Micranthuosides I and II, two novel 1,10-secograyanane diterpenoids and their analogues from the leaves and twigs of *Rhododendron micranthum*

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Electronic supplementary information

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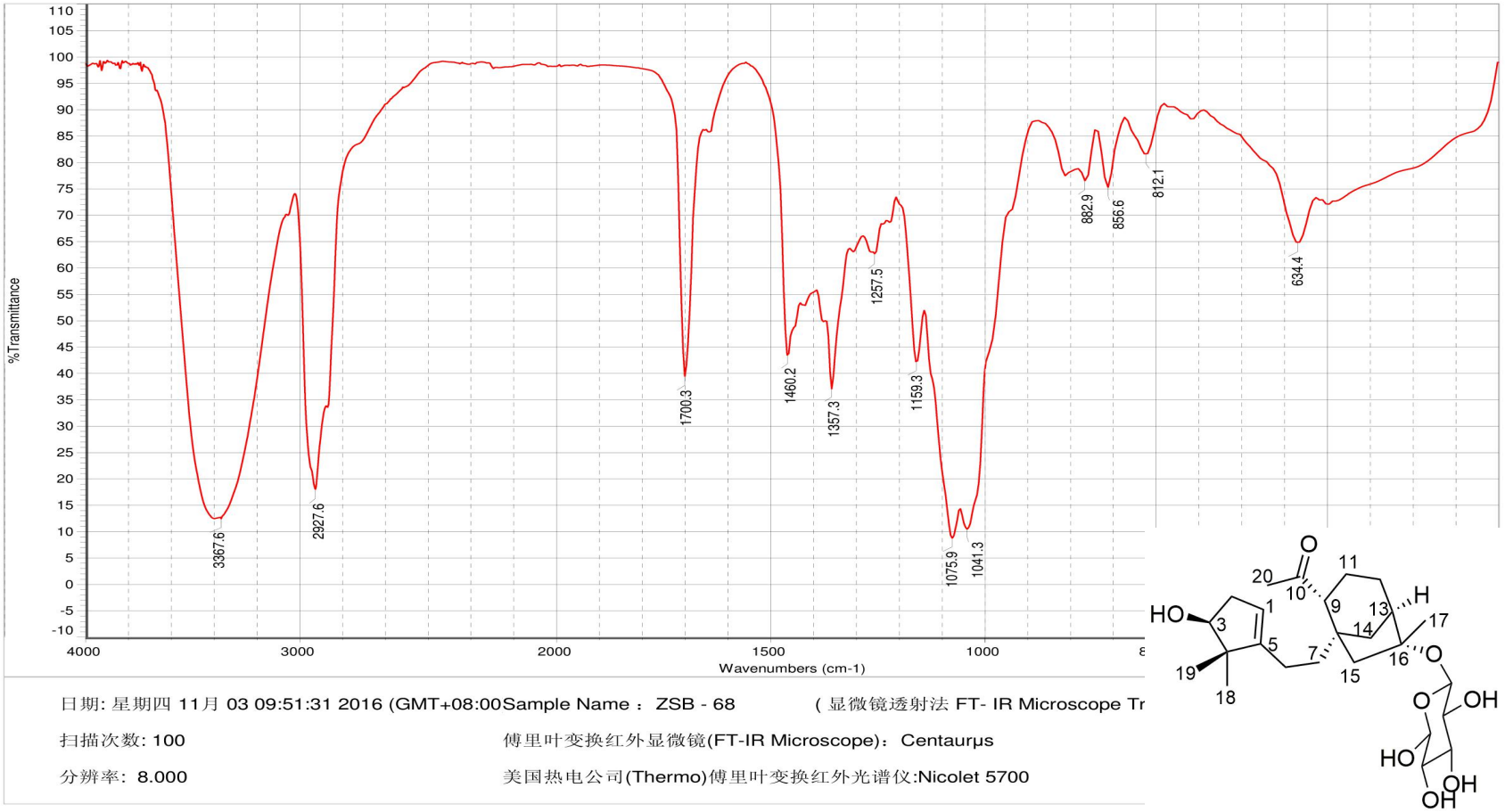
Attached spectra

CD spectra of compounds 1, 2, 12, and 15

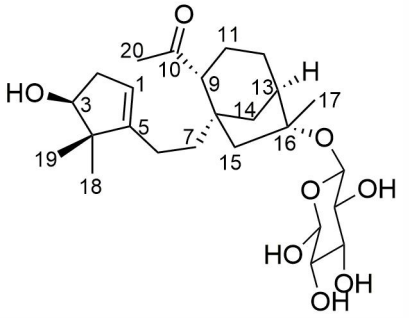


The IR spectrum of **1**

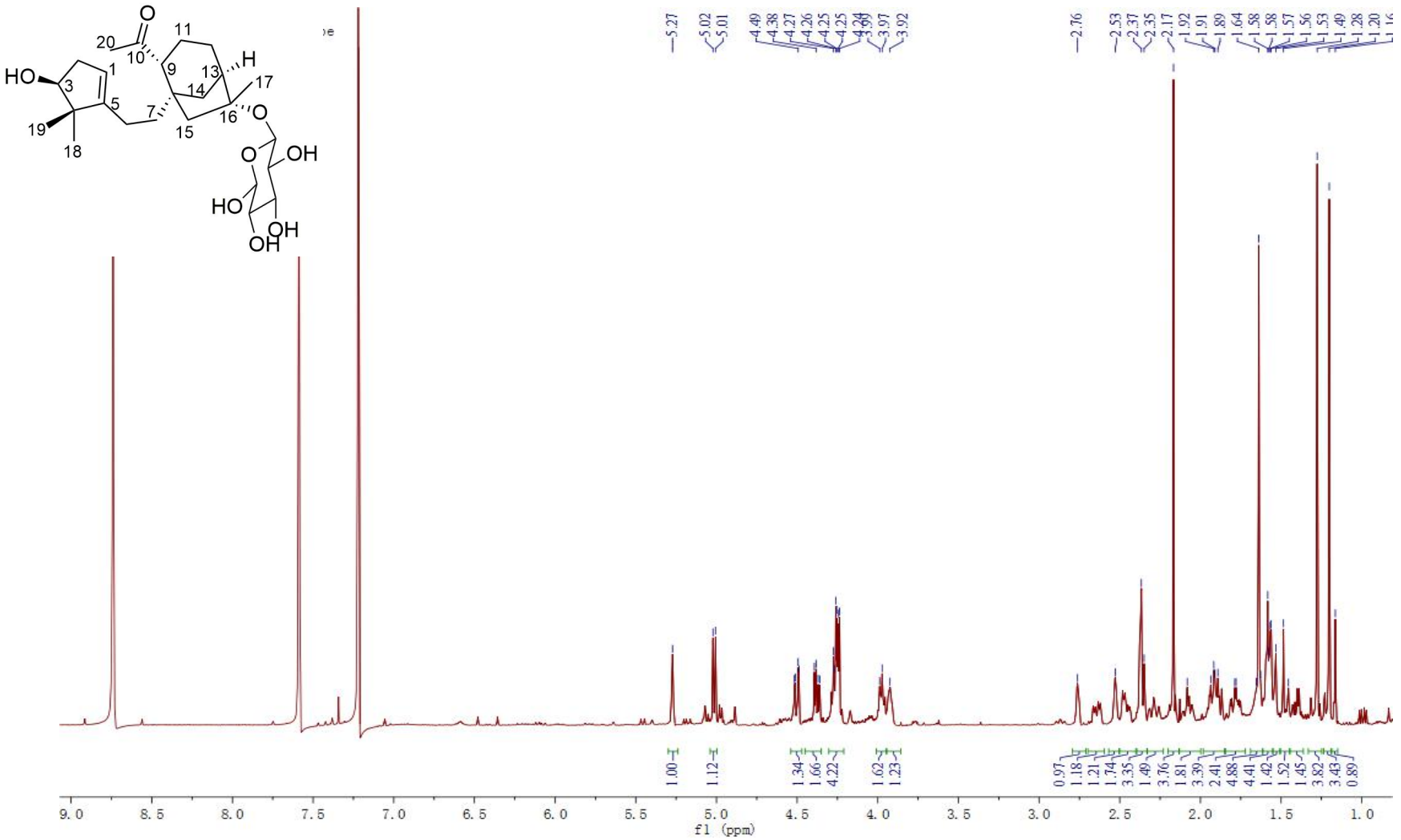
MS Formula Results: + Scan (6.414 min) Sub (2015102206.d)

	m/z	Ion	Formula	Abundance
-	505.2786	(M+Na)+	C26 H42 Na O8	1400111.6

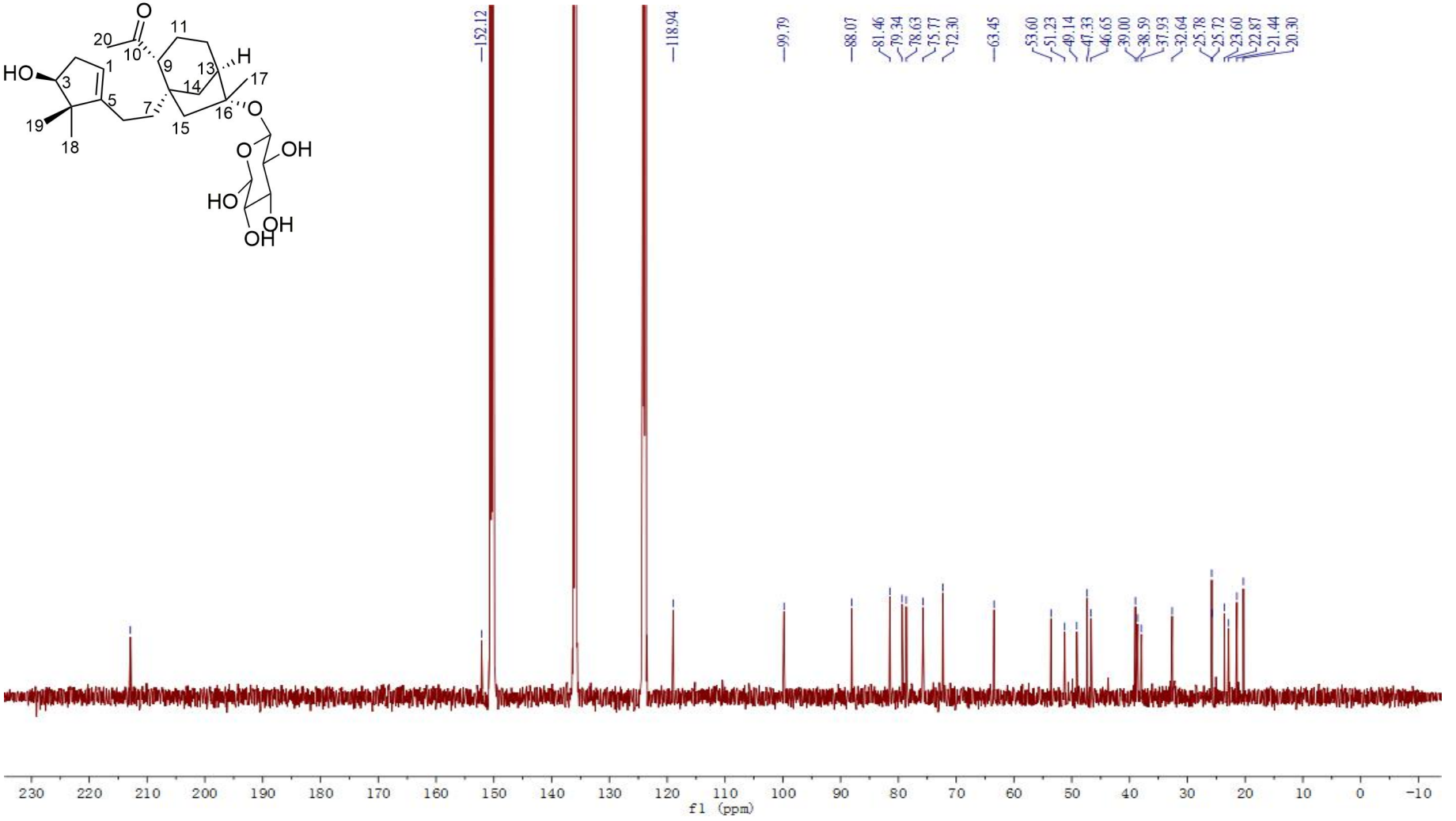
	Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
+	☑	C26 H42 O8	C26 H42 Na O8	99.78		482.2893	482.288	505.2772	-2.83	2.83	99.75	99.67	99.98	6
+	☐	C27 H38 N4 O4	C27 H38 N4 Na O4	99.96		482.2893	482.2893	505.2785	-0.07	0.07	100	99.89	99.99	11
+	☐	C23 H46 O8 S	C23 H46 Na O8 S	98.54		482.2893	482.2913	505.2806	4.15	4.15	99.46	96.03	99.7	1
+	☐	C19 H42 N6 O6 S	C19 H42 N6 Na O6 S	98.28		482.2894	482.2887	505.2779	-1.45	1.45	99.93	94.49	99.53	2
+	☐	C27 H46 O3 S2	C27 H46 Na O3 S2	97.8		482.2893	482.2888	505.2781	-1.04	1.04	99.97	92.82	99.45	5



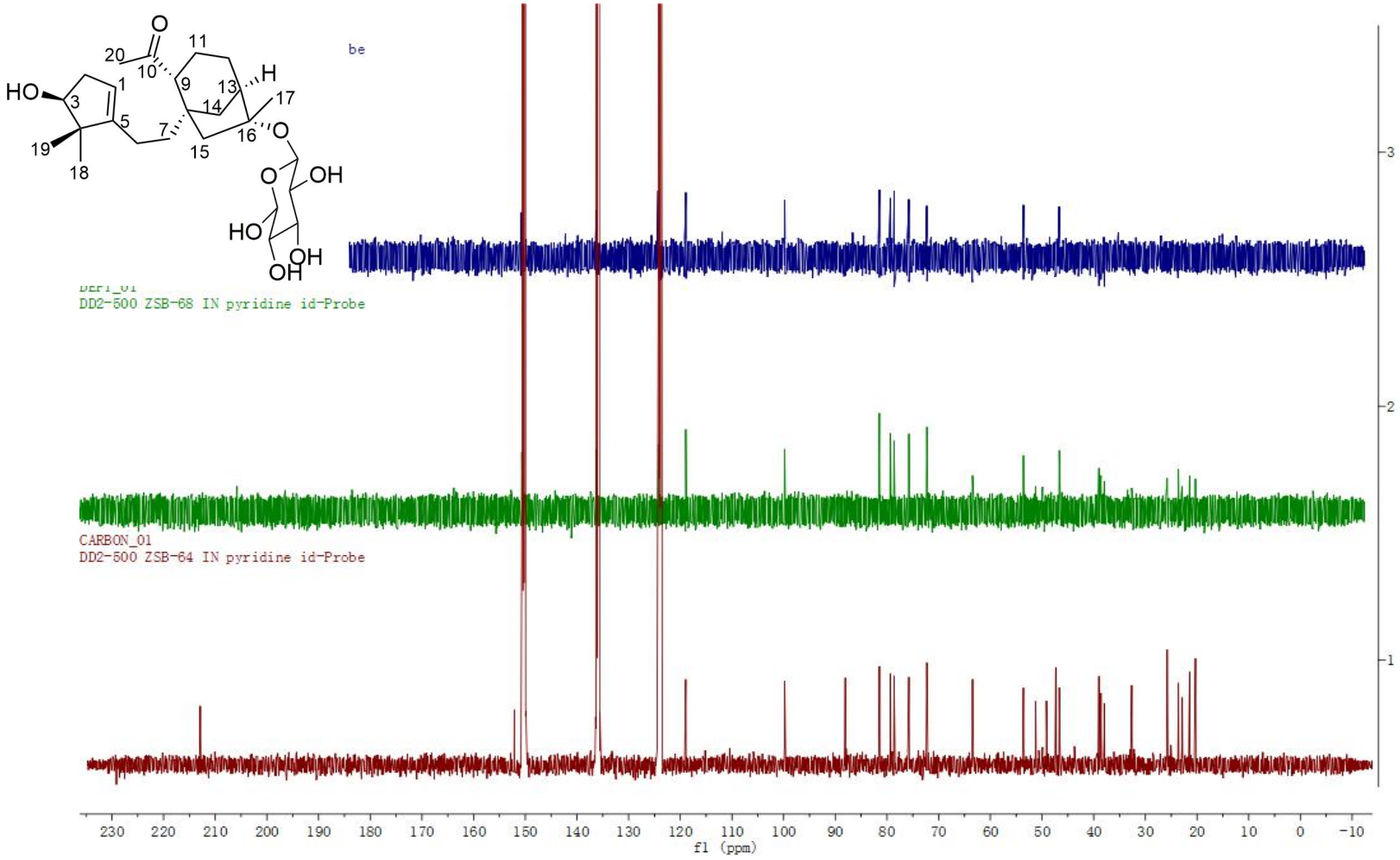
The HRESIMS spectrum of **1**



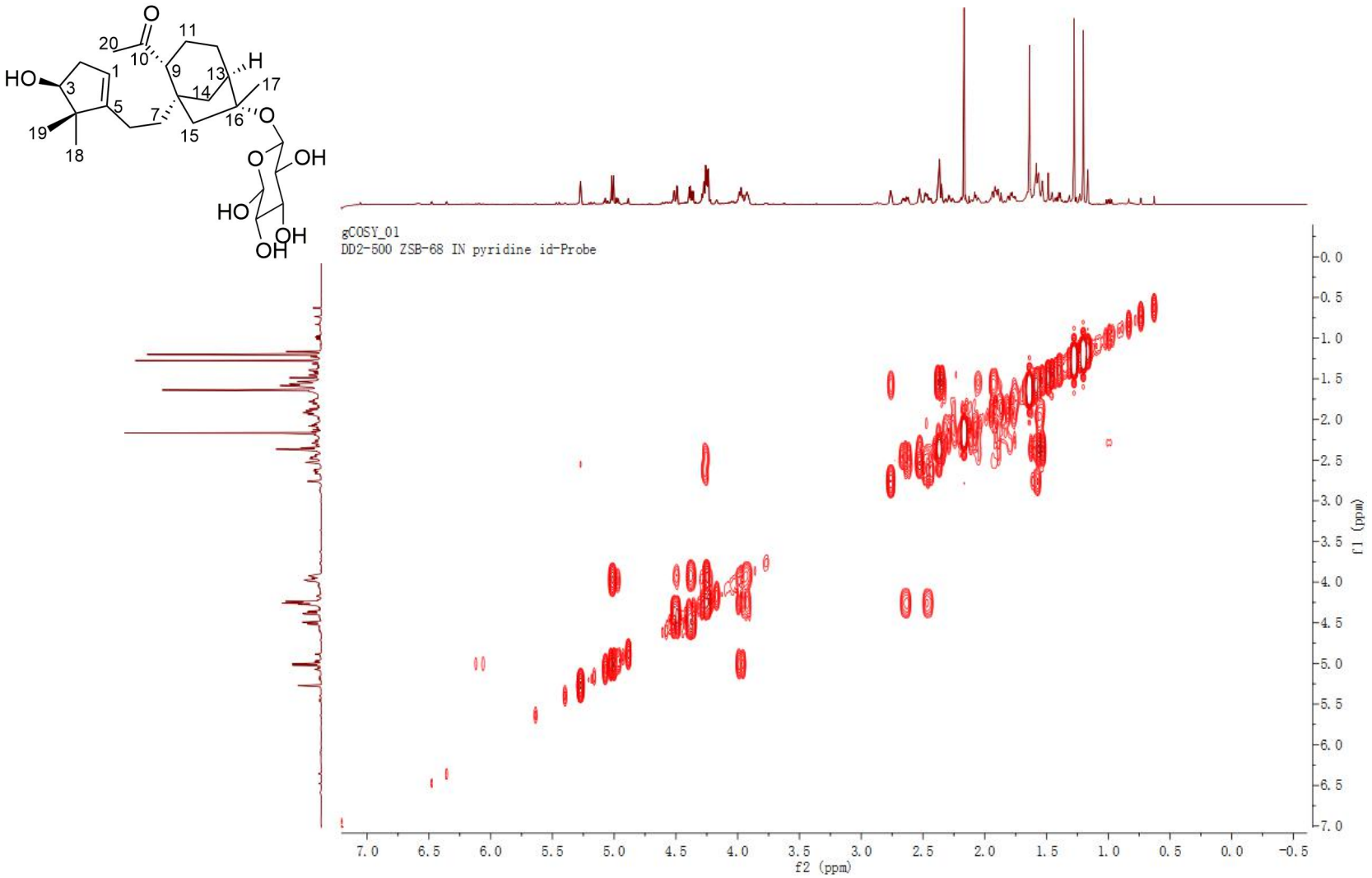
The ^{1}H NMR spectrum of **1** in C_5D_5N (500 MHz)



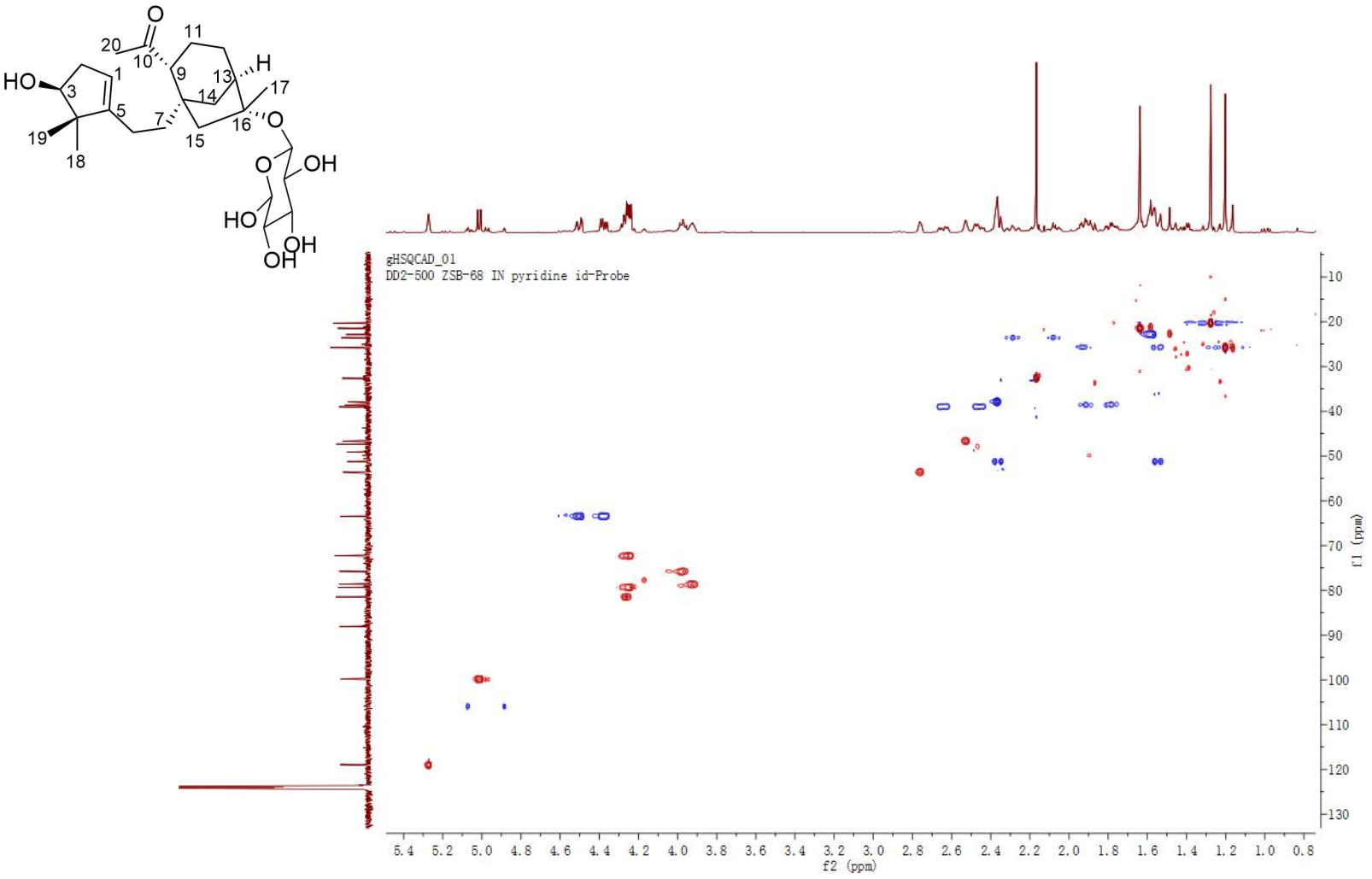
The ^{13}C NMR spectrum of **1** in C_5D_5N (125 MHz)



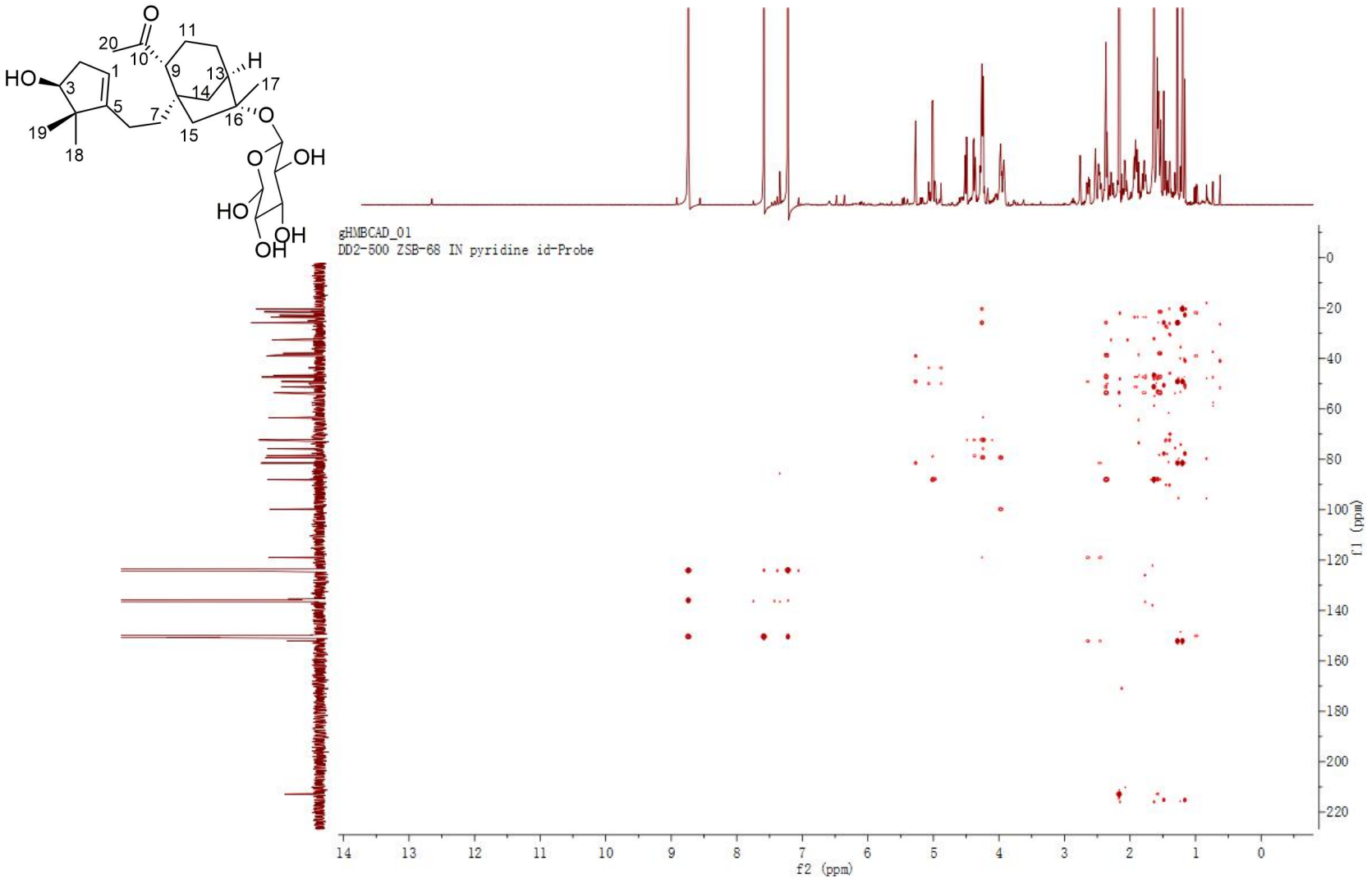
The DEPT spectrum of **1** in C_5D_5N (125 MHz)



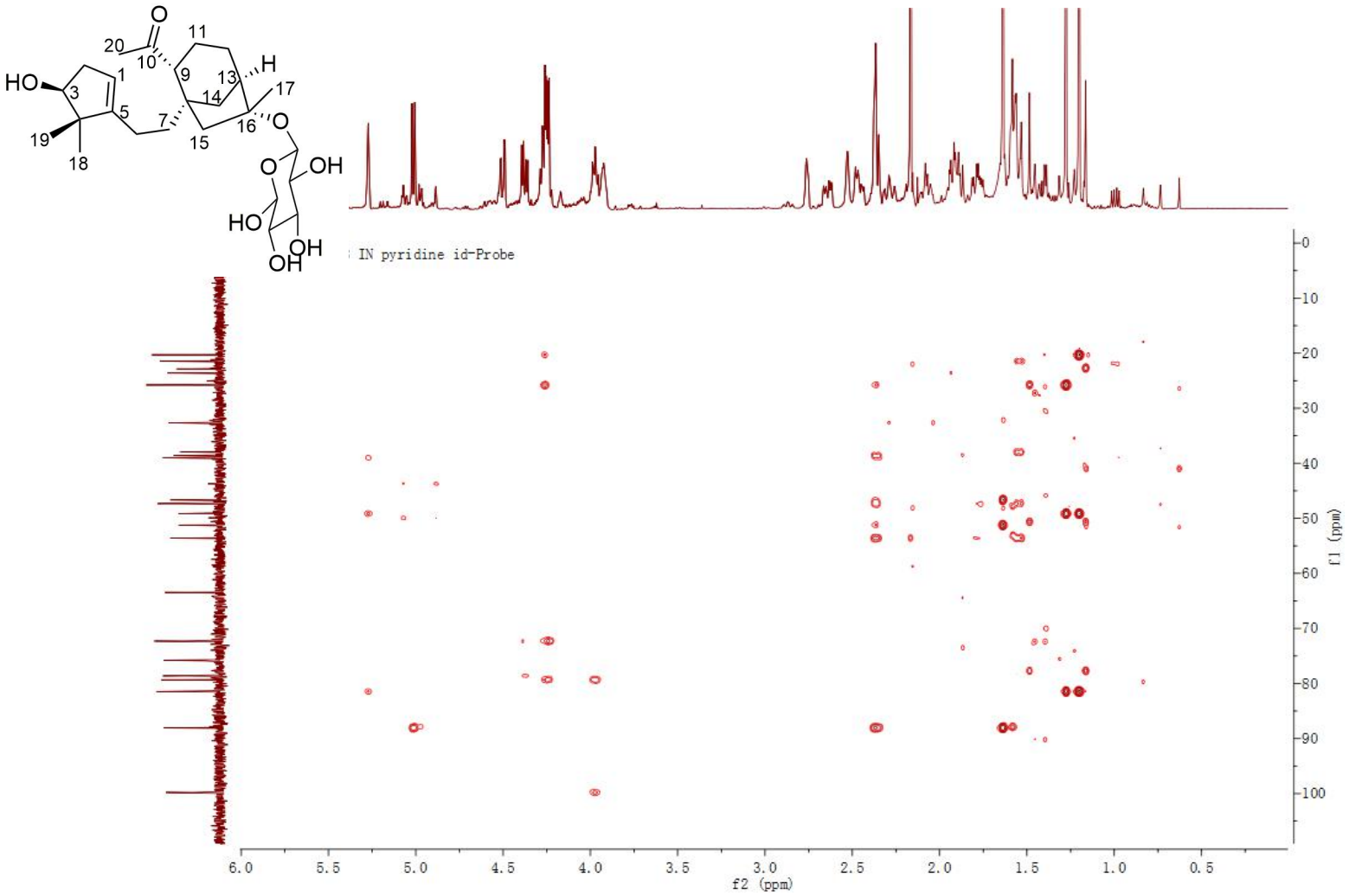
The COSY spectrum of **1** in C_5D_5N (500 MHz)



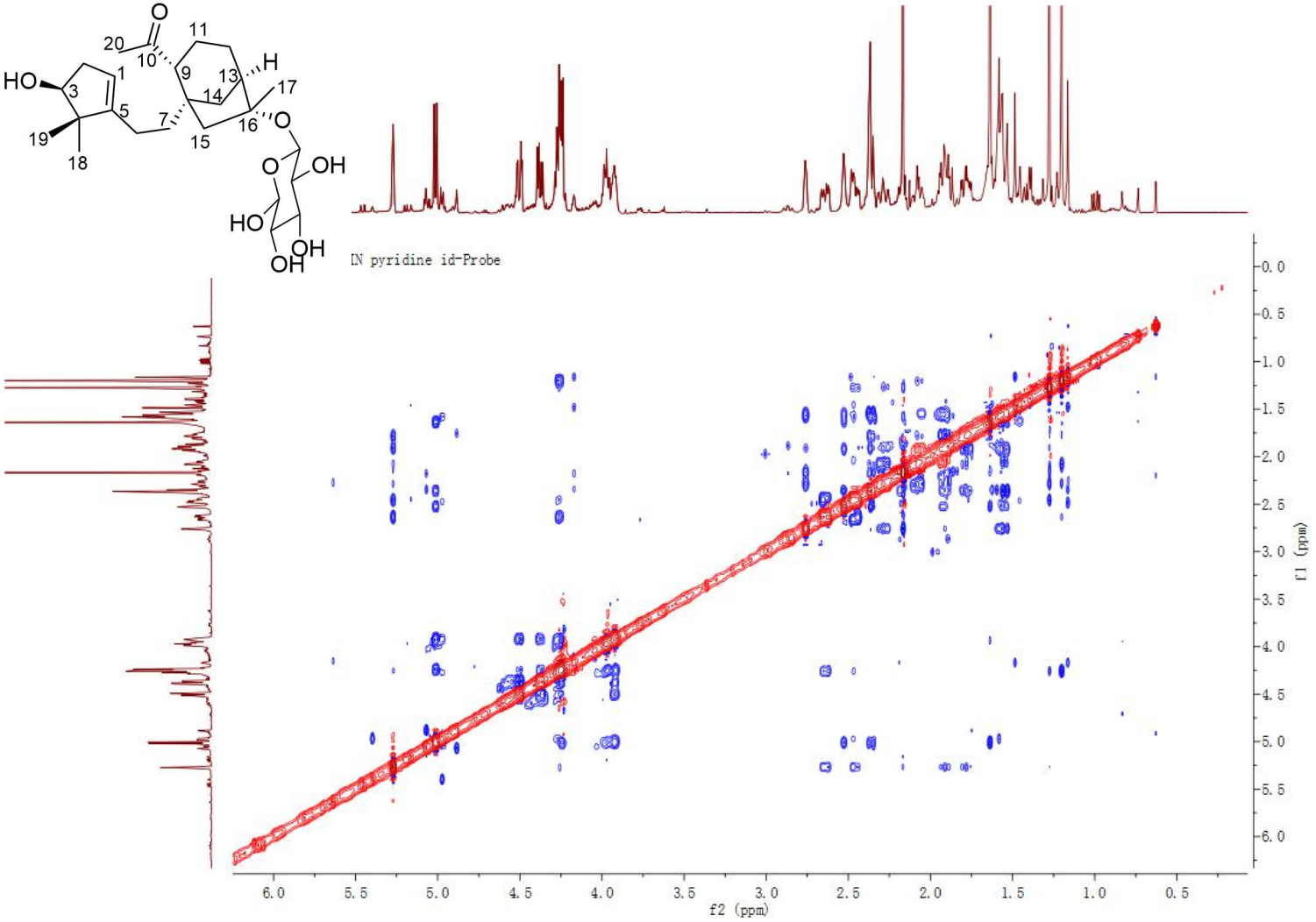
The HSQC of **1** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



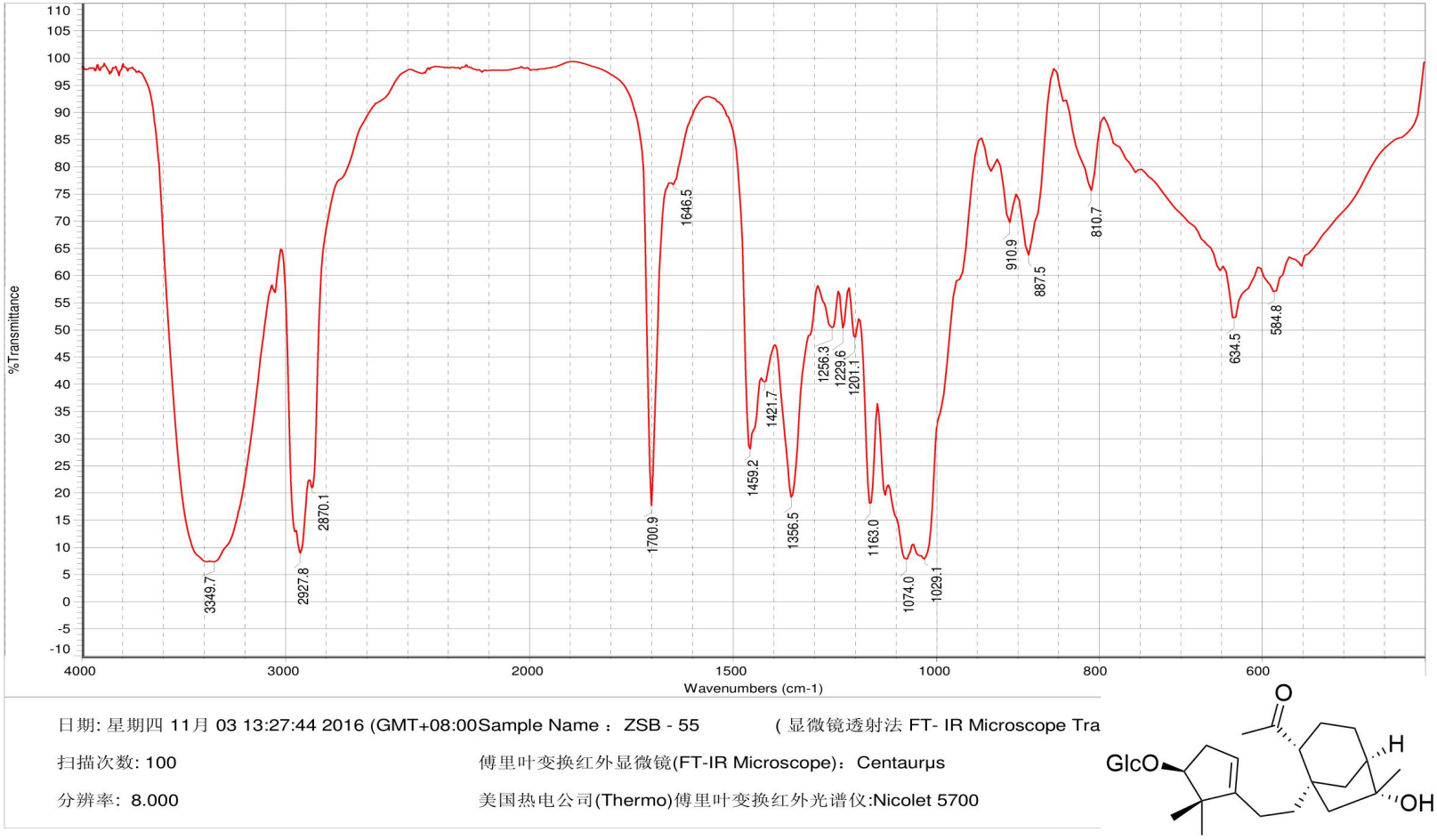
The HMBC spectrum of **1** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The HMBC spectrum (amplified) of **1** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The NOESY spectrum of **1** in C_5D_5N (500 MHz)

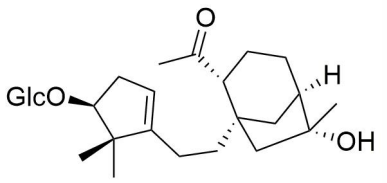


The IR spectrum of **2**

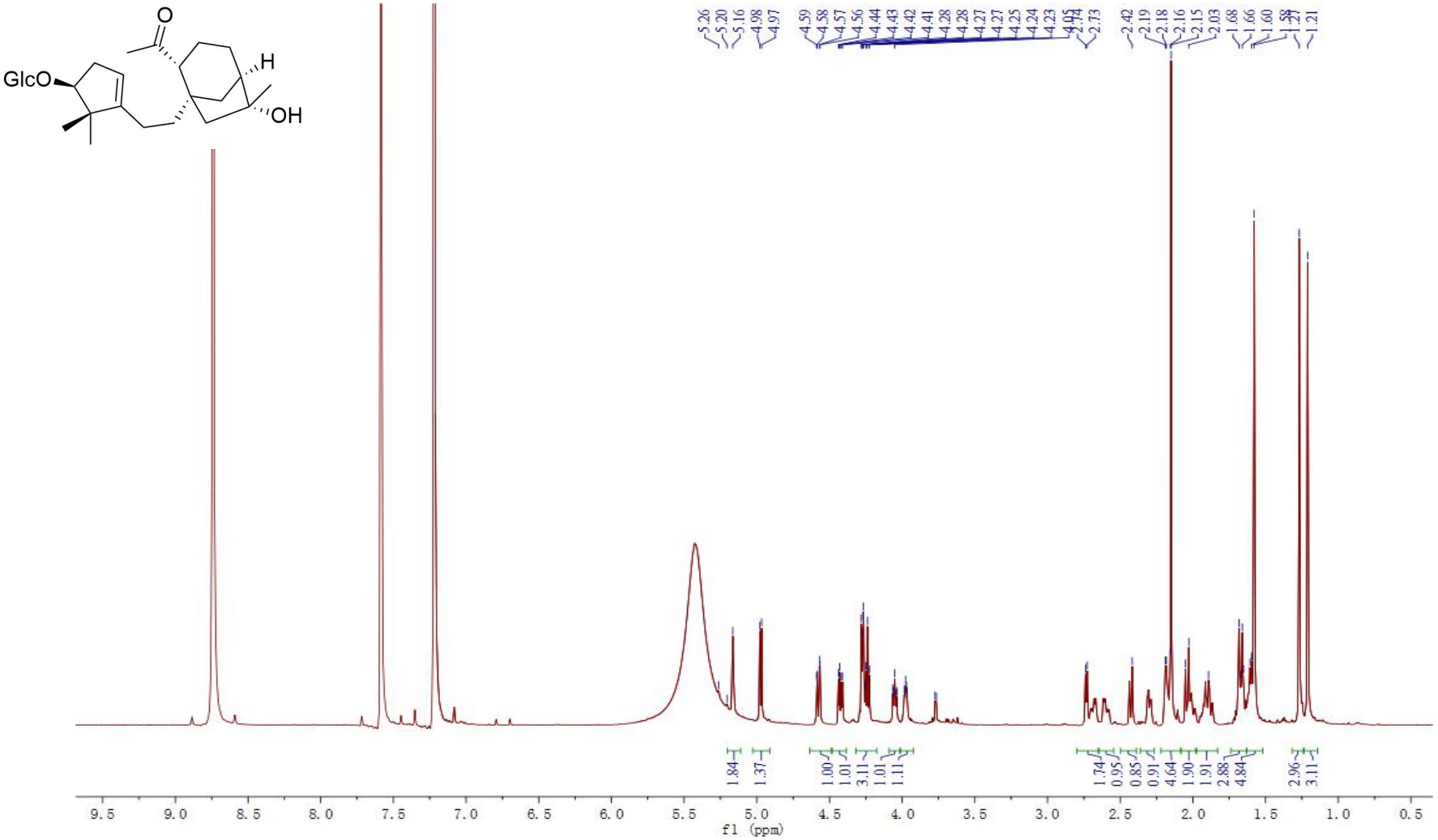
MS Formula Results: + Scan (6.470 min) Sub (2015101203.d)

m/z	Ion	Formula	Abundance
505.2781	(M+Na)+	C26 H42 Na O8	593222.4

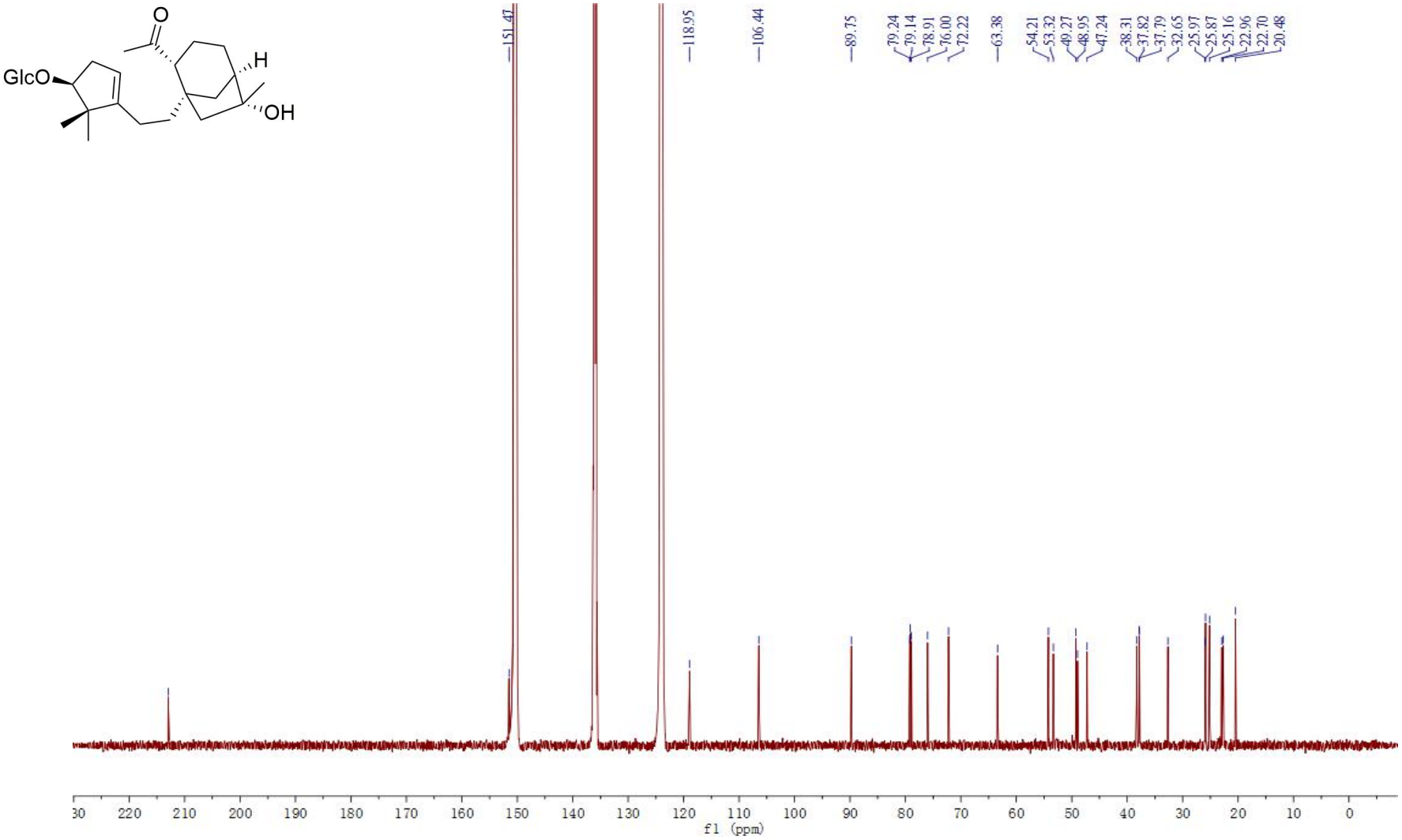
Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
✔	C26 H42 O8	C26 H42 Na O8	99.91		482.2888	482.288	505.2772	-1.77	1.77	99.9	99.89	99.94	6
	C27 H38 N4 O4	C27 H38 N4 Na O4	99.85		482.2888	482.2893	505.2785	0.99	0.99	99.97	99.53	99.98	11



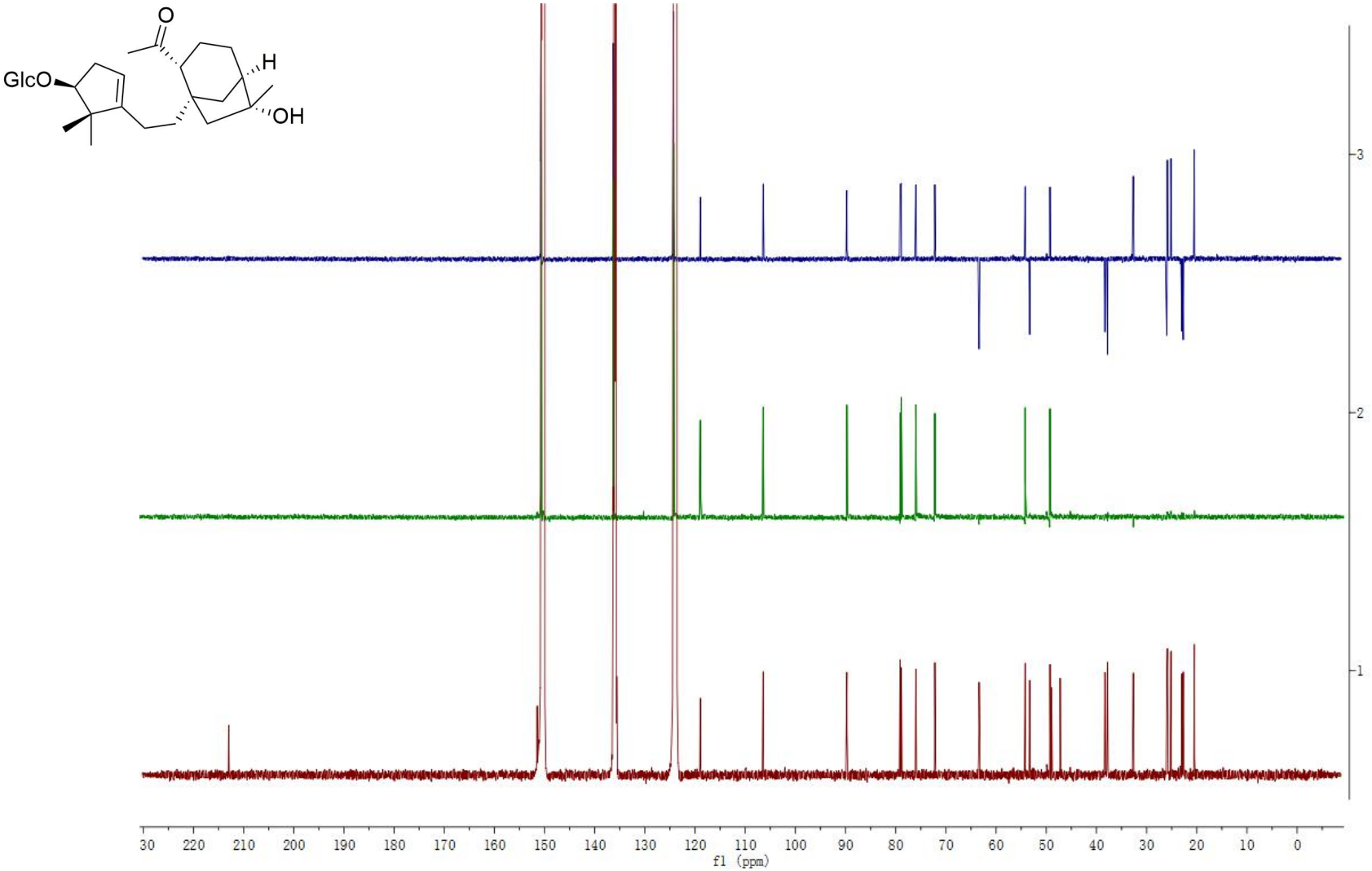
The HRESIMS spectrum of **2**



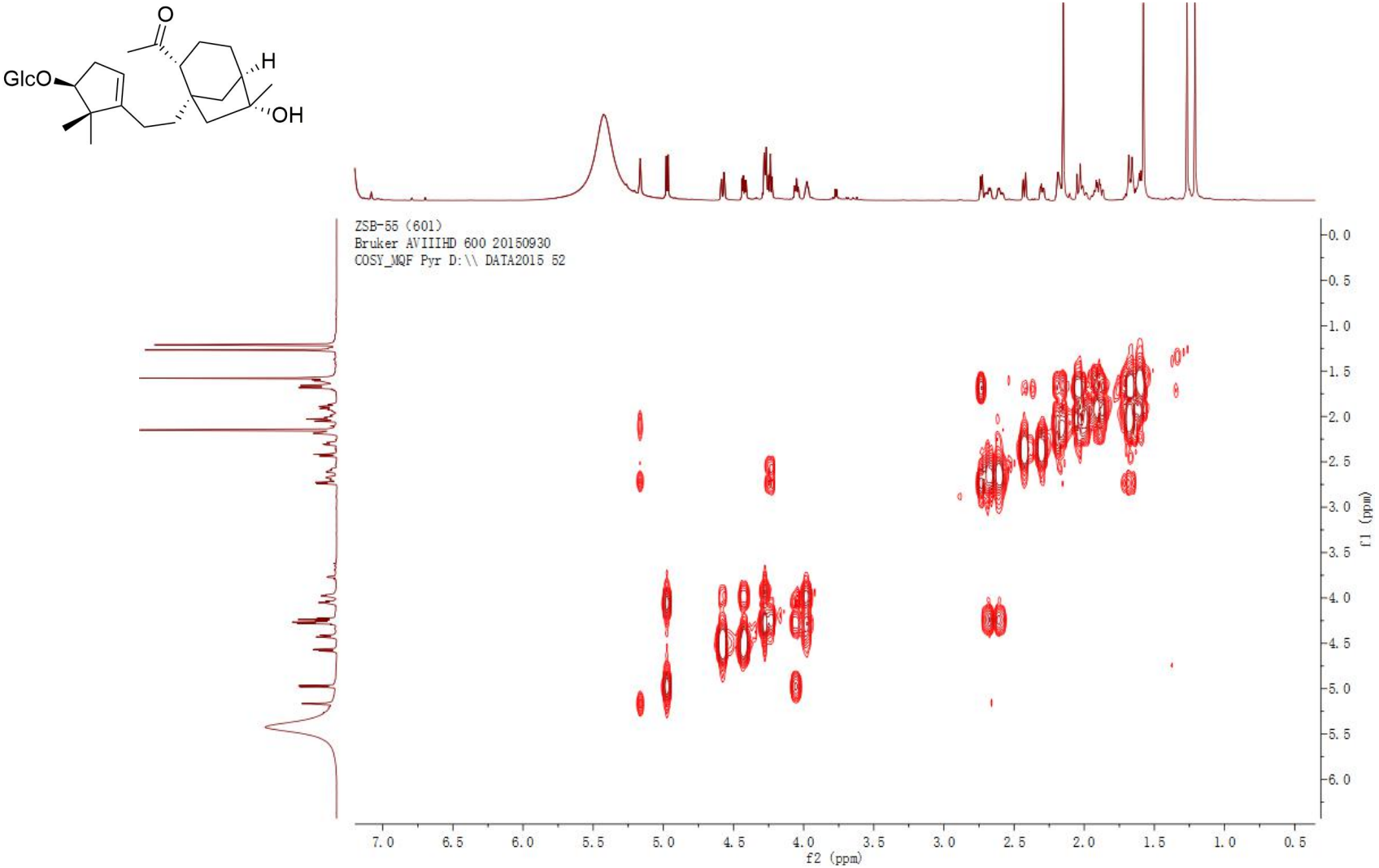
The ^{1}H NMR spectrum of **2** in C_5D_5N (600 MHz)



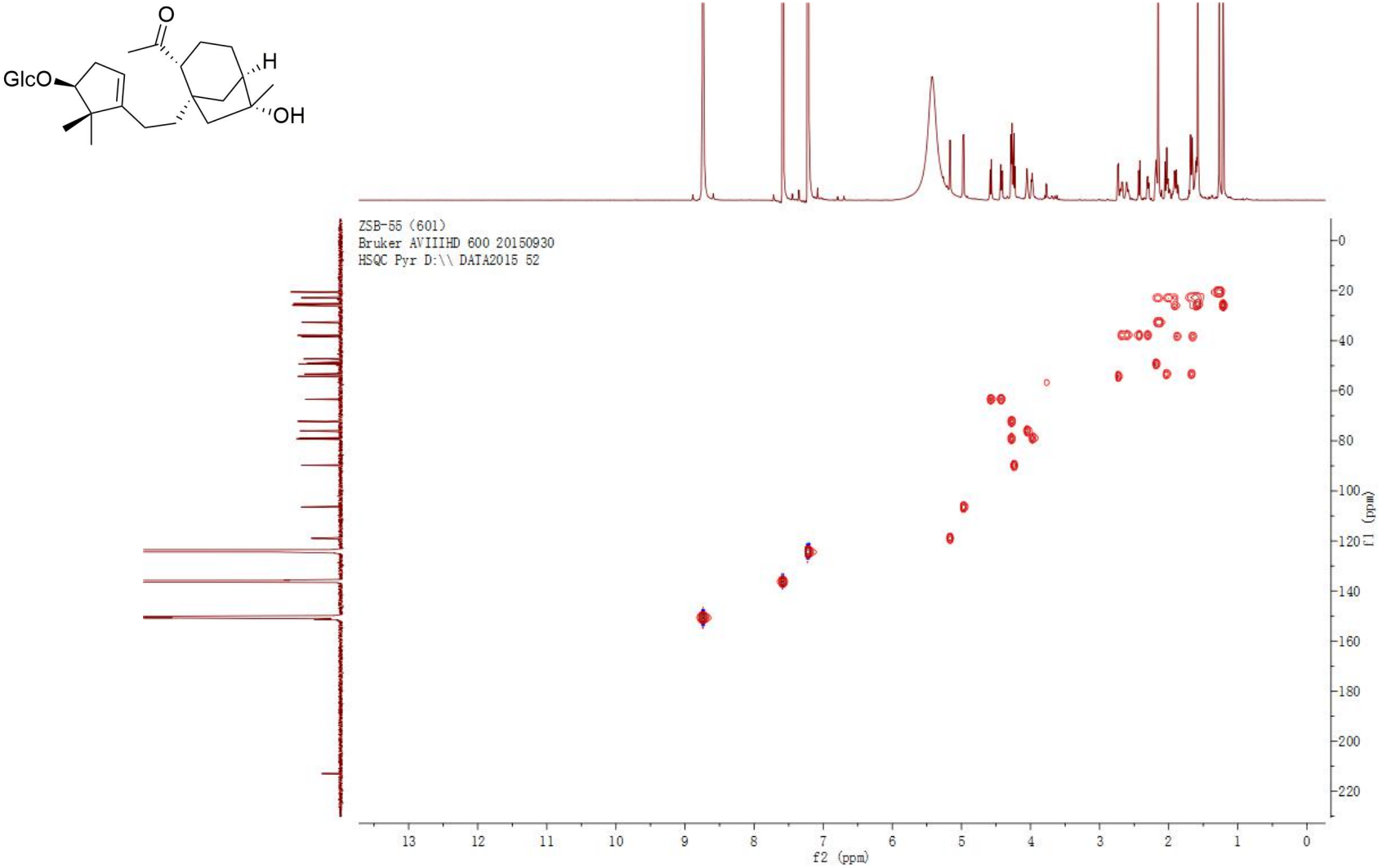
The ^{13}C NMR spectrum of **2** in C_5D_5N (150 MHz)



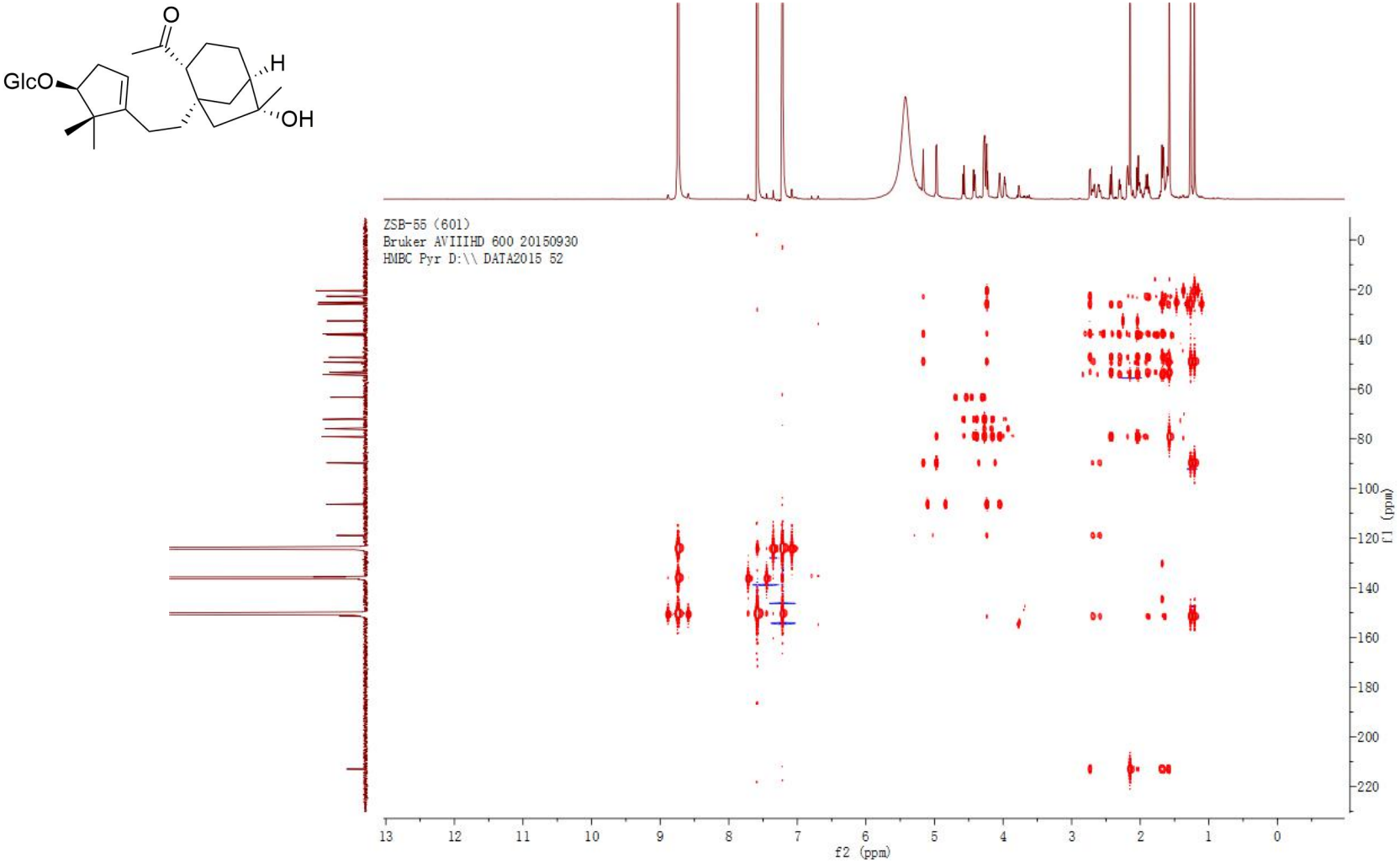
The DEPT spectrum of **2** in C_5D_5N (150 MHz)



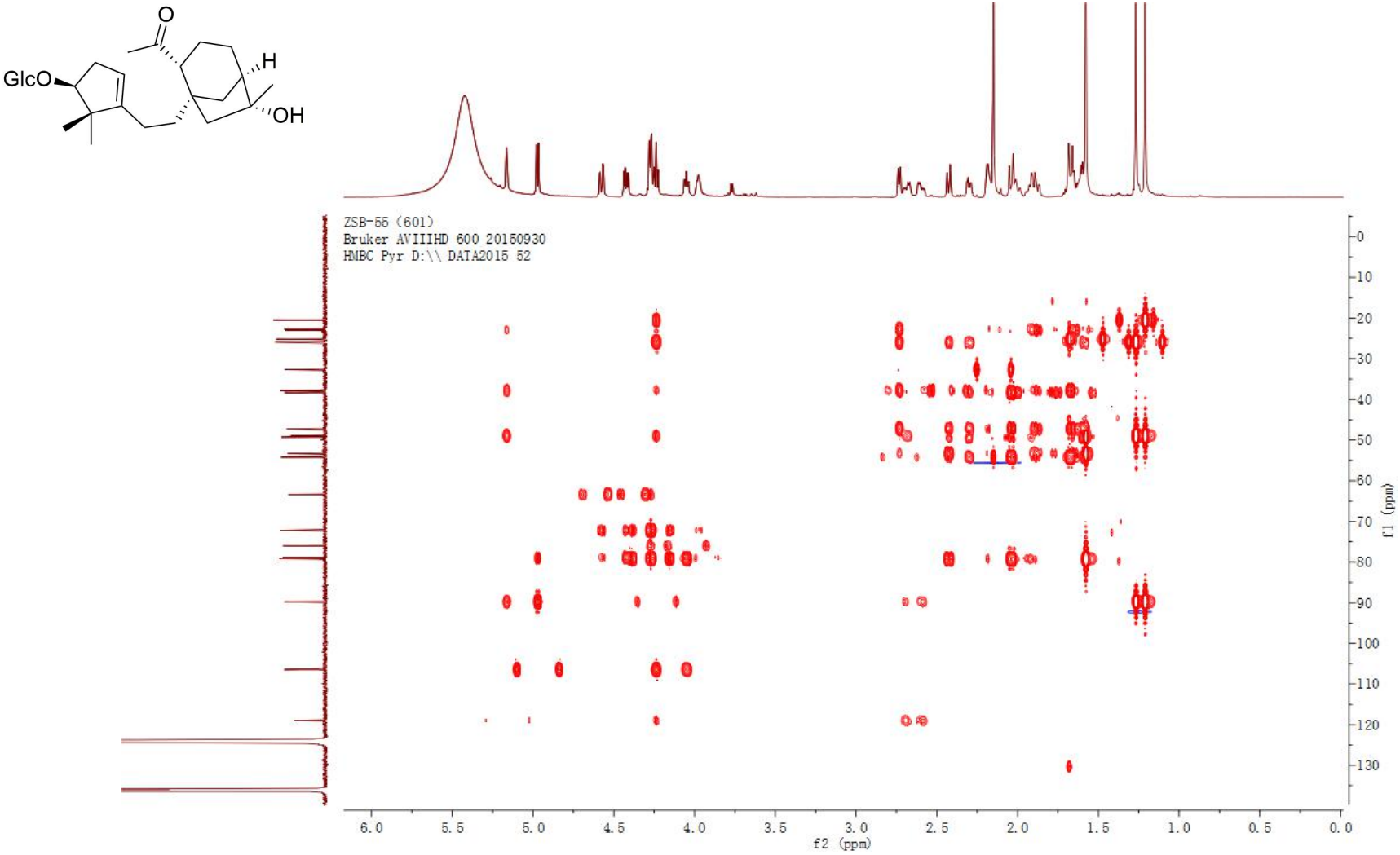
The COSY spectrum of **2** in C_5D_5N (600 MHz)



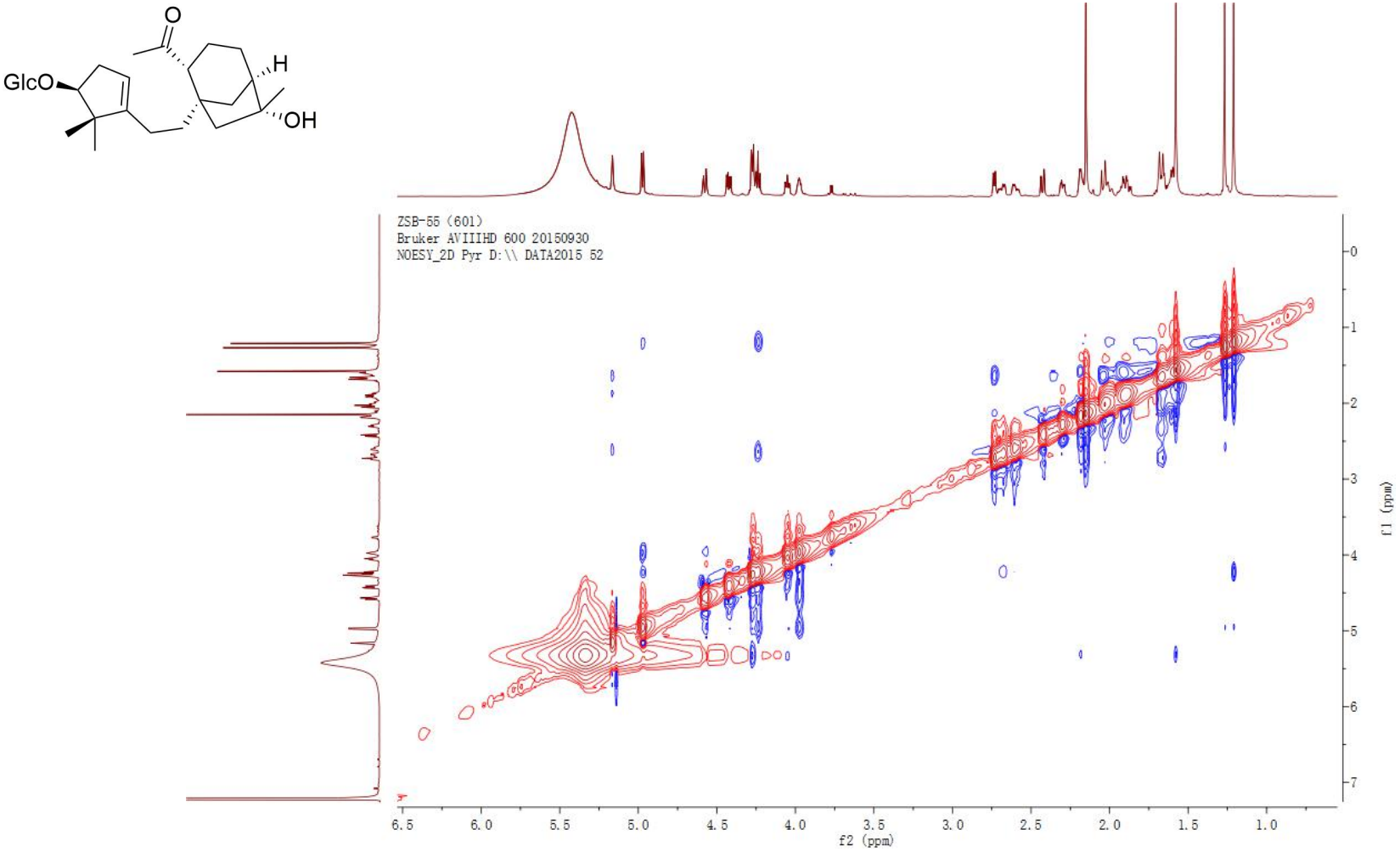
The HSQC of **2** in C_5D_5N (^1H: 600 MHz, ^{13}C: 150 MHz)



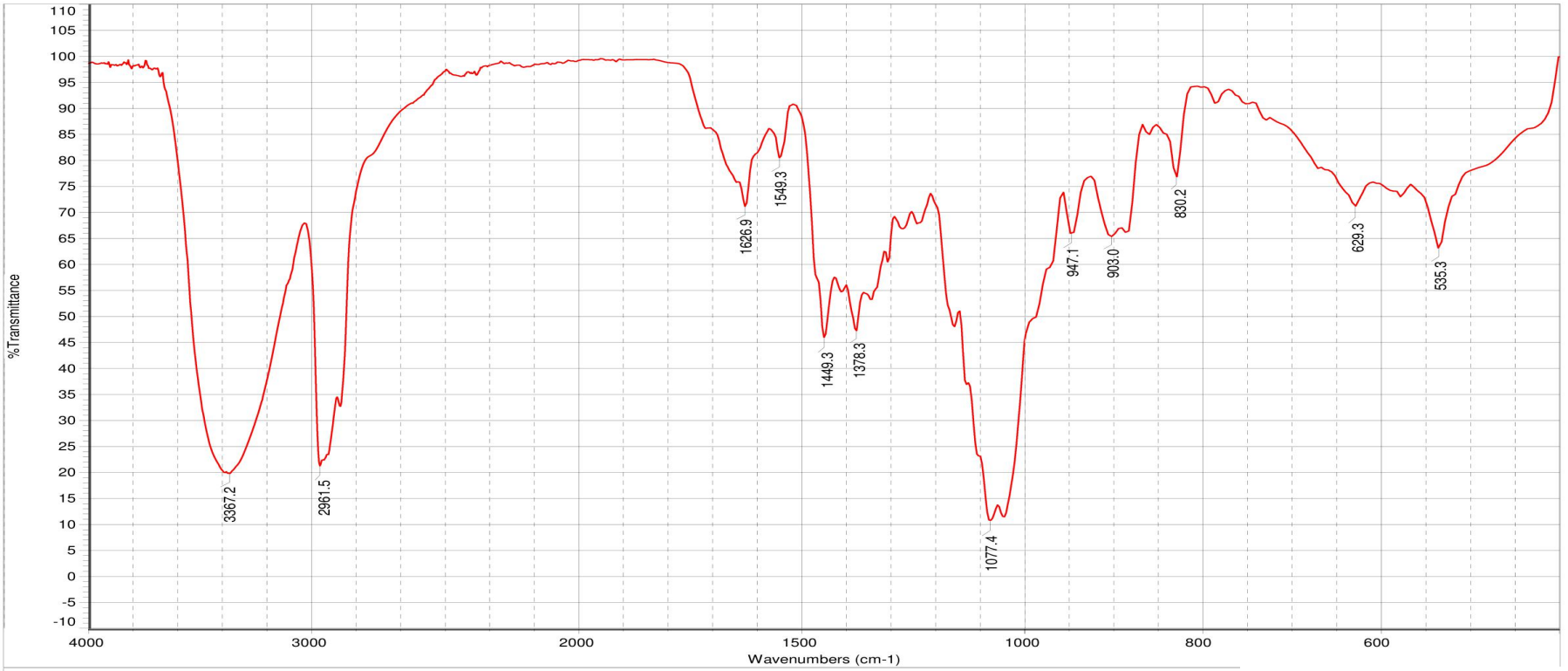
The HMBC spectrum of **2** in C_5D_5N (^1H: 600 MHz, ^{13}C: 150 MHz)

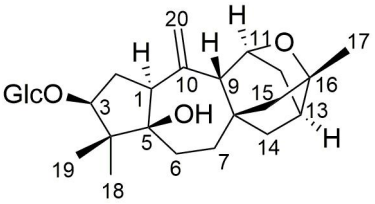


The HMBC spectrum (amplified) of **2** in C_5D_5N (^1H: 600 MHz, ^{13}C: 150 MHz)



The NOESY spectrum of **2** in C_5D_5N (600 MHz)





The IR spectrum of **3**

MS Formula Results: + Scan (7.152 min) Sub (2016061502.d)

	m/z	Ion	Formula	Abundance
-	503.2623	(M+Na)+	C26 H40 Na O8	938446.8

	Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
+	☑	C26 H40 O8	C26 H40 Na O8	99.56		480.2731	480.2723	503.2615	-1.58	1.58	99.92	98.8	99.73	7
+	☐	C23 H44 O8 S	C23 H44 Na O8 S	98.99		480.2731	480.2757	503.2649	5.43	5.43	99.08	99.48	98.22	2
+	☐	C27 H44 O3 S2	C27 H44 Na O3 S2	98.42		480.2731	480.2732	503.2624	0.21	0.21	100	96.55	97.53	6

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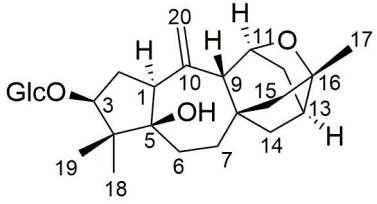
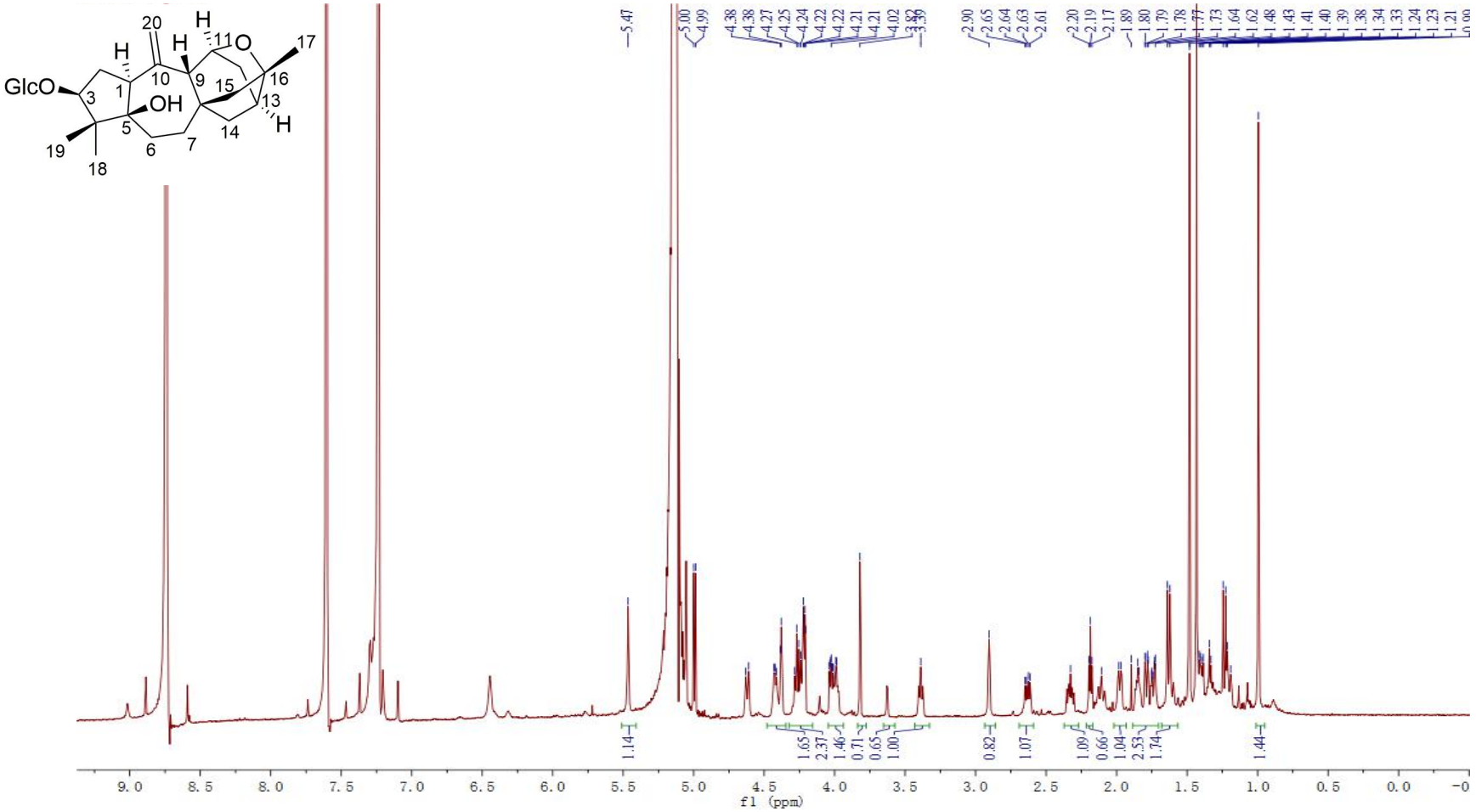
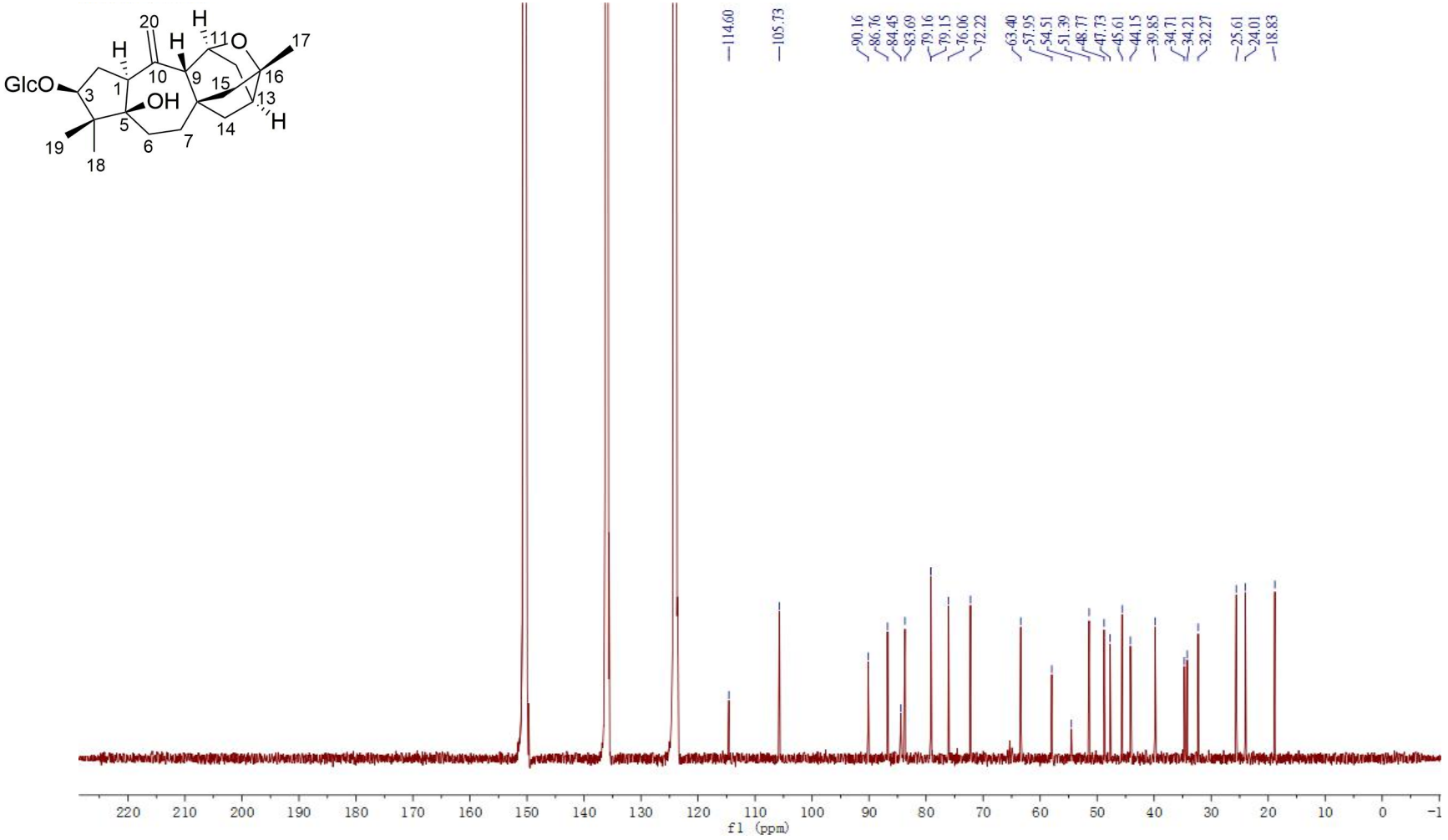


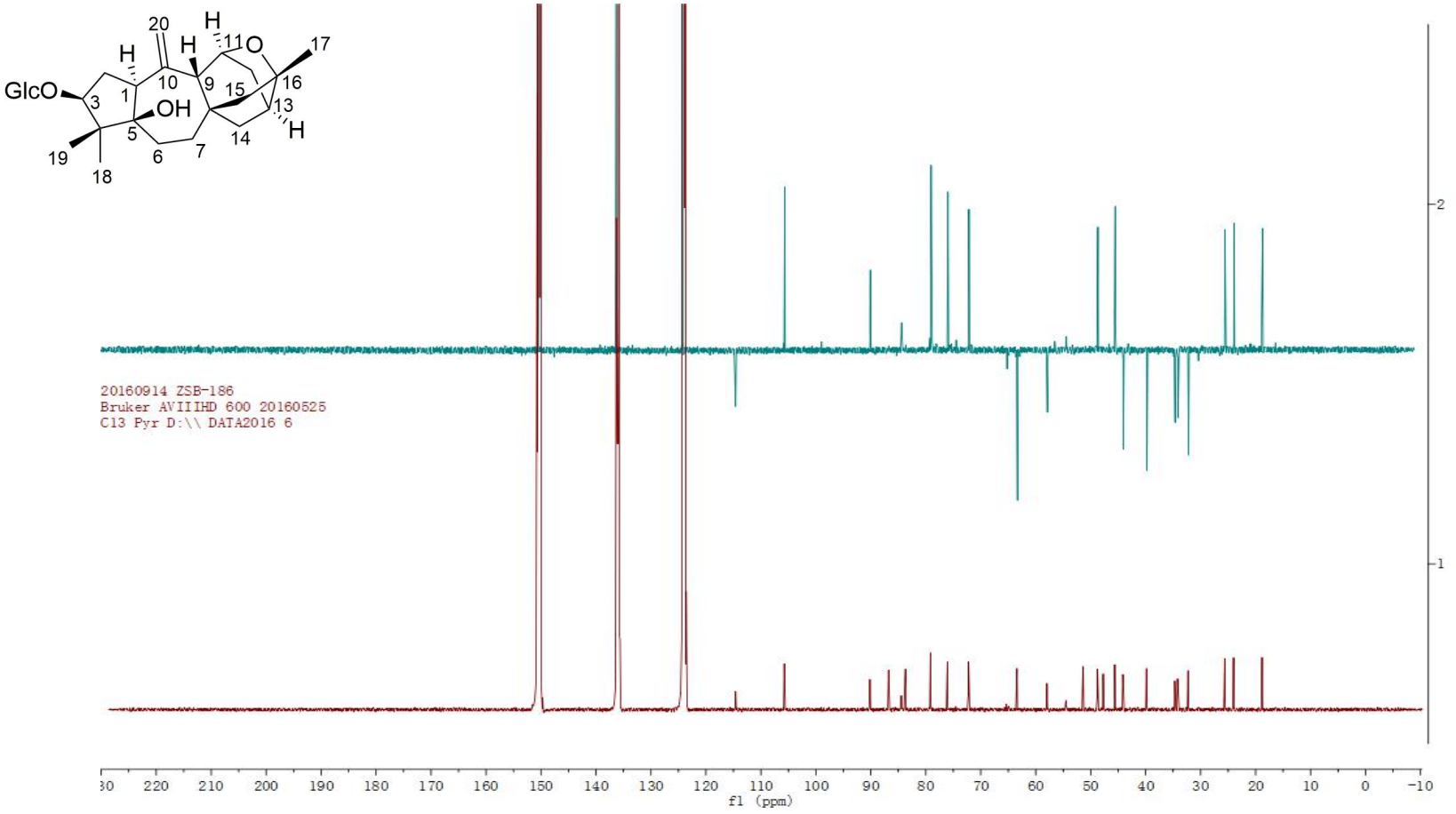
The HRESIMS spectrum of **3**



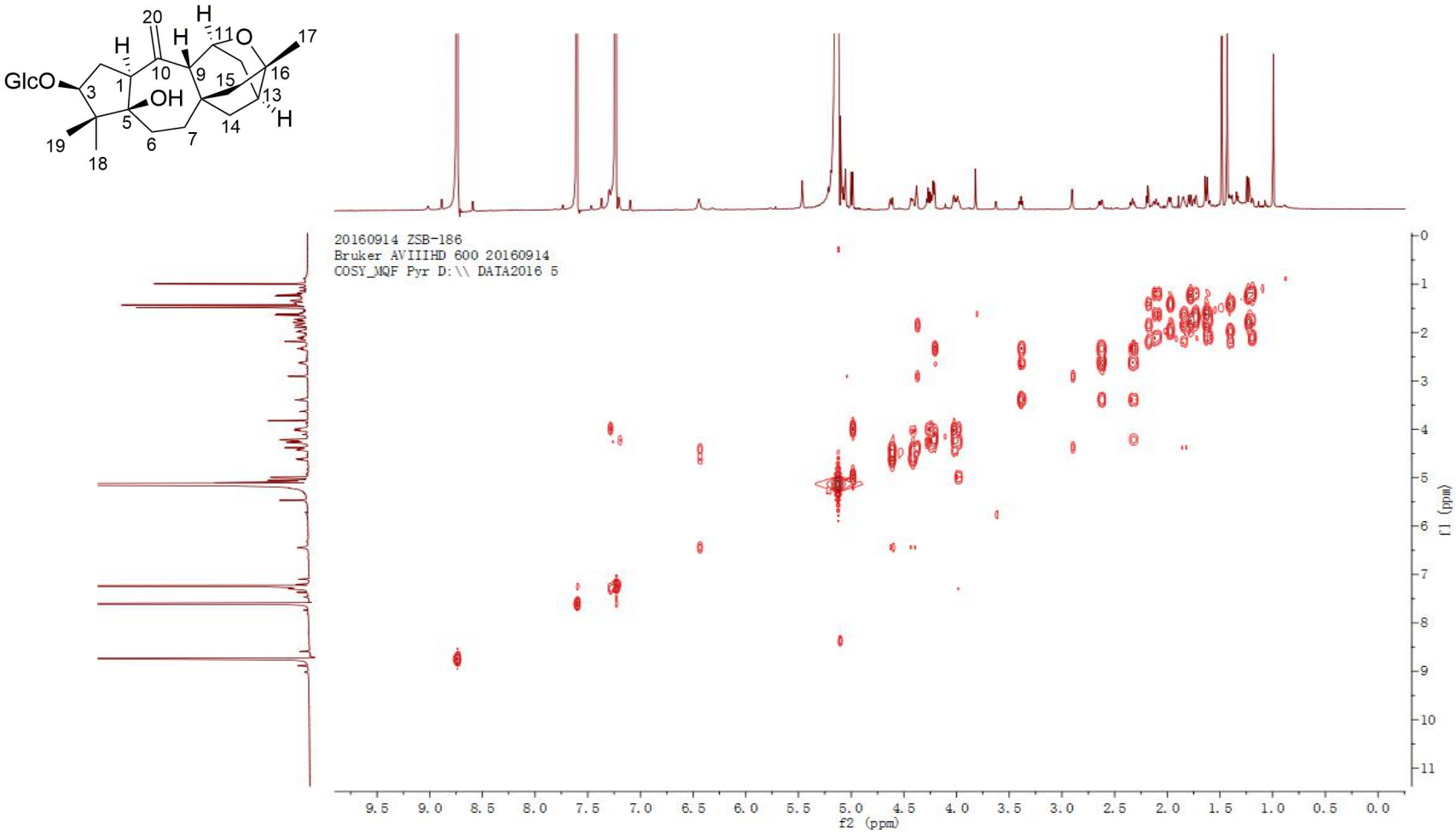
The ^{1}H NMR spectrum of **3** in C_5D_5N (600 MHz)



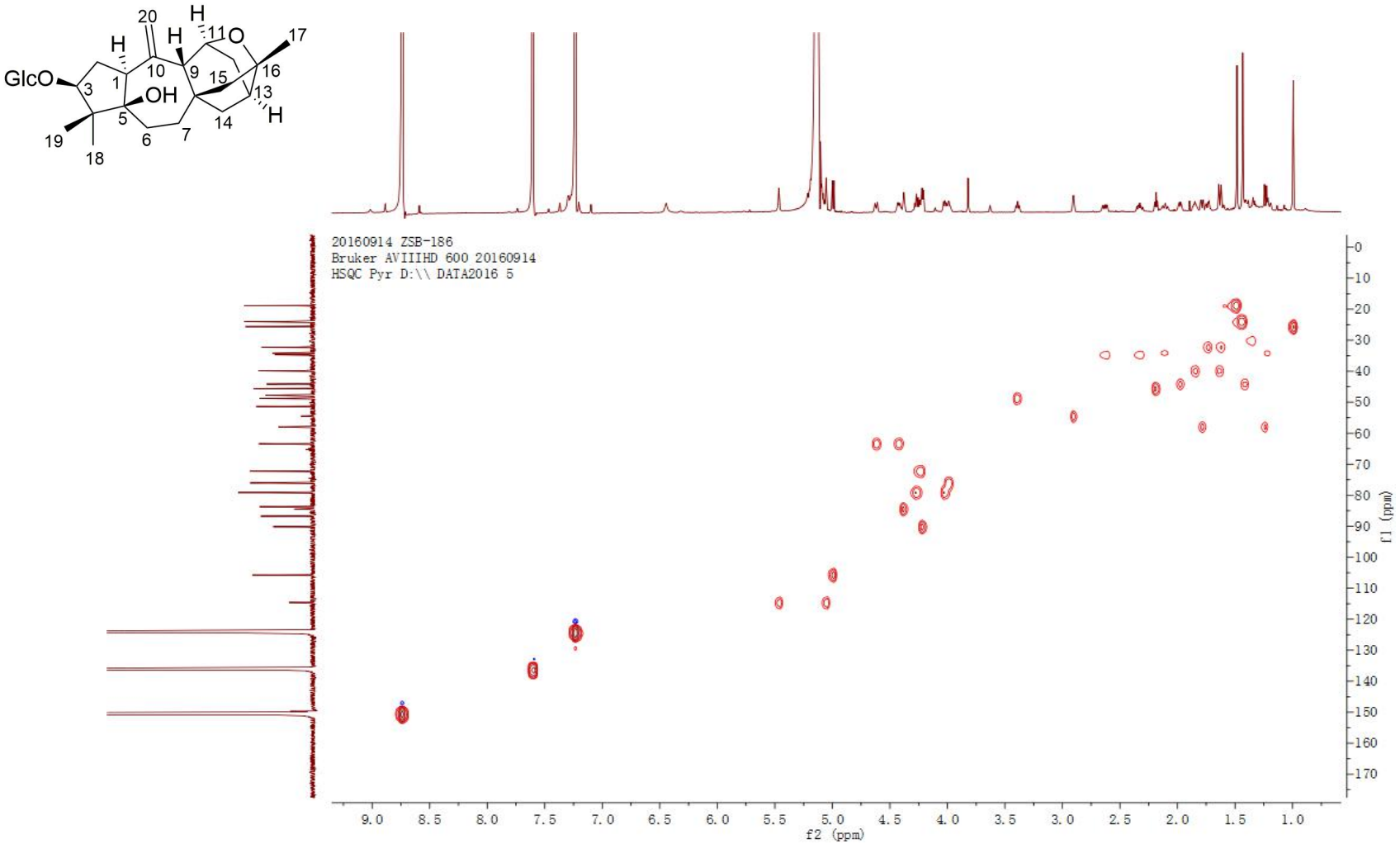
The ^{13}C NMR spectrum of **3** in C_5D_5N (150 MHz)



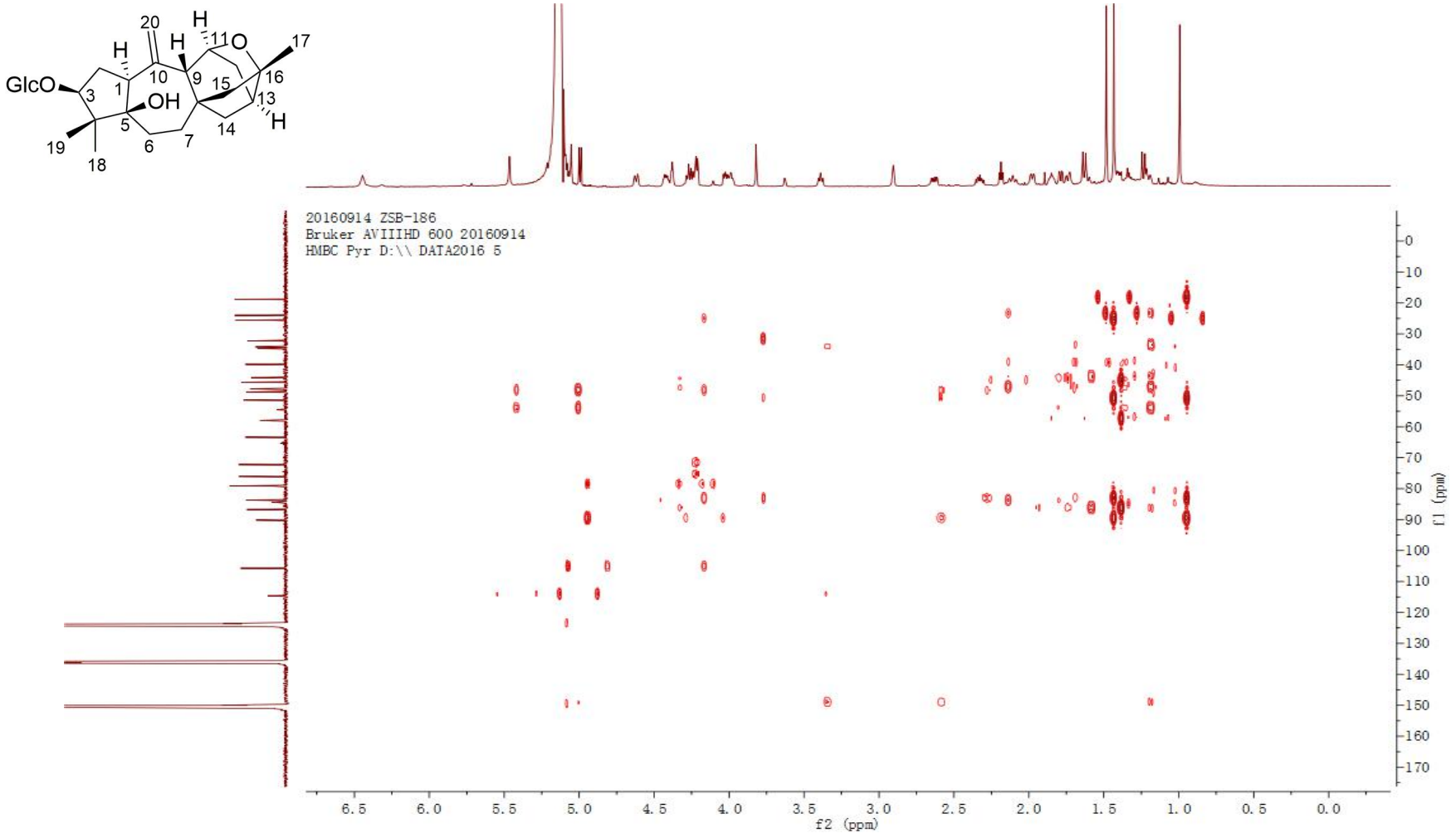
The DEPT (135˚) spectrum of **3** in C_5D_5N (150 MHz)



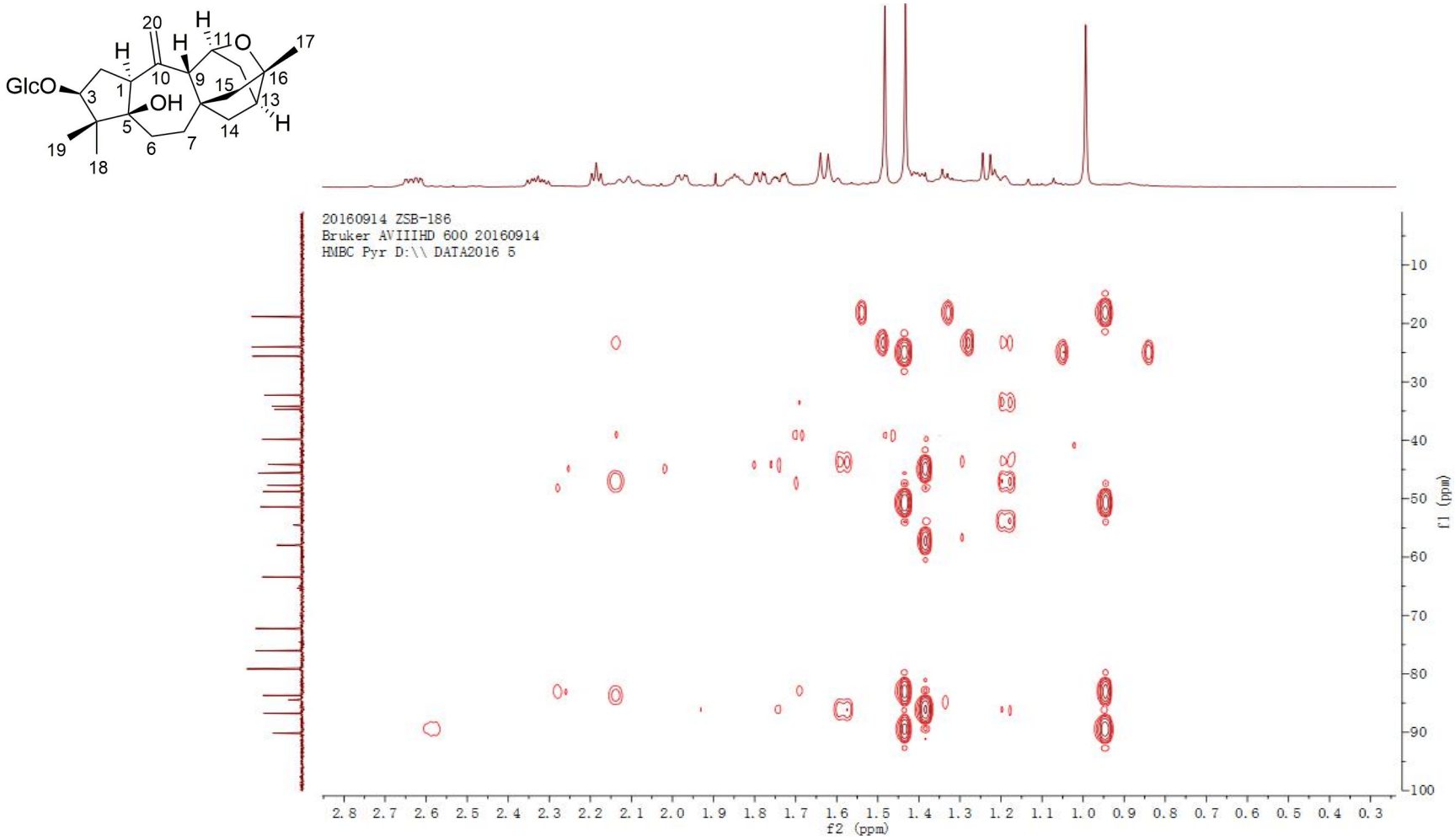
The COSY spectrum of **3** in C_5D_5N (600 MHz)



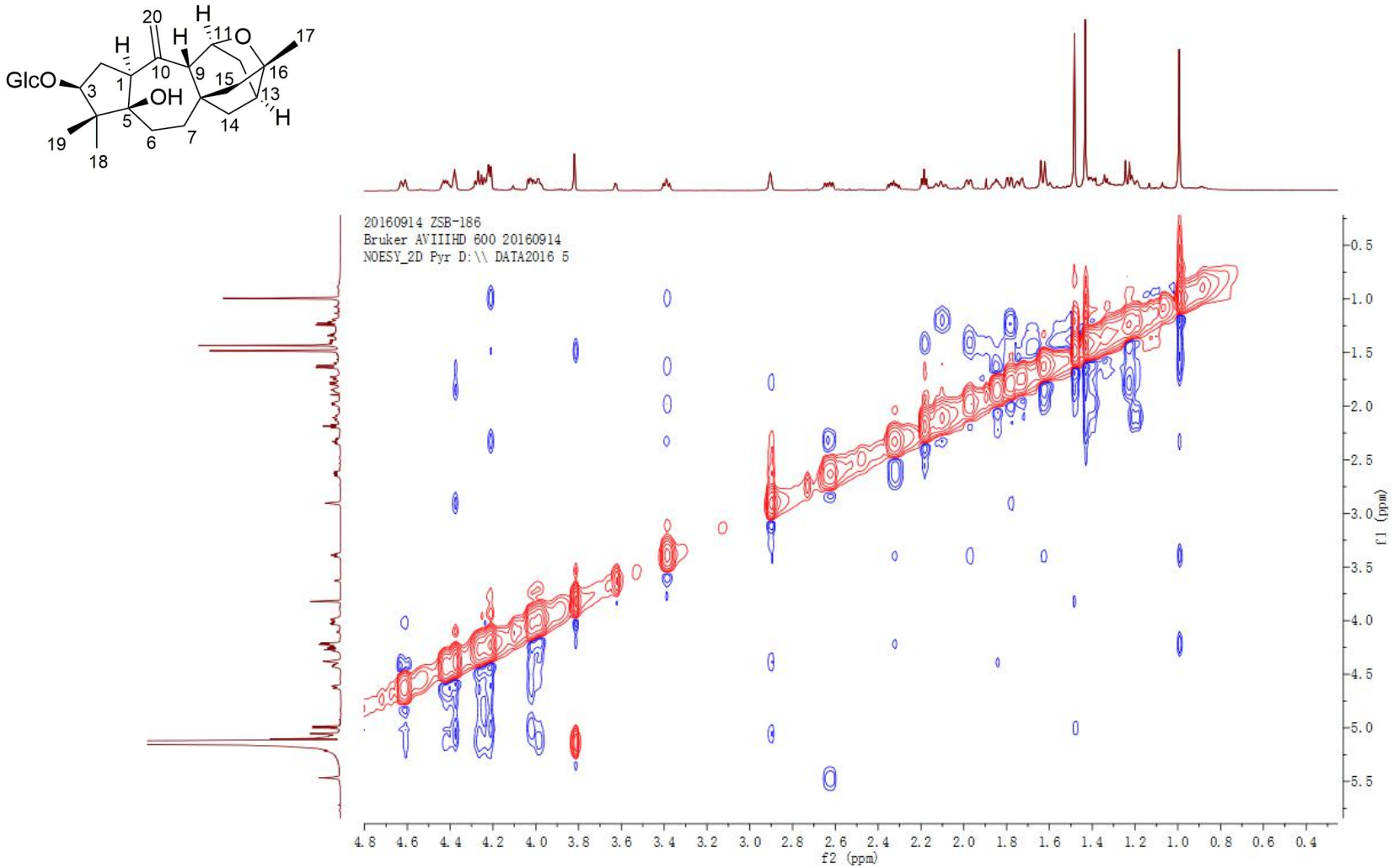
The HSQC of **3** in C_5D_5N (^1H: 600 MHz, ^{13}C: 150 MHz)



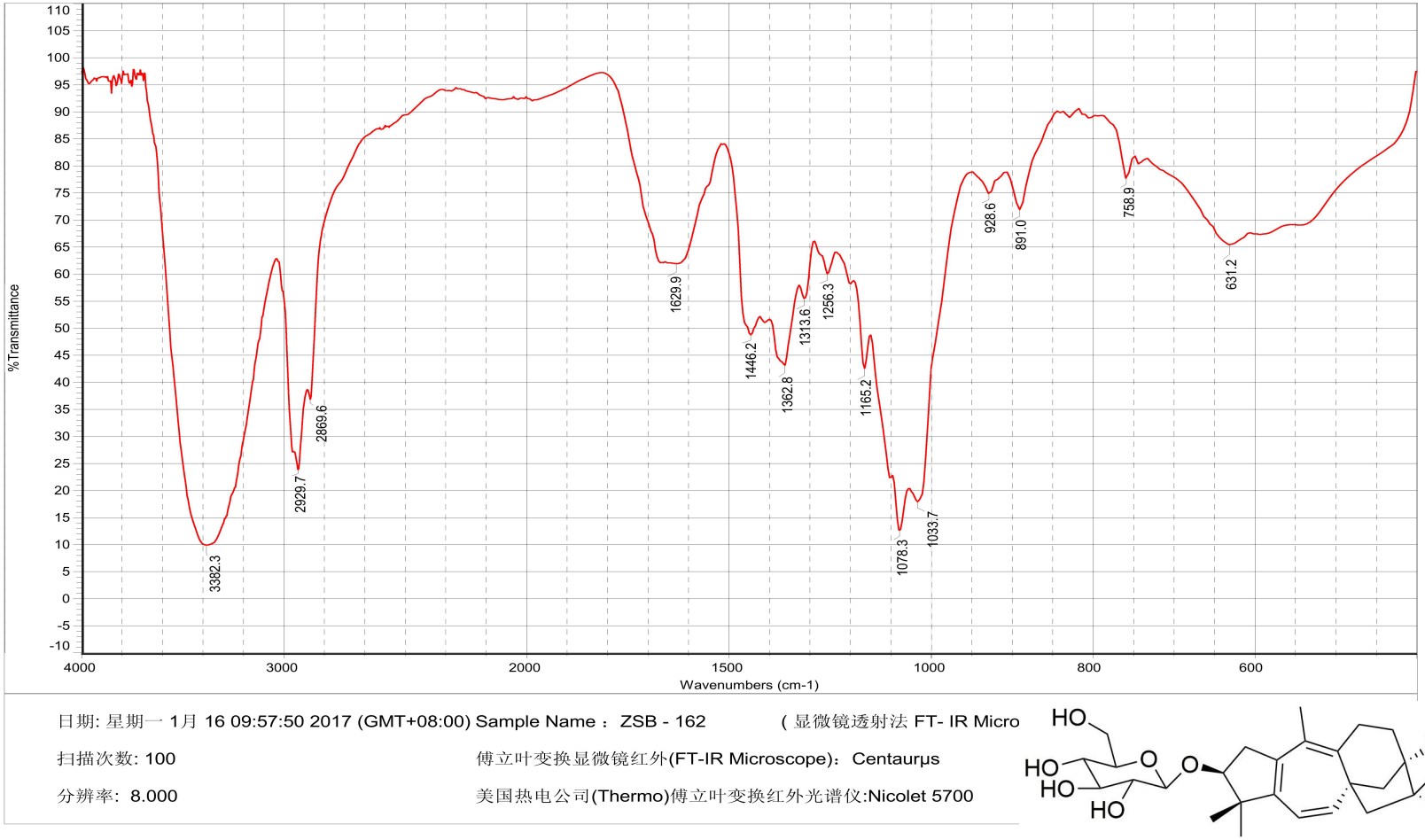
The HMBC spectrum of **3** in C_5D_5N (^1H: 600 MHz, ^{13}C: 150 MHz)



The HMBC spectrum (amplified) of **3** in C_5D_5N (^1H: 600 MHz, ^{13}C: 150 MHz)



The NOESY spectrum of **3** in C_5D_5N (600 MHz)



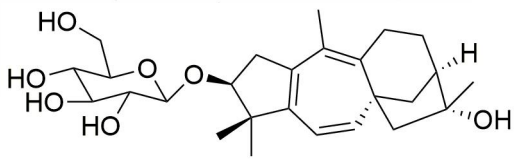
The IR spectrum of **4**

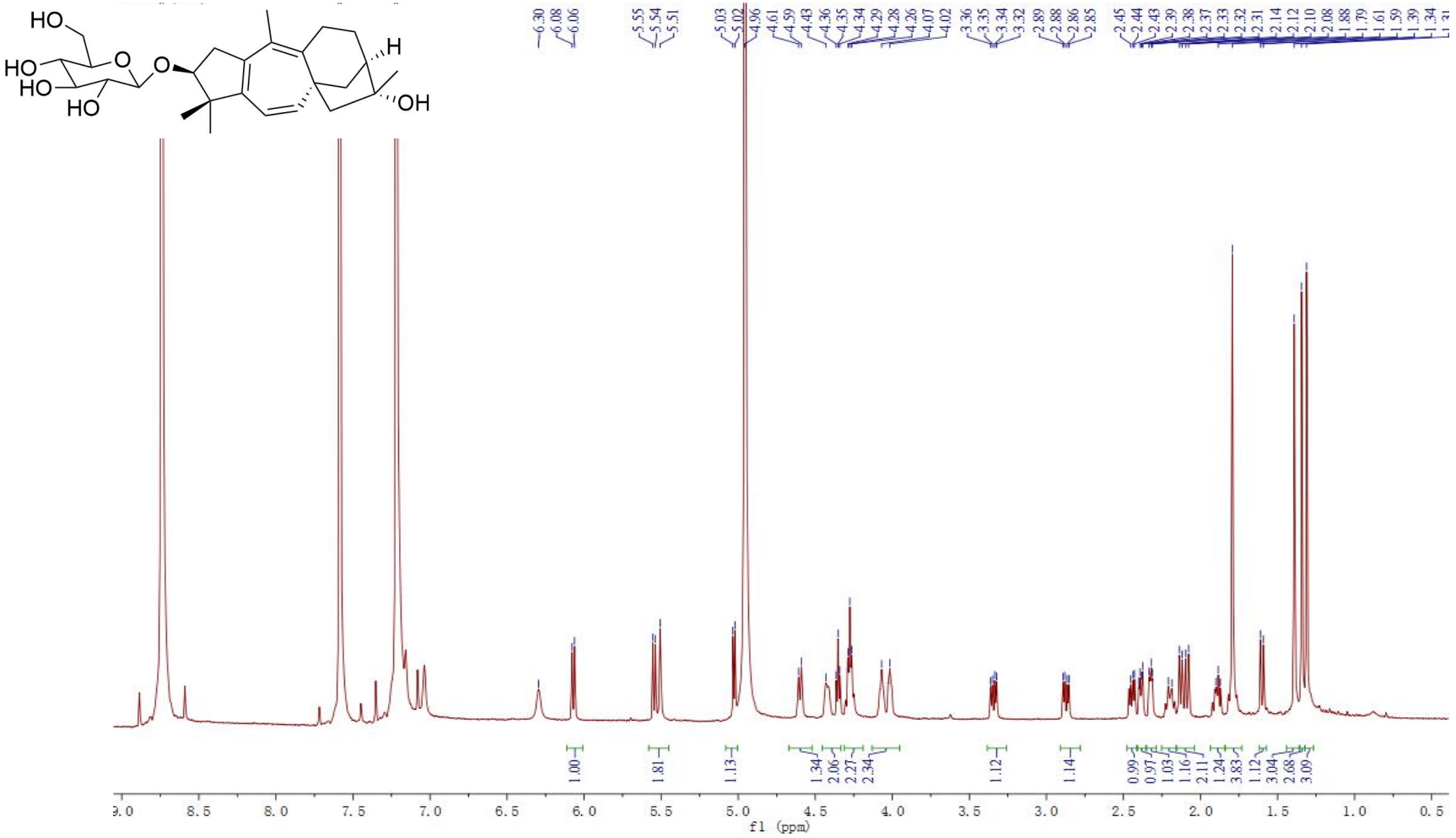
MS Formula Results: + Scan (7.432 min) Sub (2016050405.d)

	m/z	Ion	Formula	Abundance
-	485.2492	(M+Na)+	C26 H38 Na O7	510472.4

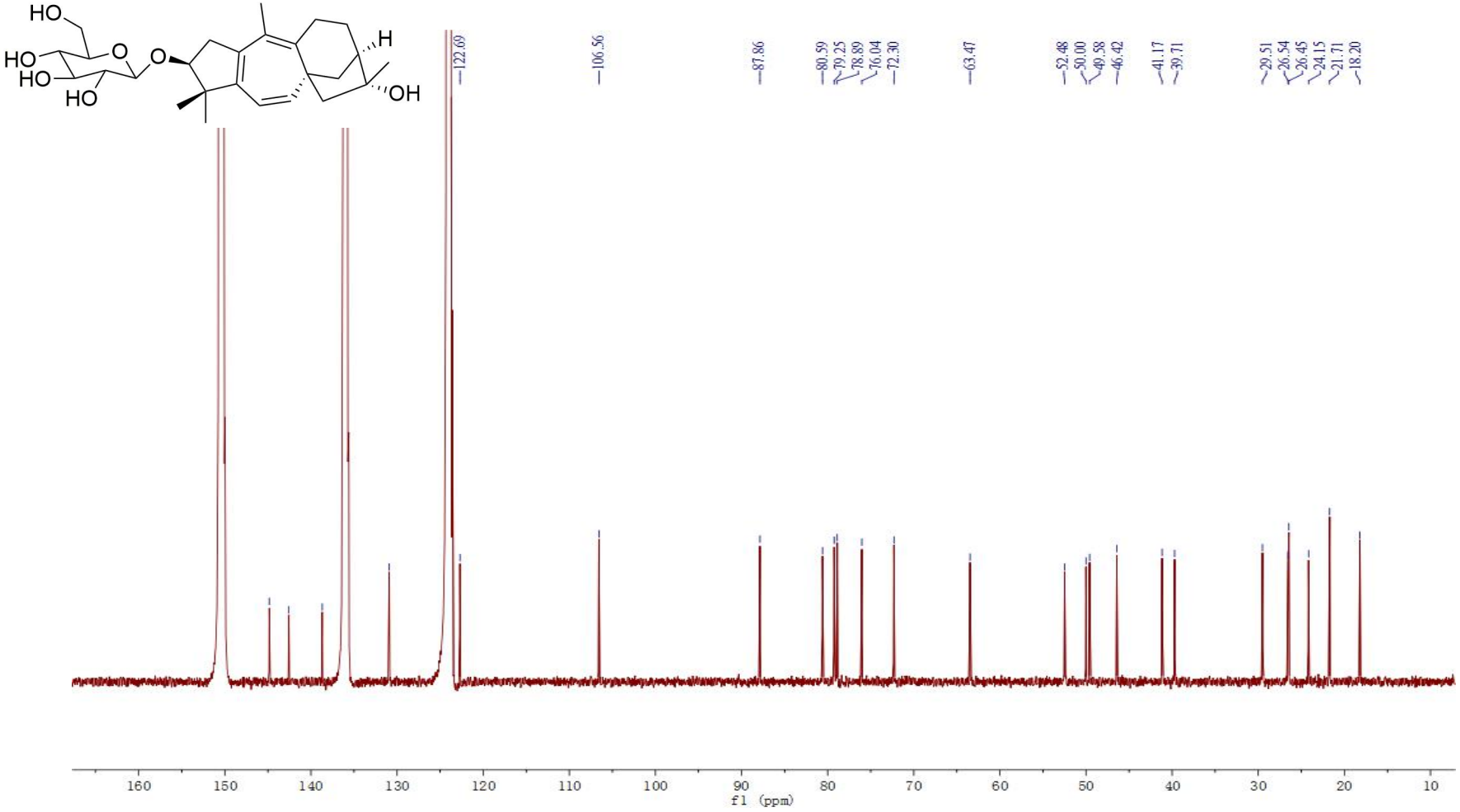
	Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
+	☑	C26 H38 O7	C26 H38 Na O7	99.7		462.26	462.2618	485.251	3.81	3.81	99.55	99.71	99.97	8
+	☐	C21 H38 N2 O9	C21 H38 N2 Na O9	99.44		462.26	462.2577	485.247	-4.9	4.9	99.26	99.3	99.99	4
+	☐	C30 H38 O2 S	C30 H38 Na O2 S	98.74		462.26	462.2593	485.2485	-1.61	1.61	99.92	95.83	99.86	12
+	☐	C22 H42 N2 O4 S2	C22 H42 N2 Na O4 S2	97.65		462.26	462.2586	485.2478	-3.04	3.04	99.71	92.71	99.44	3
+	☐	C27 H42 O2 S2	C27 H42 Na O2 S2	97.28		462.26	462.2626	485.2518	5.67	5.67	99.01	92.49	99.56	7

The HRESIMS spectrum of **4**

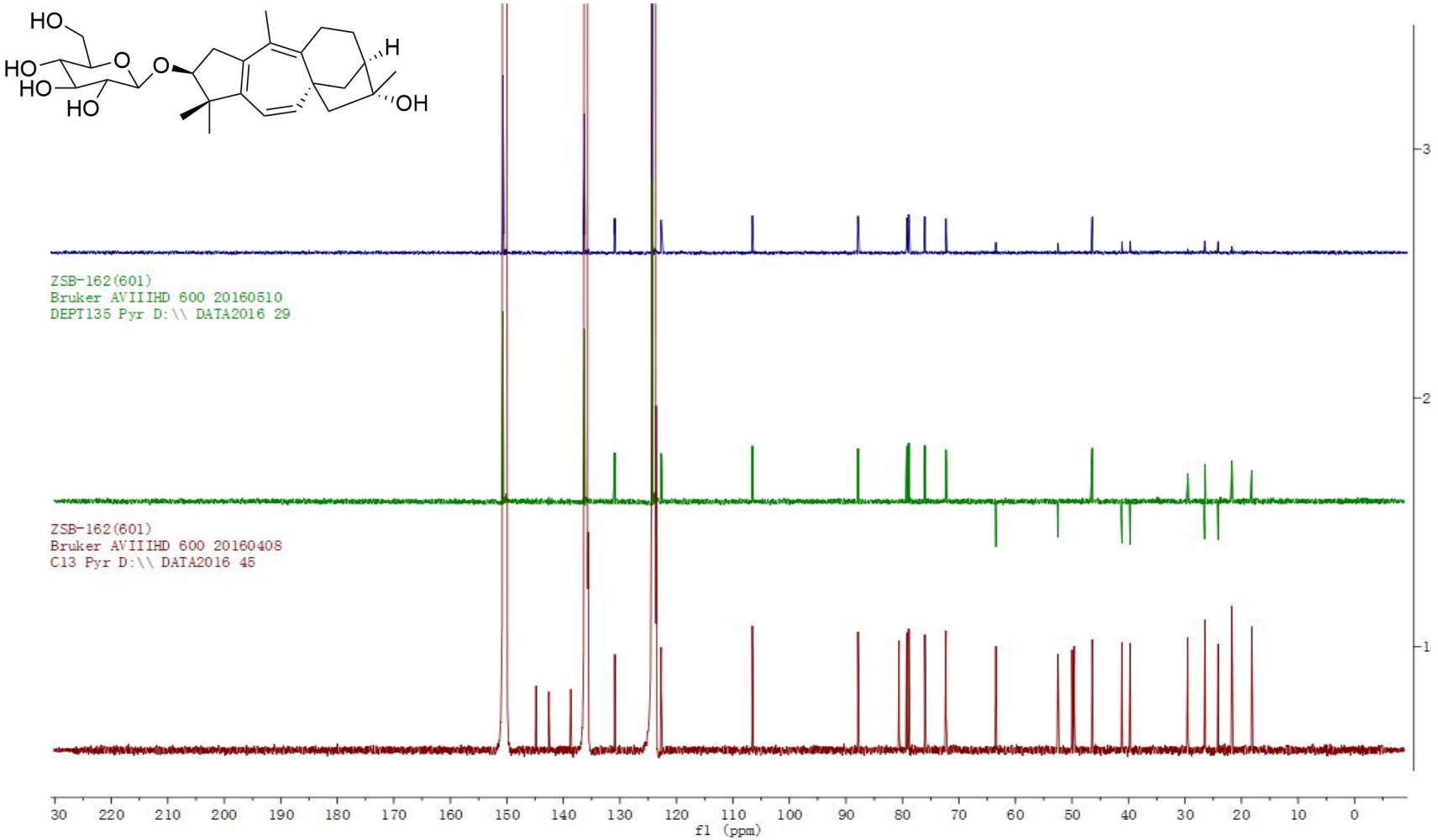




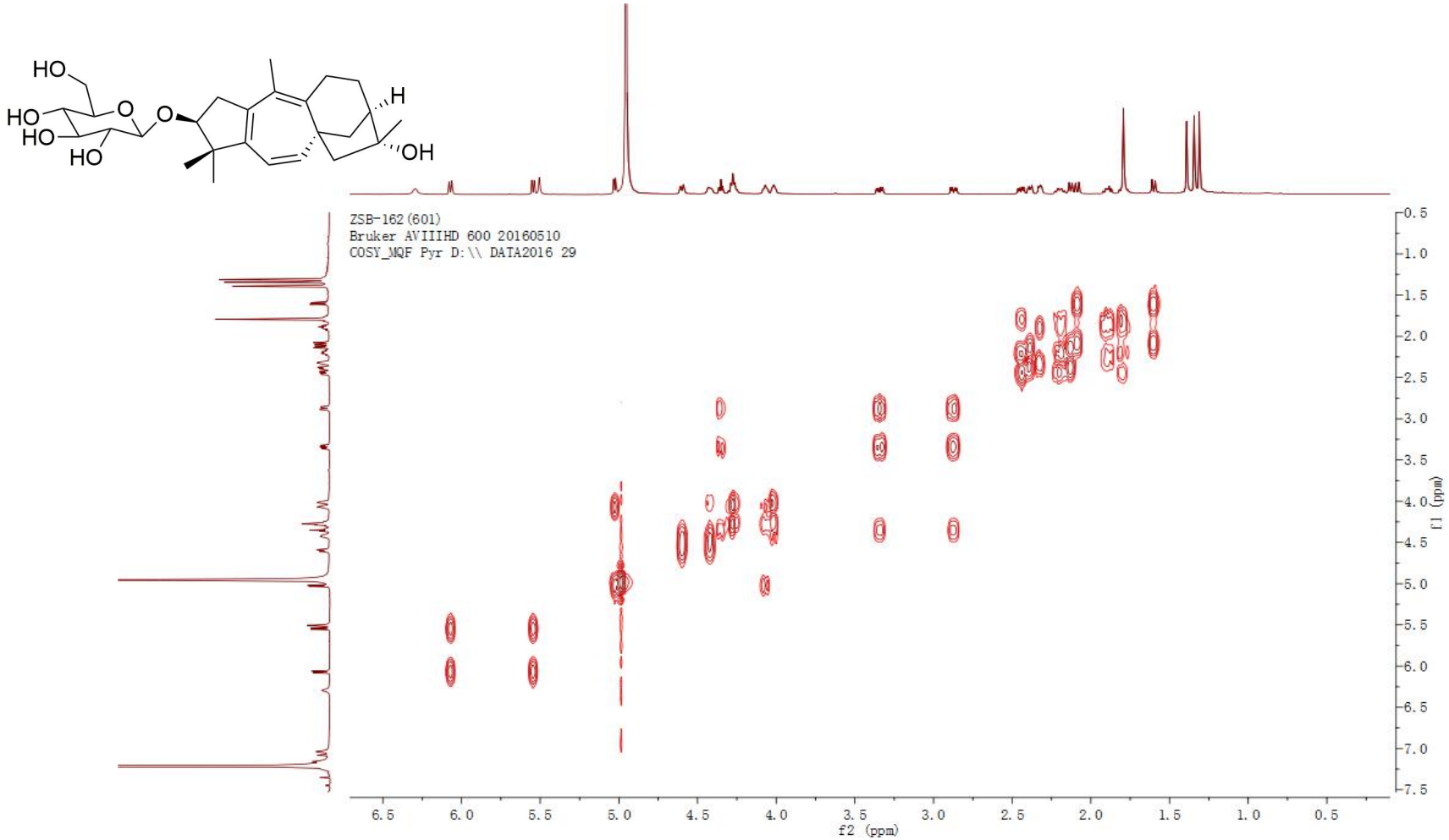
The ^{1}H NMR spectrum of **4** in C_5D_5N (600 MHz)



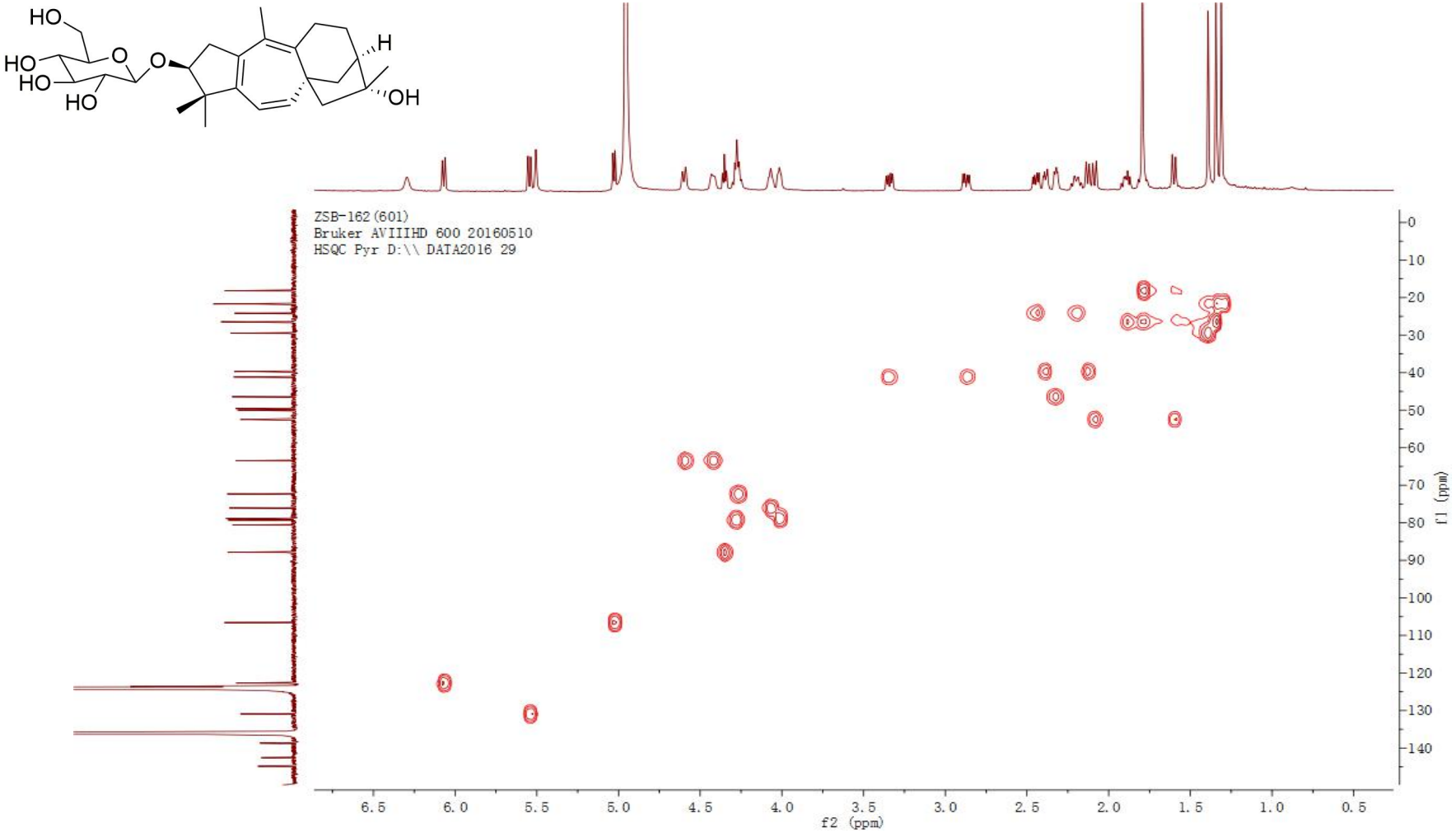
The ^{13}C NMR spectrum of **4** in C_5D_5N (150 MHz)



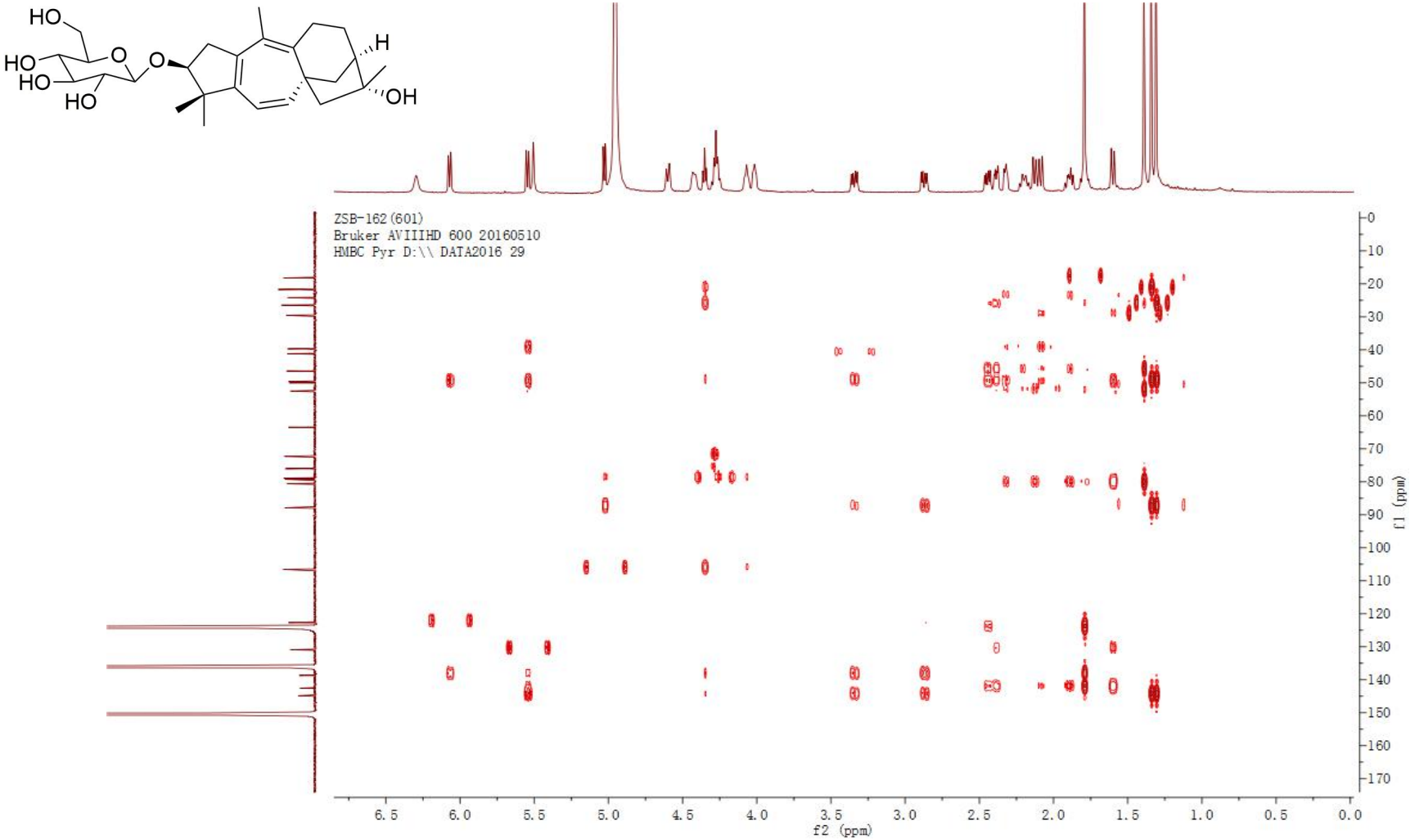
The DEPT spectrum of **4** in C_5D_5N (150 MHz)



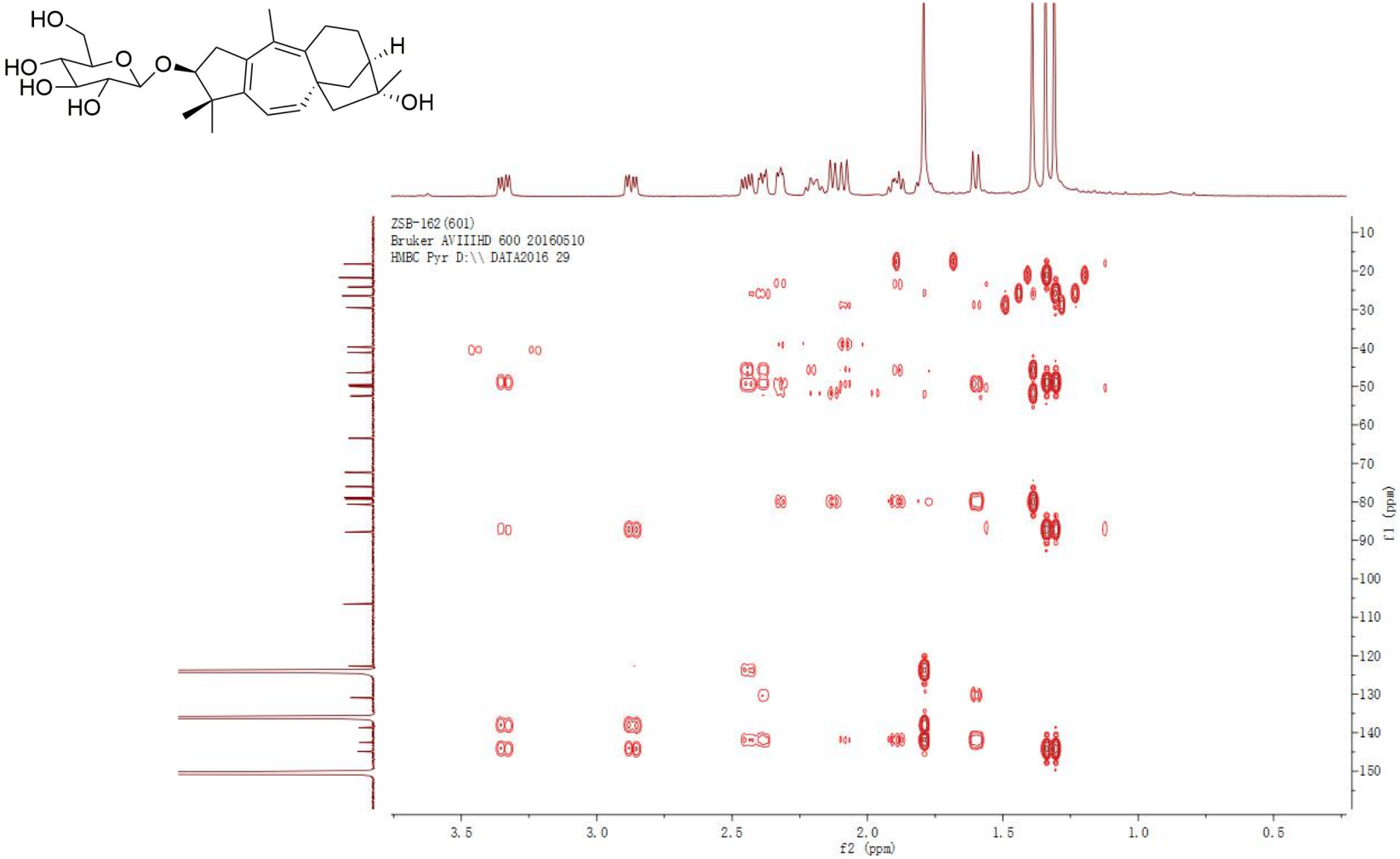
The COSY spectrum of **4** in C_5D_5N (600 MHz)



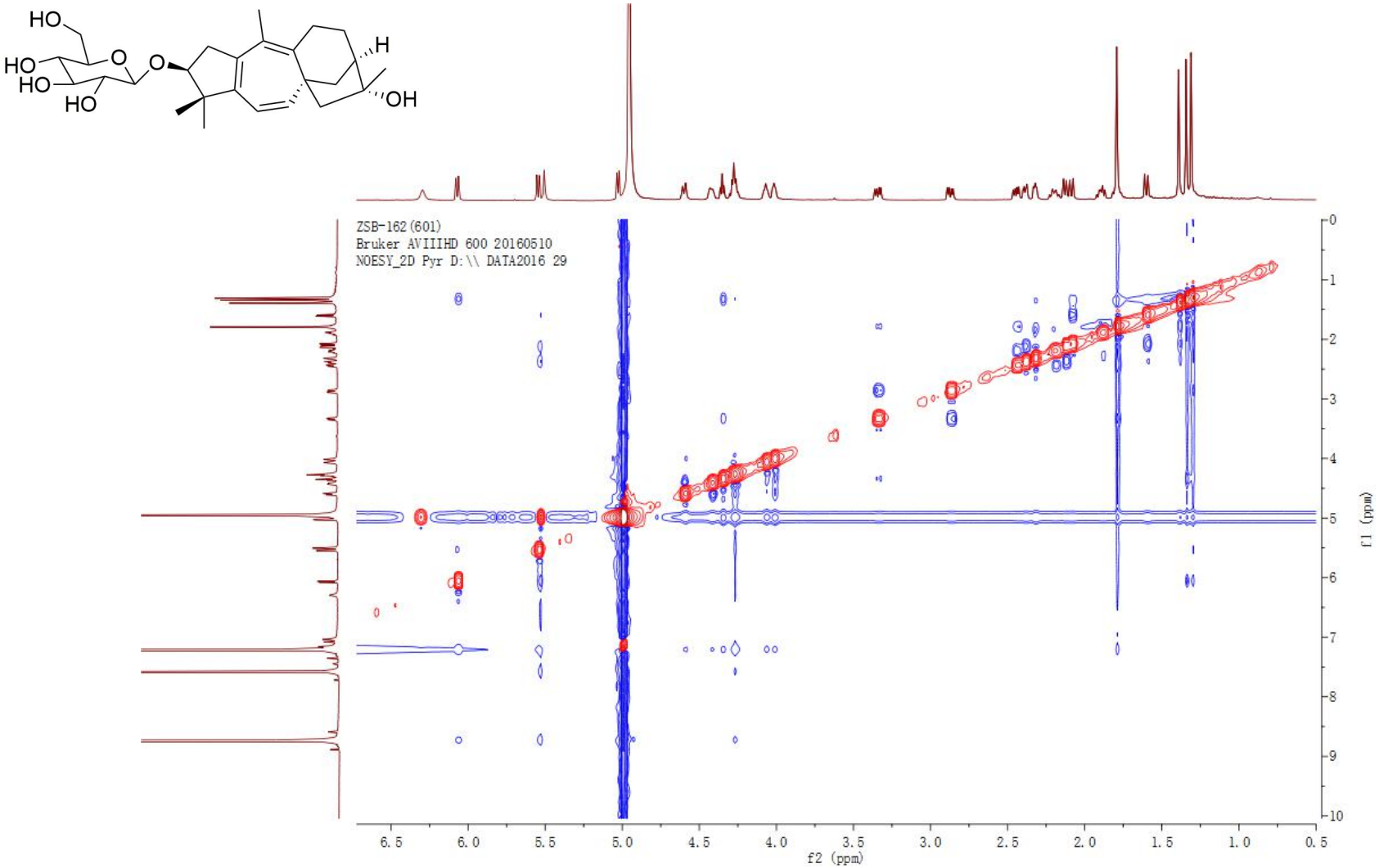
The HSQC spectrum of **4** in C_5D_5N (^1H: 600 MHz, ^{13}C: 150 MHz)



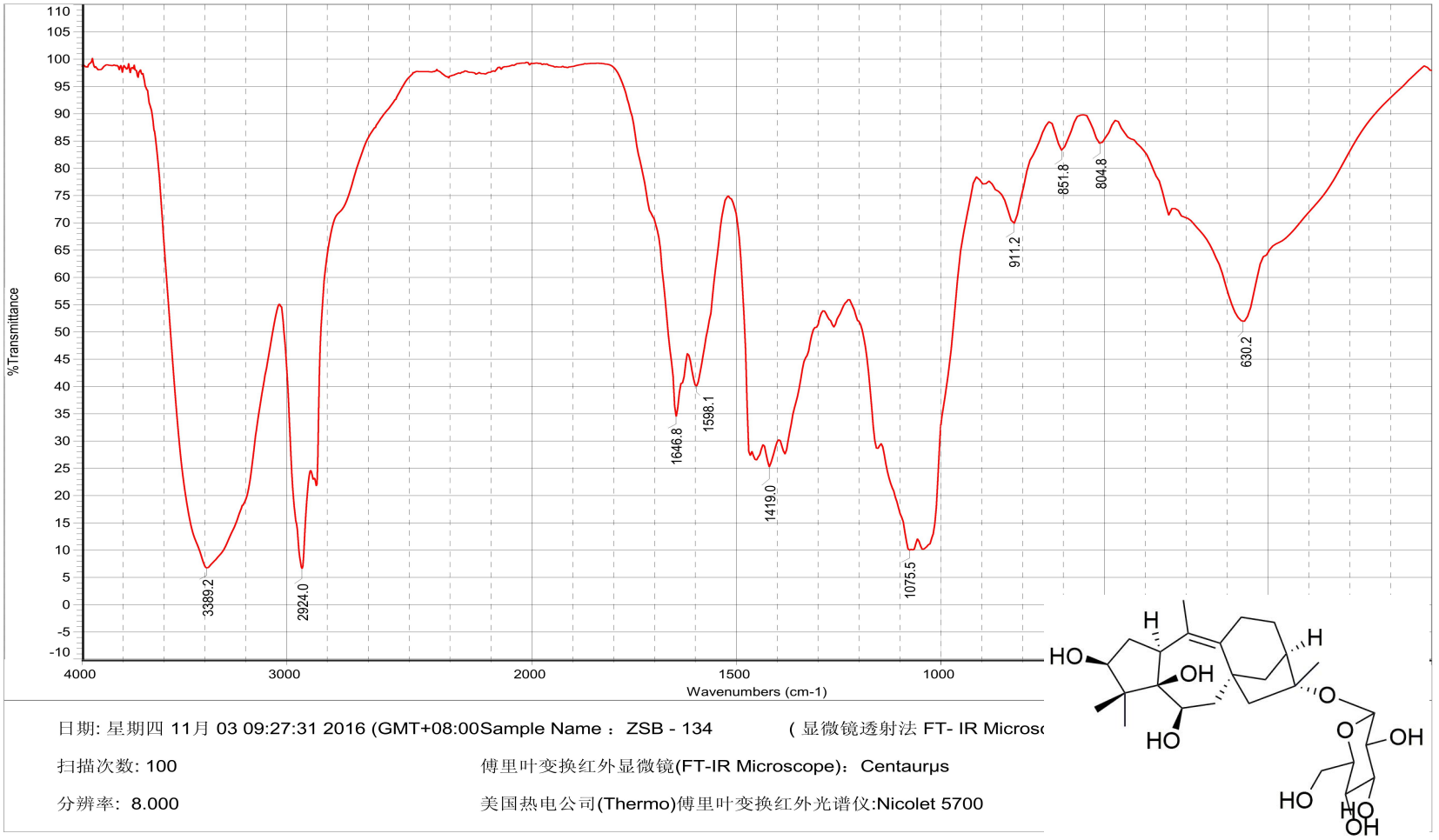
The HMBC spectrum of **4** in C_5D_5N (^1H: 600 MHz, ^{13}C: 150 MHz)



The HMBC spectrum (amplified) of **4** in C_5D_5N (^1H: 600 MHz, ^{13}C: 150 MHz)



The NOESY spectrum of **4** in C_5D_5N (600 MHz)

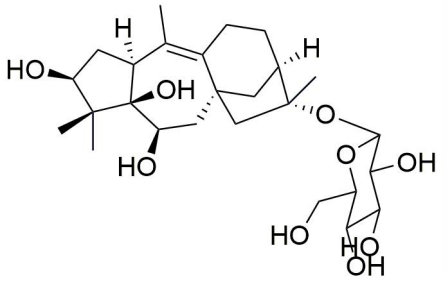


The IR spectrum of **5**

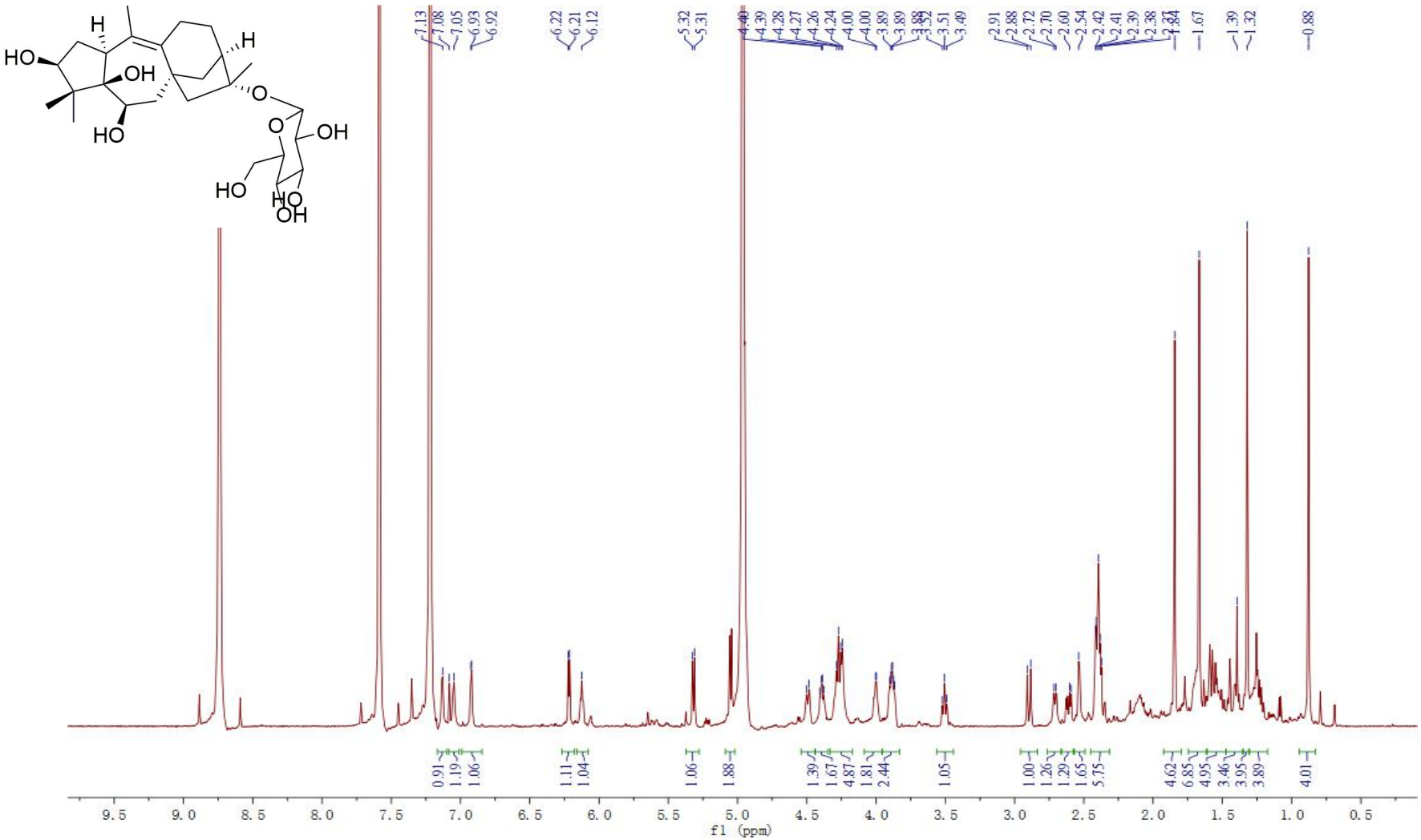
MS Formula Results: + Scan (6.410 min) Sub (2016032905.d)

m/z	Ion	Formula	Abundance
521.2722	(M+Na)+	C26 H42 Na O9	182458.1

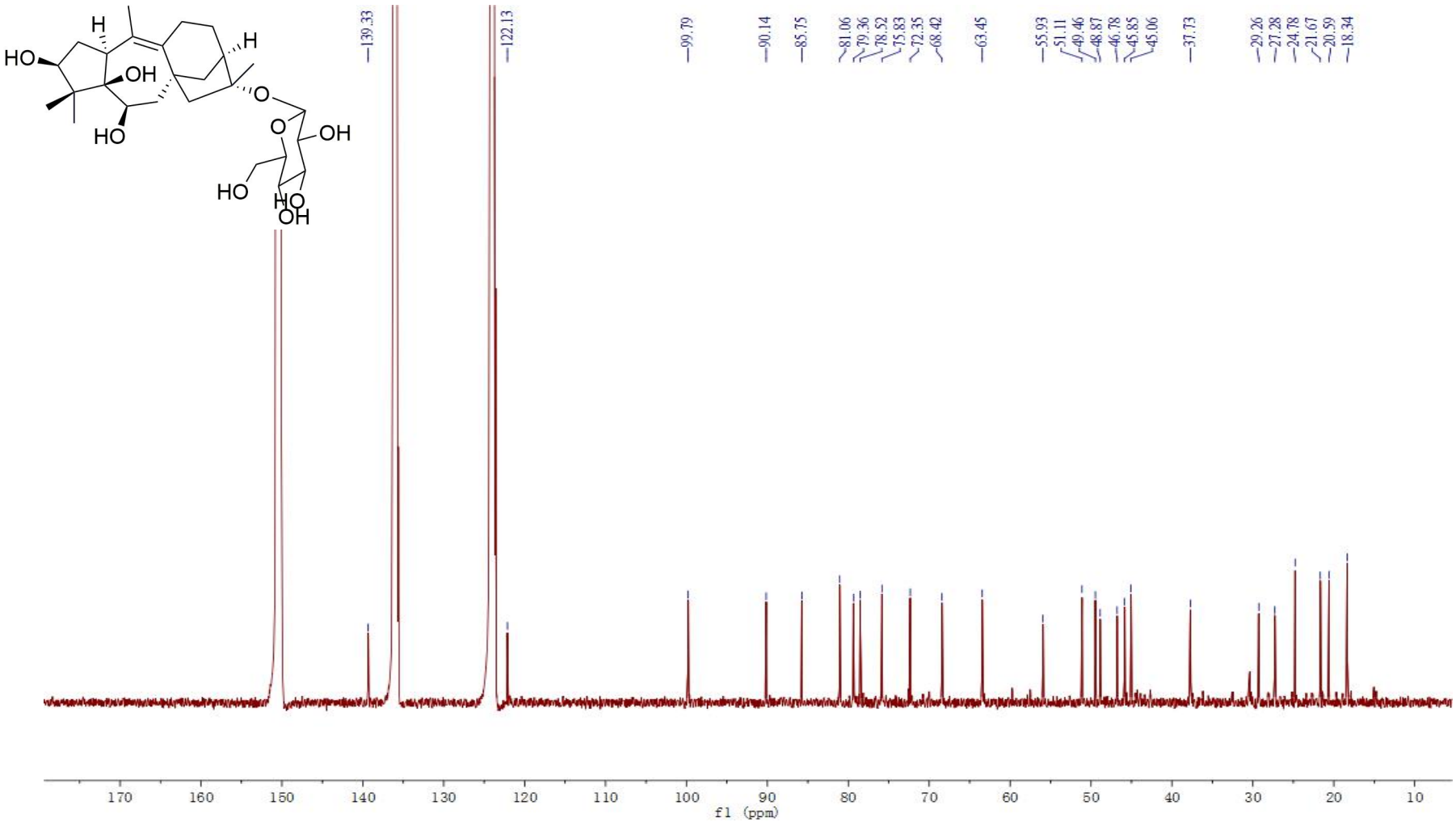
Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
☑	C26 H42 O9	C26 H42 Na O9	99.85		498.283	498.2829	521.2721	-0.27	0.27	100	99.65	99.79	6
☐	C30 H42 O4 S	C30 H42 Na O4 S	98.5		498.283	498.2804	521.2696	-5.29	5.29	99.12	96.22	99.99	10
☐	C27 H46 O4 S2	C27 H46 Na O4 S2	98		498.283	498.2838	521.273	1.47	1.47	99.93	93.24	99.84	5
☐	C26 H46 O5 S Si	C26 H46 Na O5 S Si	97.81		498.283	498.2835	521.2727	0.99	0.99	99.97	92.48	99.9	5
☐	C29 H42 O5 Si	C29 H42 Na O5 Si	97.65		498.283	498.2802	521.2694	-5.77	5.77	98.96	93.51	99.99	10
☐	C25 H46 O6 Si2	C25 H46 Na O6 Si2	97.24		498.283	498.2833	521.2725	0.51	0.51	99.99	90.45	99.91	5
☐	C30 H46 S2 Si	C30 H46 Na S2 Si	95		498.283	498.281	521.2702	-4.04	4.04	99.49	83.5	99.82	9
☐	C29 H46 O S Si2	C29 H46 Na O S Si2	94.3		498.283	498.2808	521.27	-4.51	4.51	99.36	81.26	99.84	9
☐	C21 H50 N2 O3 S2 Si2	C21 H50 N2 Na O3 S2 Si2	93.78		498.283	498.2801	521.2694	-5.83	5.83	98.93	80.35	99.58	0
☐	C26 H50 O S2 Si2	C26 H50 Na O S2 Si2	93.44		498.283	498.2842	521.2734	2.25	2.25	99.84	77.55	99.7	4
☐	C28 H46 O2 Si3	C28 H46 Na O2 Si3	93.4		498.283	498.2806	521.2698	-4.98	4.98	99.22	78.33	99.83	9
☐	C25 H50 O2 S Si3	C25 H50 Na O2 S Si3	93		498.283	498.2839	521.2732	1.78	1.78	99.9	75.92	99.69	4
☐	C33 H39 Cl N2	C33 H39 Cl N2 Na	85.11		498.283	498.2802	521.2694	-5.71	5.71	98.98	49.84	99.71	15
☐	C29 H43 Cl N2 O Si	C29 H43 Cl N2 Na O Si	84.06		498.283	498.2833	521.2725	0.58	0.58	99.99	44.51	99.66	10
☐	C30 H43 Cl N2 S	C30 H43 Cl N2 Na S	83.58		498.283	498.2835	521.2728	1.05	1.05	99.96	42.9	99.63	10
☐	C32 H44 Cl2	C32 H44 Cl2 Na	75.9		498.283	498.282	521.2712	-2.03	2.03	99.87	16.24	99.57	10
☐	C28 H48 Cl2 O Si	C28 H48 Cl2 Na O Si	75.24		498.283	498.2851	521.2744	4.25	4.25	99.43	14.64	99.56	5
☐	C23 H48 Cl2 N2 O3 Si	C23 H48 Cl2 N2 Na O3 Si	74.91		498.283	498.2811	521.2703	-3.83	3.83	99.54	13.35	99.52	1
☐	C29 H48 Cl2 S	C29 H48 Cl2 Na S	74.82		498.283	498.2854	521.2746	4.73	4.73	99.3	13.42	99.54	5
☐	C22 H52 Cl2 N2 Si3	C22 H52 Cl2 N2 Na Si3	74.76		498.283	498.2815	521.2708	-3.04	3.04	99.71	12.64	99.38	0
☐	C24 H48 Cl2 N2 O2 S	C24 H48 Cl2 N2 Na O2 S	74.56		498.283	498.2814	521.2706	-3.35	3.35	99.65	11.95	99.51	1



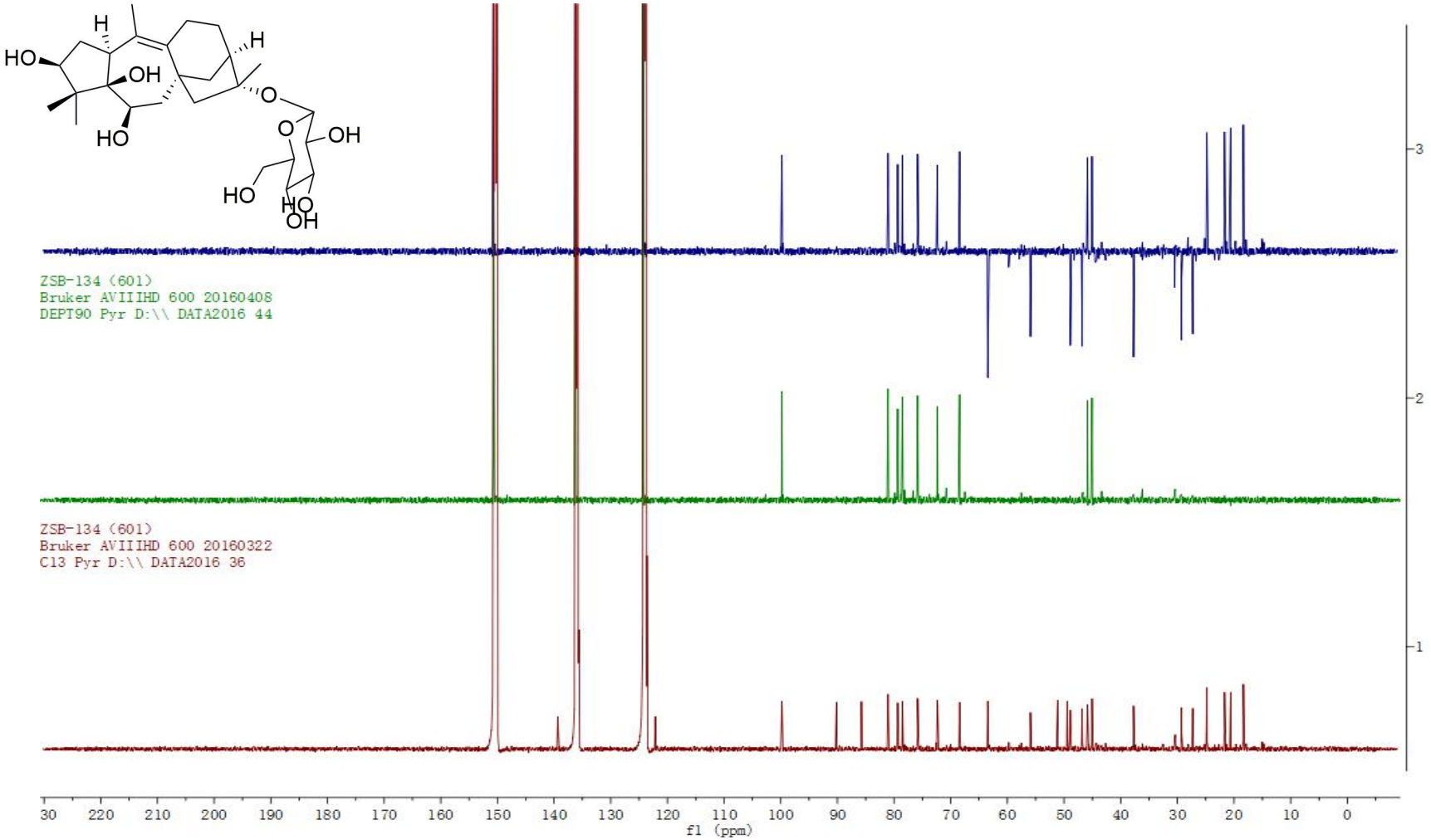
The HRESIMS spectrum of **5**



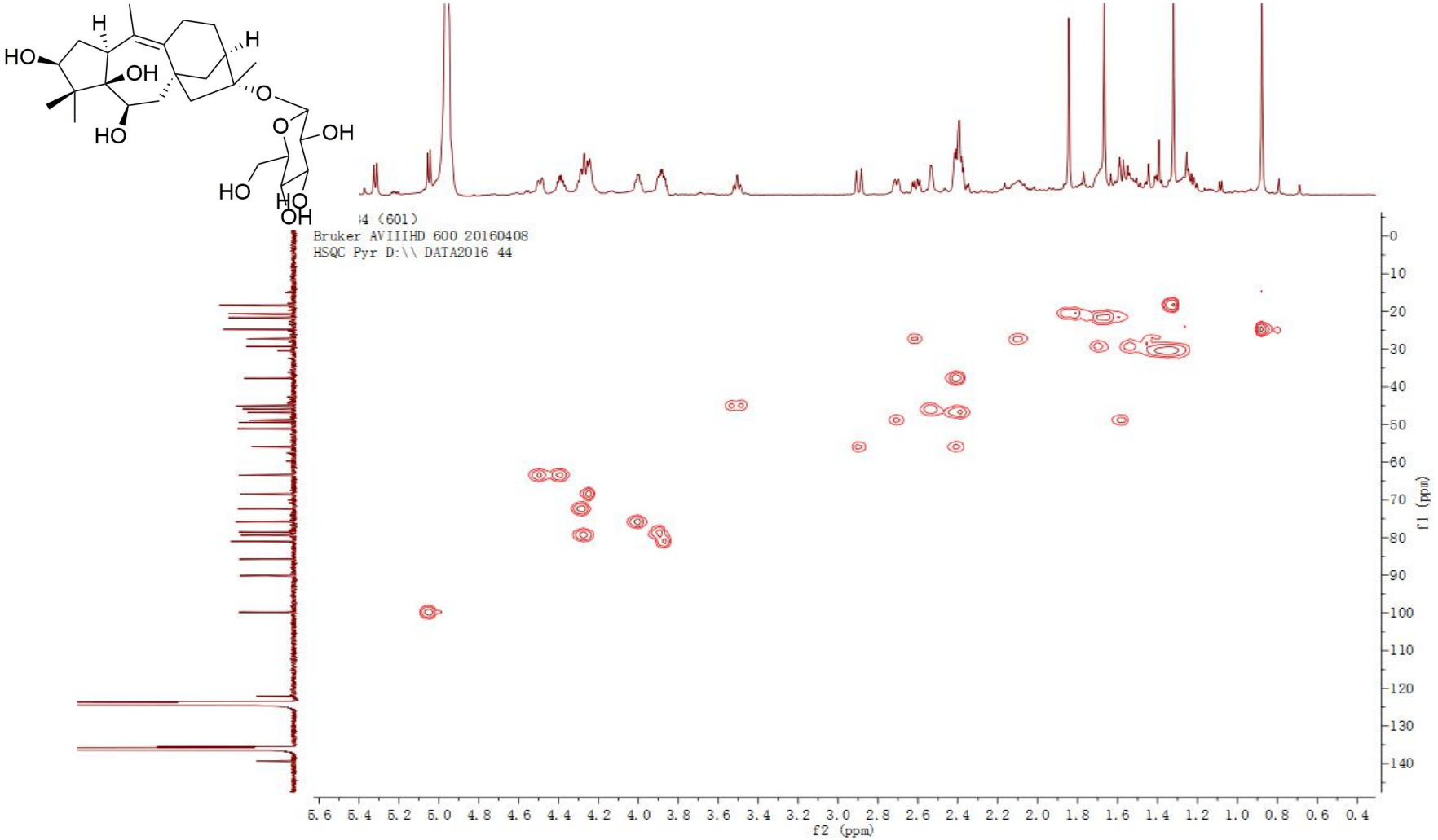
The ^{1}H NMR spectrum of **5** in C_5D_5N (600 MHz)



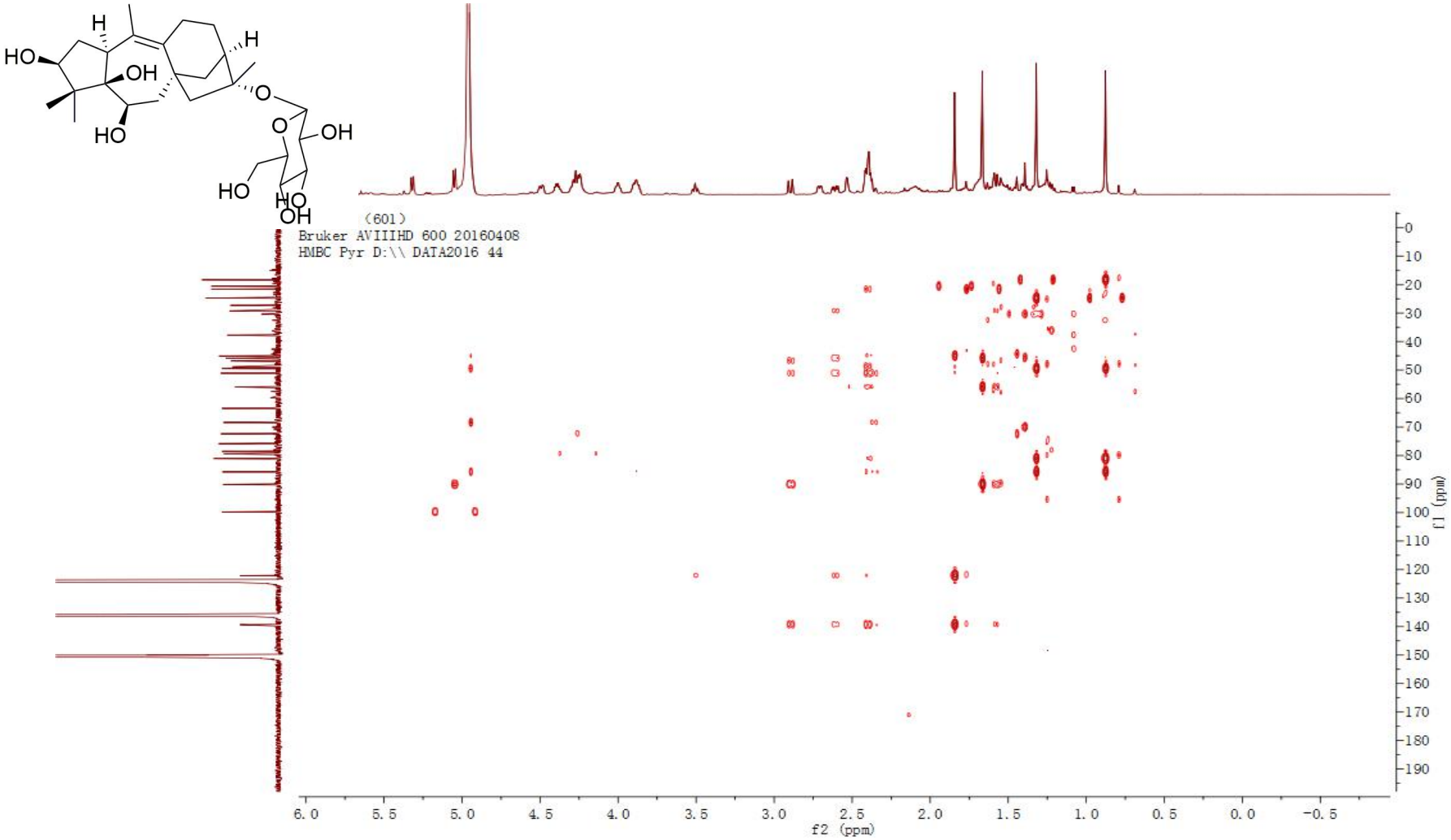
The ^{13}C NMR spectrum of **5** in C_5D_5N (150 MHz)



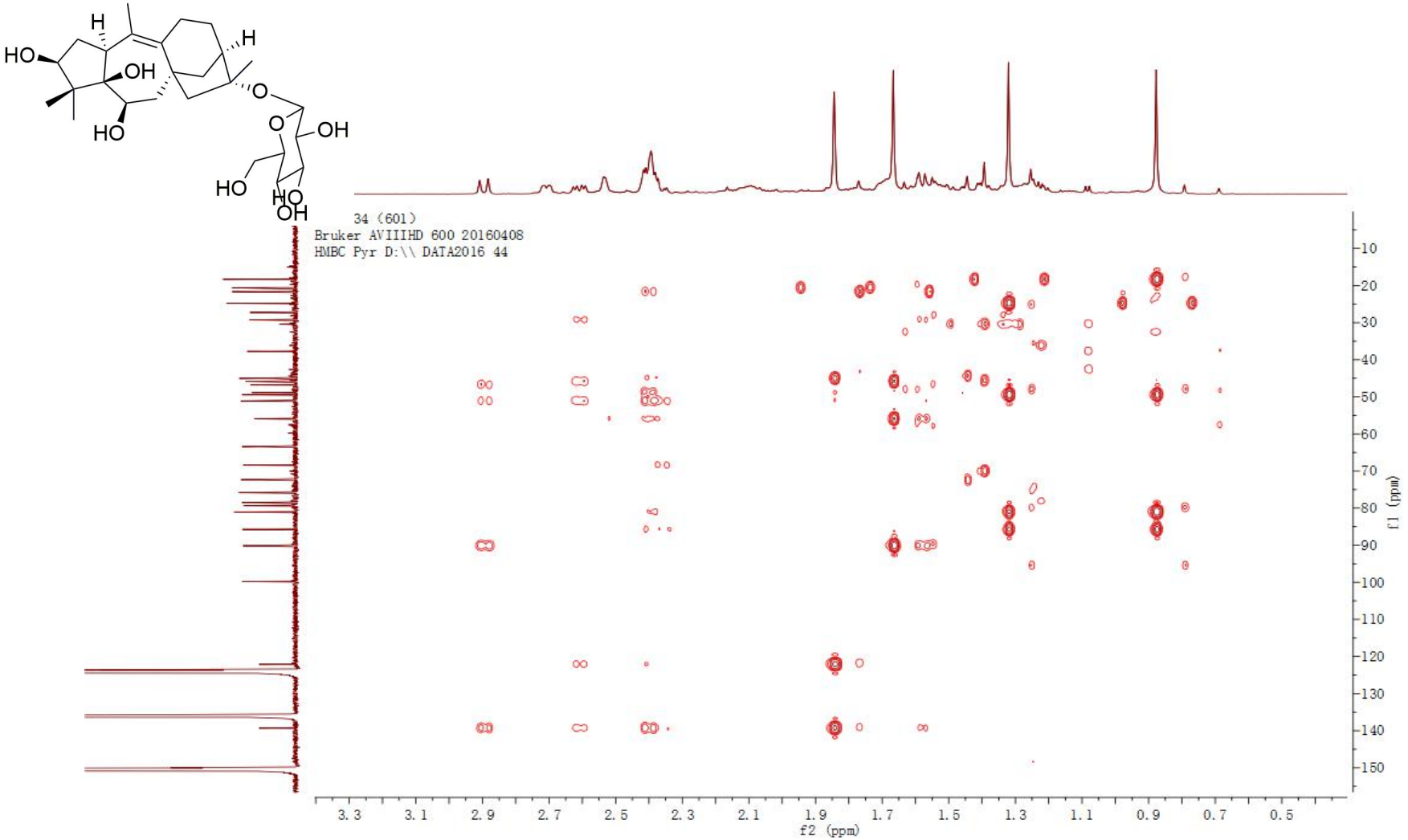
The DEPT spectrum of **5** in C_5D_5N (150 MHz)



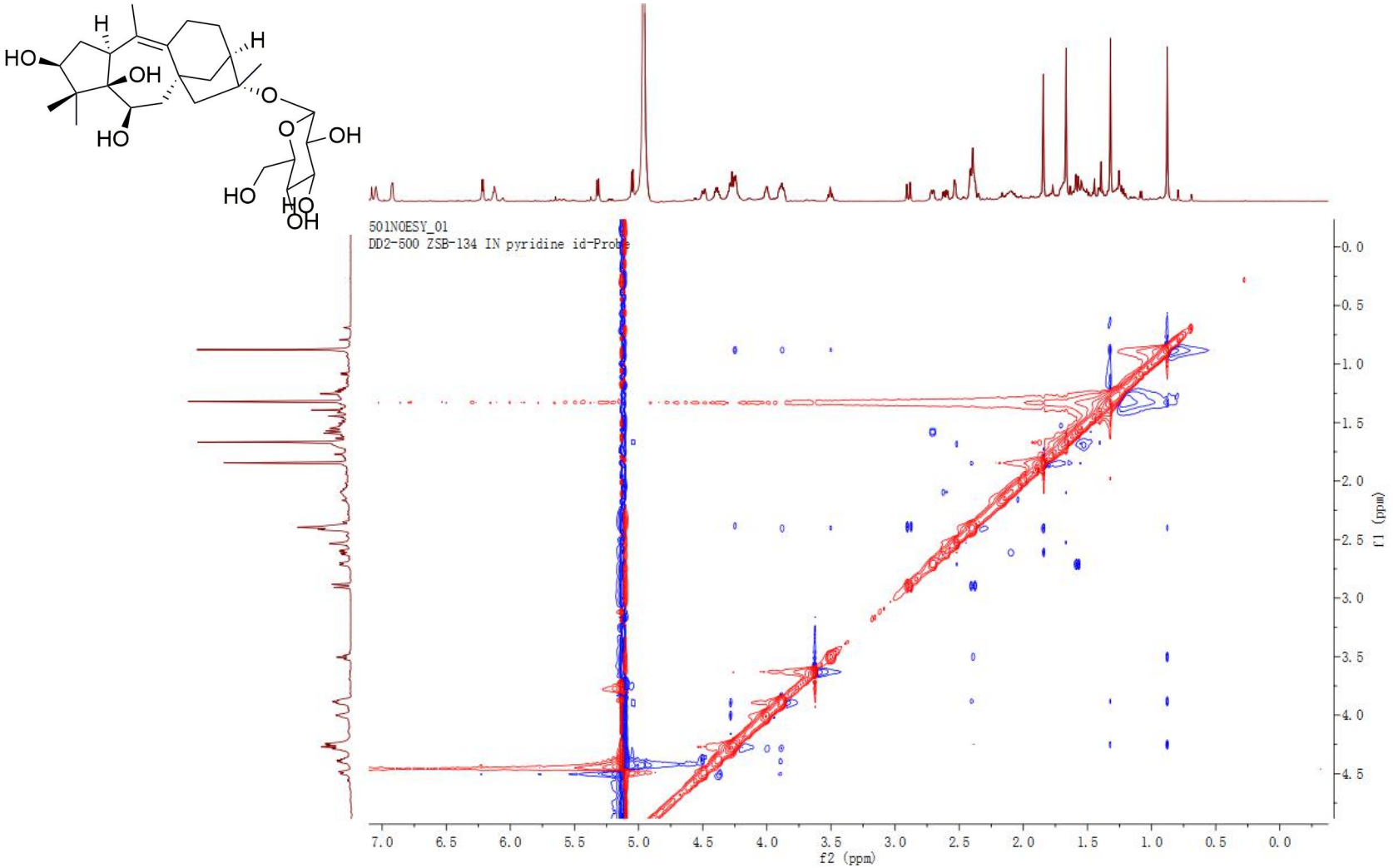
The HSQC spectrum of **5** in C_5D_5N (^1H: 600 MHz, ^{13}C: 150 MHz)



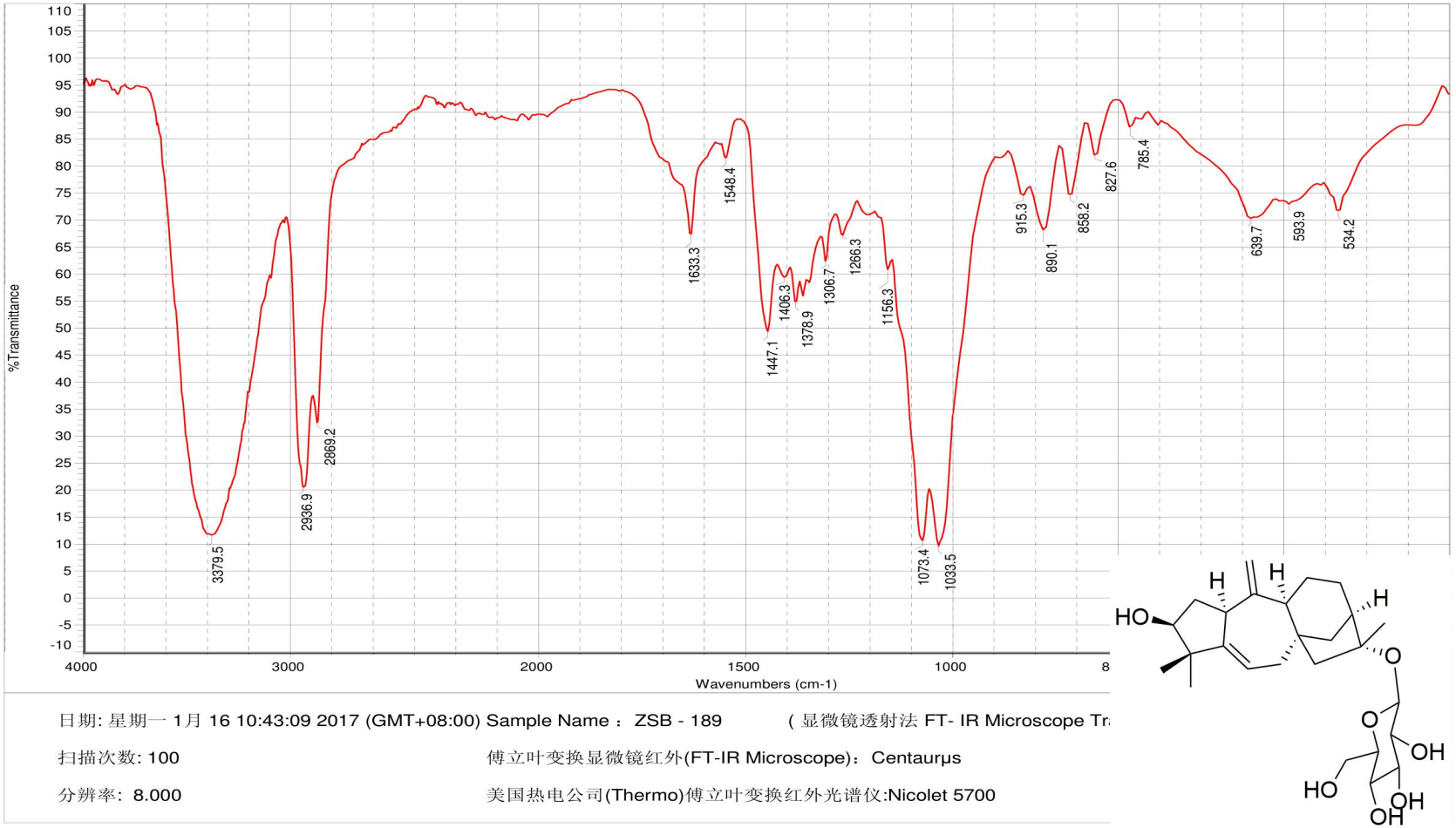
The HMBC spectrum of **5** in C_5D_5N (^1H: 600 MHz, ^{13}C: 150 MHz)



The HMBC spectrum (amplified) of **5** in C_5D_5N (^1H: 600 MHz, ^{13}C: 150 MHz)



The NOESY spectrum of **5** in C_5D_5N (600 MHz)

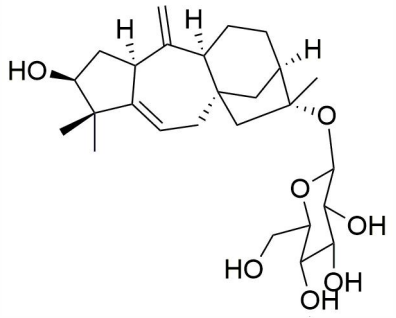


The IR spectrum of **6**

MS Formula Results: + Scan (6.973 min) Sub (2016052604.d)

	m/z	Ion	Formula	Abundance
-	487.2676	(M+Na)+	C26 H40 Na O7	360201.6

	Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
+	☑	C26 H40 O7	C26 H40 Na O7	99.81		464.2783	464.2774	487.2666	-1.95	1.95	99.88	99.86	99.63	7
+	☐	C23 H44 O7 S	C23 H44 Na O7 S	98.86		464.2783	464.2808	487.27	5.3	5.3	99.13	97.69	99.7	2
+	☐	C27 H44 O2 S2	C27 H44 Na O2 S2	97.75		464.2783	464.2783	487.2675	-0.09	0.09	100	92.46	99.6	6



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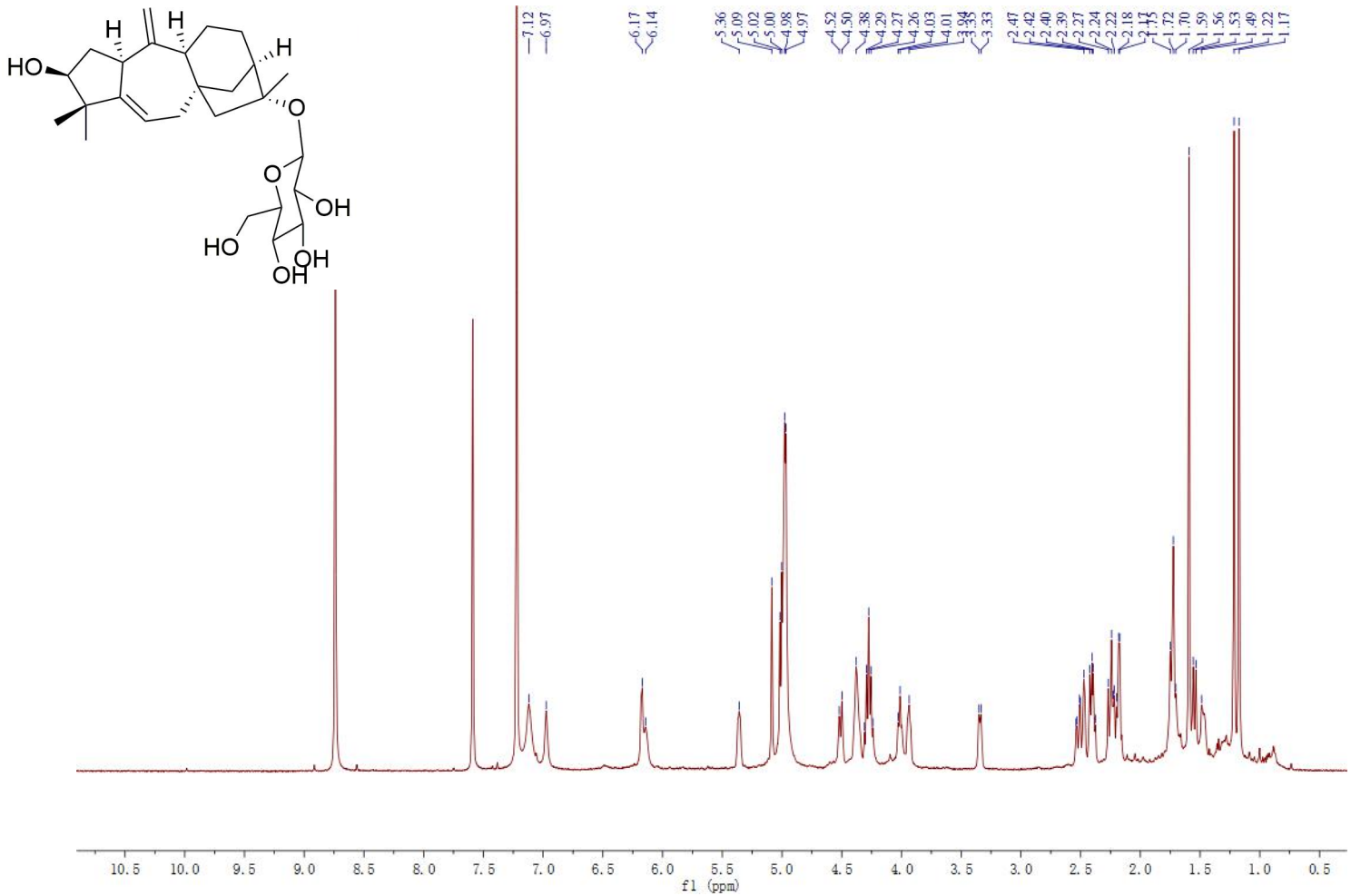
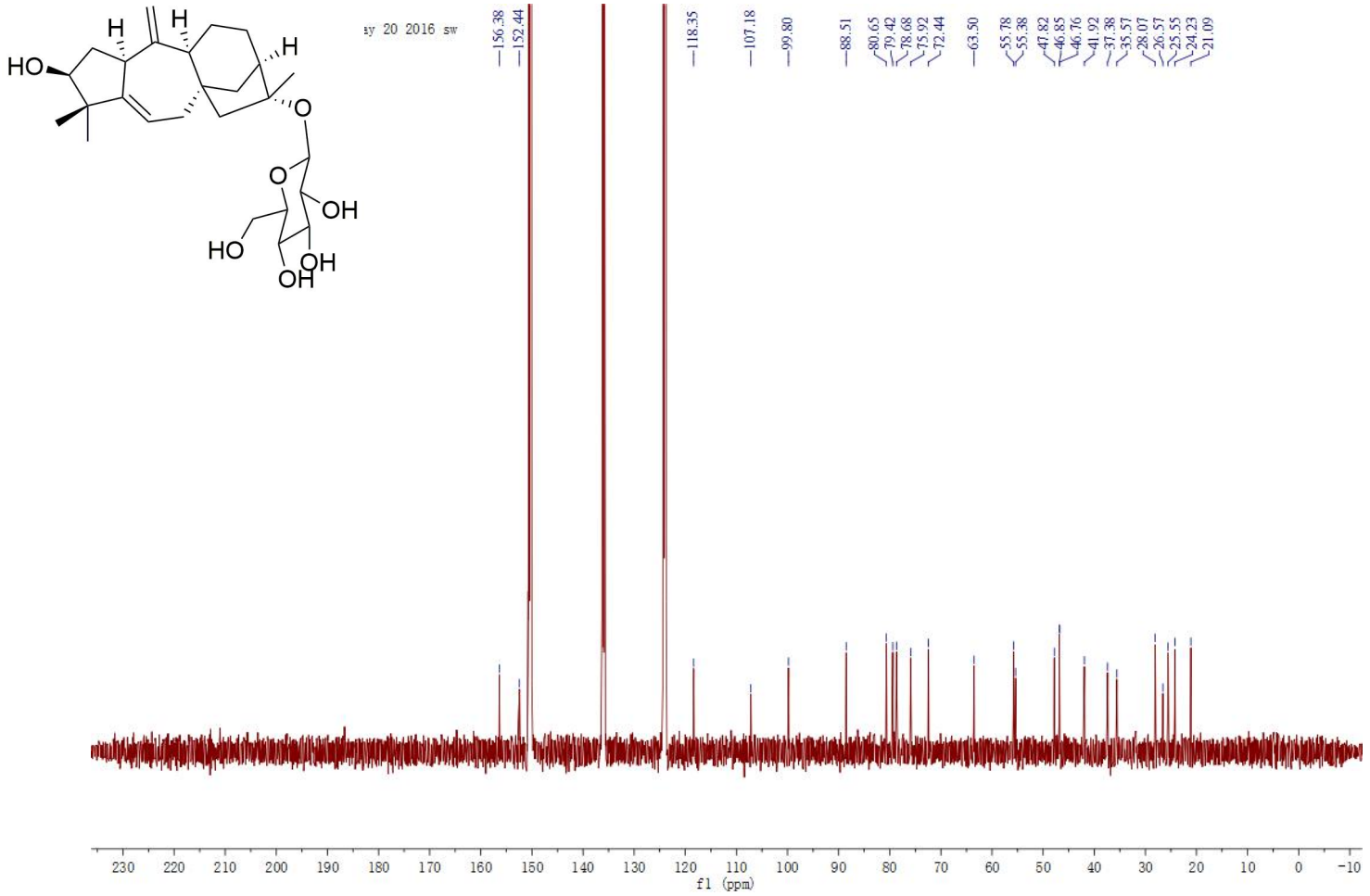
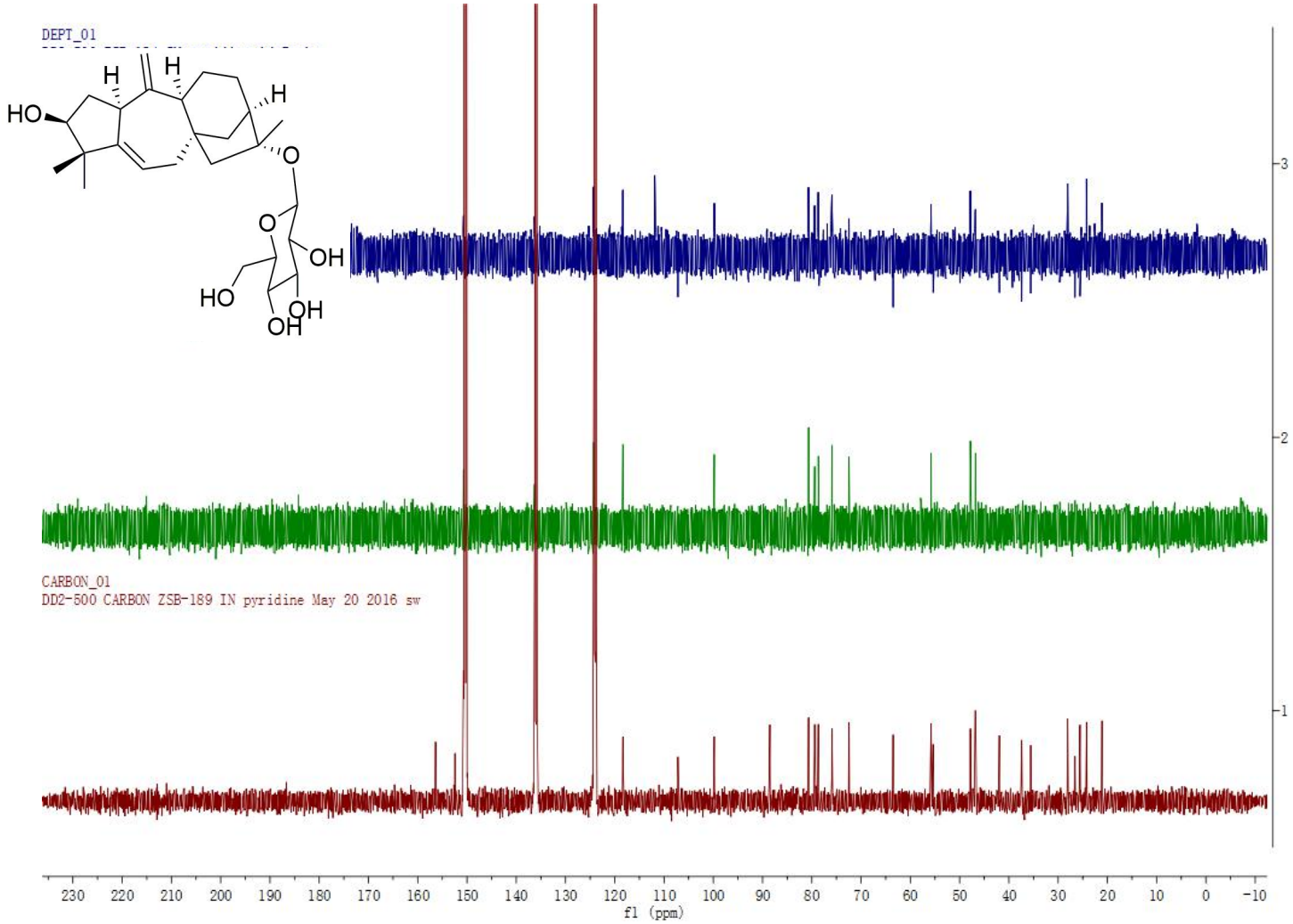
The HRESIMS spectrum of **6**



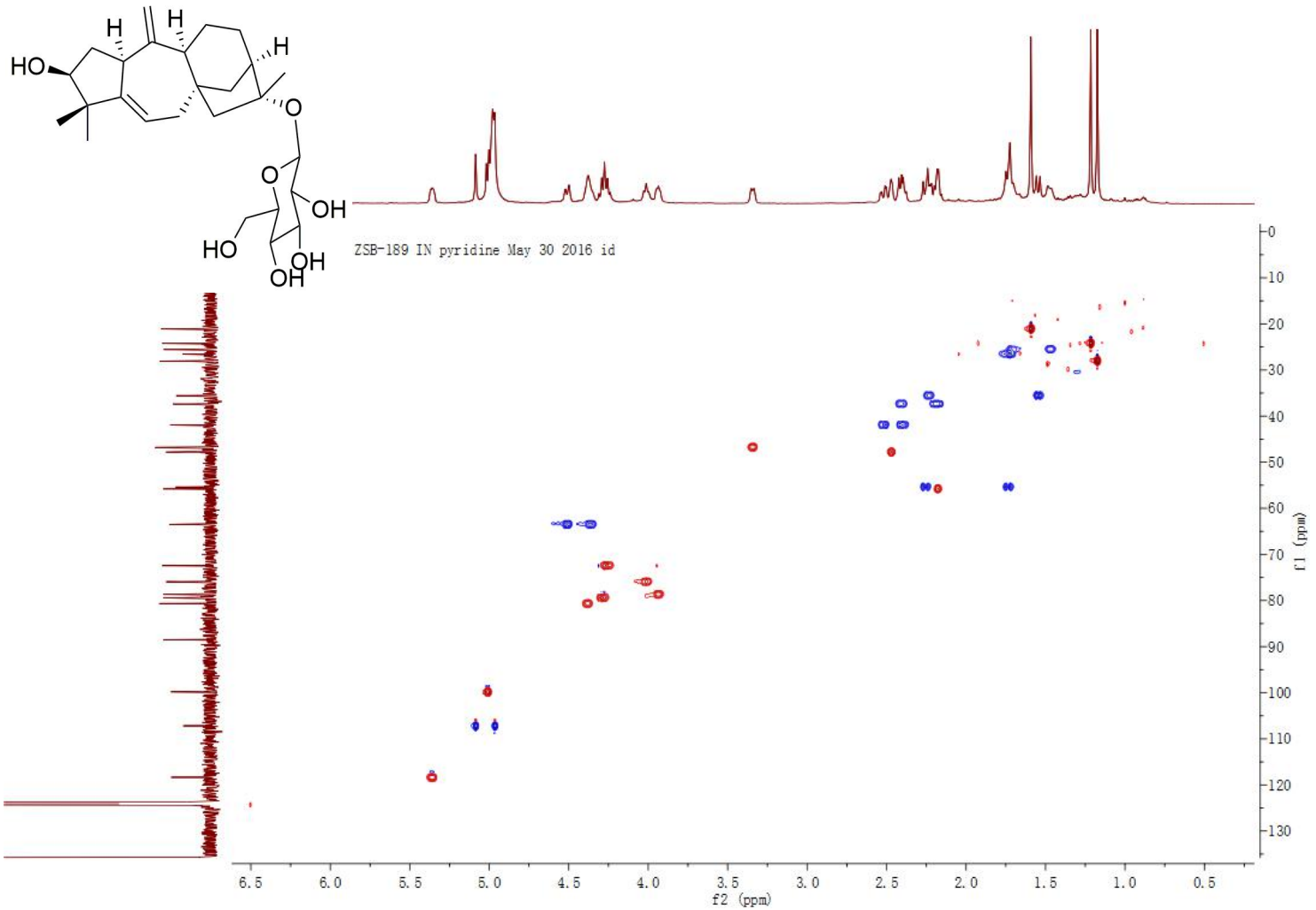
The ^{1}H NMR spectrum of **6** in C_5D_5N (500 MHz)



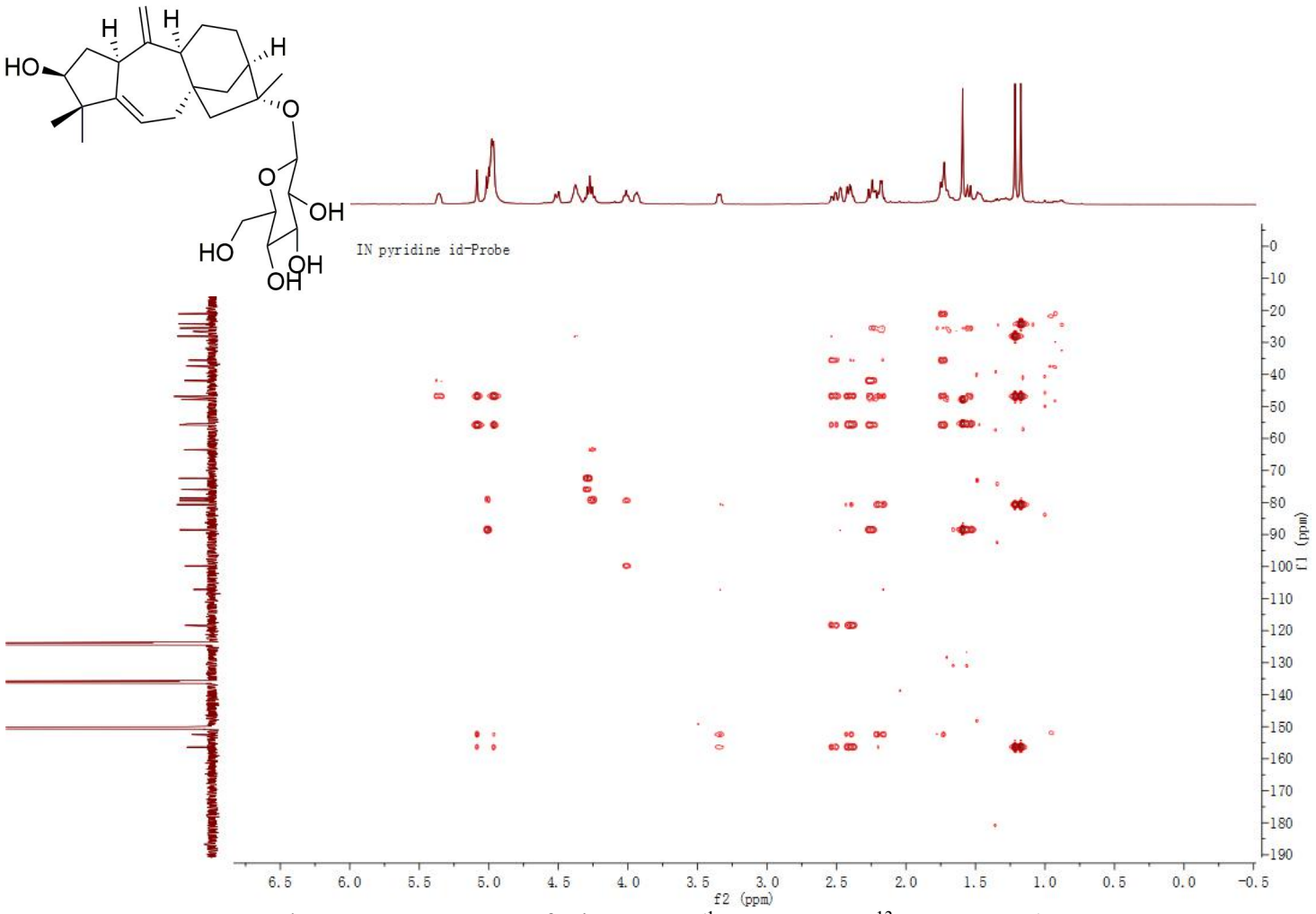
The ^{13}C NMR spectrum of **6** in C_5D_5N (125 MHz)



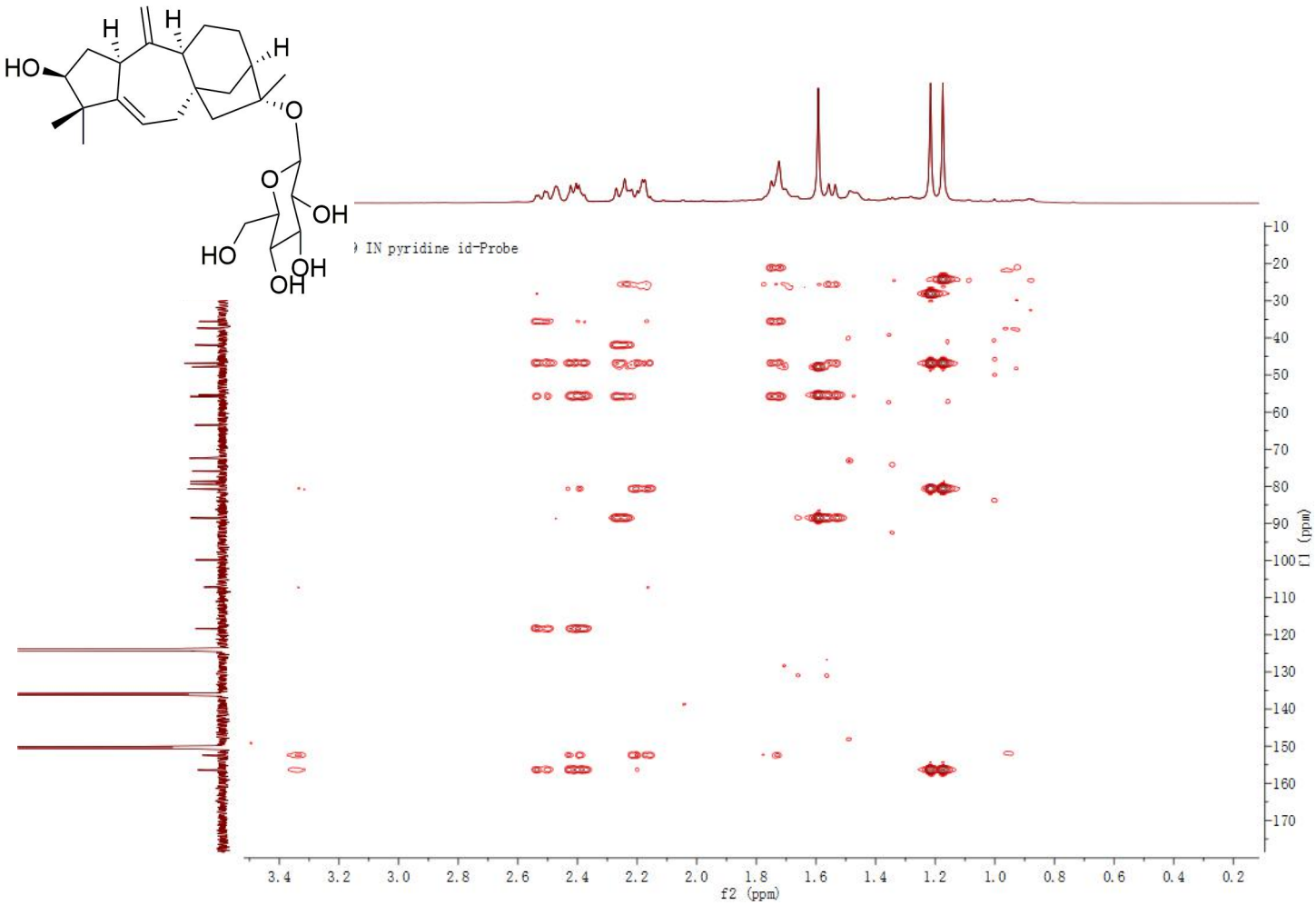
The DEPT spectrum of **6** in C_5D_5N (125 MHz)



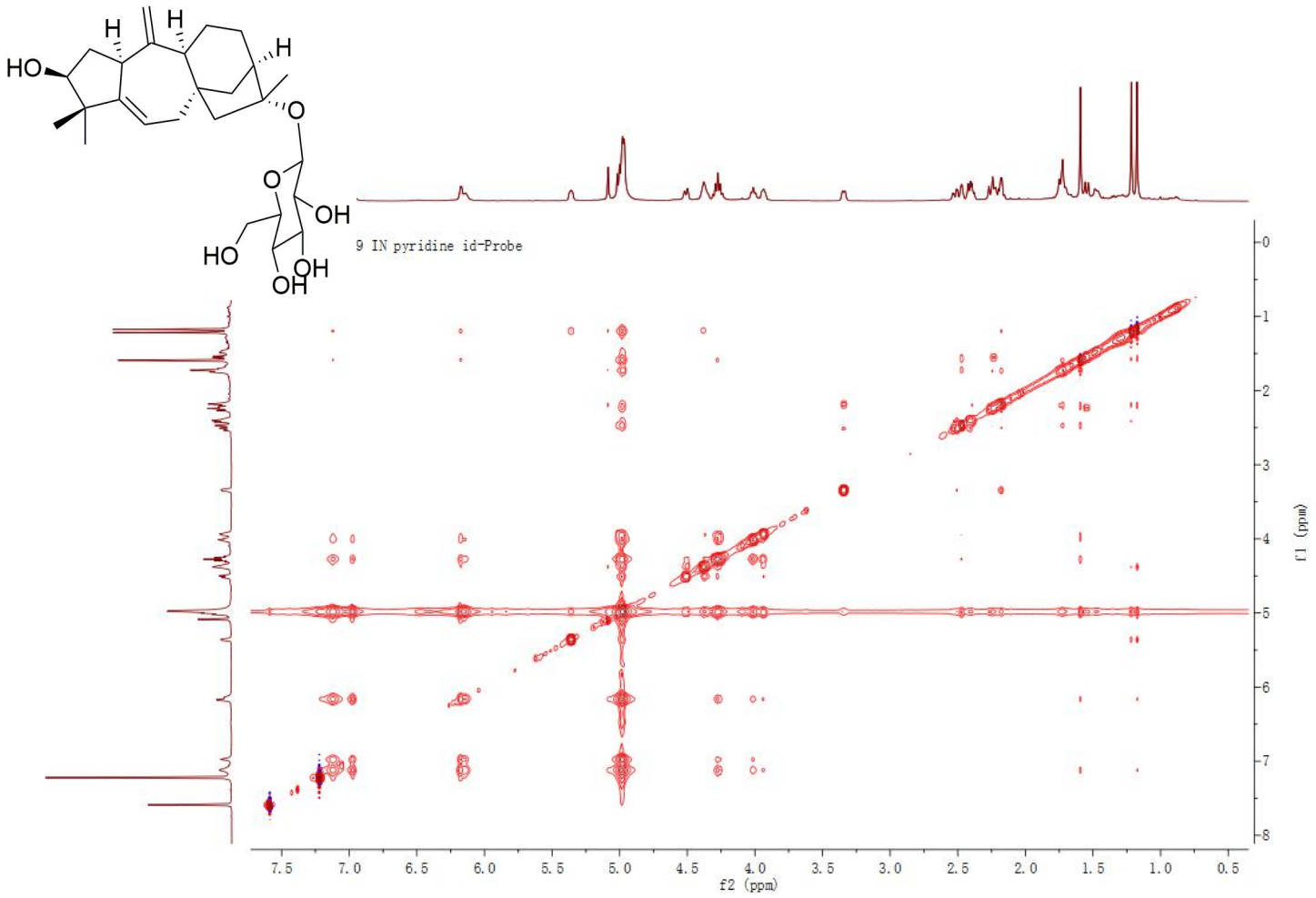
The HSQC spectrum of **6** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



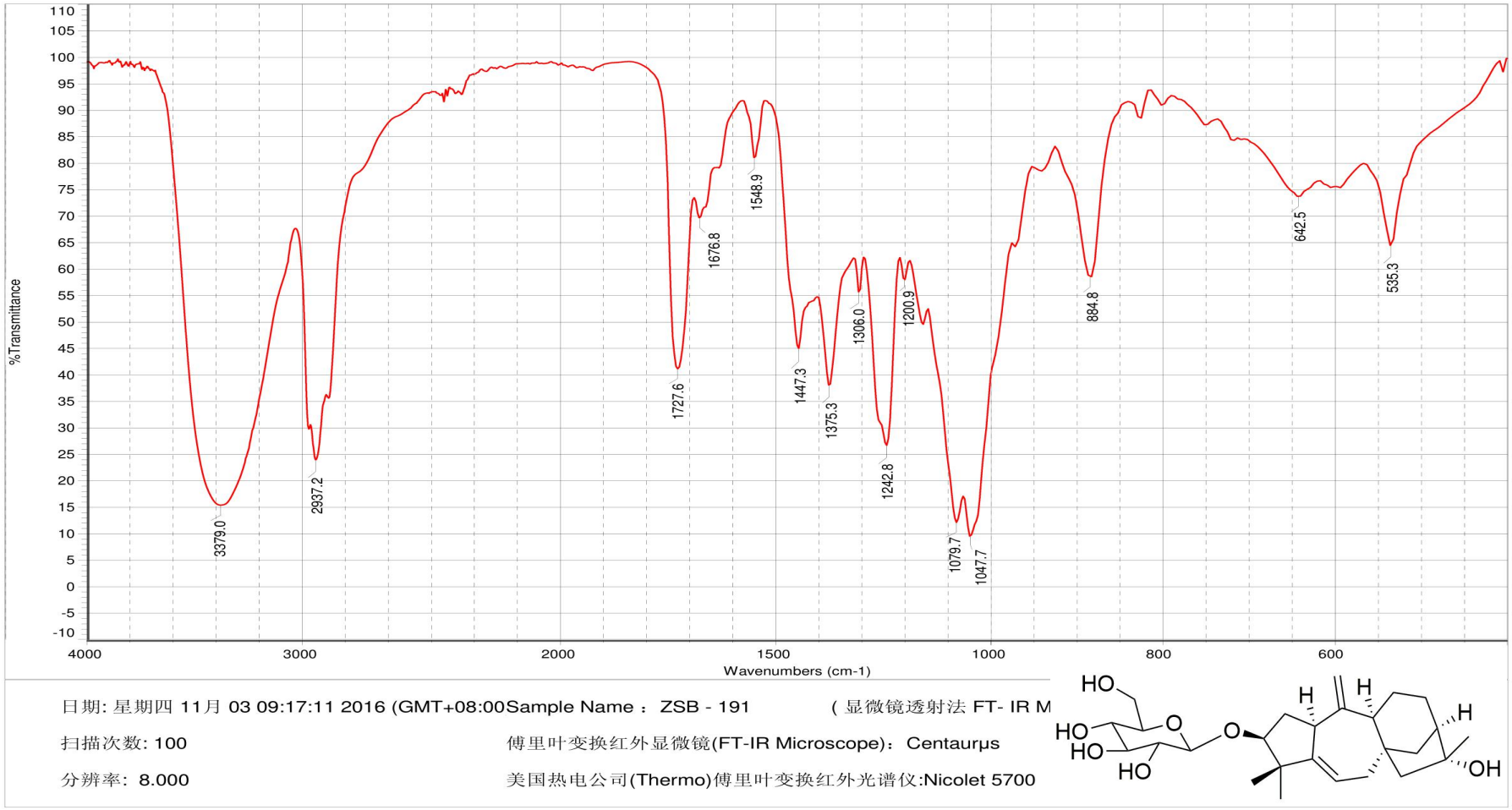
The HMBC spectrum of **6** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The HMBC spectrum (amplified) of **6** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The NOESY spectrum of **6** in C_5D_5N (500 MHz)

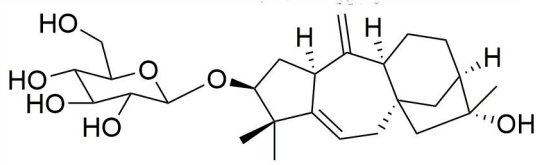


The IR spectrum of **7**

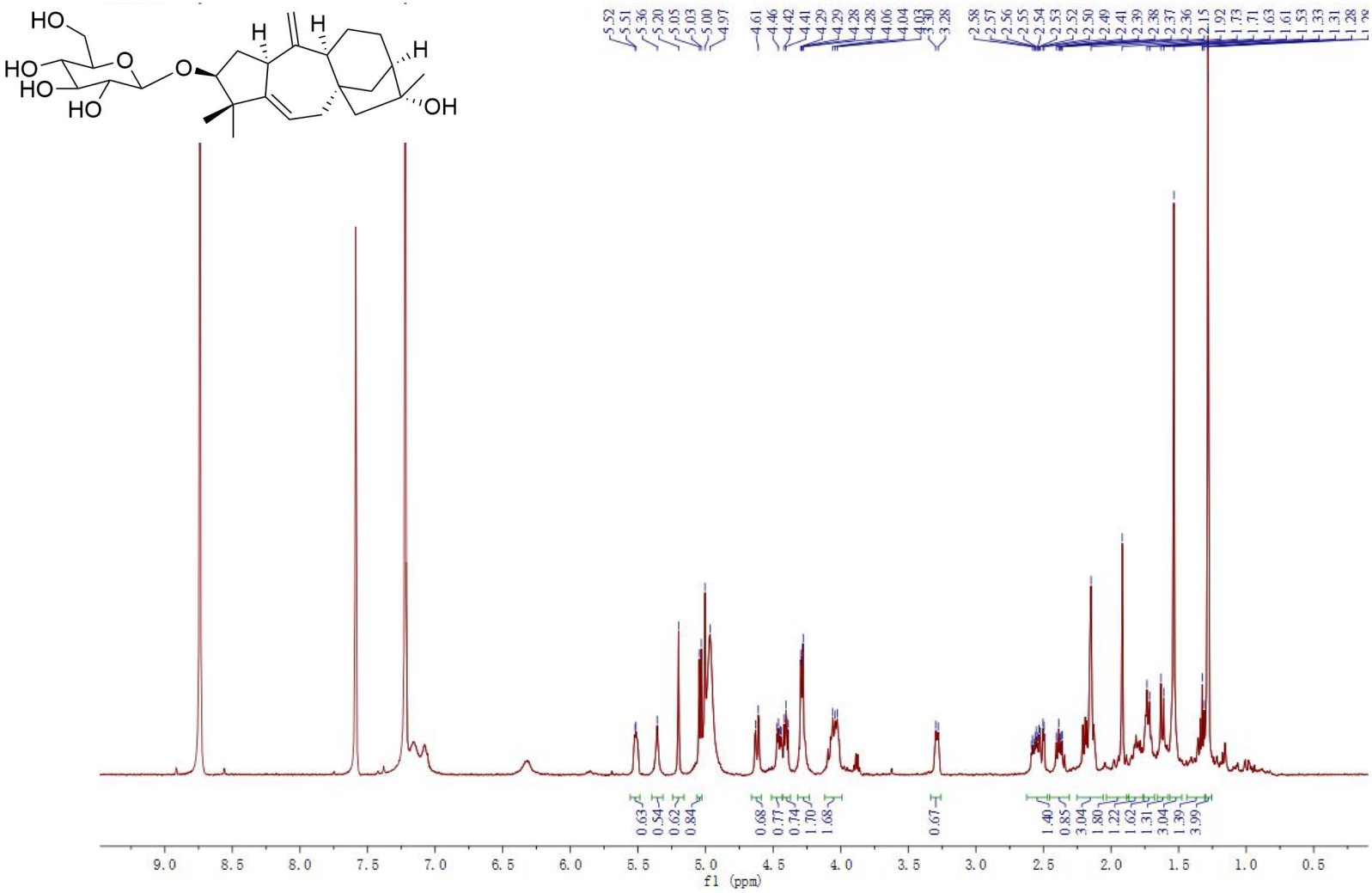
MS Formula Results: + Scan (6.927 min) Sub (2016052607.d)

	m/z	Ion	Formula	Abundance
-	487.2671	(M+Na)+	C26 H40 Na O7	406239.9

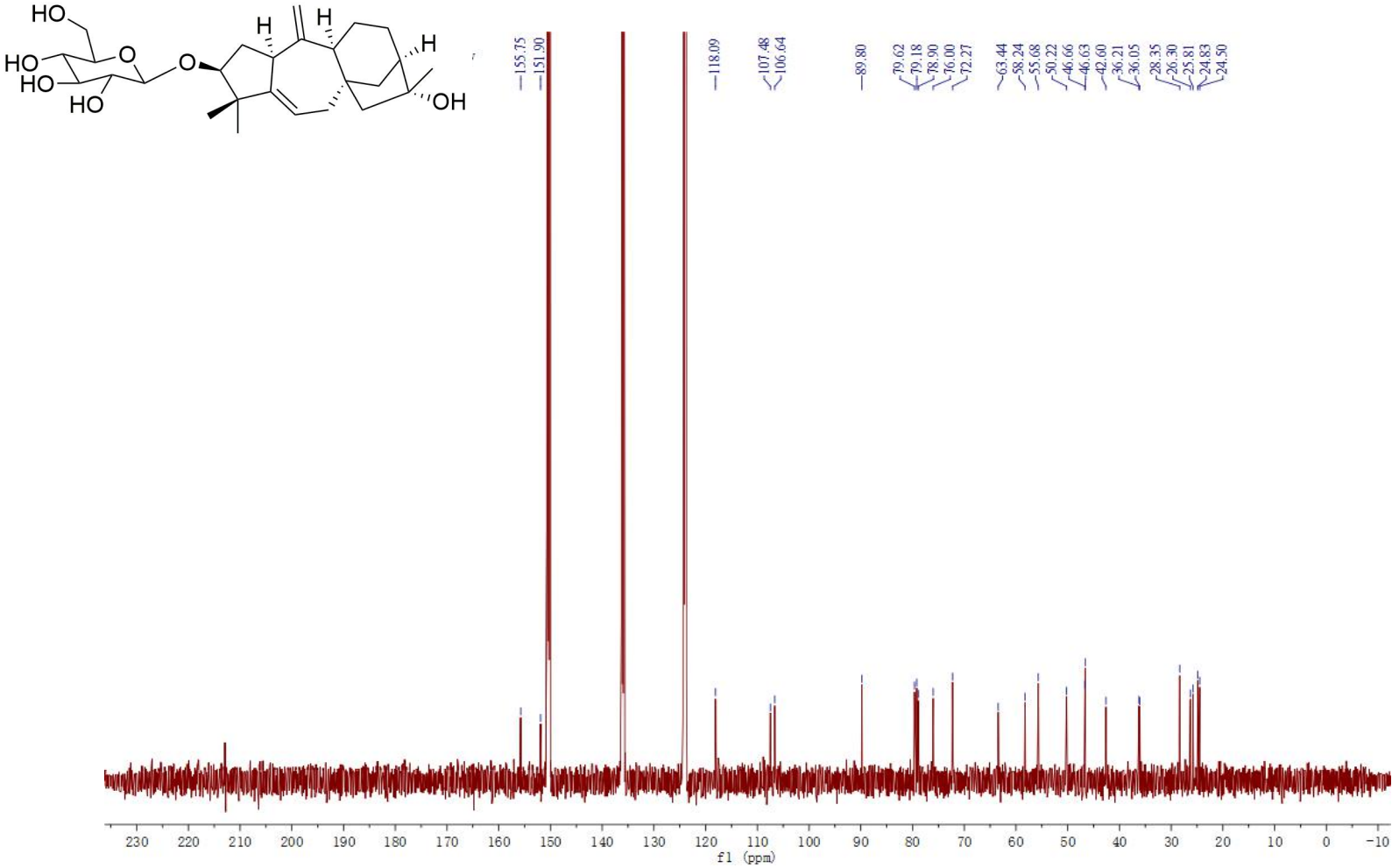
	Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
+	☑	C26 H40 O7	C26 H40 Na O7	99.84		464.2779	464.2774	487.2666	-1.04	1.04	99.97	99.67	99.8	7
+	☐	C27 H44 O2 S2	C27 H44 Na O2 S2	97.92		464.2779	464.2783	487.2675	0.82	0.82	99.98	93.16	99.49	6



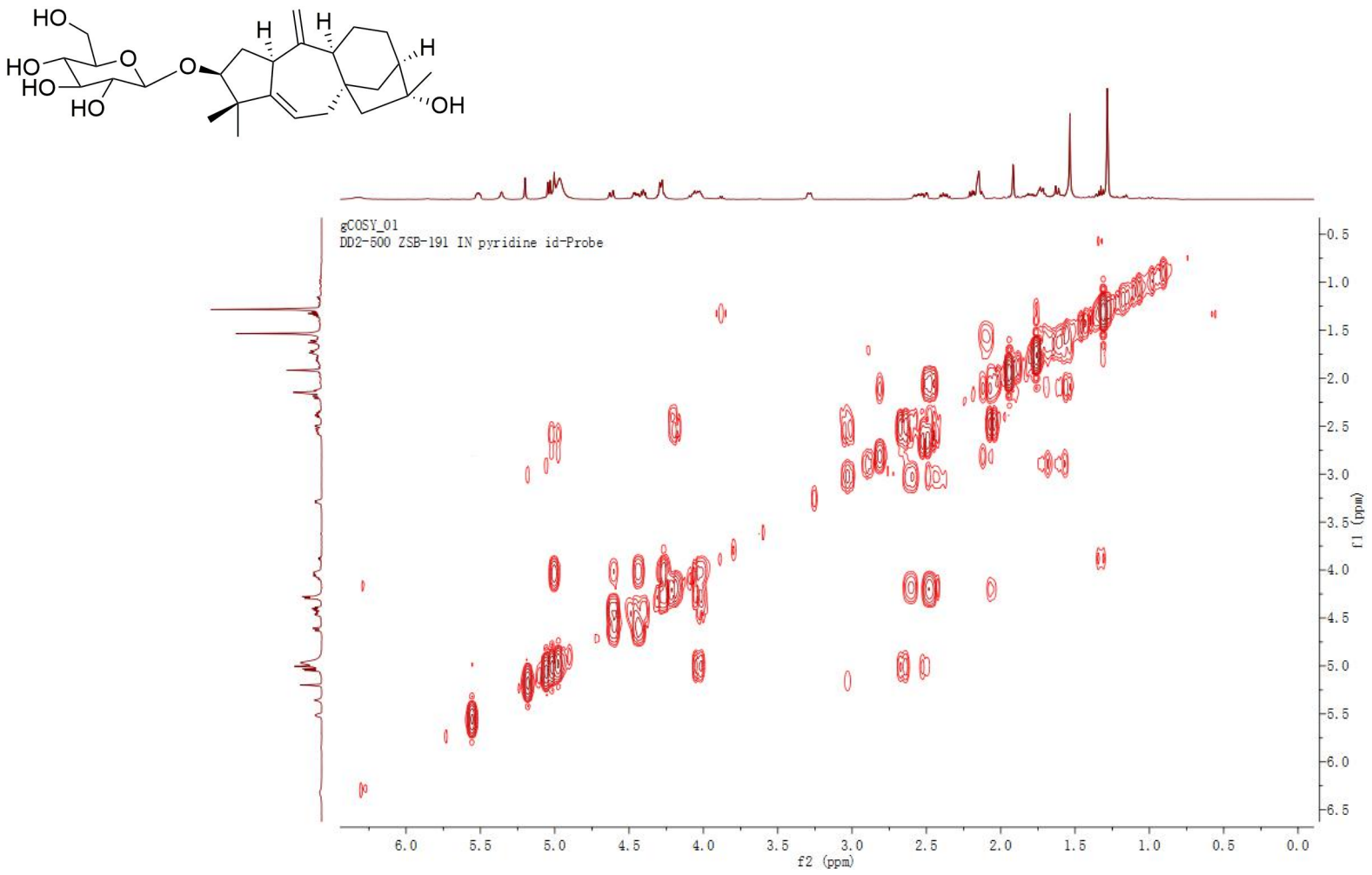
The HRESIMS spectrum of **7**



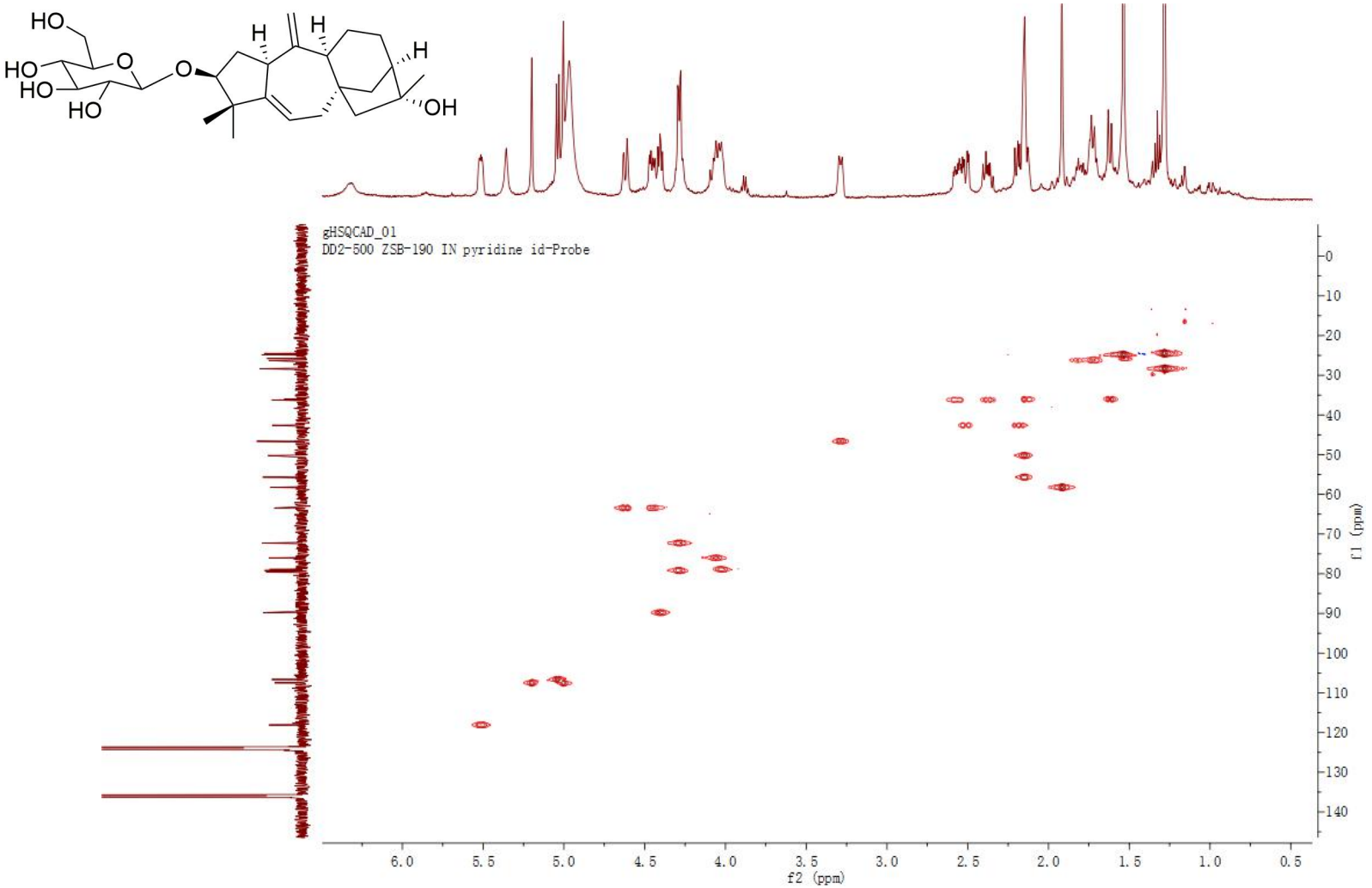
The ^{1}H NMR spectrum of **7** in C_5D_5N (500 MHz)



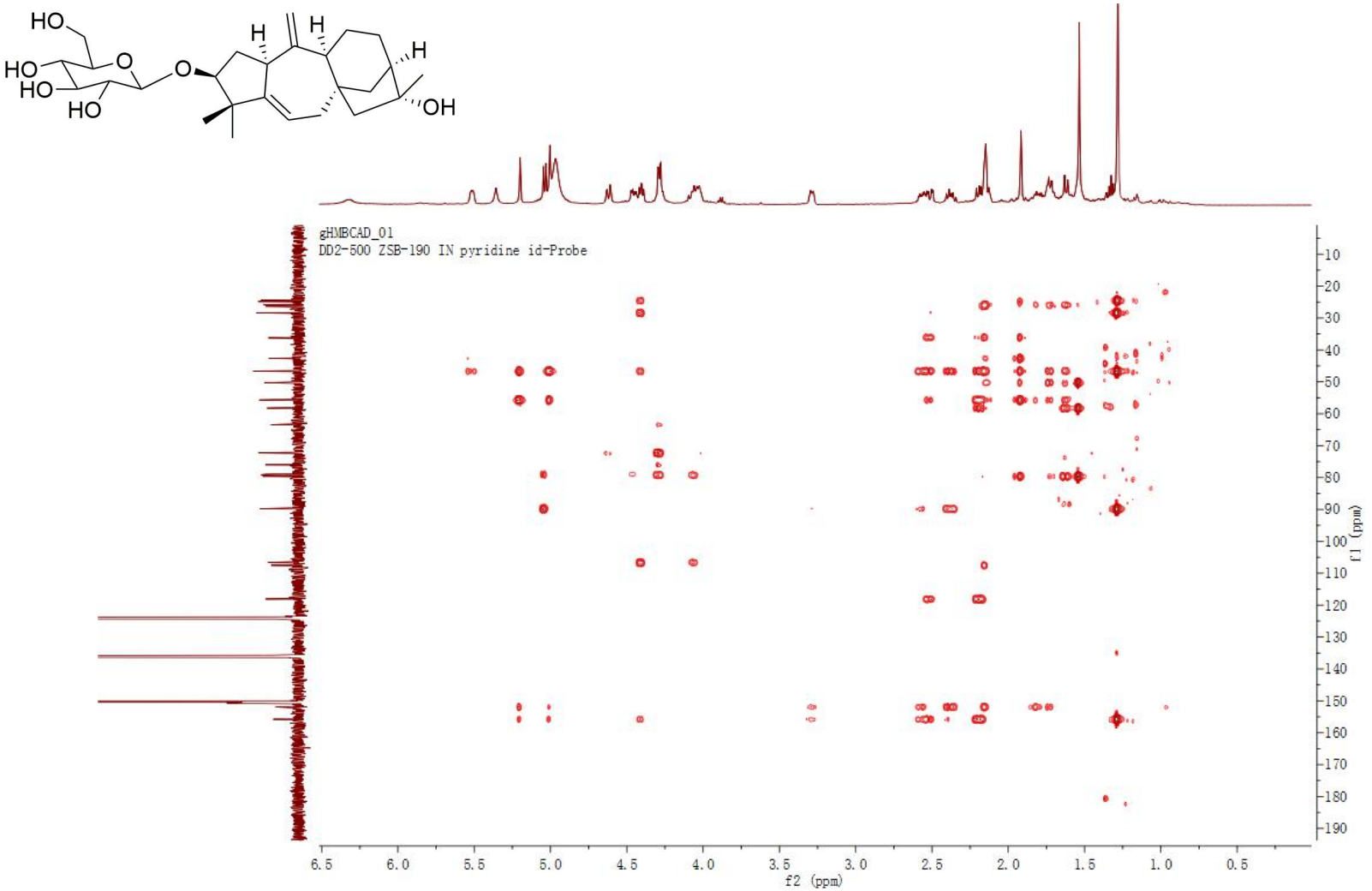
The ^{13}C NMR spectrum of **7** in C_5D_5N (125 MHz)



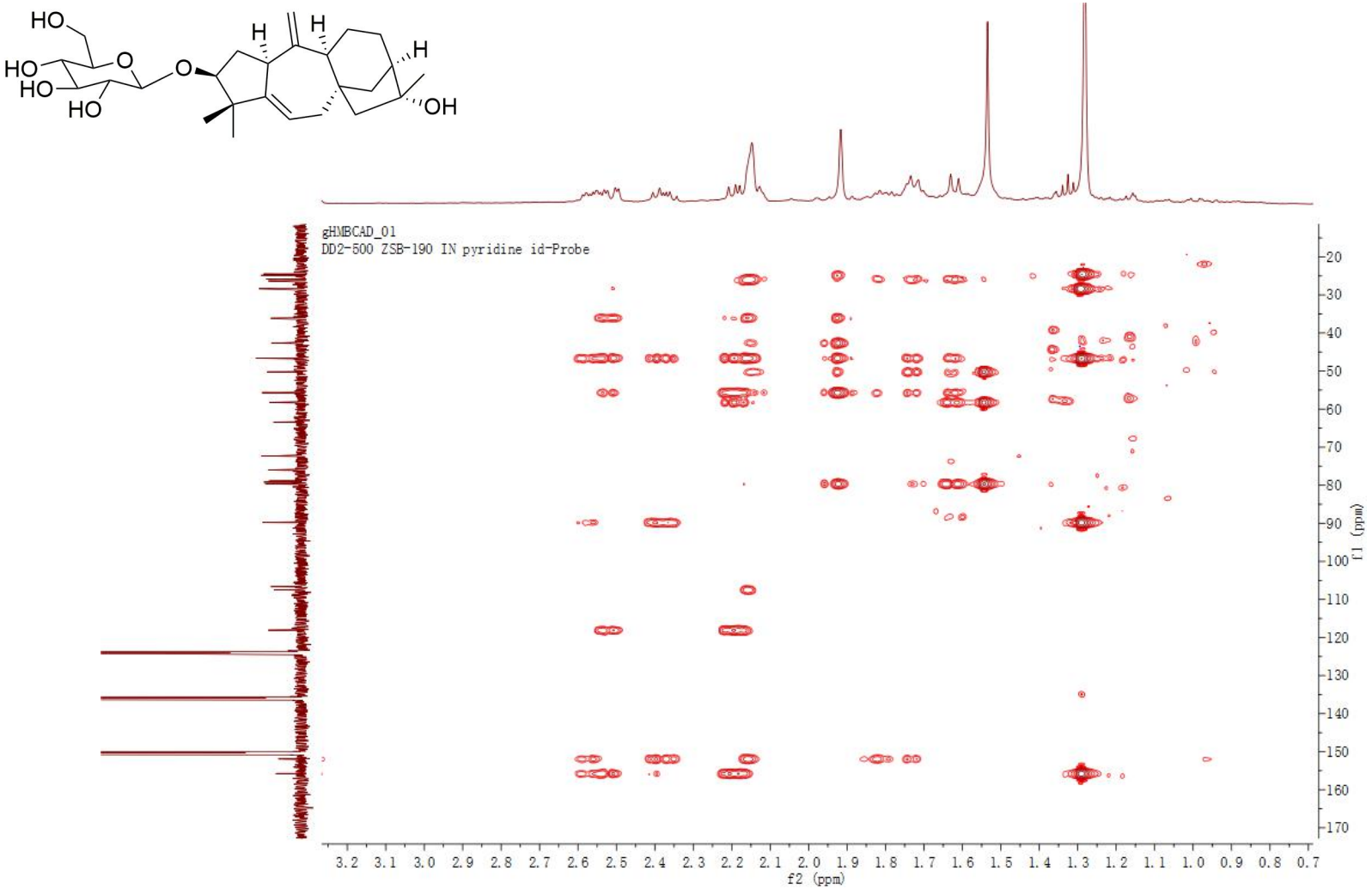
The COSY spectrum of **7** in C_5D_5N (500 MHz)



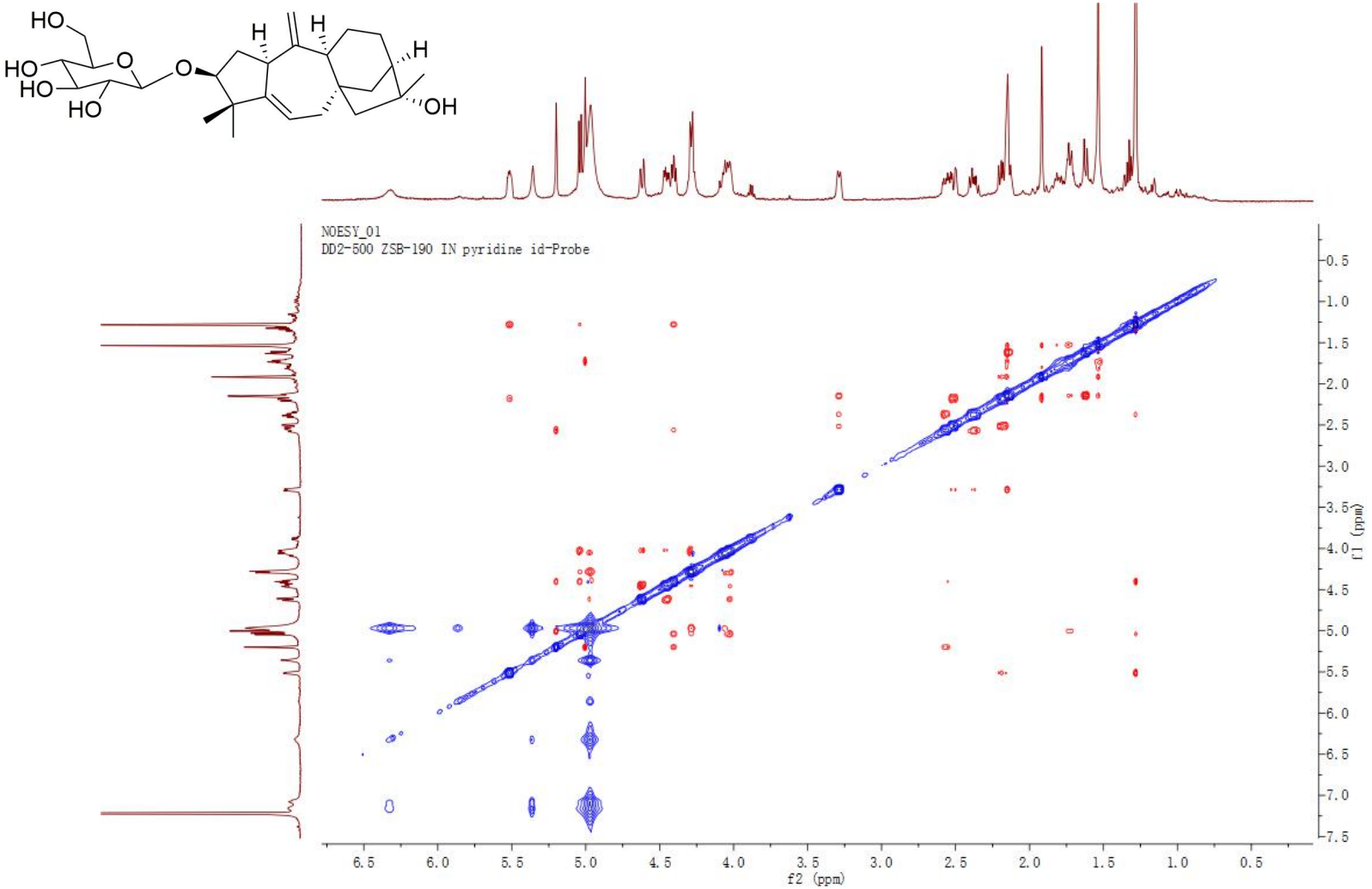
The HSQC spectrum of **7** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



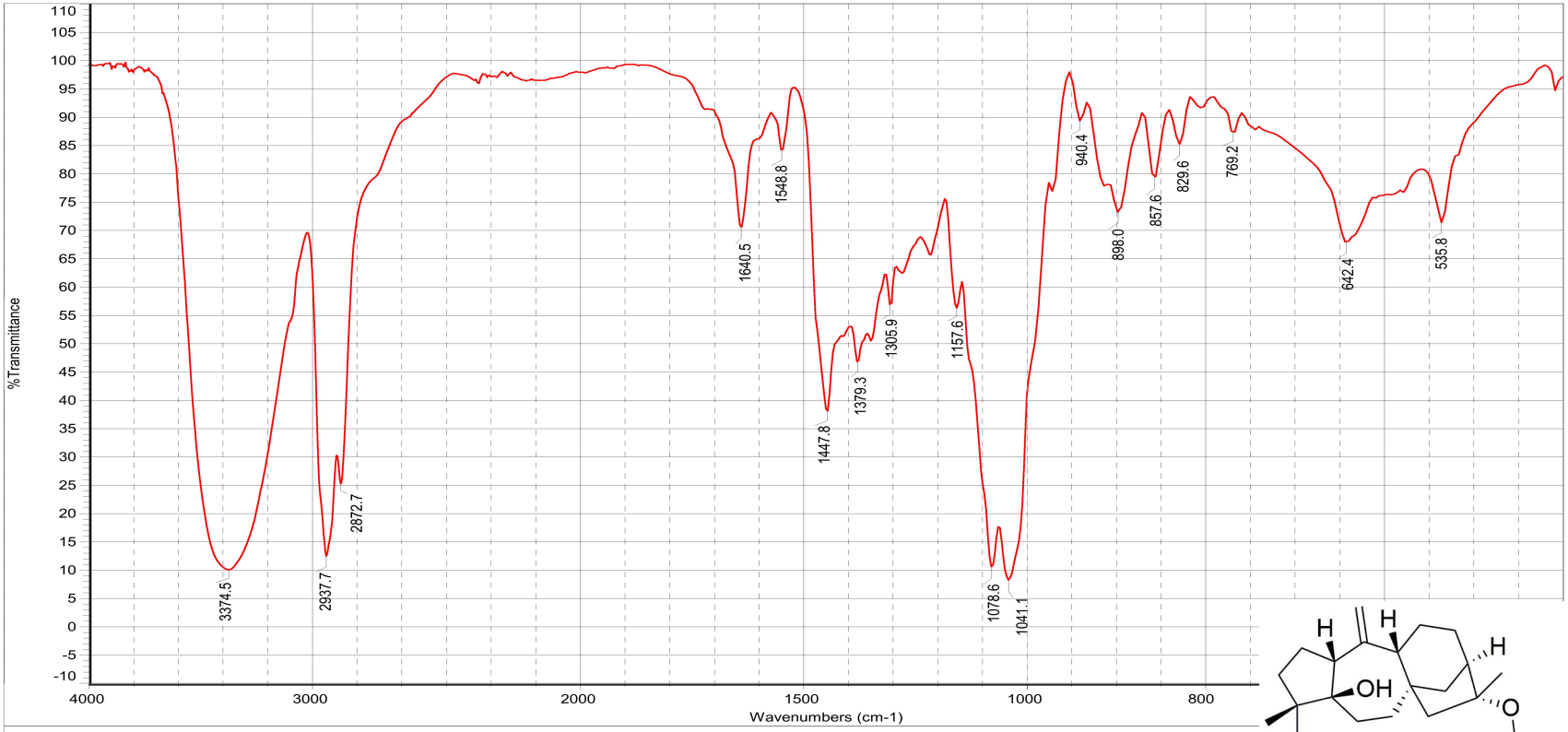
The HMBC spectrum of **7** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The HMBC spectrum (amplified) of **7** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The NOESY spectrum of **7** in C_5D_5N (500 MHz)

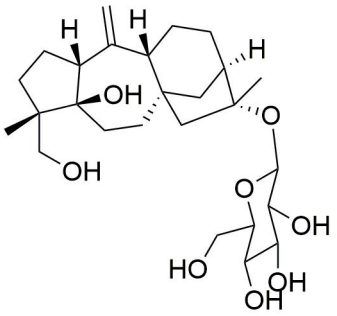


The IR spectrum of **8**

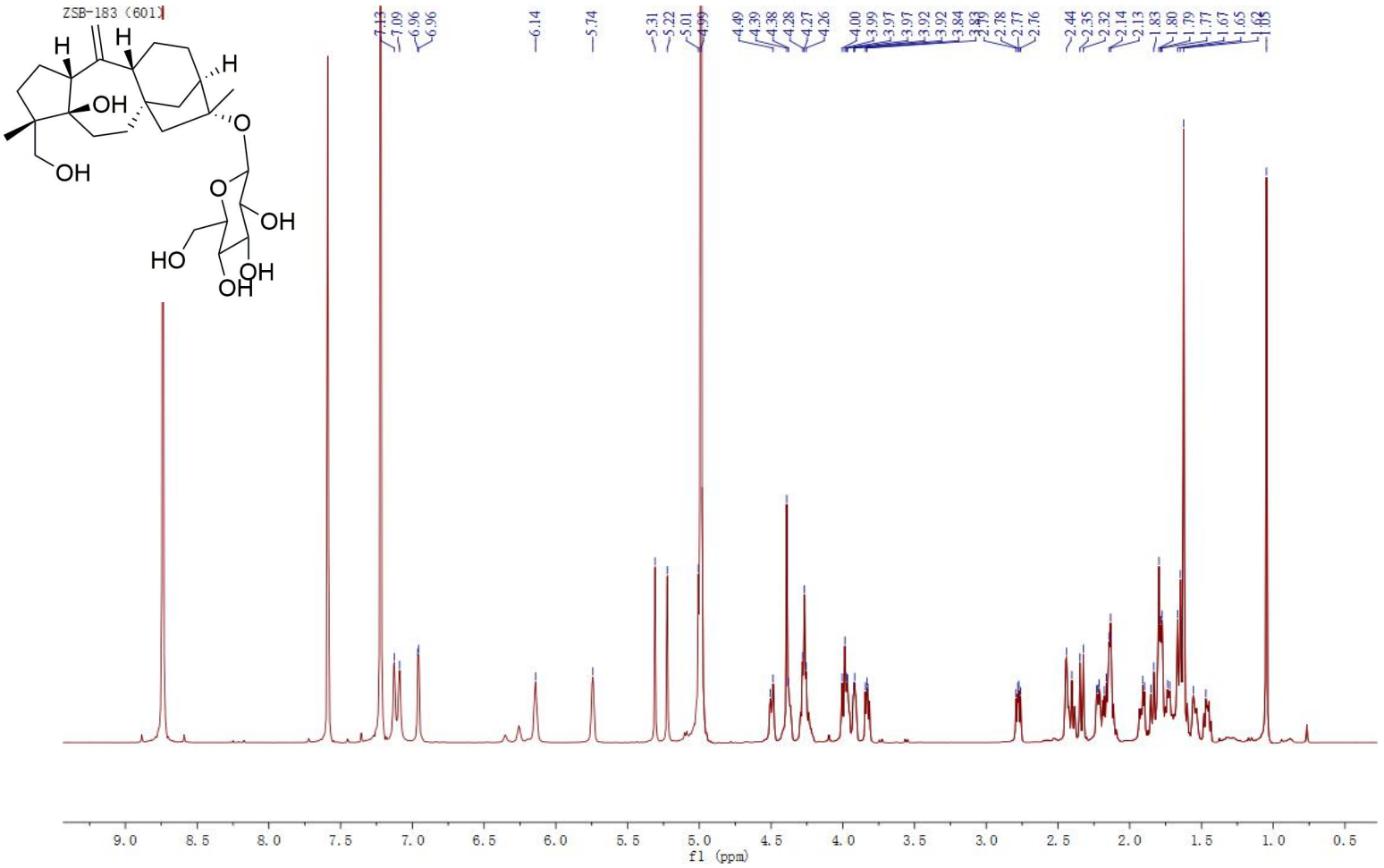
MS Formula Results: + Scan (7.433 min) Sub (2016061501.d)

	m/z	Ion	Formula	Abundance
-	505.2788	(M+Na)+	C26 H42 Na O8	512537.3

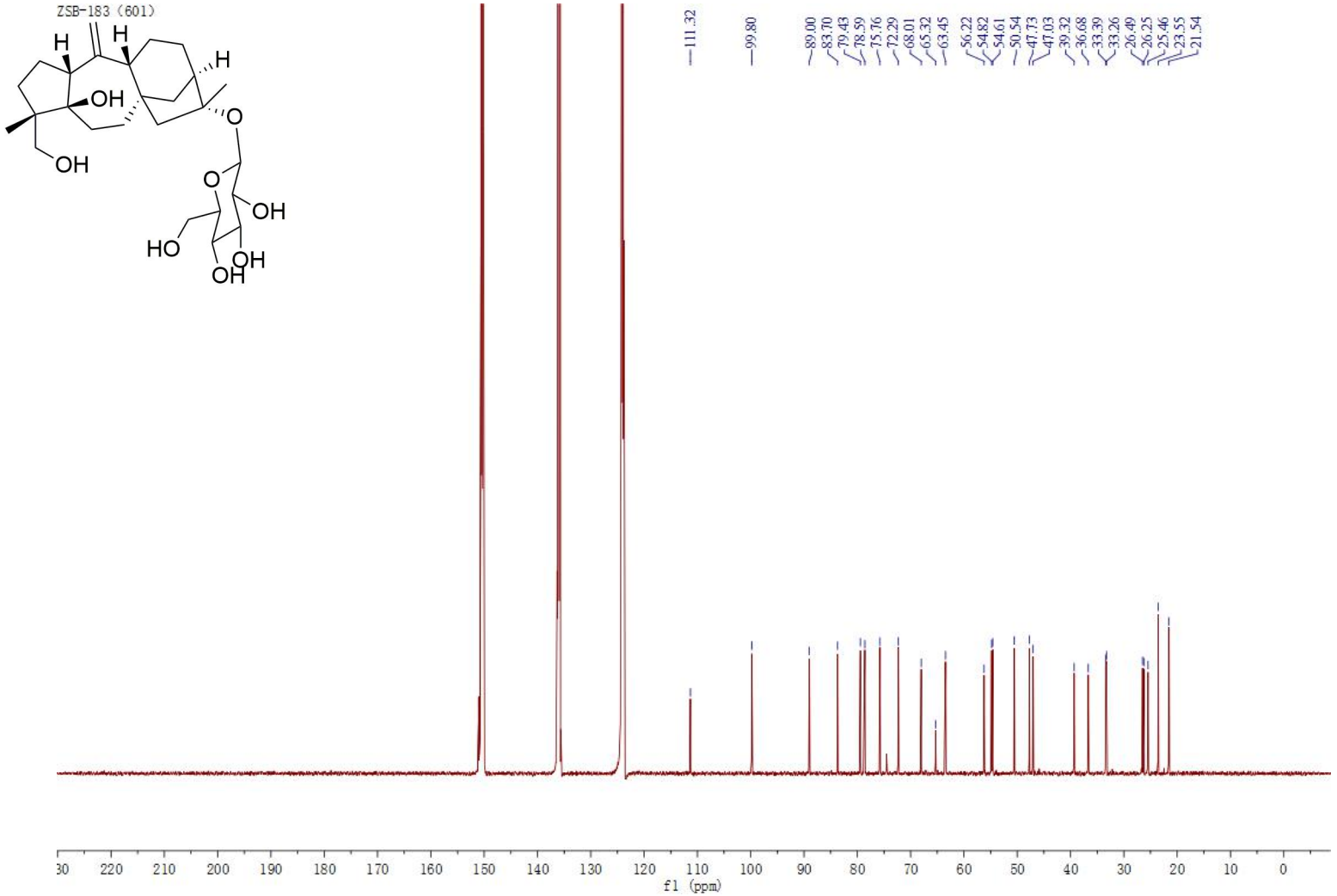
	Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
+	✔	C26 H42 O8	C26 H42 Na O8	99.82		482.2896	482.288	505.2772	-3.29	3.29	99.66	99.95	99.98	6
+		C23 H46 O8 S	C23 H46 Na O8 S	98.91		482.2896	482.2913	505.2806	3.69	3.69	99.58	97.18	99.66	1
+		C27 H46 O3 S2	C27 H46 Na O3 S2	97.6		482.2896	482.2888	505.2781	-1.51	1.51	99.93	92.18	99.44	5
+		C24 H50 O3 S3	C24 H50 Na O3 S3	94.83		482.2896	482.2922	505.2814	5.48	5.48	99.07	84.14	99.19	0



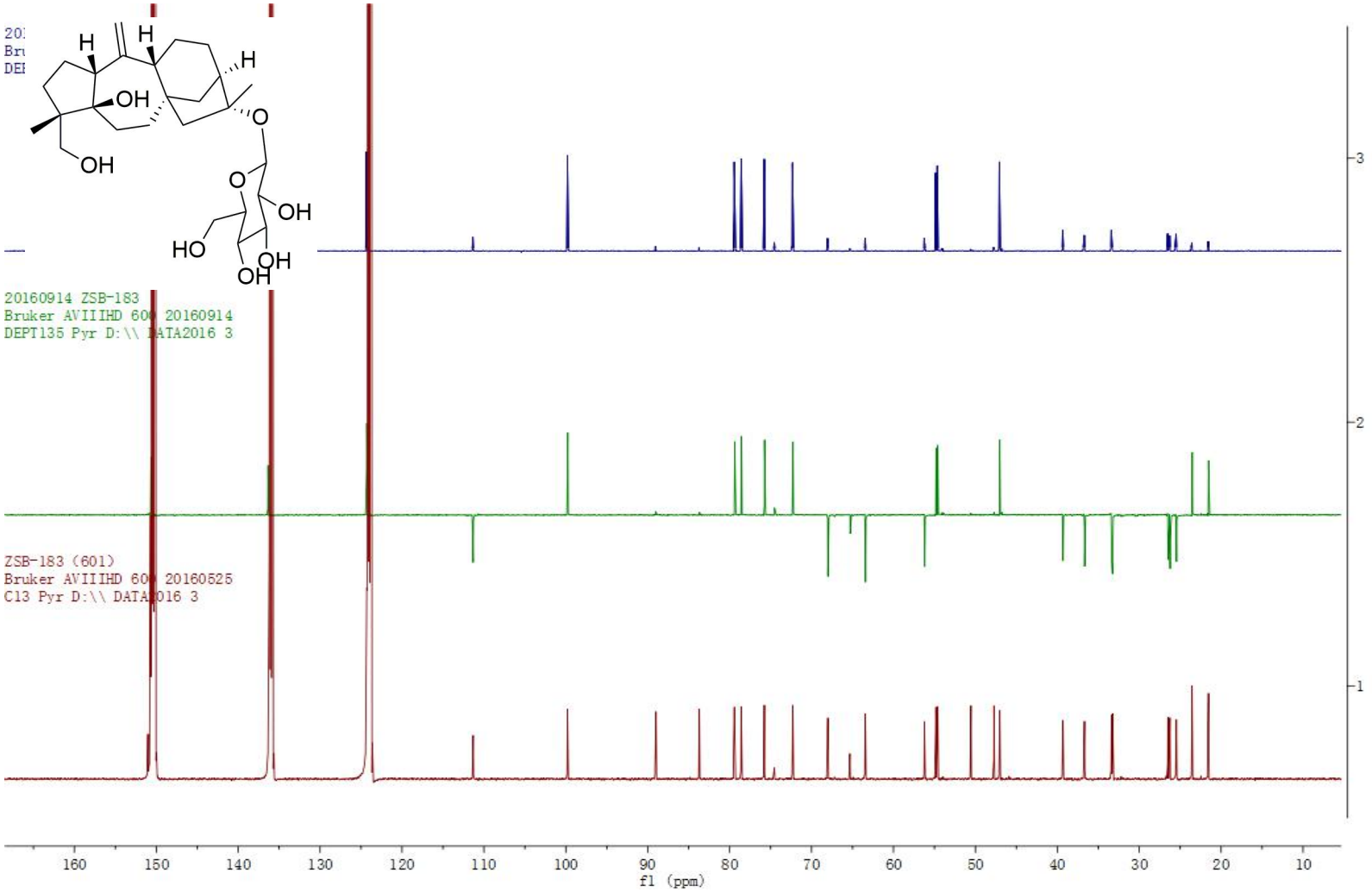
The HRESIMS spectrum of **8**



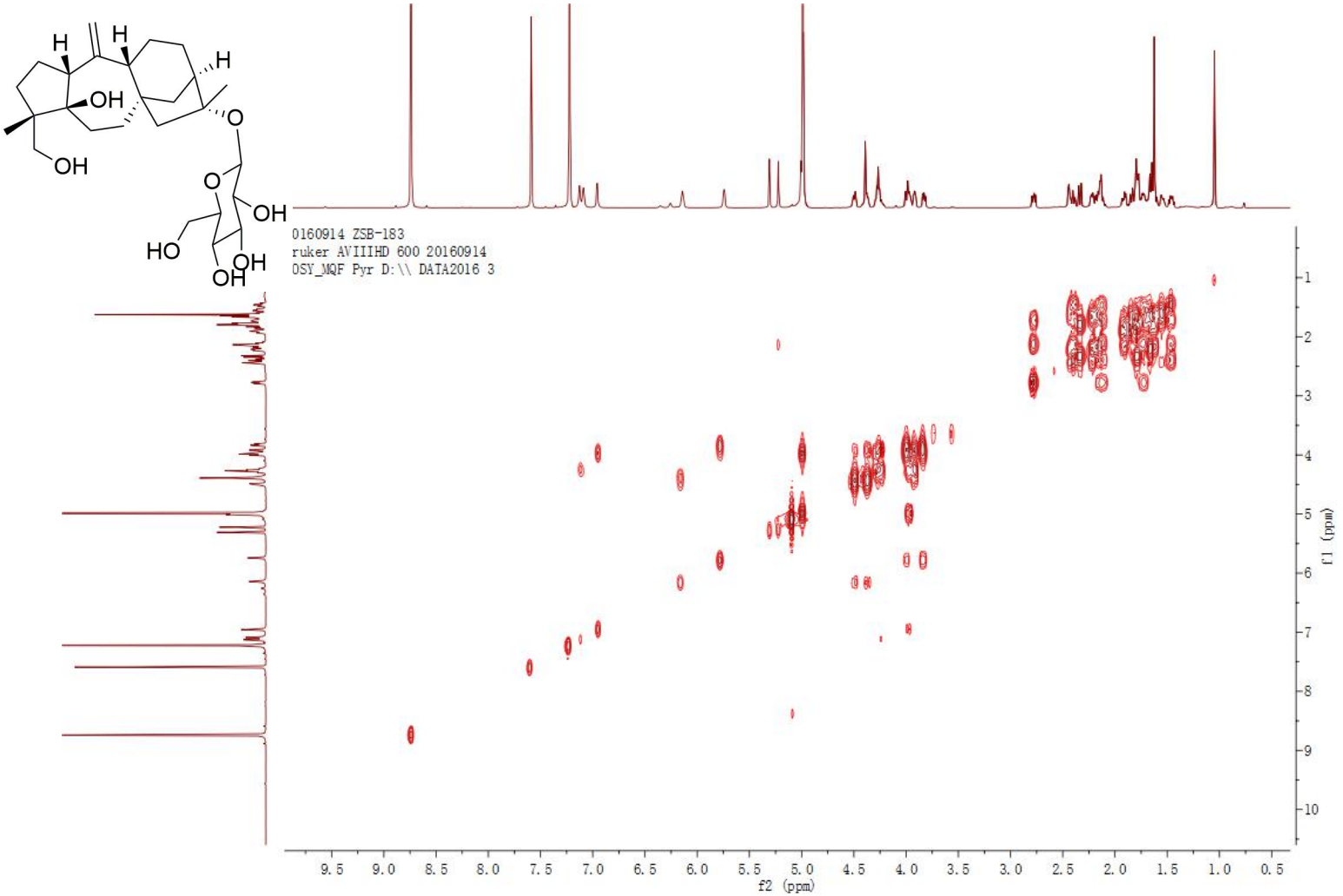
The ^{1}H NMR spectrum of **8** in C_5D_5N (600 MHz)



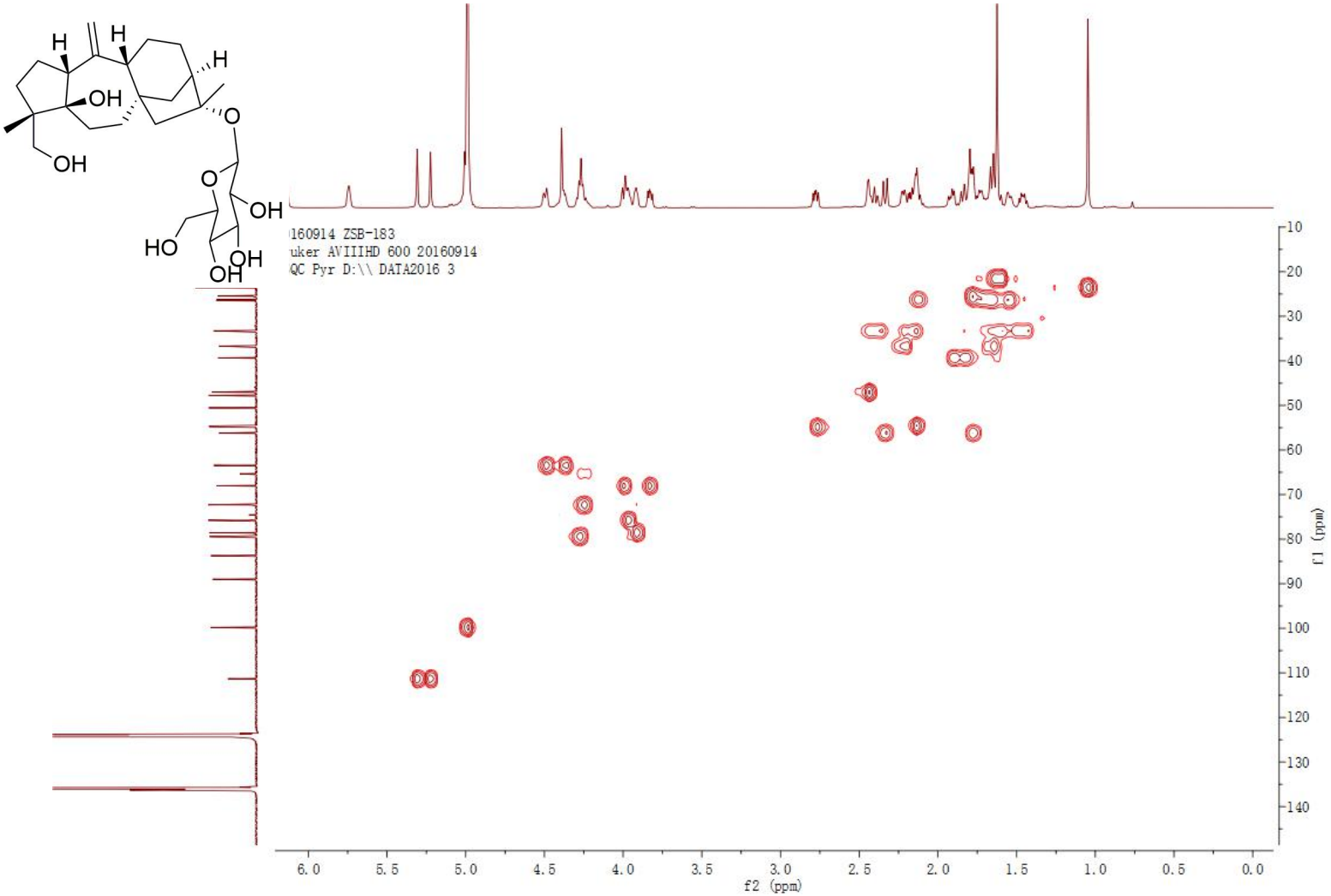
The ^{13}C NMR spectrum of **8** in C_5D_5N (150 MHz)



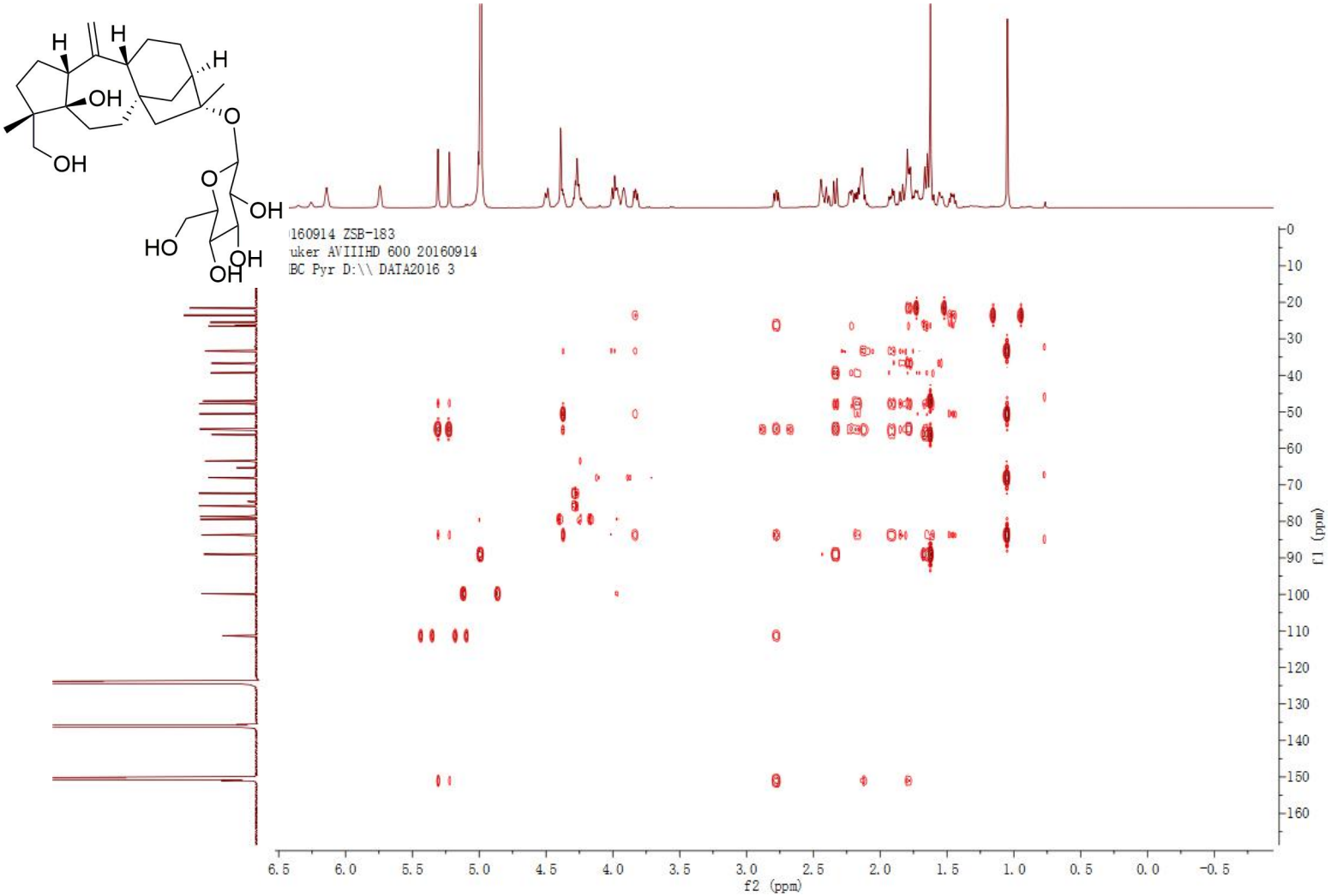
The DEPT spectrum of **8** in C_5D_5N (150 MHz)



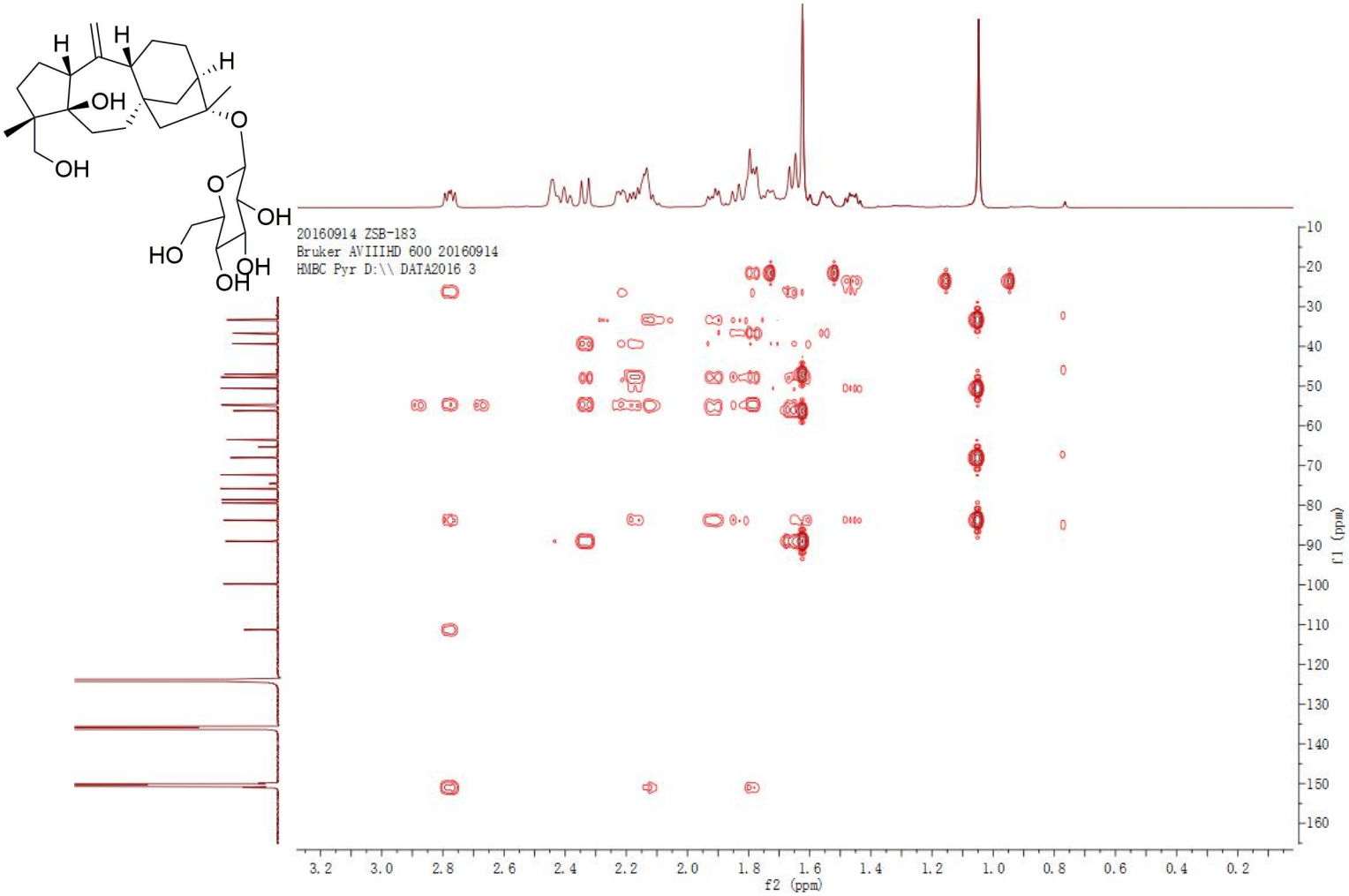
The COSY spectrum of **8** in C_5D_5N (600 MHz)



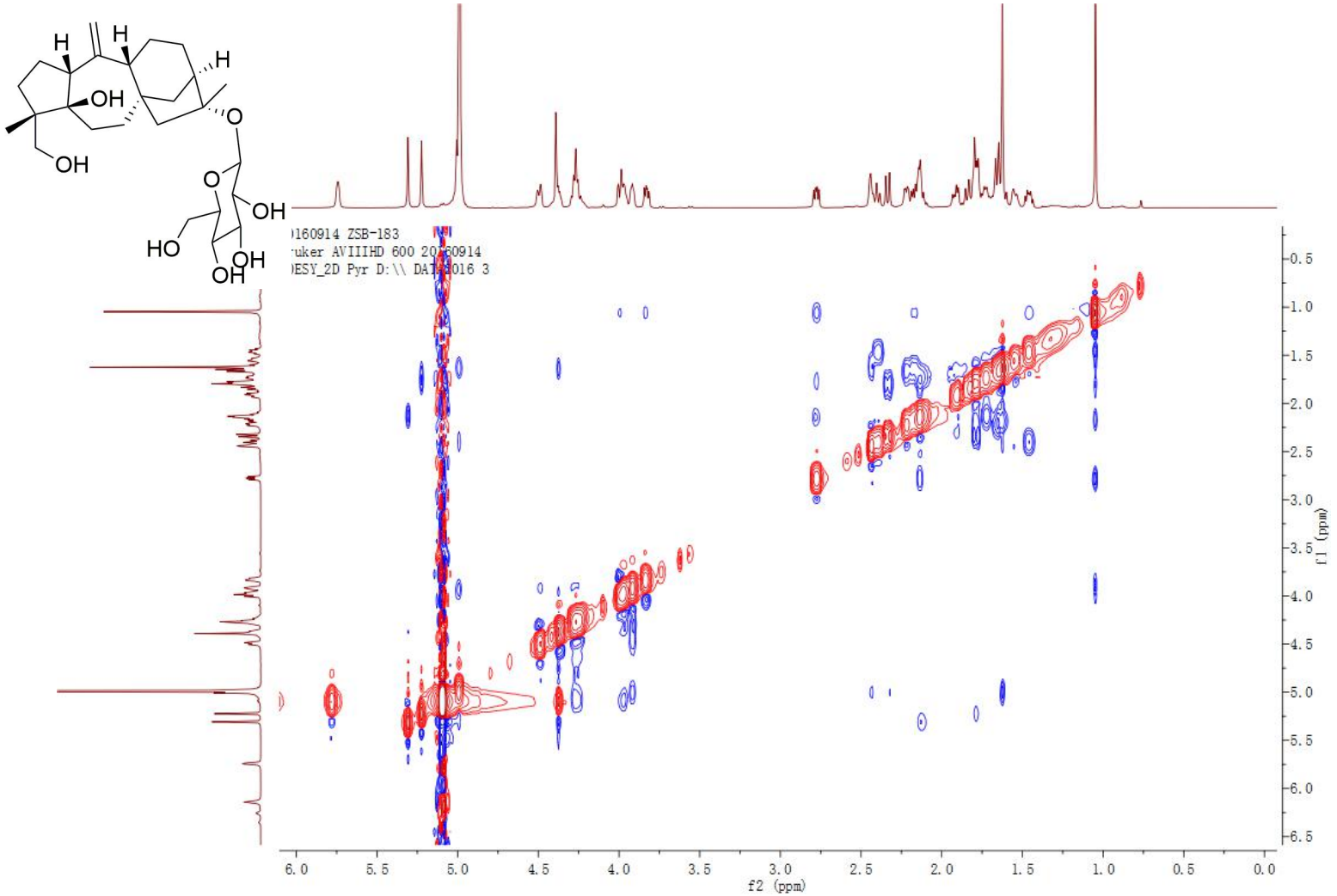
The HSQC spectrum of **8** in C_5D_5N (^1H: 600 MHz, ^{13}C: 150 MHz)



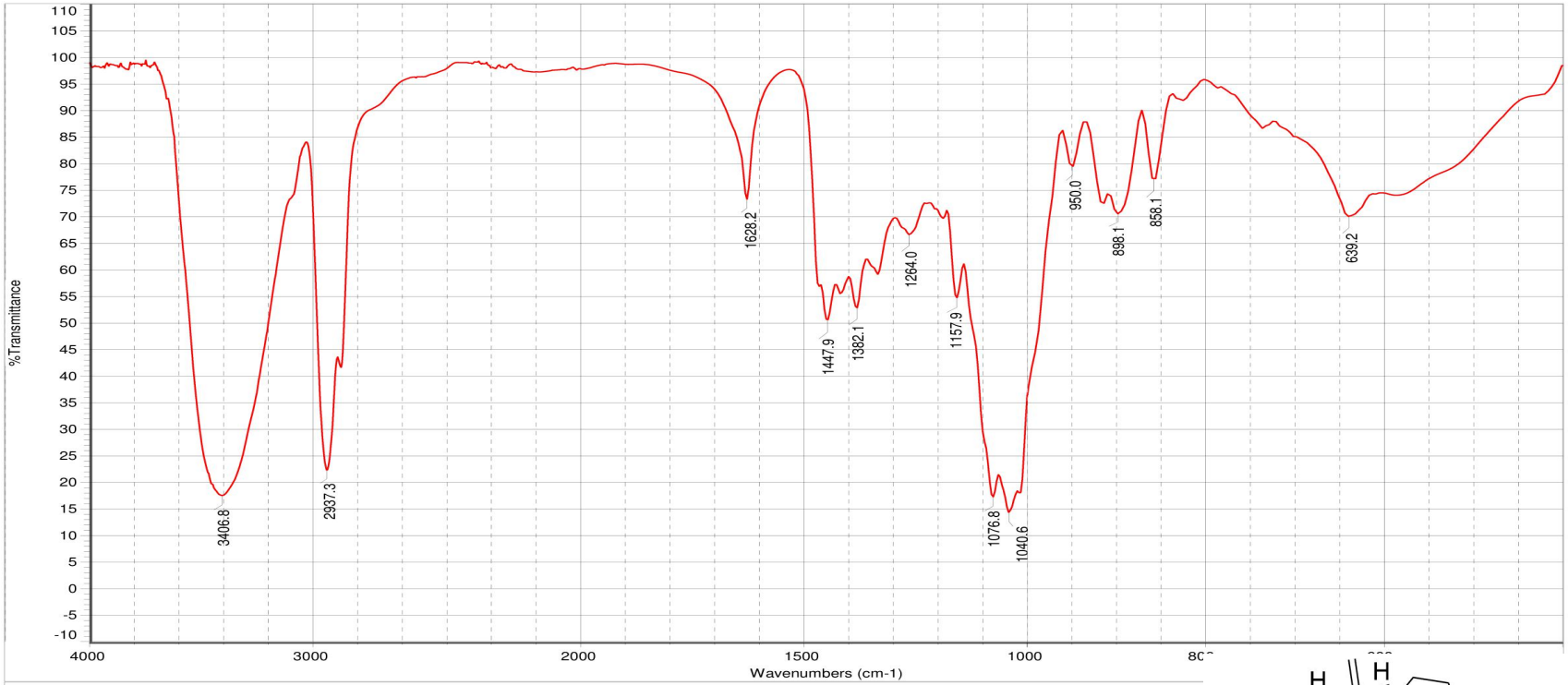
The HMBC spectrum of **8** in C_5D_5N (^1H: 600 MHz, ^{13}C: 150 MHz)

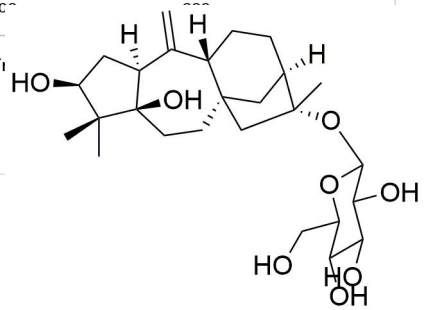


The HMBC spectrum (amplified) of **8** in C_5D_5N (^1H: 600 MHz, ^{13}C: 150 MHz)



The NOESY spectrum of **8** in C_5D_5N (600 MHz)



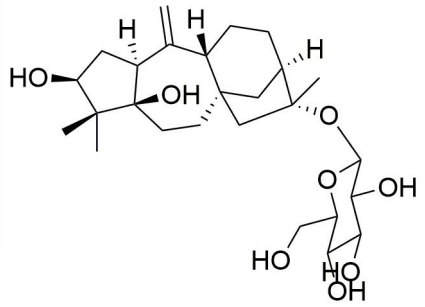


The IR spectrum of **9**

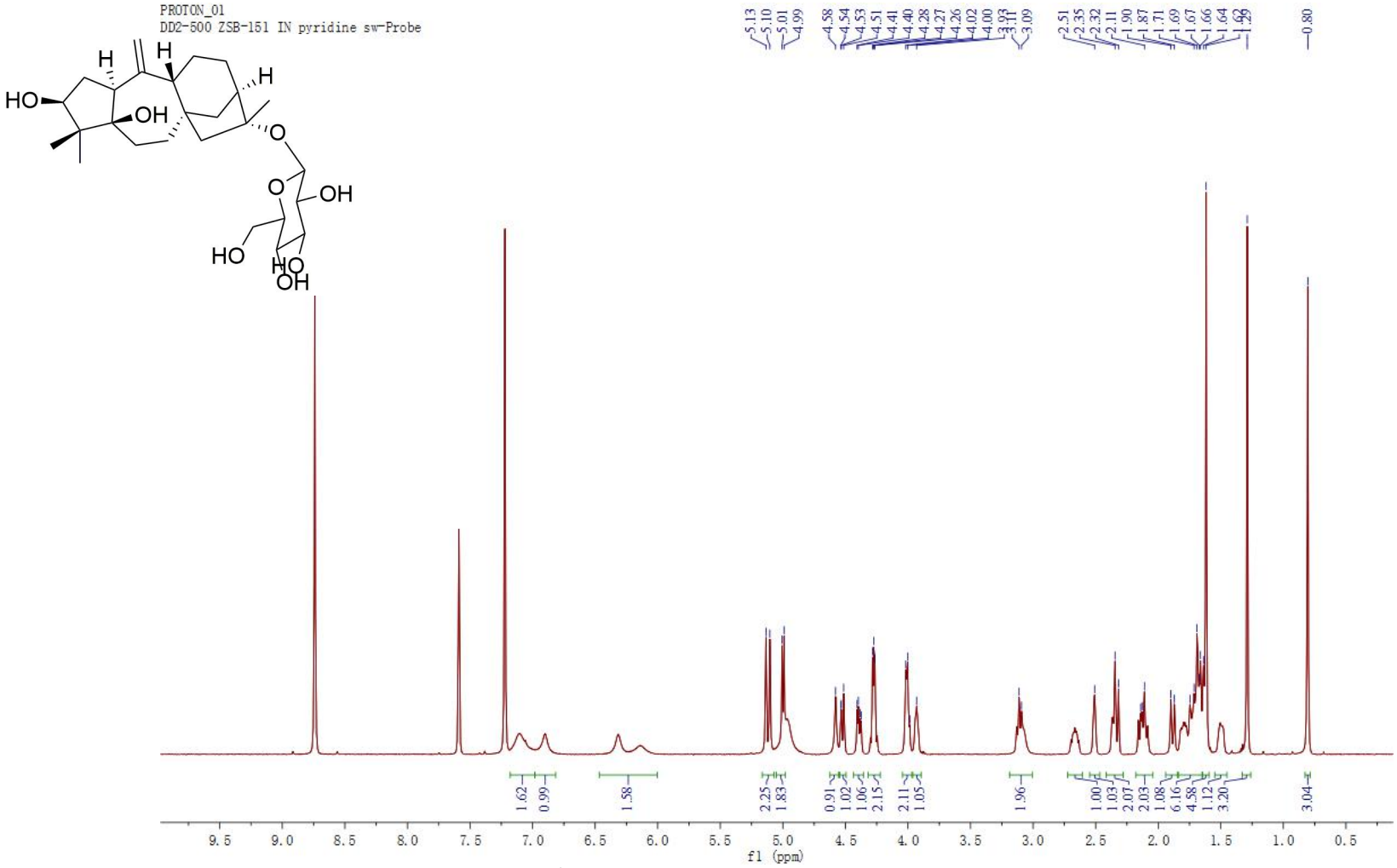
MS Formula Results: + Scan (6.399 min) Sub (2016032906.d)

m/z	Ion	Formula	Abundance
505.2775	(M+Na)+	C26 H42 Na O8	35799.6

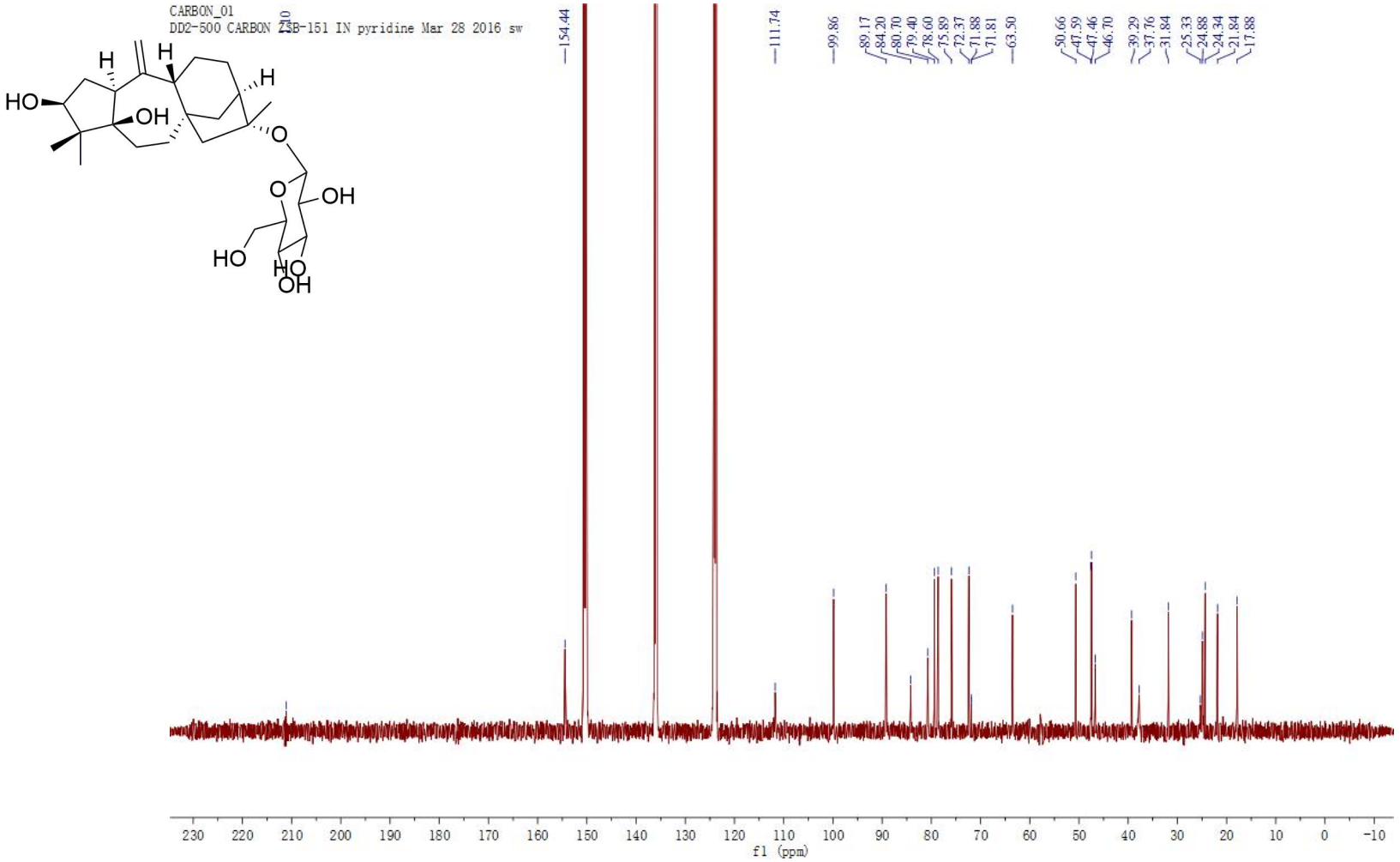
Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
☑	C26 H42 O8	C26 H42 Na O8	99.35		482.2882	482.288	505.2772	-0.47	0.47	99.99	99.67	97.7	6
☐	C30 H42 O3 S	C30 H42 Na O3 S	98.51		482.2882	482.2855	505.2747	-5.67	5.67	99	97.17	99.13	10
☐	C27 H46 O3 S2	C27 H46 Na O3 S2	98.1		482.2882	482.2888	505.2781	1.31	1.31	99.95	93.77	99.61	5
☐	C26 H46 O4 S Si	C26 H46 Na O4 S Si	98.02		482.2882	482.2886	505.2778	0.82	0.82	99.98	93.46	99.57	5
☐	C25 H46 O5 Si2	C25 H46 Na O5 Si2	97.54		482.2882	482.2884	505.2776	0.32	0.32	100	91.84	99.47	5
☐	C29 H46 S Si2	C29 H46 Na S Si2	94.58		482.2882	482.2859	505.2751	-4.86	4.86	99.26	82.54	99.66	9
☐	C28 H46 O Si3	C28 H46 Na O Si3	93.71		482.2882	482.2856	505.2749	-5.35	5.35	99.11	79.84	99.58	9
☐	C26 H50 S2 Si2	C26 H50 Na S2 Si2	93.68		482.2882	482.2892	505.2785	2.12	2.12	99.86	78.24	99.83	4
☐	C25 H50 O S Si3	C25 H50 Na O S Si3	93.28		482.2882	482.289	505.2782	1.63	1.63	99.92	76.78	99.78	4
☐	C29 H43 Cl N2 Si	C29 H43 Cl N2 Na Si	83.85		482.2882	482.2884	505.2776	0.39	0.39	100	43.62	99.85	10
☐	C28 H48 Cl2 Si	C28 H48 Cl2 Na Si	74.68		482.2882	482.2902	505.2795	4.19	4.19	99.45	12.39	99.89	5
☐	C23 H48 Cl2 N2 O2 Si	C23 H48 Cl2 N2 Na O2 Si	74.37		482.2882	482.2862	505.2754	-4.16	4.16	99.46	11.27	99.93	1
☐	C24 H48 Cl2 N2 O S	C24 H48 Cl2 N2 Na O S	74.05		482.2882	482.2864	505.2757	-3.66	3.66	99.58	9.99	99.85	1



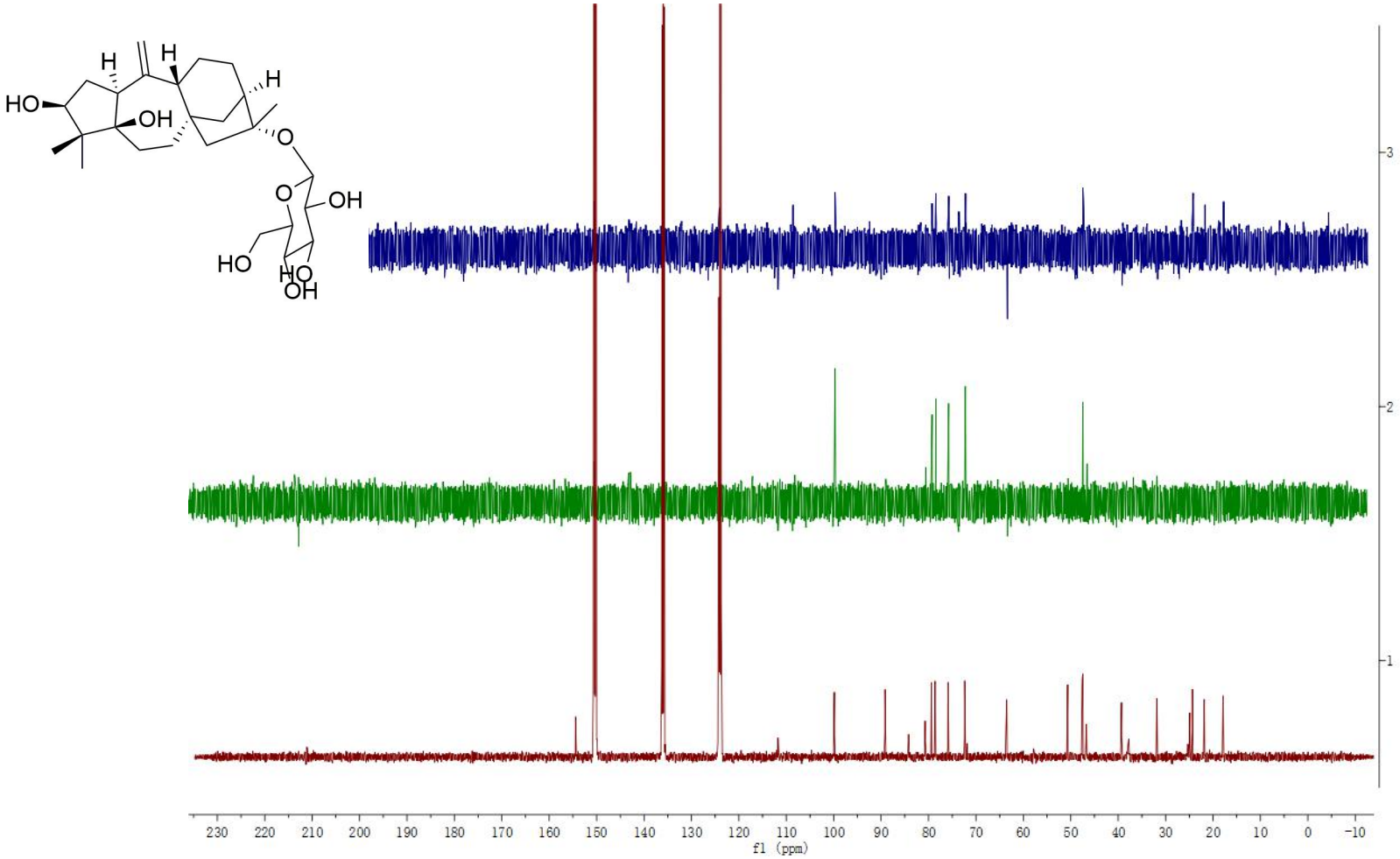
The HRESIMS spectrum of **9**



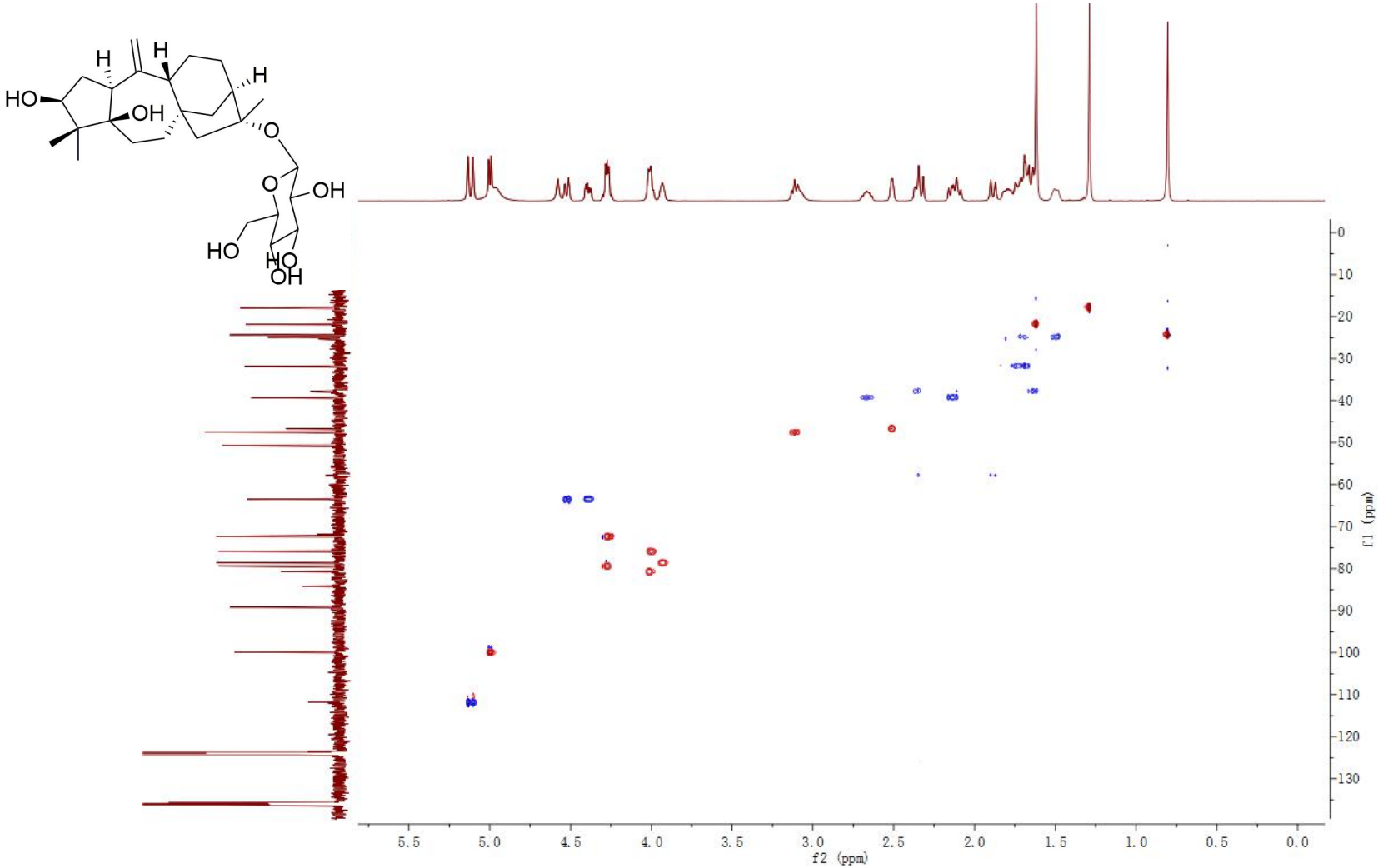
The ^{1}H NMR spectrum of **9** in C_5D_5N (500 MHz)



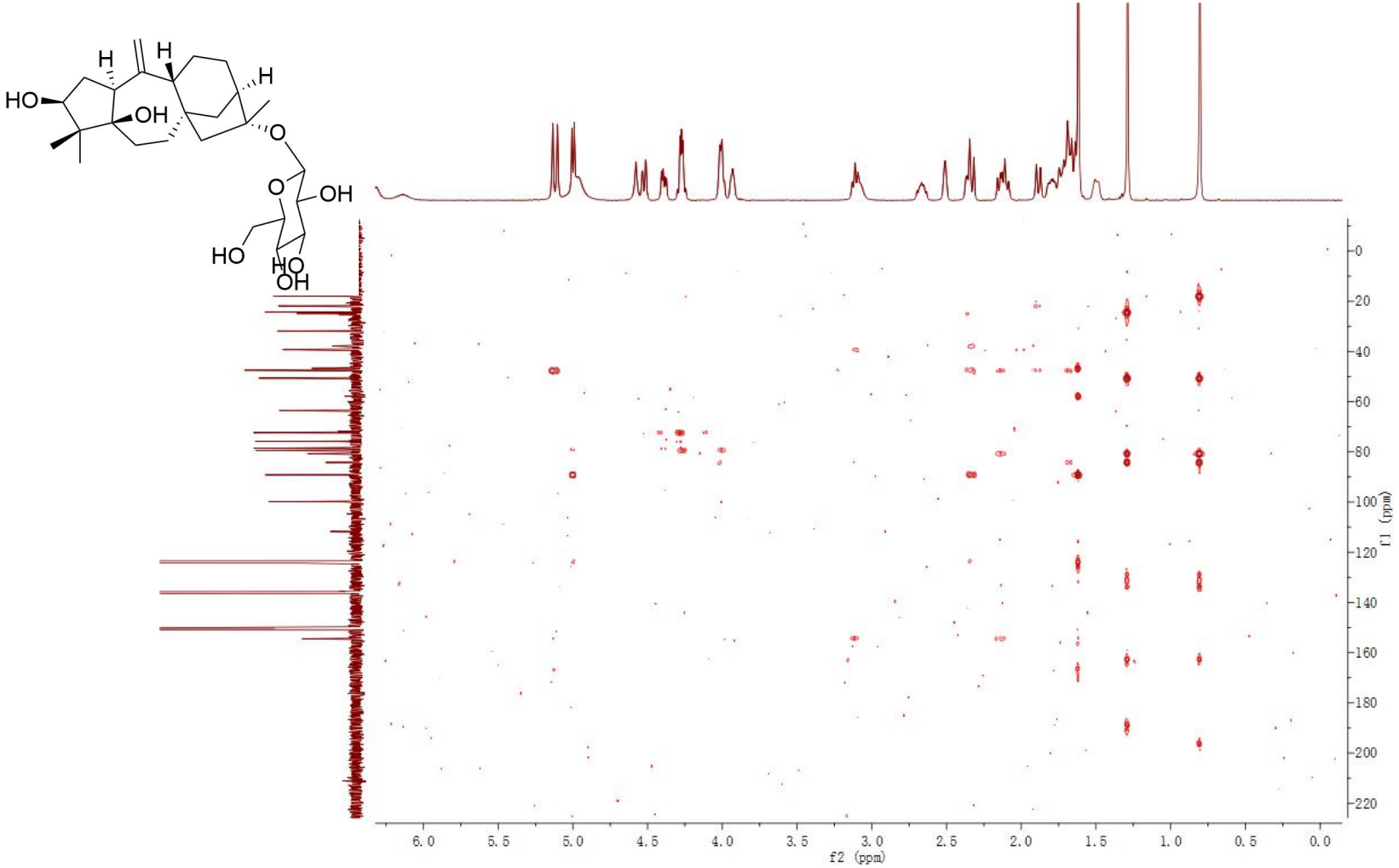
The ^{13}C NMR spectrum of **9** in C_5D_5N (125 MHz)



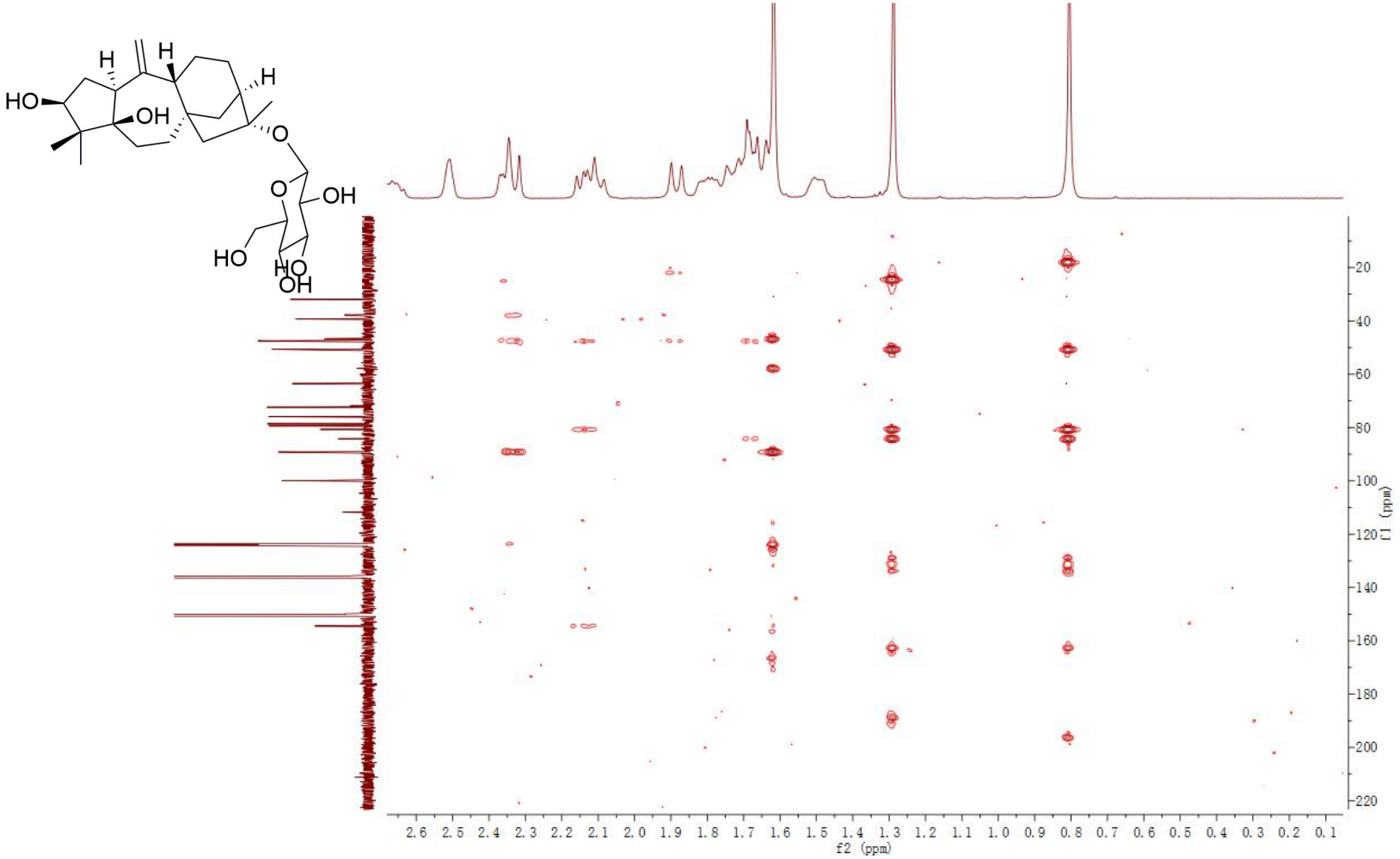
The DEPT spectrum of **9** in C_5D_5N (125 MHz)



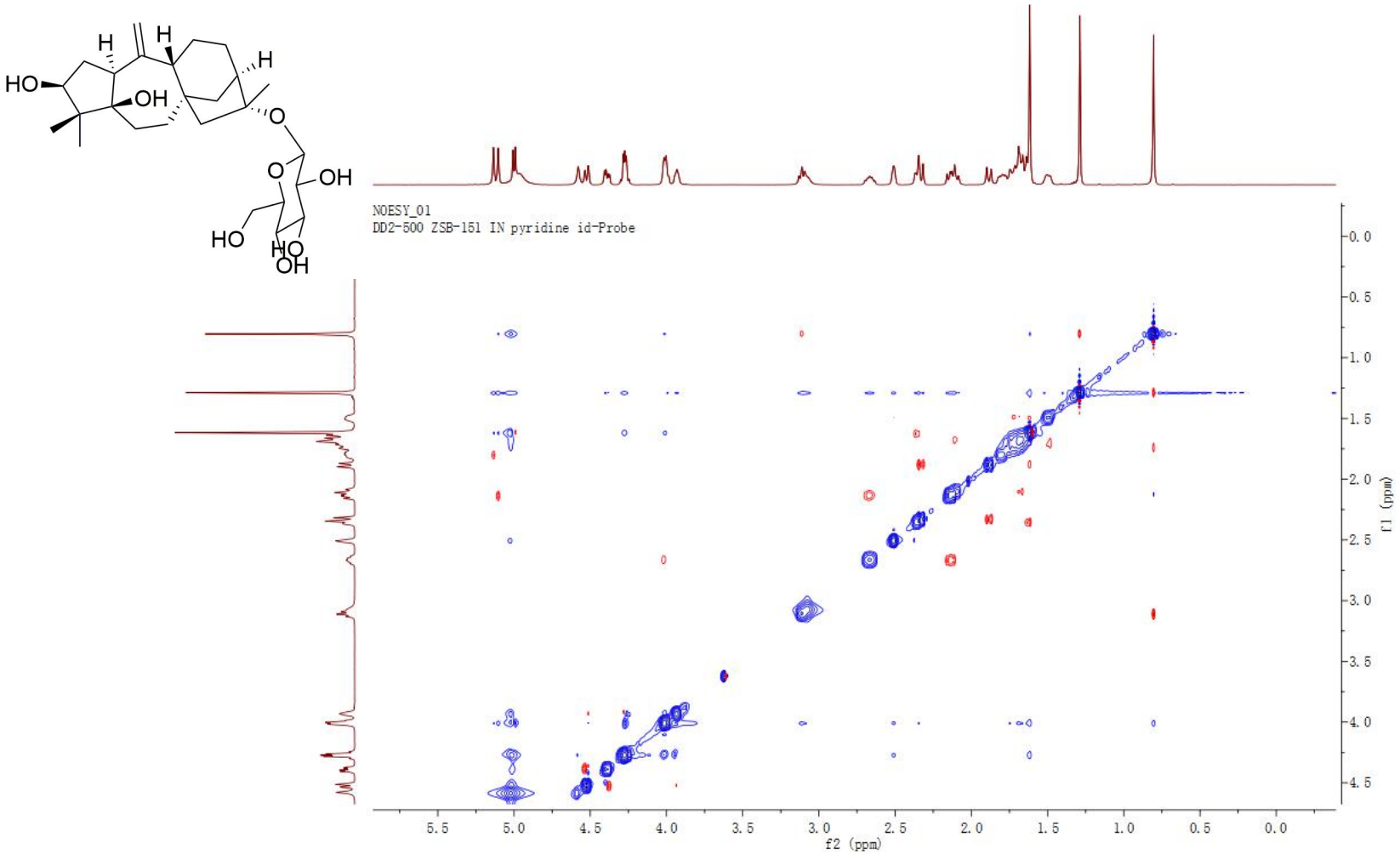
The HSQC spectrum of **9** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



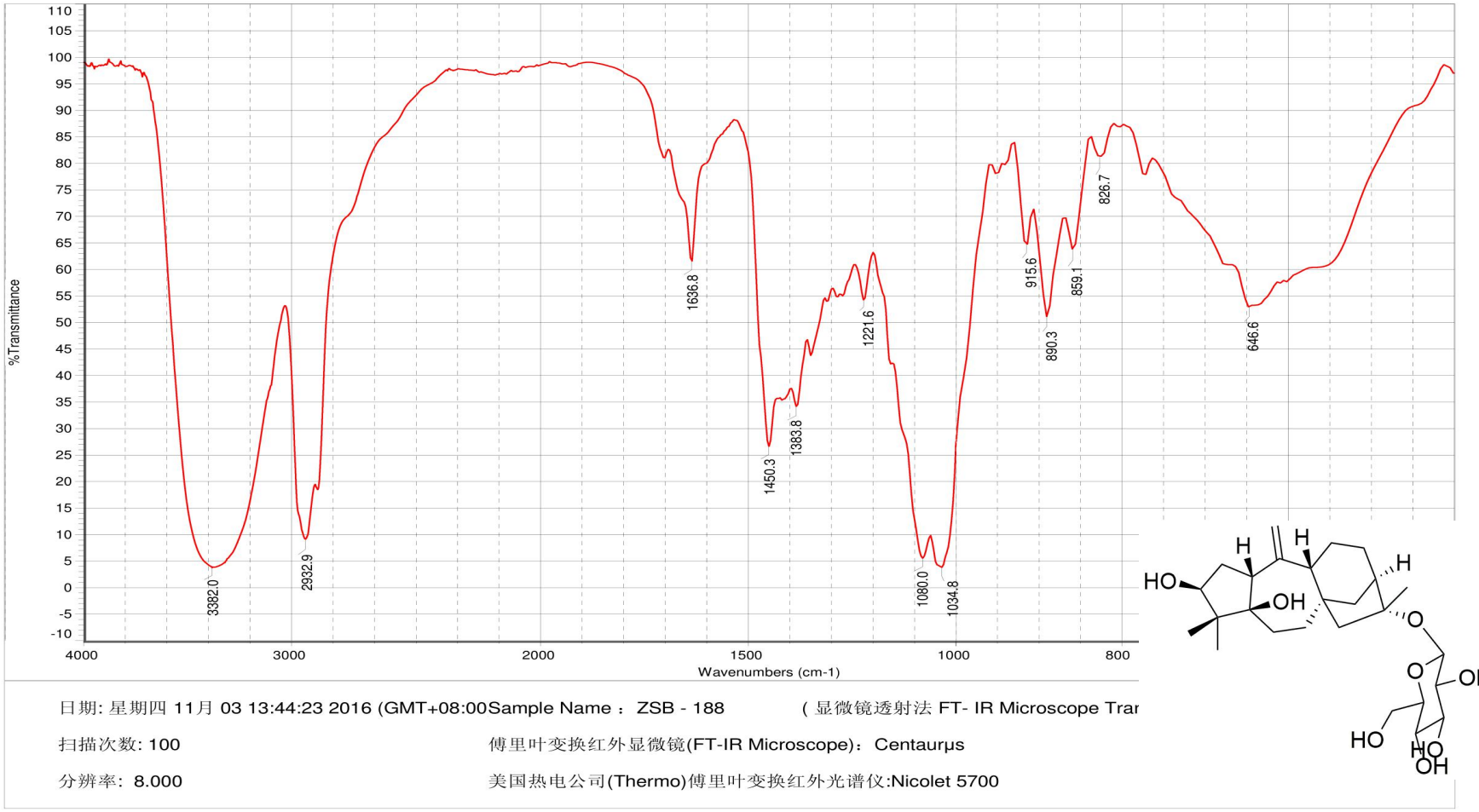
The HMBC spectrum of **9** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The HMBC spectrum (amplified) of **9** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The NOESY spectrum of **9** in C_5D_5N (500 MHz)



The IR spectrum of **10**

MS Formula Results: + Scan (7.005 min) Sub (2016052603.d)

m/z	Ion	Formula	Abundance
505.2766	(M+Na)+	C26 H42 Na O8	71321.1

Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
✔	C26 H42 O8	C26 H42 Na O8	99.67		482.2874	482.288	505.2772	1.25	1.25	99.95	99.63	99.16	6
	C30 H42 O3 S	C30 H42 Na O3 S	98.79		482.2874	482.2855	505.2747	-3.95	3.95	99.51	98.55	97.65	10
	C27 H46 O3 S2	C27 H46 Na O3 S2	97.44		482.2874	482.2888	505.2781	3.03	3.03	99.71	94.43	96.52	5
	C22 H46 N2 O5 S2	C22 H46 N2 Na O5 S2	96.55		482.2874	482.2848	505.274	-5.32	5.32	99.12	92.63	96.13	1

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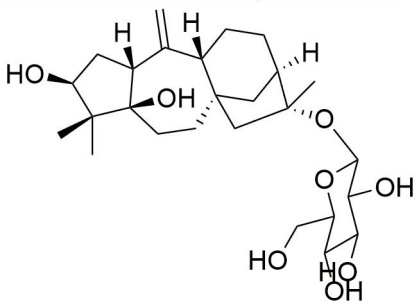
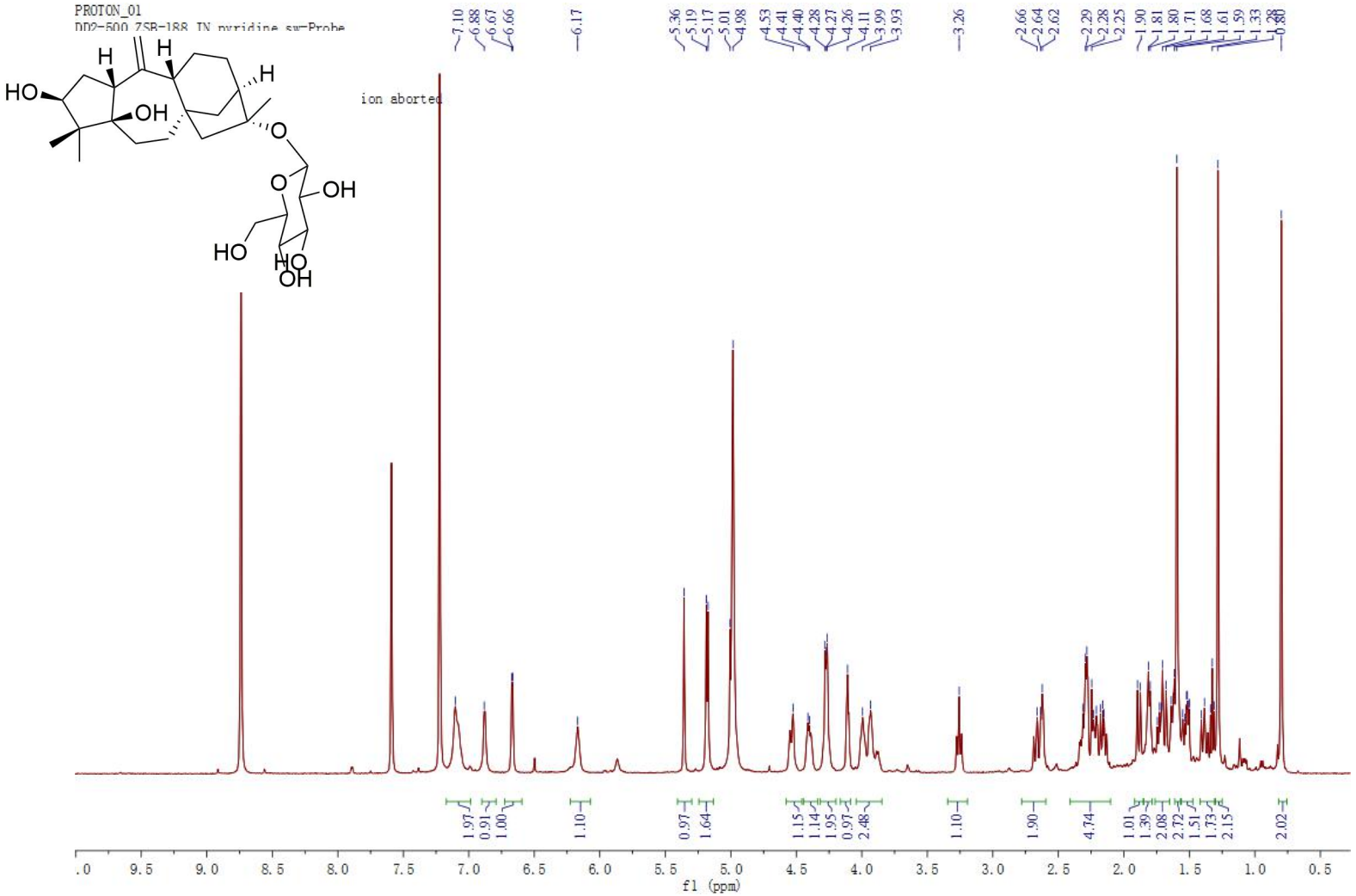
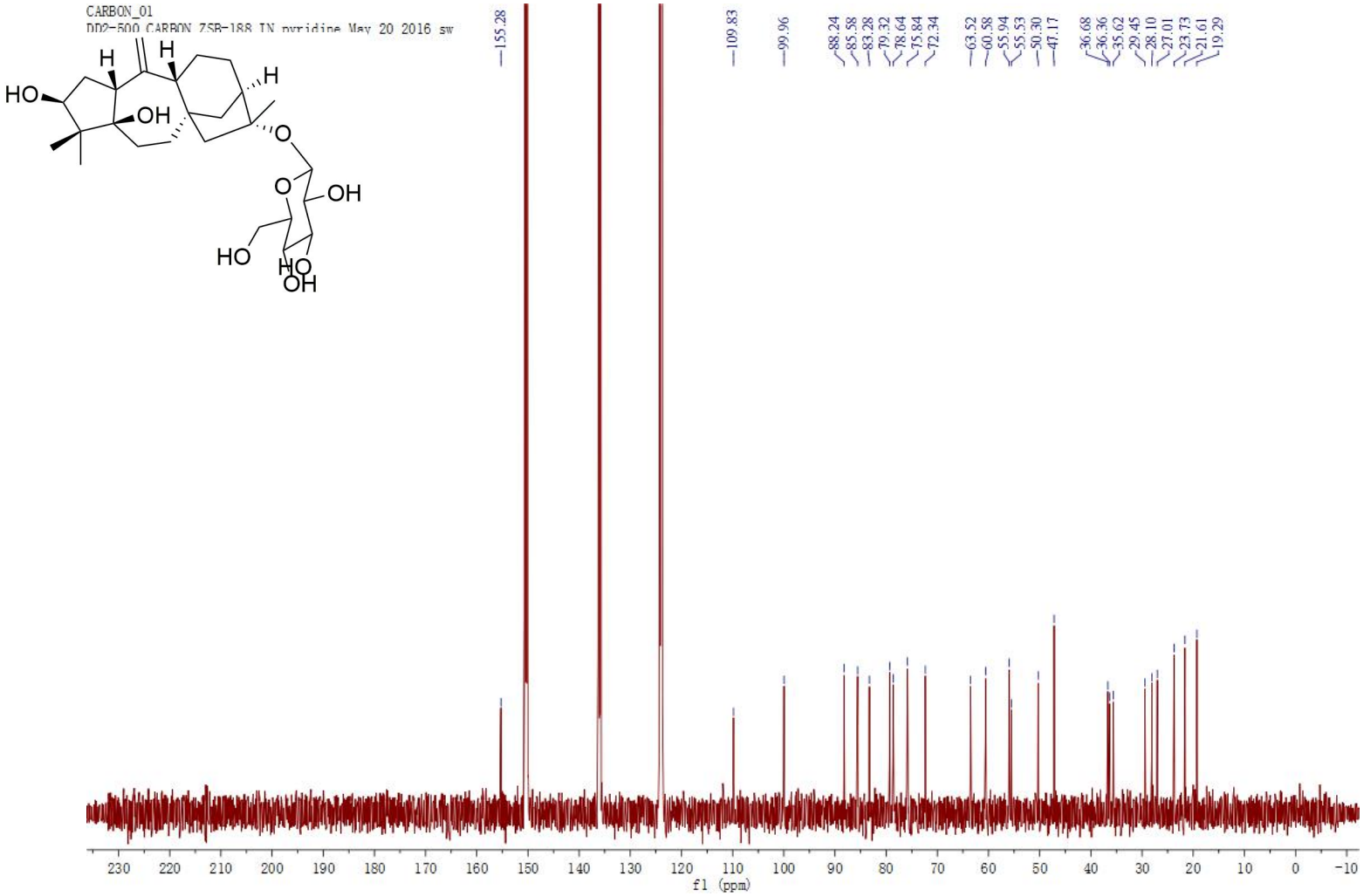


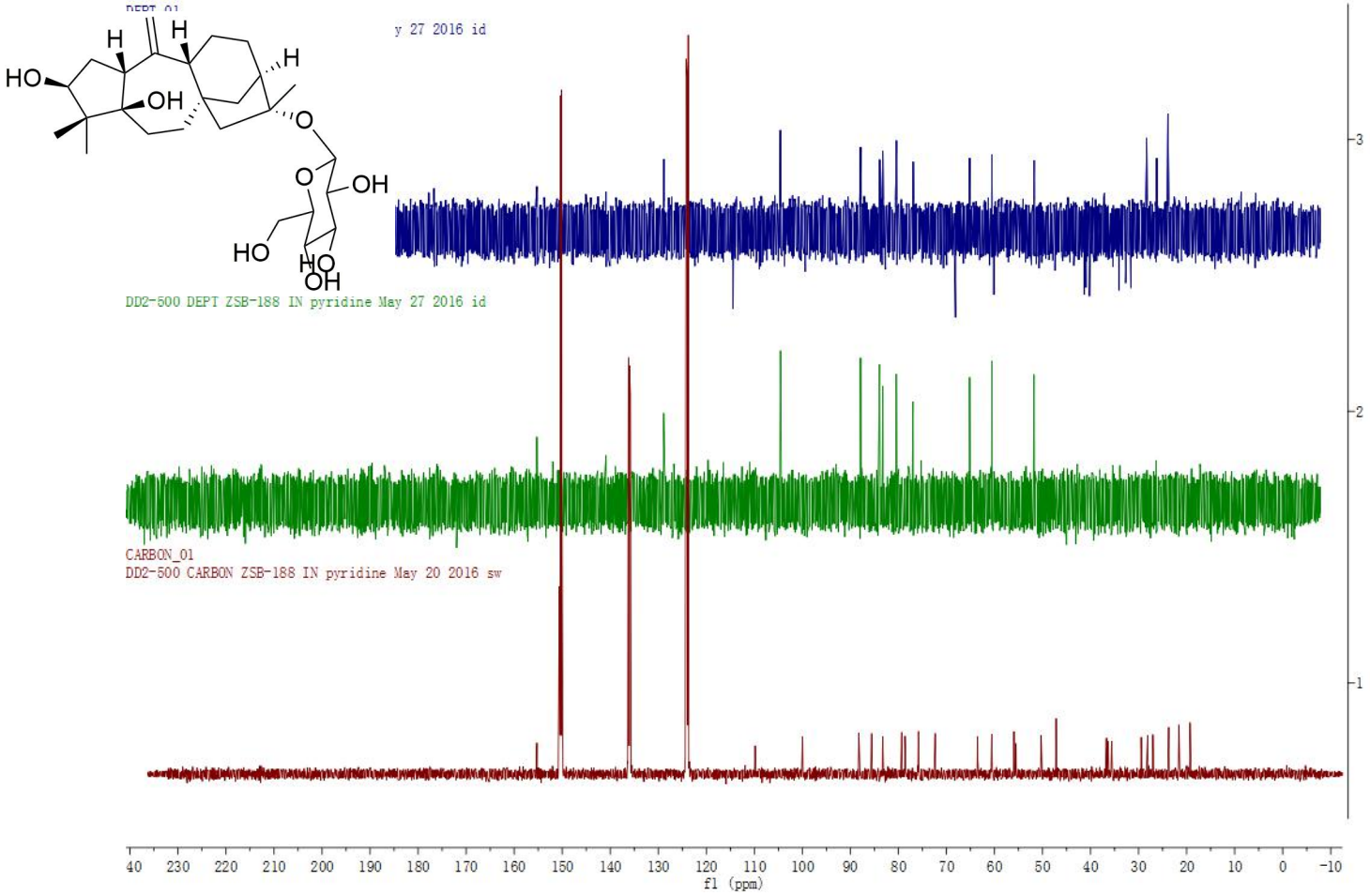
The HRESIMS spectrum of **10**



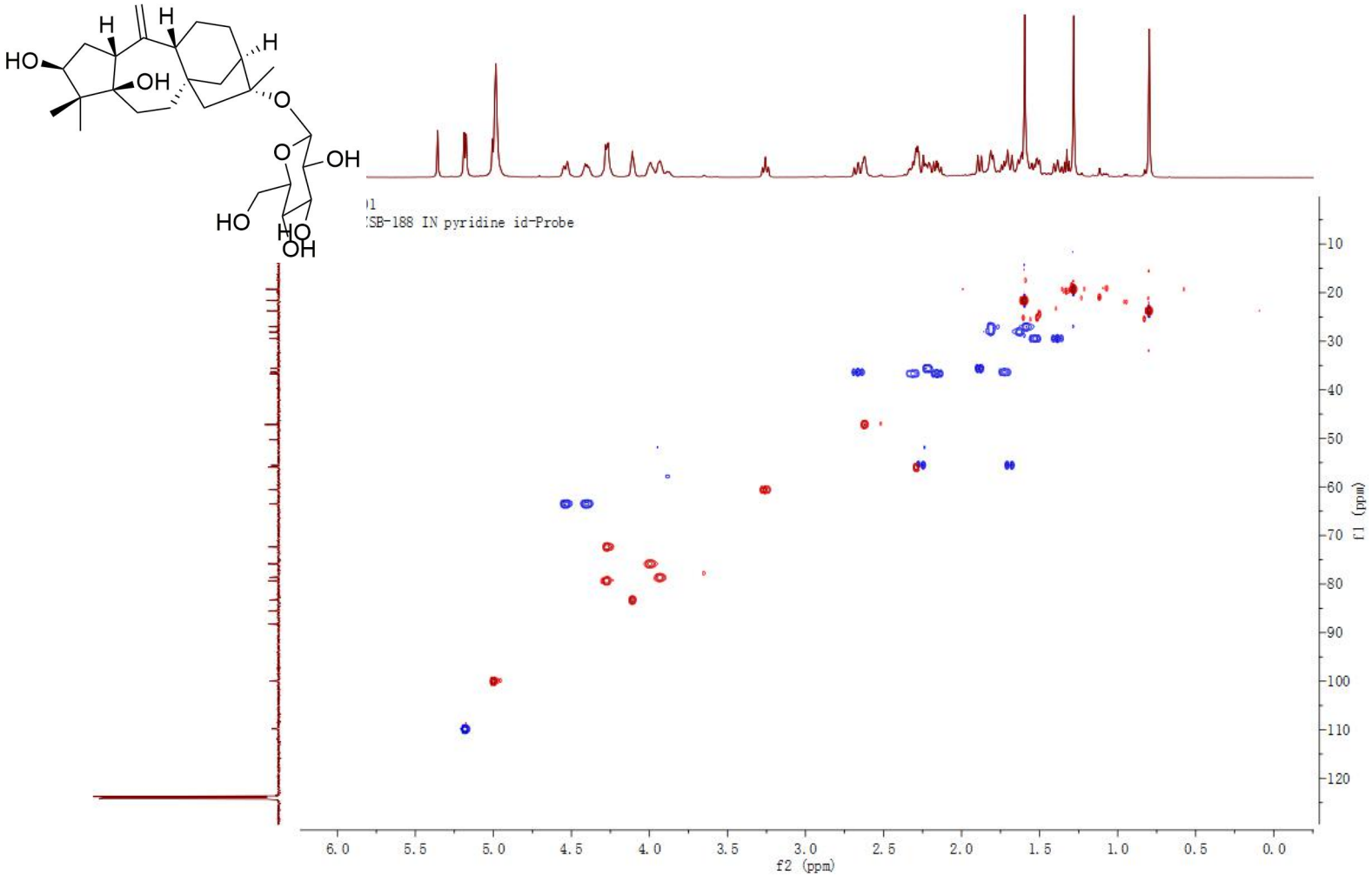
The ^{1}H NMR spectrum of **10** in C_5D_5N (500 MHz)



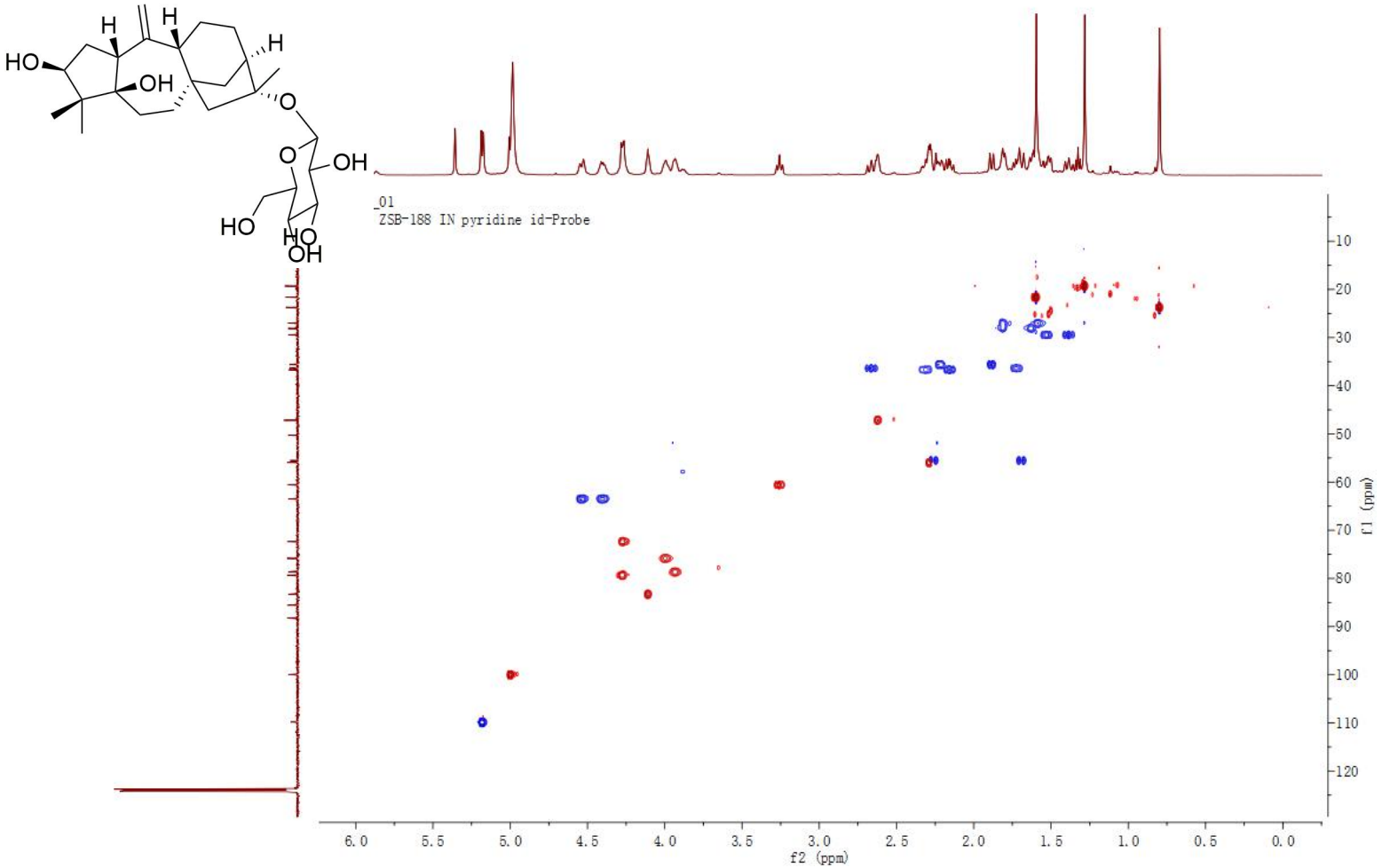
The ^{13}C NMR spectrum of **10** in C_5D_5N (125 MHz)



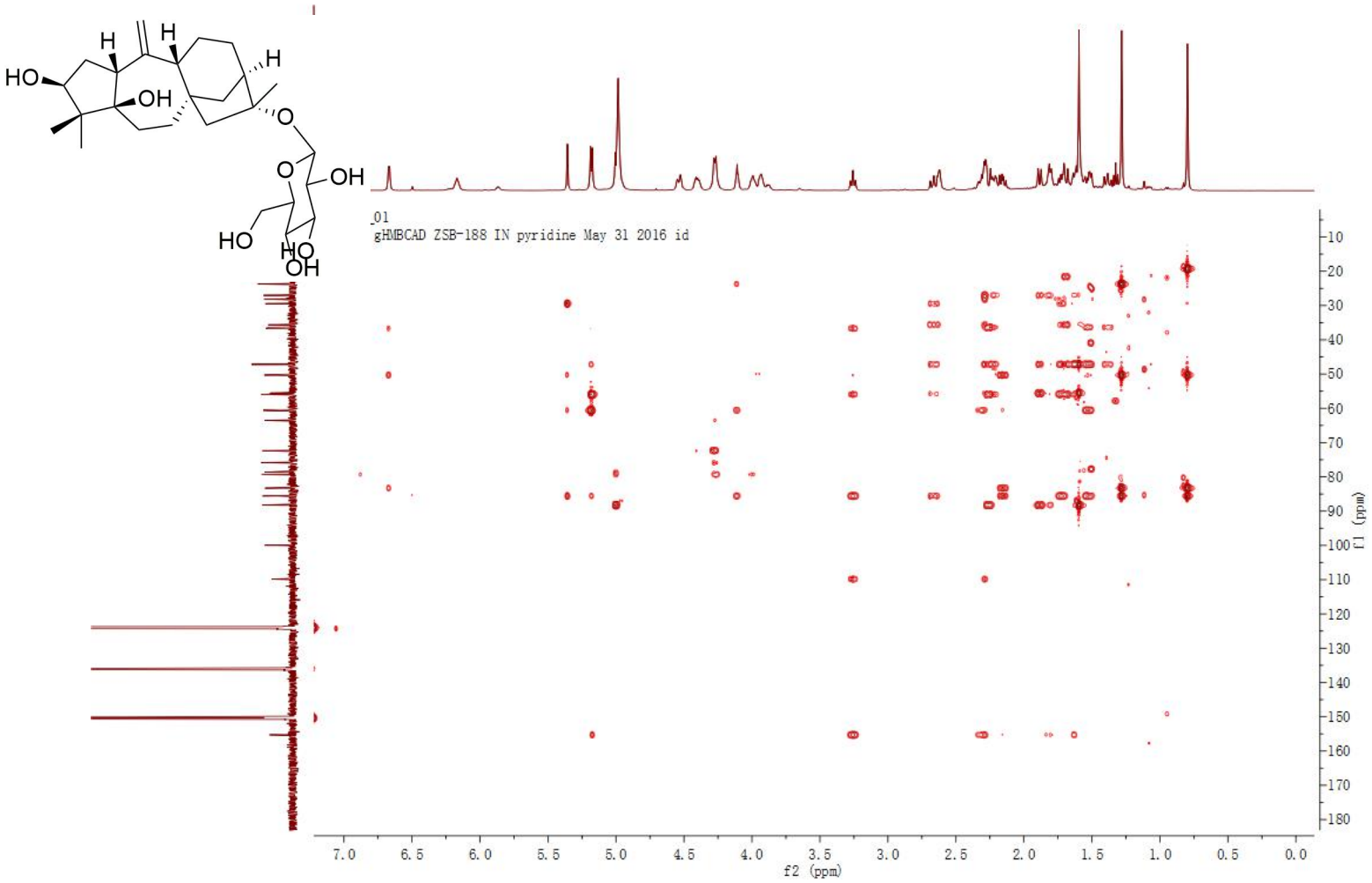
The DEPT spectrum of **10** in C_5D_5N (125 MHz)



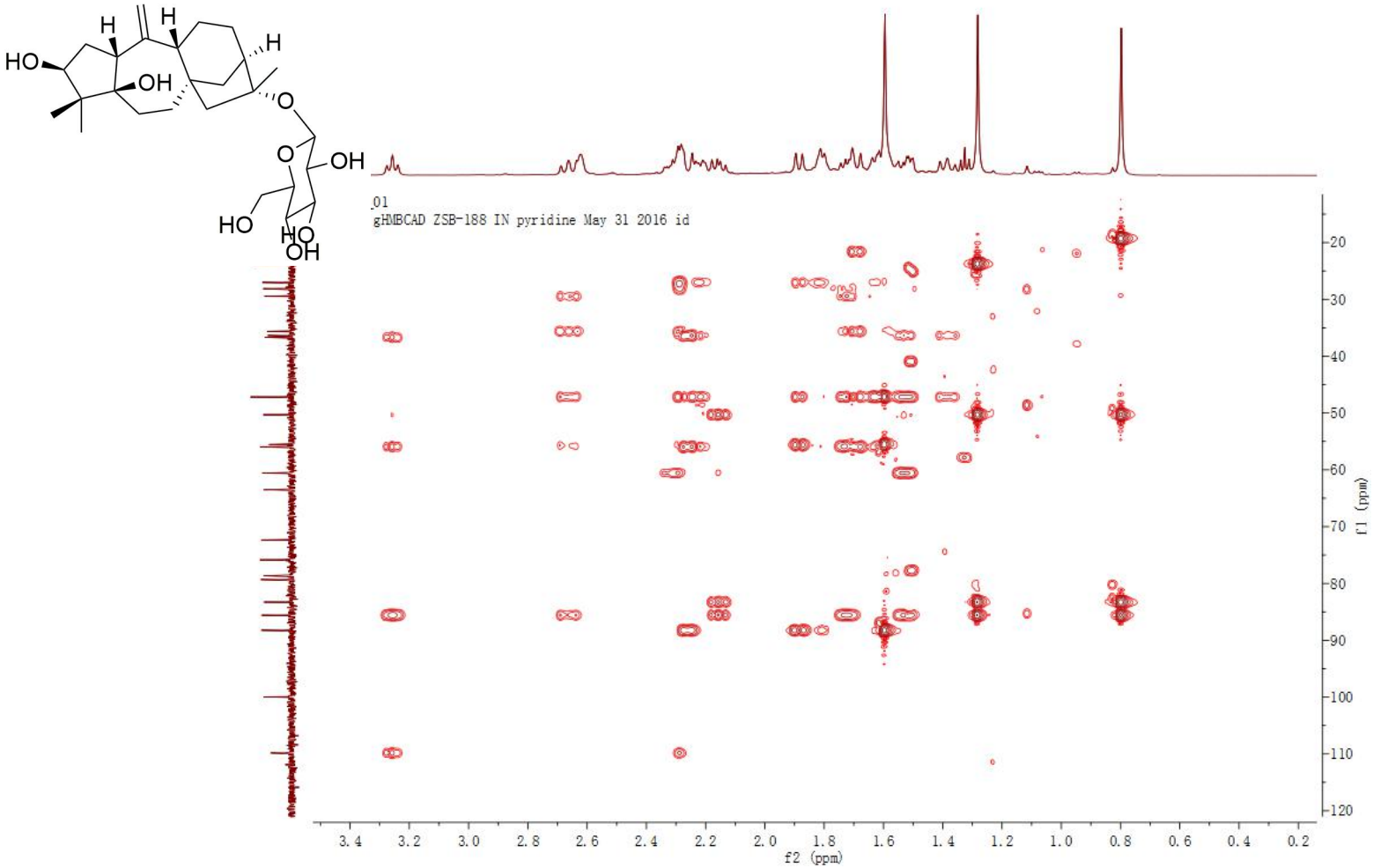
The COSY spectrum of **10** in C_5D_5N (500 MHz)



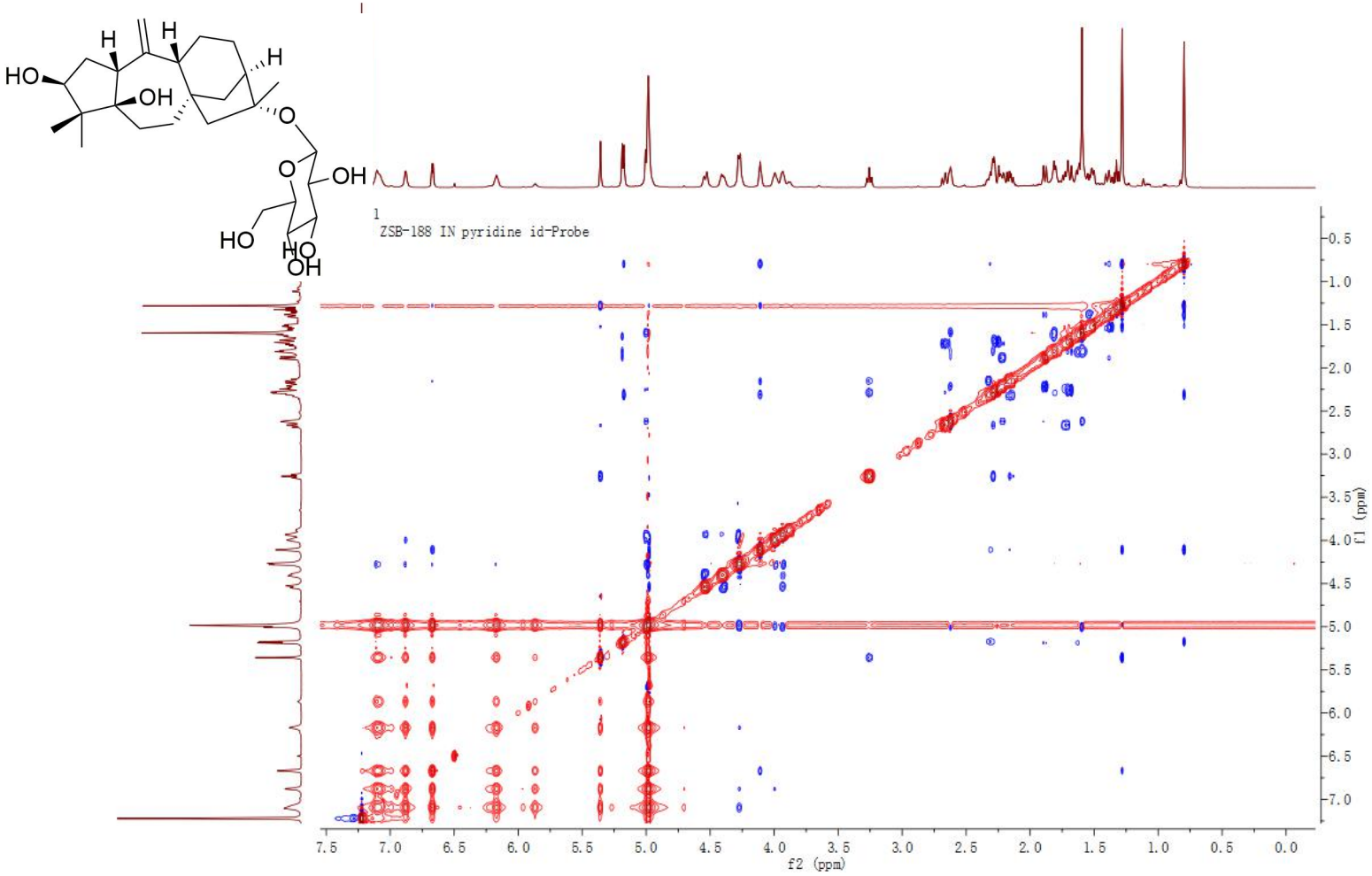
The HSQC spectrum of **10** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



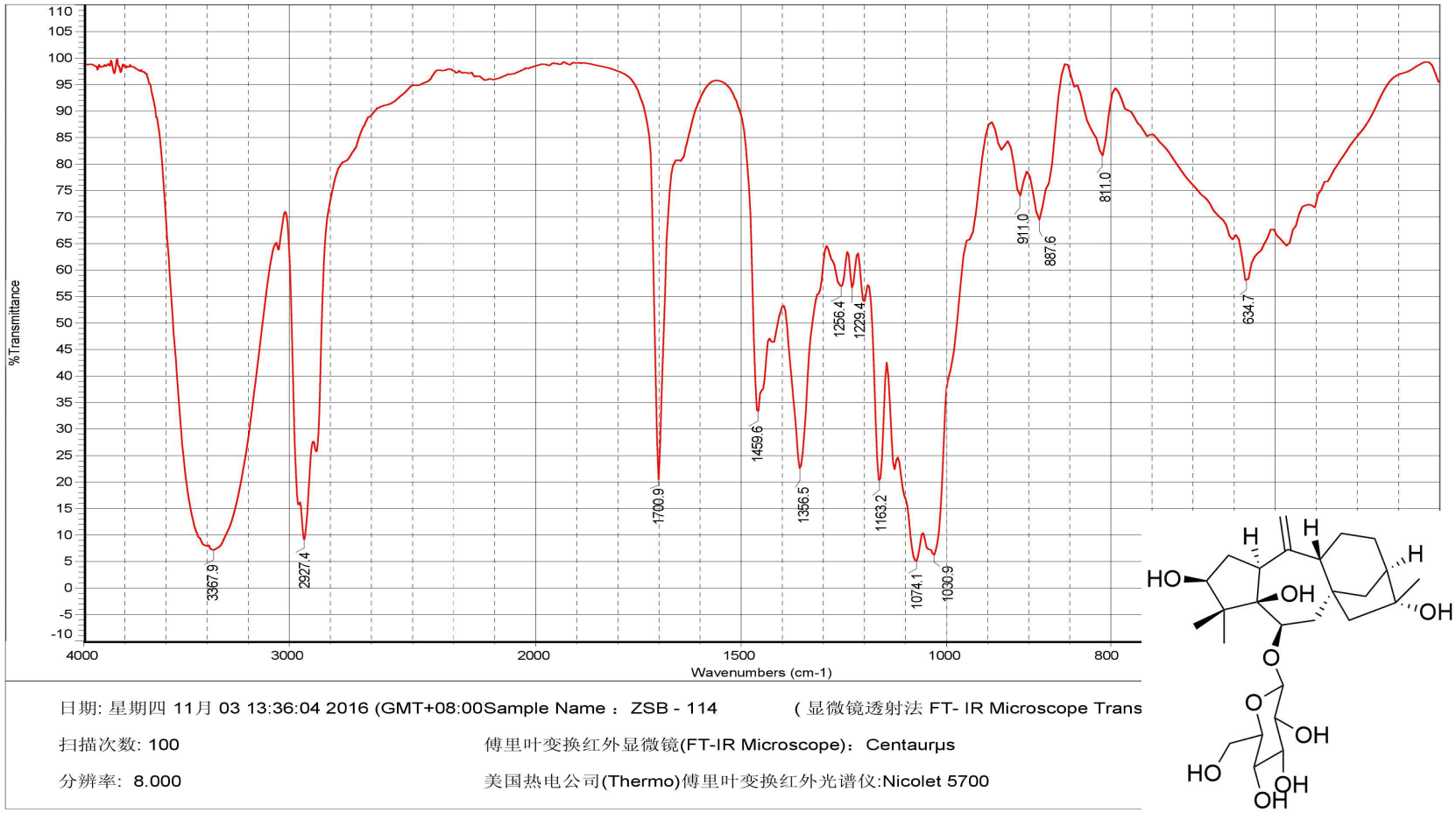
The HMBC spectrum of **10** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The HMBC spectrum (amplified) of **10** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The NOESY spectrum of **10** in C_5D_5N (500 MHz)

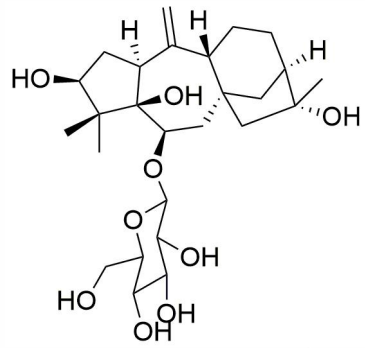


The IR spectrum of **11**

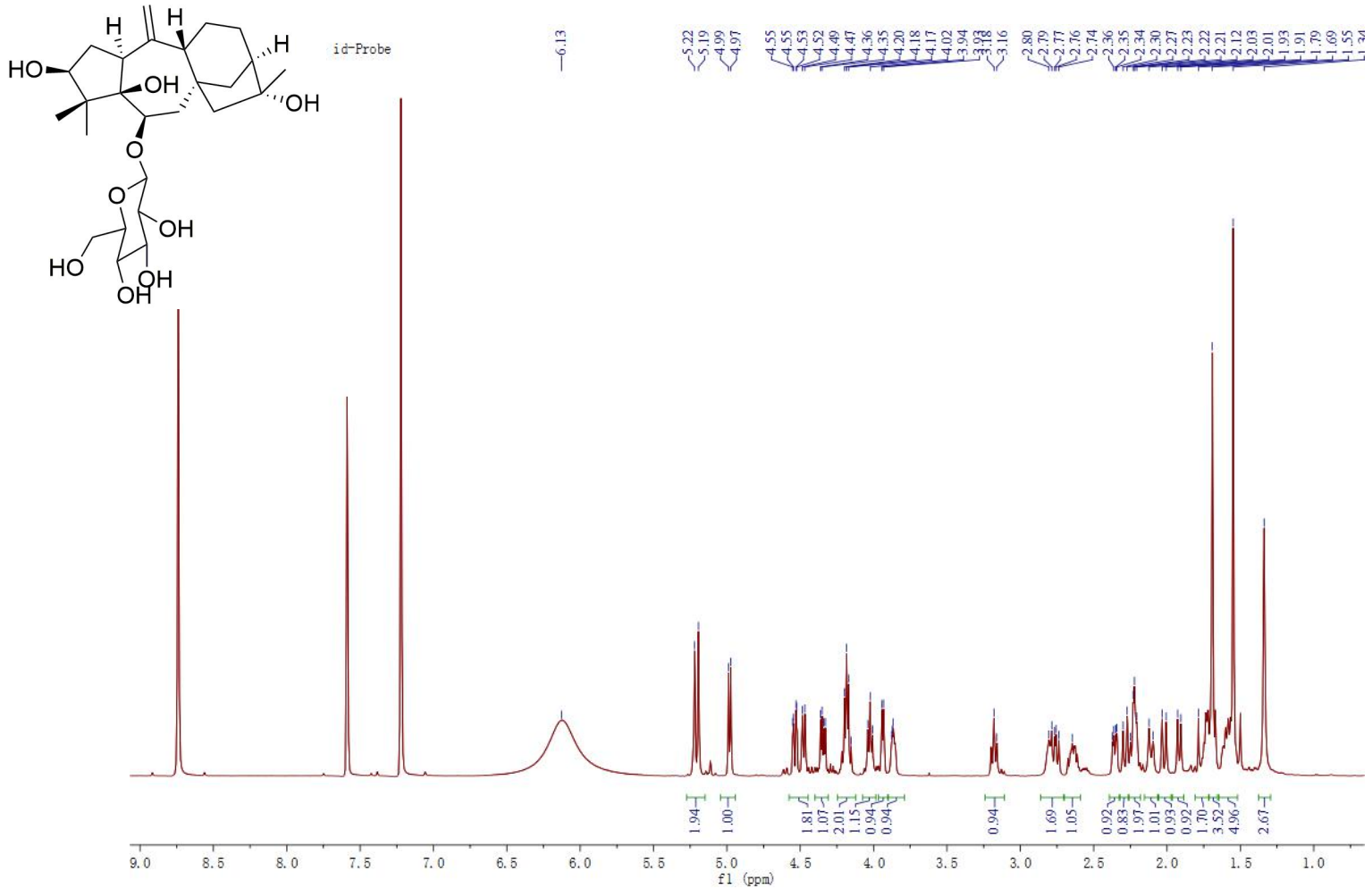
MS Formula Results: + Scan (6.461 min) Sub (2015123103.d)

	m/z	Ion	Formula	Abundance
-	521.2721	(M+Na)+	C26 H42 Na O9	2216676.5

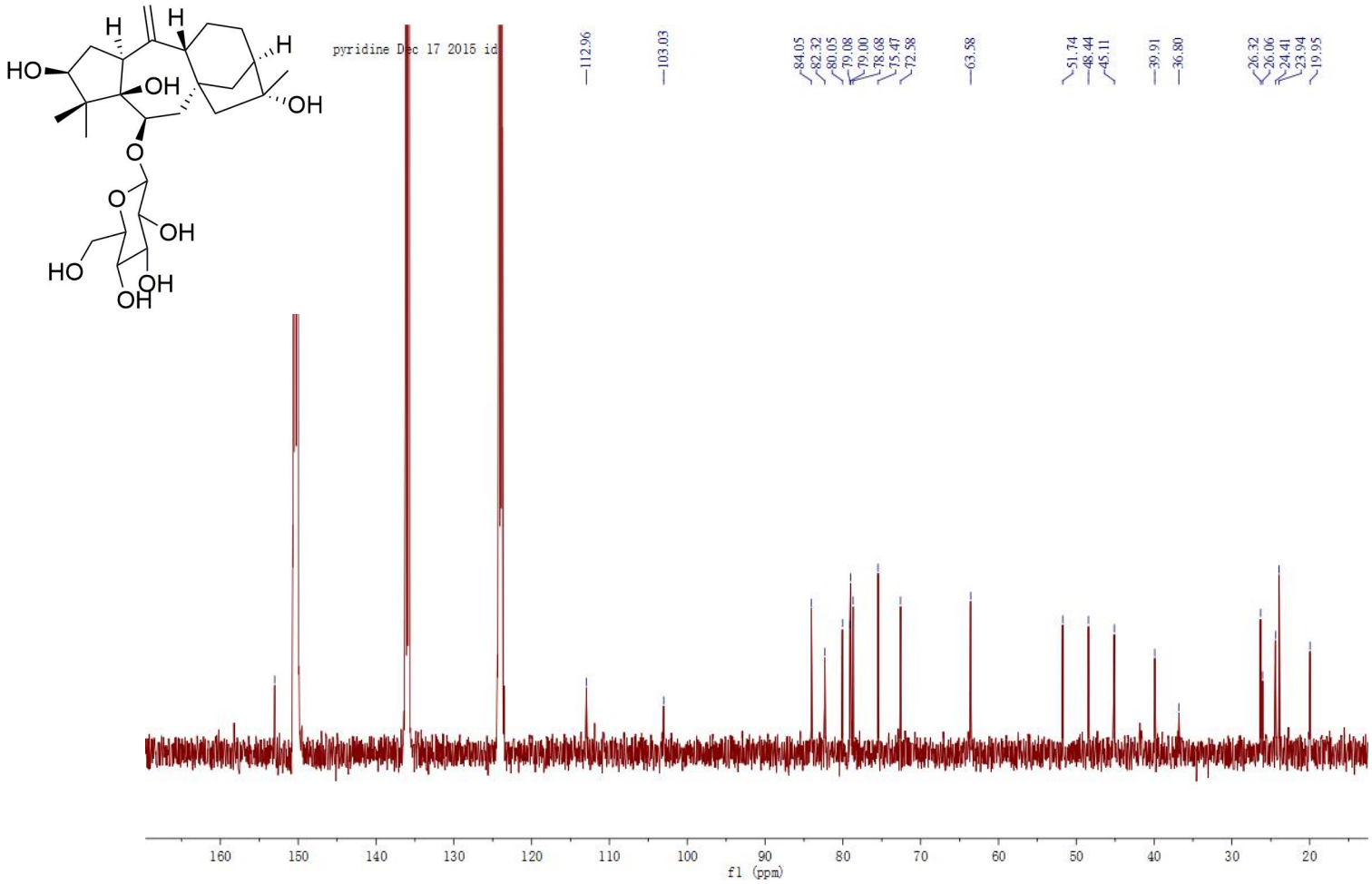
	Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
+	✔	C26 H42 O9	C26 H42 Na O9	98.03		498.2829	498.2829	521.2721	-0.06	0.06	100	93.15	99.95	6
+		C27 H38 N4 O5	C27 H38 N4 Na O5	96.87		498.2829	498.2842	521.2734	2.62	2.62	99.78	89.47	99.93	11
+		C27 H46 O4 S2	C27 H46 Na O4 S2	95.6		498.2829	498.2838	521.273	1.68	1.68	99.91	84.93	99.78	5
+		C30 H42 O4 S	C30 H42 Na O4 S	95.39		498.2829	498.2804	521.2696	-5.09	5.09	99.19	85.26	99.94	10
+		C28 H42 N4 S2	C28 H42 N4 Na S2	94.67		498.2829	498.2851	521.2743	4.36	4.36	99.4	82.54	99.74	10
+		C31 H38 N4 S	C31 H38 N4 Na S	94.64		498.2829	498.2817	521.2709	-2.41	2.41	99.82	81.62	99.91	15



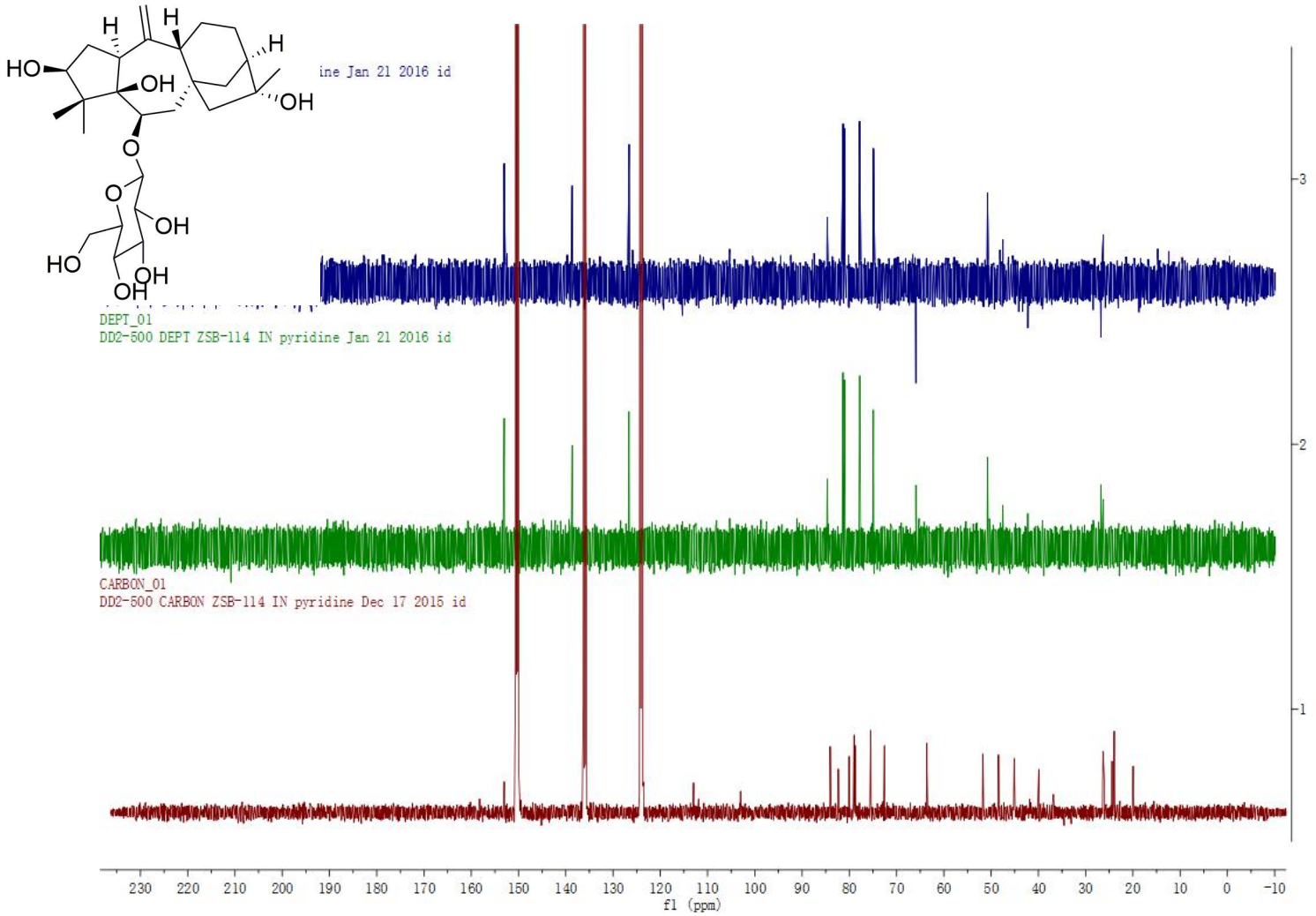
The HRESIMS spectrum of **11**



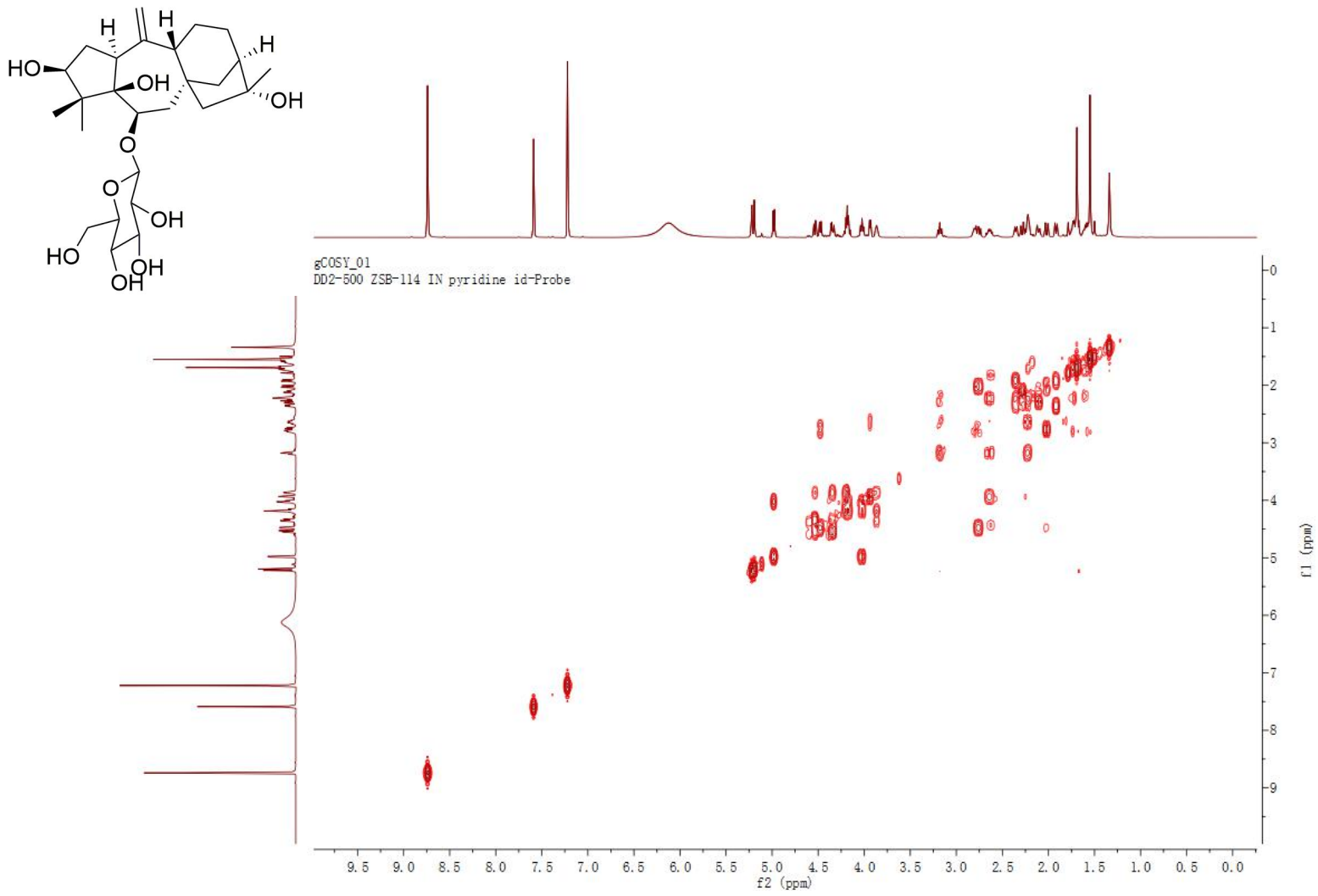
The ^{1}H NMR spectrum of **11** in C_5D_5N (500 MHz)



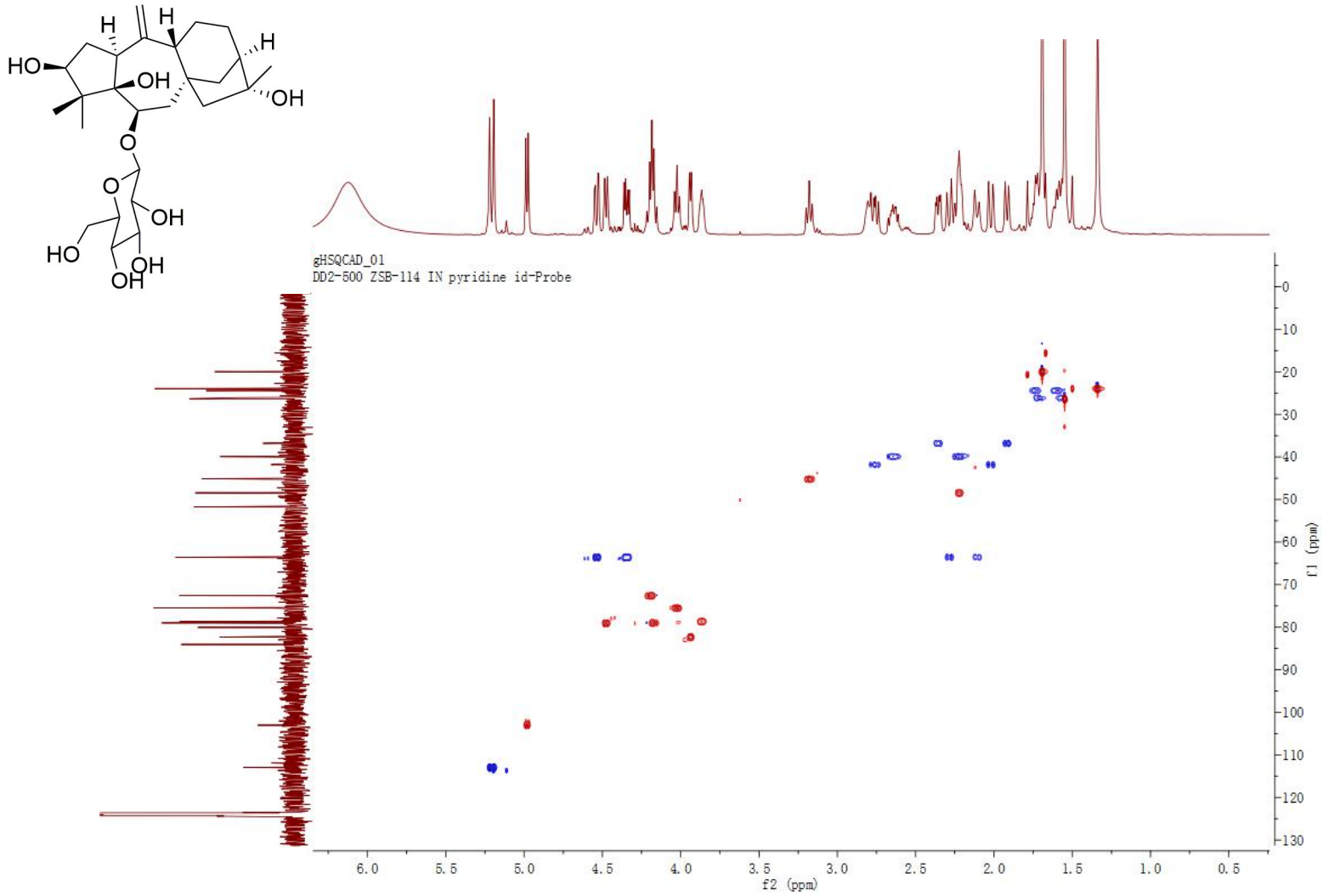
The ^{13}C NMR spectrum of **11** in C_5D_5N (125 MHz)



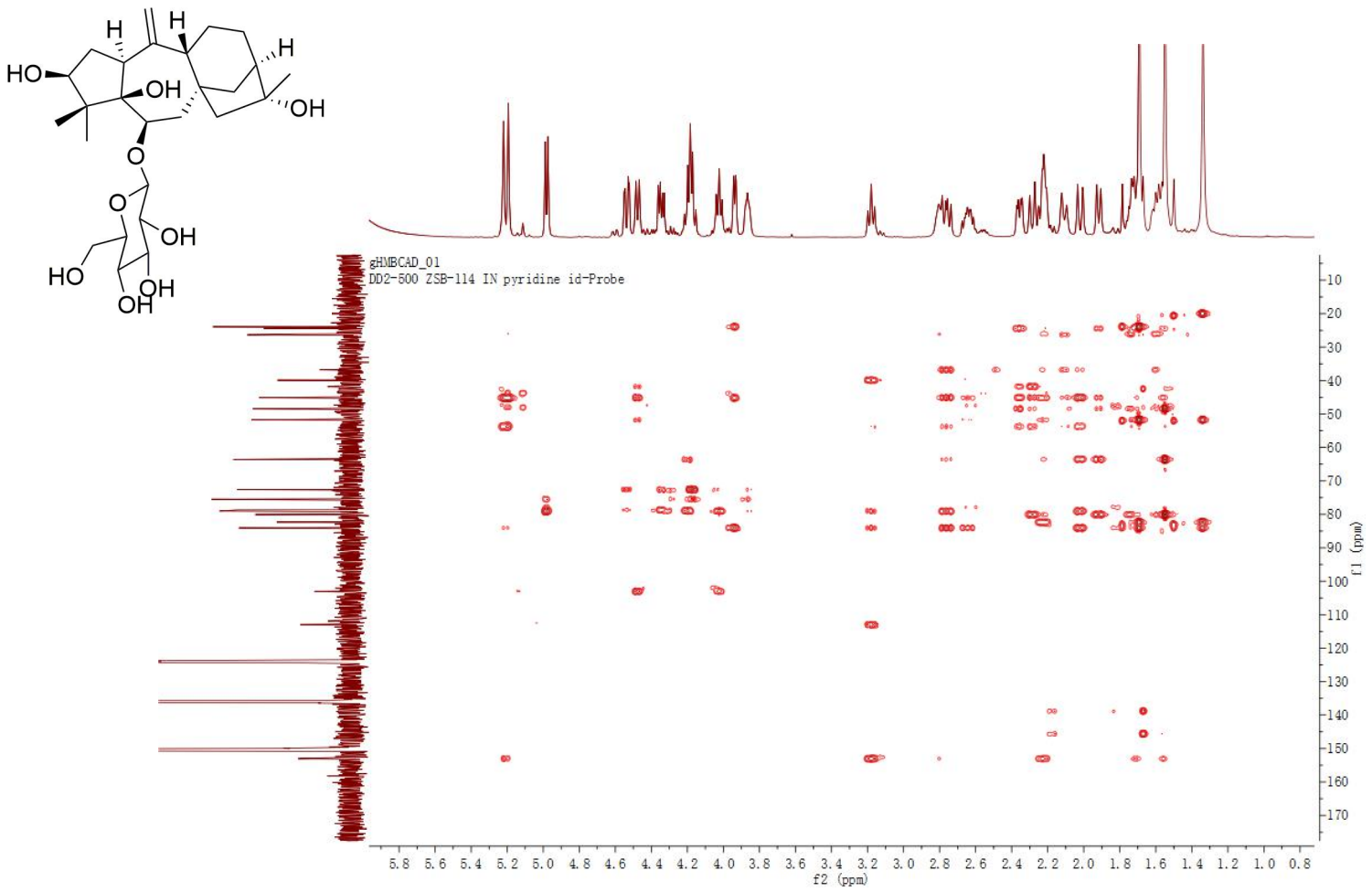
The DEPT spectrum of **11** in C_5D_5N (125 MHz)



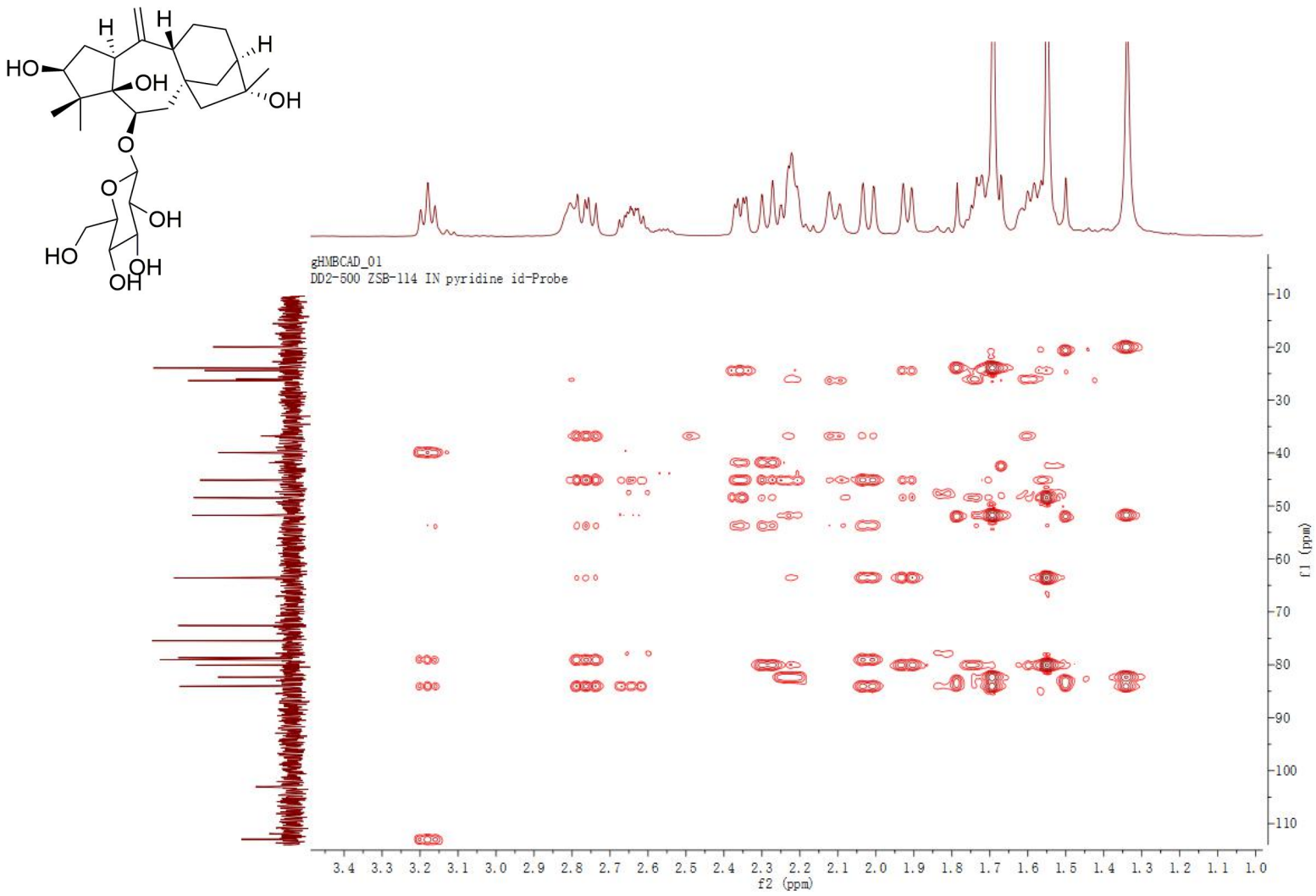
The COSY spectrum of **11** in C_5D_5N (500 MHz)



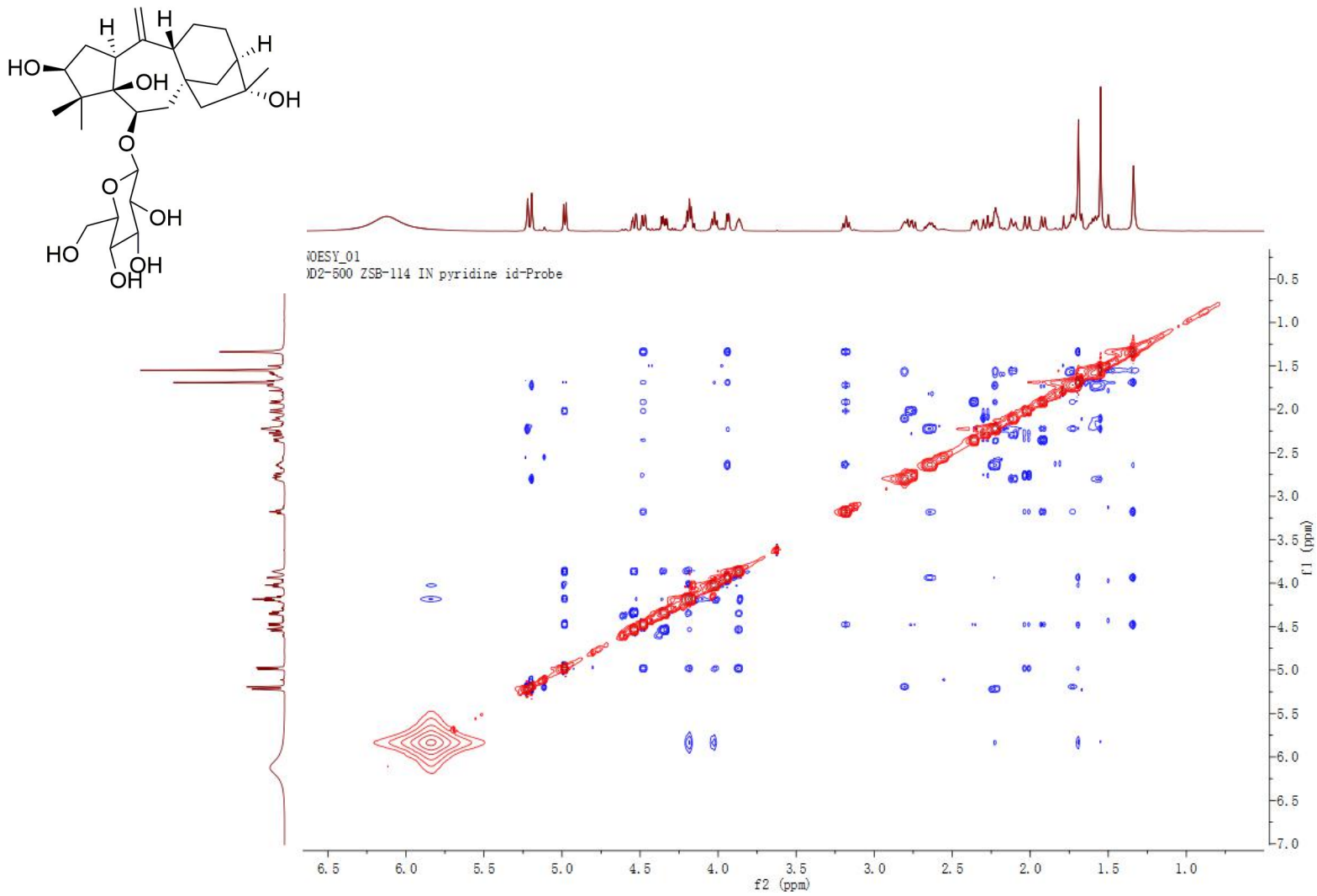
The HSQC spectrum of **11** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



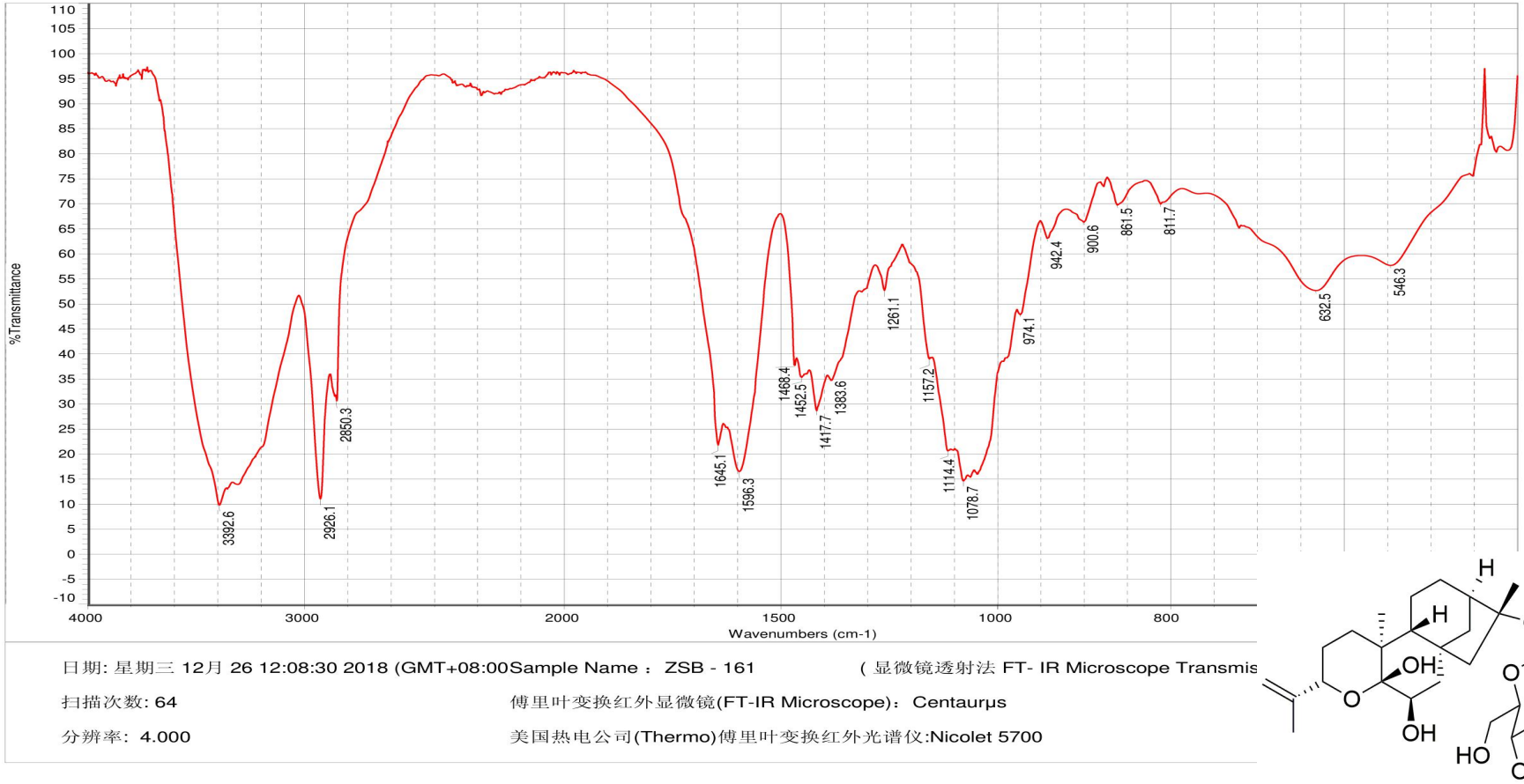
The HMBC spectrum of **11** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The HMBC spectrum (amplified) of **11** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The NOESY spectrum of **11** in C_5D_5N (500 MHz)

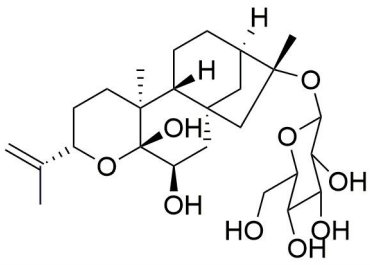


The IR spectrum of **12**

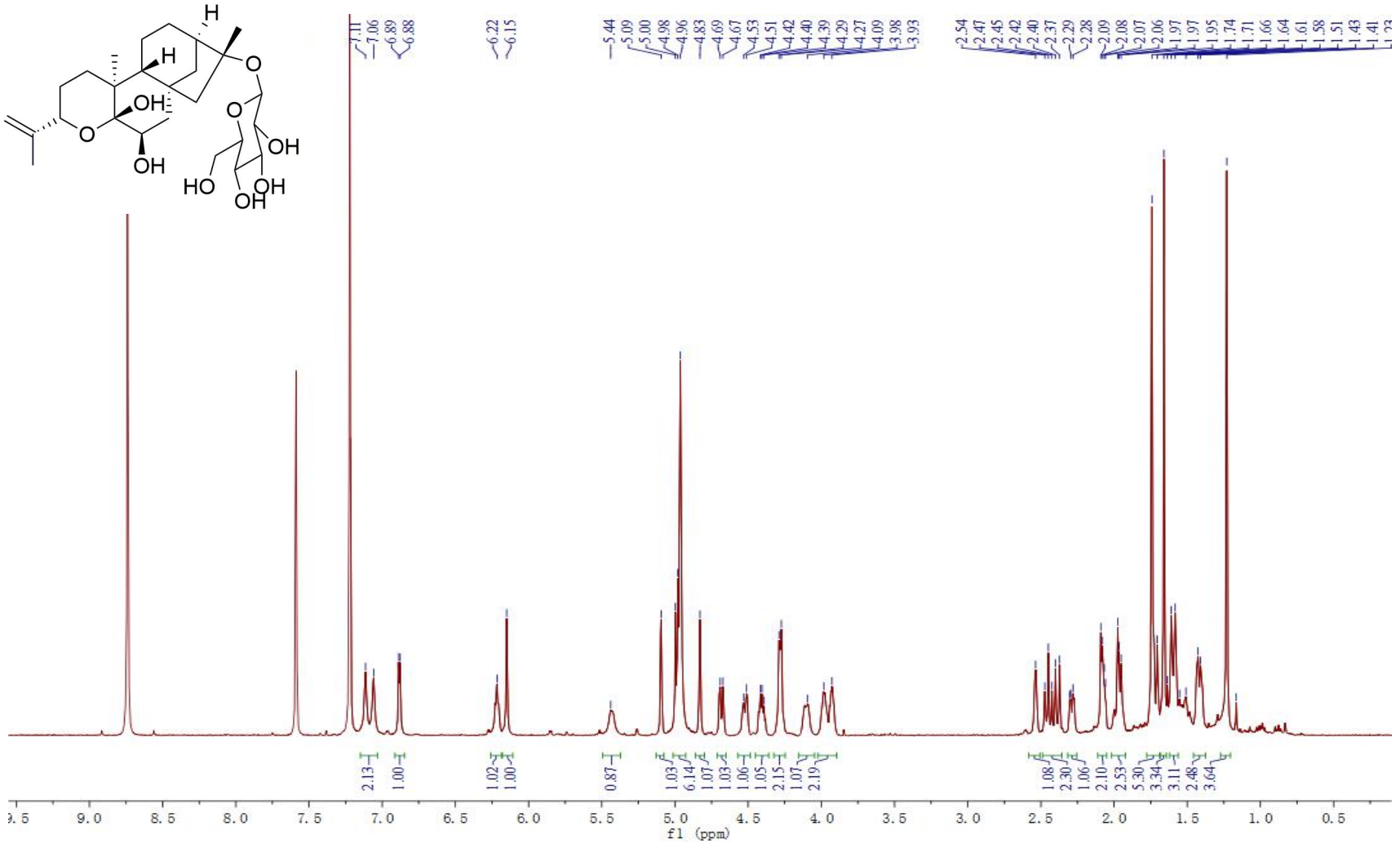
MS Formula Results: + Scan (7.390 min) Sub (2016050404.d)

	m/z	Ion	Formula	Abundance
-	521.2708	(M+Na)+	C26 H42 Na O9	469797.6

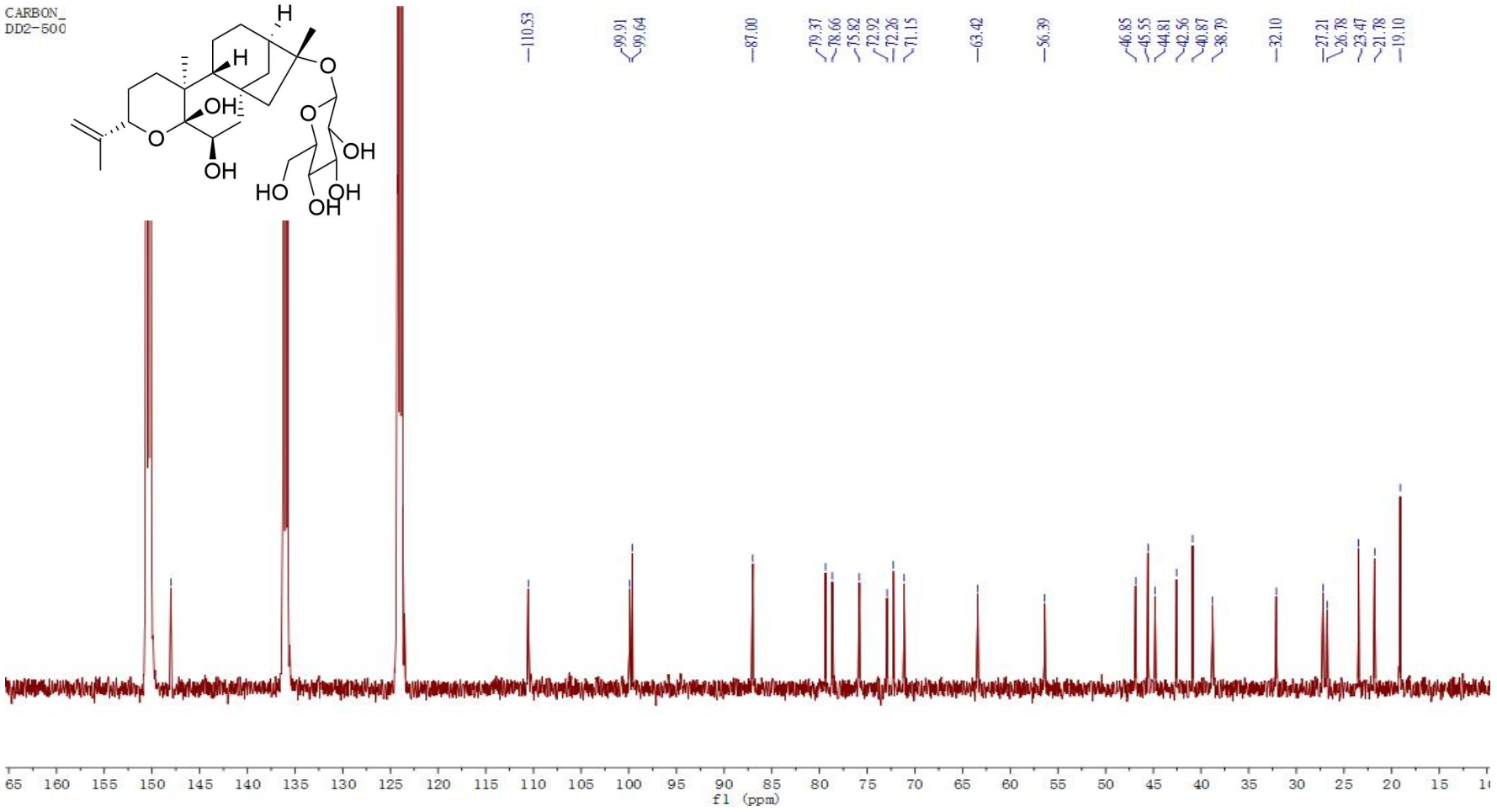
	Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
+	☑	C26 H42 O9	C26 H42 Na O9	99.83		498.2816	498.2829	521.2721	2.56	2.56	99.79	99.89	99.83	6
+	☐	C21 H42 N2 O11	C21 H42 N2 Na O11	99.17		498.2816	498.2789	521.2681	-5.52	5.52	99.04	98.79	99.89	2
+	☐	C30 H42 O4 S	C30 H42 Na O4 S	98.98		498.2816	498.2804	521.2696	-2.47	2.47	99.81	96.78	99.96	10
+	☐	C27 H46 O4 S2	C27 H46 Na O4 S2	97.73		498.2816	498.2838	521.273	4.29	4.29	99.42	93.19	99.79	5
+	☐	C22 H46 N2 O6 S2	C22 H46 N2 Na O6 S2	97.66		498.2816	498.2797	521.2689	-3.79	3.79	99.55	92.81	99.72	1



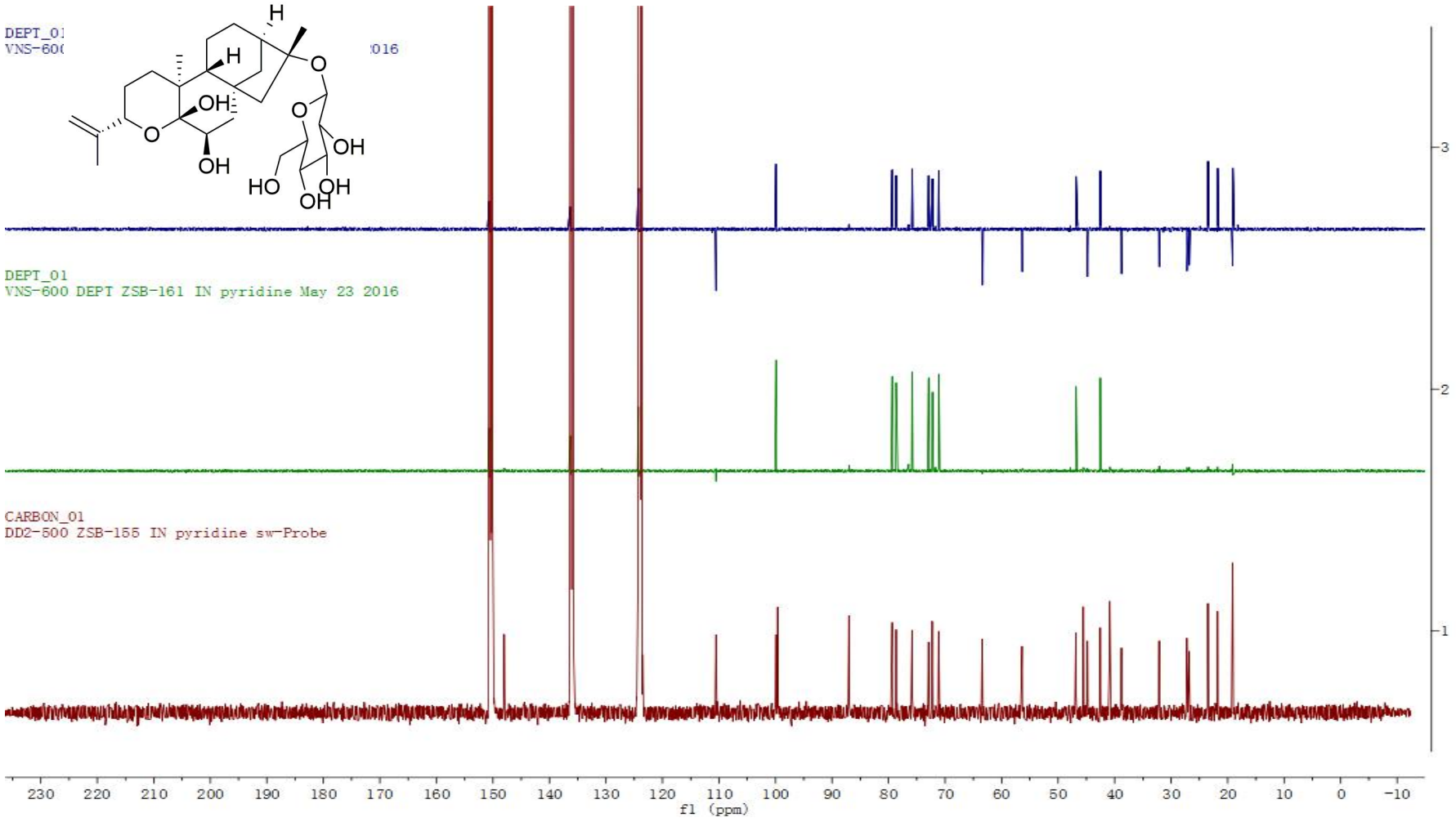
The HRESIMS spectrum of **12**



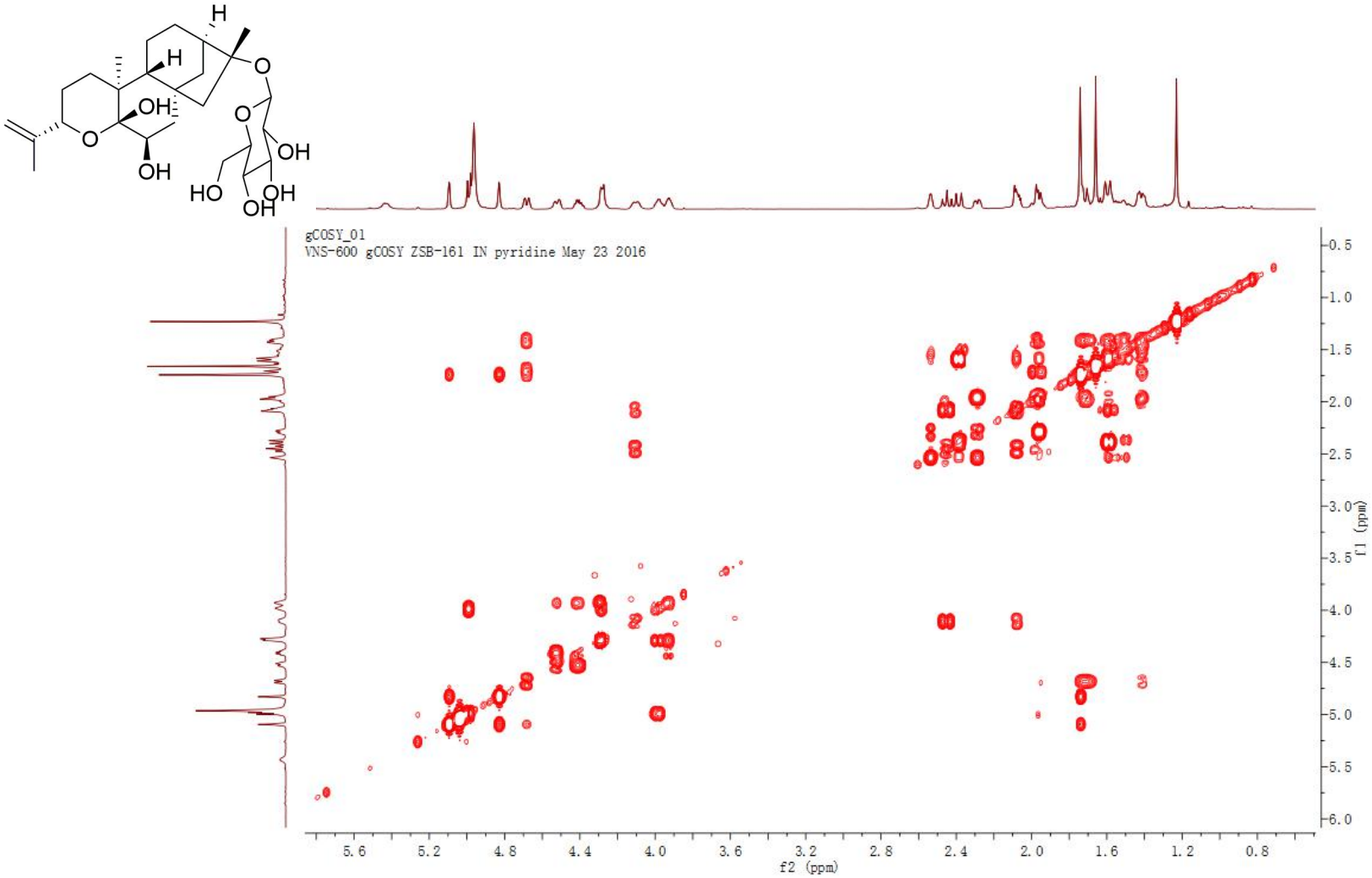
The ^{1}H NMR spectrum of **12** in C_5D_5N (500 MHz)



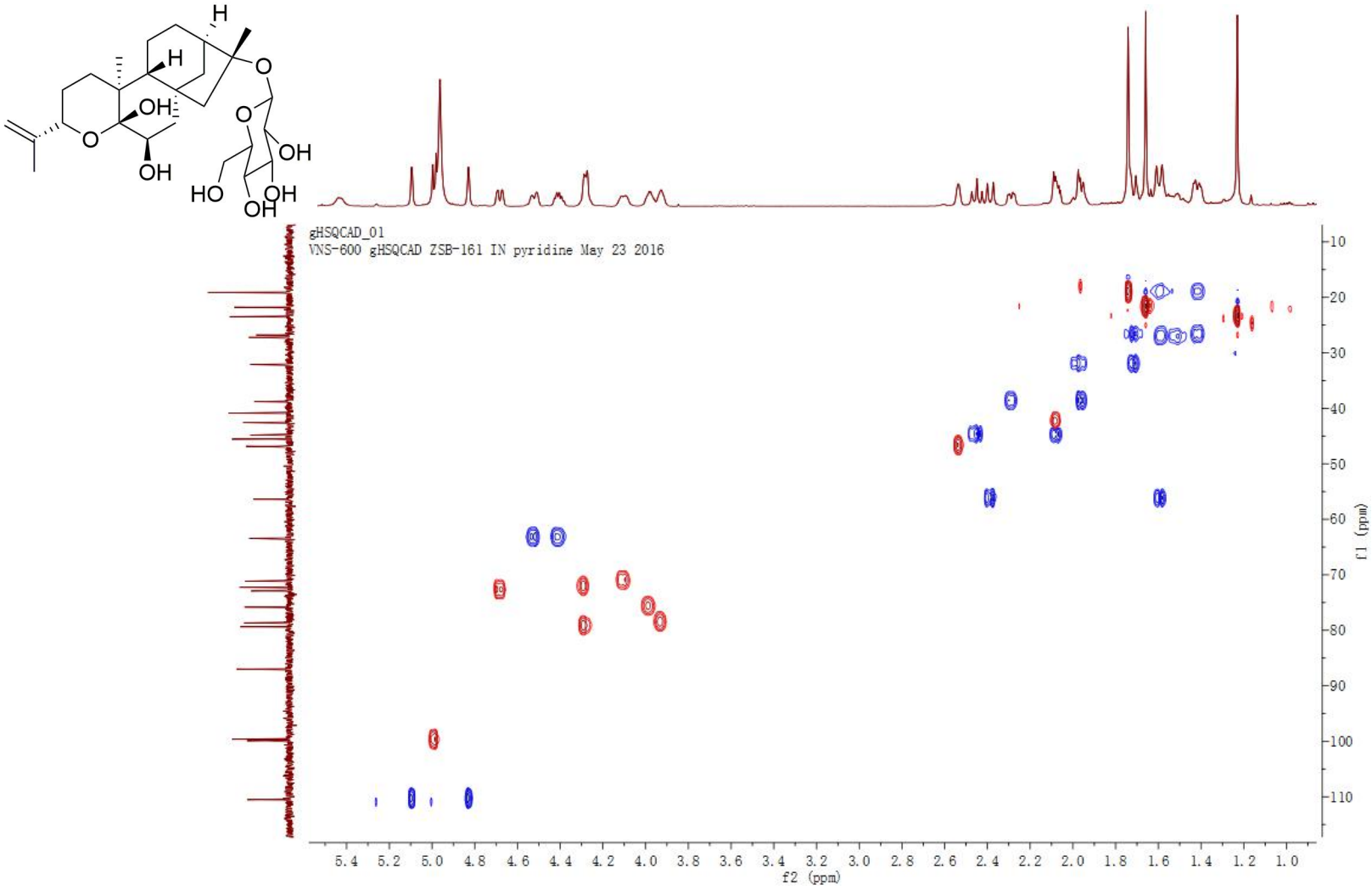
The ^{13}C NMR spectrum of **12** in C_5D_5N (125 MHz)



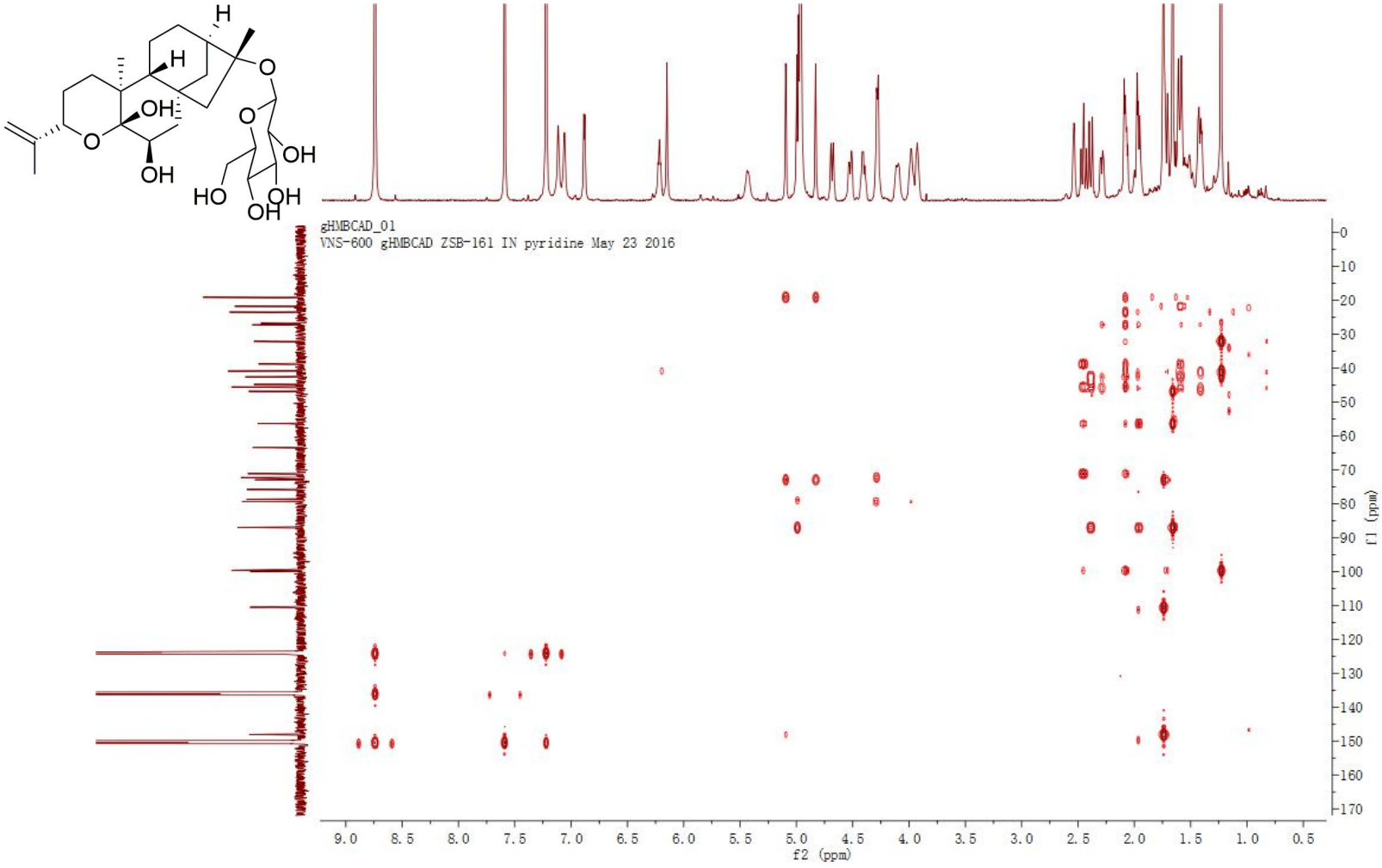
The DEPT spectrum of **12** in C_5D_5N (125 MHz)



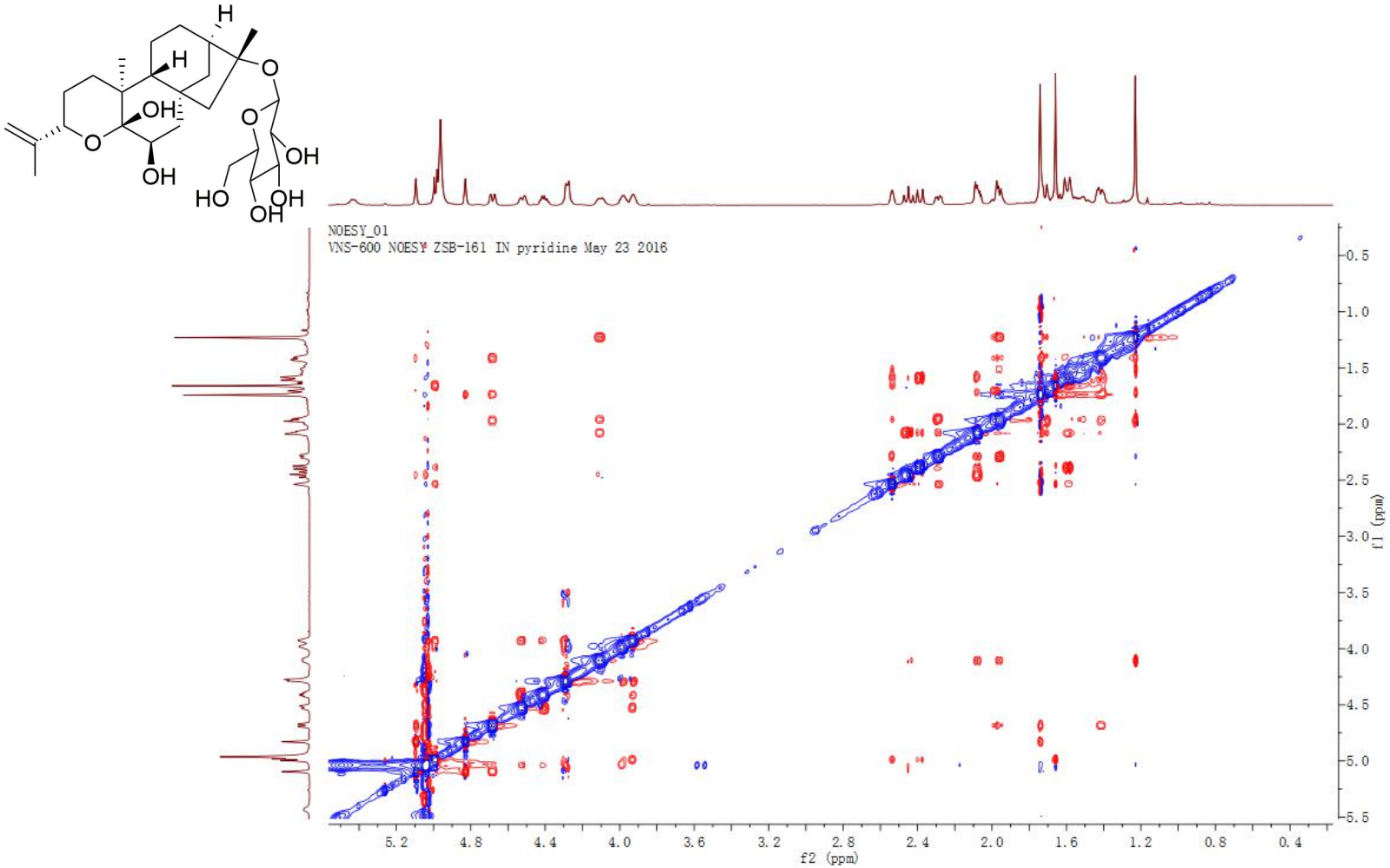
The COSY spectrum of **12** in C_5D_5N (500 MHz)



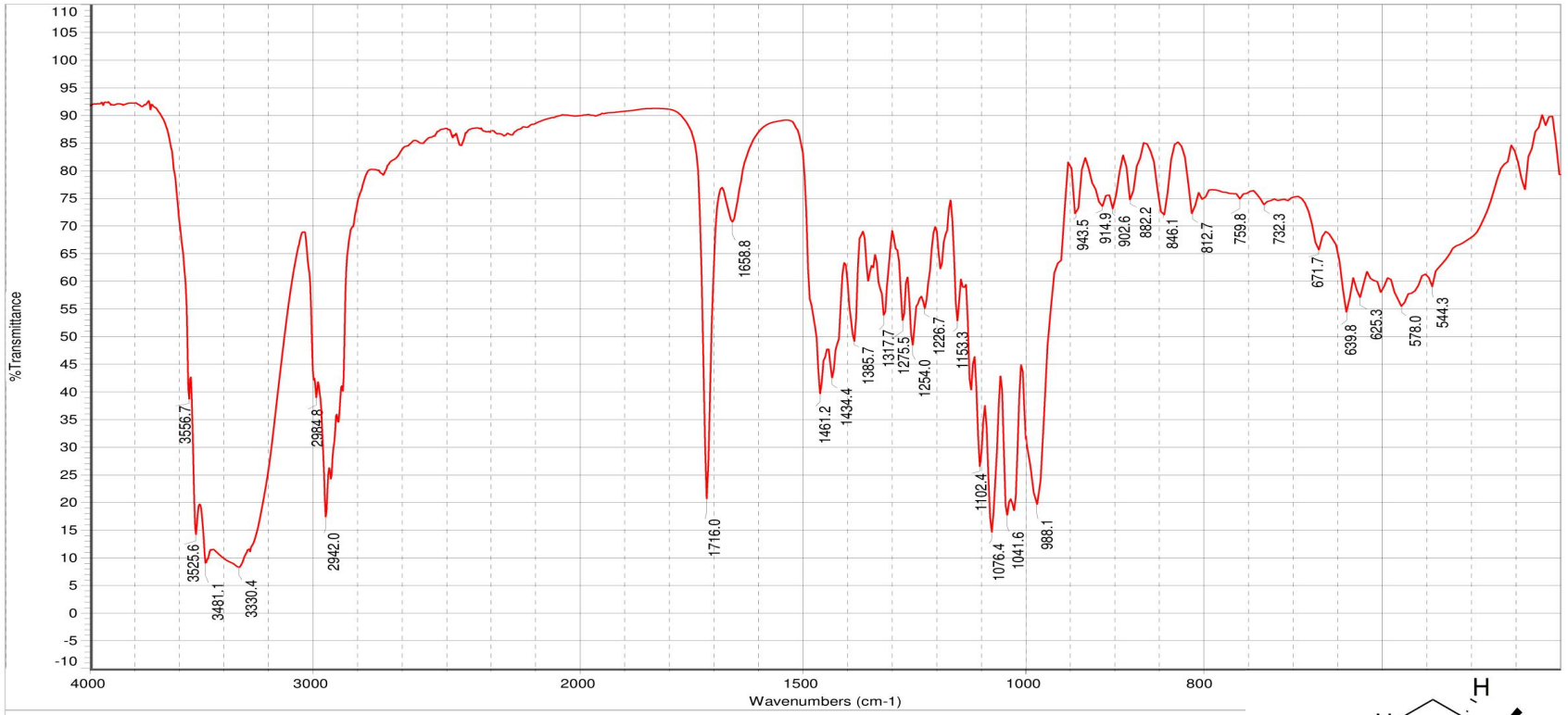
The HSQC spectrum of **12** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)

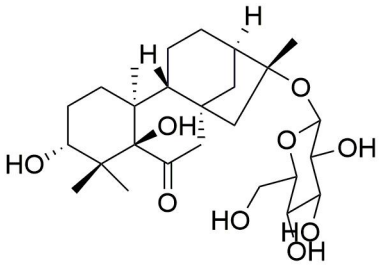


The HMBC spectrum of **12** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The NOESY spectrum of **12** in C_5D_5N (500 MHz)



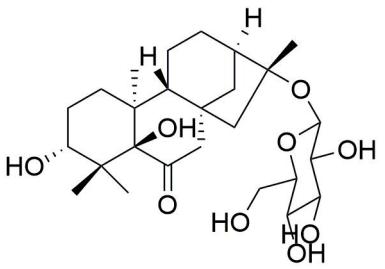


The IR spectrum of **13**

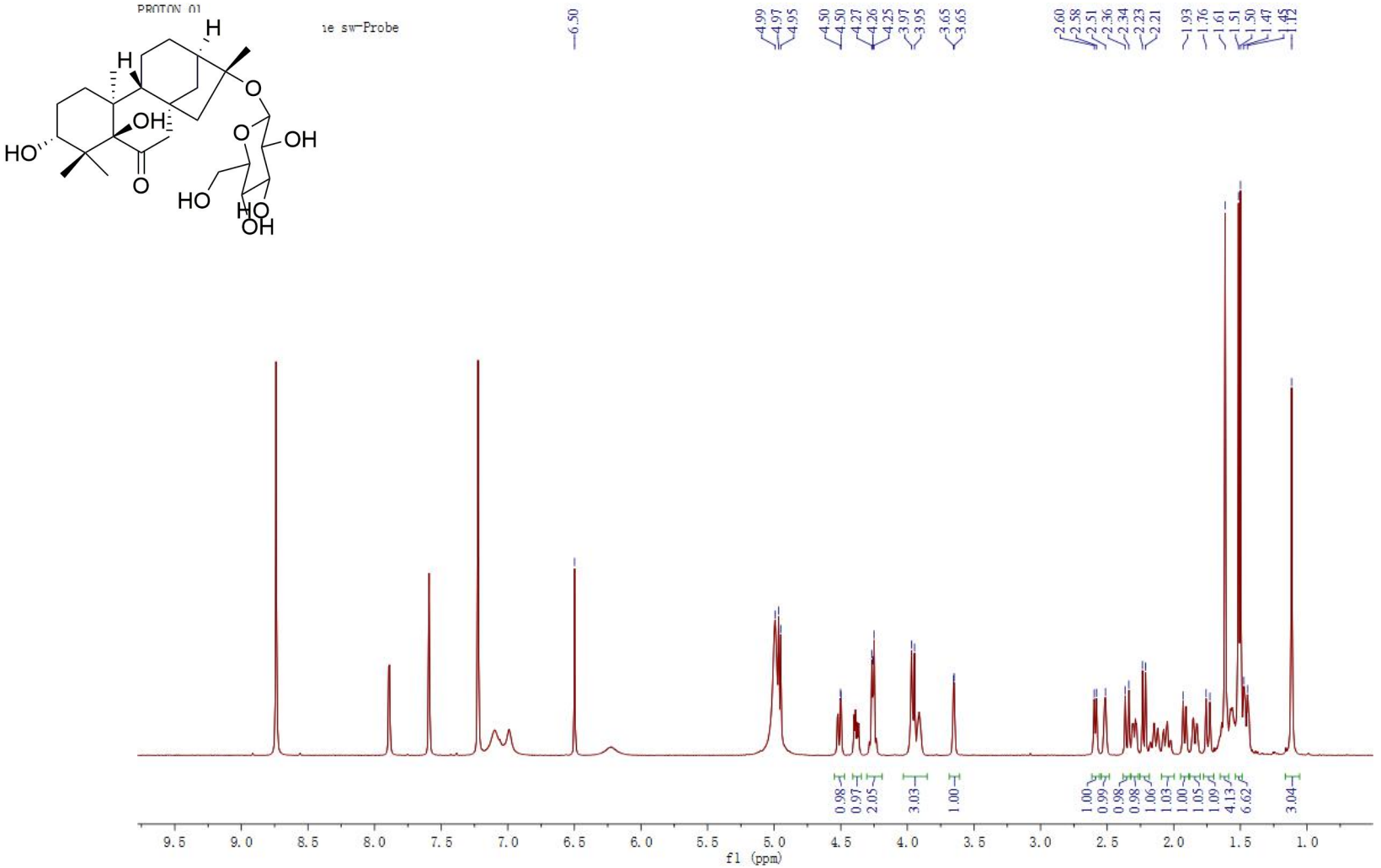
MS Formula Results: + Scan (6.856 min) Sub (2016053102.d)

	m/z	Ion	Formula	Abundance
-	521.2719	(M+Na)+	C26 H42 Na O9	129910.7

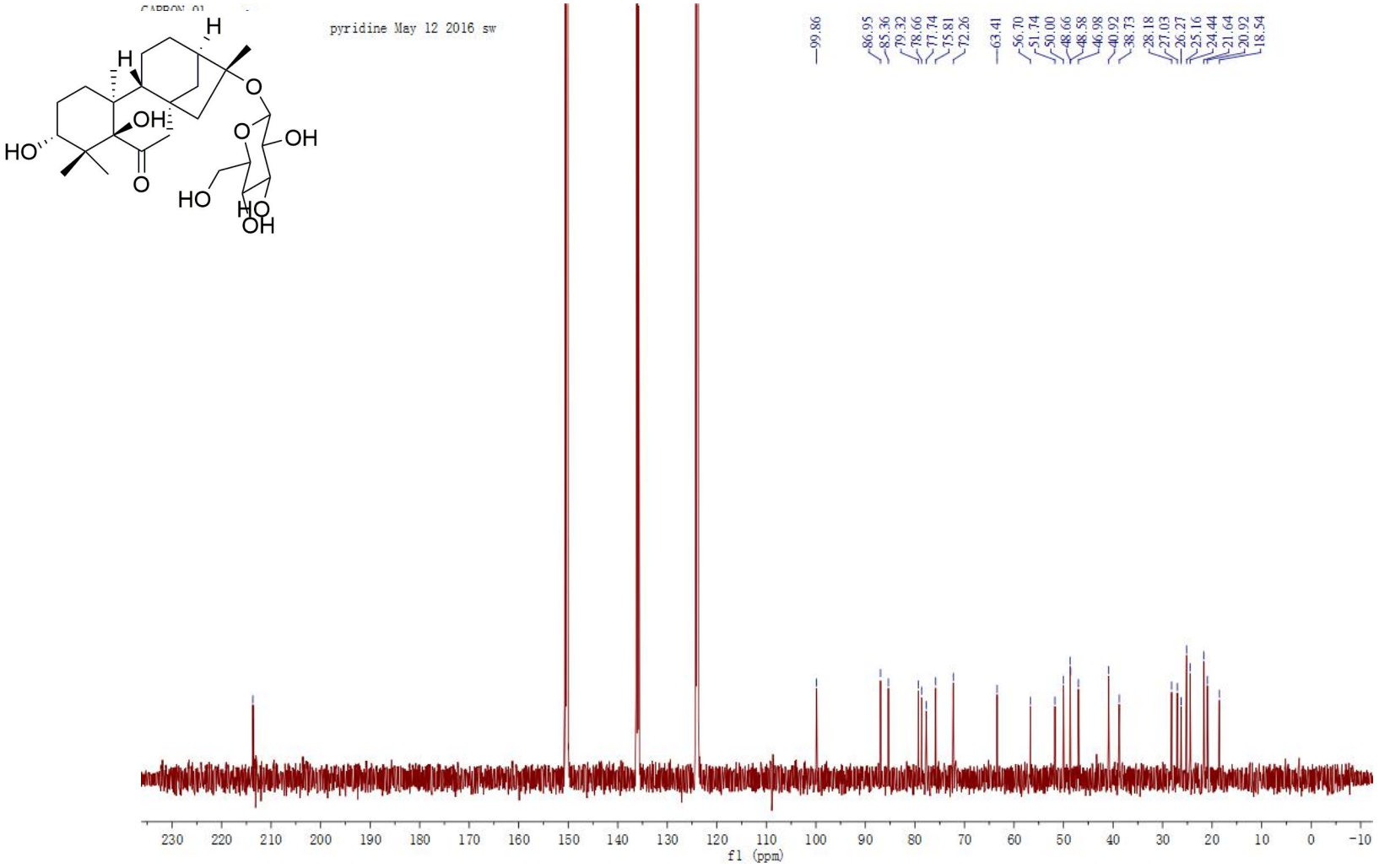
	Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
+	☑	C26 H42 O9	C26 H42 Na O9	99.89		498.2827	498.2829	521.2721	0.42	0.42	99.99	99.65	99.99	6
+	☐	C30 H42 O4 S	C30 H42 Na O4 S	99.1		498.2827	498.2804	521.2696	-4.61	4.61	99.33	98.22	99.7	10
+	☐	C27 H46 O4 S2	C27 H46 Na O4 S2	98.34		498.2827	498.2838	521.273	2.15	2.15	99.85	95.12	99.18	5
+	☐	C22 H46 N2 O6 S2	C22 H46 N2 Na O6 S2	97.56		498.2827	498.2797	521.2689	-5.93	5.93	98.9	94.13	98.98	1



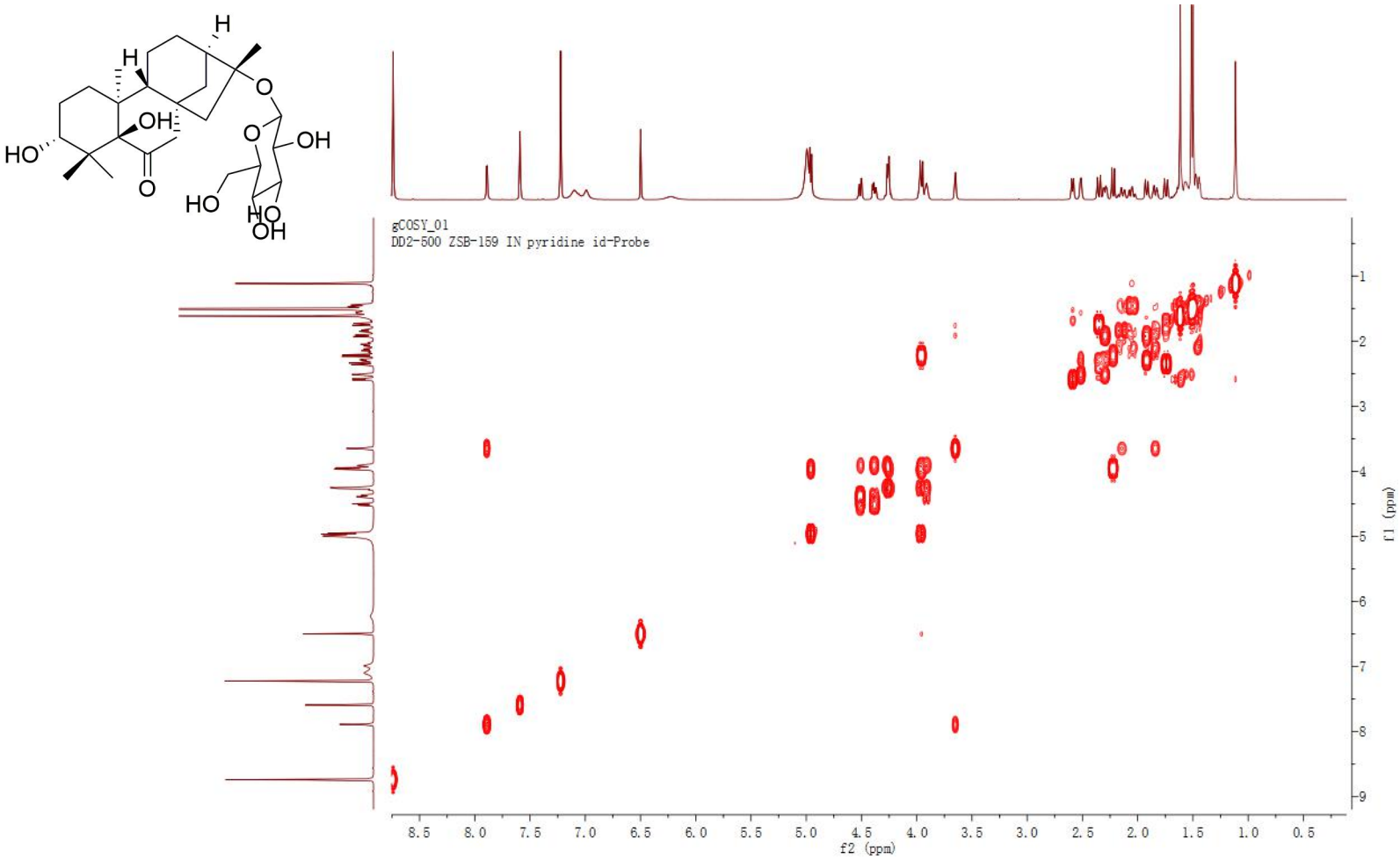
The HRESIMS spectrum of **13**



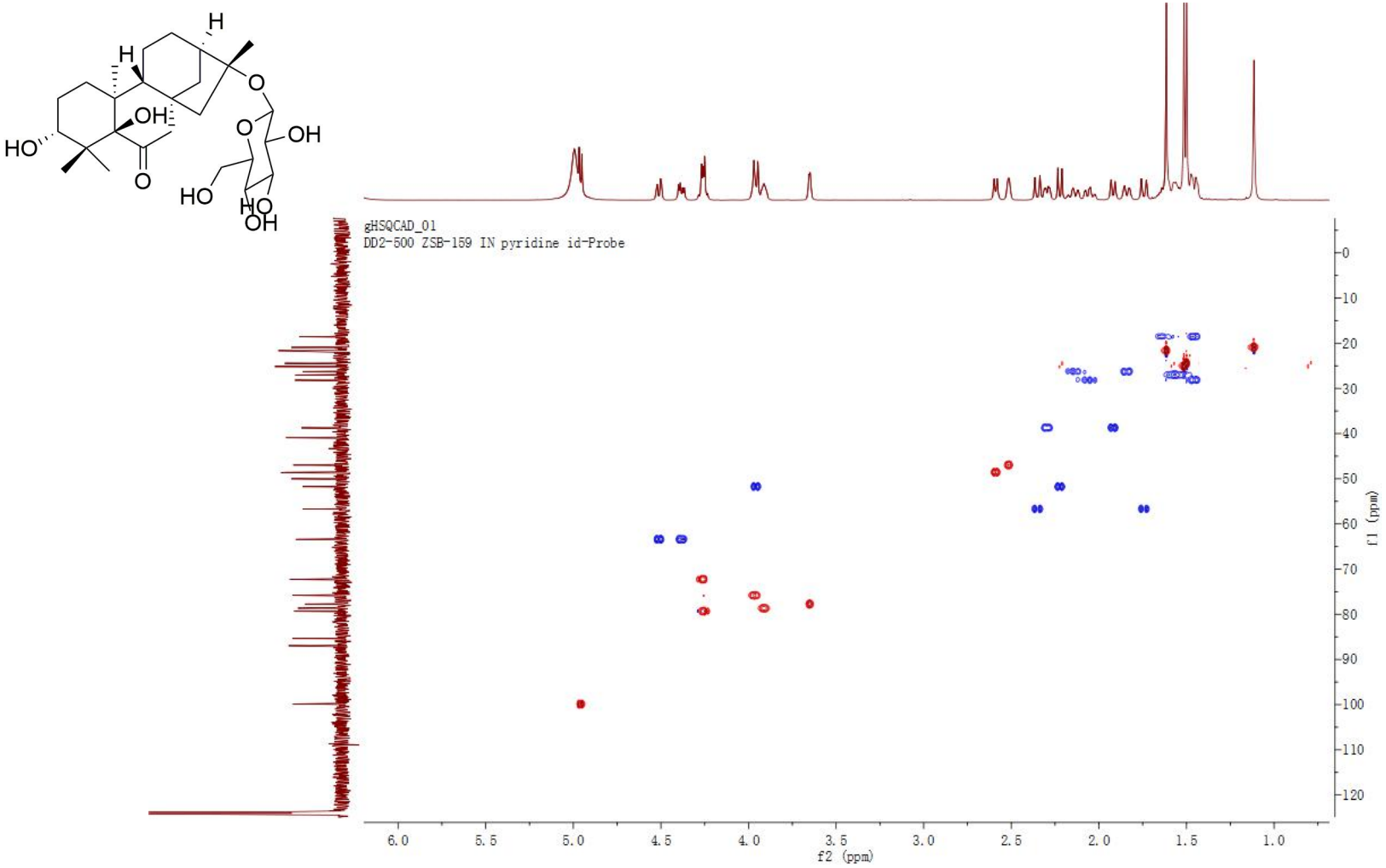
The ^{1}H NMR spectrum of **13** in C_5D_5N (500 MHz)



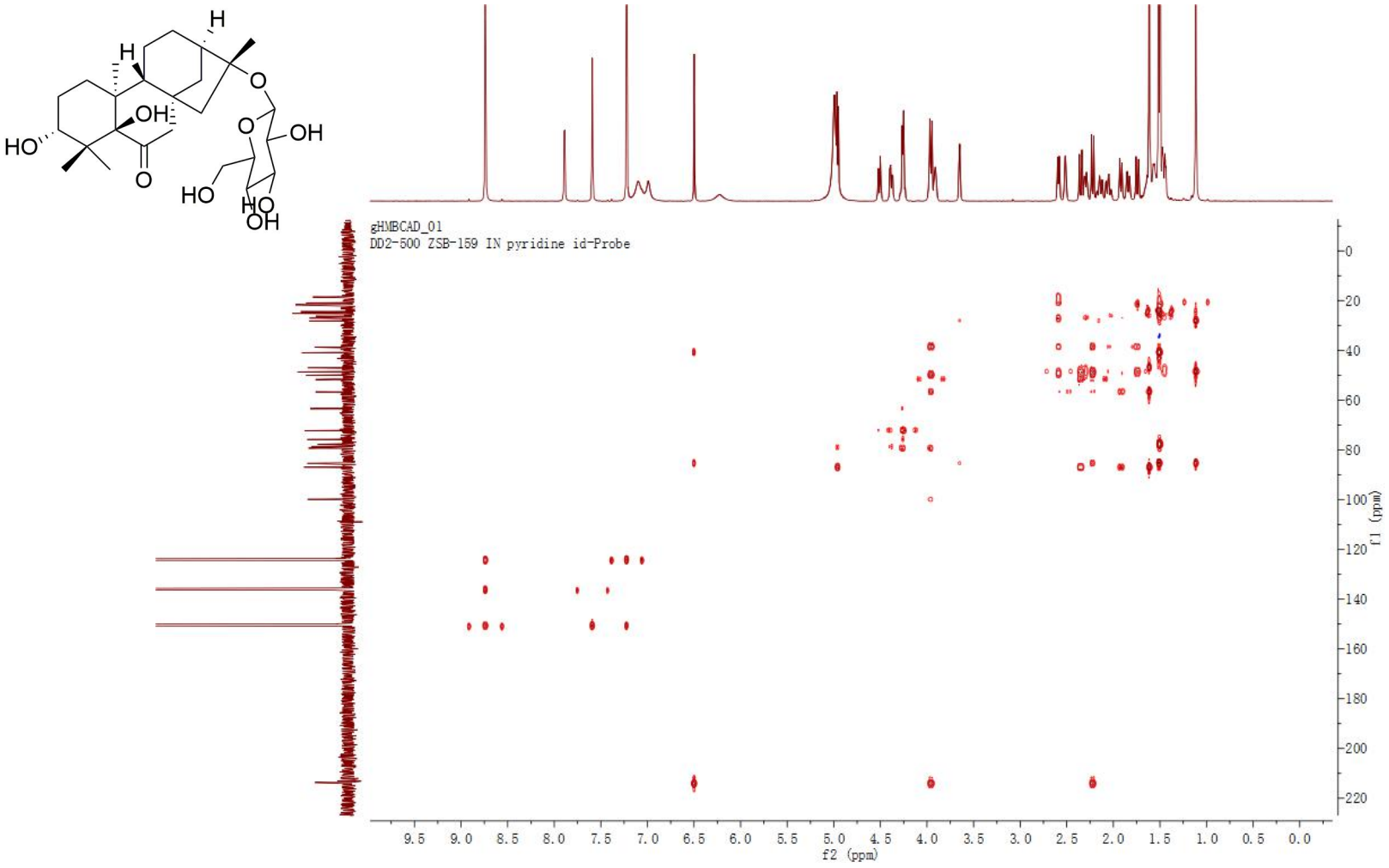
The ^{13}C NMR spectrum of **13** in C_5D_5N (125 MHz)



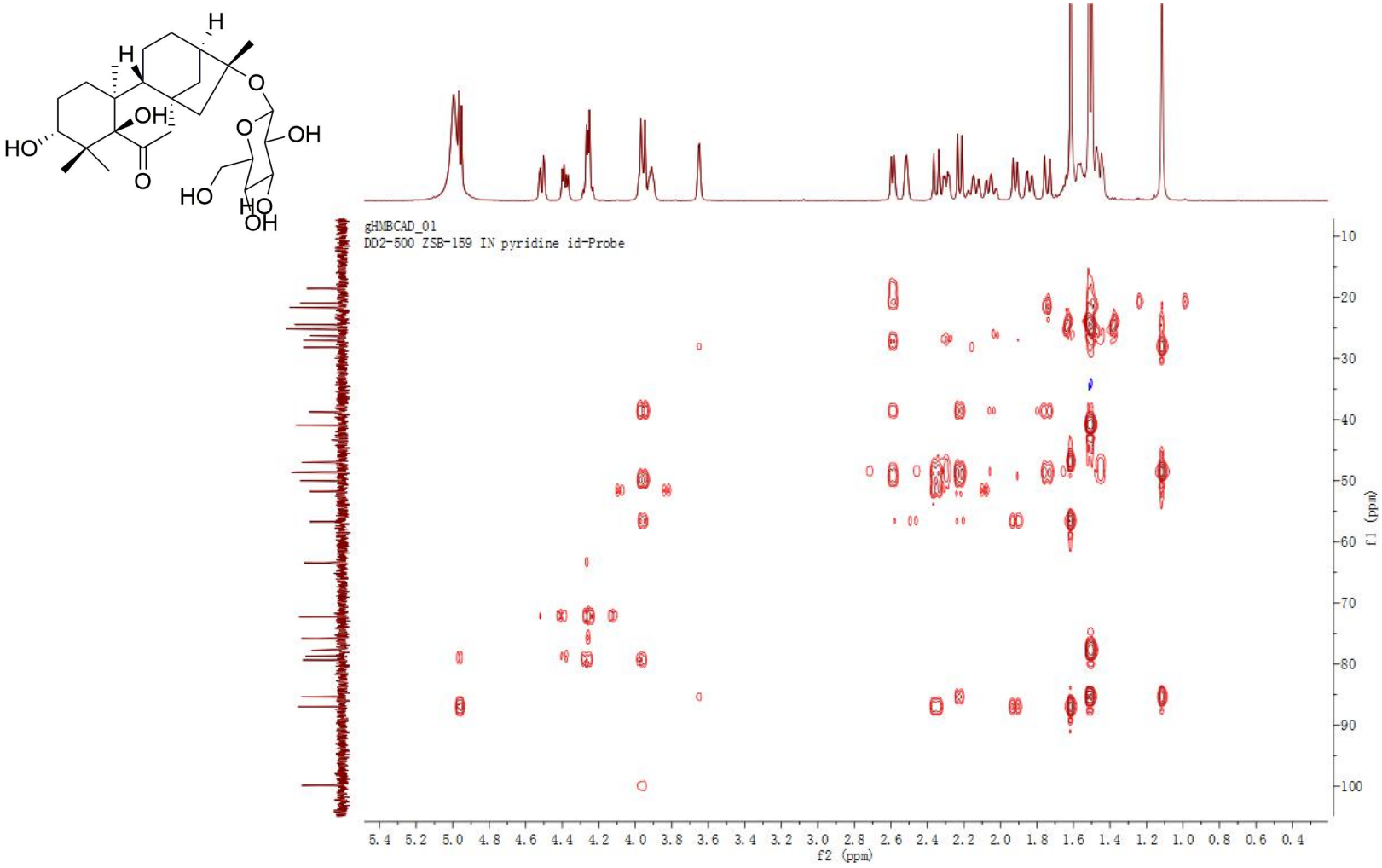
The COSY spectrum of **13** in C_5D_5N (500 MHz)



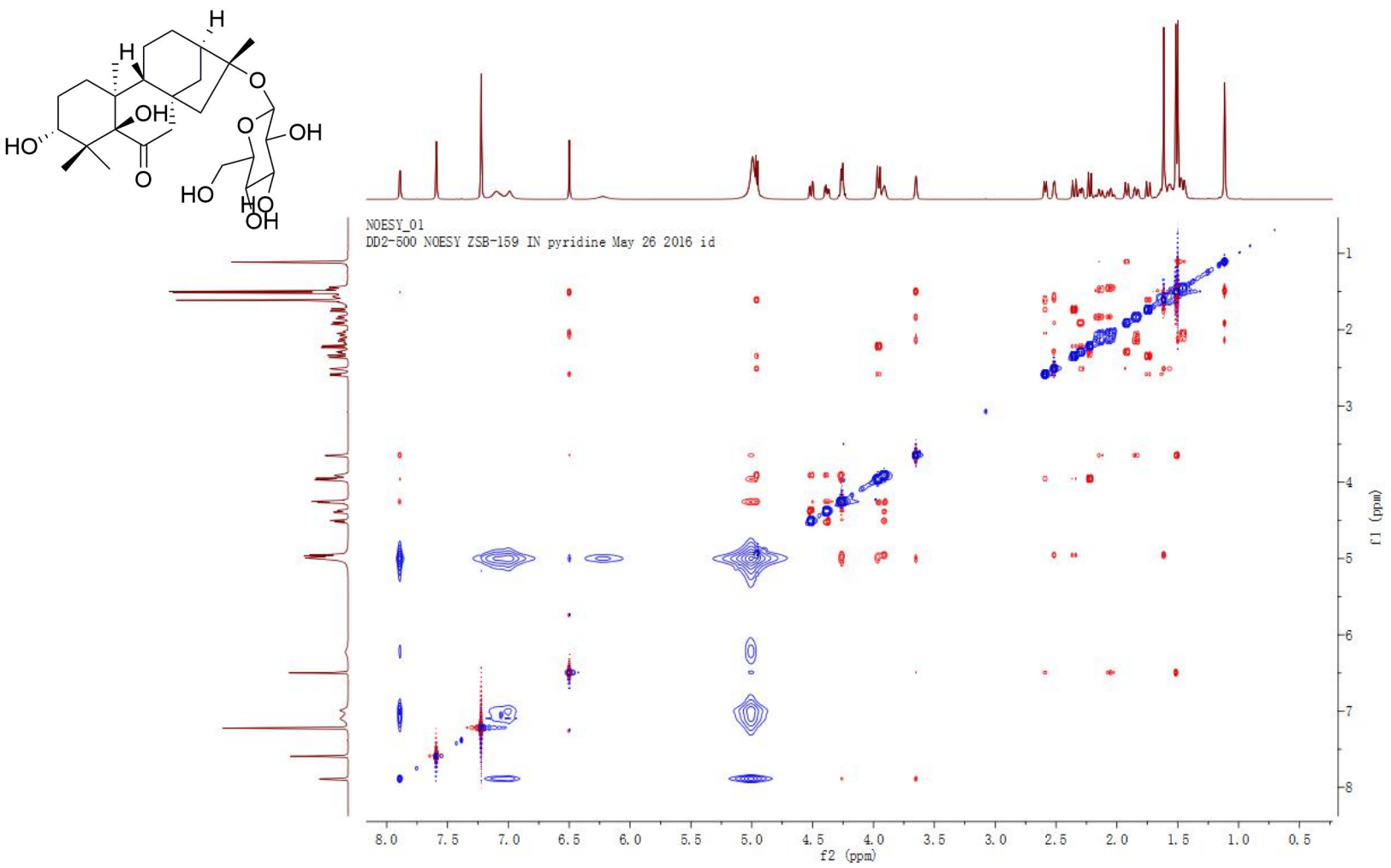
The HSQC spectrum of **13** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



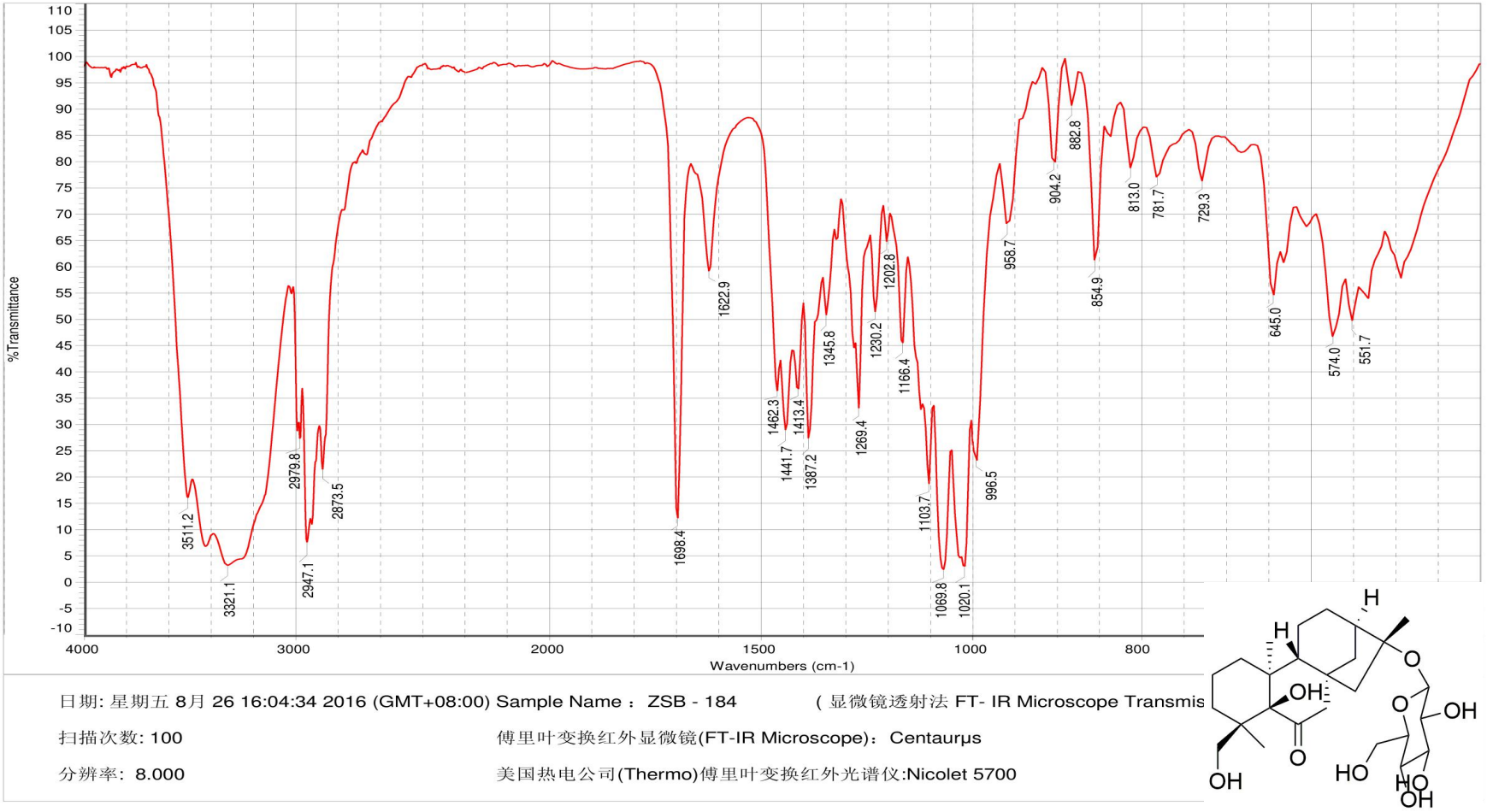
The HMBC spectrum of **13** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The HMBC spectrum (amplified) of **13** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The NOESY spectrum of **13** in C_5D_5N (500 MHz)

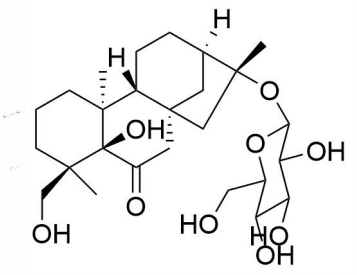


The IR spectrum of **14**

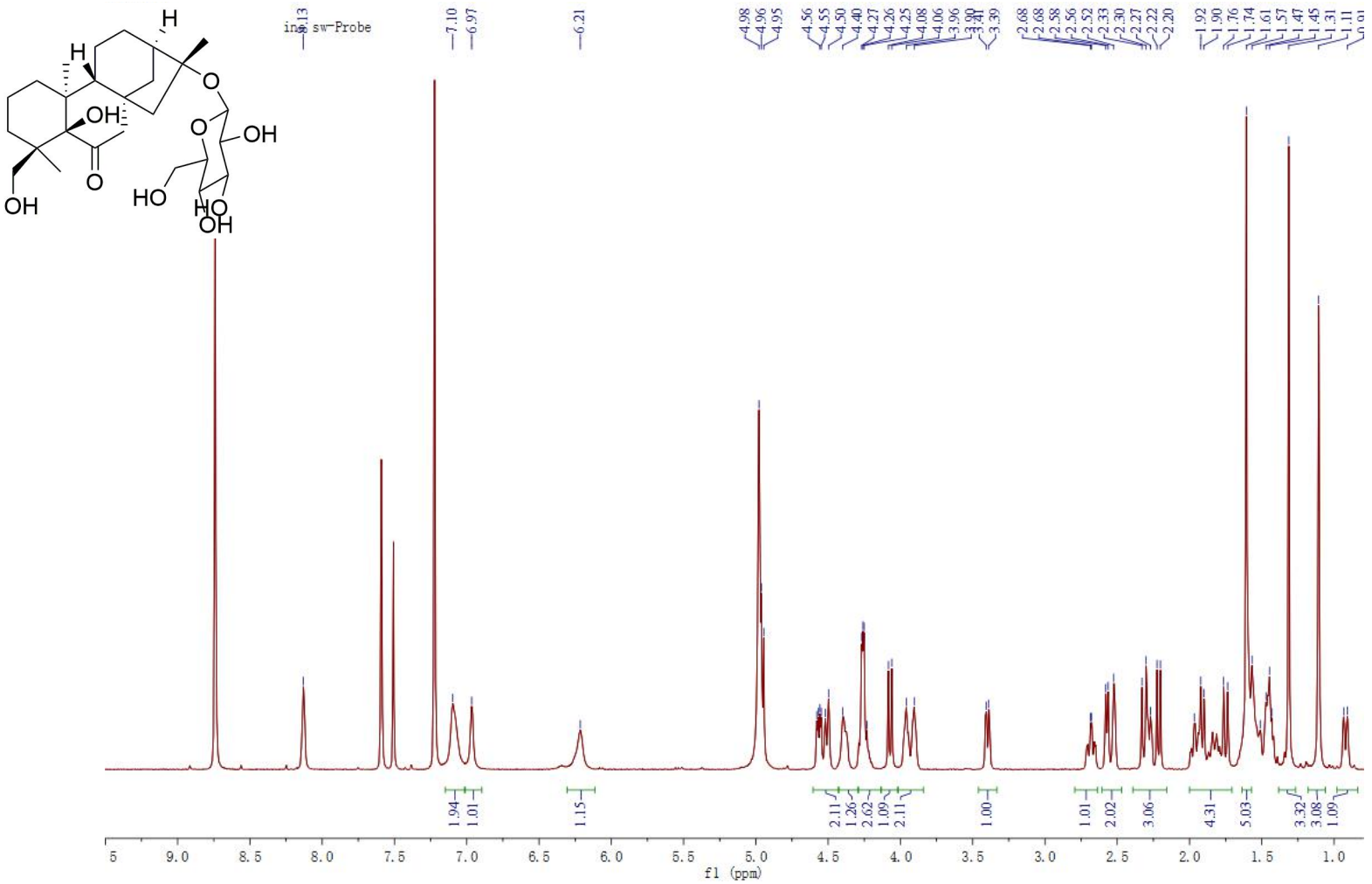
MS Formula Results: + Scan (7.428 min) Sub (2016052602.d)

	m/z	Ion	Formula	Abundance
-	521.2711	(M+Na)+	C26 H42 Na O9	140097.7

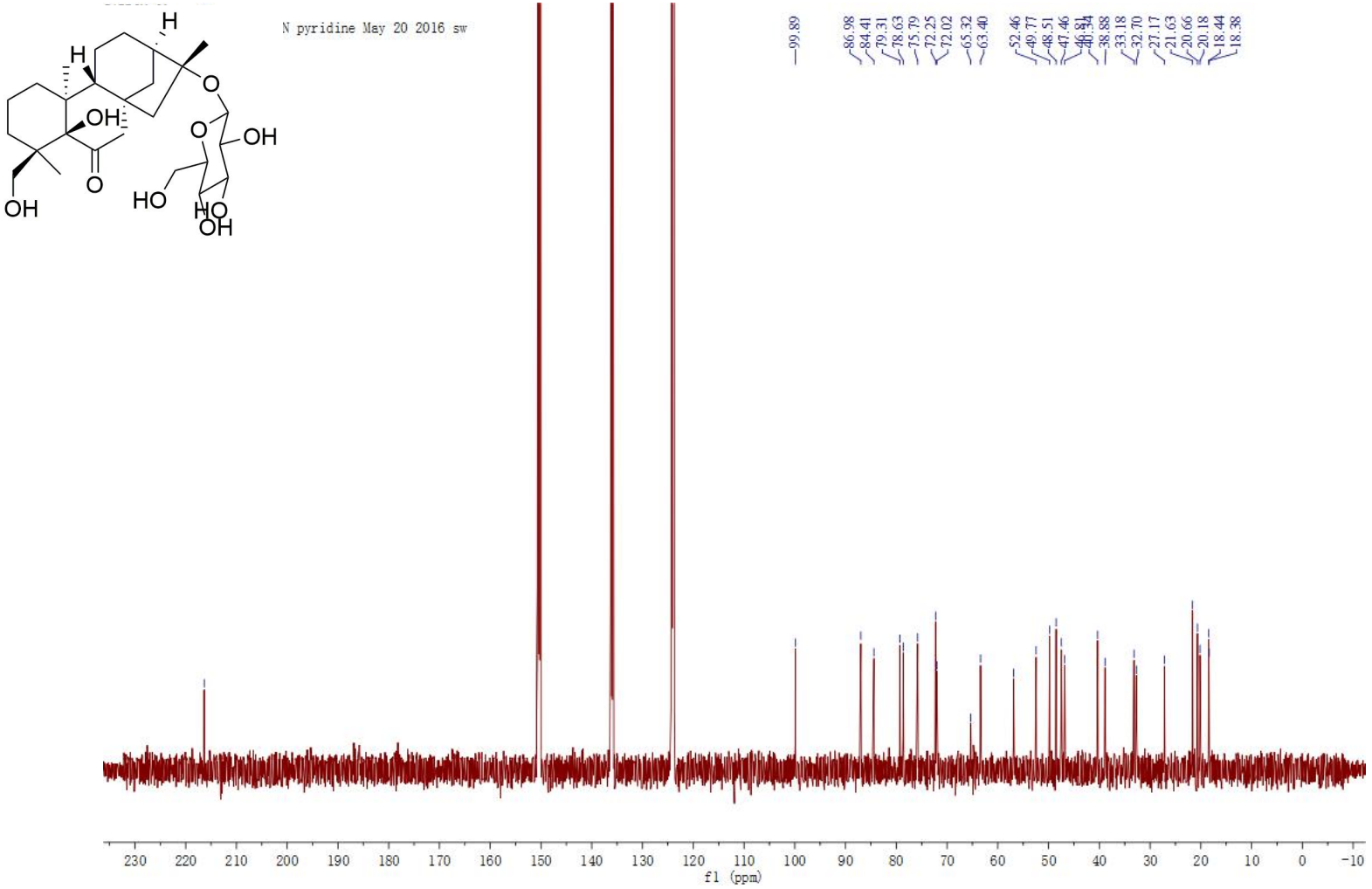
	Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
+	☑	C26 H42 O9	C26 H42 Na O9	99.13		498.2819	498.2829	521.2721	2.04	2.04	99.87	97.96	99.05	6
+	☐	C30 H42 O4 S	C30 H42 Na O4 S	98.79		498.2819	498.2804	521.2696	-2.99	2.99	99.72	98.56	97.2	10
+	☐	C27 H46 O4 S2	C27 H46 Na O4 S2	98.17		498.2819	498.2838	521.273	3.76	3.76	99.55	97.94	95.68	5
+	☐	C22 H46 N2 O6 S2	C22 H46 N2 Na O6 S2	97.84		498.2819	498.2797	521.2689	-4.32	4.32	99.41	97.37	95.27	1



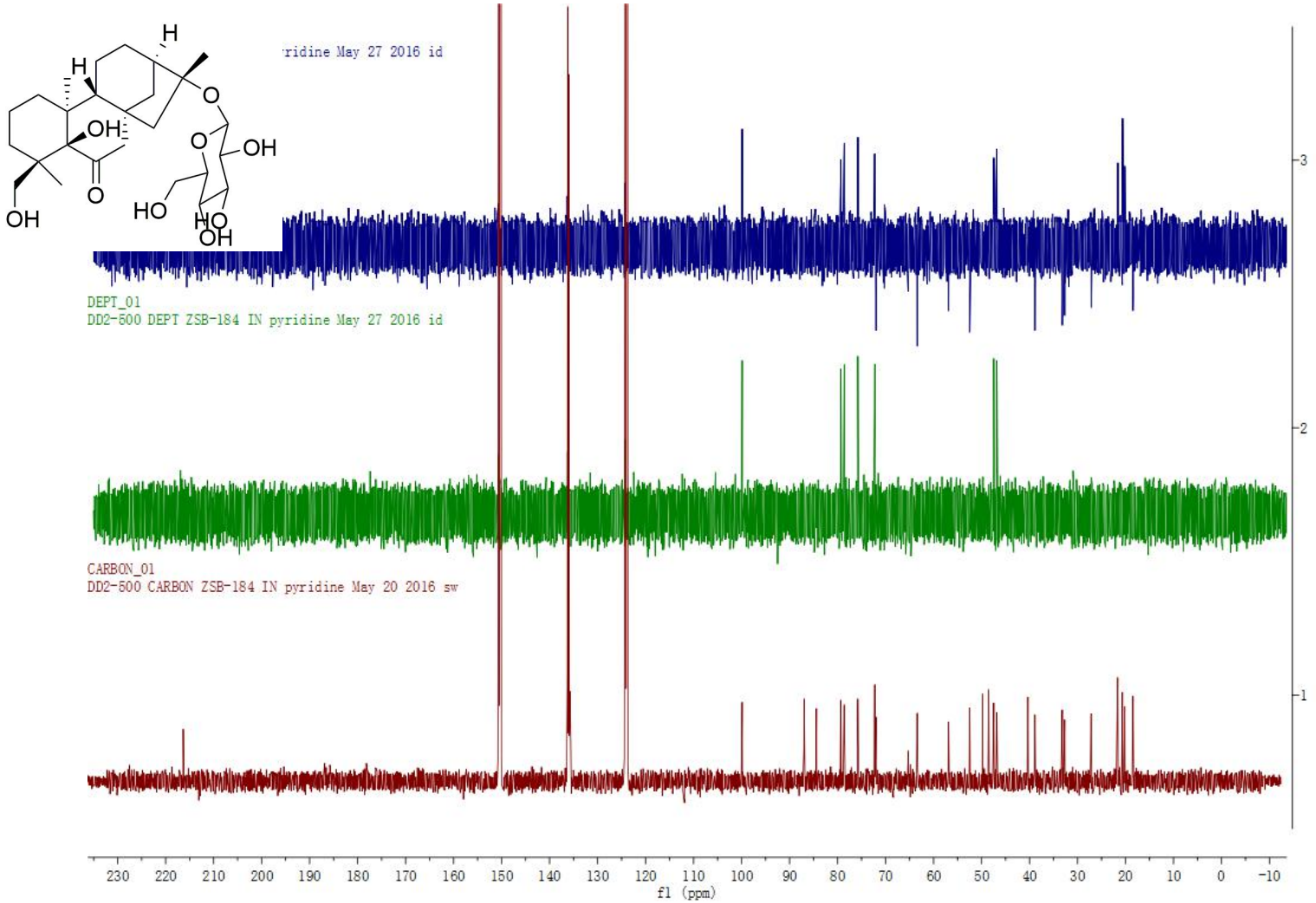
The HRESIMS spectrum of **14**



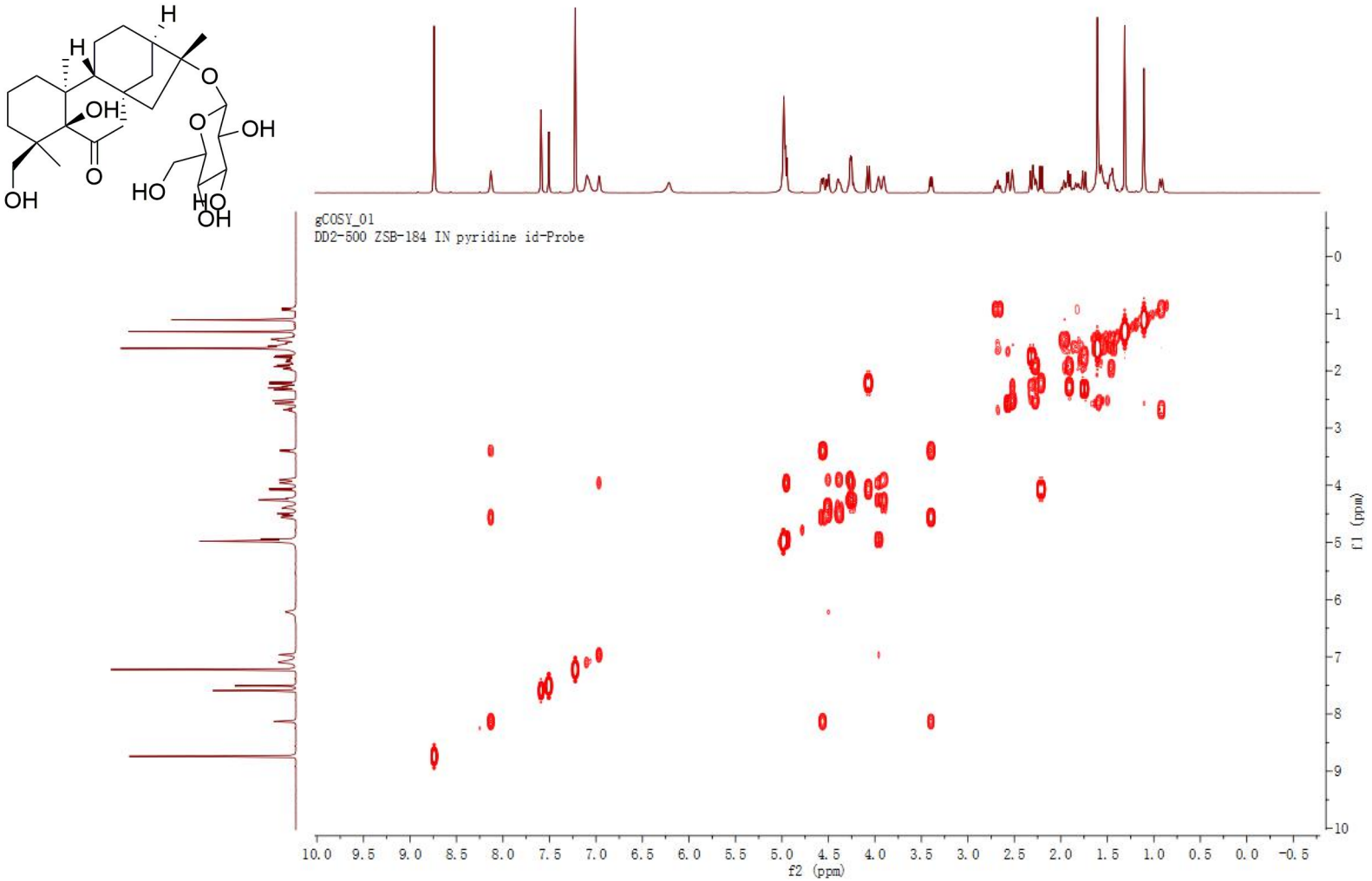
The ^{1}H NMR spectrum of **14** in C_5D_5N (500 MHz)



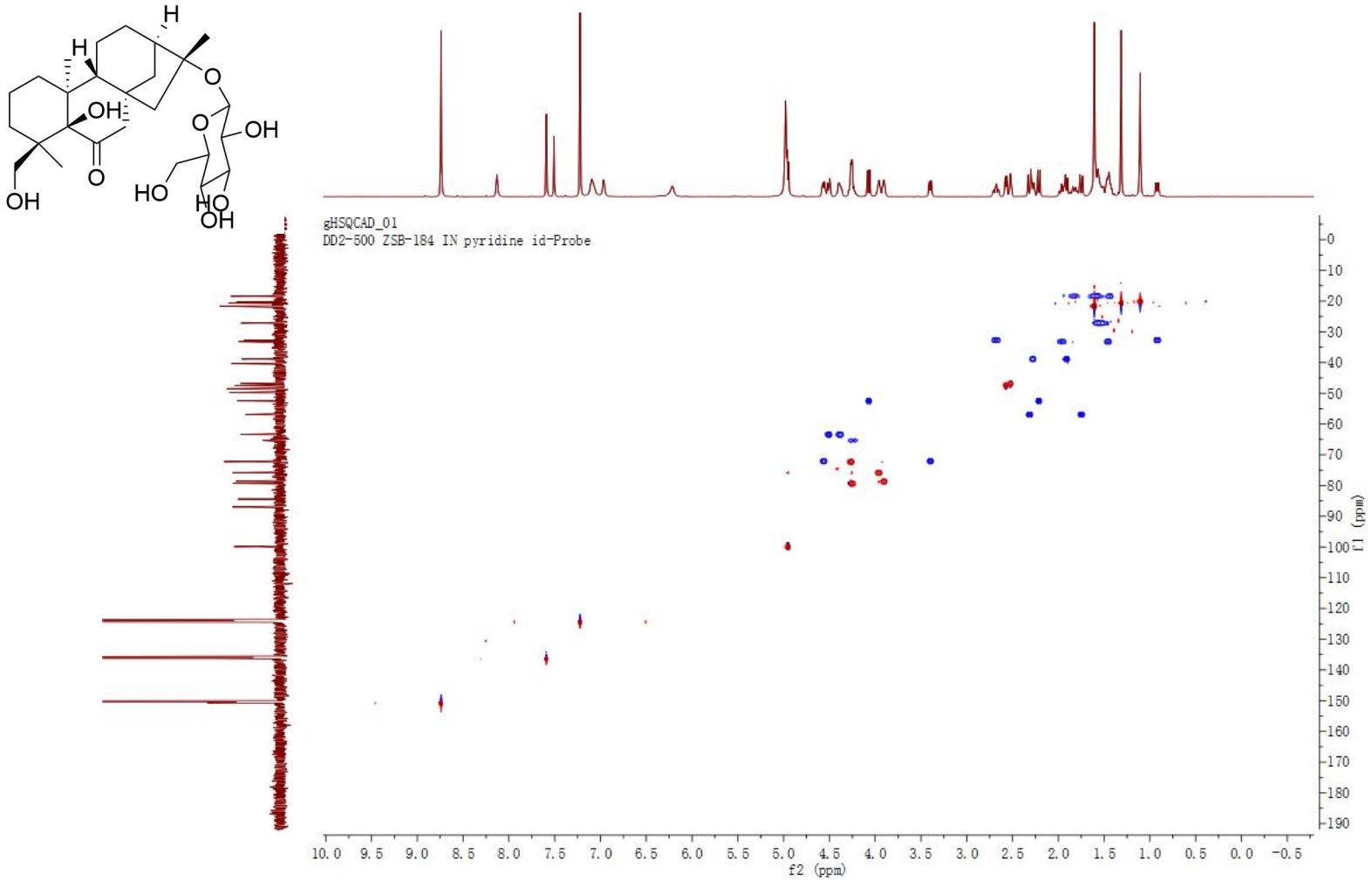
The ^{13}C NMR spectrum of **14** in C_5D_5N (125 MHz)



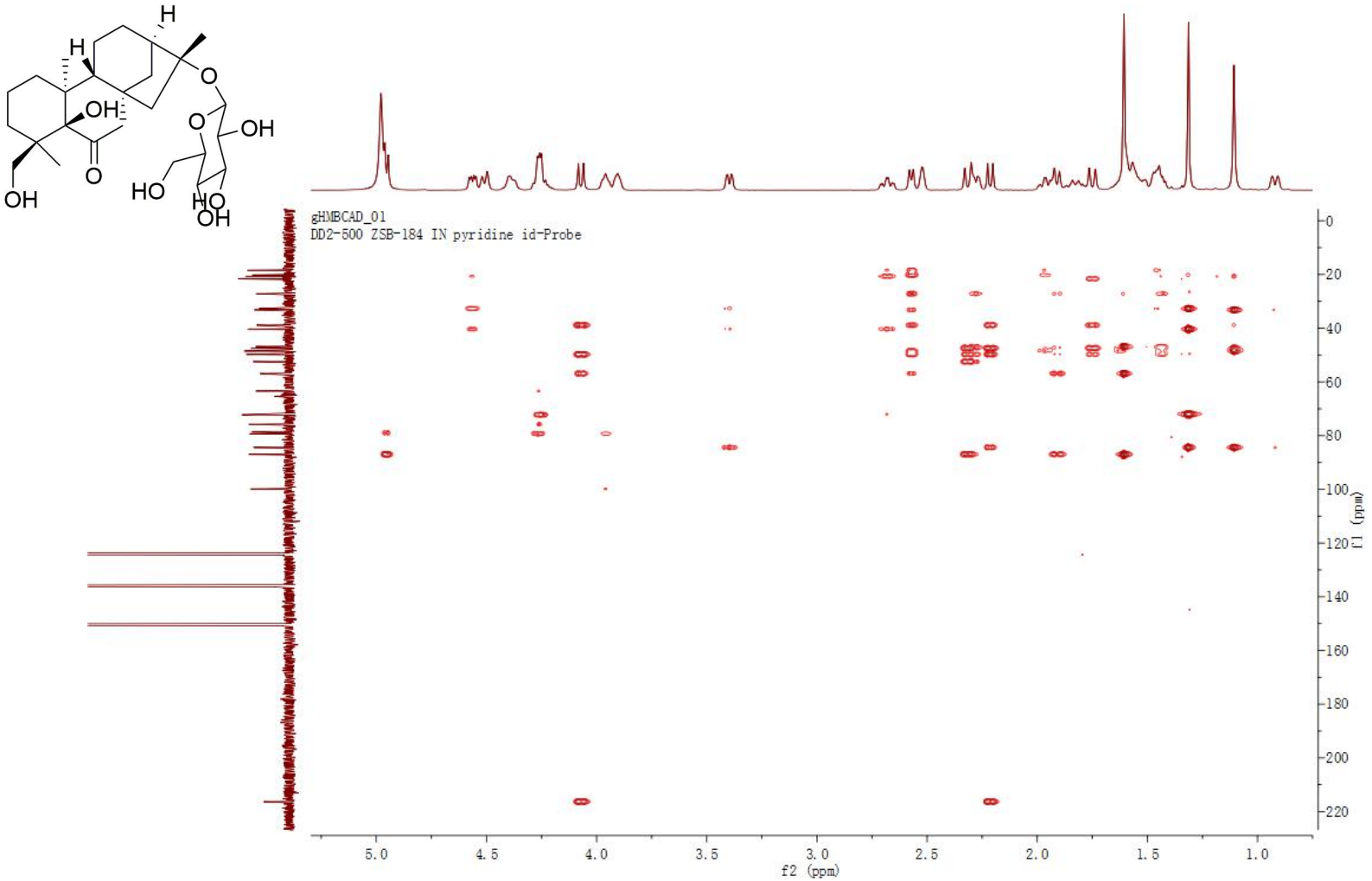
The DEPT spectrum of **14** in C_5D_5N (125 MHz)



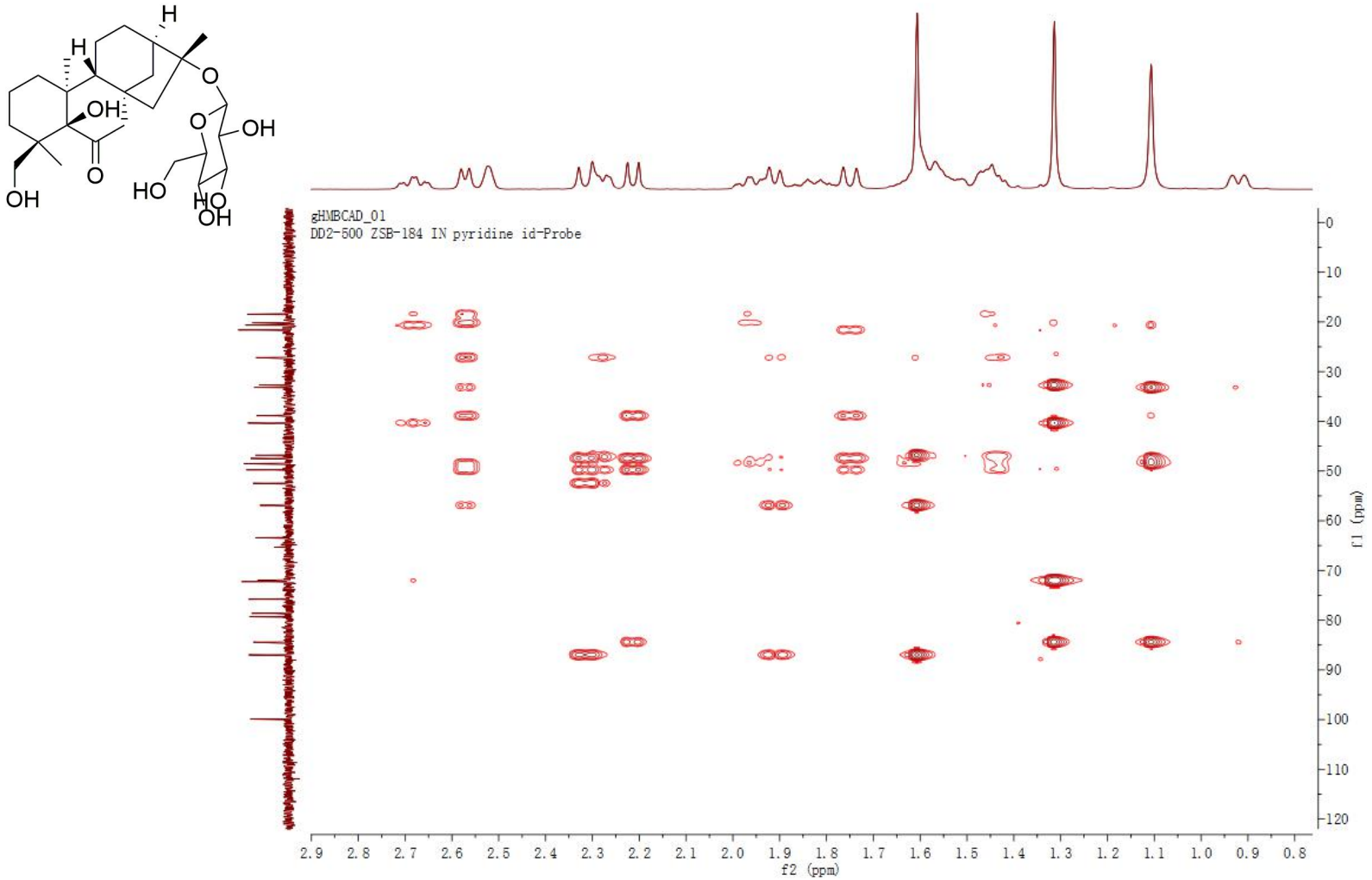
The COSY spectrum of **14** in C_5D_5N (500MHz)



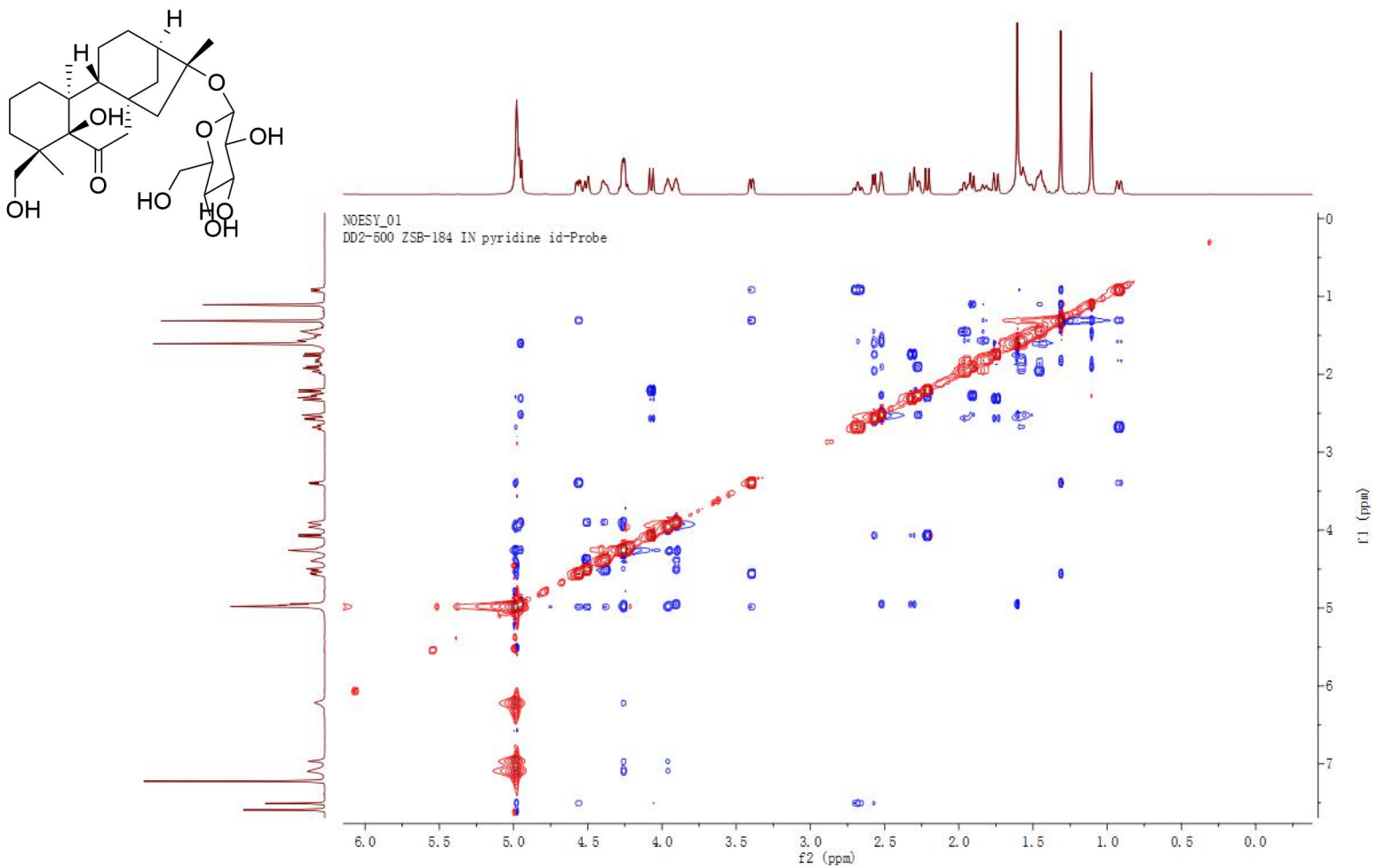
The HSQC spectrum of **14** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



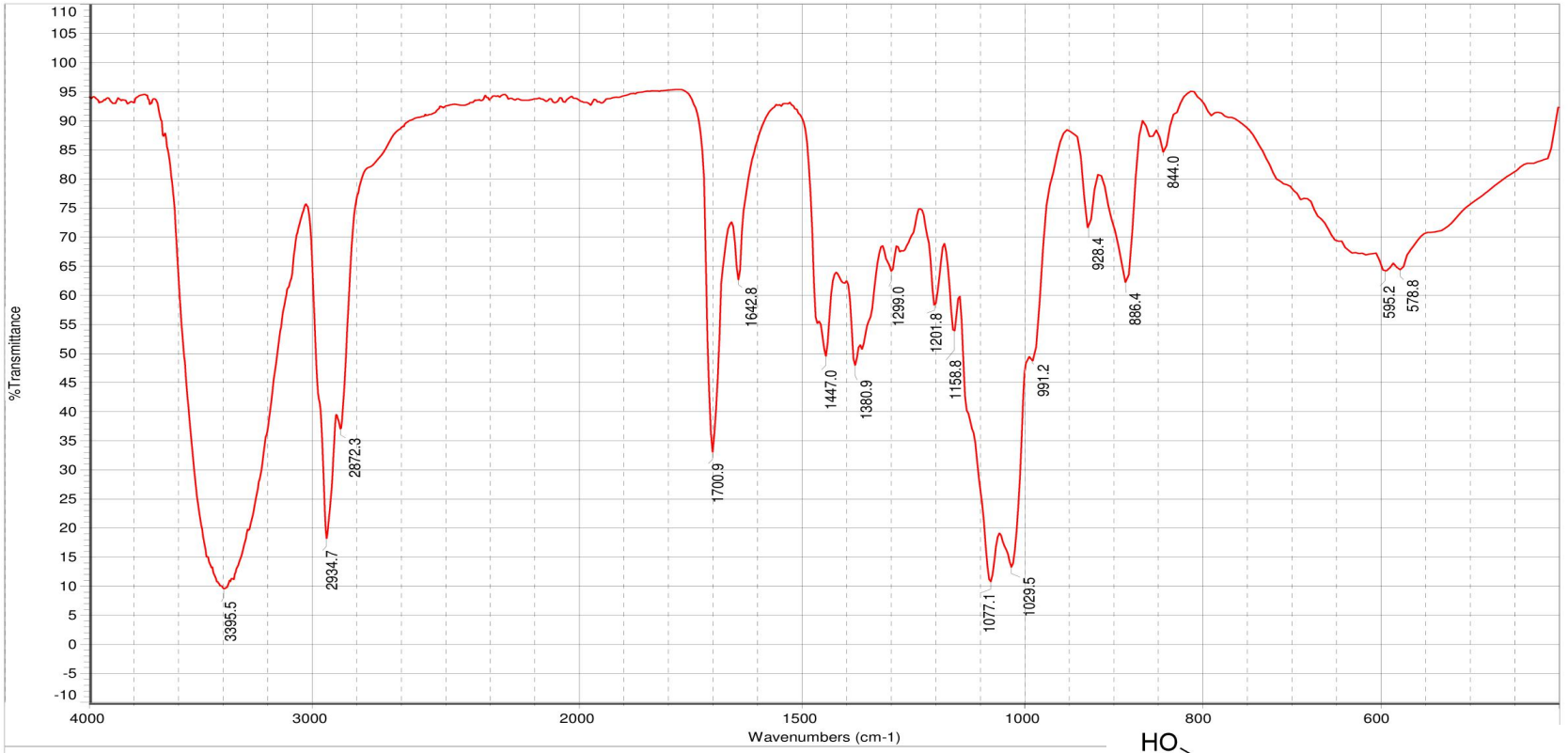
The HMBC spectrum of **14** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The HMBC spectrum (amplified) of **14** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



The NOESY spectrum of **14** in C_5D_5N (500MHz)

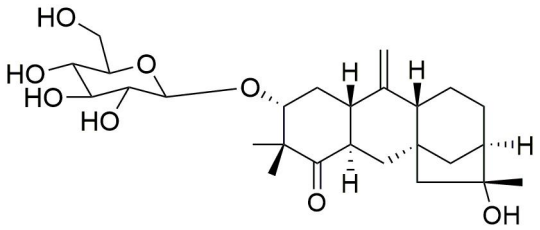


The IR spectrum of **15**

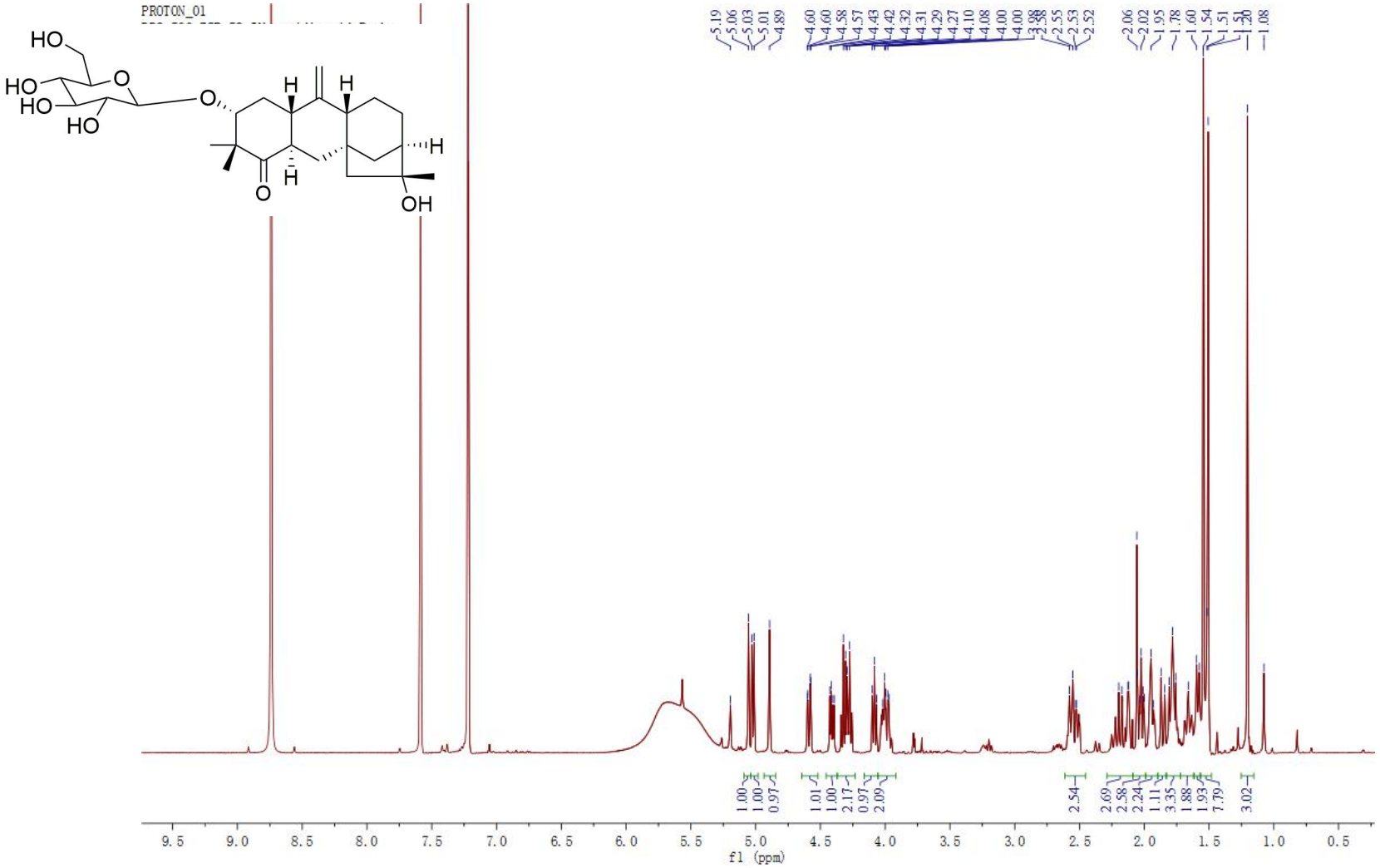
MS Formula Results: + Scan (6.184 min) Sub (2015092903.d)

m/z	Ion	Formula	Abundance
503.2615	(M+Na)+	C26 H40 Na O8	2388776.3

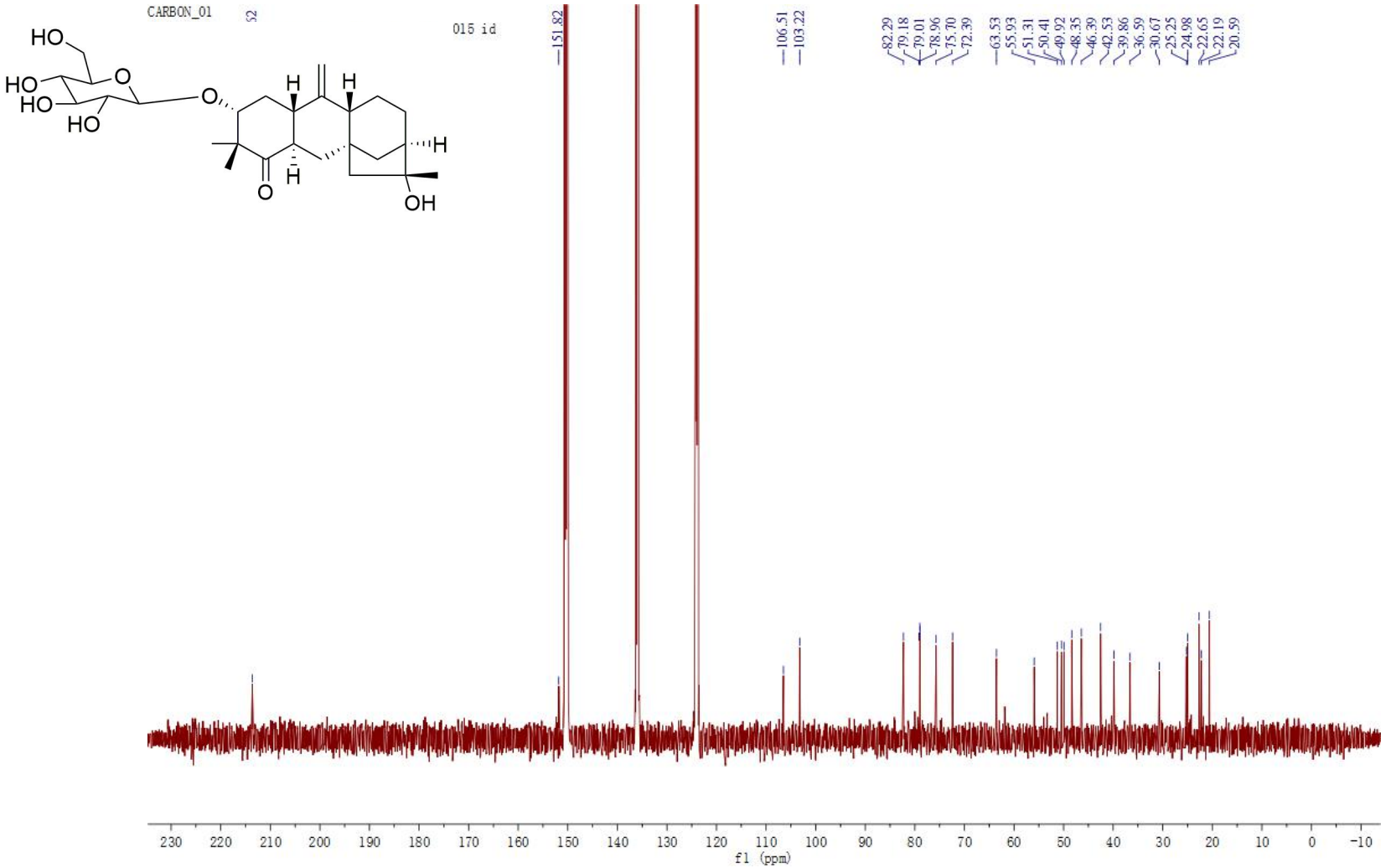
Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
☑	C26 H40 O8	C26 H40 Na O8	99.83		480.2723	480.2723	503.2615	0.05	0.05	100	99.53	99.85	7
☐	C27 H36 N4 O4	C27 H36 N4 Na O4	99.79		480.2723	480.2737	503.2629	2.82	2.82	99.75	99.89	99.76	12
☐	C22 H36 N6 O6	C22 H36 N6 Na O6	98.95		480.2723	480.2696	503.2589	-5.57	5.57	99.03	98.22	99.67	8



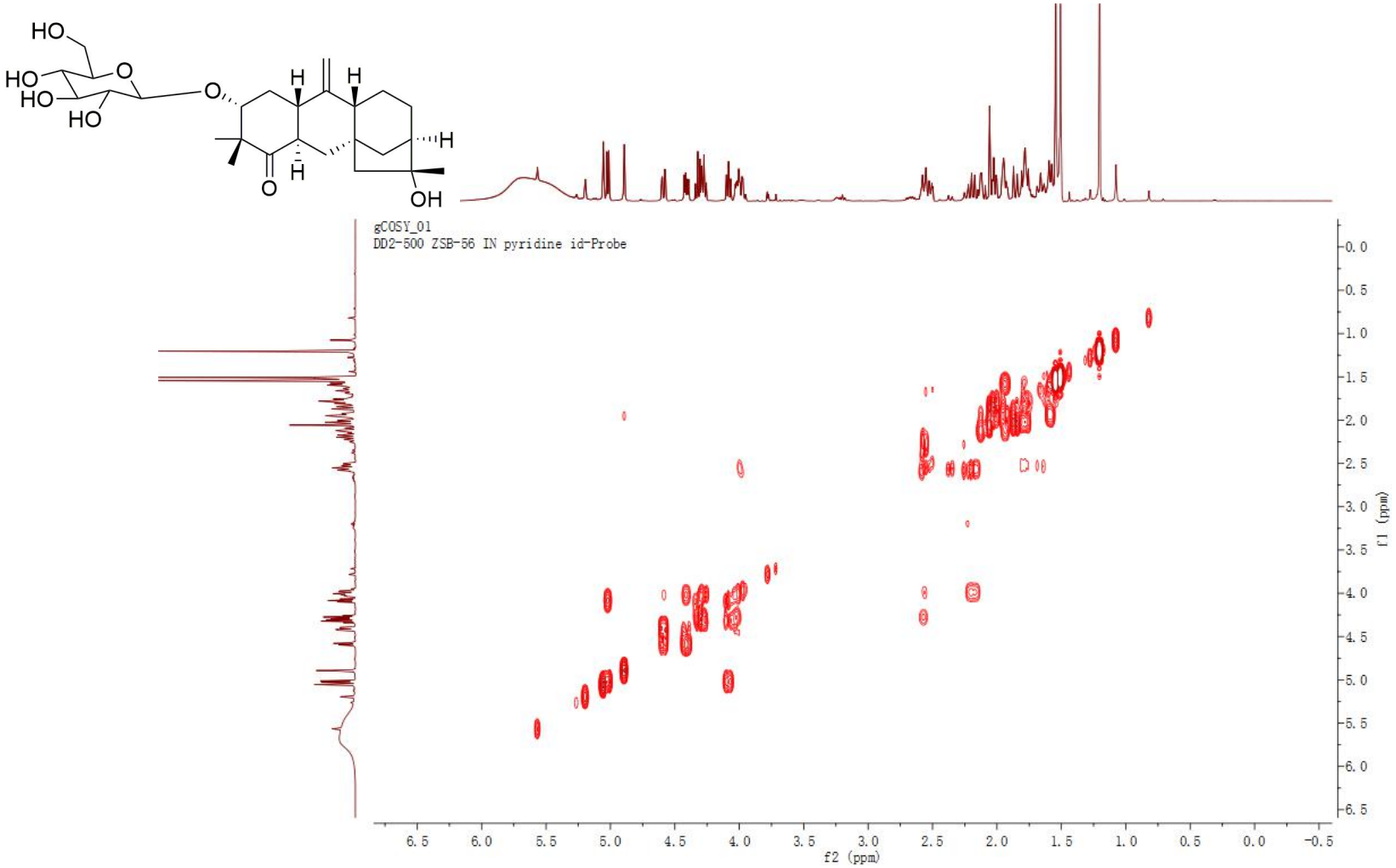
The HRESIMS spectrum of **15**



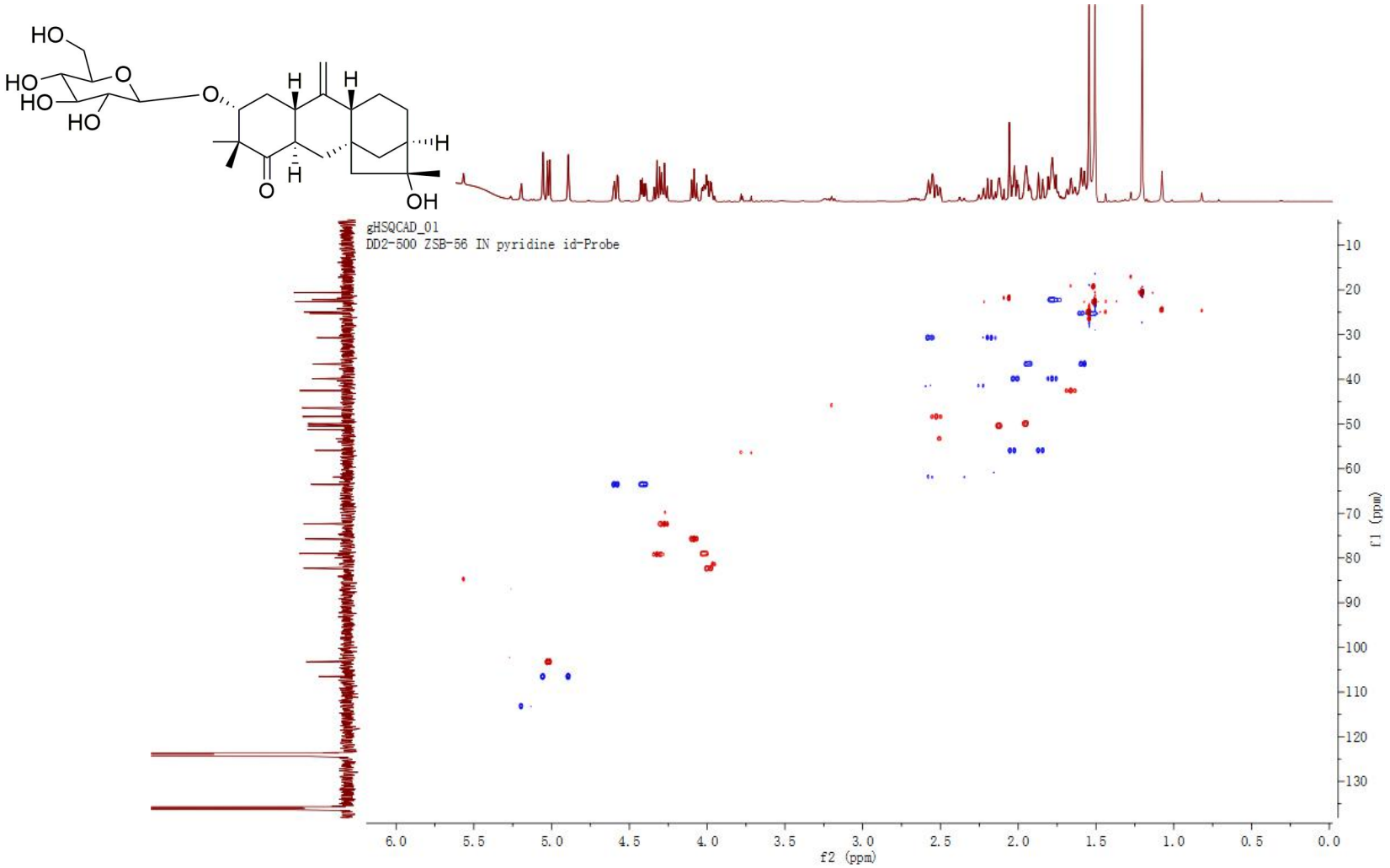
The ^{1}H NMR spectrum of **15** in C_5D_5N (500 MHz)



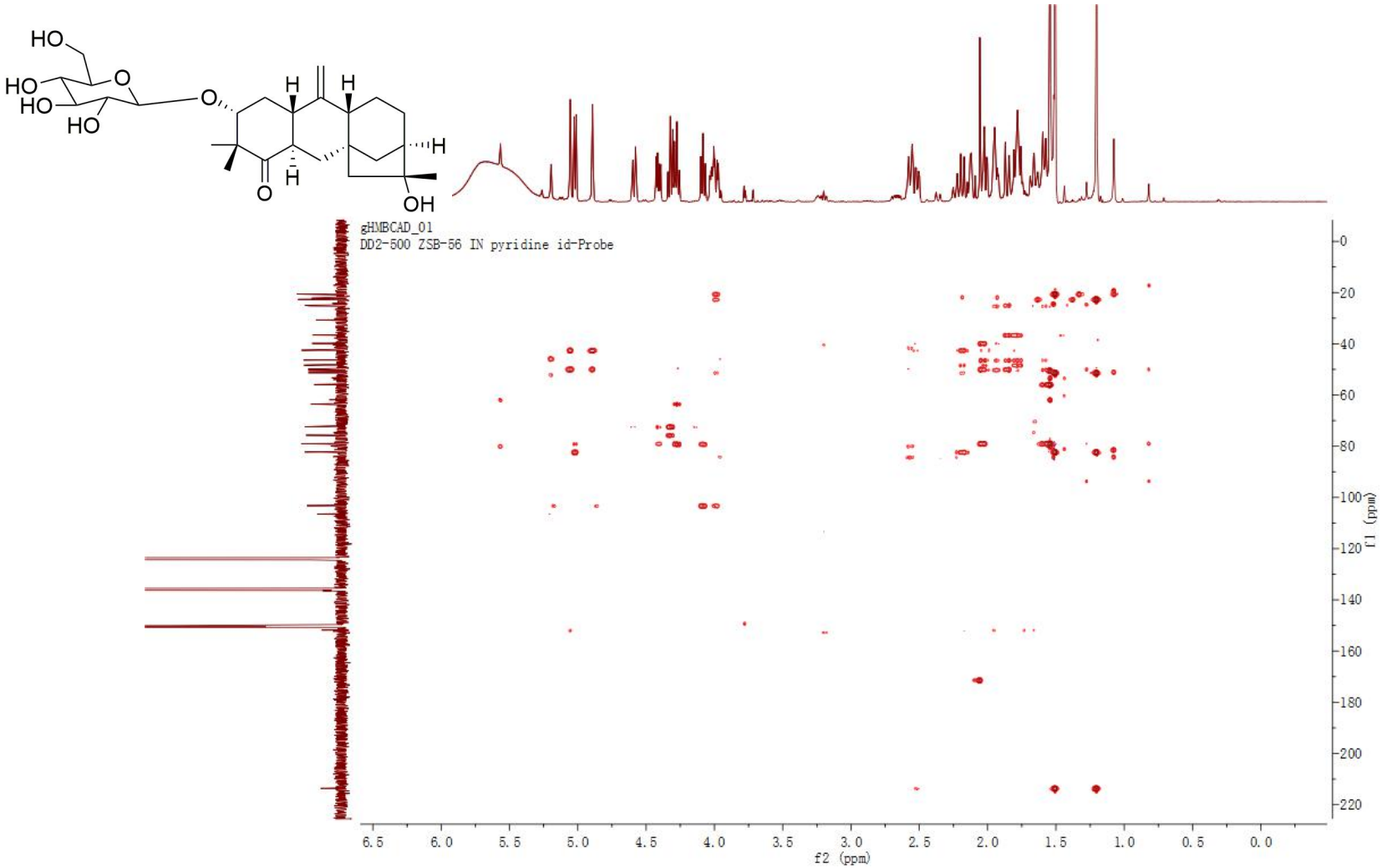
The ^{13}C NMR spectrum of **15** in C_5D_5N (125 MHz)



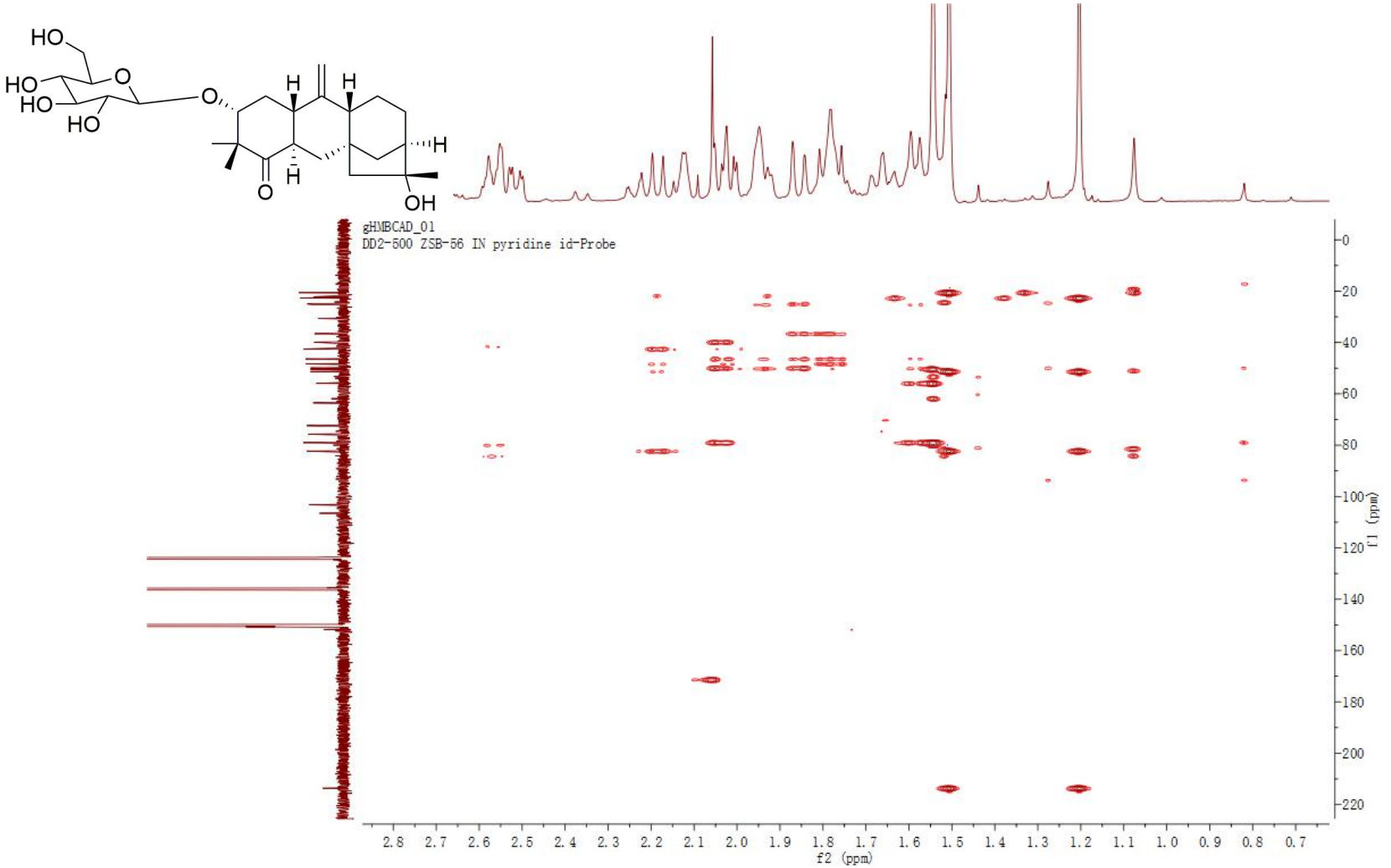
The COSY spectrum of **15** in C_5D_5N (500 MHz)



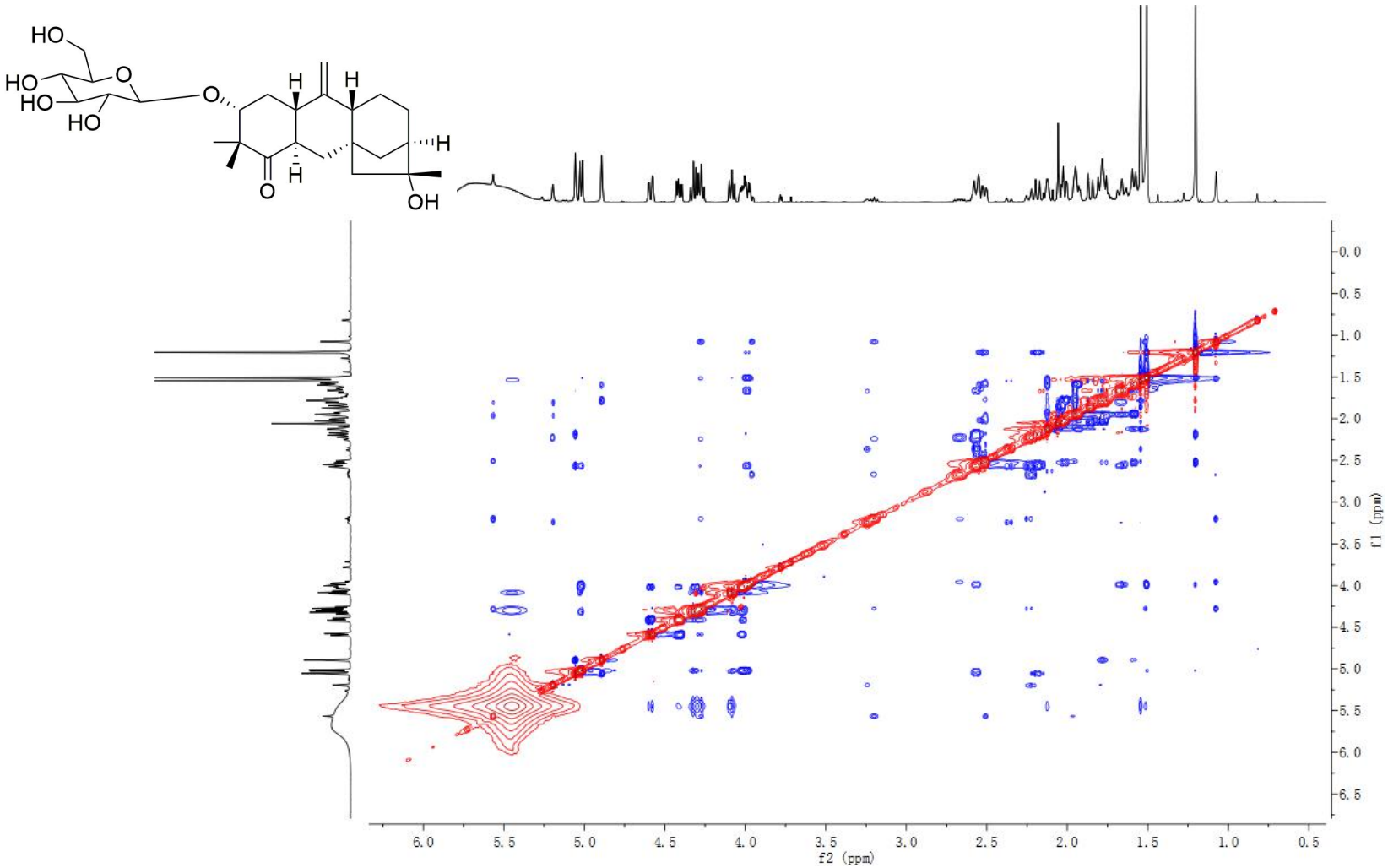
The HSQC spectrum of **15** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



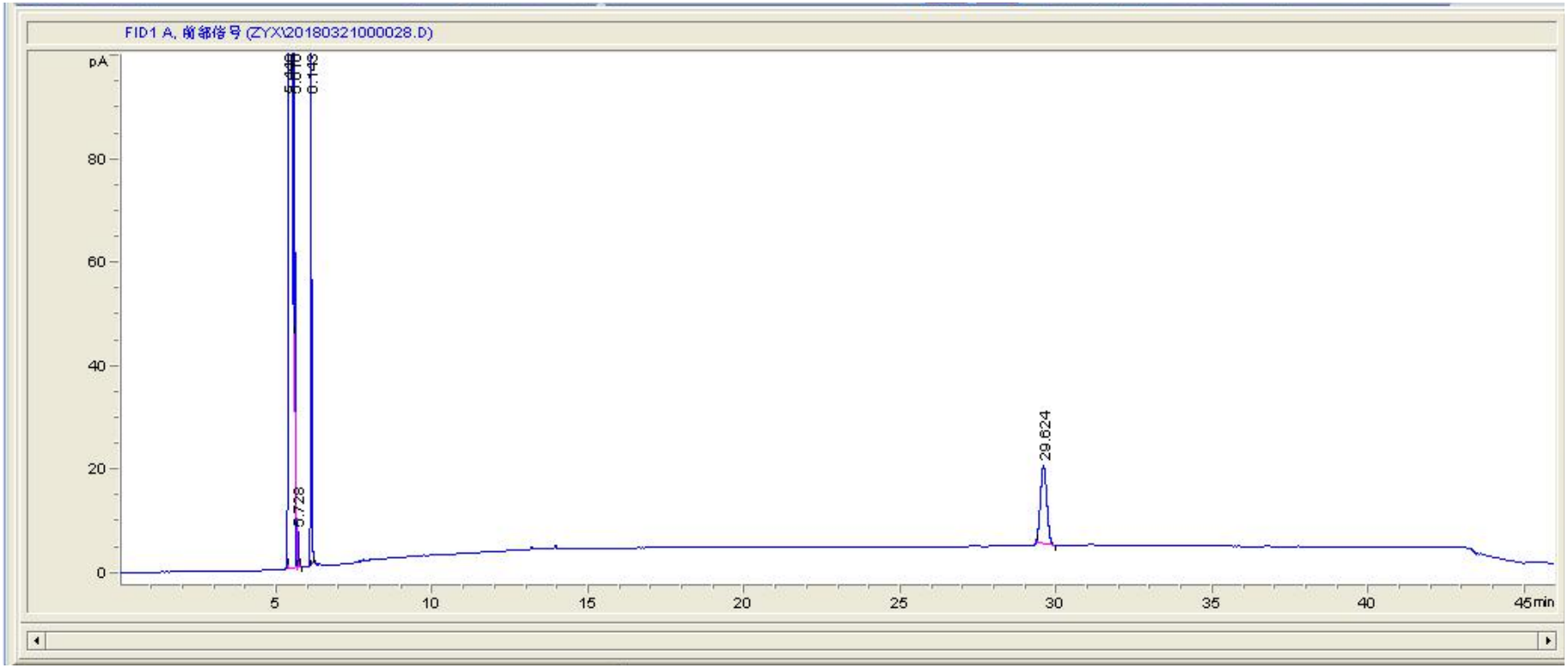
The HMBC spectrum of **15** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125MHz)



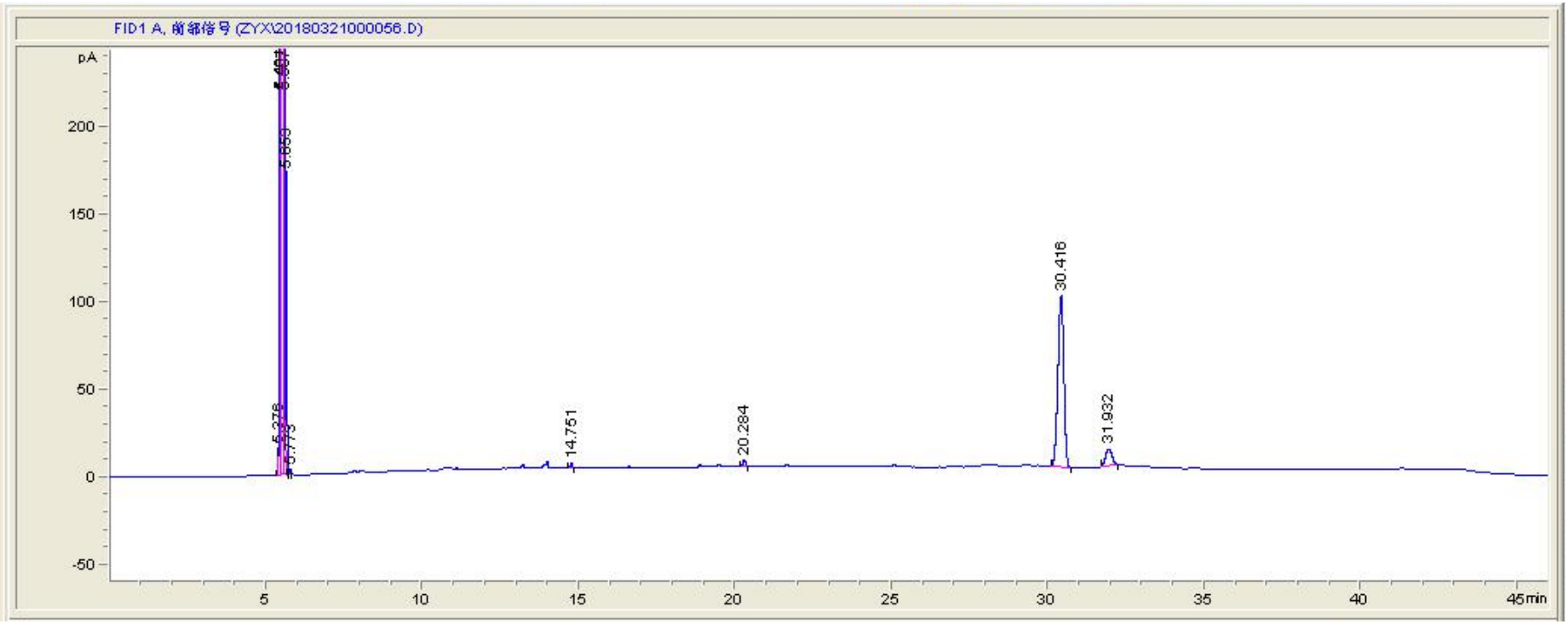
The HMBC spectrum (amplified) of **15** in C_5D_5N (^1H: 500 MHz, ^{13}C: 125 MHz)



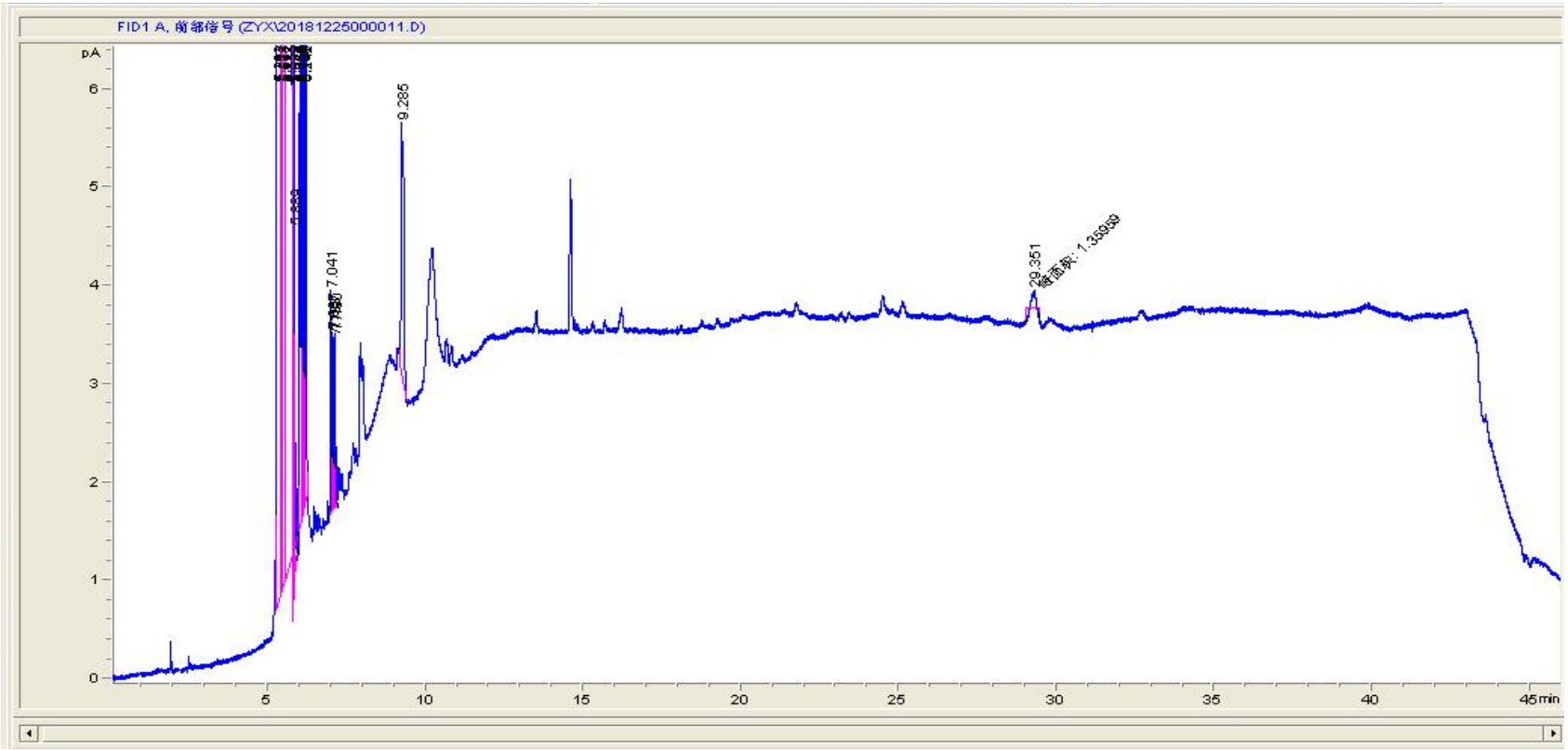
The NOESY spectrum of **15** in C_5D_5N (500 MHz)



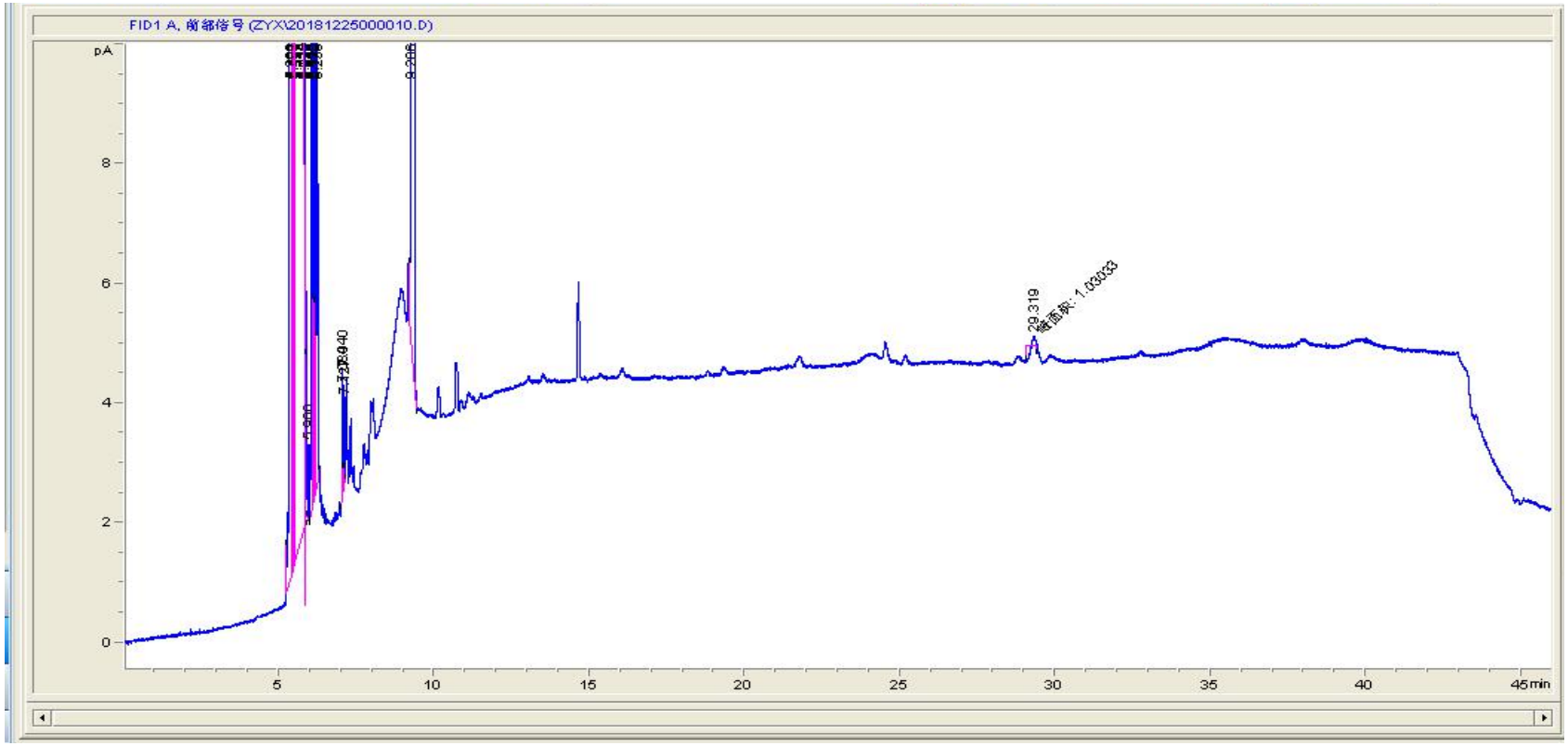
GC analysis of the standard D-glucose



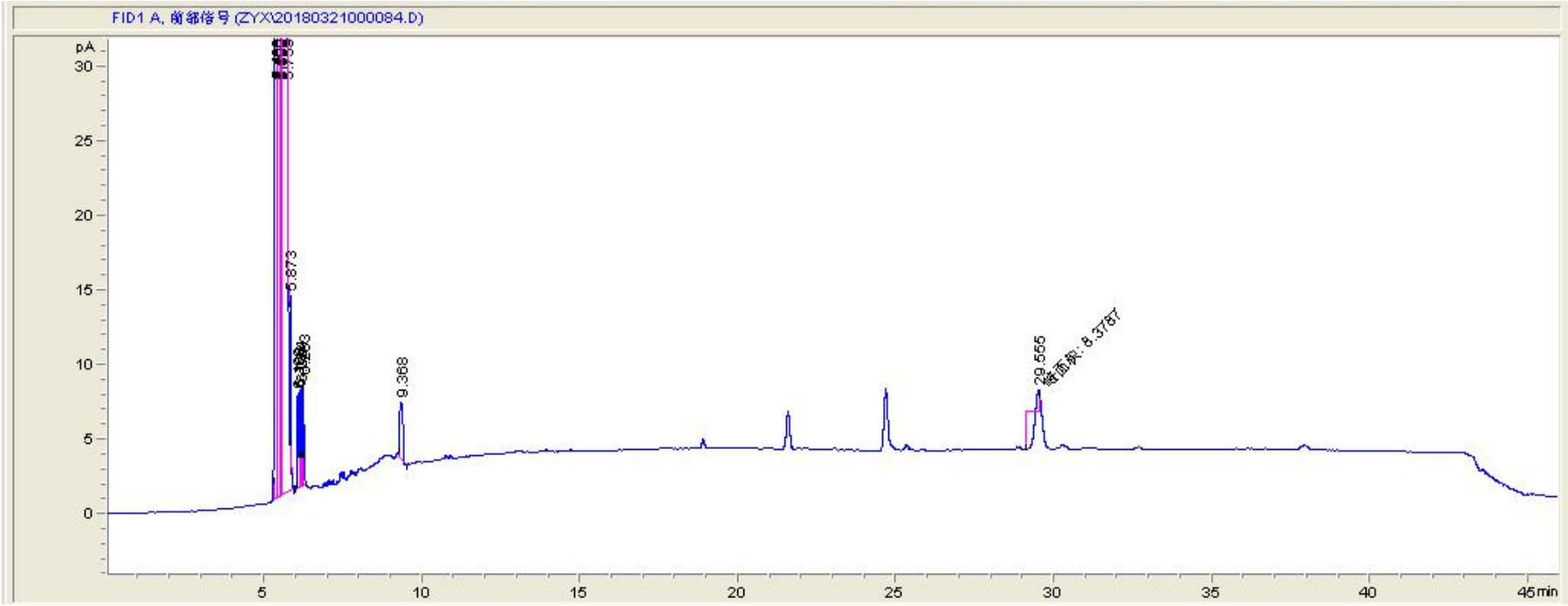
GC analysis of the standard $_{L}$-glucose



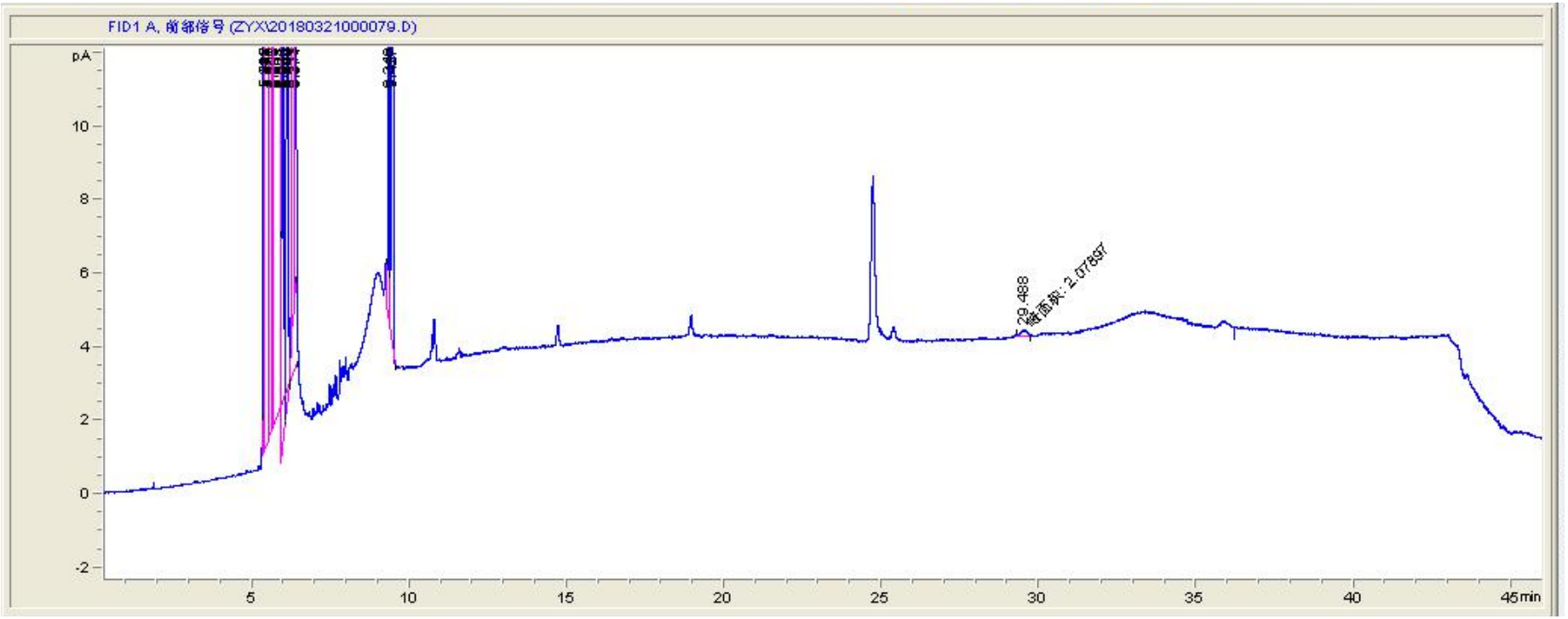
GC analysis of the sugar moiety of **1**



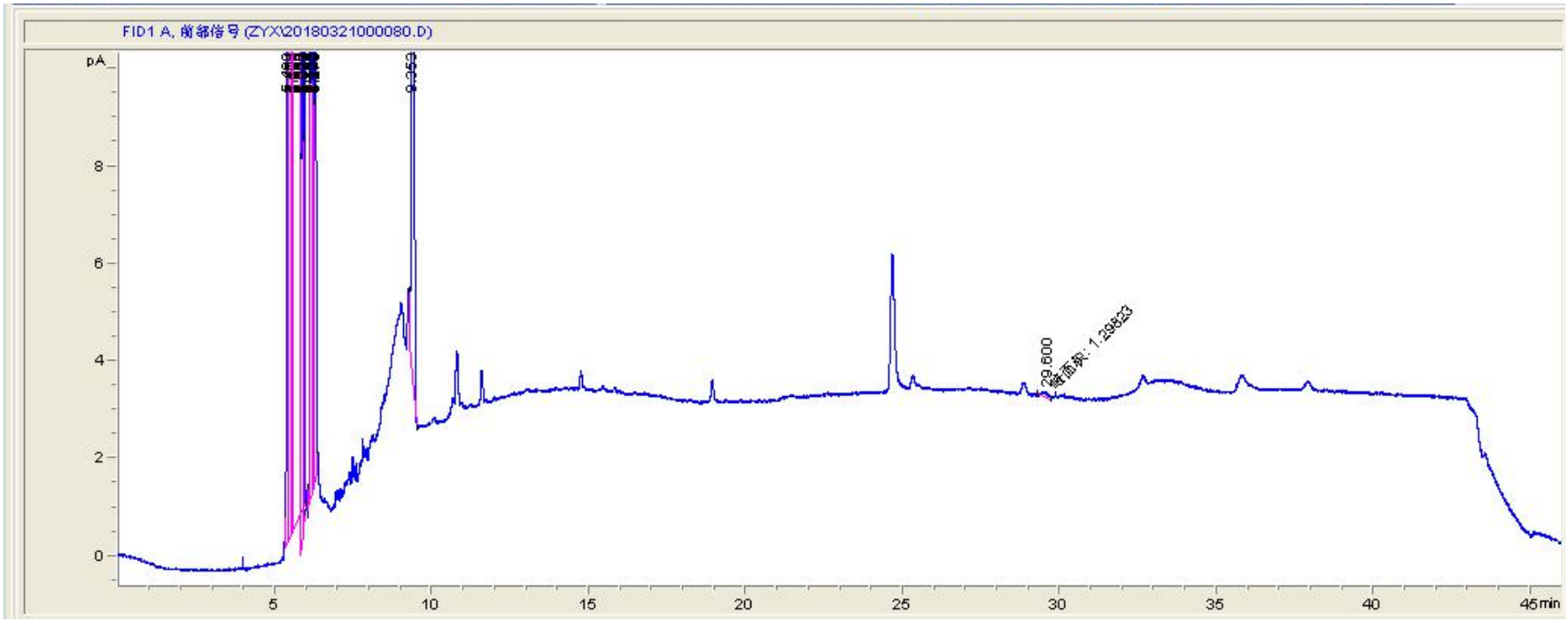
GC analysis of the sugar moiety of **2**



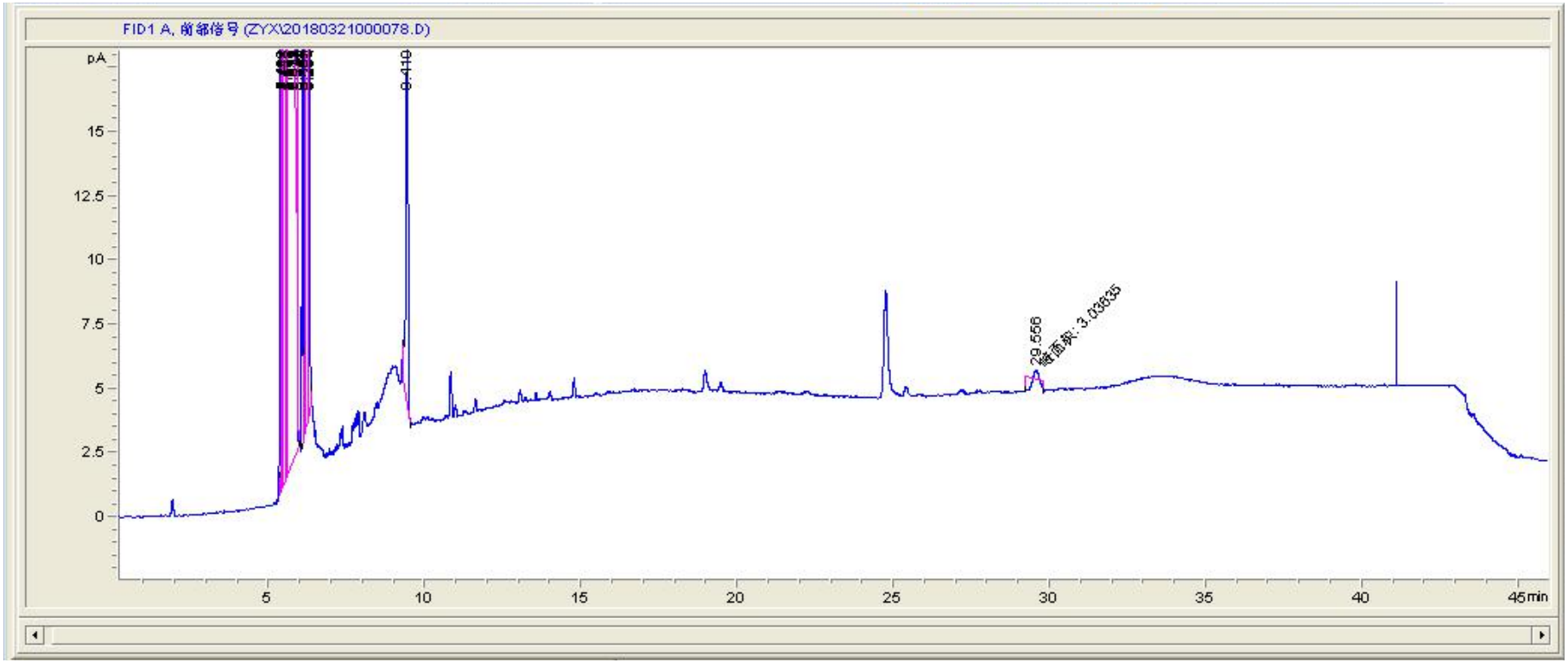
GC analysis of the sugar moiety of **3**



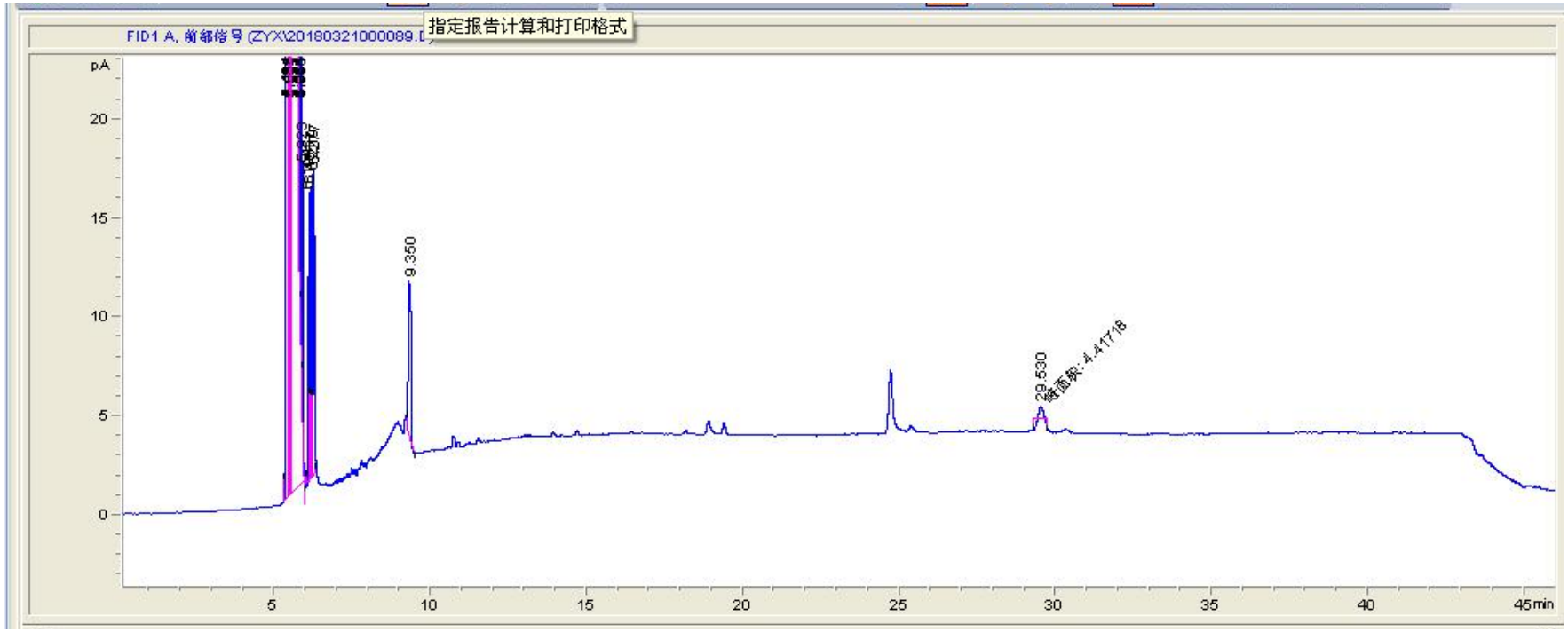
GC analysis of the sugar moiety of **4**



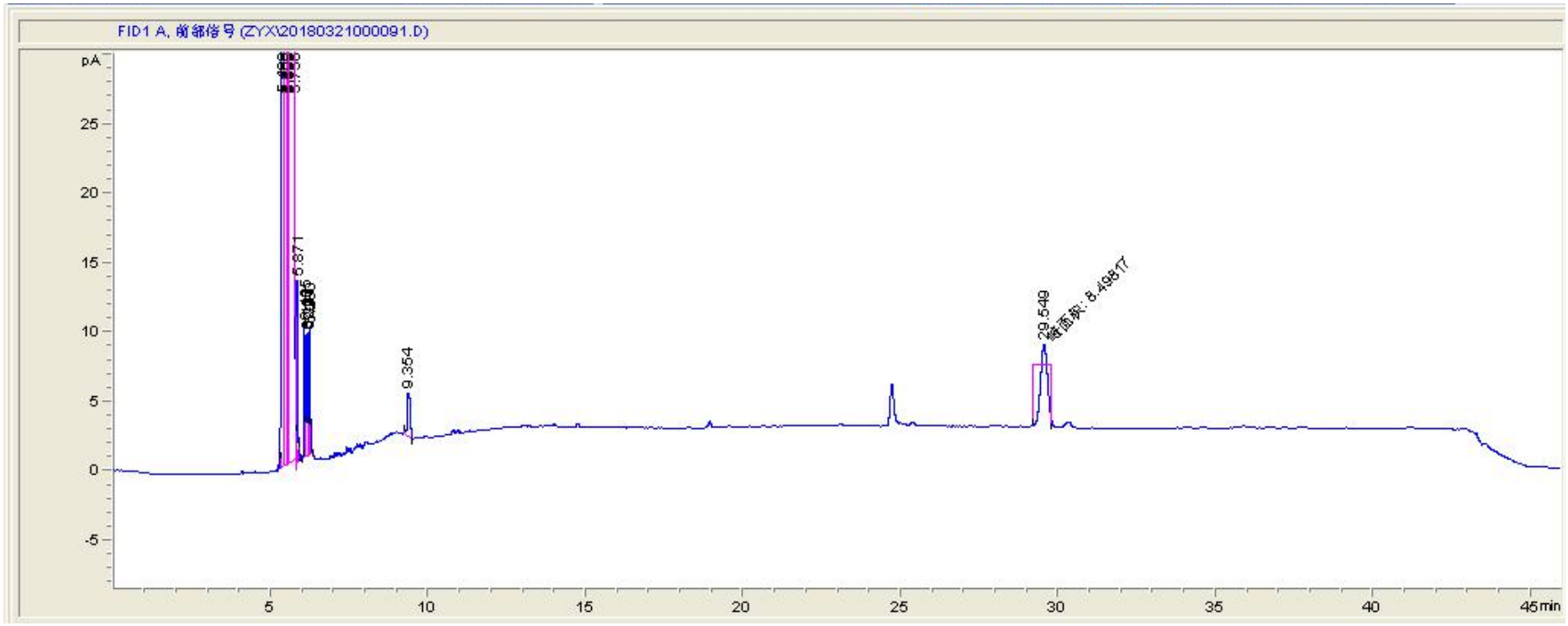
GC analysis of the sugar moiety of **5**



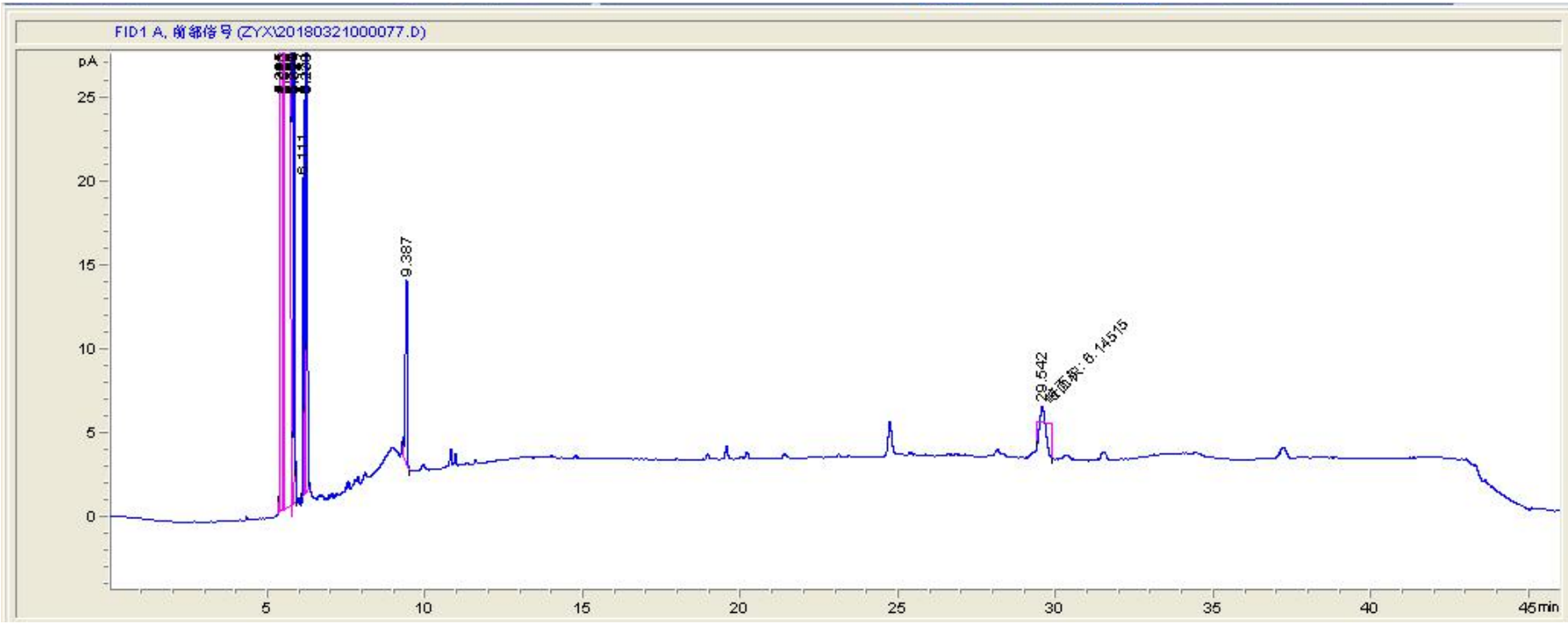
GC analysis of the sugar moiety of **6**



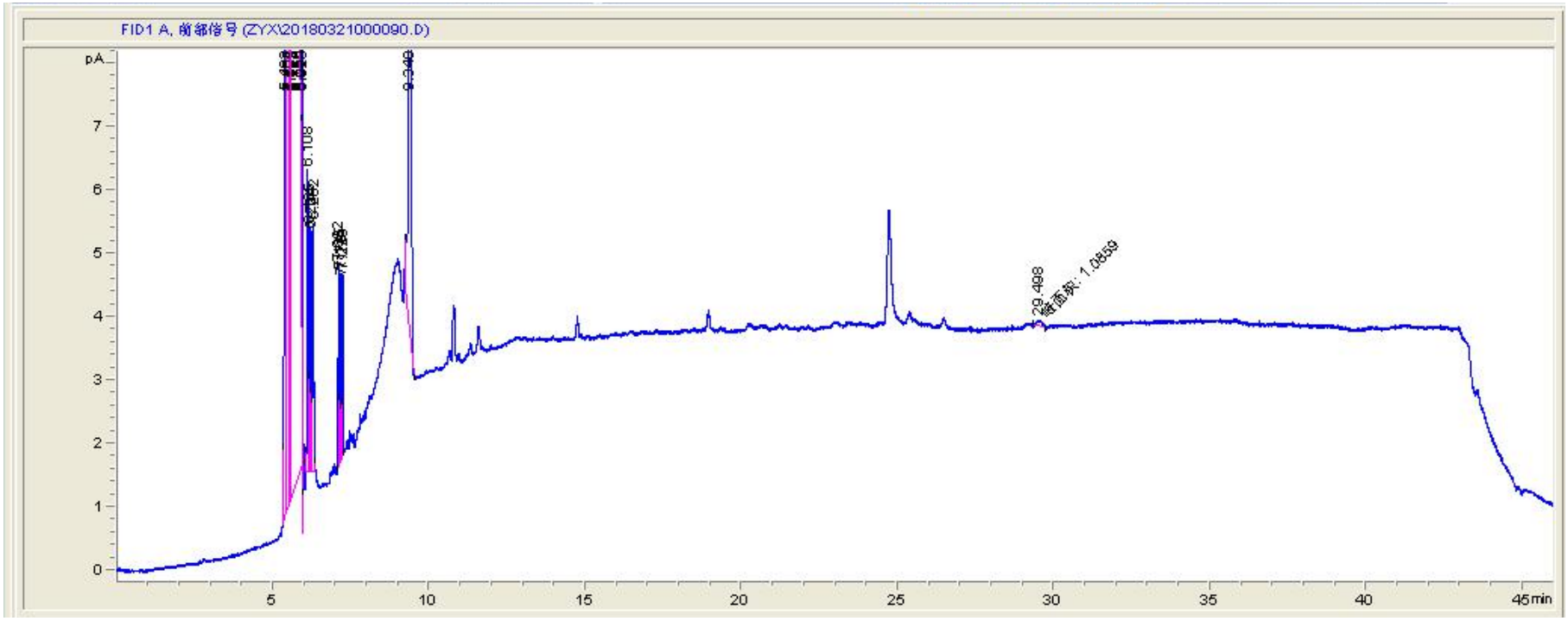
GC analysis of the sugar moiety of **9**



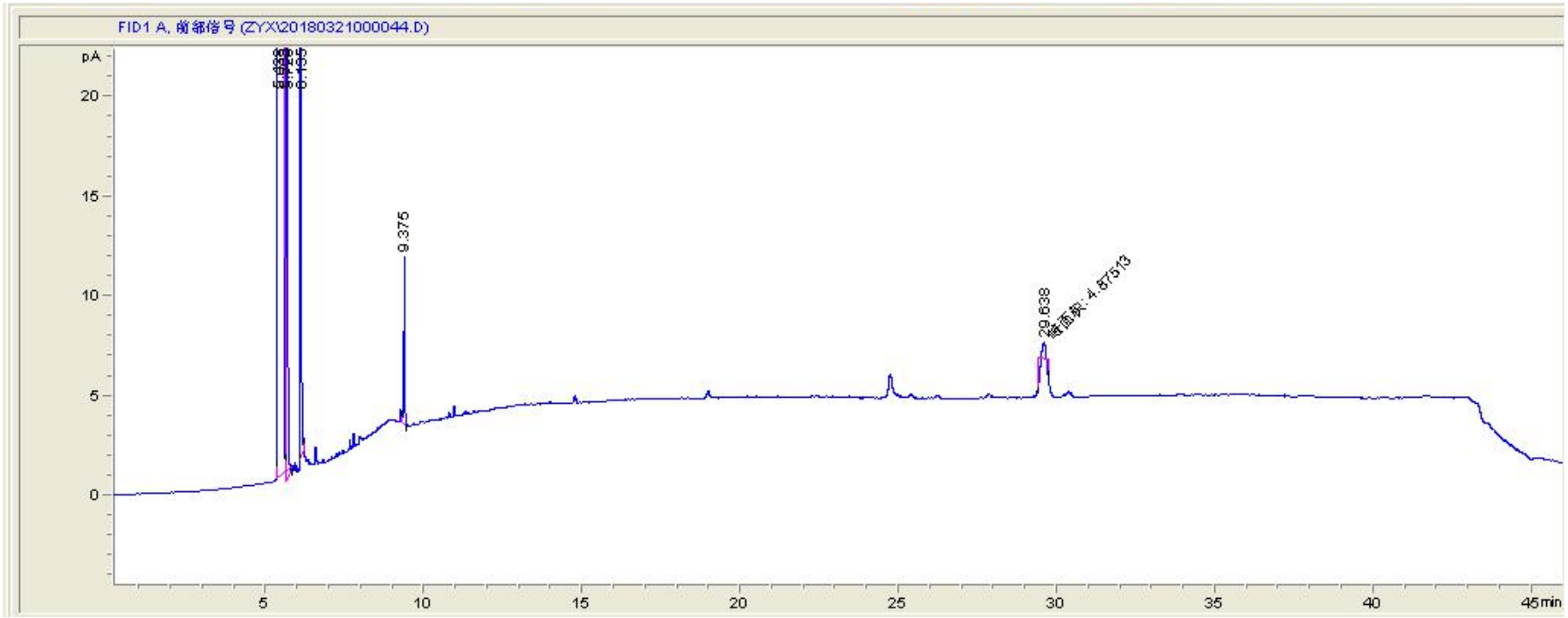
GC analysis of the sugar moiety of **10**



GC analysis of the sugar moiety of **13**

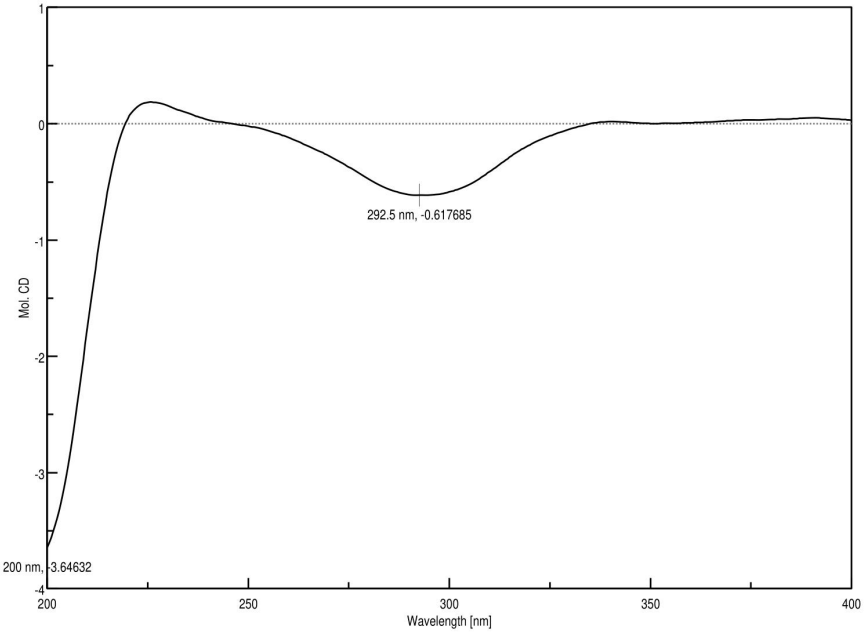


GC analysis of the sugar moiety of **14**



GC analysis of the sugar moiety of **15**

CD spectrum of **1**



[Comments]
Sample name ZSB-68
Comment

[Measurement Information]
Instrument Name J-815
Control Name J-815soft
Serial No. A024461168

Accessory Standard
Accessory S/N A024461168
Cell Length 1 mm

Measurement date 2018/12/11 16:03

Photometric Mode CD, HT, Abs
Measure Range 400 - 200 nm
Data pitch 0.5 nm
Sensitivity Standard
D.I.T. 1 sec
Bandwidth 1.00 nm
Start Mode Immediately
Scanning Speed 100 nm/min
Baseline Correction Baseline
Shutter Control Auto
CD Detector PMT
PMT Voltage Auto
Accumulations 2
Solvent MEOH
Concentration 0.5 (w/v)%

[Detailed Information]
Creation date 2018/12/12 15:27

Data array type Linear data array * 3
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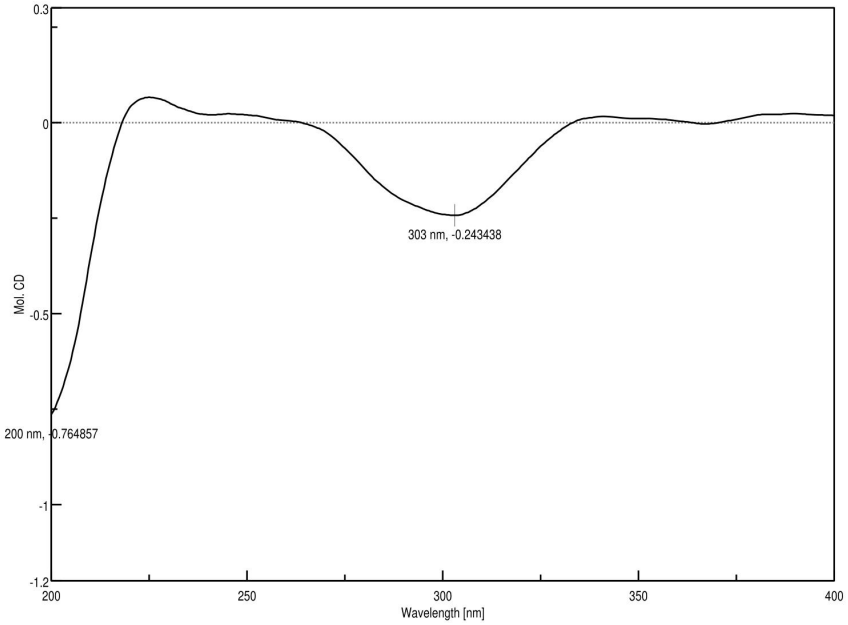
Vertical axis(1) Mol. CD
Vertical axis(2) HT [V]
Vertical axis(3) Abs
Start 400 nm
End 200 nm
Data interval 0.5 nm
Data points 401

CD spectrum of **2**



[Comments]
Sample name ZSB-55
Comment

[Measurement Information]
Instrument Name J-815
Model Name J-815
Serial No. A024461168

Accessory Standard
Accessory S/N A024461168
Cell Length 1 mm

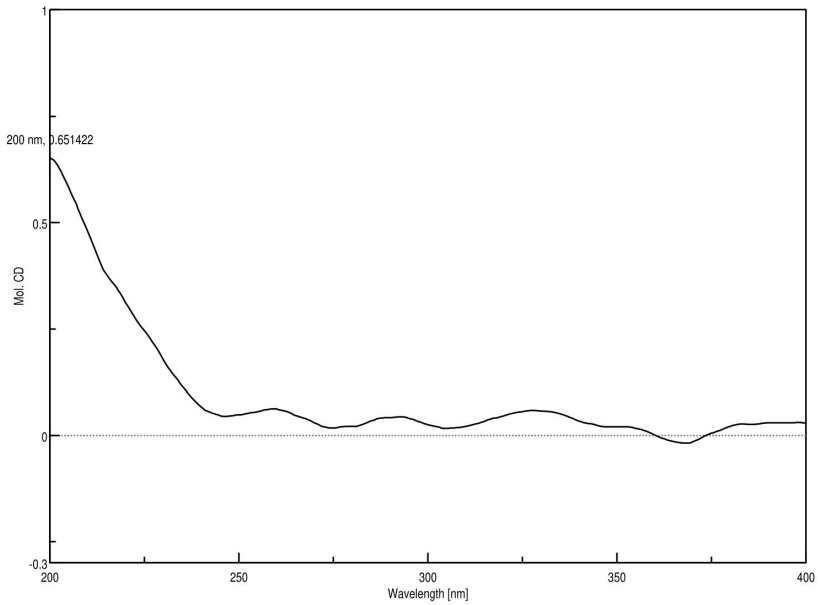
Measurement date 2018/12/11 15:55

Photometric Mode CD, HT, Abs
Measure Range 400 - 200 nm
Data pitch 0.5 nm
Sensitivity Standard
D.I.T. 1 sec
Bandwidth 1.00 nm
Start Mode Immediately
Scanning Speed 100 nm/min
Baseline Correction Baseline
Shutter Control Auto
CD Detector PMT
PMT Voltage Auto
Accumulations 2
Solvent MEOH
Concentration 0.84 (w/v)%

[Detailed Information]
Creation date 2018/12/12 15:19

Data array type Linear data array * 3
Horizontal axis Wavelength [nm]
Vertical axis(1) Mol. CD
Vertical axis(2) HT [V]
Vertical axis(3) Abs
Start 400 nm
End 200 nm
Data interval 0.5 nm
Data points 401

CD spectrum of **12**



[Comments]
Sample name ZSB-161
Comment

[Measurement Information]
Instrument Name J-815
Control Name Matrisoft
Serial No. A024461168

Accessory Standard
Accessory S/N A024461168
Cell Length 1 mm

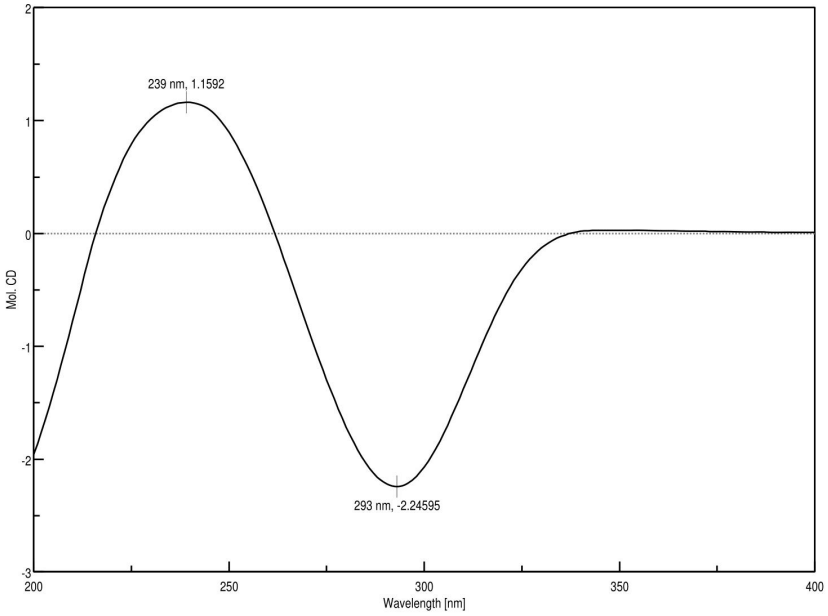
Measurement date 2018/12/11 16:13

Photometric Mode CD, HT, Abs
Measure Range 400 - 200 nm
Data pitch 0.5 nm
Sensitivity Standard
D.I.T. 1 sec
Bandwidth 1.00 nm
Start Mode Immediately
Scanning Speed 100 nm/min
Baseline Correction Baseline
Shutter Control Auto
CD Detector PMT
PMT Voltage Auto
Accumulations 2
Solvent MEOH
Concentration 0.5 (w/v)%

[Detailed Information]
Creation date 2018/12/12 15:46

Data array type Linear data array * 3
Horizontal axis Wavelength [nm]
Vertical axis(1) Mol. CD
Vertical axis(2) HT [V]
Vertical axis(3) Abs
Start 400 nm
End 200 nm
Data interval 0.5 nm
Data points 401

CD spectrum of **15**



ZSB-52-1-s-m.jws

[Measurement Information]

Instrument Name	J-815
Model Name	J-815
Serial No.	A024461168
Accessory	Standard
Accessory S/N	A024461168
Cell Length	1 mm
Measurement date	2018/4/3 15:01
Photometric Mode	CD, HT, Abs
Measure Range	400 - 200 nm
Data pitch	1 nm
Sensitivity	Standard
D.I.T.	1 sec
Bandwidth	1.00 nm
Start Mode	Immediately
Scanning Speed	100 nm/min
Baseline Correction	Baseline
Shutter Control	Auto
CD Detector	PMT
PMT Voltage	Auto
Accumulations	2
Solvent	MEOH
Concentration	0.4 (w/v)%