

General solvent-free highly selective *N*-*tert*-butyloxycarbonylation strategy using protic ionic liquid as an efficient catalyst

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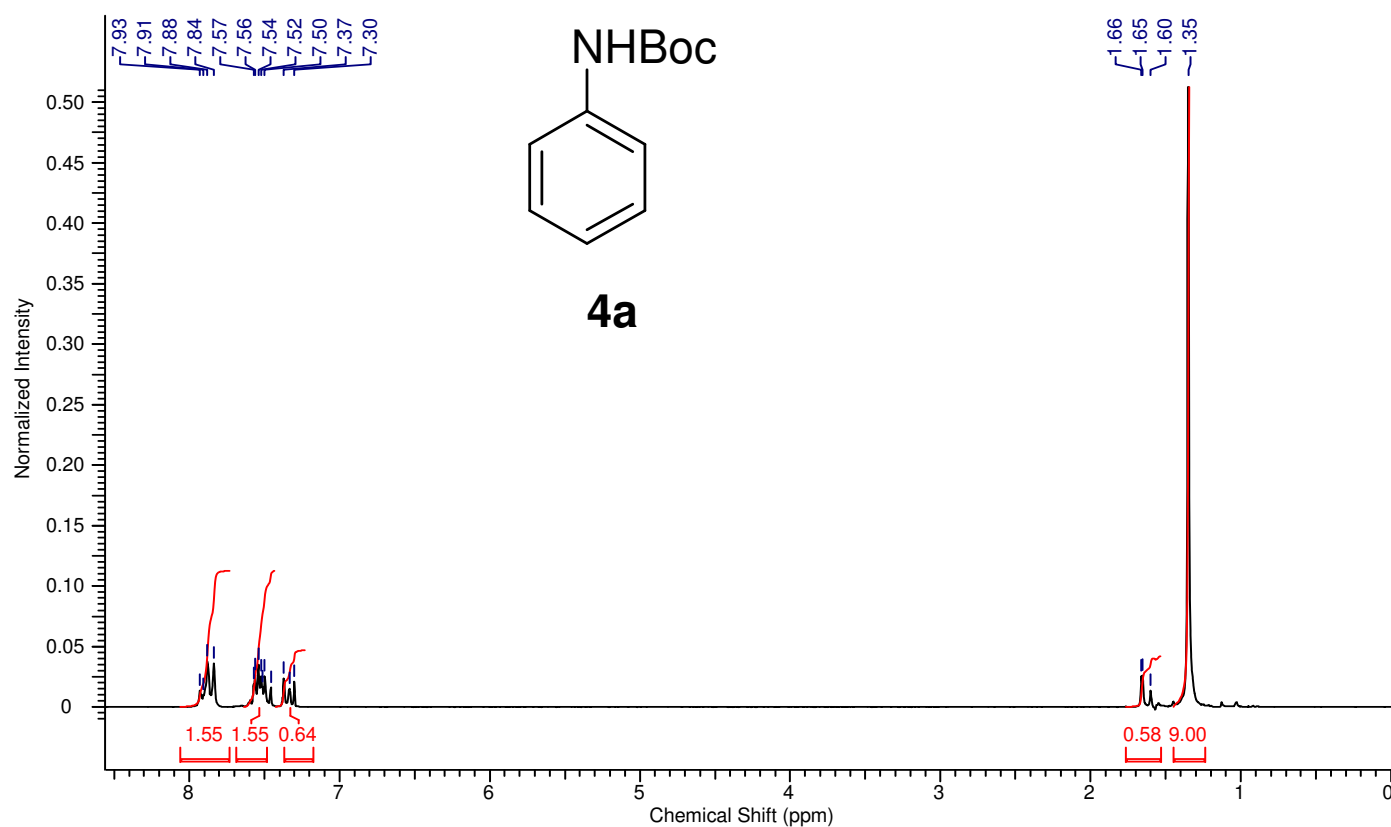
General procedure for *N*-*tert*-butyloxycarbonylation of amines: A mixture of Boc₂O (5.0 mmol), protic ionic liquid (5 mol%) and an amine (5.0 mmol) was stirred at room temperature or 70°C for the time indicated in Table 2. After completion of reaction as revealed by TLC, the mixture was diluted with water (5 ml) and extracted with ether or ethyl acetate (3 x 10 ml). The aqueous layer was recycled. The combined organic layer was washed with water, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude products were essentially pure but for analytical data, the samples were passed through short pad silica-gel (60-120 mesh) to remove any trace impurities.

3-(*N*-*tert*-butyloxy carbonyl)amino-1-propanol (5h): Table 3, entry 8): Yield: 99%; colourless syrup; IR (neat) 3368, 2978, 1689, 1526 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 4.97 (bs, 1H), 3.60 (bs, 2H), 3.41 (bs, 1H), 3.24-3.18 (m, 2H), 1.66 – 1.58 (m, 2H), 1.39 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz) δ 157.1, 79.5, 59.2, 37.0, 32.7, 28.3; EIMS m/z 176 (M⁺+1), 175 (M⁺), 145, 120, 89, 76; HRMS Calcd for C₈H₁₇NO₃ 175.2263 found 175.2260

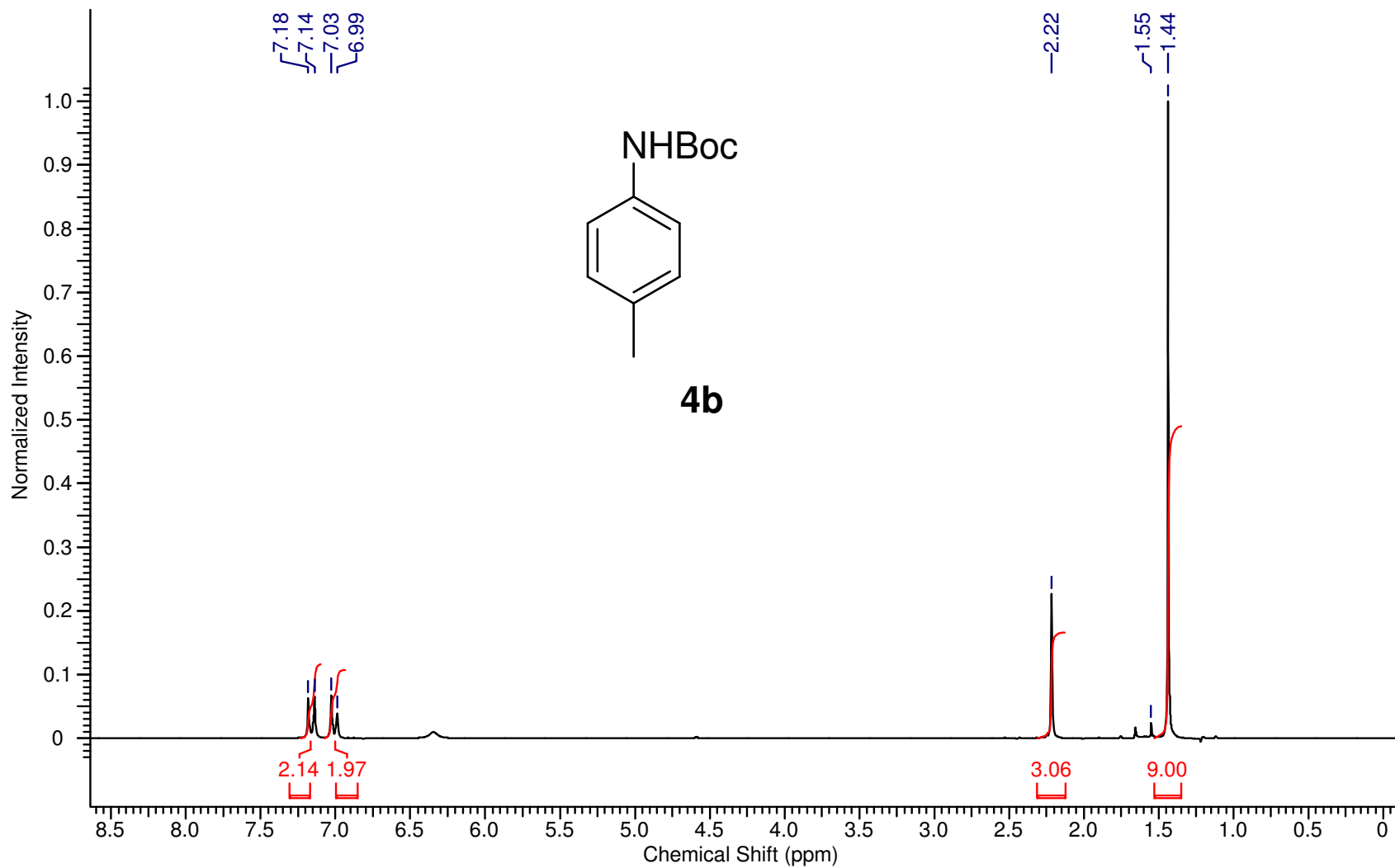
***Tert*-butyl-[3-(*N*-*tert*-butyloxy carbonyl)amino propyl] carbonate (5i):** Table 3, entry 9): Yield: 98%; colourless syrup; IR (neat) 3369, 2980, 2932, 1742, 1696, 1394, 1369 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 4.76 (bs, 1H), 4.08 (t, *J* = 6.3 Hz, 2H); 3.20-3.14 (m, 2H); 1.87-1.76 (m, 2H), 1.44 (s, 9H), 1.40 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz) δ 155.9, 153.6, 82.0, 79.2, 64.4, 37.2, 29.1, 28.8, 27.9; EIMS m/z 276 (M⁺+1), 275 (M⁺); 219, 204, 163, 102, 56; HRMS Calcd for C₁₃H₂₅NO₅ 275.3427 found 275.3422.

N-tert-Butyloxycarbonyl L-Leucinol (6a: Table 4, entry 1): yield: 97%, colourless syrup; $[\alpha]_D^{25}$ -28° (c 2, MeOH) {lit $[\alpha]_D^{20}$ $-27.5 \pm 1^\circ$ (c 2, MeOH), Fisher Scientific Ltd., Catalogue No. AC37620-0050}; IR (neat) 3367, 2928, 2873, 1690 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 4.71 (bs, 1H), 3.66-3.58 (m, 2H), 3.49-3.43 (m, 1H), 2.98 (bs, 1H), 1.68-1.56 (m, 1H), 1.41 (s, 9H), 1.31-1.19 (m, 2H), 0.90 (d, $J = 5.7$ Hz, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 156.50, 79.50, 66.4, 51.1, 40.5, 28.3, 24.7, 23.0; EI MS m/z 218 ($\text{M}^+ + 1$), 186, 162, 144, 130, 86.

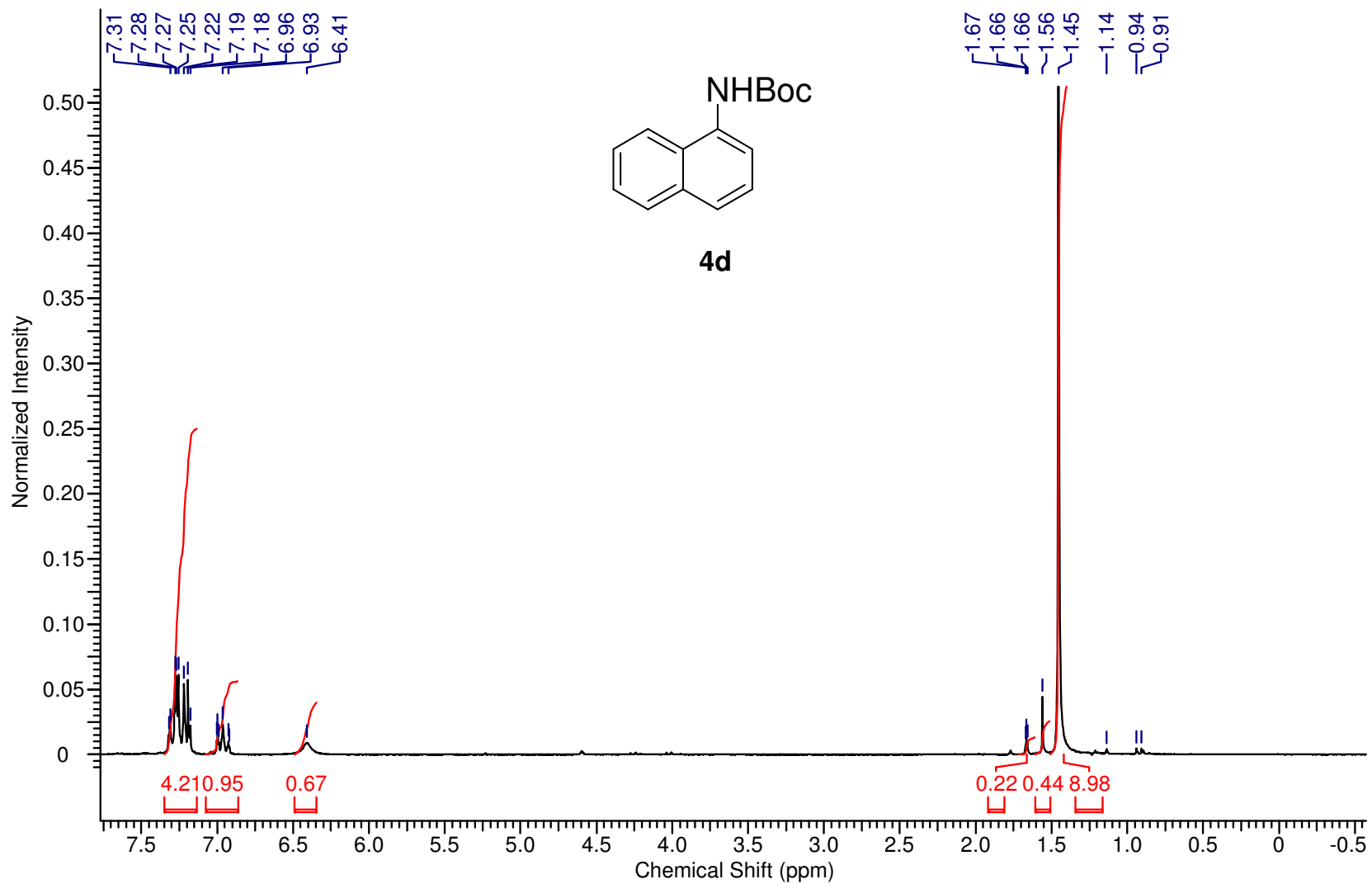
^1H NMR spectra of 4a



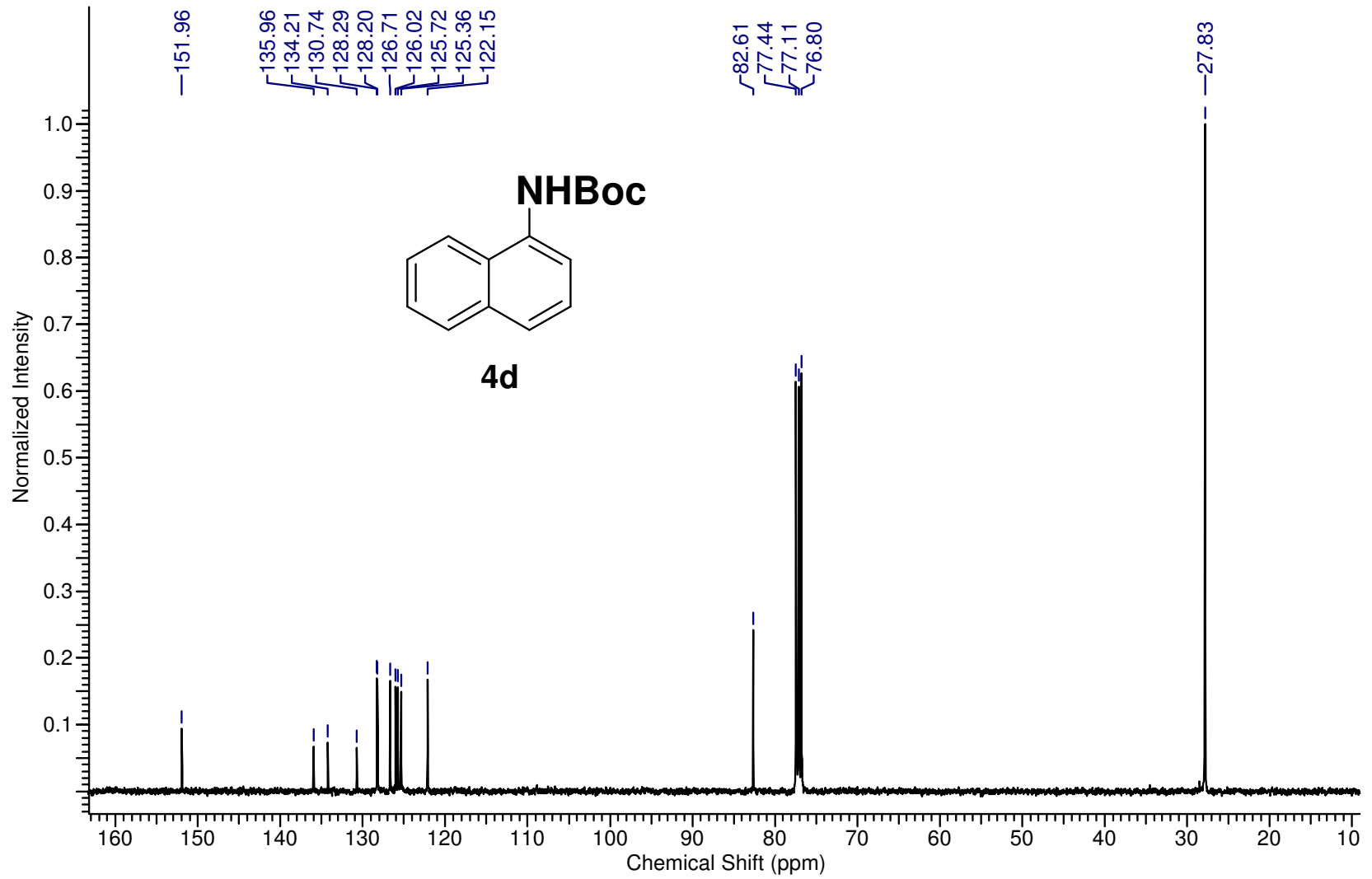
¹H NMR spectra of 4b

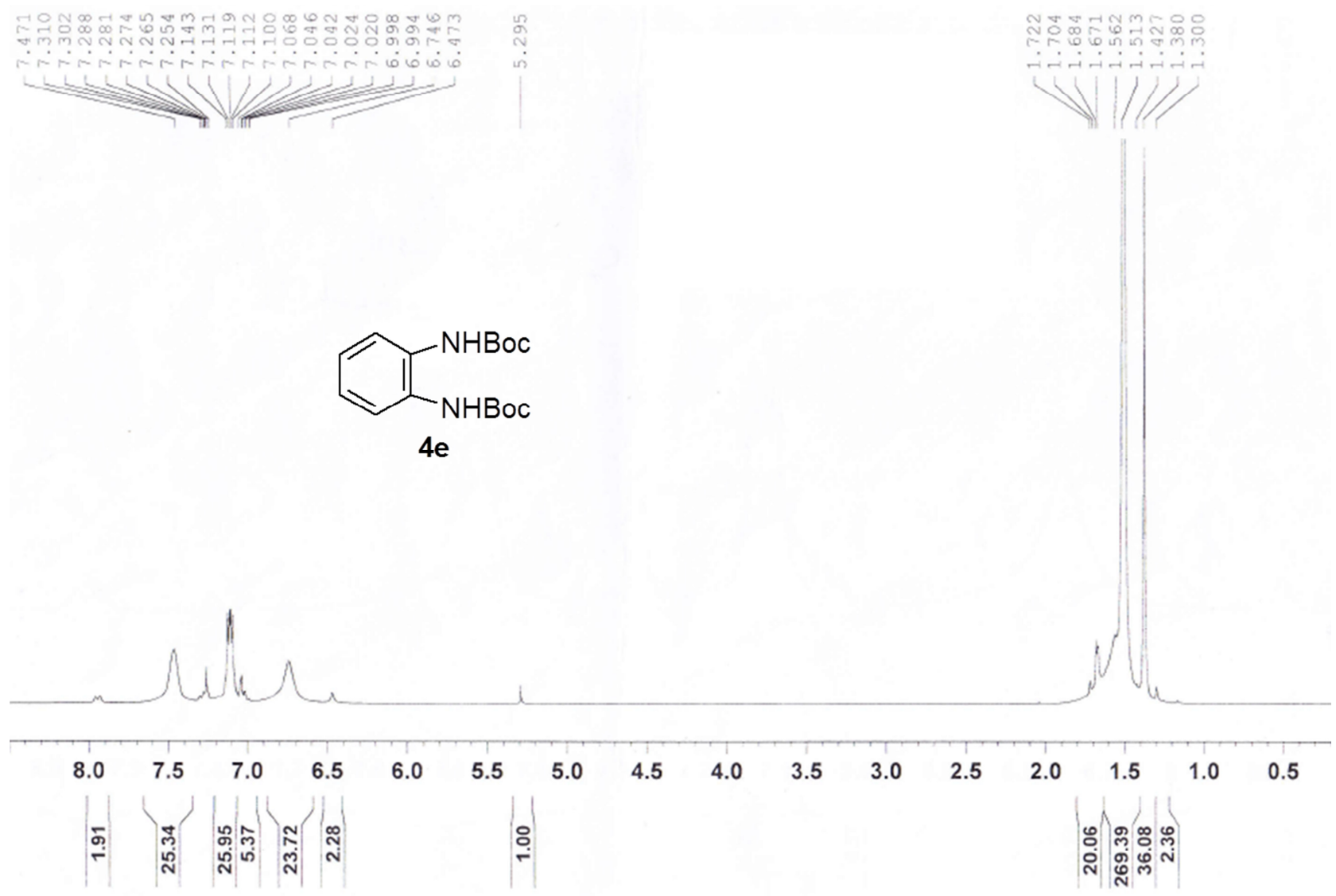


¹H NMR spectra of 4d

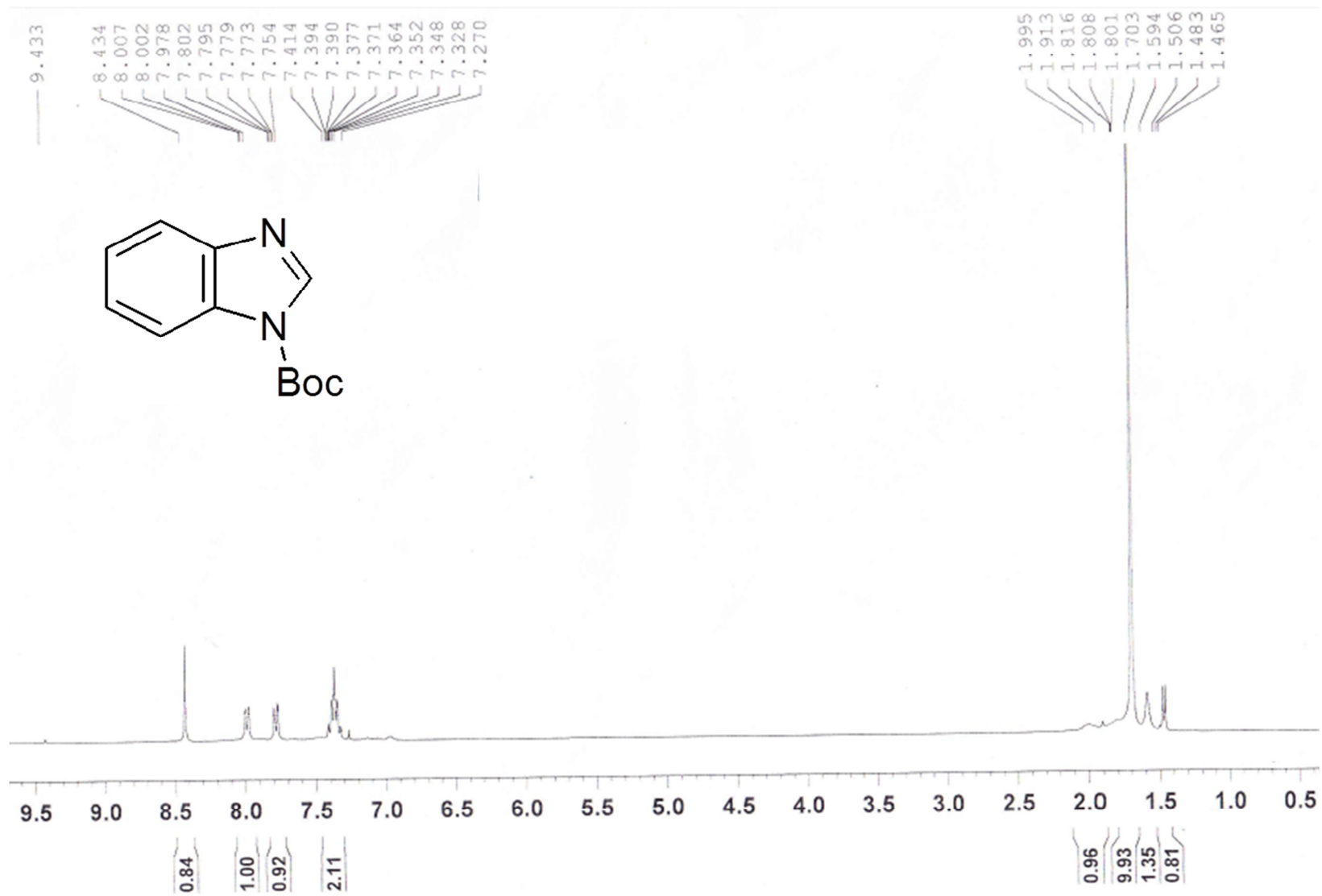


¹³C NMR spectra of 4d

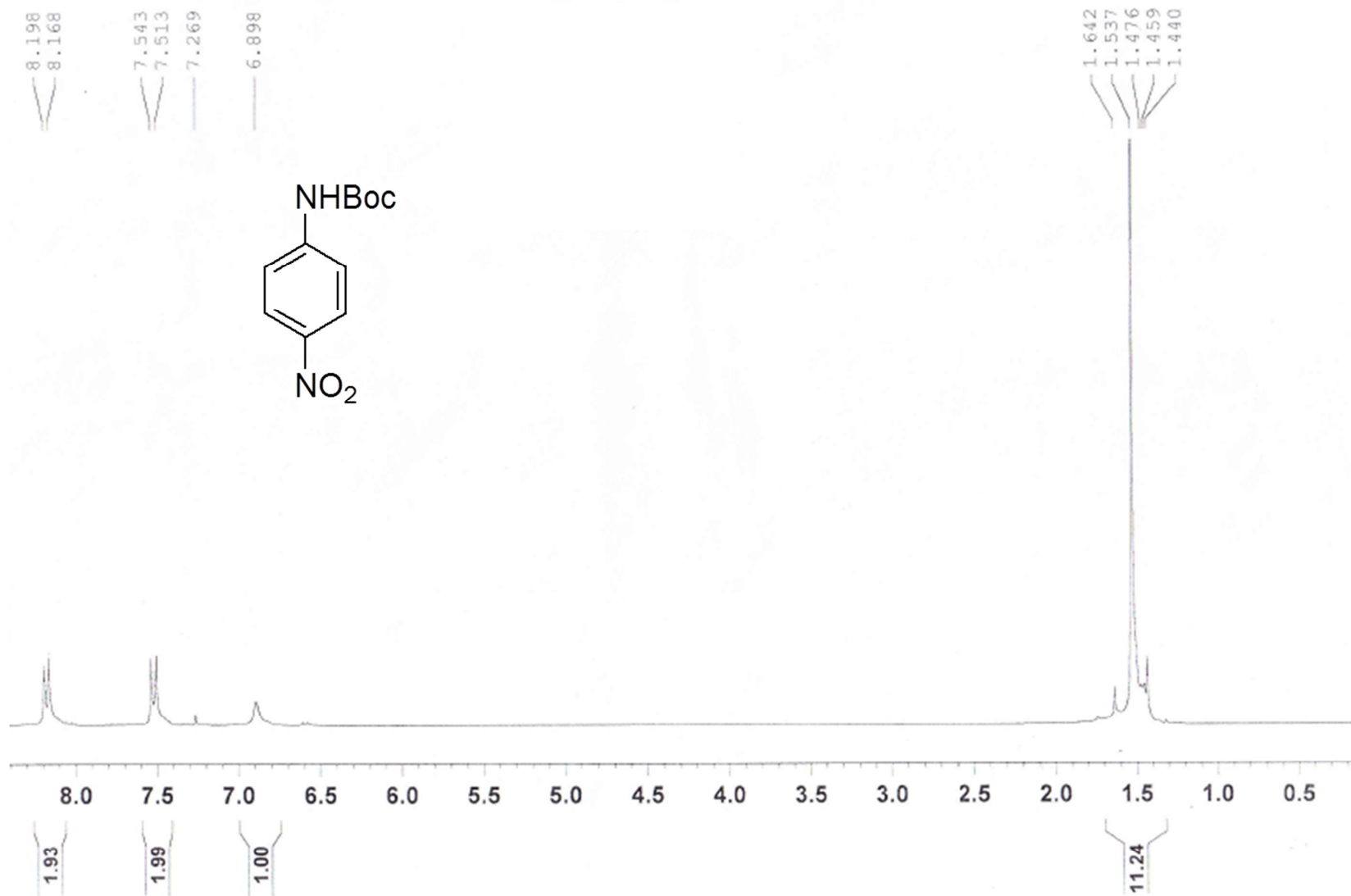




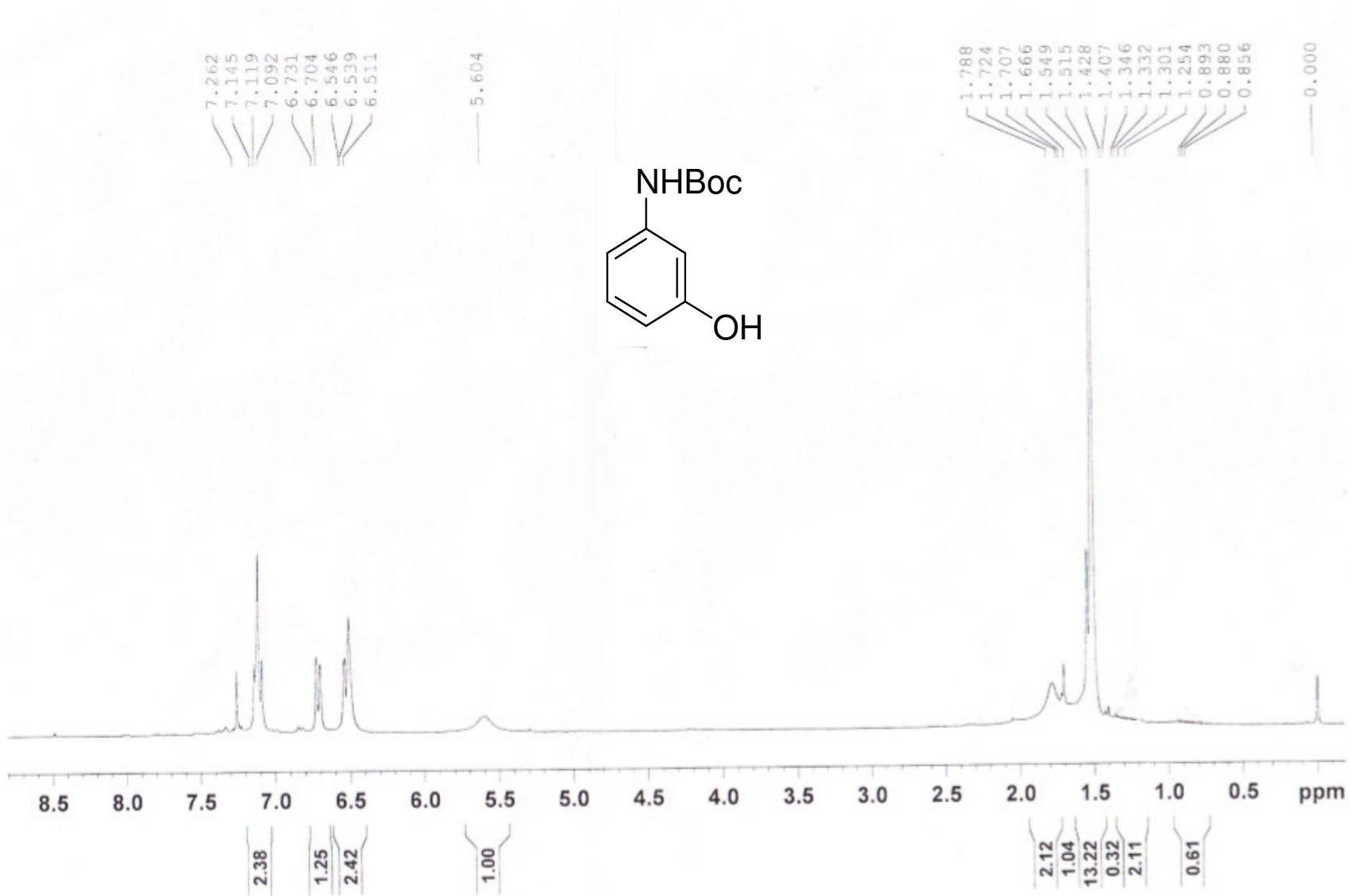
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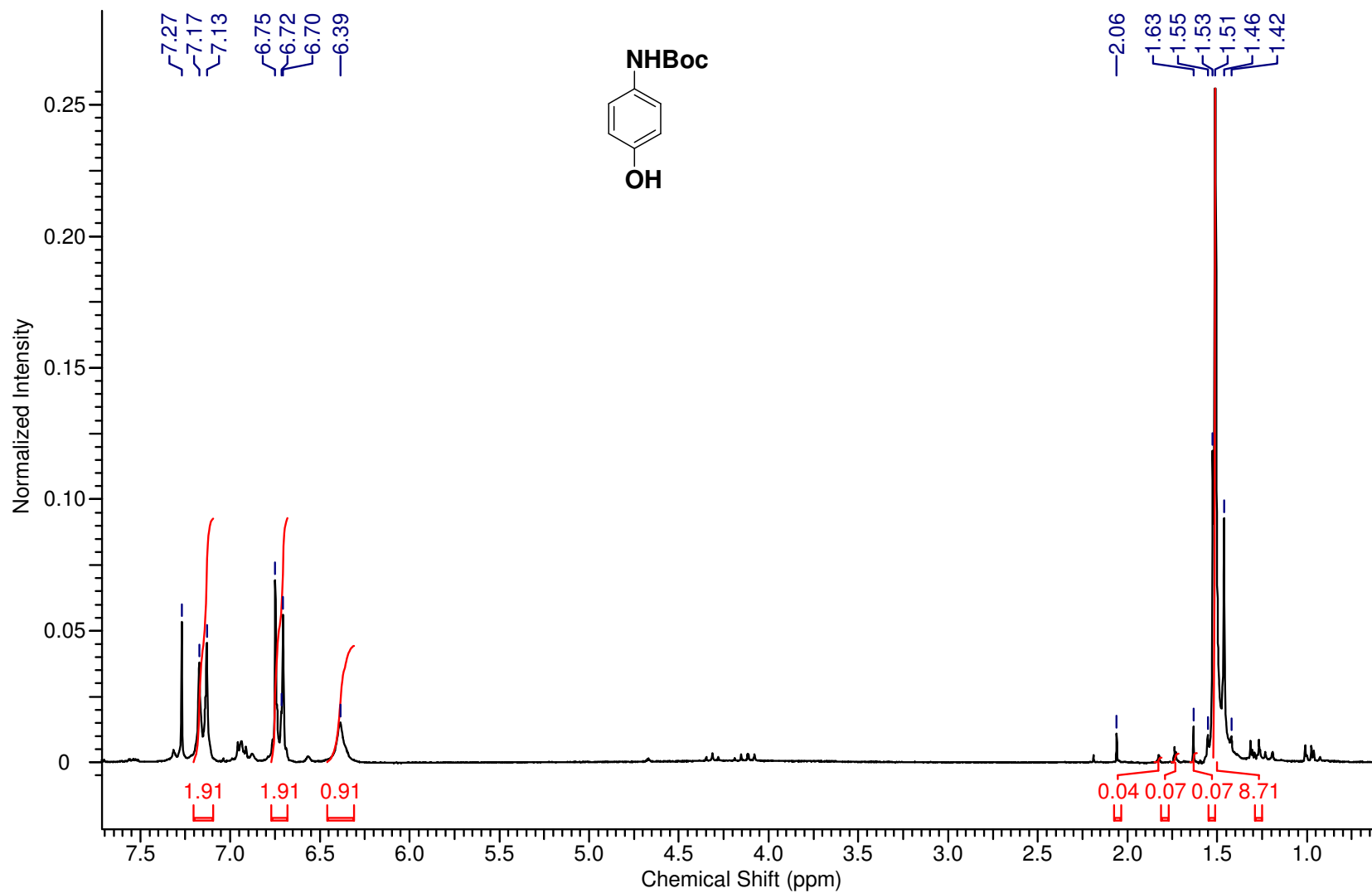
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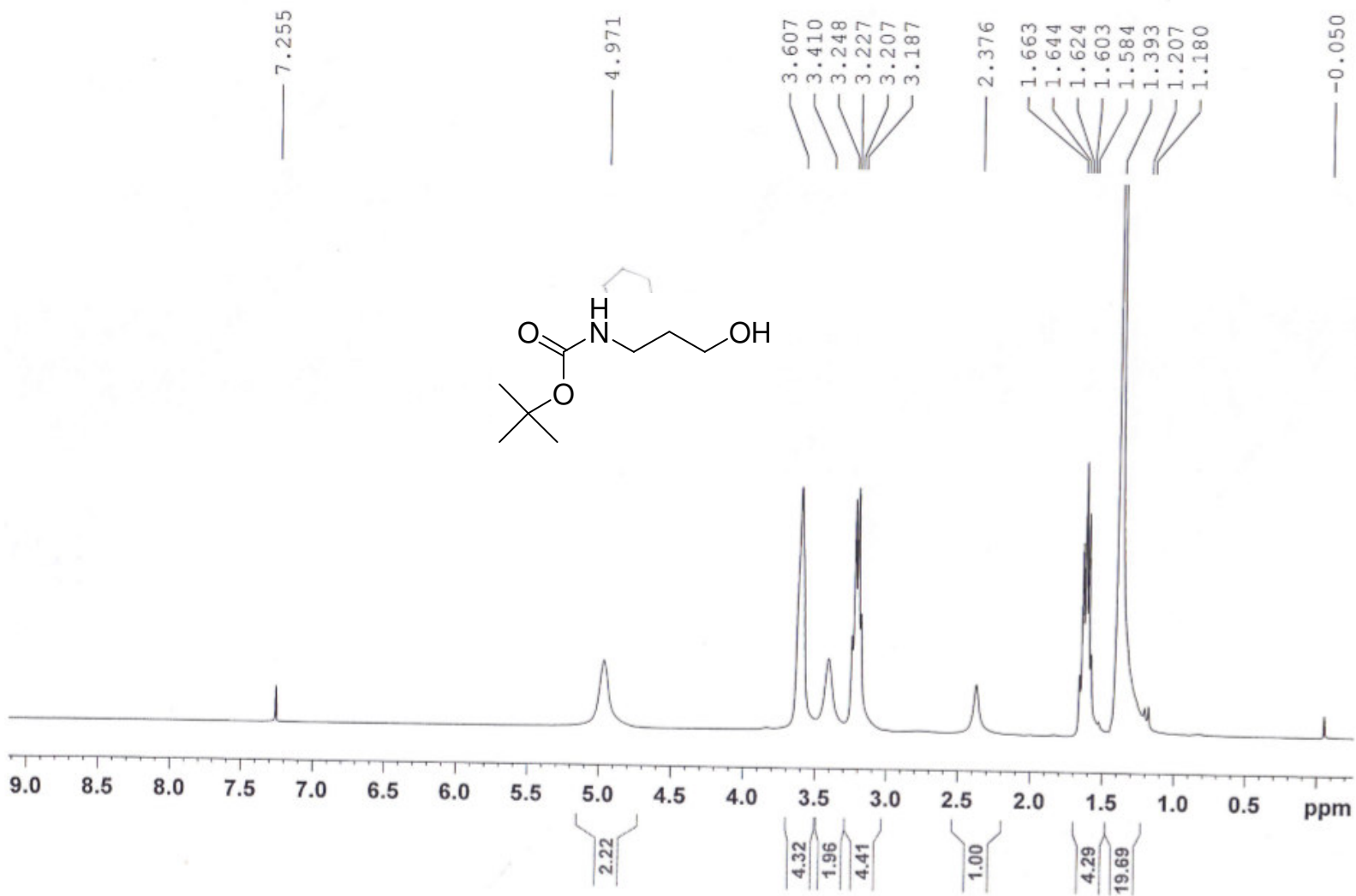
¹H NMR spectra of 5f



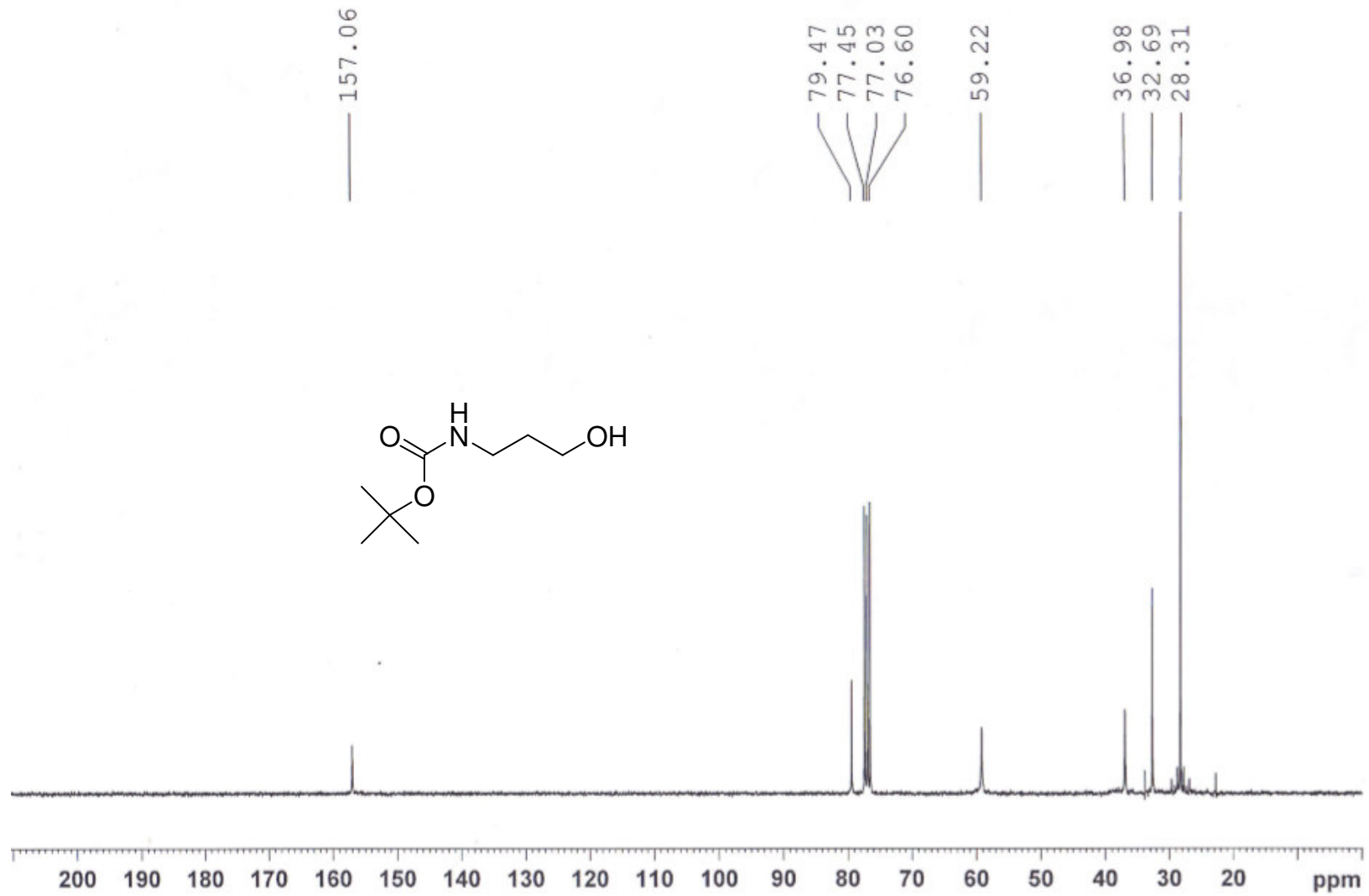
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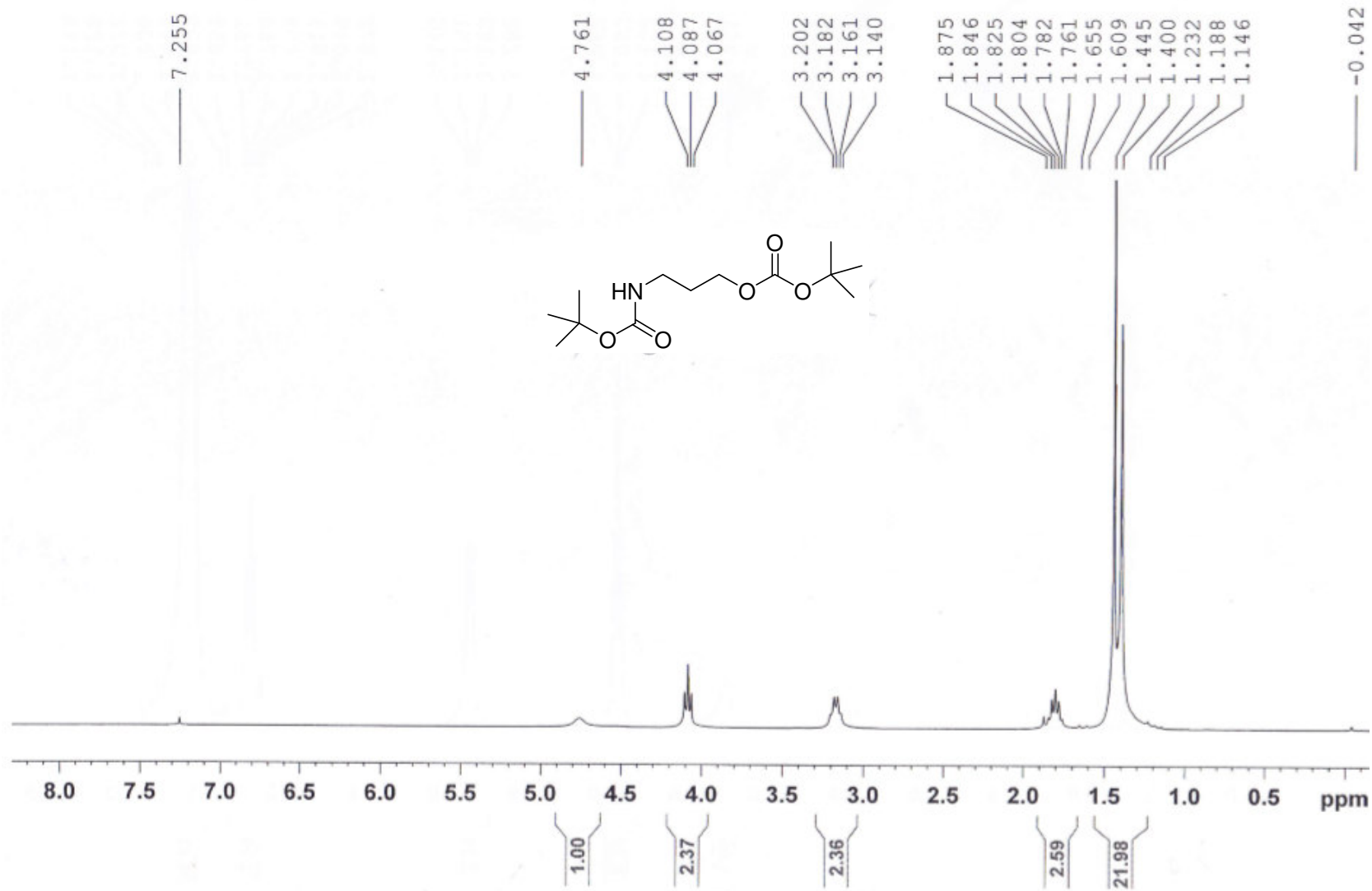
¹H NMR spectra of 5h



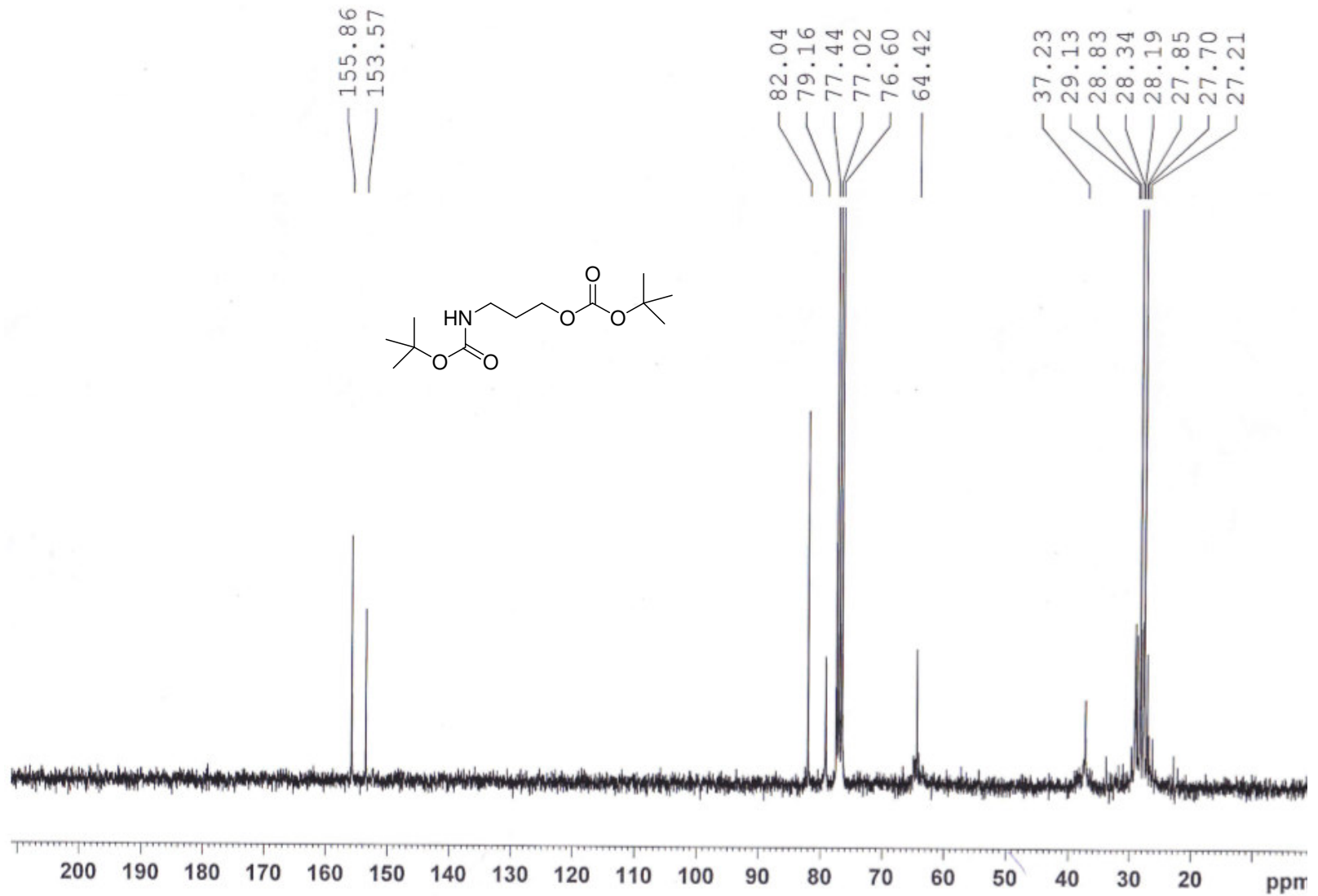
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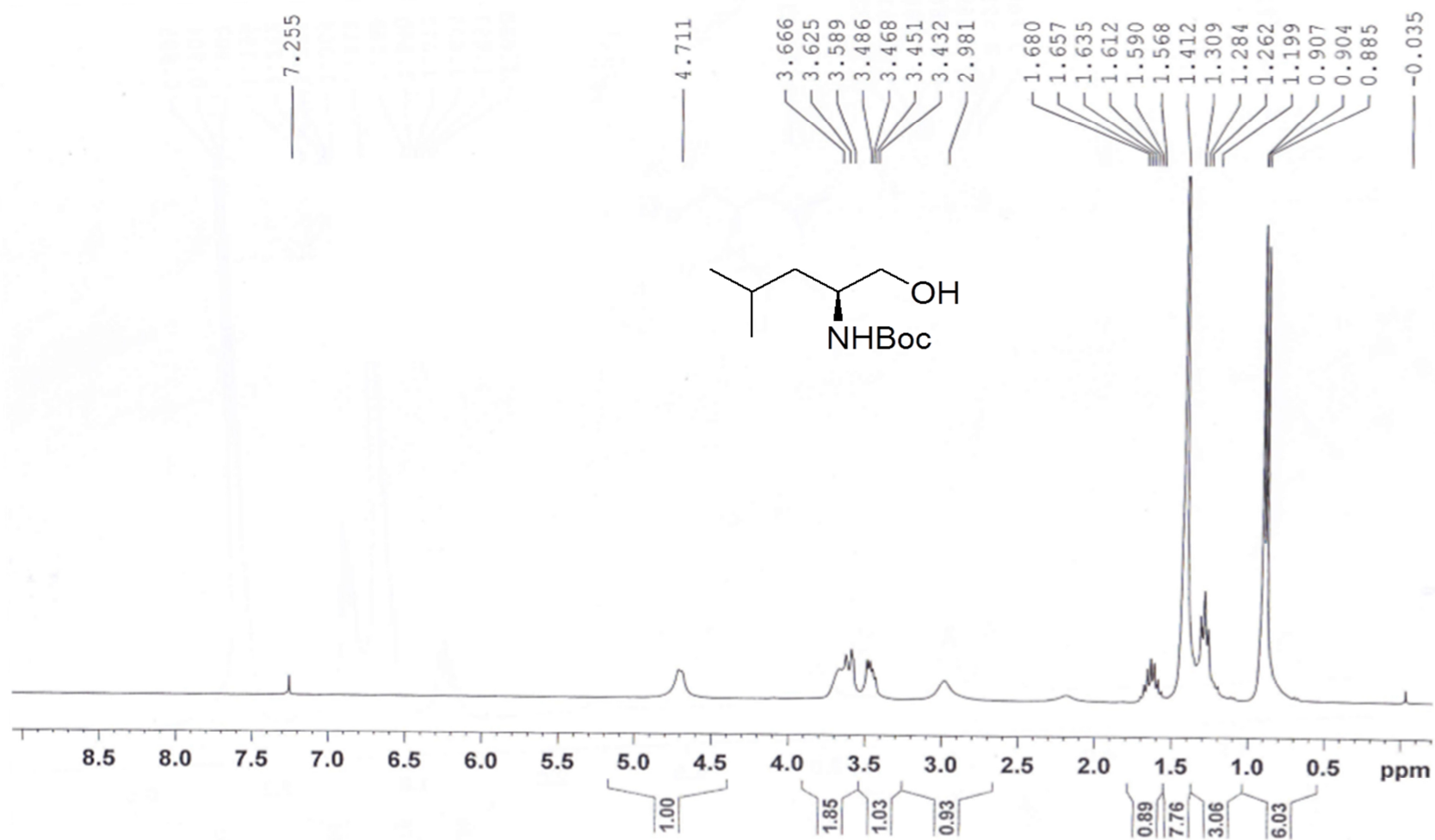
¹H NMR spectra of 5i



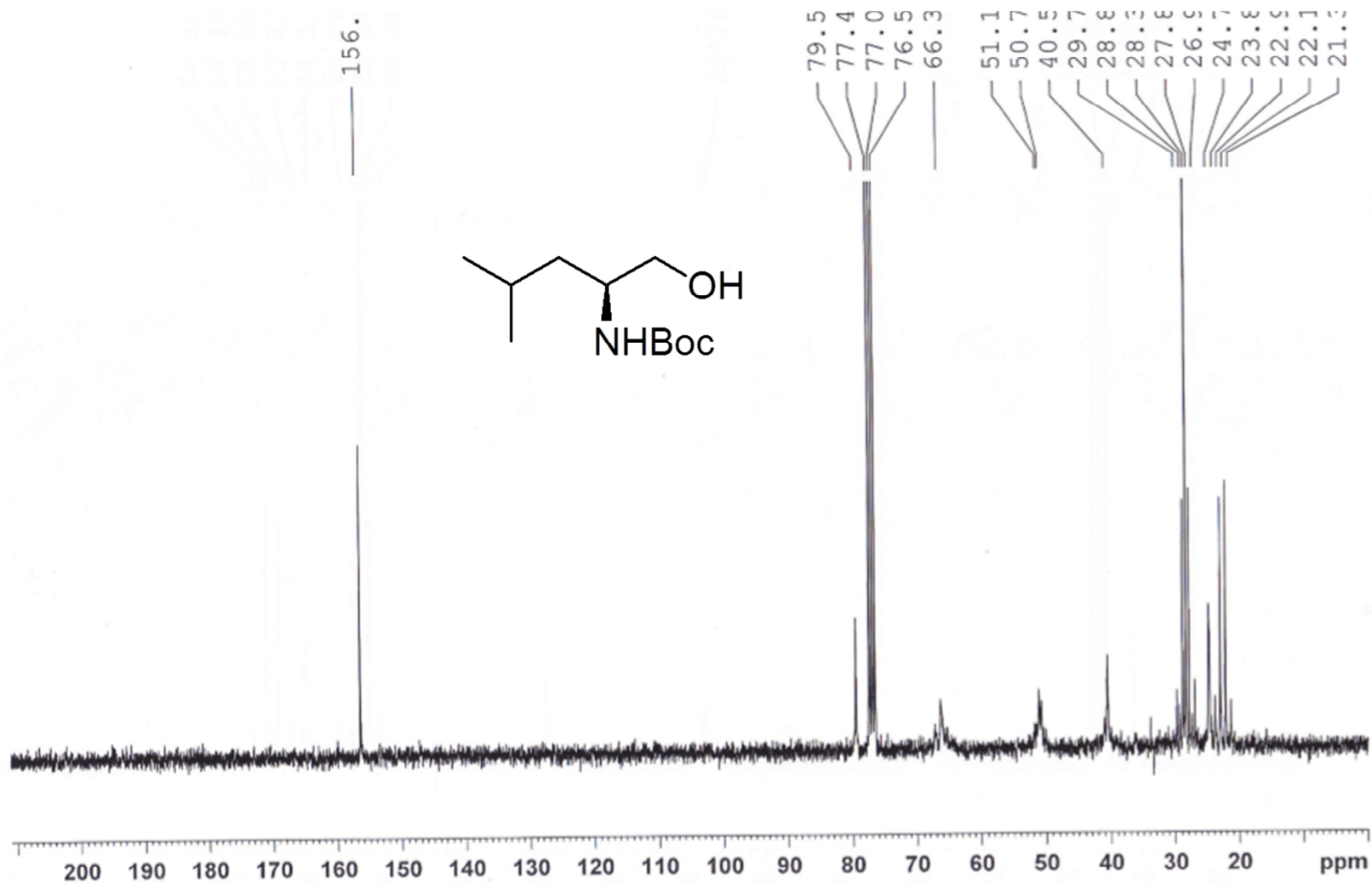
¹³C NMR spectra of 5i



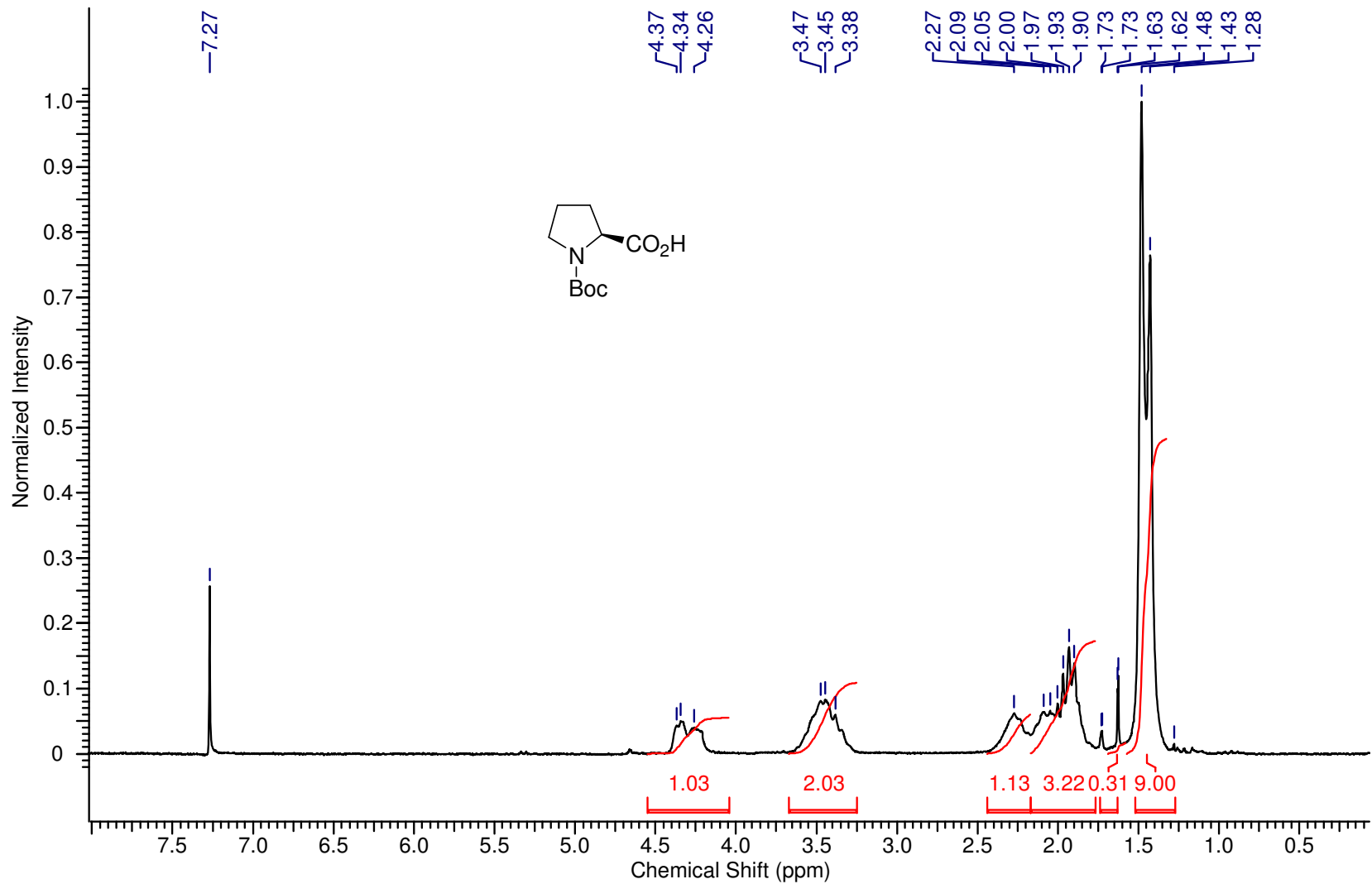
¹H NMR spectra of 6a



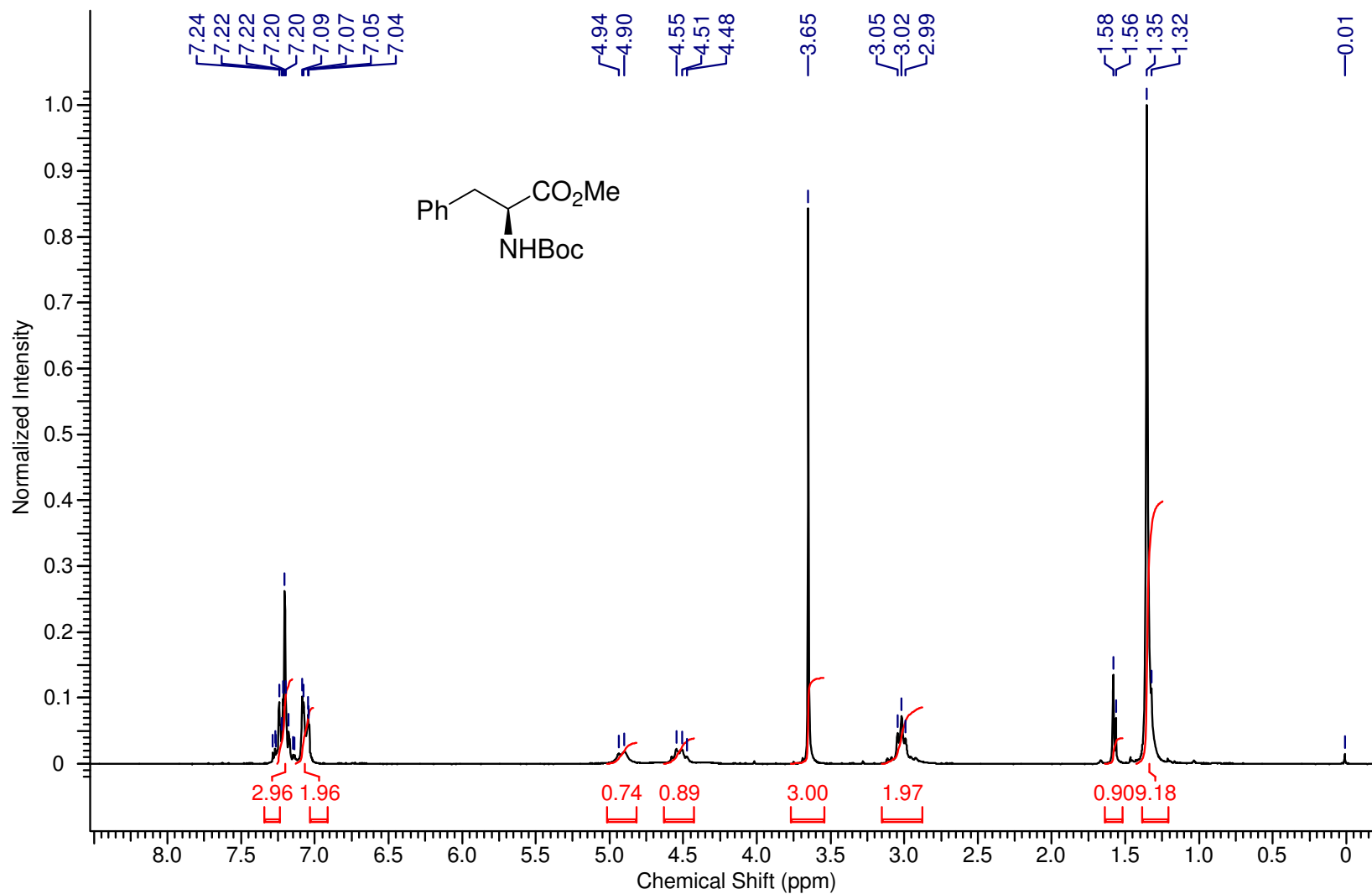
^{13}C NMR spectra of 6a



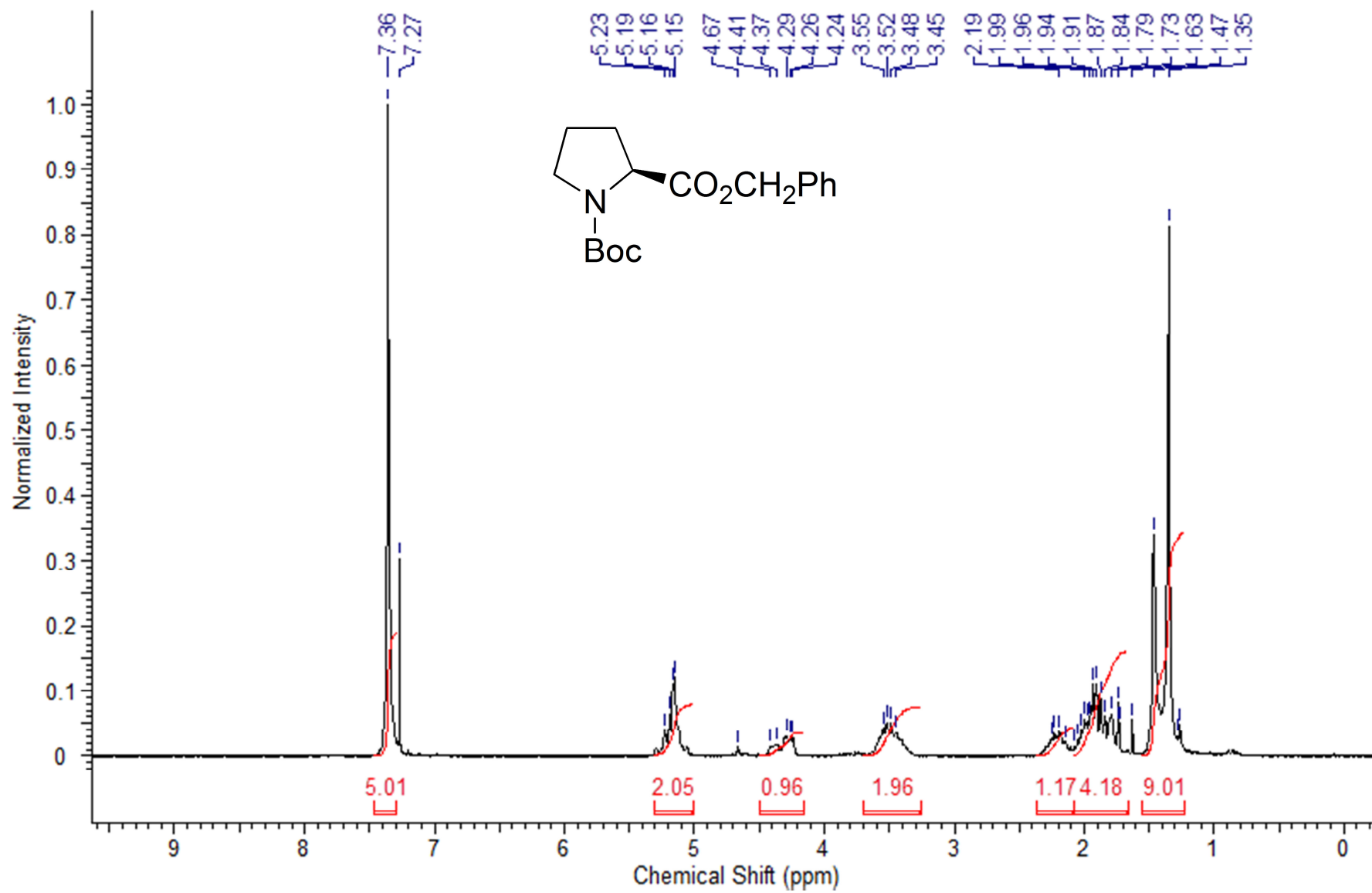
¹H NMR spectra of 6b



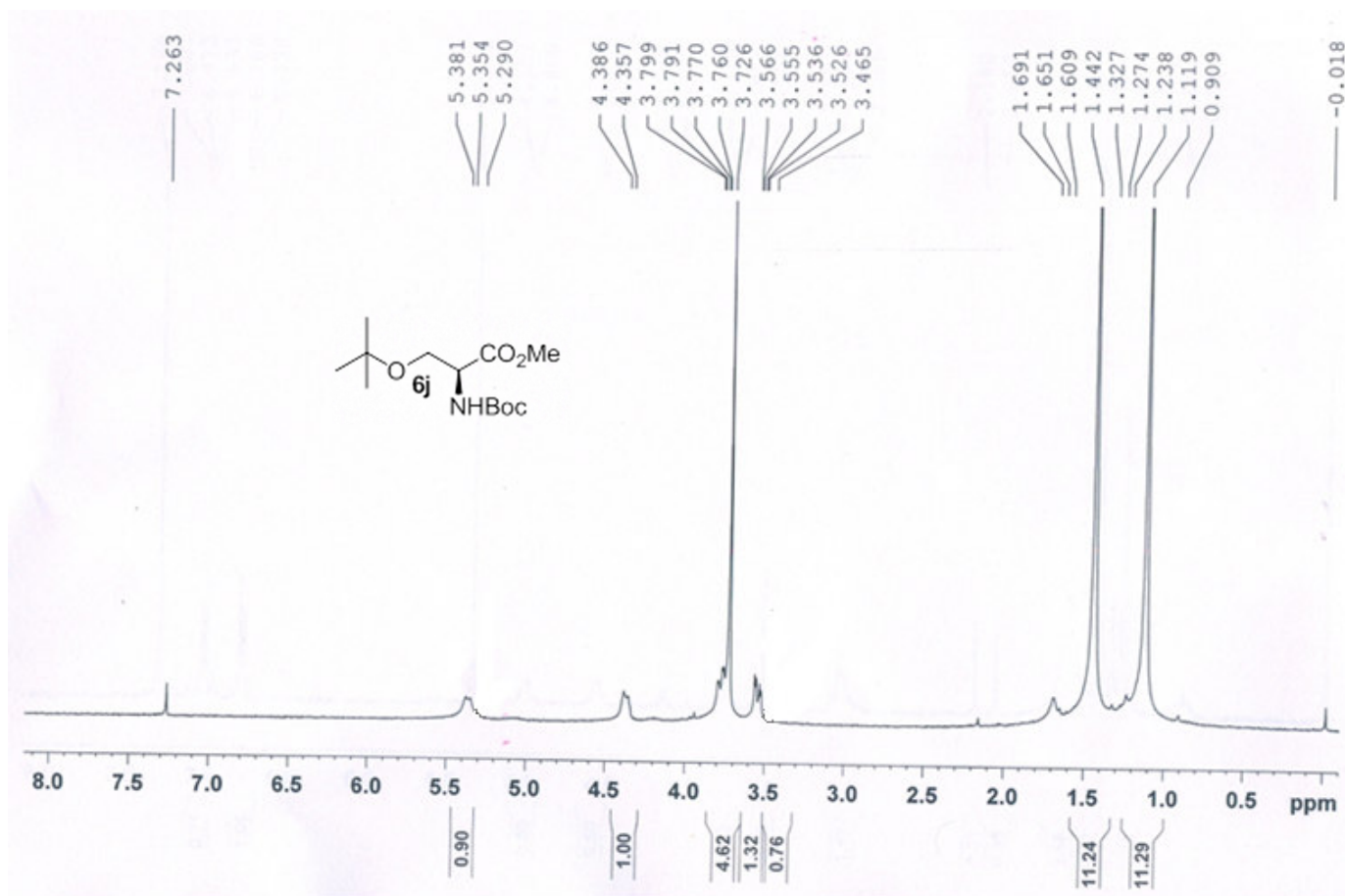
¹H NMR spectra of 6g



^1H NMR spectra of 6i



¹H NMR spectra of 6j



¹H NMR spectra of 6k

