Supplemental file for manuscript Petko I. Bozov, Plamen N. Penchev, Yoana P. Georgieva and Velizar K. Gochev, Clerodane diterpenoids from *Teucrium scordium* L. subsp. *scordioides* (Shreb.) Maire et Petitmengin

Contents

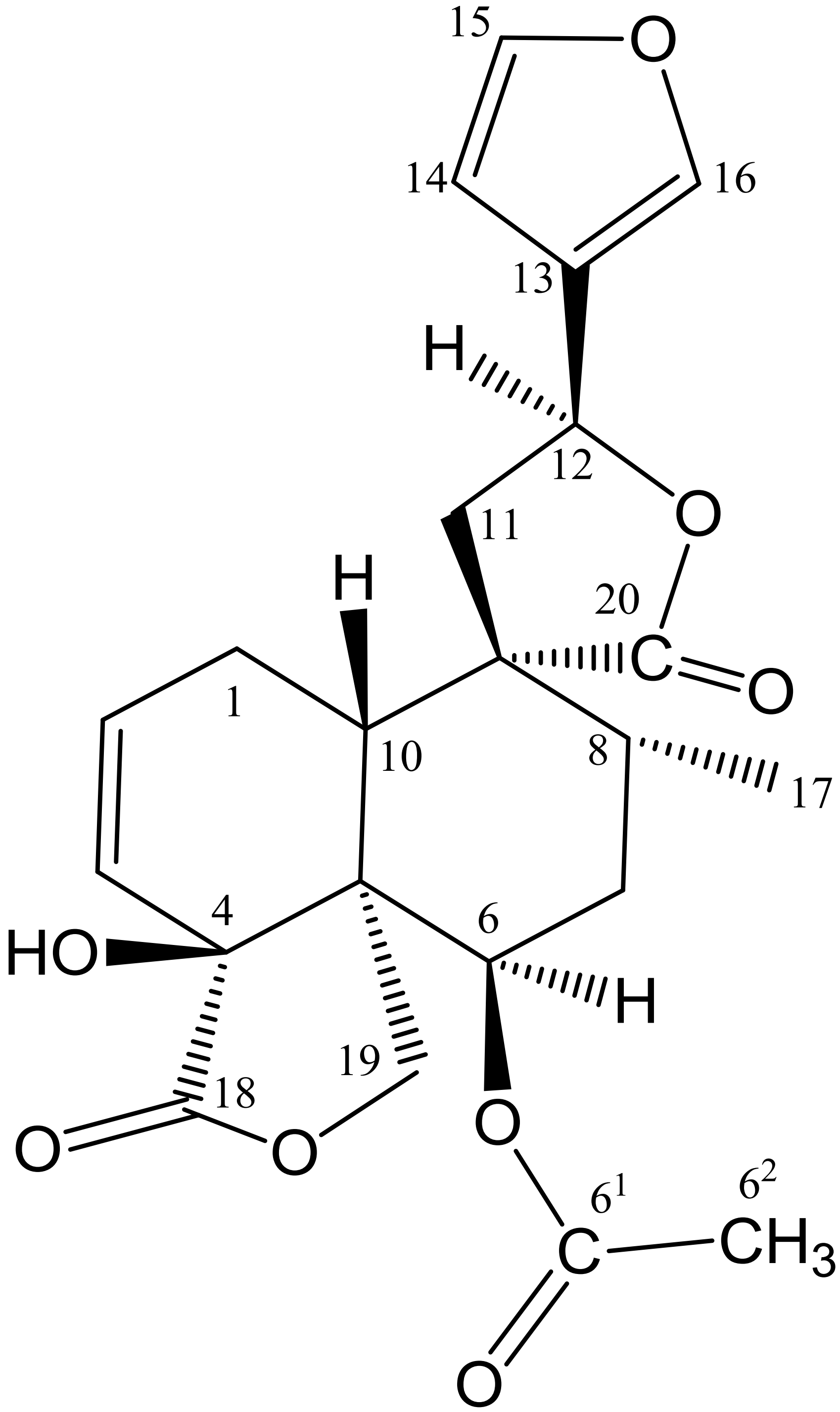

Figure 1. Structure of 6-acetyl teucrin F (**1**)

Table 1. ^{1}H and ^{13}C NMR spectral data, ^{1}H-^{1}H COSY, HMBC and NOESY correlations for 6-acetyl teucrin F (**1**) [600.13 MHz (^{1}H) and 150.903 MHz (^{13}C)][a]

position	δ ^{13}C, nH	δ ^{1}H	m, *J* (in Hz)	^{1}H-^{1}H COSY	HMBC	NOESY
1	25.19, CH_2	2.085	m	2, 3	-	2, 19b
		2.589	m [c]	2, 3	3, 4, 5, 6, 9, 11, 20	2, 12
2	129.85, CH	6.098	ddd, 10.0, 5.3, 2.2	1α, 1β, 3,	-	1α, 1β, 3
3	125.56, CH	5.547	ddd, 9.9, 2.8, 1.4	1α, 1β , 2	-	2
4	75.85, C	-	-	-	-	-
5	47.84, C	-	-	-	-	-
6	68.04, CH	5.411 (α)	dd, 4.0, 2.1	7β, 1β	3, 6^1, 8, 10	7α, 7β, 19a
7	31.84, CH_2	2. 343 (α)	ddd, 14.8, 12.7, 2.0	6, 7β, 8	8	6α, 17, 19a
		1.694 (β)	dt, 14.9; 4.0	7α	5, 6, 8, 9, 17	6α, 7α, 8β, 17
8	32.88, CH	2.179-2.095	m	7β, 17	20	7β, 11β, 17
9	51.57, C	-	-	-	-	-
10	37.23, CH	2.653-2.596	m	1, 2	1, 3, 4, 5, 9, 11[b], 20	-
11	42.57, CH_2	2.570 A	dd, 14.3, 8.6	11β,12	8, 9, 10, 12, 13, 20	12
		2.474 B	dd, 14.2, 8.9	11α	7, 8, 9, 12, 13	8β, 14, 16, 17
12	72.21, CH	5.427	d, 9.0	11α	11, 13, 14, 16	1β, 11α, 14, 16
13	124.59, C	-	-	-	-	-
14	107.98, CH	6.406	dd, 1.8; 0.8	15 or 16	13, 15, 16	11β, 12, 15, 17
15	144.33, CH	7.459	t, 1.8	12, 14, 16	16	11β, 14
16	139.62, CH	7.477	dt, 1.7; 0.9	14, 15	13, 14, 15	11β, 12, 17
17	16.44, CH_3	1.004	d, 6.8	8, 7α	6, 8, 9	7α, 7β, 8, 11β, 14, 16
18	176.04, C	-	-	-	-	-
19	68.99, CH_2	4.536 B[b]	d, 11.3	19b	4, 6, 9, 18	6, 7α
		4.118 A	d, 11.3	19a	6, 9, 10, 18	1α
20	177.51, C	-	-	-	-	-
6^1 (C = O)	170.15, C	-	-	-	-	-
6^2 (CH3)	21.48, CH_3	2.041	s	-	6, 6^1	

[a] $CDCl_3$, ^{1}H 600.13 MHz, δ_{ref} 7.26; ^{13}C 150.9 MHz, δ_{ref} 77.0 ppm, TMS as an internal standard; [b] endo hydrogen with respect to ring B; [c] δ_H data from HSQC; ov – overlapped signal.

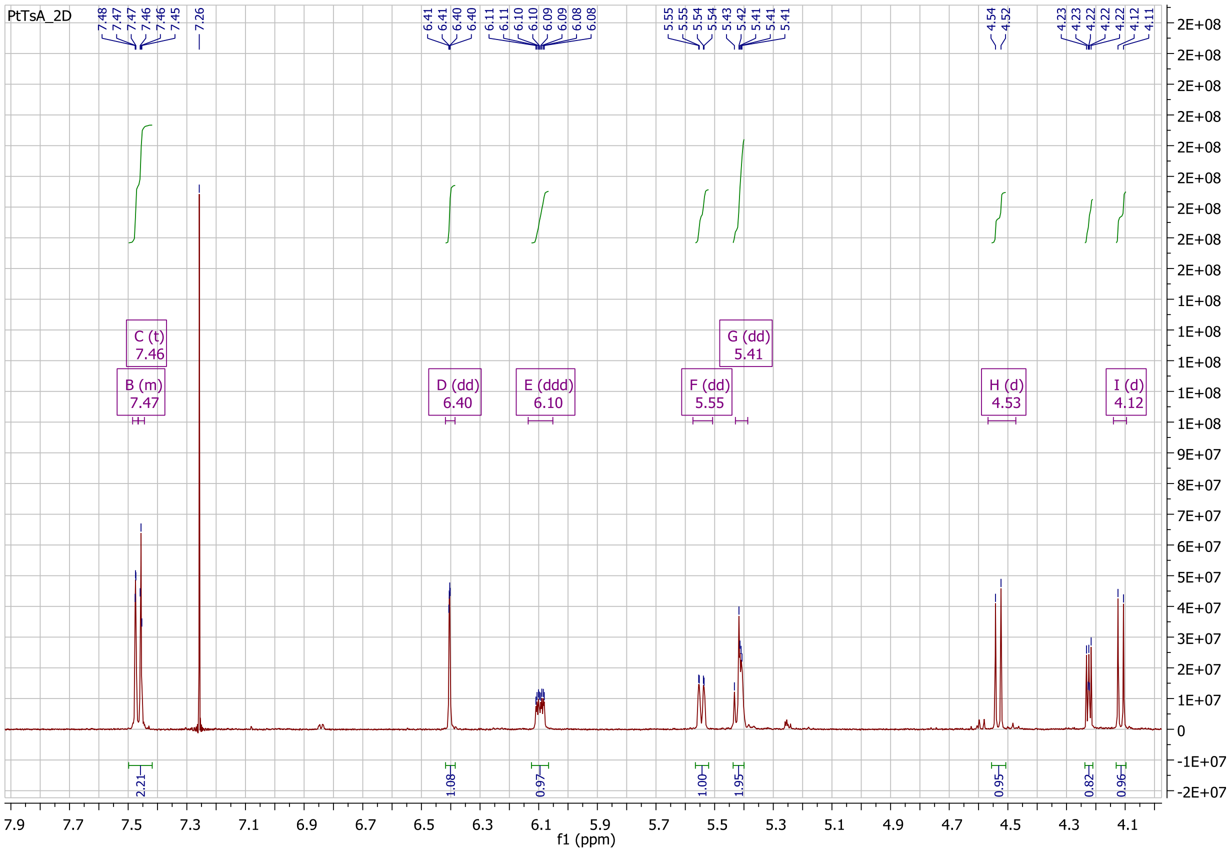

Figure 2. Part of the ^{1}H NMR spectrum of 6-acetyl teucrin F (**1**)

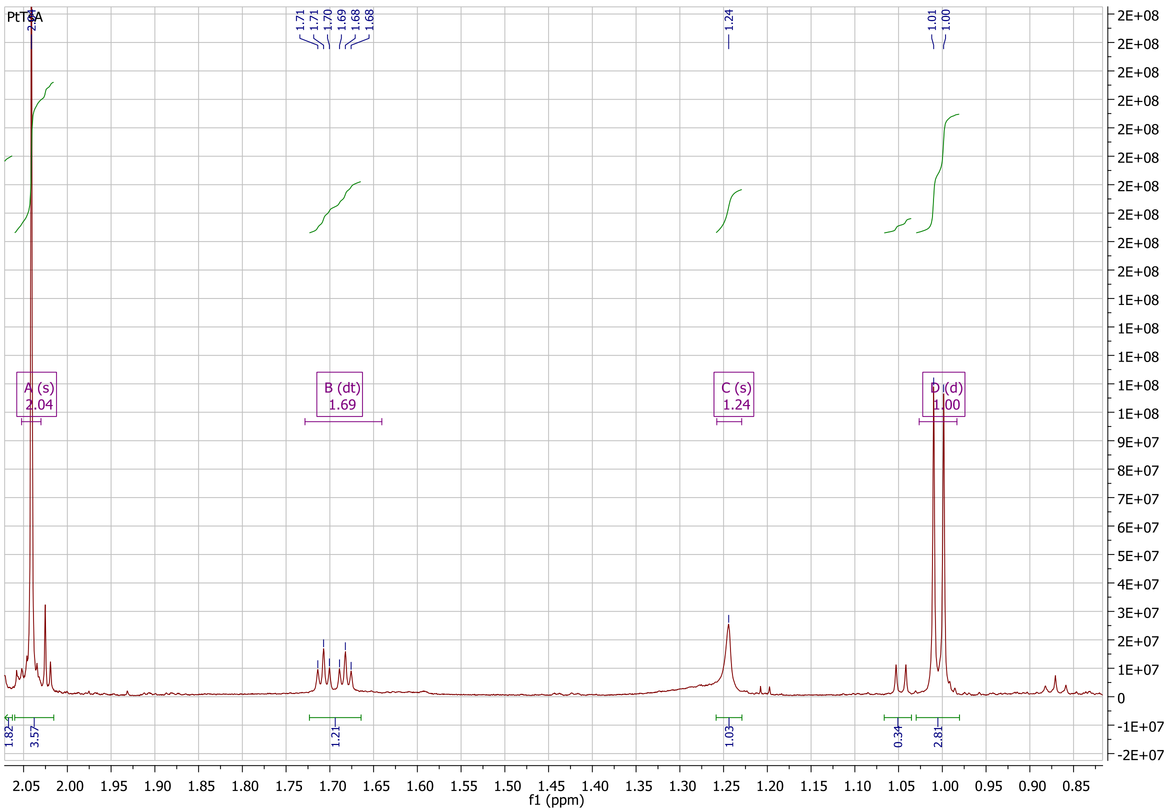

Figure 3. Part of the ^{1}H NMR spectrum of 6-acetyl teucrin F (**1**)

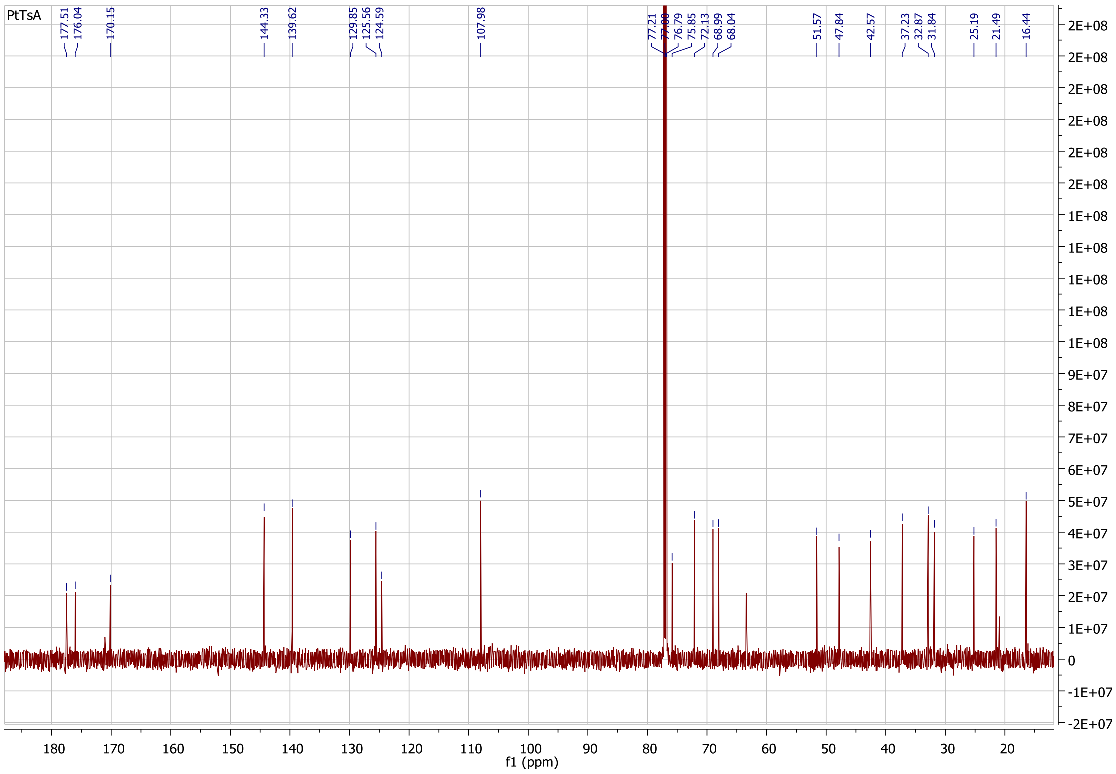

Figure 4. The [1]H-broadband-decoupled [13]C NMR spectrum of 6-acetyl teucrin F (**1**)

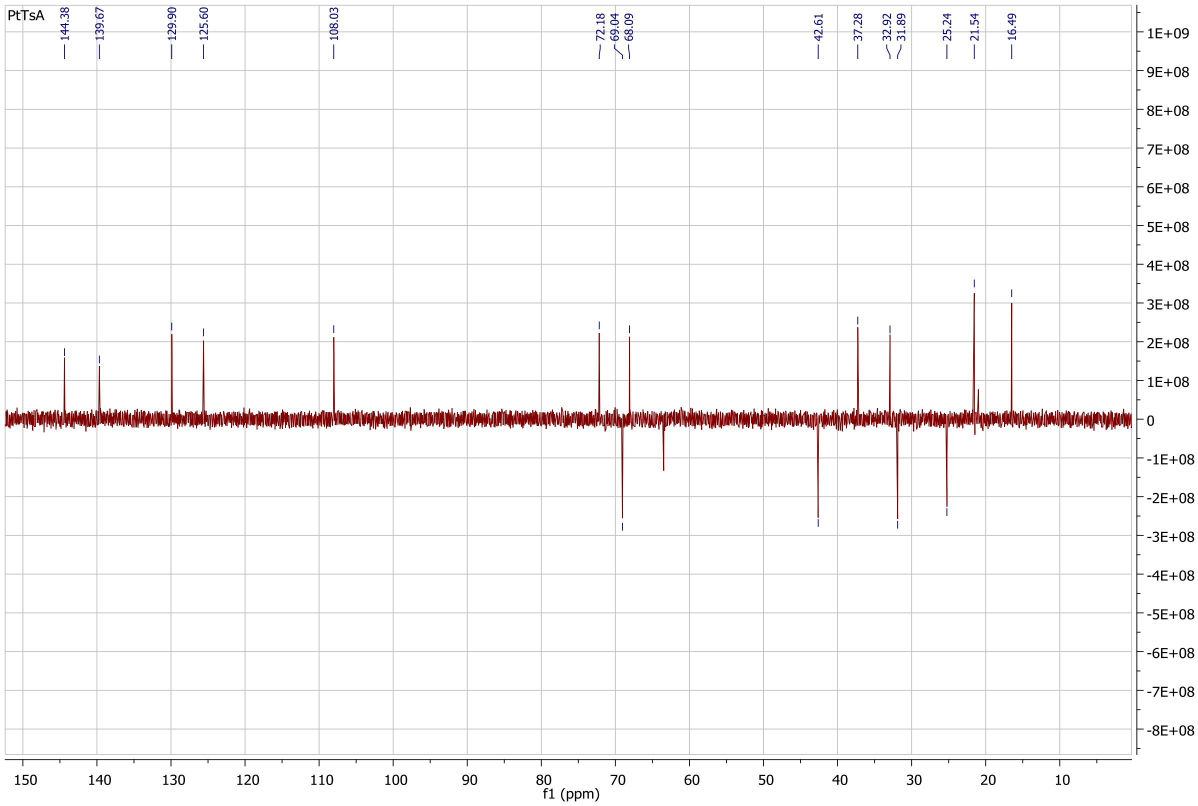

Figure 5. The DEPT 135º [13]C NMR spectrum of 6-acetyl teucrin F (**1**)

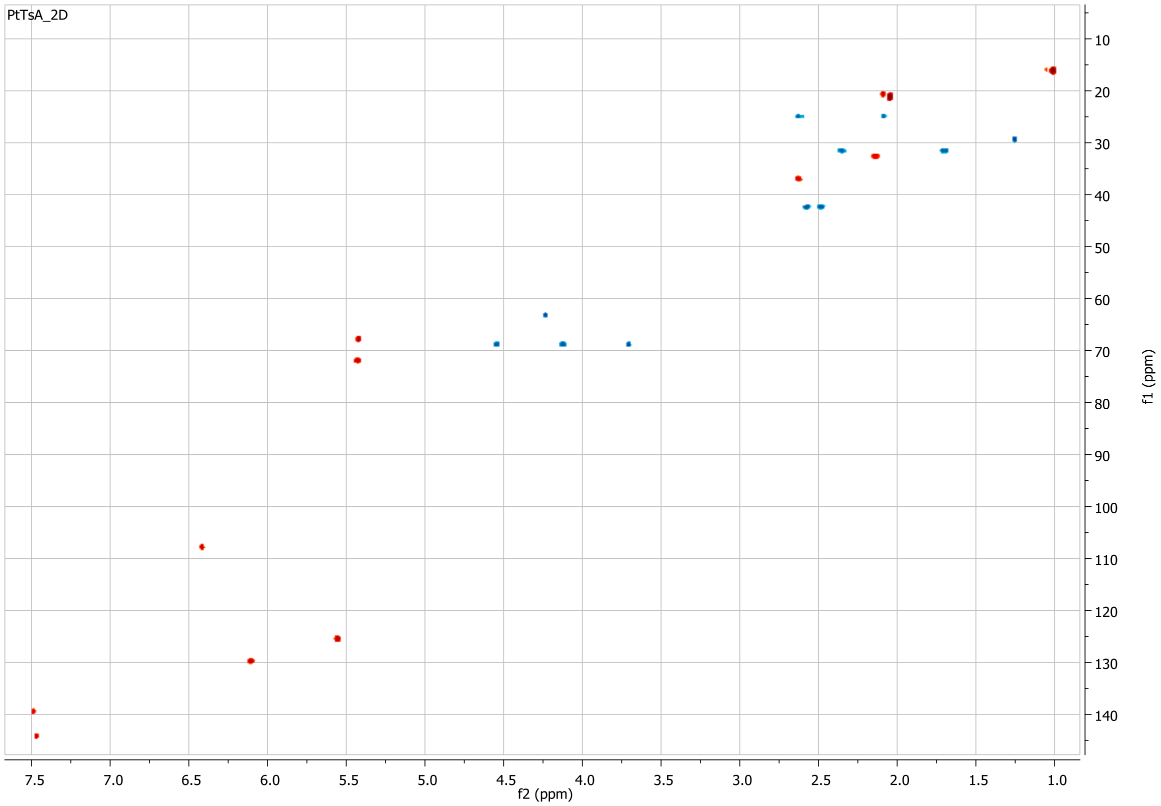

Figure 6. The HSQC spectrum of 6-acetyl teucrin F (**1**). The resonances denoted in blue are negative and are for CH_2 groups.

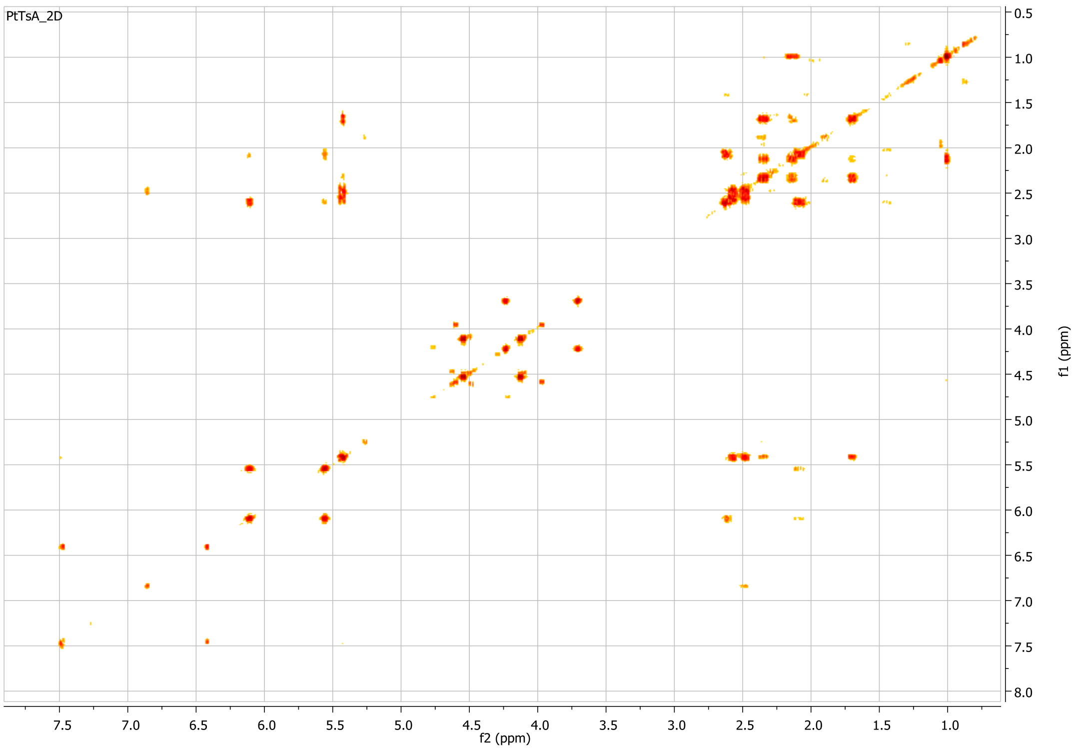

Figure 7. The COSY spectrum of teuscordesin A.

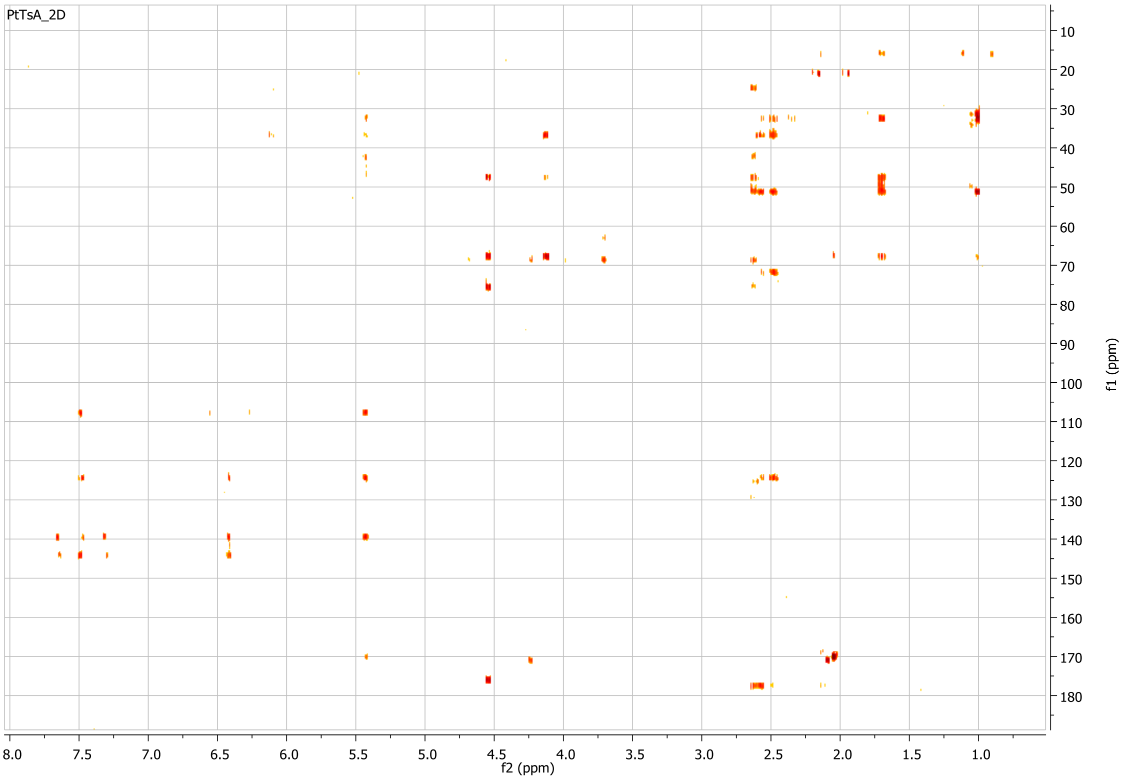

Figure 8. The HMBC spectrum of **1**.

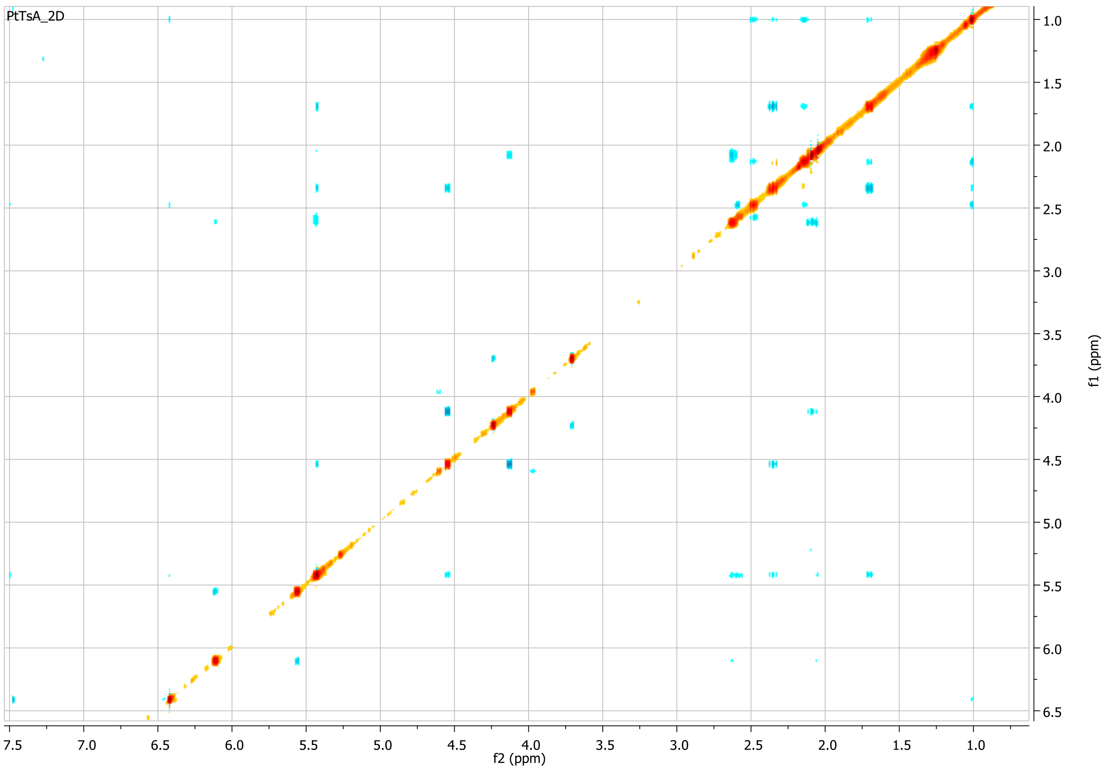

Figure 9. The NOESY spectrum of **1**.

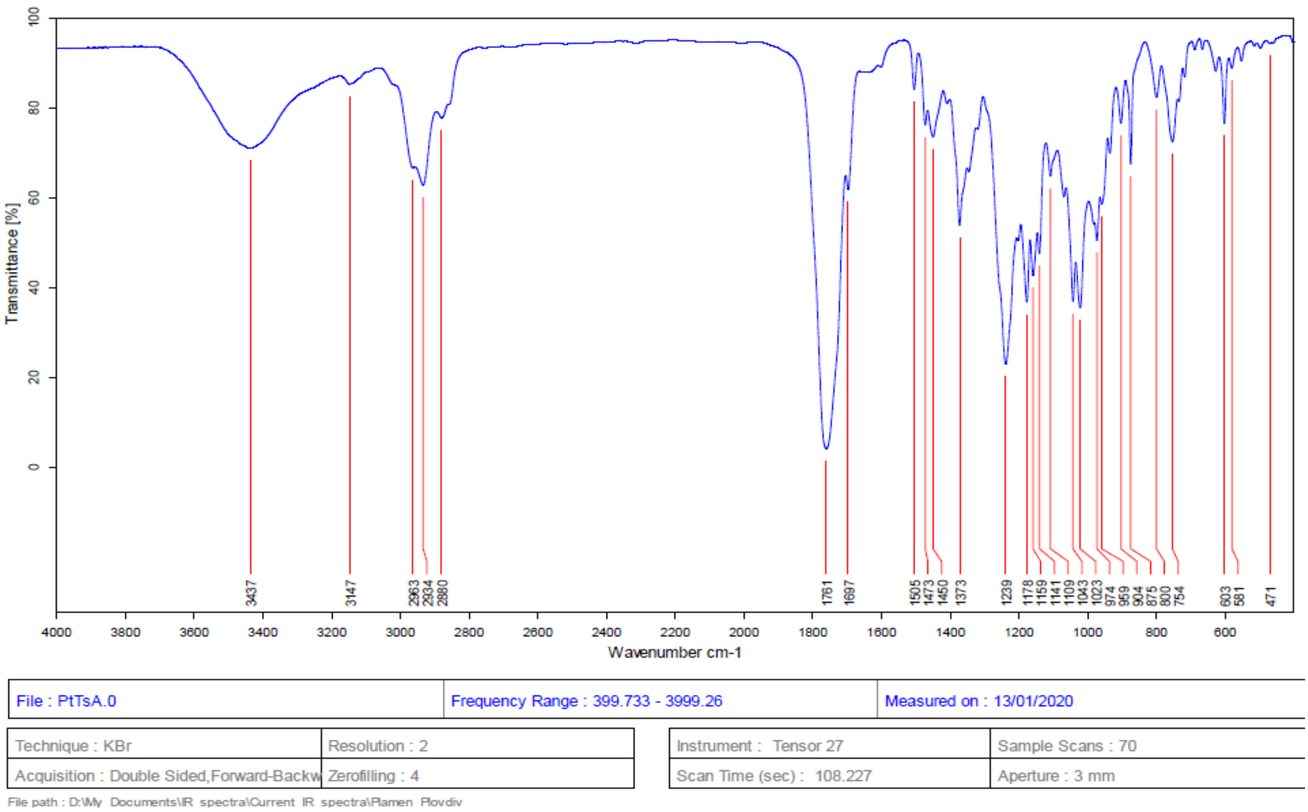

Figure 10. IR spectrum of **1**.

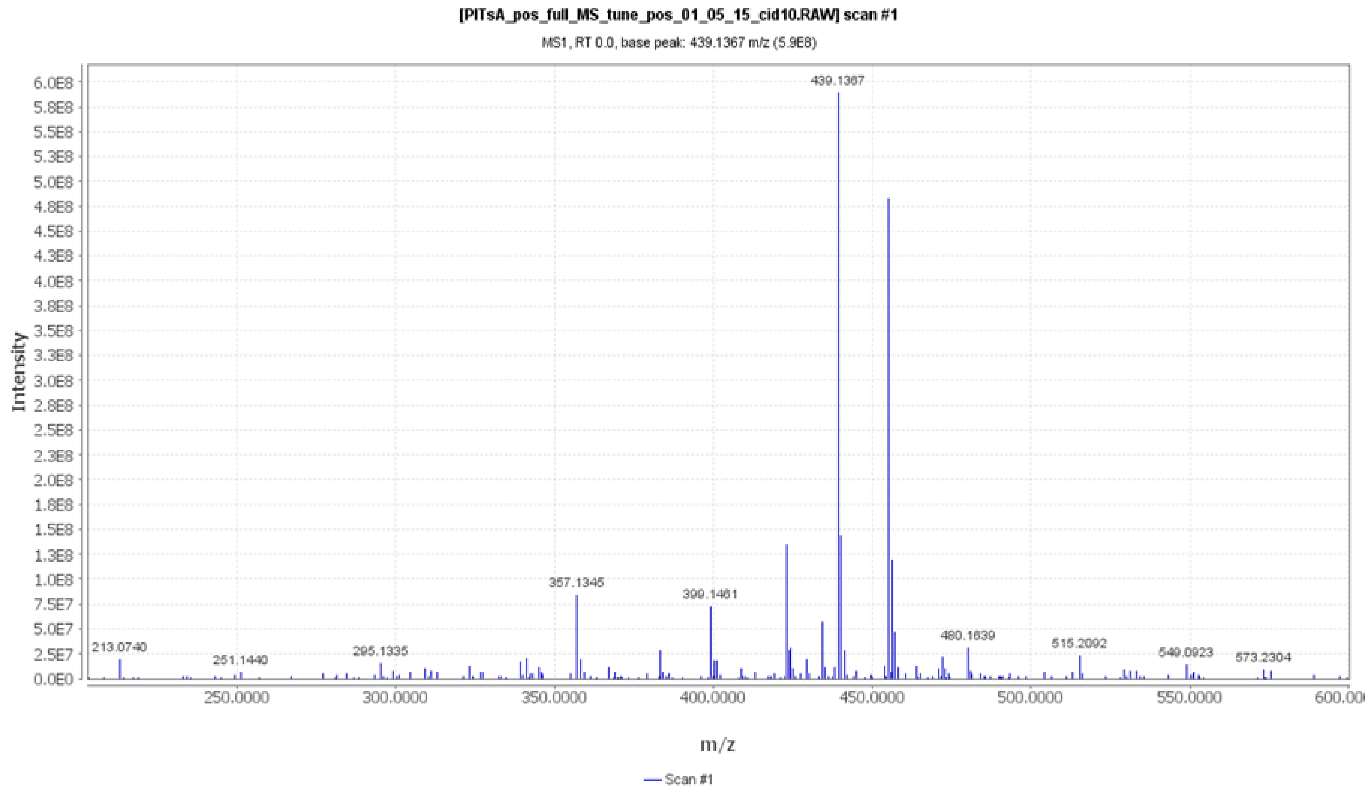

Figure 11. HRESIMS spectrum of **1**.

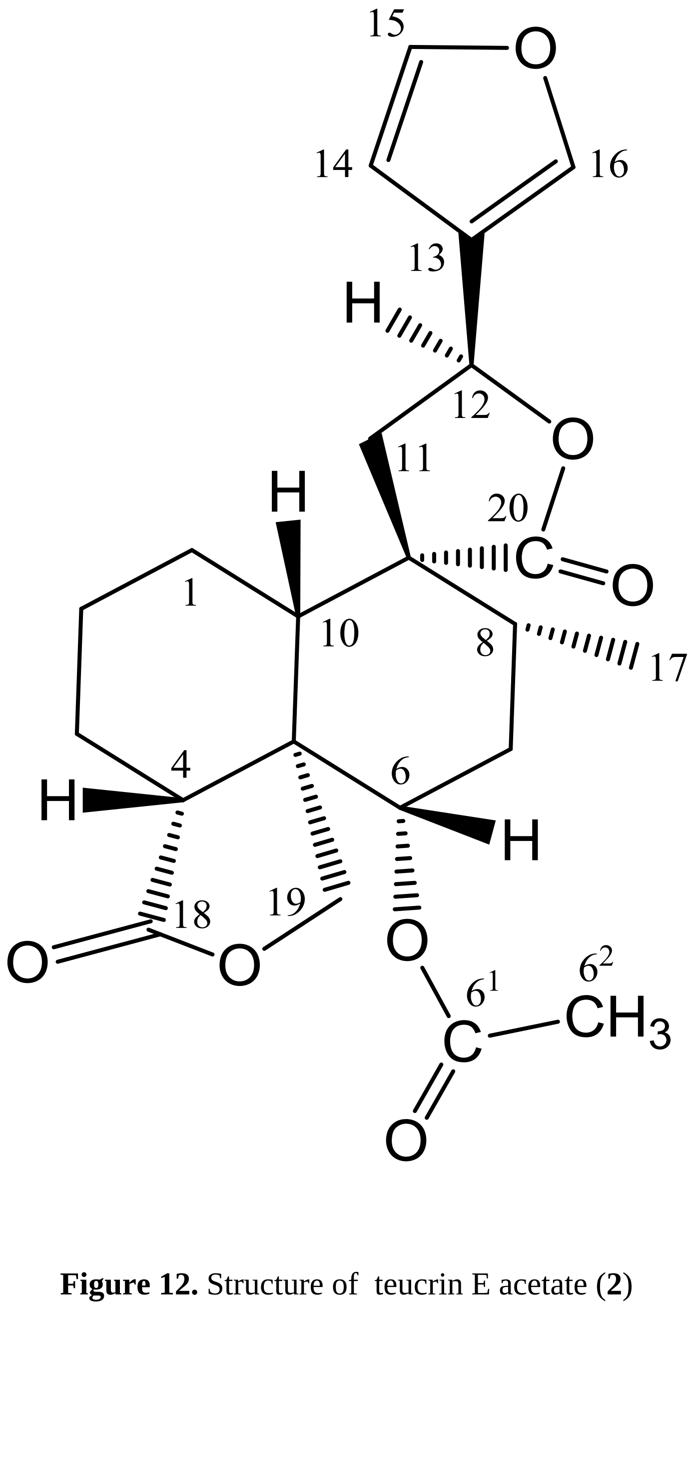

Figure 12. Structure of teucrin E acetate (**2**)

Table 2. ^{1}H and ^{13}C NMR spectral data and ^{1}H-^{1}H COSY, HMBC and NOESY correlations for **2**. [600.13 MHz (^{1}H) and 150.903 MHz (^{13}C)][a]

position	δ ^{13}C, nH	δ ^{1}H	m, *J* (in Hz)	^{1}H-^{1}H COSY	HMBC	NOESY
1	25.0, CH_2	1.57 (α)	m[c]	2α, 3β	2	19b
		2.06 (β)	ov m[c]	1α, 2β, 3α, 3β, 8, 10	2, 4, 5, 20	2β, 11α
2	22.5, CH_2	2.03 (α)	ov[c]	1α, 3α, 3β, 4, 10	-	3α
		1.51 (β)	m[c]	1β, 3β,10	3	1β, 10β, 3β, 4β
3	23.1, CH_2	1.45 (α)	m[c]	1β, 2α, 3β	-	2α, 19b
		1.90 (β)	m[c]	1α, 1β, 2α, 2β, 3α	-	2β
4	46.01, CH	2.18 (β)	br s	2α, 6, 10, 19A	3, 6	2β, 6β, 10β
5	45.98, C	-	-	-	-	-
6	78.3, CH	4.75 (β)	dd, 12.1; 3.8	4, 7α, 7β, 8	4, 6^1, 7, 19	4β, 8β, 10β
7	31.8, CH_2	1.81 (α)	ov	6, 8	5, 17, 19, 20	19a, 6^2, 17
		2.20 (β)	dt, 13.1; 3.8	6	5, 6, 8, 9, 10, 17, 18	
8	47.4, CH	1.80 (β)	ov	6, 7α, 17	5, 6, 9, 10, 17, 19	6, 11β
9	50.9, C	-	-	-	-	-
10	38.0, CH	1.80 (β)	ov	1β, 2α, 2β, 4, 19A	7 , 9, 17, 18	4β, 6β, 11β
11	41.7, CH_2	2.45 A	dd, 14.5; 8.9	12	8, 9, 10, 12, 13, 20	1β, 12
		2.37 B	dd, 14.5; 8.9	12	8, 9, 10, 12, 13	8, 10, 12, 14, 16, 17
12	71.9, CH	5.37 (α)	t, 8.9	11A, 11B	13, 14, 16	1β, 11α
13	124.7, C	-	-	-	-	-
14	107.9, CH	6.39	dd, 1.8; 0.8	15 or 16	13, 15, 16	11β, 12, 15, 17
15	144.3, CH	7.45	br d, 1.8	14	16	14
16	139.6, CH	7.46	m	14	13,14, 15	12, 11β, 17
17	16.4, CH_3	1.03	d, 6.6	8	6, 7, 9, 10	7α, 11β, 14, 16
18	176.5, C	-	-	-	-	-
19	68.4, CH_2	4.80 B[b]	d, 11.3	4, 10, 19A	4, 6, 20	6″, 7α
		4.32 A	d, 11.3	19B	4, 6, 20	1α
20	178.5, C	-	-	-	-	-
6^1 (CO)	170.8, C	-	-	-	-	-
6^2 (CH_3)	21.0, CH_3	2.04	s	-	1, 6, 6^1, 9,	7α, 19a

[a] $CDCl_3$, ^{1}H 600.13 MHz, δ_{ref} 7.26; ^{13}C 150.9 MHz, δ_{ref} 77.0 ppm, TMS as an internal standard; [b] endo hydrogen with respect to ring B; [c] δ_H data from HSQC; ov – overlapped signal.

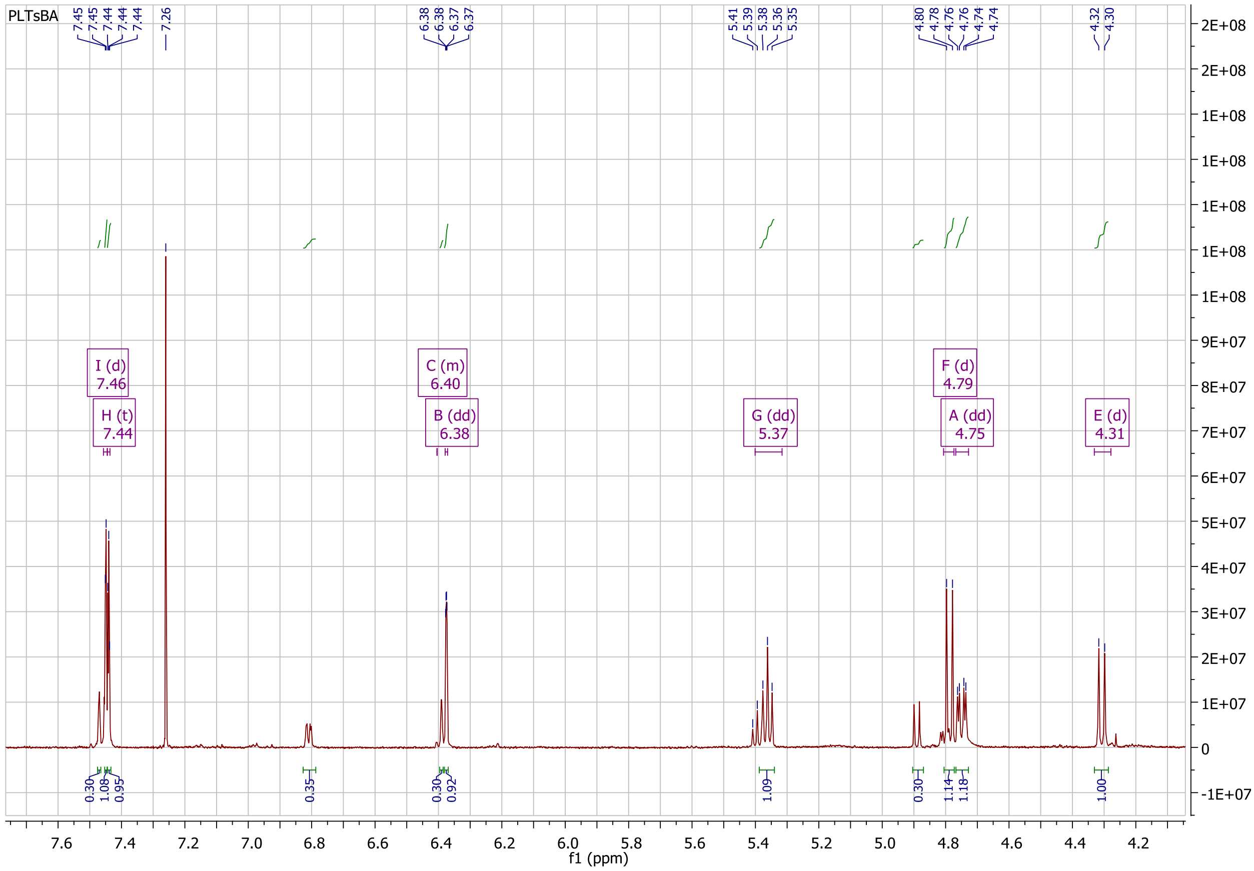

Figure 13. Part of the [1]H NMR spectrum of **2**.

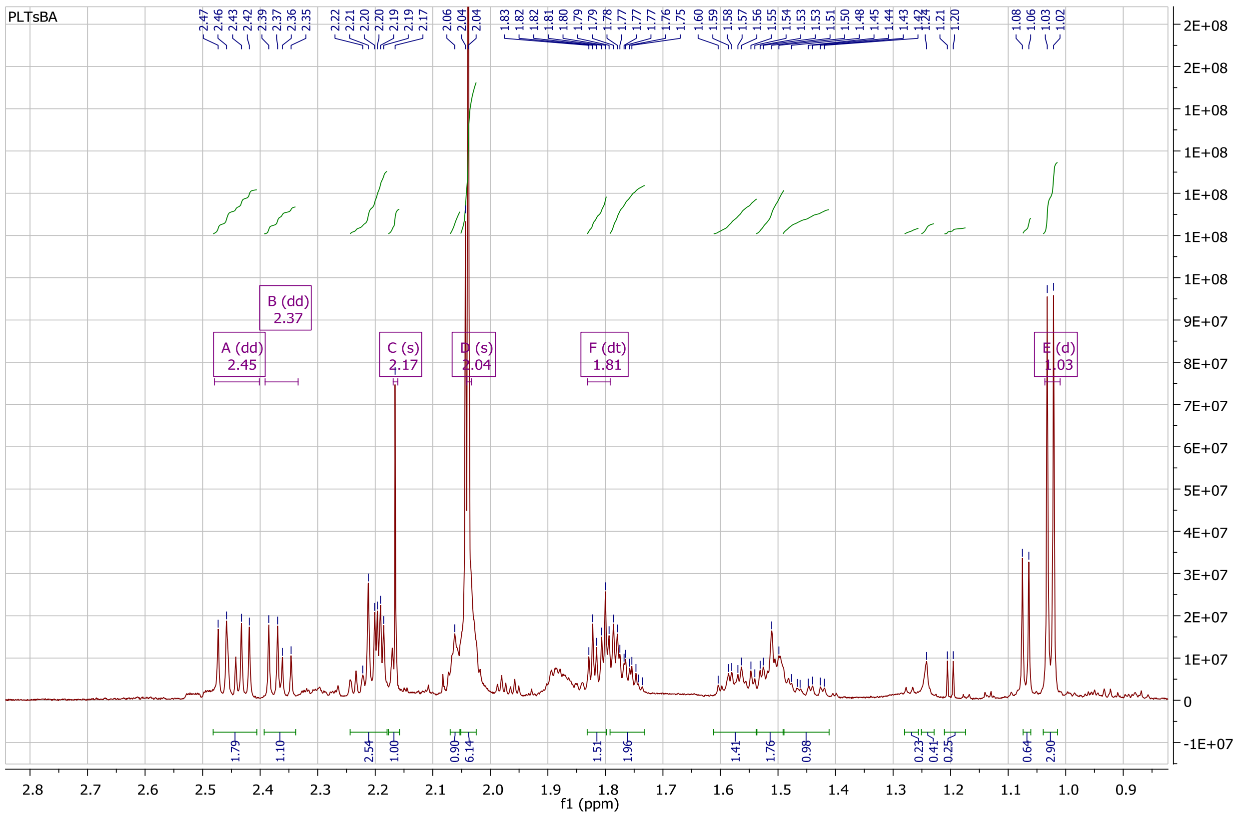

Figure 14. Part of the [1]H NMR spectrum of **2**.

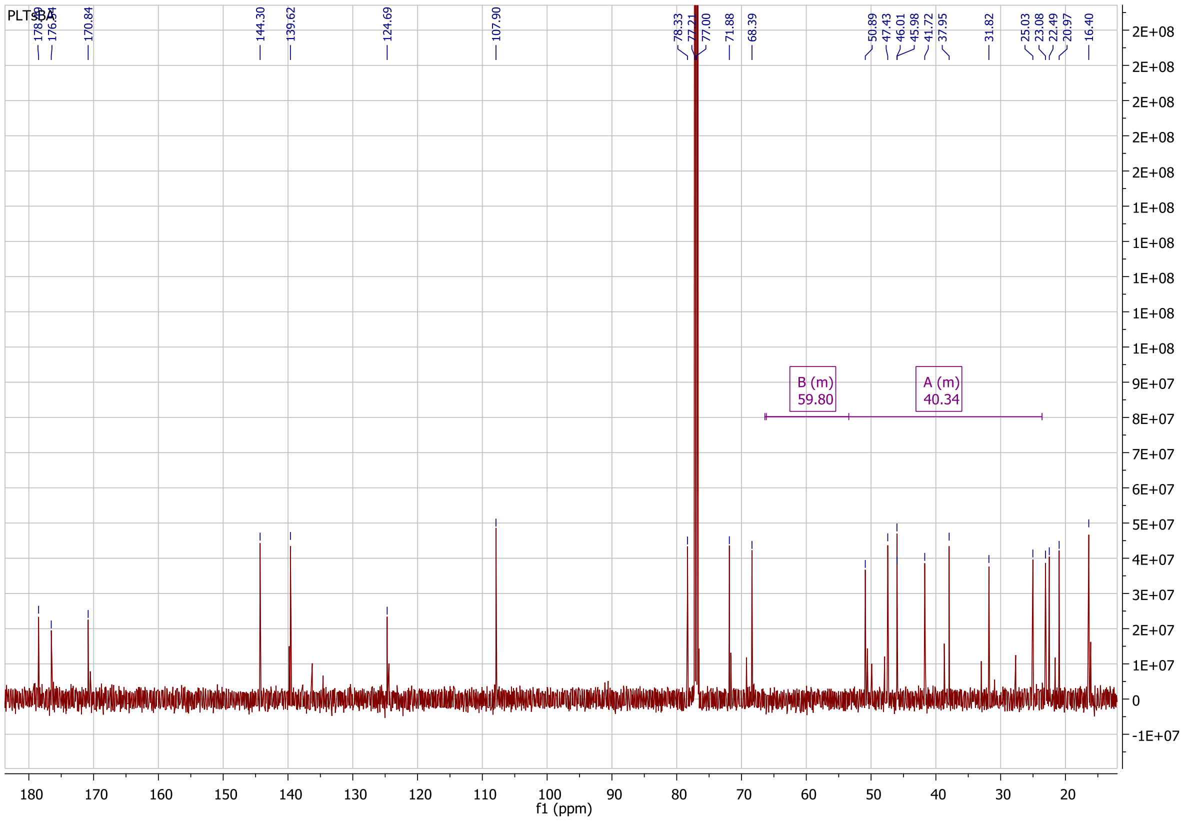

Figure 15. The [1]H-broadband-decoupled [13]C NMR spectrum of **2**.

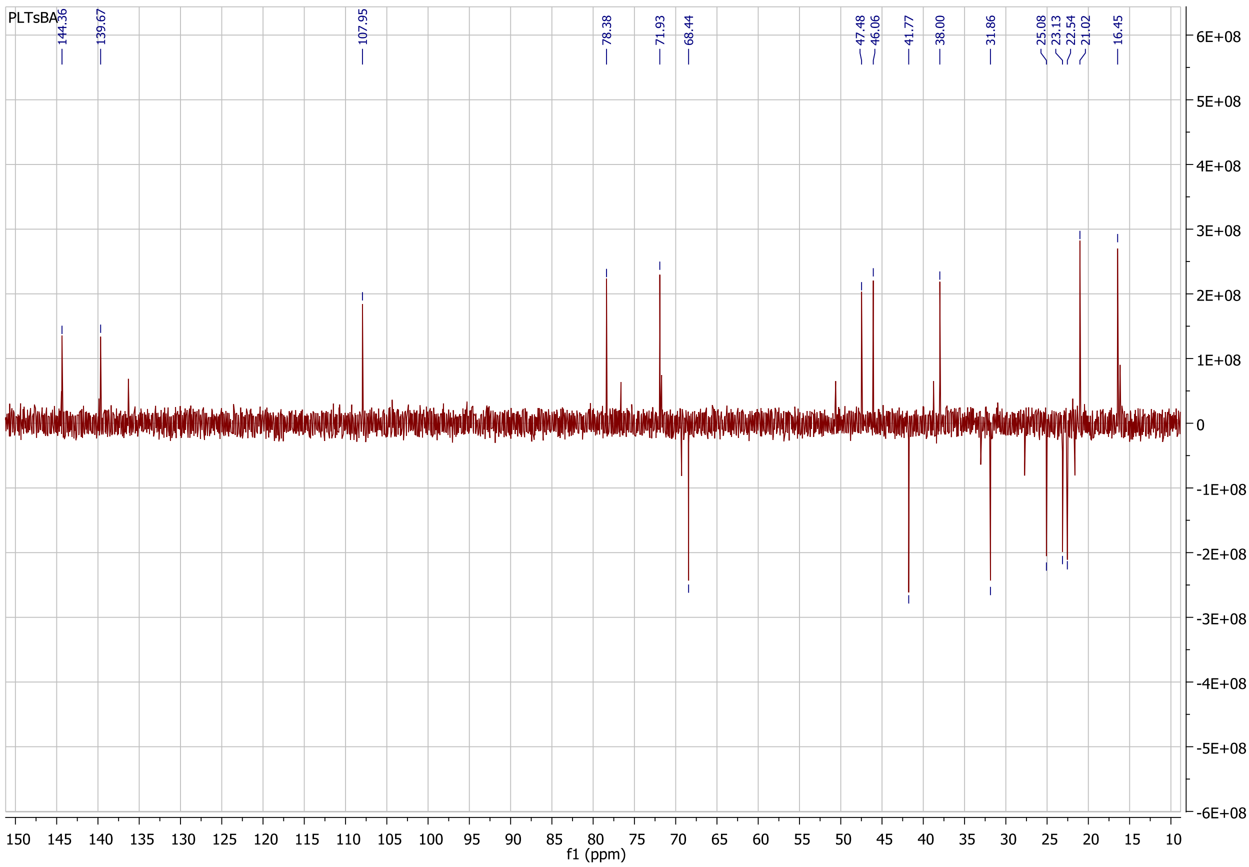

Figure 16. The DEPT 135° [13]C NMR spectrum of **2**.

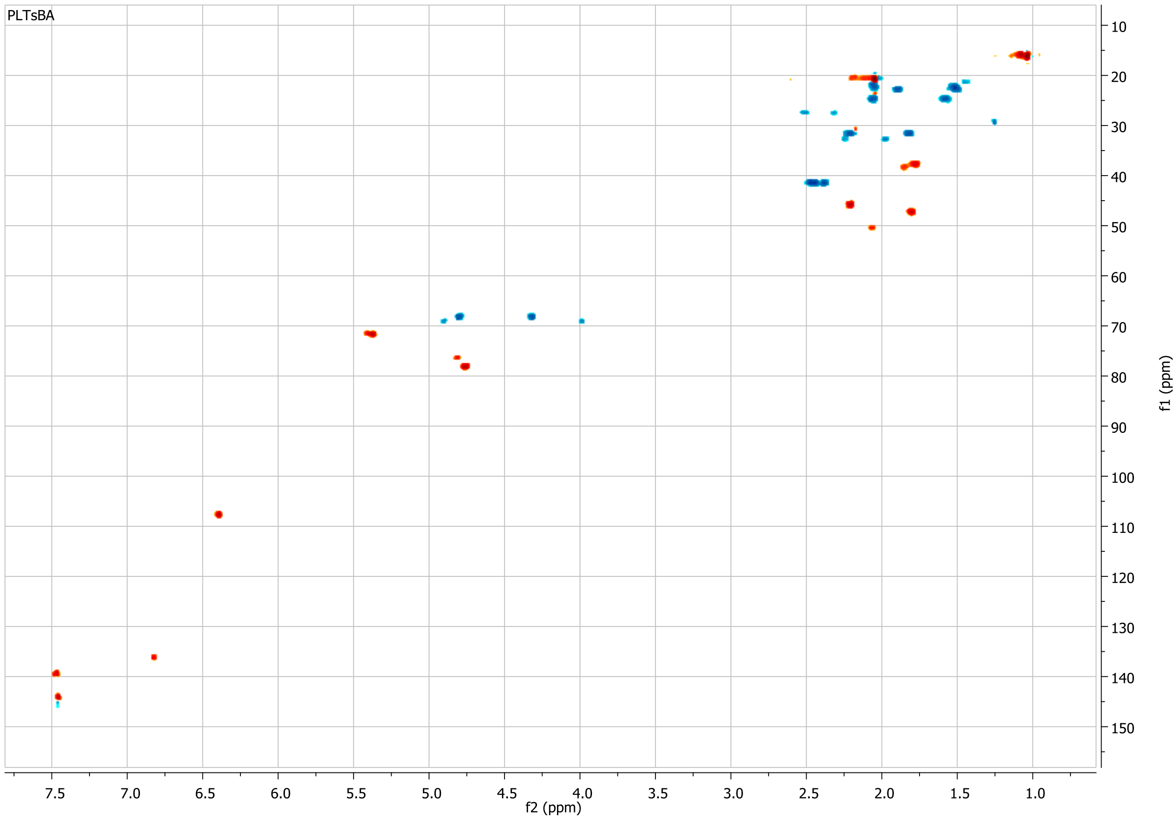

Figure 17. The HSQC spectrum of **2**. The resonances denoted in blue are negative and are for CH_2 groups.

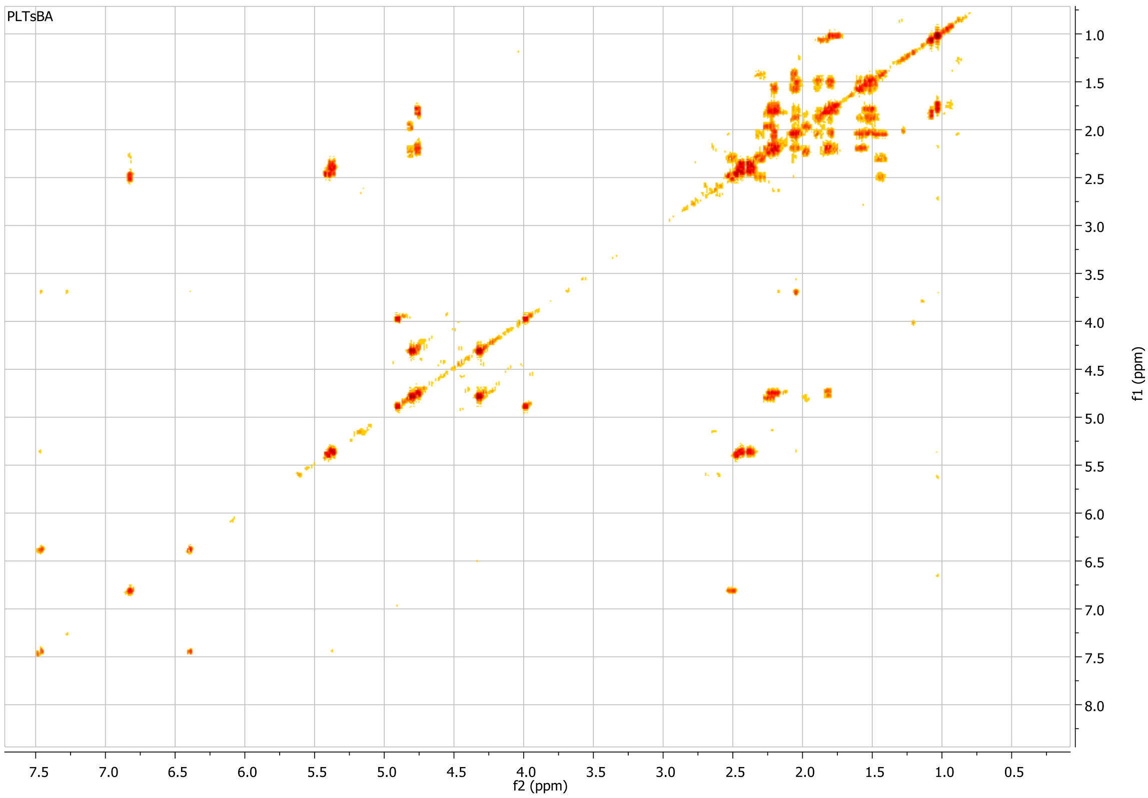

Figure 18. The COSY spectrum of **2**.

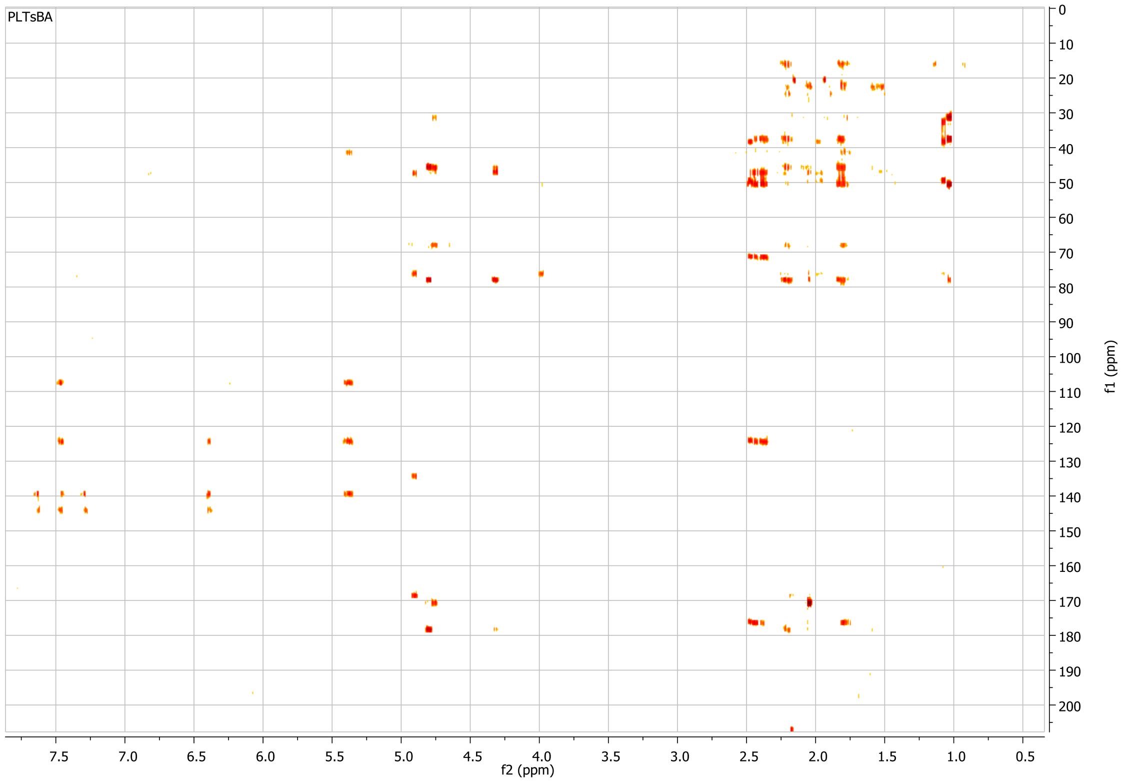

Figure 19. The HMBC spectrum of **2**.

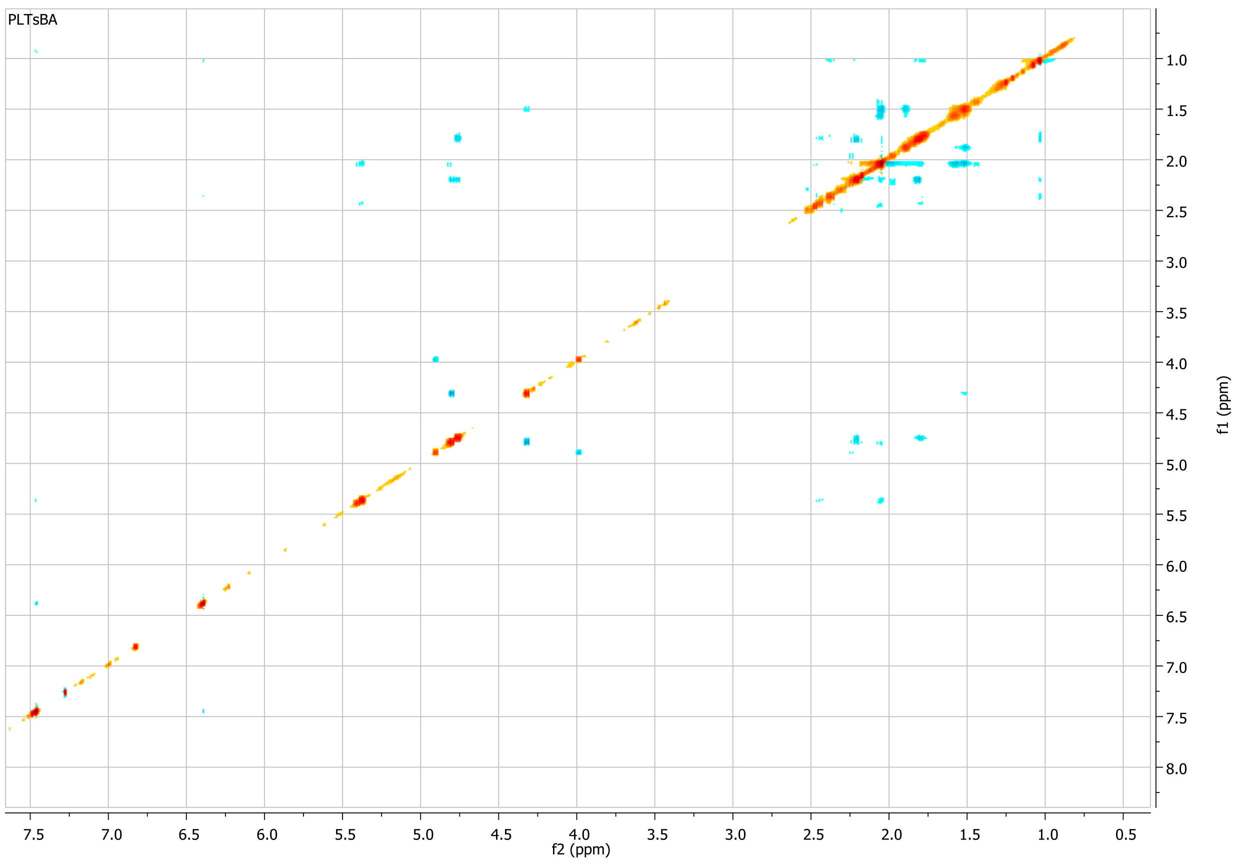

Figure 20. The NOESY spectrum of **2**.

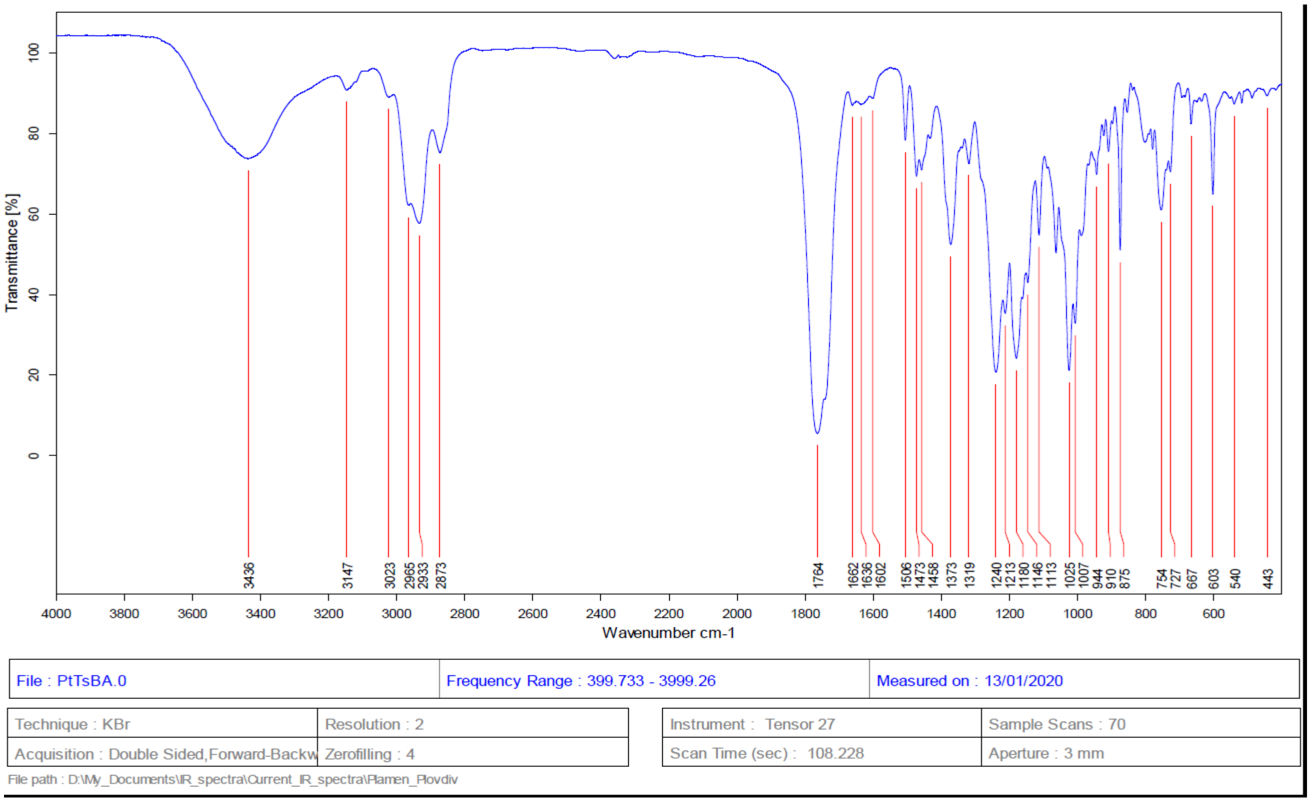

Figure 21. IR spectrum of **2**.

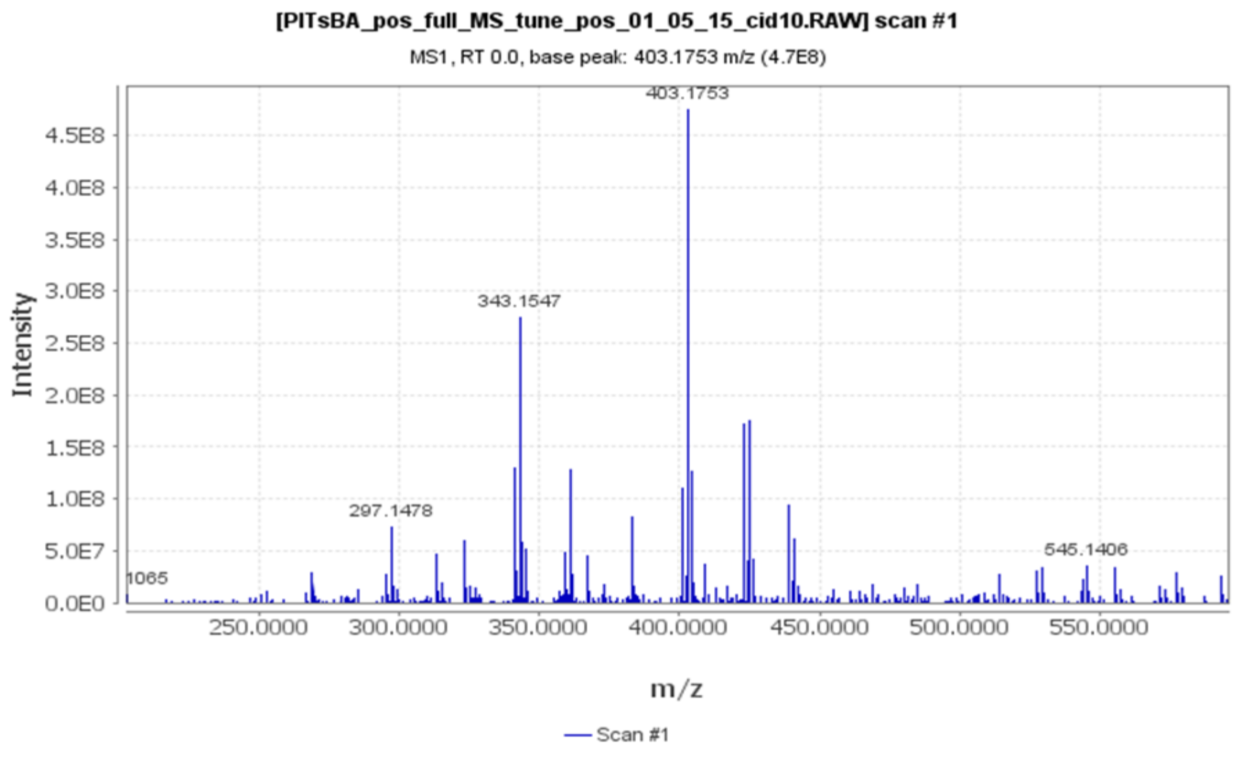

Figure 22. HRESIMS spectrum of **2**.

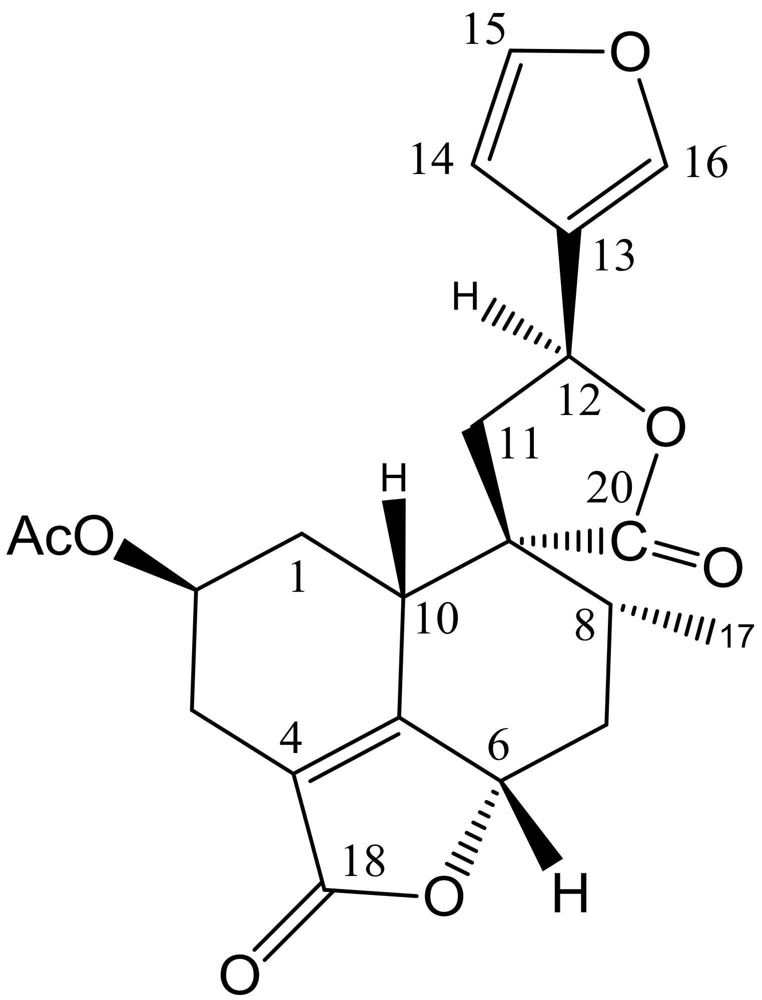

Figure 23. Structure of teuscordesin (**3**)

Table 3. ^{1}H and ^{13}C NMR spectral data[a,] and ^{1}H-^{1}H COSY, HMBC and NOESY correlations for **3**

position	**δ ^{13}C, nH**	**δ ^{1}H**	**m, *J* (in Hz)**	**^{1}H-^{1}H COSY**	**HMBC**	NOESY
1	27.9, CH_2	2.17 (α)[c] 1.68 (β)	ov m[c] ov m[c]	1β, 2α, 3α, 3β, 10β 1α, 2α, 10β	7^2 -	1β, 2β, 3β 1α, 2β, 3β, 10β
2	60.4, CH	5.60 eq (α)	br s	1α, 1β, 10β	-	1α, 1β, 3α, 3β
3	19.9, CH_2	2.13 (α) 1.66 (β)	ov m[c] ov m[c]	1β, 2α 1α, 2α	7^2 -	2β 1β, 2β, 10β
4	124.7, C	-	-	-	-	-
5	167.5, C	-	-	-	-	-
6	78.0, CH	4.82 (β)	dd, 10.1; 7.4	7α, 7β	-	7β, 8β, 10β
7	34.8, CH_2	2.24 (α) 2.37 (β)	ddd, 14.2;12.6;10.1 m[c]	6β, 7β, 8β 6β, 7α, 8β	- 6, 8	7β, 17 6β, 7α, 17
8	35.7, CH	1.94 (β)	ddq, 12.6; 3.3; 6.8	7β, 7α, 17	-	6β, 10β, 11, 17
9	53.6, C	-	-	-	-	-
10	42.0, CH	2.68 (β)	m	1α, 1β, 2β	-	1β, 3β, 6β, 8β, 11
11	40.7, CH_2	2.58 A 2.58 B	d, 8.5 d, 8.5	12	8, 9, 10, 12, 13, 20	8β,10β, 12, 14, 16, 17
12	71.2, CH	5.46	t, 8.5	11	13, 14, 16	11, 14, 16
13	124.1, C	-	-	-	-	-
14	107.9, CH	6.40	br s	15 or 16	13, 15, 16	11, 12, 15, 17
15	144.3, CH	7.46	t, 1.6	14	16	14,
16	139.6, CH	7.47	br s	14	13, 14, 15	11, 12, 17
17	16.9, CH_3	1.09	d, 6.8	8	6, 7, 9	7α, 7β, 8β, 11β, 14, 16
18	170.7, C	-	-	-	-	-
20	174.9, C	-	-	-	-	-
7^1 (CO)	170.5, C	-	-	-	-	-
7^2 (CH_3)	21.2, CH_3	2.15	s	-	7^1, 7	3α

[a] $CDCl_3$, ^{1}H 600.01 MHz, δ_{ref} 7.26; ^{13}C 150.89 MHz, δ_{ref} 77.0 ppm, TMS as an internal standard; [b] δ_H data from HSQC; ov – overlapped signal.

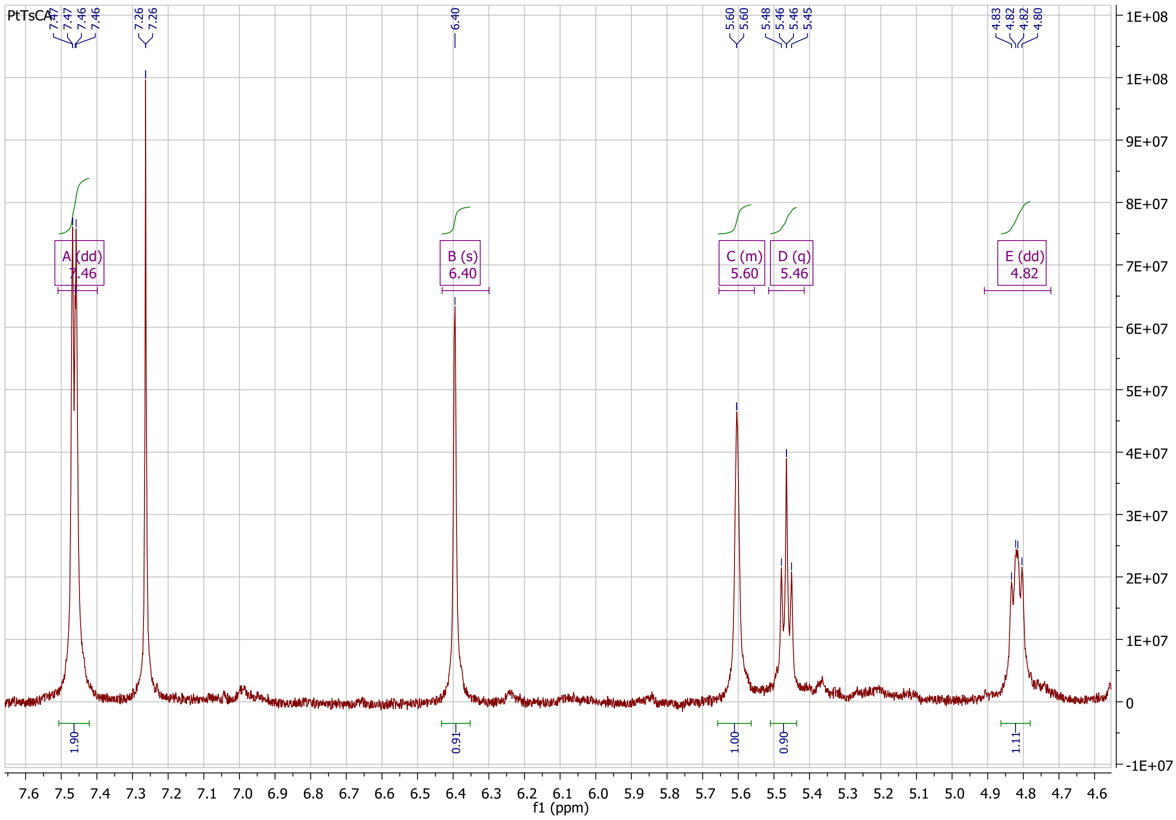

Figure 24. Part of the ^{1}H NMR spectrum of **3**.

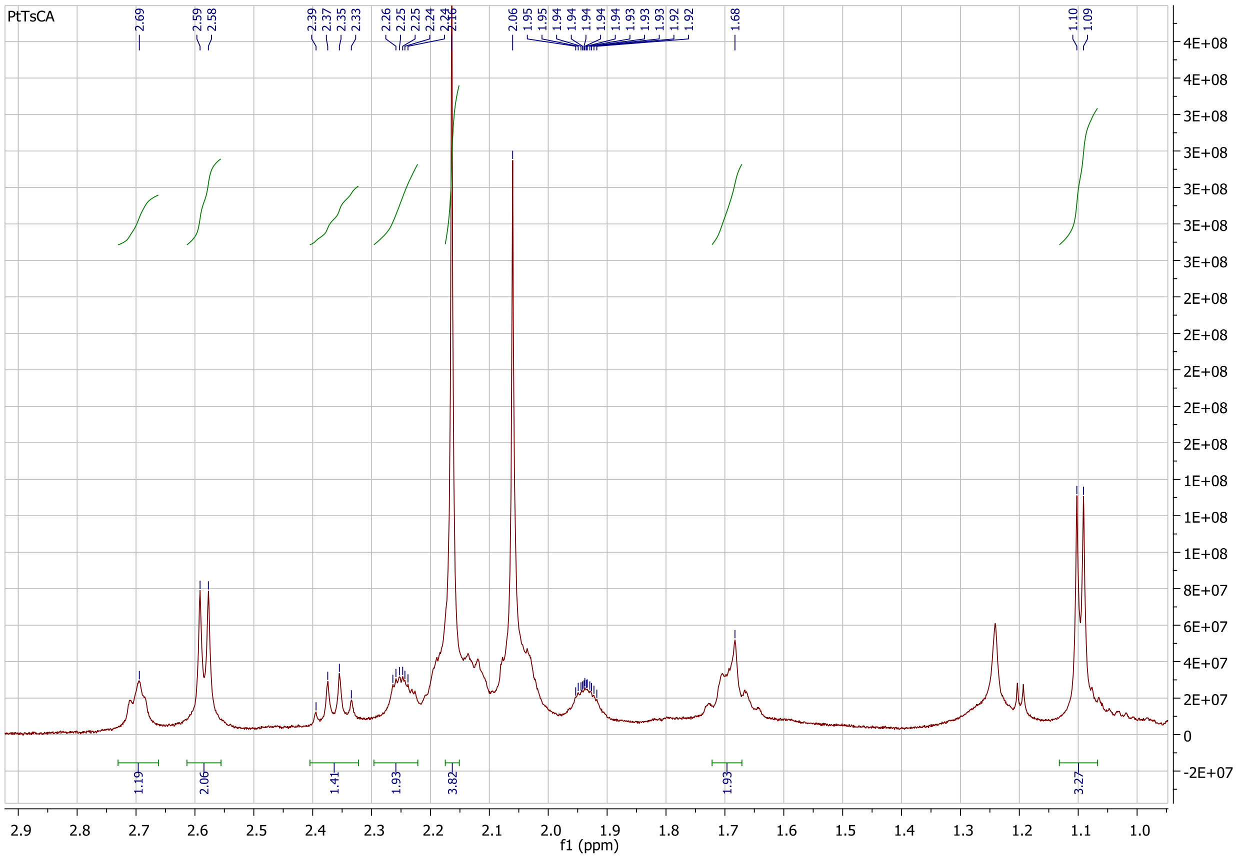

Figure 25. Part of the ^{1}H NMR spectrum of **3**.

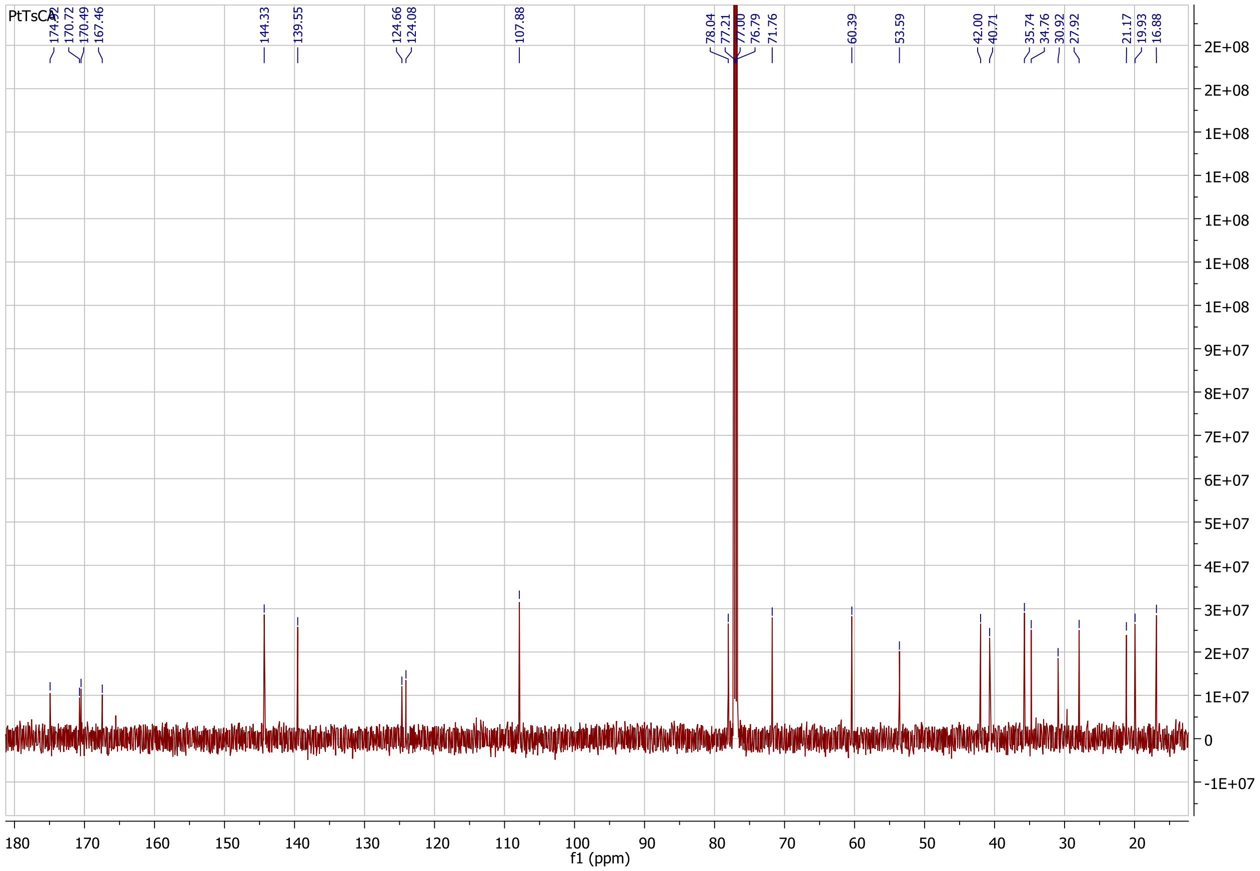

Figure 26. The ^{1}H-broadband-decoupled ^{13}C NMR spectrum of **3**.

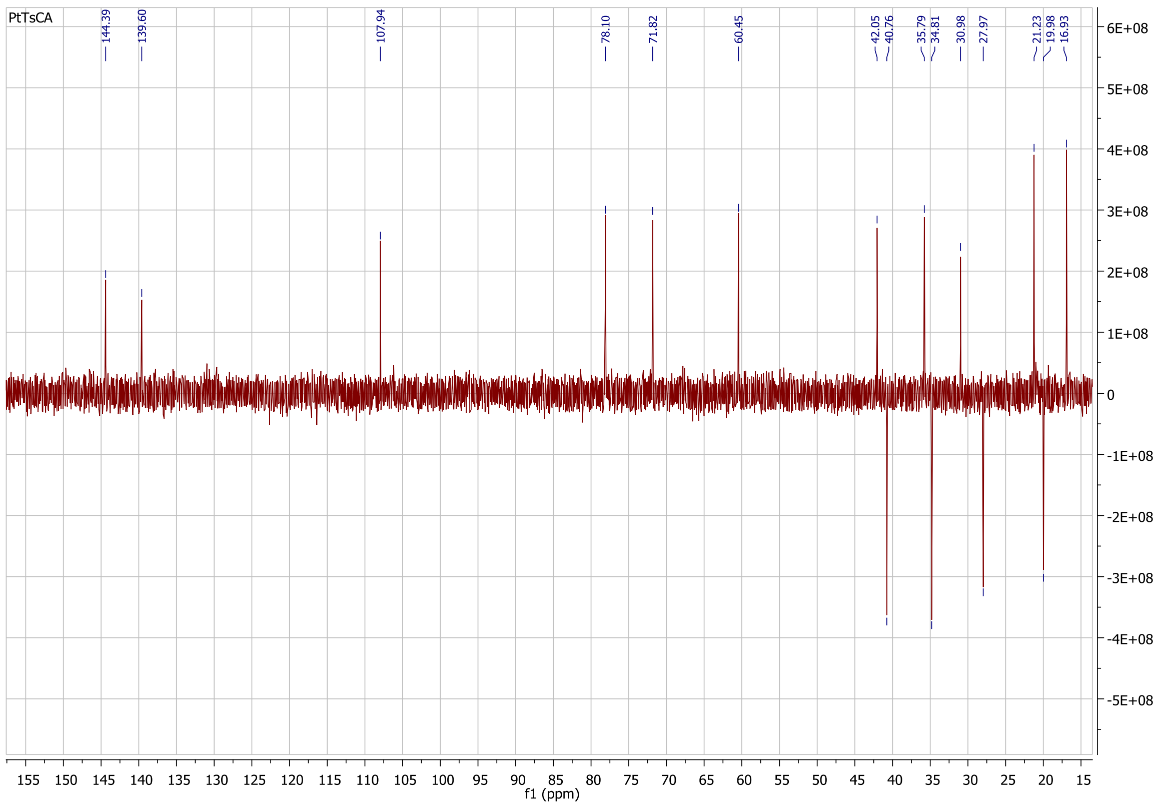

Figure 27. The DEPT 135^{o} ^{13}C NMR spectrum of **3**.

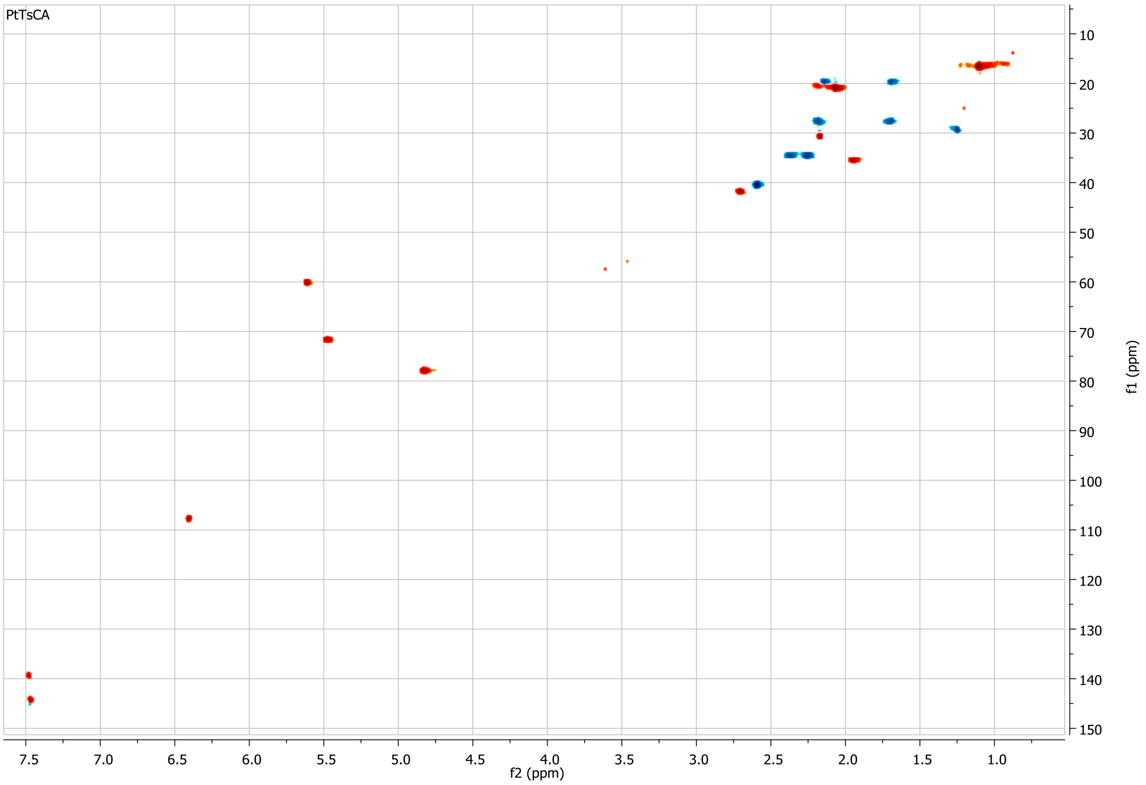

Figure 28. The HSQC spectrum of **3**. The resonances denoted in blue are negative and are for CH_2 groups.

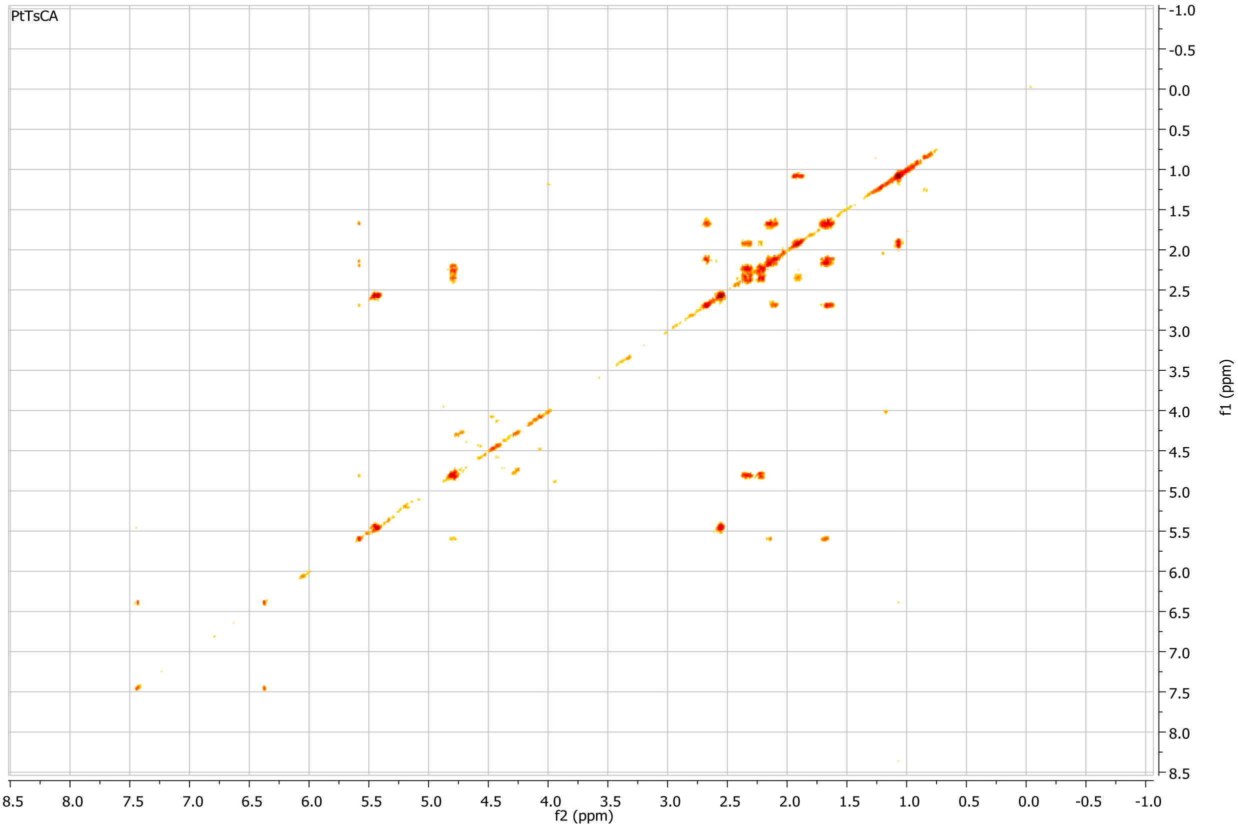

Figure 29. The COSY spectrum of **3**.

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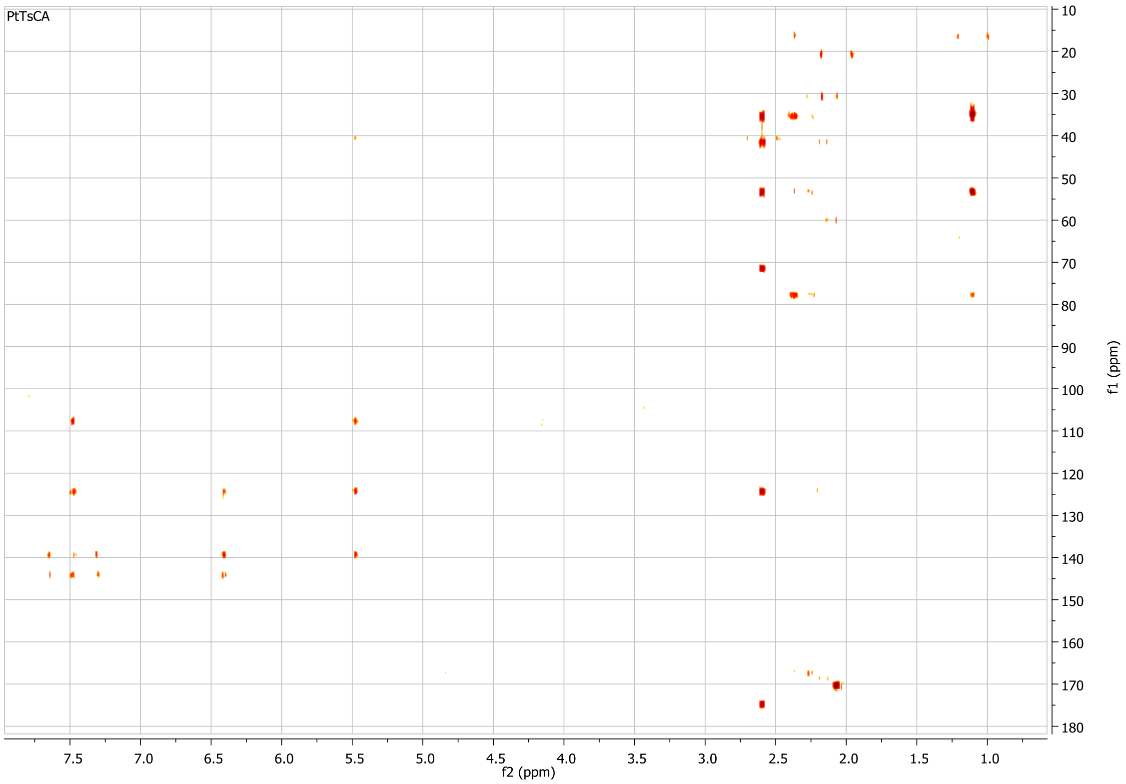

Figure 30. The HMBC spectrum of **3**.

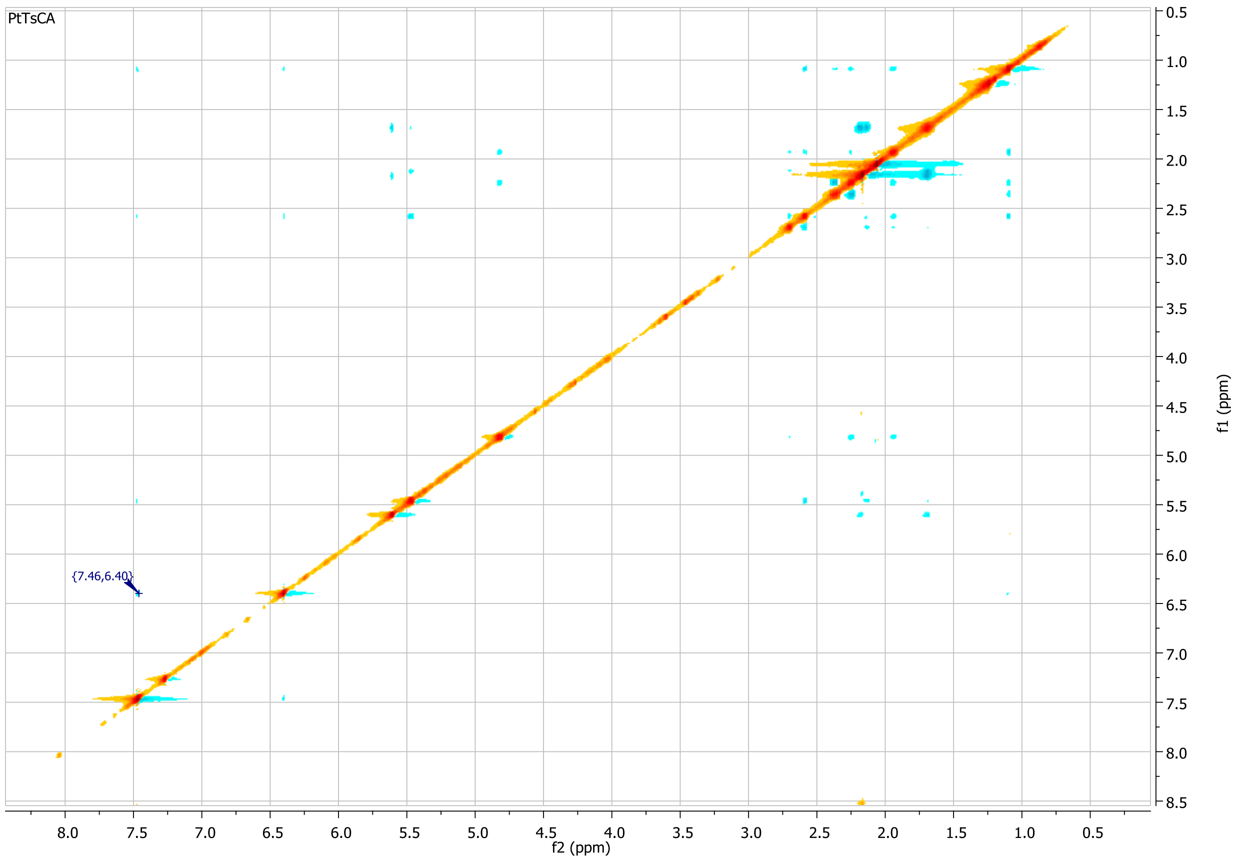

Figure 31. The NOESY spectrum of **3**.

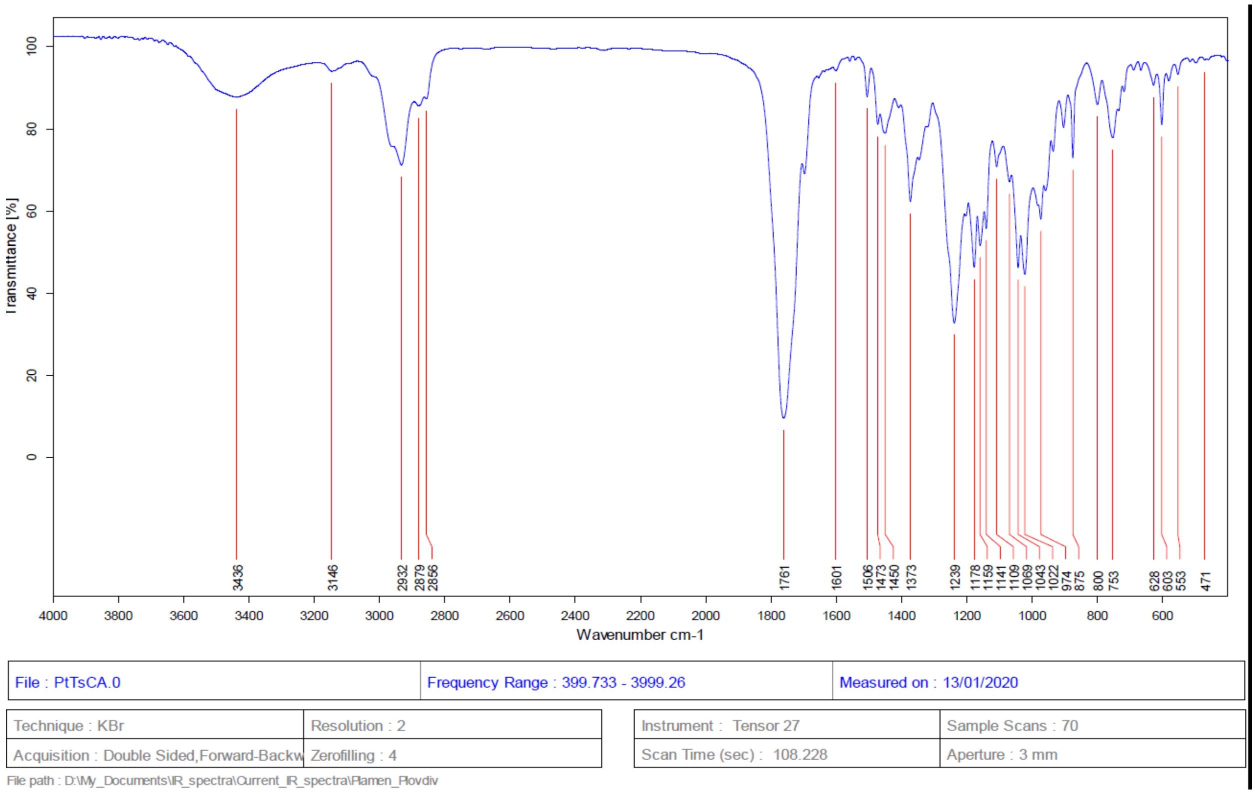

Figure 32. IR spectrum of **3**.

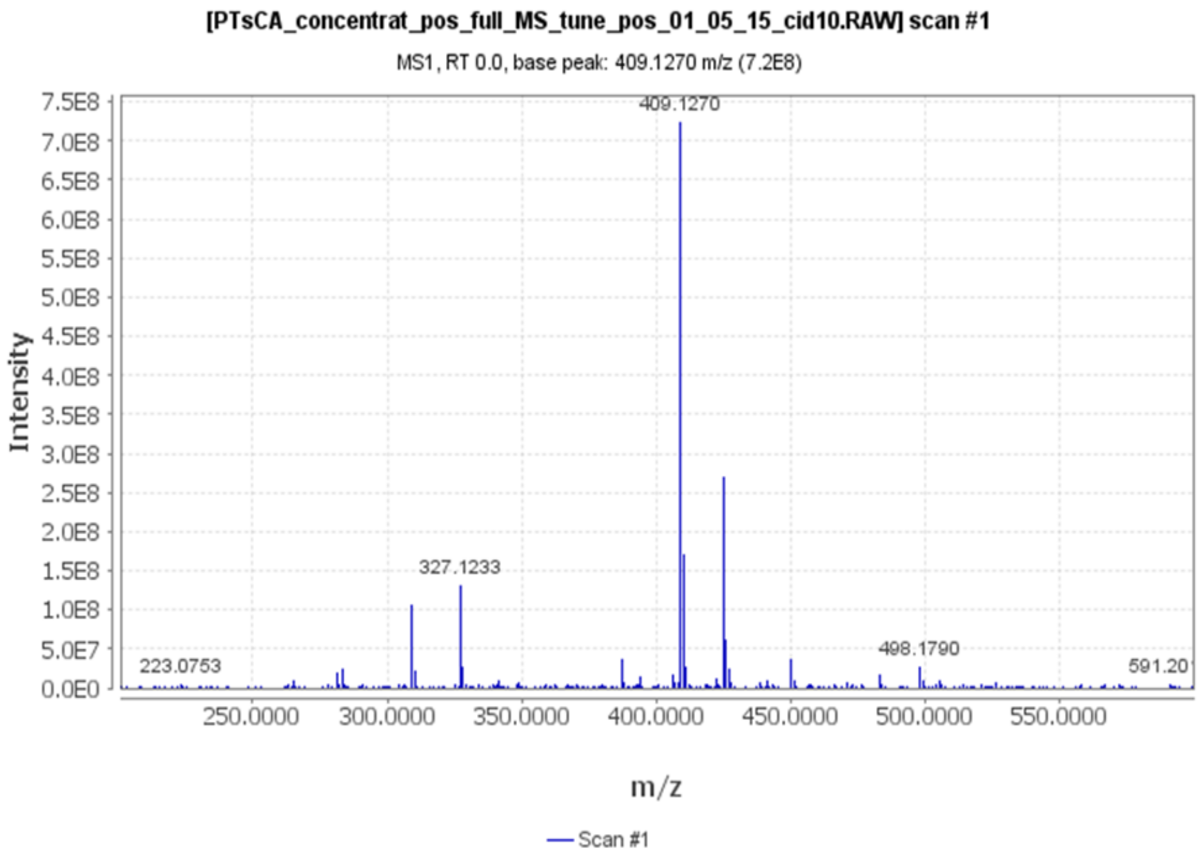

Figure 33. HRESIMS spectrum of **3**.