Supplementary Data

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A New Iridoid Glycoside Isolated from *Valeriana officinalis* L.

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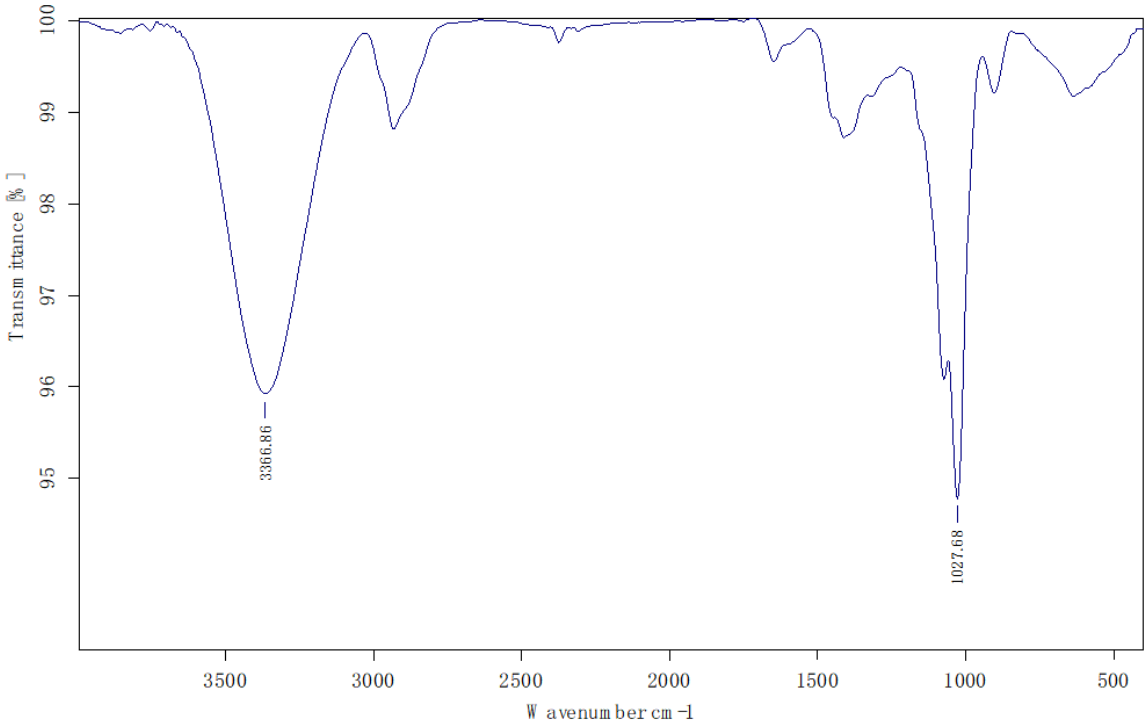


Figure S1: The IR spectrum of 1 (in KBr)

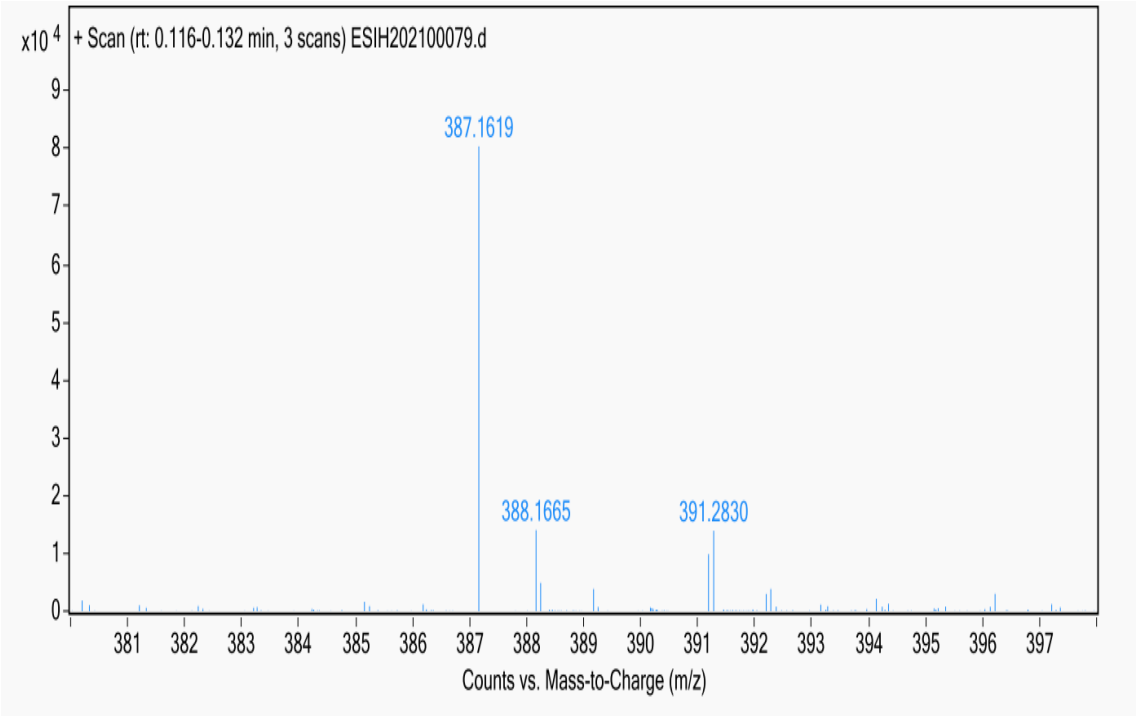


Figure S2: The HR-ESI-MS spectrum of **1** (in MeOH）

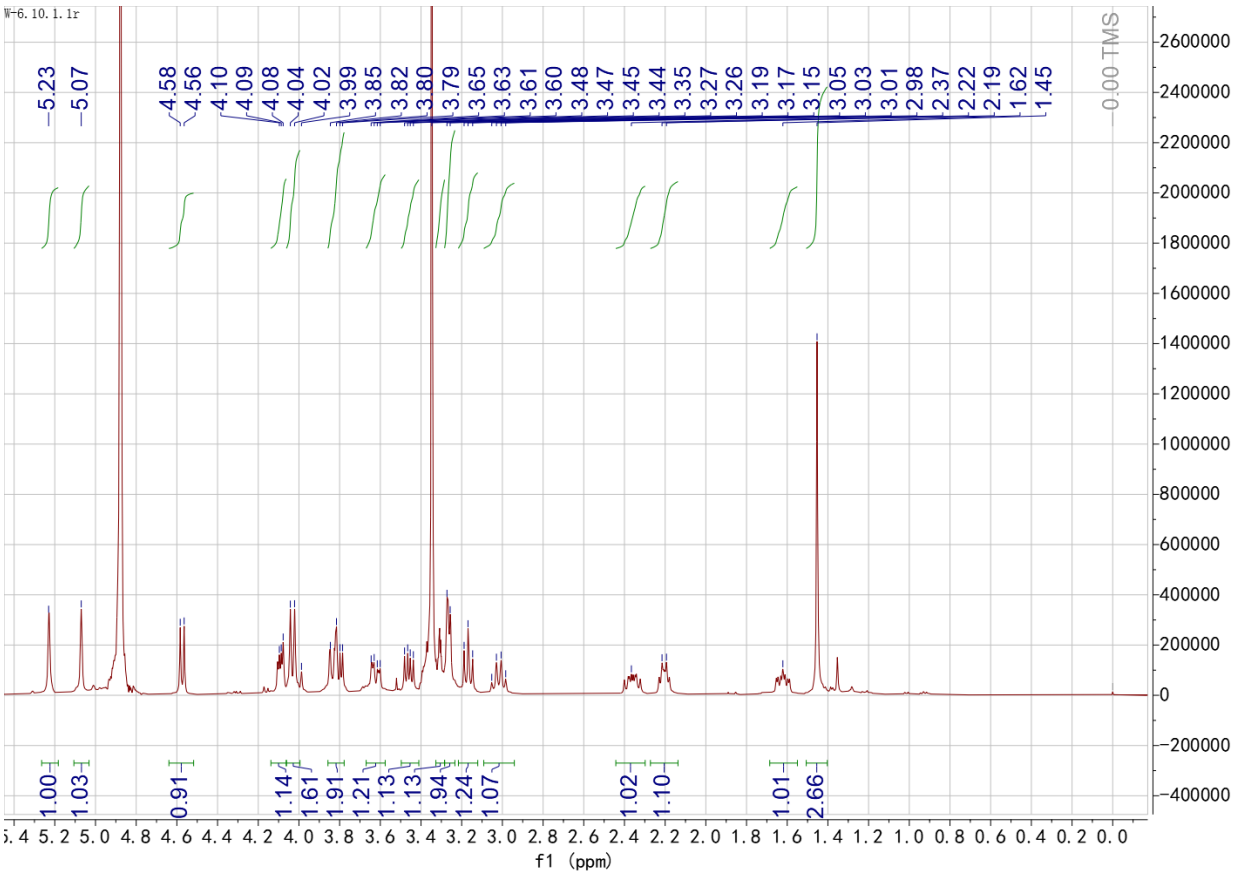


Figure S3: The ^{1}H NMR spectrum of **1** (in MeOD)

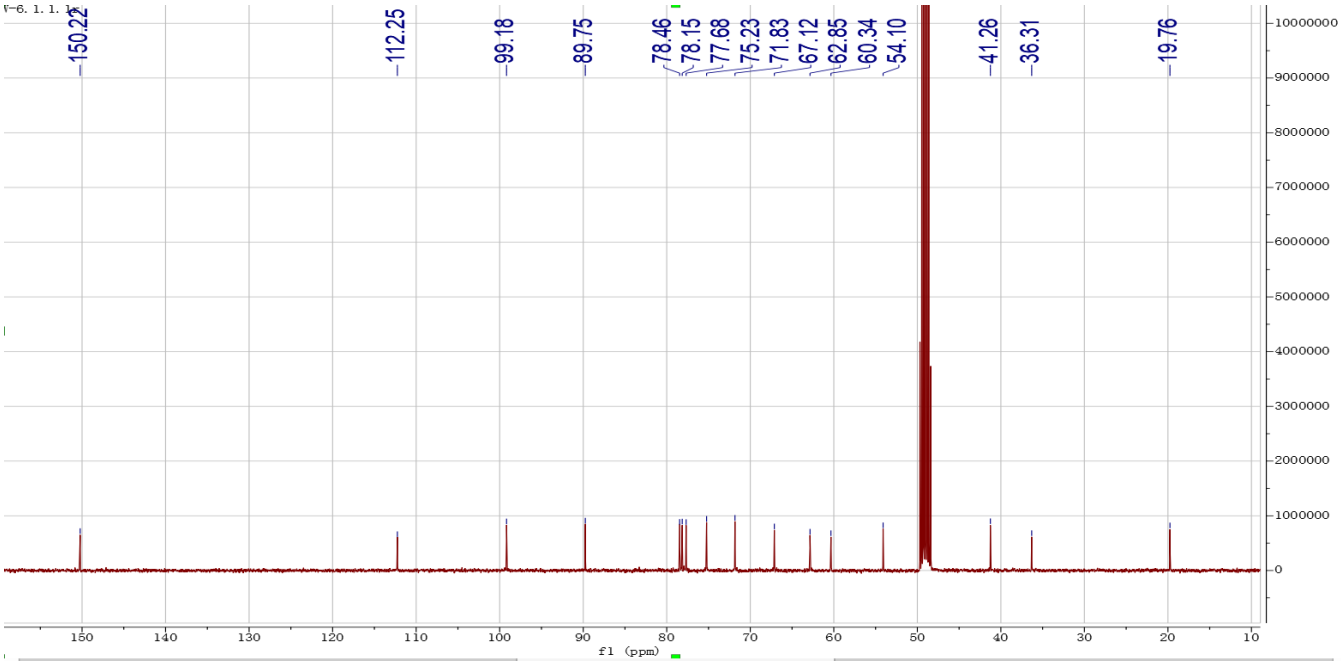


Figure S4: The ^{13}C NMR spectrum of **1** (in MeOD)

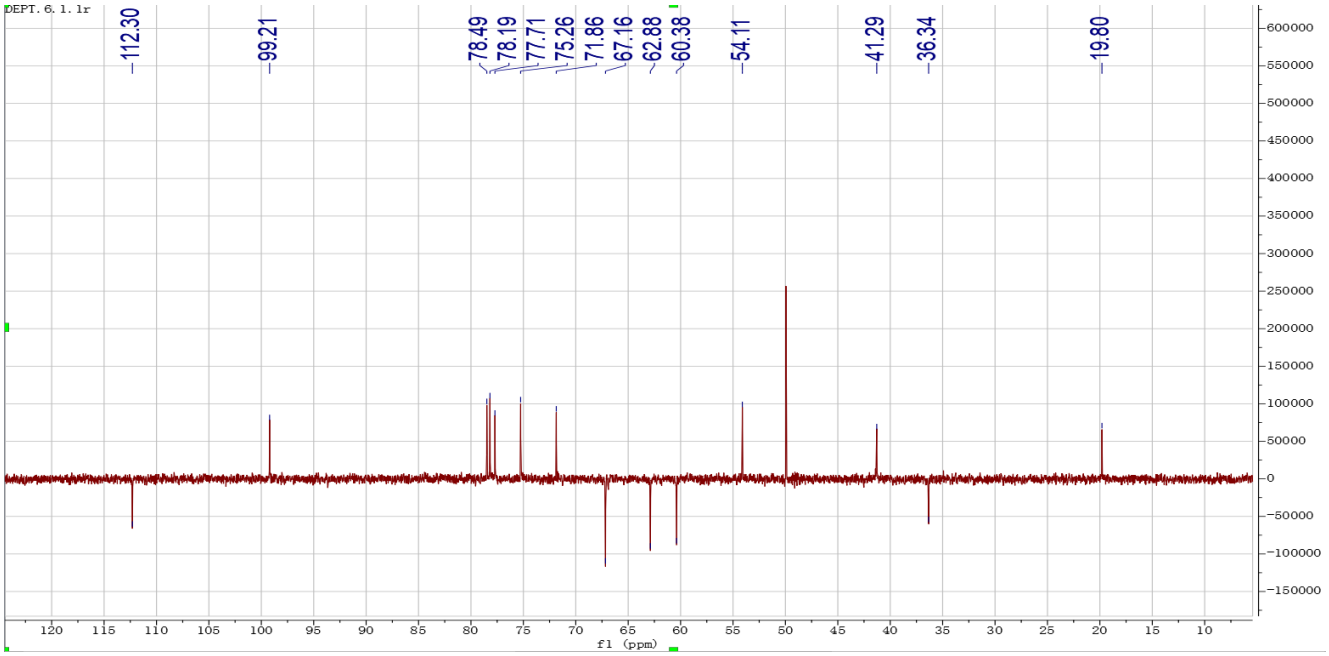


Figure S5: The DEPT spectrum of **1** (in MeOD)

Figure S6: The HSQC spectrum of **1** (in MeOD)

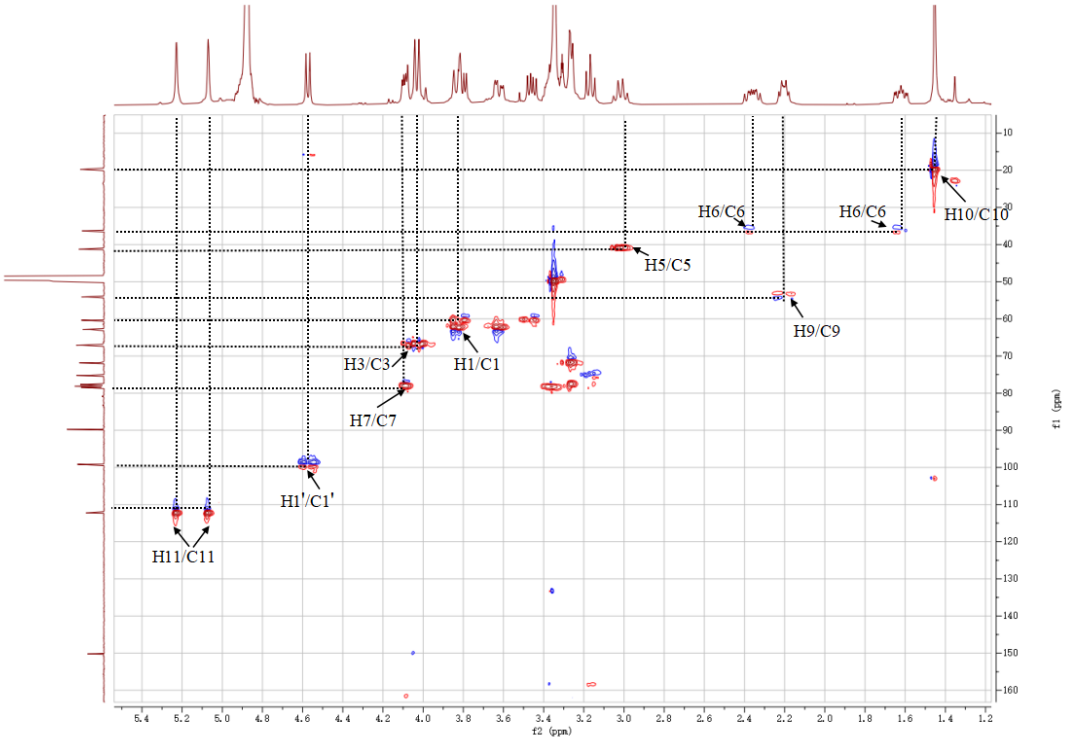


Figure S7: The HSQC spectrum of **1** (in MeOD) (From δ_C 90 ppm to δ_C 160 ppm)

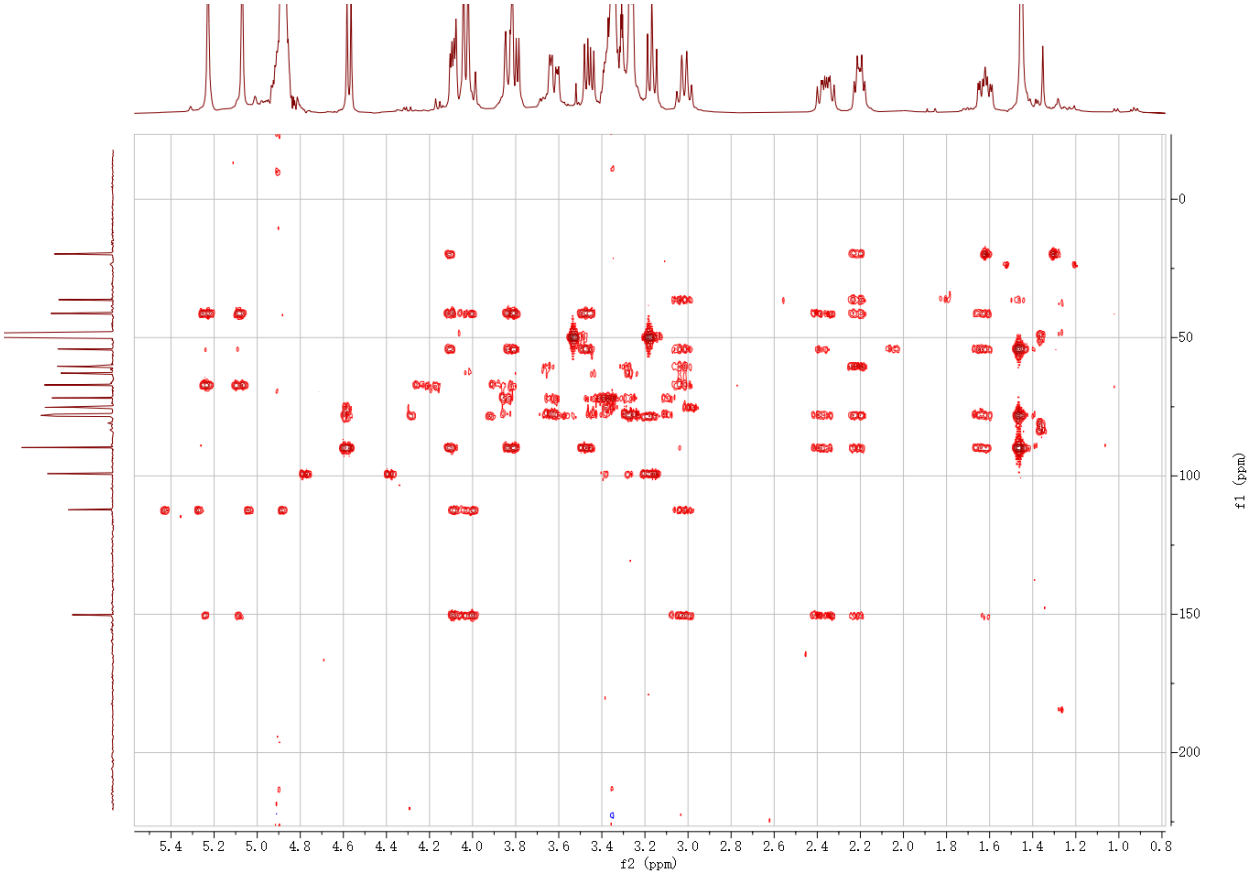


Figure S8: The HMBC spectrum of **1** (in MeOD)

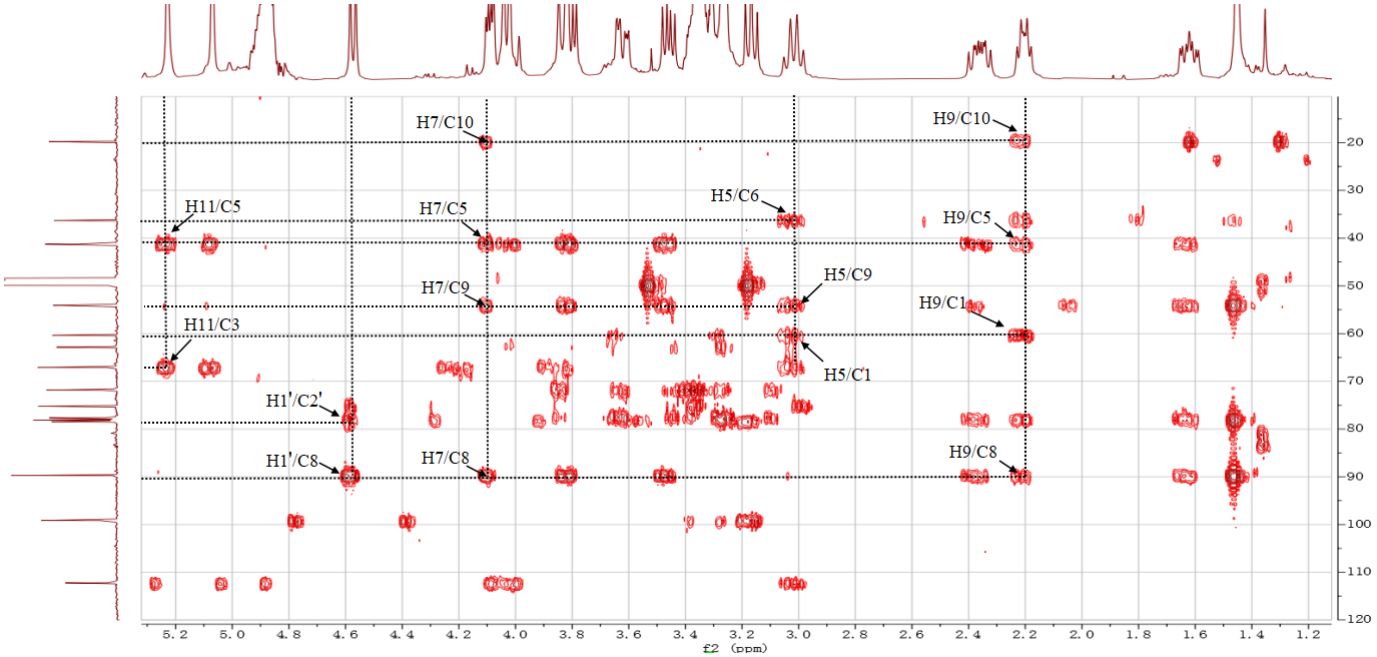


Figure S9: The HMBC spectrum of **1** (in MeOD) (From δ_C20ppm to δ_C 120 ppm)

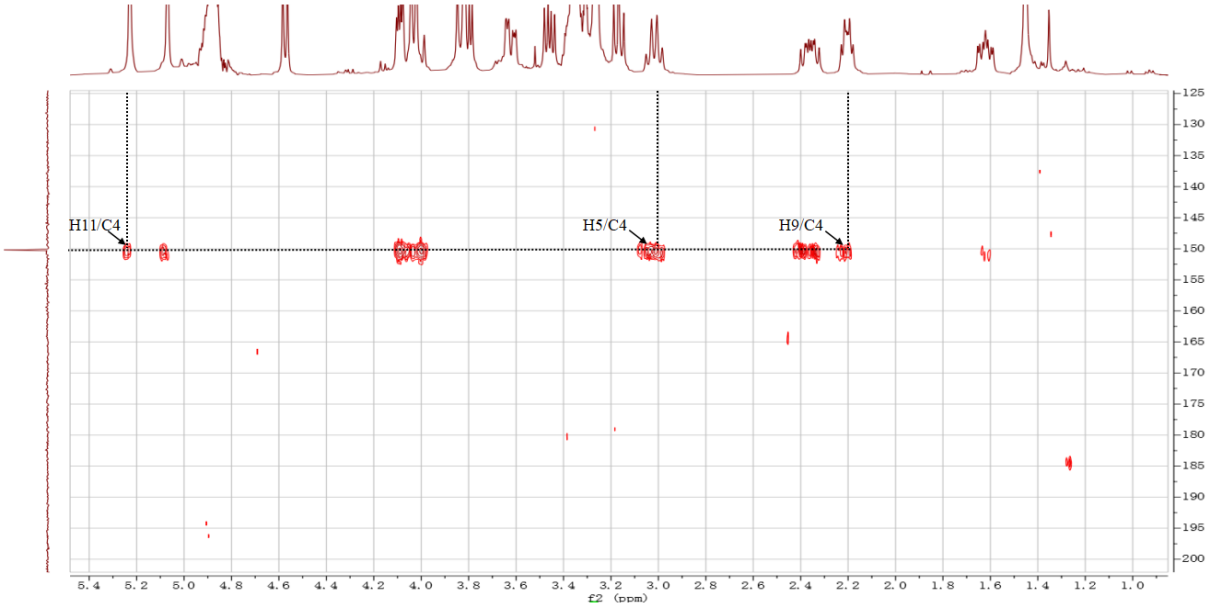


Figure S10: The HMBC spectrum of **1** (in MeOD) (From δ_C125ppm to δ_C 200 ppm

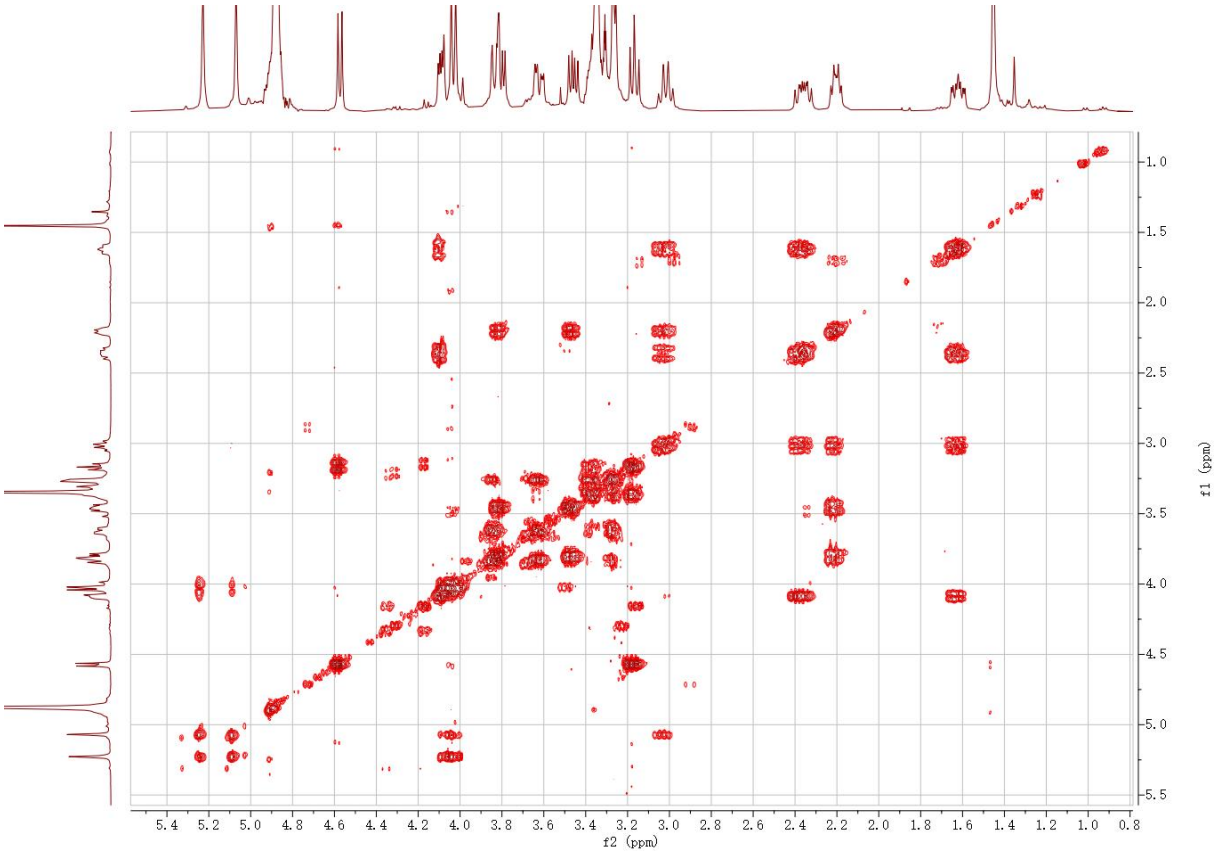


Figure S11: The ^{1}H-^{1}H COSY spectrum of **1** (in MeOD)

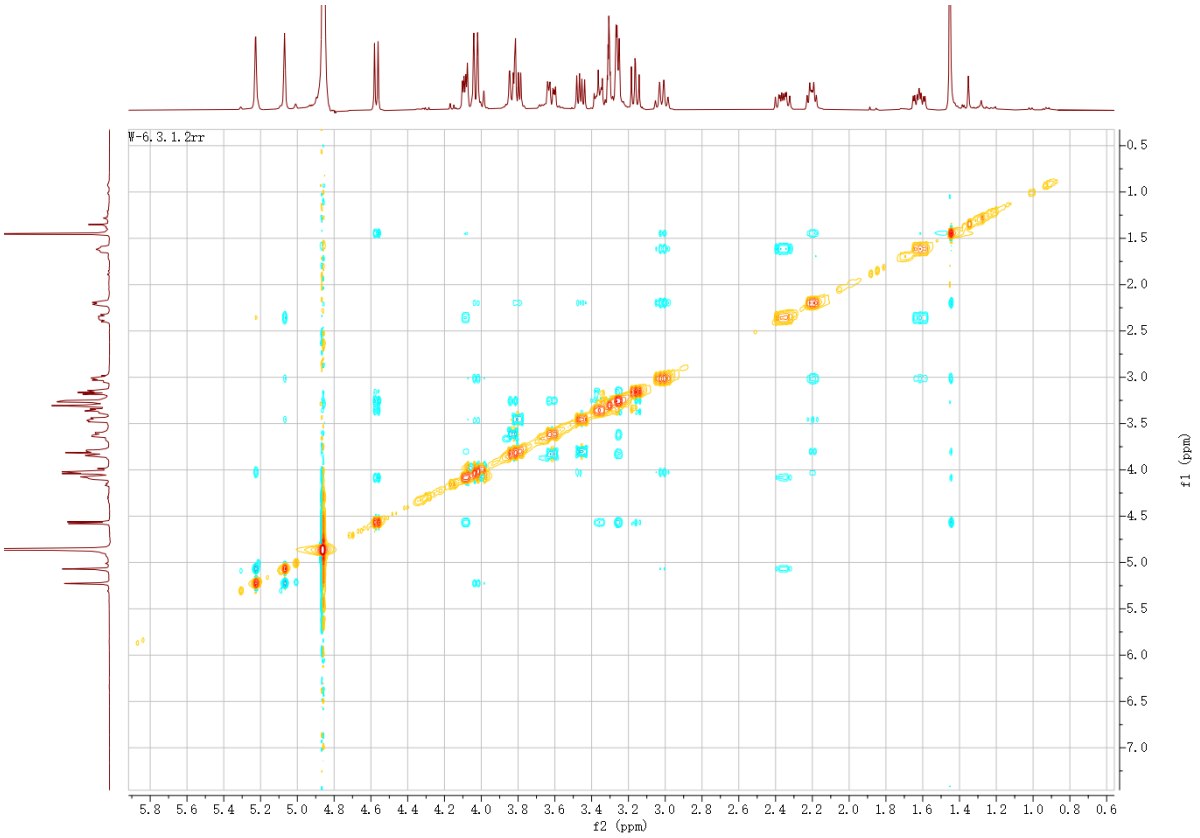
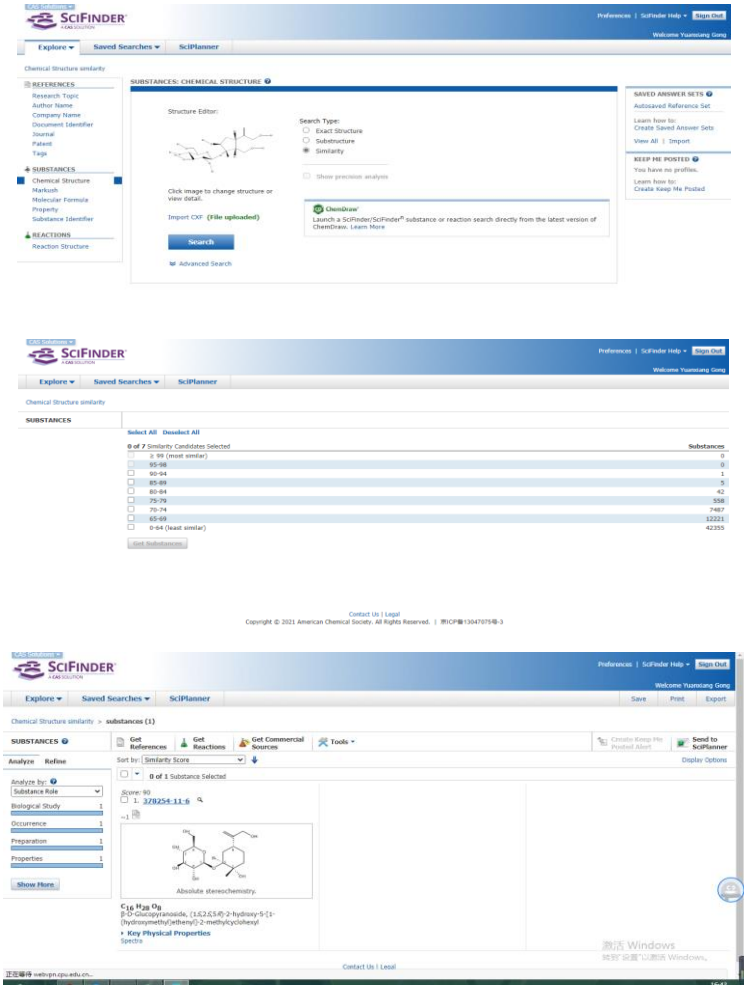
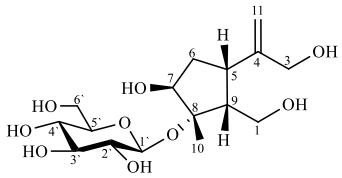


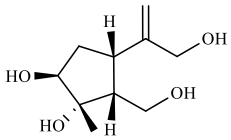
Figure S12: The NOESY spectrum of **1** (in MeOD)



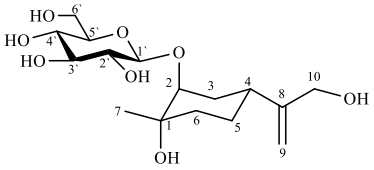
S1: Search report of SciFinder of **1**



1



3



simialr compound

Table 1: ^{13}C NMR data for compound **1** and similar compound

	1	**3**	**similar compound**
Position	δ_C	δ_C	δ_C
1	60.4	61.0	70.4
2	-	-	84.1
3	67.1	67.5	33.9
4	150.2	150.6	34.4
5	41.3	41.5	27.6
6	36.3	38.9	35.3
7	78.2	81.0	28.3
8	89.8	83.5	156.1
9	54.1	51.3	107.0
10	19.8	23.5	64.8
11	112.3	112.4	-
1'	99.2		106.3
2'	75.2		75.7
3'	77.7		78.7
4'	71.8		71.7
5'	78.5		78.3
6'	62.9		62.9

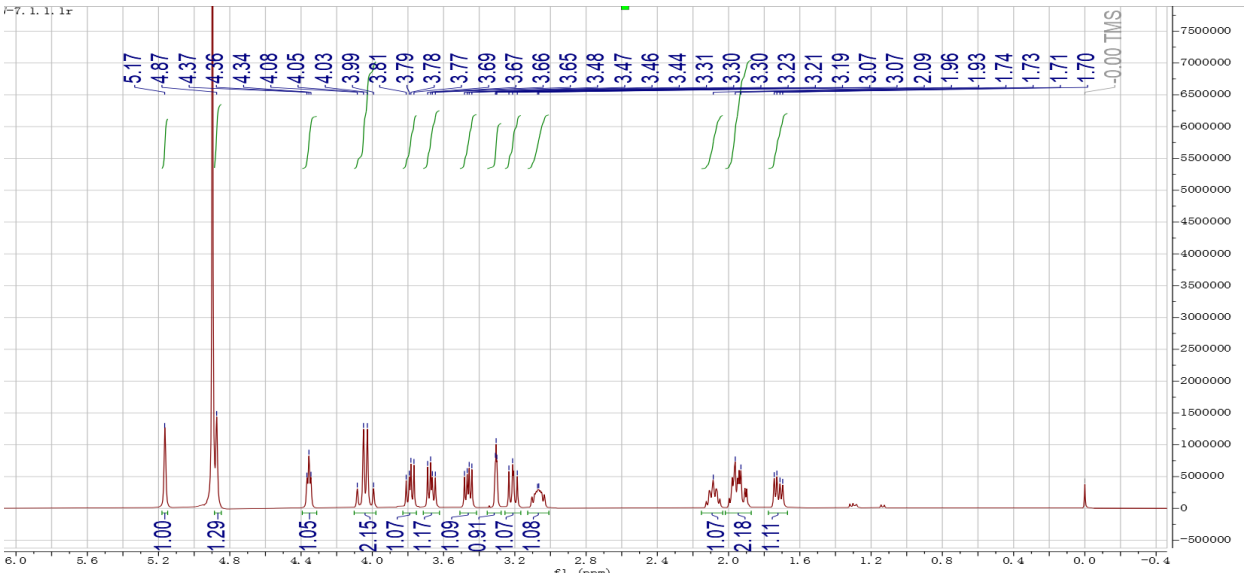


Figure S13: The ^{1}H NMR spectrum of **2** (in MeOD)

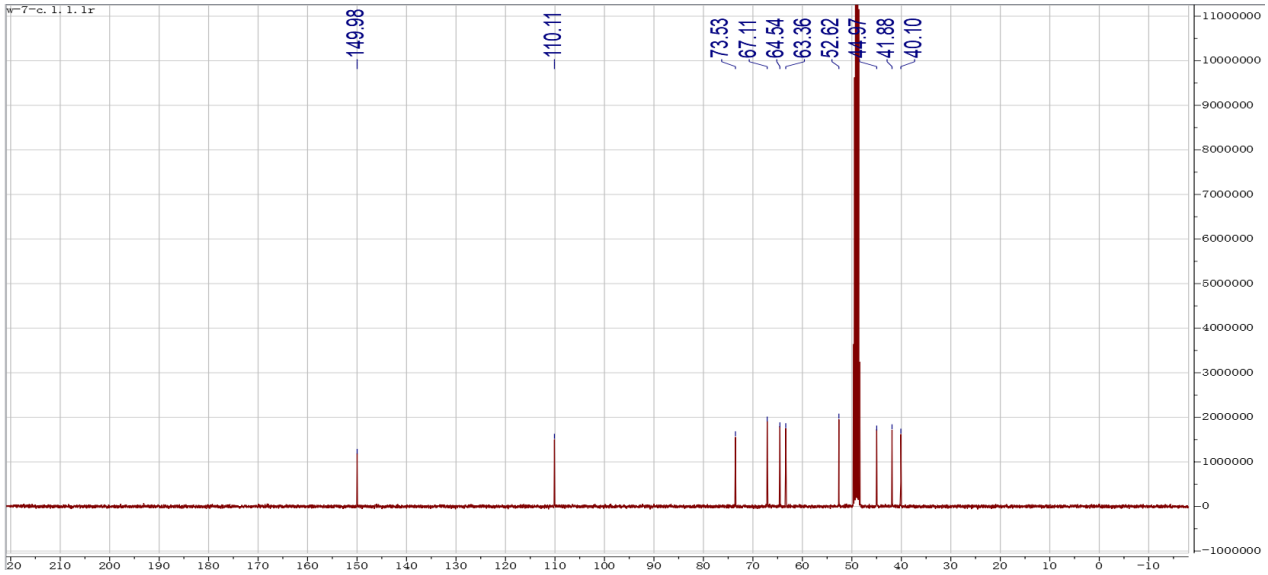


Figure S14: The ^{13}C NMR spectrum of **2** (in MeOD)

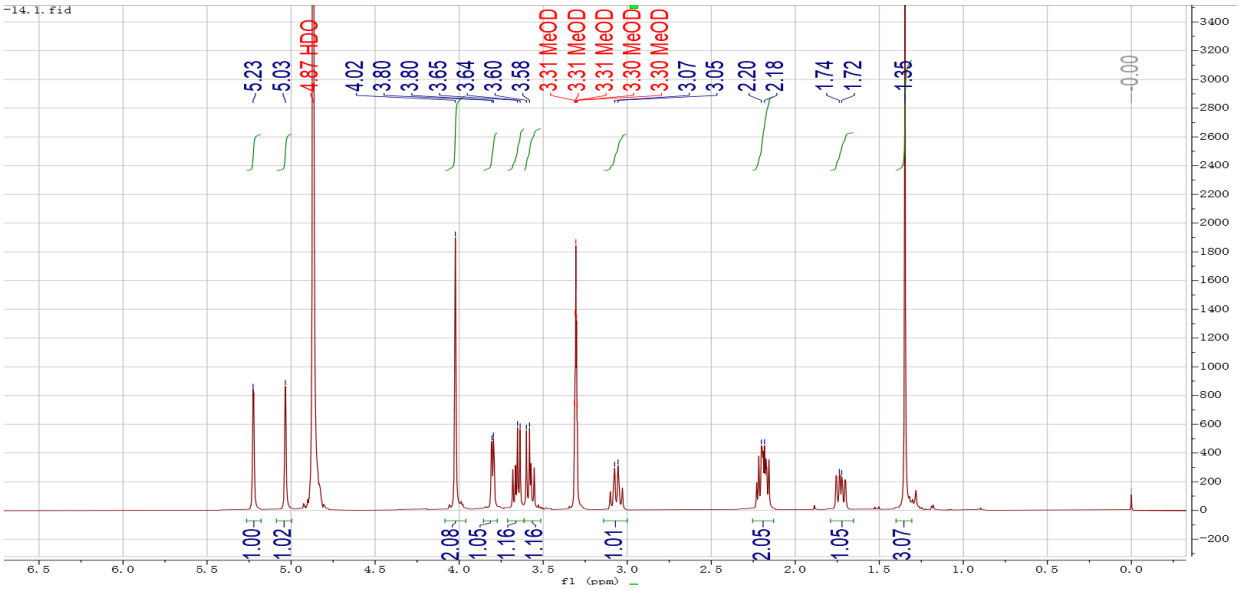


Figure S15: The ^{1}H NMR spectrum of **3** (in MeOD)

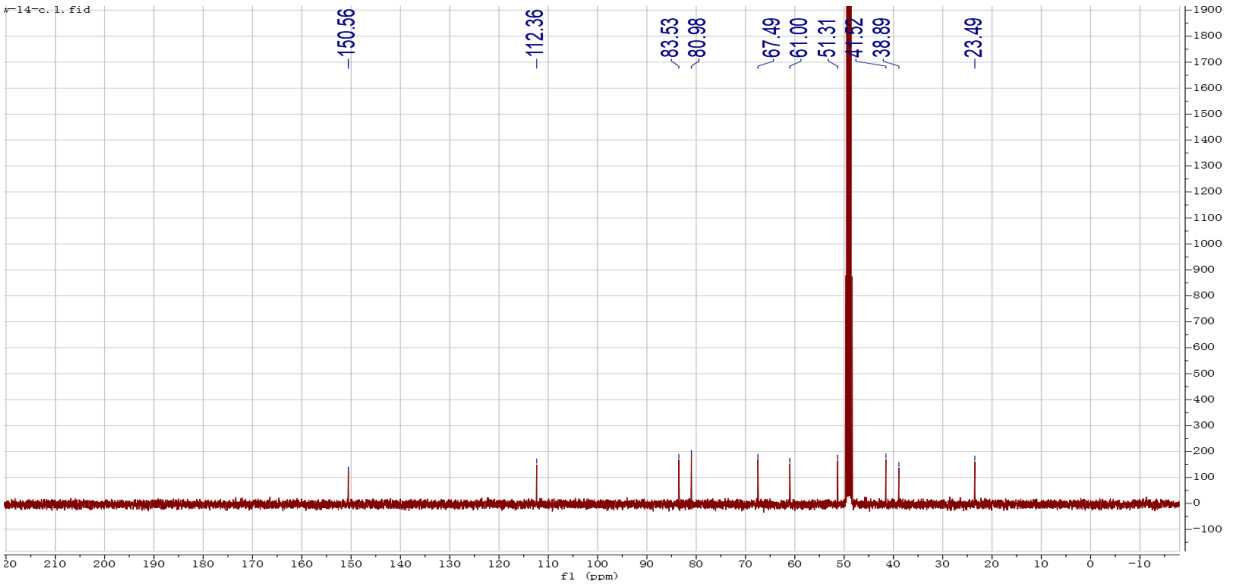


Figure S16: The ^{13}C NMR spectrum of **3** (in MeOD**)**

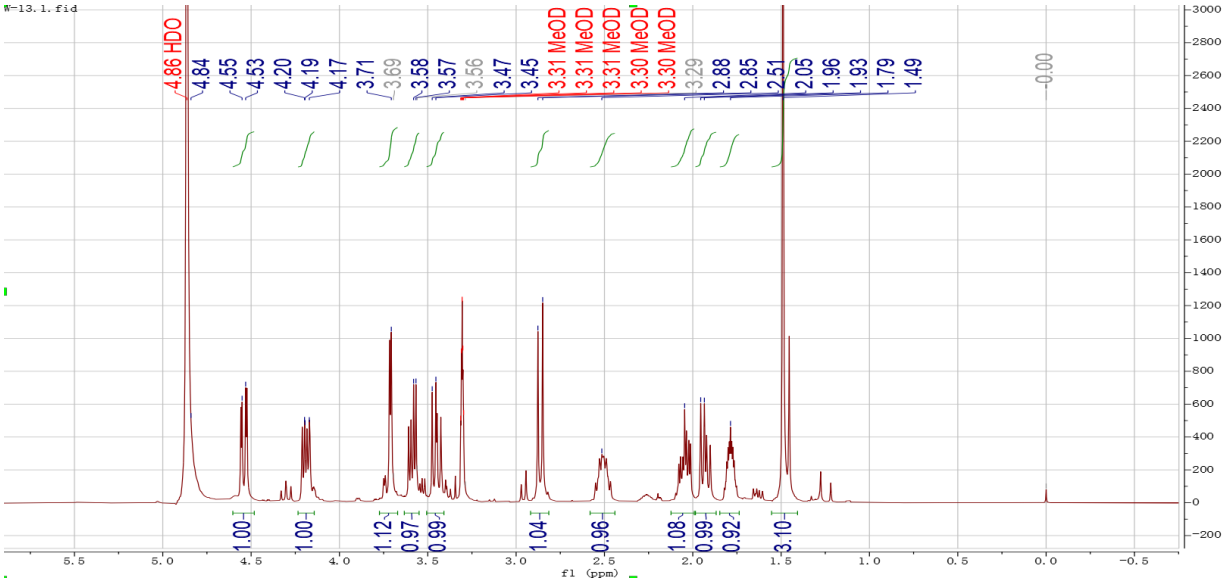


Figure S17: The ^{1}H NMR spectrum of **4** (in MeOD)

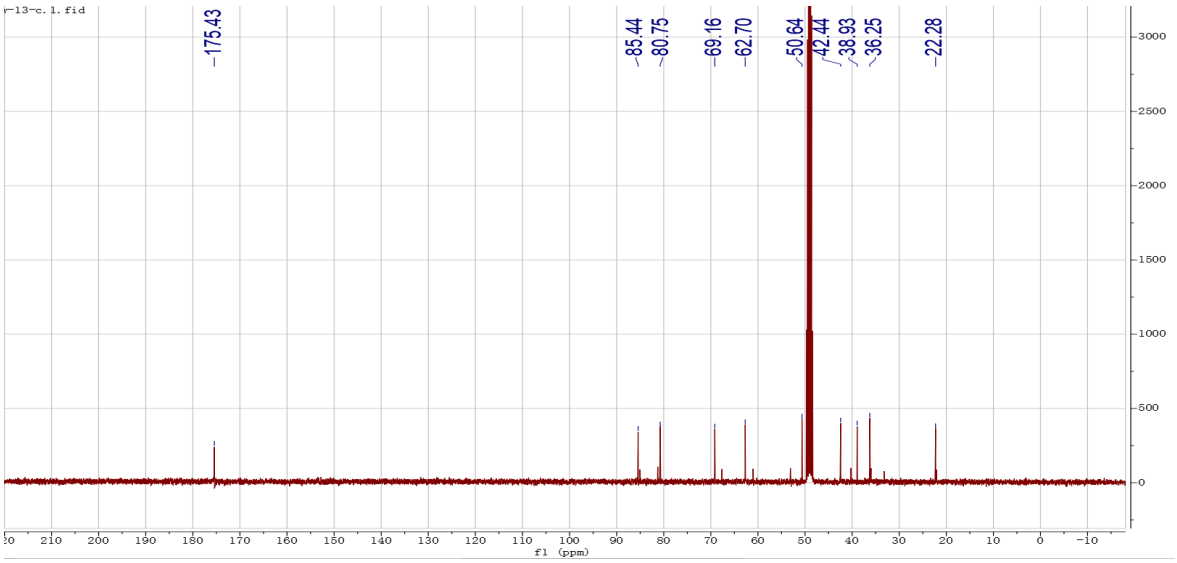


Figure S18: The ^{13}C NMR spectrum of **4** (in MeOD)

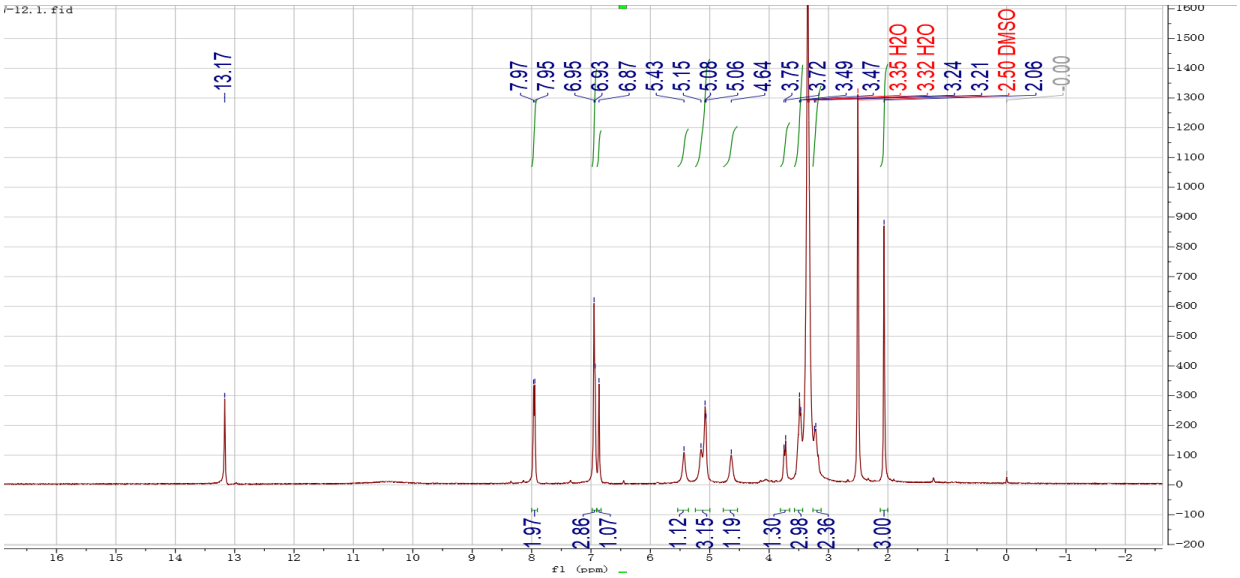


Figure S19: The ^{1}H NMR spectrum of **5** (in DMSO-d_6)

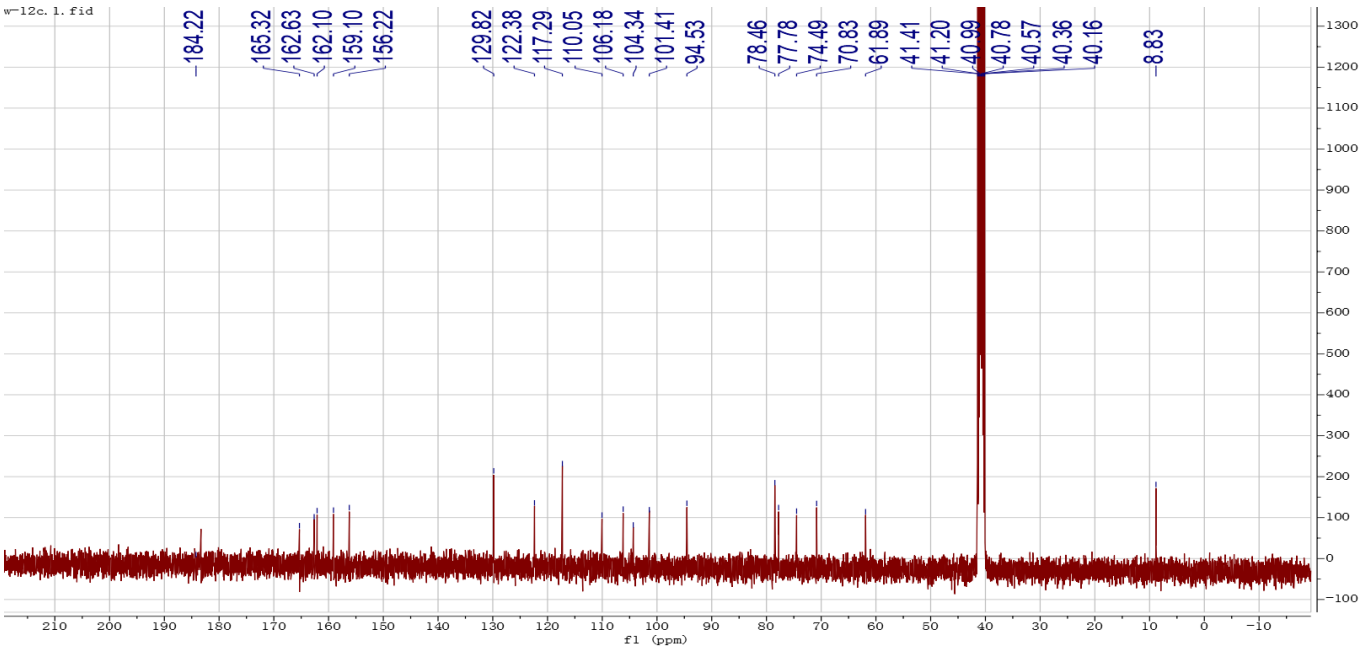


Figure S20: The ^{13}C NMR spectrum of **5** (in DMSO-d_6)

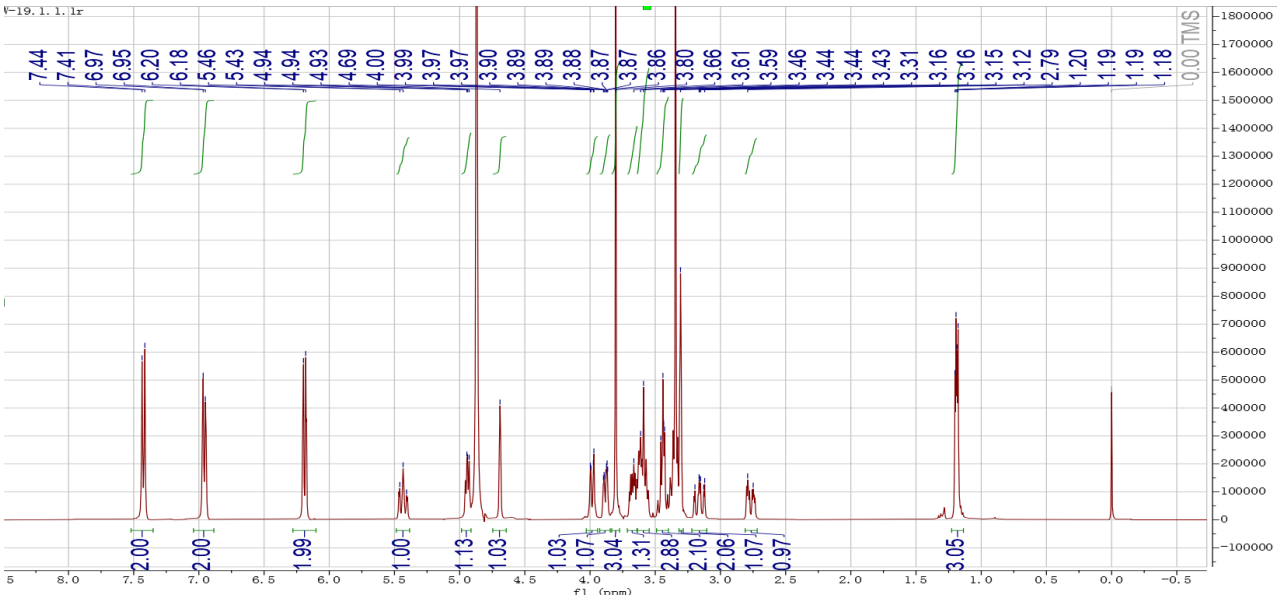


Figure S21: The ^{1}H NMR spectrum of **6** (in MeOD)

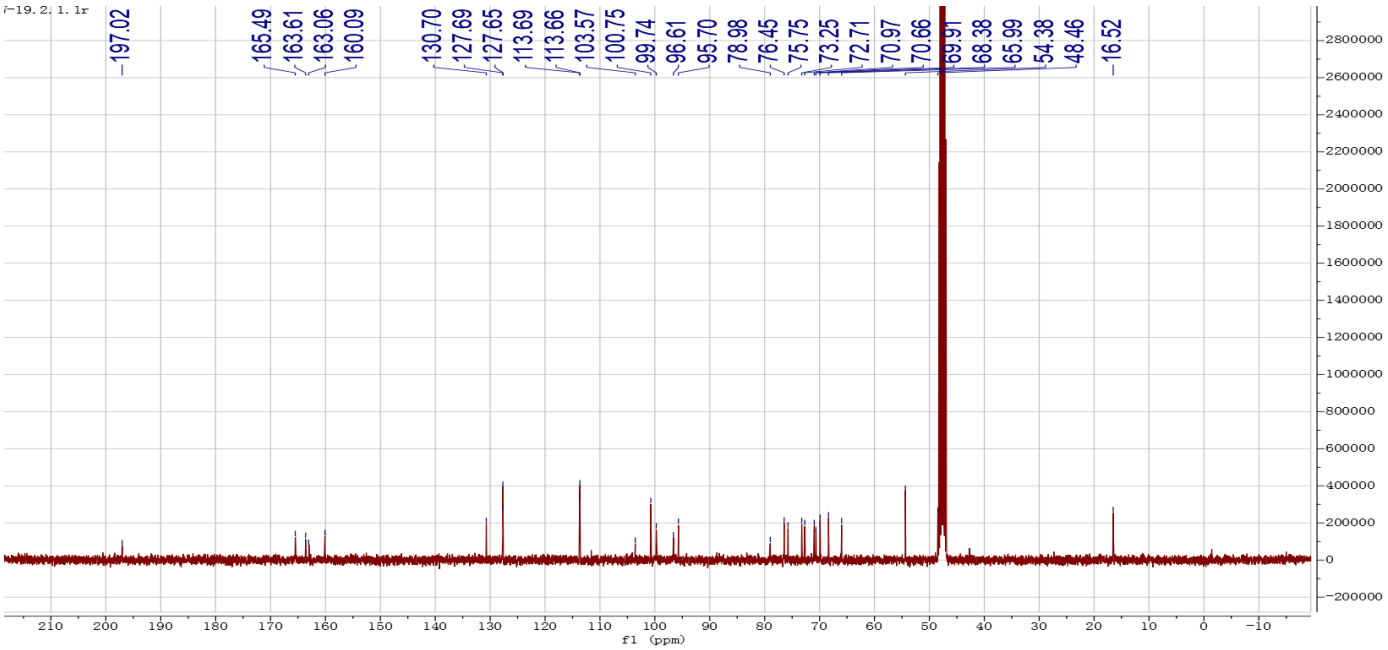


Figure S22: The ^{1}H NMR spectrum of **6** (in MeOD)

S2: Spectroscopic Data of 2-6

Dioscoridin A ***(2):***, $C_{10}H_{18}O_4$, colorless oil, $[\alpha]_D^{27}$ = +8.0 (c 0.1, MeOH), HR-ESI-MS *m/z* 225.1095 ($[M+Na]^+$). ^{1}H-NMR (400 MHz, MeOD) δ_H: 5.17 (1H, s, H-11a), 4.87 (1H, s, H-11b), 3.46 (1H, dd, *J* = 10.6, 6.1 Hz, H-1a), 3.21 (1H, dd, *J* = 10.6, 8.2 Hz, H-1b), 4.06 (2H, dd, *J* = 14.0, 8.6 Hz, H-3), 3.07 (1H, m, H-5), 1.92 (1H, dd, *J* = 13.0, 4.0 Hz, H-6a), 1.72 (1H, dd, *J* = 13.0, 6.1 Hz, H-6b), 4.36 (1H, t, *J* = 4.6 Hz, H-7), 1.97 (1H, m, H-8), 2.09 (1H, m, H-9), 3.79 (1H, dd, *J* = 10.6, 6.9 Hz, H-10a), 3.67 (1H, dd, *J* = 10.6, 6.7 Hz, H-10b). ^{13}C-NMR (100 MHz, MeOD) δ_C: 64.5 (C-1), 67.1 (C-3), 149.9 (C-4), 41.9 (C-5), 40.1 (C-6), 73.5 (C-7), 52.6 (C-8), 45.0 (C-9), 63.4 (C-10), 110.1 (C-11).

Jatamanin J ***(3):*** $C_{10}H_{18}O_4$, yellow oil, $[\alpha]_D^{20}$ +87.0 (c 0.36, MeOH), HR-ESI-MS *m/z* 225.1102 ($[M+Na]^+$). ^{1}H-NMR (400 MHz, MeOD) δ_H: 3.66 (1H, dd, *J* = 11.1, 6.3 Hz, H-1a), 3.58 (1H, dd, *J* = 11.1, 7.4 Hz, H-1b), 4.02 (2H, s, H-3), 3.06 (1H, dd, *J* = 10.4, 7.9 Hz, H-5), 2.19 (1H, ddd, *J* = 13.2, 9.6, 4.8 Hz, H-6a), 1.72 (1H, ddd, *J* = 13.2, 7.9, 1.8 Hz, H-6b), 3.80 (1H, dd, *J* = 5.2, 1.8 Hz, H-7), 2.19 (1H, ddd, *J* = 10.2, 7.2, 6.0 Hz, H-9), 1.34 (3H, s, H-10), 5.23 (1H, s, H-11a), 5.03 (1H, s, H-11b). ^{13}C-NMR (100 MHz, MeOD) δ_C: 61.0 (C-1), 67.5 (C-3), 150.6 (C-4), 41.5 (C-5), 38.9 (C-6), 81.0 (C-7), 83.5 (C-8), 51.3 (C-9), 23.5 (C-10), 112.4 (C-11).

Longiflorone ***(4):*** $C_{10}H_{16}O_5$, yellow oil, $[\alpha]_D^{20}$ +61.9 (c 1.1, MeOH), DCI-MS *m/z* 234.1 ($[M+NH_3+H]^+$). ^{1}H-NMR (400 MHz, MeOD) δ_H: 4.54 (1H, dd, *J* = 10.9, 2.9 Hz, H-3a), 4.19 (1H, dd, *J* = 10.9, 5.7 Hz, H-3b), 1.76 (1H, m, H-4), 2.52 (1H, m, H-5), 2.05 (1H, ddd, *J* = 13.4, 9.4, 4.0 Hz, H-6a), 1.93 (1H, dd, *J* = 13.4, 8.3 Hz, H-6b), 3.71 (1H, d, *J* = 3.9 Hz, H-7), 2.86 (1H, d, *J* = 10.9 Hz, H-9), 1.49 (3H, s, H-10), 3.59 (1H, dd, *J* = 11.2, 5.4 Hz, H-11a), 3.45 (1H, dd, *J* = 11.2, 8.4 Hz, H-11b). ^{13}C-NMR (100 MHz, MeOD) δ_C: 175.4 (C-1), 69.2 (C-3), 42.4 (C-4), 36.2 (C-5), 38.9 (C-6), 80.8 (C-7), 85.4 (C-8), 50.6 (C-9), 22.3 (C-10), 62.7 (C-11).

Apigenin-8-O-β-D-glucopyranoside ***(5):*** $C_{22}H_{23}O_{10}$, colorless oil, $[\alpha]_D^{20}$ -115.8 (c 0.41, MeOH), HR-FAB-MS *m/z* 447.1285 ($[M+H]^+$). ^{1}H-NMR (400 MHz, MeOD) δ_H: 6.87 (1H, s, H-3), 7.96 (1H, d, *J* = 8.4 Hz, H-6), 7.96 (1H, d, *J* = 8.4 Hz, H-8), 6.93 (1H, d, *J* = 2.1 Hz, H-2'), 6.94 (1H, d, *J* = 7.3 Hz, H-5'), 6.94 (1H, dd, *J* = 7.3, 2.1 Hz, H-6'), 5.08 (1H, d, *J* = 7.5 Hz, H-1″), 4.64 (1H, m, H-2″), 3.75 (1H, m, H-3″), 3.49 (1H, m, H-4″), 3.49 (1H, m, H-5″), 3.24 (2H, m, H-6″), 2.06 (3H, s, Me-3'). ^{13}C-NMR (100 MHz, MeOD) δ_C: 162.6 (C-2), 106.2 (C-3), 184.2 (C-4), 159.1 (C-5), 104.3 (C-6), 94.5 (C-7), 165.3 (C-8), 162.1 (C-9), 110.1 (C-10), 129.8 (C-1'), 117.3 (C-2'), 129.8 (C-3'), 156.2 (C-4'), 117.3 (C-5'), 122.4 (C-6'), 101.4 (C-1″), 77.8 (C-2″), 74.5 (C-3″), 70.8 (C-4″), 78.5 (C-5″), 61.9 (C-6″), 8.8 (3'-CH_3).

*Isosakuranetin-5-O-rutinoside (**6**):* $C_{28}H_{34}O_{14}$, white needles, $[\alpha]_D^{20}$ -105.3 (c 0.16, MeOH), FAB-MS *m/z* 594.2 ($[M]^+$). ^{1}H-NMR (400 MHz, MeOD) δ_H: 7.43 (2H, d, *J* = 8.7 Hz, H-2', 6'), 6.96 (2H, d, *J* = 8.8 Hz, H-3', 5'), 6.20 (1H, d, *J* = 2.2 Hz, H-6), 6.18 (1H, d, *J* = 2.2 Hz, H-8), 5.57 (1H, dd, *J* = 11.9, 2.9 Hz, H-2), 4.96 (1H, d, *J* = 7.5 Hz, H-1″), 4.51 (1H, brs, H-1‴), 3.80 (3H, s, 4'-OCH_3), 1.19 (3H, m, H-6‴). ^{13}C-NMR (100 MHz, MeOD) δ_C: 78.9 (C-2), 48.5 (C-3), 197.0 (C-4), 163.6 (C-5), 96.6 (C-6), 165.5 (C-7), 95.7 (C-8), 163.1 (C-9), 103.6 (C-10), 130.7 (C-1'), 127.6 (C-2'), 113.6 (C-3'), 160.1 (C-4'), 113.7 (C-5'), 127.7 (C-6'), 100.7 (C-1″), 73.2 (C-2″), 75.8 (C-3″), 69.9 (C-4″), 76.4 (C-5″), 66.0 (C-6″), 99.7 (C-1‴), 70.9 (C-2‴), 70.7 (C-3‴), 72.7 (C-4‴), 68.4 (C-5‴), 16.5 (C-6‴), 54.4 (4'-OCH_3).