Supporting Information

Koilodenoids A–G, Immunosuppressive Spiro Dimers of Diterpenoids from *Koilodepas hainanense*: Structural Elucidation and Biomimetic Transformation

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Structure elucidation for compounds 5−7

Koilodenoid E (**5**) had a molecular formular of $C_{40}H_{62}O_6$ as deduced from the HRESIMS and ^{13}C NMR data. The NMR data of **5** (Table S4) resembled those of **4**, except that the chloride group at C-16′ in **4** was replaced by a hydroxy group in **5**, which was supported by the relatively downfield chemical shift of C-16′ (δ_C 62.7 in **5** vs δ_C 48.3 in **4**) and the ^1H-^1H COSY correlations of H-15′/H_2-16′ (Figure S4). The relative and absolute configurations of **5** except for C-15′, were elucidated to be identical to those of **4** based on the NOESY data (Figure S4B) and thire highly compatible ECD curves (Figure S5). Finally, the absolute configuration of C-15′ was determined as *R* by Snatzke's method. As shown in Figure S6, the ECD spectrum of compound **5** and $Mo_2(OAc)_4$ in DMSO exhibits a negative Cotton effect at 310 nm, corresponding to a negative dihedral angle of the O−C−C−O moiety.

Koilodenoid F (**6**) gave a molecular formula of $C_{40}H_{58}O_7$. Comparison of the 1D NMR data of compounds **6** and **2** (Tables S1 and S5) revealed their structural closeness. In-depth scrutiny of the NMR data (Figure S7), especially the HMBC correlations from H-1 and H-10 to C-2 (δ_C 193.1) and the downfield chemical shift of C-4 (δ_C 143.2 in **6** vs δ_C 116.8 in **2**), revealed that an additional carbonyl was located at C-2 and conjugated to the Δ^3 double bond in **6**. Correspondingly, an absorption band at λ_{max} 276 nm in the UV spectrum (Figure S5) and two absorption peaks at 1676 and 1620 cm^{-1} in the IR spectrum further confirmed the presence of an enone moiety in **6**. The absolute configuration of **6** was determined as delineated by comparison of the ECD spectra (Figure S5). Compound **6** was therefore identified as a 2-oxo derivative of **2**.

Koilodenoid G (**7**) exhibited a molecular formula of $C_{39}H_{58}O_6$. The ^1H and ^{13}C NMR data of **7** (Table S6) were very similar to those of **2**, except for the presence of a carboxyl

group at δ_C 184.8 and the disappearance of an α-hydroxy ketone motif in **7**. The carboxyl group was assigned to C-15 based on the HMBC correlation from H_3-17 to C-15 (Figure S8). The absolute configuration of **7** was established as 5*R*, 8*S*, 9*S*, 10*R*, 13*S*, 4′*R*, 5′*R*, 8′*S*, 9′*S*, 10′*R*, 13′*S* by single-crystal X-ray diffraction with a Flack parameter of 0.06 (10) (Figure S9).

Table S1. ^{1}H (400 MHz) and ^{13}C (125 MHz) NMR Data for Compound **2** in $CDCl_3$.

No.	δ_H, multiplets (*J* in Hz)	δ_C, type	No.	δ_H, multiplets (*J* in Hz)	δ_C, type
1	1.46, m	17.5, CH_2	1′	1.55, m	23.5, CH_2
	1.65, overlap			1.91, m	
2	1.99, overlap	29.6, CH_2	2′	2.08, m	38.3, CH_2
	2.20, m			2.70, m	
3		143.6, C	3′		213.4, C
4		116.8, C	4′		85.0, C
5		37.0, C	5′		46.0, C
6	1.04, m	37.0, CH_2	6′	1.34, m	32.2, CH_2
	1.65, overlap			1.73, m	
7	1.15, m	25.5, CH_2	7′	1.10, m	25.7, CH_2
	1.30, m			1.31, m	
8	1.24, m	41.4, CH	8′	1.33, m	40.9, CH
9		36.4, C	9′		36.7, C
10	0.95, dd (12.4, 2.0)	54.0, CH	10′	2.24, m	46.4, CH
11	β 0.99, m	34.1, CH_2	11′	β 1.22, m	34.8, CH_2
	α 1.61, m			α 1.57, m	
12	β 1.35, overlap	28.0, CH_2	12′	β 1.35, overlap	28.0, CH_2
	α 1.82, overlap			α 1.82, overlap	
13		45.7, C	13′		45.7, C
14	β 1.13, overlap	35.1, CH_2	14′	β 1.13, overlap	35.2, CH_2
	α 1.52, overlap			α 1.52, overlap	
15		215.4, C	15′		215.5, C
16	4.34, overlap	63.9, CH_2	16′	4.34, overlap	63.9, CH_2
17	1.16, s	20.8, CH_3	17′	1.24, s	20.7, CH_3
18	α 1.73, m	16.9, CH_2	18′	2.00-2.10, m (2H)	19.4, CH_2
	β 1.99, overlap				
19	0.90, s	20.7, CH_3	19′	0.78, s	15.7, CH_3
20	0.69, s	12.3, CH_3	20′	0.71, s	12.5, CH_3

Table S2. ^{1}H (400 MHz) and ^{13}C (125 MHz) NMR Data for Compound **3** in $CDCl_3$.

No.	δ_H, multiplets (*J* in Hz)	δ_C, type	No.	δ_H, multiplets (*J* in Hz)	δ_C, type
1	1.94, m	17.2, CH_2	1′	1.59, m	23.6, CH_2
	2.01, m			1.93, m	
2	1.97, m	25.8, CH_2	2′	2.11, m	38.2, CH_2
	2.24, m			2.70, m	
3		145.6, C	3′		213.2, C
4		113.7, C	4′		85.1, C
5		37.0, C	5′		45.7, C
6	1.11, m	37.7, CH_2	6′	1.36, m	32.2, CH_2
	1.89, m			1.73, m	
7	1.19, m	25.6, CH_2	7′	1.08, m	27.1, CH_2
	1.36, m			1.44, m	
8	1.33, m	41.2, CH	8′	1.35, m	40.9, CH
9		37.8, C	9′		36.8, C
10	1.06, m	52.2, CH	10′	2.24, dd (11.6, 3.6)	46.5, CH
11	1.15, m	34.8, CH_2	11′	1.18, m	34.9, CH_2
	1.58, m			1.59, m	
12	β 1.42, m	28.2, CH_2	12′	β 1.34, m	28.2, CH_2
	α 1.84, m			α 1.93, m	
13		45.9, C	13′		45.8, C
14	1.20, m	35.2, CH_2	14′	1.15, m	35.2, CH_2
	1.59, m			1.56, m	
15		215.5, C	15′		215.7, C
16	4.38, overlap	64.0, CH_2	16′	4.38, overlap	64.0 CH_2
17	1.27, s	21.0, CH_3	17′	1.21, s	20.7, CH_3
18	1.86, m	18.5, CH_2	18′	1.42, m	20.4, CH_2
	2.06, m			2.15, m	
19	0.90, s	34.1, CH_3	19′	0.82, s	15.9, CH_3
20	0.88, s	12.0, CH_3	20′	0.75, s	12.6, CH_3

Table S3. ^{1}H (400 MHz) and ^{13}C (125 MHz) NMR Data for Compound **4** in $CDCl_3$.

No.	δ_H, multiplets (*J* in Hz)	δ_C, type	No.	δ_H, multiplets (*J* in Hz)	δ_C, type
1	1.50, m	17.7, CH_2	1′	1.60, m	23.8, CH_2
	1.73, m			1.93, m	
2	2.05, m	29.7, CH_2	2′	2.11, m	38.6, CH_2
	2.25, m			2.74, m	
3		143.8, C	3′		213.8, C
4		116.9, C	4′		85.2, C
5		37.2, C	5′		46.2, C
6	1.07, m	37.2, CH_2	6′	1.34, m	32.4, CH_2
	1.67, m			1.75, m	
7	1.14, m	25.9, CH_2	7′	1.15, overlap	25.8, CH_2
	1.31, m			1.36, m	
8	1.28, m	41.6, CH	8′	1.28, m	41.3, CH
9		36.9, C	9′		36.6, C
10	1.00, m	54.2, CH	10′	2.25, m	46.5, CH
11	1.04, m	34.3, CH_2	11′	1.15, overlap	35.3, CH_2
	1.62, m			1.57, m	
12	β 1.38, m	29.1, CH_2	12′	β 1.41, m	28.1, CH_2
	α 1.87, overlap			α 1.87, overlap	
13		45.8, C	13′		38.0, C
14	1.15, overlap	35.5, CH_2	14′	1.17, m	36.9, CH_2
	1.58, overlap			1.60, m	
15		215.7, C	15′	3.39, dd (10.2, 2.6)	80.9, CH
16	4.39, s (2H)	64.0, CH_2	16′	3.48, dd (10.8, 10.2)	48.3, CH_2
				3.78, dd (10.8, 2.6)	
17	1.20, s	20.9, CH_3	17′	0.99, s	19.0, CH_3
18	α 1.75, m	17.0, CH_3	18′	2.03, m	19.5, CH_2
	β 2.01, m			2.05, m	
19	0.94, s	20.8, CH_3	19′	0.82, s	15.8, CH_3
20	0.73, overlap	12.4, CH_3	20′	0.73, overlap	12.6, CH_3

Table S4. ^{1}H (400 MHz) and ^{13}C (125 MHz) NMR Data for Compound **5** in $CDCl_3$.

No.	δ_H, multiplets (*J* in Hz)	δ_C, type	No.	δ_H, multiplets (*J* in Hz)	δ_C, type
1	1.51, m	17.7, CH_2	1′	1.58, m	23.8, CH_2
	1.70, m			1.94, m	
2	2.05, m	29.7, CH_2	2′	2.11, m	38.6, CH_2
	2.25, m			2.74, m	
3		143.8, C	3′		213.8, C
4		116.9, C	4′		85.2, C
5		37.2, C	5′		46.2, C
6	1.10, m	37.2, CH_2	6′	1.34, m	32.4, CH_2
	1.67, m			1.75, m	
7	1.16, m	25.9, CH_2	7′	1.15, m	25.8, CH_2
	1.33, m			1.36, m	
8	1.30, m	41.6, CH	8′	1.32, m	41.2, CH
9		37.0, C	9′		36.8, C
10	1.00, m	54.2, CH	10′	2.23, m	46.6, CH
11	1.04, m	34.3, CH_2	11′	1.15, m	35.4, CH_2
	1.64, m			1.58, overlap	
12	β 1.38, m	29.1, CH_2	12′	β 1.41, m	28.1, CH_2
	α 1.58, overlap			α 1.87, m	
13		45.8, C	13′		36.6, C
14	1.16, m	35.4, CH_2	14′	0.84, m	36.5, CH_2
	1.58, m			1.33, m	
15		215.7, C	15′	3.34, dd (9.4, 2.8)	81.4, CH
16	4.38, s (2H)	64.0, CH_2	16′	3.53, dd (10.8, 9.4)	62.7, CH_2
				3.78, dd (10.8, 2.8)	
17	1.20, s	20.9, CH_3	17′	0.99, s	19.2, CH_3
18	α 1.75, m	17.0, CH_3	18′	2.05, m	19.5, CH_2
	β 2.01, m			2.11, m	
19	0.94, s	20.8, CH_3	19′	0.82, s	15.8, CH_3
20	0.73, s	12.4, CH_3	20′	0.73, s	12.6, CH_3

Table S5. ^{1}H (400 MHz) and ^{13}C (125 MHz) NMR Data for Compound **6** in $CDCl_3$.

No.	δ_H, multiplets (*J* in Hz)	δ_C, type	No.	δ_H, multiplets (*J* in Hz)	δ_C, type
1	1.61, m	34.9, CH_2	1′	1.60, m	23.4, CH_2
	2.45, m			1.98, m	
2		193.1, C	2′	2.10, m	37.8, CH_2
				2.74, m	
3		142.4, C	3′		212.7, C
4		143.2, C	4′		85.4, C
5		39.4, C	5′		46.3, C
6	1.32, m	35.9, CH_2	6′	1.37, m	32.1, CH_2
	1.77, m			1.82, m	
7	1.22, overlap	25.1, CH_2	7′	1.22, overlap	25.4, CH_2
	1.40, overlap			1.40, overlap	
8	1.36, m	41.0, CH	8′	1.51, m	40.5, CH
9		36.3, C	9′		36.7, C
10	1.58, m	52.6, CH	10′	2.55, dd (12.8, 3.2)	46.0, CH
11	1.08, m	33.7, CH_2	11′	1.20, m	34.7, CH_2
	1.60, m			1.56, m	
12	β 1.43, m	28.0, CH_2	12′	β 1.48, m	27.7, CH_2
	α 1.86, m			α 1.86, m	
13		45.7, C	13′		45.5, C
14	1.18, m	35.1, CH_2	14′	1.20, m	35.1, CH_2
	1.56, m			1.56, m	
15		215.5, C	15′		215.1, C
16	4.38, overlap	63.9, CH_2	16′	4.38, overlap	63.9, CH_2
17	1.20, s	20.8, CH_3	17′	1.28, s	20.6, CH_3
18	2.19, m	18.8, CH_3	18′	2.04, m	18.6, CH_2
	2.40, m			2.08, m	
19	1.10, s	19.1, CH_3	19′	0.85, s	15.9, CH_3
20	0.76, s	12.1, CH_3	20′	0.81, s	12.5, CH_3

Table S6. ^{1}H (400 MHz) and ^{13}C (125 MHz) NMR Data for Compound **7** in $CDCl_3$.

No.	δ_H, multiplets (*J* in Hz)	δ_C, type	No.	δ_H, multiplets (*J* in Hz)	δ_C, type
1	1.49, m	17.7, CH_2	1′	1.60, m	23.7, CH_2
	1.69, m			1.94, m	
2	2.01, m	29.8, CH_2	2′	2.13, m	38.4, CH_2
	2.22, m			2.74, m	
3		143.7, C	3′		213.6, C
4		117.1, C	4′		85.1, C
5		37.2, C	5′		45.8, C
6	1.09, m	37.2, CH_2	6′	1.38, m	32.3, CH_2
	1.64, m			1.77, m	
7	1.17, m	25.7, CH_2	7′	1.12, m	25.6, CH_2
	1.36, m			1.38, m	
8	1.22, m	41.7, CH	8′	1.36, m	41.0, CH
9		36.8, C	9′		36.5, C
10	0.98, dd (12.6, 1.8)	54.2, CH	10′	2.26, dd (13.0, 3.4)	46.5, CH
11	1.02, m	34.5, CH_2	11′	1.22, m	34.9, CH_2
	1.65, m			1.60, m	
12	β 1.47, m	28.9, CH_2	12′	β 1.41, m	28.1, CH_2
	α 2.00, m			α 1.86, m	
13		42.0, C	13′		46.1, C
14	1.24, m	36.1, CH_2	14′	1.20, m	35.2, CH_2
	1.66, m			1.56, m	
15		184.6, C	15′		215.5, C
			16′	4.39, s (2H)	64.0, CH_2
17	1.26, s	20.9, CH_3	17′	1.24, s	21.4, CH_3
18	1.77, m	17.0, CH_3	18′	2.07, m	19.5, CH_2
	2.01, m			2.14, m	
19	0.94, s	20.9. CH_3	19′	0.82, s	15.8, CH_3
20	0.74, s	12.4, CH_3	20′	0.75, s	12.6, CH_3

Table S7. X-ray Crystallographic Data for Compound **2**[a]

Identification code	cu_20211157_0m
Empirical formula	$C_{40}H_{60}O_6$
Formula weight	636.88
Temperature/K	170.0
Crystal system	triclinic
Space group	P1
a/Å	6.58220 (10)
b/Å	7.3678 (2)
c/Å	19.2597 (5)
α/°	82.8040 (10)
β/°	83.0410 (10)
γ/°	67.3320 (10)
Volume/Å^3	852.37 (4)
Z	1
ρ_{calc} g/cm^3	1.241
μ/mm^{-1}	0.640
F(000)	348.0
Crystal size/mm^3	0.12 × 0.08 × 0.05
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	4.64 to 148.97
Index ranges	-8 ≤ h ≤ 8, -9 ≤ k ≤ 8, -23 ≤ l ≤ 24
Reflections collected	17711
Independent reflections	6389 [R_{int} = 0.0497, R_{sigma} = 0.0520]
Data/restraints/parameters	6389/3/426
Goodness-of-fit on F^2	1.033
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0392, ωR_2 = 0.0977
Final *R* indexes [all data]	R_1 = 0.0414, ωR_2 = 0.1001
Largest diff. peak/hole/e Å^{-3}	0.22/−0.20
Flack parameter	−0.07 (10)

[a]Crystals of **2** were obtained from CH_2Cl_2.

Table S8. X-ray Crystallographic Data for Compound **3**[a]

Identification code	cu_2022189_0m
Empirical formula	$C_{40}H_{60}O_6$
Formula weight	636.88
Temperature/K	150.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.9518 (2)
b/Å	14.2638 (3)
c/Å	17.5248 (4)
α/°	90
β/°	93.3940 (10)
γ/°	90
Volume/Å^3	1734.70 (7)
Z	2
ρ_{calc} g/cm^3	1.219
μ/mm^{-1}	0.629
F(000)	696.0
Crystal size/mm^3	0.08 × 0.05 × 0.03
Radiation	Cu K*α* (λ = 1.54178)
2Θ range for data collection/°	5.052 to 149.04
Index ranges	-8 ≤ h ≤ 8, -17 ≤ k ≤ 17, -21 ≤ l ≤ 21
Reflections collected	30435
Independent reflections	6985 [R_{int} = 0.0428, R_{sigma} = 0.0316]
Data/restraints/parameters	6985/1/426
Goodness-of-fit on F^2	1.045
Final *R* indexes [I>=2*σ* (I)]	R_1 = 0.0288, ωR_2 = 0.0730
Final R indexes [all data]	R_1 = 0.0301, ωR_2 = 0.0739
Largest diff. peak/hole/e Å^{-3}	0.21/−0.17
Flack parameter	0.01 (5)

[a]Crystals of **3** were obtained from CH_2Cl_2.

Table S9. X-ray Crystallographic Data for Compound **4**[a]

Identification code	mo_20211202_0m
Empirical formula	$C_{40}H_{61}ClO_5$
Formula weight	657.33
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.4779 (3)
b/Å	39.9833 (16)
c/Å	7.3091 (3)
α/°	90
β/°	110.8930 (10)
γ/°	90
Volume/Å^3	1768.64 (13)
Z	2
ρ_{calc} g/cm^3	1.234
μ/mm^{-1}	0.151
F(000)	716.0
Crystal size/mm^3	0.11 × 0.06 × 0.03
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.074 to 54.652
Index ranges	-8 ≤ h ≤ 8, -51 ≤ k ≤ 50, -8 ≤ l ≤ 9
Reflections collected	17791
Independent reflections	7158 [R_{int} = 0.0448, R_{sigma} = 0.0577]
Data/restraints/parameters	7158/1/423
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0441, ωR_2 = 0.0827
Final R indexes [all data]	R_1 = 0.0615, ωR_2 = 0.0922
Largest diff. peak/hole/e Å^{-3}	0.19/−0.27
Flack parameter	−0.06 (4)

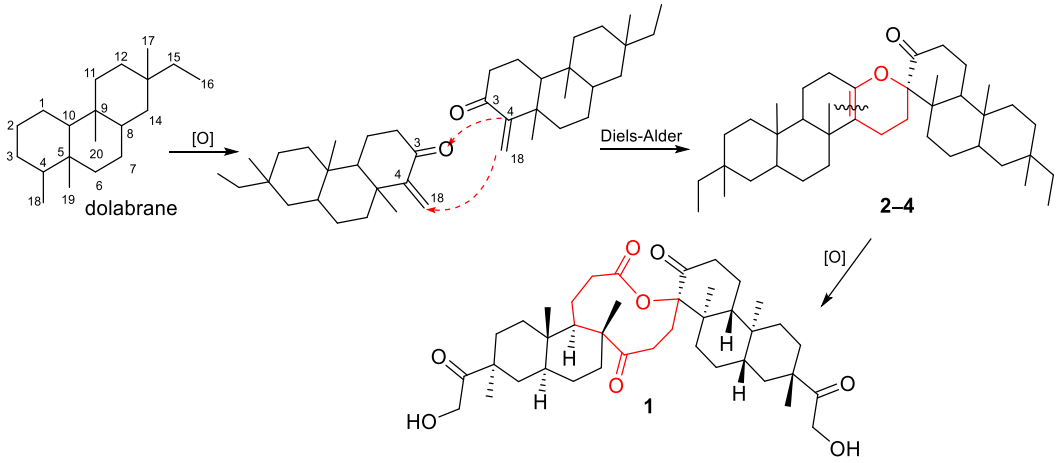
[a]Crystals of **4** were obtained from CH_2Cl_2.

Table S10. X-ray Crystallographic Data for Compound **7**[a]

Identification code	20220561_0m_sq
Empirical formula	$C_{39}H_{58}O_6$
Formula weight	622.85
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	19.4735 (6)
b/Å	7.8392 (2)
c/Å	24.0193 (8)
α/°	90
β/°	107.264 (2)
γ/°	90
Volume/Å^3	3501.51 (19)
Z	4
*ρ*calc g/cm^3	1.182
μ/mm^{-1}	0.613
F(000)	1360.0
Crystal size/mm^3	0.09 × 0.05 × 0.04
Radiation	Cu K*α* (*λ* = 1.54178)
2Θ range for data collection/°	4.752 to 149.498
Index ranges	-24 ≤ h ≤ 24, -9 ≤ k ≤ 9, -29 ≤ l ≤ 30
Reflections collected	58386
Independent reflections	14096 [R_{int} = 0.0598, R_{sigma} = 0.0448]
Data/restraints/parameters	14096/62/865
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2*σ* (I)]	R_1 = 0.0616, ωR_2 = 0.1705
Final R indexes [all data]	R_1 = 0.0734, ωR_2 = 0.1821
Largest diff. peak/hole/e Å^{-3}	0.48/−0.36
Flack parameter	0.06 (10)

[a]Crystals of **7** were obtained from CH_2Cl_2.

Scheme S1. Plausible biosynthetic pathway for 1−4.



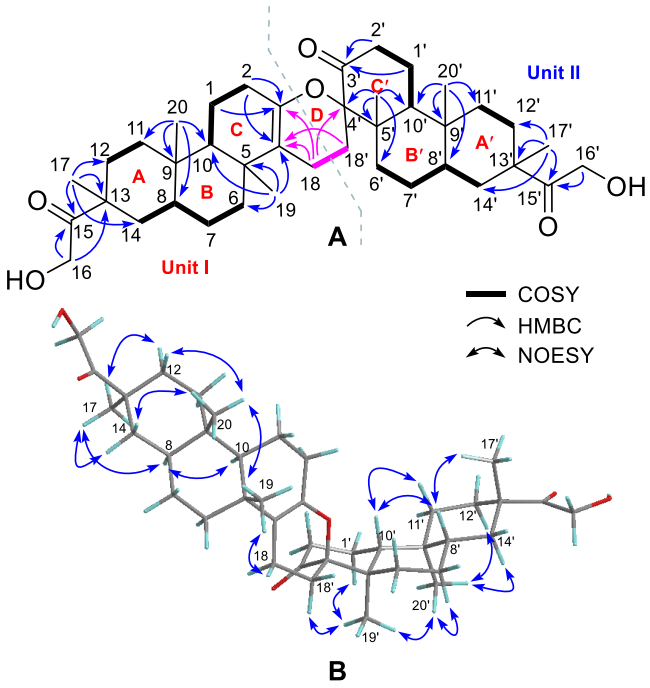


Figure S1. Key COSY, HMBC, and NOESY correlations of **2**.

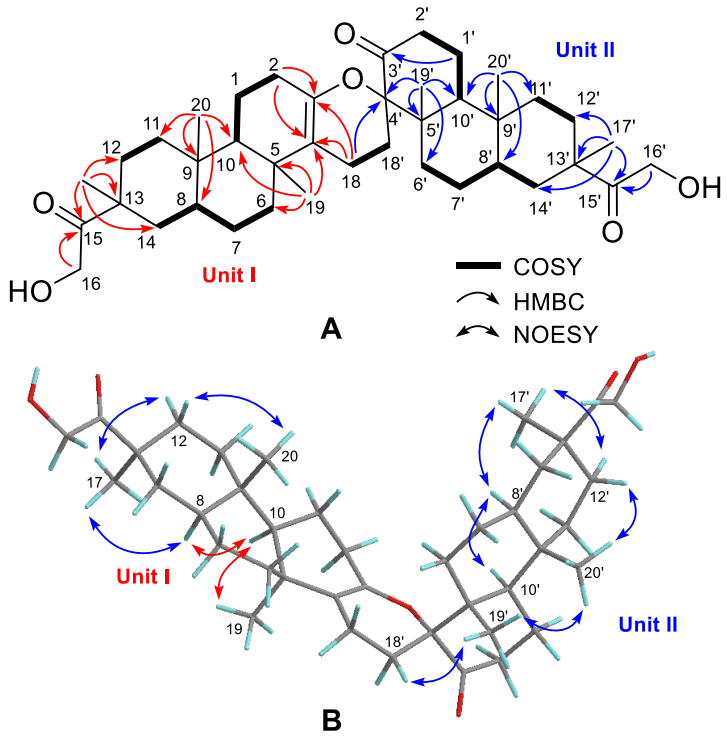


Figure S2. Key COSY, HMBC, and NOESY correlations of **3**.

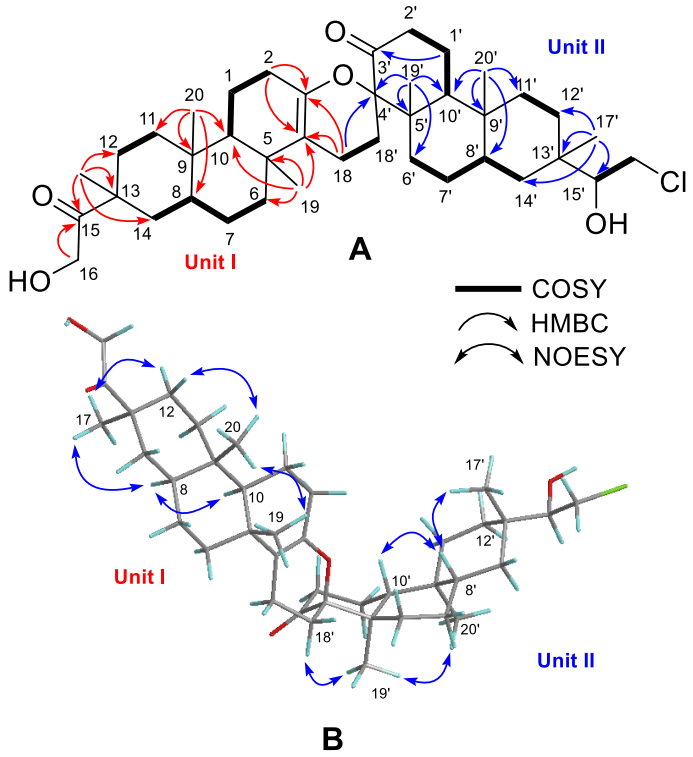


Figure S3. Key COSY, HMBC, and NOESY correlations of **4**.

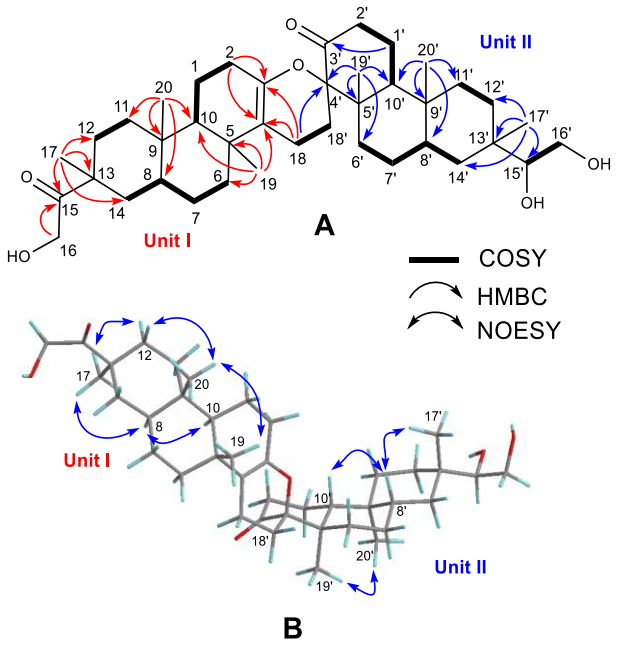


Figure S4. Key COSY, HMBC, and NOESY correlations of **5**.

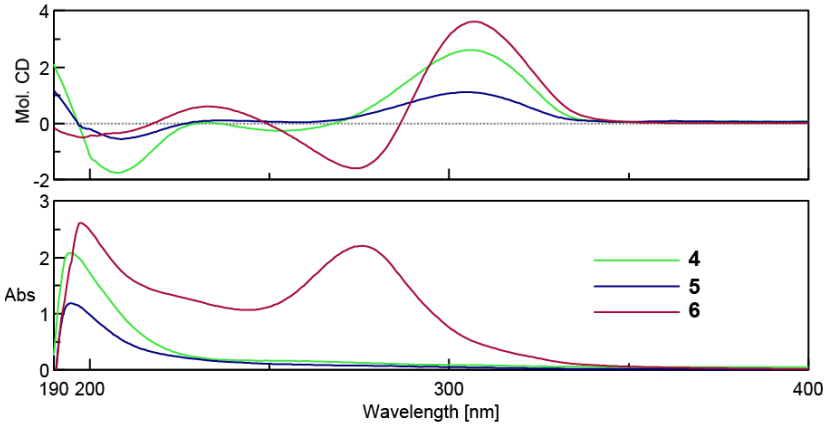


Figure S5. The ECD spectra of compounds **4**–**6**.

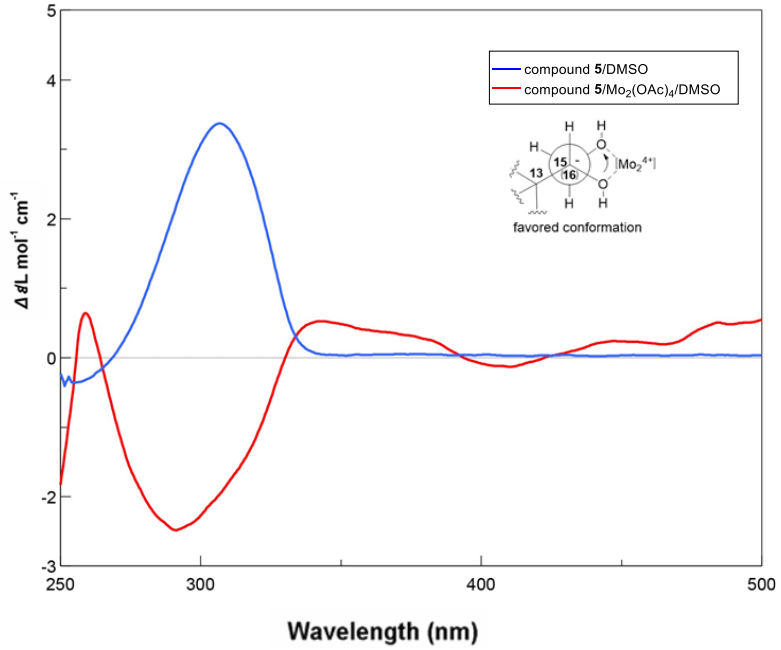


Figure S6. ECD spectra of compound **5** in a DMSO solution (blue) and in a DMSO solution of $Mo_2(OAc)_4$ (red) (The inherent ECD was subtracted).

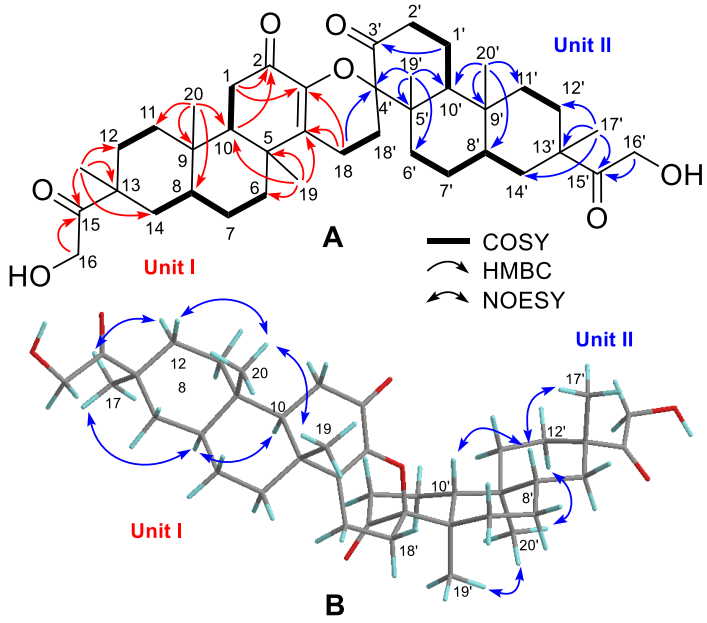


Figure S7. Key COSY, HMBC, and NOESY correlations of **6**.

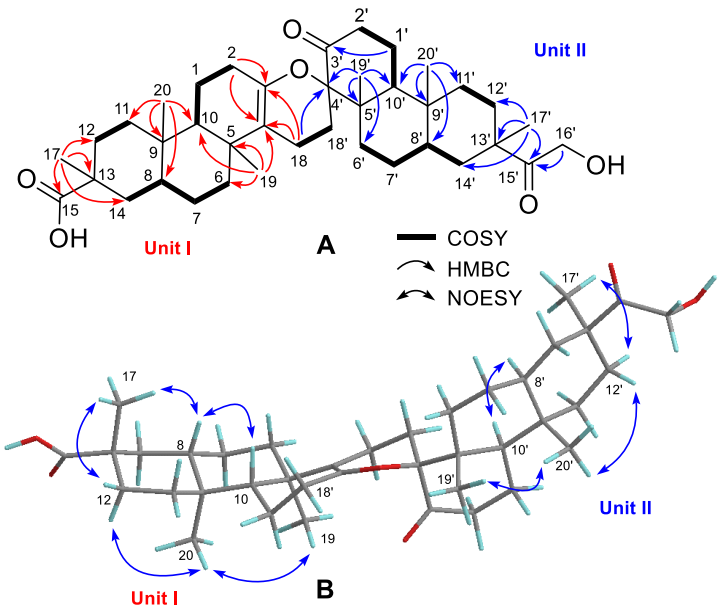


Figure S8. Key COSY, HMBC, and NOESY correlations of **7**.

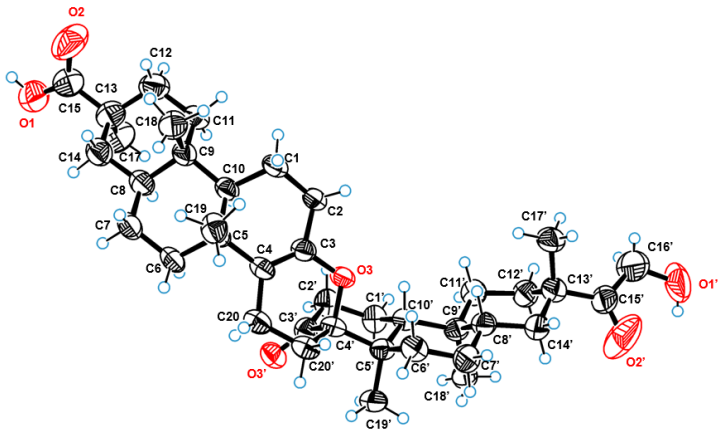


Figure S9. X-ray ORTEP drawing of **7**.

Figure S10. ^{1}H NMR spectrum of natural Koilodenoid A (**1**) in $CDCl_3$.

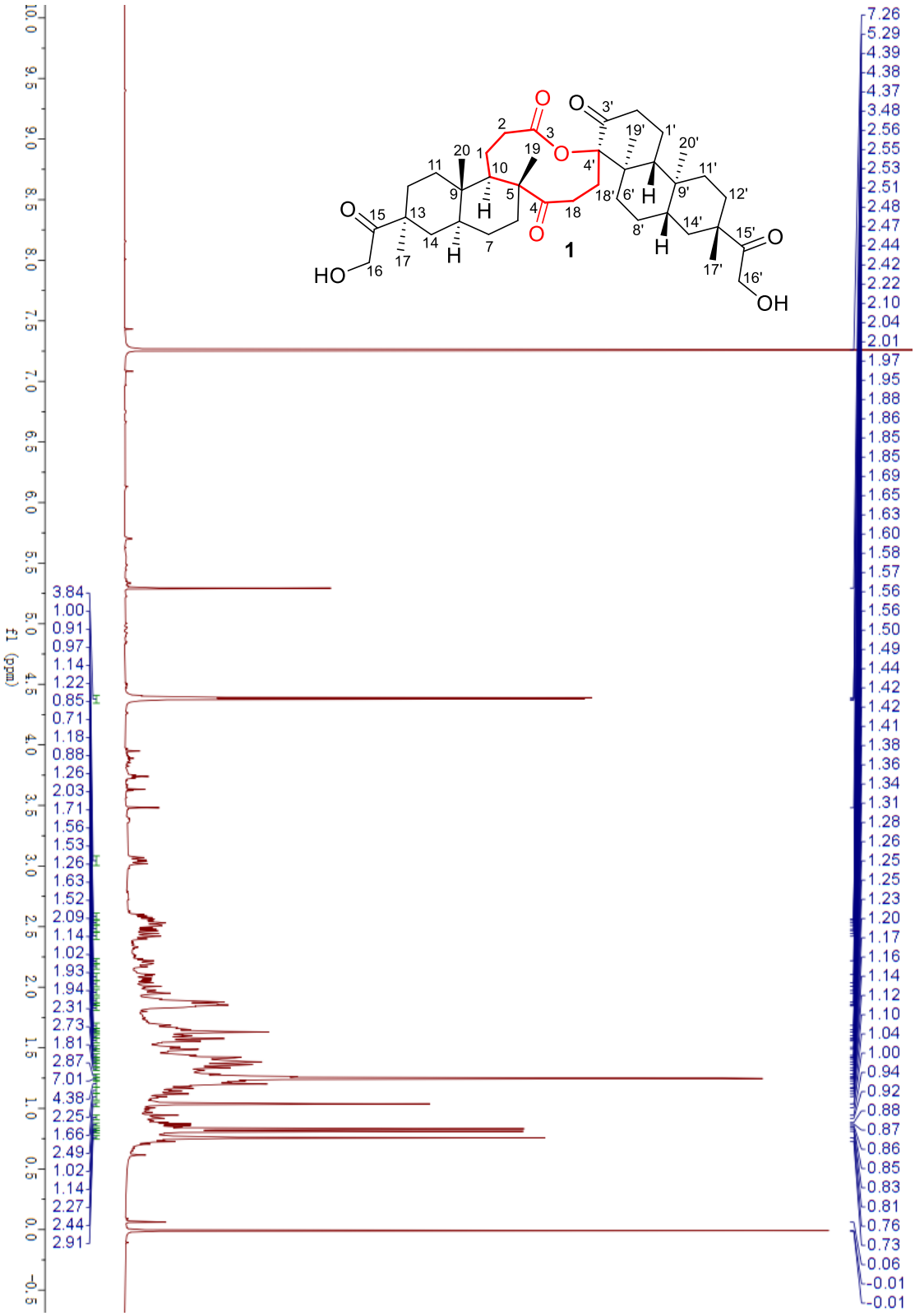


Figure S11. ^{13}C NMR spectrum of natural Koilodenoid A (**1**) in $CDCl_3$.

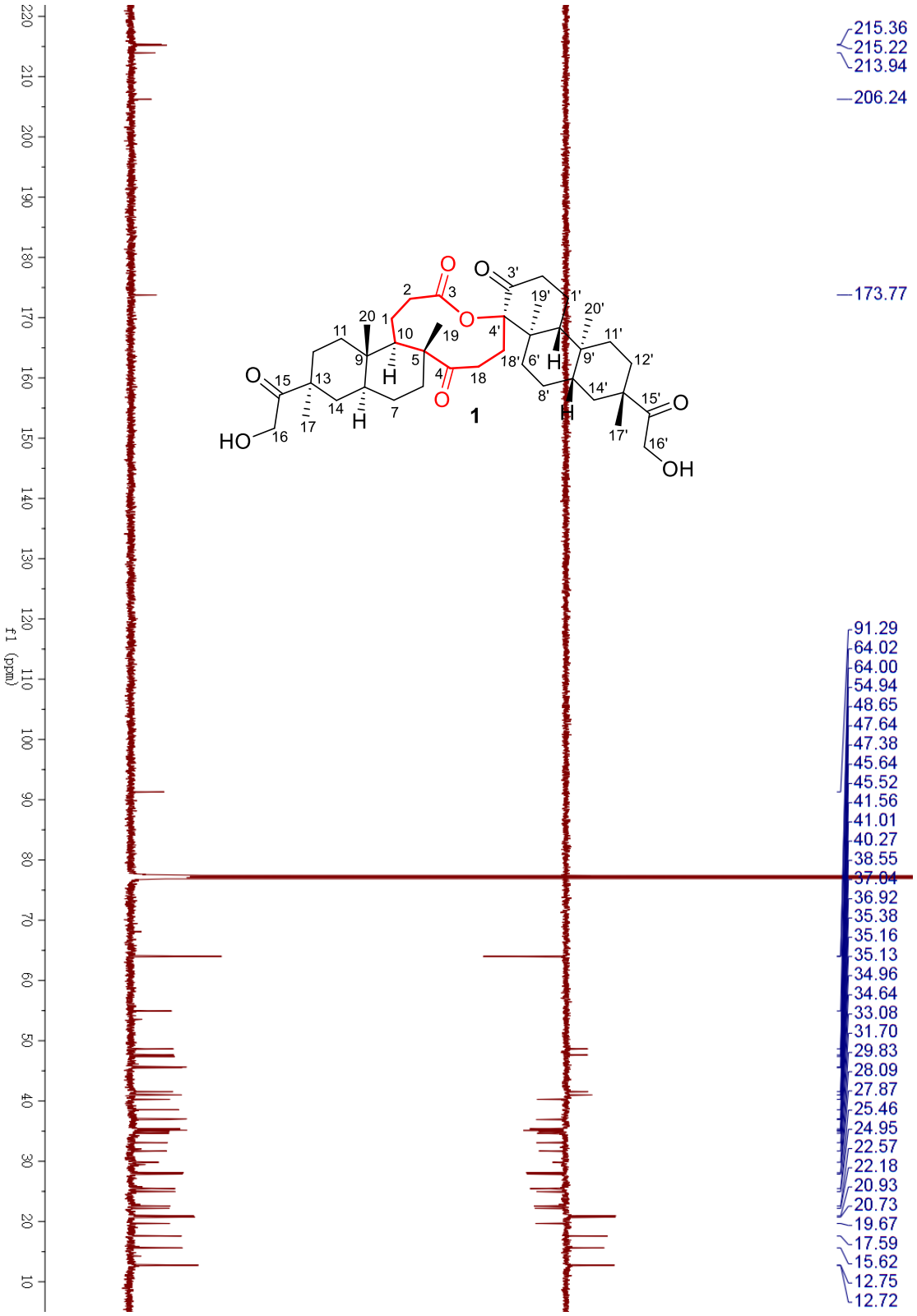


Figure S12. HSQC spectrum of natural Koilodenoid A (**1**) in $CDCl_3$.

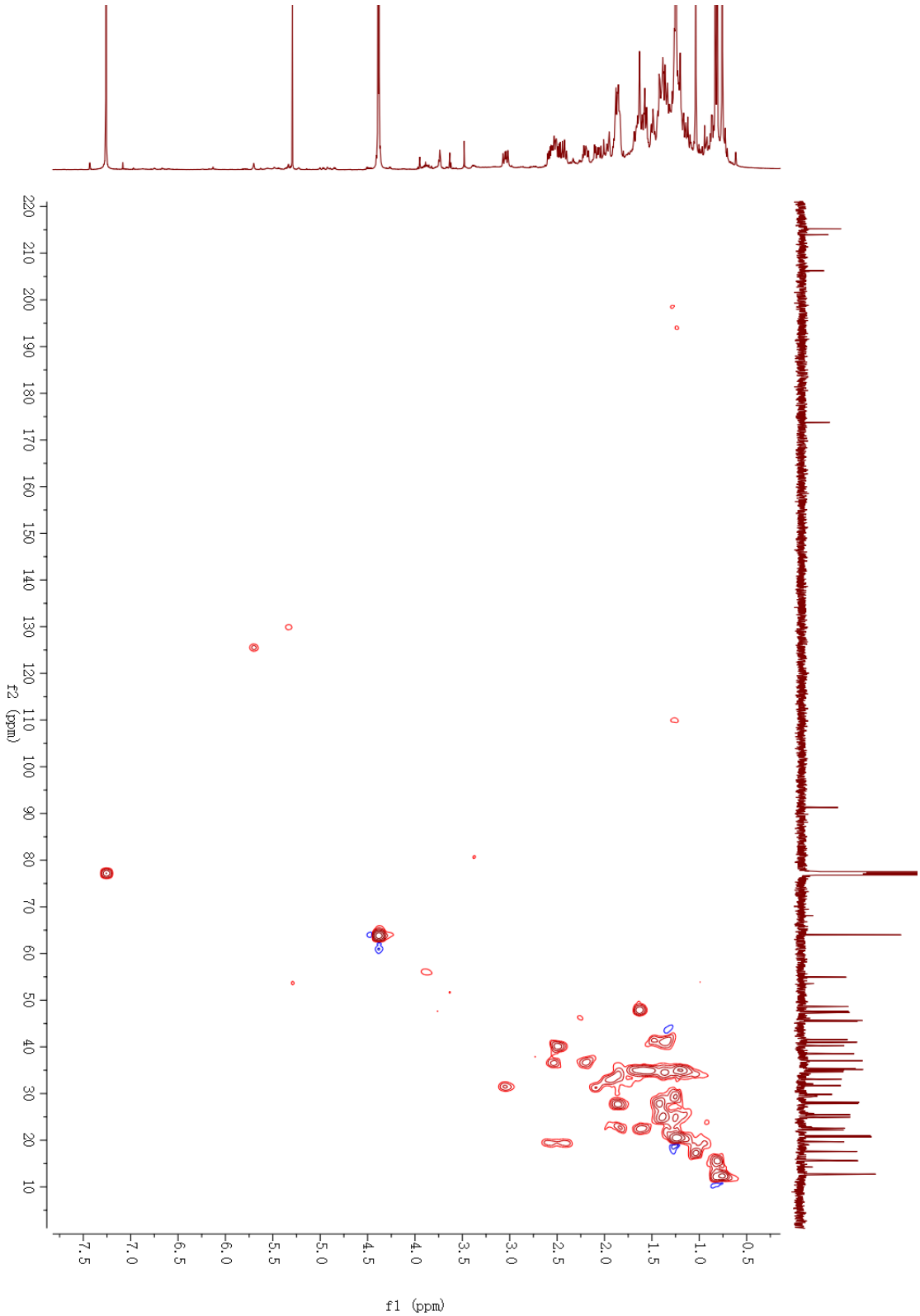


Figure S13. ^{1}H-^{1}H COSY NMR spectrum of natural Koilodenoid A (**1**) in $CDCl_3$.

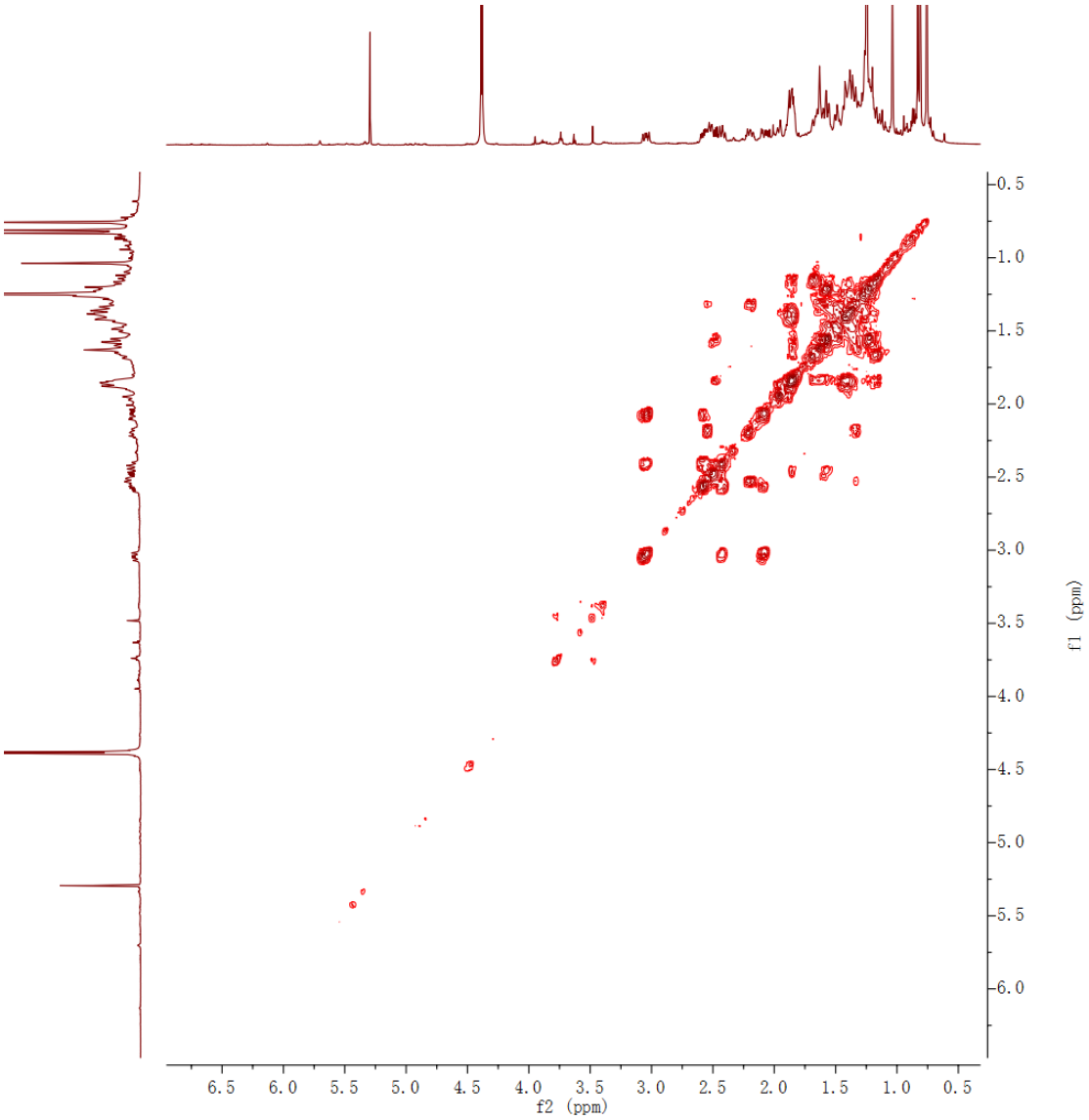


Figure S14. HMBC spectrum of natural Koilodenoid A (**1**) in $CDCl_3$.

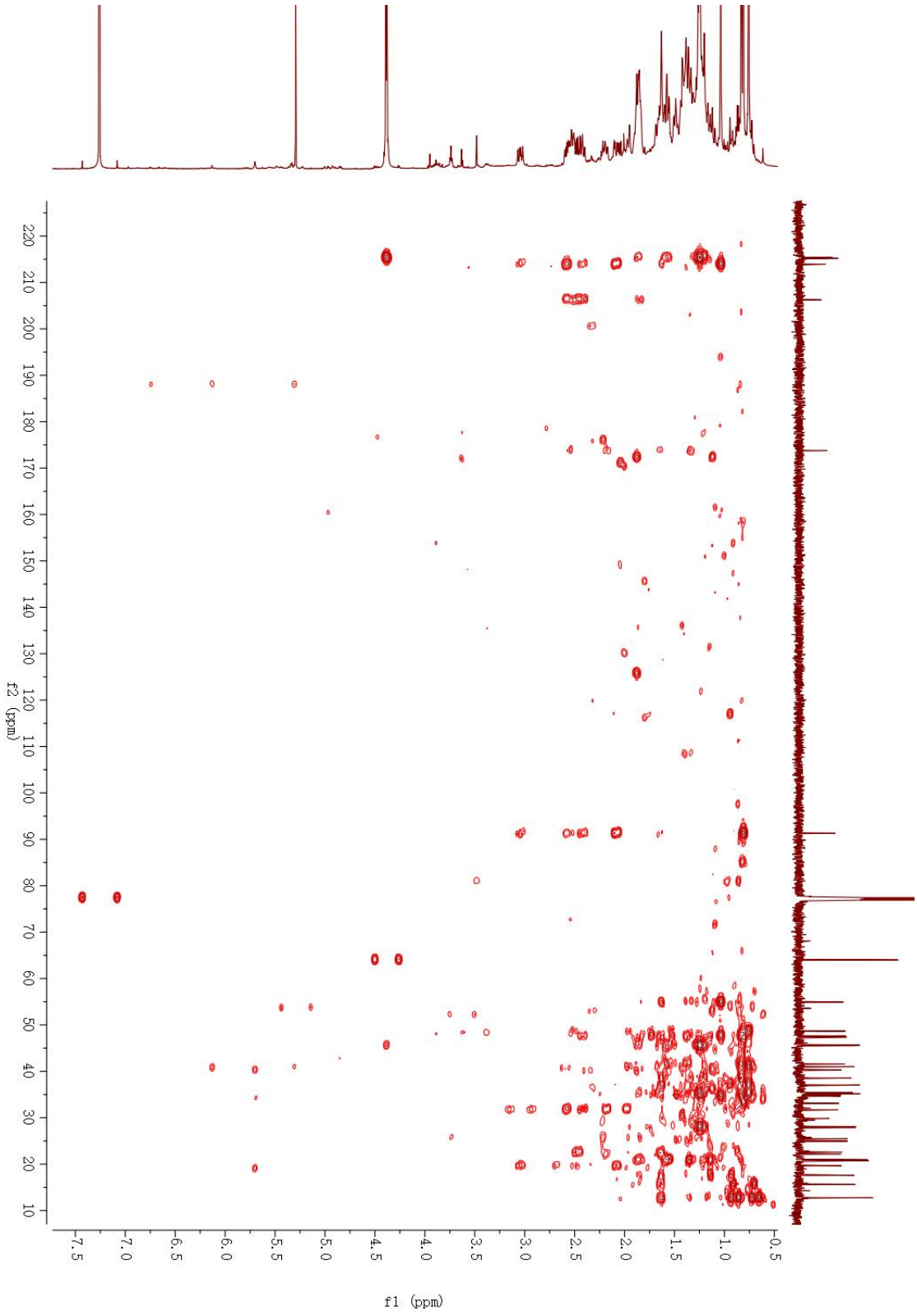


Figure S15. NOESY spectrum of natural Koilodenoid A (**1**) in $CDCl_3$.

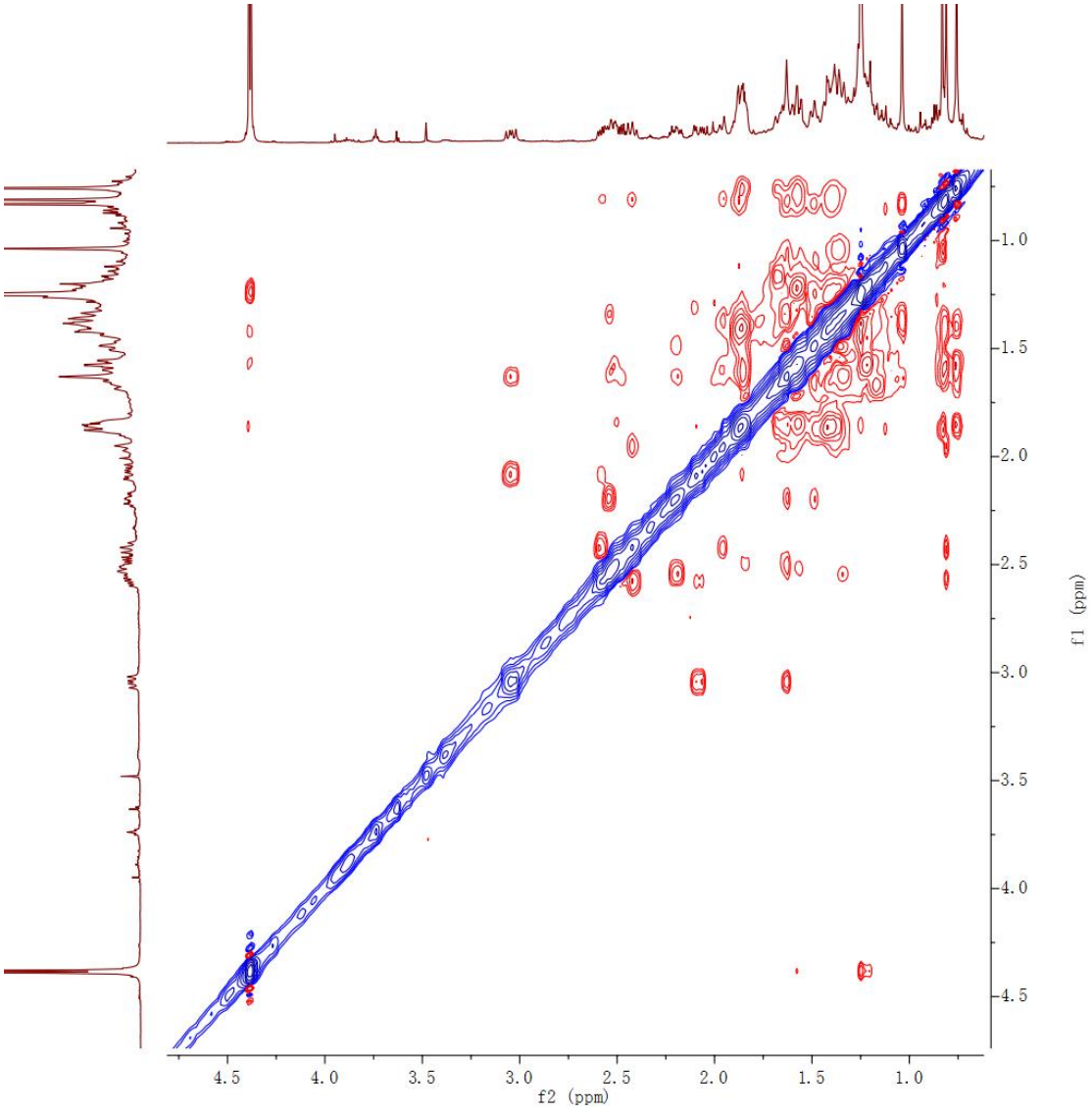


Figure S16. (+)-ESIMS spectrum of natural Koilodenoid A (**1**).

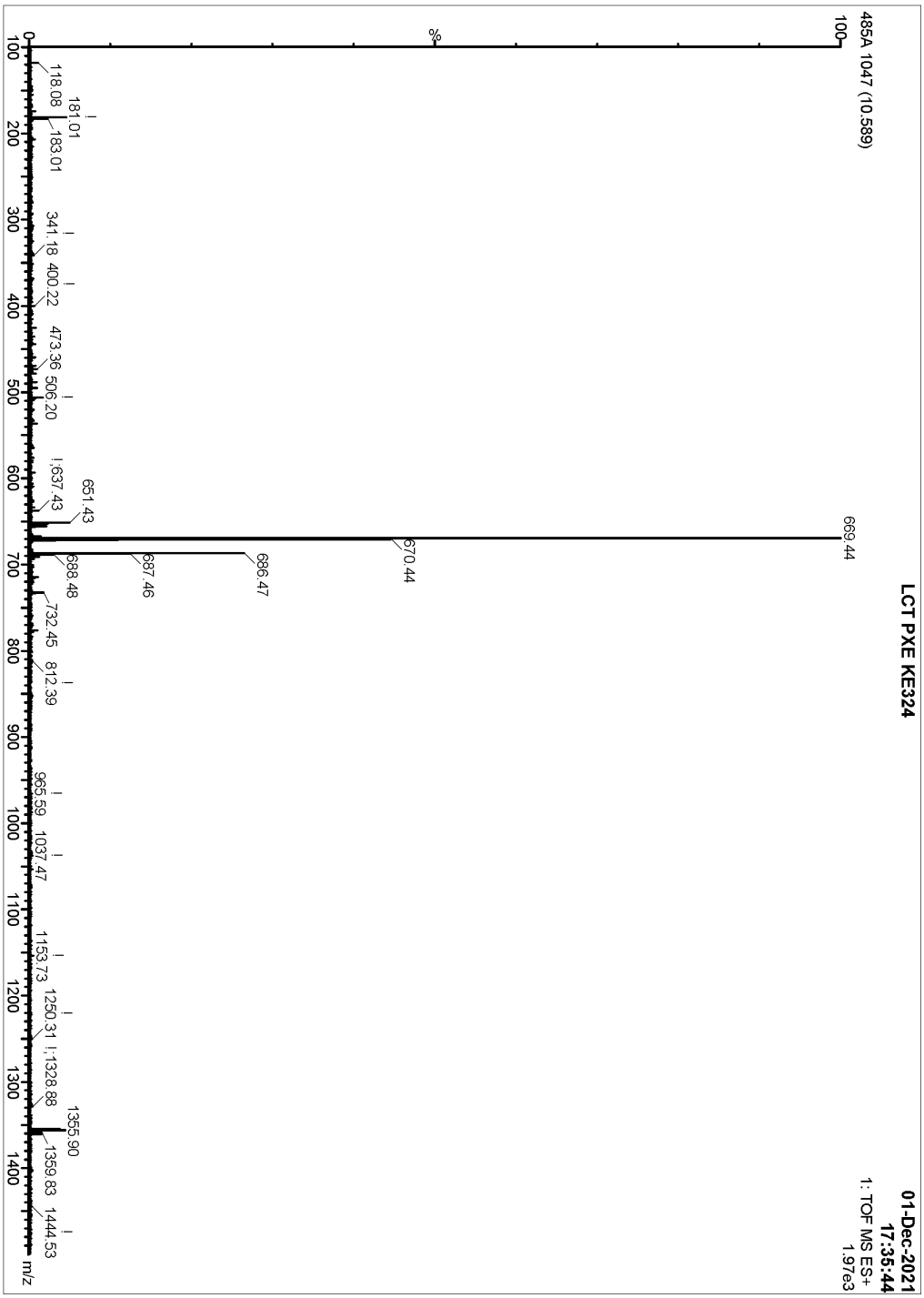


Figure S17. (+)-HRESIMS spectrum of natural Koilodenoid A (**1**).

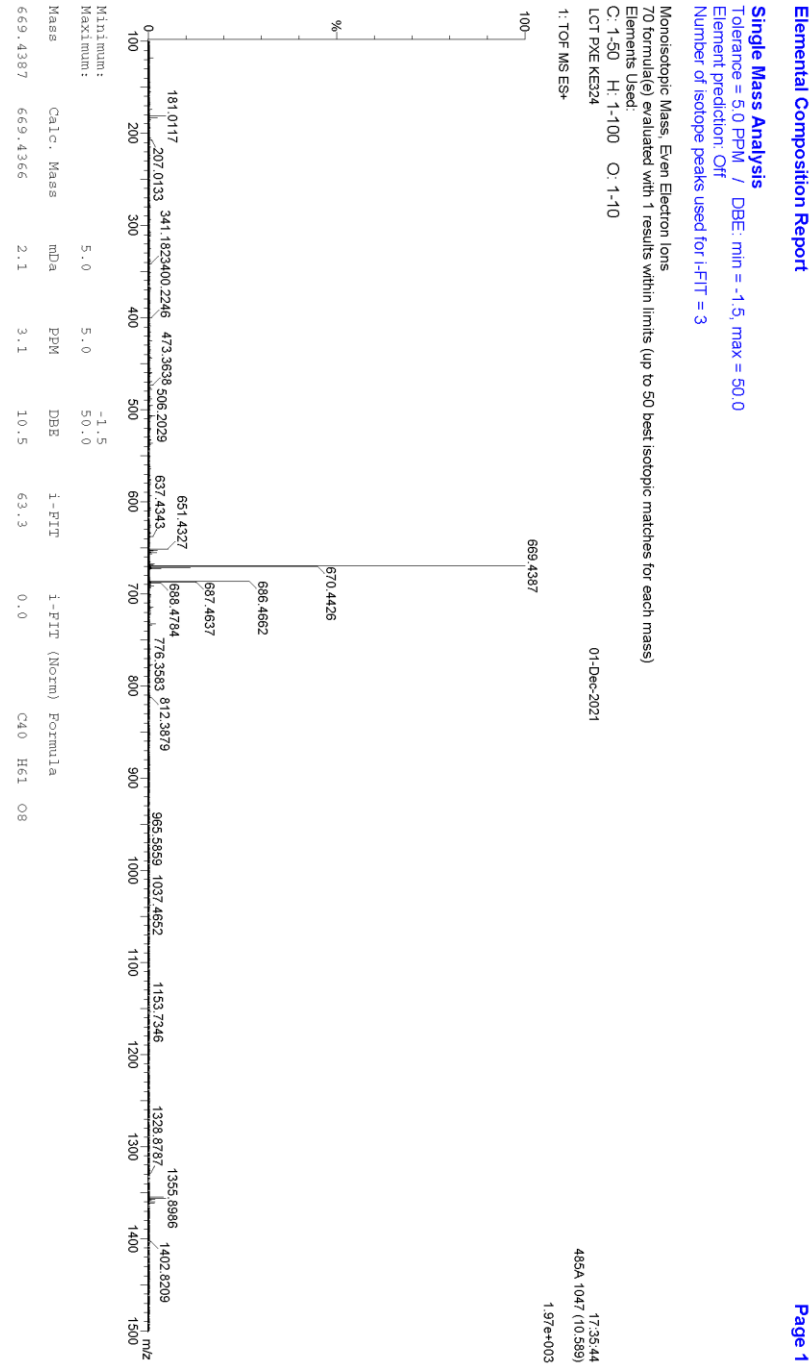


Figure S18. IR spectrum of natural Koilodenoid A (**1**).

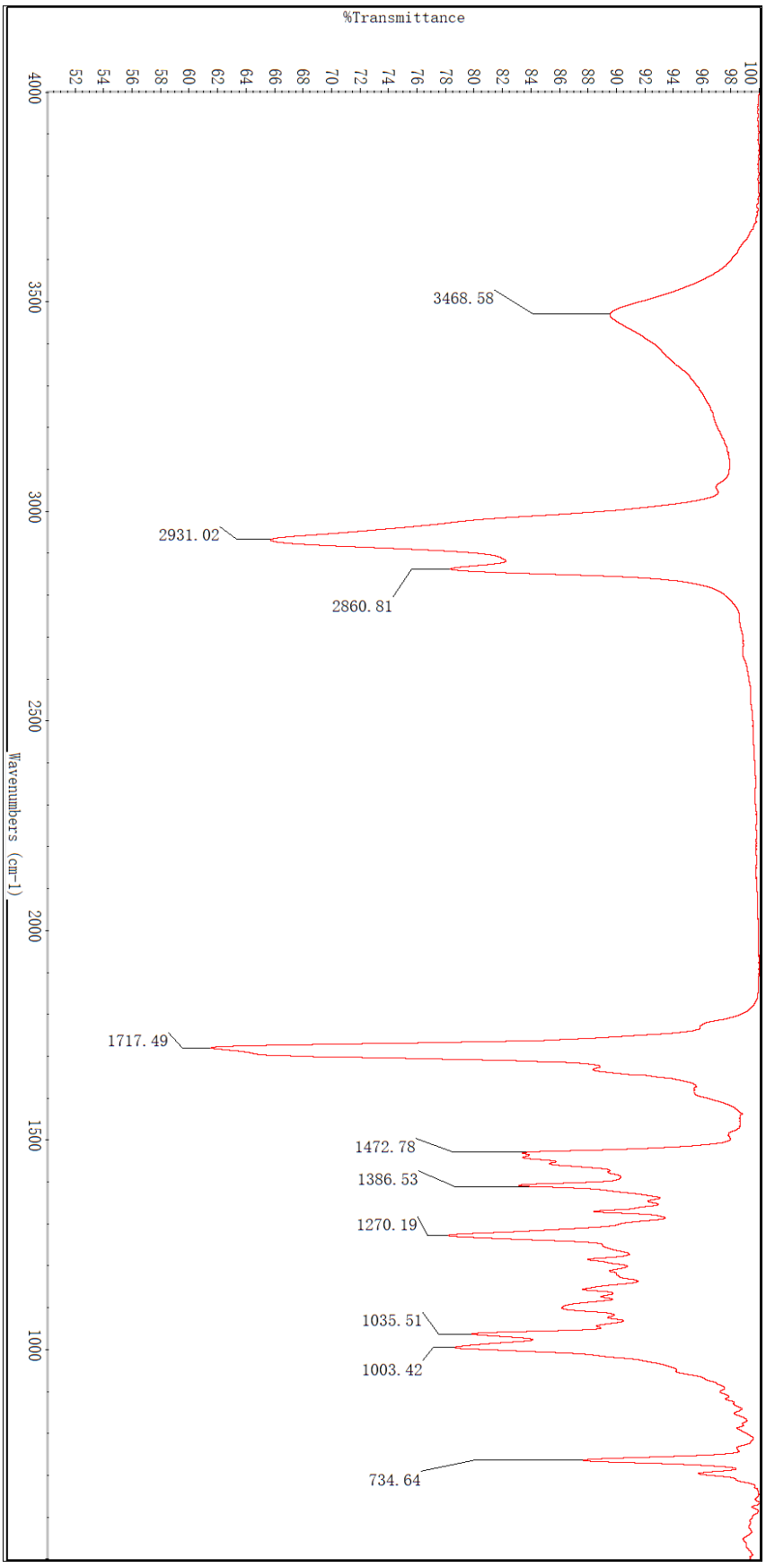


Figure S19. ^{1}H NMR spectrum of Koilodenoid B (**2**) in $CDCl_3$.

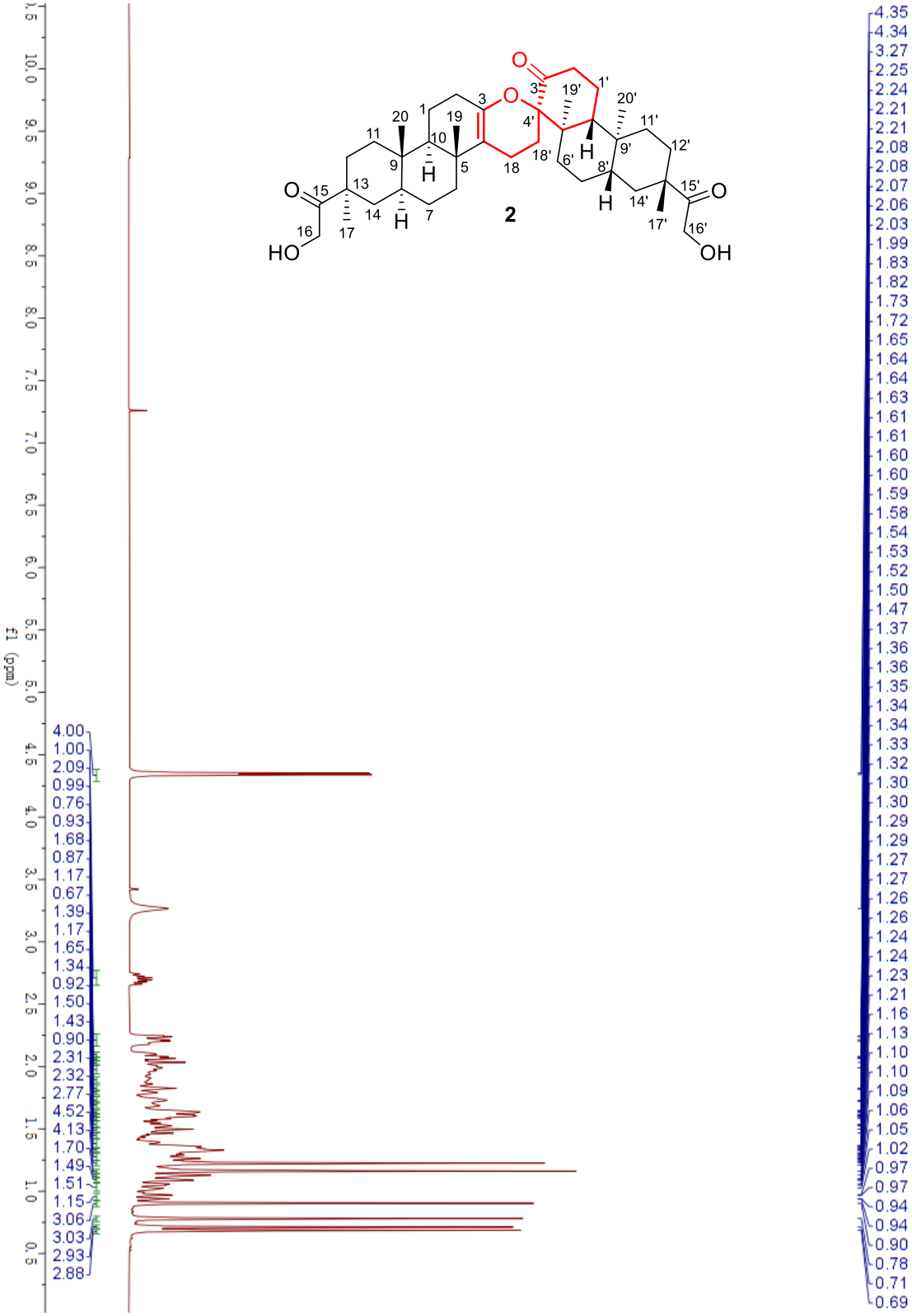


Figure S20. ^{13}C NMR spectrum of Koilodenoid B (**2**) in $CDCl_3$.

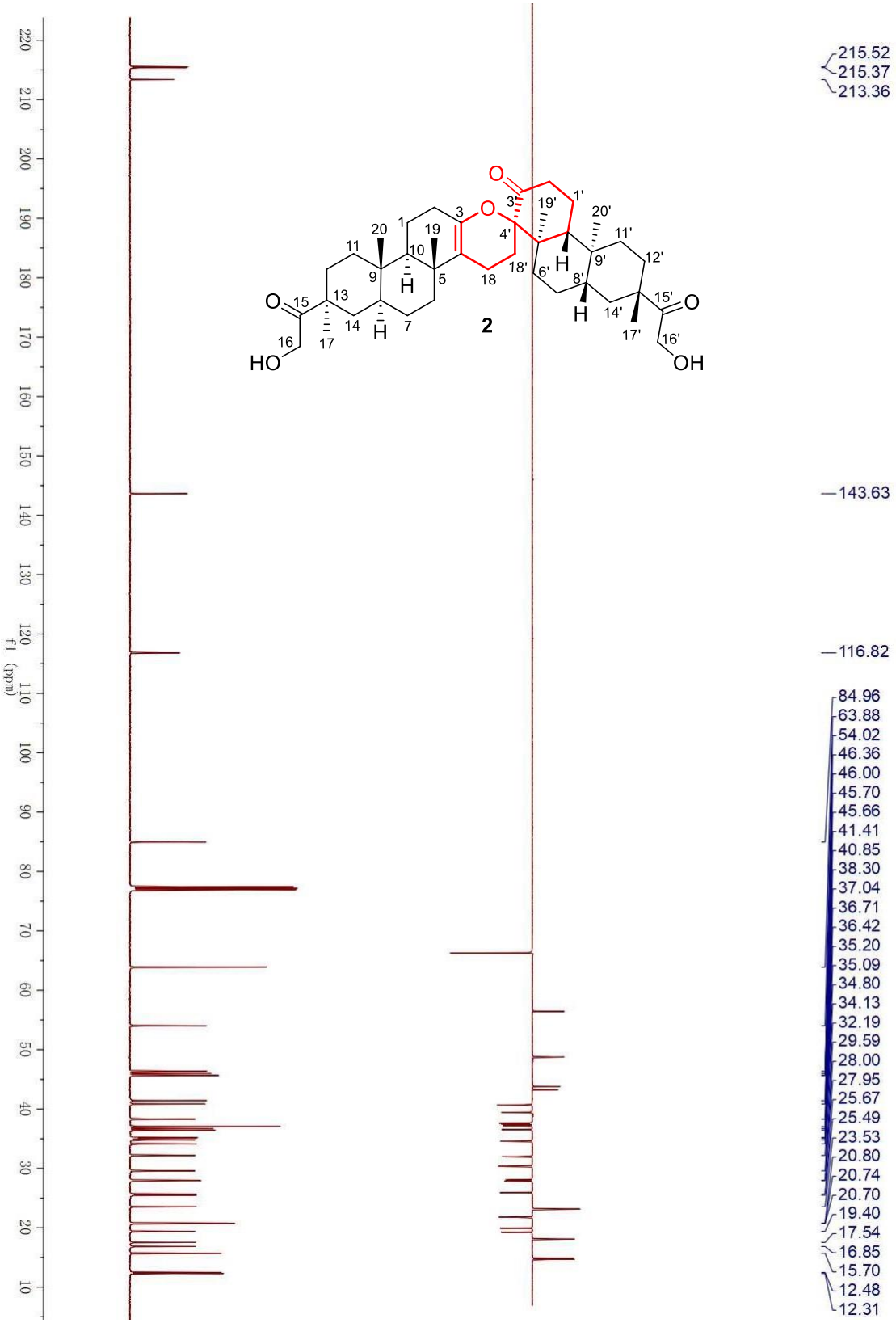


Figure S21. HSQC spectrum of Koilodenoid B (**2**) in $CDCl_3$.

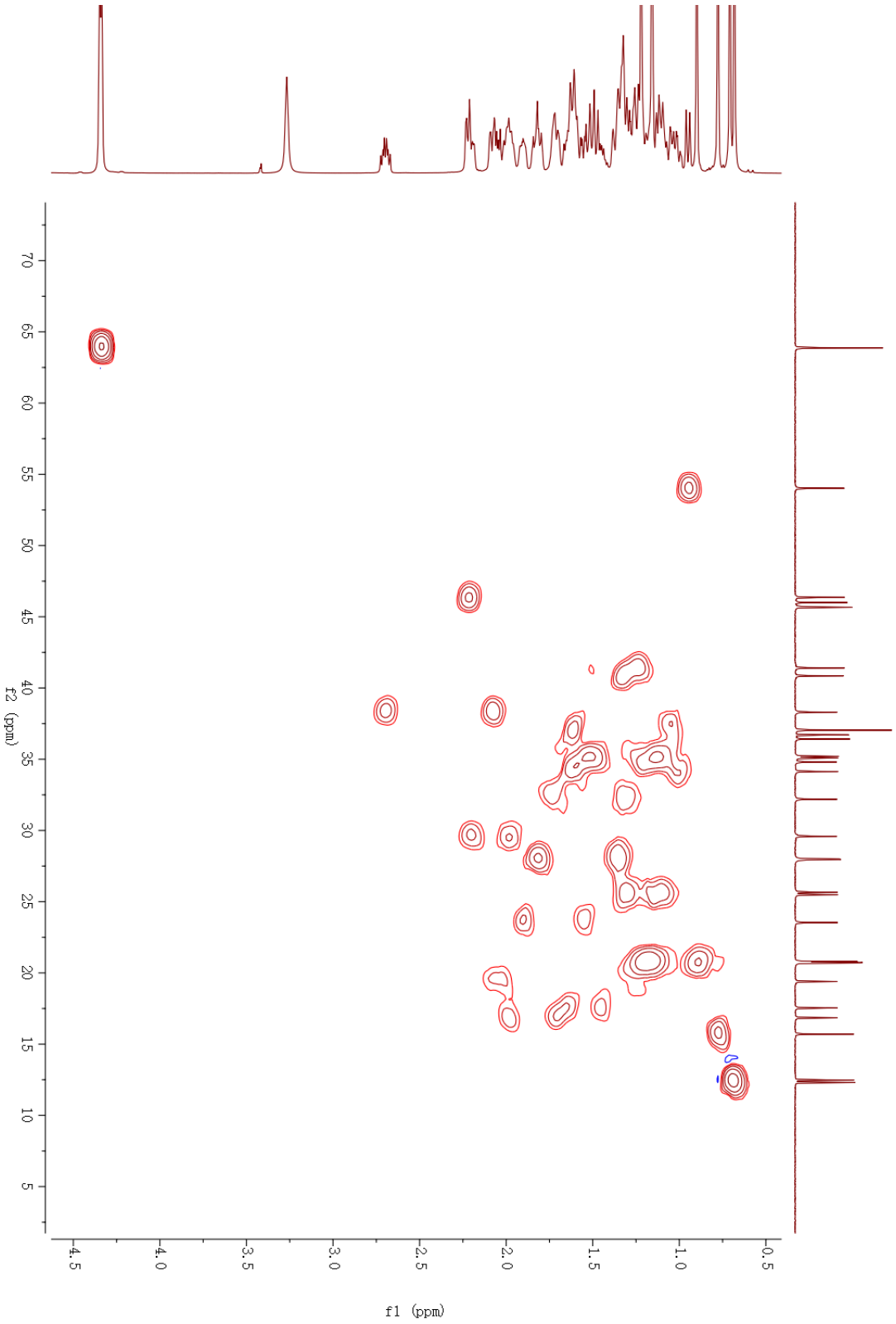


Figure S22. $^{1}H-^{1}H$ COSY spectrum of Koilodenoid B (**2**) in $CDCl_3$.

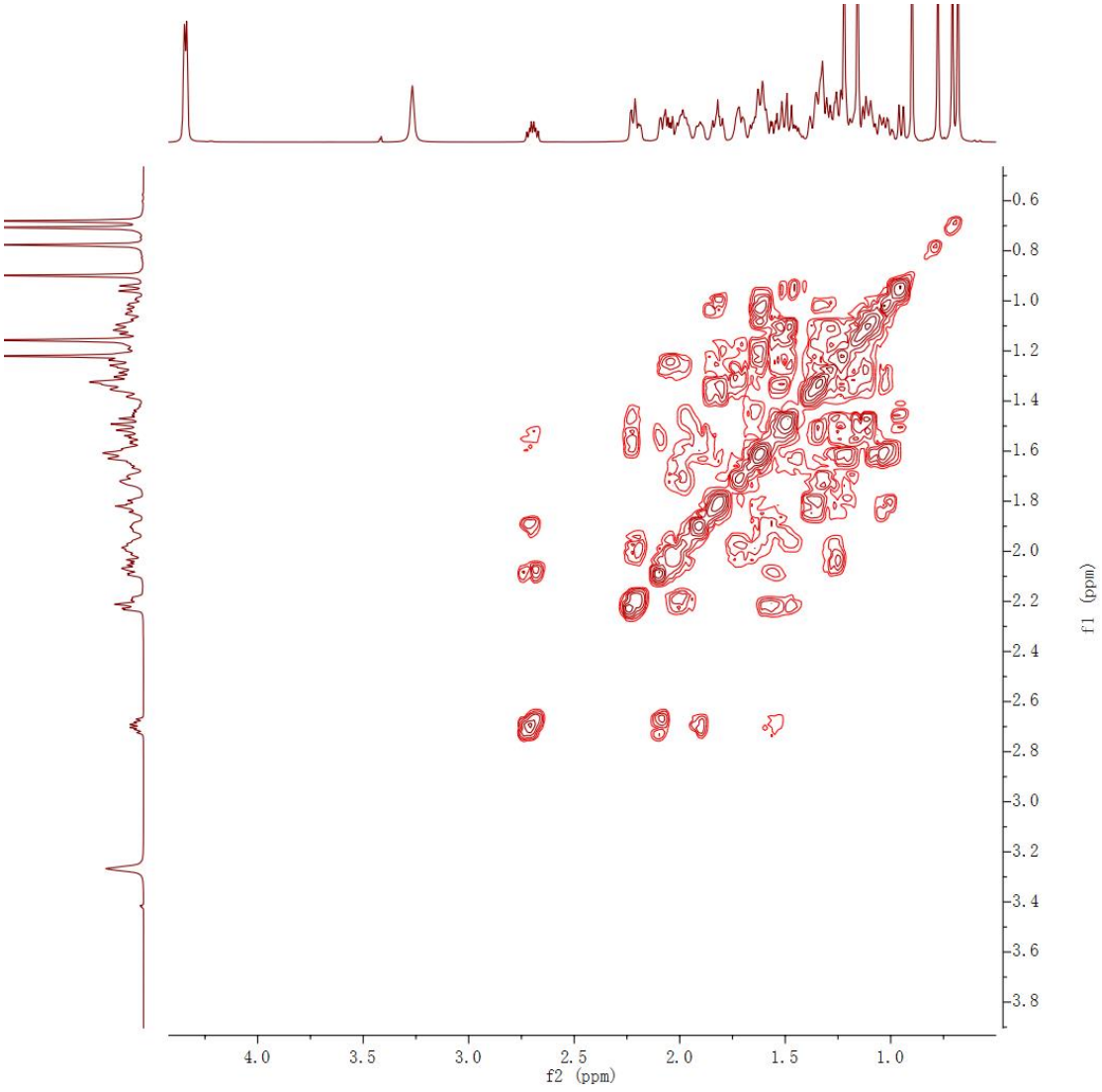


Figure S23. HMBC spectrum of Koilodenoid B (**2**) in $CDCl_3$.

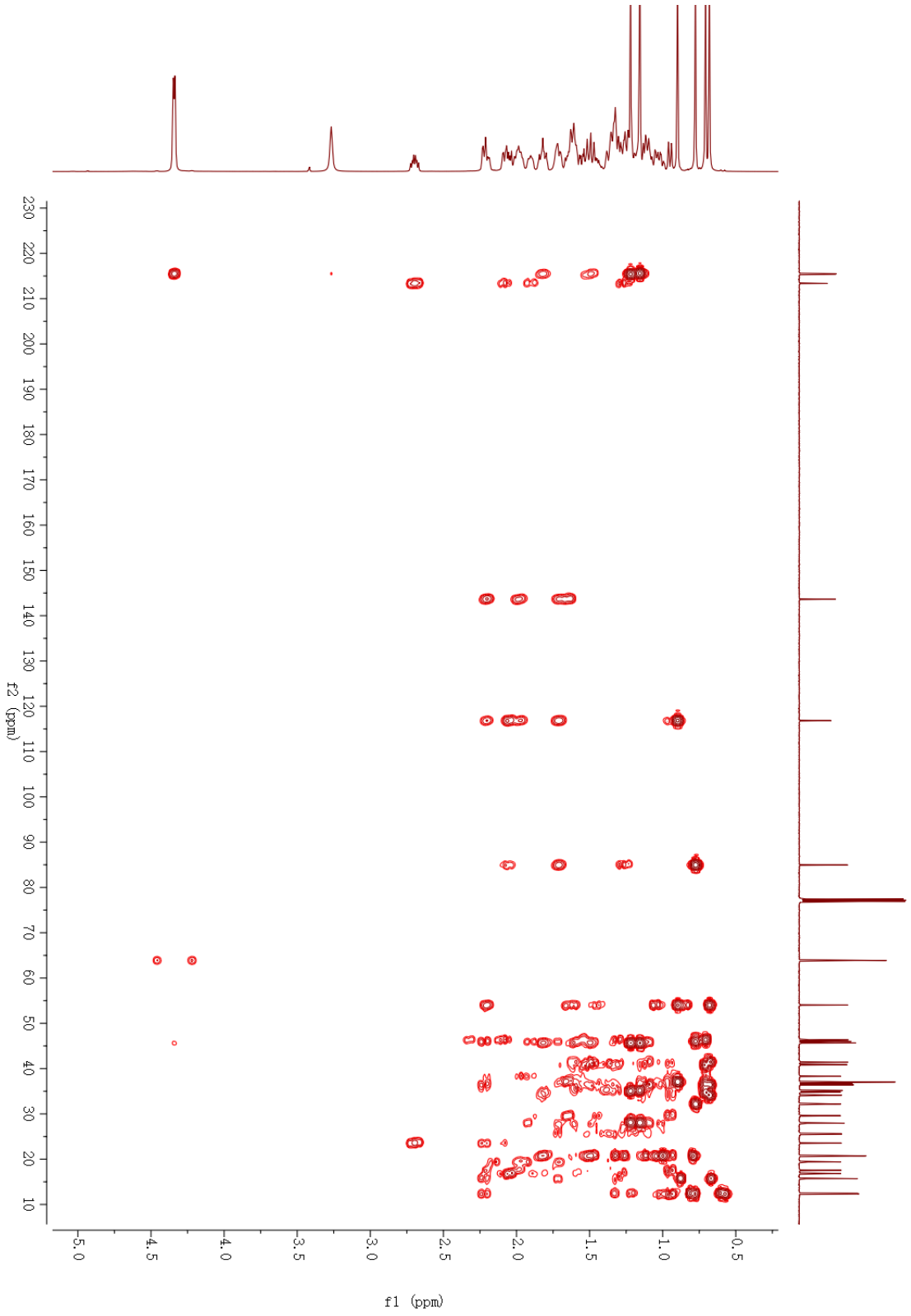


Figure S24. NOESY spectrum of Koilodenoid B (**2**) in $CDCl_3$.

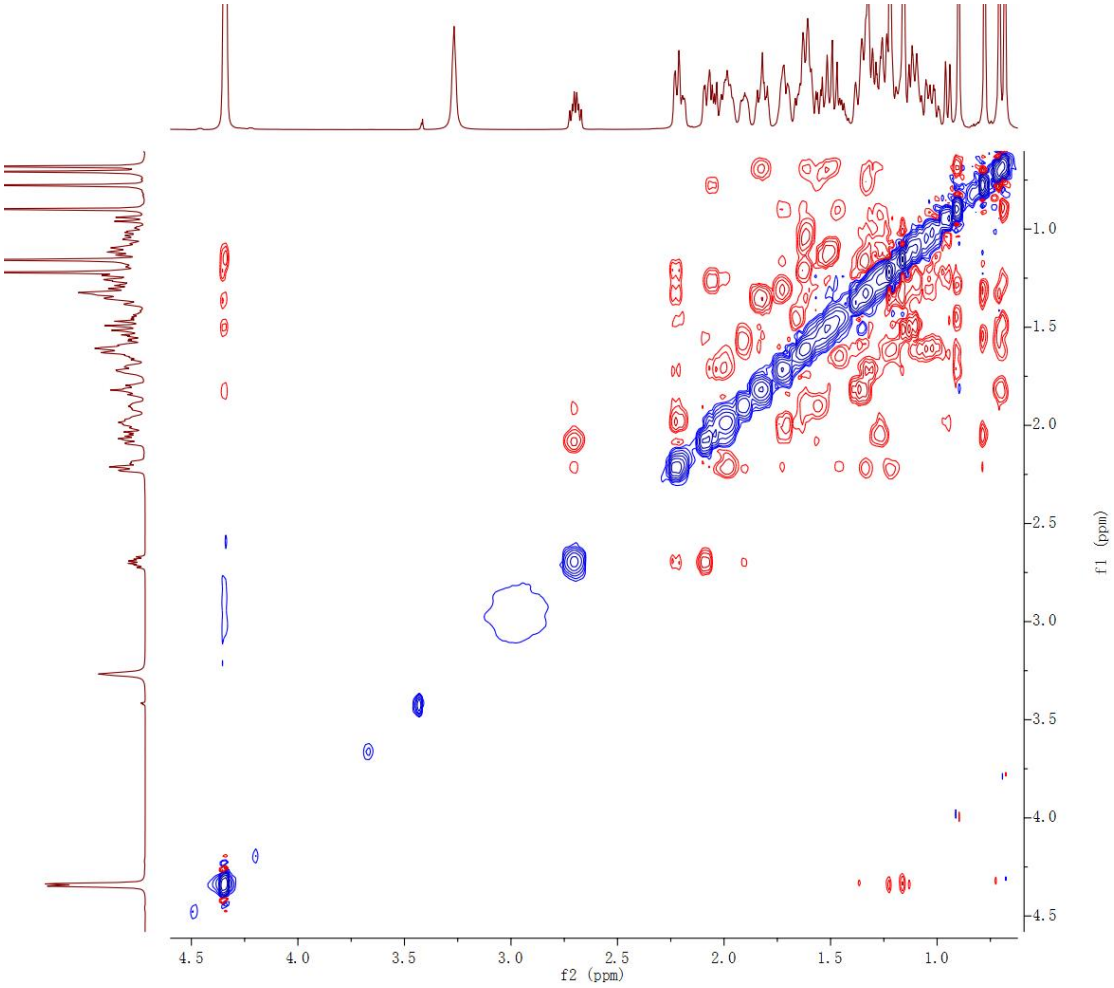


Figure S25. (+)-ESIMS spectrum of Koilodenoid B (**2**).

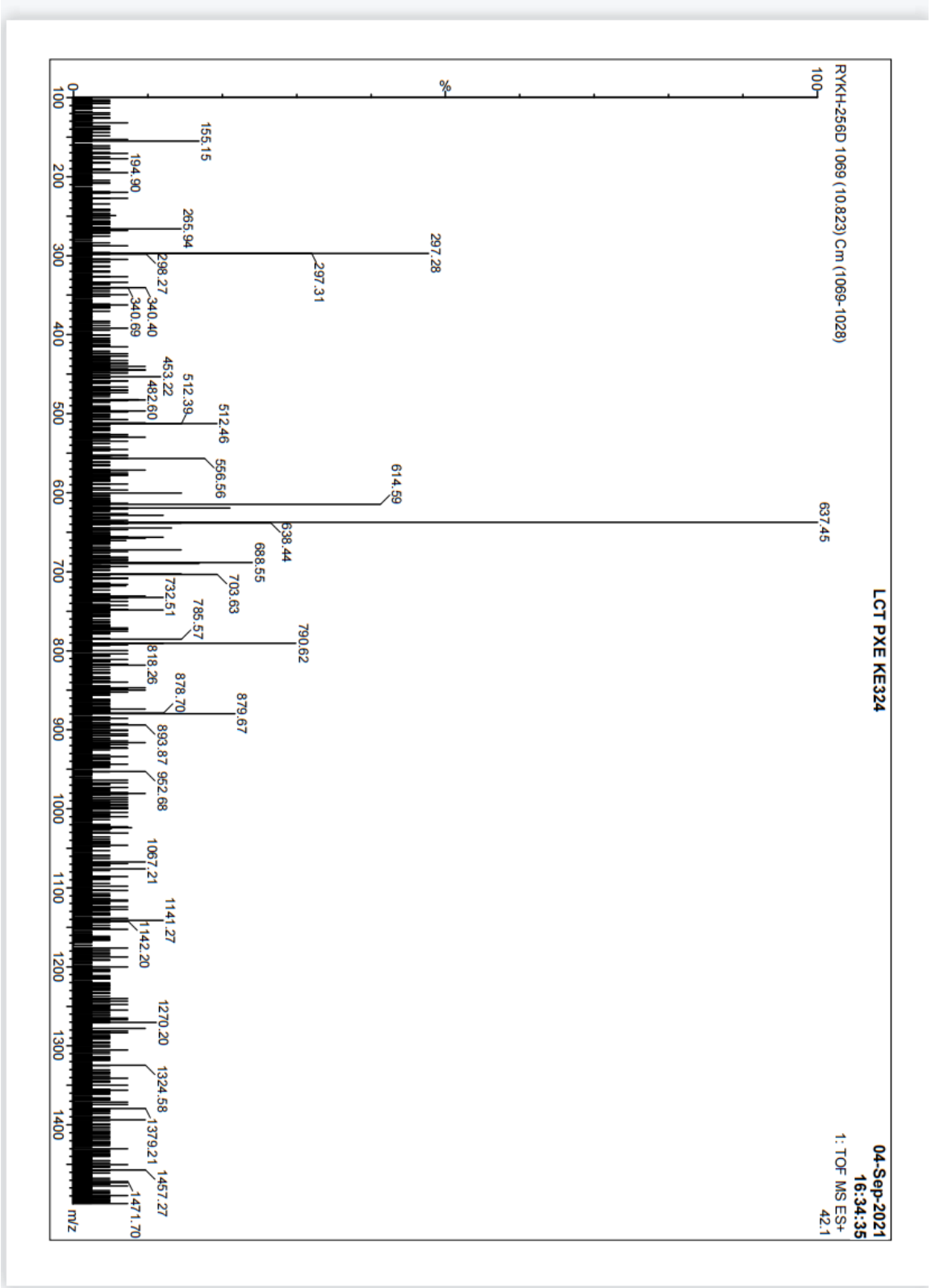


Figure S26. (+)-HRESIMS spectrum of Koilodenoid B (**2**).

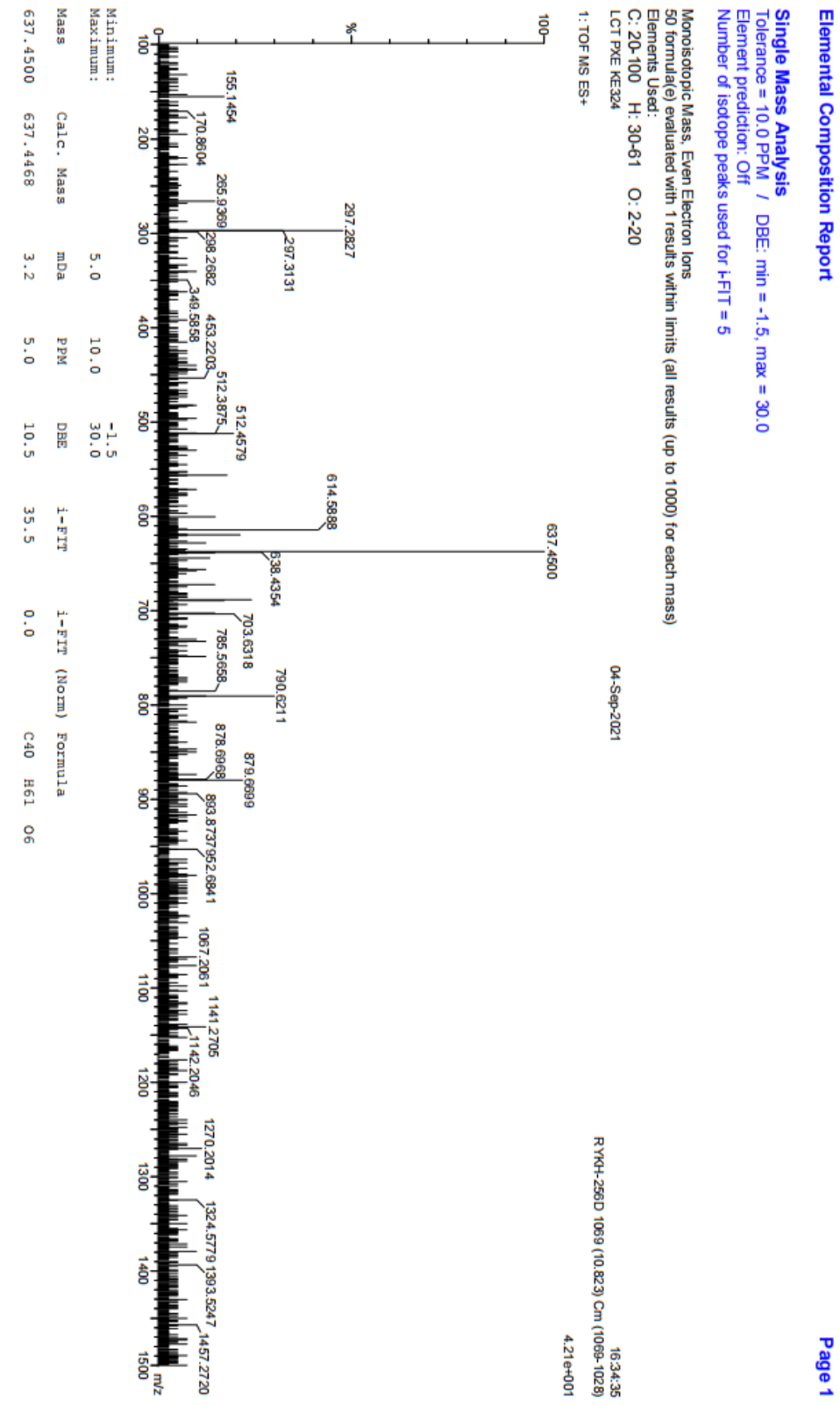


Figure S27. IR spectrum of Koilodenoid B (**2**).

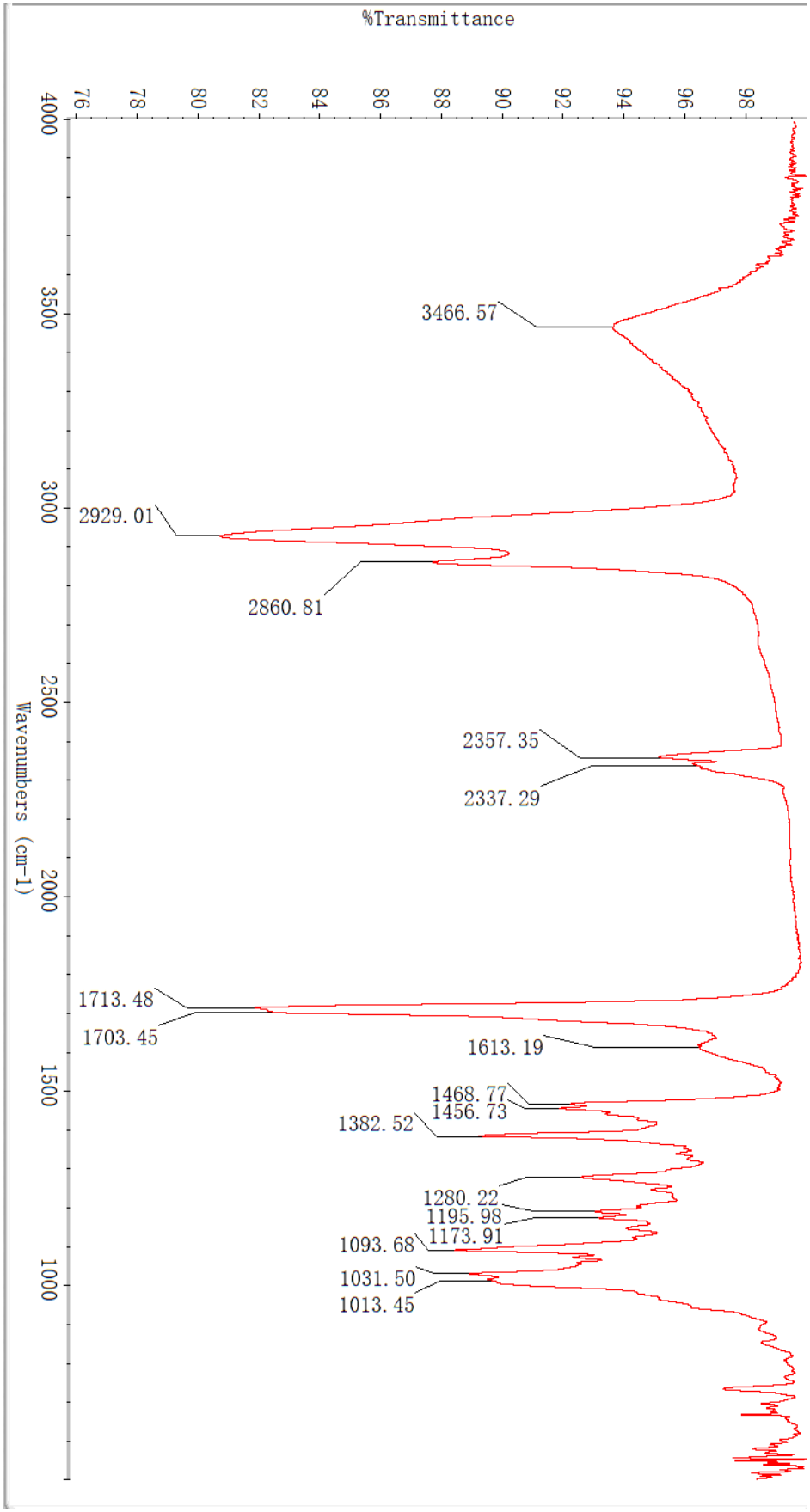


Figure S28. ^{1}H NMR spectrum of Koilodenoid C (**3**) in $CDCl_3$.

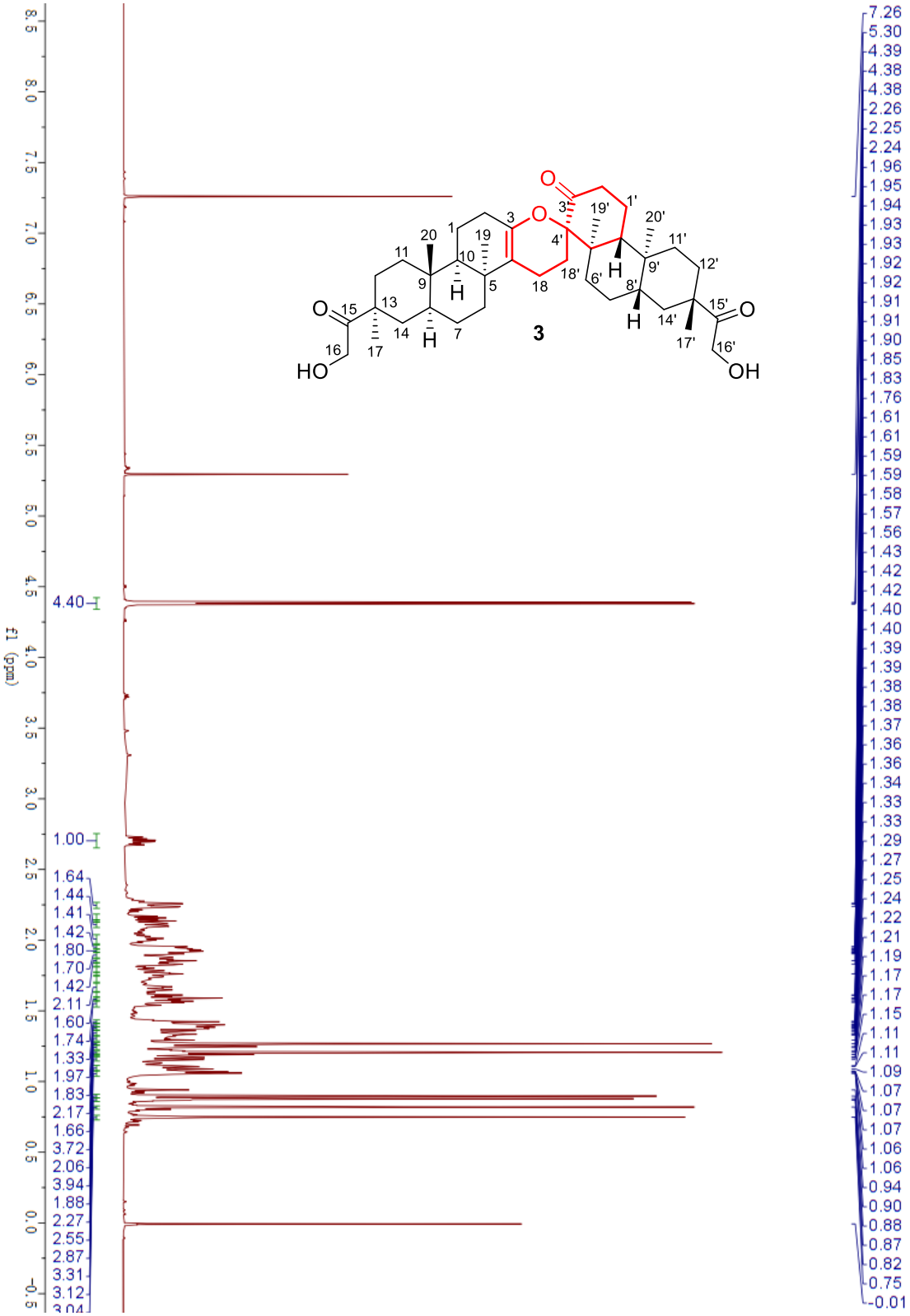


Figure S29. ^{13}C NMR spectrum of Koilodenoid C (**3**) in $CDCl_3$.

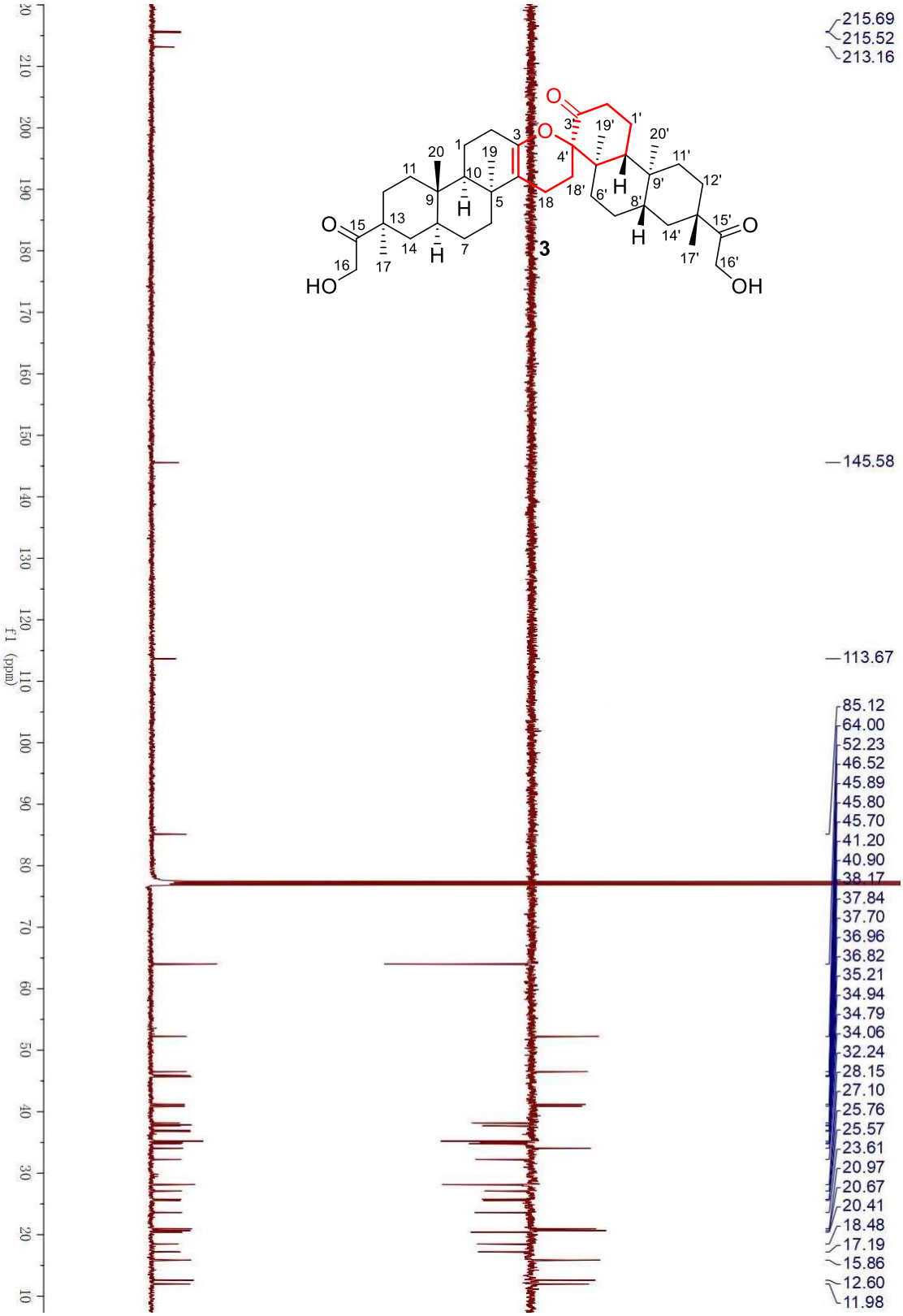


Figure S30. HSQC spectrum of Koilodenoid C (**3**) in $CDCl_3$.

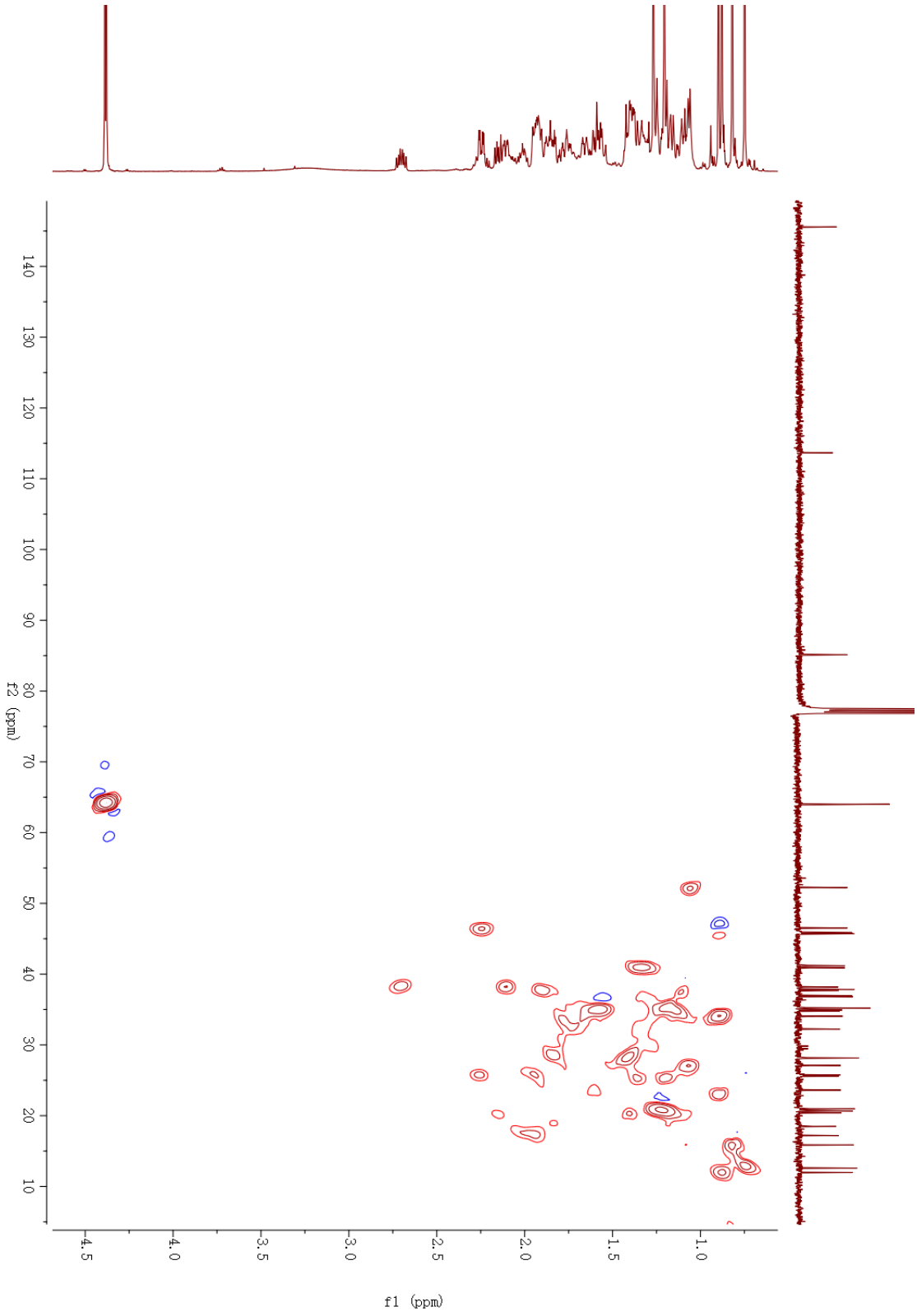


Figure S31. ^{1}H-^{1}H COSY NMR spectrum of Koilodenoid C (**3**) in $CDCl_3$.

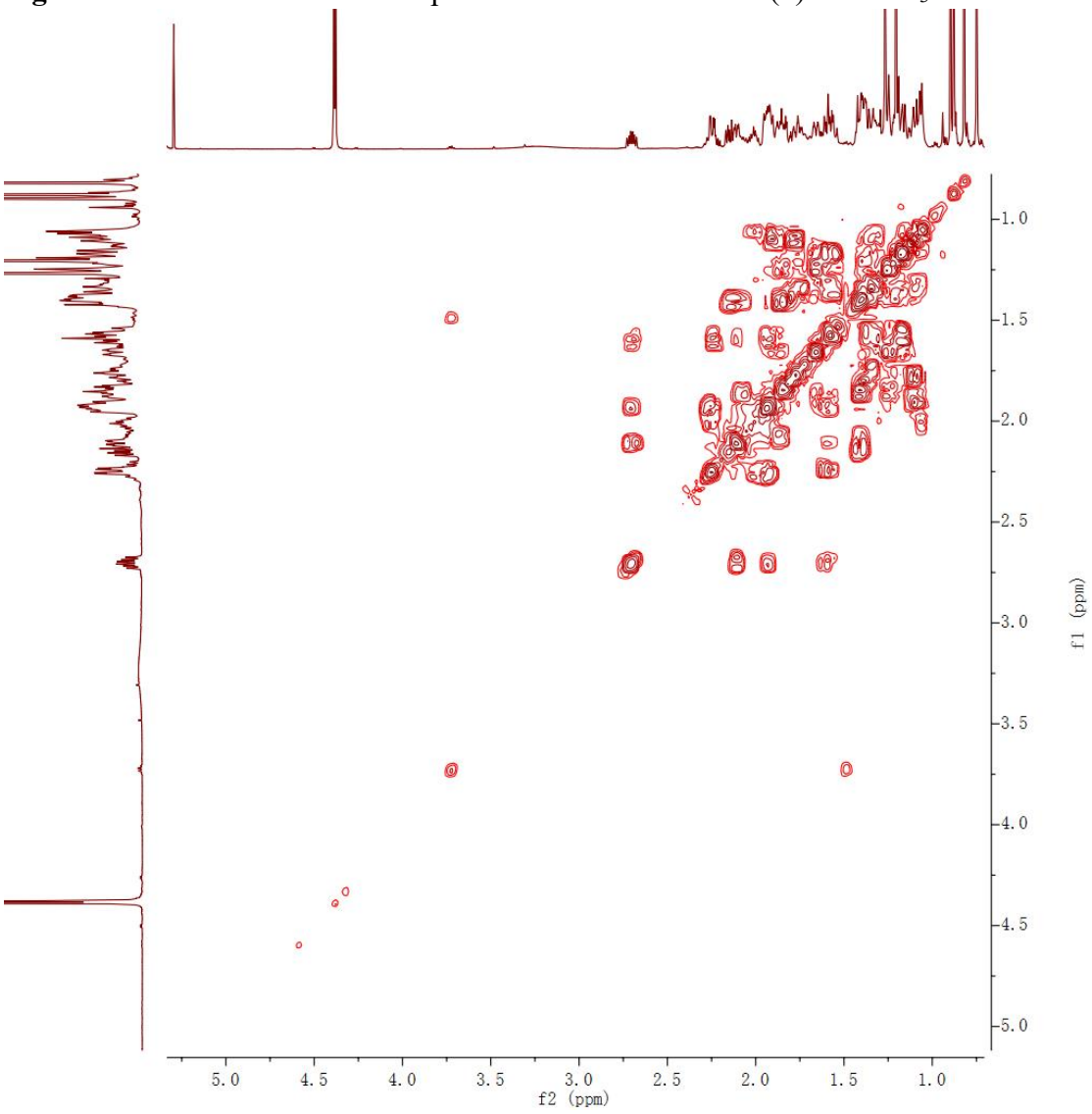


Figure S32. HMBC spectrum of Koilodenoid C (**3**) in $CDCl_3$.

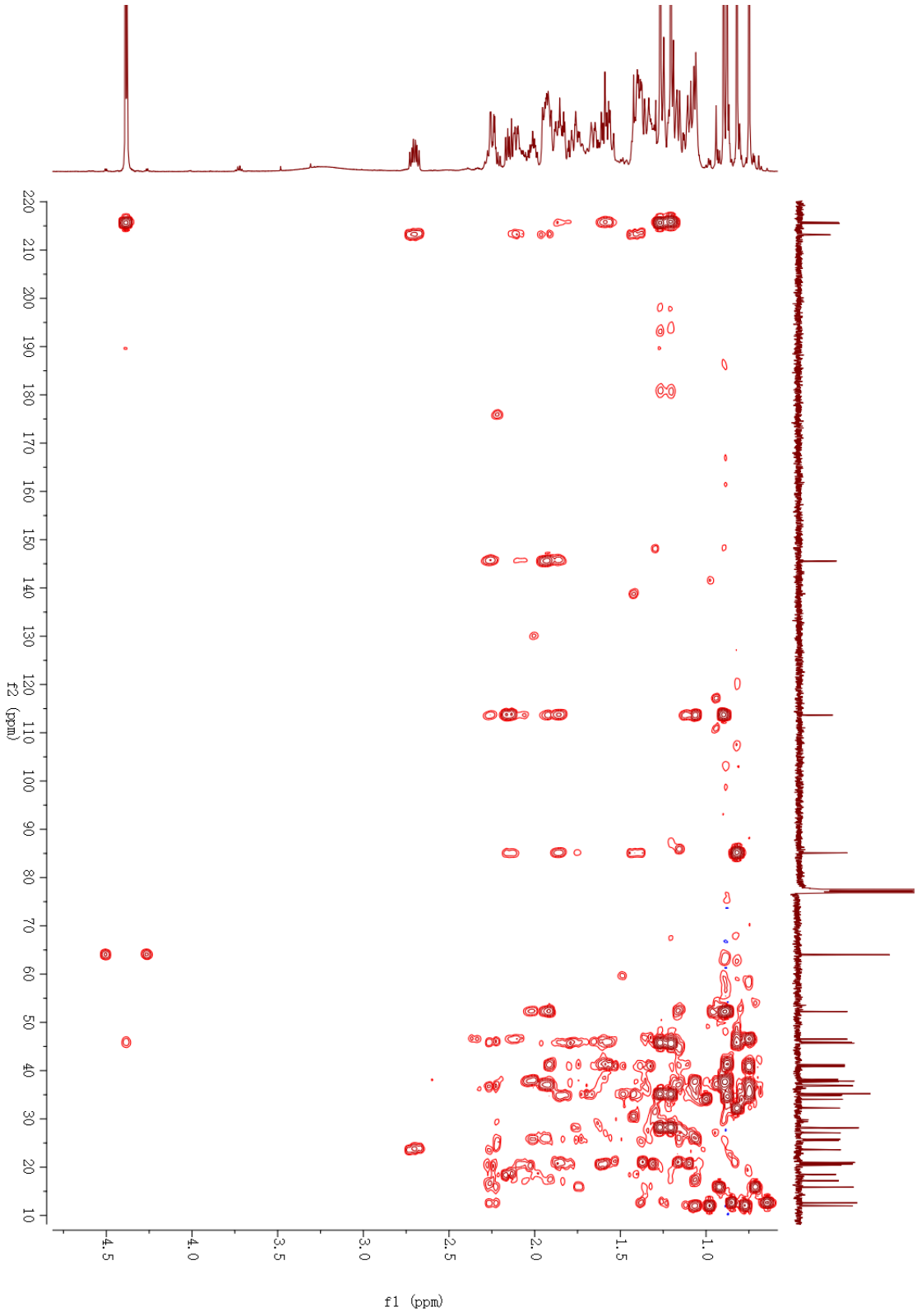


Figure S33. NOESY spectrum of Koilodenoid C (**3**) in $CDCl_3$.

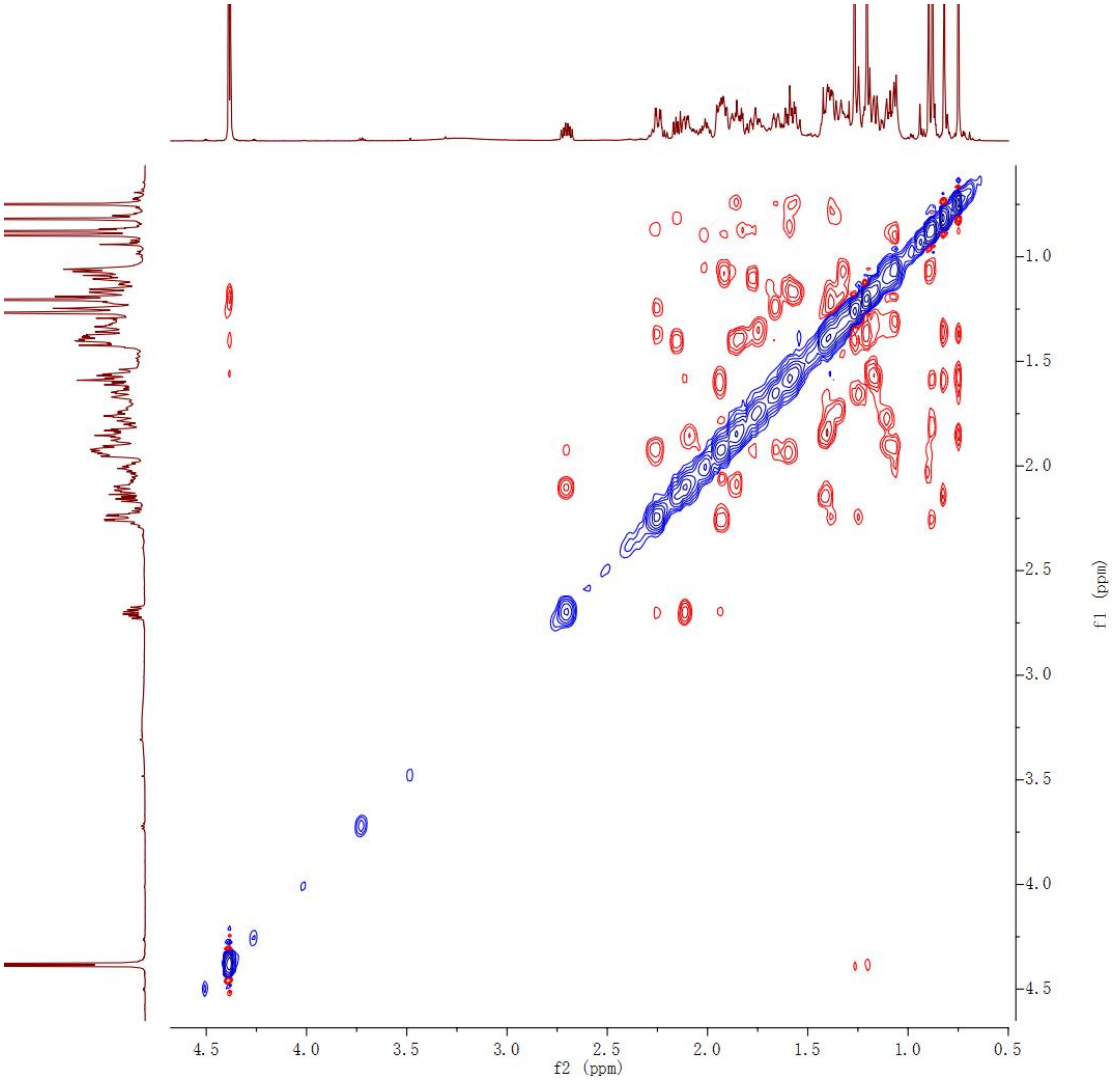


Figure S34. (+)-ESIMS spectrum of Koilodenoid C (**3**).

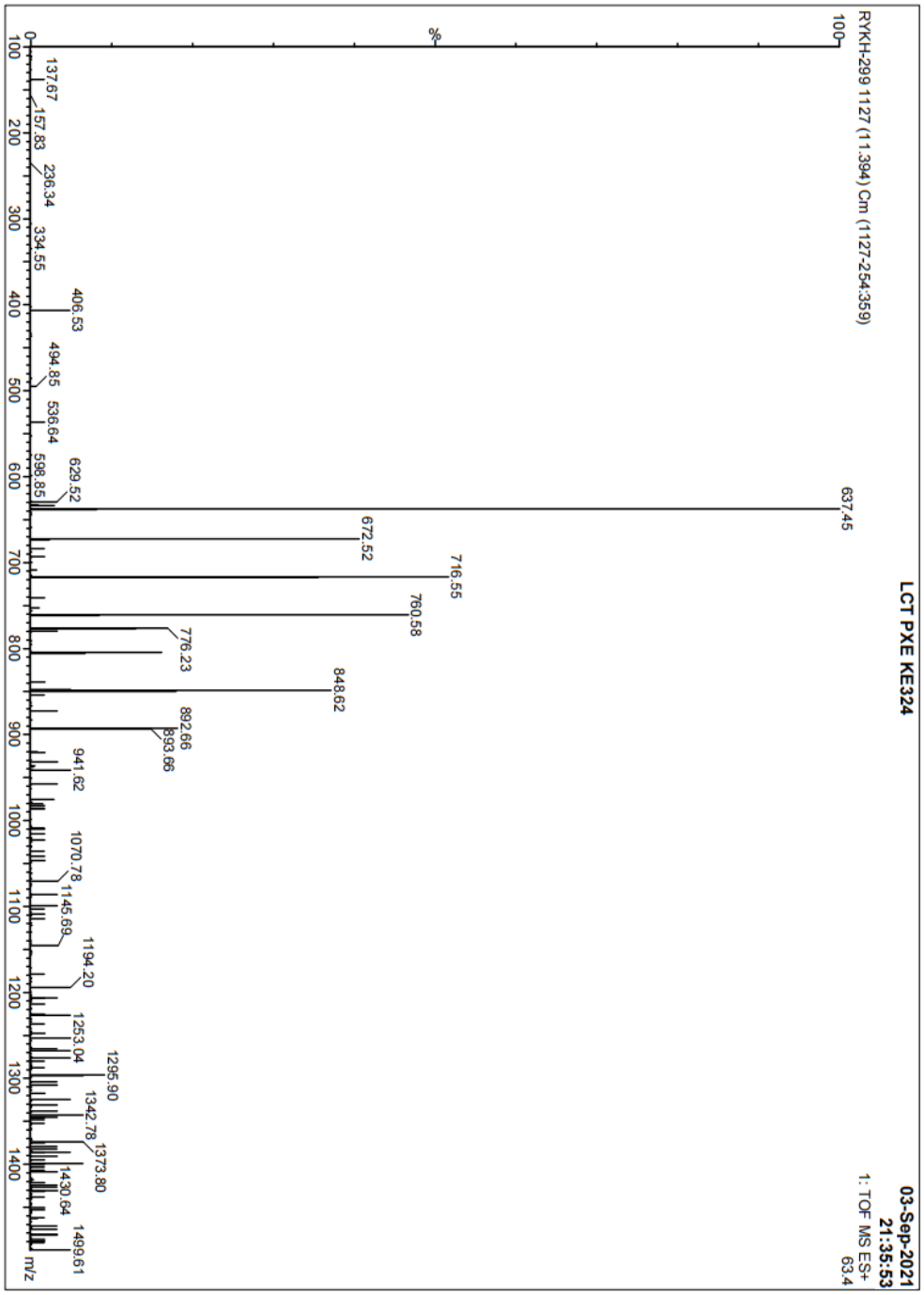


Figure S35. (+)-HRESIMS spectrum of Koilodenoid C (**3**).

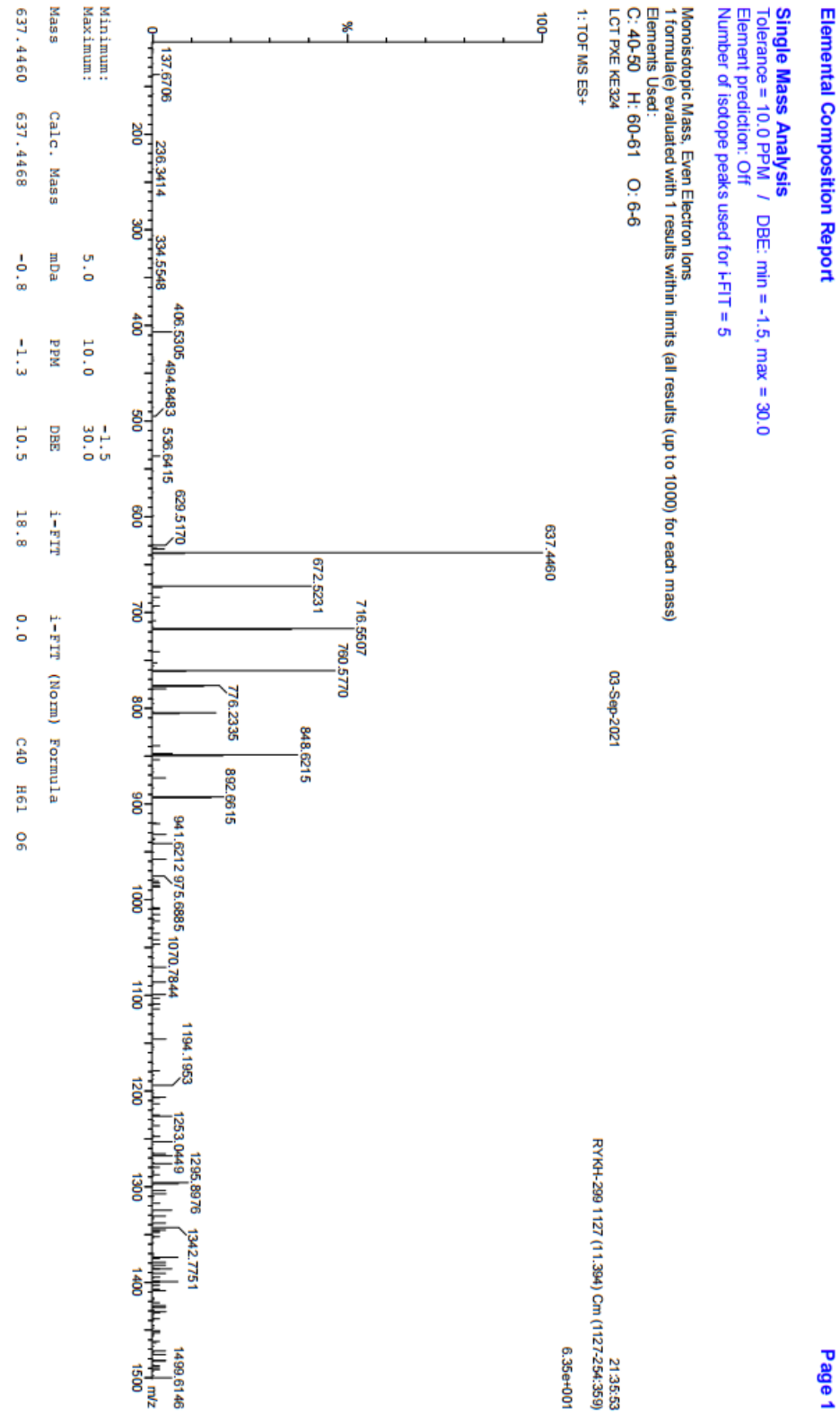


Figure S36. IR spectrum of Koilodenoid C (**3**).

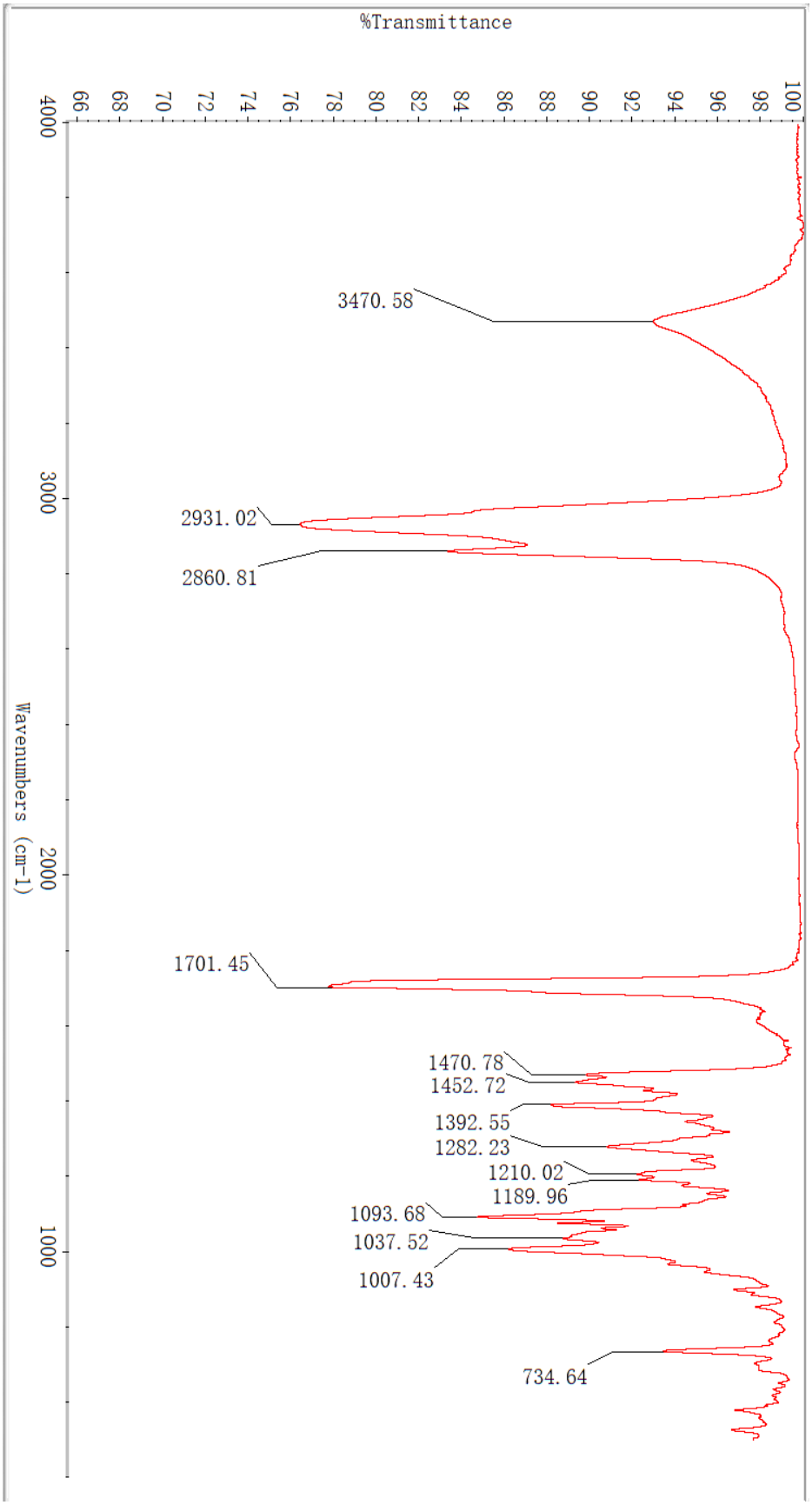


Figure S37. ^{1}H NMR spectrum of Koilodenoid D (**4**) in $CDCl_3$.

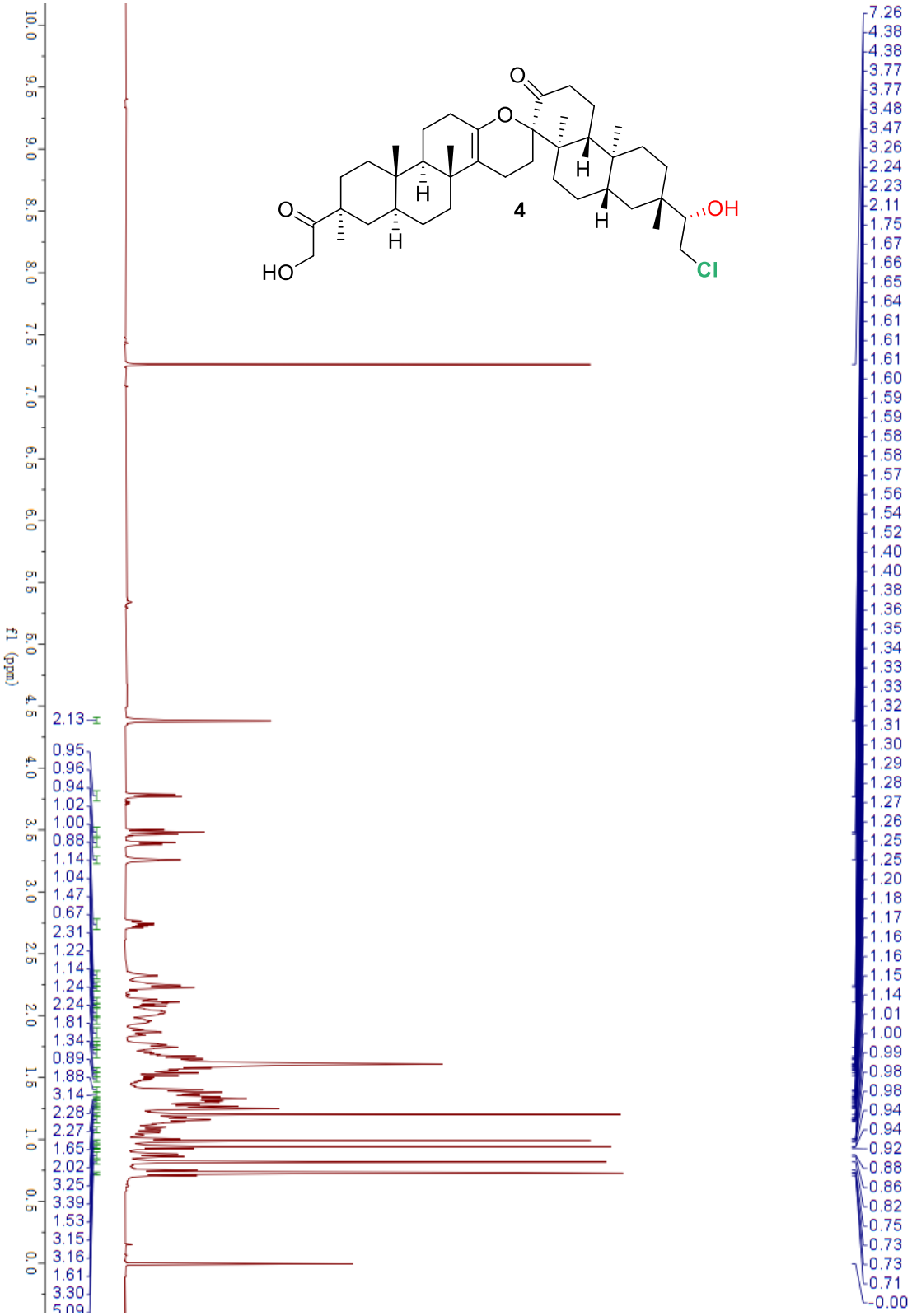


Figure S38. ^{13}C NMR spectrum of Koilodenoid D (**4**) in $CDCl_3$.

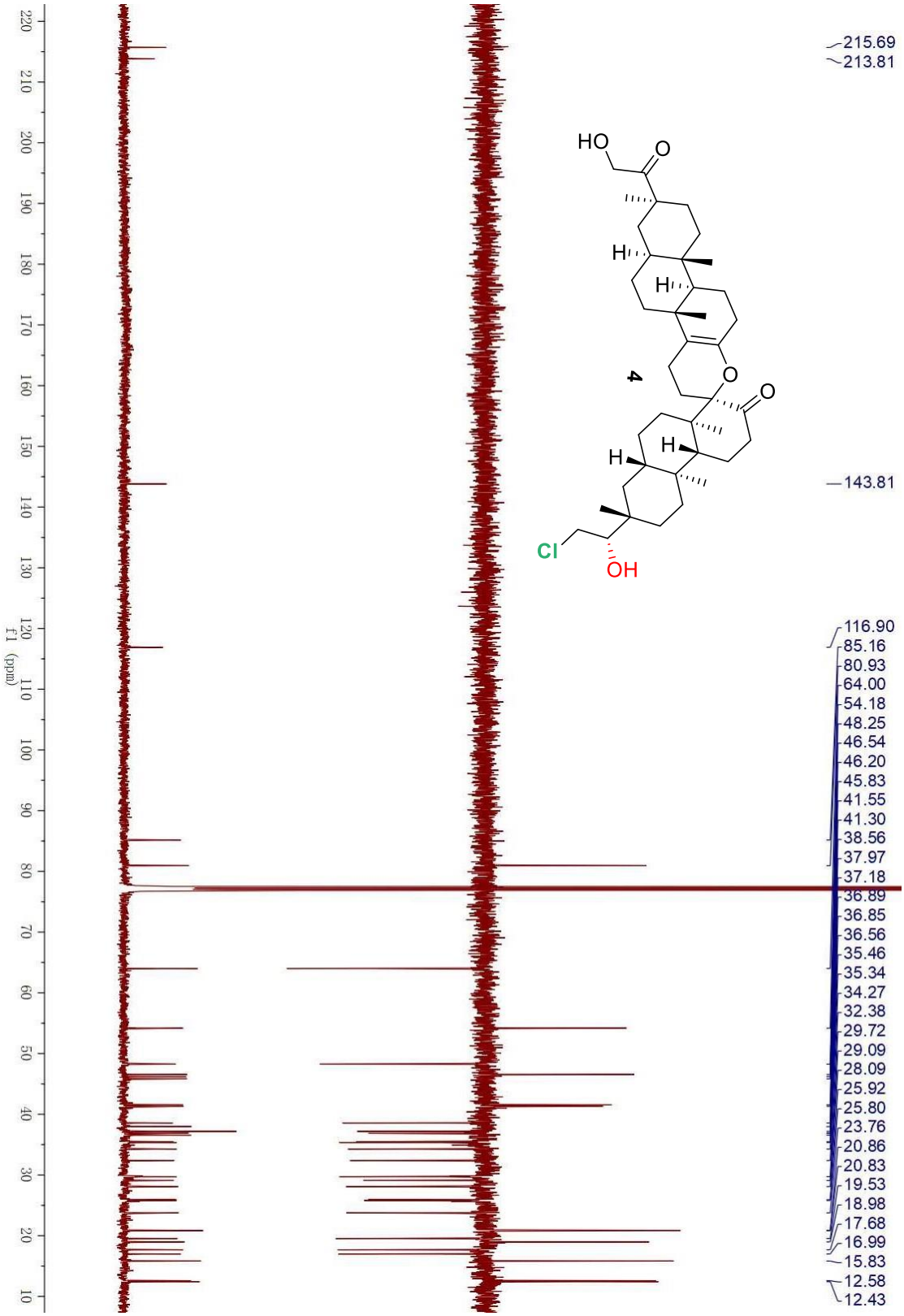


Figure S39. HSQC spectrum of Koilodenoid D (**4**) in $CDCl_3$.

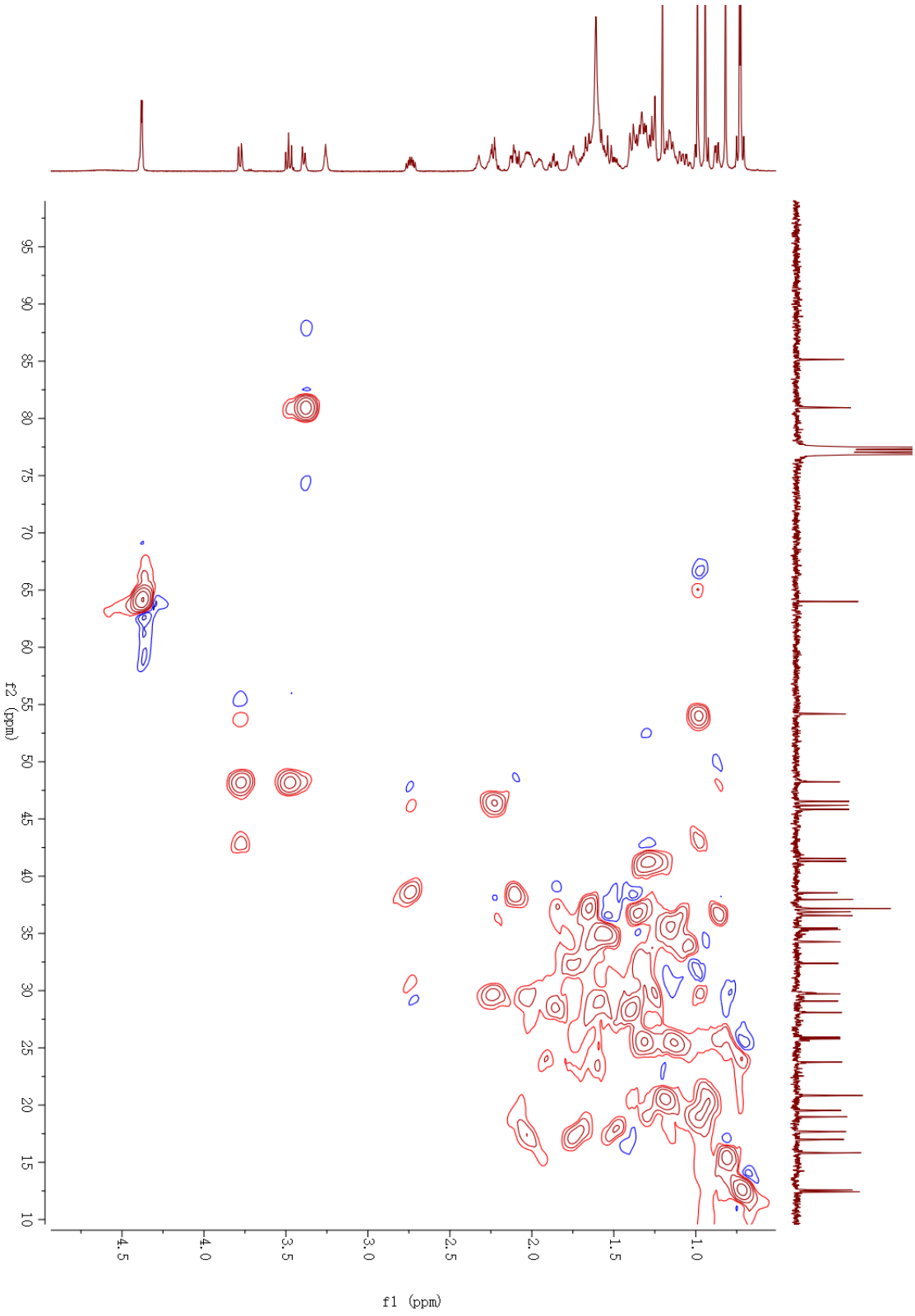


Figure S40. ^{1}H-^{1}H COSY NMR spectrum of Koilodenoid D (**4**) in $CDCl_3$.

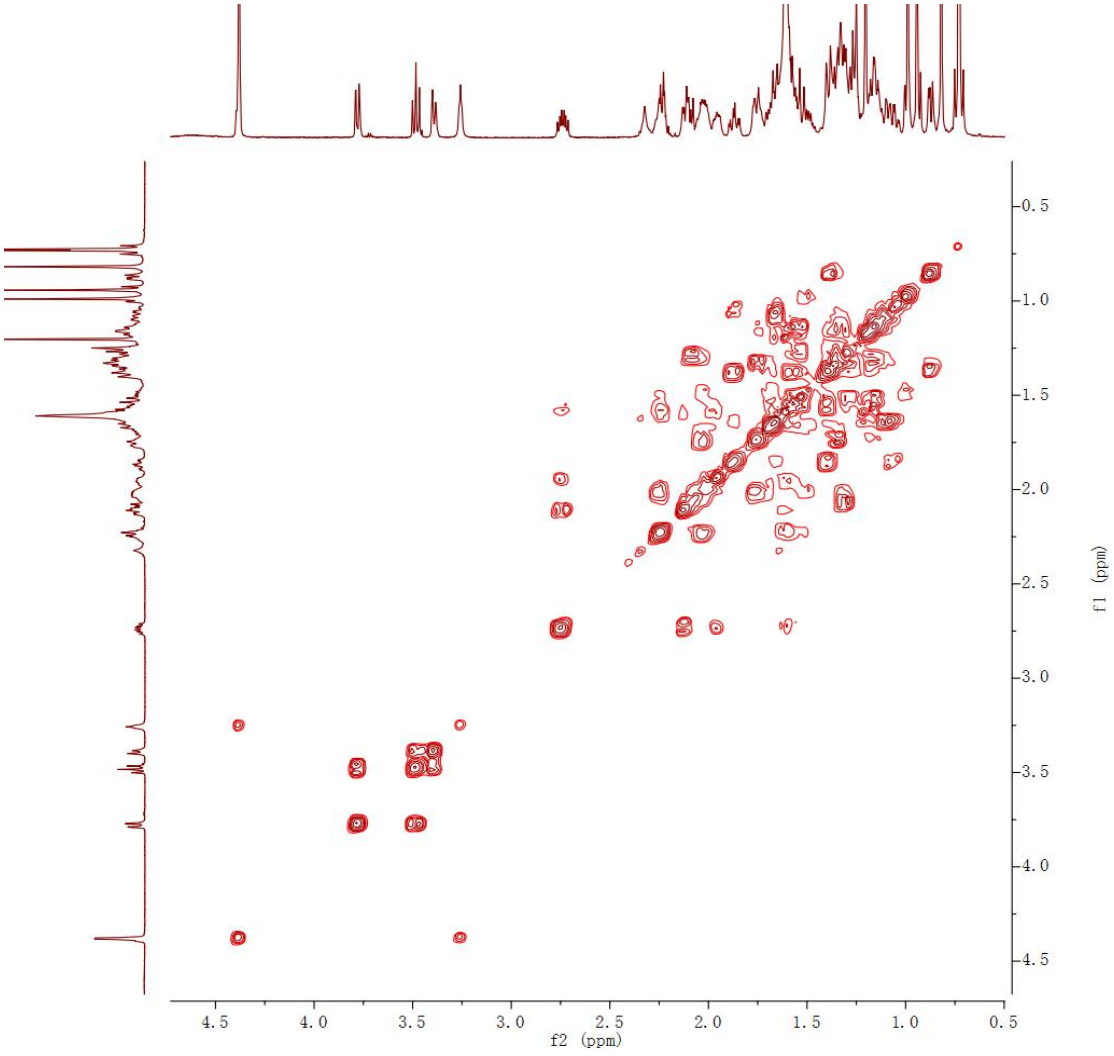


Figure S41. HMBC spectrum of Koilodenoid D (**4**) in $CDCl_3$.

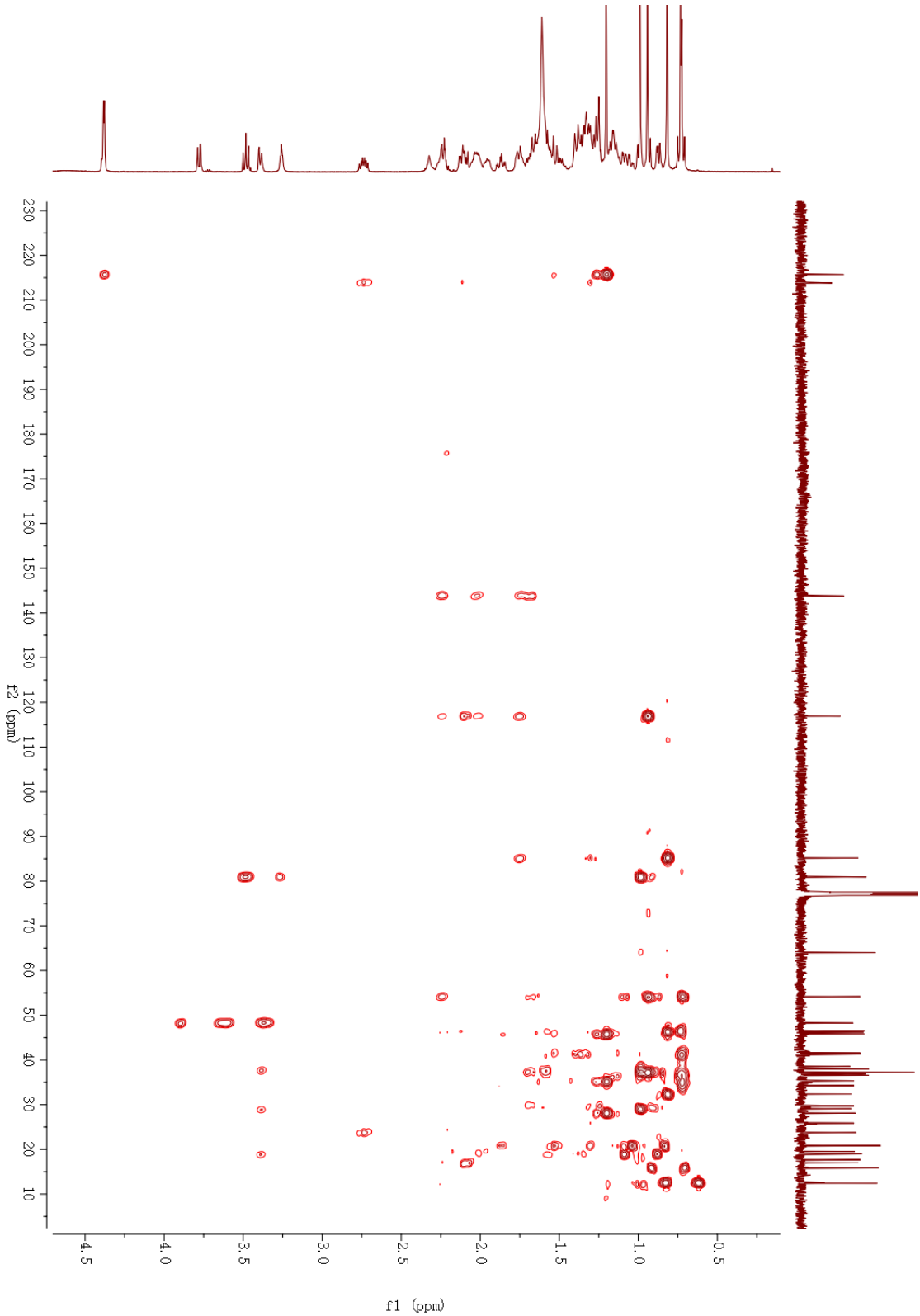


Figure S42. NOESY spectrum of Koilodenoid D (**4**) in $CDCl_3$.

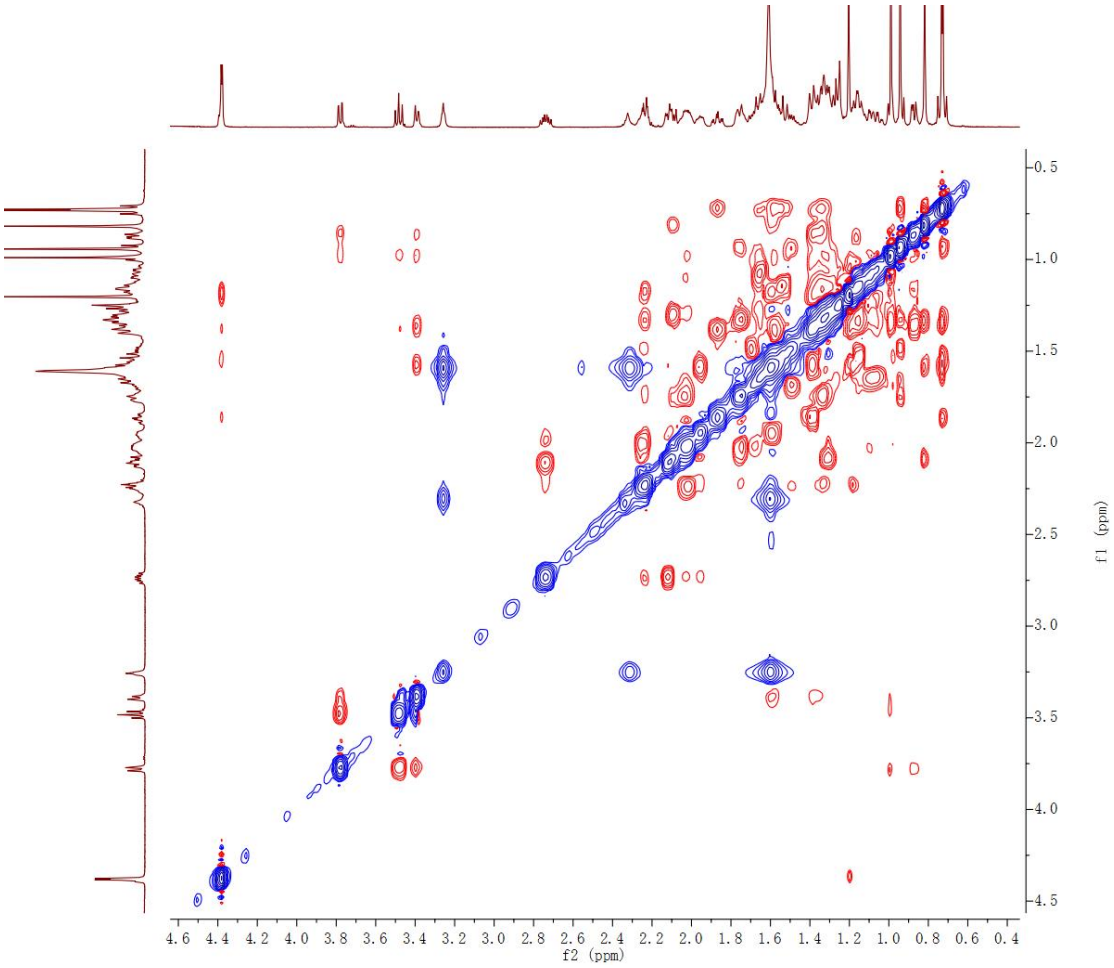


Figure S43. (+)-ESIMS spectrum of Koilodenoid D (**4**).

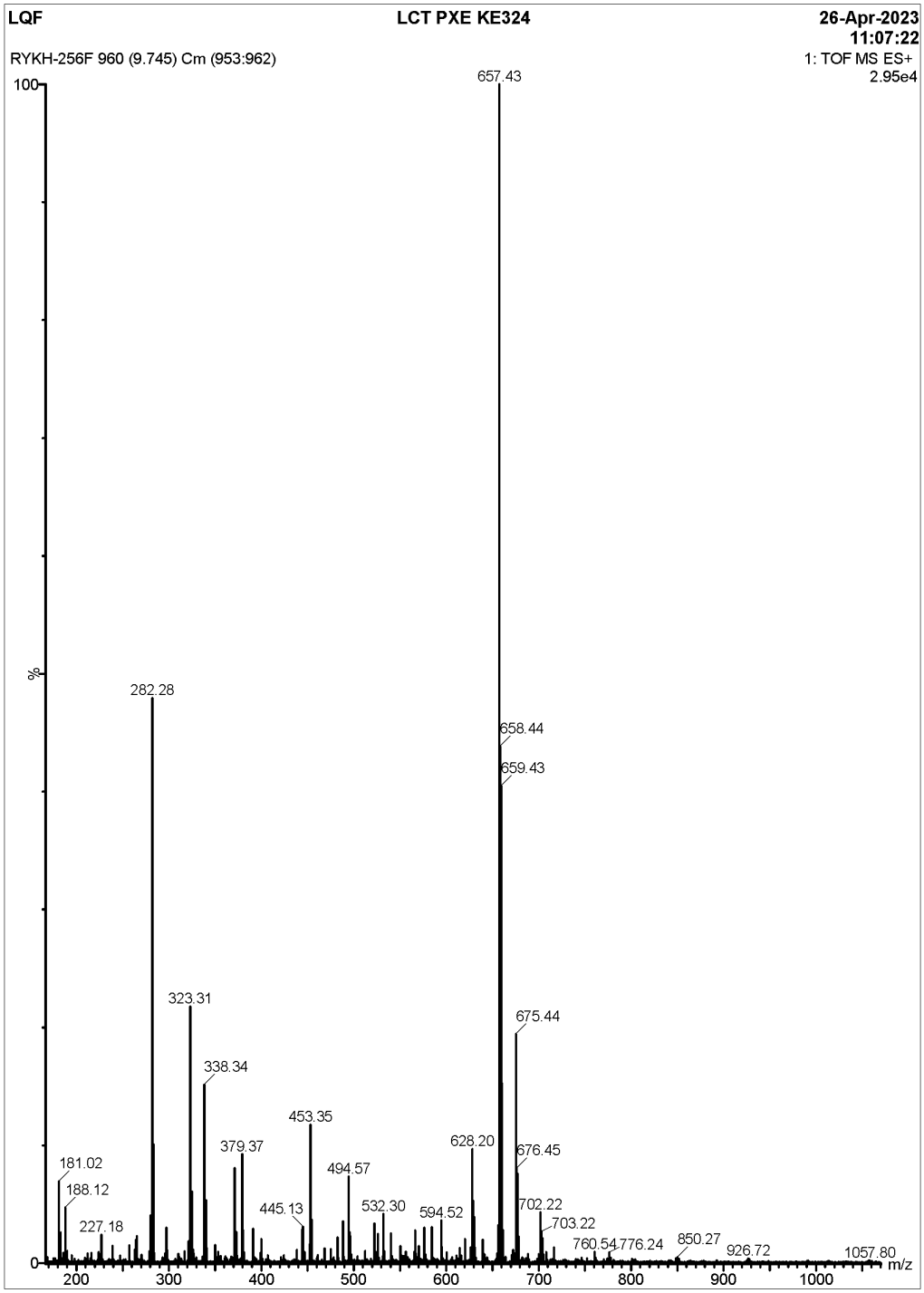


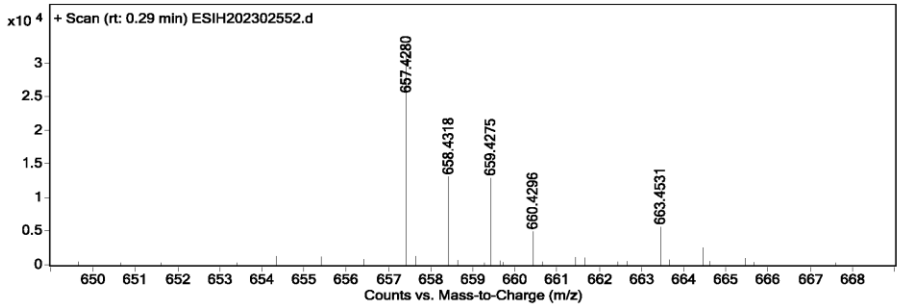
Figure S44. (+)-HRESIMS spectrum of Koilodenoid D (**4**).

Qualitative Analysis Report

Data Filename	ESIH202302552.d	**Sample Name**	D4-RYKH-256F
Sample ID		**Position**	P1-A1
Instrument Name	Agilent 6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	4/14/2023 14:24:47	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by fangsu

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
657.428	657.428	0	0.01	C40 H62 Cl O5	(M+H)+

--- End Of Report ---

Figure S45. IR spectrum of Koilodenoid D (**4**).

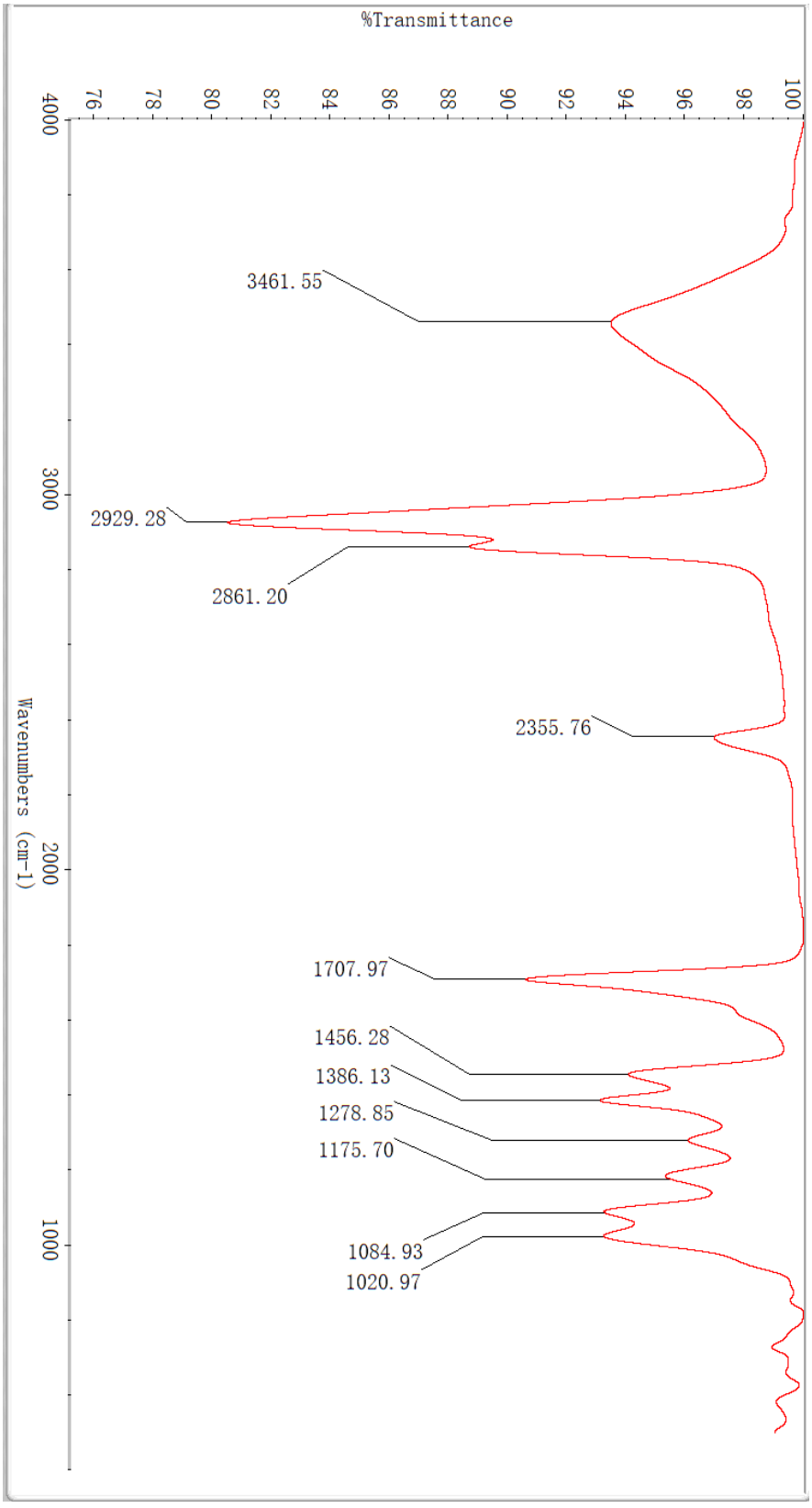


Figure S46. ^{1}H NMR spectrum of Koilodenoid E (**5**) in $CDCl_3$.

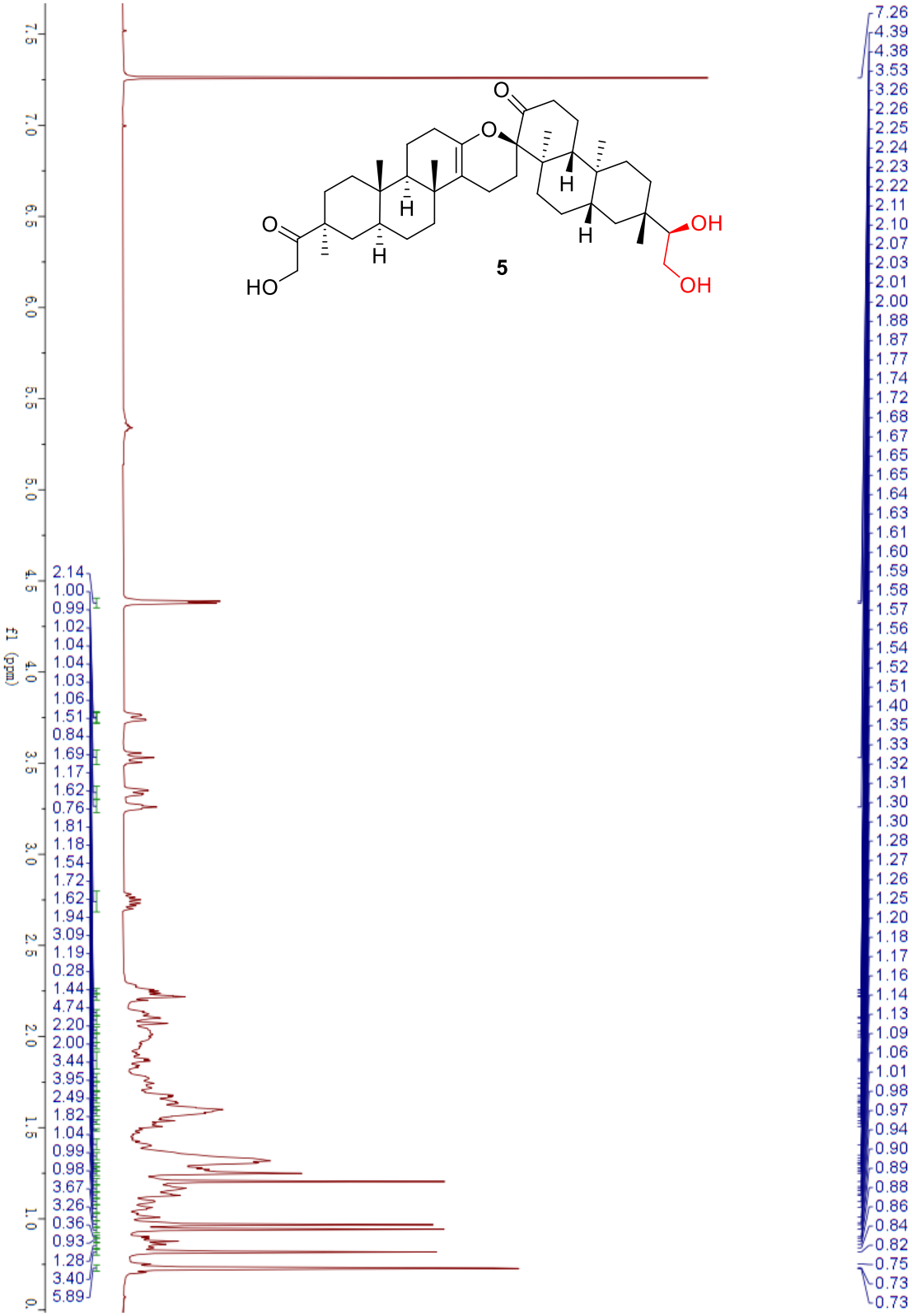


Figure S47. ^{13}C NMR spectrum of Koilodenoid E (**5**) in $CDCl_3$.

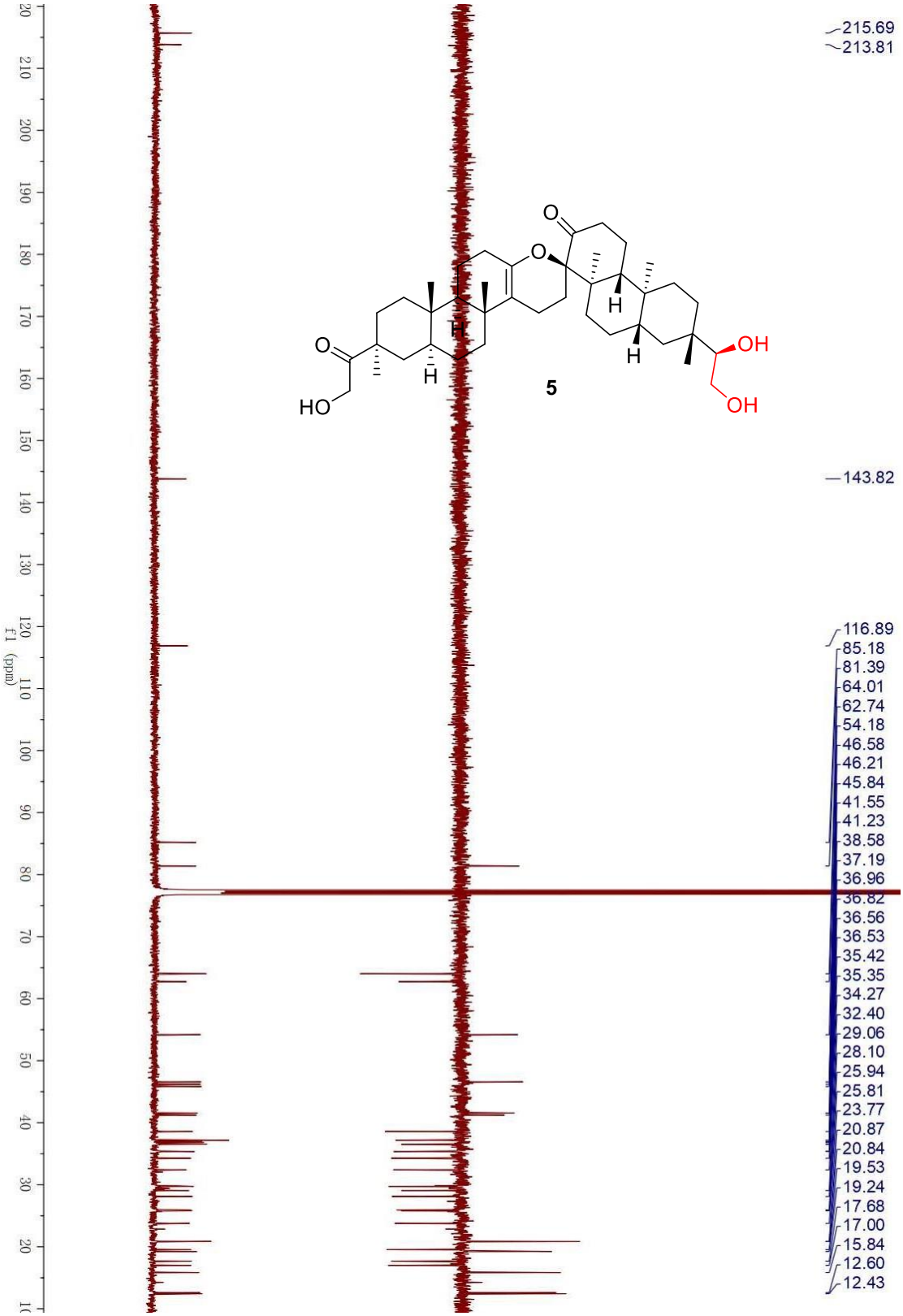


Figure S48. HSQC spectrum of Koilodenoid E (**5**) in $CDCl_3$.

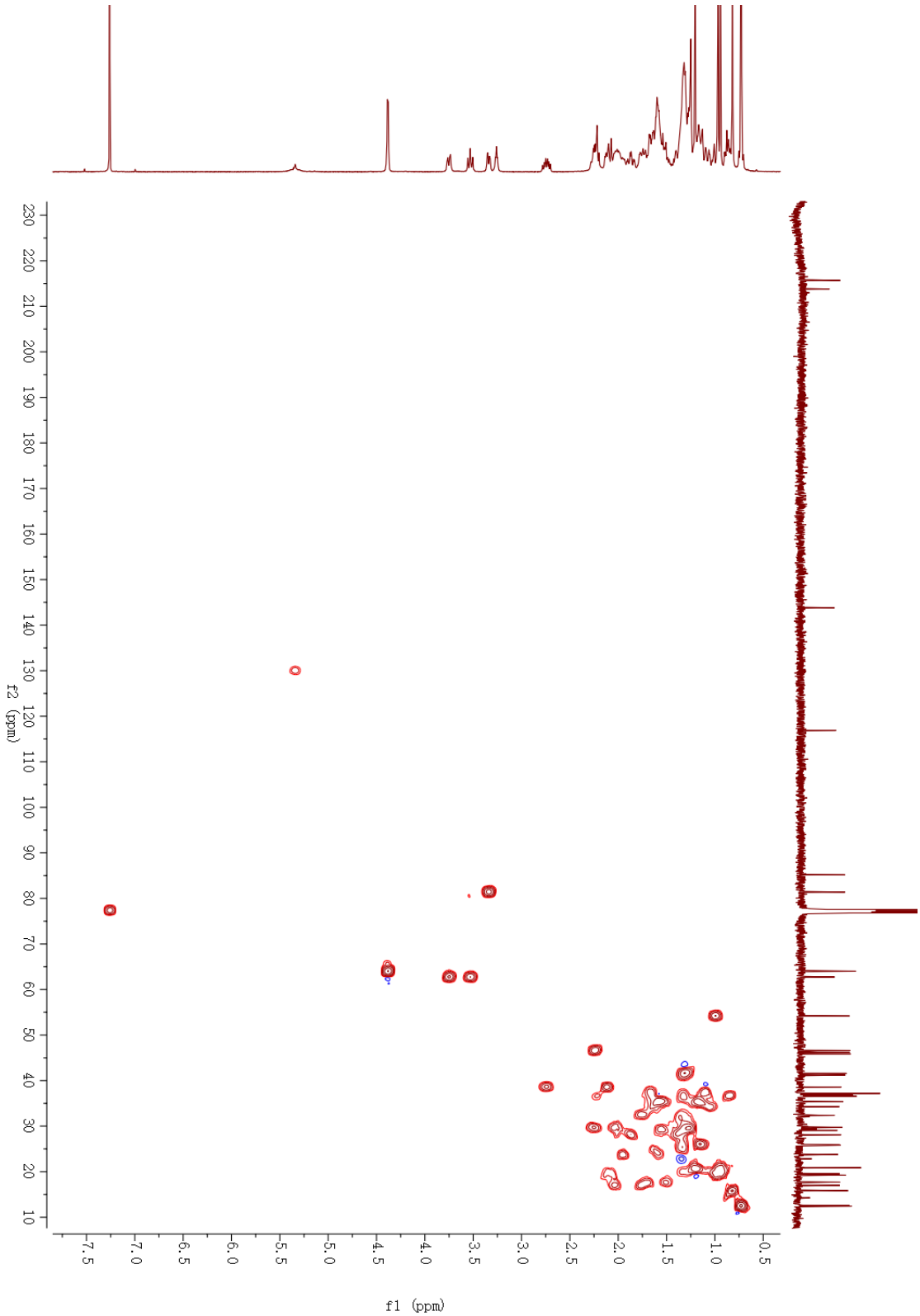


Figure S49. ^{1}H-^{1}H COSY NMR spectrum of Koilodenoid E (**5**) in $CDCl_3$.

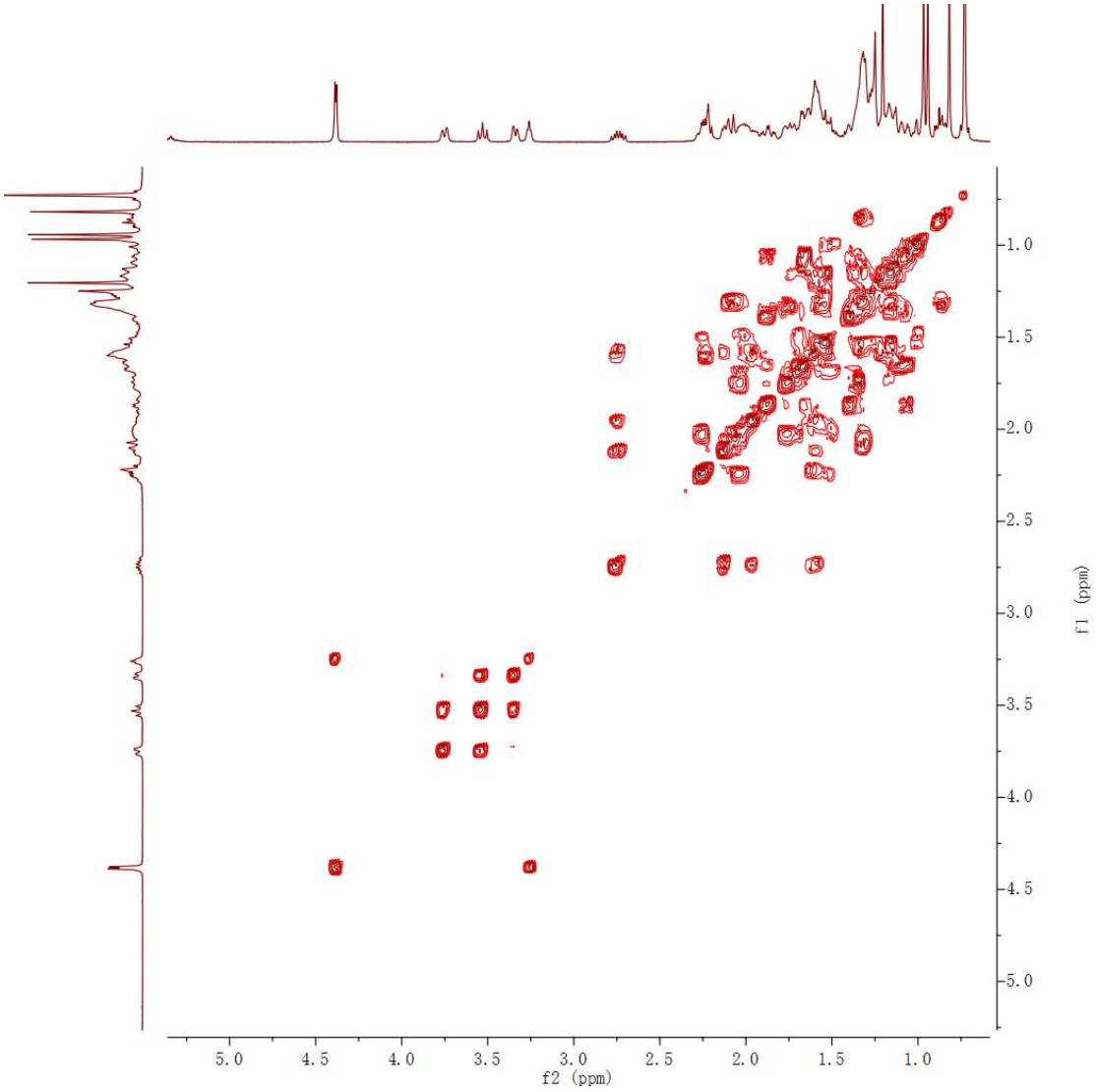


Figure S50. HMBC spectrum of Koilodenoid E (**5**) in $CDCl_3$.

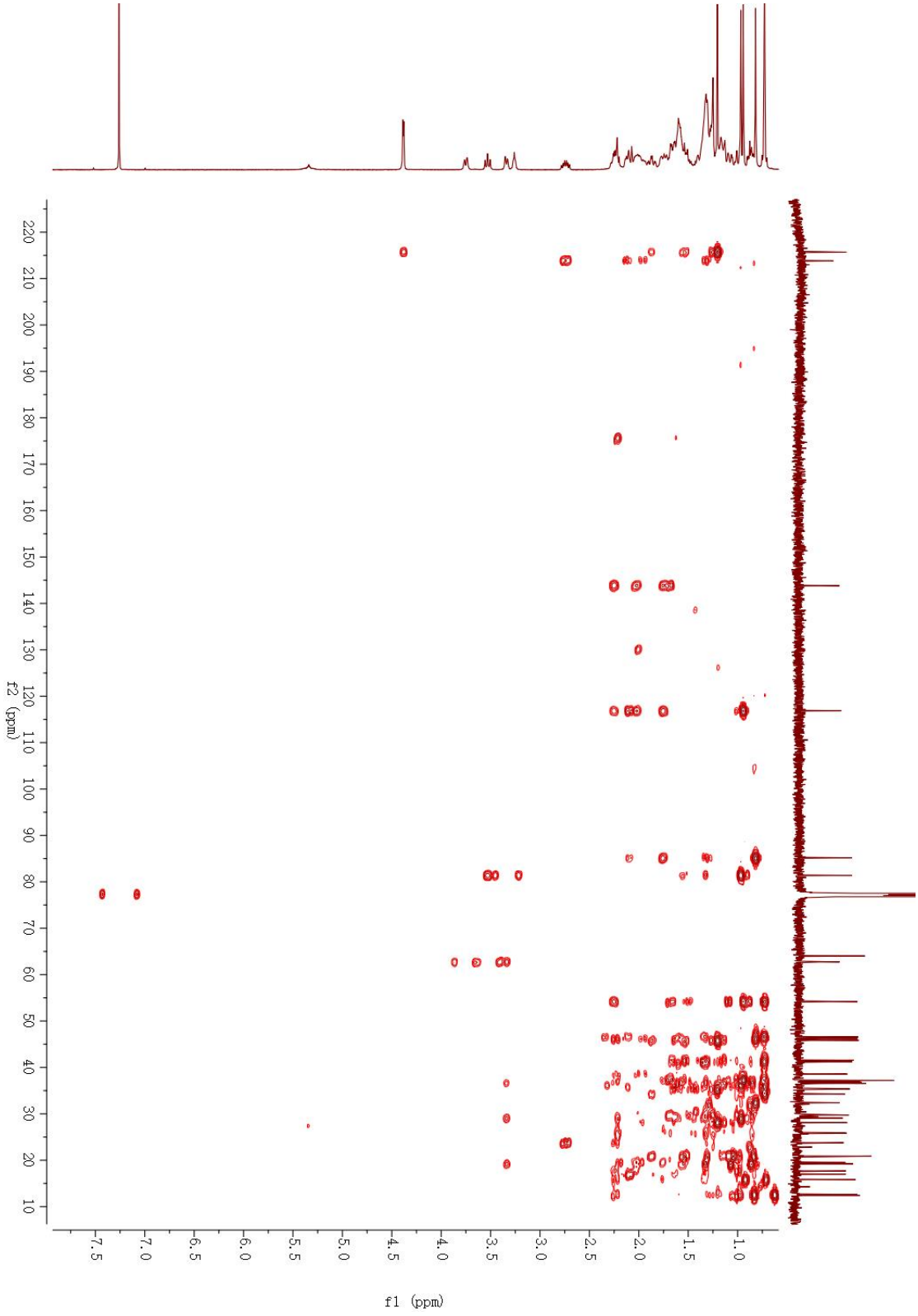


Figure S51. NOESY spectrum of Koilodenoid E (**5**) in $CDCl_3$.

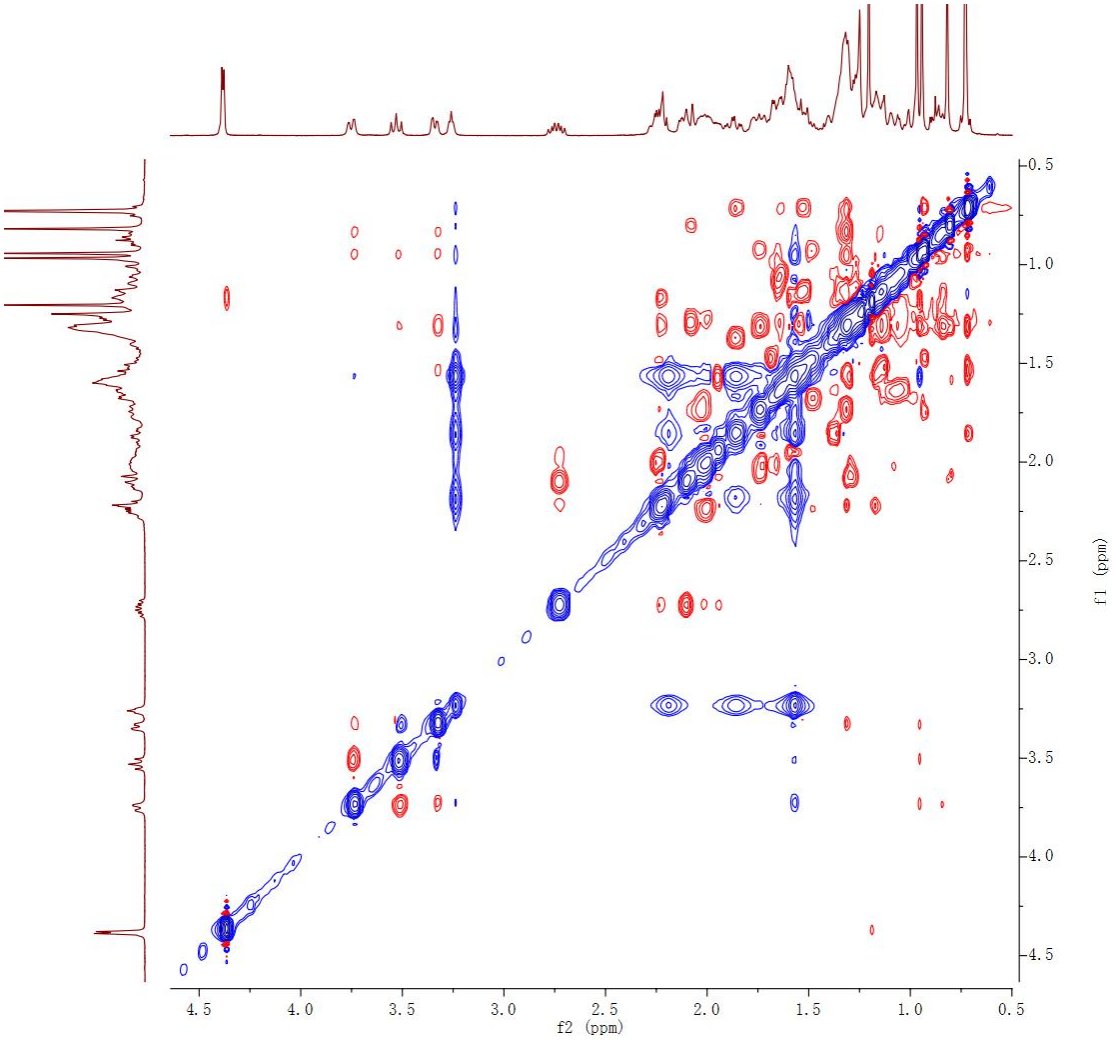


Figure S52. (+)-ESIMS spectrum of Koilodenoid E (**5**).

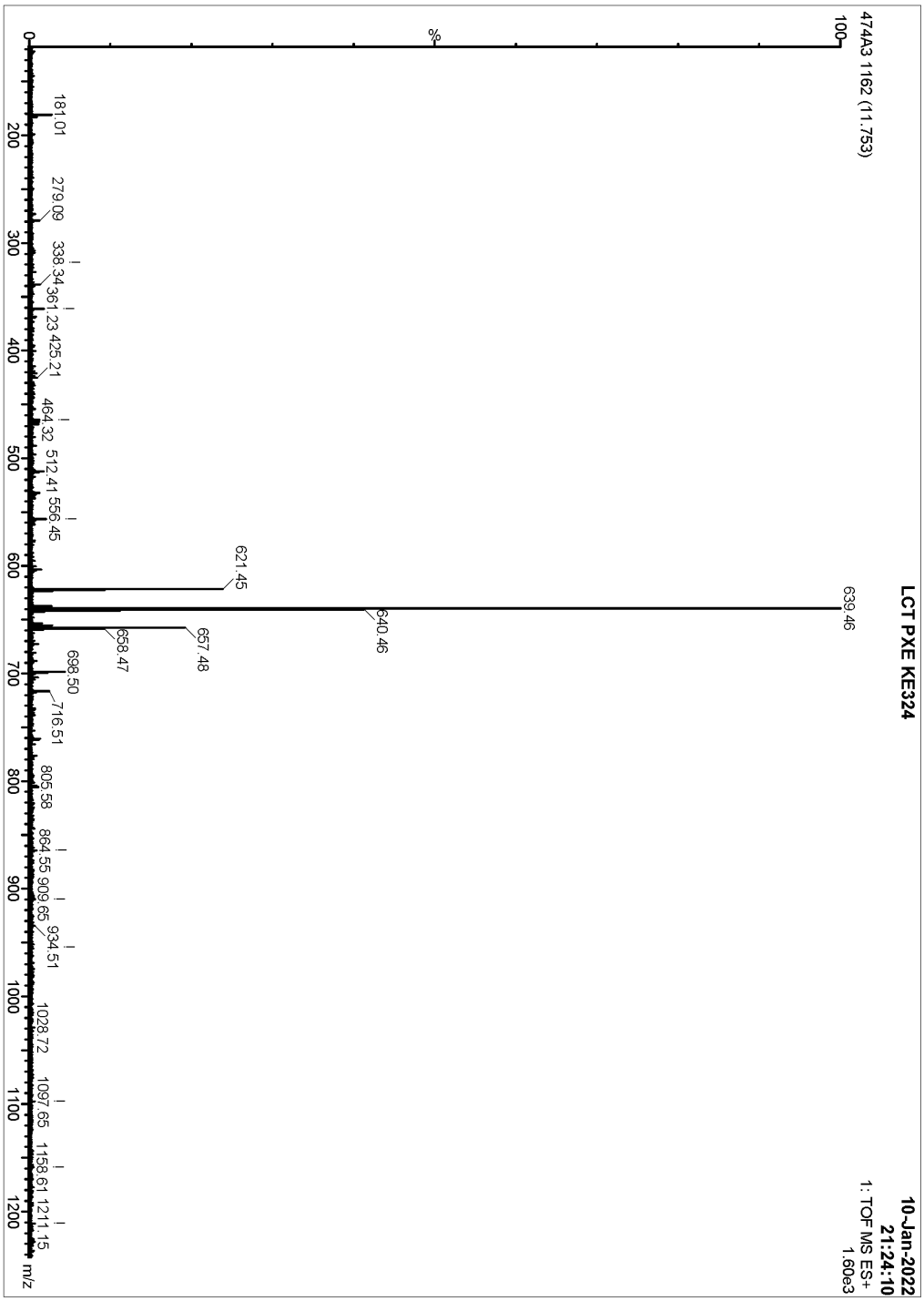


Figure S53. (+)-HRESIMS spectrum of Koilodenoid E (**5**).

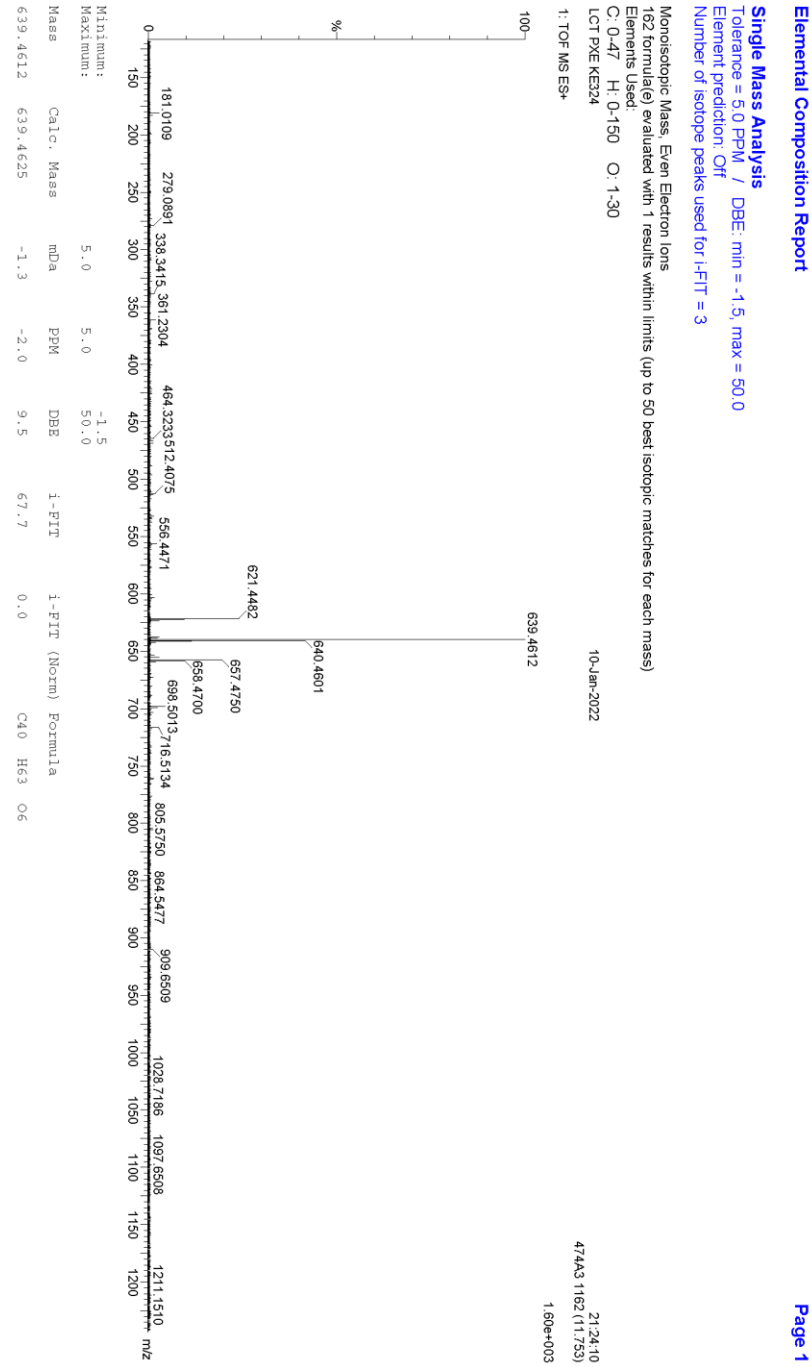


Figure S54. IR spectrum of Koilodenoid E (**5**).

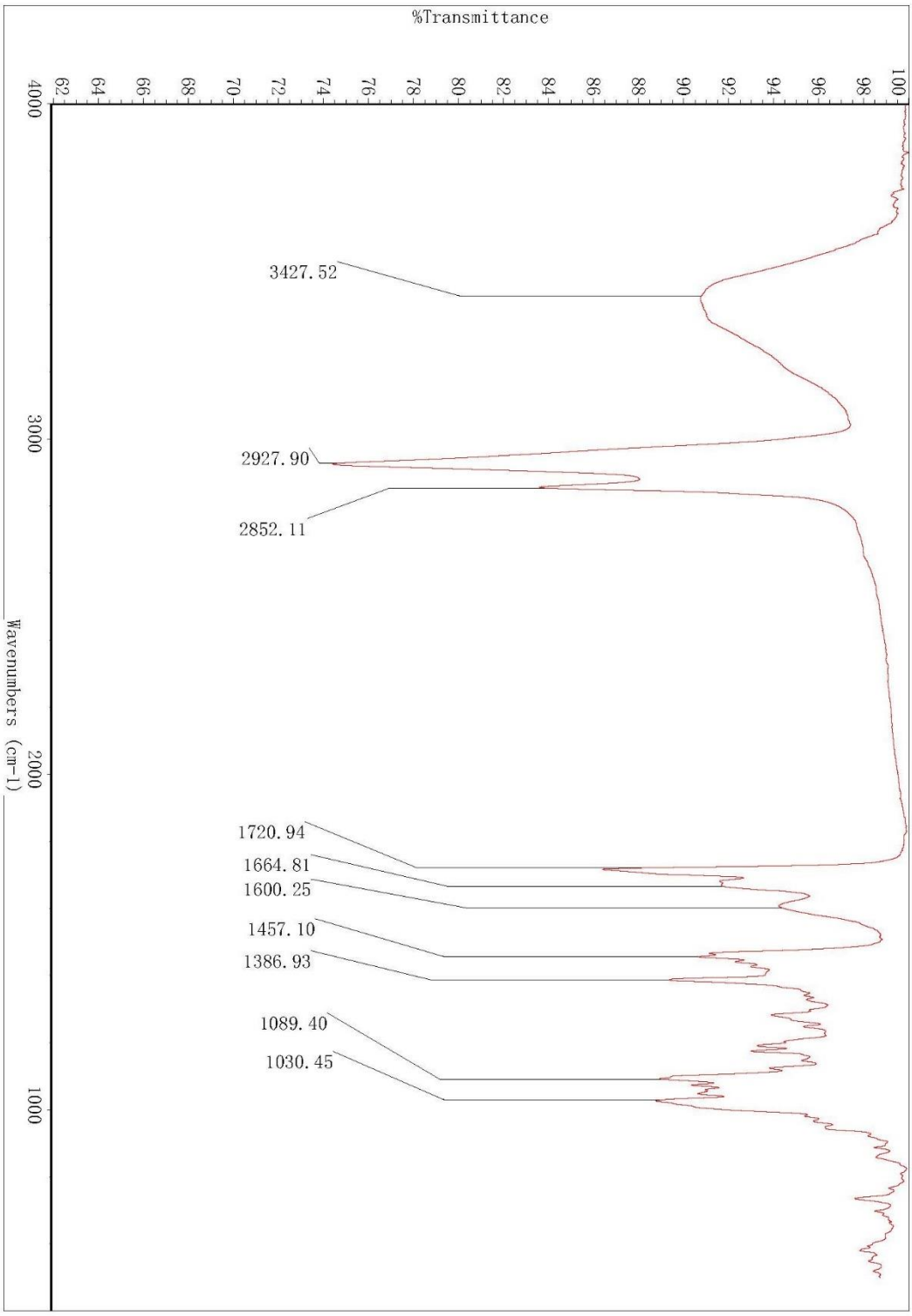


Figure S55. ^{1}H NMR spectrum of Koilodenoid F (**6**) in $CDCl_3$.

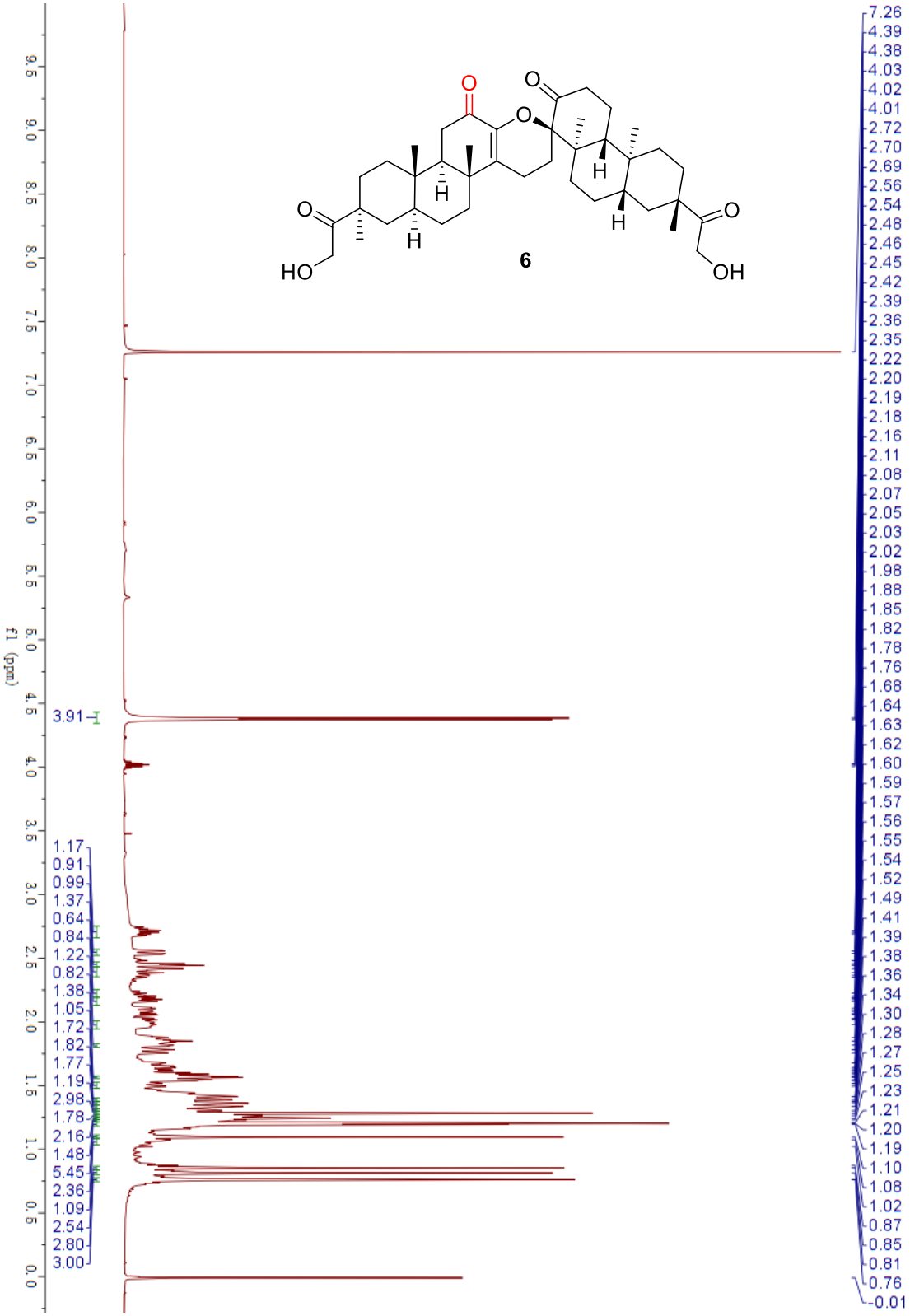


Figure S56. ^{13}C NMR spectrum of Koilodenoid F (**6**) in $CDCl_3$.

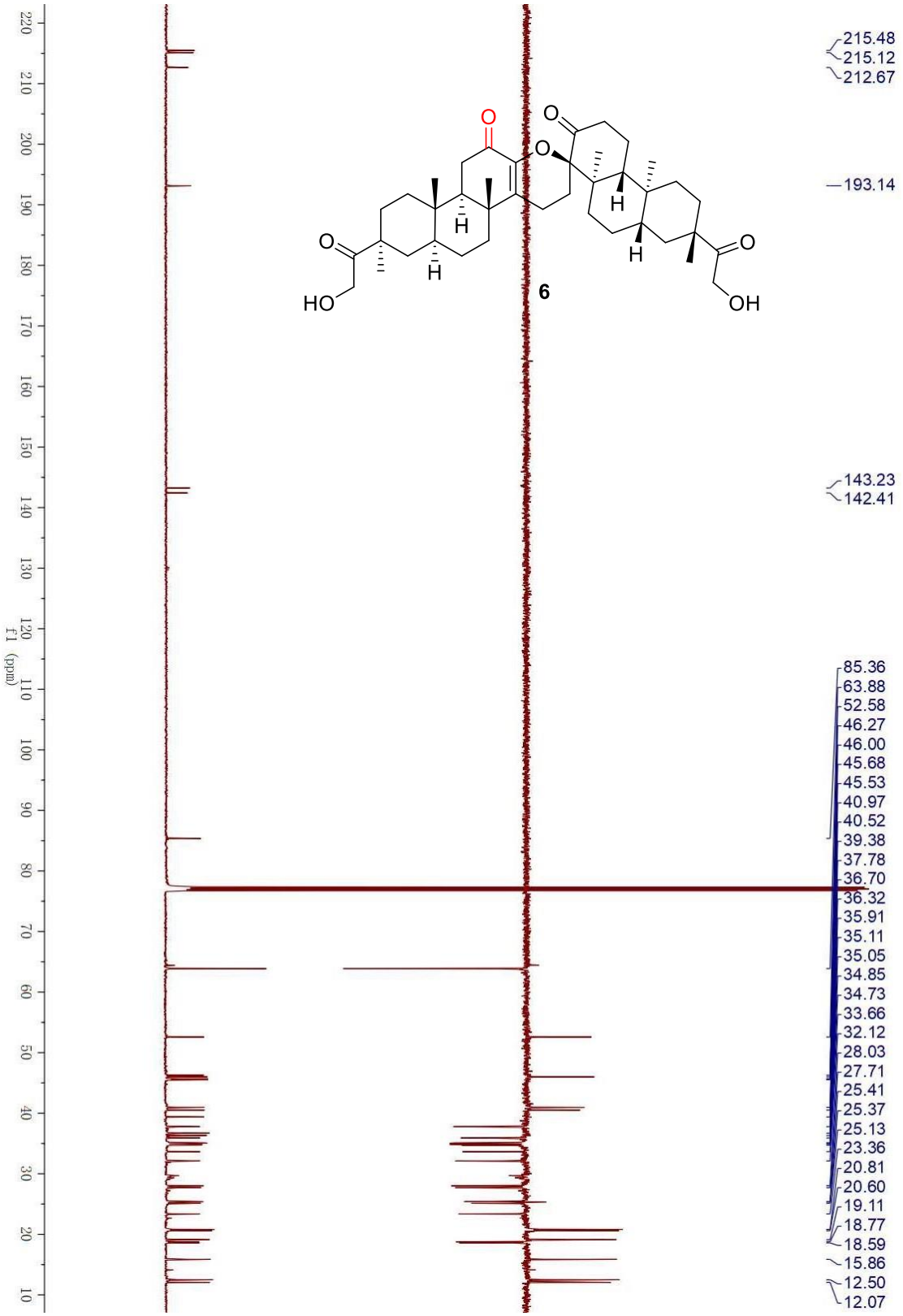


Figure S57. HSQC spectrum of Koilodenoid F (**6**) in $CDCl_3$.

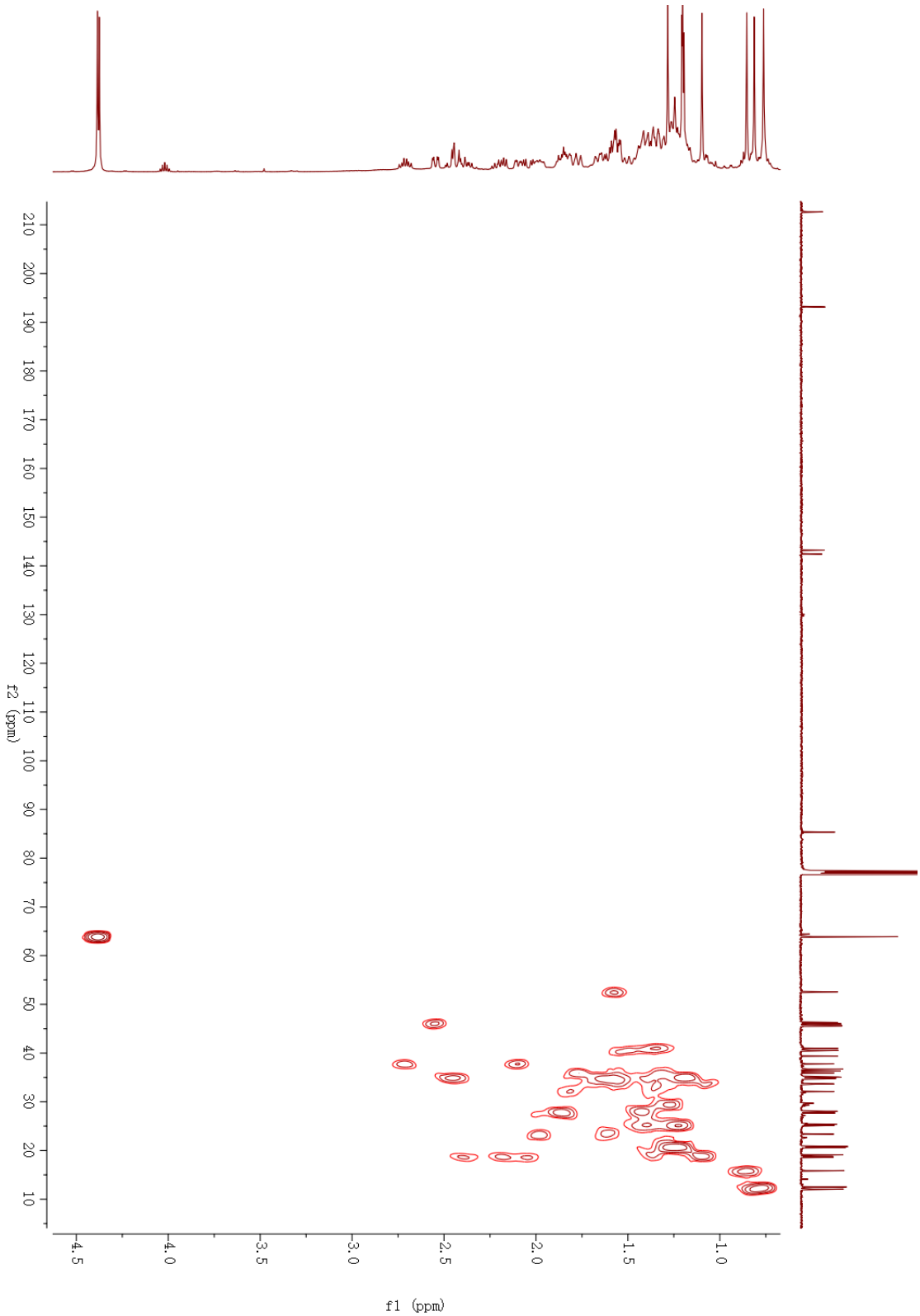


Figure S58. ^{1}H-^{1}H COSY NMR spectrum of Koilodenoid F (**6**) in $CDCl_3$.

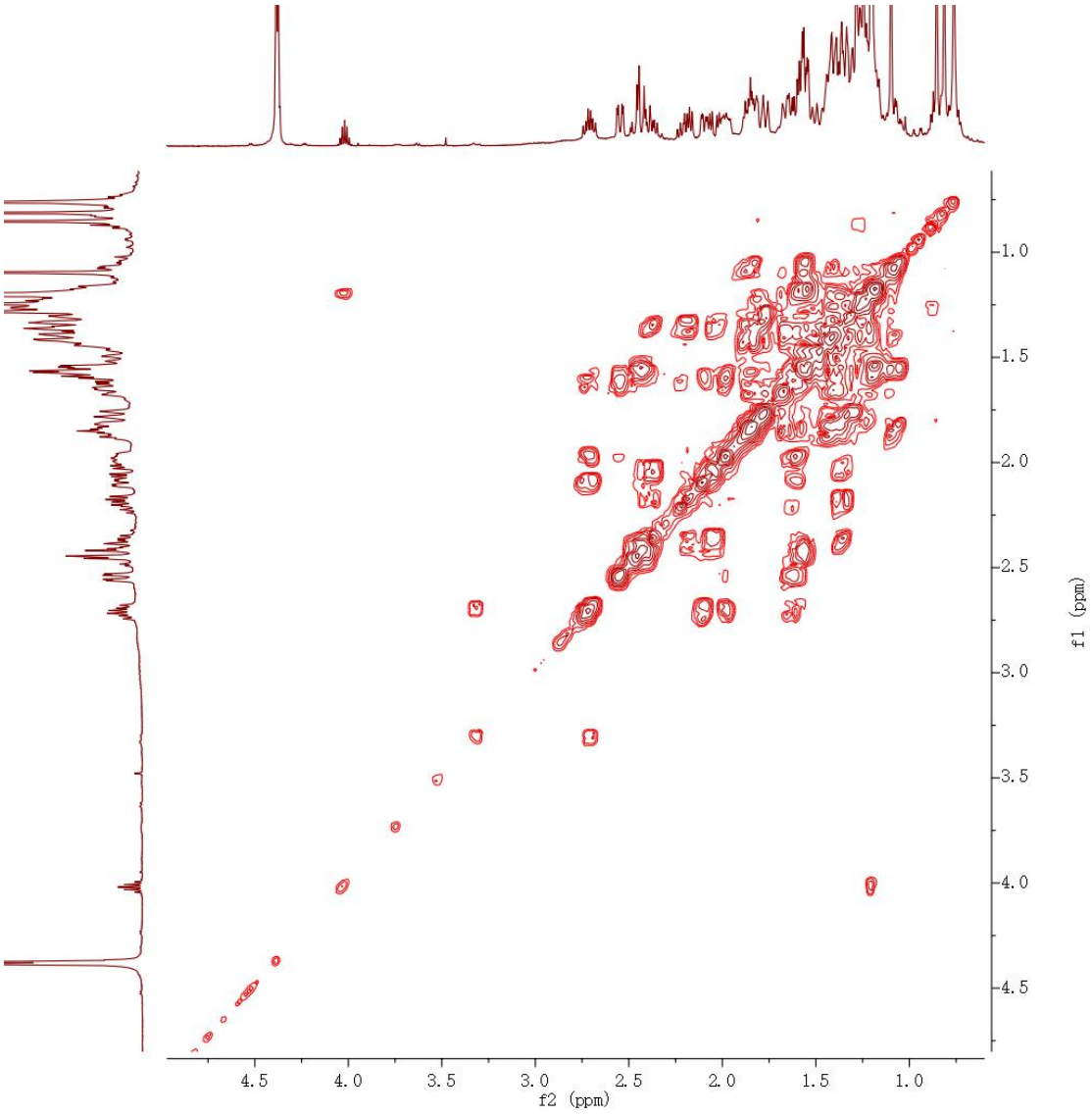


Figure S59. HMBC spectrum of Koilodenoid F (**6**) in $CDCl_3$.

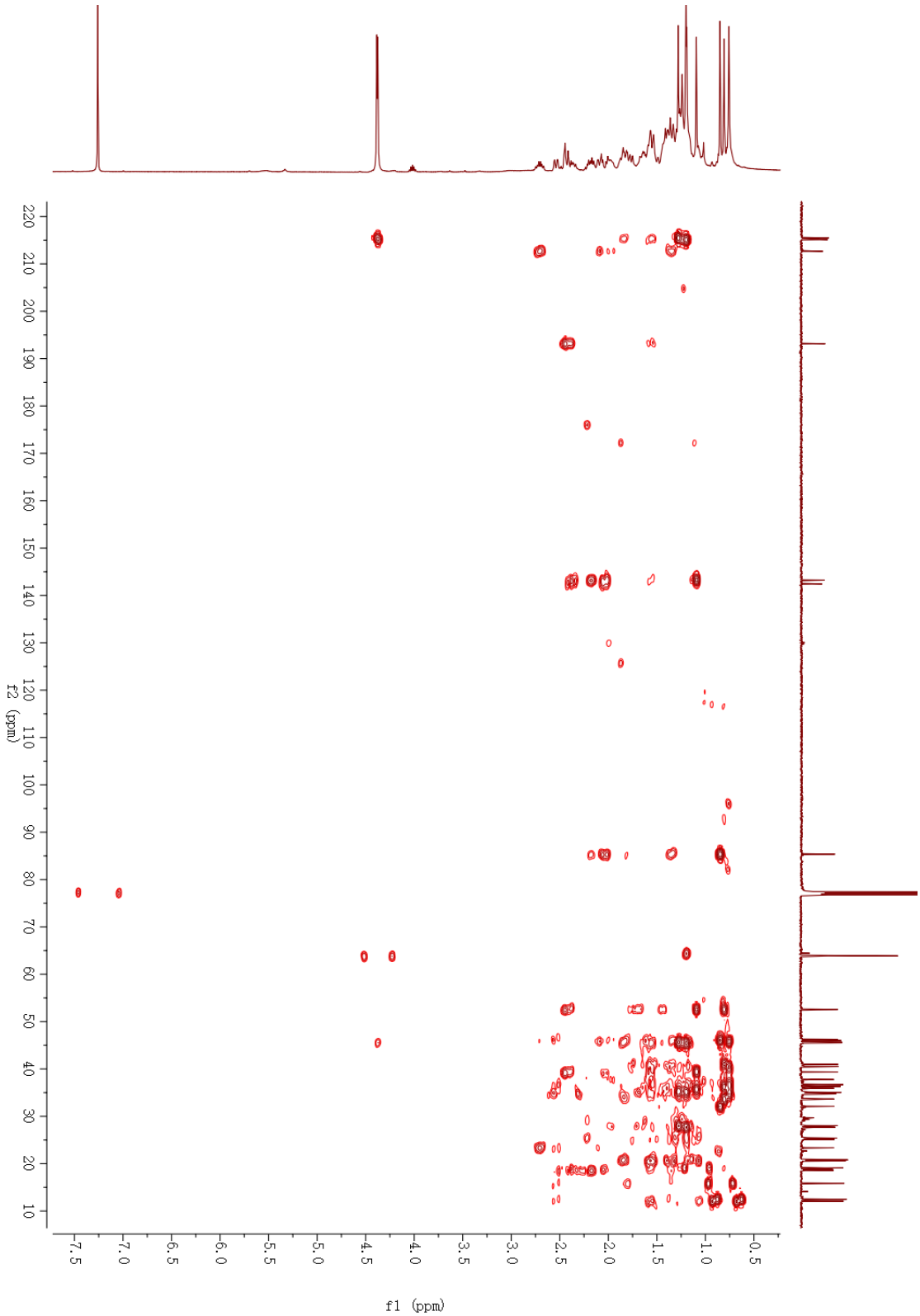


Figure S60. NOESY spectrum of Koilodenoid F (**6**) in $CDCl_3$.

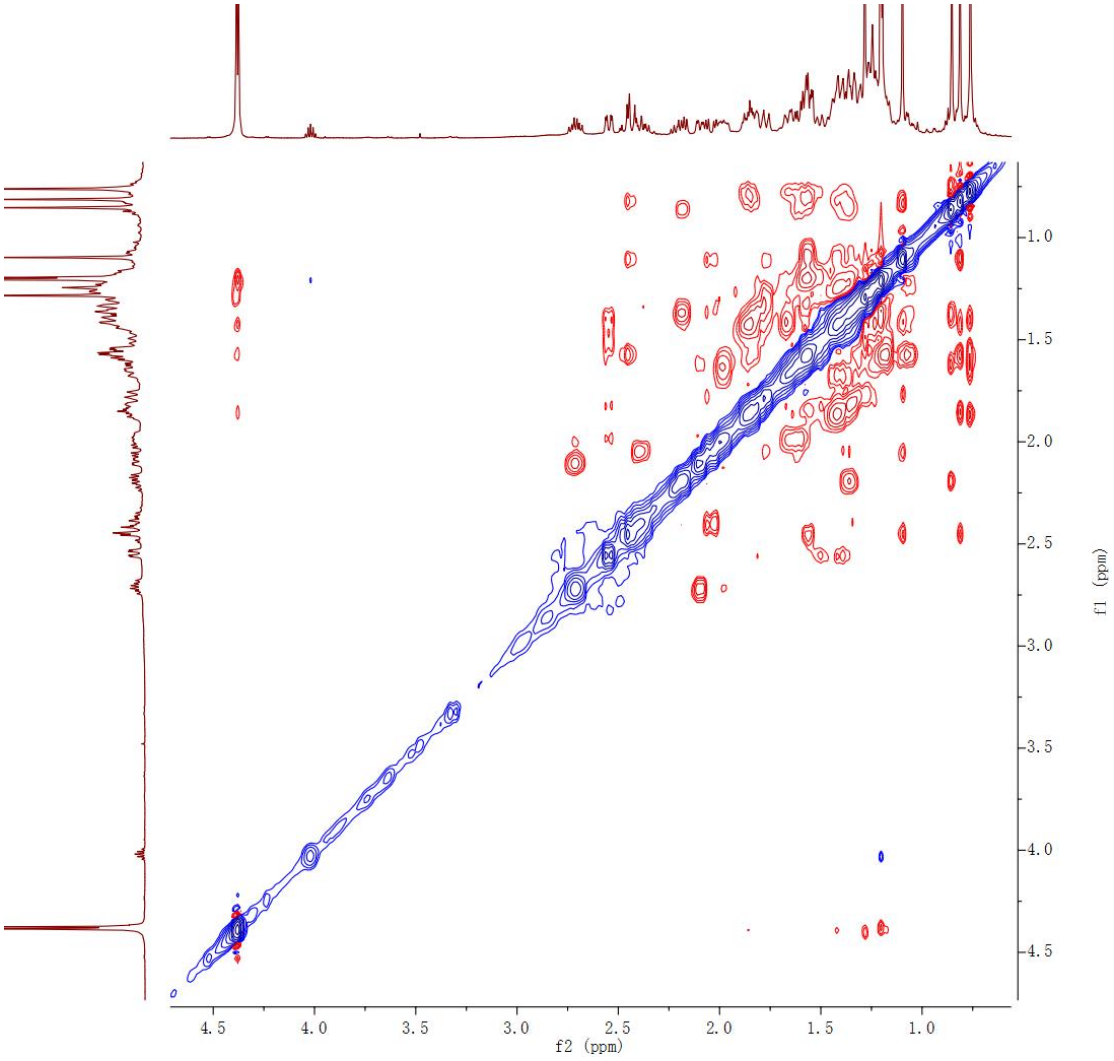


Figure S61. (+)-ESIMS spectrum of Koilodenoid F (**6**).

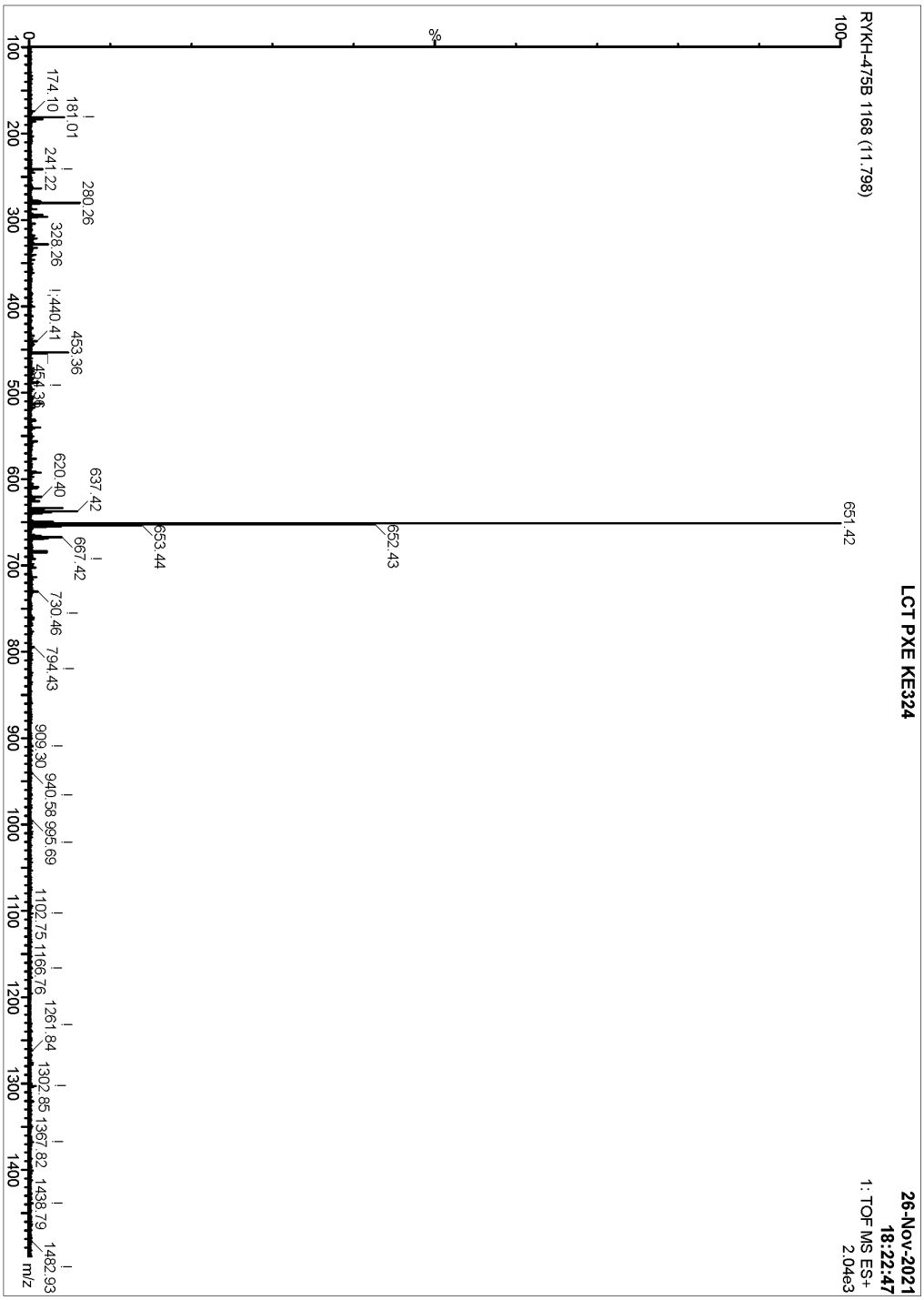


Figure S62. (+)-HRESIMS spectrum of Koilodenoid F (**6**).

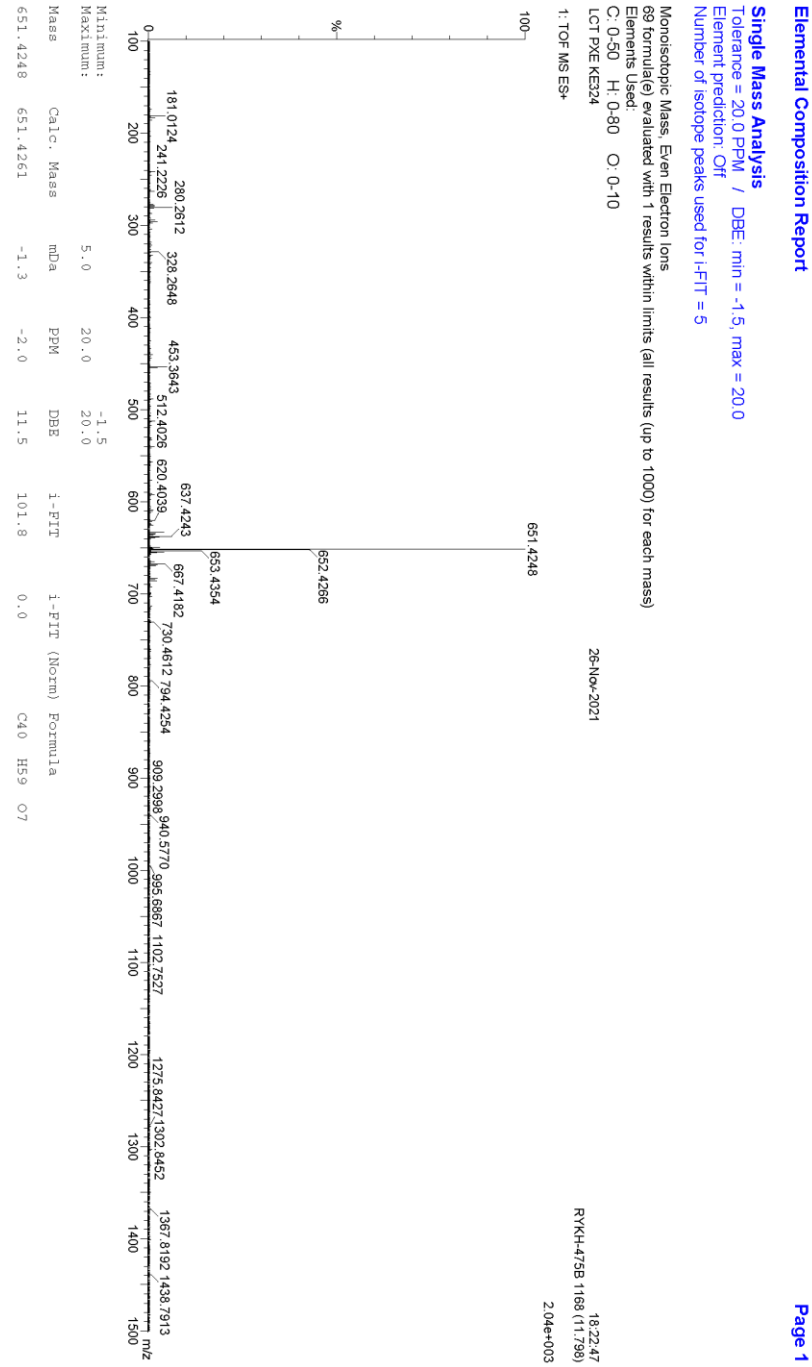


Figure S63. IR spectrum of Koilodenoid F (**6**).

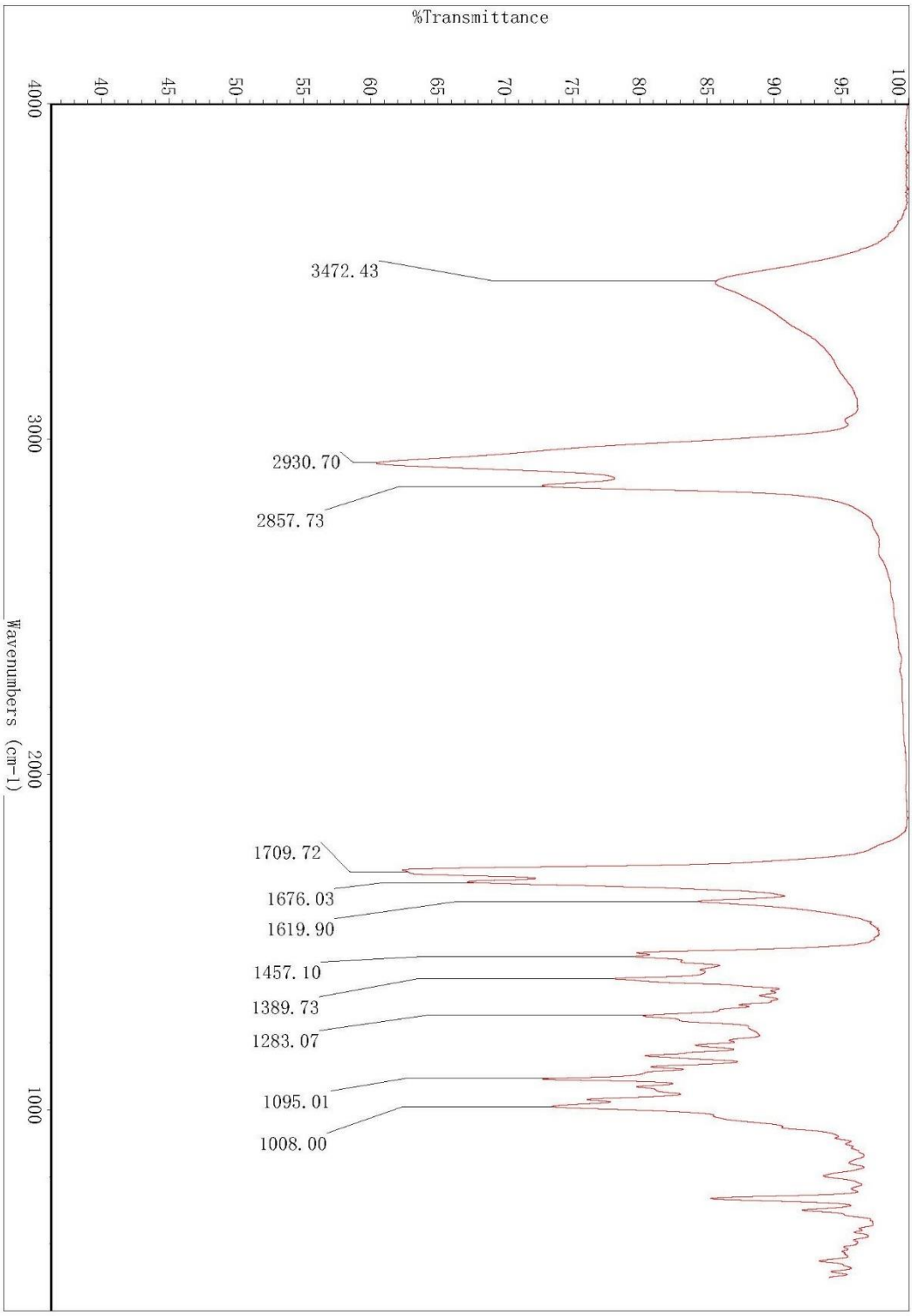


Figure S64. ^{1}H NMR spectrum of Koilodenoid G (**7**) in $CDCl_3$.

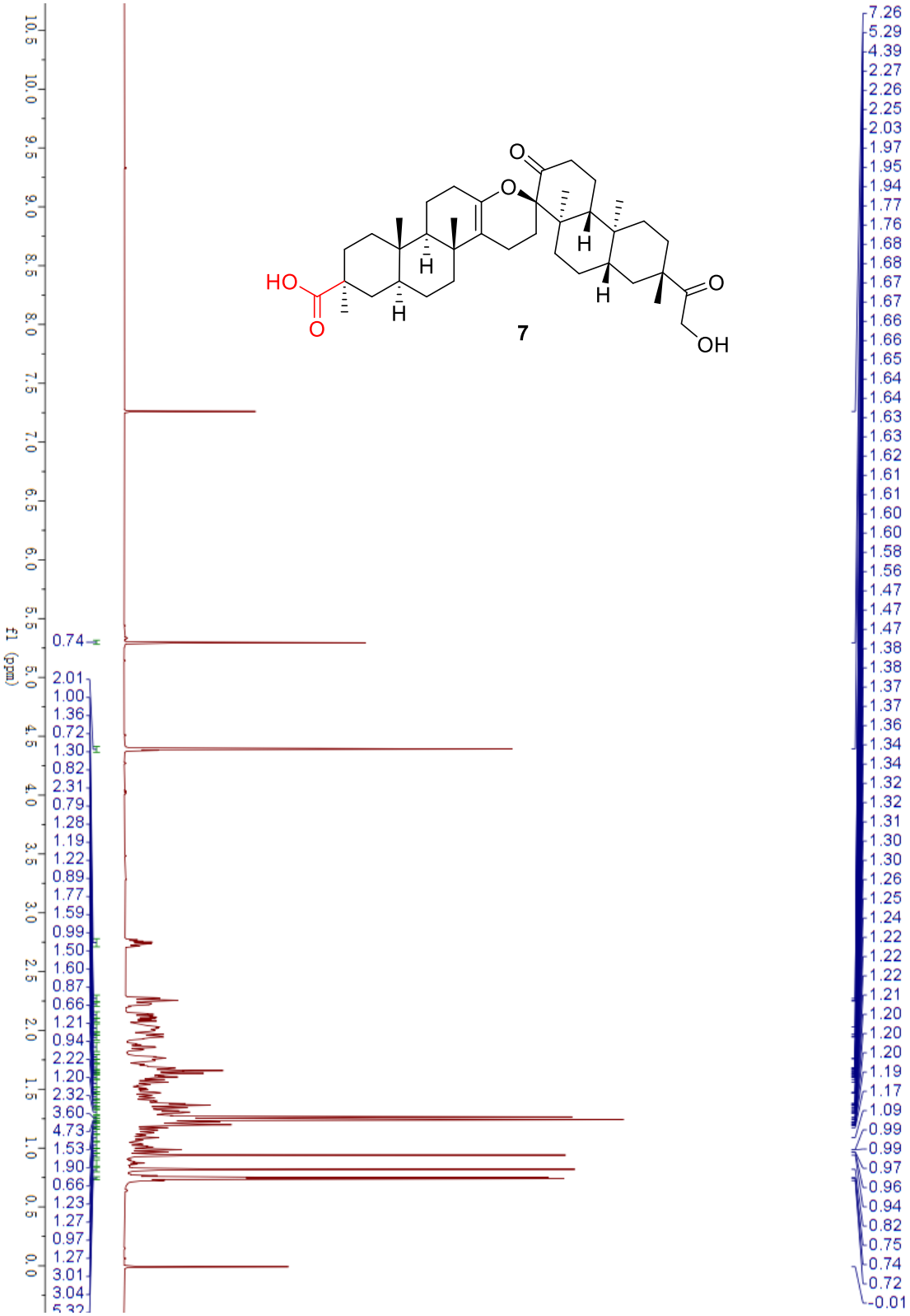


Figure S65. ^{13}C NMR spectrum of Koilodenoid G (**7**) in $CDCl_3$.

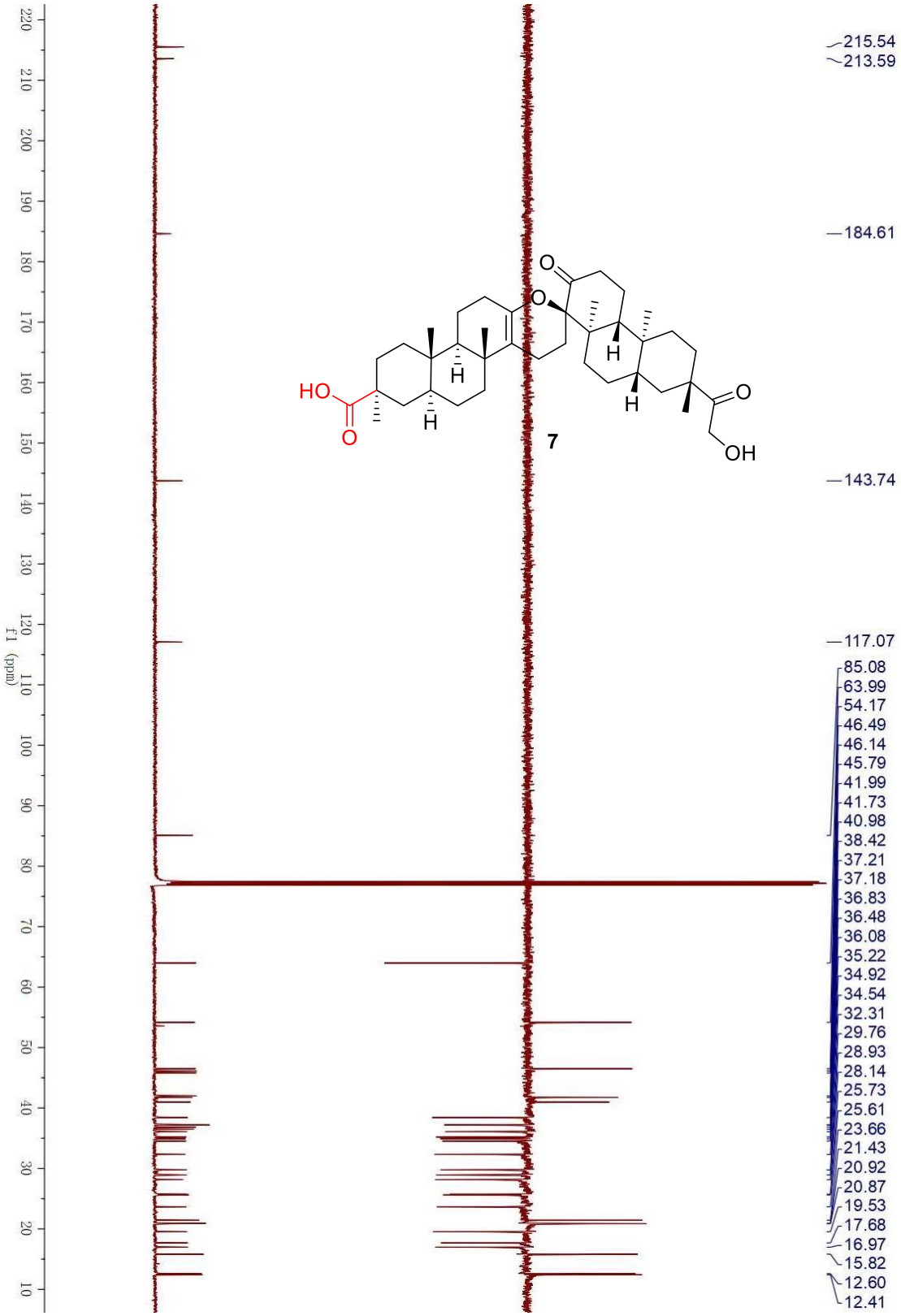


Figure S66. HSQC spectrum of Koilodenoid G (**7**) in $CDCl_3$.

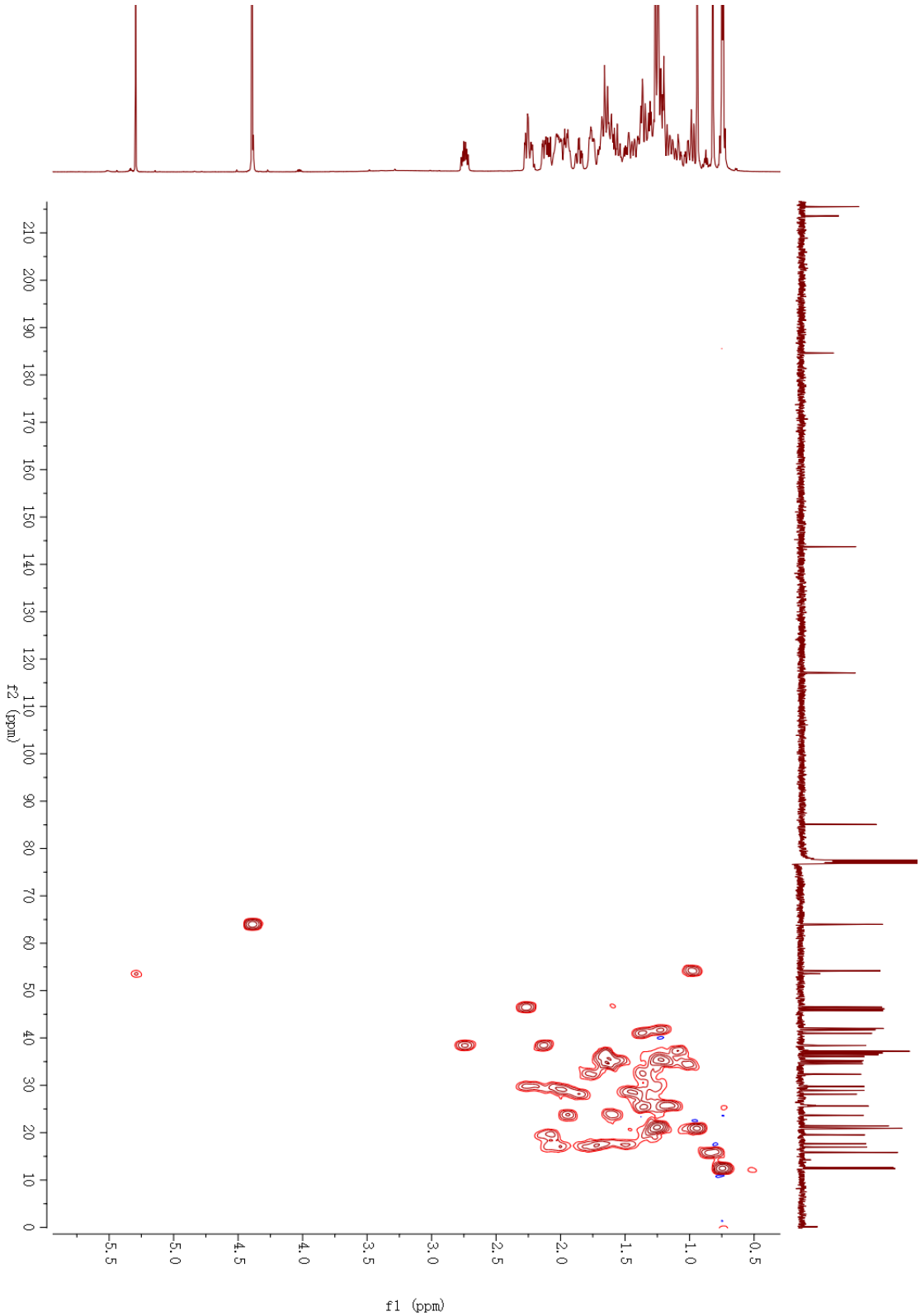


Figure S67. ^{1}H-^{1}H COSY NMR spectrum of Koilodenoid G (**7**) in $CDCl_3$.

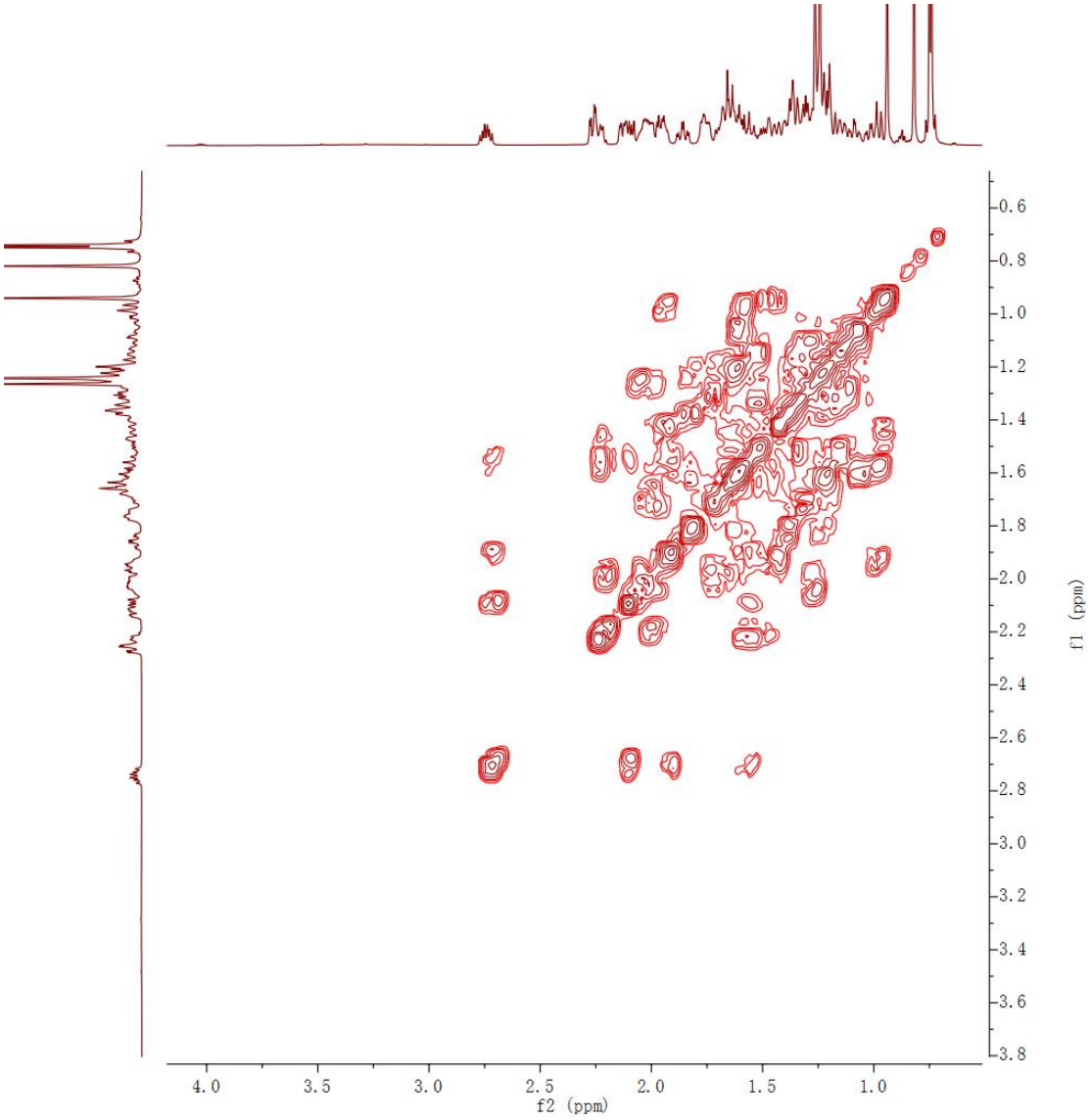


Figure S68. HMBC spectrum of Koilodenoid G (**7**) in $CDCl_3$.

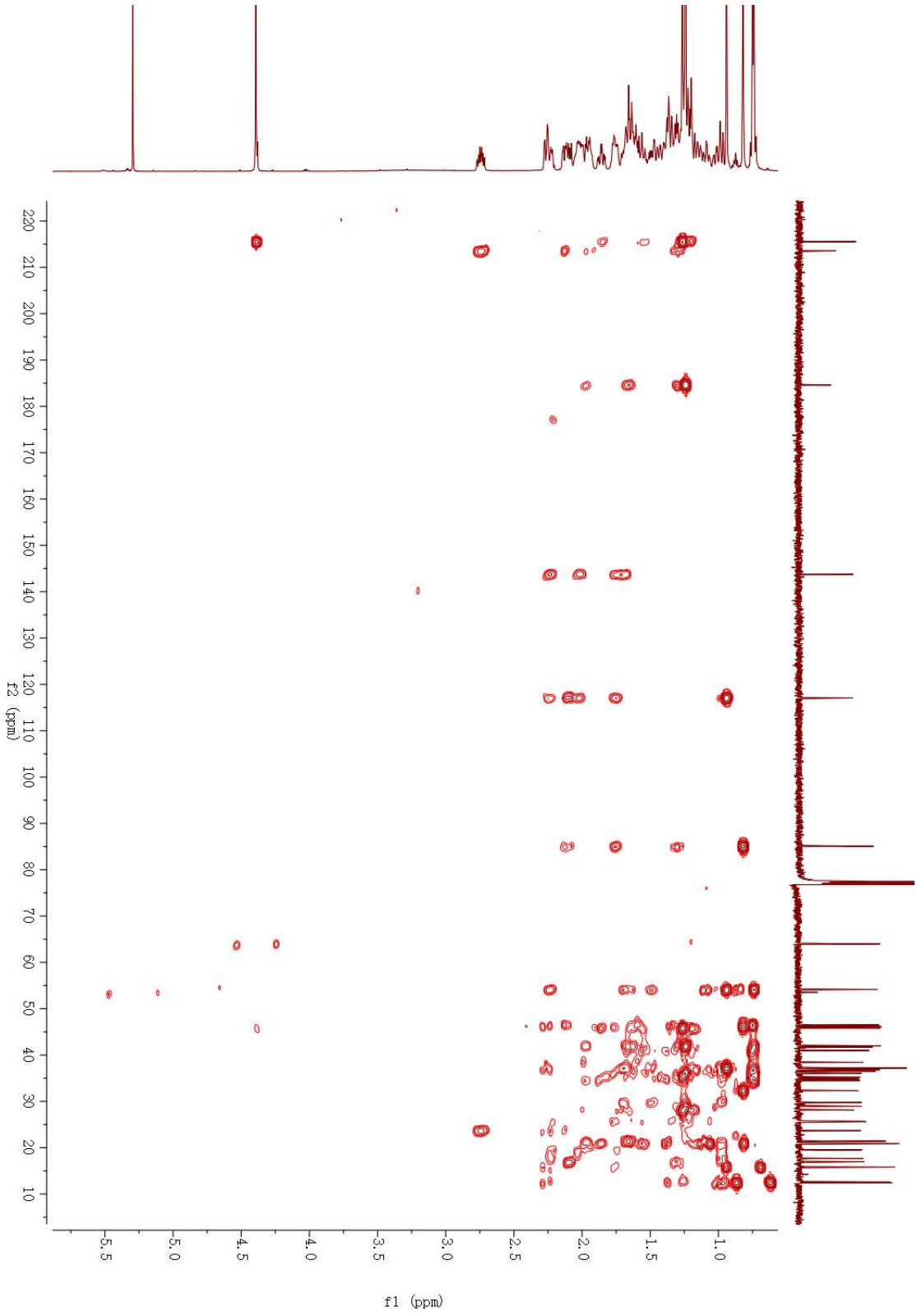


Figure S69. NOESY spectrum of Koilodenoid G (**7**) in $CDCl_3$.

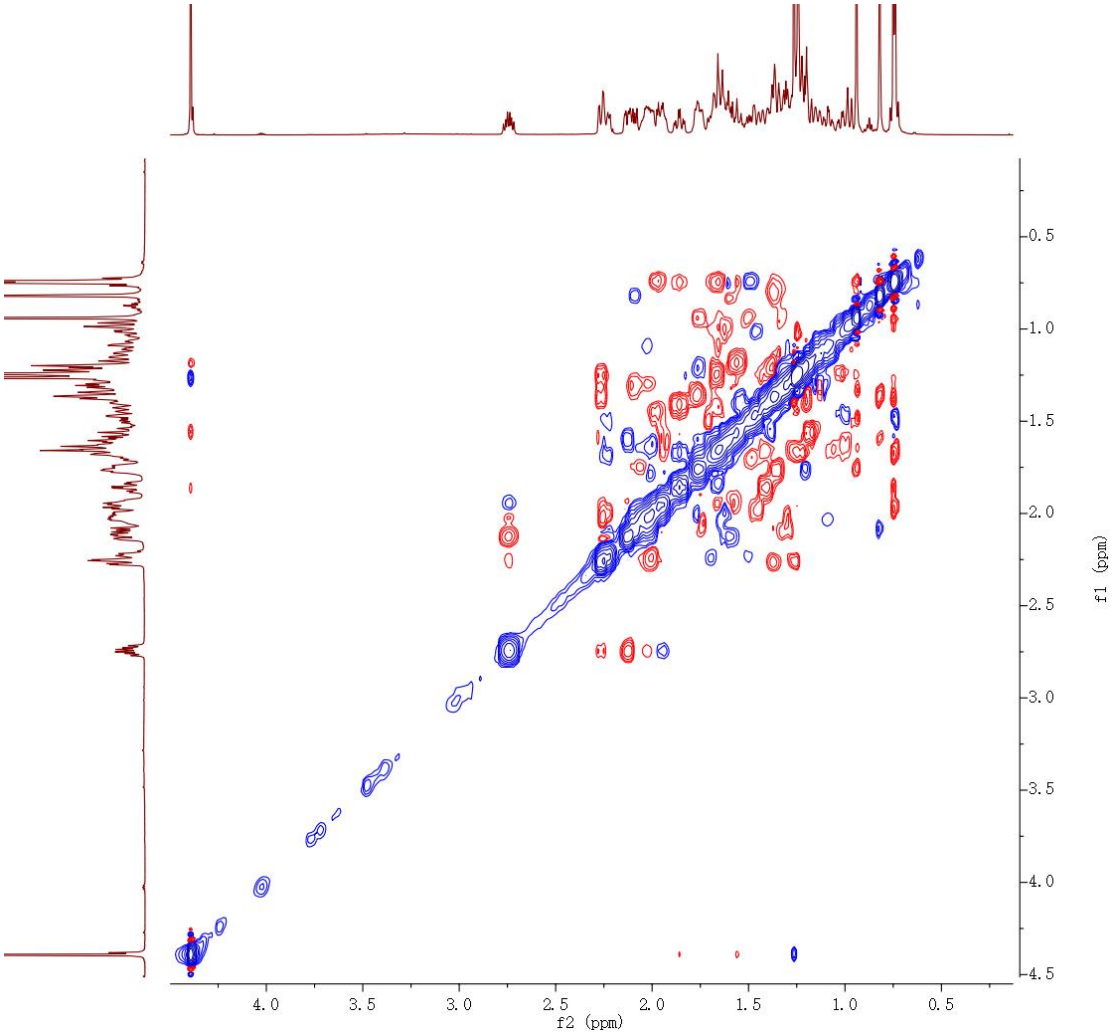


Figure S70. (+)-ESIMS spectrum of Koilodenoid G (**7**).

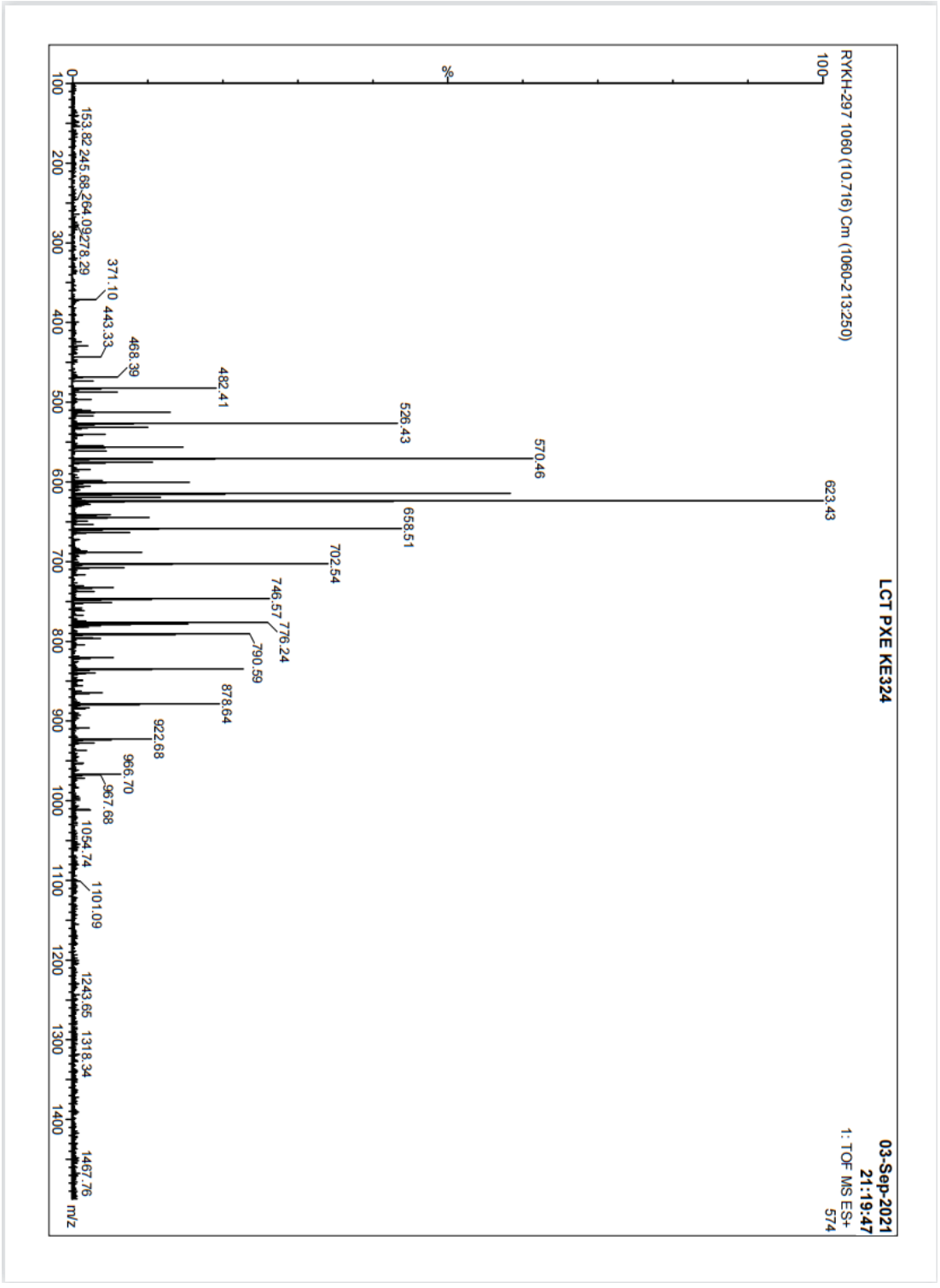


Figure S71. (+)-HRESIMS spectrum of Koilodenoid G (**7**).

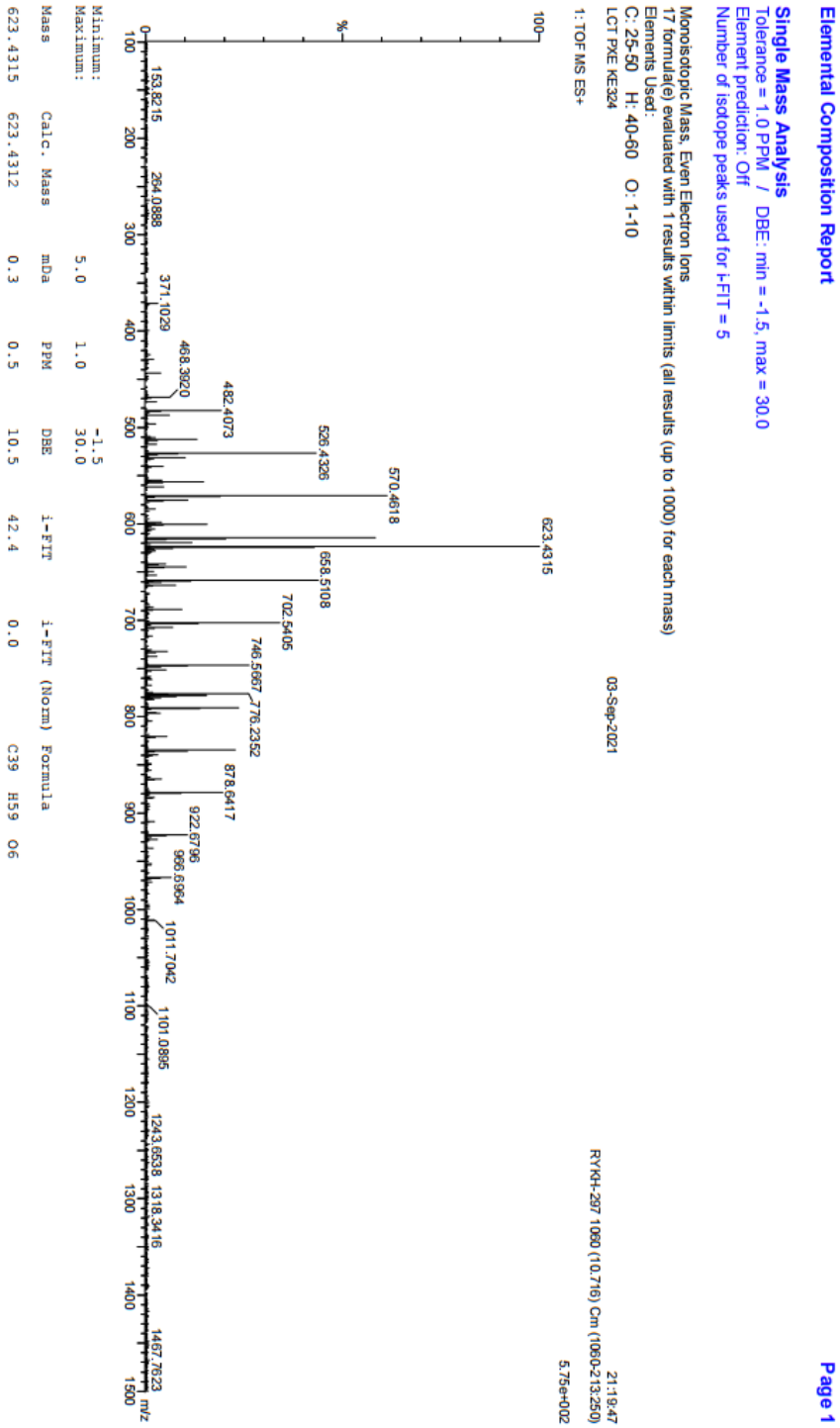


Figure S72. IR spectrum of Koilodenoid G (**7**).

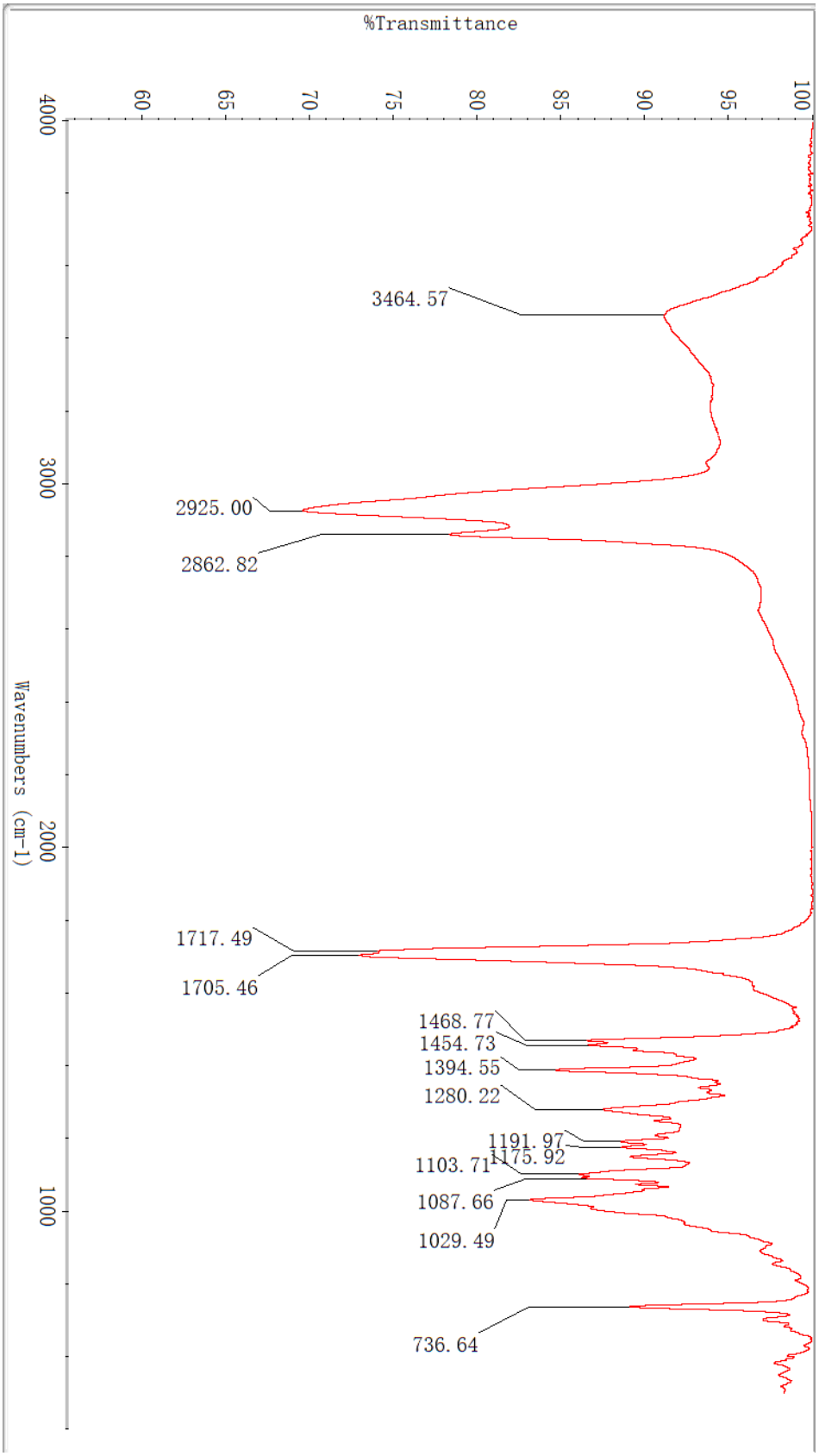


Figure S73. ^{1}H NMR spectrum of compound **9** in $CDCl_3$.

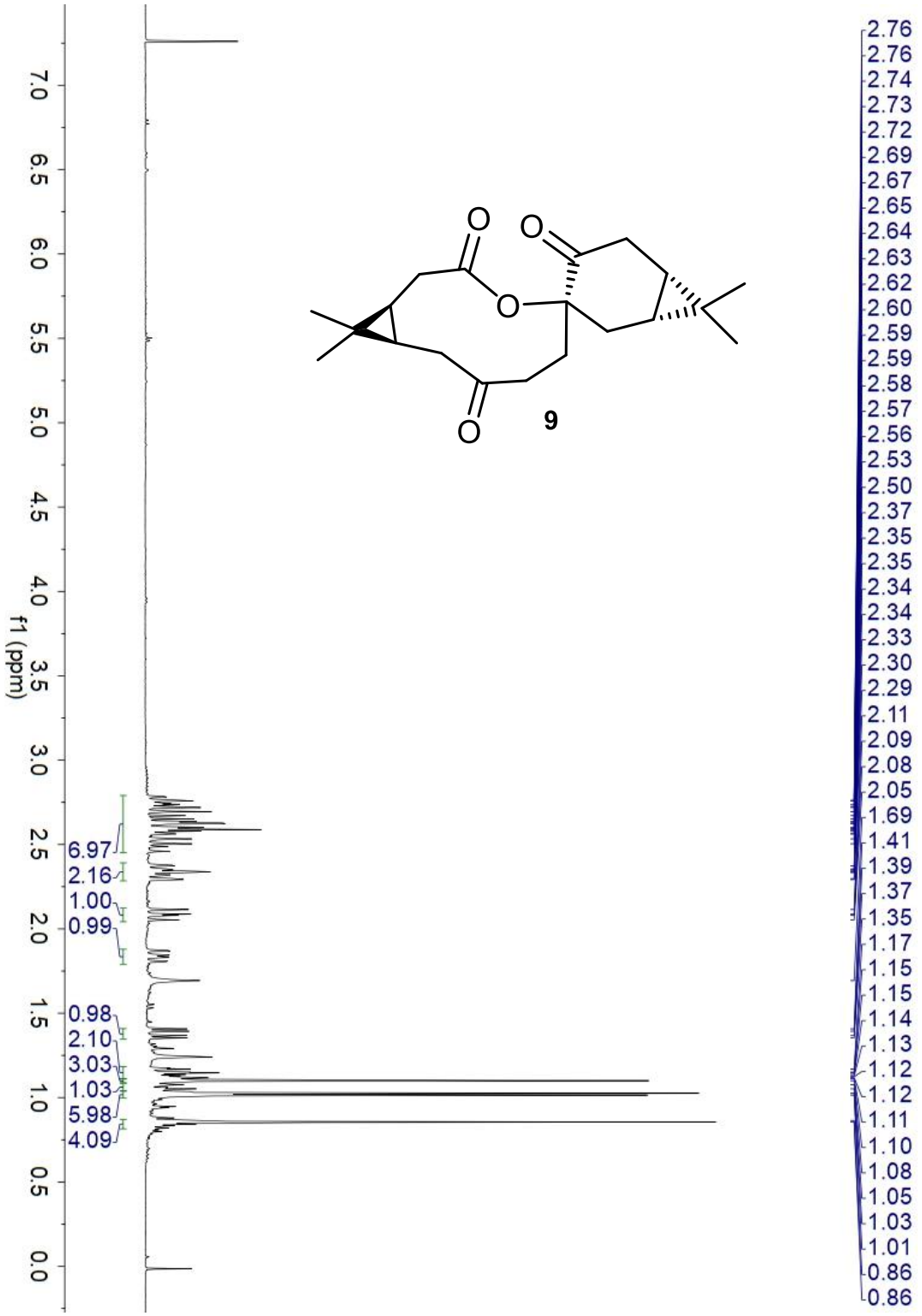


Figure S74. ^{13}C NMR spectrum of compound **9** in $CDCl_3$.

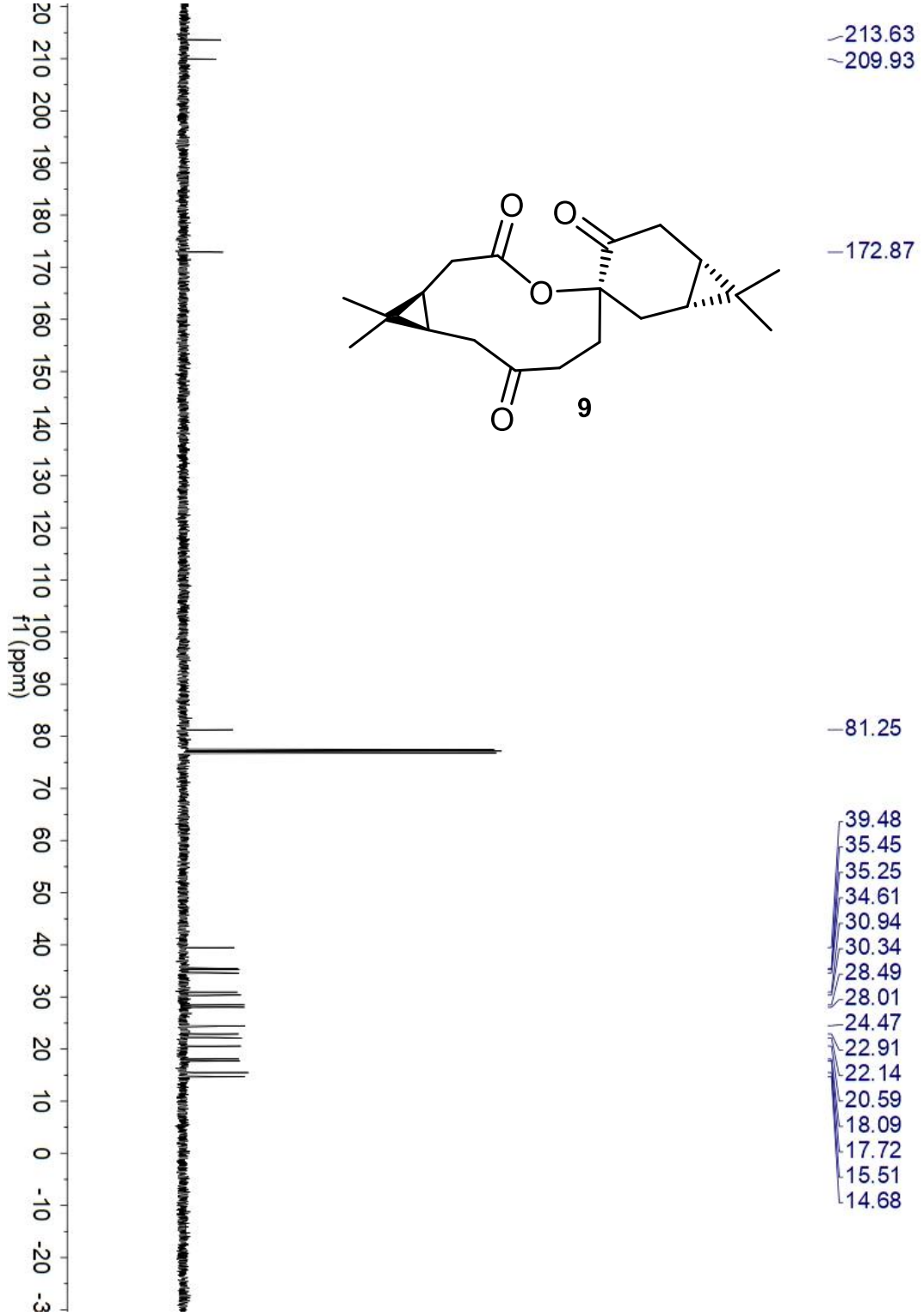


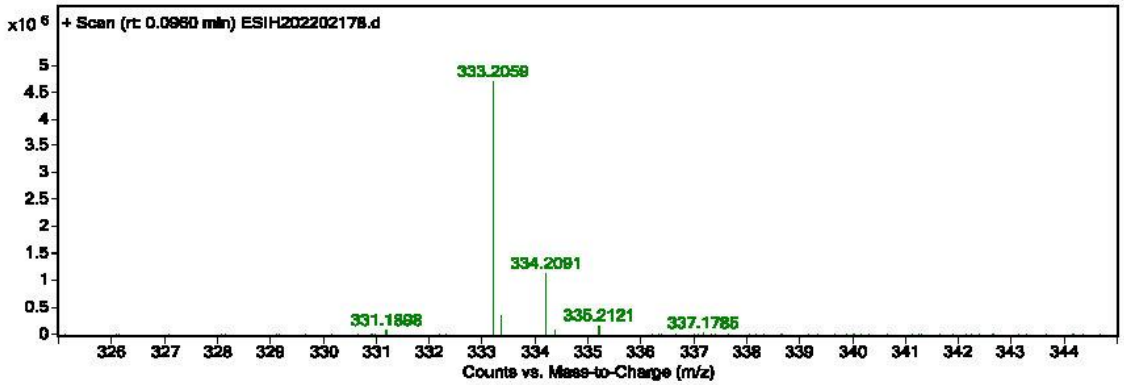
Figure S75. (+)-HRESIMS spectrum of compound **9**.

Qualitative Analysis Report

Data Filename	ESIH202202178.d	**Sample Name**	D4-OA5
Sample ID		**Position**	P1-A2
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	7/7/2022 10:47:21	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by fangsu

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
333.2059	333.206	0.09	0.28	C20 H29 O4	(M+H)+

--- End Of Report ---

Figure S76. ^{1}H NMR spectrum of synthetic Koilodenoid A (**1**) in $CDCl_3$.

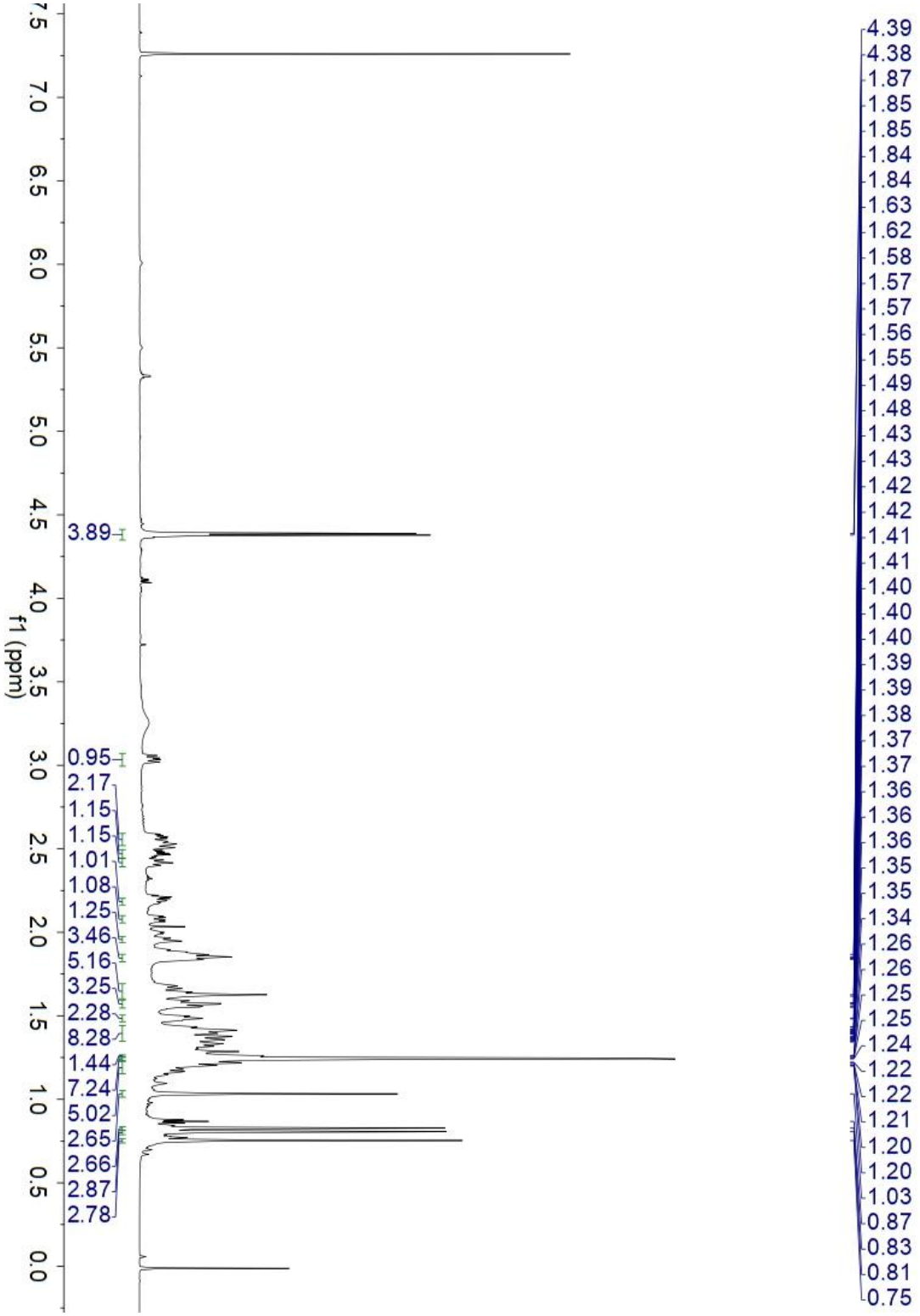


Figure S77. ^{13}C NMR spectrum of synthetic Koilodenoid A (**1**) in $CDCl_3$.

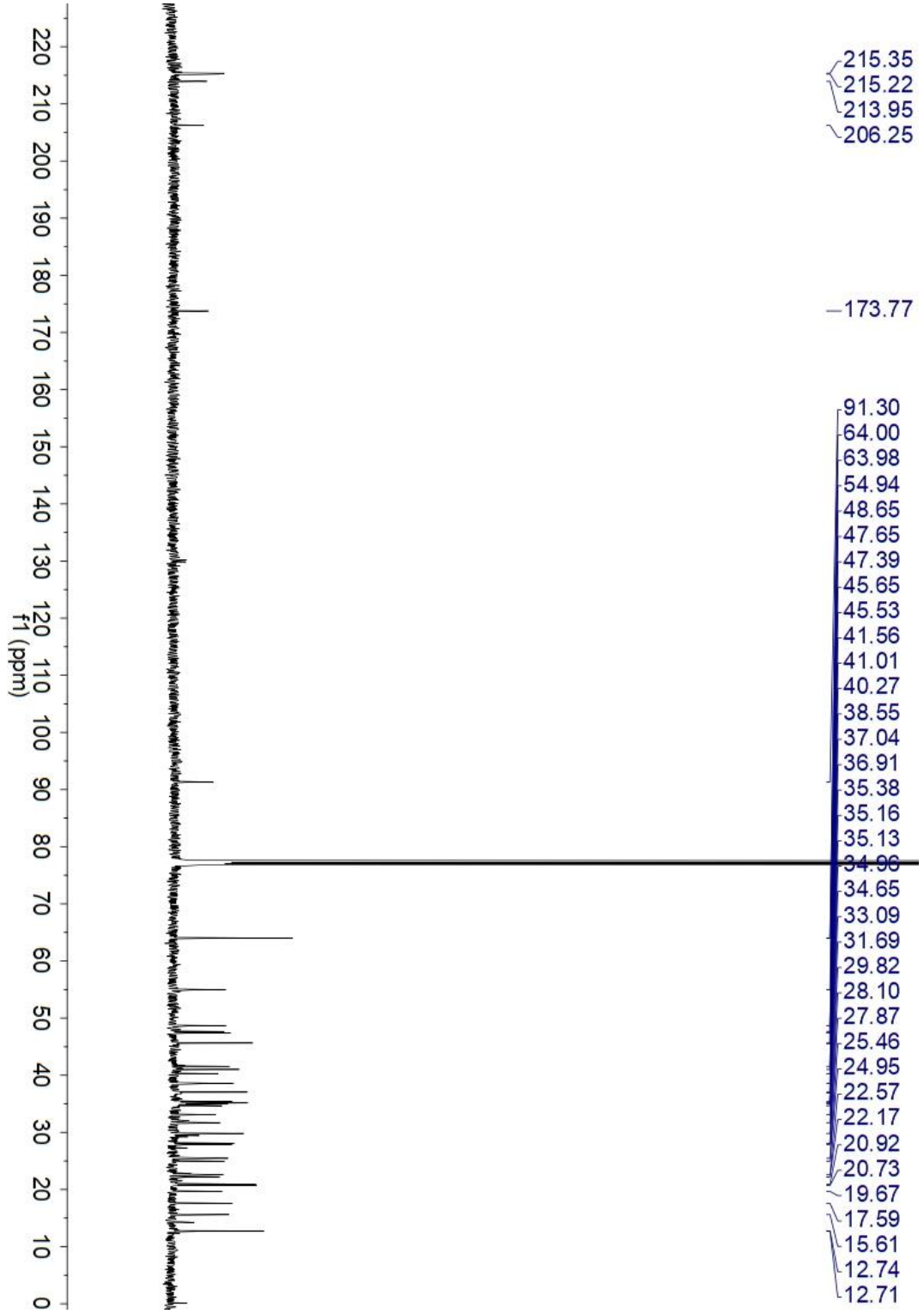


Figure S78. (+)-HRESIMS spectrum of synthetic Koilodenoid A (**1**).