Electronic Supplementary Information

A novel strategy for screening new natural products by combination of reversed-phase liquid chromatography fractionation and ^{13}C NMR pattern recognition: the discovery of new anti-cancer flavone dimers from *Dysosma versipellis* (Hance)

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Legends for Supplementary figures and tables

Fig. S1† (A-X) The ^{13}C NMR spectra of the fractions obtained by RPLC fractionation.

Table S1† The relative intensity of ^{13}C NMR signals of the fractions by RPLC fractionation (Level 0.005)

Table S2† Validation of the ^{13}C chemical shifts of the recognized and unrecognized podophyllotoxins (δC, ppm)[a,b]

Table S3† Validation of the ^{13}C chemical shifts of recognized and unrecognized flavonoids (δC, ppm)[a,b,c]

Fig. S2† ESI-MS, ESI-MS/MS, ESI-TOF-MS, and 1D and 2D NMR spectra of compound **9.**

Table S4† 1D and 2D NMR data of compound **9** (DMSO-*d6*, 500MHz for ^{1}H)

Fig. S3† ESI-MS, ESI-MS/MS, ESI-TOF-MS, and 1D and 2D NMR spectra of compound **12**.

Table S5† 1D and 2D NMR data of compound **12** (DMSO-*d6*, 500MHz for ^{1}H)

Fig. S4† ESI-MS, ESI-MS/MS, ESI-TOF-MS, and 1D and 2D NMR spectra of compound **13**.

Table S6† 1D and 2D NMR data of compound **13** (DMSO-*d6*, 500MHz for ^{1}H)

Fig. S5† ^{13}C NMR map-based pattern recognition of the metabolites of RPLC fractions. The minimum intensity threshold of ^{13}C NMR signals of fractions was set at 0.002.

Fig. S6† The known and new compounds identified by this strategy from *Dysosma versipellis* (Hance)

Fig. S7† ESI-MS, ESI-MS/MS, ESI-TOF-MS, and 1D and 2D NMR spectra of compound **10.**

Table S7† 1D and 2D NMR data of compound **10** (DMSO-*d6*, 500MHz for ^{1}H)

Fig. S8† ESI-MS, ESI-MS/MS, ESI-TOF-MS, and 1D and 2D NMR spectra of compound **11**.

Table S8† 1D and 2D NMR data of compound **11** (DMSO-*d6*, 600MHz for ^{1}H)

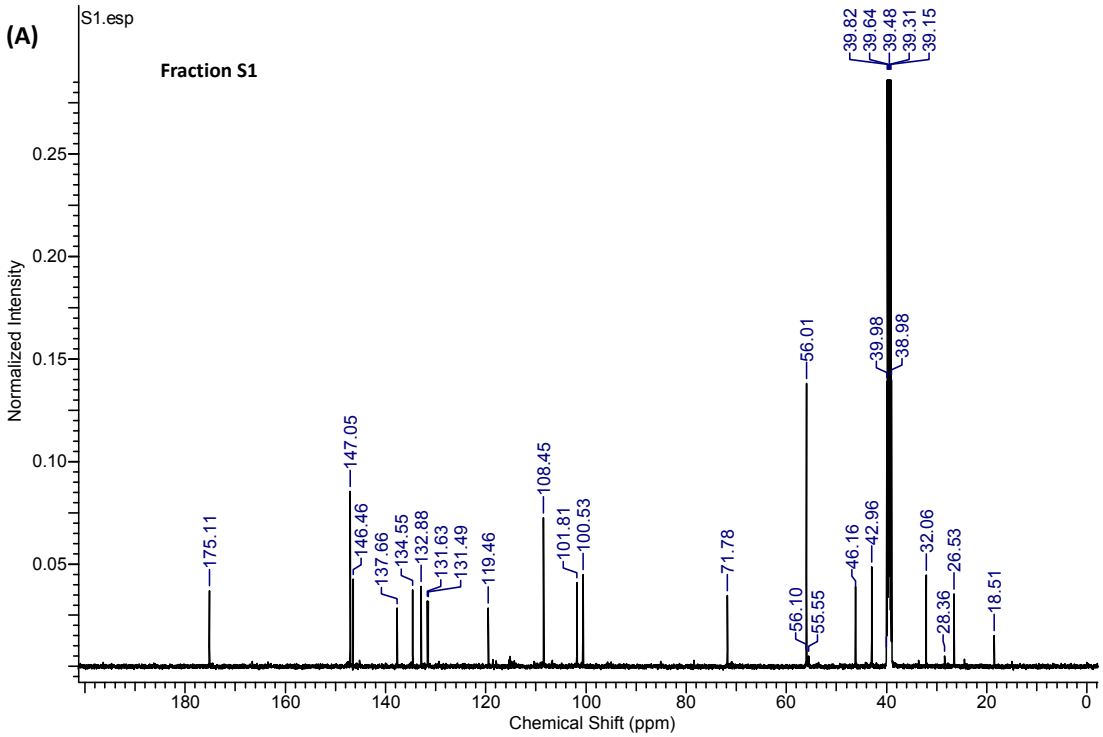
Fig. S9† ESI-MS, ESI-MS/MS, ESI-TOF-MS, and 1D and 2D NMR spectra of compound **14**.

Table S9† 1D and 2D NMR data of compound **14** (DMSO-*d6*, 600MHz for ^{1}H)

Fig. S10† ESI-MS, ESI-MS/MS, ESI-TOF-MS, and 1D and 2D NMR spectra of compound **15**.

Table S10† 1D and 2D NMR data of compound **15** (DMSO-*d6*, 600MHz for ^{1}H)

Fig. S11† CD spectra of compounds **10**-**15**. The samples were dissolved in ethanol at concentrations of 0.1 mg/mL. The CD signal was recorded every 0.5 nm with a 0.5s signal averaging for each point. Each spectrum was recorded twice and averaged.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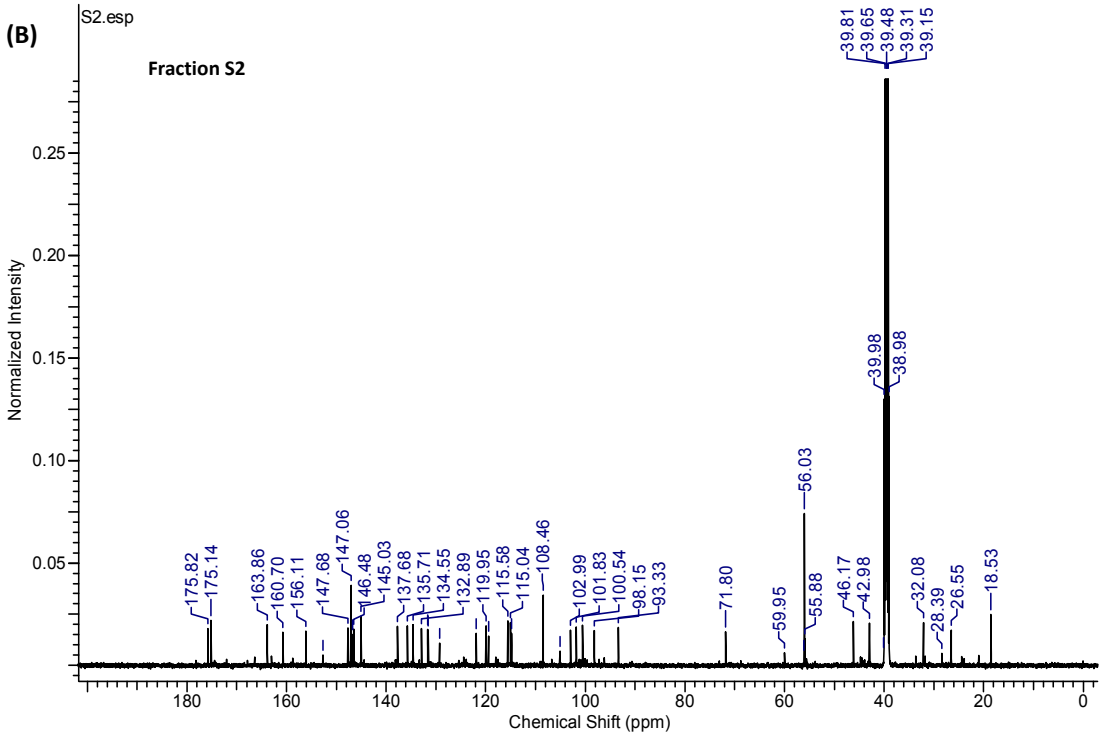
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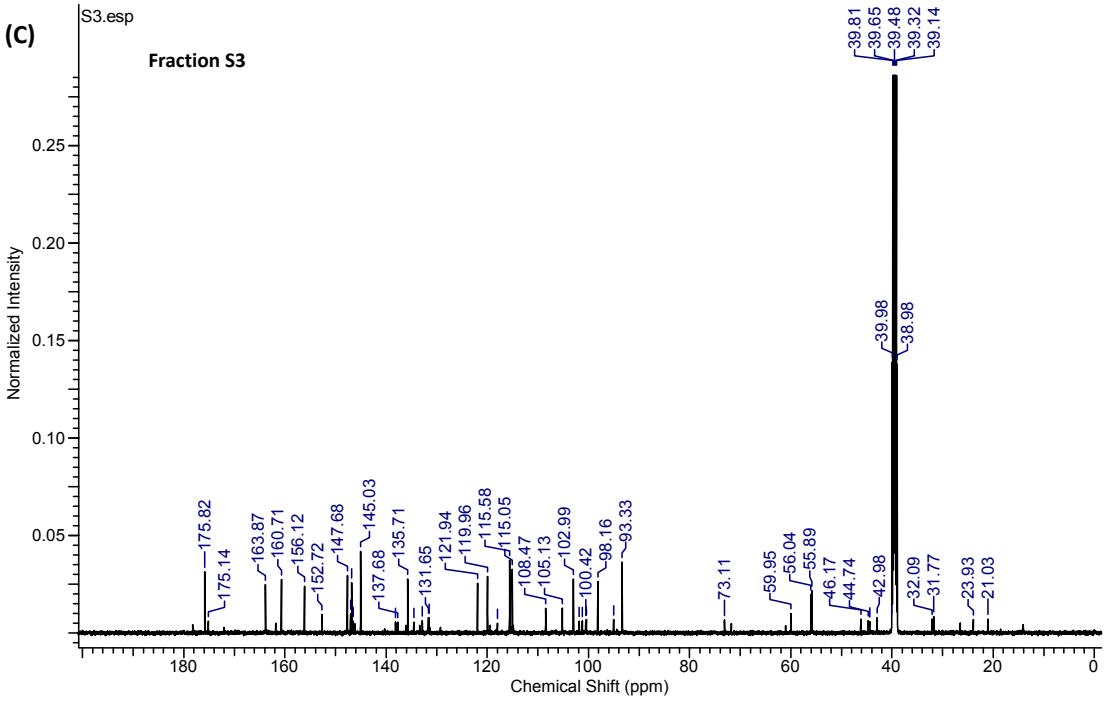
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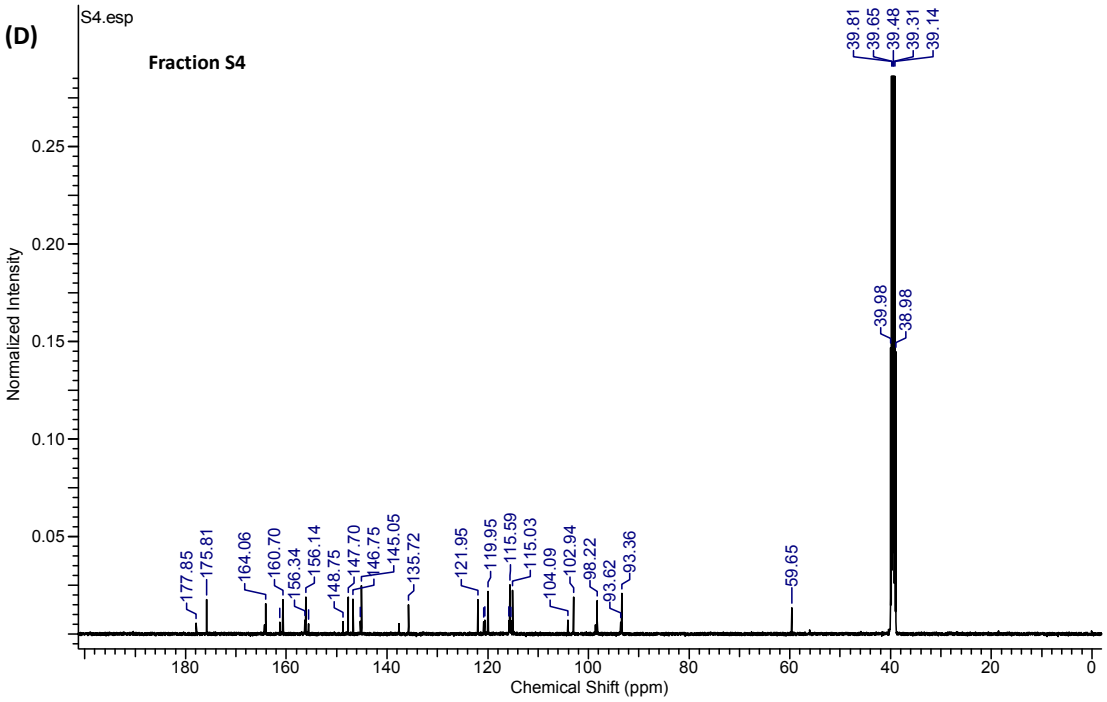
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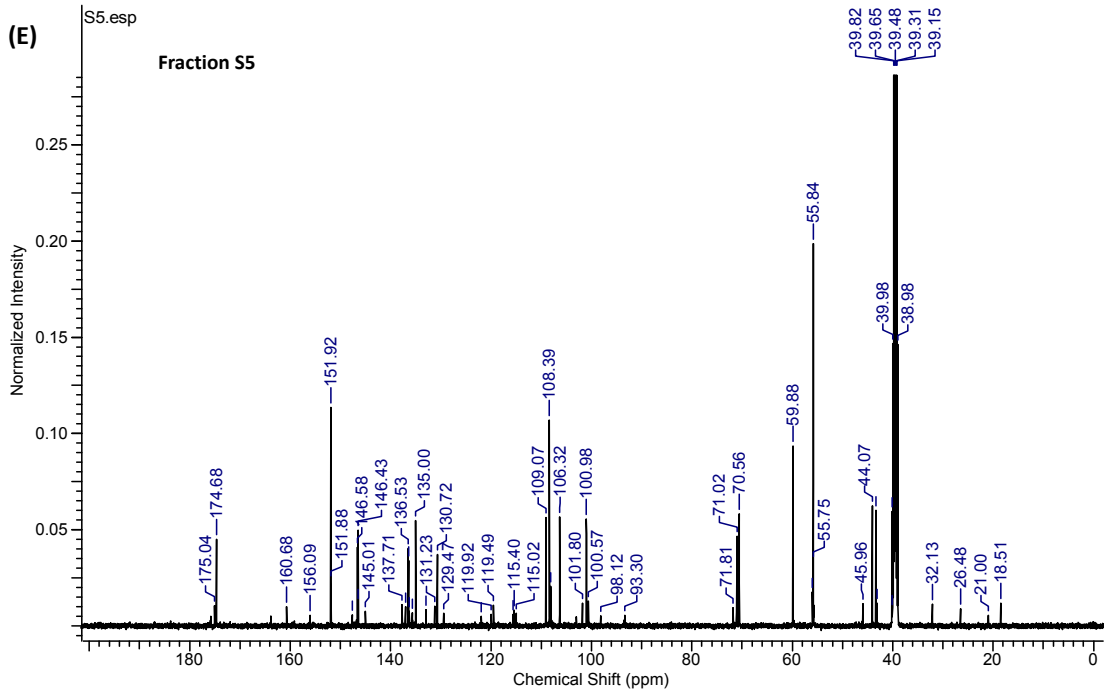
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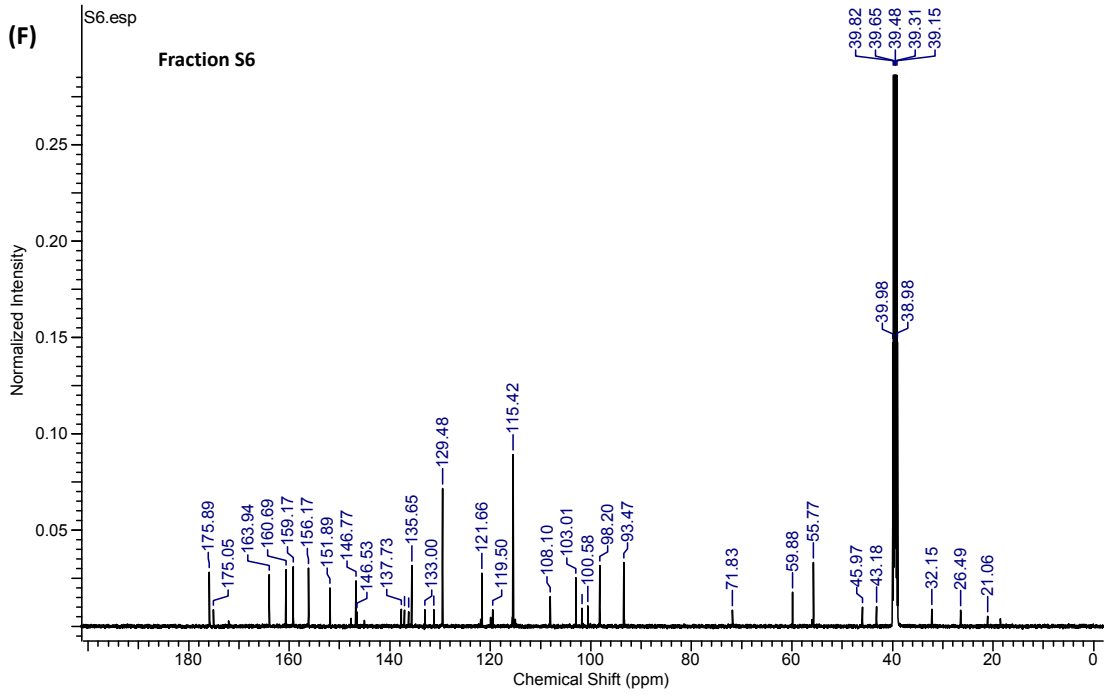
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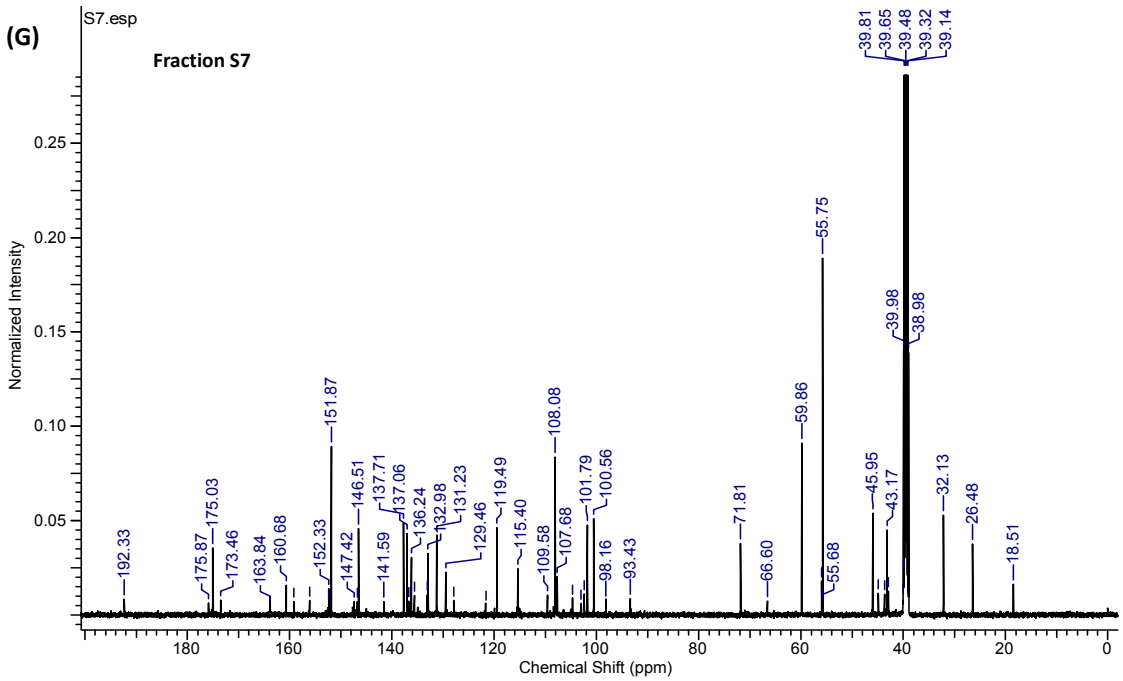
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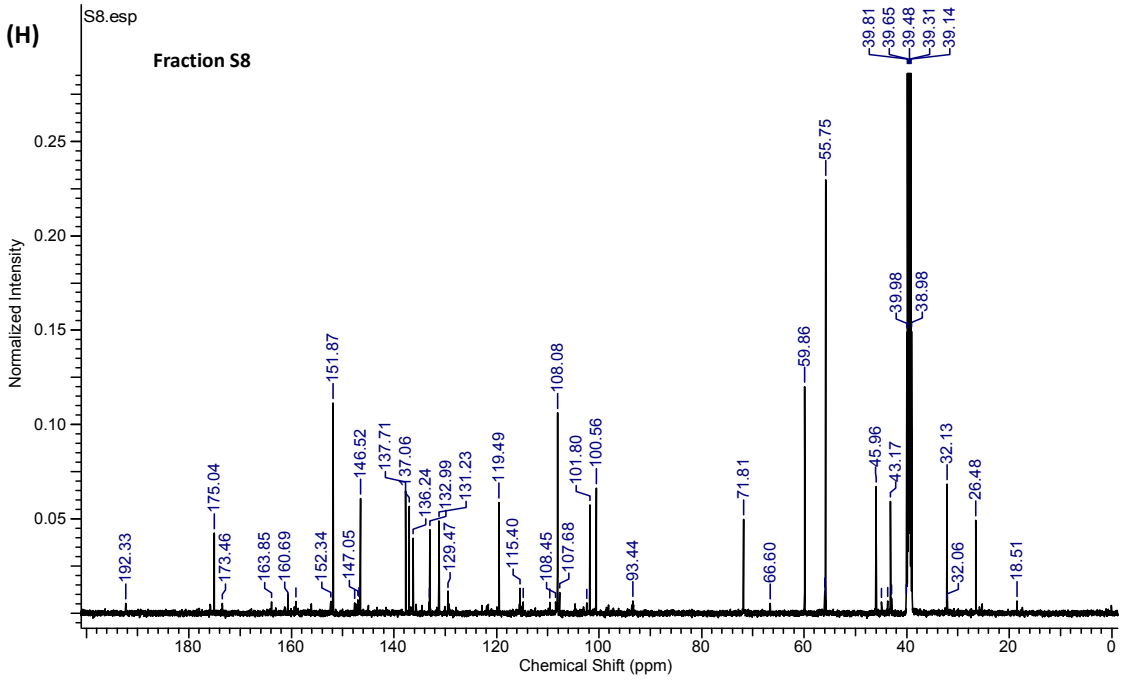
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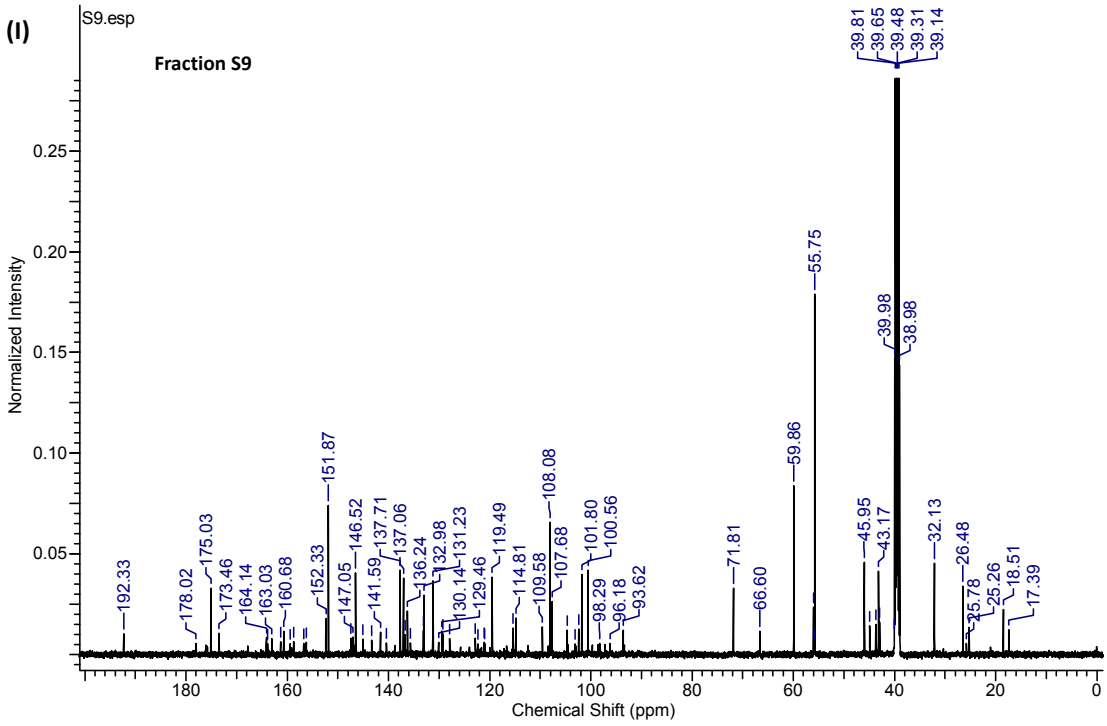
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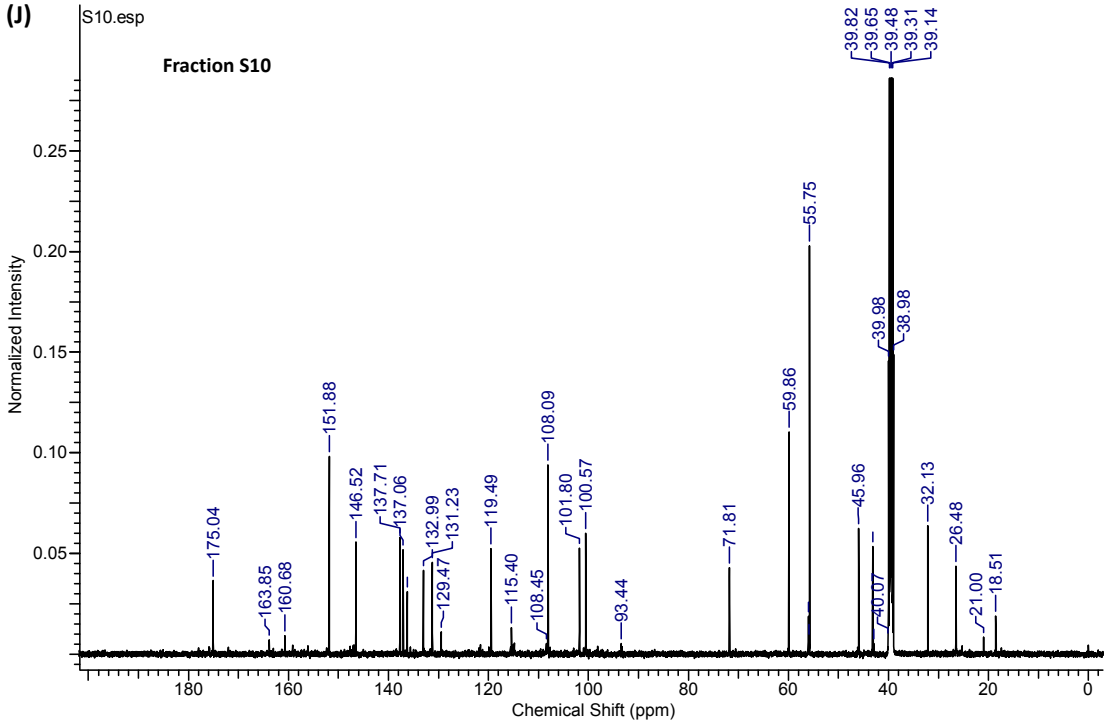
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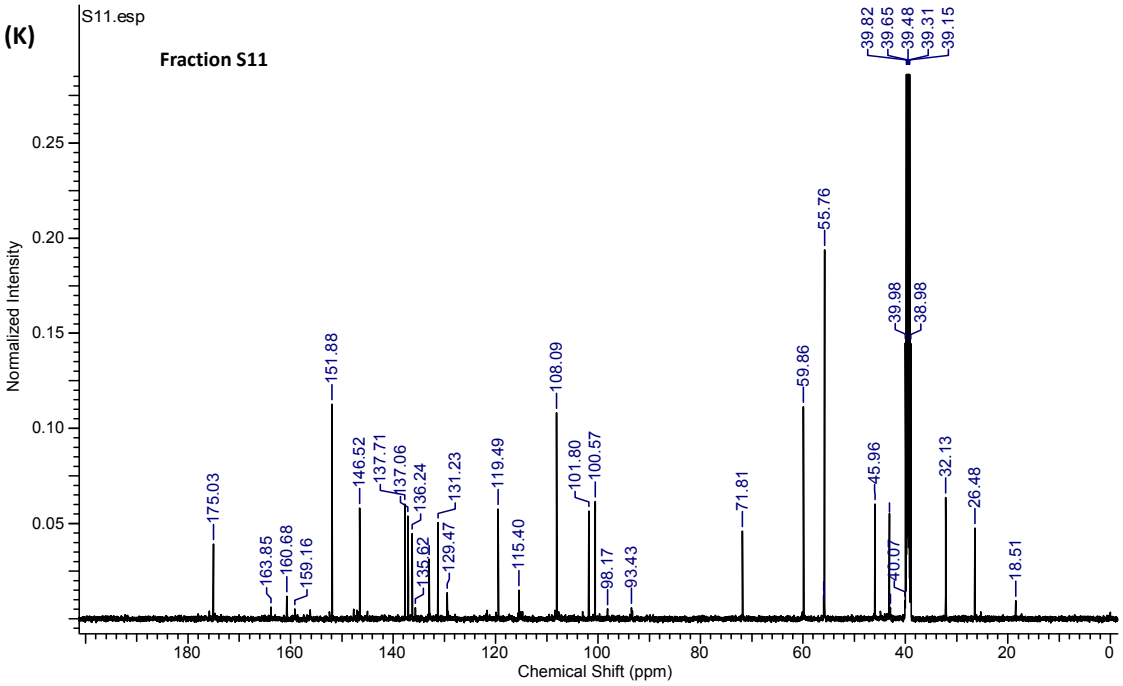
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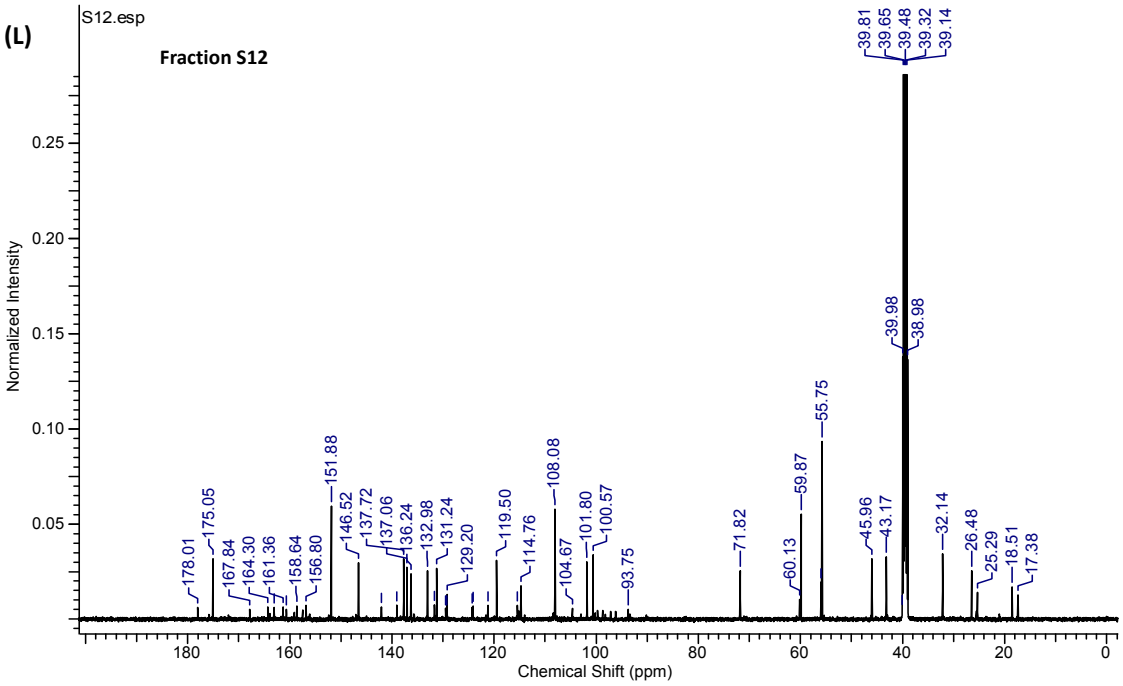
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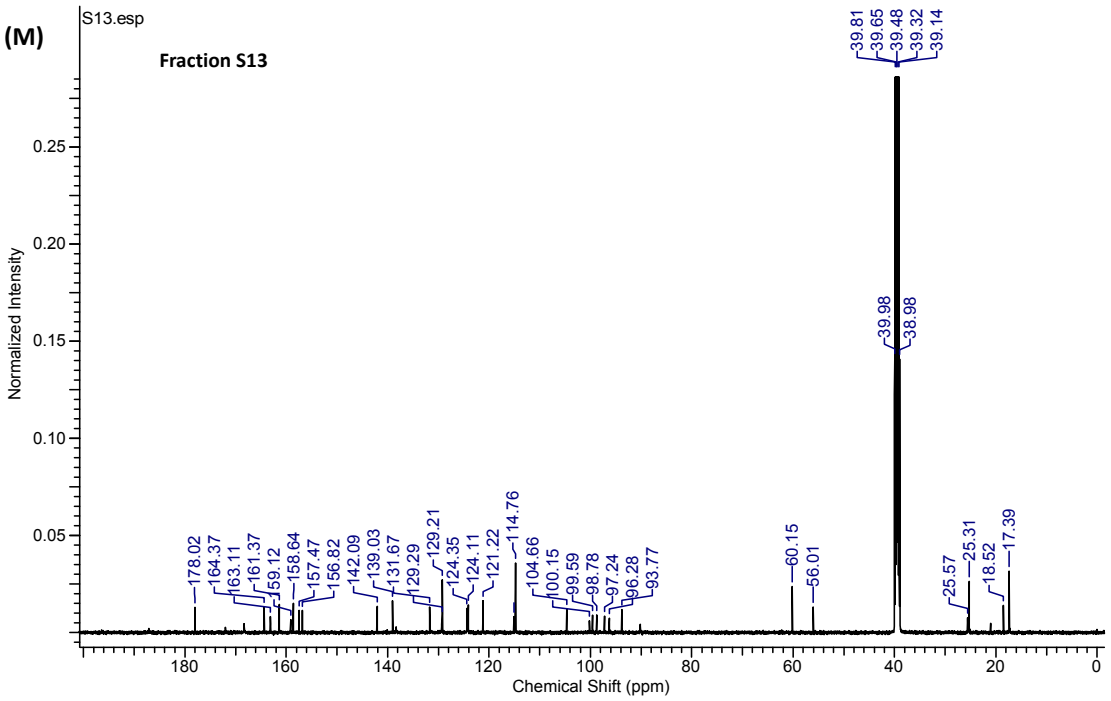
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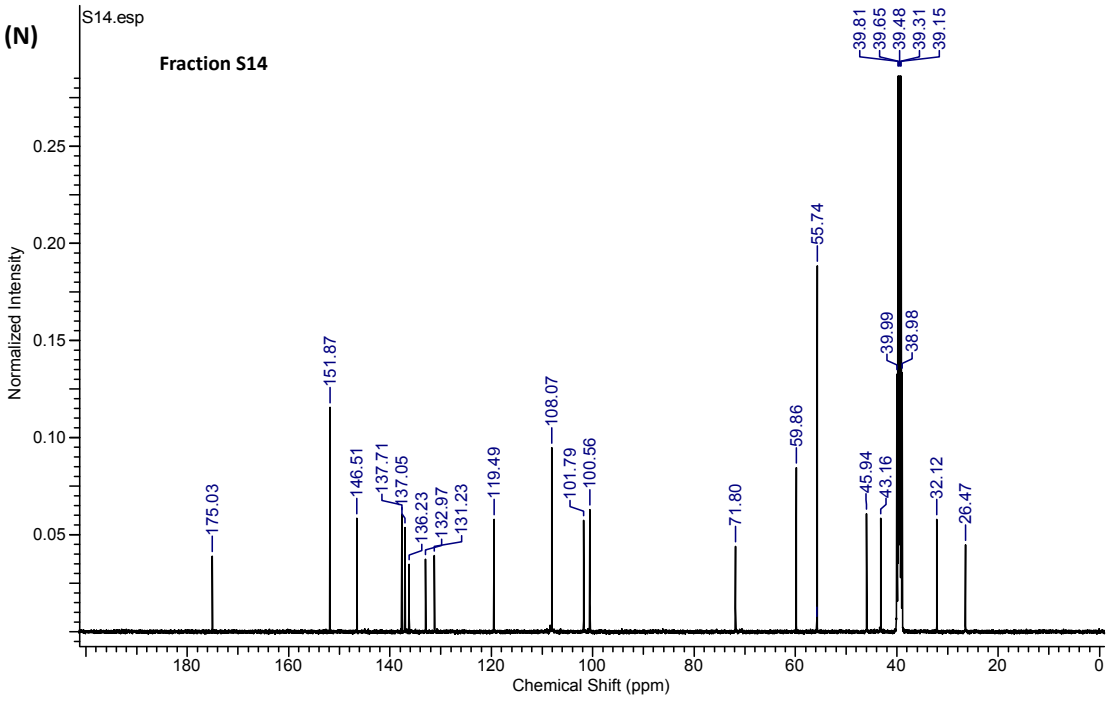
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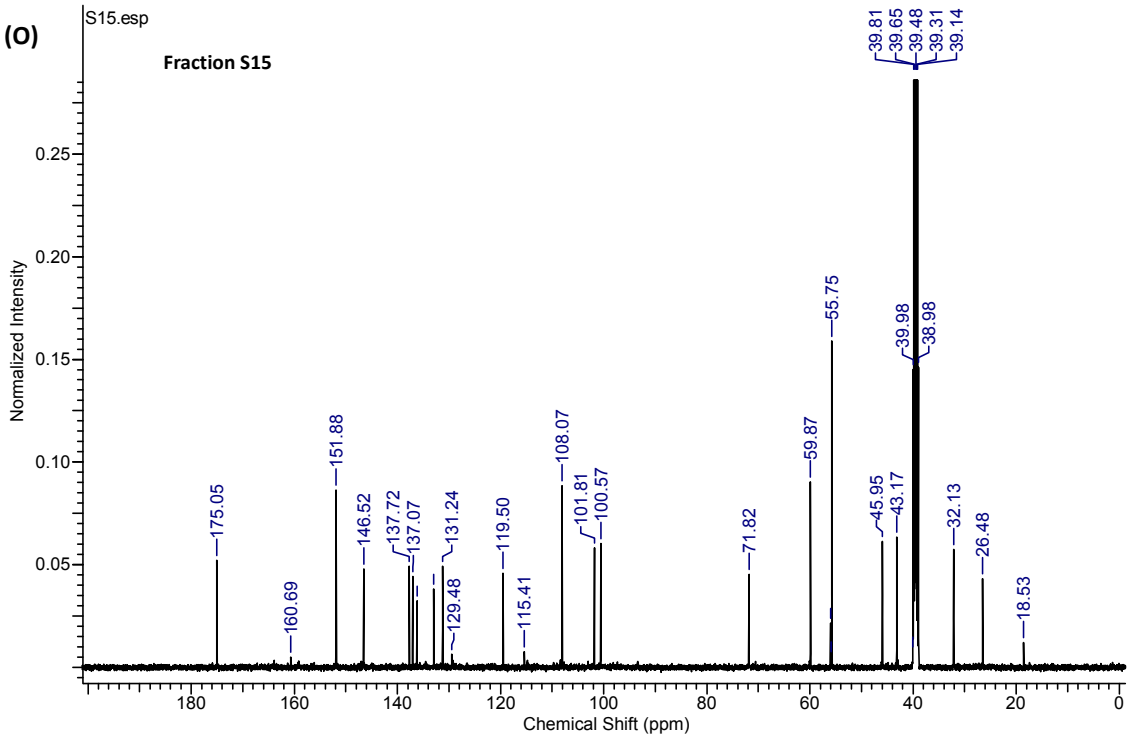
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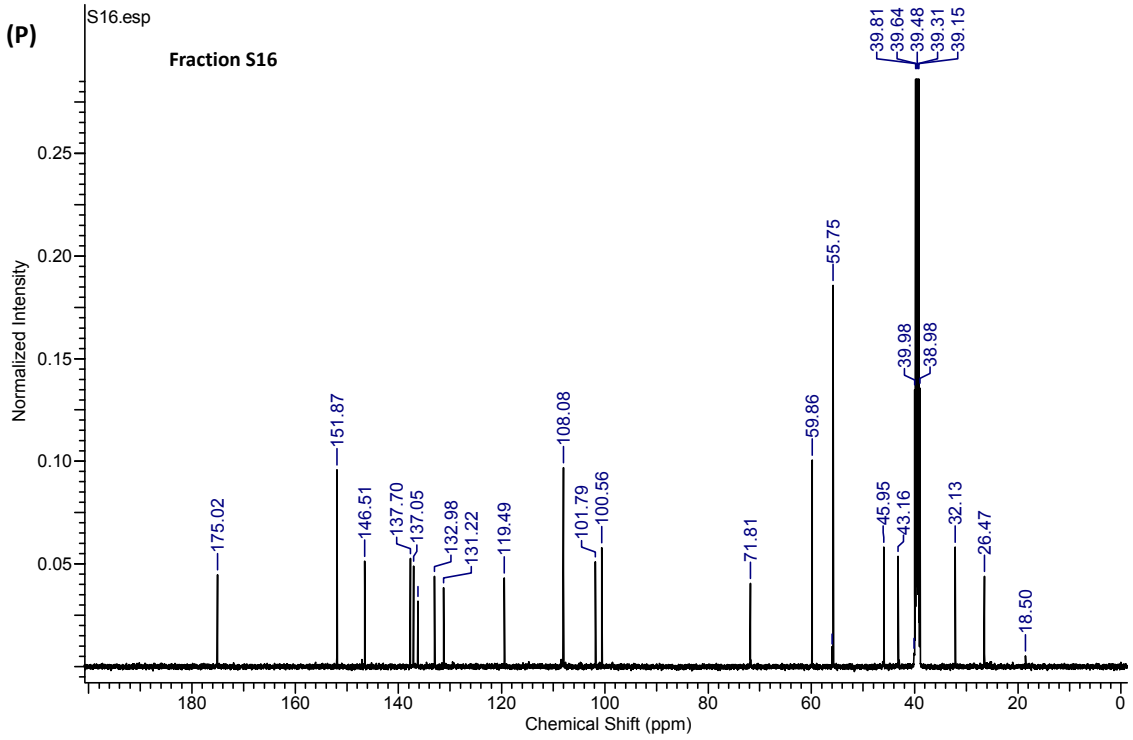
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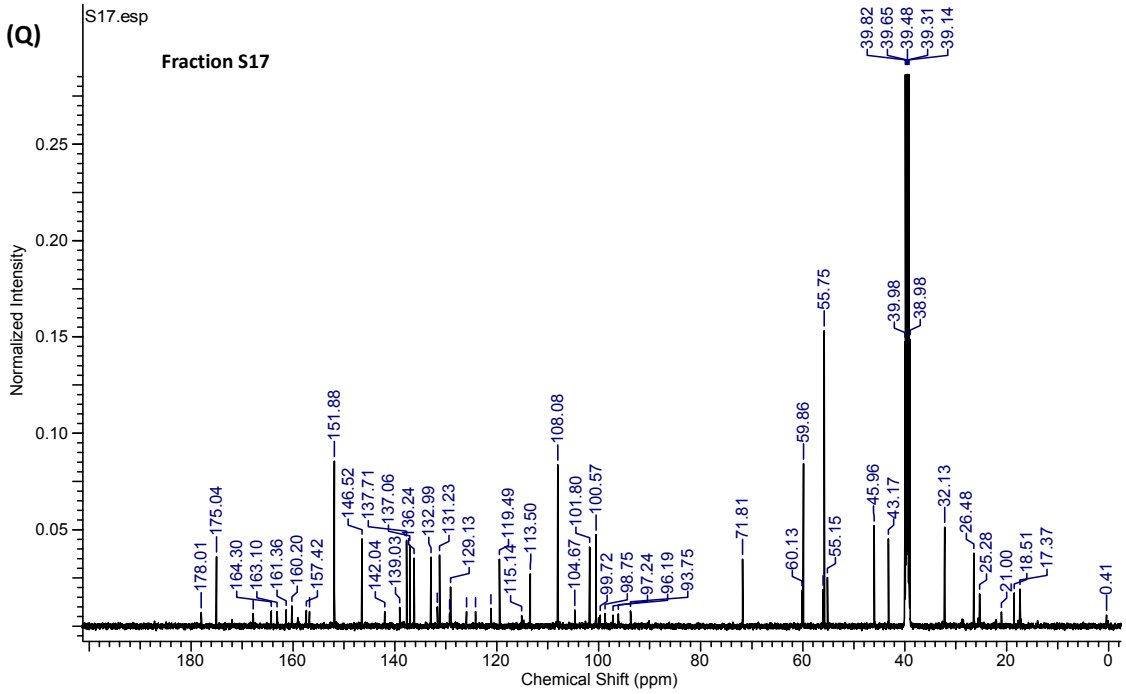
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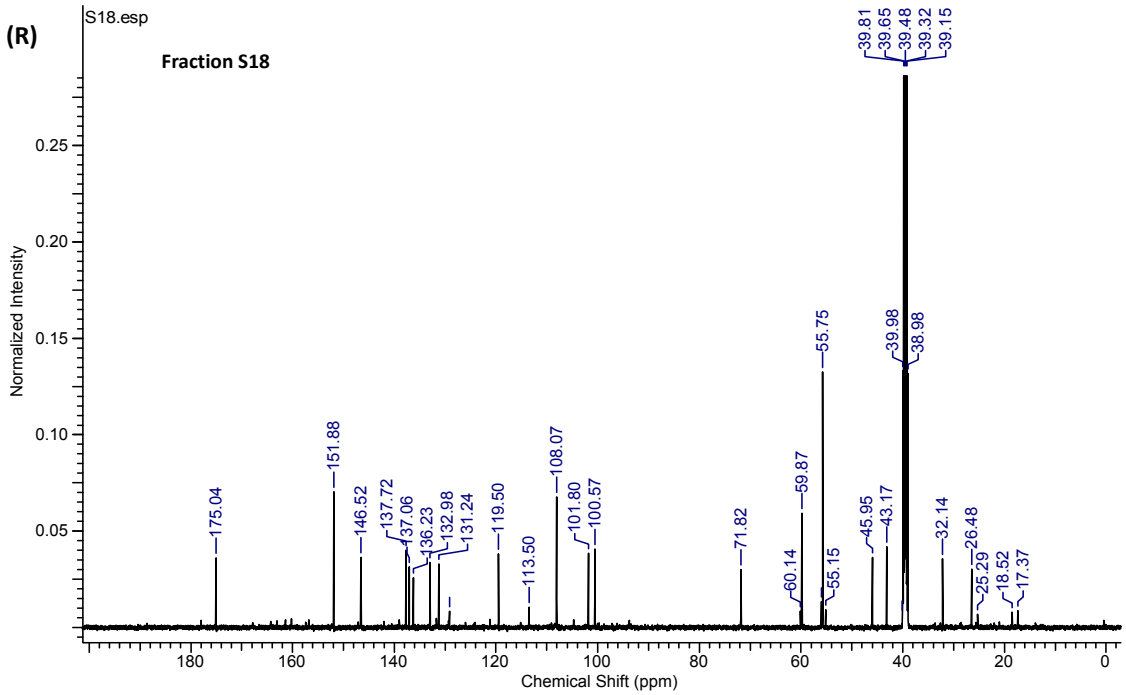
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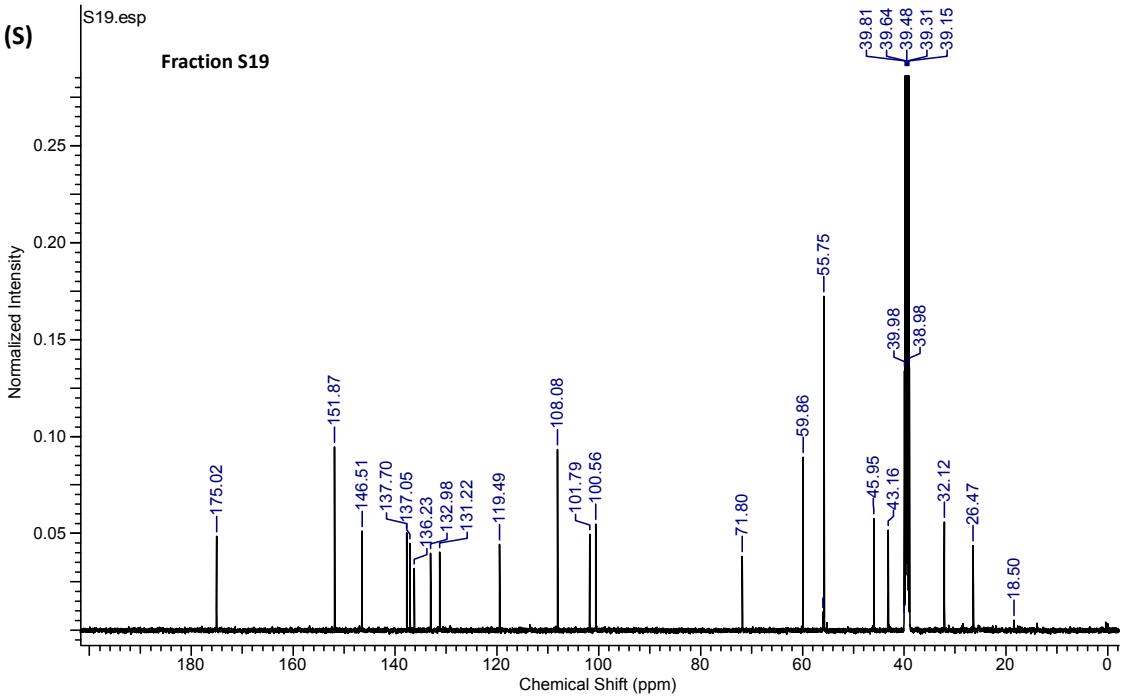
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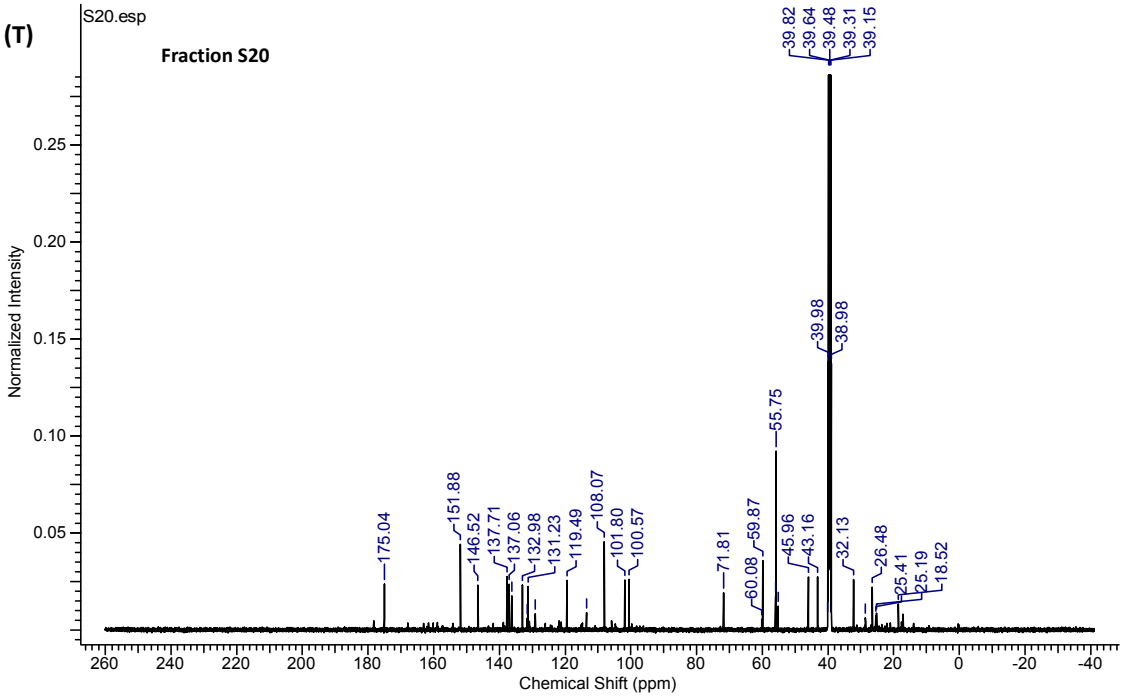
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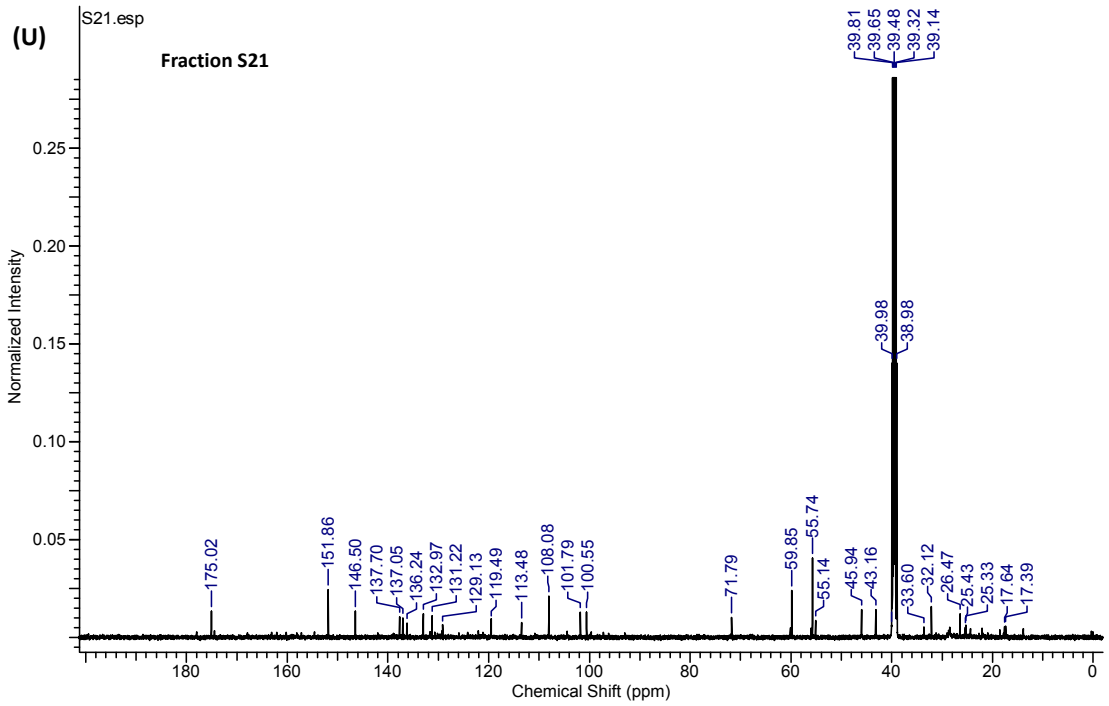
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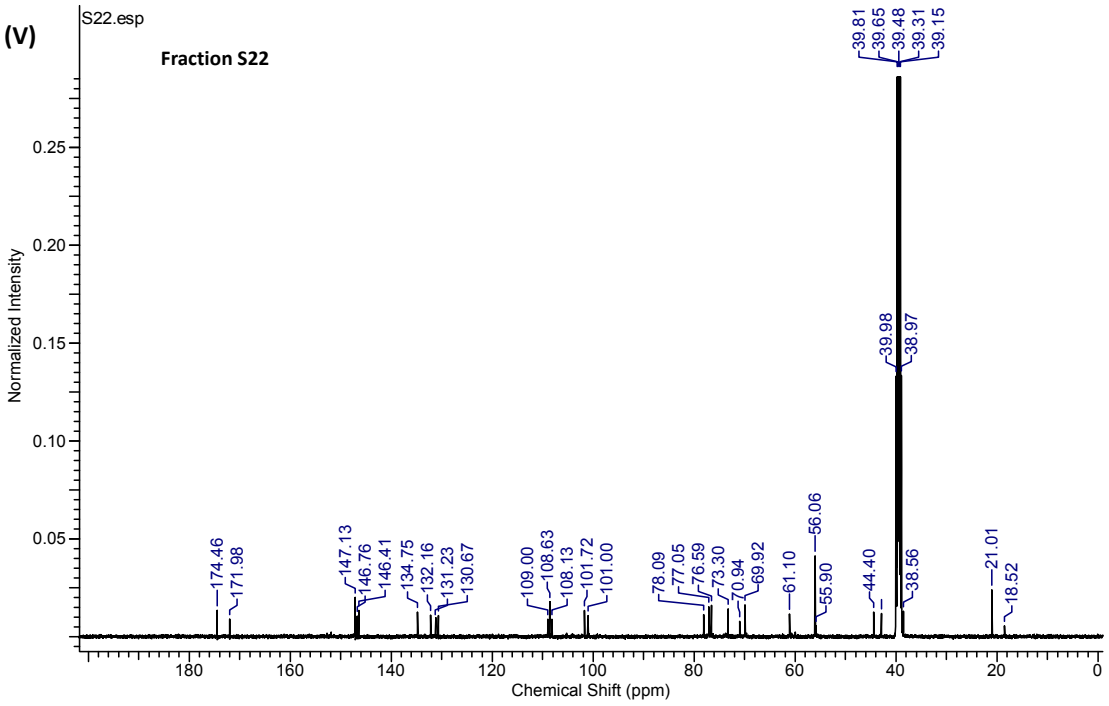
113.48
108.08
101.79
100.55
71.79
59.85
55.74
55.14
45.94
43.16
33.60
32.12
26.47
25.43
25.33
17.64
17.39


(V)
S22.esp
Fraction S22
Normalized Intensity
Chemical Shift (ppm)
39.81
39.65
39.48
39.31
39.15
39.98
38.97
174.46
171.98
147.13
146.76
146.41
134.75
132.16
131.23
130.67
109.00
108.63
108.13
101.72
101.00
78.09
77.05
76.59
73.30
70.94
69.92
61.10
56.06
55.90
44.40
38.56
21.01
18.52

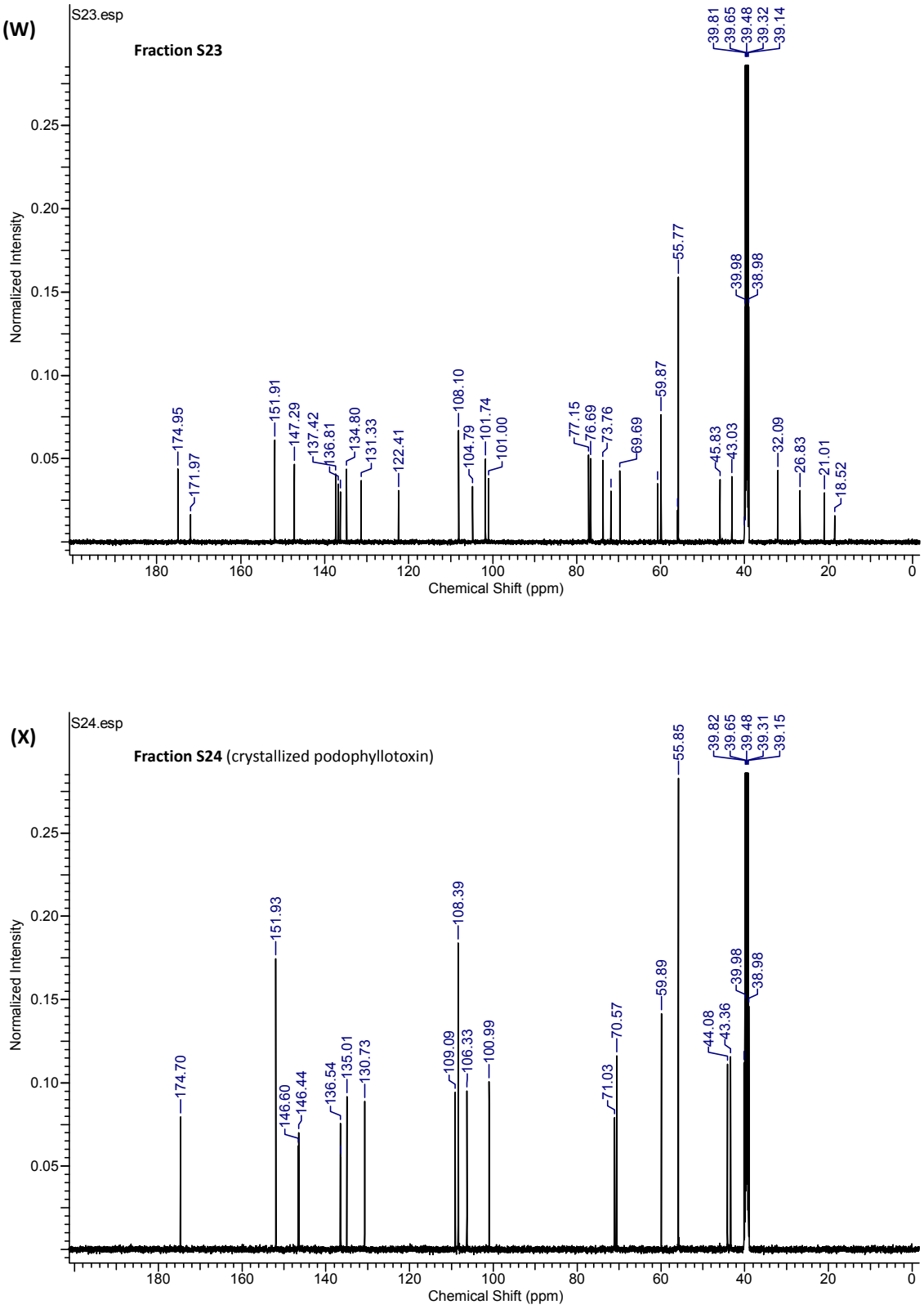


Fig. S1[†] **(A-X)** The ^{13}C NMR spectra of the fractions obtained by RPLC fractionation

Table S1[†] The relative intensity of ^{13}C NMR signals of the fractions by RPLC fractionation (Level 0.005)

NO.	^{13}C NMR shifts	RPLC fractions																						6
		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24
1	0.409	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.006	0	0	0	0	0	0	0
2	17.383	0	0	0	0	0	0	0	0	0.012	0	0	0.013	0.032	0	0	0	0.019	0.009	0	0	0.006	0	0	0
3	17.642	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.006	0	0	0
4	18.514	0.015	0.025	0	0	0.012	0	0.016	0.007	0.023	0.019	0.01	0.017	0.014	0	0.012	0.005	0.017	0.008	0.005	0.013	0	0.005	0.016	0
5	21.015	0	0	0.007	0	0.006	0.005	0	0	0	0.008	0	0	0	0	0	0	0.007	0	0	0	0	0.024	0.03	0
6	23.929	0	0	0.007	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
7	25.279	0	0	0	0	0	0	0	0	0.014	0	0	0.014	0.026	0	0	0	0.017	0.007	0	0.009	0.006	0	0	0
8	25.546	0	0	0	0	0	0	0	0	0.006	0	0	0	0.008	0	0	0	0	0	0	0.007	0.005	0	0	0
9	26.502	0.035	0.017	0	0	0.009	0.008	0.038	0.049	0.034	0.044	0.048	0.025	0	0.045	0.043	0.044	0.038	0.03	0.044	0.022	0.012	0	0.031	0
10	28.448	0.005	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.006	0	0	0	0
11	31.770	0	0	0.008	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
12	32.076	0.045	0.021	0.007	0	0	0	0	0.005	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.043	0
13	32.131	0	0	0	0	0.011	0.009	0.053	0.068	0.045	0.064	0.064	0.034	0	0.058	0.057	0.058	0.051	0.036	0.056	0.026	0.016	0	0	0
14	33.599	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.005	0	0	0
15	38.561	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.013	0	0
16	39.905	0	0	0	0	0	0	0.023	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
17	40.072	0.007	0.007	0.007	0	0.009	0	0.009	0.008	0.01	0.008	0.009	0.006	0	0	0.008	0.007	0.008	0.007	0.007	0.007	0.006	0	0.008	0.01
18	40.147	0	0	0	0	0.059	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.11
19	42.964	0.049	0.021	0.008	0	0	0	0.013	0.008	0.016	0.005	0.006	0	0	0	0	0	0	0	0	0	0	0.012	0.039	0
20	43.167	0	0	0	0	0.012	0.01	0.045	0.059	0.041	0.053	0.054	0.033	0	0.058	0.064	0.054	0.045	0.042	0.052	0.027	0.014	0	0	0
21	43.551	0	0	0	0	0.06	0	0.011	0.006	0.015	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.12
22	44.245	0	0	0.006	0	0.062	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.012	0	0.11
23	44.837	0	0	0.006	0	0	0	0.012	0.006	0.014	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
24	45.980	0.037	0.022	0.007	0	0.012	0.01	0.054	0.067	0.046	0.062	0.06	0.032	0	0.061	0.061	0.058	0.052	0.036	0.058	0.027	0.014	0	0.037	0
25	55.147	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.025	0.009	0	0.012	0.009	0	0	0
26	55.617	0.005	0	0	0	0	0	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
27	55.753	0	0	0	0	0.034	0.033	0.189	0.23	0.179	0.203	0.194	0.093	0	0.189	0.159	0.186	0.153	0.133	0.172	0.092	0.04	0	0.159	0
28	55.854	0	0.013	0.022	0	0.199	0	0.008	0.007	0.005	0.008	0.008	0	0	0.006	0.005	0	0	0	0	0	0	0.005	0	0.28
29	55.997	0.138	0	0	0	0.018	0	0.018	0.012	0.023	0.019	0.012	0.019	0.013	0	0.022	0.009	0.019	0.013	0.01	0.017	0	0	0.019	0
30	56.042	0	0.074	0.02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.041	0	0
31	56.103	0.006	0.005	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
32	59.865	0	0.006	0.01	0.013	0.094	0.018	0.091	0.12	0.084	0.11	0.112	0.055	0	0.084	0.09	0.101	0.084	0.059	0.089	0.036	0.024	0	0.076	0.14
33	60.123	0	0	0	0	0	0	0	0	0	0	0	0.01	0.024	0	0	0	0.019	0.009	0	0.006	0	0	0	0
34	60.903	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.012	0.035	0
35	66.600	0	0	0	0	0	0	0.007	0.005	0.012	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
36	69.806	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.016	0.043	0
37	70.568	0	0	0	0	0.058	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.12
38	71.000	0	0	0	0	0.047	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.008	0	0.08
39	71.810	0.035	0.017	0	0	0.009	0.008	0.038	0.05	0.033	0.043	0.046	0.026	0	0.044	0.045	0.041	0.035	0.03	0.038	0.019	0.01	0	0.031	0
40	73.202	0	0	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.014	0	0
41	73.760	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.049	0
42	76.640	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.016	0.05	0
43	77.100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.015	0.052	0
44	78.087	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.011	0	0
45	93.394	0	0.018	0.036	0.021	0.006	0.033	0.008	0.007	0	0.005	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0
46	93.701	0	0	0	0.006	0	0	0	0	0.012	0	0	0.005	0.012	0	0	0	0.008	0	0	0	0	0	0	0
47	95.048	0	0	0.007	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
48	96.217	0	0	0	0	0	0	0	0	0.006	0	0	0	0.007	0	0	0	0.006	0	0	0	0	0	0	0
49	97.237	0	0	0	0	0	0	0	0	0	0	0	0	0.008	0	0	0	0.006	0	0	0	0	0	0	0
50	98.184	0	0.017	0.026	0.017	0.005	0.032	0.008	0	0.005	0	0.005	0	0	0	0	0	0	0	0	0	0	0	0	0
51	98.767	0	0	0	0	0	0	0	0	0	0	0	0	0.009	0	0	0	0.007	0	0	0	0	0	0	0
52	99.654	0	0	0	0	0	0	0	0	0	0	0	0	0.009	0	0	0	0.006	0	0	0	0	0	0	0
53	100.283	0	0	0.007	0	0	0	0	0	0	0	0	0	0.006	0	0	0	0	0	0	0	0	0	0	0
54	100.562	0.045	0.019	0.006	0	0.013	0.01	0.051	0.066	0.042	0.06	0.062	0.034	0	0.063	0.06	0.058	0.047	0.041	0.055	0.026	0.013	0	0	0
55	101.044	0	0	0.006	0	0.056	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.011	0.038	0.1
56	101.795	0.041	0.019	0.006	0	0.012	0.01	0.048	0.057	0.04	0.053	0.057	0.03	0	0.057	0.058	0.051	0.041	0.039	0.05	0.026	0.013	0.013	0.05	0
57	102.393	0	0	0	0	0	0	0.011	0.006	0.013	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
58	103.015	0	0.017	0.028	0.019	0	0.025	0.006	0	0.005	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
59	104.095	0	0	0	0.007	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
60	104.697	0	0	0	0	0	0	0.009	0	0.012	0	0	0.006	0.012	0	0	0	0.008	0	0	0	0	0	0.033	0
61	105.126	0	0.007	0.013	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
62	106.325	0	0	0	0	0.057	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.1
63	107.679	0	0	0	0	0	0	0.02	0.011	0.026	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

64	108.084	0	0	0	0	0.021	0.016	0.084	0.106	0.066	0.094	0.108	0.058	0	0.095	0.088	0.097	0.084	0.068	0.093	0.046	0.021	0.009	0.067	0
65	108.461	0.073	0.034	0.013	0	0.107	0	0	0.006	0	0.005	0	0	0	0	0	0	0	0	0	0	0	0.018	0	0.18
66	109.052	0	0	0	0	0.056	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.009	0	0.09
67	109.582	0	0	0	0	0	0	0.01	0.006	0.014	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
68	113.489	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.027	0.011	0	0.009	0.007	0	0	0
69	114.796	0	0.016	0	0	0	0	0	0.006	0.018	0	0	0.018	0.036	0	0	0	0	0	0	0	0	0	0	0
70	115.066	0	0.021	0.033	0.022	0.006	0	0	0	0	0	0	0	0.008	0	0	0	0.006	0	0	0	0	0	0	0
71	115.403	0	0	0	0.007	0.008	0.089	0.024	0.013	0.013	0.013	0.015	0.007	0	0	0.008	0	0	0	0	0	0	0	0	0
72	115.577	0	0.022	0.037	0.025	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
73	115.759	0	0	0	0.007	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
74	118.000	0	0	0.005	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
75	119.489	0.029	0.014	0	0	0.011	0.009	0.046	0.059	0.039	0.052	0.058	0.031	0	0.058	0.046	0.043	0.035	0.038	0.044	0.025	0.009	0	0	0
76	119.945	0	0.019	0.029	0.022	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
77	120.567	0	0	0	0.007	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
78	120.769	0	0	0	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
79	120.989	0	0	0	0	0	0	0	0	0.005	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
80	121.166	0	0	0	0	0	0	0	0	0.006	0	0	0.007	0.016	0	0	0	0.009	0	0	0	0	0	0	0
81	121.841	0	0.016	0.025	0.018	0.005	0.028	0.005	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
82	122.395	0	0	0	0	0	0	0	0	0.005	0	0	0	0	0	0	0	0	0	0	0	0	0	0.031	0
83	122.818	0	0	0	0	0	0	0	0	0.008	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
84	124.132	0	0	0	0	0	0	0	0	0	0	0	0.007	0.014	0	0	0	0.008	0	0	0	0	0	0	0
85	124.324	0	0	0	0	0	0	0	0	0	0	0	0.006	0.012	0	0	0	0	0	0	0	0	0	0	0
86	125.972	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.008	0	0	0	0	0	0	0
87	127.873	0	0	0	0	0	0	0.008	0	0.008	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
88	129.145	0	0	0	0	0	0	0	0	0	0	0	0.013	0.027	0	0	0	0.02	0.009	0	0.008	0.006	0	0	0
89	129.290	0	0.011	0	0	0	0	0	0	0.01	0	0	0.005	0.008	0	0	0	0.007	0	0	0	0	0	0	0
90	129.470	0	0	0	0	0.007	0.072	0.023	0.011	0.012	0.011	0.014	0.005	0	0	0.006	0	0	0	0	0	0	0	0	0
91	130.135	0	0	0	0	0	0	0	0	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
92	130.702	0	0	0	0	0.037	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.011	0	0.09
93	131.235	0	0	0	0	0.01	0.009	0.042	0.049	0.037	0.046	0.051	0.027	0	0.039	0.049	0.038	0.037	0.033	0.04	0.022	0.011	0.009	0.037	0
94	131.507	0.032	0.017	0.008	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
95	131.655	0.032	0.018	0.008	0	0	0	0	0	0	0	0	0.007	0.013	0	0	0	0.01	0	0	0.006	0	0	0	0
96	132.163	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.011	0	0
97	132.967	0.039	0.018	0.006	0	0.009	0.009	0.033	0.044	0.03	0.042	0.031	0.026	0	0.037	0.038	0.044	0.036	0.034	0.04	0.023	0.012	0	0	0
98	133.113	0	0	0	0	0	0	0.011	0.006	0.012	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
99	134.644	0.037	0.02	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.013	0.044	0
100	135.004	0	0	0	0	0.055	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.09
101	135.670	0	0.019	0.028	0.015	0.007	0.032	0.01	0	0.006	0	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0
102	136.239	0	0	0	0	0.008	0.008	0.03	0.04	0.022	0.031	0.045	0.024	0	0.035	0.033	0.032	0.035	0.026	0.032	0.018	0.007	0	0.03	0
103	136.415	0	0	0	0	0.034	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.06
104	136.660	0	0	0	0	0.04	0	0.007	0	0.01	0	0	0	0	0	0	0	0	0	0	0	0	0	0.035	0.08
105	137.059	0	0	0	0	0.01	0.008	0.043	0.057	0.038	0.052	0.054	0.027	0	0.054	0.044	0.049	0.042	0.031	0.045	0.024	0.01	0	0	0
106	137.691	0.028	0.019	0.005	0	0.011	0.009	0.049	0.065	0.042	0.058	0.06	0.032	0	0.061	0.049	0.053	0.045	0.04	0.05	0.028	0.01	0	0.041	0
107	138.140	0	0	0.005	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
108	139.033	0	0	0	0	0	0	0	0	0	0	0	0.007	0.016	0	0	0	0.01	0	0	0	0	0	0	0
109	140.375	0	0	0	0	0	0	0	0	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
110	141.588	0	0	0	0	0	0	0.007	0	0.011	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
111	142.069	0	0	0	0	0	0	0	0	0	0	0	0.006	0.013	0	0	0	0.008	0	0	0	0	0	0	0
112	143.289	0	0	0	0	0	0	0	0	0.007	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
113	145.035	0	0.024	0.042	0.025	0.008	0	0	0	0.008	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
114	145.257	0	0	0	0.007	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
115	146.451	0.042	0.018	0.006	0	0.05	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.013	0	0.07
116	146.517	0	0	0	0	0.012	0.007	0.046	0.061	0.04	0.055	0.058	0.03	0	0.058	0.048	0.051	0.045	0.036	0.051	0.023	0.013	0	0	0
117	146.731	0	0.015	0.026	0.018	0.041	0.024	0.007	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0	0.011	0	0.06
118	147.069	0.086	0.039	0.01	0	0	0	0	0.007	0.009	0	0	0	0	0	0	0	0	0	0	0	0	0.02	0	0
119	147.379	0	0	0	0	0	0	0.007	0	0.008	0	0	0	0	0	0	0	0	0	0	0	0	0	0.047	0
120	147.675	0	0.018	0.03	0.019	0.006	0	0	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
121	148.749	0	0	0	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
122	151.875	0	0	0	0	0.024	0	0.089	0.111	0.074	0.098	0.113	0.059	0	0.116	0.086	0.096	0.086	0.07	0.095	0.044	0.024	0	0	0
123	151.915	0	0	0	0	0.114	0.02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.061	0.18
124	152.334	0	0	0	0	0	0	0.014	0.006	0.018	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
125	152.553	0	0.005	0.01	0	0	0	0.006	0	0.009	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
126	155.561	0	0	0	0.005	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
127	156.127	0	0.017	0.024	0.019	0.005	0.03	0.008	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
128	156.300	0	0	0	0.007	0	0	0	0	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
129	156.787	0	0	0	0	0	0	0	0	0.006	0	0	0.007	0.011	0	0	0	0.008	0	0	0	0	0	0	0
130	157.445	0	0	0	0	0	0	0	0	0	0	0	0	0.011	0	0	0	0.008	0	0	0	0	0	0	0
131	158.663	0	0	0	0	0	0	0	0	0.006	0	0	0.007	0.015	0	0	0	0	0	0	0	0	0	0	0
132	159.196	0	0	0	0	0	0.031	0.007	0.006	0.005	0	0.005	0	0.007	0	0	0	0	0	0	0	0	0	0	0

133	160.204	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.01	0	0	0	0	0	0	0
134	160.689	0	0.016	0.027	0.018	0.01	0.029	0.016	0.006	0.012	0.009	0.012	0.005	0	0	0.005	0	0	0	0	0	0	0	0
135	161.334	0	0	0	0.006	0	0	0	0	0.006	0	0	0.006	0.015	0	0	0	0.008	0	0	0	0	0	0	0
136	163.081	0	0	0	0	0	0	0	0	0.008	0	0	0.006	0.008	0	0	0	0.008	0	0	0	0	0	0	0
137	163.865	0	0.02	0.025	0	0	0.027	0.005	0.006	0.005	0.007	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0
138	164.235	0	0	0	0.016	0	0	0	0	0.008	0	0	0.007	0.013	0	0	0	0.008	0	0	0	0	0	0	0
139	167.845	0	0	0	0	0	0	0	0	0	0	0	0.005	0	0	0	0	0.007	0	0	0	0	0	0	0
140	171.975	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.009	0.016	0
141	173.457	0	0	0	0	0	0	0.008	0.005	0.01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
142	174.612	0	0	0	0	0.045	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.013	0	0.08
143	175.045	0.037	0.022	0.006	0	0.01	0.009	0.036	0.042	0.033	0.036	0.039	0.032	0	0.039	0.052	0.045	0.036	0.036	0.049	0.024	0.013	0	0.044	0
144	175.841	0	0.018	0.031	0.018	0	0.028	0.006	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
145	177.979	0	0	0	0.005	0	0	0	0	0.006	0	0	0.006	0.013	0	0	0	0.007	0	0	0	0	0	0	0
146	192.328	0	0	0	0	0	0	0.008	0.005	0.01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table S2[†] Validation of the ^{13}C chemical shifts of the recognized and unrecognized podophyllotoxins (δ_C, ppm)[a,b]

Atom	Recognized podophyllotxins										Unrecognized podophyllotxins	
	6		5		2		1		3		8	
	Cluster A	Purified	Cluster B	Purified	Cluster C	Purified	Cluster D	Purified	Cluster E	Purified	Cluster K	Purified
1	43.55	43.43	43.16	43.16	42.96	42.93	42.96	42.88	42.96	43.03	*43.55*	43.7
2	44.24	44.15	45.98	45.95	45.98	46.14	44.24	44.39	45.98	45.84	44.84	44.89
3	40.15	39.98	32.13	32.13	32.07	32.04	38.56	38.53	32.07	32.09	*42.96*	42.97
4	70.56	70.64	26.5	26.47	26.5	26.51	78.08	78.05	26.5	26.83	192.33	192.35
5	106.32	106.39	137.69	137.06	137.69	137.88	108.46	108.57	137.69	137.42	*104.7*	104.71
6	146.45	146.53	132.96	132.99	131.51	131.47	146.45	146.38	134.64	134.8	*147.38*	147.43
7	146.73	146.67	146.51	146.51	146.45	146.4	146.73	146.73	147.37	147.42	152.55	152.35
8	109.05	109.15	101.79	101.77	101.79	101.59	109.05	108.97	101.79	101.74	109.58	109.59
9	135	135.05	131.23	131.22	131.66	131.54	131.23	131.2	131.23	131.33	141.59	141.61
10	130.7	130.8	119.48	119.81	119.48	119.49	130.7	130.63	122.39	122.42	127.87	127.89
2a	174.61	174.79	175.04	175.04	175.04	175.04	174.61	174.44	175.04	174.96	173.46	173.47
3a	71	71.11	71.81	71.81	71.81	71.73	71	70.92	71.81	71.84	66.6	66.61
1'	136.41	136.53	136.23	136.23	132.96	132.89	134.64	134.7	136.66	136.82	133.11	133.12
2'	108.46	108.45	108.08	108.08	108.46	108.49	108.08	108.1	108.08	108.09	107.68	107.67
3'	151.91	152	151.87	151.87	147.07	147.07	147.06	147.09	151.91	151.9	152.33	152.35
3'-OCH_3	55.85	55.9	55.75	55.74	56.1	56	56.04	56.02	55.75	55.71	55.62	55.68
4'	136.66	136.6	137.05	137.77	134.64	134.56	132.16	132.13	136.23	136.37	*136.66*	136.71
4'-OCH_3	*59.86*	59.96	59.86	59.85					59.86	59.88	*59.86*	59.88
5'	151.91	152	151.87	151.87	147.07	147.07	147.06	147.09	151.91	151.9	152.33	152.35
5'-OCH_3	55.85	55.9	55.75	55.74	55.99	56	56.04	56.02	55.75	55.71	55.62	55.68
6'	108.46	108.45	108.08	108.08	108.46	108.49	108.08	108.1	108.08	108.06	107.68	107.67
–OCH_2O–	101.04	101.06	100.56	100.54	100.56	100.41	101.04	100.98	101.04	101	102.39	102.41
1"							101.79	101.69	104.69	104.79		
2"							73.2	73.26	73.76	73.73		
3"							76.64	76.55	76.64	76.62		
4"							69.8	69.88	69.8	69.64		
5"							77.1	77.03	77.1	77.14		
6"							60.9	61.06	60.9	60.7		

[a] The signals out of the clusters were marked in green zone.

[b] Using DMSO-*d6* as a solvent with δ_C of 39.48 ppm.

Table S3[†] Validation of the ^{13}C chemical shifts of recognized and unrecognized flavonoids (δ_C, ppm)[a,b,c]

Atom	Recognized clusters				Unrecognized clusters					
	4		7		9		12		13	
	Cluster F	Purified	Cluster G	Purified	Cluster J	Purified	Cluster H	Purified	Cluster I	Purified
1										
2	*146.73*	146.7	*146.73*	146.65	*159.16*	159.33	157.44	157.49	157.44	157.43
3	135.67	135.62	135.67	135.67	/	138.63	/	138.38	/	139.03
3-OCH_3					*59.86*	59.8	60.12	60.17	60.12	60.14
4	175.84	175.73	175.84	175.84	177.98	177.96	177.98	178.05	177.98	178.01
5	160.68	160.63	160.68	160.65	161.33	161.29	161.33	161.41	161.33	161.36
6	98.18	98.16	98.18	98.28	96.22	98.59	98.77	98.81	98.77	98.76
7	163.86	164.03	163.86	164.33	164.24	164.24	164.24	164.36	164.24	164.32
8	93.39	93.29	93.39	93.49	93.7	93.62	93.7	93.79	93.7	93.75
9	156.12	156.08	156.12	156.18	156.79	156.73	156.79	156.84	156.79	156.8
10	103.01	102.86	103.01	102.85	*104.69*	104.46	*104.69*	104.71	*104.69*	104.67
1'	121.84	121.88	121.84	121.67	120.99	120.97	124.32	124.36	124.74	124.23
2'	115.06	114.98	129.47	129.43	*127.87*	127.76	129.29	129.34	129.29	129.3
3'	145.03	144.99	115.4	115.41	143.29	143.27	139.03	139.07	139.03	138.28
4'	147.67	147.64	159.19	159.15	*147.38*	147.04	142.07	142.12	142.07	142.04
5'	115.57	115.52	115.4	115.41	/	112.45	*115.07*	115.14	*115.07*	115.15
6'	119.94	119.88	129.47	129.43	121	121.05	124.13	124.18	124.13	124.16
1"					25.55	25.76	25.55	25.6	25.55	25.56
2"					122.82	122.79	121.17	121.25	121.17	121.16
3"					130.14	130.08	*131.66*	131.71	*131.66*	131.69
4"					17.38	17.34	17.38	17.42	17.38	17.38
5"					25.28	25.22	25.28	25.33	25.28	25.3
1"'										
2"'							*100.28*	100.23	/	100.02
3"'							90.19	90.24	/	90.13
4"'							/	187.37	/	187.14
5"'							163.08	163.14	163.08	163.10
6"'							97.24	97.23	97.24	97.26
7"'							/	168	/	167.97
8"'							96.22	96.25	96.22	96.22
9"'							*159.2*	159.17	/	159.05
10"'							99.65	99.74	99.65	99.69
1""							124.32	124.18	125.97	125.99
2"",6""							129.15	129.24	129.15	129.14
3"",5""							114.8	114.81	113.49	113.5
4""							158.66	158.68	160.2	160.2
4""-OCH3									55.15	55.15

[a] The signals out of the clusters were marked in green zone.

[b] "/" means that the signal was not detected in the fraction.

[c] Using DMSO-*d6* as a solvent with δ_C of 39.48 ppm.

Structure identification of compound 9

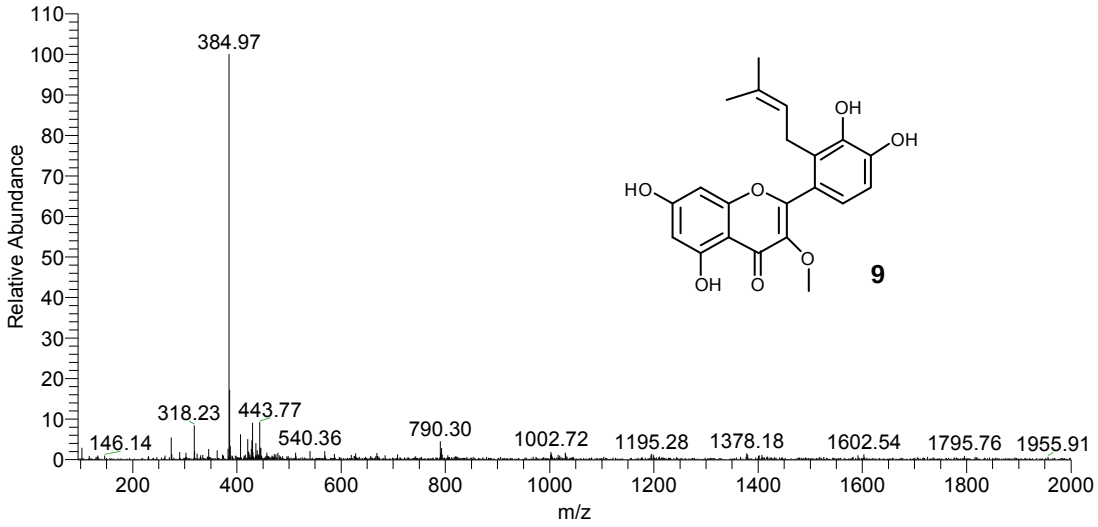
ESI-MS spectra of the compound **9** showed that it had prominent ions of $[M+H]^+$ at *m/z* 385 , suggesting that its molecular weight was 384 (Fig. S2A†). Further high resolution ESI-TOF-MS analysis indicated that its molecular formula was $C_{21}H_{20}O_7$ (Fig. S2C†). As shown in Fig. S2B†, in the positive ESI-MS^2 spectrum the prominent fragment at *m/z* 353 closely corresponded to the loss of the OCH_3 while the fragments at *m/z* 329 and 317 corresponded to the loss of prenyl group in the molecular.

^1H NMR spectrum showed that it had two CH_3 at δ 1.33 and 1.48, a CH_2 at δ 3.26 (d, *J*=6.7Hz), and a CH at δ 5.02 (t, *J*=6.7Hz). Several coupling correlations among the signals were found in the ^1H-^1H COSY and HMBC spectra, confirming the existence of a prenyl group. The ^1H NMR spectrum also showed four strong single signals at δ 3.57 (OCH_3), 6.20 (1H), 6.30 (1H), and 6.76 (2H) and ^{13}C NMR data showed 21 ^{13}C signals. Therefore, the compound **9** was a prenylated flavonoid.

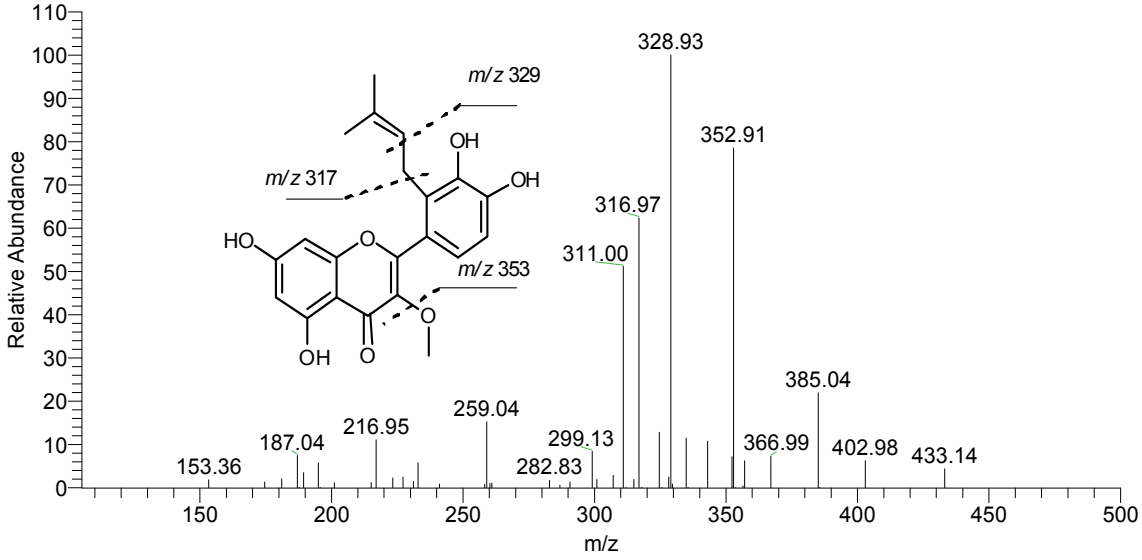
The position of prenyl group was confirmed by HMBC, which showed three critical correlations between C1″ of the prenyl group and C1′, C2′ and C3′ of the phenyl of the flavonoid. Thus the prenyl group was located at C2′. In addition, the strong Nuclear Overhauser Effects (NOE) between H1″ (δ 3.25) and H4″ (δ 1.33), and H2″ (δ 5.02) and H5″ (δ 1.48) were observed in the Nuclear Overhauser effect spectroscopy (NOESY), which confirmed the configuration of prenyl group of **9** as shown in Fig. 4. Similarly, the position of OCH_3 was determined at C3 due to the strong NOE between δ 3.57 (OCH_3) and δ 6.76 (H6′) in the NOESY spectrum.

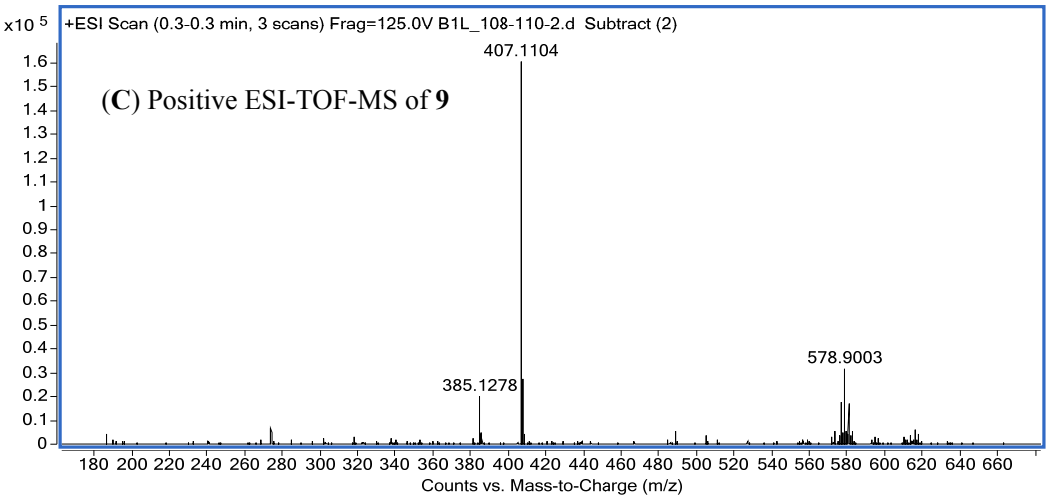
The characteristic OH signal (δ 12.65, 1H) was observed in the ^1H NMR spectrum, which indicated that the compound was a C5-OH flavone. Other signals were designated based on 1D and 2D NMR data. On-line ^{13}C data screening indicated that the compound was a known compound: podoverine A. Its 1D and 2D data were summarized in Table S4†.

(A) Positive ESI-MS of **9**



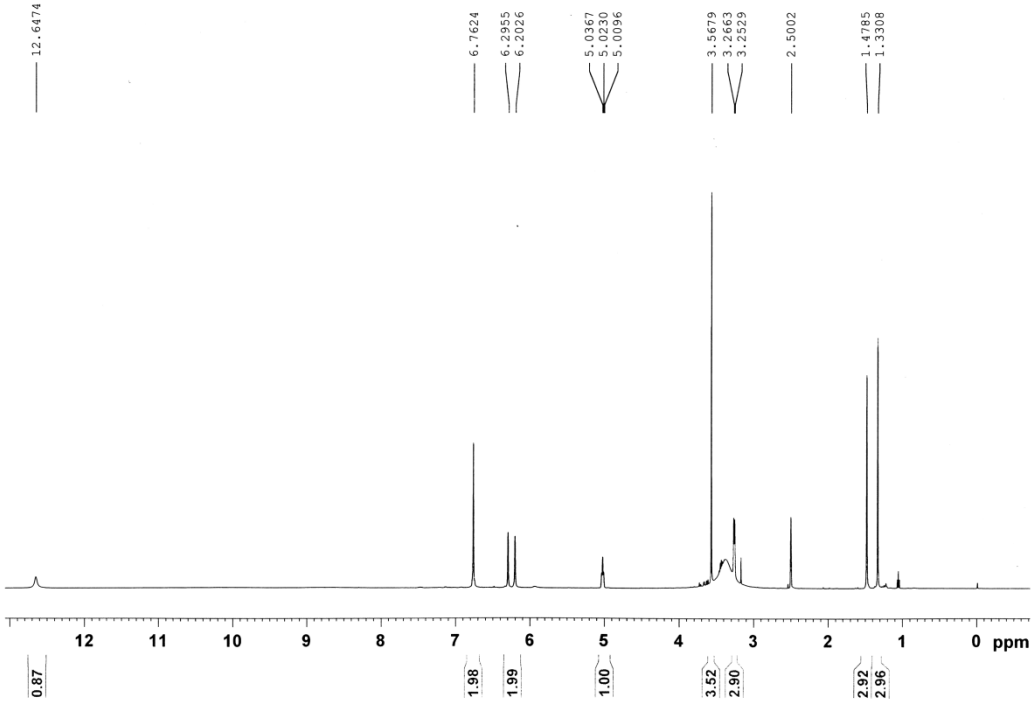
(**B**) Positive ESI-MS/MS of **9** (*m/z* 385→)



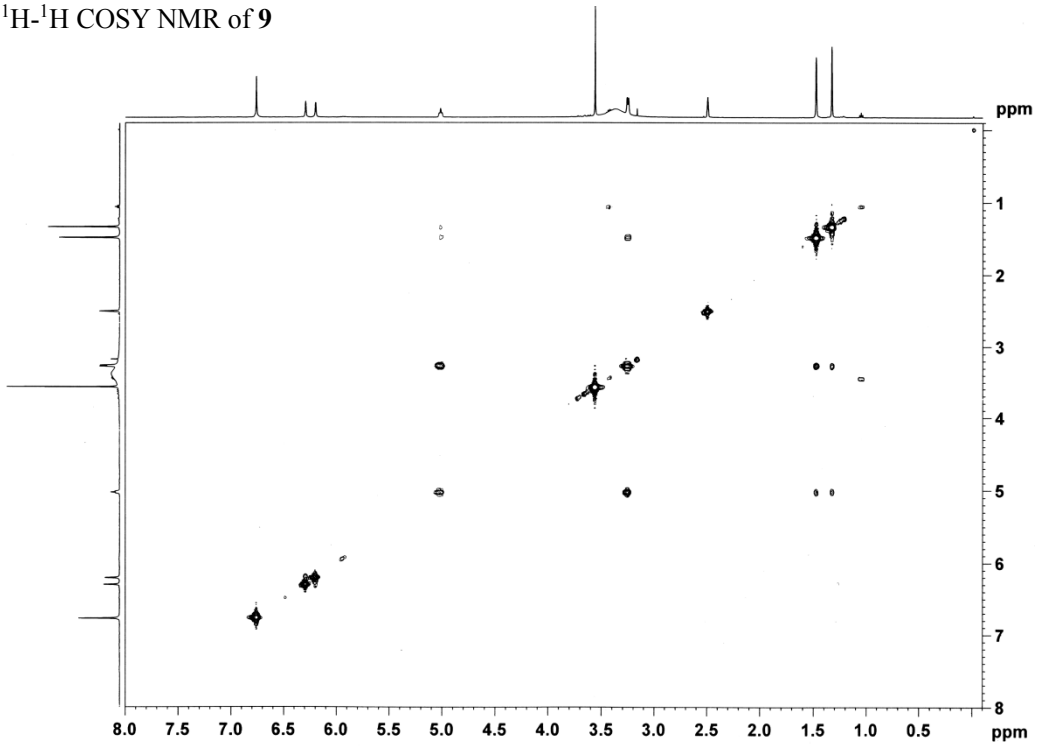


Ion Formula	m/z	Calc m/z	Diff (ppm)	DBE
C21 H20 Na O7	407.1104	407.1107	0.67	11.5

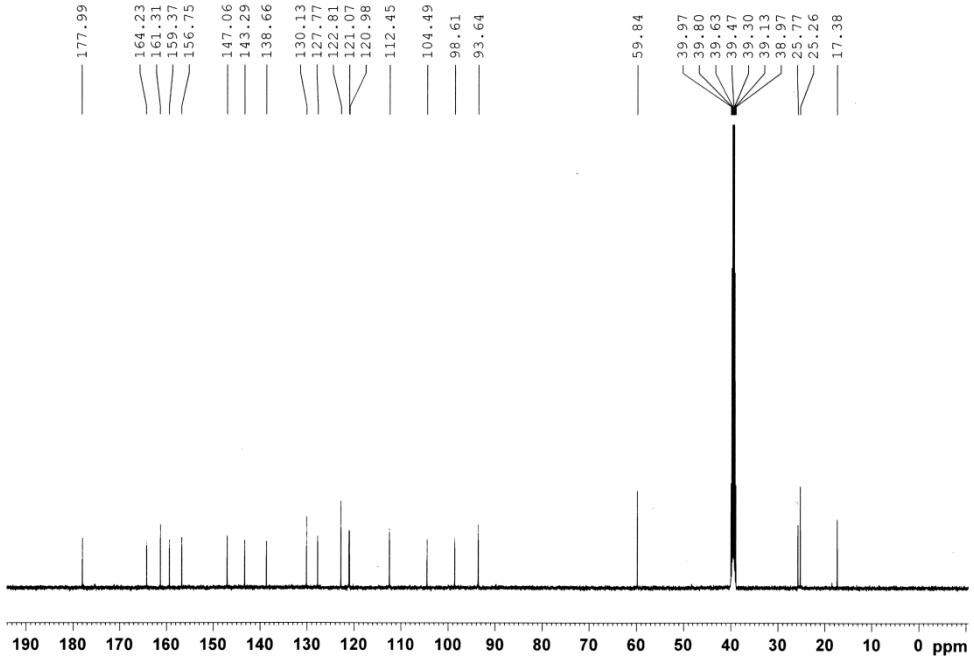
(**D**) ^{1}H NMR of **9**



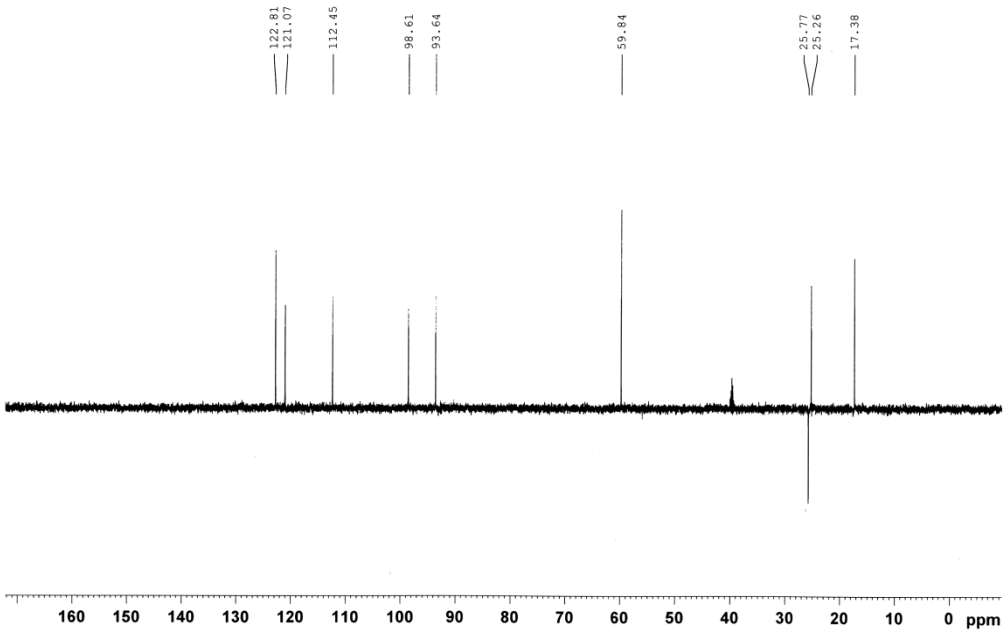
(**E**) ^{1}H-^{1}H COSY NMR of **9**



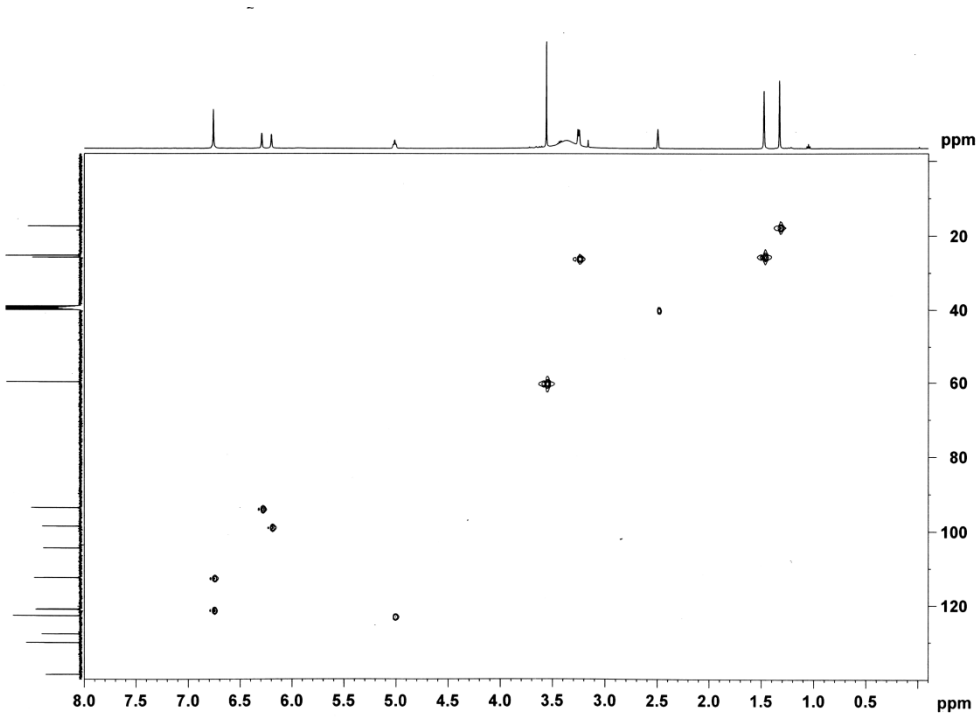
(**F**) ^{13}C NMR of **9**



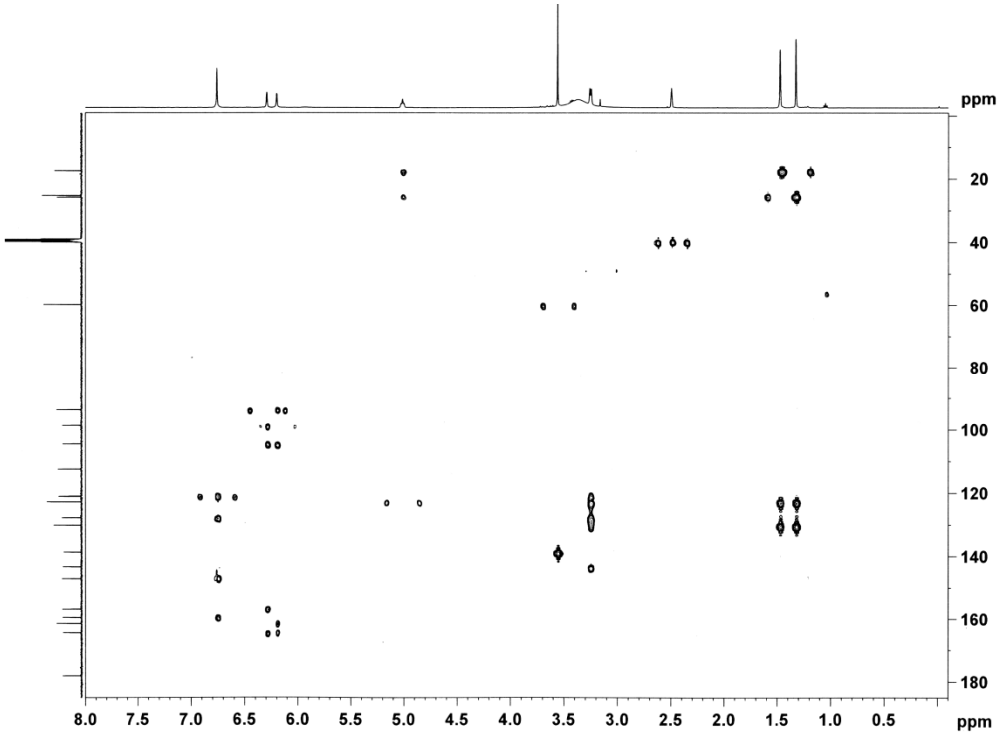
(**G**) DEPT135 NMR of **9**



(**H**) HSQC NMR of **9**



(**I**)HMBC NMR of **9**



(**J**) NOESY NMR of **9**

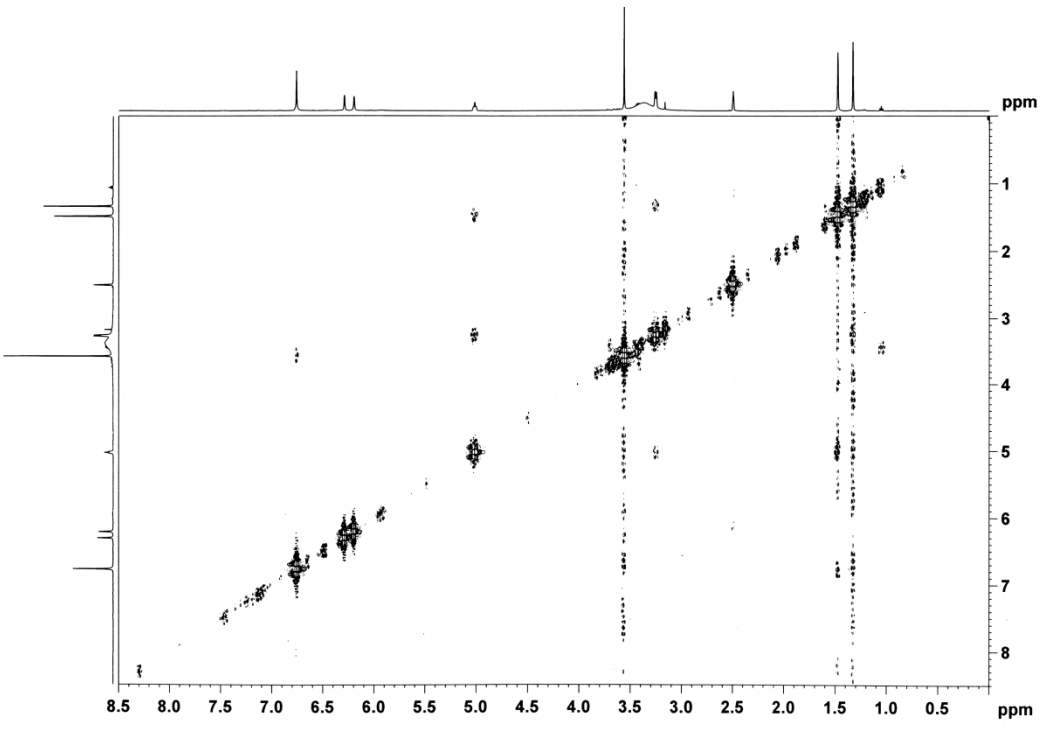


Fig. S2† ESI-MS, ESI-MS/MS, ESI-TOF-MS, and 1D and 2D NMR spectra of compound **9.**

Table S4† 1D and 2D NMR data of compound **9** (DMSO-*d6*, 500MHz for ^{1}H)

Atom	9				
	δ_C (ppm)	**DEPT[a]**	**HMQC** δ_H (ppm)	**HMBC** correlation with	**^{1}H-^{1}H COSY** correlation with
1					
2	159.33	q[b]		H-6'	
3	138.63	q		H-3-OCH_3	
3-OCH_3	59.8		3.57 (3H, s)		
4	177.96	q			
5	161.29	q		H-6	
5-OH			12.65 (1H, s)		
6	98.59	CH	6.20 (1H, s)	H-8	H-8
7	164.24	q		H-6, H-8	
8	93.62	CH	6.29 (1H, s)	H-6	H-6
9	156.73	q		H-8	
10	104.46	q		H-6, H-8	
1'	120.97	q		H-5', H-1"	
2'	127.76	q		H-6', H-1"	
3'	143.27	q		H-1"	
4'	147.04	q		H-5', H-6'	
5'	112.45	CH	6.76 (1H, o[a])		H-6'
6'	121.05	CH	6.76 (1H, o)	H-5'	H-5'
1"	25.76	CH_2	3.25 (2H, d, *J*= 6.7 Hz)	H-2"	H-2"
2"	122.79	CH	5.02 (1H, t, *J* = 6.7 Hz)	H-1", H-4", H-5"	H-1",H-4",H-5"
3"	130.08	q		H-1", H-4", H-5"	
4"	17.34	CH_3	1.33 (3H, s)	H-2", H-5"	H-2",H-5"
5"	25.22	CH_3	1.47 (3H, s)	H-2", H-4"	H-2",H-4"

[a] overlapped signals

Structure identification of compound 12

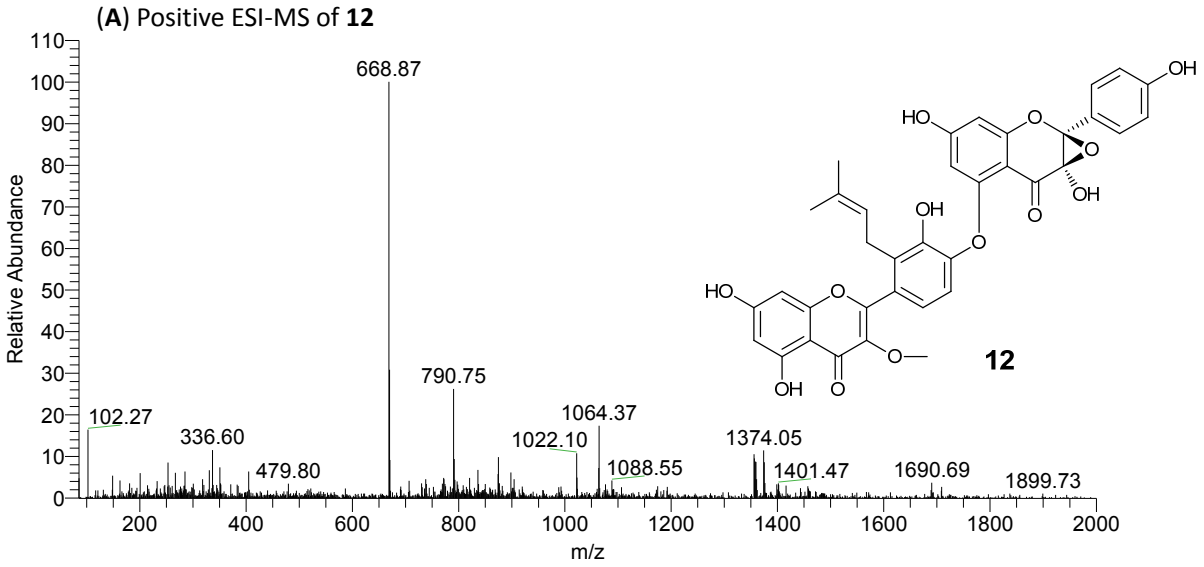
The compound **12** had prominent ions of $[M-H]^-$ at *m/z* 667 (40%), $[2M-H]^-$ at *m/z* 1335 (100%) and $[M+H]^+$ at *m/z* 669 (100%), suggesting that its molecular weight was 668 (Fig. S3A, C†). The high resolution ESI-TOF-MS analysis indicated that its molecular formula was $C_{36}H_{28}O_{13}$ (Fig. S3E†). The positive ESI-MS^2 spectrum showed the compound **12** was easily broken into two monomer with positive ions at *m/z* 383 (100%) and *m/z* 287 (22%). Similar monomers were observed at *m/z* 381 (13%) and 283 (100%) in the negative ESI-MS spectrum (Fig. S3B, D†). The loss of the prenyl groups was also observed at *m/z* 601 and *m/z* 613 in the positive ESI-MS/MS spectrum. Due to the existence of prenyl group, the prenylated monomer (*m/z* 383) had strong positive ion signal (100%) and relative weak negative ion signal (13%).

The ^{13}C NMR spectrum showed that the compound **12** had 33 C signals. However, on-line ^{13}C data screening in MICRONMR database and manual searching in CA could not hit any structures. By comparison with the cluster J (peak 9) together with above ESI-MS^n analyses, the compound **12** was defined as a flavone dimer and compound **9** was one possible monomer, which was supported by further 1D and 2D NMR spectra. ^1H NMR spectrum showed several characteristic signals such as two CH_3 δ 1.27 (H4″) and 1.49 (H5″), a CH_2 δ 3.26 (d, *J*=6.7Hz, H1″), a CH δ 5.03 (t, *J*=6.7Hz, H2″), a CH_3 δ 3.57 (3-OCH_3), two aromatic H δ 7.02 (d, *J*=8.4 Hz, H5′), 7.14 (d, *J*=8.4 Hz, H6′), and a characteristic OH signal (δ 12.56, C5-OH), which were closely agreement with the structure of compound **9**. Several key coupling correlations among the signals in the ^1H-^1H COSY and HMBC spectra were listed in Fig. 4, which confirmed that compound **12** contained podoverine A (**9**) as a subunit.

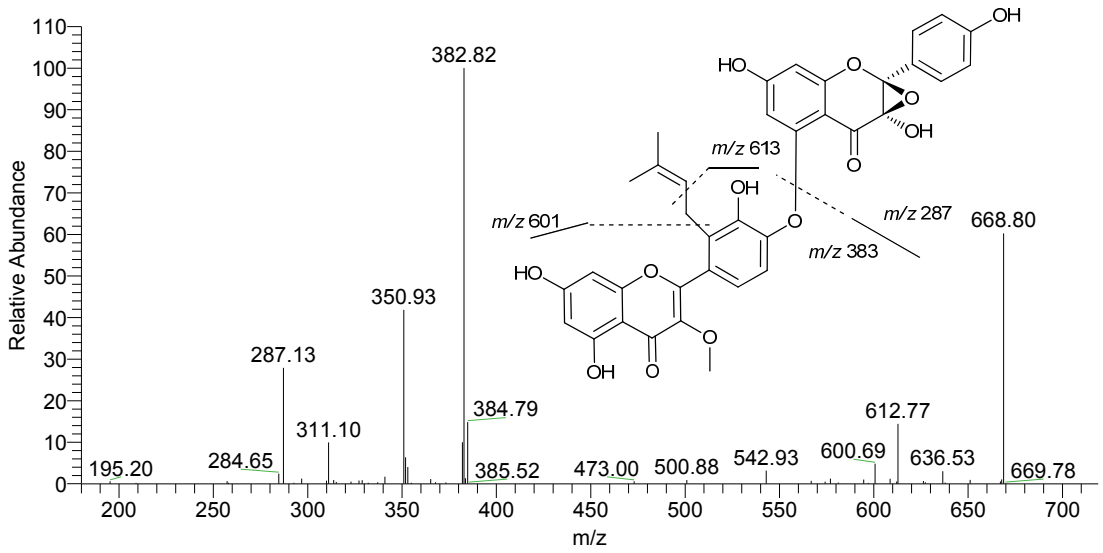
Besides the subunit of podoverine A, another subunit in the compound **12** seemed a kaemferol-derived oxidation product based on the evidences: a heterocyclic ring bearing a carbonyl (δ_C 187.37) and a 2,3-epoxy ring with signals at δ_C 100.23 (C2‴) and 90.24 (C3‴). Due to the existence of 2,3-epoxy ring, its shifts of C2‴ and C3‴ were different from the ones of reported dimers with the phenyl replacement at C3 position (δ_C 119.3 and 81.8)[1]. A 3-OH-(2,3-epoxy)flavone moiety was proposed as part of the structure of **12**, which was fully supported by 1D and 2D NMR data (Table S5†).

However, there were no any signals about the connection of two subunit moieties of the dimer **12** in the HMBC or NOESY spectra. Fortunately, the two relative flavones including podoverine A (**9**) and kaemferol (**7**) were both identified in the current work. As shown in Table Supp. 3, the biggest δ_C change of the moiety of podoverine A was at C4′ position on the ring B while the signals on the ring A and C were almost not changed. For the moiety of 3-OH-(2,3-epoxy)flavonone, δ_C signals on the ring B' were almost not changed by comparison with the data of kaemferol (**7**). Its major changes were on the A' and C' rings. Due to the existence of 3‴-OH, there were only two possible positions at C5‴-OH and C7‴-OH for the connection. ^1H NMR spectrum showed the compound **12** had only one C-OH signal at δ_C 12.56 (1H, C5-OH). Thus C5‴-OH was a unique position for connection of two monomers.

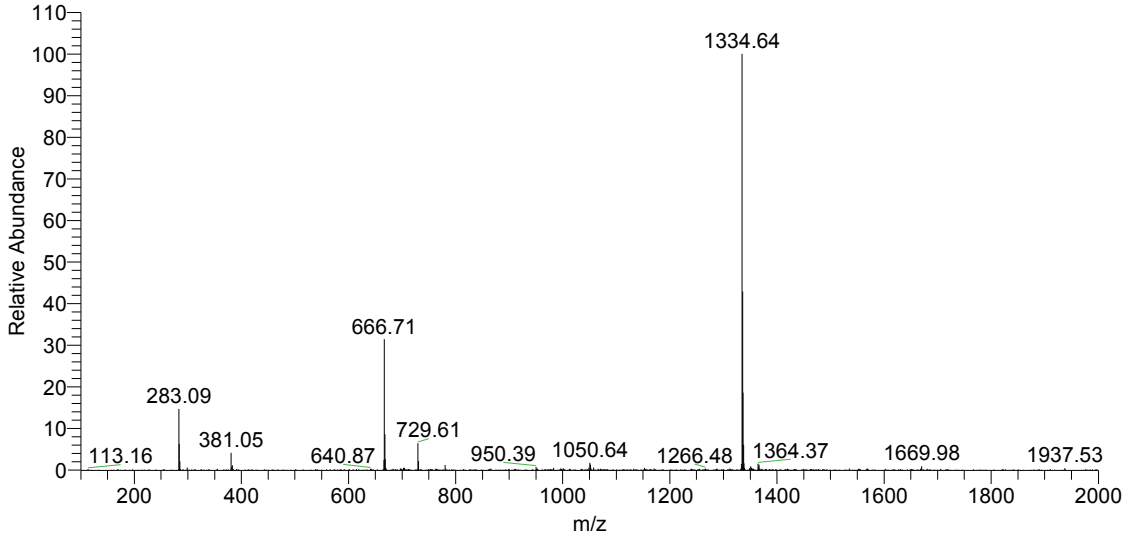
Therefore, the structure of **12** was established as Fig. 4. Because it was a dimer of podoverine A and an analogue of podoverine B and C were isolated from *Podophyllum versipelle* Hance,[2] we named the compound **12** as podoverine D.



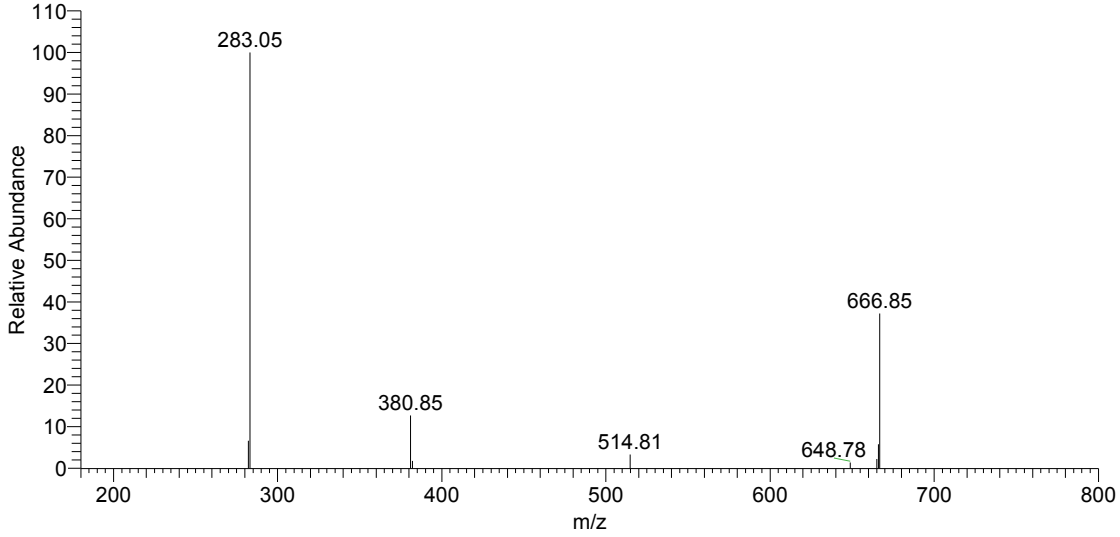
(**B**) Positive ESI-MS/MS of **12** (*m/z* 669→)

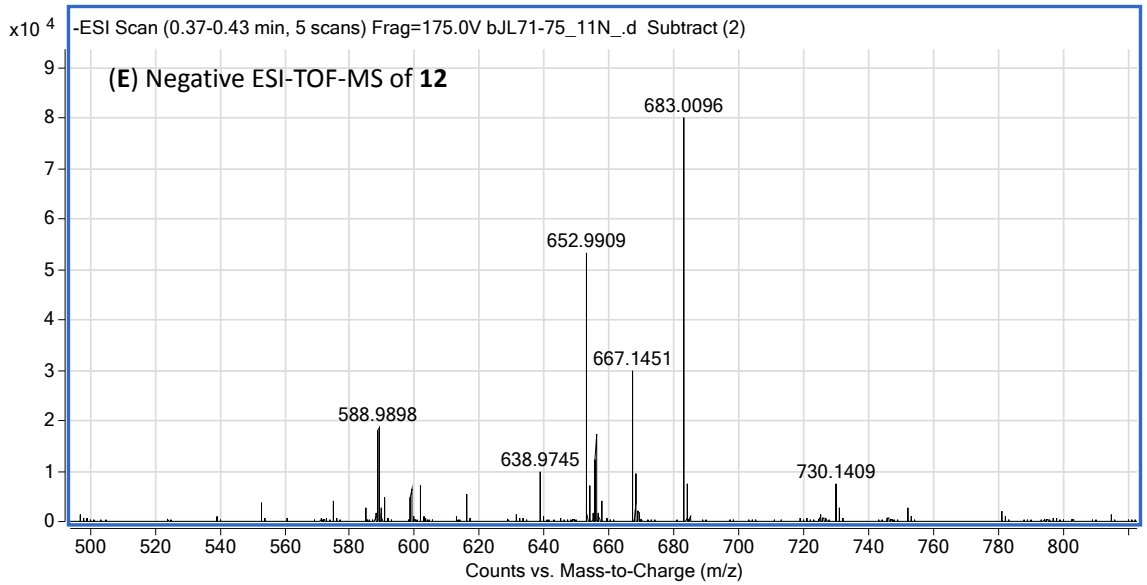


(**C**) Negative ESI-MS of **12**



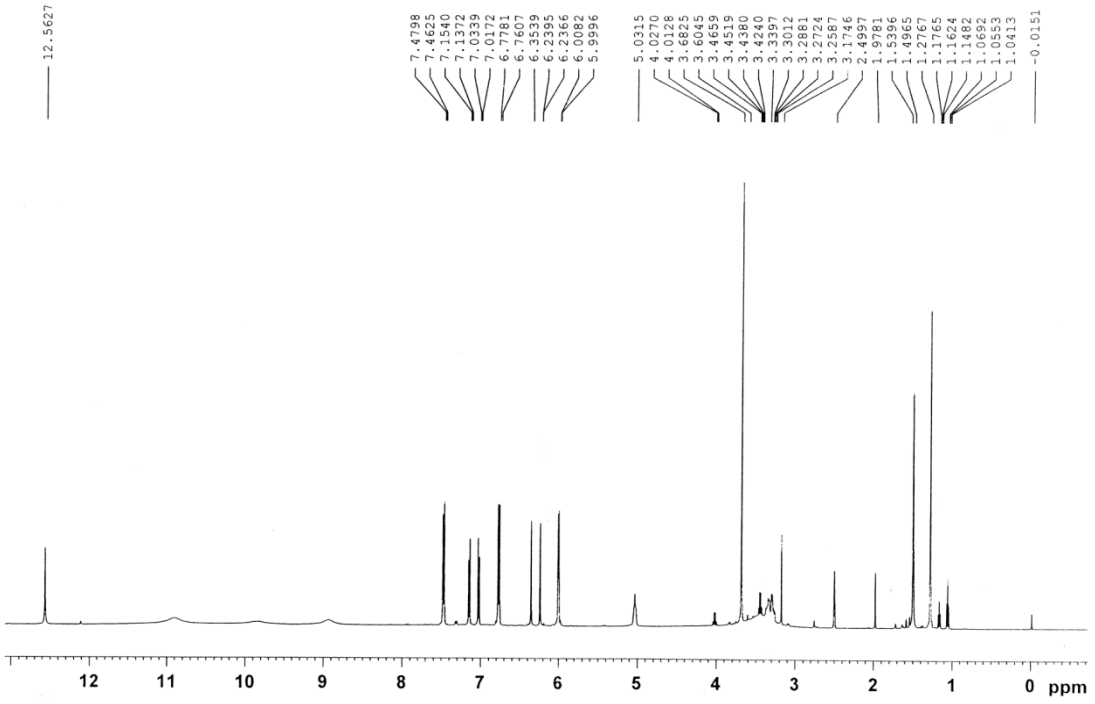
(**D**) Negative ESI-MS/MS of **12** (*m/z* 667→)



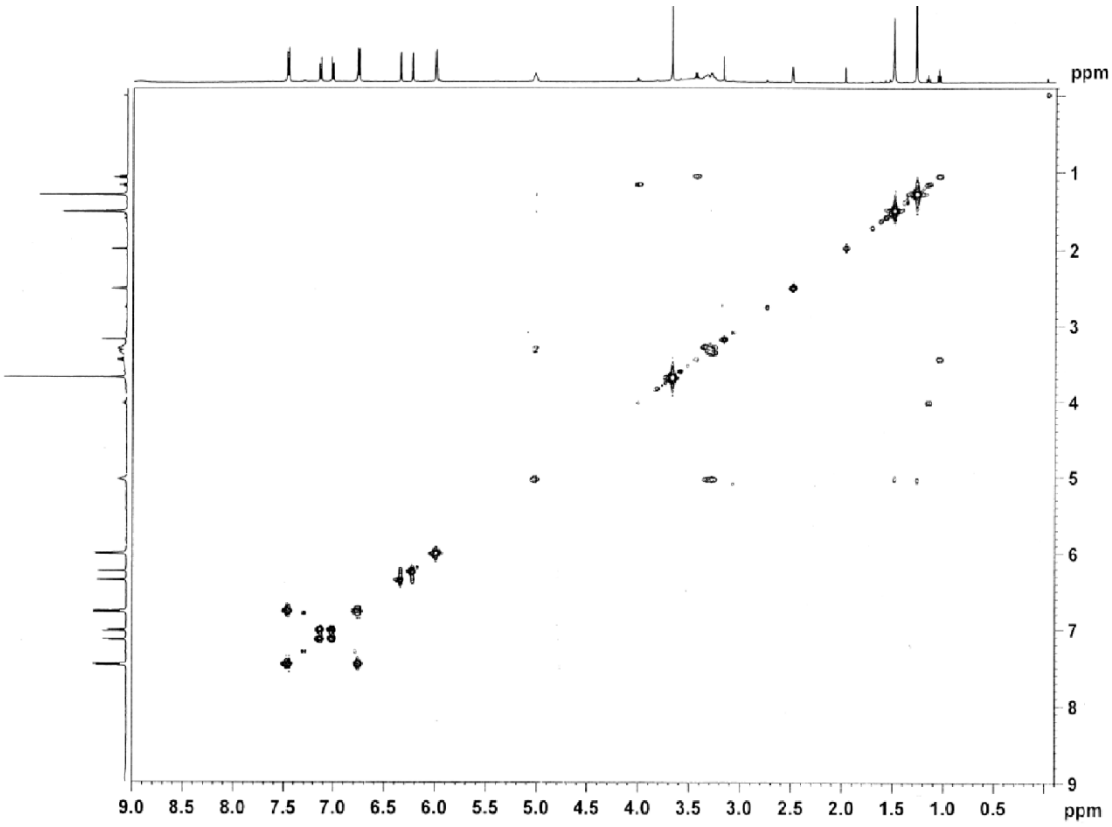


Ion Formula	m/z	Calc m/z	Diff (ppm)	DBE
C36 H27 O13	667.1451	667.1452	0.1	23.5

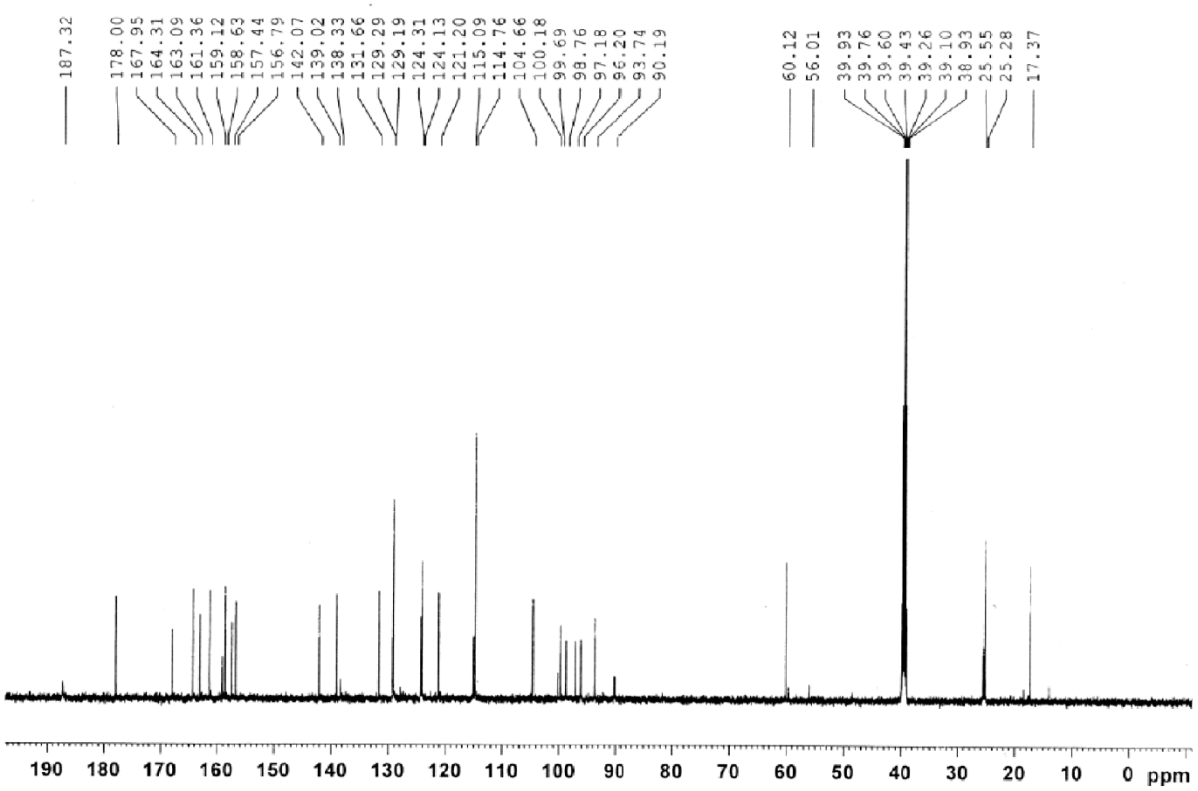
(**F**) ^{1}H NMR of **12**



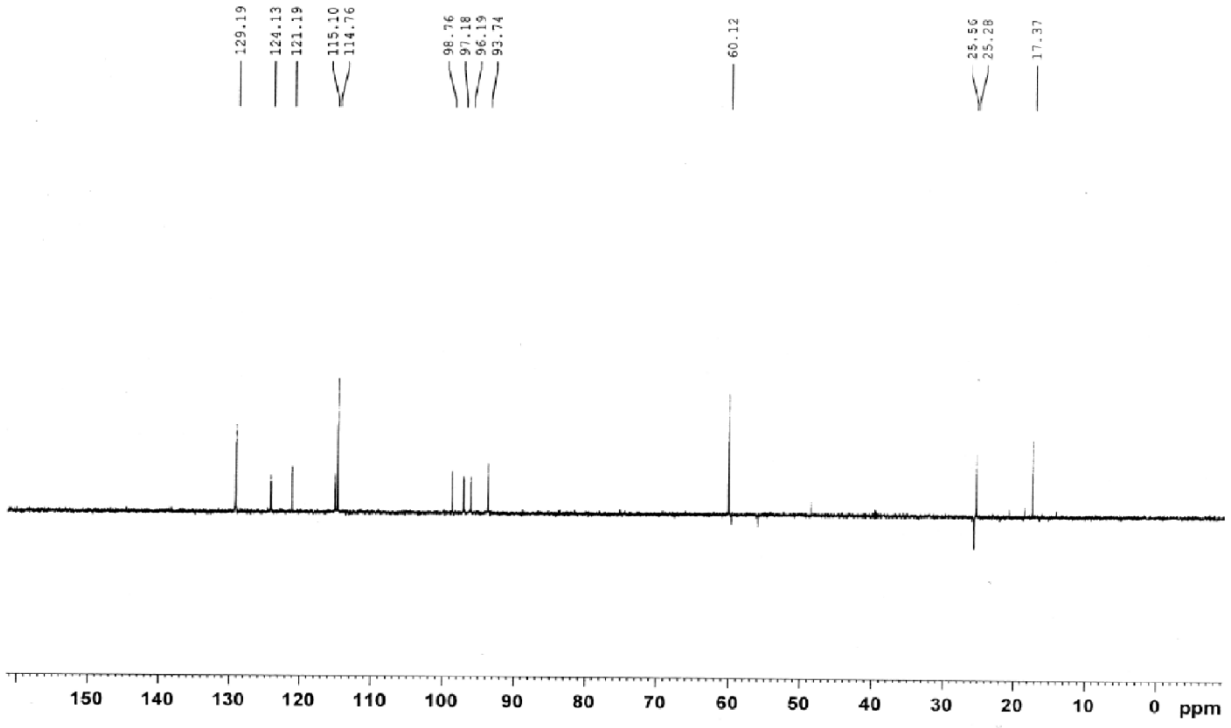
(**G**) ^{1}H-^{1}H COSY NMR of **12**



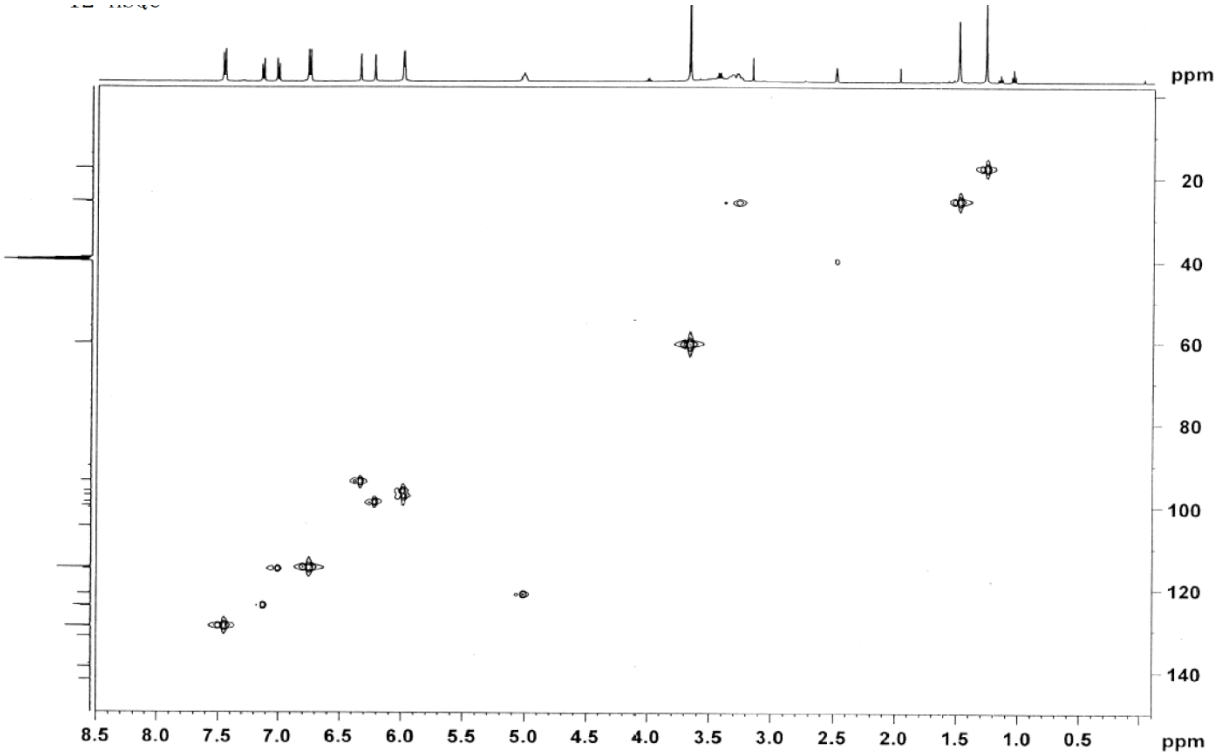
(**H**) ^{13}C NMR of **12**



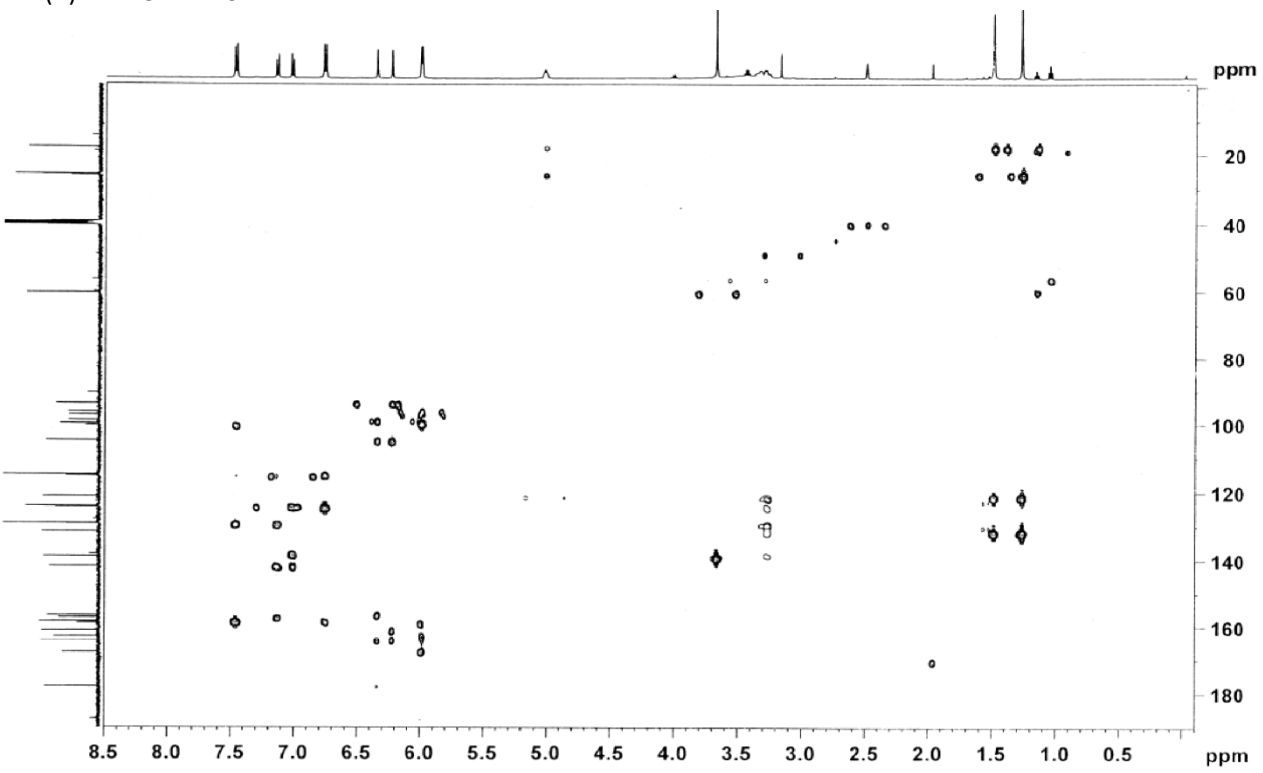
(**I**) DEPT135 NMR of **12**



(**J**) HSQC NMR of **12**



(**K**) HMBC NMR of **12**



(**L**) NOESY NMR of **12**

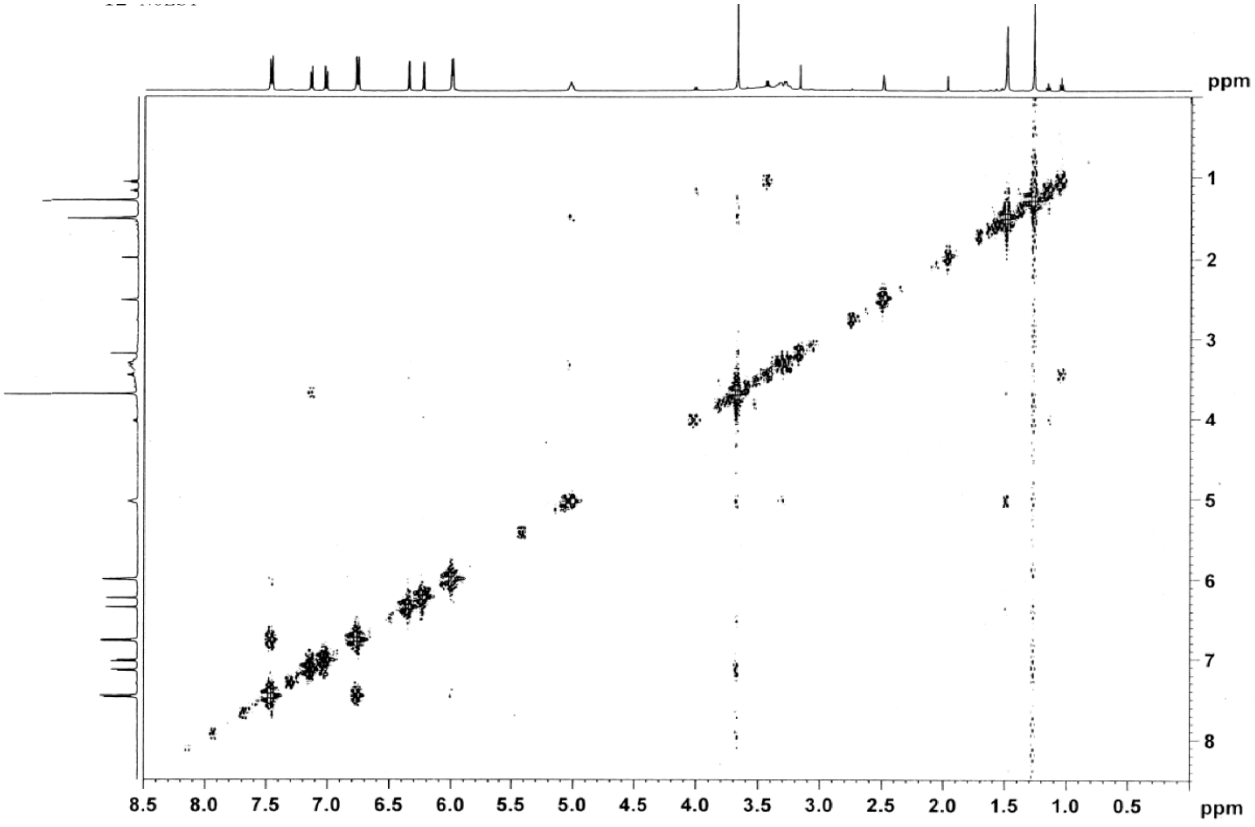


Fig. S3† ESI-MS, ESI-MS/MS, ESI-TOF-MS, and 1D and 2D NMR spectra of compound **12**.

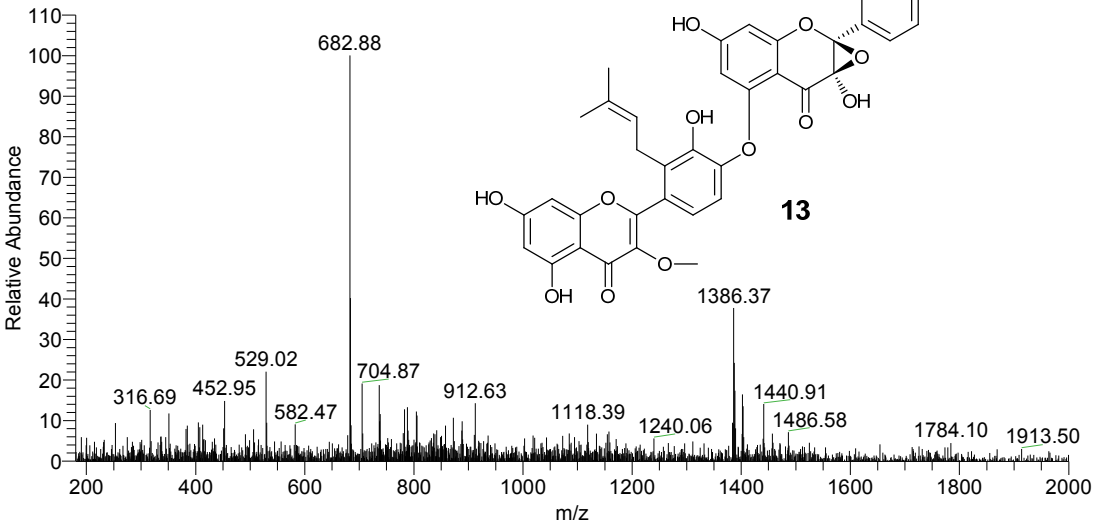
Table S5† 1D and 2D NMR data of compound **12** (DMSO-*d6*, 500MHz for ^{1}H)

Atom	12				
	δ_C (ppm)	DEPT[a]	HMQC	HMBC	^{1}H-^{1}H COSY
			δ_H (ppm)	correlation with	correlation with
2	157.49	q		H-6'	
3	138.38	q		H-3-OCH_3	
3-OCH_3	60.17	CH_3	3.68 (3H, s)		
4	178.05	q			
5	161.41	q		H-6	
5-OH			12.56 (1H, s)		
6	98.81	CH	6.23（1H，d, *J* = 1.45 Hz）	H-8	H-8
7	164.36	q		H-6, H-8	
8	93.79	CH	6.35（1H，s）	H-6	H-6
9	156.84	q		H-8	
10	104.71	q		H-6, H-8	
1'	124.36	q		H-5', H-1"	
2'	129.34	q		H-6', H-1"	
3'	139.07	q		H-5', H-1"	
4'	142.12	q		H-5', H-6'	
5'	115.14	CH	7.02（1H，d, *J* = 8.35 Hz）	H-6'	H-6'
6'	124.18	CH	7.14（1H，d, *J* = 8.4 Hz）	H-5'	H-5'
1"	25.6	CH_2	3.26 (2H, dd, *J* = 6.55 Hz, *J* = 14.7 Hz)	H-2"	H-2"
2"	121.25	CH	5.0 3 (1H, s)	H-1", H-4", H-5"	H-1", H-4", H-5"
3"	131.71	q		H-1", H-4", H-5"	
4"	17.42	CH_3	1.27 (3H, s)	H-2", H-5"	H-2", H-5"
5"	25.33	CH_3	1.49 (3H, s)	H-2", H-4"	H-2", H-4"
2"'	100.23	q		H-2"", H-6""	
3"'	90.24	q			
4"'	187.37	q			
5"'	163.14	q		H-6"'	
6"'	97.23	CH	5.99（1H，s）	H-8"'	H-8"'
7"'	168	q		H-6"', H-8"'	
8"'	96.25	CH	6.01（1H，s）	H-6"'	H-6"'
9"'	159.17	q		H-8"'	
10"'	99.74	q		H-6"', H-8"'	
1""	124.18	q		H-3"", H-5""	
2"", 6""	129.24	CH	7.47（2H，d, *J* = 8.65 Hz）	H-6"" for C-2"", H-2"" for C-6""	H-2""
3"", 5""	114.81	CH	6.77（2H，d, *J* = 8.7 Hz）	H-5"" for C-3"", H-3"" for C-5""	H-2""
4""	158.68	q		H-2"", H-3"", H-5"", H-6""	

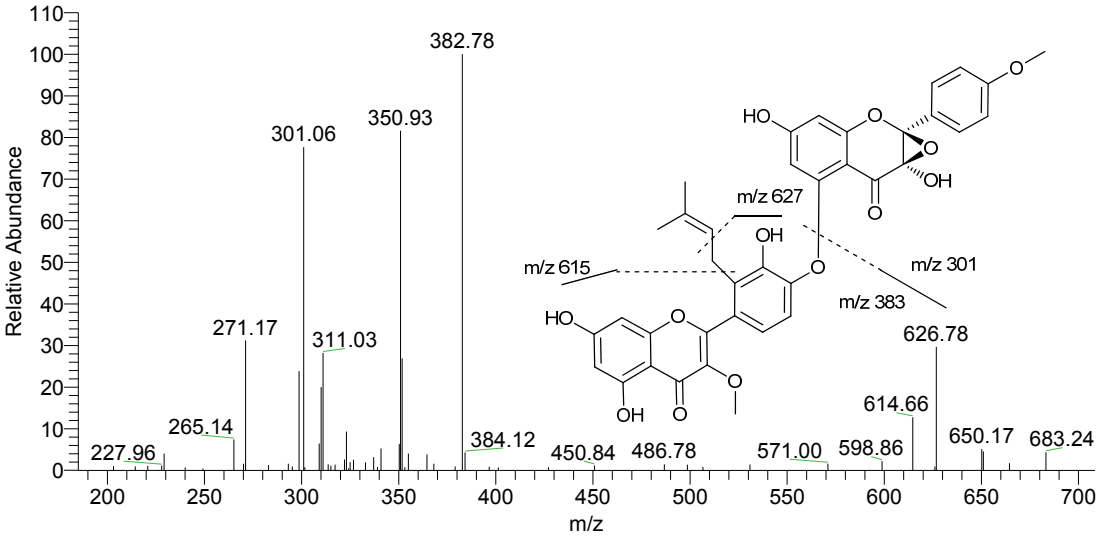
Structure identification of compound 13

The compound **13** had prominent ions of $[M-H]^-$ at *m/z* 681, $[2M-H]^-$ at *m/z* 1363 and $[M+H]^+$ at *m/z* 683, suggesting that its molecular weight was 682 (Fig. S4A, C†). The high resolution ESI-TOF-MS analysis indicated that its molecular formula was $C_{37}H_{30}O_{13}$ (Fig. 4E). The positive ESI-MS^2 spectrum showed that the compound **13** was easily broken into two monomers with positive ions at *m/z* 383 (100%) and *m/z* 301 (38%). Similar monomers fragments was observed at *m/z* 381 (100%) and 299 (1%) in the negative ESI-MS spectrum (Fig. S 4B, D†). The loss of the prenyl groups was also observed at *m/z* 615 and *m/z* 627 in the positive ESI-MS/MS spectrum. Clearly, the positive ion intensity of two monomer fragments was both strong. ^1H and ^{13}C NMR data showed there were minor differences between compounds **12** and **13** except for an OCH_3 at C4′′′′ position (δ_C 55.15, δ_H 3.75). The key coupling correlations were illustrated in the Fig. 4. All assignments of H and C atoms were confirmed by 1D and 2D NMR data (Table. S6†). Therefore, the structure of **13** was established and named as podoverine E

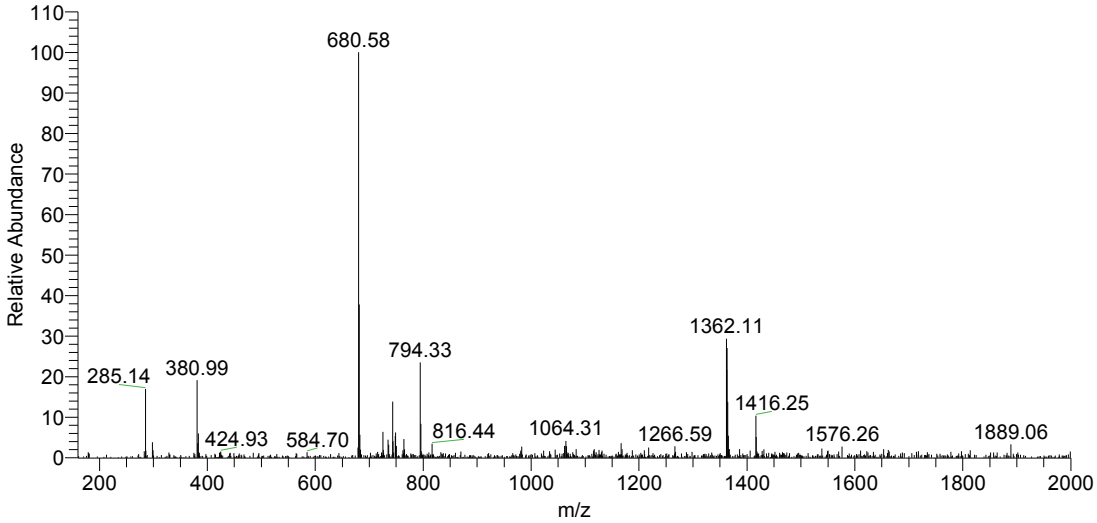
(A) Positive ESI-MS of **13**



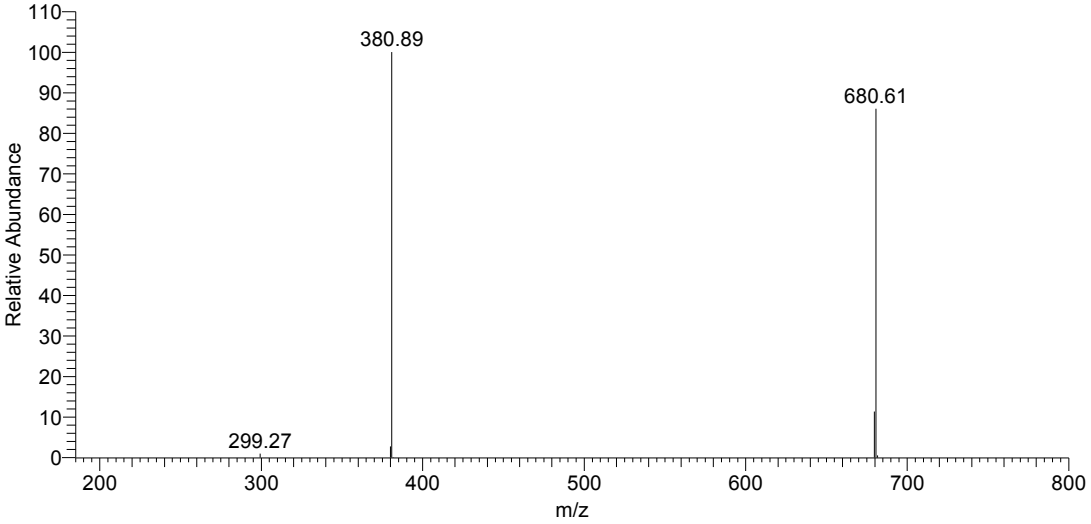
(**B**) Positive ESI-MS/MS of **13** (*m/z* 683→)

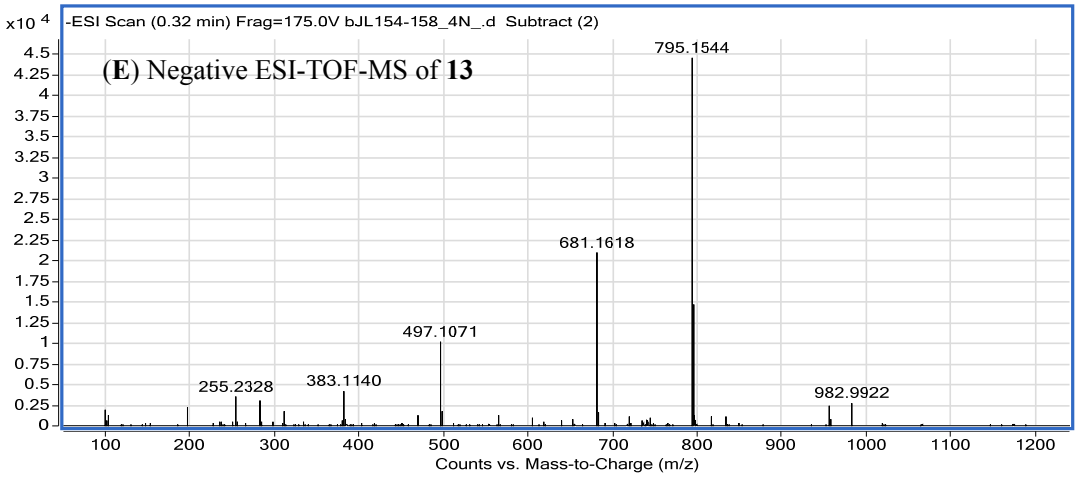


(**C**) Negative ESI-MS of **13**



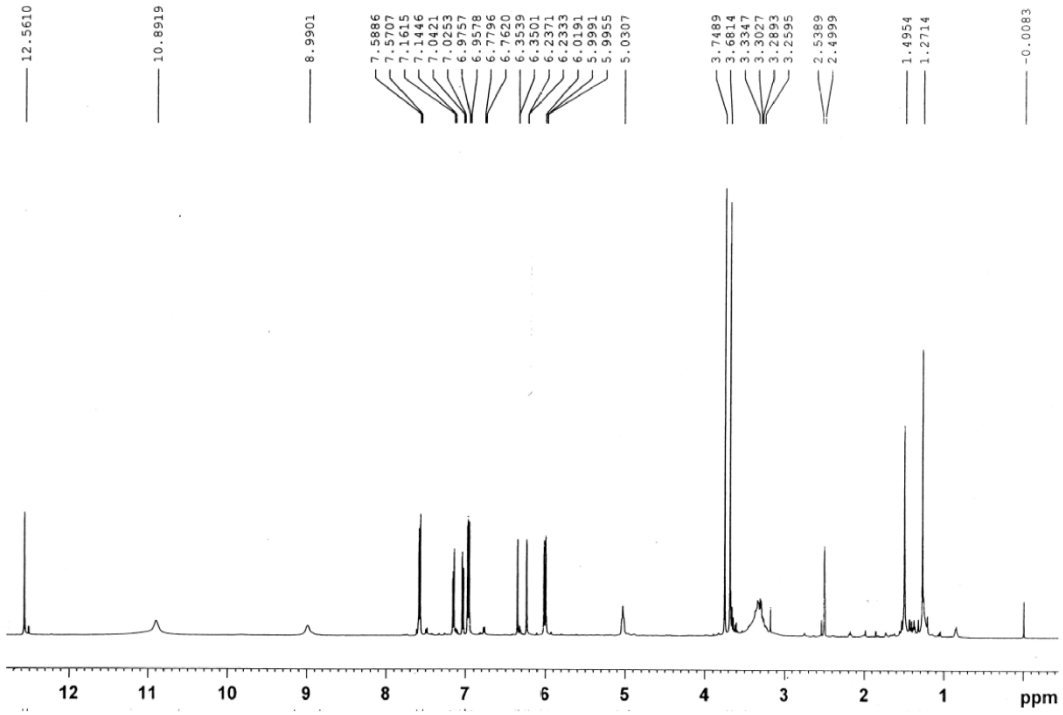
（**D**）Negative ESI-MS/MS of **13** (*m/z* 681→)



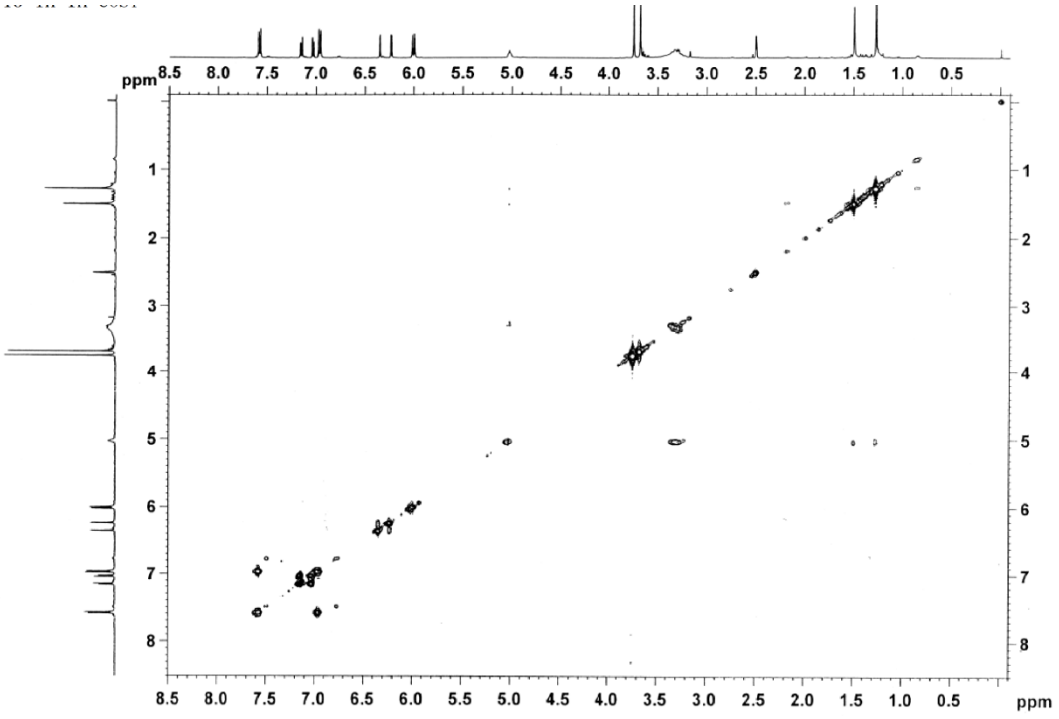


Ion Formula	m/z	Calc m/z	Diff (ppm)	DBE
C37 H29 O13	681.1618	681.1608	-1.44	23.5

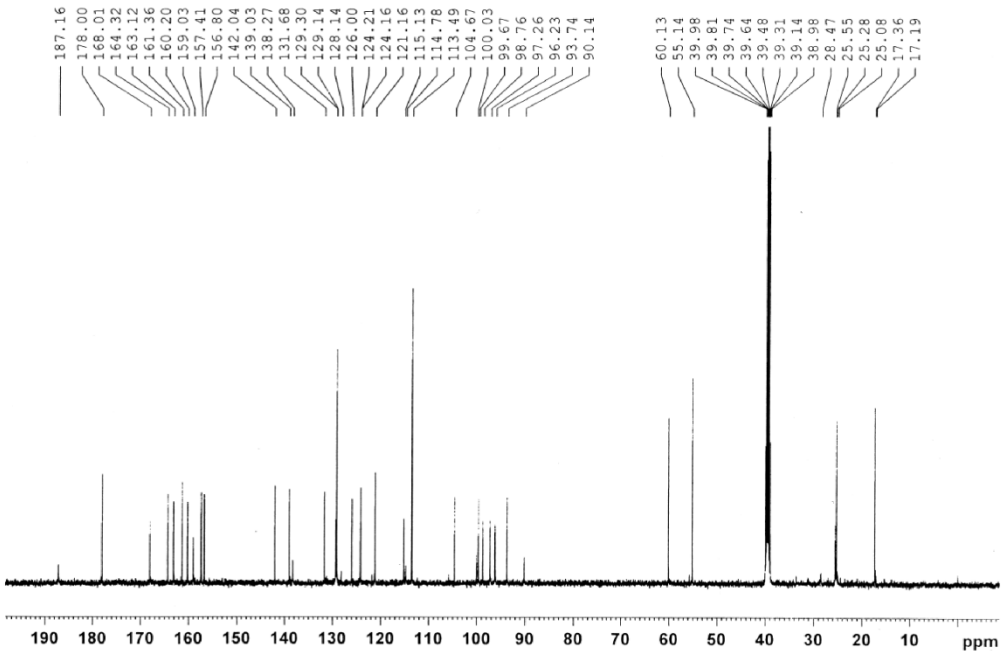
(**F**) ^{1}H NMR of **13**



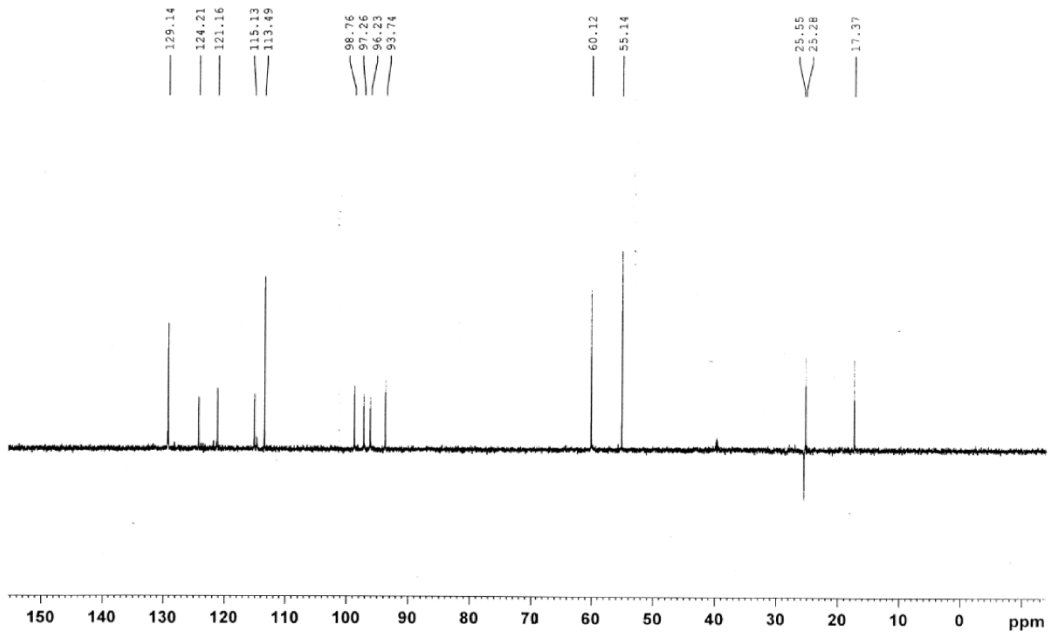
(**G**) ^{1}H-^{1}H COSY NMR of **13**



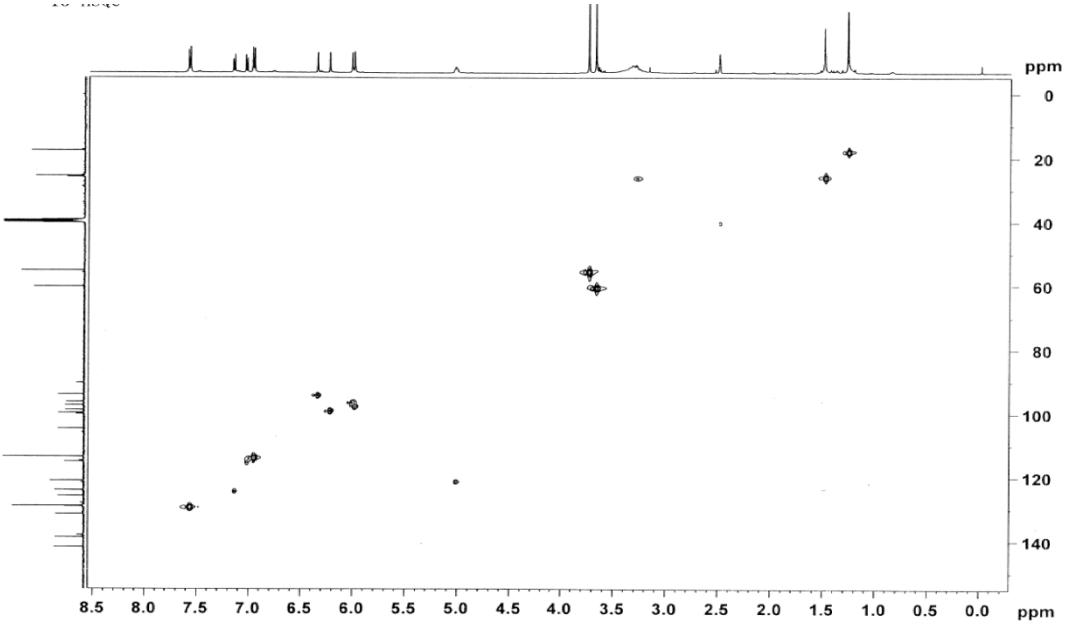
(**H**) ^{13}C NMR of **13**



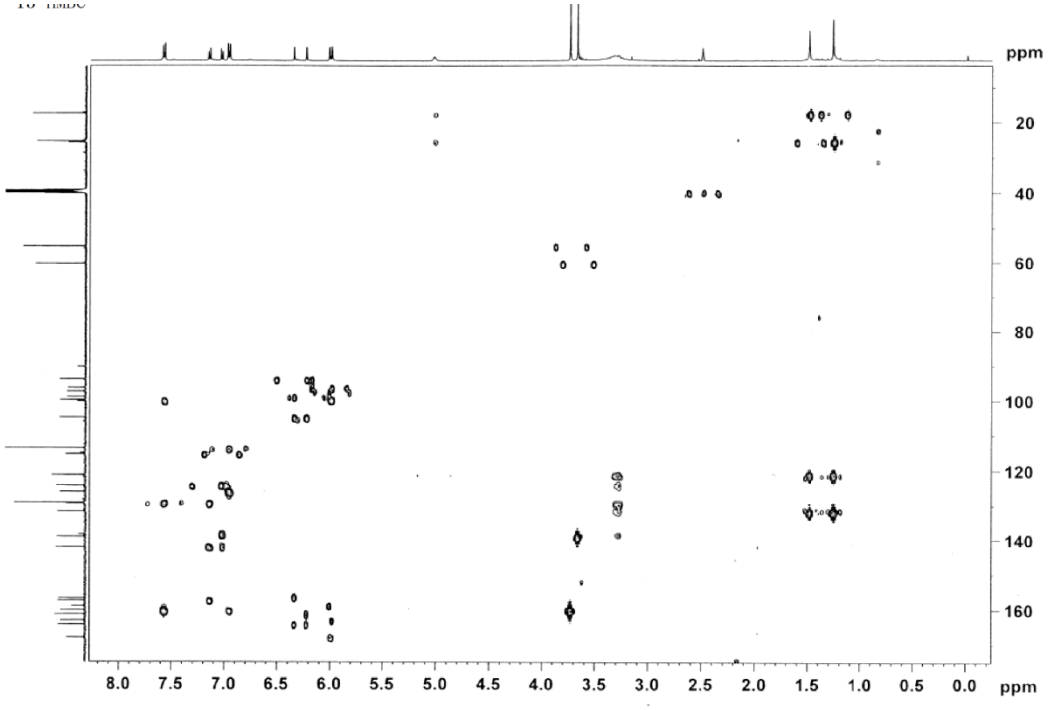
(**I**) DEPT135 NMR of **13**



(**J**) HSQC NMR of **13**



(**K**) HMBC NMR of **13**



(**L**) NOESY NMR of **13**

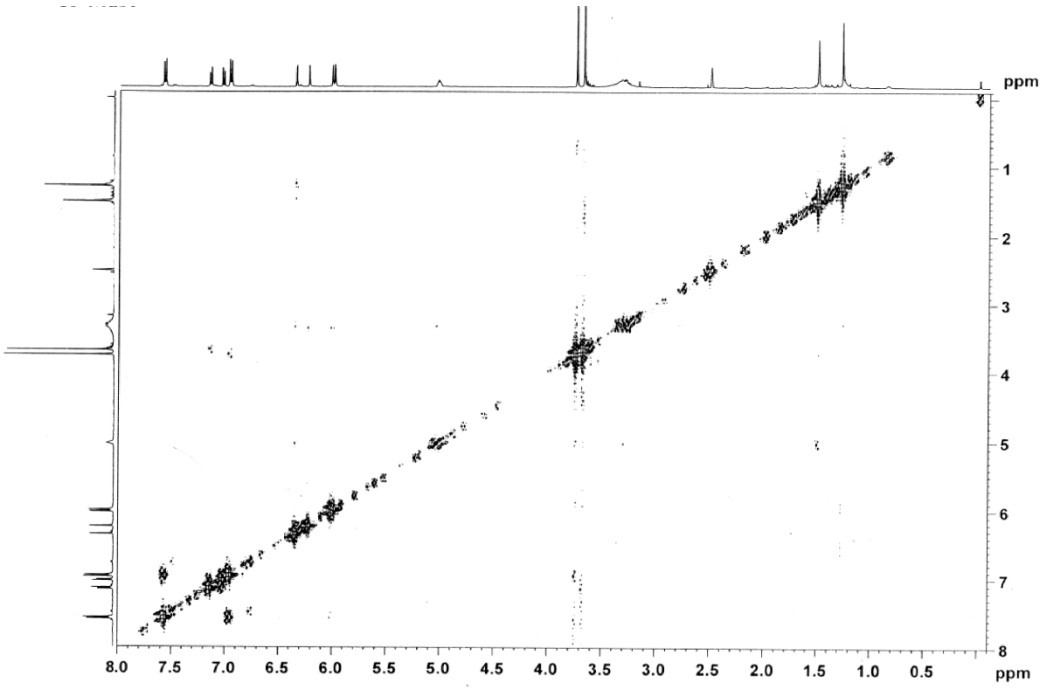


Fig. S4† ESI-MS, ESI-MS/MS, ESI-TOF-MS, and 1D and 2D NMR spectra of compound **13**.

Table S6† 1D and 2D NMR data of compound **13** (DMSO-*d6*, 500MHz for ^{1}H)

Atom	**13**				
	δ_C (ppm)	DEPT[a]	HMQC	HMBC	^{1}H-^{1}H COSY
			δ_H (ppm)	correlation with	correlation with
2	157.43	q		H-6'	
3	138.28	q		H-3-OCH$_3$	
3-OCH$_3$	60.14	CH$_3$	3.68 (3H, s)		
4	178.01	q			
5	161.36	q		H-6	
5-OH			12.56 (1H, s)		
6	98.76	CH	6.23（1H，d, *J* = 1.9 Hz）	H-8	H-8
7	164.32	q		H-6, H-8	
8	93.75	CH	6.35（1H，d, *J* = 1.9 Hz）	H-6	H-6
9	156.8	q		H-8	
10	104.67	q		H-6, H-8	
1'	124.23	q		H-5', H-1"	
2'	129.3	q		H-6', H-1"	
3'	139.03	q		H-5', H-1"	
4'	142.04	q		H-5', H-6'	
5'	115.15	CH	7.03（1H，d, *J* = 8.4Hz,）	H-6'	H-6'
6'	124.16	CH	7.15（1H，d, *J* = 8.45 Hz）	H-5'	H-5'
1"	25.56	CH$_2$	3.26 (2H, dd, *J* = 6.7 Hz, 16 Hz)	H-2"	H-2"
2"	121.16	CH	5.03 (1H, s)	H-1", H-4", H-5"	H-1", H-4", H-5"
3"	131.69			H-1", H-4", H-5"	
4"	17.38	CH$_3$	1.27 (3H, s)	H-2", H-5"	H-2", H-5"
5"	25.3	CH$_3$	1.48 (3H, s)	H-2", H-4"	H-2", H-4"
2"'	100.02	q		H-2"", H-6""	
3"'	90.13	q			
4"'	187.14	q			
5"'	163.10	q		H-6"'	
6"'	97.26	CH	5.99（1H，d, *J* = 1.8 Hz）	H-8"'	H-8"'
7"'	167.97	q		H-6"', H-8"'	
8"'	96.22	CH	6.01（1H，d, *J* = 1.8 Hz）	H-6"'	H-6"'
9"'	159.05	q		H-8"'	
10"'	99.69	q		H-6"', H-8"'	
1""	125.99	q		H-3"", H-5""	
2"", 6""	129.14	CH	7.58（2H，d, *J* = 8.9 5Hz）	H-6"" for C-2"", H-2"" for C-6""	H-2""
3"", 5""	113.5	CH	6.96（2H，d, *J* = 8.95 Hz）	H-5"" for C-3"", H-3"" for C-5""	H-2""
4""	160.2	q		H-2"", H-3"", H-5"", H-6"", H-4""-OCH$_3$	
4""-OCH$_3$	55.15	CH$_3$	3.75 (3H, s)		

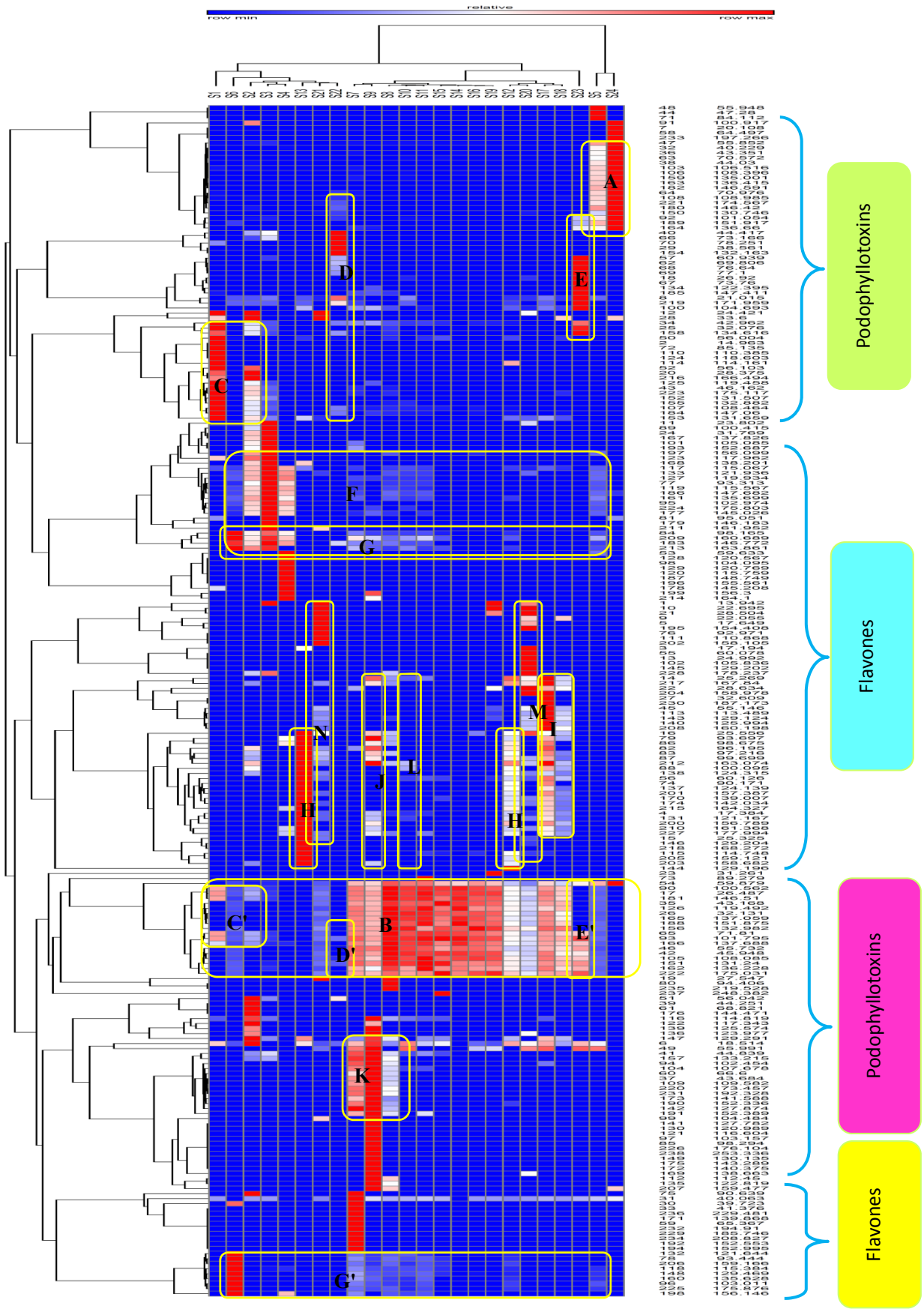


Fig. S5† ^{13}C NMR map-based pattern recognition of the metabolites of RPLC fractions. The minimum intensity threshold of ^{13}C NMR signals of fractions was set at 0.002.

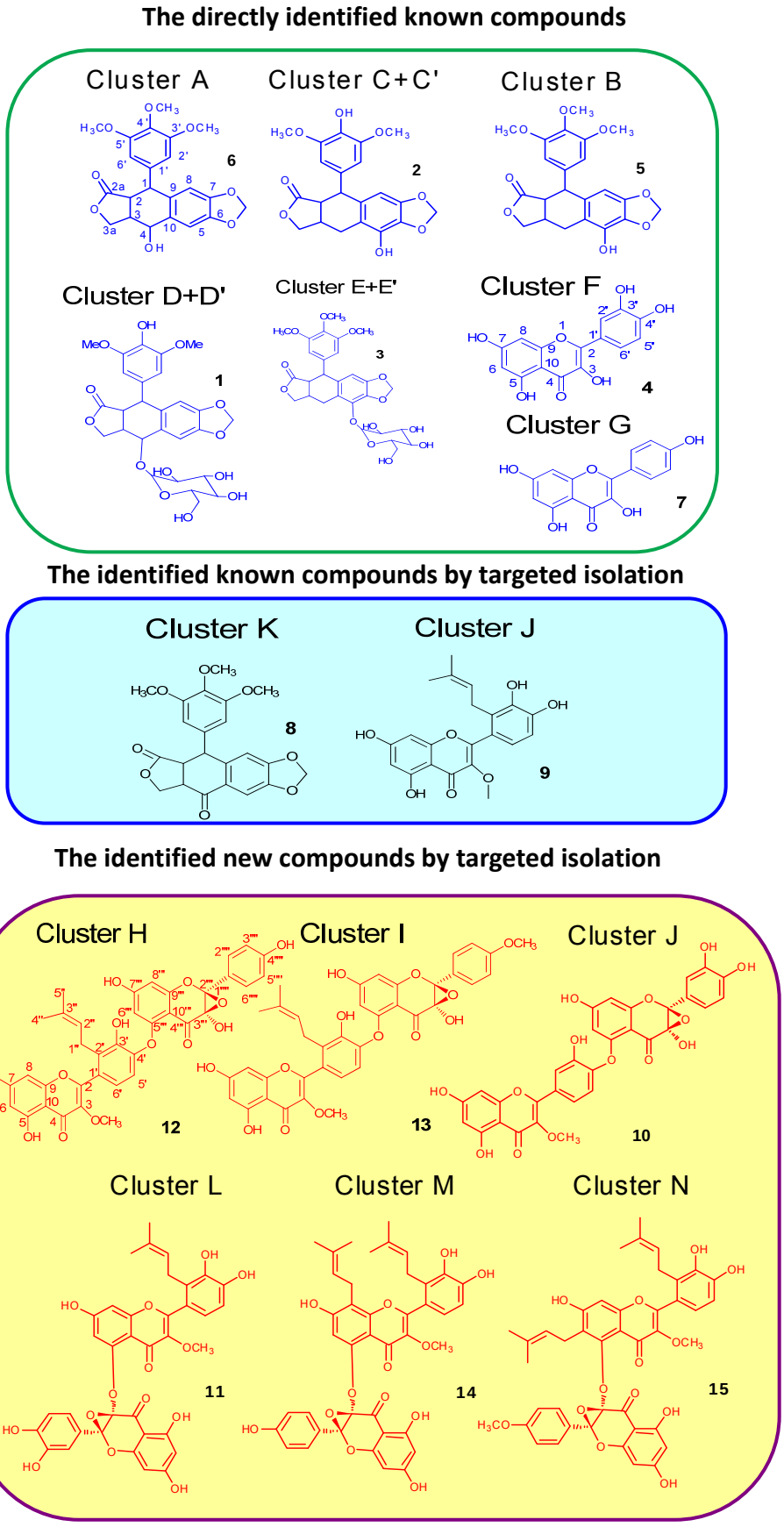
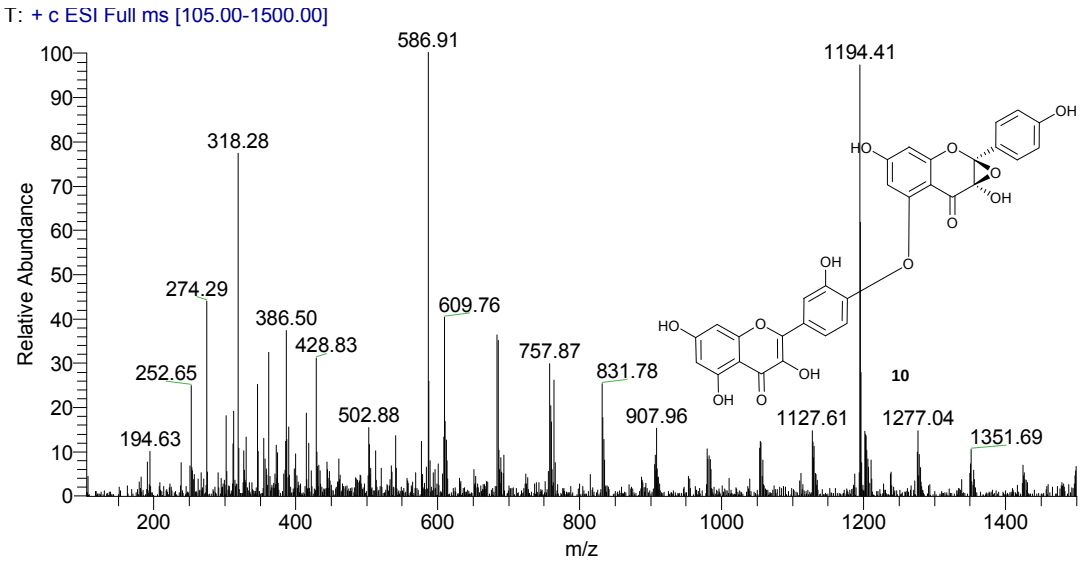


Fig. S6† The known and new compounds identified from *Dysosma versipellis* (Hance)

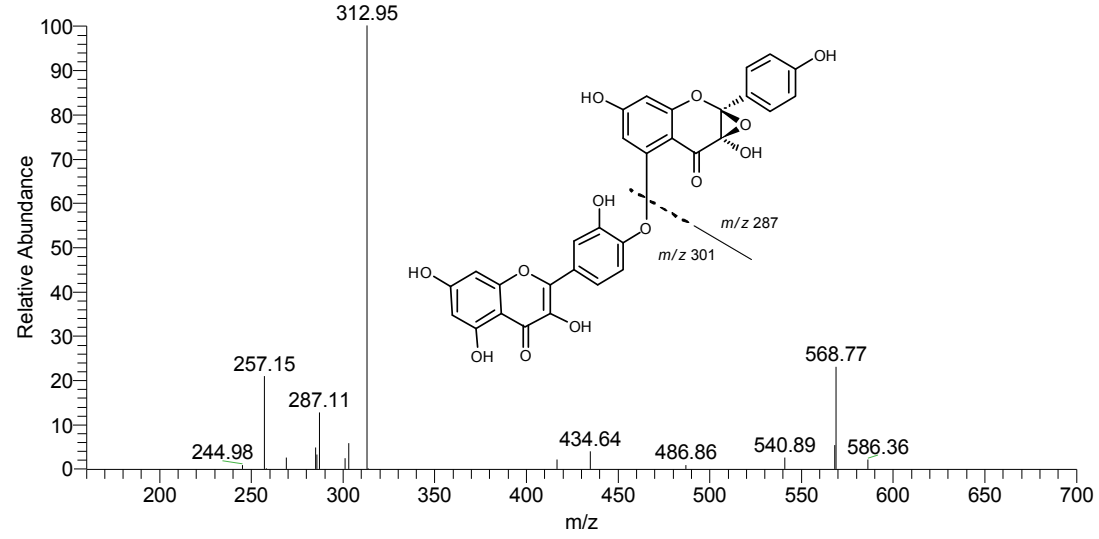
Structure identification of compound 10

ESI-MS spectra of compound **10** showed that it had prominent ions of $[M-H]^-$ at *m/z* 585 (82%), $[2M-H]^-$ at *m/z* 1171 (100%) and $[M+H]^+$ at *m/z* 587 (100%)(Fig. S7A, C†), suggesting that its molecular weight was 586. The high resolution ESI-TOF-MS analysis indicated that its molecular formula was $C_{30}H_{18}O_{13}$ (Fig. S7E†). Its 1D and 2D NMR data were similar with those of compounds **12** and **13**, but ESI-MS/MS analysis indicated that there was no prenyl group signals. The structure of **10** was illustrated in the Fig. 4, which was fully supported by 1D and 2D NMR data (Table S7†). Similarly, it was named as podoverine F.

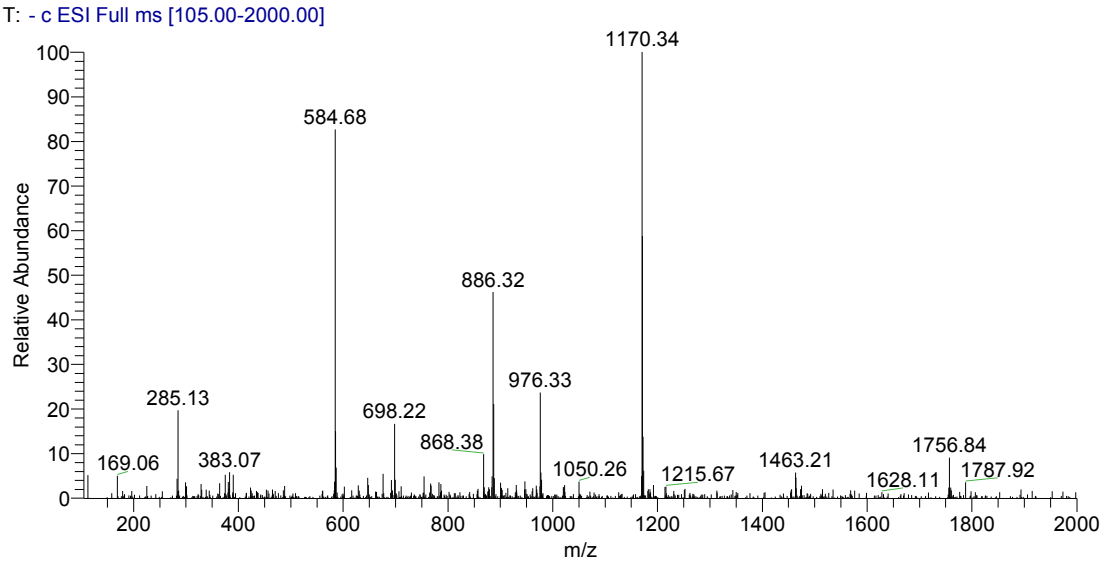
(**A**)Positive ESI-MS of **10**



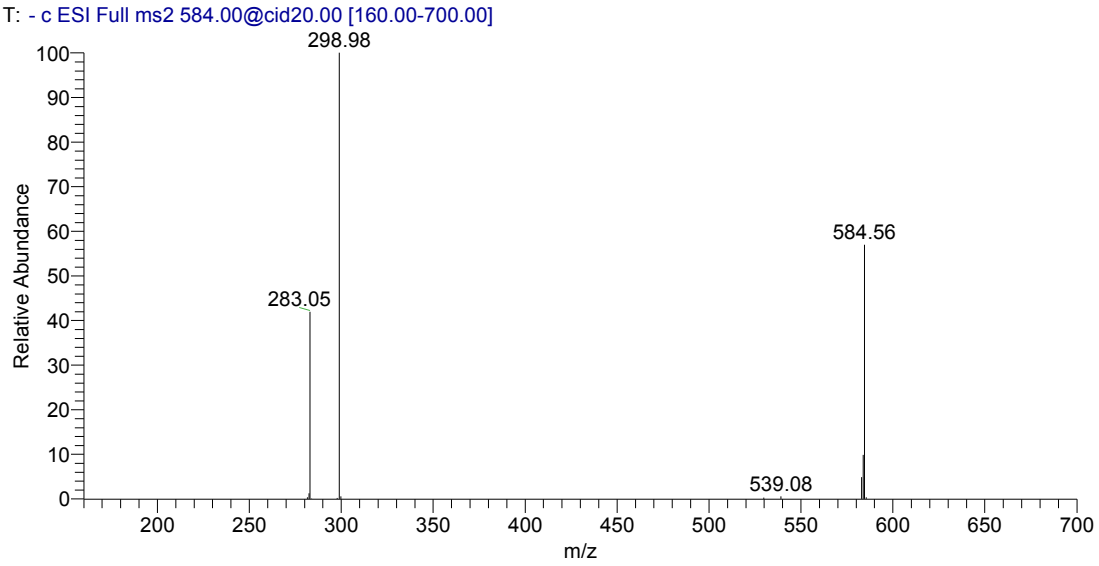
(**B**) Positive ESI-MS/MS of **10** (*m/z* 587→)



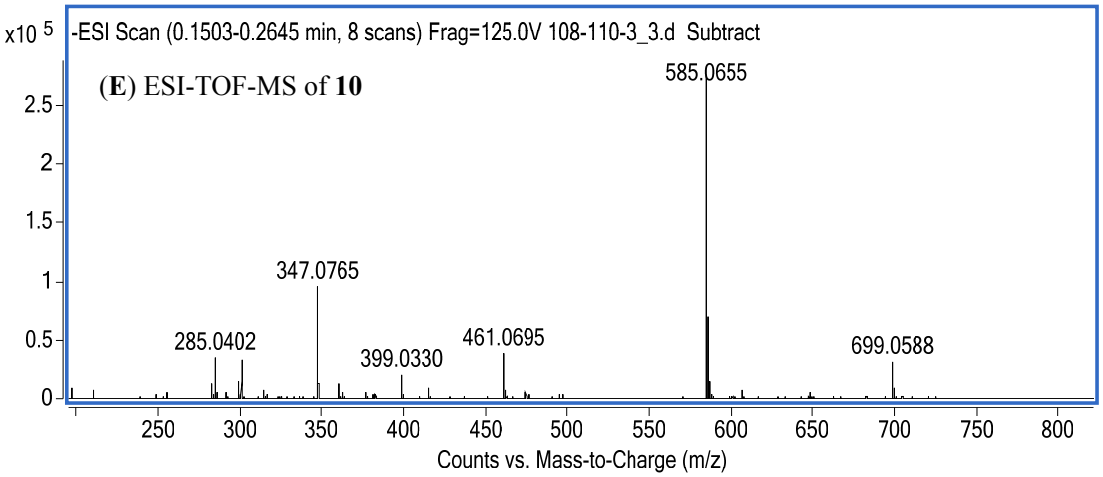
(**C**) Negative ESI-MS of **10**



(**D**) Negative ESI-MS/MS of **10** (*m/z* 585→)

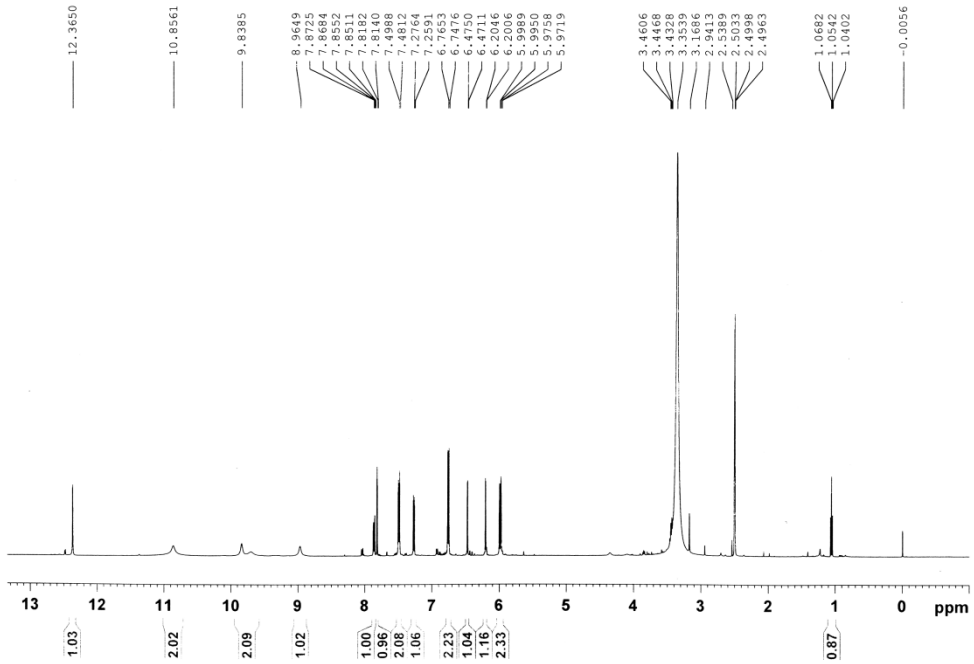


(**E**) ESI-TOF-MS of **10**

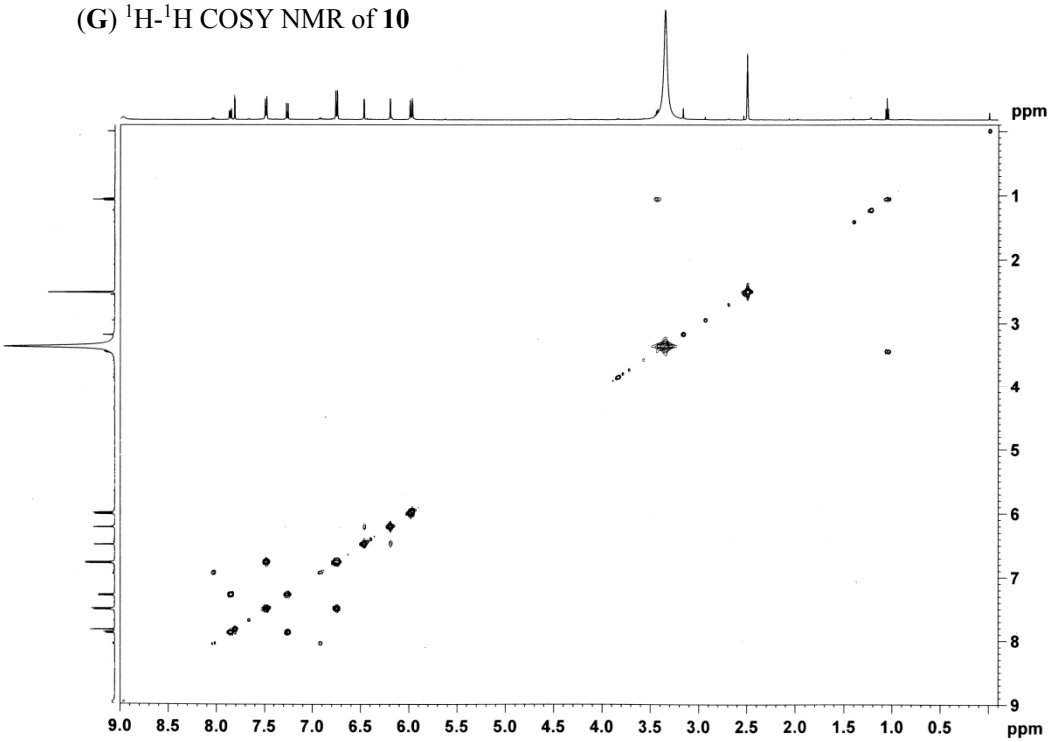


Ion Formula	m/z	Calc m/z	Diff (ppm)	DBE
C30 H17 O13	585.0655	585.0669	2.42	22.5

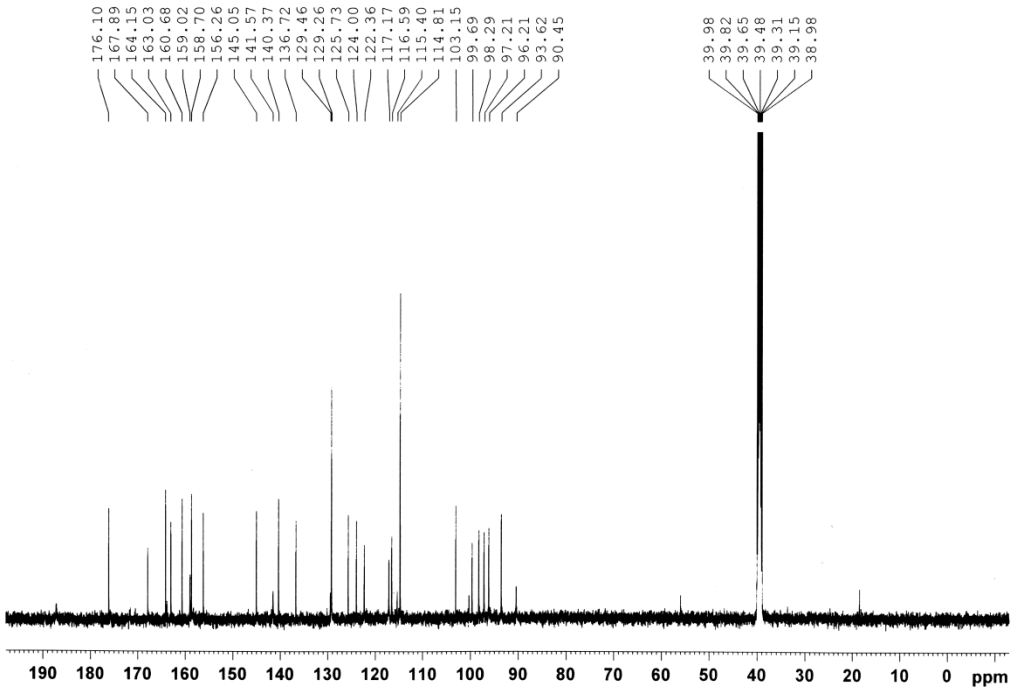
(**F**) ^{1}H NMR of **10**



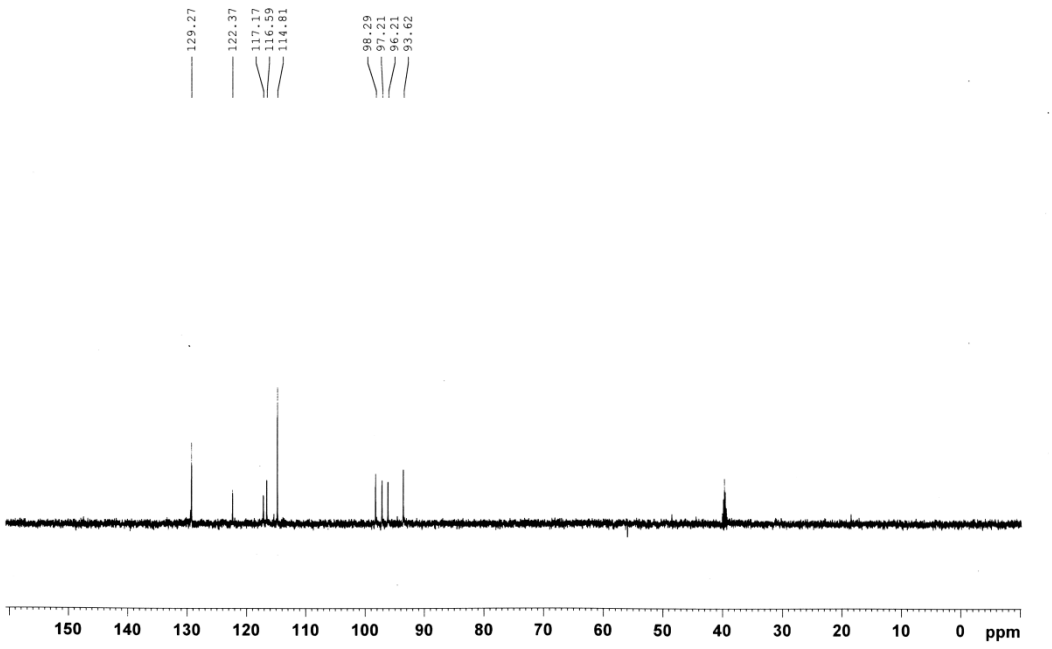
(**G**) ^{1}H-^{1}H COSY NMR of **10**



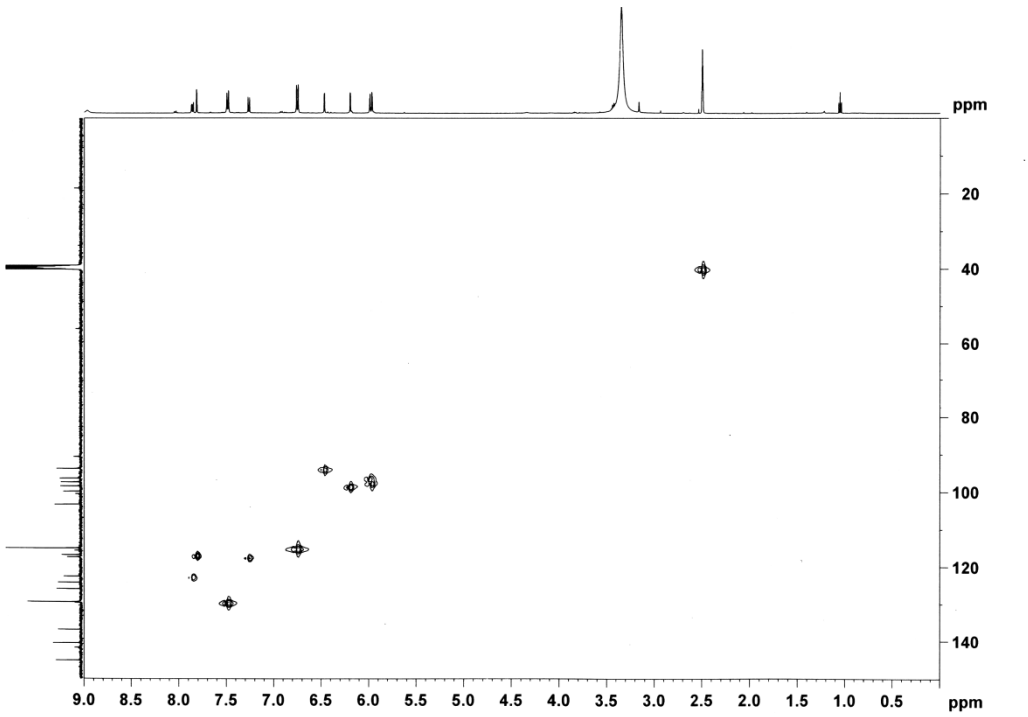
(**H**) ^{13}C NMR of **10**



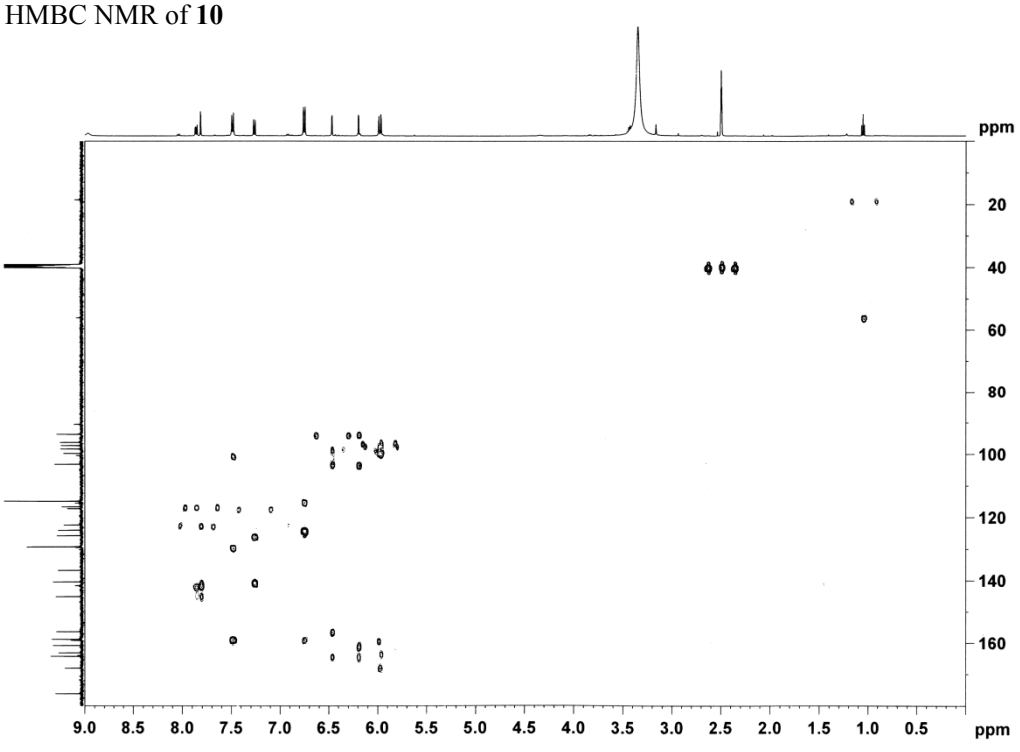
(**I**) DEPT 135 NMR of **10**



(**J**) HSQC NMR of **10**



(**K**) HMBC NMR of **10**



(**L**) NOESY NMR of **10**

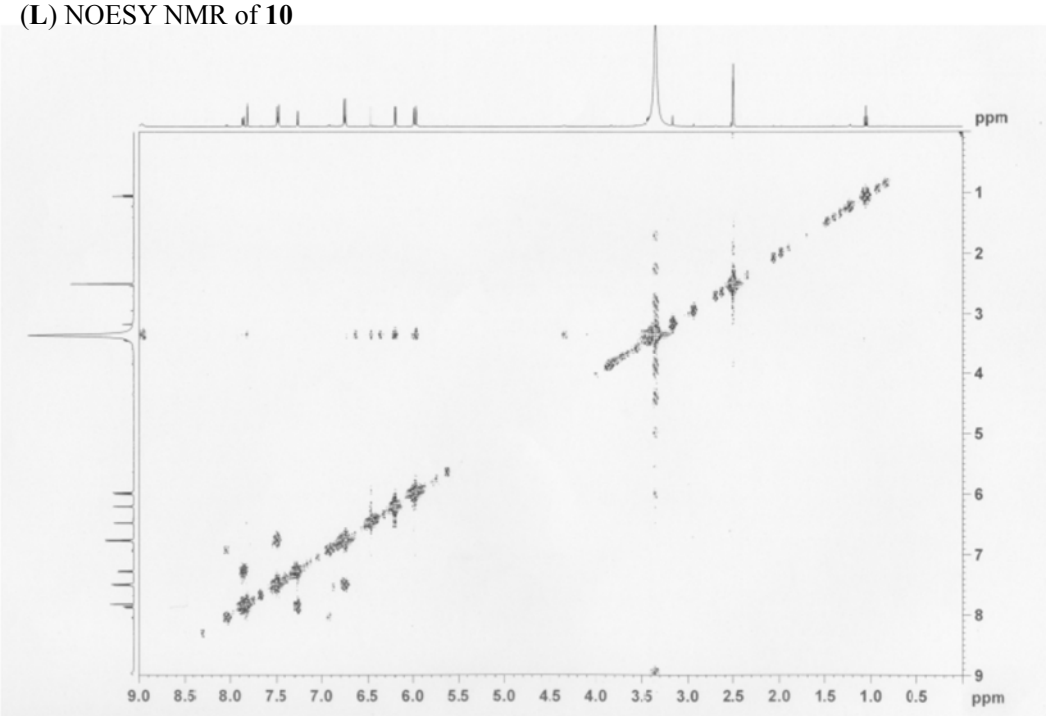


Fig. S7† ESI-MS, ESI-MS/MS, ESI-TOF-MS, and 1D and 2D NMR spectra of compound **10.**

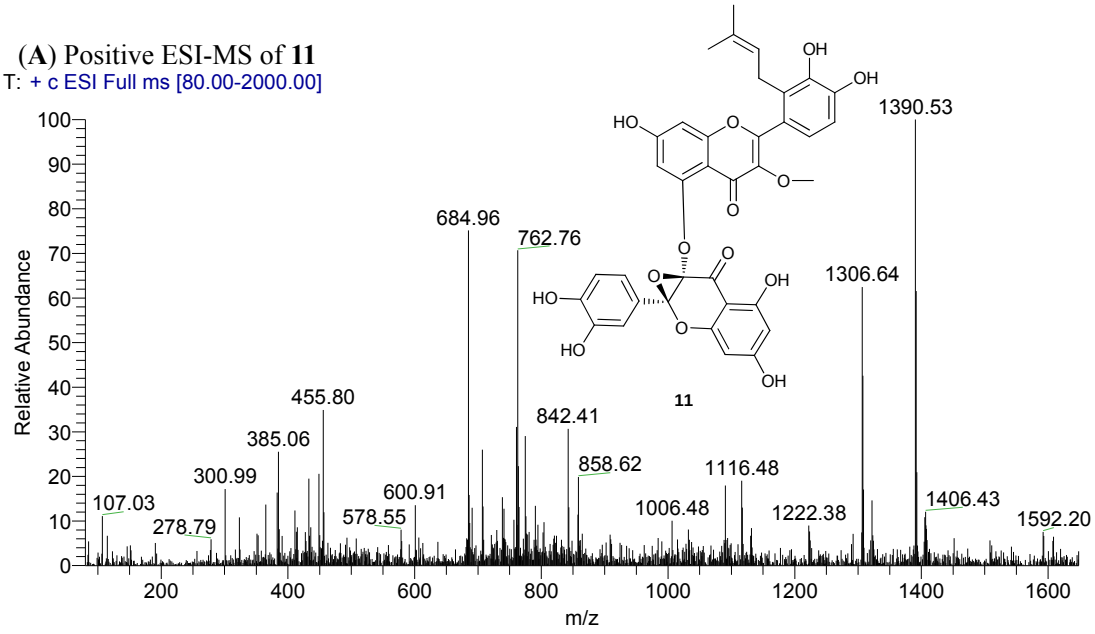
Table S7[†] 1D and 2D NMR data of compound **10** (DMSO-*d6*, 500MHz for ^{1}H)

Atom	**10**				
	δ_C (ppm)	DEPT[a]	HMQC	HMBC	^{1}H-^{1}H COSY
			δ_H (ppm)	correlation with	correlation with
1					
2	145.03	q		H-2', H-6'	
3	136.68	q			
4	176.08	q			
5	160.66	q		H-6	
5-OH			12.37 (1H, s)		
6	98.26	CH	6.20 (1H, d, *J* = 2.0 Hz)	H-8	H-8
7	164.13	q		H-6, H-8	
8	93.59	CH	6.47 (1H, d, *J* = 1.95 Hz)	H-6	H-6
9	156.24	q		H-8	
10	103.12	q		H-6, H-8	
1'	125.7	q		H-5'	
2'	116.56	CH	7.81 (1H, d, *J* = 2.1 Hz)	H-6'	H-6'
3'	140.35	q		H-2', H-5'	
4'	141.56	q		H-2', H-5', H-6'	
5'	117.12	CH	7.26 (1H, d, *J* = 8.65 Hz)	H-6'	H-6'
6'	122.32	CH	7.86 (1H, d, *J* = 8.65 Hz, *J* = 2.05 Hz)	H-2'	H-2', 5'
1"					
2"	100.3	q		H-2"', H-6"'	
3"	90.43	q			
4"	187.11	q			
5"	163.02	q		H-6"	
6"	97.2	CH	5.97 (1H, d, *J* = 1.9 Hz)	H-8"	H-8"
7"	168	q		H-6", H-8"	
8"	96.22	CH	5.99 (1H, d, *J* = 1.95 Hz)	H-6"	H-6"
9"	158.98	q		H-8"	
10"	99.61	q		H-6", H-8"	
1"'	124	q		H-3"', H-5"'	
2"',6"'	129.22	CH	7.49 (2H, d, *J* = 8.8 Hz)	H-6"' for C-2"', H-2"' for C-6"'	H-3"' for H-2"' and H-5"' for H-6"'
3"',5"'	114.77	CH	6.75 (2H, d, *J* = 8.85 Hz)	H-5"' for C-3"', H-3"' for C-5"'	H-2"' for H-3"' and H-6"' for H-5"'
4"'	158.66	q		H-2"', H-3"', H-5"', H-6"'	

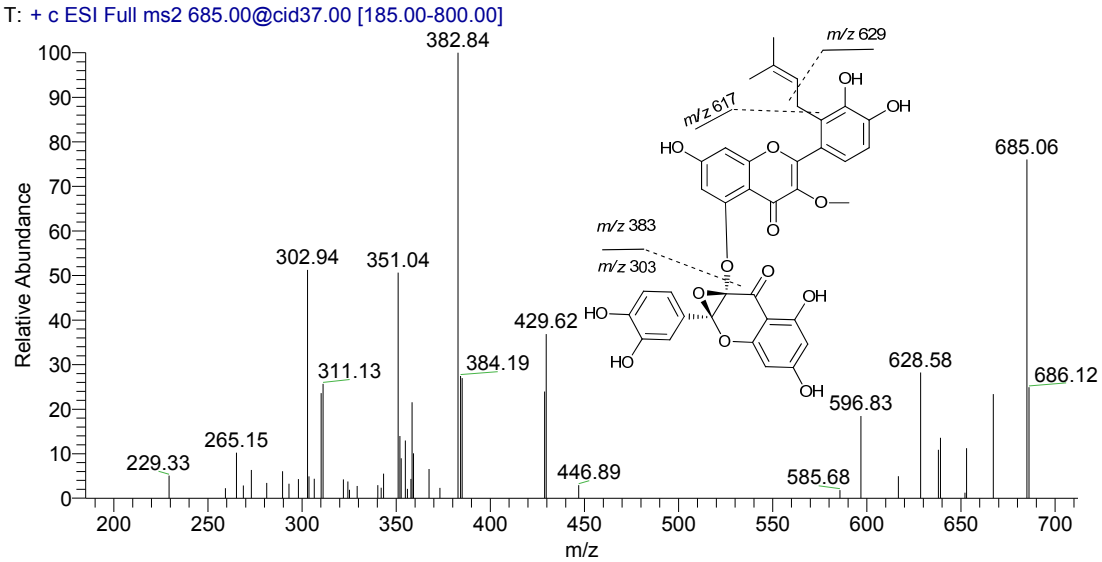
Structure identification of compound 11

ESI-MS spectra of compound **11** showed that it had prominent ions of $[M-H]^-$ at *m/z* 683 (100%), $[2M-H]^-$ at *m/z* 1367 (34%) and $[M+H]^+$ at *m/z* 685 (75%), $[2M+Na]^+$ at *m/z* 1391 (100%) (Fig. S8A, C†), suggesting that its molecular weight was 684. The high resolution ESI-TOF-MS analysis indicated that its molecular formula was $C_{36}H_{28}O_{14}$ (Fig. S8E†). The NMR data and ESI-MS/MS analysis showed that it had podoverine A as a subunit moiety, and the other one was a 6,8,5′,6′-tetrahydroxy-(2,3-epoxy)flavonone. However, compared with compounds **12** and **13**, the ^{13}C NMR signals of the C in carbonyl of the 6,8,5′,6′-tetrahydroxy-(2,3-epoxy)flavonone moiety moved toward high field about 15ppm, affected by the phenyl of another moiety, implied that the link location of the moiety was at C3‴-OH. In addition, there was also only one C-OH signal at δ_C 12.58 (1H, C5‴-OH), so the other link location was at C5-OH. The structure of **11** was established as Fig. 4 and its 1D and 2D NMR were summarized in Table S8†. And it was named as podoverine G.

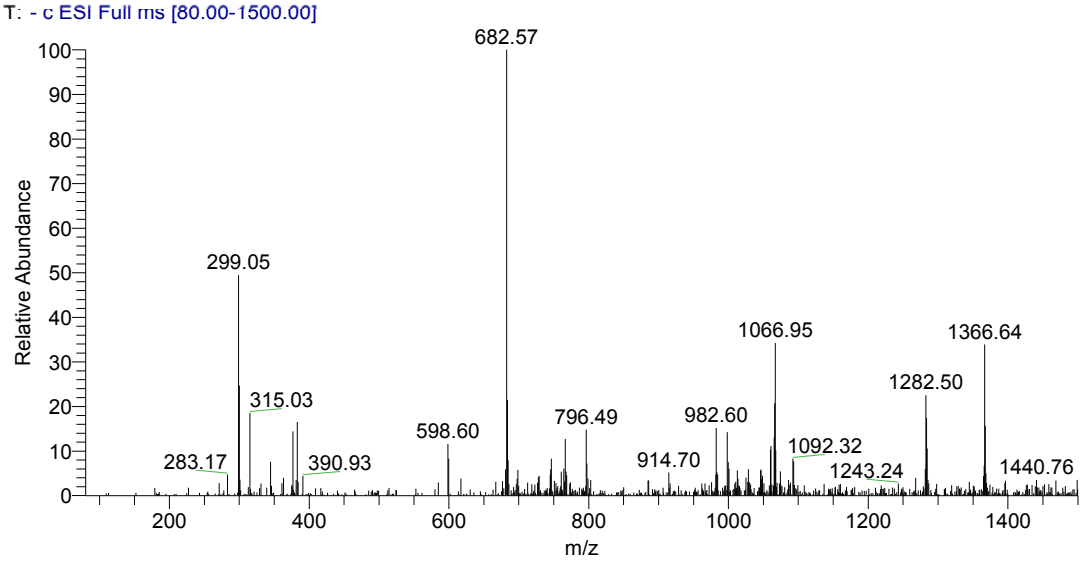
(**A**) Positive ESI-MS of **11**



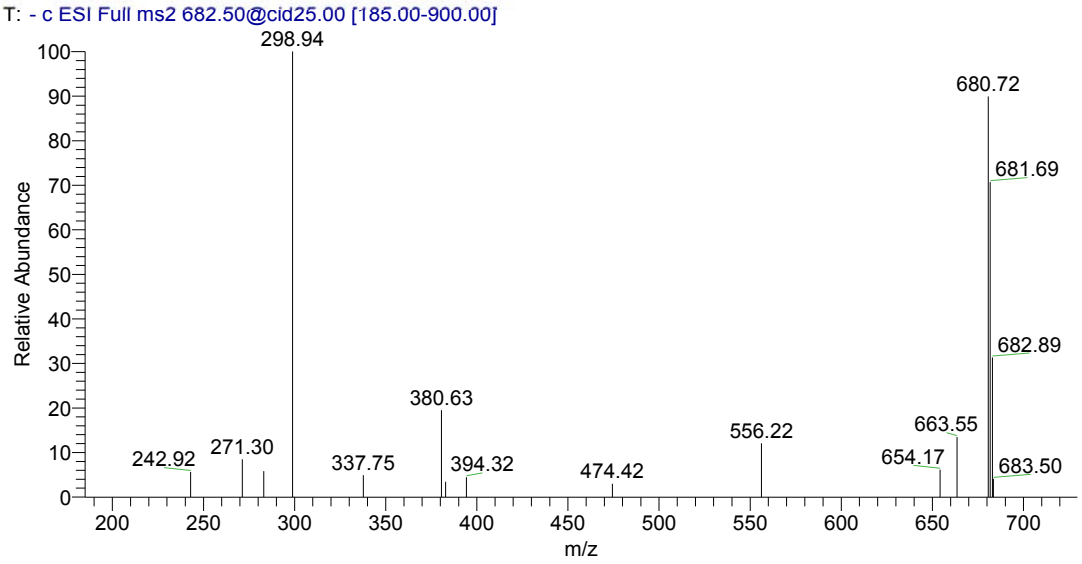
(**B**) Positive ESI-MS/MS of **11** (*m/z* 685→)

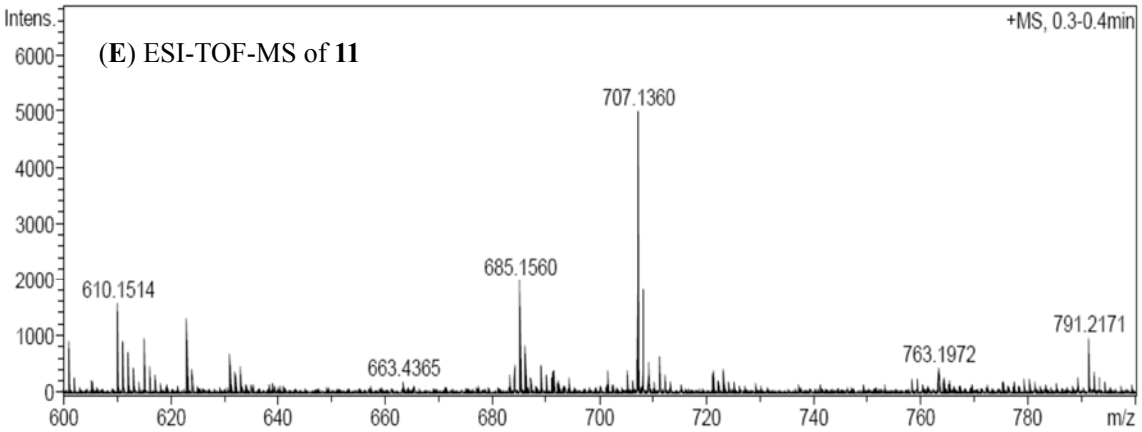


(**C**) Negative ESI-MS of **11**



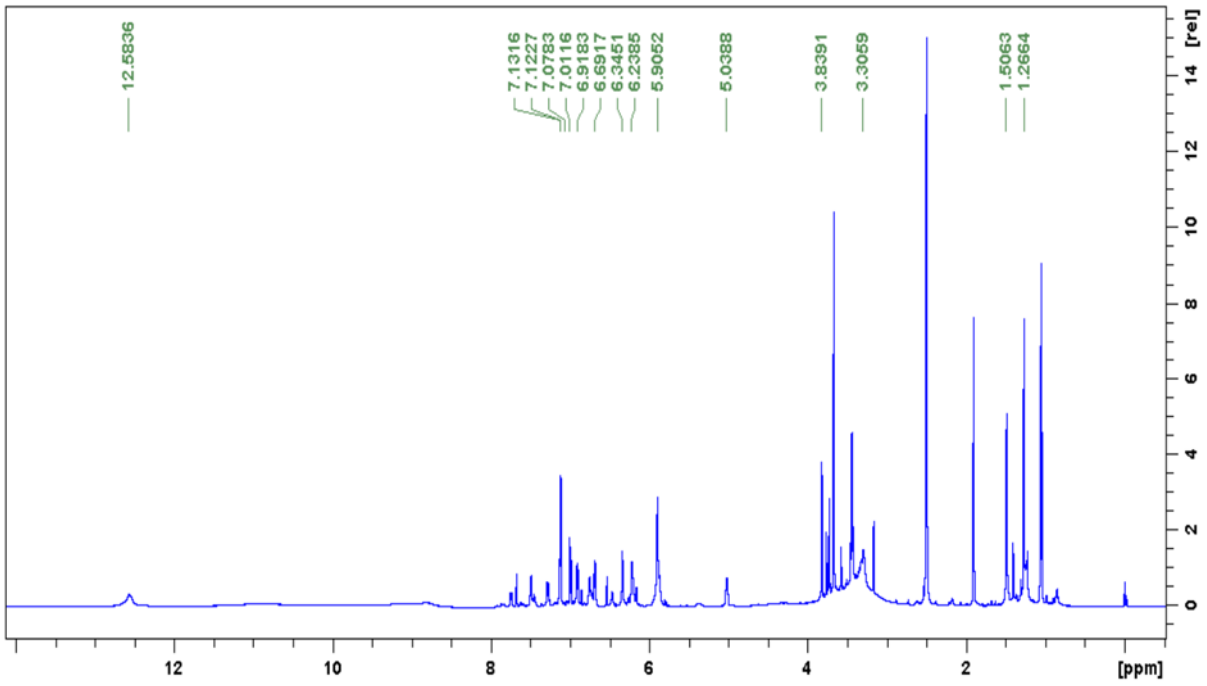
(**D**) Negative ESI-MS/MS of **11** (*m/z* 683→)



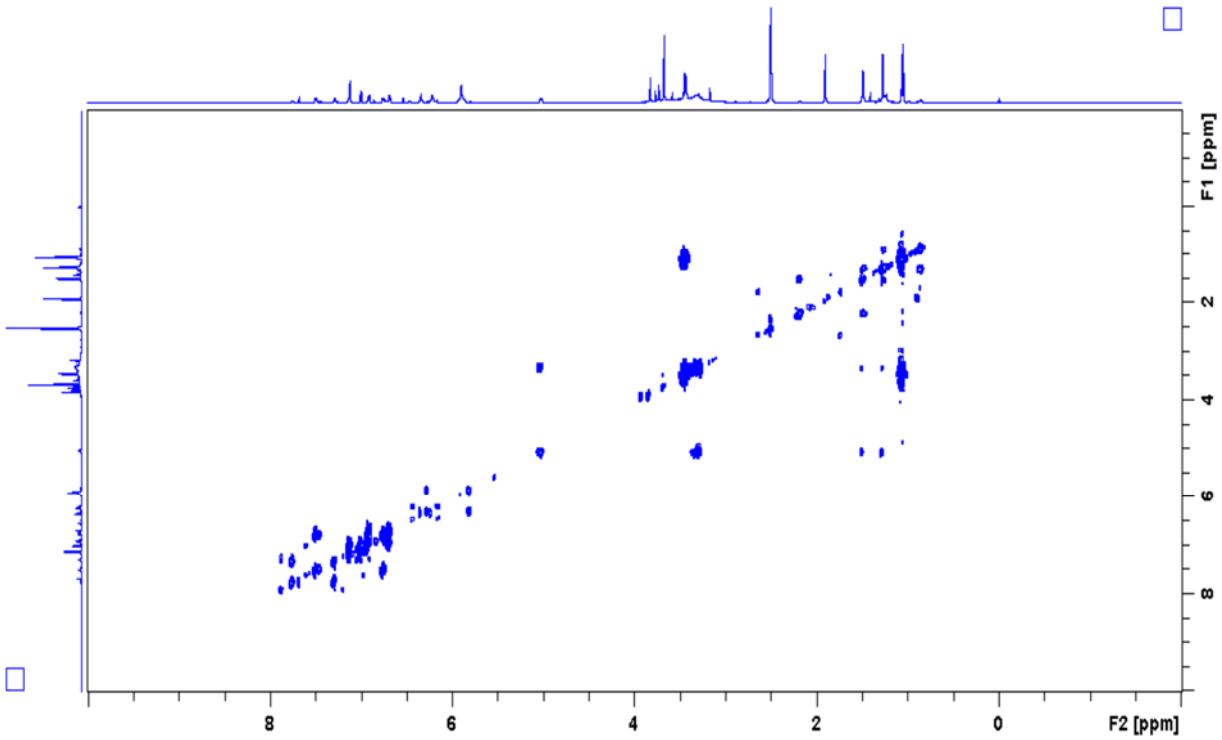


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
685.1560	1	C 36 H 29 O 14	100.00	685.1552	-0.8	-1.2	21.9	22.5	even	ok
707.1360	1	C 36 H 28 Na O 14	100.00	707.1371	1.1	1.6	16.6	22.5	even	ok

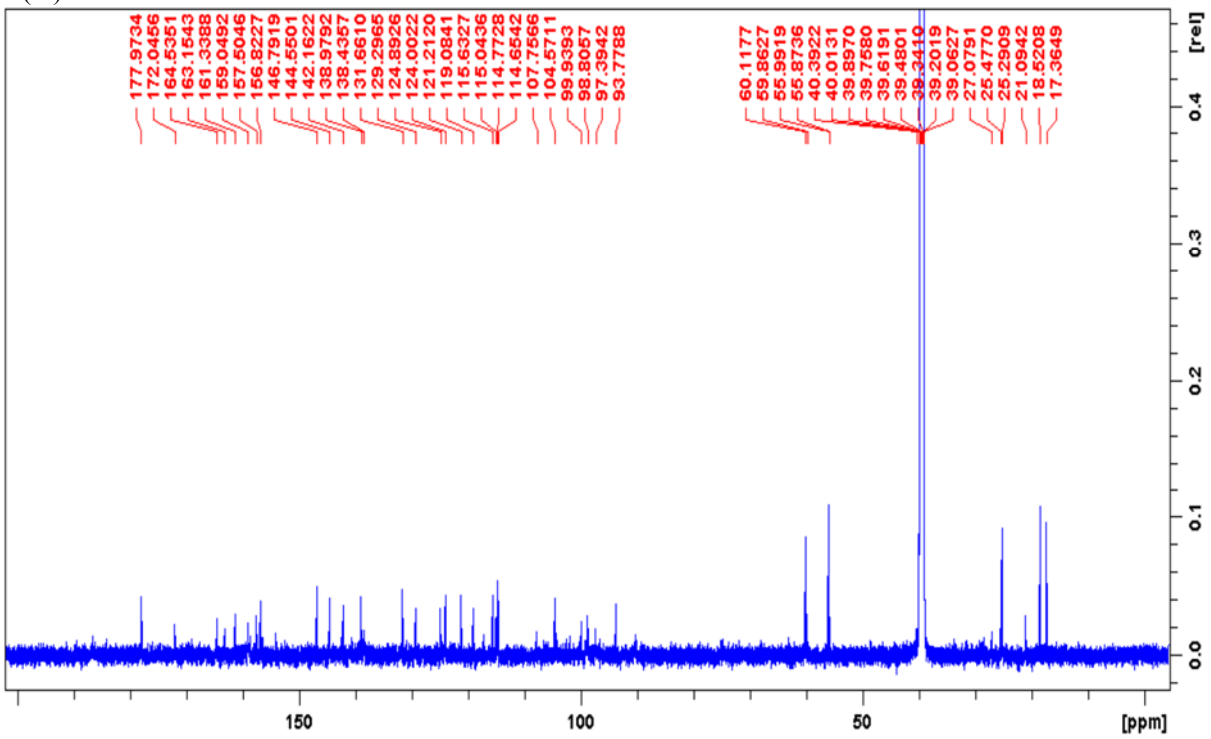
(**F**) ^{1}H NMR of **11**



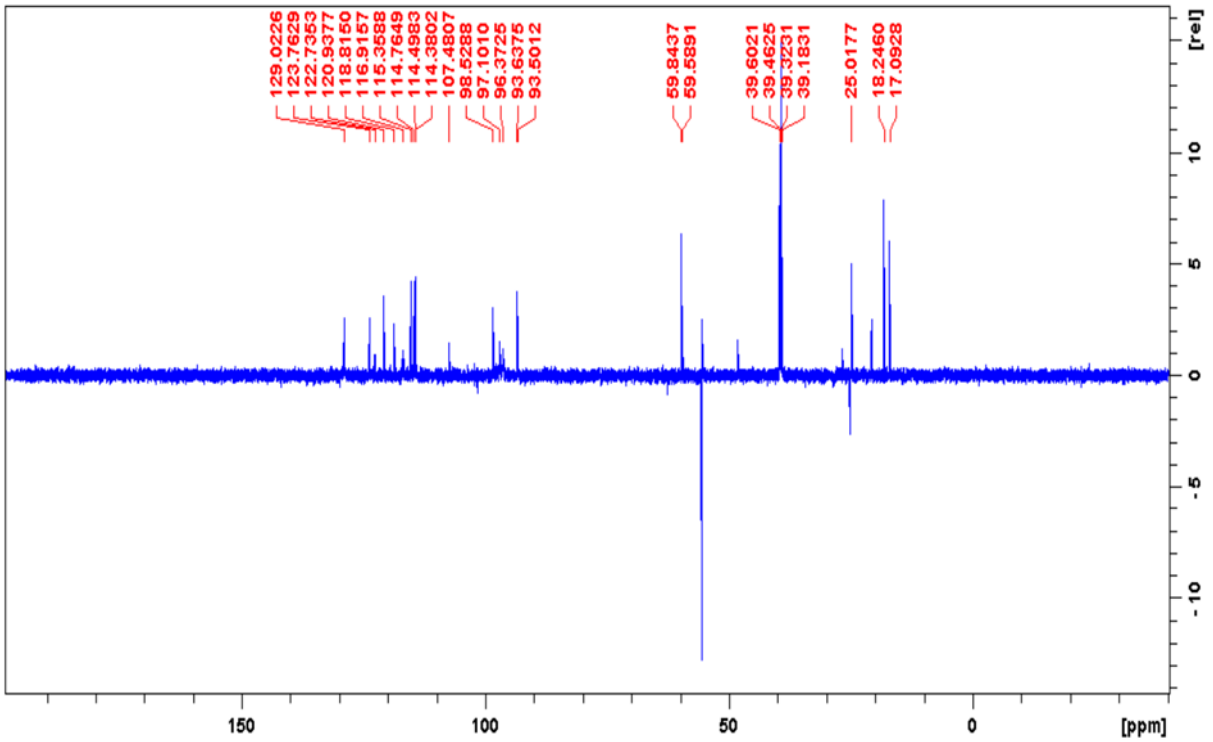
(**G**) ^{1}H-^{1}H COSY NMR of **11**



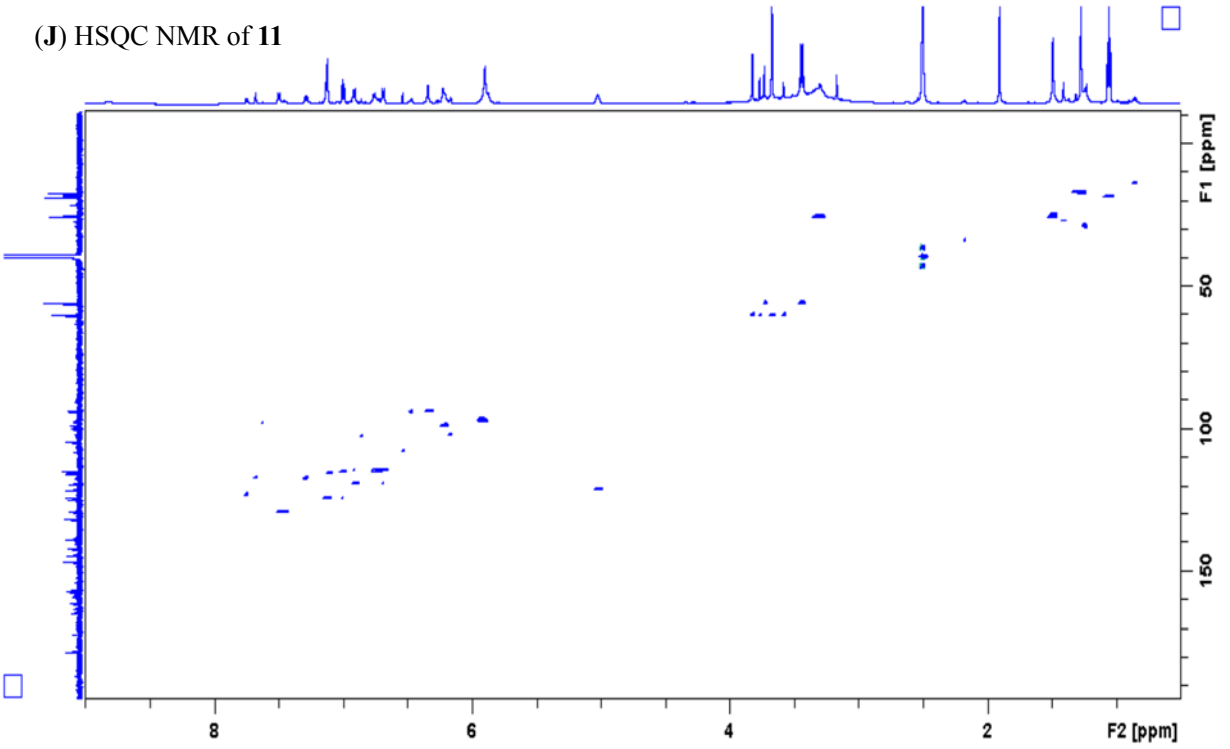
(**H**) ^{13}C NMR of **11**



(**I**) DEPT135 NMR of **11**



(**J**) HSQC NMR of **11**



(**K**) HMBC NMR of **11**

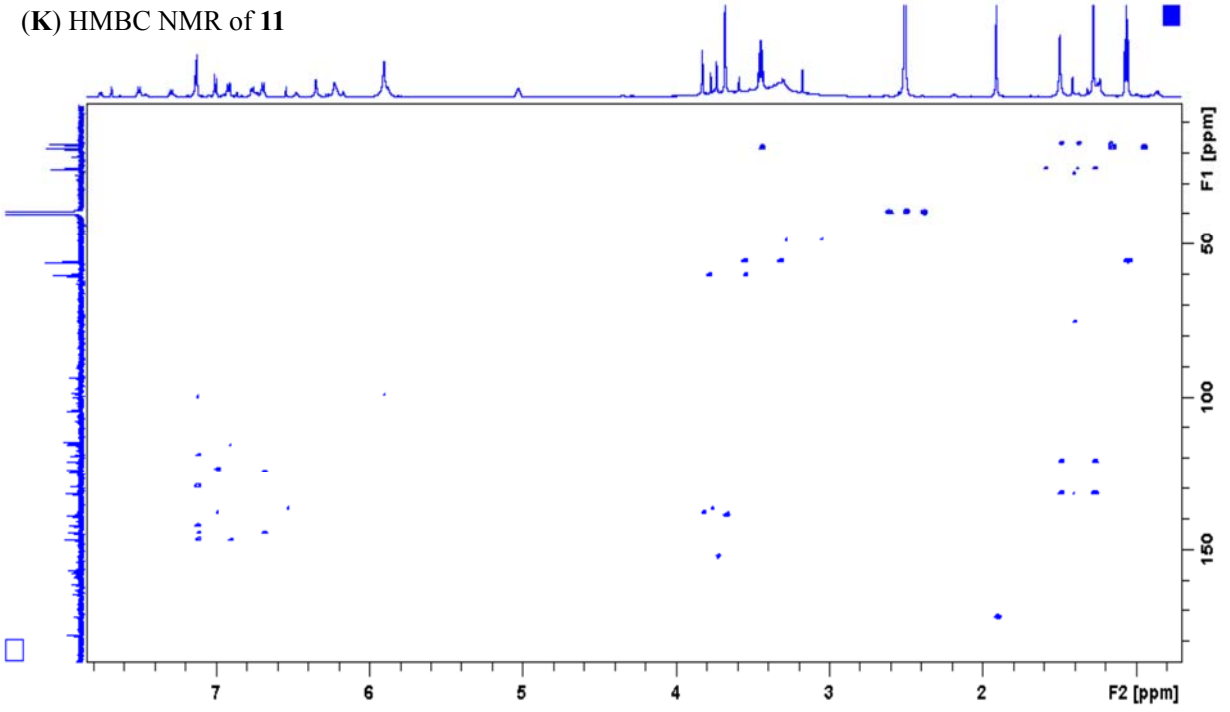


Fig. S8† ESI-MS, ESI-MS/MS, ESI-TOF-MS, and 1D and 2D NMR spectra of compound **11**.

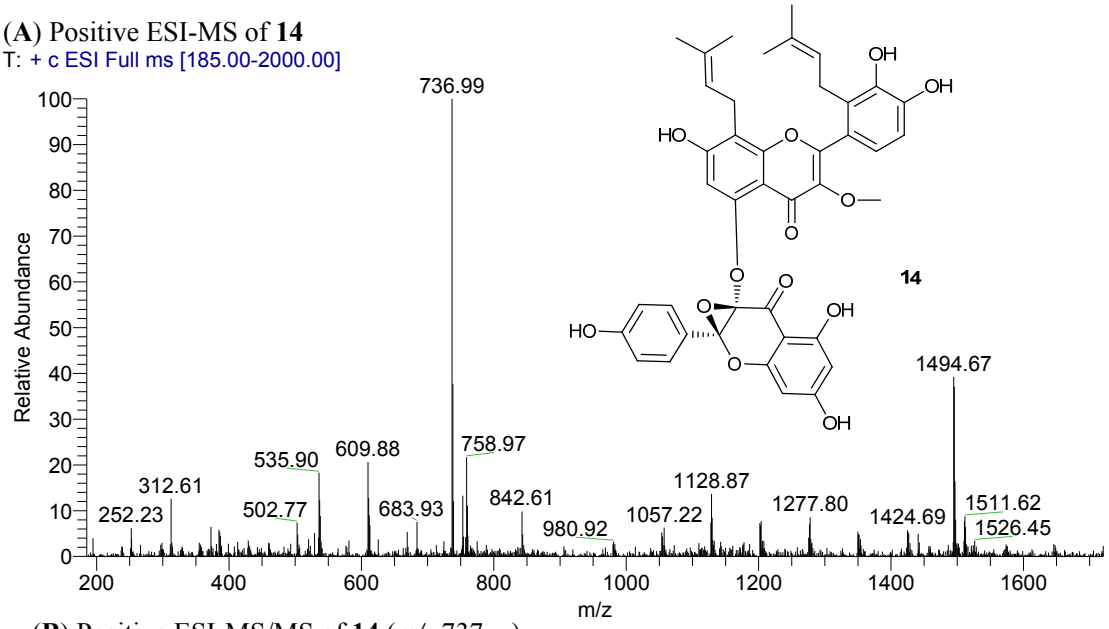
Table S8† 1D and 2D NMR data of compound **11** (DMSO-*d6*, 600MHz for ^{1}H)

Atom	**11**				
	δ_C (ppm)	DEPT[a]	HMQC	HMBC	^{1}H-^{1}H COSY
			δ_H (ppm)	correlation with	correlation with
1					
2	157.5	q		H-6'	
3	138.43	q		H-3-OCH_3	
3-OCH_3	60.12	CH_3	3.83(1H,s)		
4	177.97	q			
5	158.68	q			
6	98.81	CH	6.23(1H,s)	H-8	H-8
7	164.53	q		H-8	
8	93.78	CH	6.35(1H,s)	H-6	H-6
9	156.82	q		H-8	
10	104.57	q		H-6, H-8	
1'	124	q		H-5', H-1"	
2'	129.22	q		H-6', H-1"	
3'	138.98	q		H-5', H-1"	
4'	142.16	q		H-5', H-6'	
5'	115.04	CH	7.01(1H,d,*J*=8.4Hz)	H-6'	H-6'
6'	124	q	7.13(1H,s)	H-5'	H-5'
1"	25.56	CH_2	3.31(2H,m)	H-2"	H-2"
2"	121.21	CH	5.03(1H,s)	H-1", H-4", H-5"	H-1", H-4", H-5"
3"	131.66	q		H-1", H-4", H-5"	
4"	17.36	CH_3	1.49(3H.s)	H-2", H-5"	H-2", H-5"
5"	25.29	CH_3	1.28(3H,s)	H-2", H-4"	H-2", H-4"
1"'					
2"'	99.94	q		H-2"", H-6""	
3"'	90.25	q			
4"'	172.05	q			
5"'	161.34				
5"'-OH			12.58 (1H, s)		
6"'	97.39	CH	5.90(1H,o)	H-8"'	H-8"'
7"'	163.15	q			
8"'	96.62	CH	5.90(1H,o)	H-6"'	H-6"'
9"'	159.05	q		H-8"'	
10"'	101.95	q			
1""	124.89	q		H-5""	
2""	115.63	CH	7.12(1H,d,*J*=2.34Hz）	H-6""	
3""	144.55	q		H-2"", H-5""	
4""	146.79	q		H-2"", H-5"", H-6""	
5""	114.65	CH	6.70(1H,d,*J*=8.34Hz）	H-6""	H-6""
6""	119.09	CH	6.91(1H,dd,*J*=1.8Hz,*J*=8.34Hz)	H-2""	H-5""

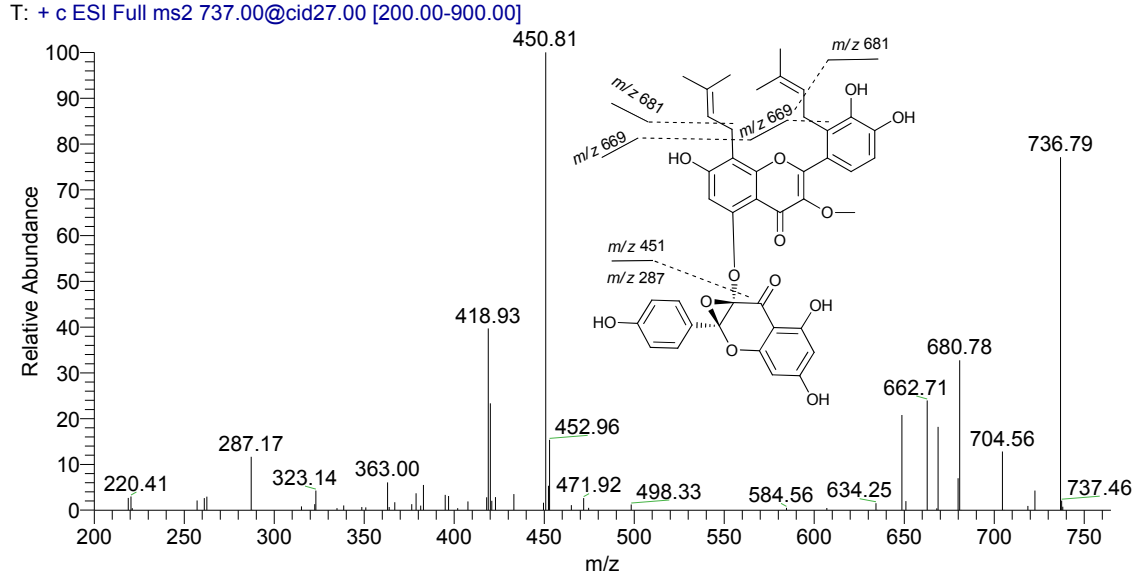
Structure identification of compound 14

ESI-MS spectra of compound **14** showed that it had prominent ions of $[M-H]^-$ at *m/z* 735 (100%), $[2M-H]^-$ at *m/z* 1471 (88%) and $[M+H]^+$ at *m/z* 737 (100%), $[2M+Na]^+$ at *m/z* 1495 (40%) (Fig. S9A, C†), suggesting that its molecular weight was 736. The high resolution ESI-TOF-MS analysis indicated that its molecular formula was $C_{41}H_{36}O_{13}$ (Fig. S9E†). ESI-MS/MS analysis indicated it also contained two moieties. ^{1}H NMR spectrum showed that it had two prenyl group: four CH_3 at δ 1.23 (3H, s), δ 1.44 (6H, s) and δ 1.55 (3H, s), two CH_2 at δ 3.24 (d, *J*=6.84Hz), δ 3.34 (d, *J*=6.3Hz), and two CH at δ 4.94 (s), δ 5.02 (t, *J*=7.2Hz). The position of the two prenyl groups were confirmed by HMBC, which showed three critical correlations between C1″ of one prenyl group and C7, C8 and C9 of the phenyl of the flavonoid and another three critical correlations between C1‴ of the other prenyl group and C1′, C2′ and C3′ of the phenyl of the flavonoid (Fig. 4). Thus the two prenyl group was located at C8 and C2′. And the link mode of the compound **14** was the same with **11**. So the structure of **14** was established as Fig. 4. Its NMR spectra were summarized in Table S9†. And it was named as podoverine H.

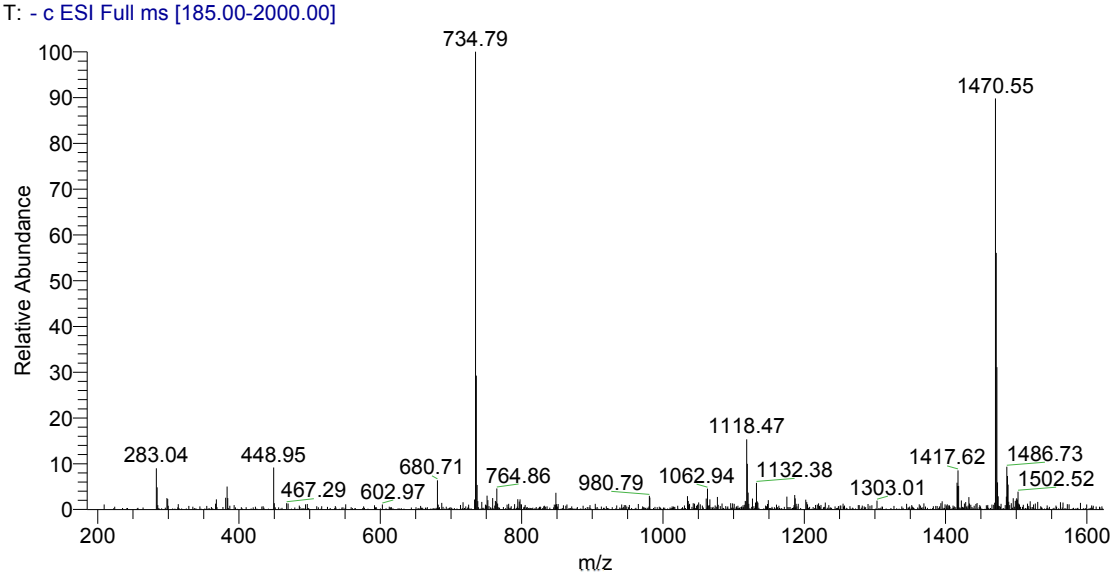
(**A**) Positive ESI-MS of **14**



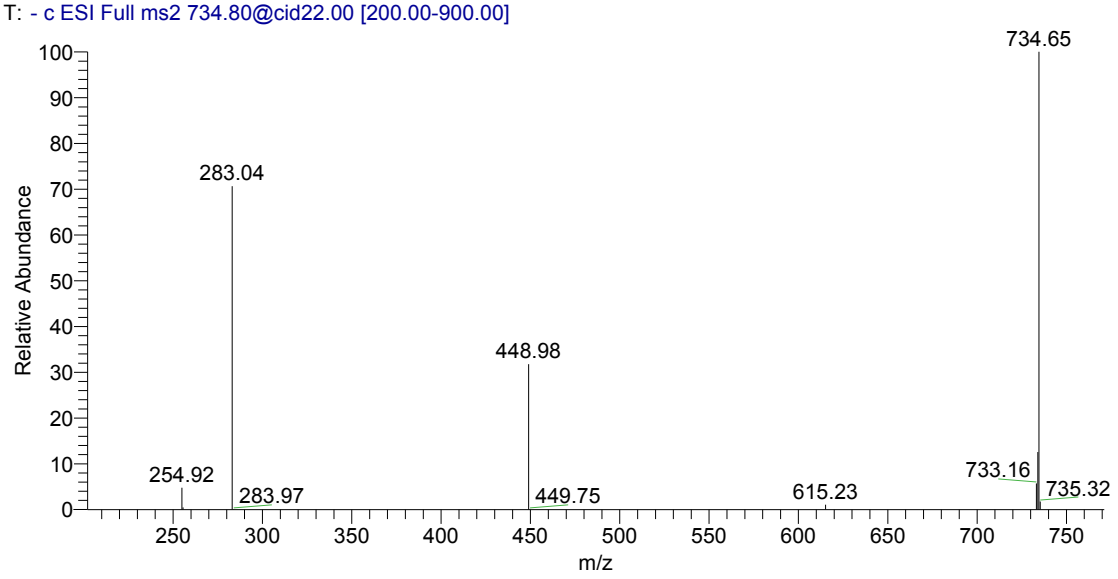
(**B**) Positive ESI-MS/MS of **14** (*m/z* 737→)



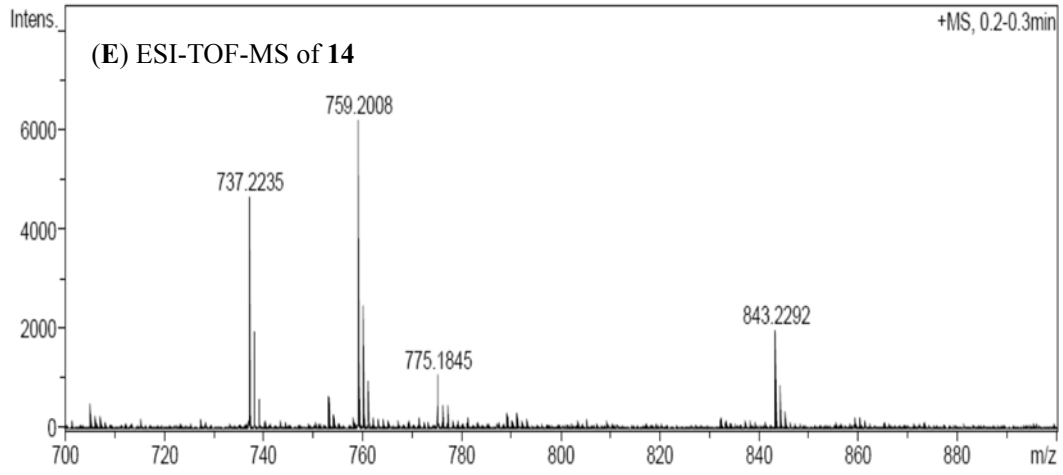
(**C**) Negative ESI-MS of **14**



(**D**) Negative ESI-MS/MS of **14** (*m/z* 735→)

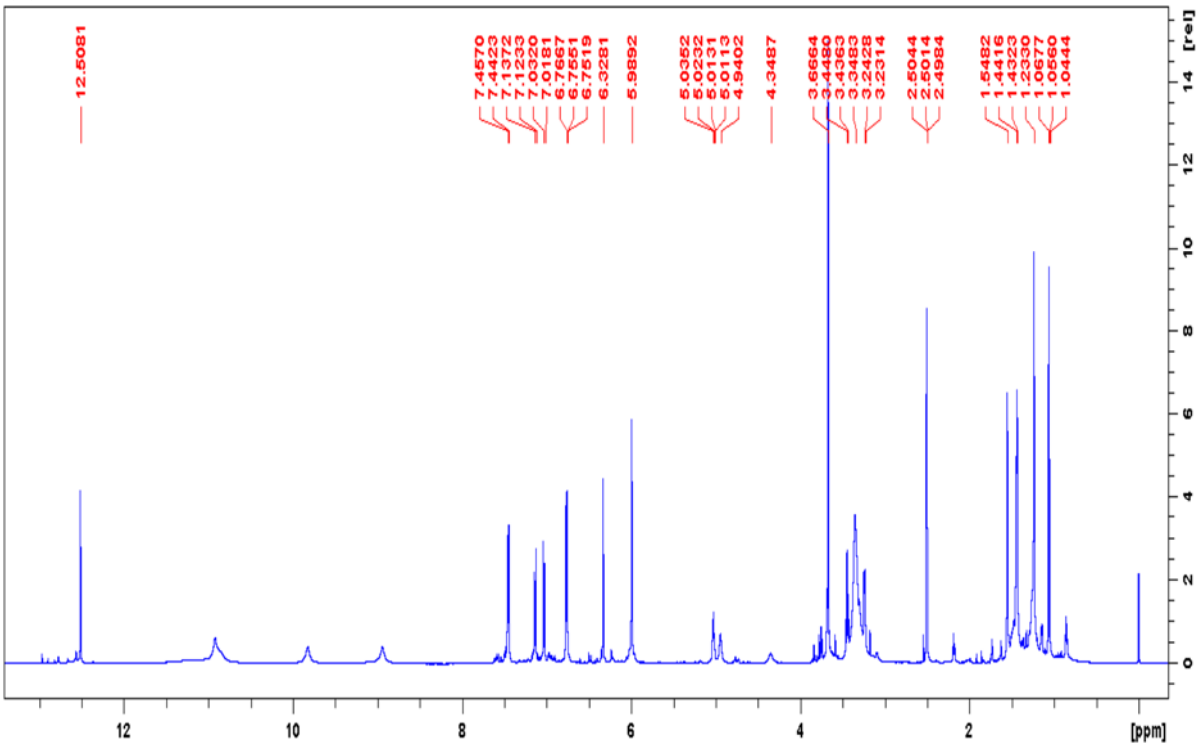


(**E**) ESI-TOF-MS of **14**

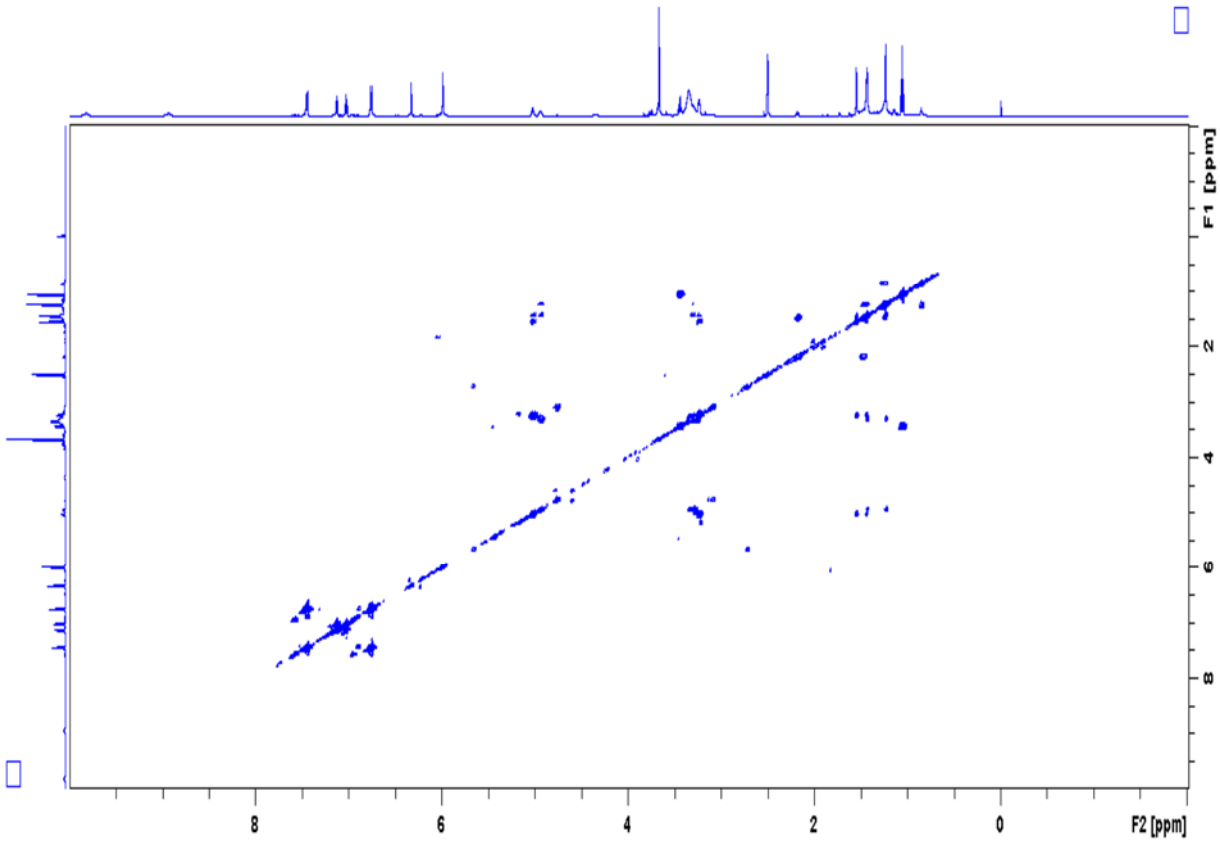


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
737.2235	1	C 41 H 37 O 13	100.00	737.2229	-0.7	-0.9	22.3	23.5	even	ok
759.2008	1	C 41 H 36 Na O 13	100.00	759.2048	4.0	5.3	33.0	23.5	even	ok

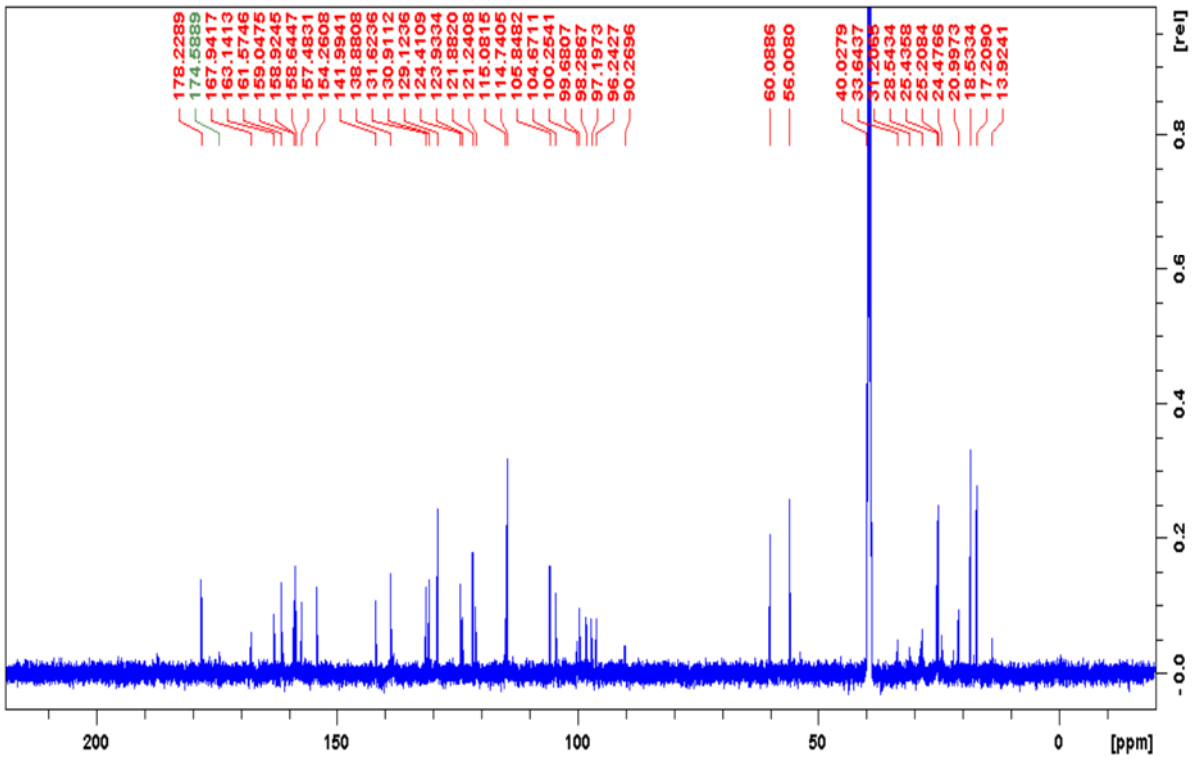
(**F**) ^{1}H NMR of **14**



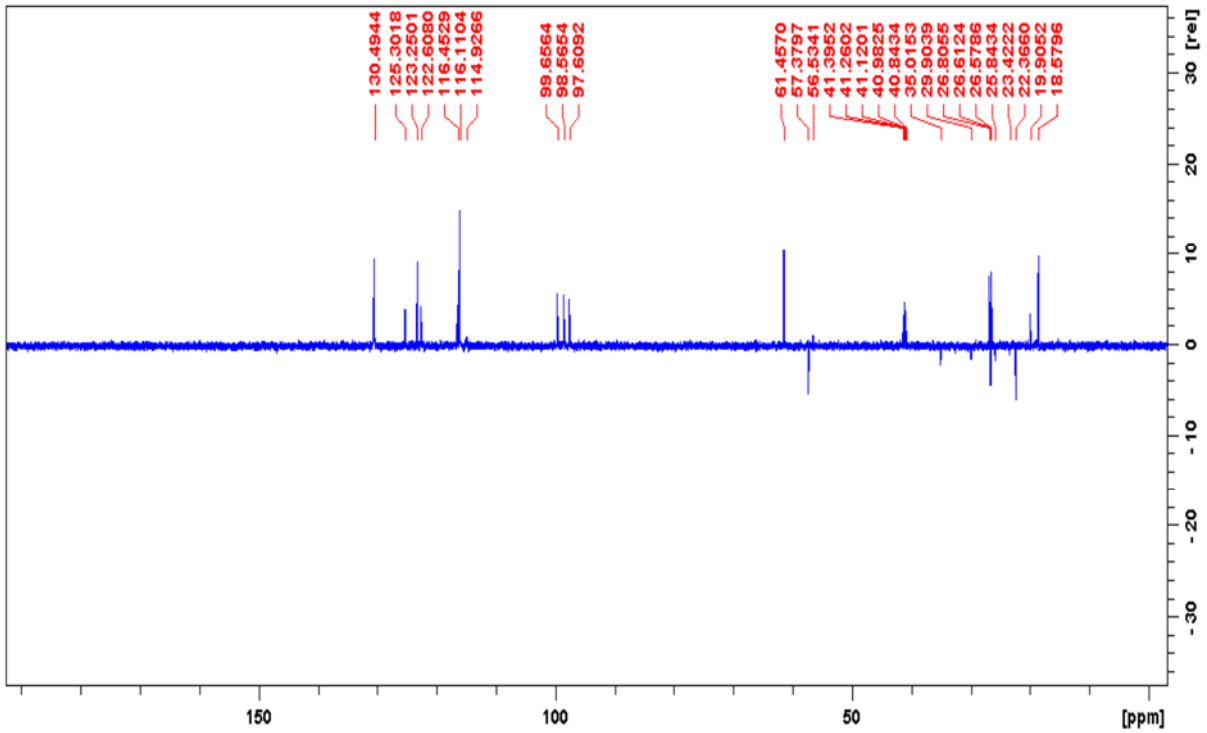
(**G**) ^{1}H-^{1}H COSY NMR of **14**



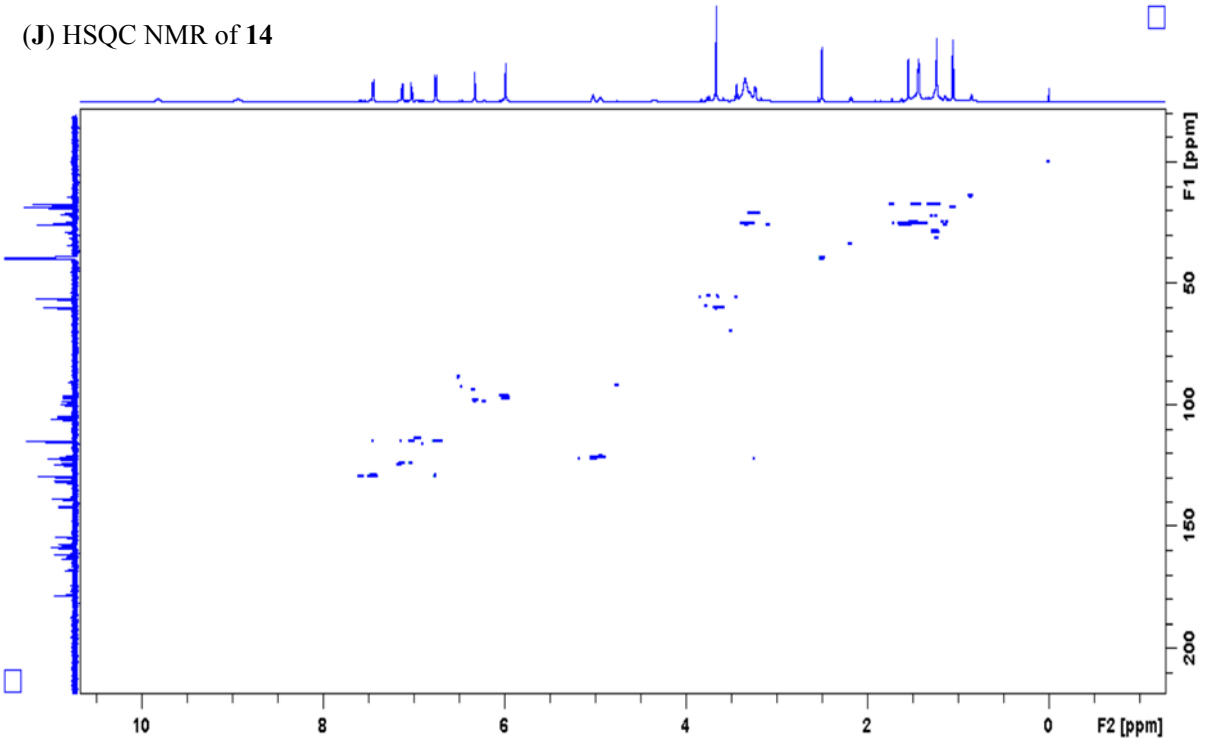
(**H**) ^{13}C NMR of **14**



(**I**) DEPT135 NMR of **14**



(**J**) HSQC NMR of **14**



(**K**) HMBC NMR of **14**

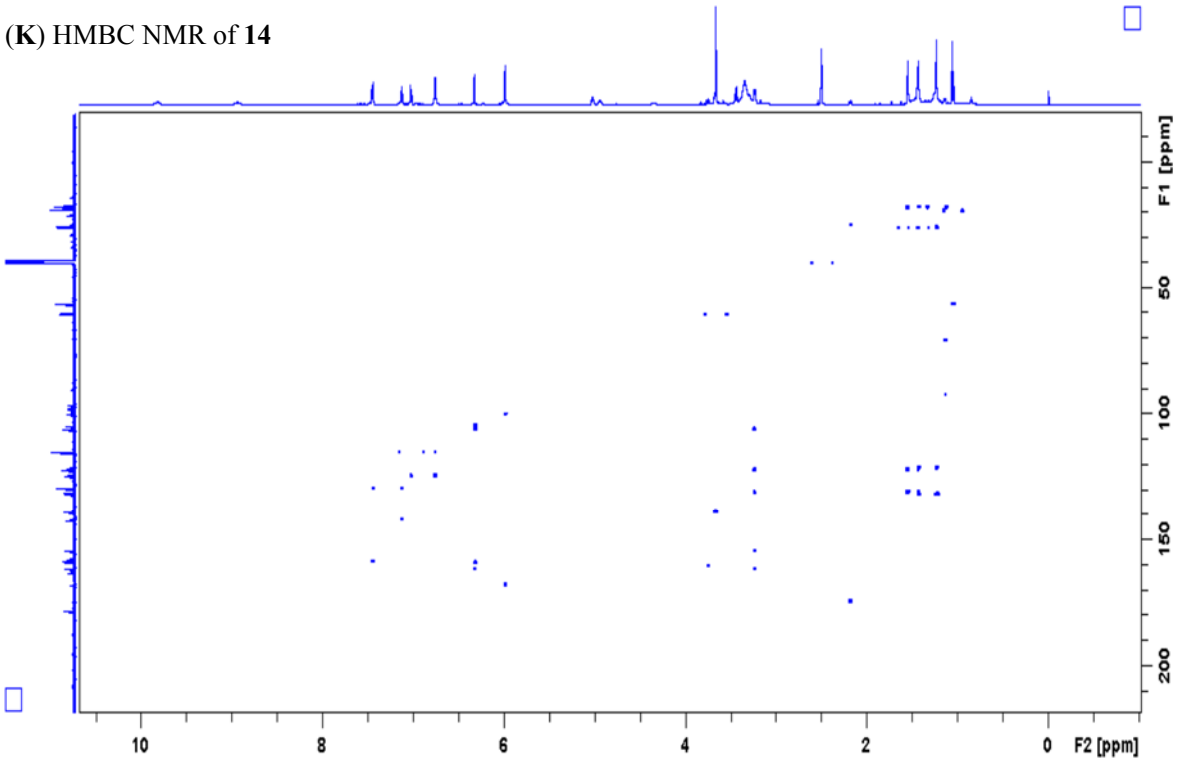


Fig. S9† ESI-MS, ESI-MS/MS, ESI-TOF-MS, and 1D and 2D NMR spectra of compound **14**.

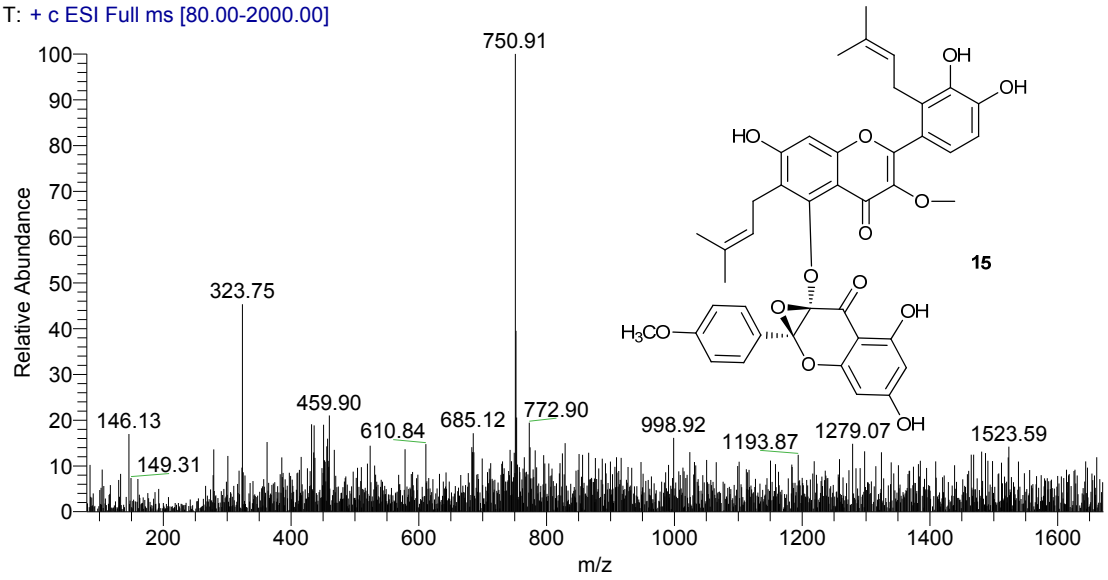
Table S9† 1D and 2D NMR data of compound **14** (DMSO-*d6*, 600MHz for ^{1}H)

Atom	**14**				
	δ_C (ppm)	DEPT[a]	HMQC	HMBC	^{1}H-^{1}H COSY
			δ_H (ppm)	correlation with	correlation with
2	157.47	q		H-6'	
3	138.26	q		H-3-OCH_3	
3-OCH_3	60.08	CH3	3.67(3H, s)		
4	178.22	q			
5	158.92	q		H-6	
6	98.28	CH	6.33(1H,s)		
7	161.56	q		H-6, H-1"	
8	104.66	q		H-6, H-1"	
9	154.25	q		H-1"	
10	105.84	q		H-6	
1'	124.4	q		H-5', H-1'''	
2'	129.19	q		H-6', H-1'''	
3'	138.87	q		H-5', H-1'''	
4'	141.98	q		H-5', H-6'	
5'	115.07	CH	7.02(1H,d,*J*=8.34Hz)	H-6'	H-6'
6'	123.92	CH	7.13(1H,d,*J*=8.34Hz)	H-5'	H-5'
1"	25.23	CH_2	3.24(2H,d,*J*=6.84Hz)	H-2"	H-2"
2"	121.87	CH	5.02(1H,t,*J*=7.2Hz)	H-1", H-4", H-5"	H-1", H-4", H-5"
3"	130.9	q		H-1", H-4", H-5"	
4"	17.2	CH_3	1.55((3H,s)	H-2", H-5"	H-2", H-5"
5"	25.43	CH_3	1.44(3H,s)	H-2", H-4"	H-2", H-4"
1'''	25.23	CH_2	3.34(2H,d,*J*=6.3Hz)	H-2'''	H-2'''
2'''	121.23	CH	4.94(1H,s)	H-1''', H-4''', H-5'''	H-1''', H-4''', H-5'''
3'''	131.62	q		H-1''', H-4''', H-5'''	
4'''	17.2	CH_3	1.44(3H,s)	H-2''', H-5'''	H-2''', H-5'''
5'''	25.19	CH_3	1.23(3H,s)	H-2''', H-4'''	H-2''', H-4'''
2''''	100.24	q		H-2'''', H-6''''	
3''''	90.24	q			
4''''	174.47	q			
5''''	163.13	q		H-6''''	
5''''-OH			12.51 (1H, s)		
6''''	97.18	CH	5.99(1H,s）	H-8''''	H-8''''
7''''	167.93			H-6'''', H-8''''	
8''''	96.23	CH	5.99(1H,S)	H-6''''	H-6''''
9''''	158.63	q		H-8''''	
10''''	99.67	q		H-6'''', H-8''''	
1'''''	124.4	q		H-3'''', H-5'''''	
2'''',6'''''	129.11	CH	7.45(2H,d,*J*=8.82Hz)	H-6''''' for C-2'''', H-2''''' for C-6'''''	H-3'''' for H-2'''' , H-5'''' for H-6''''
3'''',5'''''	114.73	CH	6.75(2H,d,*J*=8.88Hz)	H-5''''' for C-3'''', H-3''''' for C-5'''''	H-2'''' for H-3'''' , H-6'''' for H-5''''
4'''''	159.03	q		H-2''''', H-3'''', H-5''''', H-6'''''	

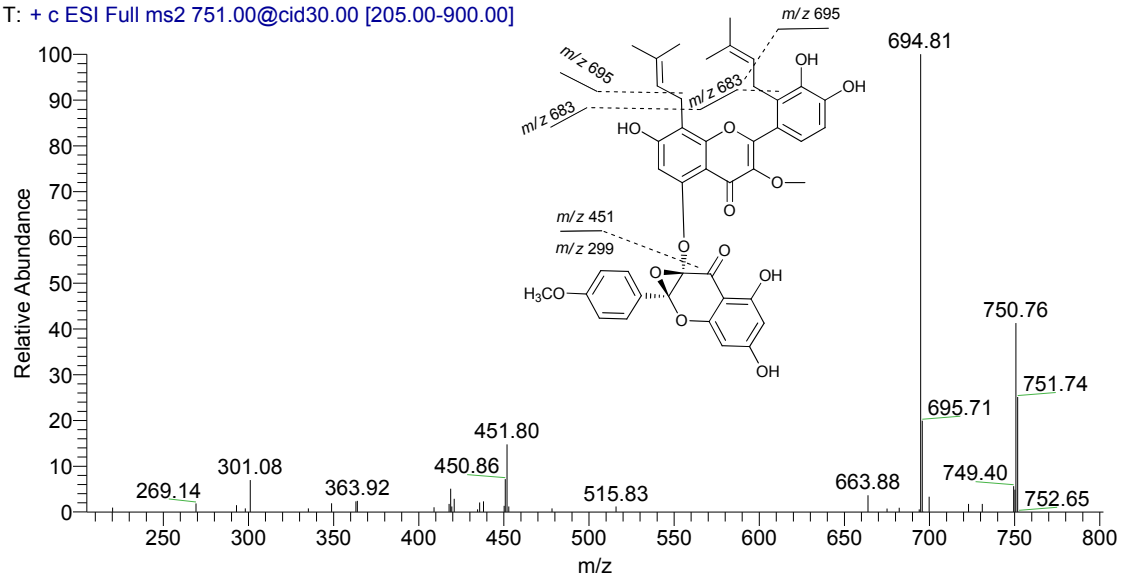
Structure identification of compound 15

ESI-MS spectra of compound **15** showed that it had prominent ions of $[M-H]^-$ at *m/z* 749 (100%), $[2M-H]^-$ at *m/z* 1499 (14%) and $[M+H]^+$ at *m/z* 751 (100%)(Fig. S10A, C†), suggesting that its molecular weight was 750. The high resolution ESI-TOF-MS analysis indicated that its molecular formula was $C_{42}H_{38}O_{13}$ (Fig. S10E†). ESI-MS/MS analysis indicated it also contained two moieties. ^1H and ^{13}C NMR showed that there was also two prenyl group. One was located at C2′. The position of the other prenyl group was located at C6. And it was confirmed by HMBC, which showed three critical correlations between C1″ of the prenyl group and C5, C6 and C7 of the phenyl of the flavonoid. The rest signals of **15** were very similar with **14** except a OCH_3 signal (δ_C 55.14, δ_H 3.75) at the C4‴″position. The structure of **15** was established as Fig. 4. Its NMR data were summarized in Table S10†. And it was named as podoverine I.

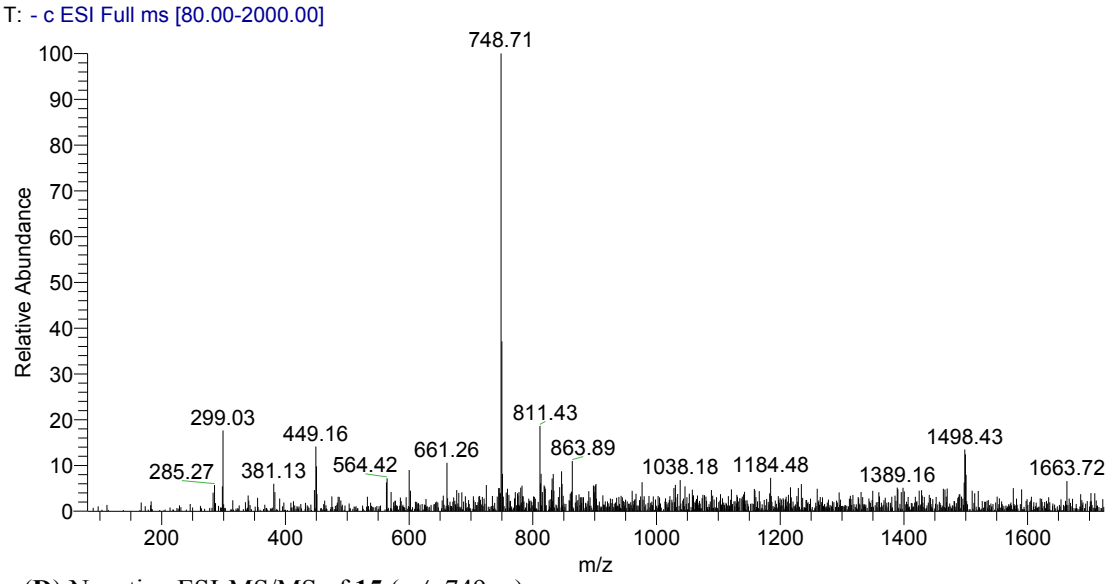
(**A**) Positive ESI-MS of **15**



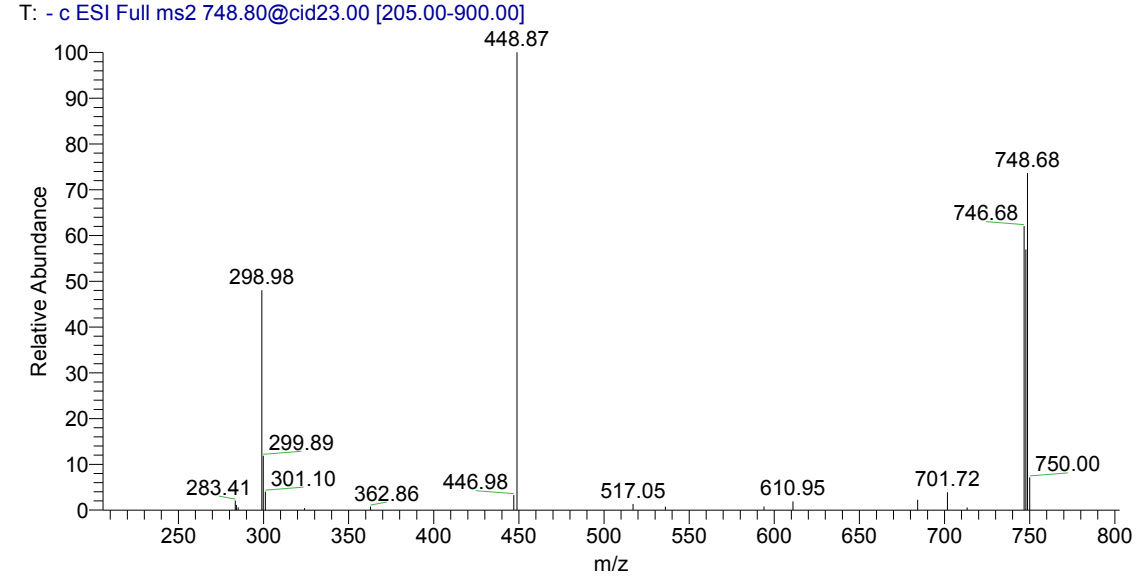
(**B**) Positive ESI-MS/MS of **15** (*m/z* 751→)



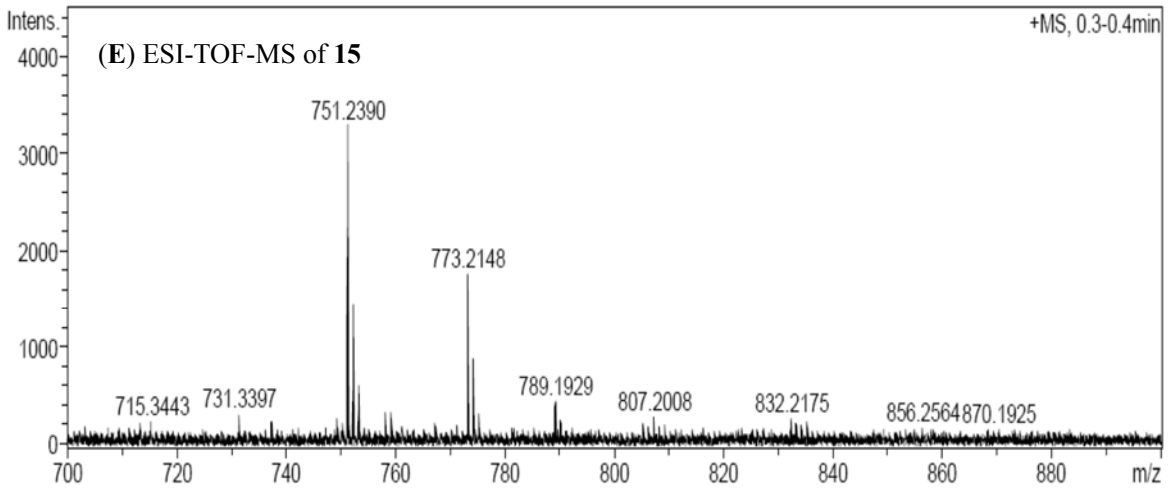
(**C**) Negative ESI-MS of **15**



(**D**) Negative ESI-MS/MS of **15** (*m/z* 749→)

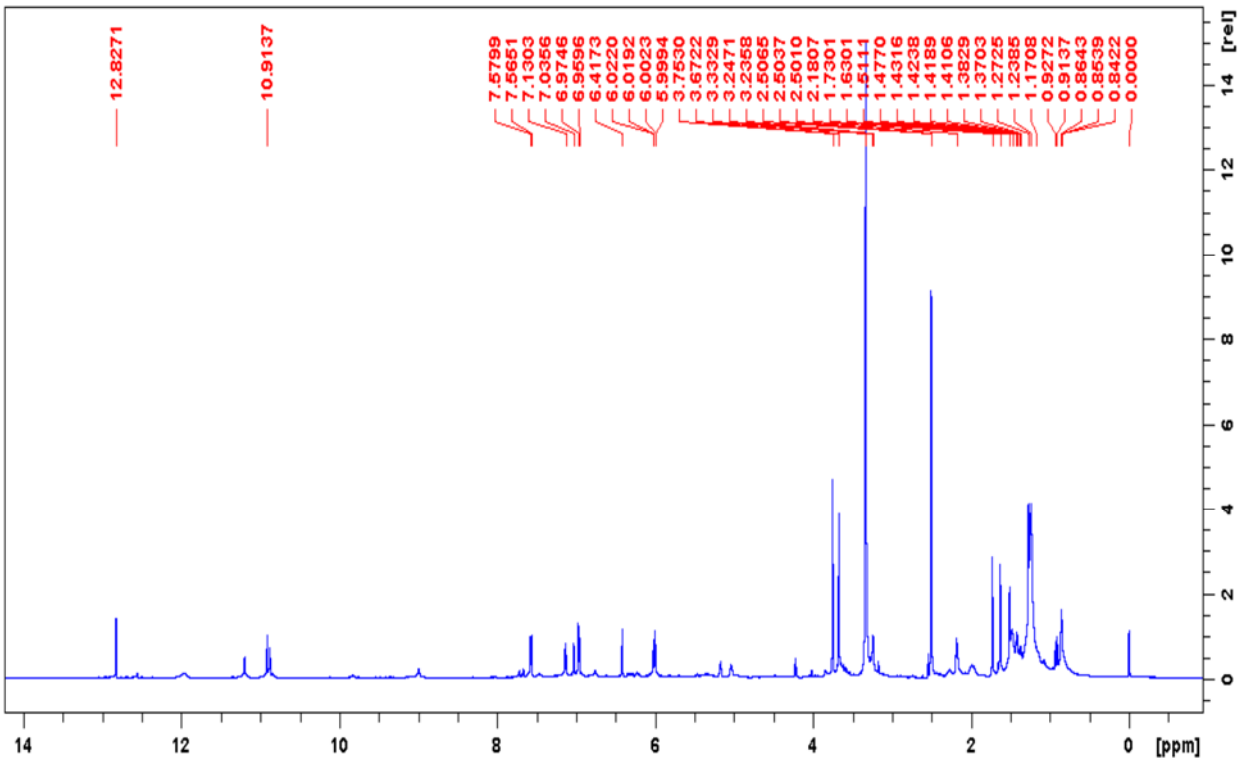


(**E**) ESI-TOF-MS of **15**

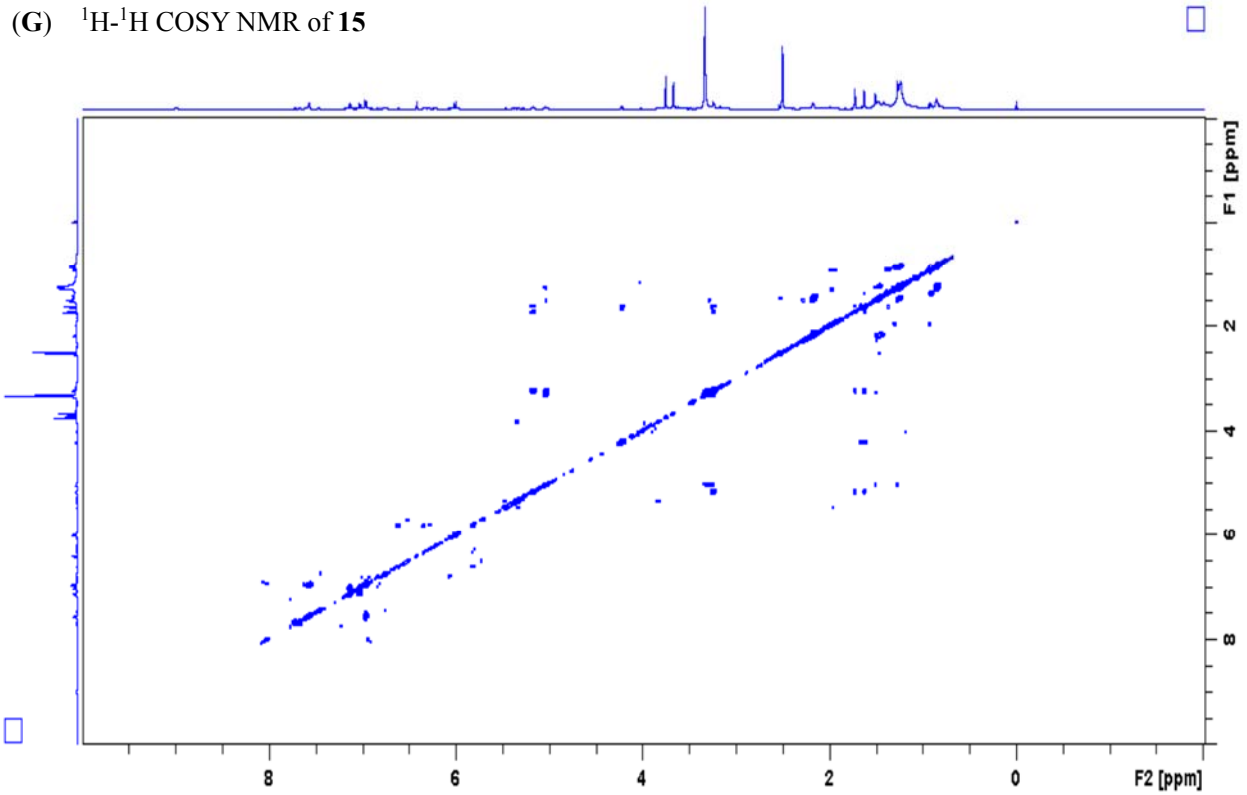


Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
751.2390	1	C 42 H 39 O 13	100.00	751.2385	-0.5	-0.6	33.5	23.5	even	ok
773.2148	1	C 42 H 38 Na O 13	100.00	773.2205	5.6	7.3	36.7	23.5	even	ok

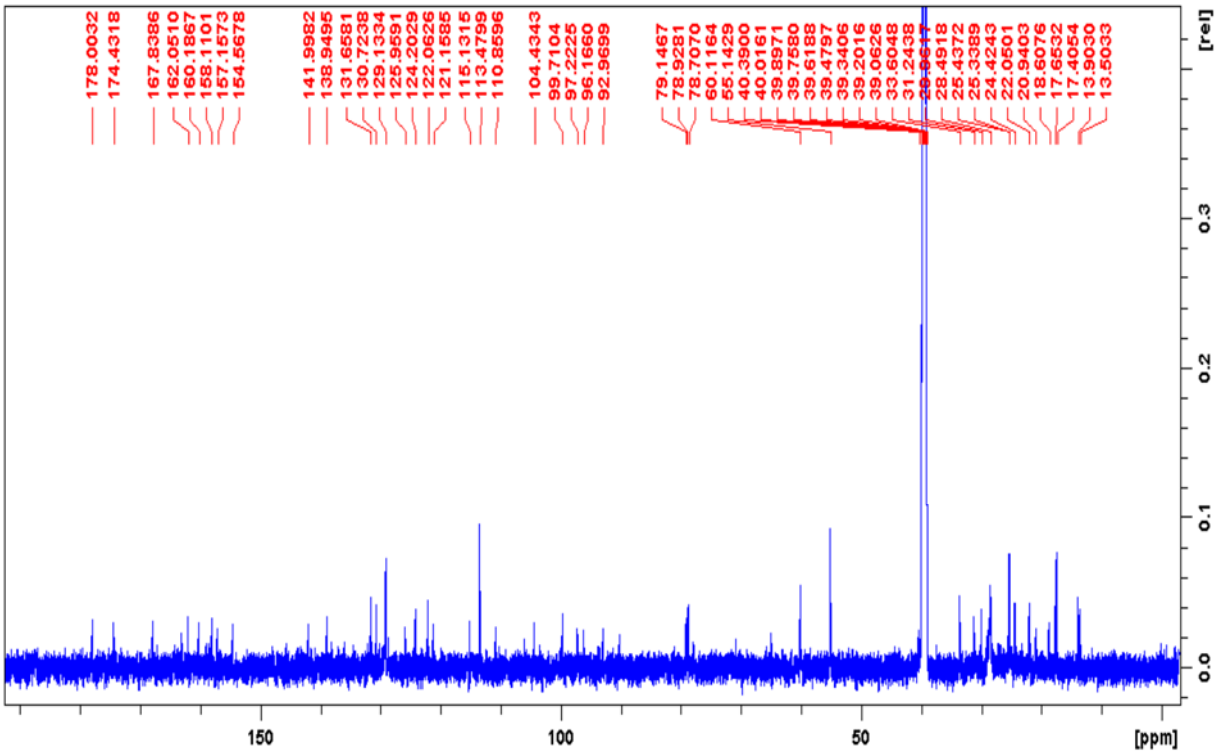
(**F**) ^{1}H NMR of **15**



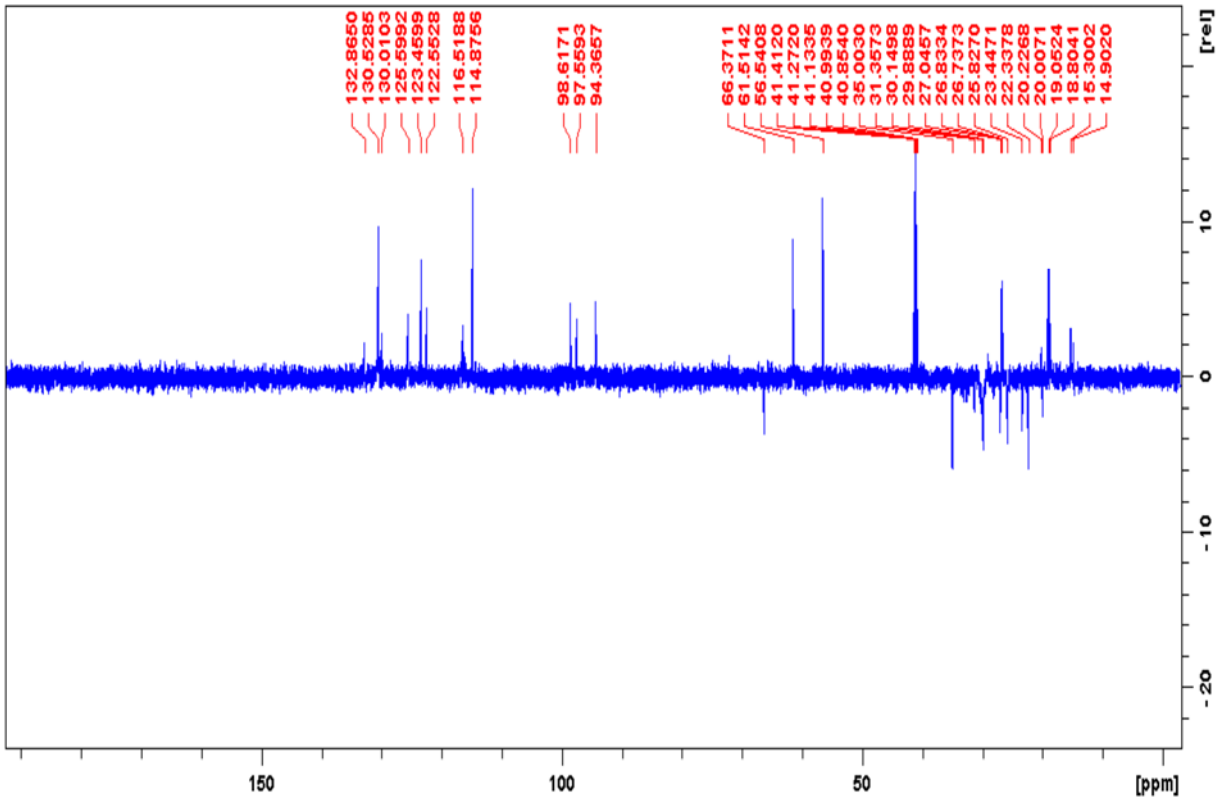
(**G**) ^{1}H-^{1}H COSY NMR of **15**



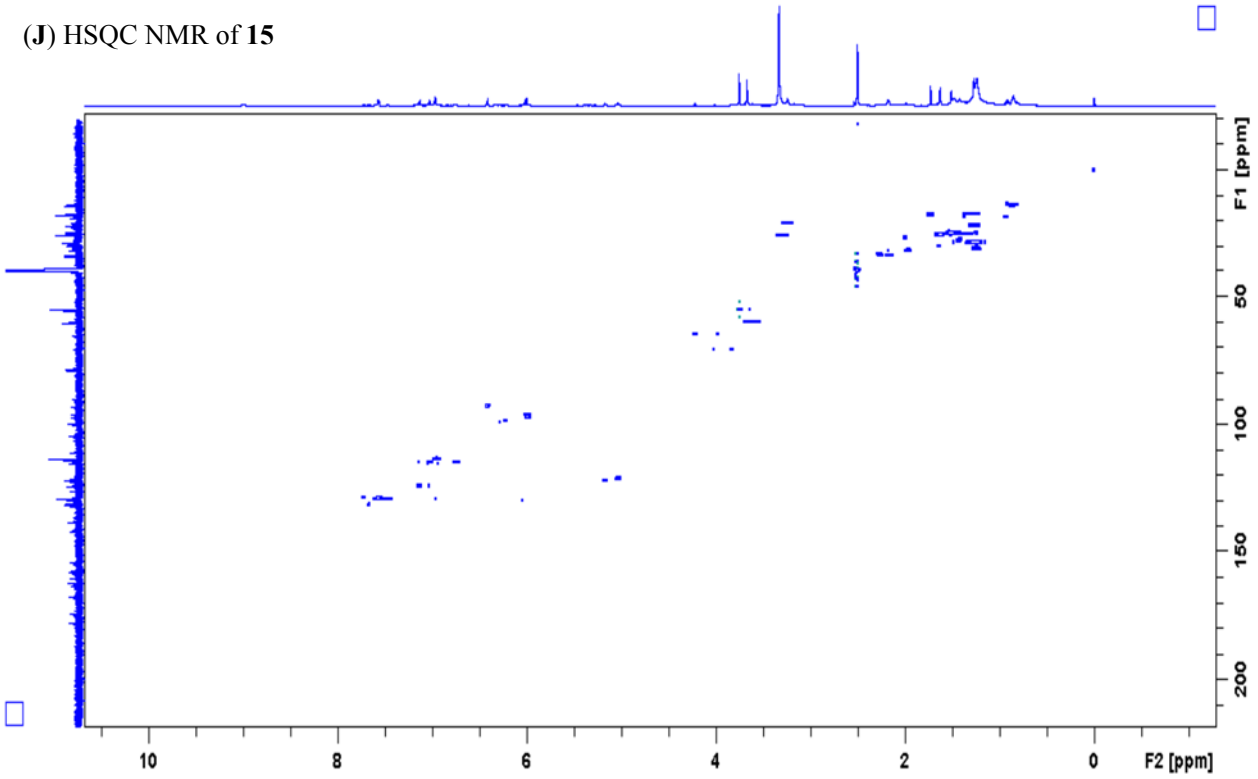
(**H**) ^{13}C NMR of **15**



(**I**) DEPT135 NMR of **15**



(**J**) HSQC NMR of **15**



(**K**) HMBC NMR of **15**

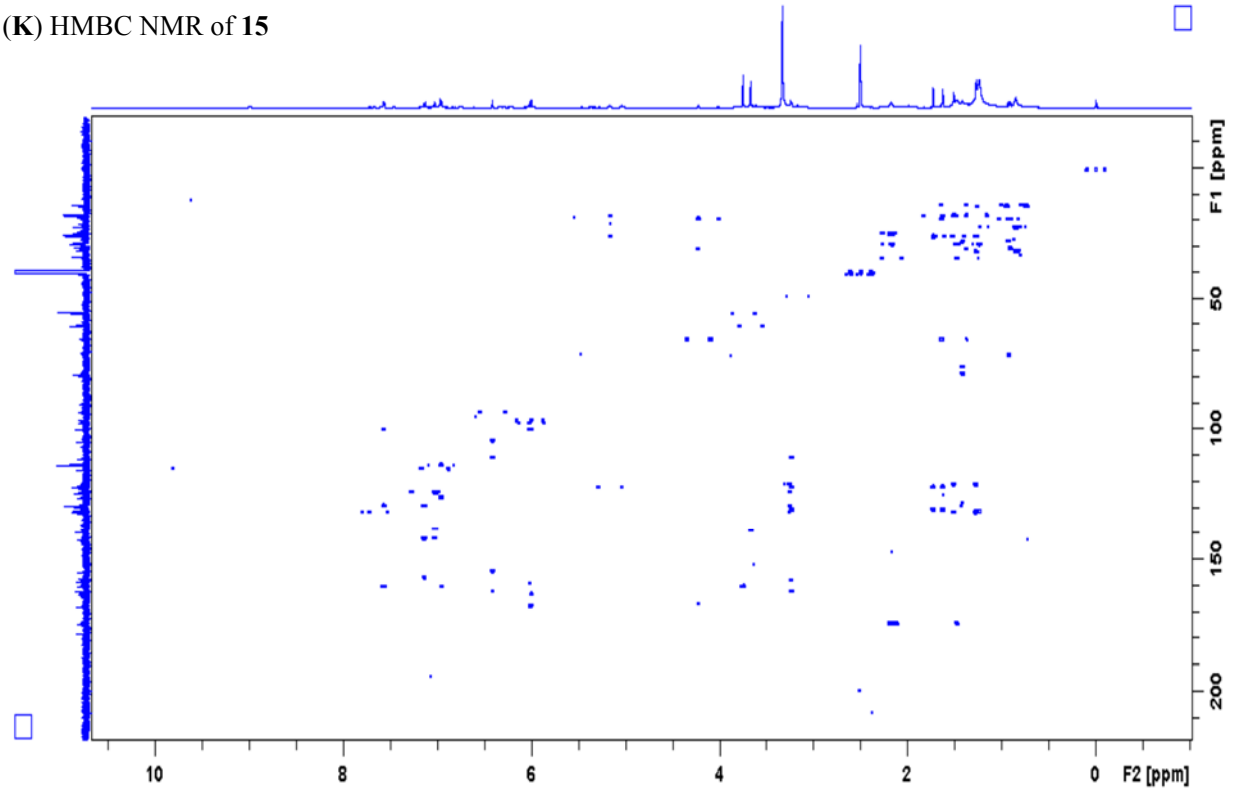


Fig. S10† ESI-MS, ESI-MS/MS, ESI-TOF-MS, and 1D and 2D NMR spectra of compound **15**.

Table S10[†] 1D and 2D NMR data of compound **15** (DMSO-*d6*, 600MHz for ^{1}H)

Atom	15				
	δ_C (ppm)	DEPT[a]	HMQC	HMBC	^{1}H-^{1}H COSY
			δ_H (ppm)	correlation with	correlation with
2	157.16	q		H-6'	
3	138.95	q		H-3-OCH_3	
3-OCH_3	60.12	CH_3	3.67(1H,s)		
4	178.01	q			
5	158.11	q		H-1"	
6	104.44	q		H-8, H-1"	
7	162.05	q		H-8, H-1"	
8	92.97	CH	6.42(1H,s)		
9	154.57	q		H-8	
10	110.86	q		H-8	
1'	124.21	q		H-5', H-1'''	
2'	129.29	q		H-6', H-1'''	
3'	138.98	q		H-5', H-1'''	
4'	142	q		H-5', H-6'	
5'	115.13	CH	7.03(1H,d,*J*=8.4Hz)	H-6'	H-6'
6'	124.21	CH	7.13(1H,s,*J*=8.4Hz)	H-5'	H-5'
1"	25.62	CH_2	3.24(2H,d,*J*=6.78Hz)	H-2"	H-2"
2"	122.06	CH	5.18(1H,t,*J*=7.02Hz)	H-1", H-4", H-5"	H-1", H-4", H-5"
3"	130.73	q		H-1", H-4", H-5"	
4"	17.65	CH_3	1.73(3H.s)	H-2", H-5"	H-2", H-5"
5"	25.44	CH_3	1.63(3H,s)	H-2", H-4"	H-2", H-4"
1'''	24.42	CH_2	3.26(2H,d,*J*=7.02Hz)	H-2'''	H-2'''
2'''	121.16	CH	5.04(1H,s)	H-1''', H-4''', H-5'''	H-1''', H-4''', H-5'''
3'''	131.66	q		H-1''', H-4''', H-5'''	
4'''	17.41	CH_3	1.51(3H,s)	H-2''', H-5'''	H-2''', H-5'''
5'''	25.34	CH_3	1.27(3H,s)	H-2''', H-4'''	H-2''', H-4'''
2''''	99.71	q		H-2'''', H-6''''	
3''''	90.15	q			
4''''	174.43	q			
5''''	163.08	q		H-6''''	
5''''-OH			12.87 (1H, s)		
6''''	97.23	CH	6.0(1H,d,*J*=1.74Hz)	H-8''''	H-8'''
7''''	167.84	q		H-6'''', H-8''''	
8''''	96.17	CH	6.02(1H,d,*J*=1.68Hz)	H-6''''	H-6'''
9''''	159.04	q		H-8''''	
10''''	99.71	q		H-6'''', H-8''''	
1'''''	125.96	q		H-3''''', H-5'''''	
2''''',6'''''	129.14	CH	7.57(2H,d,*J*=8.88Hz}	H-6''''' for C-2''''', H-2''''' for C-6'''''	H-3'''' for H-2'''' , H-5'''' for H-6''''
3''''',5'''''	113.49	CH	6.96(2H,s,*J*=9Hz)	H-5''''' for C-3''''', H-3''''' for C-5'''''	H-2'''' for H-3'''' , H-6'''' for H-5''''
4'''''	160.19	q		H-2''''', H-3''''', H-5''''', H-6''''', H-4'''''-OCH_3	
4''''' -OCH_3	55.14	CH_3	3.75(3H,s)		

Assignment of absolute configuration of new flavones dimers

There were two chiral centers at C2‴ (or C‴″) and C3‴ (or C‴″) on the ring C′ of the compounds **10-15**, and therefore they had four possible stereoisomers. CD measurements (Fig. S11†) showed that the compounds **10-15** both had a positive Cotton effect in the 310 nm region and a negative Cotton effect at 265 nm. Therefore the absolute configuration had to be (*2R,3R*) or (*2R,3S*)[3]. However, due to the existence of the *2,3-epoxy* ring at C2‴ and C3‴, its absolute configuration had to be (*2R,3S*). Therefore, the stereochemistry of compounds **10-15** were illustrated in Fig. 4.

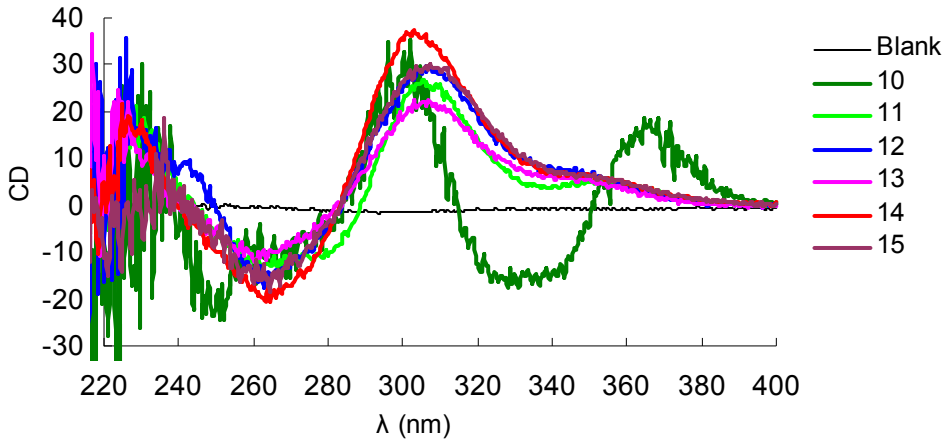


Fig. S11† CD spectrum of compounds **10-15**. The samples were dissolved in ethanol at concentrations of 0.1 mg/mL. The CD signal was recorded every 0.5 nm with a 0.5s signal averaging for each point. Each spectrum was recorded twice and averaged.

References

1. F. A. Ramos, Y. Takaishi, M. Shirotori, Y. Kawaguchi, K. Tsuchiya, H. Shibata, T. Higuti, T. Tadokoro and M. Takeuchi, *J. Agr. Food Chem.*, 2006, **54**, 3551-3557.
2. H. Arens, B. Ulbrich, H. Fischer, M. J. Parnham and A. Romer, *Planta Med.*, 1986, 468-473.
3. D. Slade, D. Ferreira and J. P. J. Marais, *Phytochemistry*, 2005, **66**, 2177-2215.