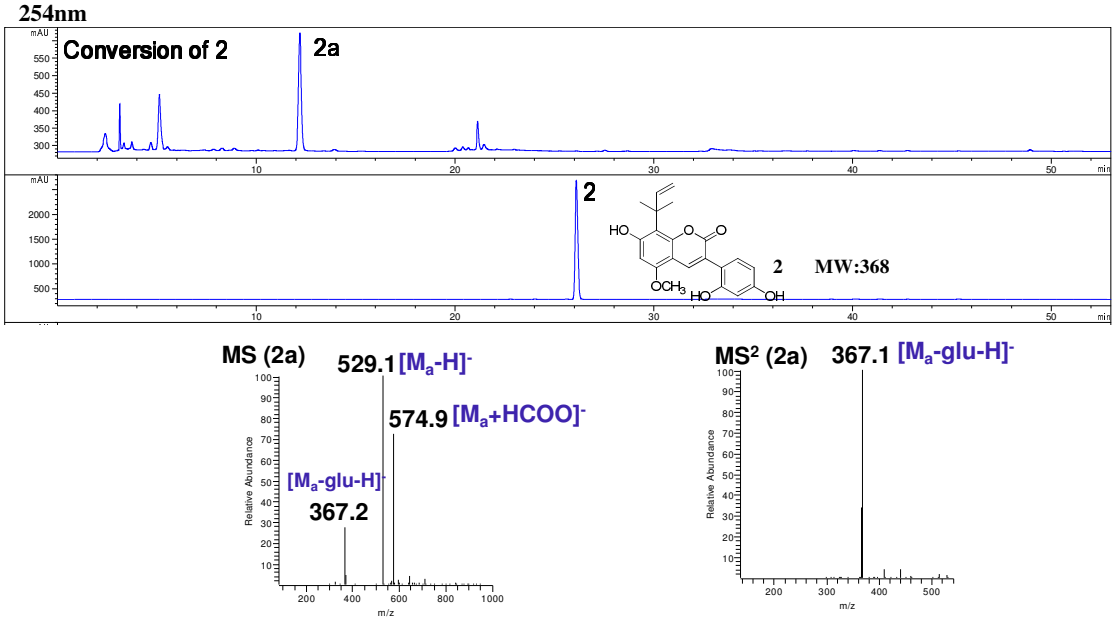


Figure S4. HPLC and ESI-MS/MS analysis for **2** in *M. hiemalis*.

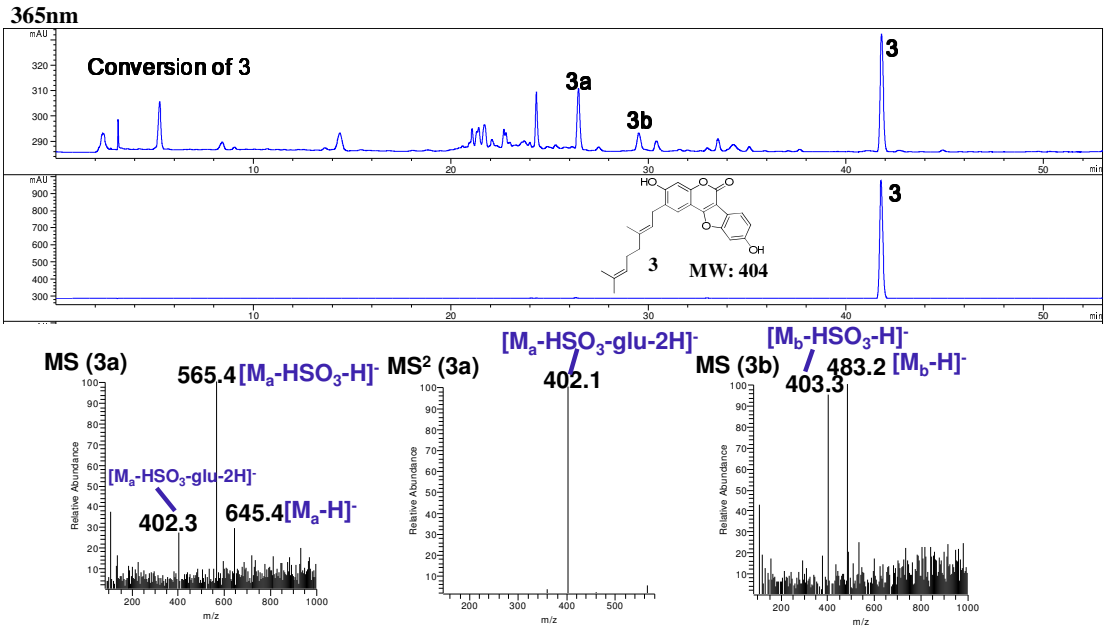


Figure S5. HPLC and ESI-MS/MS analysis for **3** in *M. hiemalis*.

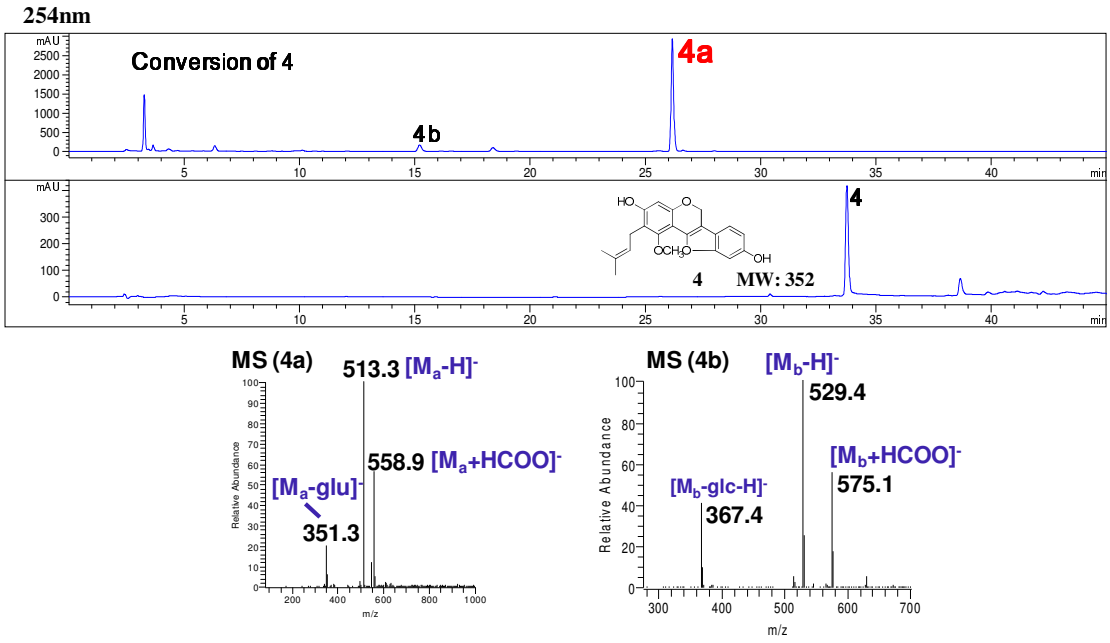


Figure S6. HPLC and ESI-MS/MS analysis for **4** in *M. hiemalis*.

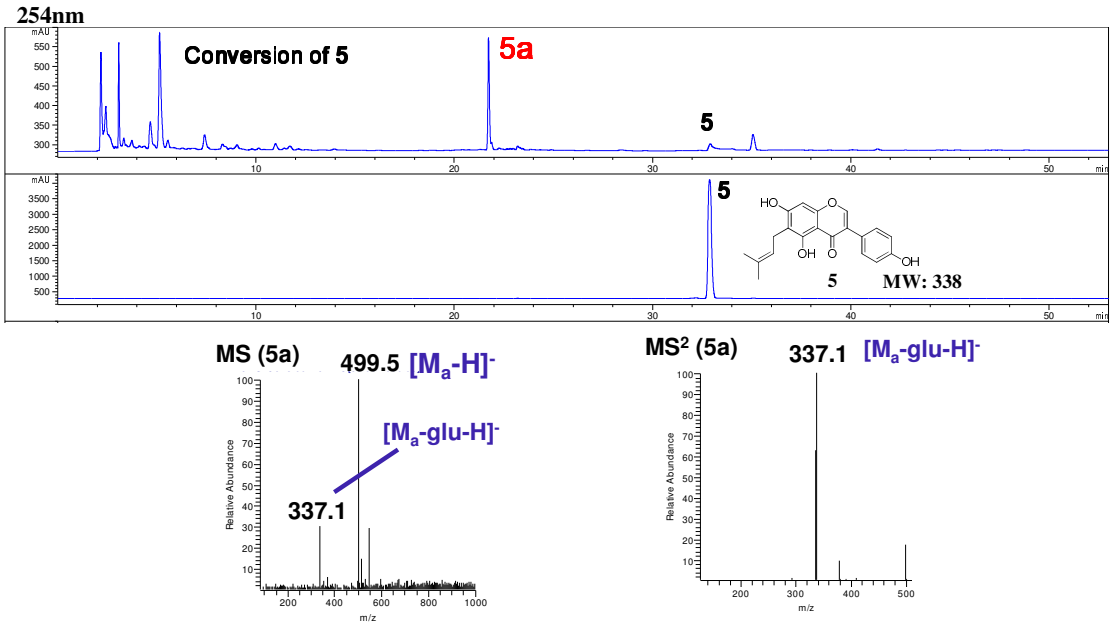


Figure S7. HPLC and ESI-MS/MS analysis for **5** in *M. hiemalis*.

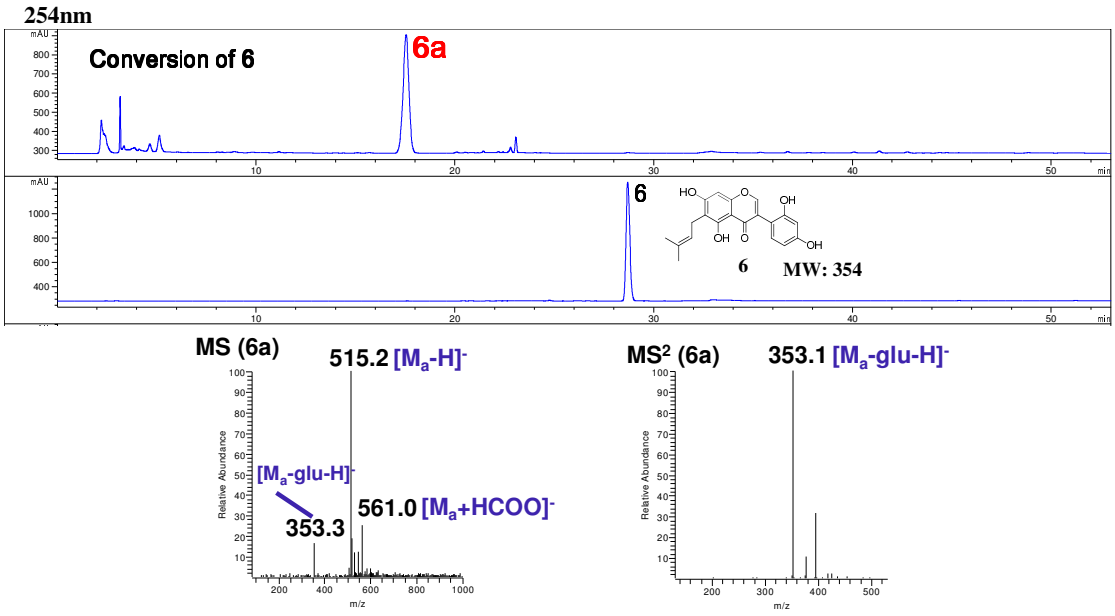


Figure S8. HPLC and ESI-MS/MS analysis for **6** in *M. hiemalis*.

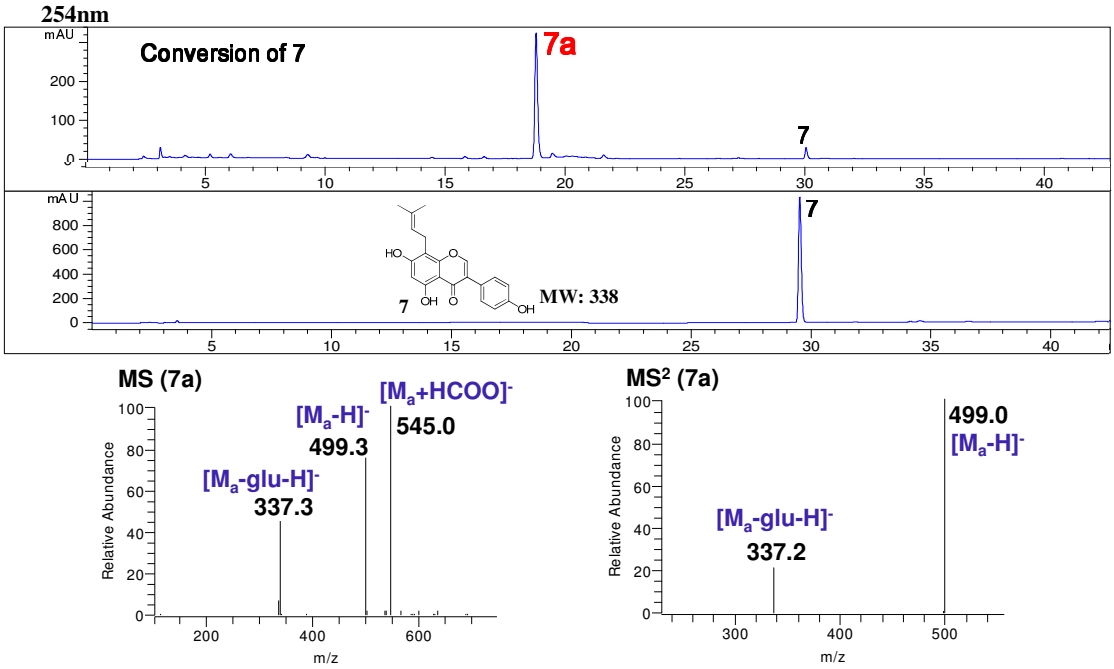


Figure S9. HPLC and ESI-MS/MS analysis for **7** in *M. hiemalis*.

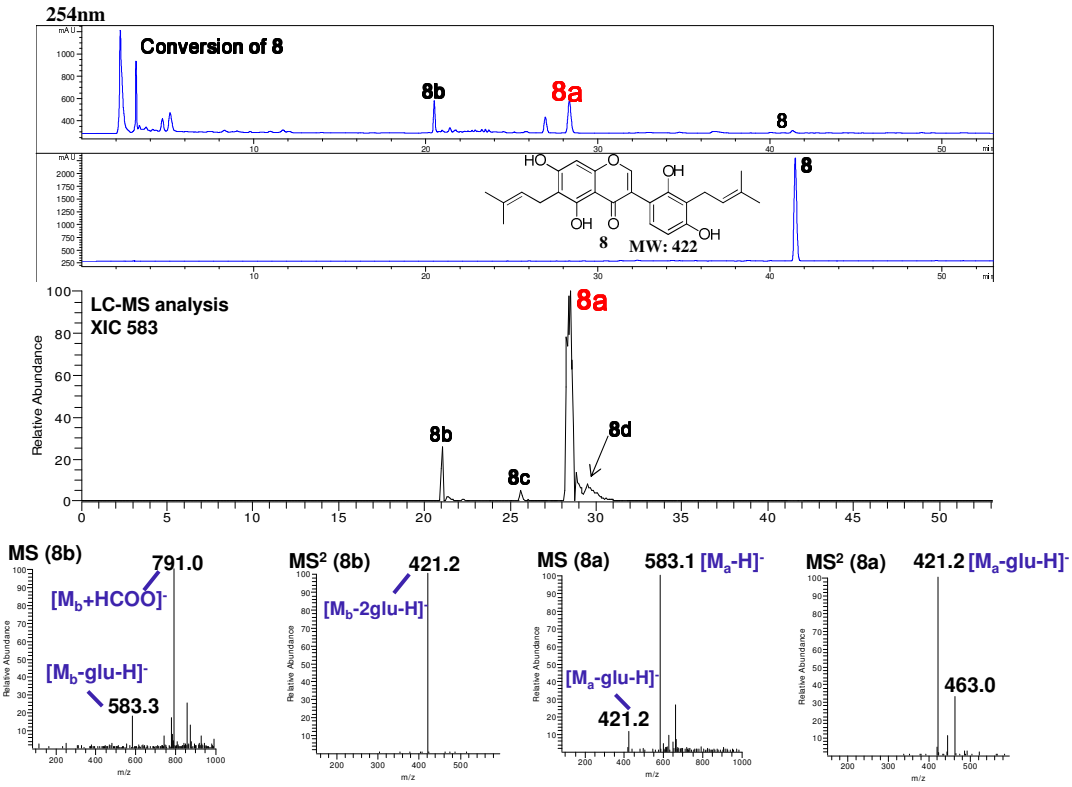


Figure S10. HPLC and ESI-MS/MS analysis for **8** in *M. hiemalis*.

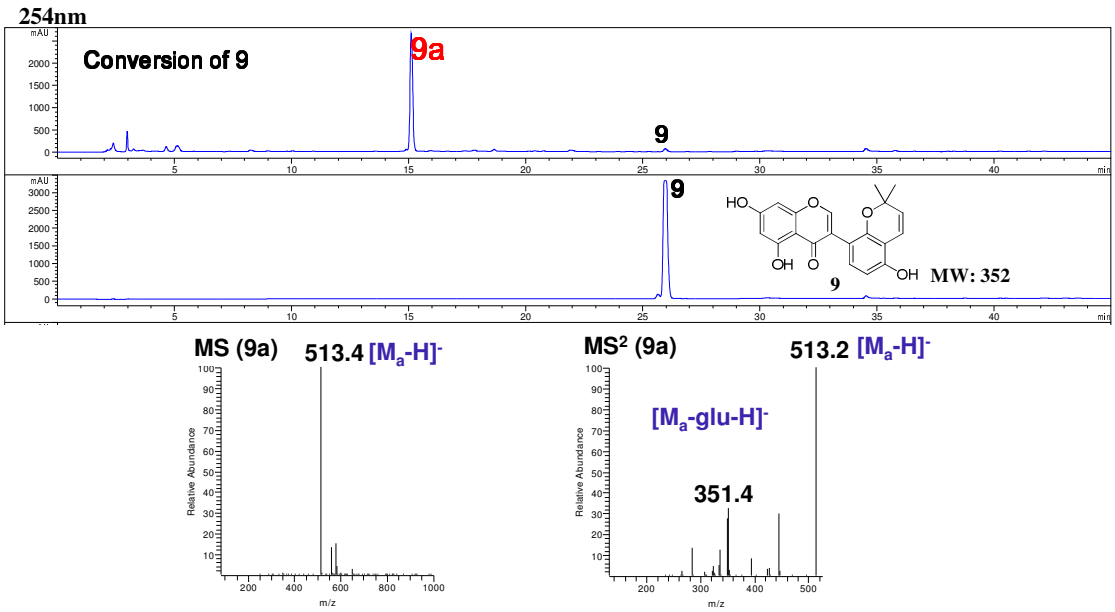


Figure S11. HPLC and ESI-MS/MS analysis for **9** in *M. hiemalis*.

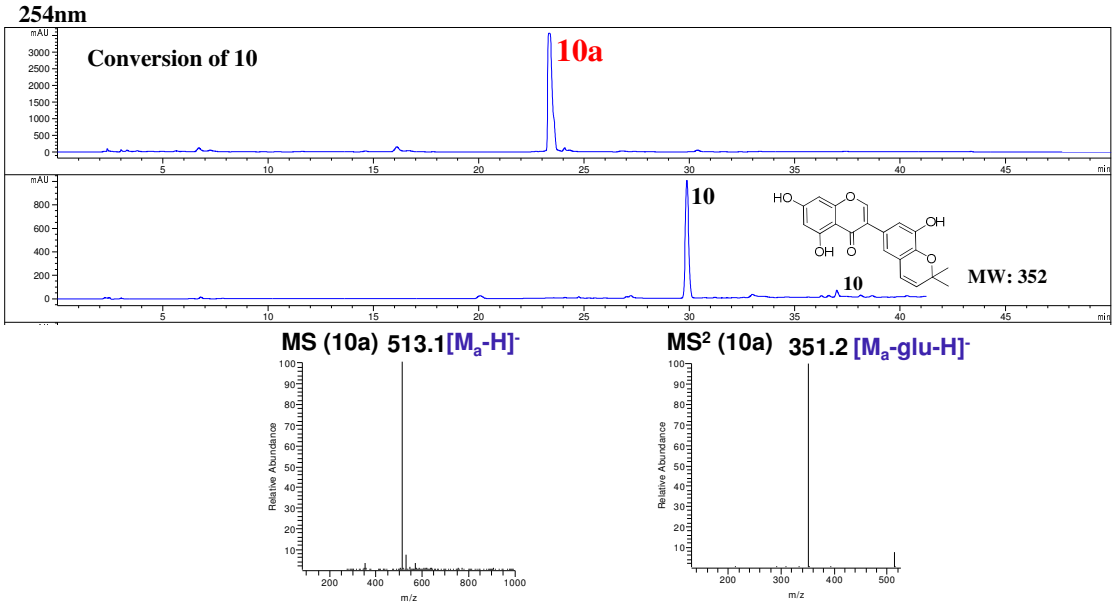


Figure S12. HPLC and ESI-MS/MS analysis for **10** in *M. hiemalis*.

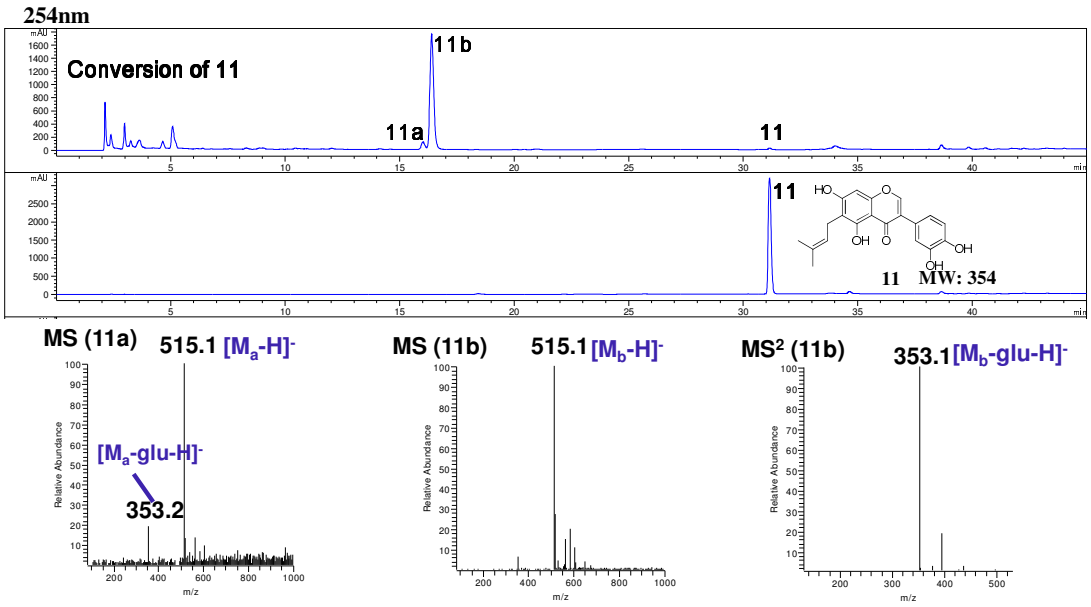


Figure S13. HPLC and ESI-MS/MS analysis for **11** in *M. hiemalis*.

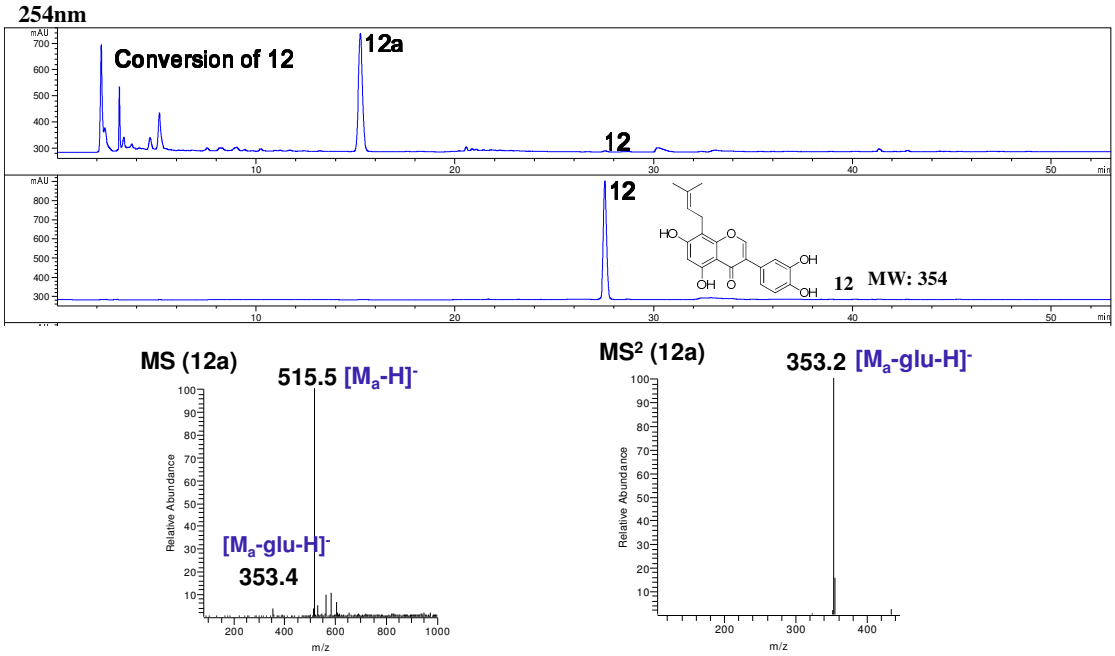


Figure S14. HPLC and ESI-MS/MS analysis for **12** in *M. hiemalis*.

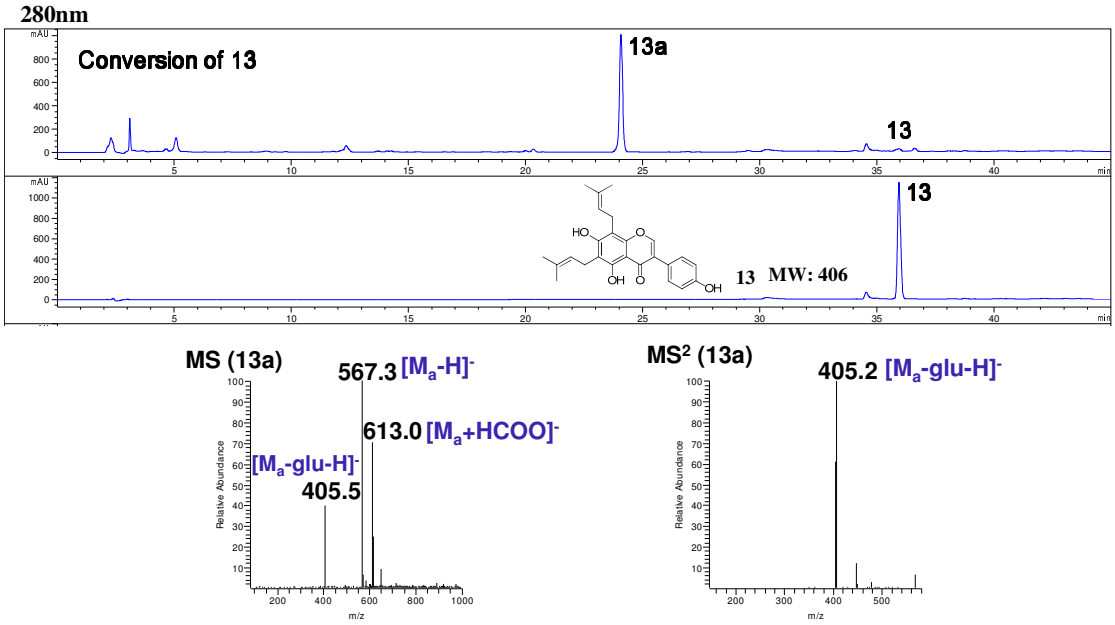


Figure S15. HPLC and ESI-MS/MS analysis for **13** in *M. hiemalis*.

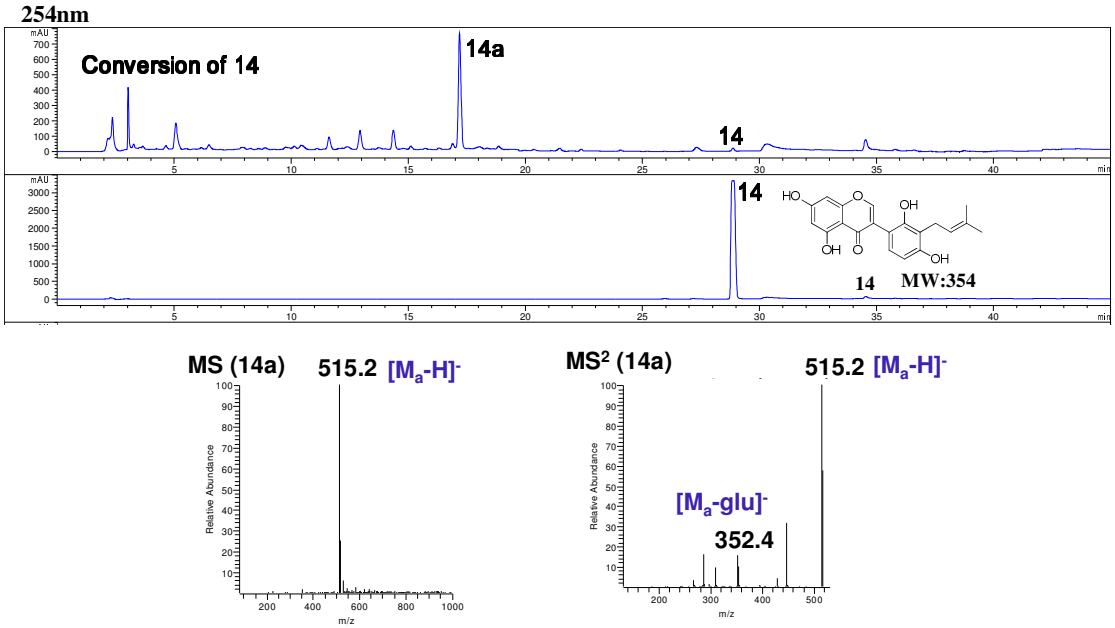


Figure S16. HPLC and ESI-MS/MS analysis for **14** in *M. hiemalis*.

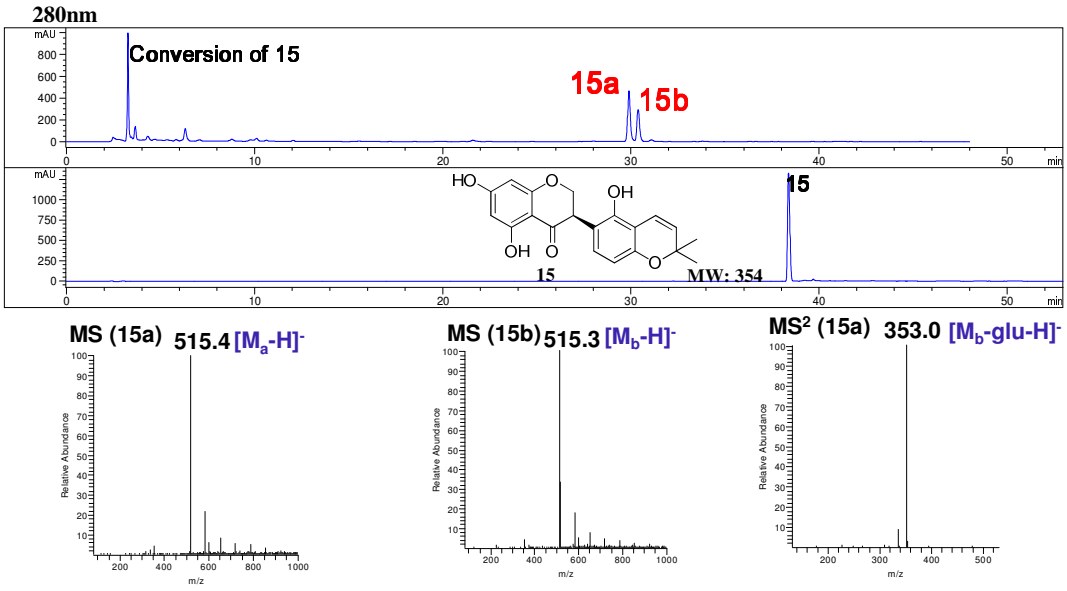


Figure S17. HPLC and ESI-MS/MS analysis for **15** in *M. hiemalis*.

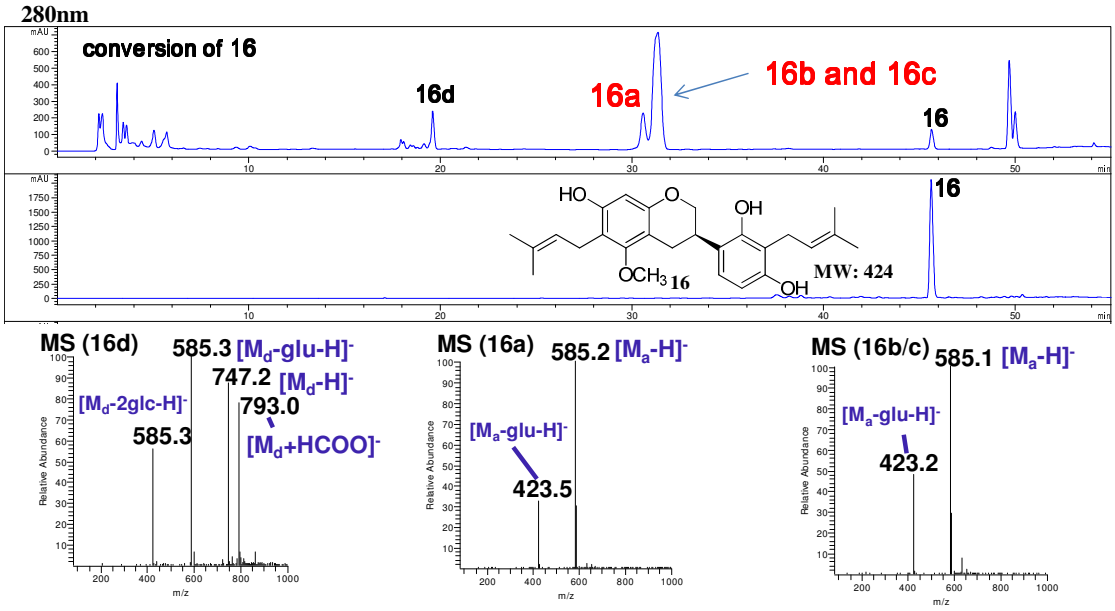


Figure S18. HPLC and ESI-MS/MS analysis for **16** in *M. hiemalis*.

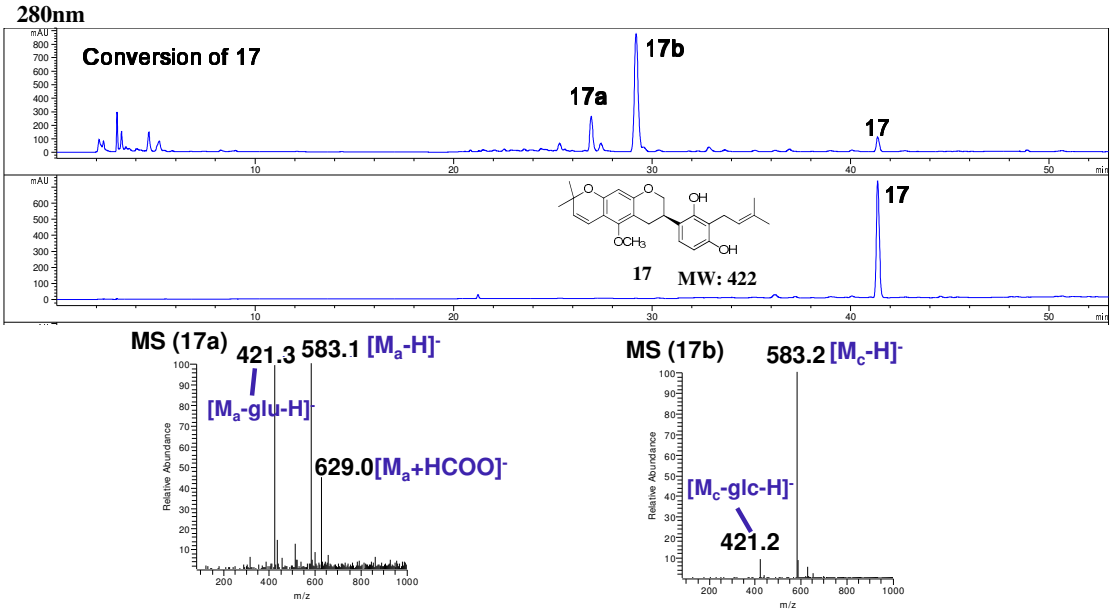


Figure S19. HPLC and ESI-MS/MS analysis for **17** in *M. hiemalis*.

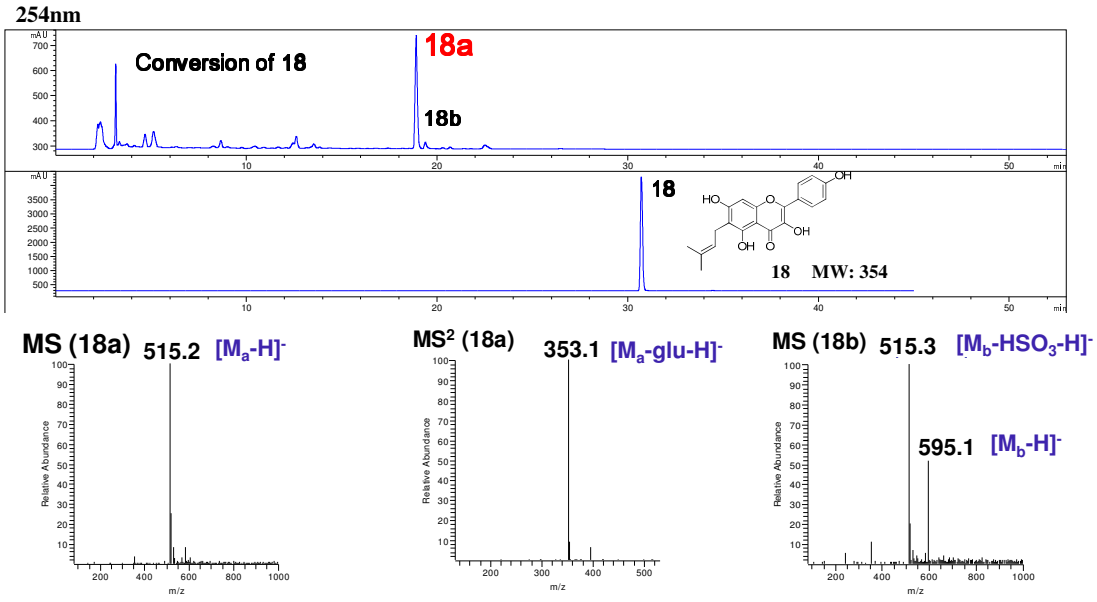


Figure S20. HPLC and ESI-MS/MS analysis for **18** in *M. hiemalis*.

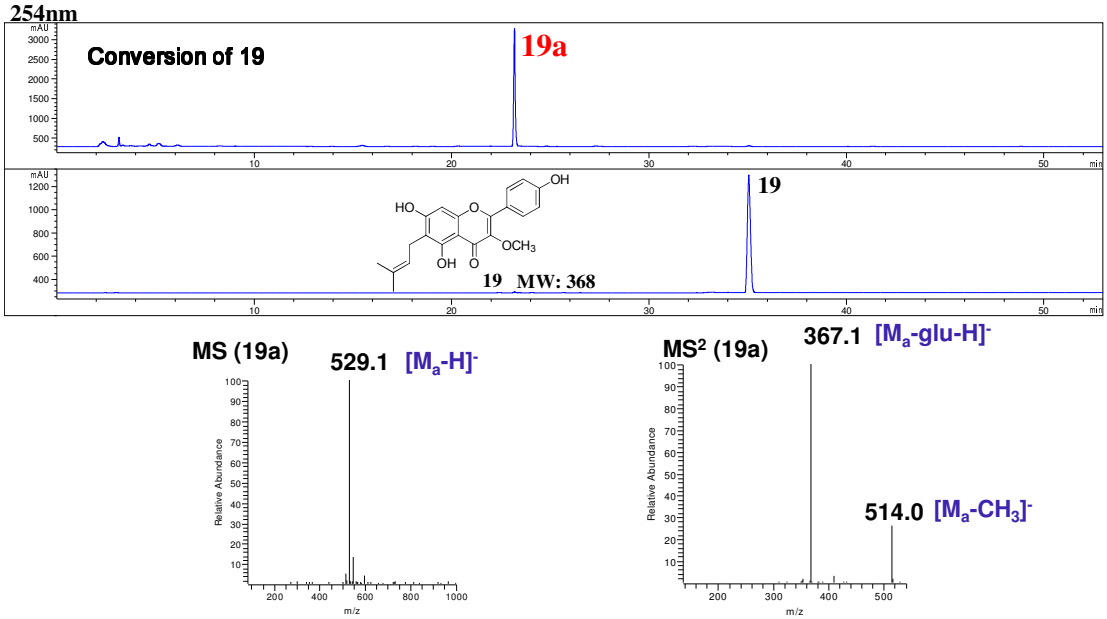


Figure S21. HPLC and ESI-MS/MS analysis for **19** in *M. hiemalis*.

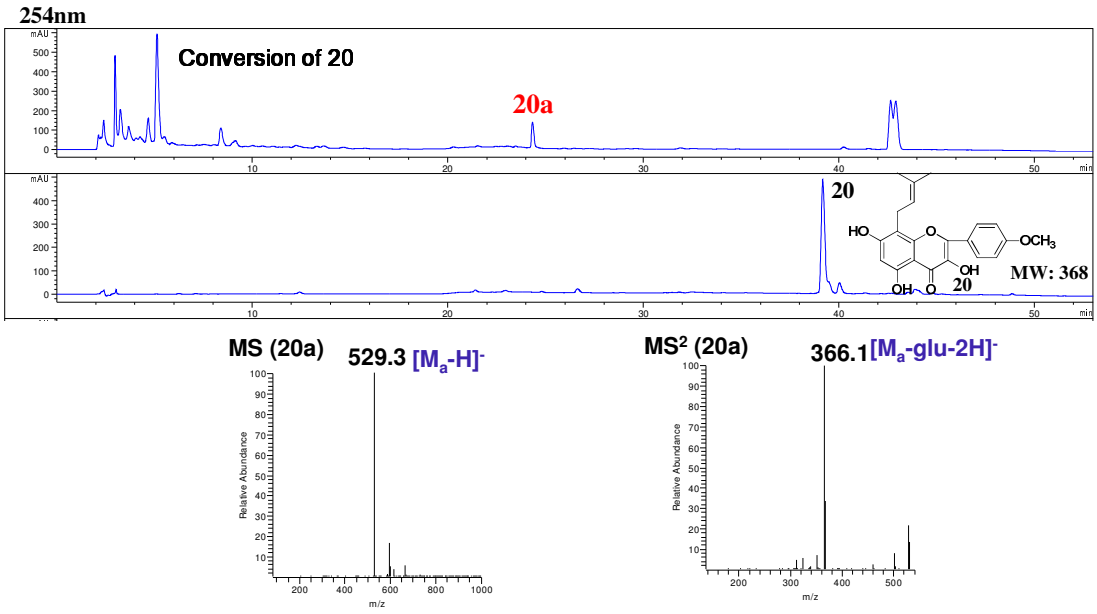


Figure S22. HPLC and ESI-MS/MS analysis for **20** in *M. hiemalis*.

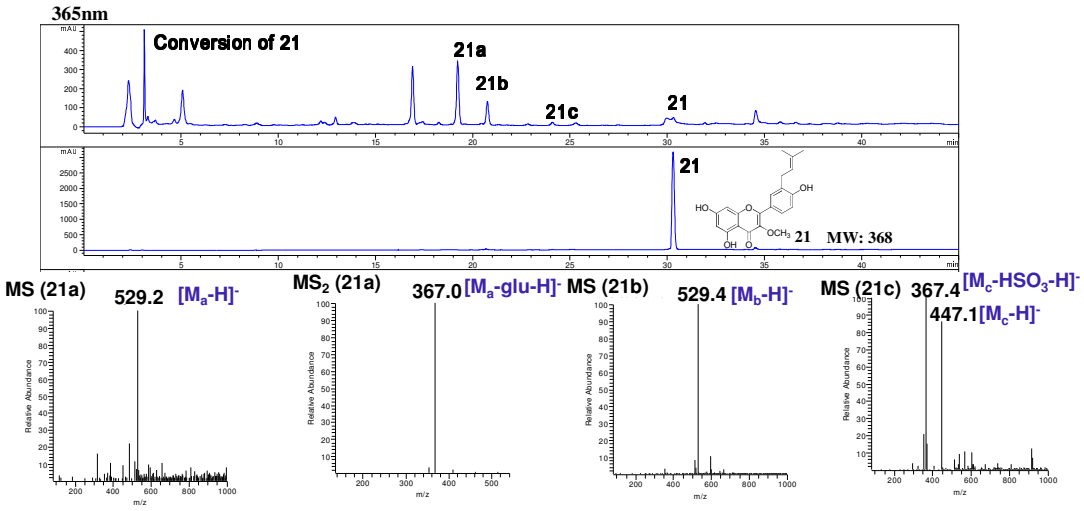


Figure S23. HPLC and ESI-MS/MS analysis for **21** in *M. hiemalis*.

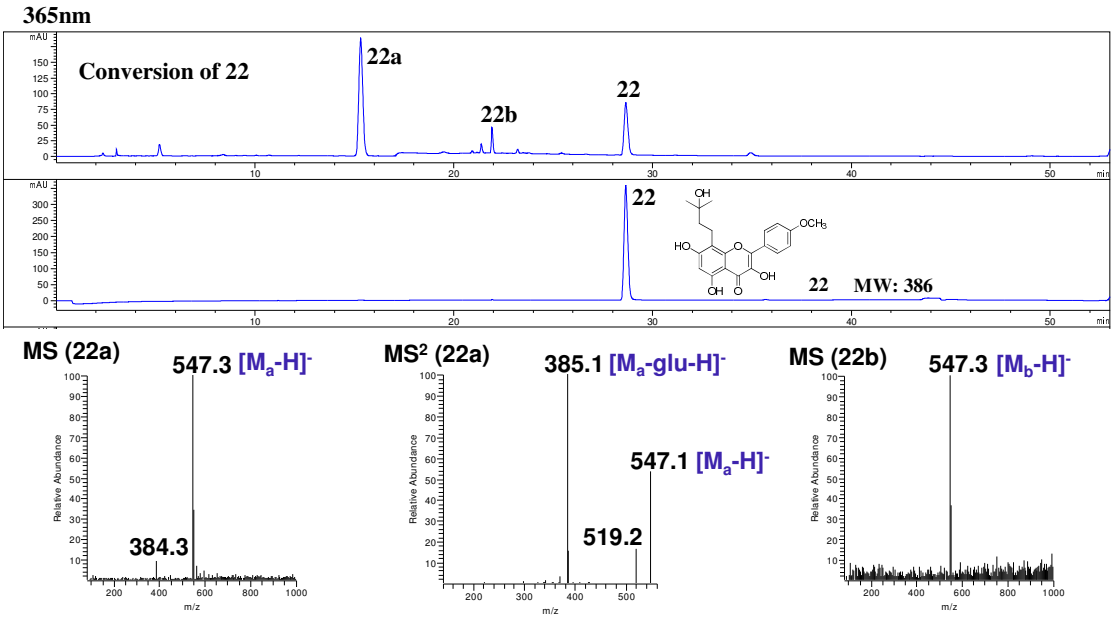


Figure S24. HPLC and ESI-MS/MS analysis for **22** in *M. hiemalis*.

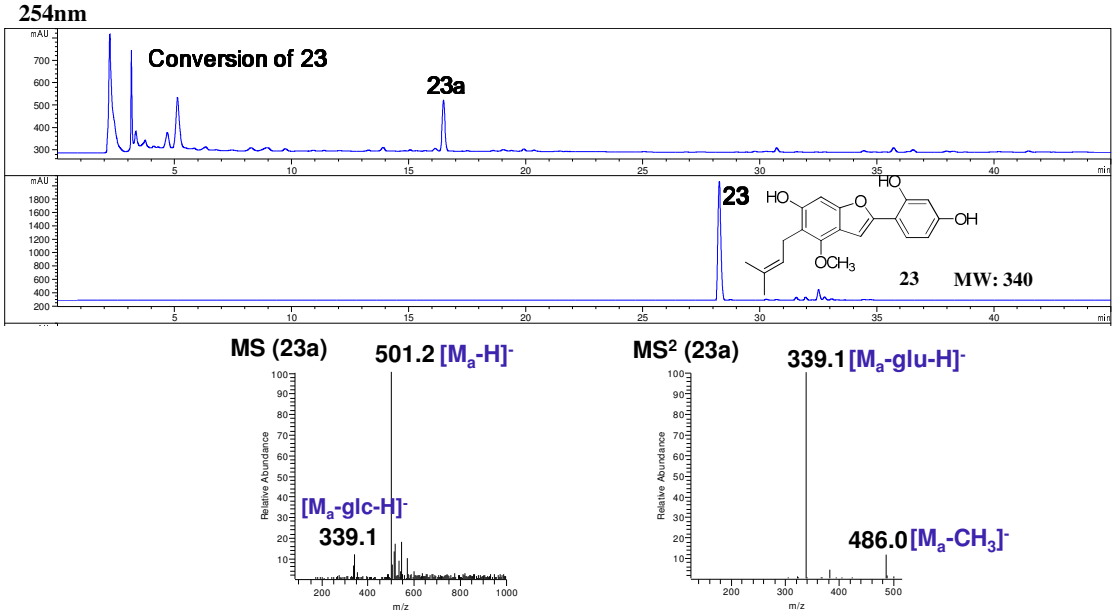


Figure S25. HPLC and ESI-MS/MS analysis for **23** in *M. hiemalis*.

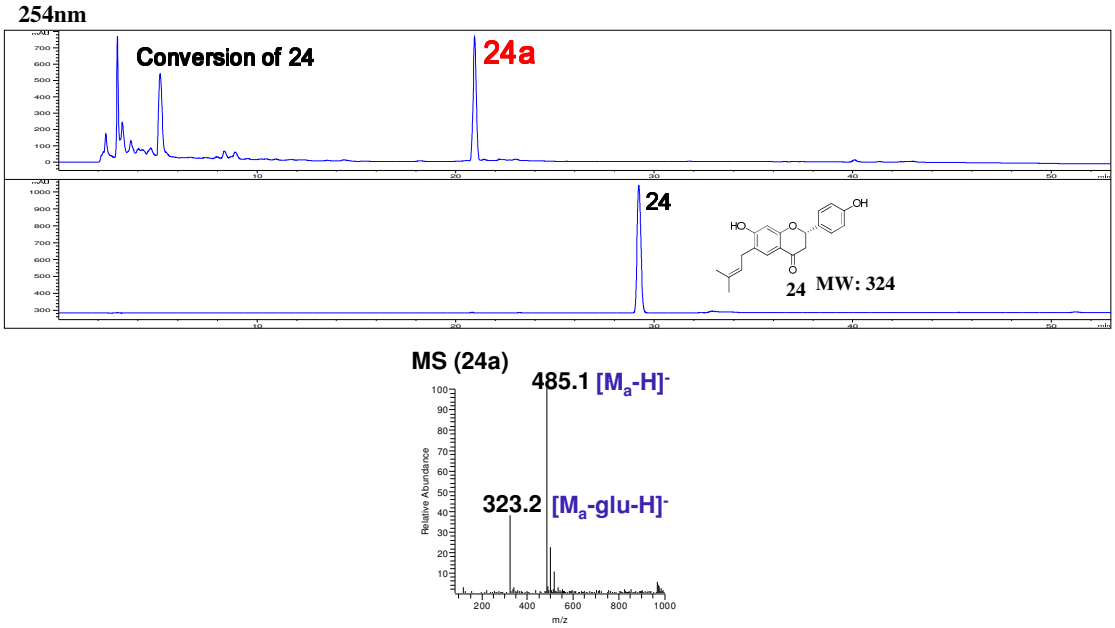


Figure S26. HPLC and ESI-MS/MS analysis for **24** in *M. hiemalis*.

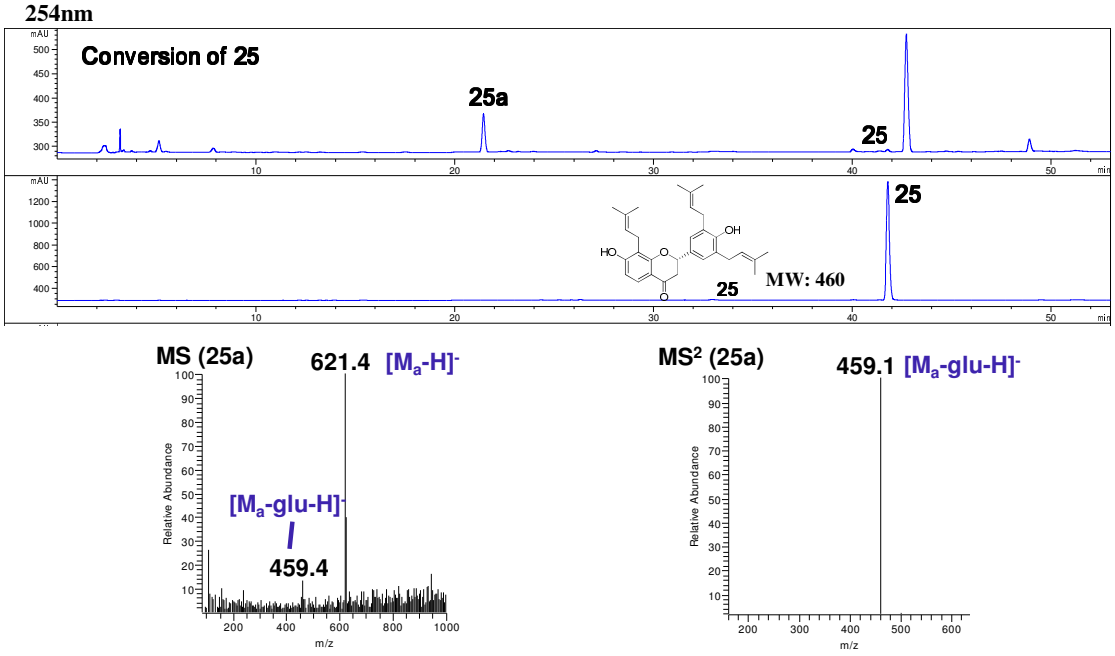


Figure S27. HPLC and ESI-MS/MS analysis for **25** in *M. hiemalis*.

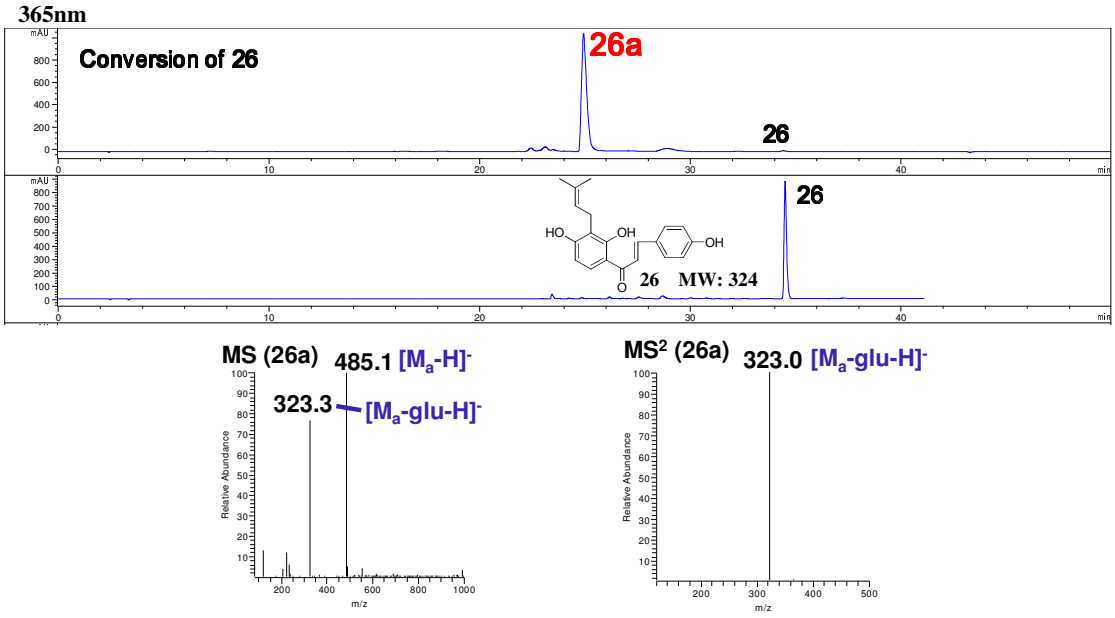


Figure S28. HPLC and ESI-MS/MS analysis for **26** in *M. hiemalis*.

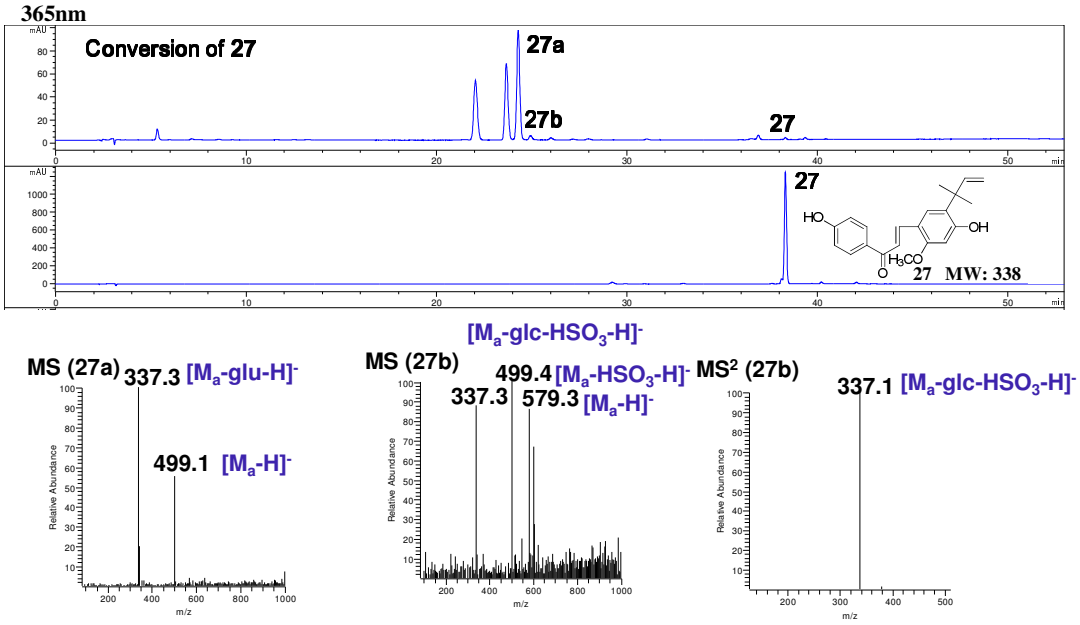


Figure S29. HPLC and ESI-MS/MS analysis for **27** in *M. hiemalis*.

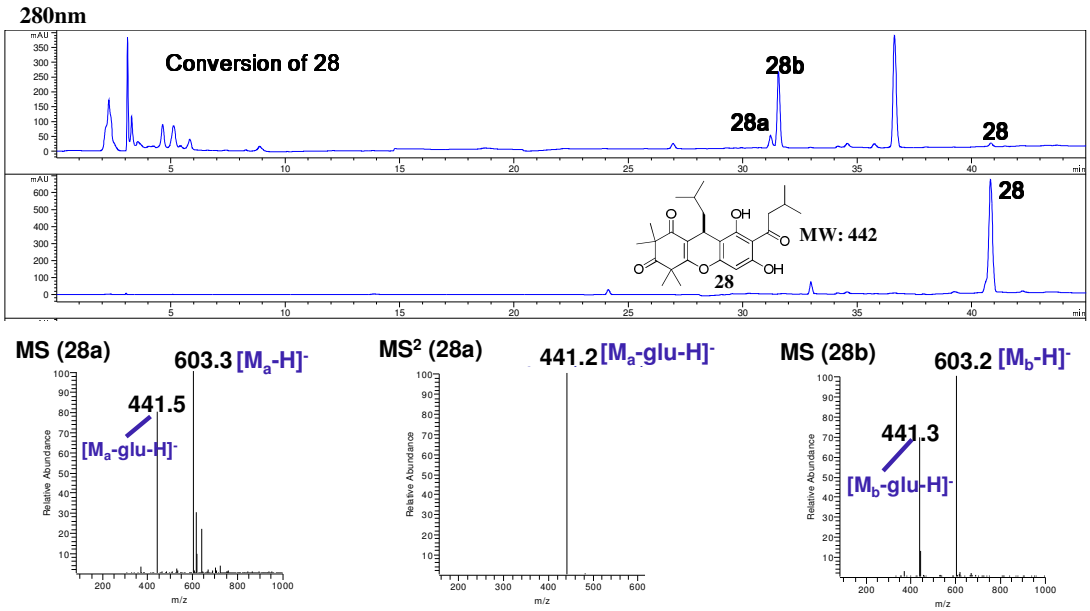


Figure S30. HPLC and ESI-MS/MS analysis for **28** in *M. hiemalis*.

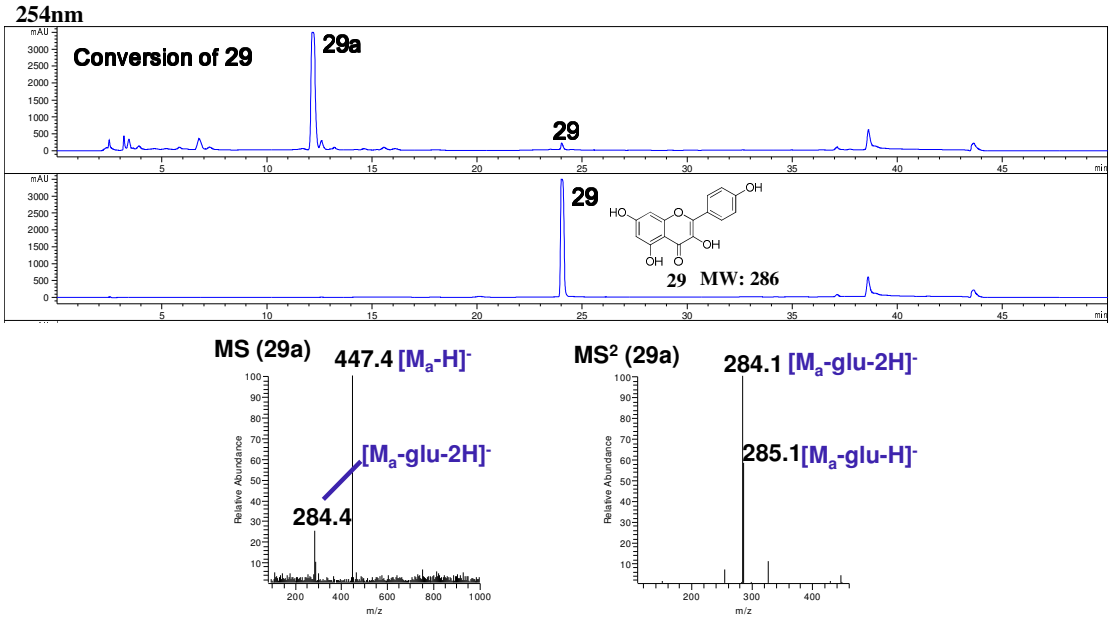


Figure S31. HPLC analysis for **29** in *M. hiemalis*

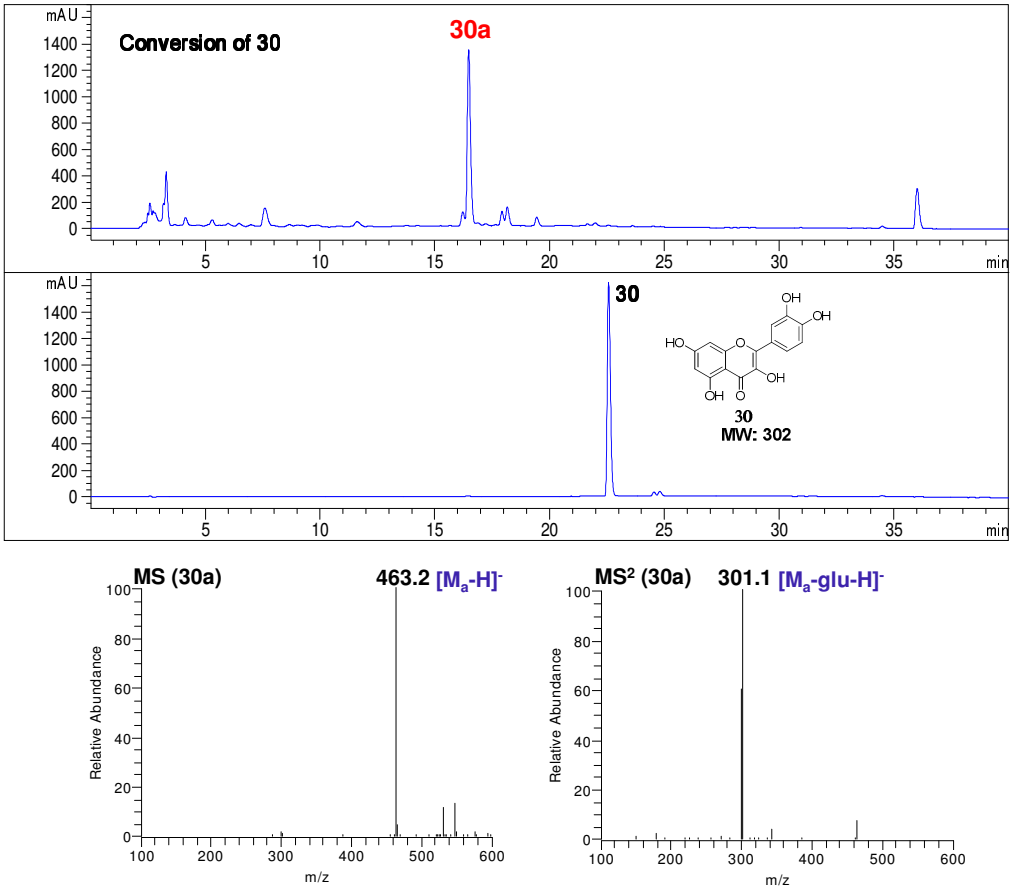


Figure S32. HPLC analysis for **30** in *M. hiemalis*

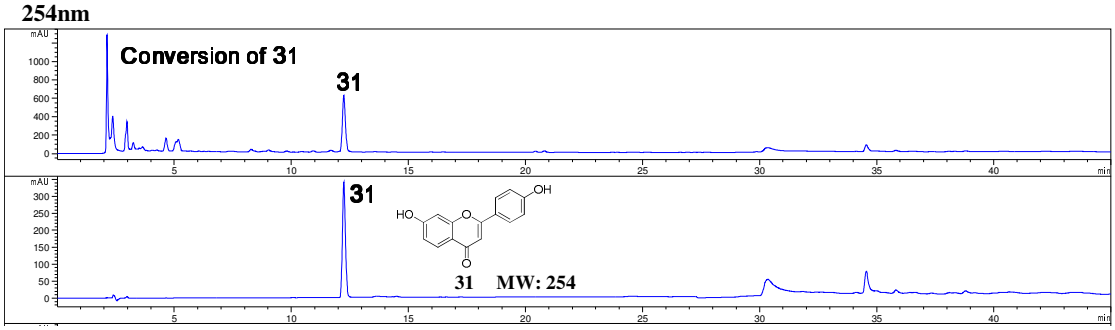


Figure S33. HPLC analysis for **31** in *M. hiemalis*

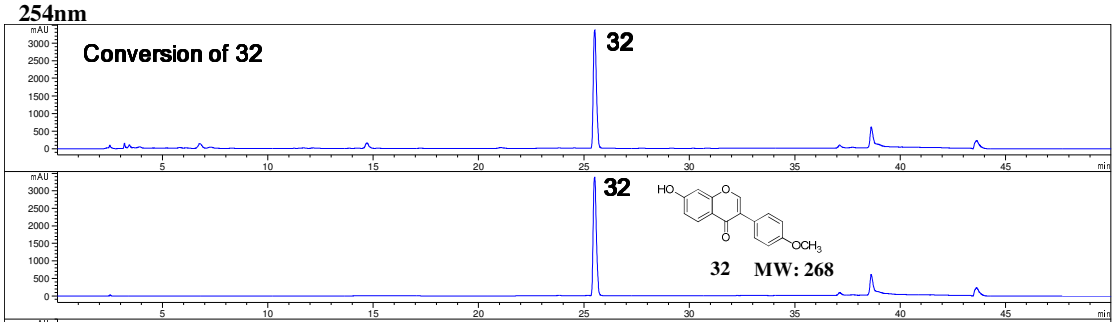


Figure S34. HPLC analysis for **32** in *M. hiemalis*

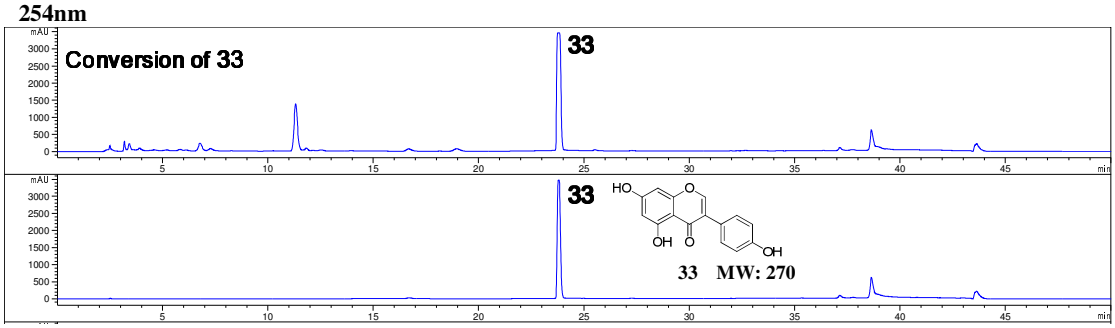


Figure S35. HPLC analysis for **33** in *M. hiemalis*

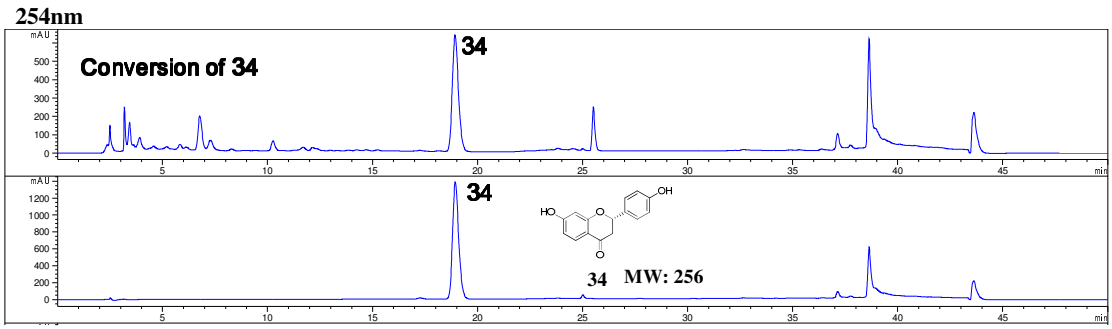


Figure S36. HPLC analysis for **34** in *M. hiemalis*

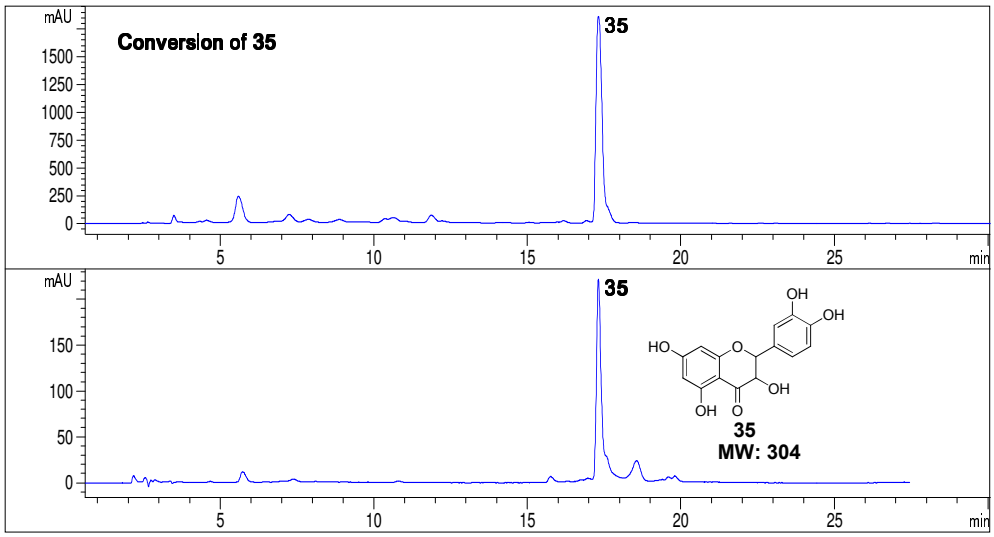


Figure S37. HPLC analysis for **35** in *M. hiemalis*

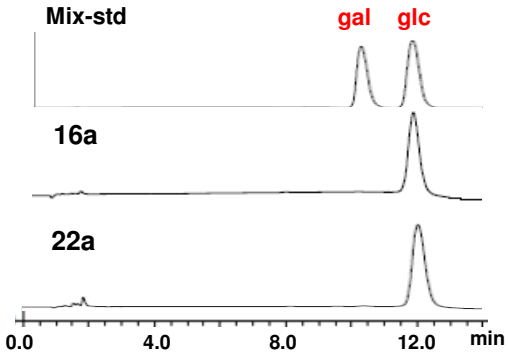


Figure S38. IC-PAD analysis for sugar residue of **16a** and **22a**. gal: galactose; glc: glucose.

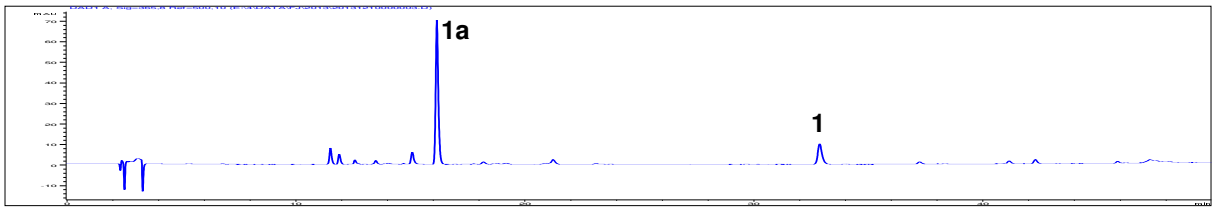


Figure S39. HPLC analysis for crude enzyme catalysis of **1**.

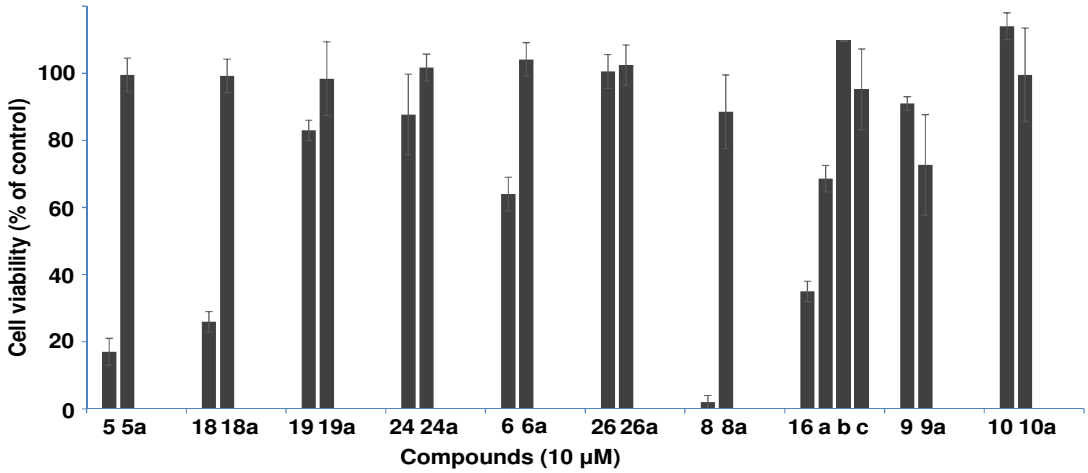


Figure S40. Cytotoxicities of several pairs of substrates and their glycosylated products against HepG2 cells at 10 μM. a, **16a**; b, **16b**, c, **16c**.

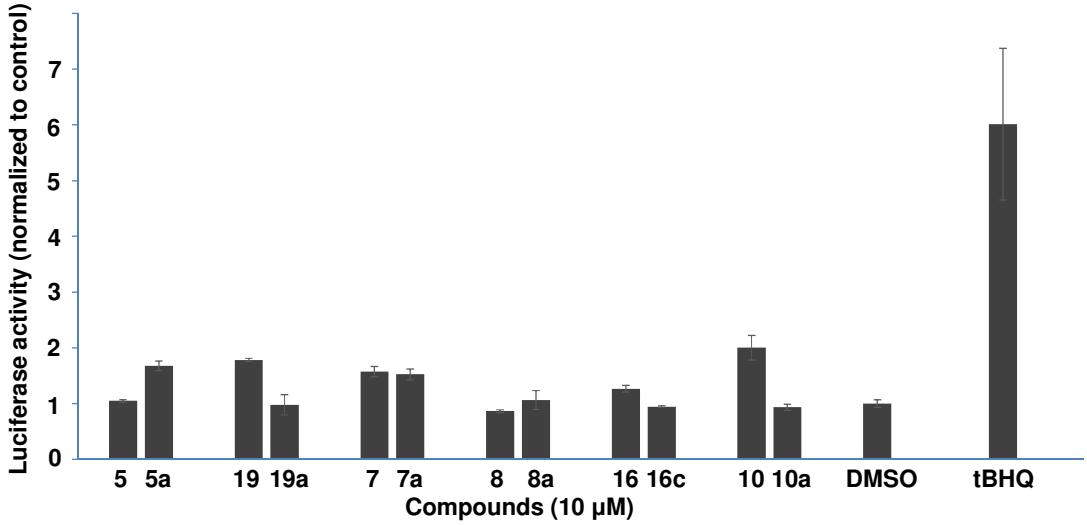


Figure S41. Effects of several pairs of substrates and their glycosylated products on Nrf2 transcription in HepG2 cells at 10 μM.

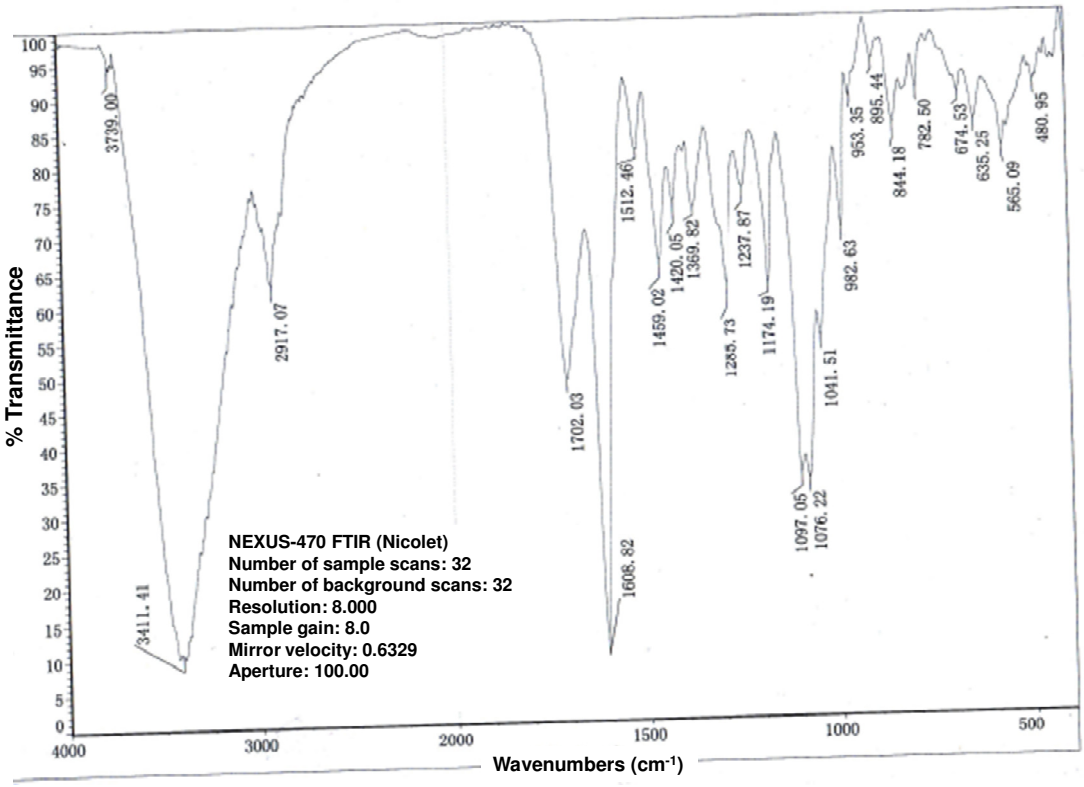


Figure S42. The IR spectrum of **1a**.

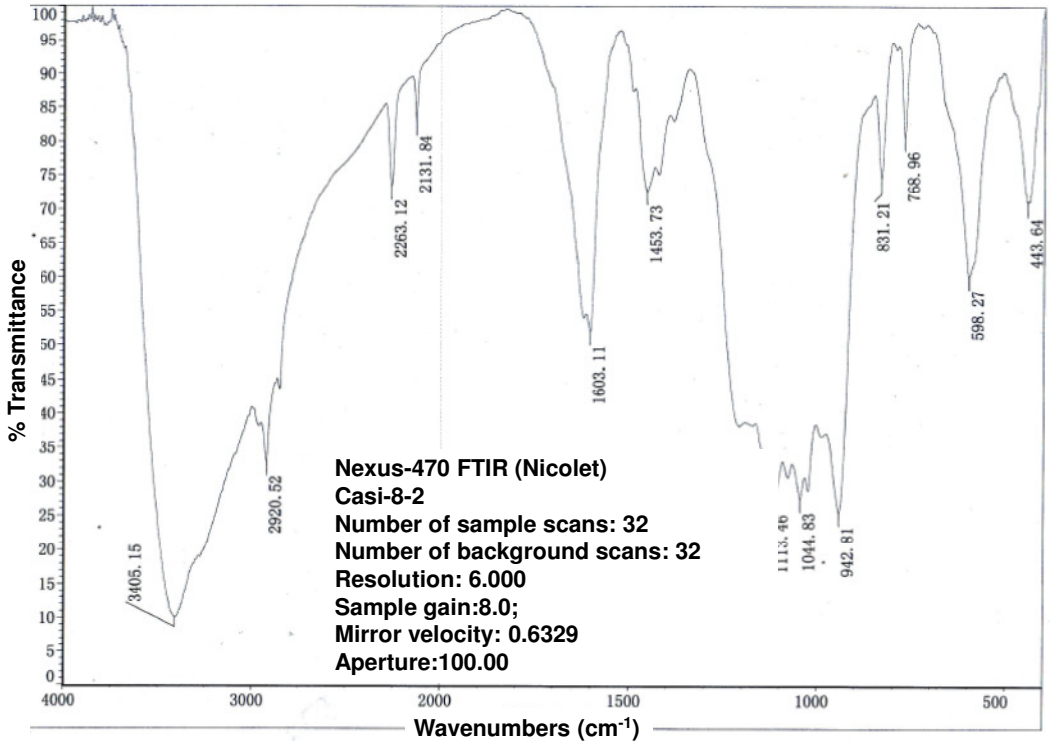


Figure S43. The IR spectrum of **4a**.

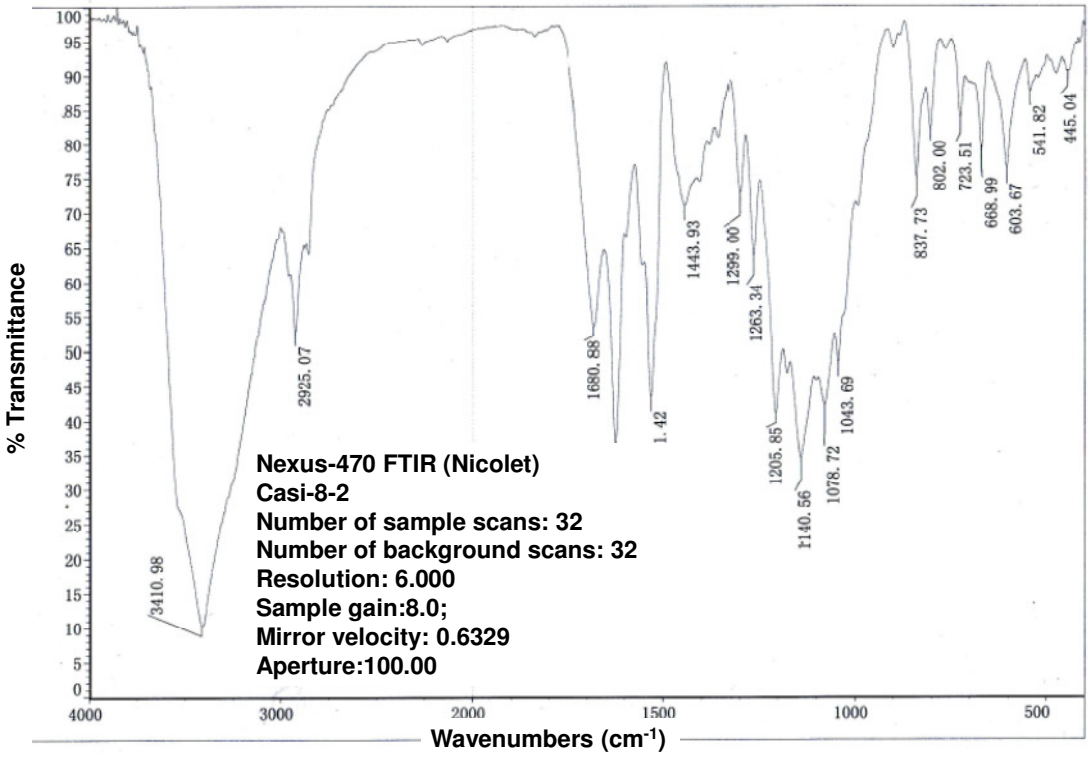


Figure S44. The IR spectrum of **7a**.

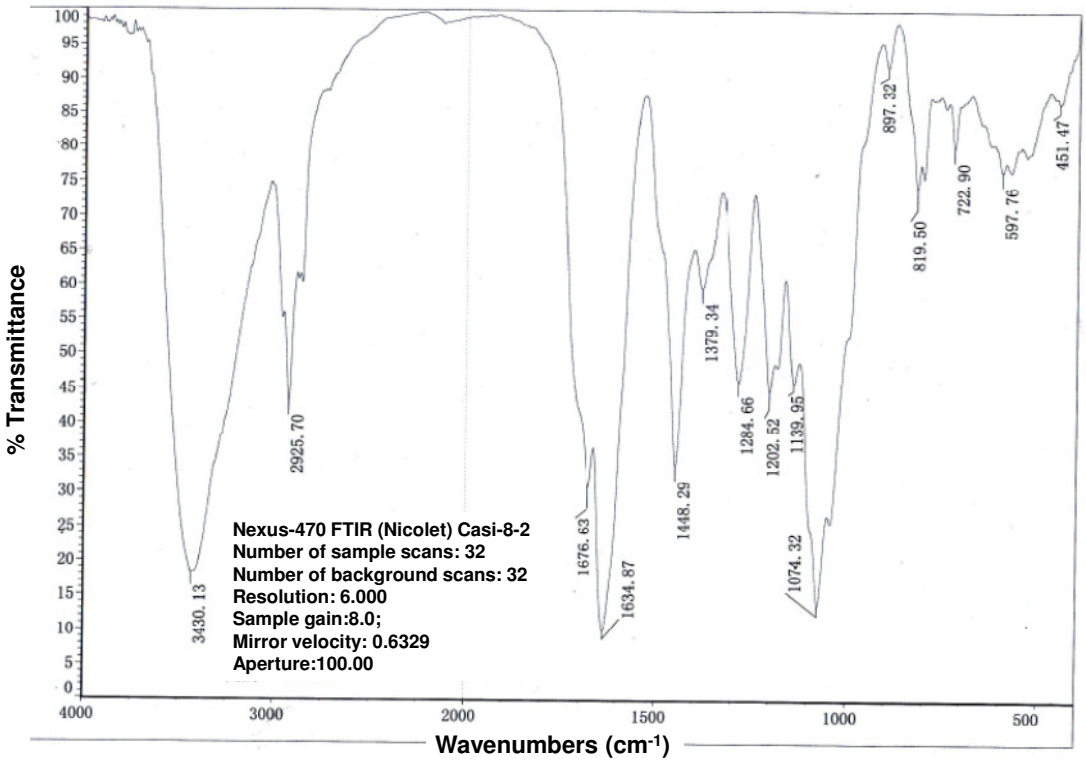


Figure S45. The IR spectrum of **8a**.

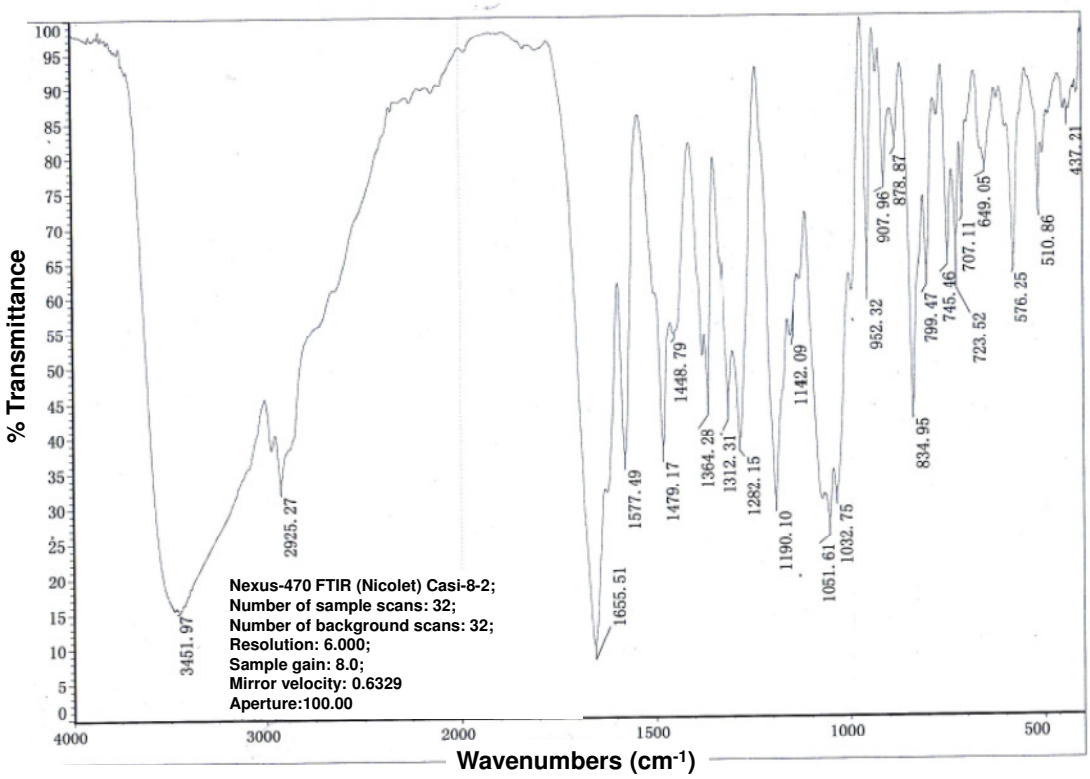


Figure S46. The IR spectrum of **9a**.

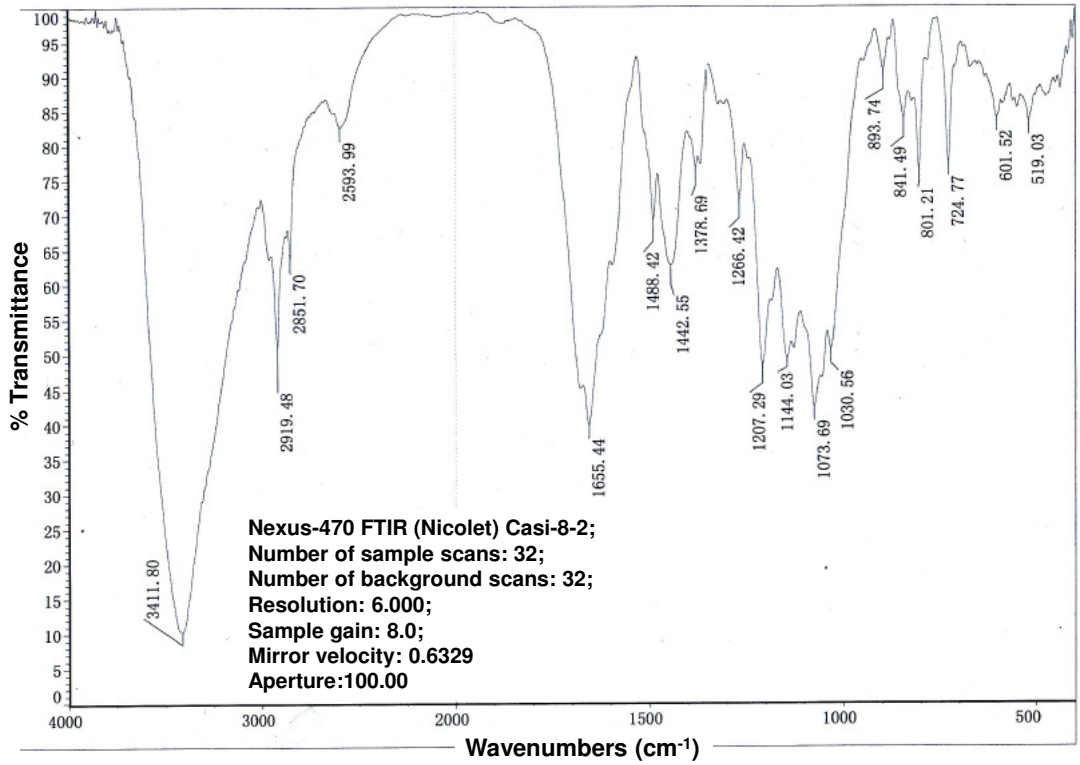


Figure S47. The IR spectrum of **10a**.

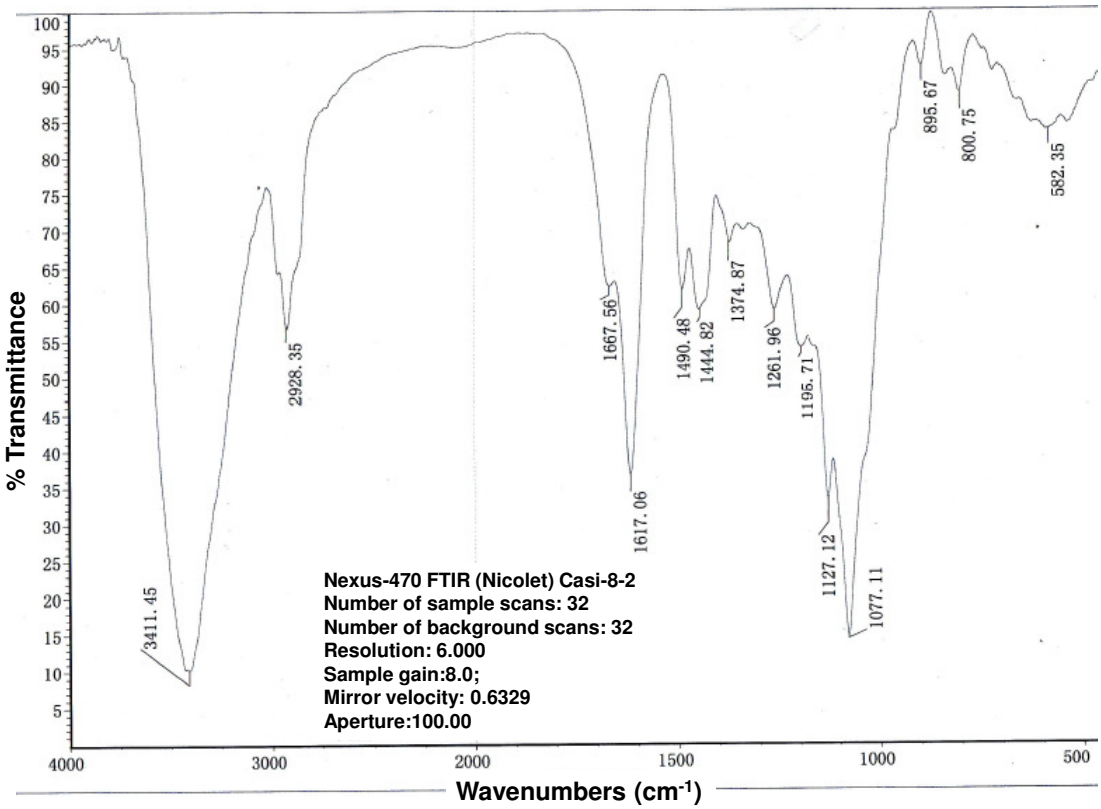


Figure S48. The IR spectrum of **16a**.

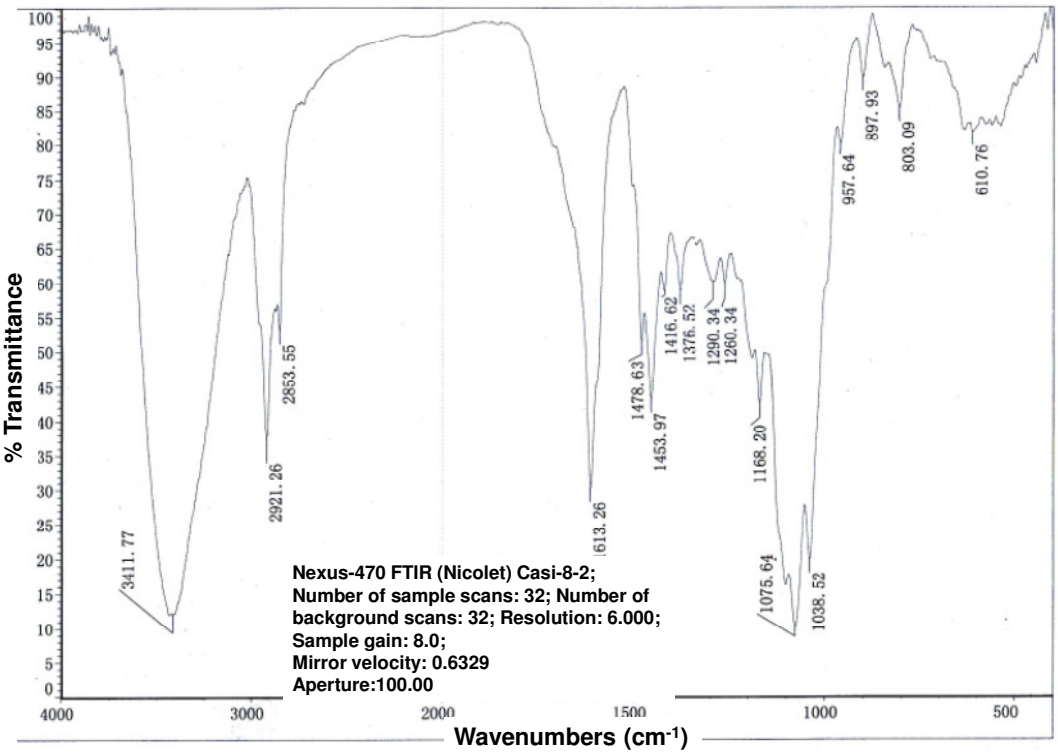


Figure S49. The IR spectrum of **16b**.

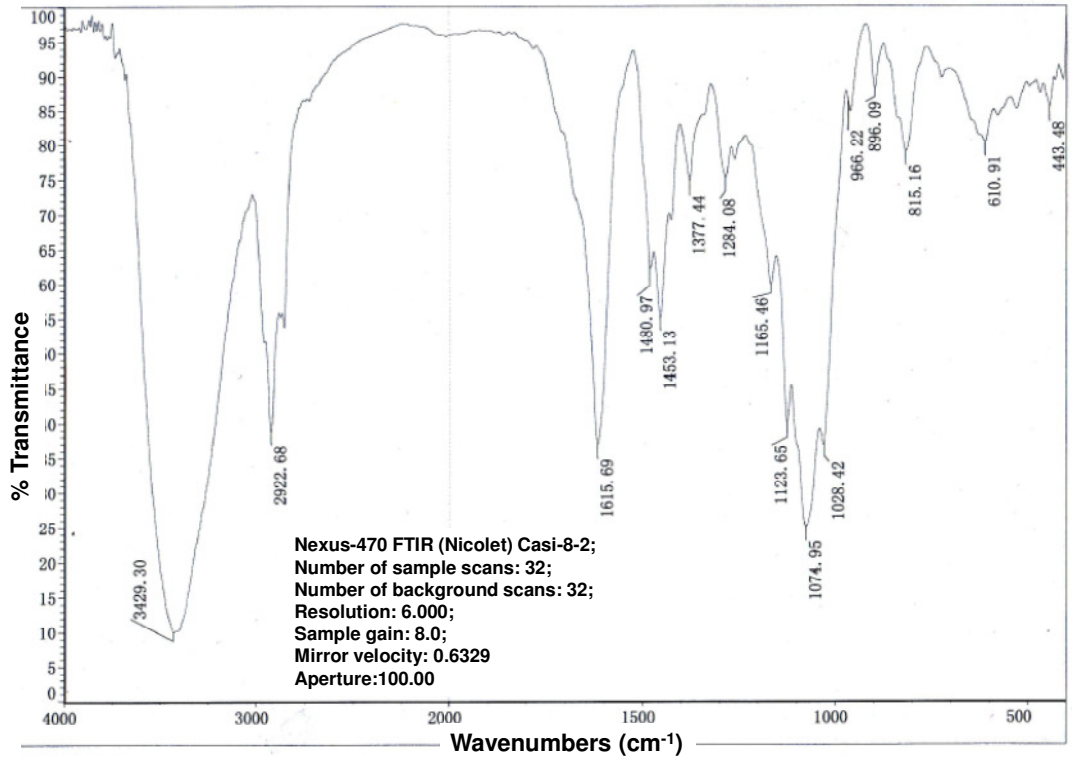


Figure S50. The IR spectrum of **16c**.

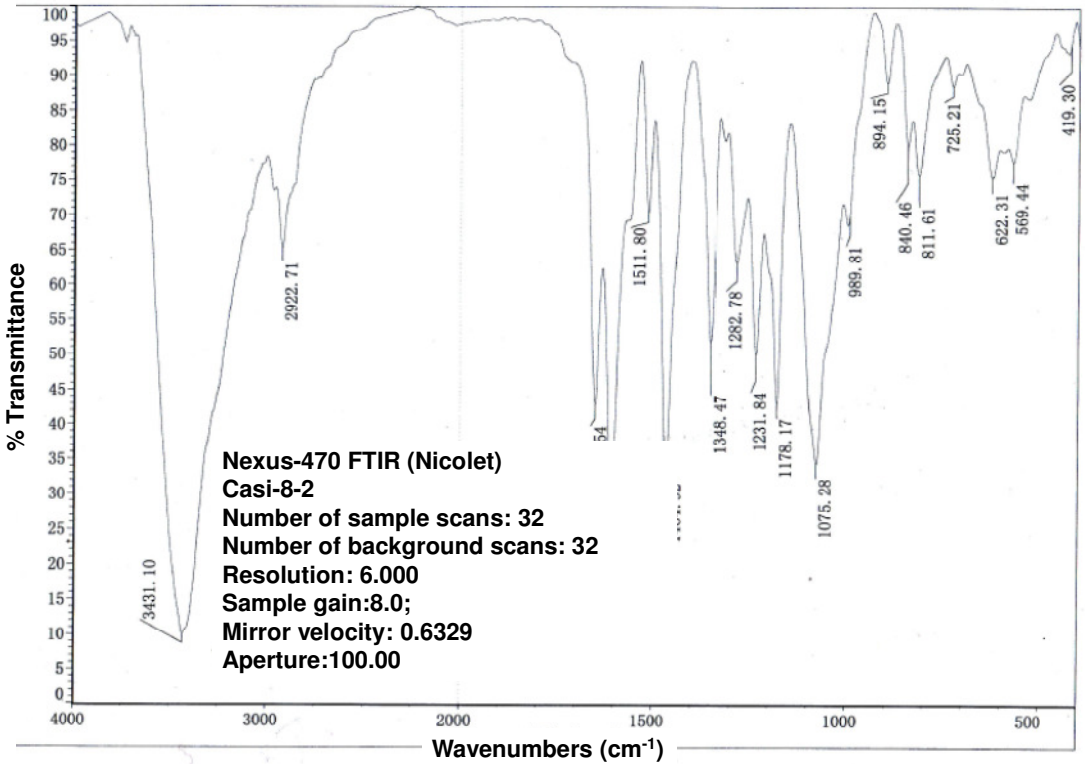


Figure S51. The IR spectrum of **19a**.

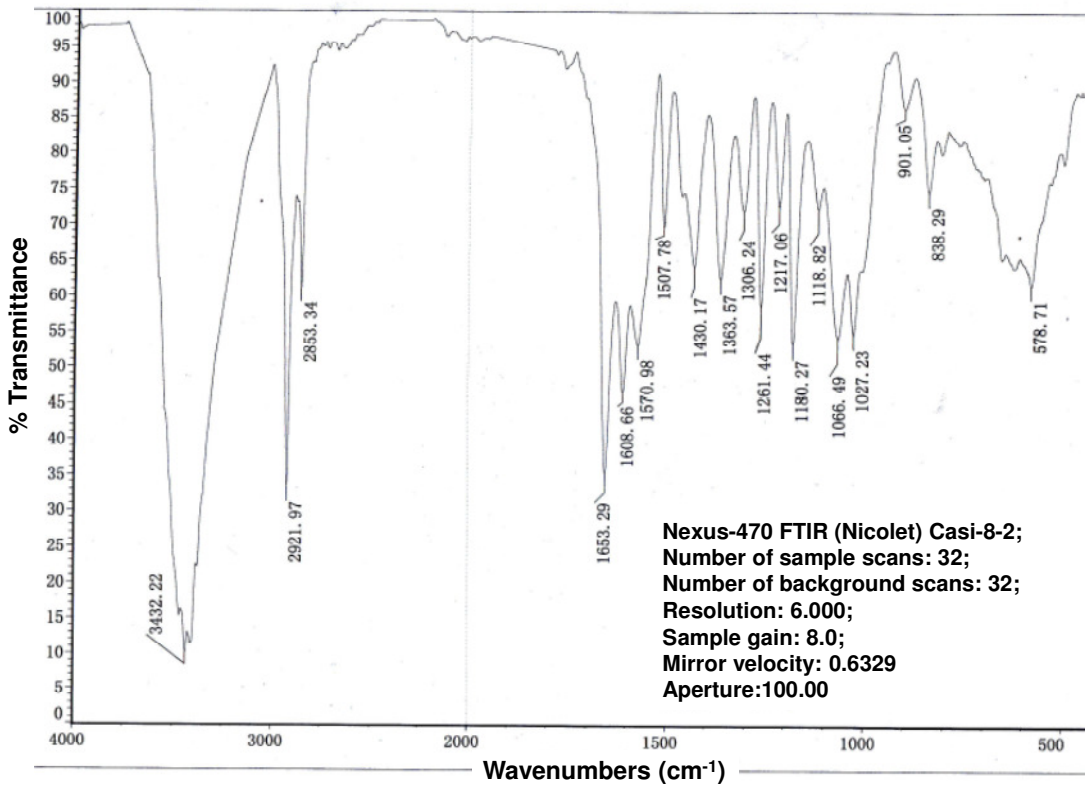


Figure S52. The IR spectrum of **22a**.

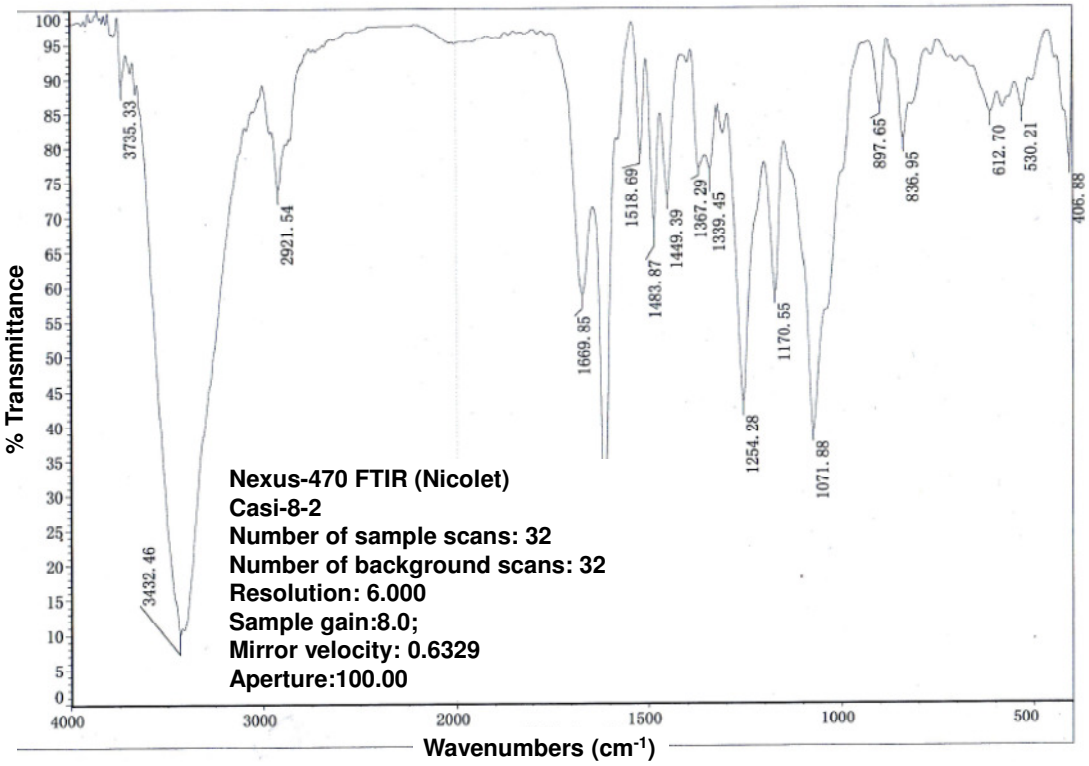


Figure S53. The IR spectrum of **24a**.

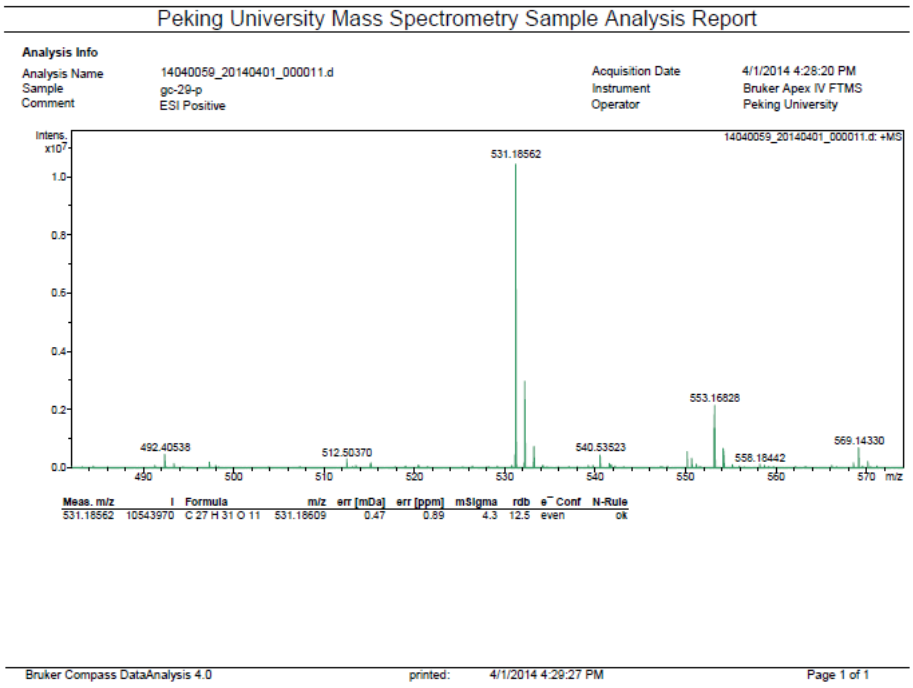


Figure S54. HRESIMS spectrum of **1a**.

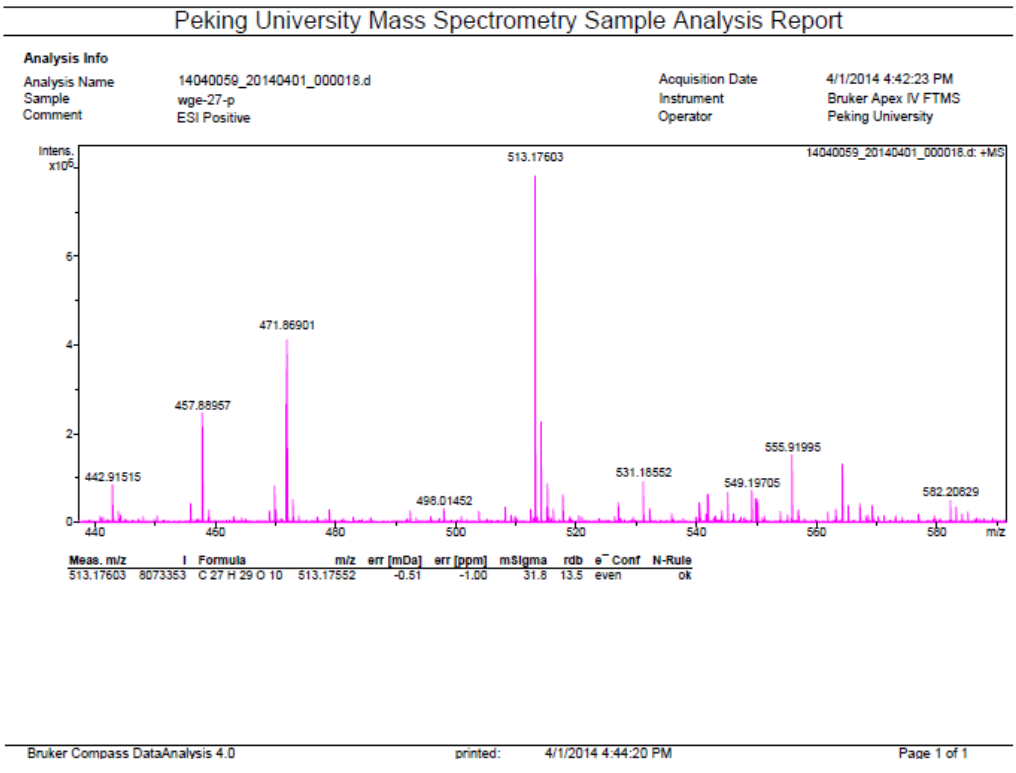


Figure S55. HRESIMS spectrum of **4a**.

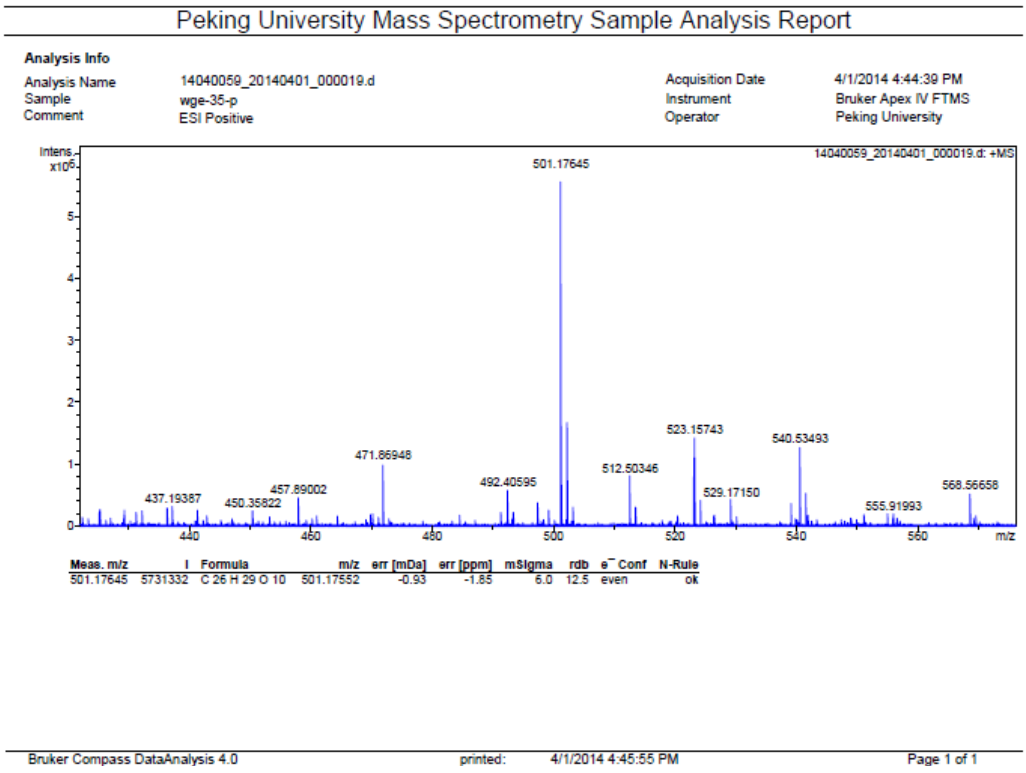


Figure S56. HRESIMS spectrum of **7a**.

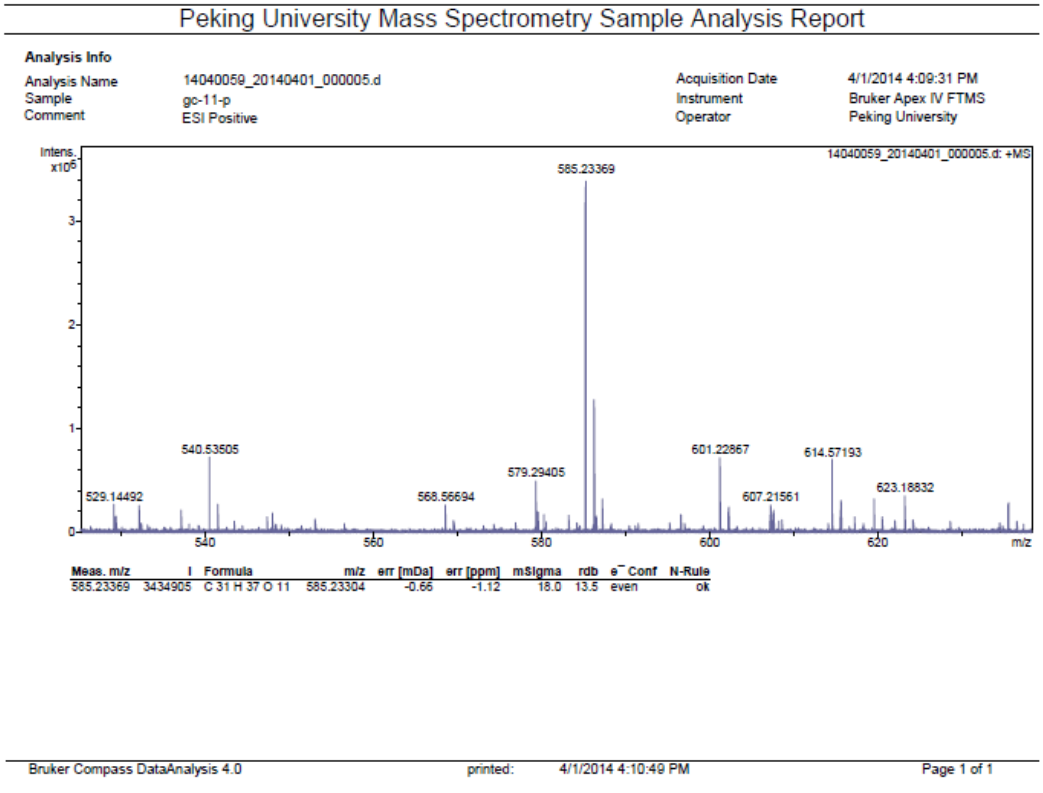


Figure S57. HRESIMS spectrum of **8a**.

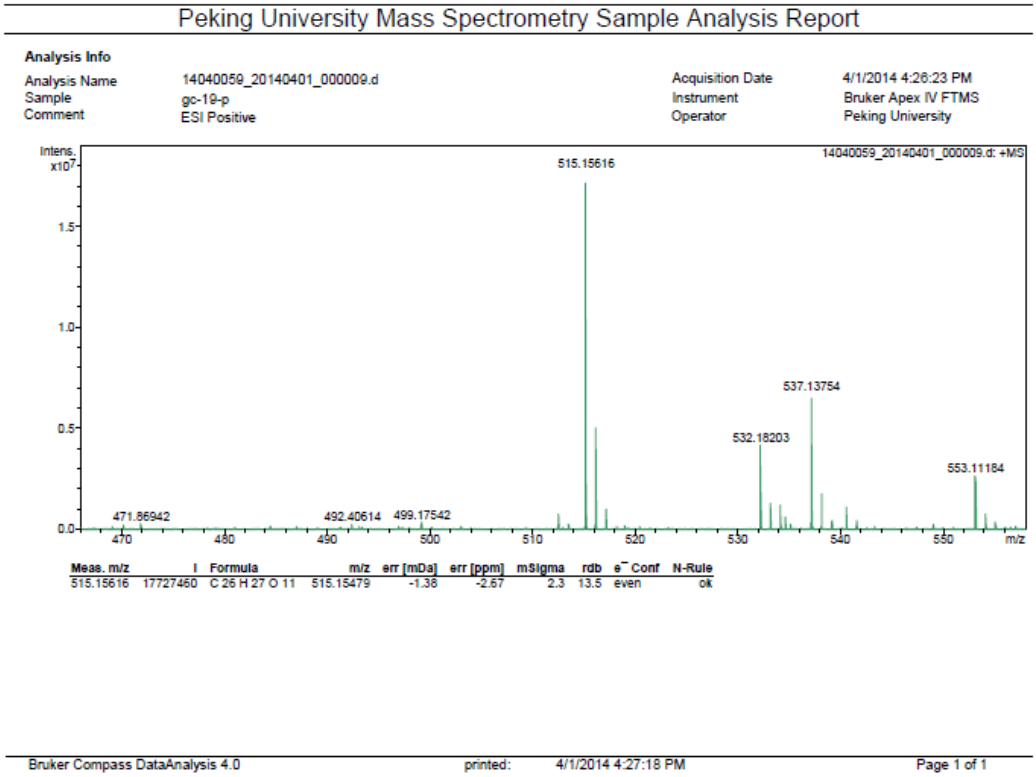


Figure S58. HRESIMS spectrum of **9a**.

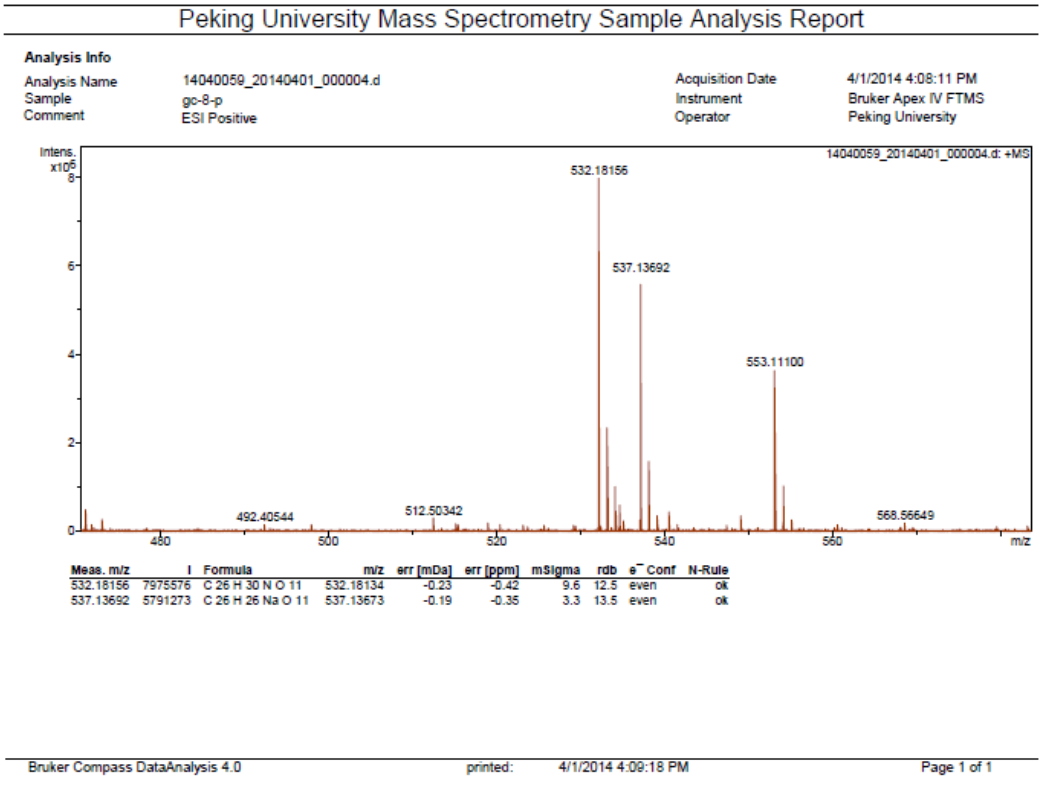


Figure S59. HRESIMS spectrum of **10a**.

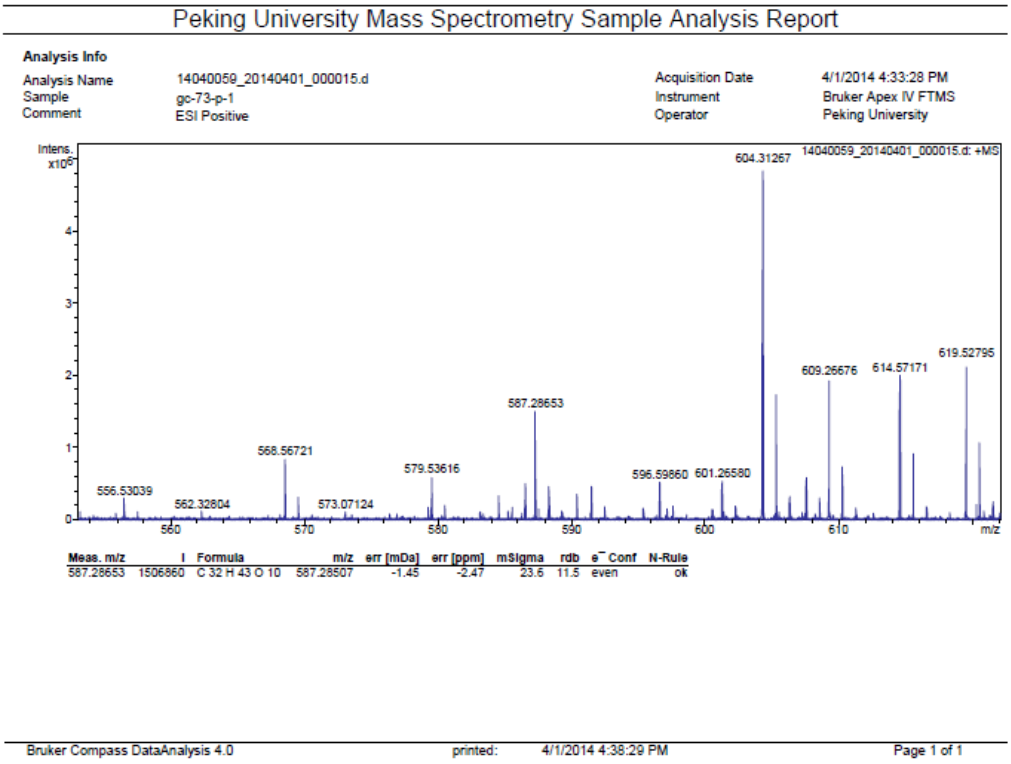


Figure S60. HRESIMS spectrum of **16a**.

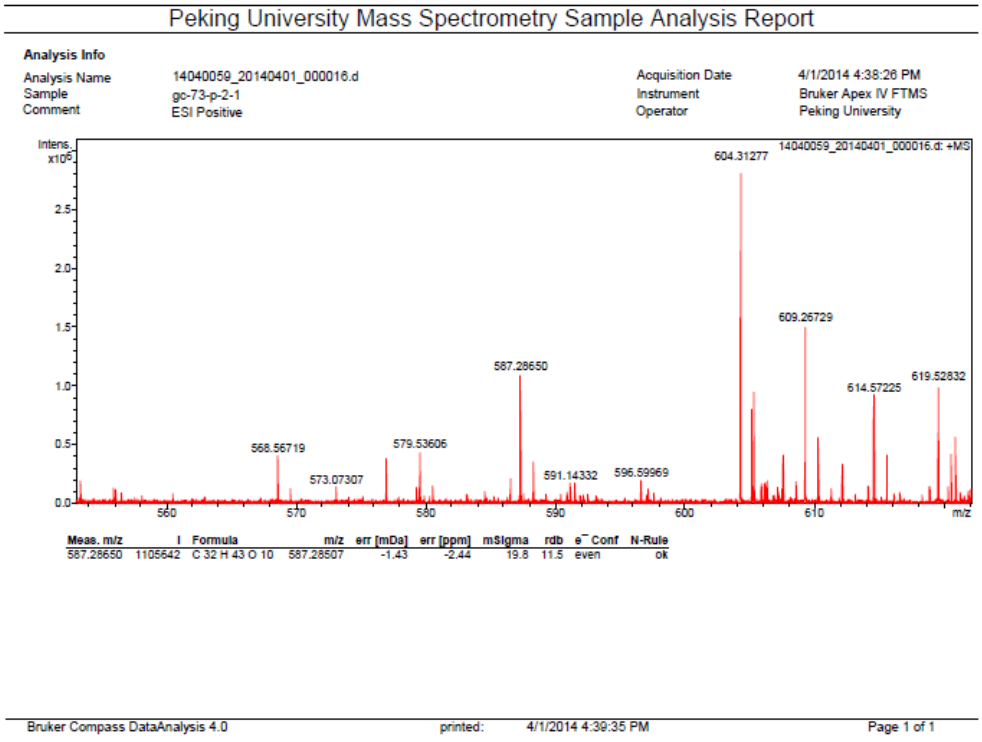


Figure S61. HRESIMS spectrum of **16b**.

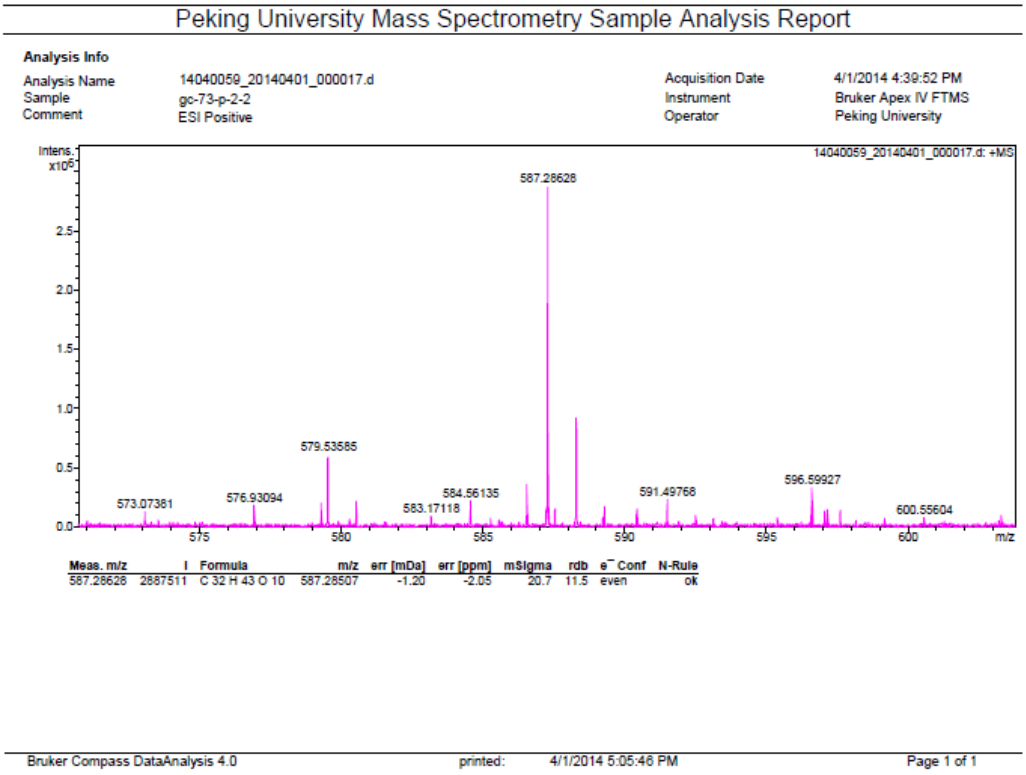


Figure S62. HRESIMS spectrum of **16c**.

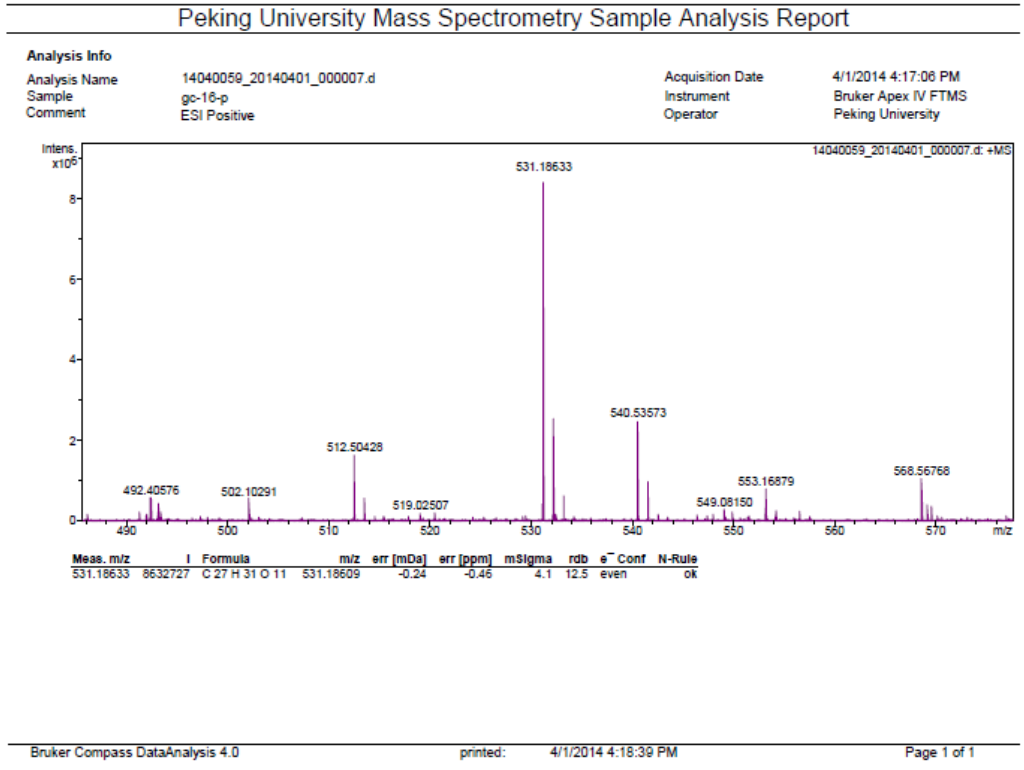


Figure S63. HRESIMS spectrum of **19a**.

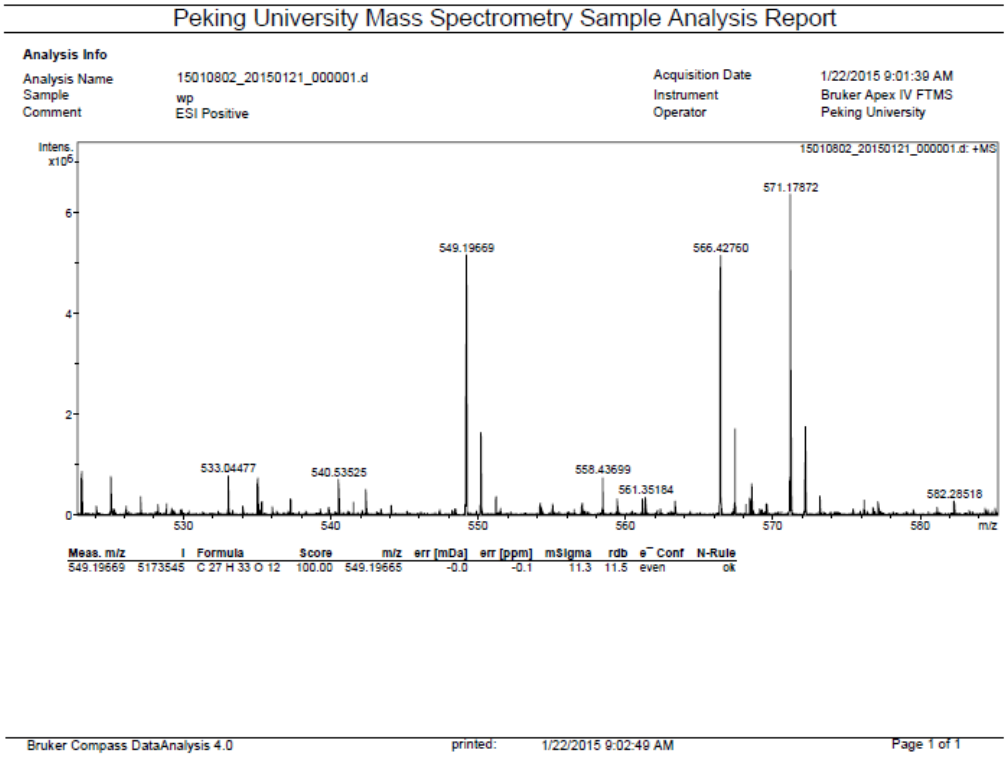


Figure S64. HRESIMS spectrum of **22a**.

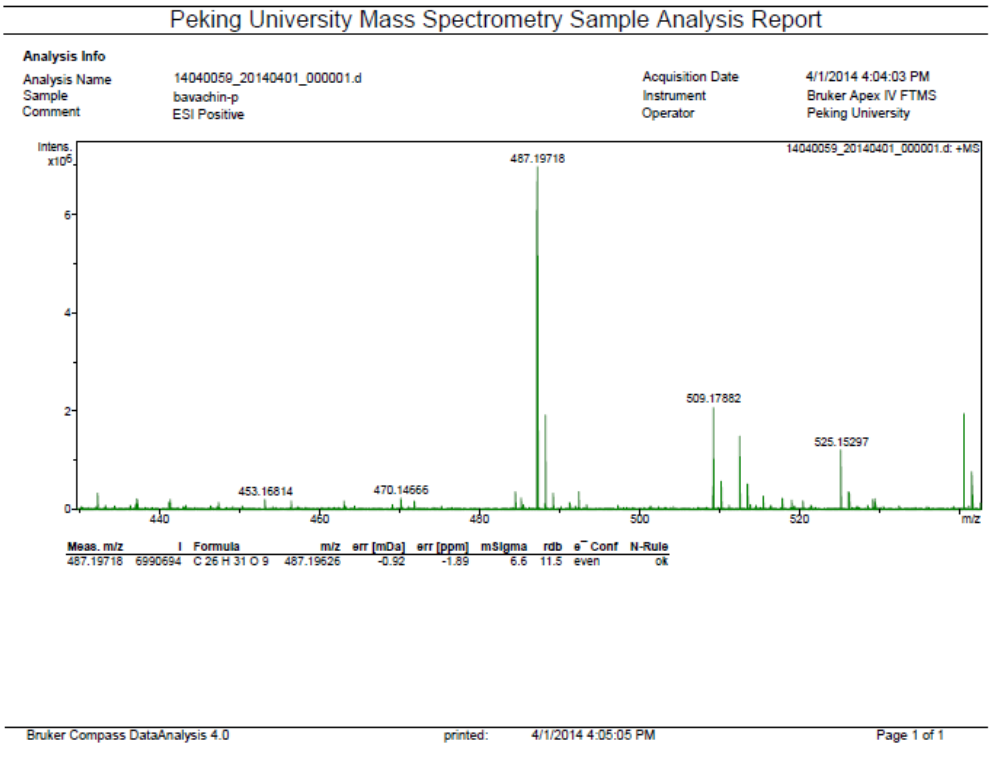


Figure S65. HRESIMS spectrum of **24a**.

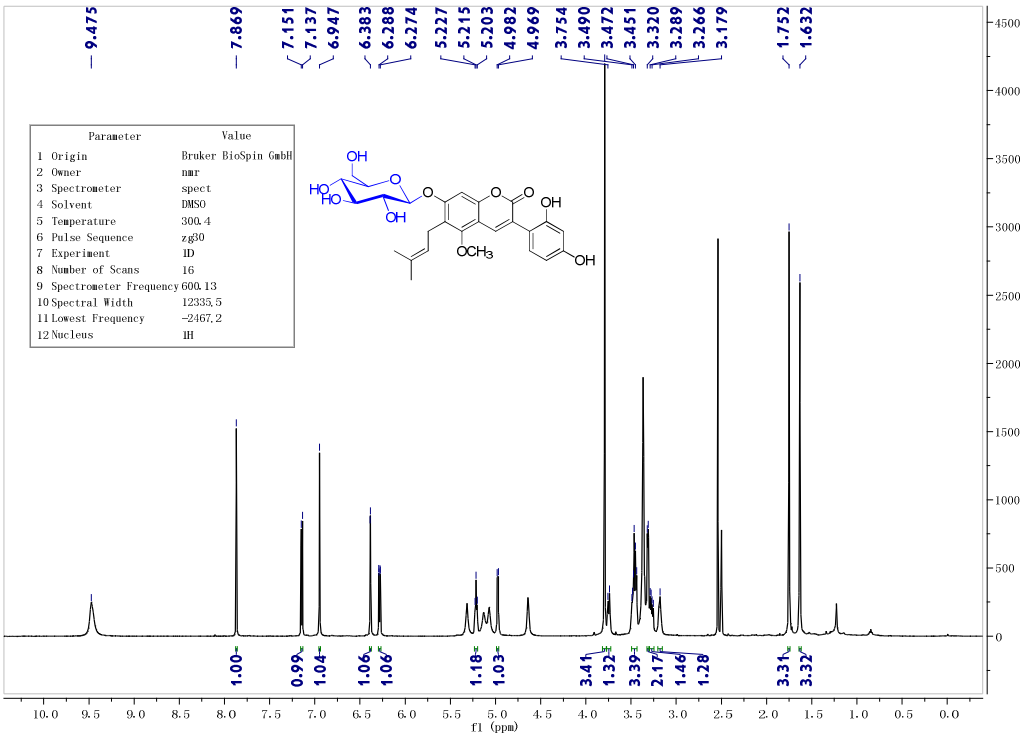


Figure S66. ^{1}H NMR spectrum of **1a** (600 MHz, DMSO-d_6).

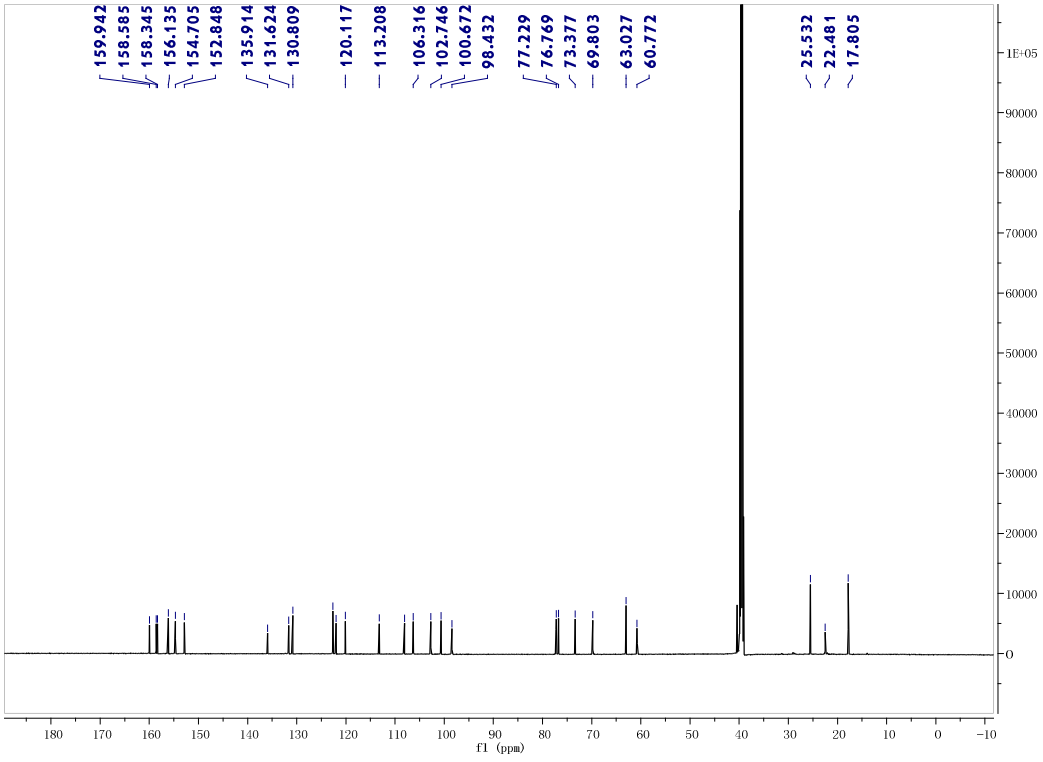


Figure S67. ^{13}C NMR spectrum of **1a** (150 MHz, DMSO-d_6).

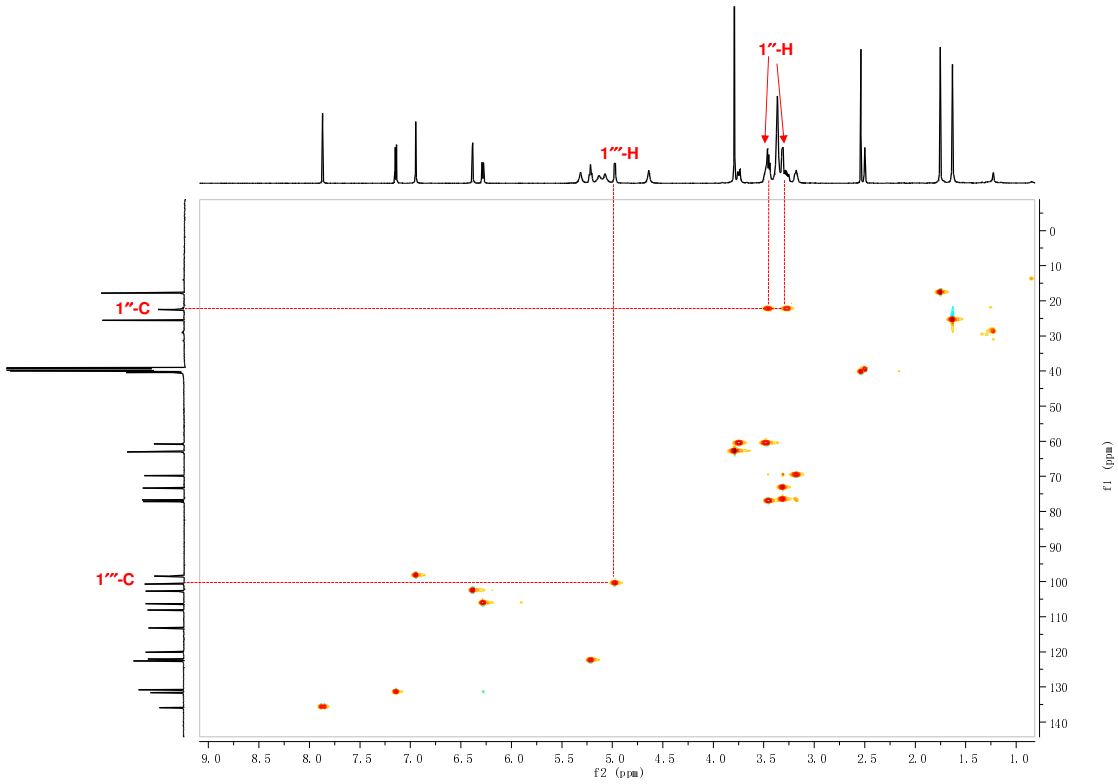


Figure S68. HSQC spectrum of **1a** (600 MHz, DMSO-d_6).

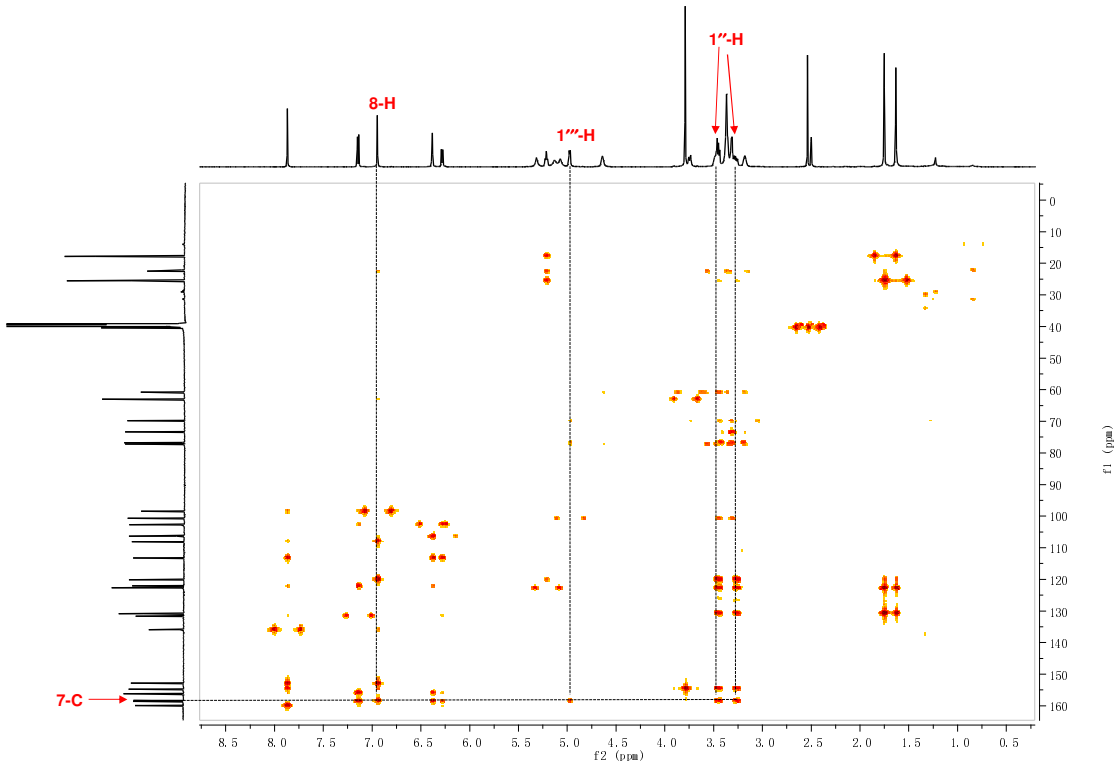


Figure S69. HMBC spectrum of **1a** (600 MHz, DMSO-d_6).

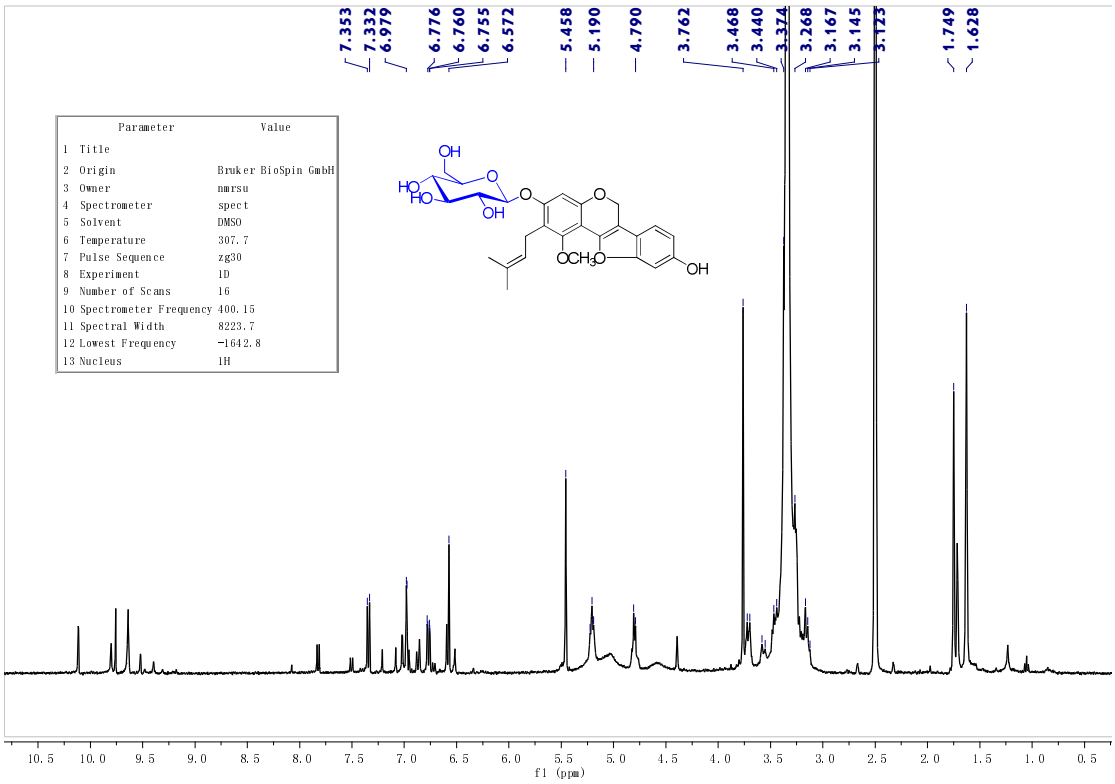


Figure S70. ^{1}H NMR spectrum of **4a** (400 MHz, DMSO-d_6).

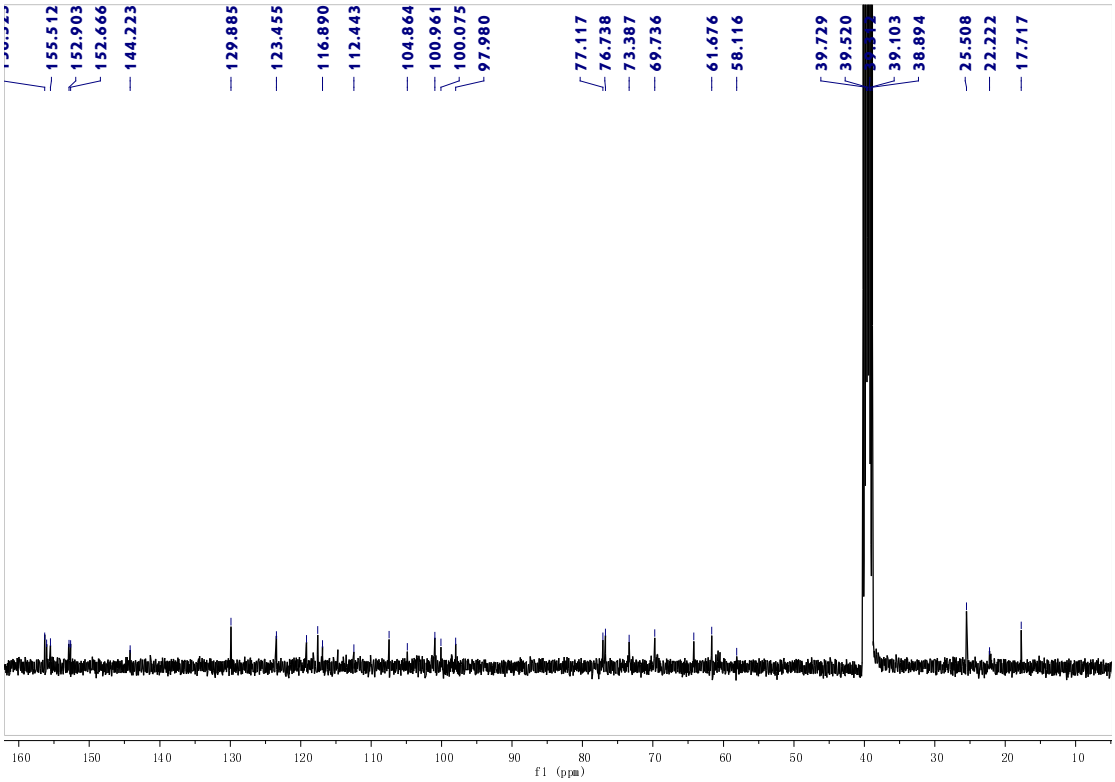


Figure S71. ^{13}C NMR spectrum of **4a** (100 MHz, DMSO-d_6).

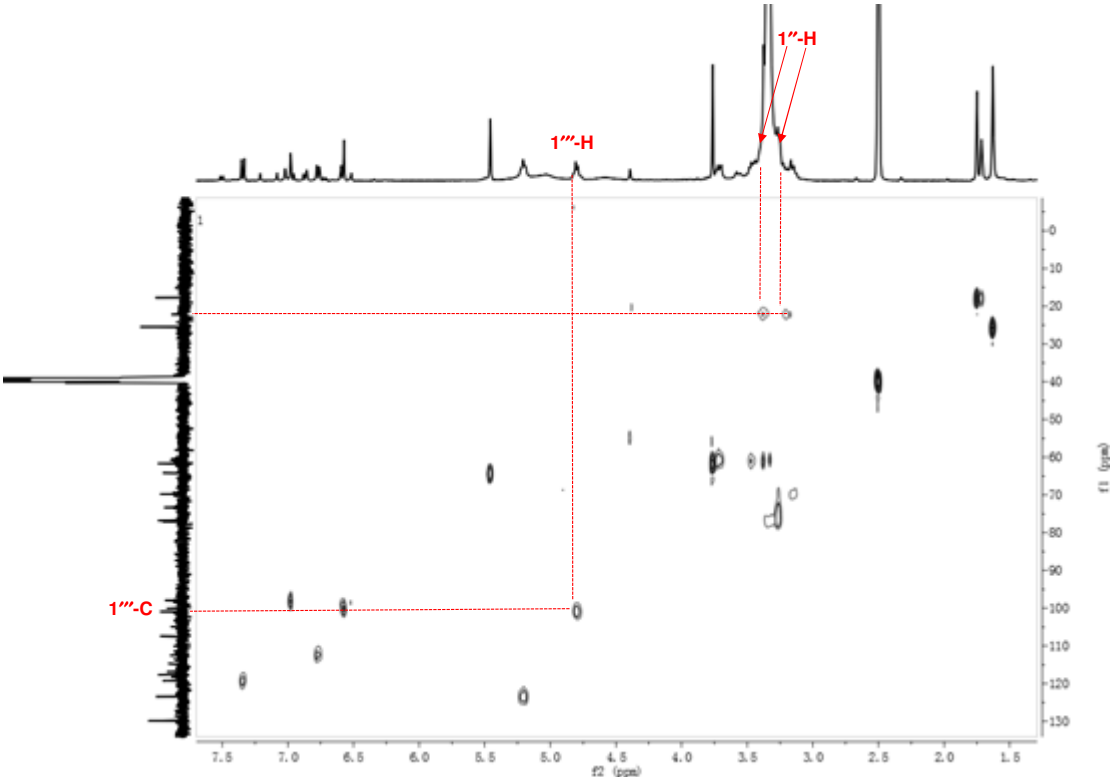


Figure S72. HSQC spectrum of **4a** (400 MHz, DMSO-d_6).

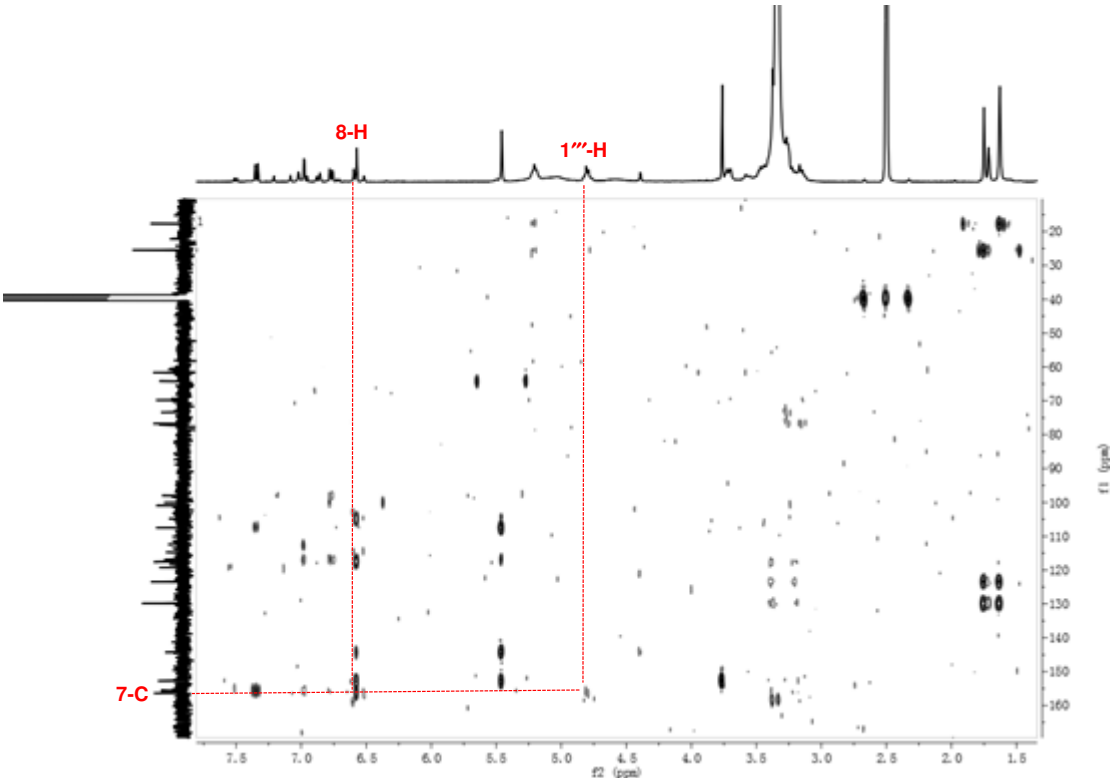


Figure S73. HMBC spectrum of **4a** (400 MHz, DMSO-d_6).

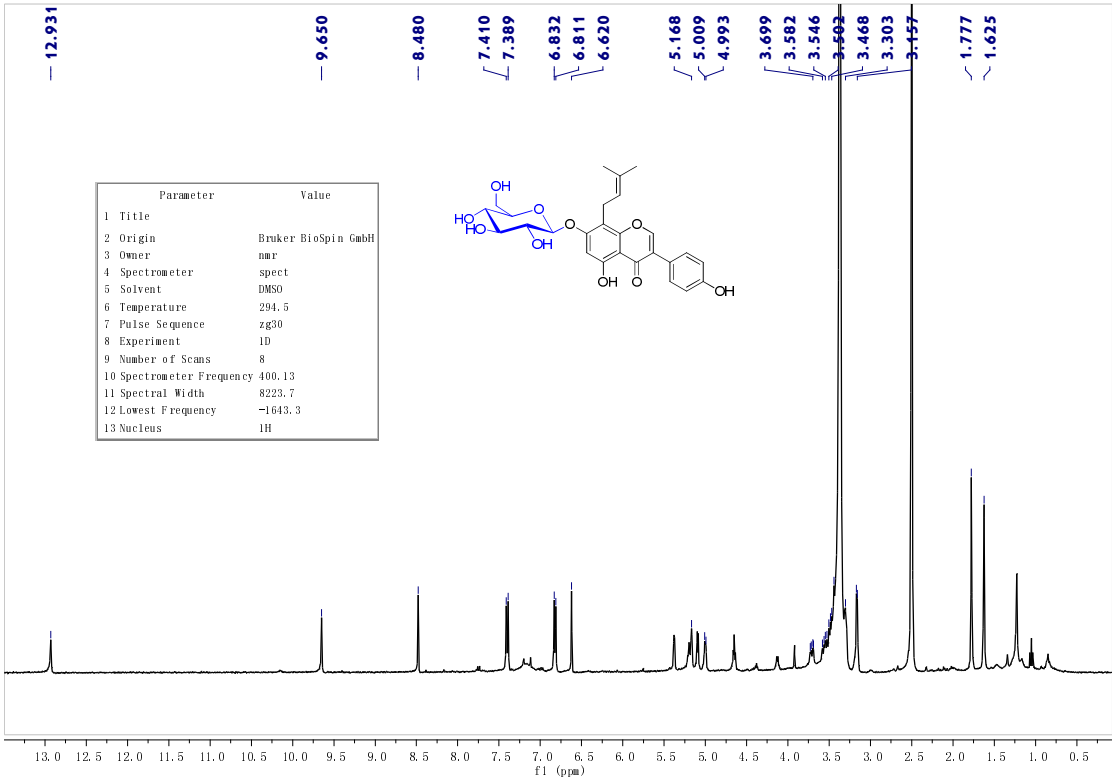


Figure S74. ^{1}H NMR spectrum of **7a** (400 MHz, DMSO-d_6).

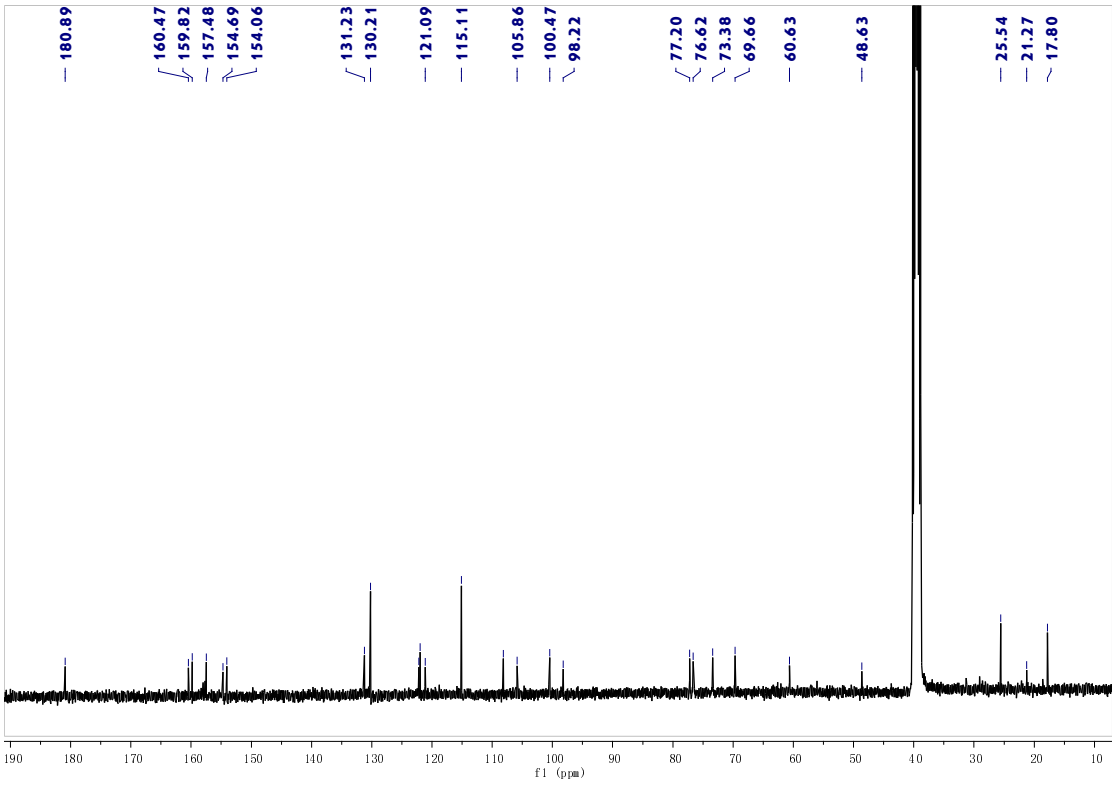


Figure S75. ^{13}C NMR spectrum of **7a** (100 MHz, DMSO-d_6).

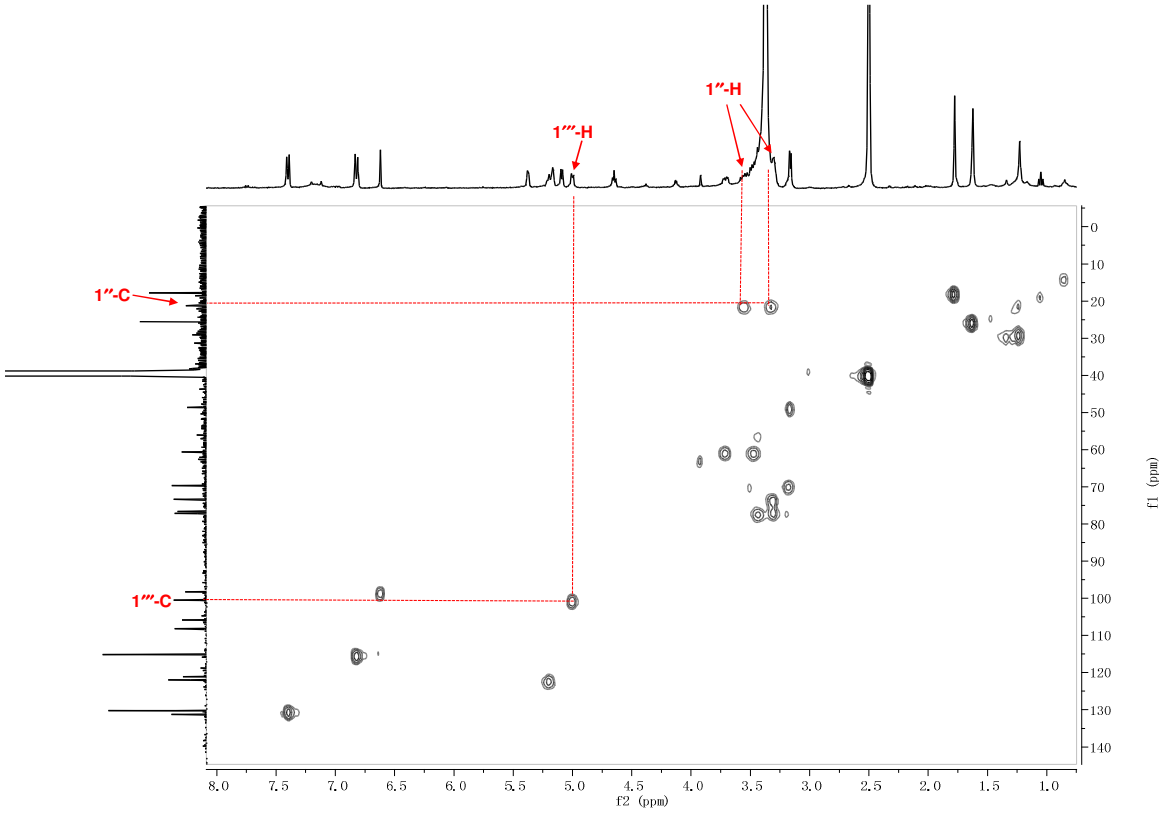


Figure S76. HSQC spectrum of **7a** (400 MHz, DMSO-d_6).

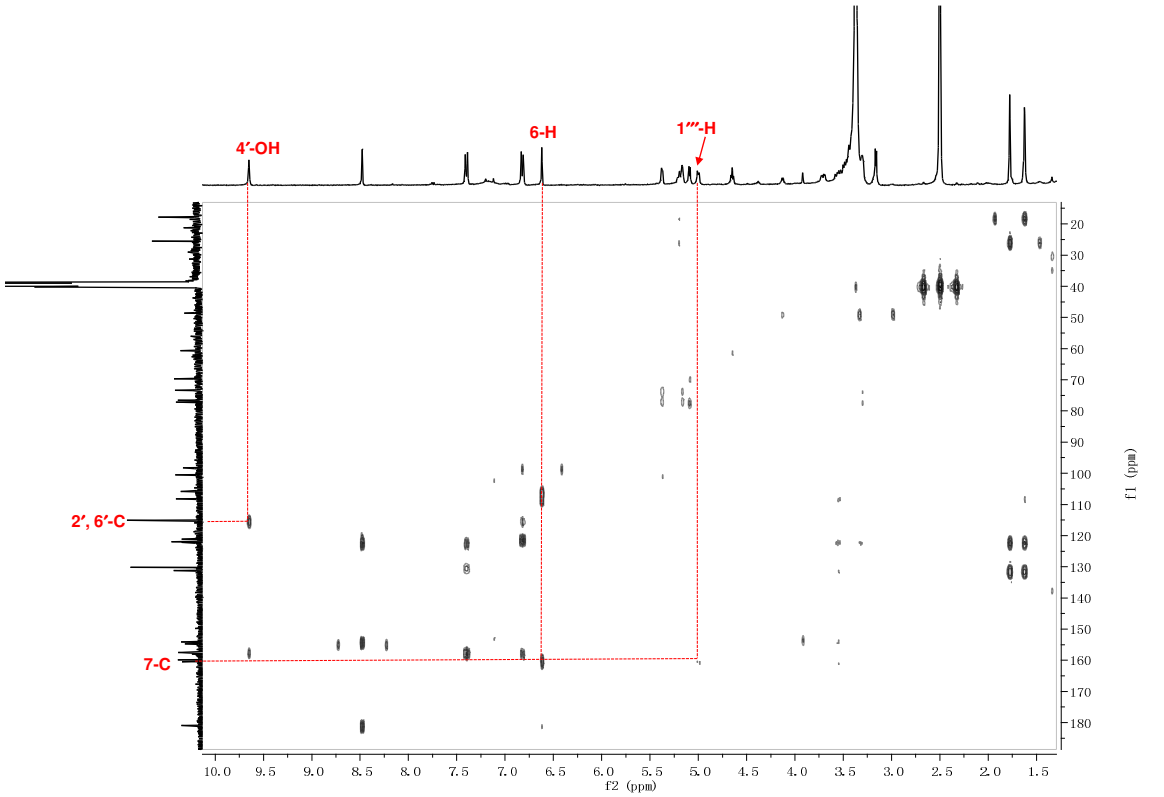


Figure S77. HMBC spectrum of **7a** (400 MHz, DMSO-d_6).

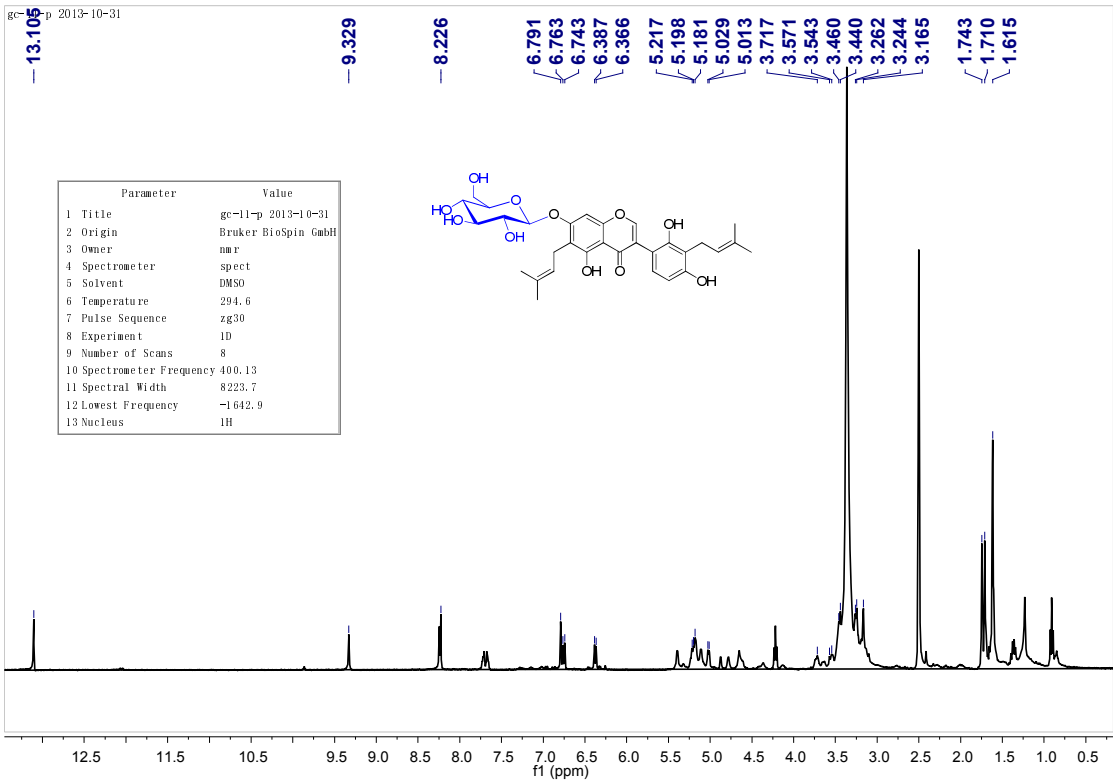


Figure S78. ^{1}H NMR spectrum of **8a** (400 MHz, DMSO-d_6).

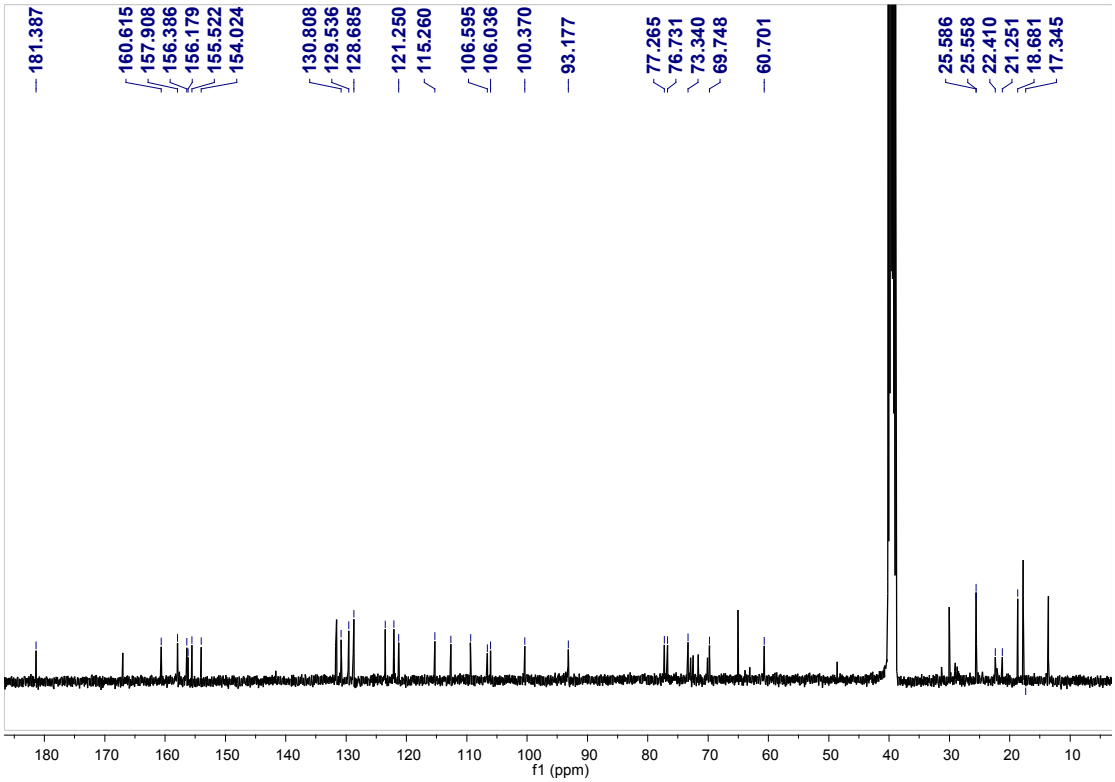


Figure S79. ^{13}C NMR spectrum of **8a** (100 MHz, DMSO-d_6).

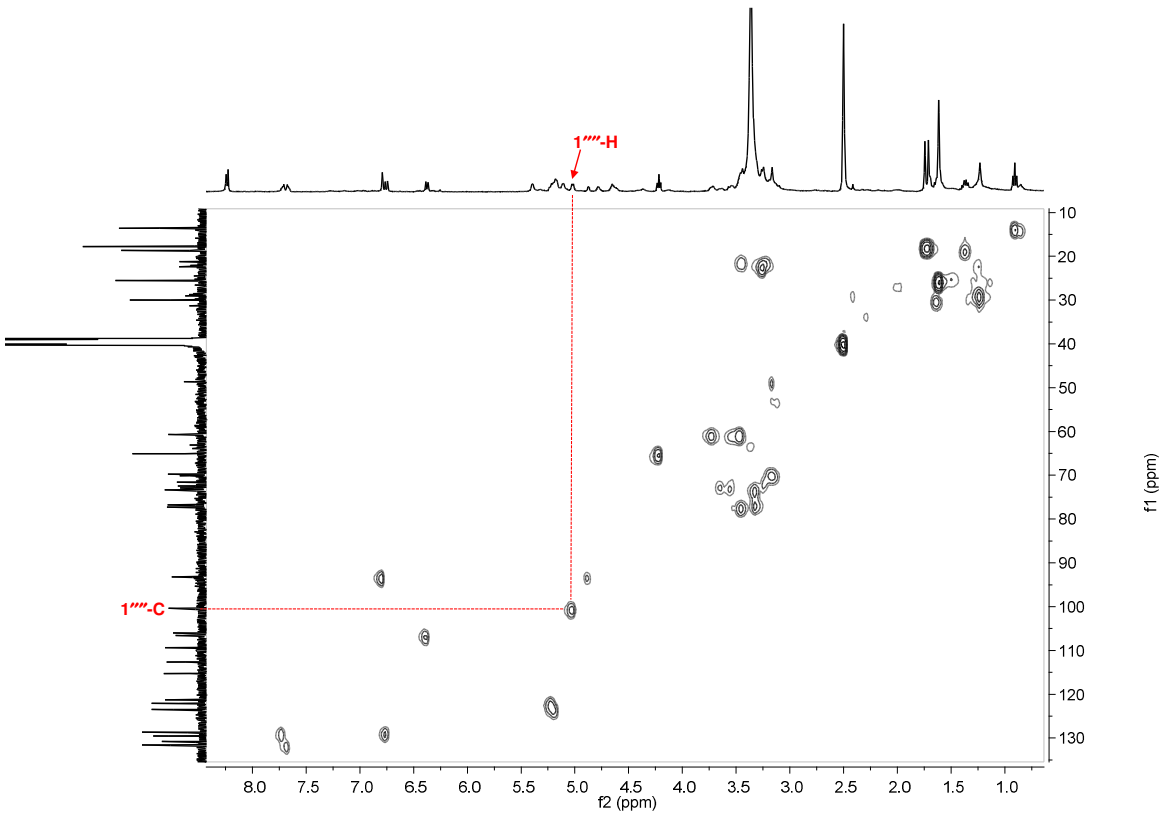


Figure S80. HSQC spectrum of **8a** (400 MHz, DMSO-d_6).

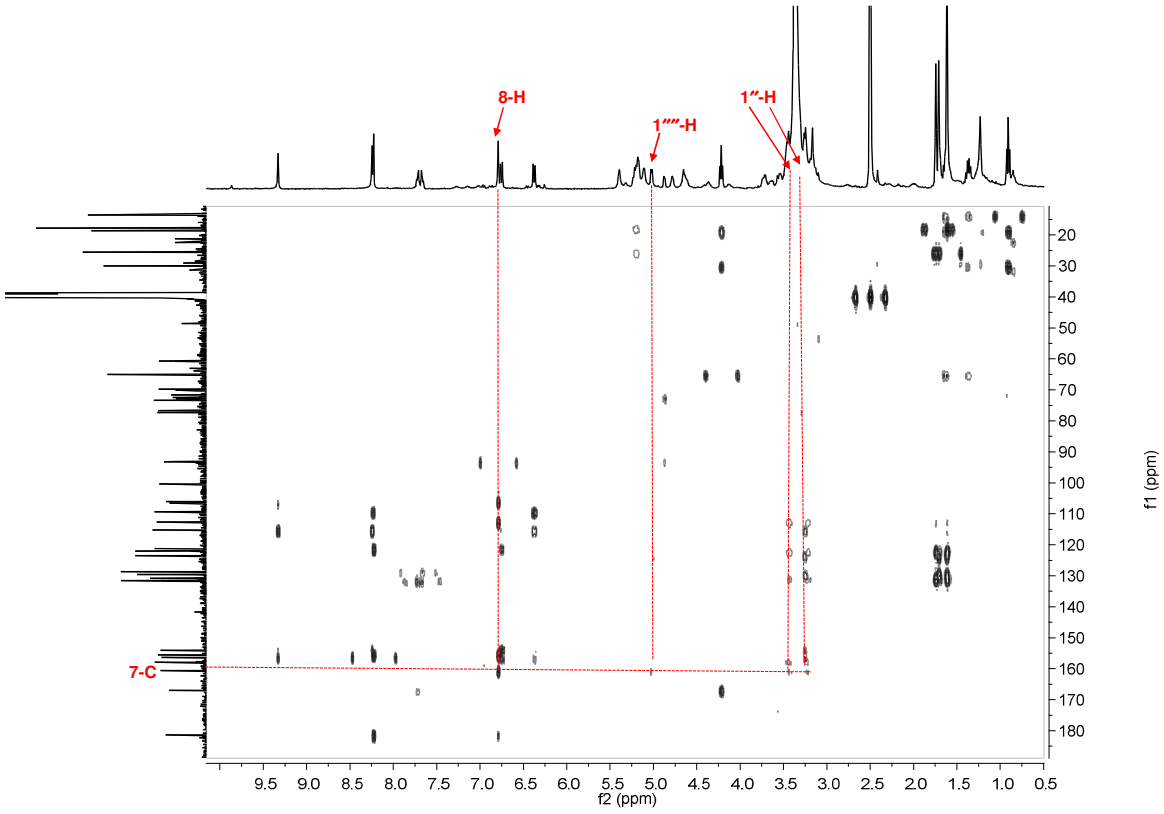


Figure S81. HMBC spectrum of **8a** (400 MHz, DMSO-d_6).

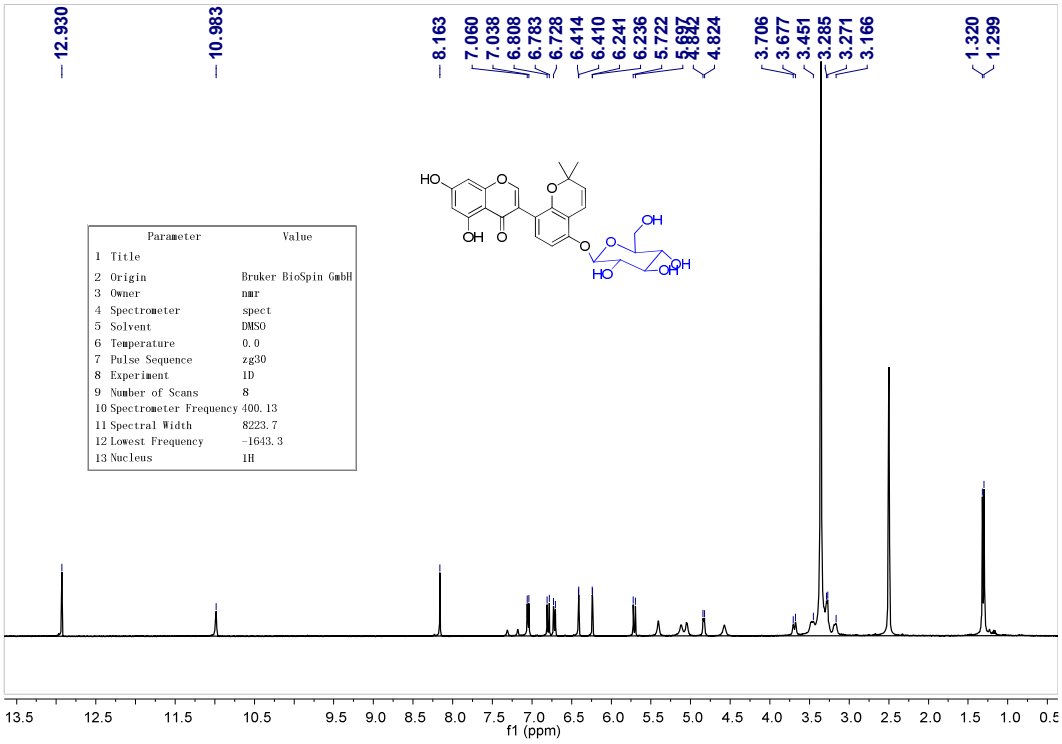


Figure S82. ^{1}H NMR spectrum of **9a** (400 MHz, DMSO-d_6).

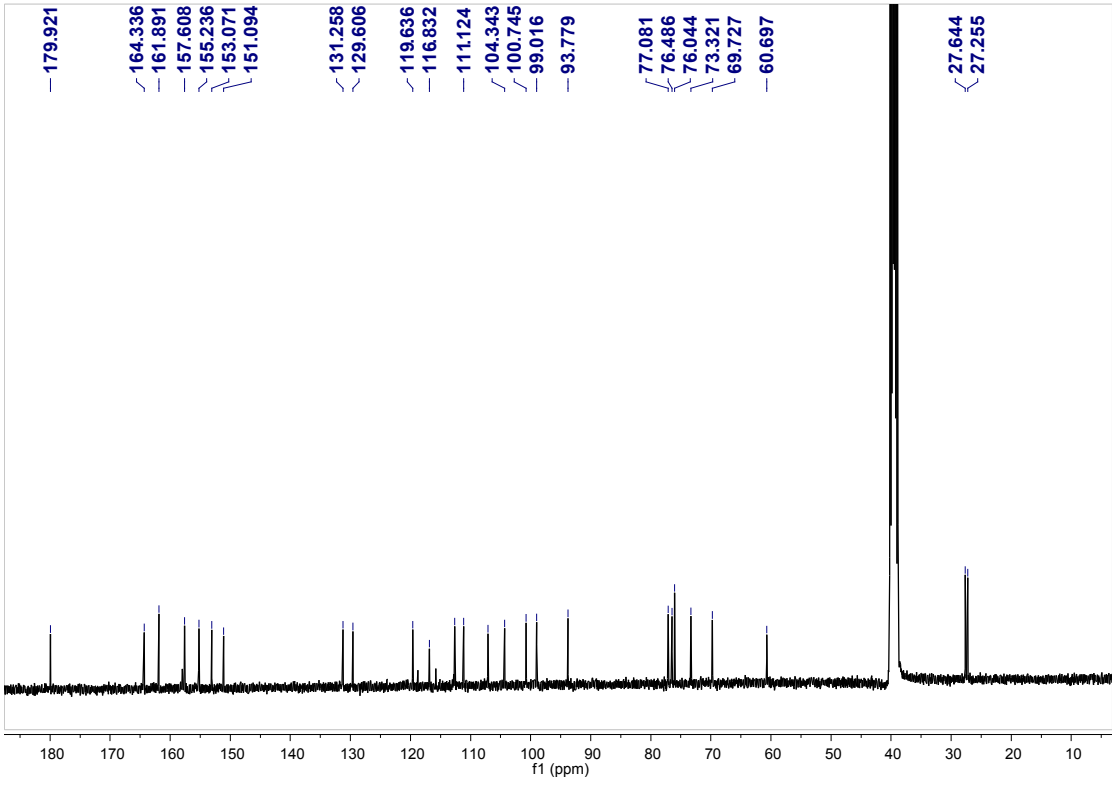


Figure S83. ^{13}C NMR spectrum of **9a** (100 MHz, DMSO-d_6).

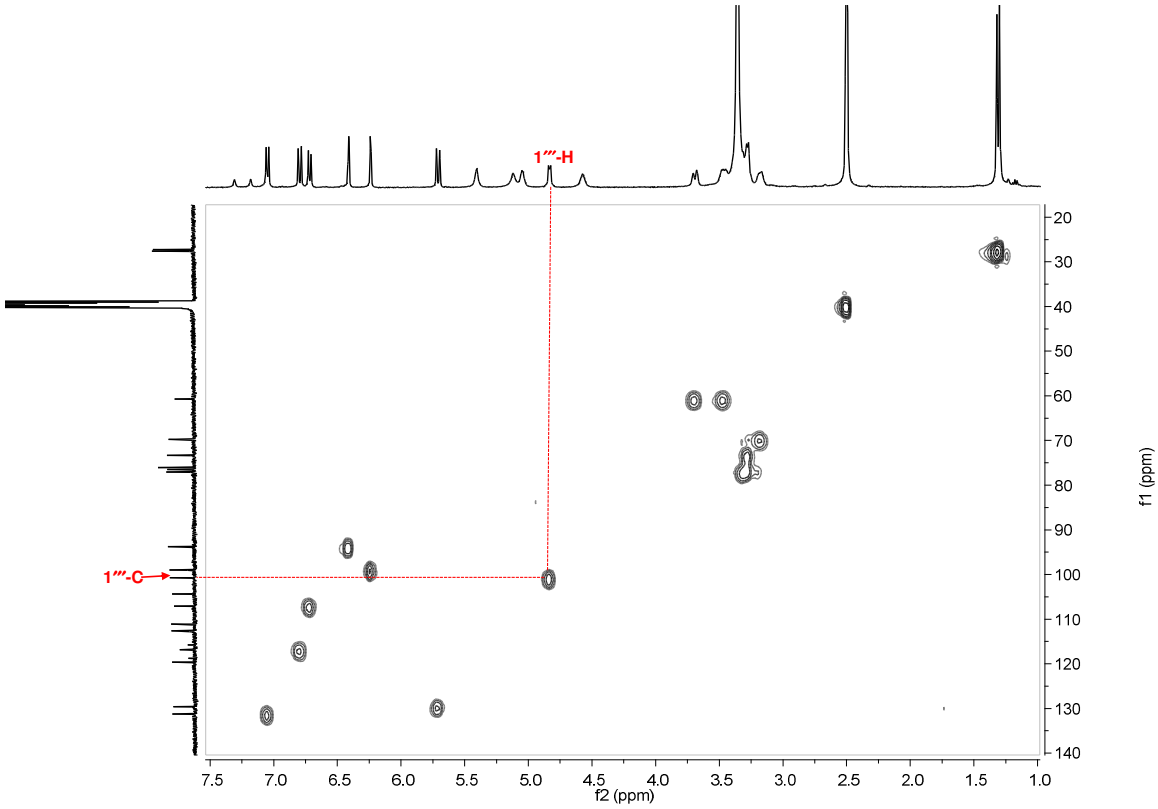


Figure S84. HSQC spectrum of **9a** (400 MHz, DMSO-d_6).

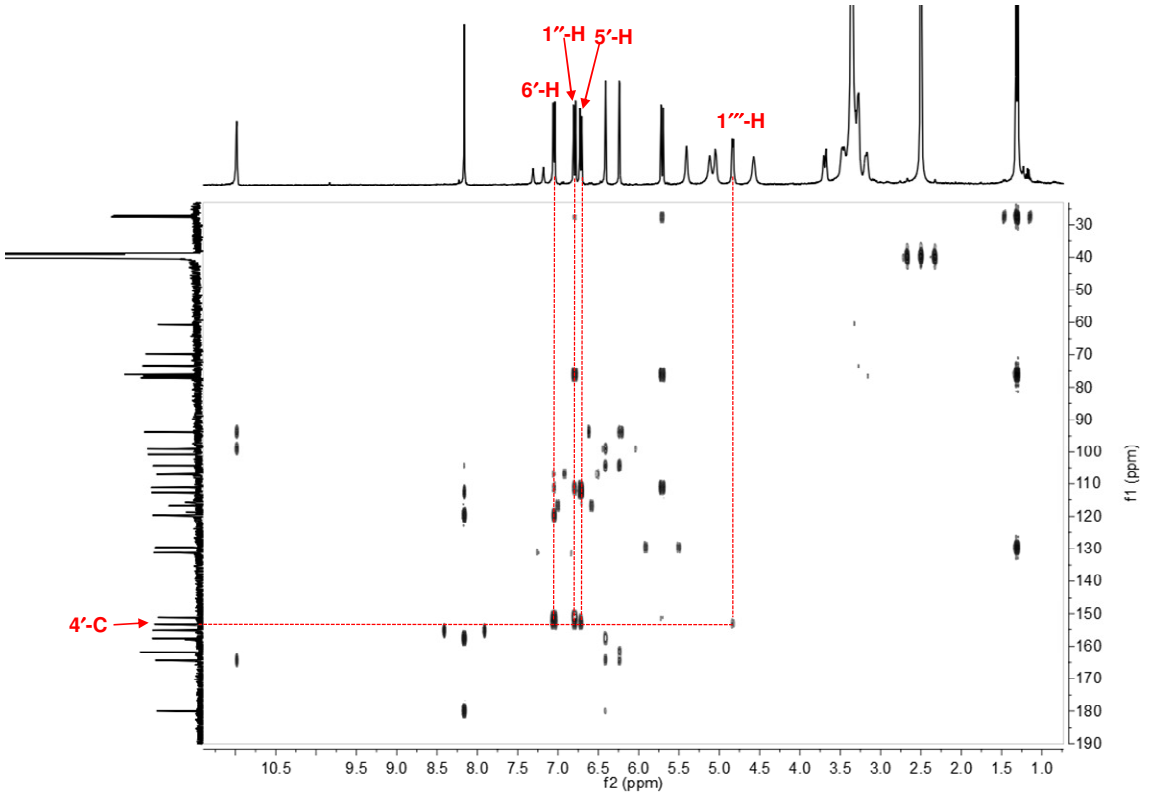


Figure S85. HMBC spectrum of **9a** (400 MHz, DMSO-d_6).

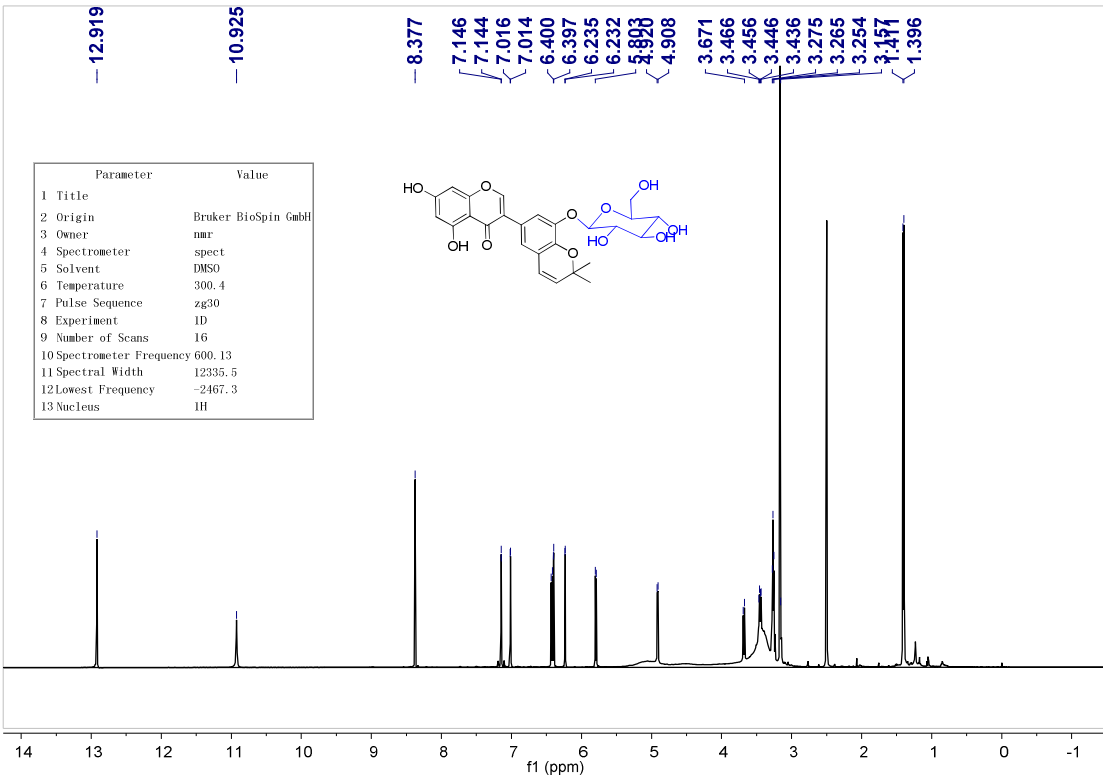


Figure S86. ^{1}H NMR spectrum of **10a** (600 MHz, DMSO-d_6).

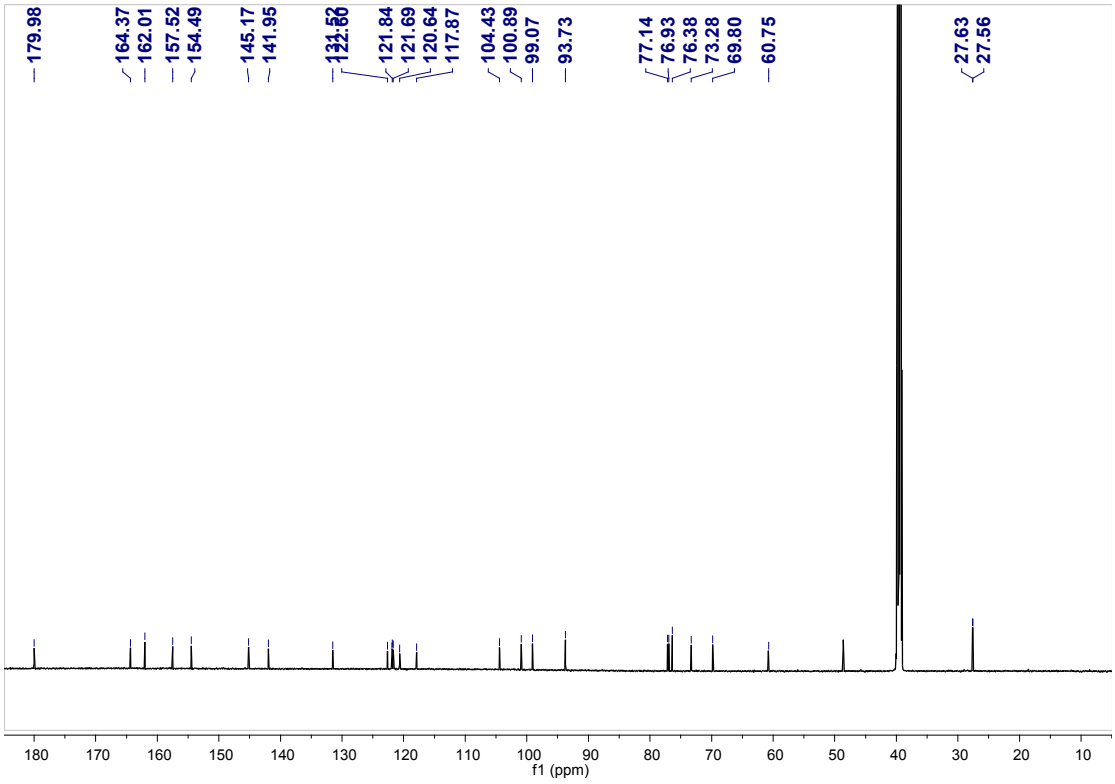


Figure S87. ^{13}C NMR spectrum of **10a** (150 MHz, DMSO-d_6).

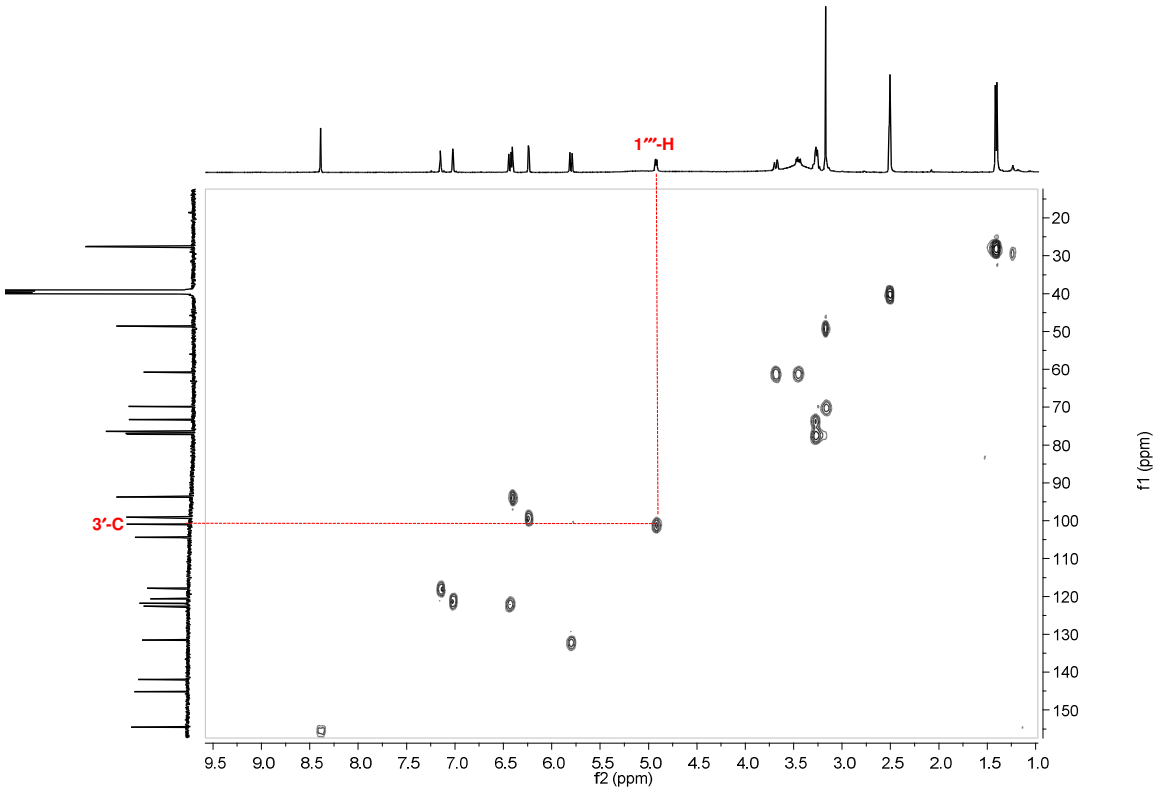


Figure S88. HSQC spectrum of **10a** (600 MHz, DMSO-d_6).

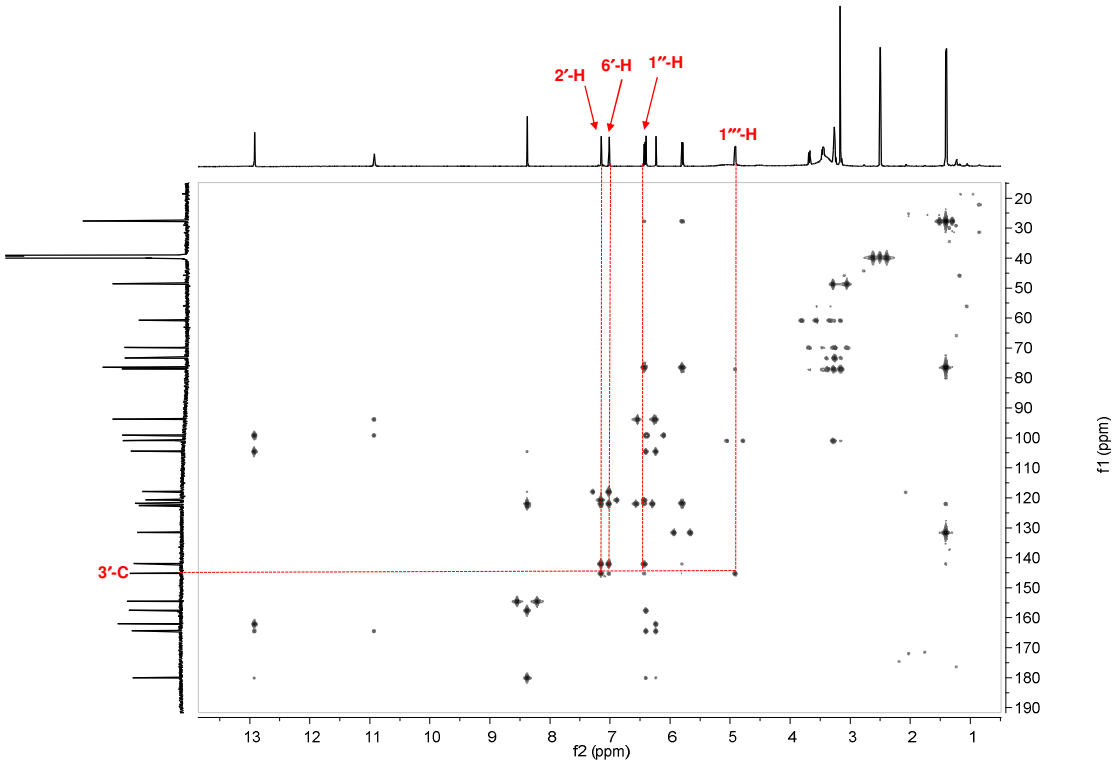


Figure S89. HMBC spectrum of **10a** (600 MHz, DMSO-d_6).

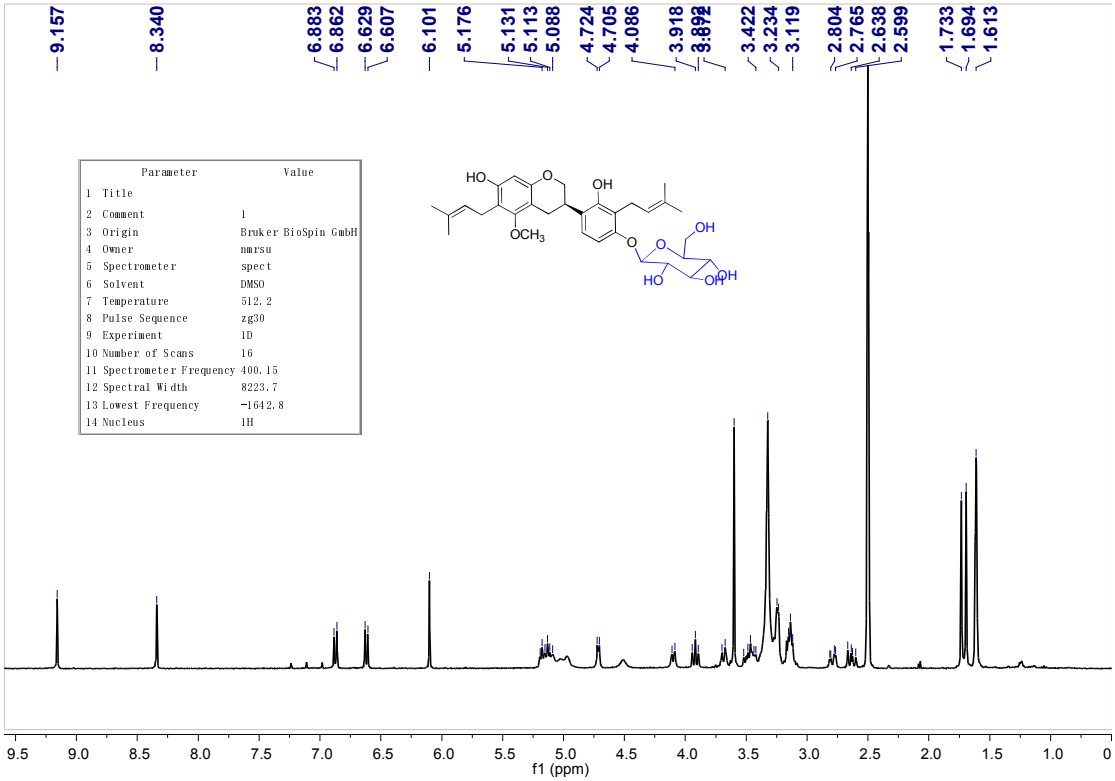


Figure S90. ^{1}H NMR spectrum of **16a** (400 MHz, DMSO-d_6).

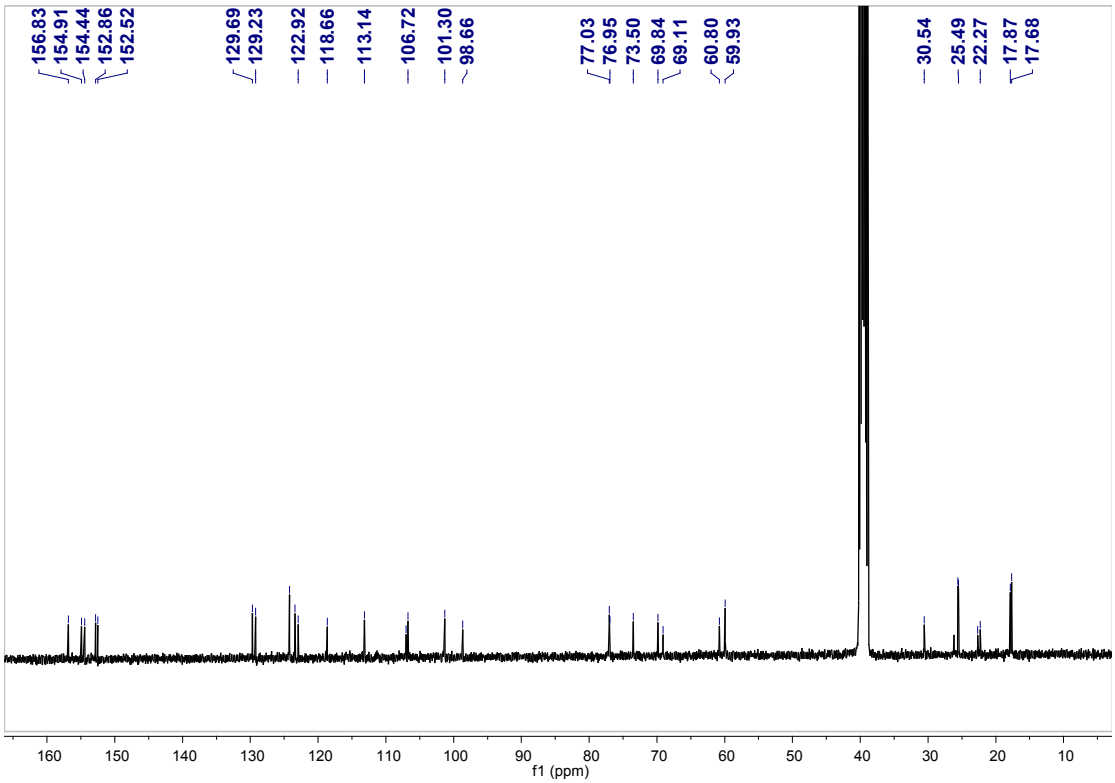


Figure S91. ^{13}C NMR spectrum of **16a** (100 MHz, DMSO-d_6).

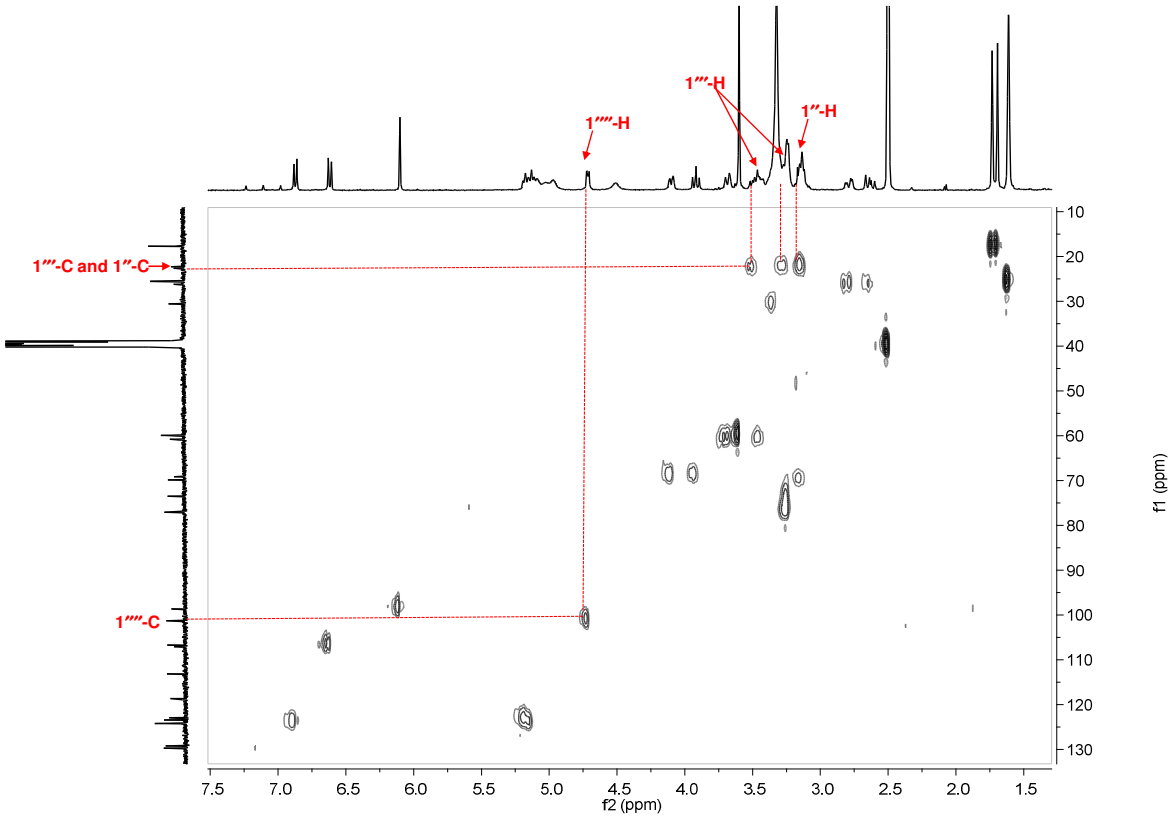


Figure S92. HSQC spectrum of **16a** (400 MHz, DMSO-d_6).

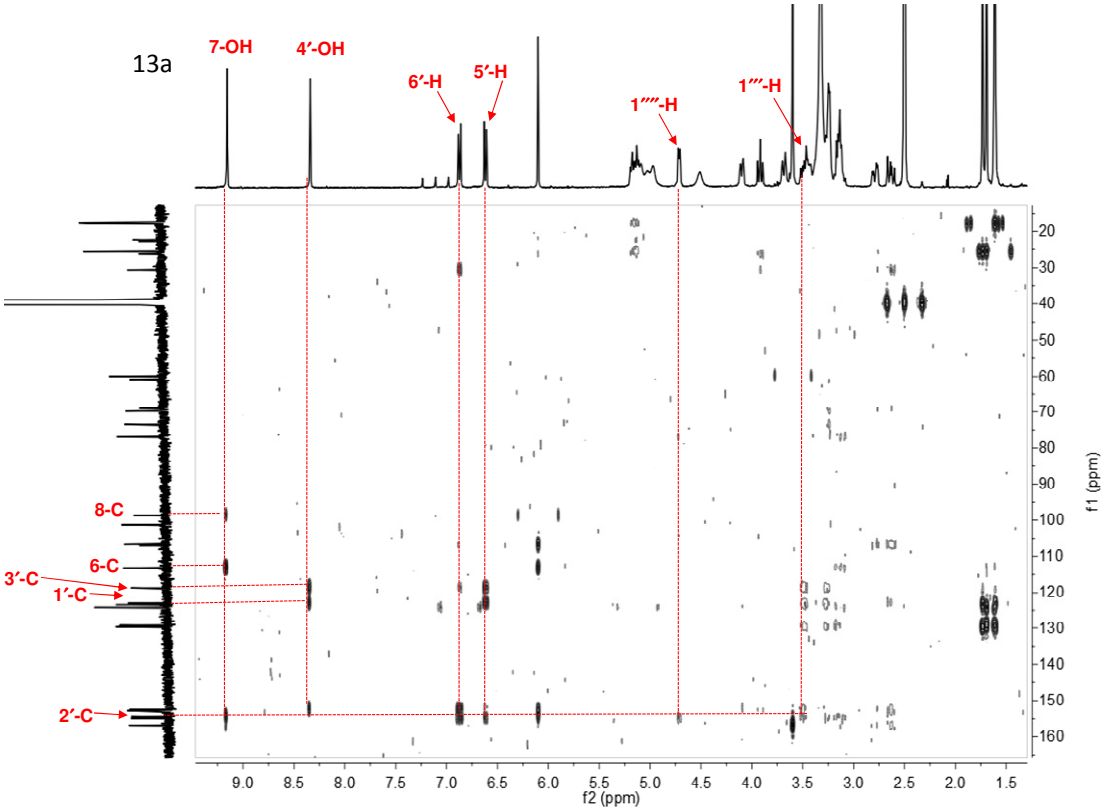


Figure S93. HMBC spectrum of **16a** (400 MHz, DMSO-d_6).

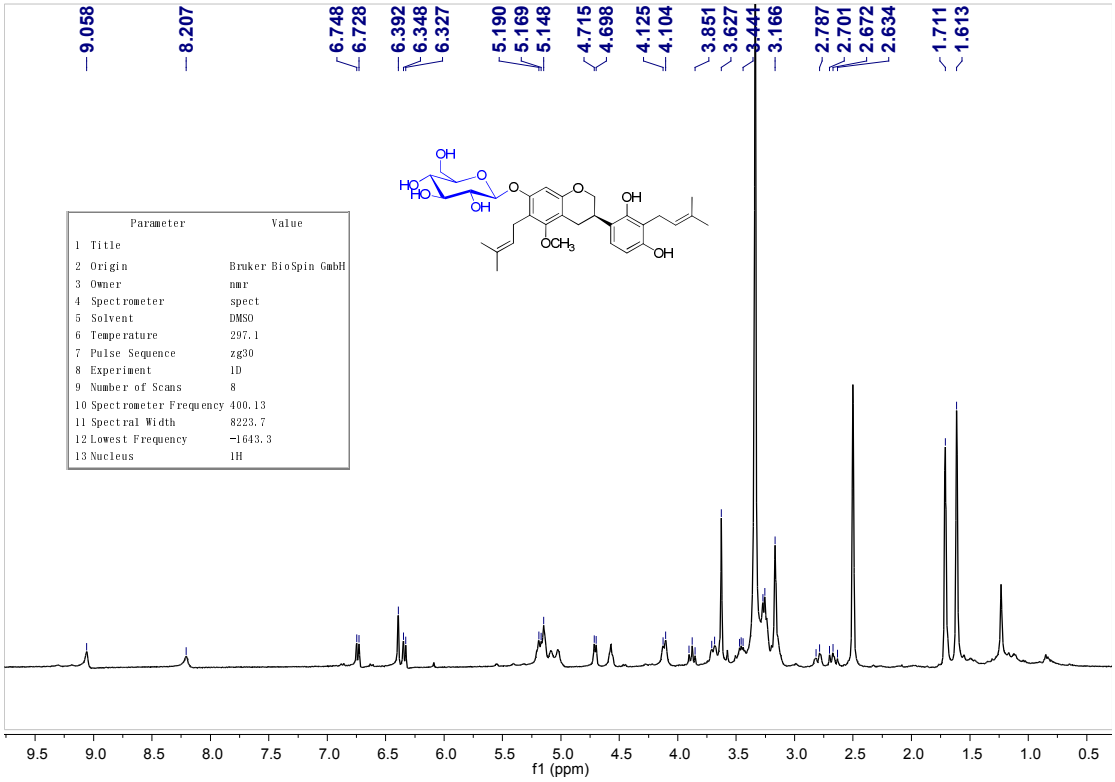


Figure S94. ^{1}H NMR spectrum of **16b** (400 MHz, DMSO-d_6).

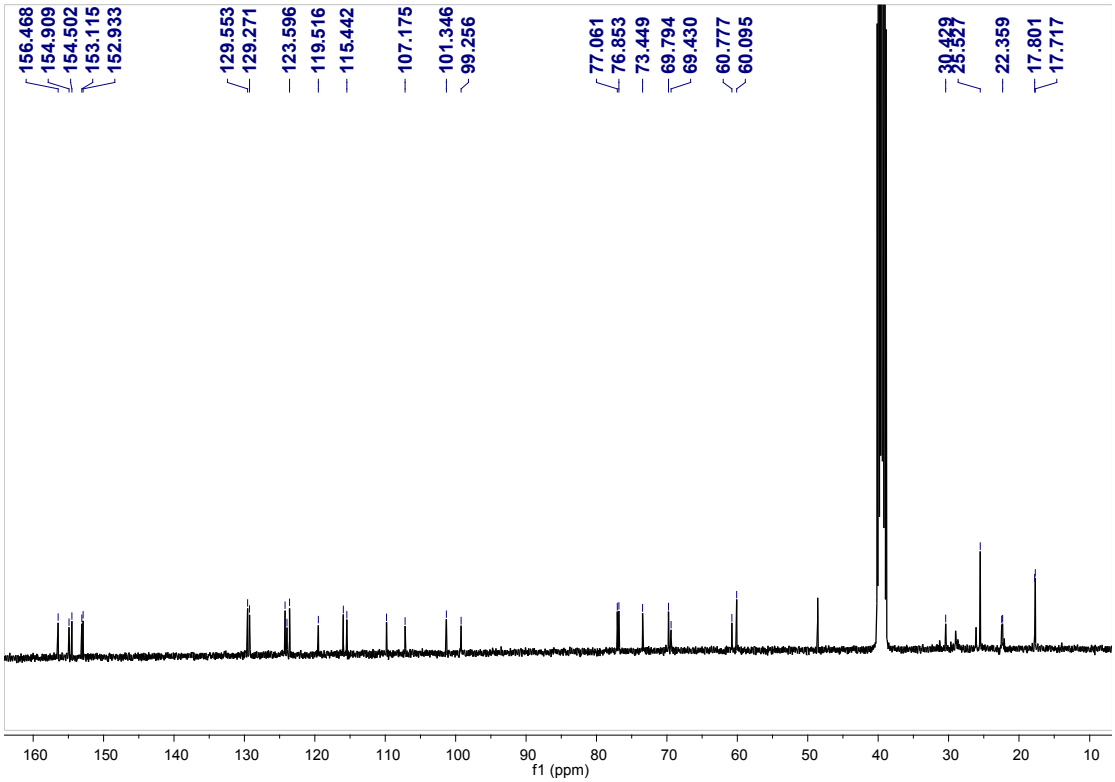


Figure S95. ^{13}C NMR spectrum of **16b** (100 MHz, DMSO-d_6).

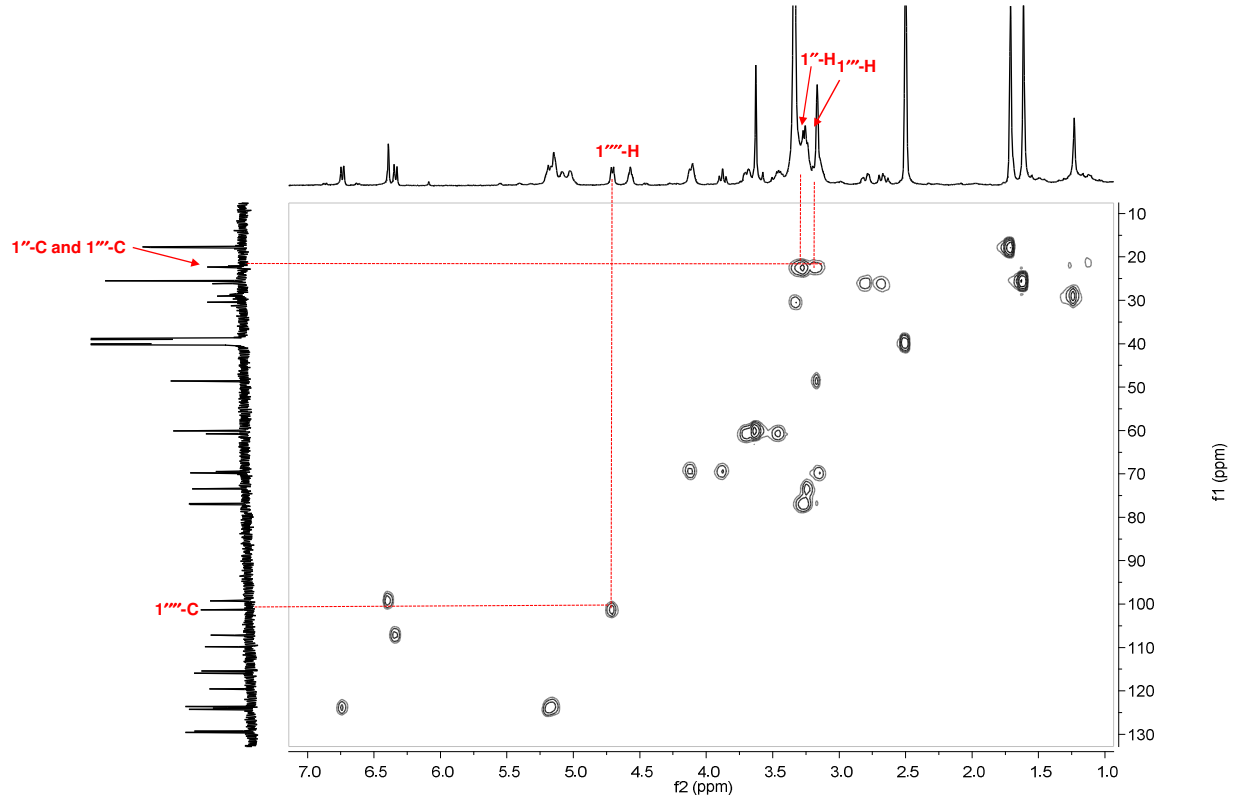


Figure S96. HSQC spectrum of **16b** (400 MHz, DMSO-d_6).

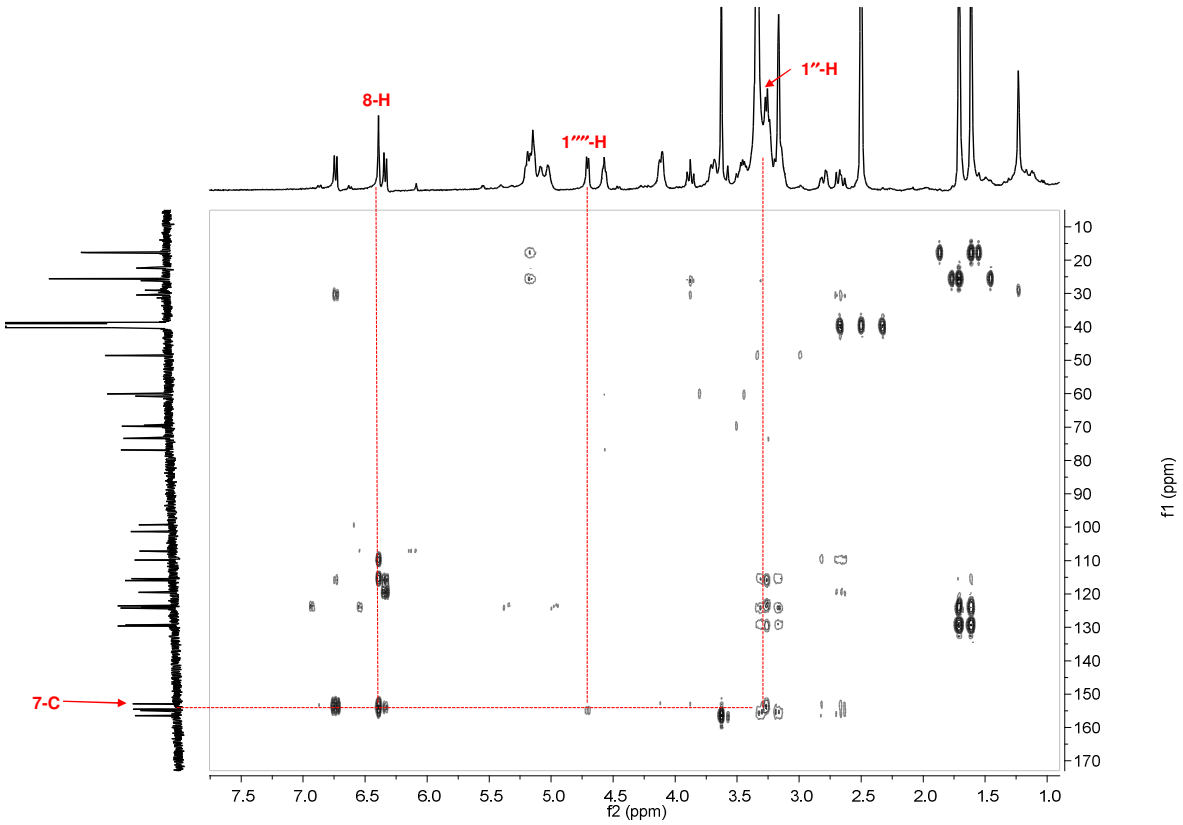


Figure S97. HMBC spectrum of **16b** (400 MHz, DMSO-d_6).

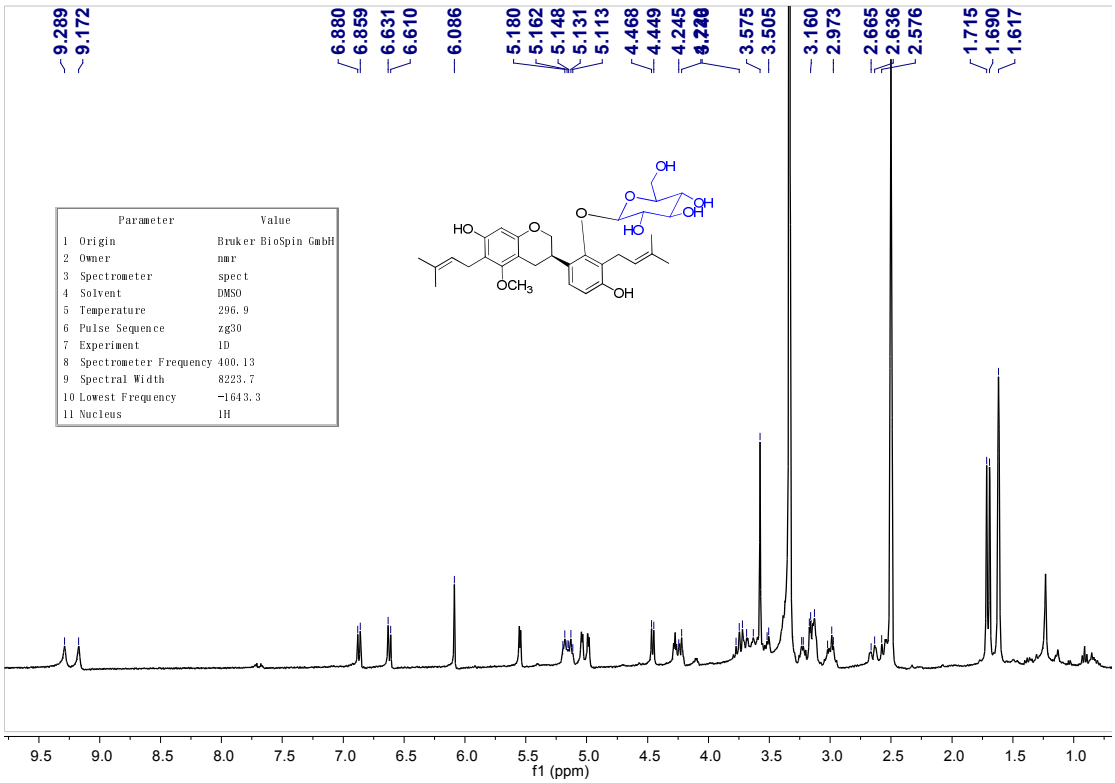


Figure S98. ^{1}H NMR spectrum of **16c** (400 MHz, DMSO-d_6).

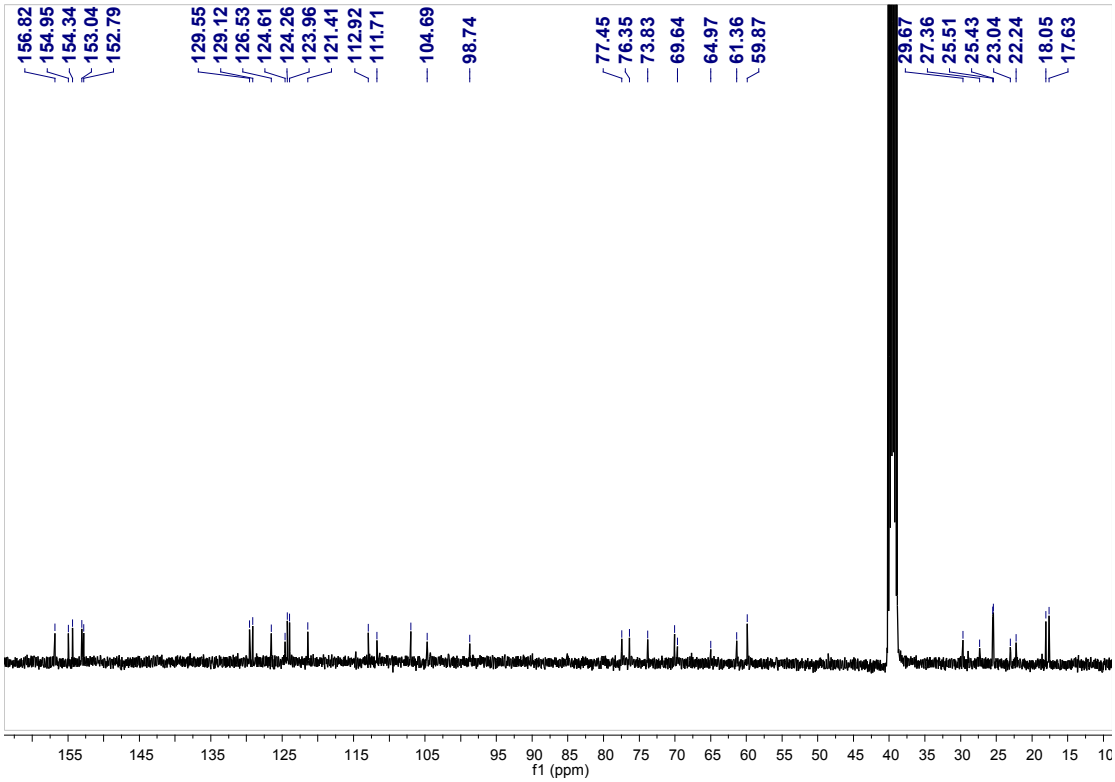


Figure S99. ^{13}C NMR spectrum of **16c** (100 MHz, DMSO-d_6).

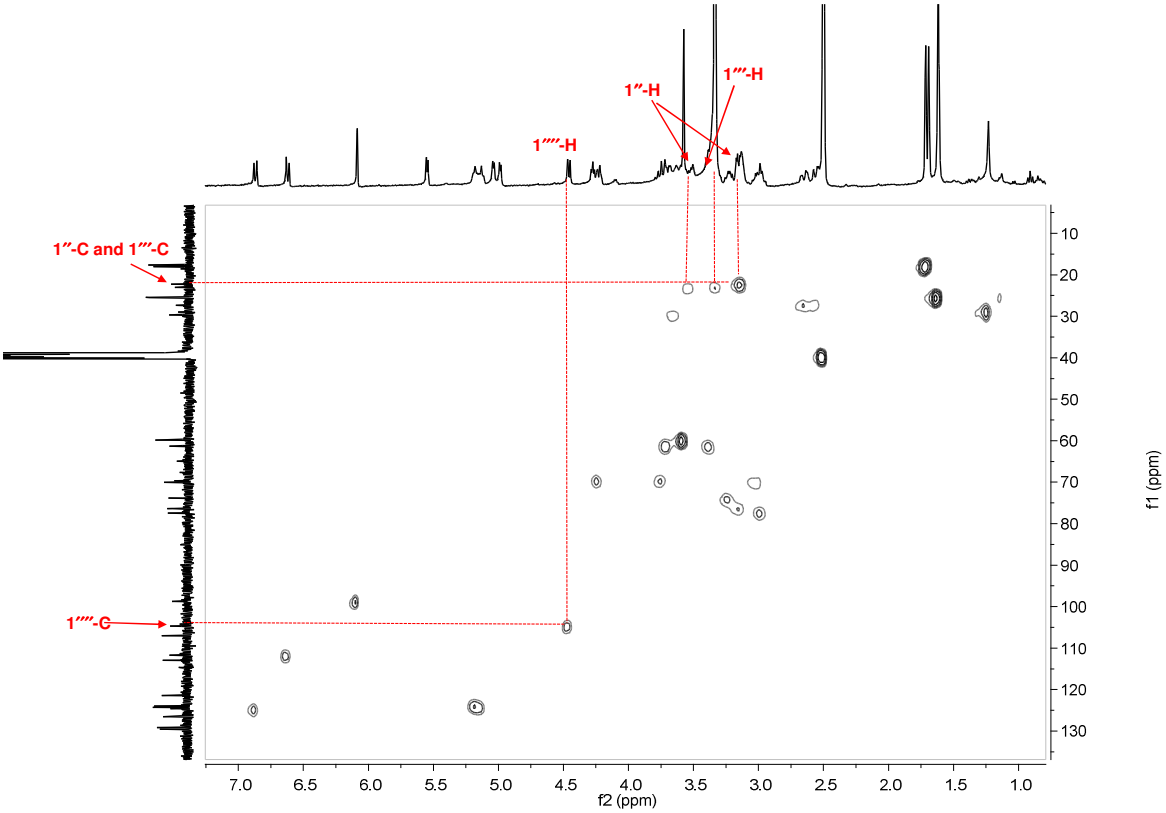


Figure S100. HSQC spectrum of **16c** (400 MHz, DMSO-d_6).

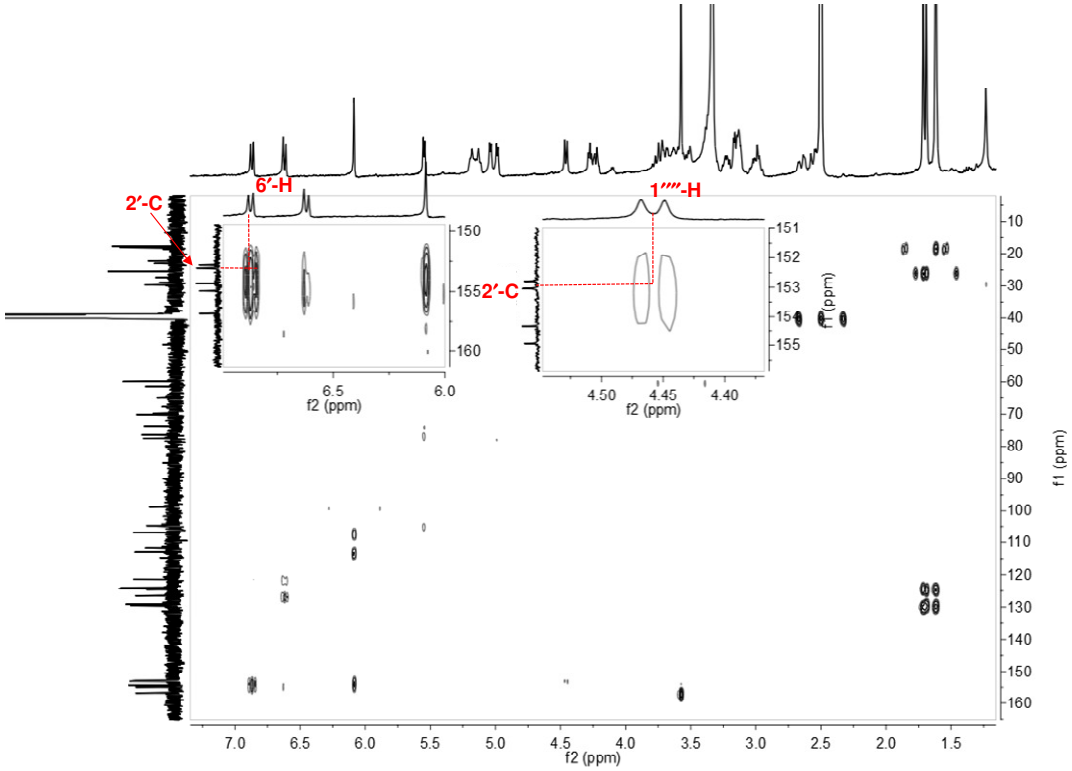


Figure S101. HMBC spectrum of **16c** (400 MHz, DMSO-d_6).

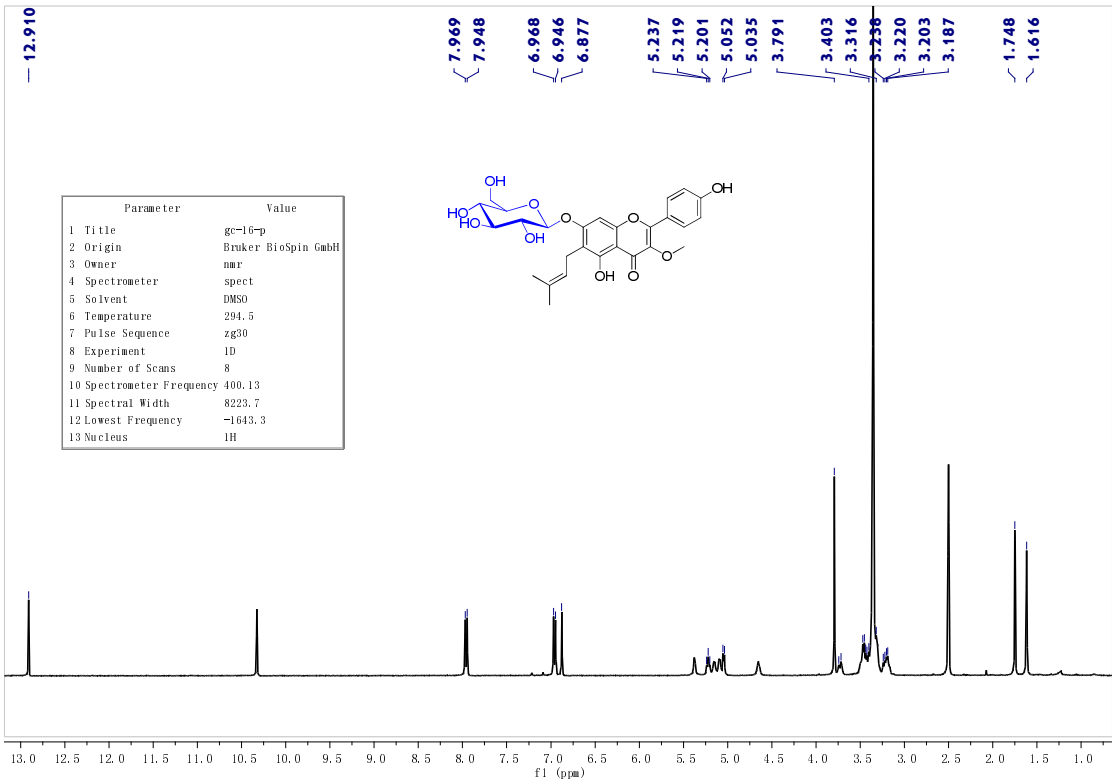


Figure S102. ^{1}H NMR spectrum of **19a** (400 MHz, DMSO-d_6).

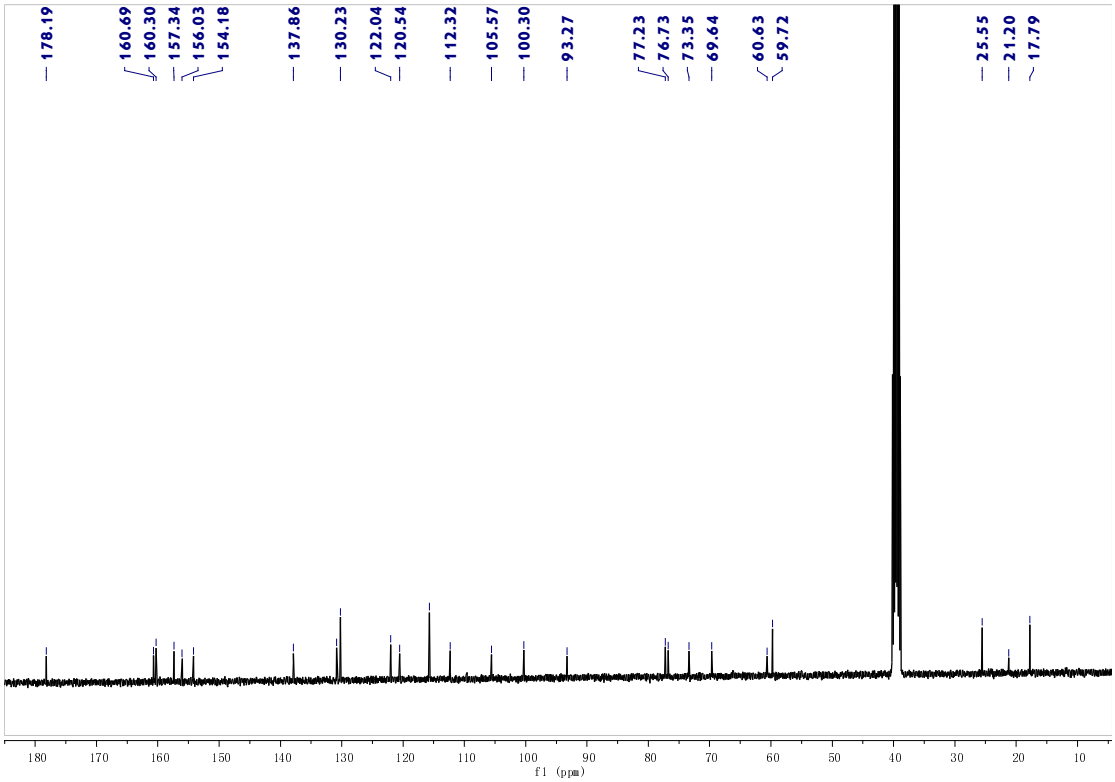


Figure S103. ^{13}C NMR spectrum of **19a** (100 MHz, DMSO-d_6).

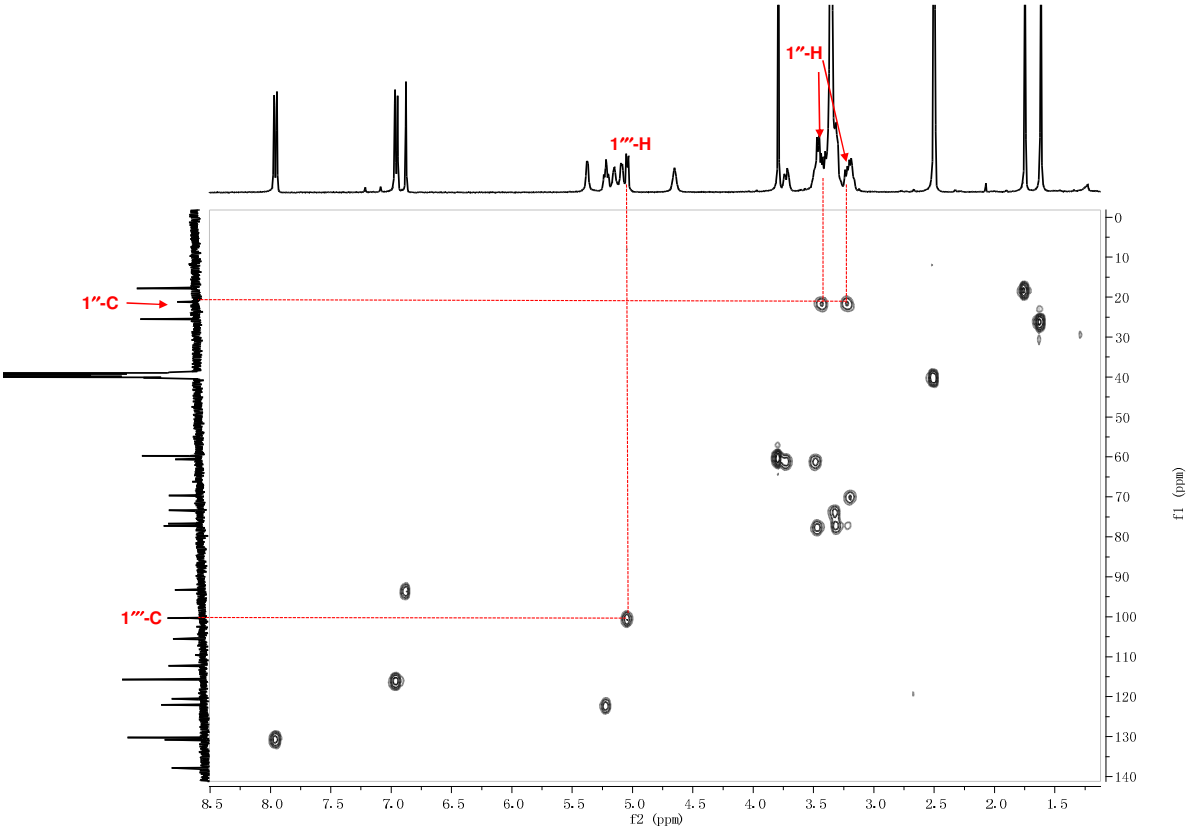


Figure S104. HSQC spectrum of **19a** (400 MHz, DMSO-d_6).

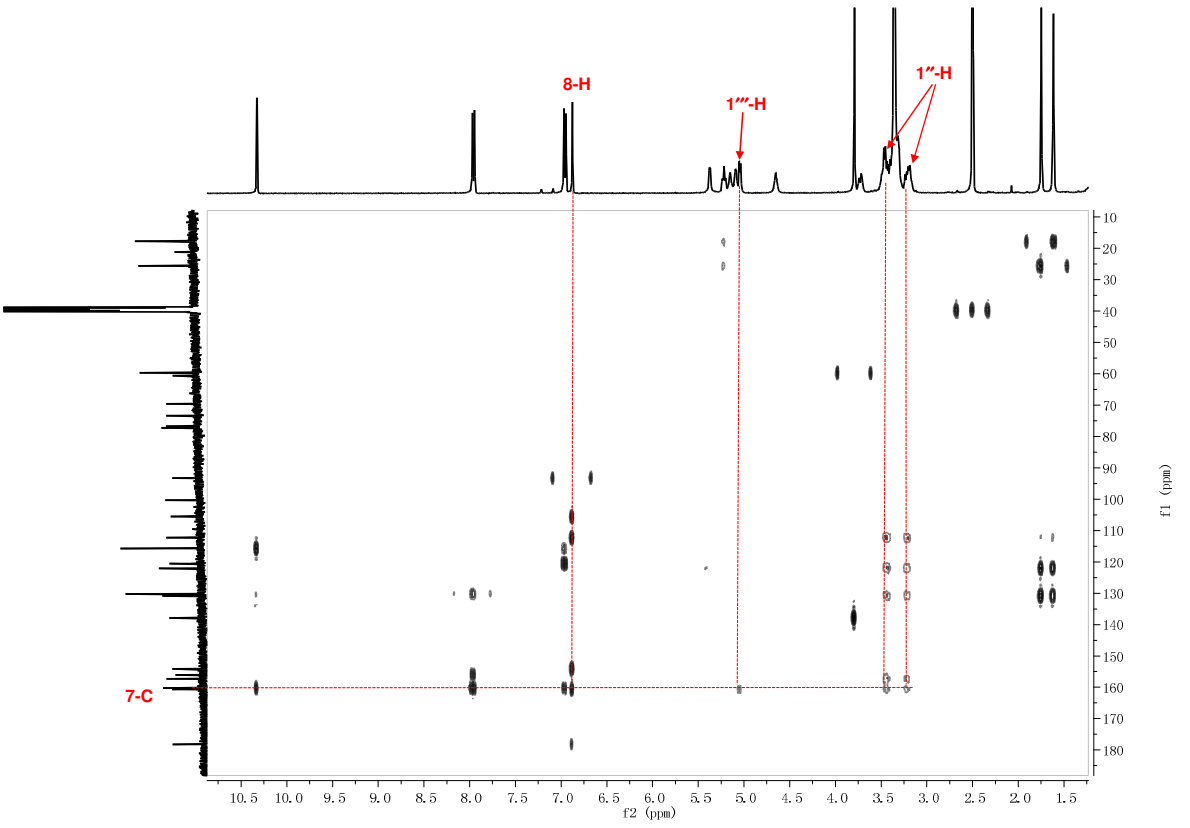


Figure S105. HMBC spectrum of **19a** (400 MHz, DMSO-d_6).

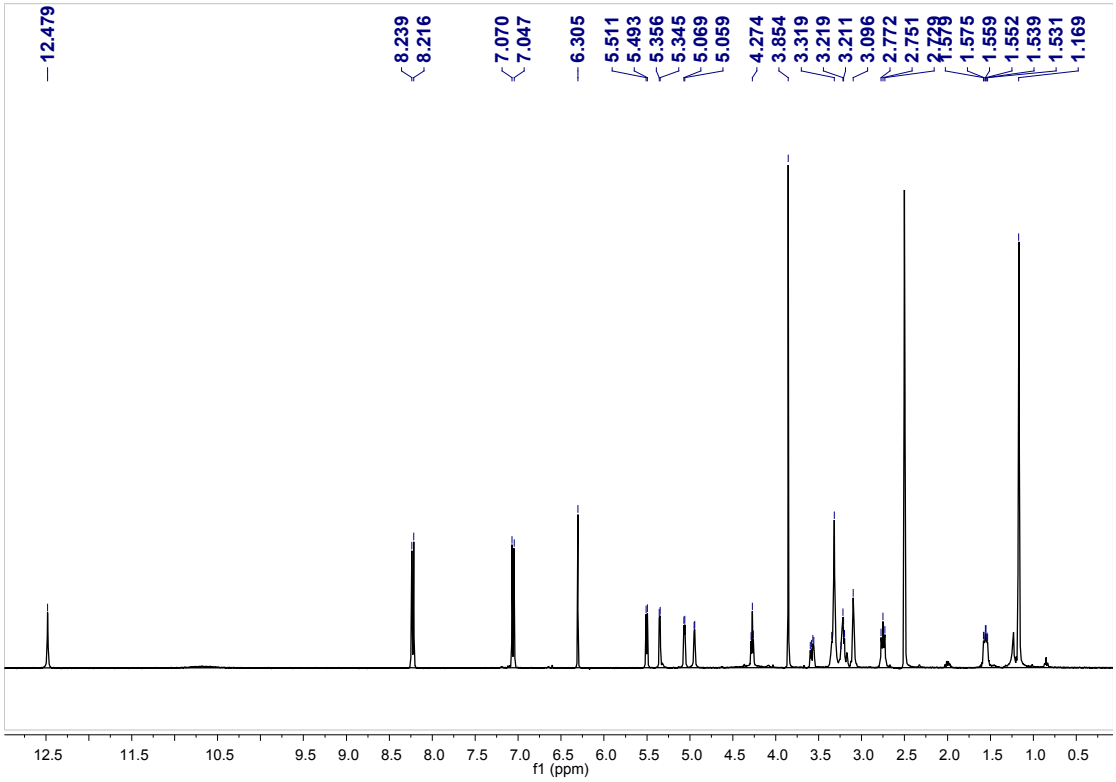


Figure S106. ^{1}H NMR spectrum of **22a** (400 MHz, DMSO-d_6).

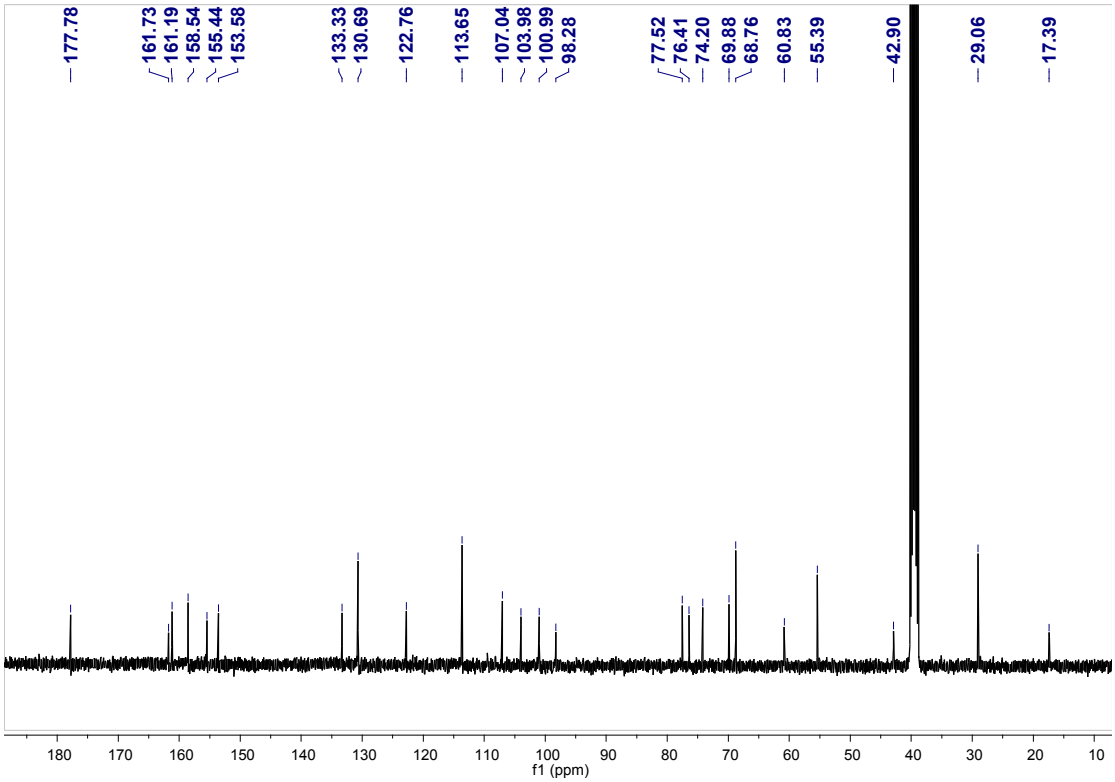


Figure S107. ^{13}C NMR spectrum of **22a** (100 MHz, DMSO-d_6)

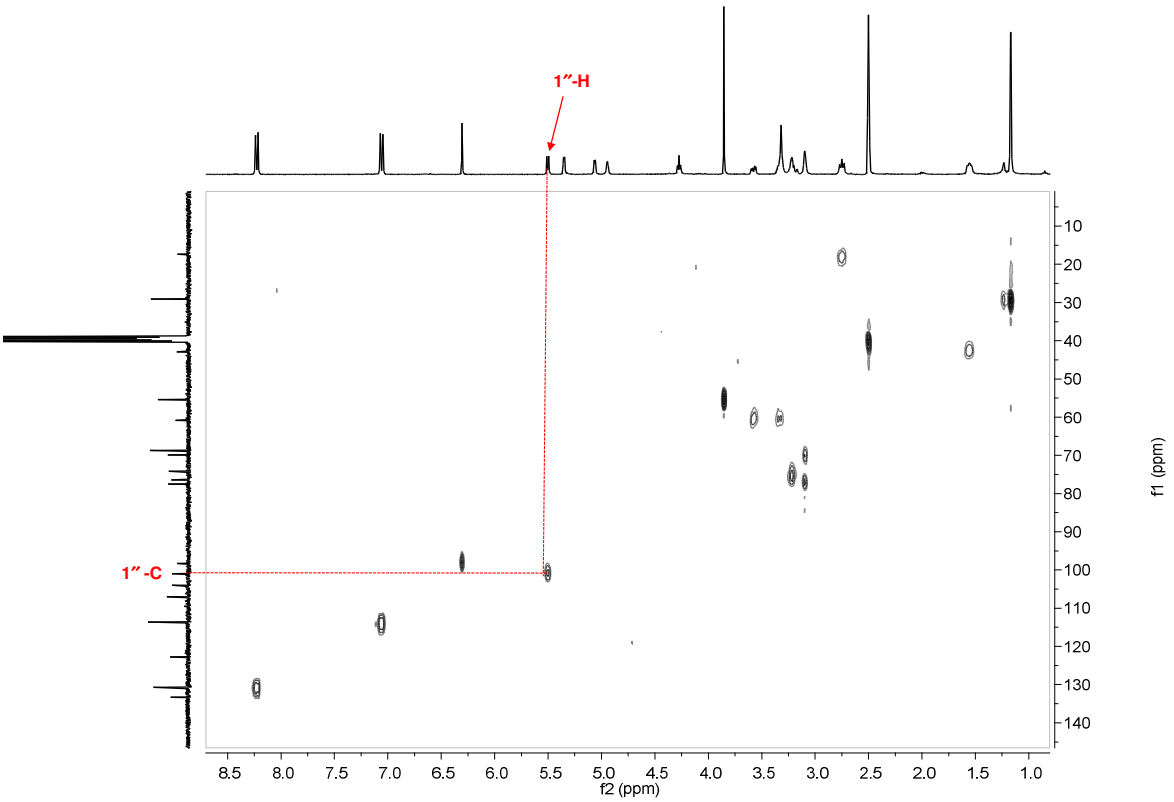


Figure S108. HSQC spectrum of **22a** (400 MHz, DMSO-d_6).

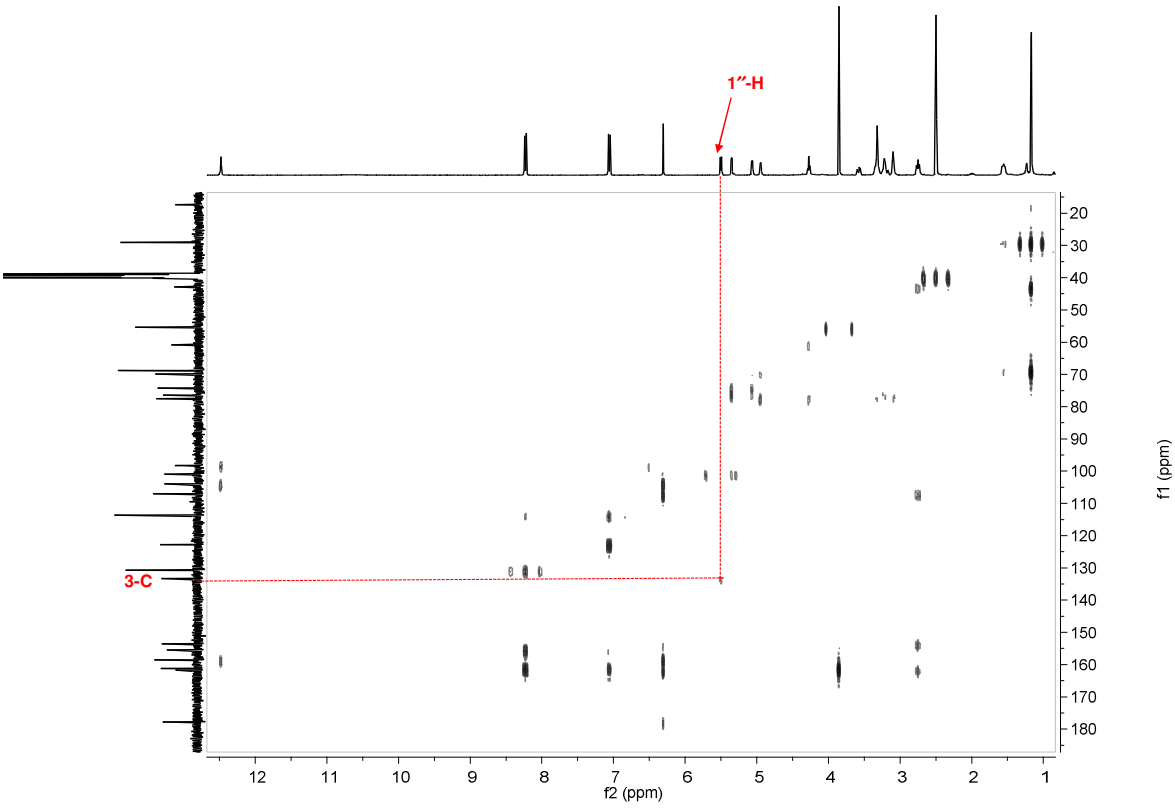


Figure S109. HMBC spectrum of **22a** (400 MHz, DMSO-d_6)

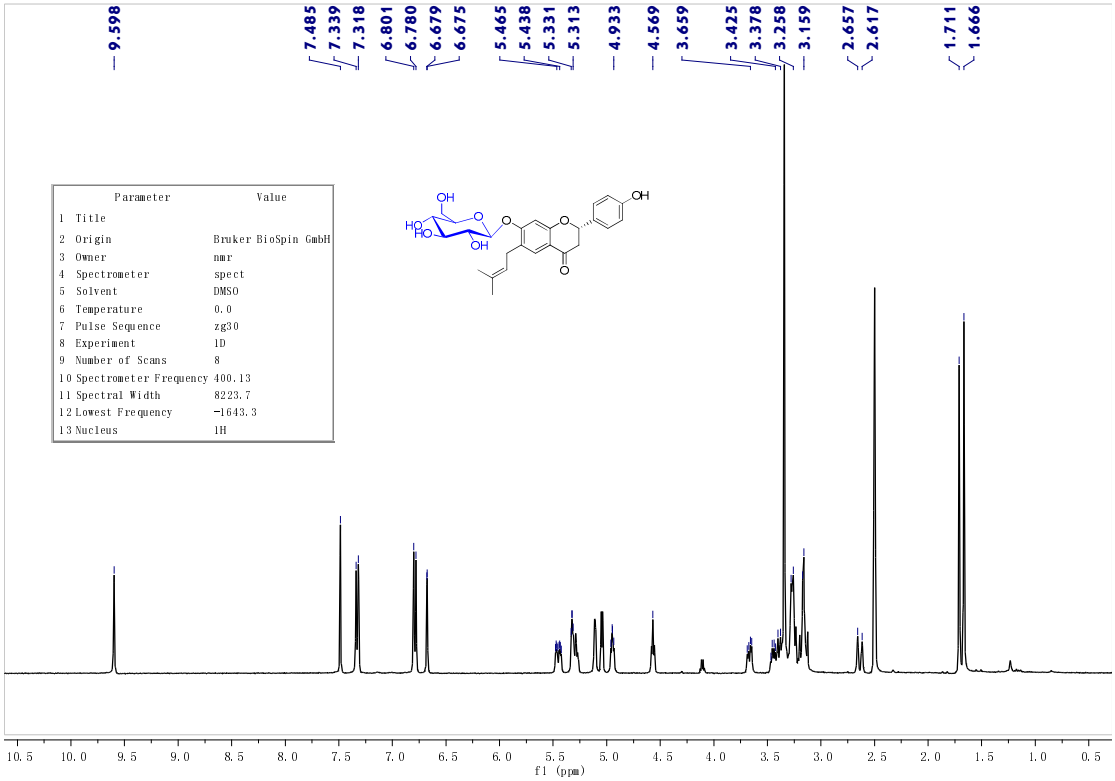


Figure S110. ^{1}H NMR spectrum of **24a** (400 MHz, DMSO-d_6).

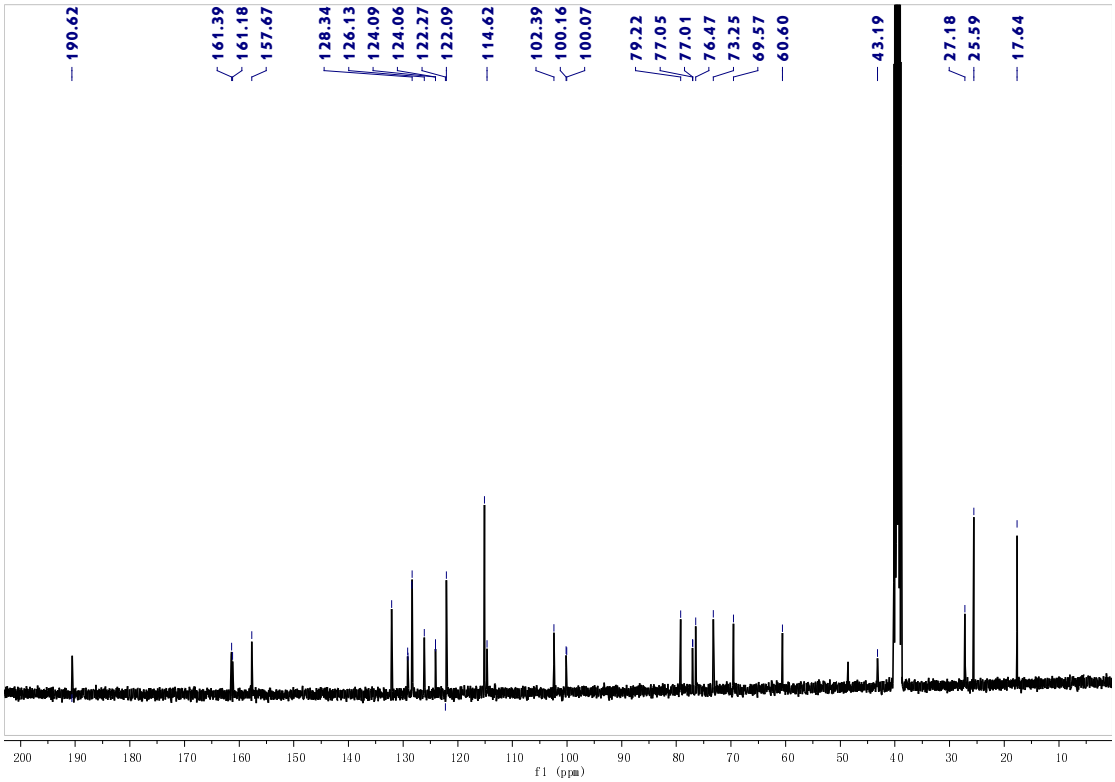


Figure S111. ^{13}C NMR spectrum of **24a** (100 MHz, DMSO-d_6).

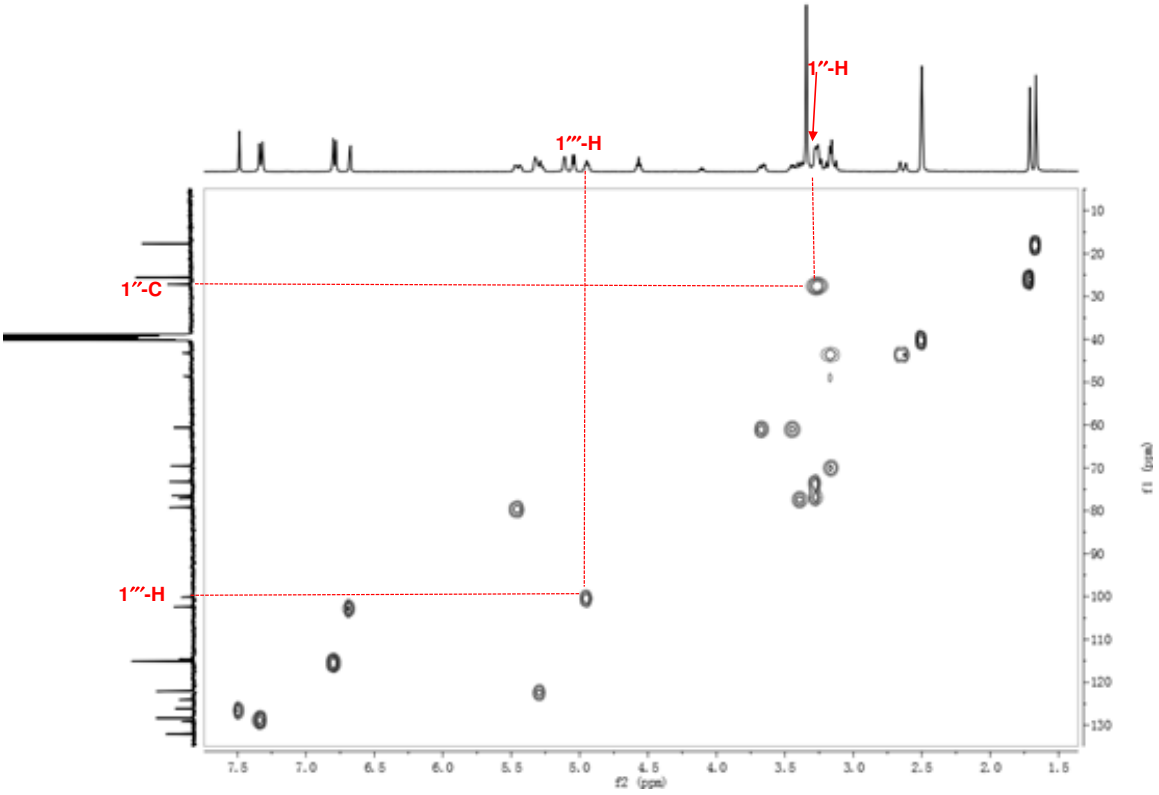


Figure S112. HSQC spectrum of **24a** (400 MHz, DMSO-d_6).

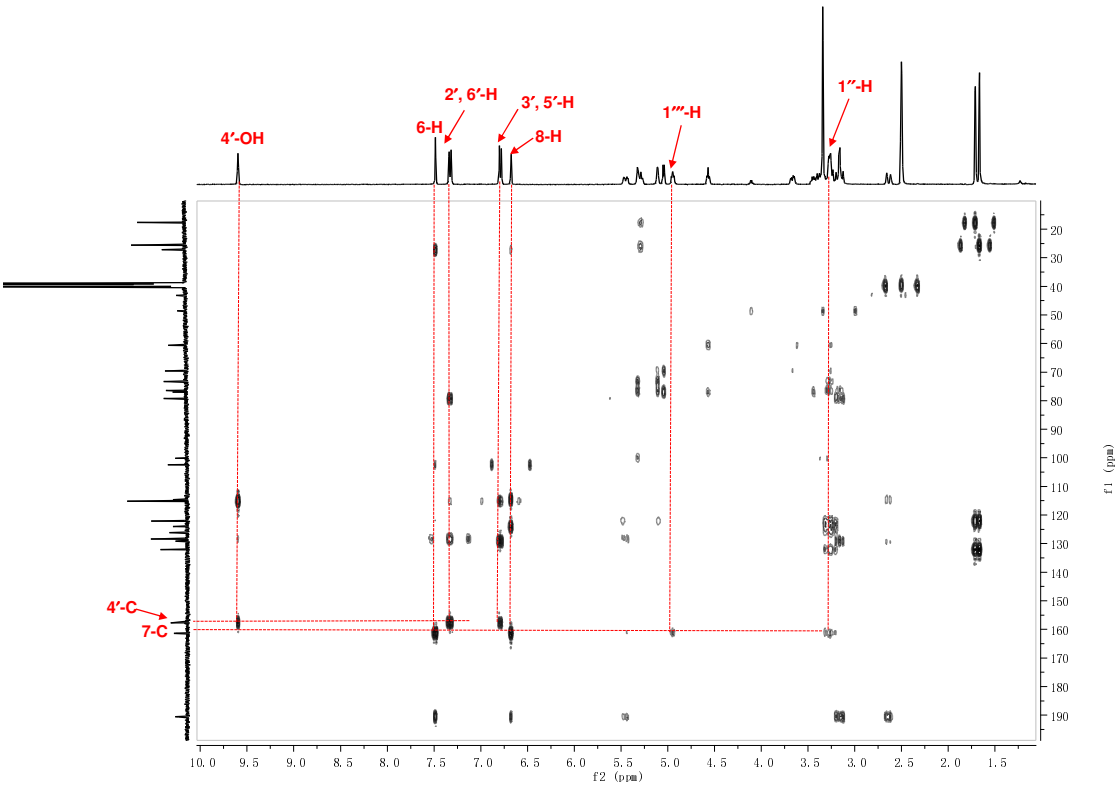


Figure S113. HMBC spectrum of **24a** (400 MHz, DMSO-d_6).