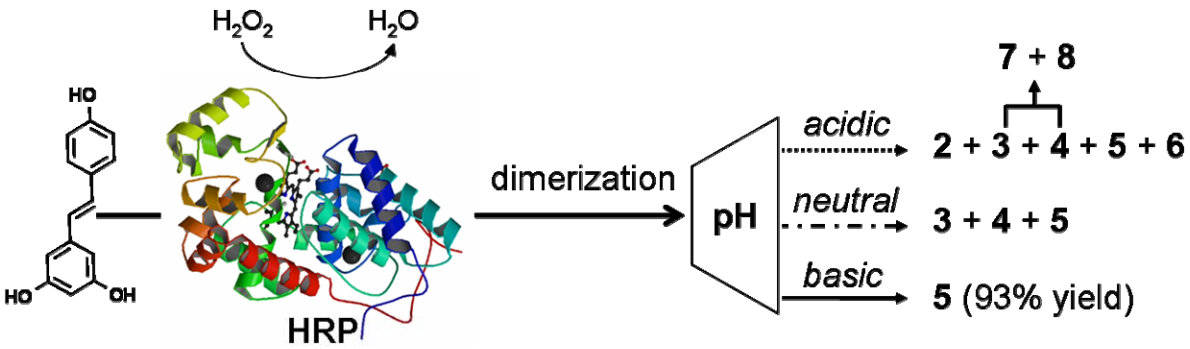
Electronic Supplementary Material (ESI) for Green Chemistry

pH Switched HRP Catalyzed Dimerization of Resveratrol: A Selective Biomimetic Synthesis

*Chang Li, Jing Lu, Xiaofei Xu, Ruilin Hu and Yuanjiang Pan **

Department of Chemistry, Zhejiang University, Hangzhou, 310027, P. R. China
E-mail: panyuanjiang@zju.edu.cn



Supporting Information

Experimental Procedures and Spectroscopic Data of the Products

General Procedures. All reagents were purchased at the highest commercial quality and used without further purification. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) or high performance liquid chromatography (HPLC). HPLC analysis were carried out on a Agilent 1100 system including a G1311A QuatPump, a G1322 degasser, a G1314A variable-wavelength detector (VWD), a model 7725 injection valve with 20μL loop. And the HPLC column used was Capcell PAK C18 (250mm × 4.6mm i.d., 5μm, Shisheido). Purification of compounds was carried out with silica gel (academic grade, 200-300) and a preparative HPLC (Varian ProStar 215 and Shimadzu Shimpack-C18 column, 250× 20mm i.d). NMR spectra were recorded on Bruker 500 MHz instrument. Mass spectroscopic data were obtained using Waters GCT Premier oa-TOF mass spectrometer.

Horseradish Peroxidase Catalyzed dimerization of 1. All buffers (pH 3.0-10.0) were prepared according to handbooks with citric acid – sodium citrate (pH 3.0, 4.0, 5.0, 6.0 and 7.0), PBS salts (pH 6.0, 7.0 and 8.0) and glycine – NaOH (9.0 and 10.0). All pH values were adjusted with monitoring by a pH-adjuster (PHS-3B, Shanghai INESA Scientific Instrument Co. Ltd.). To perform the reaction, a mixture of **1** (0.4 mmol, 91.2 mg) and HRP (160μL, 1mg/mL aqueous solution) was added to acetone (2 mL) – buffer (2 mL), stirred at 40℃ for 30 min. Then 60 μL fresh 30% H_2O_2 was added to the solution. After one hour, the reaction solution was extracted with EtOAc. The organic layer was washed by brine and water, dried over anhydrous sodium sulphate and concentrated. Analysis of

the product solution was carried out on HPLC with a C-18 column (Shisheido, column temperature, 25℃; mobile phase, methanol and water at the gradient: methanol, 0-8 min, 40%-53%, 8-15 min, 53%, 15-20 min, 53%-90%; flow rate, 0.8 mL/min; detection, 280 nm UV). HPLC yields were calculated by peak area, assuming all dimers share the same absorption at 280 nm. Representative chromatograms were shown in the main text. Separation was carried out on a preparative HPLC with a C-18 column (Shimadzu), using gradient elution (methanol, 0-24 min, 40%-53%; 24-40 min, 53%; 40-60 min, 53%-90%) and detected at 280 nm UV. Isolation of pH 8.0 reaction solution got **5** (80.8 mg, 89.0% yield), Isolation of pH 6.0 reaction got a mixture of **3** and **4** (22.6 mg, 24.0% yield). Isolation of pH 5.0 reaction solution got **2** (16.8 mg, 18.5% yield), and isolation of pH 4.0 reaction solution obtained 6 (23.4 mg, 25.8% yield).

Pallidol (2) was obtained as a brown amorphous powder. ^{1}H NMR (500 MHz, acetone) δ 8.19 (s, 2H), 8.15 (s, 2H), 7.92 (s, 2H), 7.05 (d, J = 10.0 Hz, 4H), 6.77 (d, J = 10.0 Hz, 4H), 6.70 (s, 2H), 6.26 (s, 2H), 4.63 (s, 2H), 3.88 (s, 2H); ^{13}C NMR (125 MHz, acetone) δ 159.0, 155.1, 150.2, 137.6, 129.0, 123.2, 115.8, 103.3, 102.4, 60.3, 53.8. HRMS(EI) calcd for $C_{28}H_{22}O_6^+$ [M^+] 454.1416, found 454.1417.

L**eachianol F (3) and leachianol G (4)** was obtained as a brown amorphous powder. The product got was a 1:2 mixture. Data of **3**: ^{1}H NMR (500 MHz, acetone) δ 7.99 (br, 5H), 7.47 (s, 1H), 6.84 - 6.88 (m, 4H), 6.70 - 6.73 (m, 2H), 6.67 (d, J = 5.0 Hz, 2H), 6.58 (d, 1H), 6.30 (d, J = 5.0 Hz, 1H), 6.12 (m, 1H), 5.92 (d, 1H), 4.48 (m, 1H), 4.22 (d, J = 5.0 Hz, 1H), 4.08 (d, J = 5.0 Hz, 1H), 3.36 (m, 1H), 2.94 (t, J = 5.0 Hz, 1H); ^{13}C NMR (125 MHz, acetone) δ 159.1, 158.8, 157.1, 156.3, 155.0, 150.6, 148.7, 137.4, 136.1, 129.3, 128.8, 122.5, 115.6, 115.4, 106.1, 106.0, 102.4, 101.2, 76.6, 61.8, 59.4, 55.6. HRMS(EI) calcd for $C_{28}H_{24}O_7^+$ [$(M-H_2O)^+$] 454.1416, found 454.1419. Data of **4**: ^{1}H NMR (500 MHz, acetone) δ 8.10 (br, 5H), 7.44 (s, 1H), 7.07 (d, J = 10.0, 2H), 6.85 (m, 2H), 6.67 (m, 4H), 6.22 (d, 2H), 6.16 (d, 2H), 6.14 (d, J = 5.0 Hz, 2H), 5.74 (d, J = 5.0 Hz, 1H), 4.48 (m, 1H), 4.26 (d, 1H), 4.14 (d, 1H), 3.48 (t, J = 5.0 Hz, 1H), 3.40 (m, 1H); ^{13}C NMR (125 MHz, acetone) δ 159.2, 158.5, 157.2, 156.2, 154.8, 151.4, 147.3, 138.0, 135.7, 129.4, 129.3, 106.2, 105.6, 102.4, 101.0, 77.3, 62.5, 59.0, 56.0. HRMS(EI) calcd for $C_{28}H_{24}O_7^+$ [$(M-H_2O)^+$] 454.1419, found 454.1419.

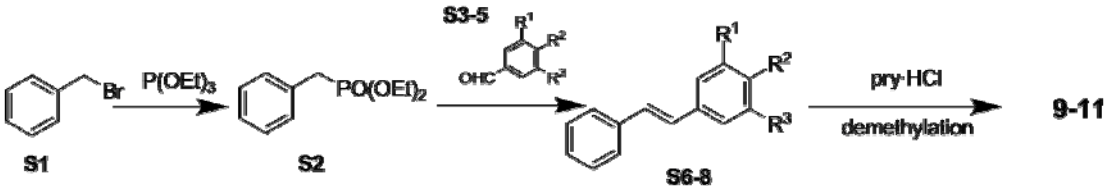
***trans*-δ-viniferin (5)** was obtained as a yellow amorphous powder. ^{1}H NMR (500 MHz, acetone) δ 8.48 (s, 1H), 8.24 (s, 2H), 8.20 (s, 2H), 7.44 (d, J = 5.0 Hz, 1H), 7.26 (m, 3H), 7.06 (d, J = 15.0 Hz, 1H), 6.92 (d, J = 15.0 Hz, 1H), 6.87 (m, 3H), 6.55 (d, 2H), 6.28 (d, J = 10.0 Hz, 2H), 6.20 (d, J = 5.0 Hz, 2H), 5.46 (d, J = 5.0 Hz, 1H), 4.48 (d, J = 5.0 Hz, 1H); ^{13}C NMR (125 MHz, acetone) δ 160.6, 159.7, 159.5, 158.4, 145.2, 140.8, 132.5, 132.1, 131.7, 129.1, 128.6, 127.2, 123.9, 116.2, 110.1, 107.4, 105.7, 102.7, 102.3, 94.0, 57.8, 55.4. HRMS(EI) calcd for $C_{28}H_{22}O_6^+$ [M^+] 454.1416, found 454.1414.

***cis*-δ-viniferin (6)** was obtained as a yellow amorphous powder. After isolation, the product turned to be a mixture of **5** and **6** (1:3), which is in the equilibrium state of *cis-/trans-* isomerization. ^{1}H NMR (500 MHz, acetone) δ 8.26 (br, 5H), 7.23 (d, J = 10.0 Hz, 2H), 6.96 (s, 1H), 6.84 – 6.86 (m, 3H), 6.76 (d, J = 5.0 Hz, 1H), 6.48 (d, J = 10.0 Hz, 1H), 6.32 – 6.36 (m, 3H), 6.24 (m, 2H), 6.13 (m, 2H), 5.37 (d, J = 10.0 Hz, 1H), 4.42 (d, J = 10.0 Hz, 1H); ^{13}C NMR (125 MHz, acetone) δ 160.0, 159.6, 159.0, 156.4, 144.6. 140.3. 132.2, 131.1, 131.0, 130.7, 130.2, 129.3, 128.7, 128.6, 127.1, 116.1, 109.7, 108.2, 107.4, 102.6,

102.4, 94.0, 57.8, 55.4. HRMS(EI) calcd for $C_{28}H_{22}O_6^+$ [M^+] 454.1416, found 454.1418.

Synthesis of resveratrol analogs (9, 10 and 11): The synthetic route (shown bellow) was designed according to Kim[1] and Heynekamp's[2] work with modifications.

*Scheme S1. Synthesis of resveratrol analogs **9-11***



	R^1	R^2	R^3
S3	H	OMe	H
S4	OMe	H	H
S5	OMe	H	OMe
S6	H	OMe	H
S7	OMe	H	H
S8	OMe	H	OMe

General Procedures of methoxyl stilbene synthesis. A mixture of benzyl bromide (**S1**, 10 mmol, 1.71g) and triethyl phosphite (30 mmol, 4.98g) was heated at reflux in an oil bath for 8h. After the mixture was cooled, the excess triethyl phosphite was removed in vacuo. The product **S2** was further used without purification. To an ice-cooled well-stirred suspension of **S2** and potassium *tert*-butoxide (12 mmol, 1.344g) in DMF (10 mL), methoxyl substituted aldehydes (**S3 - S5**, 11 mmol) were added respectively. The reaction was stirred at 0℃ to room temperature for 5h. The mixture was diluted in 10 mL EtOAc, and extracted by water (50 mL) for three times. The organic layer was further washed by brine (2 × 15 mL), dried by Na_2SO_4, and the solvent was removed in vacuo. The residue was subjected to silica gel and eluted by petroleum ether – EtOAc (10:1) to give methoxyl stilbene **S6** – **S8**.

4-methoxyl stilbene (**S6**) was obtained as a white powder (1.33 g, 62.8% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 10.0 Hz, 2H), 7.50 (d, J = 5.0 Hz, 2H), 7.38 (t, J = 10.0 Hz, 2H), 7.28 (m, 2H), 7.10 (d, J = 15.0 Hz, 1H), 7.02 (d, J = 15.0 Hz, 1H), 6.94 (d, J = 10.0 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 137.8, 130.3, 128.8, 128.3, 127.9, 127.3, 126.7, 126.4, 114.3, 55.5. HRMS(EI) calcd for $C_{15}H_{14}O^+$ [M^+] 210.1045, found 210.1045.

3-methoxyl stilbene (**S7**) was got as a white powder (721.8 mg, 34.0% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 5.0 Hz, 2H), 7.27 (t, J = 10.0 Hz, 2H), 7.18 (q, J = 10.0 Hz, 2H), 7.00 – 7.04 (m, 3H), 6.97 (m, 1H), 6.74 (d, J = 5.0 Hz, 3H), 3.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 138.9, 137.7. 129.7, 129.1, 128.8, 128.7, 127.6, 126.7, 119.4, 113.4, 111.9, 55.3. HRMS(EI) calcd for $C_{15}H_{14}O^+$ [M^+] 210.1045, found 210.1045.

3,5-dimethoxyl stilbene (**S8**) was got as a white powder (1.10 g, 48.7% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 5.0 Hz, 2H), 7.33 (t, J = 5.0 Hz, 2H), 7.24 (t, J = 10.0 Hz,

1H), 7.07 (d, J = 20.0 Hz, 1H), 7.01 (d, J = 15.0 Hz, 1H), 6.66 (d, J = 0, 2H), 6.39 (t, J = 5.0 Hz, 1H), 3.79 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1, 139.5, 137.2, 129.3, 128.8, 127.8, 126.7, 104.7, 100.1, 55.4. HRMS(EI) calcd for $C_{16}H_{16}O_2^+$ [M^+] 240.1150, found 240.1153.

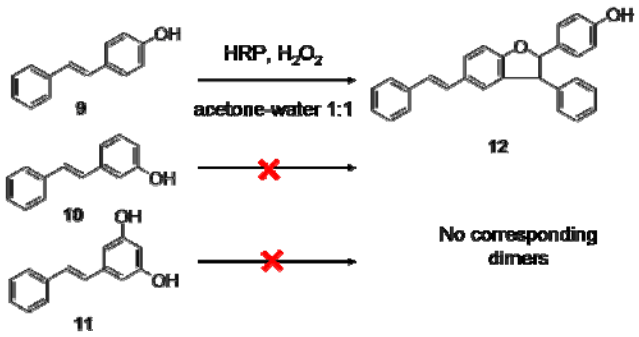
General procedure of demethylation. Methoxyl stilbenes (**S6**, **S7** and **S8**) were heated with pyridine hydrochloride (5 equiv) at 200℃. After 5h, the hot dark syrup was poured into 20 mL saturated HCl, and further extracted with ethyl acetate (2 × 20 mL). The organic layer was collected and washed with brine, dried by Na_2SO_4, and the solvent was removed in vacuo. The residue was subjected to silica gel and eluted by petroleum ether – EtOAc (3:1) to give hydroxylstilbenes **9** –**11**.

4-hydroxyl stilbene (**9**) was got as a white powder (72% yield). ^{1}H NMR (500 MHz, Acetone) δ 8.50 (s, 1H), 7.54 (d, J = 5.0 Hz, 2H), 7.46 (d, J = 10.0 Hz, 2H), 7.34 (t, J = 10.0 Hz, 2H), 7.22 (t, J = 10.0 Hz, 2H), 7.17 (d, J = 20.0 Hz, 1H), 7.04 (d, J = 15.0 Hz, 1H), 6.86 (d, J = 10.0 Hz, 2H); ^{13}C NMR (125 MHz, acetone) δ 158.2, 138.9, 130.0, 129.5, 129.4, 128.8, 127.8, 127.0, 126.5, 116.5. HRMS(EI) calcd for $C_{14}H_{12}O^+$ [M^+] 196.0888, found 196.0891.

3-hydroxyl stilbene (**10**) was got as a white powder (69% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 10.0 Hz, 2H), 7.60 (t, J = 10.0 Hz, 2H), 7.45 – 7.52 (m, 2H), 7.33 (d, J = 10.0 Hz, 1H), 7.30 (d, J = 10.0 Hz, 2H), 7.23 (t, J = 10.0 Hz, 1H), 6.98 (m, 1H), 5.17 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 139.2, 137.3, 130.0, 129.4, 128.8, 128.4, 127.9, 126.7, 119.6, 114.8, 113.1. HRMS(EI) calcd for $C_{14}H_{12}O^+$ [M^+] 196.0888, found 196.0891.

3,5-dihydroxyl stilbene (**11**) was got as a white powder (52% yield). ^{1}H NMR (500 MHz, acetone) δ 8.24 (s, 2H), 7.53 (d, J = 10.0 Hz, 2H), 7.32 (t, J = 10.0 Hz, 2H), 7.21 (t, J = 10.0 Hz, 1H), 7.06 (s, 1H), 6.57 (d, J = 0 Hz, 2H), 6.29 (t, J = 0 Hz, 1H); ^{13}C NMR (125 MHz, acetone) δ 159.6, 140.4, 138.3, 129.7, 129.5, 129.2, 128.3, 127.3, 106.0, 103.2. HRMS(EI) calcd for $C_{14}H_{12}O_2^+$ [M^+] 212.0837, found 212.0842.

Treatment of hydroxyl stilbenes (9 - 11) with Horseradish Peroxidase and hydroperoxide.



General Procedure. To perform the reaction, a mixture of hydroxylstilbenes **(9 - 11)** (0.4 mmol) and HRP (160μL, 1mg/mL aqueous solution) was added to acetone (2 mL) – water (2 mL), stirred at 40℃ for 30 min. Then 60 μL fresh 30% H_2O_2 was added to the solution. After one hour, the reaction solution was extracted with EtOAc. The organic layer was

washed by brine and water, dried over anhydrous sodium sulphate and concentrated. Analysis of the product solution was carried out using TLC. It appeared that no reaction occurred in **10** and **11** cases, only **9** produced 72% (112.3 mg) **12**, obtained as a pale yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 10.0 Hz, 2H), 7.21 – 7.30 (m, 6H), 7.10 – 7.14 (m, 6H), 6.94 (d, J = 15.0 Hz, 2H), 6.80 – 6.86 (m, 2H), 6.72 (d, J = 10.0 Hz, 2H), 5.41 (d, J = 10.0 Hz, 1H), 4.90 (s, 1H), 4.48 (d, J = 5.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ159.8, 155.8, 141.6, 137.8, 132.8, 131.2, 131.1, 129.1, 128.8, 128.6, 128.5, 128.0, 127.8, 127.5, 127.3, 126.5, 126.3, 123.1, 115.6, 109.9, 93.5, 57.8. HRMS(EI) calcd for $C_{16}H_{16}O_2^+$ [M^+] 390.1620, found 390.1643.

Derivative Synthesis of Parthenocissin A (7) and Quadrangularin A (8) from leachianol F & G (3 & 4).

Parthenocissin A (**7**). Leachianol F (**3**) & G (**4**) was accumulated by repeated synthesis and isolation using HRP and resveratrol (**1**) in acetone – pH 6.0 buffer. 60.0 mg mixture of 3 and 4 (1:2) was well stirred in 2 mL CH_2Cl_2 in ice bath, then 1 equivalent BF_3•Et_2O was added dropwisely. After 2hours' stirring of the reaction solution at room temperature, it was quenched by adding 1 mL water. The product solution was diluted in 15 mL EtOAc and extracted with water, further washed with saturated brine. After removing the solvent in vacuo, the residue was subjected on a gel column (Sephadex LH-20) and eluted with MeOH to give **7** (52.0 mg, 90%). ^{1}H NMR (500 MHz, acetone) δ 8.24 (s, br, 6H), 7.24 (d, J = 10.0 Hz, 2H), 6.83 (d, J = 10.0 Hz, 2H), 6.76 (d, J = 10.0 Hz, 2H), 6.55 (d, J = 0, 2H), 6.34 (s, 1H), 6.29 (d, J = 0, 1H), 6.23 (s, 1H), 4.28 (s, 1H), 3.77 (s, 1H); ^{13}C NMR (125 MHz, acetone) δ 159.3, 158.4, 157.1, 156.4, 155.3, 149.8, 145.5, 142.8, 137.4, 130.6, 129.8, 128.9, 127.8, 125.2, 115.9, 115.8, 106.5, 104.0, 103.1, 101.4, 64.3, 54.9. HRMS(EI) calcd for $C_{28}H_{22}O_6^+$ [M^+] 454.1419, found 454.1419.

Quadrangularin A (**8**). 40.0 mg of **7** was dissolved in 5 mL MeOH and put in a Pyrex glass-made reactor (30 mL), thermostated at 25℃. The stirred solution was irradiated by a Mercury lamp (300 W, λ > 320 nm, Shanghai Yamin), which had been turned on for at least 30 min. After 2 hours, the solvent was removed in vacuo, and the residue was subjected to preparative HPLC to get 30.2 mg quadrangularin A (**8**, yield 77.0%). ^{1}H NMR (500 MHz, acetone) δ 8.42 (s, 1H), 8.29 (s, 1H), 8.20 (s, 2H), 8.09 (s, 1H), 7.93 (s, 1H), 7.24 (d, J = 10.0 Hz, 2H), 7.08 (s, 1H), 6.95 (d, J = 10.0 Hz, 2H), 6.82 (m, 1H), 6.69 - 6.71 (m, 4H), 6.34 (m, 2H), 6.32 (m, 2H), 6.22 (m, 1H), 4.30 (s, 1H), 4.17 (s, 1H); ^{13}C NMR (125 MHz, acetone) δ 159.6, 159.5, 157.2, 156.4, 155.8, 149.0, 147.3, 142.6, 137.7, 131.0, 129.7, 128.7, 124.5, 123.0, 116.0, 115.8, 106.2, 103.7, 101.5, 98.3, 66.5, 57.5. HRMS(EI) calcd for $C_{16}H_{16}O_2^+$ [M^+] 454.1419, found 454.1413.

Parallel reactions to identity the influence of pH to proportion of resveratrol radical mesomers.

A mixture of **1** (0.05 mmol, 11.4 mg) and oxidant (AgOAc 9.0 mg or $PhI(OAc)_2$ 10.0 mg) was added to acetone (1 mL) – buffer (pH 3.0, 5.0 or 8.0, 1 mL), stirred at 50℃ for 3 hours. The reaction solution was extracted with EtOAc. The organic layer was washed by brine and water, dried over anhydrous sodium sulphate and concentrated. Analysis of the product solution was carried out on HPLC in the same chromatographic condition. The

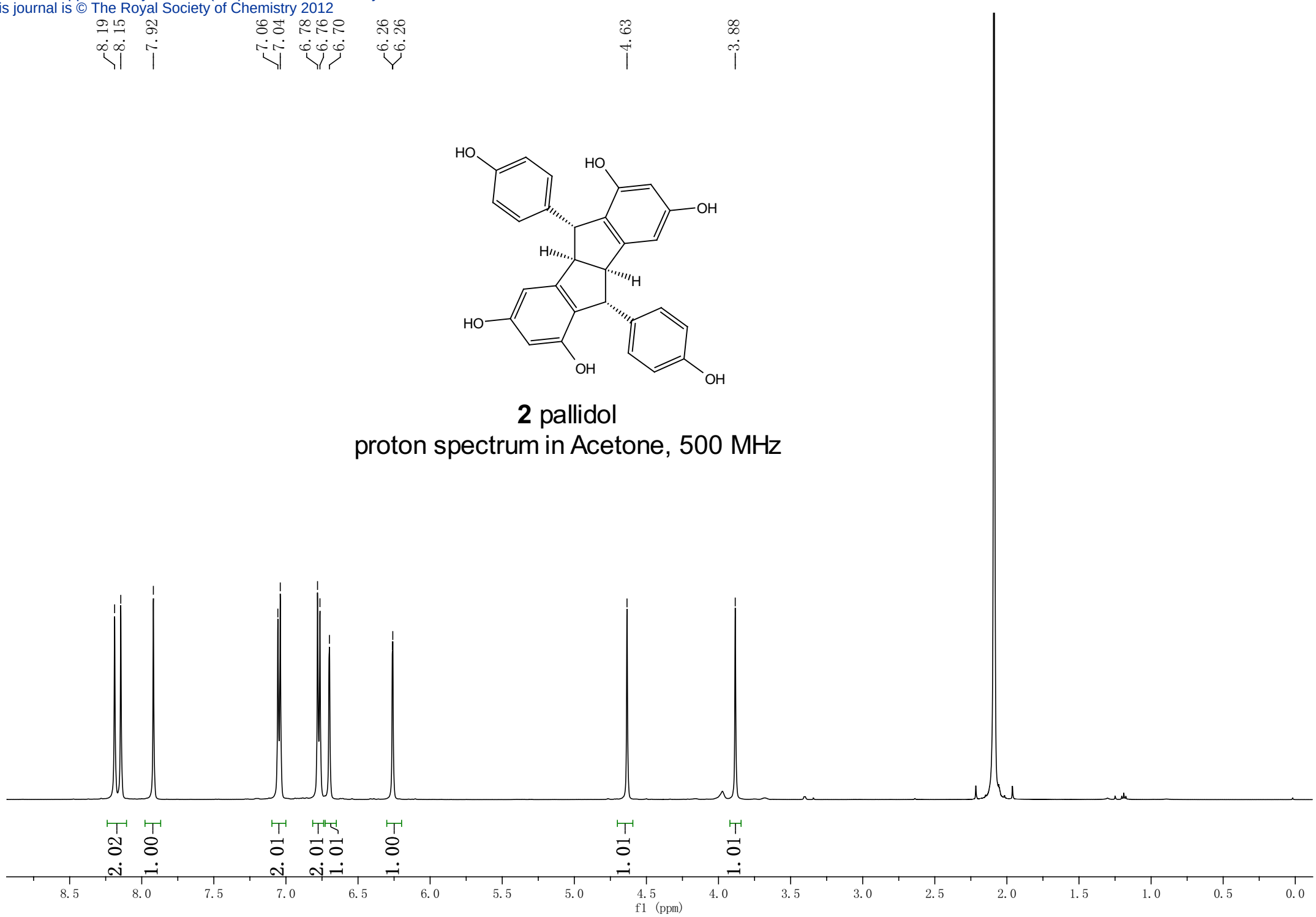
result shows there're no such distinct results as in HRP/ H_2O_2 case.

Characterization of HRP's conformation in various pH buffer with circular dichroism spectrometer.

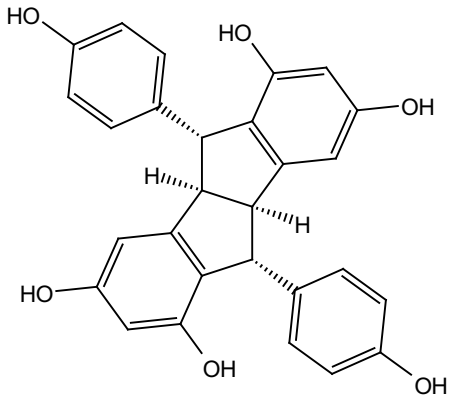
HRP (160μL, 1mg/mL aqueous solution) was added to 2 mL buffer (pH 3.0, 5.0 and 8.0, respectively). The solution was incubated at 40℃ for 8h as in the enzymatic reaction. A JASCO J-820 spectrometer was used for CD spectroscopy, spectra were recorded at 25℃ in corresponding buffer solution, using a path length of 1.0 cm. Spectra were recorded in the range of 200 - 300 nm.

[1] S. Kim, H. Ko, J. E. Park, S. Jung, S. K. Lee, Y. J. Chun, *J. Med. Chem.*, **2002**, *45*, 160-164.

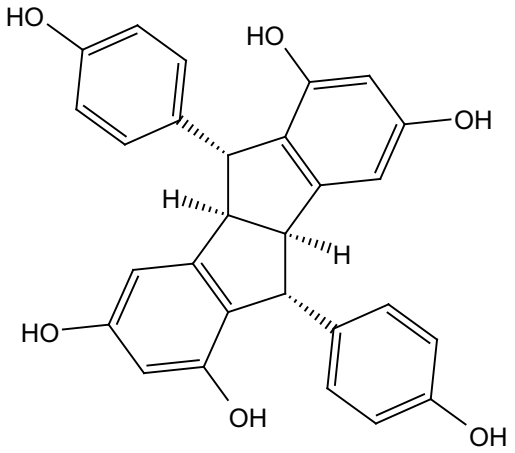
[2] J. J. Heynekamp, W. M. Weber, L. A. Hunsaker, A. M. Gonzales, R. A. Orlando, L. M. Deck, D. L. V. Jagt, *J. Med. Chem.*, **2006**, *49*, 7182-7189.



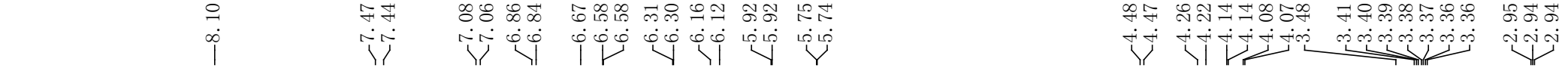
2 pallidol
proton spectrum in Acetone, 500 MHz

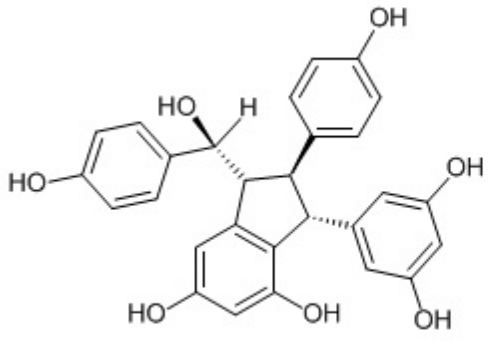


2 pallidol
carbon spectrum in Acetone, 125 MHz

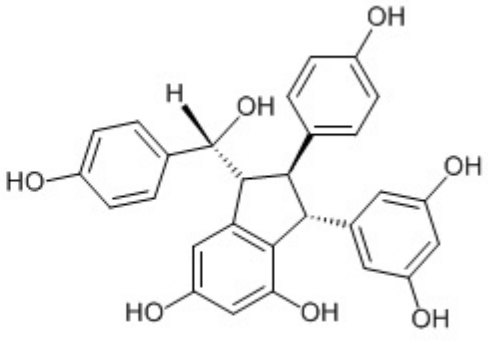


2 pallidol
DEPT-135 spectrum in Acetone,
125 MHz



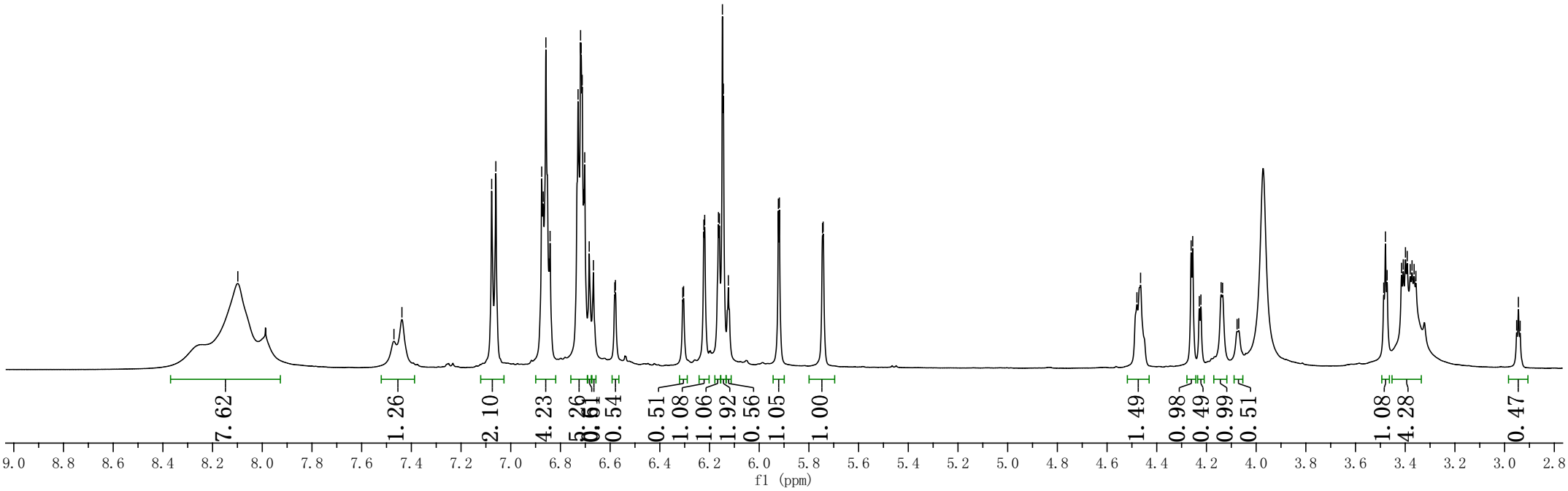


3: leachianols F

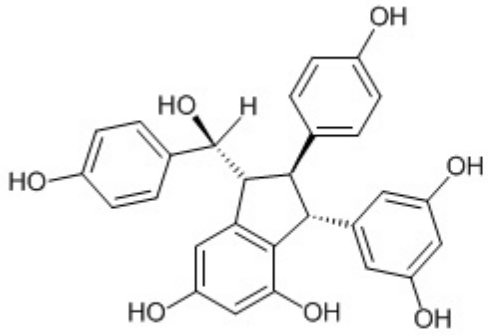


4: leachianols G

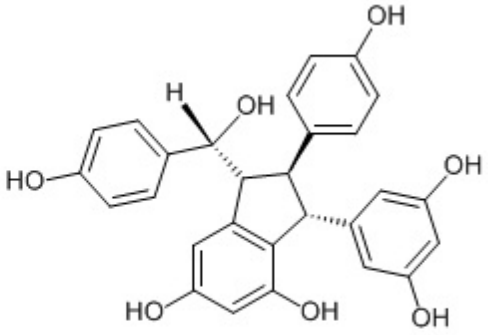
mixture of **3** and **4** (1:2)
proton spectrum in acetone, 500MHz



159.20
159.12
158.49
157.24
156.18
154.85
151.43
147.27
137.97
135.67
129.43
129.29
129.26
128.81
123.09
115.63
115.59
115.40
115.25
106.19
106.01
105.60
102.36
101.05
77.29
69.85
62.54
58.97
55.95
55.35

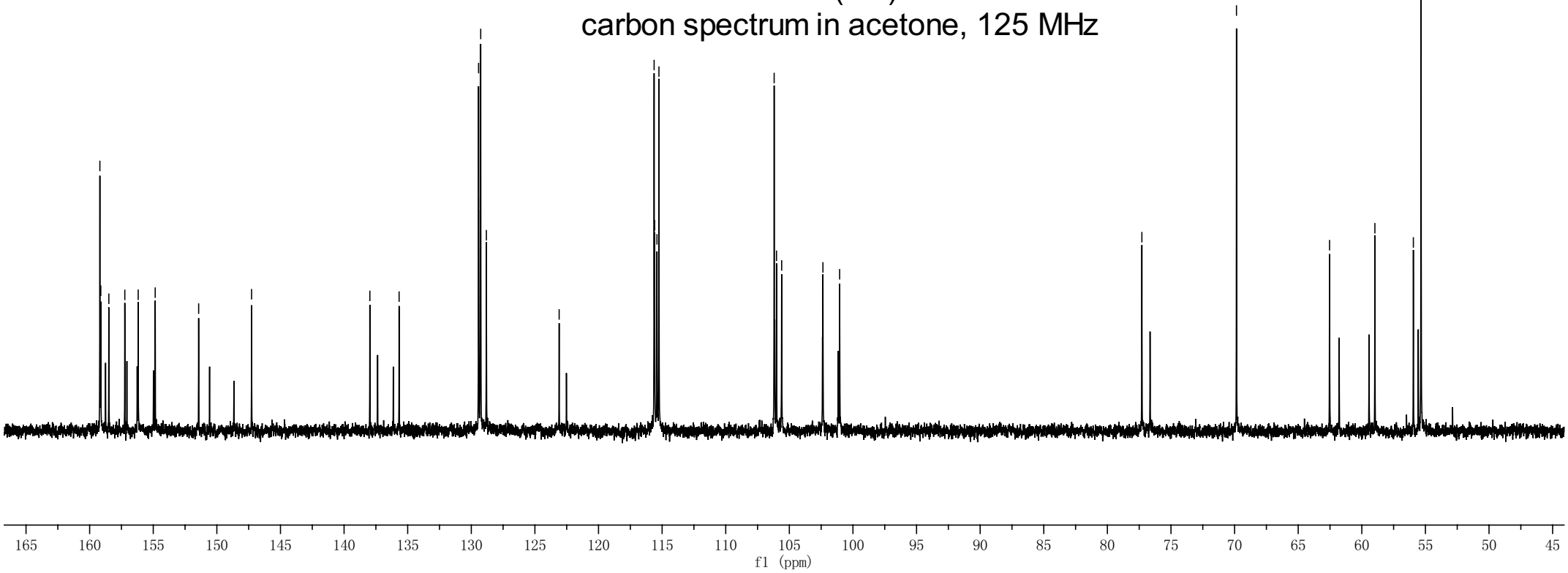


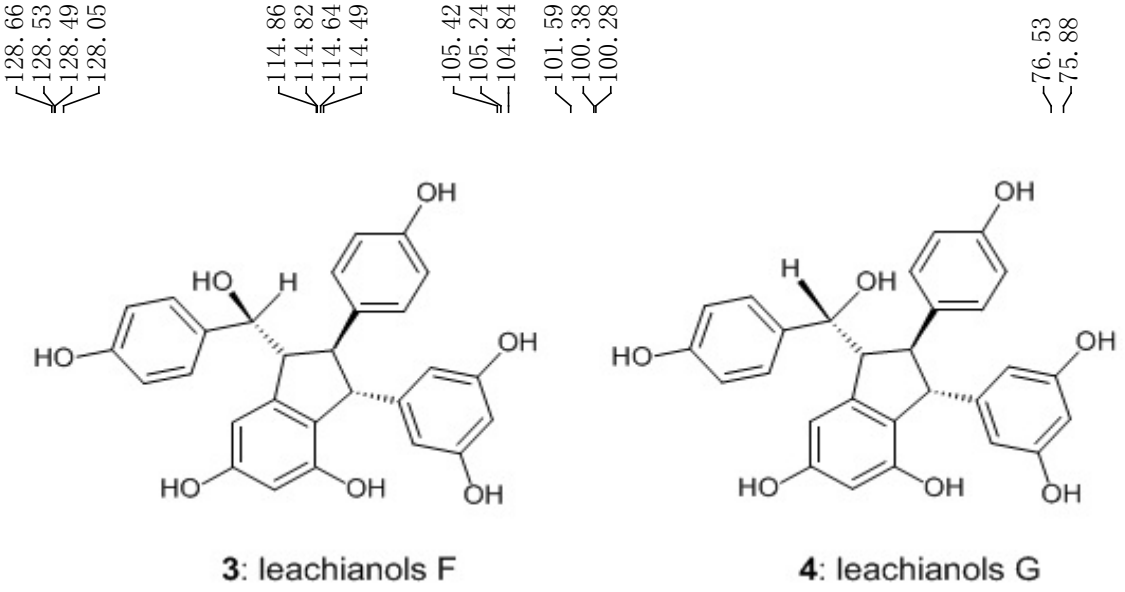
3: leachianols F



4: leachianols G

mixture of **3** and **4** (1:2)
carbon spectrum in acetone, 125 MHz

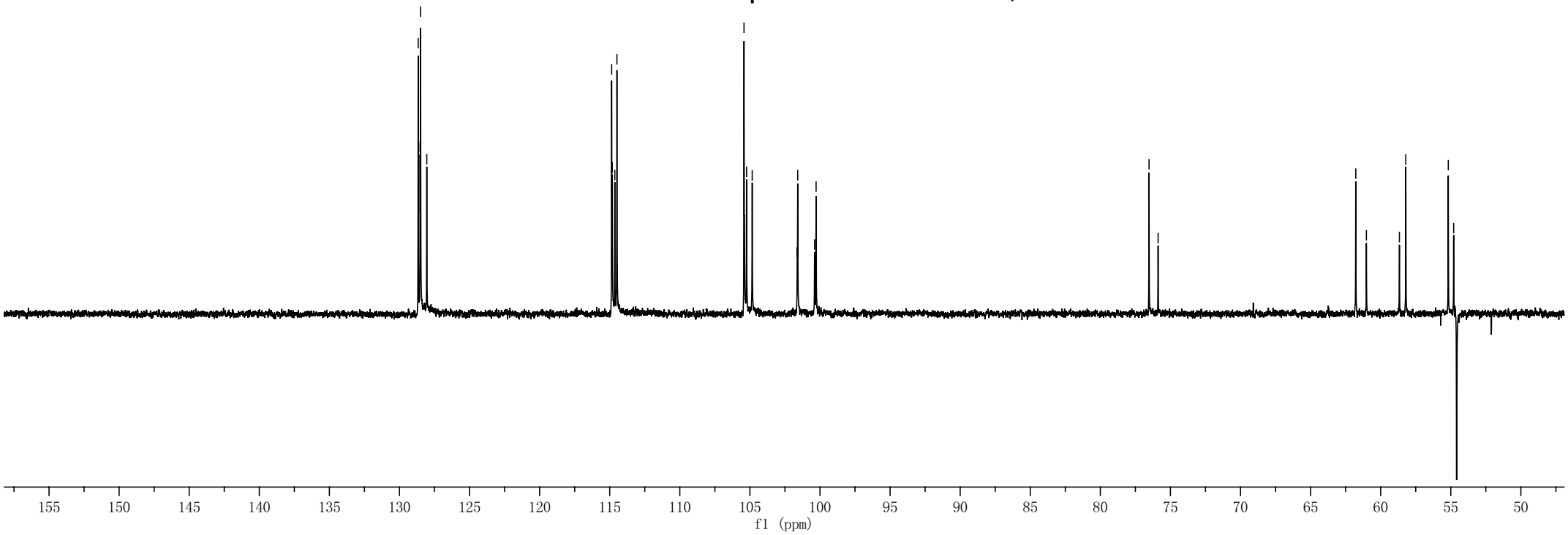


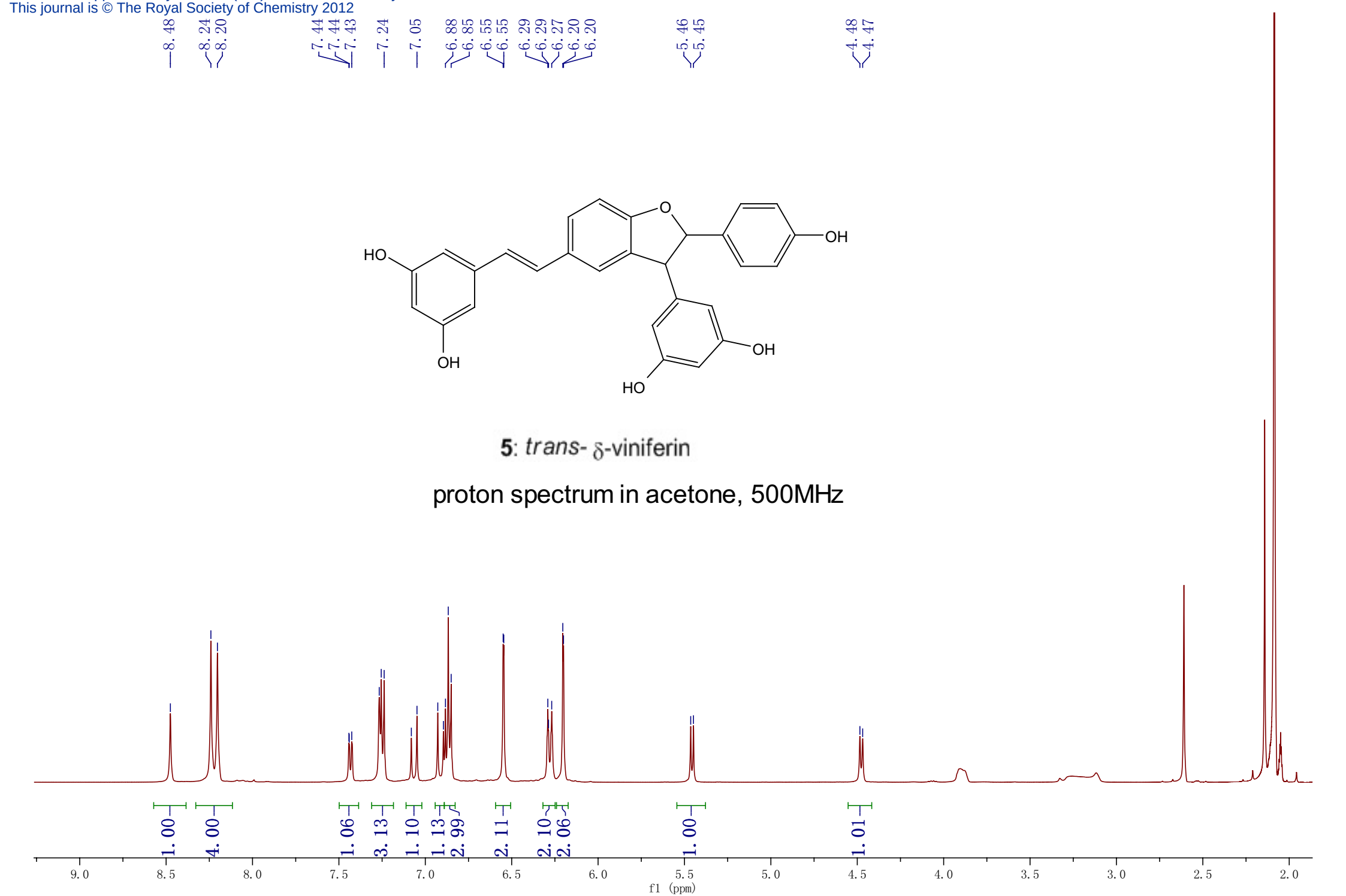


3: leachianols F

4: leachianols G

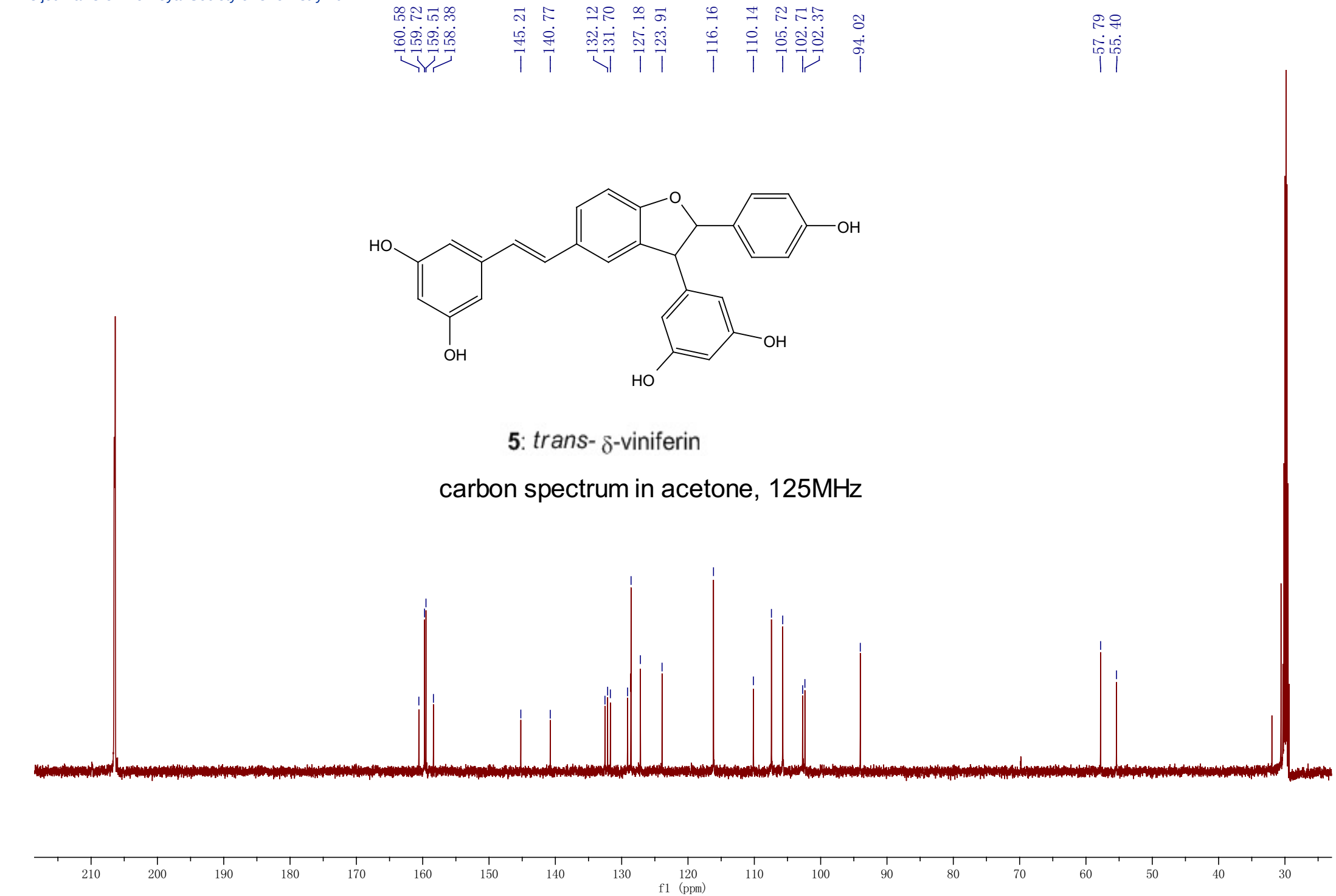
mixture of **3** and **4** (1:2)
DEPT-135 spectrum in acetone, 125 MHz





5: *trans*- δ-viniferin

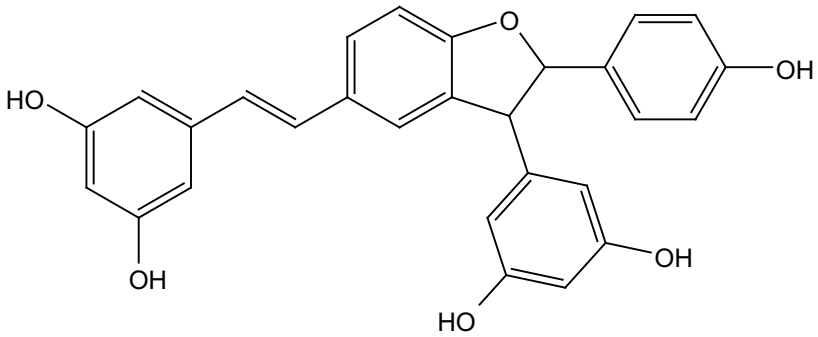
proton spectrum in acetone, 500MHz



5: *trans*- δ-viniferin

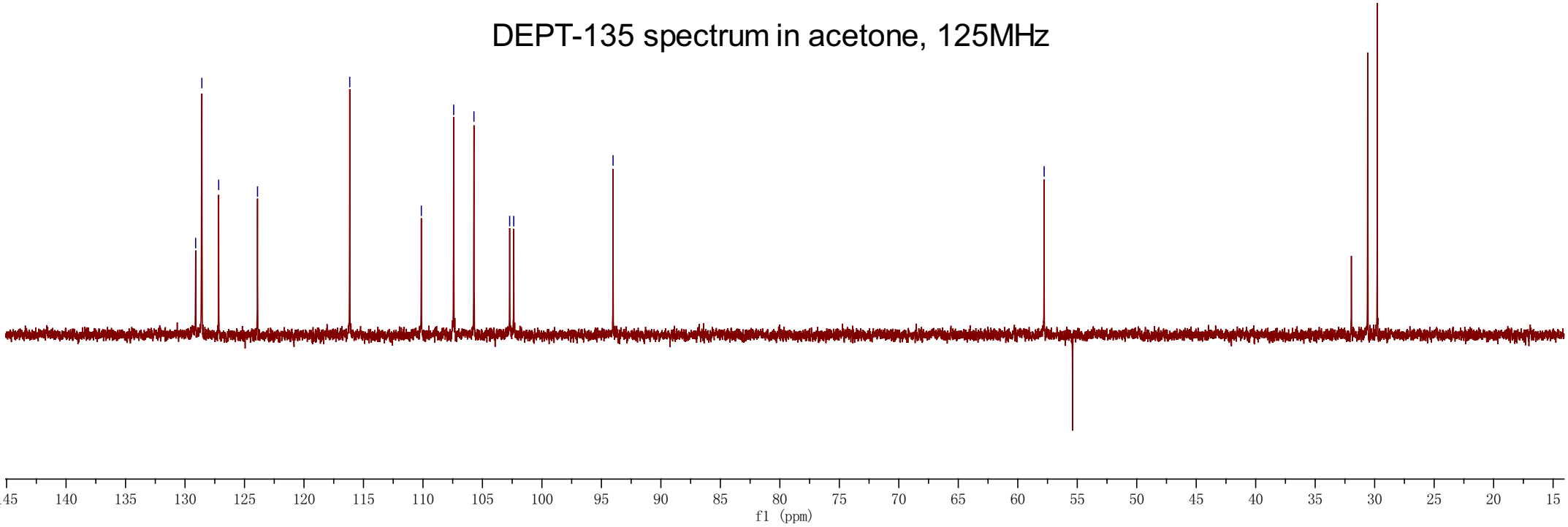
carbon spectrum in acetone, 125MHz

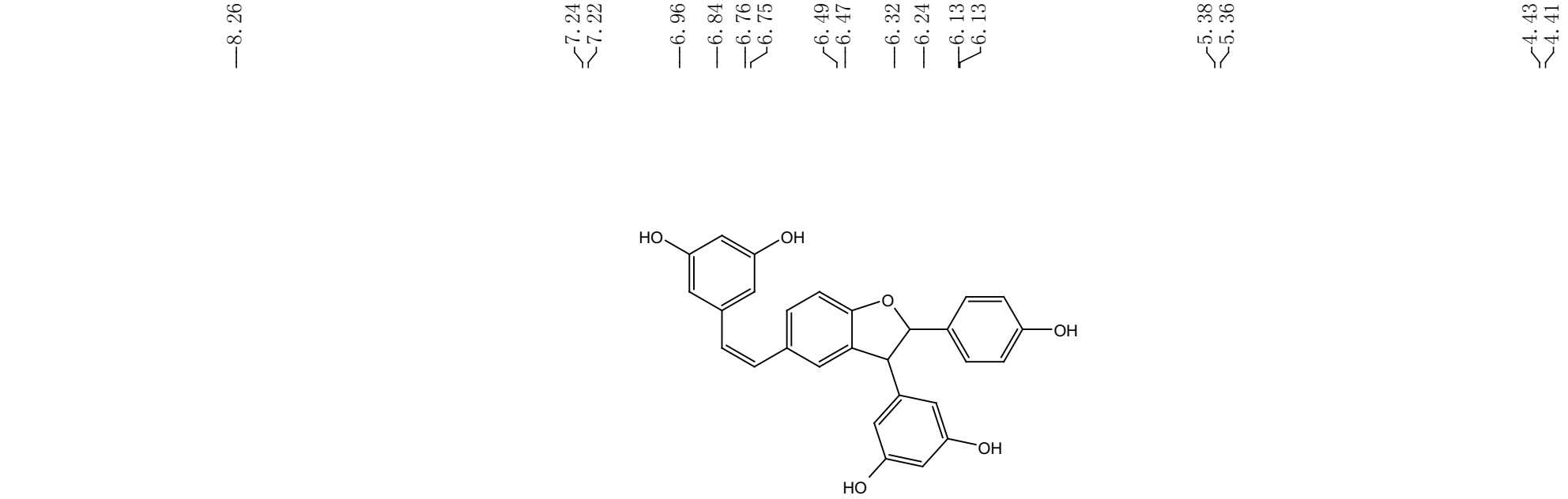
129.11
128.58
127.17
123.91
116.15
110.14
107.42
105.71
102.71
102.37
94.02
57.78



5: *trans*- δ-viniferin

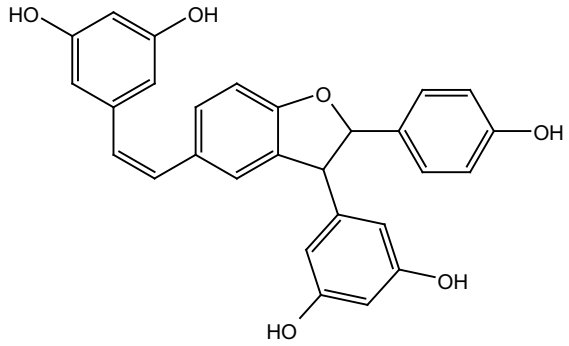
DEPT-135 spectrum in acetone, 125MHz



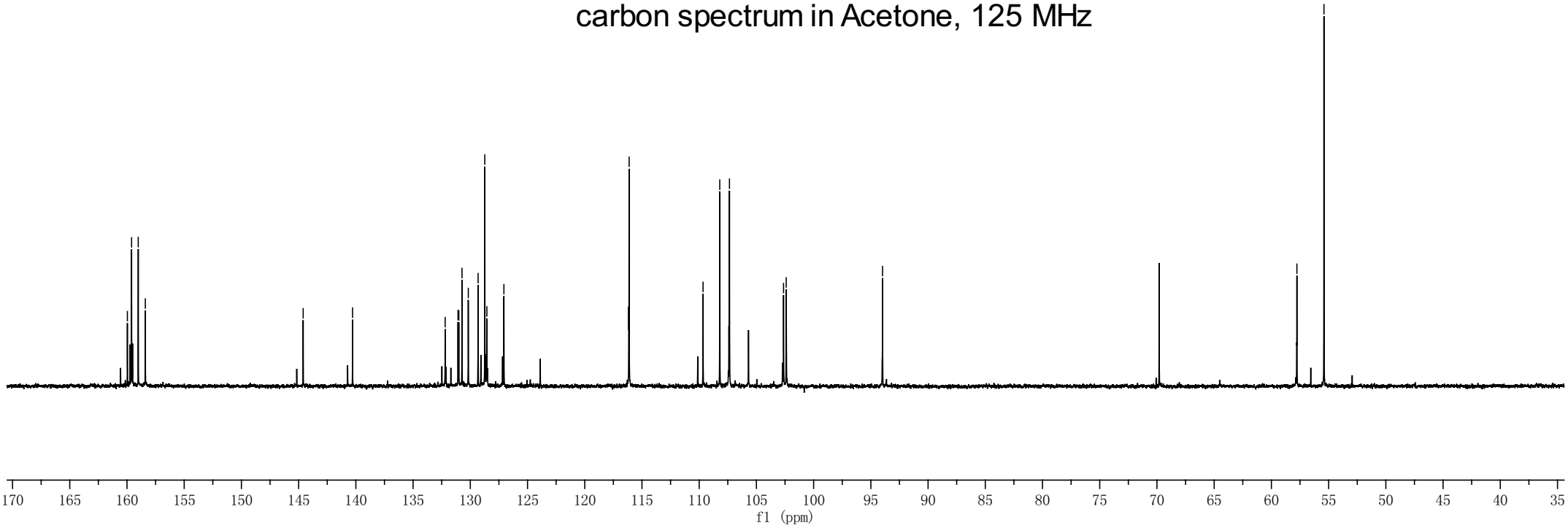


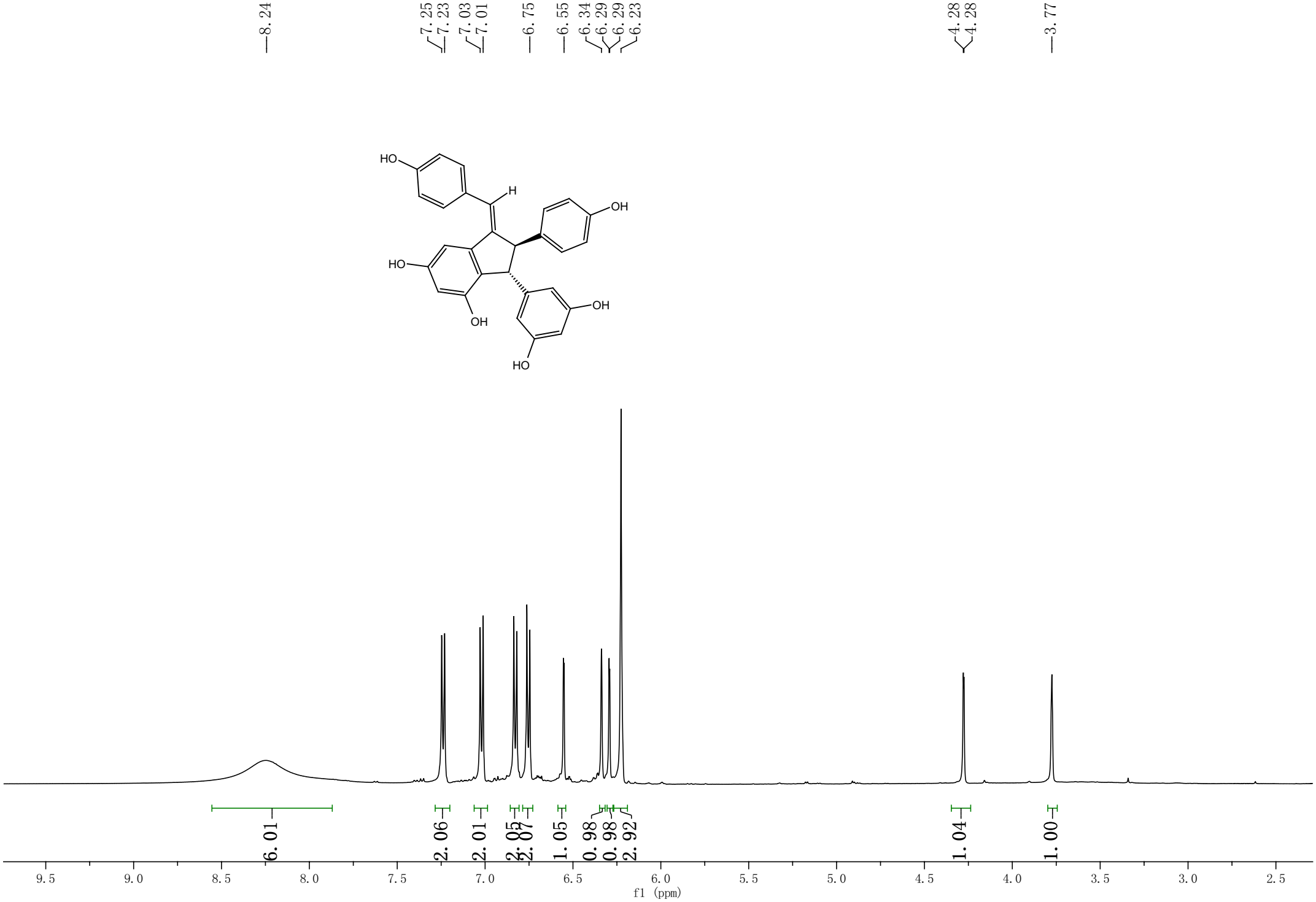
6 *cis*-δ-viniferin
proton spectrum in Acetone, 500 MHz

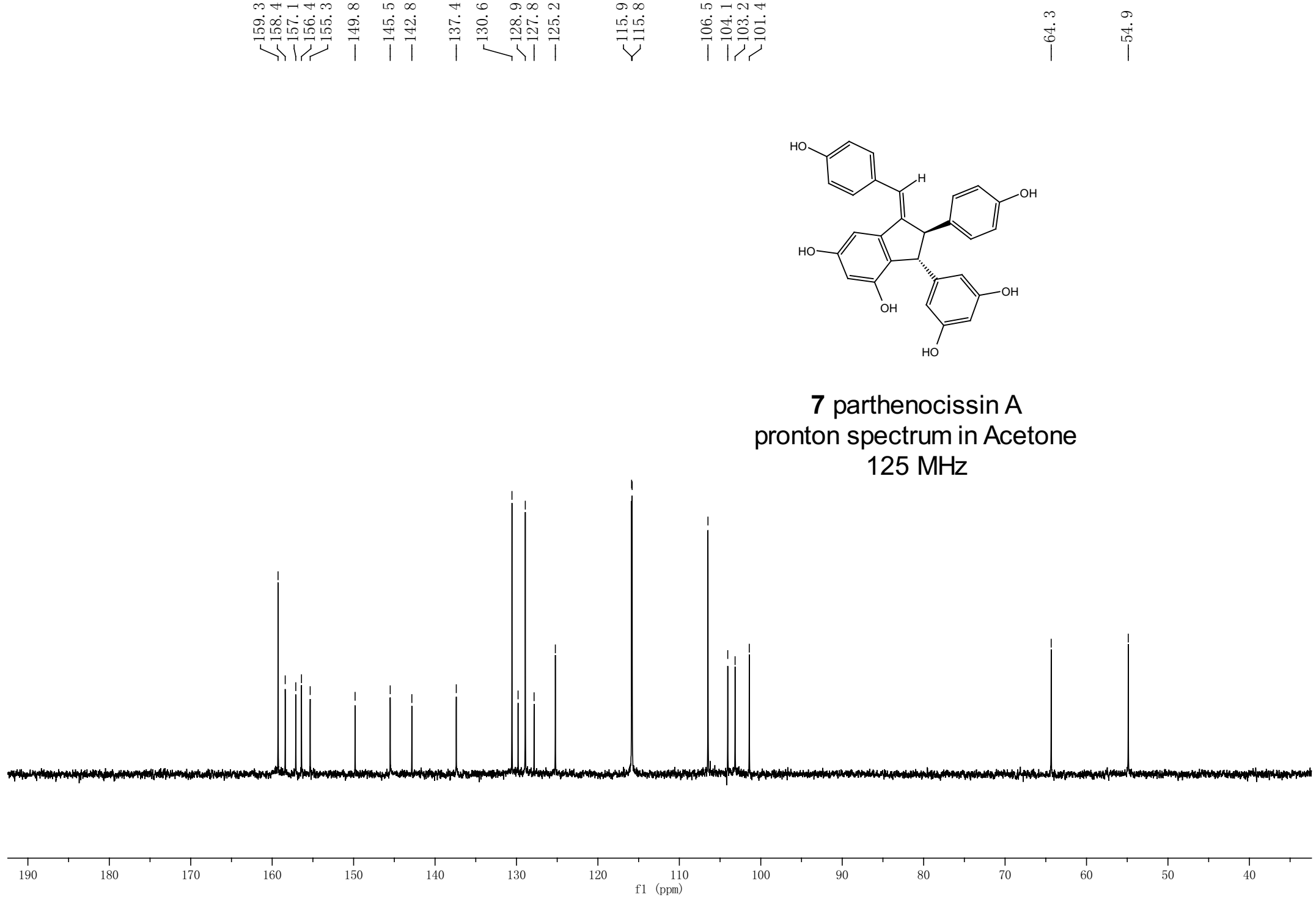
160.0
159.6
159.0
158.4
144.6
140.3
132.2
131.1
131.0
130.7
130.2
129.3
128.7
128.6
127.1
116.1
109.7
108.2
107.4
102.6
102.4
94.0
57.8
55.4

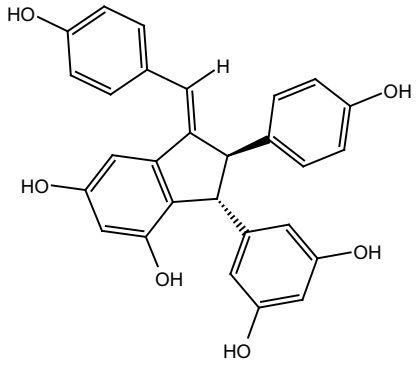


6 *cis*-δ-viniferin
carbon spectrum in Acetone, 125 MHz

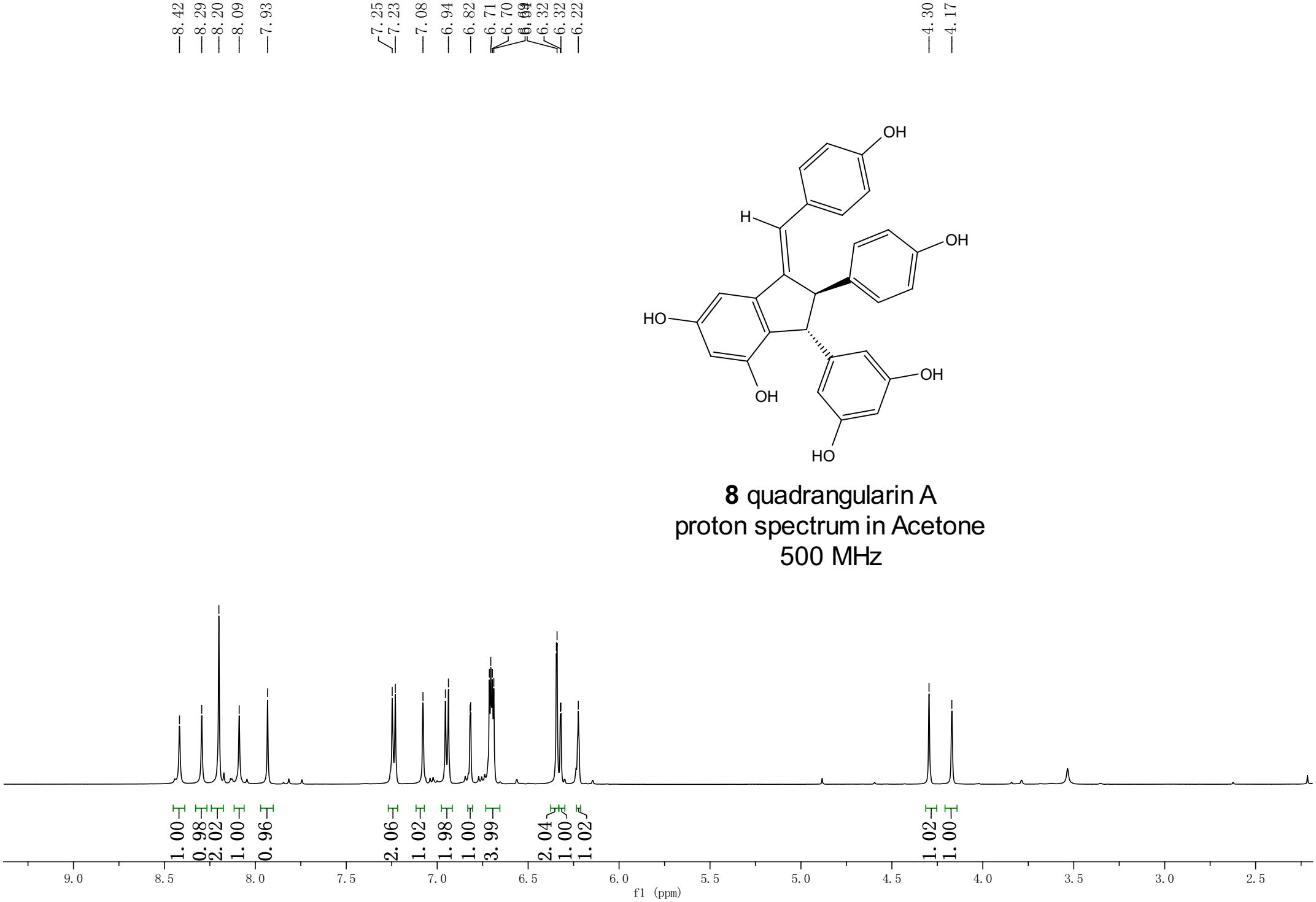




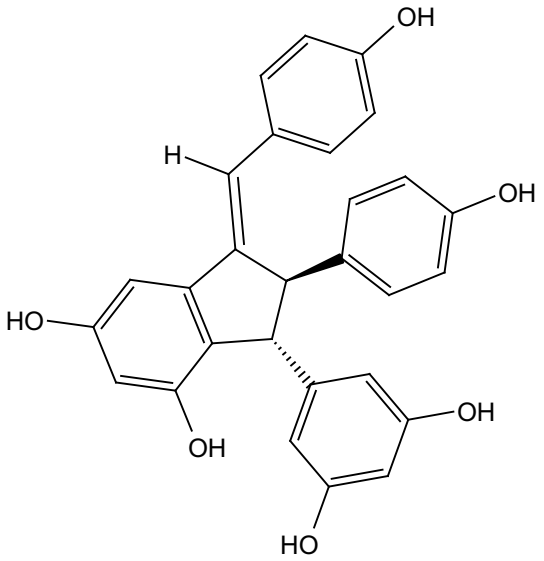




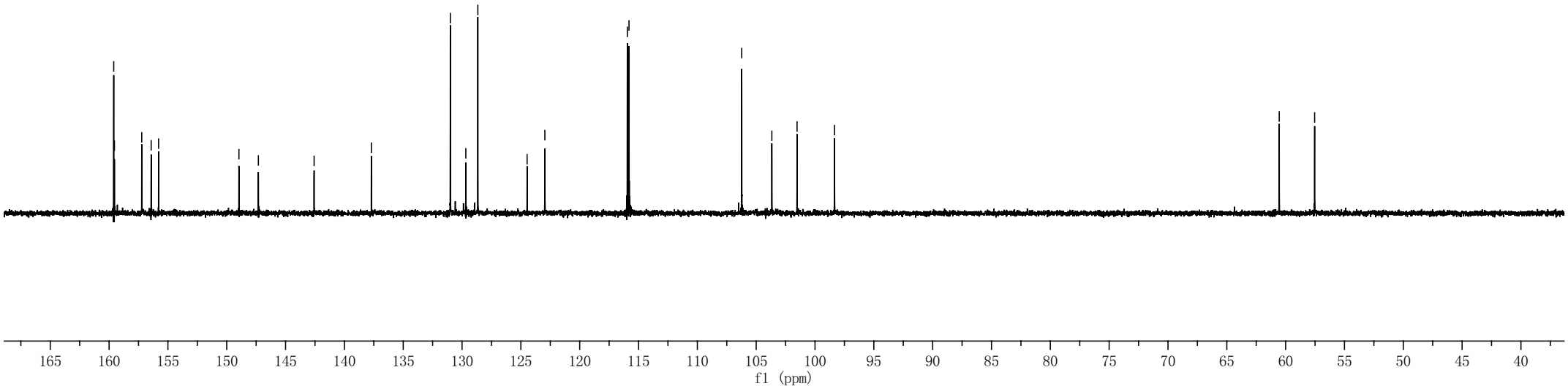
7 parthenocissin A
pronton spectrum in Acetone
125 MHz

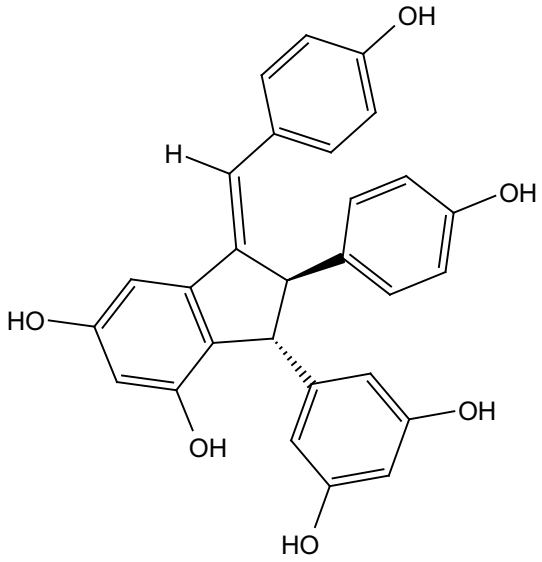


159.61
159.55
157.22
156.42
155.79
148.96
147.31
142.57
137.71
130.99
129.68
128.66
124.47
122.96
115.95
115.81
106.23
103.67
101.53
98.34
60.55
57.54

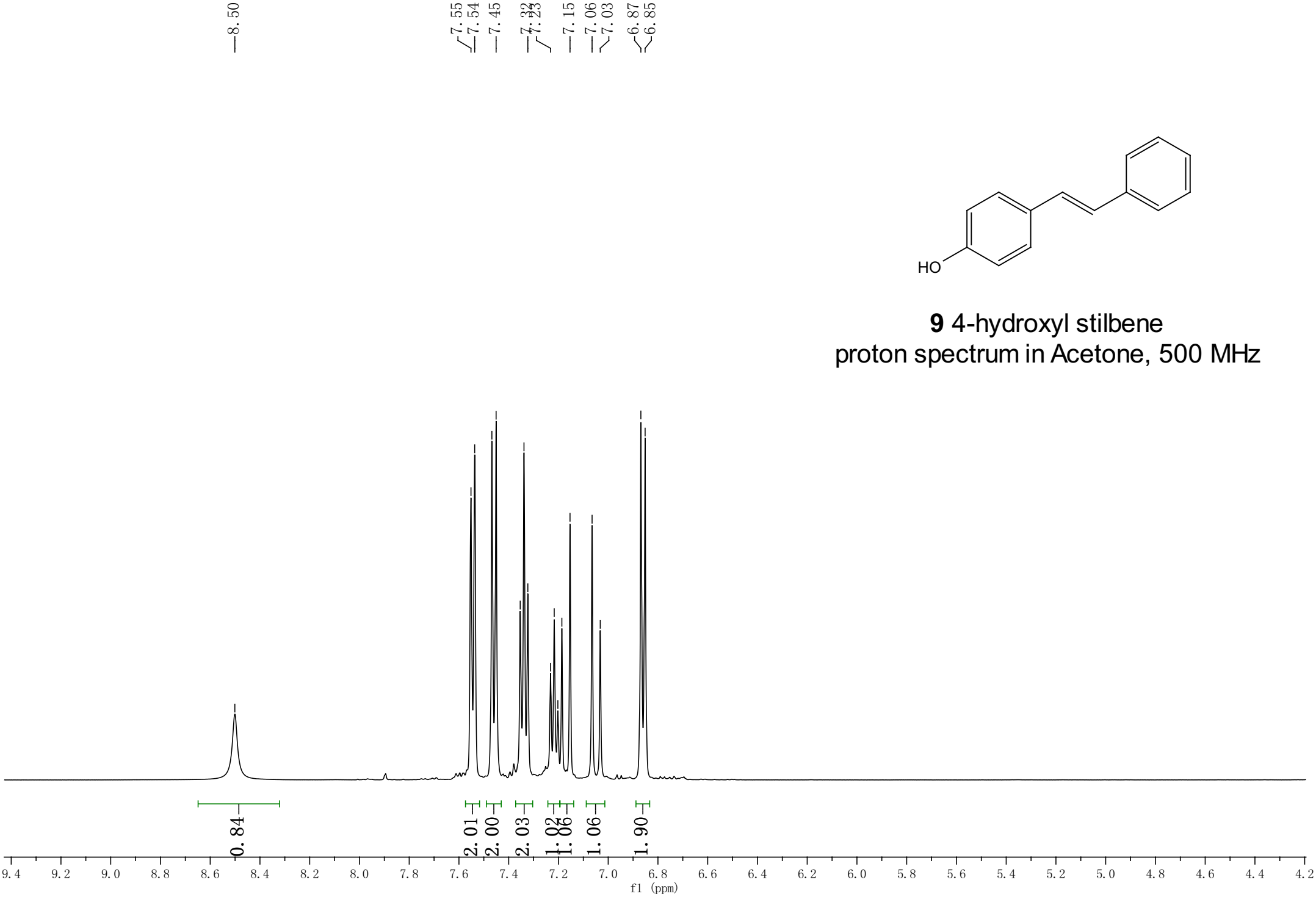


8 quadrangularin A
carbon spectrum in Acetone
125 MHz



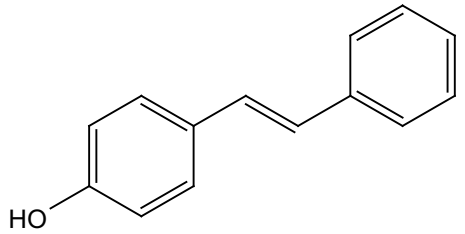


8 quadrangularin A
DEPT-135 spectrum in Acetone
125 MHz

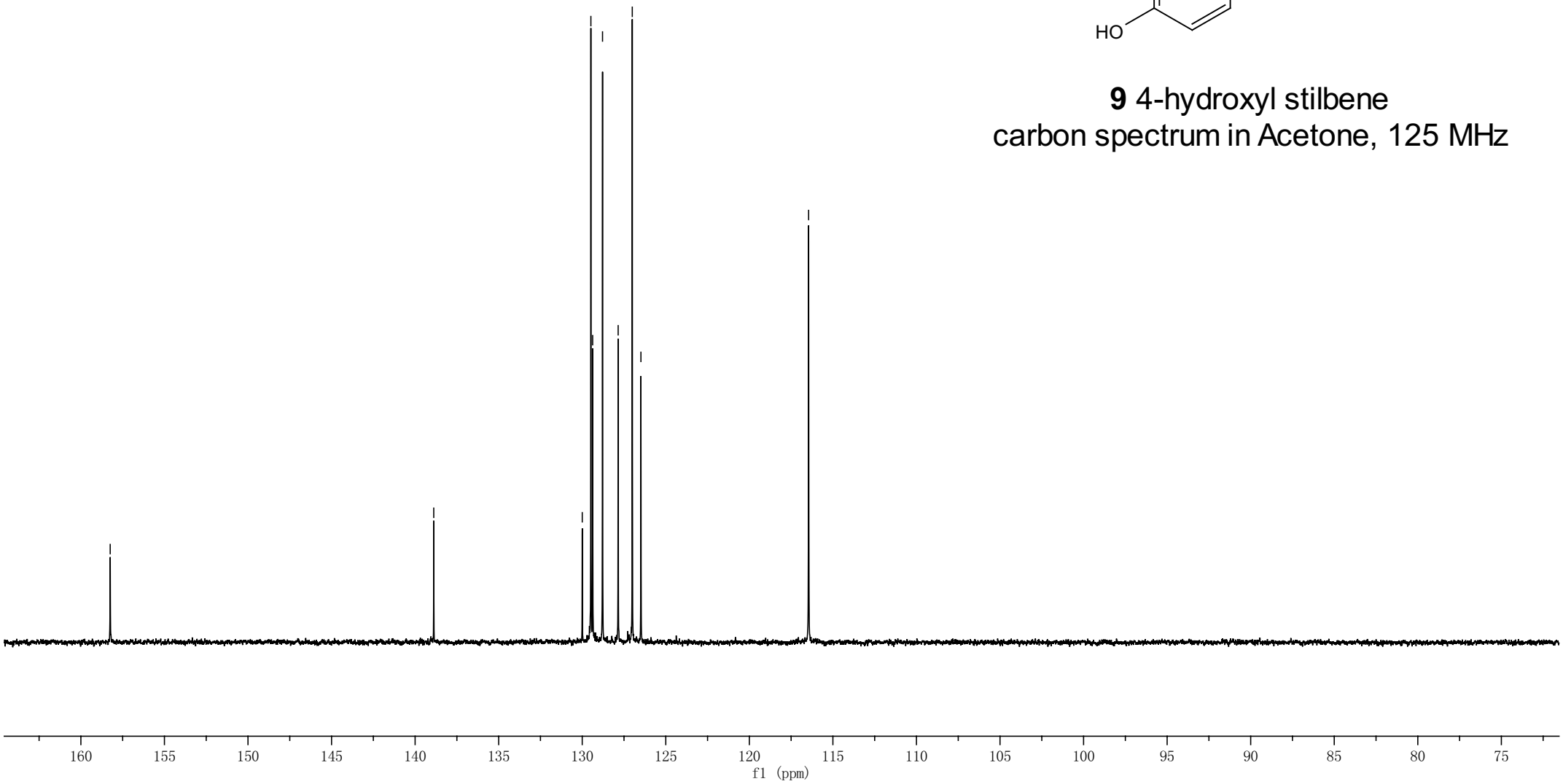


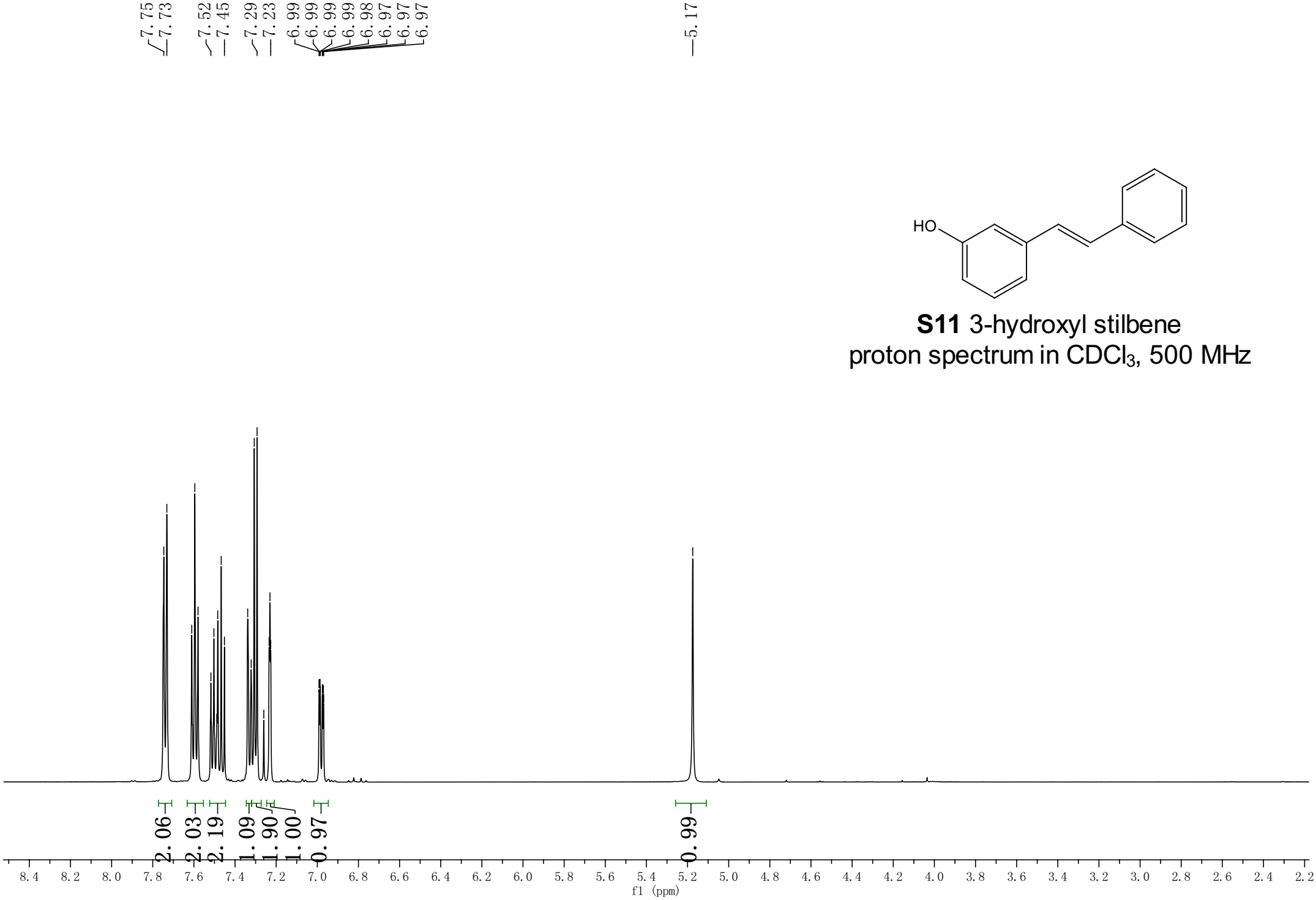
9 4-hydroxyl stilbene
proton spectrum in Acetone, 500 MHz

158.2
138.9
130.0
129.5
129.4
128.8
127.8
127.0
126.5
116.5

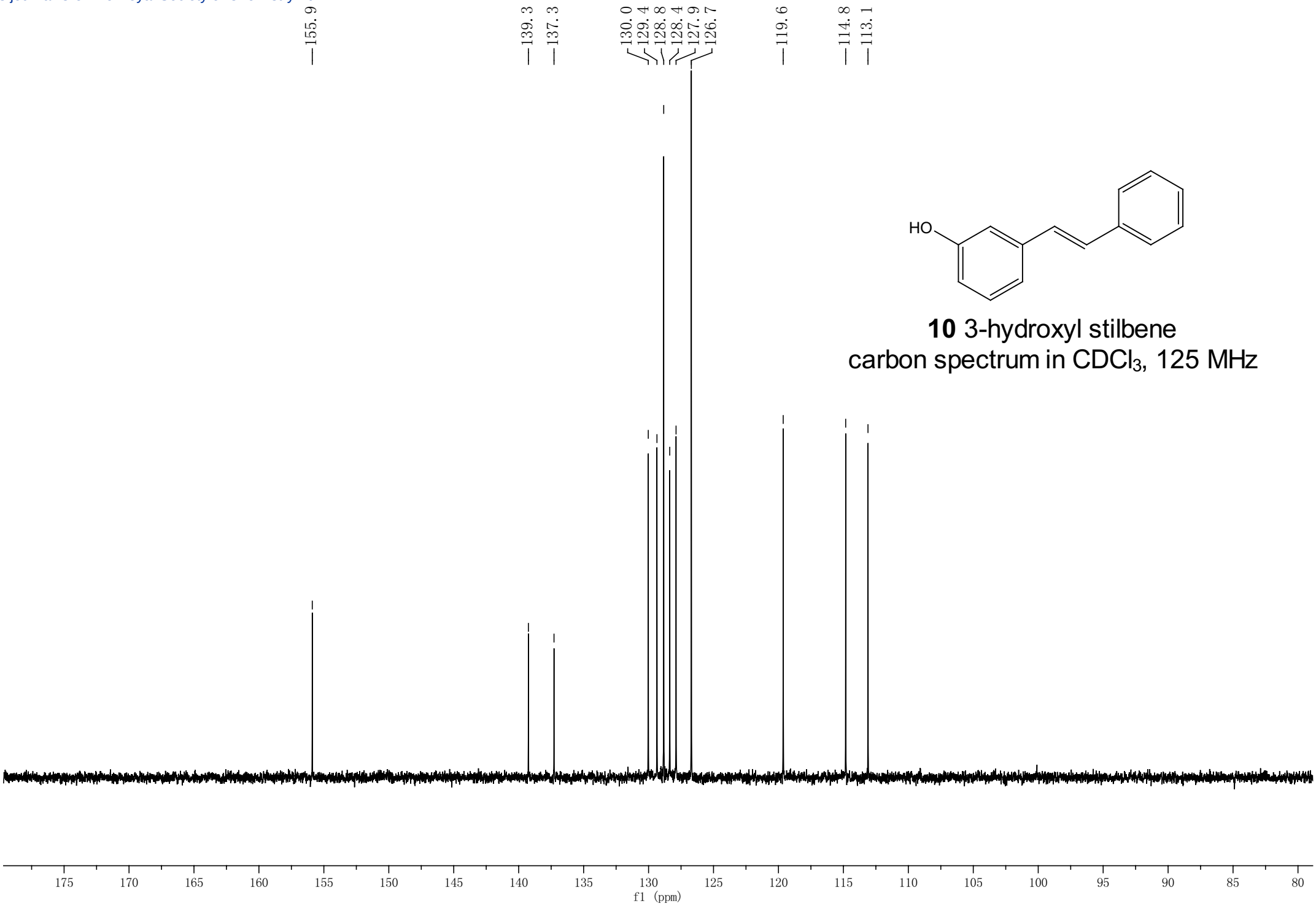


9 4-hydroxyl stilbene
carbon spectrum in Acetone, 125 MHz

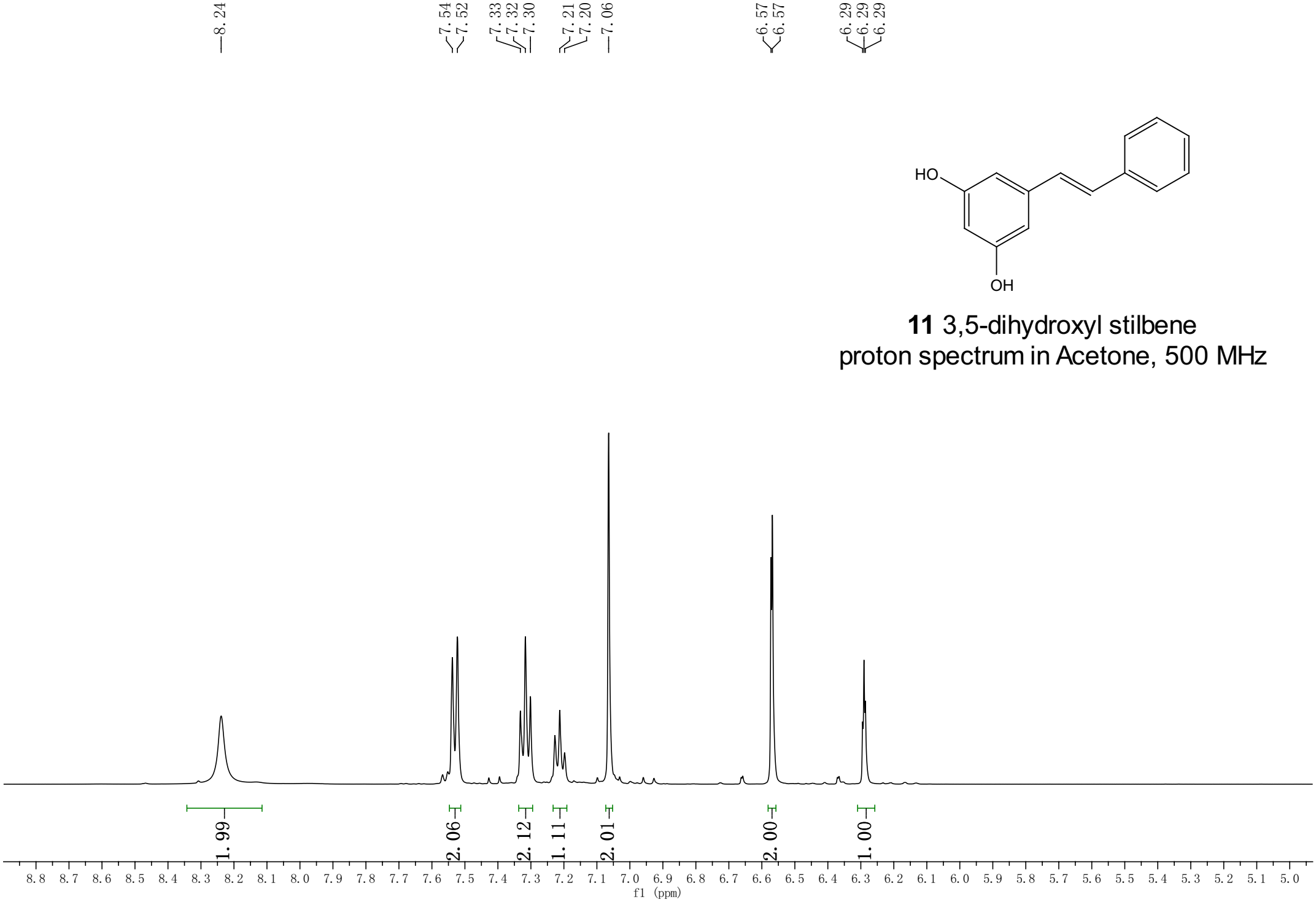




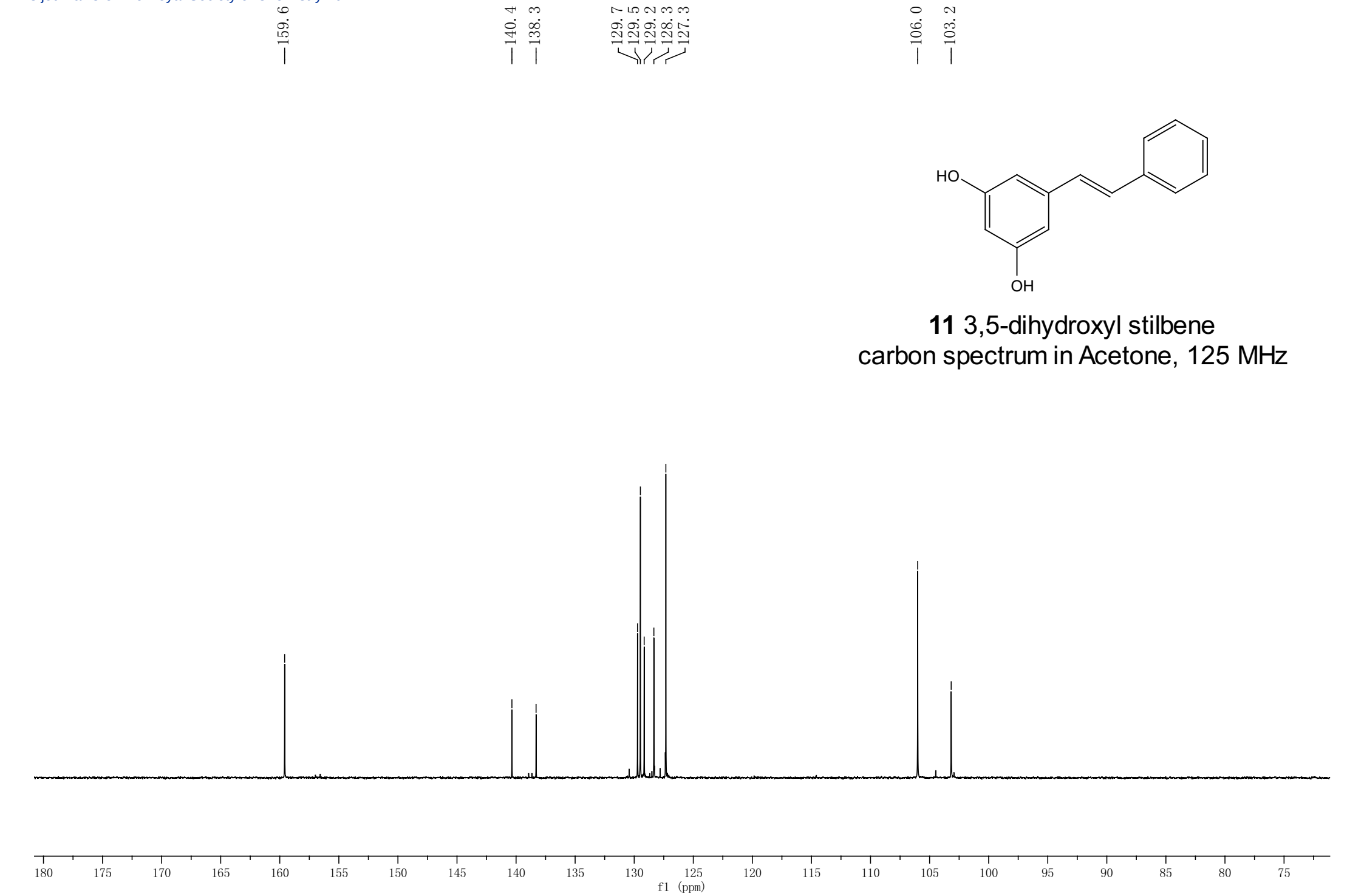
S11 3-hydroxyl stilbene
proton spectrum in $CDCl_3$, 500 MHz



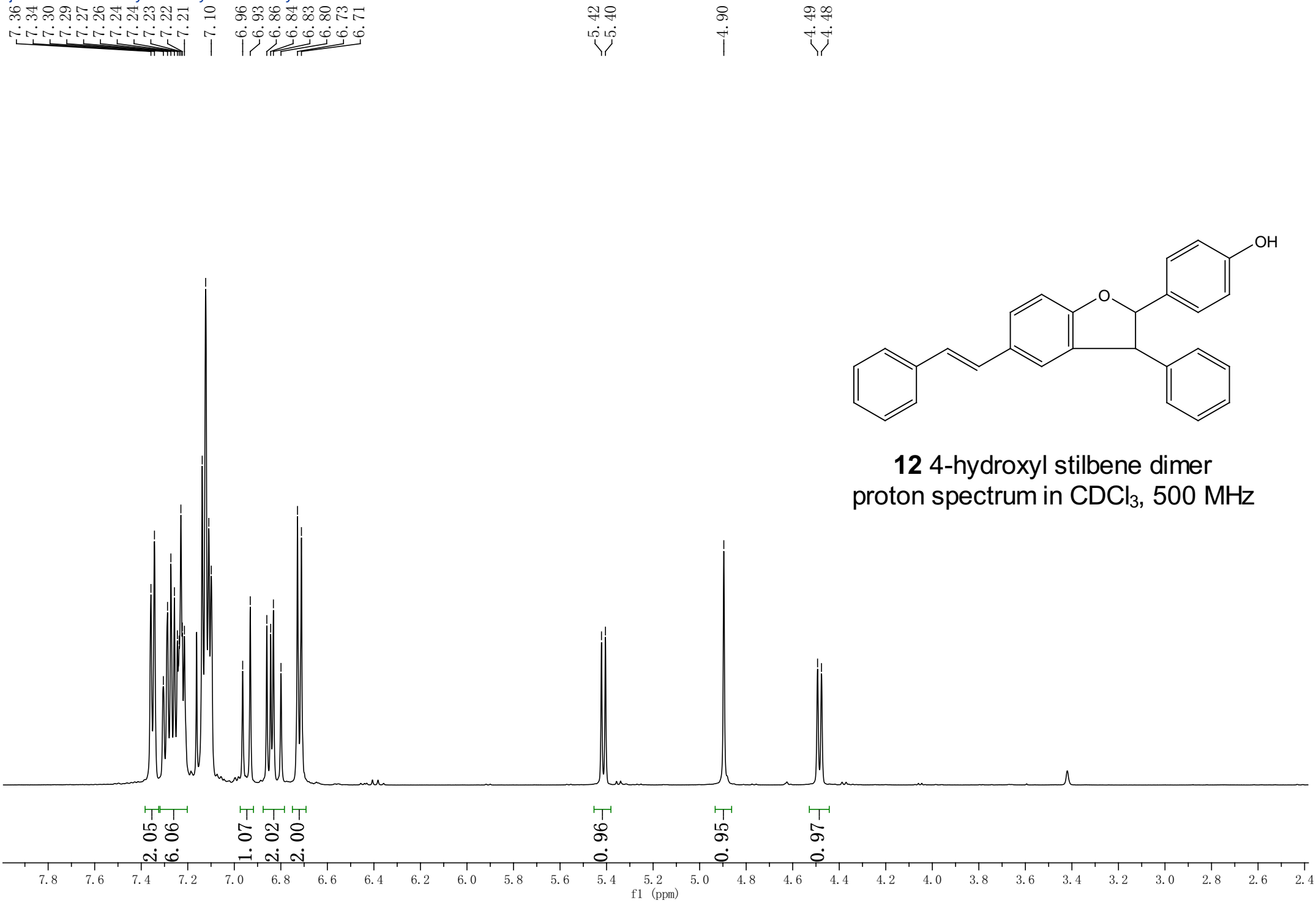
10 3-hydroxyl stilbene
carbon spectrum in $CDCl_3$, 125 MHz



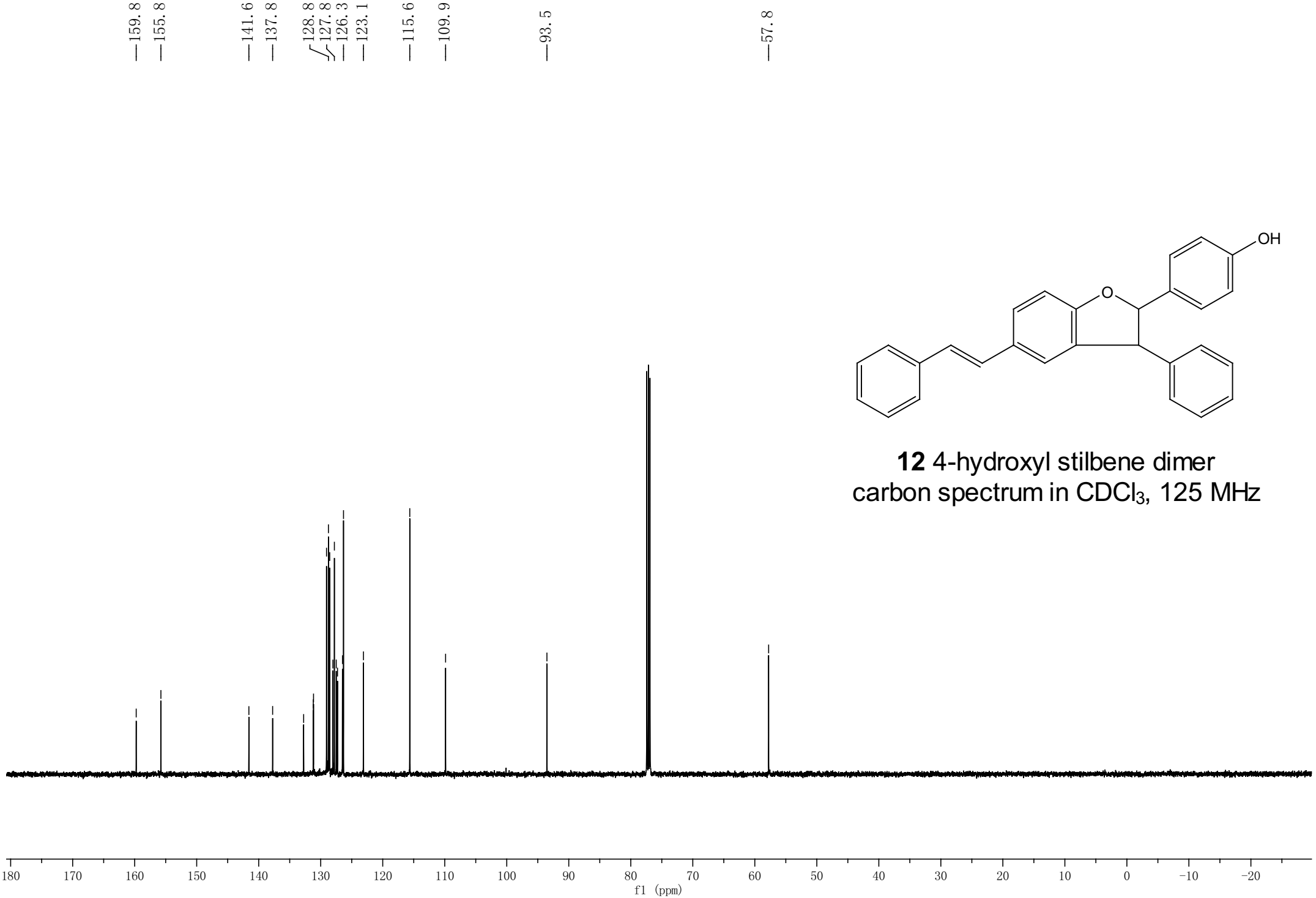
11 3,5-dihydroxyl stilbene
proton spectrum in Acetone, 500 MHz



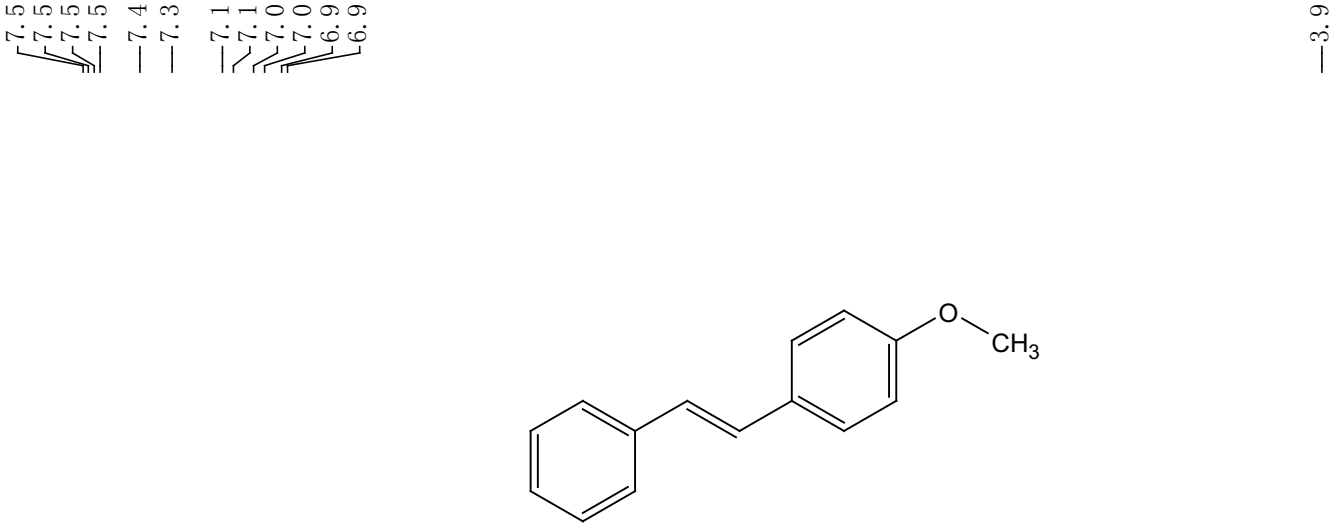
11 3,5-dihydroxyl stilbene
carbon spectrum in Acetone, 125 MHz



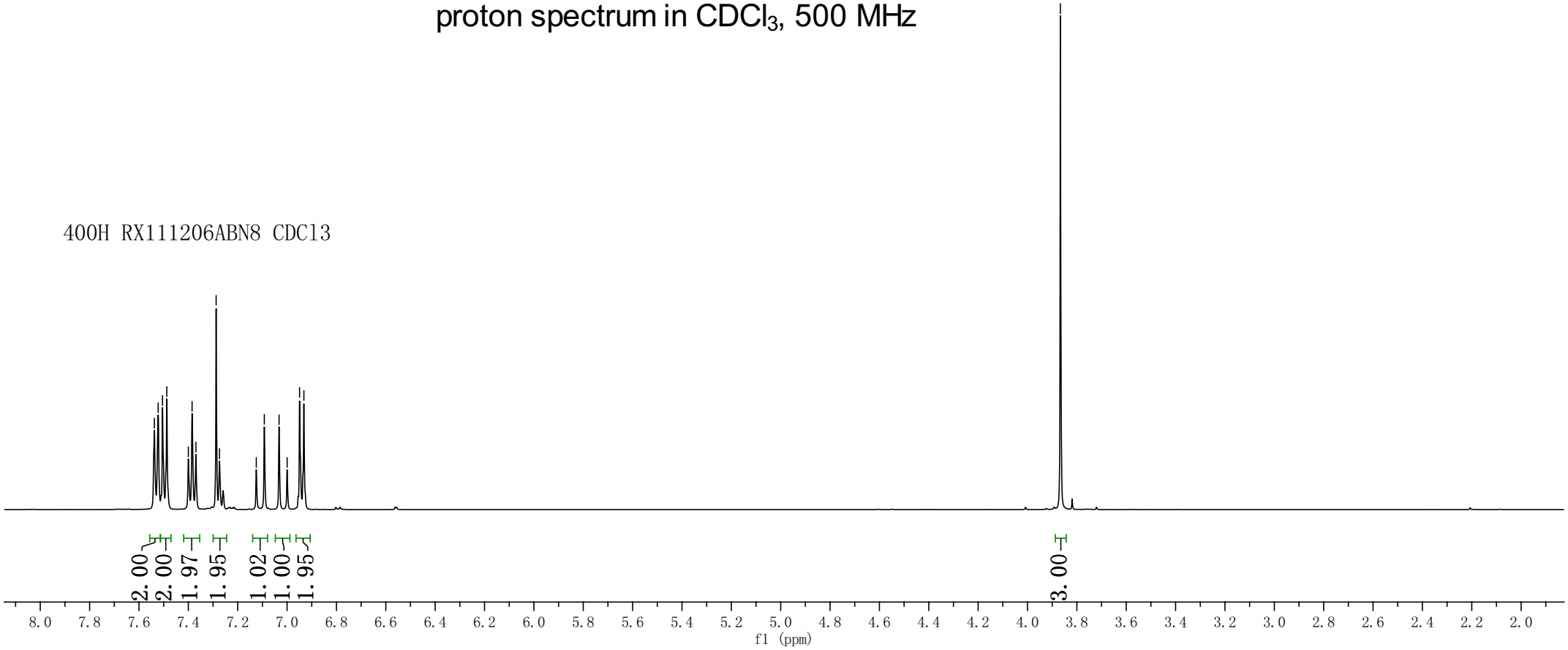
12 4-hydroxyl stilbene dimer
proton spectrum in $CDCl_3$, 500 MHz

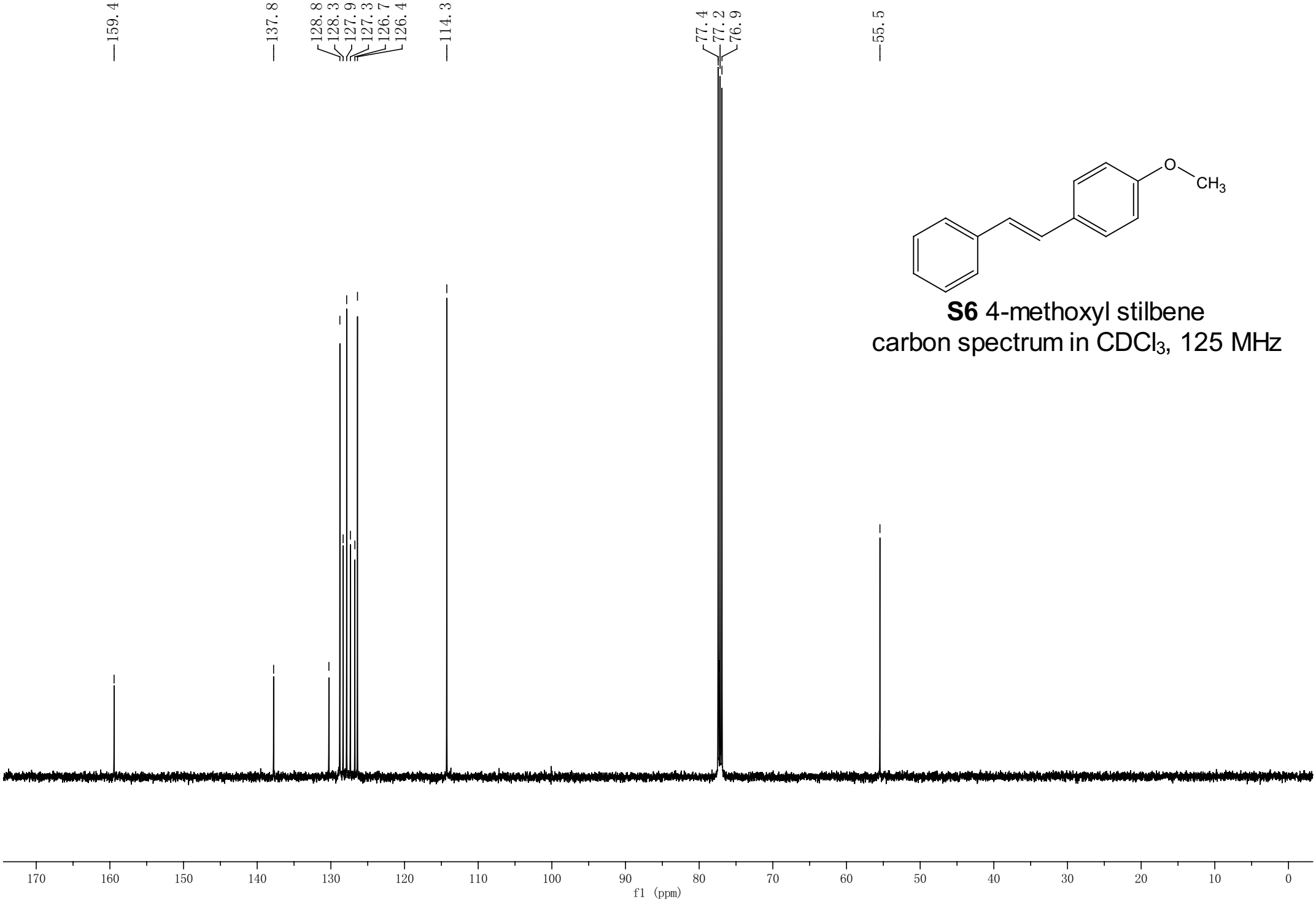


12 4-hydroxyl stilbene dimer
carbon spectrum in $CDCl_3$, 125 MHz

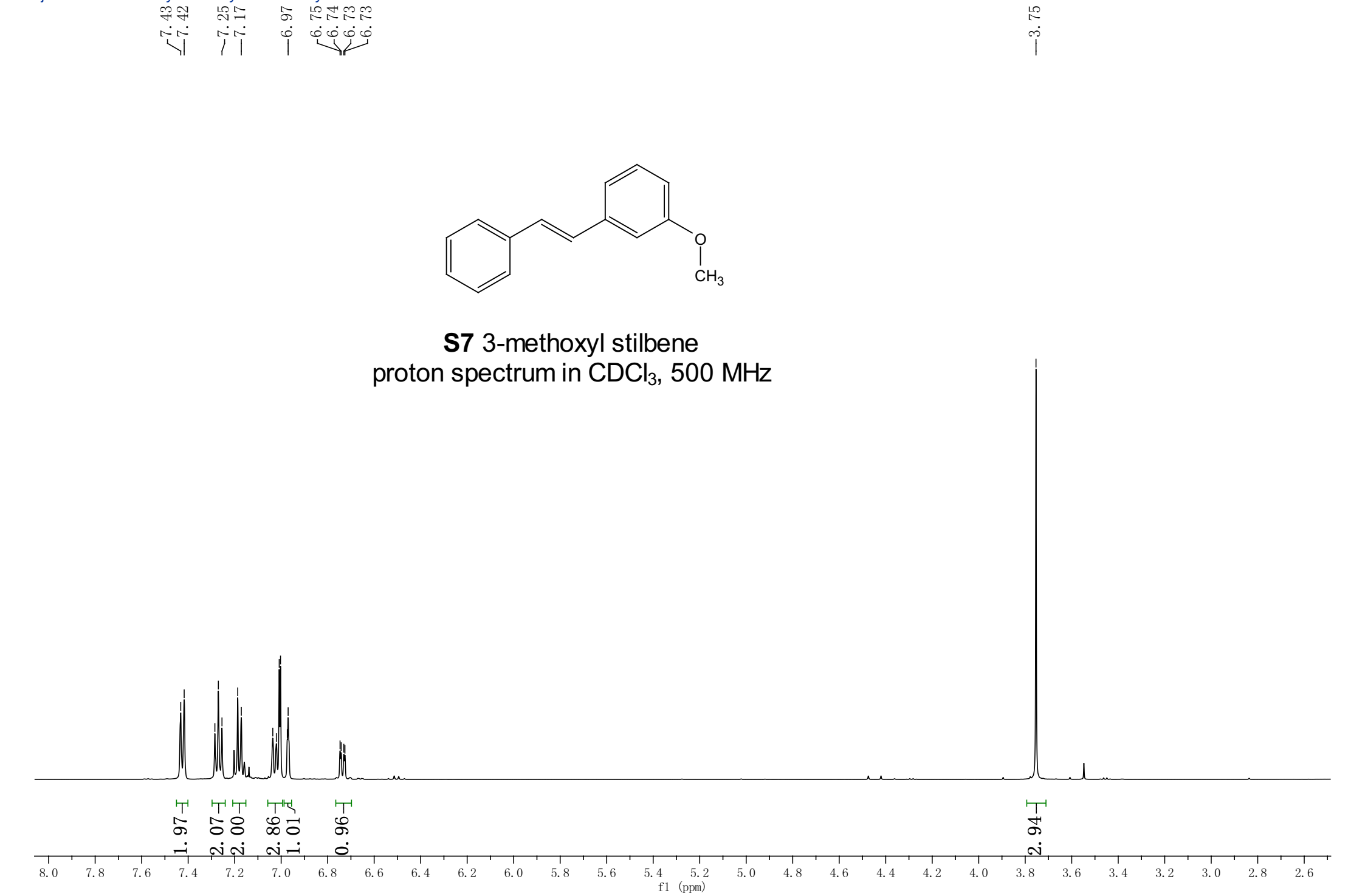


S6 4-methoxyl stilbene
proton spectrum in $CDCl_3$, 500 MHz

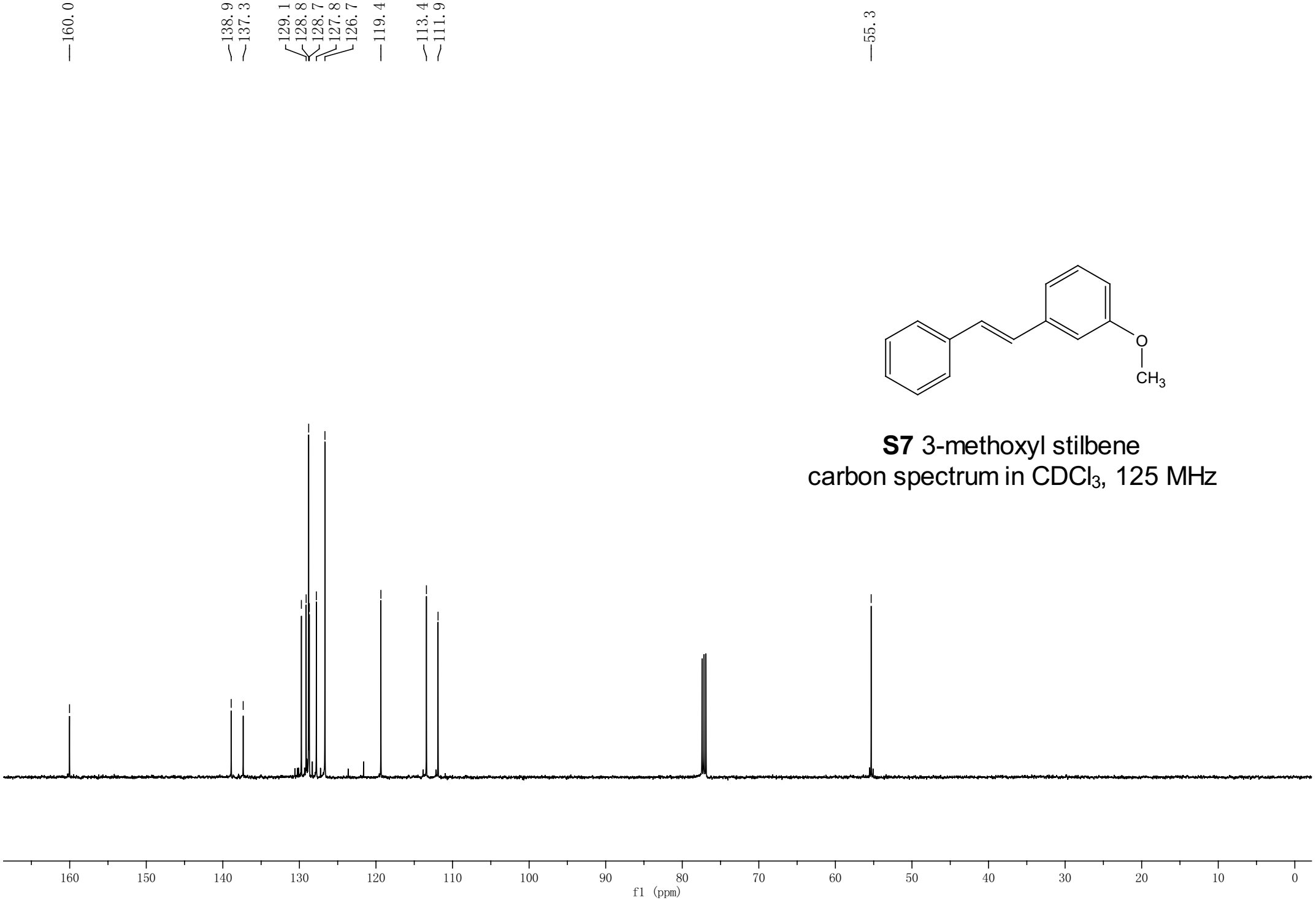




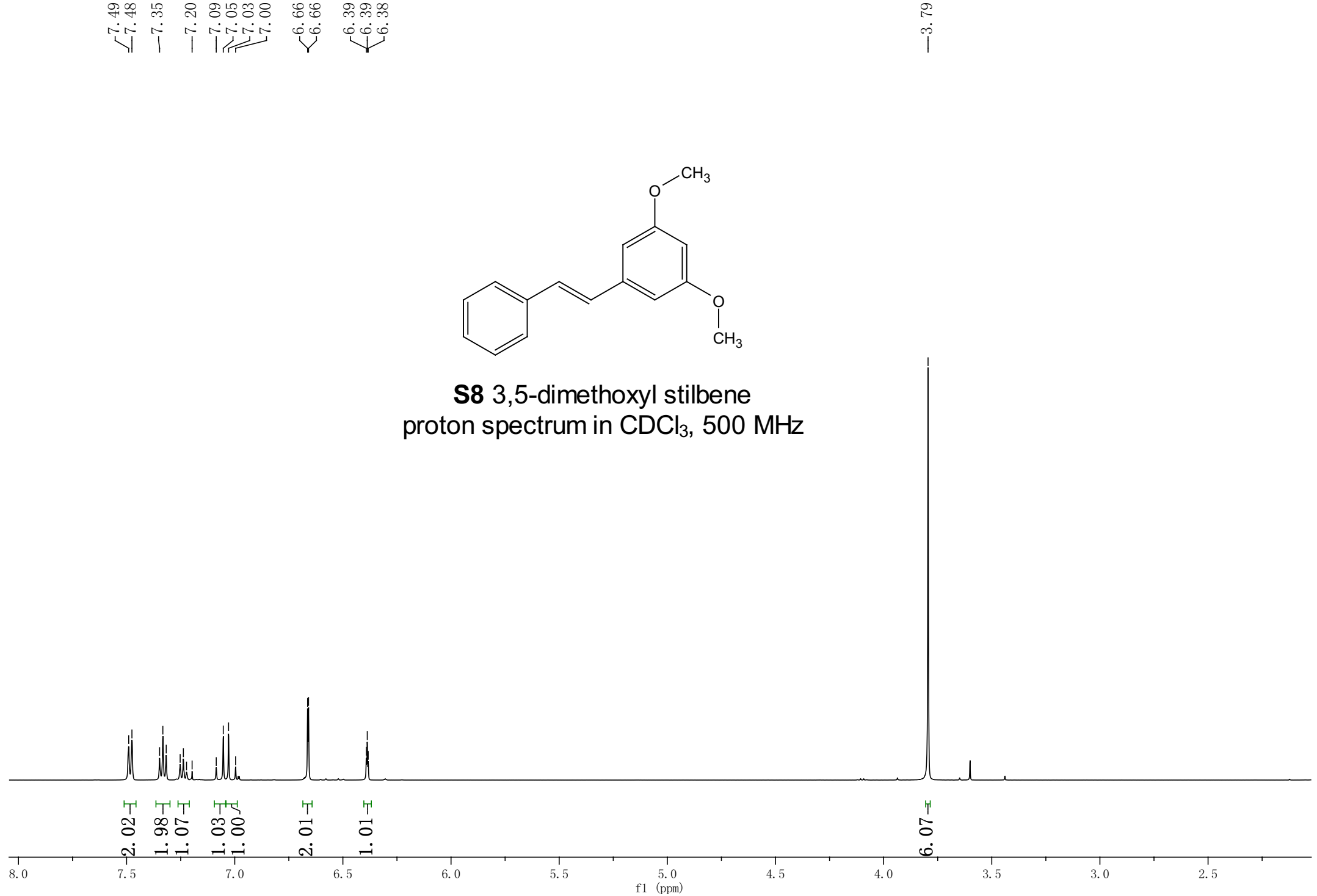
S6 4-methoxyl stilbene
carbon spectrum in $CDCl_3$, 125 MHz



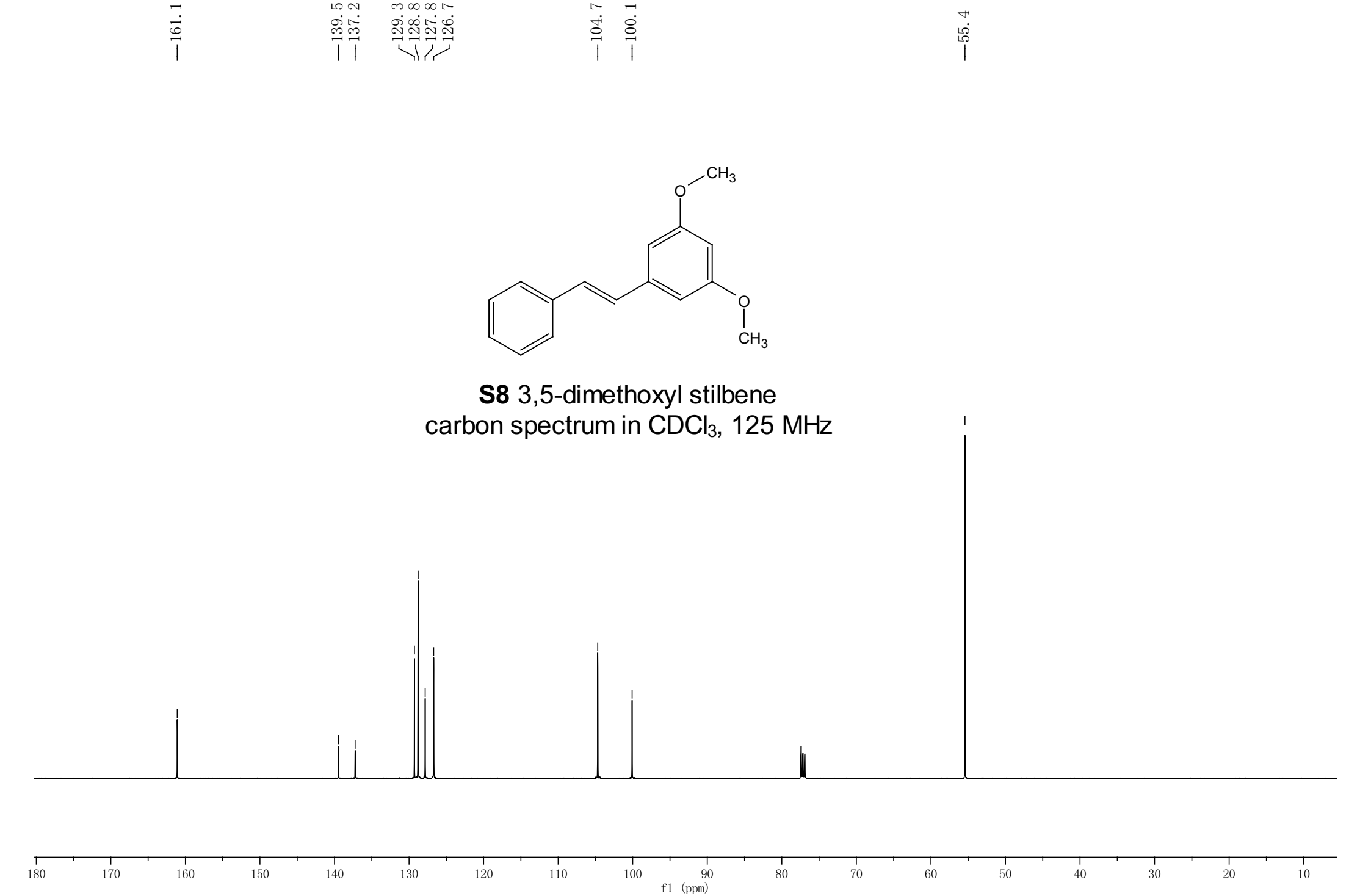
S7 3-methoxyl stilbene
proton spectrum in $CDCl_3$, 500 MHz



S7 3-methoxyl stilbene
carbon spectrum in $CDCl_3$, 125 MHz



S8 3,5-dimethoxyl stilbene
proton spectrum in $CDCl_3$, 500 MHz



S8 3,5-dimethoxyl stilbene
carbon spectrum in $CDCl_3$, 125 MHz