Supporting Information

Total Synthesis of (-)-Indolactam V

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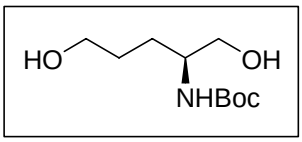
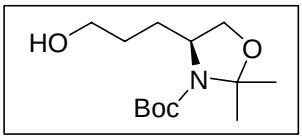
Experimental procedure and physical data



(2*S*)-2-*tert*-Butoxycarbonylamino-1,5-dihydroxypentane 19.[1] To a suspension of L-glutamic acid (15.0 g, 102 mmol) in dry methanol (170 mL) was added TMSCl (56.9 mL, 449 mmol) dropwise in ice-cooled bath, and then the reaction mixture was stirred at room temperature overnight. Then Et_3N (92.4 mL, 663 mmol) and Boc_2O (24.5 g, 112 mmol) were sequentially added, and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure, and the residue was dissolved in water. The aqueous phase was extracted with EtOAc, and the combined organic phases were washed sequentially with water, brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure to give crude *N*-Boc glutamic acid dimethyl ester **18**, which was dissolved in THF/MeOH (5:1, 300 mL) followed by addition of $NaBH_4$ (15.4 g, 408 mmol) at 0℃. Then the reaction mixture was stirred at room temperature for 24 h until the starting material consumed. The solvent was removed under reduced pressure, and water was added to the residue. The mixture was adjusted to pH 6-7 by citric acid, and then extracted with EtOAc until no product was detected in the aqueous phase. The combined organic phased were dried over Na_2SO_4 and evaporated to dryness to give the crude **19**, which could be used for the next step without further purifications. An analytical sample was purified by FCC (DCM-MeOH, 15:1) to provide pure **19** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 (d, J = 7.2 Hz, 1H), 4.01 (br s, 1H), 3.72 (br s, 1H), 3.54-3.58 (m, 5H), 1.39-1.60 (m, 4H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 79.4, 64.7, 62.0, 52.1, 28.6, 28.3, 27.8; ^{1}H NMR (300 MHz, CD_3OD) δ 3.42-3.58 (m, 5H), 1.32-1.69 (m, 4H), 1.43 (s, 9H); ^{13}C NMR (75 MHz, CD_3OD) δ 158.5, 79.3, 65.5, 62.8, 53.5, 30.1, 28.7.



(4*S*)-*tert*-Butyl-4-(3-hydroxypropyl)-2,2-dimethyloxazolidine-3-carxoylate S1.[2] The crude **19** was dissolved in acetone/2,2-DMP (10:3, 260 mL), to which catalytic amount of $BF_3{\cdot}Et_2O$ (250 μL) was added. The resulting mixture was stirred at room temperature for 24 h until the starting material consumed, and the solvent was removed in vacuo. The residue oil was dissolved in water and the

[1] (a) S.-H. Moon, S. Lee, *Synth. Commun.* 1998, **28**, 3919-3926. (b) L. J. Breña-Valle, R. Cruz-Almanza, F. O. Guadarrama-Morales, *Synth. Commun.* 2001, **31**, 697-706.

[2] C. Truchot, Q. Wang, N. A. Sasaki, *Eur. J. Org. Chem.* 2005, 1765-1776.

pH was adjusted to 6-7 by adding sat. aq. $NaHCO_3$. The aqueous phase was extracted with EtOAc, and the combined organic phases were washed sequentially with water, brine, and dried over Na_2SO_4. Purification with FCC (DCM-MeOH, 30:1) afforded the desired **S1** (19.0 g, 72% from L-glutamic acid) as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) showed the presence of two rotamers, δ 3.53-3.82 (m, 5H), 3.21 (br s, 0.5H), 2.85 (br s, 0.5H), 1.36-1.71 (m, 19H); ^{13}C NMR (75 MHz, $CDCl_3$), all rotemers shown, δ 152.3, 151.8, 93.5, 93.1, 80.0, 79.3, 66.8, 66.7, 62.0, 61.9, 57.0, 29.8, 29.2, 29.1, 28.8, 28.1, 27.2, 26.4, 24.2, 22.9.

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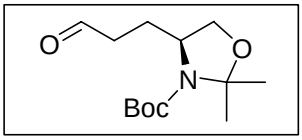
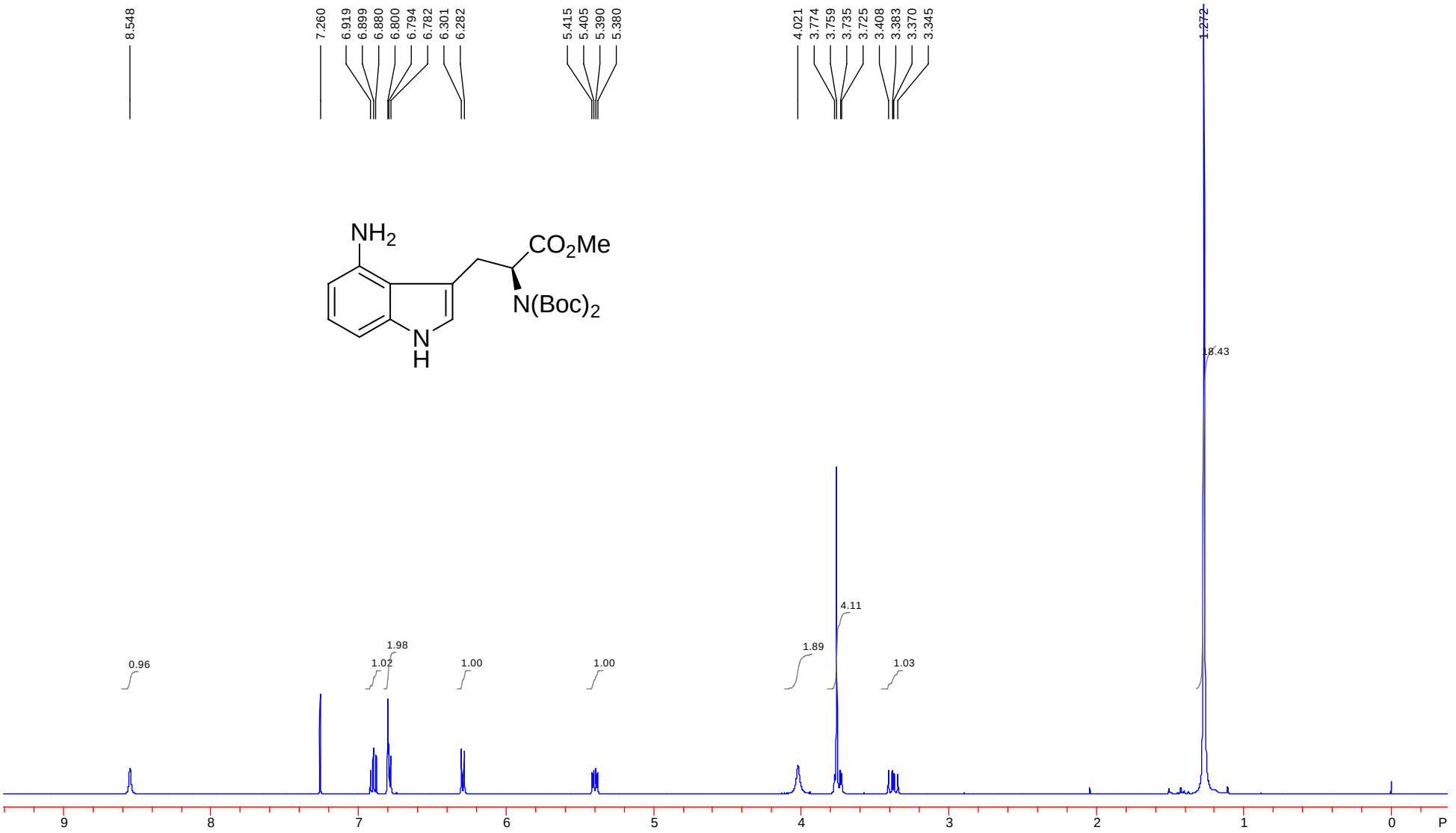


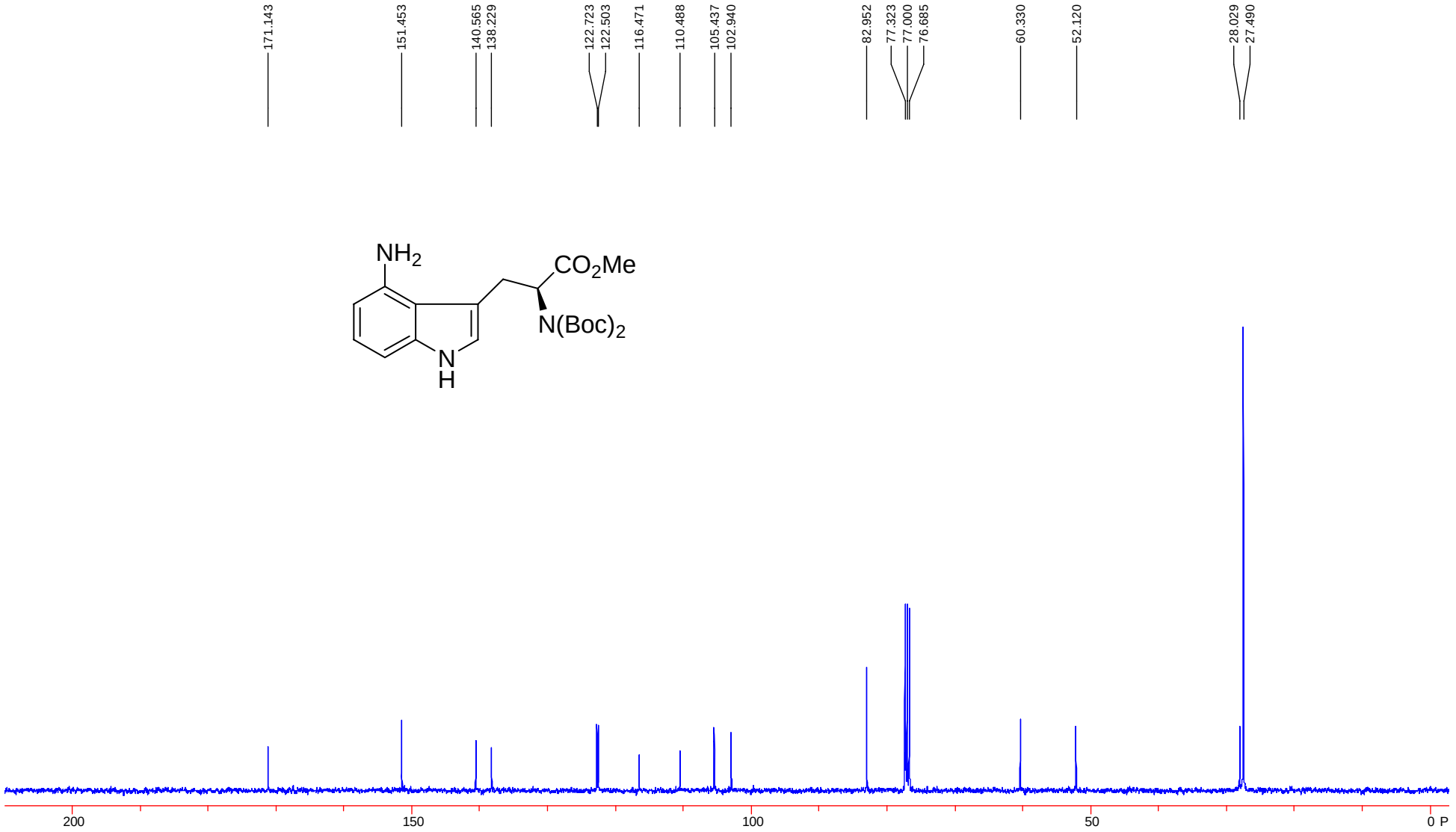
Aldehyde 7.[2-3] Oxalyl chloride (552 μL) was added dropwise to a solution of DMSO (984 μL) in dry DCM (25 mL) at -78℃. The reaction mixture was stirred at -78℃ for 15 min, and a solution of **S1** (1.09 g, 4.2 mmol) in dry DCM (3.6 mL) was added dropwise. The reaction mixture was stirred at -78℃ for another 45 min, followed by addition of Et_3N (4.0 mL) at the same temperature. The cooling bath was then removed, and the reaction was stirred at room temperature for 1 h. Then water was added, and the aqueous phase was extracted with DCM. The combined organic phases were washed successively with 1M aq. HCl, sat. $NaHCO_3$ and brine, then dried over Na_2SO_4. Purification with FCC (PE-EtOAc, 4:1) afforded the desired aldehyde **7** (1.02 g, 94%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) show the presence of two rotamers, δ 9.71 (br s, 1H), 3.80-3.90 (m, 2H), 3.62 (d, J = 8.0 Hz, 1H), 2.40-2.44 (m, 2H), 1.79-1.99 (m, 2H), 1.49-1.53 (m, 3H), 1.41 (br s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) all rotamers shown, δ 201.4, 201.1, 152.4, 151.7, 93.9, 93.4, 80.1, 79.7, 66.9, 56.5, 56.1, 40.3, 40.1, 28.3, 27.4, 26.6, 25.8, 24.2, 22.9.

[3] X. Feng, E. D. Edstrom, *Tetrahedron: Asymmetry*, 1999, **10**, 99-105.

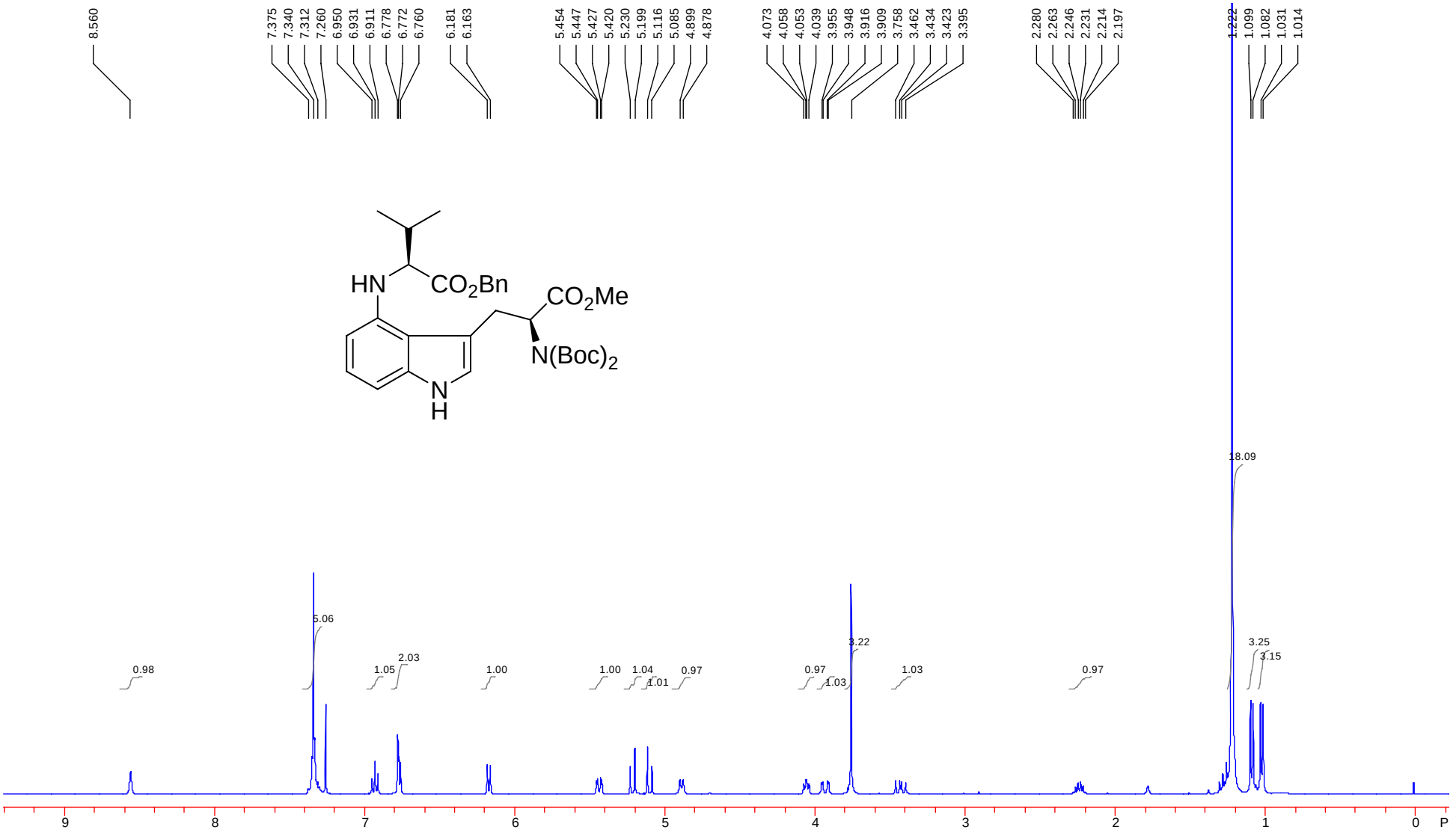
^{1}H-NMR of compound 8 (400 MHz, $CDCl_3$)



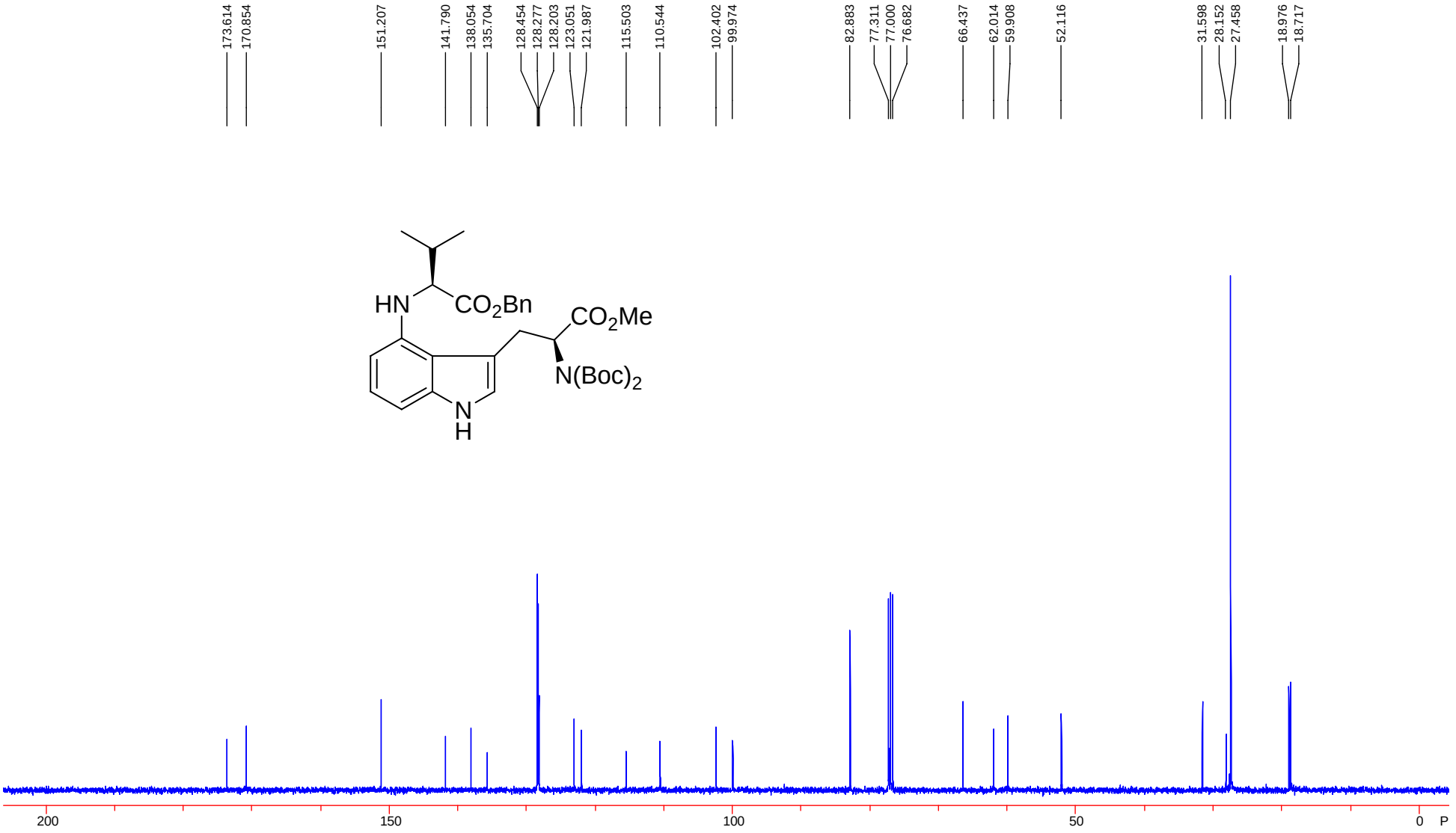
^{13}C-NMR of compound 8 (100 MHz, $CDCl_3$)



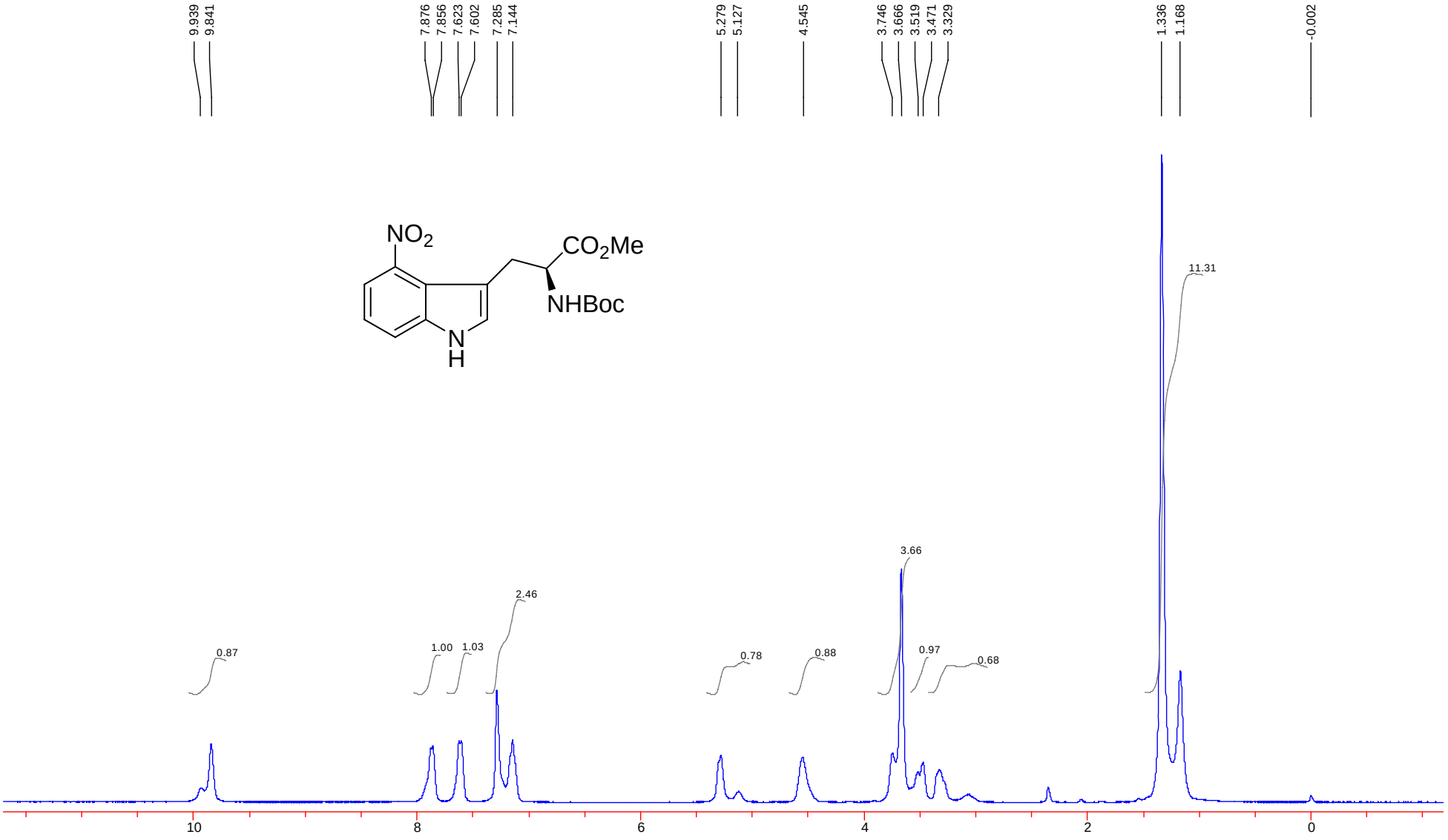
^{1}H-NMR of compound 9 (400 MHz, $CDCl_3$)



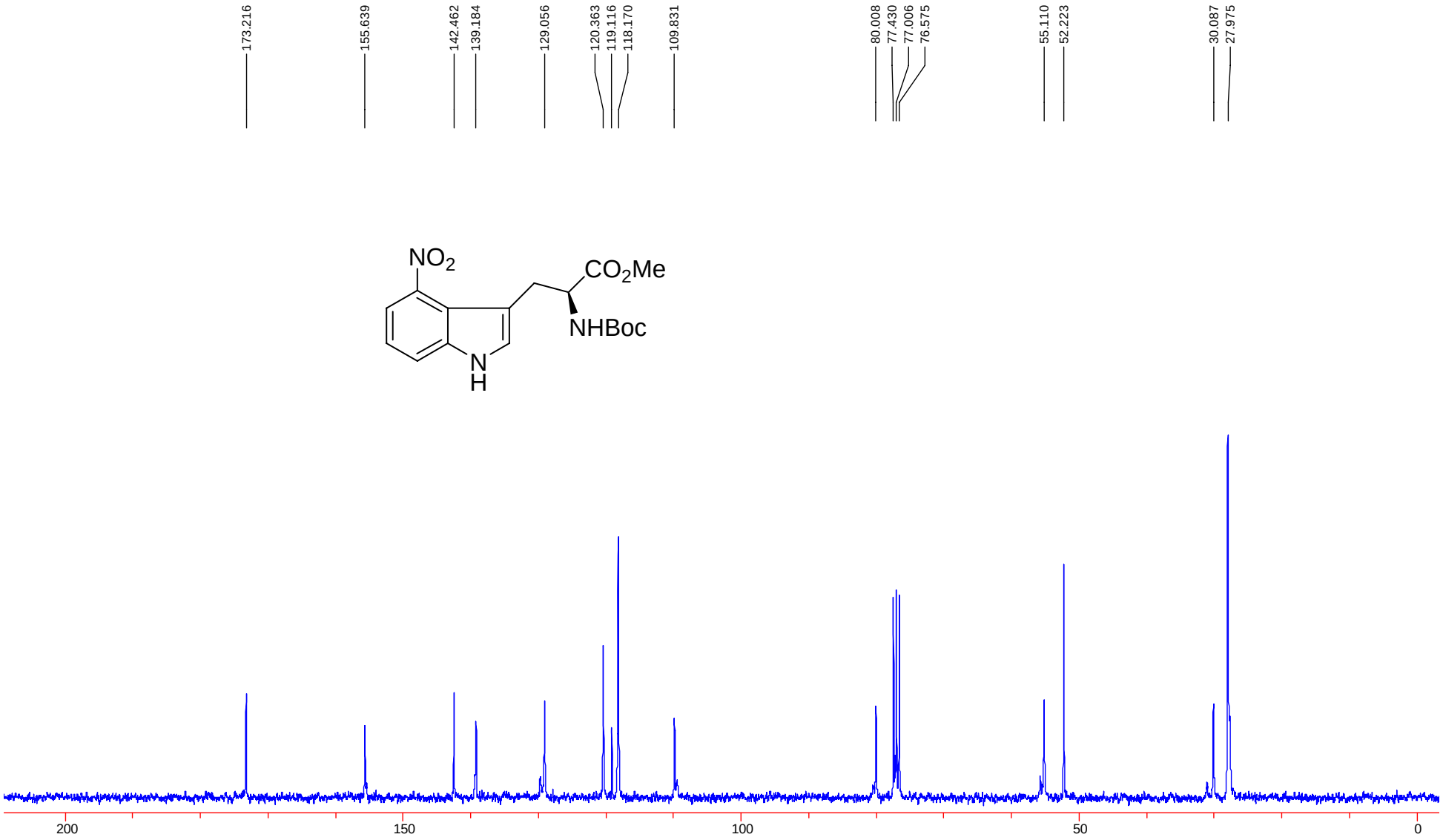
^{13}C-NMR of compound 9 (100 MHz, $CDCl_3$)



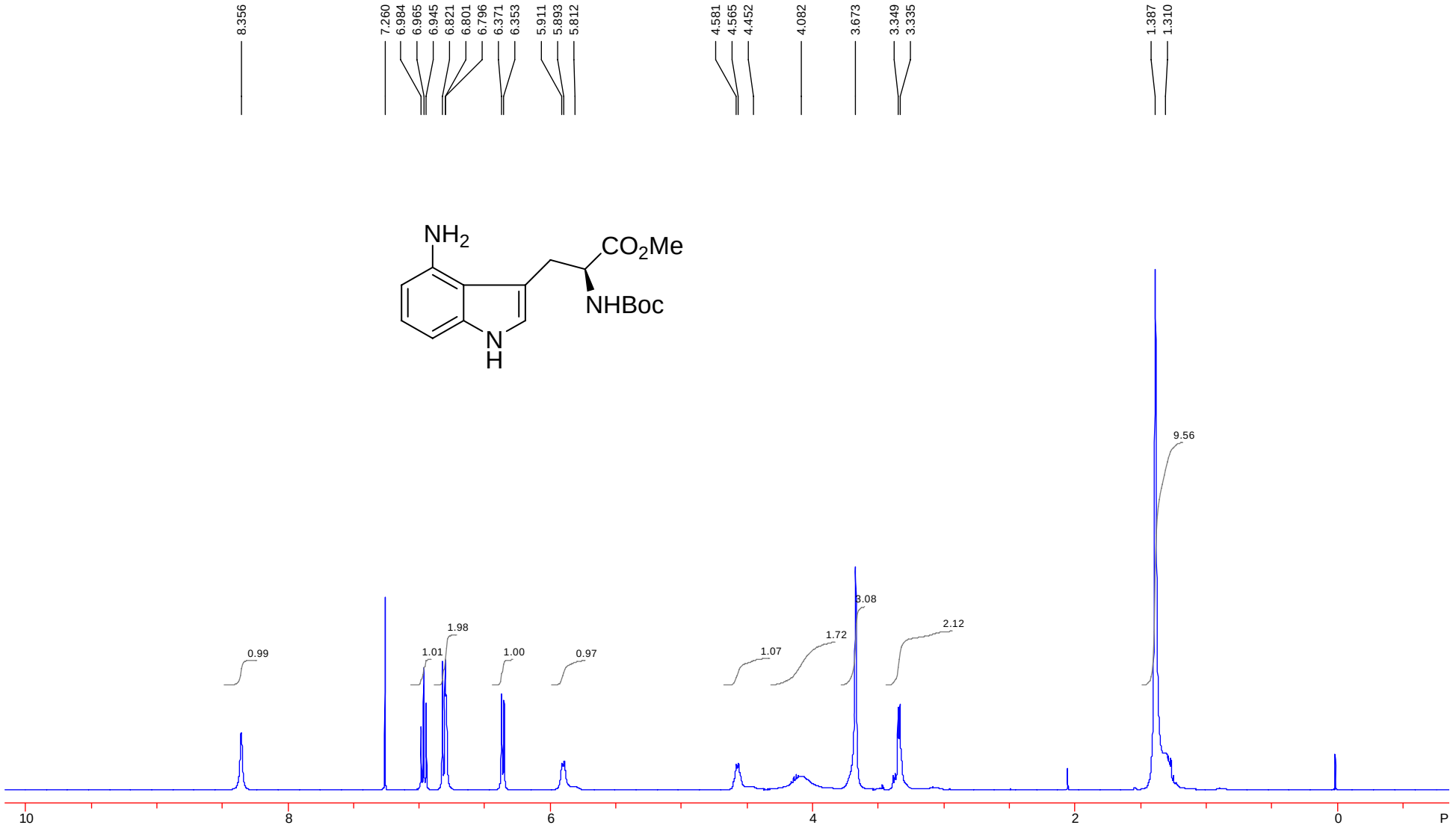
^{1}H-NMR of compound 10 (300 MHz, $CDCl_3$)



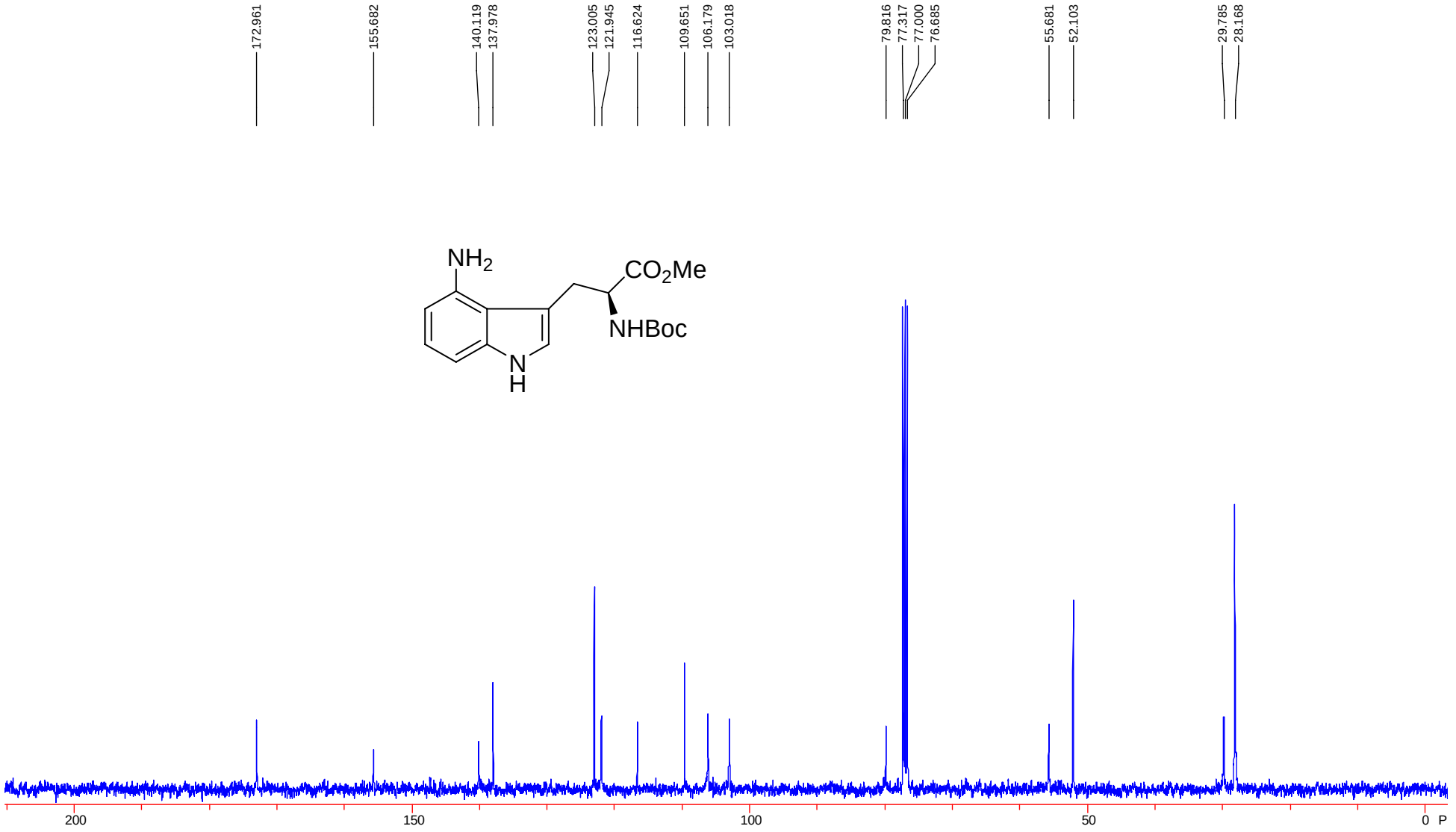
^{13}C-NMR of compound 10 (75 MHz, $CDCl_3$)



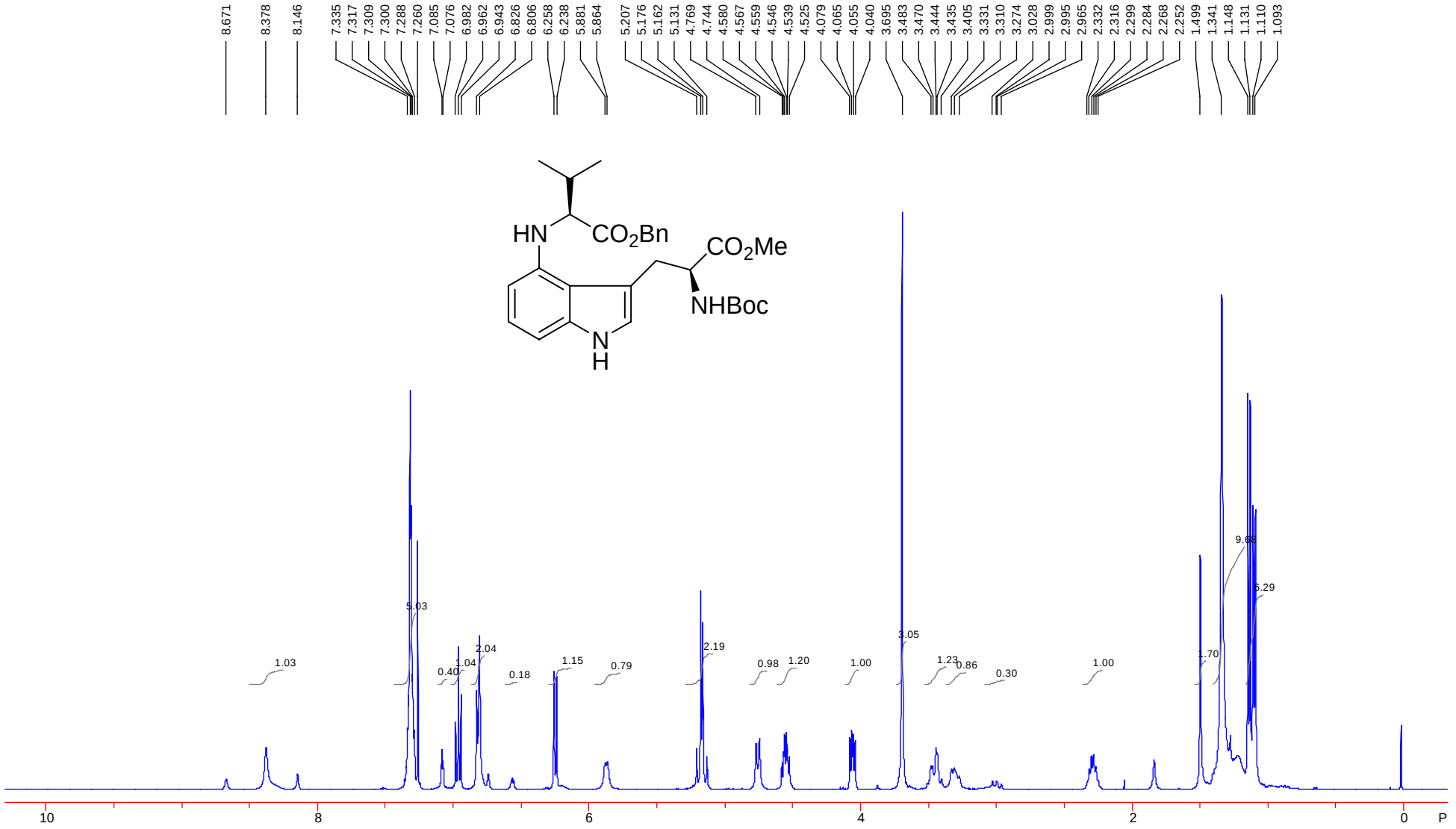
^{1}H-NMR of compound 11 (400 MHz, $CDCl_3$)



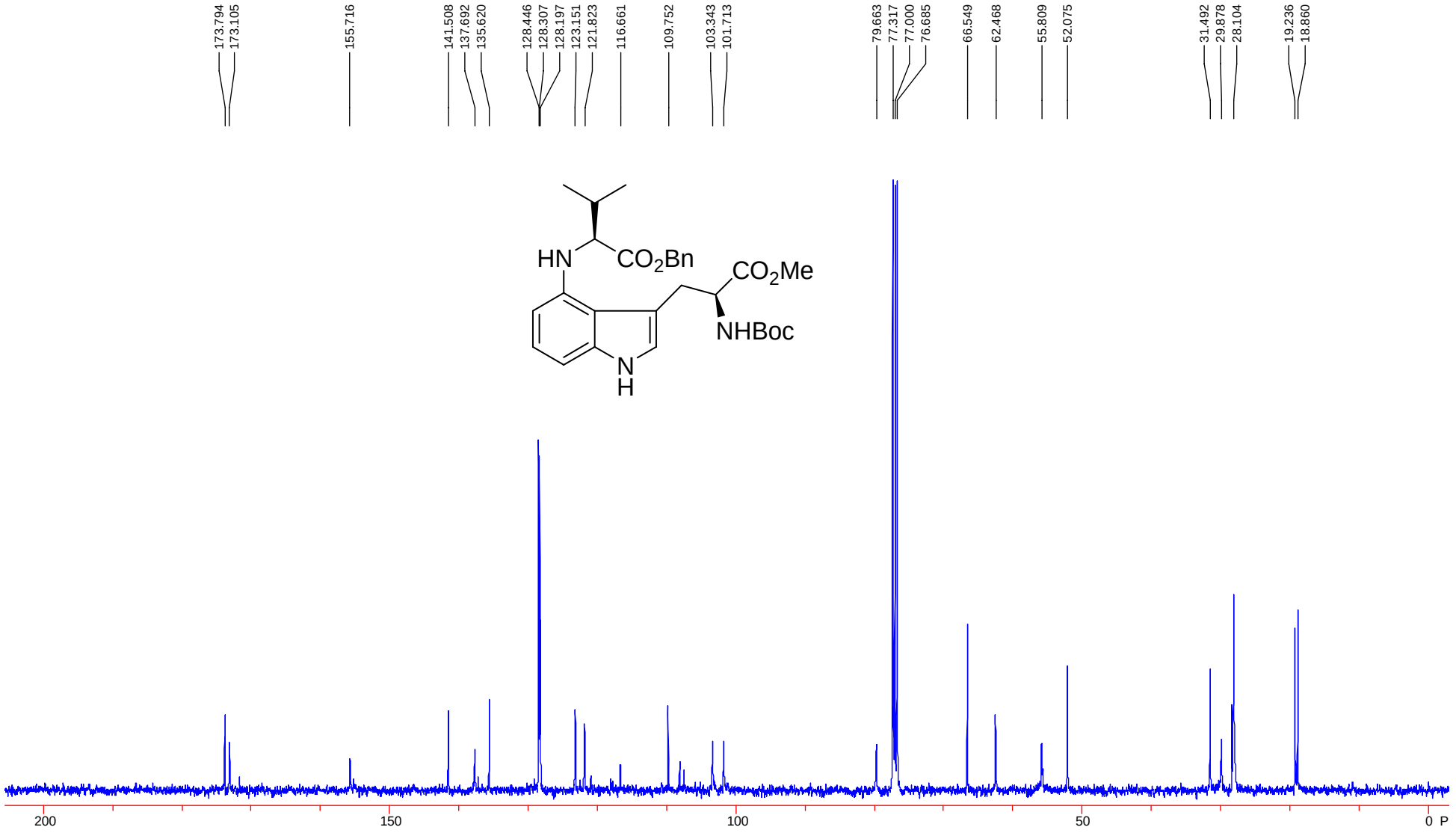
^{13}C-NMR of compound 11 (100 MHz, $CDCl_3$)



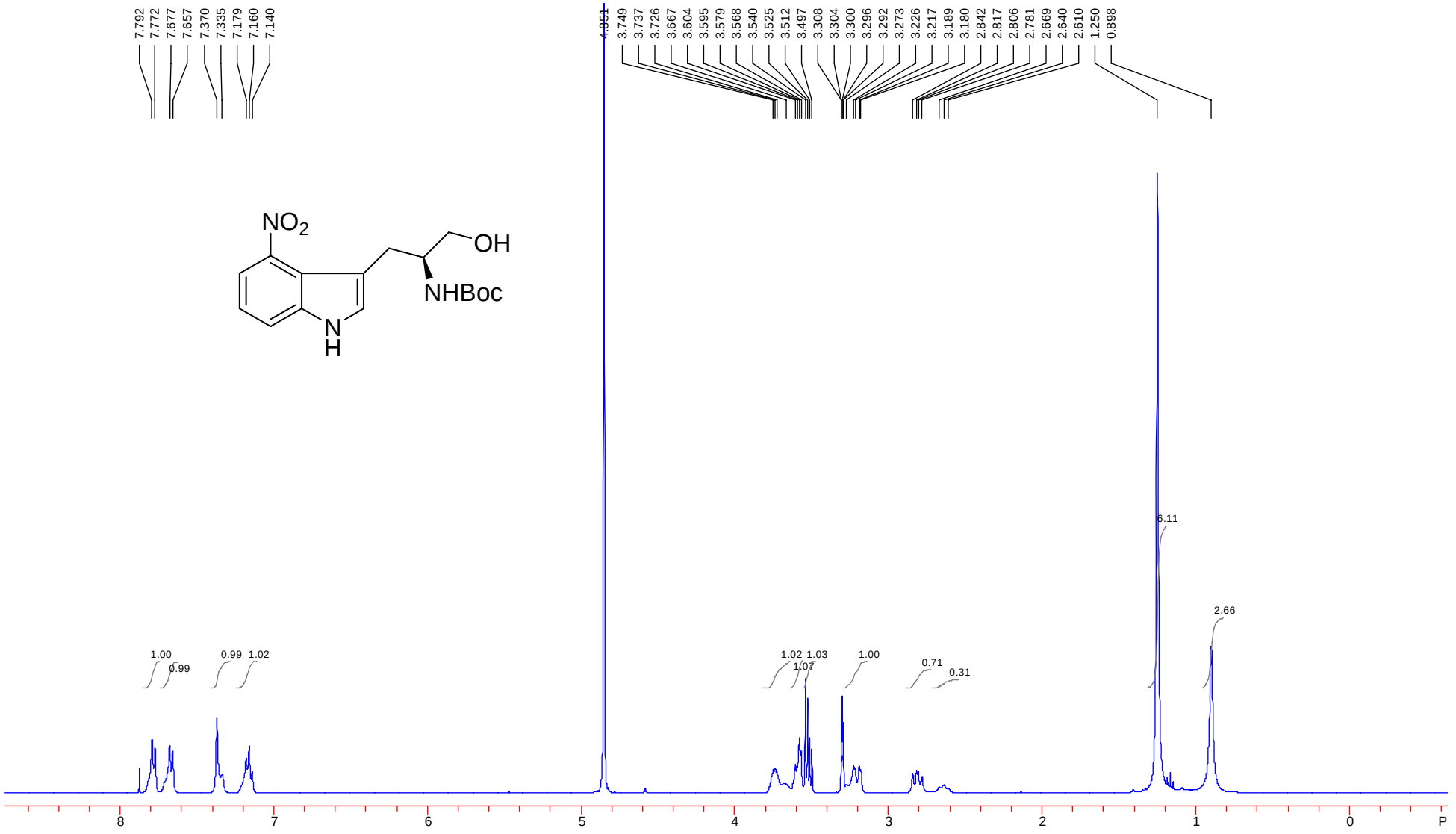
^{1}H-NMR of compound 12 (400 MHz, $CDCl_3$)



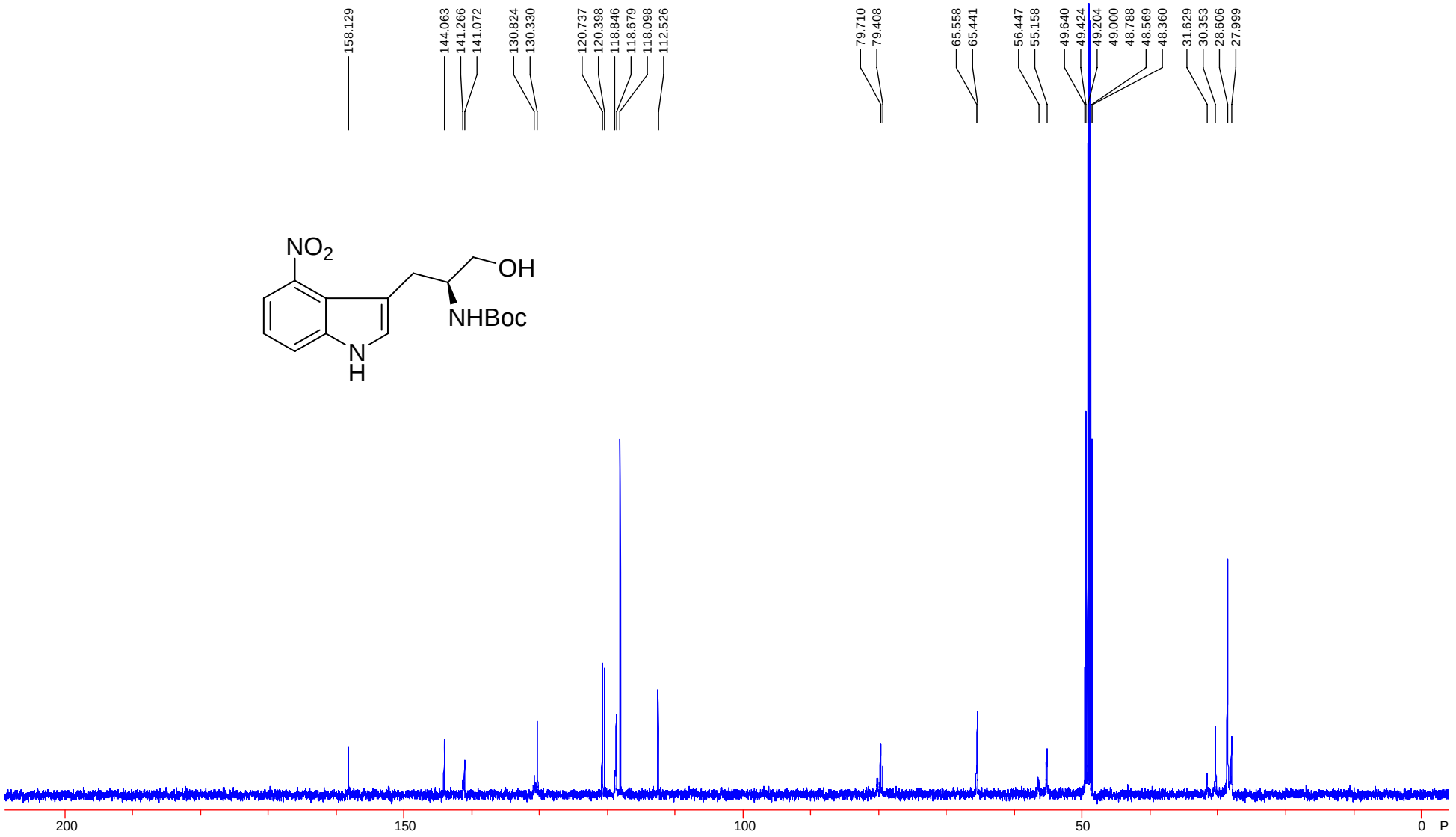
^{13}C-NMR of compound 12 (100 MHz, $CDCl_3$)



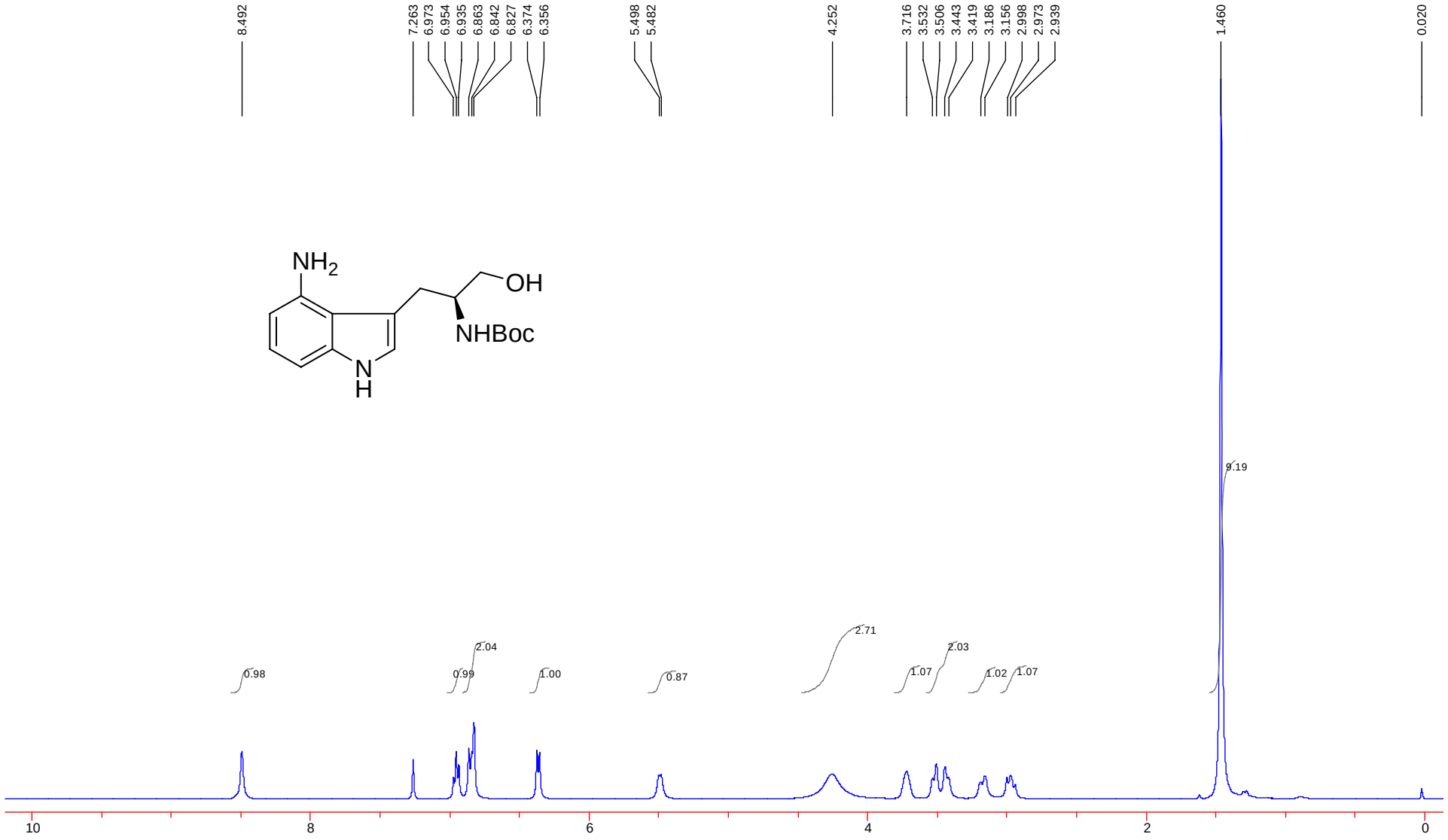
^{1}H-NMR of compound 13 (400 MHz, CD_3OD)



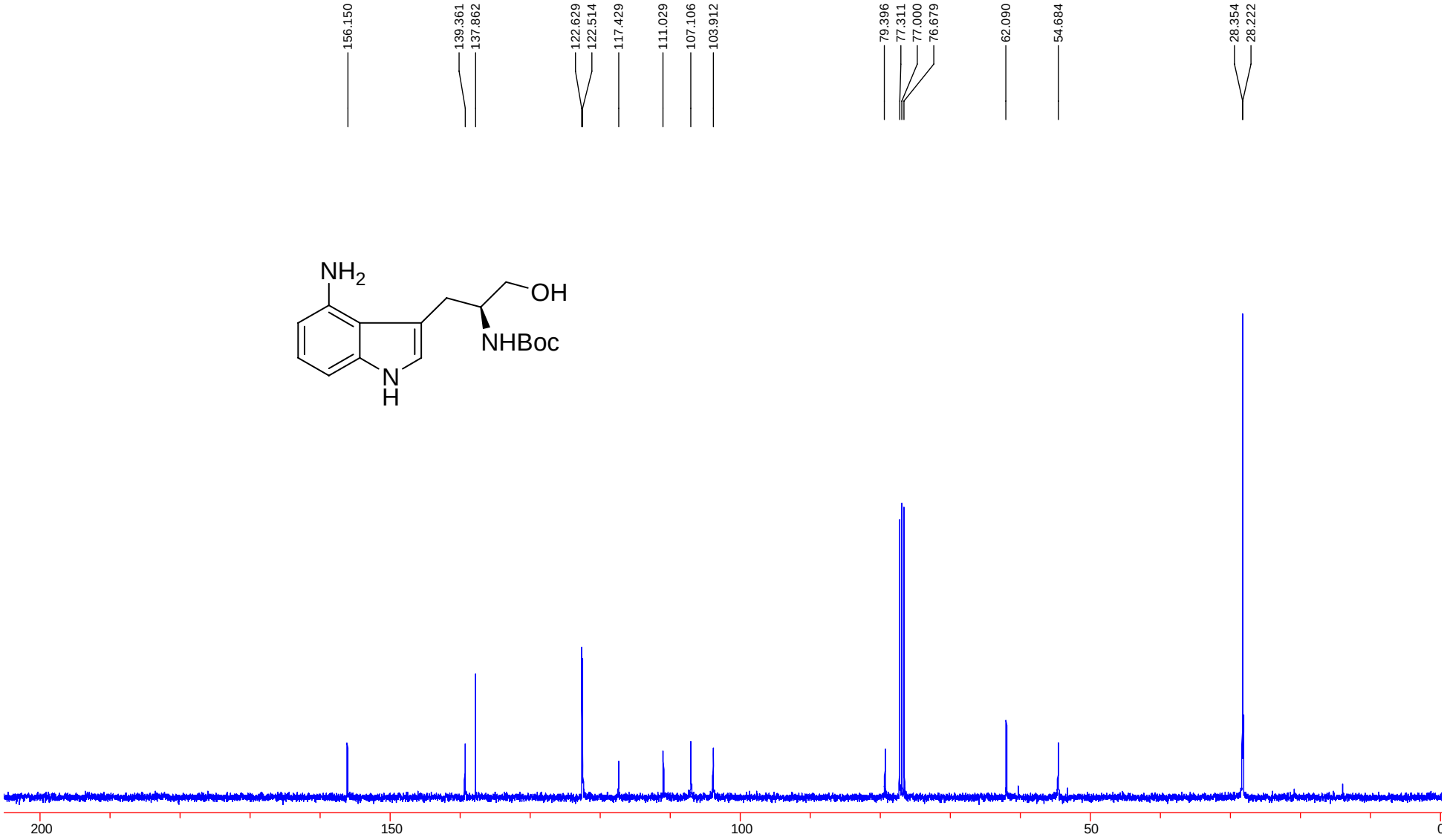
^{13}C-NMR of compound 13 (100 MHz, CD_3OD)



^{1}H-NMR of compound 14 (400 MHz, $CDCl_3$)



^{13}C-NMR of compound 14 (100 MHz, $CDCl_3$)



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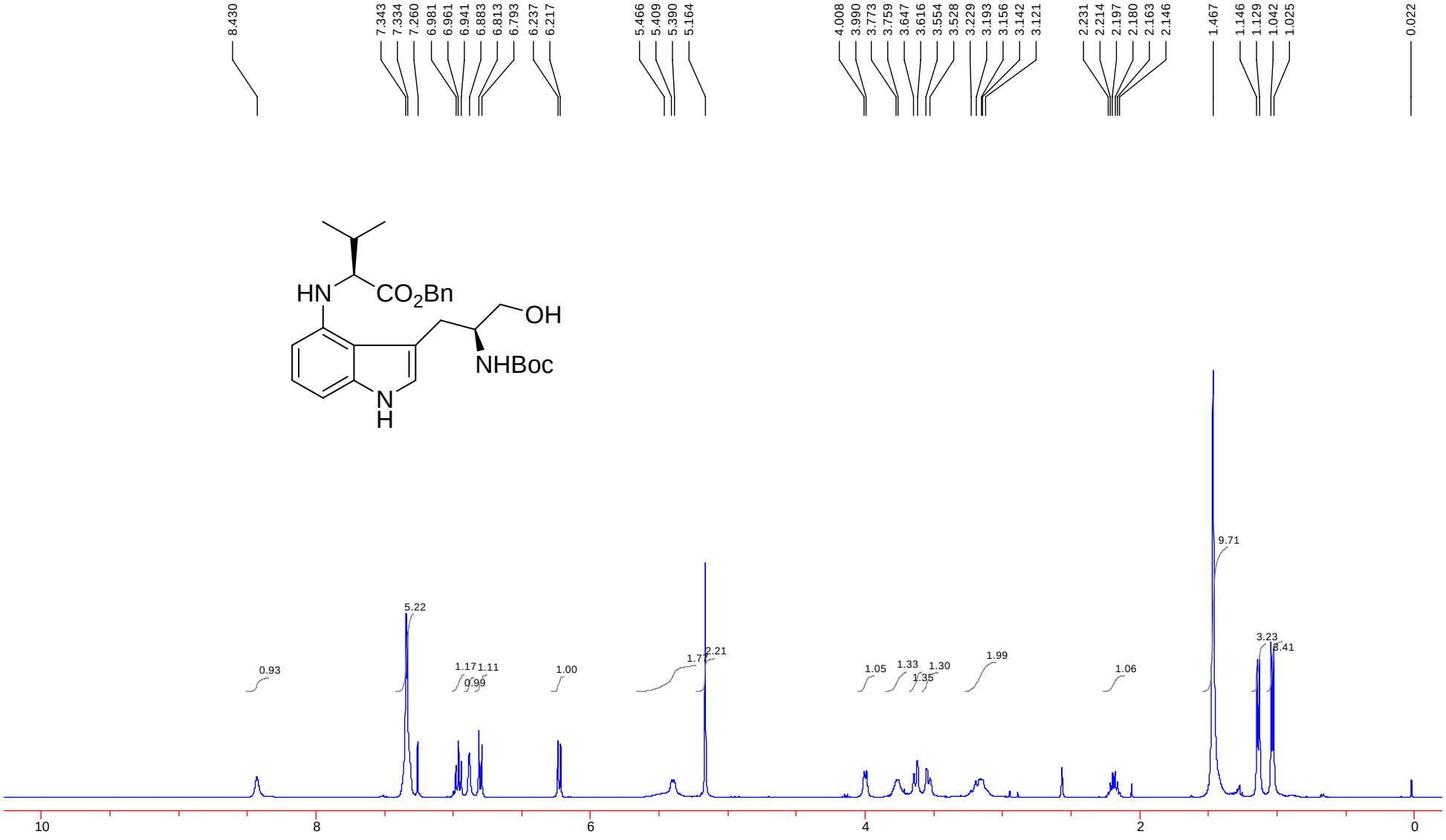
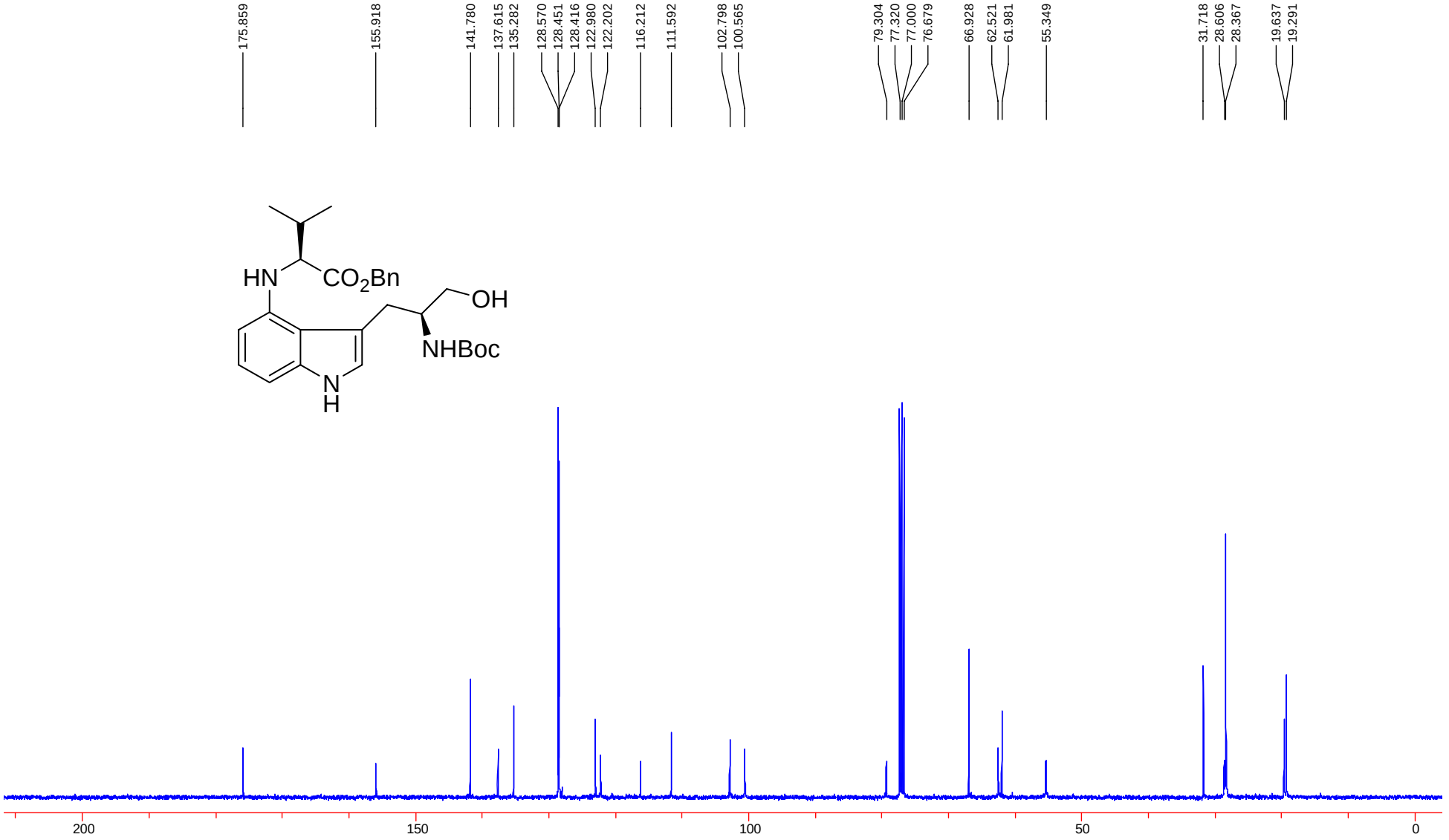
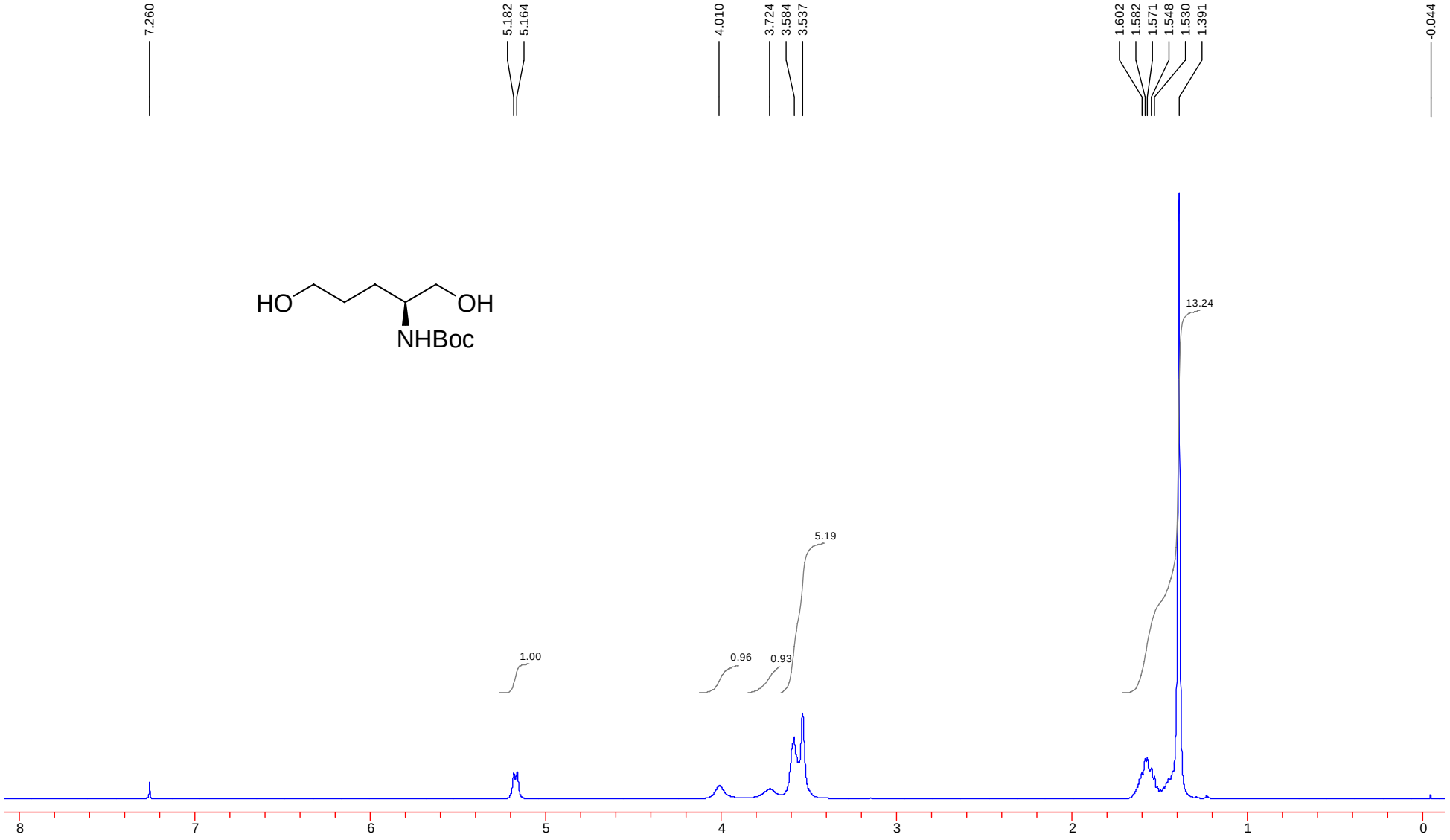


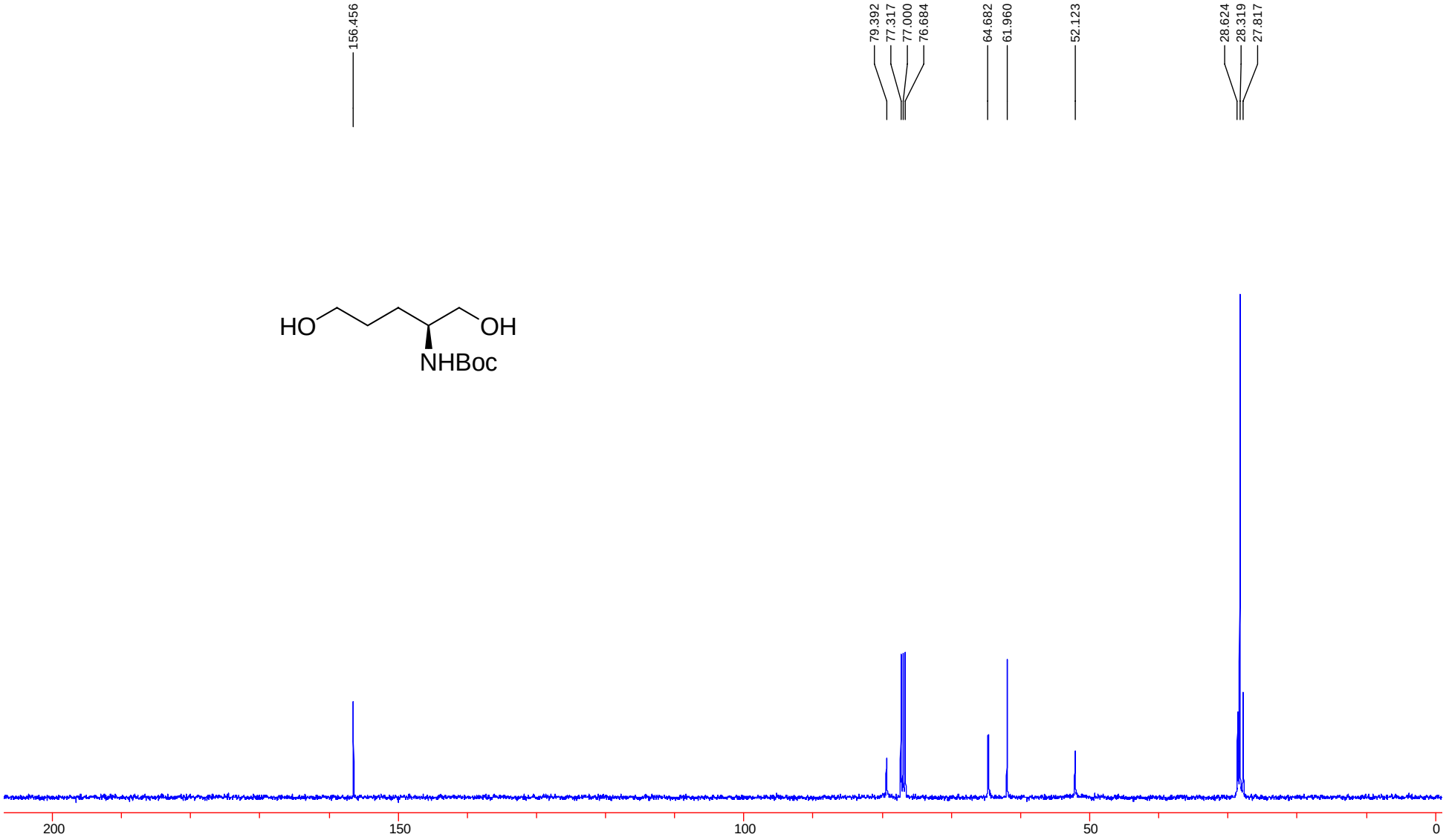
^{13}C-NMR of compound 15 (100 MHz, $CDCl_3$)



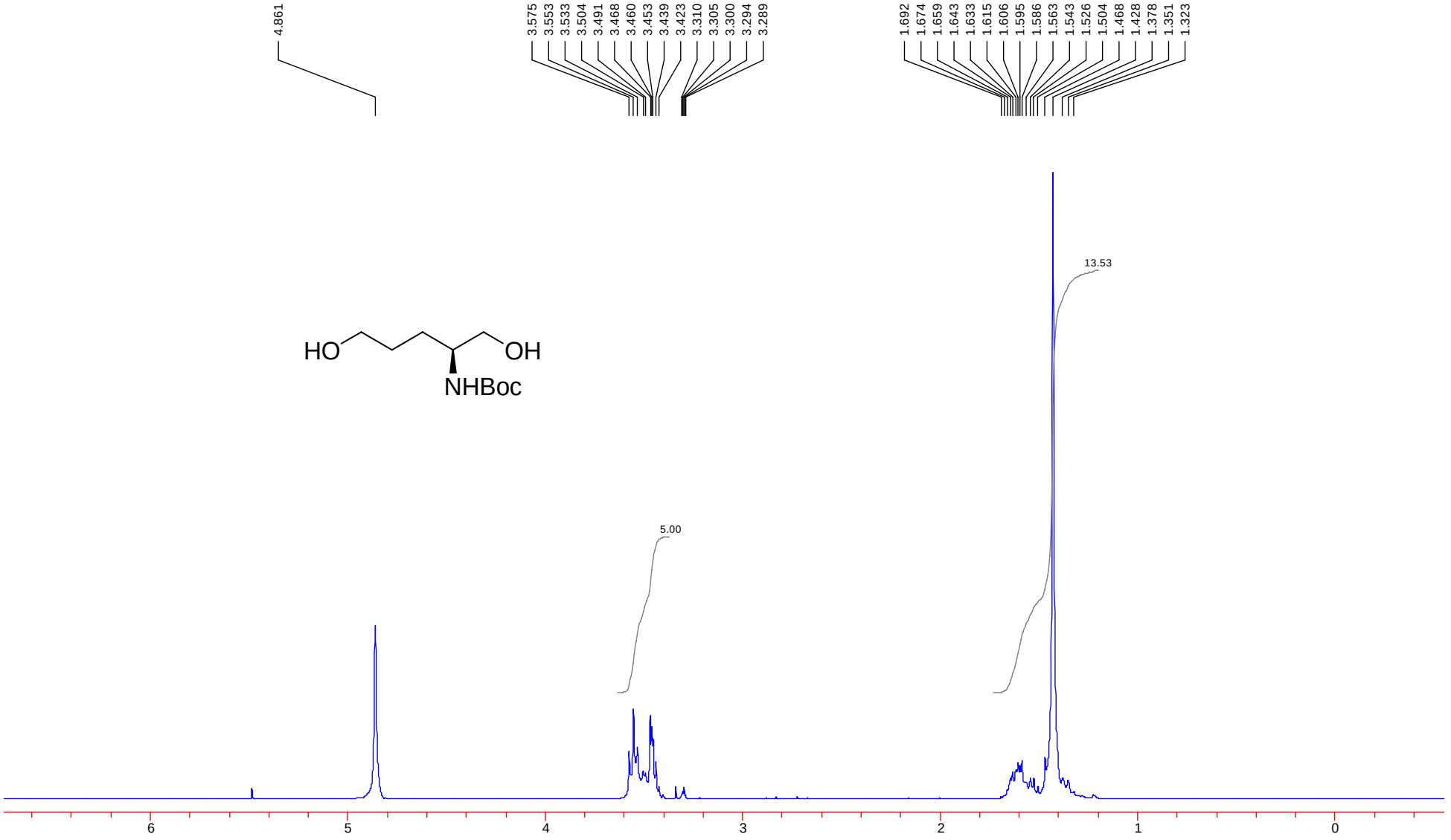
^{1}H-NMR of compound 19 (400 MHz, $CDCl_3$)



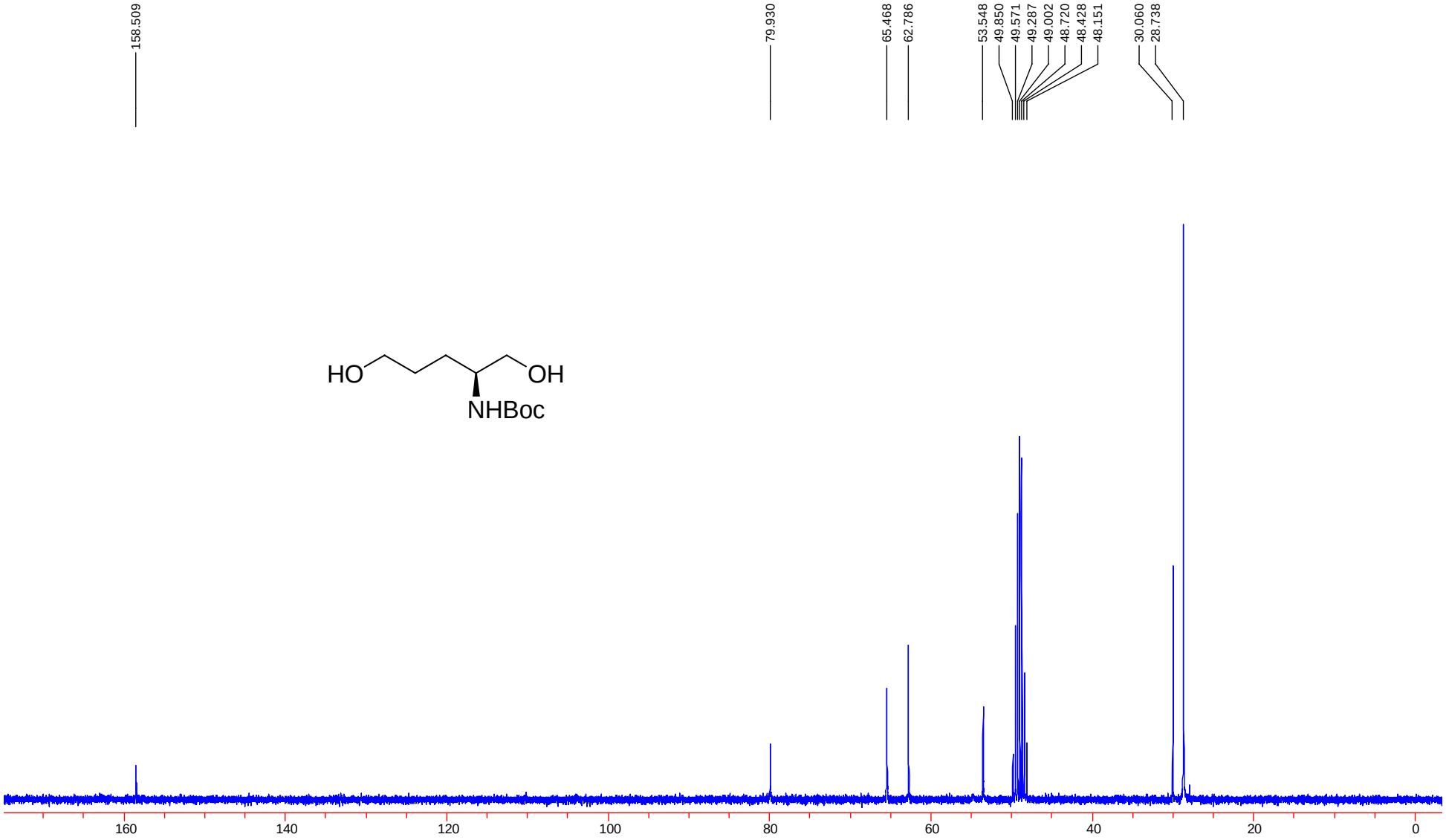
^{13}C-NMR of compound 19 (100 MHz, $CDCl_3$)



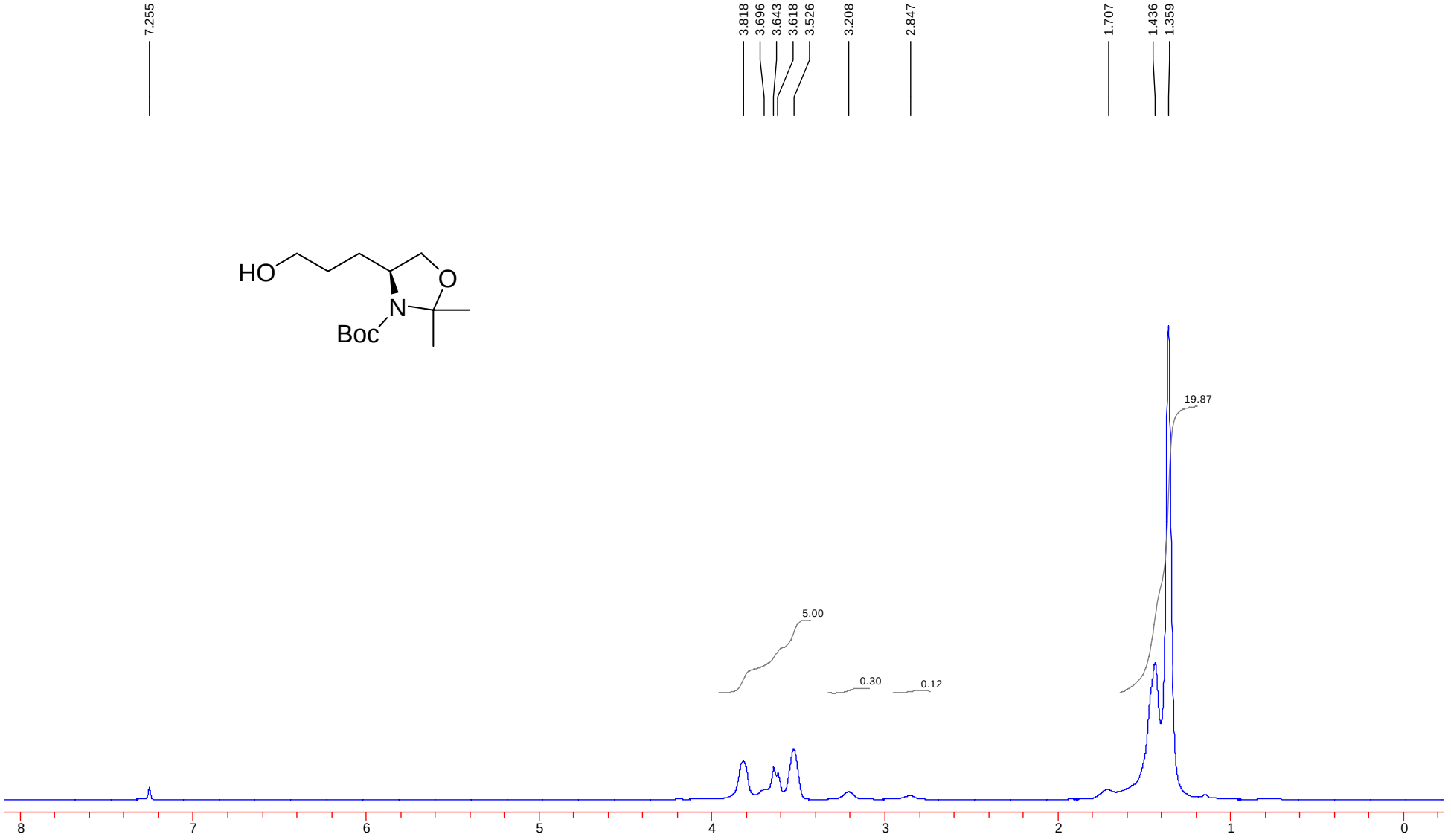
^{1}H-NMR of compound 19 (300 MHz, CD_3OD)



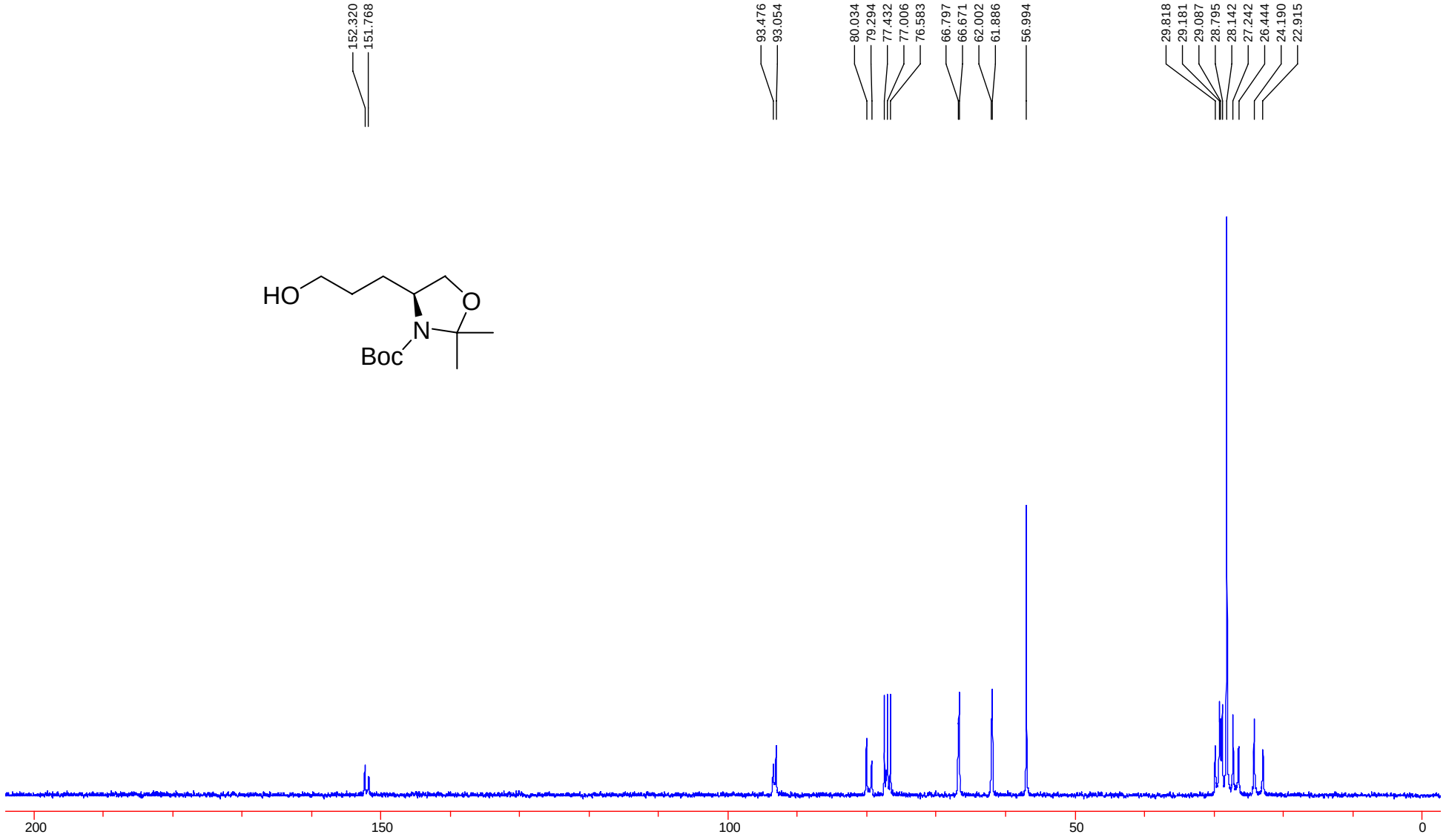
^{13}C-NMR of compound 19 (75 MHz, CD_3OD)



^{1}H-NMR of compound S1 (300 MHz, $CDCl_3$)

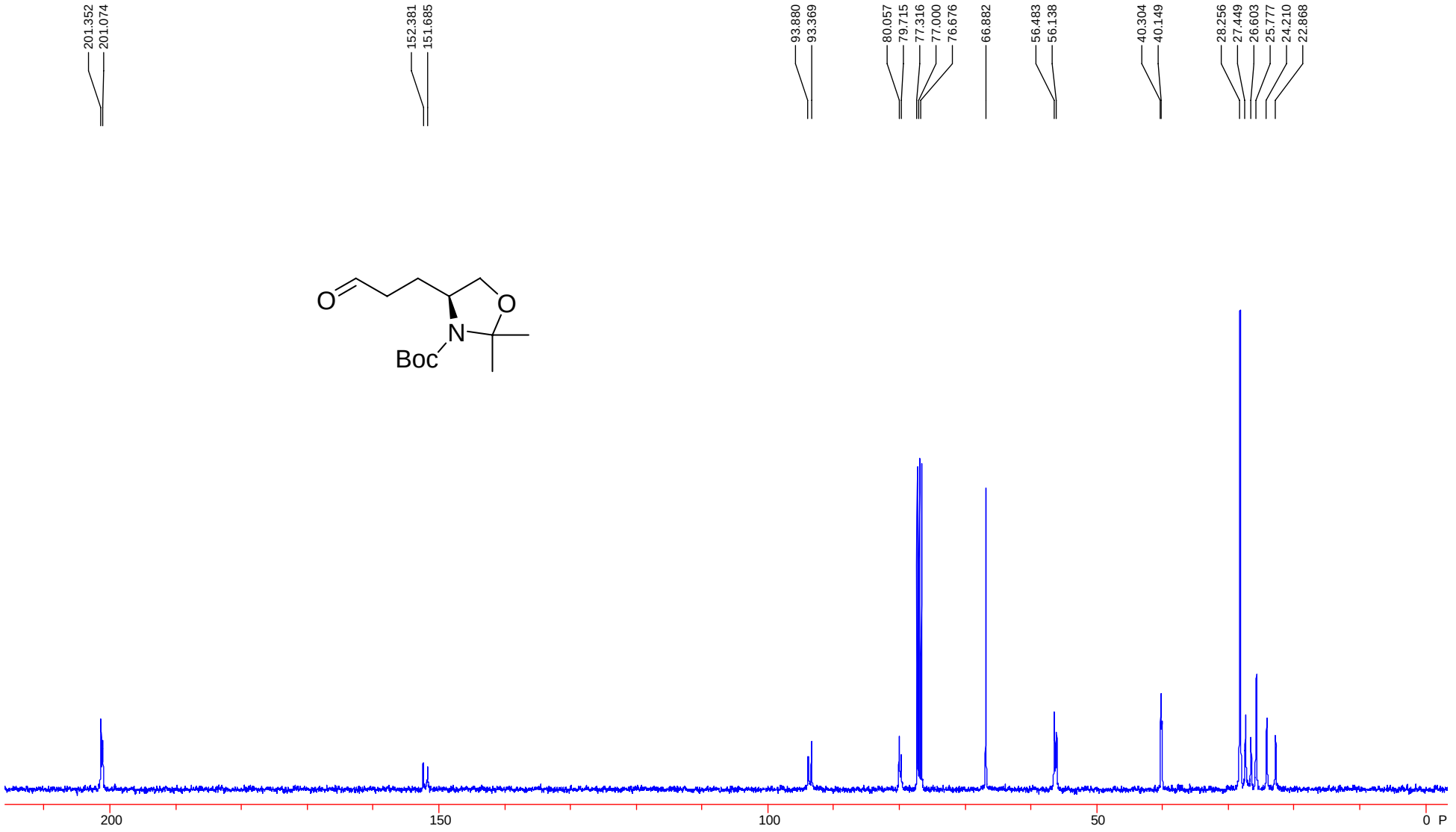


^{13}C-NMR of compound S1 (75 MHz, $CDCl_3$)

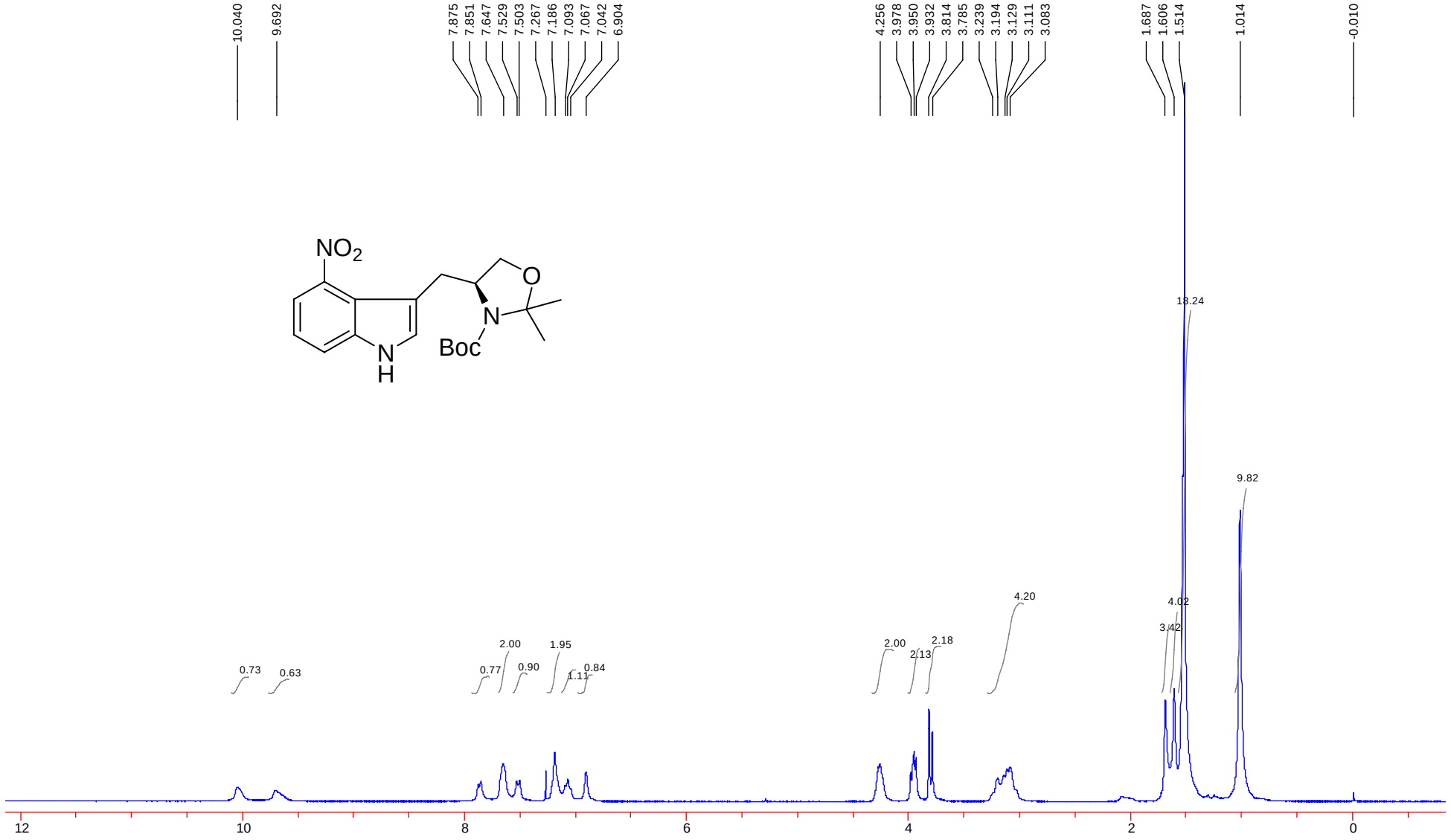


^{1}H-NMR of compound 7 (400 MHz, $CDCl_3$)

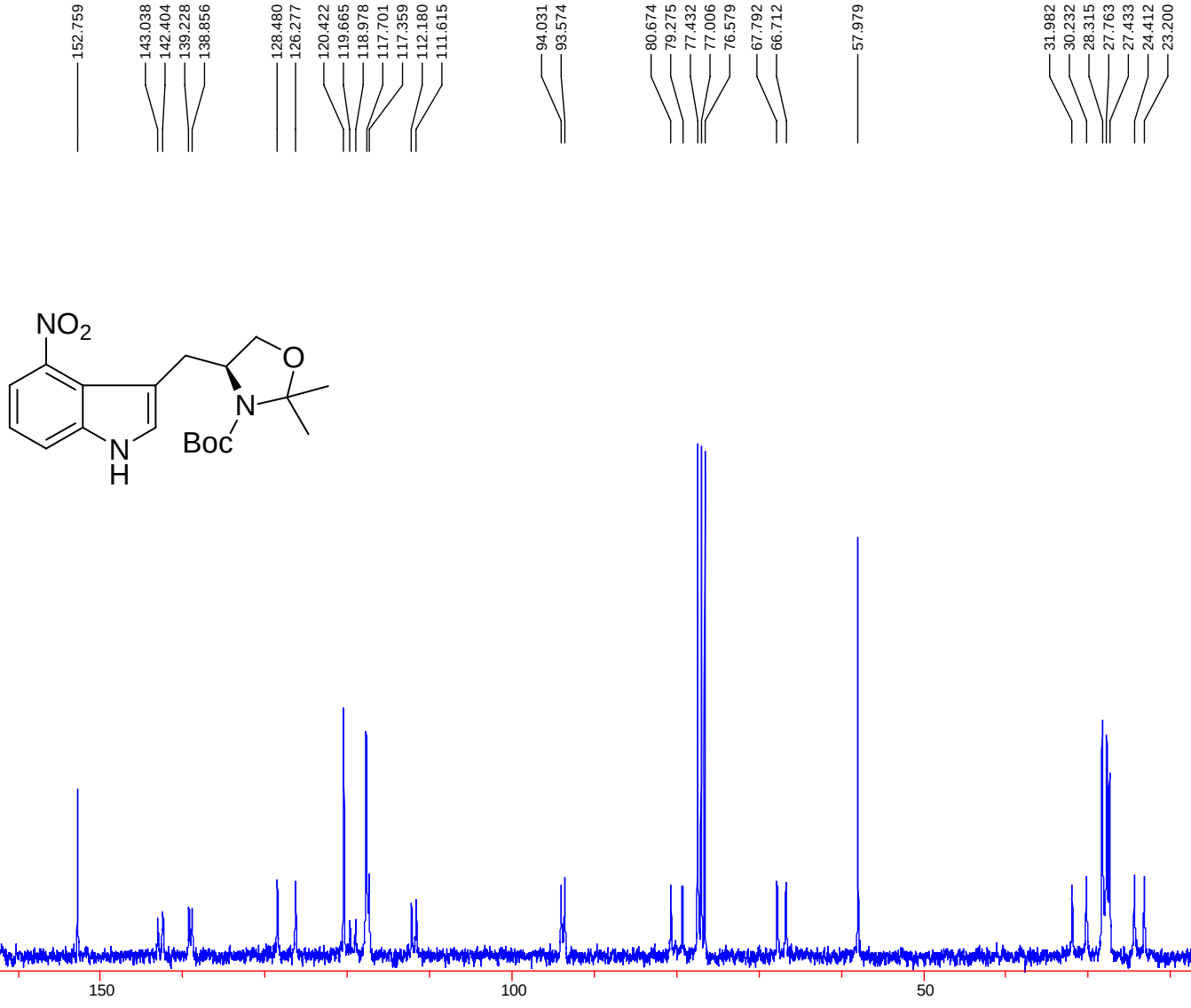
^{13}C-NMR of compound 7 (100 MHz, $CDCl_3$)



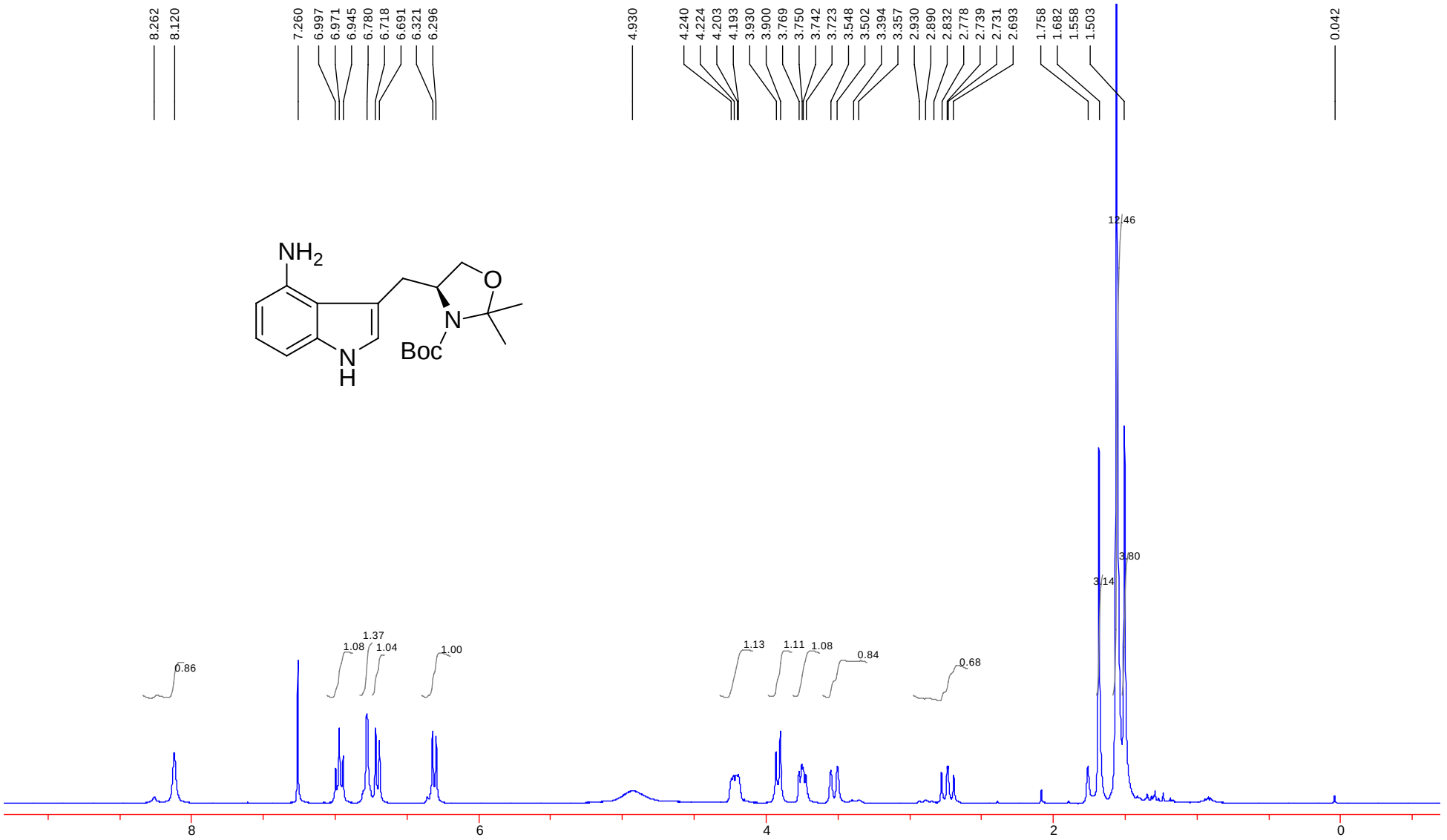
^{1}H-NMR of compound 4 (300 MHz, $CDCl_3$)



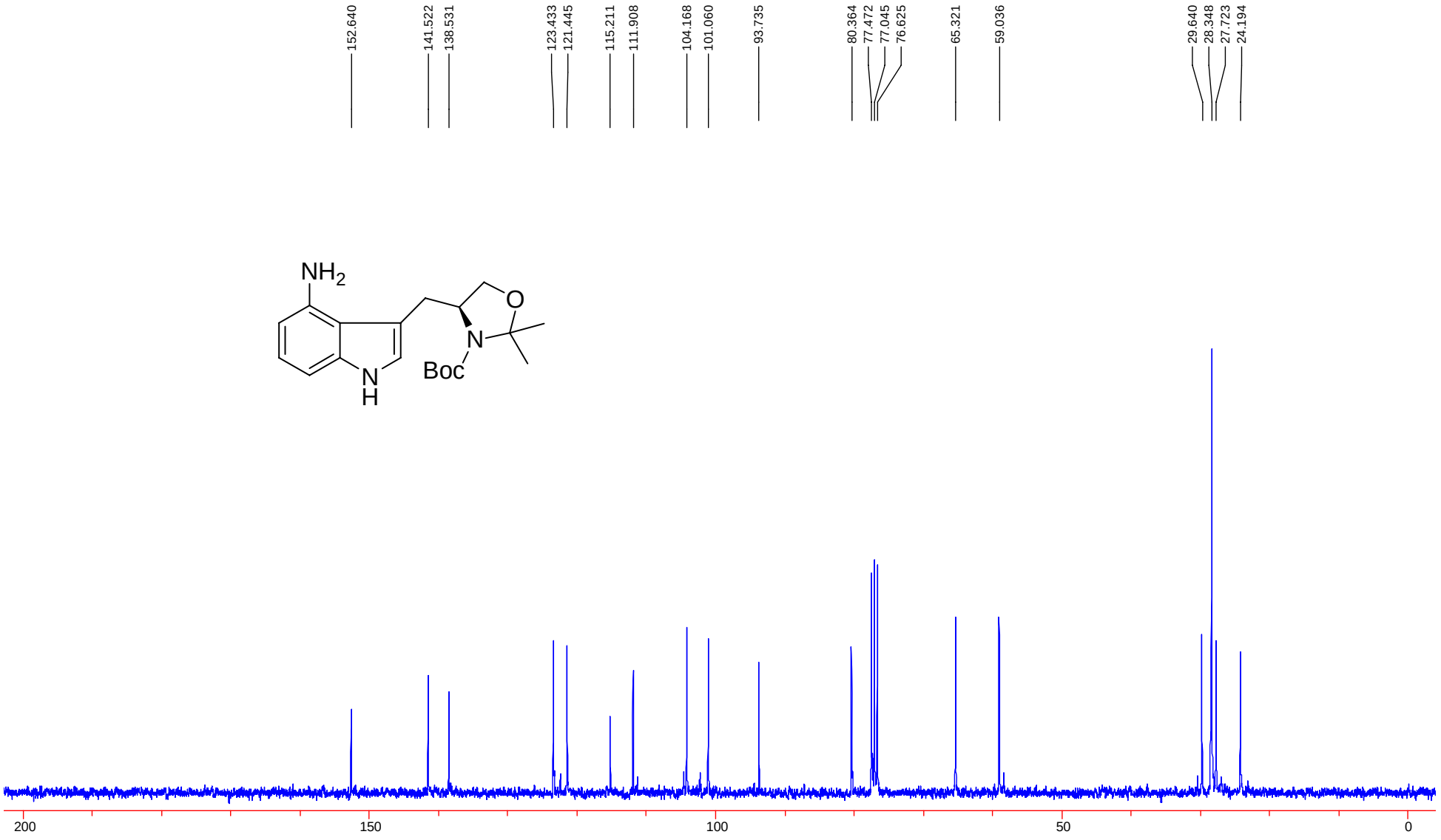
^{13}C-NMR of compound 4 (75 MHz, $CDCl_3$)



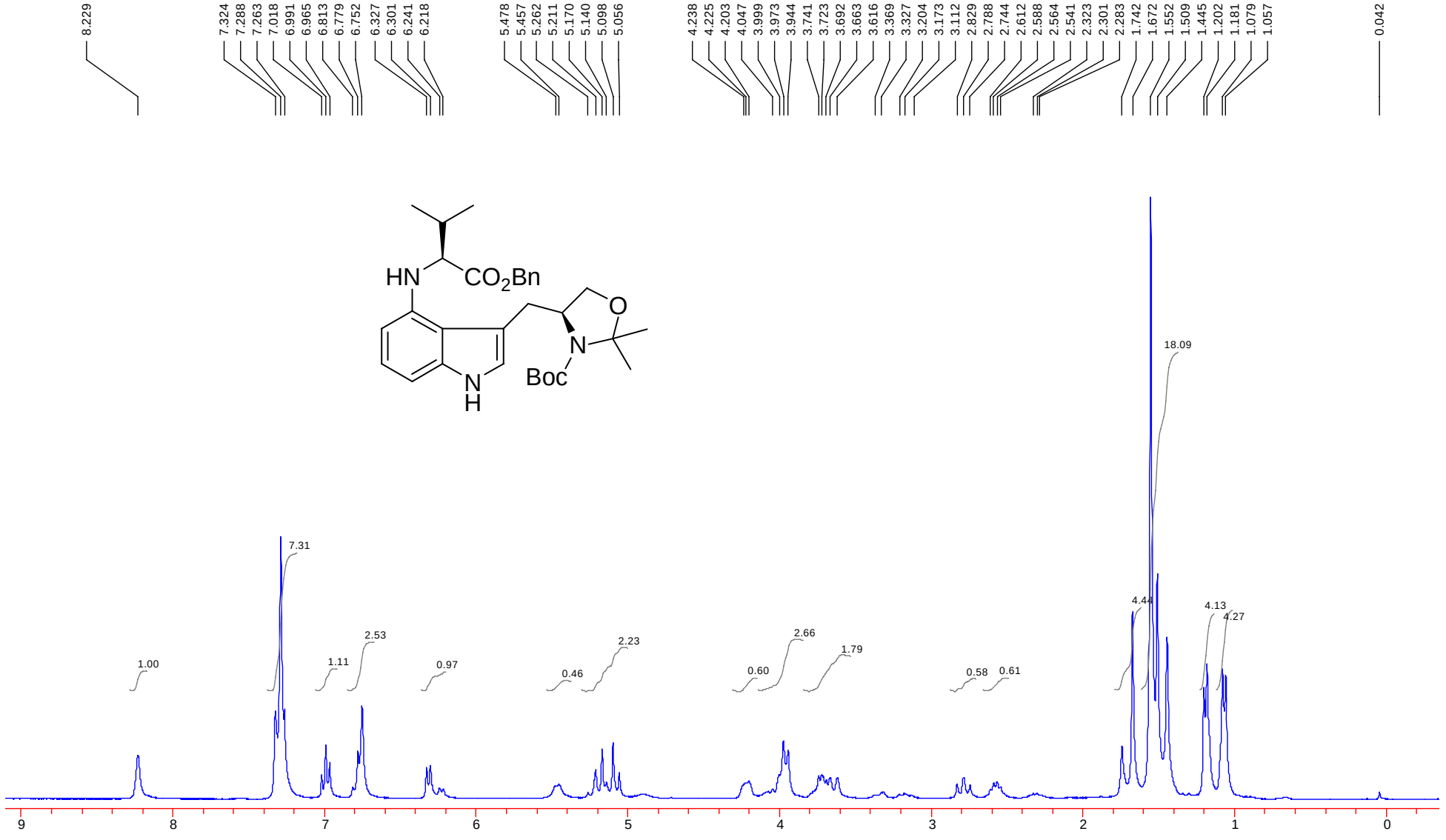
^{1}H-NMR of compound 20 (300 MHz, $CDCl_3$)



^{13}C-NMR of compound 20 (75 MHz, $CDCl_3$)



^{1}H-NMR of compound 21 (300 MHz, $CDCl_3$)



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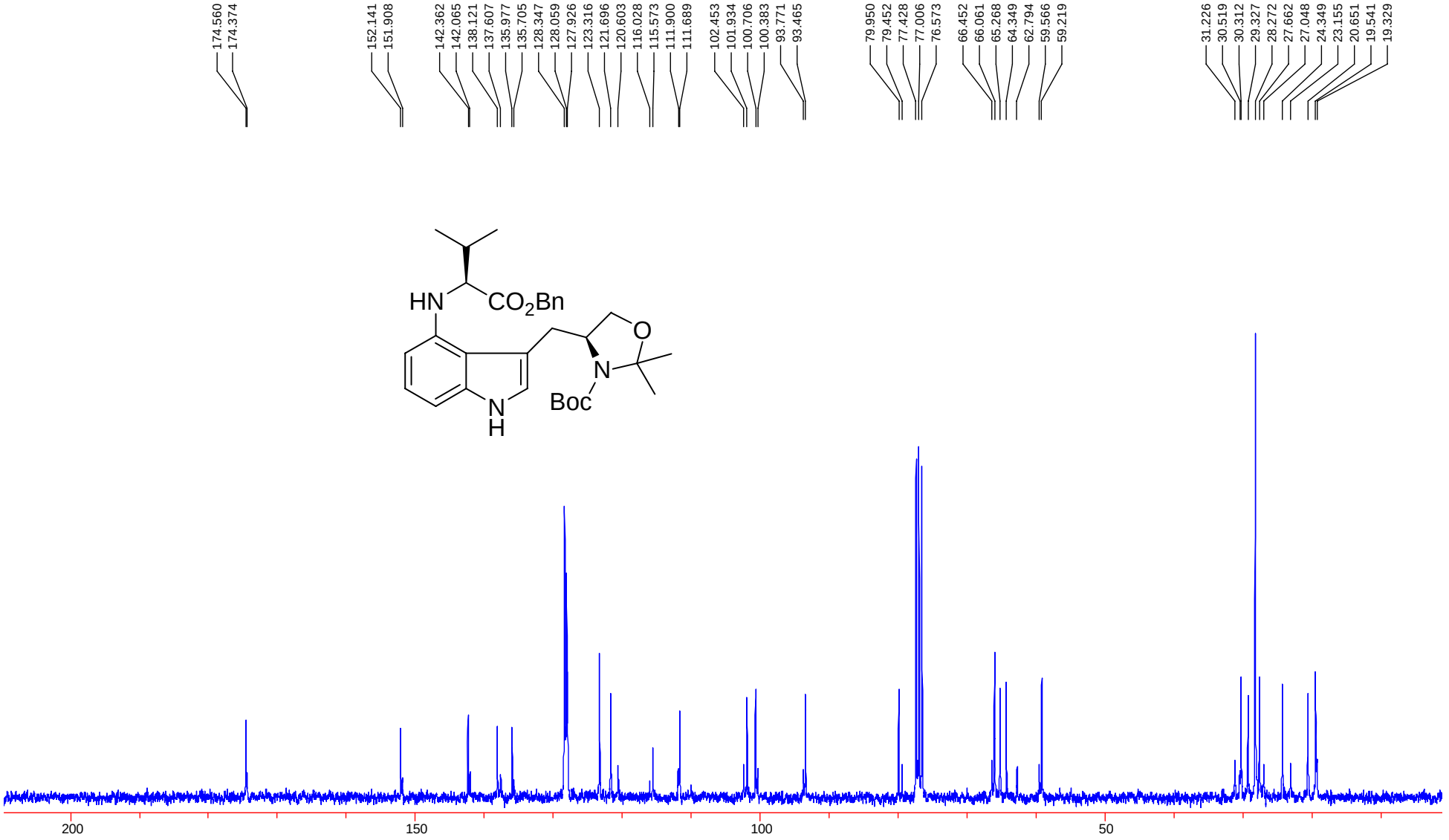
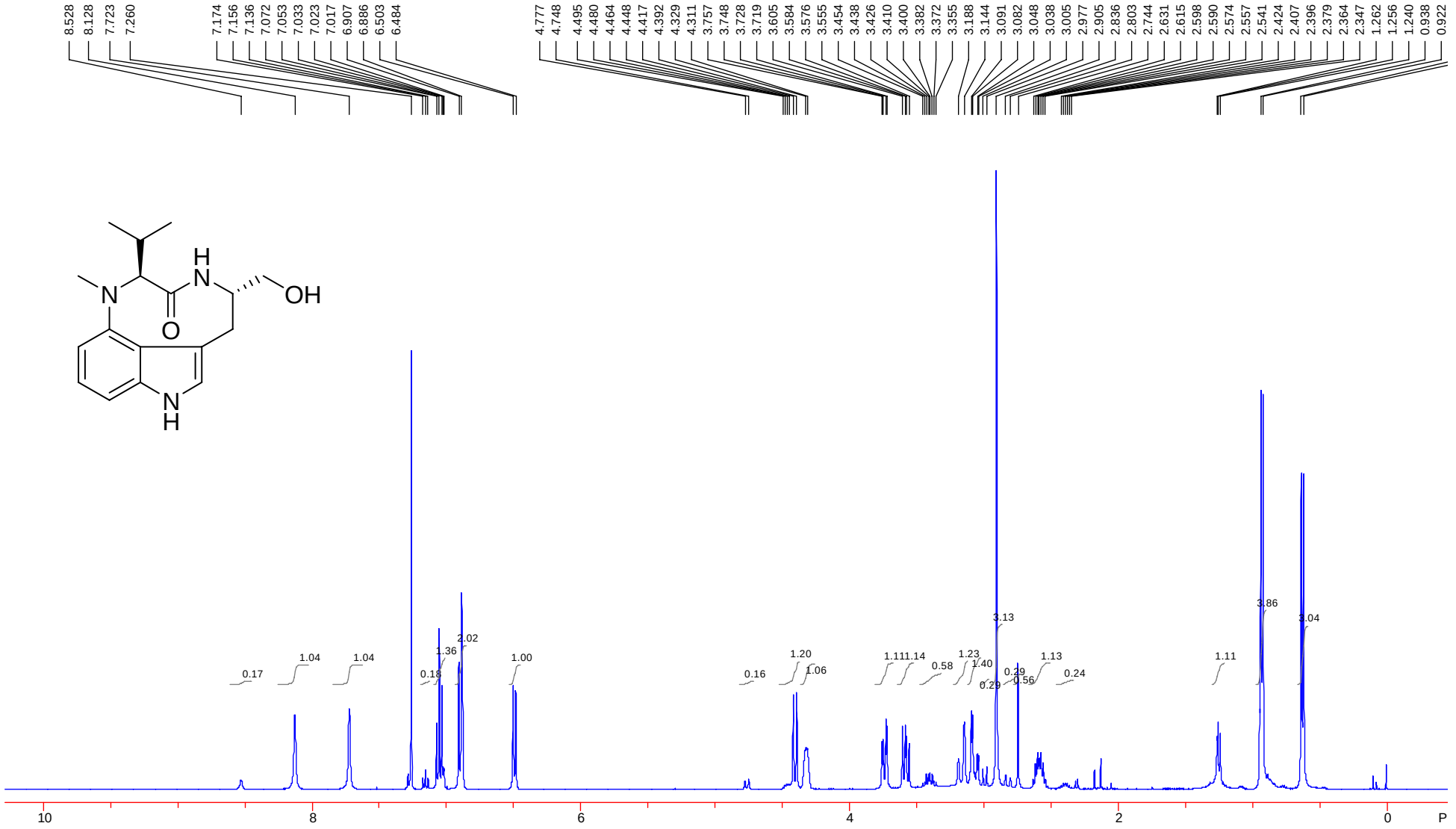


^{1}H-NMR of compound (-)-indolactam V (1) (400 MHz, $CDCl_3$)



^{13}C-NMR of compound (-)-indolactam V (1) (75 MHz, $CDCl_3$)