Supporting Information for

Stereoselective C-terminal peptide elongation from Chan-Lam-Evans reaction generated isopropenyl esters

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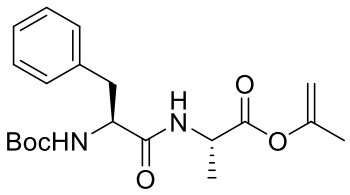
General Information and Materials

NMR spectra were recorded using a Bruker AV-300 or AV-400 MHz spectrometers and calibrated on residual undeuterated solvent signals as internal standard. The data are reported as follows: chemical shift in ppm on the δ scale, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were recorded on a Mass spectra were collected on an AccuTOF GC v 4g, JMS-T100GCV Mass spectrometer (JEOL, Japan). FD/FI probe equipped with FD Emitter, Carbotec or Linden (Germany), FD 10 µm. Current rate 51.2 mA/min over 1.2 min machine using field desorption (FD) as ionization method. Depending on the molecule, either the $(M)^+$ or $(M+H)^+$ were observed. Reactions were monitored with thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254). SilaFlash® P60 (particle size 40-63 µm) was used for silica column chromatography. Dried CH_2Cl_2 and CH_3CN were obtained by distilling these solvents with CaH_2 as drying agent. Dried THF and Et_2O were obtained by distillation with sodium. All dried solvents were stored under N_2 atmosphere. Dry DMF on 4Å molecular sieves was obtained from Sigma-Aldrich and stored under N_2 atmosphere. Reagents were purchased with the highest purity (usually >98%) from Sigma Aldrich and Fluorochem and used as received. Melting points were recorded on a Wagner & Munz Polytherm A melting point apparatus and are uncorrected. IR spectra were recorded on a Bruker Alpha FTIR machine. All reactions were performed in normal glassware, without drying. Unless stated elsewhere, all reactions were performed under air. Boc-protected dipeptide acids were synthesised according the procedure described by Popovic *et al*. See: S. Popovic, H. Bieraugel, R. J. Detz, A. M. Kluwer, J. A. A. Koole, D. E. Streefkerk, H. Hiemstra, J. H. van Maarseveen, *Chem. Eur. J.* **2013**, *19*, 16934-16937.

General procedure 1: Synthesis of isopropenyl esters 2a-f *via* the Chan-Lam-Evans reaction

$Cu(OTf)_2$ and 1,3-diethylurea (both 1.0 equivalent) were placed in a round bottom flask and dissolved in dry THF to make a 0.1M solution. Next, Et_3N (1.0 equivalent) was added, giving a very dark green solution. After stirring for 2 minutes, the *N*-Boc dipeptide acid (1.0 equivalent) was added in one portion, leading to a green or brown solution. After stirring for 2 minutes, isopropenylboroxine pyridine complex (0.66 equiv) was added in one portion. A balloon was filled with air and attached to the round bottom flask *via* a septum and the reaction was heated to 50°C and stirred overnight at ~800 rpm. After stirring for ca. 1h the reaction usually turned faint green or blue. After stirring overnight a precipitate had formed on the walls and the reaction usually turned green again. The mixture was cooled to room temperature and silica was added (ca. 1 gram per 150 mg substrate) and the solution was concentrated *in vacuo* (use dust filter). The dry-loaded product was directly purified *via* column chromatography, eluting with a mixture of PE 40-60 and EtOAc.

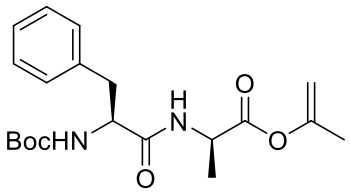
Boc-Phe-Ala-O-isopropenyl 2a



Synthesised according to general procedure 1, starting with 2.0 mmol Boc-Phe-Ala-OH. Column chromatography with PE/EtOAc 5:1 → 3:1 to give an off-white solid. Yield: 691 mg (1.84 mmol, 92%). Melting point: 79-85 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.32-7.21 (m, 5H), 6.65 (d, 1H), 5.13 (d, 1H), 4.74 (s, 1H), 4.71 (s, 1H), 4.57 (quint, 1H), 4.41 (m, 1H), 3.08 (d, 2H), 1.92 (s, 3H), 1.41 (s, 12H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.1, 170.8, 155.5, 152.8, 136.6, 129.5, 128.7, 127.0,

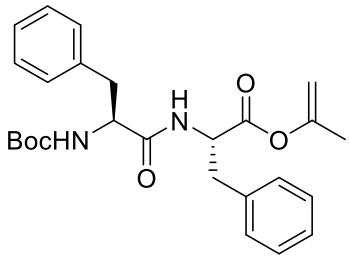
102.5, 80.3, 64.2, 55.6, 48.3, 38.5, 28.3, 19.4, 18.2; IR (cm^{-1}) 3318, 2981, 2931, 1759, 1681, 1654, 1526; HRMS (FD) calcd for $C_{20}H_{28}N_2O_5$ [M^+]: 376.1993, found: 376.2003

Boc-Phe-D-Ala-O-isopropenyl 2b



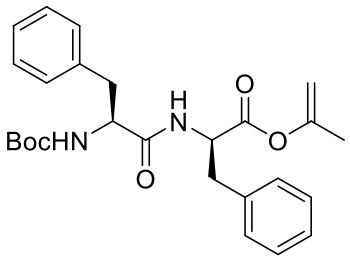
Synthesised according to general procedure 1, starting with 2.0 mmol Boc-Phe-D-Ala-OH. Column chromatography with PE/EtOAc 5:1 → 3:1 to give a white solid. Yield: 682 mg (1.81 mmol, 91%). Melting point: 108-110 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.32-7.20 (m, 5H), 6.47 (d, 1H), 5.18 (d, 1H), 4.72 (s, 1H), 4.70 (s, 1H), 4.55 (quint, 1H), 4.40 (q, 1H), 3.07 (d, 2H), 1.91 (s, 3H), 1.40 (s, 9H), 1.34 (d, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.9, 170.8, 155.5, 152.7, 136.7, 129.4, 128.7, 127.0, 102.4, 80.2, 55.8, 48.1, 38.7, 28.3, 19.3, 18.0; IR (cm^{-1}) 3323, 2973, 2925, 1749, 1697, 1649, 1521; HRMS (FD) calcd for $C_{20}H_{28}N_2O_5$ [M^+]: 376.1993, found: 376.1997

Boc-Phe-Phe-O-isopropenyl 2c



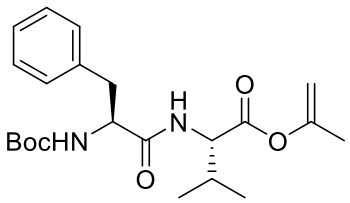
Synthesised according to general procedure 1, starting with 2.0 mmol Boc-Phe-Phe-OH. Column chromatography with PE/EtOAc 6:1 → 4:1 to give a faint yellow solid. Yield: 784 mg (1.73 mmol, 87%). Melting point: 106-109 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.33-7.20 (m, 8H), 7.09 (d, 2H), 6.50 (d, 1H), 5.13 (d, 1H), 4.84 (q, 1H), 4.70 (s, 1H), 4.60 (s, 1H), 4.40 (q, 1H), 3.08 (m, 4H), 1.85 (s, 3H), 1.41 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.0, 169.2, 155.3, 152.6, 136.5, 135.5, 129.4, 128.7, 128.6, 127.2, 127.0, 102.5, 80.2, 55.7, 53.4, 38.3, 37.9, 28.3, 19.3; IR (cm^{-1}) 3333, 2971, 2929, 1749, 1682, 1654, 1519; HRMS (FD) calcd for $C_{26}H_{32}N_2O_5$ [M^+]: 452.2306, found: 452.2320

Boc-Phe-D-Phe-O-isopropenyl 2d



Synthesised according to general procedure 1, starting with 2.0 mmol Boc-Phe-D-Phe-OH. Column chromatography with PE/EtOAc 6:1 → 4:1 to give a colorless waxy solid. Yield: 877 mg (1.94 mmol, 97%). Melting point: 90-93 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.33-7.16 (m, 8H), 7.05 (d, 2H), 6.66 (d, 1H), 5.16 (d, 1H), 4.89 (q, 1H), 4.69 (s, 1H), 4.61 (s, 1H), 4.45 (q, 1H), 3.15-2.97 (m, 4H), 1.85 (s, 3H), 1.40 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.1, 169.4, 155.4, 152.7, 136.6, 135.4, 129.3, 128.6, 127.2, 126.9, 102.4, 80.1, 55.7, 53.2, 38.3, 37.8, 28.2, 19.3; IR (cm^{-1}) 3338, 2970, 2929, 1746, 1679, 1664, 1650, 1515 ; HRMS (FD) calcd for $C_{26}H_{32}N_2O_5$ [M^+]: 452.2306, found: 452.2316

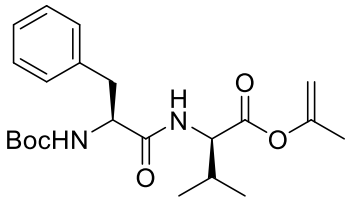
Boc-Phe-Val-O-isopropenyl 2e



Synthesised according to general procedure 1, starting with 1.0 mmol Boc-Phe-Val-OH. Column chromatography with PE/EtOAc 8:1 → 6:1 to give a white solid. Yield: 353 mg (0.873 mmol, 87%). Melting point: 117-119 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.31-7.20 (m, 5H), 6.55 (d, 1H), 5.17 (d, 1H), 4.73 (s, 1H), 4.68 (s, 1H), 4.53 (dd, 1H), 4.41 (q, 1H), 3.08 (m, 2H), 2.20 (sext, 1H), 1.92 (s, 3H), 1.42 (s, 9H), 0.92 (dd, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.4, 169.6, 155.5, 152.7,

136.7, 129.4, 128.7, 127.0, 102.5, 80.2, 57.2, 55.8, 38.0, 31.3, 28.3, 19.5, 18.9, 17.7; IR (cm^{-1}) 3308, 2969, 2930, 1754, 1681, 1650, 1529; HRMS (FD), calcd for $C_{22}H_{32}N_2O_5$ [M^+]: 404.2306, found: 404.2313

Boc-Phe-D-Val-O-isopropenyl 2f

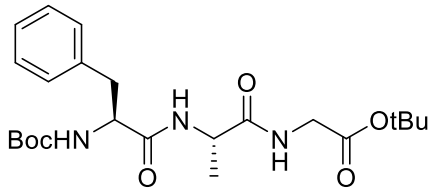


Synthesised according to general procedure 1, starting with 1.0 mmol Boc-Phe-D-Val-OH. Column chromatography with PE/EtOAc 8:1 → 6:1 to give a white solid. Yield: 369 mg (0.912 mmol, 91%). Melting point: 84-86 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.34-7.22 (m, 5H), 6.50 (d, 1H), 5.06 (d, 1H), 4.73 (s, 1H), 4.69 (s, 1H), 4.53 (dd, 1H), 4.44 (q, 1H), 3.10 (d, 2H), 2.15 (sext, 1H), 1.92 (s, 3H), 1.42 (s, 9H), 0.85 (dd, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.4, 169.8, 155.5, 152.8, 136.7, 129.3, 128.8, 127.1, 102.5, 80.4, 57.2, 56.0, 38.3, 31.2, 28.3, 19.5, 18.9, 17.6; IR (cm^{-1}) 3337, 2962, 2929, 1748, 1678, 1658, 1520; HRMS (FD), calcd for $C_{22}H_{32}N_2O_5$ [M^+]: 404.2306, found: 404.2242

General procedure 2: Synthesis of tripeptides 3a-x *via* aminolysis of dipeptide isopropenyl esters 22a-f

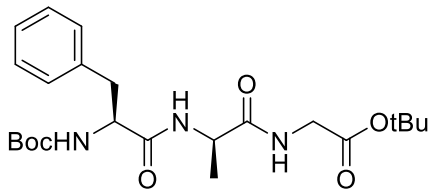
The dipeptide isopropenyl ester (0.10 mmol), amino acid *tert*-butyl ester free base (0.20 mmol, 2.0 equiv) and 34 mg pyrazole (0.50 mmol, 5.0 equiv) were dissolved in 2 mL anhydrous $PhCH_3$. Next, 10 µL of a 1M solution of DBU in $PhCH_3$ (0.01 mmol, 10 mol%) was added and the reaction was stirred overnight at room temperature (except C-terminal valine, see below). The mixture was diluted with 20 mL Et_2O and washed with 10 mL 1M $KHSO_4$, 10 mL $NaHCO_3$, 10 mL brine, dried over $MgSO_4$ and concentrated *in vacuo* to give the tripeptide as a colorless solid or foam. In almost all cases, no further purification was required.

Boc-Phe-Ala-Gly-OtBu 3a



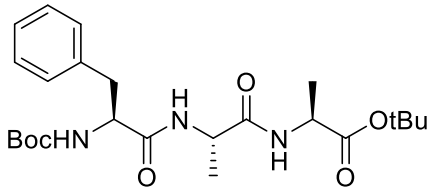
Synthesised according to general procedure 2. Yield: 43 mg (0.096 mmol, 96%) as a colorless solid. Melting point: 157-160 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.31-7.19 (m, 5H), 6.83 (m, 2H), 5.28 (d, 1H), 4.58 (quint, 1H), 4.43 (q, 1H), 3.87 (d, 2H), 3.11-3.04 (m, 2H), 1.48 (s, 9H), 1.40 (s, 9H), 1.36 (d, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 172.0, 171.4, 168.7, 155.8, 136.6, 129.5, 128.7, 127.0, 82.2, 80.4, 55.9, 48.8, 42.1, 38.6, 28.4, 28.2, 18.4; IR (cm^{-1}) 3296, 2978, 2932, 1678, 1639, 1532; HRMS (FD), calcd for $C_{23}H_{35}N_3O_6$ [M^+]: 449.2520, found: 449.2516 (Δ 0.9 ppm); d.e. (determined by chiral HPLC): 97.1%

Boc-Phe-D-Ala-Gly-OtBu 3b



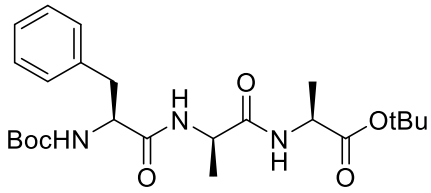
Synthesised according to general procedure 2. Yield: 44 mg (0.098 mmol, 98%) as a colorless foam. Melting point: 58-65 °C (stays thick oil). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.32-7.19 (m, 5H), 7.13 (bs, 1H), 6.66 (d, 1H), 5.37 (d, 1H), 4.54 (quint, 1H), 4.33 (q, 1H), 4.00-3.78 (m, 2H), 3.09-3.03 (m, 2H), 1.47 (s, 9H), 1.40 (s, 9H), 1.23 (d, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 172.2, 171.4, 168.9, 155.6, 136.7, 129.4, 128.7, 127.1, 82.2, 80.3, 56.4, 48.7, 42.0, 38.7, 28.4, 28.1, 17.9; IR (cm^{-1}) 3284, 2977, 2933, 1644, 1521; HRMS (FD), calcd for $C_{23}H_{35}N_3O_6$ [M^+]: 449.2520 found: 449.2513 (Δ 1.6 ppm); d.e. (determined by chiral HPLC): 98.4%

Boc-Phe-Ala-Ala-OtBu 3c



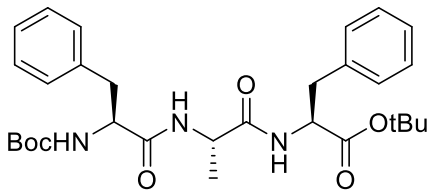
Synthesised according to general procedure 2. Yield: 47 mg (0.100 mmol, 100%) as a glassy solid. Melting point: 137-140 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.31-7.17 (m, 5H), 7.01 (d, 1H), 6.83 (d, 1H), 5.24 (d, 1H), 4.57 (quint, 1H), 4.43 (quint, 2H), 3.10-3.03 (m, 2H), 1.48 (s, 9H), 1.40 (s, 9H), 1.37 (d, 3H), 1.34 (d, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.9, 171.4, 171.2, 155.5, 136.6, 129.4, 128.7, 127.0, 82.0, 80.2, 55.7, 48.91, 48.85, 38.6, 28.4, 28.1, 18.7, 18.5; IR (cm^{-1}) 3298, 2979, 2931, 1637, 1519; HRMS (FD), calcd for $C_{24}H_{37}N_3O_6$: 463.2682 [M^+], found: 463.2677 (Δ 1.1 ppm); d.e. (determined by chiral HPLC): 98.8%

Boc-Phe-D-Ala-Ala-OtBu 3d



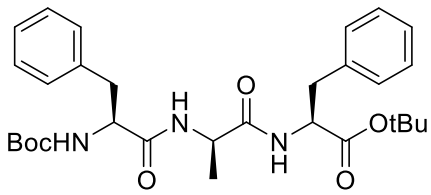
Synthesised according to general procedure 2. Yield: 43 mg (0.093 mmol, 93%) as a colorless solid. Melting point: 114-117 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.32-7.19 (m, 5H), 7.12 (d, 1H), 6.53 (d, 1H), 5.36 (d, 1H), 4.50 (quint, 1H), 4.43 (t, 1H), 4.35 (q, 1H), 3.07 (d, 2H), 1.46 (s, 9H), 1.40 (s, 9H), 1.36 (d, 3H), 1.19 (d, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 172.0, 171.4, 171.2, 155.5, 136.7, 129.4, 128.7, 127.0, 81.9, 80.2, 56.5, 48.7, 48.6, 38.7, 28.4, 28.1, 18.4, 18.0; IR (cm^{-1}) 3278, 2977, 2933, 1657, 1643, 1519; HRMS (FD), calcd for $C_{24}H_{37}N_3O_6$ [M^+]: 463.2677, found: 463.2692 (Δ 3.2 ppm); d.e. (determined by chiral HPLC): 98.9%

Boc-Phe-Ala-Phe-OtBu 3e



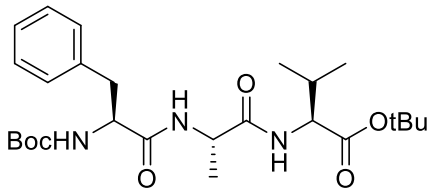
Synthesised according to general procedure 2. Yield: 51 mg (0.095 mmol, 95%) as a glassy solid. Melting point: 75-78 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.32-7.16 (m, 10H), 6.78 (d, 1H), 6.72 (d, 1H), 5.17 (d, 1H), 4.70 (q, 1H), 4.48 (quint, 1H), 4.43 (q, 1H), 3.09-3.03 (m, 4H), 1.41 (s, 9H), 1.40 (s, 9H), 1.32 (d, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.4, 171.2, 170.4, 155.5, 136.7, 136.2, 129.6, 129.5, 128.7, 128.5, 127.1, 127.0, 82.5, 80.3, 55.7, 53.9, 49.0, 38.4, 38.1, 28.4, 28.0, 18.6; IR (cm^{-1}) 3286, 2976, 2930, 1694, 1638, 1516; HRMS (FD), calcd for $C_{30}H_{41}N_3O_6$: 539.2990 [M^+], found: 539.2995 (Δ 0.9 ppm); d.e. (determined by chiral HPLC): 99.1%

Boc-Phe-D-Ala-Phe-OtBu 3f



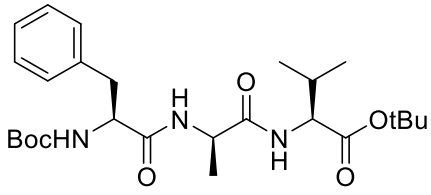
Synthesised according to general procedure 2. Yield: 51 mg (0.095 mmol, 95%) as a colorless foam. Melting point: 57-59 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.31-7.10 (m, 10H), 7.07 (d, 1H), 6.50 (d, 1H), 5.38 (d, 1H), 4.74 (q, 1H), 4.54 (quint, 1H), 4.33 (q, 1H), 3.14-2.98 (m, 4H), 1.42 (s, 9H), 1.41 (s, 9H), 1.10 (d, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.5, 171.0, 170.6, 136.8, 136.3, 129.6, 129.4, 128.7, 128.4, 127.04, 126.98, 82.5, 80.1, 56.3, 53.6, 48.6, 39.0, 38.2, 28.4, 28.1, 18.4; IR (cm^{-1}) 3282, 2976, 2929, 1637, 1513, 1497; HRMS (FD), calcd for $C_{30}H_{41}N_3O_6$ [M^+]: 539.2990, found: 539.2983 (Δ 1.3 ppm); d.e. (determined by chiral HPLC): 98.9%

Boc-Phe-Ala-Val-OtBu 3g



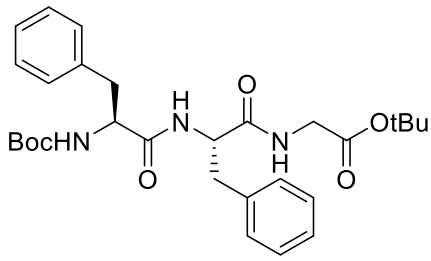
Synthesised according to general procedure 2. Yield: 45 mg (0.092 mmol, 92%) as a colorless foam. Melting point: 66-68 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.31-7.18 (m, 5H), 6.88 (d, 1H), 6.81 (d, 1H), 5.21 (d, 1H), 4.59 (quint, 1H), 4.40 (m, 2H), 3.10-3.02 (m, 2H), 2.17 (sext, 1H), 1.48 (s, 9H), 1.39 (s, 9H), 1.35 (d, 3H), 0.92 (t, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.8, 171.2, 170.8, 155.5, 136.6, 129.4, 128.7, 127.0, 82.0, 80.2, 57.7, 55.7, 49.1, 38.5, 31.4, 28.3, 28.1, 19.0, 18.6, 17.8; IR (cm^{-1}) 3281, 2973, 2932, 1693, 1641, 1519; HRMS (FD), calcd for $C_{26}H_{41}N_3O_6$ [M^+]: 491.2990, found: 491.2971 (Δ 3.9 ppm); d.e. (determined by chiral HPLC): 99.3%

Boc-Phe-D-Ala-Val-OtBu 3h



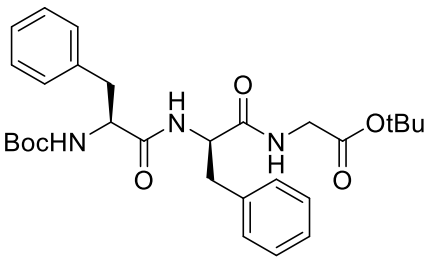
Synthesised according to general procedure 2. Yield: 48 mg (0.098 mmol, 98%) as a glassy solid. Melting point: 66-69 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.31-7.18 (m, 6H), 6.61 (d, 1H), 5.55 (d, 1H), 4.69 (quint, 1H), 4.46 (dd, 1H), 4.39 (q, 1H), 3.08-3.01 (m, 2H), 2.17 (sext, 1H), 1.47 (s, 9H), 1.40 (s, 9H), 1.21 (d, 3H), 0.94 (t, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 172.1, 171.1, 171.0, 155.5, 136.9, 129.4, 128.7, 126.9, 82.1, 80.0, 57.3, 56.3, 48.9, 39.2, 31.6, 28.4, 28.2, 19.1, 18.9, 17.7; IR (cm^{-1}) 3291, 2970, 2931, 1713, 1695, 1638, 1510; HRMS (FD), calcd for $C_{26}H_{41}N_3O_6$ [M^+]: 491.2990, found: 491.2978 (Δ 2.4 ppm); d.e. (determined by chiral HPLC): 97.8%

Boc-Phe-Phe-Gly-OtBu 3i



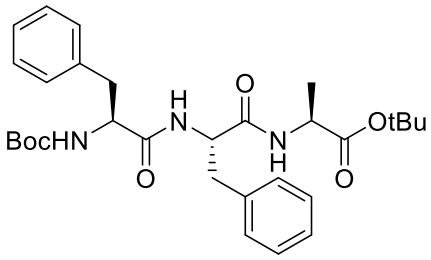
Synthesised according to general procedure 2. Yield: 50 mg (0.095 mmol, 95%) as a colorless solid. Melting point: 178-180 °C. ^{1}H-NMR (300 MHz, DMSO-d6) δ 8.40 (t, 1H), 8.01 (d, 1H), 7.27-7.14 (m, 10H), 6.86 (d, 1H), 4.60 (q, 1H), 4.11 (q, 1H), 3.74 (m, 2H), 3.07 (dd, 1H), 2.83 (m, 2H), 2.62 (t, 1H), 1.41 (s, 9H), 1.28 (s, 9H); ^{13}C-NMR (75 MHz, DMSO-d6) δ 171.5, 168.8, 155.1, 138.1, 137.7, 129.4, 129.2, 128.12, 128.06, 126.4, 126.6, 80.8, 78.3, 56.0, 38.0, 37.7, 28.2, 27.8; IR (cm^{-1}) 3306, 3274, 2978, 2929, 1751, 1646, 1563; HRMS (FD), calcd for $C_{29}H_{39}N_3O_6$ [M^+]: 525.2833, found: 525.2821 (Δ 2.3 ppm); d.e. (determined by chiral HPLC): 96.8%

Boc-Phe-D-Phe-Gly-OtBu 3j



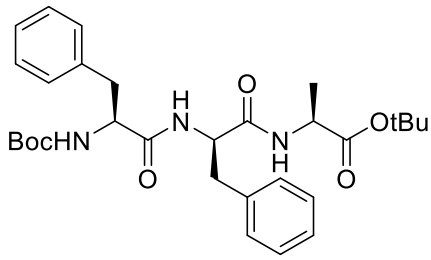
Synthesised according to general procedure 2. Yield: 49 mg (0.093 mmol, 93%) as a colorless solid. Melting point: 160-163 °C. ^{1}H-NMR (300 MHz, DMSO-d6) δ 8.53-8.36 (m, 2H), 7.29-7.06 (m, 10H), 6.70 (d, 1H), 4.59 (m, 1H), 4.16 (m, 1H), 3.78 (d, 2H), 3.10 (d, 1H), 2.78 (t, 1H), 2.63 (d, 1H), 2.44 (d, 1H), 1.42 (s, 9H), 1.28 (s, 9H); ^{13}C-NMR (75 MHz, DMSO-d6) δ 171.6, 171.5, 168.7, 155.2, 138.0, 137.9, 129.3, 129.2, 128.1, 127.9, 126.4, 126.1, 80.8, 78.1, 55.5, 37.9, 37.4, 28.2, 27.8; IR (cm^{-1}) 3295, 2979, 2931, 1752, 1708, 1644, 1483; HRMS (FD), calcd for $C_{29}H_{39}N_3O_6$ [M^+]: 525.2833, found: 525.2797 (Δ 6.9 ppm); d.e. (determined by chiral HPLC): 99.9%

Boc-Phe-Phe-Ala-OtBu 3k



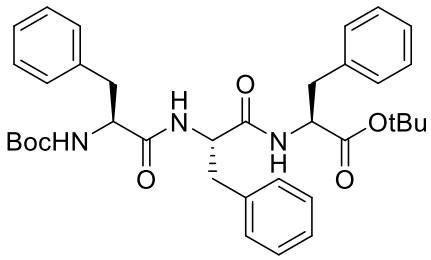
Synthesised according to general procedure 2. Yield: 48 mg (0.090 mmol, 90%) as colorless foam. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.32-7.18 (m, 9H), 7.08 (d, 2H), 6.58 (bs, 2H), 4.98 (s, 1H), 4.70 (t, 1H), 4.35 (quint, 1H), 3.15-2.92 (m, 4H), 1.47 (s, 9H), 1.36 (s, 9H), 1.30 (d, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.5, 171.0, 169.8, 136.5, 136.3, 129.43, 129.39, 128.8, 128.7, 127.2, 127.1, 82.0, 80.4, 55.9, 54.1, 48.9, 38.1, 28.3, 28.0, 18.4; IR (cm^{-1}) 3292, 2980, 2931, 1645, 1518; HRMS (FD), calcd for $C_{30}H_{41}N_3O_6$ [M^+]: 539.2990, found: 539.3002 (Δ 2.2 ppm); d.e. (determined by chiral HPLC): 96.5%

Boc-Phe-D-Phe-Ala-OtBu 3l



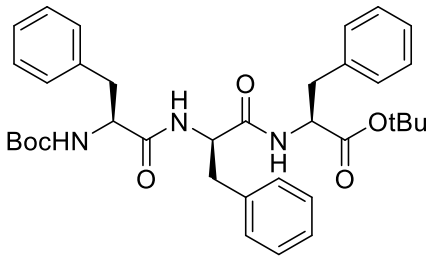
Synthesised according to general procedure 2. Yield: 47 mg (0.088 mmol, 88%) as a colorless foam. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.35-7.16 (m, 9H), 7.03 (d, 2H), 6.60 (d, 1H), 6.48 (d, 1H), 5.15 (d, 1H), 4.70 (q, 1H), 4.37 (quint, 1H), 4.24 (q, 1H), 3.13-2.92 (m, 3H), 2.78 (dd, 1H), 1.43 (s, 9H), 1.39 (s, 9H), 1.21 (d, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.8, 171.2, 169.8, 155.5, 136.6, 136.4, 129.54, 129.45, 128.8, 128.7, 127.2, 127.1, 81.9, 80.3, 56.6, 54.1, 48.7, 38.4, 38.0, 28.4, 28.0, 18.2; IR (cm^{-1}) 3291, 2979, 2930, 1641, 1516, 1497; HRMS (FD), calcd for $C_{30}H_{41}N_3O_6$ [M^+]: 539.2990, found: 539.3005 (Δ 2.8 ppm); d.e. (determined by chiral HPLC): 98.2%

Boc-Phe-Phe-Phe-OtBu 3m



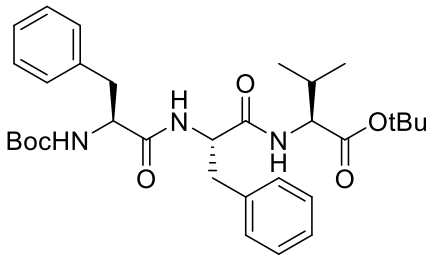
Synthesised according to general procedure 2. Yield: 54 mg (0.088 mmol, 88%) as a colorless glassy solid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.32-7.09 (m, 15H), 6.63 (d, 1H), 6.47 (d, 1H), 5.03 (d, 1H), 4.65 (sext, 2H), 4.39 (q, 1H), 3.03-2.98 (m, 6H), 1.40 (s, 9H), 1.38 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.1, 170.0, 169.9, 155.4, 136.6, 136.3, 136.1, 129.5, 129.4, 128.8, 128.7, 128.5, 127.1, 127.0, 82.4, 80.3, 55.8, 54.4, 54.0, 38.4, 38.3, 28.3, 28.0; IR (cm^{-1}) 3272, 2977, 2928, 1693, 1641, 1519; HRMS (FD), calcd for $C_{36}H_{45}N_3O_6$ [M^+]: 615.3303, found: 615.3306 (Δ 0.5 ppm); d.e. (determined by chiral HPLC): 97.8%

Boc-Phe-D-Phe-Phe-OtBu 3n



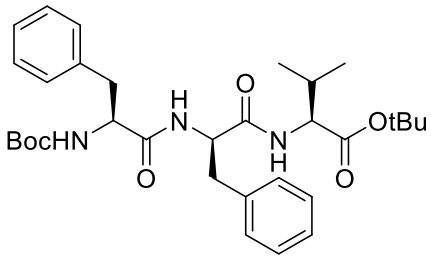
Synthesised according to general procedure 2. Yield: 58 mg (0.094 mmol, 94%) as a colorless solid. Melting point: 173-178 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.34-7.21 (m, 9H), 7.14 (d, 2H), 7.02 (d, 4H), 6.78 (d, 1H), 6.60 (d, 1H), 5.21 (d, 1H), 4.71 (quint, 2H), 4.30 (q, 1H), 3.02-2.90 (m, 6H), 1.40 (s, 9H), 1.35 (s, 9H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.2, 170.3, 170.0, 155.4, 136.6, 136.4, 136.2, 129.5, 129.4, 128.71, 128.67, 128.4, 127.10, 127.05, 127.0, 82.3, 80.2, 56.3, 54.1, 53.8, 38.5, 38.3, 37.9, 28.4, 28.0; IR (cm^{-1}) 3294, 2979, 2929, 1688, 1649, 1519; HRMS (FD), calcd for $C_{36}H_{45}N_3O_6$ [M^+]: 615.3303, found: 614.3287 (Δ 2.6 ppm); d.e. (determined by chiral HPLC): 97.0%

Boc-Phe-Phe-Val-OtBu 3o



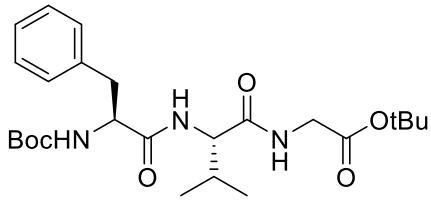
Synthesised according to general procedure 2. Yield: 51 mg (0.090 mmol, 90%) as a colorless foam. Melting point: 132-138 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.32-7.17 (m, 8H), 7.11 (d, 2H), 6.71 (d, 1H), 6.56 (d, 1H), 5.08 (d, 1H), 4.72 (q, 1H), 4.40-4.30 (m, 2H), 3.10-2.95 (m, 4H), 2.09 (sext, 1H), 1.47 (s, 9H), 1.38 (s, 9H), 0.87 (t, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.2, 170.4, 170.3, 155.6, 136.6, 136.3, 129.4, 128.73, 128.65, 127.1, 82.0, 80.1, 57.8, 54.5, 38.3, 31.4, 28.3, 28.1, 18.9, 17.9; IR (cm^{-1}) 3271, 2966, 2929, 1693, 1643, 1519; HRMS (FD), calcd for $C_{32}H_{45}N_3O_6$ [M^+]: 567.3303, found: 567.3312 (Δ 1.6 ppm); d.e. (determined by chiral HPLC): 98.5%

Boc-Phe-D-Phe-Val-OtBu 3p



Synthesised according to general procedure 2. Yield: 58 mg (0.094 mmol, 94%) as a colorless foam. Melting point: 91-97°C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.33-7.11 (m, 10H), 6.69 (d, 1H), 6.59 (d, 1H), 5.23 (d, 1H), 4.78 (q, 1H), 4.33 (q, 2H), 3.09-2.82 (m, 4H), 2.00 (sext, 1H), 1.44 (s, 9H), 1.39 (s, 9H), 0.77 (dd, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.3, 170.6, 170.4, 155.5, 136.7, 136.5, 129.4, 128.7, 127.1, 127.0, 82.1, 80.2, 57.8, 56.2, 54.4, 38.7, 38.2, 31.3, 28.4, 28.1, 18.7, 17.8; IR (cm^{-1}) 3272, 2966, 2929, 1716, 1639, 1496; HRMS (FD), calcd for $C_{32}H_{45}N_3O_6$ [M^+]: 567.3303, found: 567.3294 (Δ 1.6 ppm); d.e. (determined by chiral HPLC): 96.8%

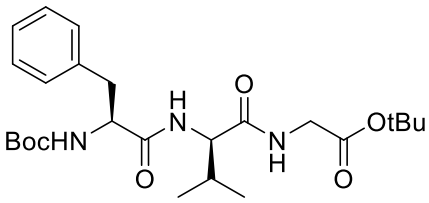
Boc-Phe-Val-Gly-OtBu 3q



Synthesised according to general procedure 2, except by stirring overnight at 50°C. Yield: 44 mg (0.092 mmol, 92%) as a colorless solid. Melting point: 185-189 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.31-7.20 (m, 5H), 6.83-6.75 (m, 2H), 5.32 (d, 1H), 4.46-4.36 (m, 2H), 3.87 (s, 2H), 3.09 (m, 2H), 2.19 (q, 1H), 1.47 (s, 9H), 1.40 (s, 9H), 0.92 (dd, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.7, 171.0, 168.7, 155.8, 136.7, 129.4, 128.7, 126.9, 82.1, 80.3, 58.4, 56.1, 42.0, 38.1, 30.7, 28.4, 28.1, 19.3, 17.9; IR (cm^{-1}) 3286, 2974, 2931, 1745, 1692, 1640, 1519; HRMS

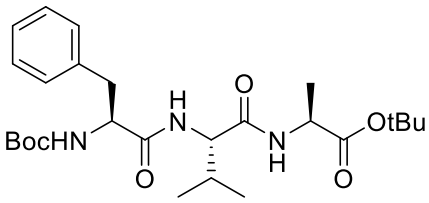
(FD), calcd for $C_{25}H_{39}N_3O_6$ [M^+]: 477.2833, found: 477.2840 (Δ 1.4 ppm); d.e. (determined by chiral HPLC): 98.7%

Boc-Phe-D-Val-Gly-OtBu 3r



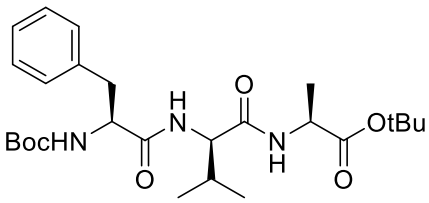
Synthesised according to general procedure 2, except by stirring overnight at 50°C. Yield: 43 mg (0.090 mmol, 90%) as a colorless foam. Melting point: 62-65 °C (stays oily). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.30-7.20 (m, 5H), 7.12 (bs, 1H), 6.75 (d, 1H), 5.35 (d, 1H), 4.38 (q, 1H), 3.90 (m, 2H), 3.13-2.99 (m, 2H), 2.16 (q, 1H), 1.46 (s, 9H), 1.39 (s, 9H), 0.79 (d, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.8, 171.1, 168.8, 155.7, 136.6, 129.4, 128.8, 127.0, 82.1, 80.3, 58.4, 56.5, 42.0, 38.3, 30.3, 28.4, 28.1, 19.2, 17.7; IR (cm^{-1}) 3291, 2967, 2931, 1744, 1693, 1641, 1514, 1498; HRMS (FD), calcd for $C_{25}H_{39}N_3O_6$ [M^+]: 477.2833, found: 477.2847 (Δ 1.9 ppm); d.e. (determined by chiral HPLC): 98.8%

Boc-Phe-Val-Ala-OtBu 3s



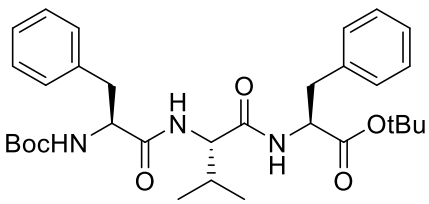
Synthesised according to general procedure 2, except by stirring overnight at 50°C. Yield: 47 mg (0.096 mmol, 96%) as a colorless foam. Melting point: 83-88 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.30-7.18 (m, 5H), 6.81 (dd, 2H), 5.25 (d, 1H), 4.45 (quint, 2H), 4.33 (t, 1H), 3.15-3.00 (m, 2H), 2.12 (sext, 1H), 1.47 (s, 9H), 1.42-1.35 (m, 12H), 0.92 (dd, 6H). Note: rotamers present; ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.9, 171.5, 170.2, 155.6, 136.7, 129.4, 128.7, 127.0, 82.0, 80.2, 58.5, 57.3, 55.9, 48.8, 38.1, 31.2, 28.4, 28.1, 19.2, 18.4, 18.1; IR (cm^{-1}) 3278, 2975, 2931, 1718, 1689, 1642, 1522; HRMS (FD), calcd for $C_{26}H_{41}N_3O_6$ [M^+]: 491.2990, found: 491.2981 (Δ 1.8 ppm); d.e. (determined by chiral HPLC): 96.7%

Boc-Phe-D-Val-Ala-OtBu 3t



Synthesised according to general procedure 2, except by stirring overnight at 50°C. Yield: 40 mg (0.082 mmol, 82%) as a colorless solid. Melting point: 114-117 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.32-7.19 (m, 5H), 6.97 (bs, 1H), 6.60 (d, 1H), 5.24 (d, 1H), 4.74-4.30 (m, 3H), 3.15-3.04 (m, 2H), 2.10 (sext, 1H), 1.47 (s, 9H), 1.42-1.37 (m, 12H), 0.88-0.76 (m, 6H). Note: rotamers present; ^{13}C-NMR (75 MHz, $CDCl_3$) δ 172.0, 171.5, 170.2, 155.6, 136.7, 129.4, 128.8, 127.0, 82.0, 80.3, 58.2, 56.6, 48.8, 38.3, 30.5, 28.4, 28.1, 19.5, 19.1, 18.5, 17.7; IR (cm^{-1}) 3274, 2966, 2930, 1732, 1694, 1639, 1518; HRMS (FD), calcd for $C_{26}H_{41}N_3O_6$ [M^+]: 491.2990, found: 491.2991 (Δ 0.2 ppm); d.e. (determined by chiral HPLC): 97.1%

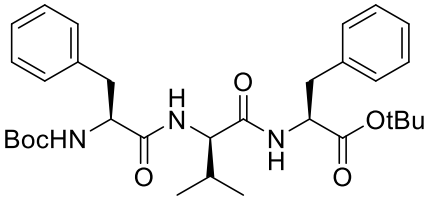
Boc-Phe-Val-Phe-OtBu 3u



Synthesised according to general procedure 2, except by stirring overnight at 80°C. Yield: 51 mg (0.090 mmol, 90%) as a faint yellow foam. Melting point: 64-68 °C (stays oily). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.32-7.16 (m, 10H), 6.71 (m, 2H), 5.23 (d, 1H), 4.75 (q, 1H), 4.43 (q, 1H), 4.32 (t, 1H), 3.14-2.99 (m, 4H), 2.08 (sext, 1H), 1.41

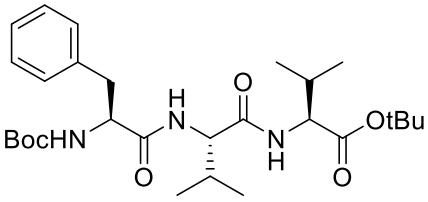
(bs, 18H), 0.88 (dd, 6H). Note: rotamers present; ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.5, 170.4, 170.3, 155.6, 136.8, 136.2, 129.6, 129.4, 128.7, 128.5, 127.1, 127.0, 82.4, 80.2, 58.5, 55.9, 53.8, 38.3, 38.1, 31.2, 28.4, 28.0, 19.1, 18.1; IR (cm^{-1}) 3272, 2974, 2931, 1732, 1691, 1640, 1519; HRMS (FD), calcd for $C_{32}H_{45}N_3O_6$ [M^+]: 567.3303, found: 567.3305 (Δ 0.4 ppm); d.e. (determined by chiral HPLC): 98.0%

Boc-Phe-D-Val-Phe-OtBu 3v



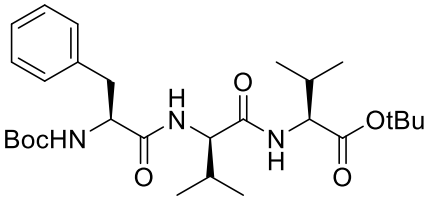
Synthesised according to general procedure 2, except by stirring overnight at 80°C. Yield: 45 mg (0.079 mmol, 79%) as a colorless solid. Melting point: 122-124 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.30-7.17 (m, 10H), 6.83 (bs, 1H), 6.62 (d, 1H), 5.21 (d, 1H), 4.75 (q, 1H), 4.39 (q, 1H), 4.32 (t, 1H), 3.12-3.02 (m, 4H), 1.99 (sext, 1H), 1.40 (bs, 18H), 0.70 (dd, 6H). Note: rotamers present; ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.5, 170.6, 170.4, 155.4, 136.7, 136.4, 129.5, 129.3, 128.8, 128.6, 128.5, 127.0, 82.4, 80.2, 58.2, 56.3, 53.8, 38.5, 30.7, 28.4, 28.0, 19.1, 17.5; IR (cm^{-1}) 3261, 2970, 2930, 1727, 1691, 1636, 1518; HRMS (FD), calcd for $C_{32}H_{45}N_3O_6$ [M^+]: 567.3303, found: 567.3284 (Δ 3.7 ppm); d.e. (determined by chiral HPLC): 94.0%

Boc-Phe-Val-Val-OtBu 3w



Synthesised according to general procedure 2, except by stirring at 50°C for 3 days. The product was purified by column chromatography (PE/EtOAc 7:1 → 5:1 → 3:1) to give a colorless oil, which solidified upon standing. Yield: 40 mg (0.077 mmol, 77%). Melting point: 125-132 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.31-7.19 (m, 5H), 6.75 (d, 1H), 6.69 (d, 1H), 5.27 (d, 1H), 4.47-4.33 (m, 3H), 3.15-3.00 (m, 2H), 2.13 (oct, 2H), 1.48 (s, 9H), 1.40 (s, 9H), 0.95-0.89 (m, 12H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.5, 170.8, 170.7, 155.6, 136.8, 129.4, 128.7, 126.9, 82.0, 80.2, 58.8, 57.7, 55.8, 38.0, 31.4, 31.2, 28.4, 28.1, 19.2, 19.1, 18.3, 17.9; IR (cm^{-1}) 3270, 2964, 1731, 1691, 1641, 1519; HRMS (FD), calcd for $C_{28}H_{45}N_3O_6$ [M^+]: 519.3303, found: 519.3285 (Δ 3.5 ppm); d.e. (determined by chiral HPLC): 90.8%

Boc-Phe-D-Val-Val-OtBu 3x



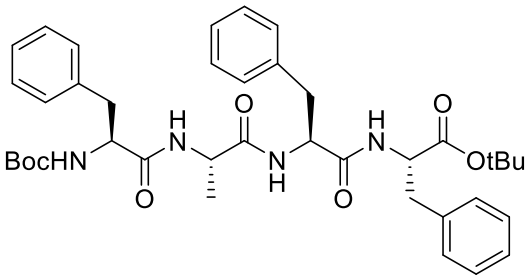
Synthesised according to general procedure 2, except by stirring at 50°C for 3 days. The product was isolated as a colorless foam. Yield: 44 mg (0.085 mmol, 85%). Melting point: 120-123 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.31-7.19 (m, 5H), 6.77 (d, 1H), 6.67 (d, 1H), 5.27 (d, 1H), 4.41 (m, 3H), 3.15-3.01 (m, 2H), 2.15 (sext, 1H), 2.04 (sext, 1H), 1.47 (s, 9H), 1.40 (s, 9H), 0.94 (t, 6H), 0.81 (d, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.4, 170.8, 170.7, 155.5, 136.8, 129.4, 128.8, 127.0, 82.2, 80.2, 58.4, 57.7, 56.3, 38.6, 31.5, 30.9, 28.4, 28.2, 19.11, 19.07, 17.94, 17.86; IR (cm^{-1}) 3283, 2964, 2930, 1717, 1698, 1638, 1515; HRMS (FD), calcd for $C_{28}H_{45}N_3O_6$ [M^+]: 519.3303, found: 519.3301 (Δ 0.4 ppm); d.e. (determined by chiral HPLC): 94.5%

General procedure 3: **Synthesis of tetrapeptides Boc-Phe-AA-Phe-Phe-OtBu 4a-f**

The dipeptide isopropenyl ester (0.20 mmol), 147 mg H-Phe-Phe-OtBu (0.40 mmol, 2.0 equiv) and 69 mg pyrazole (1.00 mmol, 5.0 equiv) were dissolved in 4 mL anhydrous $PhCH_3$. Next, 20 µL of a 1M solution of DBU in $PhCH_3$ (0.02 mmol, 10 mol%) was added and the reaction was stirred overnight at room temperature (except C-terminal Valine, see below). The mixture was diluted with 20 mL Et_2O and washed with 10 mL H_2O, 10 mL 1M NaOH, 10 mL brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was dissolved in 4 mL dry CH_2Cl_2 and 87 mg Boc_2O (0.40 mmol, 2.0 equiv) and 55 µL Et_3N (0.40 mmol, 2.0 equiv) were added. The reaction was stirred overnight at room temperature, diluted with 20 mL CH_2Cl_2 and washed with 10 mL 1M HCl, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography, eluting with a CH_2Cl_2/CH_3OH mixture.

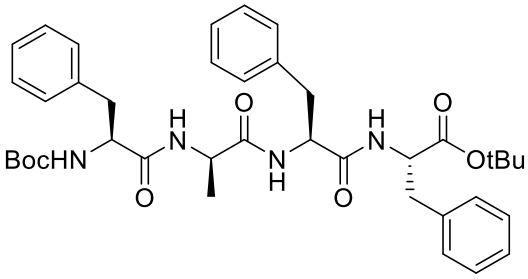
-Note: for purification purposes it was necessary to transform the excess H-Phe-Phe-OtBu (which could not be washed away with acid) into the more apolar Boc-Phe-Phe-OtBu to ensure good separation with column chromatography.

Boc-Phe-Ala-Phe-Phe-OtBu 4a



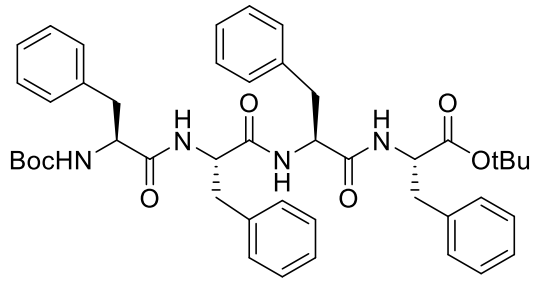
Synthesised according to general procedure 3. Purified by column chromatography (CH_2Cl_2/CH_3OH 99.5 : 0.5 → 99.3 : 0.7 → 99.1 : 0.9) to give a colorless solid. Yield: 93 mg (0.135 mmol, 68%). Melting point: 210-213 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.44 (d, 1H), 7.30-7.11 (m, 17H), 7.01 (d, 1H), 5.55 (d, 1H), 4.90 (q, 1H), 4.75-4.66 (m, 2H), 4.52 (q, 1H), 3.14-2.93 (m, 6H), 1.40 (s, 9H), 1.39 (s, 9H), 1.29 (d, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 172.1, 171.5, 170.4, 170.2, 155.7, 136.8, 136.6, 136.3, 129.6, 129.5, 129.4, 128.6, 128.4, 127.0, 126.91, 126.87, 82.3, 80.0, 55.7, 54.4, 53.9, 48.9, 38.7, 38.3, 28.4, 28.0, 19.0; IR (cm^{-1}) 3276, 2977, 2929, 1731, 1690, 1635, 1520; HRMS (FD), calcd for $C_{39}H_{50}N_4O_7$ [M^+]: 686.3674, found: 686.3712 (Δ 5.5 ppm); d.e. (determined by chiral HPLC): 98.5%

Boc-Phe-D-Ala-Phe-Phe-OtBu 4b



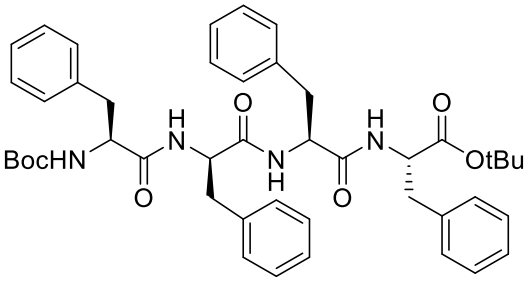
Synthesised according to general procedure 3. Purified by column chromatography (CH_2Cl_2/CH_3OH 99.5 : 0.5 → 99.25 : 0.75 → 99 : 1) to give a colorless powder. Yield: 108 mg (0.157 mmol, 79%). Melting point: 142-144 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.35-7.15 (m, 15H), 7.09 (d, 2H), 6.85 (d, 1H), 6.76 (d, 1H), 5.72 (d, 1H), 4.77-4.69 (m, 2H), 4.50 (quint, 1H), 4.43 (d, 1H), 3.16-2.86 (m, 6H), 1.38 (bs, 18H), 1.06 (d, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.9, 171.4, 170.6, 170.4, 155.6, 136.9, 136.6, 136.1, 129.5, 129.4, 128.5, 128.4, 126.9, 126.8, 82.4, 80.0, 56.0, 54.4, 53.8, 53.5, 48.6, 38.8, 38.2, 28.4, 28.0, 18.0; IR (cm^{-1}) 3273, 2977, 2929, 1732, 1693, 1633, 1520; HRMS (FD), calcd for $C_{39}H_{50}N_4O_7$ [M^+]: 686.3674, found: 686.3712 (Δ 5.5 ppm); d.e. (determined by chiral HPLC): 98.6%

Boc-Phe-Phe-Phe-Phe-OtBu 4c



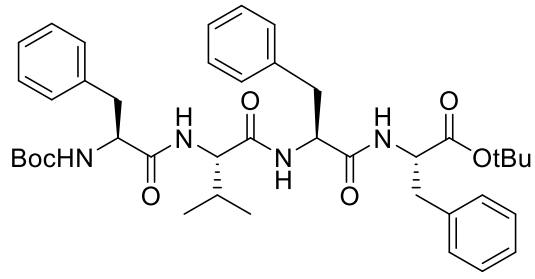
Synthesised according to general procedure 3. Purified by column chromatography (CH_2Cl_2/CH_3OH 99.4 : 0.6 → 99.2 : 0.8 → 99 : 1) to give a colorless solid. Yield: 106 mg (0.139 mmol, 69%). Melting point: 170-178 °C. ^{1}H-NMR (300 MHz, DMSO-d6) δ 8.47 (d, 1H), 8.24 (d, 1H), 7.89 (d, 1H), 7.31-7.15 (m, 20H), 6.87 (d, 1H), 4.64 (t, 1H), 4.58 (t, 1H), 4.41 (q, 1H), 4.10 (t, 1H), 3.08-2.98 (m, 4H), 2.86-2.58 (m, 4H), 1.32 (s, 9H), 1.27 (s, 9H). Note: rotamers also present; ^{13}C-NMR (75 MHz, DMSO-d6) δ 171.3, 170.9, 170.7, 170.4, 155.0, 138.2, 137.5, 137.1, 129.4, 129.2, 129.1, 128.2, 128.0, 127.9, 126.6, 126.3, 126.2, 126.1, 80.7, 78.1, 55.8, 54.2, 53.5, 37.8, 37.7, 37.6, 37.0, 28.1, 27.5; IR (cm^{-1}) 3272, 2976, 2927, 1733, 1689, 1639, 1522; HRMS (FD), calcd for $C_{45}H_{54}N_4O_7$ [M$^+$]: 762.3987, found: 762.4001 (Δ 1.8 ppm); d.e. (determined by chiral HPLC): 93.0%

Boc-Phe-D-Phe-Phe-Phe-OtBu 4d



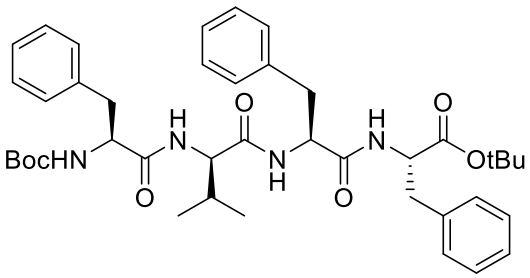
Synthesised according to general procedure 3. Purified by column chromatography (CH_2Cl_2/CH_3OH 99.5 : 0.5 → 99.3 : 0.7 → 99.1 : 0.9) to give a colorless solid. Yield: 105 mg (0.138 mmol, 69%). Melting point: 172-175 °C. ^{1}H-NMR (300 MHz, DMSO-d6) δ 8.53 (d, 1H), 8.49 (d, 1H), 8.08 (d, 1H), 7.36-6.98 (m, 20H), 6.62 (d, 1H), 4.69 (t, 1H), 4.61 (t, 1H), 4.40 (q, 1H), 4.18 (t, 1H), 3.10 (d, 1H), 3.01 (d, 2H), 2.78-2.59 (m, 3H), 2.43 (t, 2H), 1.32 (s, 9H), 1.26 (s, 9H). Note: rotamers also present; ^{13}C-NMR (75 MHz, DMSO-d6) δ 171.3, 171.1, 170.6, 170.4, 155.0, 138.1, 137.8, 137.5, 137.1, 129.5, 129.3, 129.21, 129.18, 128.2, 128.0, 127.8, 126.5, 126.4, 126.2, 126.0, 80.6, 77.9, 55.3, 54.4, 53.6, 38.1, 37.7, 36.9, 28.1, 27.5; IR (cm^{-1}) 3281, 3027, 2977, 2929, 1733, 1692, 1668, 1638, 1523; HRMS (FD), calcd for $C_{45}H_{54}N_4O_7$ [M$^+$]: 762.3987, found: 762.4029 (Δ 5.5 ppm); d.e. (determined by chiral HPLC): 94.8%

Boc-Phe-Val-Phe-Phe-OtBu 4e

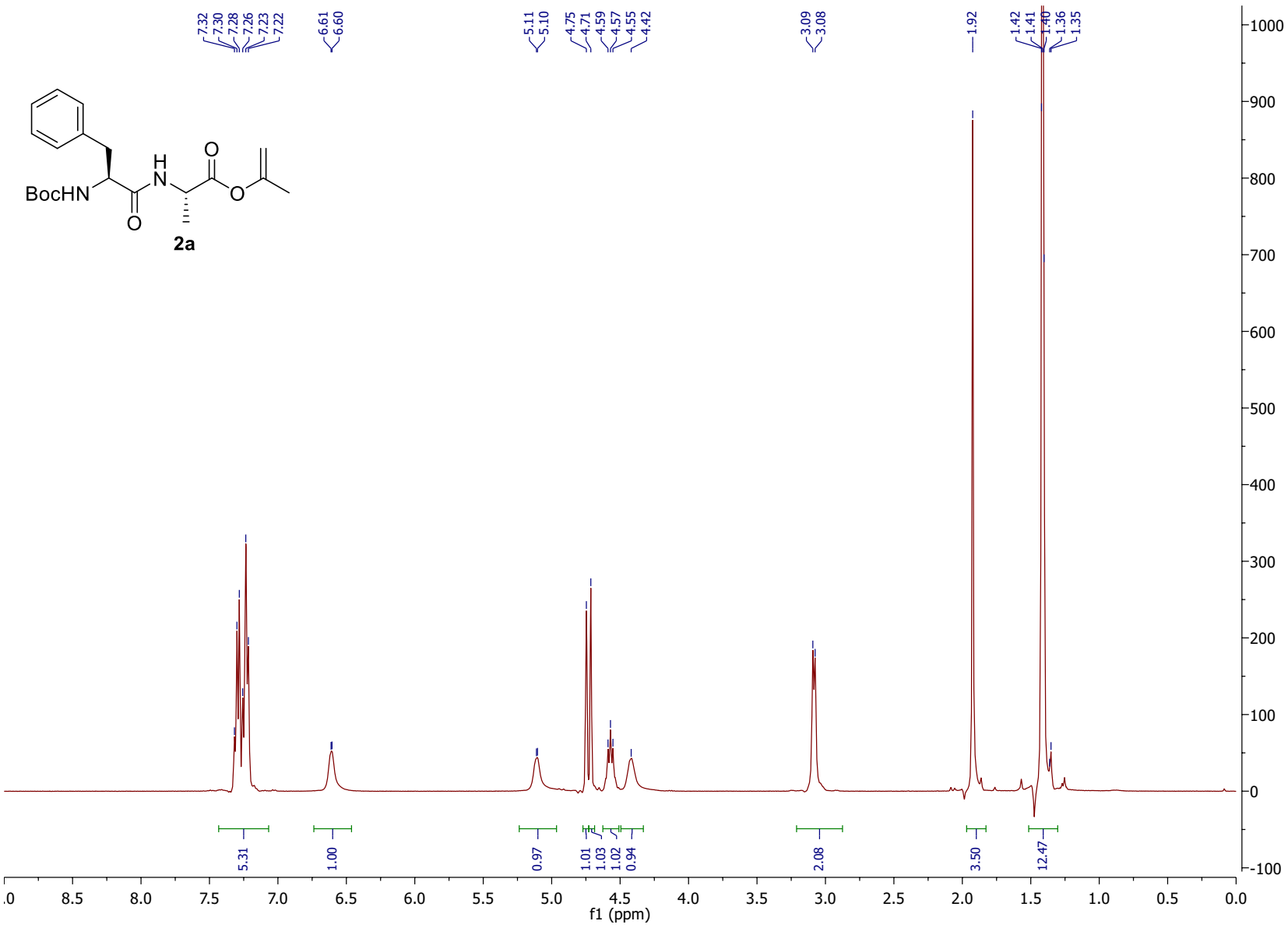


Synthesised according to general procedure 3, except by stirring overnight at 70 °C. Purified by column chromatography (CH_2Cl_2/CH_3OH 99.5 : 0.5 → 99.3 : 0.7 → 99.1 : 0.9) to give a colorless solid. Yield: 67 mg (0.094 mmol, 47%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.33-7.18 (m, 14H), 7.11 (d, 2H), 6.80 (d, 1H), 6.61 (d, 2H), 5.13 (d, 1H), 4.75 (q, 1H), 4.67 (q, 1H), 4.34 (q, 1H), 4.24 (t, 1H), 3.12-2.97 (m, 6H), 2.09 (sext, 1H), 1.42 (s, 9H), 1.39 (s, 9H), 0.83-0.72 (dd, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 171.9, 170.7, 170.2, 170.1, 155.8, 136.7, 136.6, 136.4, 129.6, 129.4, 129.3, 128.9, 128.7, 128.5, 127.2, 127.1, 127.0, 82.3, 80.6, 59.0, 56.2, 54.3, 54.01, 38.2, 37.9, 28.4, 28.0, 19.3, 17.6; IR (cm^{-1}) 3271, 2975, 2928, 1715, 1634, 1517, 1497; HRMS (FD), calcd for $C_{41}H_{54}N_4O_7$ [M$^+$]: 714.3987, found: 714.3996 (Δ 1.3 ppm); d.e. (determined by chiral HPLC): 94.6%

Boc-Phe-D-Val-Phe-Phe-OtBu 4f



Synthesised according to general procedure 3, except by stirring overnight at 70 °C. Purified by column chromatography (CH_2Cl_2/CH_3OH 99.5 : 0.5 → 99.3 : 0.7 → 99.1 : 0.9) to give a colorless solid. Yield: 75 mg (0.105 mmol, 52%). ^{1}H-NMR (300 MHz, DMSO-d6) δ 8.43 (d, 1H), 8.35 (d, 1H), 7.77 (d, 1H), 7.30-7.16 (m, 15H), 6.86 (d, 1H), 4.67 (t, 1H), 4.39 (q, 1H), 4.29 (q, 1H), 4.17 (t, 1H), 3.12-2.93 (m, 4H), 2.76-2.68 (m, 2H), 1.72 (sext, 1H), 1.31 (s, 9H), 1.29 (s, 9H), 0.48 (dd, 6H). Note: rotamers present; ^{13}C-NMR (75 MHz, DMSO-d6) δ 171.5, 171.4, 170.5, 170.4, 155.0, 138.1, 137.8, 137.1, 129.22, 129.17, 128.2, 128.0, 127.9, 126.5, 126.2, 126.1, 80.6, 78.1, 57.3, 55.9, 54.4, 53.7, 37.9, 37.7, 36.9, 30.8, 28.1, 27.5, 18.9, 17.3; IR (cm^{-1}) 3266, 2970, 2927, 1725, 1636; HRMS (FD), calcd for $C_{41}H_{54}N_4O_7$ [M^+]: 714.3987, found: 714.3983 (Δ 0.6 ppm); d.e. (determined by chiral HPLC): 96.6%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O
O
O
2a
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7.23
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6.60
5.11
5.10
4.75
4.71
4.59
4.57
4.55
4.42
3.09
3.08
1.92
1.42
1.41
1.40
1.36
1.35
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1.03
1.02
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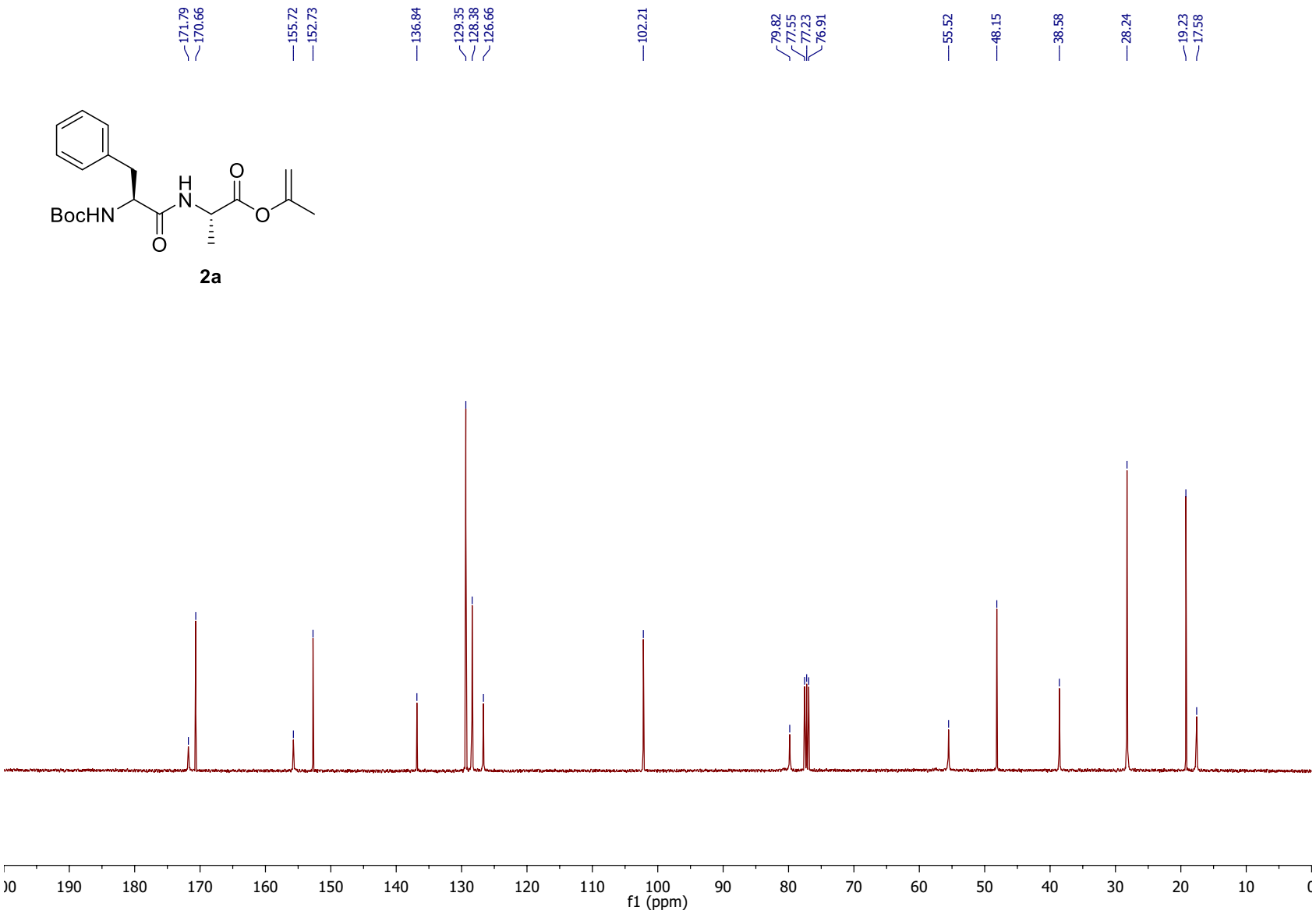
f1 (ppm)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55.52
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28.24
19.23
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N
O
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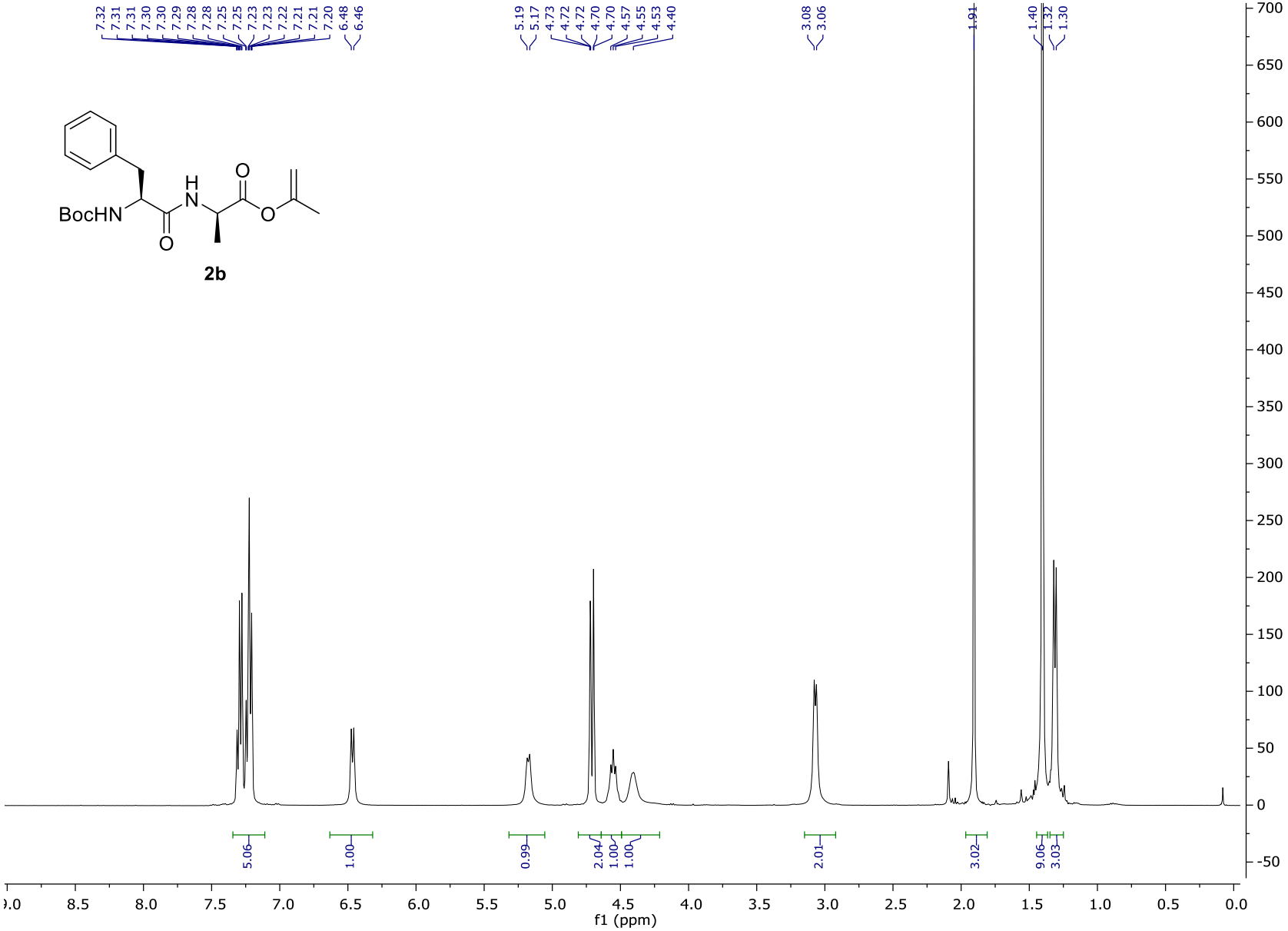
O
O
f1 (ppm)

2a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4.72
4.72
4.70
4.70
4.57
4.55
4.53
4.40
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3.06
1.91
1.40
1.32
1.30
BocHN
H
N
O
O
O
O
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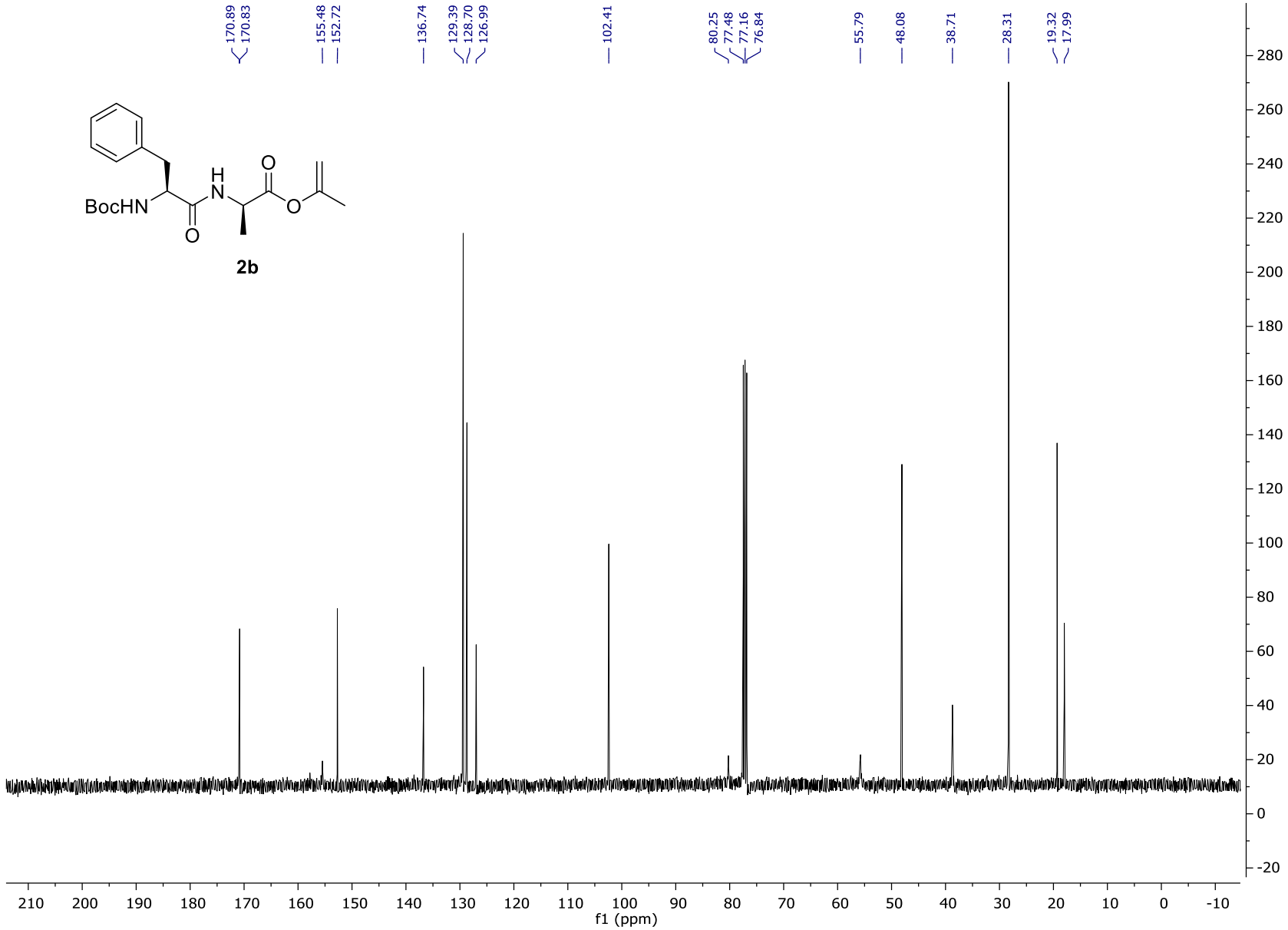
f1 (ppm)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76.84
55.79
48.08
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28.31
19.32
17.99
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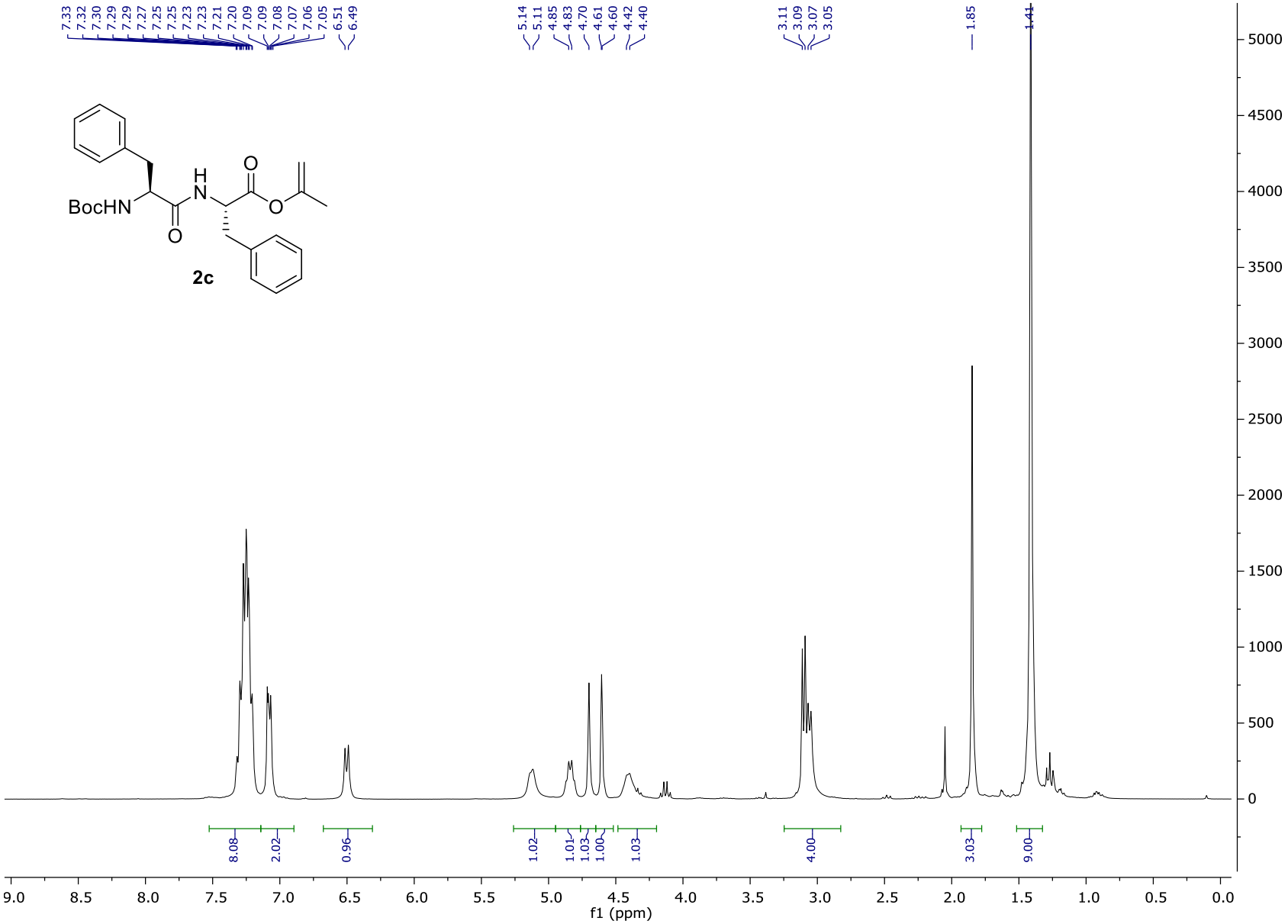
H
N
O
O
O
2b
f1 (ppm)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7.09
7.09
7.08
7.07
7.06
7.05
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6.49
5.14
5.11
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4.70
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H
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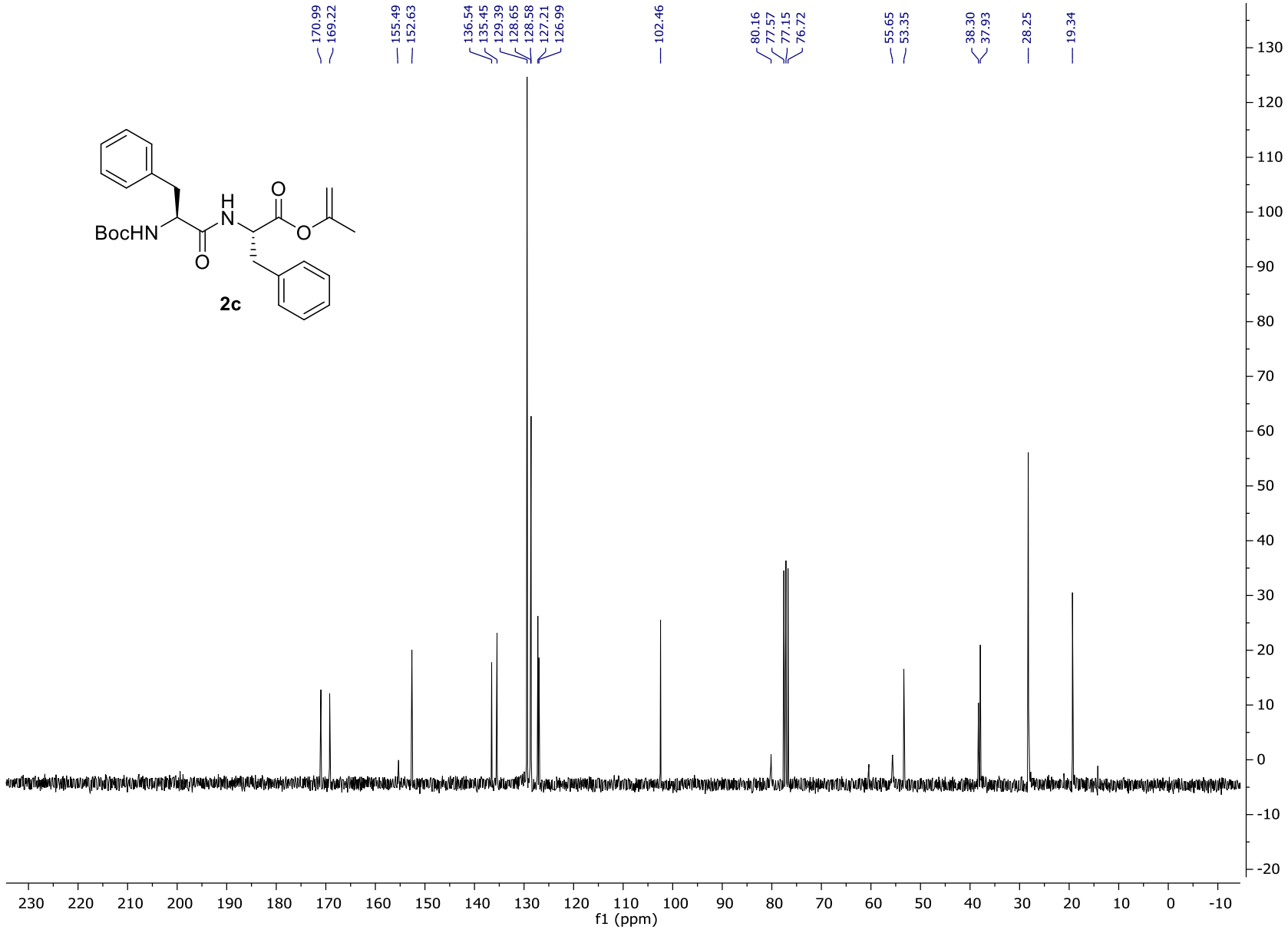
f1 (ppm)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77.15
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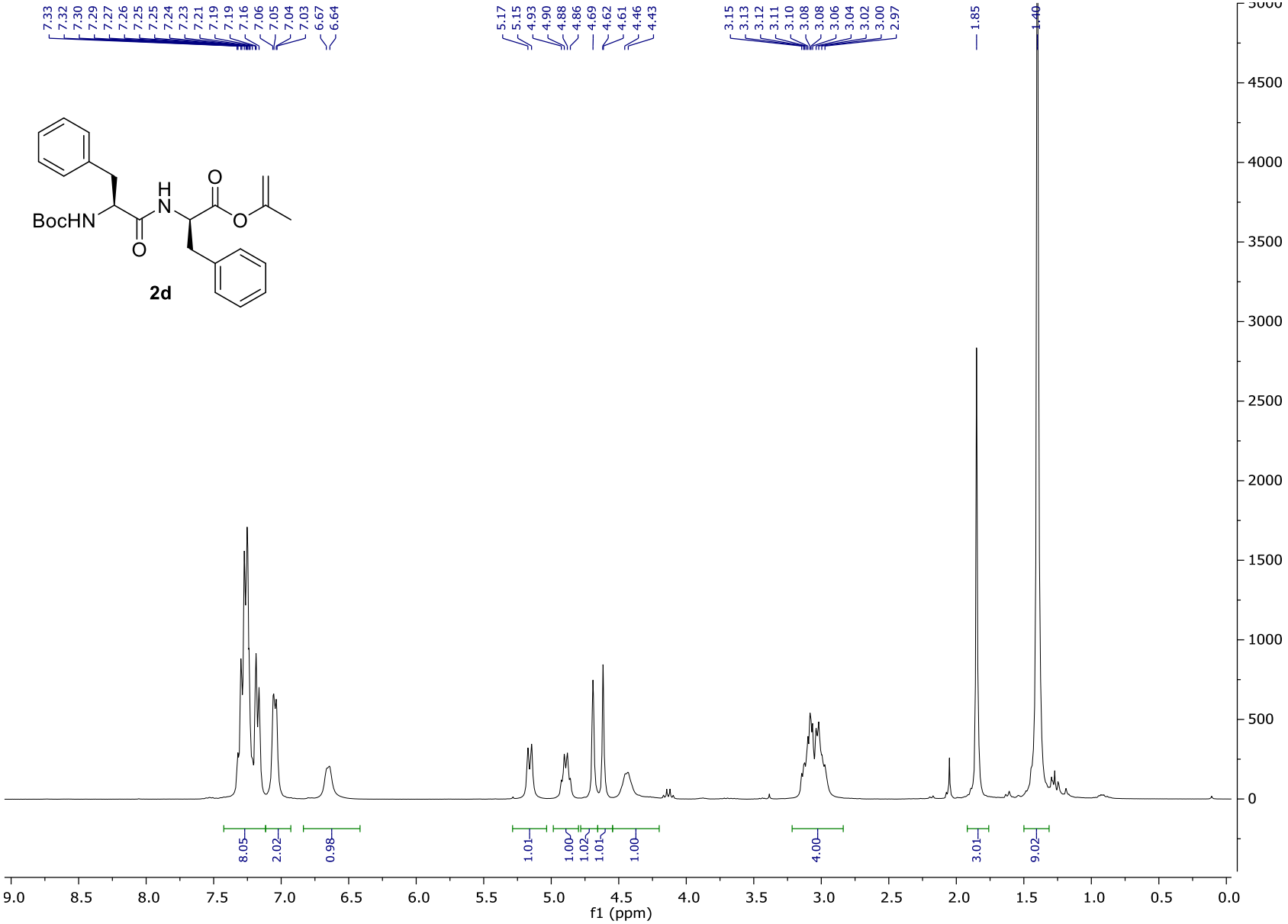
H
N
O
O
O
O
2c
f1 (ppm)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7.25
7.24
7.23
7.21
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7.19
7.16
7.06
7.05
7.04
7.03
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5.15
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4.61
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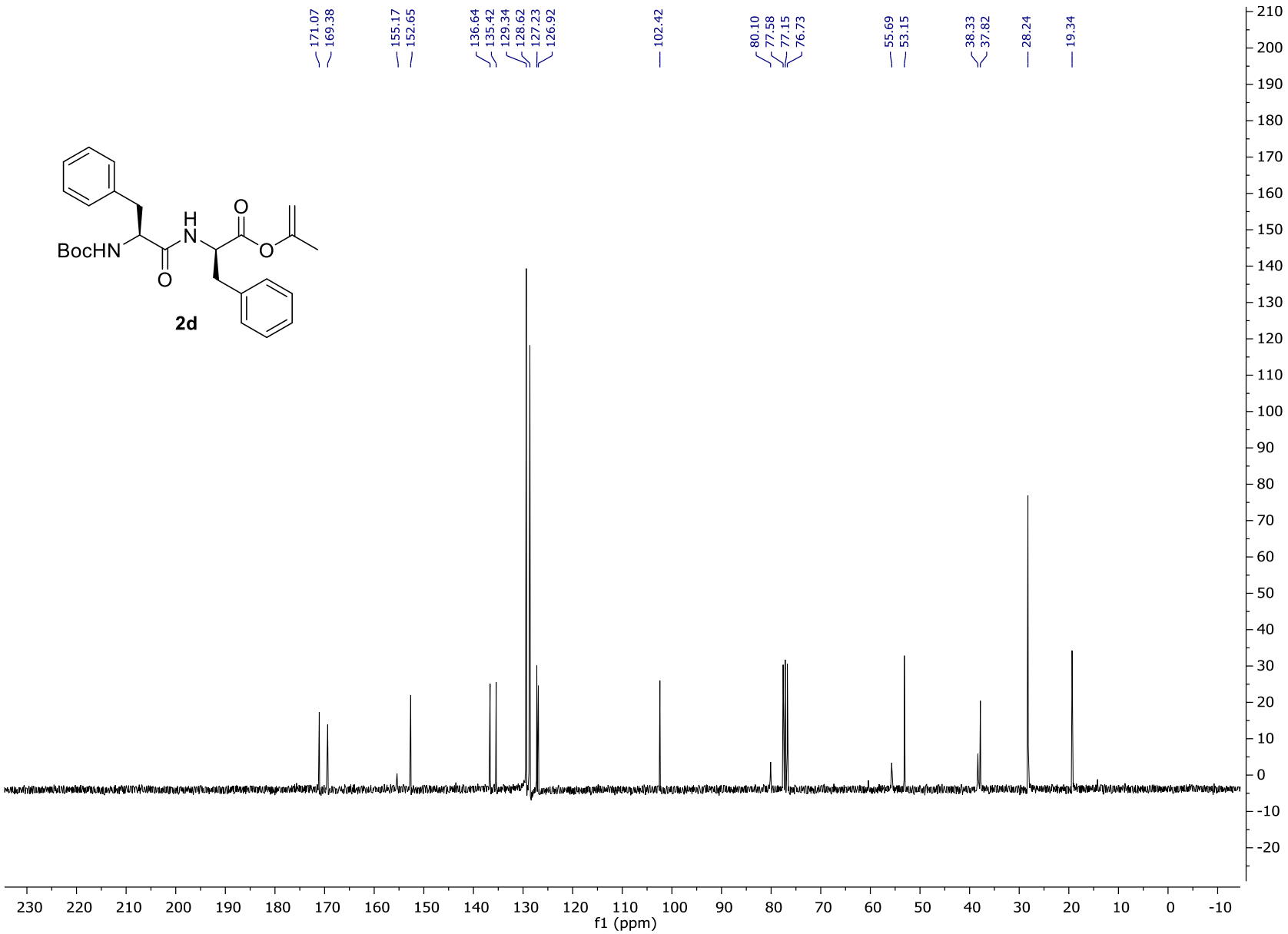
f1 (ppm)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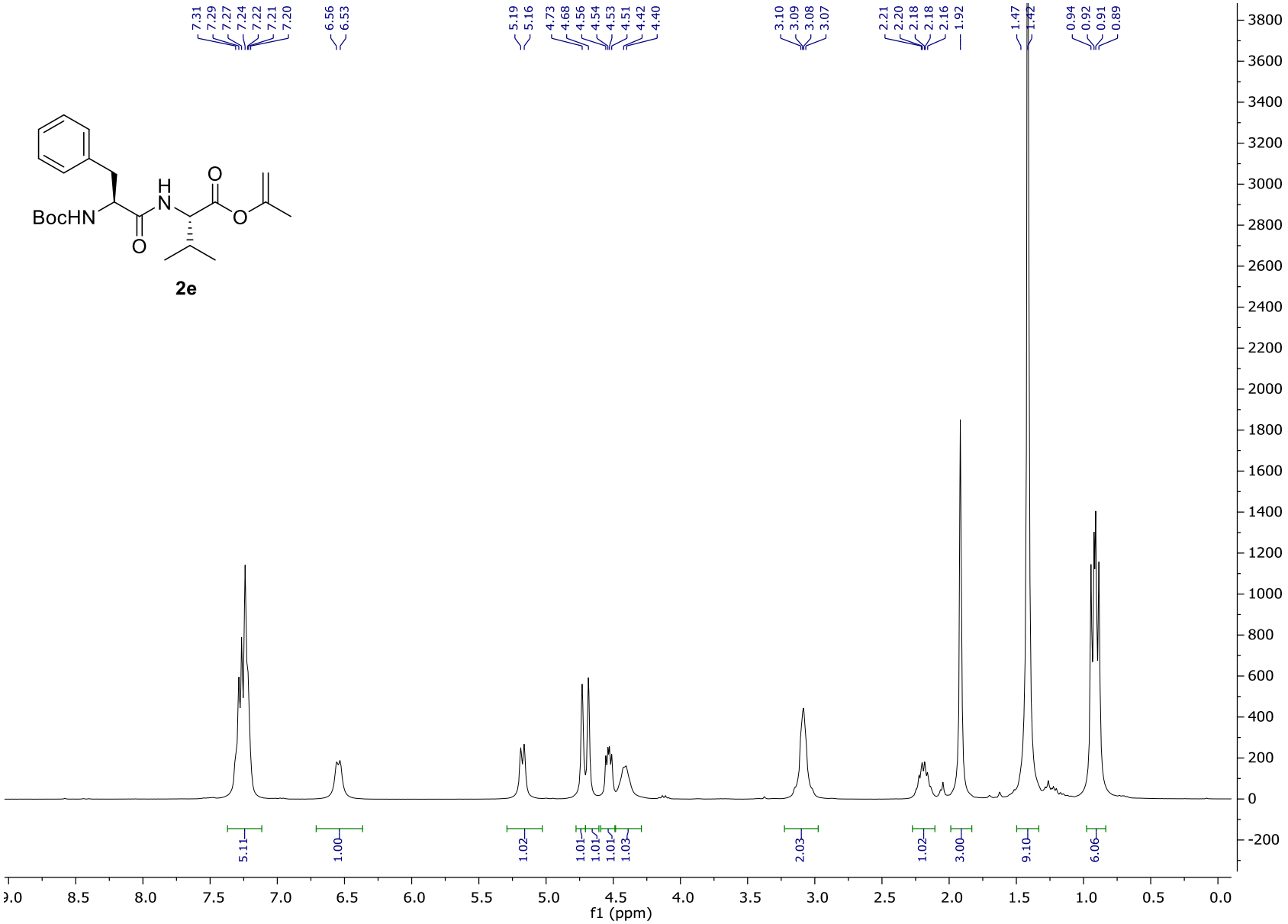
H
N
O
O
O
O
2d
f1 (ppm)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0.91
0.89
BocHN
H
N
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O
O
O
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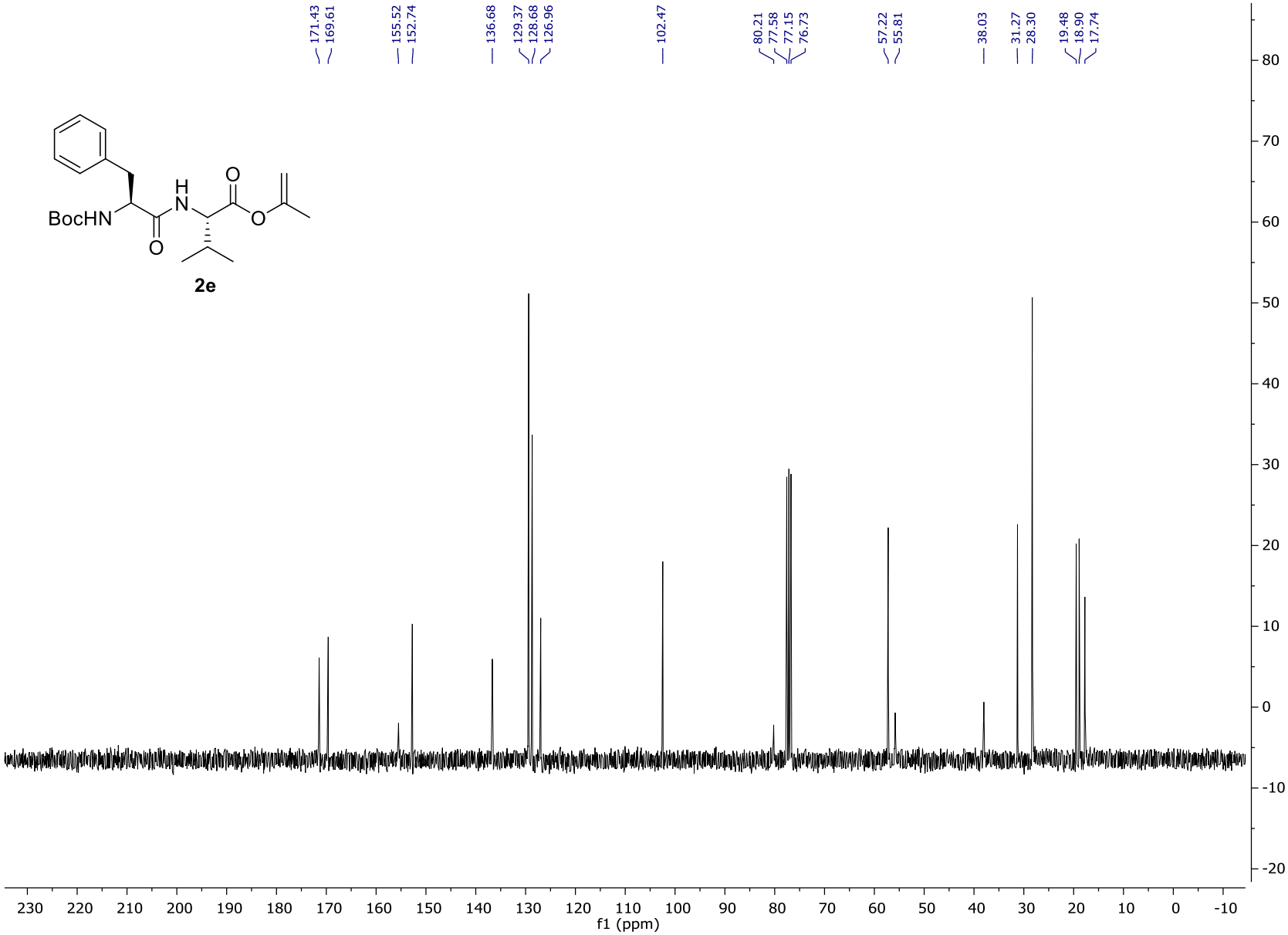
f1 (ppm)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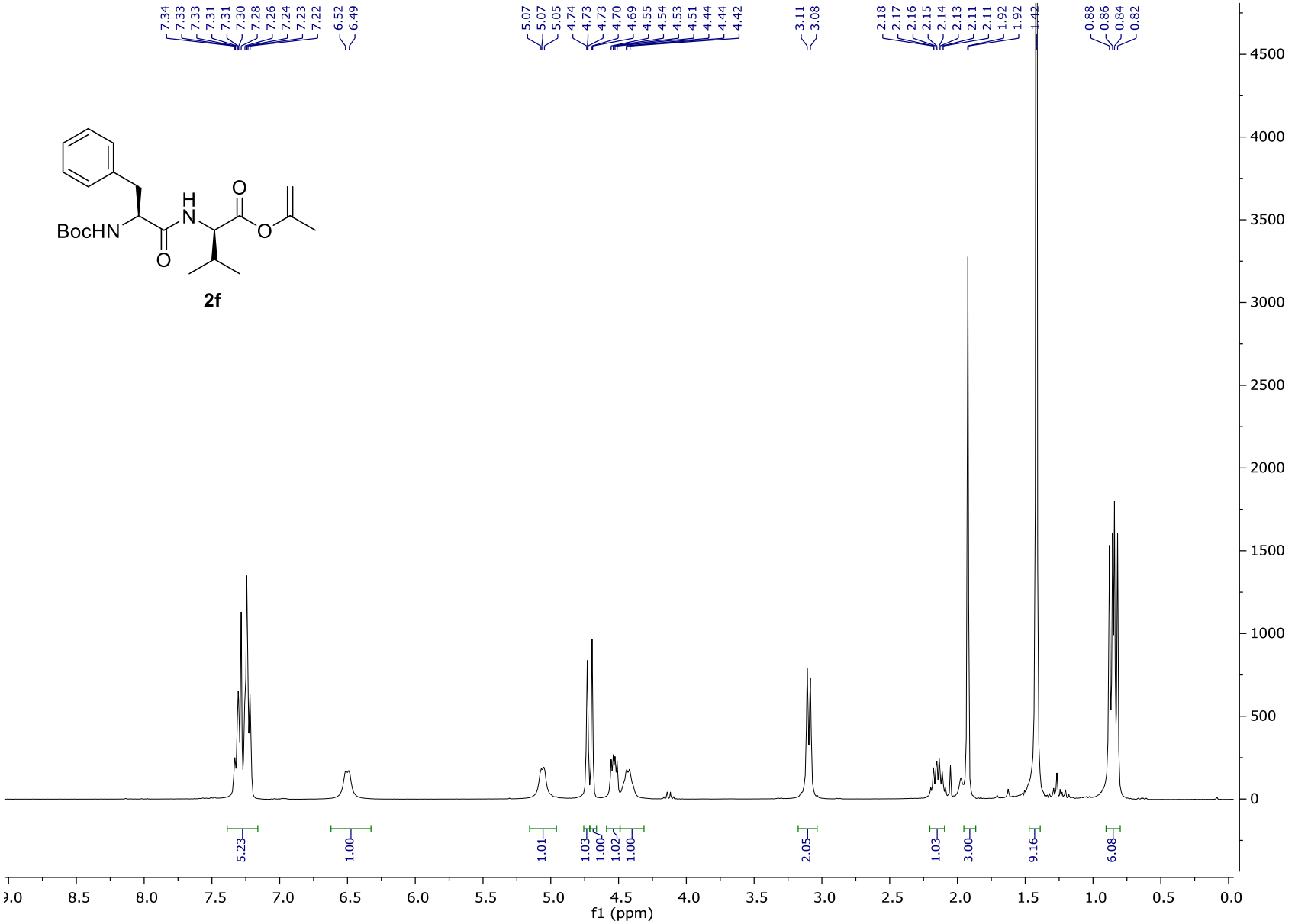
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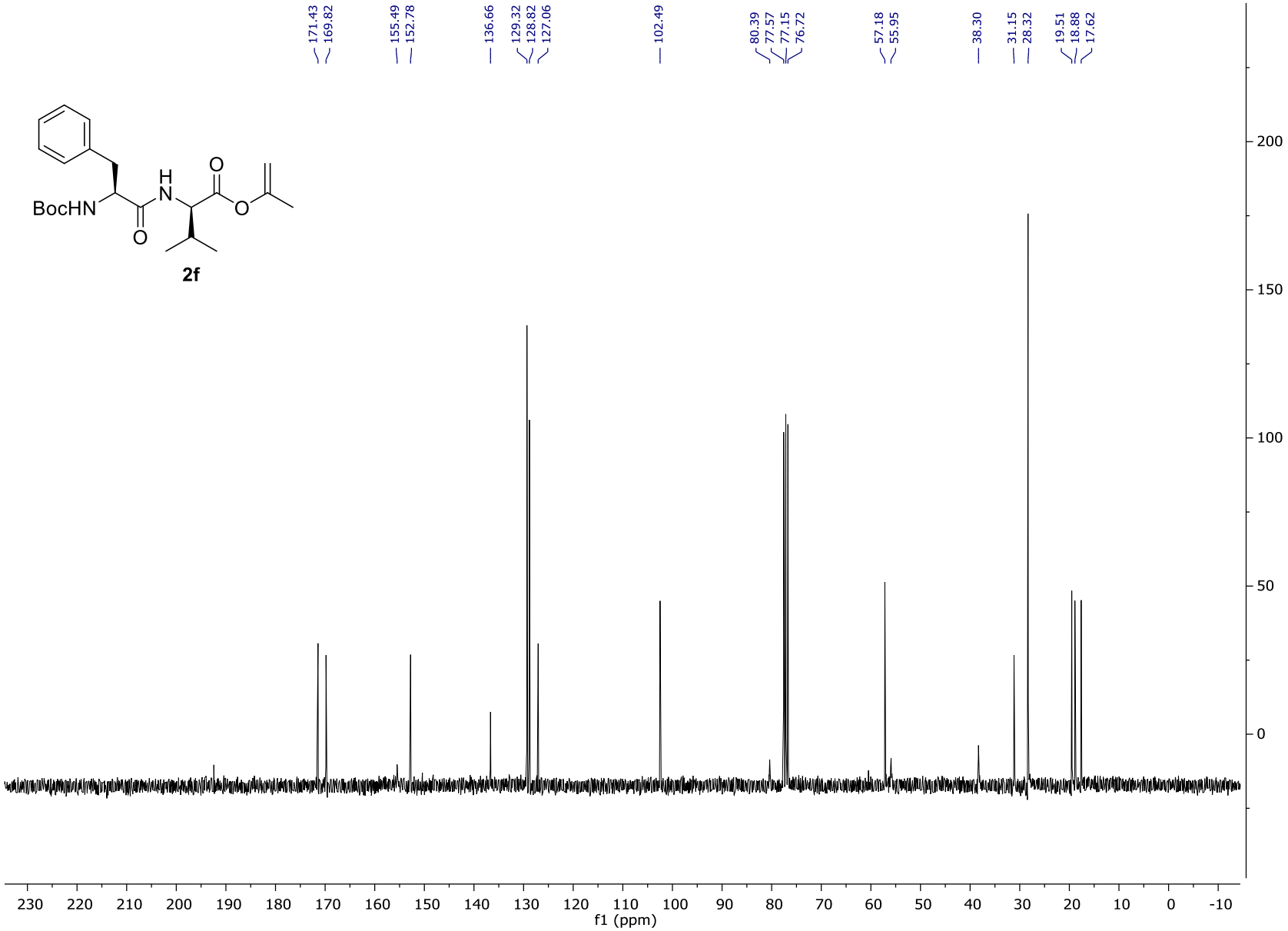
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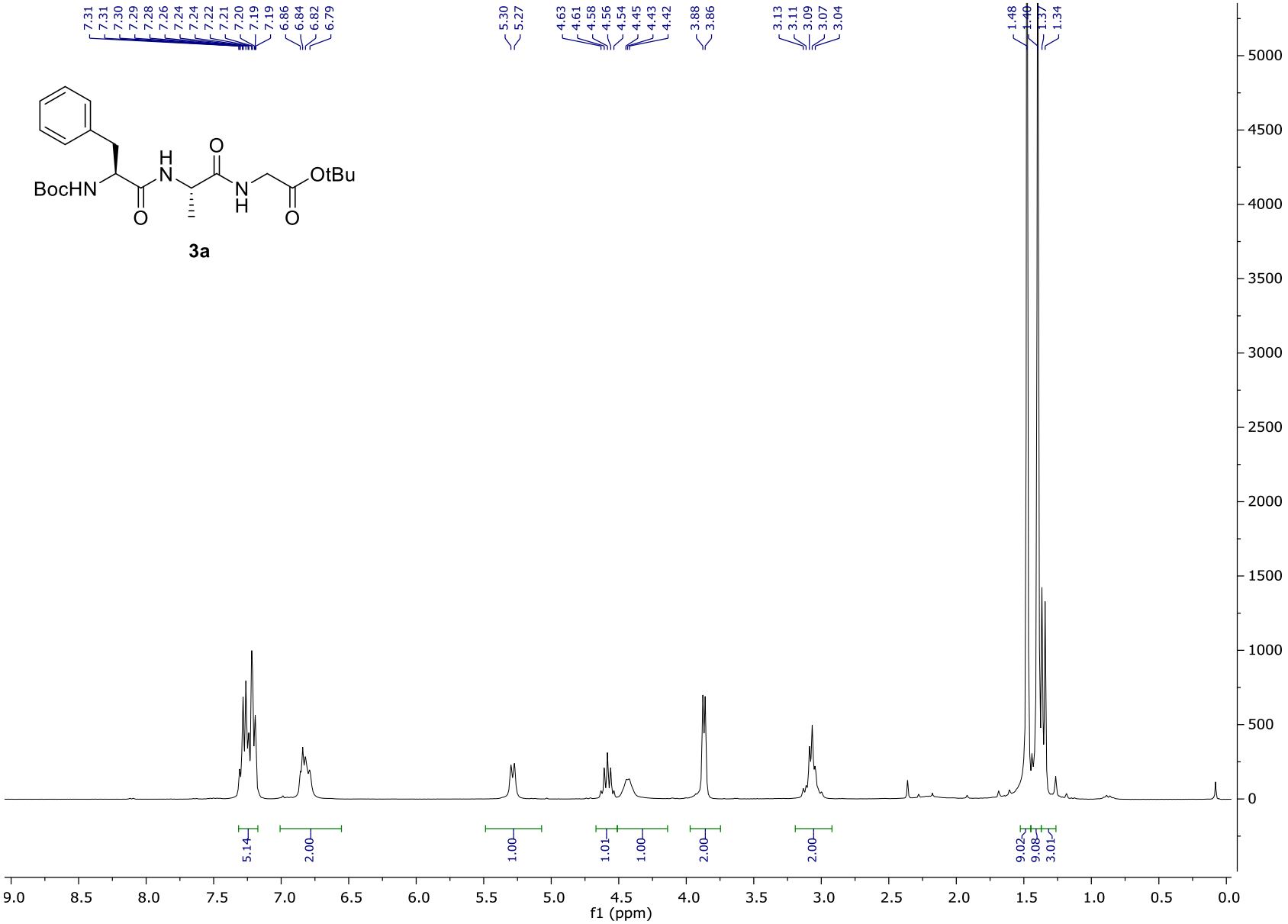
f1 (ppm)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1.34
BocHN
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O
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H
O
OtBu
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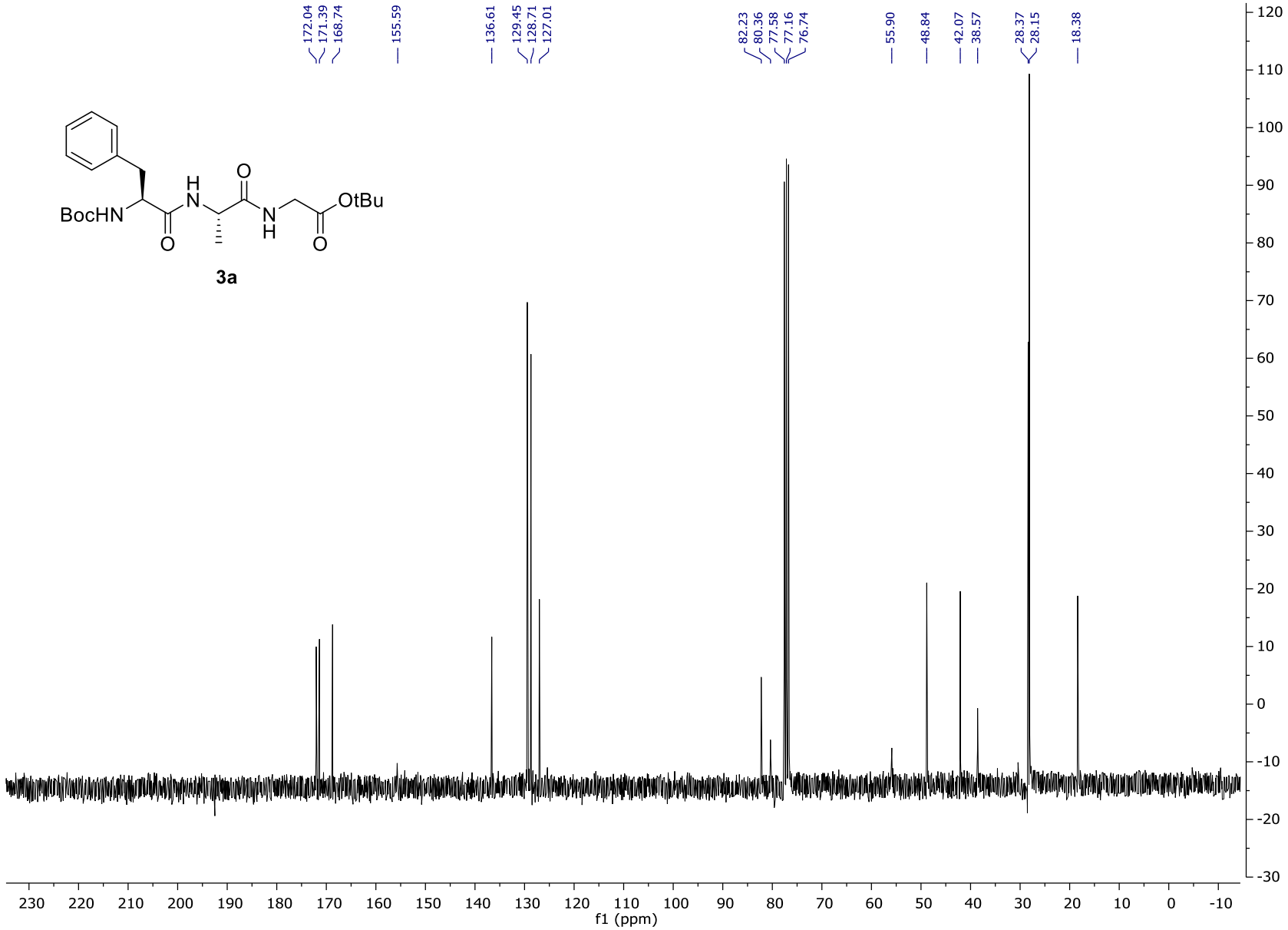
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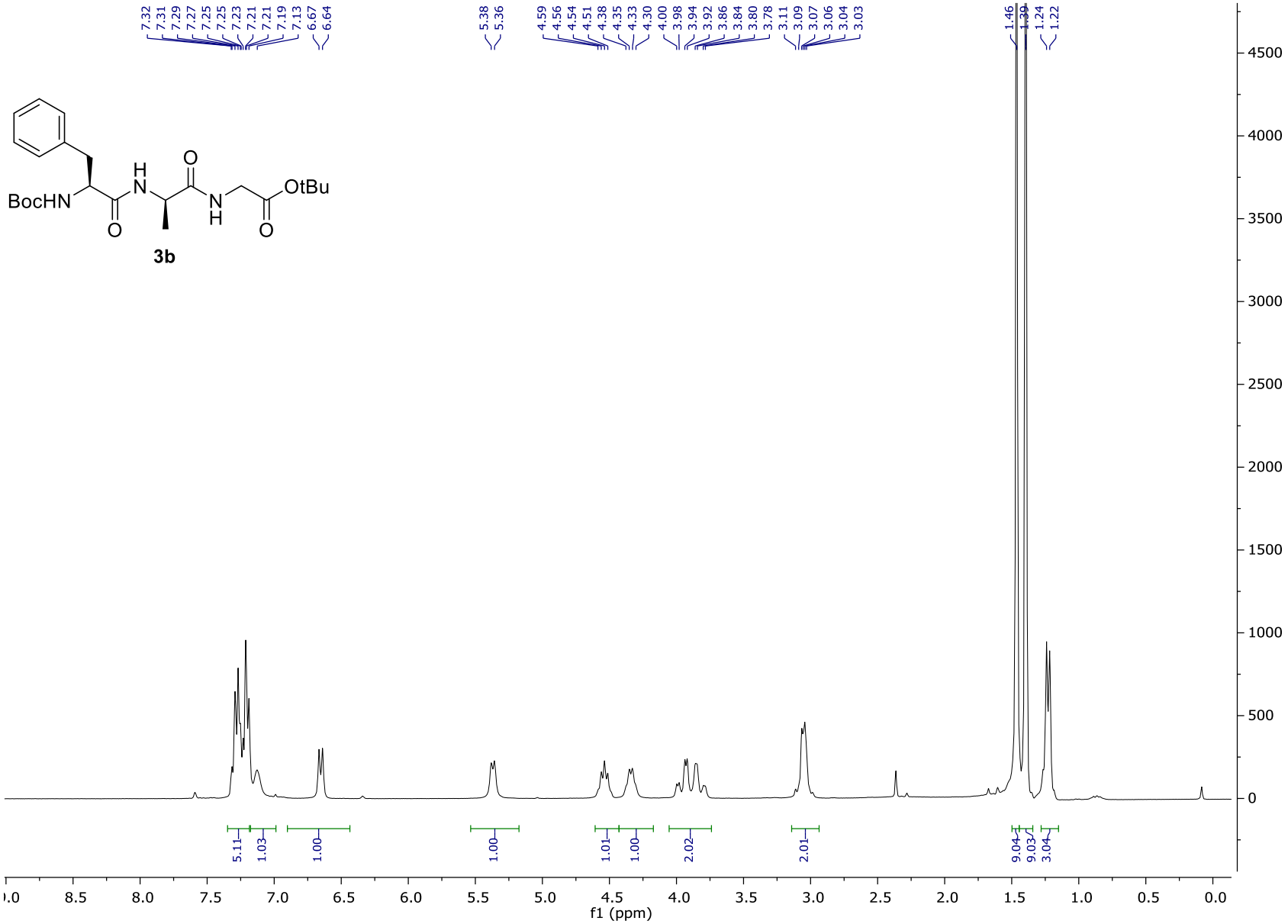
f1 (ppm)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4.59
4.56
4.54
4.51
4.38
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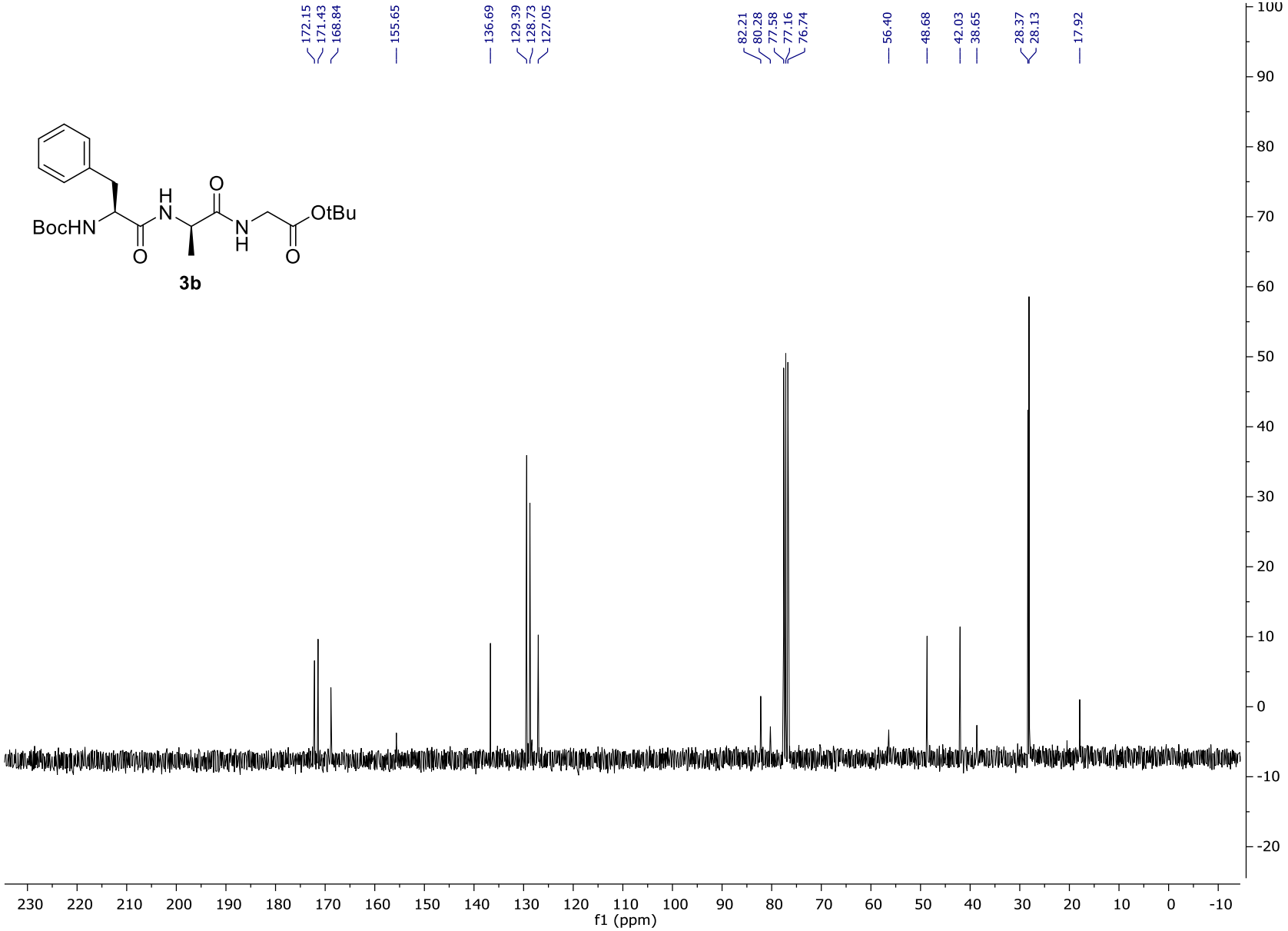
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42.03
38.65
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17.92
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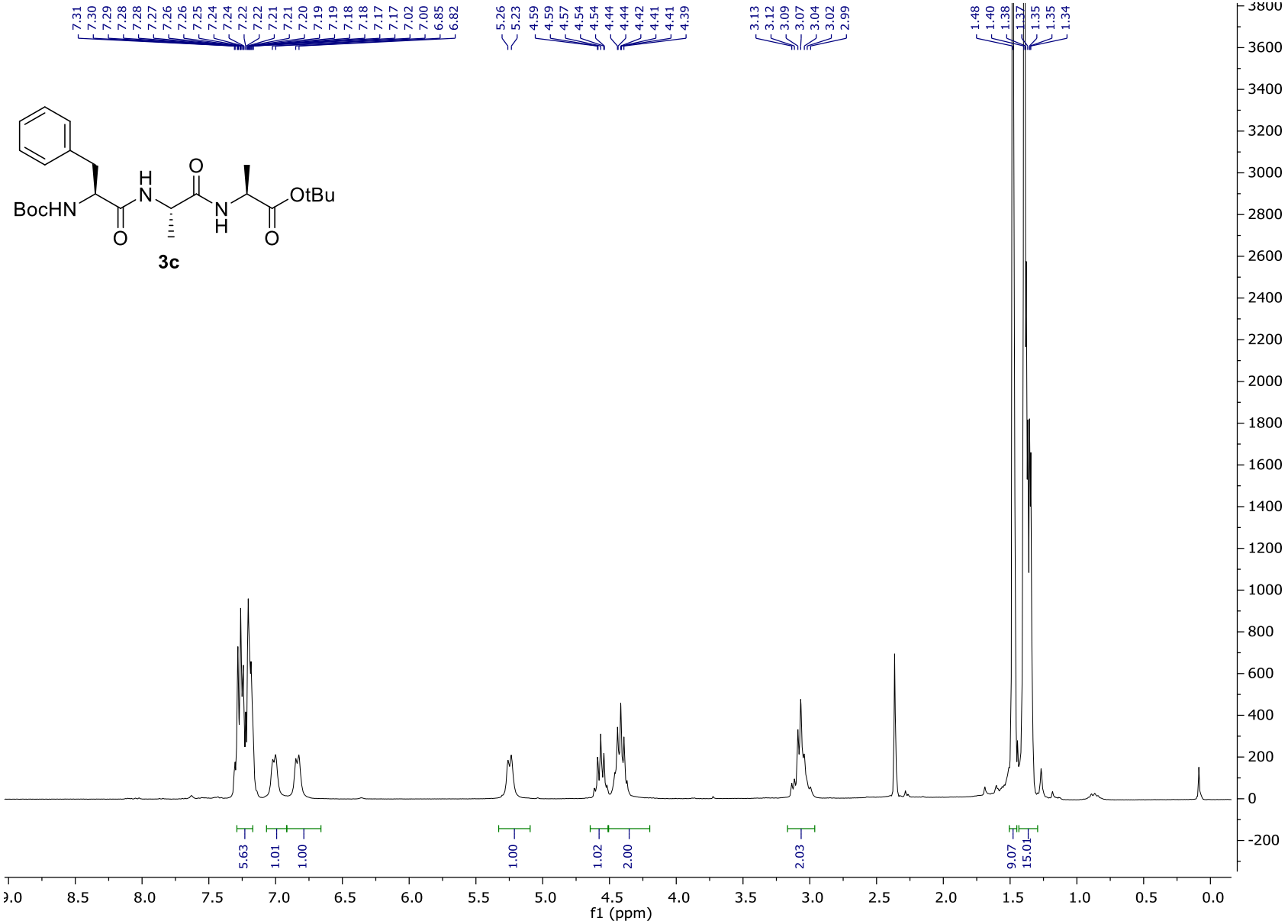
O
N
H
O
OtBu
O
3b
f1 (ppm)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5.26 5.23
4.59 4.59 4.57 4.54 4.54 4.44 4.44 4.42 4.41 4.41 4.39
3.13 3.12 3.09 3.07 3.04 3.02 2.99
1.48 1.40 1.38 1.37 1.35 1.35 1.34
BocHN
H
N
O
O
N
H
O
OtBu
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1.02
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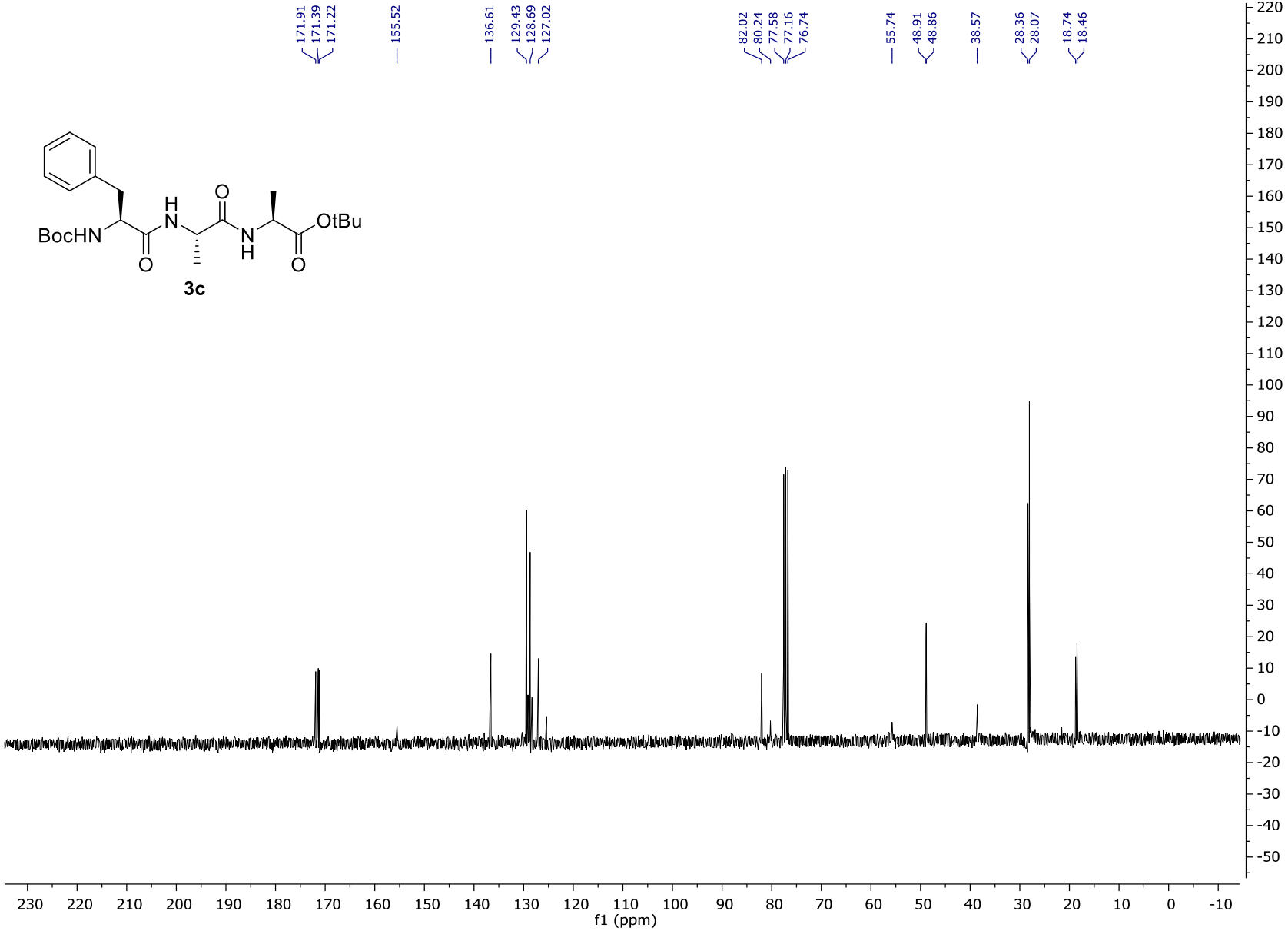
15.01
f1 (ppm)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OtBu
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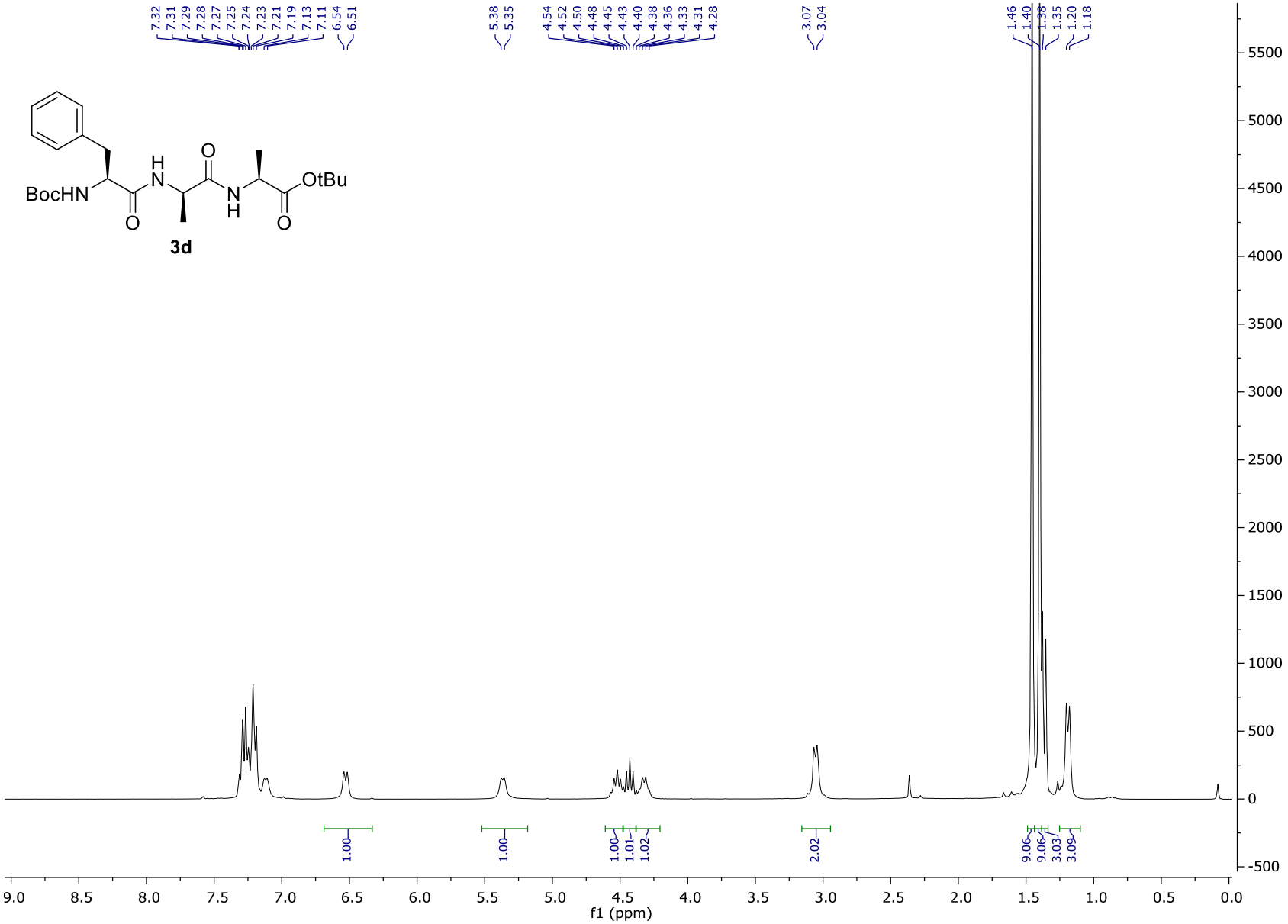
3c
f1 (ppm)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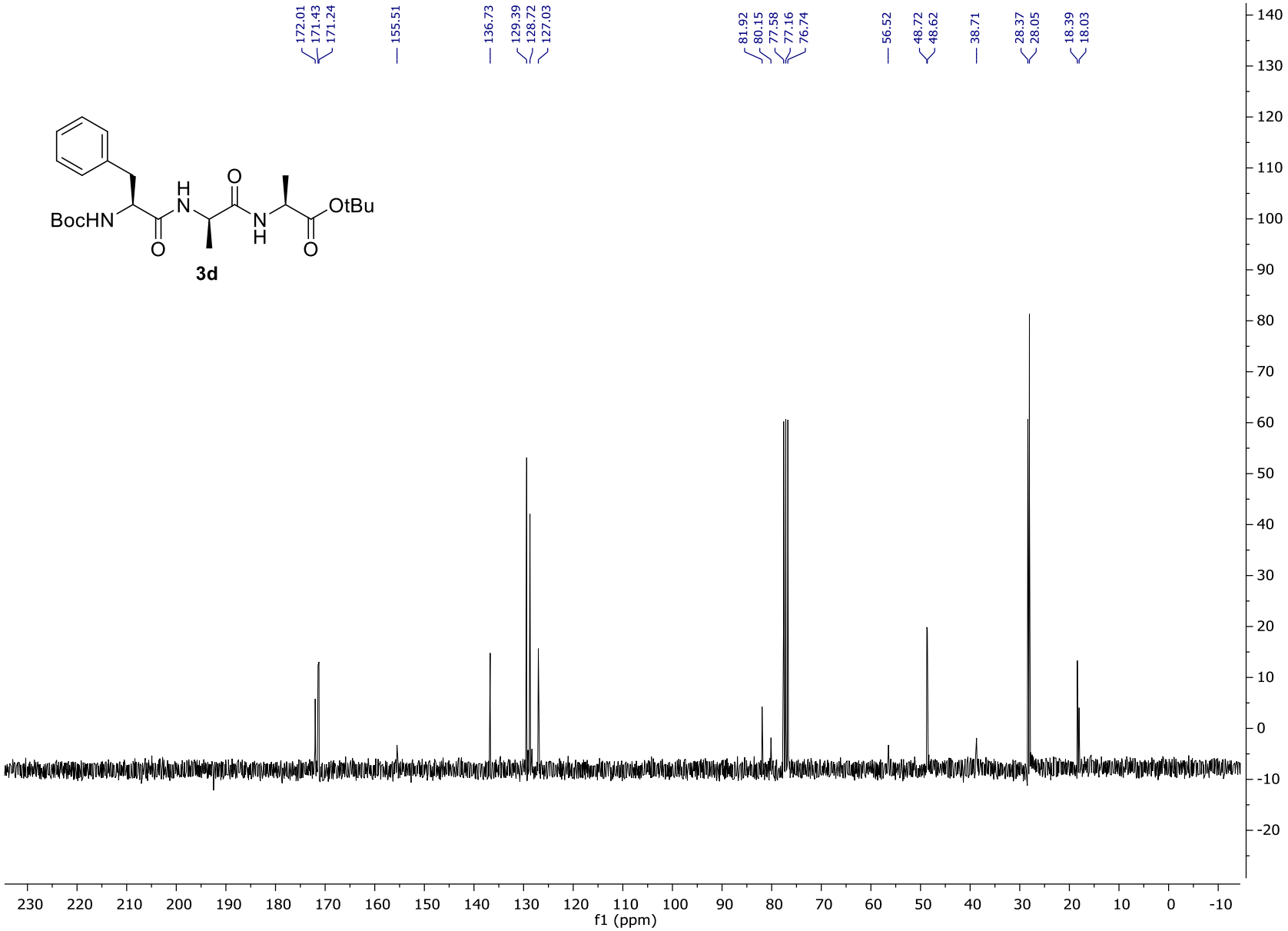
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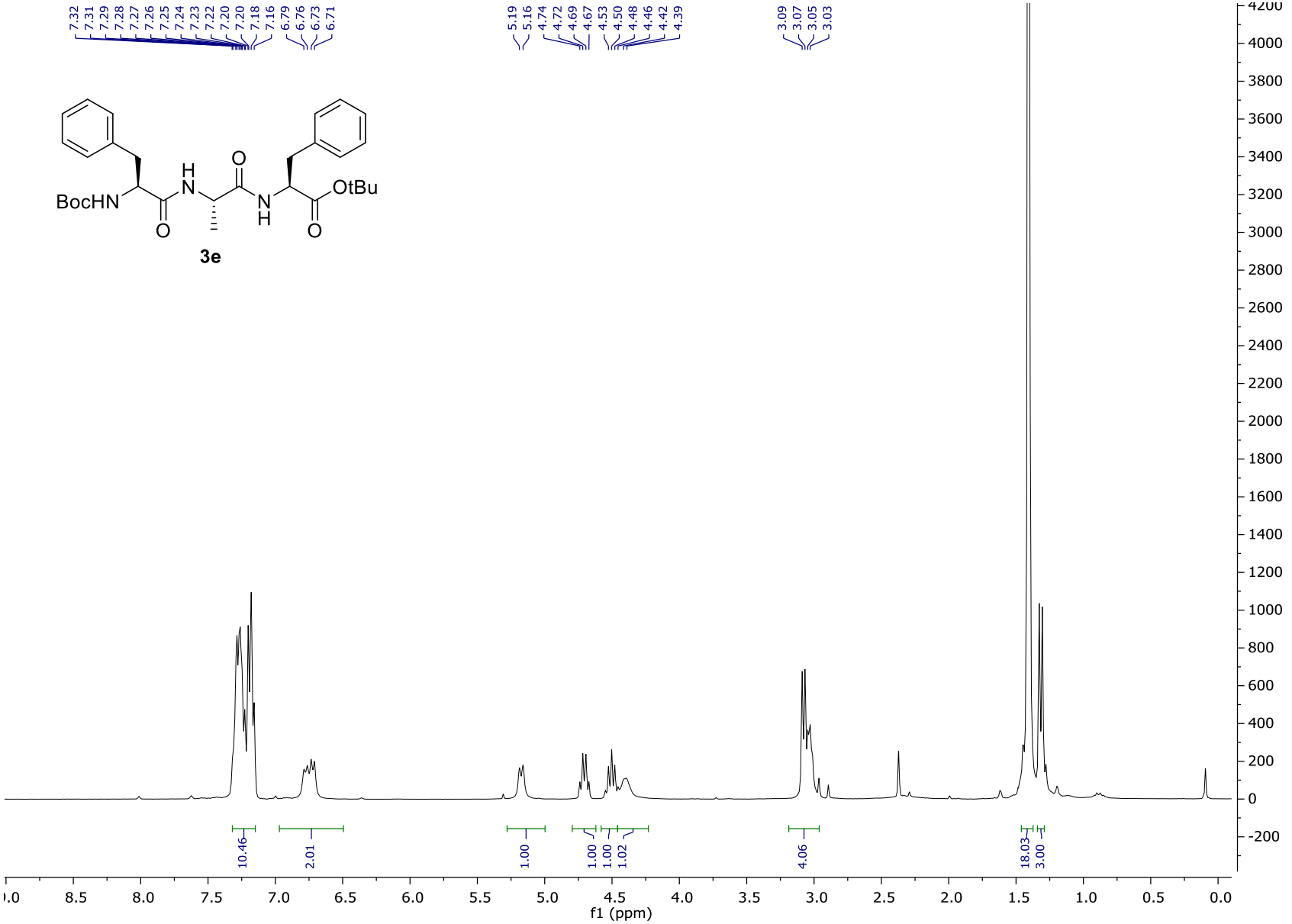
3d
f1 (ppm)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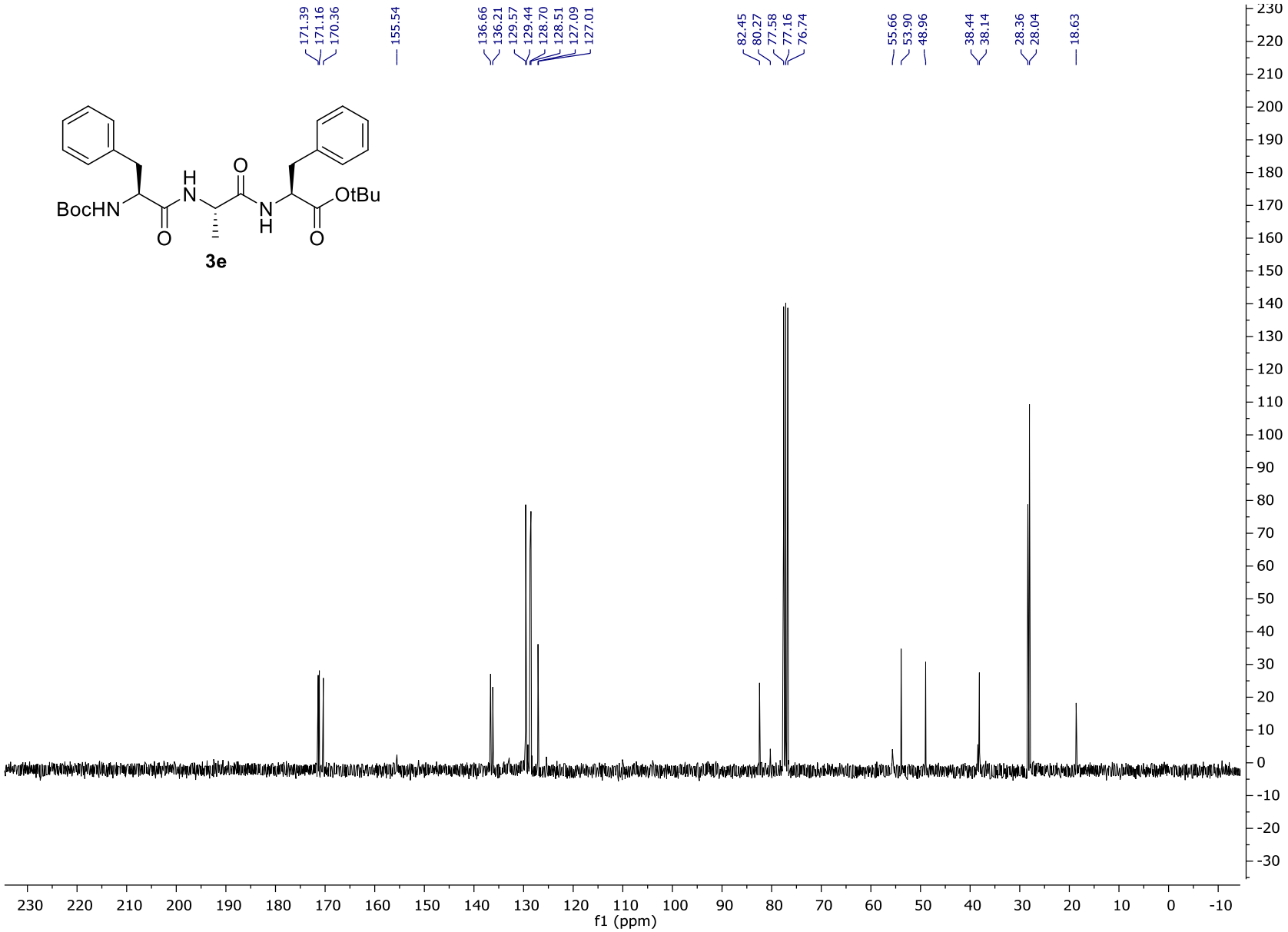
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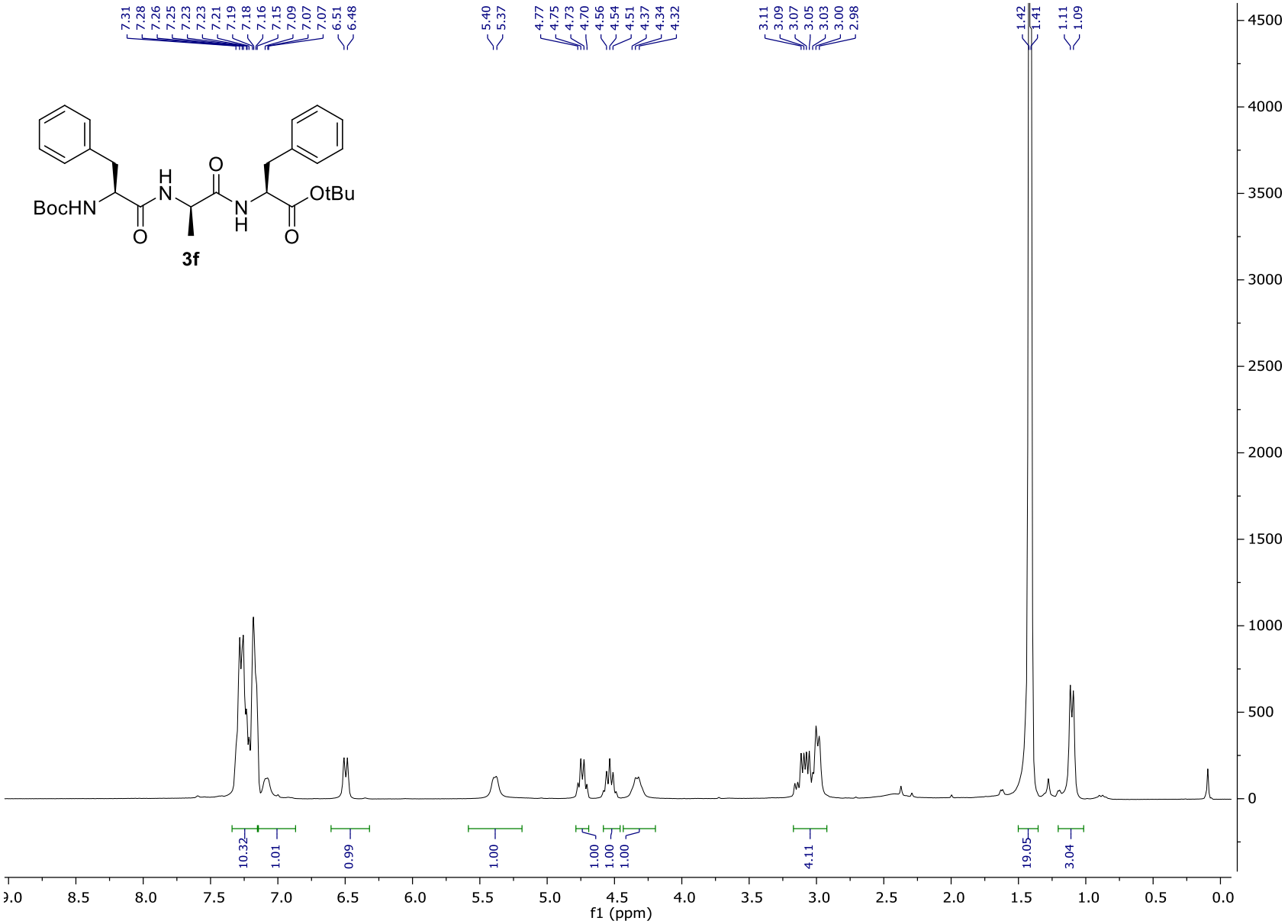
3e
f1 (ppm)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1.11
1.09
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O
N
H
O
OtBu
O
3f
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3000
2500
2000
1500
1000
500
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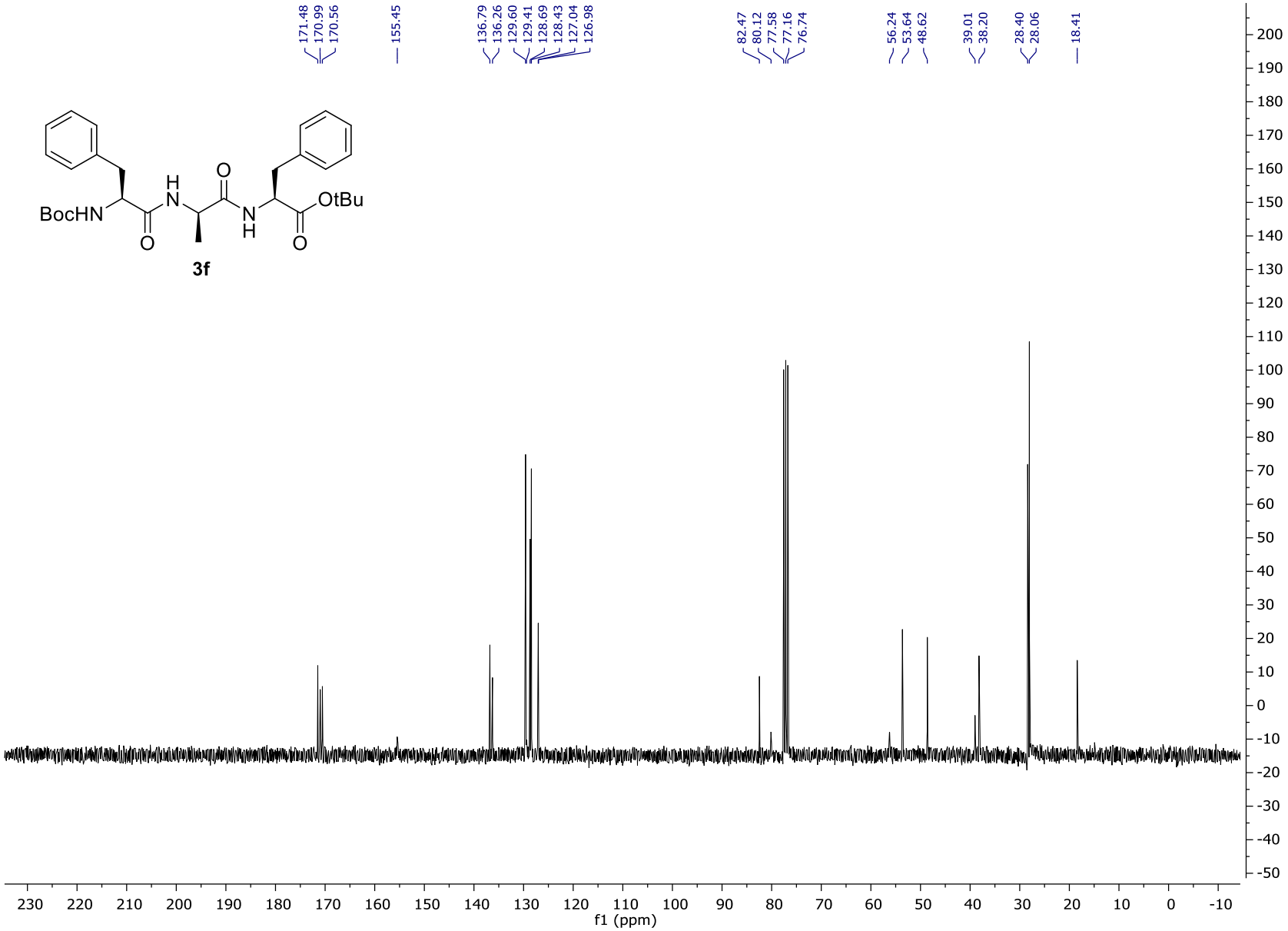
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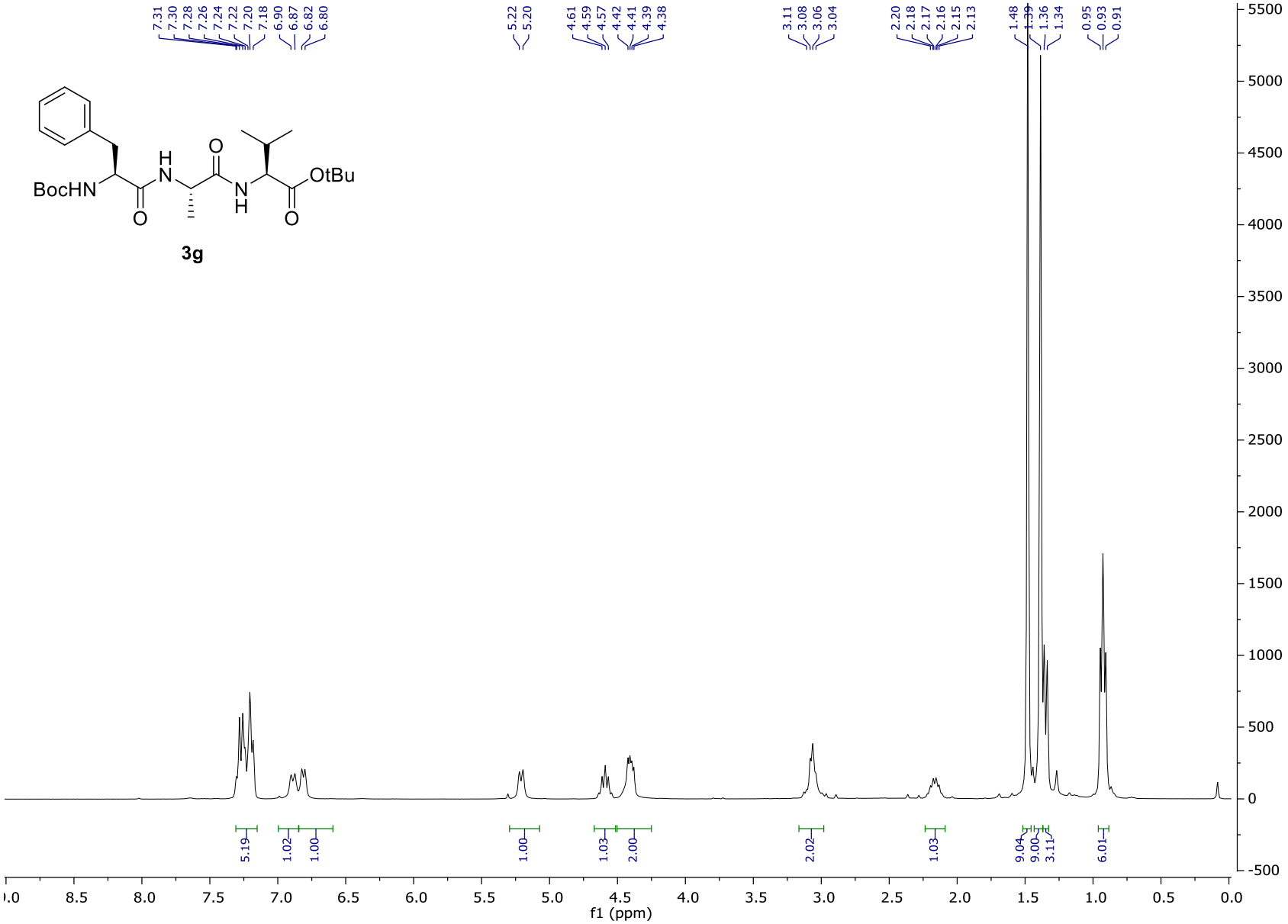
f1 (ppm)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H
O
OtBu
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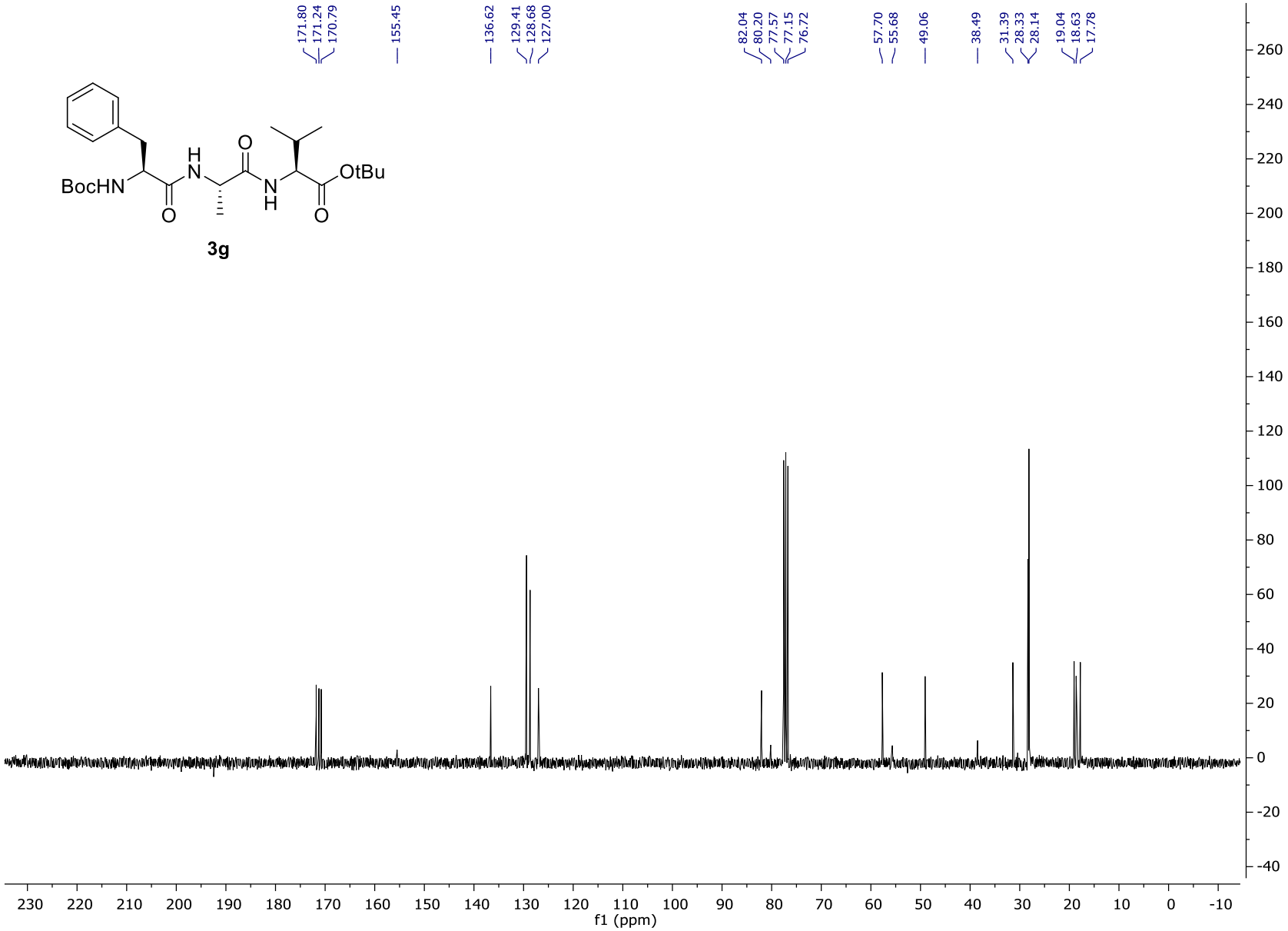
f1 (ppm)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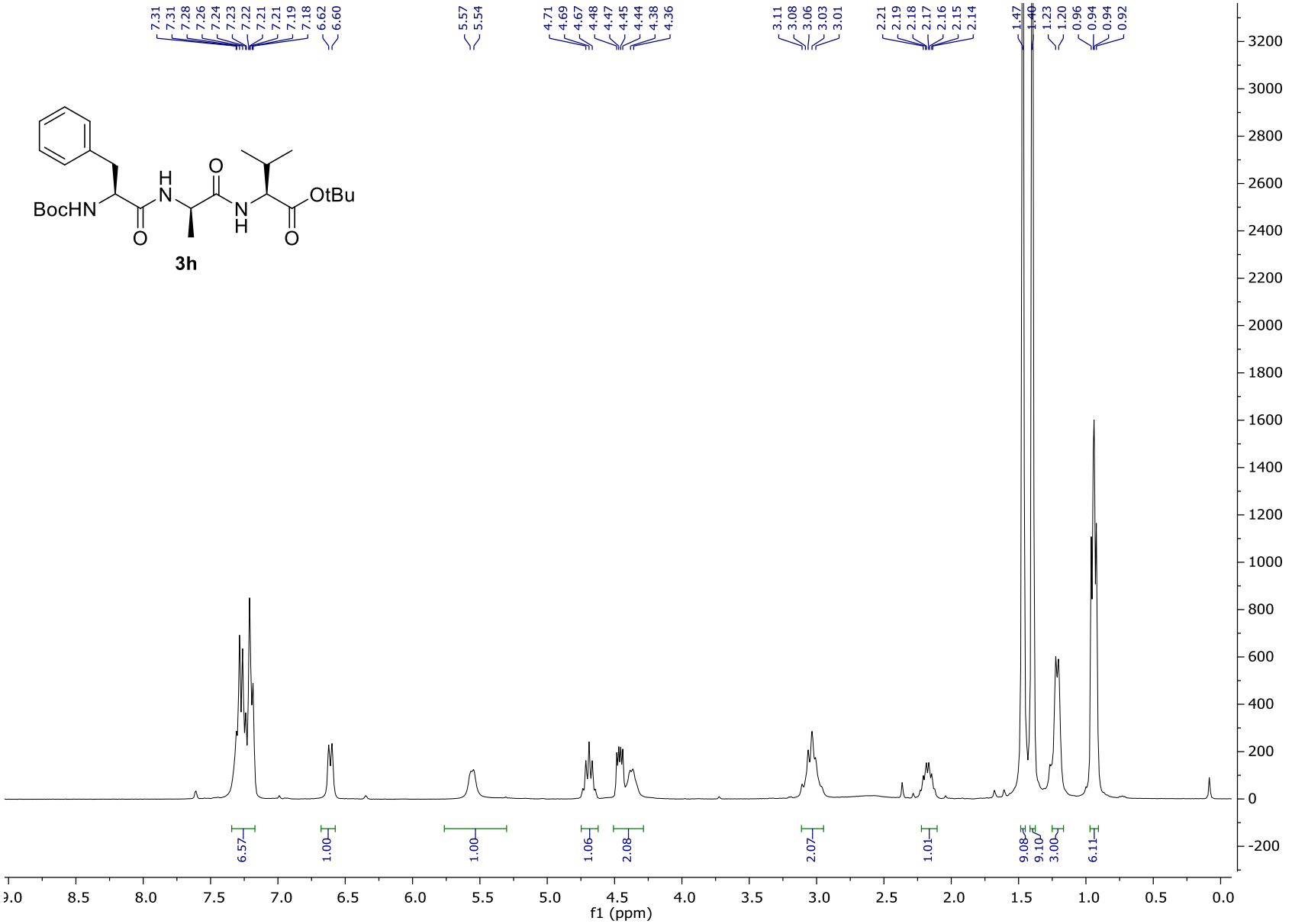
f1 (ppm)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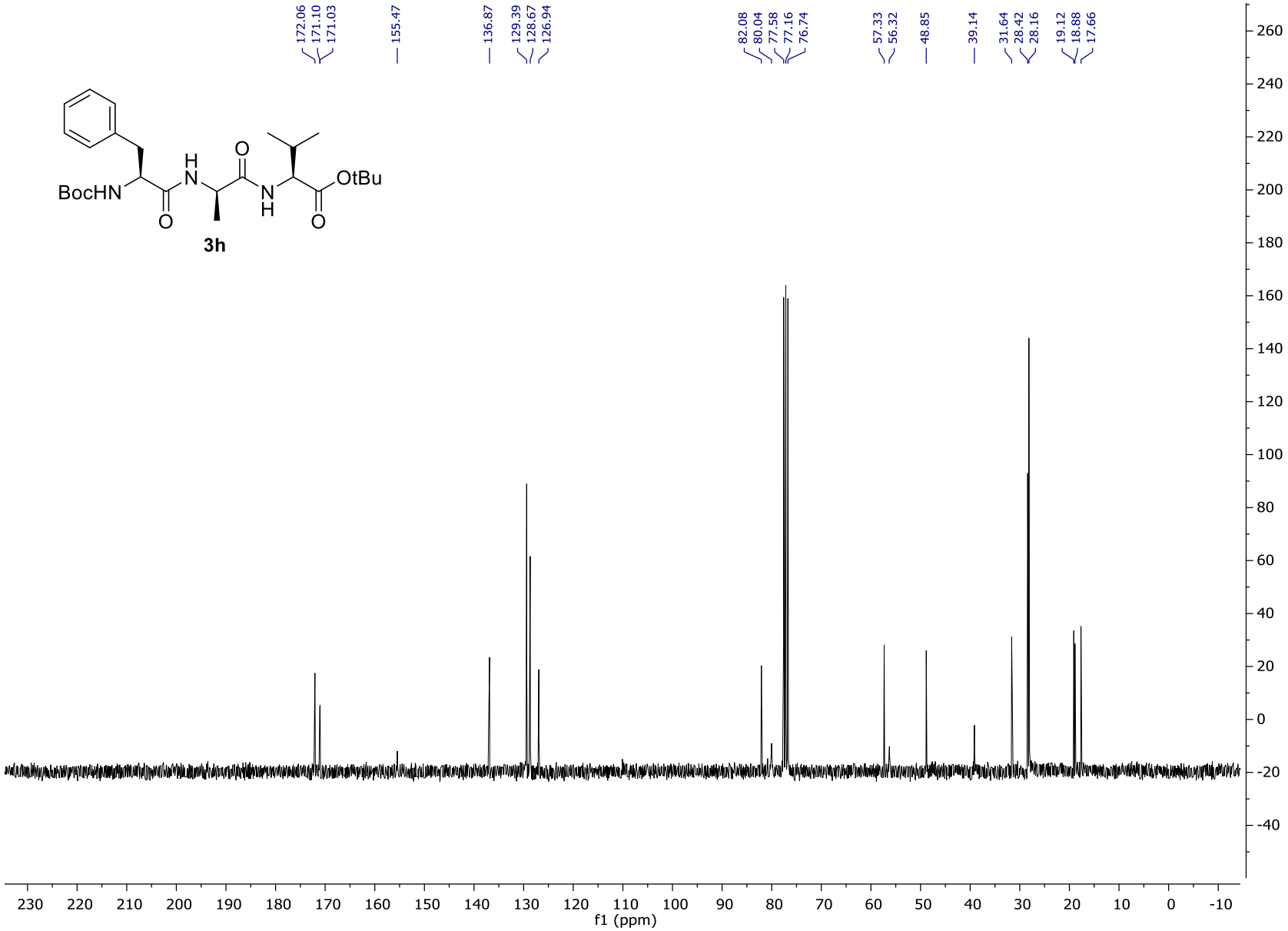
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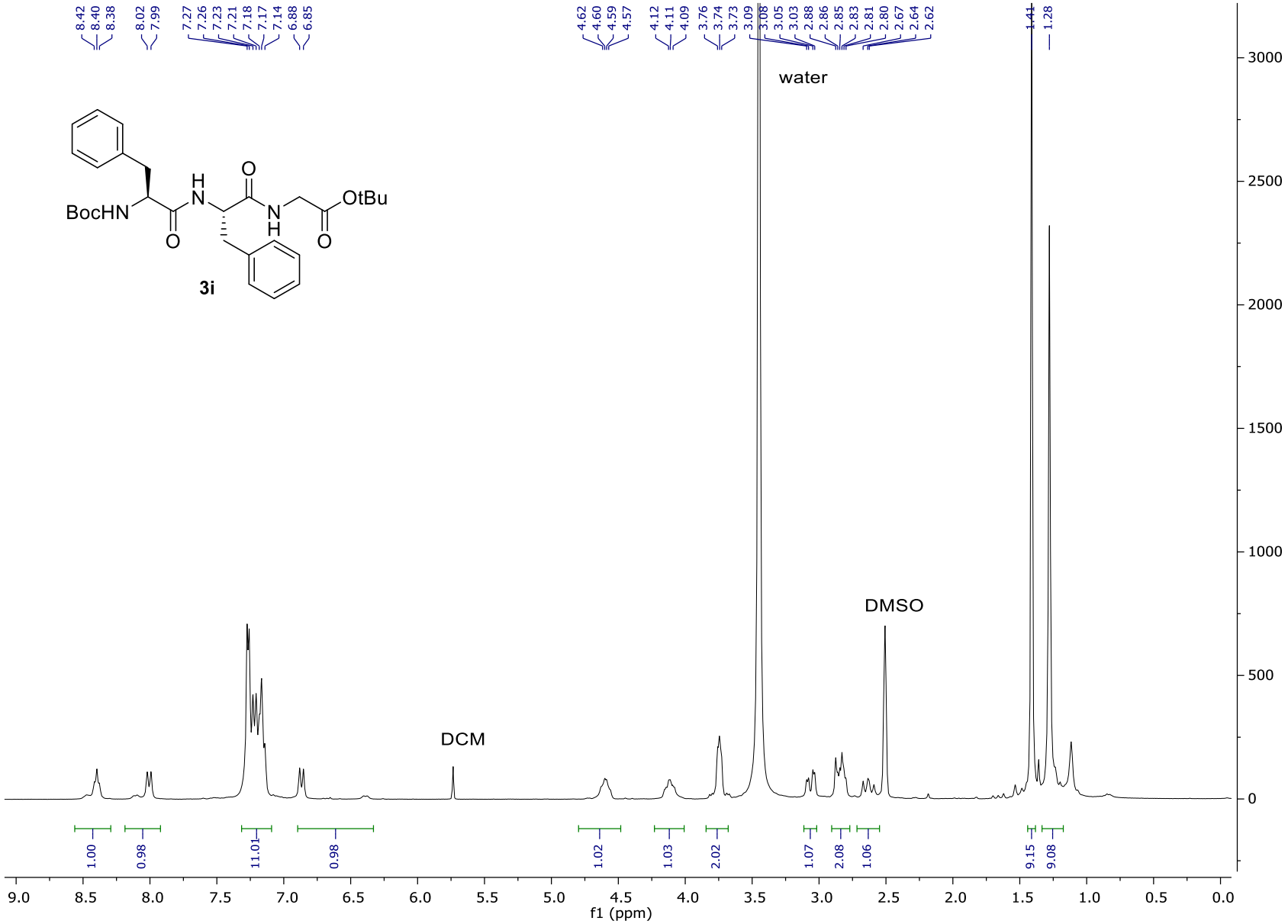
3h
f1 (ppm)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water
DMSO
DCM
BocHN
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3i
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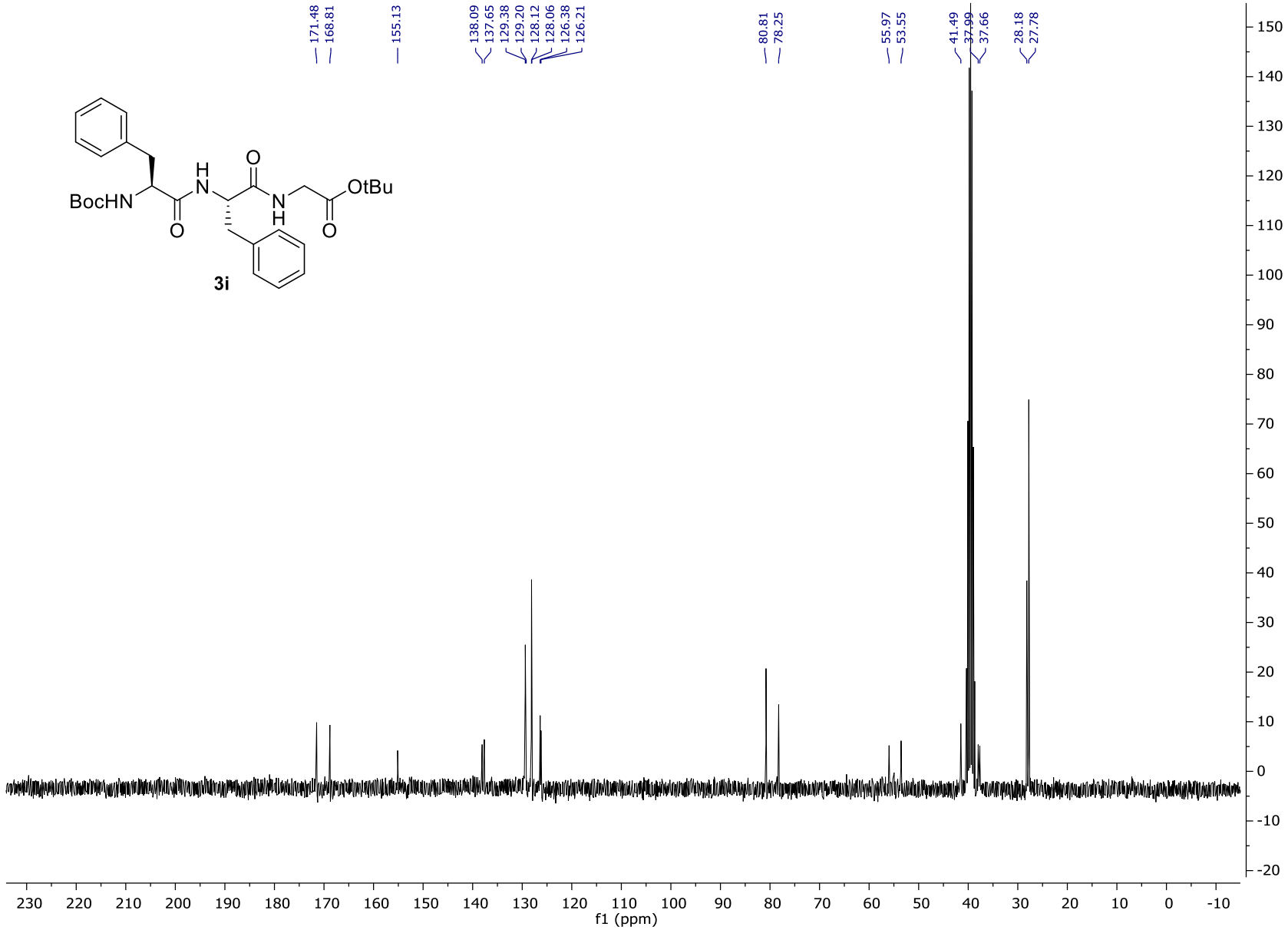
9.08
f1 (ppm)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27.78
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N
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O
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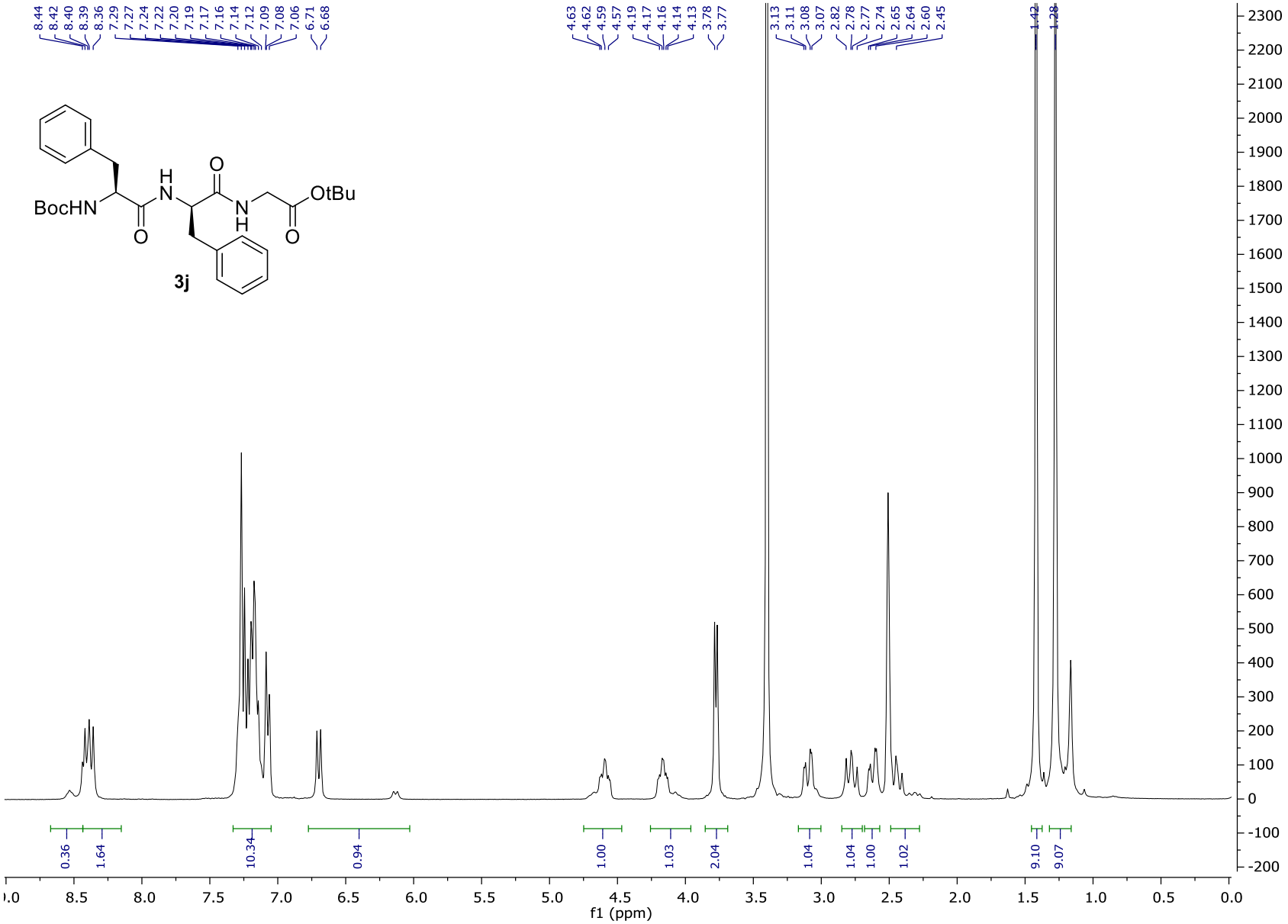
3i
f1 (ppm)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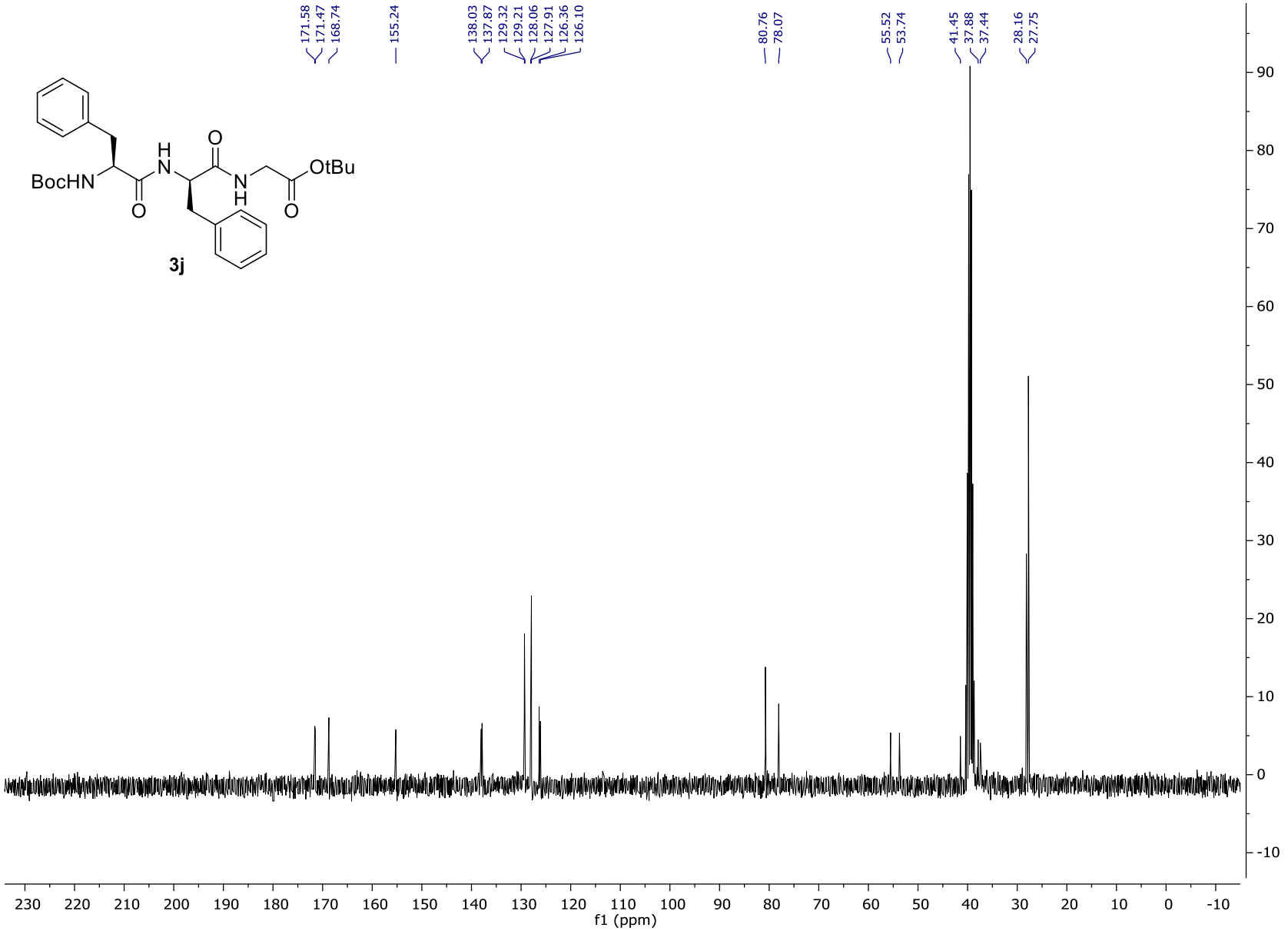
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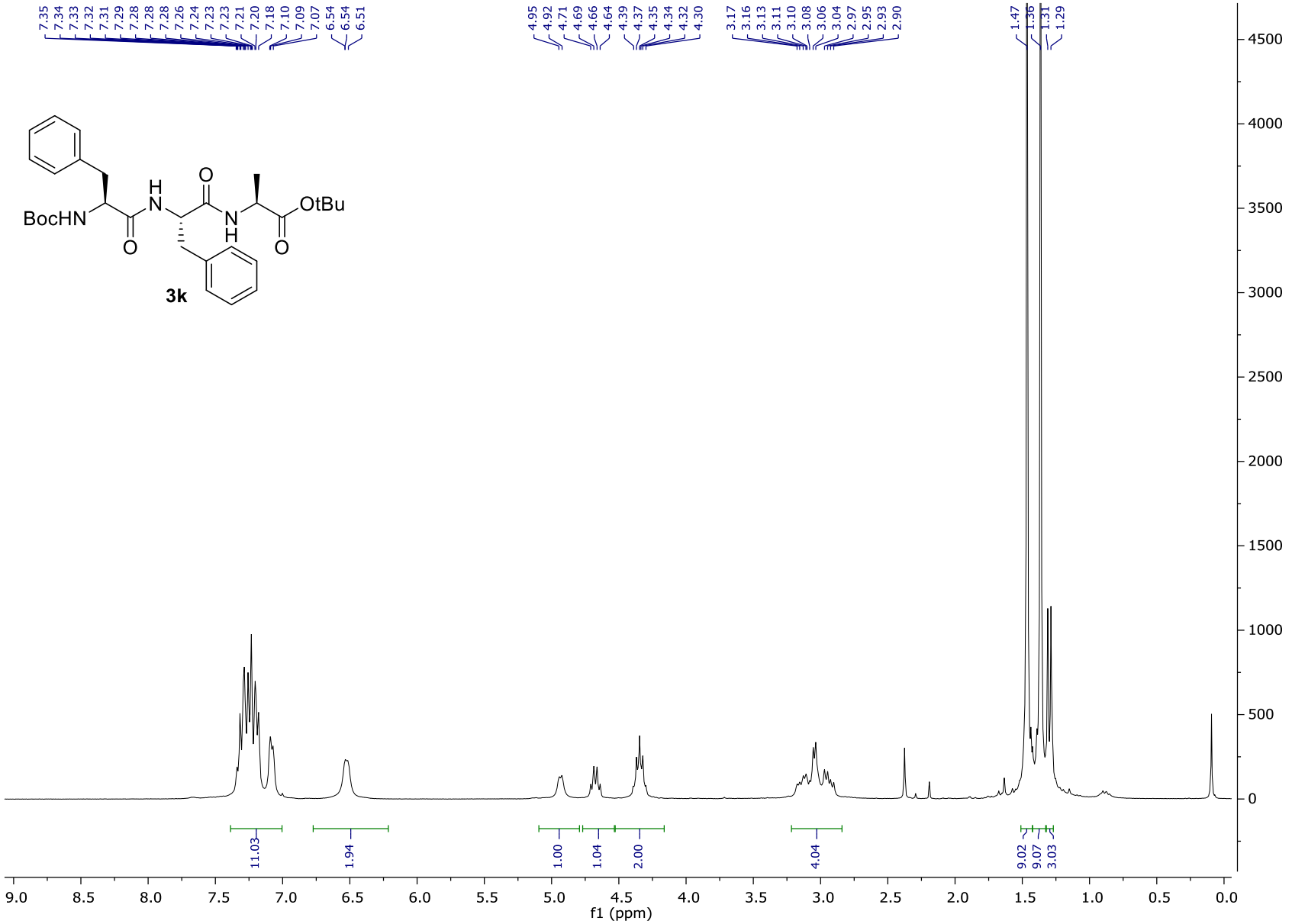
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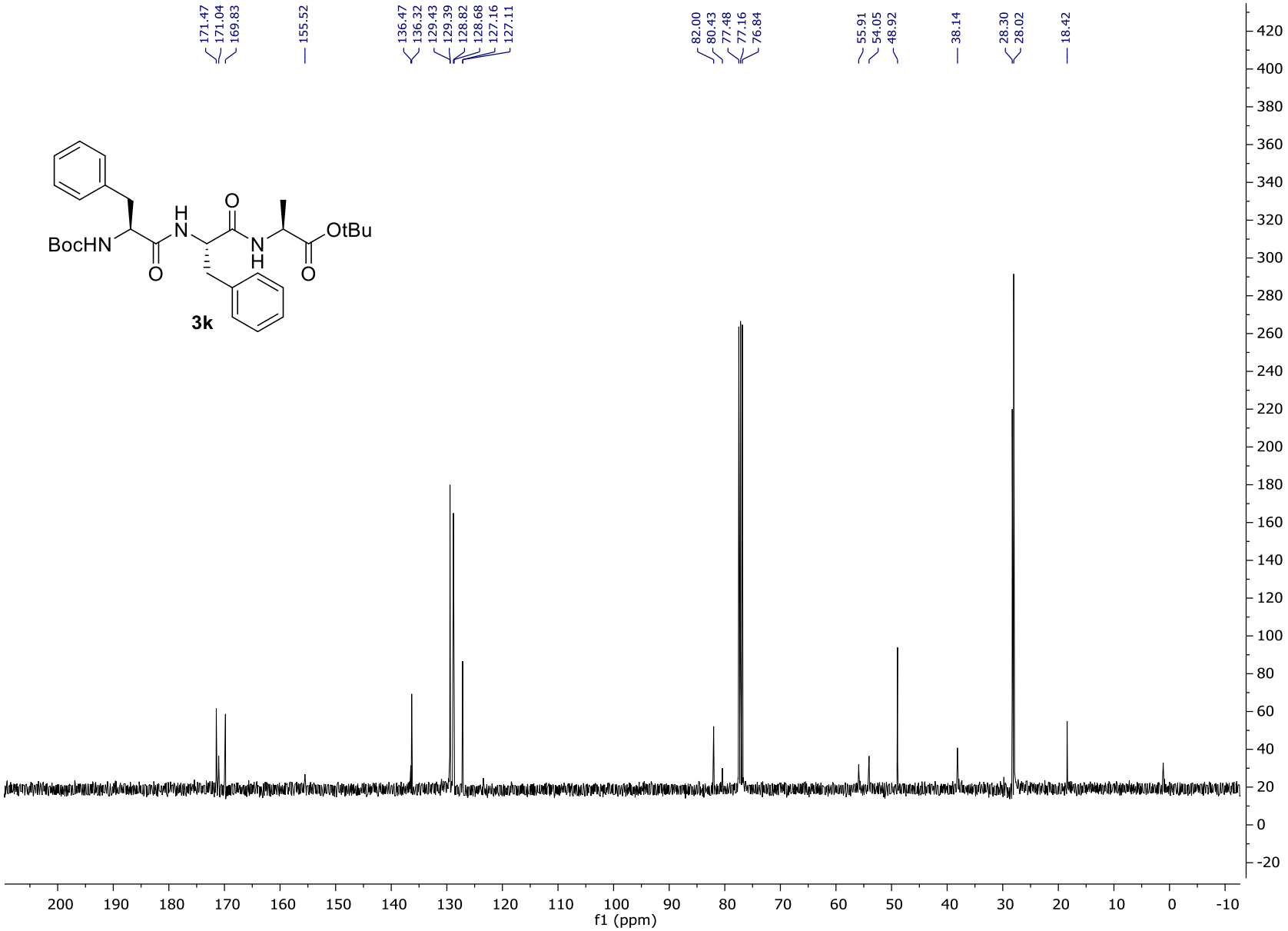
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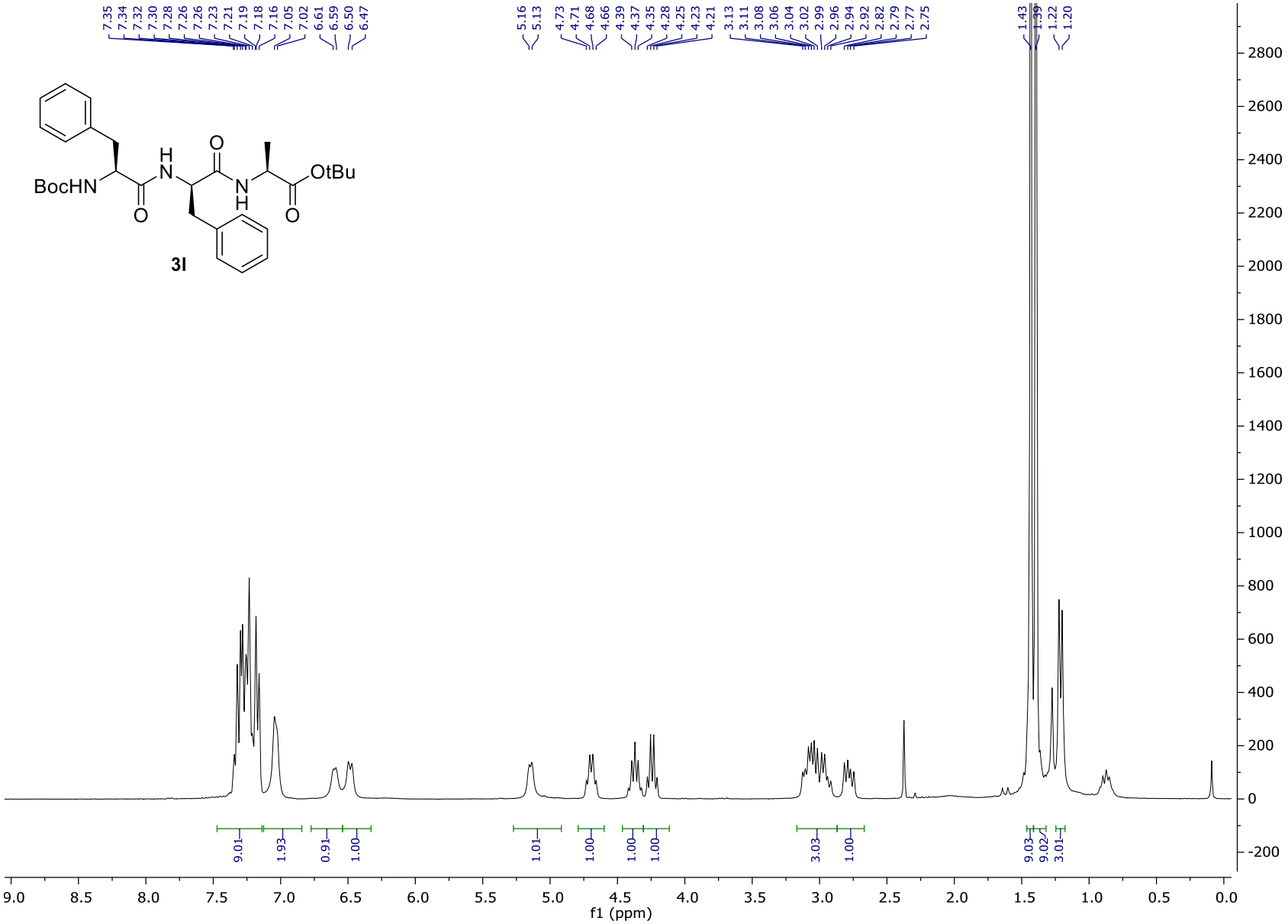
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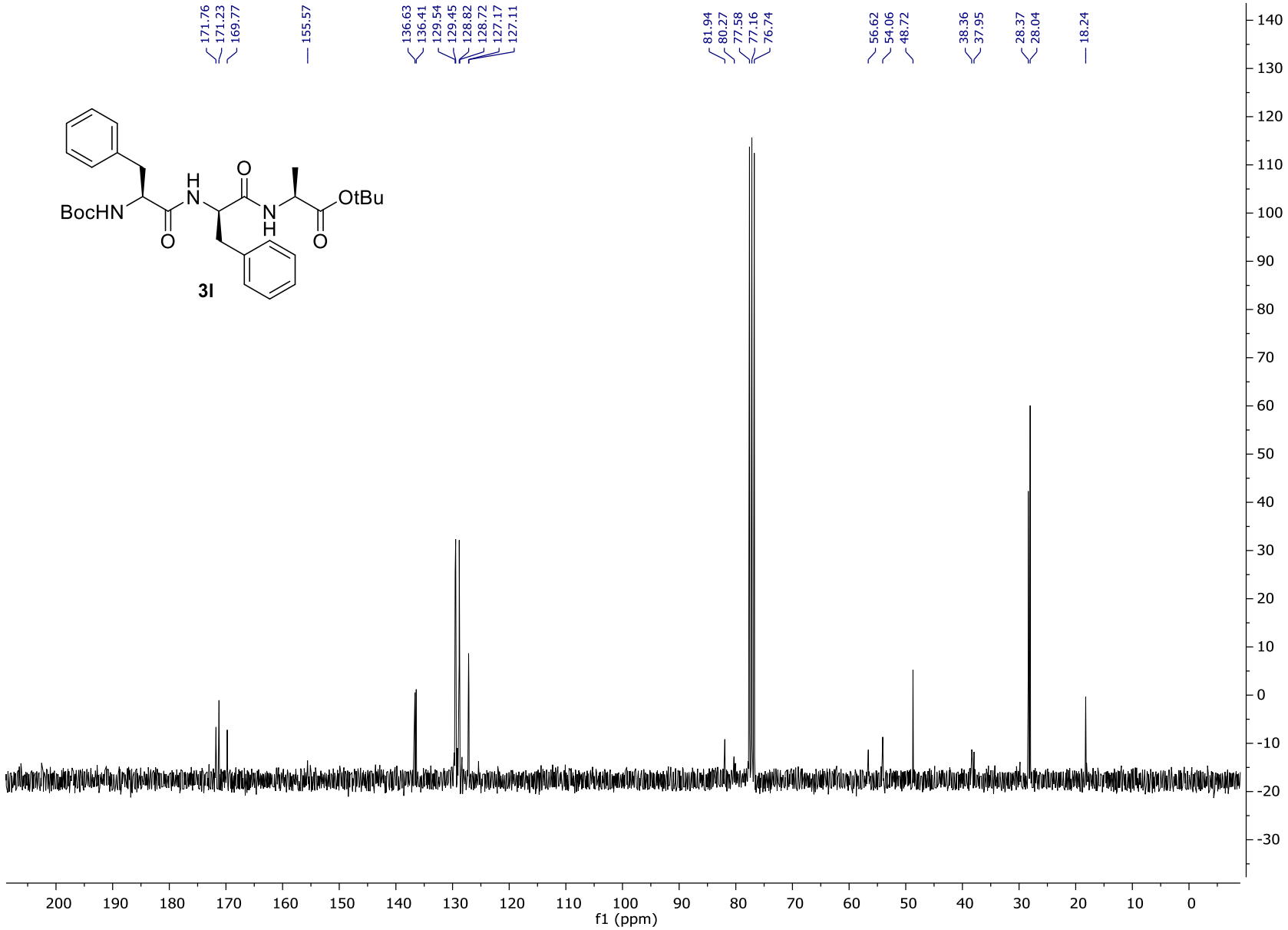
f1 (ppm)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OtBu
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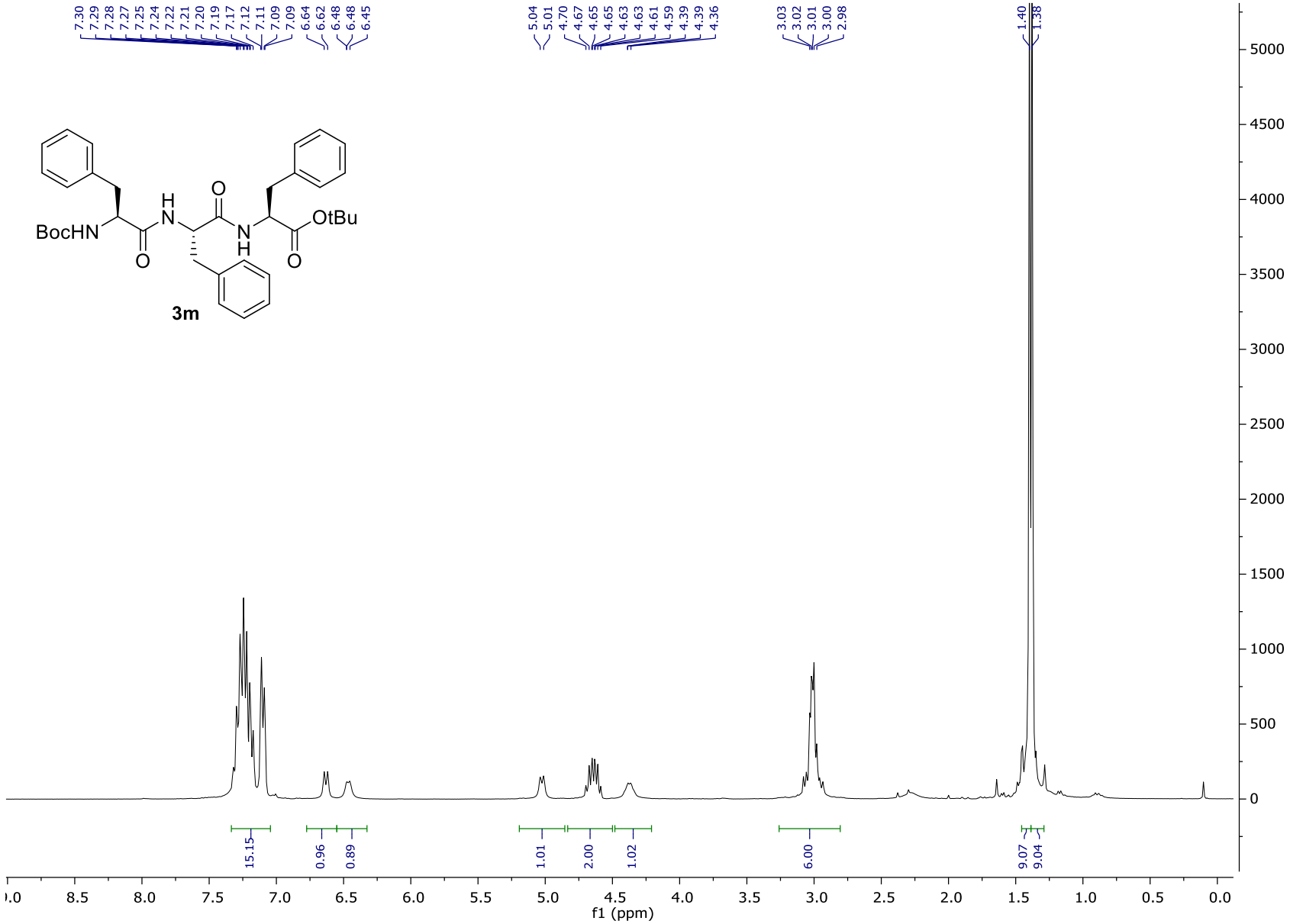
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H
O
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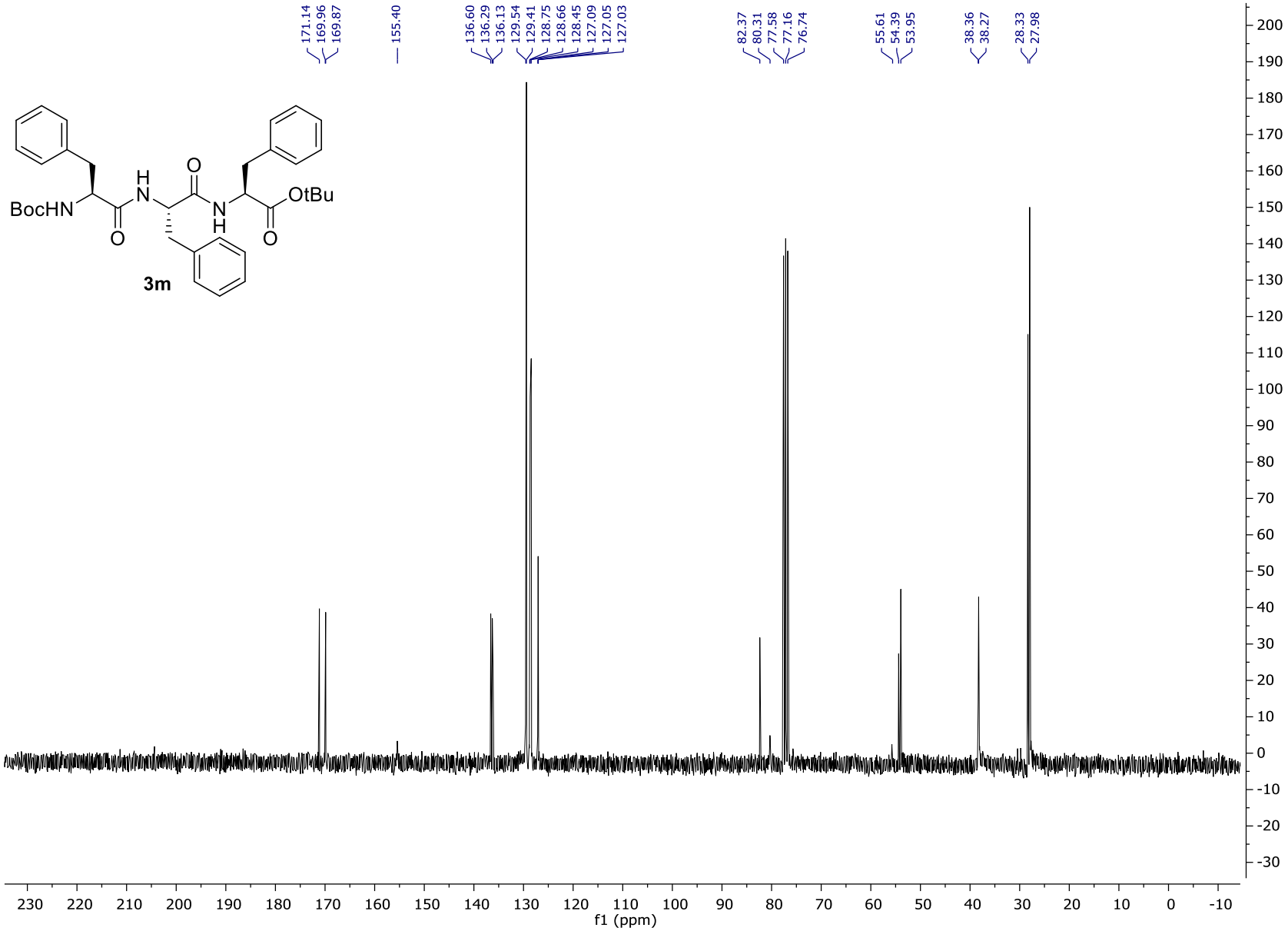
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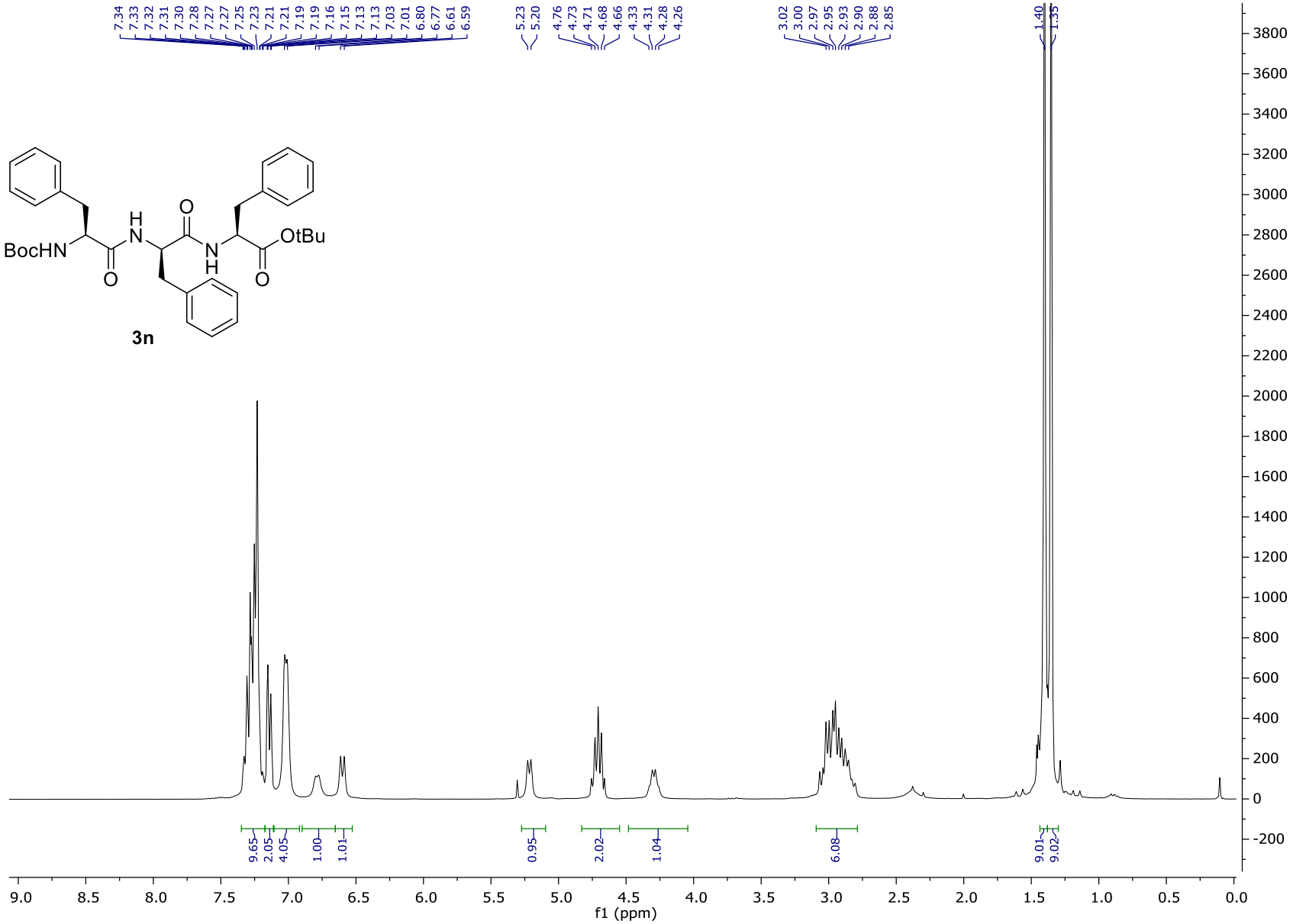
f1 (ppm)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N
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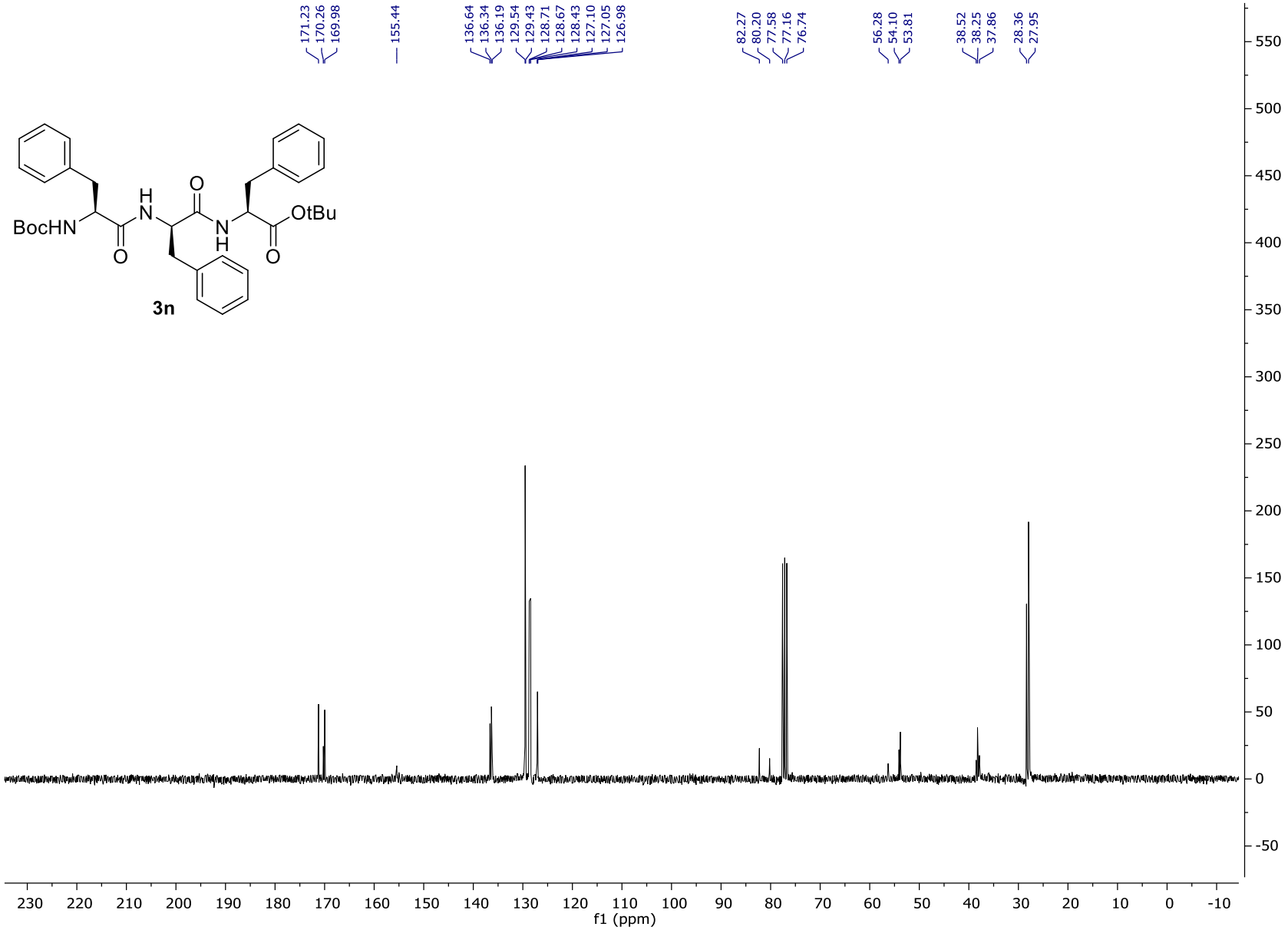
9.02
f1 (ppm)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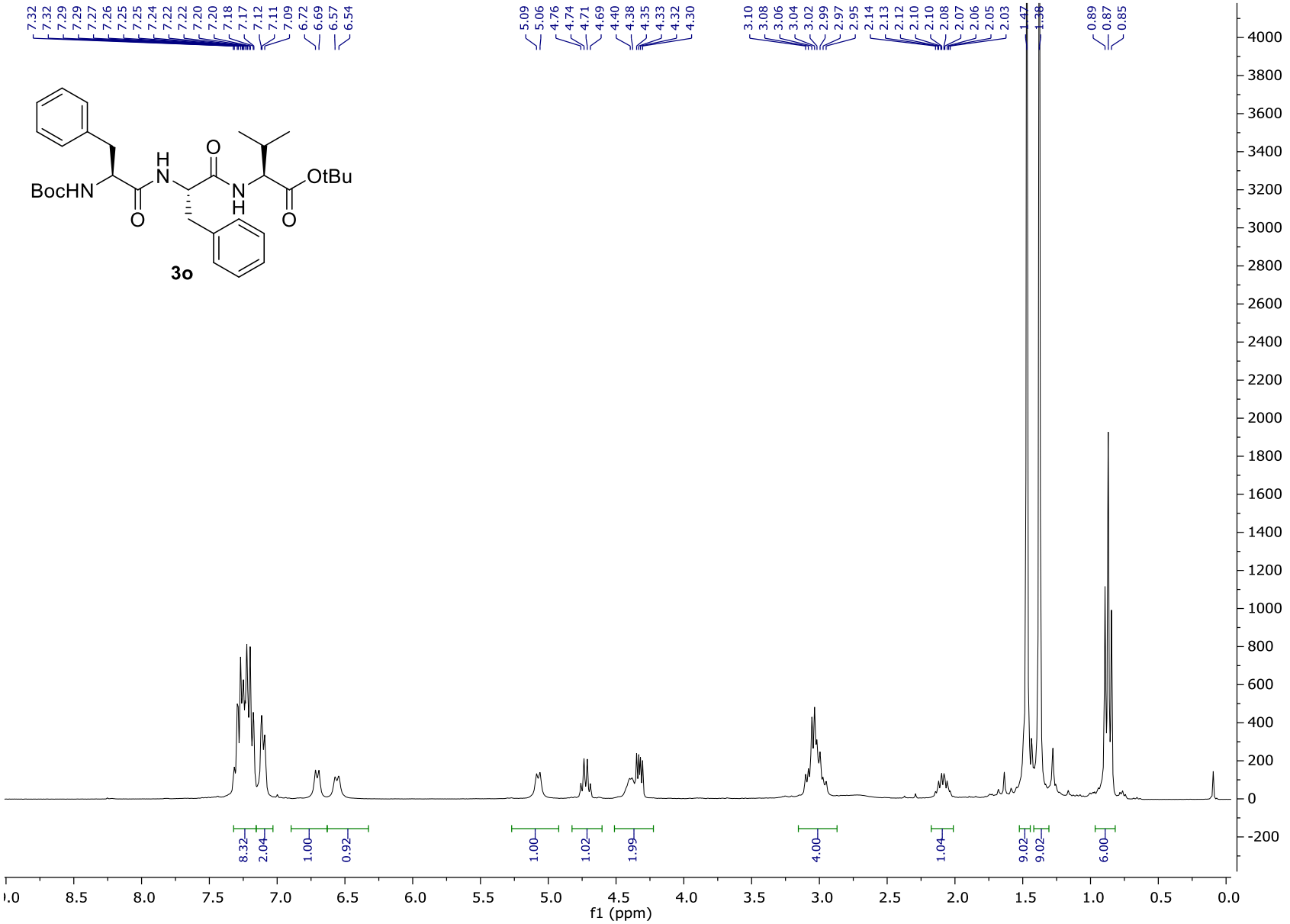
f1 (ppm)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H
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OtBu
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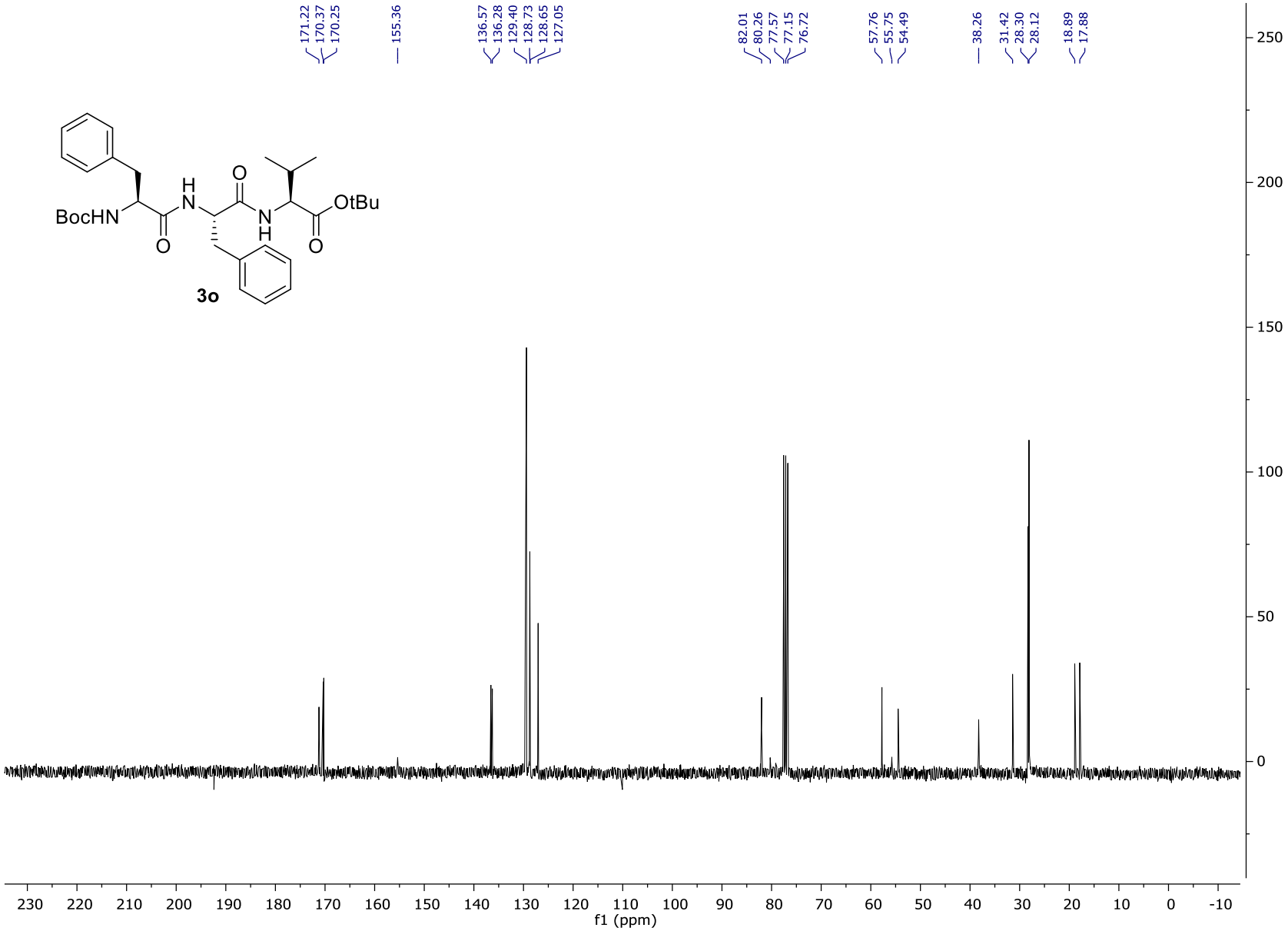
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H
O
OtBu
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100
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0
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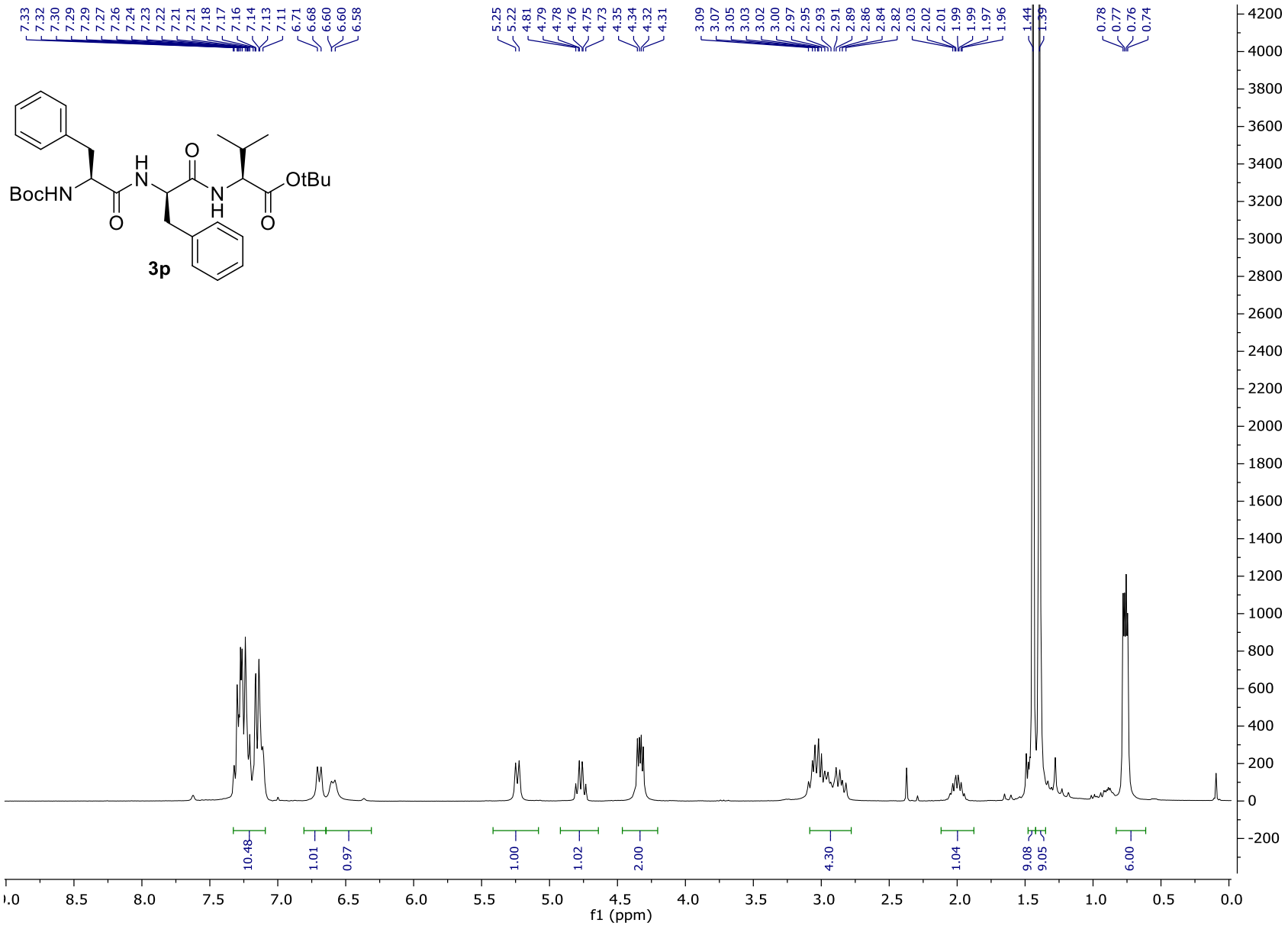
f1 (ppm)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3p
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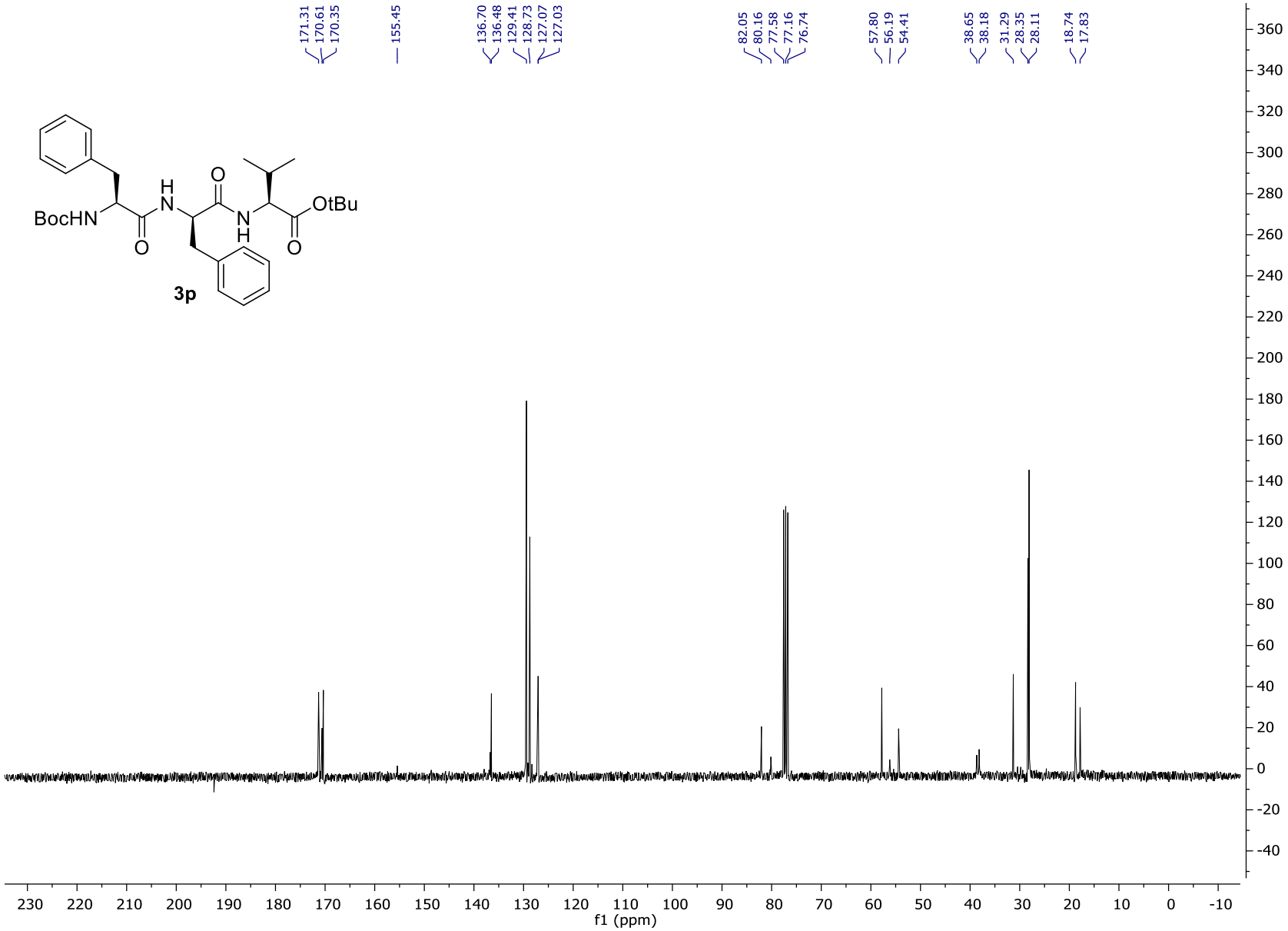
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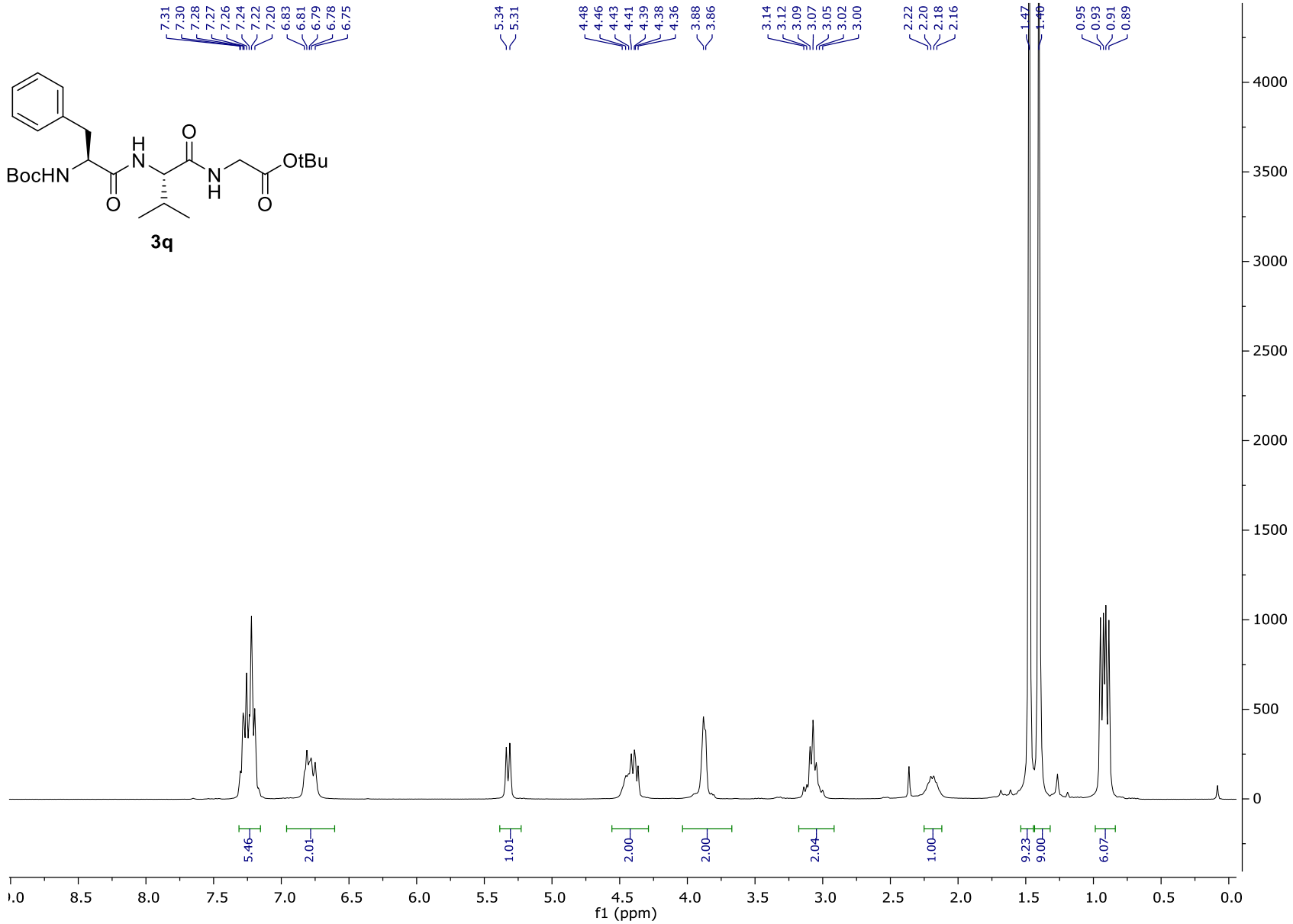
f1 (ppm)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0.91
0.89
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O
N
H
O
OtBu
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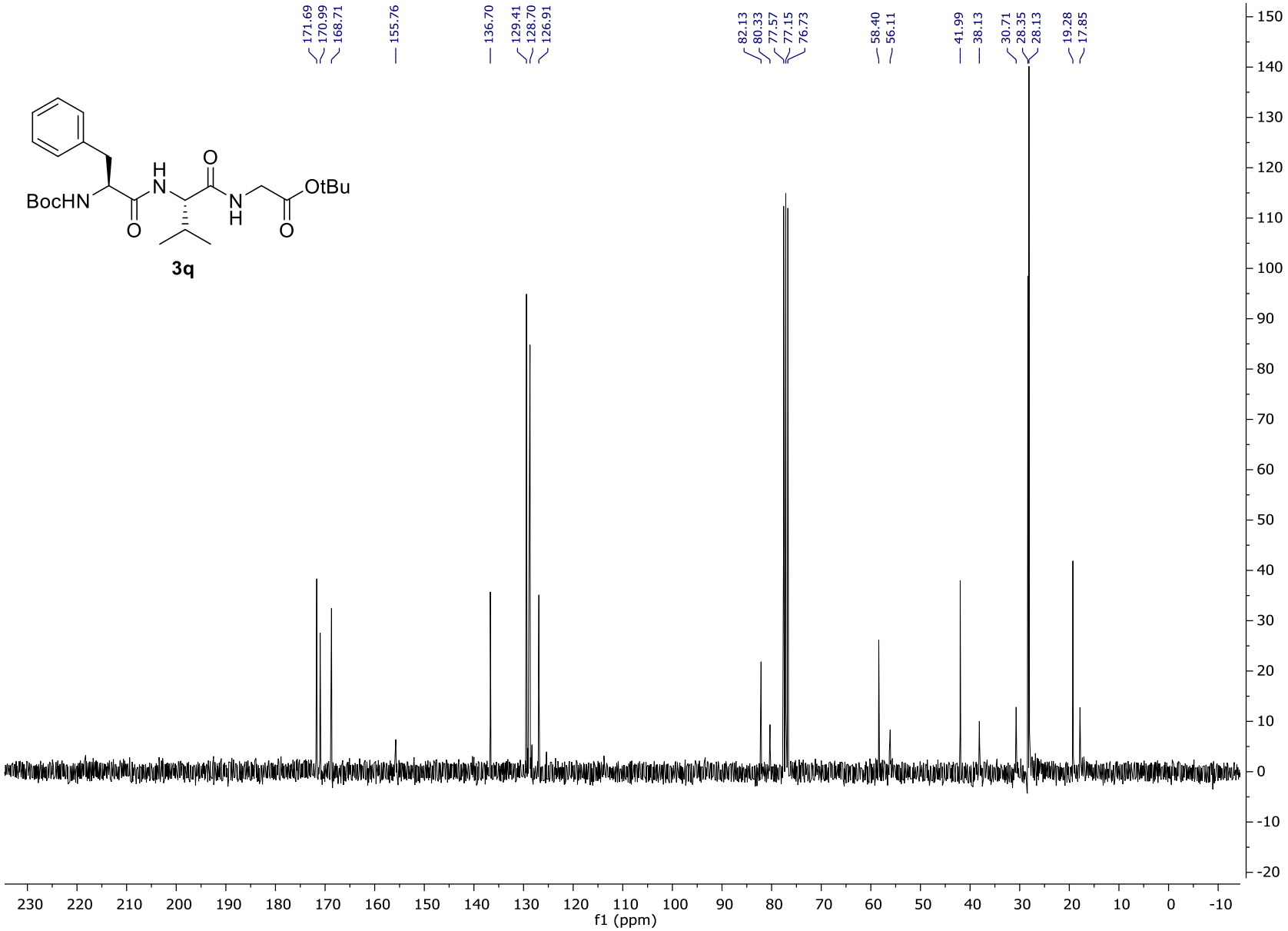
6.07
f1 (ppm)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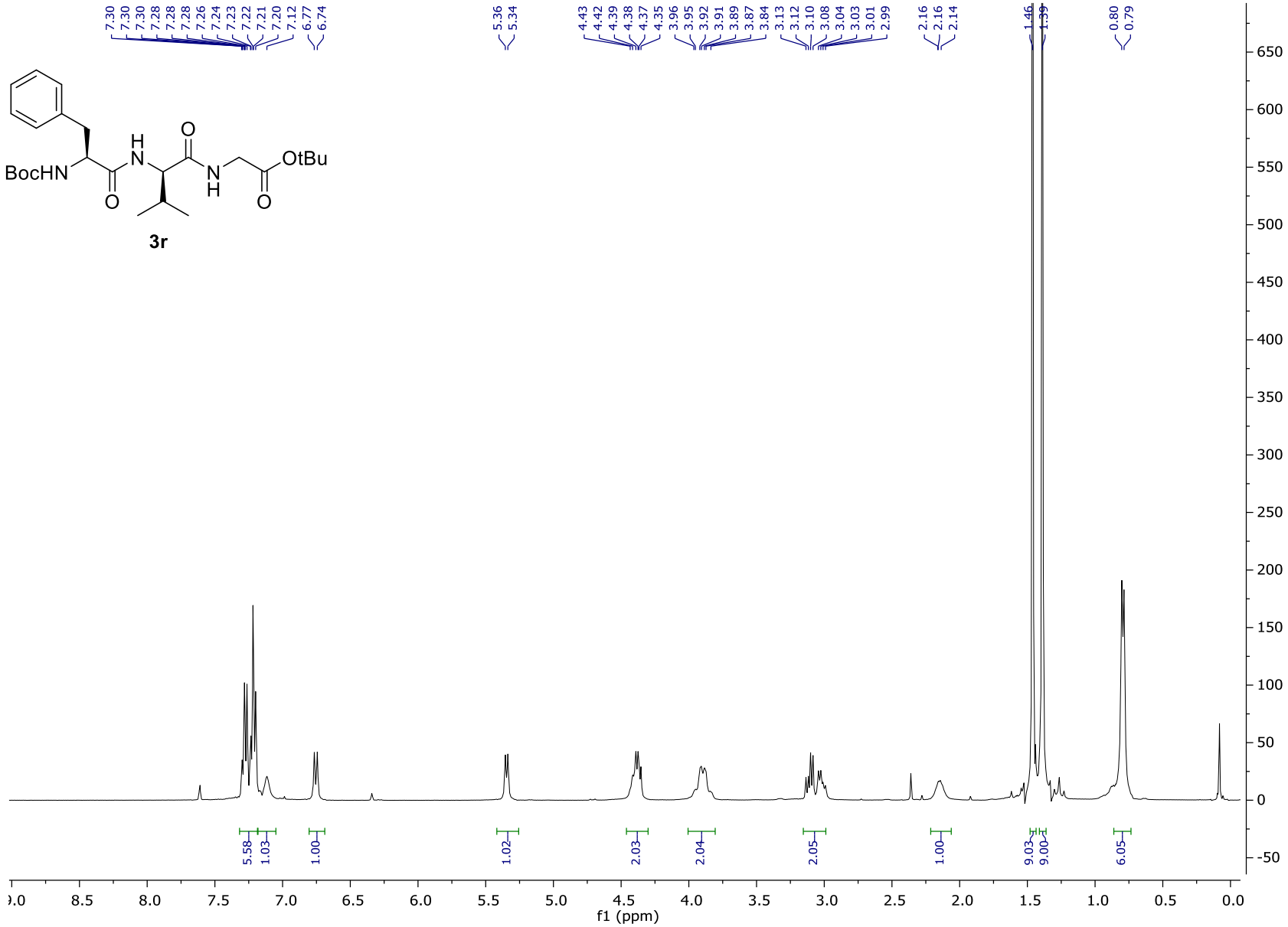
3q
f1 (ppm)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OtBu
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50
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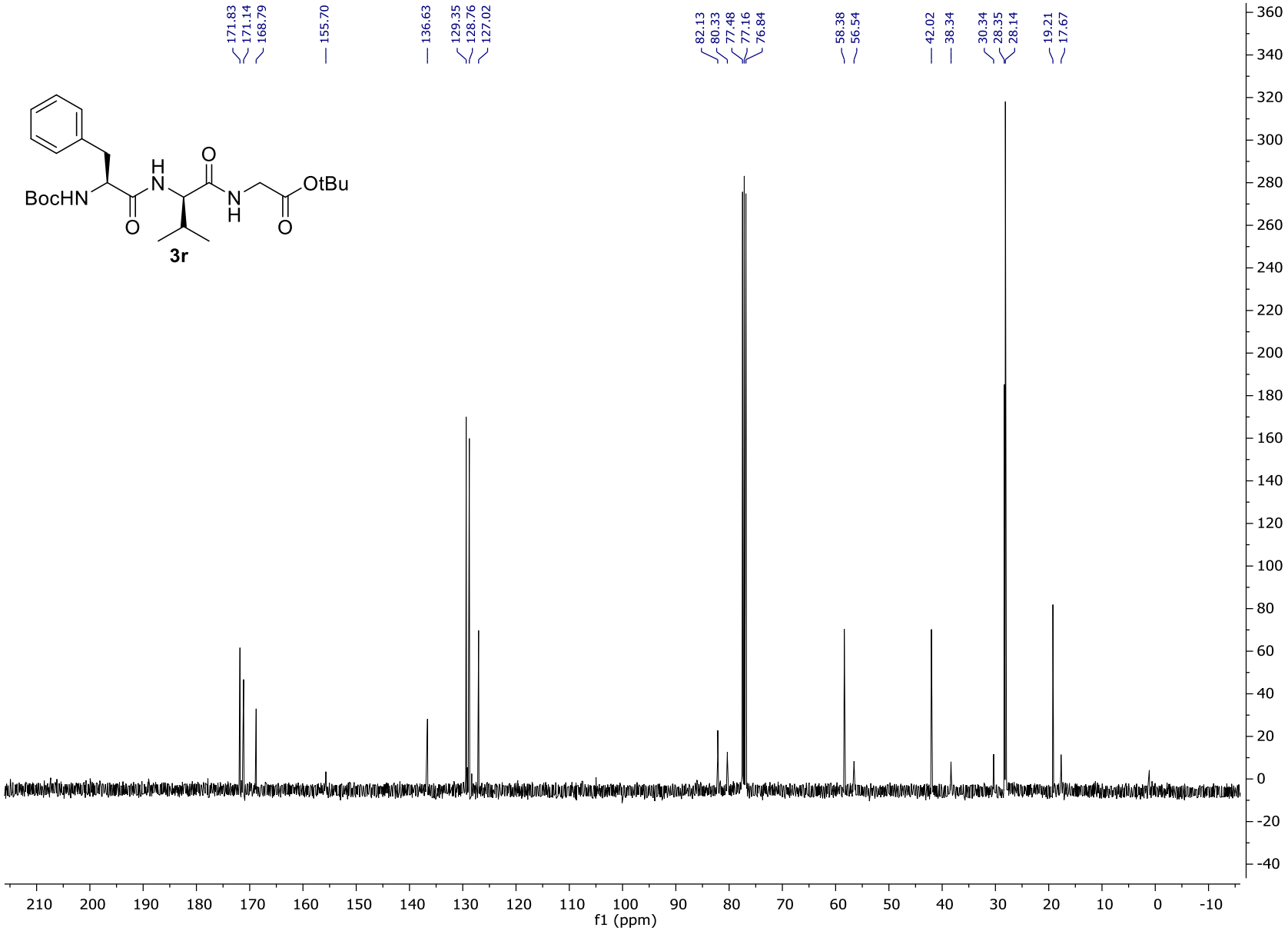
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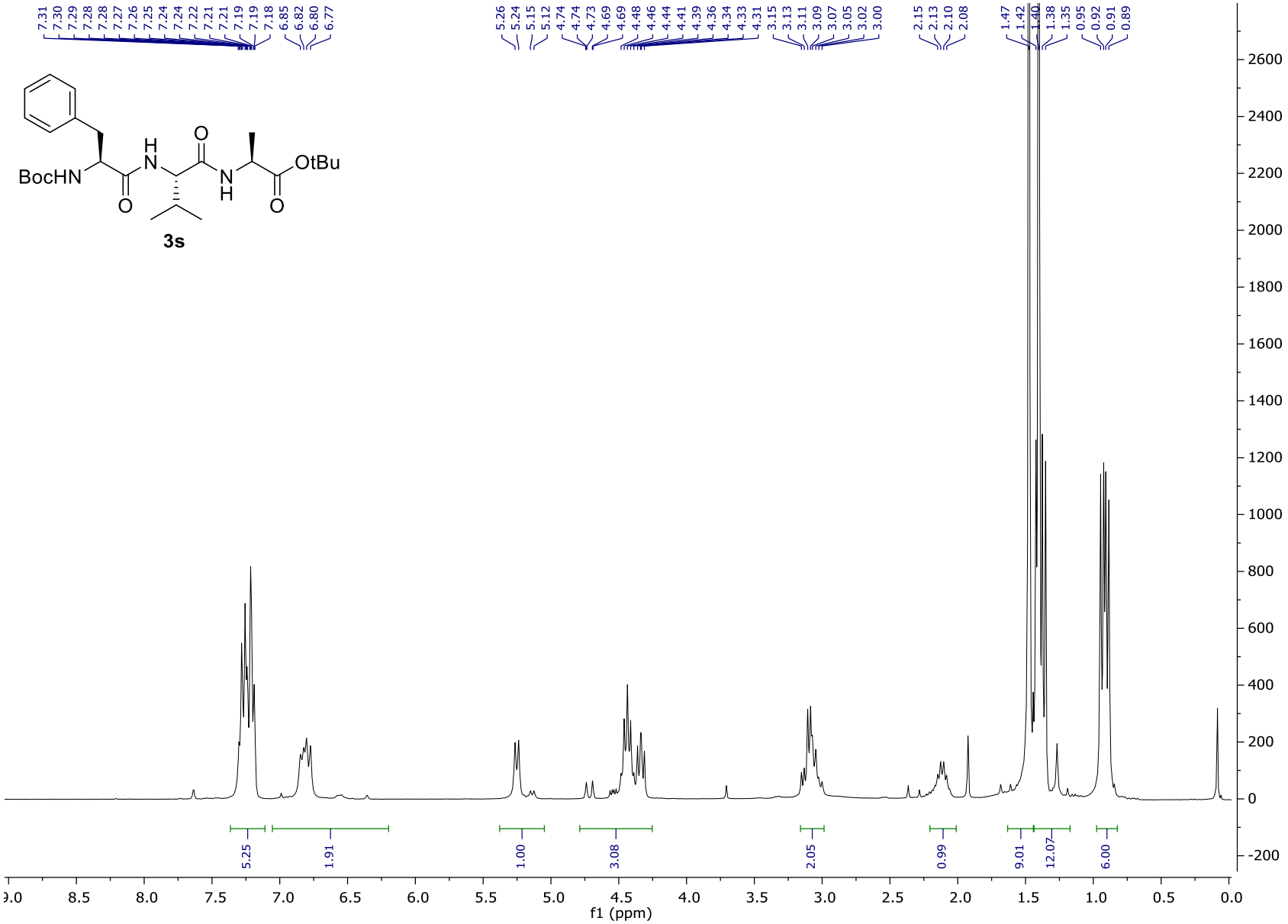
3r
f1 (ppm)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2.15 2.13 2.10 2.08
1.47 1.42 1.40 1.38 1.35 0.95 0.92 0.91 0.89
BocHN
H
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OtBu
3s
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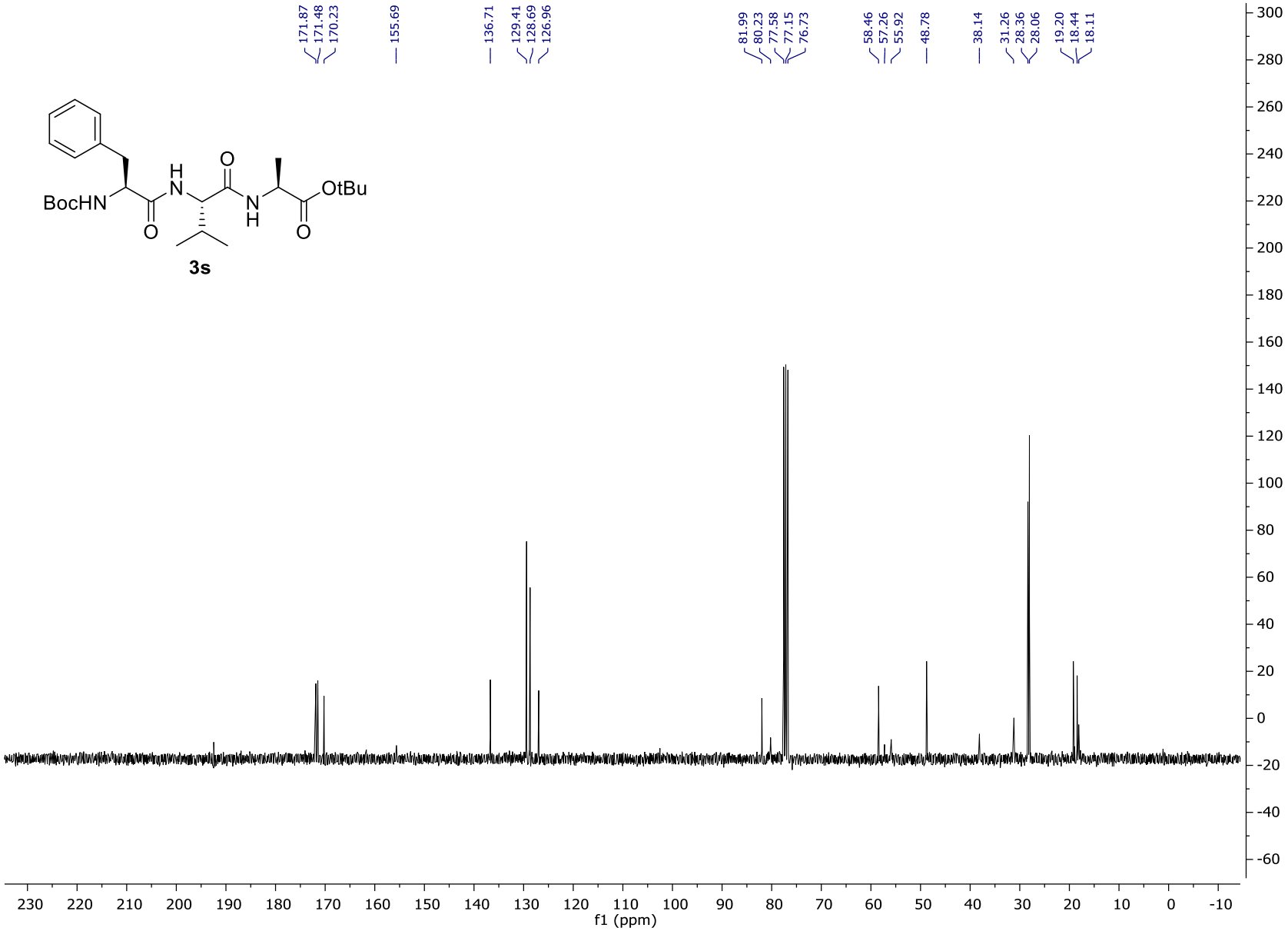
f1 (ppm)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57.26
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31.26
28.36
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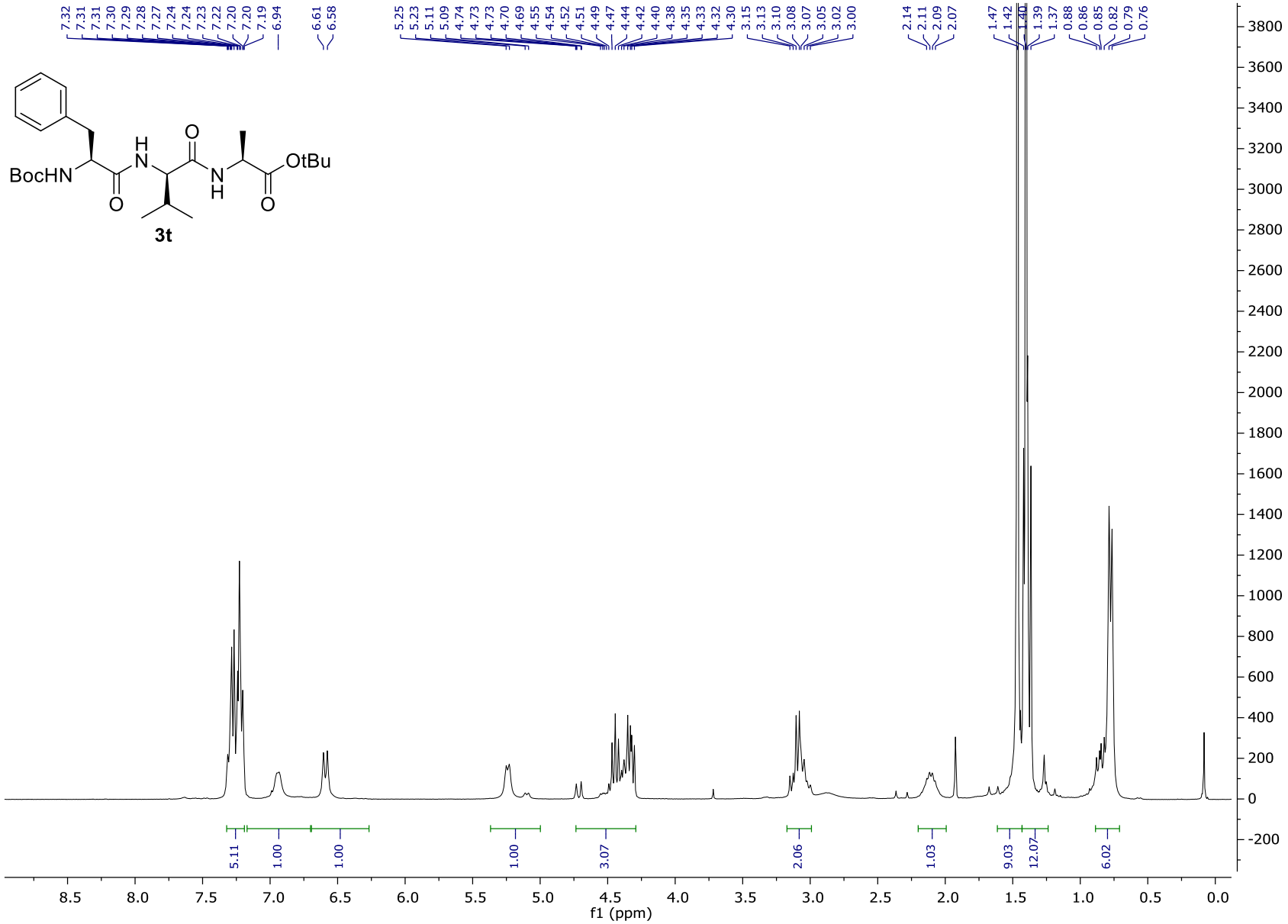
N
H
O
OtBu
3s
f1 (ppm)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H
O
OtBu
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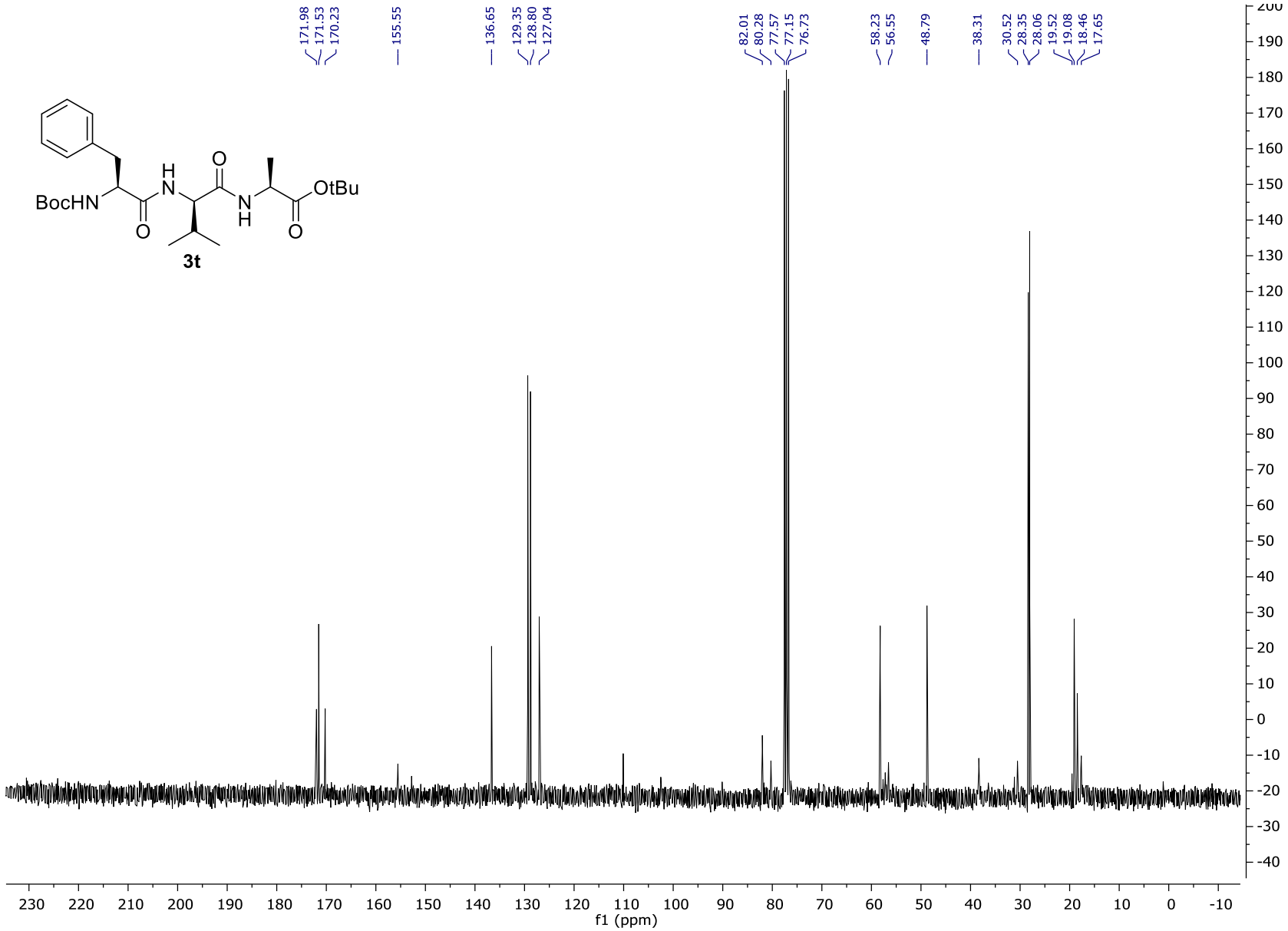
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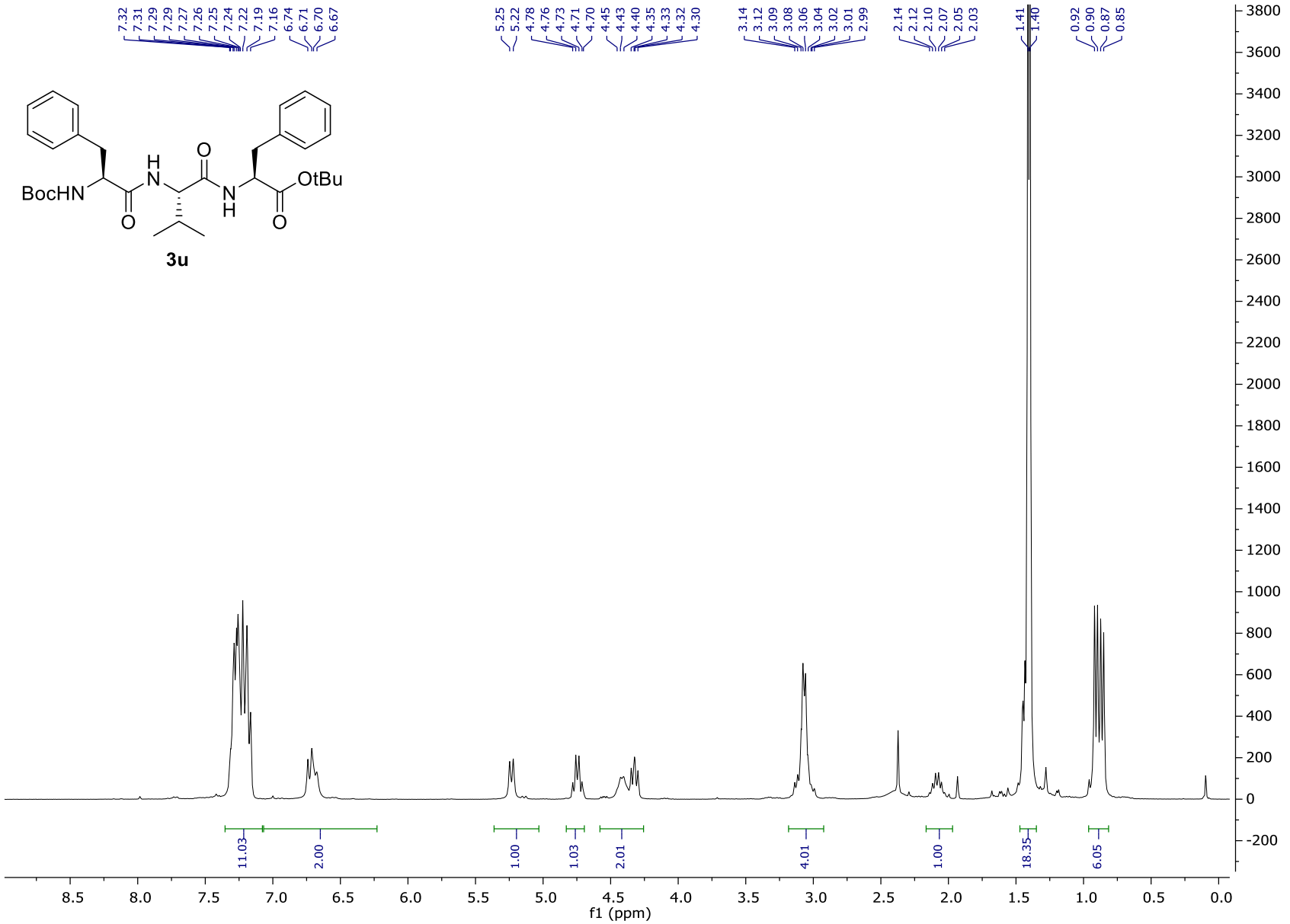
3t
f1 (ppm)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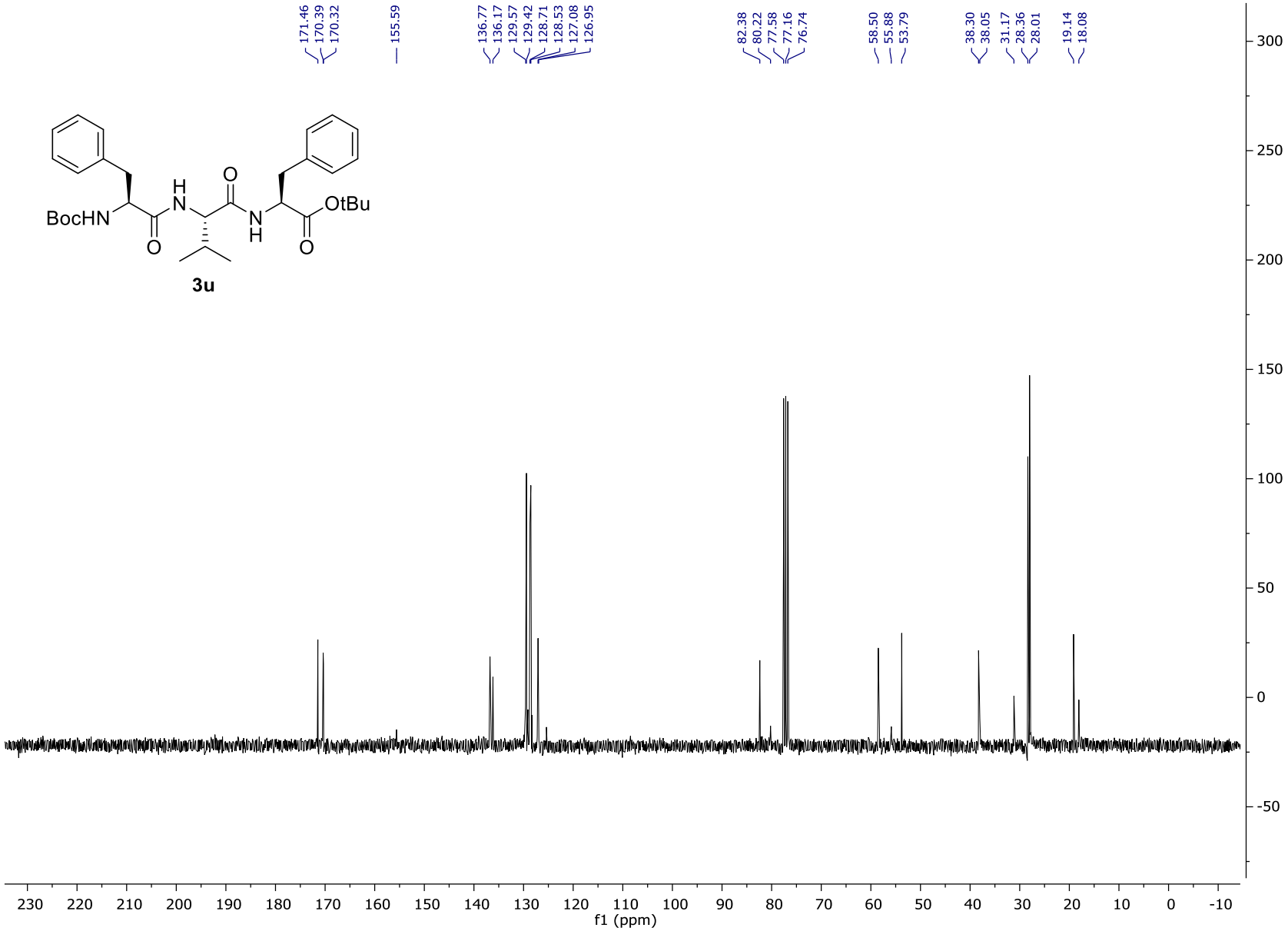
6.70
6.67
5.25
5.22
4.78
4.76
4.73
4.71
4.70
4.45
4.43
4.40
4.35
4.33
4.32
4.30
3.14
3.12
3.09
3.08
3.06
3.04
3.02
3.01
2.99
2.14
2.12
2.10
2.07
2.05
2.03
1.41
1.40
0.92
0.90
0.87
0.85
BocHN
O
H
N
O
N
H
O
OtBu
O
3u
11.03
2.00
1.00
1.03
2.01
4.01
1.00
18.35
6.05
f1 (ppm)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129.42
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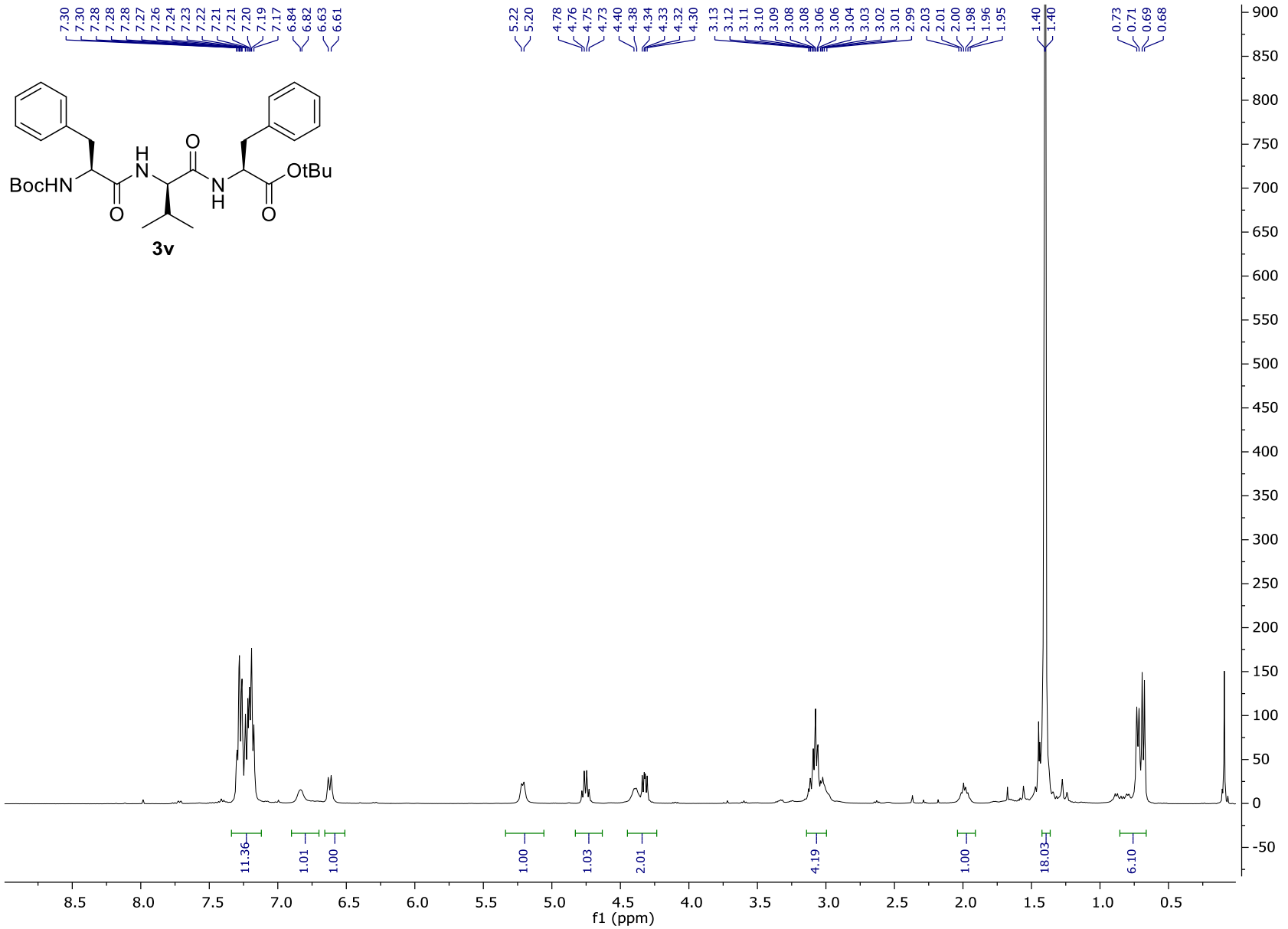
127.08
126.95
82.38
80.22
77.58
77.16
76.74
58.50
55.88
53.79
38.30
38.05
31.17
28.36
28.01
19.14
18.08
BocHN
H
N
O
O
N
H
O
OtBu
O
3u
300
250
200
150
100
50
0
-50
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.24
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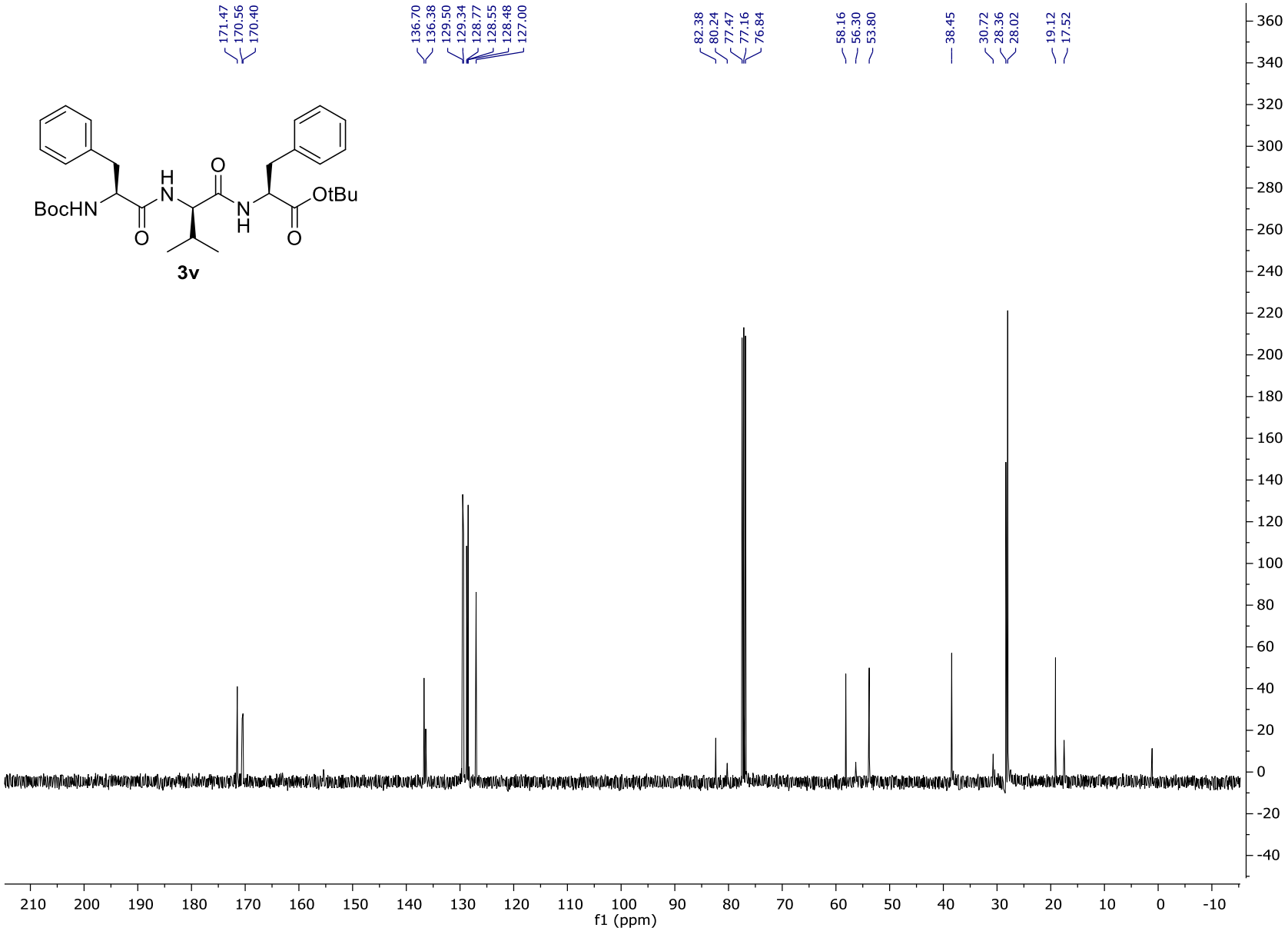
7.20
7.19
7.17
6.84
6.82
6.63
6.61
5.22
5.20
4.78
4.76
4.75
4.73
4.40
4.38
4.34
4.33
4.32
4.30
3.13
3.12
3.11
3.10
3.09
3.08
3.08
3.06
3.06
3.04
3.03
3.02
3.01
2.99
2.03
2.01
2.00
1.98
1.96
1.95
1.40
1.40
0.73
0.71
0.69
0.68
BocHN
H
N
O
O
N
H
O
OtBu
O
3v
11.36
1.01
1.00
1.00
1.03
2.01
4.19
1.00
18.03
6.10
f1 (ppm)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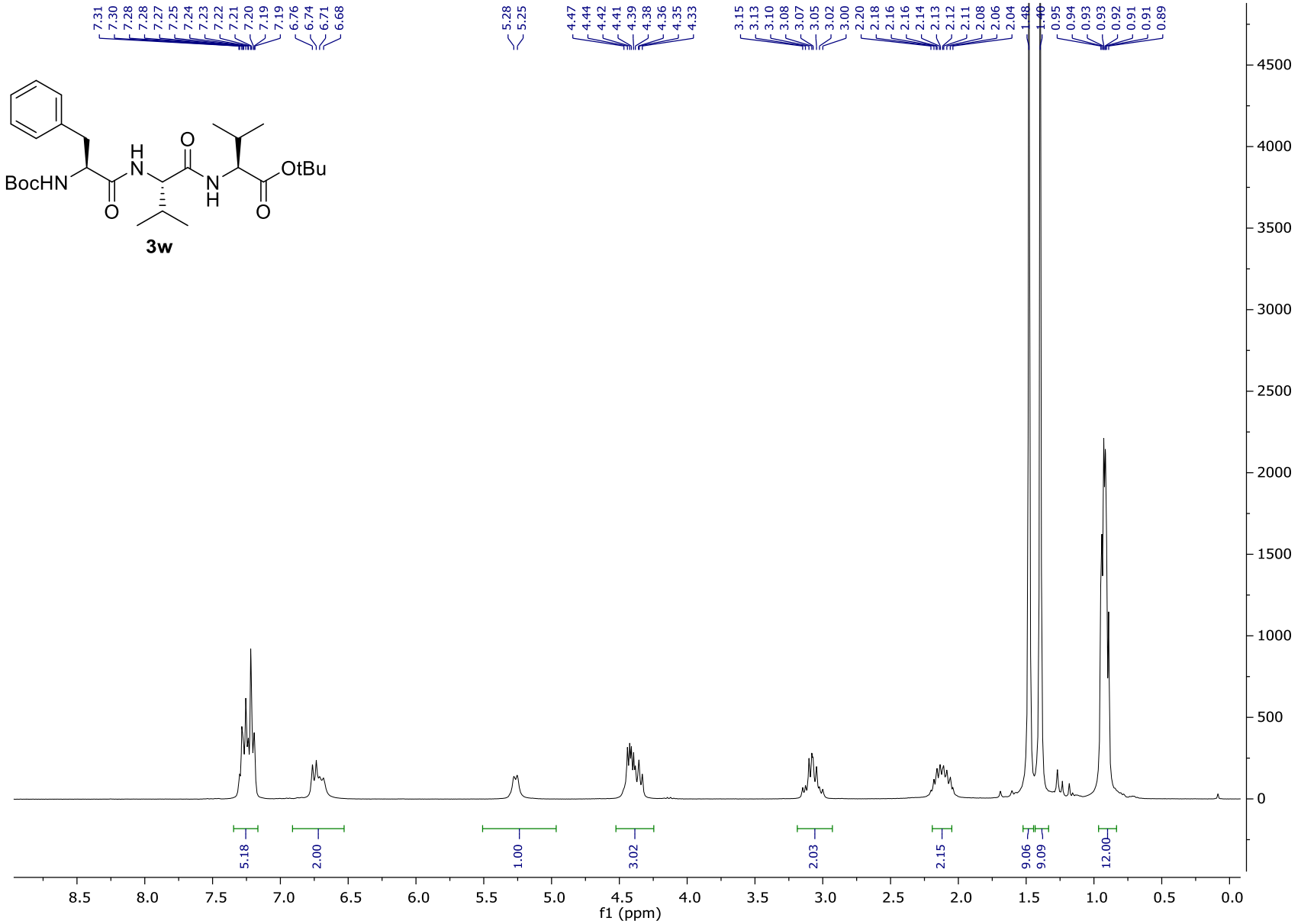
80.24
77.47
77.16
76.84
58.16
56.30
53.80
38.45
30.72
28.36
28.02
19.12
17.52
BocHN
H
N
O
O
N
H
O
OtBu
O
3v
f1 (ppm)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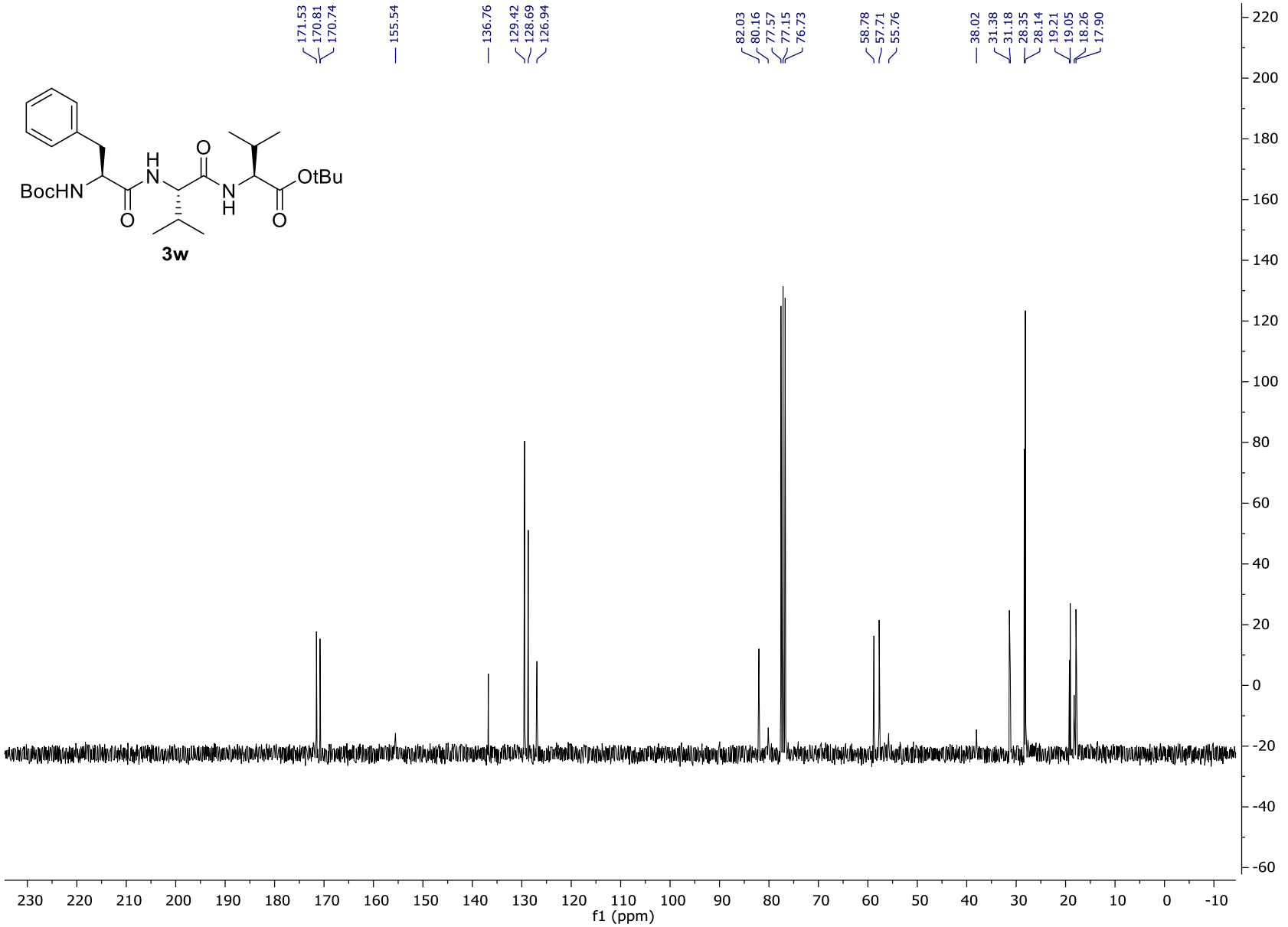
7.19
6.76
6.74
6.71
6.68
5.28
5.25
4.47
4.44
4.42
4.41
4.39
4.38
4.36
4.35
4.33
3.15
3.13
3.10
3.08
3.07
3.05
3.02
3.00
2.20
2.18
2.16
2.16
2.14
2.13
2.12
2.11
2.08
2.06
2.04
1.48
1.40
0.95
0.94
0.93
0.93
0.92
0.91
0.91
0.89
BocHN
O
H
N
O
N
H
O
OtBu
O
3w
4500
4000
3500
3000
2500
2000
1500
1000
500
0
5.18
2.00
1.00
3.02
2.03
2.15
9.06
9.09
12.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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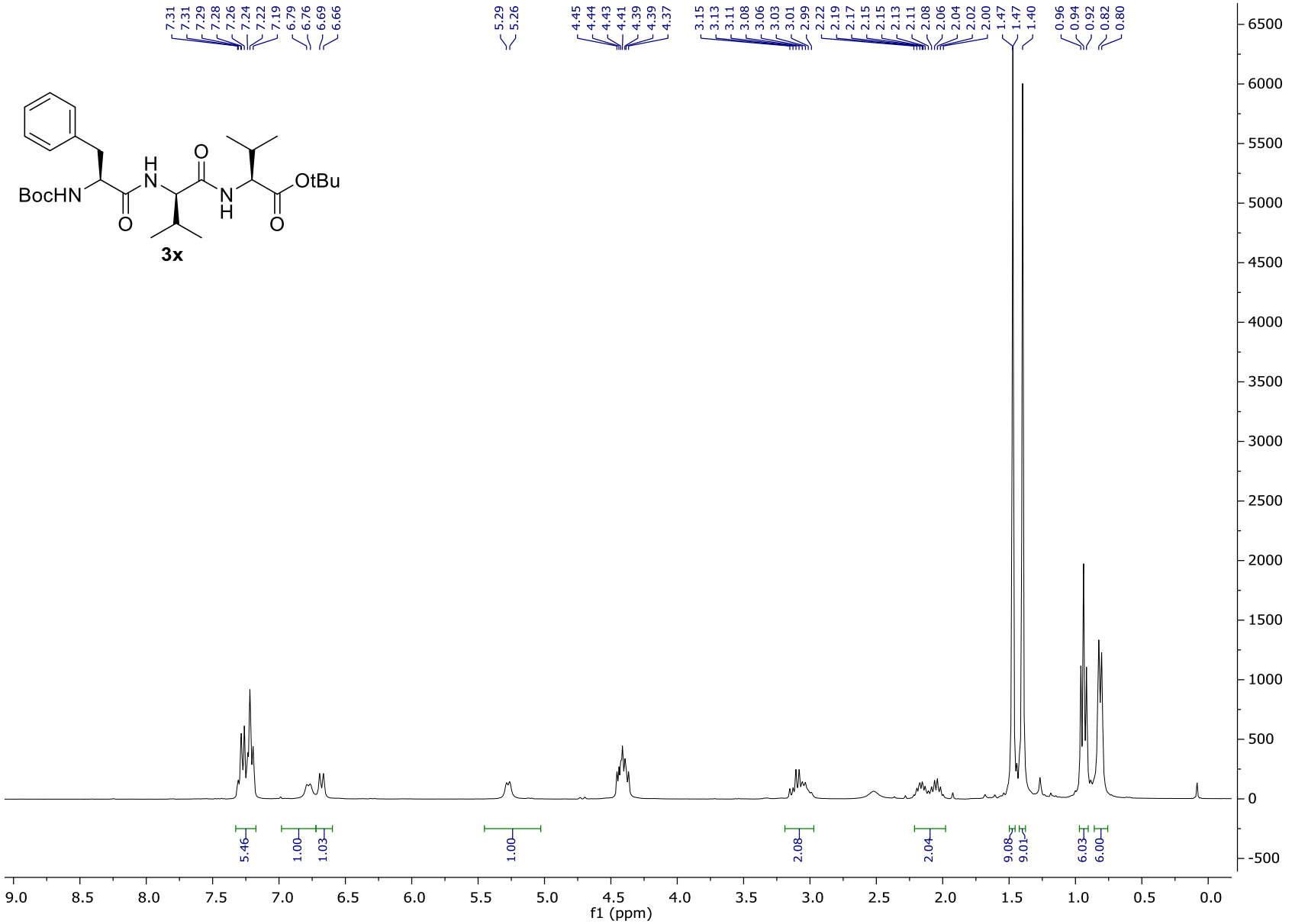
77.15
76.73
58.78
57.71
55.76
38.02
31.38
31.18
28.35
28.14
19.21
19.05
18.26
17.90
BocHN
H
N
O
O
N
H
O
OtBu
O
3w
f1 (ppm)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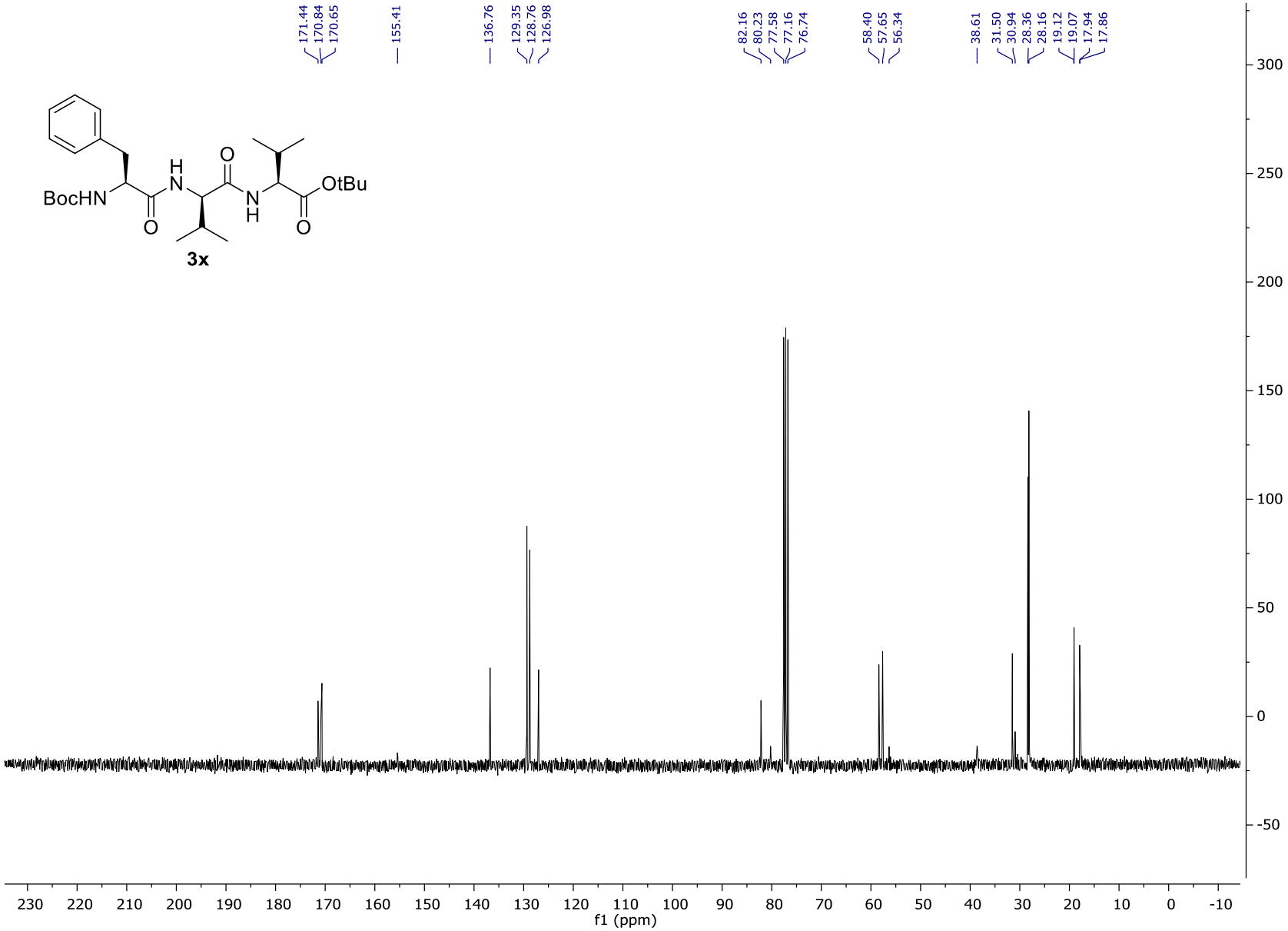
6.69
6.66
5.29
5.26
4.45
4.44
4.43
4.41
4.39
4.39
4.37
3.15
3.13
3.11
3.08
3.06
3.03
3.01
2.99
2.22
2.19
2.17
2.15
2.15
2.13
2.11
2.08
2.06
2.04
2.02
2.00
1.47
1.47
1.40
0.96
0.94
0.92
0.82
0.80
BocHN
H
N
O
O
N
H
O
OtBu
3x
5.46
1.00
1.03
1.00
2.08
2.04
9.08
9.01
6.03
6.00
f1 (ppm)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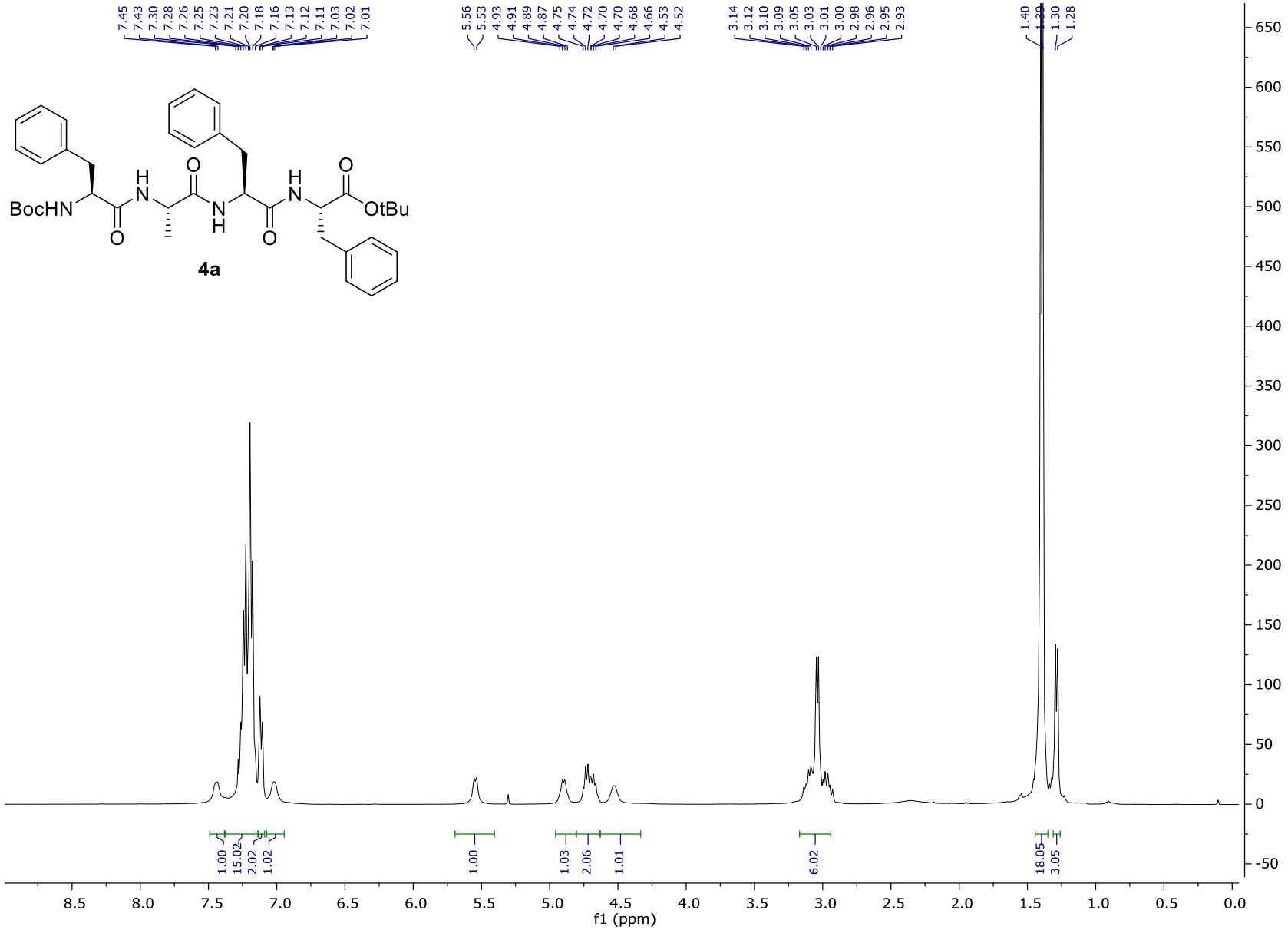
77.58
77.16
76.74
58.40
57.65
56.34
38.61
31.50
30.94
28.36
28.16
19.12
19.07
17.94
17.86
BocHN
H
N
O
O
N
H
O
OtBu
O
3x
300
250
200
150
100
50
0
-50
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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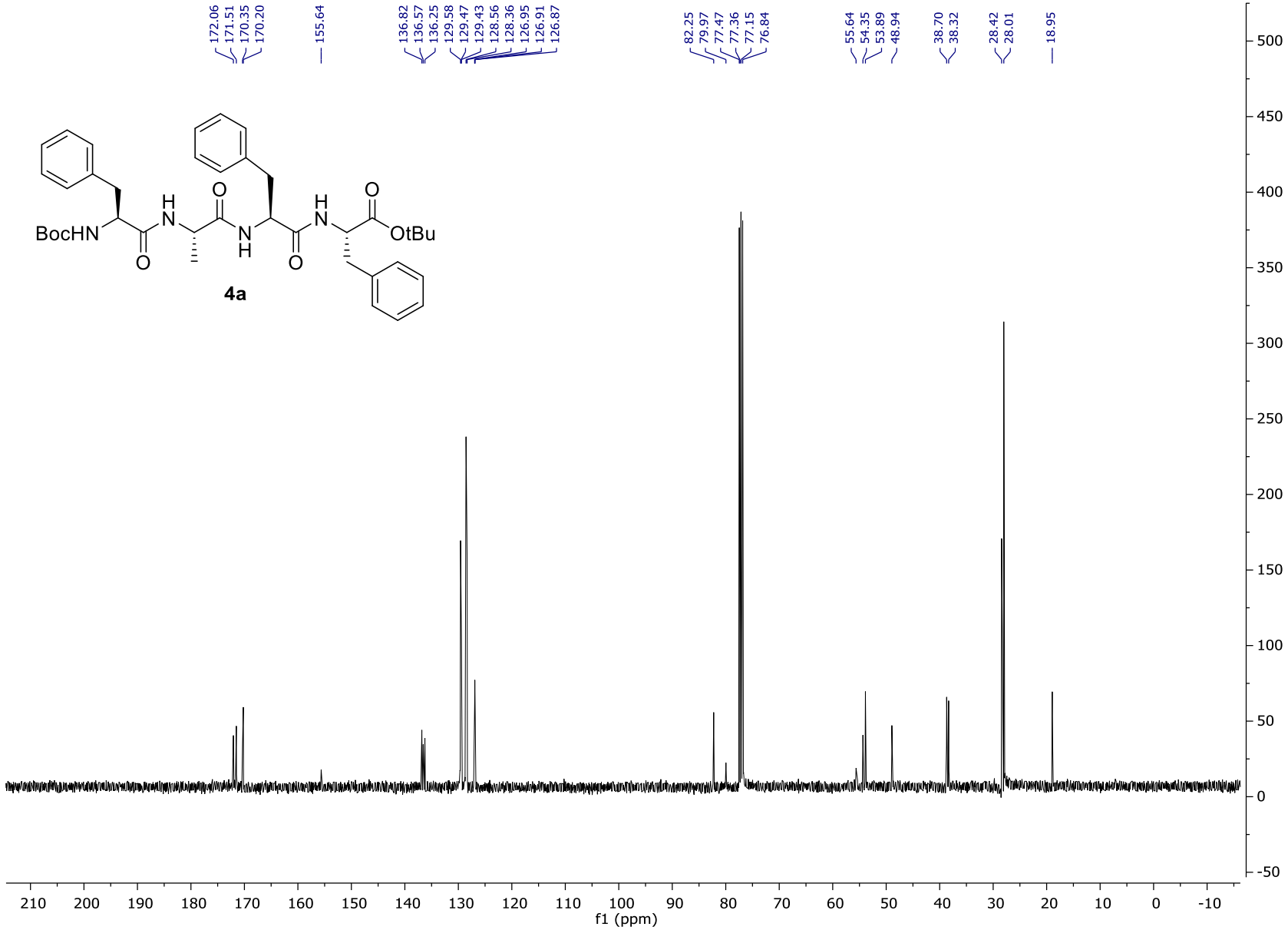
7.23
7.21
7.20
7.18
7.16
7.13
7.12
7.11
7.03
7.02
7.01
5.56
5.53
4.93
4.91
4.89
4.87
4.75
4.74
4.72
4.70
4.70
4.68
4.66
4.53
4.52
3.14
3.12
3.10
3.09
3.05
3.03
3.01
3.00
2.98
2.96
2.95
2.93
1.40
1.39
1.30
1.28
BocHN
OtBu
4a
1.00
15.02
2.02
1.02
1.00
1.03
2.06
1.01
6.02
18.05
3.05
f1 (ppm)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136.25
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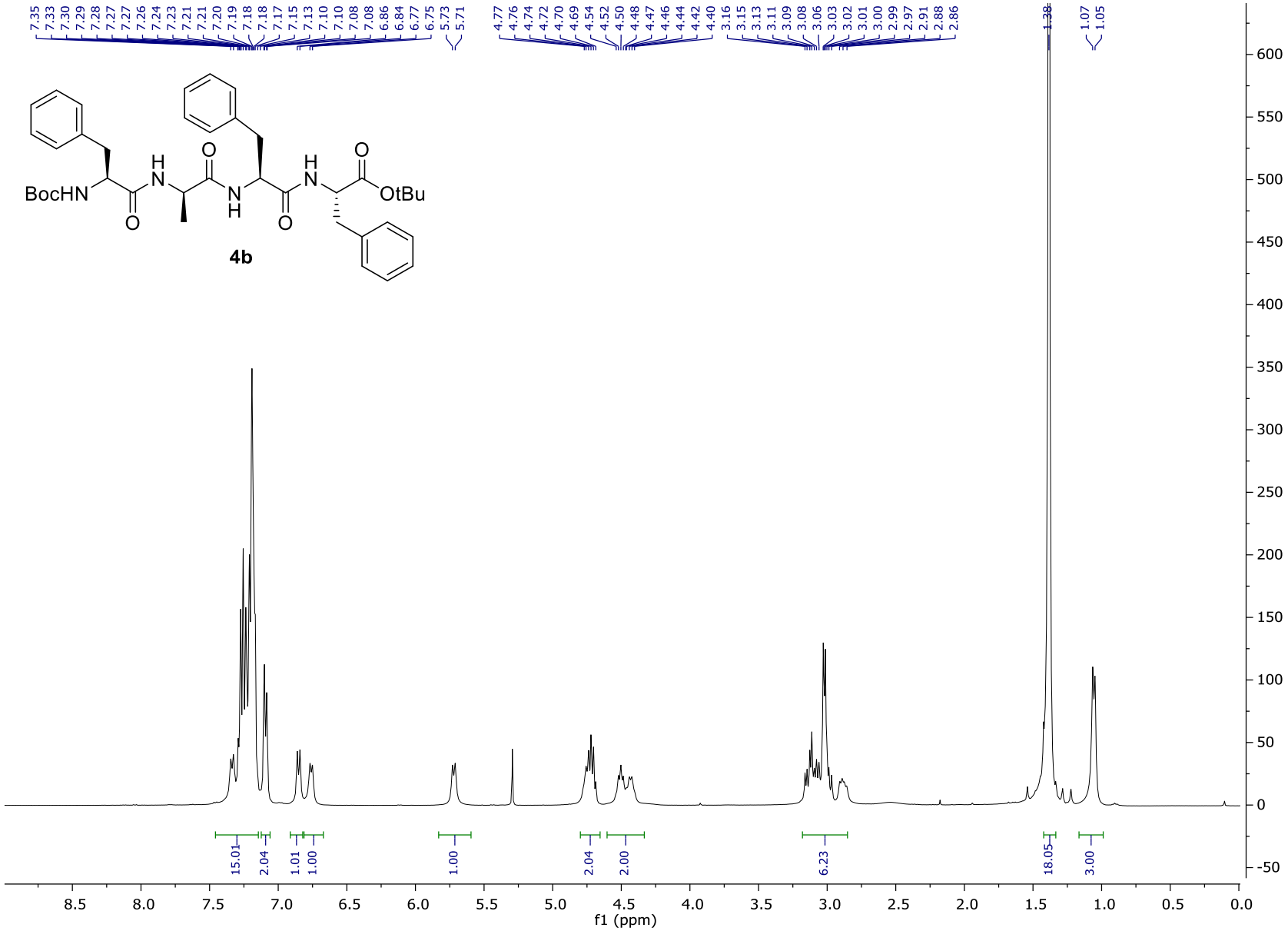
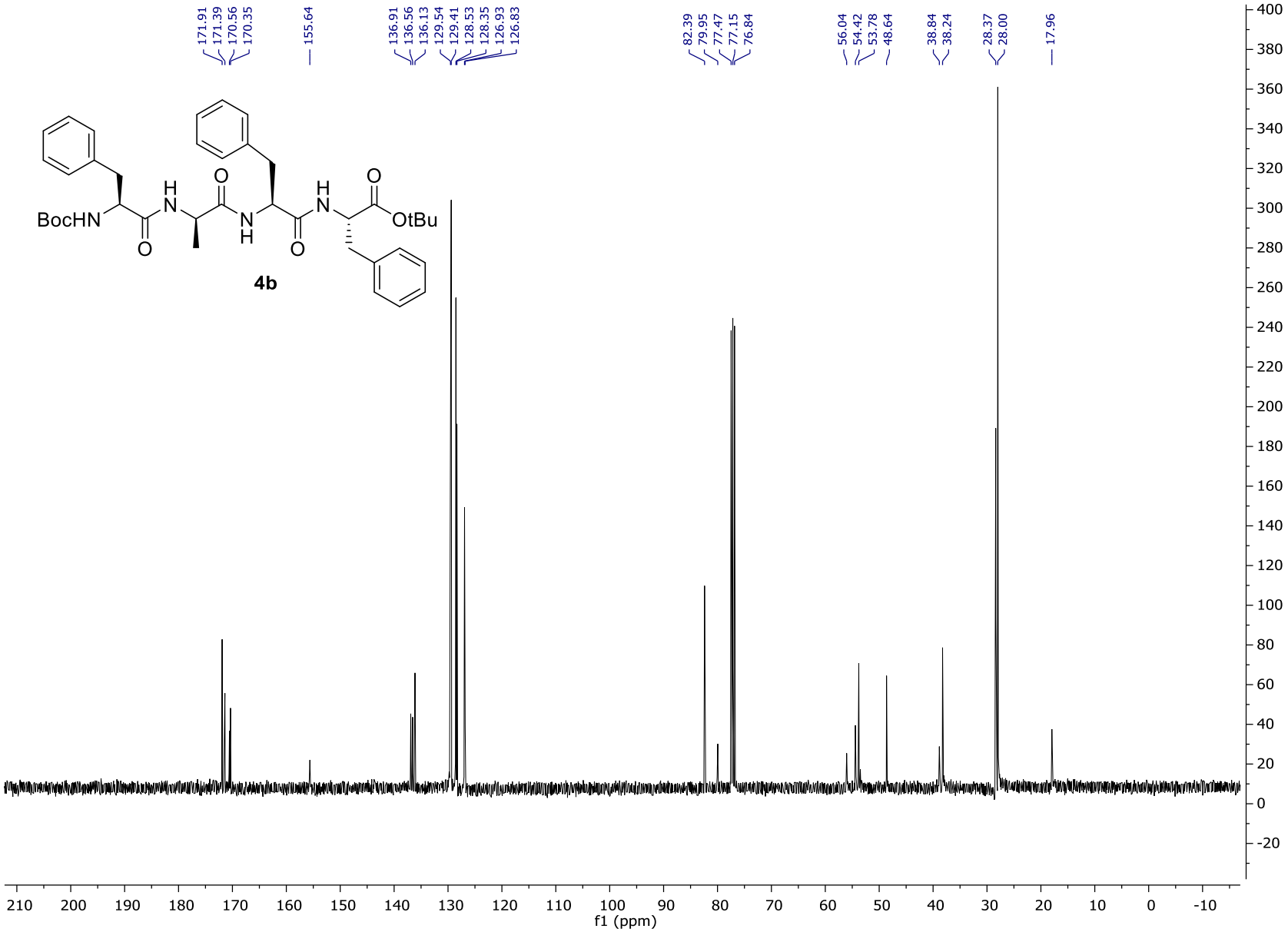
129.47
129.43
128.56
128.36
126.95
126.91
126.87
82.25
79.97
77.47
77.36
77.15
76.84
55.64
54.35
53.89
48.94
38.70
38.32
28.42
28.01
18.95
BocHN
OtBu
4a
f1 (ppm)


7.35 7.33 7.30 7.29 7.28 7.27 7.27 7.26 7.24 7.23 7.21 7.21 7.20 7.19 7.18 7.18 7.17 7.15 7.13 7.10 7.10 7.08 7.08 6.86 6.84 6.77 6.75 5.73 5.71
4.77 4.76 4.74 4.72 4.70 4.69 4.54 4.52 4.50 4.48 4.47 4.46 4.44 4.42 4.40
3.16 3.15 3.13 3.11 3.09 3.08 3.06 3.03 3.02 3.01 3.00 2.99 2.97 2.91 2.88 2.86
1.38 1.07 1.05
BocHN
OtBu
4b
15.01 2.04 1.01 1.00 1.00 2.04 2.00 6.23 18.05 3.00
f1 (ppm)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136.13
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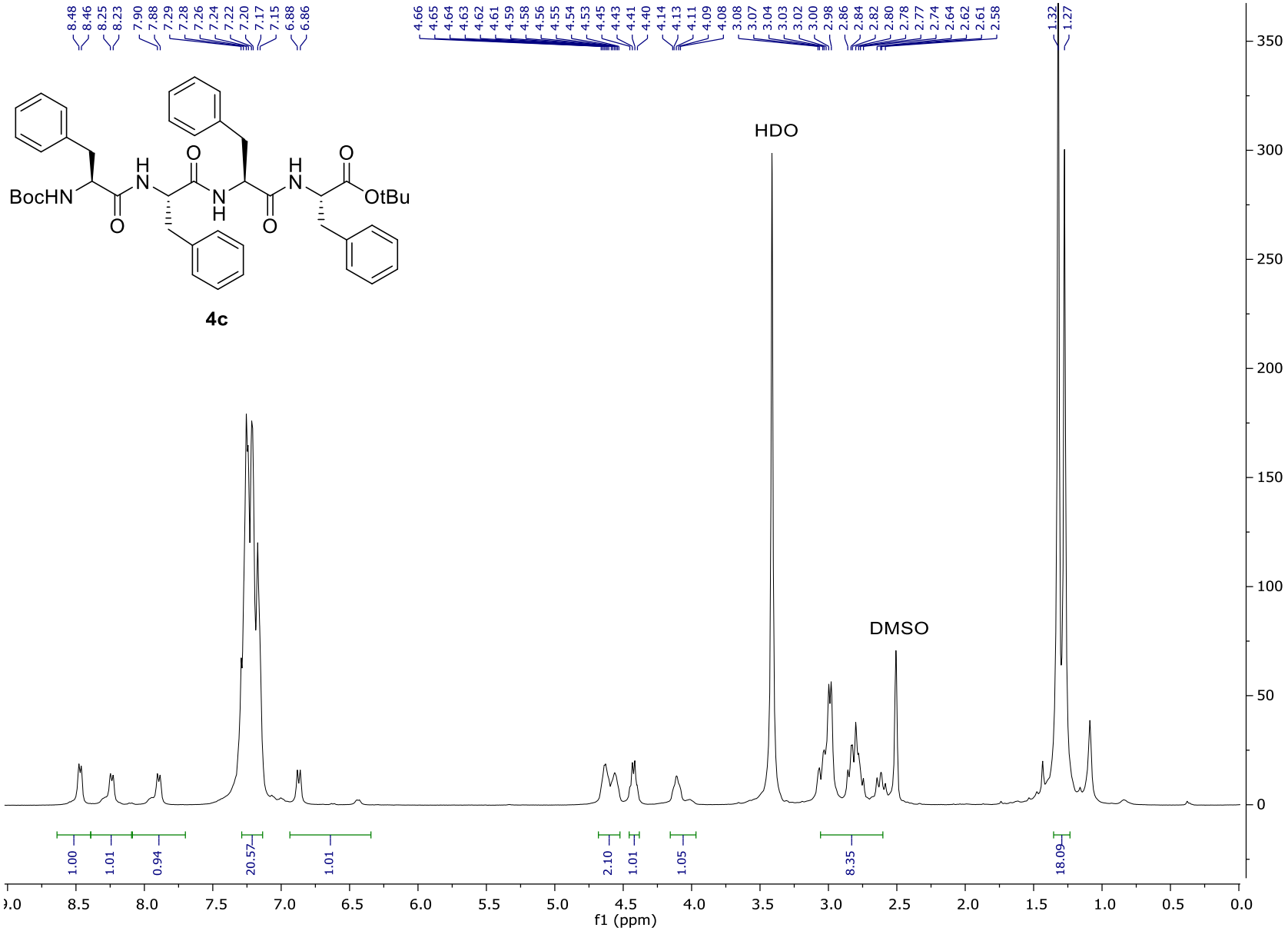
129.41
128.53
128.35
126.93
126.83
82.39
79.95
77.47
77.15
76.84
56.04
54.42
53.78
48.64
38.84
38.24
28.37
28.00
17.96
BocHN
OtBu
4b
f1 (ppm)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7.20
7.17
7.15
6.88
6.86
4.66
4.65
4.64
4.63
4.62
4.61
4.59
4.58
4.56
4.55
4.54
4.53
4.45
4.43
4.41
4.40
4.14
4.13
4.11
4.09
4.08
3.08
3.07
3.04
3.03
3.02
3.00
2.98
2.86
2.84
2.82
2.80
2.78
2.77
2.74
2.64
2.62
2.61
2.58
1.32
1.27
BocHN
OtBu
4c
HDO
DMSO
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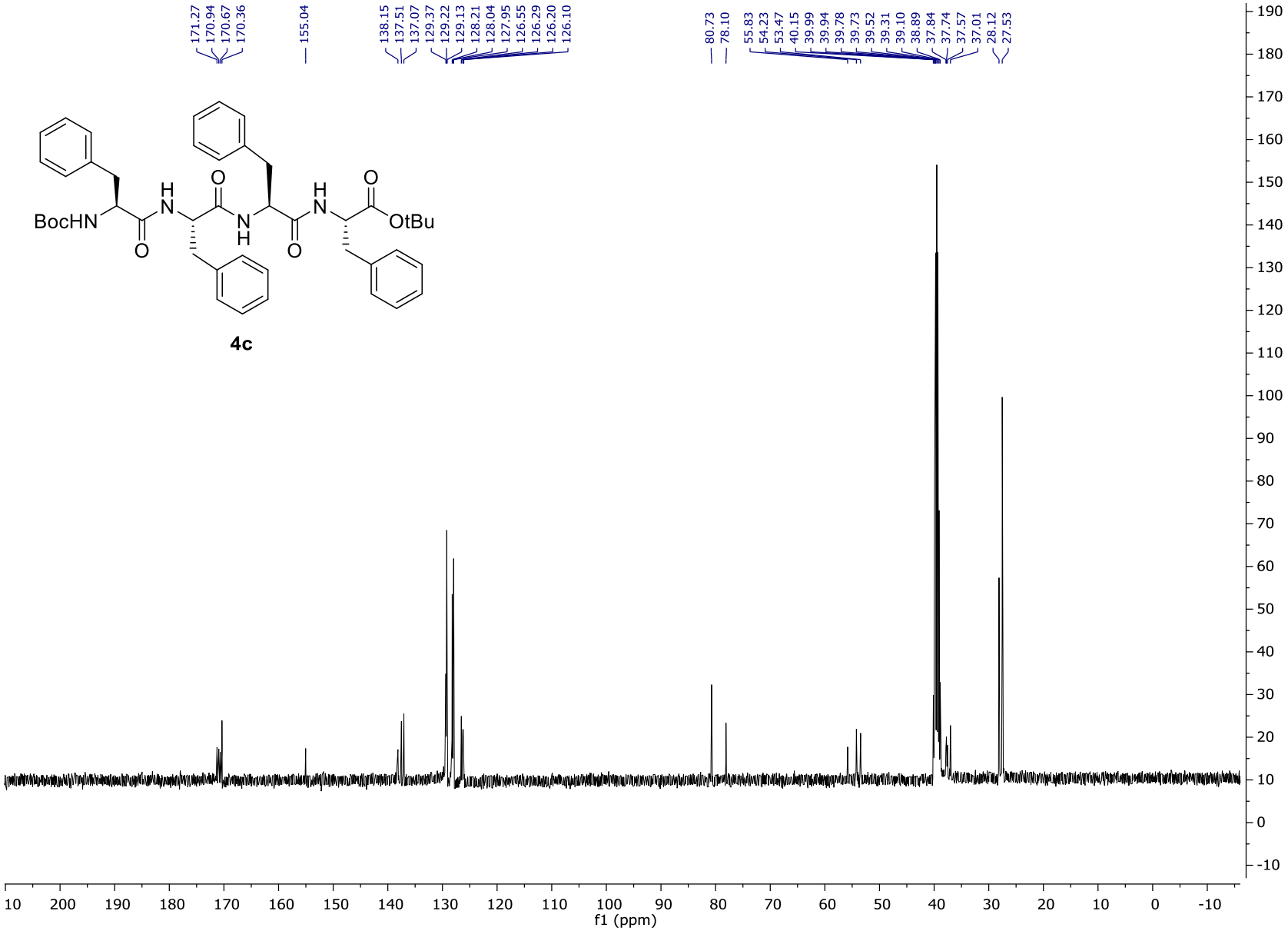
1.01
0.94
20.57
1.01
2.10
1.01
1.05
8.35
18.09
f1 (ppm)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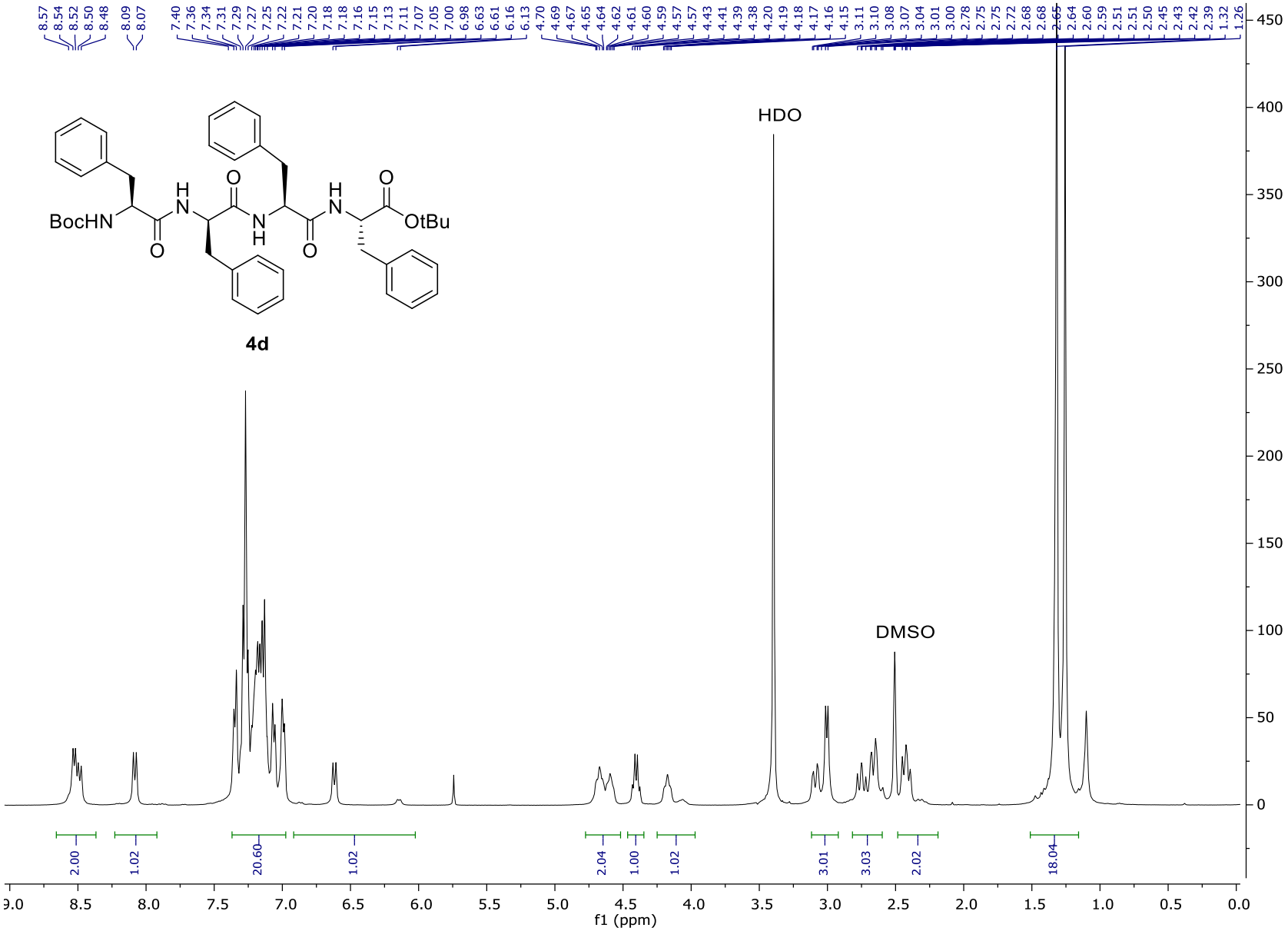
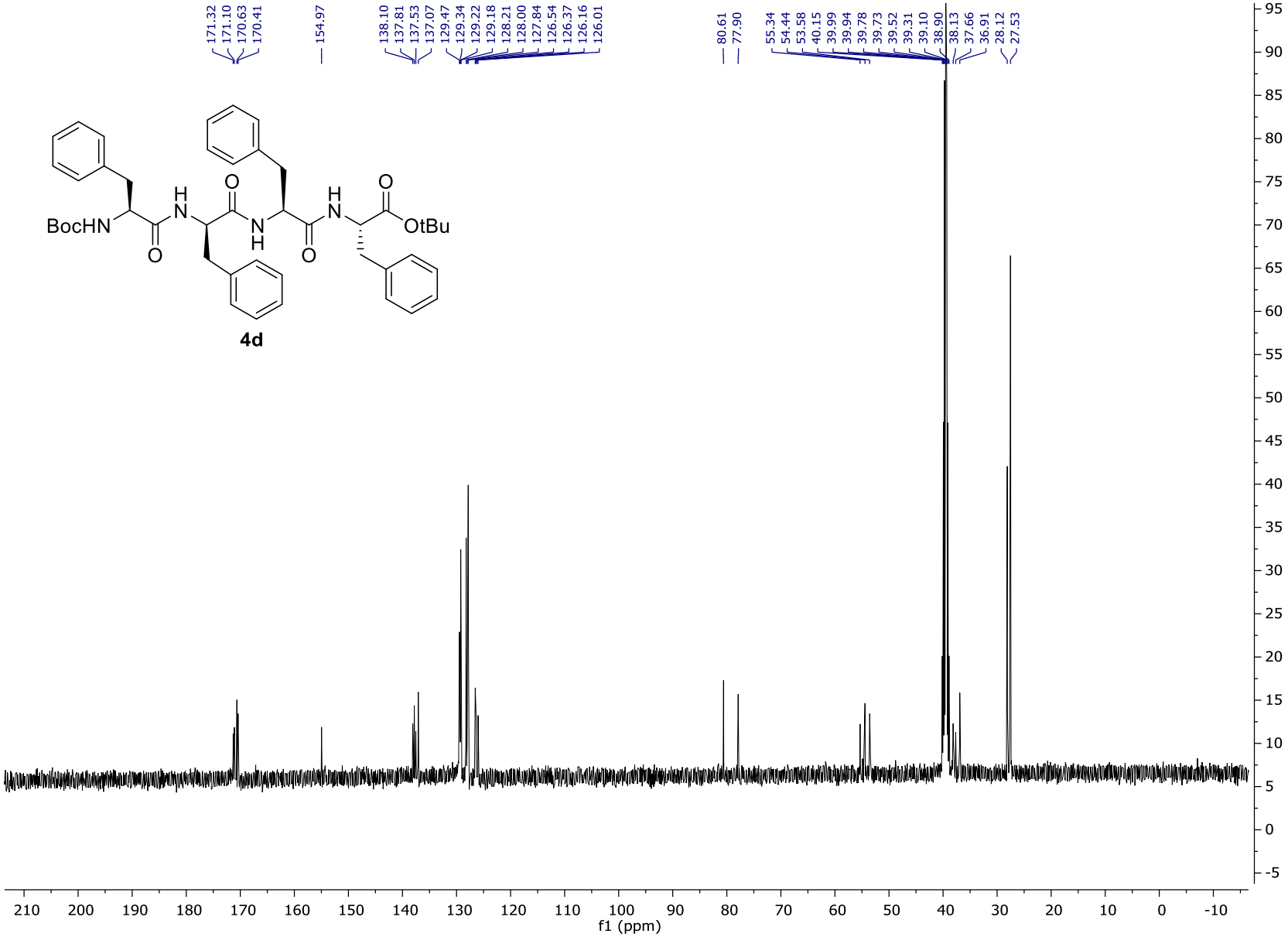
128.04
127.95
126.55
126.29
126.20
126.10
80.73
78.10
55.83
54.23
53.47
40.15
39.99
39.94
39.78
39.73
39.52
39.31
39.10
38.89
37.84
37.74
37.57
37.01
28.12
27.53
BocHN
OtBu
4c
f1 (ppm)


HDO
DMSO
BocHN
OtBu
4d
f1 (ppm)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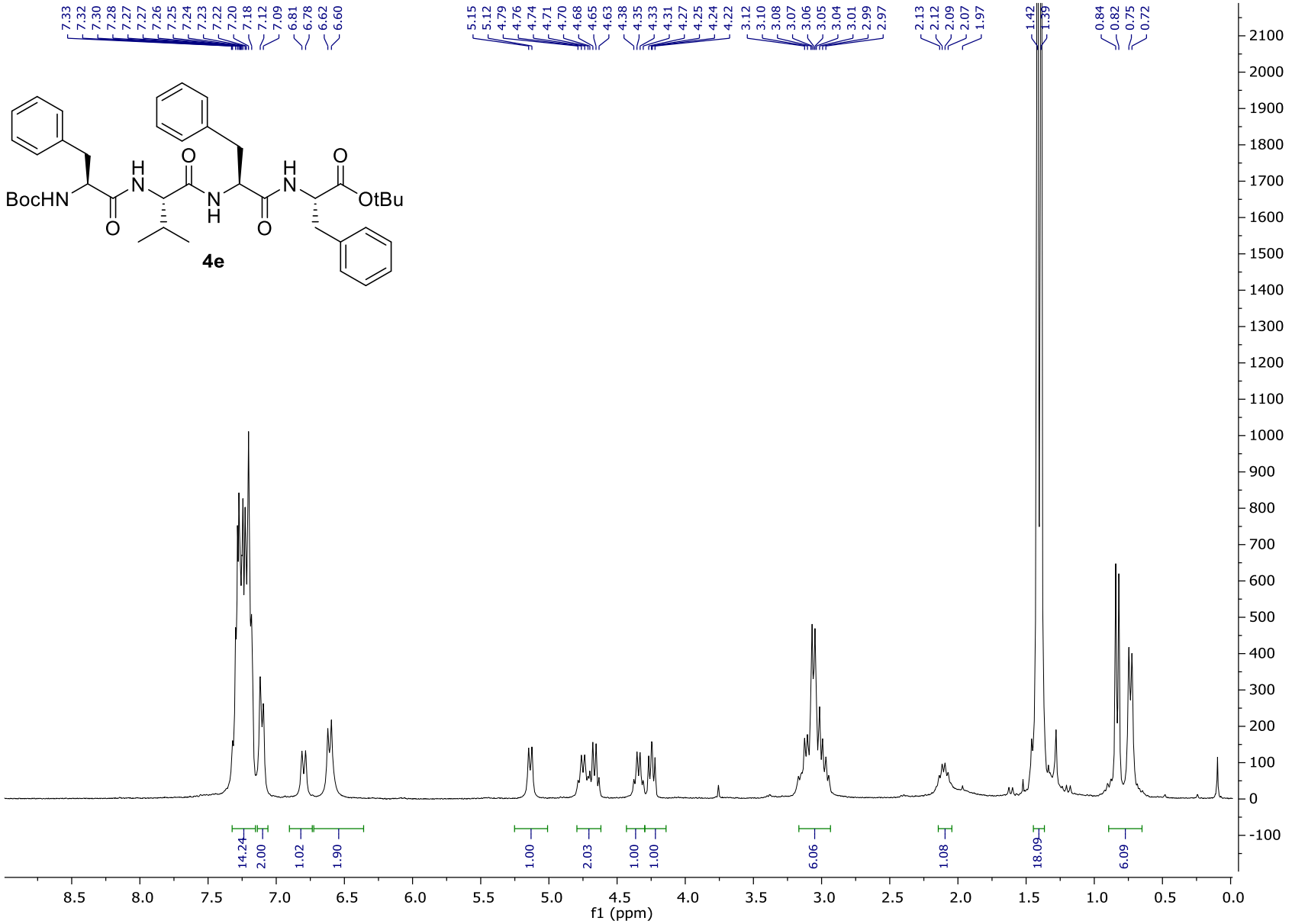
137.53
137.07
129.47
129.34
129.22
129.18
128.21
128.00
127.84
126.54
126.37
126.16
126.01
80.61
77.90
55.34
54.44
53.58
40.15
39.99
39.94
39.78
39.73
39.52
39.31
39.10
38.90
38.13
37.66
36.91
28.12
27.53
BocHN
OtBu
4d
f1 (ppm)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7.23
7.22
7.20
7.18
7.12
7.09
6.81
6.78
6.62
6.60
5.15
5.12
4.79
4.76
4.74
4.71
4.70
4.68
4.65
4.63
4.38
4.35
4.33
4.31
4.27
4.25
4.24
4.22
3.12
3.10
3.08
3.07
3.06
3.05
3.04
3.01
2.99
2.97
2.13
2.12
2.09
2.07
1.97
1.42
1.39
0.84
0.82
0.75
0.72
BocHN
OtBu
4e
14.24
2.00
1.02
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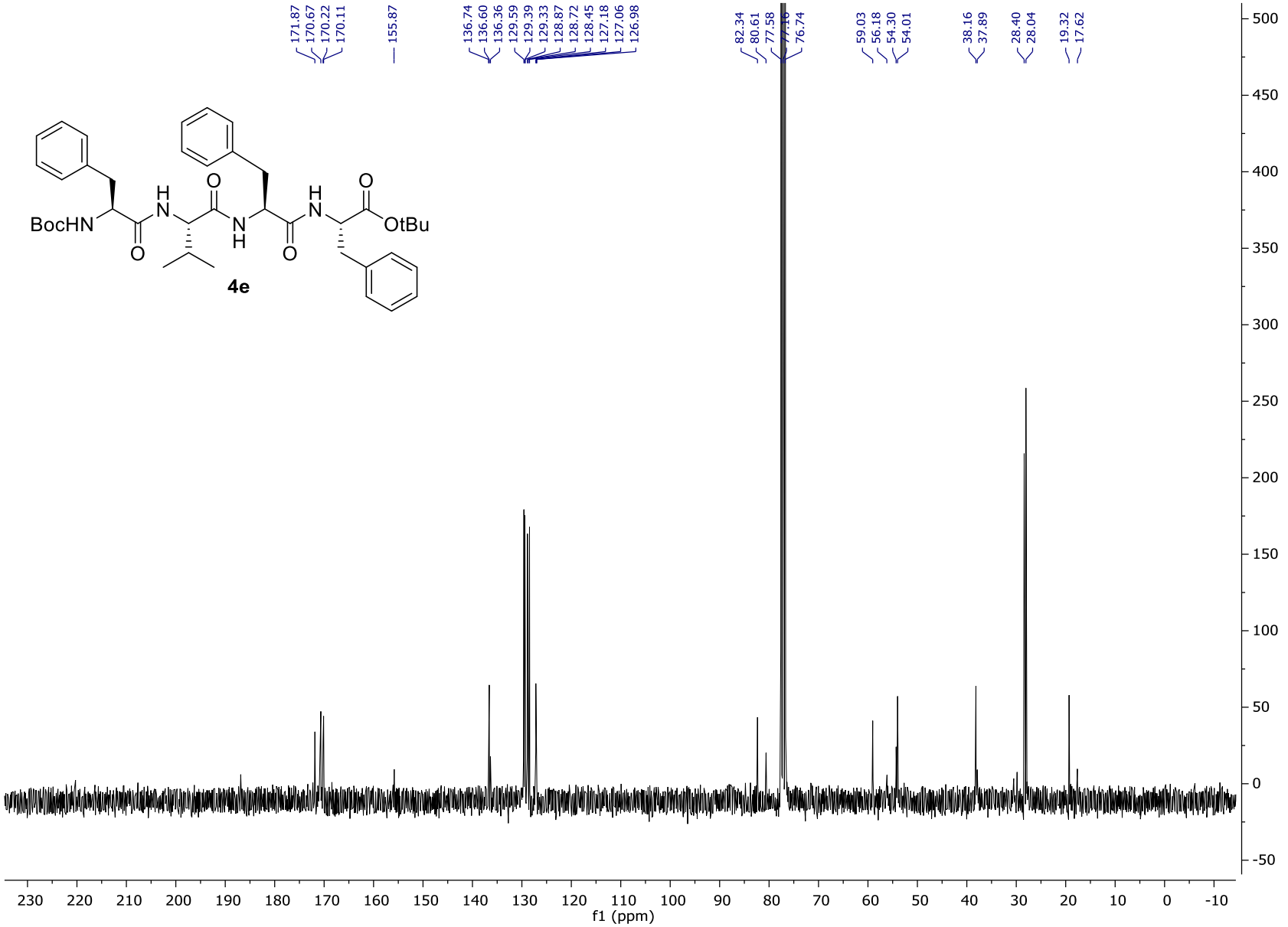
1.00
2.03
1.00
1.00
6.06
1.08
18.09
6.09
f1 (ppm)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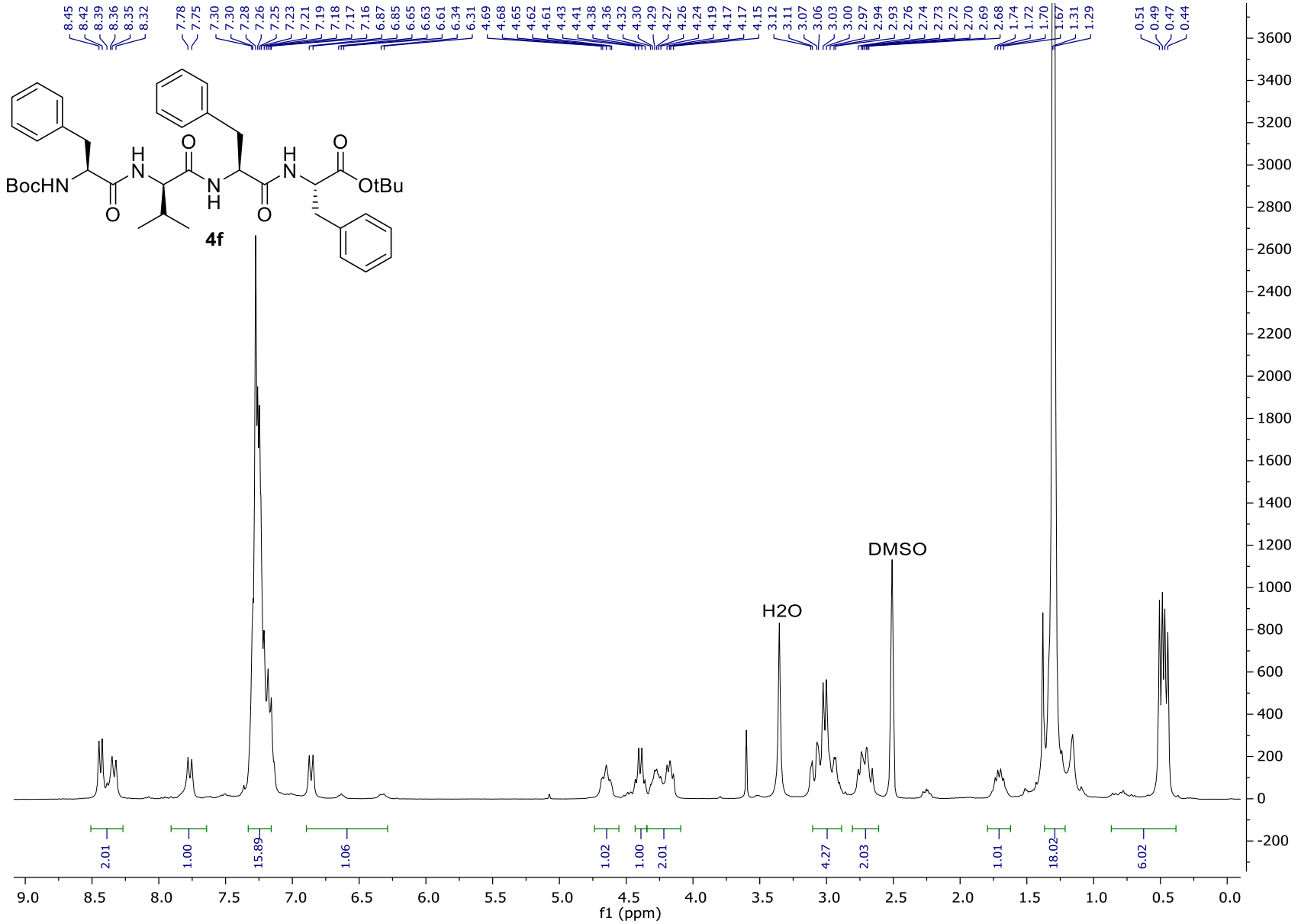
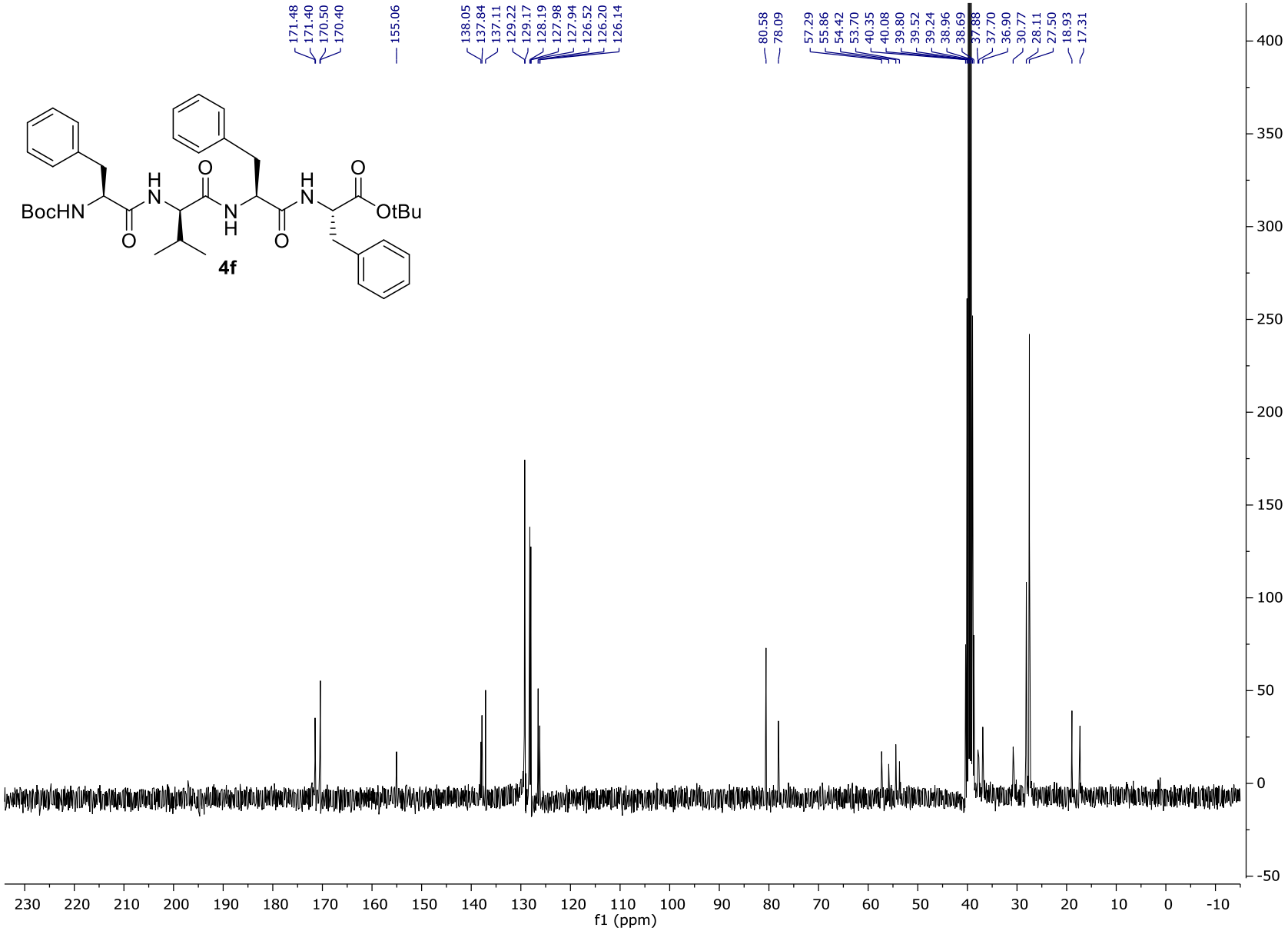
136.60
136.36
129.59
129.39
129.33
128.87
128.72
128.45
127.18
127.06
126.98
82.34
80.61
77.58
77.16
76.74
59.03
56.18
54.30
54.01
38.16
37.89
28.40
28.04
19.32
17.62
BocHN
OtBu
4e
f1 (ppm)


BocHN
OtBu
4f
H2O
DMSO
f1 (ppm)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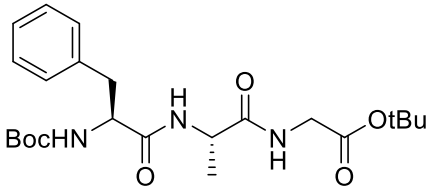
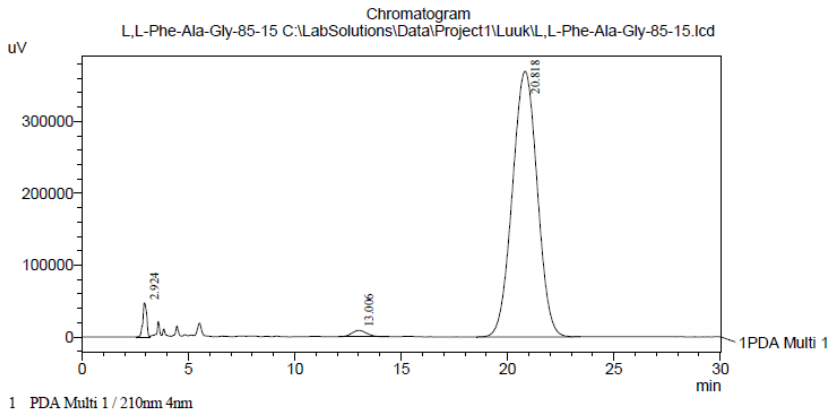
128.19
127.98
127.94
126.52
126.20
126.14
80.58
78.09
57.29
55.86
54.42
53.70
40.35
40.08
39.80
39.52
39.24
38.96
38.69
37.88
37.70
36.90
30.77
28.11
27.50
18.93
17.31
BocHN
OtBu
4f
f1 (ppm)



3a

		Method
Acquired by	: Admin	[Pump A Mobile Phase A]
Sample Name	: L,L-Phe-Ala-Gly-85-15	Heptane
Sample ID	: L,L-Phe-Ala-Gly-85-15	Pump A: Heptane, B: 2-Propanol
Vail #	:	Pump A :LC-20AD
Injection Volume	: 10 uL	Total Flow :1.0000 mL/min
Data File Name	: L,L-Phe-Ala-Gly-85-15.lcd	B.Conc :0.0 %
Method File Name	: Remko1.lcm	C.Conc :85.0 %
Batch File Name	:	D.Conc :15.0 %
Report File Name	: remko-report.lcr	PressMax :100 bar
Data Acquired	: 6/26/2017 3:39:40 PM	PressMin :0 bar
Data Processed	: 6/26/2017 4:09:42 PM	

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

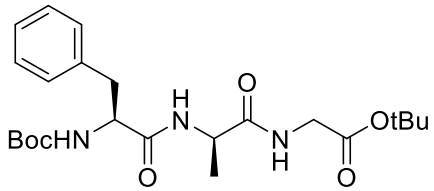
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.924	597158	47422	1.917	11.131
2	13.006	443680	8915	1.424	2.093
3	20.818	30116788	369683	96.659	86.776
Total		31157627	426020	100.000	100.000

d.r. = 96.659 / (96.659 + 1.424) = 98.55 : 1.45

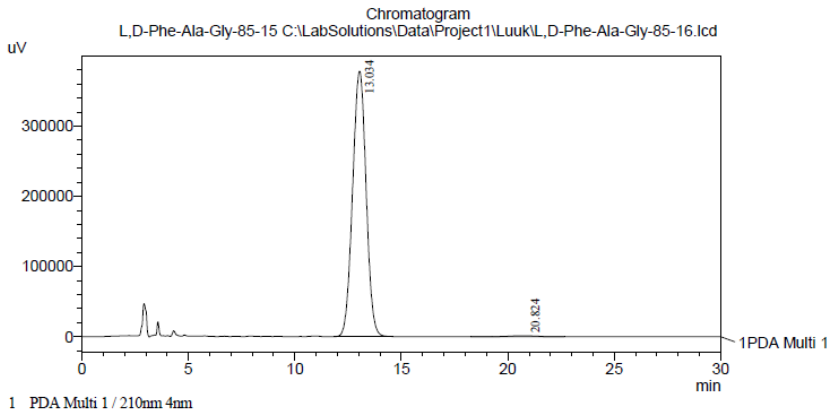
d.e. = 97.1%



3b

		Method
Acquired by	: Admin	[Pump A Mobile Phase A]
Sample Name	: L,D-Phe-Ala-Gly-85-15	Heptane
Sample ID	: L,D-Phe-Ala-Gly-85-15	Pump A: Heptane, B: 2-Propanol
Vail #	:	Pump A :LC-20AD
Injection Volume	: 10 uL	Total Flow :1.0000 mL/min
Data File Name	: L,D-Phe-Ala-Gly-85-16.lcd	B.Conc :0.0 %
Method File Name	: Remko1.lcm	C.Conc :85.0 %
Batch File Name	:	D.Conc :15.0 %
Report File Name	: remko-report.lcr	PressMax :100 bar
Data Acquired	: 6/26/2017 4:10:42 PM	PressMin :0 bar
Data Processed	: 6/26/2017 4:40:44 PM	

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

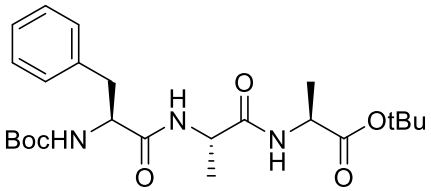
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.034	16706625	378056	99.184	99.605
2	20.824	137519	1501	0.816	0.395
Total		16844144	379557	100.000	100.000

d.r. = 99.18 : 0.82

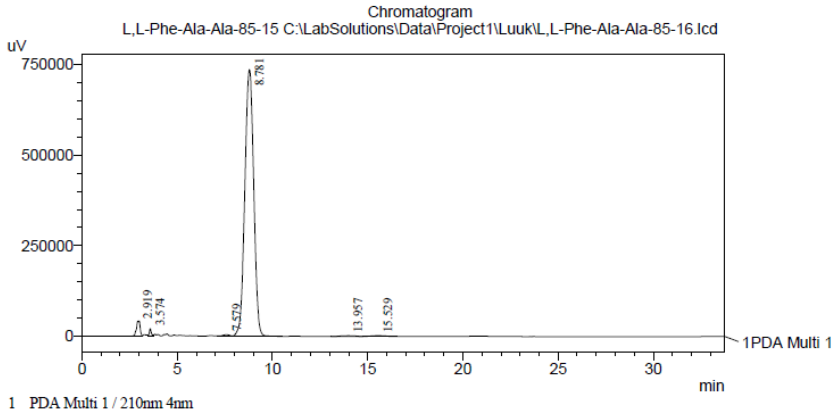
d.e. = 98.4%



3c

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,L-Phe-Ala-Ala-85-15	Heptane	
Sample ID	: L,L-Phe-Ala-Ala-85-15	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,L-Phe-Ala-Ala-85-16.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:85.0 %
Batch File Name	:	D.Conc	:15.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 6/27/2017 10:05:37 AM	PressMin	:0 bar
Data Processed	: 6/27/2017 10:39:23 AM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

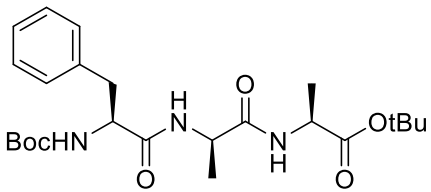
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.919	580825	41304	2.319	5.111
2	3.574	145929	20787	0.583	2.572
3	7.579	121300	4365	0.484	0.540
4	8.781	23939654	736663	95.579	91.153
5	13.957	121621	2351	0.486	0.291
6	15.529	137645	2690	0.550	0.333
Total		25046975	808159	100.000	100.000

d.r. = 95.579 / (95.579 + 0.550) = 99.43 : 0.57

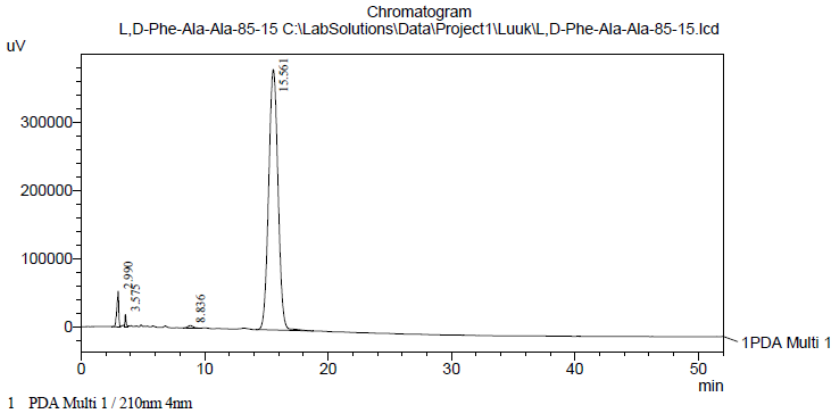
d.e. = 98.8%



3d

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,D-Phe-Ala-Ala-85-15	Heptane	
Sample ID	: L,D-Phe-Ala-Ala-85-15	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,D-Phe-Ala-Ala-85-15.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:85.0 %
Batch File Name	:	D.Conc	:15.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 6/27/2017 9:12:19 AM	PressMin	:0 bar
Data Processed	: 6/27/2017 10:04:23 AM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

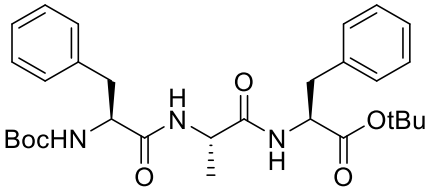
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.990	561476	52594	2.682	11.507
2	3.575	131310	18702	0.627	4.092
3	8.836	111212	3642	0.531	0.797
4	15.561	20134523	382119	96.160	83.604
Total		20938520	457057	100.000	100.000

d.r. = 96.160 / (96.160 + 0.531) = 99.45 : 0.55

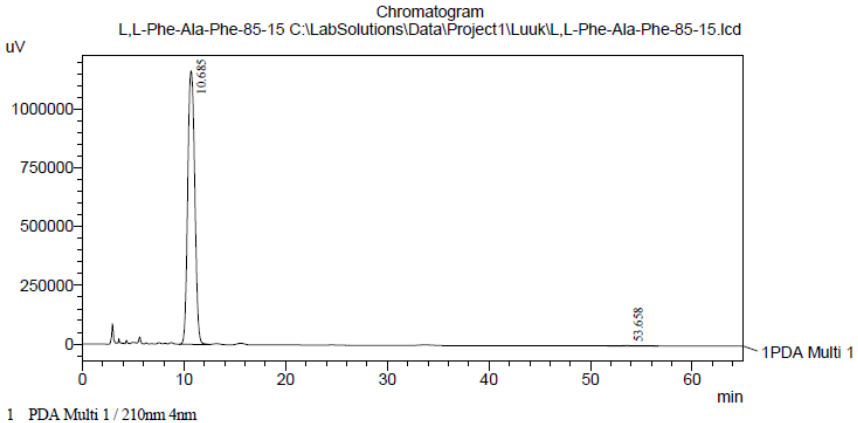
d.e. = 98.9%



3e

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,L-Phe-Ala-Phe-85-15	Heptane	
Sample ID	: L,L-Phe-Ala-Phe-85-15	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,L-Phe-Ala-Phe-85-15.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:85.0 %
Batch File Name	:	D.Conc	:15.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 6/28/2017 9:42:12 AM	PressMin	:0 bar
Data Processed	: 6/28/2017 10:47:14 AM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

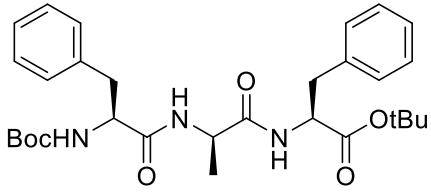
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.685	56145376	1163799	99.529	99.860
2	53.658	265941	1628	0.471	0.140
Total		56411318	1165427	100.000	100.000

d.r. = 99.53 : 0.47

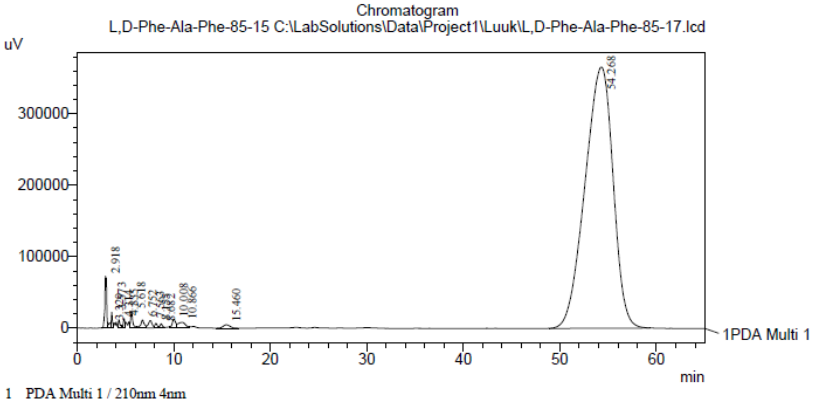
d.e. = 99.1%



3f

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,D-Phe-Ala-Phe-85-15	Heptane	
Sample ID	: L,DPhe-Ala-Phe-85-15	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,D-Phe-Ala-Phe-85-17.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:85.0 %
Batch File Name	:	D.Conc	:15.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 6/27/2017 11:53:29 AM	PressMin	:0 bar
Data Processed	: 6/27/2017 12:58:31 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

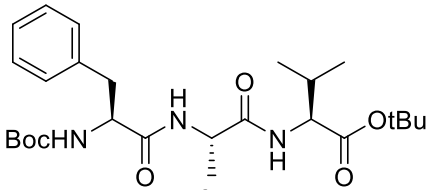
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.918	970508	72870	1.249	12.694
2	3.329	103751	7112	0.134	1.239
3	3.573	199481	22333	0.257	3.890
4	4.314	141779	11840	0.182	2.062
5	4.835	163751	13177	0.211	2.295
6	5.618	340587	22651	0.438	3.946
7	6.752	299925	11204	0.386	1.952
8	7.563	275146	10353	0.354	1.804
9	8.155	115140	6492	0.148	1.131
10	8.682	113899	5885	0.147	1.025
11	10.008	313793	12108	0.404	2.109
12	10.866	406805	7646	0.524	1.332
13	15.460	236432	4772	0.304	0.831
14	54.268	74016811	365622	95.262	63.690
Total		77697807	574066	100.000	100.000

d.r. = 95.262 / (95.262 + 0.524) = 99.45 : 0.55

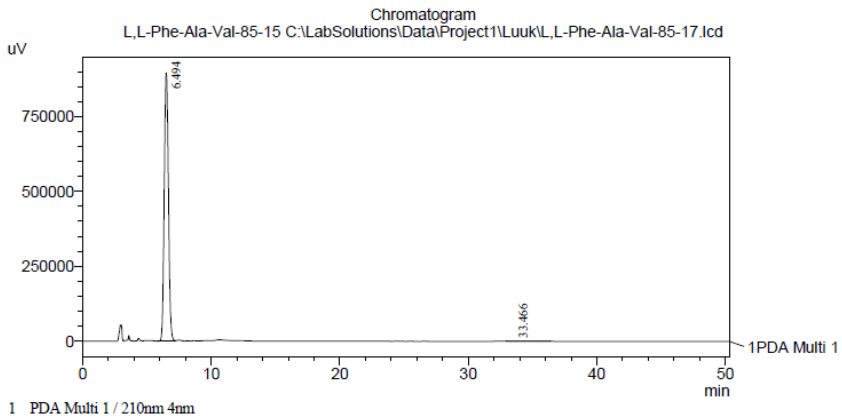
d.e. = 98.9%



3g

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,L-Phe-Ala-Val-85-15	Heptane	
Sample ID	: L,L-Phe-Ala-Val-85-15	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,L-Phe-Ala-Val-85-17.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:85.0 %
Batch File Name	:	D.Conc	:15.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 6/28/2017 1:20:44 PM	PressMin	:0 bar
Data Processed	: 6/28/2017 2:11:06 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

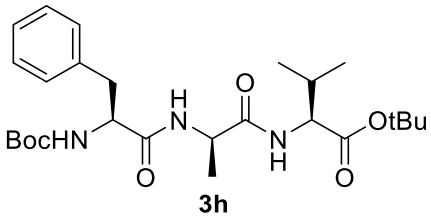
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.494	20426143	896248	99.628	99.960
2	33.466	76227	354	0.372	0.040
Total		20502371	896603	100.000	100.000

d.r. = 99.63 : 0.37

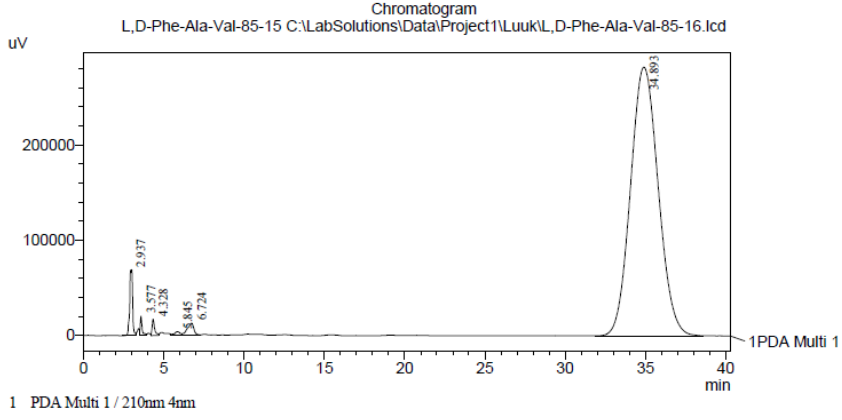
d.e. = 99.3%



3h

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,D-Phe-Ala-Val-85-15	Heptane	
Sample ID	: L,D-Phe-Ala-Val-85-15	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,D-Phe-Ala-Val-85-16.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:85.0 %
Batch File Name	:	D.Conc	:15.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 6/28/2017 12:39:24 PM	PressMin	:0 bar
Data Processed	: 6/28/2017 1:19:43 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

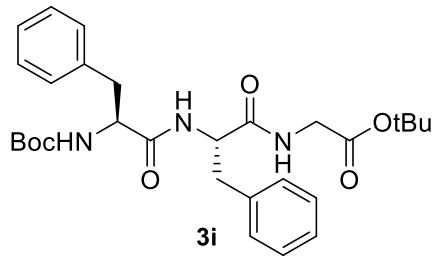
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.937	879810	68964	2.471	17.007
2	3.577	170437	20383	0.479	5.027
3	4.328	191750	17169	0.539	4.234
4	5.845	101946	3894	0.286	0.960
5	6.724	376601	13020	1.058	3.211
6	34.893	33884108	282070	95.168	69.561
Total		35604652	405500	100.000	100.000

d.r. = 95.168 / (95.168 + 1.058) = 98.90 : 1.10

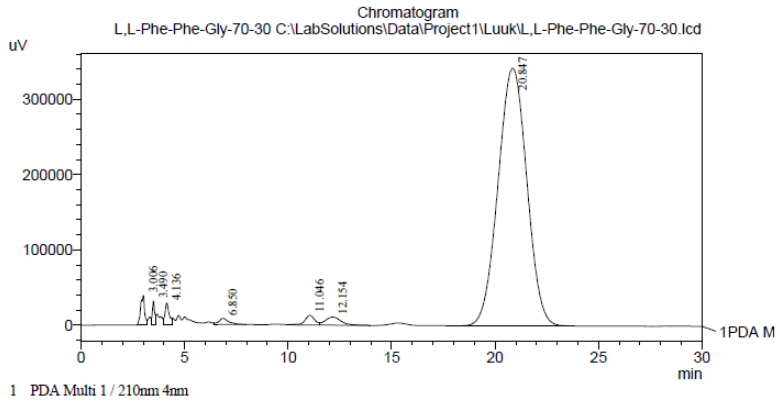
d.e. = 97.8%



3i

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,L-Phe-Phe-Gly-70-30	Heptane	
Sample ID	: L,L-Phe-Phe-Gly-70-30	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,L-Phe-Phe-Gly-70-30.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:70.0 %
Batch File Name	:	D.Conc	:30.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 6/26/2017 11:12:40 AM	PressMin	:0 bar
Data Processed	: 6/26/2017 11:42:42 AM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

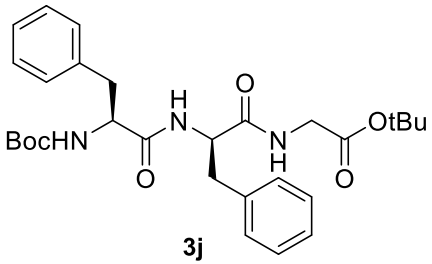
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.006	520239	39219	1.464	8.274
2	3.490	255126	31787	0.718	6.706
3	4.136	411213	29036	1.157	6.126
4	6.850	277787	8255	0.782	1.742
5	11.046	427096	12799	1.202	2.700
6	12.154	555490	10703	1.563	2.258
7	20.847	33089685	342197	93.114	72.194
Total		35536636	473996	100.000	100.000

d.r. = 93.11/(93.114+1.563) = 98.4 : 1.6

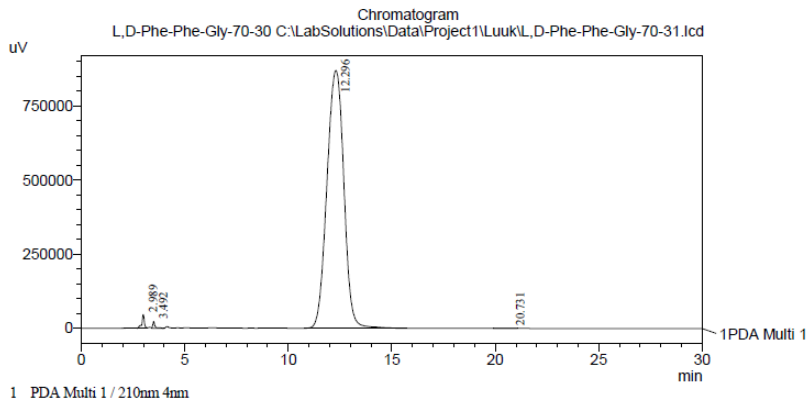
d.e. = 96.8%



3j

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,D-Phe-Phe-Gly-70-30	Heptane	
Sample ID	: L,D-Phe-Phe-Gly-70-30	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,D-Phe-Phe-Gly-70-31.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:70.0 %
Batch File Name	:	D.Conc	:30.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 6/26/2017 11:46:40 AM	PressMin	:0 bar
Data Processed	: 6/26/2017 12:16:42 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

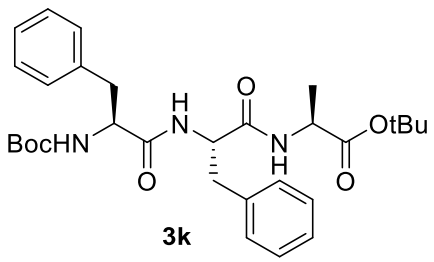
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.989	383718	46265	0.767	4.924
2	3.492	178262	23492	0.356	2.500
3	12.296	49477007	869540	98.850	92.544
4	20.731	13752	301	0.027	0.032
Total		50052739	939599	100.000	100.000

d.r. = 98.850/(98.850+0.027) = 99.96 : 0.04

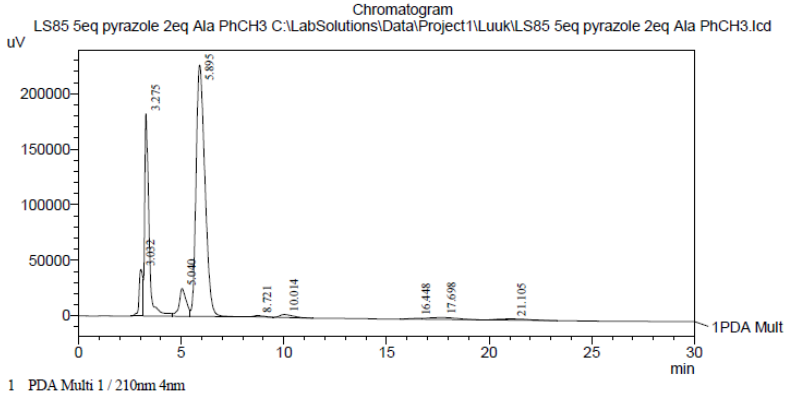
d.e. = 99.9%



3k

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: LS85 5eq pyrazole 2eq Ala PhCH	Heptane	
Sample ID	: LS85 5eq pyrazole 2eq Ala PhCH	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: LS85 5eq pyrazole 2eq Ala PhCH	B.Conc	:30.0 %
Method File Name	: Remko1.lcm	C.Conc	:0.0 %
Batch File Name	:	D.Conc	:0.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 5/4/2017 11:26:23 AM	PressMin	:0 bar
Data Processed	: 5/4/2017 11:56:26 AM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

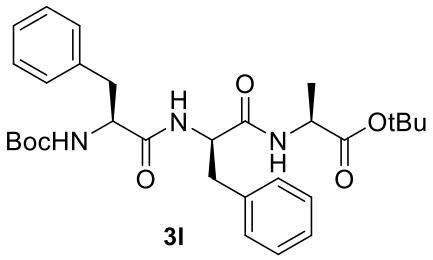
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.032	539689	42063	4.894	8.702
2	3.275	2625998	182166	23.814	37.687
3	5.040	602644	25075	5.465	5.188
4	5.895	6769525	226361	61.391	46.830
5	8.721	40168	1232	0.364	0.255
6	10.014	120439	2727	1.092	0.564
7	16.448	31426	709	0.285	0.147
8	17.698	177240	1856	1.607	0.384
9	21.105	119769	1175	1.086	0.243
Total		11026898	483364	100.000	100.000

d.r. = 61.391 / (61.391+1.086) = 98.2 : 1.8

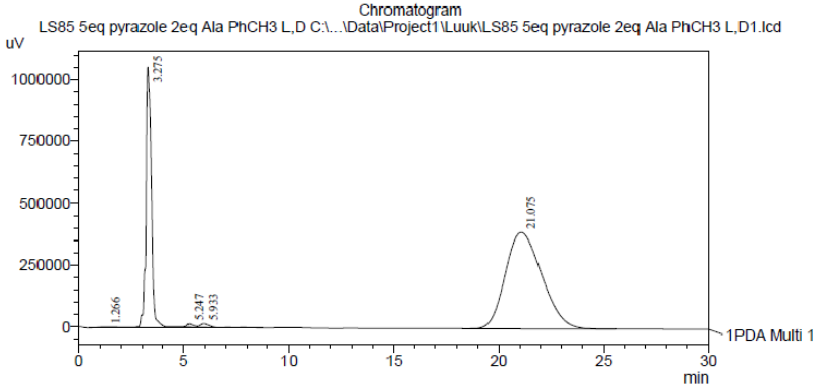
d.e. = 96.5%



3l

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: LS85 5eq pyrazole 2eq Ala PhCH	Heptane	
Sample ID	: LS85 5eq pyrazole 2eq Ala PhCH	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: LS85 5eq pyrazole 2eq Ala PhCH	B.Conc	:30.0 %
Method File Name	: Remko1.lcm	C.Conc	:0.0 %
Batch File Name	:	D.Conc	:0.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 5/11/2017 10:42:33 AM	PressMin	:0 bar
Data Processed	: 5/11/2017 11:12:35 AM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

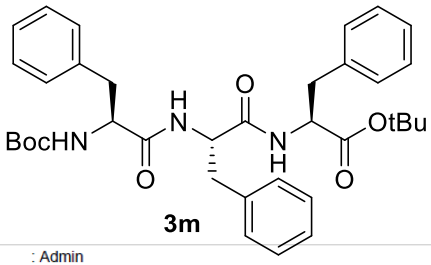
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	1.266	292438	3345	0.431	0.226
2	3.275	19416777	1055331	28.643	71.448
3	5.247	266475	13301	0.393	0.901
4	5.933	443156	15065	0.654	1.020
5	21.075	47370249	390012	69.879	26.405
Total		67789096	1477054	100.000	100.000

d.r. = 69.879 / (69.879+0.654) = 99.1 : 0.9

d.e.= 98.2%



3m

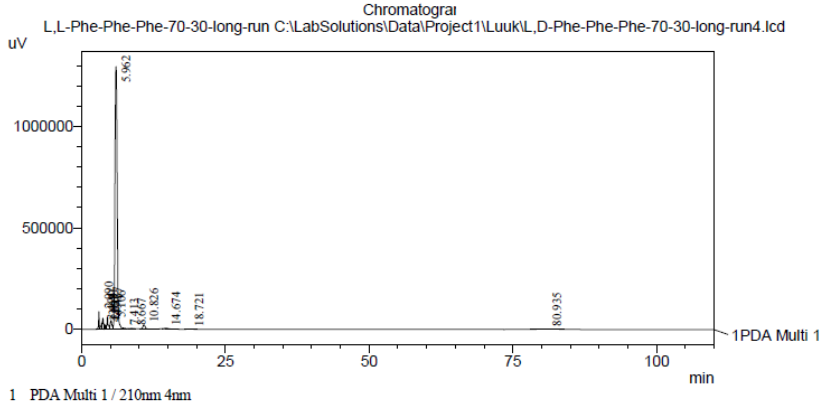
Acquired by	: Admin
Sample Name	: L,L-Phe-Phe-Phe-70-30-long-run
Sample ID	: L,L-Phe-Phe-Phe-70-30-long-run
Vail #	:
Injection Volume	: 10 uL
Data File Name	: L,D-Phe-Phe-Phe-70-30-long-run
Method File Name	: Remko1.lcm
Batch File Name	:
Report File Name	: remko-report.lcr
Data Acquired	: 6/21/2017 12:02:51 PM
Data Processed	: 6/21/2017 1:52:55 PM

Method

[Pump A Mobile Phase A]
Heptane
Pump A: Heptane, B: 2-Propanol

Pump A	:LC-20AD
Total Flow	:1.0000 mL/min
B.Conc	:0.0 %
C.Conc	:70.0 %
D.Conc	:30.0 %
PressMax	:100 bar
PressMin	:0 bar

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

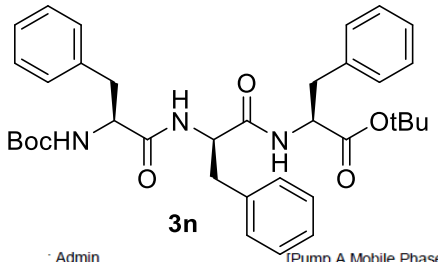
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.990	698151	87161	1.750	5.321
2	3.494	412671	31801	1.035	1.941
3	3.681	660218	54406	1.655	3.321
4	3.893	303779	24567	0.762	1.500
5	4.201	242071	18950	0.607	1.157
6	4.457	792245	55761	1.986	3.404
7	5.106	882275	41793	2.212	2.551
8	5.962	34639903	1294463	86.849	79.025
9	7.413	12032	872	0.030	0.053
10	8.667	59110	2228	0.148	0.136
11	10.826	565190	19592	1.417	1.196
12	14.674	177261	3790	0.444	0.231
13	18.721	61451	926	0.154	0.057
14	80.935	378733	1729	0.950	0.106
Total		39885091	1638039	100.000	100.000

d.r. = 86.849 / (86.849 + 0.950) = 98.94 : 1.06

d.e. = 97.8%



3n

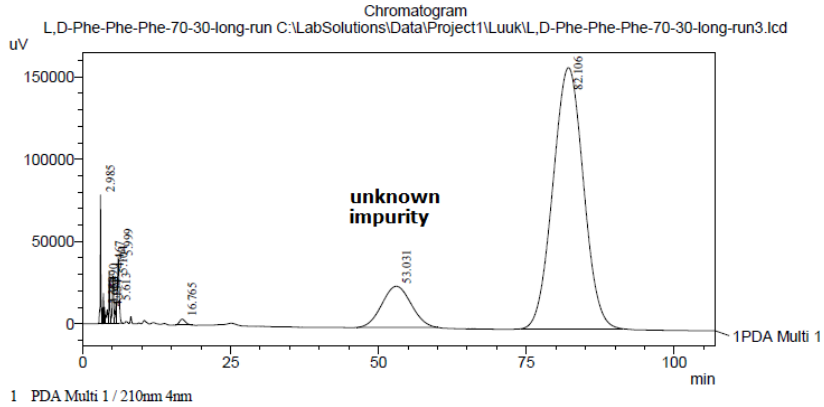
Acquired by	: Admin
Sample Name	: L,D-Phe-Phe-Phe-70-30-long-run
Sample ID	: L,D-Phe-Phe-Phe-70-30-long-run
Vail #	:
Injection Volume	: 10 uL
Data File Name	: L,D-Phe-Phe-Phe-70-30-long-run
Method File Name	: Remko1.lcm
Batch File Name	:
Report File Name	: remko-report.lcr
Data Acquired	: 6/21/2017 10:14:36 AM
Data Processed	: 6/21/2017 12:01:34 PM

Method

[Pump A Mobile Phase A]
Heptane
Pump A: Heptane, B: 2-Propanol

Pump A	:LC-20AD
Total Flow	:1.0000 mL/min
B.Conc	:0.0 %
C.Conc	:70.0 %
D.Conc	:30.0 %
PressMax	:100 bar
PressMin	:0 bar

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

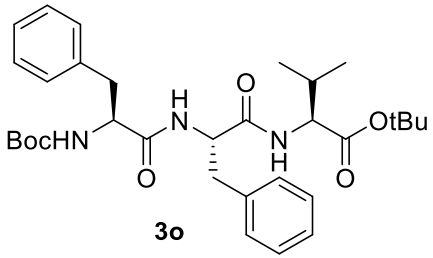
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.985	599327	78251	0.872	18.422
2	3.369	107124	9914	0.156	2.334
3	3.490	133465	18399	0.194	4.332
4	3.652	107797	10015	0.157	2.358
5	4.134	149650	8476	0.218	1.995
6	4.467	348812	31982	0.507	7.529
7	5.104	463475	28663	0.674	6.748
8	5.613	170036	12409	0.247	2.921
9	5.999	875084	39498	1.273	9.299
10	16.765	251683	3563	0.366	0.839
11	53.031	8622660	25035	12.544	5.894
12	82.106	56909731	158564	82.791	37.329
Total		68738845	424768	100.000	100.000

d.r. = 82.791 / (82.791 + 1.273) = 98.47 : 1.53

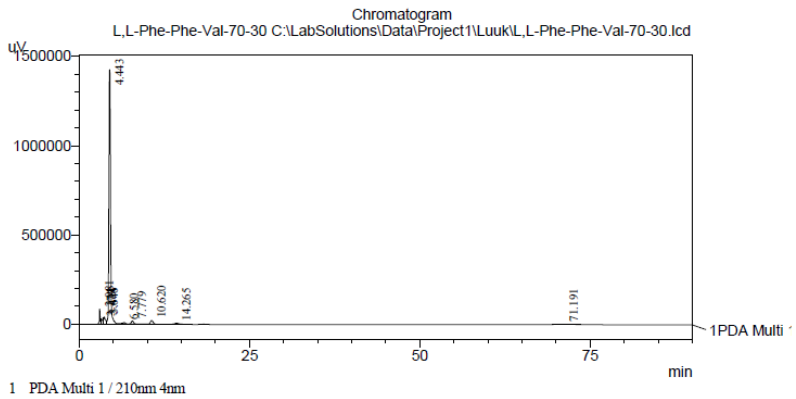
d.e. = 97.0%



3o

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,L-Phe-Phe-Val-70-30	Heptane	
Sample ID	: L,L-Phe-Phe-Val-70-30	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,L-Phe-Phe-Val-70-30.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:70.0 %
Batch File Name	:	D.Conc	:30.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 6/22/2017 3:08:10 PM	PressMin	:0 bar
Data Processed	: 6/22/2017 4:38:15 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

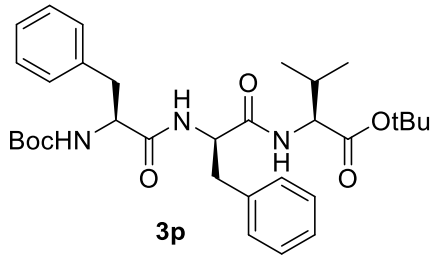
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.981	642746	86479	2.235	5.165
2	3.174	206980	31293	0.720	1.869
3	3.474	485111	36474	1.687	2.178
4	3.646	791863	41527	2.754	2.480
5	4.443	24952093	1425760	86.783	85.151
6	6.580	163184	7107	0.568	0.424
7	7.779	406630	17725	1.414	1.059
8	10.620	586651	20797	2.040	1.242
9	14.265	331633	6046	1.153	0.361
10	71.191	185493	1178	0.645	0.070
Total		28752383	1674386	100.000	100.000

d.r. = 86.783 / (86.783 + 0.645) = 99.26 : 0.76

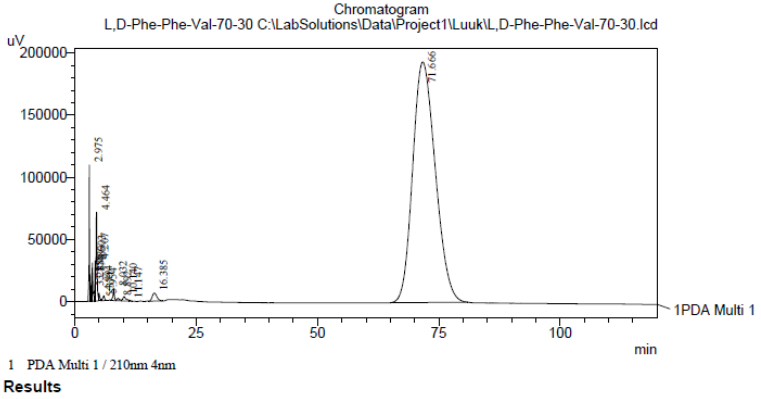
d.e. = 98.5%



3p

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,D-Phe-Phe-Val-70-30	Heptane	
Sample ID	: L,D-Phe-Phe-Val-70-30	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,D-Phe-Phe-Val-70-30.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:70.0 %
Batch File Name	:	D.Conc	:30.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 6/21/2017 2:28:23 PM	PressMin	:0 bar
Data Processed	: 6/21/2017 4:28:27 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

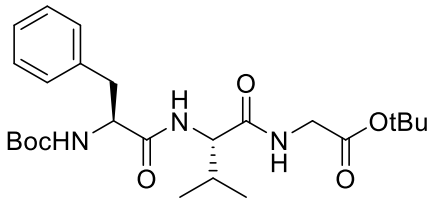
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.975	847895	109653	1.268	21.118
2	3.158	89668	14614	0.134	2.815
3	3.288	82604	10611	0.124	2.043
4	3.480	134347	22548	0.201	4.342
5	3.603	338576	30747	0.506	5.921
6	4.207	418971	32441	0.626	6.248
7	4.464	1006654	71412	1.505	13.753
8	4.994	100617	6097	0.150	1.174
9	5.371	16328	1281	0.024	0.247
10	5.954	97836	3980	0.146	0.766
11	8.032	193852	9586	0.290	1.846
12	8.892	77949	1950	0.117	0.376
13	10.140	165473	3545	0.247	0.683
14	11.147	17088	824	0.026	0.159
15	16.385	426495	6453	0.638	1.243
16	71.666	62861100	193505	93.997	37.267
Total		66875453	519247	100.000	100.000

d.r. = 93.997 / (93.997 + 1.505) = 98.42 : 1.58

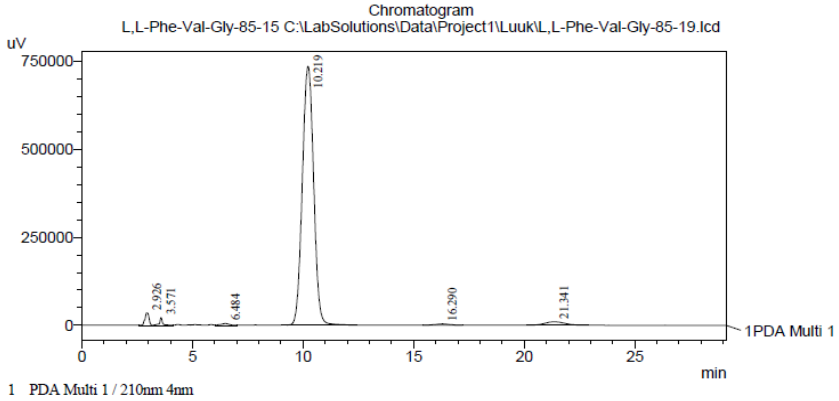
d.e. = 96.8%



3q

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,L-Phe-Val-Gly-85-15	Heptane	
Sample ID	: L,L-Phe-Val-Gly-85-15	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,L-Phe-Val-Gly-85-19.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:85.0 %
Batch File Name	:	D.Conc	:15.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 6/28/2017 4:11:24 PM	PressMin	:0 bar
Data Processed	: 6/28/2017 4:40:32 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

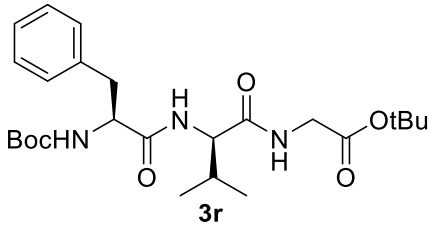
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.926	461590	35685	1.654	4.390
2	3.571	238926	22470	0.856	2.764
3	6.484	150181	5362	0.538	0.660
4	10.219	26241269	735825	94.053	90.515
5	16.290	172413	3626	0.618	0.446
6	21.341	636072	9960	2.280	1.225
Total		27900451	812929	100.000	100.000

d.r. = 94.053 / (94.053 + 0.618) = 99.35 : 0.65

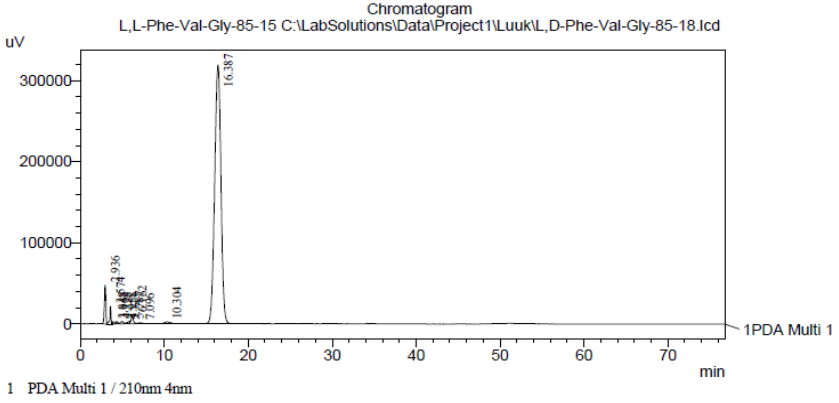
d.e. = 98.7%



3r

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,L-Phe-Val-Gly-85-15	Heptane	
Sample ID	: L,L-Phe-Val-Gly-85-15	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,D-Phe-Val-Gly-85-18.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:85.0 %
Batch File Name	:	D.Conc	:15.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 6/28/2017 2:48:39 PM	PressMin	:0 bar
Data Processed	: 6/28/2017 4:05:26 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

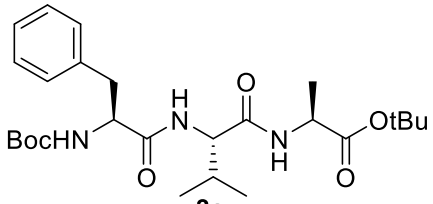
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.936	600664	47986	3.343	11.434
2	3.574	217913	22177	1.213	5.284
3	3.818	19417	2931	0.108	0.698
4	3.962	36414	2960	0.203	0.705
5	4.325	61403	3441	0.342	0.820
6	4.958	71091	3137	0.396	0.748
7	5.323	10153	1159	0.057	0.276
8	5.787	68658	3175	0.382	0.757
9	6.162	187441	10547	1.043	2.513
10	7.096	29551	1099	0.164	0.262
11	10.304	96374	1962	0.536	0.468
12	16.387	16566255	319085	92.212	76.034
Total		17965335	419659	100.000	100.000

d.r. = 92.212 / (92.212 + 0.536) = 99.42 : 0.58

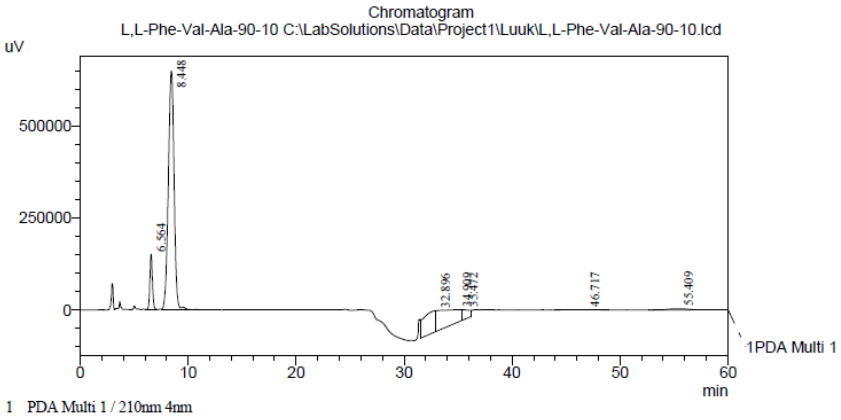
d.e. = 98.8%



3s

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,L-Phe-Val-Ala-90-10	Heptane	
Sample ID	: L,L-Phe-Val-Ala-90-10	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,L-Phe-Val-Ala-90-10.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:90.0 %
Batch File Name	:	D.Conc	:10.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 6/29/2017 12:35:23 PM	PressMin	:0 bar
Data Processed	: 6/29/2017 1:35:25 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

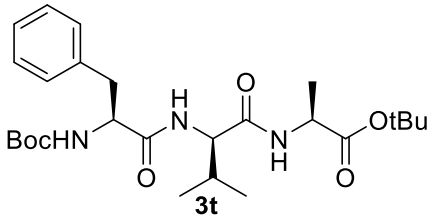
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.564	2547019	151349	6.518	16.379
2	8.448	24029358	649418	61.488	70.280
3	32.896	4659855	57149	11.924	6.185
4	34.909	6140193	34556	15.712	3.740
5	35.472	1160391	27305	2.969	2.955
6	46.717	135514	1136	0.347	0.123
7	55.409	407135	3128	1.042	0.339
Total		39079465	924041	100.000	100.000

d.r. = 61.488 / (61.488+1.042) = 98.33 : 1.67

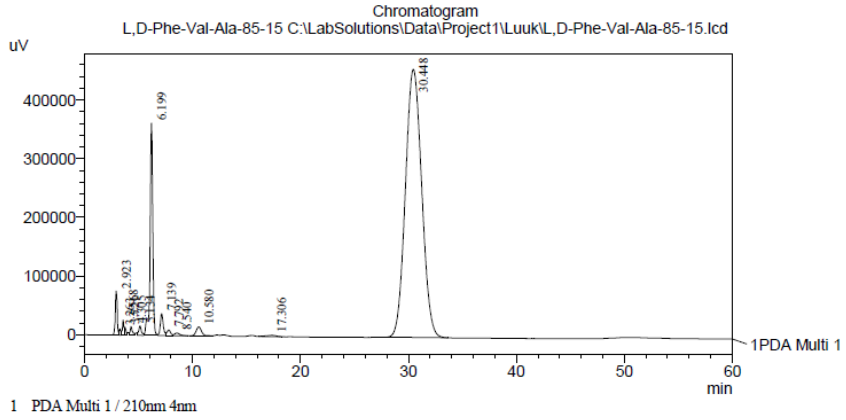
d.e. = 96.7%



3t

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,D-Phe-Val-Ala-85-15	Heptane	
Sample ID	: L,D-Phe-Val-Ala-85-15	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,D-Phe-Val-Ala-85-15.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:85.0 %
Batch File Name	:	D.Conc	:15.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 6/29/2017 9:15:48 AM	PressMin	:0 bar
Data Processed	: 6/29/2017 10:15:51 AM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

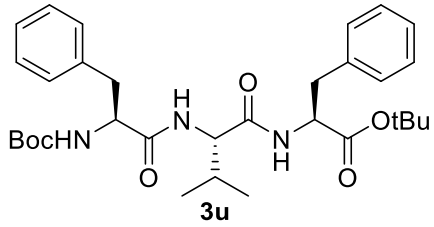
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.923	930734	74891	1.606	7.172
2	3.263	105509	10550	0.182	1.010
3	3.568	240599	25648	0.415	2.456
4	3.721	159298	13782	0.275	1.320
5	4.305	209842	14875	0.362	1.425
6	5.134	279464	16071	0.482	1.539
7	6.199	6328099	362274	10.917	34.695
8	7.139	704926	37182	1.216	3.561
9	7.792	228556	9672	0.394	0.926
10	8.540	160059	4678	0.276	0.448
11	10.580	518256	15115	0.894	1.448
12	17.306	156226	2350	0.270	0.225
13	30.448	47944786	457081	82.711	43.775
Total		57966353	1044168	100.000	100.000

d.r. = 82.711 / (82.711+1.216) = 98.55 : 1.45

d.e. = 97.1%

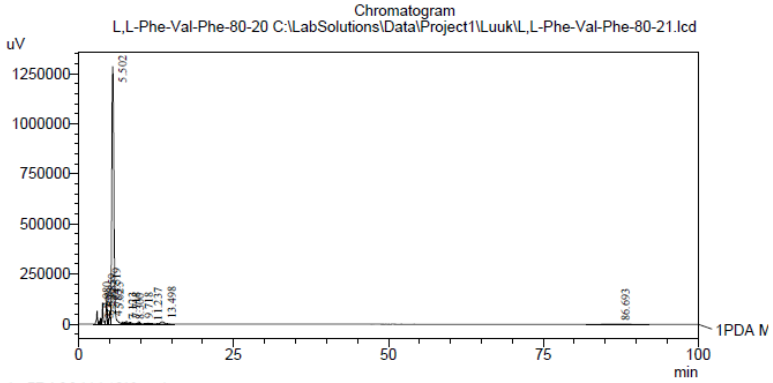


3u

Method

Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,L-Phe-Val-Phe-80-20	Heptane	
Sample ID	: L,L-Phe-Val-Phe-80-20	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,L-Phe-Val-Phe-80-21.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:80.0 %
Batch File Name	:	D.Conc	:20.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 7/13/2017 12:54:35 PM	PressMin	:0 bar
Data Processed	: 7/13/2017 2:34:38 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

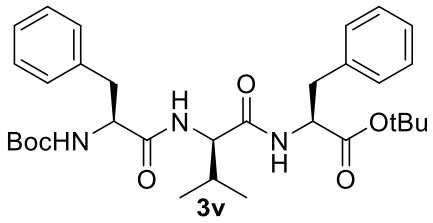
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.980	729792	65310	1.939	3.683
2	3.362	129207	14314	0.343	0.807
3	3.526	286693	28368	0.762	1.600
4	3.859	1007812	105925	2.677	5.973
5	4.519	1628750	133729	4.327	7.540
6	4.783	263759	27153	0.701	1.531
7	5.025	626758	62195	1.665	3.507
8	5.502	31309410	1286257	83.179	72.526
9	7.123	108713	6060	0.289	0.342
10	7.718	211953	10325	0.563	0.582
11	8.300	191486	7142	0.509	0.403
12	9.718	247643	11322	0.658	0.638
13	11.237	116246	3275	0.309	0.185
14	13.498	471258	11073	1.252	0.624
15	86.693	311467	1060	0.827	0.060
Total		37640947	1773507	100.000	100.000

d.r. = 83.179 / (83.179+0.827) = 99.01 : 0.99

d.e. = 98.0%

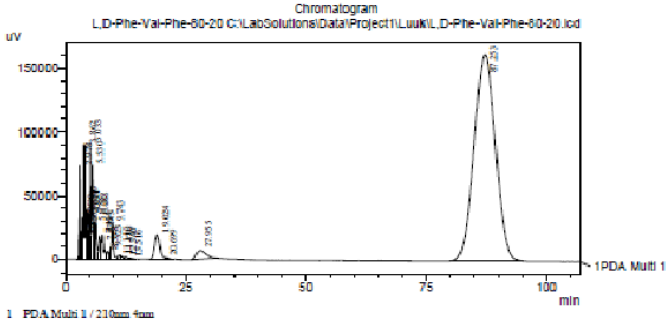


3v

Method

Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,D-Phe-Val-Phe-80-20	Heptane	
Sample ID	: L,D-Phe-Val-Phe-80-20	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,D-Phe-Val-Phe-80-20.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:80.0 %
Batch File Name	:	D.Conc	:20.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 7/13/2017 11:05:36 AM	PressMin	:0 bar
Data Processed	: 7/13/2017 12:53:34 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

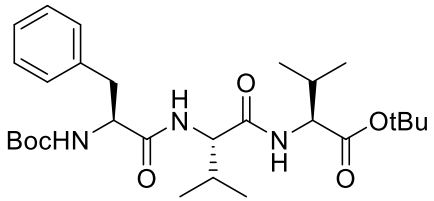
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.833	165457	20026	0.263	2.202
2	2.978	597767	73565	0.950	8.090
3	3.190	129933	19076	0.206	2.098
4	3.362	249013	22557	0.396	2.480
5	3.530	374806	32969	0.595	3.625
6	3.862	930373	90311	1.478	9.931
7	4.156	126274	18683	0.201	2.054
8	4.299	374177	38550	0.594	4.239
9	4.621	522533	35905	0.830	3.948
10	4.797	346965	35717	0.550	3.928
11	5.033	1035213	91200	1.645	10.029
12	5.530	1550441	73944	2.463	8.131
13	5.922	411177	28800	0.653	3.167
14	6.286	846732	34066	1.345	3.746
15	7.134	394457	18757	0.627	2.063
16	7.435	112994	13622	0.180	1.498
17	7.743	515676	19469	0.819	2.143
18	8.558	242222	6710	0.385	0.738
19	9.323	195024	8577	0.310	0.943
20	9.743	755825	28291	1.217	3.111
21	11.110	97795	3159	0.155	0.347
22	11.476	58244	2948	0.155	0.324
23	12.340	83321	2066	0.132	0.227
24	13.516	56251	954	0.089	0.105
25	19.024	1566559	19709	2.489	2.167
26	25.698	22451	535	0.036	0.059
27	27.955	1015967	7363	1.620	0.812
28	87.253	50116999	151983	79.618	17.813
Total		62947153	909376	100.000	100.000

d.r = 79.618 / (79.618+2.463) = 97.00 : 3.00

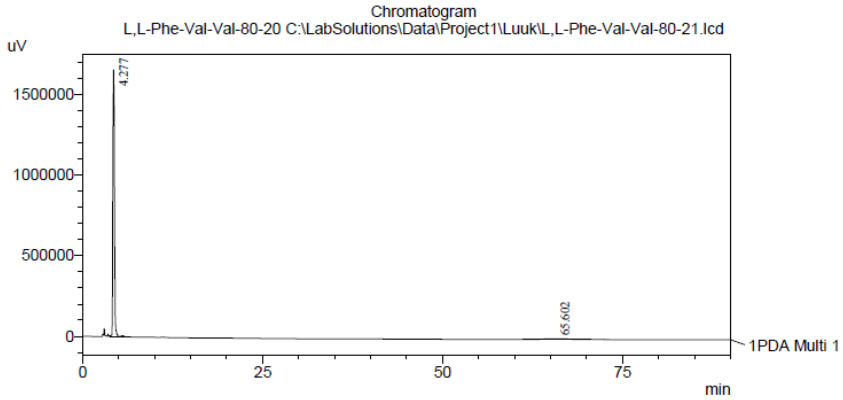
d.e. = 94.0%



3w

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,L-Phe-Val-Val-80-20	Heptane	
Sample ID	: L,L-Phe-Val-Val-80-20	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,L-Phe-Val-Val-80-21.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:80.0 %
Batch File Name	:	D.Conc	:20.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 7/14/2017 8:41:13 AM	PressMin	:0 bar
Data Processed	: 7/14/2017 10:11:16 AM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

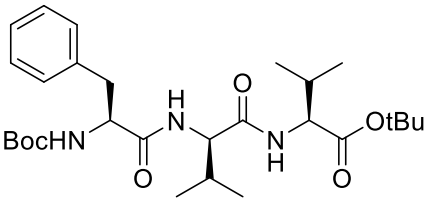
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.277	25665737	1653530	95.397	99.679
2	65.602	1238468	5323	4.603	0.321
Total		26904205	1658854	100.000	100.000

d.r. = 95.40 : 4.60

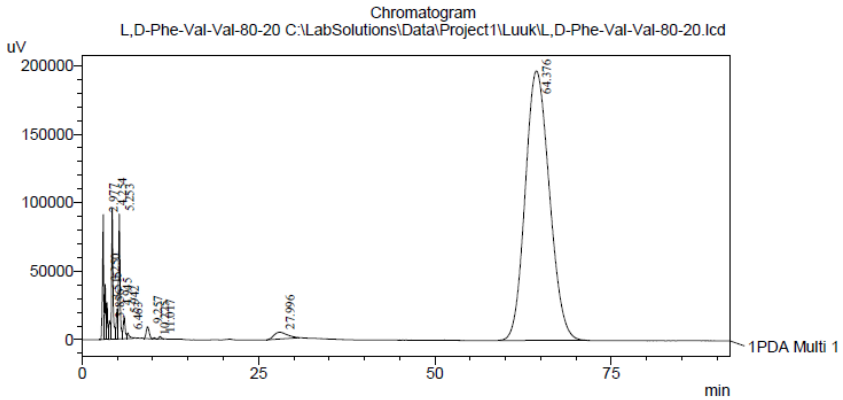
d.e. = 90.8%



3x

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,D-Phe-Val-Val-80-20	Heptane	
Sample ID	: L,D-Phe-Val-Val-80-20	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,D-Phe-Val-Val-80-20.lcd	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:80.0 %
Batch File Name	:	D.Conc	:20.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 7/13/2017 2:57:20 PM	PressMin	:0 bar
Data Processed	: 7/13/2017 4:29:12 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

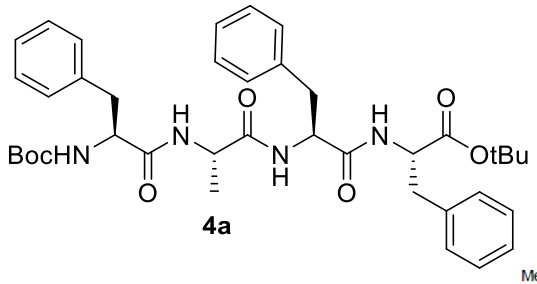
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.977	1041664	91152	1.956	14.850
2	3.250	447329	40221	0.840	6.552
3	3.515	243020	26879	0.456	4.379
4	3.856	238781	13768	0.448	2.243
5	4.254	1330765	95468	2.499	15.553
6	4.945	316652	22026	0.595	3.588
7	5.253	1311231	91251	2.463	14.866
8	5.942	311766	16177	0.586	2.635
9	6.463	102908	4146	0.193	0.675
10	9.257	257540	8667	0.484	1.412
11	10.225	12982	744	0.024	0.121
12	11.017	41647	1820	0.078	0.296
13	27.996	655751	4975	1.232	0.810
14	64.376	46931176	196543	88.145	32.019
Total		53243210	613837	100.000	100.000

d.r. = 88.145 / (88.145 + 2.499) = 97.24 : 2.76

d.e. = 94.5%

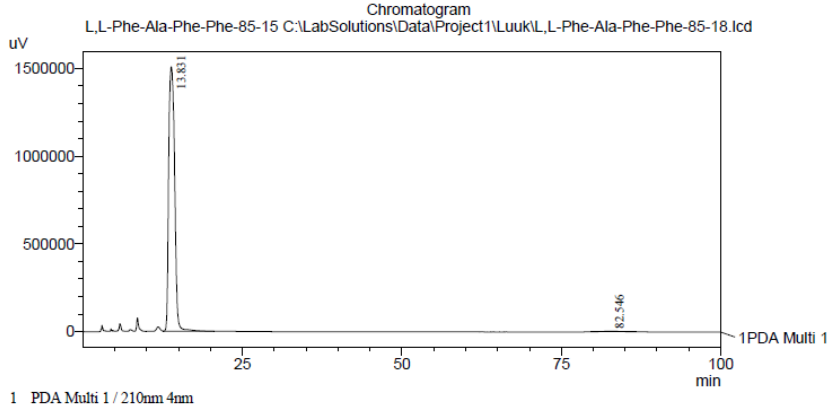


4a

Method

Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,L-Phe-Ala-Phe-Phe-85-15	Heptane	
Sample ID	: L,L-Phe-Ala-Phe-Phe-85-15	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,L-Phe-Ala-Phe-Phe-85-18.lcd	B.Conc	:0.0 %
Method File Name	: Remko2.lcm	C.Conc	:85.0 %
Batch File Name	:	D.Conc	:15.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 8/23/2017 1:18:12 PM	PressMin	:0 bar
Data Processed	: 8/23/2017 2:58:14 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

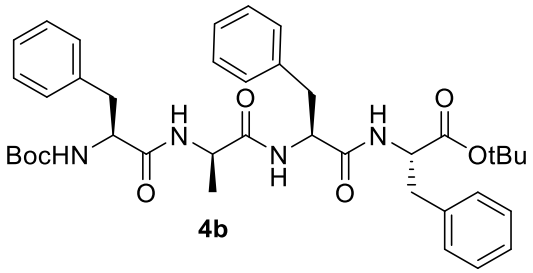
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.831	98314689	1507375	99.241	99.790
2	82.546	751782	3171	0.759	0.210
Total		99066471	1510546	100.000	100.000

d.r. = 99.24 : 0.76

d.e. = 98.5%

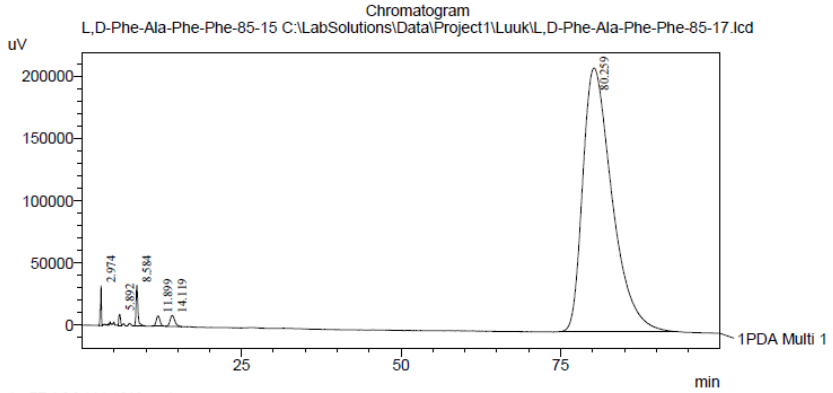


4b

Method

Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,D-Phe-Ala-Phe-Phe-85-15	Heptane	
Sample ID	: L,D-Phe-Ala-Phe-Phe-85-15	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,D-Phe-Ala-Phe-Phe-85-17.lcd	B.Conc	:0.0 %
Method File Name	: Remko2.lcm	C.Conc	:85.0 %
Batch File Name	:	D.Conc	:15.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 8/23/2017 11:37:09 AM	PressMin	:0 bar
Data Processed	: 8/23/2017 1:17:05 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

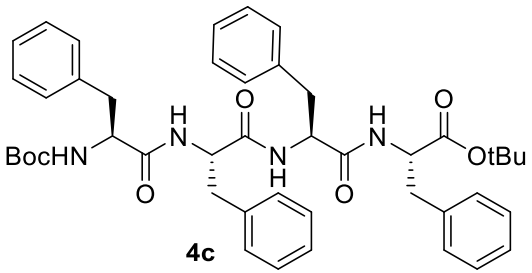
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.974	339475	31905	0.487	10.512
2	5.892	184700	9309	0.265	3.067
3	8.584	676293	32799	0.970	10.807
4	11.899	338873	8405	0.486	2.769
5	14.119	468274	8894	0.672	2.930
6	80.259	67697107	212197	97.120	69.915
Total		69704722	303509	100.000	100.000

d.r. = 97.120 / (97.120 + 0.672) = 99.31 : 0.69

d.e. = 98.6%

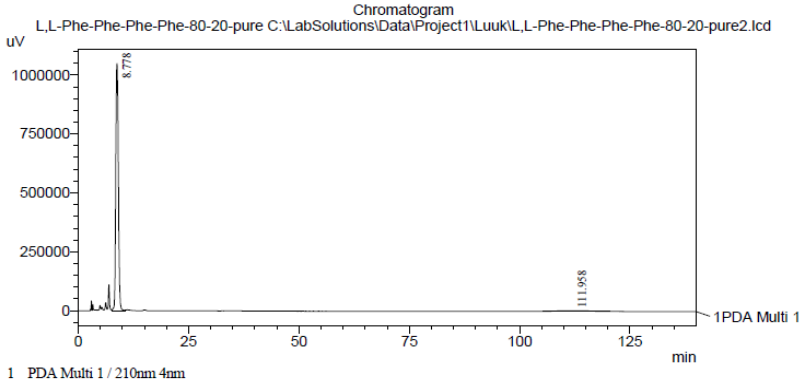


4c

Method

Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,L-Phe-Phe-Phe-Phe-80-20-pure	Heptane	
Sample ID	: L,L-Phe-Phe-Phe-Phe-80-20-pure	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,L-Phe-Phe-Phe-Phe-80-20-pure	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:80.0 %
Batch File Name	:	D.Conc	:20.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 7/21/2017 12:31:48 PM	PressMin	:0 bar
Data Processed	: 7/21/2017 2:51:51 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

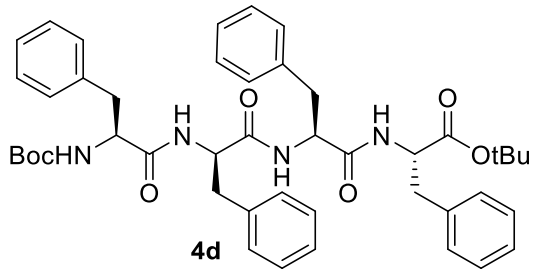
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.778	42829882	1048443	96.517	99.699
2	111.958	1545742	3169	3.483	0.301
Total		44375624	1051612	100.000	100.000

d.r. = 96.52 : 3.48

d.e. = 93.0%

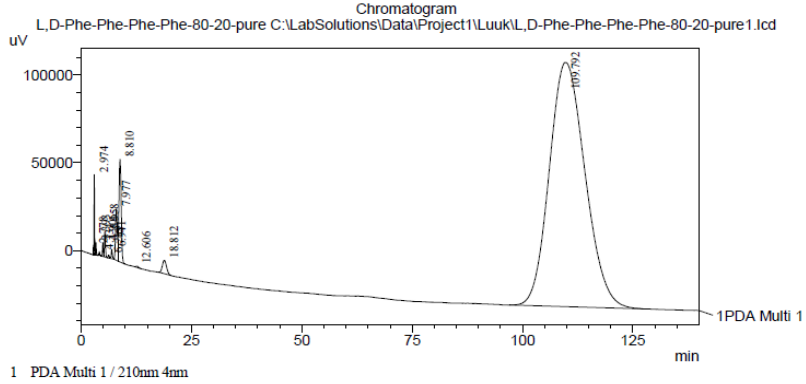


4d

Method

Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,D-Phe-Phe-Phe-Phe-80-20-pure	Heptane	
Sample ID	: L,D-Phe-Phe-Phe-Phe-80-20-pure	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,D-Phe-Phe-Phe-Phe-80-20-pure	B.Conc	:0.0 %
Method File Name	: Remko1.lcm	C.Conc	:80.0 %
Batch File Name	:	D.Conc	:20.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 7/21/2017 9:58:15 AM	PressMin	:0 bar
Data Processed	: 7/21/2017 12:18:17 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

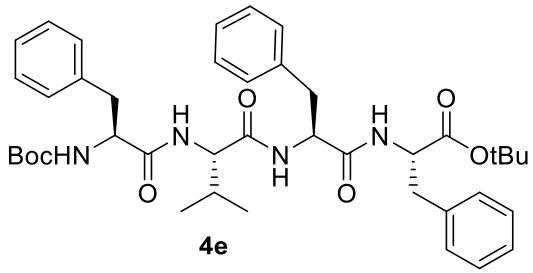
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	2.778	31092	5507	0.038	1.697
2	2.974	305794	45593	0.370	14.053
3	3.393	45614	7000	0.055	2.158
4	4.131	20690	2269	0.025	0.699
5	4.906	98037	7897	0.119	2.434
6	5.358	235214	14132	0.285	4.356
7	6.219	32303	1687	0.039	0.520
8	6.941	95852	5312	0.116	1.637
9	7.977	812770	29273	0.984	9.023
10	8.810	2075367	58385	2.512	17.996
11	12.606	26749	715	0.032	0.220
12	18.812	500870	7623	0.606	2.350
13	109.792	78347031	139044	94.820	42.857
Total		82627385	324438	100.000	100.000

d.r = 94.820 / (94.820 + 2.512) = 97.42 : 2.58

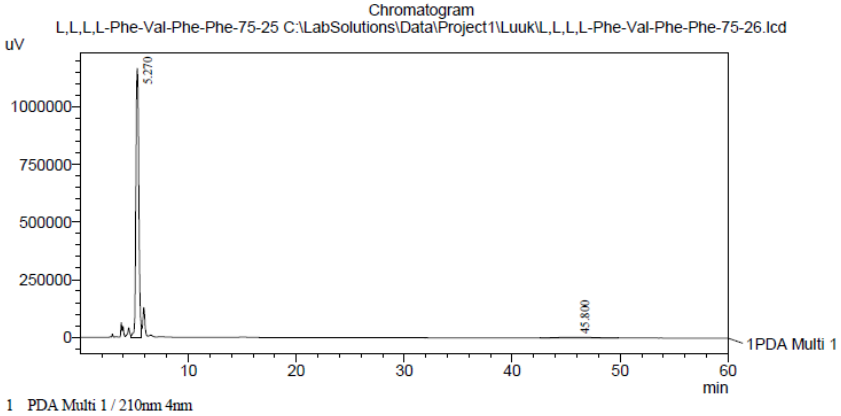
d.e. = 94.8%



4e

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,L,L,L-Phe-Val-Phe-Phe-75-25	Heptane	
Sample ID	: L,L,L,L-Phe-Val-Phe-Phe-75-25	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,L,L,L-Phe-Val-Phe-Phe-75-26.lc	B.Conc	:0.0 %
Method File Name	: Remko2.lcm	C.Conc	:75.0 %
Batch File Name	:	D.Conc	:25.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 9/20/2017 12:52:36 PM	PressMin	:0 bar
Data Processed	: 9/20/2017 1:52:38 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

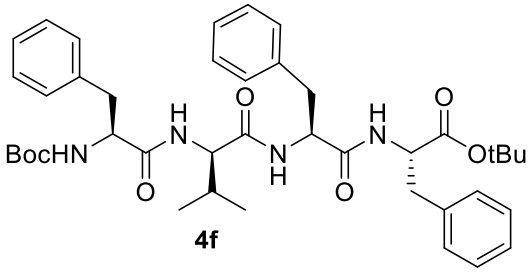
PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.270	22080489	1167336	97.307	99.751
2	45.800	611023	2916	2.693	0.249
Total		22691512	1170252	100.000	100.000

d.r. = 97.31 : 2.69

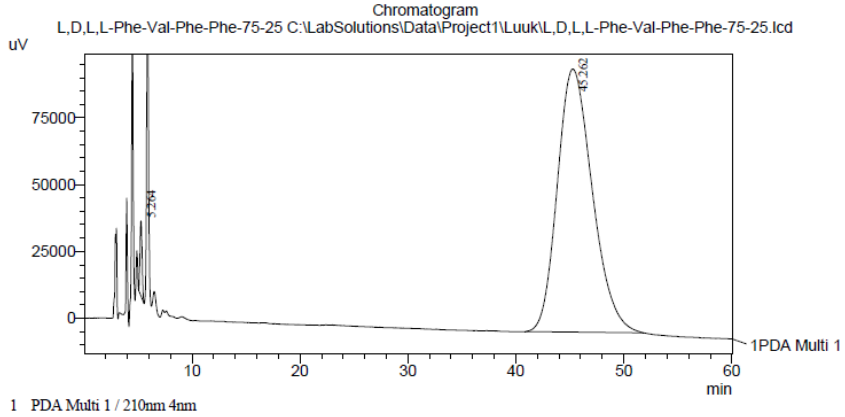
d.e. = 94.6%



4f

		Method	
Acquired by	: Admin	[Pump A Mobile Phase A]	
Sample Name	: L,D,L,L-Phe-Val-Phe-Phe-75-25	Heptane	
Sample ID	: L,D,L,L-Phe-Val-Phe-Phe-75-25	Pump A: Heptane, B: 2-Propanol	
Vail #	:	Pump A	:LC-20AD
Injection Volume	: 10 uL	Total Flow	:1.0000 mL/min
Data File Name	: L,D,L,L-Phe-Val-Phe-Phe-75-25.l	B.Conc	:0.0 %
Method File Name	: Remko2.lcm	C.Conc	:75.0 %
Batch File Name	:	D.Conc	:25.0 %
Report File Name	: remko-report.lcr	PressMax	:100 bar
Data Acquired	: 9/20/2017 11:42:39 AM	PressMin	:0 bar
Data Processed	: 9/20/2017 12:42:42 PM		

Chromatogram



1 PDA Multi 1 / 210nm 4nm

Results

PeakTable

PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.264	381637	28057	1.686	22.176
2	45.262	22255705	98460	98.314	77.824
Total		22637343	126517	100.000	100.000

d.r. = 98.31 : 1.69

d.e. = 96.6%