

Supporting Information

Convenient approach to polyoxygenated dibenzo[*c,e*]pyrrolo[1,2-*a*]azepines from donor-acceptor cyclopropanes

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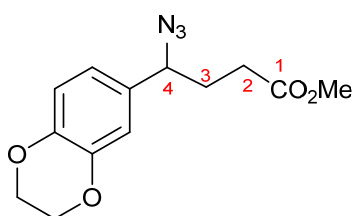
General Information

NMR spectra were recorded on Bruker Avance 500 MHz and Bruker Avance 400 MHz spectrometers at room temperature; the chemical shifts δ were measured in ppm with respect to solvent (CDCl₃: ¹H: δ = 7.27 ppm, ¹³C: δ = 77.0 ppm; CD₃OD-d₆: δ_{H} = 3.35 ppm, ¹³C: δ = 49.9 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, double doublet. Coupling constants (*J*) are given in Hz. The structures of synthesized compounds were elucidated with the aid of 1D NMR (¹H, ¹³C) and 2D NMR (COSY ¹H-¹H, HSQC and HMBC ¹H-¹³C, HMBC ¹H-¹⁵N, NOESY ¹H-¹H) spectroscopies. Infrared spectra were recorded on Thermo Nicolet IR200 FT-IR. High resolution and accurate mass measurements were carried out using a Bruker microTOF-QTM ESI-TOF (Electro Spray Ionization / Time of Flight) and Thermo ScientificTM LTQ Orbitrap mass spectrometers. Elemental analyses were performed with Fisons EA-1108 CHNS elemental analyser instrument. Melting points (m.p.) were determined using Electrothermal 9100 capillary melting point apparatus, the values are uncorrected. Microwave reactions were performed in a Monowave 300 – Anton Paar microwave reactor in sealed reaction vessels. The temperature was monitored with installed IR detector. X-Ray analysis was performed on STOE STADI VARI PILATUS-100K diffractometer and corrected for absorption using the *SADABS* program;^[S1] calculations were carried out using the *SHELXTL* program.^[S2] Analytical thin layer chromatography (TLC) was carried out with silica gel plates (silica gel 60, F₂₅₄, supported on aluminium); the visualization was performed by UV lamp (365 nm) and chemical staining (iodine vapor or aqueous potassium permanganate solution). Column chromatography was performed on silica gel 60 (230-400 mesh, Macherey-Nagel). All the reactions were carried out using freshly distilled and dry solvents from solvent stills. 2-Substituted cyclopropane-1,1-diesters **1a-d** were prepared by Knoevenagel/Corey-Chaykovsky reactions sequence from the corresponding aldehydes.^{S1,S2} Spectra and physical data of azides **2a,b** are consistent well with data published earlier.^{S3,S4}

Synthesis of methyl 4-azido-4-arylbutyrates 2a-d

Cyclopropane **1** (1 equiv, 0.4 M in DMSO), sodium azide (2.75 equiv), and triethylamine hydrochloride (2.25 equiv) were mixed in a glass vial and heated in a microwave reactor for 1.5 h at 100 °C. The reaction vessel was cooled to r.t. Water (1 equiv.) was added and the reaction mixture was heated in a microwave reactor at 125 °C for another 4 h followed by quenching with water and extraction with ethyl acetate (3×10 mL). The combined organic extracts were washed with brine, dried with anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography on a silica gel to afford the desired product.

Methyl 4-azido-4-(2,3-dihydro[1,4]benzodioxin-6-yl)butanoate (2c) was obtained from cyclopropane **1c** (585 mg, 2 mmol), NaN₃ (358 g, 5.5 mmol) and triethylamine hydrochloride (620 g, 4.5 mmol) in DMSO (5 mL) as a colorless oil; yield 344 mg (62%); *R_f* = 0.32 (diethyl ether : petroleum ether; 1:1).

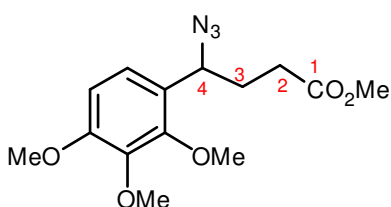


¹H NMR (CDCl₃, 500 MHz) δ = 1.99–2.13 (m, 2H, C(3)H₂), 2.38 (t, ³*J* = 7.5 Hz, 2H, C(2)H₂), 3.69 (s, 3H, CH₃O), 4.28 (s, 4H, OC₂H₄O), 4.42 (dd, ³*J* = 8.1 Hz, ³*J* = 6.6 Hz, 1H, C(4)H), 6.79 (dd, ³*J* = 8.2 Hz, ⁴*J* = 2.1 Hz, 1H, Ar), 6.84 (d, ⁴*J* = 2.1 Hz, 1H, Ar), 6.88 (d, ³*J* = 8.2 Hz, 1H, Ar).

¹³C NMR (CDCl₃, 125 MHz) δ = 30.6 (CH₂), 31.2 (CH₂), 51.7 (CH₃O), 64.3 (2×CH₂O), 64.8 (CHN₃), 115.9 (CH, Ar), 117.5 (CH, Ar), 120.0 (CH, Ar), 132.1 (C, Ar), 143.66 (C, Ar), 143.71 (C, Ar), 173.2 (CO₂Me).

Anal. calcd for C₁₃H₁₅N₃O₄: C, 56.31; H, 5.45; N, 15.15. Found: C, 56.24; H, 5.63; N, 15.01.

Methyl 4-azido-4-(2,3,4-trimethoxyphenyl)butanoate (2d) was obtained from cyclopropane **1d** (389 mg, 1.2 mmol), NaN₃ (215 mg, 3.3 mmol) and triethylamine hydrochloride (372 mg, 2.7 mmol) in DMSO (3 mL) as colorless oil; yield **2d** (238 mg, 64%); *R_f* = 0.50 (ethyl acetate: petroleum ether; 1:2).



¹H NMR (CDCl₃, 500 MHz) δ = 2.02 (dddd, ²*J* = 14.0 Hz, ³*J* = 8.2 Hz, ³*J* = 6.7 Hz, ³*J* = 6.1 Hz, 1H, C(3)H₂), 2.10 (dddd, ²*J* = 14.0 Hz, ³*J* = 8.5 Hz, ³*J* = 7.9 Hz, ³*J* = 6.7 Hz, 1H, C(3)H₂), 2.35 (ddd, ²*J* = 16.2 Hz, ³*J* = 7.9 Hz, ³*J* = 6.7 Hz, 1H, C(2)H₂), 2.38 (ddd, ²*J* = 16.2 Hz, ³*J* = 8.2 Hz, ³*J* = 6.7 Hz, 1H, C(2)H₂), 3.64 (s, 3H, CH₃O), 3.84 (s, 3H, CH₃O), 3.85 (s, 3H, CH₃O), 3.90 (s, 3H, CH₃O), 4.84 (dd, ³*J* = 8.5 Hz, ³*J* = 6.1 Hz, 1H, CH), 6.68 (d, ³*J* = 8.7 Hz, 1H, Ar), 6.98 (d, ³*J* = 8.7 Hz, 1H, Ar).

^{13}C NMR (CDCl_3 , 125 MHz) δ = 30.1 (CH_2), 30.6 (CH_2), 51.4 (CH_3O), 55.8 (CH_3O), 58.9 (CHN_3), 60.5 (CH_3O), 61.1 (CH_3O), 107.3 (CH , Ar), 121.4 (CH , Ar), 124.4 (C , Ar), 141.8 (C , Ar), 151.5 (C , Ar), 153.5 (C), 173.0 (CO_2Me).

IR (film, cm^{-1}) 2998, 2943, 2100, 1737, 1592, 1509, 1423, 1278, 1198, 1150, 1129, 1007.

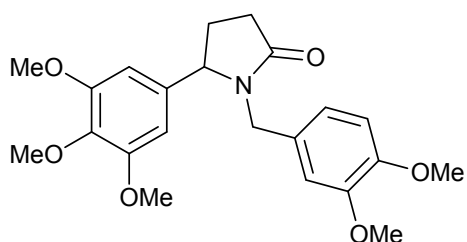
Anal. calcd for $\text{C}_{14}\text{H}_{19}\text{N}_3\text{O}_5$: C, 54.36; H, 6.19; N, 13.58. Found: C, 54.14; H, 5.83; N, 13.41.

Synthesis of pyrrolidones 4a-l

General procedure A: A suspension of azide **2** (1 equiv, 0.4 M) and polymer-bound triphenylphosphine (1.1 equiv) in dichloroethane was stirred at room temperature for 45 minutes. After that, aldehyde **3** (3 equiv) was added, and the resulting mixture was heated in a microwave reactor at 90 °C for 15 h. The resin was filtered off and washed with dichloroethane; the filtrate was concentrated in vacuo. The residue was dissolved in methanol (60–70 equiv) and treated with sodium cyanoborohydride (6 equiv.) and glacial acetic acid (12 equiv). The reaction mixture was refluxed for 4 h, followed by quenching with conc. aqueous NaHCO_3 and extraction with ethyl acetate (3×10 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on a silica gel to afford the desired product.

General procedure B: To a mixture of azide **2** (1 equiv, 0.1 M), aldehyde **3** (1.5 equiv) and molecular sieves (4Å) in methanol 10% Pd/C (10 wt. %) was carefully added. After that, the flask was evacuated and filled with hydrogen. The hydrogenation was carried out at room temperature under hydrogen (1 atm) and vigorous stirring for 4.5 h. The additional quantity of aldehyde **3** (1–1.5 equiv) was added and the reaction mixture was further stirred for 4.5 h. The catalyst was removed by filtration through a short pad of silica gel and washed with a portion of methanol. The filtrate was treated with acetic acid (5 mol %) and heated in a microwave reactor for 45 minutes at 65 °C. The residue was purified by column chromatography on a silica gel to afford the desired product.

1-(3,4-Dimethoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4a) was synthesized by **General procedure A** from azide **2a** (186 mg, 0.6 mmol), polymer-bound triphenylphosphine (210 mg, 0.7 mmol) and 3,4-dimethoxybenzaldehyde (300 mg, 1.8 mmol) in DCE (1.3 mL). The reductive cyclization with sodium cyanoborohydride (226 mg, 3.6 mmol) and glacial acetic acid (0.41 mL, 7.2 mmol) in MeOH (1.6 mL) yielded **4a** (154 mg, 64%) as a colorless viscous oil; R_f



= 0.40 (ethyl acetate).

^1H NMR (CD_3OD , 500 MHz) δ = 1.86–1.99 (m, 1H, CH_2), 2.36–2.69 (m, 3H, CH_2), 3.73 (s, 3H, CH_3O), 3.77 (s, 3H, CH_3O), 3.78 (s, 6H, $2\times\text{CH}_3\text{O}$), 3.79 (s, 3H, CH_3O),

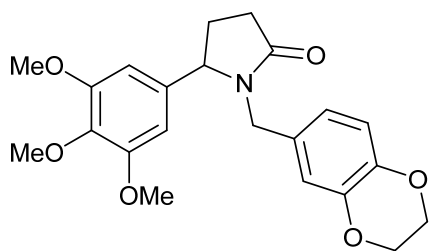
3.82 (d, $^2J = 14.5$ Hz, 1H, CH₂), 4.47 (dd, $^3J = 7.5$ Hz, $^3J = 6.7$ Hz, 1H, C(5)H), 4.66 (d, $^2J = 14.5$ Hz, 1H, CH₂), 6.41 (s, 2H, Ar), 6.60 (dd, $^3J = 6.5$ Hz, $^5J = 1.9$ Hz, 1H, Ar), 6.62 (br. s, 1H, Ar), 6.81 (dd, $^3J = 6.5$ Hz, $^4J = 2.4$ Hz, 1H, Ar).

¹³C NMR (CD₃OD, 125 MHz) $\delta = 29.0$ (C(4)H₂), 31.3 (C(3)H₂), 45.7 (CH₂N), 56.3 (CH₃O), 56.4 (CH₃O), 56.6 (2×CH₃O), 61.1 (CH₃O), 64.0 (C(5)H), 105.2 (2×CH, Ar), 112.7 (CH, Ar), 113.3 (CH, Ar), 122.0 (CH, Ar), 130.3 (C, Ar), 137.7 (C, Ar), 138.5 (C, Ar), 149.6 (C, Ar), 150.1 (C, Ar), 154.6 (2×C, Ar), 177.7 (C=O).

IR (cm⁻¹) 3471, 2937, 2837, 2592, 2172, 2003, 1729, 1687, 1593, 1514, 1463, 1357, 1327, 1239, 1124, 1026.

HRMS (ESI/Q-TOF) m/z [M + H]⁺ Calcd for C₂₂H₂₈NO₆ 402.1911; Found 402.1915.

1-[(2,3-Dihydro[1,4]benzodioxin-6-yl)methyl]-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4b) was synthesized by *General procedure A* from azide **2a** (591 mg, 1.9 mmol), polymer-bound triphenylphosphine (690 g, 2.3 mmol) and 2,3-dihydro[1,4]benzodioxine-6-carbaldehyde (936 mg, 5.7 mmol) in DCE (4 mL). The reductive cyclization with sodium cyanoborohydride (754 mg, 12 mmol) and glacial acetic acid (1.4 mL, 24.5 mmol) in MeOH (5 mL) yielded **4b** (496 mg, 65%) as a colorless viscous oil; $R_f = 0.50$ (ethyl acetate : petroleum ether; 2:1).



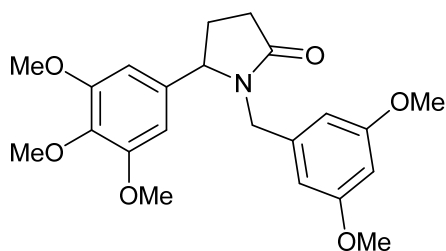
¹H NMR (CDCl₃, 500 MHz) $\delta = 1.84$ – 1.91 (m, 1H, C(4)H₂), 2.34– 2.50 (m, 2H, C(4)H₂, C(3)H₂), 2.60 (ddd, $^2J = 16.7$ Hz, $^3J = 10.4$ Hz, $^3J = 5.4$ Hz, 1H, C(3)H₂), 3.50 (d, $^2J = 14.4$ Hz, 1H, CH₂), 3.81 (s, 6H, 2×CH₃O), 3.83 (s, 3H, CH₃O), 4.20 (br. s, 4H, OC₂H₄O), 4.35 (dd, $^3J = 8.0$ Hz, $^3J = 6.4$ Hz, 1H, C(5)H), 4.86 (d, $^2J = 14.4$ Hz, 1H, CH₂), 6.30 (s, 2H, Ar), 6.53 (br. d, $^3J = 8.0$ Hz, 1H, Ar), 6.57 (br. s, 1H, Ar), 6.72 (d, $^3J = 8.0$ Hz, 1H, Ar).

¹³C NMR (CDCl₃, 125 MHz) $\delta = 28.0$ (CH₂), 30.3 (CH₂), 43.9 (CH₂N), 56.0 (2×CH₃O), 60.7 (CH₃O), 61.9 (CH), 64.2 (2×CH₂O), 103.5 (2×CH, Ar), 117.0 (CH, Ar), 117.2 (CH, Ar), 121.5 (CH, Ar), 129.3 (C, Ar), 136.2 (C, Ar), 137.4 (C, Ar), 142.9 (C, Ar), 143.3 (C, Ar), 153.5 (2×C, Ar), 175.6 (C=O).

IR (film, cm⁻¹) 3996, 3644, 3501, 3363, 3046, 2939, 2878, 2845, 2587, 2396, 2359, 2251, 2209, 1961, 1687, 1592, 1506, 1465, 1428, 1361, 1248, 1239, 1205, 1126, 1067, 1001.

HRMS (ESI/Q-TOF) m/z [M + H]⁺ Calcd for C₂₂H₂₆NO₆ 400.1755; Found 400.1761.

1-(3,5-Dimethoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4c) was synthesized by *General procedure B* from azide **2a** (180 mg, 0.58 mmol) and 3,5-dimethoxybenzaldehyde (2×145 mg, 1.74 mmol) in MeOH (5.8 mL) using 60 mg 10% Pd/C. Product was obtained as a colorless viscous oil (182 mg, 78%). $R_f = 0.58$ (methanol : ethyl acetate; 1:9).



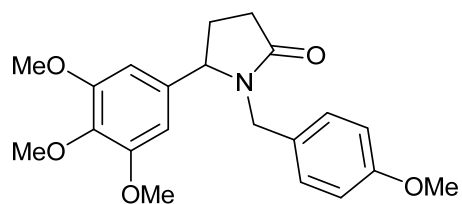
$^1\text{H NMR}$ (CDCl_3 , 500 MHz) $\delta = 1.79\text{--}1.87$ (m, 1H, CH_2), 2.29–2.46 (m, 2H, CH_2), 2.56 (ddd, $^2J = 15.0$ Hz, $^3J = 9.2$ Hz, $^3J = 4.8$ Hz, 1H, CH_2), 3.47 (d, $^2J = 14.5$ Hz, 1H, CH_2), 3.65 (s, 6H, $2\times\text{CH}_3\text{O}$), 3.75 (s, 6H, $2\times\text{CH}_3\text{O}$), 3.78 (s, 3H, CH_3O), 4.30 (dd, $^3J = 7.9$ Hz, $^3J = 6.6$ Hz, 1H, CH), 4.90 (d, $^2J = 14.5$ Hz, 1H, CH_2), 6.16 (d, $^4J = 2.3$ Hz, 2H, Ar), 6.26 (s, 2H, Ar), 6.27 (t, $^4J = 2.3$ Hz, 1H, Ar).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz) $\delta = 28.0$ (CH_2), 30.2 (CH_2), 44.5 (CH_2), 55.1 ($2\times\text{CH}_3\text{O}$), 55.9 ($2\times\text{CH}_3\text{O}$), 60.6 (CH_3O), 61.7 (CH), 99.2 (CH, Ar), 103.3 ($2\times\text{CH}$, Ar), 106.2 ($2\times\text{CH}$, Ar), 136.2 ($2\times\text{C}$, Ar), 137.3 (C, Ar), 138.5 ($2\times\text{C}$, Ar), 153.4 (C, Ar), 160.6 (C, Ar), 175.1 (C=O).

IR (cm^{-1}): 2941, 2838, 1688, 1594, 1506, 1465, 1352, 1237, 1205, 1126, 1072, 1009.

HRMS (ESI/Q-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{28}\text{NO}_6$ 402.1911; Found 402.1911.

1-(4-Methoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4d) was synthesized by *General procedure A* from azide **2a** (433 mg, 1.4 mmol), polymer-bound triphenylphosphine (510 mg, 1.7 mmol) and 4-methoxybenzaldehyde (572 mg, 4.2 mmol) in DCE (2.8 mL). The reductive cyclization with sodium cyanoborohydride (528 mg, 8.4 mmol) and glacial acetic acid (1 mL, 17.5 mmol) in MeOH (3.4 mL) yielded **4d** (338 mg, 65%) as a colorless viscous oil; $R_f = 0.52$ (petroleum ether : ethyl acetate; 1:1).



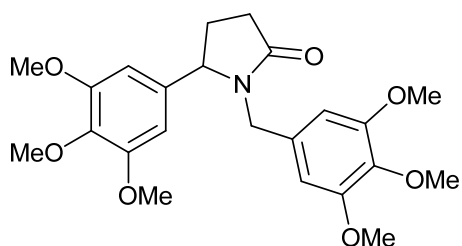
$^1\text{H NMR}$ (CDCl_3 , 500 MHz) $\delta = 1.81\text{--}1.91$ (m, 1H, $\text{C}(4)\text{H}_2$), 2.30–2.40 (m, 1H, $\text{C}(4)\text{H}_2$), 2.44 (ddd, $^2J = 16.4$ Hz, $^3J = 9.7$ Hz, $^3J = 7.6$ Hz, 1H, $\text{C}(3)\text{H}_2$), 2.59 (ddd, $^2J = 16.4$ Hz, $^3J = 10.4$ Hz, $^3J = 5.7$ Hz, 1H, $\text{C}(3)\text{H}_2$), 3.53 (d, $^2J = 14.6$ Hz, 1H, CH_2), 3.74 (s, 3H, CH_3O), 3.78 (s, 6H, $2\times\text{CH}_3\text{O}$), 3.83 (s, 3H, CH_3O), 4.30 (dd, $^3J = 7.6$ Hz, $^3J = 5.7$ Hz, 1H, C(5)H), 4.90 (d, $^2J = 14.6$ Hz, 1H, CH_2), 6.28 (s, 2H, Ar), 6.75 (br. d, $^3J = 8.6$ Hz, 2H, Ar), 6.95 (br. d, $^3J = 8.6$ Hz, 2H, Ar).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz) $\delta = 28.1$ (CH_2), 30.5 (CH_2), 44.0 (CH), 55.2 (CH_2), 56.2 ($2\times\text{CH}_3\text{O}$), 60.9 (CH_3O), 61.9 (CH_3O), 103.7 ($2\times\text{CH}$, Ar), 113.8 ($2\times\text{CH}$, Ar), 128.3 (C, Ar), 129.8 ($2\times\text{CH}$, Ar), 136.3 (C, Ar), 137.5 (C, Ar), 153.5 ($2\times\text{C}$), 159.0 (C, Ar), 176.7 (C=O).

IR (film, cm^{-1}) 2930, 2837, 1710, 1681, 1593, 1513, 1463, 1435, 1420, 1328, 1242, 1126, 1002.

HRMS (ESI/Q-TOF) m/z $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{25}\text{NNaO}_5$ 394.1625; Found 394.1633.

1-(3,4,5-Trimethoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4e) was obtained by *General procedure A* from azide **2a** (495 mg, 1.6 mmol), polymer-bound triphenylphosphine (546 g, 1.8 mmol) and 3,4,5-trimethoxybenzaldehyde (942 g, 4.8 mmol) in DCE (3.2 mL). The reductive cyclization with sodium cyanoborohydride (602 mg, 9.6 mmol) and glacial acetic acid (1.1 mL, 19.2 mmol) in MeOH (3.9 mL) yielded **4e** (463 mg, 67%) as a colorless solid; m.p. 135–137 °C (CH₃OH); *R_f* = 0.52 (ethyl acetate : methanol; 10:1).



¹H NMR (CDCl₃–CD₃OD, 500 MHz) δ = 1.86–1.93 (m, 1H, C(4)H₂), 2.38–2.52 (m, 2H, C(4)H₂, C(3)H₂), 2.60–2.65 (m, 1H, C(3)H₂), 3.64 (d, ²*J* = 14.2 Hz, 1H, CH₂), 3.74 (s, 6H, 2×CH₃O), 3.76 (s, 3H, CH₃O), 3.79 (s, 6H, 2×CH₃O), 3.83 (s, 3H, CH₃O), 4.38 (dd, ³*J* = 7.3 Hz, ³*J* = 6.2 Hz, 1H, C(5)H), 4.80 (d, ²*J* = 14.2 Hz, 1H, CH₂), 6.25 (br. s, 2H, Ar), 6.31 (br. s, 2H, Ar).

¹³C NMR (CDCl₃–CD₃OD, 125 MHz) δ = 28.1 (C(4)H₂), 30.1 (C(3)H₂), 44.9 (CH₂N), 55.7 (2×CH₃O), 55.8 (2×CH₃O), 60.38 (CH₃O), 60.43 (CH₃O), 62.2 (C(5)H), 103.3 (2×CH, Ar), 105.5 (2×CH, Ar), 131.7 (C, Ar), 136.0 (C, Ar), 136.9 (C, Ar), 137.3 (C, Ar), 152.8 (2×C, Ar), 153.3 (2×C, Ar), 175.9 (C=O).

IR (film, cm⁻¹) 3478, 2994, 2942, 2841, 2567, 2366, 2209, 2160, 1958, 1682, 159, 1508, 1461, 1422, 1330, 1236, 1175, 1127, 1002.

HRMS (ESI/Q-TOF) *m/z* [M + H]⁺ Calcd for C₂₃H₃₀NO₇ 432.2017; Found 432.2019.

Anal. Calcd for C₂₃H₂₉NO₇: C, 64.02; H, 6.77; N, 3.25. Found: C, 63.69; H, 6.76; N, 3.28.

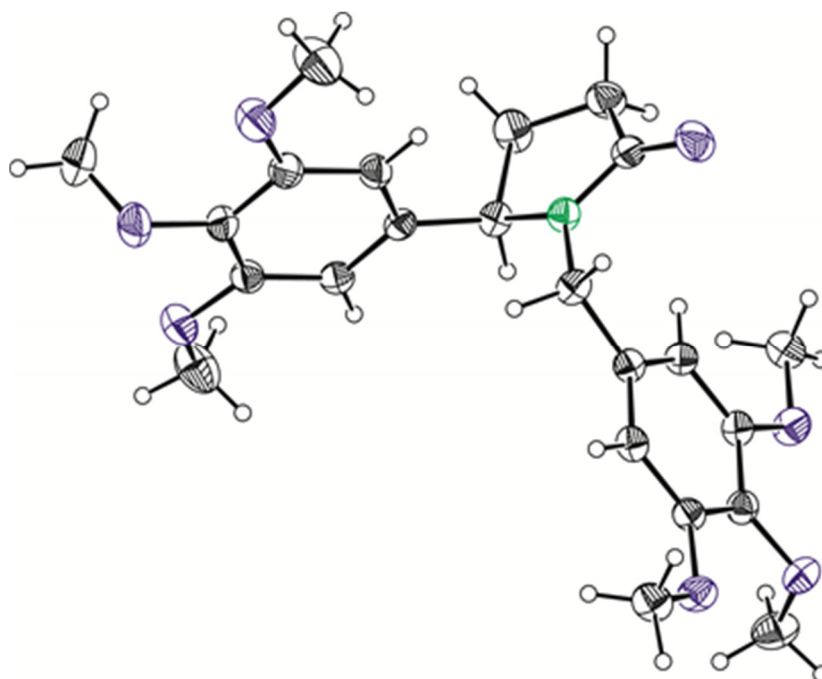
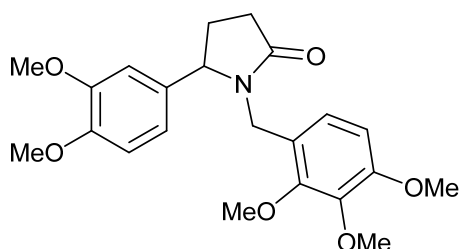


Figure S1. Molecular structure (ORTEP-3^[S5]) from single crystal X-ray study of **4e**.

5-(3,4-Dimethoxyphenyl)-1-(2,3,4-trimethoxybenzyl)pyrrolidin-2-one (4f) was synthesized by *General procedure B* from azide **2b** (279 mg, 1.0 mmol) and 2,3,4-trimethoxybenzaldehyde (294 mg and then 196 mg, 2.5 mmol) in MeOH (10.7 mL) using 100 mg 10% Pd/C. Product was obtained as a colorless viscous oil (269 mg, 67%). $R_f = 0.58$ (ethyl acetate : methanol; 10:1).



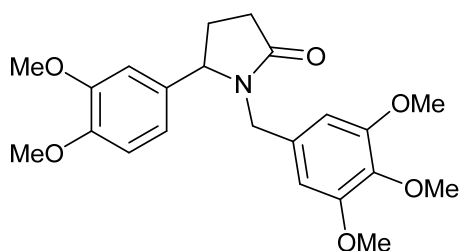
$^1\text{H NMR}$ ($\text{CDCl}_3\text{-CD}_3\text{OD}$, 500 MHz) $\delta = 1.81\text{--}1.88$ (m, 1H, CH_2), 2.33–2.41 (m, 1H, CH_2), 2.46 (ddd, $^2J = 16.6$ Hz, $^3J = 9.8$ Hz, $^3J = 7.0$ Hz, 1H, CH_2), 2.60 (ddd, $^2J = 16.6$ Hz, $^3J = 9.5$ Hz, $^3J = 5.8$ Hz, 1H, CH_2), 3.63 (d, $^2J = 14.7$ Hz, 1H, CH_2), 3.65 (s, 3H, CH_3O), 3.80 (s, 3H, CH_3O), 3.81 (s, 6H, $2\times\text{CH}_3\text{O}$), 3.85 (s, 3H, CH_3O), 4.35 (dd, $^3J = 8.5$ Hz, $^3J = 5.5$ Hz, 1H, CH), 4.84 (d, $^2J = 14.7$ Hz, 1H, CH_2), 6.55 (d, $^3J = 8.5$ Hz, 1H, Ar), 6.58 (br. s, 1H, Ar), 6.66 (d, $^3J = 8.2$ Hz, 1H, Ar), 6.67 (d, $^3J = 8.5$ Hz, 1H, Ar), 6.81 (d, $^3J = 8.2$ Hz, 1H, Ar).

$^{13}\text{C NMR}$ ($\text{CDCl}_3\text{-CD}_3\text{OD}$, 125 MHz) $\delta = 27.8$ (CH_2), 29.9 (CH_2), 39.2 (CH_2), 55.5 ($3\times\text{CH}_3\text{O}$), 60.21 (CH_3O), 60.24 (CH_3O), 61.6 (CH), 106.8 (CH, Ar), 109.4 (CH, Ar), 111.2 (CH, Ar), 118.8 (CH, Ar), 121.2 (C, Ar), 124.2 (CH, Ar), 132.9 (C, Ar), 141.6 (C, Ar), 148.4 (C, Ar), 149.0 (C, Ar), 151.6 (C, Ar), 153.0 (C, Ar), 175.8 (C=O).

IR (film, cm^{-1}) 2933, 2875, 2834, 1684, 1591, 1508, 1508, 1462, 1414, 1288, 1261, 1238, 1147, 1068, 1026.

HRMS (ESI/Q-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{28}\text{NO}_6$ 402.1911; Found 402.1916.

1-(3,4-Dimethoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4g) was synthesized by *General procedure B* from azide **2b** (280 mg, 1 mmol) and 3,4,5-trimethoxybenzaldehyde (2×294 mg, 3.0 mmol) in MeOH (10.4 mL) using 110 mg 10% Pd/C. Product was obtained as a colorless viscous oil (249 mg, 62%). $R_f = 0.61$ (methanol : ethyl acetate; 1:9).



$^1\text{H NMR}$ (CDCl_3 , 500 MHz) $\delta = 1.86\text{--}1.93$ (m, 1H, CH_2), 2.36–2.44 (m, 1H, CH_2), 2.46–2.52 (m, 1H, CH_2), 2.64 (ddd, $^2J = 14.7$ Hz, $^3J = 9.7$ Hz, $^3J = 4.8$ Hz, 1H, CH_2), 3.51 (d, $^2J = 14.2$ Hz, 1H, CH_2), 3.78 (s, 6H, $2\times\text{CH}_3\text{O}$), 3.83 (s, 3H, CH_3O), 3.84 (s, 3H, CH_3O), 3.90 (s, 3H, CH_3O), 4.38 (dd, $^3J = 7.2$ Hz, $^3J = 6.9$ Hz, 1H, C(5)H), 4.97 (d, $^2J = 14.2$ Hz, 1H, CH_2), 6.28 (s, 2H, Ar), 6.62 (d, $^4J = 1.9$ Hz, 1H, Ar), 6.71 (dd, $^3J = 8.1$ Hz, $^4J = 1.9$ Hz, 1H, Ar), 6.86 (d, $^3J = 8.1$ Hz, 1H, Ar).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz) $\delta = 28.5$ ($\text{C}(4)\text{H}_2$), 30.5 ($\text{C}(3)\text{H}_2$), 44.8 (CH_2N), 55.93 (CH_3O), 55.94 (CH_3O), 56.1 ($2\times\text{CH}_3\text{O}$), 60.8 (CH_3O), 61.4 (CH), 105.8 ($2\times\text{CH}$, Ar), 109.5 (CH, Ar),

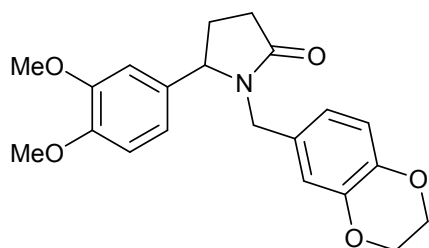
111.2 (CH, Ar), 119.3 (CH, Ar), 132.1 (C, Ar), 133.2 (C, Ar), 137.2 (C, Ar), 148.9 (C, Ar), 149.6 (C, Ar), 153.2 (2×C, Ar), 175.2 (C=O).

IR (film, cm^{-1}) 2999, 2939, 2837, 1682, 1593, 1516, 1464, 1419, 1352, 1329, 1261, 1238, 1128, 1026, 1009.

HRMS (ESI/Q-TOF) m/z $[M + H]^+$ Calcd for $\text{C}_{22}\text{H}_{28}\text{NO}_6$ 402.1911; Found 402.1911.

1-[(2,3-Dihydro[1,4]benzodioxin-6-yl)methyl]-5-(3,4-dimethoxyphenyl)pyrrolidin-2-one

(4h) was synthesized by *General procedure B* from azide **2b** (279 mg, 1.0 mmol) and 2,3-dihydro[1,4]benzodioxine-6-carbaldehyde (2×246 mg, 3.0 mmol), in MeOH (10.7 mL) using 100 mg 10% Pd/C. Product was obtained as a colorless viscous oil (259 mg, 70%). $R_f = 0.59$ (ethyl acetate).



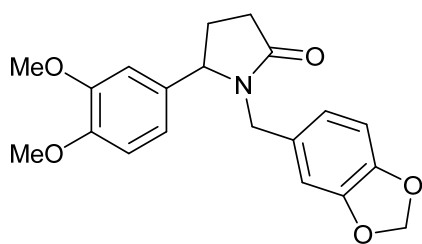
$^1\text{H NMR}$ (CDCl_3 , 400 MHz) $\delta = 1.86$ (dddd, $^2J = 13.0$ Hz, $^3J = 9.8$ Hz, $^3J = 7.2$ Hz, $^3J = 6.0$ Hz, 1H, CH_2), 2.35 (dddd, $^2J = 13.0$ Hz, $^3J = 9.6$ Hz, $^3J = 7.6$ Hz, $^3J = 5.0$ Hz, 1H, CH_2), 2.45 (ddd, $^2J = 16.4$ Hz, $^3J = 9.6$ Hz, $^3J = 7.2$ Hz, 1H, CH_2), 2.60 (ddd, $^2J = 16.4$ Hz, $^3J = 9.8$ Hz, $^3J = 5.0$ Hz, 1H, CH_2), 3.39 (d, $^2J = 14.5$ Hz, 1H, CH_2), 3.82 (s, 3H, CH_3O), 3.87 (s, 3H, CH_3O), 4.21 (br. s, 4H, $\text{OC}_2\text{H}_4\text{O}$), 4.35 (dd, $^3J = 7.6$ Hz, $^3J = 6.0$ Hz, 1H, CH), 4.90 (d, $^2J = 14.5$ Hz, 1H, CH_2), 6.54 (dd, $^3J = 8.2$ Hz, $^4J = 2.0$ Hz, 1H, Ar), 6.57 (d, $^4J = 2.0$ Hz, 1H, Ar), 6.58 (d, $^4J = 2.0$ Hz, 1H, Ar), 6.67 (dd, $^3J = 8.2$ Hz, $^4J = 2.0$ Hz, 1H, Ar), 6.72 (d, $^3J = 8.2$ Hz, 1H, Ar), 6.82 (d, $^3J = 8.2$ Hz, 1H, Ar).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) $\delta = 28.3$ (CH_2), 30.5 (CH_2), 43.7 (CH_2N), 55.88 (CH_3O), 55.90 (CH_3O), 61.2 (CH), 64.2 (2× CH_2O), 109.3 (CH, Ar), 111.1 (CH, Ar), 117.1 (CH, Ar), 117.3 (CH, Ar), 119.3 (CH, Ar), 121.6 (CH, Ar), 129.7 (C, Ar), 133.1 (C, Ar), 142.9 (C, Ar), 143.3 (C, Ar), 148.8 (C, Ar), 149.4 (C, Ar), 175.1 (C=O).

IR (film, cm^{-1}): 2933, 2875, 2835, 1684, 1591, 1508, 1462, 1414, 1288, 1261, 1238, 1205, 1147, 1140, 1126, 1068, 1026.

HRMS (ESI/Q-TOF) m/z $[M + H]^+$ Calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_5$ 370.1649; Found 370.1655.

1-([1,3]Benzodioxol-5-ylmethyl)-5-(3,4-dimethoxyphenyl)pyrrolidin-2-one (4i) was obtained by *General procedure A* from azide **2b** (447 mg, 1.6 mmol), polymer-bound triphenylphosphine (539 g, 1.8 mmol) and [1,3]benzodioxole-5-carbaldehyde (721 g, 4.8 mmol) in DCE (3.3 mL). The reductive cyclization with sodium cyanoborohydride (601 mg, 9.6 mmol) and glacial acetic acid (1.1 mL, 19.2 mmol) in MeOH (4.0 mL) yielded **4i** (279 mg, 49%) as a yellow thick oil; $R_f = 0.48$ (ethyl acetate).



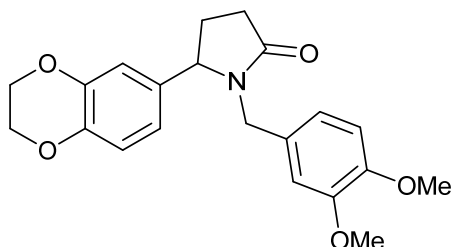
^1H NMR (CDCl_3 , 500 MHz) δ = 1.78–1.85 (m, 1H, CH_2), 2.26–2.33 (m, 1H, CH_2), 2.35–2.42 (m, 1H, CH_2), 2.53 (ddd, $^2J = 14.9$ Hz, $^3J = 10.1$ Hz, $^3J = 4.8$ Hz, 1H, CH_2), 3.38 (d, $^2J = 14.5$ Hz, 1H, CH_2), 3.75 (s, 3H, CH_3O), 3.80 (s, 3H, CH_3O), 4.30 (dd, $^3J = 7.5$ Hz, $^3J = 6.5$ Hz, 1H, CH), 4.79 (d, $^2J = 14.5$ Hz, 1H, CH_2), 5.80 (s, 2H, OCH_2O), 6.37 (dd, $^3J = 7.8$ Hz, $^4J = 1.5$ Hz, 1H, Ar), 6.50 (d, $^4J = 1.5$ Hz, 1H, Ar), 6.54 (d, $^4J = 2.0$ Hz, 1H, Ar), 6.56 (d, $^3J = 7.8$ Hz, 1H, Ar), 6.62 (dd, $^3J = 8.1$ Hz, $^4J = 2.0$ Hz, 1H, Ar), 6.78 (d, $^3J = 8.1$ Hz, 1H, Ar).

^{13}C NMR (CDCl_3 , 125 MHz) δ = 27.8 (CH_2), 30.2 (CH_2), 43.7 (CH_2N), 55.8 ($2\times\text{CH}_3\text{O}$), 60.5 (CH), 100.6 (OCH_2O), 107.6 (CH, Ar), 108.4 (CH, Ar), 109.3 (CH, Ar), 111.0 (CH, Ar), 119.0 (CH, Ar), 121.4 (CH, Ar), 129.7 (C, Ar), 132.5 (C, Ar), 146.5 (C, Ar), 147.4 (C, Ar), 148.3 (C, Ar), 148.9 (C, Ar), 175.2 (C=O).

IR (cm^{-1}) 3016, 2944, 2907, 1679, 1605, 1520, 1513, 1447, 1368, 1306, 1235, 1100, 1025, 929.

HRMS (ESI/Q-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_5$ 356.1492; Found 356.1490.

5-(2,3-Dihydro[1,4]benzodioxin-6-yl)-1-(3,4-dimethoxybenzyl)pyrrolidin-2-one (4j) was synthesized by *General procedure B* from azide **2c** (277 mg, 1.0 mmol) and 3,4-dimethoxybenzaldehyde (2×249 mg, 3.0 mmol), in MeOH (11.4 mL) using 100 mg 10% Pd/C. Product was obtained as a colorless viscous oil (259 mg, 70%). R_f = 0.55 (ethyl acetate:petroleum ether; 2:1).



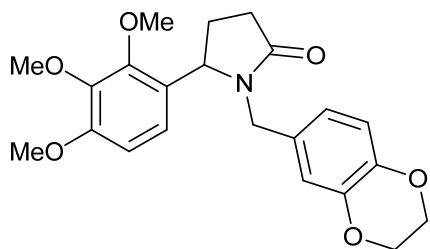
^1H NMR (CDCl_3 , 500 MHz) δ = 1.72–1.79 (m, 1H, CH_2), 2.22–2.27 (m, 1H, CH_2), 2.31–2.38 (m, 1H, CH_2), 2.49 (ddd, $^2J = 15.1$ Hz, $^3J = 9.6$ Hz, $^3J = 5.4$ Hz, 1H, CH_2), 3.39 (d, $^2J = 14.4$ Hz, 1H, CH_2), 3.69 (s, 3H, CH_3O), 3.73 (s, 3H, CH_3O), 4.14 (br. s, 4H, $\text{OC}_2\text{H}_4\text{O}$), 4.21 (dd, $^3J = 7.7$ Hz, $^3J = 6.1$ Hz, 1H, C(5)H), 4.86 (d, $^2J = 14.4$ Hz, 1H, CH_2), 6.49–6.52 (m, 4H, Ar), 6.66 (br. d, $^3J = 7.8$, 1H, Ar), 6.73 (d, $^3J = 8.1$ Hz, 1H, Ar).

^{13}C NMR (CDCl_3 , 125 MHz) δ = 27.7 (CH_2), 30.0 (CH_2), 43.7 (CH_2N), 55.3 (CH_3O), 55.4 (CH_3O), 60.7 (CH), 63.92 (CH_2O), 63.94 (CH_2O), 110.7 (CH, Ar), 111.4 (CH, Ar), 115.2 (CH, Ar), 117.2 (CH, Ar), 119.4 (CH, Ar), 120.6 (CH, Ar), 128.4 (C, Ar), 133.2 (C, Ar), 143.0 (C, Ar), 143.5 (C, Ar), 147.9 (C, Ar), 148.4 (C, Ar), 175.4 (C=O).

IR (film, cm^{-1}): 2999, 2937, 2875, 2837, 1666, 1593, 1516, 1464, 1417, 1286, 1263, 1238, 1155, 1140, 1028.

HRMS (ESI/Q-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_5$ 370.1649; Found 370.1652.

1-[(2,3-Dihydro[1,4]benzodioxin-6-yl)methyl]-5-(2,3,4-trimethoxyphenyl)pyrrolidin-2-one (4k) was synthesized by *General procedure B* from azide **2d** (495 mg, 1.6 mmol) and 2,3-dihydro[1,4]benzodioxine-6-carbaldehyde (2×394 mg, 4.8 mmol), in MeOH (16.2 mL) using 161 mg 10% Pd/C. Product was obtained as a colorless viscous oil (416 mg, 70%). $R_f = 0.58$ (ethyl acetate : petroleum ether; 1:1).

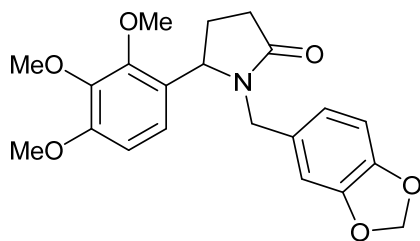


$^1\text{H NMR}$ (CDCl_3 , 400 MHz) $\delta = 1.74\text{--}1.81$ (m, 1H, CH_2), 2.26–2.43 (m, 2H, CH_2), 2.49–2.58 (m, 1H, CH_2), 3.36 (d, $^2J = 14.5$ Hz, 1H, CH_2), 3.68 (s, 3H, CH_3O), 3.80 (s, 3H, CH_3O), 3.81 (s, 3H, CH_3O), 4.15 (br. s, 4H, $\text{OC}_2\text{H}_4\text{O}$), 4.64 (dd, $^3J = 8.1$ Hz, $^3J = 4.5$ Hz, 1H, CH), 4.93 (d, $^2J = 14.5$ Hz, 1H, CH_2), 6.51 (dd, $^3J = 8.3$ Hz, $^4J = 1.9$ Hz, 1H, Ar), 6.56 (d, $^4J = 1.9$ Hz, 1H, Ar), 6.60 (br. d, $^3J = 8.6$ Hz, 1H, Ar), 6.66 (d, $^3J = 8.6$ Hz, 1H, Ar), 6.68 (d, $^3J = 8.3$ Hz, 1H, Ar).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) $\delta = 27.0$ (CH_2), 30.1 (CH_2), 43.6 (CH_2N), 55.8 (CH_3O , CH), 60.6 (CH_3O), 60.7 (CH_3O), 64.1 ($\text{OC}_2\text{H}_4\text{O}$), 107.0 (CH, Ar), 117.0 (2×CH, Ar), 121.3 (2×CH, Ar), 126.1 (C, Ar), 129.5 (C, Ar), 142.2 (C, Ar), 142.7 (C, Ar), 143.3 (C, Ar), 151.6 (C, Ar), 153.3 (C, Ar), 175.3 (C=O).

HRMS (ESI/Q-TOF) m/z [$\text{M} + \text{H}$] $^+$ Calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_6$ 400.1755; Found 400.1760.

1-([1,3]Benzodioxol-5-ylmethyl)-5-(2,3,4-trimethoxyphenyl)pyrrolidin-2-one (4l) was synthesized by *General procedure B* from azide **2d** (464 mg, 1.5 mmol) and [1,3]benzodioxole-5-carbaldehyde (2×338 mg, 4.5 mmol), in MeOH (15.0 mL) using 150 mg 10% Pd/C. Product was obtained as a yellow thick oil (353 mg, 61%). $R_f = 0.49$ (ethyl acetate : methanol, 10:1).



$^1\text{H NMR}$ (CDCl_3 , 500 MHz) $\delta = 1.78\text{--}1.85$ (m, 1H, CH_2), 2.28–2.36 (m, 1H, CH_2), 2.40 (ddd, $^2J = 16.4$ Hz, $^3J = 10.0$ Hz, $^3J = 5.0$ Hz, 1H, CH_2), 2.56 (ddd, $^2J = 16.4$ Hz, $^3J = 10.4$ Hz, $^3J = 7.2$ Hz, 1H, CH_2), 3.43 (d, $^2J = 14.5$ Hz, 1H, CH_2), 3.72 (s, 3H, CH_3O), 3.82 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 4.67 (dd, $^3J = 8.6$ Hz, $^3J = 4.8$ Hz, 1H, CH), 4.93 (d, $^2J = 14.5$ Hz, 1H, CH_2), 5.87 (s, 2H, OCH_2O), 6.49 (dd, $^3J = 7.9$ Hz, $^4J = 1.4$ Hz, 1H, Ar), 6.60 (d, $^4J = 1.4$ Hz, 1H, Ar), 6.63 (d, $^3J = 8.5$ Hz, 1H, Ar), 6.64 (d, $^3J = 7.9$ Hz, 1H, Ar), 6.68 (d, $^3J = 8.5$ Hz, 1H, Ar).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz) $\delta = 26.9$ (CH_2), 30.0 (CH_2), 43.9 (CH_2N), 55.8 (CH_3O , CH), 60.5 (CH_3O), 60.7 (CH_3O), 100.8 (OCH_2O), 107.1 (CH, Ar), 107.8 (CH, Ar), 108.6 (CH, Ar), 121.3 (CH, Ar), 121.6 (CH, Ar), 126.0 (C, Ar), 130.2 (C, Ar), 142.2 (C, Ar), 146.7 (C, Ar), 147.6 (C, Ar), 151.6 (C, Ar), 153.3 (C, Ar), 175.2 (C=O).

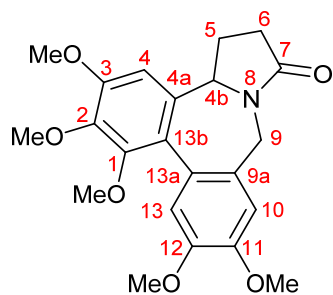
IR (film, cm^{-1}) 2940, 2836, 1685, 1599, 1492, 1471, 1444, 1244, 1096, 1037, 924.

HRMS (ESI/Q-TOF) m/z $[M + H]^+$ Calcd for $C_{21}H_{24}NO_6$ 385.1598; Found 386.1605.

Synthesis of dibenzazepines **5**

General procedure C: A solution of pyrrolidone **4** (1 equiv, 0.1 M), DDQ (1.2 equiv), and $BF_3 \cdot Et_2O$ (12 equiv) in dry chlorobenzene was refluxed for 0.5–0.75 h followed by quenching with conc. aqueous $NaHCO_3$ and extraction with ethyl acetate (3×10 mL). The combined organic extracts were washed with brine, dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on a silica gel to afford product **5**.

1,2,3,11,12-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5a) was obtained from **4a** (101 mg, 0.25 mmol) after reflux for 0.5 h with DDQ (68 mg, 0.3 mmol) and $BF_3 \cdot Et_2O$ (0.37 mL, 3 mmol) in PhCl (2.5 mL). Product was isolated as a colorless solid with bluish shimmer; yield 74 mg (74%); m.p. 188–190 °C ($CHCl_3$); R_f = 0.54 (ethyl acetate : petroleum ether; 1:1).



1H NMR ($CDCl_3$, 500 MHz) δ = 2.19–2.25 (m, 1H, C(5)H₂), 2.37–2.46 (m, 1H, C(5)H₂), 2.46–2.59 (m, 2H, C(6)H₂), 3.56 (d, 2J = 13.6 Hz, 1H, C(9)H₂), 3.58 (s, 3H, CH₃O), 3.90 (s, 3H, CH₃O), 3.93 (s, 3H, CH₃O), 3.95 (s, 3H, CH₃O), 3.96 (s, 3H, CH₃O), 4.22 (dd, 3J = 9.3 Hz, 3J = 6.3 Hz, 1H, C(4b)H), 4.81 (d, 2J = 13.6 Hz, 1H, C(9)H₂), 6.75 (s, 1H, C(4)H), 6.90 (s, 1H, C(10)H), 7.12 (s, 1H, C(13)H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ = 22.0 (C(5)H₂), 31.7 (C(6)H₂), 43.7 (C(9)H₂), 55.9 (CH₃O), 56.0 (CH₃O), 56.1 (CH₃O), 57.5 (C(4b)H), 60.8 (CH₃O), 61.1 (CH₃O), 104.2 (C(4)H), 111.5 (C(10)H), 113.7 (C(13)H), 125.9 (C(4a)), 126.1 (C(9a)), 127.8 (C(13a)), 130.3 (C(13b)), 142.5 (C(3)), 147.9 (C(12)), 148.4 (C(11)), 151.1 (C(1)), 152.9 (C(2)), 172.1 (C=O).

IR (film, cm^{-1}) 3087, 2988, 2965, 2868, 2839, 1680, 1601, 1518, 1466, 1429, 1369, 1320, 1244, 1199, 1066, 1033, 991, 978.

HRMS (ESI/Q-TOF) m/z $[M + H]^+$ Calcd for $C_{22}H_{26}NO_6$ 400.1755; Found 400.1759.

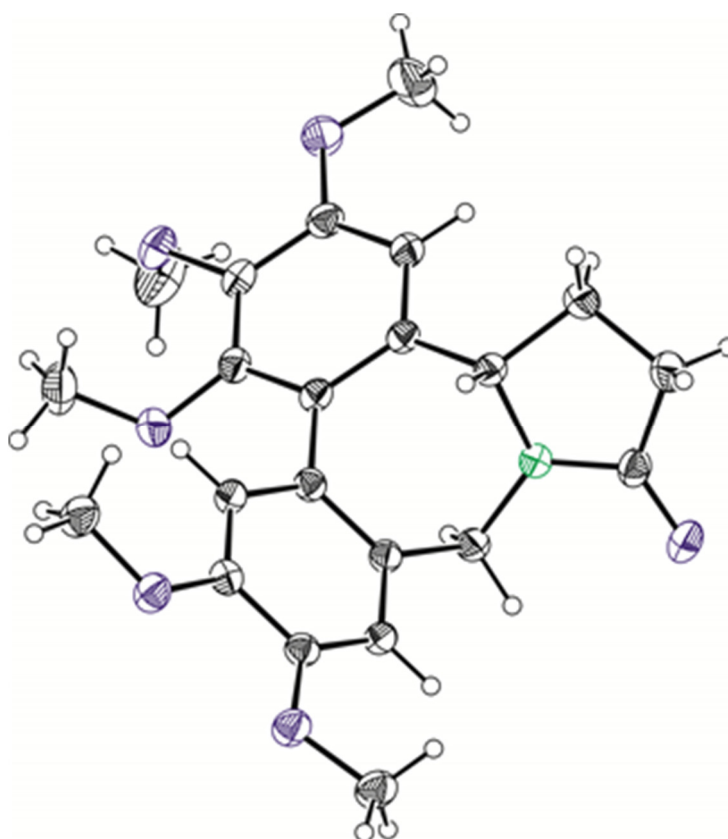
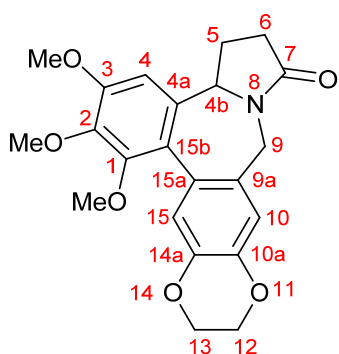


Figure S2. Molecular structure (ORTEP-3^[S51]) from single crystal X-ray study of **5a**.

1,2,3-Trimethoxy-4b,5,6,9,12,13-hexahydro-7H-[1,4]dioxino[2',3':4,5]benzo[1,2-*e*]benzo[*c*]pyrrolo[1,2-*a*]azepin-7-one (5b) was obtained from **4b** (200 mg, 0.5 mmol) after reflux for 0.75 h with DDQ (136 mg, 0.6 mmol) and BF₃·Et₂O (0.75 mL, 6 mmol) in PhCl (5 mL). Product was isolated as orange thick oil; yield 120 mg (60%); *R_f* = 0.50 (ethyl acetate : petroleum ether; 2:1).

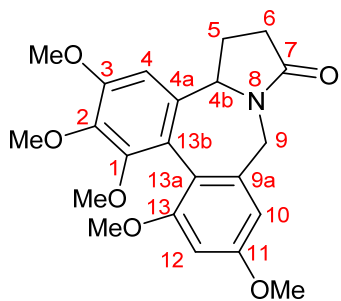


¹H NMR (CDCl₃, 500 MHz) δ = 2.18–2.24 (m, 1H, C(5)H₂), 2.34–2.43 (m, 1H, C(5)H₂), 2.43–2.54 (m, 2H, C(6)H₂), 3.51 (d, ²*J* = 13.8 Hz, 1H, C(9)H₂), 3.66 (s, 3H, CH₃O), 3.94 (s, 6H, 2×CH₃O), 4.24–4.34 (m, 1H, C(4b)H + 4H, OC₂H₄O), 4.81 (d, ²*J* = 13.8 Hz, 1H, C(9)H₂), 6.73 (s, 1H, C(4)H), 6.91 (s, 1H, C(10)H), 7.08 (s, 1H, C(15)H).

¹³C NMR (CDCl₃, 125 MHz) δ = 21.9 (C(5)H₂), 31.7 (C(6)H₂), 43.6 (C(9)H₂), 56.2 (CH₃O), 57.4 (C(4b)H), 60.9 (CH₃O), 61.0 (CH₃O), 64.35 (CH₂O), 64.40 (CH₂O), 104.0 (C(4)H), 117.3 (C(10)H), 119.5 (C(15)H), 125.9 (C(15b)), 126.9 (C(9a)), 128.5 (C(15a)), 130.3 (C(4a)), 142.5 (C(3)), 142.7 (C(14a)), 143.1 (C(10a)), 151.3 (C(1)), 152.9 (C(2)), 172.0 (C=O).

HRMS (ESI/Q-TOF) *m/z* [M + H]⁺ Calcd for C₂₂H₂₄NO₆ 398.1598; Found 398.1602.

1,2,3,11,13-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5c) was obtained from **4c** (327 mg, 0.81 mmol) after reflux for 0.75 h with DDQ (219 mg, 0.97 mmol) and BF₃·Et₂O (1.2 mL, 9.7 mmol) in PhCl (9 mL). Product was isolated as orange thick oil; yield 27 mg (8%); *R_f* = 0.55 (ethyl acetate).



¹H NMR (CDCl₃, 500 MHz) δ = 2.19–2.26 (m, 1H, C(5)H₂), 2.37–2.59 (m, 1H, C(5)H₂ + 2H, C(6)H₂), 3.53 (d, ²*J* = 13.4 Hz, 1H, C(9)H₂), 3.74 (s, 3H, CH₃O), 3.81 (s, 3H, CH₃O), 3.87 (s, 3H, CH₃O), 3.92 (s, 3H, CH₃O), 3.96 (s, 3H, CH₃O), 4.31 (dd, ³*J* = 9.4 Hz, ³*J* = 6.6 Hz, 1H, C(4b)H), 4.83 (d, ²*J* = 13.4 Hz, 1H, C(9)H₂), 6.56 (d, ⁴*J* = 2.3 Hz, 1H, CH, Ar), 6.57 (d, ⁴*J* = 2.3 Hz, 1H, CH, Ar),

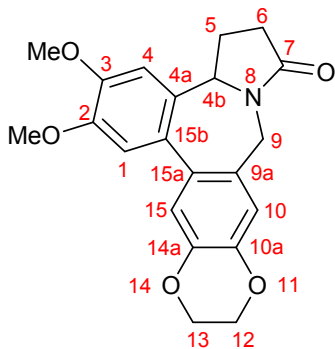
6.73 (s, 1H, C(4)H).

¹³C NMR (CDCl₃, 125 MHz) δ = 21.8 (CH₂), 31.7 (CH₂), 44.4 (CH₂), 55.5 (CH₃O), 55.8 (CH₃O), 56.2 (CH₃O), 57.7 (CH), 60.8 (CH₃O), 60.9 (CH₃O), 98.6 (CH, Ar), 103.5 (CH, Ar), 104.8 (CH, Ar), 111.7 (C, Ar), 117.2 (C, Ar), 121.4 (C, Ar), 122.3 (C, Ar), 130.3 (C, Ar), 135.5 (C, Ar), 153.3 (C, Ar), 157.9 (C, Ar), 160.8 (C, Ar), 172.2 (C=O).

IR (film, cm⁻¹): 2954, 2924, 2852, 1680, 1601, 1566, 1460, 1408, 1362, 1323, 1284, 1242, 1203, 1157, 1093, 1074, 1039, 1007.

HRMS (ESI/Q-TOF) *m/z* [M + H]⁺ Calcd for C₂₂H₂₆NO₆ 400.1755; Found 400.1761.

2,3-Dimethoxy-4b,5,6,9,12,13-hexahydro-7H-[1,4]dioxino[2',3':4,5]benzo[1,2-*e*]benzo[*c*]pyrrolo[1,2-*a*]azepin-7-one (5d) was obtained from **4h** (148 mg, 0.4 mmol) after reflux for 0.75 h with DDQ (113 mg, 0.5 mmol) and BF₃·Et₂O (0.62 mL, 5 mmol) in PhCl (6.7 mL). Product was isolated as brown thick oil; yield 104 mg (71%); *R_f* = 0.45 (ethyl acetate).



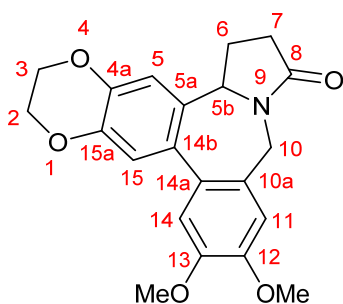
¹H NMR (CDCl₃, 500 MHz) δ = 2.20–2.28 (m, 1H, C(5)H₂), 2.38–2.46 (m, 1H, C(5)H₂), 2.46–2.59 (m, 2H, C(6)H₂), 3.54 (d, ²*J* = 13.6 Hz, 1H, C(9)H₂), 3.93 (s, 3H, CH₃O), 3.95 (s, 3H, CH₃O), 4.29 (s, 4H, 2×CH₂O), 4.31 (dd, ³*J* = 9.3 Hz, ³*J* = 6.3 Hz, 1H, C(4b)H), 4.77 (d, ²*J* = 13.6 Hz, 1H, C(9)H₂), 6.90 (s, 2H, C(4)H, C(10)H), 6.96 (s, 2H, C(1)H, C(15)H).

¹³C NMR (CDCl₃, 125 MHz) δ = 22.3 (C(5)H₂), 31.7 (C(6)H₂), 43.5 (C(9)H₂), 56.0 (CH₃O), 56.1 (CH₃O), 57.4 (C(4b)H), 64.35 (CH₂O), 64.42 (CH₂O), 108.2 (C(4)H), 112.2 (C(15)H), 117.2 (C(1)H), 117.8 (C(10)H), 126.4 (C(15b)), 126.6 (C(15a)), 132.7 (C(4a)), 133.6 (C(9a)), 143.1, 143.4 (C(10a), C(14a)), 148.5, 148.9 (C(2), C(3)), 172.0 (C=O).

HRMS (ESI/Q-TOF) *m/z* [M + H]⁺ Calcd for C₂₁H₂₂NO₅ 368.1492; Found 368.1492.

Analysis of the reaction mixture NMR spectra revealed the presence of a second isomer (NMR yield was ca. 16%) that was not isolated in a pure form.

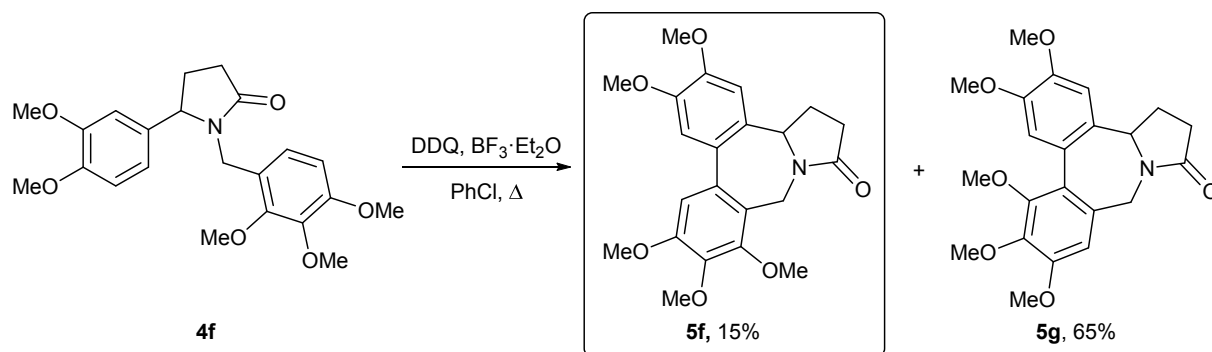
12,13-Dimethoxy-2,3,5b,6,7,10-hexahydro-8H-[1,4]dioxino[2',3':4,5]benzo[1,2-c]pyrrolo[1,2-a]azepin-8-one (5e) was obtained from **4j** (122 mg, 0.33 mmol) after reflux for 0.75 h with DDQ (91 mg, 0.4 mmol) and BF₃·Et₂O (0.5 mL, 4 mmol) in PhCl (3.5 mL). Product was isolated as yellowish foam; yield 81 mg (67%); *R*_f = 0.32 (ethyl acetate).



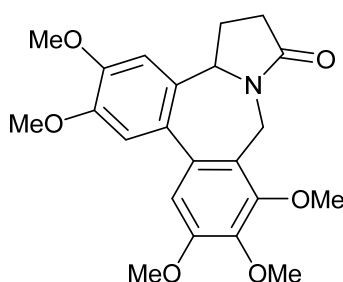
¹H NMR (CDCl₃, 500 MHz) δ = 2.19–2.24 (m, 1H, C(6)H₂), 2.34–2.43 (m, 1H, C(6)H₂), 2.46–2.59 (m, 2H, C(7)H₂), 3.62 (d, ²*J* = 13.7 Hz, 1H, C(10)H₂), 3.66 (s, 3H, CH₃O), 3.93 (s, 3H, CH₃O), 4.31 (dd, ³*J* = 9.4 Hz, ³*J* = 6.1 Hz, 1H, C(5b)H), 4.34 (s, 4H, 2×CH₂O), 4.85 (d, ²*J* = 13.7 Hz, 1H, C(10)H₂), 6.91 (s, 1H, C(11)H), 6.92 (s, 1H, C(14)H), 6.94 (s, 1H, C(5)H), 7.03 (s, 1H, C(15)H).

¹³C NMR (CDCl₃, 125 MHz) δ = 22.4 (C(6)H₂), 31.7 (C(7)H₂), 43.8 (C(10)H₂), 56.2 (2×CH₃O), 57.3 (C(5b)H), 64.5 (2×CH₂O), 112.0 (C(11)H), 112.2 (C(14)H), 114.0 (C(5)H), 117.5 (C(15)H), 125.5 (C(14b)), 127.7 (C(5a)), 132.3 (C(14a)), 133.9 (C(10a)), 143.1 (C(15a)), 143.4 (C(4a)), 148.6 (C(13)), 148.8 (C(12)), 172.4 (C=O).

HRMS (ESI/Q-TOF) *m/z* [M + H]⁺ Calcd for C₂₁H₂₂NO₅ 368.1492; Found 368.1493.



2,3,10,11,12-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5f) was obtained together with **5g** from **4f** (209 mg, 0.52 mmol) after reflux for 0.75 h with DDQ (141 mg, 0.62 mmol) and BF₃·Et₂O (0.77 mL, 6.2 mmol) in PhCl (5.5 mL). NMR yield of **5f** 15%. Product **5g** was isolated in 65% yield (135 mg).



¹H NMR (CDCl₃, 500 MHz) δ = 2.20–2.29 (m, 1H, CH₂), 2.37–2.58 (m, 3H, CH₂), 3.16 (d, ²*J* = 13.5 Hz, 1H, C(9)H₂), 3.87 (s, 3H, CH₃O), 3.88 (s, 3H, CH₃O), 3.90 (s, 3H, CH₃O), 3.91 (s, 3H, CH₃O), 3.94 (s, 3H, CH₃O), 4.29 (dd, ³*J* = 8.9 Hz, ³*J* = 6.4 Hz, 1H, C(4b)H), 5.42 (d, ²*J* = 13.5 Hz, 1H, C(9)H₂), 6.72 (s, 1H, CH), 6.91

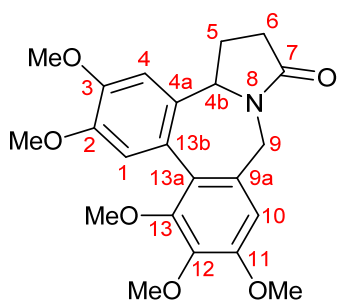
(s, 1H, CH), 6.97 (s, 1H, CH).

^{13}C NMR (CDCl_3 , 125 MHz) δ = 22.3 (CH_2), 31.7 (CH_2), 35.9 (CH_2N), 56.17 ($2\times\text{CH}_3\text{O}$), 56.21 (CH), 57.3 (CH_3O), 60.9 (CH_3O), 61.8 (CH_3O), 108.0 (CH, Ar), 108.2 (CH, Ar), 112.3 (CH, Ar), 120.0 (C, Ar), 126.8 (C, Ar), 133.1 (C, Ar), 136.4 (C, Ar), 141.9 (C, Ar), 148.88 (C, Ar), 148.94 (C, Ar), 151.1 (C, Ar), 153.1 (C, Ar), 171.9 (C=O).

HRMS (ESI/Q-TOF) m/z $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{25}\text{NNaO}_6$ 422.1574; Found 422.1577.

2,3,11,12,13-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5g)

was obtained from **4g** (241 mg, 0.6 mmol) after reflux for 0.5 h with DDQ (170 mg, 0.75 mmol) and $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.9 mL, 7.3 mmol) in PhCl (6 mL). Product was isolated as colorless solid; yield 156 mg (65%); m.p. 192–193 °C (petroleum ether : ethyl acetate, 1:1); R_f = 0.63 (CH_3OH : ethyl acetate; 1:3).



^1H NMR (CDCl_3 , 500 MHz) δ = 2.22–2.29 (m, 1H, C(5) H_2), 2.39–2.45 (m, 1H, C(5) H_2), 2.46–2.58 (m, 2H, C(6) H_2), 3.42 (d, 2J = 13.4 Hz, 1H, C(9) H_2), 3.59 (s, 3H, CH_3O), 3.88 (s, 3H, CH_3O), 3.90 (s, 3H, CH_3O), 3.91 (s, 3H, CH_3O), 3.95 (s, 3H, CH_3O), 4.32 (dd, 3J = 9.5 Hz, 3J = 6.4 Hz, 1H, C(4b)H), 4.78 (d, 2J = 13.4 Hz, 1H, C(9) H_2), 6.72 (s, 1H, C(10)H), 6.91 (s, 1H, C(4)H), 7.16 (s, 1H, C(1)H).

^{13}C NMR (CDCl_3 , 125 MHz) δ = 22.0 (C(5) H_2), 31.7 (C(6) H_2), 44.0 (C(9) H_2), 55.92 ($2\times\text{CH}_3\text{O}$), 55.94 (CH_3O), 55.95 (CH_3O), 57.3 (C(4b)H), 60.7 (CH_3O), 107.5 (C(4)H), 108.1 (C(10)H), 114.0 (C(1)H), 125.5 (C(13a)), 126.6 (C(4a)), 128.4 (C(13b)), 129.3 (C(9a)), 142.1 (C(11)), 148.1 (C(2)), 148.4 (C(3)), 151.0 (C(13)), 152.9 (C(11)), 172.0 (C=O).

HRMS (ESI/Q-TOF) m/z $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{25}\text{NNaO}_6$ 422.1574; Found 422.1577.

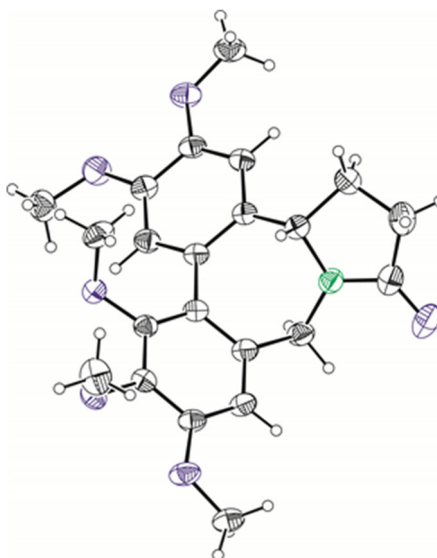


Figure S3. Molecular structure (ORTEP-3^[S5]) from single crystal X-ray study of **5g**.

Cell assays

HEK-293, MCF7, A549, PC3 and VA13 cell lines

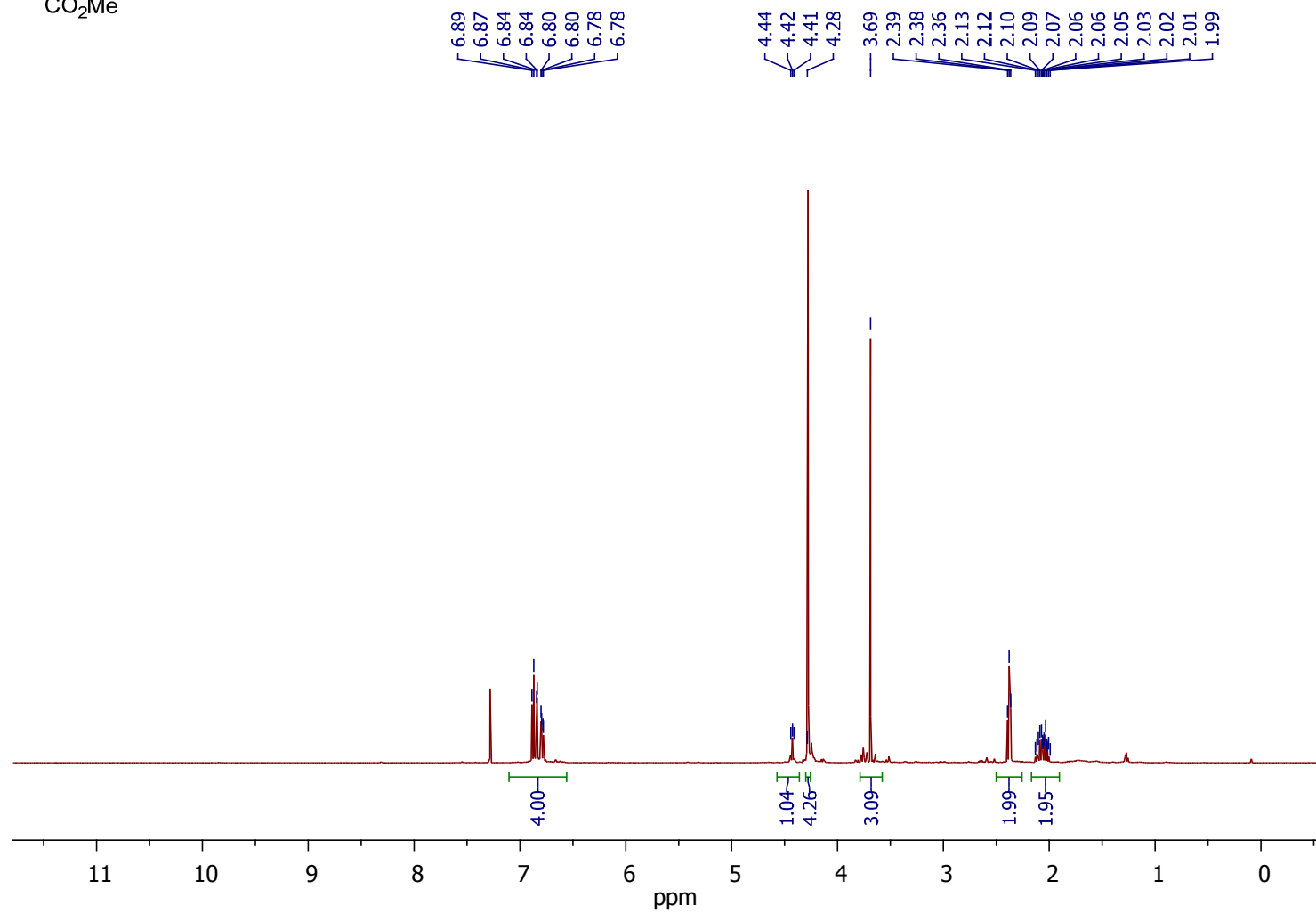
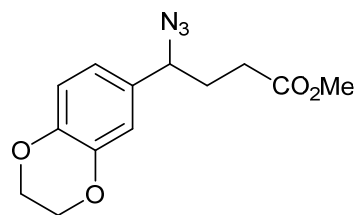
The cytotoxicity of tested compounds was assessed using the MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay^[S6] with some modifications. 4000 cells per well were plated out in 100 mL of DMEM media containing 10% FBS in 96-well plate and incubated at 37 °C in 5% CO₂ incubator for 24 h. Then 10 mL of water-DMSO solution of tested compound was added to the cells (DMSO concentration in the media was kept below 1%) in such way that effective concentrations of studied compounds were in a range of 50 nM to 100 mM (eight dilutions). Doxorubicin (3 nM to 6 mM) was used as a control. After incubation for 72 h 10 mL MTT solution in PBS (5 mg/ml) was added, cells were incubated for 2 h. Medium was removed and 100 mL of DMSO was added. Samples were incubated for 15 min with shaking to completely solubilize formazan. Cell survival was measured spectrophotometrically at 565 nm.

References

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- S6. M. Ferrari, M.C. Fornasiero, A.M. Isetta, *J. Immunol. Methods*, 1990, 131, 165-172.

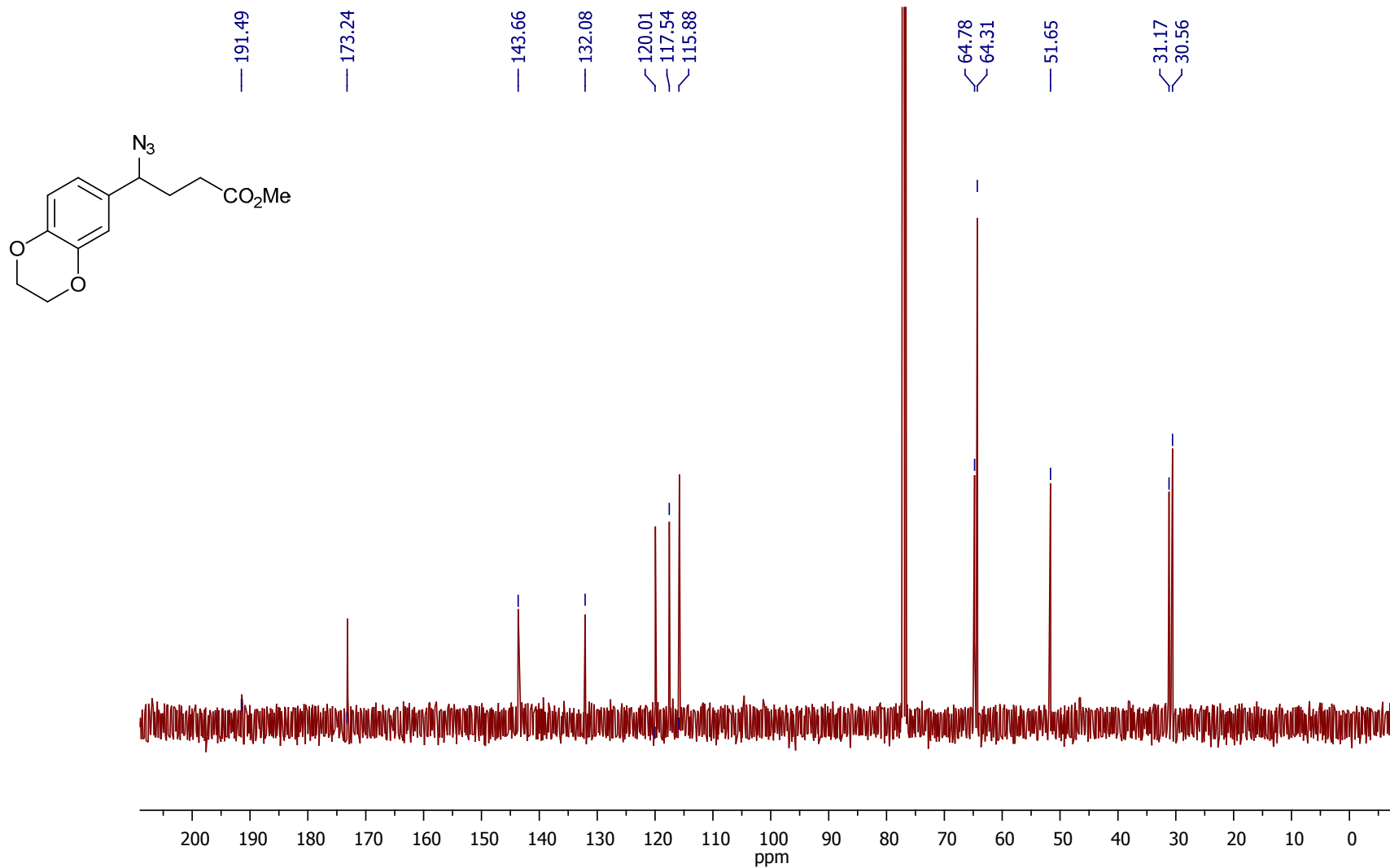
Methyl 4-azido-4-(2,3-dihydro[1,4]benzodioxin-6-yl)butanoate (2c)

^1H NMR (CDCl_3 , 500 MHz)



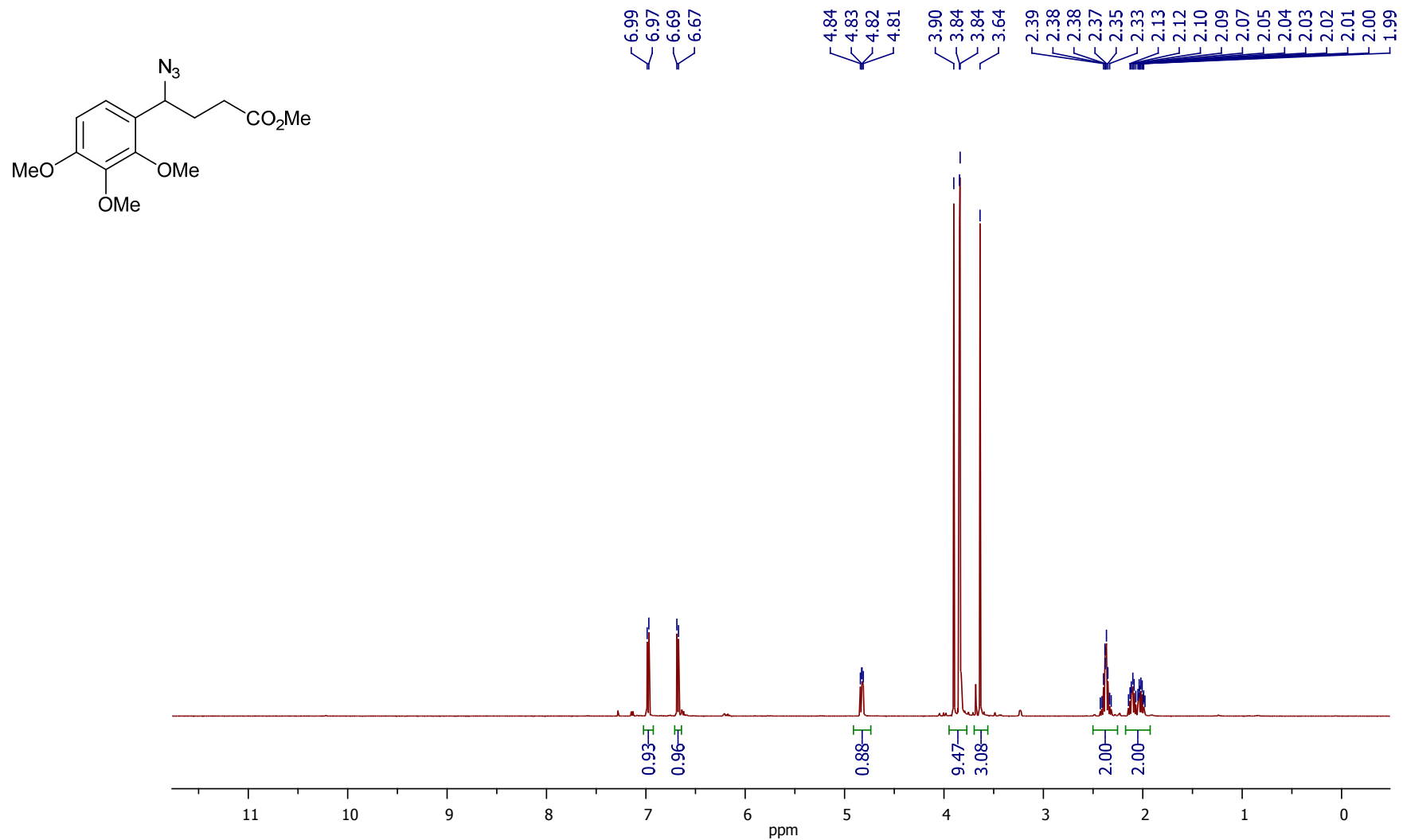
Methyl 4-azido-4-(2,3-dihydro[1,4]benzodioxin-6-yl)butanoate (2c)

^{13}C NMR (CDCl_3 , 125 MHz)



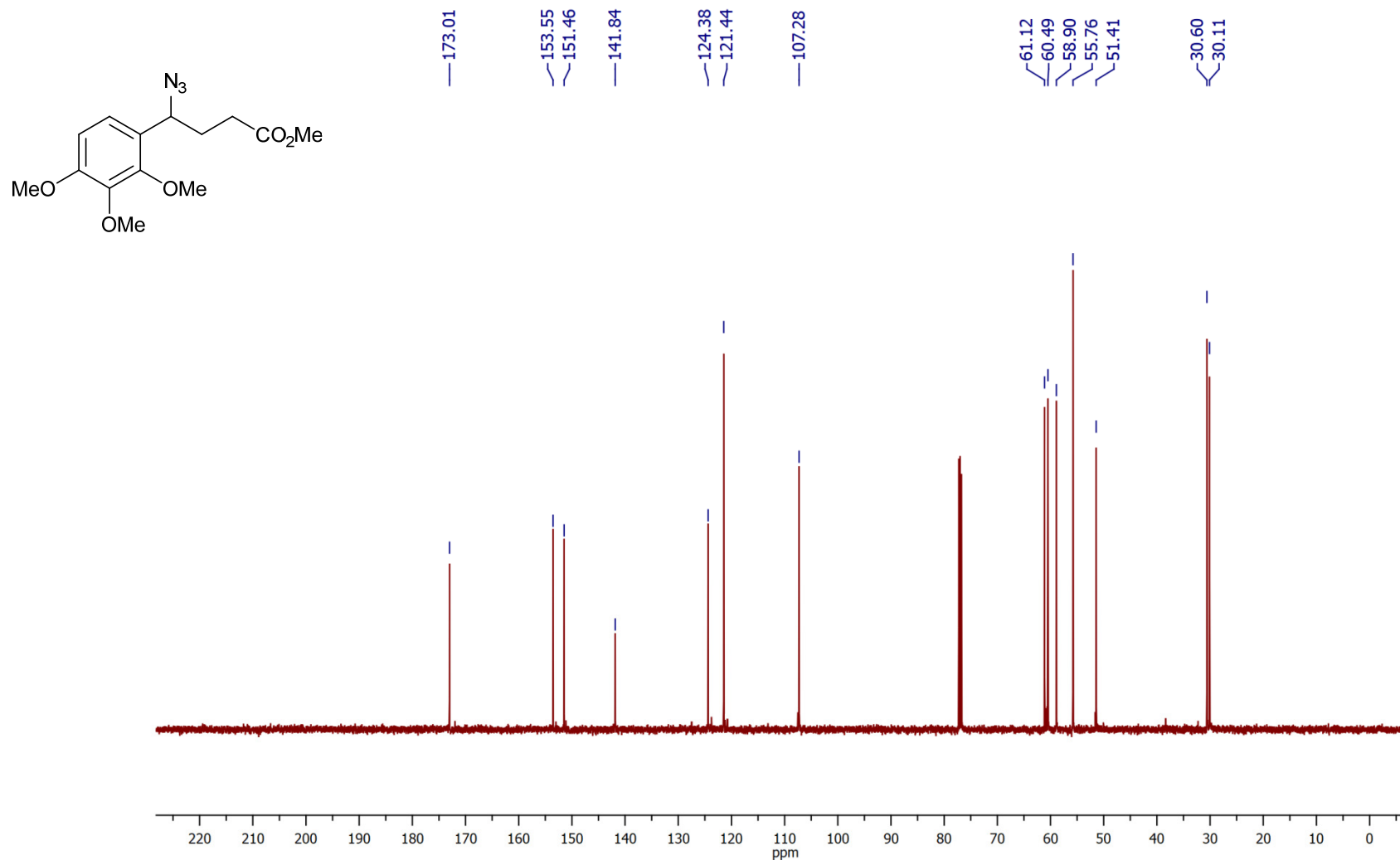
Methyl 4-azido-4-(2,3,4-trimethoxyphenyl)butanoate (2d)

^1H NMR (CDCl_3 , 500 MHz)



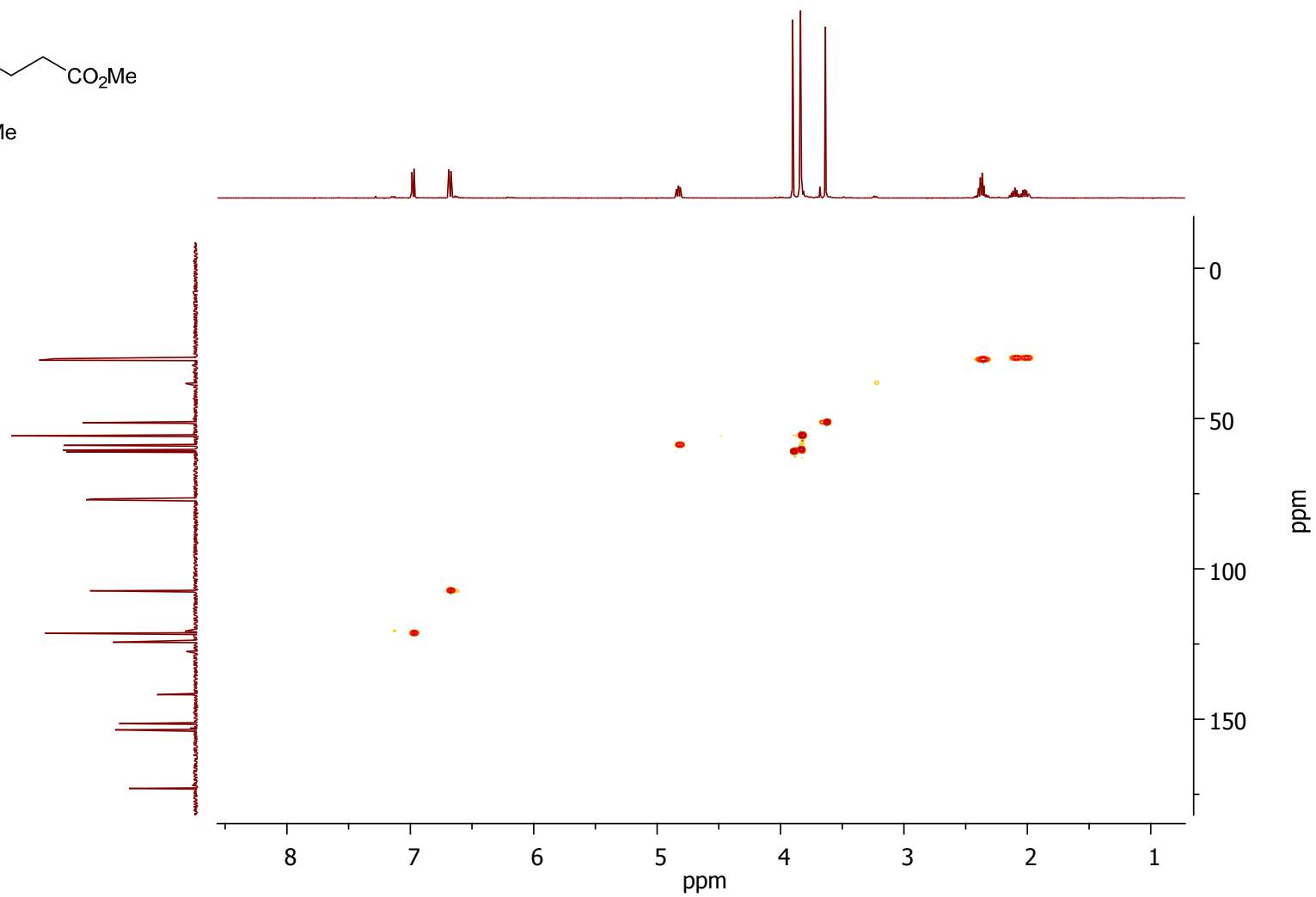
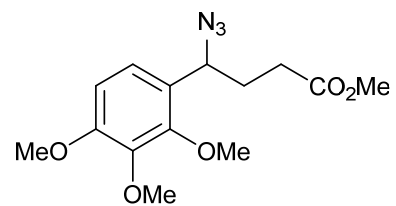
Methyl 4-azido-4-(2,3,4-trimethoxyphenyl)butanoate (2d)

¹³C NMR (CDCl₃, 125 MHz)



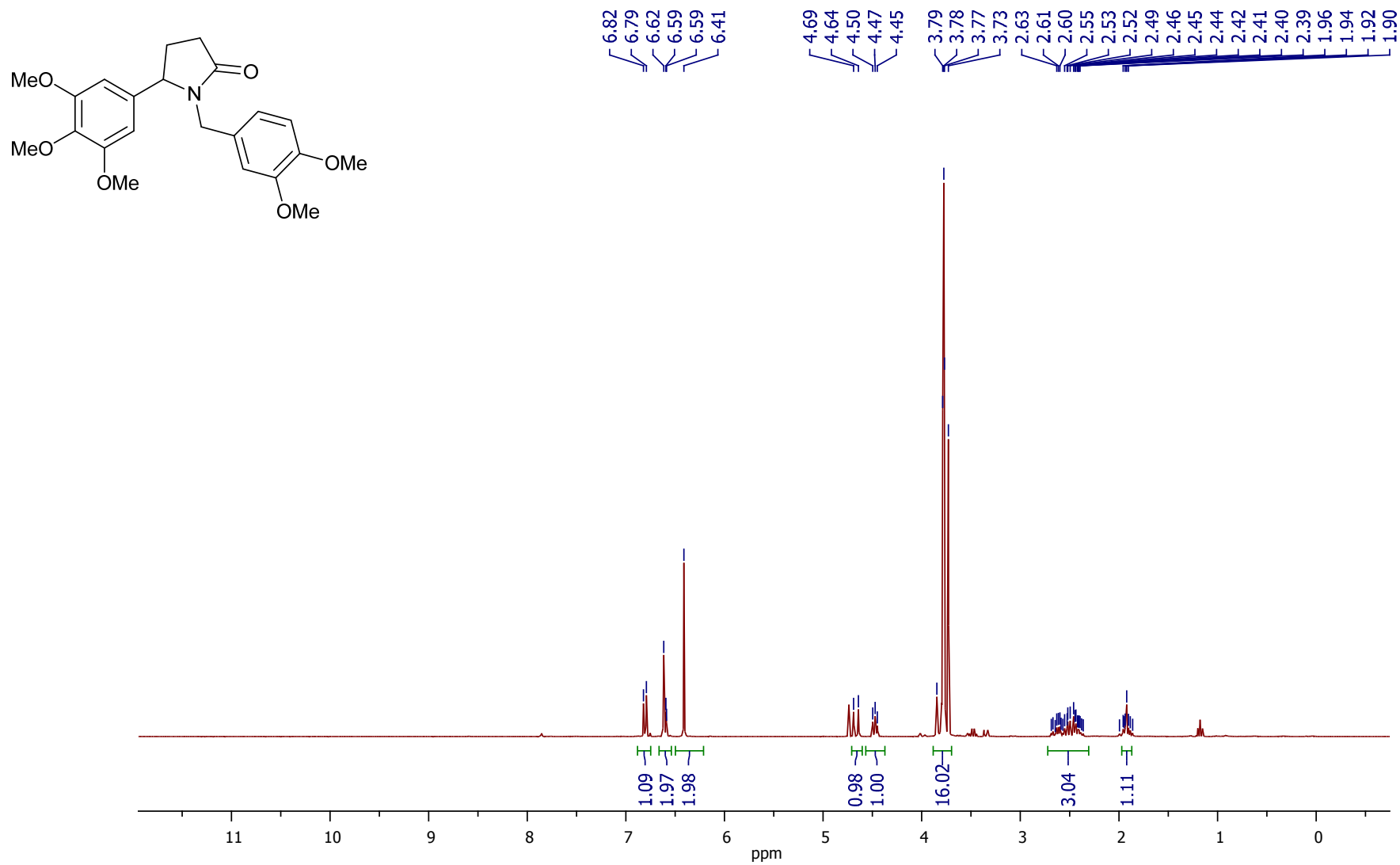
Methyl 4-azido-4-(2,3,4-trimethoxyphenyl)butanoate (2d)

HSQC ^1H - ^{13}C (CDCl_3)



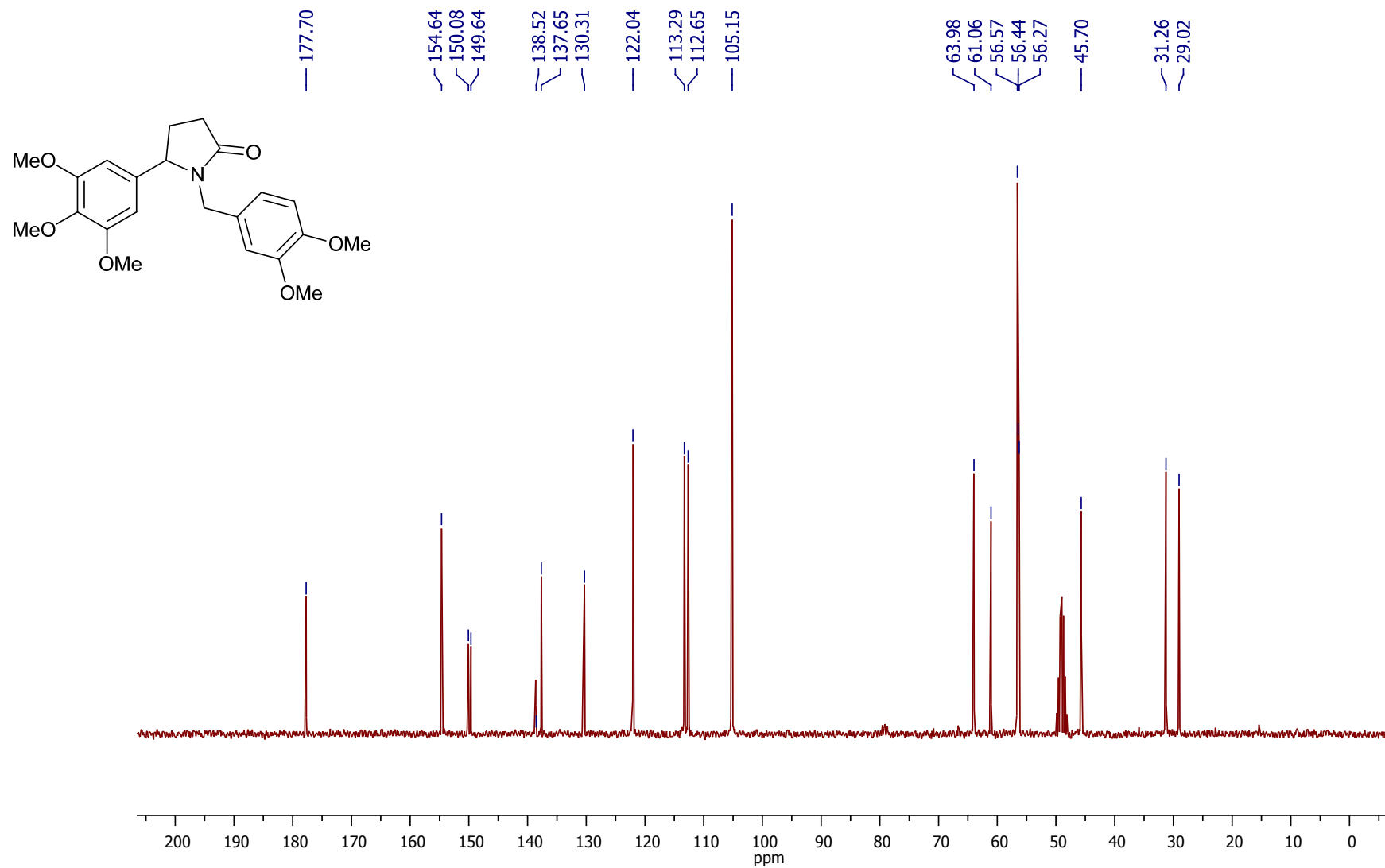
1-(3,4-Dimethoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4a)

¹H NMR (CD₃OD, 500 MHz)



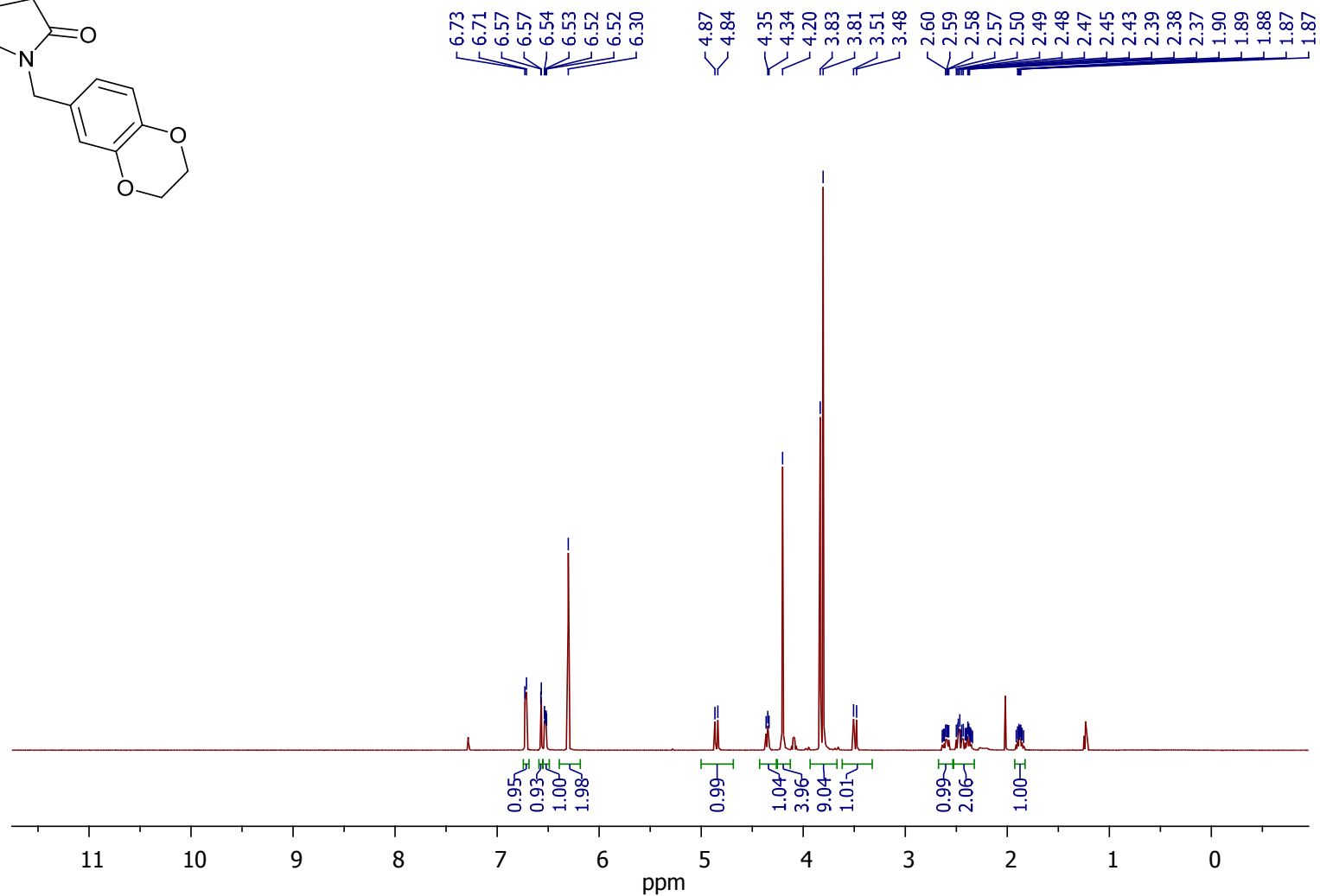
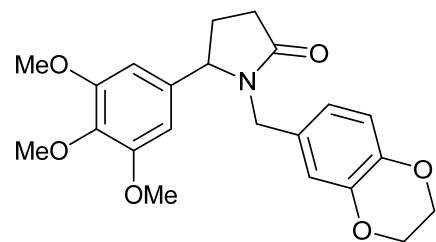
1-(3,4-Dimethoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4a)

^{13}C NMR (CD_3OD , 125 MHz)



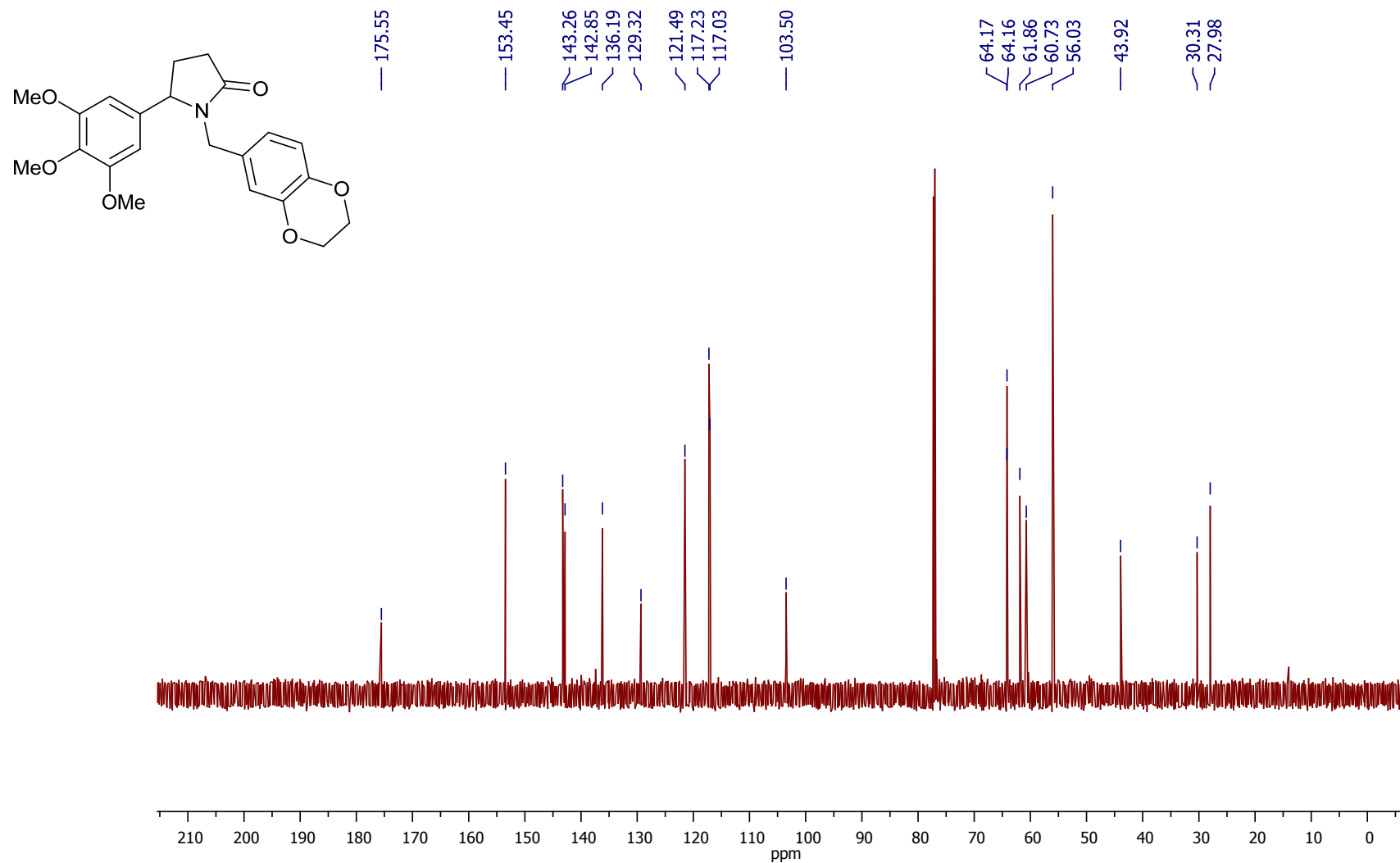
1-[(2,3-Dihydro[1,4]benzodioxin-6-yl)methyl]-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4b)

¹H NMR (CDCl₃, 500 MHz)



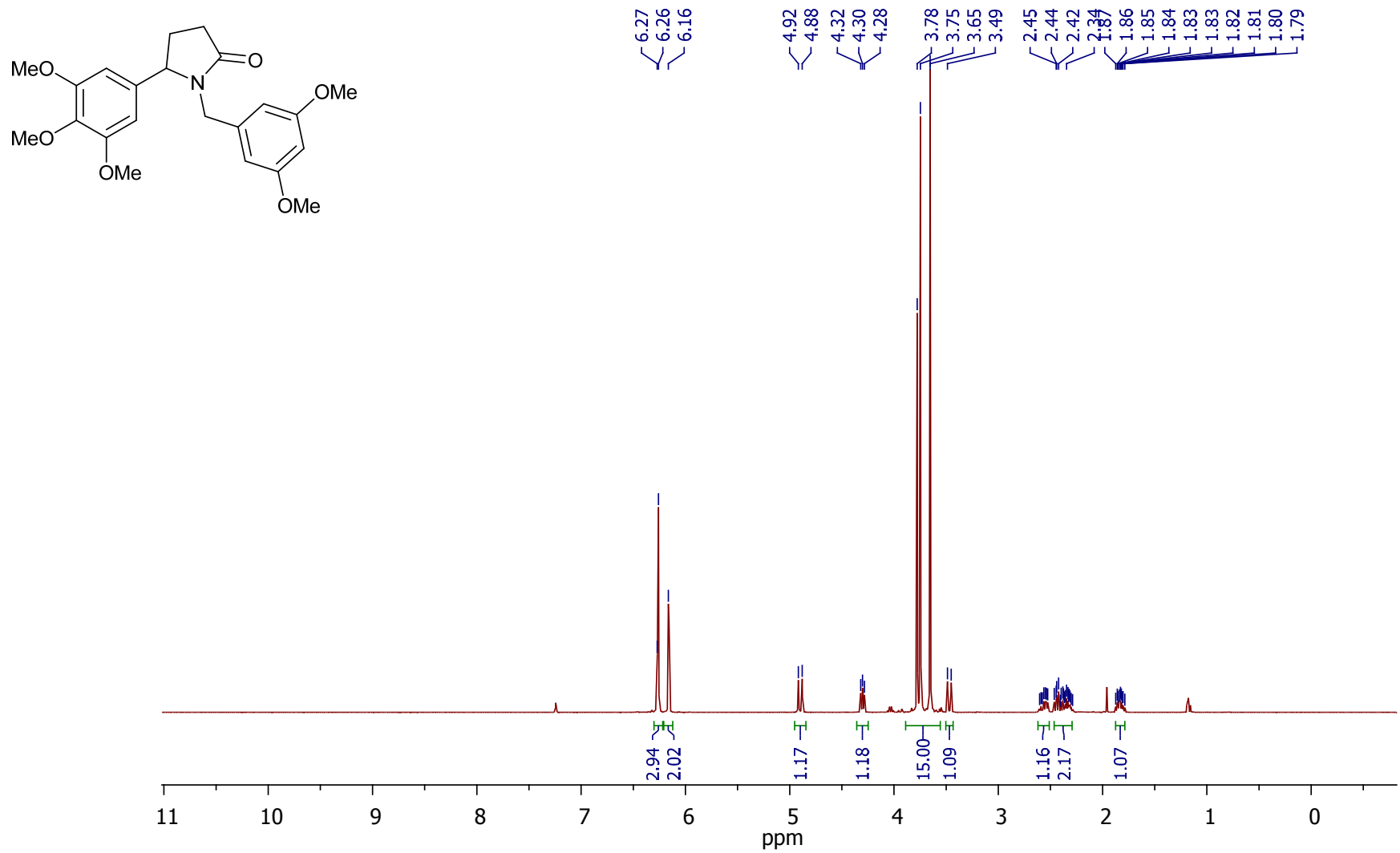
1-[(2,3-Dihydro[1,4]benzodioxin-6-yl)methyl]-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4b)

^{13}C NMR (CDCl_3 , 125 MHz)



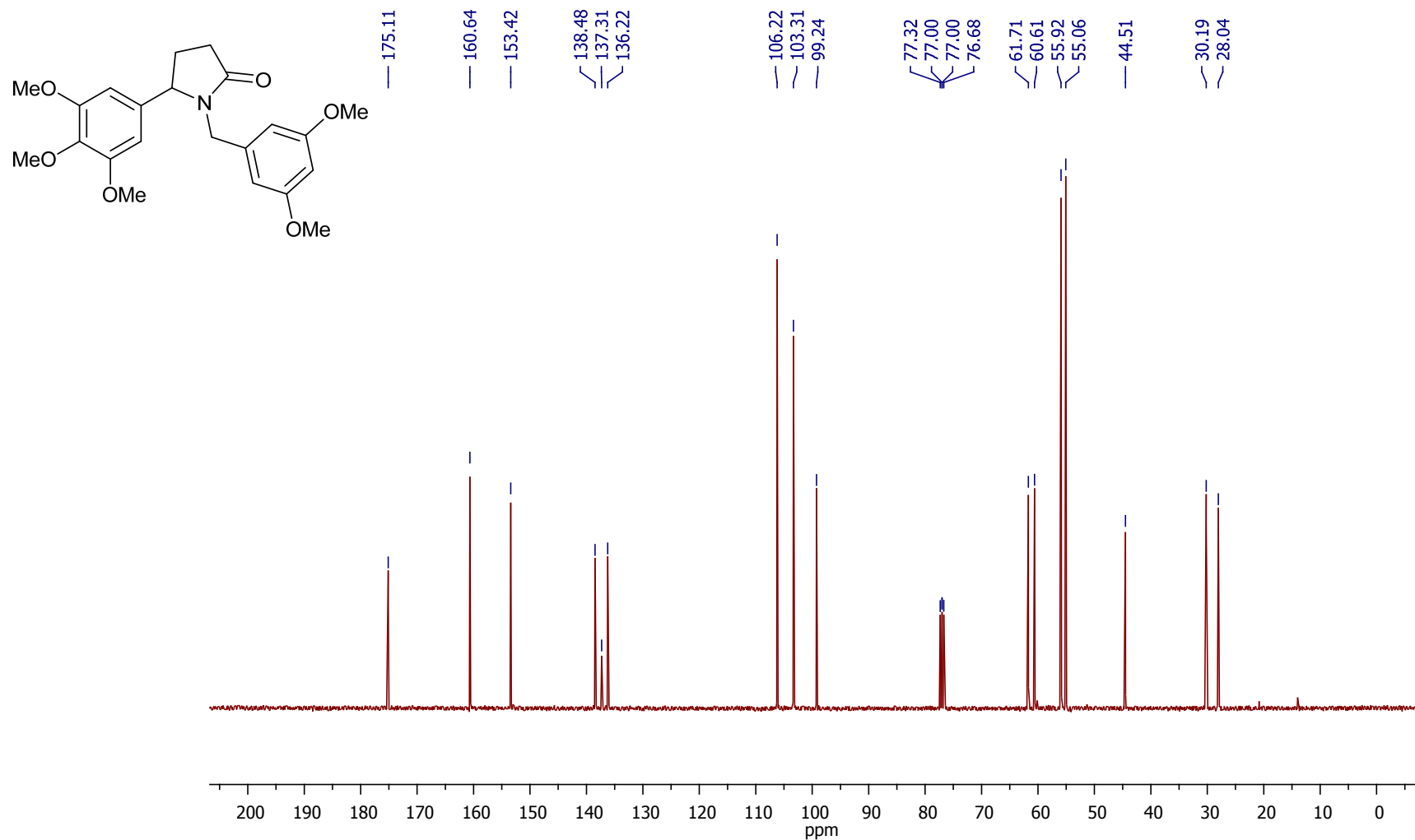
1-(3,5-Dimethoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4c)

¹H NMR (CDCl₃, 500 MHz)



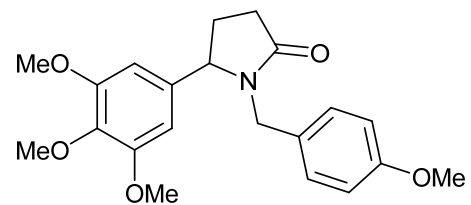
1-(3,5-Dimethoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4c)

^{13}C NMR (CDCl_3 , 125 MHz)

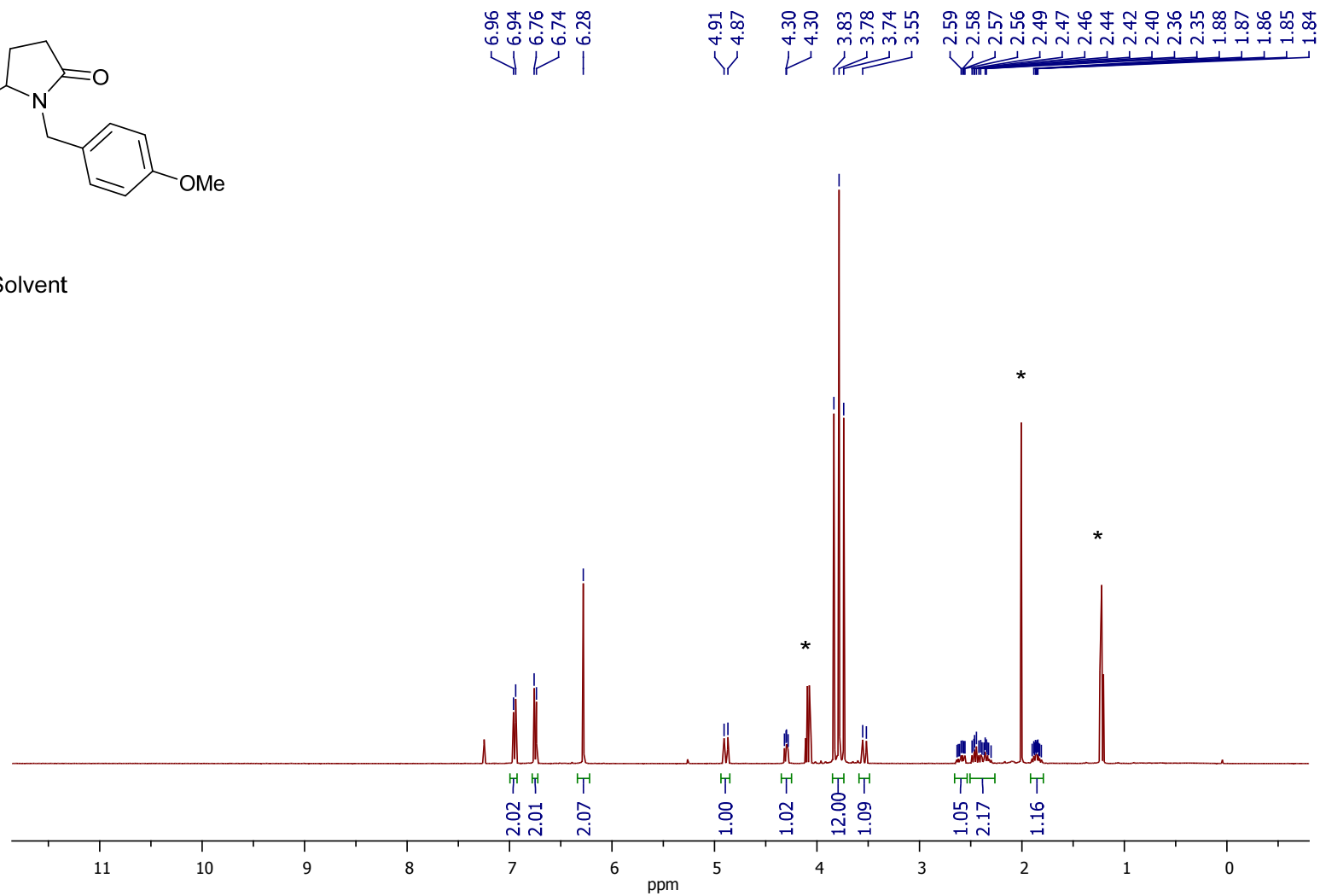


1-(4-Methoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4d)

^1H NMR (CDCl_3 , 500 MHz)

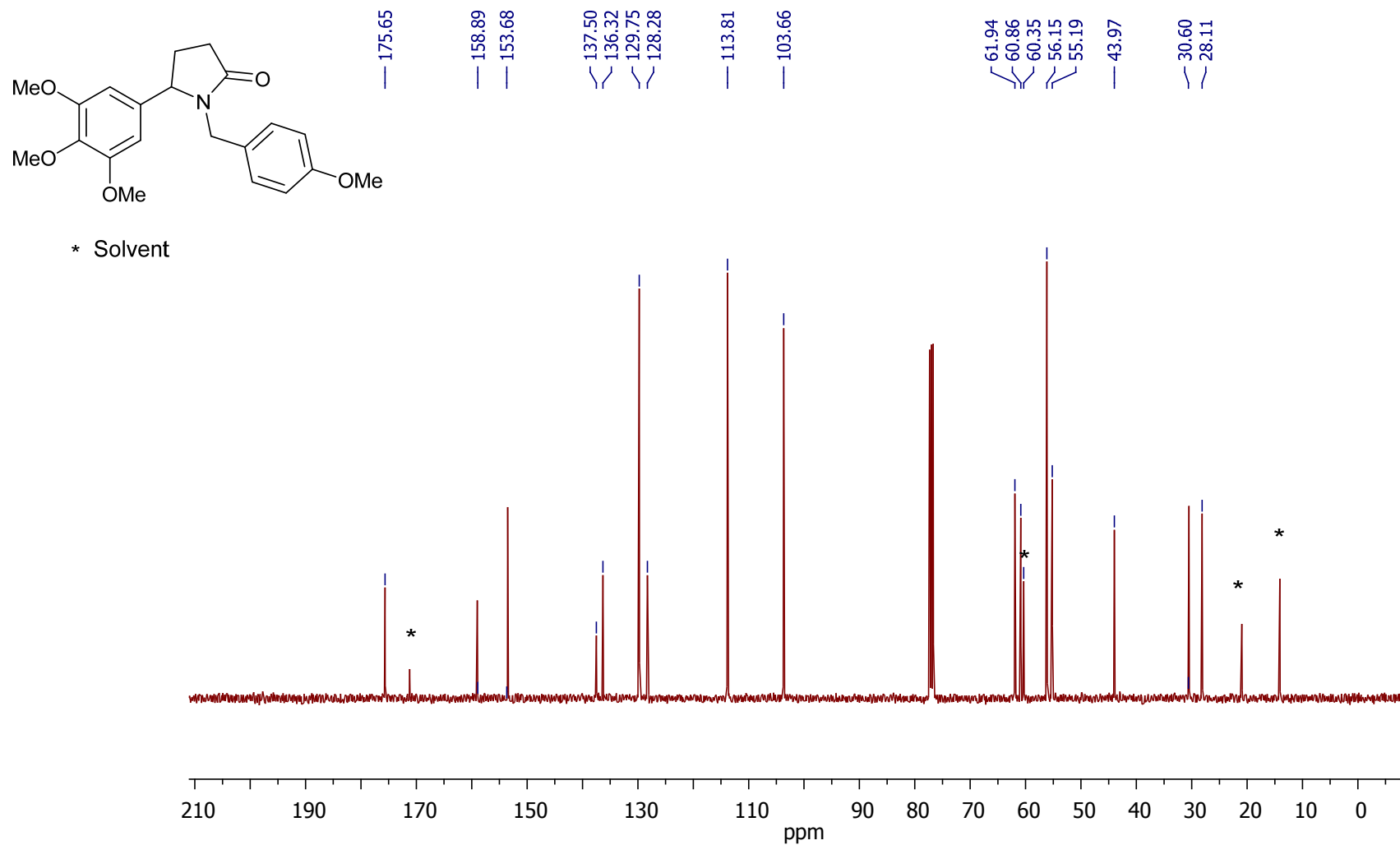


* Solvent



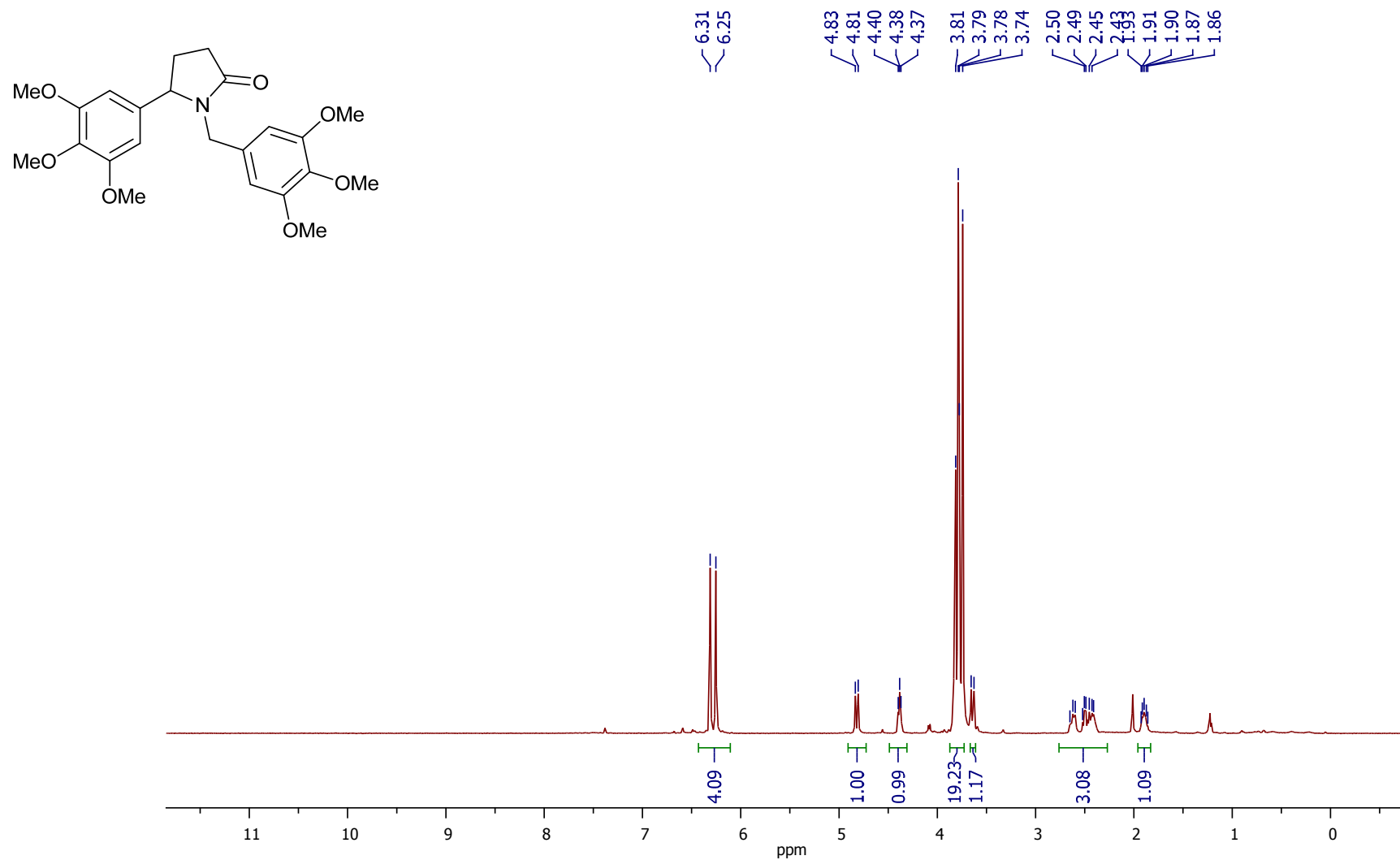
1-(4-Methoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4d)

^{13}C NMR (CDCl_3 , 125 MHz)



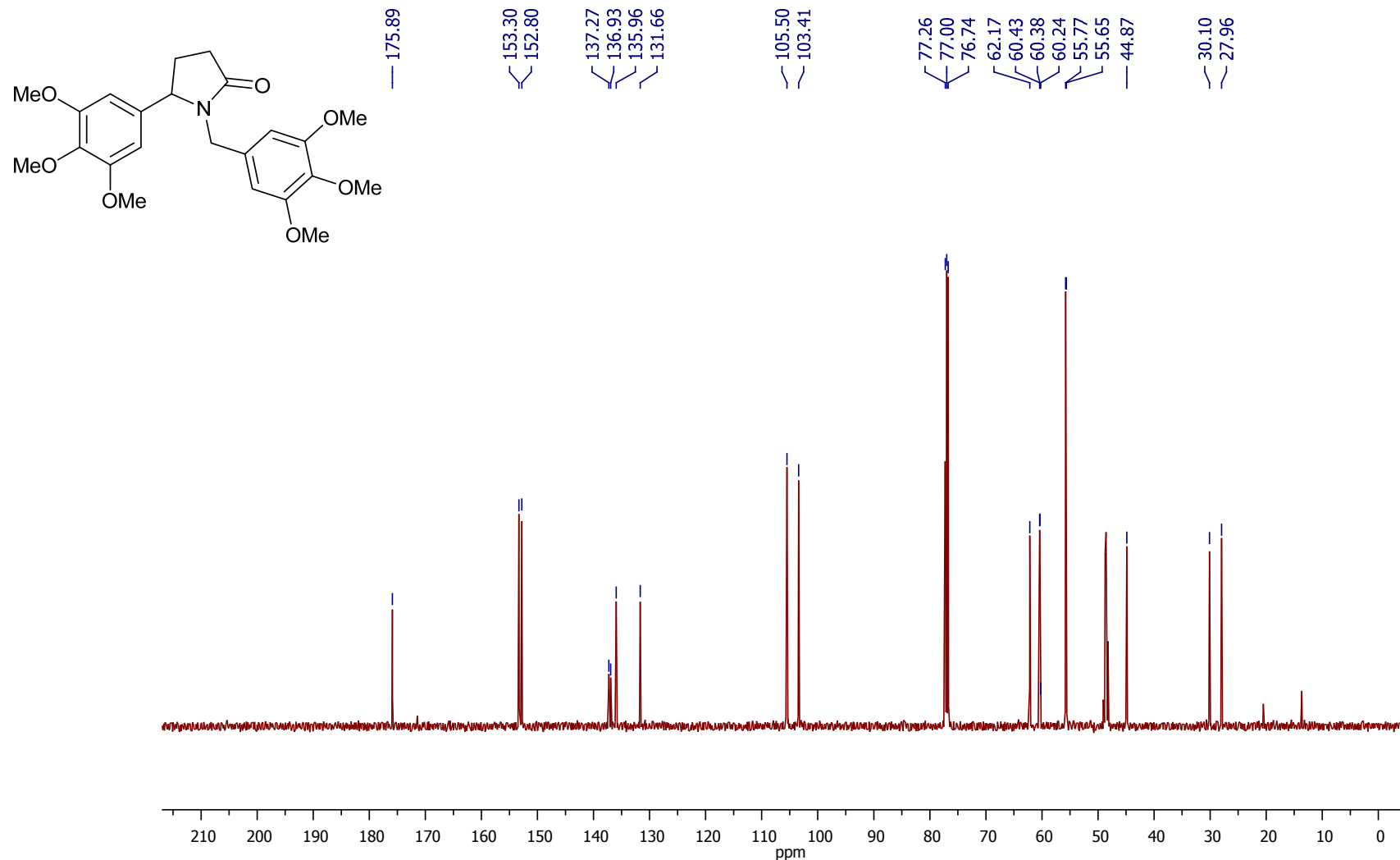
1-(3,4,5-Trimethoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4e)

¹H NMR (CDCl₃-CD₃OD, 500 MHz)



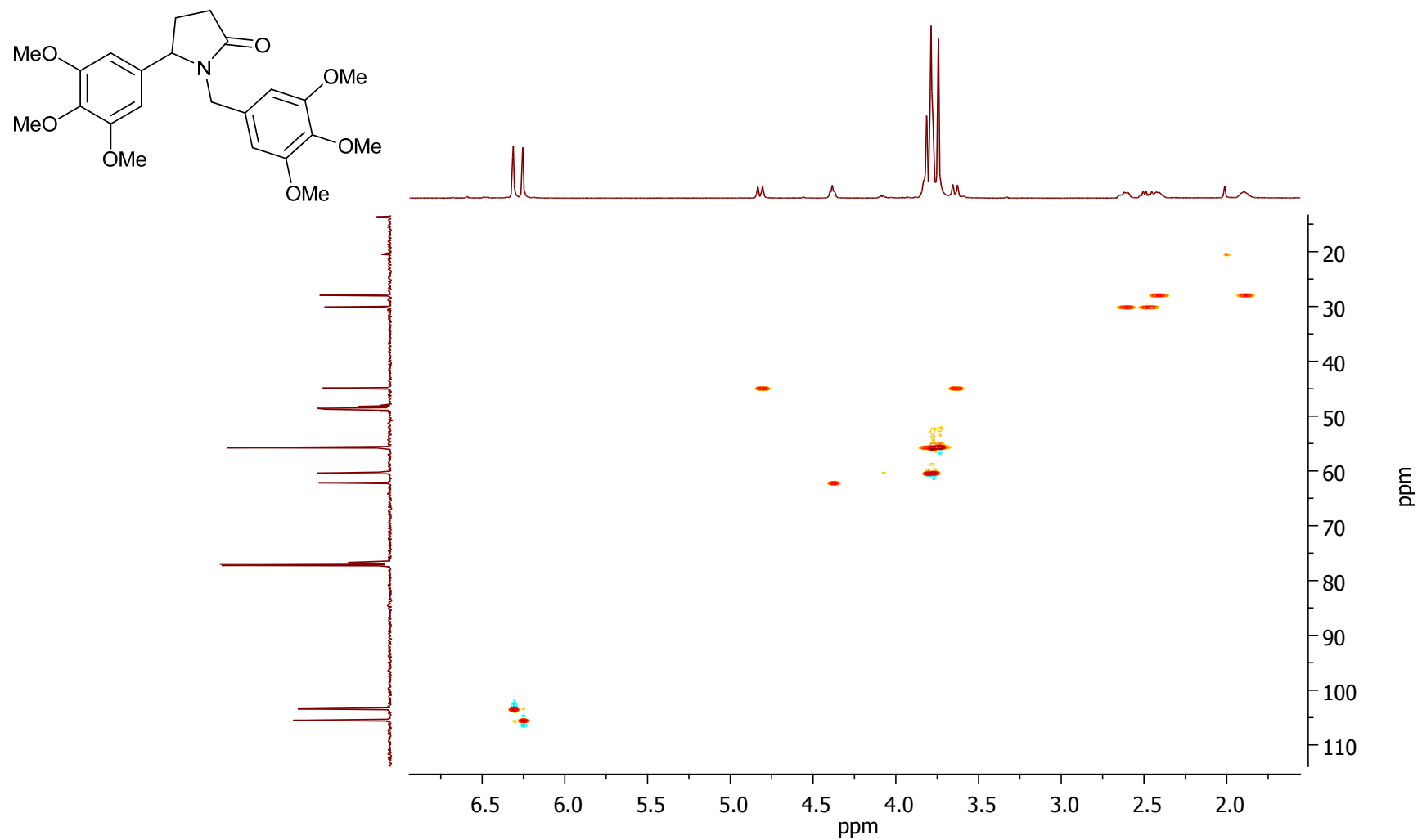
1-(3,4,5-Trimethoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4e)

^{13}C NMR ($\text{CDCl}_3\text{-CD}_3\text{OD}$, 125 MHz)



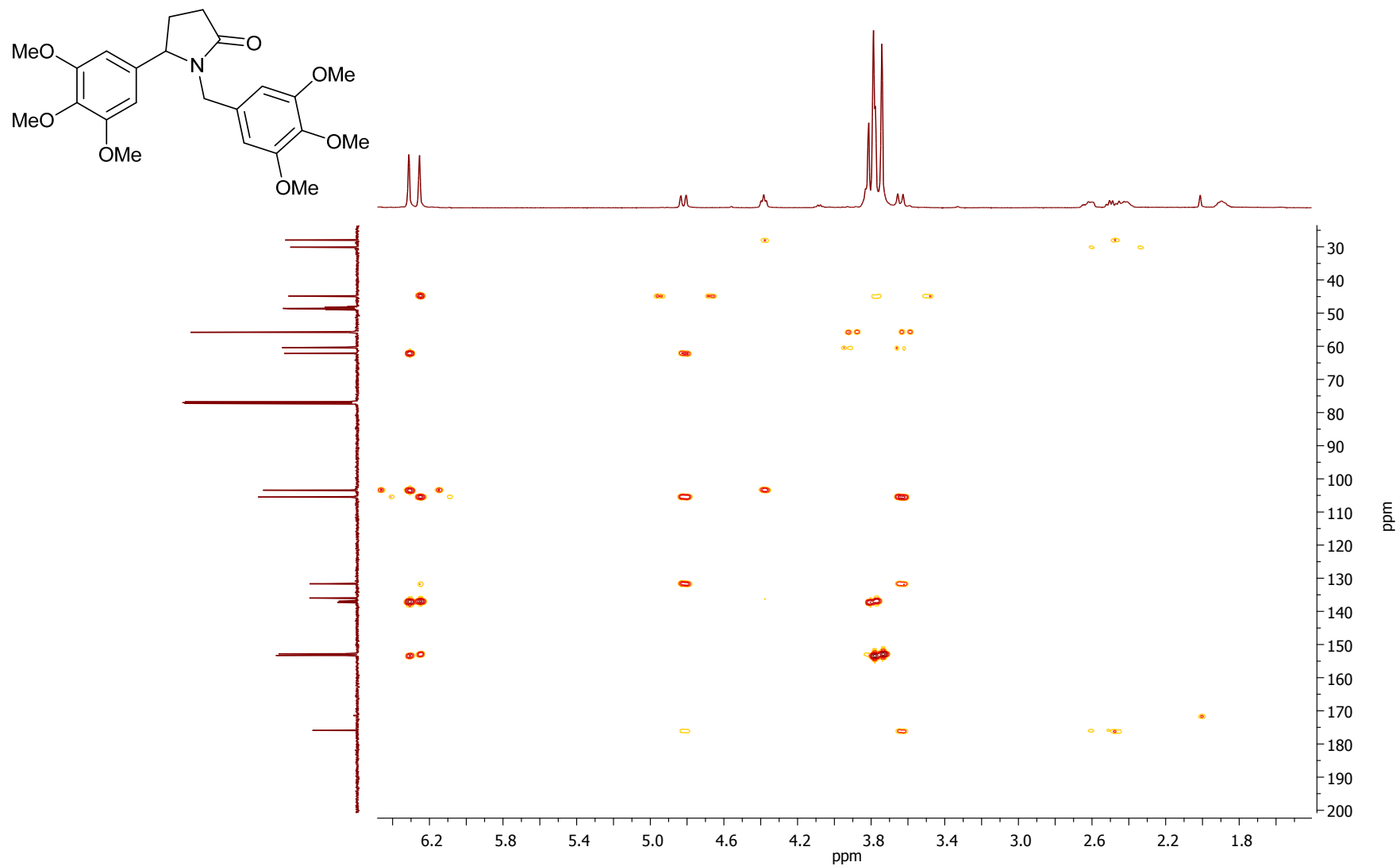
1-(3,4,5-Trimethoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4e)

HSQC ^1H - ^{13}C (CDCl_3 - CD_3OD)



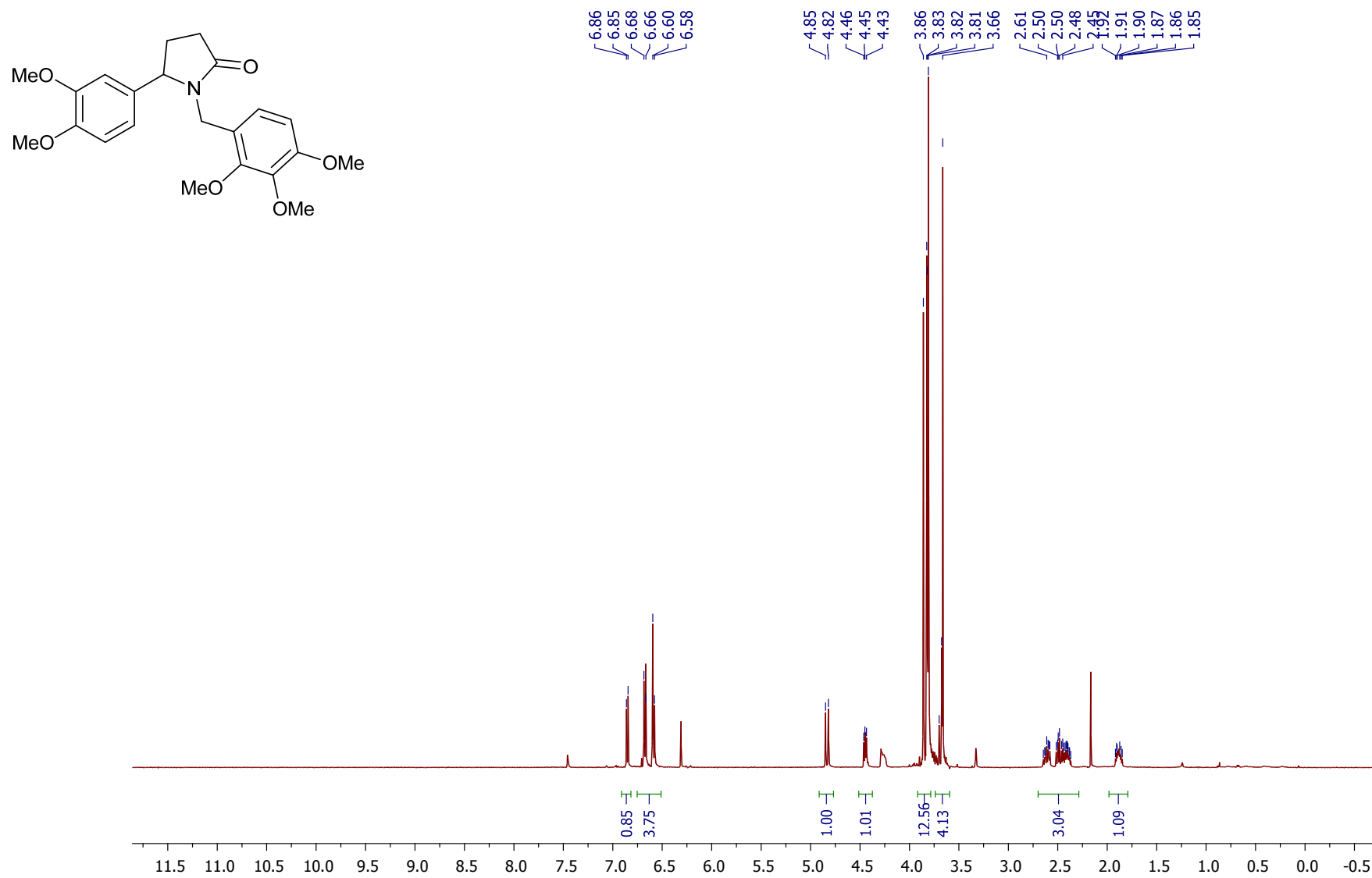
1-(3,4,5-Trimethoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4e)

HMBC ^1H - ^{13}C (CDCl_3 - CD_3OD)



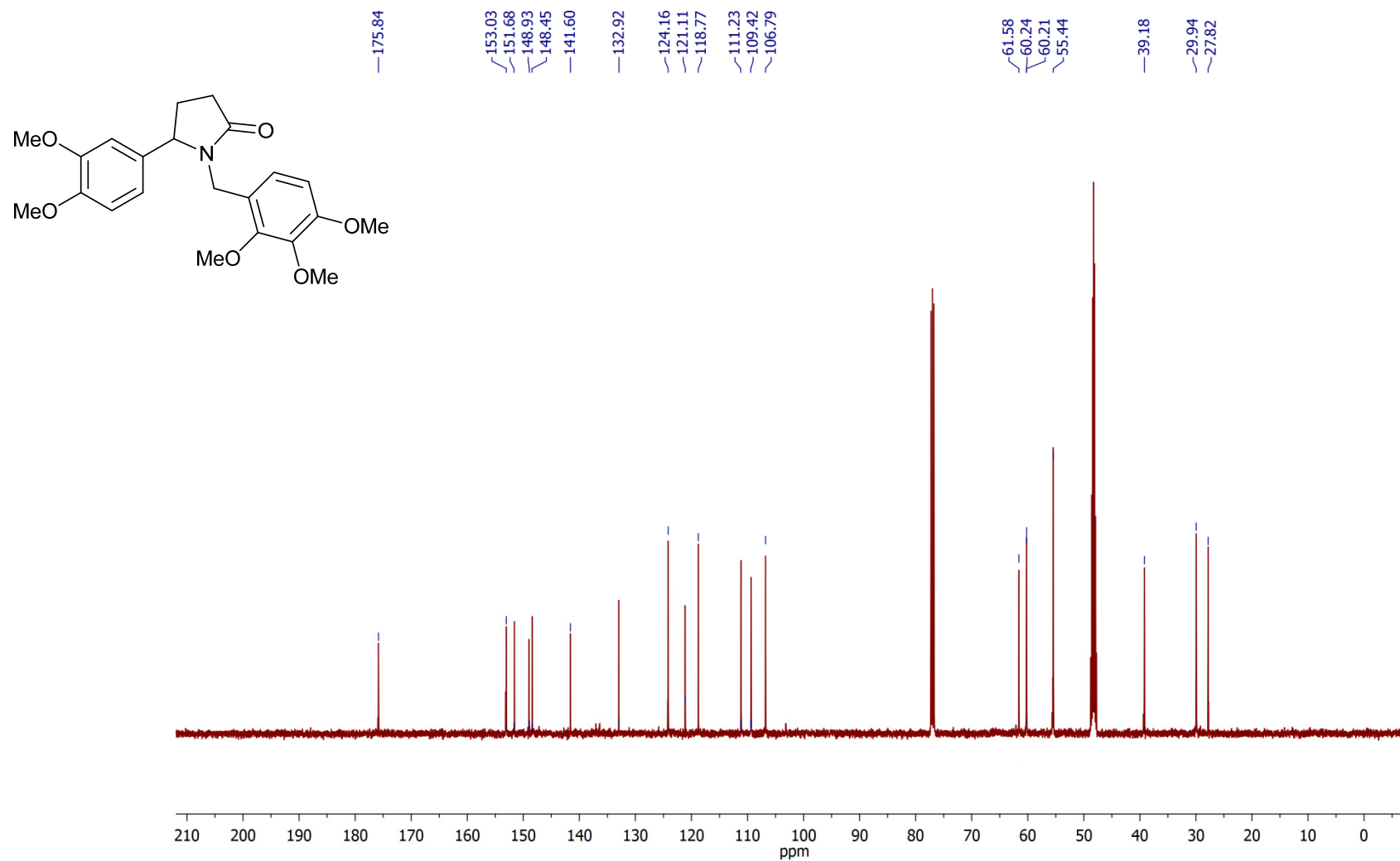
5-(3,4-Dimethoxyphenyl)-1-(2,3,4-trimethoxybenzyl)pyrrolidin-2-one (4f)

^1H NMR ($\text{CDCl}_3\text{-CD}_3\text{OD}$, 500 MHz)



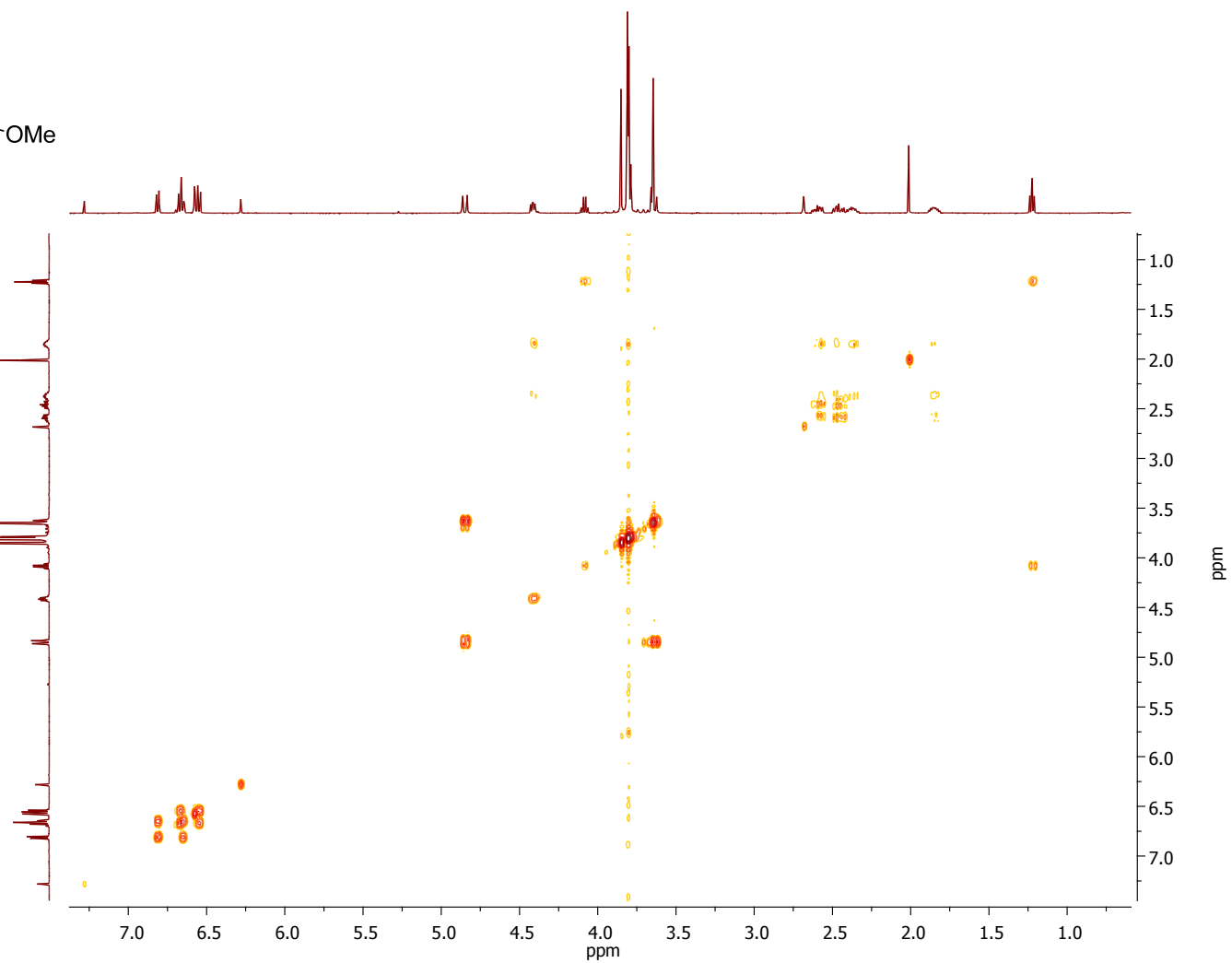
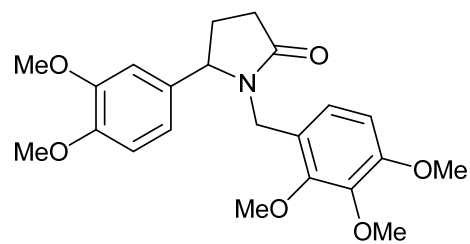
5-(3,4-Dimethoxyphenyl)-1-(2,3,4-trimethoxybenzyl)pyrrolidin-2-one (4f)

^{13}C NMR ($\text{CDCl}_3\text{-CD}_3\text{OD}$, 125 MHz)



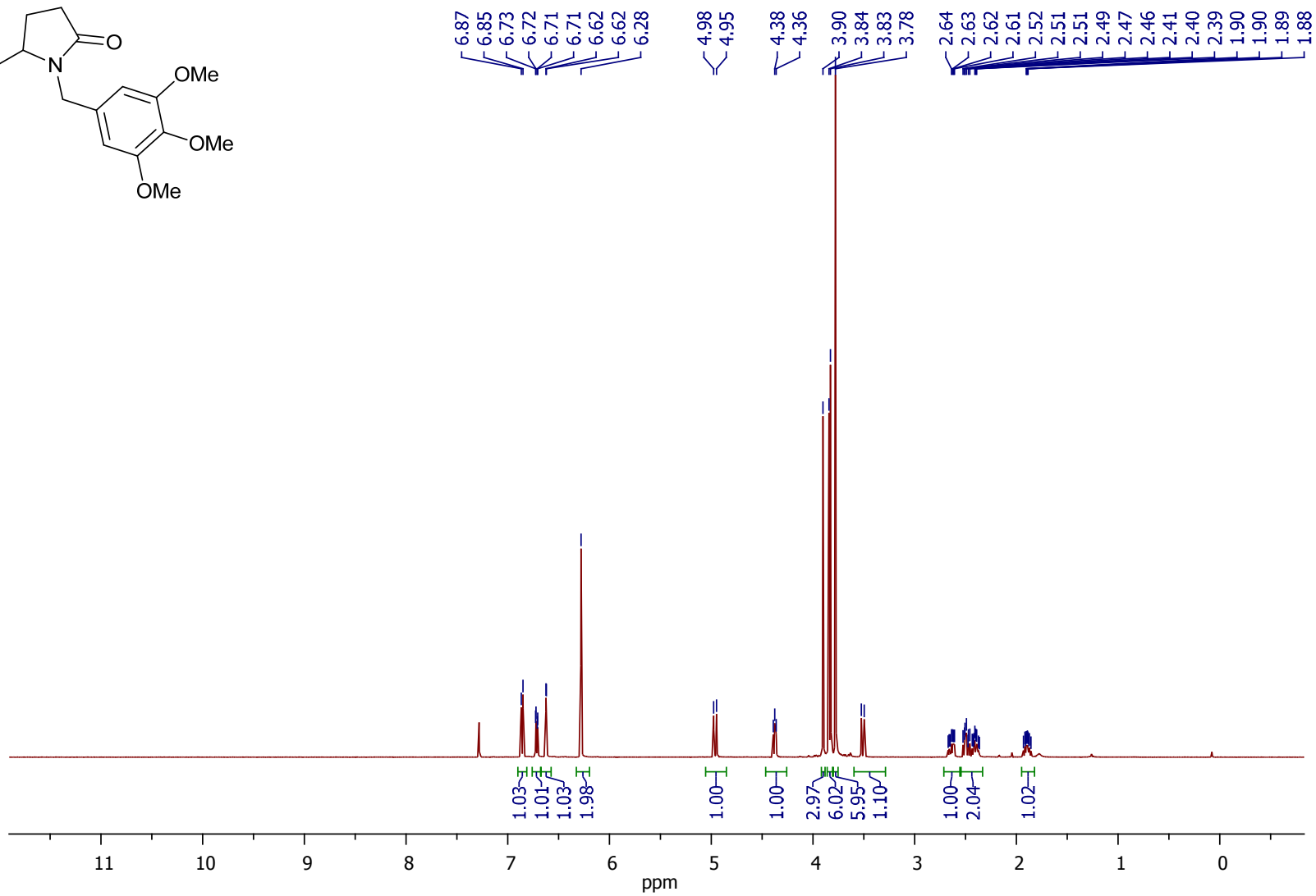
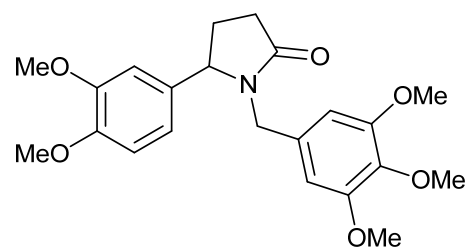
5-(3,4-Dimethoxyphenyl)-1-(2,3,4-trimethoxybenzyl)pyrrolidin-2-one (4f)

COSY ^1H - ^1H (CDCl_3 - CD_3OD)



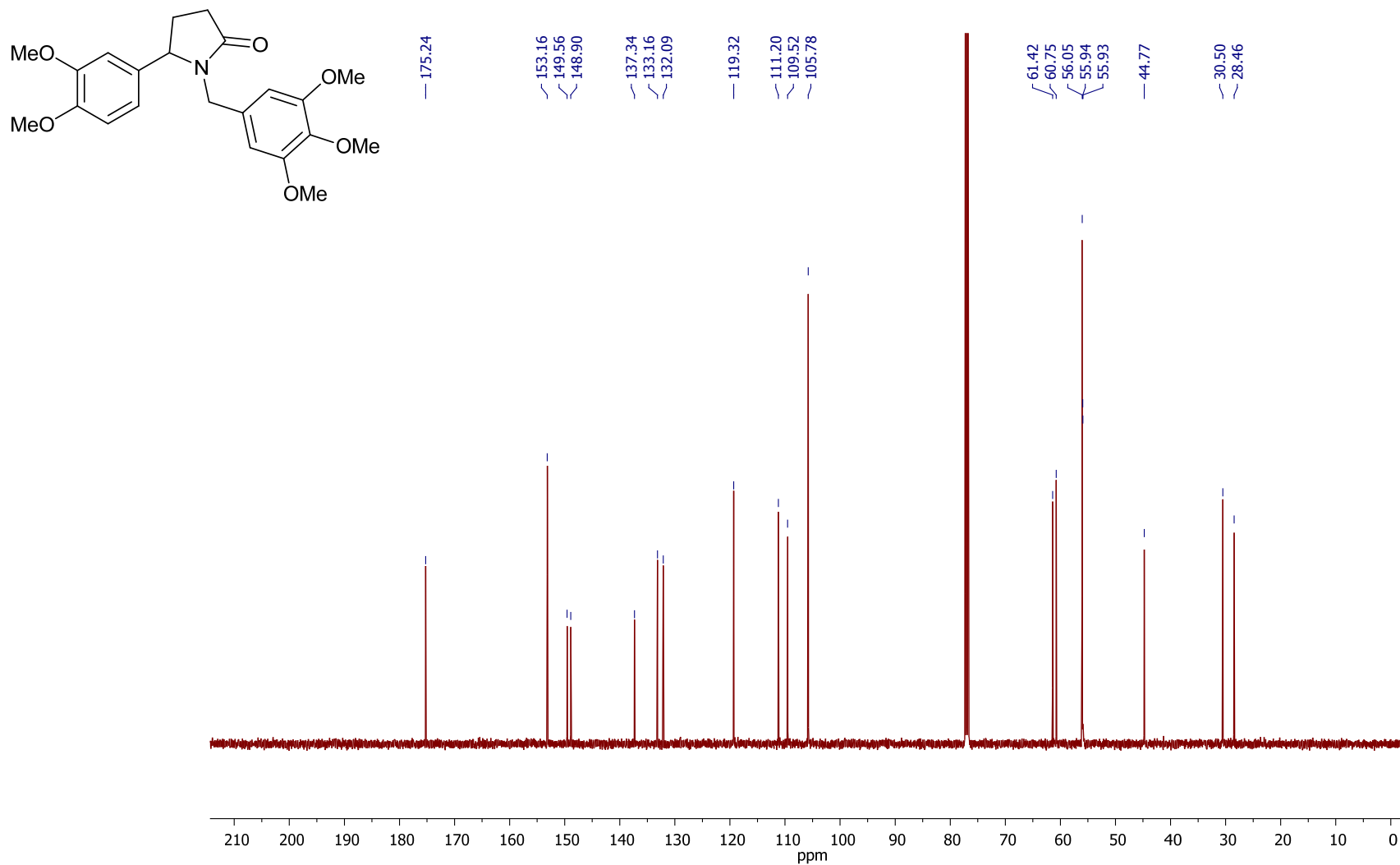
1-(3,4-Dimethoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4g)

¹H NMR (CDCl₃, 500 MHz)



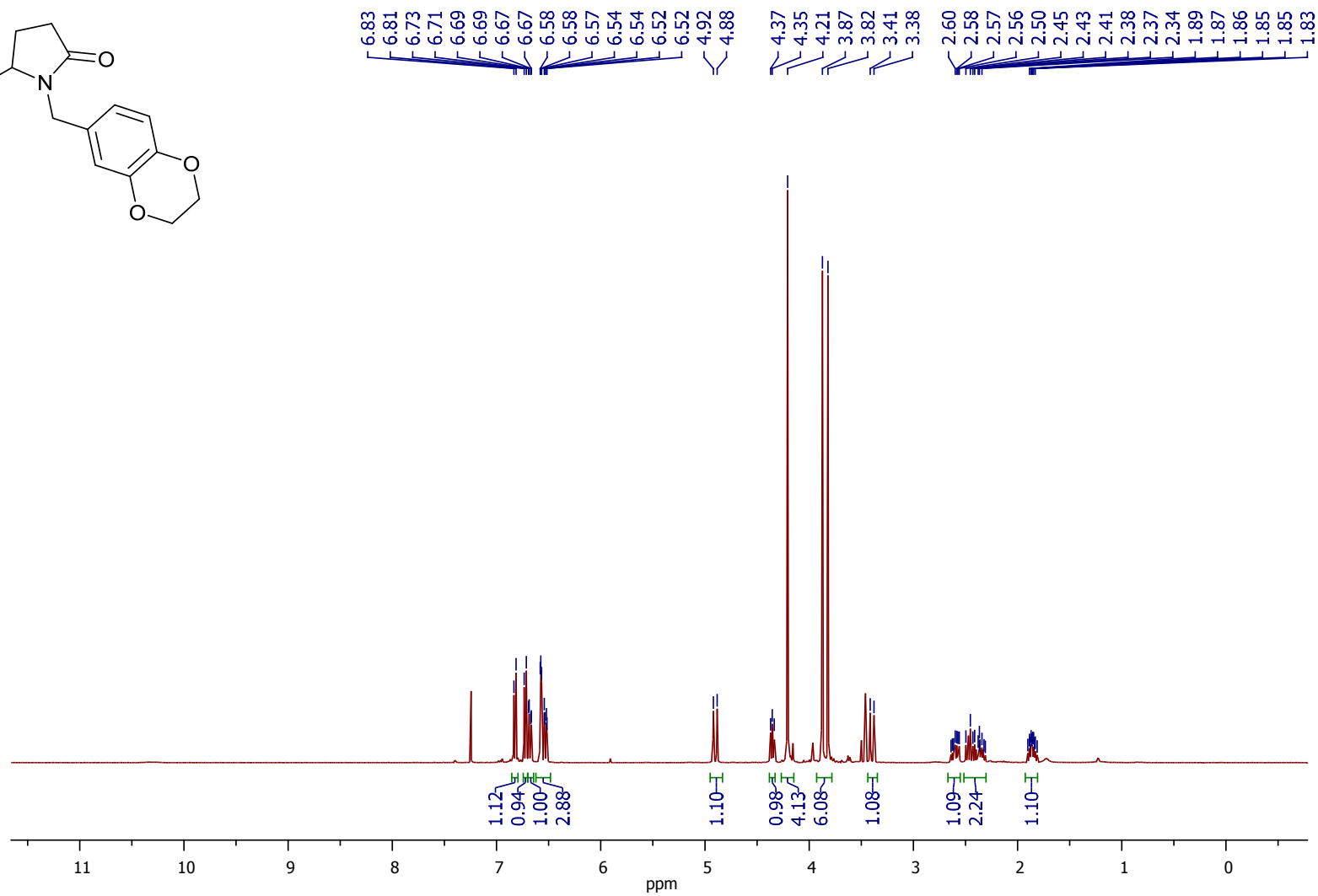
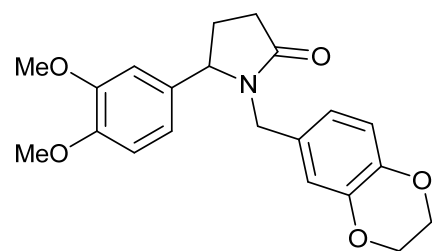
1-(3,5-Dimethoxybenzyl)-5-(3,4,5-trimethoxyphenyl)pyrrolidin-2-one (4g)

^{13}C NMR (CDCl_3 , 125 MHz)



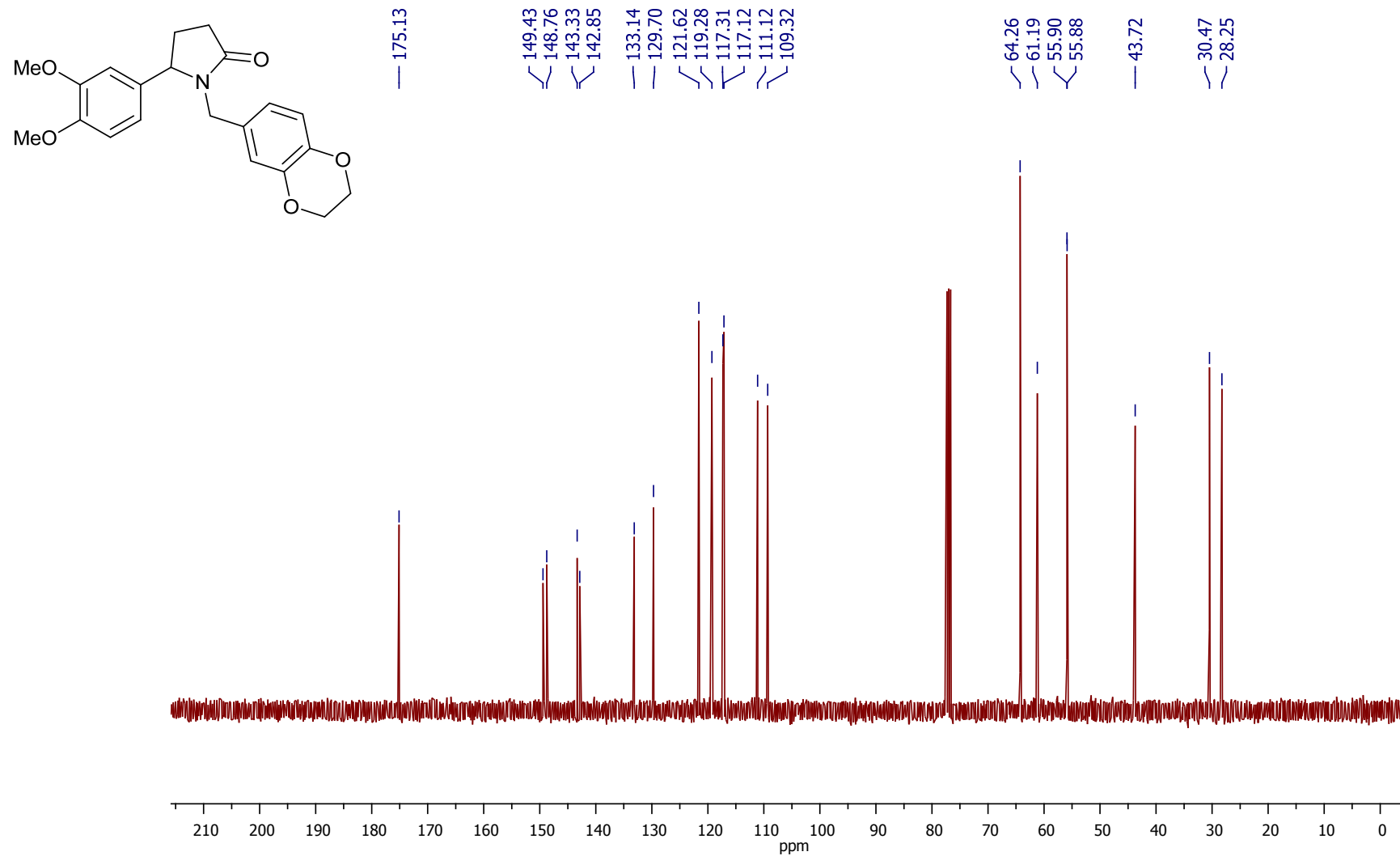
1-[(2,3-Dihydro[1,4]benzodioxin-6-yl)methyl]-5-(3,4-dimethoxyphenyl)pyrrolidin-2-one (4h)

¹H NMR (CDCl₃, 400 MHz)



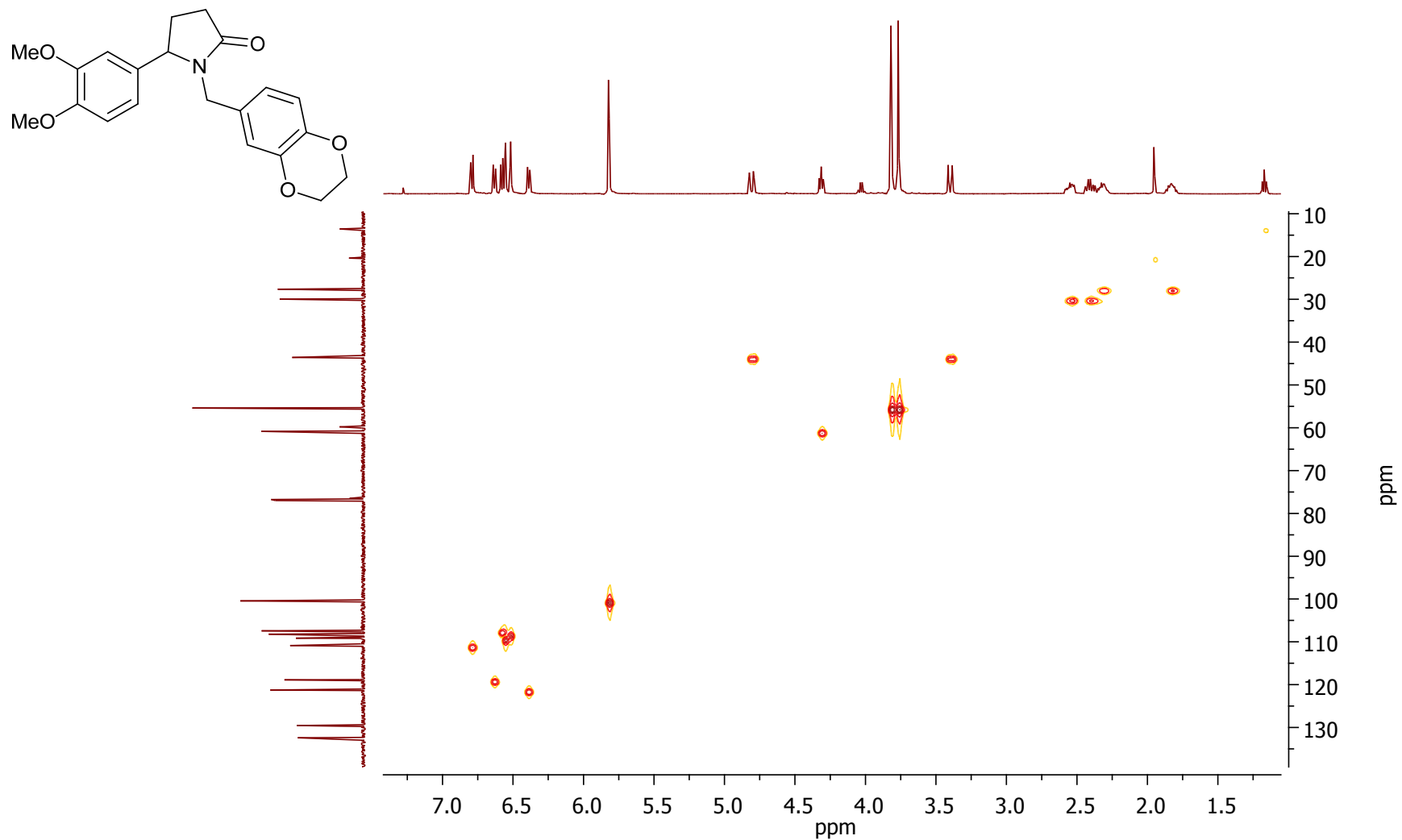
1-[(2,3-Dihydro[1,4]benzodioxin-6-yl)methyl]-5-(3,4-dimethoxyphenyl)pyrrolidin-2-one (4h)

¹³C NMR (CDCl₃, 100 MHz)



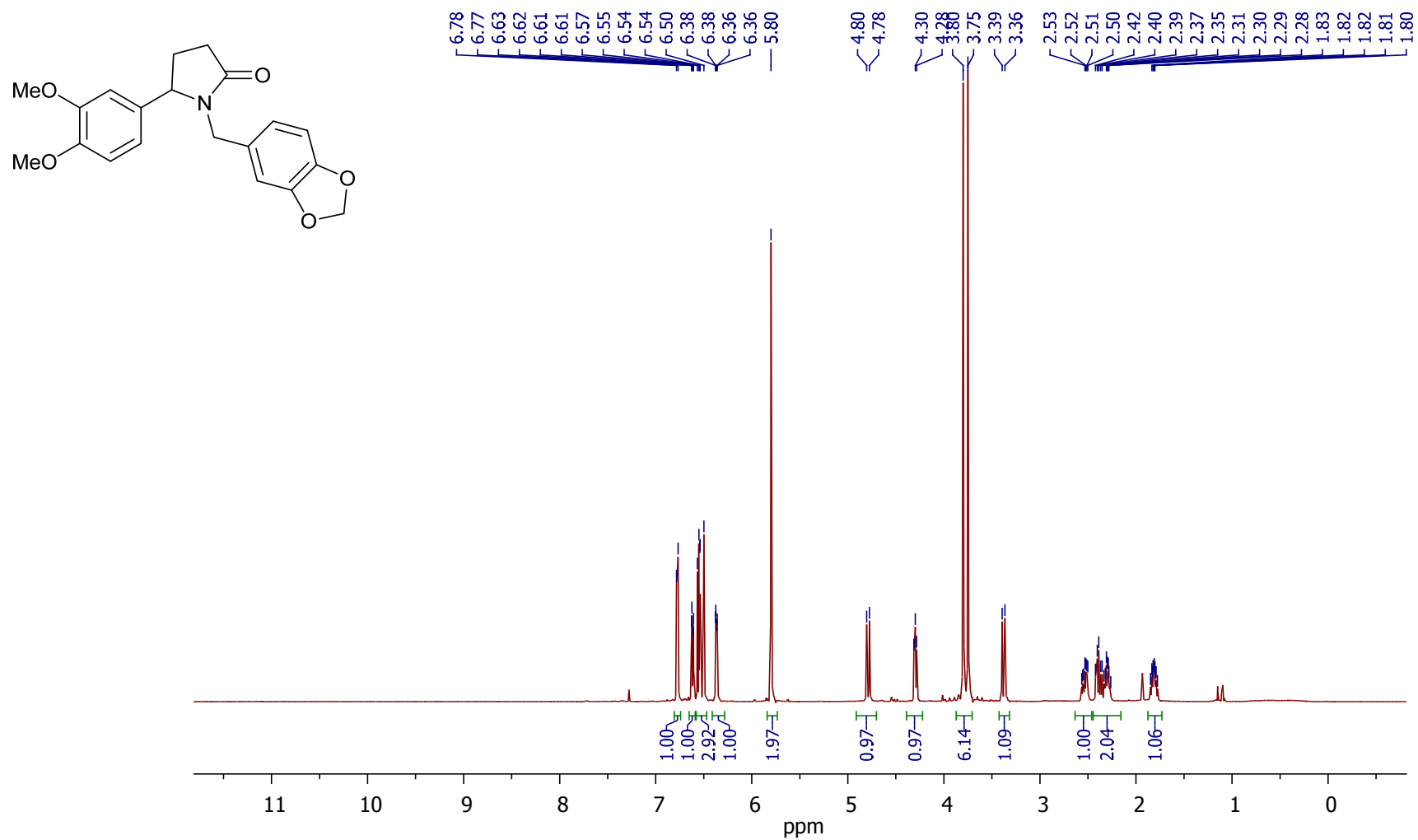
1-[(2,3-Dihydro[1,4]benzodioxin-6-yl)methyl]-5-(3,4-dimethoxyphenyl)pyrrolidin-2-one (4h)

HSQC ^1H - ^{13}C (CDCl_3)



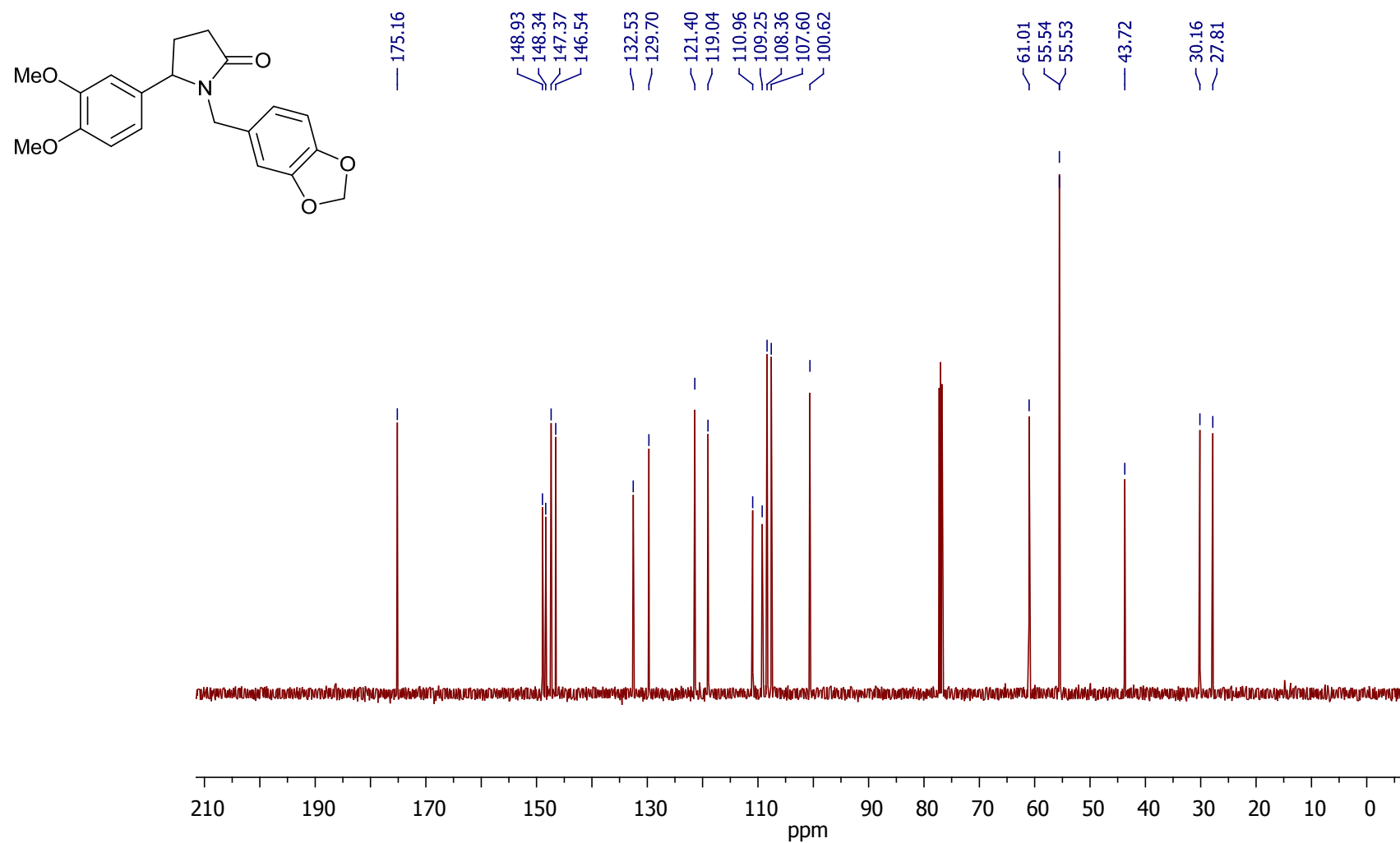
1-([1,3]Benzodioxol-5-ylmethyl)-5-(3,4-dimethoxyphenyl)pyrrolidin-2-one (4i)

^1H NMR (CDCl_3 , 500 MHz)



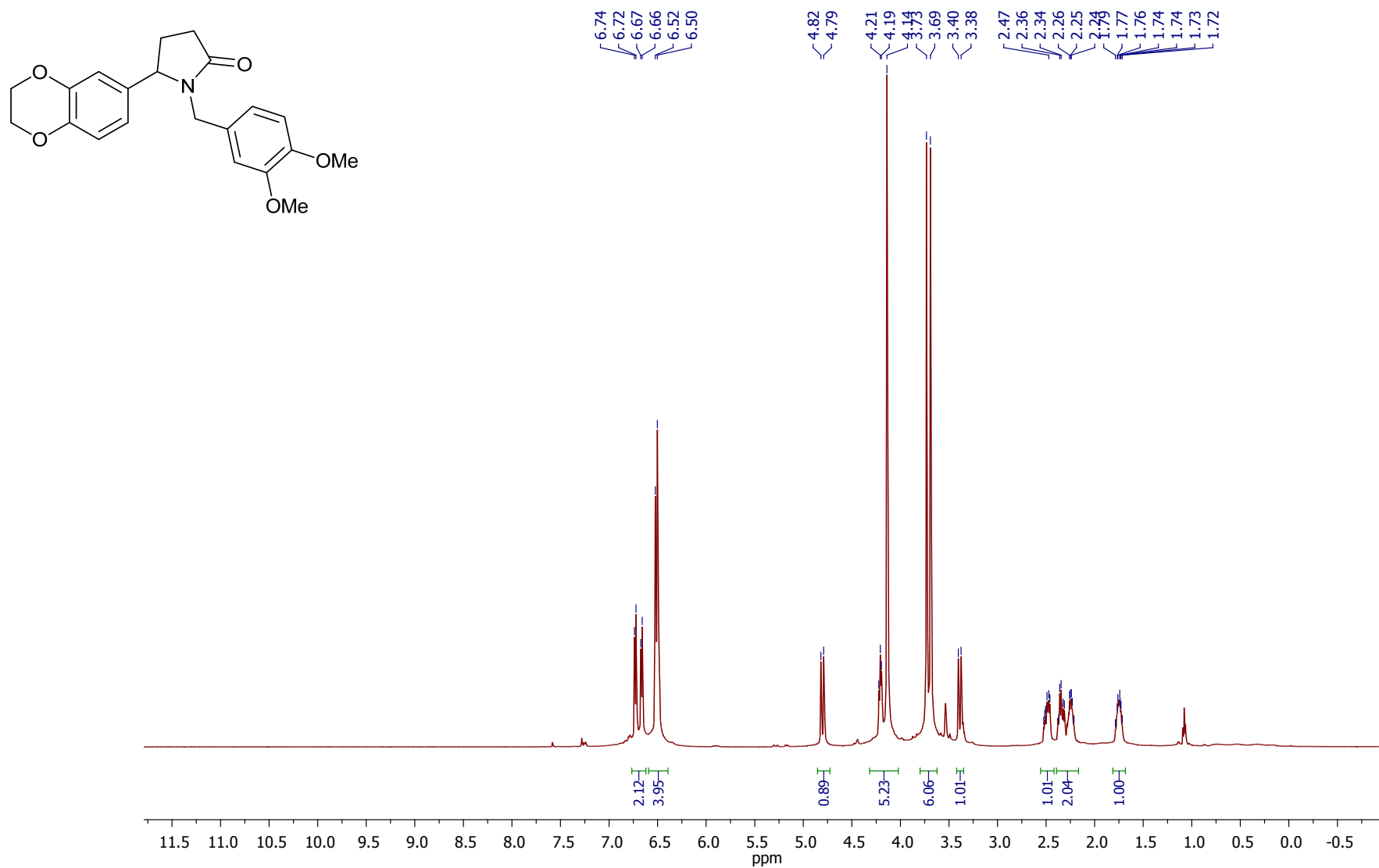
1-([1,3]Benzodioxol-5-ylmethyl)-5-(3,4-dimethoxyphenyl)pyrrolidin-2-one (4i)

^{13}C NMR (CDCl_3 , 125 MHz)



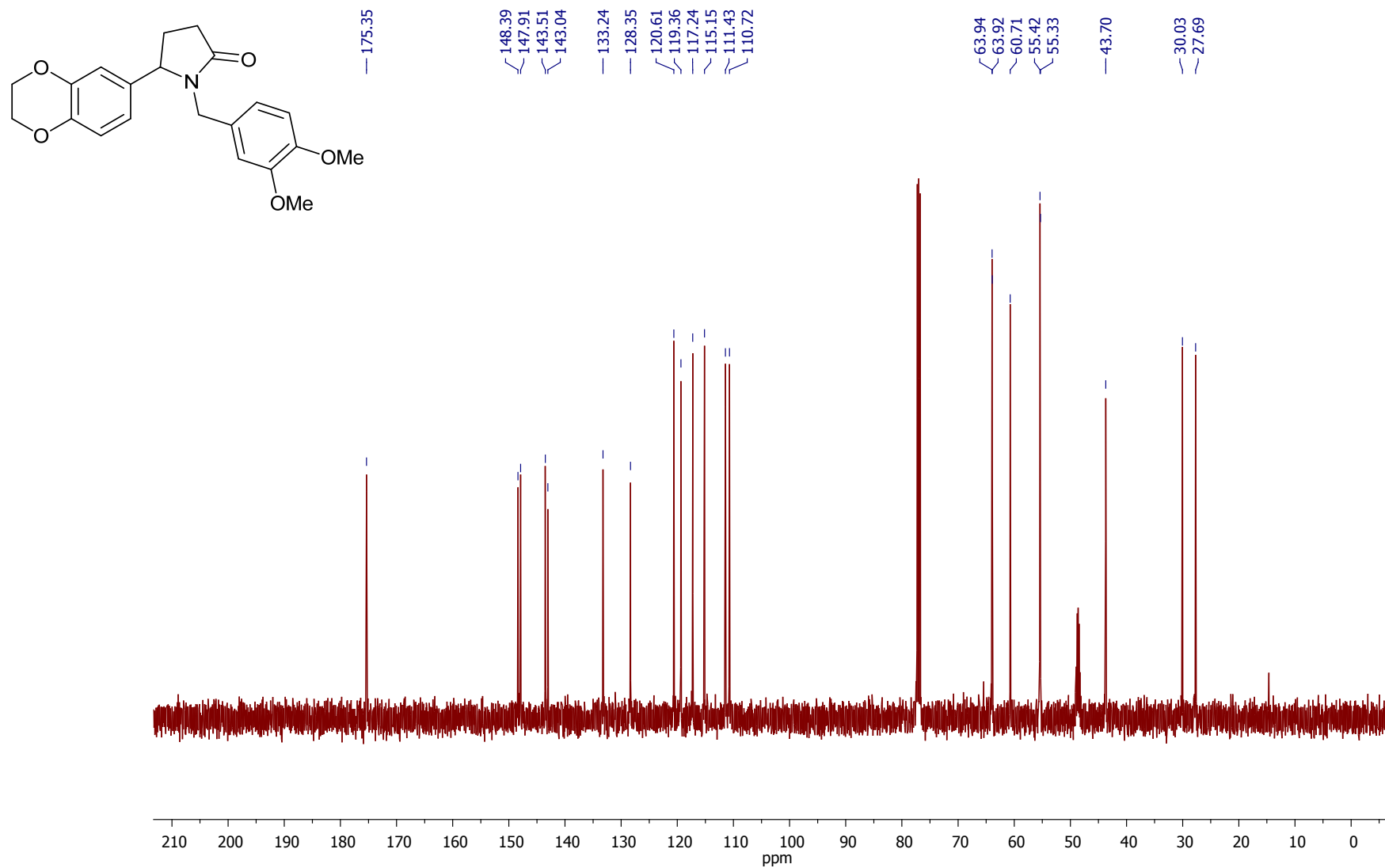
5-(2,3-Dihydro[1,4]benzodioxin-6-yl)-1-(3,4-dimethoxybenzyl)pyrrolidin-2-one (4j)

¹H NMR (CDCl₃, 500 MHz)



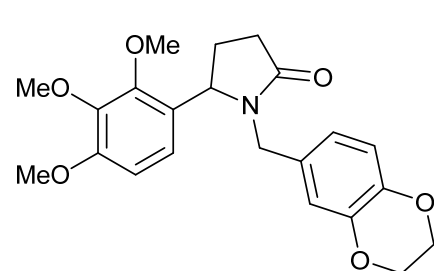
5-(2,3-Dihydro[1,4]benzodioxin-6-yl)-1-(3,4-dimethoxybenzyl)pyrrolidin-2-one (4j)

^{13}C NMR (CDCl_3 , 125 MHz)

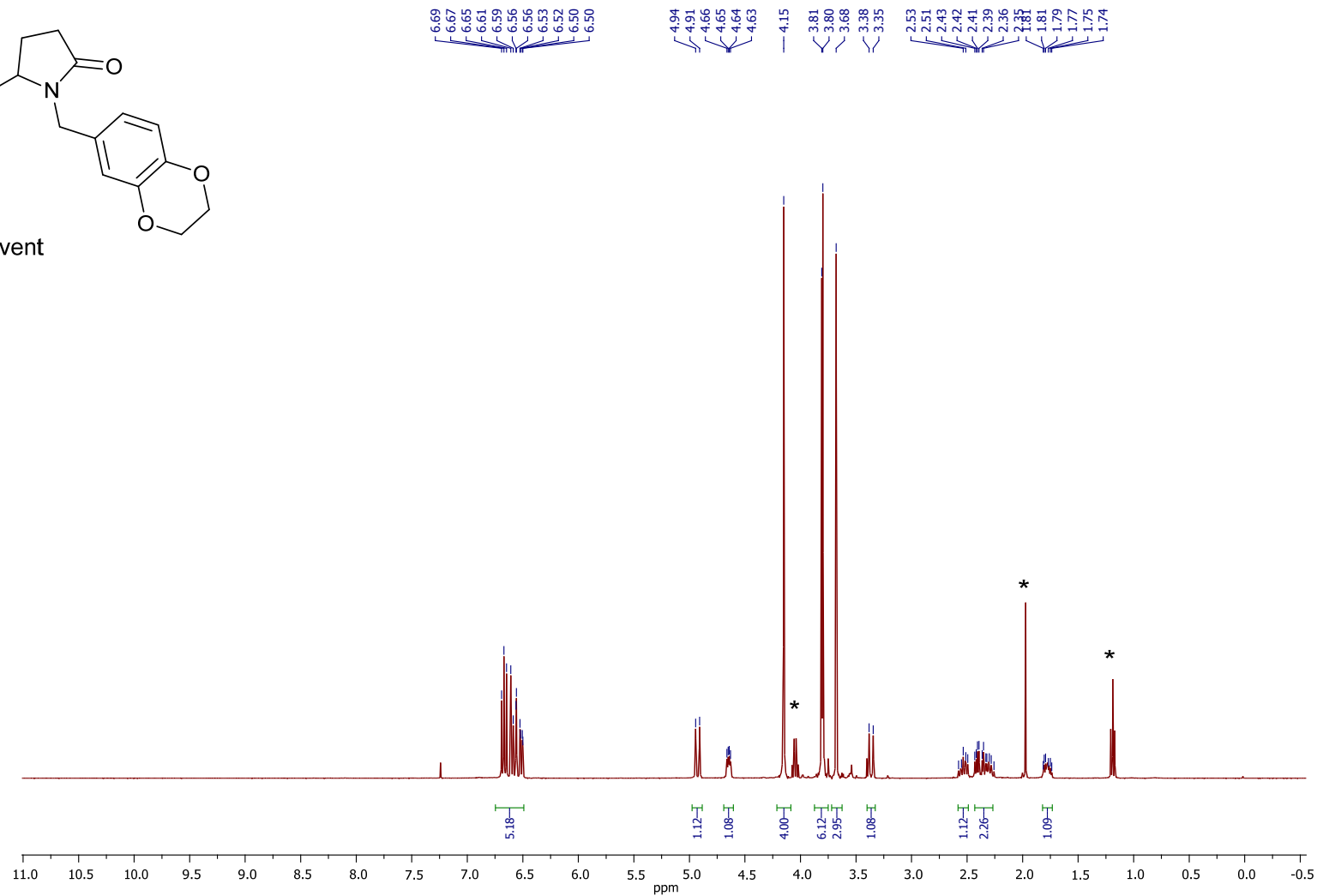


1-[(2,3-Dihydro[1,4]benzodioxin-6-yl)methyl]-5-(2,3,4-trimethoxyphenyl)pyrrolidin-2-one (4k)

¹H NMR (CDCl₃, 400 MHz)

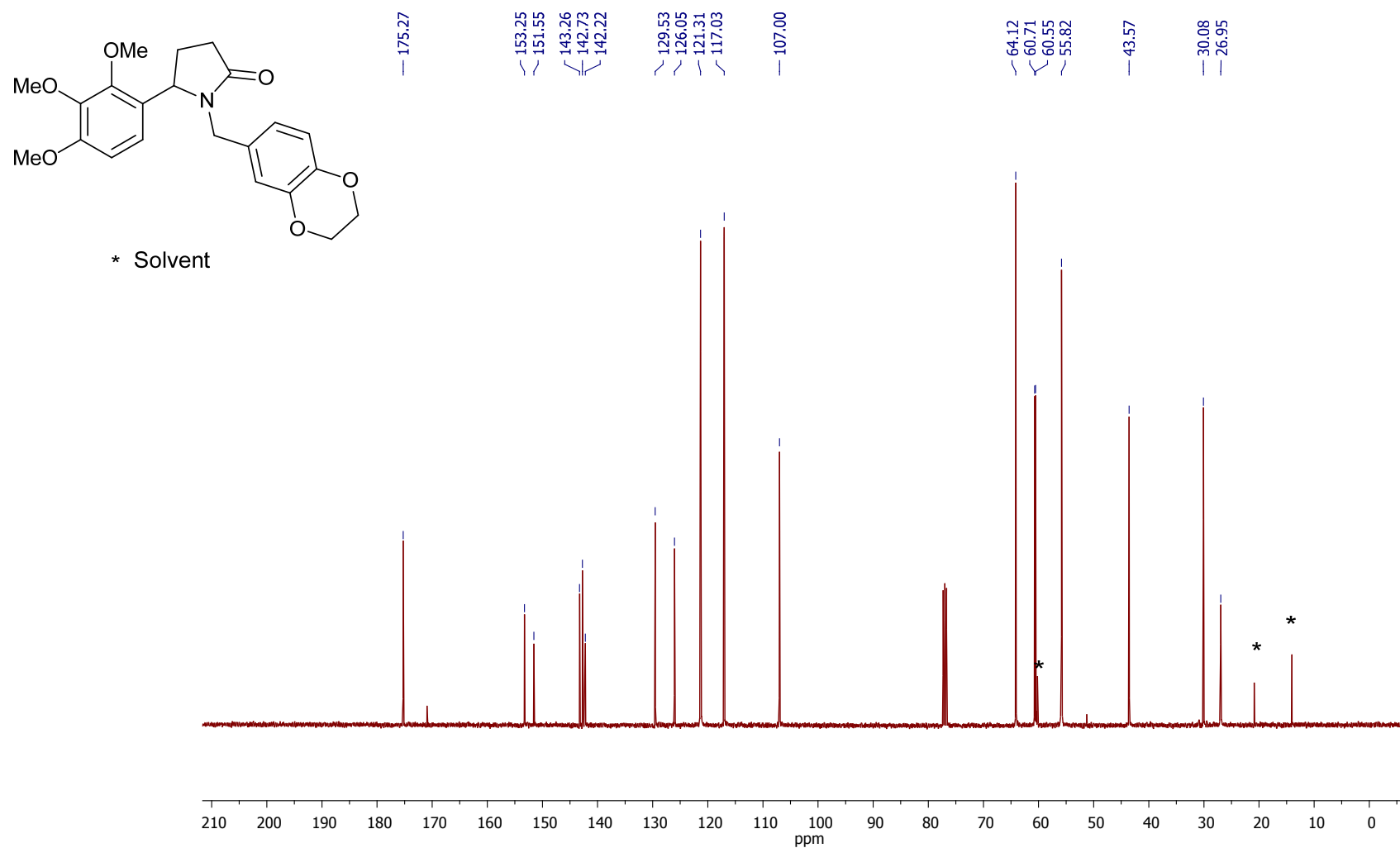


* Solvent



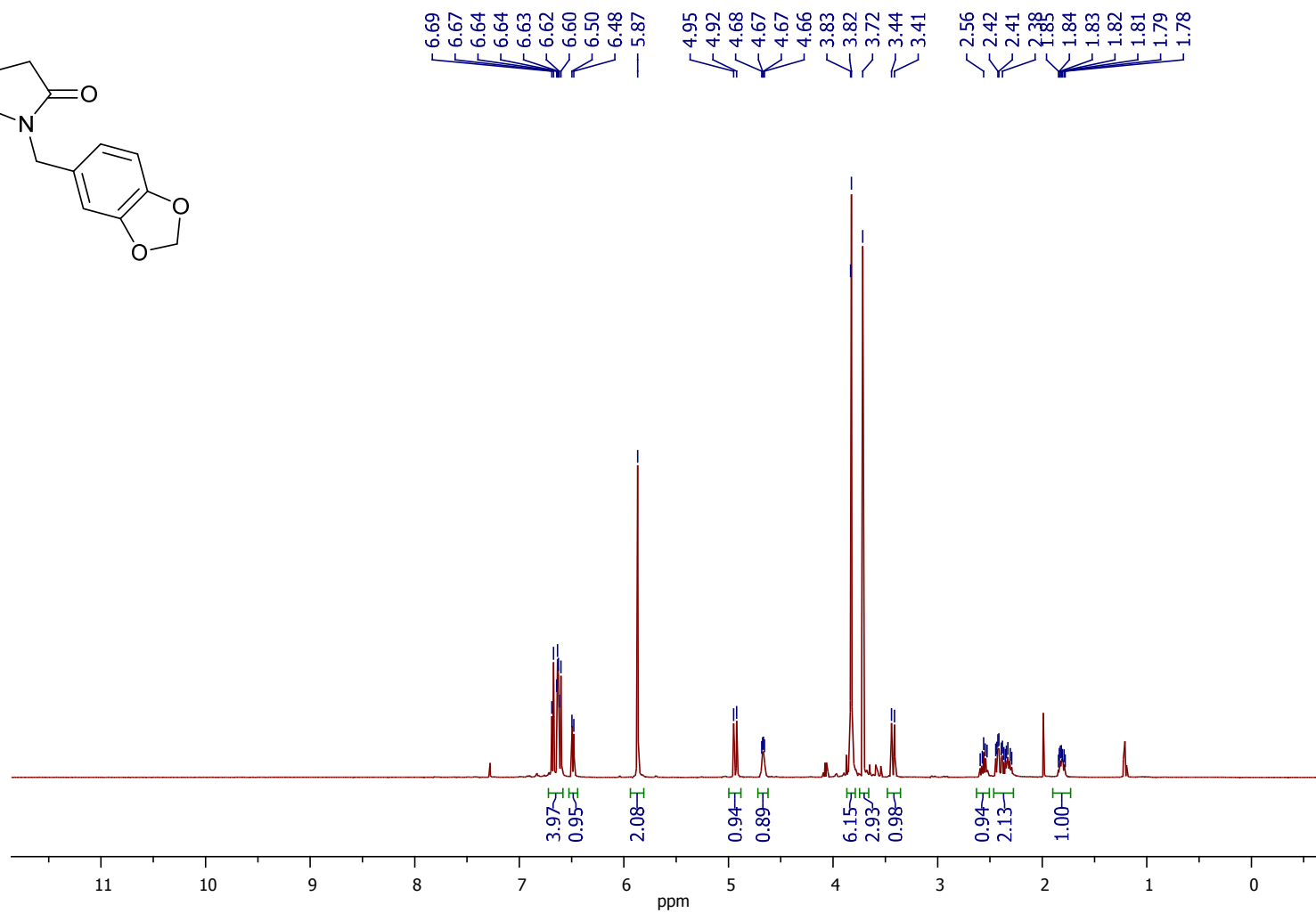
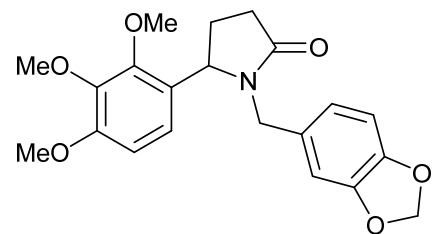
1-[(2,3-Dihydro[1,4]benzodioxin-6-yl)methyl]-5-(2,3,4-trimethoxyphenyl)pyrrolidin-2-one (4k)

^{13}C NMR (CDCl_3 , 100 MHz)



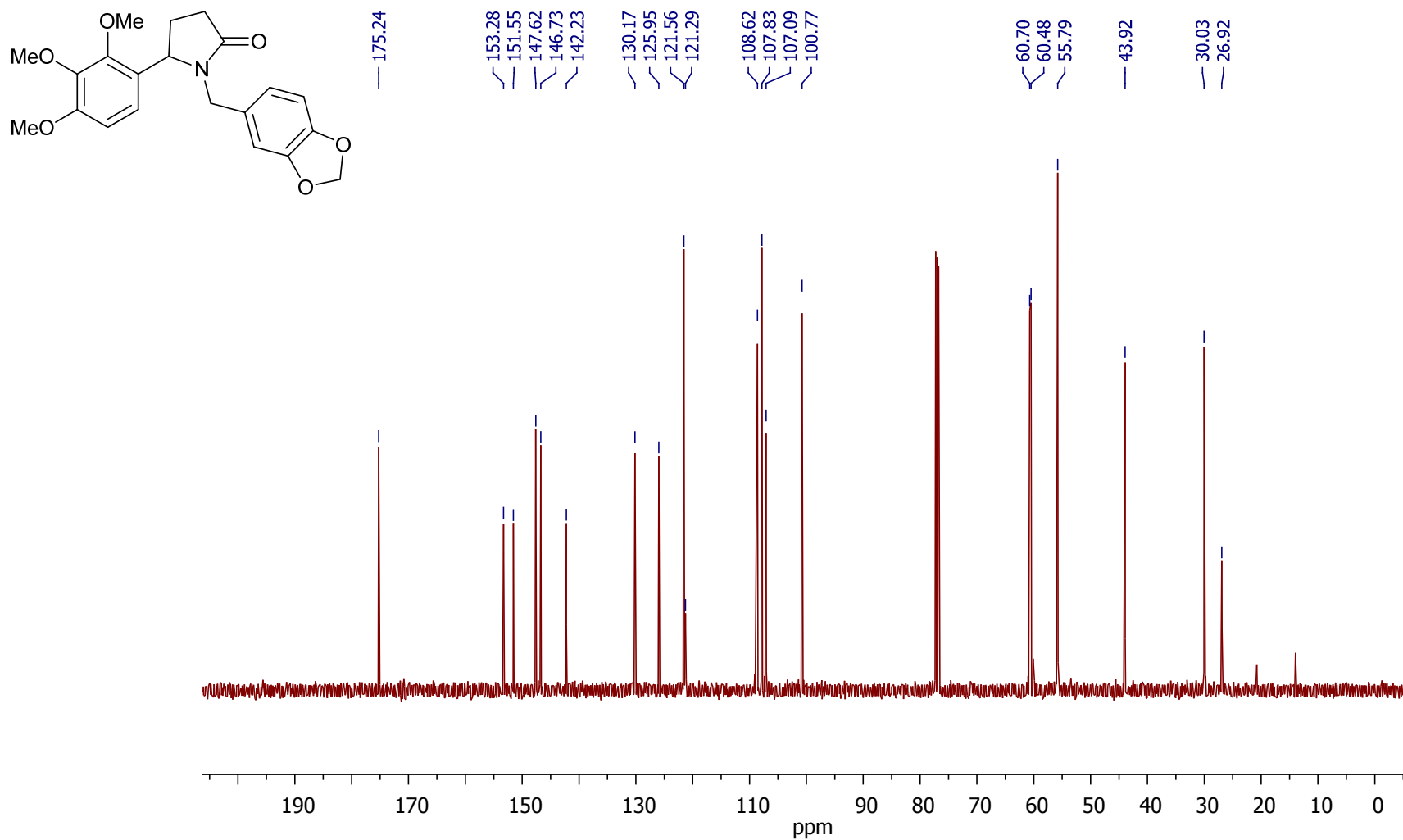
1-([1,3]Benzodioxol-5-ylmethyl)-5-(2,3,4-trimethoxyphenyl)pyrrolidin-2-one (4l)

¹H NMR (CDCl₃, 500 MHz)



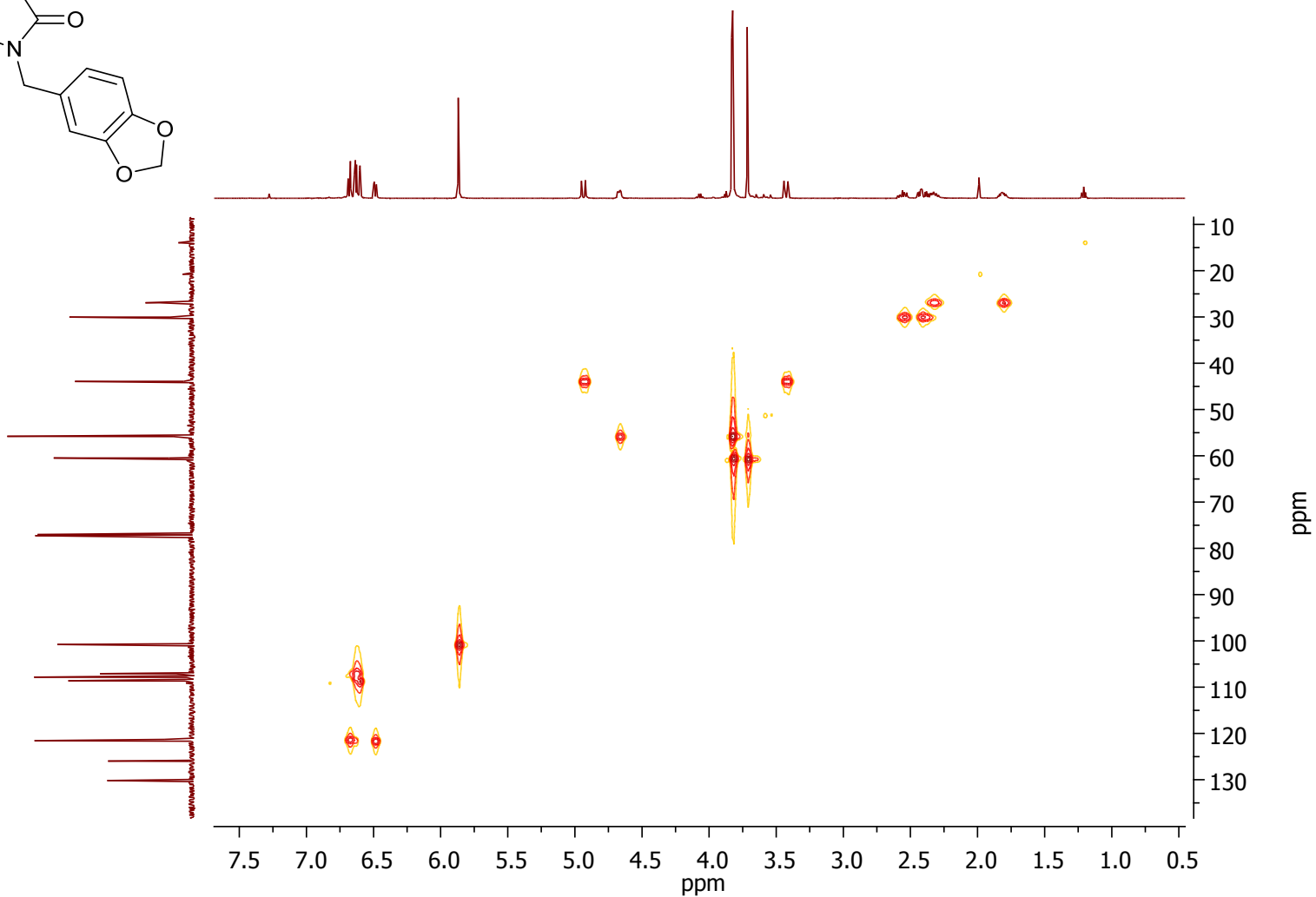
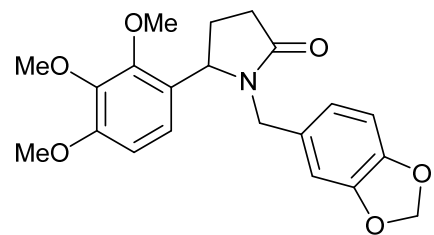
1-([1,3]Benzodioxol-5-ylmethyl)-5-(2,3,4-trimethoxyphenyl)pyrrolidin-2-one (4l)

¹³C NMR (CDCl₃, 125 MHz)



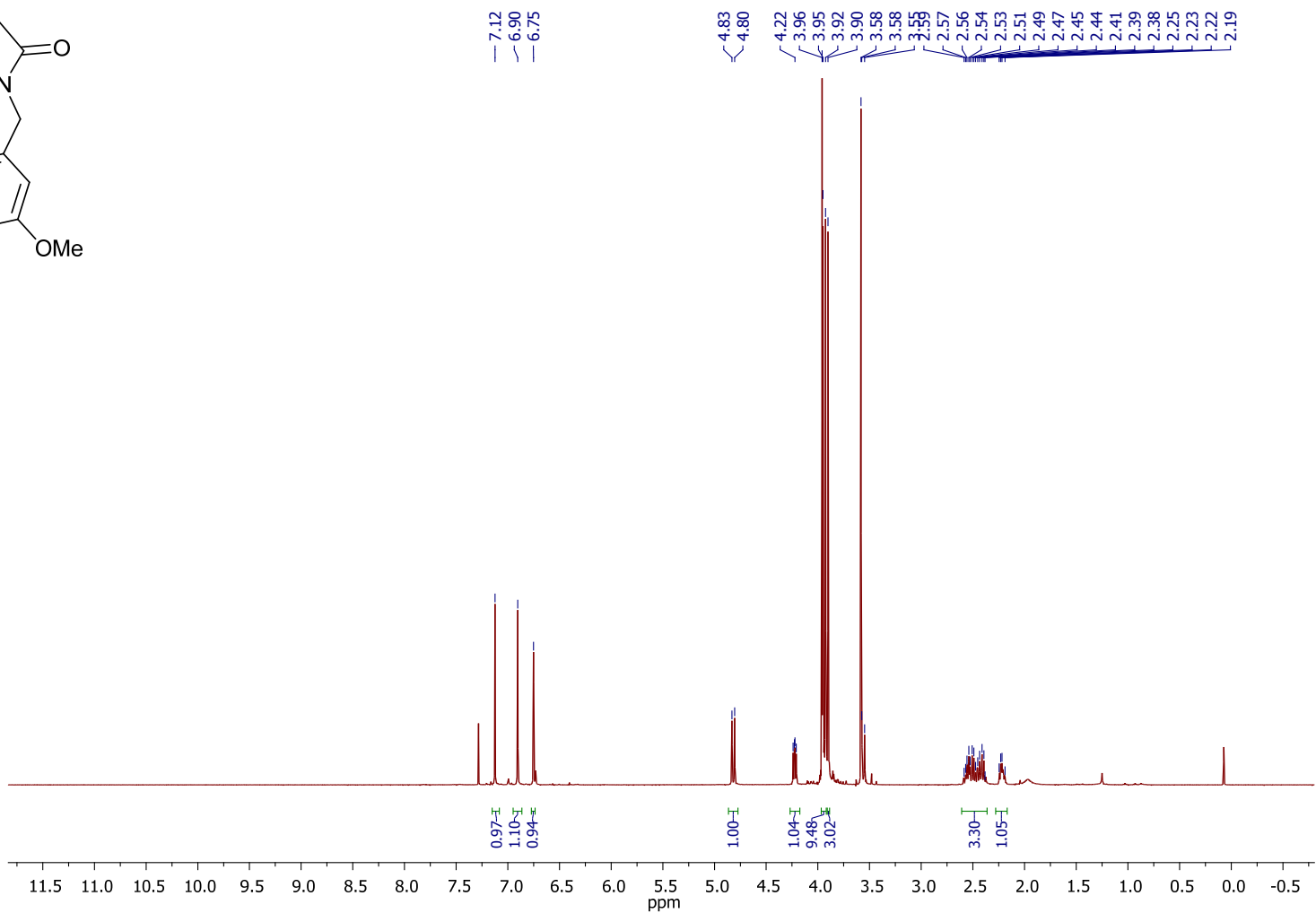
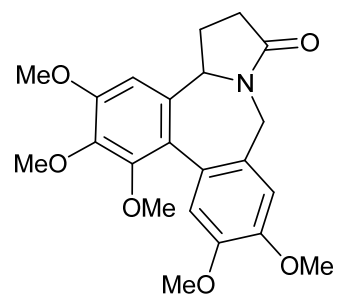
1-([1,3]Benzodioxol-5-ylmethyl)-5-(2,3,4-trimethoxyphenyl)pyrrolidin-2-one (4l)

HSQC ^1H - ^{13}C (CDCl_3)



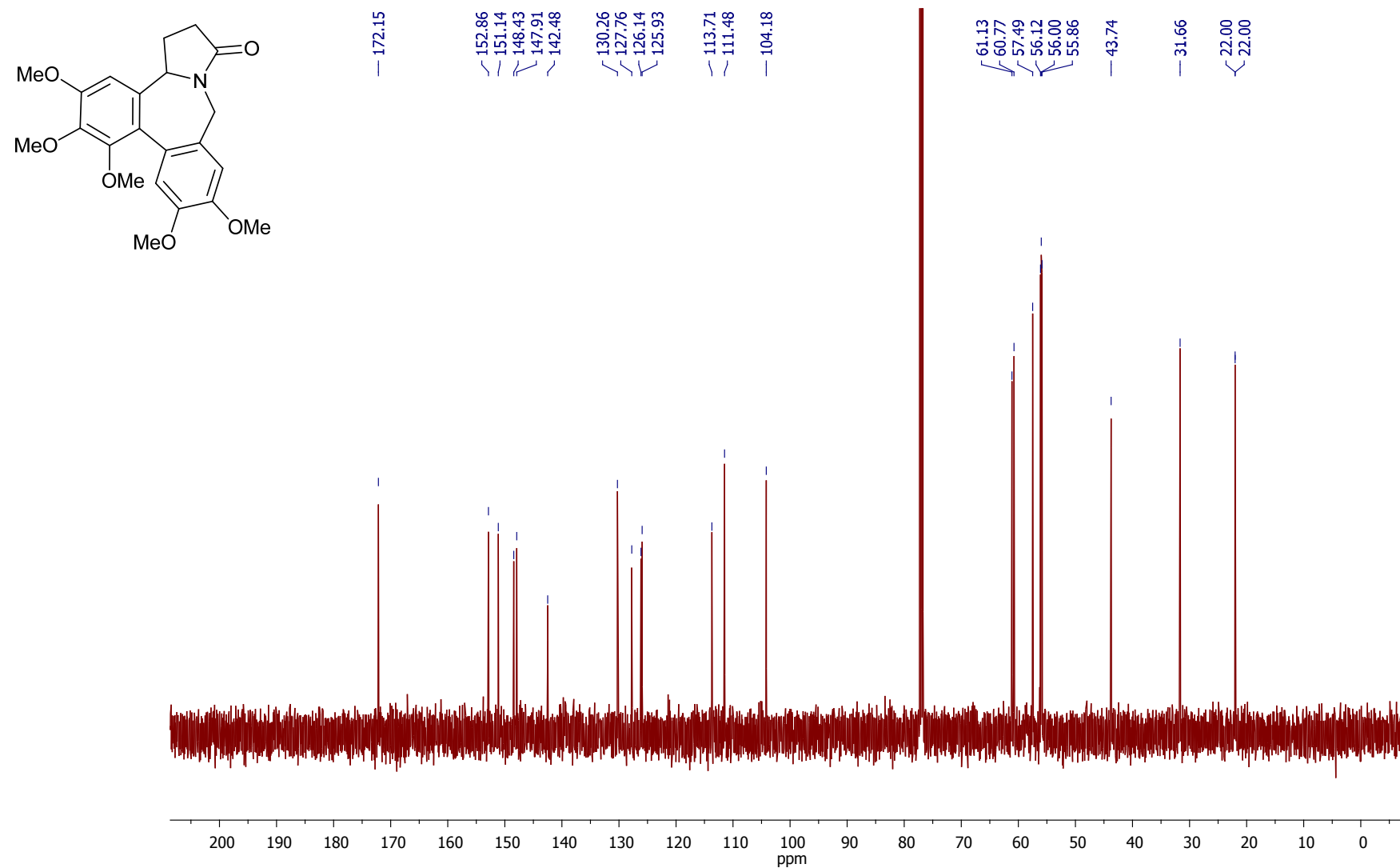
1,2,3,11,12-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5a)

¹H NMR (CDCl₃, 500 MHz)



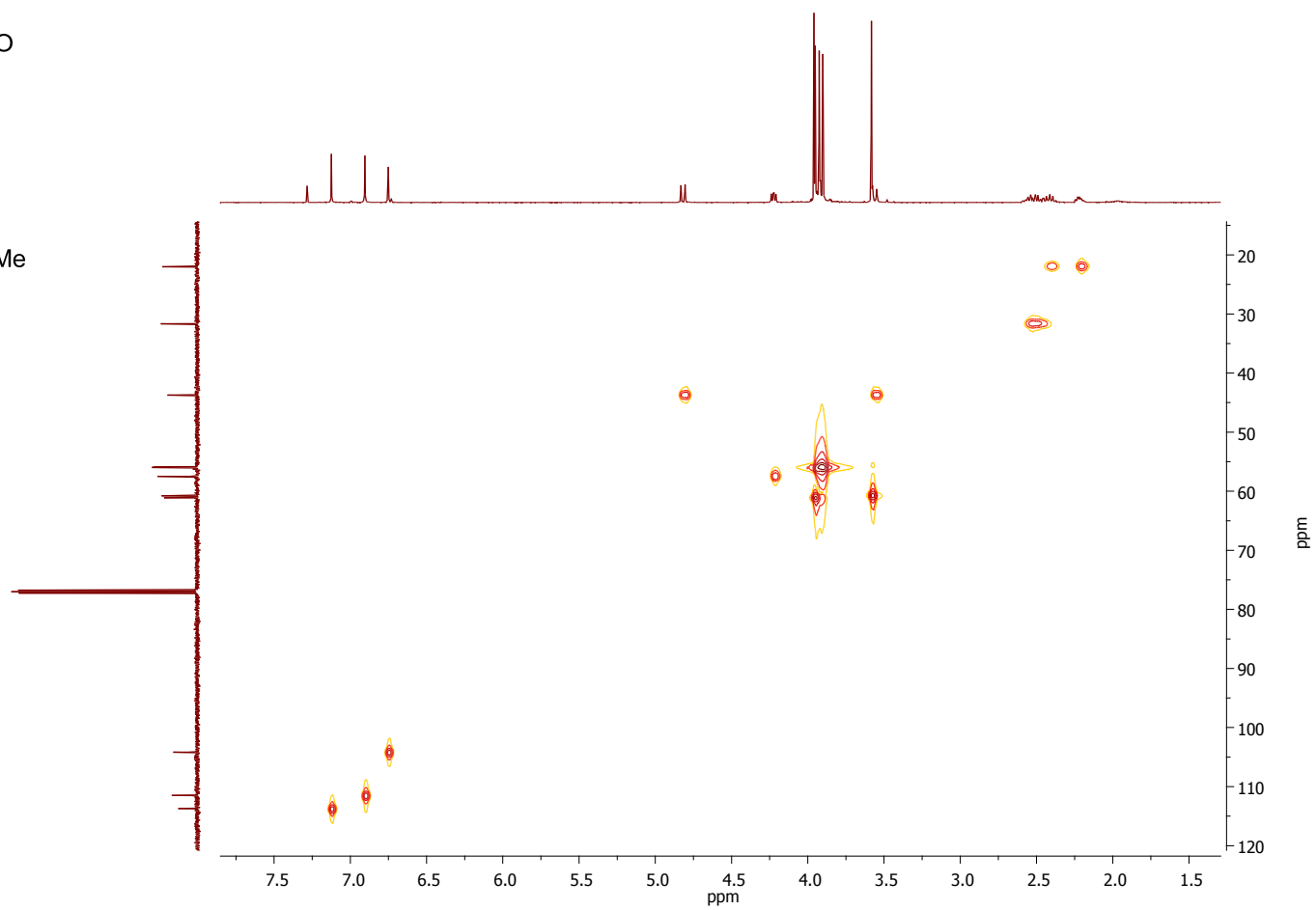
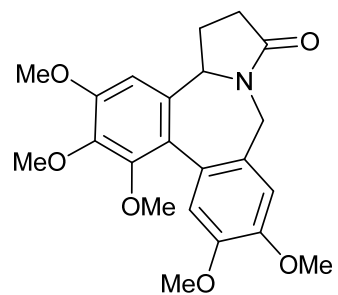
1,2,3,11,12-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5a)

^{13}C NMR (CDCl_3 , 125 MHz)



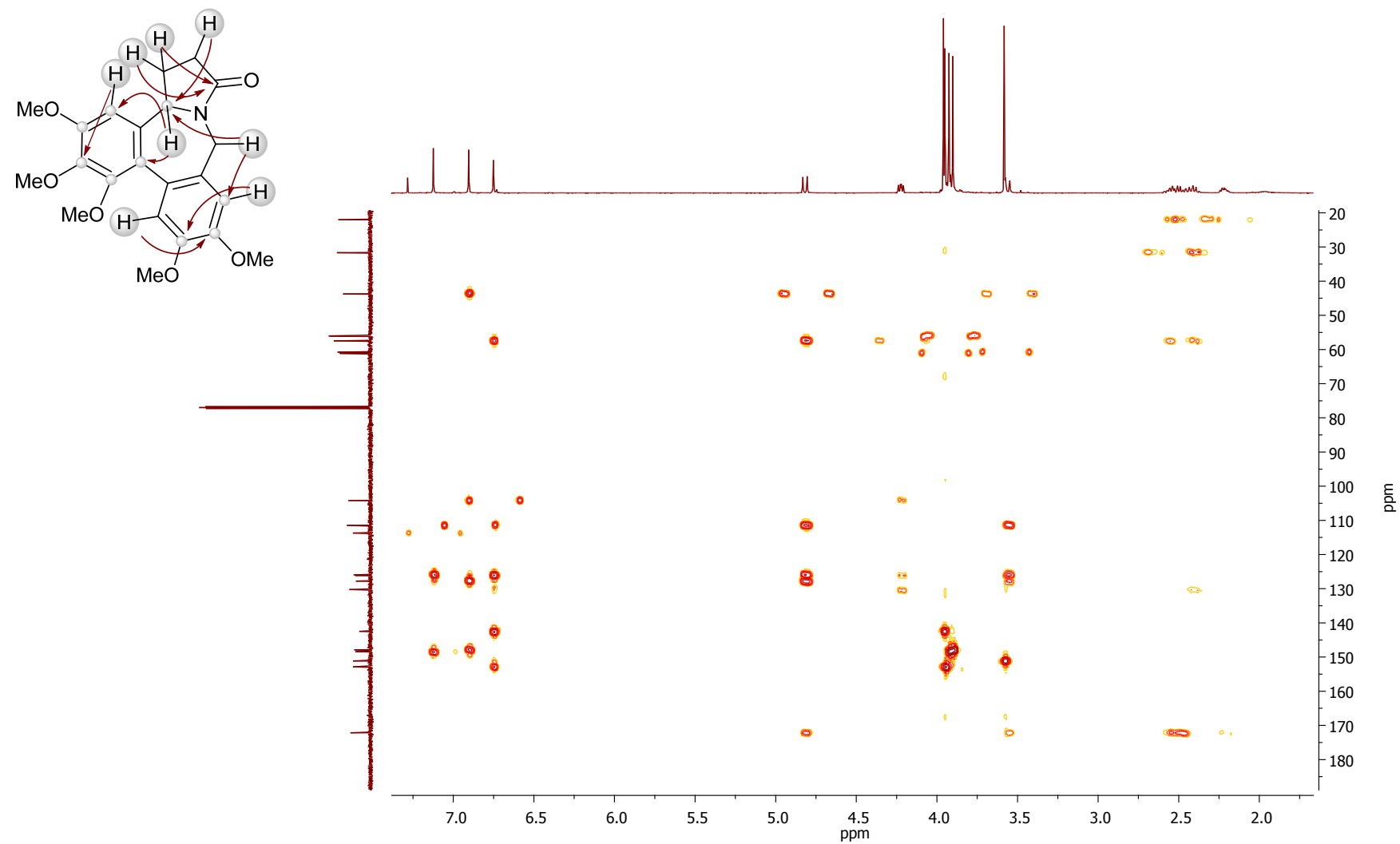
1,2,3,11,12-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5a)

HSQC ^1H - ^{13}C (CDCl_3)



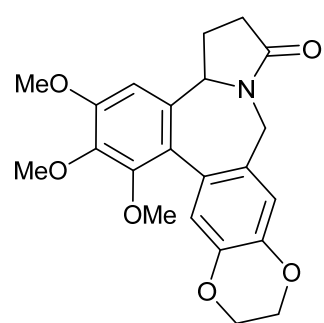
1,2,3,11,12-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]zepin-7-one (5a)

HMBC ^1H - ^{13}C (CDCl_3)

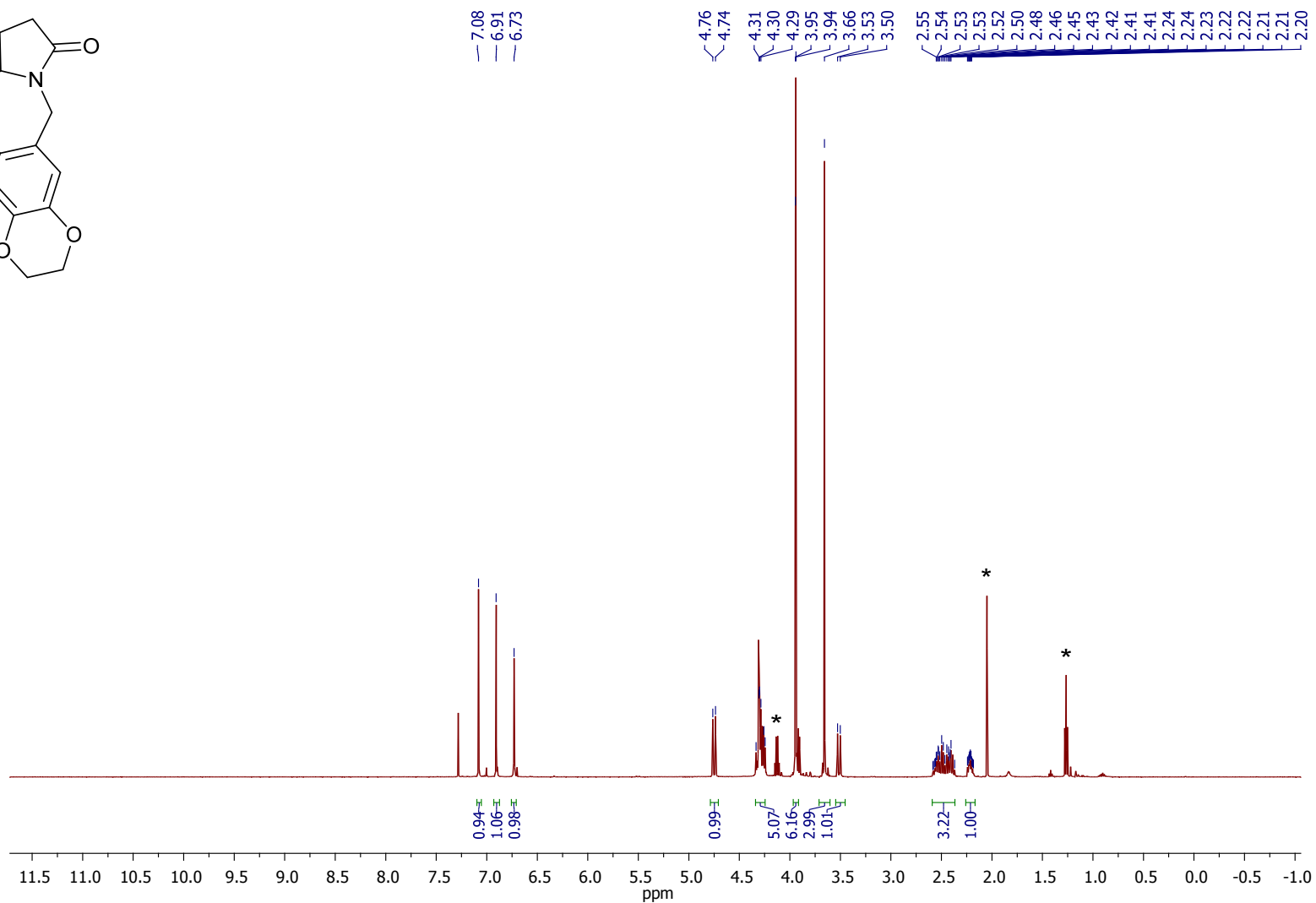


1,2,3-Trimethoxy-4b,5,6,9,12,13-hexahydro-7H-[1,4]dioxino[2',3':4,5]benzo[1,2-e]benzo[c]pyrrolo[1,2-a]azepin-7-one (5b)

¹H NMR (CDCl₃, 500 MHz)

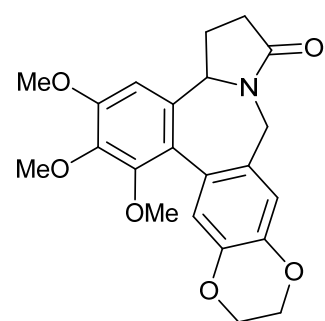


* Solvent

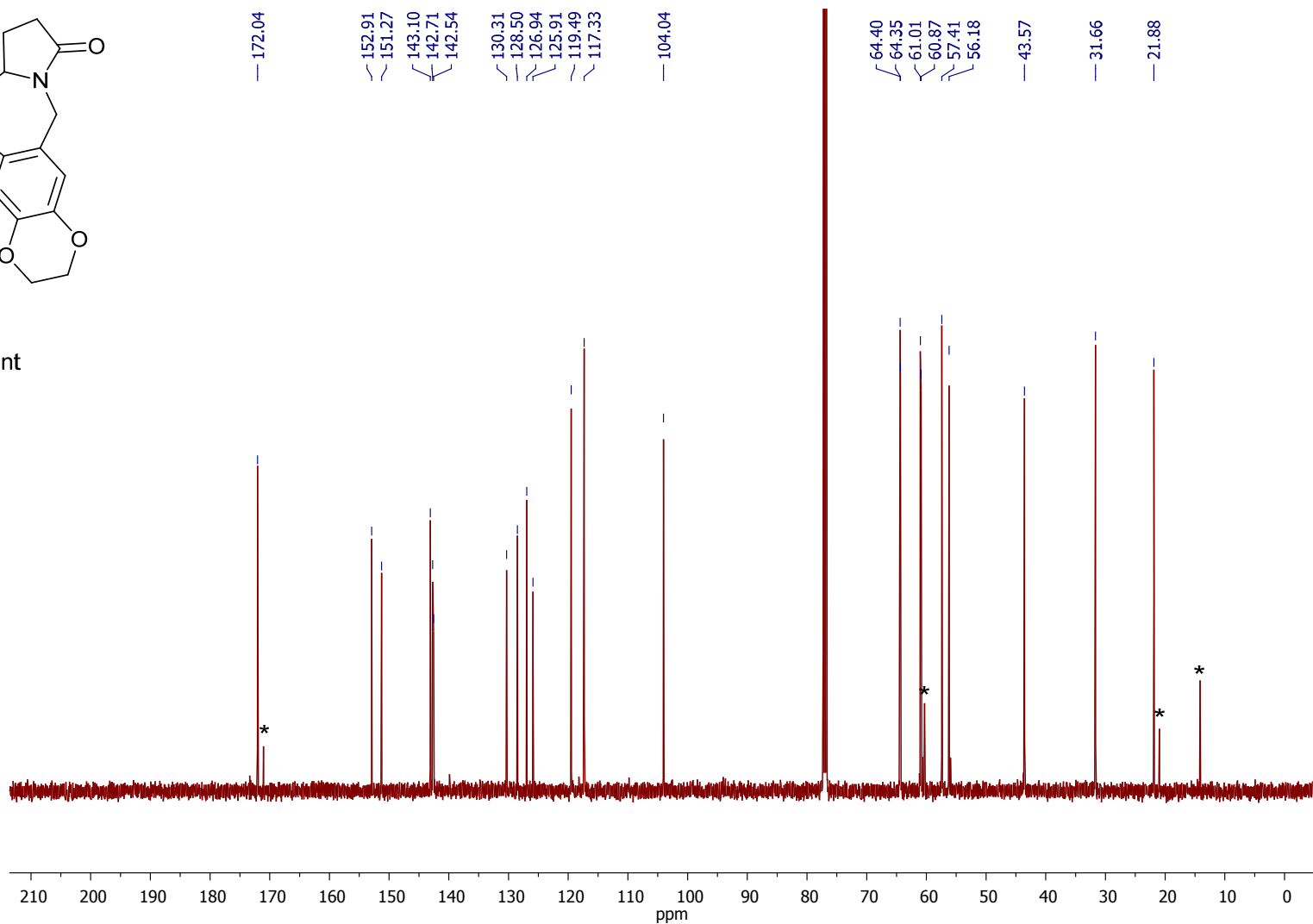


1,2,3-Trimethoxy-4b,5,6,9,12,13-hexahydro-7H-[1,4]dioxino[2',3':4,5]benzo[1,2-e]benzo[c]pyrrolo[1,2-a]azepin-7-one (5b)

^{13}C NMR (CDCl_3 , 125 MHz)

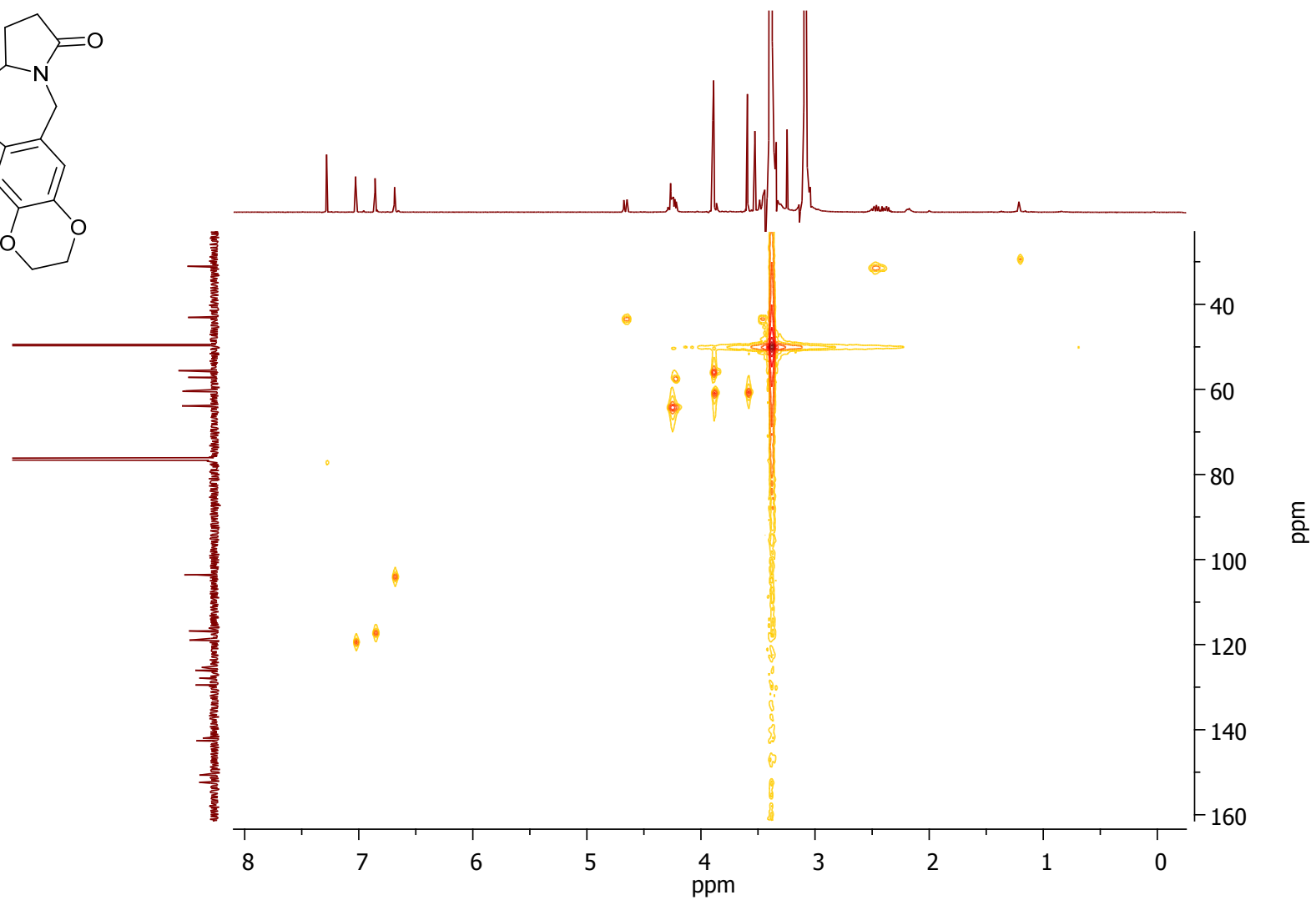
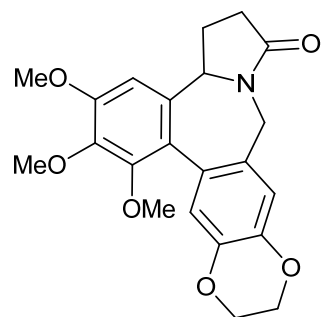


* Solvent



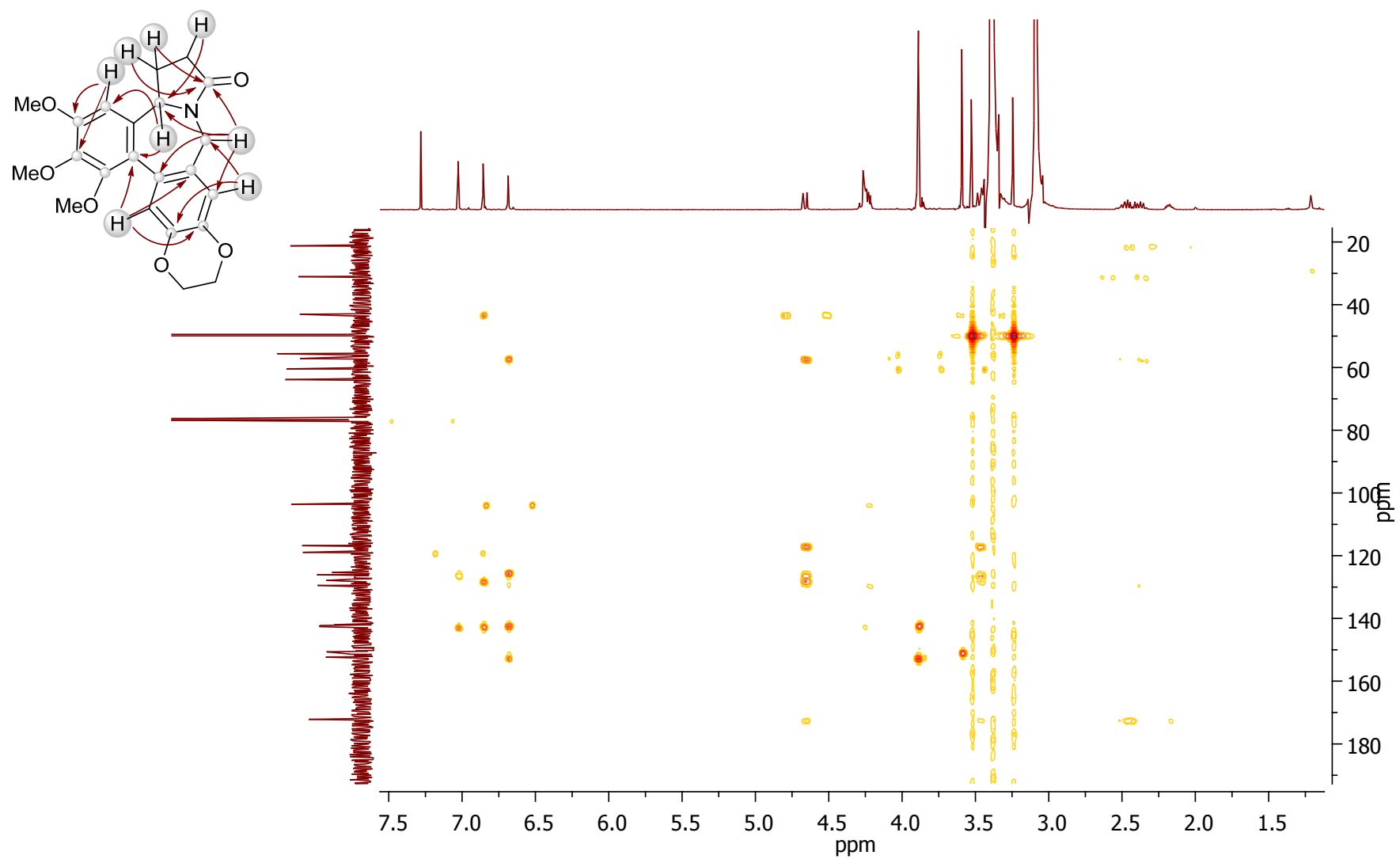
1,2,3-Trimethoxy-4b,5,6,9,12,13-hexahydro-7H-[1,4]dioxino[2',3':4,5]benzo[1,2-e]benzo[c]pyrrolo[1,2-a]azepin-7-one (5b)

HSQC ^1H - ^{13}C (CDCl_3)



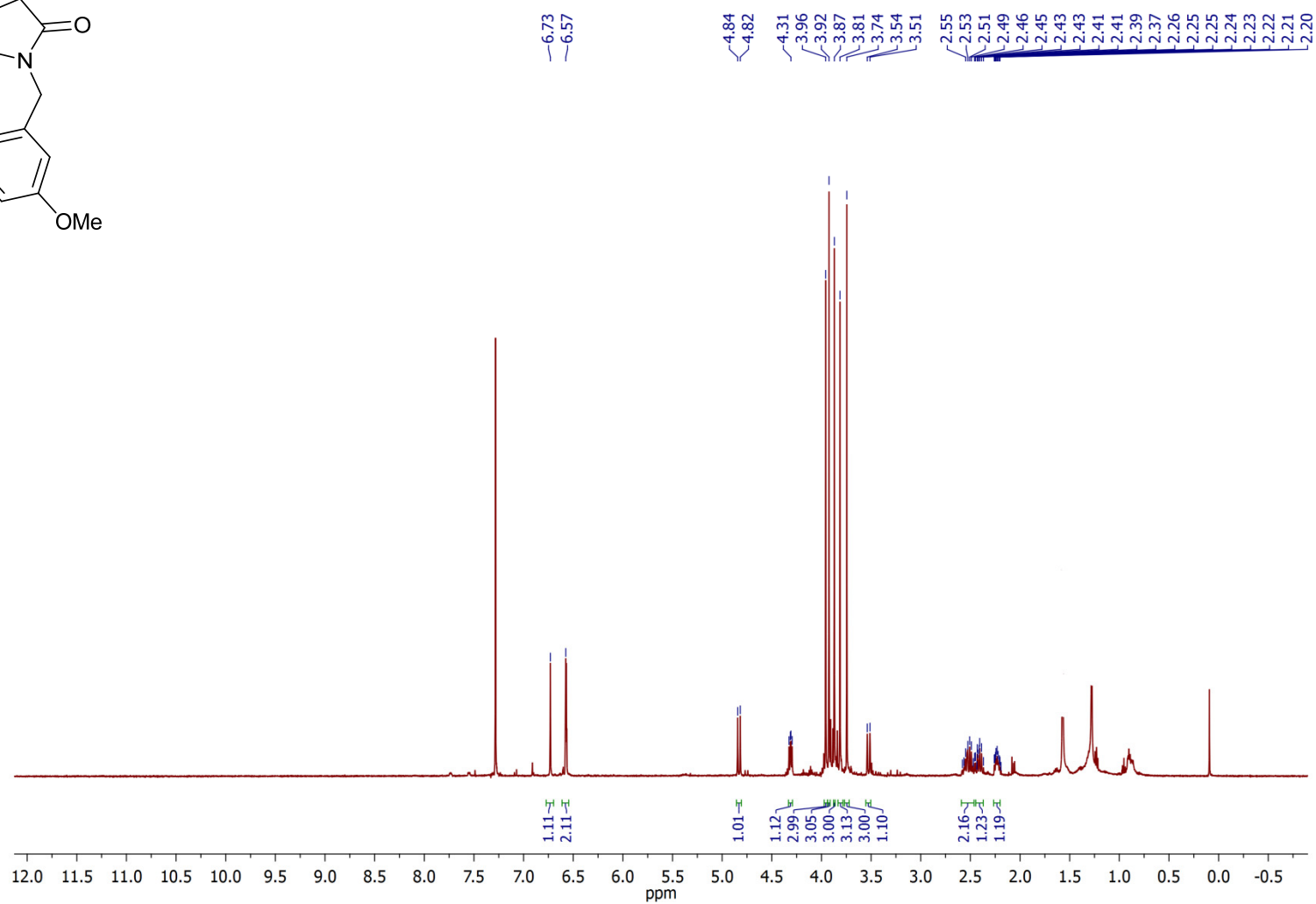
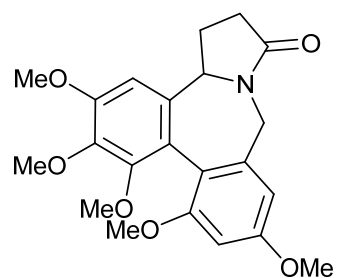
1,2,3-Trimethoxy-4b,5,6,9,12,13-hexahydro-7H-[1,4]dioxino[2',3':4,5]benzo[1,2-e]benzo[c]pyrrolo[1,2-a]azepin-7-one (5b)

HMBC ^1H - ^{13}C (CDCl_3)



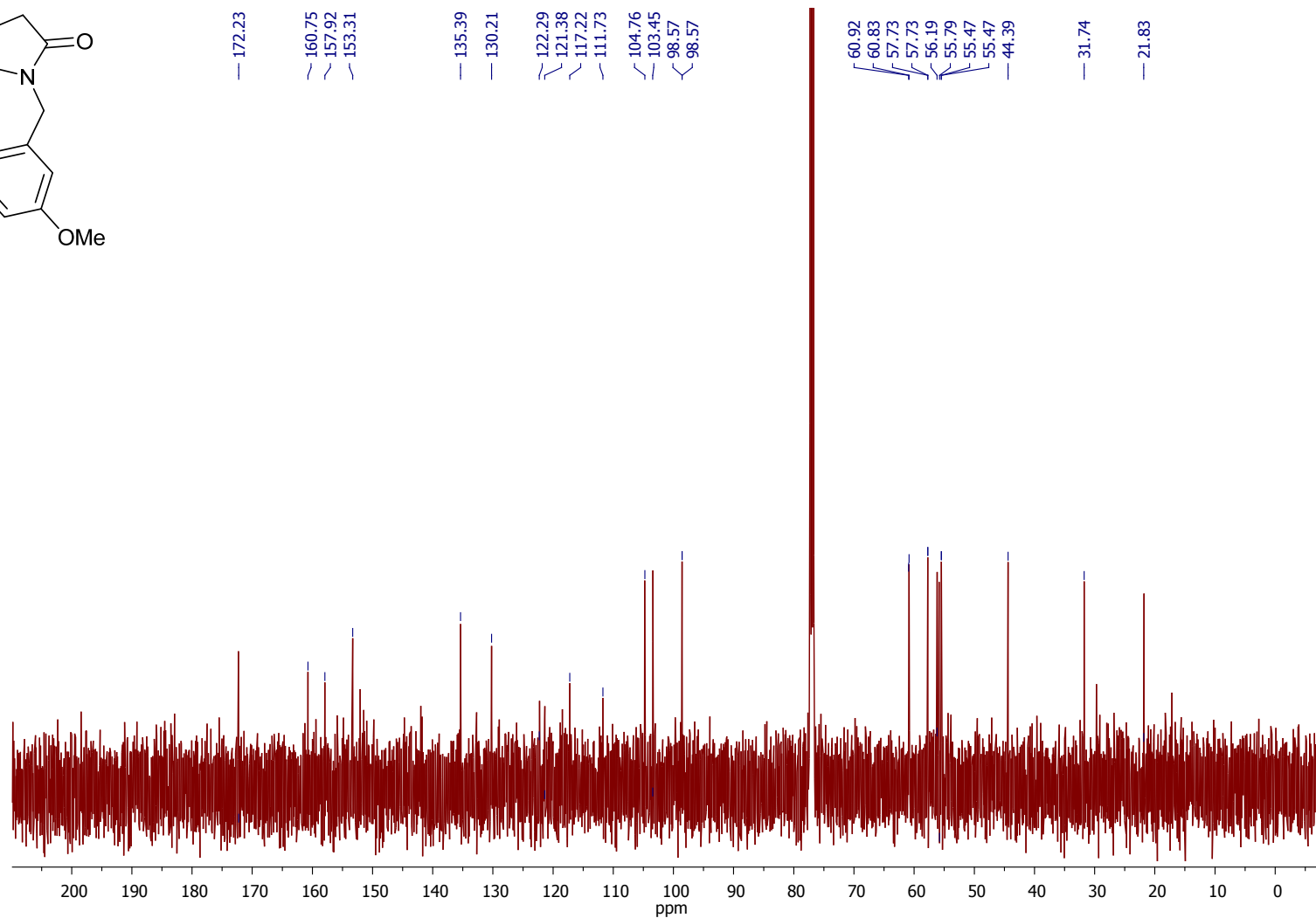
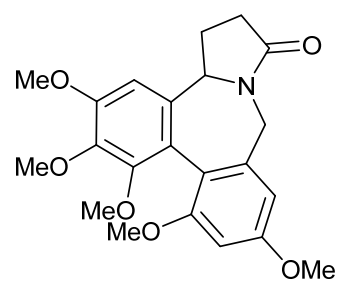
1,2,3,11,13-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5c)

¹H NMR (CDCl₃, 500 MHz)



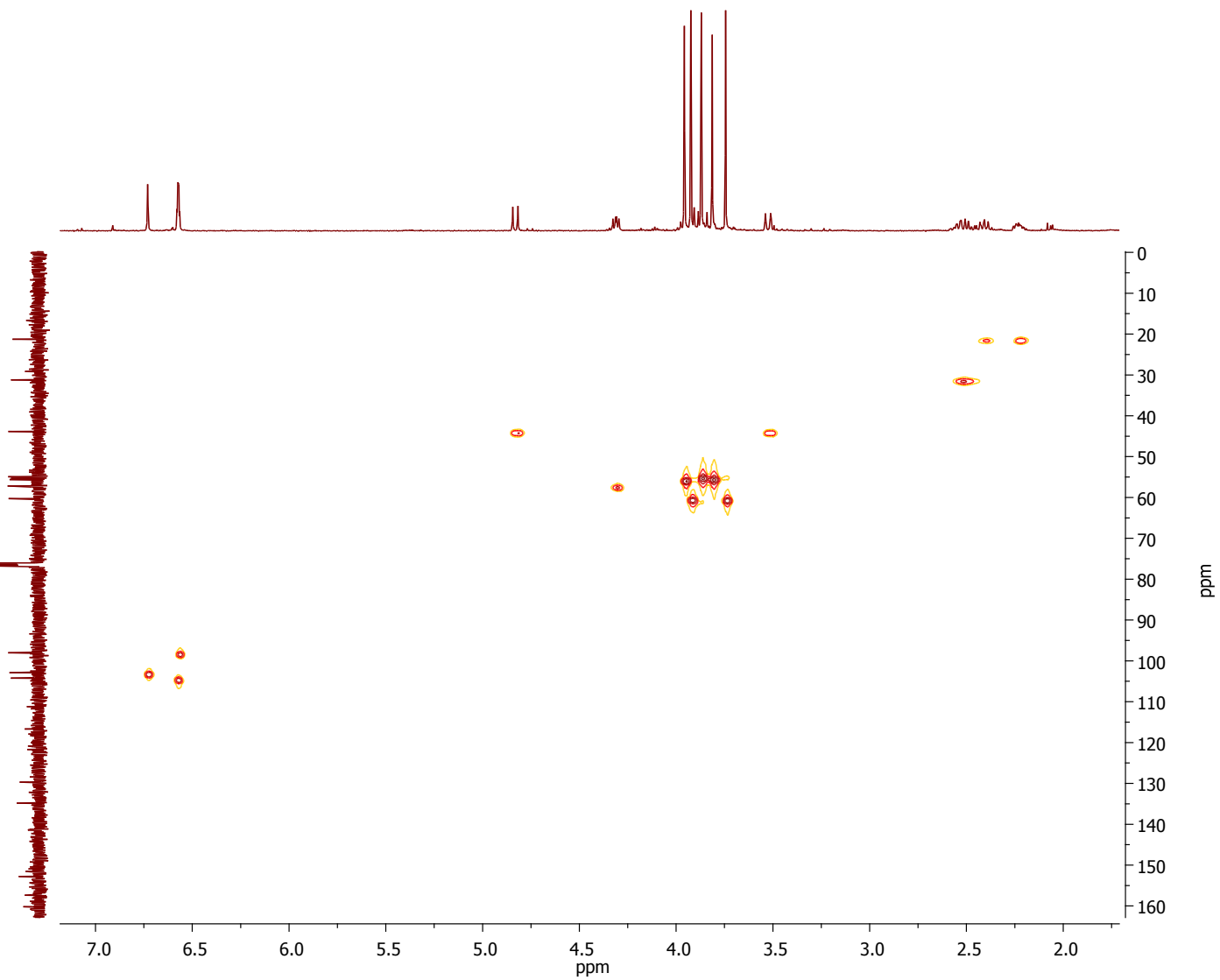
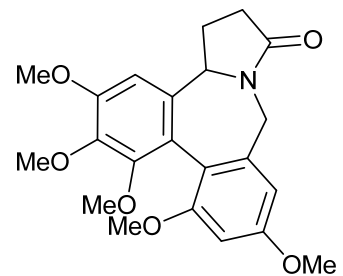
1,2,3,11,13-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5c)

^{13}C NMR (CDCl_3 , 125 MHz)



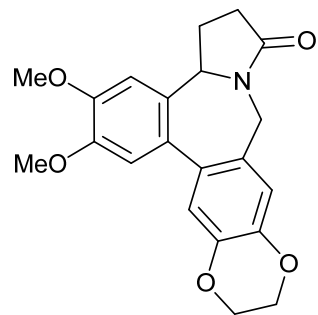
1,2,3,11,13-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5c)

HSQC ^1H - ^{13}C (CDCl_3)

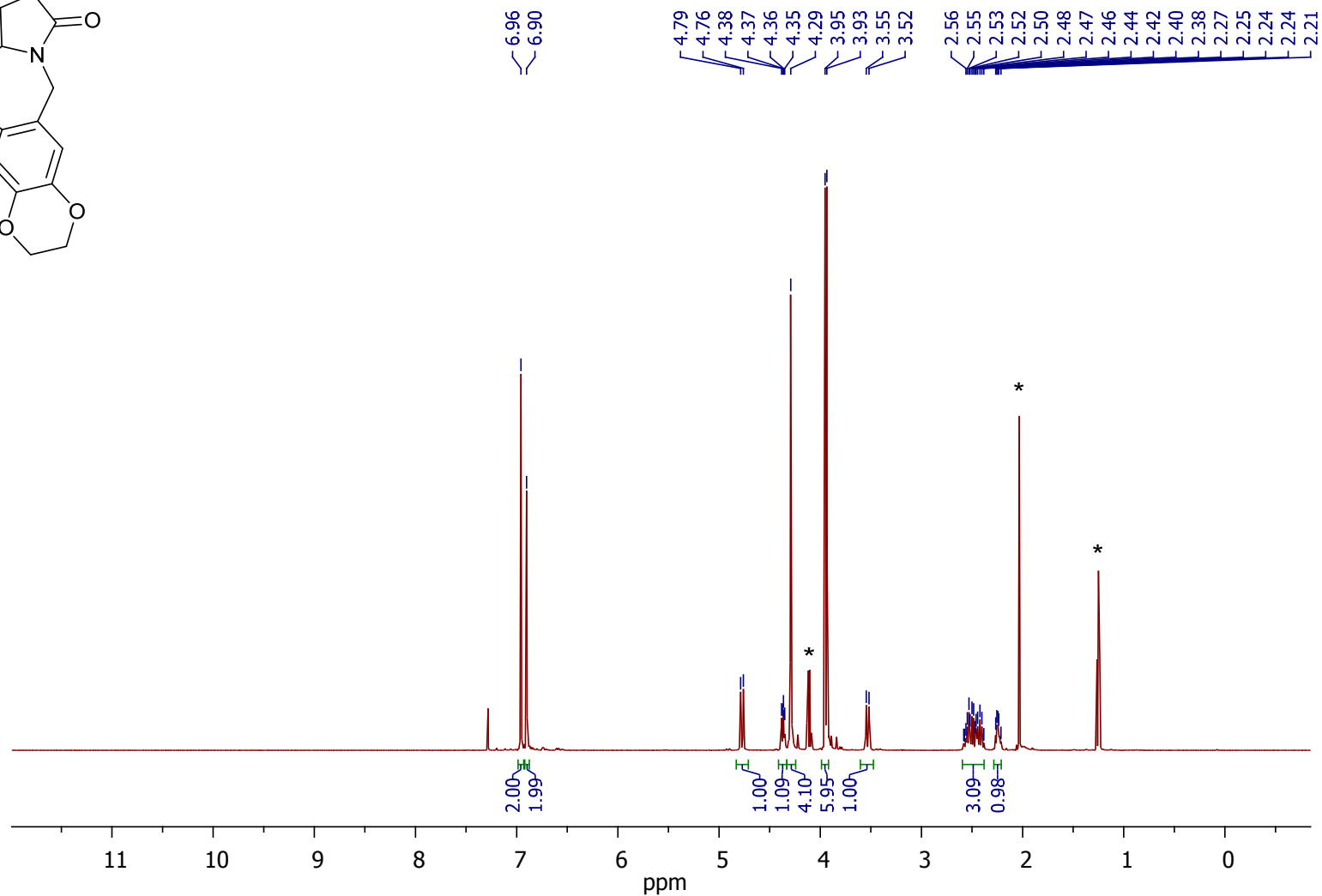


2,3-Dimethoxy-4b,5,6,9,12,13-hexahydro-7H-[1,4]dioxino[2',3':4,5]benzo[1,2-e]benzo[c] pyrrolo[1,2-a]azepin-7-one (5d)

¹H NMR (CDCl₃, 500 MHz)

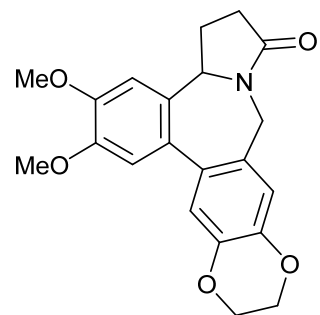


* Solvent

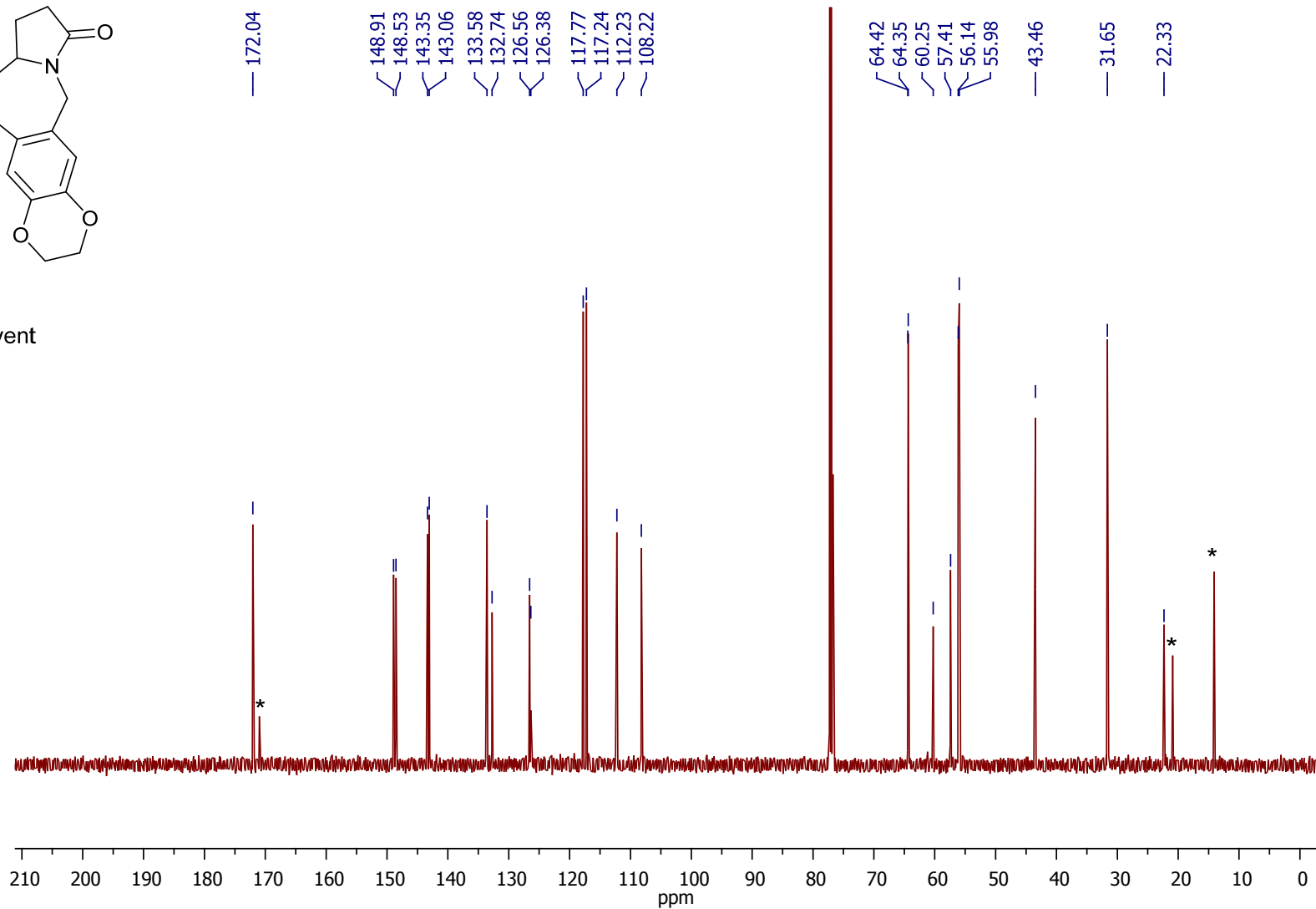


2,3-Dimethoxy-4b,5,6,9,12,13-hexahydro-7H-[1,4]dioxino[2',3':4,5]benzo[1,2-e]benzo[c] pyrrolo[1,2-a]azepin-7-one (5d)

^{13}C NMR (CDCl_3 , 125 MHz)

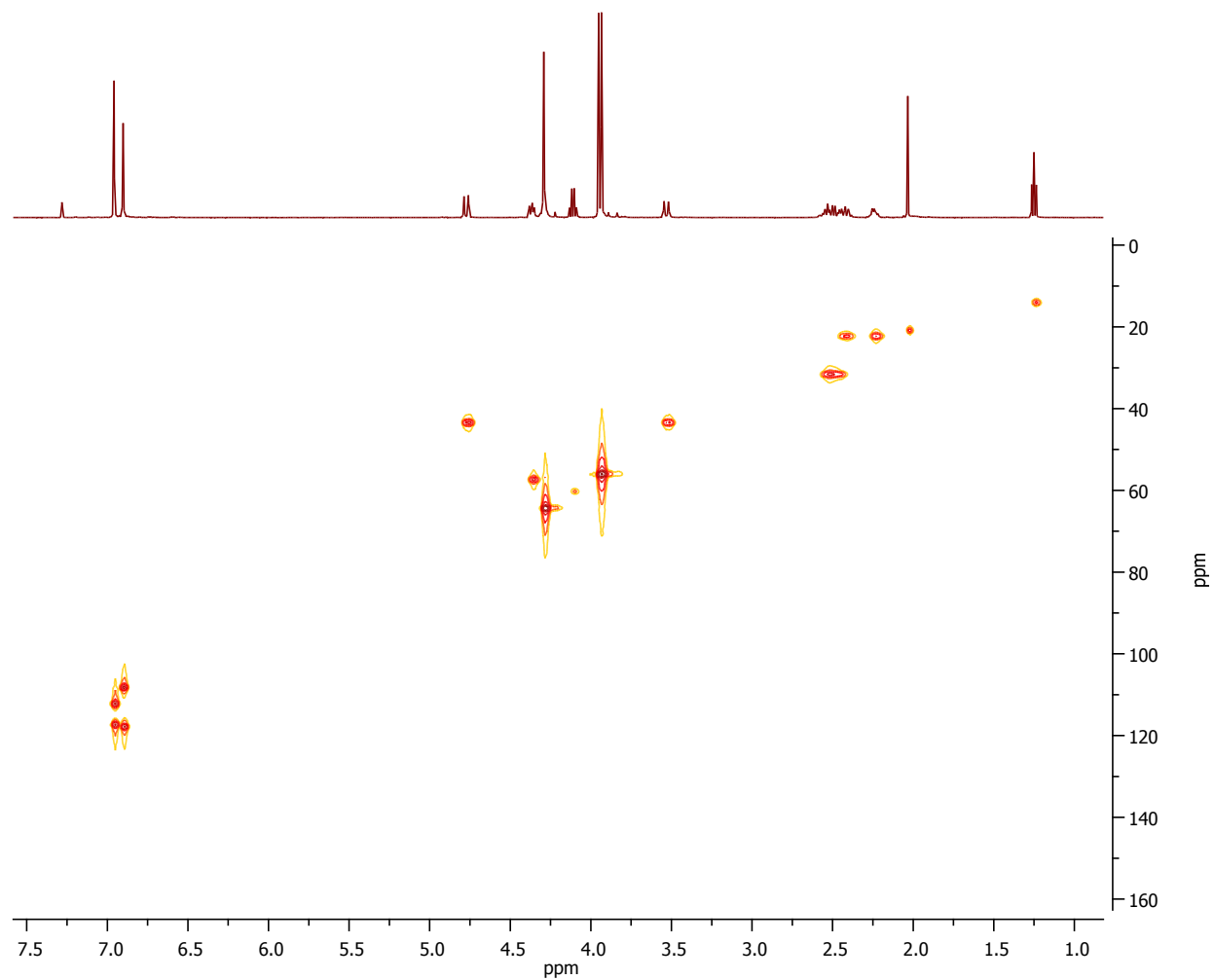
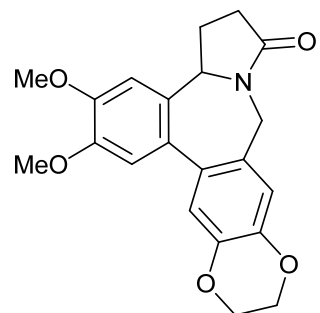


* Solvent



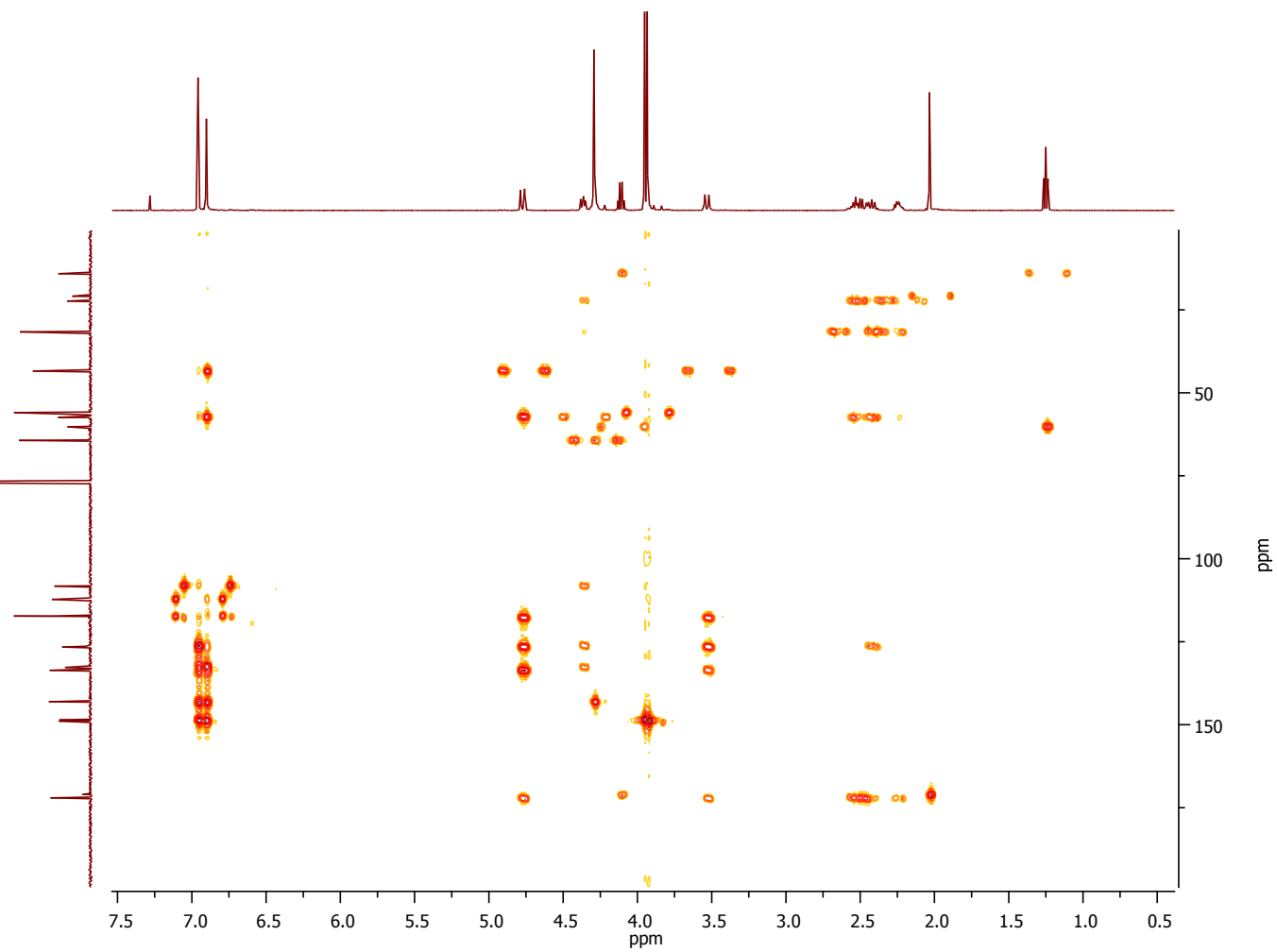
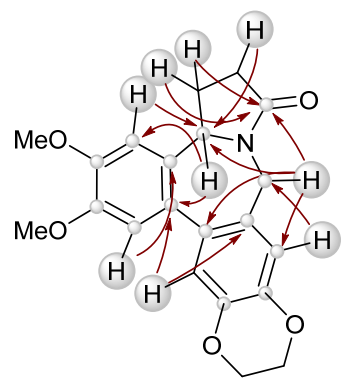
2,3-Dimethoxy-4b,5,6,9,12,13-hexahydro-7H-[1,4]dioxino[2',3':4,5]benzo[1,2-e]benzo[c] pyrrolo[1,2-a]azepin-7-one (5d)

HSQC ^1H - ^{13}C (CDCl_3)



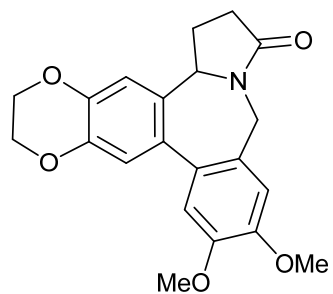
2,3-Dimethoxy-4b,5,6,9,12,13-hexahydro-7H-[1,4]dioxino[2',3':4,5]benzo[1,2-*e*]benzo[*c*]pyrrolo[1,2-*a*]azepin-7-one (5d)

HMBC ^1H - ^{13}C (CDCl_3)

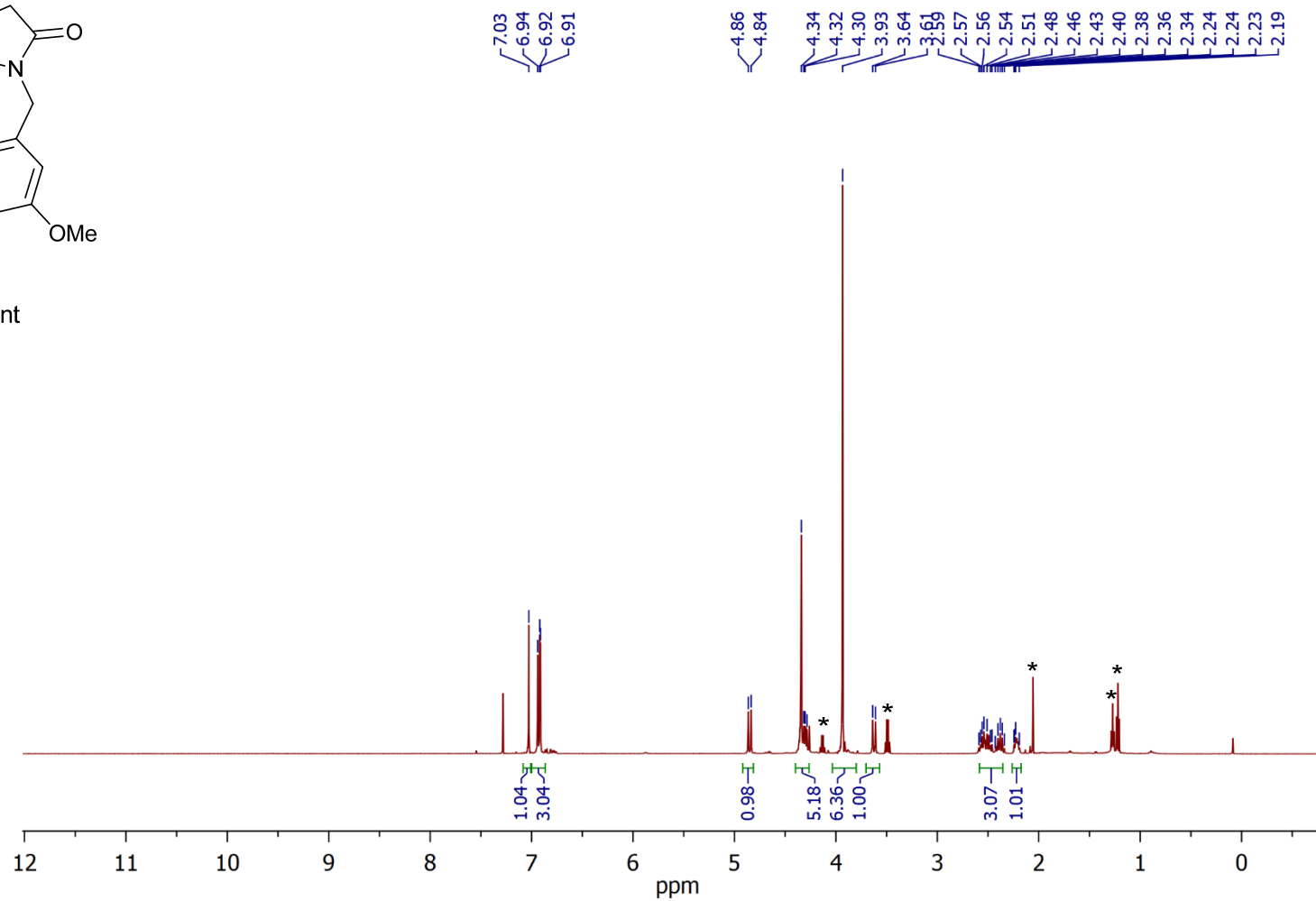


12,13-Dimethoxy-2,3,5b,6,7,10-hexahydro-8H-[1,4]dioxino[2',3':4,5]benzo[1,2-c]pyrrolo[1,2-a]azepin-8-one (5e)

¹H NMR (CDCl₃, 500 MHz)

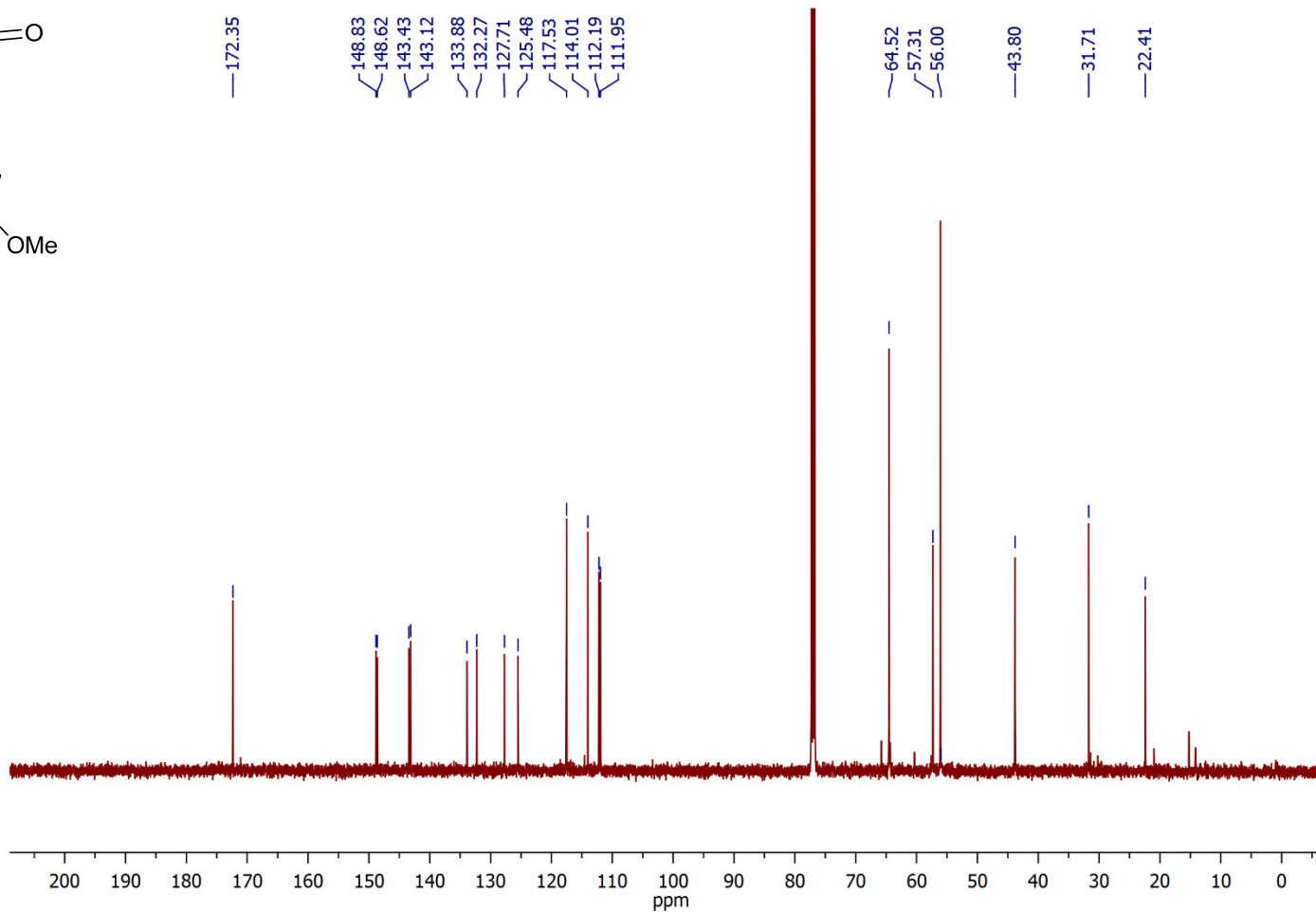
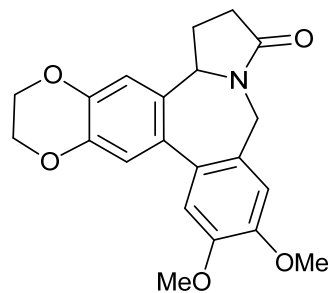


* Solvent



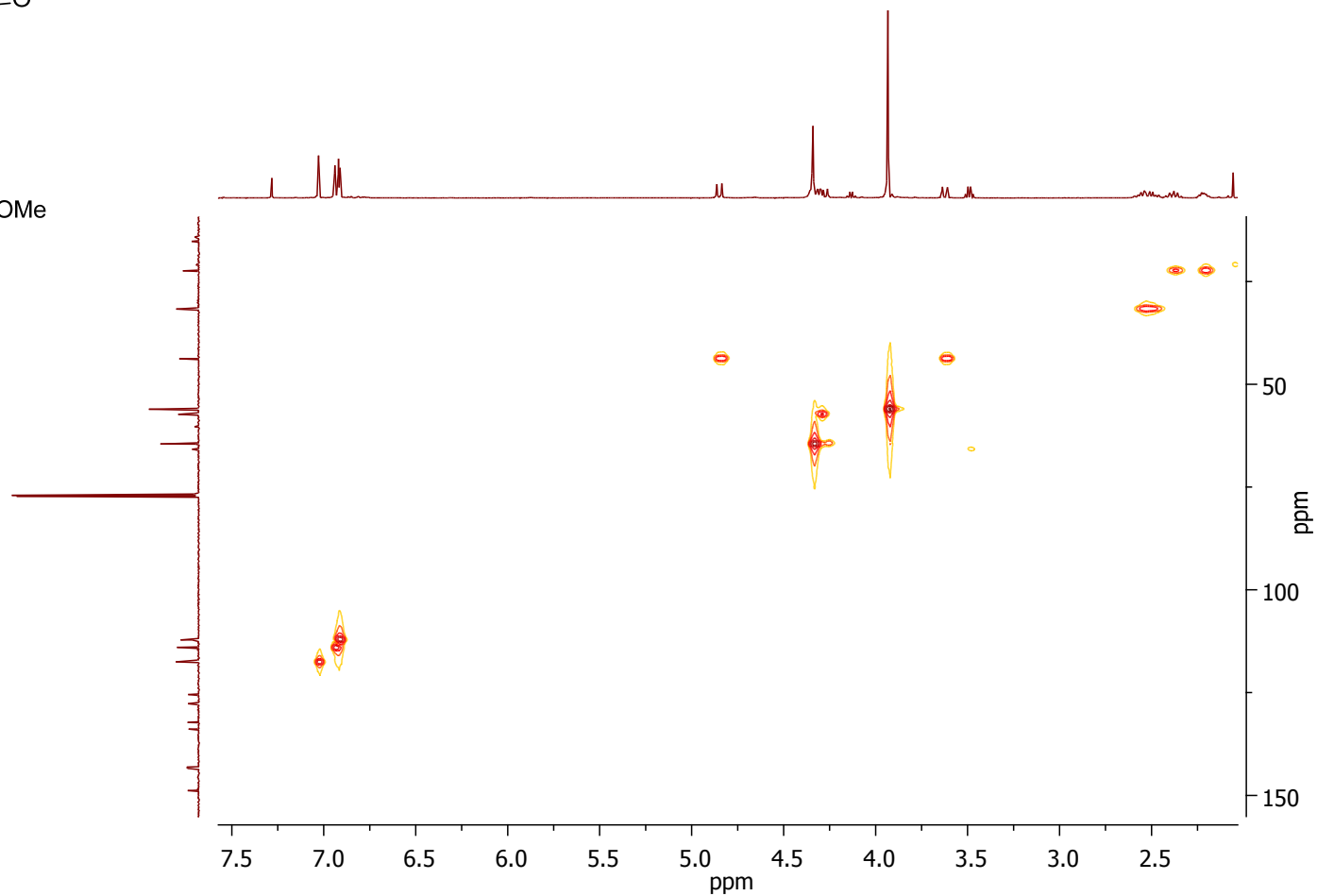
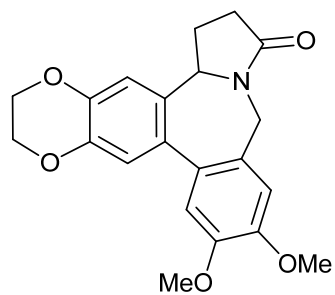
12,13-Dimethoxy-2,3,5b,6,7,10-hexahydro-8H-[1,4]dioxino[2',3':4,5]benzo[1,2-c]pyrrolo[1,2-a]azepin-8-one (5e)

^{13}C NMR (CDCl_3 , 125 MHz)



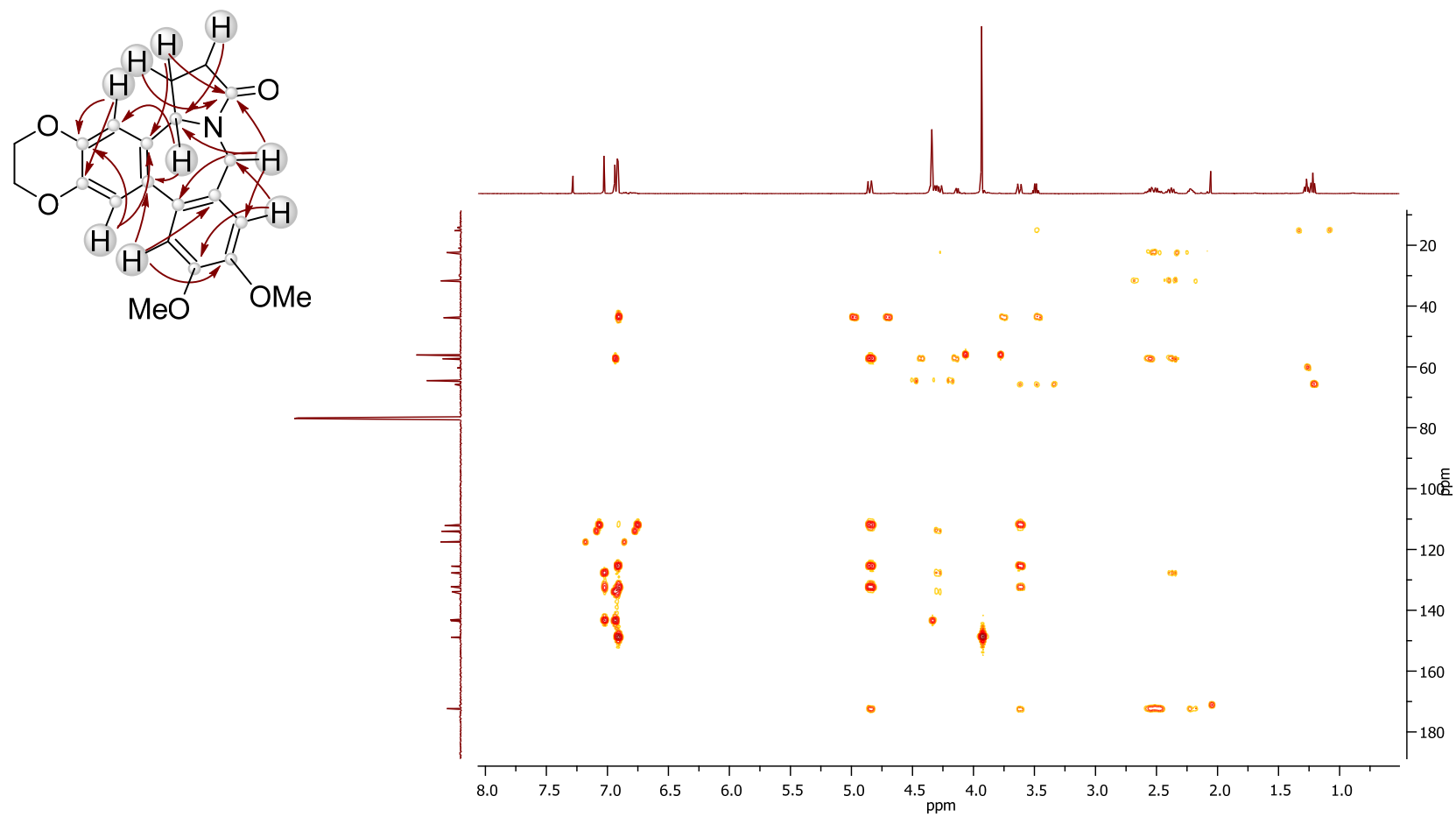
12,13-Dimethoxy-2,3,5b,6,7,10-hexahydro-8*H*-[1,4]dioxino[2',3':4,5]benzo[1,2-*c*]pyrrolo[1,2-*a*]azepin-8-one (5e)

HSQC ^1H - ^{13}C (CDCl_3)



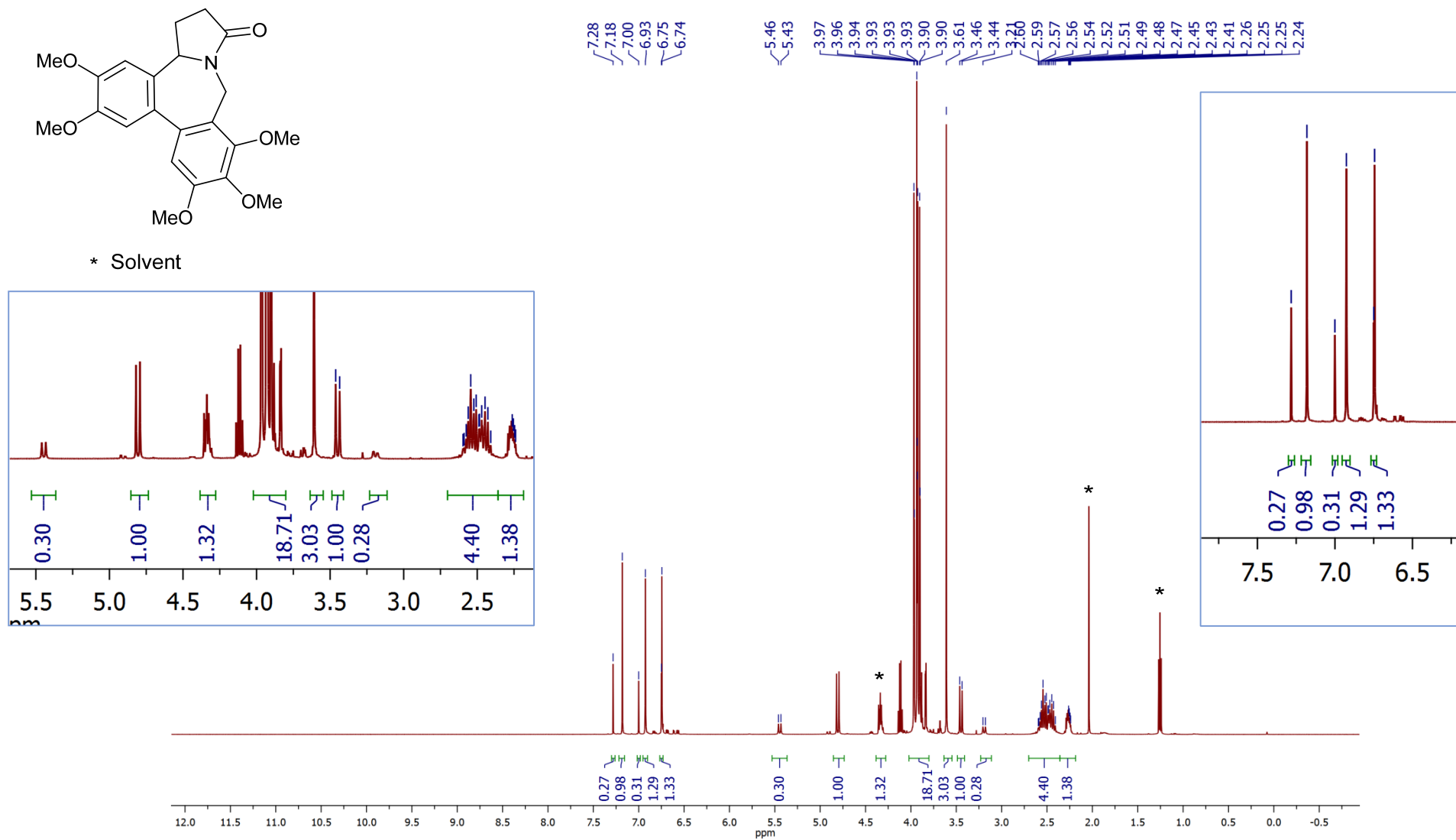
12,13-Dimethoxy-2,3,5b,6,7,10-hexahydro-8*H*-[1,4]dioxino[2',3':4,5]benzo[1,2-*c*]pyrrolo[1,2-*a*]azepin-8-one (5e)

HMBC ^1H - ^{13}C (CDCl_3)



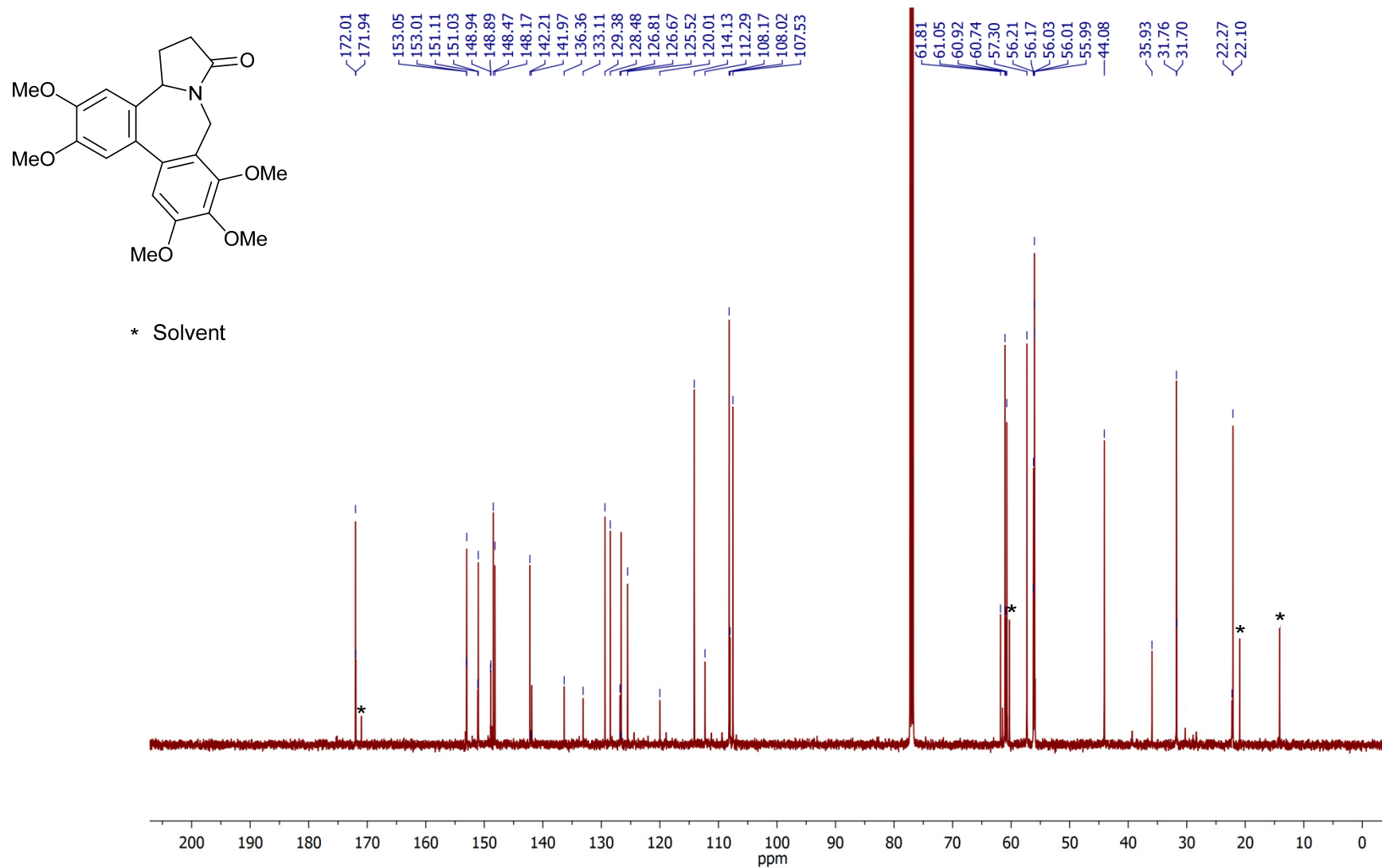
2,3,10,11,12-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5f) (as a mixture with 5g in a ratio of 23:77)

^1H NMR (CDCl_3 , 500 MHz)



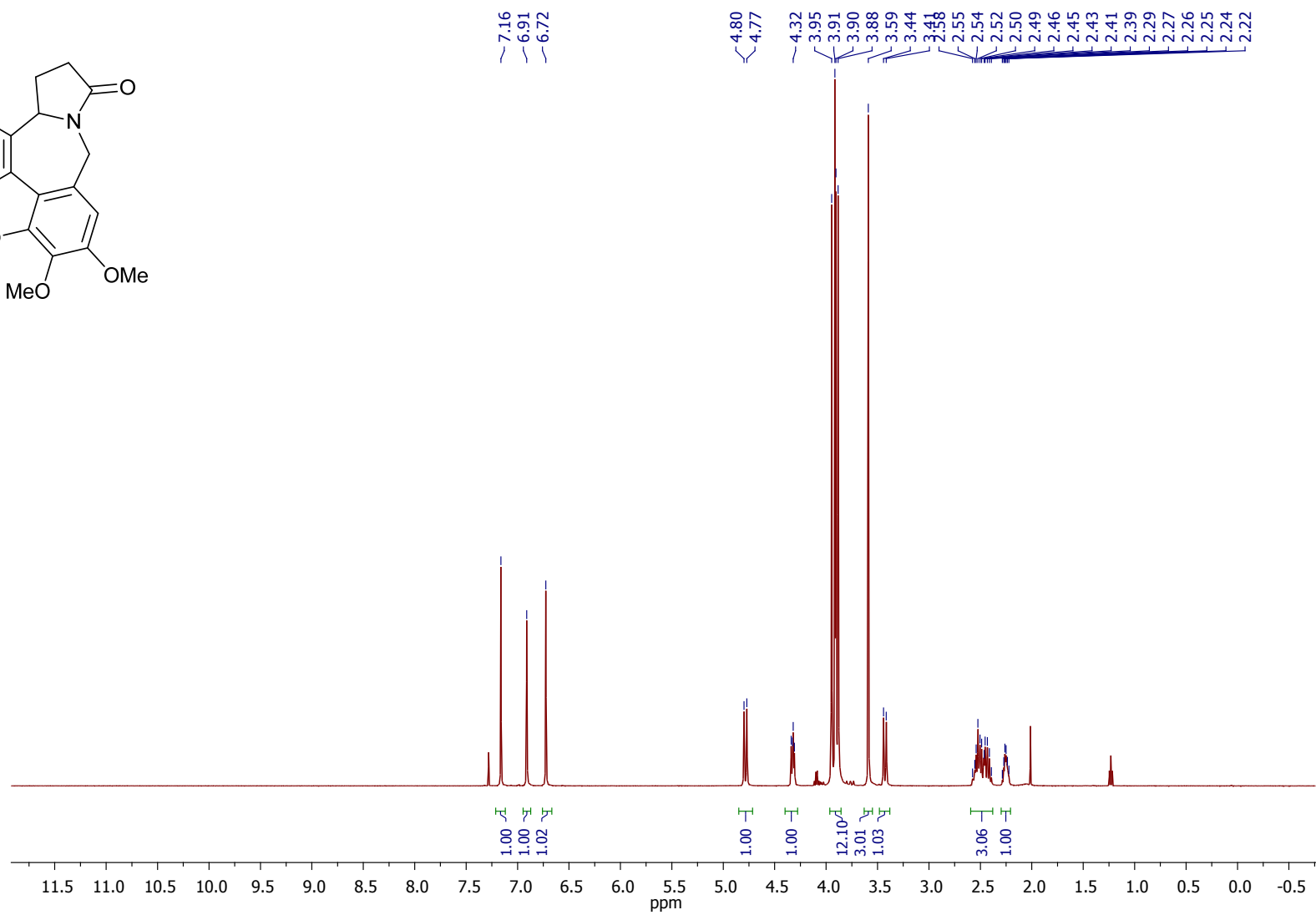
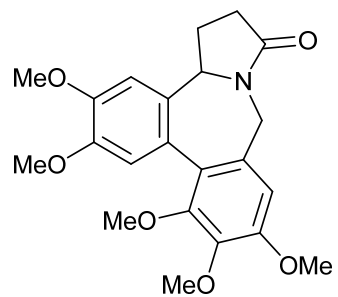
2,3,10,11,12-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5f) (as a mixture with 5g in a ratio of 23:77)

¹³C NMR (CDCl₃, 125 MHz)



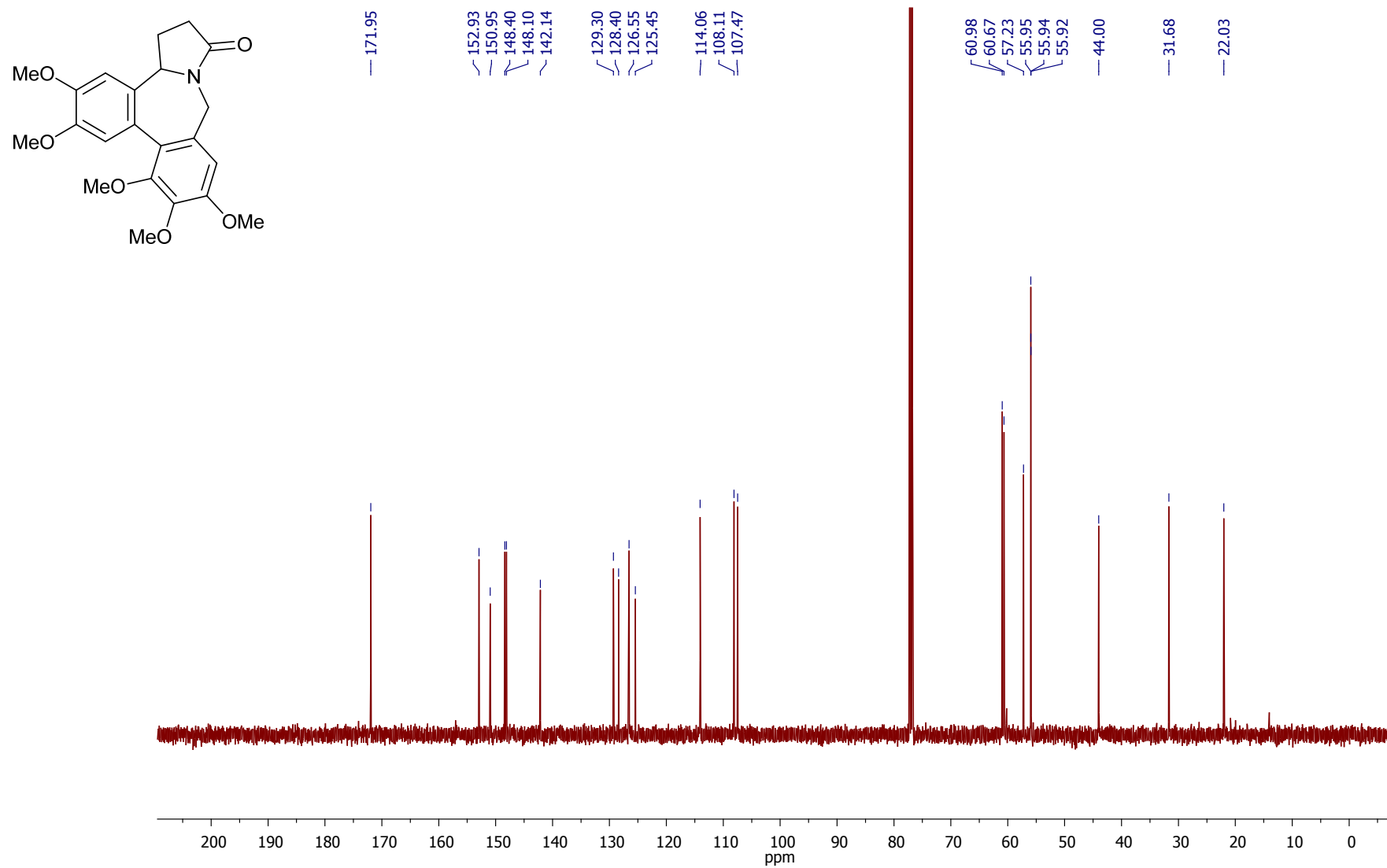
2,3,11,12,13-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5g)

¹H NMR (CDCl₃, 500 MHz)



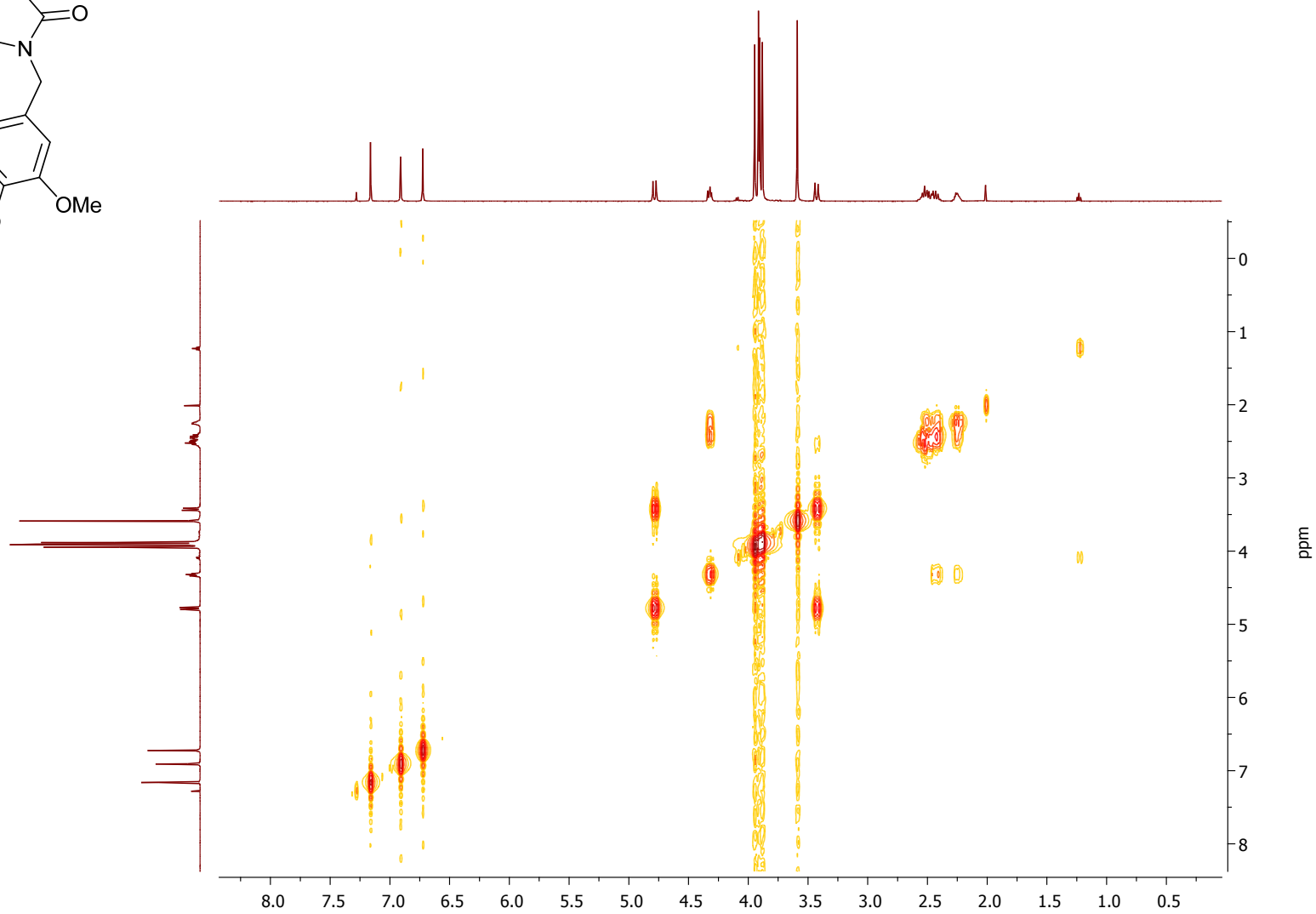
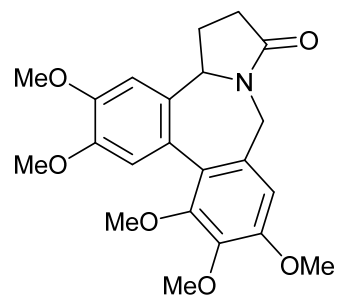
2,3,11,12,13-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5g)

¹³C NMR (CDCl₃, 125 MHz)



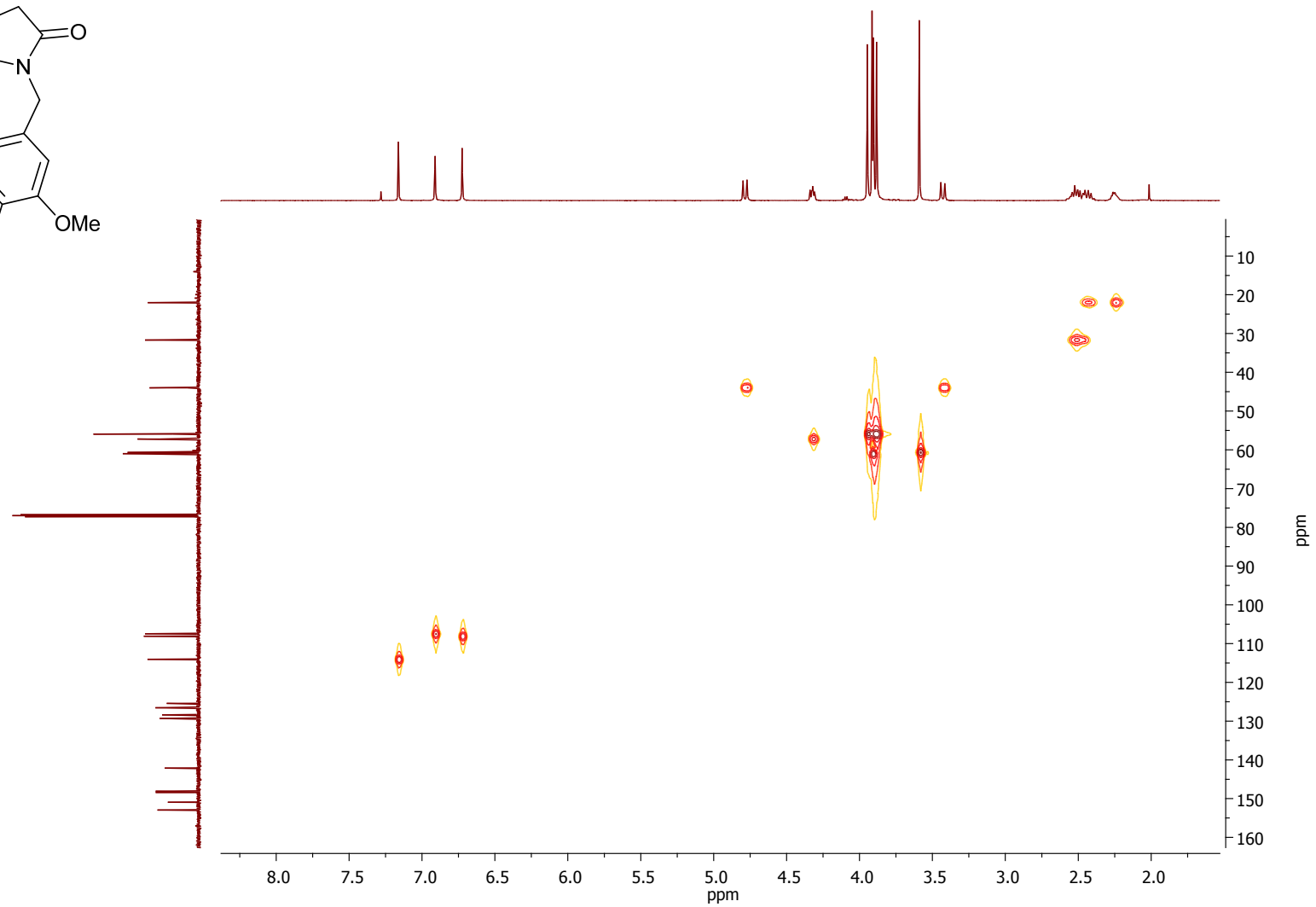
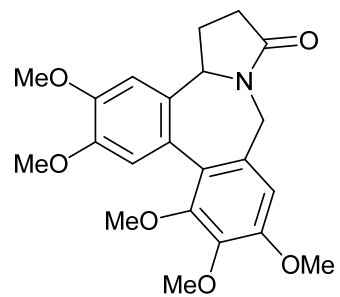
2,3,11,12,13-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5g)

NOESY ^1H - ^1H (CDCl_3)



2,3,11,12,13-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5g)

HSQC ^1H - ^{13}C (CDCl_3)



2,3,11,12,13-Pentamethoxy-4b,5,6,9-tetrahydrodibenzo[*c,e*]pyrrolo[1,2-*a*]azepin-7-one (5g)

HMBC ^1H - ^{13}C (CDCl_3)

