Supplementary Information

Structural Elucidation of New Compounds

Due to the limited quantities obtained during the purification process in a single chromatographic step, mainly to allow the biological activity of the extracts to be deconvoluted, structural elucidation was carried out as extensively as possible. Among the unreported compounds, compound **33** is the only rotenoid. Compound **33** was isolated as an amorphous powder with a $[M\text{-}C_2H_4O_2+H]^+$ of *m/z* 353.1012 and a molecular formula of $C_{22}H_{20}O_8$. NMR data show that this compound is a member of the rotenoid family and, in particular, bears a close resemblance to that of 12-deoxo-12α-acetoxyelliptone (**34**). The ^{1}H-NMR and HSQC spectra indicated the presence of three methyl groups: two methoxyl (δ_H 3.85, δ_C 56.1, 3′-OCH_3 and δ_H 3.87, δ_C 56.5, 2′-OCH_3) and one acetoxy group (δ_H 1.78, s, δ_C 20.9, 12-OAc), this latter was not observed in MS because of in-source fragmentation. Four aromatic protons are also visible, in the form of two singulets (δ_H 6.39, δ_C 99.9 and 7.07, δ_C 108.6, CH-4 and CH-1 respectively) and two ortho protons (*J* = 8.5 Hz) at δ_H 7.16, δ_C 106.0 for CH-10 and δ_H 7.22, δ_C 127.0 for CH-11. Also, two benzofuranic protons were observed at δ_H 6.88, δ_C 104.2, for CH-3′ and δ_H 7.58, δ_C 144.6, for CH-2′. The HSQC spectrum indicated the presence of an oxymethylene (δ_H 4.42, dd, *J* = 10.7, 5.4 Hz, and 4.67, dd, 11.3, 10.7 Hz, δ_C 64.7, CH_2-6) and two oxymethines: one in the form of a doublet of doublet of doublets (δ_H 4.86, ddd, *J* = 11.3, 5.4, 1.8 Hz, δ_C 75.4, CH-6a) and one in the form of a doublet (δ_H 6.27, d, *J* = 1.8 Hz, δ_C 70.4, CH-12). Finally, a singlet was observed at δ_H 2.39 on the ^{1}H NMR spectrum recorded in $CDCl_3$. It was assigned to a hydroxy group and positioned in C-12a thanks to its HMBC to C-12a (δ_C 69.1), C-12, and C-1a (δ_C 112.6). The relative configuration between CH-6a, CH-12, and OH-12a was established based on the ROESY correlations observed from H-6a to OH-12a and H-12 and from OH-12a to H-12 and H-1. The ^4J W-coupling of 1.8 Hz between H-6a and H-12 confirms the equatorial position of these protons. The absolute configuration of **33** could not be determined based on the data obtained. Compound **33** was identified as 12-deoxo-12α-acetoxy-12aβ-hydroxyelliptone.

Compound **1** was isolated as an amorphous powder with a $[M+H]^+$ of *m/z* 341.1742 and a molecular formula of $C_{21}H_{24}O_4$. The ^{1}H-NMR spectrum indicated that **1** was a close analog of bavaisoflavanol (**2)** and manuifolin H (**3**) . When compared to manuifolin H, an additional methoxy signal is observed at δ_H 3.80 (δ_C 55.8, 2′-OCH_3), confirming the information obtained from the HRMS. The ROESY correlation between 2'-OCH_3 and H-3' (δ_H 6.44, d, *J* = 2.6 Hz) and the HMBC correlation from 2'-OCH_3 to C-2′ (δ_C 159.6) and from H-6′ (δ_H 6.92, d, *J* = 8.3 Hz) to C-2′ allowed to determine the position of the methoxyl in C-2′. The absolute configuration of **1** was deduced as 3*R* based on the negative optical rotation value ($[\alpha]_D^{20}$ -70.5), which was on the same sign as that of manuifolin H (**3**). Compound **1** was identified as 2′-*O*-methylmanuifolin H.

Compound **6** was isolated as an amorphous powder with a $[M+H]^+$ of *m/z* 357.1700 and a molecular formula of $C_{21}H_{24}O_5$. The NMR data of **6** indicated a structure analog to 2′-*O*-methylmanuifolin H (**1)**, except for the allylic group. The two methyl groups are still observed (δ_H 1.21, s, H_3-12) and (δ_H 1.23, s, H_3-13) but with a slightly higher field than those of **1**. The HMBC spectrum showed that the carbon atom bearing the two methyl groups (C-11) was shifted at a higher field (δ_C 72.5) compared to the one of **1** (δ_C 132.3). The same shielded chemical shift could be observed for CH-10 (δ_C 90.9) compared to the one of **1** (δ_C 124.6) and indicates the loss of the olefin group. In addition, the chemical shifts of CH-10 and C-11 indicated that both atoms were bearing an oxygen atom. Because of the obtained molecular formula, an ether link should arise between C-10 and C-7 or between C-11 and C-7. A comparison of the chemical shift values of H-10, C-10, and C-11 with those of rautandiol A which contain a 3-hydroxy-2,2dimethyldihydropyran moiety and B which contain a hydroxyisopropyldihydrofuran moiety [1] indicated that these values are closer to those of rautandiol B, and thus an ether between C-10 and C-7 occurred. Because of the distance between the two chiral carbon atoms CH-3 and CH-10, the relative configuration of **6** could not be established based on the data obtained. Compound **6** was identified as 4-(2-(2-hydroxypropan-2-yl)-2,3,6,7-tetrahydro-5H-furo[3,2-g]chromen-6-yl)-3-methoxyphenol.

Compound **13** was isolated with an $[M+H]^+$ of *m/z* 397.1648 corresponding to a molecular formula of $C_{23}H_{24}O_6$. The NMR data of **13** showed the same signals as those obtained for the flavanone part of purpurine (**11**): a hydroxy methine at δ_H 5.56 (dd, *J* = 13.8, 3.0 Hz, H-2), a methylene at δ_H 2.85 (dd, *J* = 17.0, 3.0 Hz, H-3b) and 2.96 (dd, *J* = 17.0, 13.8 Hz, H-3a), phenyl protons at δ_H 7.38 (t, *J* = 7.7 Hz, H-4'), 7.45 (t, *J* = 7.7 Hz, H-3', H-5'), and 7.61 (d, *J* = 7.7 Hz, H-2', H-6'), and two ortho coupled aromatics at δ_H 6.54 (d, *J* = 8.4 Hz, H-6) and 7.81 (d, *J* = 8.4 Hz, H-5). The signals for the ditetrahydrofuran part of purpurine are different in **13**. In this latter, they consist of two methyl groups at δ_H 1.22 and 1.23 linked to quaternary carbon bearing an oxygen atom (δ_C 73.0, C-5″), a methine bearing an acetoxy group at δ_H 4.94 and 1.88 for the acetate, a methine at δ_H 3.86 (t, *J* = 7.7 Hz, H-3″) and a methylene at δ_H 4.62 (t, *J* = 8.8 Hz, H-2″b) and 4.82 (overlapped, H-2″a). This information indicated that the dihydrofurane of purpurin was open in **13** between the oxygen linked to C-5″ and C-2″. The HMBC correlations are in agreement with this structure. Due to the opening of the dihydrofuran ring, the relative configuration of **13** could not be established. Based on these data, the structure of **13** was established as 2-hydroxy-2-methyl-1-(4-oxo-2-phenyl-3,4,8,9-tetrahydro-2H-furo[2,3-h]chromen-9-yl) propyl acetate.

Compound **12** was isolated with an $[M+H]^+$ *m/z* 413.1586 corresponding to a molecular formula of $C_{23}H_{24}O_7$. The NMR data of **12** showed close similarities to those of **13** except for the phenyl group, which appeared in **12** as a para-substituted phenol as indicated by the four

aromatic protons at δ_H 6.84 (d, *J* = 8.5 Hz, H-3', H-5'), and 7.41 (2H, d, *J* = 8.5 Hz, H-2', H-6'). This structure is consistent with the HRMS data. Based on this data, the structure of **12** was established as 2-hydroxy-1-(2-(4-hydroxyphenyl)-4-oxo-3,4,8,9-tetrahydro-2H-furo[2,3-h]chromen-9-yl)-2-methylpropyl acetate. As for compound **13**, the relative configuration of **12** could not be established.

Compound **14** was isolated with an $[M+H]^+$ of *m/z* 485.1964 corresponding to a molecular formula of $C_{30}H_{28}O_6$. The HRMS data of **14** indicated a C_7H_4 increment compared with **13**. Compared to **13**, the ^{1}H-NMR spectrum indicated that the acetyl signal was missing and that the signals corresponding to a styrene group were observed at δ_H 6.31 (d, *J* = 16.0 Hz, H-9'') and 7.46 (m, H-10") for the vinyl and δ_H 7.39 for the phenyl protons. The HMBC correlations from H4", H-9", and H-10" to C-8" (δ_H 167.4) allowed us to link this group to C-4". Based on this data, the structure of **14** was established as 2-hydroxy-2-methyl-1-(4-oxo-2-phenyl-3,4,8,9-tetrahydro-2H-furo[2,3-h]chromen-9-yl)propyl cinnamate. As for compounds **12** and **13**, the relative configuration of **14** could not be established based on the data obtained.

Compound **21** was isolated as an amorphous powder with a $[M+H]^+$ of *m/z* 353.1020 and a molecular formula of $C_{20}H_{16}O_6$. The NMR and HRMS data of **21** showed that when compared to glabrone (**20**) ($C_{20}H_{16}O_5$), an additional phenol group positioned in C-6 was observed. This is confirmed by the presence of two aromatic singlets at δ_H 6.91 and 7.49 for H-8 and H-5, respectively. Based on this data, the structure of **21** was established as 5',6,7-trihydroxy-2',2'-dimethyl-2'H,4H-[3,6'-bichromen]-4-one. Compound **21** was named 6-hydroxy-glabrone.

Table S1: ^{1}H-NMR ($CDCl_3$, 600 MHz) and ^{13}C-NMR ($CDCl_3$, 151 MHz) data of compounds **33**

Position	**33 ($CDCl_3$)**	
	δ_H (J in Hz)	δ_C, Type
1	7.07 (s)	108.6, CH
1a	-	112.6, C
2	-	144.1, C
3	-	150.6, C
4	6.39 (s)	99.9, CH
4a	-	148.8, C
6	4.42 (dd, 10.7, 5.4 Hz), 4.67 (dd, 11.3, 10.7 Hz)	64.7, CH_2
6a	4.86 (ddd, 11.3, 5.4, 1.8 Hz)	75.4, CH
7a	-	146.1, C
8	-	117.1, C
9	-	157.0, C
10	7.16 (dd, 8.5, 0.9 Hz)	106.0, CH
11	7.22 (d, 8.5 Hz)	127.0, CH
11a	-	110.3, C
12	6.27 (d, 1.8 Hz)	70.4, CH
12a	2.39 (s, OH)	69.1, C
2-OCH_3	3.87 (s)	56.5, CH_3
3-OCH_3	3.85 (s)	56.1, CH_3
3'	6.88 (dd, 2.2, 0.9 Hz)	104.2, CH
2'	7.58 (d, 2.2 Hz)	144.6, CH
12-OAc	-	169.7, C
12-OAc	1.78 (s)	20.9, CH_3

Table S2: ^{1}H-NMR (CD_3OD, 600 MHz) and ^{13}C-NMR (CD_3OD, 151 MHz) data of compounds **20** and **21**

Position	**20 (glabrone)**		**21**	
	δ_H (J in Hz)	δ_C, Type	δ_H (J in Hz)	δ_C, Type
2	8.00 (s)	156.2, CH	8.20 (s)	156.0, CH
3	-	*NO*	-	123.9, C
4	-	178.3, C	-	178.9, C
5	8.04 (d, 8.8 Hz)	128.5, CH	7.49 (s)	107.8, CH
6	6.94 (m)	116.3, CH	-	146.8 , C
7	-	164.4, C	-	154.0, C
8	6.87 (d, 2.3 Hz)	103.3, CH	6.91 (s)	102.9, CH
9	-	159.8, C	-	153.8, C
10	-	*NO*	-	*NO*
1'	-	112.5, C	-	114.5, C
2'	-	154.5, C	-	152.9, C
3'	-	110.9, C	-	112.4, C
4'	-	153.1, C	-	155.6, C
5'	6.40 (d, 8.3 Hz)	108.3, CH	6.38 (d, 8.4 Hz)	109.5, CH
6'	6.94 (m)	132.3, CH	6.98 (d, 8.4 Hz)	130.8, CH
1''	6.68 (d, 10.0 Hz)	118.2, CH	6.77 (d, 10.0 Hz)	118.2, CH
2''	5.60 (d, 10.0 Hz)	129.6, CH	5.65 (d, 10.0 Hz)	129.6, CH
3''	-	77.1, C	-	76.7, C
4''	1.35 (s)	28.0, CH_3	1.41 (s)	27.8, CH_3
5''	1.35 (s)	28.0, CH_3	1.41 (s)	27.8, CH_3

Table S3: ^{1}H-NMR (CD_3OD, 600 MHz) and ^{13}C-NMR (CD_3OD, 151 MHz) data of compounds **3**, **2**, **1** and **6**

	3 (manuifolin H)		**2 (bavaisoflavanol)**		**1**		**6**	
Position	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	3.89 (t, 10.1 Hz), 4.18 (dt, 10.1, 2.9 Hz)	71.2, CH_2	3.47 (m), 4.17 (dd, 9.2, 2.4 Hz)	67.7, CH_2	3.87 (td, 10.0, 2.8 Hz), 4.14 (dd, 10.0, 2.7 Hz)	71.2, CH_2	3.90 (t, 10.4 Hz), 4.16 (dt, 10.4, 2.4 Hz)	71.2, CH_2
3	3.40 (m)	33.2, CH	3.47 (m)	41.0, CH	-	33.0, CH	-	32.9, CH
4	2.73 (ddd, 15.6, 5.3, 1.9 Hz), 2.90 (dd, 15.6, 11.0 Hz)	31.5, CH_2	5.40 (d, 5.7 Hz),	80.2, CH	2.71 (dd, 15.0, 4.8 Hz), 2.87 (ddd, 15.0, 10.9, 2.7 Hz)	31.5, CH_2	2.77 (dd, 15.5, 5.4 Hz), 2.91 (dd, 15.5, 10.7 Hz)	32.0, CH_2
4a	-	114.6, C	-	112.4, C	-	114.4, C	-	115.2, C
5	6.70 (s)	131.0, CH	7.11 (s)	132.4, CH	6.69 (s)	130.9, CH	6.84 (s)	126.2, CH
6	-	121.7, C	-	123.6, C	-	121.8, C	-	120.5, C
7	-	154.8, C	-	157.5, C	-	154.9, C	-	160.5, C
8	6.21 (s)	103.5, CH	6.30 (s)	103.5, CH	6.21 (s)	103.5, CH	6.16 (s)	98.2, CH
8a	-	154.2, C	-	155.9, C	-	154.1, C	-	155.4, C
9	3.19 (d, 7.3 Hz)	28.6, CH_2	3.24 (d, 7.5 Hz)	28.6, CH_2	3.18 (d, 7.4 Hz)	28.6, CH_2	3.06 (m)	30.9, CH_2
10	5.29 (t, 7.3 Hz)	124.7, CH	5.33 (t, 7.5 Hz)	124.1, CH	5.28 (t, 7.4 Hz)	124.6, CH	4.54 (t, 8.8 Hz)	90.9 , CH
11	-	132.3, C	-	132.9, C	-	132.3, C	-	72.5, C
12	1.70 (s)	17.8, CH_3	1.73 (s)	17.8, CH_3	1.69 (s)	17.8, CH_3	1.21 (s)	25.1, CH_3
13	1.72 (s)	26.0, CH_3	1.76 (s)	26.0, CH_3	1.72 (s)	25.9, CH_3	1.23 (s)	25.3, CH_3
1'	-	120.3, C	-	119.7, C	-	121.7, C	-	121.7, C
2'	-	157.2, C	-	161.9, C	-	159.6, C	-	159.6, C
3'	6.31 (d, 2.4 Hz)	103.5, CH	6.26 (d, 2.3 Hz)	98.7, CH	6.44 (d, 2.6 Hz)	99.9, CH	6.44 (d, 2.4 Hz)	100.0, CH
4'	-	157.9, C	-	159.7, C	-	158.4, C	-	158.5, C
5'	6.25 (dd, 8.3, 2.4 Hz)	107.6, CH	6.32 (dd, 8.2, 2.3 Hz)	108.6, CH	6.34 (dd, 8.3, 2.6 Hz)	108.0, CH	6.34 (dd, 8.3, 2.4 Hz)	108.0, CH
6'	6.86 (d, 8.3 Hz)	128.8, CH	7.06 (d, 8.2 Hz	126.0, CH	6.92 (d, 8.3 Hz)	128.6, CH	6.92 (d, 8.3 Hz)	128.7, CH
-OCH_3	-	-	-	-	3.80 (s)	55.8, CH_3	3.80 (s)	55.9, CH_3

Table S4: ^{1}H-NMR (CD_3OD, 600 MHz) and ^{13}C-NMR (CD_3OD, 151 MHz) data of compounds **11**, **13**, **12** and **14**

	11 ((-)-purpurin)		**13**		**12**		**14**	
Position	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	5.69 (dd, 11.7, 3.4 Hz)	81.0, CH	5.56 (dd, 13.8, 3.0 Hz)	81.0, CH	5.44 (dd, 13.8, 2.8 Hz)	81.0, CH	5.44 (dd, 12.2, 3.2 Hz)	80.7, CH
3	2.93 (dd, 16.0, 3.4 Hz), 3.06 (dd, 16.0, 11.7 Hz)	45.2, CH_2	2.85 (dd, 17.0, 3.0 Hz), 2.96 (dd, 17.0, 13.8 Hz)	45.8, CH_2	2.79 (dd, 17.0, 2.8 Hz), 2.99 (dd, 17.0, 13.8 Hz)	45.5, CH_2	2.73 (dd, 16.9, 3.2 Hz), 2.90 (dd,16.9, 12.2 Hz)	44.8, CH_2
4	-	192.4, C	-	192.5, C	-	193.0, C	-	192.5, C
5	7.85 (d, 8.6 Hz)	131.2, CH	7.81 (d, 8.4 Hz)	130.8, CH	7.79 (d, 8.5 Hz)	130.8, CH	7.73 (d, 8.6 Hz)	130.9, CH
6	6.56 (d, 8.6 Hz)	105.8, CH	6.54 (d, 8.4 Hz)	105.9, CH	6.52 (d, 8.5 Hz)	105.8, CH	6.53 (d, 8.6 Hz)	106.0, CH
7	-	167.1, C	-	170.4, C	-	169.9, C	-	170.3, C
8	-	114.6, C	-	115.9, C	-	116.3, C	-	115.6, C
9	-	159.8, C	-	161.4, C	-	161.7, C	-	161.1, C
10	-	117.0, C	-	116.3, C	-	NO	-	116.5, C
1'	-	140.6, C	-	140.7, C	-	131.3, C	-	140.4, C
2'	7.52 (d, 8.0 Hz)	127.1, CH	7.61 (d, 7.7 Hz)	127.0, CH	7.41 (d, 8.5 Hz)	128.7, CH	7.46 (m)	126.8, CH
3'	7.41 (t, 8.0 Hz)	129.7, CH	7.45 (t, 7.7 Hz)	129.7, CH	6.84 (d, 8.5 Hz)	116.3, CH	7.39 (m)	129.8, CH
4'	7.35 (t, 8.0 Hz)	129.5, CH	7.38 (t, 7.7 Hz)	129.5, CH	-	159.2, C	7.39 (m)	129.4, CH
5'	7.41 (t, 8.0 Hz)	129.7, CH	7.45 (t, 7.7 Hz)	129.7, CH	6.84 (d, 8.5 Hz)	116.3, CH	7.39 (m)	129.8, CH
6'	7.52 (d, 8.0 Hz)	127.1, CH	7.61 (d, 7.7 Hz)	127.0, CH	7.41 (d, 8.5 Hz)	128.7, CH	7.46 (m)	126.8, CH
2''	6.52 (d, 6.7 Hz)	113.9, CH	4.62 (t, 8.8 Hz), 4.82 (overlapped)	80.0, CH_2	4.62 (t, 9.4, 8.0 Hz), 4.83 (overlapped)	80.0, CH_2	4.64 (t, 9.4, 8.0 Hz), 4.95 (dd, 9.4, 2.1 Hz)	79.7, CH_2
3''	4.12 (dd, 6.7, 2.9 Hz)	53.4, CH	3.86 (t, 7.7 Hz)	41.5, CH	3.84 (td, 8.0, 2.4 Hz)	41.5, CH	4.02 (td, 8.0, 2.1 Hz)	41.7, CH
4''	5.51 (d, 2.9 Hz)	81.8, CH	4.95 (overlapped)	81.7, CH	4.91 (d, 7.8 Hz)	81.8, CH	5.04 (d, 8.0 Hz)	81.5, CH
5''	-	88.7, C	-	73.0, C	-	73.0, C	-	73.2, C
6''	1.23 (s)	23.5, CH_3	1.23 (s)	24.6, CH_3	1.20 (s)	24.7, CH_3	1.30 (s)	24.8, CH_3
7''	1.01 (s)	27.7, CH_3	1.22 (s)	27.3, CH_3	1.19 (s)	27.3, CH_3	1.23 (s)	27.7, CH_3
8''	-	171.5, C	-	171.8, C	-	171.8, C	-	167.4, C
9''	2.08 (s)	20.6, CH_3	1.88 (s)	21.0, CH_3	1.86 (s)	21.0, CH_3	6.31 (d, 16.0 Hz)	118.6, CH
10''	-	-	-	-	-	-	7.46 (m)	146.5, CH
11''	-	-	-	-	-	-	-	135.3, C
12''	-	-	-	-	-	-	7.39 (m)	131.8, CH
13''	-	-	-	-	-	-	7.39 (m)	129.3, CH
14''	-	-	-	-	-	-	7.39 (m)	130.1, CH
15''	-	-	-	-	-	-	7.39 (m)	129.3, CH
16''	-	-	-	-	-	-	7.39 (m)	131.8, CH

Isolated compounds details

(-)-(3*R*)-2′-*O*-methylmanuifolin H (**1**): HRESIMS *m/z* 341.1742 $[M+H]^+$ (calcd for $C_{21}H_{25}O_4$, 341.1753). $[\alpha]_D^{20}$ -70.9 (*c* 0.0127, MeOH). UV (MeOH) λ_{max} (log ε) 230 (3.55) nm, 287 (3.46) nm. For NMR data, see Table 3. For NMR spectra, see Figures S10 to S15.

(-)-(3*S*,4*R*)-bavaisoflavanol (**2**) : HRESIMS *m/z* 325.1431 $[M-H_2O+H]^+$ (calcd for $C_{20}H_{21}O_4$, 325.1440). $[\alpha]_D^{20}$ -154.6 (*c* 0.0087, MeOH). UV (MeOH) λ_{max} (log ε) 231 (3.52) nm, 287 (3.45) nm. For NMR data, see Table 3.

(-)-(3*R*)-manuifolin H (**3**): HRESIMS *m/z* 327.1594 $[M+H]^+$ (calcd for $C_{20}H_{23}O_4$, 327,1596). $[\alpha]_D^{20}$ -86.7 (*c* 0.0060, MeOH). For NMR data, see Table 3.

(-)-(3*S*)-7,4′-dihydroxy-2′-methoxyisoflavan (**4**): HRESIMS *m/z* 273.1116 $[M+H]^+$ (calcd for $C_{16}H_{17}O_4$, 273.1127). $[\alpha]_D^{20}$ -71.2 (*c* 0.0027, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 2.75 (1H, dd, *J* = 15.6, 5.2 Hz, H_2-4eq), 2.90 (1H, dd, *J* = 15.6, 10.9 Hz, H_2-4ax), 3.42 (1H, overlapped, H-3), 3.80 (3H, s, 2'OCH_3), 3.91 (1H, t, *J* = 10.3 Hz, H_2-2ax), 4.17 (1H, dt, *J* = 10.3, 2.6 Hz, H_2-2eq), 6.22 (1H, d, *J* = 2.5 Hz, H-8), 6.31 (1H, dd, *J* = 8.1, 2.5 Hz, H-6), 6.34 (1H, dd, *J* = 8.3, 2.4 Hz, H-5'), 6.45 (1H, d, *J* = 2.4 Hz, H-3'), 6.86 (1H, d, *J* = 8.1 Hz, H-5), 6.93 (1H, d, *J* = 8.3 Hz, H-6'); ^{13}C NMR (CD_3OD, 151 MHz) δ 31.5 (CH_2-4), 2.9 (CH-3), 71.3 (CH_2-2), 100.0 (CH-3'), 103.9 (CH-8), 108.1 (CH-5'), 109.0 (CH-6), 114.9 (C-10), 121.7 (C-1'), 128.7 (CH-6'), 131.1 (CH-5), 156.3 (C-9), 157.6 (C-7), 158.7 (C-4'), 159.6 (C-2').

(-)-astraciceran (**5**): HRESIMS *m/z* 301.1068 $[M+H]^+$ (calcd for $C_{17}H_{17}O_5$, 301.1076). $[\alpha]_D^{20}$ -75 (*c* 0.0040, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 2.78 (1H, ddd, *J* = 15.5, 5.3, 1.9 Hz, H_2-4b), 2.87 (1H, dd, *J* = 15.5, 10.4 Hz, H_2-4a), 3.49 (1H, tt, *J* = 10.4, 5.3, 3.5 Hz, H-3), 3.80 (3H, s, 2'OCH_3), 3.93 (1H, t, *J* = 10.4 Hz, H_2-2b), 4.16 (1H, ddd, *J* = 10.4, 3.5, 1.9 Hz, H_2-2a), 5.86 (1H, d, *J* = 1.2 Hz, H_2-7'b), 5.87 (1H, d, *J* = 1.2 Hz, H_2-7'a), 6.22 (1H, d, *J* = 2.5 Hz, H-8), 6.32 (1H, dd, *J* = 8.2, 2.5 Hz, H-6), 6.67 (1H, s, H-3'), 6.68 (1H, s, H-6'), 6.87 (1H, d, *J* = 8.2 Hz, H-5); ^{13}C NMR (CD_3OD, 151 MHz) δ 31.6 (CH_2-4), 33.2 (CH-3), 57.0 (2'OCH_3), 71.1 (CH_2-2), 95.9 (CH-3'), 102.3 (CH_2-7'), 103.8 (CH-8), 108.1 (CH-6'), 109.1 (CH-6), 114.6 (C-10), 123.1 (C-1'), 131.2 (CH-5), 142.7 (C-4'), 148.2 (C-5'), 153.8 (C-2'), 156.3 (C-9), 157.6 (C-7).

4-(2-(2-hydroxypropan-2-yl)-2,3,6,7-tetrahydro-5H-furo[3,2-g]chromen-6-yl)-3-methoxyphenol (**6**): HRESIMS *m/z* 357.1700 $[M+H]^+$ (calcd for $C_{21}H_{25}O_5$, 357.1702). $[\alpha]_D^{20}$ - 60.0 (*c* 0.0027, MeOH). UV (MeOH) λ_{max} (log ε) 211 (3.93) nm, 293 (3.60) nm. For NMR data, see Table 3. For NMR spectra, see Figures S16 to S20.

isobavachalcone (**7**): HRESIMS *m/z* 325.1438 $[M+H]^+$ (calcd for $C_{20}H_{21}O_4$, 325.1440). NMR data: ^{1}H NMR (CD3OD, 600 MHz) δ 1.66 (3H, s, H_3-5''), 1.78 (3H, s, H_3-4''), 3.32 (2H, overlapped,

H_2-1''), 5.23 (1H, t, *J* = 7.4 Hz, H-2''), 6.44 (1H, d, *J* = 8.7 Hz, H-5'), 6.85 (2H, d, *J* = 8.2 Hz, H-3, H-5), 7.63 (3H, m, H-2, H-6, H-8), 7.78 (1H, d, *J* = 15.2 Hz, H-7), 7.84 (1H, d, *J* = 8.7 Hz, H-6'); ^{13}C NMR (CD3OD, 151 MHz) δ 17.9 (CH_3-4''), 22.5 (CH_2-1''), 26.0 (CH_3-5''), 108.2 (CH-5'), 114.5 (C-1'), 116.6 (C-3'), 116.9 (CH-3, CH-5), 118.6 (CH-8), 123.6 (CH-2''), 127.9 (C-1), 130.4 (CH-6'), 131.8 (CH-2, CH-6), 131.9 (C-3''), 145.4 (CH-7), 161.5 (C-4), 163.7 (C-4'), 165.1 (C-2'), 193.8 (C-9).

pongamol (**8**): HRESIMS *m/z* 295.0964 $[M+H]^+$ (calcd for $C_{18}H_{15}O_4$, 295,0970). $[\alpha]_D^{20}$ -27.9 (*c* 0.0187, MeOH). NMR data: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 4.15 (3H, s, OCH_3), 7.00 (1H, t, *J* = 2.2, 0.9 Hz, H-15), 7.17 (1H, s, H-8), 7.32 (1H, dd, *J* = 8.7, 0.9 Hz, H-12), 7.49 (2H, tt, *J* = 7.5, 1.2 Hz, H-3, H-5), 7.54 (1H, tt, *J* = 7.5, 1.2 Hz, H-4), 7.63 (1H, d, *J* = 2.2 Hz, H-14), 7.88 (1H, d, *J* = 8.7 Hz, H-11), 7.98 (2H, d, *J* = 7.5 Hz, H-2, H-6); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 61.4 (OCH_3), 98.1 (CH-8), 105.4 (CH-15), 107.2 (CH-12), 119.8 (C-16), 122.4 (C-10), 126.6 (CH-11), 127.3 (CH-2, CH-6), 128.8 (CH-3, CH-5), 132.3 (CH-4), 135.8 (C-1), 145.0 (CH-14), 153.9 (C-17), 158.9 (C-13), 184.4 (C-7), 186.3 (C-9).

(-)-dehydroisoderricin (**9**): HRESIMS *m/z* 321.1488 $[M+H]^+$ (calcd for $C_{21}H_{21}O_3$, 321.1491). $[\alpha]_D^{20}$ -82.1 (*c* 0.0113, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 1.90 (3H, d, *J* = 1.3 Hz, H_3-4''), 2.90 (1H, dd, *J* = 16.8, 3.0 Hz, H_2-3b), 3.10 (1H, dd, *J* = 16.8, 12.8 Hz, H_2-3a), 3.97 (3H, s, 7OCH_3), 4.91 (1H, s, H_2-5''b), 5.00 (1H, t, *J* = 1.9 Hz, H_2-5''a), 5.61 (1H, dd, *J* = 12.8, 3.0 Hz, H-2), 6.80 (1H, d, *J* = 16.6 Hz, H-1''), 6.83 (1H, d, *J* = 8.9 Hz, H-6), 7.36 (1H, d, *J* = 16.6 Hz, H-2''), 7.39 (1H, m, H-4'), 7.44 (2H, t, *J* = 7.4 Hz, H-3', H-5'), 7.56 (2H, d, *J* = 7.4 Hz, H-2', H-6'), 7.82 (1H, d, *J* = 8.9 Hz, H-5); ^{13}C NMR (CD_3OD, 151 MHz) δ 18.2 (CH_3-4''), 44.9 (CH_2-3), 56.7 (7OCH_3), 81.1 (CH-2), 106.4 (CH-6), 115.5 (C-8), 116.5 (C-10), 117.4 (CH_2-5''), 119.4 (CH-1''), 127.2 (CH-2', CH-6'), 128.1 (CH-5), 129.6 (CH-4'), 129.8 (CH-3', CH-5'), 137.7 (CH-2''), 140.6 (C-1'), 144.6 (C-3''), 161.9 (C-9), 165.0 (C-7), 193.6 (C-4).

lanceolatin B (**10**): HRESIMS *m/z* 263.0701 $[M+H]^+$ (calcd for $C_{17}H_{11}O_3$, 263.0708). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 7.01 (1H, s, H-3), 7.44 (1H, d, *J* = 2.0 Hz, H-1''), 7.62 (3H, m, H-3', H-4', H-5'), 7.69 (1H, d, *J* = 8.8 Hz, H-6), 8.02 (1H, d, *J* = 2.0 Hz, H-2''), 8.11 (1H, d, *J* = 8.8 Hz, H-5), 8.14 (2H, m, H-2', H-6'); ^{13}C NMR (CD_3OD, 151 MHz) δ 105.2 (CH-1''), 108.1 (CH-3), 111.6 (CH-6), 118.7 (C-8), 120.0 (C-10), 122.2 (CH-5), 127.5 (CH-2', CH-6'), 130.4 (CH-3', CH-5'), 132.7 (C-1'), 133.1 (CH-4'), 148.2 (CH-2''), 152.4 (C-9), 160.1 (C-7), 165.3 (C-2), 180.5 (C-4).

(-)-purpurin (**11**): HRESIMS *m/z* 395.1465 $[M+H]^+$ (calcd for $C_{23}H_{23}O_6$, 395.1495). $[\alpha]_D^{20}$ -79.3 (*c* 0.0047, MeOH). For NMR data, see Table 4.

2-hydroxy-1-(2-(4-hydroxyphenyl)-4-oxo-3,4,8,9-tetrahydro-2H-furo[2,3-h]chromen-9-yl)-2-methylpropyl acetate (**12**): HRESIMS *m/z* 413.1586 $[M+H]^+$ (calcd for $C_{23}H_{25}O_7$, 413.1600). $[\alpha]_D^{20}$ -63.0 (*c* 0.0067, MeOH). UV (MeOH) λ_{max} (log ε) 225 (3.72) nm, 282 (3.65) nm. For NMR data, see Table 4. For NMR spectra, see Figures S21 to S25.

2-hydroxy-2-methyl-1-(4-oxo-2-phenyl-3,4,8,9-tetrahydro-2H-furo[2,3-h]chromen-9-yl) propyl acetate (**13**): HRESIMS *m/z* 397.1648 $[M+H]^+$ (calcd for $C_{23}H_{24}O_6$, 396.1573). $[\alpha]_D^{20}$ -63.3 (*c* 0.0060, MeOH). UV (MeOH) λ_{max} (log ε) 222 (3.74) nm, 239 (3.71) nm, 286 (3.63) nm. For NMR data, see Table 4. For NMR spectra, see Figures S26 to S30.

2-hydroxy-2-methyl-1-(4-oxo-2-phenyl-3,4,8,9-tetrahydro-2H-furo[2,3-h]chromen-9-yl)propyl cinnamate (**14**): HRESIMS *m/z* 485.1964 $[M+H]^+$ (calcd for $C_{30}H_{29}O_6$, 485.1964). $[\alpha]_D^{20}$ - 132.9 (*c* 0.0047, MeOH). UV (MeOH) λ_{max} (log ε) 223 (3.88) nm, 241 (3.85) nm, 279 (3.82) nm. For NMR data, see Table 4. For NMR spectra, see Figures S31 to S36.

(-)-(6a*R*,11a*R*)-medicarpin (**15)**: HRESIMS *m/z* 271.0975 $[M+H]^+$ (calcd for $C_{16}H_{15}O_4$, 271.0970). $[\alpha]_D^{20}$ -240.0 (*c* 0.0020, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 3.54 (2H, m, H-6'', H-6a), 3.74 (3H, s, 9OCH_3), 4.22 (1H, d, *J* = 5.8 Hz, H-6'), 5.48 (1H, d, *J* = 6.4 Hz, H-11a), 6.31 (1H, d, *J* = 2.4 Hz, H-4), 6.38 (1H, d, *J* = 2.3 Hz, H-10), 6.45 (1H, dd, *J* = 8.1, 2.3 Hz, H-8), 6.49 (1H, dd, *J* = 8.4, 2.4 Hz, H-2), 7.17 (1H, d, *J* = 8.1 Hz, H-7), 7.29 (1H, d, *J* = 8.4 Hz, H-1); ^{13}C NMR (CD_3OD, 151 MHz) δ 40.9 (CH-6a), 55.9 (9OCH_3), 67.6 (CH_2-6), 80.1 (CH-11a), 97.6 (CH-10), 104.1 (CH-4), 107.2 (CH-8), 110.7 (CH-2), 112.9 (C-11b), 120.9 (C-6b), 126.0 (CH-7), 133.2 (CH-1), 158.1 (C-4a), 160.1 (C-3), 162.1 (C-10a), 162.6 (C-9).

(-)-(6a*R*,11a*R*)-maackiain (**16)**: HRESIMS *m/z* 285.0753 $[M+H]^+$ (calcd for $C_{16}H_{13}O_5$, 285.0763). $[\alpha]_D^{20}$ -103.1 (*c* 0.0053, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 3.48 (1H, ddd, *J* = 10.9, 6.9, 4.8 Hz, H-6a), 3.56 (1H, t, *J* = 10.9 Hz, H-6''), 4.22 (1H, dd, *J* = 10.9, 4.8 Hz, H-6'), 5.45 (1H, d, *J* = 6.9 Hz, H-11a), 5.85 (1H, d, *J* = 1.1 Hz, OCH_2O''), 5.88 (1H, d, *J* = 1.1 Hz, OCH_2O'), 6.30 (1H, d, *J* = 2.4 Hz, H-4), 6.37 (1H, s, H-10), 6.48 (1H, dd, *J* = 8.3, 2.4 Hz, H-2), 6.81 (1H, s, H-7), 7.26 (1H, d, *J* = 8.3 Hz, H-1); ^{13}C NMR (CD_3OD, 151 MHz) δ 41.6 (CH-6a), 67.4 (CH_2-6), 80.1 (CH-11a), 94.2 (CH-10), 102.5 (OCH_2O), 104.1 (CH-4), 106.0 (CH-7), 110.7 (CH-2), 112.9 (C-11b), 119.8 (C-6b), 133.1 (CH-1), 143.1 (C-8), 149.5 (C-9), 155.6 (C-10a), 158.0 (C-4a), 160.1 (C-3).

(-)-(6a*R*,11a*R*,2'*R*)-emoroidocarpan (**17**): HRESIMS m/z 351.1214 $[M+H]^+$ (calcd for $C_{21}H_{19}O_5$, 351.1233). $[\alpha]_D^{20}$ -273.0 (c 0.0100, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 1.75 (3H, t, J = 1.2 Hz, H_3-4'), 2.99 (1H, ddd, J = 15.3, 7.7, 1.3 Hz, H-1'b), 3.33 (1H, dd, J = 15.3, 9.2 Hz, H-1'a), 3.49 (1H, ddd, J = 10.7, 7.0, 4.8 Hz, H-6a), 3.57 (1H, t, J = 10.7 Hz, H-6''), 4.22 (1H, dd, J = 10.7, 4.8 Hz, H-6'), 4.88 (1H, p, J = 1.2 Hz, H-5'b), 5.05 (1H, p, J = 1.2 Hz, H-5'a), 5.20 (1H, t, J = 9.2, 7.1 Hz, H-2'), 5.47 (1H, d, J = 7.0 Hz, H-11a), 5.86 (1H, d, J = 1.2 Hz, OCH_2O''), 5.88 (1H, d, J = 1.2 Hz, OCH_2O'), 6.27 (1H, s, H-4), 6.37 (1H, s, H-10), 6.81 (1H, s, H-7), 7.23 (1H, s, H-1); ^{13}C NMR (CD_3OD, 151 MHz) δ 17.2 (CH_3-4'), 34.9 (CH_2-1'), 41.6 (CH-6a), 67.6 (CH_2-6), 80.4 (CH-11a), 87.9 (CH-2'), 94.2 (CH-10), 98.6 (CH-4), 102.5 (OCH_2O), 106.0 (CH-7), 112.1 (CH_2-5'), 113.7 (C-11b), 119.8 (C-6b), 122.0 (C-2), 127.8 (CH-1), 143.1 (C-8), 145.8 (C-3'), 149.5 (C-9), 155.5 (C-10a), 157.5 (C-4a), 162.5 (C-3).

(-)-(6a*R*,11a*R*,2'*R*)-4'-hydroxyemoroidocarpan (**18**): HRESIMS *m/z* 367.1190 $[M+H]^+$ (calcd for $C_{21}H_{19}O_6$, 367.1182). $[\alpha]_D^{20}$ -222.0 (*c* 0.0033, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 3.07 (1H, dd, *J* = 15.3, 7.9 Hz, H-1'b), 3.37 (1H, dd, *J* = 15.3, 9.6 Hz, H-1'a), 3.49 (1H, ddd, *J* = 10.7, 7.0, 4.8 Hz, H-6a), 3.57 (1H, t, *J* = 10.8 Hz, H-6''), 4.15 (2H, s, H_2-4'), 4.22 (1H, dd, *J* = 10.8, 4.8 Hz, H-6'), 5.21 (2H, s, H-5'), 5.31 (1H, t, *J* = 9.6, 7.9 Hz, H-2'), 5.47 (1H, d, *J* = 7.0 Hz, H-11a), 5.86 (1H, s, OCH_2O''), 5.88 (1H, s, OCH_2O'), 6.29 (1H, s, H-4), 6.37 (1H, s, H-10), 6.81 (1H, s, H-7), 7.24 (1H, s, H-1); ^{13}C NMR (MeOD, 151 MHz) δ 35.3 (CH_2-1'), 41.5 (CH-6a), 62.6 (CH_2-4'), 67.6 (CH_2-6), 80.3 (CH-11a), 85.4 (CH-2'), 94.2 (CH-10), 98.7 (CH-4), 102.5 (OCH_2O), 106.0 (CH-7), 110.8 (CH_2-5'), 113.8 (C-11b), 119.8 (C-6b), 121.9 (C-2), 127.9 (CH-1), 143.1 (C-8), 149.5 (C-9), 149.7 (C-3'), 155.5 (C-10a), 157.5 (C-4a), 162.2 (C-3).

(-)-(2'*R*)-tephcalostan (**19**): HRESIMS *m/z* 363.0883 $[M+H]^+$ (calcd for $C_{21}H_{15}O_6$, 363.0869). $[\alpha]_D^{20}$ -30.0 (*c* 0.0047, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 1.79 (3H, t, *J* = 1.2 Hz, H_3-4'), 3.18 (1H, ddd, *J* = 15.9, 7.9, 1.3 Hz, H-1'b), 3.54 (1H, ddd, *J* = 15.9, 9.5, 0.7 Hz, H-1'a), 4.96 (1H, p, *J* = 1.2 Hz, H-5'b), 5.13 (1H, p, *J* = 1.2 Hz, H-5'a), 5.40 (1H, t, *J* = 9.5, 7.9 Hz, H-2'), 6.08 (2H, s, OCH_2O), 6.92 (1H, s, H-4), 7.28 (1H, s, H-10), 7.35 (1H, s, H-7), 7.84 (1H, t, *J* = 1.3, 0.7 Hz, H-1); ^{13}C NMR (CD_3OD, 151 MHz) δ 16.9 (CH_3-4'), 34.3 (CH_2-4'), 88.6 (CH-2'), 94.8 (CH-10), 98.6 (CH,4), 100.1 (CH-7), 103.1 (OCH_2O), 106.8 (C-11b), 112.5 (CH_2-5'), 117.8 (C-6b), 118.0 (CH-1), 127.0 (C-2), 144.7 (C-3'), 147.4 (C-8), 148.8 (C-9), 151.7 (C-10a), 155.7 (C-4a), 161.7 (C-11a), 164.5 (C-3).

glabrone (**20**): HRESIMS *m/z* 337.1070 $[M+H]^+$ (calcd for $C_{20}H_{17}O_5$, 337.1076). For NMR data, see Table 2.

6-hydroxy-glabrone (**21**): HRESIMS *m/z* 353.1020 $[M+H]^+$ (calcd for $C_{20}H_{17}O_6$, 353.1025). UV (MeOH) λ_{max} (log ε) 226 (4.43) nm, 258 (4.02) nm, 330 (3.80) nm. For NMR data, see Table 2. For NMR spectra, see Figures S37 to S41.

formononetin (**22**): HRESIMS *m/z* 269.0802 $[M+H]^+$ (calcd for $C_{16}H_{13}O_4$, 269.0814). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 3.83 (3H, s, 4'OCH_3), 6.86 (1H, d, *J* = 2.3 Hz, H-8), 6.94 (1H, dd, *J* = 8.8, 2.3 Hz, H-6), 6.99 (3H, d, *J* = 8.8 Hz, H-3', H-5'), 7.47 (2H, d, *J* = 8.8 Hz, H-2', H-6'), 8.06 (1H, d, *J* = 8.8 Hz, H-5), 8.16 (1H, s, H-2); ^{13}C NMR (CD_3OD, 151 MHz) δ 55.7 (4'OCH_3), 103.3 (CH-8), 114.8 (CH-3', CH-5'), 116.6 (CH-6), 118.1 (C-10), 125.6 (C-1'), 125.7 (C-3), 128.5 (CH-5), 131.4 (CH-2', CH-6'), 154.8 (CH-2), 160.0 (C-9), 161.3 (C-4'), 165.0 (C-7), 178.1 (C-4).

munetone (**23**): HRESIMS *m/z* 417.1962 $[M+H]^+$ (calcd for $C_{26}H_{24}O_5$, 417.1702). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 1.43 (6H, s, H_3-5''', H_3-6'''), 1.49 (6H, s, H_3-5'', H_3-6''), 3.58 (3H, s, 2'OCH_3), 5.76 (1H, d, *J* = 10.0 Hz, H-3'''), 5.90 (1H, d, *J* = 10.0 Hz, H-3''), 6.54 (1H, d, *J* = 10.0 Hz, H-4''), 6.61 (1H, d, *J* = 8.3 Hz, H-5'), 6.63 (1H, d, *J* = 10.0 Hz, H-4'''), 6.88 (1H, s, H-8), 7.06 (1H, d, *J* = 8.3 Hz, H-6'), 7.81 (1H, s, H-5), 8.10 (1H, s, H-2); ^{13}C NMR (CD_3OD, 151 MHz) δ 28.0 (CH_3-5''',

CH_3-6'''), 28.7 (CH_3-5'', CH_3-6''), 62.3 (2'O CH_3), 77.1 (C-2'''), 79.4 (C-2''), 105.0 (CH-8), 113.3 (CH-5'), 116.3 (C-3'), 118.1 (CH-4'''), 118.6 (C-1'), 119.3 (C-10), 121.7 (C-6), 121.9 (CH-4''), 123.3 (C-3), 124.0 (CH-5), 131.8 (CH-3'''), 132.8 (CH-6'), 133.6 (CH-3''), 155.8 (C-4'), 156.1 (C-2'), 156.2 (CH-2), 159.3 (C-9), 159.9 (C-7), 178.1 (C-4).

acicerone (**24**): HRESIMS *m/z* 313.0708 $[M+H]^+$ (calcd for $C_{17}H_{13}O_6$, 313.0712). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 4.01 (3H, d, *J* = 2.6 Hz, 7OCH_3), 5.98 (2H, d, *J* = 2.6 Hz, OCH_2O), 6.88 (1H, d, *J* = 8.0 Hz, H-5'), 6.99 (1H, d, *J* = 8.0 Hz, H-6'), 7.07 (1H, s, H-2'), 7.13 (1H, s, H-8), 7.48 (1H, s, H-5), 8.20 (1H, s, H-2); ^{13}C NMR (CD_3OD, 151 MHz) δ 57.0 (7OCH_3), 100.7 (CH-8), 102.5 (OCH_2O), 108.9 (CH-5), 109.1 (CH-5'), 110.8 (CH-2'), 119.0 (C-10), 123.8 (CH-6'), 125.3 (C-3), 127.3 (C-1'), 146.8 (C-6), 149.1 (C-3', C-4'), 153.6 (C-9), 154.9 (C-2), 155.6 (C-7), 177.8 (C-4).

alfalone (**25**): HRESIMS *m/z* 299.0921 $[M+H]^+$ (calcd for $C_{17}H_{15}O_5$, 299.0920). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 3.83 (3H, s, 4'OCH_3), 4.01 (3H, s, 7OCH_3), 6.99 (2H, d, *J* = 8.4 Hz, H-3', H-5'), 7.13 (1H, s, H-8), 7.47 (2H, d, *J* = 8.4 Hz, H-2', H-6'), 7.49 (1H, s, H-5), 8.20 (1H, s, H-2); ^{13}C NMR (CD_3OD, 151 MHz) δ 55.7 (4'OCH_3), 57.0 (7OCH_3), 100.8 (CH-8), 108.9 (CH-5), 114.9 (CH-3', CH-5'), 119.1 (C-10), 125.3 (C-3), 125.7 (C-1'), 131.4 (CH-2', CH-6'), 146.7 (C-6), 153.7 (C-9), 154.7 (CH-2), 155.6 (C-7), 161.2 (C-4'), 178.0 (C-4).

afrormosin (**26**): HRESIMS *m/z* 299.0921 $[M+H]^+$ (calcd for $C_{17}H_{15}O_5$, 299.0920). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 3.83 (3H, s, 4'OCH_3), 3.97 (3H, s, 6OCH_3), 6.95 (1H, s, H-8), 6.99 (2H, d, *J* = 8.7 Hz, H-3', H-5'), 7.48 (2H, d, *J* = 8.7 Hz, H-2', H-6'), 7.58 (1H, s, H-5), 8.18 (1H, s, H-2); ^{13}C NMR (CD_3OD, 151 MHz) δ 55.7 (4'OCH_3), 56.6 (7OCH_3), 103.9 (CH-8), 105.4 (CH-5), 114.8 (CH-3', CH-5'), 117.9 (C-10), 125.7 (C-1'), 131.4 (CH-2', CH-6'), 148.6 (C-6), 154.5 (CH-2), 161.2 (C-4'), 177.8 (C-4).

wighteone (**27**): HRESIMS *m/z* 339.1218 $[M+H]^+$ (calcd for $C_{20}H_{19}O_5$, 339.1233). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 1.66 (3H, s, H_3-4''), 1.78 (3H, s, H_3-5''), 3.32 (2H, overlapped, H_2-1''), 5.23 (1H, t, *J* = 7.6 Hz, H-2''), 6.39 (1H, s, H-8), 6.85 (2H, d, *J* = 7.7 Hz, H-3', H-5'), 7.37 (2H, d, *J* = 7.7 Hz, H-2', H-6'), 8.04 (1H, s, H-2); ^{13}C NMR (CD_3OD, 151 MHz) δ 17.9 (CH_3-5''), 22.3 (CH_2-1''), 26.0 (CH_3-4''), 93.9 (CH-8), 106.1 (C-10), 113.1 (C-6), 116.3 (CH-3', CH-5'), 123.2 (C-1'), 123.3 (CH-2''), 124.5 (C-3), 131.4 (CH-2', CH-6'), 132.2 (C-3''), 154.6 (CH-2), 157.6 (C-9), 158.8 (C-4'), 160.5 (C-5), 163.7 (C-7), 182.4 (C-4).

dehydroneotenone (**28**): HRESIMS *m/z* 337.0712 $[M+H]^+$ (calcd for $C_{19}H_{13}O_6$, 337.0712). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 3.73 (3H, s, 2'OCH_3), 5.96 (2H, s, OCH_2O), 6.76 (1H, s, H-3'), 6.80 (1H, s, H-6'), 7.07 (1H, d, *J* = 2.3 Hz, H-3''), 7.77 (1H, s, H-8), 7.96 (1H, d, *J* = 2.3 Hz, H-2''), 8.19 (1H, s, H-2), 8.48 (1H, s, H-5); ^{13}C NMR (CD_3OD, 151 MHz) δ 57.1 (2'OCH_3), 96.3 (CH-3'), 101.0 (CH-8), 102.8 (OCH_2O), 108.0 (CH-3''), 112.0 (CH-6'), 114.0 (C-1'), 119.4 (CH-5), 121.9

(C-10), 122.8 (C-3), 127.9 (C-6), 142.6 (C-5'), 149.7 (CH-2''), 150.1 (C-4'), 154.6 (C-2'), 155.8 (C-9), 157.3 (CH-2), 159.0 (C-7), 178.9 (C-4).

(-)-12a-hydroxypachyrrhizone (**29**): HRESIMS *m/z* 365.0652 $[M-H_20+H]^+$ (calcd for $C_{20}H_{13}O_7$, 365.0661). $[\alpha]_D^{20}$ -46.1 (*c* 0.0093, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 4.04 (3H, s, 8OCH_3), 4.50 (1H, d, *J* = 11.6 Hz, H-6''), 4.63 (1H, d, *J* = 11.6 Hz, H-6'), 4.65 (1H, s, H6a), 5.79 (1H, s, OCH_2O''), 5.85 (1H, s, OCH_2O'), 6.44 (1H, s, H-4), 6.55 (1H, s, H-1), 6.86 (1H, s, H-3'), 7.74 (1H, s, H-2'), 7.89 (1H, s, H-11); ^{13}C NMR (CD_3OD, 151 MHz) δ 61.5 (8OCH_3), 65.0 (CH_2-6), 69.9 (C-12a), 77.6 (CH-6a), 99.6 (CH-4), 102.7 (OCH_2O), 107.3 (CH-1), 108.3 (CH-3'), 109.9 (C-12b), 115.0 (CH-11), 118.2 (C-11a), 125.7 (C-10), 134.6 (C-8), 143.4 (C-2), 148.0 (CH-2'), 150.6 (C-7a), 150.9 (C-3), 151.3 (C-4a), 152.6 (C-9), 194.5 (C-12).

(-)-12a-hydroxydolineone (**30**): HRESIMS *m/z* 335.0558 $[M-H_20+H]^+$ (calcd for $C_{19}H_{11}O_6$, 335.0556). $[\alpha]_D^{20}$ -41.3 (*c* 0.0053, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 4.48 (1H, dd, *J* = 12.2, 1.1 Hz, H-6''), 4.57 (1H, dd, *J* = 12.2, 2.4 Hz, H-6'), 4.64 (1H, dd, *J* = 2.4, 1.1 Hz, H-6a), 5.79 (1H, d, *J* = 1.1 Hz, OCH_2O''), 5.85 (1H, d, *J* = 1.1 Hz, OCH_2O'), 6.43 (1H, s, H-4), 6.56 (1H, s, H-1), 6.86 (1H, d, *J* = 2.3 Hz, H-3'), 7.02 (1H, s, H-8), 7.71 (1H, d, *J* = 2.3 Hz, H-2'), 8.18 (1H, s, H-11); ^{13}C NMR (CD_3OD, 151 MHz) δ 65.0 (CH_2-6), 69.8 (C-12a), 77.5 (CH-6a), 99.7 (CH-4), 100.4 (CH-8), 102.7 (OCH_2O), 107.4 (CH-1), 107.9 (CH-3'), 110.0 (C-12b), 117.0 (C-11a), 121.8 (CH-11), 124.6 (C-10), 143.2 (C-2), 148.0 (CH-2'), 150.9 (C-3), 151.3 (C-4a), 159.6 (C-7a), 161.4 (C-9), 194.5 (C-12).

(+)-12a-hydroxyerosone (**31**): HRESIMS *m/z* 351.0867 $[M-H_20+H]^+$ (calcd for $C_{20}H_{15}O_6$, 351.0869). $[\alpha]_D^{20}$ 97.5 (*c* 0.0067, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 3.66 (3H, s, 2OCH_3), 3.77 (3H, s, 3OCH_3), 4.50 (1H, dd, *J* = 12.1, 3.4 Hz, H-6''), 4.59 (1H, dd, *J* = 12.1, 1.6 Hz, H-6'), 4.65 (1H, s, H-6a), 6.54 (1H, s, H-4), 6.70 (1H, s, H-1), 6.85 (1H, s, H-3'), 7.02 (1H, s, H-8), 7.71 (1H, s, H-2'), 8.19 (1H, s, H-11); ^{13}C NMR (CD_3OD, 151 MHz) δ 56.3 (3OCH_3), 57.1 (2OCH_3), 65.0 (CH_2-6), 69.7 (C-12a), 77.8 (CH-6a), 100.4 (CH-8), 102.3 (CH-4), 107.9 (CH-3'), 109.3 (C-12b), 112.6 (CH-1), 117.0 (C-11a), 121.7 (CH-11), 124.6 (C-10), 144.9 (C-2), 148.1 (CH-2'), 150.6 (C-4a), 152.9 (C-3), 159.5 (C-7a), 161.4 (C-9), 194.5 (C-12).

(+)-erosone (**32**): HRESIMS *m/z* 353.1016 $[M+H]^+$ (calcd for $C_{20}H_{17}O_6$, 353.1025). $[\alpha]_D^{20}$ 46.7 (*c* 0.0060, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 3.67 (3H, s, 2OCH_3), 3.76 (3H, s, 3OCH_3), 3.96 (1H, d, *J* = 3.8 Hz, H-12a), 4.23 (1H, d, *J* = 12.2 Hz, H-6''), 4.59 (1H, dd, *J* = 12.2, 3.0 Hz, H-6'), 5.03 (1H, t, *J* = 3.8, 3.0 Hz, H-6a), 6.50 (1H, s, H-4), 6.73 (1H, s, H-1), 6.85 (1H, d, *J* = 2.4 Hz, H-3'), 7.07 (1H, s, H-8), 7.71 (1H, d, *J* = 2.4 Hz, H-2'), 8.20 (1H, s, H-11); ^{13}C NMR (CD_3OD, 151 MHz) δ 46.0 (CH-12a), 56.4 (3OCH_3), 57.2 (2OCH_3), 67.5 (CH_2-6), 73.8 (CH-6a), 100.4 (CH-8), 102.5 (CH-4), 106.2 (C-12b), 107.9 (CH-3'), 112.5 (CH-1), 117.4 (C-11a), 121.7 (CH-11), 124.5 (C-10), 145.0 (C-2), 148.0 (CH-2'), 149.7 (C-4a), 151.3 (C-3), 160.8 (C-7a), 161.3 (C-9), 192.9 (C-12).

12-deoxo-12α-acetoxy-12aβ-hydroxyelliptone (**33**): HRESIMS *m/z* 353.1012 $[M\text{-}C_2H_4O_2+H]^+$ (calcd for $C_{20}H_{17}O_6$, 353.1025). $[\alpha]_D^{20}$ - 80.6 (*c* 0.0053, MeOH). UV (MeOH) λ_{max} (log ε) 225 (3.82) nm, 326 (3.61) nm. For NMR data, see Table 1. For NMR spectra, see Figures S42 to S46.

(-)-12-deoxo-12α-acetoxyelliptone (**34**): HRESIMS *m/z* 337.1065 $[M\text{-}C_2H_4O_2+H]^+$ (calcd for $C_{20}H_{17}O_5$, 337.1076). $[\alpha]_D^{20}$ -293.0 (*c* 0.0187, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 1.74 (3H, s, Ac), 3.75 (1H, tt, *J* = 6.2, 4.6, 1.4 Hz, H-12a), 3.78 (3H, s, $2OCH_3$), 3.79 (3H, s, $3OCH_3$), 4.30 (1H, ddd, *J* = 10.1, 5.1, 1.4 Hz, H-6), 4.50 (1H, t, *J* = 11.2, 10.1 Hz, H-6), 5.01 (1H, dtd, *J* = 11.2, 6.2, 5.1, 1.1 Hz, H-6a), 6.47 (1H, s, H-4), 6.47 (1H, d, *J* = 4.6 Hz, H-12), 6.89 (1H, dd, *J* = 2.2, 0.9 Hz, H-3'), 6.89 (1H, s, H-1), 7.10 (1H, dd, *J* = 8.4, 0.9 Hz, H-10), 7.17 (1H, d, *J* = 8.4 Hz, H-11), 7.68 (1H, d, *J* = 2.2 Hz, H-2'); ^{13}C NMR (CD_3OD, 151 MHz) δ 20.7 (Ac), 37.6 (CH-12a), 56.4 ($3OCH_3$), 57.2 ($2OCH_3$), 65.4 (CH_2-6), 68.5 (CH-12), 70.6 (CH-6a), 101.5 (CH-4), 104.8 (CH-3'), 105.8 (CH-10), 110.5 (C-12b), 112.9 (C-11a), 114.6 (CH-1), 118.2 (C-8), 127.7 (CH-11), 144.8 (C-2), 145.8 (CH-2'), 148.2 (7C-a), 150.4 (C-4a), 151.1 (C-3), 158.2 (C-9), 171.8 (CO).

(-)-(6a*R*,12a*R*)-elliptone (**35**): HRESIMS *m/z* 353.1015 $[M+H]^+$ (calcd for $C_{20}H_{17}O_6$, 353.1025). $[\alpha]_D^{20}$ -31.4 (*c* 0.0073, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 3.67 (3H, s, $2OCH_3$), 3.75 (3H, s, $3OCH_3$), 3.98 (1H, d, *J* = 4.1 Hz, H-12a), 4.28 (1H, dt, *J* = 12.3, 1.0 Hz, H-6''), 4.68 (1H, dd, *J* = 12.3, 3.1 Hz, H-6'), 5.17 (1H, td, *J* = 4.1, 3.1, 1.0 Hz, H-6a), 6.51 (1H, s, H-4), 6.72 (1H, s, H-1), 6.98 (1H, dd, *J* = 2.2, 0.9 Hz, H-3'), 7.19 (1H, dd, *J* = 8.8, 0.9 Hz, H-10), 7.75 (1H, d, *J* = 2.2 Hz, H-2'), 7.86 (1H, d, *J* = 8.8 Hz, H-11); ^{13}C NMR (CD_3OD, 151 MHz) δ 45.8 (CH-12a), 56.4 ($3OCH_3$), 57.2 ($2OCH_3$), 67.3 (CH_2-6), 74.4 (CH-6a), 102.6 (CH-4), 105.5 (CH-3'), 106.3 (C-12b), 107.4 (CH-10), 112.5 (CH-1), 114.7 (C-11a), 118.4 (C-8), 124.8 (CH-11), 145.1 (C-2), 146.9 (CH-2'), 149.6 (C-4a), 151.3 (C-3), 157.5 (C-7a), 161.8 (C-9), 192.1 (C-12).

(+)-(6a*S*,12a*S*)-12a-hydroxyelliptone (**36**): HRESIMS *m/z* 351.0856 $[M\text{-}H_20+H]^+$ (calcd for $C_{20}H_{15}O_6$, 351.0869). $[\alpha]_D^{20}$ 23.3 (*c* 0.0060, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 3.66 (3H, s, $2OCH_3$), 3.76 (3H, s, $3OCH_3$), 4.54 (1H, dd, *J* = 12.3, 1.1 Hz, H-6''), 4.68 (1H, dd, *J* = 12.3, 2.5 Hz, H-6'), 4.78 (1H, dd, *J* = 2.5, 1.1 Hz, H-6a), 6.54 (1H, s, H-4), 6.70 (1H, s, H-1), 6.95 (1H, dd, *J* = 2.2, 0.9 Hz, H-3'), 7.21 (1H, dd, *J* = 8.8, 0.9 Hz, H-10), 7.75 (1H, d, *J* = 2.2 Hz, H-2'), 7.85 (1H, d, *J* = 8.8 Hz, H-11); ^{13}C NMR (CD_3OD, 151 MHz) δ 56.3 ($3OCH_3$), 57.1 ($2OCH_3$), 64.9 (CH_2-6), 69.3 (C-12a), 78.3 (CH-6a), 102.3 (CH-4), 105.4 (CH-3'), 107.6 (CH-10), 109.5 (C-12b), 112.5 (CH-1), 114.3 (C-11a), 118.3 (C-8), 124.7 (C-H11), 145.0 (C-2), 147.0 (CH-2'), 150.5 (C-4a), 152.9 (C-3), 156.6 (C-7a), 161.8 (C-9), 193.9 (C-12).

(-)-(6a*S*,11a*S*,2'*R*)-rotenone (**37**): HRESIMS *m/z* 395.1488 $[M+H]^+$ (calcd for $C_{23}H_{23}O_6$, 395.1495). $[\alpha]_D^{20}$ -223.3 (*c* 0.0060, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 1.76 (3H, t, *J* = 1.2 Hz, H_3-6'), 2.95 (1H, dd, *J* = 15.8, 8.0 Hz, H-3'b), 3.33 (1H, overlapped, H-3'a), 3.67 (3H, s, $2OCH_3$), 3.77 (3H, s, $3OCH_3$), 3.87 (1H, d, *J* = 4.0 Hz, H-12a), 4.22 (1H, dt, *J* = 12.3, 1.0 Hz, H-6), 4.58 (1H, dd, *J* = 12.3, 3.0 Hz, H-6), 4.92 (1H, p, *J* = 1.2 Hz, H-5'b), 5.01 (1H, td, *J* = 4.0, 3.0, 1.0 Hz, H-6a),

5.06 (1H, p, *J* = 1.2 Hz, H-5'a), 5.31 (1H, t, *J* = 9.7, 8.0 Hz, H-2'), 6.49 (1H, s, H-4), 6.51 (1H, d, *J* = 8.6 Hz, H-10), 6.71 (1H, s, H-1), 7.80 (1H, d, *J* = 8.6 Hz, H-11); ^{13}C NMR (CD_3OD, 151 MHz) δ 16.7 (CH_3-6'), 31.7 (CH_2-3'), 45.4 (CH-12a), 56.1 ($3OCH_3$), 56.8 ($2OCH_3$), 67.0 (CH_2-6), 73.3 (CH-6a), 89.0 (CH-2'), 102.2 (CH-4), 105.3 (CH-10), 106.4 (C-13a), 112.2 (CH-1), 112.4 (CH_2-5'), 114.2 (C-8), 130.5 (CH-11), 144.8 (C-2, C-4'), 149.3 (C-4a), 151.1 (C-3), 159.4 (C-7a), 168.6 (C-9), 191.3 (C-12).

(-)-(6a*R*,12a*R*)-tephrosin (**38**): HRESIMS *m/z* 393.1320 $[M\text{-}H_20+H]^+$ (calcd for $C_{23}H_{21}O_6$, 393.1338). $[\alpha]_D^{20}$ -47.9 (*c* 0.0140, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 1.36 (3H, s, H_3-6'), 1.43 (3H, s, H_3-5'), 3.67 (3H, s, $2OCH_3$), 3.78 (3H, s, $3OCH_3$), 4.48 (1H, dd, *J* = 12.7, 1.6 Hz, H-6''), 4.60 (1H, t, *J* = 2.4, 1.6 Hz, H-6a), 4.60 (1H, dd, *J* = 12.7, 2.4 Hz, H-6'), 5.66 (1H, d, *J* = 10.1 Hz, H-3'), 6.45 (1H, d, *J* = 8.8 Hz, H-10), 6.54 (1H, s, H-4), 6.59 (1H, d, *J* = 10.1 Hz, H-4'), 6.70 (1H, s, H-1), 7.69 (1H, d, *J* = 8.8 Hz, H-11); ^{13}C NMR (CD_3OD, 151 MHz) δ 28.2 (CH_3-6'), 28.6 (CH_3-5'), 56.3 ($3OCH_3$), 57.1 ($2OCH_3$), 64.9 (CH_2-6), 69.0 (12a), 77.9 (CH-6a), 79.0 (C-2'), 102.3 (CH-4), 109.6 (C-12b), 110.3 (C-8), 112.5 (CH-10), 112.6 (CH-1), 113.4 (C-11a), 116.2 (CH-4'), 129.3 (CH-11), 130.4 (CH-3'), 145.0 (C-2), 150.5 (C-4a), 152.9 (C-3), 157.6 (C-7a), 161.6 (C-9), 193.1 (C-12).

(-)-(6a*S*,12a*S*)-deguelin (**39**): HRESIMS *m/z* 395.1481 $[M+H]^+$ (calcd for $C_{23}H_{23}O_6$, 395.1495). $[\alpha]_D^{20}$ -79.5 (*c* 0.0267, MeOH). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 1.35 (3H, s, H_3-6'), 1.42 (3H, s, H_3-5'), 3.68 (3H, s, $2OCH_3$), 3.75 (3H, s, $3OCH_3$), 3.86 (1H, d, *J* = 4.0 Hz, H-12a), 4.21 (1H, dt, *J* = 12.2, 1.0 Hz, H-6), 4.60 (1H, dd, *J* = 12.2, 3.0 Hz, H-6), 4.98 (1H, td, *J* = 4.0, 3.0, 1.0 Hz, H-6a), 5.65 (1H, d, *J* = 10.1 Hz, H-3'), 6.43 (1H, dd, *J* = 8.7, 0.7 Hz, H-10), 6.49 (1H, s, H-4), 6.63 (1H, dd, *J* = 10.1, 0.7 Hz, H-4'), 6.72 (1H, d, *J* = 1.0 Hz, H-1), 7.69 (1H, d, *J* = 8.7 Hz, H-11); ^{13}C NMR (CD_3OD, 151 MHz) δ 28.2 (CH_3-6'), 28.6 (CH_3-5'), 45.4 (CH-12a), 56.4 ($3OCH_3$), 57.2 ($2OCH_3$), 67.3 (CH_2-6), 73.9 (CH-6a), 78.9 (C-2'), 102.6 (CH-4), 106.4 (C-12b), 110.4 (C-8), 112.3 (CH-10), 112.5 (CH-1), 113.8 (C-11a), 116.4 (CH-1'), 129.3 (CH-11), 130.3 (CH-3'), 145.0 (C-2), 149.5 (C-4a), 151.2 (C-3), 158.5 (C-7a), 161.5 (C-9), 191.6 (C-12).

norisojamaicin (**40**): HRESIMS *m/z* 365.1026 $[M+H]^+$ (calcd for $C_{21}H_{17}O_6$, 365.1025). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 1.50 (6H, s, H_3-5'', H_3-6''), 5.87 (1H, d, *J* = 10.1 Hz, H-3''), 5.95 (2H, s, OCH_2O), 6.62 (1H, s, H-2'), 6.65 (1H, s, H-6'), 6.88 (1H, d, *J* = 10.1 Hz, H-4''), 6.91 (0H, d, *J* = 8.5 Hz, H-6), 7.98 (1H, d, *J* = 8.5 Hz, H-5), 8.22 (1H, s, H-2); ^{13}C NMR (CD_3OD, 151 MHz) δ 28.4 (CH_3-5'', CH_3-6''), 79.2 (C-2''), 102.5 (OCH_2O), 102.9 (CH-2'), 110.6 (C-8), 113.4 (CH-6'), 115.5 (CH-4''), 116.6 (CH-6), 119.1 (C-10), 126.1 (C-1'), 127.3 (CH-5), 132.1 (CH-3''), 135.8 (C-4'), 142.0 (C-5'), 150.4 (C-3'), 153.8 (C-9), 155.0 (C-2), 159.4 (C-7), 177.8 (C-4).

3′-hydroxy-4′-*O*-metyhlerrone (**41**): HRESIMS *m/z* 367.118 $[M+H]^+$ (calcd for $C_{21}H_{19}O_6$, 367.1182). NMR data: ^{1}H NMR (CD_3OD, 600 MHz) δ 1.47 (6H, s, H_3-5'', H_3-6''), 3.89 (3H, s, $4'OCH_3$), 5.70 (1H, d, *J* = 10.0 Hz, H-3''), 6.22 (1H, s, H-6), 6.74 (1H, d, *J* = 10.0 Hz, H-4''), 6.99 (2H, m, H-5', H-6'), 7.06 (1H, d, *J* = 1.8 Hz, H-2'), 8.17 (1H, s, H-2); ^{13}C NMR (CD_3OD, 151 MHz) δ 28.3 (CH_3-5'', CH_3-6''), 56.2 ($4'OCH_3$), 79.3 (C-2''), 100.6 (CH-6), 102.4 (C-8), 106.7 (C-10), 112.5 (CH-5'), 115.1 (CH-4''),

117.2 (CH-2'), 121.5 (CH-6'), 124.6 (C-3), 128.7 (CH-3''), 147.3 (C-3'), 149.1 (C-4'), 153.4 (C-9), 154.9 (CH-2), 160.6 (C-7), 163.1 (C-5), 182.2 (C-4).

Isolated Compounds Biological Source

Table S5: Occurrence of each compound in each extract (x = isolated from the corresponding extract)

Compound	*C. palala* roots	*C. grevei* roots bark	*P.erosus* leaves	*D. heterophyllum* u.g
1			x	
2			x	
3			x	
4			x	
5			x	
6			x	
7			x	
8				x
9				x
10				x
11				x
12				x
13				x
14				x
15	x			
16	x			
17		x		
18		x		
19		x		
20		x		
21		x		
22	x			
23		x		
24			x	
25			x	
26			x	
27			x	
28			x	
29			x	
30			x	
31			x	
32			x	
33	x			
34	x			
35	x			
36	x			
37		x	x	x
38	x			
39	x	x		x
40		x		
41		x		

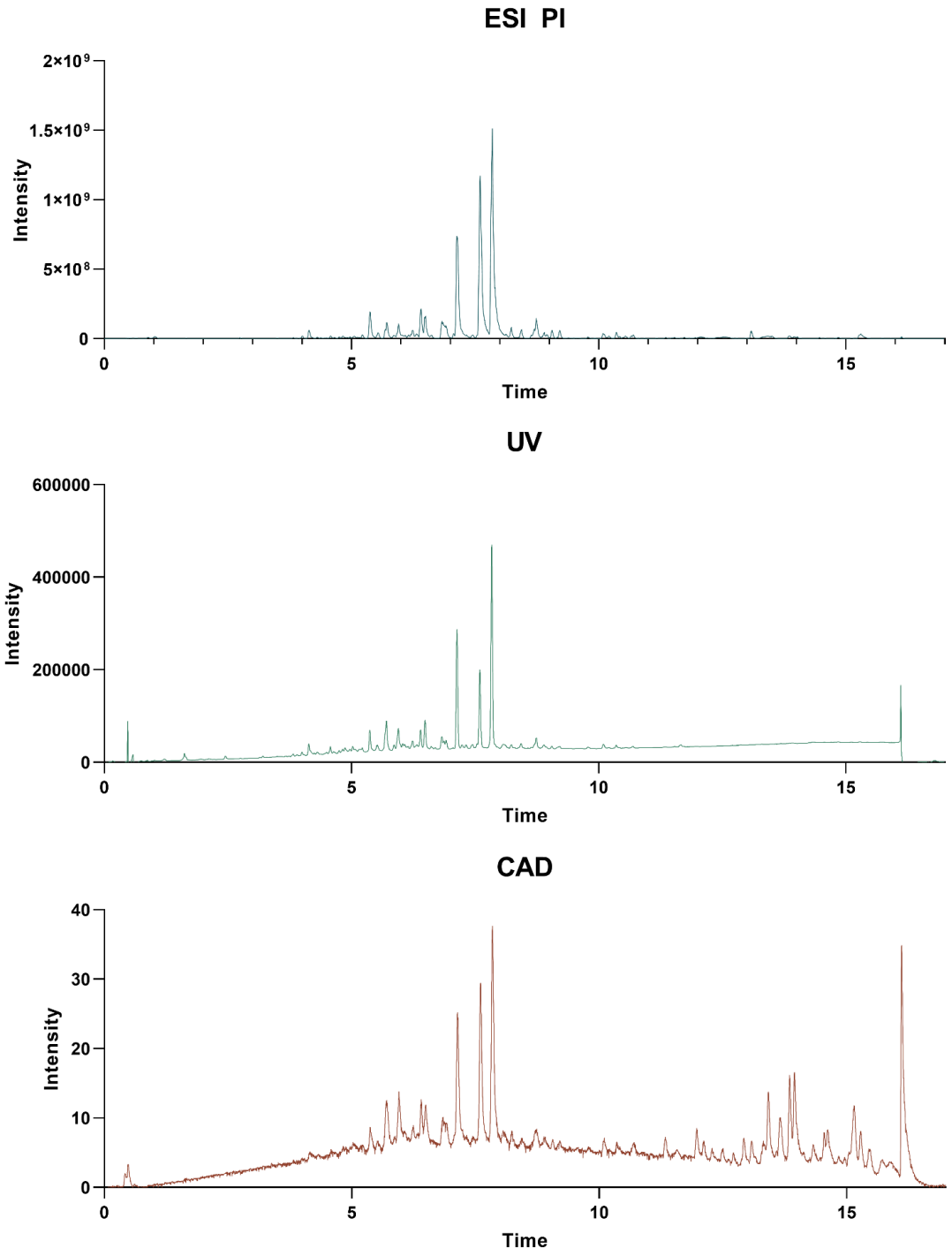


Figure S1: UHPLC-MS-PDA-CAD profile of *Cnestis palala* branches EtOAc extract.

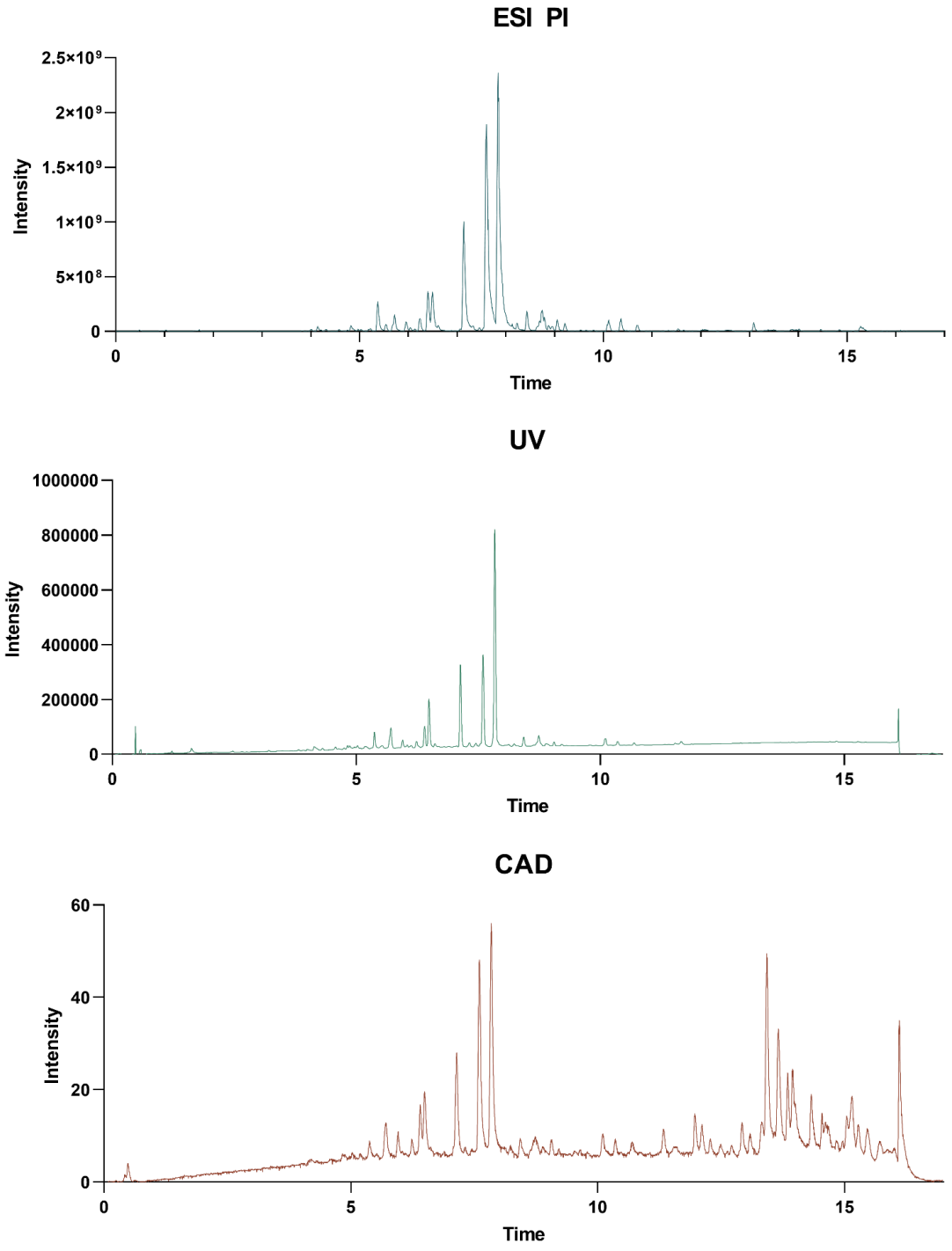


Figure S2: UHPLC-MS-PDA-CAD profile of *Cnestis palala* roots EtOAc extract.

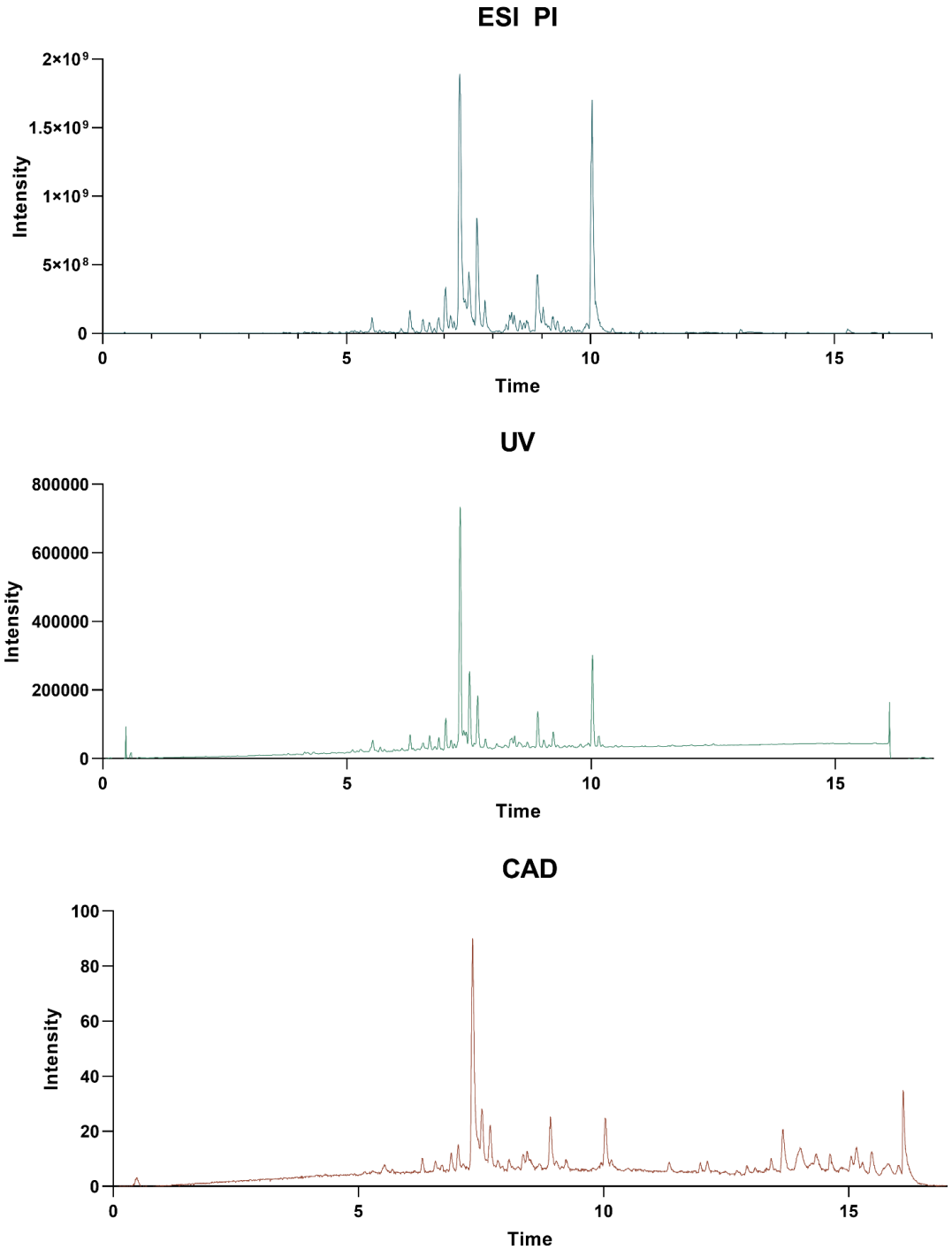


Figure S3: UHPLC-MS-PDA-CAD profile of *Chadsia grevei* roots bark EtOAc extract.

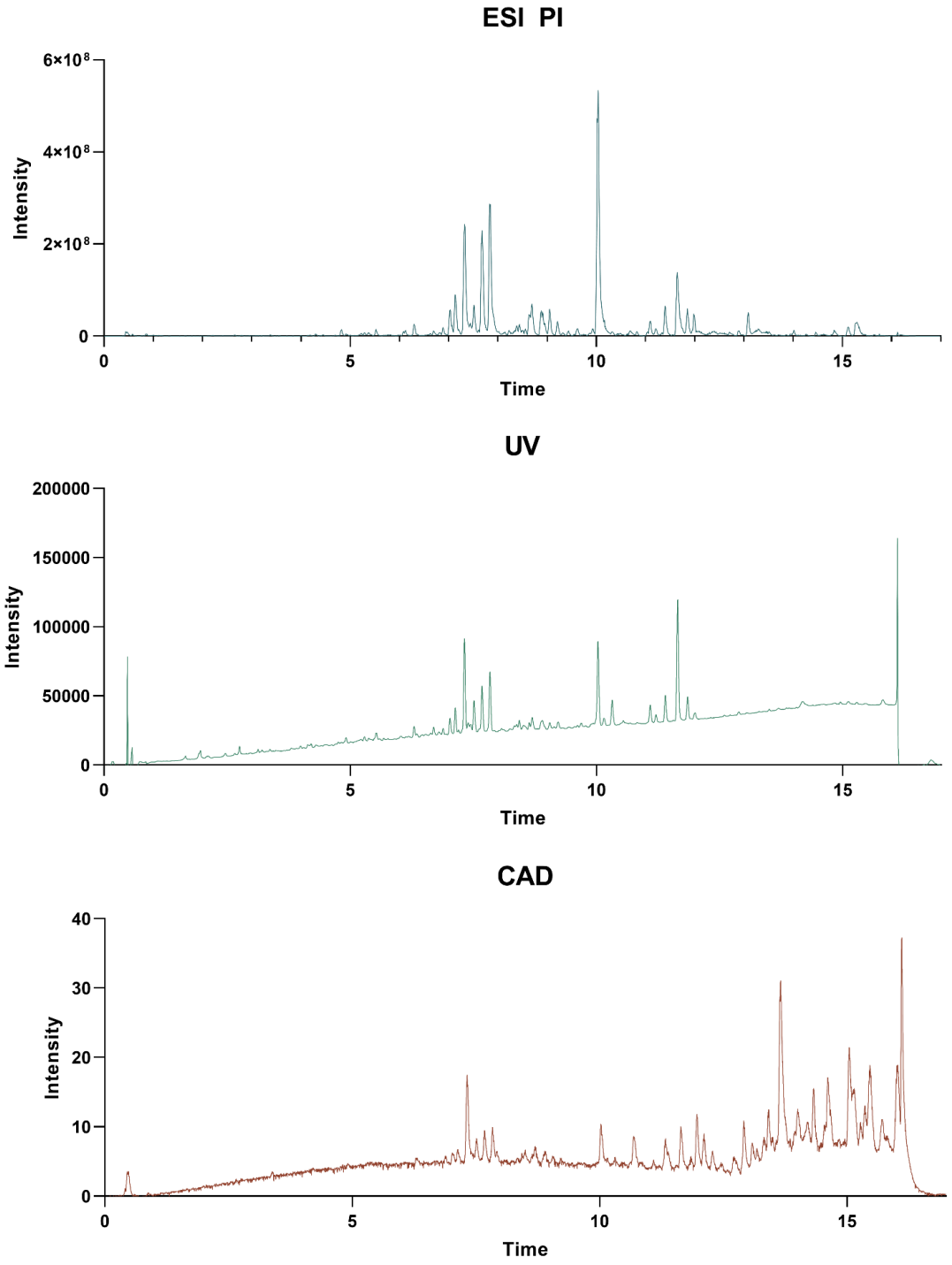


Figure S4: UHPLC-MS-PDA-CAD profile of *Chadsia grevei* trunk bark EtOAc extract.

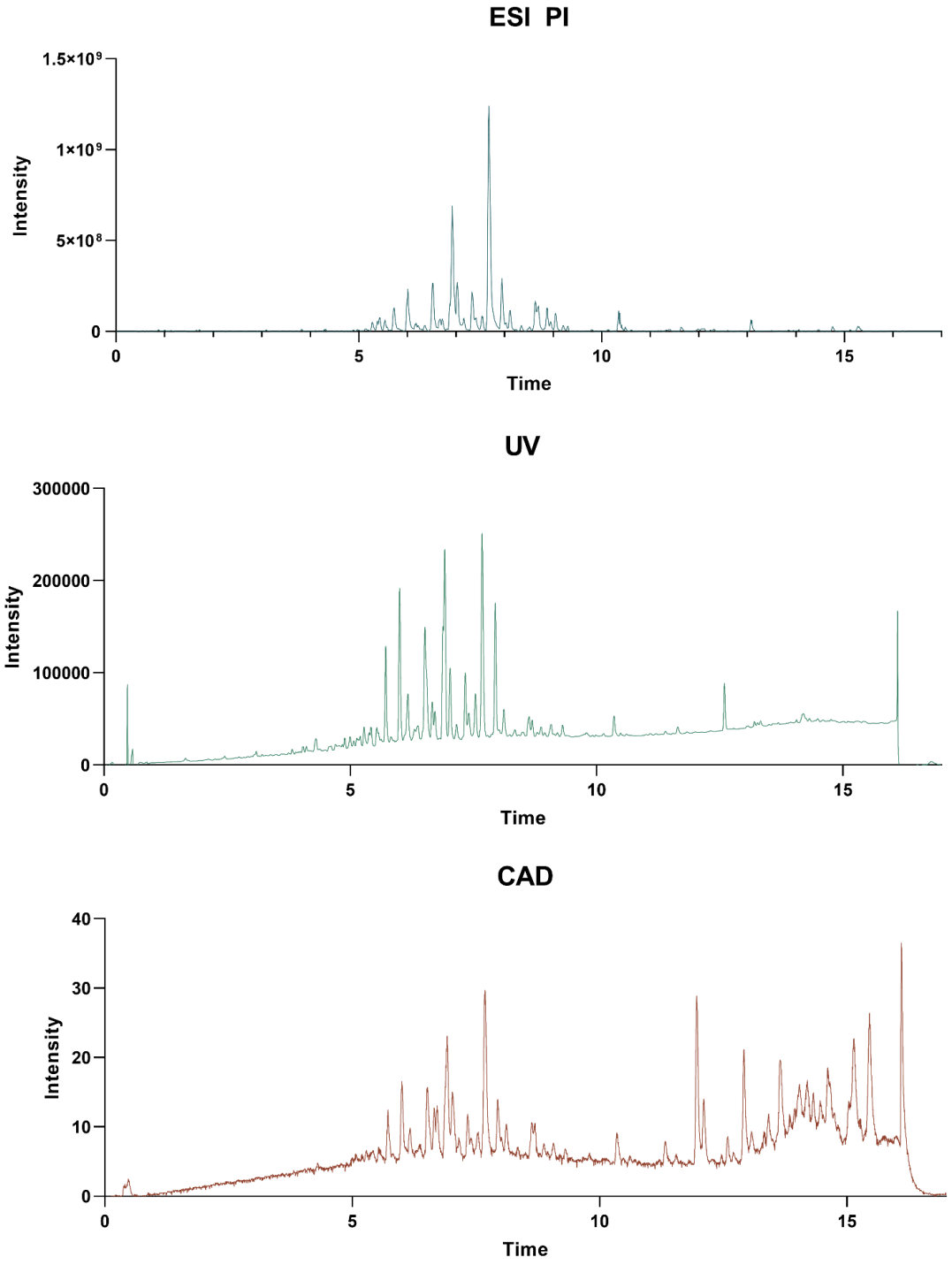


Figure S5: UHPLC-MS-PDA-CAD profile of *Pachyrhizus erosus* leaves EtOAc extract.

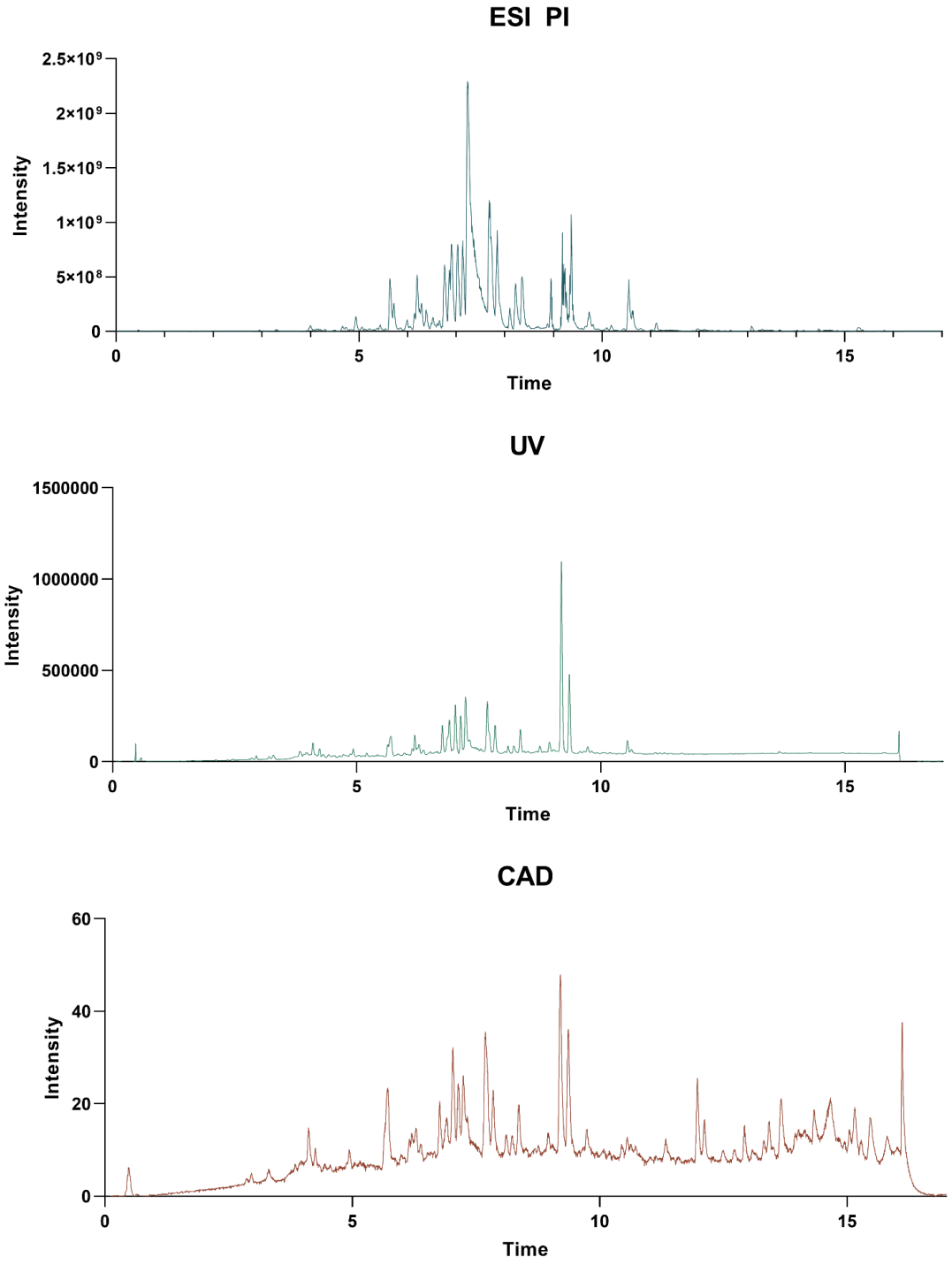


Figure S6: UHPLC-MS-PDA-CAD profile of *Desmodium heterophyllum* underground parts EtOAc extract.

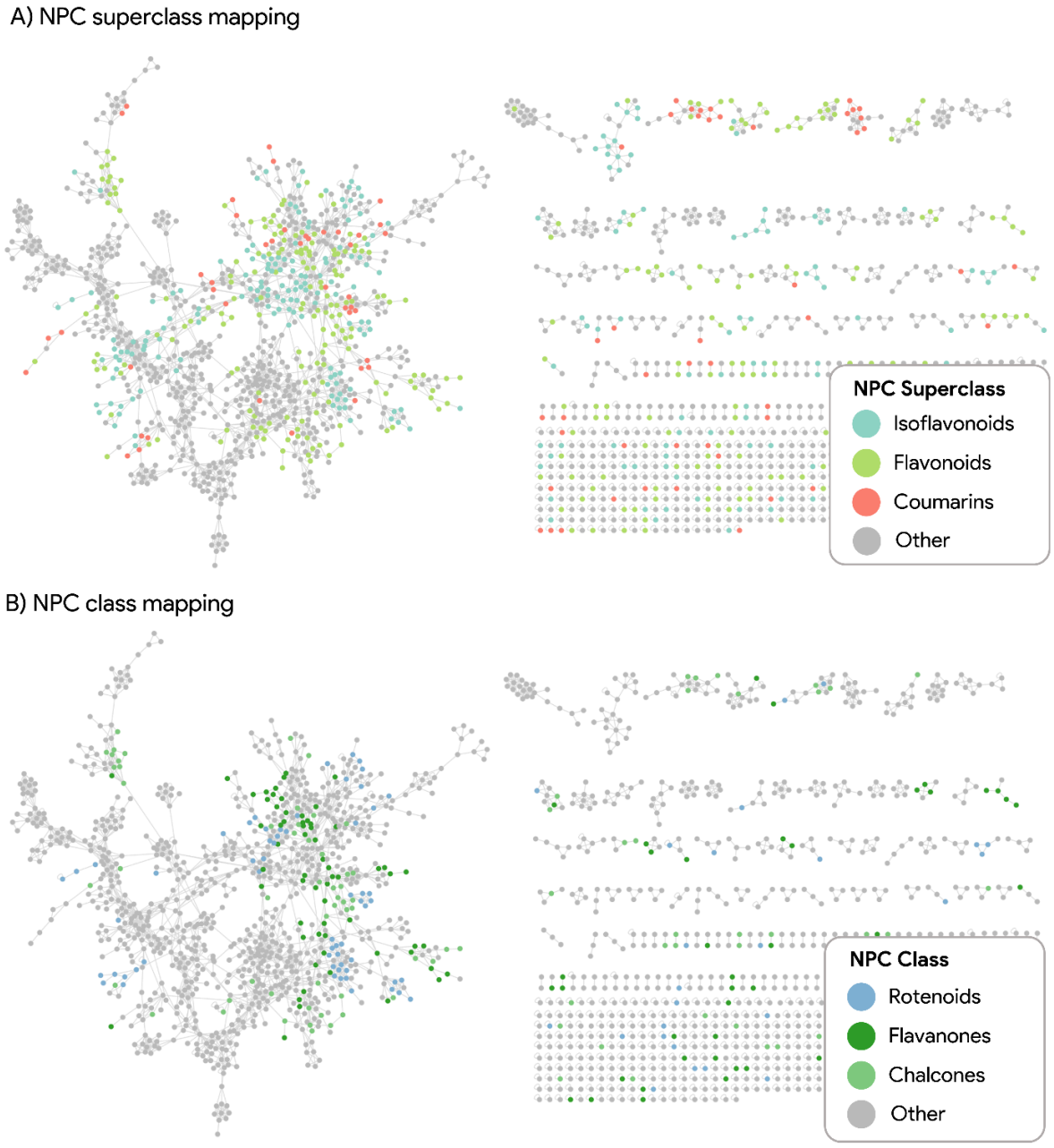
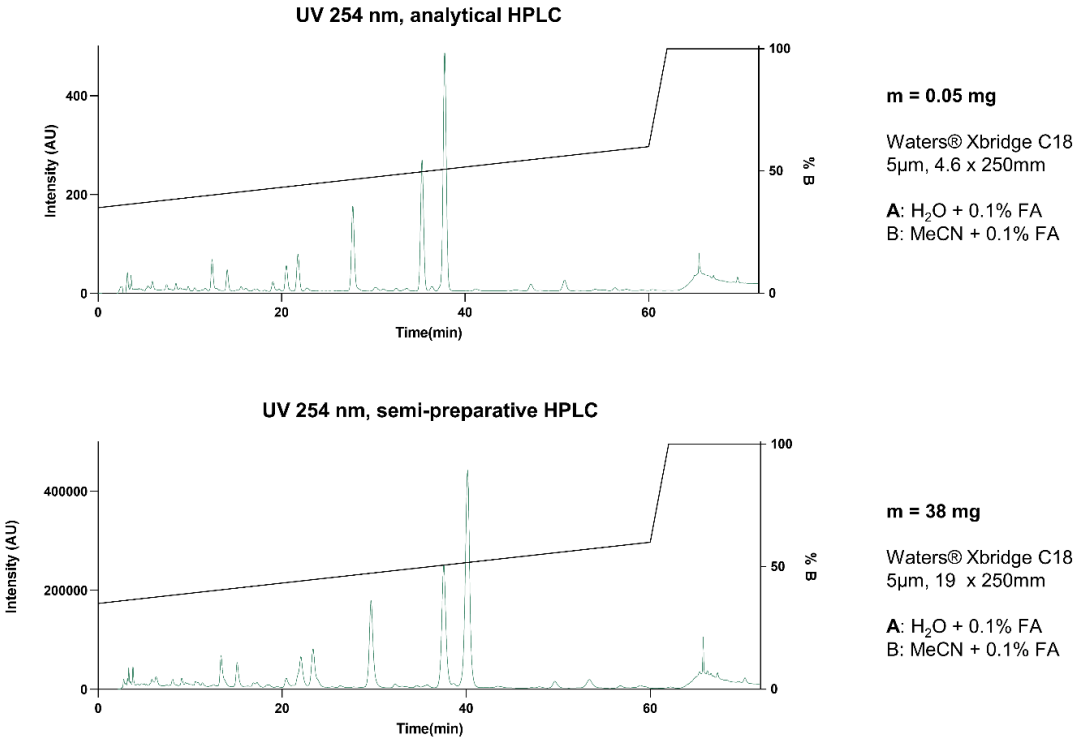


Figure S7: IIN MN of the six active extracts with mapping of the three main chemical NPClassifier superclasses (A) and classes (B).

Semi-Preparative HPLC chromatograms

A) *Cnestis palala* roots



B) *Chadsia grevei* roots bark

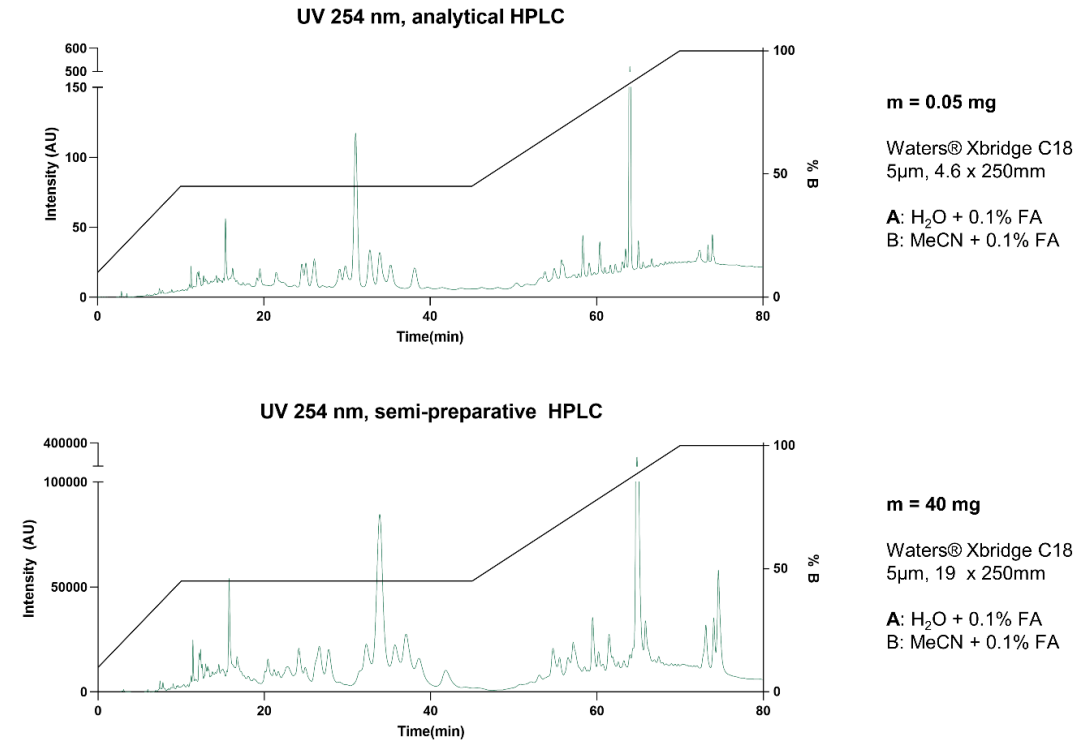
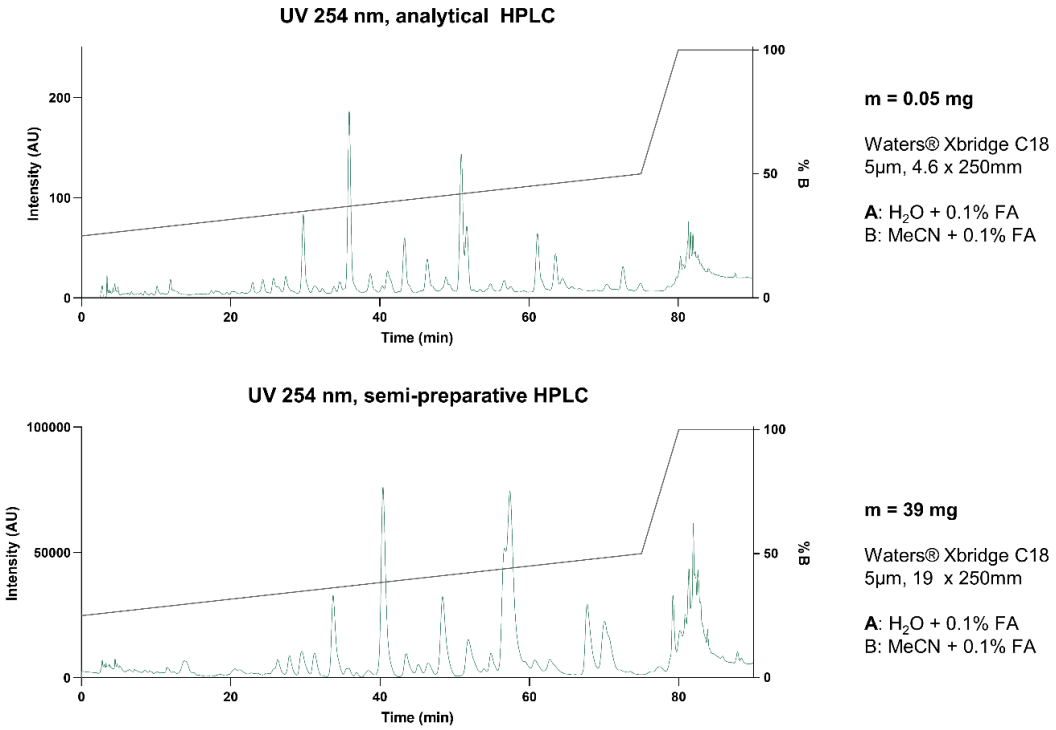


Figure S8: HPLC chromatograms (analytical and semi-preparative scale) of *Cnestis palala* roots (A) and *Chadsia grevei* roots bark (B) extracts. *m = amount of extract injected*.

A) *Pachyrhizus erosus leaves*



B) *Desmodium heterophyllum* underground parts

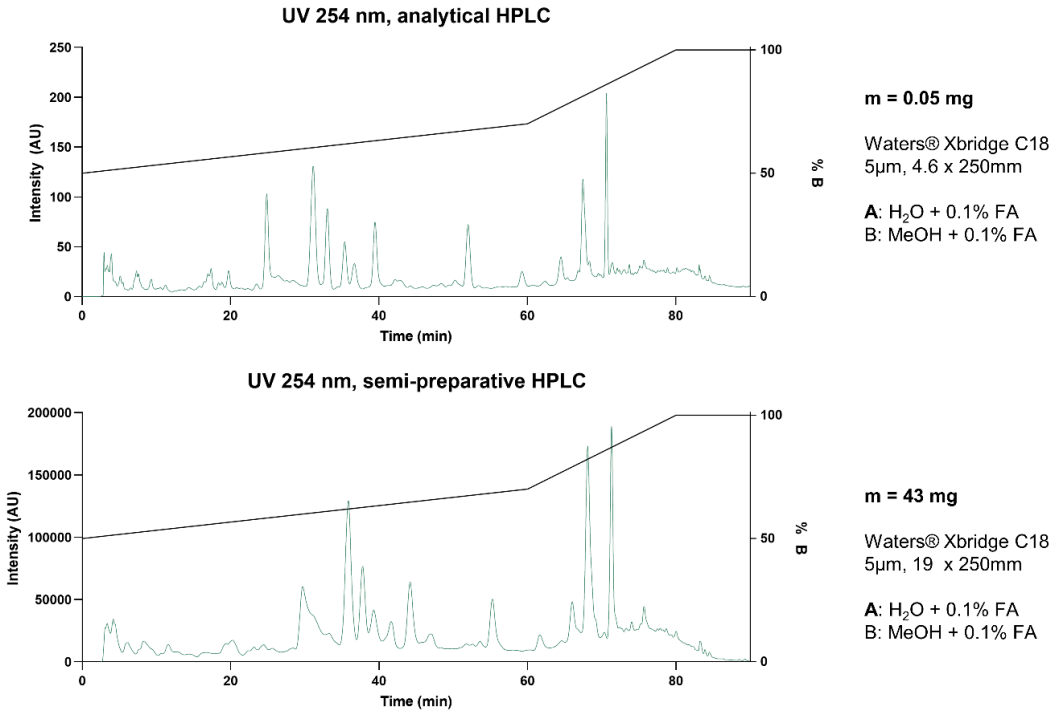


Figure S9: HPLC chromatograms (analytical and semi-preparative scale) of *Pachyrhizus erosus* leaves(A) and *Desmodium heterophyllum* underground parts (B) extracts. *m = amount of extract injected*.

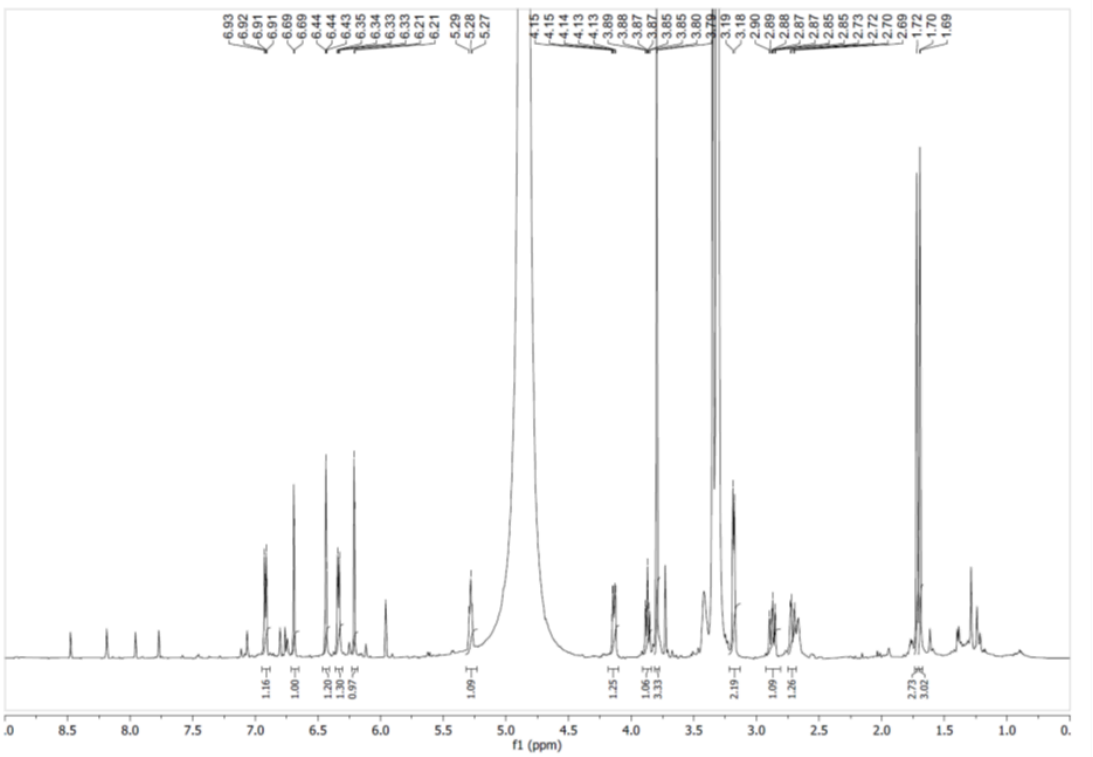


Figure S10: 1H NMR spectrum of compound **1** in CD3OD at 600 MHz

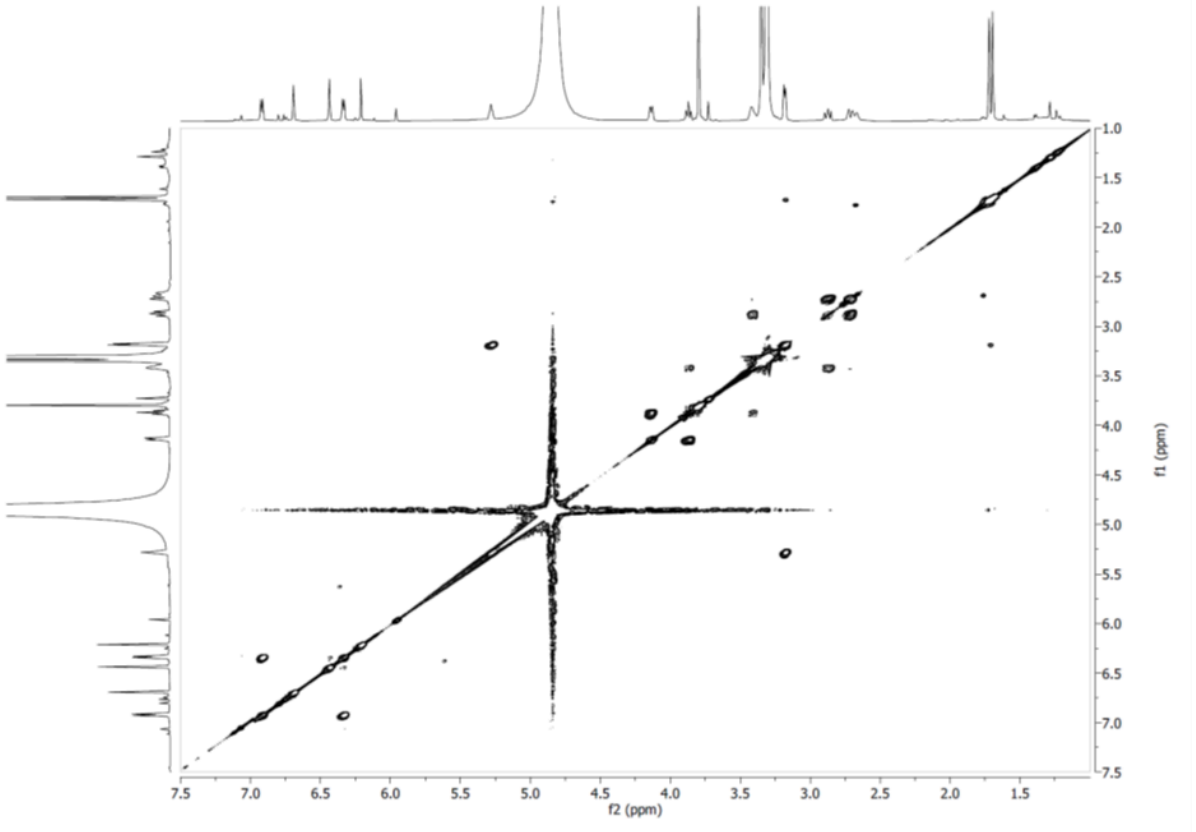


Figure S11: COSY NMR spectrum of compound **1** in CD_3OD

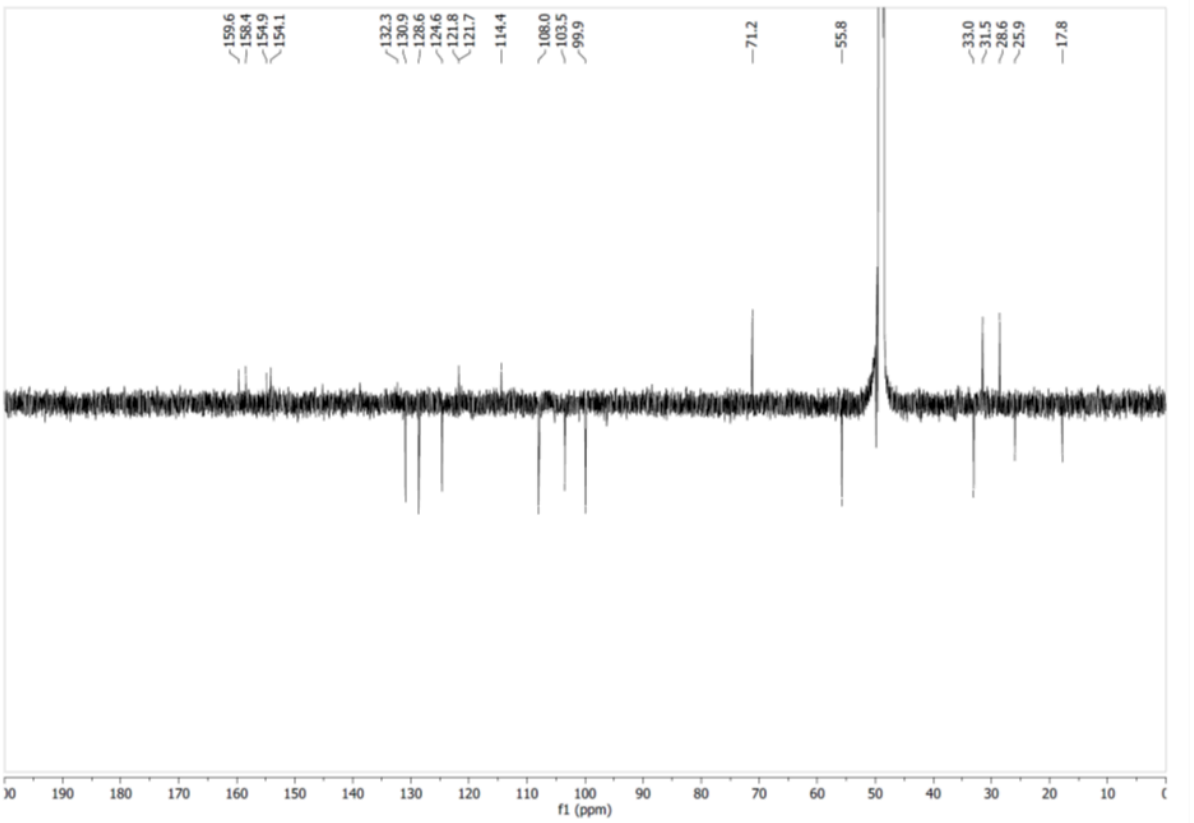


Figure S12: ^{13}C-DEPTQ NMR spectrum of compound **1** in CD_3OD at 151 MHz

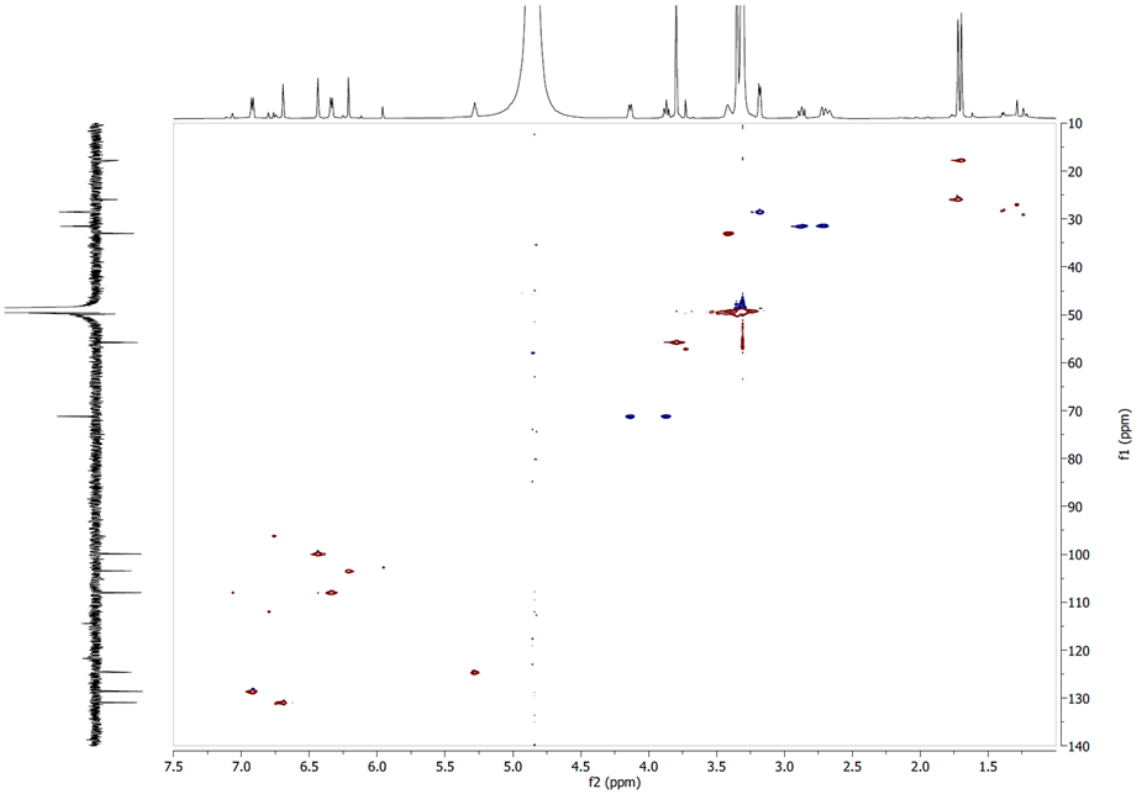


Figure S13: Edited HSQC NMR spectrum of compound **1** in CD_3OD

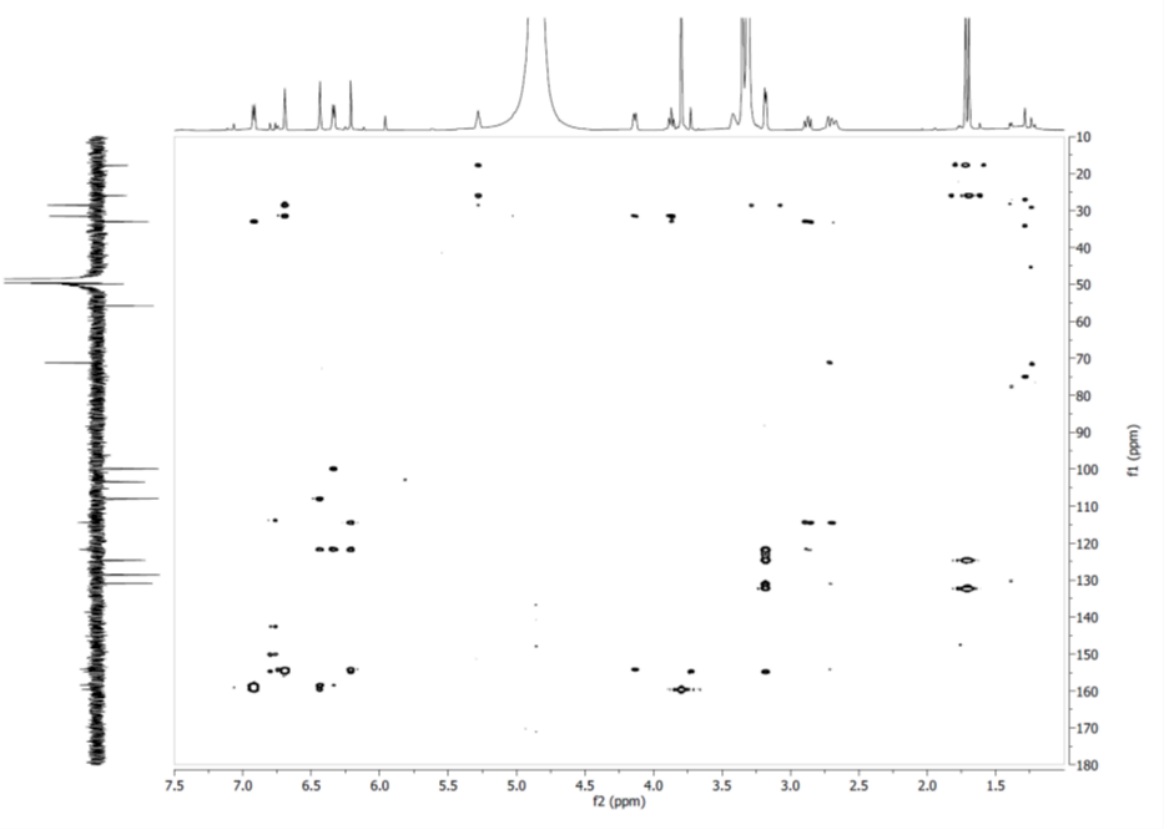


Figure S14: HMBC NMR spectrum of compound **1** in CD_3OD

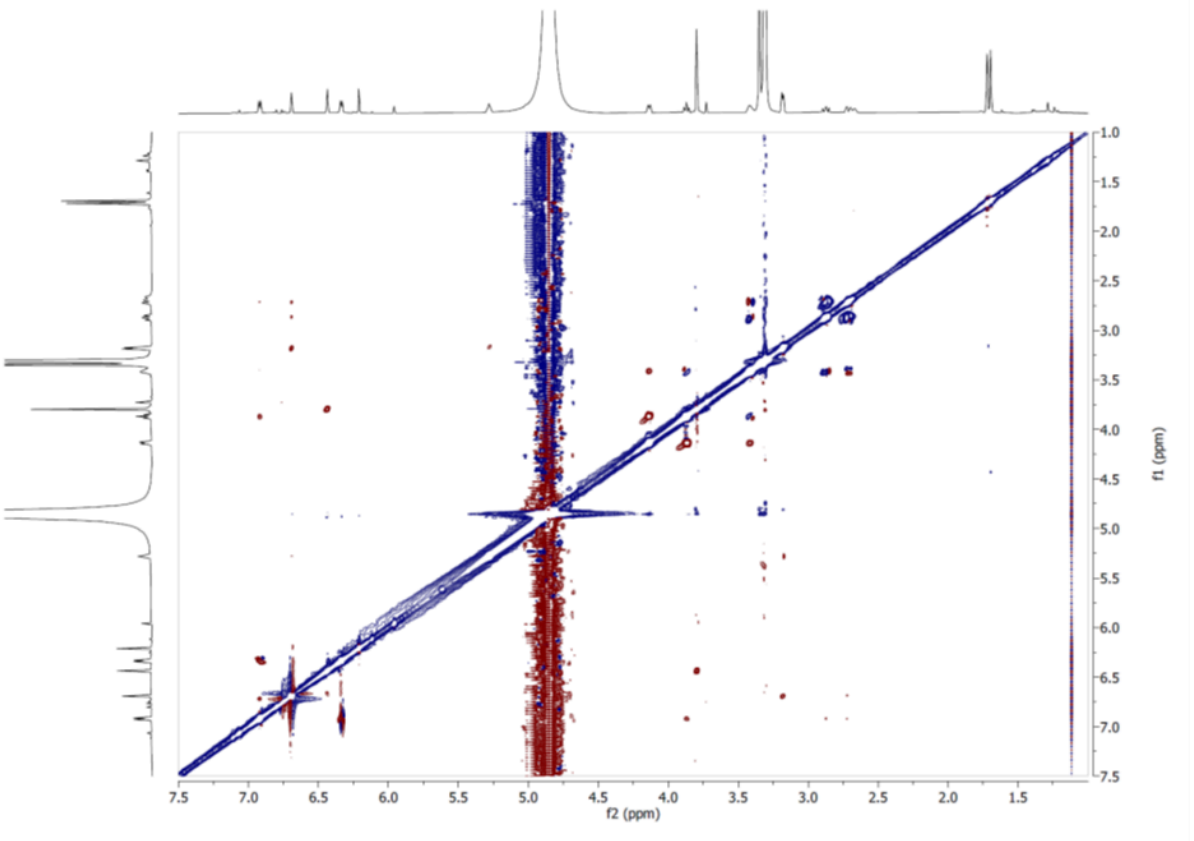


Figure S15: ROESY NMR spectrum of compound **1** in CD_3OD

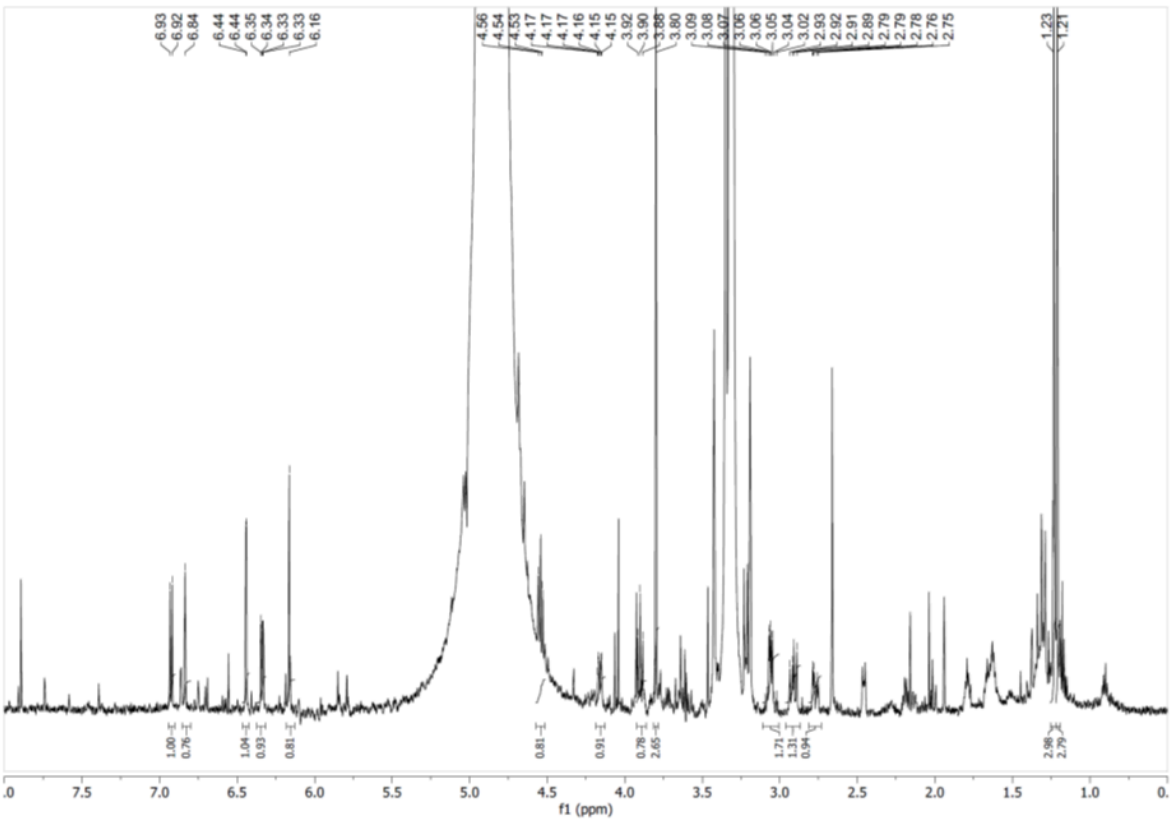


Figure S16: ^{1}H NMR spectrum of compound **6** in CD_3OD at 600 MHz

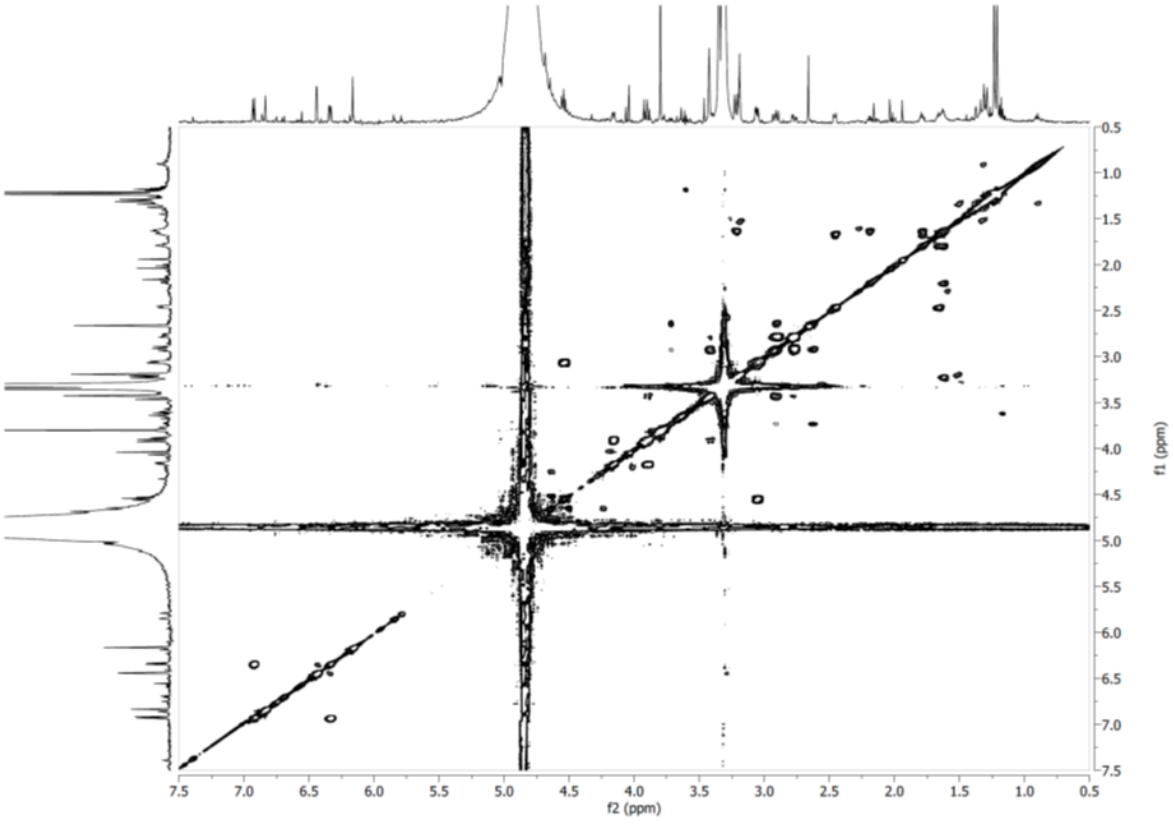


Figure S17: COSY NMR spectrum of compound **6** in CD_3OD

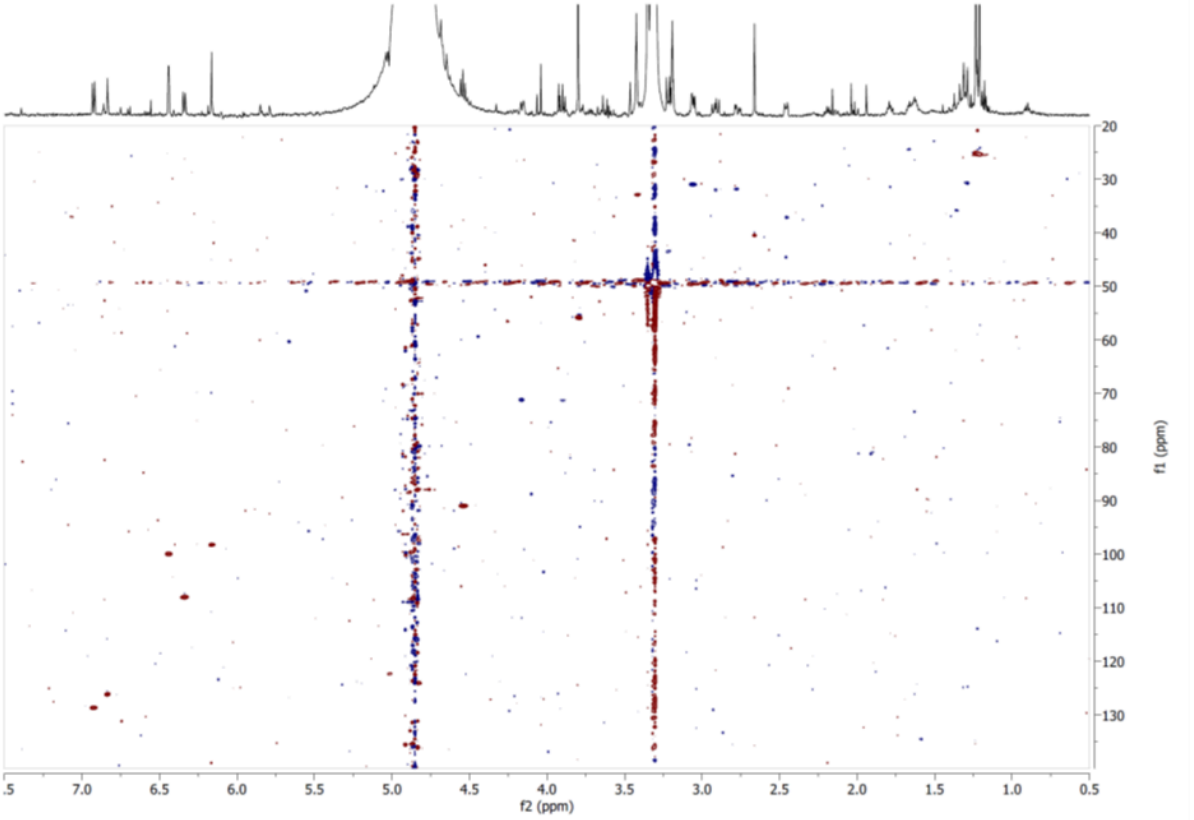


Figure S18: Edited HSQC NMR spectrum of compound **6** in CD_3OD

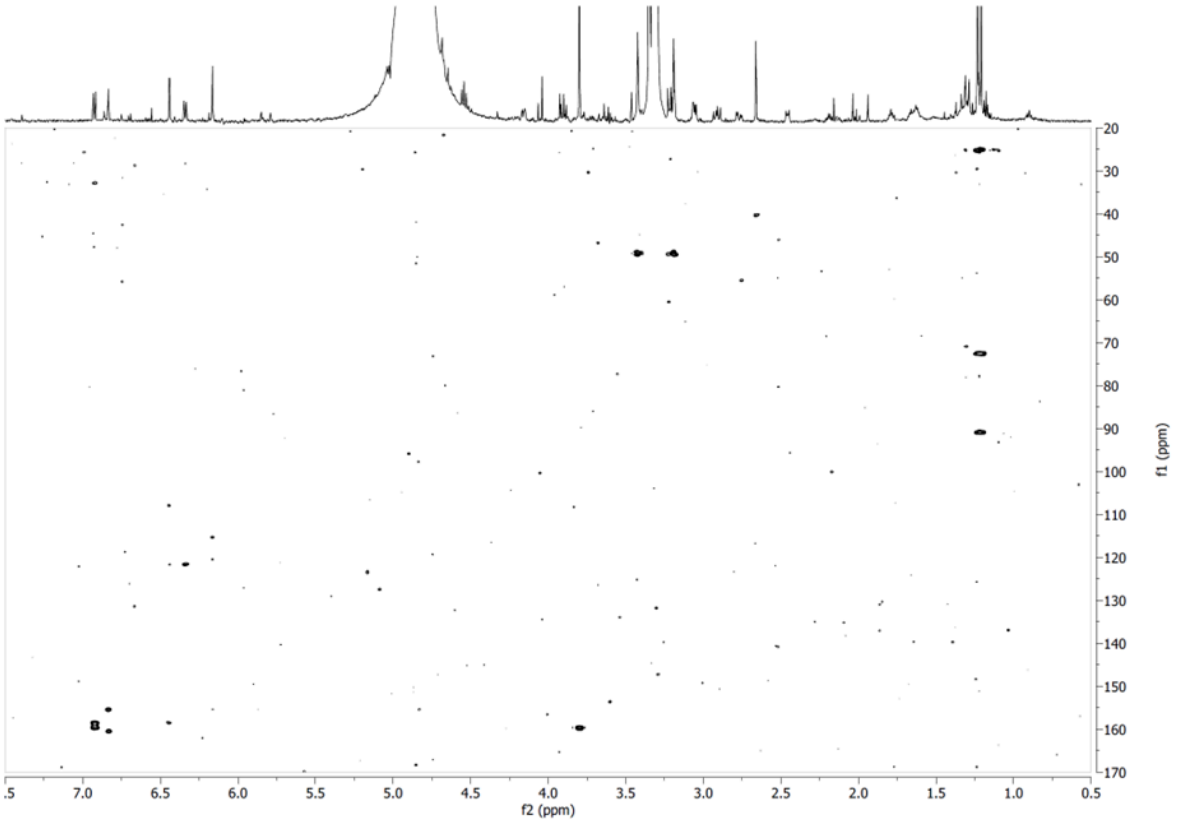


Figure S19: HMBC NMR spectrum of compound **6** in CD_3OD

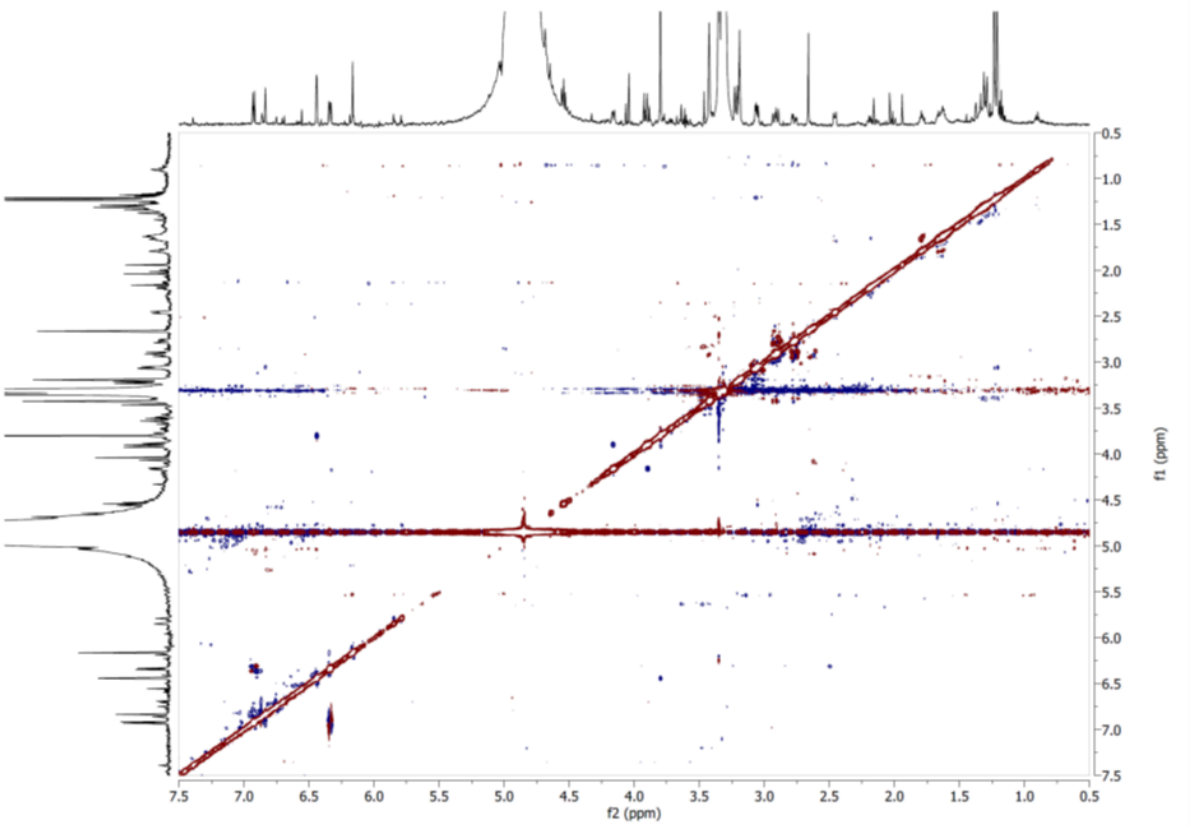


Figure S20: ROESY NMR spectrum of compound **6** in CD_3OD

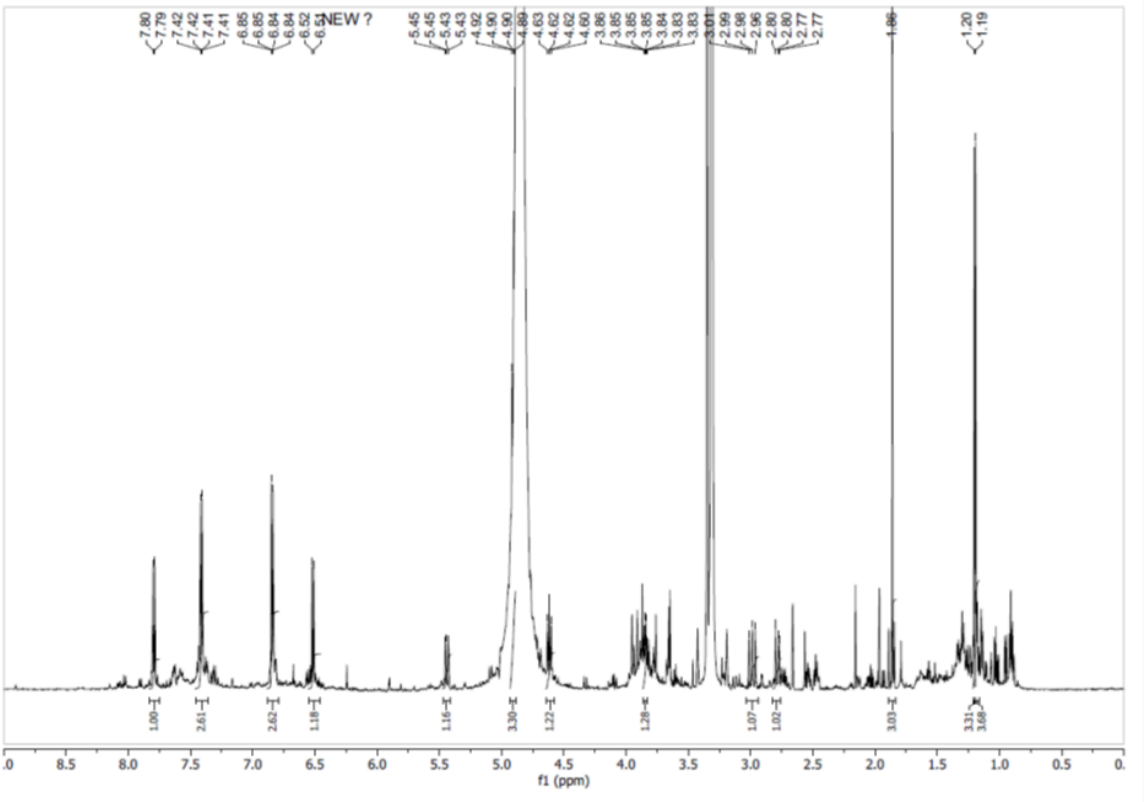


Figure S21: ^1H NMR spectrum of compound **12** in CD_3OD at 600 MHz

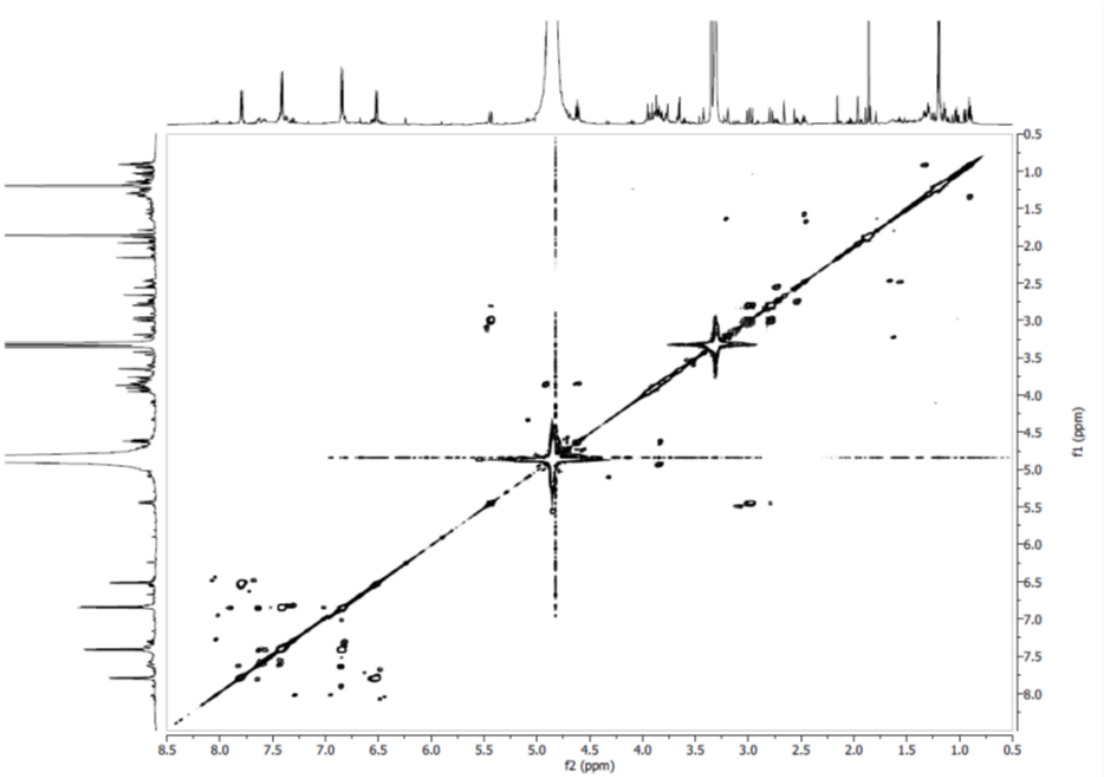


Figure S22: COSY NMR spectrum of compound **12** in CD_3OD

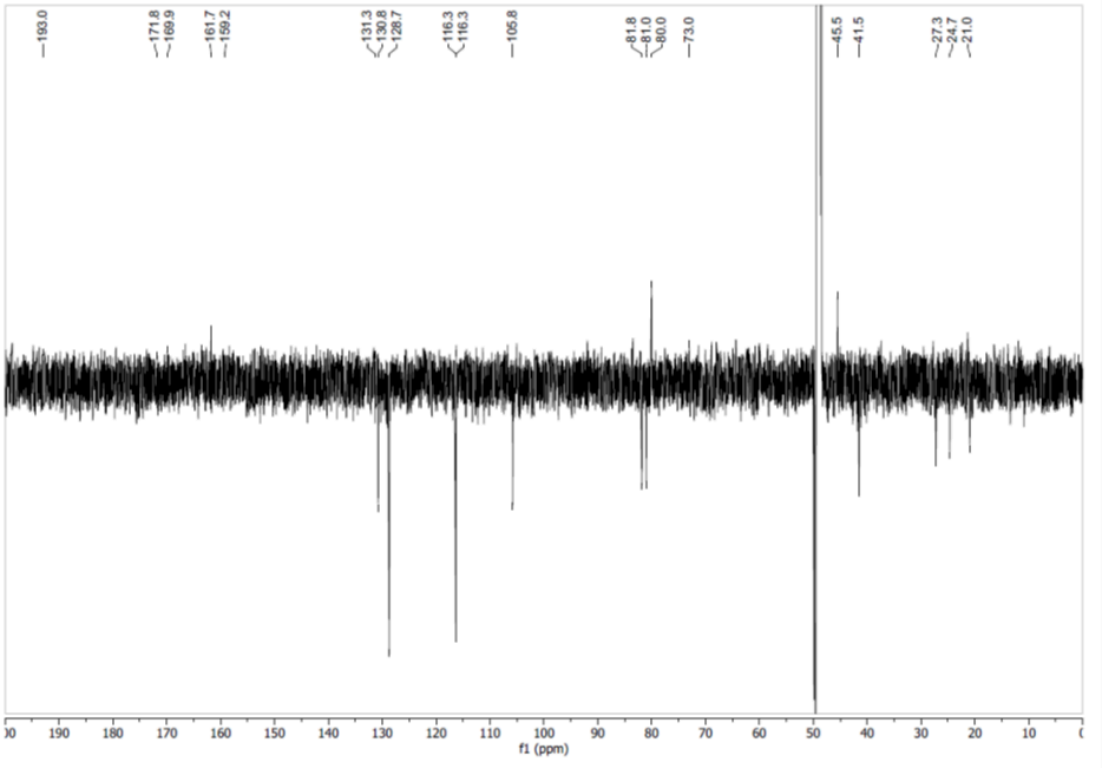


Figure S23: ^{13}C-DEPTQ NMR spectrum of compound **12** in CD_3OD at 151 MHz

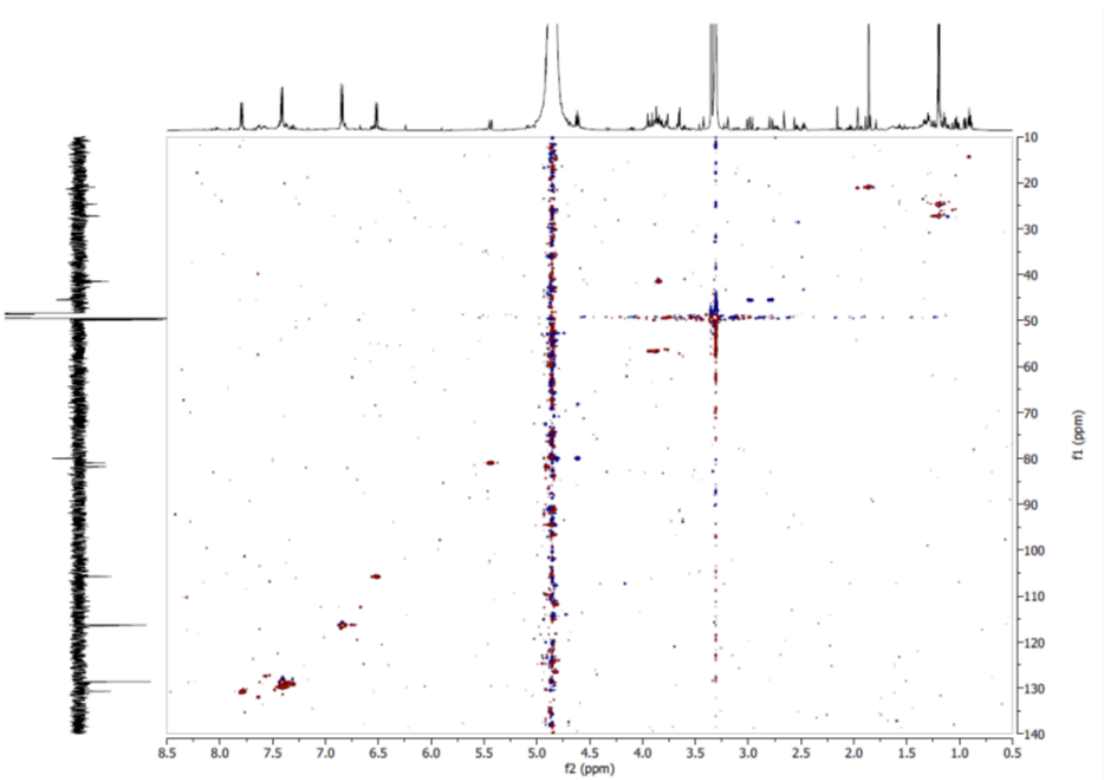


Figure S23: Edited HSQC NMR spectrum of compound **12** in CD_3OD

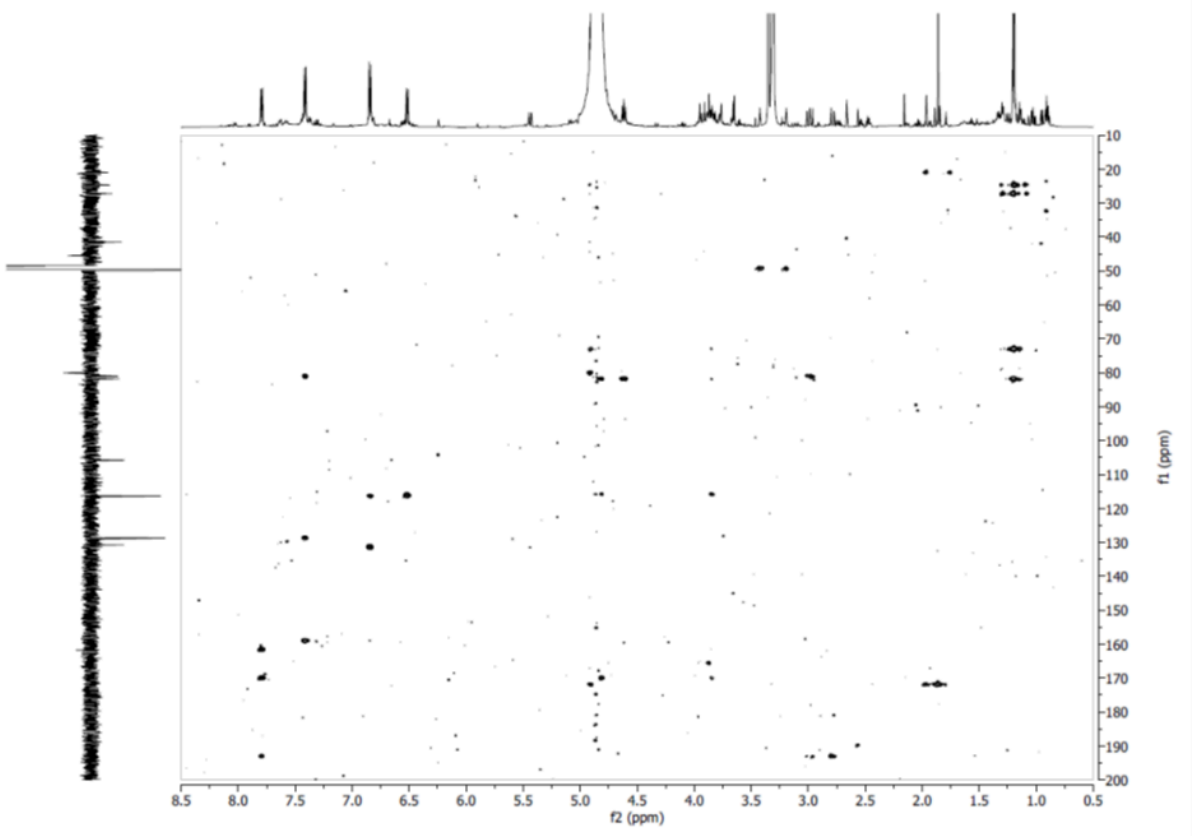


Figure S24: HMBC NMR spectrum of compound **12** in CD_3OD

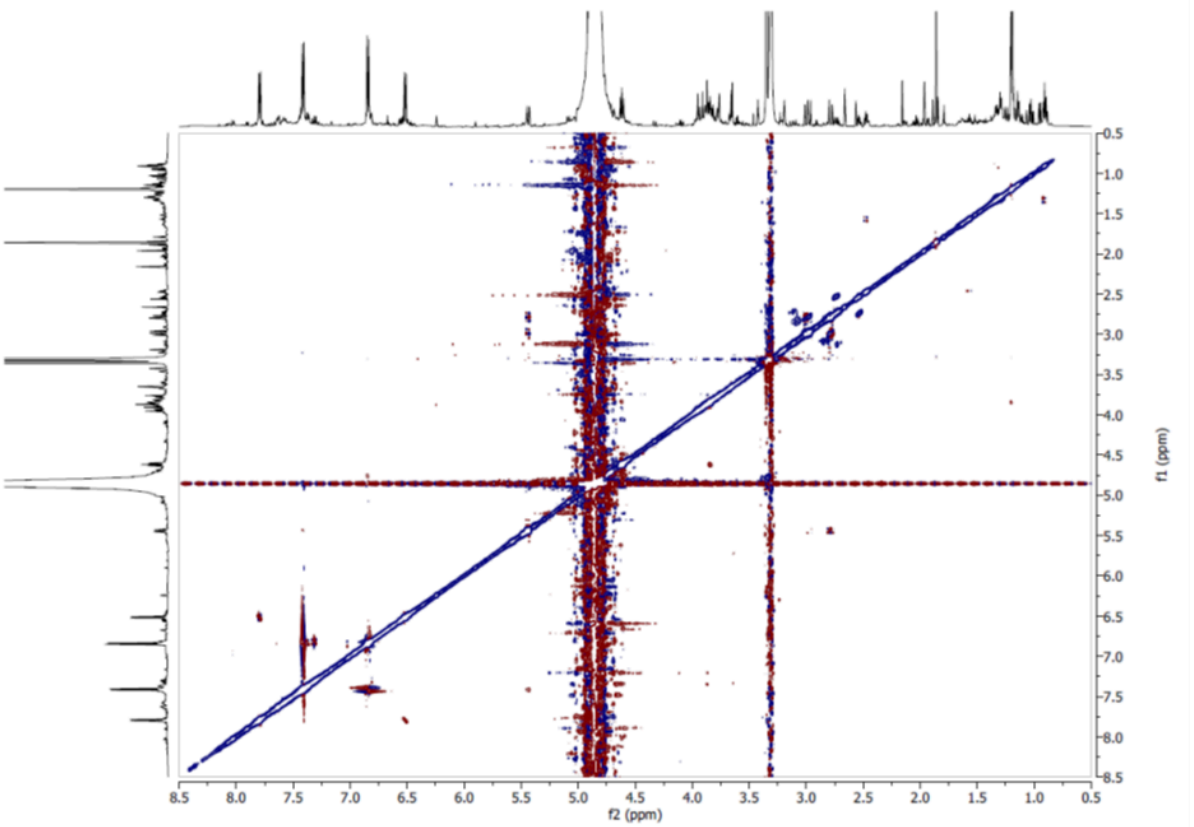


Figure S25: ROESY NMR spectrum of compound **12** in CD_3OD

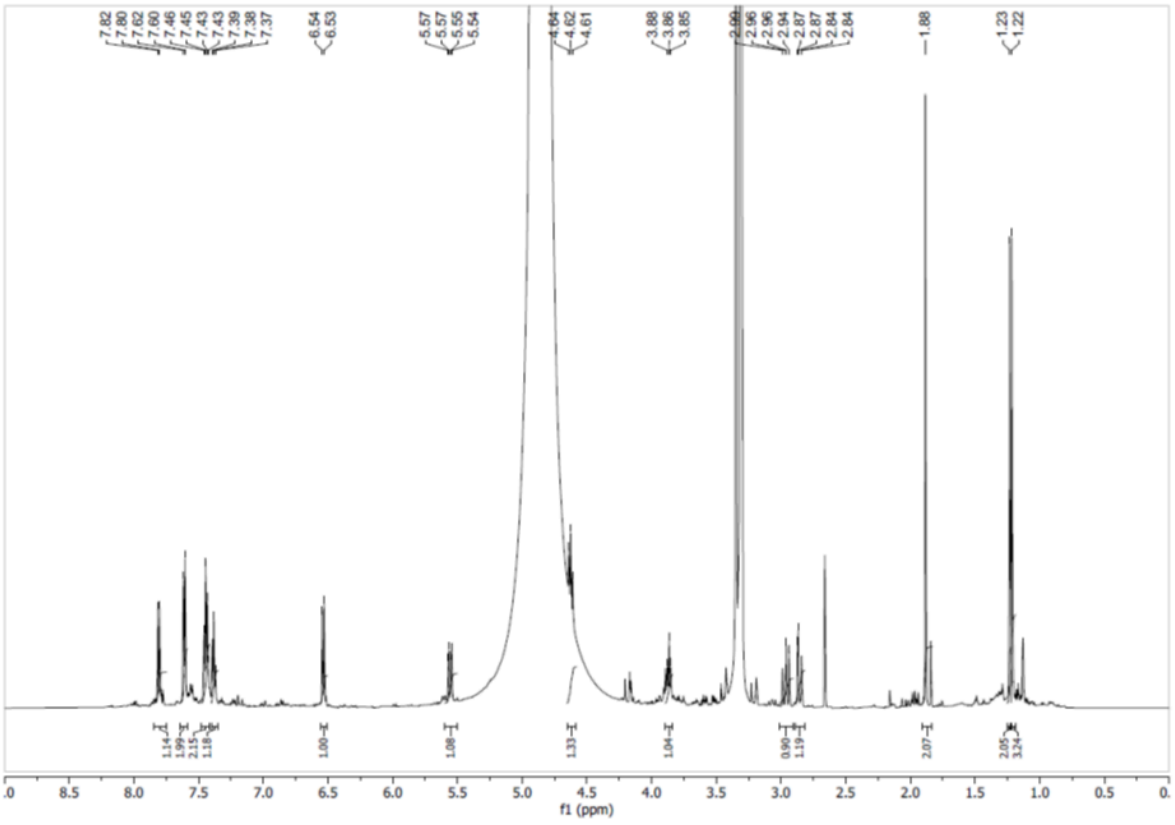


Figure S26: ^1H NMR spectrum of compound **13** in CD_3OD at 600 MHz

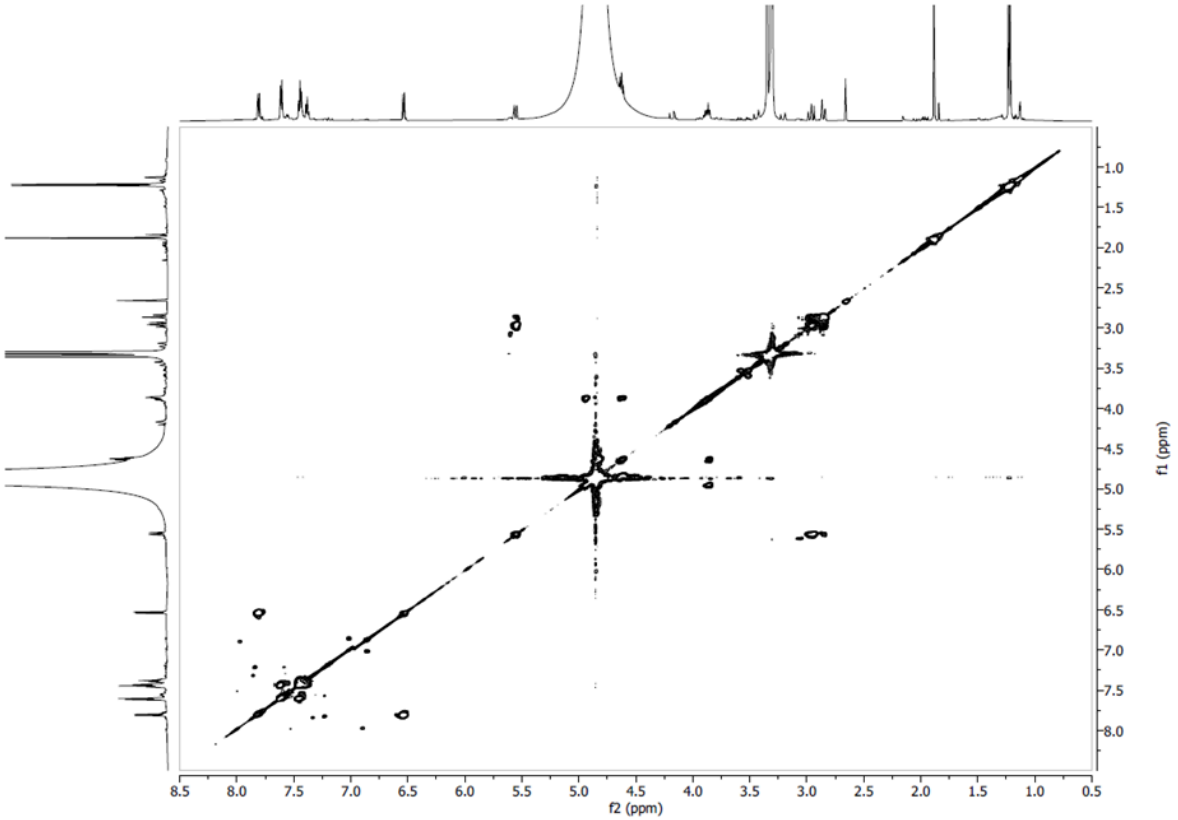


Figure S27: COSY NMR spectrum of compound **13** in CD_3OD

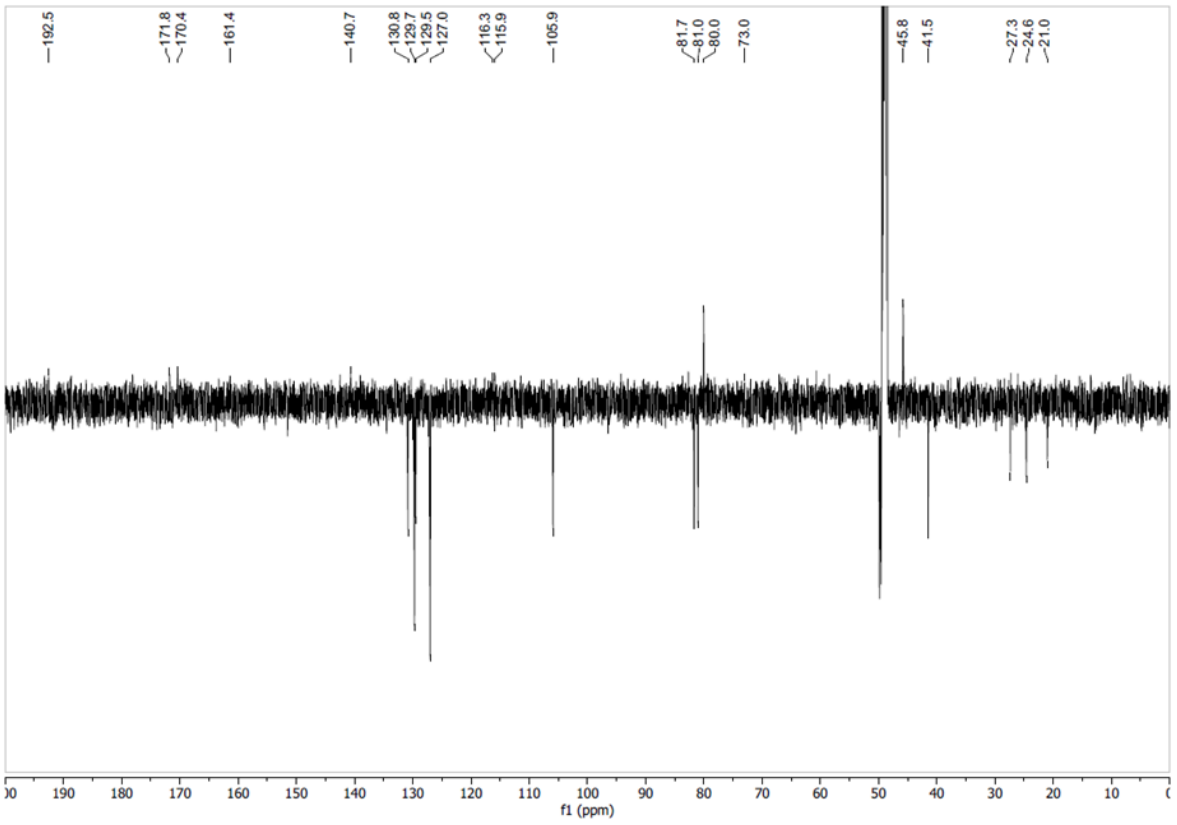


Figure S27: ^{13}C-DEPTQ NMR spectrum of compound **13** in CD_3OD at 151 MHz

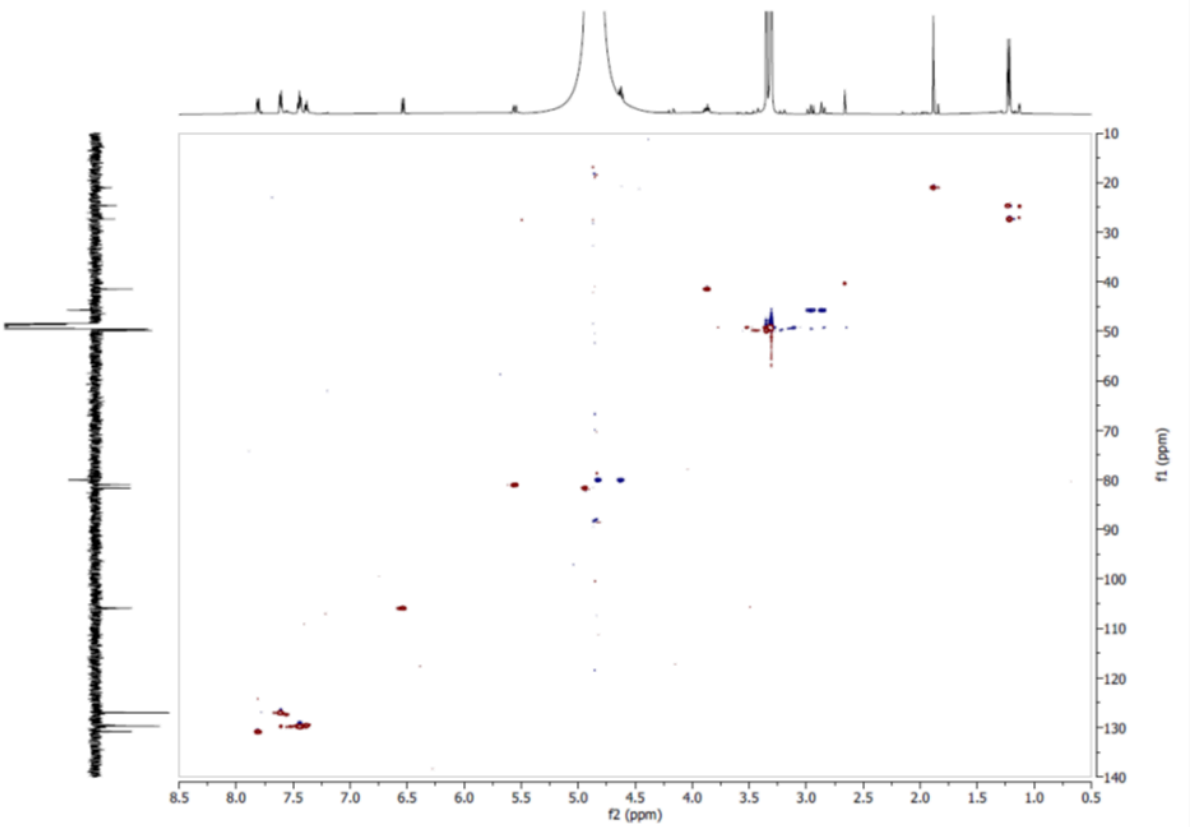


Figure S28: Edited HSQC NMR spectrum of compound **13** in CD_3OD

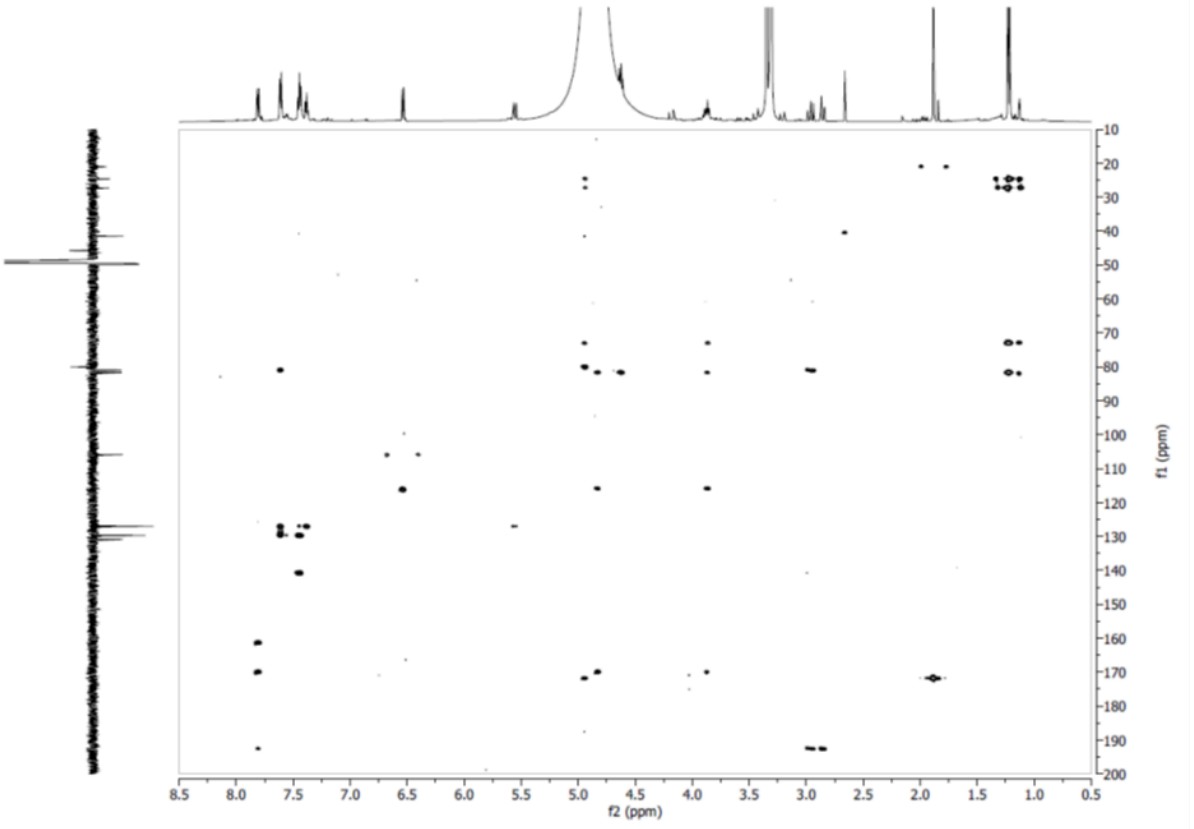


Figure S29: HMBC NMR spectrum of compound **13** in CD_3OD

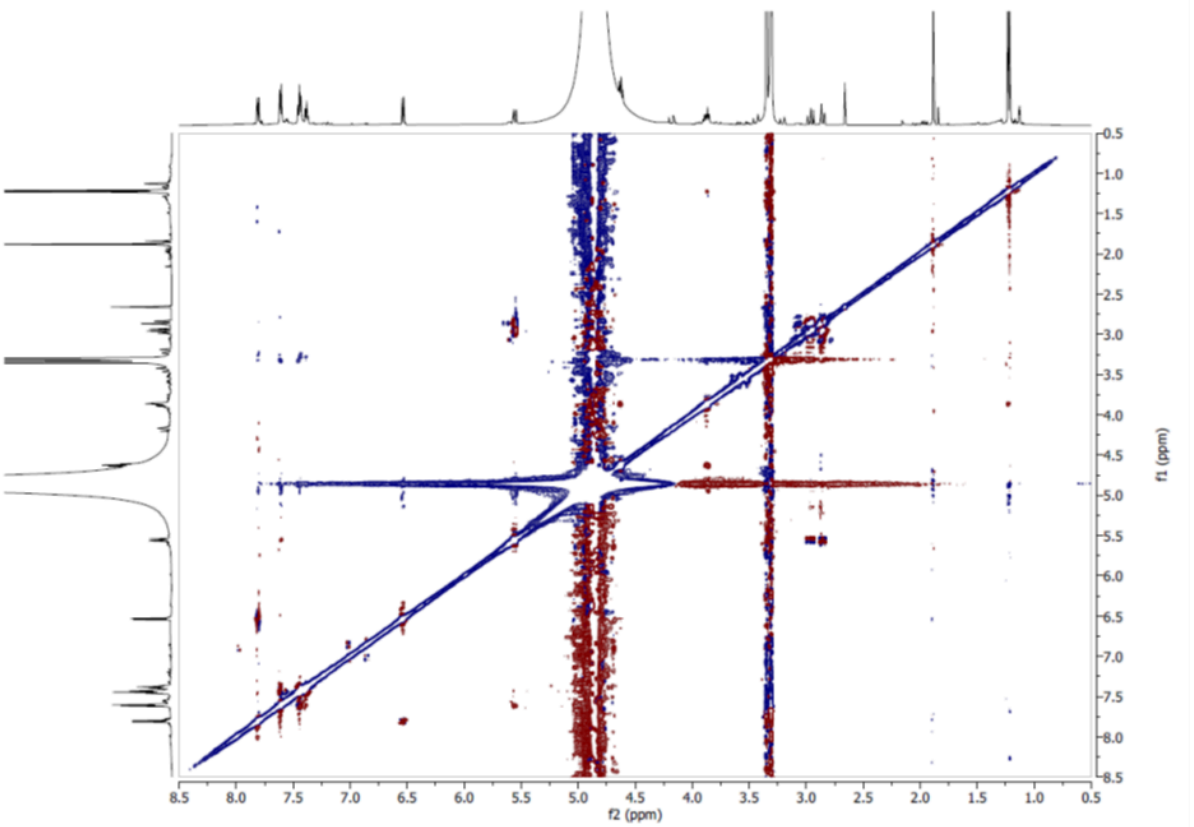


Figure S30: ROESY NMR spectrum of compound **13** in CD_3OD

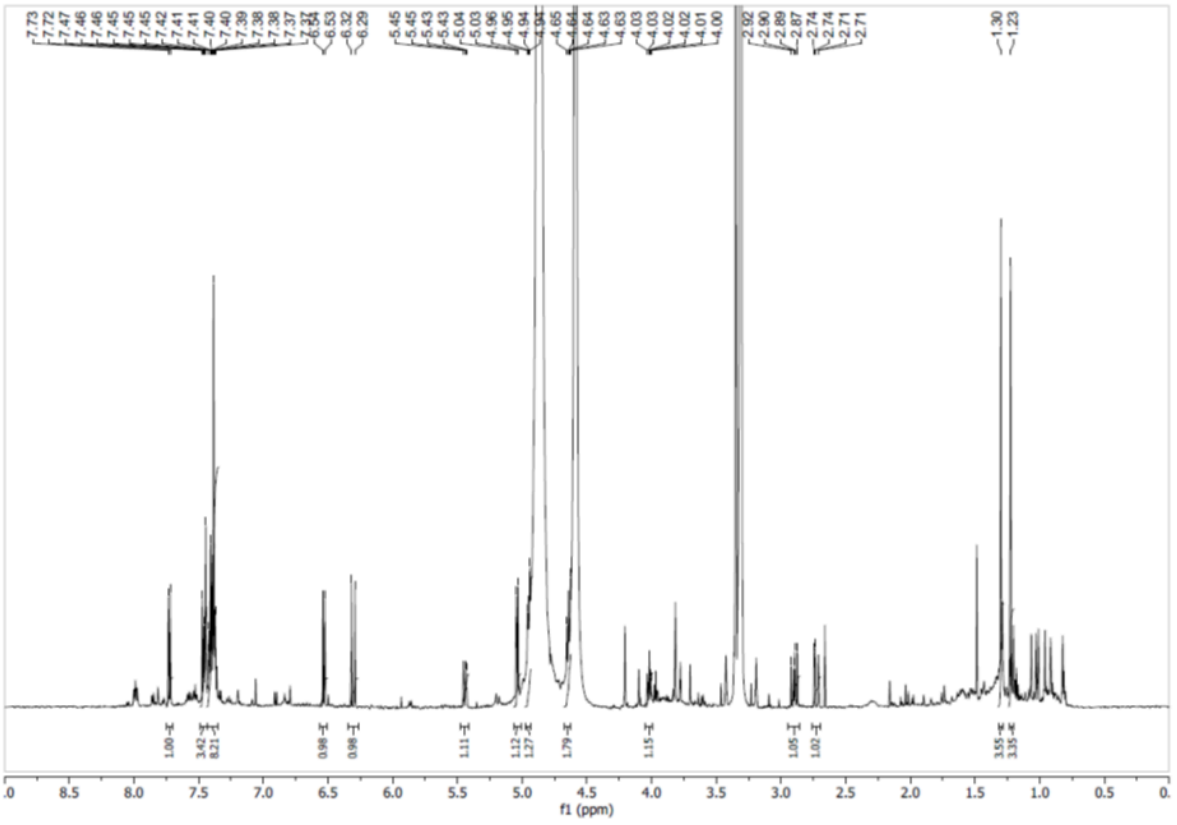


Figure S31: ^1H NMR spectrum of compound **14** in CD_3OD at 600 MHz

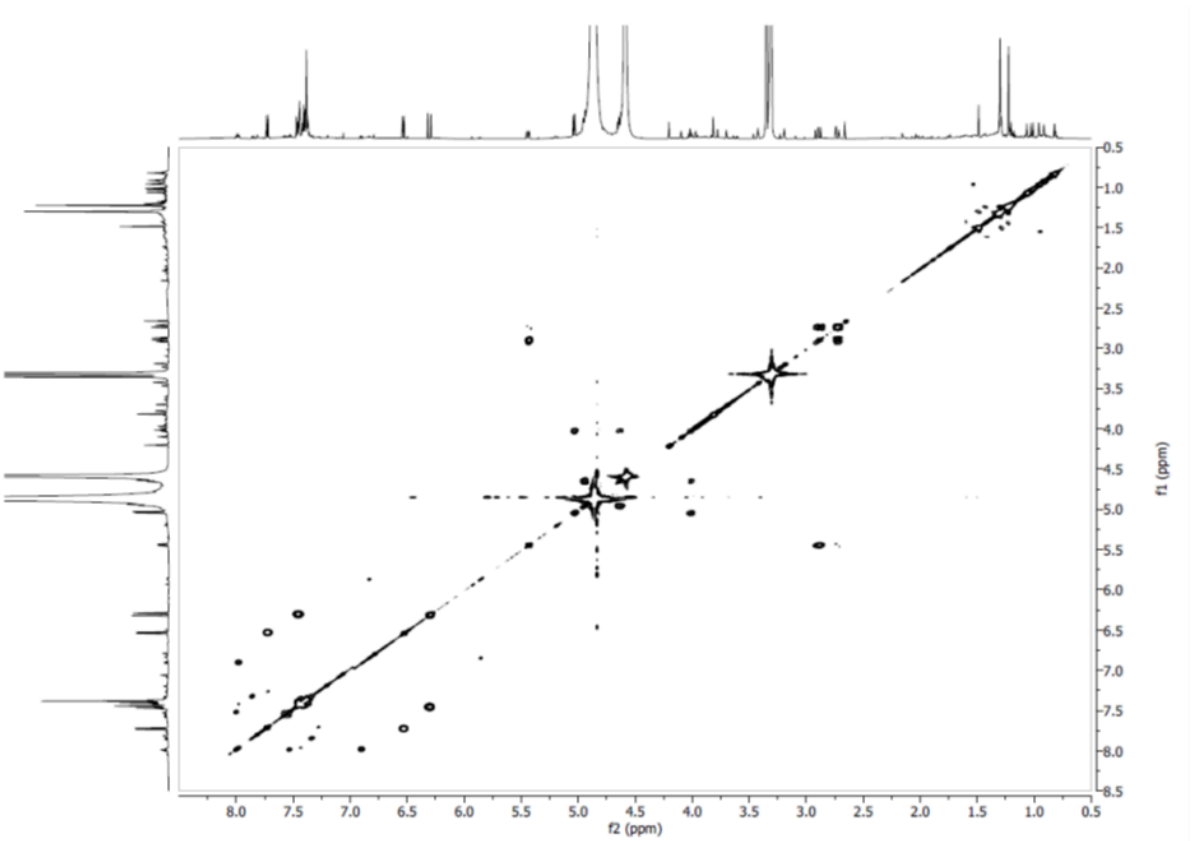


Figure S32: COSY NMR spectrum of compound **14** in CD_3OD

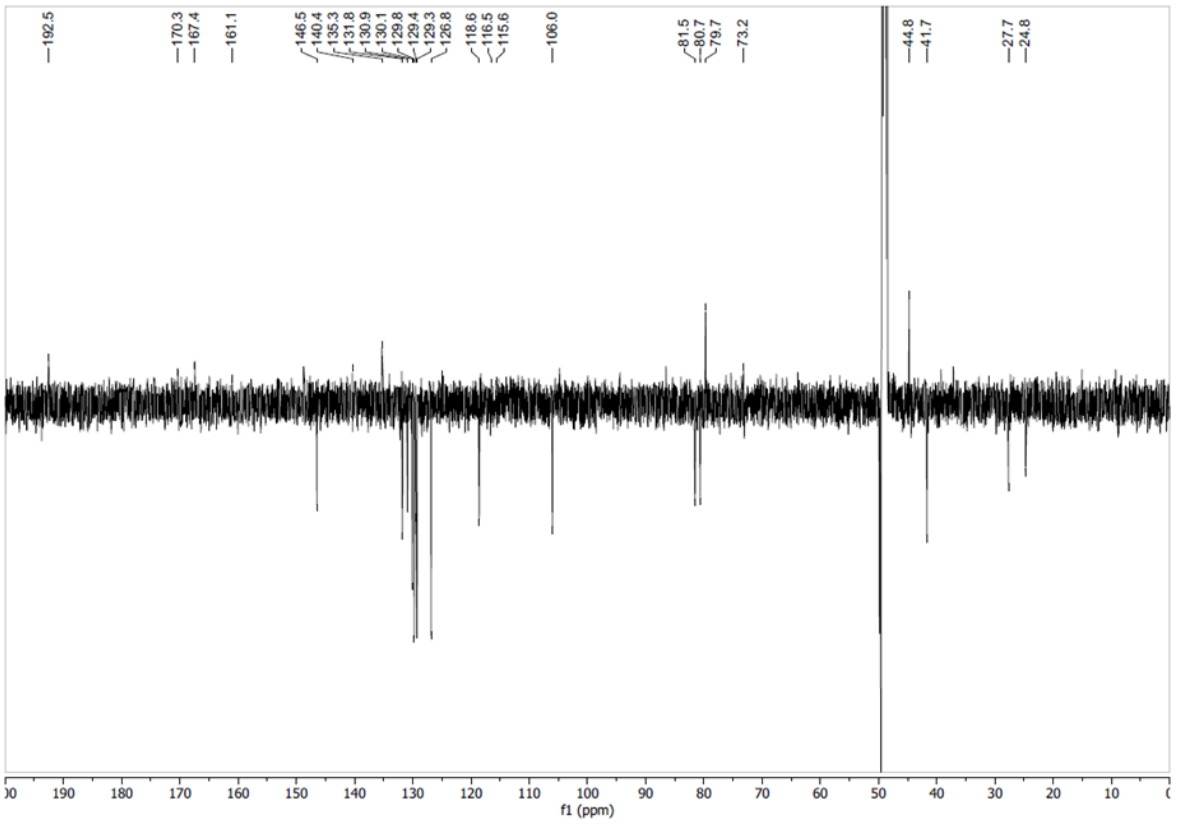


Figure S33: ^{13}C-DEPTQ NMR spectrum of compound **14** in CD_3ODat 151 MHz

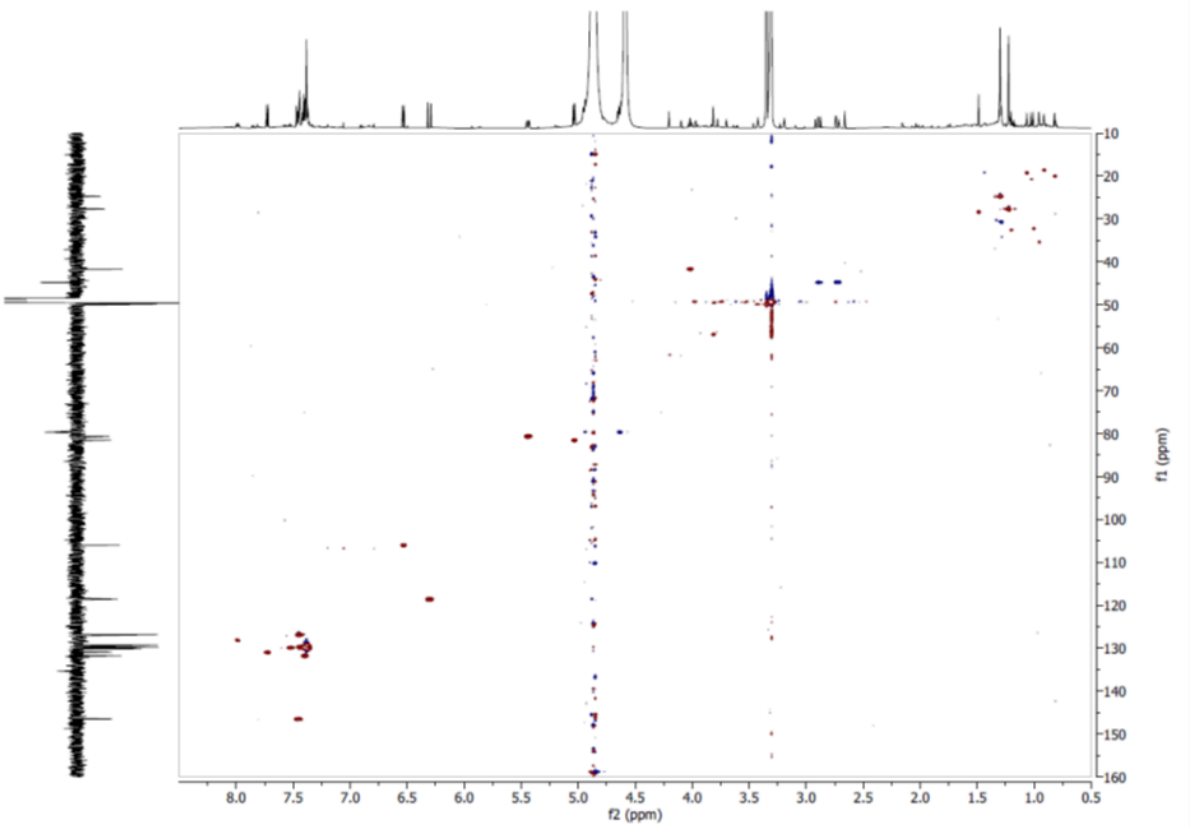


Figure S34: Edited HSQC NMR spectrum of compound **14** in CD_3OD

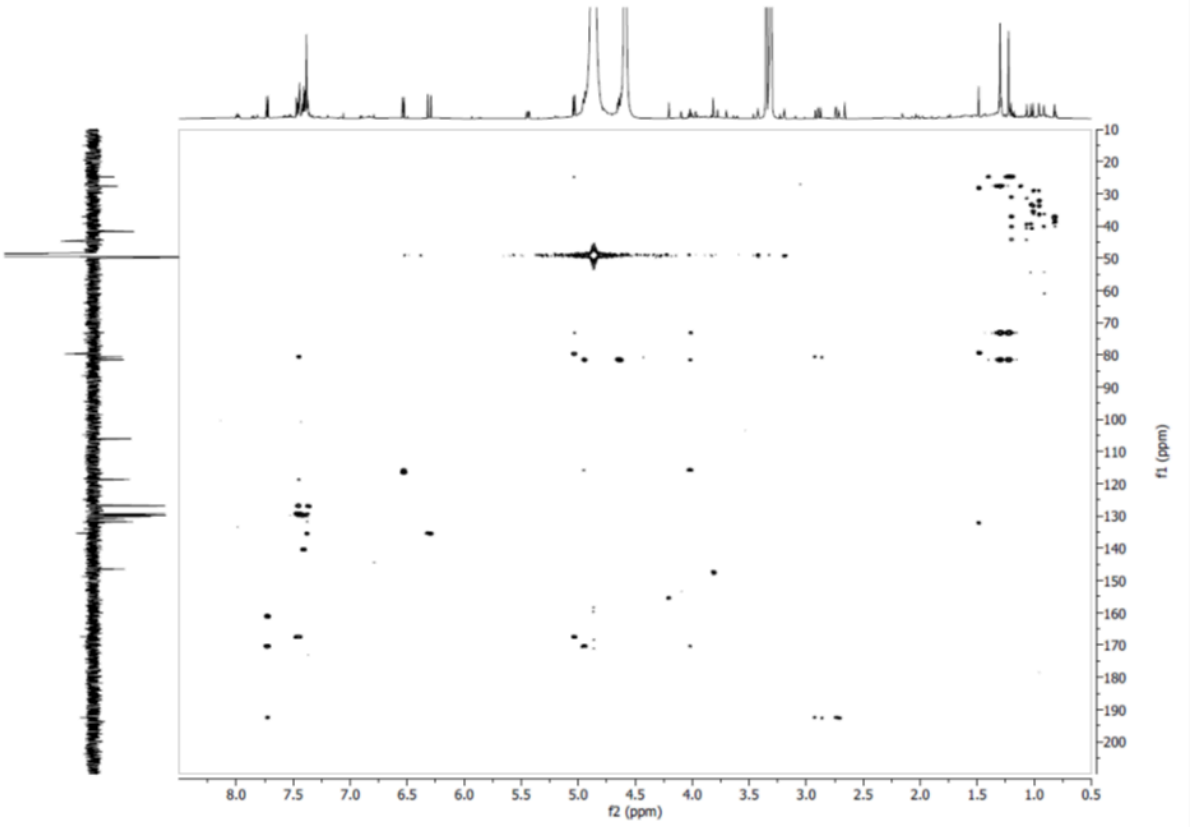


Figure S35: HMBC NMR spectrum of compound **14** in CD_3OD

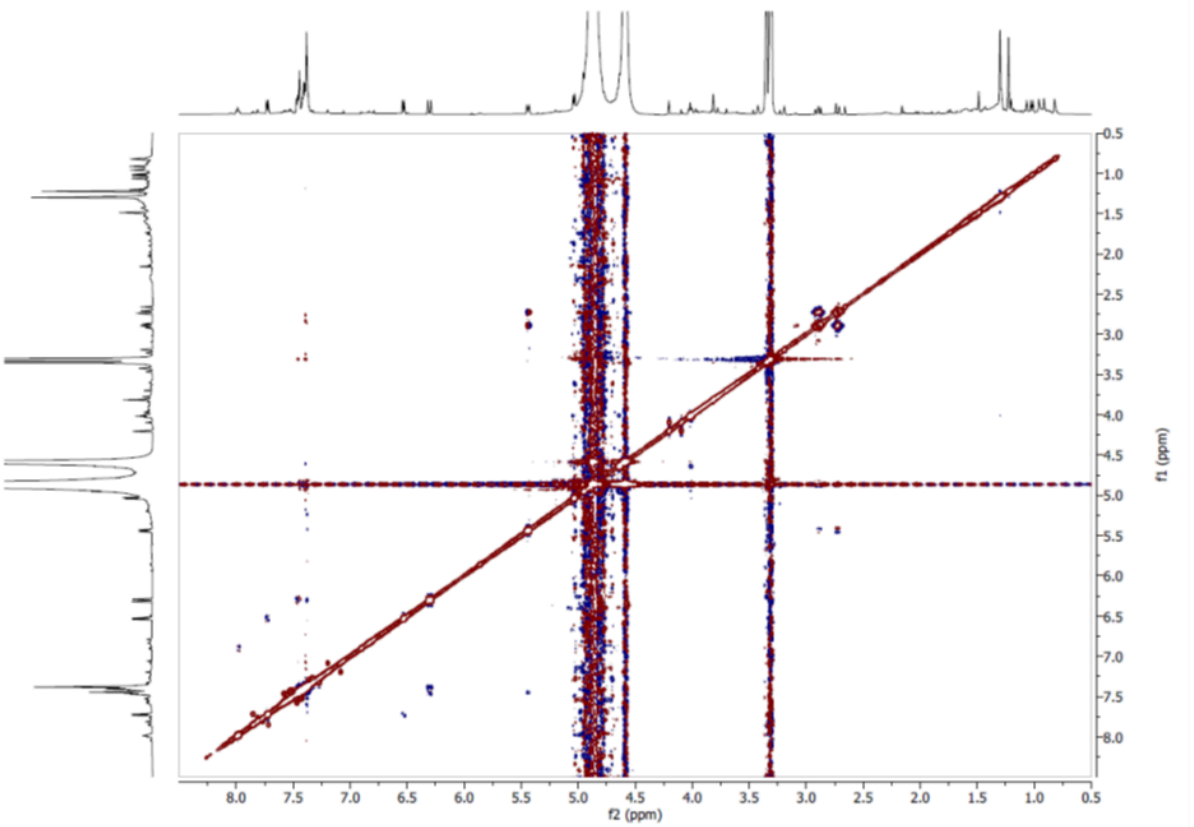


Figure S36: ROESY NMR spectrum of compound **14** in CD_3OD

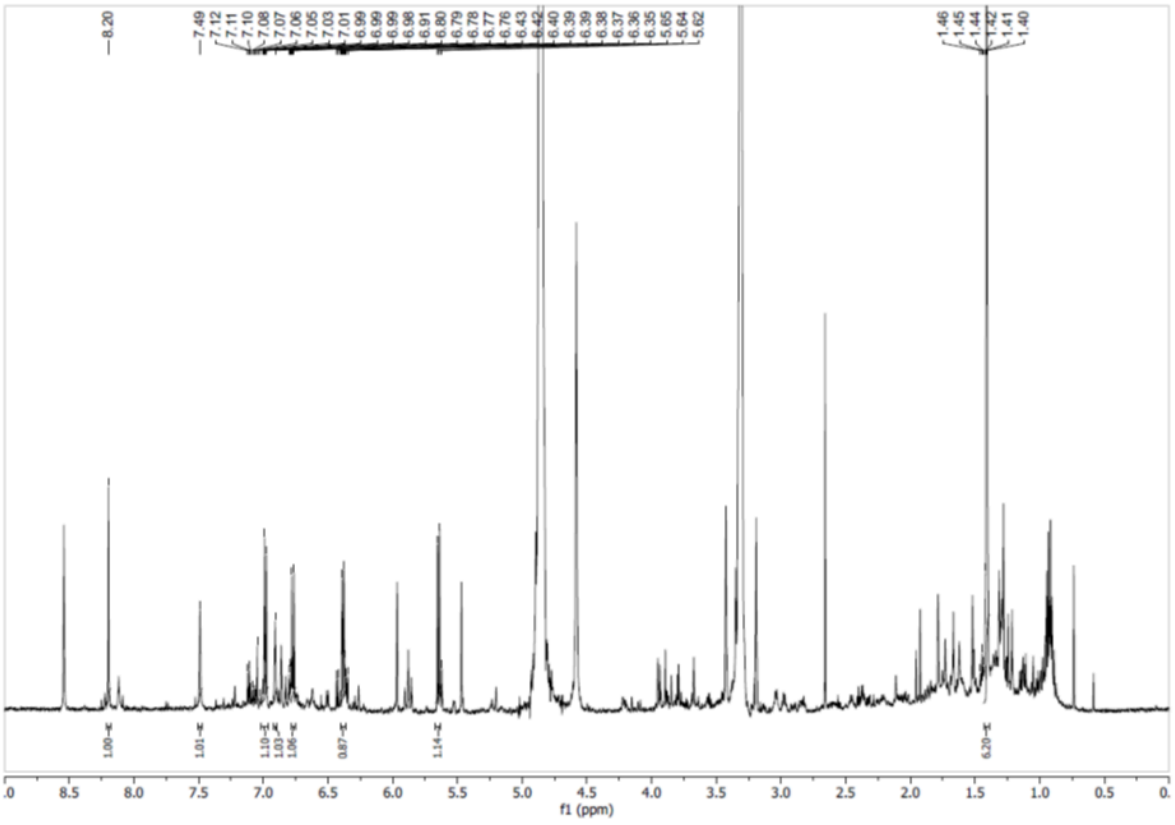


Figure S37: ^1H NMR spectrum of compound **21** in CD_3OD at 600 MHz

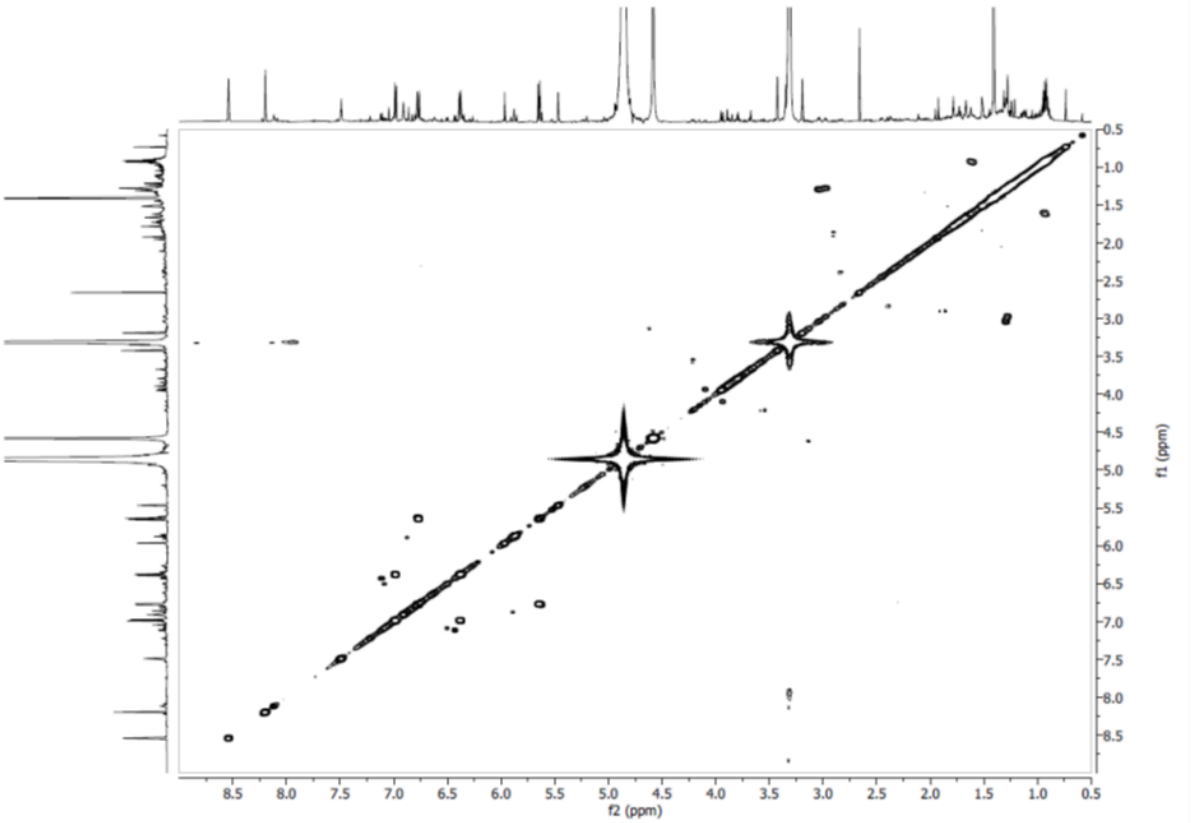


Figure S38: COSY NMR spectrum of compound **21** in CD_3OD

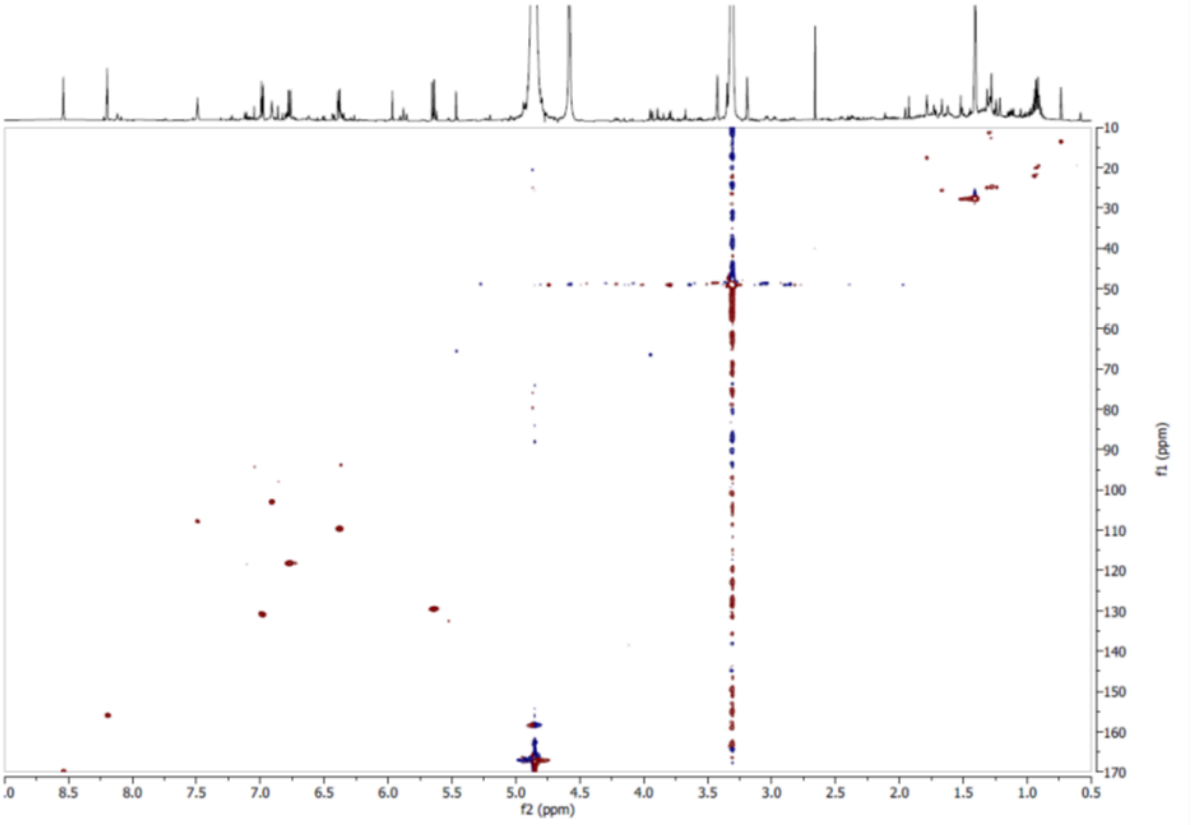


Figure S39: Edited HSQC NMR spectrum of compound **21** in CD_3OD

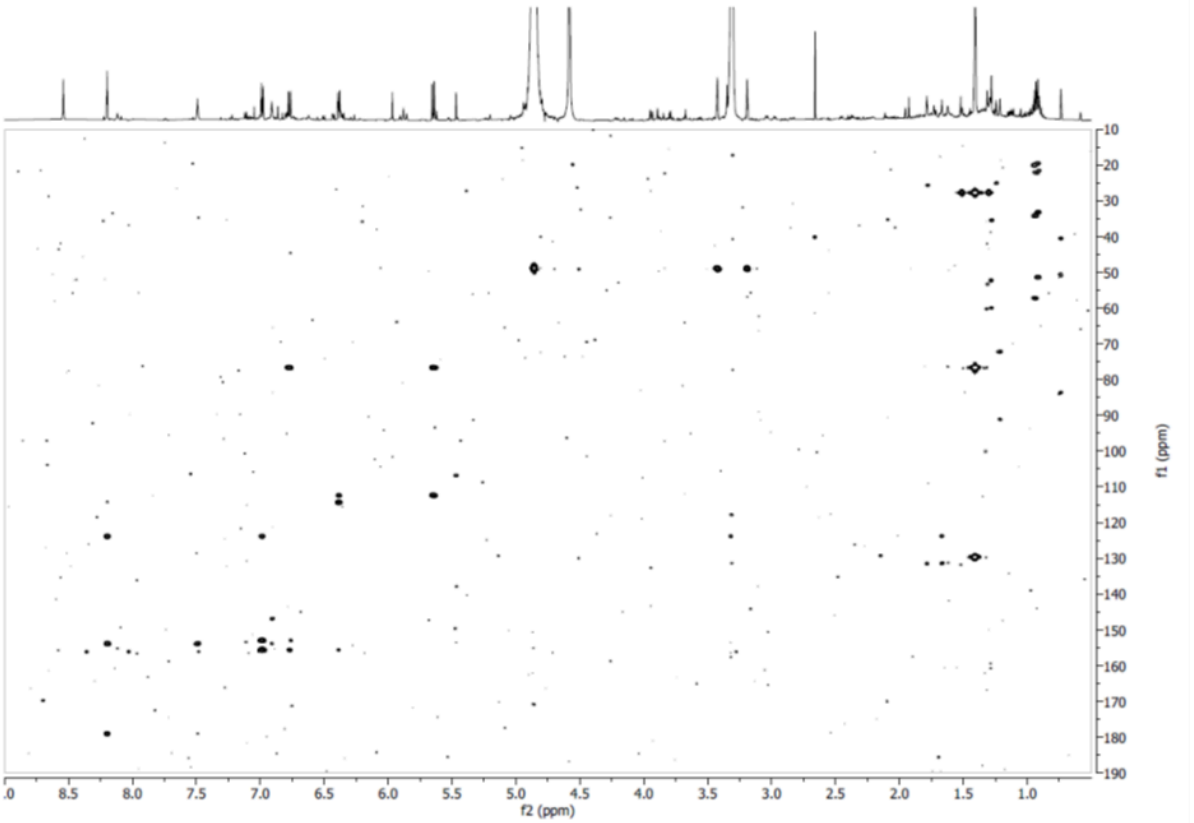


Figure S40: HMBC NMR spectrum of compound **21** in CD_3OD

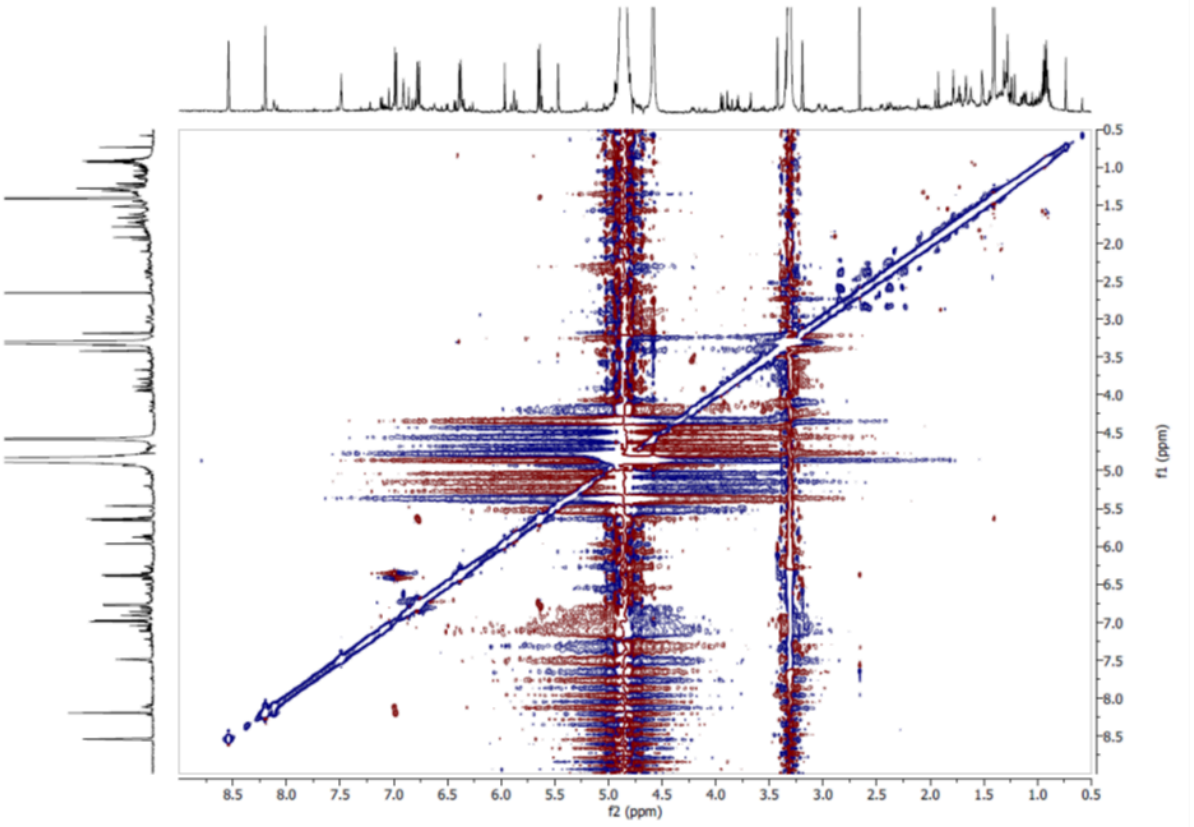


Figure S41: ROESY NMR spectrum of compound **21** in CD_3OD

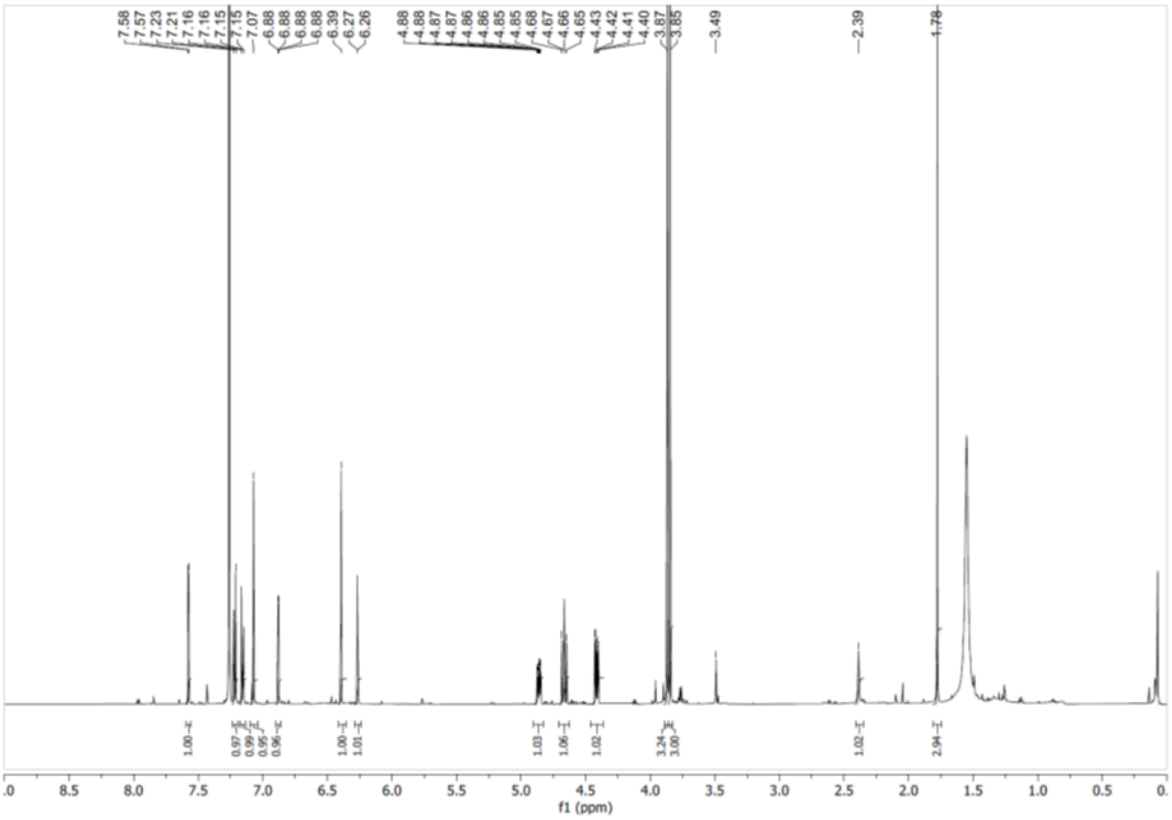


Figure S42: ^{1}H NMR spectrum of compound **33** in $CDCl_3$ at 600 MHz

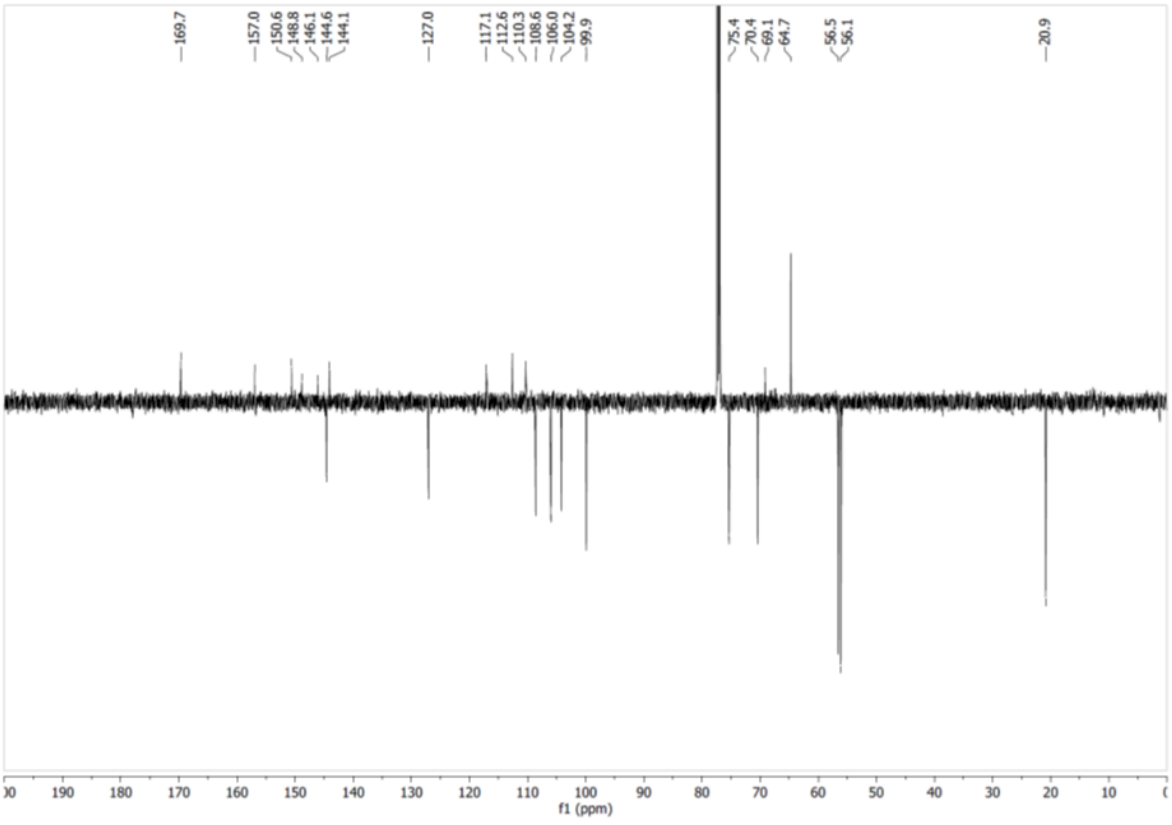


Figure S43: ^{13}C-DEPTQ NMR spectrum of compound **33** in $CDCl_3$ at 151 MHz

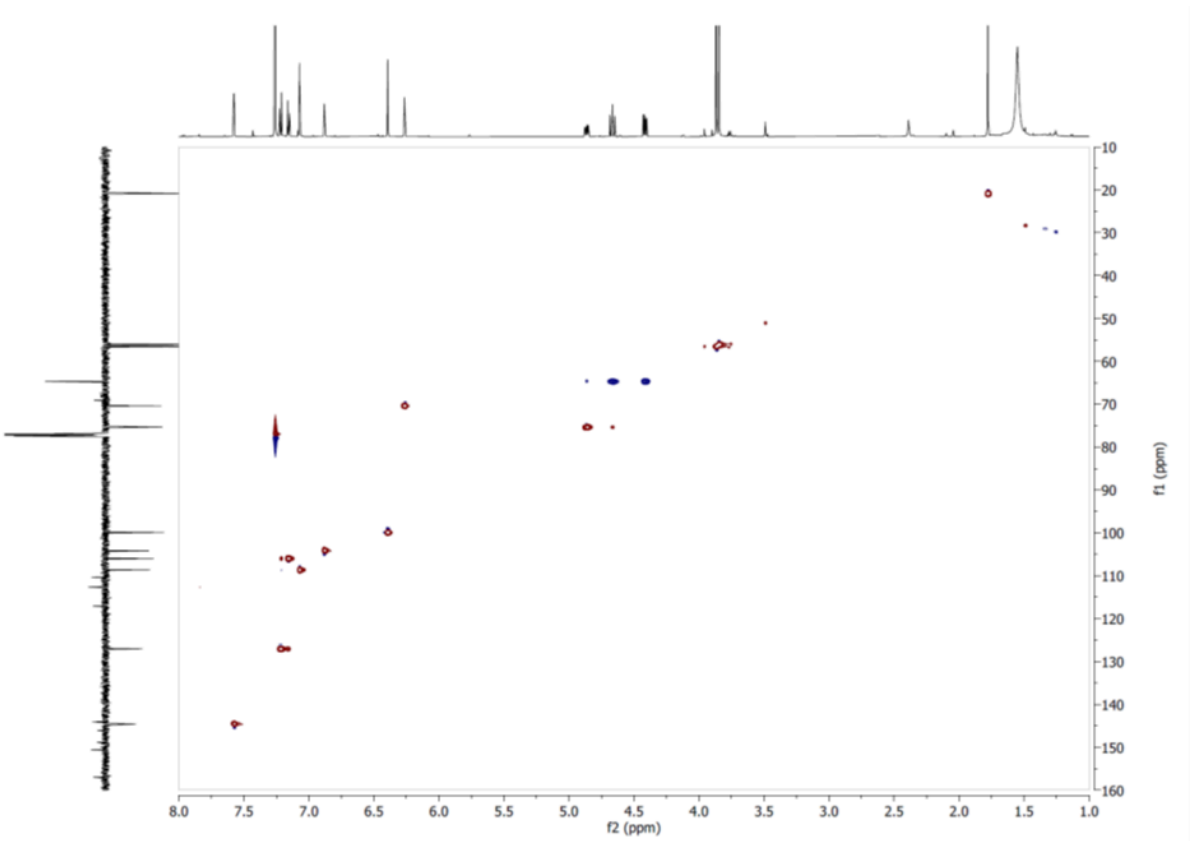


Figure S44: Edited HSQC NMR spectrum of compound **33** in $CDCl_3$

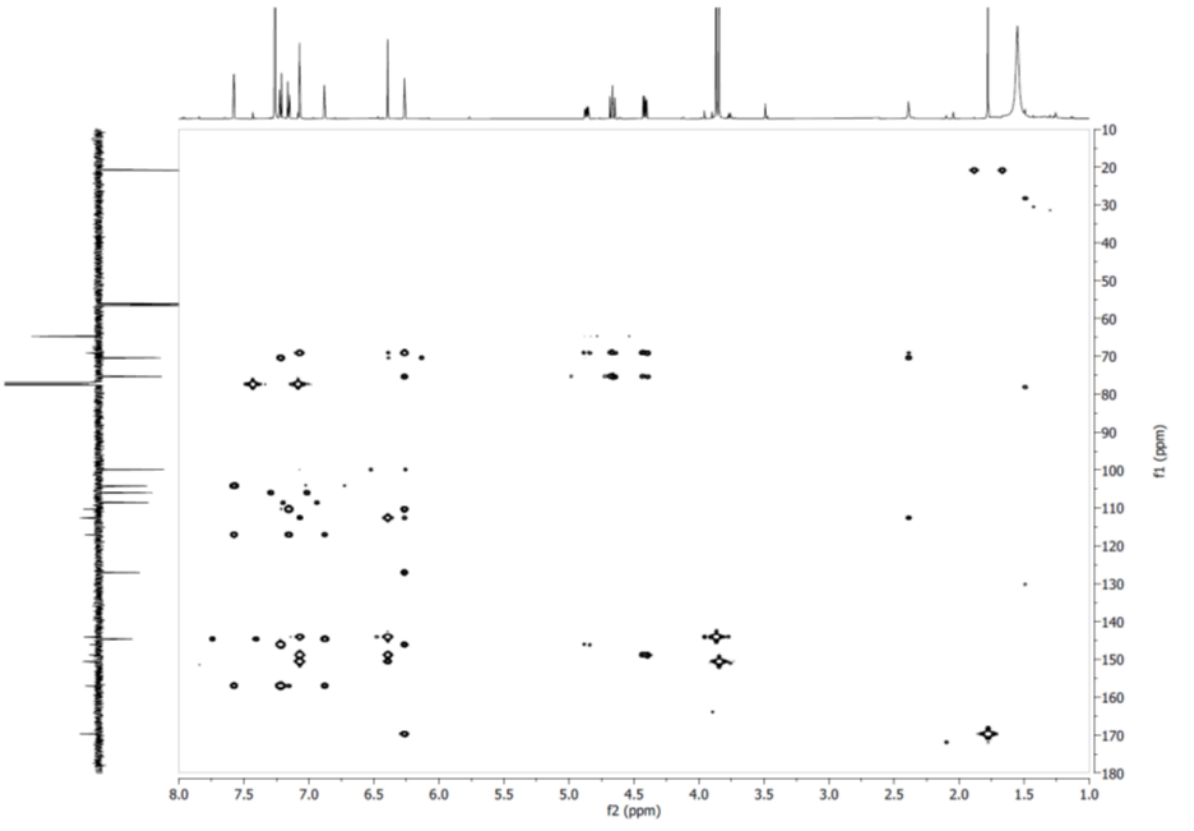


Figure S45: HMBC NMR spectrum of compound **33** in $CDCl_3$

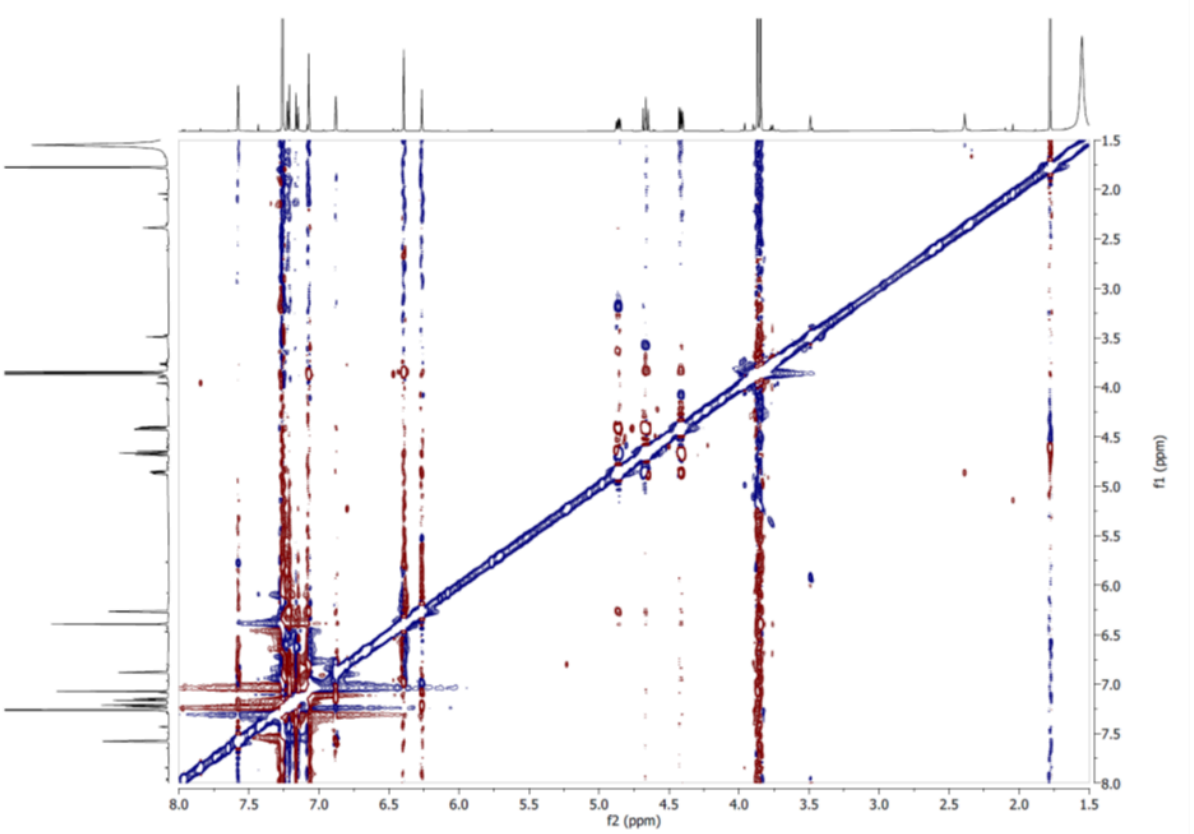


Figure S46: ROESY NMR spectrum of compound **33** in $CDCl_3$

Reference

1. Sakurai Y, Sakurai N, Taniguchi M, Nakanishi Y, Bastow KF, Wang X, et al. Rautandiols A and B, pterocarpans and cytotoxic constituents from *Neorautanenia mitis*. J Nat Prod. 2006;69: 397–399.