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General Information

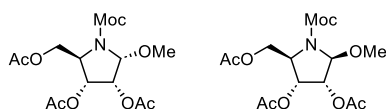
All the reagents and solvents were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) carried out on Merck precoated silica gel F₂₅₄ plates (thickness 0.25 mm), with detection by UV absorption (254 nm) and by heating the plates after dipping in ceric ammonium molybdate solution (contains H₂SO₄) or ninhydrin solution. Silica gel (particle size 40–50 µm) was used for column chromatography. ¹H and ¹³C{¹H} NMR spectra were collected on JEOL ECA-600 (¹H 600 MHz, ¹³C{¹H} 150 MHz). Chemical shifts were reported in ppm (δ) relative to residual non-deuterated solvent as an internal standard. Coupling constants (*J*) were reported in hertz (Hz). Abbreviations of multiplicity were as follows; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. High-resolution mass spectra (HRMS) were obtained on time-of-flight (TOF) spectrometers (JEOL JMS T-100LP).

Synthesis and Characterization Data

General Procedure for the Electrochemical Oxidation.

Bu₄NBF₄ was dried in vacuum oven at 150 °C under reduced pressure. Undivided cell and the electrodes were dried in oven at 100 °C. To a solution of Bu₄NBF₄ (140 mg, 0.40 mmol) in dry CH₃OH (4.0 mL) was added prolinol (0.10 mmol). The resulting reaction mixture was electrolyzed at constant current (2.5 mA/cm²) in undivided cell equipped with glassy carbon plate (10 mm x 10 mm) as anode and Pt plate (10 mm x 10 mm) as cathode with stirring at room temperature under argon atmosphere. After electrolysis (6.0 F/mol), the reaction mixture was concentrated in vacuo.

(2*R*,3*R*,4*R*,5*R*)-2-(Acetoxymethyl)-5-methoxy-1-(methoxycarbonyl)pyrrolidine-3,4-diyl diacetate (4*α*) and (2*R*,3*R*,4*R*,5*S*)-2-(acetoxymethyl)-5-methoxy-1-(methoxycarbonyl)pyrrolidine-3,4-diyl diacetate (4*β*).



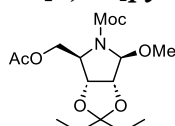
The prolinol **1**^[1] (33.0 mg, 0.104 mmol) was subjected to General Procedure. The title compounds were afforded after purification by silica gel column chromatography (*n*-hexane/ethyl acetate = 2:3) as a colorless oil (**4α**: 15.2 mg, 0.0438 mmol; **4β**: 11.8 mg, 0.0340 mmol, 75% yield).

4α: ¹H NMR (DMSO-*d*₆, 90 °C, 600 MHz): δ 5.29 (d, *J* = 4.8 Hz, 1H), 5.14-5.11 (m, 2H), 4.28 (dd, *J* = 11.7, 5.5 Hz, 1H), 4.19 (dd, *J* = 11.3, 3.1 Hz, 1H), 4.00 (dd, *J* = 5.5, 3.4 Hz, 1H), 3.70 (s, 3H), 3.41 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H); ¹³C{¹H} NMR (DMSO-*d*₆, 90 °C, 150 MHz): δ 169.3, 169.2, 168.9, 154.0, 86.9, 71.5, 69.8, 61.2, 60.2, 57.9, 52.0, 20.1, 19.9, 19.7; HRMS [*M* + Na]⁺ calcd for C₁₄H₂₁NNaO₉ 370.1109, found 370.1132.

4β: ¹H NMR (DMSO-*d*₆, 90 °C, 600 MHz): δ 5.31 (dd, *J* = 6.7, 5.0 Hz, 1H), 5.13 (dd, *J* = 4.8, 1.4 Hz, 1H), 5.05 (s, 1H), 4.42 (dd, *J* = 11.7, 4.8 Hz, 1H), 4.15 (dd, *J* = 11.7, 4.1 Hz, 1H),

4.00 (m, 1H), 3.72 (s, 3H), 3.32 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 90 °C, 150 MHz): δ 169.4, 168.8 (2C), 154.7, 90.6, 72.6, 71.2, 61.3, 58.3, 54.8, 52.4, 19.9, 19.8, 19.7; HRMS $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{21}\text{NNaO}_9$ 370.1109, found 370.1124.

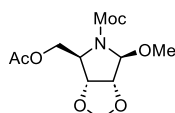
Methyl (3aR,4R,6S,6aR)-4-(acetoxymethyl)-2,2-diethyl-6-methoxytetrahydro-5H-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate (5).



The prolinol **2** (29.6 mg, 0.098 mmol) was subjected to General Procedure. The title compound was afforded after purification by silica gel column chromatography (*n*-hexane/ethyl acetate = 2:1) as a colorless oil (32.4 mg, 0.098 mmol, 100% yield).

^1H NMR (DMSO- d_6 , 90 °C, 600 MHz): δ 5.15 (s, 1H), 4.68 (d, J = 5.5 Hz, 1H), 4.58 (d, J = 6.2 Hz, 1H), 4.24 (t, J = 6.9 Hz, 1H), 4.14 (dd, J = 11.0, 6.9 Hz, 1H), 3.93 (dd, J = 11.0, 6.2 Hz, 1H), 3.67 (s, 3H), 3.27 (s, 3H), 2.02 (s, 3H), 1.59-1.52 (m, 4H), 0.83 (t, J = 7.6 Hz, 3H), 0.75 (t, J = 7.2 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 90 °C, 150 MHz): δ 169.4, 154.7, 114.6, 93.1, 83.6, 80.6, 63.1, 62.8, 54.5, 52.2, 28.8, 27.8, 20.0, 7.7, 6.0; HRMS $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{25}\text{NNaO}_7$ 354.1523, found 354.1507.

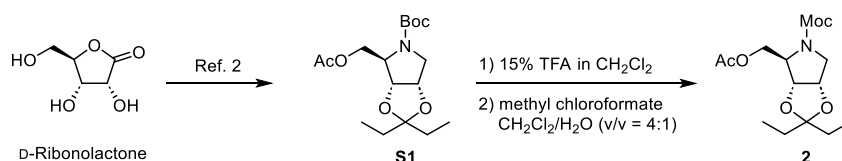
Methyl (3aR,4R,6S,6aR)-4-(acetoxymethyl)-6-methoxytetrahydro-5H-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate (6).



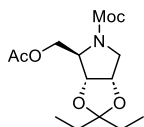
The prolinol **3** (26.2 mg, 0.107 mmol) was subjected to General Procedure. The title compound was afforded after purification by silica gel column chromatography (*n*-hexane/ethyl acetate = 2:1) as a colorless oil (28.0 mg, 0.102 mmol, 94% yield).

^1H NMR (DMSO- d_6 , 90 °C, 600 MHz): δ 5.15 (s, 1H), 4.96 (s, 1H), 4.76 (s, 1H), 4.63 (d, J = 6.2 Hz, 1H), 4.48 (d, J = 5.5 Hz, 1H), 4.22-4.16 (m, 2H), 3.98 (dd, J = 10.7, 5.5 Hz, 1H), 3.69 (s, 3H), 3.29 (s, 3H), 2.03 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 90 °C, 150 MHz): δ 169.4, 154.3, 94.8, 92.1, 82.6, 80.1, 62.7, 62.1, 54.6, 52.3, 19.9; HRMS $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{11}\text{H}_{17}\text{NNaO}_7$ 298.0897, found 298.0926.

Scheme S1. Preparation of the prolinol 2



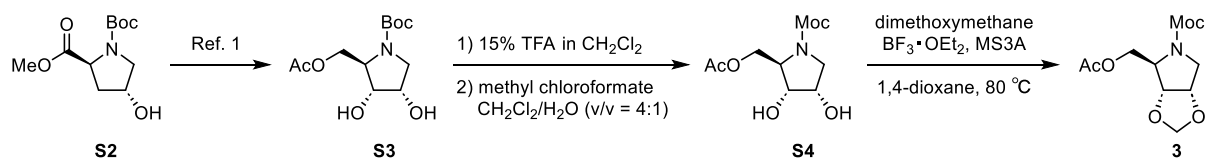
Methyl (4R)-4-(acetoxymethyl)-2,2-diethyltetrahydro-5H-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate (2).



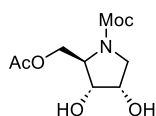
The prolinol **S1**^[2] (223.6 mg, 0.651 mmol) was added to a 15% trifluoroacetic acid solution in CH₂Cl₂ (6.5 mL) and the reaction mixture was stirred at room temperature. After 1 hour, the reaction mixture was concentrated in vacuo and the crude product was dissolved in CH₂Cl₂/water (6.5 mL, v/v = 4:1). NaHCO₃ (283.4 mg, 3.37 mmol) and methyl chloroformate (65 μ L, 0.846 mmol) were added to the solution and the reaction mixture was stirred vigorously for 1 hour. The mixture was extracted with CH₂Cl₂ (10 mL x 3), the combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The title compound was afforded after purification by silica gel column chromatography (*n*-hexane/ethyl acetate = 2:1) as a colorless oil (183.8 mg, 0.610 mmol, 94% yield).

¹H NMR (DMSO-*d*₆, 90 °C, 600 MHz): δ 4.78 (t, *J* = 5.5 Hz, 1H), 4.61 (d, *J* = 6.2 Hz, 1H), 4.16 (t, *J* = 5.2 Hz, 1H), 4.09 (m, 2H), 3.71 (d, *J* = 13.1 Hz, 1H), 3.61 (s, 3H), 3.42 (dd, *J* = 12.4, 4.8 Hz, 1H), 2.02 (s, 3H), 1.56 (m, 4H), 0.83 (t, *J* = 7.6 Hz, 3H), 0.79 (t, *J* = 7.6 Hz, 3H); ¹³C{¹H} NMR (DMSO-*d*₆, 90 °C, 150 MHz): δ 169.5, 154.1, 114.5, 81.5, 78.7, 78.7, 62.2, 62.0, 51.7, 28.7, 28.1, 20.0, 7.7, 6.2; HRMS [M + Na]⁺ calcd for C₁₄H₂₃NNaO₆ 324.1418, found 324.1402.

Scheme S2. Preparation of the prolinol 3



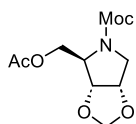
Methyl (2R,3R,4S)-2-(acetoxymethyl)-3,4-dihydroxypyrrolidine-1-carboxylate (S4).



The prolinol **S3**^[1] (1.90 g, 6.91 mmol) was added to a 15% trifluoroacetic acid solution in CH₂Cl₂ (30 mL) and the reaction mixture was stirred at room temperature. After 1 hour, the reaction mixture was concentrated in vacuo and the crude product was dissolved in CH₂Cl₂/water (50 mL, v/v = 4:1). NaHCO₃ (3.48 g, 41.5 mmol) and methyl chloroformate (1.38 mL, 18.0 mmol) were added to the solution and the reaction mixture was stirred vigorously for 20 hours. The mixture was extracted with ethyl acetate (20 mL x 5), the combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The title compound was afforded after purification by silica gel column chromatography (*n*-hexane/ethyl acetate = 1:15) as a colorless oil (1.21 g, 5.18 mmol, 75% yield).

^1H NMR (DMSO- d_6 , 90 °C, 600 MHz): δ 4.71 (d, J = 4.1 Hz, 1H), 4.61 (d, J = 4.8 Hz, 1H), 4.23 (q, J = 5.7 Hz, 1H), 4.11-4.08 (m, 2H), 3.92 (q, J = 4.4 Hz, 1H), 3.73-3.71 (m, 1H), 3.60 (s, 3H), 3.38 (q, J = 5.5 Hz, 1H), 3.28 (q, J = 5.5 Hz, 1H), 2.01 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 90 °C, 150 MHz): δ 169.5, 154.8, 72.3, 68.7, 61.8, 61.6, 51.5, 50.7, 20.0; HRMS $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_9\text{H}_{15}\text{NNaO}_6$ 256.0792, found 256.0802.

Methyl (3aR,4R,6aS)-4-(acetoxymethyl)tetrahydro-5H-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate (3).



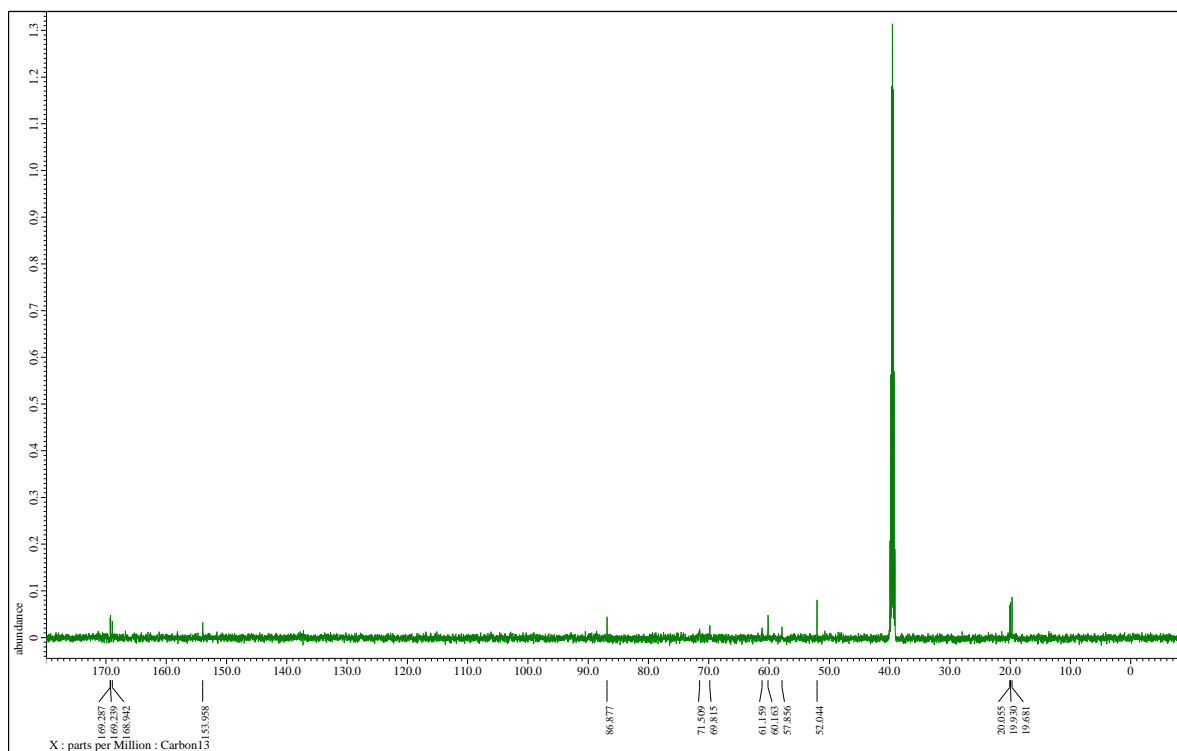
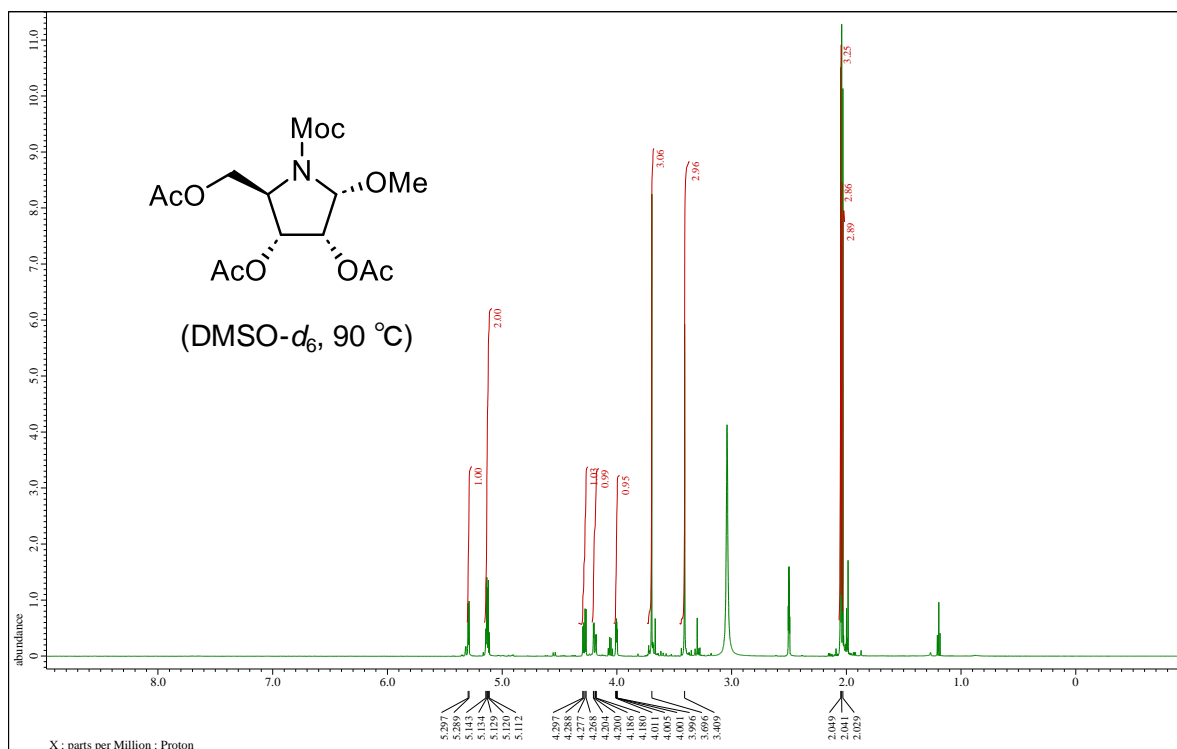
To a solution of the prolinol **S4** (893.8 mg, 3.83 mmol) in 1,4-dioxane (20 mL) were added MS3A (200 mg), boron trifluoride diethyl ether complex (1.20 mL, 9.58 mmol) and dimethoxy methane (503 μL , 5.75 mmol). The reaction was heated at 80 °C for 20 hours. The reaction was quenched with NaHCO_3 (1.0 g) and filtered by cerite pad. The filtrate was concentrated in vacuo. The title compound was afforded after purification by silica gel column chromatography (*n*-hexane/ethyl acetate = 1:1) as a colorless oil (594.0 mg, 2.42 mmol, 63% yield).

^1H NMR (DMSO- d_6 , 90 °C, 600 MHz): δ 5.00 (s, 1H), 4.79 (s, 1H), 4.74-4.72 (m, 1H), 4.53 (d, J = 6.2 Hz, 1H), 4.16-4.09 (m, 3H), 3.67-3.62 (m, 4H), 3.51 (q, J = 6.0 Hz, 1H), 2.03 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 90 °C, 150 MHz): δ 169.5, 153.8, 94.6, 78.0, 62.1, 61.1, 51.8, 51.0, 20.0; HRMS $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{10}\text{H}_{15}\text{NNaO}_6$ 268.0792, found 268.0787.

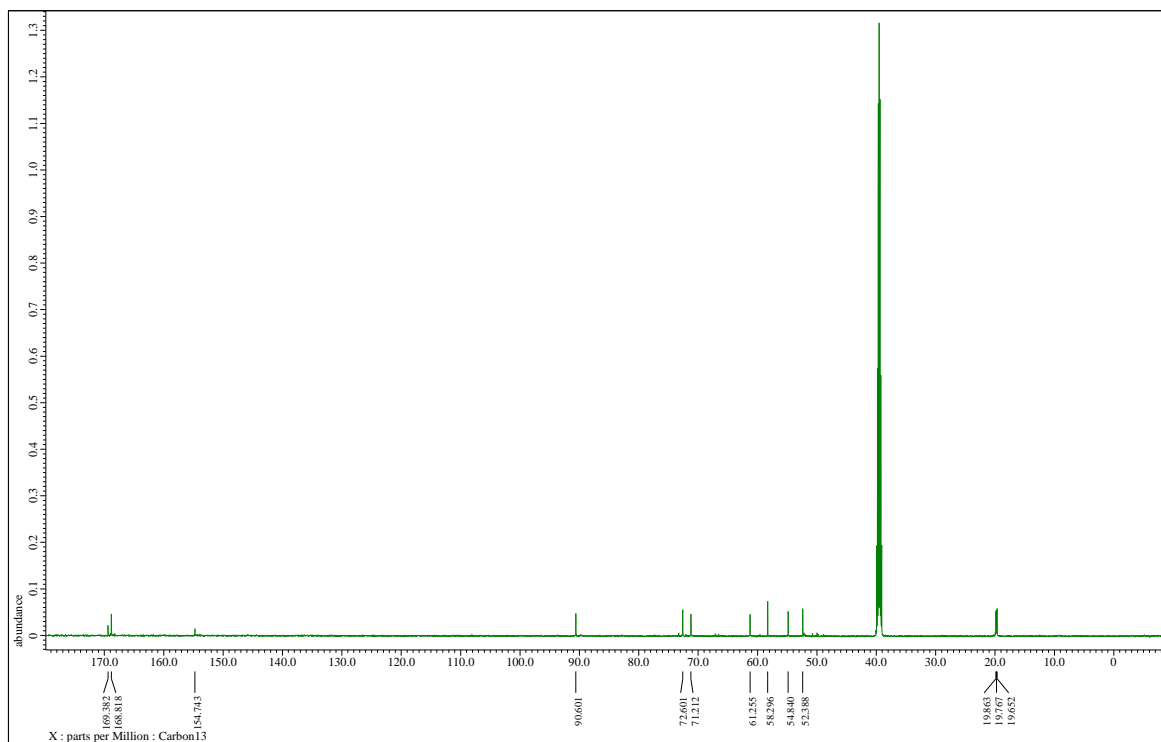
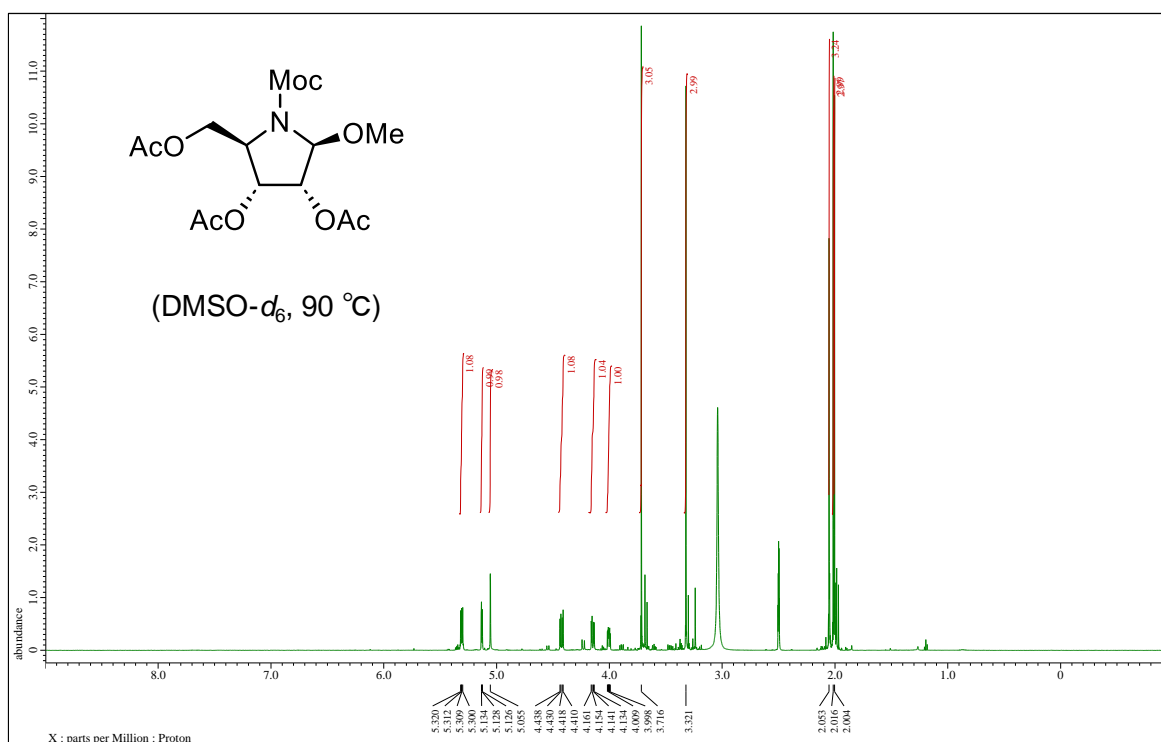
References

- [1] K. Okamoto, M. Tsutsui, H. Morizumi, Y. Kitano, K. Chiba, *Eur. J. Org. Chem.*, **17**, 2479 (2021).
- [2] H. Morizumi, K. Okamoto, S. Akahane, H. Takemae, M. Oba, Y. Okada, Y. Kitano, T. Mizutani, K. Chiba, *Eur. J. Org. Chem.*, **26**, e202201046 (2023).

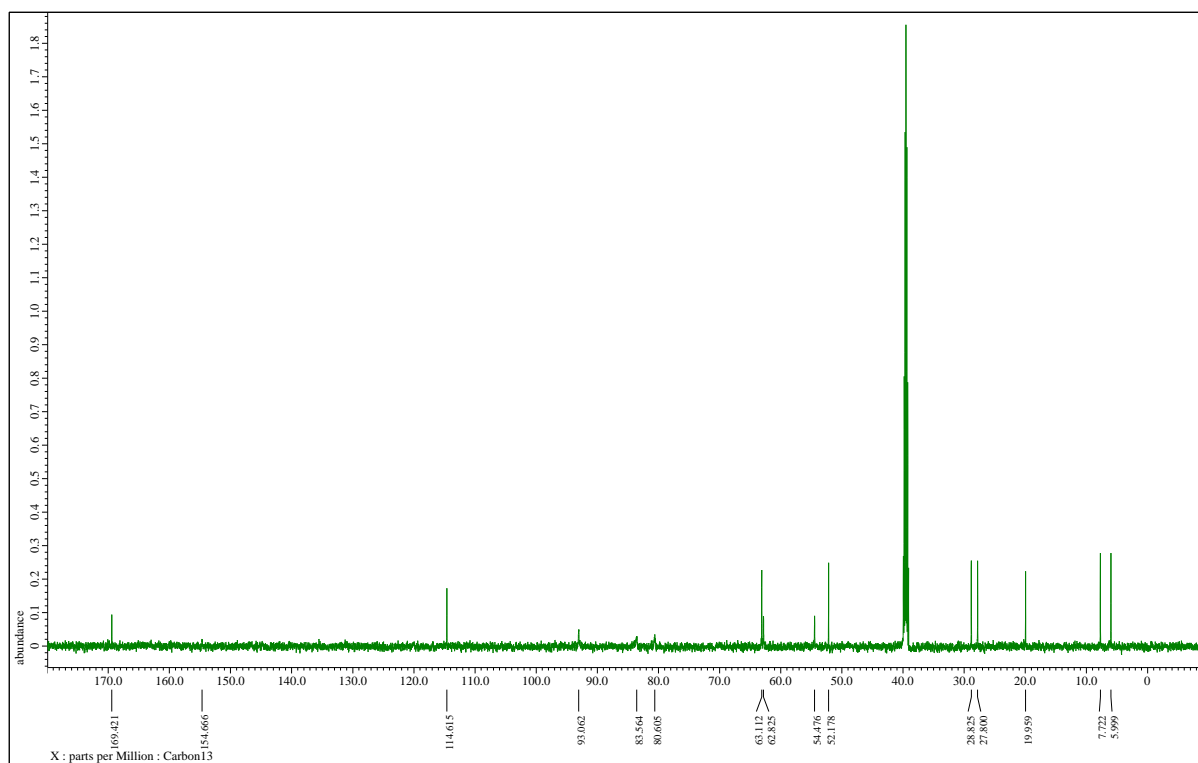
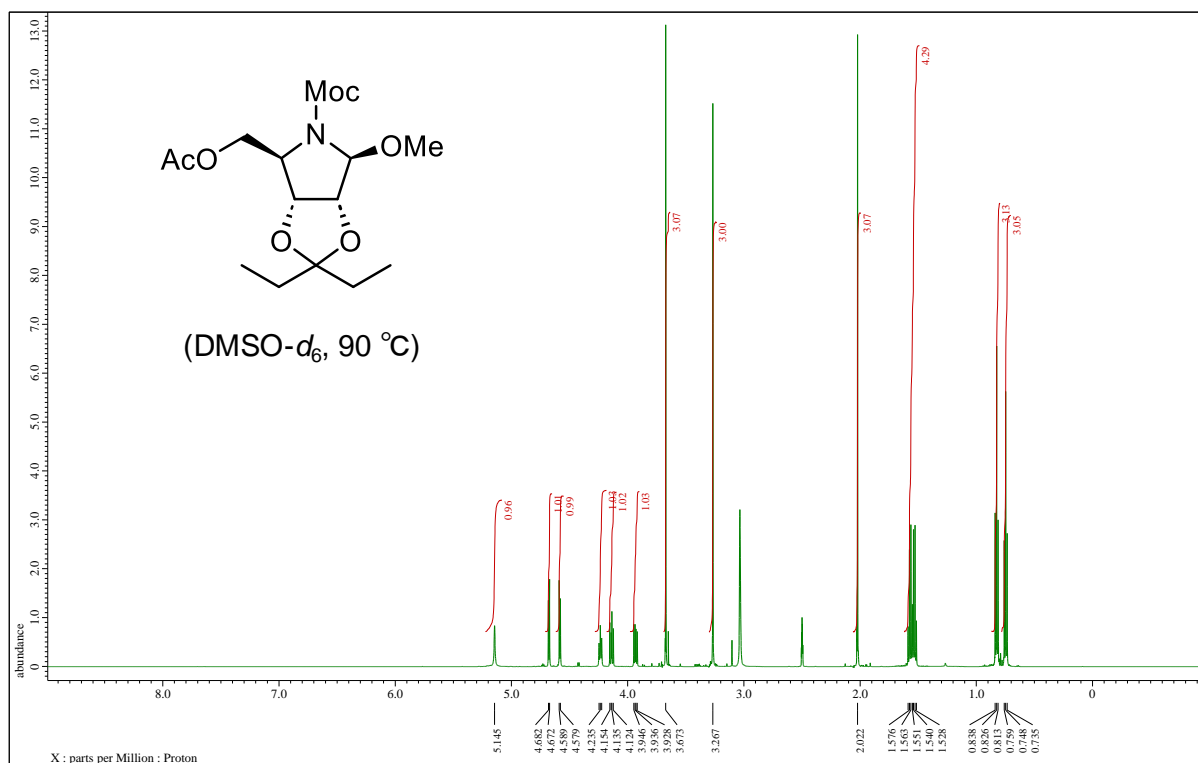
(2R,3R,4R,5R)-2-(Acetoxymethyl)-5-methoxy-1-(methoxycarbonyl)pyrrolidine-3,4-diyl diacetate



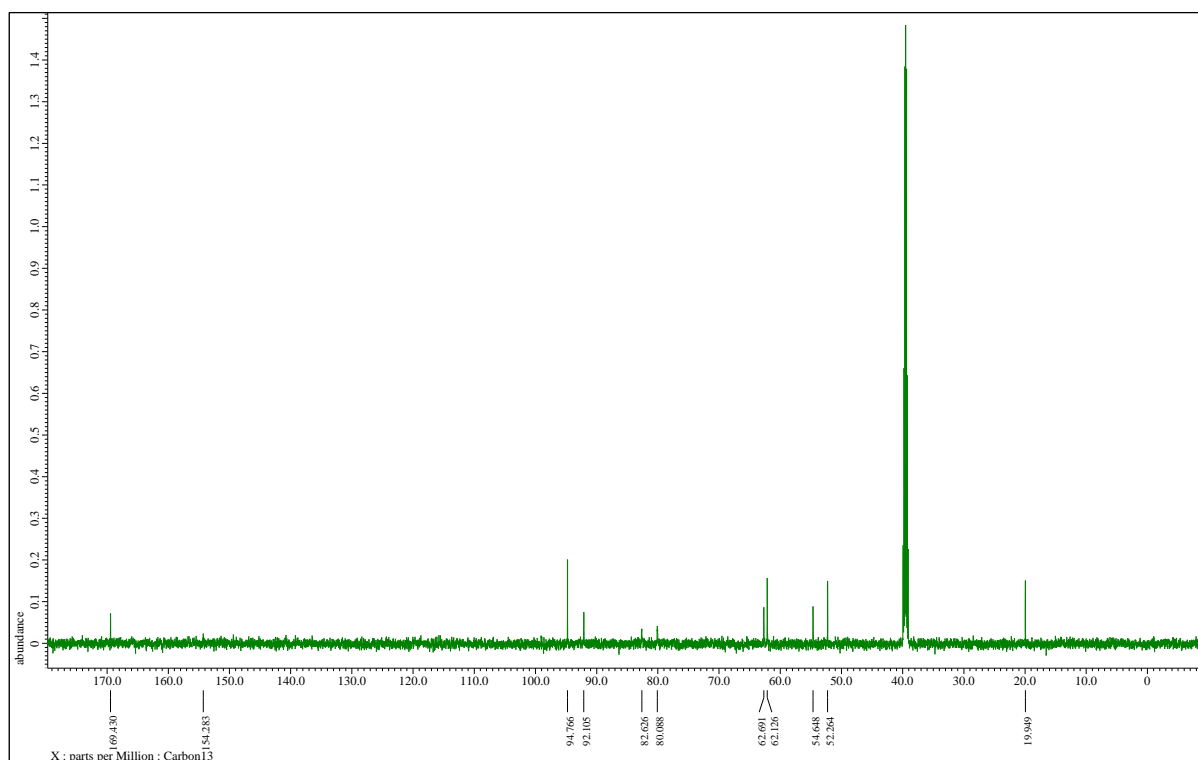
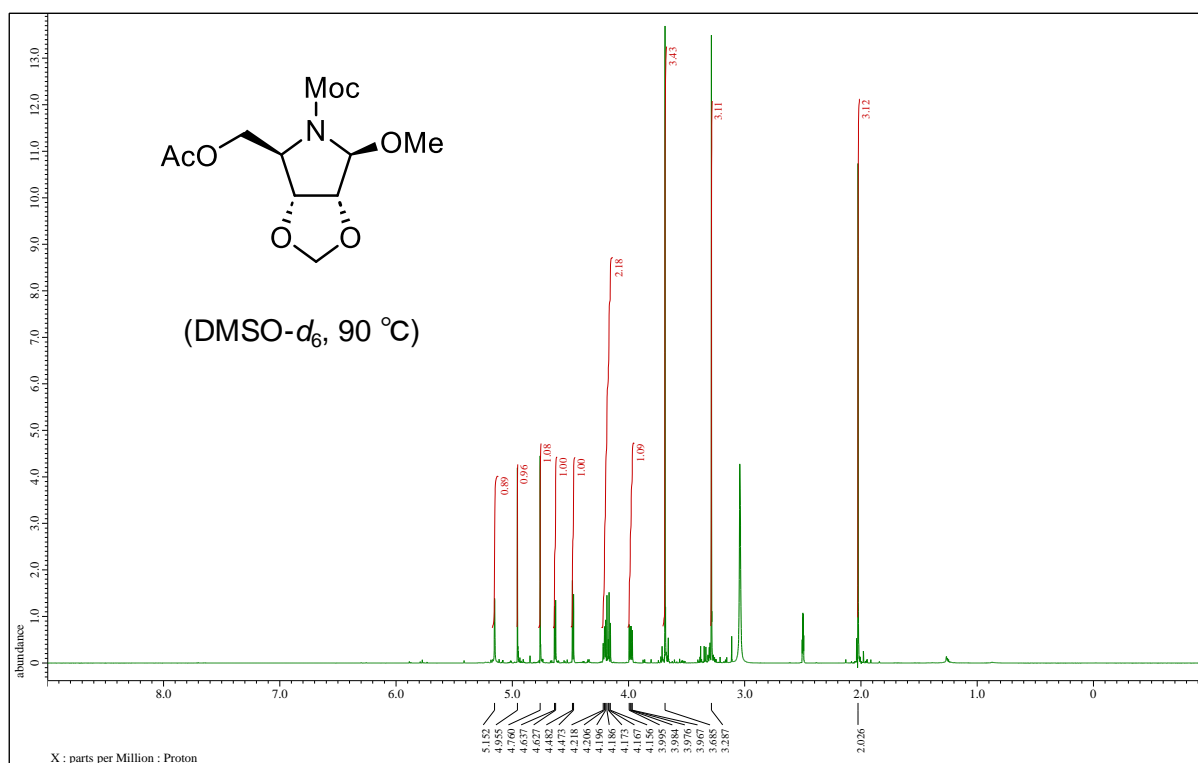
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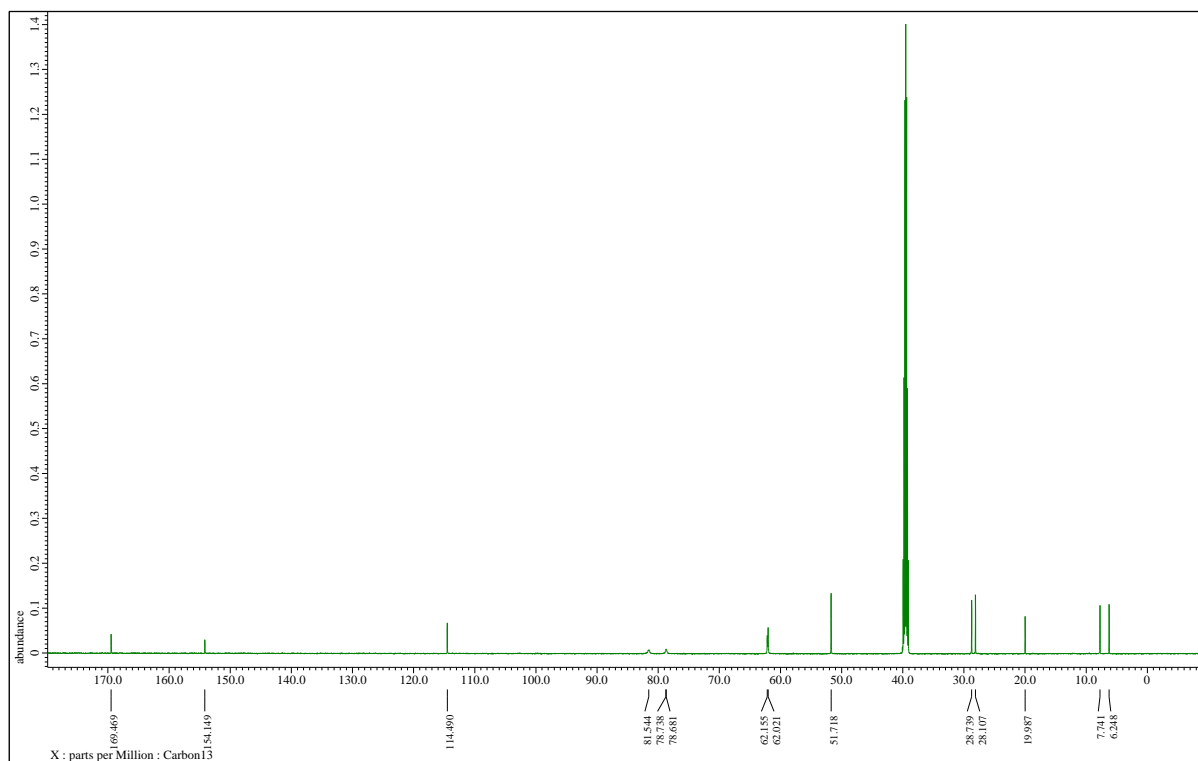
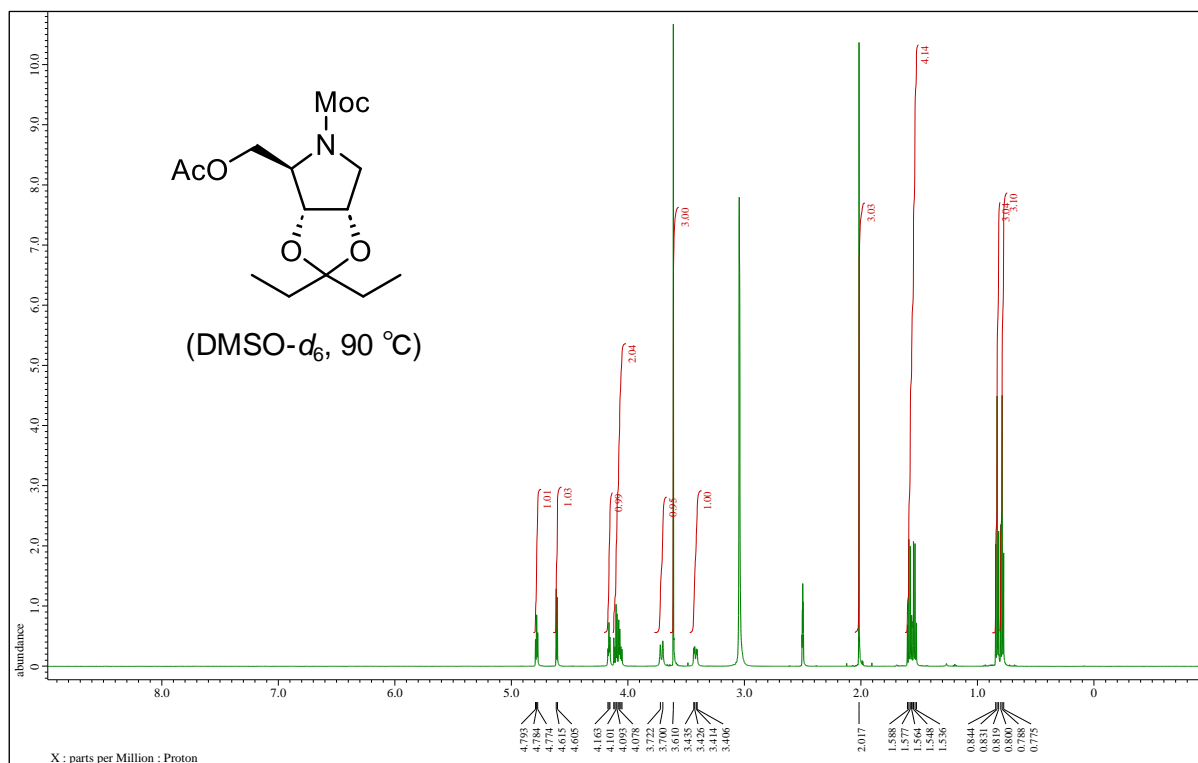
Methyl (3aR,4R,6S,6aR)-4-(acetoxymethyl)-2,2-diethyl-6-methoxytetrahydro-5H-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate



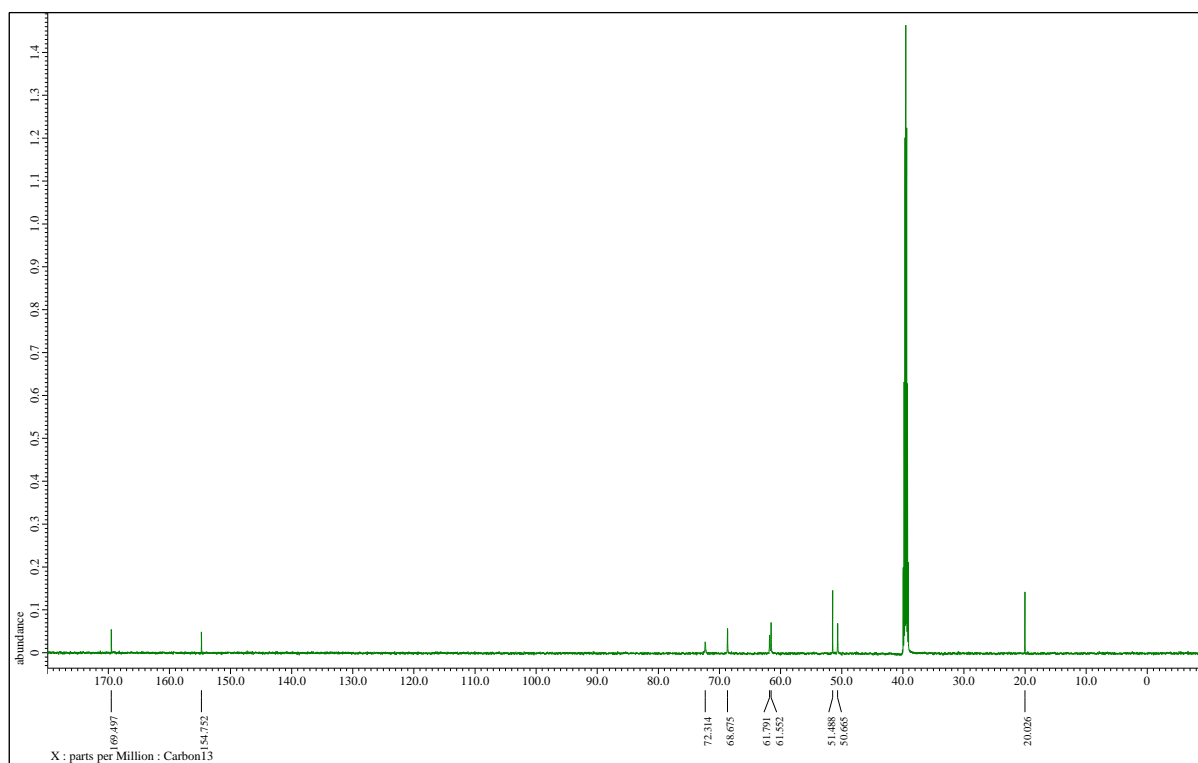
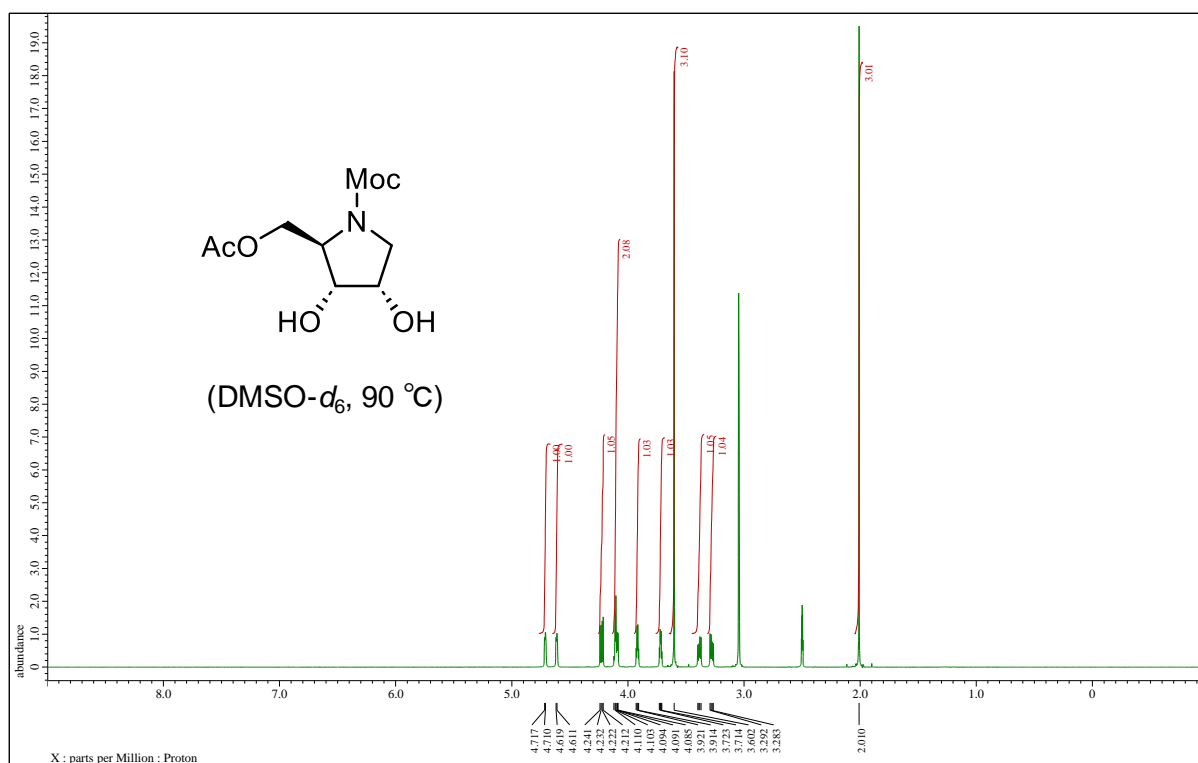
Methyl (3aR,4R,6S,6aR)-4-(acetoxymethyl)-6-methoxytetrahydro-5H-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate



Methyl (4R)-4-(acetoxymethyl)-2,2-diethyltetrahydro-5H-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate



Methyl (2R,3R,4S)-2-(acetoxymethyl)-3,4-dihydroxypyrrolidine-1-carboxylate



Methyl (3aR,4R,6aS)-4-(acetoxymethyl)tetrahydro-5H-[1,3]dioxolo[4,5-c]pyrrole-5-carboxylate

