

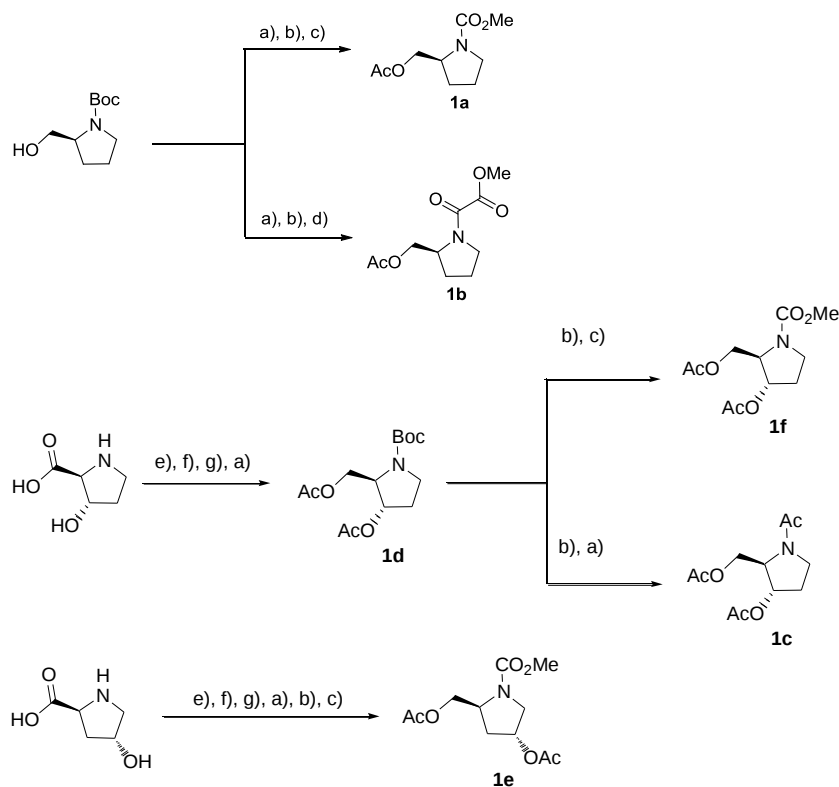
Supporting information

1. General information

^1H and ^{13}C NMR spectra were recorded in CDCl_3 or dimethyl sulfoxide- D_6 on JEOL ECA-600 spectrometer (^1H 600 MHz, ^{13}C 150MHz) or JEOL ECA-400 spectrometer (^1H 400 MHz, ^{13}C 100MHz). Mass spectra were obtained on JEOL JMS T-100LP mass spectrometer. IR spectra were measured with a JEOL JIR-WINSPEC50. Cyclic voltammetry (CV) was carried out HOKUTO DENKO HSV-100. Measurement was carried out in 0.2 M $\text{LiClO}_4/\text{CH}_3\text{NO}_2$ -10 mM acetic acid using grassy carbon as anode, platinum wire as cathode and Ag/AgCl as reference electrode. TCI precoated silica gel F₂₅₄ plates (thickness 0.25 mm) was used for thin-layer chromatography (TLC) analysis. Diastereomers were isolated by silicagel chromatography or HPLC. All materials were obtained from TCI fine chemicals, Wako Pure Chemical Industries, Kanto Chemical and Acros Organics and used without further purification.

Abbreviations: *t*Bu, *tert*-butyl; Me, methyl; AcO, acetoxy; Ac, acetyl; Ac_2O , acetic anhydride; TEA, triethylamine; DMAP, *N,N*-dimethyl-4-aminopyridine; DMDC, dimethyl dicarbonate; Boc_2O , di-*tert*-butyl dicarbonate; THF, tetrahydrofuran.

2. Preparation of electrolytic substrates



Scheme 1. a) Ac₂O, TEA, DMAP/CH₂Cl₂, b) 4 N HCl/Dioxane, c)DMDC, TEA, DMAP/CH₂Cl₂, d) MeO(CO)₂Cl, TEA, DMAP/CH₂Cl₂, e) SOCl₂/MeOH, f) Boc₂O, TEA, DMAP/CH₂Cl₂, g) LiAlH₄/THF, 0 °C.

(S)-methyl 2-(acetoxymethyl)pyrrolidine-1-carboxylate (1a):

¹H NMR (600 MHz; CDCl₃) δ 4.17-3.97 (m, 3H, H₂ and H₆), 3.68 (s, 3H, OCH₃), 3.47-3.31 (m, 2H, H₅), 2.04 (s, 3H, CH₃CO-), 2.01-1.76 (m, 4H, H₃ and H₄); ¹³C NMR (100 MHz; CDCl₃) δ 170.7, 155.5, 155.4, 64.6, 64.2, 55.9, 55.2 54.7, 52.2, 46.7, 46.3, 28.6, 27.7, 23.7, 22.8, 20.7; IR ν_{max} (cm⁻¹, neat) 2958, 2883, 1749, 1708, 1448, 1386, 1236, 1197; HRMS calc.for [C₉H₁₅NNaO₄]⁺: 224.0899, Found: 224.0889.

(S)-Methyl 2-(2-(acetoxymethyl)pyrrolidin-1-yl)-2-oxoacetate (1b):

¹H NMR (600 MHz; CDCl₃) δ 4.64 and 4.38 (m, 1H, H₂), 4.24 and 4.03 (dd, J=10.9, 5.4 Hz and dd, J=10.9, 7.5 Hz, 1H, H_{6a}), 4.20 and 3.95 (dd, J=10.9, 4.1 Hz and dd, J=10.9, 6.1 Hz, 1H, H_{6b}), 3.89 and 3.87 (s, 3H, OCH₃), 3.70-3.54, (m, 2H, H₅), 2.07 and 2.05 (s, 3H, CH₃CO-), 2.14-1.87 (m, 4H, H₃ and H₄); ¹³C NMR (150 MHz; CDCl₃) δ 170.7, 170.4, 162.4, 162.3, 158.9, 158.8, 72.4, 71.2, 64.9, 63.3, 55.9, 52.7, 47.8, 46.0, 28.2, 27.2, 24.3, 21.5, 20.9; IR ν_{max} (cm⁻¹, neat) 2958, 2888, 1741, 1660, 1454, 1367, 1234, 1166, 1041; HRMS calc.for [C₁₀H₁₅NNaO₅]⁺: 252.0898, Found: 252.0860.

((2R,3S)-3-Acetoxy-1-acetylpyrrolidin-2-yl)methyl acetate (1c):

¹H NMR (600 MHz; CDCl₃) δ 5.21 and 5.18 (m, 1H, H₃), 4.31 and 4.03 (m, 1H, H_{6a}), 4.23 (m, 1H, H_{6b}), 4.19 and 3.88 (m, 1H, H₂), 3.70 and 3.61 (m, 1H, H_{5b}), 3.59 and 3.57 (m, 1H, H_{5a}), 2.38-2.19 (m, 1H, H_{4a}), 2.17 and 2.09 (s, 3H, CH₃CO-), 2.11 and 2.07 (s, 3H, CH₃CO-), 2.06 and 2.05 (s, 3H, CH₃CO-), 2.06-2.03 (m, 1H, H_{4b}); ¹³C NMR (150 MHz; CDCl₃) δ 170.1, 170.0, 153.9, 153.8, 79.9, 79.5, 75.1, 62.4, 61.6, 44.3, 29.5, 28.6, 28.0, 20.7, 20.4; IR ν_{max} (cm⁻¹, neat) 2977, 2933, 1749, 1697, 1398, 1367, 1236, 1168, 1124, 1043; HRMS calc.for [C₁₄H₂₃NNaO₆]⁺: 324.1423, Found: 324.1427.

(2R,3S)-tert-Butyl 3-acetoxy-2-(acetoxymethyl)pyrrolidine-1-carboxylate (1d):

¹H NMR (600 MHz; CDCl₃) δ 5.21-5.13 (m, 1H, H₃), 4.25-3.87 (m, 3H, H₂ and H₆), 3.54-3.41, (m, 2H, H₅), 2.22-2.15 (m, 1H, H_{4a}), 2.07 (s, 6H, CH₃CO-), 2.03-1.95 (m, 1H, H_{4b}), 1.48 (s, 9H, O^tBu); ¹³C NMR (150 MHz; CDCl₃) δ 170.5, 170.2, 170.5, 170.4, 170.2, 170.0, 169.9, 76.1, 75.1, 62.9, 62.6, 62.1, 61.8, 45.9, 44.2, 30.3, 28.1, 22.6, 22.0, 21.1, 20.8, 20.7; IR ν_{max} (cm⁻¹, neat) 2996, 2964, 1735, 1635, 1417, 1361, 1241, 1116, 1085, 1035; HRMS calc.for [C₁₁H₁₇NNaO₅]⁺: 266.1004, Found: 266.1081; m.p.55-57 °C.

((2S,4R)-4-Acetoxy-1-acetylpyrrolidin-2-yl)methyl acetate (1e):

^1H NMR (600 MHz; CDCl_3) δ 5.32-5.21 (m, 1H, H_4), 4.49-4.21 (m, 3H, H_2 and H_6), 3.80-3.74 (m, 1H, H_{5a}), 3.74-3.68 (m, 3H, OCH_3), 3.65-3.53 (m, 1H, H_{5b}), 2.46-2.10, (m, 2H, H_3), 2.07 (s, 3H, $\text{CH}_3\text{CO-}$), 2.05 (s, 3H, $\text{CH}_3\text{CO-}$); ^{13}C NMR (150 MHz; CDCl_3) δ 170.7, 170.5, 155.4, 155.3, 72.7, 71.9, 65.0, 64.3, 57.7, 55.0, 54.4, 52.5, 36.6, 35.6, 35.0, 34.0, 21.1, 20.9; IR ν_{max} (cm^{-1} , neat) 2989, 2958, 1741, 1704, 1448, 1386, 1230, 1124, 1043, 1024; HRMS calc.for $[\text{C}_{11}\text{H}_{17}\text{NNaO}_6]^+$: 282.0953, Found: 282.1042

(2R,3S)-Methyl 3-acetoxy-2-(acetoxymethyl)pyrrolidine-1-carboxylate (1f):

^1H NMR (600 MHz; CDCl_3) δ 5.21-5.15 (m, 1H, H_3), 4.25-3.95 (m, 3H, H_2 and H_6), 3.73 (s, 3H, OCH_3), 3.61-3.45 (m, 2H, H_5), 2.27-2.16 (m, 1H, H_{4a}), 2.08 (s, 3H $\text{CH}_3\text{CO-}$), 2.06 (s, 3H $\text{CH}_3\text{CO-}$), 2.05-2.00 (m, 1H, H_{4b}); ^{13}C NMR (150 MHz; CDCl_3) δ 170.7, 170.5, 170.4, 155.6, 155.6, 76.5, 75.5, 63.0, 62.7, 62.6, 62.1, 52.8, 52.7, 45.3, 44.8, 30.1, 29.2, 21.2, 20.6; IR ν_{max} (cm^{-1} , neat) 2989, 2958, 1749, 1704, 1454, 1386, 1236, 1130, 1043, 1024; HRMS calc.for $[\text{C}_{11}\text{H}_{17}\text{NNaO}_6]^+$: 282.0953, Found: 282.1001.

3. Anodic oxidation of prolinol derivatives

Substrate **1-6** (1.0 mmol) was dissolved in 20 ml of 1.0 M LiClO_4 + dry nitromethane. This solution was then electrolyzed at 0 °C in the presence of 50 mM acetic acid at a constant current by using an undivided cell equipped with glassy carbon plate (60 mm x 20 mm) anode and Pt cathode (10 mm x 10 mm) under Ar atmosphere, and it was quenched at 2.5 F/mole unless noted otherwise. After the completion of the electrolysis, 5.0eq of nucleophile was added, allowed to stand for 16 hr at ambient temperature to yield substituted compound.

(2S)-Methyl 2-(acetoxymethyl)-5-allylpyrrolidine-1-carboxylate (2):

^1H NMR (600 MHz, CDCl_3) δ 5.80-5.66 (m, 1H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 5.10-5.02 (m, 2H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 4.23-3.97 (m, 3H, H_2 and H_6), 3.95-3.81 (m, 1H, H_5), 3.71, 3.70 and 3.70 (s, 3H, OCH_3), 2.69-2.42 (m, 1H, $-\text{CH}_{2a}\text{CH}=\text{CH}_2$), 2.21-2.07 (m, 1H, $-\text{CH}_{2b}\text{CH}=\text{CH}_2$), 2.07, 2.06 and 2.05 (s, 3H, $\text{CH}_3\text{CO-}$), 2.05-1.69 (m, 4H, H_3 and H_4); ^{13}C NMR (100 MHz; CDCl_3) δ 170.7, 155.5, 154.9, 154.6, 154.6, 135.0, 134.9, 134.7, 117.3, 117.2, 64.3, 63.5, 57.8, 56.4, 52.3, 38.2, 36.9, 27.3, 26.3, 20.9; IR ν_{max} (cm^{-1} , neat) 3077, 2939, 1749, 1700, 1452, 1380, 1240, 1112, 1039; HRMS calc.for $[\text{C}_{12}\text{H}_{19}\text{NNaO}_4]^+$: 264.1212, Found: 264.1216.

Methyl 2-((2S)-2-(acetoxymethyl)-5-allylpyrrolidin-1-yl)-2-oxoacetate (3):

^1H NMR (600 MHz, CDCl_3) δ 5.80-5.64 (m, 1H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 5.14-5.06 (m, 2H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 4.49-4.09 (m, 3H, H_2 and H_6), 4.00-3.90 (m, 1H, H_5), 3.90, 3.90, 3.89 and 3.88 (s, 3H, OCH_3), 2.80-2.44 (m, 1H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 2.30-1.75 (m, 8H, $-\text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}_3\text{CO}-$, H_3 and H_4); ^{13}C NMR (100 MHz; CDCl_3) δ 170.7, 170.7, 170.5, 170.4, 162.6, 162.5, 162.5, 159.8, 159.7, 159.2, 159.0, 134.2, 133.7, 133.5, 118.4, 118.1, 118.0, 64.3, 63.5, 57.8, 56.4, 52.3, 38.2, 36.9, 27.3, 26.3, 20.9; IR ν_{max} (cm^{-1} , neat) 3077, 2952, 2921, 1743, 1654, 1450, 1361, 1224, 1043; HRMS calc.for $[\text{C}_{13}\text{H}_{19}\text{NNaO}_5]^+$: 292.1161, Found: 292.1220.

((2R,3S)-3-Acetoxy-1-acetyl-5-allylpyrrolidin-2-yl)methyl acetate (4):

^1H NMR (600 MHz, CDCl_3) δ 5.80-5.65 (m, 1H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 5.25-5.00 (m, 3H, $-\text{CH}_2\text{CH}=\text{CH}_2$ and H_3), 4.55-3.83 (m, 4H, H_2 , H_6 and H_5), 2.61-2.01 (m, 13H, $-\text{CH}_2\text{CH}=\text{CH}_2$, H_4 and $\text{CH}_3\text{CO}-$); ^{13}C NMR (100 MHz; CDCl_3) δ 172.2, 172.1, 171.2, 171.2, 170.9, 170.5, 170.4, 135.3, 133.9, 119.0, 117.7, 75.6, 63.8, 63.4, 63.1, 61.9, 59.0, 57.6, 39.7, 37.3, 33.4, 31.5, 23.0, 21.4, 21.3, 20.9; IR ν_{max} (cm^{-1} , neat) 3087, 2956, 2923, 1727, 1646, 1413, 1390, 1249, 1147, 1095; HRMS calc.for $[\text{C}_{14}\text{H}_{21}\text{NNaO}_5]^+$: 306.1317 Found: 306.1307.

(2R,3S)-tert-Butyl 3-acetoxy-2-(acetoxymethyl)-5-allylpyrrolidine-1-carboxylate (5):

^1H NMR (600 MHz, CDCl_3) δ 5.80-5.64 (m, 1H), 5.17-5.00 (m, 3H, $-\text{CH}_2\text{CH}=\text{CH}_2$, H_3), 4.30-3.77 (m, 4H, H_2 and H_6 and H_5), 3.01-2.70 (m, 1H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 2.28-2.13 (m, 2H, $-\text{CH}_2\text{CH}=\text{CH}_2$ and H_{4a}), 2.10, 2.08, 2.07 and 2.06 (s, 6H, $\text{CH}_3\text{CO}-$), 2.03-1.95 (m, 1H, H_{4b}), 1.47 (s, 9H, O^tBu); ^{13}C NMR (150 MHz; CDCl_3) δ 170.6, 170.5, 170.4, 170.2, 153.6, 153.2, 135.2, 135.1, 133.8, 117.9, 117.5, 117.4, 80.4, 80.2, 75.7, 63.0, 62.6, 61.9, 57.4, 57.3, 38.9, 37.6, 33.2, 32.2, 28.4, 21.3, 20.9; IR ν_{max} (cm^{-1} , neat) 3075, 2975, 2931, 1747, 1702, 1452, 1396, 1232, 1178, 1114, 1066; HRMS calc.for $[\text{C}_{17}\text{H}_{27}\text{NNaO}_6]^+$: 364.1736, Found: 364.1685.

(3R,5S)-Methyl 3-acetoxy-5-(acetoxymethyl)-2-allylpyrrolidine-1-carboxylate (6):

^1H NMR (600 MHz, CDCl_3) δ 5.88-5.67 (m, 1H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 5.40-4.98 (m, 3H, $-\text{CH}_2\text{CH}=\text{CH}_2$ and H_4), 4.47-3.88 (m, 4H, H_2 , H_6 and H_5), 3.73 and 3.72 (s, 3H, OCH_3), 2.50-2.32 (m, 1H, $-\text{CH}_2\text{CH}=\text{CH}_2$), 2.28-2.11 (m, 3H, $-\text{CH}_2\text{CH}=\text{CH}_2$ and H_3), 2.08 and 2.08 (s, 3H, $\text{CH}_3\text{CO}-$), 2.06 and 2.03 (s, 3H, $\text{CH}_3\text{CO}-$); ^{13}C NMR (150 MHz; CDCl_3) δ 170.7, 170.4, 155.9, 133.7, 117.8, 75.9, 75.4, 71.6, 64.9, 64.0, 58.2, 55.9, 55.1, 53.5, 52.4, 37.7, 32.5, 32.1, 31.2, 29.7, 21.2, 20.9; IR ν_{max} (cm^{-1} , neat) 3068, 2987, 2956, 1739, 1702, 1446, 1384, 1234, 1128, 1029; HRMS calc.for $[\text{C}_{14}\text{H}_{21}\text{NNaO}_6]^+$: 322.1267, Found: 322.1231.

(2R,3S)-Methyl 3-acetoxy-2-(acetoxymethyl)-5-(2,4,6-trimethoxyphenyl)pyrrolidine-1-carboxylate

(7):

^1H NMR (600 MHz, CDCl_3) δ 6.12 (s, 2H, Ar), 5.54 and 5.41 (dd, $J=10.9$, 6.8 Hz and $J=10.9$, 7.7 Hz, 1H, H_5), 5.20 (d, $J=4.5\text{Hz}$ 1H, H_3), 4.37-4.04 (m, 3H, H_2 and H_6), 3.86-3.74 (m, 9H, $\text{Ar}(\text{OCH}_3)_3$), 3.63 and 3.47 (s, 3H, $\text{C}(\text{O})\text{OCH}_3$), 2.65-2.55 (ddd, $J=15.5$, 11.4, 4.5 Hz, 1H, H_{4a}), 2.12 (s, 3H, $\text{CH}_3\text{CO}-$), 2.09; (s, 3H, $\text{CH}_3\text{CO}-$), 2.11-2.07 (m, 1H, H_{4b}); ^{13}C NMR (150 MHz; CDCl_3) δ 171.0, 170.5, 160.3, 159.5, 159.0, 158.9, 158.9, 156.3, 156.3, 155.4, 154.8, 154.2, 108.4, 107.9, 90.9, 75.2, 63.4, 55.4, 52.3, 33.6, 21.3, 20.9; IR ν_{max} (cm^{-1} , neat) 3079, 2973, 2929, 1745, 1695, 1394, 1365, 1240, 1176, 1114, 1058, 772; HRMS calc.for $[\text{C}_{20}\text{H}_{27}\text{NNaO}_9]^+$: 448.1583, Found: 448.1631; m.p.150-153 $^\circ\text{C}$.

(2R,3S)-Methyl 3-acetoxy-2-(acetoxymethyl)-5-(phenylthio)pyrrolidine-1-carboxylate (8):

α -anomer; ^1H NMR (600 MHz, CDCl_3) δ 7.58-7.48 (m, 2H, Ar), 7.38-7.30 (m, 3H, Ar), 5.35 (t, $J=6.9$ Hz, 1H, H_5), 5.25-5.16 (m, 1H, H_3), 4.30-3.87 (m, 3H, H_2 and H_6), 3.84-3.43 (m, 3H, OCH_3), 2.55-2.39 (m, 2H, H_4), 2.11 (s, 3H, $\text{CH}_3\text{CO}-$), 2.03 (s, 3H, $\text{CH}_3\text{CO}-$); ^{13}C NMR (150 MHz; CDCl_3) δ 170.6, 170.2 155.0, 134.8, 129.0, 128.6, 74.4, 66.0, 63.1, 62.6, 52.9, 39.0, 21.1, 21.0; IR ν_{max} (cm^{-1} , neat) 3062, 2958, 2925, 1747, 1702, 1448, 1367, 1241, 1122, 1041, 742; HRMS calc.for $[\text{C}_{17}\text{H}_{21}\text{NNaO}_6\text{S}]^+$: 390.0987, Found: 390.0966.

β -anomer; ^1H NMR (600 MHz, CDCl_3) δ 7.66-7.61 (m, 1H, Ar), 7.49-7.44 (m, 1H, Ar), 7.36-7.27 (m, 3H, Ar), 5.33-5.22 (m, 1H, H_5), 5.22-5.16 (m, 1H, H_3), 4.33-4.06 (m, 3H, H_2 and H_6), 3.78 and 3.42 (s, 3H, OCH_3), 2.82-2.46 (m, 2H, H_4), 2.16 (s, 3H, $\text{CH}_3\text{CO}-$), 2.05 (s, 3H, $\text{CH}_3\text{CO}-$); ^{13}C NMR (150 MHz; CDCl_3) δ 171.9, 170.4, 154.5, 133.2, 132.8, 128.9, 127.6, 75.0, 69.2, 68.3, 64.9, 63.2, 62.7, 61.7, 53.0 52.4, 39.6, 39.0, 21.3, 20.9; IR ν_{max} (cm^{-1} , neat) 3060, 2960, 2927, 1743, 1699, 1452, 1375, 1232, 1126, 1051, 1025, 744; HRMS calc.for $[\text{C}_{17}\text{H}_{21}\text{NNaO}_6\text{S}]^+$: 390.0987, Found: 390.0975.

(2R,3S,5R)-Methyl

3-acetoxy-2-(acetoxymethyl)-5-(4-benzamido-2-oxopyrimidin-1(2H)-yl)pyrrolidine-1-carboxylate

(α anomer) (9a):

^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 11.05 (br, 1H, ArCONH), 8.15-8.09 (m, 1H, H_6'), 8.00 (d, $J=7.5\text{Hz}$, 2H, Ar), 7.61 (t, $J=7.5\text{Hz}$, 1H, Ar), 7.50 (t, $J=7.5\text{Hz}$, 2H, Ar), 7.34-7.28 (m, 1H, H_5'), 6.13-6.09 (m, 1H, H_5), 5.14-5.11 (m, 1H, H_4), 4.47-4.26 (m, 3H, H_2 and H_6), 3.69 and 3.58 (m, 3H, OCH_3), 2.83-2.77 (m, 1H, H_{4a}), 2.06 (s, 3H, $\text{CH}_3\text{CO}-$), 2.04-1.98 (m, 1H, H_{4b}), 1.91 (s, 3H, $\text{CH}_3\text{CO}-$); ^{13}C NMR (150 MHz; $\text{DMSO}-d_6$) δ 170.6, 170.2, 160.1, 153.8, 145.7, 141.2, 133.2, 129.0, 128.9, 112.5, 74.9, 67.6, 65.6, 64.5,

53.6, 53.4, 35.0, 21.3, 21.0; IR $\nu_{\max}$ (cm⁻¹, neat) 3320, 3189, 2964, 2921, 1735, 1643, 1452, 1378, 1243, 1112, 1081, 790; HRMS calc.for [C₂₂H₂₄N₄NaO₈]⁺: 495.1492, Found: 495.1491; m.p. 125-130 °C.

(2R,3S,5S)-Methyl

3-acetoxy-2-(acetoxymethyl)-5-(4-benzamido-2-oxopyrimidin-1(2H)-yl)pyrrolidine-1-carboxylate (β anomer) (9b):

¹H NMR (600 MHz, DMSO-D₆) δ 8.06-8.04 (d, *J*=7.5 Hz, 1H, H_{6'}), 7.98-7.95 (dd, *J*=8.2, 1.3 Hz, 2H, Ar), 7.61-7.57 (ddd, *J*=8.2, 7.5, 1.3 Hz, 1H, Ar), 7.50-7.47 (dd, *J*= 8.5, 7.5 Hz, 2H, Ar), 7.32-7.26 (m, 1H, H_{5'}), 6.05 (t, *J*=7.5 Hz, 1H, H₅), 5.17-5.14 (m, 1H, H₃), 4.35-4.30 (m, 2H, H₆), 4.17-4.13 (m, 1H, H₄), 3.61 (s, 3H, OCH₃), 2.60-2.55 (m, 1H, H_{4a}), 2.46-2.42 (m, 1H, H_{4b}), 2.03 (s, 3H, CH₃CO-), 1.99 (s, 3H, CH₃CO-); ¹³C NMR (150 MHz; DMSO-D₆) δ 170.6, 170.5, 163.4, 155.5, 154.9, 145.9, 133.8, 133.3, 129.0, 128.9, 96.8, 74.3, 73.1, 64.5, 63.8, 63.4, 53.8, 37.1, 21.4, 21.1; IR $\nu_{\max}$ (cm⁻¹, neat) 3322, 3189, 2970, 2924, 1729, 1652, 1455, 1378, 1248, 1110, 1077, 793; HRMS calc.for [C₂₂H₂₄N₄NaO₈]⁺: 495.1492, Found: 495.1489; m.p. 135-141 °C.

(2R,3S)-Methyl 5-(2-acetamido-6-oxo-1H-purin-9(6H)-yl)-3-acetoxy-2-(acetoxymethyl)pyrrolidine-1-carboxylate (α anomer) (10a):

¹H NMR (600 MHz, DMSO-D₆) δ 7.94 (s, 1H, H_{8'}), 6.13 (d, *J*=7.5 Hz, 1H, H₅), 5.13 (d, *J*=5.5 Hz, 1H, H₃), 4.47-4.37 (m, 1H, H₂), 4.30-4.16 (m, 2H, H₆), 3.58 and 3.39 (s, 3H, OCH₃), 2.80-2.71 (m, 1H, H_{4a}), 2.13 (s, 3H, CH₃CO-), 2.10-2.03 (m, 1H, H_{4a}), 2.00 (s, 3H, CH₃CO-), 1.85 (s, 3H, CH₃CO-); ¹³C NMR (150 MHz, DMSO-D₆) δ 170.6, 170.3, 155.0, 134.8, 129.0, 128.6, 74.4, 66.0, 63.1, 62.6, 52.9, 39.0, 21.1, 21.0; IR $\nu_{\max}$ (cm⁻¹, neat) 3153, 2979, 2960, 1735, 1791, 1450, 1380, 1255, 1132, 1037, 781; HRMS calc.for [C₁₈H₂₂N₆NaO₈]⁺: 473.1397, Found: 473.1387; m.p. 145-151°C.

(2R,3S)-Methyl 5-(2-acetamido-6-oxo-1H-purin-9(6H)-yl)-3-acetoxy-2-(acetoxymethyl)pyrrolidine-1-carboxylate (β anomer) (10b):

¹H NMR (600 MHz, DMSO-D₆) δ 7.91 (s, 1H, H_{8'}), 6.16 (t, *J*=7.5Hz, 1H, H₅), 5.18 (d, *J*=4.8Hz, 1H, H₃), 4.40-4.28 (m, 2H, H₆), 4.12-4.05 (m, 1H, H₂), 3.50 (s, 3H, OCH₃), 2.86-2.78 (m, 1H, H_{4a}), 2.58-2.50 (m, 1H, H_{4b}), 2.12 (s, 3H, CH₃CO-), 1.99 (s, 3H, CH₃CO-), 1.96 (s, 3H, CH₃CO-); ¹³C NMR (150 MHz; DMSO-D₆) δ 173.6, 170.2, 169.9, 155.1, 154.9 148.6, 147.8, 138.0, 120.3, 73.4, 67.8, 62.9, 62.5, 53.1, 36.2, 23.9, 20.9, 20.7; IR $\nu_{\max}$ (cm⁻¹, neat) 3150, 2977, 2961, 1731, 1688, 1452, 1377, 1236, 1130, 1040, 781; HRMS calc.for [C₁₈H₂₂N₆NaO₈]⁺: 473.1397, Found: 473.1383; m.p. 135-140°C.

(2R,3S)-Methyl 3-acetoxy-2-(acetoxymethyl)-5-(6-benzamido-9H-purin-9-yl)pyrrolidine-1-

carboxylate (α anomer) (11a):

^1H NMR (600 MHz, DMSO- D_6) δ 11.09 (br, 1H, ArCONH), 8.73 (s, 1H, H_8'), 8.65-8.55 (m, 1H, H_2'), 8.05 (d, $J=7.5\text{Hz}$, 2H, Ar), 7.63 (t, $J=7.5\text{Hz}$, 1H, Ar), 7.54 (t, $J=7.5\text{Hz}$, 2H, Ar), 6.58-6.53 (m, 1H, H_5), 5.26-5.19 (m, 1H, H_3), 4.61- 4.51 (m, 1H, H_2), 4.40-4.25 (m, 2H, H_6), 3.65 and 3.42 (s, 3H, OCH₃), 3.02-2.93 (m, 1H, H_{4a}), 2.27-2.16 (m, 1H, H_{4b}), 2.10 (s, 3H, CH₃CO-), 1.93 and 1.90 (s, 3H, CH₃CO-); ^{13}C NMR (150 MHz; DMSO- D_6) δ 170.7, 170.3, 166.1, 154.0, 153.6, 152.3, 152.2, 151.9, 151.8, 150.5, 150.4, 142.9, 133.9, 132.9, 128.9, 125.9, 75.7, 74.6, 68.4, 68.0, 64.2, 63.6, 62.1, 61.6, 53.4, 38.0, 37.1, 21.4, 21.4, 21.2, 21.1; IR ν_{max} (cm^{-1} , neat) 3259, 3066, 2998, 2956, 1743, 1710, 1608, 1488, 1367, 1240, 1056, 1037, 796; HRMS calc.for $[\text{C}_{23}\text{H}_{24}\text{N}_6\text{NaO}_7]^+$: 519.1604, Found: 519.1581.

(2R,3S)-Methyl 3-acetoxy-2-(acetoxymethyl)-5-(6-benzamido-9H-purin-9-yl)pyrrolidine-1-carboxylate (β anomer) (11b):

^1H NMR (600 MHz, DMSO- D_6) δ 11.20 (br, 1H, ArCONH), 8.74 (s, 1H, H_8'), 8.52 (s, 1H, H_2'), 8.04 (d, $J=7.7\text{Hz}$, 2H, Ar), 7.65 (t, $J=7.3\text{Hz}$, 1H, Ar), 7.55 (t, $J=7.3\text{Hz}$, 2H, Ar), 6.50 (t, $J=7.3\text{Hz}$, 1H, H_5), 5.37 (d, $J=4.5\text{Hz}$, 1H, H_3), 4.66- 4.56 (m, 1H, H_{6a}), 4.47-4.38, (m, 1H, H_{6b}), 4.24-4.14 (m, 1H, H_2), 3.67-3.48 (m, 3H, OCH₃), 3.30-3.17 (m, 1H, H_{4a}), 2.75-2.63 (m, 1H, H_{4b}), 2.09 (s, 3H, CH₃CO-), 2.02 (s, 3H, CH₃CO-); ^{13}C NMR (150 MHz; DMSO- D_6) δ 170.7, 170.4, 166.2, 155.6, 151.9, 151.6, 150.8, 145.1, 135.5, 133.8, 132.9, 128.9, 126.6, 74.0, 69.2, 63.4, 62.8, 53.5, 34.9, 21.4, 21.1; IR ν_{max} (cm^{-1} , neat) 3250, 3053, 2994, 2970, 1735, 1699, 1603, 1476, 1370, 1251, 1050, 1029, 785; HRMS calc.for $[\text{C}_{23}\text{H}_{24}\text{N}_6\text{NaO}_7]^+$: 519.1604, Found: 519.1622.

(2R,3S)-Methyl 3-acetoxy-2-(acetoxymethyl)-5-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)pyrrolidine-1-carboxylate (α -anomer) (12a):

^1H NMR (600 MHz, DMSO- D_6) δ 11.16 (br, 1H, H_3'), 7.43 (s, 1H, H_6'), 6.07 (d, $J=7.3\text{Hz}$, 1H, H_5), 5.06 (d, $J=5.0\text{Hz}$, 1H, H_3), 4.48-4.35 (m, 1H, H_2), 4.32-4.11 (m, 2H, H_6), 3.63 and 3.55 (s, 3H, OCH₃), 2.79-2.66 (m, 1H, H_{4a}), 2.02 (s, 3H, CH₃CO-), 1.96-1.87 (m, 4H, H_{4b} and CH₃CO-), 1.77 (s, 3H, CH₃C₅); ^{13}C NMR (150 MHz; DMSO- D_6) δ 169.9, 169.4, 163.7, 163.6, 153.0, 150.4, 135.7, 107.9, 74.5, 73.5, 68.9, 68.4, 63.6, 63.0, 61.4, 60.4, 52.7, 36.6, 36.1, 20.7, 20.4, 11.9; IR ν_{max} (cm^{-1} , neat) 3214, 2958, 2927, 1749, 1699, 1450, 1373, 1132, 1095, 1049, 777; HRMS calc.for $[\text{C}_{16}\text{H}_{21}\text{N}_3\text{NaO}_8]^+$: 406.1226, Found: 406.1150; m.p. 84°C.

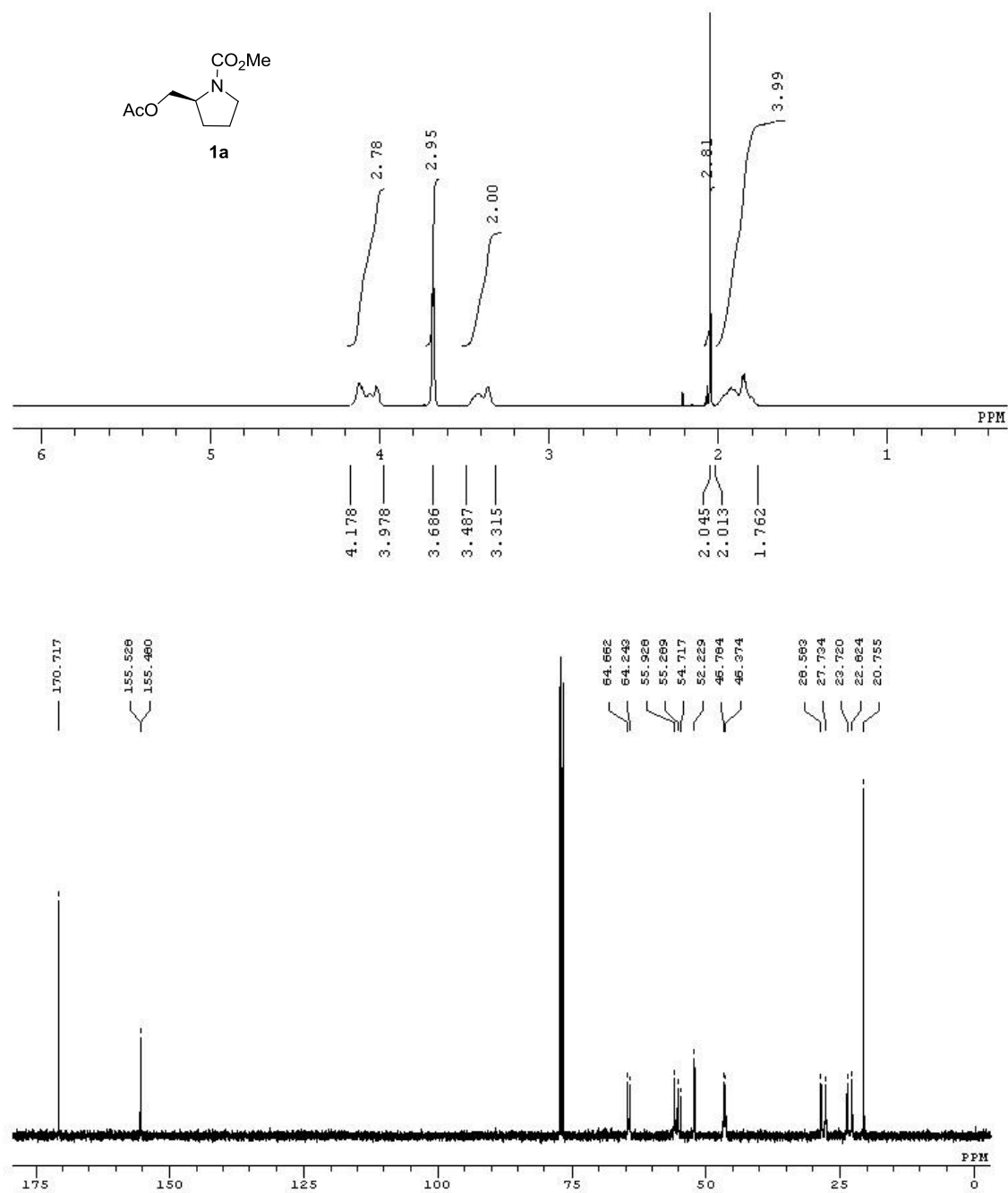
(2R,3S)-Methyl 3-acetoxy-2-(acetoxymethyl)-5-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)pyrrolidine-1-carboxylate (β -anomer) (12b):

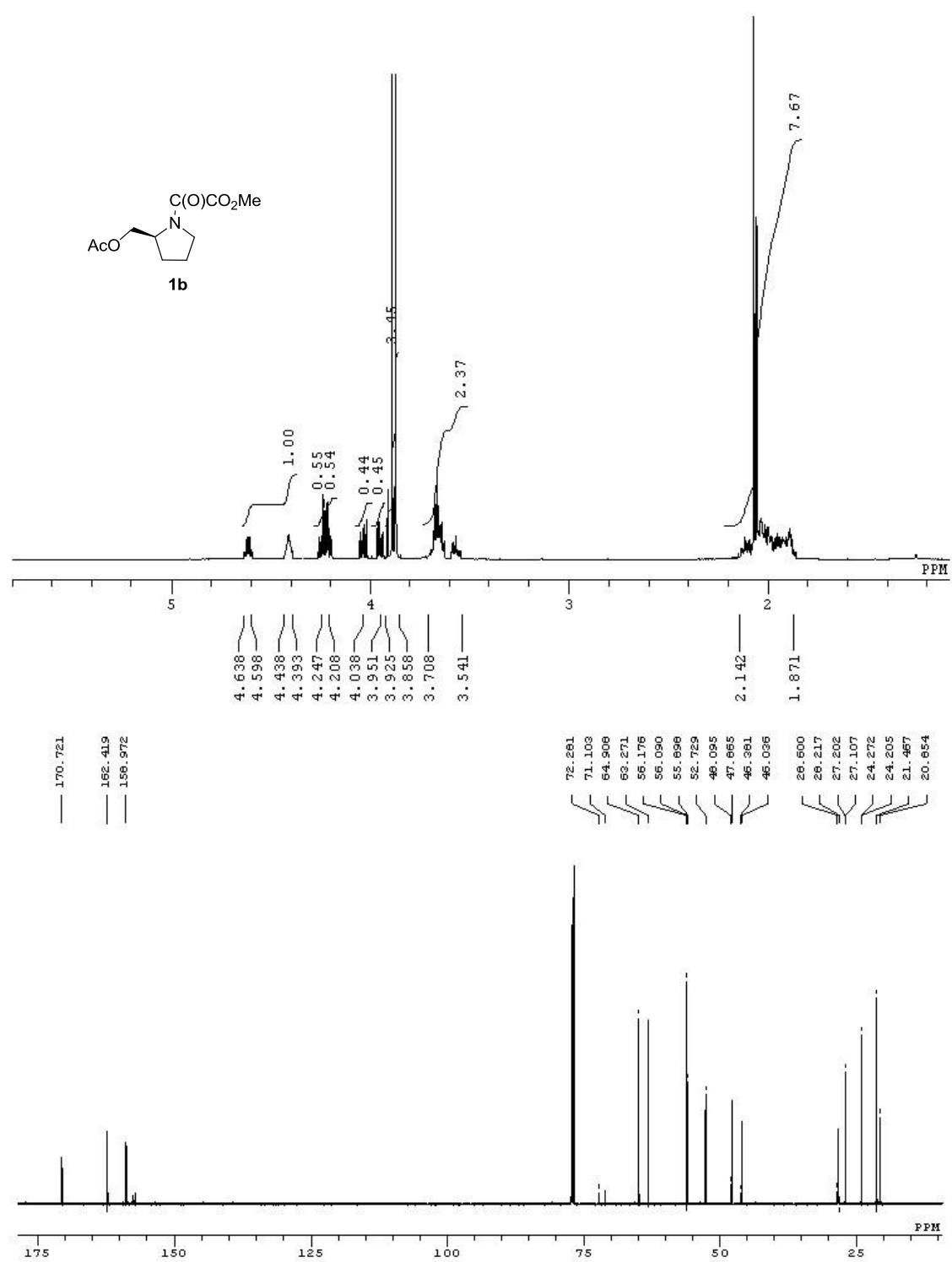
^1H NMR (600 MHz, DMSO- D_6) δ 11.23 (br, 1H, H_3 '), 7.39 (s, 1H, H_6 '), 6.05 (d, $J=7.5\text{Hz}$, 1H, H_5), 5.15 (, $J=4.8\text{Hz}$, 1H, H_3), 4.32 (m, 2H, H_6), 4.06 (m, 1H, H_2), 3.61 (s, 3H, OCH_3), 2.53-2.45 (m, 1H, H_{4a}), 2.41-2.35 (m, 1H, H_{4b}), 2.05 (s, 6H, $\text{CH}_3\text{CO-}$), 1.78 (s, 3H, CH_3C_5); ^{13}C NMR (150 MHz; DMSO- D_6) δ 169.9, 169.7, 166.9, 163.6, 154.9, 150.2, 136.3, 109.1, 73.4, 70.0, 67.4, 63.1, 62.7, 53.0, 35.3, 20.7, 20.5, 12.1; IR ν_{max} (cm^{-1} , neat) 3272, 2962, 2925, 1718, 1687, 1452, 1373, 1130, 1076, 1045, 771; HRMS calc.for $[\text{C}_{16}\text{H}_{21}\text{N}_3\text{NaO}_8]^+$: 406.1226, Found: 406.1253; m.p. 78°C .

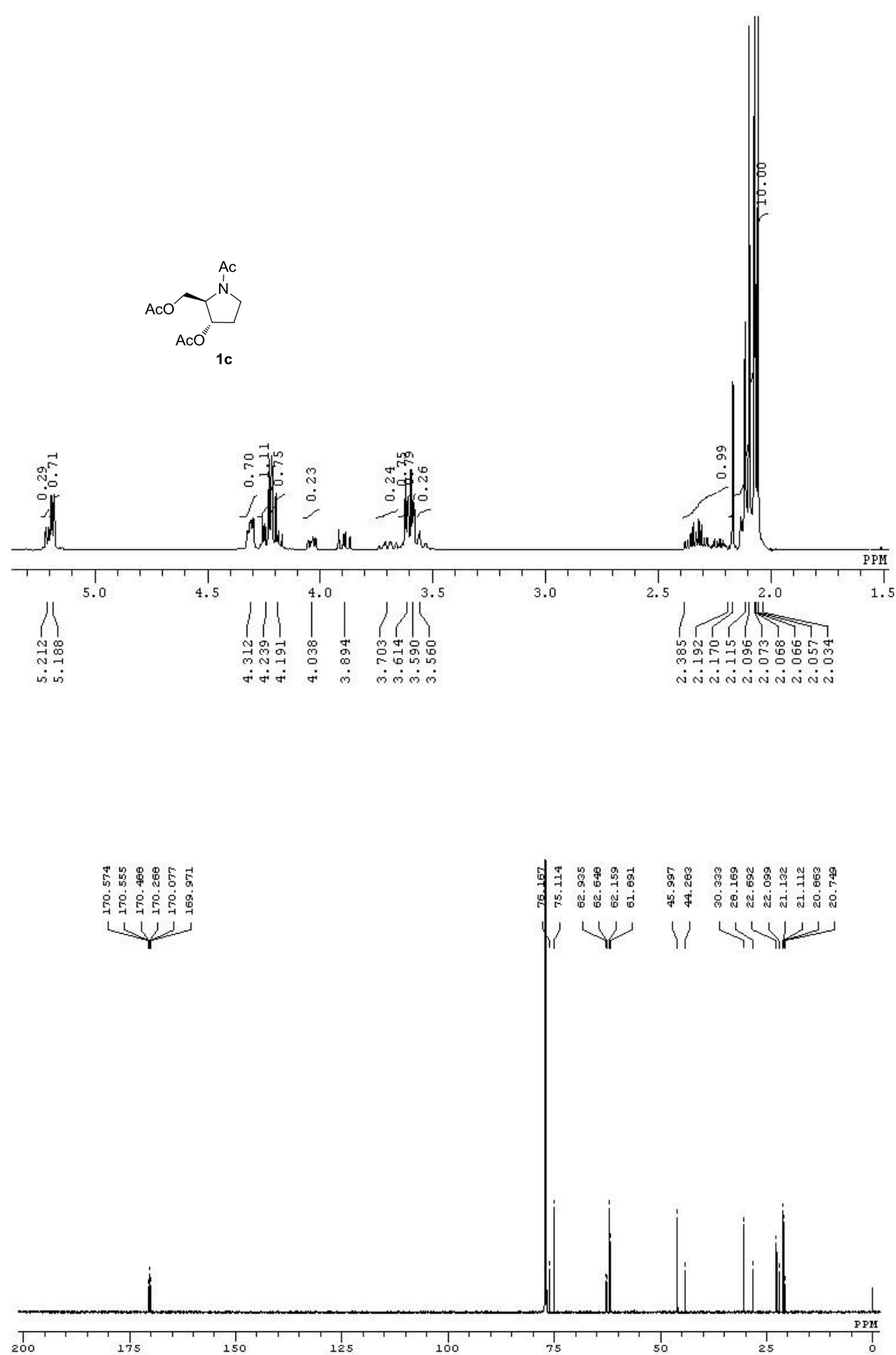
(2*R*,3*S*)-Methyl 3-acetoxy-2-(acetoxymethyl)-5-hydroxypyrrolidine-1-carboxylate (13):

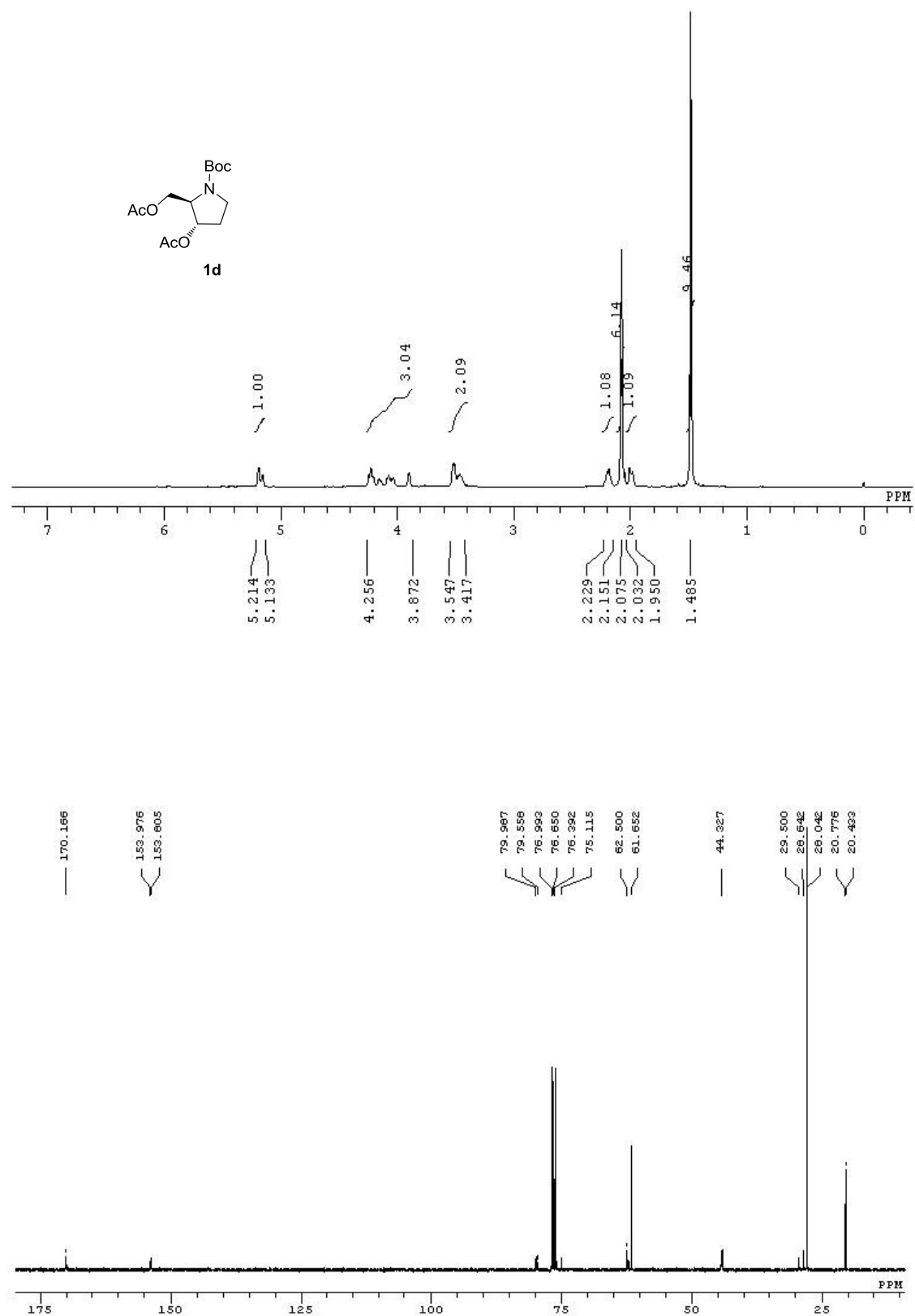
^1H NMR (600 MHz, DMSO- D_6) δ 6.07-5.72 (m, 1H, OH), 5.48-5.26 (m, 1H, H_5), 5.12-4.93 (m, 1H, H_3), 4.24-3.84 (m, 3H, H_2 and H_6), 3.58 and 3.58 (s, 3H, OCH_3), 2.34-1.73 (m, 8H, H_4 , $\text{CH}_3\text{CO-}$); ^{13}C NMR (150 MHz; DMSO- D_6) δ 170.2, 170.1, 154.5, 154.3, 81.0, 80.4, 75.5, 74.5, 62.5, 62.1, 61.9, 61.5, 61.3, 52.3, 52.2, 38.5, 37.6, 20.9, 20.8, 20.6, 20.6; IR ν_{max} (cm^{-1} , neat) 3469, 2969, 2944, 1635, 1616, 1459, 1361, 1141, 1116, 1079; HRMS calc.for $[\text{C}_{11}\text{H}_{17}\text{NNaO}_7]^+$: 298.0903, Found: 298.0915.

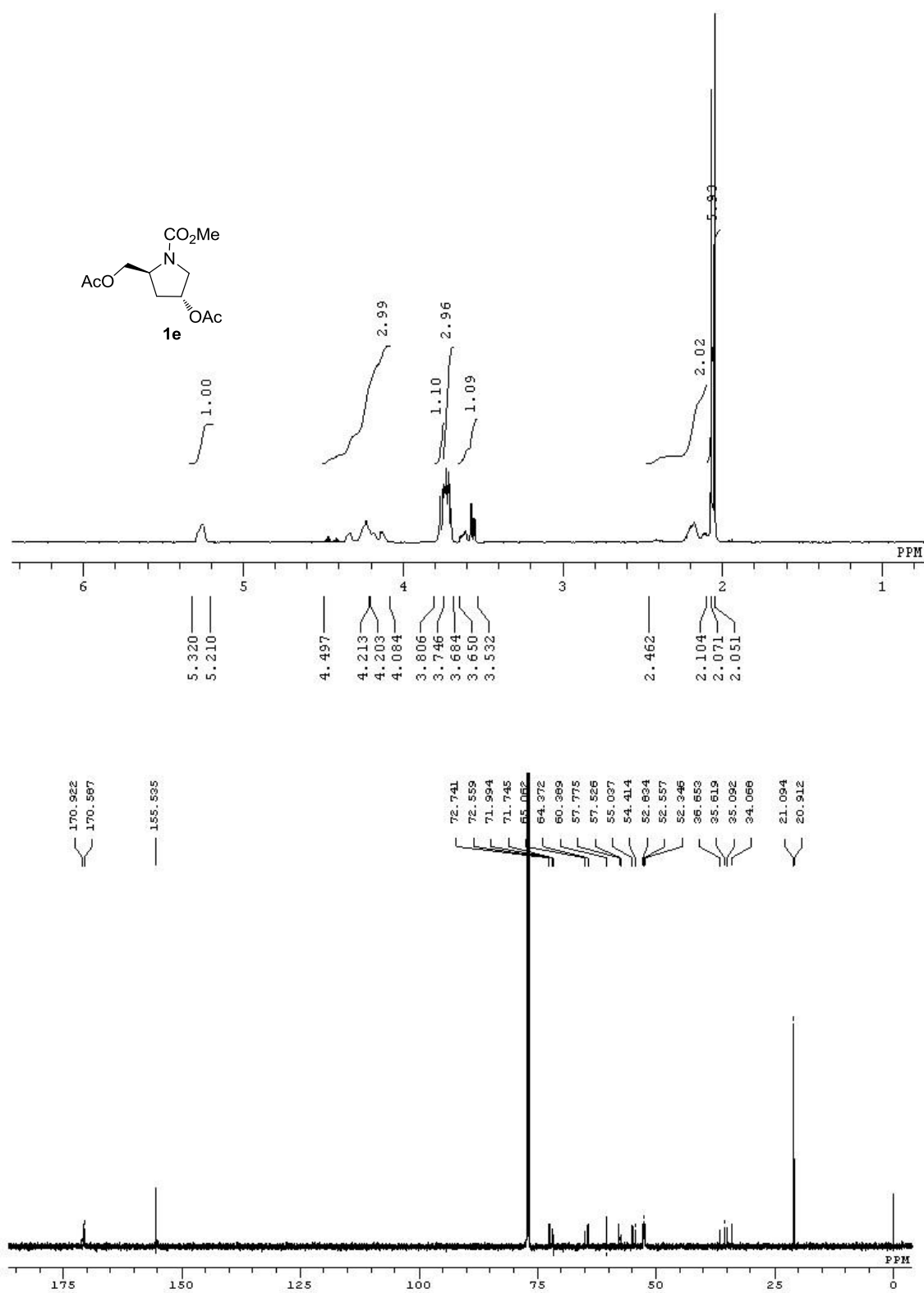
4. ^1H and ^{13}C NMR spectrum

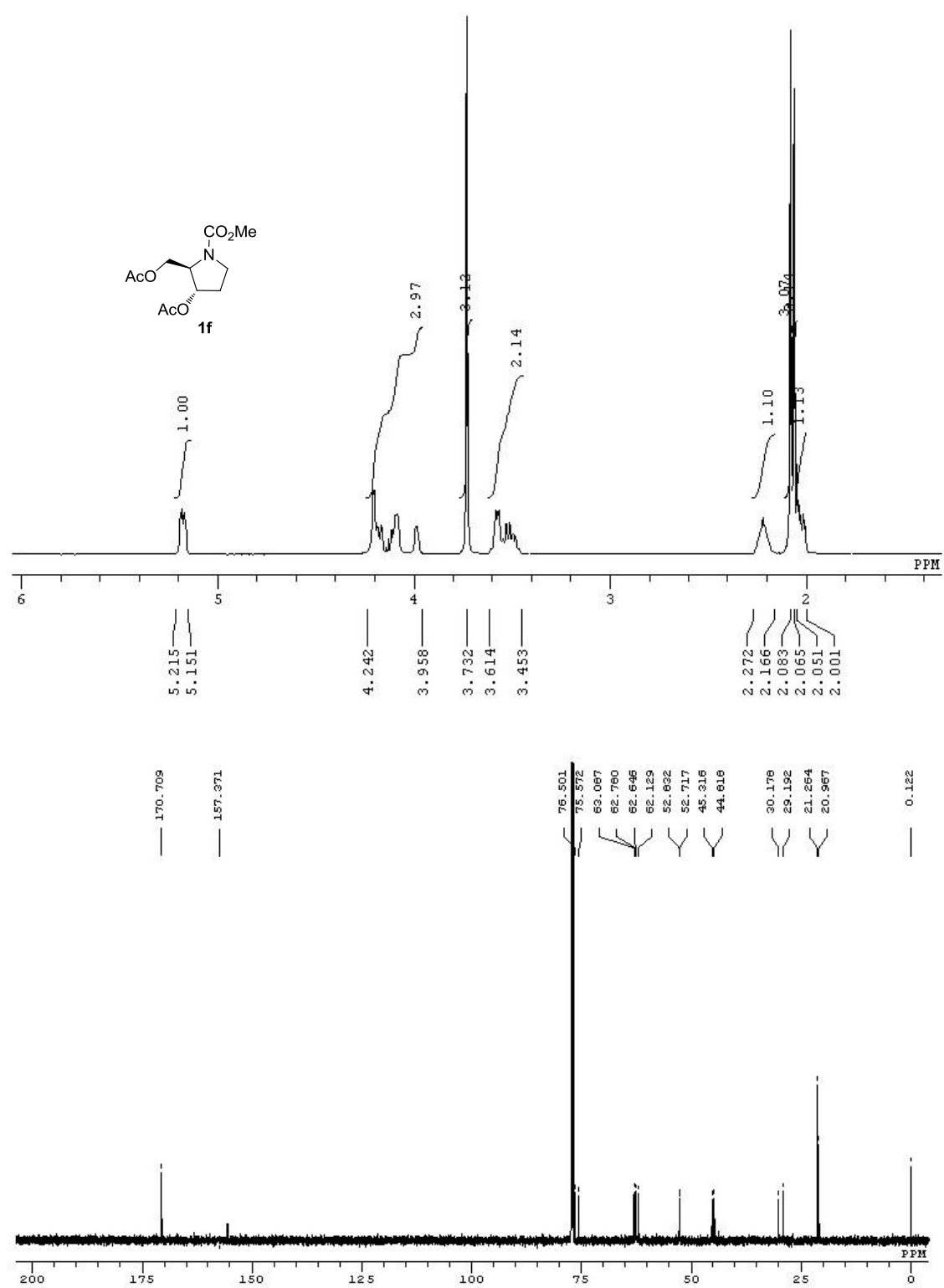


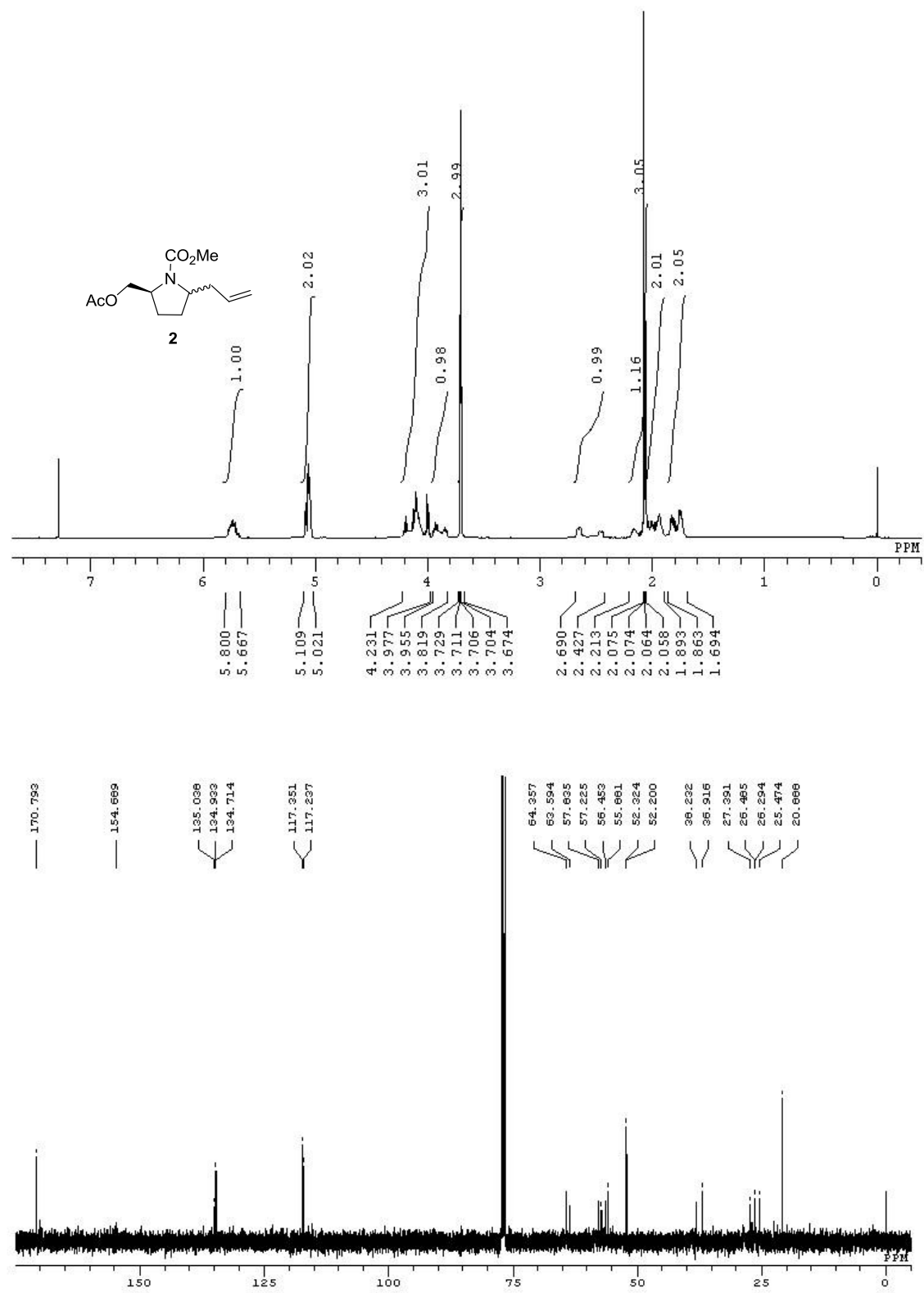


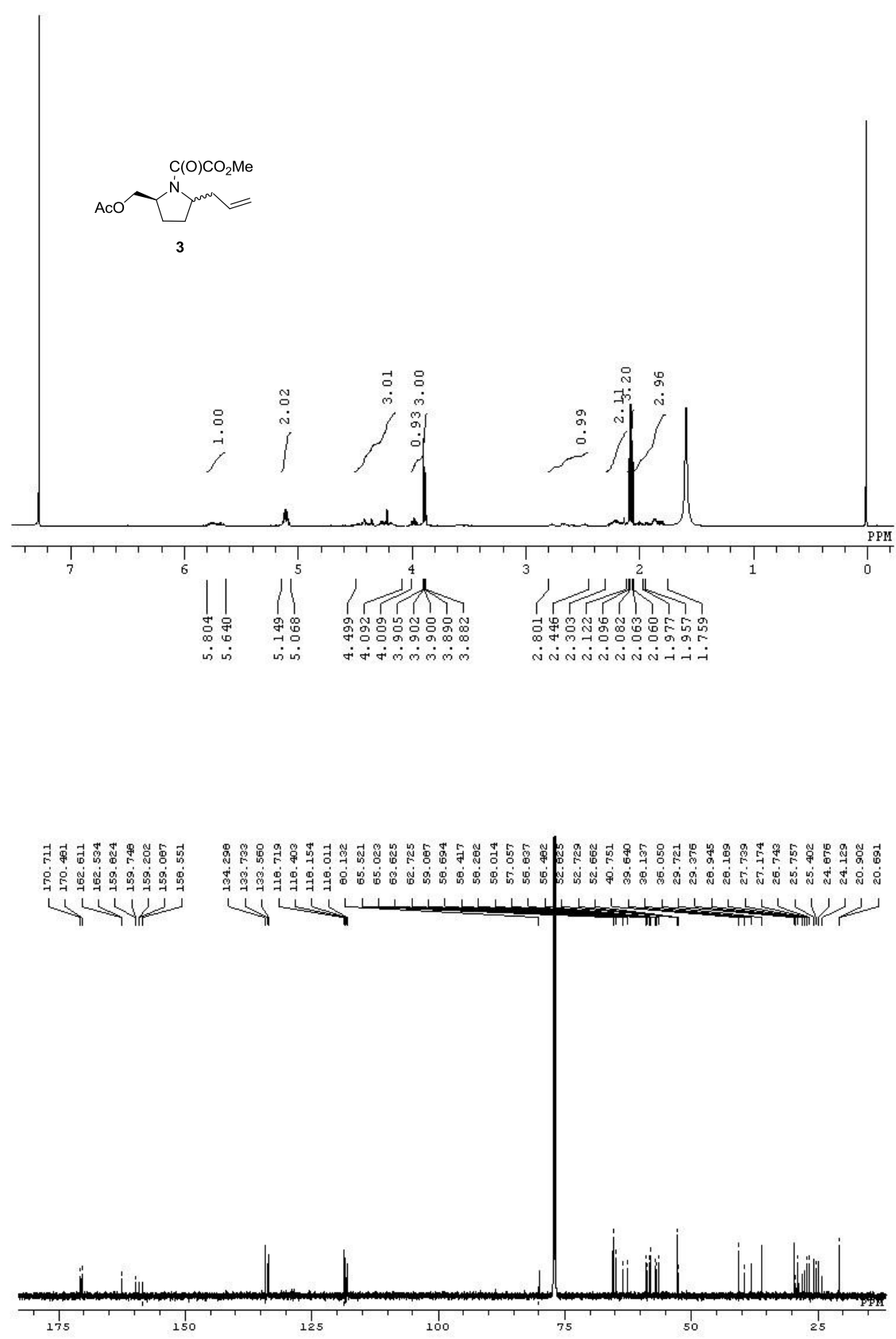


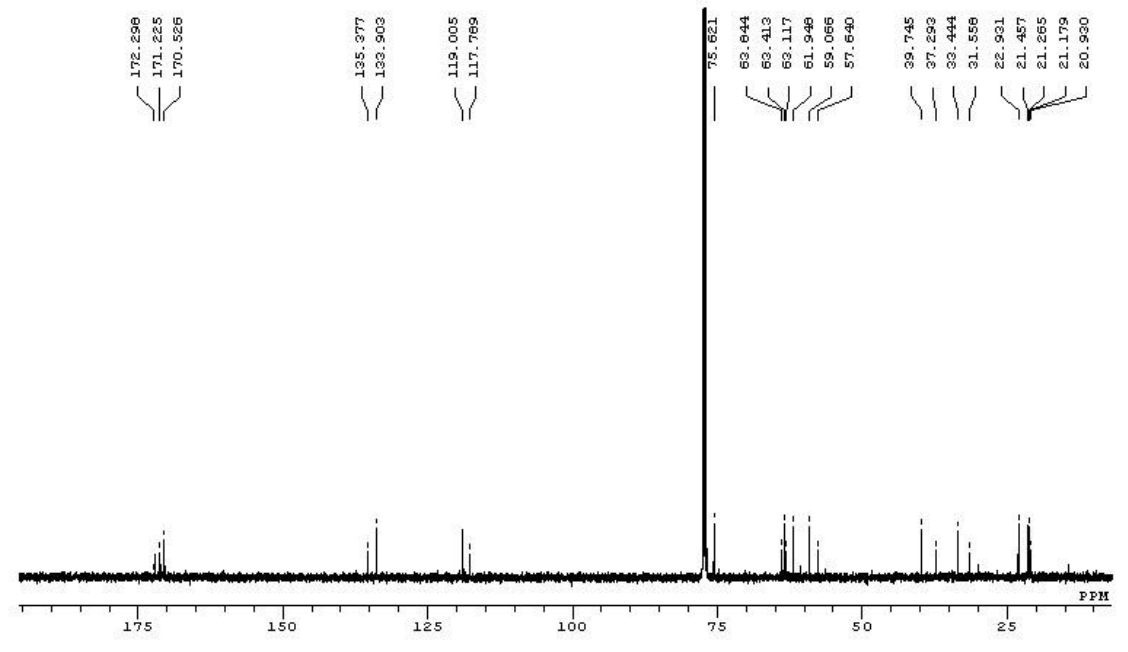
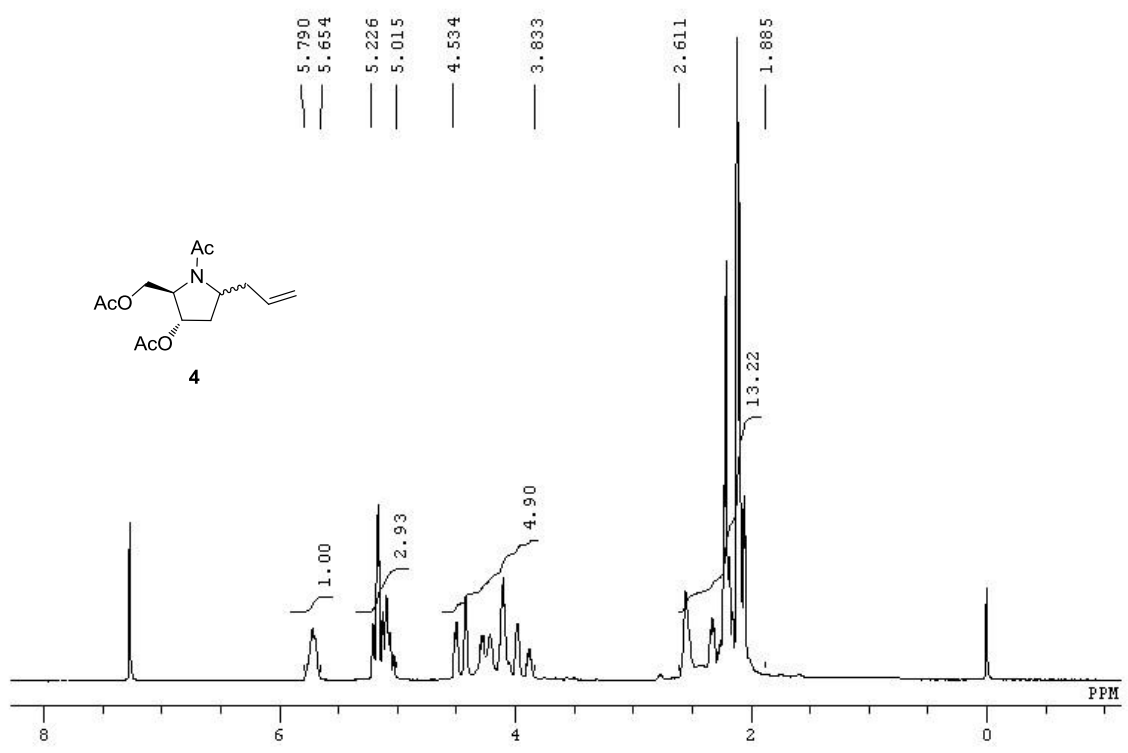


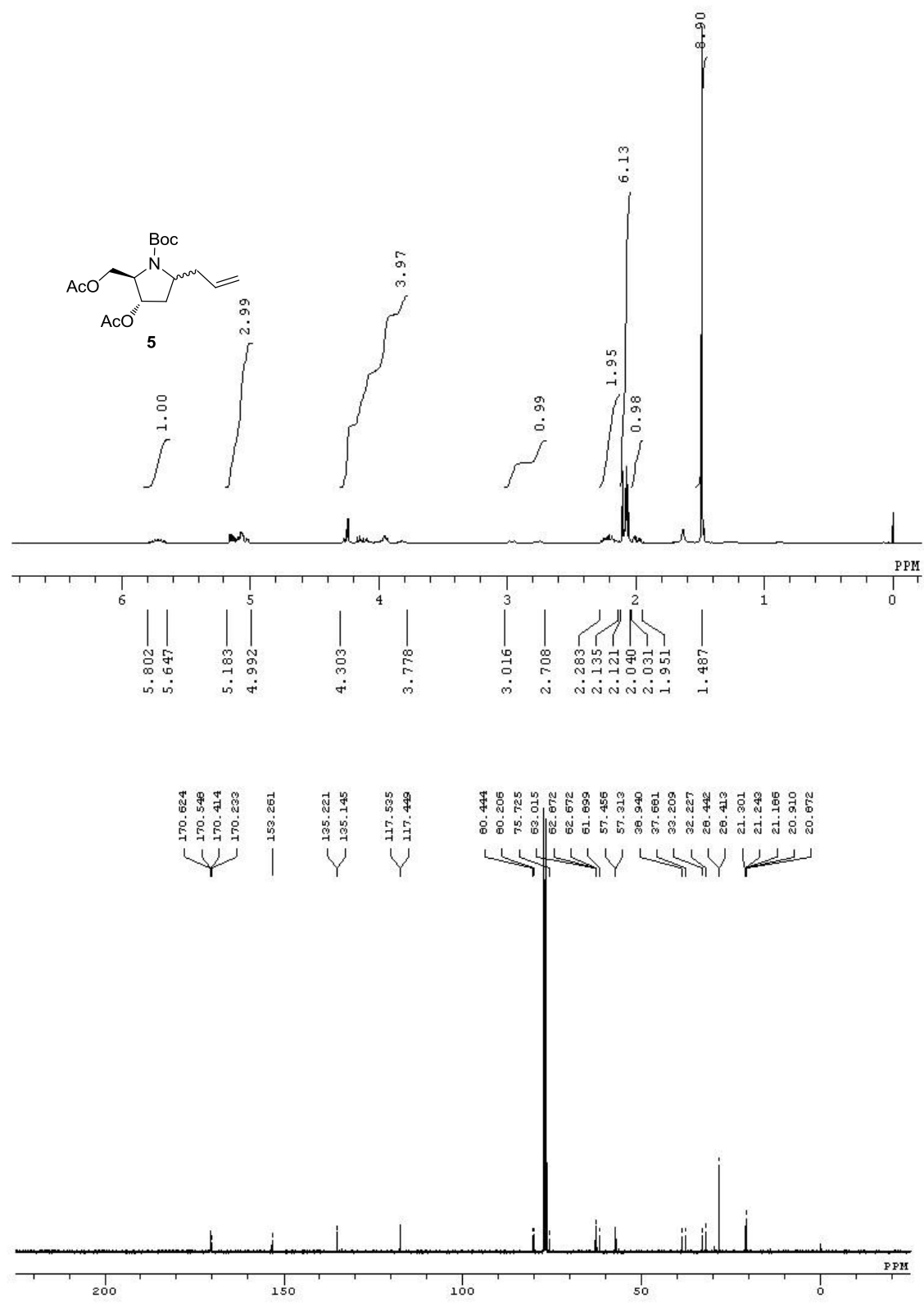


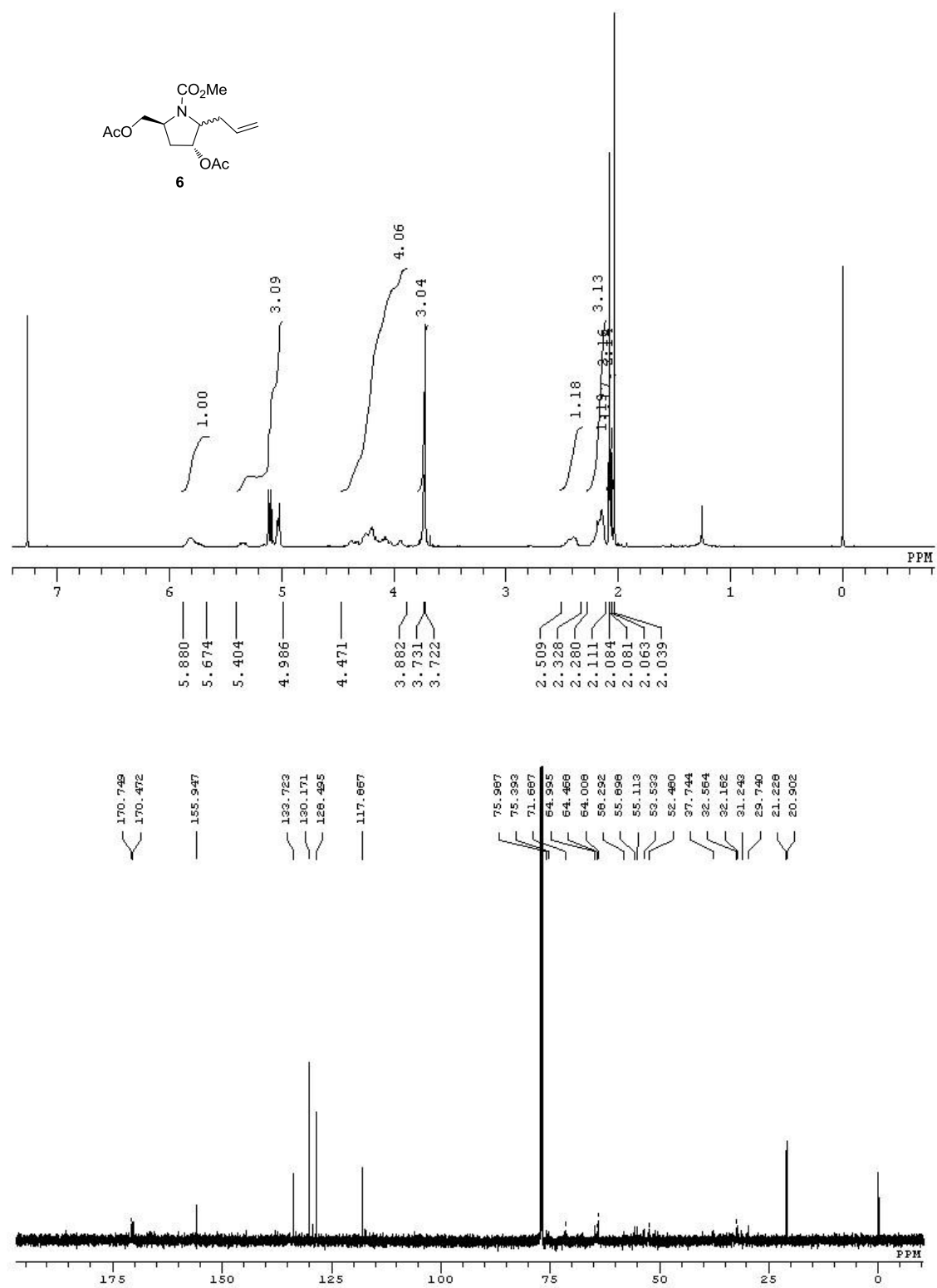


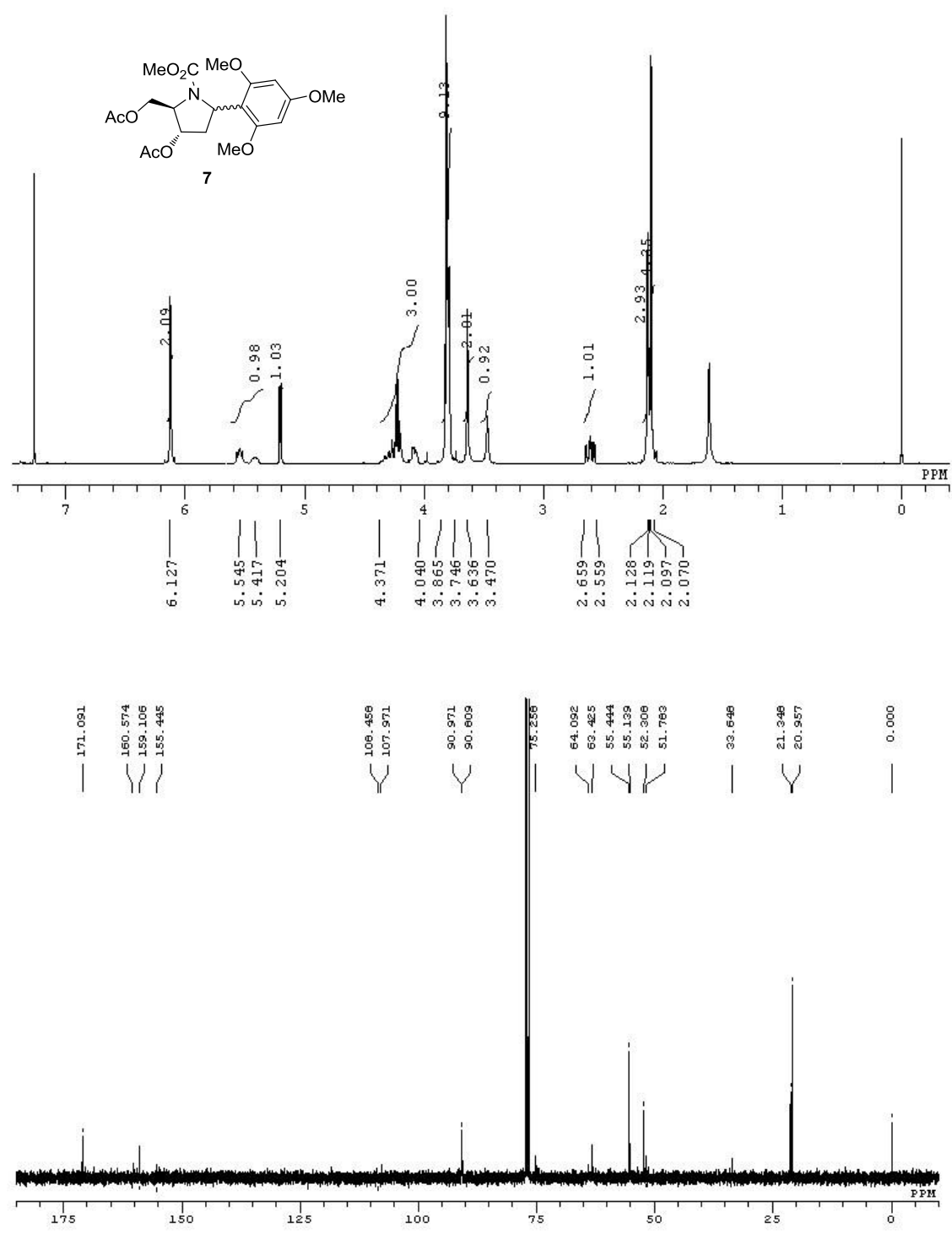


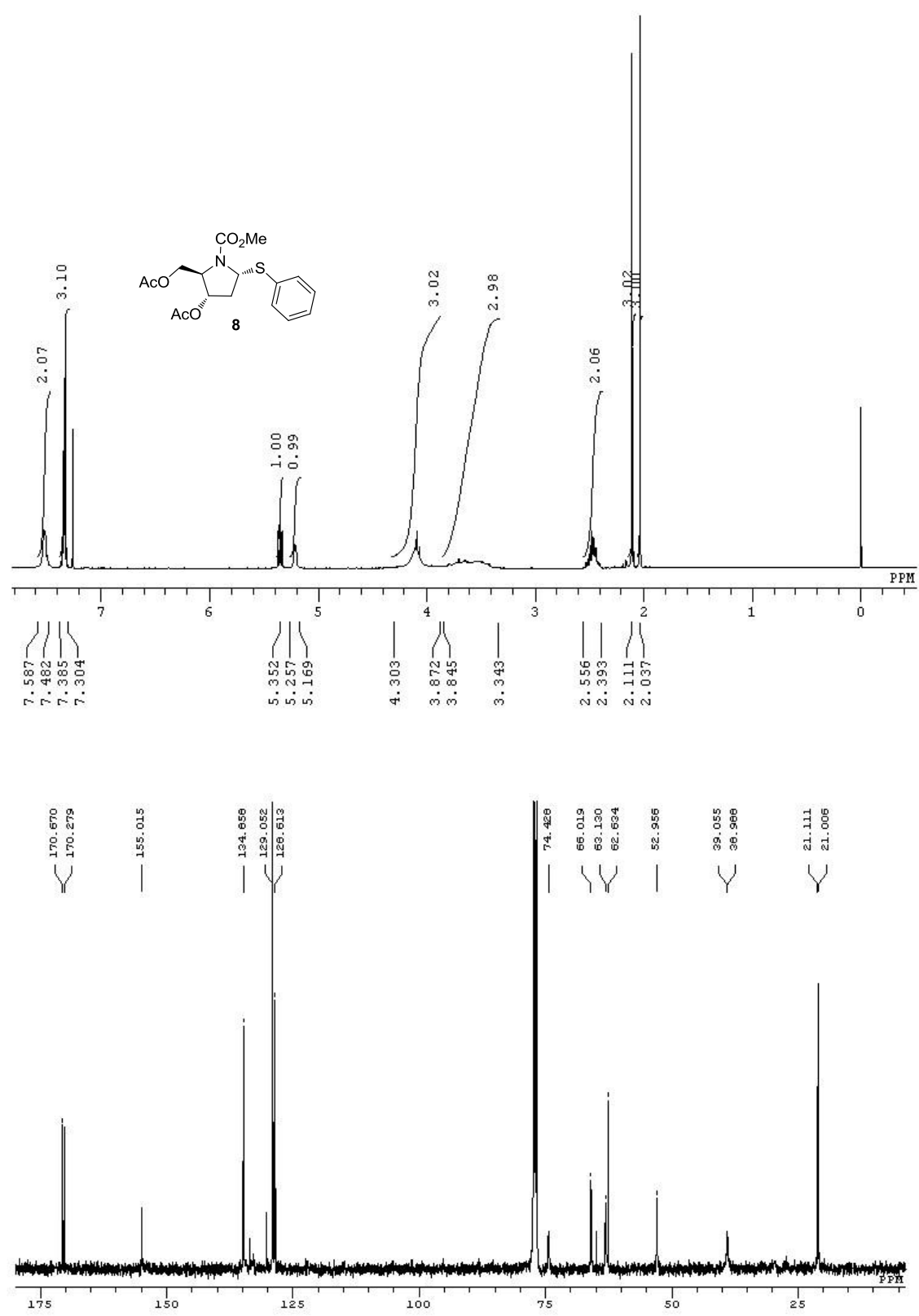


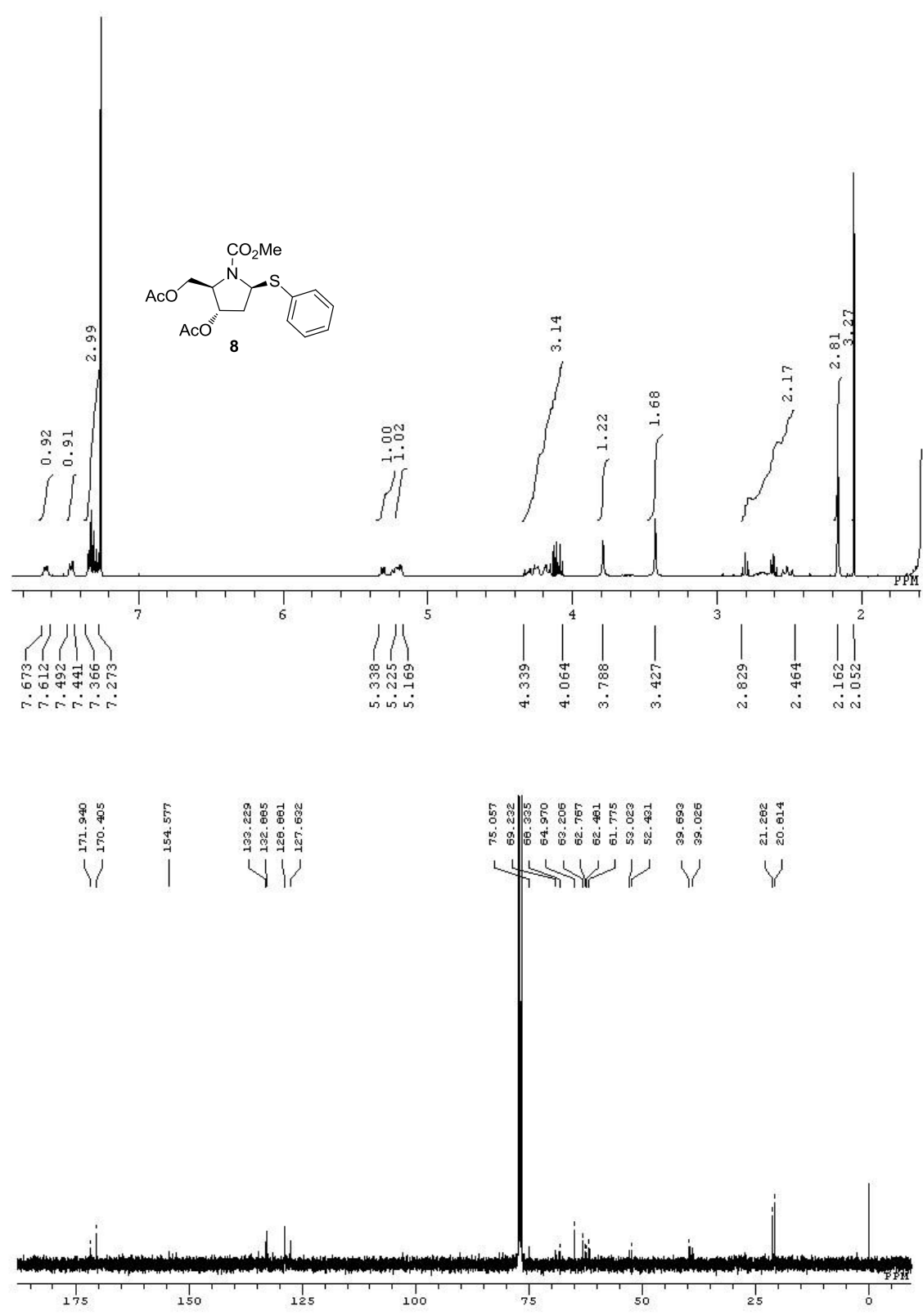


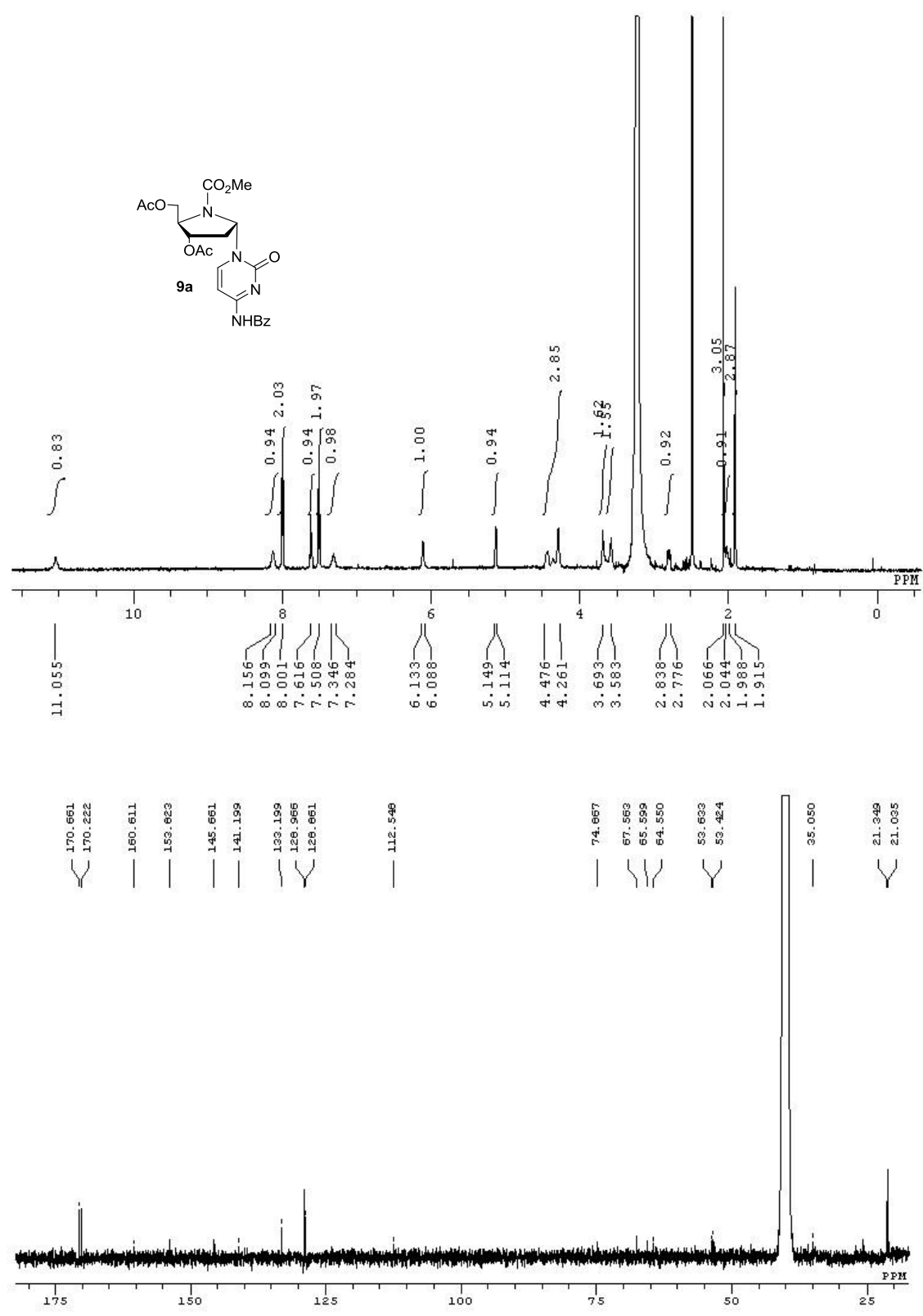


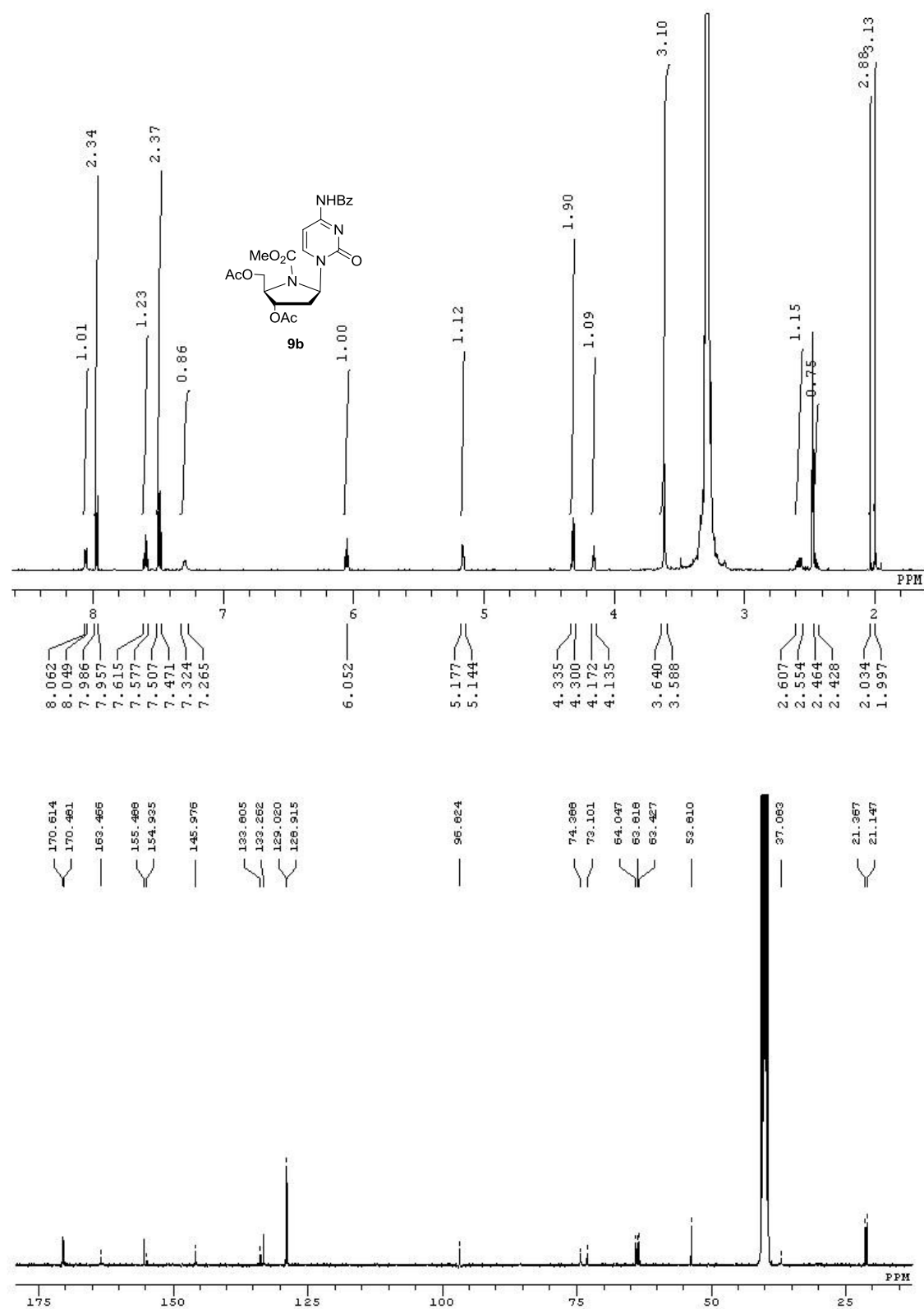


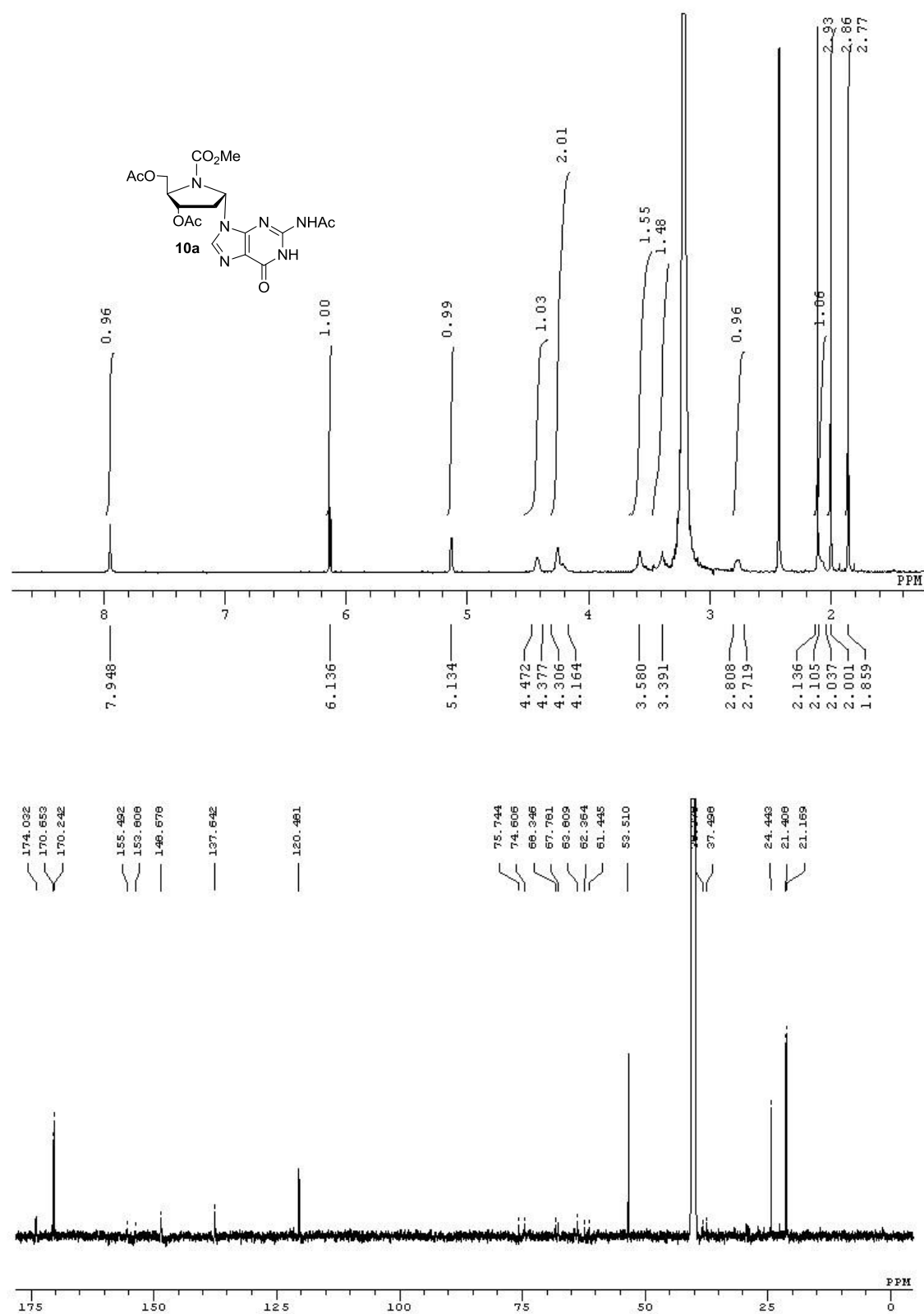


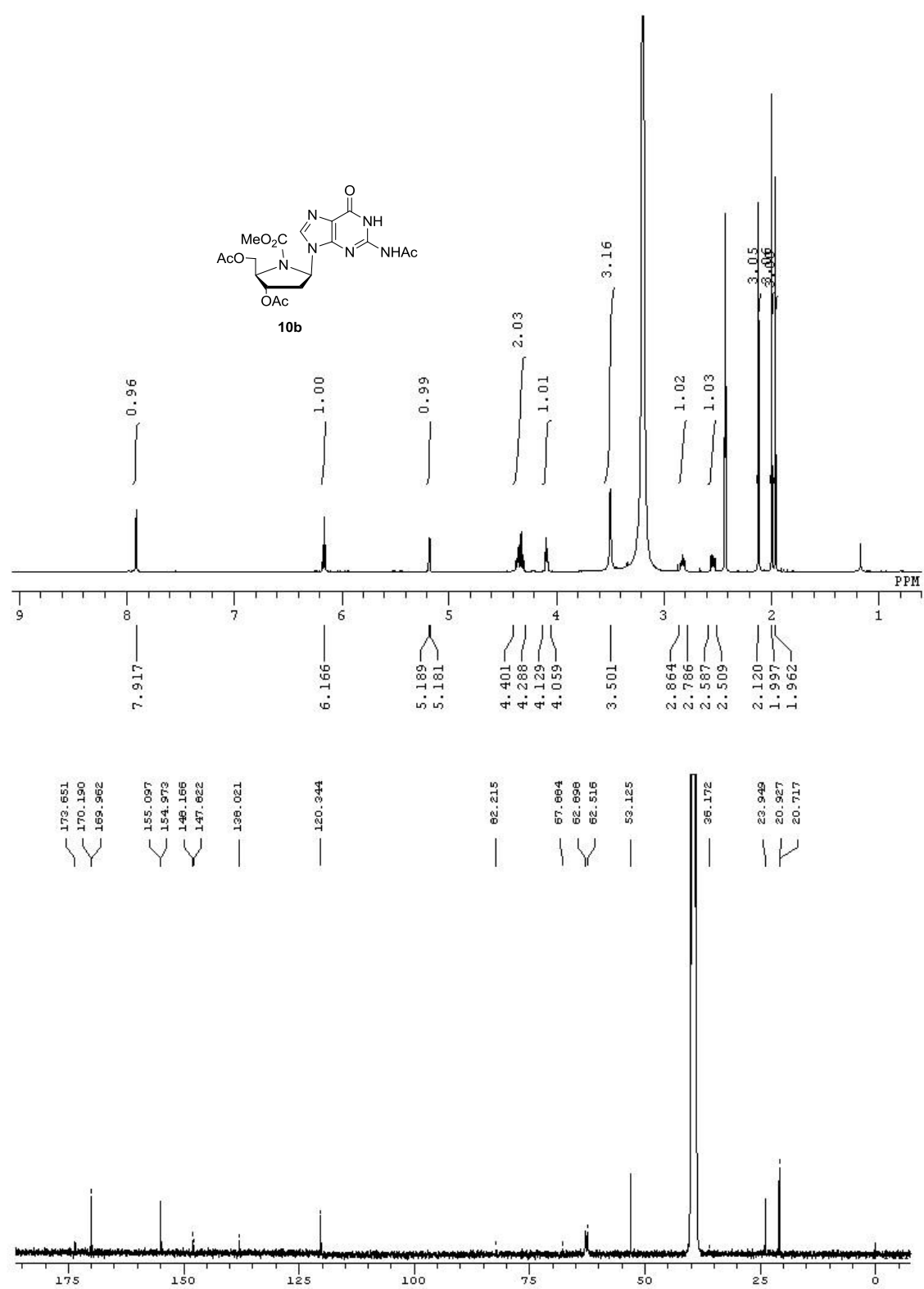


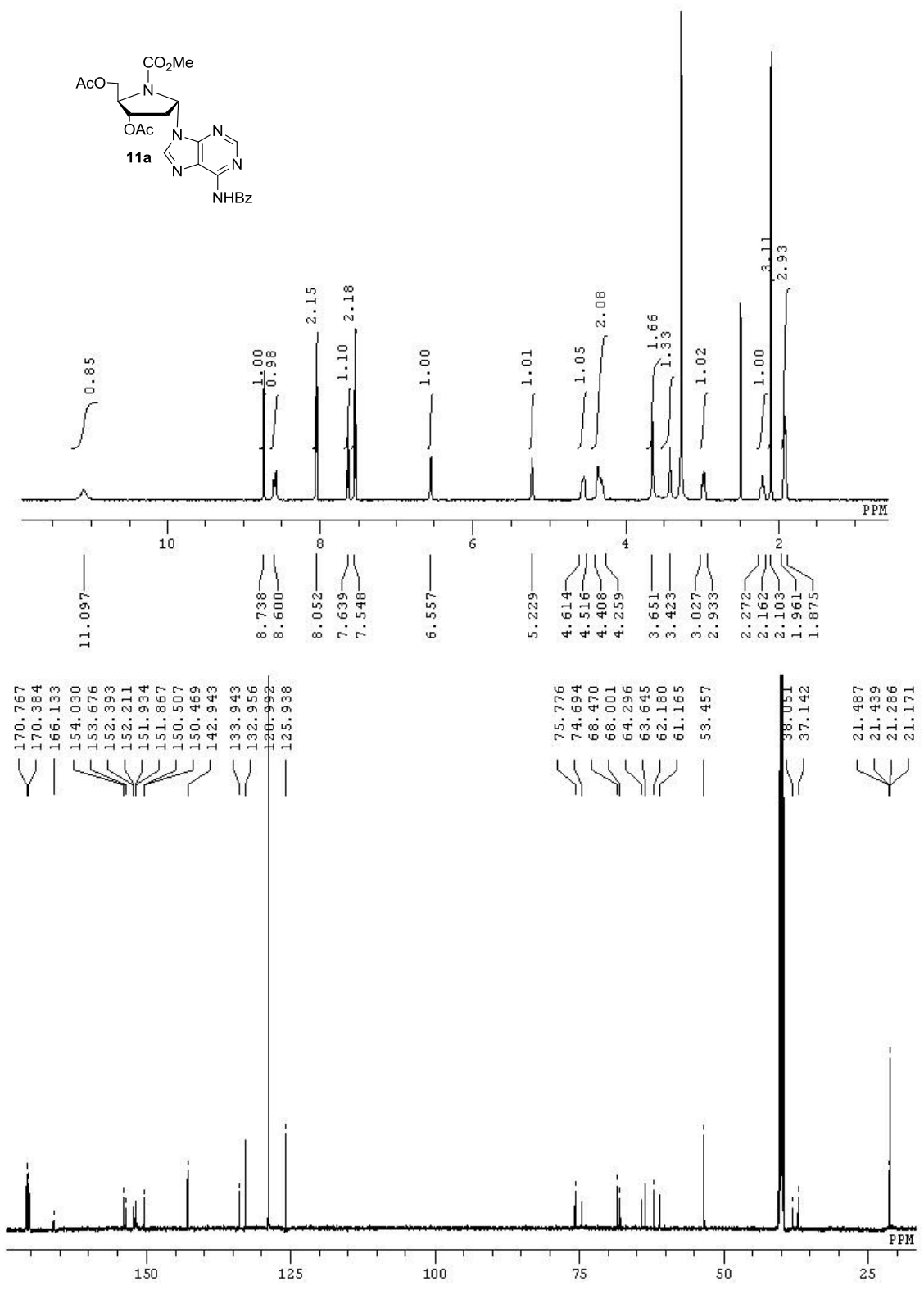


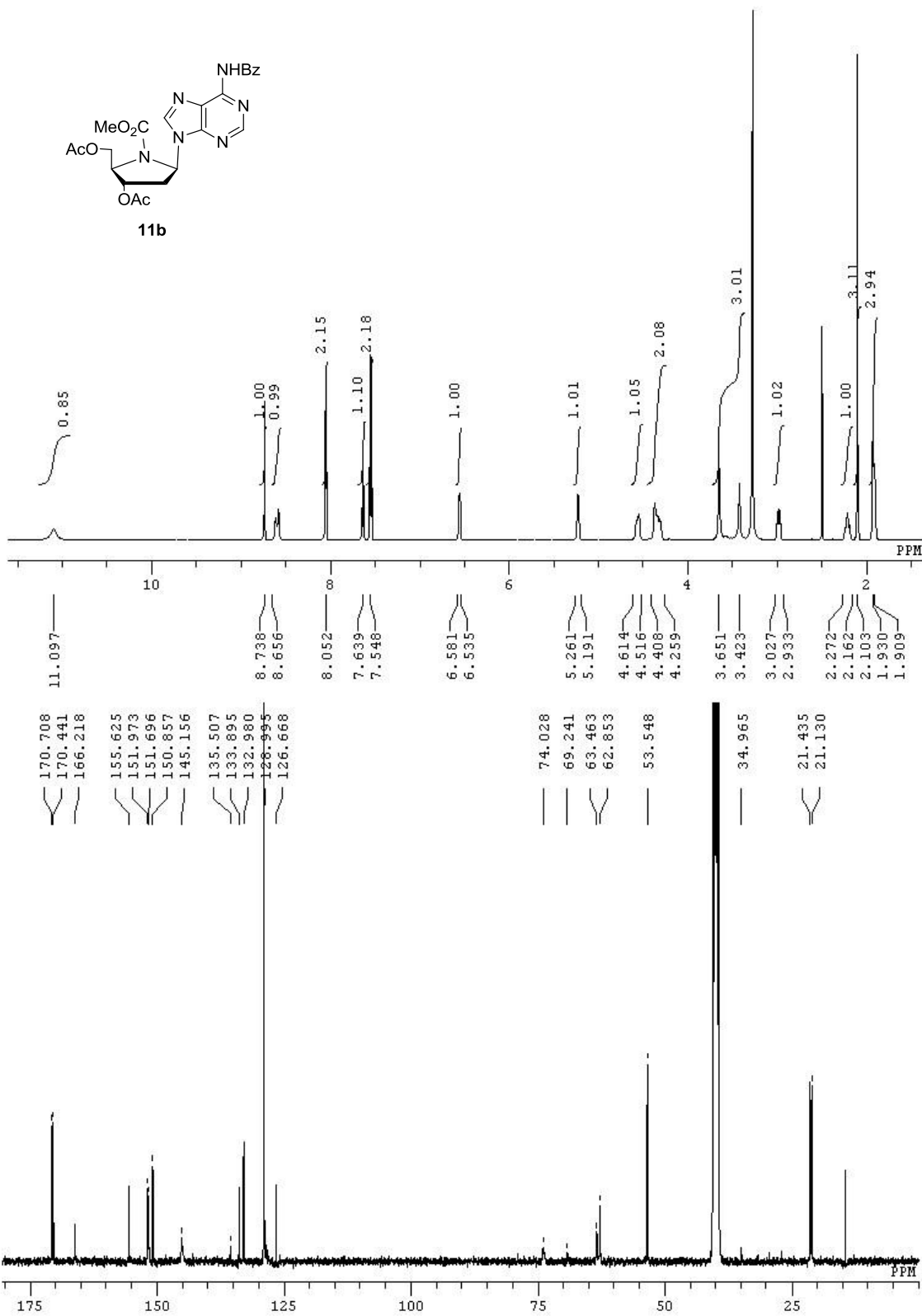


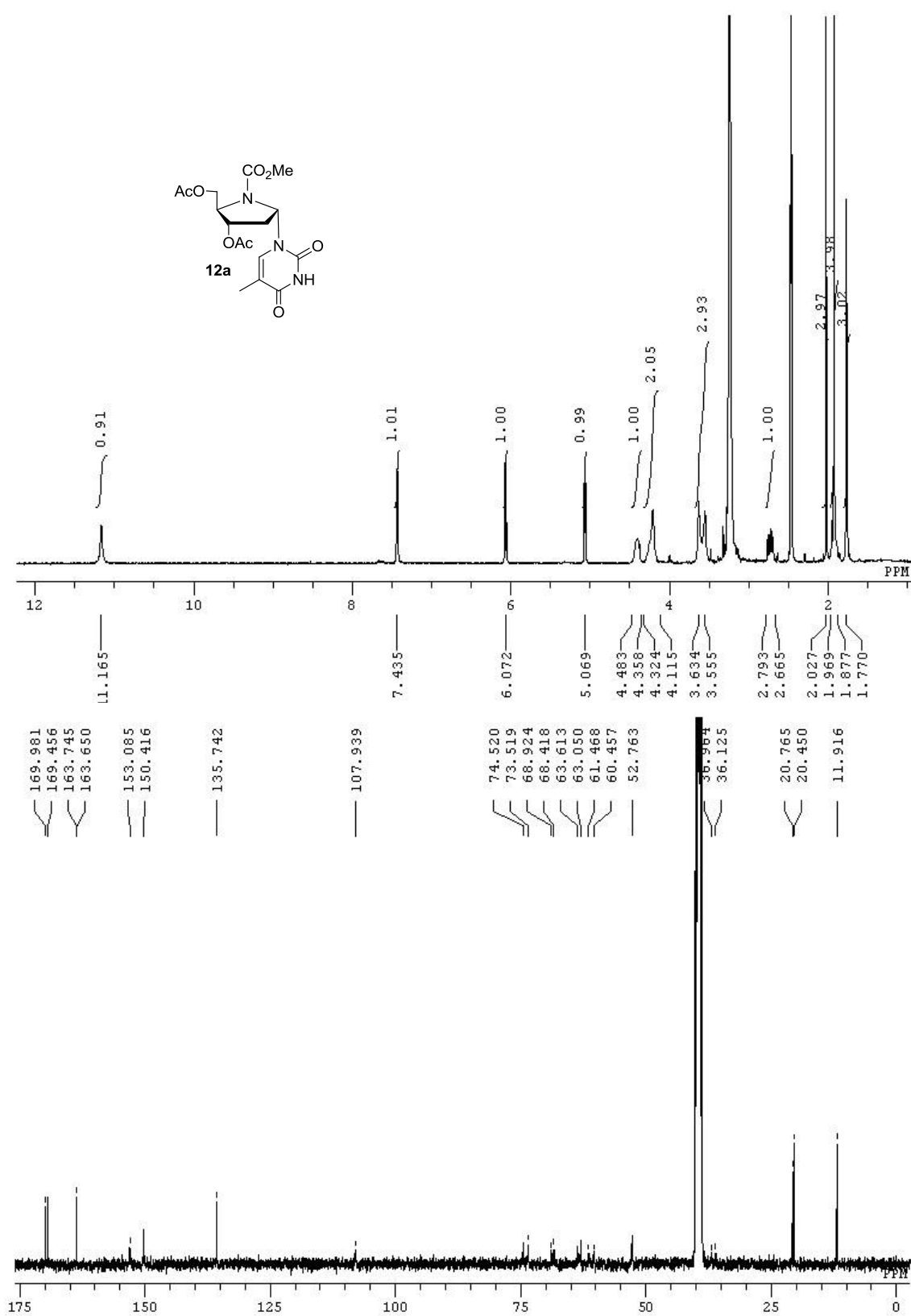


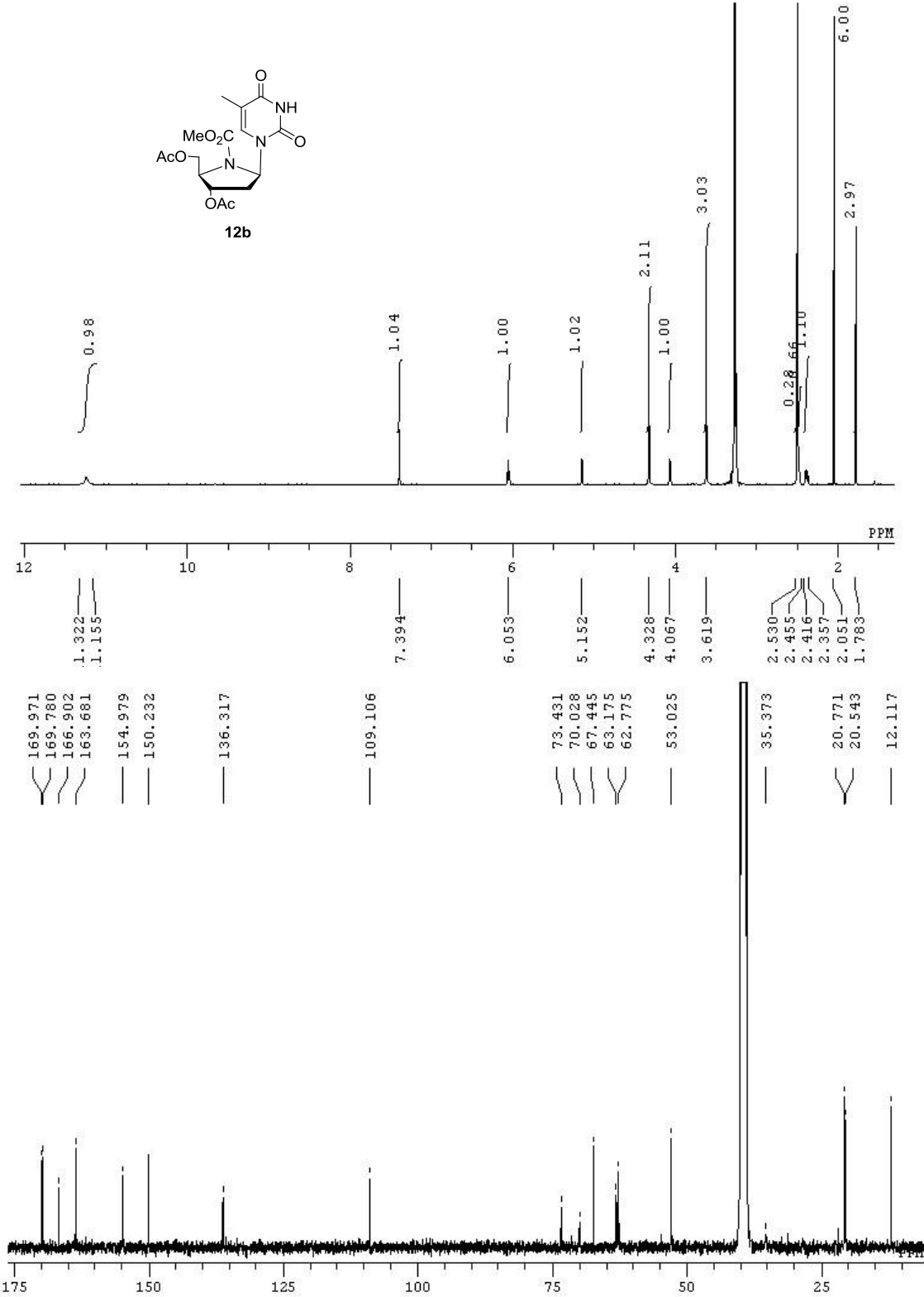


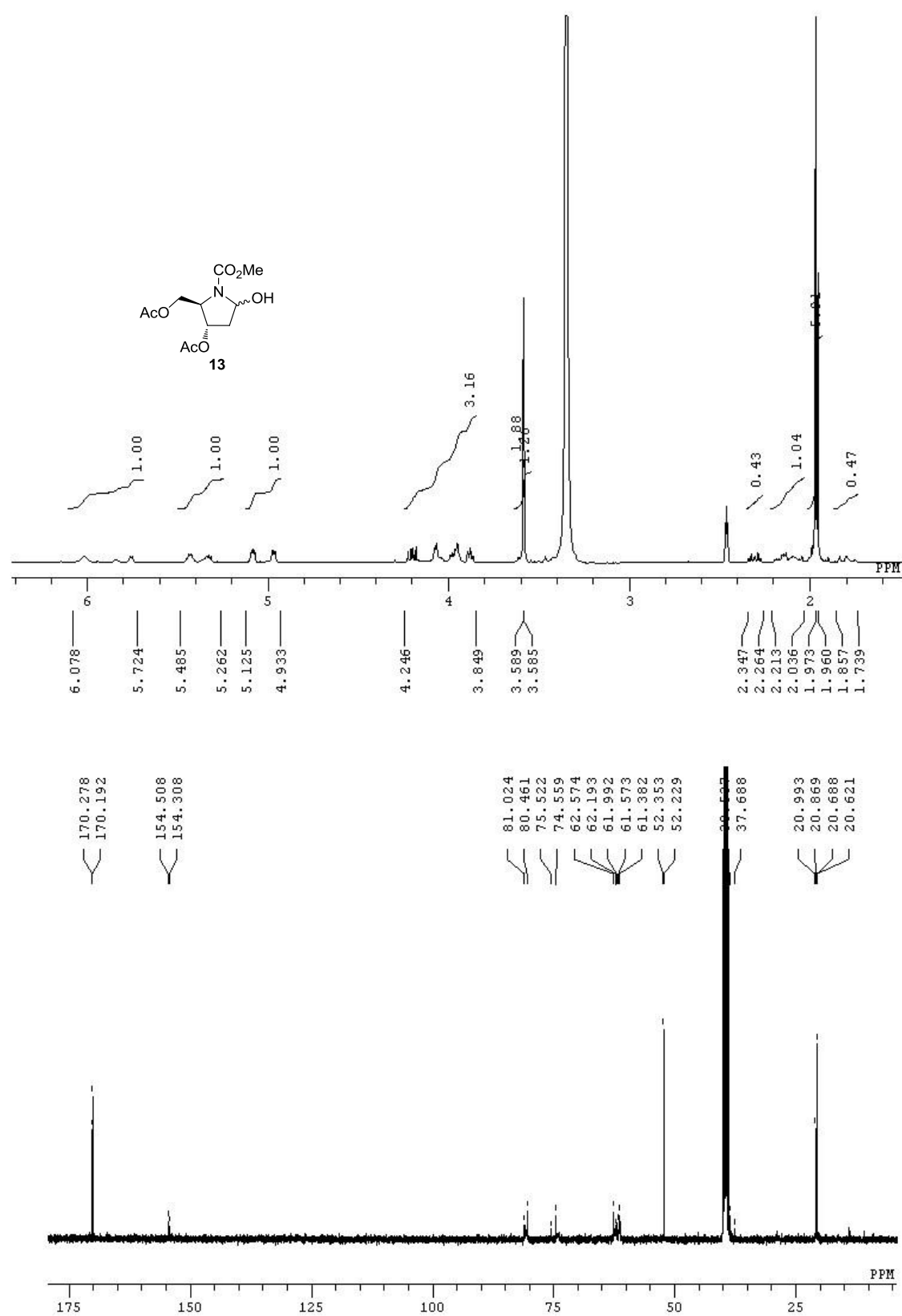












5. 1D differential NOE experiment

