

Supporting Information

A Modular and Divergent Approach for the Total Synthesis of Elaeocarpus Alkaloids

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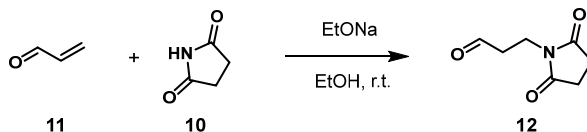
General information.

All moisture and oxygen sensitive reactions were performed in flame-dried glassware under a slight nitrogen overpressure. All reactions were stirred magnetically. Sensitive solutions, solvents or reagents were transferred via cannula or syringe. Reactions were monitored by thin-layer chromatography (TLC) or NMR of the crude mixture. Evaporations were conducted under reduced pressure at temperatures less than 35 °C, unless otherwise noted. Further dryings of the residues were accomplished using a high vacuum pump. All solvents were purchased as the highest available grade from Sinopharm Chemical, Damas-beta, Macklin, General Reagent. All other reagents were used as received from Energy Chemical, Sinopharm Chemical, Accela, Bidepharm, Macklin, 3Achem, unless otherwise noted. Thin-layer chromatography was carried out on pre-coated Leyan HPTLC Silica Gel 60 GF254 to monitor all reactions. The detection of spots was first performed by using a UV (254 nm) lamp followed by visualization by an iodine based TLC stain. Preparative column chromatography was performed with silica gel from SiliaFlash (0.040-0.063 μm , 240-400 mesh). All NMR spectra were measured on Bruker Avance III 400 or Avance III 500. Chemical shifts are given in ppm and referenced to the solvent residual peaks (Chloroform-*d* ^1H , $\delta = 7.26$ ppm, ^{13}C , $\delta = 77.16$ ppm, Methanol-*d*₄ ^1H , $\delta = 3.31$ ppm, ^{13}C , $\delta = 49.00$ ppm; Acetone-*d*₆ ^1H , $\delta = 2.05$ ppm, ^{13}C , $\delta = 29.84$ ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant *J*, integration. High-resolution mass spectra were measured on Agilent 1290/6545 UHPLC-QTOF/MS. Melting points were recorded on a SGWX-4A melting point apparatus (Shanghai instrument physical optics instrument Co., LTD.) and are uncorrected.

Experimental Procedures and Characterization Data

Compound 12

3-(2,5-dioxopyrrolidin-1-yl) propanal



The following protocols were applied according to that described in literature.^[1] Succinimide **10** (19.8 g, 200.0 mmol, 1.0 equiv) was added to a solution of EtONa (136 mg, 1 mol%) in absolute EtOH (40 mL) to give a white suspension. A solution of acrolein (13.5 mL, 1.0 equiv) in EtOH (40 mL) was then added at a rate such that the internal temperature was maintained below 30 °C (water bath). After additional 2 hours at room temperature, glacial acetic acid (0.8 mL) was added. The mixture was filtered over silica gel (20 g, 100-200 mesh), evaporated and purified by flash column chromatography (silica gel, 1:20 EtOAc:CH₂Cl₂) to give **12** as semipure viscous oil (21.4 g, 45% purity by NMR), which was directly used in the next step without further purification.

Compound S1

1-(3-hydroxy-5-(2-hydroxy-6-methylphenyl)-5-oxopentyl) pyrrolidine-2,5-dione



A solution of acetophenone **9** (5.2 g, 34.7 mmol, 1.0 equiv) in THF (70 mL) under argon was cooled to 0 °C and LDA (2.0 M in THF, 35.0 mL, 2.0 equiv) was added dropwise. After 1 hour, compound **12** (12.0 g, 1.0 equiv) was added dropwise. The resulting mixture was further stirred at 0 °C for 5 hours before quenched with saturated NH₄Cl (50 mL) and extracted with EtOAc (30 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, evaporated and purified by flash column chromatography (silica gel, 1:50 MeOH:CH₂Cl₂) to afford compound **S1** (8.7 g, 82%).

Physical State: yellow oil.

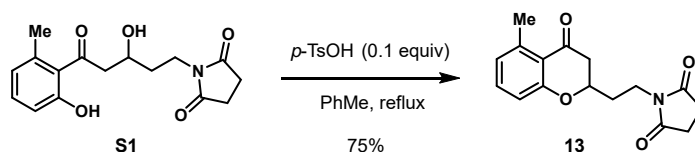
¹H NMR (400 MHz, Chloroform-*d*): δ 7.20 (t, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.69 (d, *J* = 7.5 Hz, 1H), 4.22 – 4.14 (m, 1H), 3.72 – 3.66 (m, 2H), 3.16 (dd, *J* = 16.8, 8.9 Hz, 1H), 2.87 (dd, *J* = 16.7, 3.2 Hz, 1H), 2.71 (s, 4H), 2.42 (s, 3H), 1.82 – 1.71 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 207.3, 178.1, 159.4, 138.2, 133.6, 124.4, 123.1, 116.0, 66.2, 50.7, 35.5, 34.5, 28.3, 22.9.

HRMS (ESI-TOF): calculated for C₁₆H₂₀NO₅⁺ [M+H]⁺: 306.1336; found: 306.1332.

Compound 13

1-(2-(5-methyl-4-oxochroman-2-yl) ethyl) pyrrolidine-2,5-dione



Compound **S1** (11.7 g, 38.4 mmol, 1.0 equiv), *p*-TsOH (730 mg, 0.1 equiv) and toluene (150 mL) were successively added to a Dean-stark apparatus equipped with a stir bar and the mixture was heated at reflux for 3 hours. After cooled to room temperature, the reaction mixture was neutralized with saturated NaHCO₃ (30 mL) and extracted with CH₂Cl₂ (100 mL × 3). The combined organic layers were dried over anhydrous Na₂SO₄, evaporated and purified by flash column chromatography (silica gel, 1:1 EtOAc:PE) to afford **13** (8.27 g, 75%).

Physical State: yellow oil.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.29 (t, *J* = 7.9 Hz, 1H), 6.79 (t, *J* = 8.3 Hz, 2H), 4.45 – 4.36 (m, 1H), 3.85 – 3.70 (m, 2H), 2.78 – 2.63 (m, 2H), 2.71 (s, 4H), 2.60 (s, 3H), 2.16 – 2.05 (m, 1H), 2.02 – 1.93 (m, 1H).

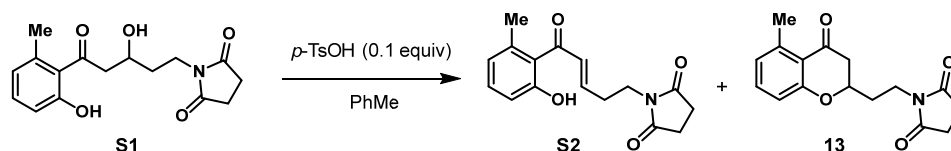
¹³C NMR (101 MHz, Chloroform-*d*): δ 193.0, 177.0, 162.1, 141.7, 134.4, 124.5, 119.3, 115.6, 74.9, 43.9, 34.9, 32.3, 28.0, 22.6.

HRMS (ESI-TOF): calculated for C₁₆H₁₈NO₄⁺ [M+H]⁺: 288.1230; found: 288.1230.

Compound S2

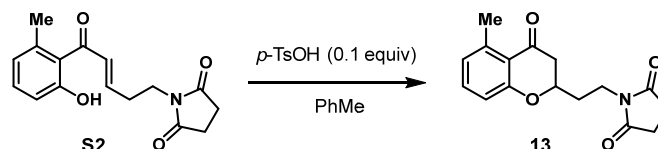
(*E*)-1-(5-(2-hydroxy-6-methylphenyl)-5-oxopent-3-en-1-yl)pyrrolidine-2,5-dione

Hydroxyketone **S1** undergoes a dehydration/oxa-Michael process to afford chromaone **13**. Enone **S2** was identified as the intermediate. Control experiments showed that the reaction is temperature dependent.



Entry	Temperature	Time	S1/S2/13 (%) ^a
1	80 °C	1 h	49/36/trace
2	80 °C	2 h	31/58/trace
3	100 °C	1 h	6/25/50

^aDetermined by crude ¹H NMR using (CHCl₂)₂ as an internal standard



Entry	Temperature	Time	S2/13 (%) ^a
1	80 °C	1 h	>95/trace
2	100 °C	1 h	15/83

^aDetermined by crude ¹H NMR using (CHCl₂)₂ as an internal standard

Physical State: yellow oil.

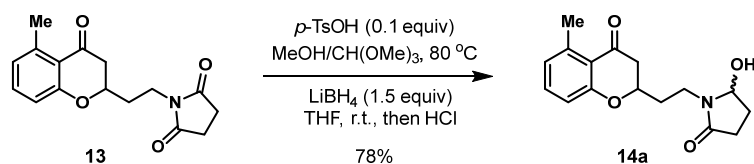
¹H NMR (500 MHz, Chloroform-*d*): δ 10.29 (s, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 6.82 (dt, *J* = 15.1, 6.9 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 6.64 (dt, *J* = 15.4, 1.4 Hz, 1H), 3.70 (t, *J* = 7.1 Hz, 2H), 2.70 (s, 4H), 2.60 (qd, *J* = 7.1, 1.4 Hz, 2H), 2.44 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*): δ 196.8, 177.1, 160.2, 143.6, 138.3, 133.8, 133.1, 123.1, 122.9, 115.5, 37.2, 30.8, 28.3, 22.9.

HRMS (ESI-TOF): calculated for C₁₆H₁₈NO₄⁺ [M+H]⁺: 288.1230; found: 288.1225.

Compound 14a

5-hydroxy-1-(2-(5-methyl-4-oxochroman-2-yl) ethyl) pyrrolidin-2-one



A mixture of compound **13** (2.18 g, 7.6 mmol, 1.0 equiv) and *p*-TsOH (144 mg, 0.1 equiv) in MeOH (16 mL) and CH(OMe)₃ (32 mL) was heated at 80 °C. After complete consumption of **13** as indicated by TLC, solvents were removed under reduced pressure. The residual was then redissolved in THF (38 mL) and added to a solution of LiBH₄ (250 mg, 11.4 mmol, 1.5 equiv) in THF (12 mL) under argon at room temperature. After 5 hours, the reaction was quenched with saturated NH₄Cl and extracted with EtOAc (50 mL × 3). The organic layers were combined, washed with brine (100 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was redissolved in THF (38 mL), and concentrated HCl (4 mL) was added. After stirring at room temperature for 1 hour, the mixture was neutralized with saturated NaHCO₃ (100 mL) and extracted with CH₂Cl₂ (50 mL × 3). The organic layers were combined, dried over anhydrous Na₂SO₄, evaporated and purified by flash column chromatography (silica gel, 2:1 EtOAc:PE) to afford hemiaminal **14a** (1.71 g, 78%) as mixture of diastereomers.

Physical State: yellow oil.

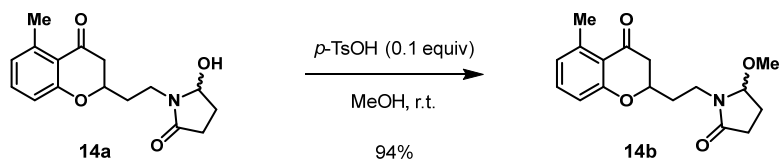
¹H NMR (400 MHz, Chloroform-*d*): δ 7.29 (dd, *J* = 8.3, 7.5 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 5.25 (t, *J* = 6.4 Hz, 1H), 4.53 – 4.37 (m, 1H), 3.94 (d, *J* = 8.0 Hz, 0.55H), 3.87 (d, *J* = 7.9 Hz, 0.45H), 3.67 – 3.46 (m, 2H), 2.76 – 2.61 (m, 2H), 2.60 (s, 3H), 2.58 – 2.51 (m, 1H), 2.39 – 2.25 (m, 2H), 2.15 – 1.88 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 193.84 (193.76), 175.21 (175.18), 162.44 (162.38), 142.25 (142.24), 134.9, 124.91 (124.90), 119.6, 115.9 (115.8), 84.1 (83.8), 75.2, 44.43 (44.40), 36.92 (36.85), 33.2 (33.0), 29.02 (28.99), 28.6 (28.5), 22.9. (The data in parentheses are peaks observed for diastereomers)

HRMS (ESI-TOF): calculated for C₁₆H₁₉NNaO₄⁺ [M+Na]⁺: 312.1206; found: 312.1201.

Compound 14b

5-methoxy-1-(2-(5-methyl-4-oxochroman-2-yl) ethyl) pyrrolidin-2-one



To a 250 mL flask equipped with a stir bar were added hemiaminal **14a** (1.15 g, 4.0 mmol, 1.0 equiv), *p*-TsOH (76 mg, 0.1 equiv) and MeOH (40 mL). The mixture was allowed to stir at room temperature overnight. After neutralizing with saturated NaHCO₃ (10 mL), the reaction mixture was extracted with CH₂Cl₂ (30 mL × 3). The organic layers were combined, dried over anhydrous Na₂SO₄, evaporated and purified by flash column chromatography (silica gel, 1:1 EtOAc:PE) to afford compound **14b** (1.14 g, 94%) as mixture of diastereomers.

Physical State: pale-yellow oil.

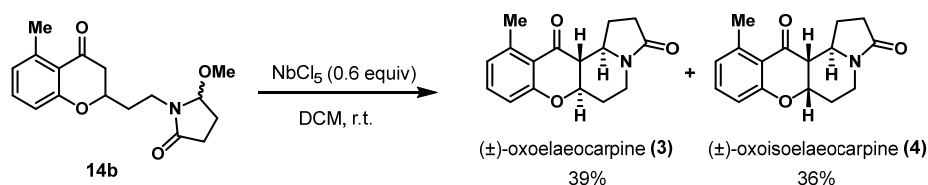
¹H NMR (400 MHz, Chloroform-*d*): δ 7.31 – 7.25 (m, 1H), 6.82 (d, *J* = 8.2 Hz, 0.45 H), 6.81 (d, *J* = 8.2 Hz, 0.55 H), 6.77 (d, *J* = 7.4 Hz, 0.55 H), 6.76 (d, *J* = 7.4 Hz, 0.45 H), 4.95 – 4.90 (m, 1H), 4.48 – 4.34 (m, 1H), 3.69

– 3.60 (m, 1H), 3.48 – 3.38 (m, 1H), 3.27 (s, 1.65 H), 3.25 (s, 1.35 H), 2.76 – 2.63 (m, 2H), 2.60 (s, 3H), 2.55 – 2.45 (m, 1H), 2.35 – 2.26 (m, 1H), 2.19 – 1.93 (m, 4H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 193.6 (193.5), 175.3 (175.2), 162.5 (162.4), 142.22 (142.15), 134.71 (134.69), 124.8 (124.7), 119.69 (119.65), 115.9 (115.8), 91.0 (90.5), 75.1 (75.0), 53.1 (53.0), 44.5, 37.3, 33.2 (33.0), 29.01 (28.96), 24.03 (23.98), 22.9. (Data in parentheses are peaks observed for diastereomers)

HRMS (ESI-TOF): calculated for C₁₇H₂₁NNaO₄⁺ [M+Na]⁺: 326.1363; found: 326.1356.

(±)-Oxoelaeocarpine (3) and (±)-oxoisoelaeocarpine (4)



NbCl₅ (278 mg, 1.0 mmol, 0.6 equiv) in CH₂Cl₂ (4 mL) was cooled to 0 °C under argon and a solution of **14b** (521 mg, 1.72 mmol, 1.0 equiv) in CH₂Cl₂ (6 mL) was added dropwise. After stirring at 0 °C for 30 minutes, the reaction mixture was allowed to raise to room temperature and stirred for another 24 hours. The reaction was neutralized with saturated NaHCO₃ (10 mL) and extracted with EtOAc (20 mL × 3). The organic layers were combined, dried over anhydrous Na₂SO₄, evaporated and purified by flash column chromatography (silica gel, 1:20 E₂O:CH₂Cl₂) to afford (±)-oxoelaeocarpine (**3**, 182 mg, 39%) and (±)-oxoisoelaeocarpine (**4**, 168 mg, 36%).

(±)-oxoelaeocarpine (**3**):

Physical State: white solid.

m.p.: 205 - 206 °C.

¹H NMR (400 MHz, Methanol-*d*₄): δ 7.35 (t, *J* = 7.9 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.82 (d, *J* = 6.9 Hz, 1H), 4.41 (td, *J* = 12.5, 4.4 Hz, 1H), 4.17 (dd, *J* = 13.5, 3.8 Hz, 1H), 3.78 (dt, *J* = 10.1, 7.3 Hz, 1H), 2.82 (t, *J* = 13.0 Hz, 1H), 2.73 – 2.63 (m, 1H), 2.67 (dd, *J* = 12.8, 10.4 Hz, 1H), 2.58 (s, 3H), 2.52 – 2.35 (m, 2H), 2.25 (d, *J* = 12.4 Hz, 1H), 2.02 – 1.90 (m, 1H), 1.89 – 1.76 (m, 1H).

¹³C NMR (101 MHz, Methanol-*d*₄): δ 194.8, 176.3, 163.3, 142.7, 135.9, 125.6, 120.5, 116.7, 78.6, 56.9, 56.1, 37.8, 31.5, 31.4, 26.3, 22.7.

HRMS (ESI-TOF): calculated for C₁₆H₁₈NO₃⁺ [M+H]⁺: 272.1281; found: 272.1287.

(±)-oxoisoelaeocarpine (**4**):

Physical State: white solid.

m.p.: 160 - 162 °C.

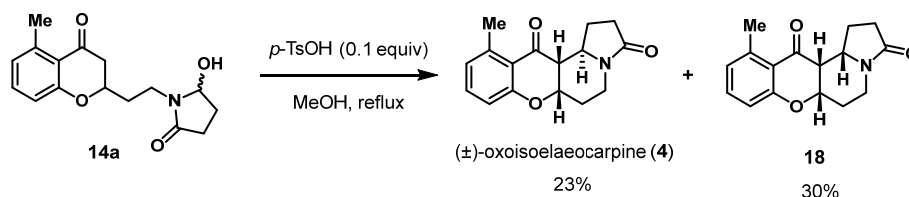
¹H NMR (400 MHz, Methanol-*d*₄): δ 7.39 (t, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 4.75 (d, *J* = 3.1 Hz, 1H), 4.01 (dd, *J* = 13.4, 5.8 Hz, 1H), 3.79 (dt, *J* = 11.2, 6.9 Hz, 1H), 3.19 (t, *J* = 12.0 Hz, 1H), 2.59 (s, 3H), 2.44 (br, d, *J* = 11.5 Hz, 1H), 2.42 – 2.29 (m, 2H), 2.17 (d, *J* = 14.6 Hz, 1H), 2.10 – 1.99 (m, 2H), 1.86 – 1.74 (m, 1H).

¹³C NMR (101 MHz, Methanol-*d*₄): δ 194.9, 176.3, 163.9, 143.7, 136.4, 126.1, 119.2, 117.1, 75.1, 55.2, 54.5, 35.6, 30.7, 29.1, 23.3, 23.1.

HRMS (ESI-TOF): calculated for C₁₆H₁₈NO₃⁺ [M+H]⁺: 272.1281; found: 272.1278.

See the following section for a full comparison of NMR data between synthetic and isolated natural products.

Compound 18



To a 100 mL flask equipped with a stir bar were added hemiaminal **14a** (1.15 g, 4.0 mmol, 1.0 equiv), *p*-TsOH (76 mg, 0.1 equiv) and MeOH (40 mL). The reaction was heated to reflux and stirred for one hour. After neutralizing with saturated NaHCO₃ (20 mL), the reaction mixture was extracted with CH₂Cl₂ (30 mL × 3). The organic layers were combined, dried over anhydrous Na₂SO₄, evaporated and purified by flash column chromatography (silica gel, 1:20 E₂O:CH₂Cl₂) to afford (\pm) -oxoisoelaecarpine (**4**, 249 mg, 23%) and compound **18** (325 mg, 30%).

Physical State: white solid.

m.p.: 157 - 158 °C.

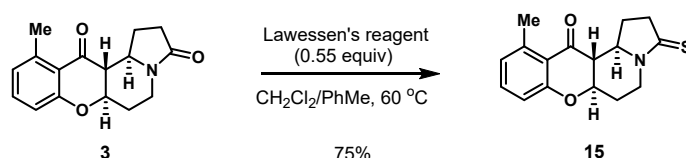
¹H NMR (400 MHz, Methanol-*d*₄): δ 7.30 (t, *J* = 7.9 Hz, 1H), 6.76 (d, *J* = 2.1 Hz, 1H), 6.75 (d, *J* = 3.3 Hz, 1H), 4.86 (t, *J* = 4.9 Hz, 1H), 4.10 (ddd, *J* = 13.5, 5.6, 1.7 Hz, 1H), 3.82 (dt, *J* = 10.5, 3.5 Hz, 1H), 3.44 – 3.41 (m, 1H), 3.00 – 2.94 (m, 1H), 2.88 – 2.82 (m, 1H), 2.50 (s, 3H), 2.47 – 2.43 (m, 1H), 2.43 – 2.38 (m, 1H), 2.25 – 2.30 (m, 1H), 1.84 – 1.80 (m, 1H), 1.77 – 1.71 (m, 1H).

¹³C NMR (101 MHz, Methanol-*d*₄): δ 195.3, 176.7, 161.0, 141.9, 136.0, 125.1, 120.6, 116.9, 77.8, 58.3, 58.2, 38.0, 31.7, 25.6, 22.4, 21.5.

HRMS (ESI-TOF): calculated for C₁₆H₁₈NO₃⁺ [M+H]⁺: 272.1281; found: 272.1280.

Compound 15

*11-methyl-3-thioxo-1,2,3,5,6,6a,12a,12b-octahydro-12H-chromeno[2,3-*g*]indolizin-12-one*



To a 25 mL flask equipped with a stir bar were added (\pm) -oxoelaecarpine **3** (542 mg, 2.0 mmol, 1.0 equiv), Lawesson's reagent (444 mg, 0.55 equiv), CH₂Cl₂ (6 mL) and toluene (10 mL). After stirring at 60 °C for 20 minutes, the mixture was evaporated and purified by flash column chromatography (silica gel, 1:5 EtOAc:PE) to afford thioamide **15** (433 mg, 75%).

Physical State: white solid.

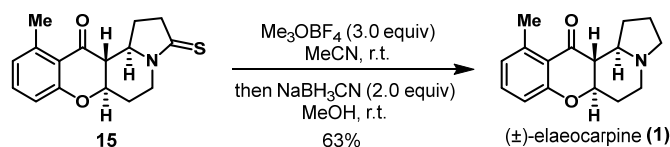
m.p.: 203 - 205 °C.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.34 (t, *J* = 8.0, 1H), 6.84 (t, *J* = 7.8, 2H), 5.10 (ddd, *J* = 14.0, 5.1, 2.2 Hz, 1H), 4.40 (ddd, *J* = 12.8, 11.2, 4.5 Hz, 1H), 3.96 (dt, *J* = 10.2, 7.7 Hz, 1H), 3.19 – 2.99 (m, 2H), 2.98 – 2.89 (m, 1H), 2.86 – 2.76 (m, 1H), 2.60 (s, 3H), 2.59 (dd, *J* = 12.8, 2.6 Hz, 1H), 2.41 – 2.33 (m, 1H), 2.07 – 1.81 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 201.6, 192.6, 161.8, 142.1, 135.2, 125.1, 119.2, 115.7, 76.7, 62.7, 55.1, 44.3, 41.9, 30.1, 27.3, 22.7.

HRMS (ESI-TOF): calculated for C₁₆H₁₈NO₂S⁺ [M+H]⁺: 288.1053; found: 288.1052.

(±)-Elaeocarpine (1)



A solution of thioamide **15** (72 mg, 0.25 mmol, 1.0 equiv) in CH_3CN (2.5 mL) was cooled to 0 °C under argon and Me_3OBF_4 (111 mg, 3.0 equiv) was added. The mixture was allowed to warm to room temperature and stirred for 2 hours. Solvent was evaporated under reduced pressure and the residue was redissolved in MeOH (2.5 mL). NaBH_3CN (32 mg, 2.0 equiv) was added and the resulting mixture was allowed to stir at room temperature for 1 hour. After quenching with saturated NH_4Cl (10 mL), the reaction mixture was extracted with EtOAc (10 mL \times 3). The organic layers were combined, washed with brine (20 mL), dried over anhydrous Na_2SO_4 , evaporated and purified by flash column chromatography (silica gel, 1:3 $\text{EtOAc}:\text{PE}$) to afford (±)-elaecarpine (**1**, 41 mg, 63%).

Physical State: white solid.

m.p.: 81 - 82 °C.

^1H NMR (400 MHz, Methanol- d_4): δ 7.31 (t, $J = 7.9$ Hz, 1H), 6.81 (d, $J = 8.4$ Hz, 1H), 6.79 (d, $J = 7.6$ Hz, 1H), 4.19 (ddd, $J = 12.6, 10.9, 5.0$ Hz, 1H), 3.17 (ddd, $J = 11.7, 4.2, 2.7$ Hz, 1H), 3.04 (td, $J = 9.2, 3.7$ Hz, 1H), 2.60 (dd, $J = 13.1, 6.4$ Hz, 1H), 2.55 (s, 3H), 2.57 – 2.50 (m, 1H), 2.28 – 2.16 (m, 3H), 2.15 – 2.03 (m, 2H), 1.91 – 1.81 (m, 2H), 1.64 – 1.51 (m, 1H).

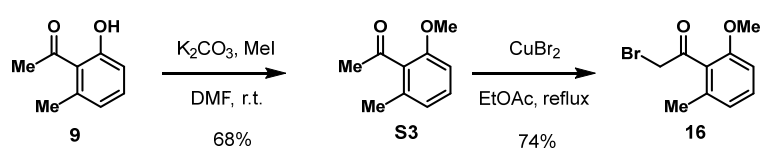
^{13}C NMR (101 MHz, Methanol- d_4): δ 195.4, 163.4, 142.6, 135.5, 125.5, 120.6, 116.6, 79.6, 63.4, 55.1, 53.5, 49.7, 32.1, 31.0, 22.8, 22.7.

HRMS (ESI-TOF): calculated for $\text{C}_{16}\text{H}_{20}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$: 258.1489; found: 258.1484.

See the following section for a full comparison of NMR data between synthetic and isolated natural products.

Compound 16

2-bromo-1-(2-methoxy-6-methylphenyl) ethan-1-one



To a 100 mL flask equipped with a stir bar were added acetophenone **9** (4.3 g, 28.7 mmol, 1.0 equiv), MeI (3.6 mL, 2.0 equiv), K_2CO_3 (7.9 g, 2.0 equiv) and DMF (58 mL). The mixture was stirred at room temperature for 6 hours. EtOAc (150 mL) was added and the resulting mixture washed with water (50 mL \times 3) and brine (50 mL) successively. The organic layer was then dried over anhydrous Na_2SO_4 , evaporated and purified by flash column chromatography (silica gel, 1:10 $\text{EtOAc}:\text{PE}$) to afford compound **S3** (3.2 g, 68%) as yellow oil.

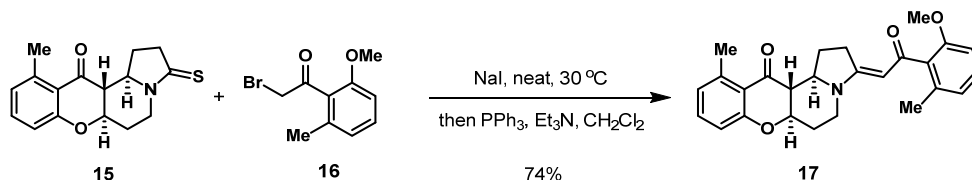
S3 (1.53 g, 9.33 mmol, 1.0 equiv), CuBr_2 (4.2 g, 2.0 equiv) and EtOAc (75 mL) were added to a 100 mL flask equipped with a stir bar. The resulting mixture was heated to reflux and stirred for 3 hours. After cooling to room temperature, the reaction mixture was filtered over a pad of celite. The filtrate was washed with brine, dried over anhydrous Na_2SO_4 , evaporated and purified by flash column chromatography (silica gel, 1:10 $\text{EtOAc}:\text{PE}$) to afford bromide **16** (1.67 g, 74%) as brown oil.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.26 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 4.36 (s, 2H), 3.82 (s, 3H), 2.27 (s, 3H).

Spectroscopic data are in accordance with that reported in the literature.^[2]

Compound 17

(6*aR*,12*aR*,12*bR*,*E*)-3-(2-(2-methoxy-6-methylphenyl)-2-oxoethylidene)-11-methyl-1,2,3,5,6,6*a*,12*a*,12*b*-octahydro-12*H*-chromeno[2,3-*g*]indolizin-12-one



To a 25 mL flask equipped with a stir bar were added thioamide **15** (574 mg, 2.0 mmol, 1.0 equiv), bromide **16** (726 mg, 1.5 equiv), NaI (30 mg, 0.1 equiv) and CH₂Cl₂ (5 mL). After stirring for 5 minutes, CH₂Cl₂ was removed under reduced pressure and the resulting mixture was stirred at 30 °C for 48 hours. A solution of PPh₃ (786 mg, 1.5 equiv) in CH₂Cl₂ (20 mL) were added and stirred for 0.5 hour before Et₃N (830 μ L, 3.0 equiv) was added. After stirring for another 3 hours, the reaction was diluted with CH₂Cl₂ (30 mL) and washed with brine (30 mL), dried over anhydrous Na₂SO₄, evaporated and purified by flash column chromatography (silica gel, 1:1 EtOAc:PE) to afford enaminone **17** (614 mg, 74%).

Physical State: yellow oil.

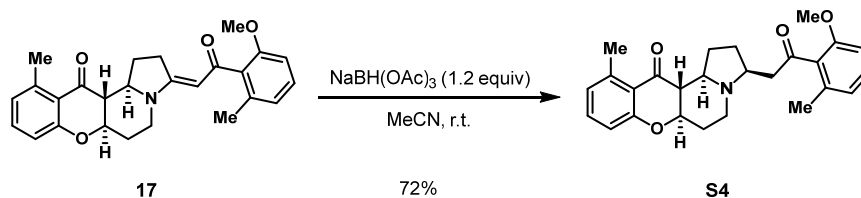
¹H NMR (400 MHz, Chloroform-*d*): δ 7.32 (t, *J* = 7.9 Hz, 1H), 7.14 (t, *J* = 7.9 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 6.9 Hz, 1H), 6.77 (d, *J* = 7.7, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 5.33 (s, 1H), 4.30 (td, *J* = 12.5, 12.0, 4.5 Hz, 1H), 3.80 (dd, *J* = 13.8, 3.3 Hz, 1H), 3.78 (s, 3H), 3.71 – 3.33 (m, 2H), 3.15 – 2.95 (m, 1H), 2.88 (t, *J* = 12.2 Hz, 1H), 2.80 – 2.73 (m, 1H), 2.60 (s, 3H), 2.50 (dd, *J* = 12.7, 10.0 Hz, 1H), 2.26 (s, 3H), 2.29 – 2.22 (m, 1H), 2.02 – 1.90 (m, 1H), 1.83 – 1.70 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 193.0, 192.4, 164.7, 161.7, 155.6, 142.0, 135.4, 134.9, 134.5, 128.3, 124.9, 122.6, 119.3, 115.6, 108.4, 93.5, 77.2, 59.8, 55.9, 54.6, 40.2, 32.8, 30.2, 28.5, 22.7, 19.2.

HRMS (ESI-TOF): calculated for C₂₆H₂₈NO₄⁺ [M+H]⁺: 418.2013; found: 418.2018.

Compound S4

3-(2-(2-methoxy-6-methylphenyl)-2-oxoethyl)-11-methyl-1,2,3,5,6,6*a*,12*a*,12*b*-octahydro-12*H*-chromeno[2,3-*g*]indolizin-12-one



To a solution of enaminone **17** (354 mg, 0.85 mmol, 1.0 equiv) in CH₃CN (17 mL) was added NaBH(OAc)₃ (216 mg, 1.2 equiv). The mixture was stirred at room temperature overnight. The reaction mixture was diluted with saturated NH₄Cl (10 mL) and extracted with EtOAc (20 mL \times 3). The organic layers were combined, washed with

brine (30 mL), dried over anhydrous Na₂SO₄, evaporated and purified by flash column chromatography (silica gel, 1:3 EtOAc:PE) to afford methylated elaeocarfoline A (**S4**, 255 mg, 72%).

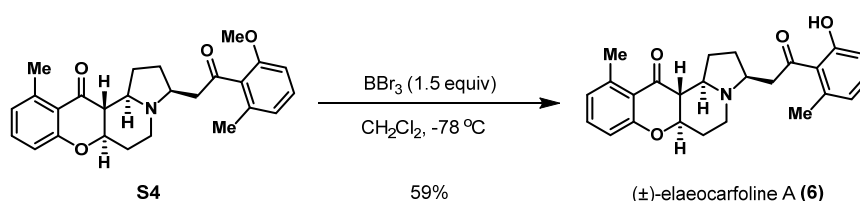
Physical State: pale-yellow oil.

¹H NMR (400 MHz, Acetone-*d*₆): δ 7.34 (t, *J* = 7.9 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.81 (t, *J* = 7.9 Hz, 3H), 4.20 (ddd, *J* = 12.4, 5, 1.2 Hz, 1H), 3.86 (s, 3H), 3.20 – 3.17 (m, 1H), 3.17 – 3.14 (m, 1H), 2.82 – 2.67 (m, 2H), 2.54 (s, 3H), 2.48 (dd, *J* = 9.6, 3.2 Hz, 1H), 2.46 – 2.42 (m, 1H), 2.20 (s, 3H), 2.20 – 2.13 (m, 2H), 2.13 – 2.07 (m, 1H), 2.03 (d, *J* = 4.0 Hz, 1H), 1.91 (m, 1H), 1.57 – 1.43 (m, 2H).

¹³C NMR (101 MHz, Acetone-*d*₆): δ 206.2, 194.8, 162.8, 157.3, 141.9, 136.3, 134.9, 132.1, 130.8, 125.0, 123.7, 120.5, 116.3, 109.5, 79.5, 63.2, 59.5, 56.0, 55.3, 49.8, 47.6, 32.4, 30.7, 29.3, 22.6, 19.2.

HRMS (ESI-TOF): calculated for C₂₆H₃₀NO₄⁺ [M+H]⁺: 420.2169; found: 420.2163.

(±)-Elaeocarfoline A (**6**)



Compound **S4** (132 mg, 0.32 mmol, 1.0 equiv) was dissolved in CH₂Cl₂ (3.6 mL) and cooled to -78 °C under argon. BBr₃ (1.0 M in CH₂Cl₂, 480 μL, 1.5 equiv) was added dropwise. After stirring at -78 °C for 5 hours, the reaction was quenched by addition of saturated NaHCO₃ (10 mL) and extracted with EtOAc (10 mL × 3). The organic layers were combined, washed with brine (20 mL), dried over anhydrous Na₂SO₄, evaporated and purified by flash column chromatography (silica gel, 1:3 EtOAc:PE) to afford (±)-elaecarfoline A (**6**, 75 mg, 59%).

Physical State: pale-yellow oil.

¹H NMR (500 MHz, Acetone-*d*₆): δ 9.40 (s, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 4.20 (ddd, *J* = 12.6, 11.1, 5.0 Hz, 1H), 3.28 (dd, *J* = 16.2, 3.8 Hz, 1H), 3.22 – 3.17 (m, 1H), 2.92 (dd, *J* = 16.2, 8.3 Hz, 1H), 2.84 – 2.78 (m, 1H), 2.54 (s, 3H), 2.52 (dd, *J* = 12.7, 9.6 Hz, 1H), 2.49 – 2.43 (m, 1H), 2.26 (s, 3H), 2.24 – 2.19 (m, 1H), 2.19 – 2.14 (m, 1H), 2.14 – 2.07 (m, 2H), 1.92 (qd, *J* = 11.9, 4.4 Hz, 1H), 1.65 – 1.55 (m, 1H), 1.55 – 1.45 (m, 1H).

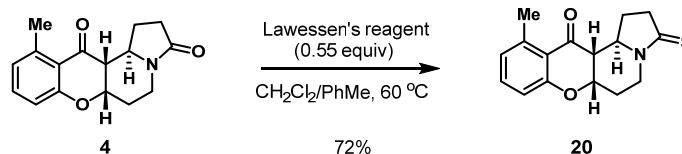
¹³C NMR (126 MHz, Acetone-*d*₆): δ 206.8, 194.8, 162.9, 155.9, 142.0, 137.2, 135.0, 131.3, 130.0, 125.0, 122.8, 120.5, 116.3, 114.8, 79.5, 63.4, 60.0, 55.3, 49.5, 47.8, 32.3, 30.5, 29.5, 22.6, 20.1.

HRMS (ESI-TOF): calculated for C₂₅H₂₈NO₄⁺ [M+H]⁺: 406.2013; found: 406.2012.

See the following section for a full comparison of NMR data between synthetic and isolated natural products.

Compound 20

11-methyl-3-thioxo-1,2,3,5,6,6a,12a,12b-octahydro-12H-chromeno[2,3-*g*]indolizin-12-one



To a 25 mL flask equipped with a stir bar were added (±)-oxisoelaecarpine **4** (227 mg, 0.84 mmol, 1.0 equiv), Lawesson's reagent (186 mg, 0.55 equiv), CH₂Cl₂ (3 mL) and toluene (5 mL). After stirring at 60 °C for 20 minutes,

the mixture was evaporated and purified by flash column chromatography (silica gel, 1:5 EtOAc:PE) to afford thioamide **20** (172 mg, 72%).

Physical State: white solid.

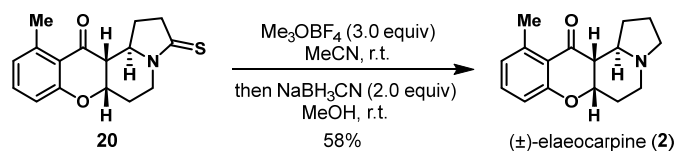
m.p.: 162 - 164 °C.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.37 (t, $J = 7.9$ Hz, 1H), 6.90 (d, $J = 8.2$ Hz, 1H), 6.85 (d, $J = 7.4$ Hz, 1H), 4.90 (dd, $J = 13.5, 5.0$ Hz, 1H), 4.73 (d, $J = 2.6$ Hz, 1H), 4.08 (dt, $J = 11.1, 7.2$ Hz, 1H), 3.43 (t, $J = 13.8$ Hz, 1H), 3.15 – 3.05 (m, 1H), 3.02 – 2.89 (m, 1H), 2.62 (s, 3H), 2.41 (dd, $J = 11.2, 2.3$ Hz, 1H), 2.35 – 2.26 (m, 1H), 2.15 – 2.07 (m, 2H), 1.95 – 1.82 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 200.9, 192.5, 162.4, 143.0, 135.5, 125.5, 118.1, 116.1, 73.0, 60.3, 54.3, 43.3, 39.7, 28.3, 23.8, 23.1.

HRMS (ESI-TOF): calculated for C₁₆H₁₈NO₂S⁺ [M+H]⁺: 288.1053; found: 288.1050.

(±)-isoeleocarpine (**2**)



A solution of thioamide **20** (86 mg, 0.3 mmol, 1.0 equiv) in CH₃CN (3 mL) was cooled to 0 °C under argon and Me₃OBF₄ (134 mg, 3.0 equiv) was added. The mixture was allowed to warm to room temperature and stirred for 2 hours. Solvent was evaporated under reduced pressure and the residue was redissolved in MeOH (3 mL). NaBH₃CN (38 mg, 2.0 equiv) was added and the resulting mixture was stirred at room temperature for 1 hour. After quenching with saturated NH₄Cl (10 mL), the reaction mixture was extracted with EtOAc (10 mL × 3). The organic layers were combined, washed with brine (20 mL), dried over anhydrous Na₂SO₄, evaporated and purified by flash column chromatography (silica gel, 1:3 EtOAc:PE) to afford (±)-isoeleocarpine (**2**, 45 mg, 58%).

Physical State: white solid.

m.p.: 51 - 52 °C.

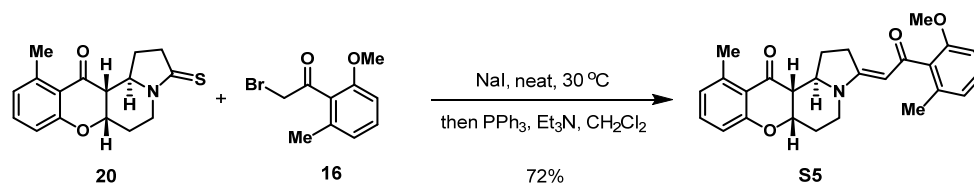
¹H NMR (400 MHz, Methanol-*d*₄): δ 7.35 (t, $J = 7.8$ Hz, 1H), 6.86 (d, $J = 8.3$ Hz, 1H), 6.81 (d, $J = 7.3$ Hz, 1H), 4.65 (s, 1H), 3.08 (t, $J = 9.0$ Hz, 1H), 3.03 (dd, $J = 11.2, 4.4$ Hz, 1H), 2.63 – 2.54 (m, 1H), 2.57 (s, 3H), 2.39 (d, $J = 11.0$ Hz, 1H), 2.33 – 2.25 (m, 1H), 2.23 – 2.17 (m, 1H), 2.17 – 2.10 (m, 1H), 2.01 – 1.90 (m, 1H), 1.85 – 1.75 (m, 1H), 1.75 – 1.60 (m, 3H).

¹³C NMR (101 MHz, Methanol-*d*₄): δ 195.9, 163.8, 143.3, 136.2, 125.8, 119.4, 117.0, 75.0, 60.2, 55.1, 54.5, 48.0, 30.5, 29.2, 23.1, 21.2.

HRMS (ESI-TOF): calculated for C₁₆H₂₀NO₂⁺ [M+H]⁺: 258.1489; found: 258.1488.

See the following section for a full comparison of NMR data between synthetic and isolated natural products.

Compound S5



To a 25 mL flask equipped with a stir bar were added thioamide **20** (143 mg, 0.5 mmol, 1.0 equiv), bromide **16** (182 mg, 1.5 equiv), NaI (8 mg, 0.1 equiv) and CH₂Cl₂ (2 mL). After stirring for 5 minutes, CH₂Cl₂ was removed under reduced pressure and the resulting mixture was stirred at 30 °C for 48 hours. A solution of PPh₃ (197 mg, 1.5 equiv) in CH₂Cl₂ (5 mL) were added and stirred for 0.5 hour before Et₃N (208 μL, 3.0 equiv) was added. After stirring for another 3 hours, the reaction was diluted with CH₂Cl₂ (10 mL) and washed with brine (10 mL), dried over anhydrous Na₂SO₄, evaporated and purified by flash column chromatography (silica gel, 1:1 EtOAc:PE) to afford enaminone **S5** (150 mg, 72%).

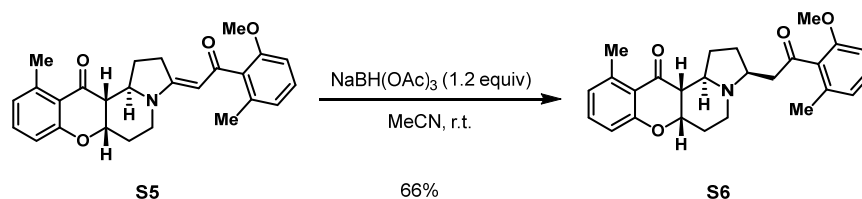
Physical State: yellow oil.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.33 (t, *J* = 7.9 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.82 (d, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 5.34 (s, 1H), 4.70 (d, *J* = 2.3 Hz, 1H), 3.76 (s, 3H), 3.72 – 3.60 (m, 2H), 3.58 – 3.31 (m, 2H), 3.13 – 2.85 (m, 1H), 2.61 (s, 3H), 2.35 (dd, *J* = 11.0, 2.2 Hz, 1H), 2.24 (s, 3H), 2.22 – 2.14 (m, 1H), 2.06 – 1.90 (m, 2H), 1.89 – 1.78 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 193.2, 192.4, 164.8, 162.2, 155.6, 142.8, 135.3, 135.2, 134.5, 128.2, 125.3, 122.6, 118.1, 115.9, 108.4, 93.8, 73.3, 57.2, 55.8, 53.9, 38.1, 31.8, 28.0, 25.5, 23.0, 19.1.

HRMS (ESI-TOF): calculated for C₂₆H₂₈NO₄⁺ [M+H]⁺: 418.2013; found: 418.2013.

Compound S6



To a solution of enaminone **S5** (184 mg, 0.44 mmol, 1.0 equiv) in CH₃CN (8 mL) was added NaBH(OAc)₃ (112 mg, 1.2 equiv). The mixture was stirred at room temperature overnight. The reaction mixture was diluted with saturated NH₄Cl (5 mL) and extracted with EtOAc (5 mL × 3). The organic layers were combined, washed with brine (10 mL), dried over anhydrous Na₂SO₄, evaporated and purified by flash column chromatography (silica gel, 1:3 EtOAc:PE) to afford methylated elaeocarfoline B (**S6**, 122 mg, 66%).

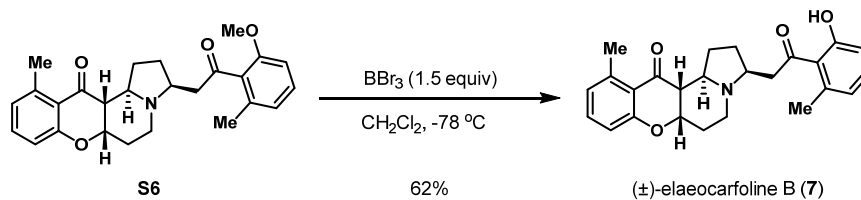
Physical State: pale-yellow oil.

¹H NMR (400 MHz, Acetone-*d*₆): δ 7.37 (t, *J* = 7.9 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 2H), 4.68 (s, 1H), 3.86 (s, 3H), 3.23 – 3.14 (m, 1H), 3.03 (ddd, *J* = 10.9, 4.9, 1.8 Hz, 1H), 2.81 – 2.77 (m, 1H), 2.76 – 2.70 (m, 1H), 2.56 (s, 3H), 2.44 – 2.36 (m, 1H), 2.36 – 2.28 (m, 2H), 2.19 (s, 3H), 2.09 (dd, *J* = 14.3, 2.4 Hz, 1H), 1.97 – 1.80 (m, 2H), 1.57 – 1.44 (m, 3H).

¹³C NMR (101 MHz, Acetone-*d*₆): δ 206.2, 194.8, 163.2, 157.3, 142.5, 136.3, 135.4, 132.1, 130.8, 125.2, 123.7, 119.3, 116.7, 109.5, 74.8, 60.9, 60.0, 56.0, 55.6, 49.8, 46.0, 30.9, 29.2, 28.1, 22.9, 19.2.

HRMS (ESI-TOF): calculated for C₂₆H₃₀NO₄⁺ [M+H]⁺: 420.2169; found: 420.2170.

(±)-Elaeocarfoline B (**7**)



Compound **S6** (121 mg, 0.29 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2.9 mL) and cooled to $-78\text{ }^\circ\text{C}$ under argon. BBr_3 (1.0 M in CH_2Cl_2 , 440 μL , 1.5 equiv) was added dropwise. After stirring at $-78\text{ }^\circ\text{C}$ for 5 hours, the reaction was quenched by addition of saturated NaHCO_3 (5 mL) and extracted with EtOAc (5 mL \times 3). The organic layers were combined, washed with brine (10 mL), dried over anhydrous Na_2SO_4 , evaporated and purified by flash column chromatography (silica gel, 1:3 EtOAc:PE) to afford (\pm)-elaeocarfoline A (**7**, 73 mg, 62%).

Physical State: pale-yellow oil.

^1H NMR (500 MHz, Acetone- d_6) δ 7.37 (t, $J = 7.9$ Hz, 1H), 7.12 (t, $J = 7.9$ Hz, 1H), 6.87 (d, $J = 8.3$ Hz, 1H), 6.83 (d, $J = 7.4$ Hz, 1H), 6.76 (d, $J = 8.2$ Hz, 1H), 6.71 (d, $J = 7.4$ Hz, 1H), 4.69 (q, like, $J = 2.3$ Hz, 1H), 3.29 (dd, $J = 16.1, 3.8$ Hz, 1H), 3.04 (ddd, $J = 11.0, 5.0, 2.0$ Hz, 1H), 2.91 (dd, $J = 16.2, 8.3$ Hz, 1H), 2.84 – 2.78 (m, 1H), 2.56 (s, 3H), 2.43 (td, $J = 12.0, 11.3, 2.8$ Hz, 1H), 2.36 – 2.31 (m, 2H), 2.24 (s, 3H), 2.11 – 2.06 (m, 1H), 1.97 – 1.90 (m, 1H), 1.90 – 1.81 (m, 1H), 1.60 – 1.51 (m, 3H).

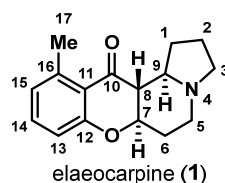
^{13}C NMR (126 MHz, Acetone- d_6) δ 206.8, 194.7, 163.3, 156.0, 142.6, 137.3, 135.5, 131.4, 130.0, 125.3, 122.8, 119.3, 116.7, 114.9, 74.8, 61.4, 60.3, 55.5, 49.6, 46.3, 30.8, 29.1, 28.1, 22.9, 20.1.

HRMS (ESI-TOF): calculated for $\text{C}_{25}\text{H}_{28}\text{NO}_4^+$ $[\text{M}+\text{H}]^+$: 406.2013; found: 406.2010.

See the following section for a full comparison of NMR data between synthetic and isolated natural products.

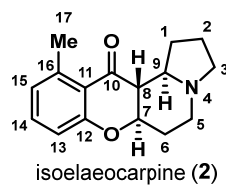
NMR Data Comparison between Synthetic and Isolated Natural Products

Table S1. Elaeocarpine (1)



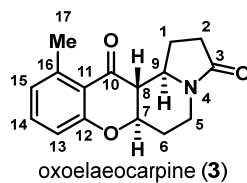
No.	δ_{H} (isolated) (500 MHz, Methanol- d_4) ^[5]	δ_{H} (synthetic) (400 MHz, Methanol- d_4)	Δ	δ_{C} (isolated) (125 MHz, Methanol- d_4) ^[5]	δ_{C} (synthetic) (101 MHz, Methanol- d_4)	Δ
1 α	1.88, m	1.91 – 1.81, m		30.2	31.0	0.8
1 β	1.57, m	1.64 – 1.51, m				
2 α	1.71, m	1.91 – 1.81, m		22.0	22.7	0.7
2 β	2.12, m	2.28 – 2.16, m				
3	3.02, t (8.8)	3.04, td (9.2, 3.7)	0.02	54.3	55.1	0.8
	2.18, m	2.28 – 2.16, m				
5 α	3.15, dd (13.2, 3.6)	3.17, ddd (11.7, 4.2, 2.7)	0.02	48.7	49.7	1.0
5 β	2.20, m	2.28 – 2.16, m				
6	2.06, m	2.15 – 2.03, m		31.3	32.1	0.8
7	4.13, m	4.19, ddd (12.6, 10.9, 5.0)	0.06	78.5	79.6	1.1
8	2.56, m	2.60, (dd, 13.1, 6.4)	0.04	52.7	53.5	0.8
9	2.53, m	2.57 – 2.50, m		61.9	63.4	1.5
10				194.5	195.4	0.9
11				119.4	120.6	1.2
12				161.9	163.4	1.5
13	6.78, d (8.4)	6.81, d (8.4)	0.03	115.4	116.6	1.2
14	7.26, t (8.4)	7.31, t (7.9)	0.05	134.1	135.5	1.4
15	6.74, d (7.6)	6.79, d (7.6)	0.05	124.3	125.5	1.2
16				141.6	142.6	1.0
17	2.60, s	2.55, s	0.05	22.6	22.8	0.2

Table S2. Isoelaecarpine (2)



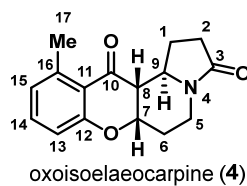
No.	δ_{H} (isolated) (400 MHz, Methanol- d_4) ^[5]	δ_{H} (synthetic) (400 MHz, Methanol- d_4)	Δ	δ_{C} (isolated) (100 MHz, Methanol- d_4) ^[5]	δ_{C} (synthetic) (101 MHz, Methanol- d_4)	Δ
1 α	1.63, m	1.75 – 1.60, m		30.8	30.5	-0.3
1 β	2.17, m	2.17 – 2.10, m				
2	1.73, m	1.75 – 1.60, m		21.5	21.2	-0.3
3	3.07, dd (11.5, 5)	3.03, dd (11.2, 4.4)	-0.04	55.2	55.1	-0.1
	2.22, m	2.23 – 2.17, m				
5 α	3.15, t (8.0)	3.08, t (9.0)	-0.07	54.6	54.5	-0.1
5 β	2.33, m	2.33 – 2.25, m				
6	2.02, m	2.01 – 1.90, m		29.3	29.2	-0.1
	1.87, m	1.85 – 1.75, m				
7	4.66, d (2.5)	4.65, s	-0.01	74.9	75.0	0.1
8	2.48 d (10.0)	2.39 d (11.0)	-0.09	47.9	48.0	0.1
9	2.63, m	2.63 – 2.54, m		59.9	60.2	0.3
10				195.5	195.9	0.4
11				119.5	119.4	-0.1
12				163.3	163.8	0.5
13	6.85, d (8.5)	6.86, d (8.3)	0.01	116.8	117.0	0.2
14	7.32, t (7.5)	7.35, t (7.8)	0.03	135.6	136.2	0.6
15	6.80, d (7.0)	6.81, d (7.3)	0.01	125.7	125.8	0.1
16				143.5	143.3	-0.2
17	2.63, s	2.57, s	-0.06	23.8	23.1	-0.7

Table S3. Oxolaecarpine (3)



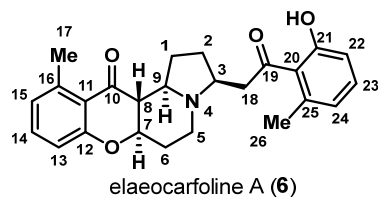
No.	δ_{H} (isolated) (500 MHz, Methanol- d_4) ^[6]	δ_{H} (synthetic) (400 MHz, Methanol- d_4)	Δ	δ_{C} (isolated) (126 MHz, Methanol- d_4) ^[6]	δ_{C} (synthetic) (101 MHz, Methanol- d_4)	Δ
1 α	2.68, m	2.73 – 2.63, m		26.3	26.3	0.0
1 β	1.92, m	2.02 – 1.90, m				
2	2.42, m	2.52 – 2.35, m		31.4	31.4	0.0
3				176.3	176.3	0.0
5 α	2.81, br dd (13.6, 13.6)	2.82, t (13.0)	0.01	37.8	37.8	0.0
5 β	4.16, ddd (13.6, 5.2, 1.9)	4.17, dd (13.5, 3.8)	0.01			
6 α	2.24, m	2.25, d (12.4)	0.01	31.5	31.5	0.0
6 β	1.82, m	1.89 – 1.76, m				
7	4.40, ddd (12.8, 11.2, 4.4)	4.41, td (12.5, 4.4)	0.01	78.6	78.6	0.0
8	2.67, dd (12.8, 10.0)	2.67, dd (12.8, 10.4)	0.00	56.1	56.1	0.0
9	3.78, ddd (10.0, 7.0, 7.0)	3.78, dt (10.1, 7.3)	0.00	56.9	56.9	0.0
10				194.8	194.8	0.0
11				120.5	120.5	0.0
12				163.3	163.3	0.0
13	6.83, br d (8.1)	6.84, d (7.9)	0.01	116.7	116.7	0.0
14	7.34, dd (8.1 7.7)	7.35, t (7.9)	0.01	135.9	135.9	0.0
15	6.82, br d (7.7)	6.82, d (6.9)	0.00	125.6	125.6	0.0
16				142.7	142.7	0.0
17	2.57, s	2.58, s	0.01	22.7	22.7	0.0

Table S4. Oxisoelaecarpine (4)



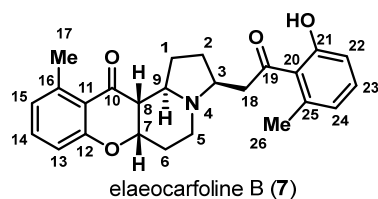
No.	δ_{H} (isolated) (400 MHz, Methanol- d_4) ^[7]	δ_{H} (synthetic) (400 MHz, Methanol- d_4)	Δ	δ_{C} (isolated) (100 MHz, Methanol- d_4) ^[7]	δ_{C} (synthetic) (101 MHz, Methanol- d_4)	Δ
1	2.13-1.99, m	2.10-1.99, m		23.4	23.3	-0.1
2	2.44-2.31, m	2.42-2.29, m		30.9	30.7	-0.2
3				176.5	176.3	-0.2
5 β	4.03, dd (13.3,5.7)	4.01, dd (13.4,5.8)	-0.02	35.8	35.6	-0.2
5 α	3.22, dd (13.3, 10.3)	3.19, t (12.0)	-0.03			
6 α	2.18, d (14.6)	2.17, d (14.6)	-0.01	29.3	29.1	-0.2
6 β	1.88-1.74, m	1.86-1.74, m				
7	4.77, d (2.4)	4.75, d (3.1)	-0.02	75.3	75.1	-0.2
8	2.47, dd (11.0, 2.4)	2.45, br d (11.5)	-0.02	55.4	55.2	-0.2
9	3.83, dt (11.0, 6.9)	3.79, dt (11.2, 6.9)	-0.04	54.7	54.5	-0.2
10				195.1	194.9	-0.2
11				119.4	119.2	-0.2
12				164.2	163.9	-0.3
13	6.94, d (7.9)	6.92, d (8.4)	-0.02	117.3	117.1	-0.2
14	7.40, t (7.9)	7.39, t (7.9)	-0.01	136.6	136.4	-0.2
15	6.87, d (7.9)	6.86, d (7.5)	-0.01	126.3	126.1	-0.2
16				143.8	143.7	-0.1
17	2.60, s	2.59, s	-0.01	23.3	23.1	-0.2

Table S5. Elaeocarfoline A (6)



No.	δ_{H} (isolated) (800 MHz, Acetone- d_6) ^[6]	δ_{H} (synthetic) (500 MHz, Acetone- d_6)	Δ	δ_{C} (isolated) (201 MHz, Acetone- d_6) ^[6]	δ_{C} (synthetic) (126 MHz, Acetone- d_6)	Δ
1	2.48, m	2.49 – 2.43, m		29.5	29.5	0.0
	1.50, m	1.55 – 1.45, m				
2 α	2.09, m	2.14 – 2.07, m		30.5	30.5	0.0
2 β	1.60, m	1.65 – 1.55, m				
3	2.81, m	2.84 – 2.78, m		59.9	60.0	0.1
5 α	2.12, m	2.14 – 2.07, m		47.7	47.8	0.1
5 β	3.20, m	3.22 – 3.17, m				
6 α	2.18, m	2.19 – 2.14, m		32.3	32.3	0.0
6 β	1.92, qd (11.9 4.7)	1.92, qd (11.9 4.4)	0.00			
7	4.22, ddd (11.9 11.1 5.0)	4.20, ddd (12.6 11.1 5.0)	-0.02	79.5	79.5	0.0
8	2.54, dd (11.1 9.8)	2.52, dd (12.7 9.6)	-0.02	55.3	55.3	0.0
9	2.22, ddd (11.1 9.8 6.0)	2.24 – 2.19, m		63.4	63.4	0.0
10				194.8	194.8	0.0
11				120.5	120.5	0.0
12				162.8	162.9	0.1
13	6.84, br d (8.2)	6.82, d (8.0)	-0.02	116.3	116.3	0.0
14	7.36, dd (8.2 7.5)	7.34, t (7.9)	-0.02	135.0	135.0	0.0
15	6.83, br d (7.5)	6.81, d (7.2)	-0.02	125.0	125.0	0.0
16				141.9	142.0	0.1
17	2.56, s	2.54, s	-0.02	22.5	22.6	0.1
18	3.29, dd (16.3, 3.8)	3.28, dd (16.2, 3.8)	-0.01	49.5	49.5	0.0
	2.93, dd (16.3 8.2)	2.92, dd (16.2 8.3)	-0.01			
19				206.8	206.8	0.0
20				130.0	130.0	0.0
21		9.40, s		155.8	155.9	0.1
22	6.78, br d (8.1)	6.77, d (8.2)	-0.01	114.7	114.8	0.1
23	7.14, dd (8.1 7.6)	7.13, t (7.9)	-0.01	131.3	131.3	0.0
24	6.74, br d (7.6)	6.73, d (7.6)	-0.01	122.8	122.8	0.0
25				137.2	137.2	0.0
26	2.27, s	2.26, s	-0.01	20.0	20.1	0.1

Table S6. Elaeocarfoline B (7)



No.	δ_{H} (isolated) (500 MHz, Acetone- d_6) ^[6]	δ_{H} (synthetic) (400 MHz, Acetone- d_6)	Δ	δ_{C} (isolated) (201 MHz, Acetone- d_6) ^[6]	δ_{C} (synthetic) (126 MHz, Acetone- d_6)	Δ
1	1.54, m	1.60 – 1.51, m		28.1	28.1	0.0
2 α	1.93, m	1.97 – 1.90, m		29.0	29.1	0.1
2 β	1.51, m	1.60 – 1.51, m				
3	2.80, m	2.84 – 2.78, m		61.3	61.4	0.1
5 α	2.42, ddd (12.0, 11.1, 2.8)	2.43, td (12.0, 11.3, 2.8)	0.01	46.2	46.3	0.1
5 β	3.03, ddd (11.1, 5.0, 2.1)	3.04, ddd (11.0, 5.2, 2.0)	0.01			
6 α	2.07, m	2.11 – 2.06, m		30.8	30.8	0.0
6 β	1.84, m	1.90 – 1.81, m				
7	4.68, q like (2.7)	4.69, q like (2.3)	0.01	74.7	74.8	0.1
8	2.34, m	2.36 – 2.31, m		55.4	55.5	0.1
9	2.36, m	2.36 – 2.31, m		60.2	60.3	0.1
10				194.7	194.7	0.0
11				119.2	119.3	0.1
12				163.2	163.3	0.1
13	6.86, br d (8.4)	6.87, d (8.3)	0.01	116.7	116.7	0.0
14	7.37 ^a , dd (8.4 7.4)	7.37, t (7.9)	0.00	135.4	135.5	0.1
15	6.82, br d (7.4)	6.83, d (7.4)	0.01	125.2	125.3	0.1
16				142.5	142.6	0.1
17	2.55, s	2.56, s	0.01	22.9	22.9	0.0
18	3.28, dd (16.0, 3.9)	3.29, dd (16.1, 3.8)	0.01	49.5	49.6	0.1
	2.90, dd (16.0 8.3)	2.91, dd (16.2 8.3)	0.01			
19				206.8	206.8	0.0
20				129.9	130.0	0.1
21				155.9	156.0	0.1
22	6.76, br d (8.2)	6.76, d (8.2)	0.00	114.8	114.9	0.1
23	7.12, dd (8.2 7.6)	7.12, t (7.9)	0.00	131.3	131.4	0.1
24	6.71, br d (7.6)	6.71, d (7.4)	0.00	122.7	122.8	0.1
25				137.2	137.3	0.1
26	2.23, s	2.24, s	0.01	20.0	20.1	0.1

^aThis number was corrected according to the spectrum reported in its *Supporting Information*^[6].

X-Ray Crystallographic Data for Compound 18

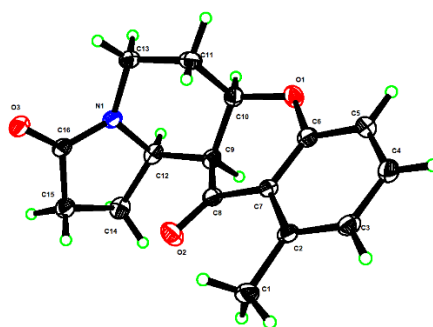


Table 1 Crystal data and structure refinement for **18**.

Identification code	CCDC 2169386
Empirical formula	C ₁₆ H ₁₇ NO ₃
Formula weight	271.30
Temperature/K	170.0
Crystal system	orthorhombic
Space group	Pbca
<i>a</i> /Å	11.002(3)
<i>b</i> /Å	9.389(3)
<i>c</i> /Å	25.890(7)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	2674.2(12)
<i>Z</i>	8
ρ_{calc} /cm ³	1.348
μ /mm ⁻¹	0.093
<i>F</i> (000)	1152.0
Crystal size/mm ³	0.15 × 0.07 × 0.06
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.86 to 52.76
Index ranges	-13 ≤ <i>h</i> ≤ 13, -9 ≤ <i>k</i> ≤ 11, -32 ≤ <i>l</i> ≤ 30
Reflections collected	18127
Independent reflections	2711 [<i>R</i> _{int} = 0.0755, <i>R</i> _{sigma} = 0.0471]
Data/restraints/parameters	2711/0/182
Goodness-of-fit on <i>F</i> ²	1.028
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0449, <i>wR</i> ₂ = 0.0964
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0713, <i>wR</i> ₂ = 0.1116

Largest diff. peak/hole / e Å⁻³ 0.16/-0.22

Table 2 Fractional Atomic Coordinates (nem⁴) and Equivalent Isotropic Displacement Parameters (Å² × a³) for 3. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{ij} tensor.

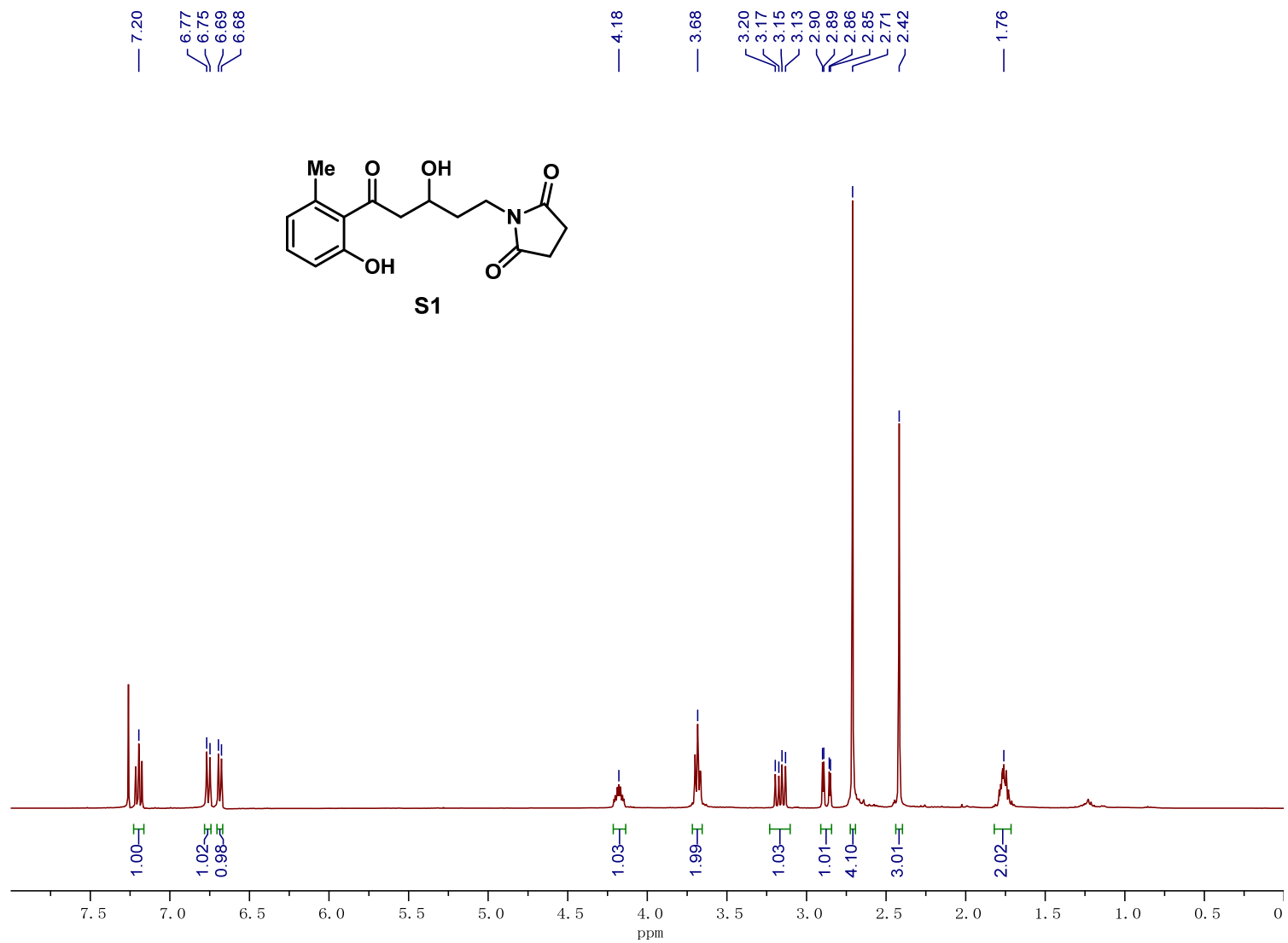
Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
O3	6403.3(11)	1899.2(14)	2976.5(5)	37.7(3)
O1	2045.5(11)	5740.1(14)	3362.3(5)	37.3(3)
O2	4546.4(11)	3537.7(16)	4212.8(5)	45.2(4)
N1	5498.6(13)	4084.8(16)	3052.6(5)	30.2(4)
C7	2480.3(15)	4208.1(19)	4100.3(6)	26.7(4)
C16	6275.0(15)	3049(2)	3196.0(6)	29.2(4)
C6	1674.0(15)	4960(2)	3779.4(6)	30.3(4)
C8	3802.3(16)	4301(2)	4000.1(6)	29.6(4)
C2	1992.2(15)	3443(2)	4527.0(6)	29.7(4)
C9	4178.5(15)	5463.5(19)	3623.0(7)	29.9(4)
C12	5458.0(16)	5318(2)	3394.1(7)	31.9(4)
C3	752.0(16)	3498(2)	4617.0(7)	33.6(4)
C10	3267.8(16)	5515(2)	3177.2(7)	32.2(4)
C4	-20.6(17)	4262(2)	4295.5(7)	36.8(5)
C5	429.8(16)	4980(2)	3873.3(7)	35.3(5)
C1	2771.3(17)	2589(2)	4891.2(7)	38.2(5)
C15	6953.7(16)	3551(2)	3667.9(7)	36.0(5)
C11	3333.1(17)	4178(2)	2846.4(7)	35.6(4)
C13	4617.1(17)	3978(2)	2634.3(7)	38.0(5)
C14	6546.9(16)	5082(2)	3758.6(7)	37.2(5)

References

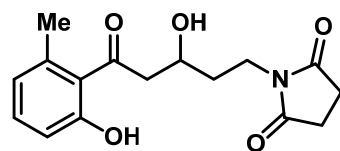
- [1] Taber, D. F., Hoerrner, R. S., Hagen, M. D. A practical preparation of the indolizidine nucleus: synthesis of (\pm)-elaekanine A. *The Journal of Organic Chemistry*, **1991**, *56*, 1287-1289
- [2] Michael, J. P., Parsons, A. S. Chemoselective reactions of vinylogous amides, and the synthesis of two Peripentadenia alkaloids. *Tetrahedron*, **1996**, *52*, 2199-2216.
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- [5] Wang, X. Y. Master's Thesis (2011). Institute of Modern Chinese Medicine (IMCM), College of Pharmaceutical Sciences, Zhejiang University, Hangzhou, P. R. China.
- [6] Hong, W., Zhang, Y., Yang, J., Xia, M. Y., Luo, J. F., Li, X. N., Wang, Y. H., Wang, J. S. Alkaloids from the Branches and Leaves of *Elaeocarpus angustifolius*. *Journal of natural products*, **2019**, *82*, 3221-3226.
- [7] Zhou, C. X., Wang, X. Y., Mo, J. X., Zhang, J., Gan, L. S. Optical resolution and structure determination of new indolizidine alkaloids from *Elaeocarpus sphaericus*. *Helvetica Chimica Acta*, **2011**, *94*, 347-354.

NMR Spectra

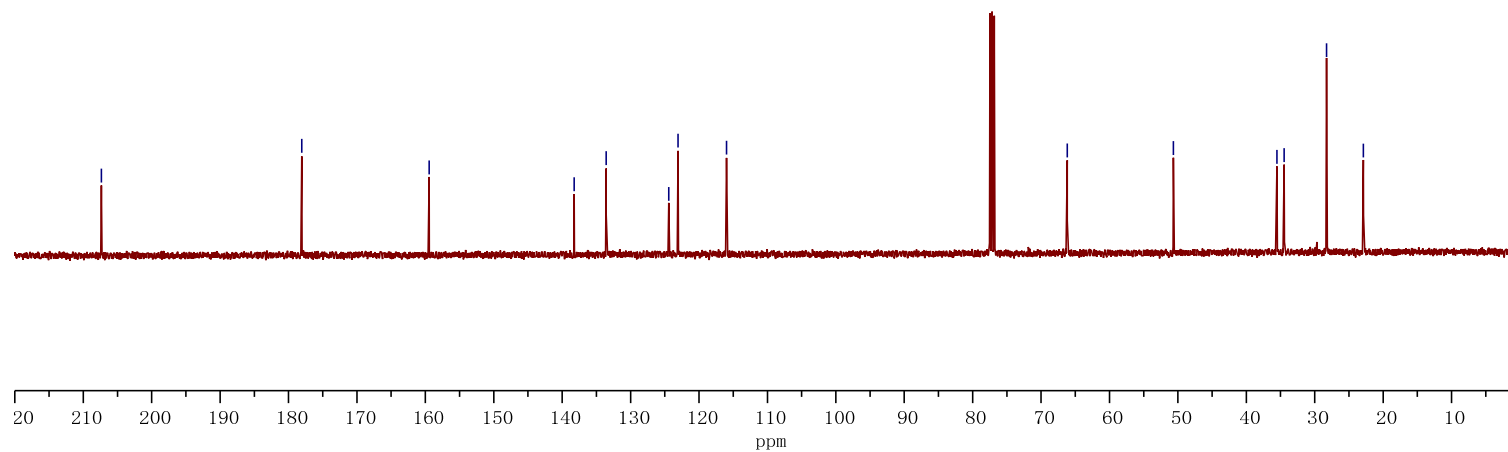
Compound S1 ¹H NMR (400 MHz, Chloroform-d)



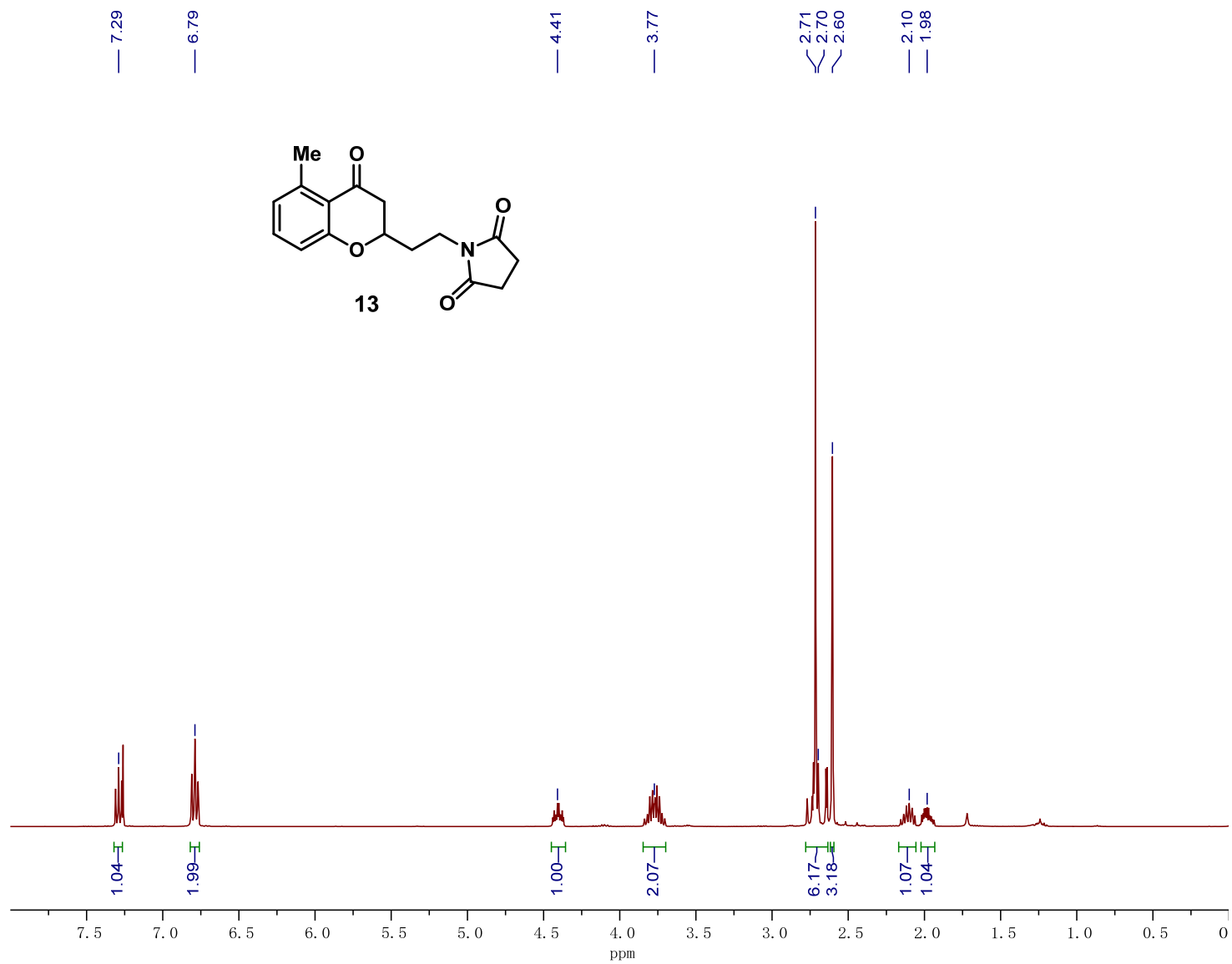
Compound S1 ¹³C NMR (101 MHz, Chloroform-*d*)



S1

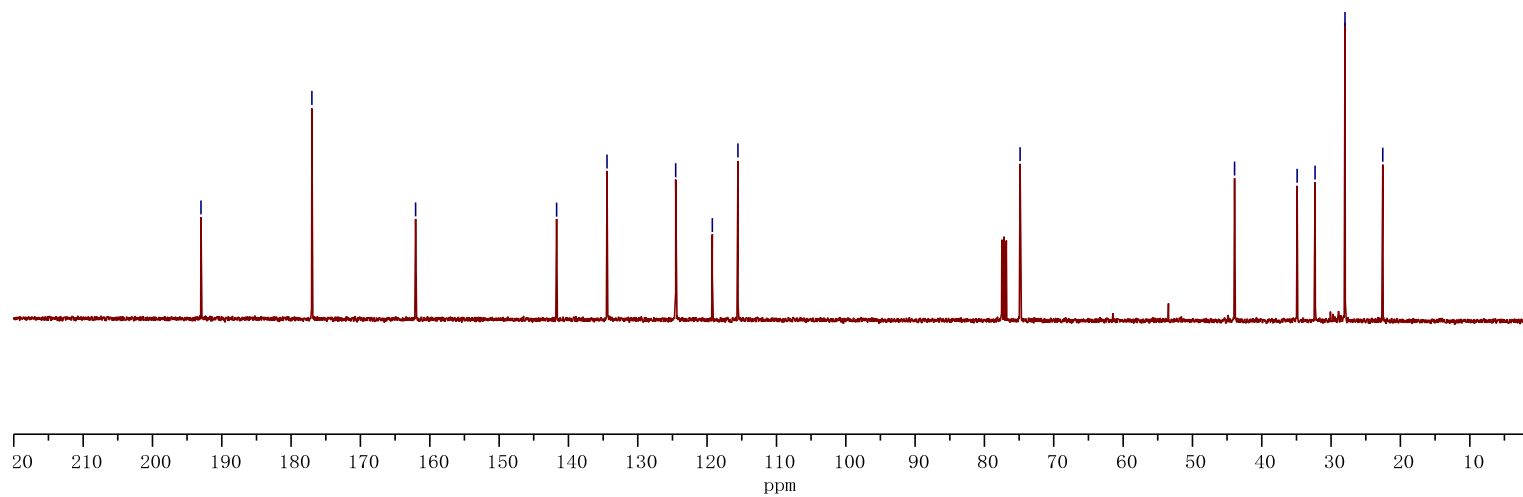
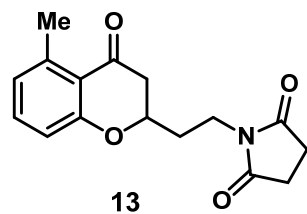


Compound 13 ¹H NMR (400 MHz, Chloroform-*d*)

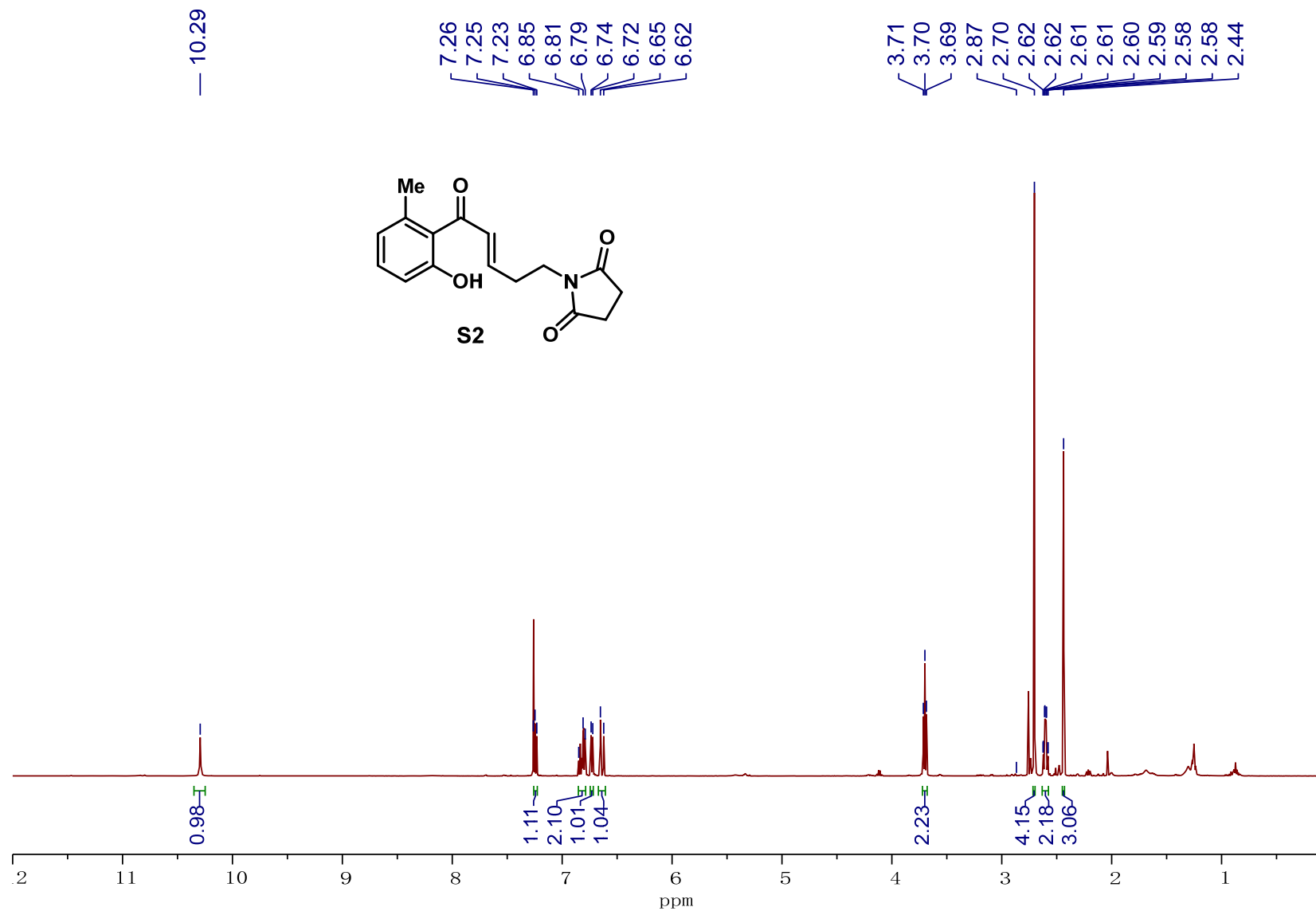


Compound 13 ¹³C NMR (101 MHz, Chloroform-*d*)

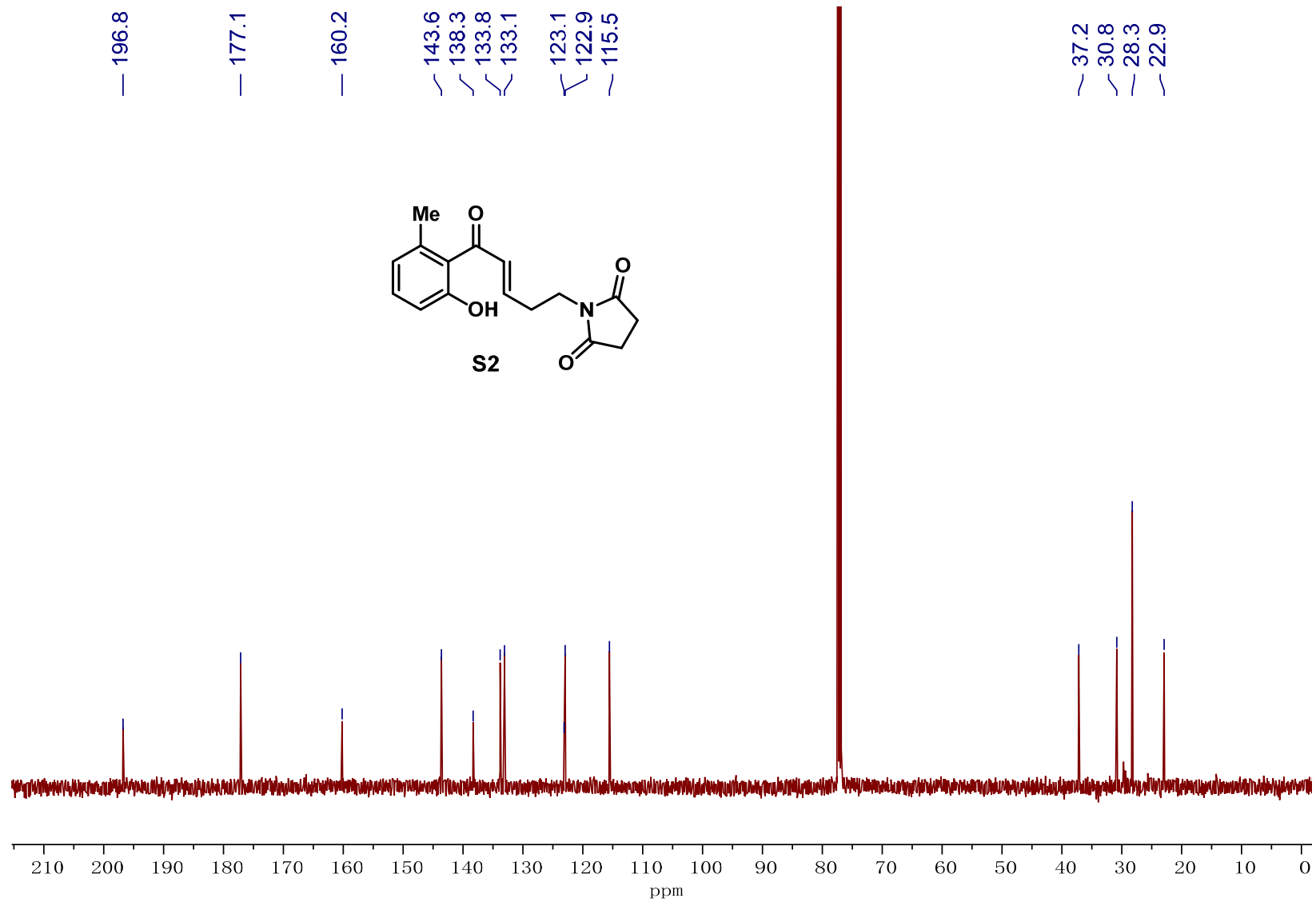
193.0
177.0
162.1
141.7
134.4
124.5
119.3
115.6
74.9
43.9
34.9
32.3
28.0
22.6



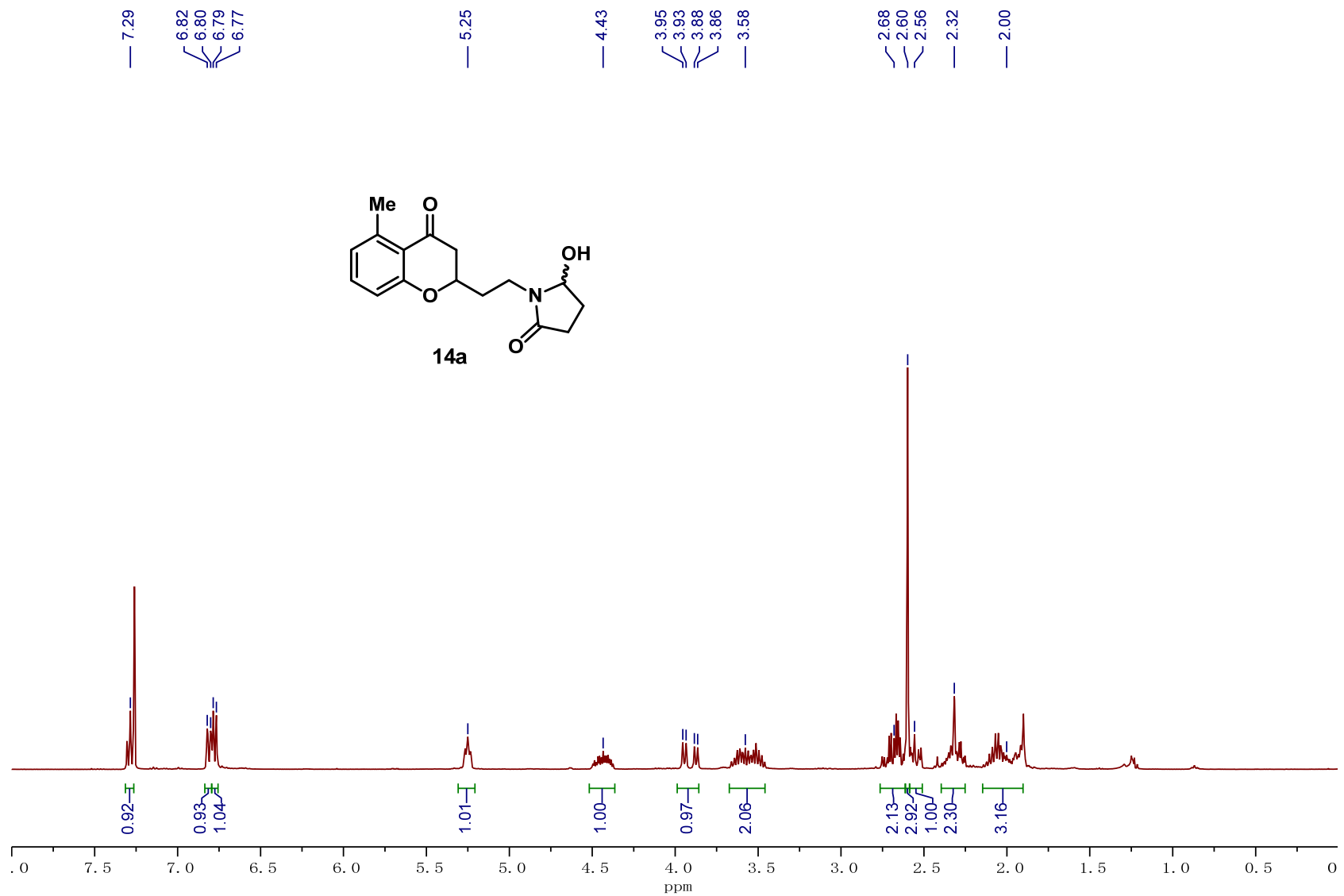
Compound S2 ¹H NMR (500 MHz, Chloroform-*d*)



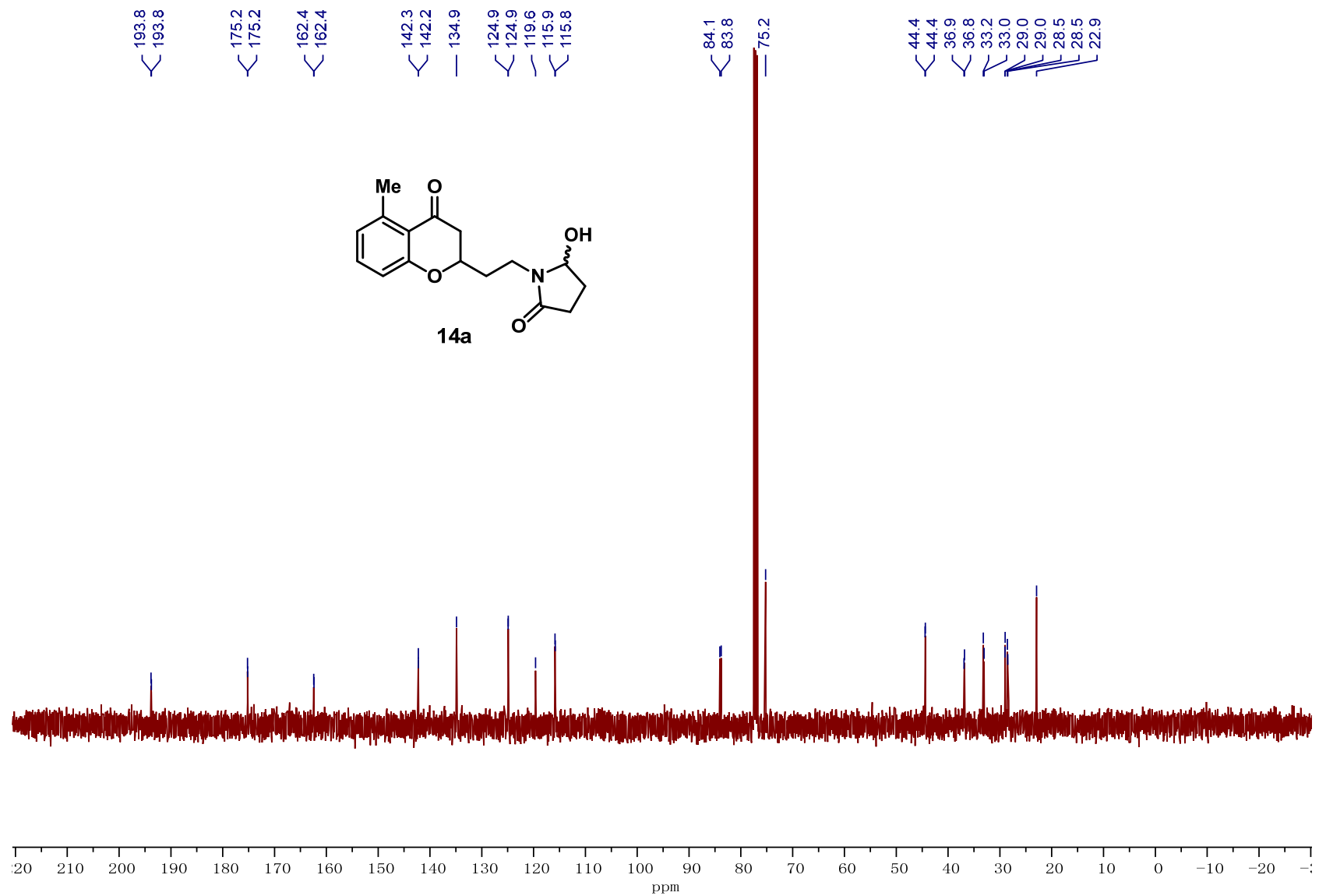
Compound S2 ¹³C NMR (126 MHz, Chloroform-*d*)



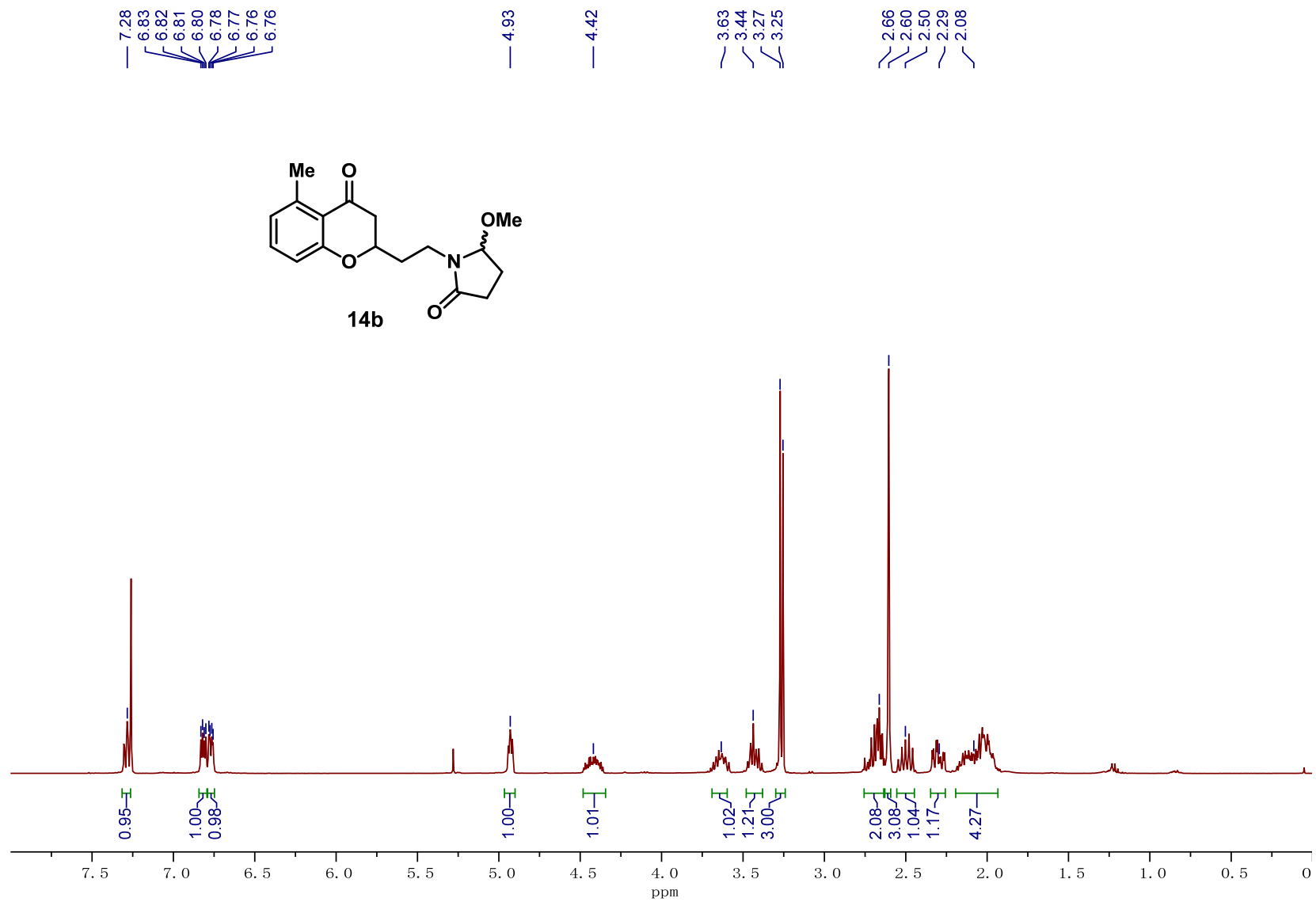
Compound 14a ¹H NMR (400 MHz, Chloroform-*d*)



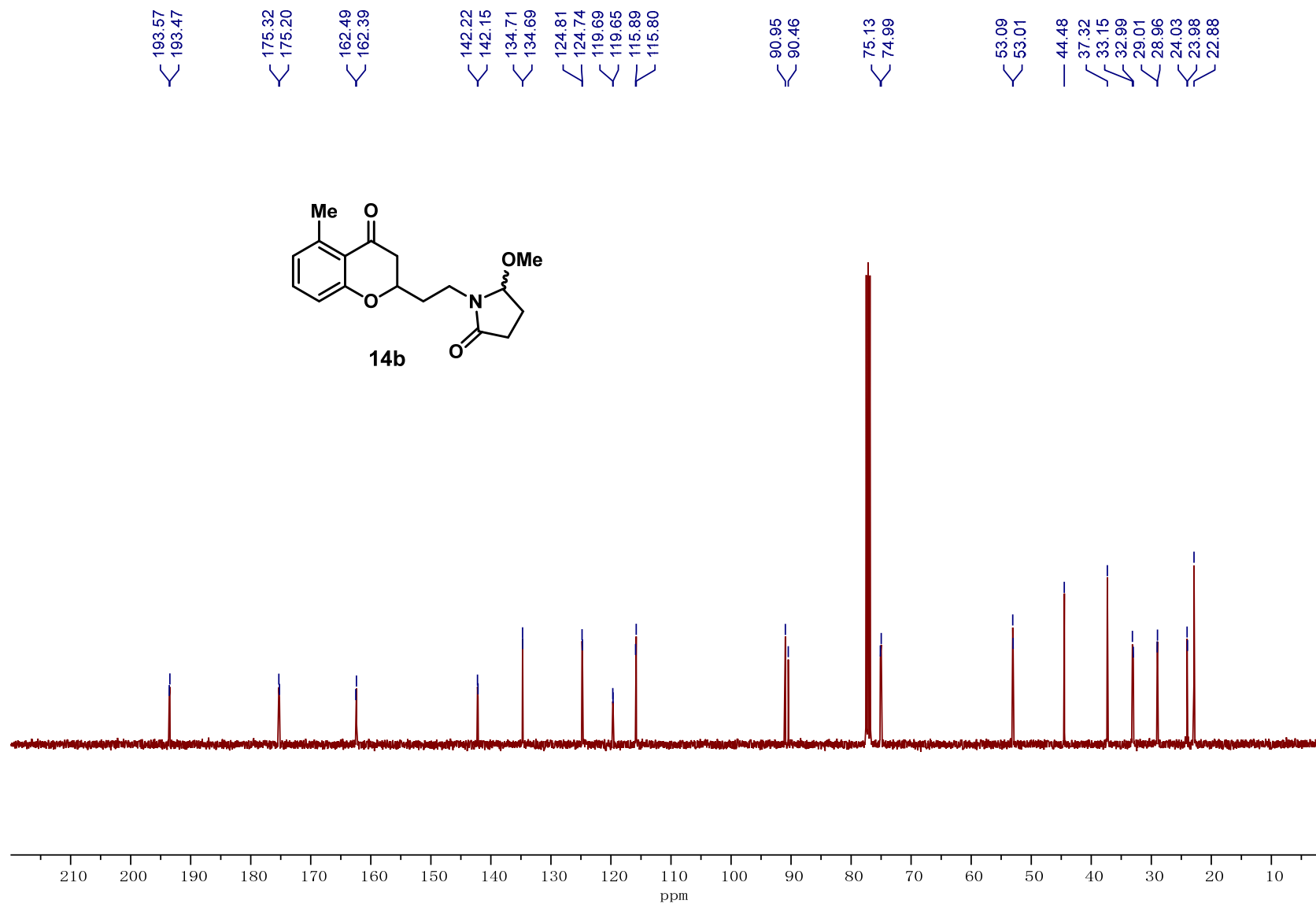
Compound 14a ¹³C NMR (101 MHz, Chloroform-*d*)



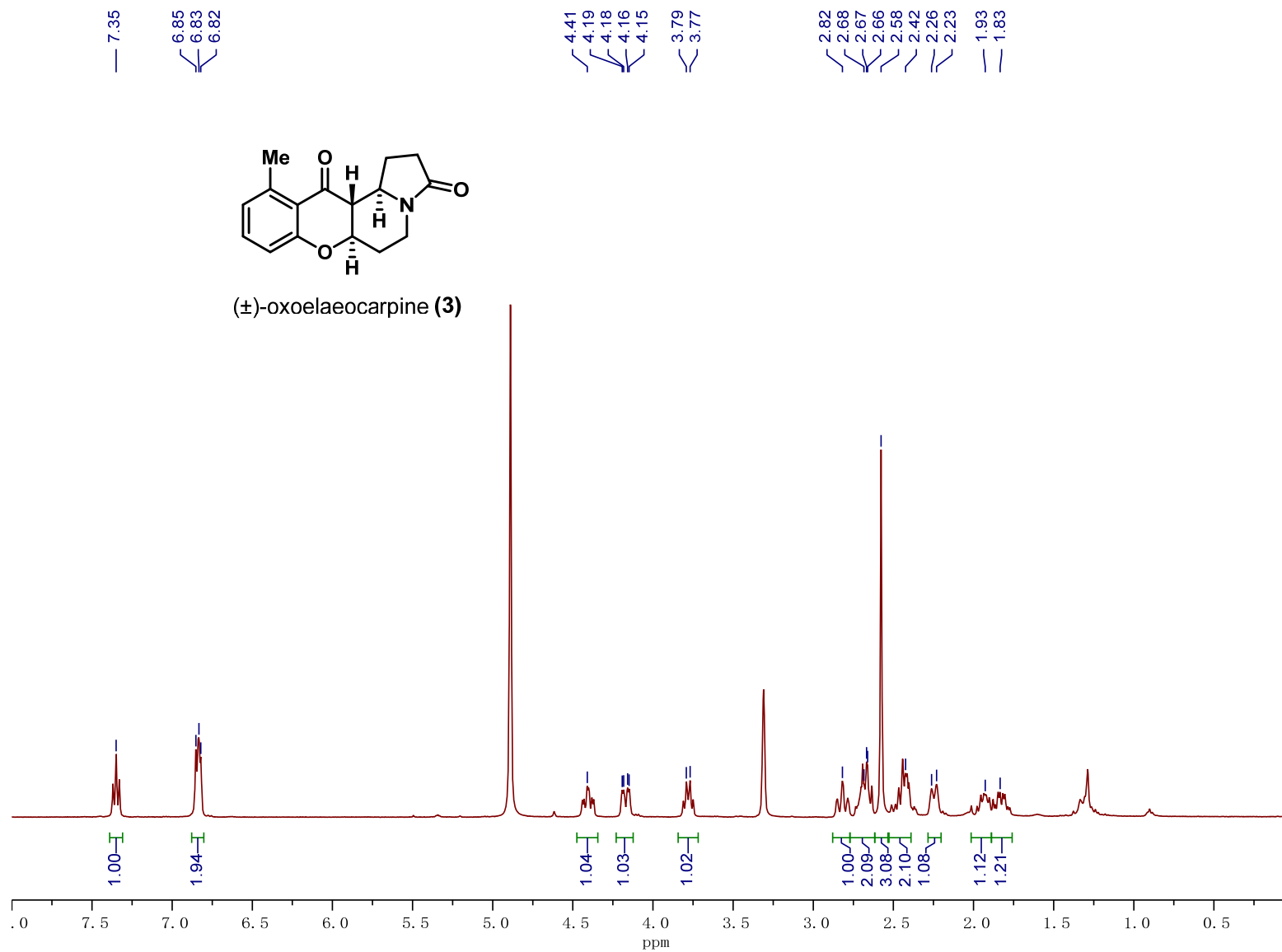
Compound 14b ¹H NMR (400 MHz, Chloroform-*d*)



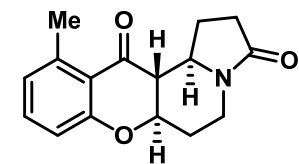
Compound 14b ¹³C NMR (101 MHz, Chloroform-*d*)



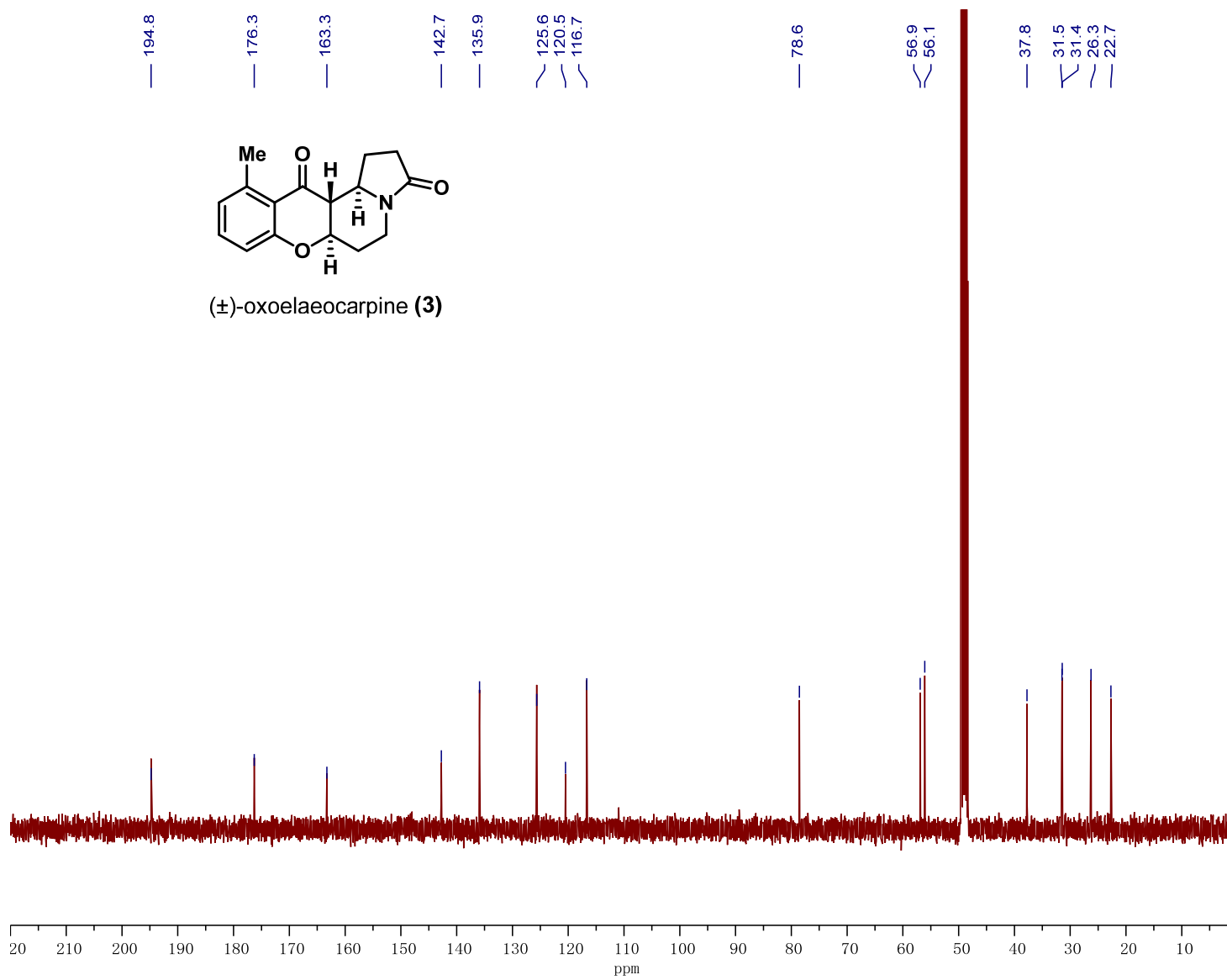
Compound 3 ¹H NMR (400 MHz, Methanol-*d*₄)



Compound 3 ¹³C NMR (101 MHz, Methanol-*d*₄)

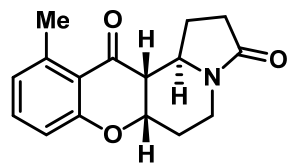


(±)-oxoelaeocarpine (3)

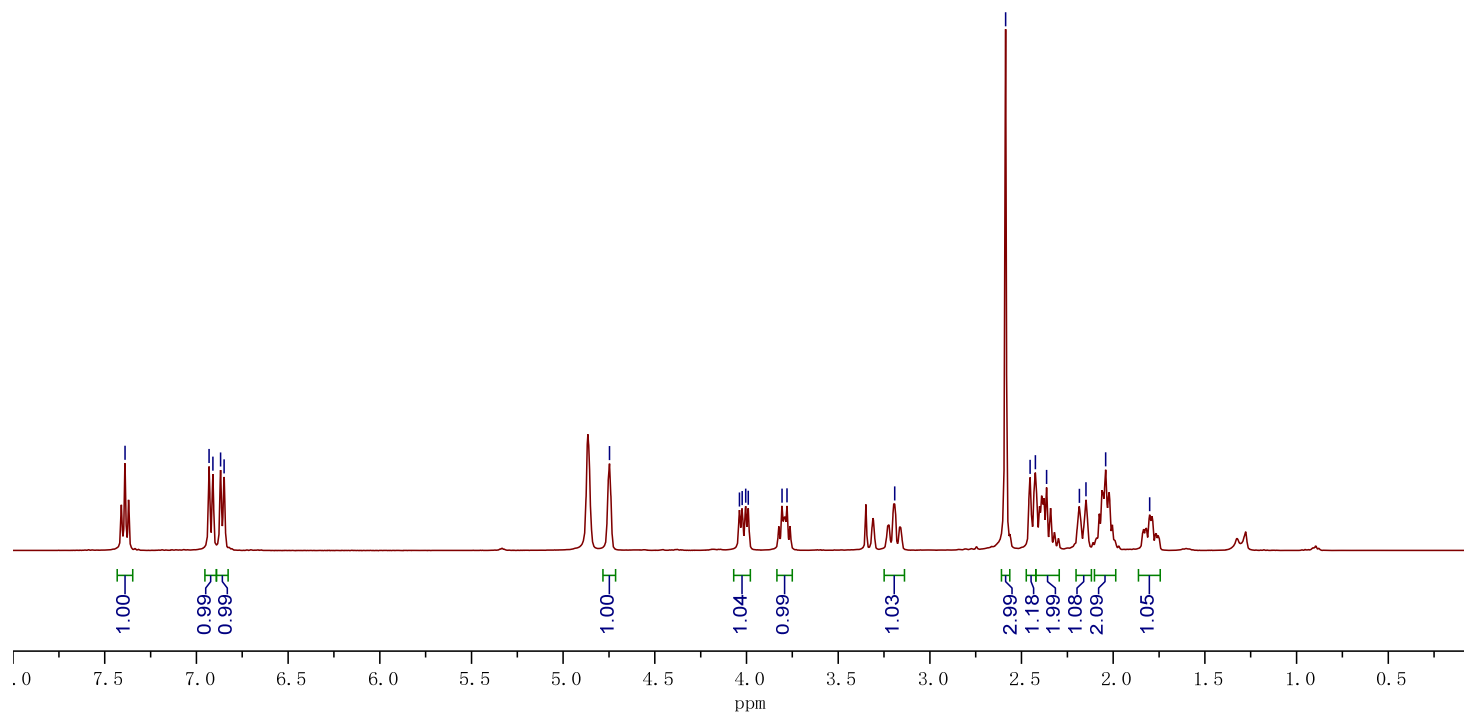


Compound **4** ^1H NMR (400 MHz, Methanol- d_4)

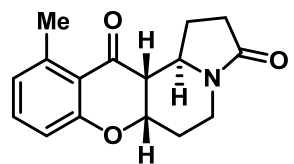
7.39
6.93
6.91
6.87
6.85
4.75
4.04
4.02
4.00
3.99
3.81
3.78
3.19
2.59
2.45
2.42
2.36
2.18
2.15
2.04
1.80



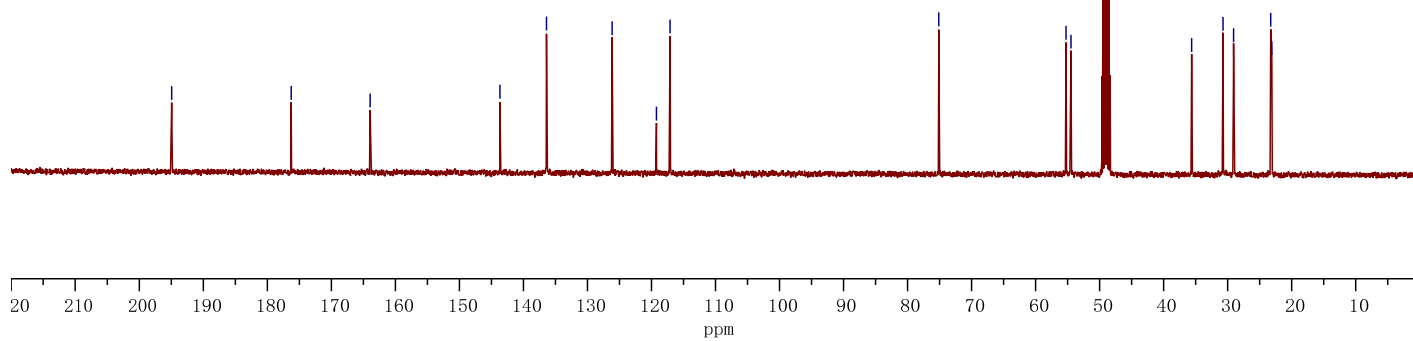
(±)-oxoisoelaecarpine (**4**)



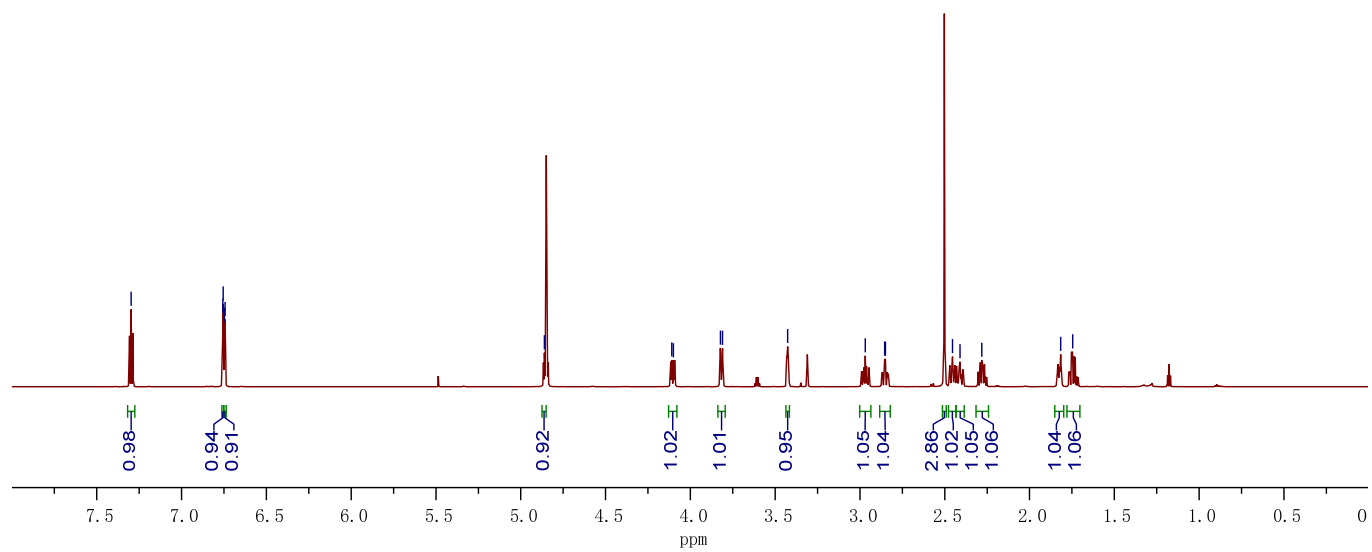
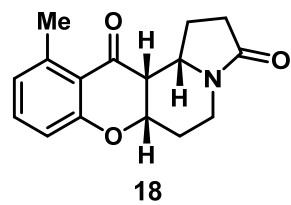
Compound **4** ^{13}C NMR (400 MHz, Methanol- d_4)



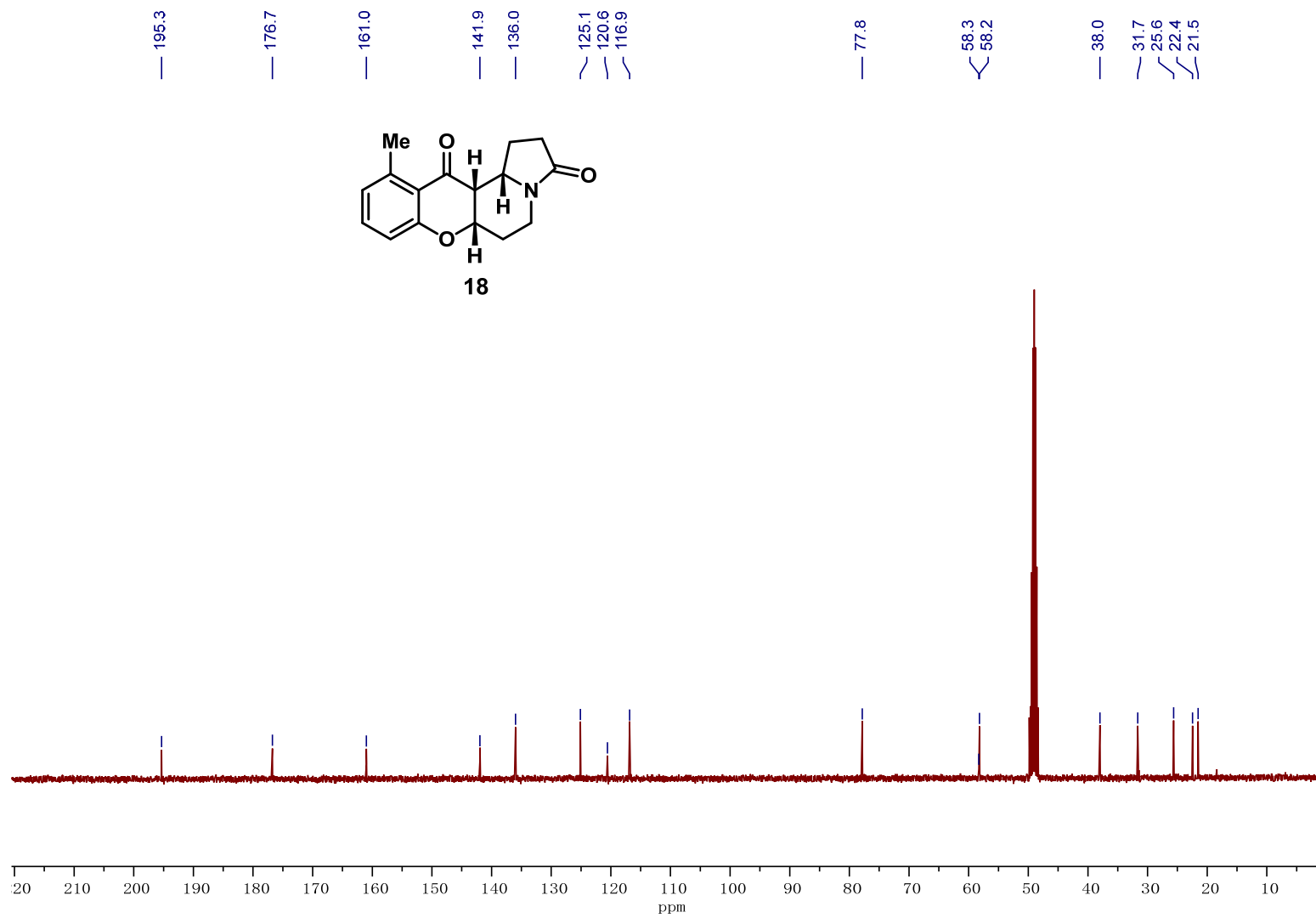
(±)-oxoisoelaecarpine (**4**)



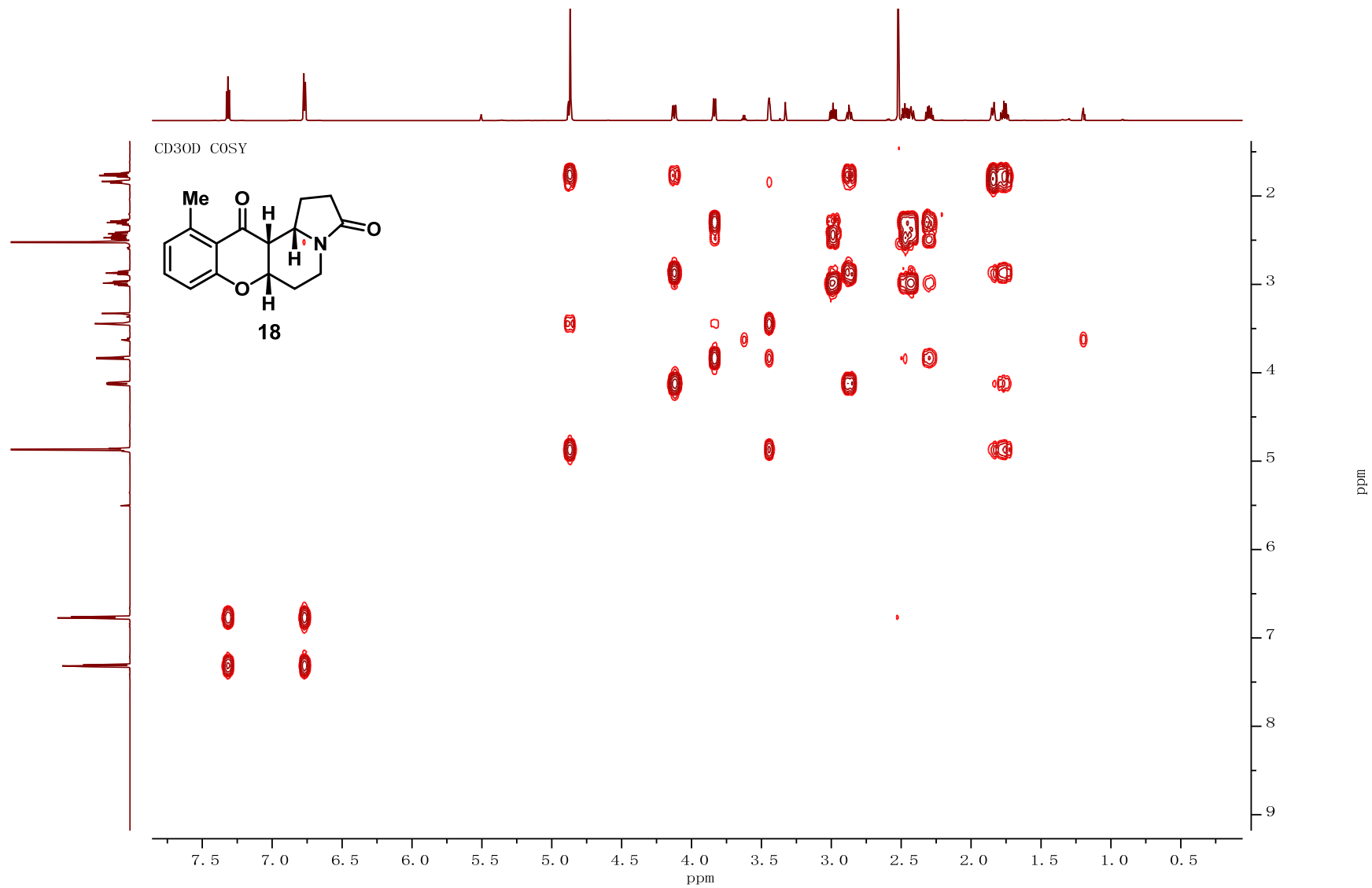
Compound 18 ¹H NMR (400 MHz, Methanol-d₄)



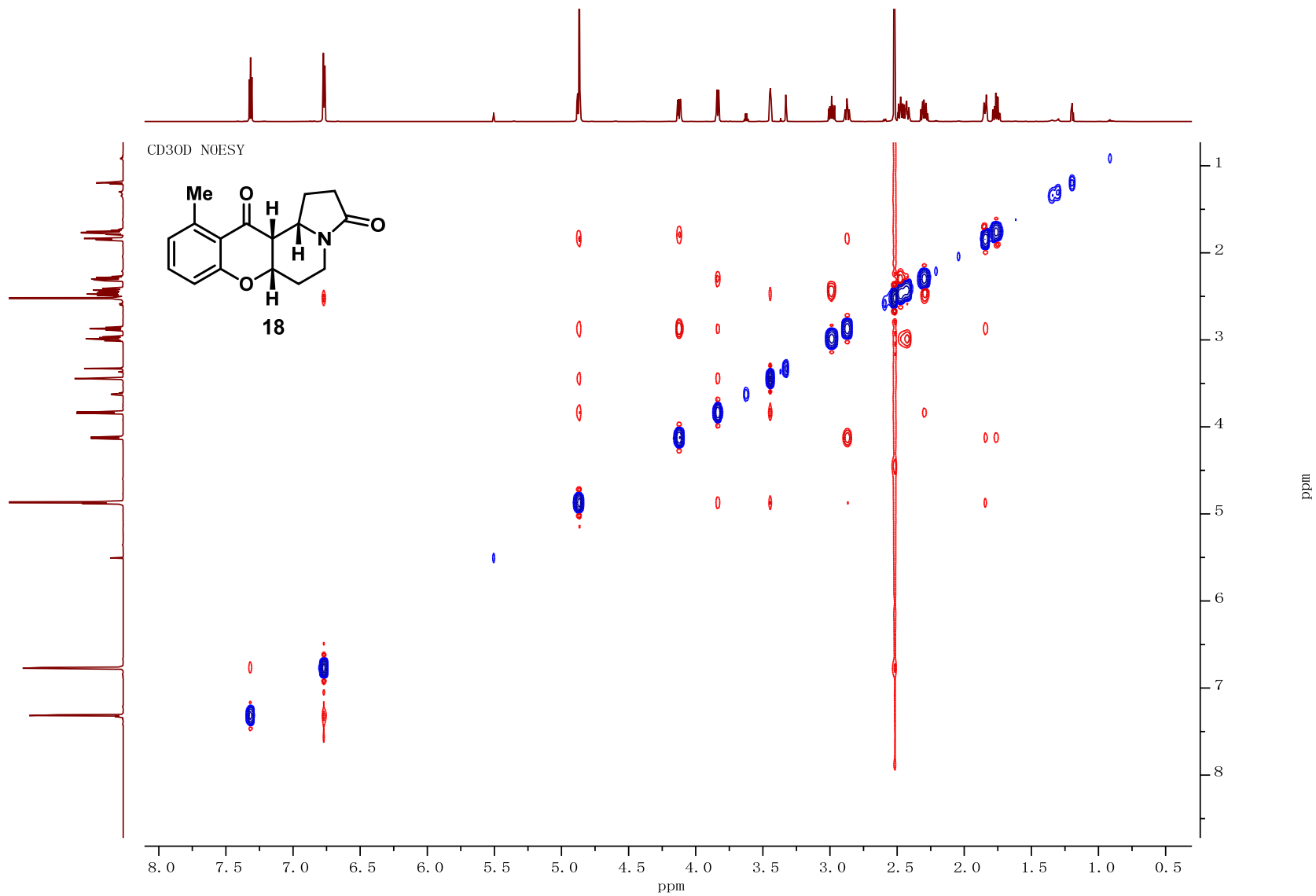
Compound 18 ¹³C NMR (101 MHz, Methanol-*d*₄)



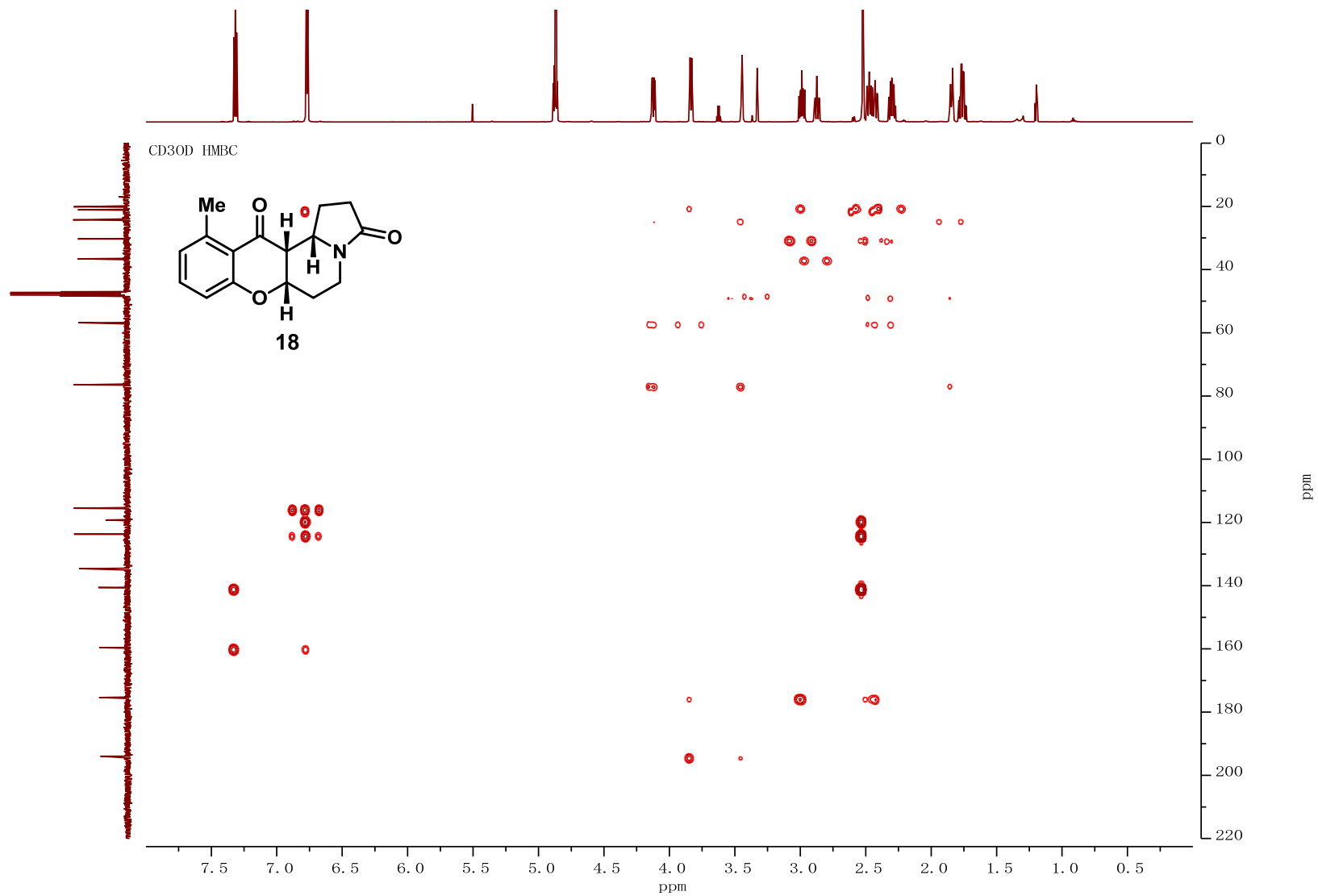
Compound 18 COSY (Methanol-*d*₄)



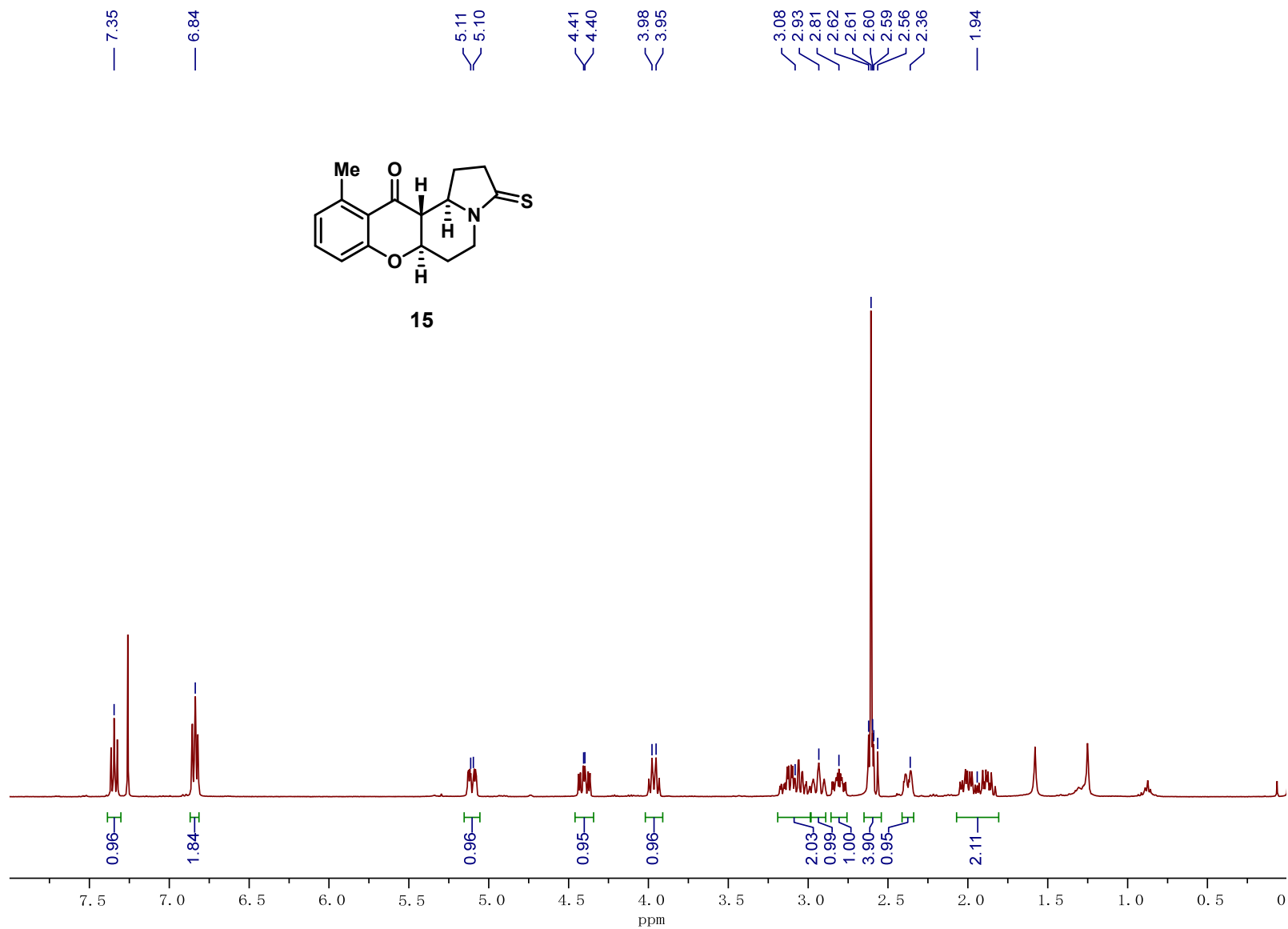
Compound 18 NOESY (Methanol-*d*₄)



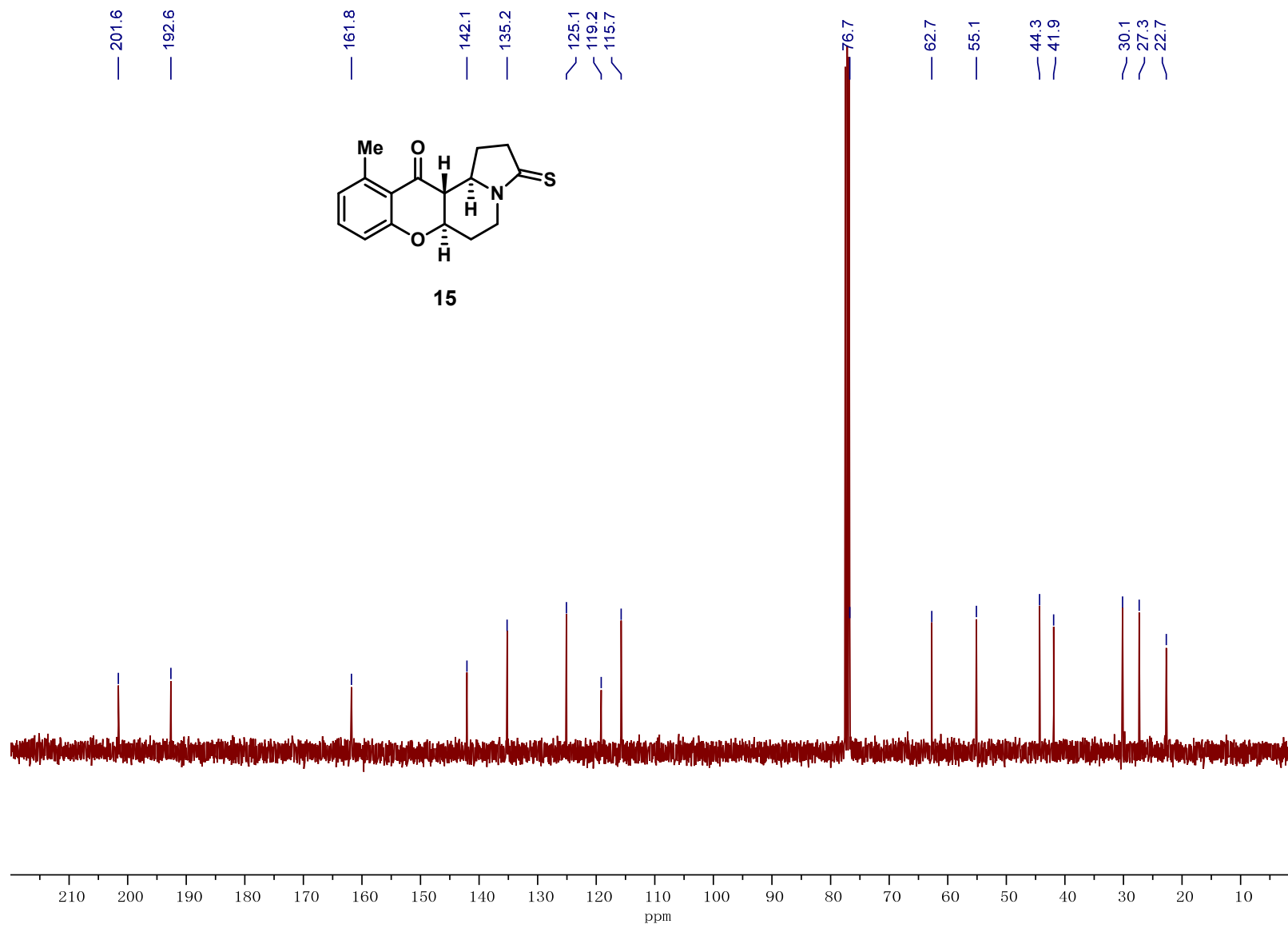
Compound 18 HMBC (Methanol-*d*₄)



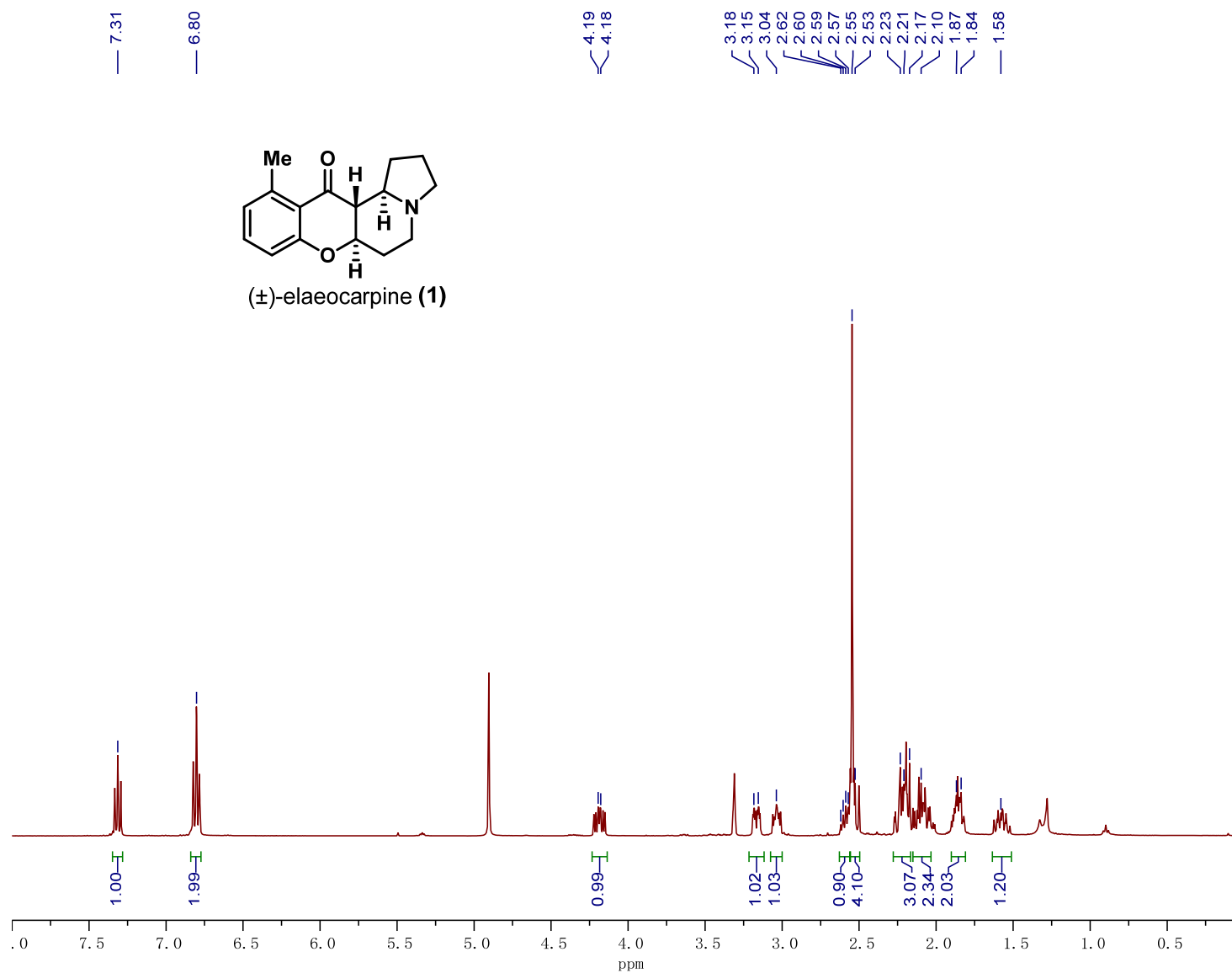
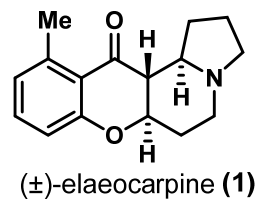
Compound 15 ¹H NMR (400 MHz, Chloroform-*d*)



Compound 15 ¹³C NMR (101 MHz, Chloroform-*d*)

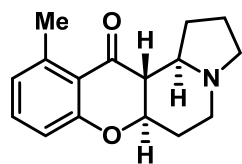


Compound 1 ¹H NMR (400 MHz, Methanol-d₄)

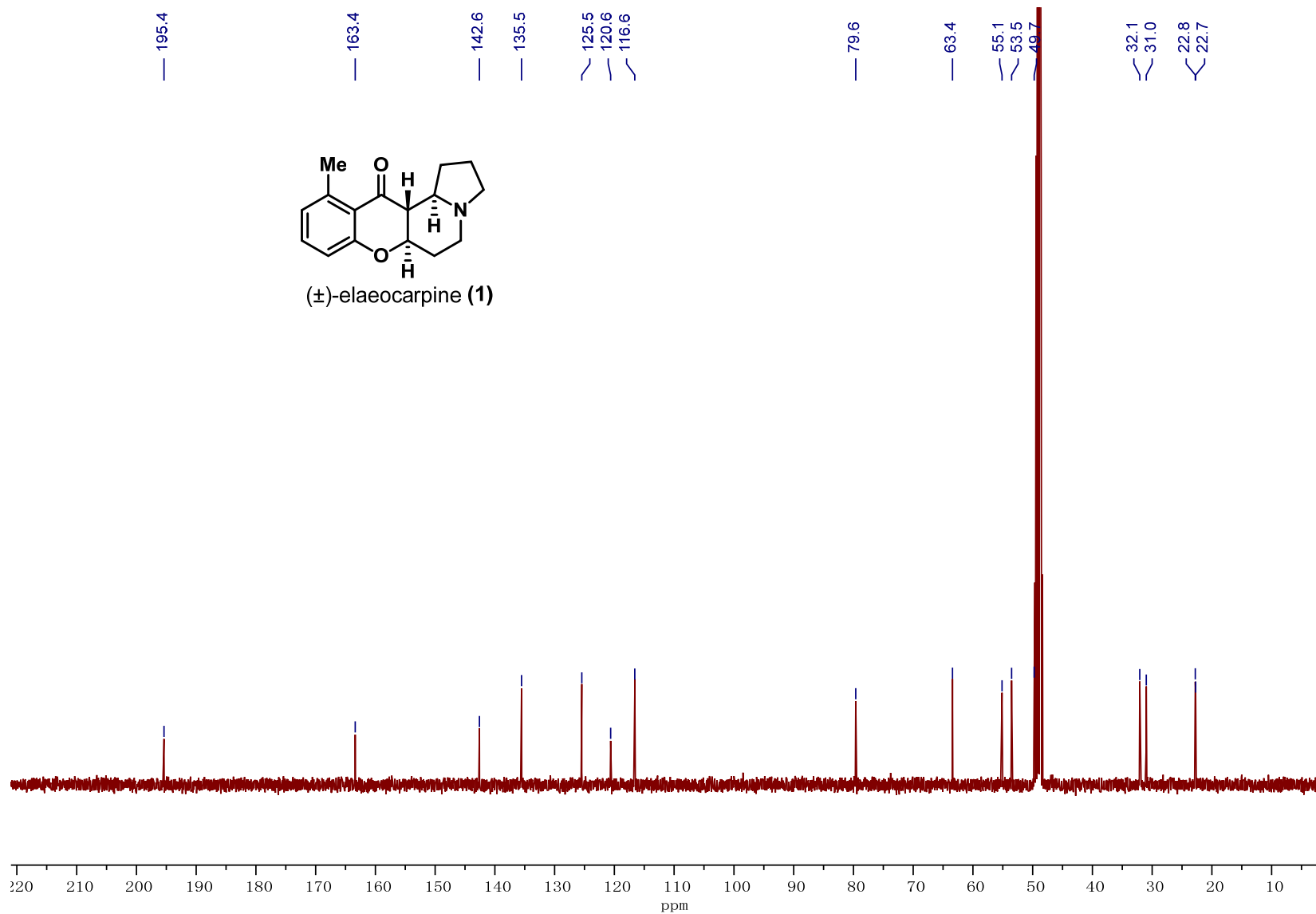


Compound 1 ¹³C NMR (101 MHz, Methanol-d₄)

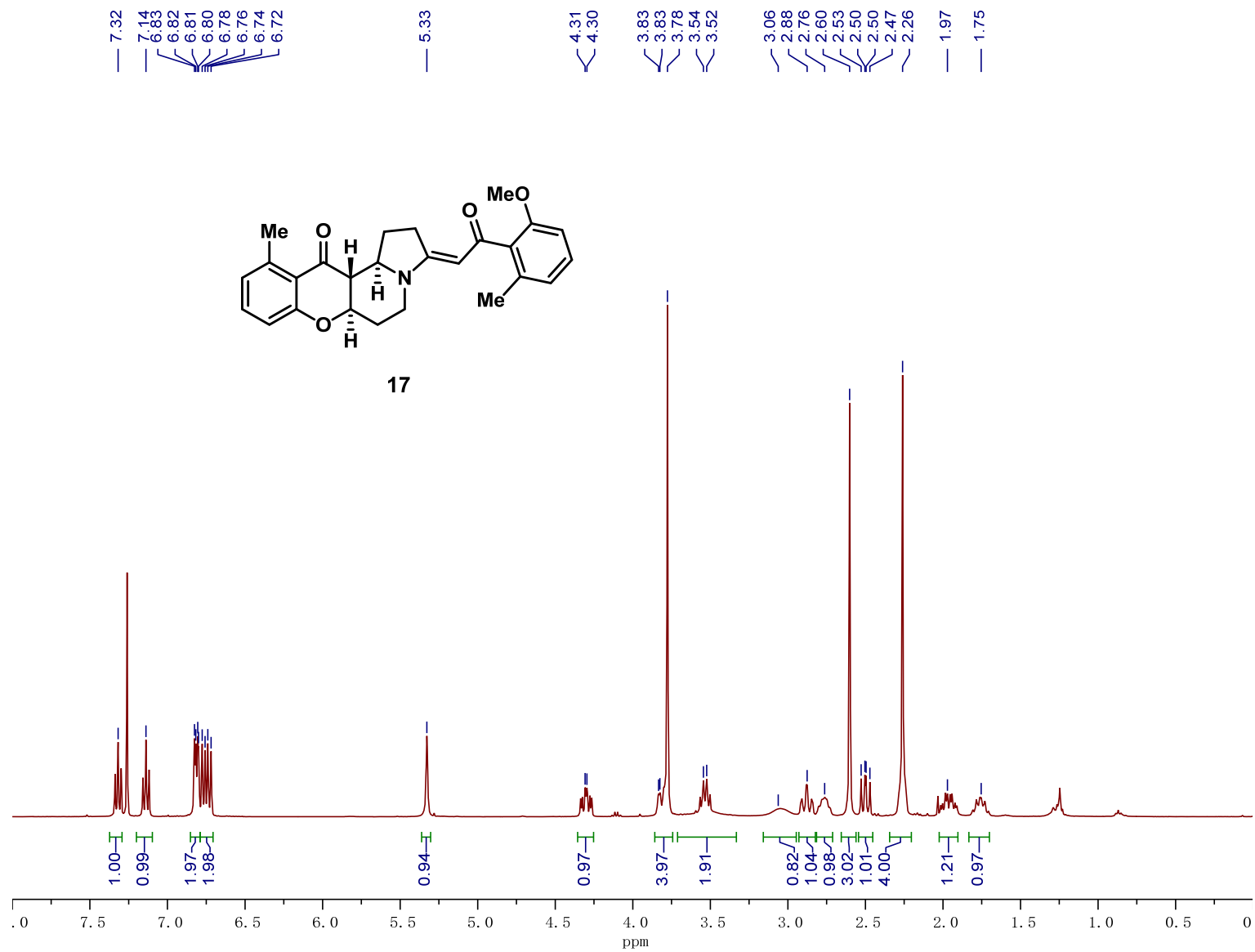
195.4
163.4
142.6
135.5
125.5
120.6
116.6
79.6
63.4
55.1
53.5
49.7
32.1
31.0
22.8
22.7



(±)-elaecarpine (1)



Compound 17 ¹H NMR (400 MHz, Chloroform-*d*)



7.32
7.14
6.82
6.81
6.80
6.78
6.76
6.74
6.72
5.33
4.31
4.30
3.83
3.83
3.78
3.54
3.52
3.06
2.88
2.76
2.60
2.53
2.50
2.50
2.47
2.26
1.97
1.75

1.00
0.99
1.97
1.98
0.94
0.97
3.97
1.91
0.82
1.04
0.98
3.02
1.01
4.00
1.21
0.97

Compound 17 ¹³C NMR (101 MHz, Chloroform-*d*)

193.0
192.4

164.7
161.7
155.6

142.0
135.4
134.9
134.5
128.3
124.9
122.6
119.3
115.6

108.4

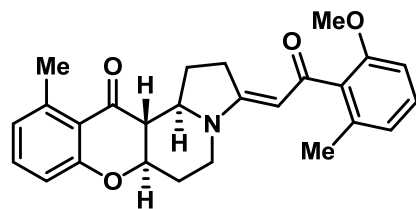
93.5

77.2

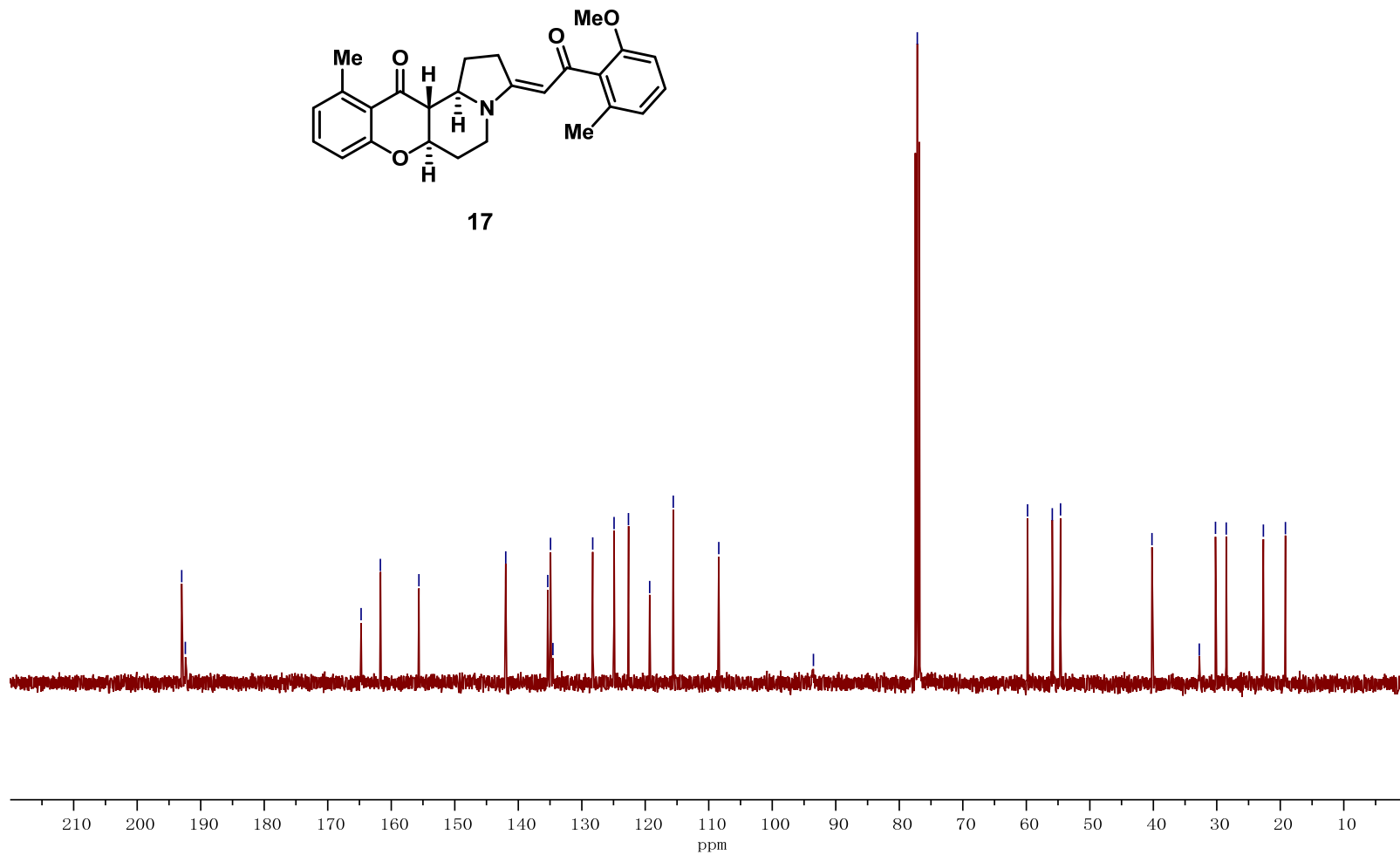
59.8
55.9
54.6

40.2

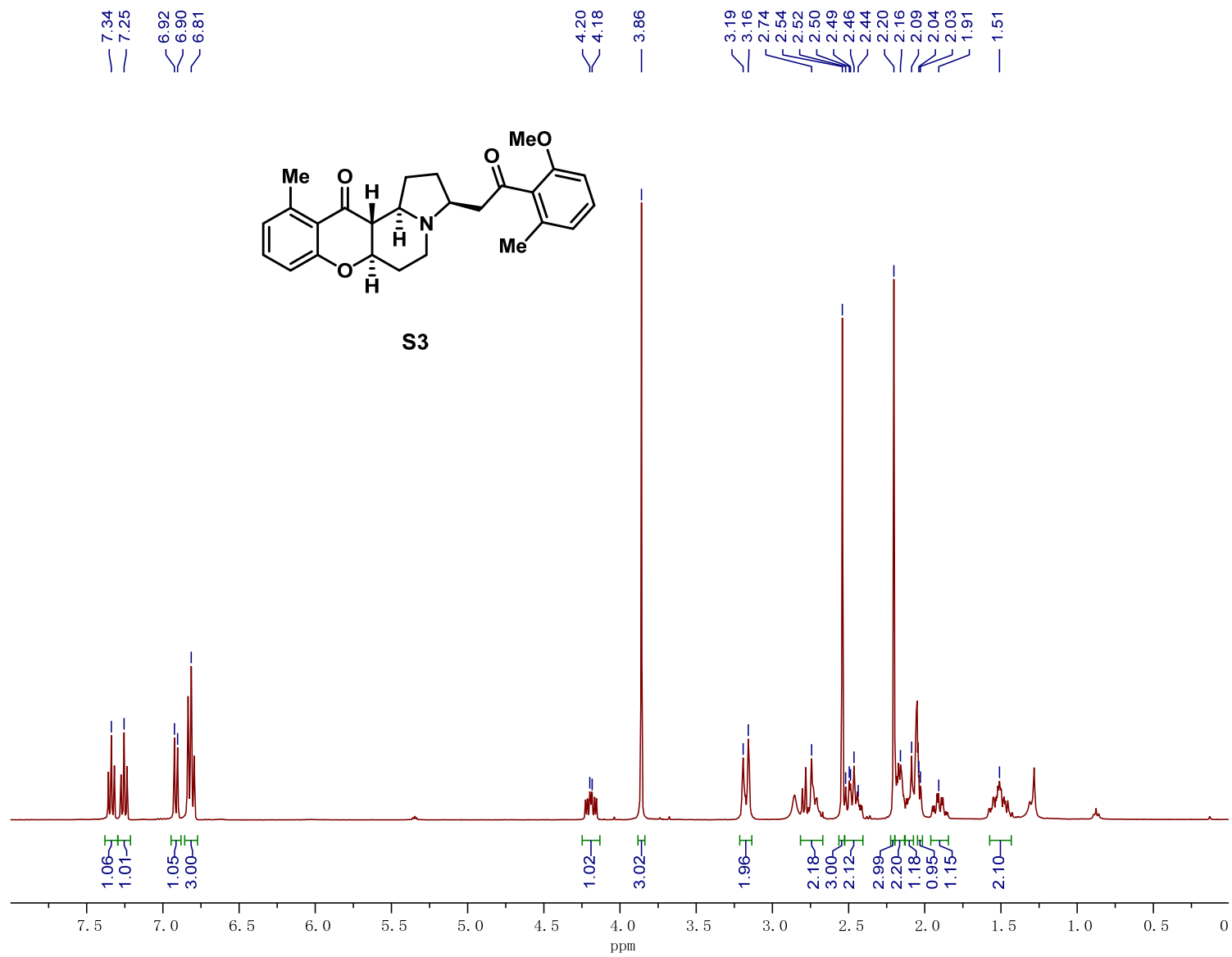
32.8
30.2
28.5
22.7
19.2



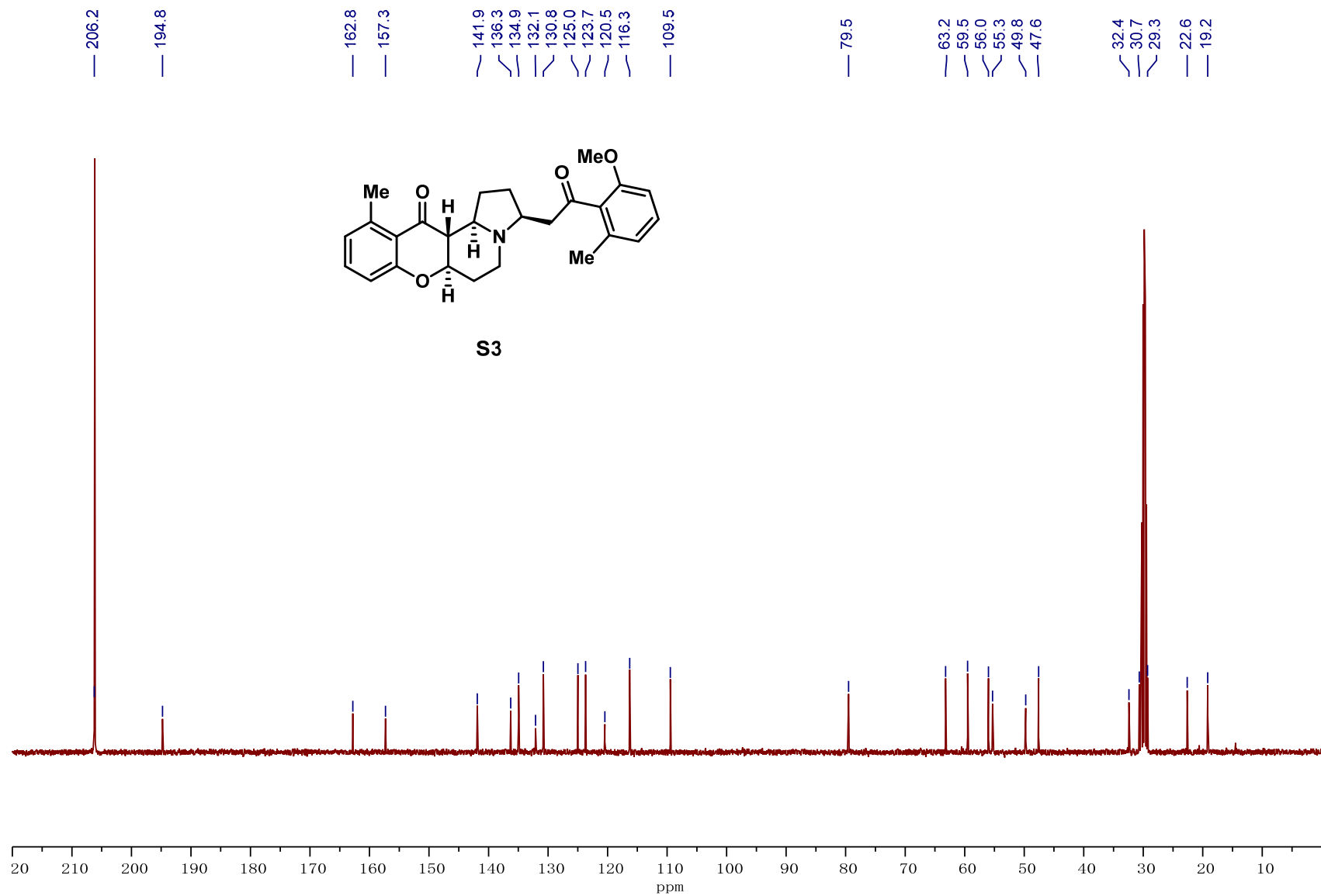
17



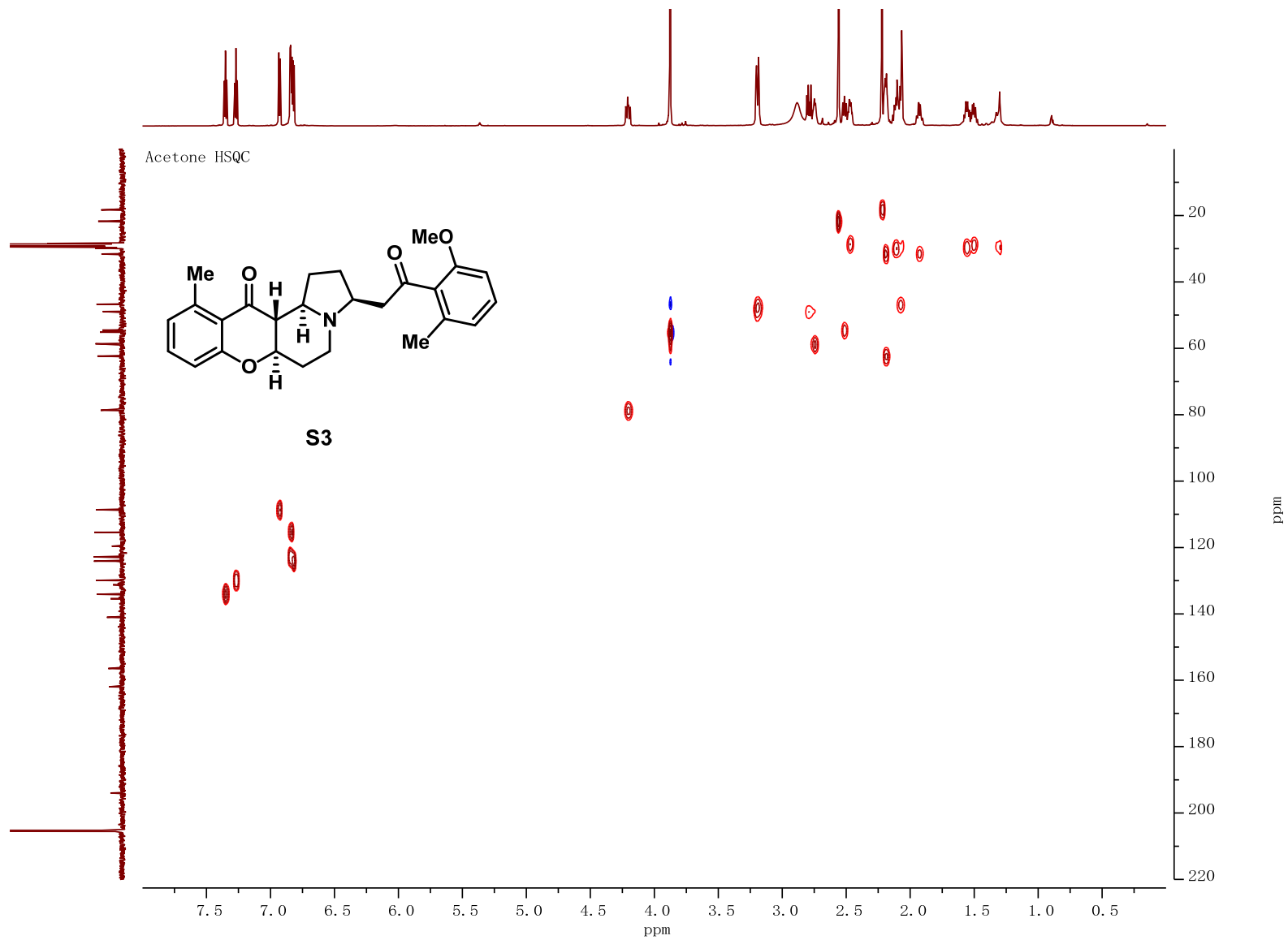
Compound S4 ¹H NMR (400 MHz, Acetone-*d*₆)



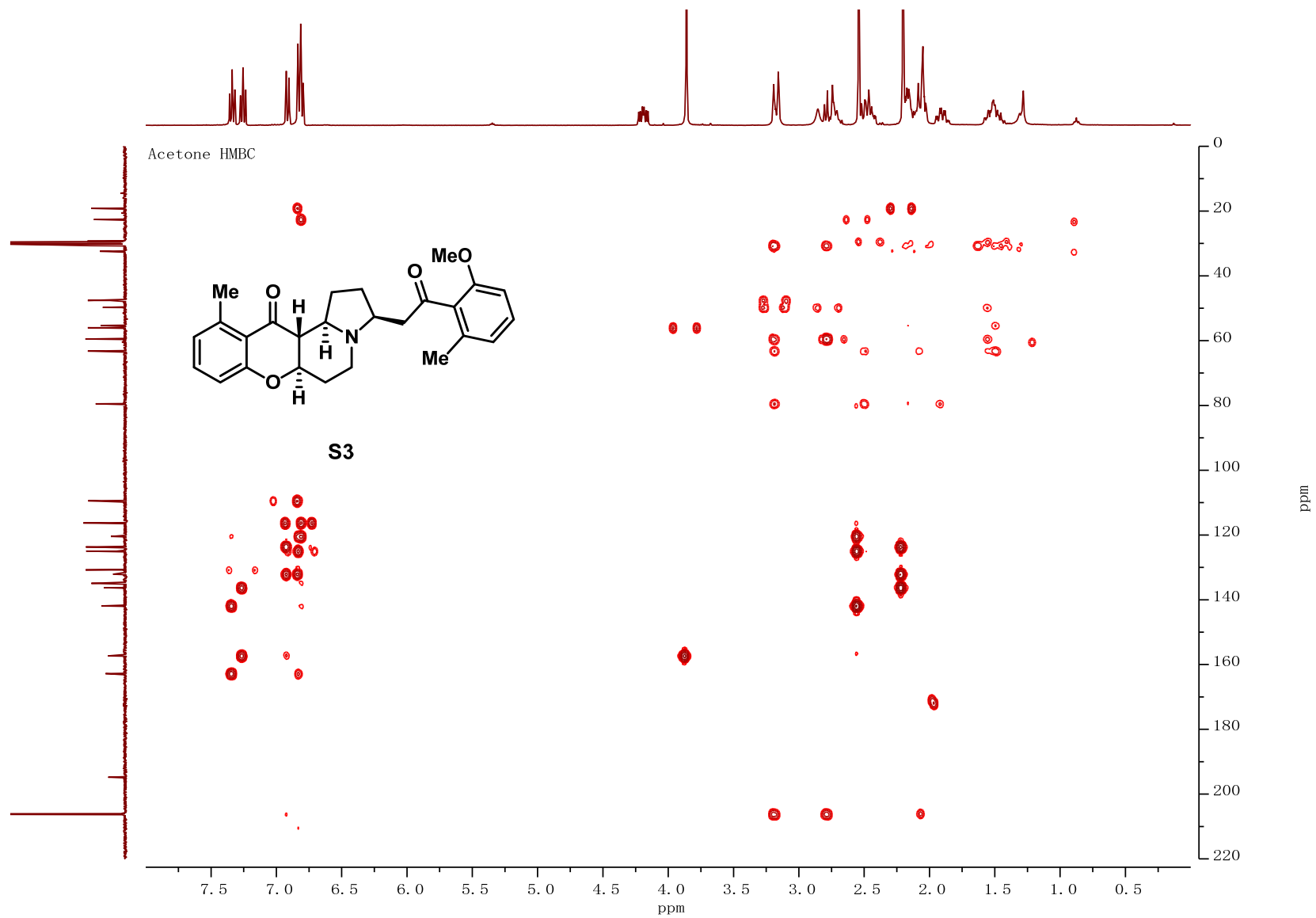
Compound S4 ¹³C NMR (101 MHz, Acetone-*d*₆)



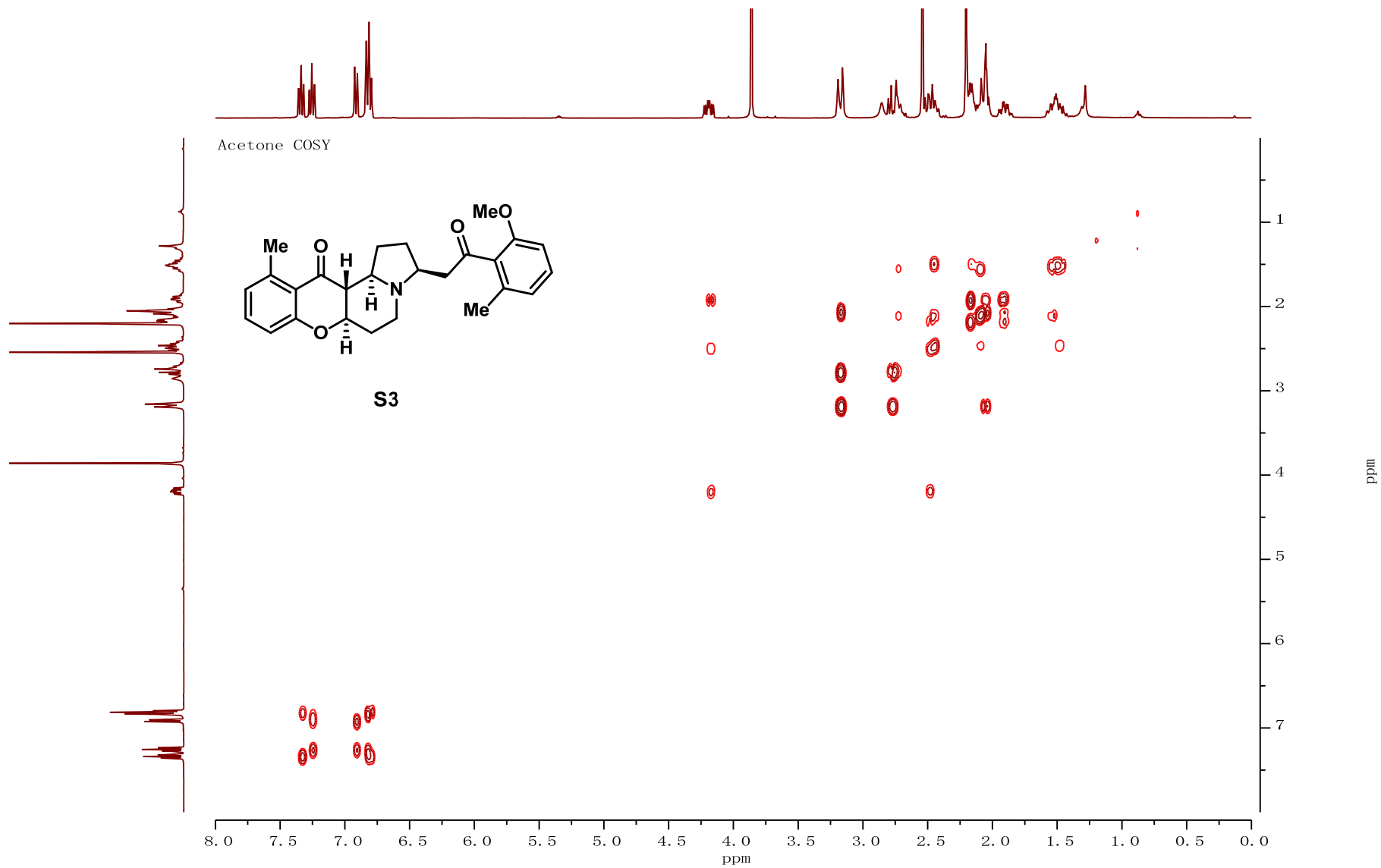
Compound S4 HSQC (Acetone-*d*₆)



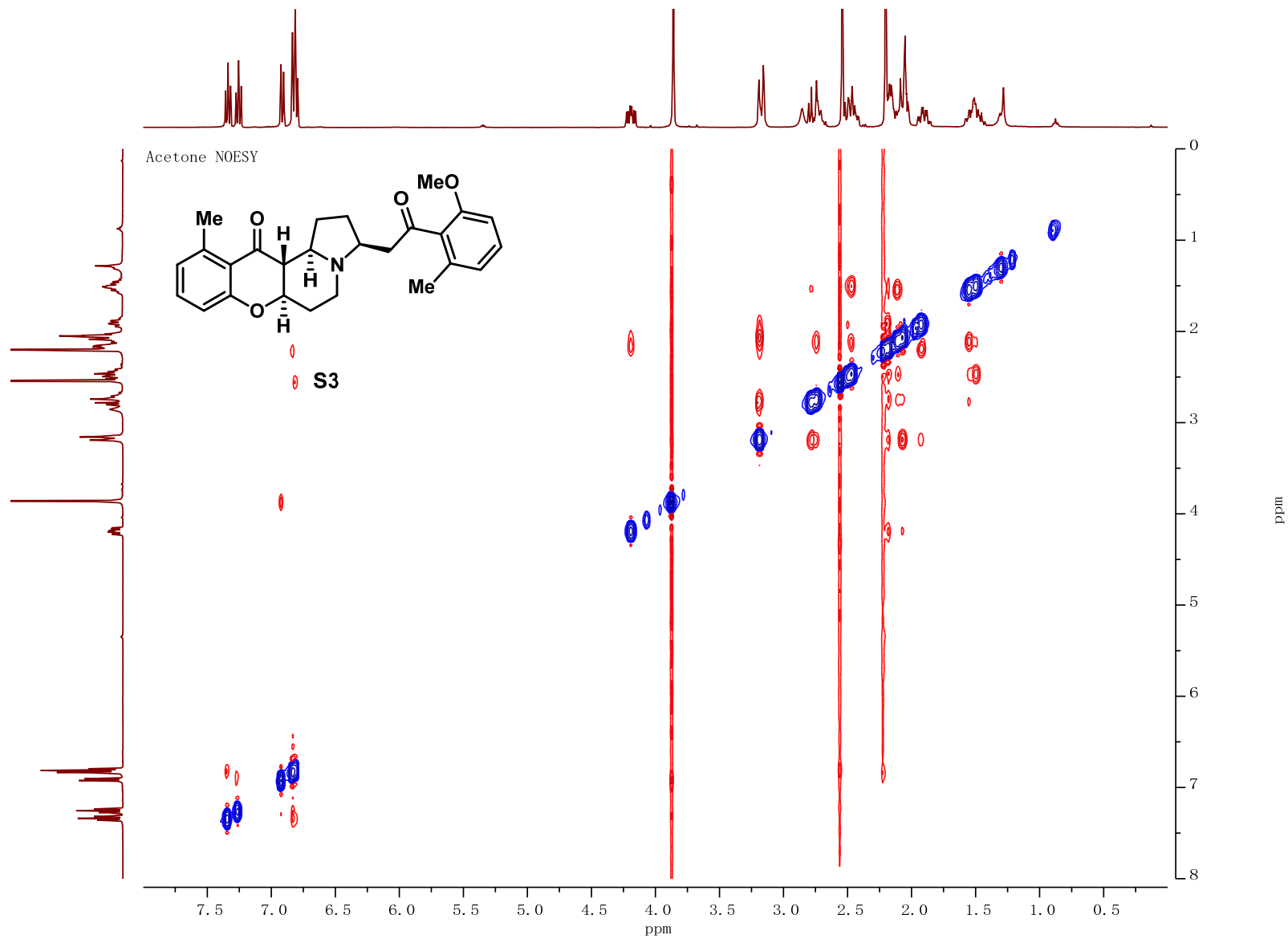
Compound S4 HMBC (Acetone-*d*₆)



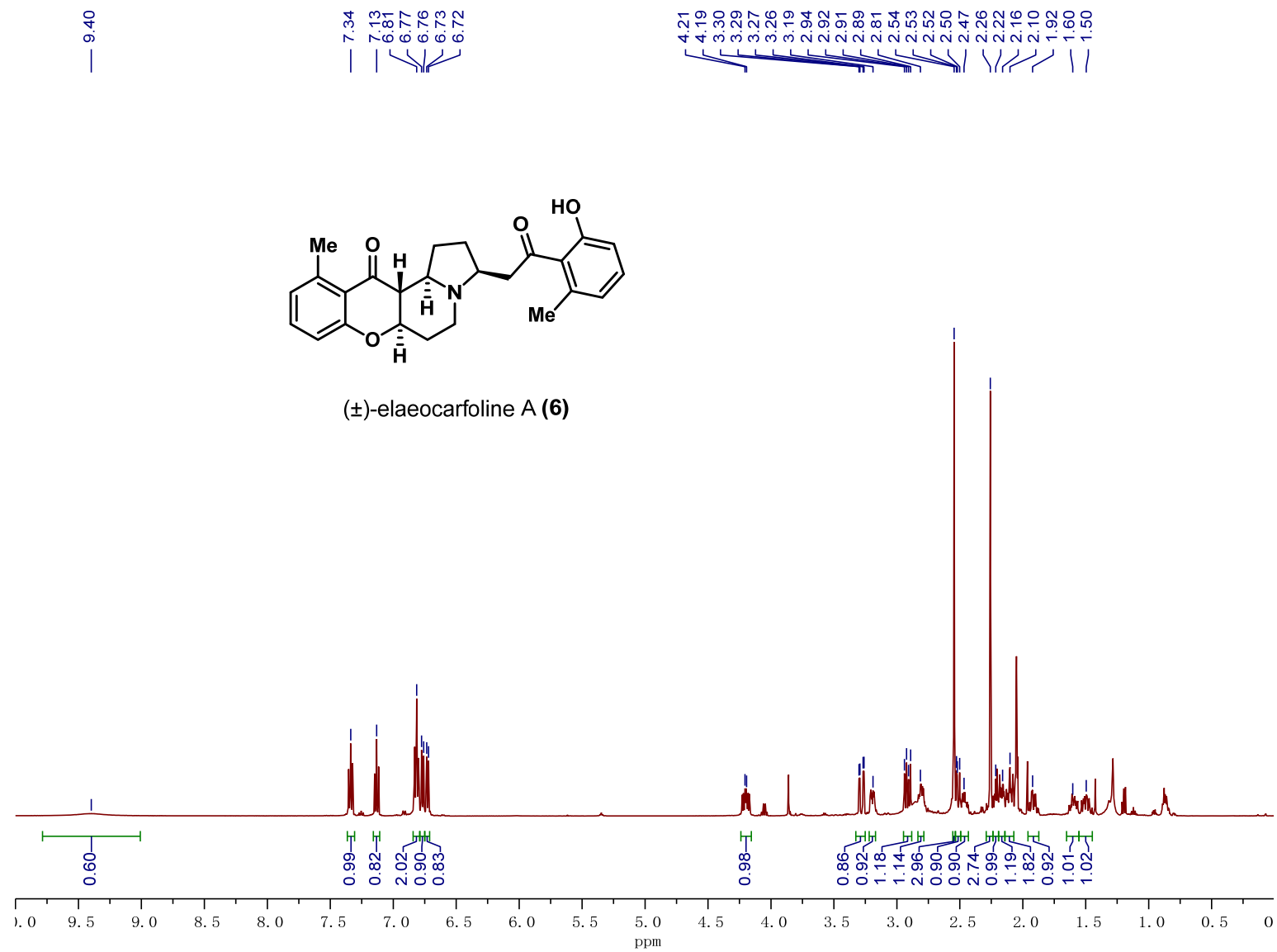
Compound S4 COSY (Acetone-*d*₆)



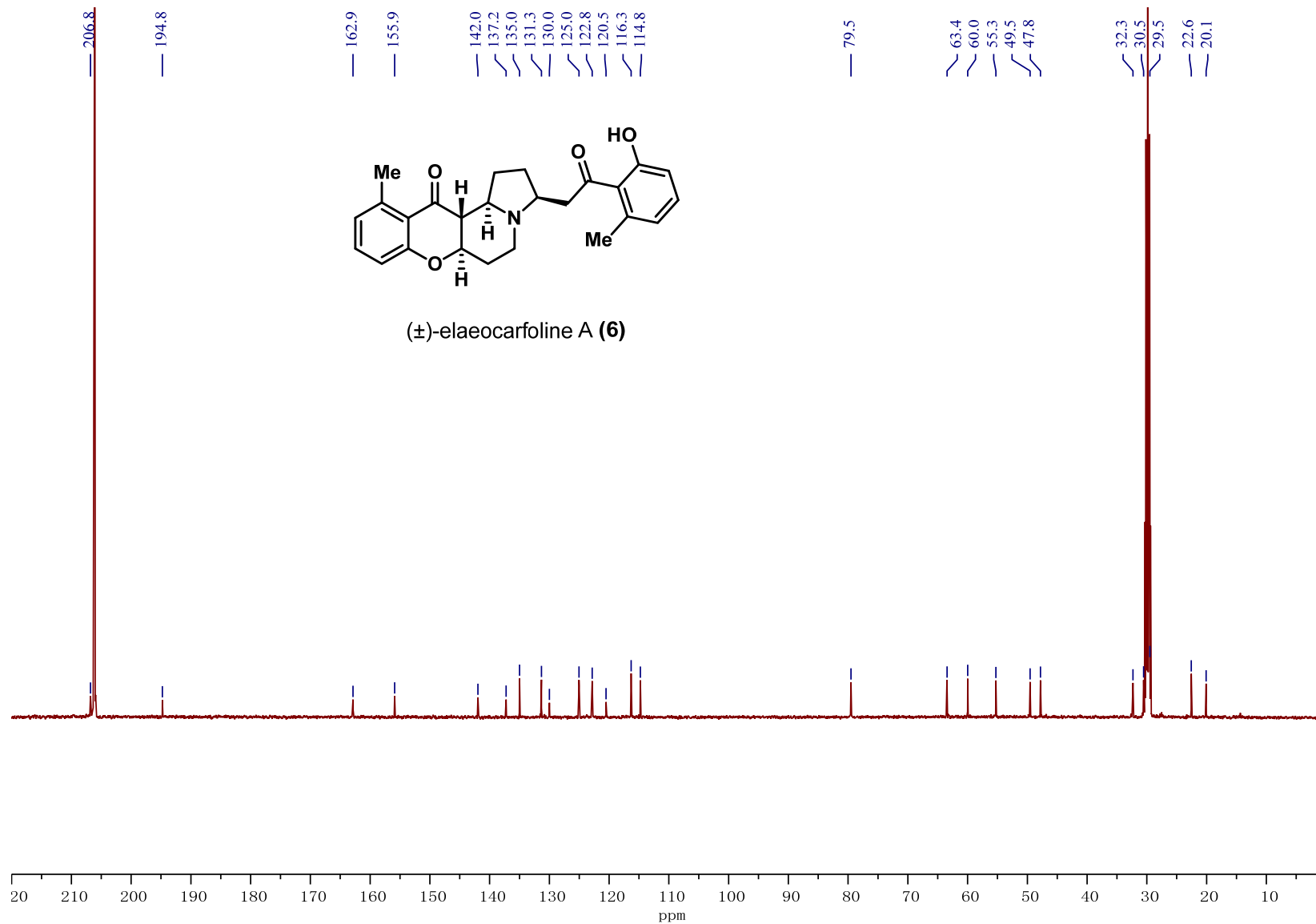
Compound S4 NOESY (Acetone-*d*₆)



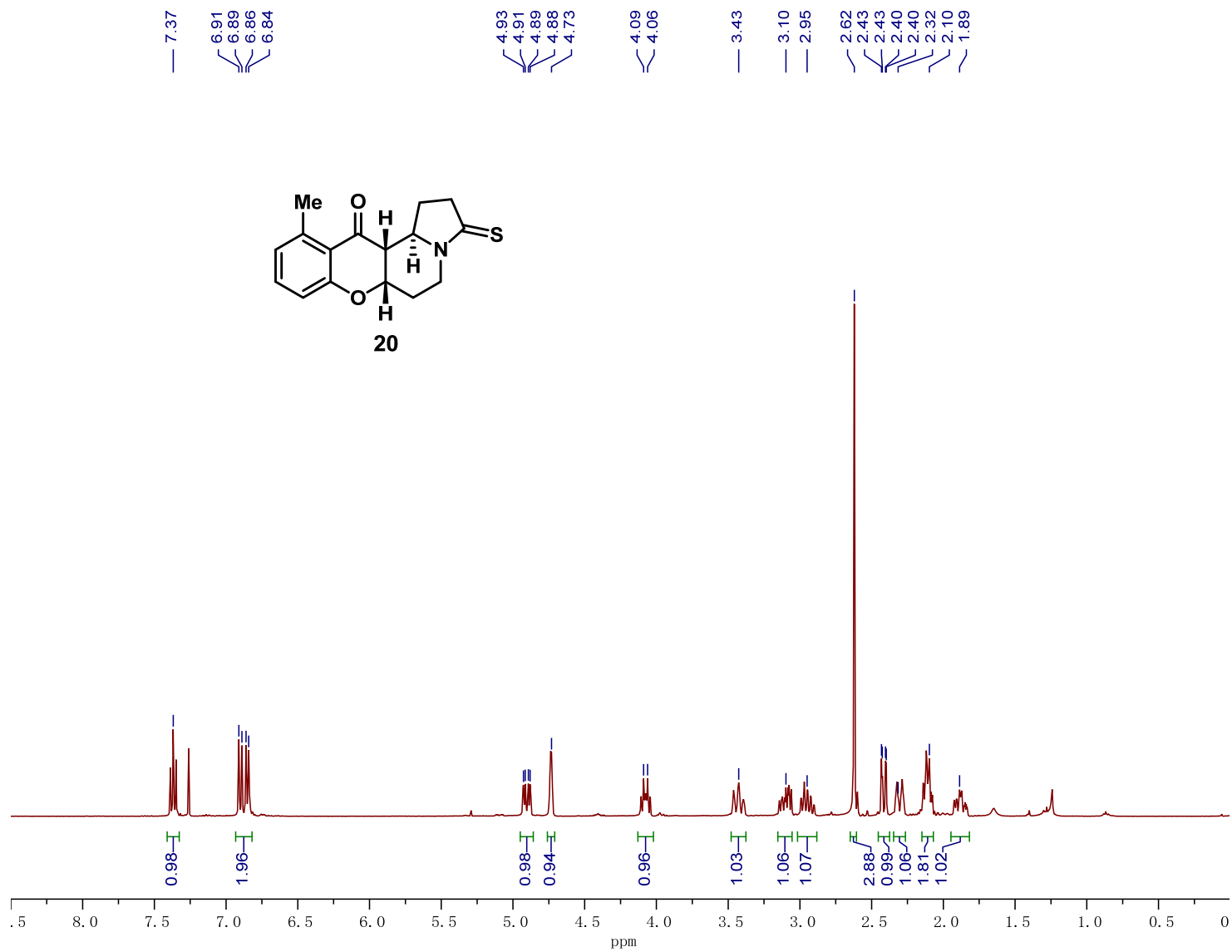
Compound 6 ¹H NMR (500 MHz, Acetone-*d*₆)



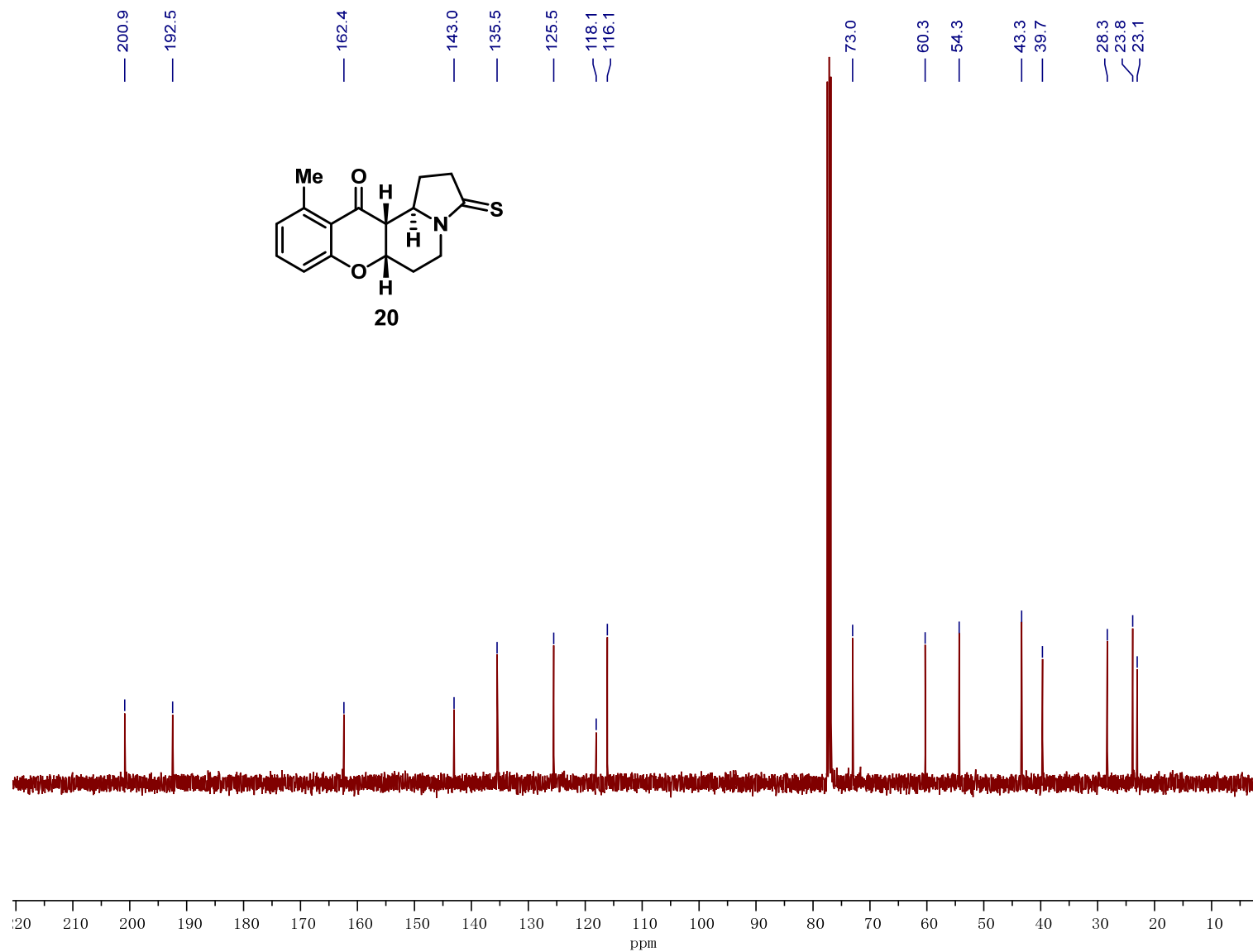
Compound 6 ^{13}C NMR (126 MHz, Acetone- d_6)



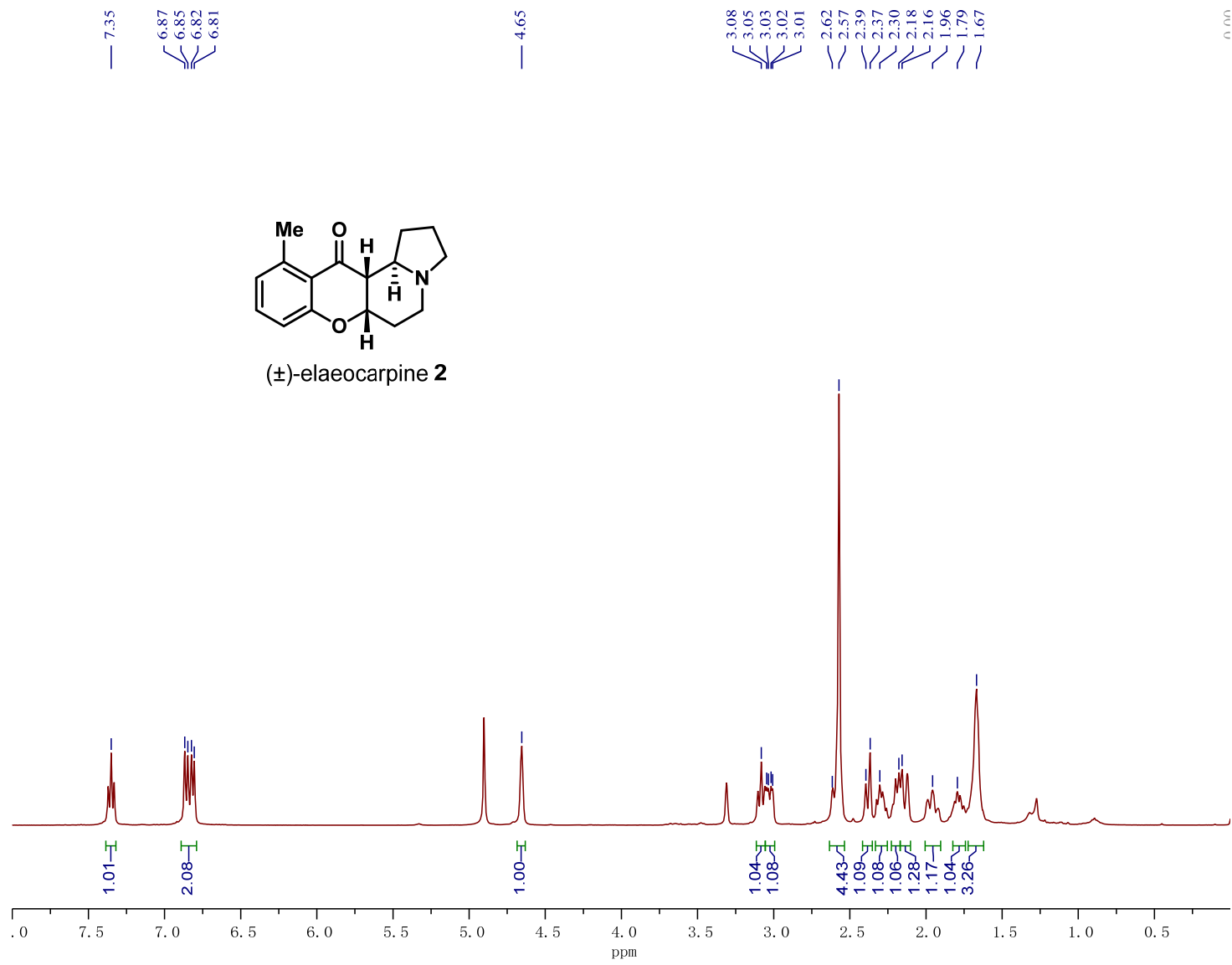
Compound 20 ^1H NMR (400 MHz, Chloroform-*d*)



Compound 20 ¹³C NMR (101 MHz, Chloroform-*d*)

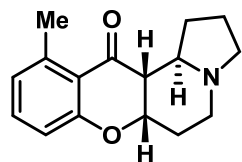


Compound 2 ¹H NMR (400 MHz, Methanol-d₄)

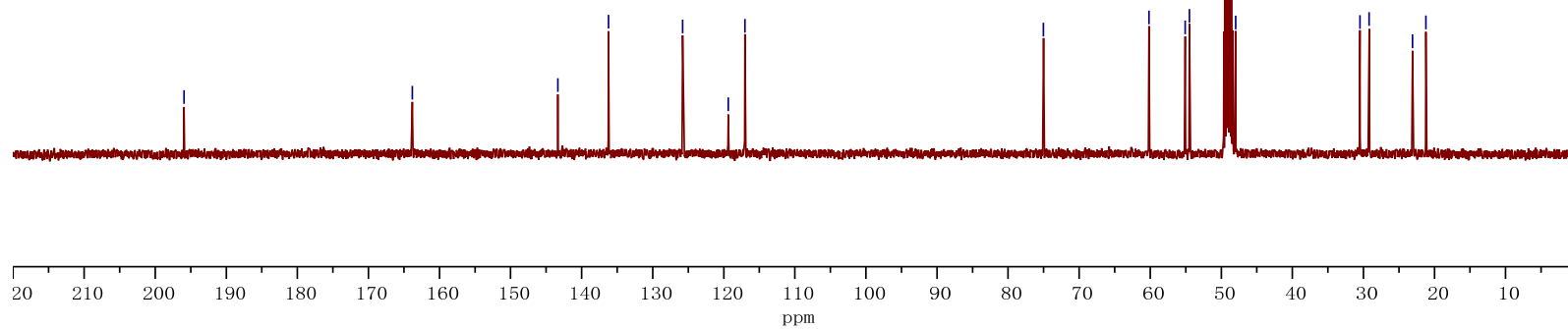


Compound 2 ¹³C NMR (101 MHz, Methanol-*d*₄)

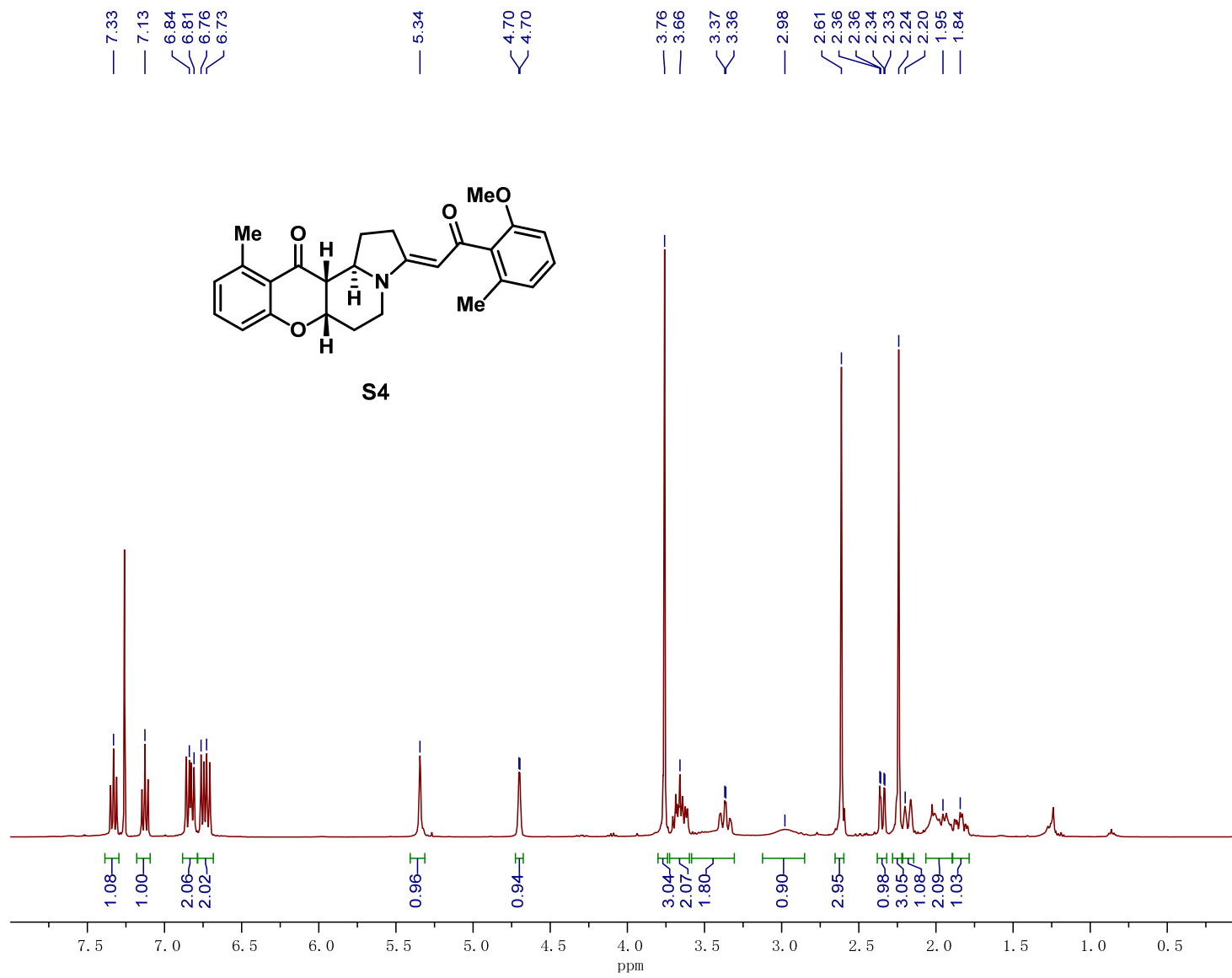
195.9
163.8
143.3
136.2
125.8
119.4
117.0
75.0
60.2
55.1
54.5
48.0
30.5
29.2
23.1
21.2



(±)-elaeocarpine 2



Compound S5 ¹H NMR (400 MHz, Chloroform-*d*)



Compound S5 ¹³C NMR (101 MHz, Chloroform-*d*)

193.2
192.4

164.8
162.2
155.6

142.8
135.3
135.2
134.5
128.2
125.3
122.6
118.1
115.9

108.4

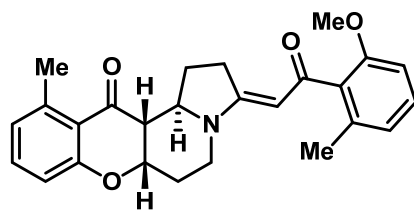
93.8

73.3

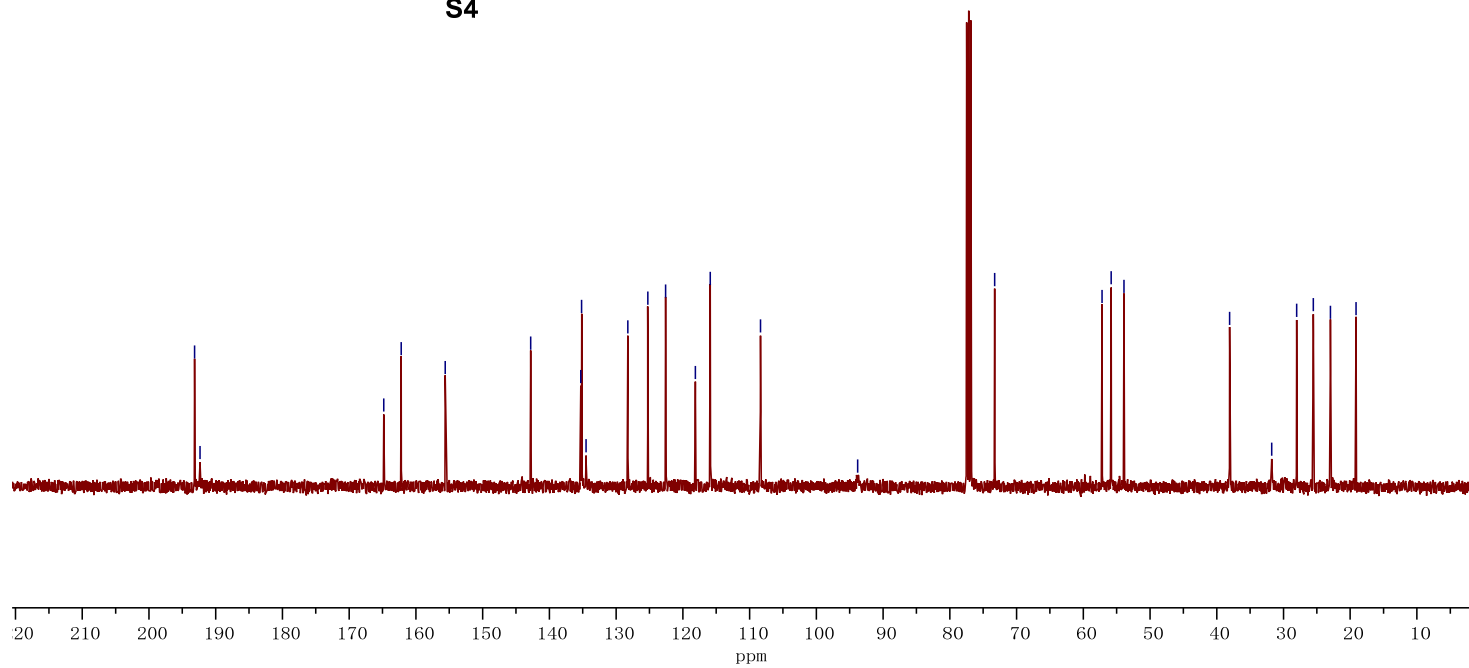
57.2
55.8
53.9

38.1

31.8
28.0
25.5
23.0
19.1



S4



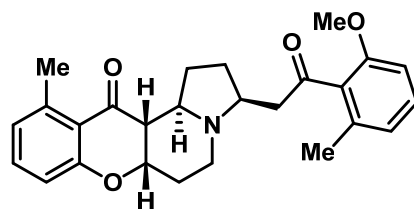
Compound S6 ¹H NMR (400 MHz, Acetone-*d*₆)

7.37
7.25
6.92
6.88
6.83
6.81

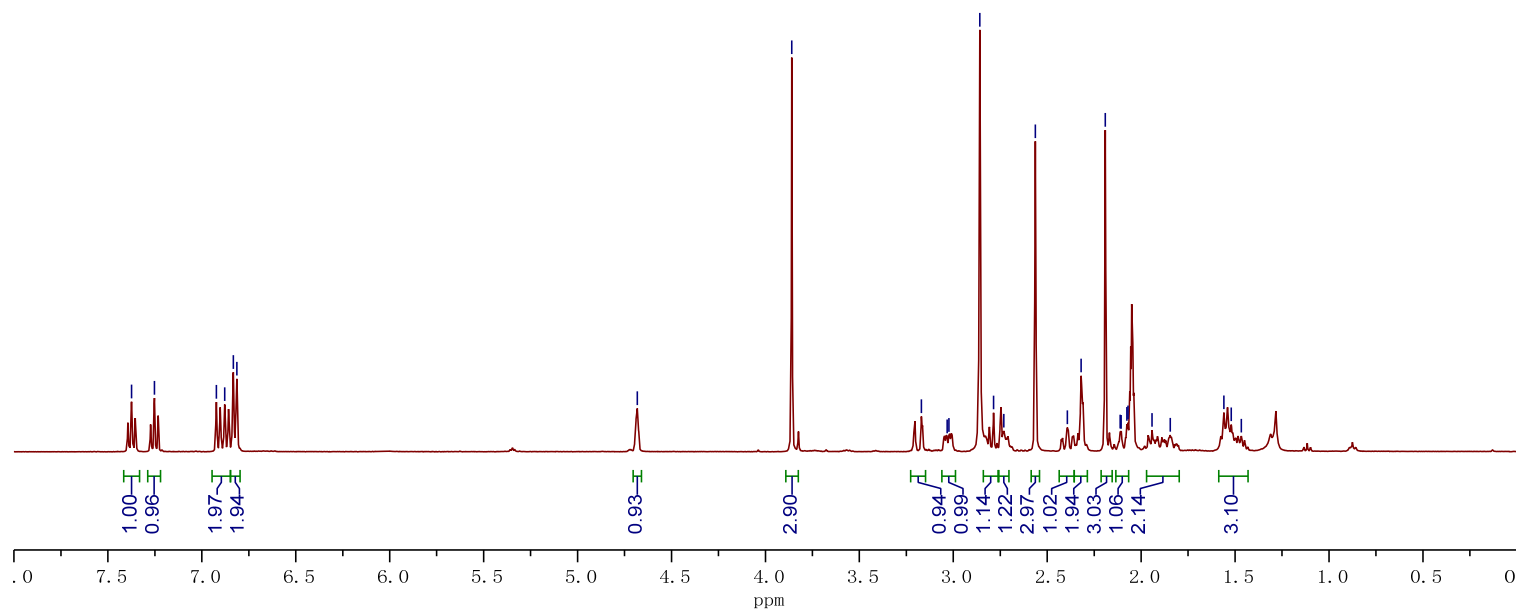
4.68

3.86

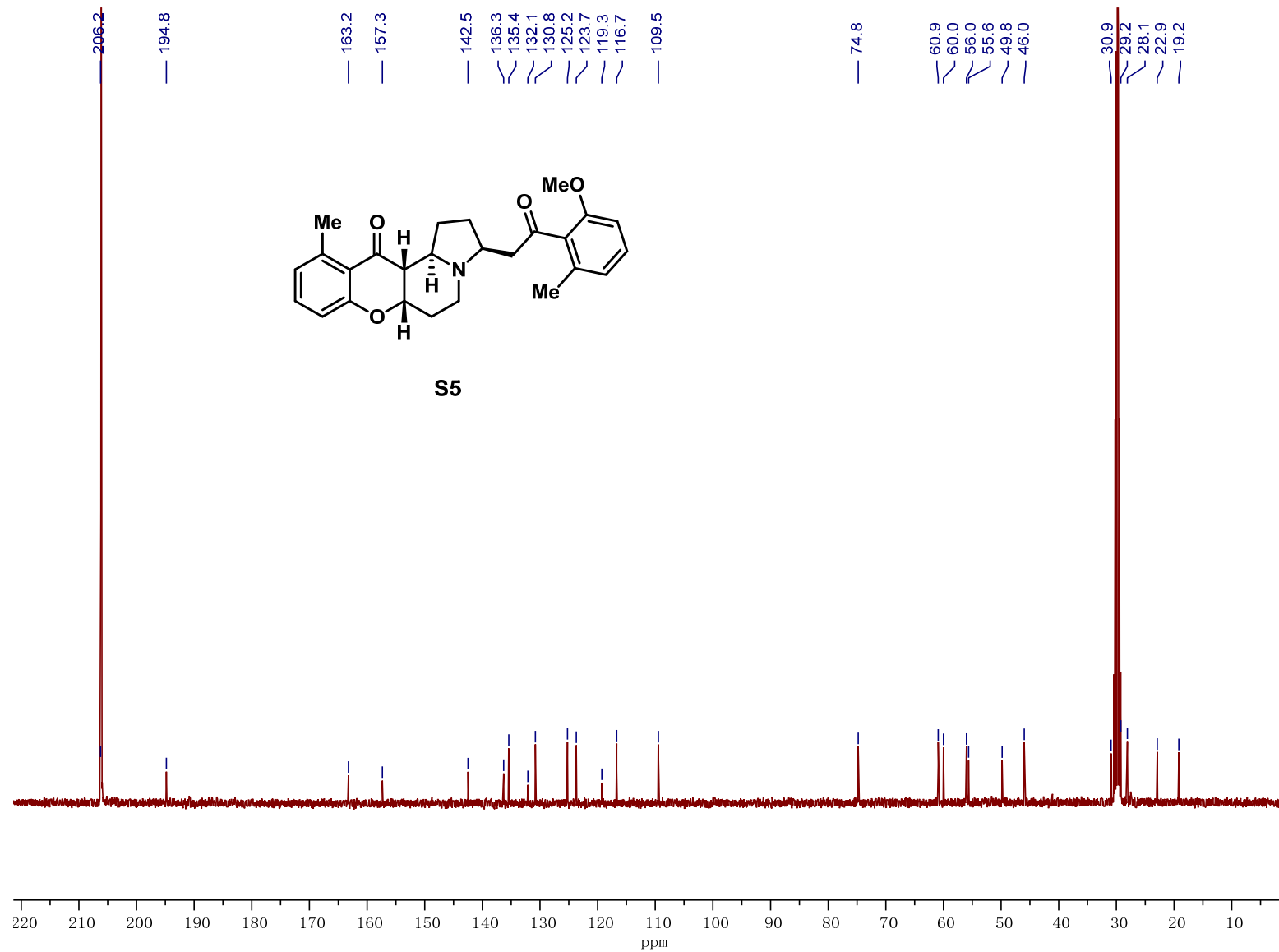
3.17
3.03
3.02
2.86
2.79
2.73
2.56
2.39
2.32
2.19
2.11
2.11
2.08
2.07
1.94
1.85
1.56
1.52
1.47



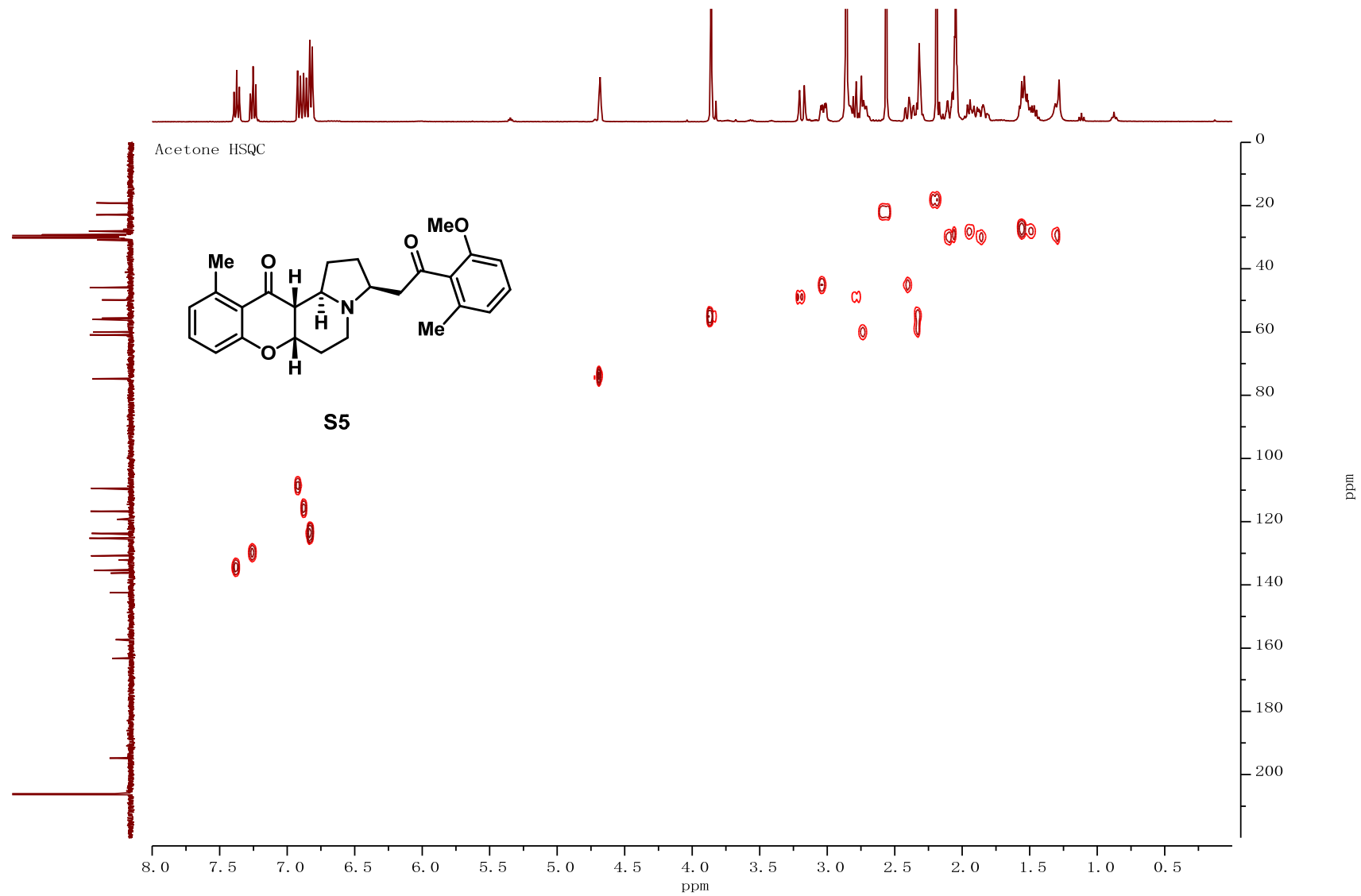
S5



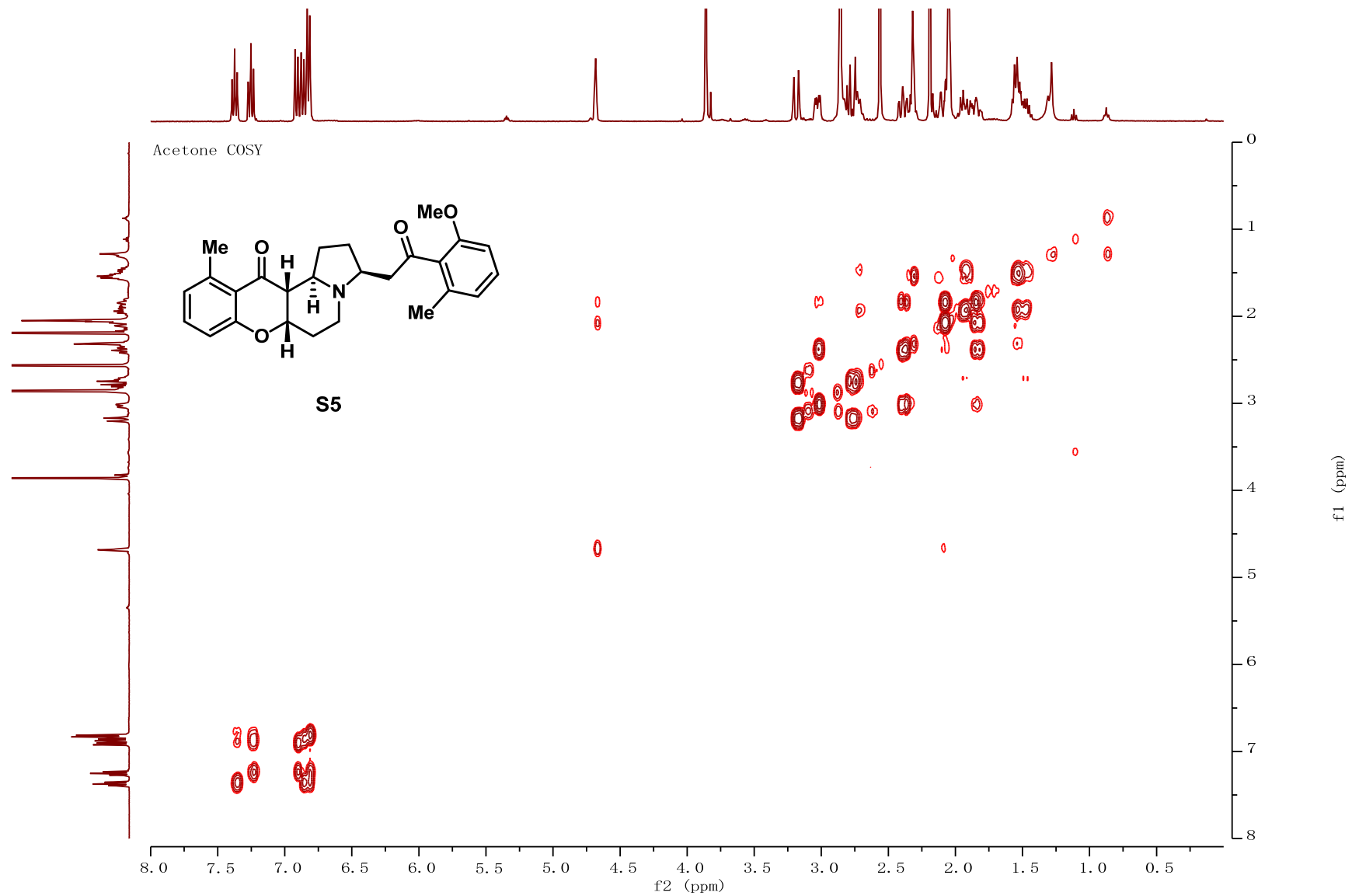
Compound S6 ¹³C NMR (101 MHz, Acetone-*d*₆)



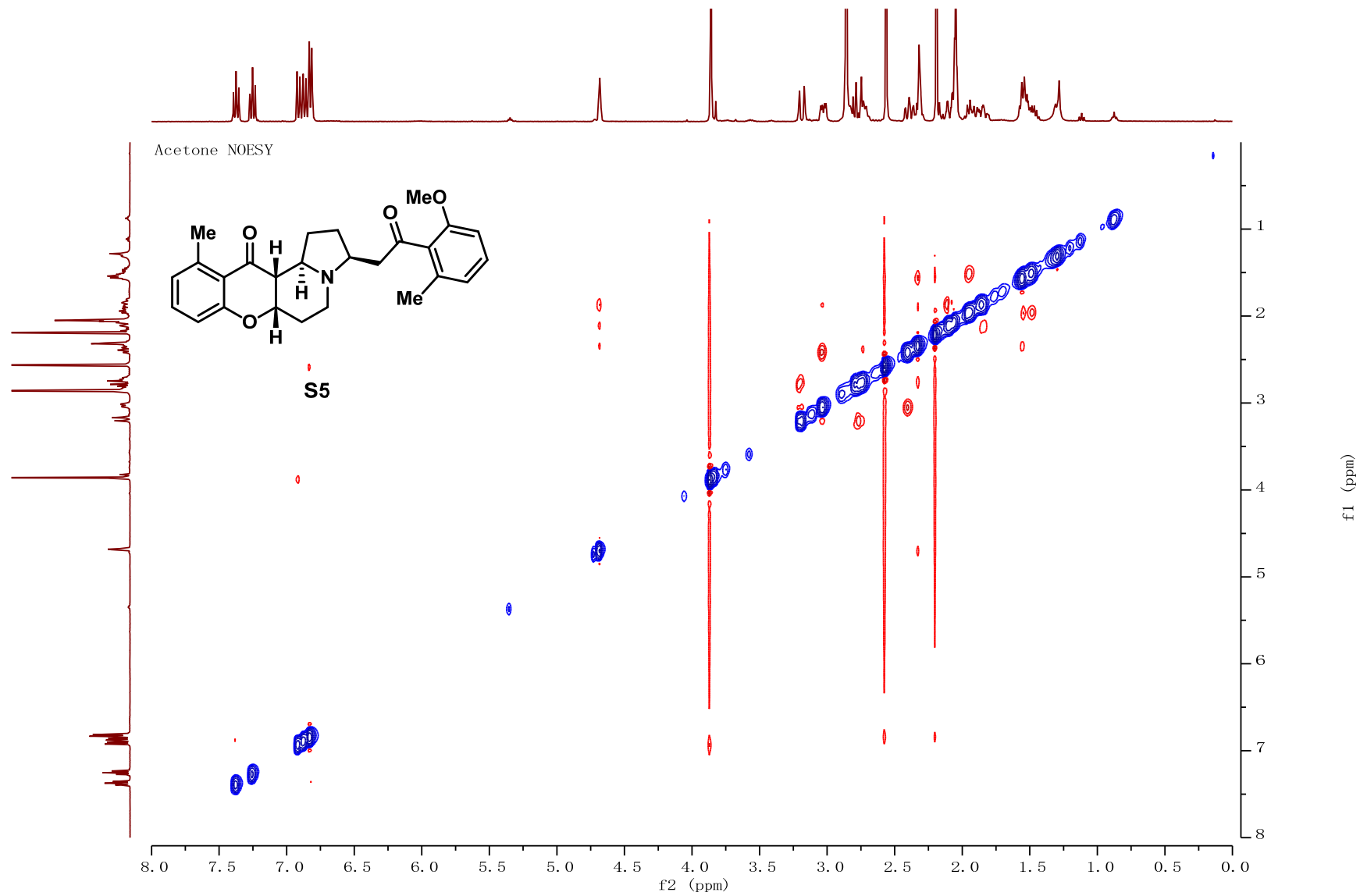
Compound S6 HSQC (Acetone-*d*₆)



Compound S6 COSY (Acetone-*d*₆)



Compound S6 NOESY (Acetone-*d*₆)

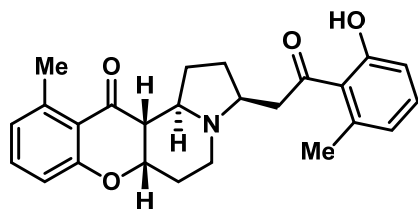


Compound 7 ¹H NMR (500 MHz, Acetone-d₆)

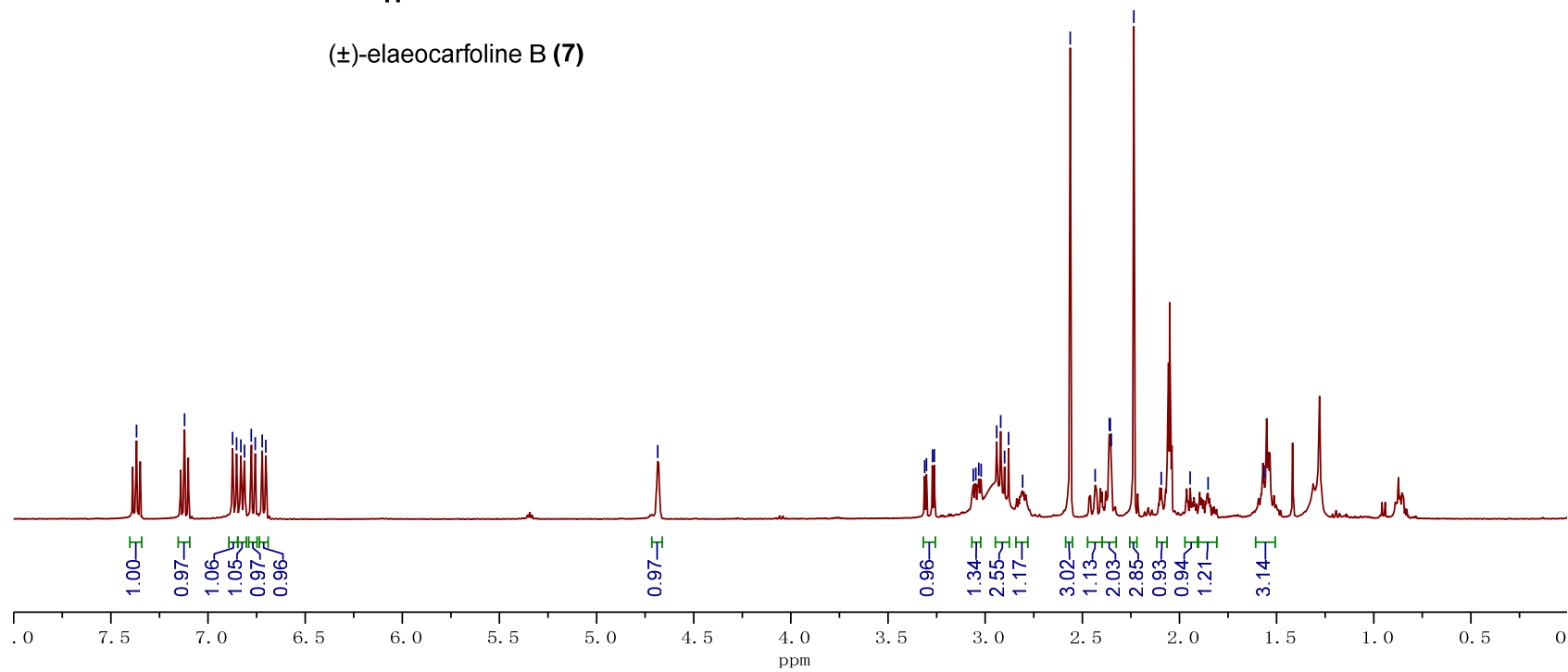
7.37
7.12
6.87
6.85
6.83
6.81
6.78
6.76
6.72
6.70

4.69

3.31
3.30
3.27
3.26
3.06
3.05
3.03
3.02
2.94
2.92
2.90
2.88
2.81
2.56
2.43
2.36
2.36
2.35
2.24
2.09
1.95
1.85
1.56



(±)-elaecarfoline B (7)



Compound 7 ¹³C NMR (126 MHz, Acetone-*d*₆)

