Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Generation and reaction of alanyl radicals in open flasks

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General Information

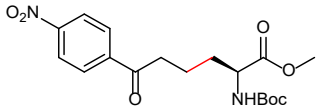
CAUTION: Although we had no incidents relating to the stability of the diazonium salts used in this work, care was taken to avoid the use of metal needles and spatulas.

All reactions were performed under air using plastic tubing, plastic syringes, and oven-dried glassware. Dimethylsulfoxide (DMSO) was dried over 3 Å molecular sieves. All other solvents and reagents were used as received from commercial sources. Melting points were determined using a Stanford Research Systems Optimelt automated melting point system and are uncorrected. Infrared spectra were acquired on a Bruker ALPHA FT-IR spectrometer as thin films, or neat. Absorption maxima are expressed in wavenumbers (cm^{-1}). Optical rotations were obtained on a Perkin-Elmer 341 polarimeter at 589 nm and 20 °C. Nuclear magnetic resonance (NMR) spectroscopy was conducted at 300 K on either a Bruker AVANCE DPX300 (1H at 300 MHz), AVANCE III 400 (1H at 400 MHz) or AVANCE III 500 (1H at 500 MHz) and processed using Bruker TopSpin 3.2 or 3.5pl7. Deuterated solvents $CDCl_3$, MeCN-d_3, MeOD-d_4, DMSO-d_6 and $(CD_3)_2CO$, were obtained from Cambridge Isotope Laboratories. Chemical shifts for all nuclei are reported as parts per million (ppm) and all coupling constants are reported in hertz (Hz) unless otherwise stated. ^1H NMR data are reported as chemical shift (ppm); relative integral; multiplicity, coupling constant (*J*), reported in Hz; chemical assignment. Chemical shifts are calibrated to residual solvent peaks: chloroform (δ = 7.26), acetone (δ = 2.05), DMSO (δ = 2.50), acetonitrile (δ = 1.94), methanol (δ = 3.31). $^{13}C\{^1H\}$ data is reported as chemical shift (ppm); degree of substitution, determined by HSQC analysis; coupling constant (if applicable) in Hz. Chemical shifts are calibrated to the residual solvent peaks: chloroform (δ = 77.16), acetone (δ = 206.26 or 29.84), DMSO (δ = 39.52), acetonitrile (δ = 118.26 or 1.32), methanol (δ = 49.00). Multiplicity is reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad and reported in decreasing magnitude of coupling constant (e.g. dt = doublet of triplets). Low-resolution mass spectrometry was carried out on a Finnigan PolarisQ ion trap mass spectrometer using the ionization mode electron impact (EI) at 40 or 70 eV or a Finnigan LCQ ion trap mass spectrometer using the ionization modes electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI). High-resolution mass spectrometry was conducted on a Bruker Apex II FTICR mass spectrometer with a 7.0 T magnet fitted with an off-axis analytical electrospray source. Column chromatography was performed using Grace Davison, Merck, or Scharlau 40-60 μm (230-400 mesh) silica gel using commercial solvents. Analytical thin-layer chromatography was performed using preconditioned plates (Merck TLC silica gel 60 F_{254} on aluminum) and visualized using UV light (254 nm and 365 nm), ethanolic anisaldehyde solution.

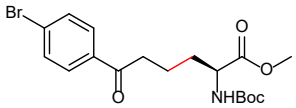
General Procedure for the reaction of iodoalanyl esters and peptides

To a solution of the desired alanyl iodide (0.35 mmol) and radical acceptor (0.70 mmol) in dry DMSO (0.2 mL), the solutions of 2,4,6-trimethylbenzenediazonium tetrafluoroborate (0.70 mmol) in dry DMSO (0.4 mL) and dibenzyl Hantzsch ester (0.70 mmol) in dry DMSO (0.4 mL) were added by syringes in one portion at room temperature under air. The resulting reaction mixture was stirred for 5 minutes and diluted with ethyl acetate (10 mL), water (20 mL) was added, and the mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over anhydrous sodium sulfate, concentrated under vacuum and the desired product was purified by column chromatography on silica get using hexane/ethyl acetate as eluent.

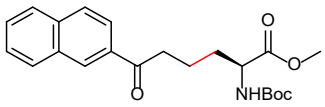
Product characterization data



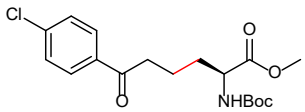
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-6-(4-nitrophenyl)-6-oxohexanoate (17): Eluent 35% ethyl acetate in hexane. Isolated as a yellow oil (56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (2H, d, J = 8.8 Hz), 8.10 (2H, d, J = 8.8 Hz), 5.11 (1H, d, J = 6.4 Hz), 4.36 (1H, d, J = 4.8 Hz), 3.75 (3H, s), 3.10-3.00 (2H, m), 1.94-1.71 (4H, m), 1.44 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 197.9, 173,0. 150.4, 141.3, 129.1, 123.9, 80.1, 53.1, 52.4, 38.3, 32.2, 29.8, 28.4, 19.6; ν_{max}/cm^{-1}: 3385, 2976, 1605, 1526, 1347, 1165, 855; HRMS (ESI) *m/z* $[M+Na]^+$ calc'd for $C_{18}H_{24}N_2O_7$: 403.14757; found: 403.14738; $[\alpha]_D^{25}$ +31 (c = 0.02, $CHCl_3$).



Methyl (*S*)-6-(4-bromophenyl)-2-((*tert*-butoxycarbonyl)amino)-6-oxohexanoate (18): Eluent 35% ethyl acetate in hexane. Isolated as a yellow oil (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (2H, d, J = 8.5 Hz), 7.58 (2H, d, J = 8.5 Hz), 5.11-5.13 (1H, m), 4.32-4.33 (1H, m), 3.72 (3H, s), 2.90-2.98 (2H, m), 1.81-1.89 (1H, m), 1.70-1.80 (3H, m), 1.42 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 198.4, 173.1, 155.4, 135.6, 131.9, 129.5, 128.2, 79.9, 53.1, 52.3, 37.6, 32.1, 29.7, 28.3, 19.8; ν_{max}/cm^{-1}: 3369, 2975, 2932, 1710, 1687, 1365, 1250, 1208, 1163, 1070, 815; HRMS (ESI) *m/z* $[M+Na]^+$ calc'd for $C_{18}H_{24}{}^{79}BrNO_5$ and $C_{18}H_{24}{}^{81}BrNO_5$: 436.07301 and 438.07096; found: 436.07277 and 438.07072. $[\alpha]_D^{25}$ +36 (c = 0.02, $CHCl_3$).

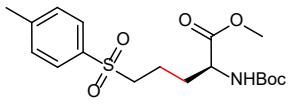


Methyl (S)-2-((*tert*-butoxycarbonyl)amino)-6-(naphthalen-2-yl)-6-oxohexanoate (19): Eluent 25% ethyl acetate in hexane. Isolated as a yellow oil (64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.4 (1H, s), 8.00 (1H, d, J = 10 Hz), 7.95 (1H, d, J = 8.0 Hz), 7.86 (2H, t, J = 7.2 Hz), 7.60-7.52 (2H, m), 5.13 (1H, d, J = 7.2 Hz), 4.37 (1H, d, J = 4.0 Hz), 3.73 (3H, s), 3.16-3.11 (2H, m), 1.94-1.78 (4H, m), 1.44 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 199.4, 173.2, 155.5, 135.6, 134.2, 132.5, 129.7, 129.6, 128.5, 127.8, 126.8, 123.8, 79.9, 53.2, 52.3, 37.7, 32.2, 28.3, 20.0; ν_{max}/cm^{-1}: 3373, 2975, 1733, 1711, 1680, 1509, 1366, 1254, 1166; HRMS (ESI) *m/z:* 408.17791 $[M+Na]^+$ $[\alpha]_D^{25}$ +34 (c = 0.02, $CHCl_3$).

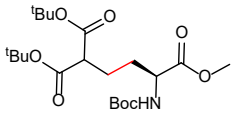


Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-6-(4-chlorophenyl)-6-oxohexanoate (20): Eluent 35% ethyl acetate in hexane. Isolated as a bright yellow oil (55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88-7.86 (2H, d, J = 8.4 Hz), 7.42-7.40 (2H, d, J = 8.4 Hz), 5.13-5.05 (1H, m), 4.34-

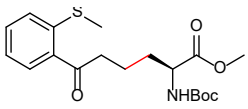
4.33 (1H, m), 3.73 (3H, s), 3.00-2.94 (2H, m), 1.90-1.71 (4H, m), 1.43 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 198.4, 173.2, 155.6, 139.7, 135.3, 129.6, 129.1, 80.1, 53.3, 52.5, 37.8, 32.3, 29.8, 28.5, 19.9; ν_{max}/cm^{-1}: 3367, 2953, 2933, 1742, 1710, 16851589, 1507, 1454, 1395, 1366, 1250, 1214, 1164, 1092, 1013; HRMS (ESI) *m/z* $[M+Na]^+$ calc'd for $C_{18}H_{24}ClNO_5$: 392.12352; found: 392.12341; $[\alpha]_D^{25}$ +5.95 (*c* = 0.63, $CHCl_3$)



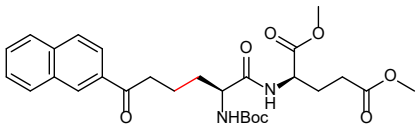
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-5-tosylpentanoate (21): Eluent 40% ethyl acetate in hexane. Isolated as a yellow oil (41%); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.76 (2H, d, *J* = 8.4 Hz), 7.34 (2H, d, *J* = 8.0 Hz), 5.05 (1H, d, *J* = 7.2 Hz), 5.24 (1H, d, *J* = 5.2 Hz), 3.70 (3H, s), 3.14-3.02 (2H, m), 2.44 (3H, s), 1.81-1.68 (4H, m), 1.41 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 172.6, 155.4, 144.8, 136.2, 130.0, 128.1, 80.2, 55.6, 52.8, 52.5, 31.5, 28.3, 27.9, 21.6, 19.1; ν_{max}/cm^{-1}: 3354, 2930, 1742, 1597, 1455, 1301, 1163, 1148, 564, 521; HRMS (ESI) *m/z* $[M+Na]^+$ calc'd for $C_{18}H_{27}NO_6S$: 408.14513; found: 408.14479; $[\alpha]_D^{25}$ +10.5 (*c* = 0.07, $CHCl_3$).



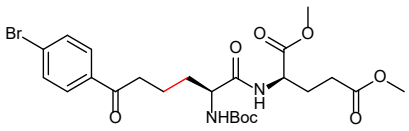
1,1-Di-*tert*-butyl 4-methyl (*S*)-4-((*tert*-butoxycarbonyl)amino)butane-1,1,4-tricarboxylate (22): Eluent 35% ethyl acetate in hexane. Isolated as a light-yellow oil (75%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 5.05 (1H, d, *J* = 7.6 Hz), 4.30 (1H, s), 3.73 (3H, s), 3.13 (1H, t, *J* = 7.2 Hz), 1.81-1.84 (3H, m), 1.45 (9H, s), 1.44 (9H, s), 1.43 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 172.7, 168.4, 168.3, 155.3, 81.5, 79.8, 53.2, 53.1, 52.3, 30.0, 28.3, 27.9, 24.4; ν_{max}/cm^{-1}: 2977, 1717, 1503, 1392, 1367, 1249, 1158, 1136, 848; HRMS (ESI+) *m/z* $[M+Na]^+$ calc'd for $C_{21}H_{37}NO_8$: 454.24114; found: 454.24087; $[\alpha]_D^{25}$ +15 (*c* = 0.02, $CHCl_3$).



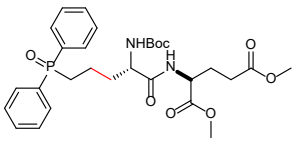
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-6-(2-(methylthio)phenyl)-6-oxohexanoate (23): Eluent 35% ethyl acetate in hexane. Isolated as a bright yellow oil (49%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.81-7.79 (1H, d, *J* = 8.0 Hz), 7.48-7.43 (1H, m), 7.32-7.30 (1H, d, *J* = 8.0 Hz), 7.19-7.15 (1H, m), 5.11-5.09 (1H, d, *J* = 8.0 Hz), 4.35-4.30 (1H, m), 3.72 (3H, s), 3.00-2.98 (2H, m), 2.42 (3H, s), 1.91-1.70 (4H, m), 1.43 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 200.7, 173.3, 155.5, 142.4, 134.4, 132.3, 130.2, 125.2, 123.6, 80.0, 55.9, 53.3, 52.4, 39.1, 32.2, 28.4, 20.1, 16.1; ν_{max}/cm^{-1}: 3364, 2925, 1740, 1707, 1671, 1619, 1587, 1558, 1511, 1453, 1434, 1391, 1365, 1272, 1249, 1215, 1163, 1078, 1047; HRMS (ESI) *m/z* $[M+Na]^+$ calc'd for $C_{19}H_{27}NO_5S$: 404.15021; found: 404.15041; $[\alpha]_D^{25}$ +4.58 (*c* = 1.0, $CHCl_3$).



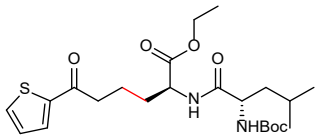
Dimethyl ((*S*)-2-((*tert*-butoxycarbonyl)amino)-6-(naphthalen-2-yl)-6-oxohexanoyl)-L-glutamate (25): Eluent 35% ethyl acetate in hexane. Isolated as a brown oil (72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.45 (1H, s), 7.99-8.01(1H, m), 7.94 (1H, d, J = 7.8 Hz), 7.84-7.87 (2H, m), 7.51-7.60 (2H, m), 7.24 (1H, d, (NH) J = 8.9 Hz), 5.36-5.38 (1H, m), 4.86-4.90 (1H, m), 4.22 (1H, brs (NH)), 3.73 (3H, s), 3.68 (3H, s), 3.31-3.37 (2H, m), 3.03 (1H, dd, J_1 = 4.6 Hz, J_2 = 17.1 Hz), 2.86 (1H, dd, J_1 = 5.6 Hz, J_2 = 17.4 Hz), 1.77-2.0 (2H, m), 1.45 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 199.7, 172.0, 171.3, 170.9, 155.6, 135.6, 134.2, 132.5, 129.7, 129.6, 128.4, 127.7, 126.7, 123.8, 80.0, 52.8, 52.0, 48.6, 37.9, 36.0, 32.1, 28.3, 20.0; ν_{max}/cm^{-1}: 3327, 2953, 2924, 2853, 1737, 1673, 1507, 1438, 1366, 1214, 1167, 477; ; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{27}H_{34}N_2O_8$: 537.22074; found: 537.22031; $[\alpha]_D^{25}$: -6.0 (c = 0.01, $CHCl_3$).



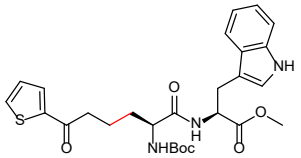
Dimethyl ((*S*)-6-(4-bromophenyl)-2-((*tert*-butoxycarbonyl)amino)-6-oxohexanoyl)-L-glutamate (26): Eluent 45% ethyl acetate in hexane. Isolated as an orange oil (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (2H, d, J = 8.6 Hz), 7.58 (2H, d, J = 8.6 Hz), 5.17-5.19 (1H, m), 4.55-4.62 (1H, m), 4.19 (1H, brs (NH)), 3.72 (3H, s), 3,65 (3H, s), 2.95-3.00 (2H, m), 2.35-2.42 (2H, m), 2.21-2.26 (2H, m), 1.96-2.00 (2H, m), 1.79-1.93 (2H, m), 1.44 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 198.7, 173.1, 172.1, 172.0, 155.6, 135.5, 131.9, 129.6, 128.3, 80.3, 52.5, 51.8, 51.6, 51.5, 37.7, 29.9, 29.7, 28.3, 27.2, 19.8; ν_{max}/cm^{-1}: 3342, 2954, 1737, 1681, 1518, 1438, 1366, 1248, 1207, 1166; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{24}H_{33}{}^{79}BrN_2O_8$ and $C_{24}H_{33}{}^{81}BrN_2O_8$: 579.13125 and 581.12921; found: 579.13079 and 581.12872.; $[\alpha]_D^{25}$ -15 (c = 0.06, $CHCl_3$).



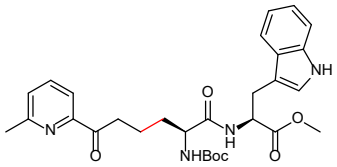
Dimethyl ((S)-2-((*tert*-butoxycarbonyl)amino)-5-(diphenylphosphoryl)pentanoyl)-L-glutamate (27): Isolated as an off-white solid (25%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64-7.69 (4H, m), 7.40-7.46 (6H, m), 5.52-5.53 (1H, m), 4.44-4.50 (1H, m), 4.21 (1H, m), 3.65 (3H, s), 3.61 (3H, s), 2.31-3.39 (3H, m), 2.12-2.16 (1H, m), 1.92-2.00 (2H, m), 1.66-1.72 (2H, m), 1.36 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 173.0, 172.3, 170.9, 132.7, 132.1, 131.8, 130.9, 130.8, 130.6, 130.5, 128.9, 128.8, 127.7, 128.6, 128.6, 79.7, 53.1, 52.3, 51.7, 51.5, 33.7, 30.0, 28.3, 27.0, 18.2; ν_{max}/cm^{-1}: 3321, 2975, 1718, 1500, 1396, 1249, 1150, 1137, 786; HRMS (ESI+) m/z $[M+Na]^+$ calc'd for $C_{29}H_{39}N_2O_8P$: 574.24440; found 574.24433; $[\alpha]_D^{25}$ -60 (c = 0.03, $CHCl_3$).



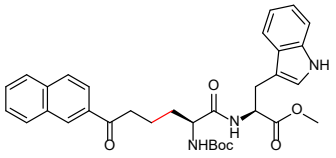
Ethyl (*S*)-2-((*S*)-2-((*tert*-butoxycarbonyl)amino)-4-methylpentanamido)-6-oxo-6-(thiophen-2-yl)hexanoate (28): Eluent 55% ethyl acetate in hexane. Isolated as a yellow oil (64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71-7.72 (1H, m), 7.61-7.62 (1H, m), 7.11-7.13 (1H, m), 6.69 (1H, d, J = 7.9 Hz), 4.88-4.90 (1H, m), 4.56-4.61 (1H, m), 4.19 (2H, q, J = 7.1 Hz), 2.91-2.96 (2H, m), 2.21-2.31 (2H, m), 1.75-1.82 (3H, m), 1.65-1.70 (2H, m), 1.43 (9H, s), 1.25-1.28 (3H, m), 0.93-0.96 (6H, m); ^{13}C NMR (101 MHz; $CDCl_3$): 192.4, 172.4, 171.9, 144.2, 133.5, 131.9, 128.1, 80.1, 61.6, 51.8, 38.3, 31.8, 29.7, 28.3, 24.7, 22.9, 19.9, 14.1; ν_{max}/cm^{-1}: 2955, 2921, 2850, 1663, 1519, 1456, 1417, 1367, 1249, 1167, 734; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{23}H_{36}N_2O_6S$:491.21863; found: 491.21906; $[\alpha]_D^{25}$ - 9.5 (c = 0.03, $CHCl_3$).



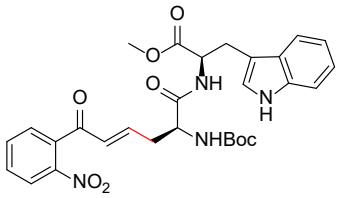
Methyl ((*S*)-2-((*tert*-butoxycarbonyl)amino)-6-oxo-6-(thiophen-2-yl)hexanoyl)-L-tryptophanate (29): Eluent 45% ethyl acetate in hexane. Isolated as a yellow oil (95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48 (1H, brs), 7.67 (1H, d, J = 4.4 Hz), 7.61 (1H, d, J = 5.2 Hz), 7.51 (1H, d, J = 7.6 Hz), 7.31 (1H, d, J = 8.0 Hz), 7.0-7.16 (4H, m), 6.77-6.80 (1H, m), 5.16 (1H, m), 1.64-1.80 (4H, m), 1.41 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 20.3, 27.6, 28.3, 32.0, 38.5, 52.4, 52.9, 80.1, 109.7, 111.4, 118.5, 119.6, 122.1, 123.2, 127.6, 128.2, 132.1, 133.6, 136.2, 144.2, 156.6, 171.7, 172.1, 192.9; ν_{max}/cm^{-1}: 3337, 2975, 1741, 1694, 1660, 1517, 1416, 1366, 1247, 1212, 1167, 742; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{27}H_{33}N_3O_6S$: 550.19823; found: 550.19833; $[\alpha]_D^{25}$ + 8.7 (c = 0.01, $CHCl_3$).



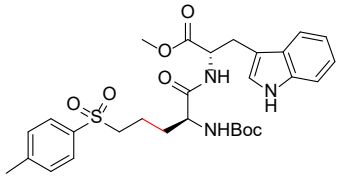
Methyl ((*S*)-2-((*tert*-butoxycarbonyl)amino)-6-(6-methylpyridin-2-yl)-6-oxohexanoyl)-L-tryptophanate (30): Eluent 35% ethyl acetate in hexane. Isolated as an orange oil (67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (1H, brs), 7.78 (1H, d, J = 7.6 Hz), 7.67 (1H, t, J = 7.8 Hz), 7.51 (1H, d, J = 7.6 Hz), 7.30 (2H, t, J = 8.4 Hz), 7.03-7.15 (3H, m), 6.70 (1H, d, J = 8.0 Hz), 5.11 (1H, s), 4.88-4.92 (1H, m), 4.11 (1H, d, J = 6.8 Hz), 3.64 (3H, s), 3.31 (2H, d, J = 5.6 Hz), 3.17-3.22 (2H, m), 2.58 (3H, s), 1.62-1.85 (4H, m), 1.40 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 202.0, 172.1, 171.7, 158.1, 152.9, 136.9, 136.2, 127.6, 126.7, 123.1, 122.12, 119.6, 118.8, 118.5, 111.3, 109.8, 79.8, 52.9, 52.3, 37.0, 32.0, 28.3, 28.0, 27.7, 24.4, 19.9; ν_{max}/cm^{-1}: 3337, 2918, 1751, 1703, 1677, 1438, 1393, 1231, 1129, 747; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{29}H_{36}N_4O_6$: 559.26348; found: 559.25959; $[\alpha]_D^{25}$ +96 (c = 0.25, $CHCl_3$)**.**



Methyl ((*S*)-2-((*tert*-butoxycarbonyl)amino)-6-(naphthalen-2-yl)-6-oxohexanoyl)-L-tryptophanate (31): Eluent 55% ethyl acetate in hexane. Isolated as an orange oil (65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42 (1H, s), 7.93-7.99 (2H, m), 7.85-7.87 (2H, d, J = 8.2 Hz), 7.51-7.61 (2H, m), 7.30-7.32 (1H, d, J = 8.2 Hz), 7.06-7.18 (2H, m), 7.01-7.04 (2H, m), 5.21-5.23 (1H, m), 4.89-4.93 (1H, m), 3.63 (3H, s), 3.30-3.32 (2H, m), 2.98-3.07 (2H, m), 1.68-1.87 (4H, m), 1.41 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 199.9, 172.1, 171.8, 155.9, 136.2, 135.6, 134.1, 132.5, 129.8, 129.6, 128.5, 128.4, 127.8, 127.6, 126.8, 123.8, 123.2, 122.1, 119.6, 118.5, 111.4, 109.7, 82.7, 52.9, 52.3, 37.9, 32.0, 28.3, 27.6, 20.0; ν_{max}/cm^{-1}: 3341, 2974, 2930, 1671, 1510, 1366, 1250, 1166, 743; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{33}H_{37}N_3O_6$: 594.25746; found: 594.25698; $[\alpha]_D^{25}$ +1.65 (c = 0.02, $CHCl_3$).

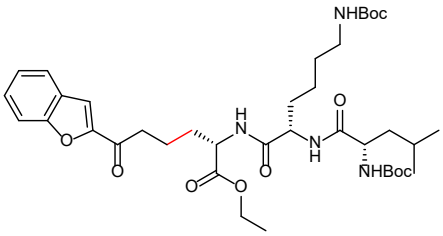


Methyl ((S, (*E/Z*))-2-((*tert*-butoxycarbonyl)amino)-6-(2-nitrophenyl)-6-oxohex-4-enoyl)-L-tryptophanate (32): Eluent 55% ethyl acetate in hexane. Isolated as an orange oil (65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (1H, brs), 8.04-8.07 (1H, m), 7.65 (1H, m), 7.63-7.65 (1H, m), 7.34 (2H, t, J = 7.6 Hz), 7.15-7.19 (1H, m), 7.06-7.11 (2H, m), 7.01 (1H, s), 6.53 (1H, d, J = 7.8 Hz), 6.35-6.40 (1H, m), 4.17 (1H, m), 3.65 (3H, s), 3.28-3.33 (2H, m), 2.60-2.66 (1H, m), 2.47-2.50 (1H, m), 1.38 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 192.6, 192.1, 171.7, 170.4, 146.7, 145.2, 136.2, 135.8, 133.9, 133.2, 130.6, 128.9, 128.2, 127.5, 124.4, 123.0, 122.3, 122.2, 119.7, 119.6, 118.5, 118.4, 111.4, 111.3, 109.6, 81.3, 80.4, 52.3, 52.9, 52.4, 35.8, 28.2, 27.5;ν_{max}/cm^{-1}: 3336, 2929, 1666, 1528, 1347, 1250, 1164, 737; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{29}H_{32}N_4O_8$: 587.21124; found: 587.21341; $[\alpha]_D^{25}$ +11.4 (c = 0.07, CH_2Cl_3).

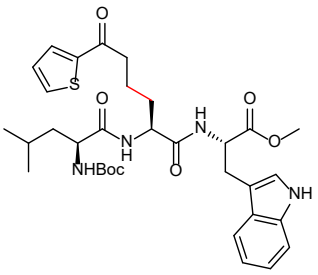


Methyl ((S)-2-((*tert*-butoxycarbonyl)amino)-5-tosylpentanoyl)-L-tryptophanate (33): Eluent 40% ethyl acetate in hexane. Isolated as an orange oil (77 %).^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (2H, d, J = 8.2 Hz), 7.50 (1H, d, J = 7.8 Hz), 7.30-7.39 (3H, m), 7.17 (1H, t, J = 7.2 Hz), 7.10 (1H, t, J = 7.2 Hz), 7.03 (1H, d, J = 1.9 Hz), 6.64 (1H, (NH), d, J = 7.7 Hz), 5.03-5.05 (1H, m), 4.83-4.90 (1H, m), 4.07 (1H, brs), 3.67 (3H, s), 3.28-3.32 (2H, m), 3.03-3.04 (2H, m), 2.42 (3H, s), 1.82-1.84 (1H, m), 1.66-1.71 (1H, m), 1.40 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 172.0, 171.3, 144.7, 136.2, 136.1, 129.9, 129.0, 127.5, 123.3, 122.1, 119.6, 118.4,

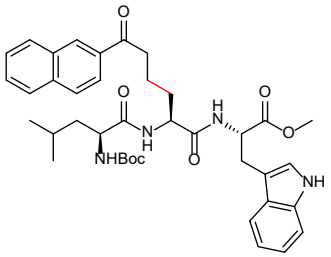
111.5, 109.5, 80.0, 52.9, 52.4, 42.6, 31.6, 28.3, 22.6, 21.6, 14.1; ν_{max}/cm^{-1}: 3348, 2929, 1665, 1286, 1248, 1162, 1146, 730; HRMS (ESI) *m/z* [M+Na]$^+$ calc'd for $C_{29}H_{37}N_3O_7S$: 594.22444; found: 594.22400; $[\alpha]_D^{25}$: +7.9 (*c* = 0.06, $CHCl_3$)



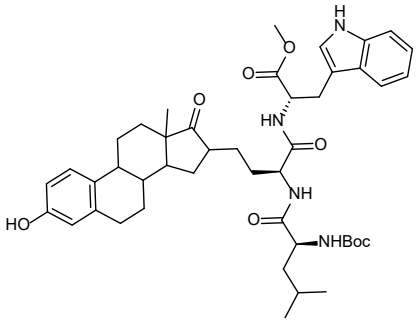
Ethyl (*6S,9S,12S*)-12-(4-(benzofuran-2-yl)-4-oxobutyl)-9-(4-((*tert*-butoxycarbonyl)amino)butyl)-6-isobutyl-2,2-dimethyl-4,7,10-trioxo-3-oxa-5,8,11-triazatridecan-13-oate (34): Eluent 60% ethyl acetate in hexane. Isolated as an off-white oil (53%). ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.70 (1H, d, *J* = 7.9 Hz), 7.54-7.57 (1H, m), 7.53 (2H, s), 7.45-7.48 (1H, m), 7.28-7.32 (1H, m), 4.79 (1H, brs), 4.83-4.84 (1H, m) 4.52-4.58 (1H, m), 4.42-4.45 (2H, m), 4.09-4.14 (2H, m), 4.09-4.13 (2H, m), 3.08 (1H, brs), 3.00-3.07 (2H, m), 1.91-1.98 (4H, m), 1.76-1.83 (4H, m), 1.50-1.51 (1H, m), 1.45 (18H, s), 1.26-1.29 (5H, m), 0.87-0.93 (6H, m); ^{13}C NMR (101 MHz; $CDCl_3$): 190.6, 172.8, 171.8, 171.3, 156.1, 155.8, 155.6, 152.5, 128.3, 127.0, 123.9, 123.3, 112.8, 112.4, 80.2, 79.0, 61.5, 52.8, 52.1, 37.9, 33.7, 31.4, 29.3, 28.5, 28.3, 24.8, 23.0, 22.4, 21.8, 19.6, 14.1; ν_{max}/cm^{-1}: 3300, 2961, 2932, 1677, 1551, 1516, 1366, 1250, 1140, 753; HRMS (ESI) *m/z* [M+Na]$^+$ calc'd for $C_{38}H_{58}N_4O_{10}$: 753.40451; found: 753.40411; $[\alpha]_D^{25}$ -20 (*c* = 0.01, $CHCl_3$).



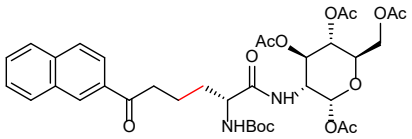
Methyl ((*S*)-2-((*S*)-2-((*tert*-butoxycarbonyl)amino)-4-methylpentanamido)-6-oxo-6-(thiophen-2-yl)hexanoyl)-L-tryptophanate (35): Eluent 45% ethyl acetate in hexane. Isolated as an orange oil (43%).^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.65 (1H, brs), 7.67 (1H, d, *J* = 4.4 Hz), 7.61 (1H, d, *J* = 5.2 Hz), 7.51 (1H, d, *J* = 7.6 Hz), 7.31 (1H, m), 7.0-7.16 (4H, m), 5.07-5.09 (1H, m), 4.84-4.89 (1H, m), 4.44-4.48 (1H, m), 4.16 (1H, brs (NH)), 3.67 (3H, s), 3.27-3.30 (2H, m), 2.87-2.93 (2H, m), 1.84-1.92 (2H, m), 1.61-1.66 (6H, m), 1.41-1.44 (1H, m), 1.44 (9H, s), 0.83-0.91 (6H, m); ^{13}C NMR (101 MHz; $CDCl_3$): 192.0, 171.9, 171.0, 169.9, 161.6, 154.9, 143.1, 135.1, 132.7, 131.2, 127.2, 127.1, 126.4, 122.5, 121.0, 121.0, 118.4, 117.4, 110.4, 110.3, 108.5, 79.4, 51.8, 51.7, 51.4, 40.3, 37.4, 30.4, 27.3, 23.8, 22.0, 20.6, 18.9; ν_{max}/cm^{-1}: 3325, 2957, 2929, 1656, 1517, 1366, 1250, 1166, 742; HRMS (ESI) *m/z* [M+Na]$^+$ calc'd for $C_{33}H_{44}N_4O_7S$: 663.28229; found: 663.28221; $[\alpha]_D^{25}$ +6.6 (*c* = 0.046, $CHCl_3$).



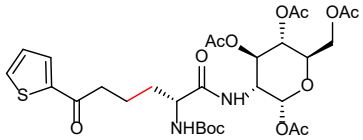
Methyl ((*S*)-2-((*S*)-2-((*tert*-butoxycarbonyl)amino)-4-methylpentanamido)-6-(naphthalen-2-yl)-6-oxohexanoyl)-L-tryptophanate (36): Eluent 55% ethyl acetate in hexane. Isolated as a yellow oil (51%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63 (1H, brs (NH)), 8.42 (1H, s), 7.93-7.99 (2H, m), 7.85-7.87 (2H, d, J = 8.2 Hz), 7.51-7.61 (2H, m), 7.30-7.32 (1H, d, J = 8.2 Hz), 7.06-7.18 (2H, m), 7.01-7.04 (2H, m), 5.09-5.12 (1H, m), 4.82-4.89 (1H, m), 4.48-4.49 (1H, m), 4.18 (1H, brs (NH)), 3.65 (3H, s), 3.39-3.31 (2H, m), 2.87-2.93 (2H, m), 1.84-1.92 (2H, m), 1.61-1.66 (6H, m), 1.41-1.44 (1H, m), 1.44 (9H, s), 0.83-0.91 (6H, m); ^{13}C NMR (101 MHz; $CDCl_3$): 200.1, 173.0, 172.0, 171.9, 155.9, 136.2, 135.6, 134.1, 132.5, 129.8, 129.6, 128.4, 127.7, 127.4, 126.8, 123.8, 123.5, 122.0, 119.41, 118.4, 111.4, 109.5, 80.4, 61.9, 52.8, 52.4, 41.3, 37.8, 31.7, 28.3, 24.8, 23.0, 21.6, 19.7; ν_{max}/cm^{-1}: 3306, 2957, 1672, 1518, 1367, 1167, 1047, 743; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{39}H_{48}N_4O_7$: 707.34152; found: 707.34149; $[\alpha]_D^{25}$ + 55 (c = 0.068, $CHCl_3$).



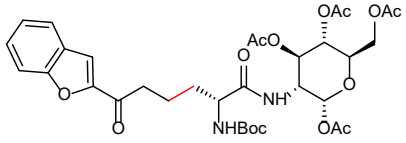
Methyl ((*2S*)-2-((*S*)-2-((*tert*-butoxycarbonyl)amino)-4-methylpentanamido)-4-(3-hydroxy-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-*6H*-cyclopenta[a]phenanthren-16-yl)butanoyl)-L-tryptophanate (37): Eluent 55% ethyl acetate in hexane. Isolated as a yellow oil (27%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48-7.52 (1H, m), 7.31-7.35 (1H, m), 6.69-7.15 (4H, m), 6.57-6.64 (2H, m), 4.97-5.03 (1H, m), 4.83-4.85(1H, m) 4.35-4.70 (1H, m (NH)), 4.11-4.13 (1H, m), 3.87 (3H, s), 3.25-3.34 (2H, m), 2.78-2.84 (2H, m), 2.21-2.33 (3H, m), 2.04-2.17 (3H, m), 1.87-1.88 (5H, m), 1.58-1.62 (5H, m), 1.42 (9H, s), 1.26-1.42 (3H, m), 0.88-0.99 (9H, m); ^{13}C NMR (125 MHz; $CDCl_3$): 222.3, 173.1, 171.9, 171.1, 155.9, 154.0, 137.8, 136.2, 131.5, 130.4, 129.5, 126.9, 126.4, 122.0, 119.5, 118.4, 115.4, 112.4, 111.4, 80.3, 53.4, 52.5, 52.4, 49.1, 48.5, 48.0, 43.9, 41.2, 37.9, 37.8, 31.9, 31.4, 30.2, 29.7, 29.6, 28.3, 26.6, 25.8, 24.8, 23.0, 22.7, 21.7, 21.2, 20.87, 20.5, 19.7, 19.2, 14.1; ν_{max}/cm^{-1}:3313, 2928, 1724, 1657, 1502, 1453, 1367, 1286, 1249, 1164, 1046, 742; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{45}H_{60}N_4O_8$: 807.43034; found: 807.43026; $[\alpha]_D^{25}$ -13 (c = 0.03, $CHCl_3$)



6-(Acetoxymethyl)-3-((*R*)-2-((*tert*-butoxycarbonyl)amino)-6-(naphthalen-2-yl)-6-oxo-hexanamido)tetrahydro-2*H*-pyran-2,4,5-triyl triacetate (39): Eluent 35% ethyl acetate in hexane. Isolated as a yellow oil (48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41 (1H, s), 7.91-8.00 (2H, m), 7.83-7.88 (2H, m), 7.51-7.60 (2H, m), 6.82-6.84 (1H, d, J = 7.6 Hz), 5.77 (1H, d, J = 8.3 Hz), 5.31-5.38 (1H, m), 5.13 (1H, t, J = 9.7 Hz), 4.30-4.40 (1H, m), 4.22-4.28 (1H, m), 4.05-4.11 (2H, m), 3.86-3.89 (1H, m), 3.09-3.11 (2H, m), 2.08 (3H, s), 2.05 (3H, s), 2.04 (6H, s), 1.75-1.80 (2H, m), 1.39-1.44 (2H, m), 1.41 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 199.6, 172.6, 171.4, 170.6, 169.4, 169.3, 155.6, 135.6, 134.0, 132.5, 129.7, 129.6, 128.6, 128.5, 127.8, 126.7, 123.7, 92.1, 80.2, 72.8, 72.6, 68.1, 61.8, 52.6, 37.7, 28.3, 20.8, 20.7, 20.6, 20.5; ν_{max}/cm^{-1}: 3354, 2974, 1750, 1677, 1514, 1454, 1367, 1221, 1164, 1122, 1076, 1040; HRMS (ESI) *m*/*z* $[M+Na]^+$ calc'd for $C_{35}H_{44}N_2O_{13}$: 723.27356; found: 723.27372; $[\alpha]_D^{25}$ + 9.1 (c = 0.02, $CHCl_3$)

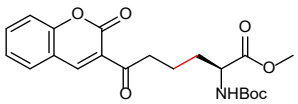


6-(Acetoxymethyl)-3-((*R*)-2-((*tert*-butoxycarbonyl)amino)-6-oxo-6-(thiophen-2-yl)-hexanamido)tetrahydro-2*H*-pyran-2,4,5-triyl triacetate (40): Eluent 35% ethyl acetate in hexane. Isolated as an off-white oil (71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68-7.69 (1H, dd, J_1 = 0.8 Hz, J_2 = 4.0 Hz), 7.61 (1H, d, J = 5.5 Hz), 7.09-7.11 (1H, dd, J_1 = 4.0 Hz, J_2 = 5.2 Hz), 5.74 (1H, d, J = 8.0 Hz), 5.35 (1H, t, J = 10 Hz), 5.14 (1H, t, J = 9.7 Hz), 4.25-4.38 (2H, m), 4.11-4.18 (1H, m), 4.01-4.04 (1H, m), 3.89-3.91 (1H, m), 2.91 (2H, t, J = 6.5 Hz), 2.09 (3H, s), 2.08 (3H, s), 2.05 (3H, s), 2.04 (3H, s), 1.72-1.76 (2H, m), 1.40-1.43 (2H, m), 1.42 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$):192.5, 172.6, 171.4, 170.6, 169.3, 155.6, 144.0, 133.8, 132.0, 128.2, 92.1, 80.1, 72.8, 72.7, 68.2, 61.8, 52.5, 38.4, 31.7, 28.3, 20.8, 20.7, 20.5, 20.3; ν_{max}/cm^{-1}: 3354, 2974, 1749, 1665, 1517, 1454, 1415, 1366, 1216, 1165, 1075, 1040, 735; HRMS (ESI) *m*/*z* $[M+Na]^+$ calc'd for $C_{29}H_{40}N_2O_{13}S$: 656.22511; found: 656.22495; $[\alpha]_D^{25}$ +136 (c = 0.16, $CHCl_3$).

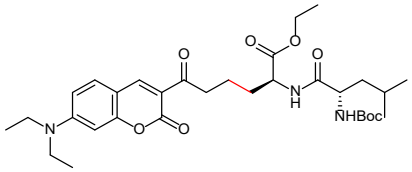


6-(Acetoxymethyl)-3-((*R*)-6-(benzofuran-2-yl)-2-((*tert*-butoxycarbonyl)amino)-6-oxo-hexanamido)tetrahydro-2*H*-pyran-2,4,5-triyl triacetate (41): Eluent 35% ethyl acetate in hexane. Isolated as an off-white oil (50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (1H, d, J = 7.8 Hz), 7.61 (1H, brd, J = 10.0 Hz), 7.53 (1H, d, J = 8.4 Hz), 7.40-7.49 (2H, m), 7.24-7.30 (1H, m),

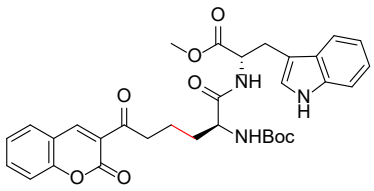
5.75 (1H, d, J = 8.5 Hz), 5.28-5.33 (1H, m), 5.11 (1H, t, J = 9.7 Hz), 4.21-4.32 (2H, m), 4.03-4.11 (2H, m), 3.85-3.87 (1H, m), 2.96-2.97 (2H, m), 2.07 (3H, s), 2.05 (3H, s), 2.02 (3H, s), 2.01 (3H, s), 1.72-1.79 (2H, m), 1.35-1.41 (2H, m), 1.40 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$):190.7, 172.5, 171.4, 170.6, 169.3, 155.6, 152.4, 128.4, 127.0, 124.0, 123.3, 112.9, 112.4, 92.1, 79.8, 72.8, 72.7, 68.1, 61.8, 52.6, 38.0, 28.4, 20.8, 20.7, 20.5, 20.0; ν_{max}/cm^{-1}: 3359, 2931, 1753, 1679, 1555, 1367, 1221, 1164, 1139, 1076, 1042, 755; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{33}H_{42}N_2O_{14}$: 713.25282; found: 713.25301; $[\alpha]_D^{25}$ +34 (c = 0.02, $CHCl_3$).



Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-6-oxo-6-(2-oxo-2*H*-chromen-3-yl)hexanoate (42): Eluent 35% ethyl acetate in hexane. Isolated as a yellow oil (58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (1H, s), 7.63-7.67 (2H, m), 7.31-7.38 (2H, m), 7.34 (1H, brs), 5.08-5.09 (1H, m), 4.32-4.34 (1H, m), 3.75 (3H, s), 3.17 (2H, t, J = 6.8 Hz), 1.73-1.78 (4H, m), 1.44 (9H, s); ^{13}C NMR (101 MHz; $CDCl_3$): 197.1,176.6, 173.4, 159.1, 155.3, 147.5, 134.4, 130.2, 125.0, 124.4, 118.3, 116.7, 80.0, 52.3, 41.8, 32.0, 29.7, 28.3, 19.6; ν_{max}/cm^{-1}: 3363, 2954, 2933, 1720, 1616, 1516, 1455, 1373, 1225, 1164, 769; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{21}H_{25}NO_7$: 426.15232; found: 426.13959; $[\alpha]_D^{25}$ +11.6 (c = 0.05, $CHCl_3$).

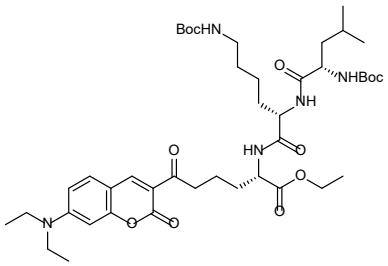


Ethyl (*S*)-2-((*S*)-2-((*tert*-butoxycarbonyl)amino)-4-methylpentanamido)-6-(7-(diethylamino)-2-oxo-2*H*-chromen-3-yl)-6-oxohexanoate (43): Eluent 60% ethyl acetate in hexane. Isolated as yellow oil (55%): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41 (1H, s), 7.38 (1H, d, J = 8.9 Hz), 6.82 (1H, d, J = 7.8 Hz), 6.60 (1H, dd, J_1 = 2.4 Hz, J_2 = 9.0 Hz), 6.44 (1H, d, J = 2.4 Hz), 5.02 (1H, d, J = 7.2 Hz), 4.52-4.56 (1H, m), 4.14-4.21 (2H, m), 4.86 (4H, q, J =7.1 Hz), 3.09 (2H, t, J = 6.9 Hz), 1.88-1.91 (1H, m), 1.76-1.81 (1H, m), 1.65-1.73 (4H, m), 1.45-1.50 (1H, m), 1.42 (9H, s), 1.21-1.28 (9H, m), 0.93 (6H, d, J = 5.4 Hz); ^{13}C NMR (101 MHz; $CDCl_3$): 197.2, 172.4, 172.0, 160.7, 158.7, 153.1, 148.1, 131.9, 115.8, 109.9, 108.2, 96.6, 61.3, 52.3, 45.1, 41.7, 31.6, 28.3, 24.7, 22.9, 19.6, 14.1, 12.4; ν_{max}/cm^{-1}: 3322, 2960, 1718, 1617, 1575, 1506, 1350, 1173, 1132; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{32}H_{47}N_3O_8$: 624.32554; found: 624.33112; $[\alpha]_D^{25}$ -13 (c = 0.01, $CHCl_3$).

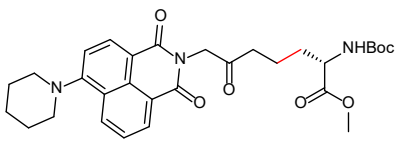


Methyl ((S)-2-((*tert*-butoxycarbonyl)amino)-6-oxo-6-(2-oxo-2H-chromen-3-yl)hexanoyl)-L-tryptophanate (44): Eluent 50% ethyl acetate in hexane. Isolated as a yellow oil (38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42 (1H, s), 8.33 (1H, brs), 7.61-7.65 (2H, m), 7.51 (1H, d, J = 7.7 Hz), 7.31-7.34 (3H, m), 7.14 (1H, t, J = 7.4 Hz), 7.04-7.08 (1H, m), 6.72 (1H (NH), d, J = 7.7 Hz),

5.05-5.09 (1H, m), 4.87-4.92 (1H, m), 4.11-4.13 (1H, brs), 3.64 (3H, s), 3.31 (2H, d, J = 5.3 Hz), 3.09-3.12 (2H, m), 1.61-1.73 (2H, m), 1.41 (9H, s); NMR (101 MHz; $CDCl_3$): 197.49, 172.04, 171.64, 159.07, 155.2, 147.5, 136.2, 134.3, 130.2, 127.6, 124.9, 123.2, 122.1, 119.6, 118.5, 118.3, 116.6, 111.3, 109.8, 80.0, 52.8, 52.4, 52.3, 41.8, 31.99, 29.7, 29.3, 27.6, 19.7; ν_{max}/cm^{-1}:3351, 2930, 1720, 1608, 1456, 1229, 1169, 757, 732; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{32}H_{35}N_3O_8$: 612.23164; found: 612.232011; $[\alpha]_D^{25}$ +3.57 (c = 0.14, CH_2Cl_2).

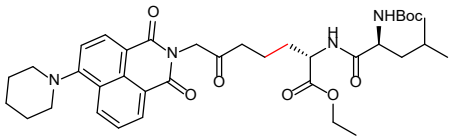


Ethyl (*6S,9S,12S*)-9-(4-((*tert*-butoxycarbonyl)amino)butyl)-12-(4-(7-(diethylamino)-2-oxo-2*H*-chromen-3-yl)-4-oxobutyl)-6-isobutyl-2,2-dimethyl-4,7,10-trioxo-3-oxa-5,8,11-triazatridecan-13-oate (49): Eluent 65% ethyl acetate in hexane. Isolated as yellow oil (55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.43 (1H, s), 8.40 (1H, d, J = 9.2 Hz), 6.61 (1H, dd, J_1 = 2.1 Hz, J_2 = 9.0 Hz), 6.44-6.45 (1H, m), 4.47-4.53 (2H, m), 4.13-4.20 (3H, m), 3.41-3.45 (6H, m), 3.08 (2H, t, J = 6.6 Hz), 2.20 (2H, brs), 1.87-1.92 (2H, m), 1.63-1.73 (4H, m), 1.47-1.51 (2H, m), 1.34-1.40 (3H, m), 1.41 (9H, s), 1.40 (9H, s), 1.20-1.24 (11H, m), 0.89-0.91 (6H, m); ^{13}C NMR (101 MHz; $CDCl_3$): 197.3, 172.7, 171.9, 171.3, 160.7, 158.7, 156.1, 153.2, 148.3, 132.0, 128.4, 115.6, 110.0, 108.3, 96.6, 80.0, 78.9, 61.4, 52.7, 52.5, 45.2, 41.6, 31.7, 31.1, 29.2, 28.4, 28.3, 24.7, 23.0, 22.2, 21.9, 19.7, 19.3, 14.2, 12.4; ν_{max}/cm^{-1}: 2973, 1717, 1617, 1574, 1506, 1350, 1175; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{43}H_{67}N_5O_{11}$: 852.47293; found: 852.48002; $[\alpha]_D^{25}$ -3.8 (c = 0.07, $CHCl_3$).

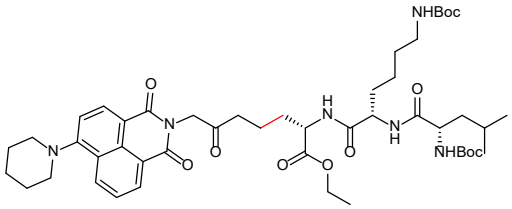


Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-7-(1,3-dioxo-6-(piperidin-1-yl)-1*H*-benzo[de] isoquinolin-2(3*H*)-yl)-6-oxoheptanoate (45): Eluent 50% ethyl acetate in hexane. Isolated as

yellow oil (42%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.55 (1H, d, J = 6.8 Hz), 8.47 (1H, d, J = 8.3 Hz), 8.40 (1H, d, J = 8.7 Hz), 7.67 (1H, t, J = 7.9 Hz), 7.17 (1H, d, J = 8.5 Hz), 5.11-5.13 (1H, m), 4.96 (2H, s), 4.30-4.31 (1H, m), 3.73 (3H, s), 3.23-3.24 (4H, m), 2.61-2.66 (2H, m), 1.86-1.90 (5H, m), 1.71-1.74 (5H, m), 1.43 (9H, s); ^{13}C NMR (125 MHz; $CDCl_3$): 202.7, 173.1, 164.3, 163.7, 157.7, 155.4, 133.1, 131.4, 131.1, 130.2, 122.6, 115.3, 114.7, 79.9, 54.6, 53.2, 52.3, 48.7, 39.3, 31.2, 28.3, 26.2, 24.3, 19.3; ν_{max}/cm^{-1}: 2917, 2850, 1694, 1655, 1588, 1452, 1377, 1235, 1164, 1081, 1028, 790; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{30}H_{37}N_3O_7$: 574.25237 ; found: 574.25233; $[\alpha]_D^{25}$ +4.3 (c = 0.06, $CHCl_3$).

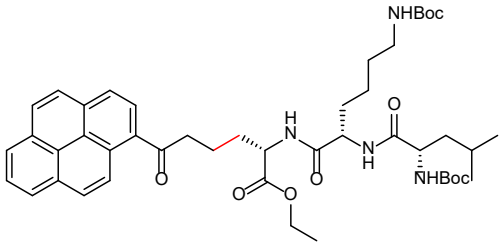


Ethyl (S)-2-((S)-2-((tert-butoxycarbonyl)amino)-4-methylpentanamido)-7-(1,3-dioxo-6-(piperidin-1-yl)-1H-benzo[de]isoquinolin-2(3H)-yl)-6-oxoheptanoate (46): Eluent 50% ethyl acetate in hexane. Isolated as yellow solid (61%); M.p.: 72-74 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (1H, d, J = 7.0 Hz), 8.47 (1H, J = 8.0 Hz), 8.39 (1H, d, J = 7.1 Hz), 7.66 (1H, t, J = 7.7 Hz), 7.16 (1H, d, J = 8.1 Hz), 6.78 (1H, brs), 5.04-5.05 (1H, m), 4.97 (2H, s), 4.54-4.57 (1H, m), 4.17 (2H, q, J = 6.9 Hz), 3.32 (4H, s), 2.55-2.69 (2H, m), 1.87-1.89 (6H, m), 1.70-1.73 (8H, m), 1.48-1.50 (1H, m), 1.42 (9H, s), 1.26 (3H, t, J = 6.9 Hz), 0.91-0.94 (6H, m); ^{13}C NMR (101 MHz; $CDCl_3$): 202.8, 172.6, 171.8, 164.3, 163.7, 157.8, 133.1, 131.4, 131.1, 130.2, 126.3, 125.3, 122.6, 115.3, 114.7, 80.0, 61.5, 54.6, 51.9, 48.5, 39.2, 31.3, 28.3, 26.2, 24.7, 24.3, 22.9, 19.5, 14.1; ν_{max}/cm^{-1}: 3330, 2924, 2852, 1696, 1651, 1375, 1234, 1163, 1011, 783; HRMS (ESI) m/z $[M+Na]^+$ calc'd for $C_{37}H_{50}N_4O_8$: 701.35210; found: 701.35341; found: $[\alpha]_D^{25}$ -16. 7 (c = 0.03, CH_2Cl_2).

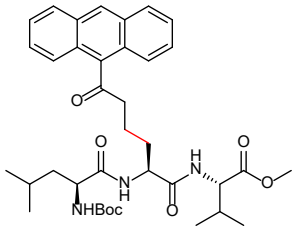


Ethyl (*6S,9S,12S*)-9-(4-((*tert*-butoxycarbonyl)amino)butyl)-12-(5-(1,3-dioxo-6-(piperidin-1-yl)-1*H*-benzo[de]isoquinolin-2(3*H*)-yl)-4-oxopentyl)-6-isobutyl-2,2-dimethyl-4,7,10-trioxo-3-oxa-5,8,11-triazatridecan-13-oate (48): Eluent 70% ethyl acetate in hexane. Isolated as yellow oil (38%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (1H, dd, J_1 = 1.0 Hz, J_2 = 7.3 Hz), 8.48 (1H, J = 8.1 Hz), 8.39 (1H, dd, J_1 = 1.1 Hz, J_2 = 8.5 Hz), 7.64-7.68 (1H, m), 7.16 (1H, d, J = 8.3 Hz), 5.04-5.08 (1H, m), 4.96 (2H, s), 4.48-4.51 (2H, m), 4.18 (2H, q, J = 6.8 Hz), 3.21-3.24 (4H, m), 3.06-3.07 (2H, m), 2.59-2.65 (2H, m), 1.86-1.87 (6H, m), 1,59-1.72 (8H, m), 1.45-1.52 (2H, m), 1.41-1.42 (1H, m), 1.41 (18H, s), 1.24-1.27 (5H, m), 0.81-0.95 (6H, m); ^{13}C NMR (101 MHz; $CDCl_3$): 203.0, 172.7, 171.8, 171.4, 164.3, 163.7, 157.8, 156.1, 155.7, 133.2,

131.5, 131.2, 130.2, 126.3, 125.3, 122.6, 115.2, 114.8, 80.0, 78.9, 65.8, 61.5, 54.5, 52.7, 52.1, 48.5, 41.0, 40.0, 39.1, 31.9, 30.8, 29.3, 28.4, 28.3, 26.2, 24.7, 24.3, 22.9, 22.3, 21.9, 19.7, 15.3, 14.1; ν_{max}/cm^{-1}: 3296, 2932, 2332, 1695, 1518, 1367, 1251, 1171, 542; HRMS (ESI) *m/z* [M+Na]$^+$ calc'd for $C_{48}H_{70}N_6O_{11}$: 929.49948; found: 929.49942; $[\alpha]_D^{25}$ -5.3 (*c* = 0.06, $CHCl_3$).

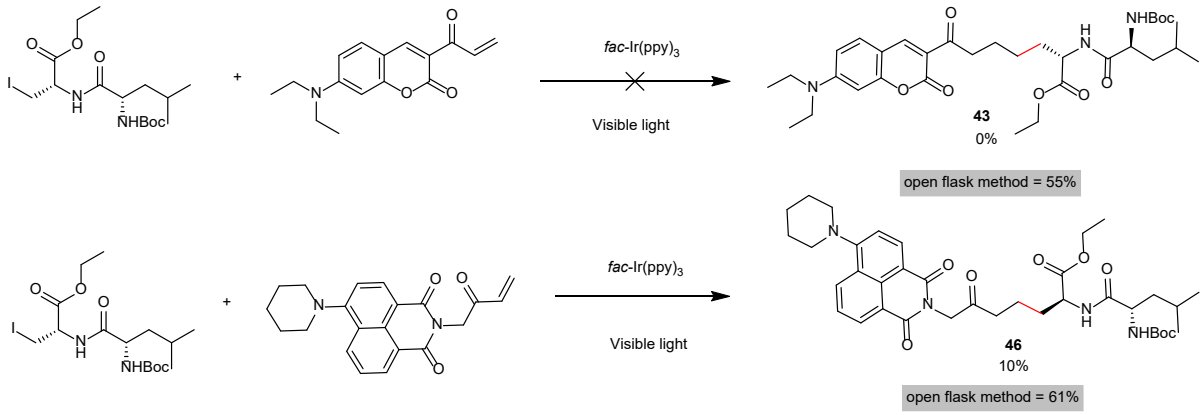


Ethyl (*6S,9S,12S*)-9-(4-((*tert*-butoxycarbonyl)amino)butyl)-6-isobutyl-2,2-dimethyl-4,7,10-trioxo-12-(4-oxo-4-(pyren-1-yl)butyl)-3-oxa-5,8,11-triazatridecan-13-oate (50): Eluent 60% ethyl acetate in hexane. Isolated as a yellow (44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.91 (1H, d, *J* = 9.2 Hz), 8.33 (1H, d, *J* = 8.0 Hz), 8.16-8.27 (6H, m), 8.05-8.09 (3H, m), 4.83-4.84 (1H, m), 4.61-4.63 (1H, m), 4.79 (1H, brs), 4.56-4.61 (1H, m), 4.47-4.51 (2H, m), 4.15-4.20 (2H, m), 4.08-4.12 (2H, m), 3.23-3.27 (2H, m), 3.07-3.08 (2H, brs), 1.95-2.00 (1H, m), 1.86-1.94 (5H, m), 1.67-1.71 (4H, m), 1.46-1.50 (1H, m), 1.42 (18H, s), 1.23-1.26 (5H, m), 0.88-0.91 (6H, m); ^{13}C NMR (101 MHz; $CDCl_3$): 204.0, 172.8, 171.9, 171.3, 156.1, 133.8, 132.2, 131.1, 130.5, 129.7, 129.5, 129.4, 127.1, 126.4,126.3, 126.2, 126.1, 125.0, 124.8, 124.7, 124.3, 124.1, 80.2, 79.0, 61.5, 53.4, 52.8, 52.2, 41.4, 31.5, 29.3, 28.5, 28.3, 24.8, 22.9, 22.4, 21.8, 20.4, 14.1; ν_{max}/cm^{-1}: 3328, 3303, 2962, 2933, 1690, 1514, 1389, 1269, 1250, 1170, 849; HRMS (ESI) *m/z* [M+Na]$^+$ calc'd for $C_{46}H_{62}N_4O_9$: 837.44090; found: 837.44041; $[\alpha]_D^{25}$ -15.6 (*c* = 0.016, $CHCl_3$)

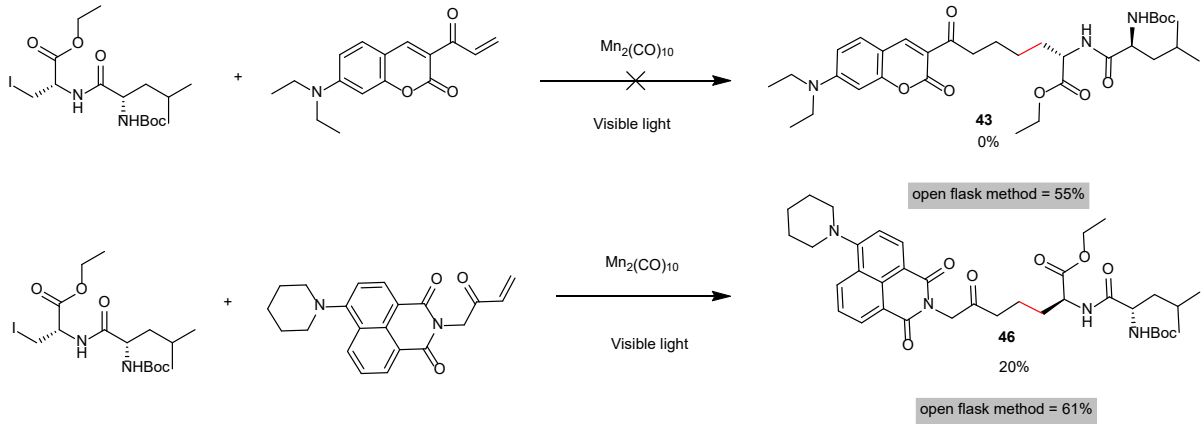


Methyl ((*S*)-6-(anthracen-9-yl)-2-((*S*)-2-((*tert*-butoxycarbonyl)amino)-4-methylpentanamido)-6-oxohexanoyl)-L-valinate (47):Eluent 55% ethyl acetate in hexane. Isolated as a yellow oil (45 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (1H, s), 8.02 (2H, d, *J* = 7.8 Hz), 7.80 (2H, d, *J* = 8.6 Hz), 7.48-7.53 (4H, m), 6.88-6.90 (1H, m, (NH)), 4.91 (1H, m), 4.48-4.55 (2H, m), 4.14 (1H, brs (NH)), 3.73 (3H, s), 3.10-3.14 (2H, m), 2.19-2.20 (1H, m), 2.04-2.06 (2H, m), 1.88-1.91 (2H, m), 1.69-1.70 (2H, m), 11.47-1.5- (1H, m), 1.43 (9H, s), 0.82-0.96 (12H, m); ^{13}C NMR (101 MHz; $CDCl_3$): 209.2, 171.8, 171.0, 170.1, 154.7, 135.3, 130.0, 127.8, 127.2, 125.9, 125.8, 124.5, 123.3, 79.3, 56.4, 52.1, 51.1, 44.7, 35.1, 30.0, 28.7, 28.0, 27.3, 23.8, 21. 9, 18.0, 16.7; ν_{max}/cm^{-1}: 3350, 2960, 1742, 1654, 1539, 1367, 1165; HRMS (ESI) *m/z* [M+Na]$^+$ calc'd for $C_{37}H_{49}N_3O_7$: 670.34627; found: 670.34598; found: $[\alpha]_D^{25}$ -191 (*c* = 0.068, $CHCl_3$)

Comparison of open flask method with photoredox catalysis



Procedure 1: To a 10 ml vial with a magnetic stir bar was added the corresponding dipeptidyl iodide (0.60 mmol, 1.0 equiv.), radical acceptor (0.6 mmol, 1.0 equiv), MeCN (6.0 ml), diethyl Hantzsch ester (DEHE) (1.2 mmol, 2.0 equiv.), tributylamine (1.2 mmol, 2.0 equiv.) and *fac*-Ir(ppy)$_3$ (0.0060 mmol, 0.010 equiv.). The reaction mixture was degassed by bubbling with Ar for 30 min with an outlet needle and the vial was sealed with PTFE cap. The mixture was stirred rapidly while irradiated with blue LED for 24 hours. The solvent was removed from the crude mixture in vacuo and the residue was dissolved in ethyl acetate. The contents were poured into a separatory funnel containing ethyl acetate (25 mL) and aqueous HCl (1 M; 25 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (2 × 25 ml). The combined organic layers were washed with sat. $NaHCO_3$ solution and brine, dried (Na_2SO_4) and concentrated in vacuo. The crude sample was subjected to NMR and MS analyses. The residue was purified by chromatography on silica gel to afford the desired product.

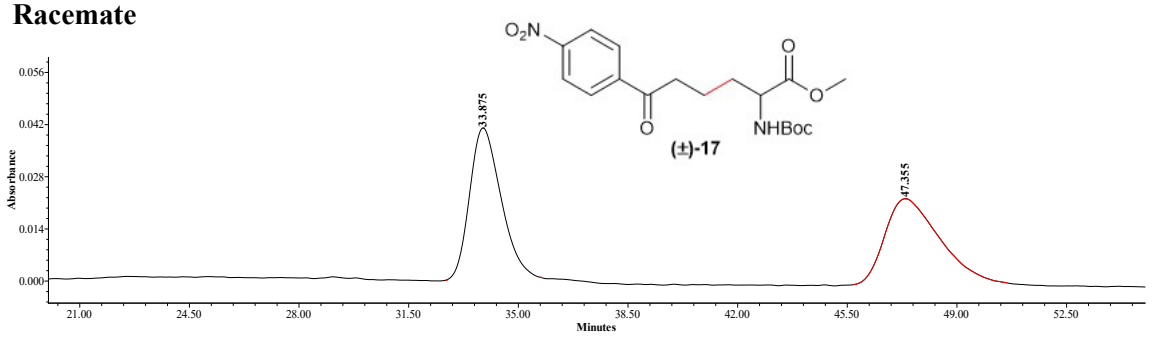


Procedure 2: To a 10 mL vial was added $Mn_2(CO)_{10}$ (11.7 mg, 0.03 mmol, 1 mol %), radical acceptor (0.3 mmol, 1.0 equiv), corresponding dipeptidyl iodide (0.6 mmol, 2.0 equiv), DEHE (114 mg, 0.45 mmol, 2.0 equiv) and 3.0 mL of DMSO. The reaction mixture was degassed by bubbling with Ar for 30 min with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with Blue LED. The progress of the reaction was monitored by TLC and mass spectrometric analysis of aliquots. After 24 hrs, the mixture was diluted with aqueous $NaHCO_3$ (1 M; 10 mL) and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude reaction mixture was subjected to NMR and MS analyses, which indicated the presence of ethyl *N*-Boc-leucyl-alaninate **54**. After identification of the targeted compound, the product was isolated using column chromatography.

HPLC traces

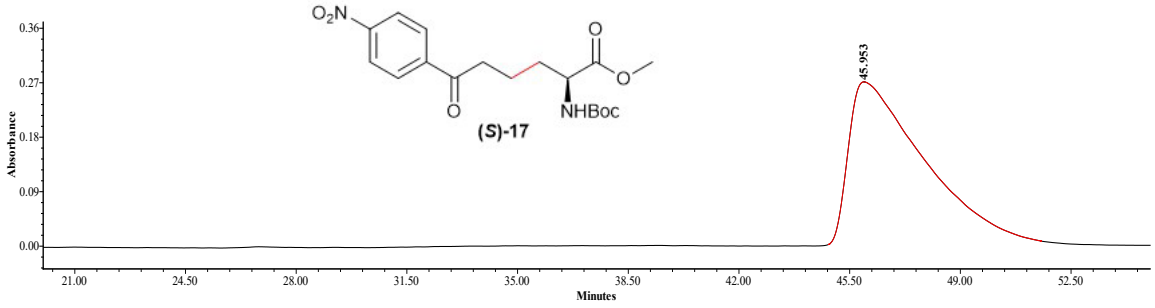
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-6-(4-nitrophenyl)-6-oxohexanoate (17): Enantioseparation of compound **17** was achieved using a Lux Amylose-2 chiral column and hexane/isopropanol (90/10) as the mobile phase (1 mL/min).

Racemate



	Retention Time	% Area
1	33.882	50.58
2	47.360	49.42

Reaction product



	Retention Time	% Area
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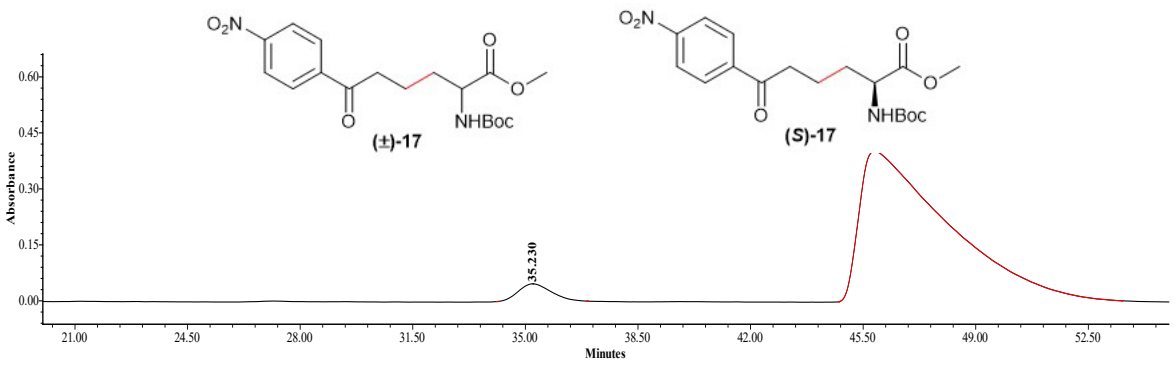
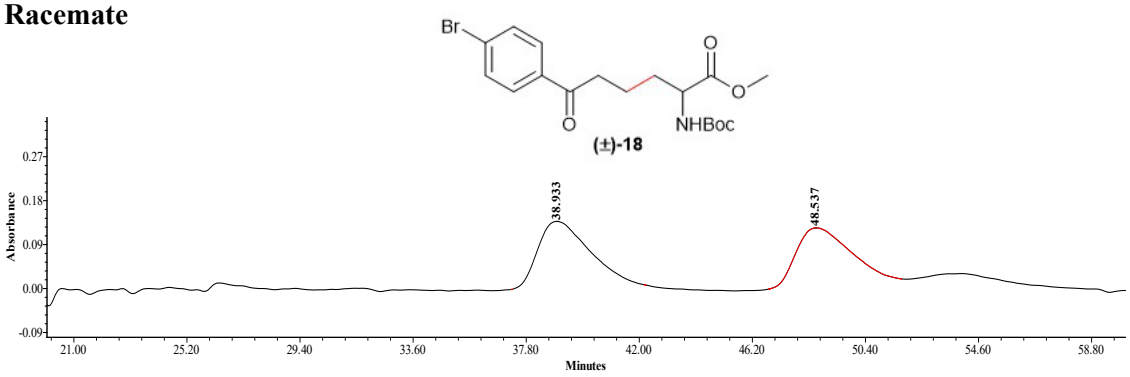
Co-injection



	Retention Time	% Area
1	35.220	4.26
2	45.851	95.74

Methyl (*S*)-6-(4-bromophenyl)-2-((*tert*-butoxycarbonyl)amino)-6-oxohexanoate (18):
Enantioseparation of compound **18** was achieved using a Lux Amylose-2 chiral column and hexane/isopropanol (90/10) as the mobile phase (0.7 mL/min).

Racemate



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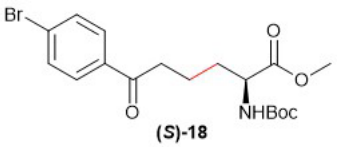
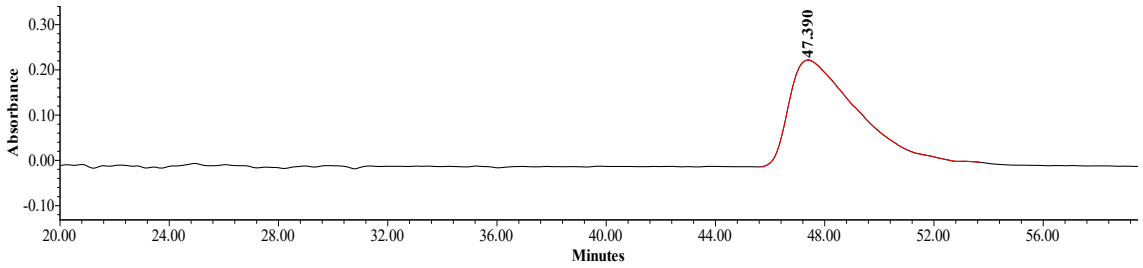
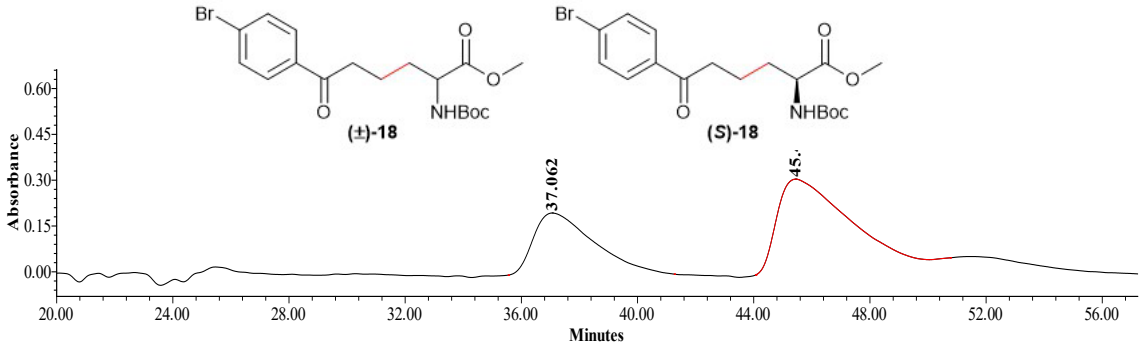
Reaction product





	Retention Time	% Area
1	47.390	100

Co-injection

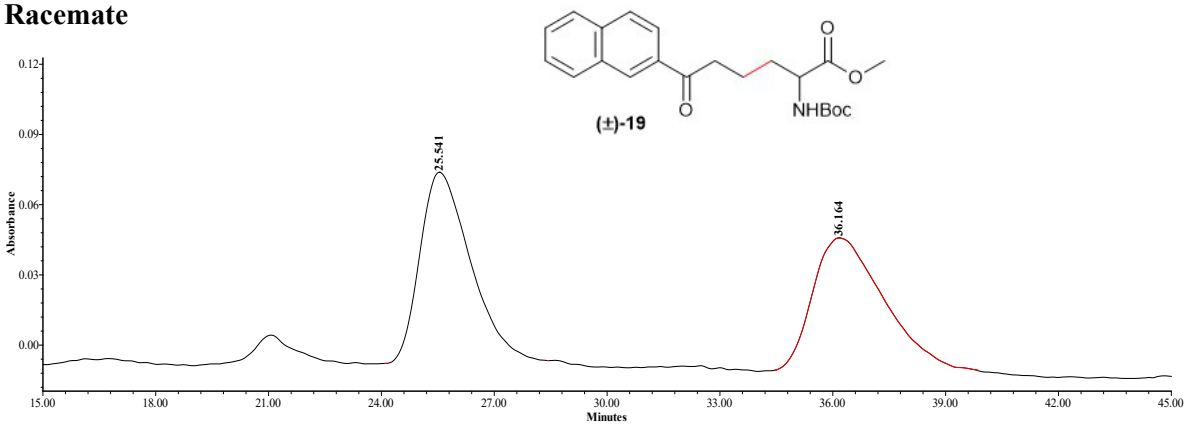


	Retention Time	% Area
1	37.062	37.29
2	45.445	62.71

Methyl (S)-2-((*tert*-butoxycarbonyl)amino)-6-(naphthalen-2-yl)-6-oxohexanoate (19):

Enantioseparation of compound **19** was achieved using a Lux Amylose-2 chiral column and hexane/isopropanol (90/10) as the mobile phase (1 mL/min).

Racemate



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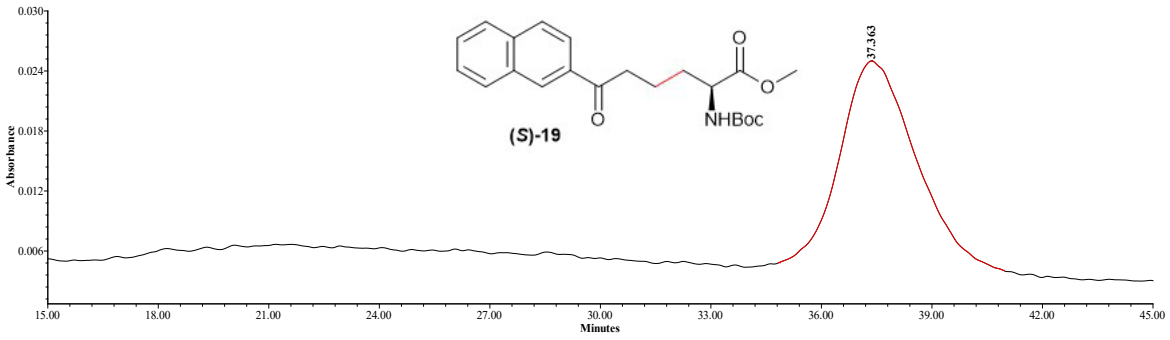
Reaction product



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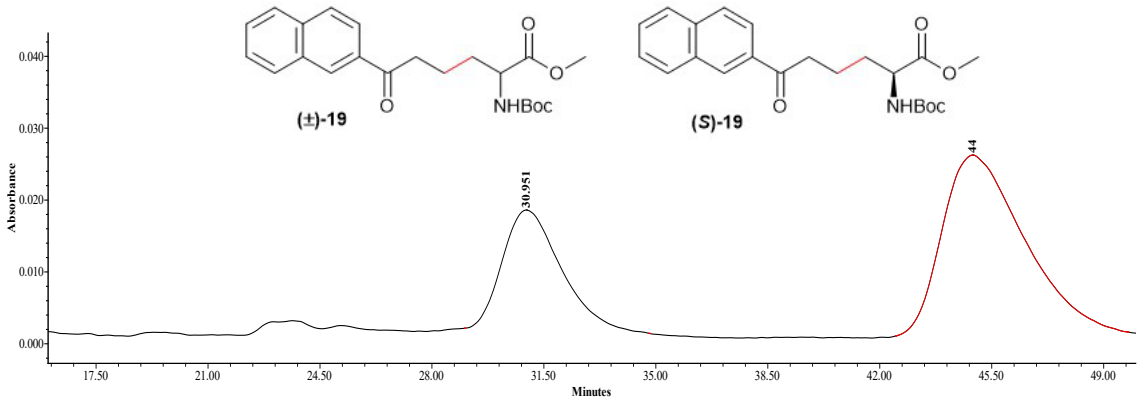
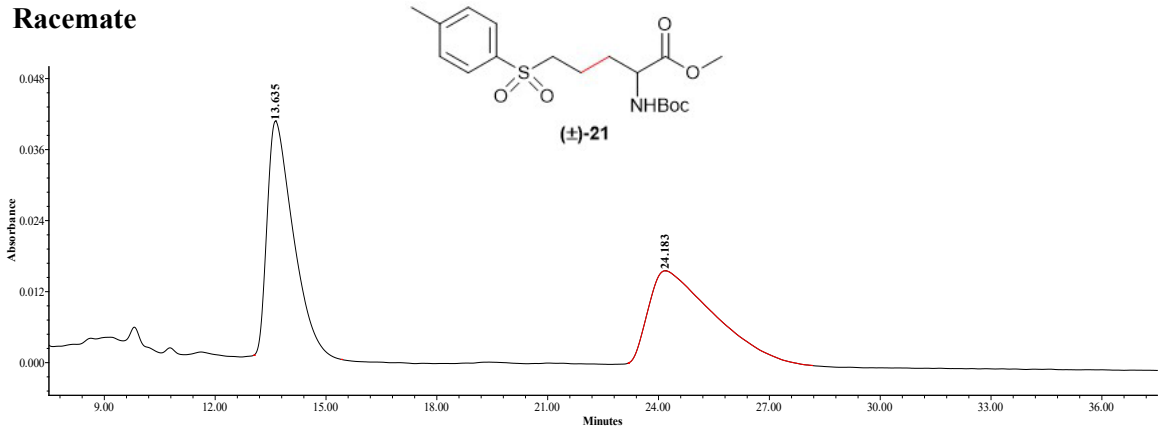
Co-injection



	Retention Time	% Area
1	30.951	31.80
2	44.908	68.20

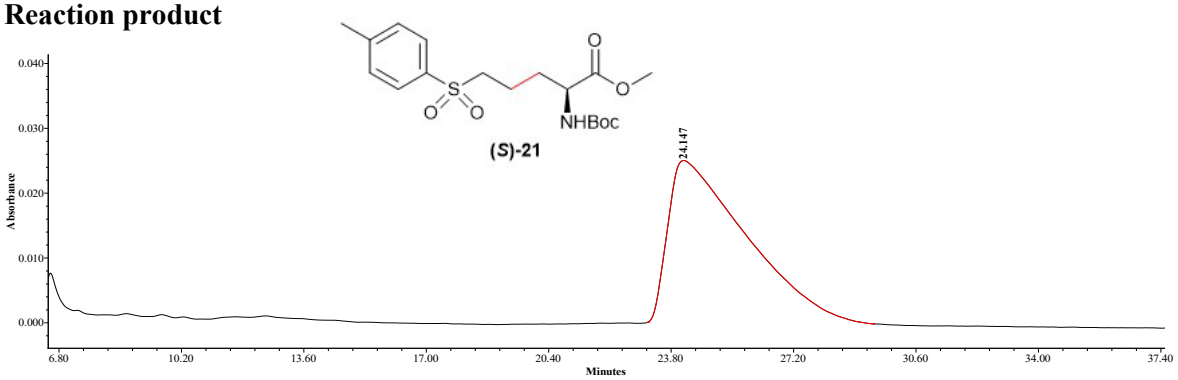
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-5-tosylpentanoate (21): Enantioseparation of compound **21** was achieved using a Lux Amylose-2 chiral column and hexane/isopropanol (60/40) as mobile phase (1 mL/min).

Racemate



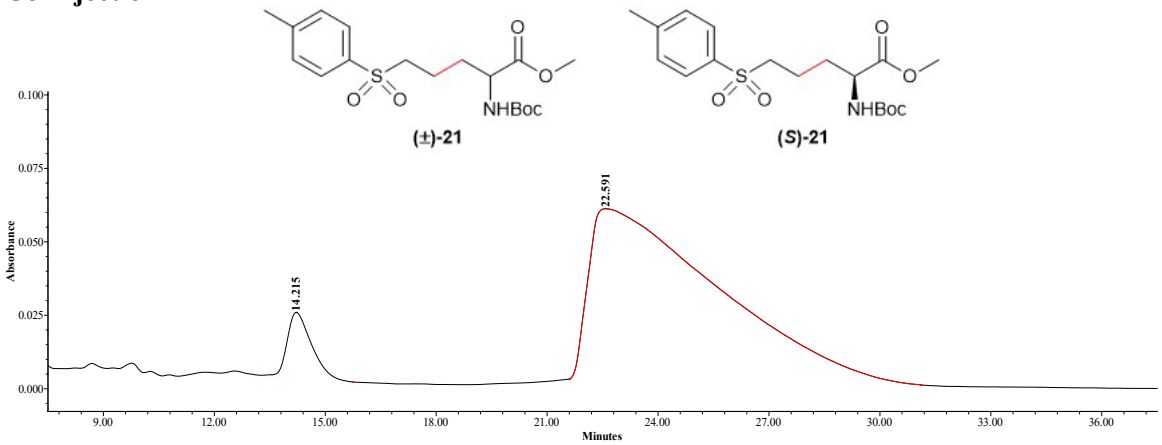
	Retention Time	% Area
1	13.635	50.35
2	24.183	49.65

Reaction product



	Retention Time	% Area
1	24.147	100

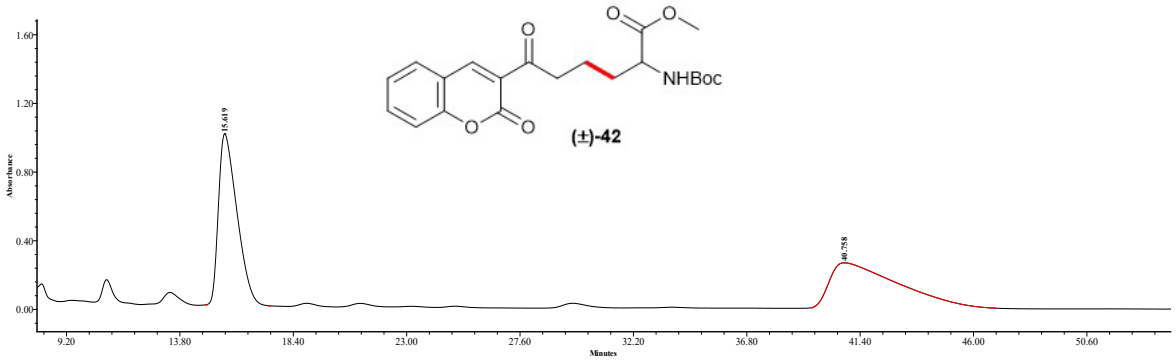
Co-injection



	Retention Time	% Area
1	14.215	6.46
2	22.591	93.54

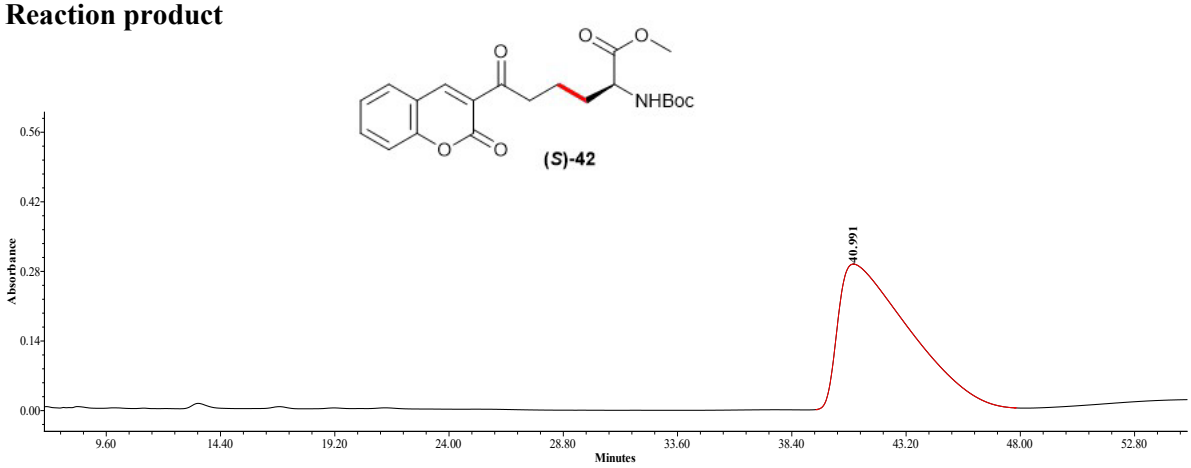
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-6-oxo-6-(2-oxo-2*H*-chromen-3-yl)hexanoate (42): Enantioseparation of compound **42** was achieved using a Lux Amylose-2 chiral column and hexane/isopropanol (40/60) as the mobile phase (1 mL/min).

Racemate



	Retention Time	% Area
1	15.619	50.88
2	40.758	49.12

Reaction product



	Retention Time	% Area
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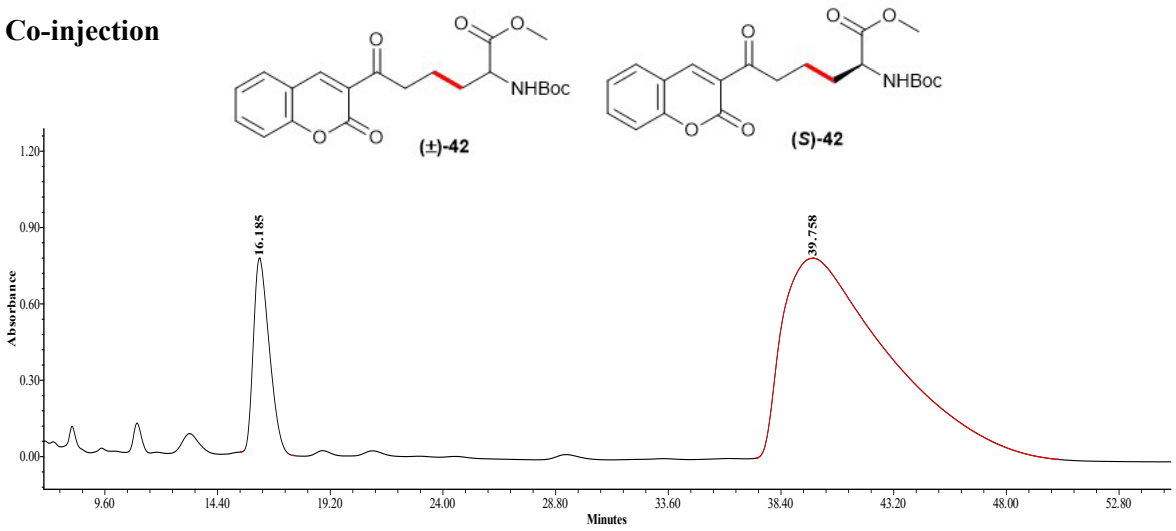
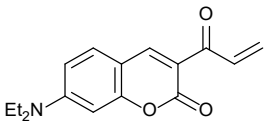
Co-injection



	Retention Time	% Area
1	16.185	12.71
2	39.758	87.29

Computational details

Standard density functional theory (DFT) calculations were carried out with Gaussian 16[1] and Q-Chem 5.[2] Geometries were optimized using the B3LYP/6-31G(d) procedure.[3] The choice of this level of theory is based on the our previous studies into the use of efficient computational chemistry methods for obtaining reliable molecular geometries.[4,5] For the calculation of electronic excitations, we used the PBE50 functional,[6] which has been shown to yield reliable excitation energies. We applied the Tamm-Dancoff approximation[7] to time-dependent DFT in our excited state calculations for its substantially improved computational efficiency with minimal impact on the reliability. The orbitals involved in the lowest-energy absorptions (i.e., the lowest-energy transitions with non-negligible intensities) are shown in the figures below. For **51**, the transition populates the acceptor alkene, making it less reactive towards further acceptance of electron density (from the donor molecule).



51

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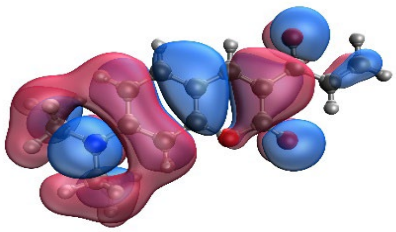
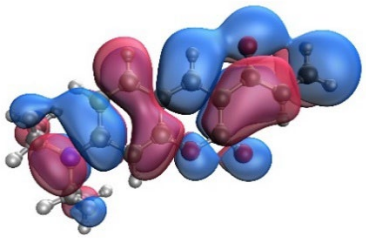
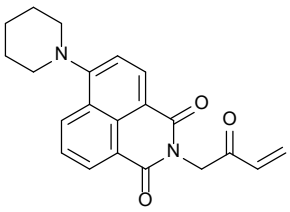
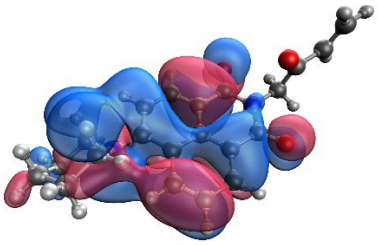
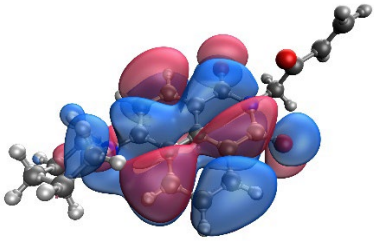
	



Originating (HOMO)	Destination (LUMO)
	

References

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Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Wallingford, CT, 2016.

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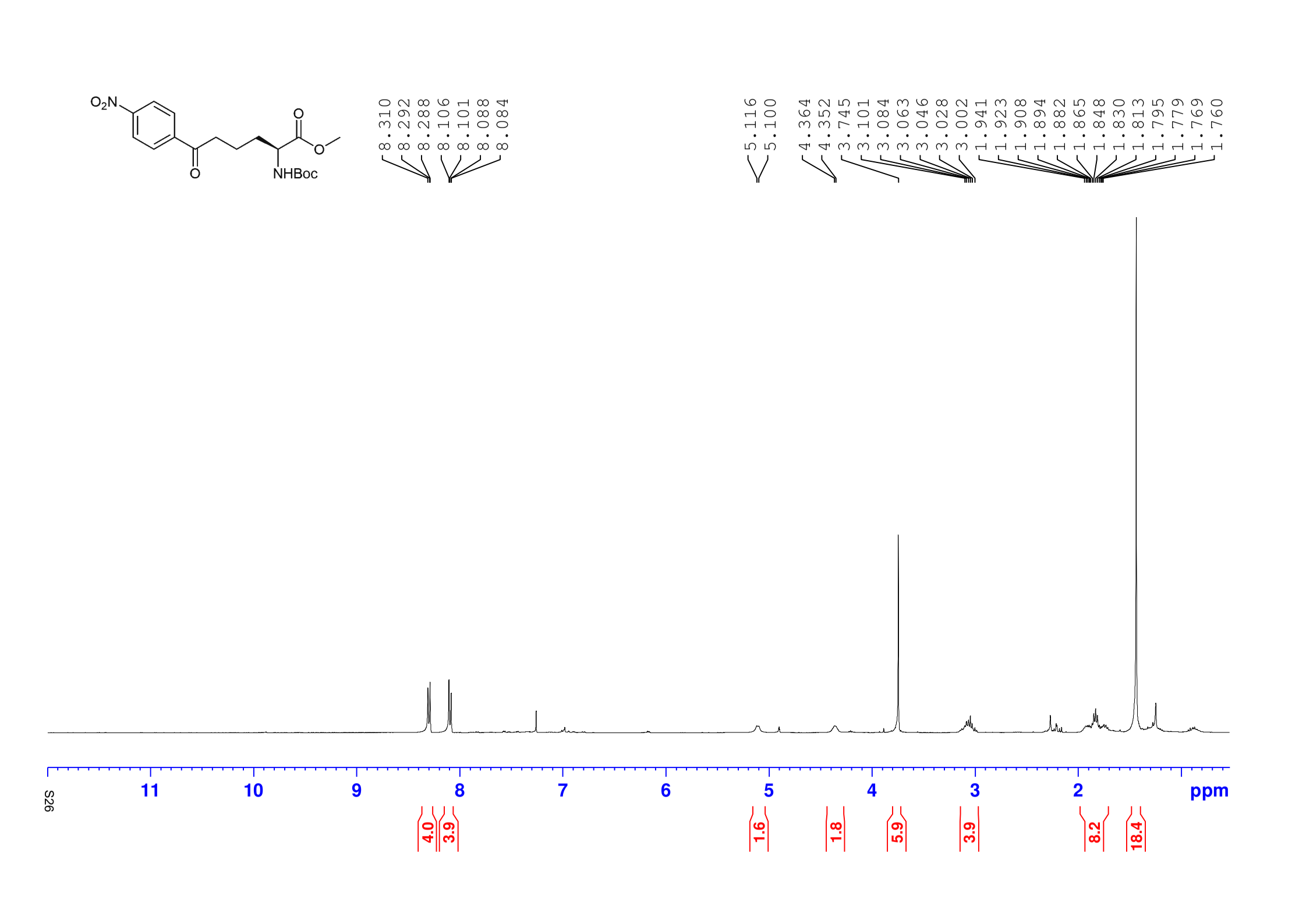
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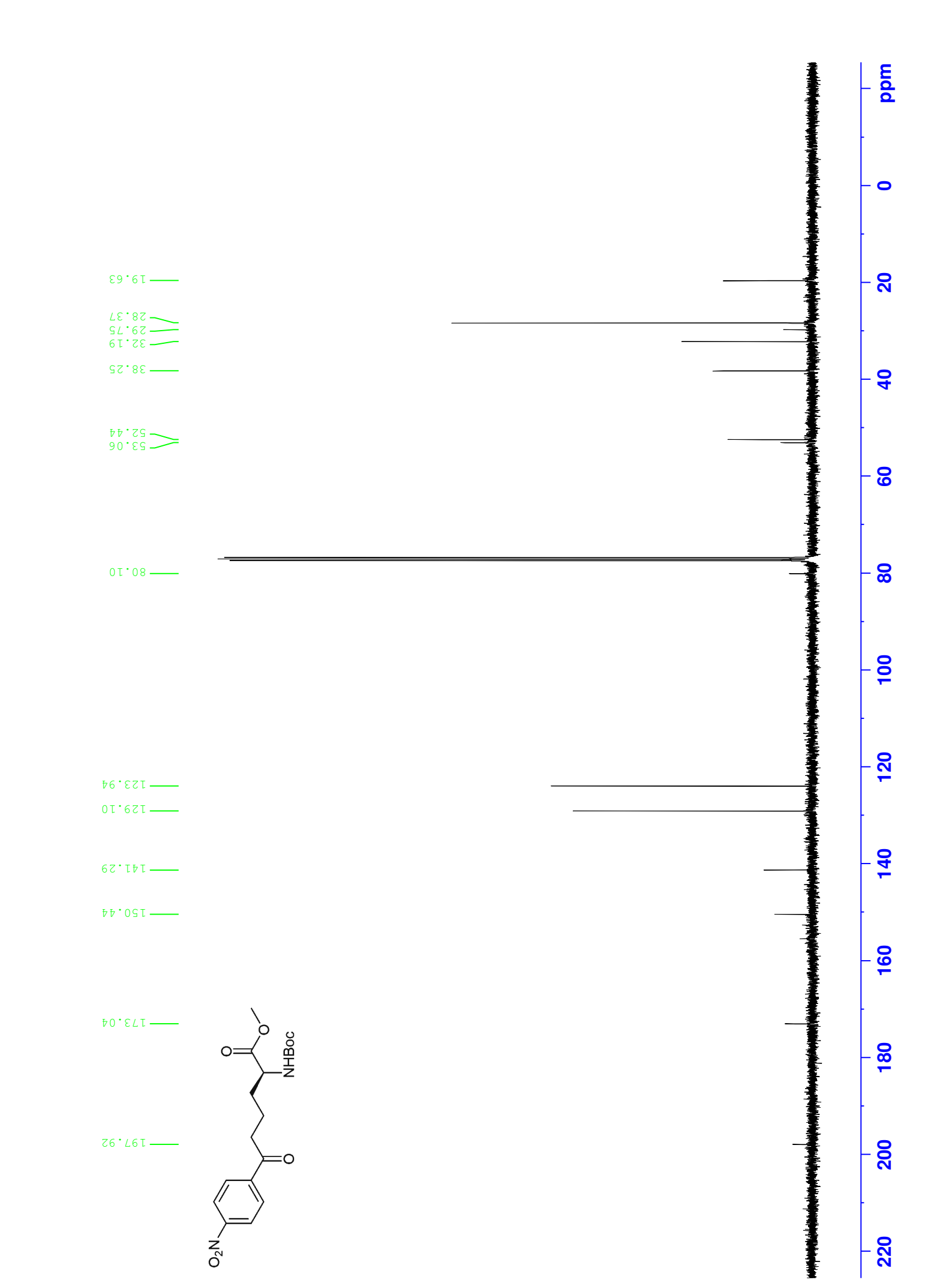
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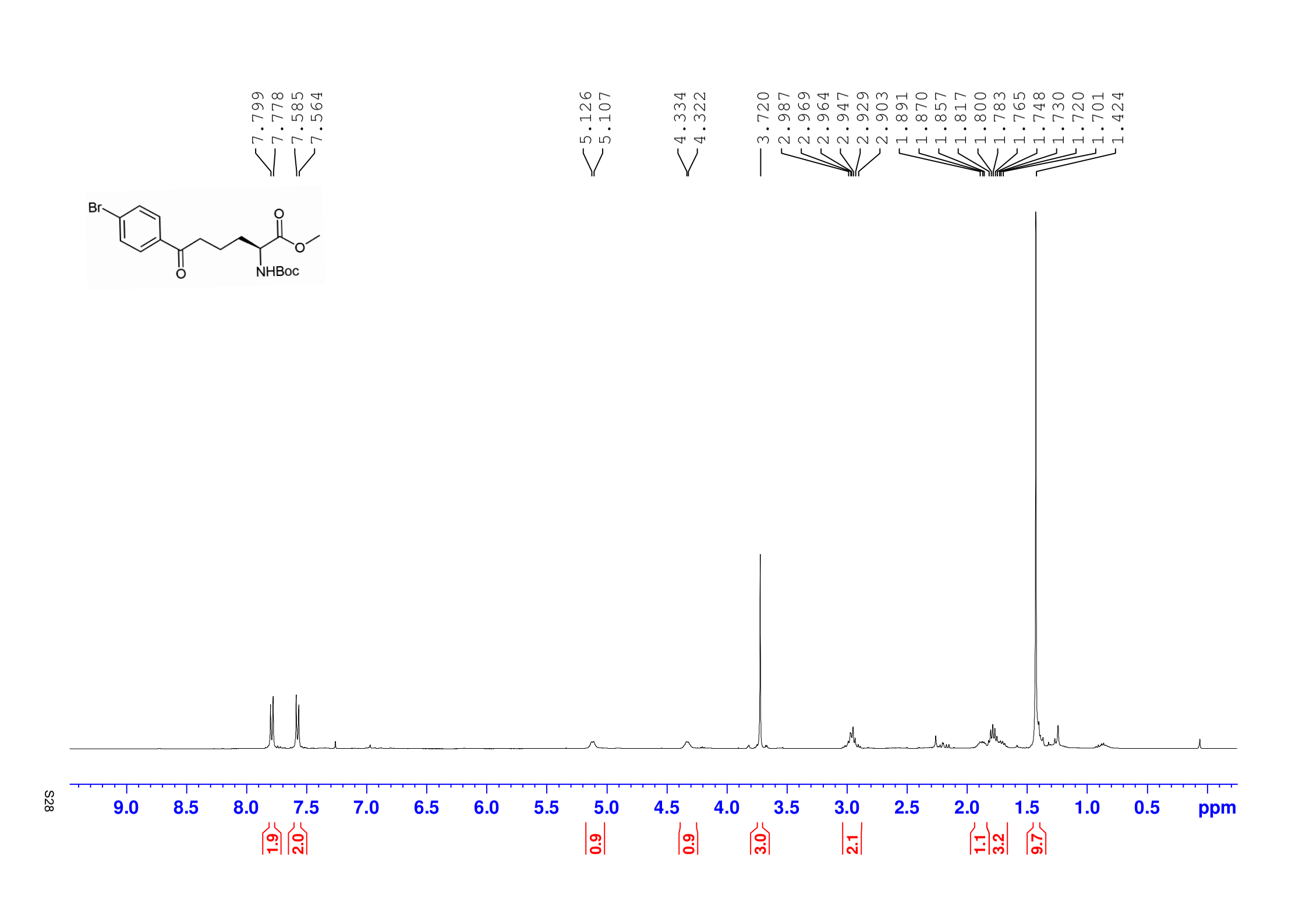
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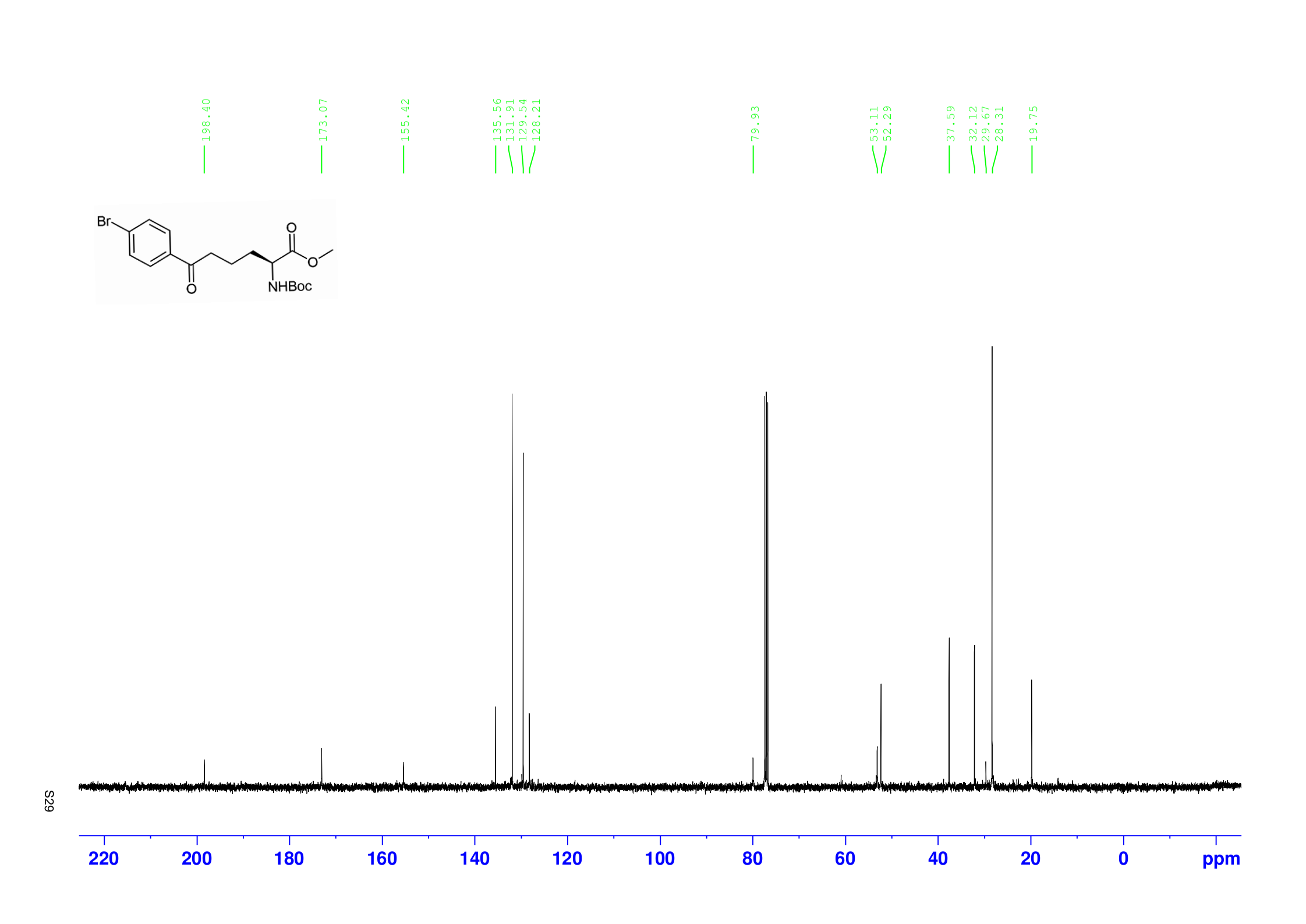
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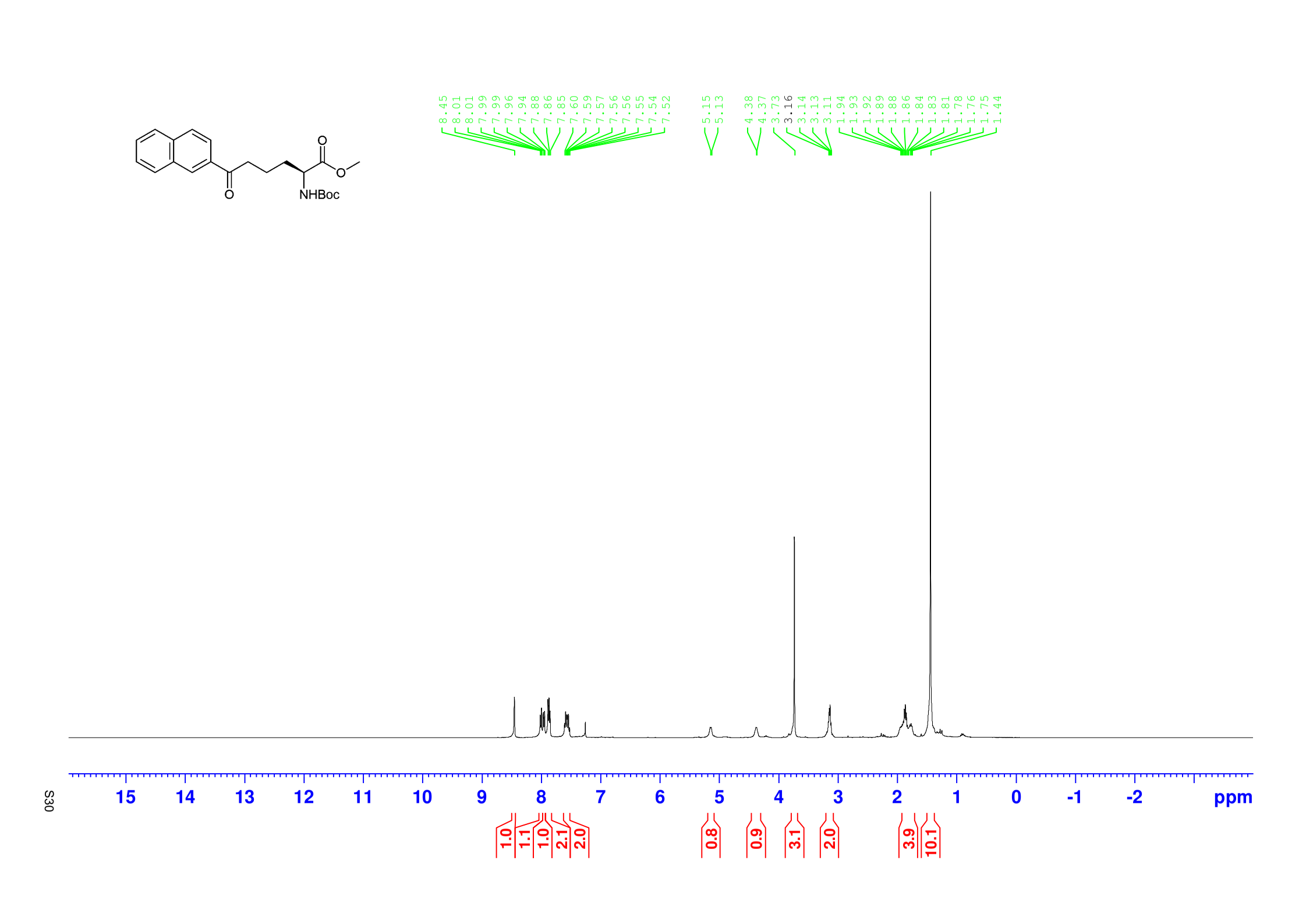
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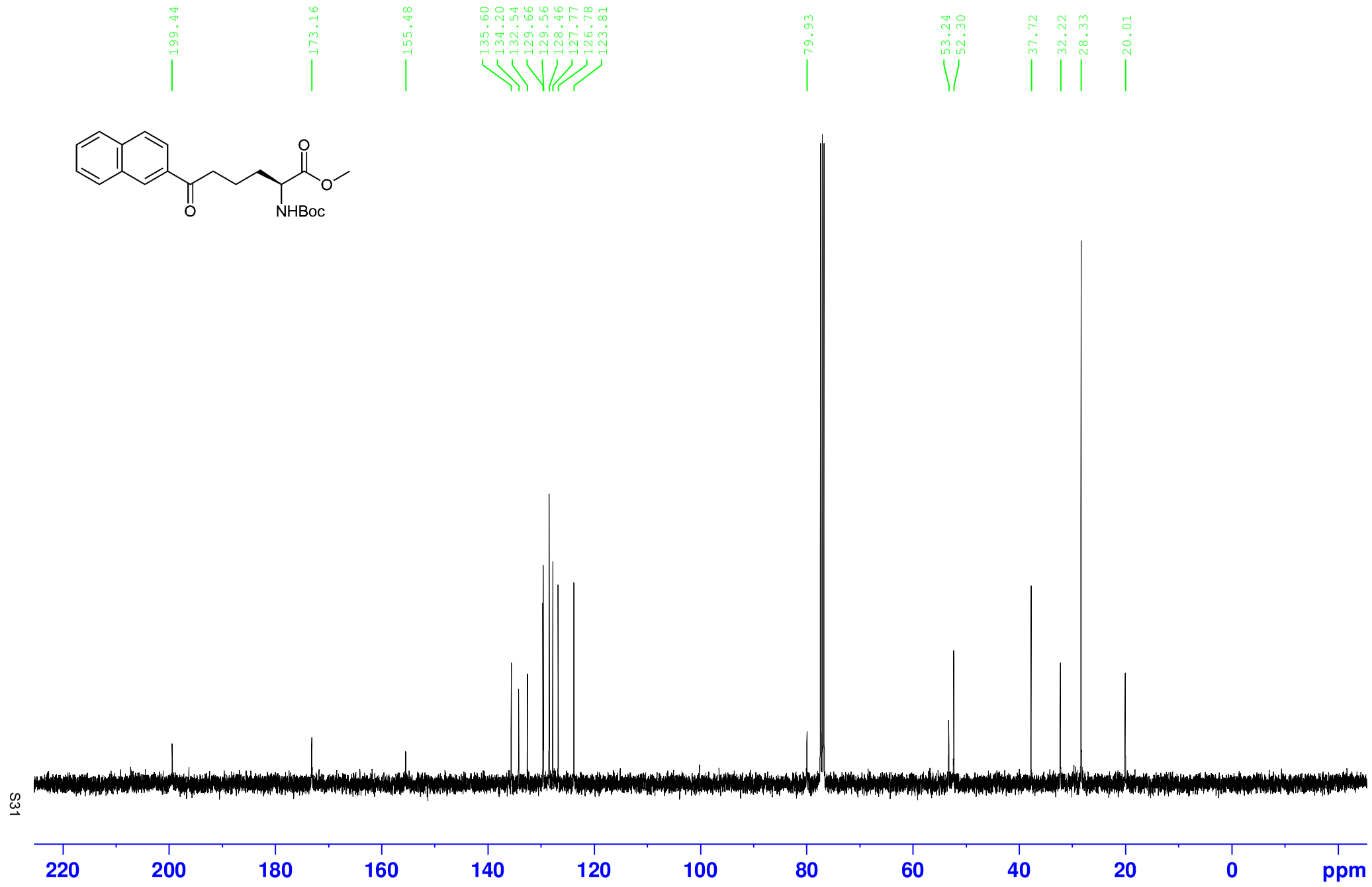
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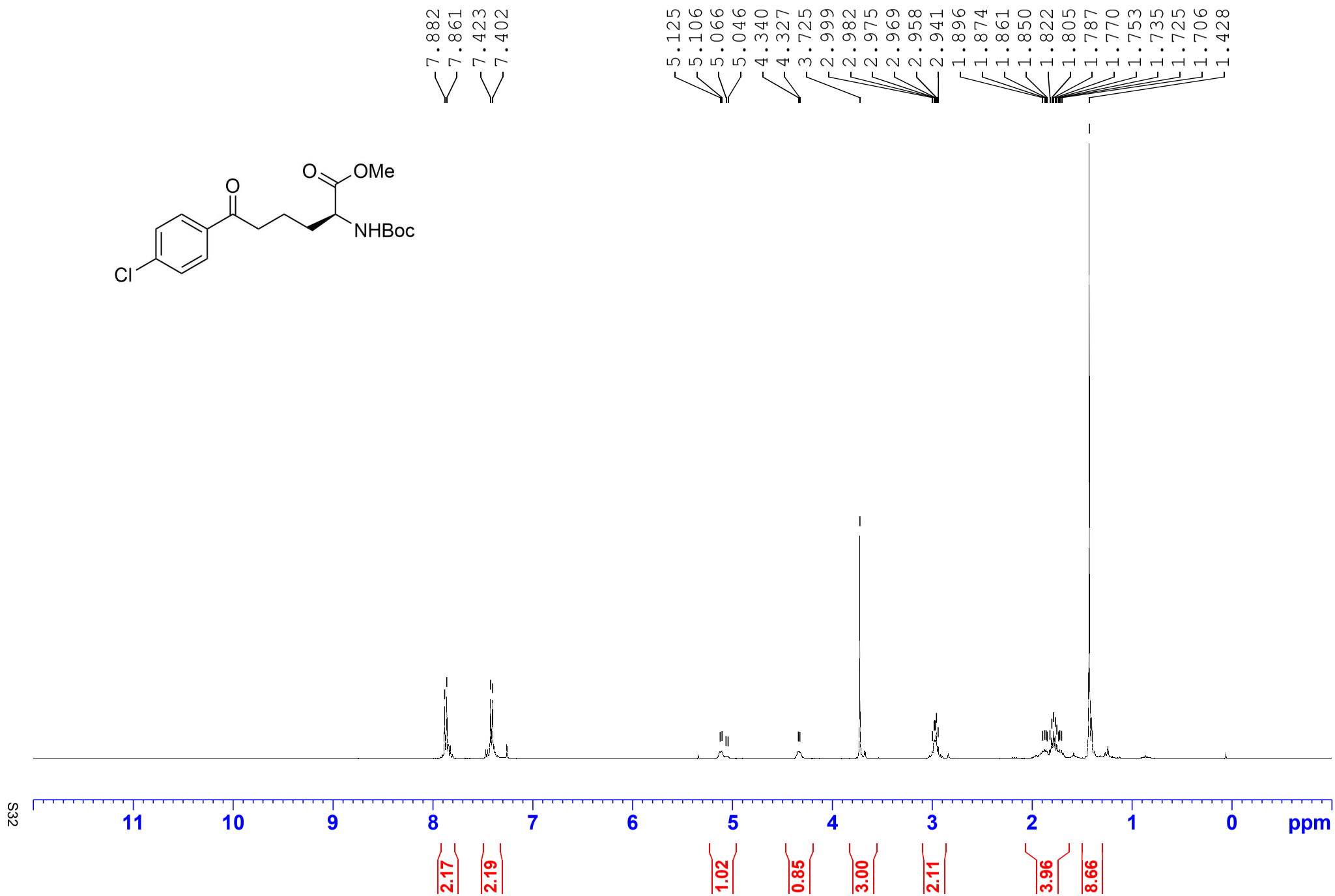
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NHBoc
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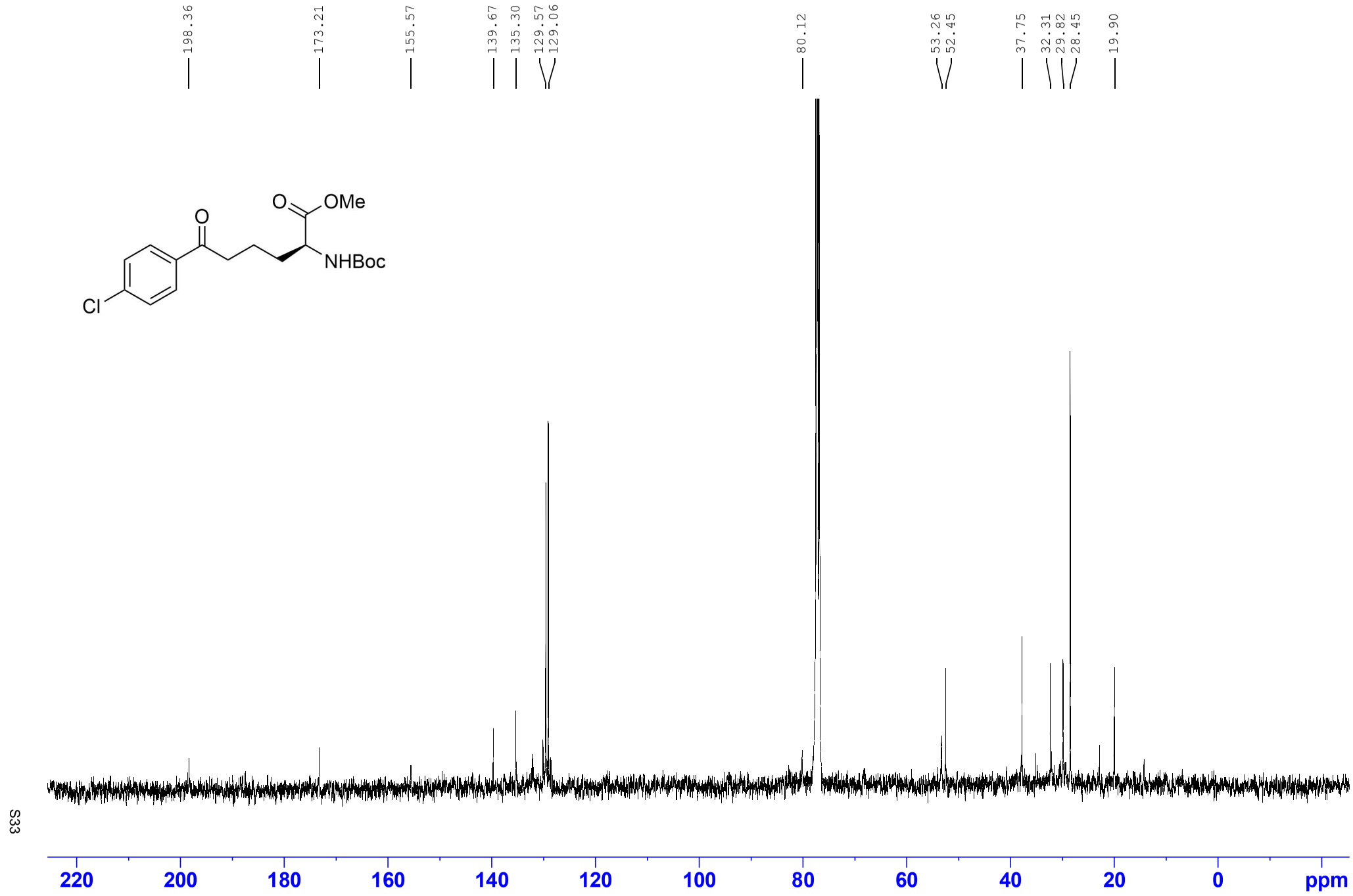
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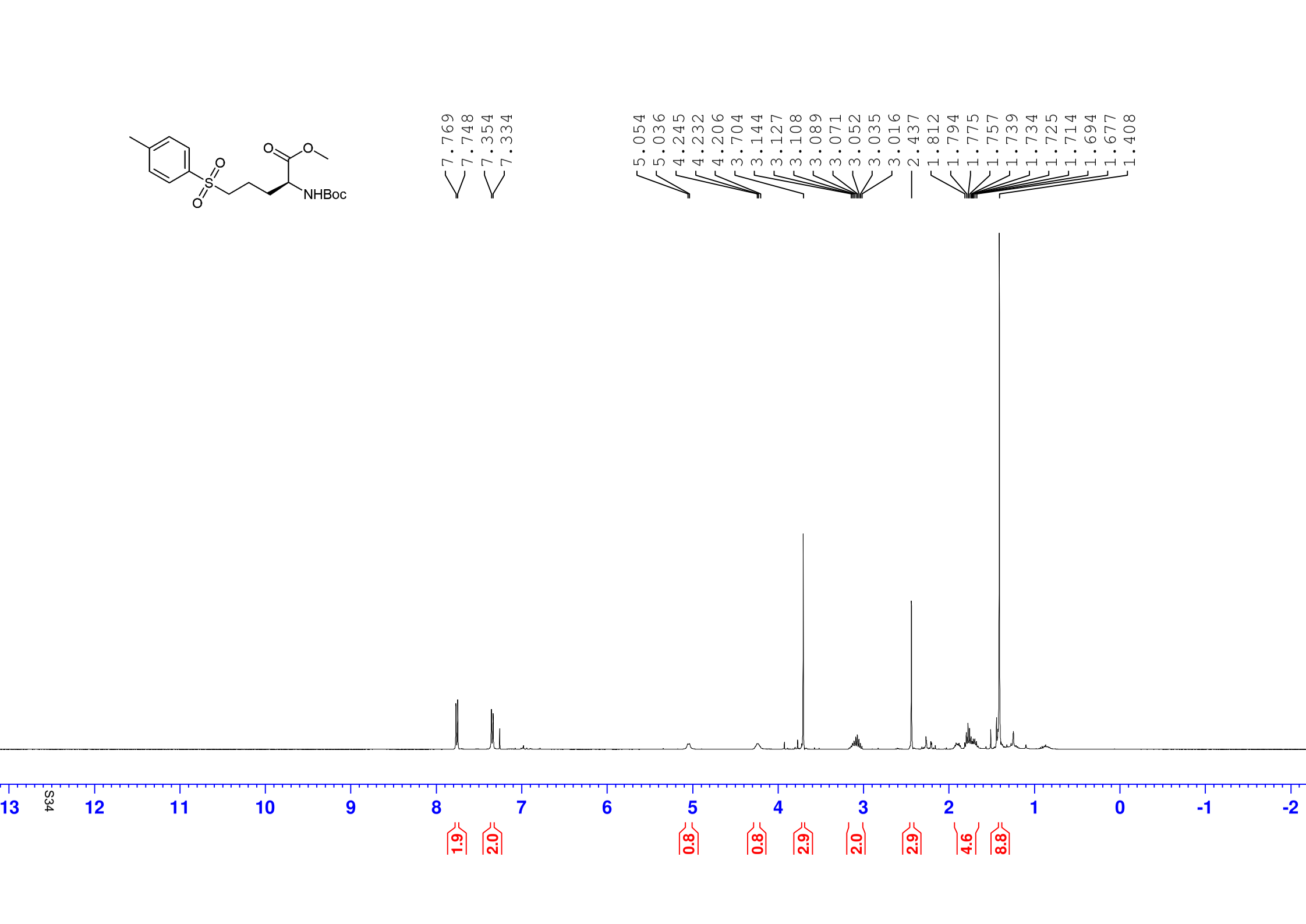
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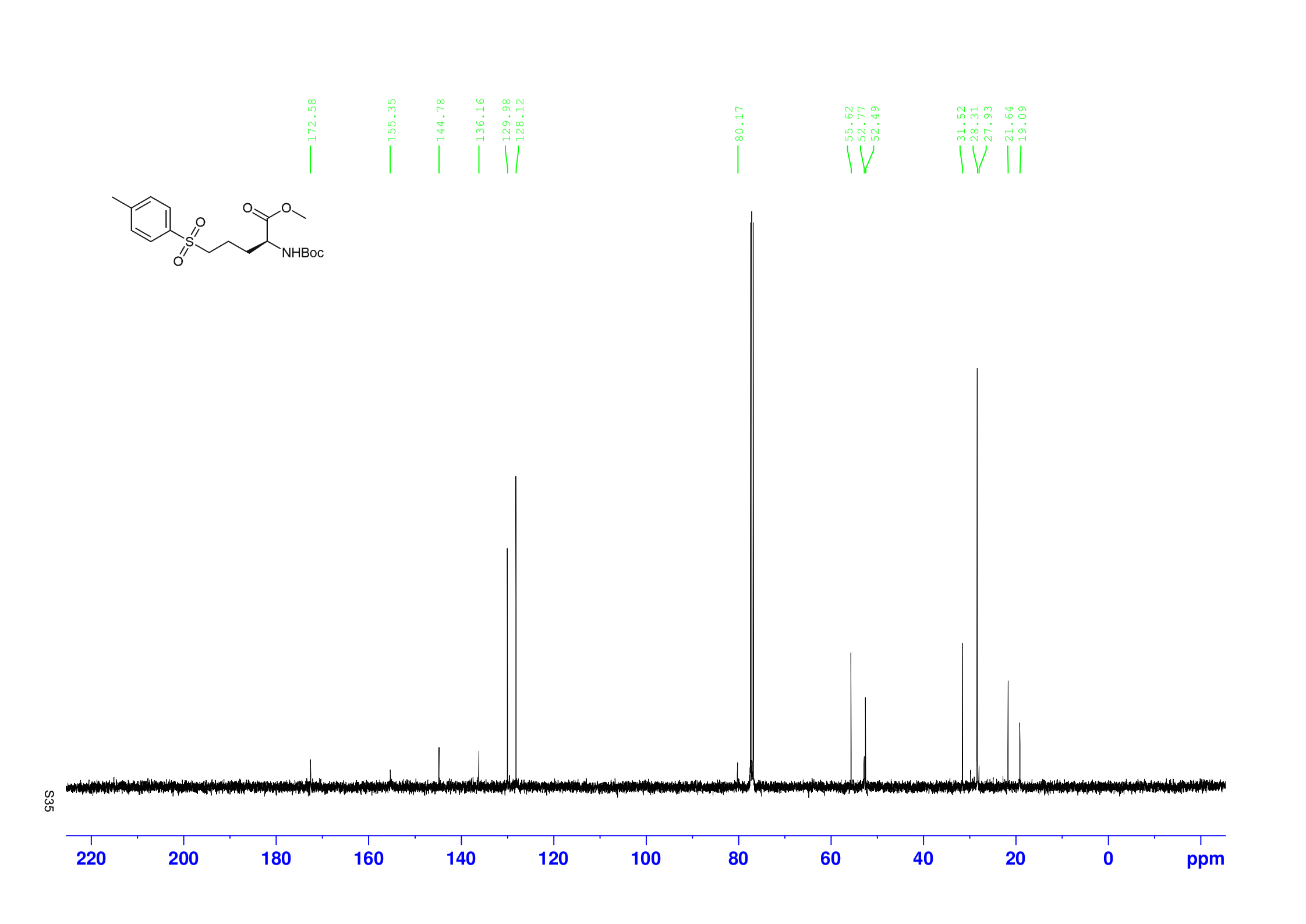
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19.09
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O
NHBoc
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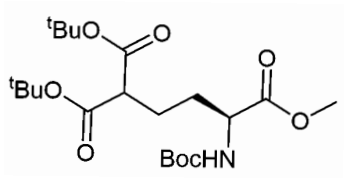

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1.433

9.0 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 ppm

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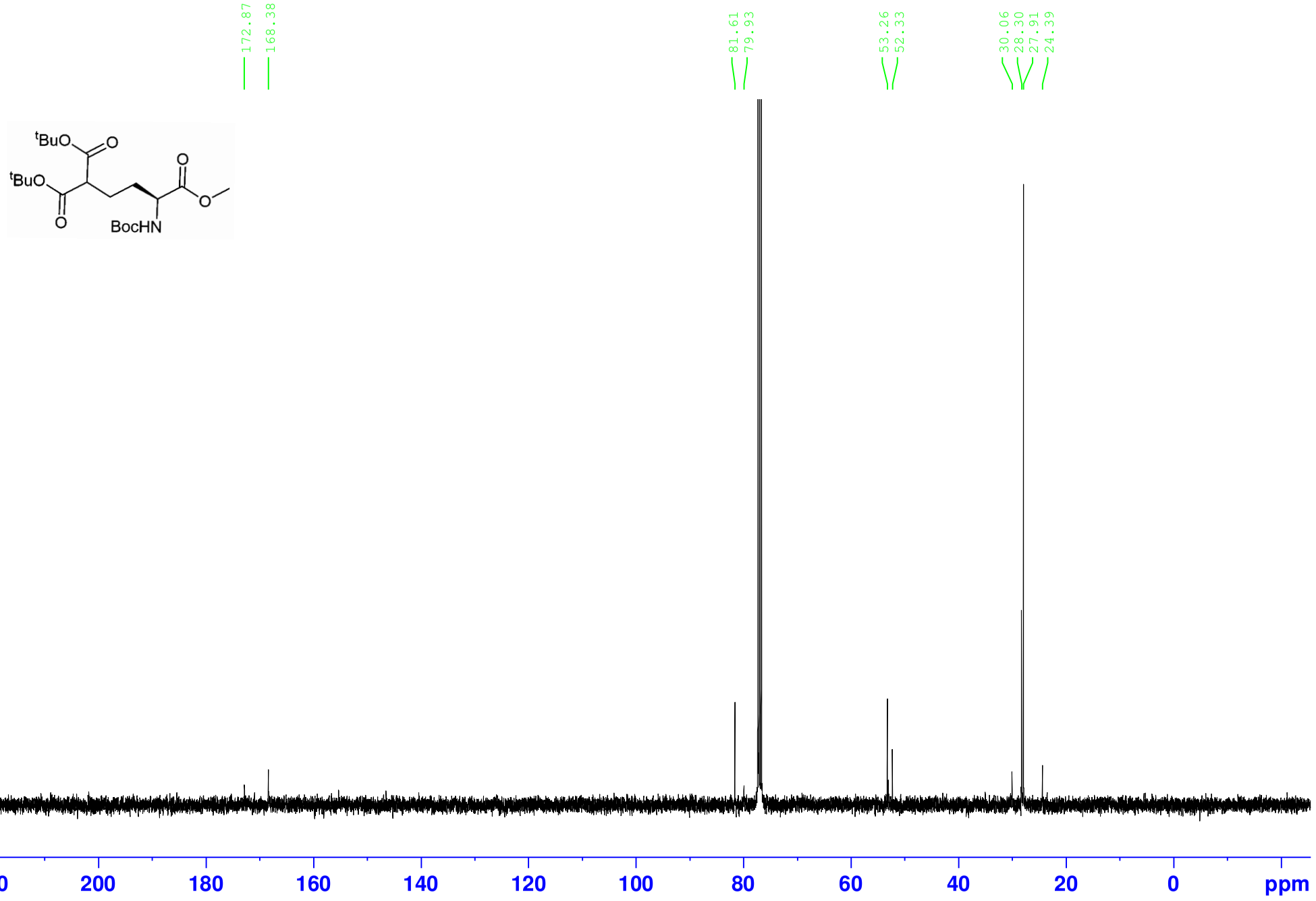
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O
BocHN
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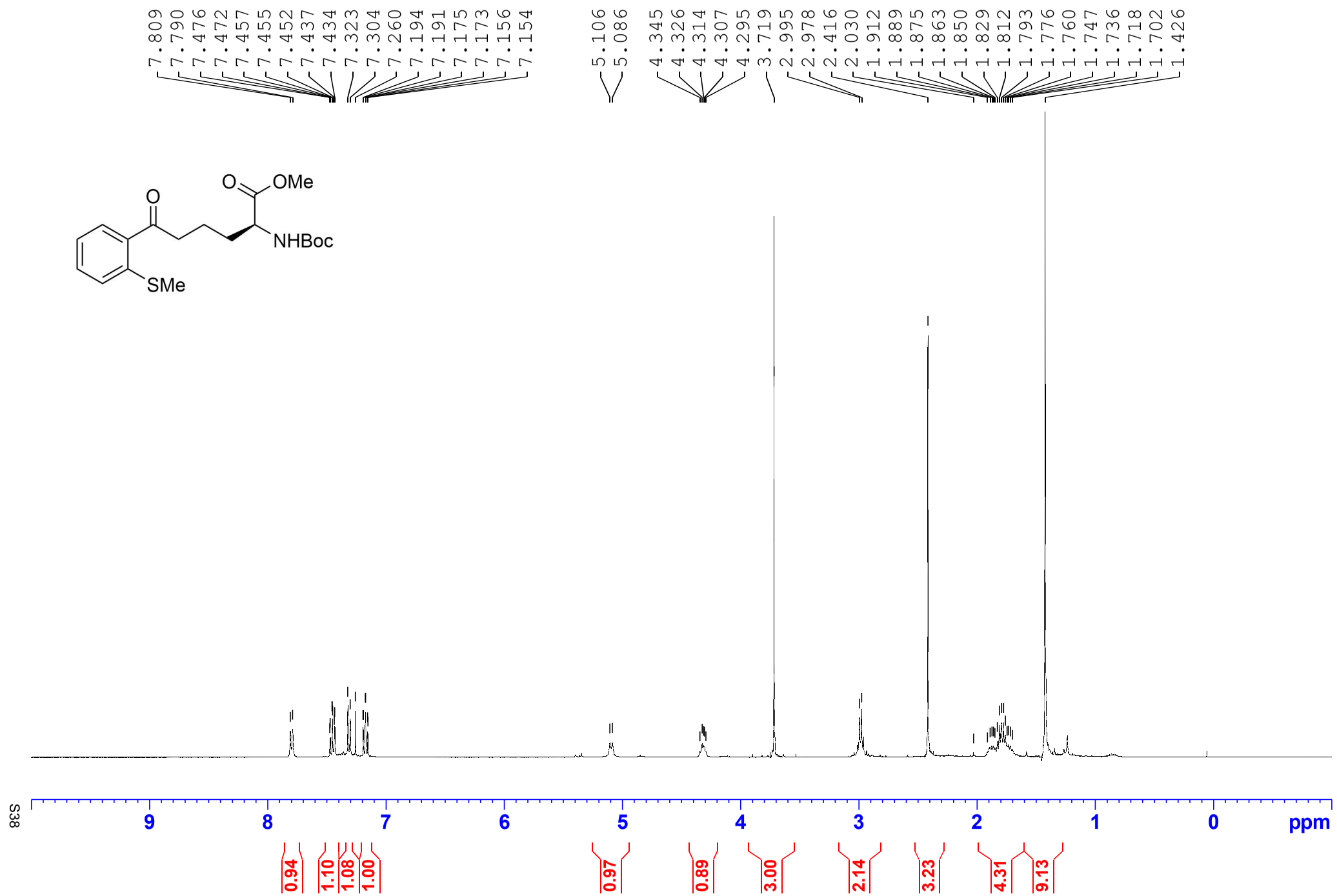
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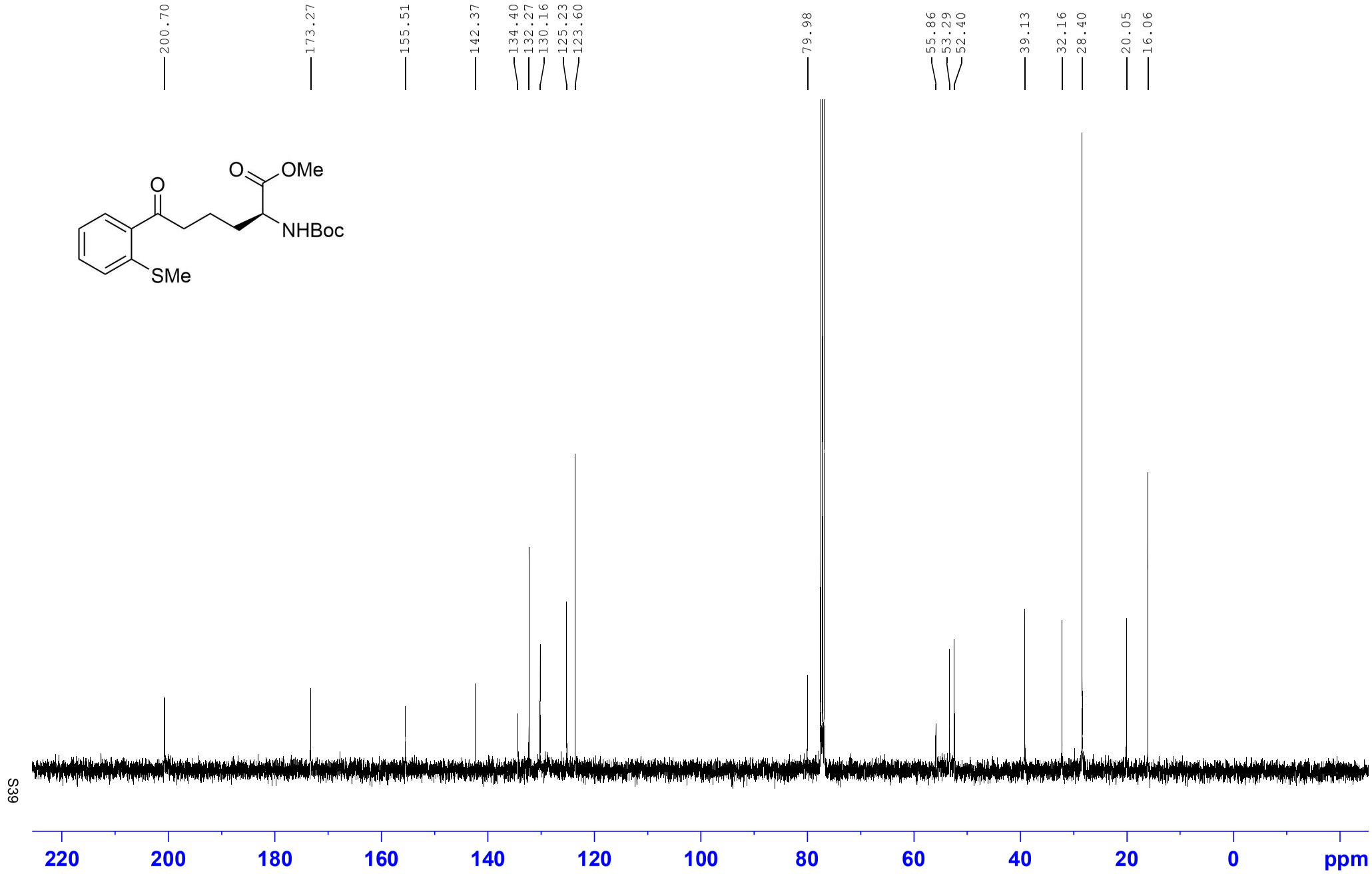
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20.05
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NHBoc
SMe
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200
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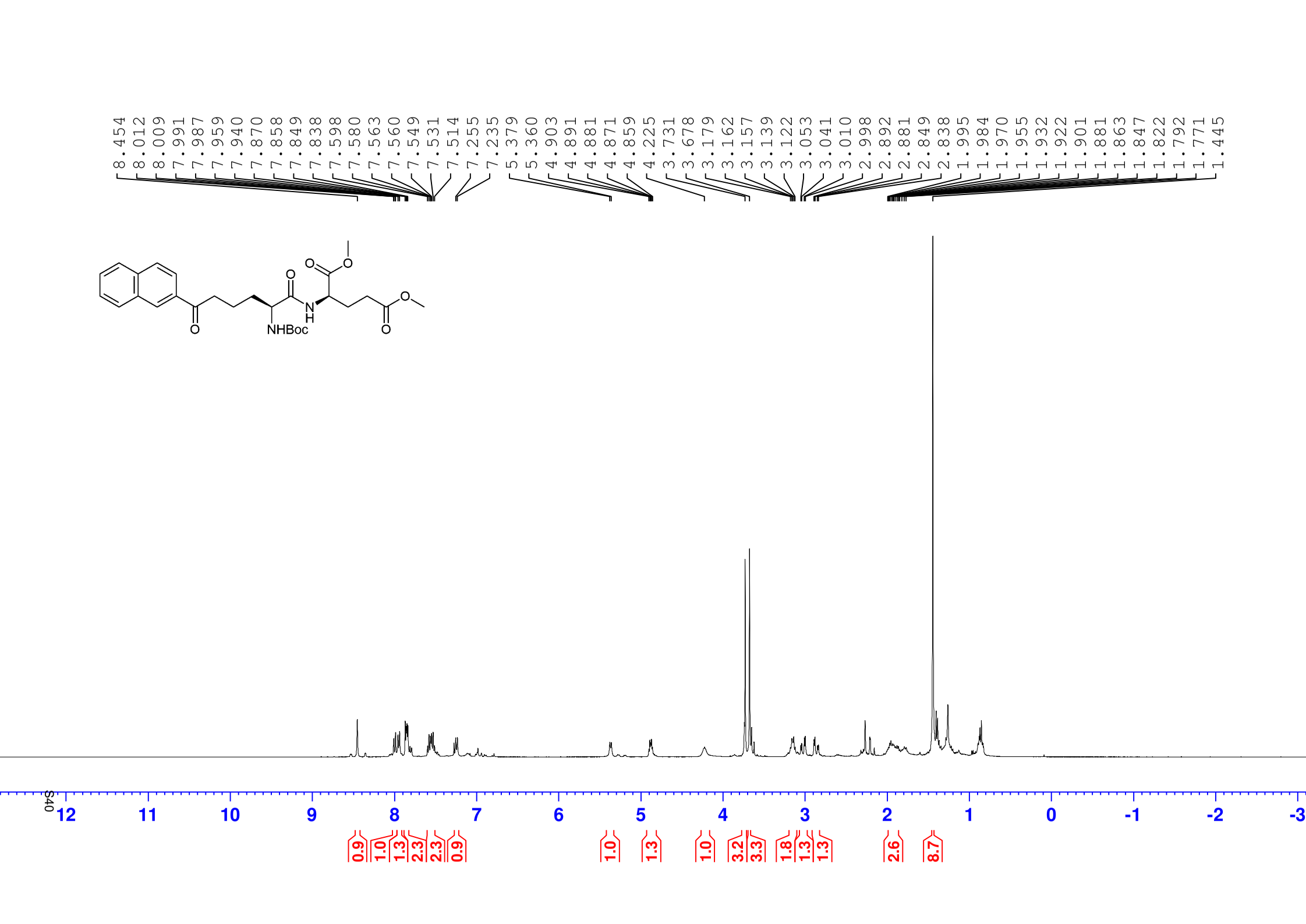
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7.549
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4.891
4.881
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1.984
1.970
1.955
1.932
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1.901
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1.792
1.771
1.445
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O
O
N
H
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NHBoc
S40
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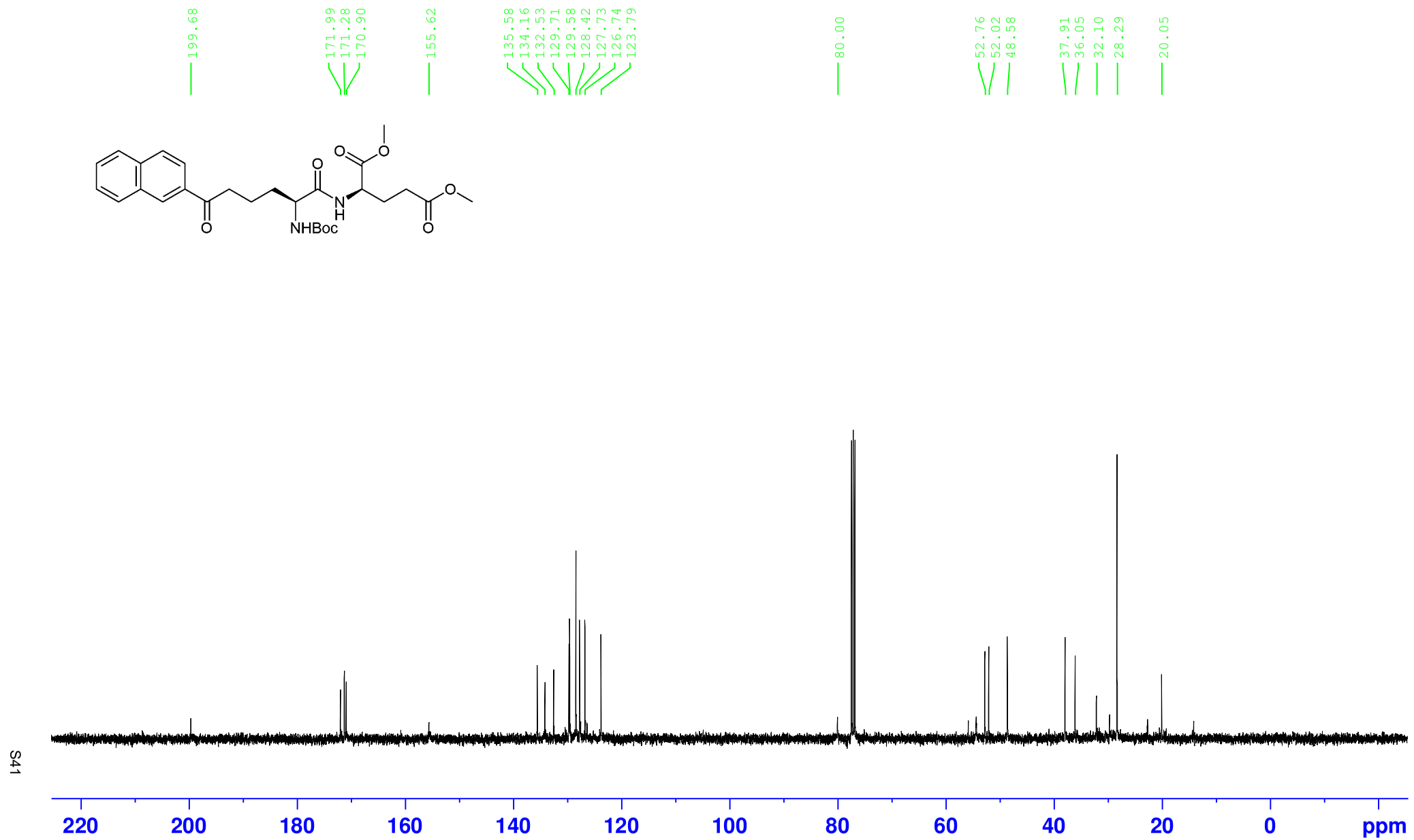
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37.91
36.05
32.10
28.29
20.05
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O
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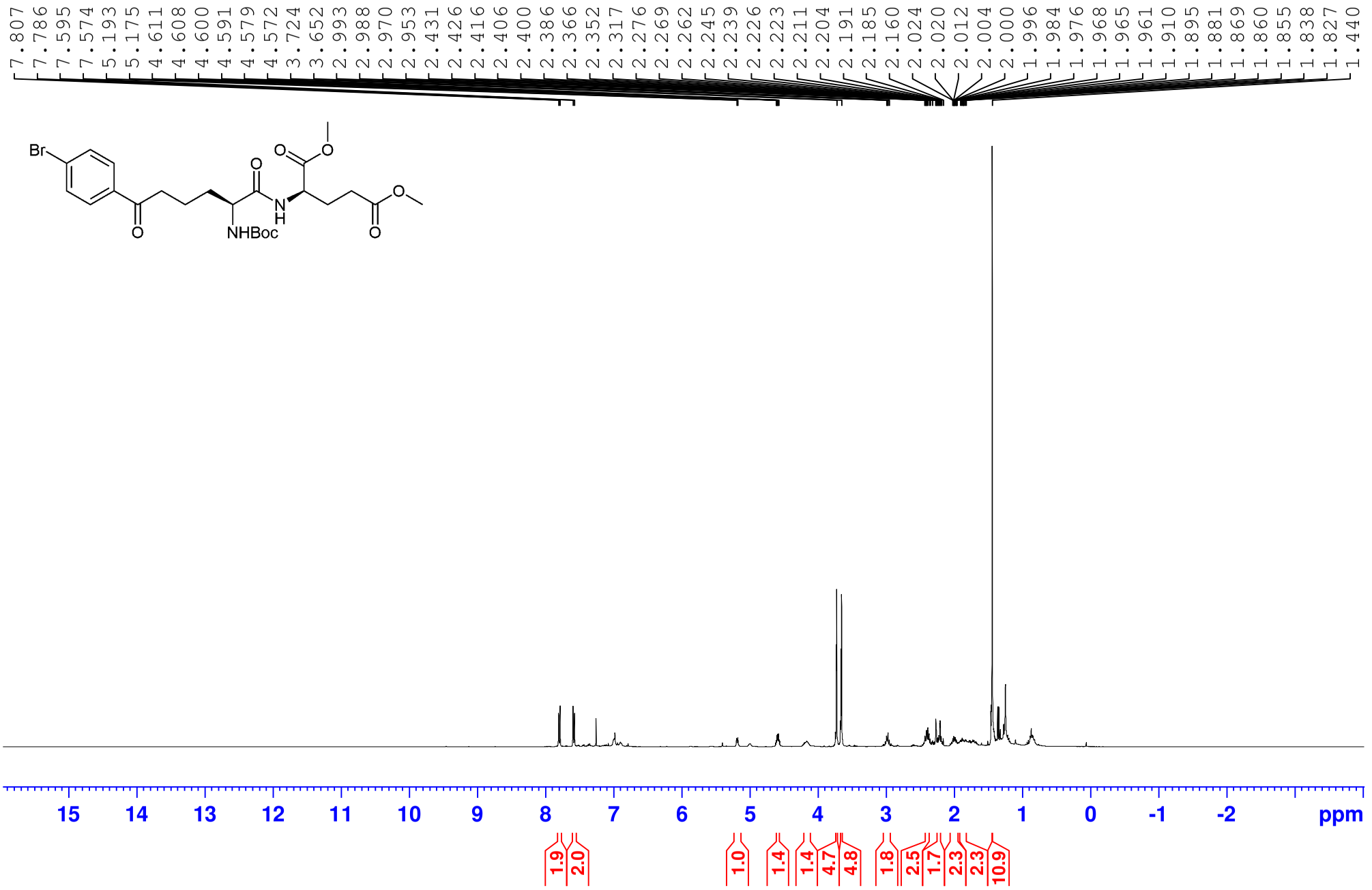
ppm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O
O
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H
O
O
NHBoc
O
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14
13
12
11
10
9
8
7
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4
3
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-2
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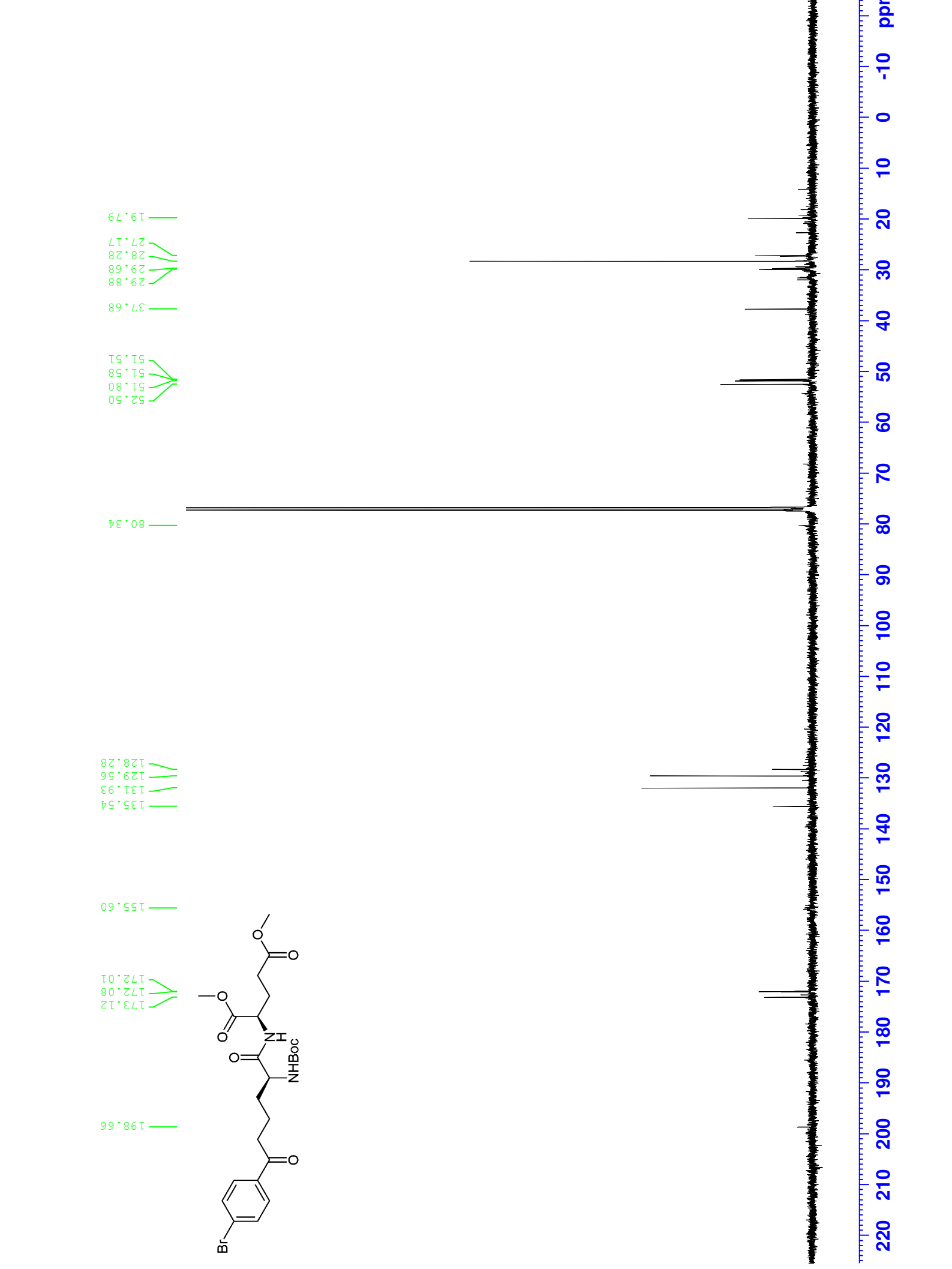
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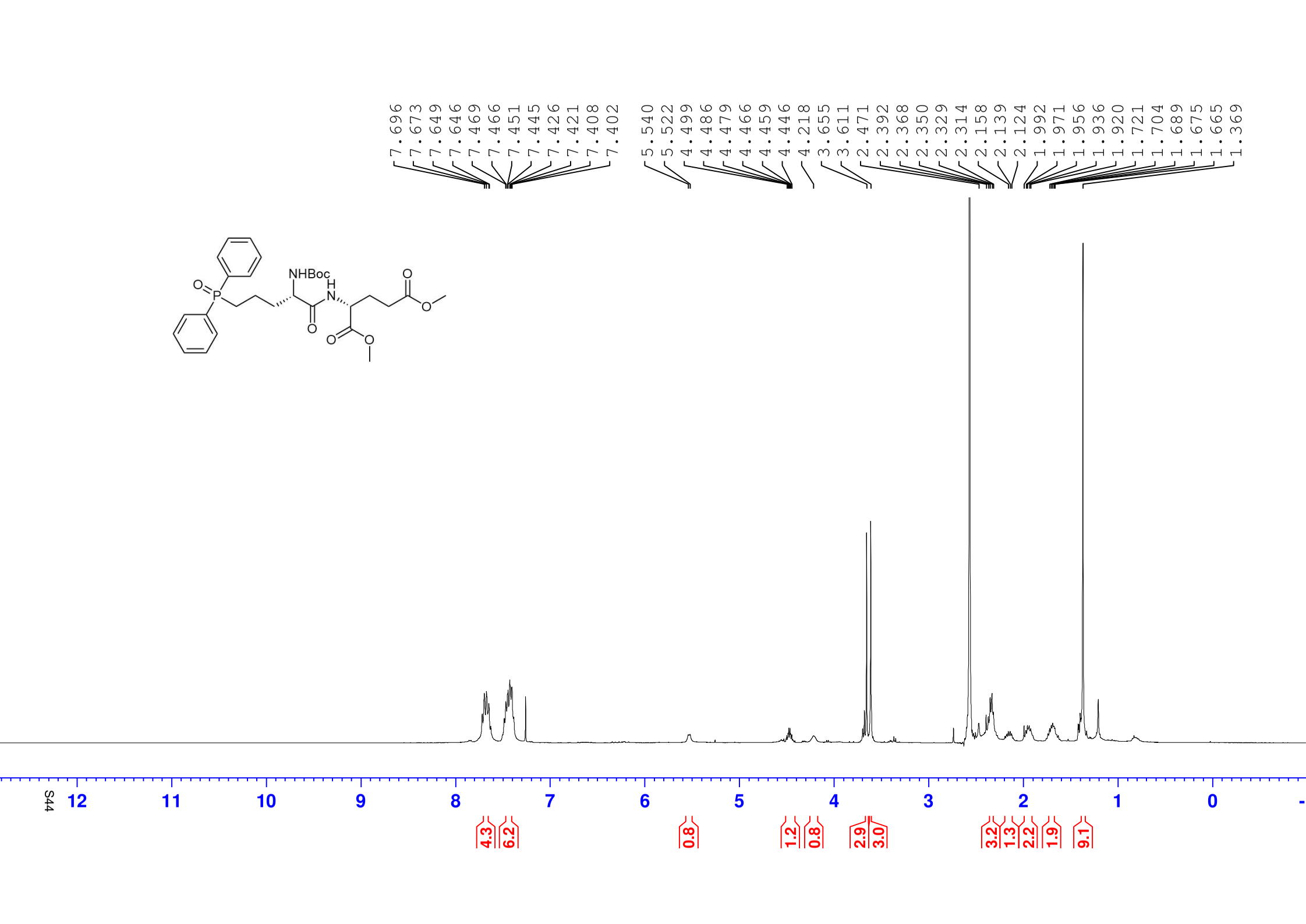
Br
O
NH
ppm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4.459
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1.369
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H
N
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P
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O
O
O
S44
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7
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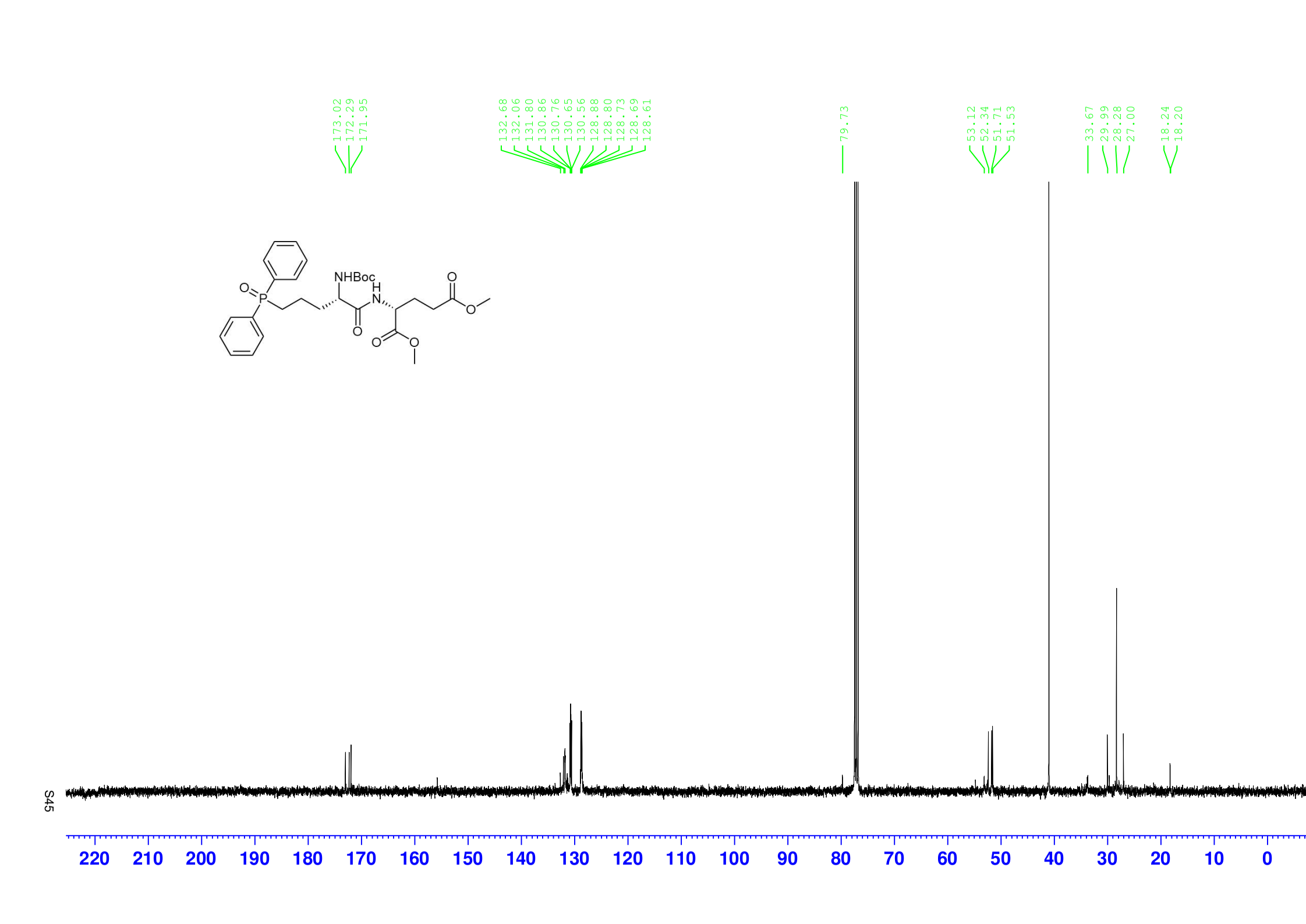
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18.20
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H
N
O
P
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O
O
O
O
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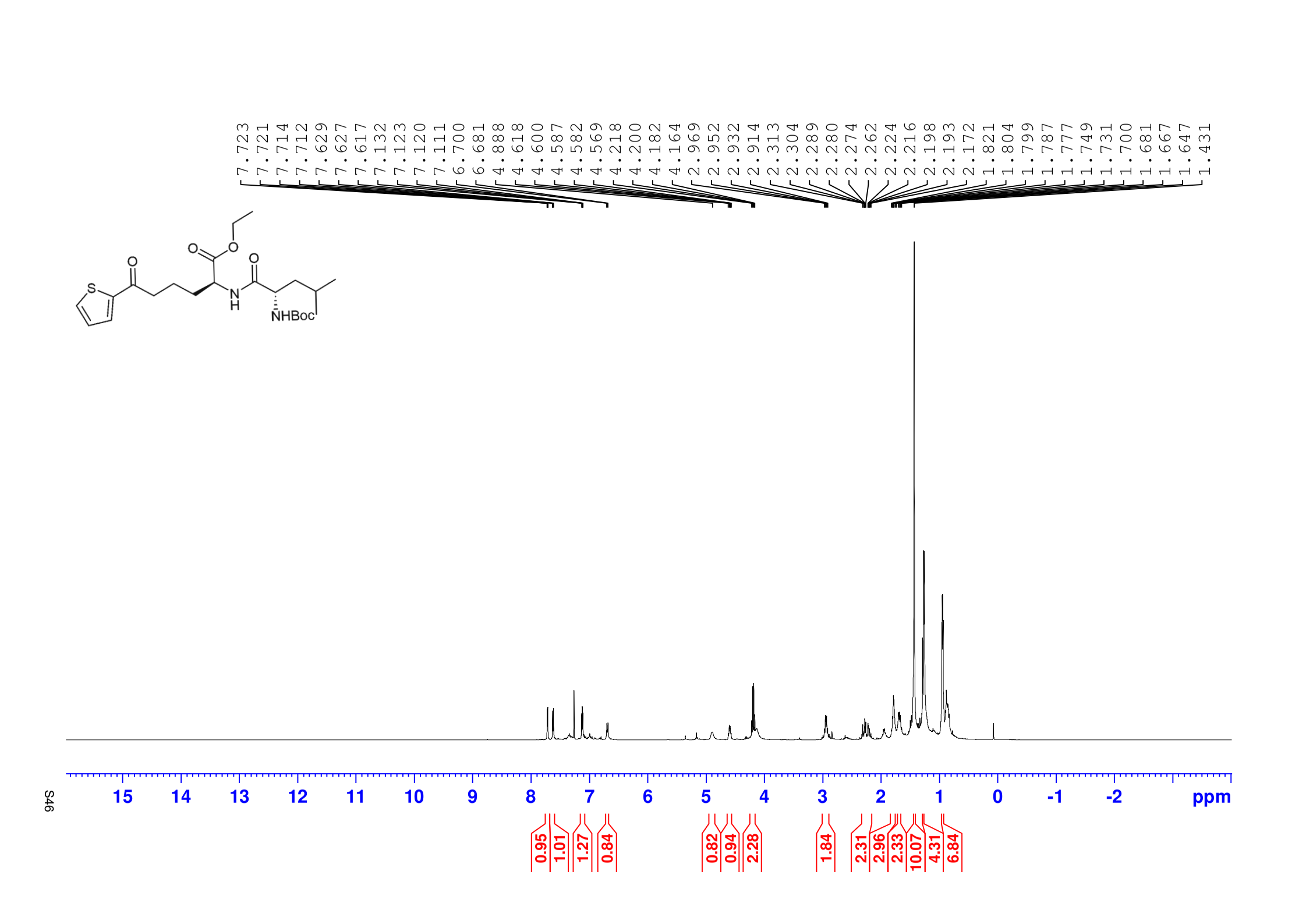
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O
O
O
S
N
H
O
NHBoc
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12
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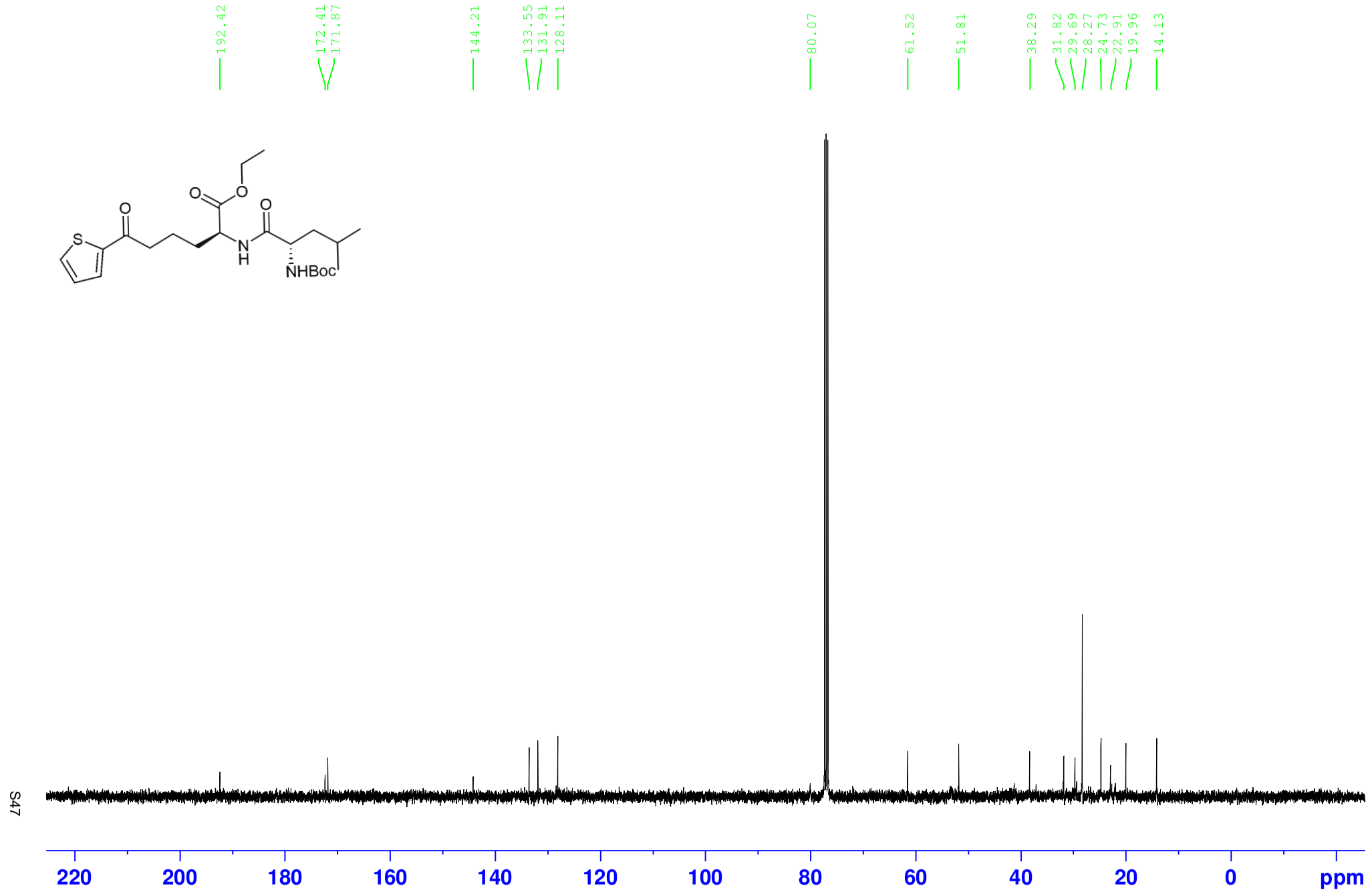
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24.73
22.91
19.96
14.13
O
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H
NHBoc
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120
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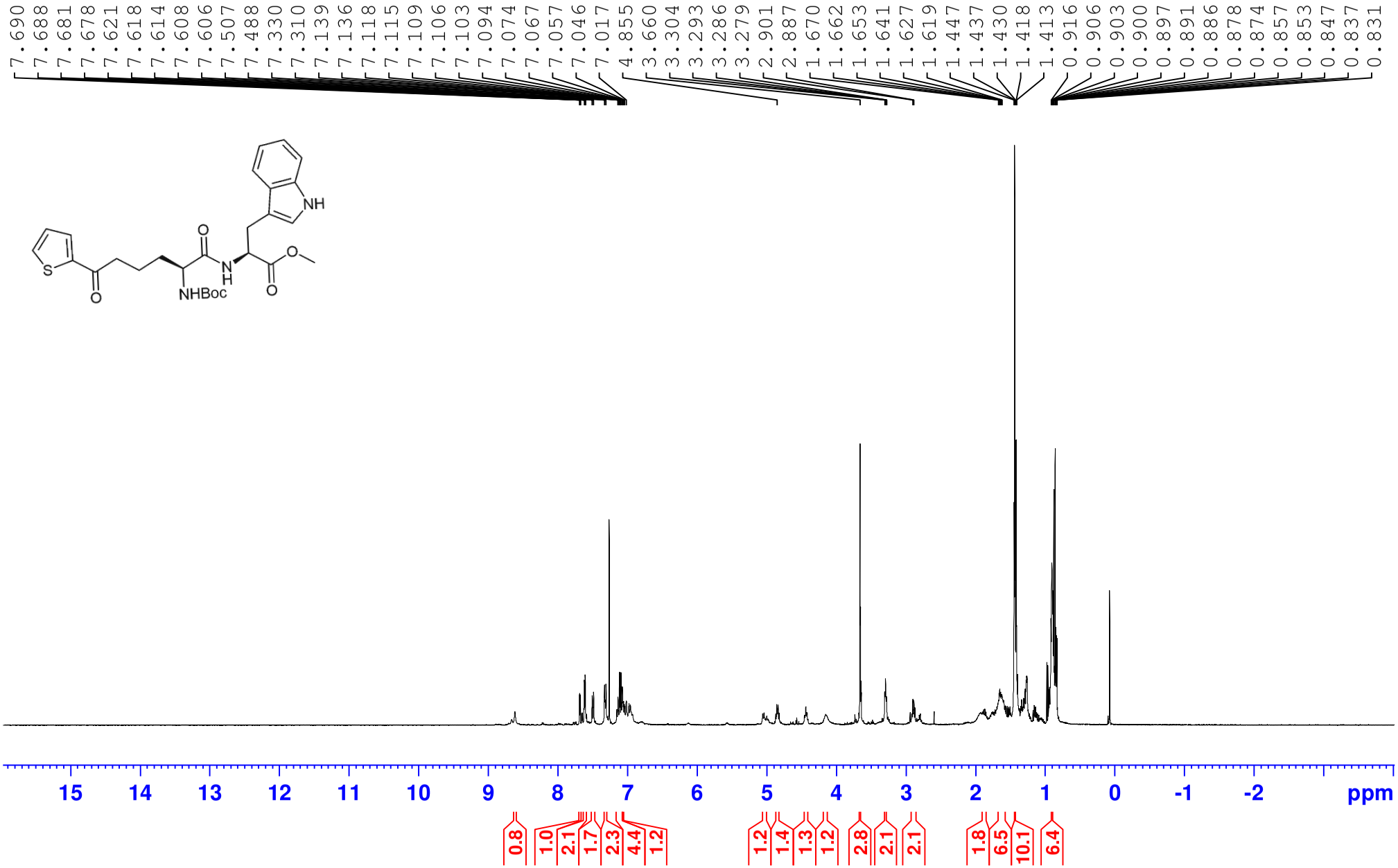
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S
O
N
H
O
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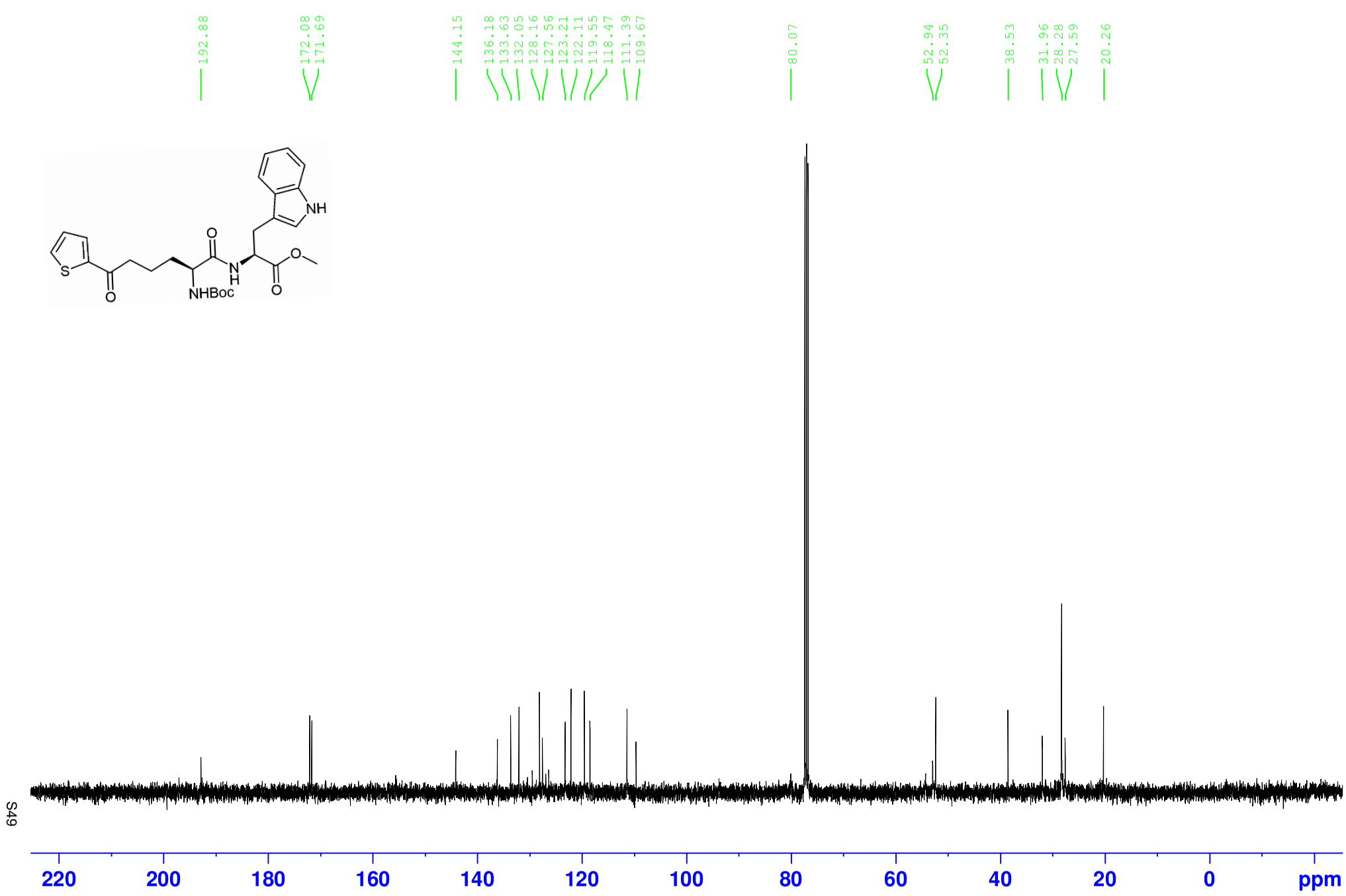
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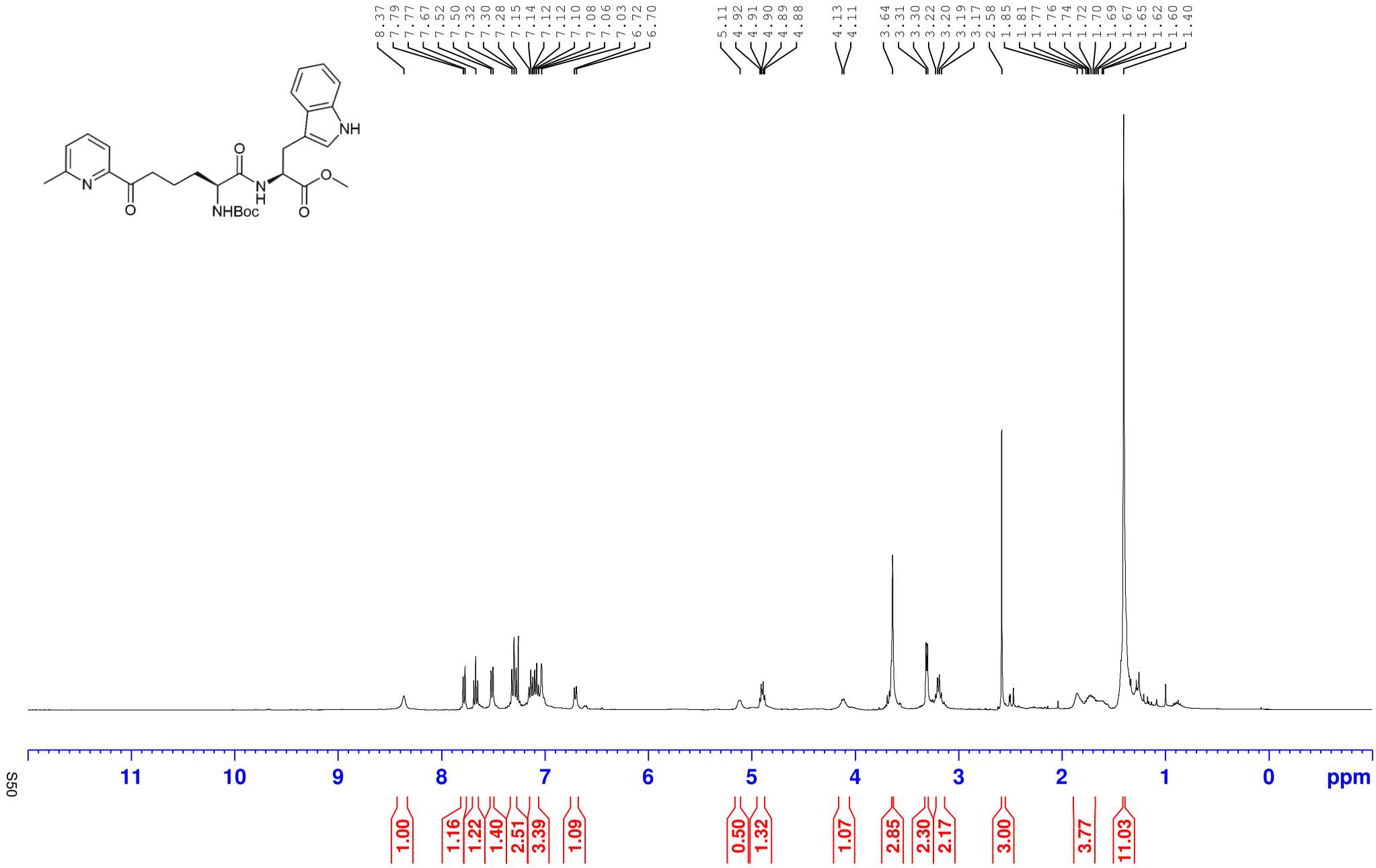
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H
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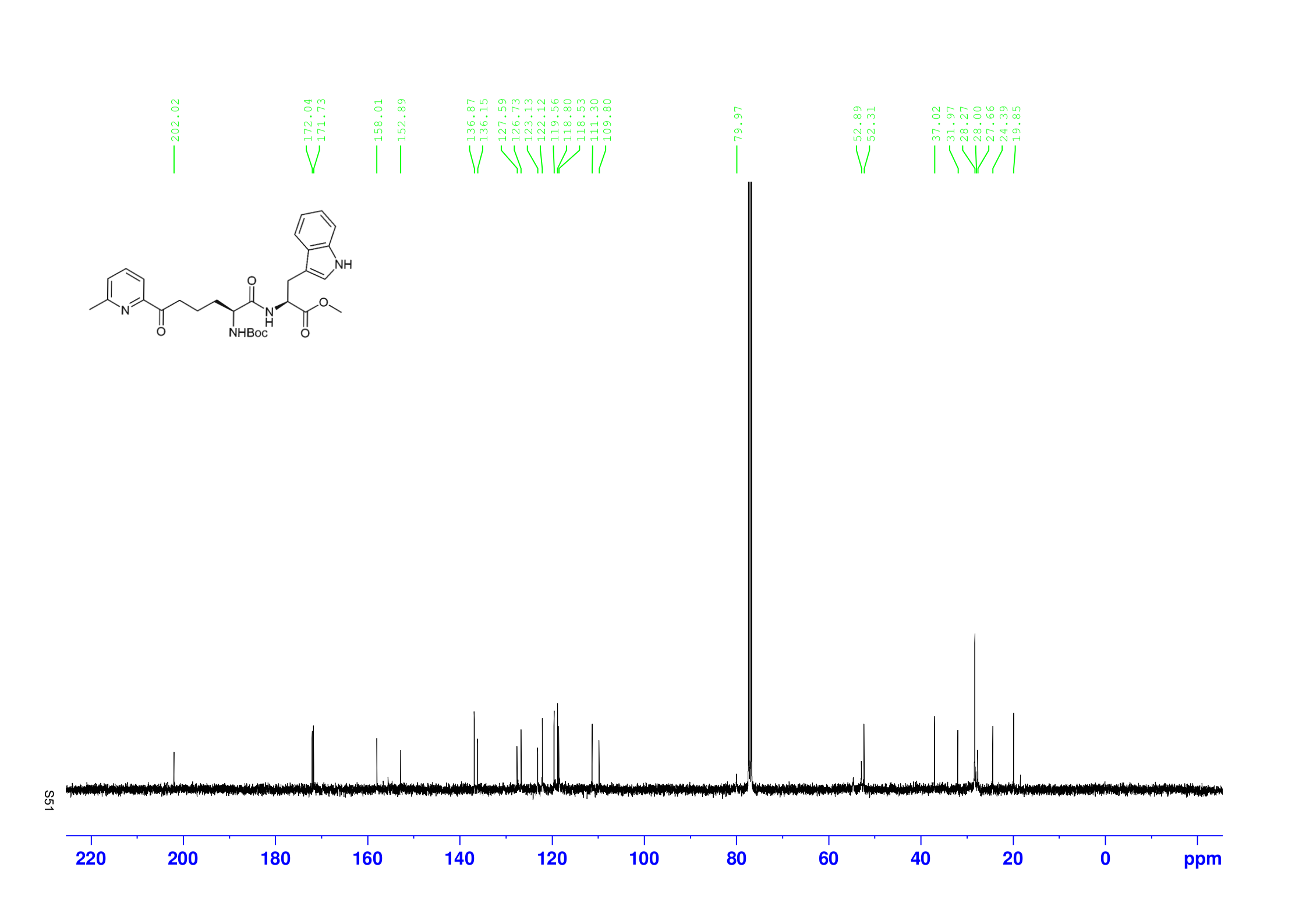
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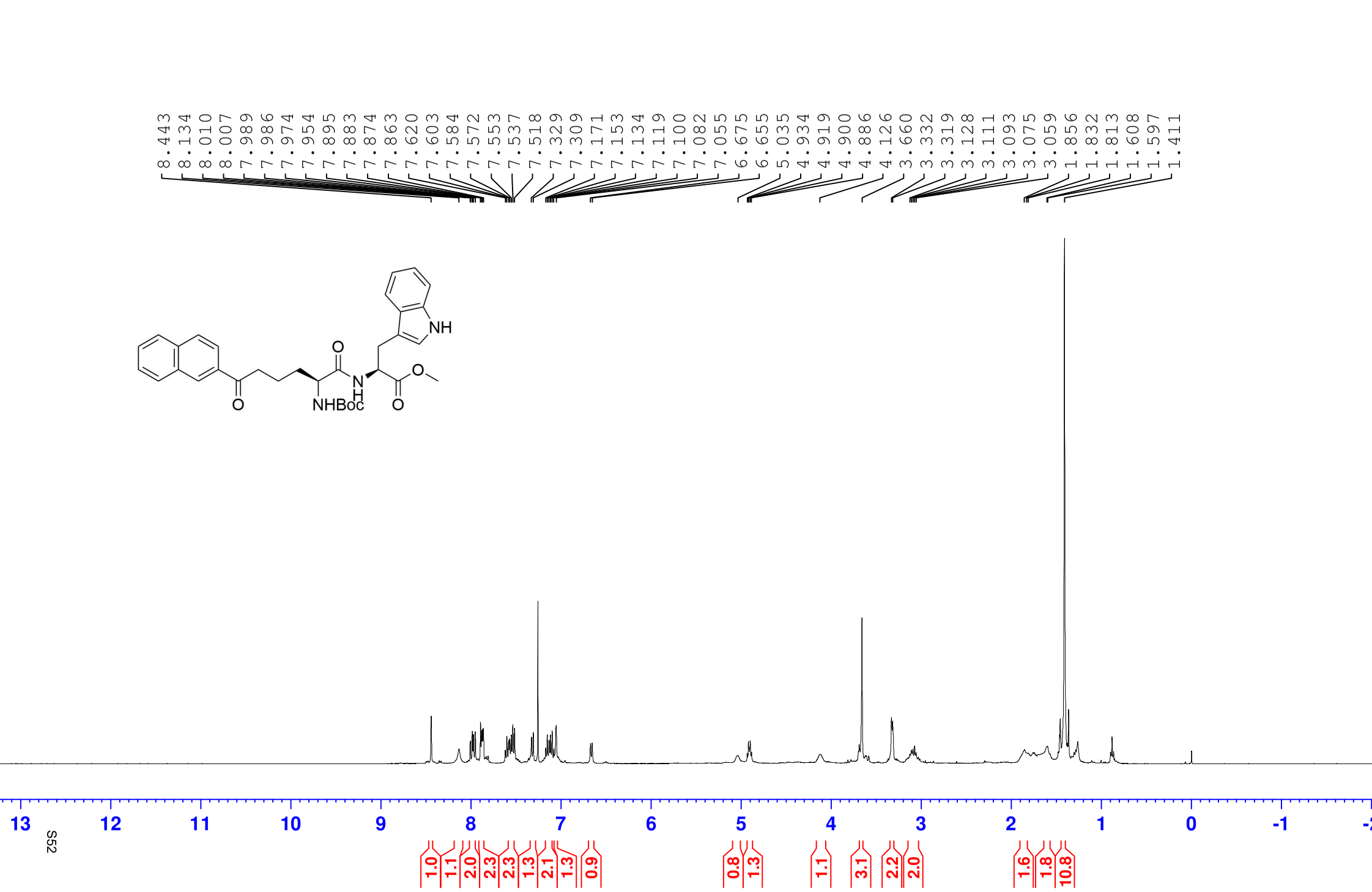
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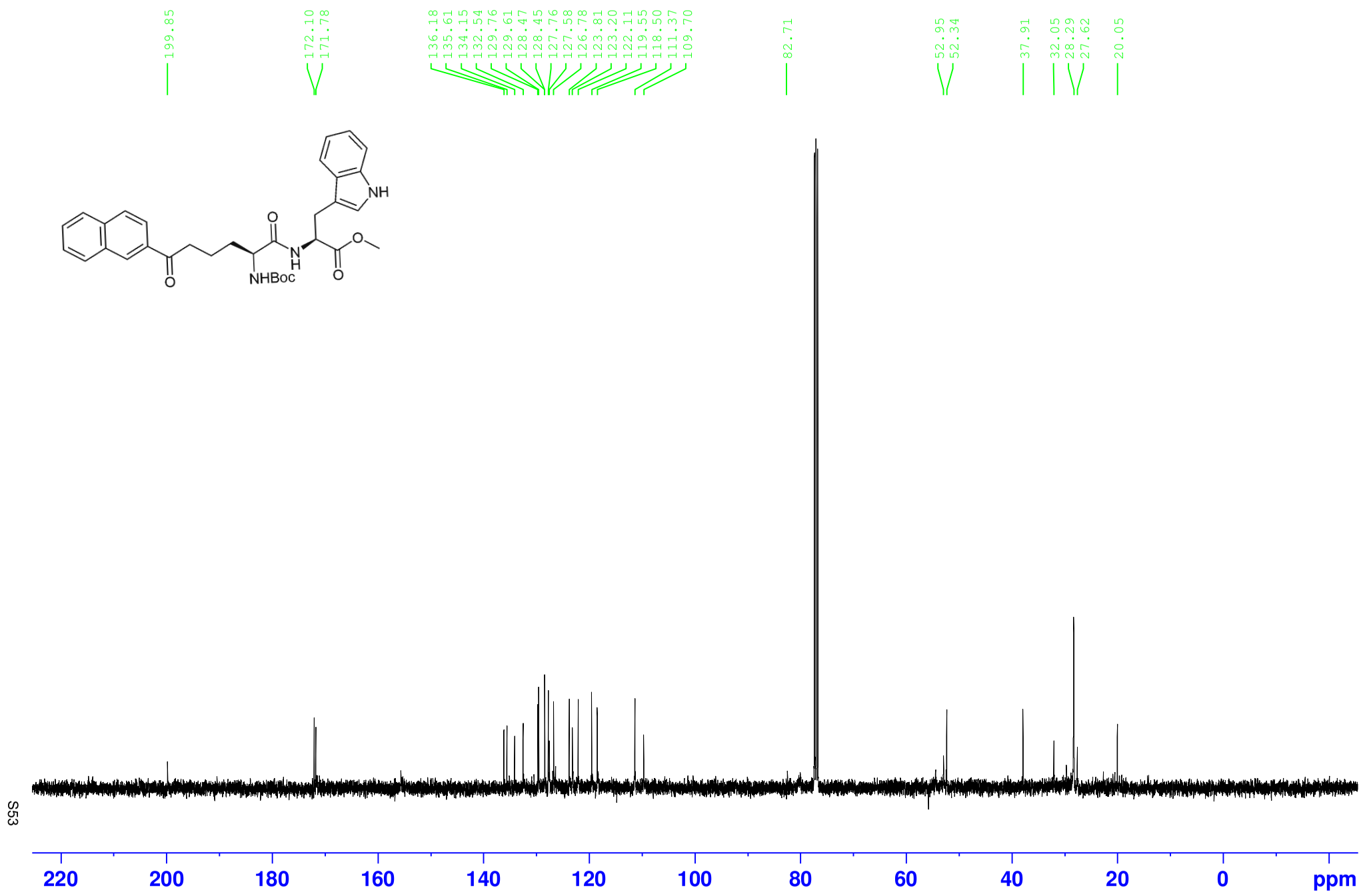
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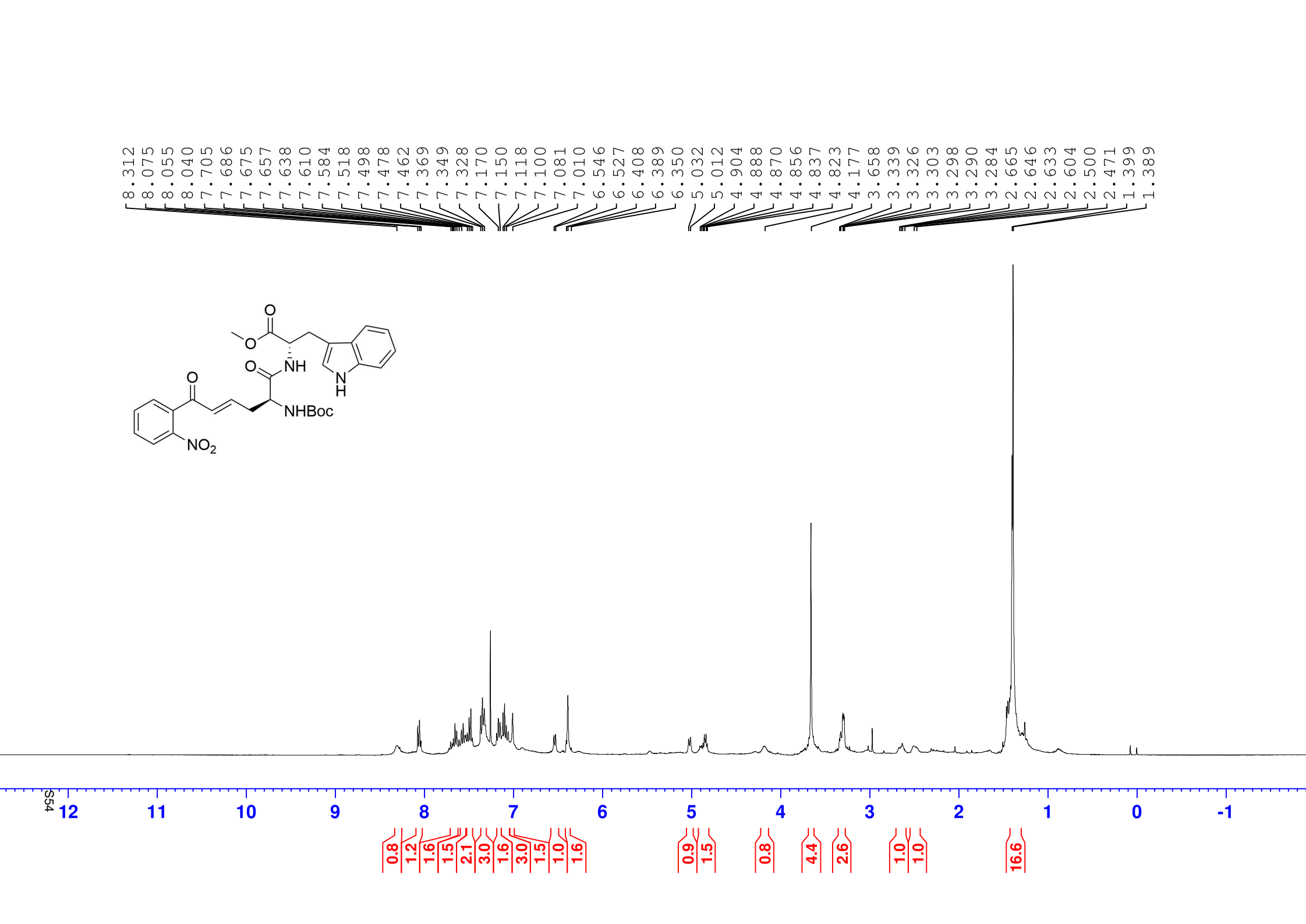
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7.150
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7.100
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2.646
2.633
2.604
2.500
2.471
1.399
1.389
O
O
NH
O
N
H
O
NHBoc
NO2
S54
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11
10
9
8
7
6
5
4
3
2
1
0
-1
0.8
1.2
1.6
1.5
2.1
3.0
1.6
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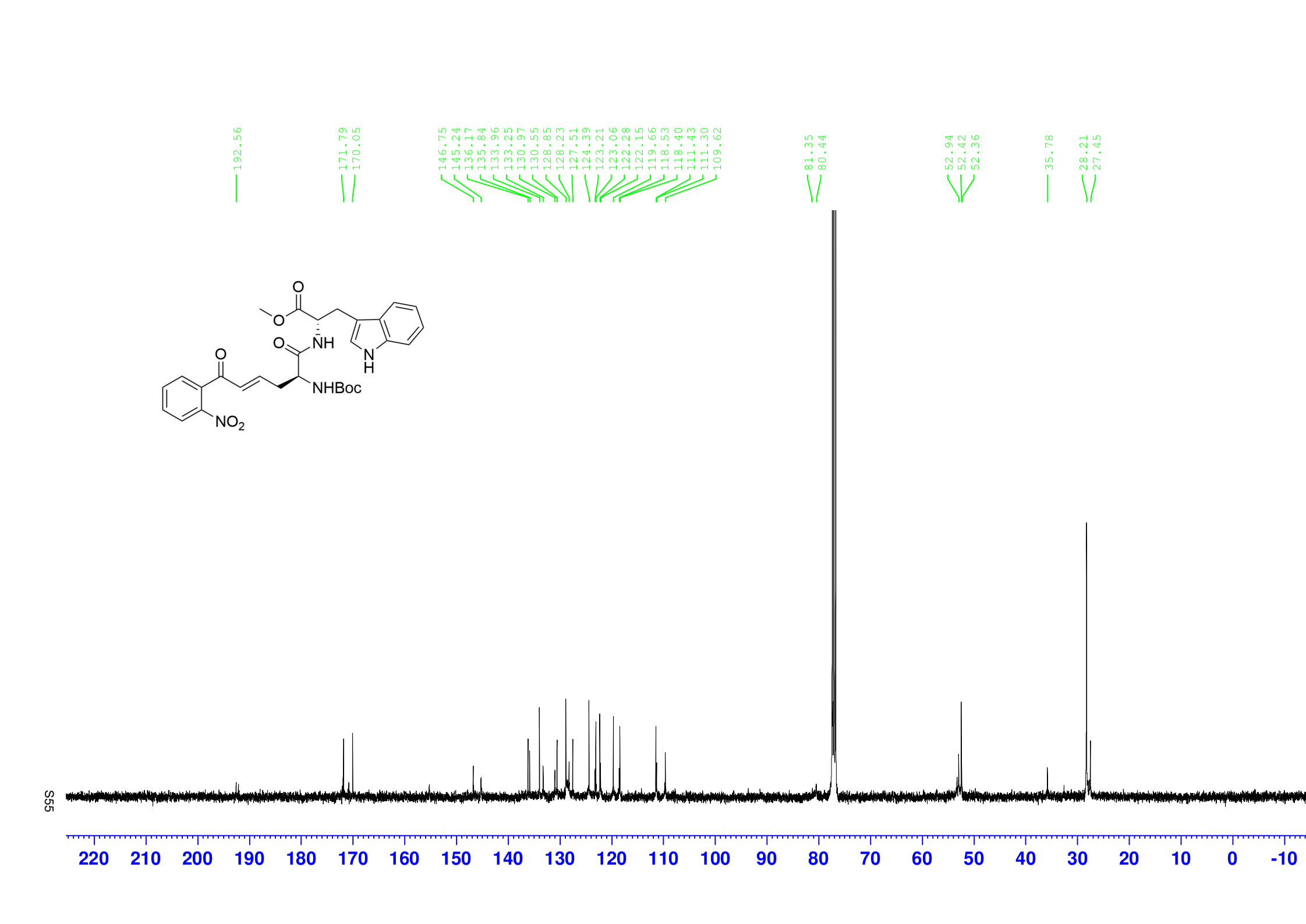
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O
O
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O
N
H
O
NHBoc
NO2
220
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200
190
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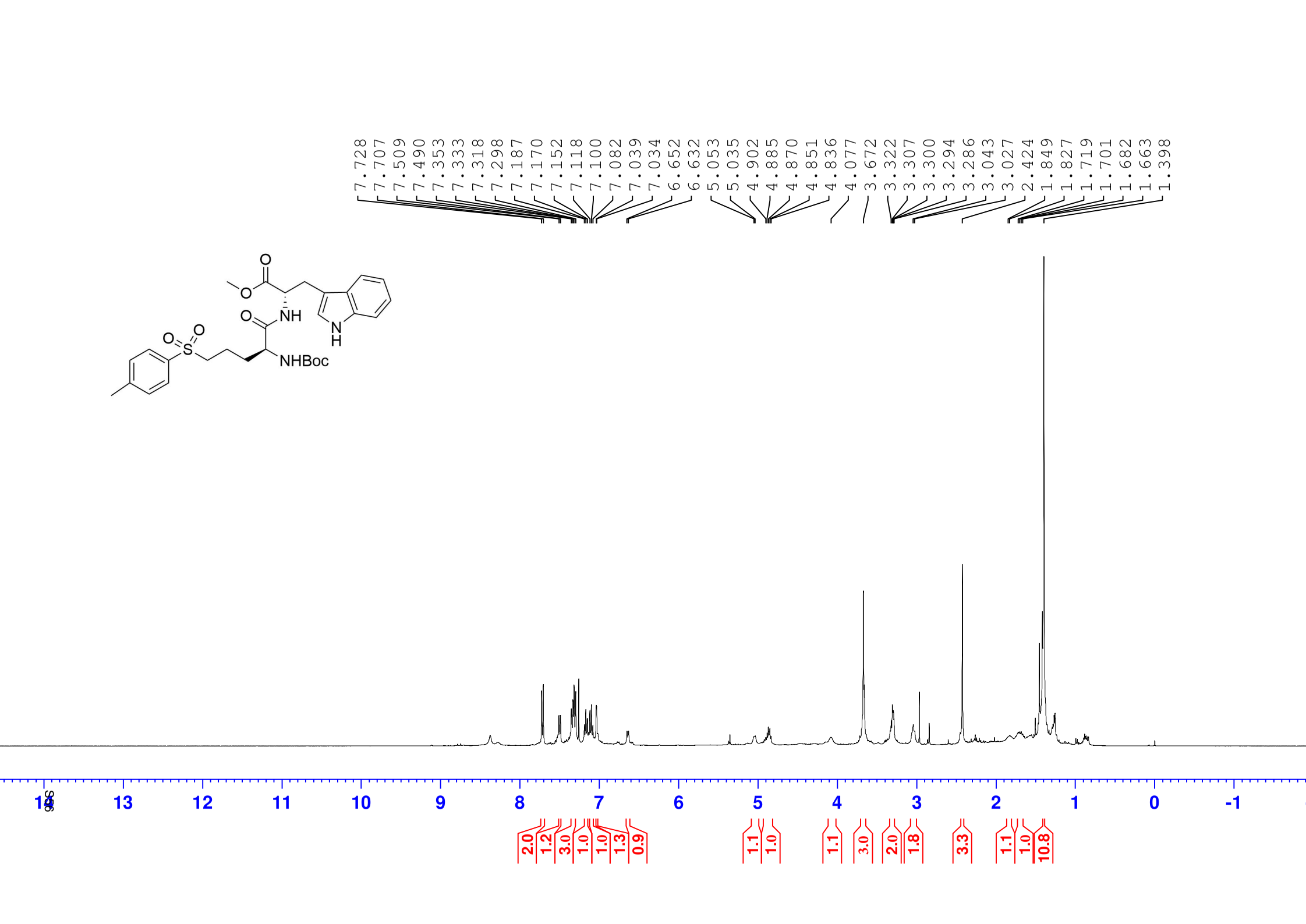
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7.039
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O
O
NH
O
N
H
O
S
O
NHBoc
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
2.0
1.2
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1.0
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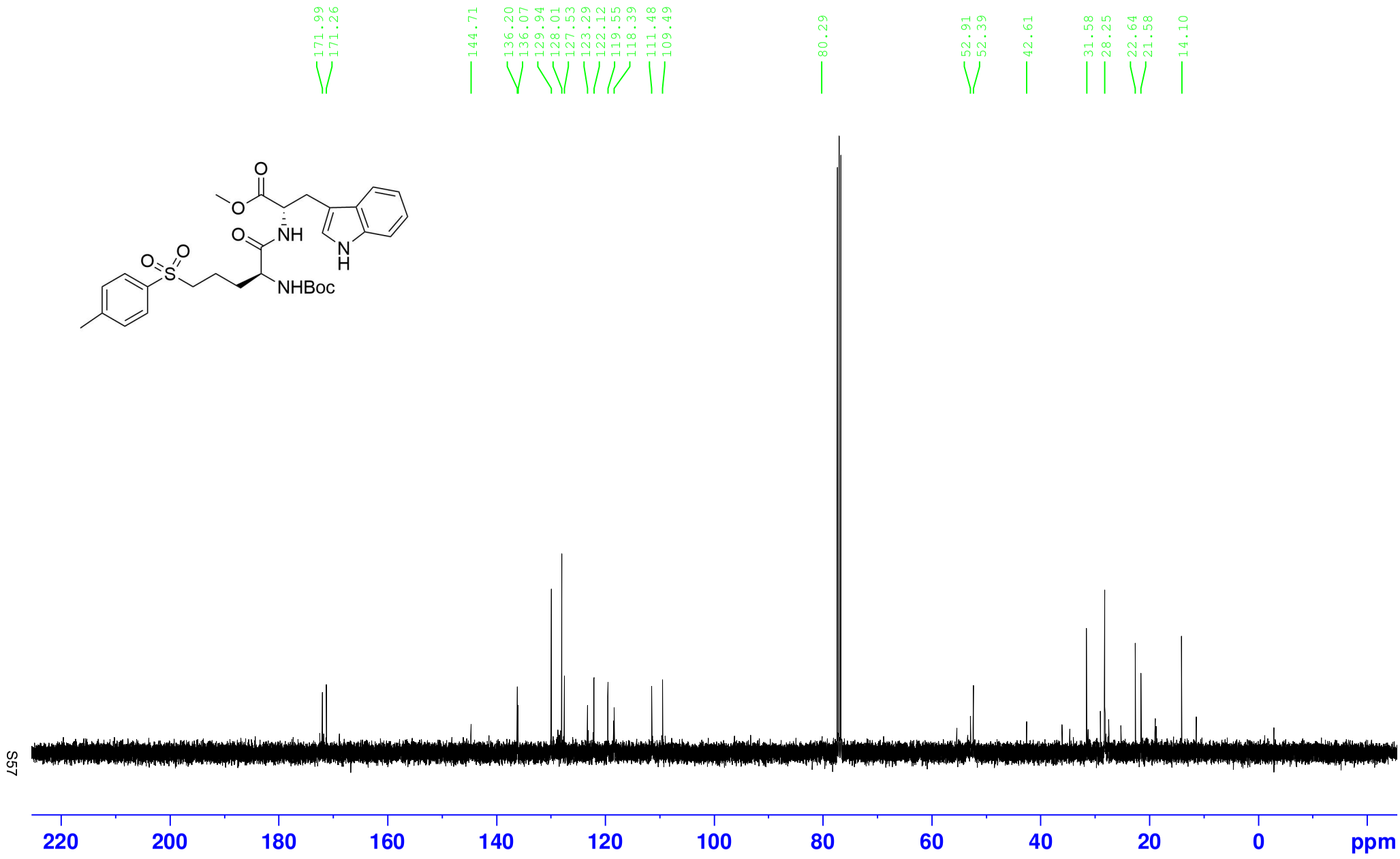
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80.29
52.91
52.39
42.61
31.58
28.25
22.64
21.58
14.10
O
O
NH
O
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H
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NHBoc
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120
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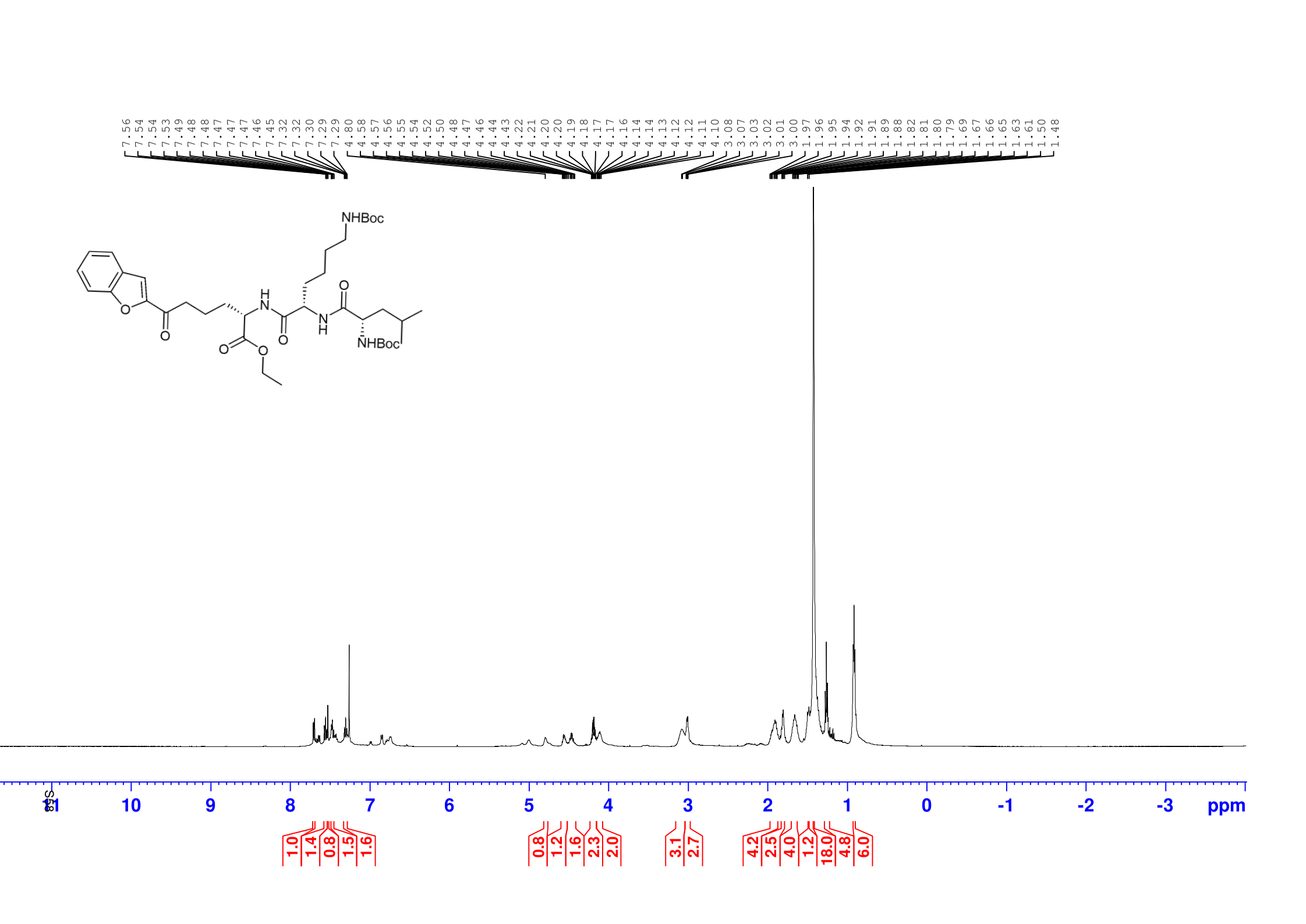
40
20
0
ppm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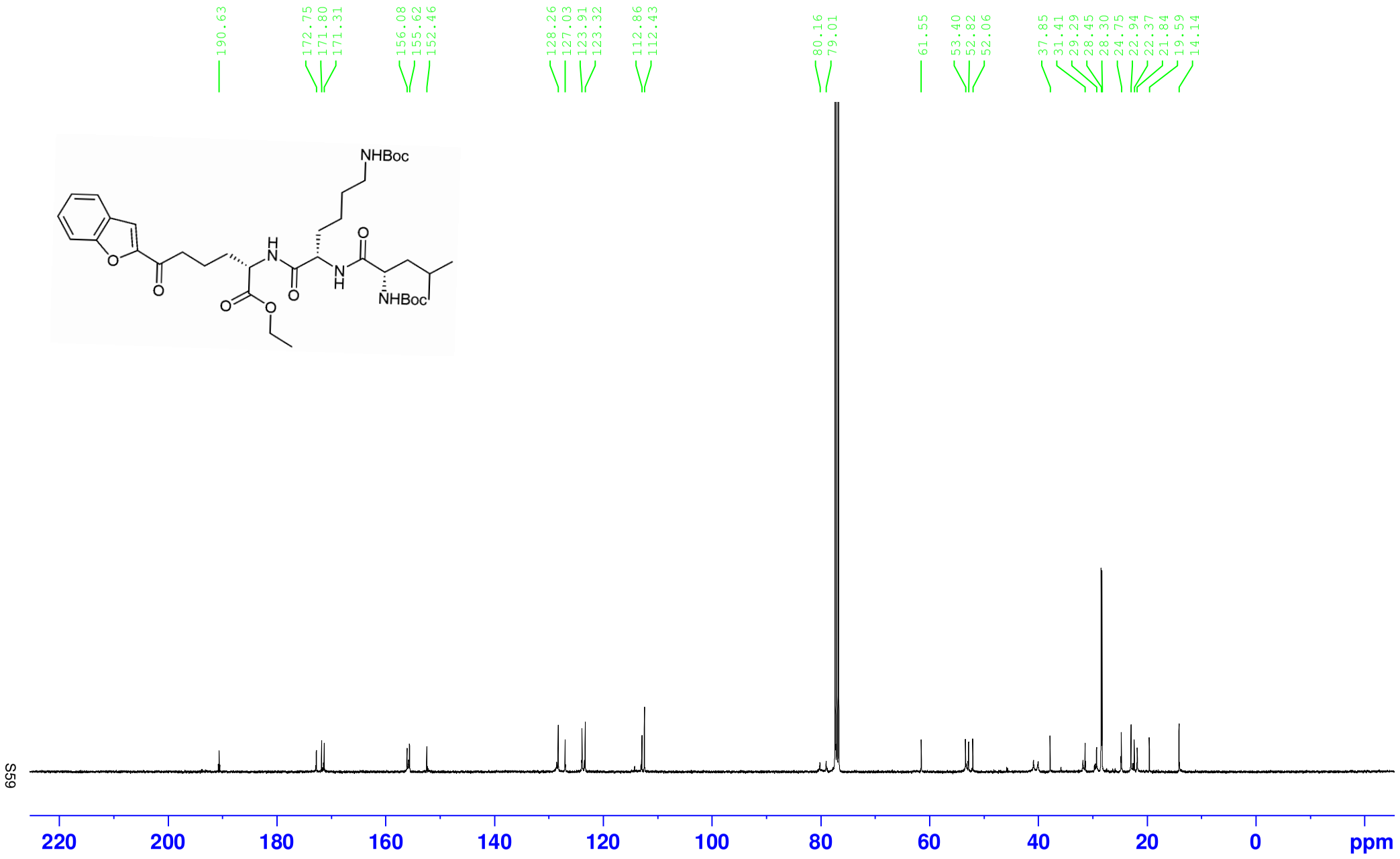
4.80 4.58 4.57 4.56 4.55 4.54 4.52 4.50 4.48 4.47 4.46 4.44 4.43 4.22 4.21 4.20 4.20 4.19 4.18 4.17 4.17 4.16 4.14 4.14 4.13 4.12 4.11 4.10
3.08 3.07 3.03 3.02 3.01 3.00
1.97 1.96 1.95 1.94 1.92 1.91 1.89 1.88 1.82 1.81 1.80 1.79 1.69 1.67 1.66 1.65 1.63 1.61 1.50 1.48
NHBoc
NHBoc
11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm
1.0 1.4 0.8 1.5 1.6
0.8 1.2 1.6 2.3 2.0
3.1 2.7
4.2 2.5 4.0 1.2 18.0 4.8 6.0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80.16
79.01
61.55
53.40
52.82
52.06
37.85
31.41
29.29
28.45
28.30
24.75
22.94
22.37
21.84
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NHBoc
NHBoc
220
200
180
160
140
120
100
80
60
40
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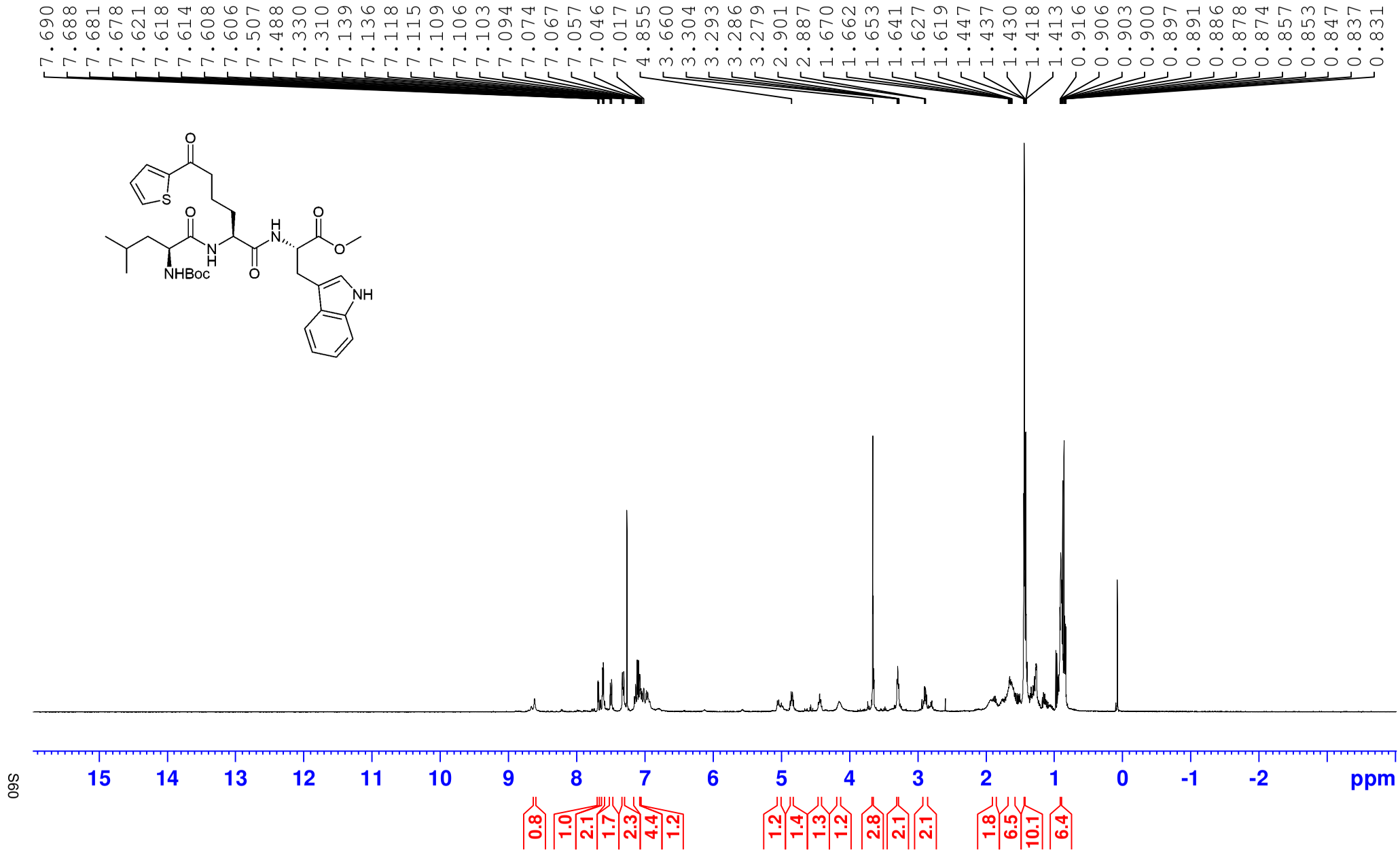
0
ppm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7.106
7.103
7.094
7.074
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7.046
7.017
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1.653
1.641
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1.430
1.418
1.413
0.916
0.906
0.903
0.900
0.897
0.891
0.886
0.878
0.874
0.857
0.853
0.847
0.837
0.831
NHBoc
NH
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
0.8
1.0
2.1
1.7
2.3
4.4
1.2
1.2
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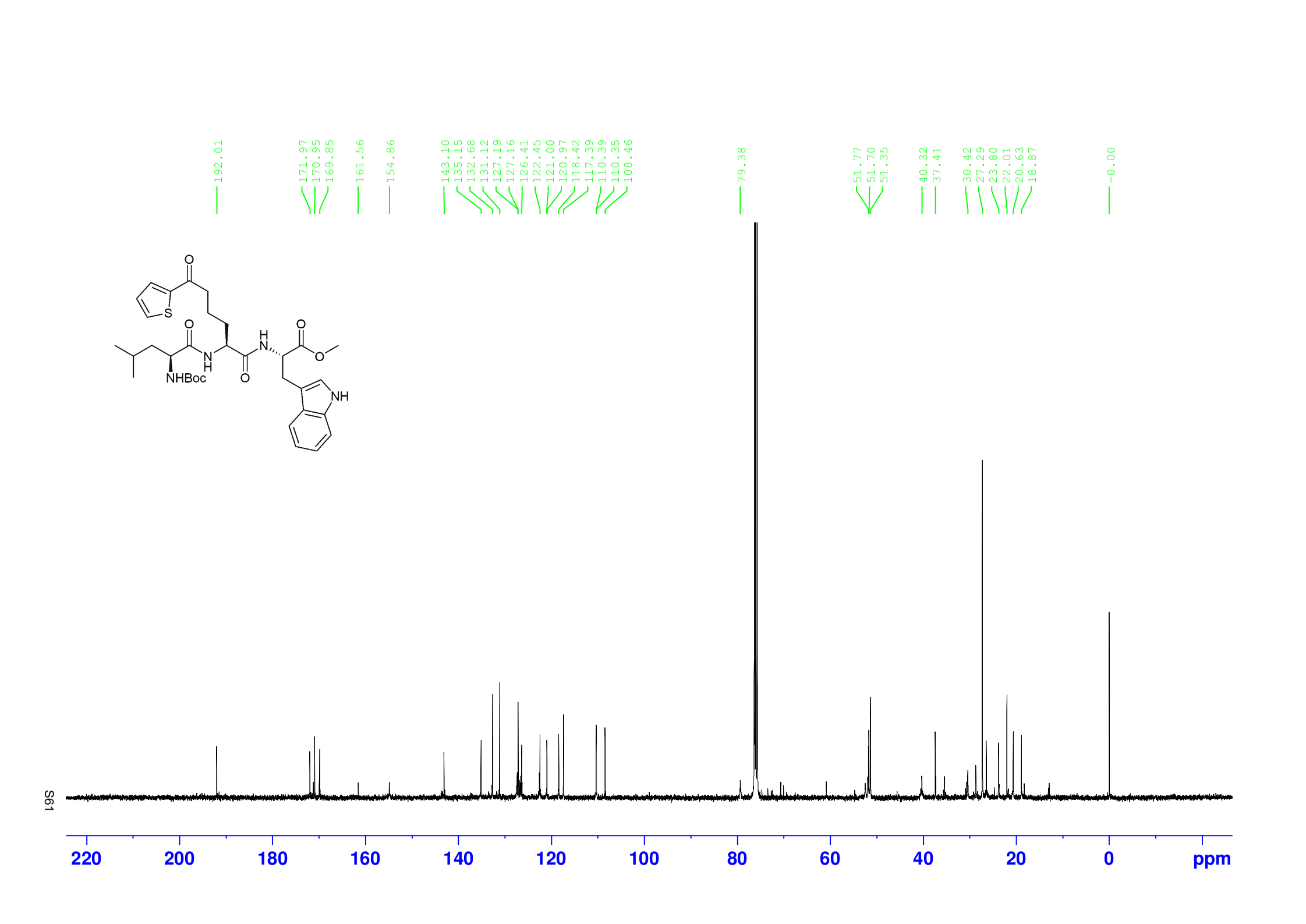
1.3
1.2
2.8
2.1
2.1
1.8
6.5
10.1
6.4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122.45
121.00
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118.42
117.39
110.39
110.35
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79.38
51.77
51.70
51.35
40.32
37.41
30.42
27.29
23.80
22.01
20.63
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O
S
O
N
H
NHBoc
O
H
N
O
O
NH
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120
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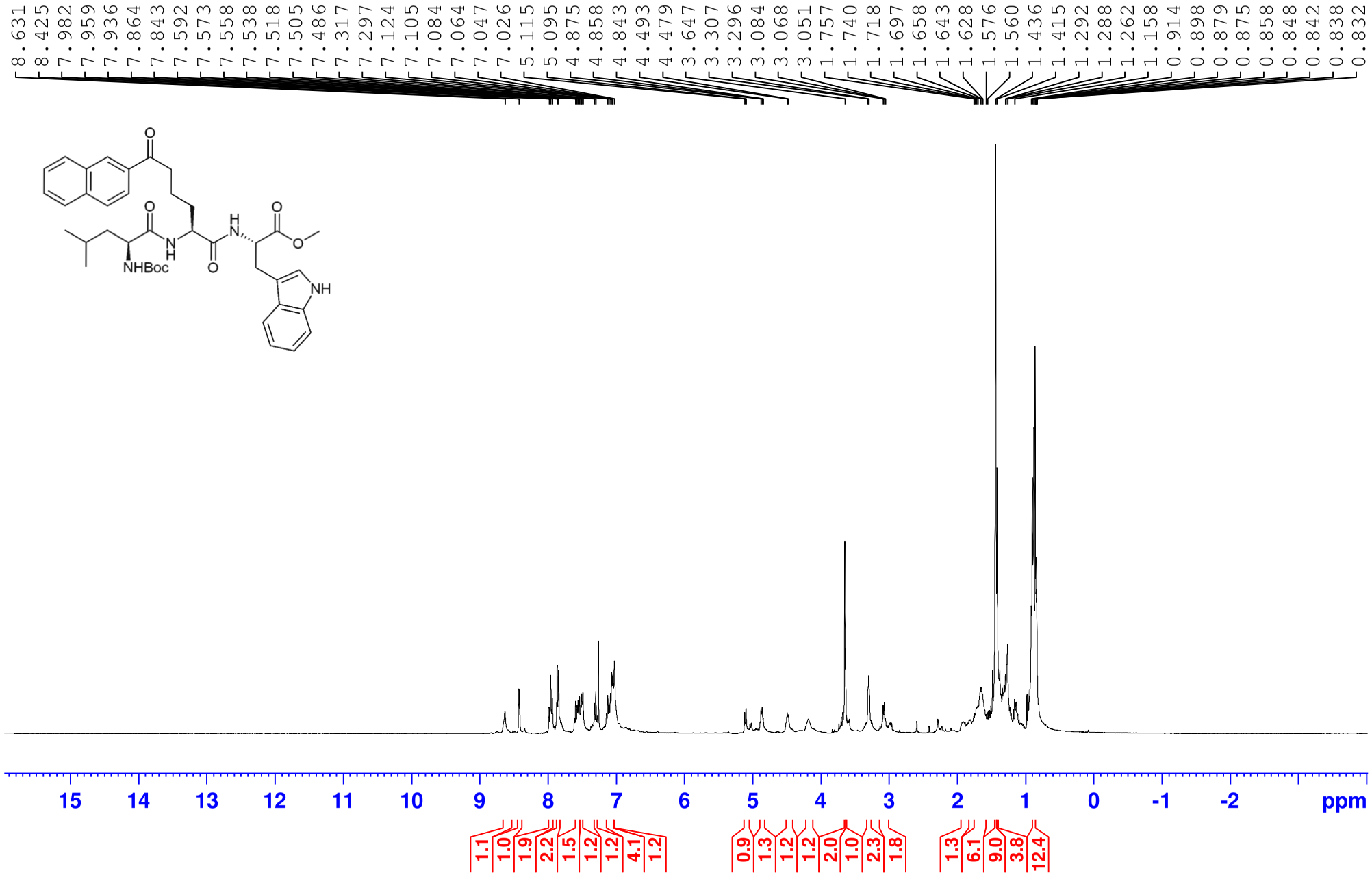
60
40
20
0
ppm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7.486
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7.064
7.047
7.026
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5.095
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3.068
3.051
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1.697
1.658
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1.628
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1.560
1.436
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1.292
1.288
1.262
1.158
0.914
0.898
0.879
0.875
0.858
0.848
0.842
0.838
0.832
O
O
N
H
O
H
N
O
O
NHBoc
NH
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
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1.0
1.9
2.2
1.5
1.2
1.2
4.1
1.2
0.9
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2.3
1.8
1.3
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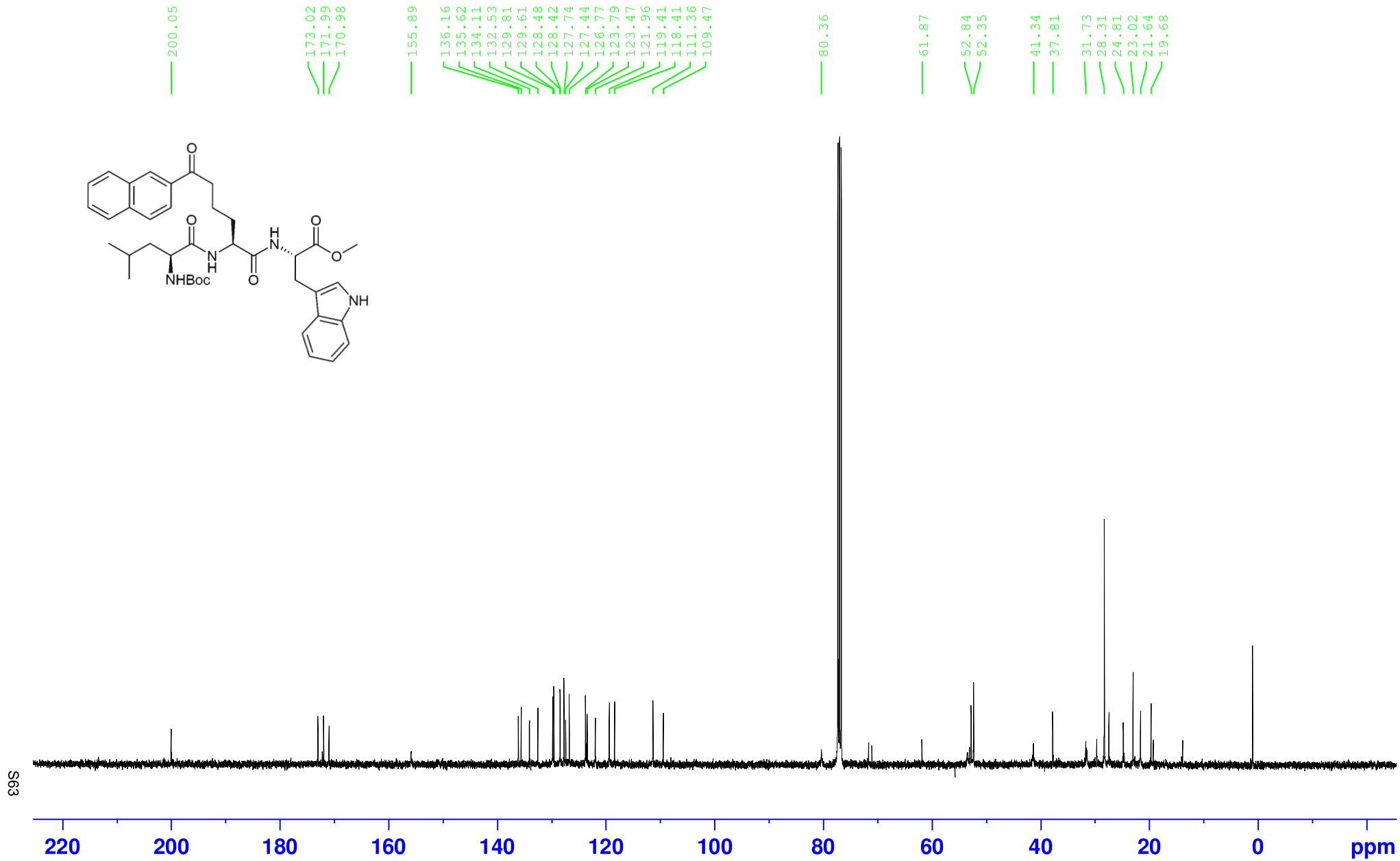
12.4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52.35
41.34
37.81
31.73
28.31
24.81
23.02
21.64
19.68
O
O
N
H
O
H
N
O
O
NHBoc
NH
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200
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120
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80
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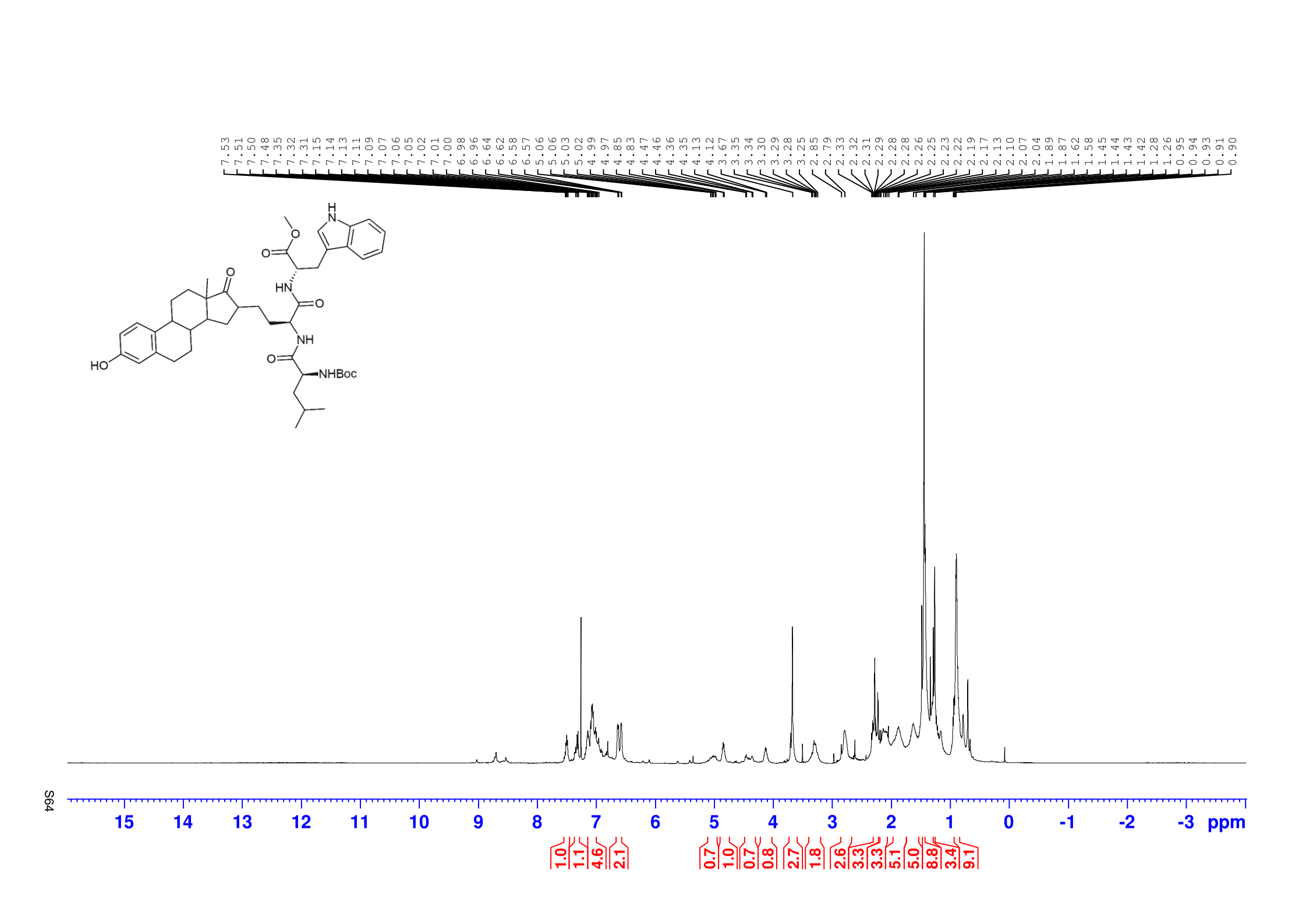
40
20
0
ppm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HO
NHBoc
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm
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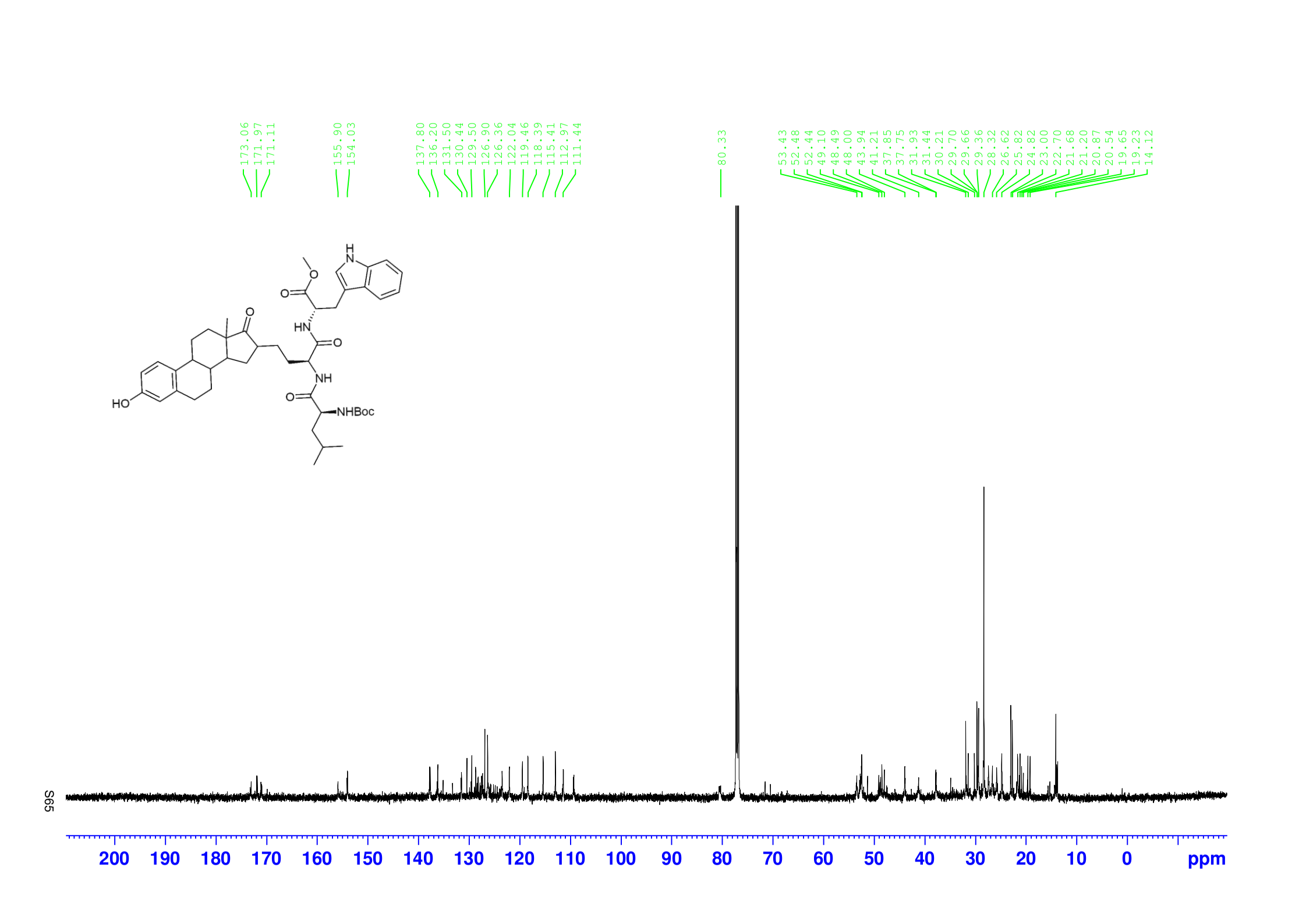
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111.44
80.33
53.43
52.48
52.44
49.10
48.49
48.00
43.94
41.21
37.85
37.75
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31.44
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29.66
29.36
28.32
26.62
25.82
24.82
23.00
22.70
21.68
21.20
20.87
20.54
19.65
19.23
14.12
HO
O
O
HN
O
NH
O
NHBoc
H
N
O
O
200
190
180
170
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150
140
130
120
110
100
90
80
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60
50
40
30
20
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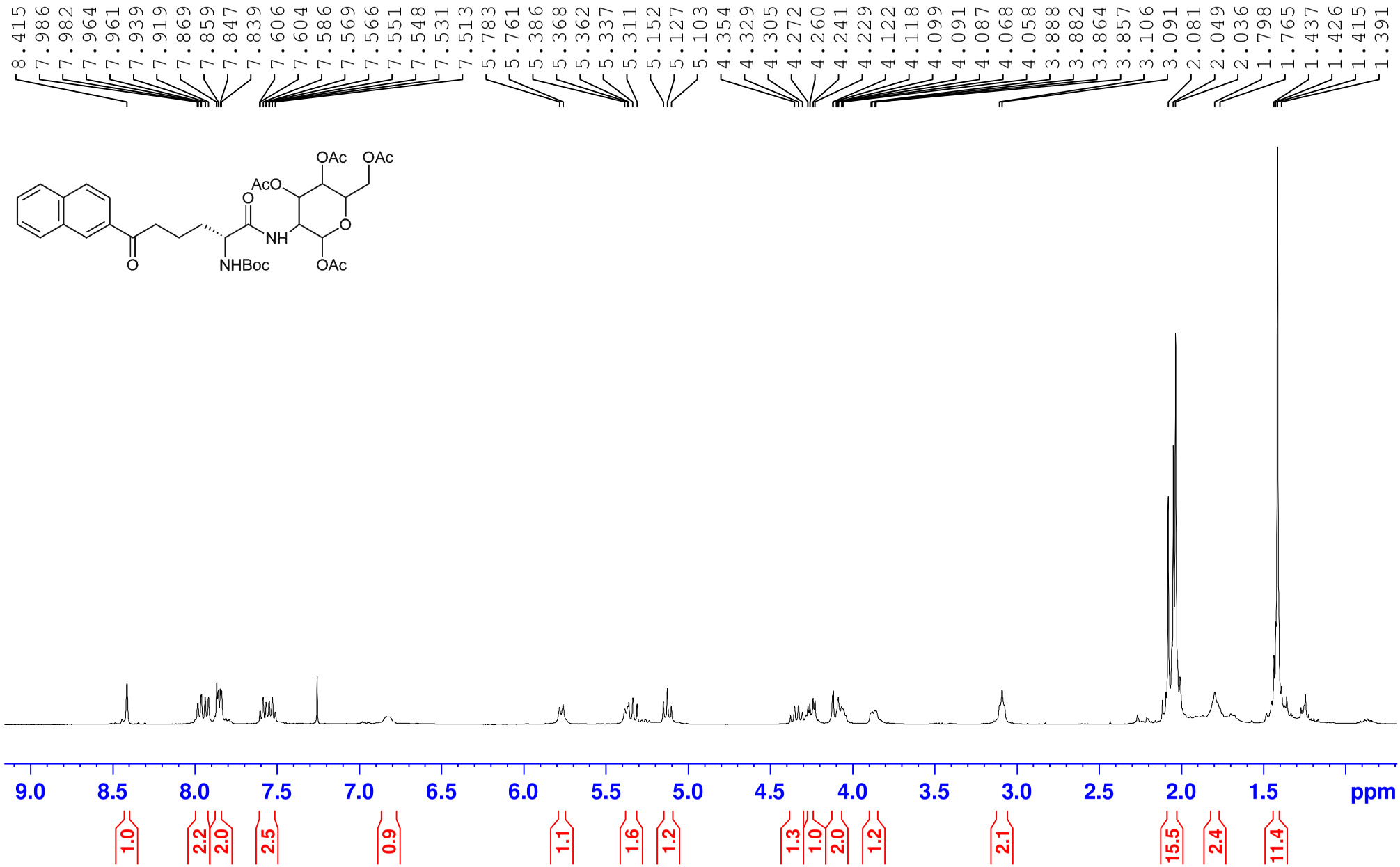
0
ppm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OAc
OAc
AcO
O
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O
O
NHBoc
OAc
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6.0
5.5
5.0
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3.0
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2.0
1.5
ppm
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2.0
2.5
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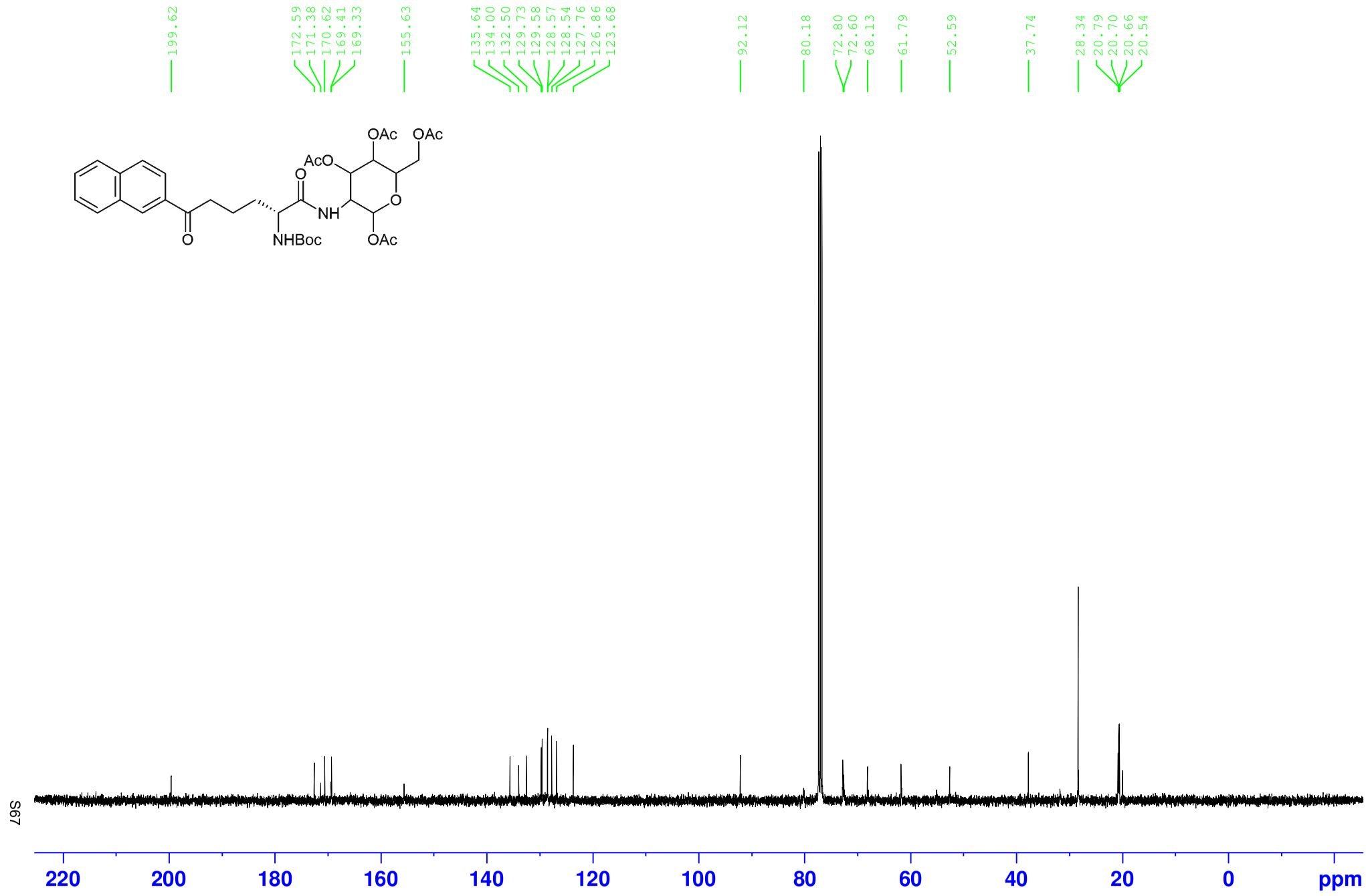
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72.60
68.13
61.79
52.59
37.74
28.34
20.79
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20.54
OAc
OAc
AcO
O
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O
O
NHBoc
OAc
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120
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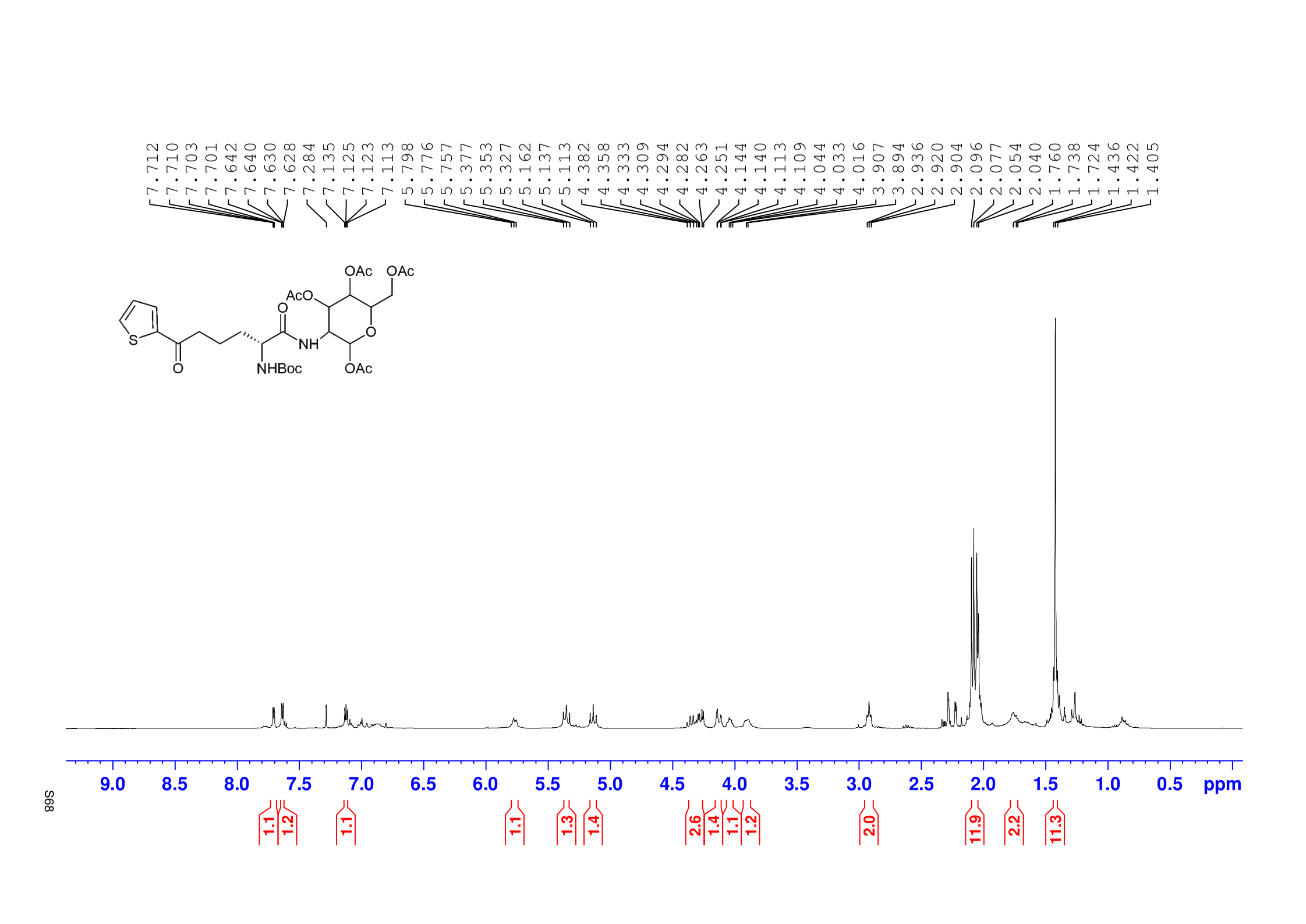
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OAc
OAc
AcO
O
NH
O
S
O
NHBoc
OAc
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ppm
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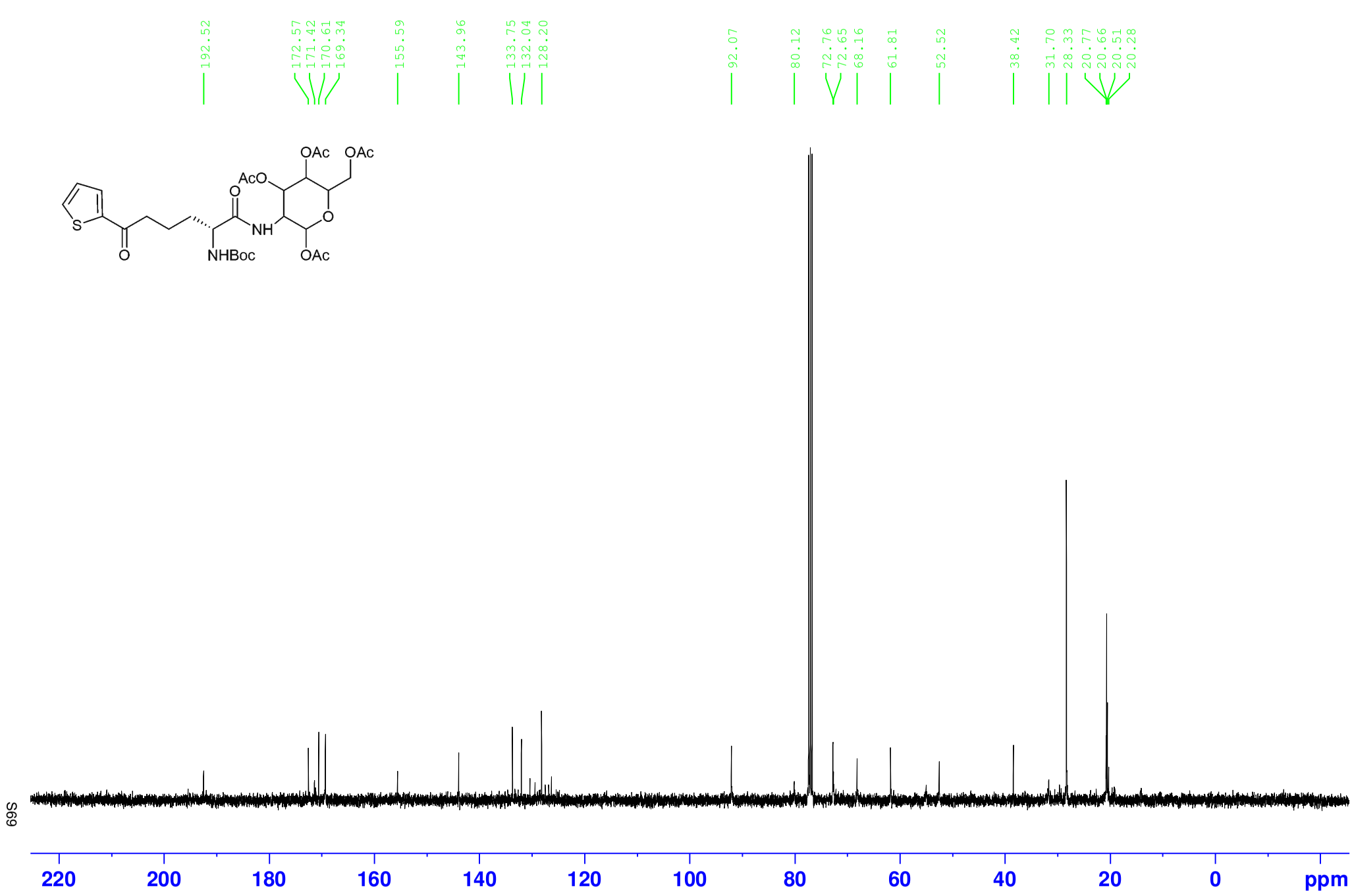
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31.70
28.33
20.77
20.66
20.51
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O
NH
O
S
O
NHBoc
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S69
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40
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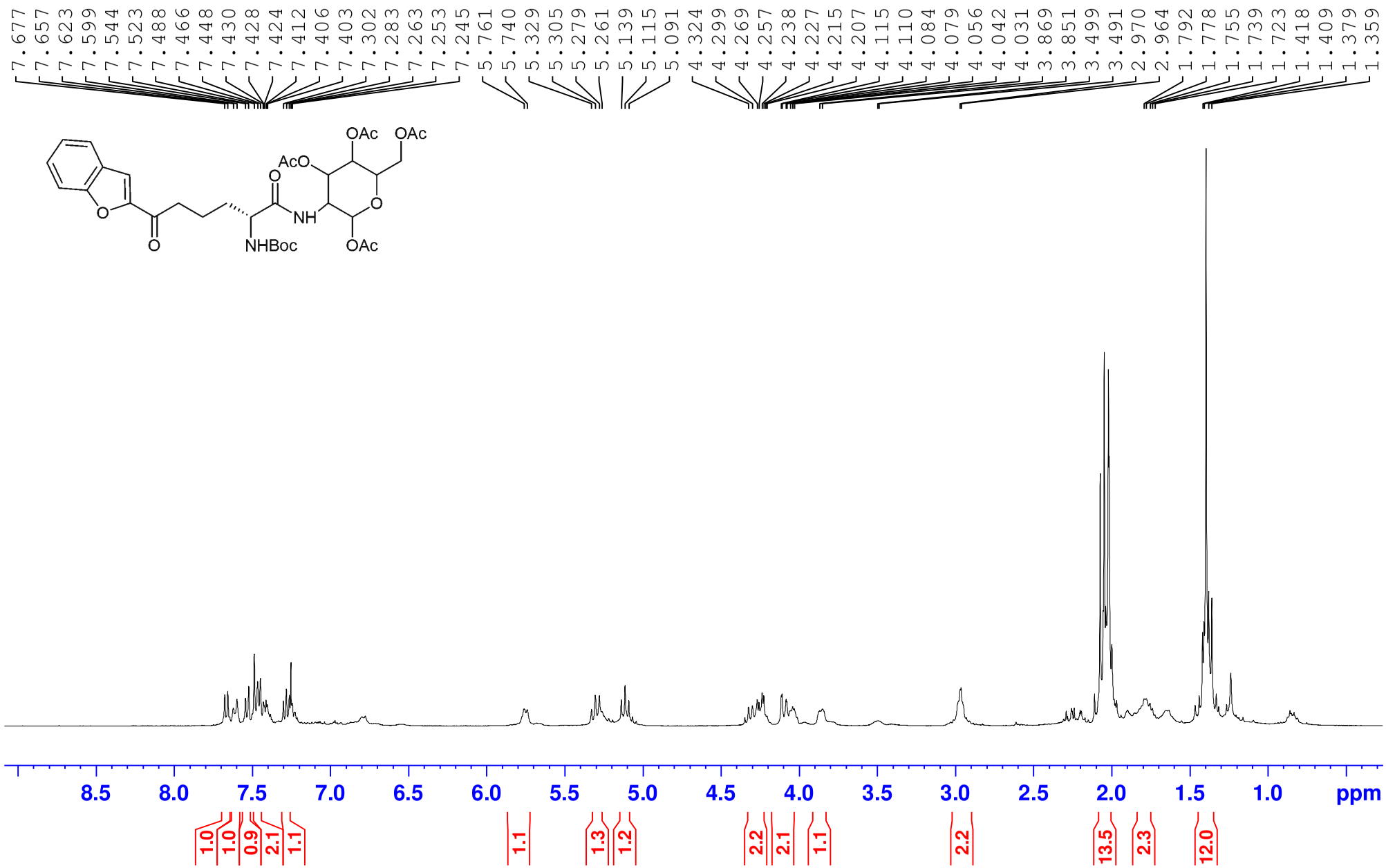
0
ppm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OAc
OAc
AcO
O
NH
O
O
O
NHBoc
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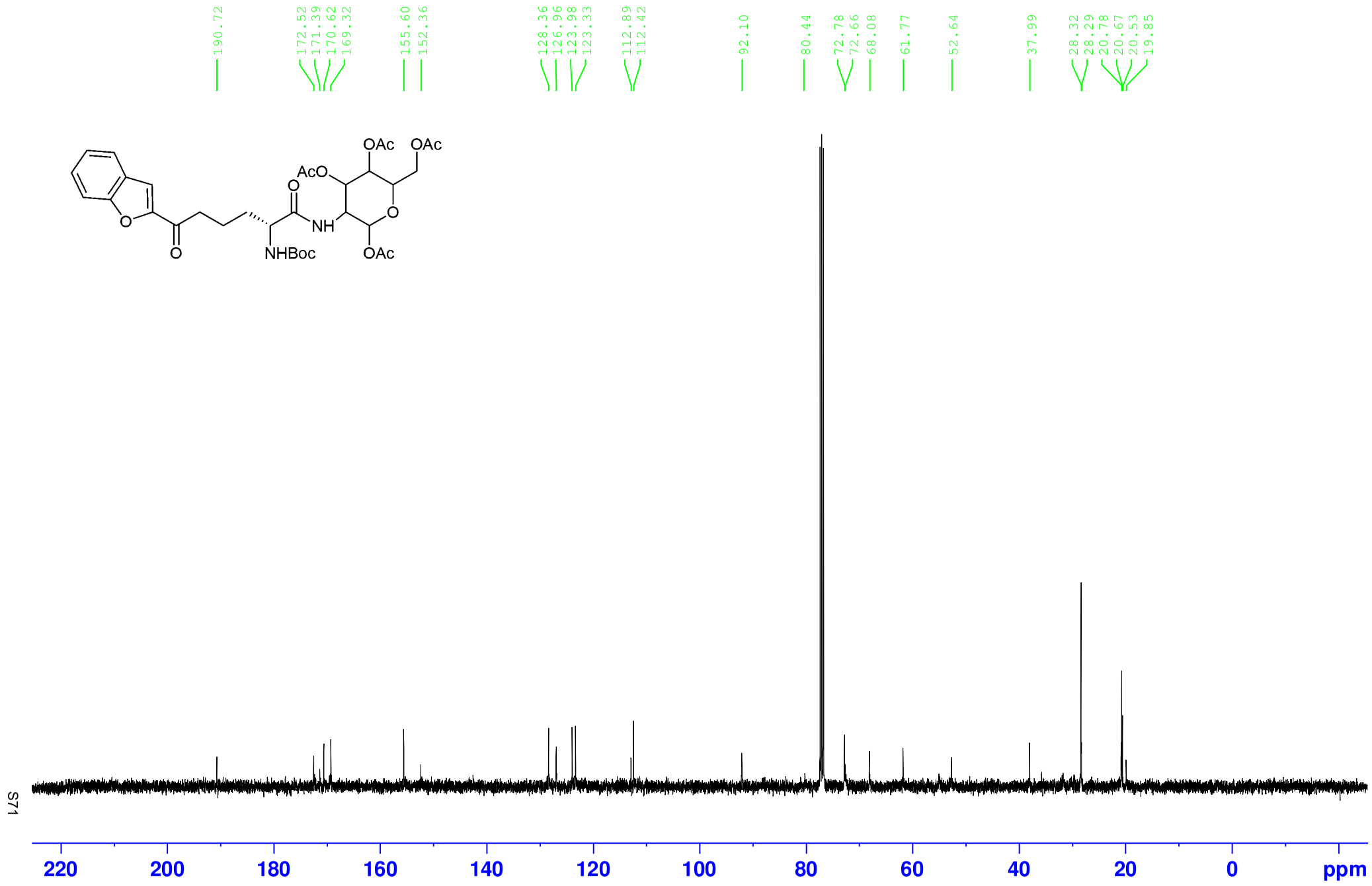
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OAc
AcO
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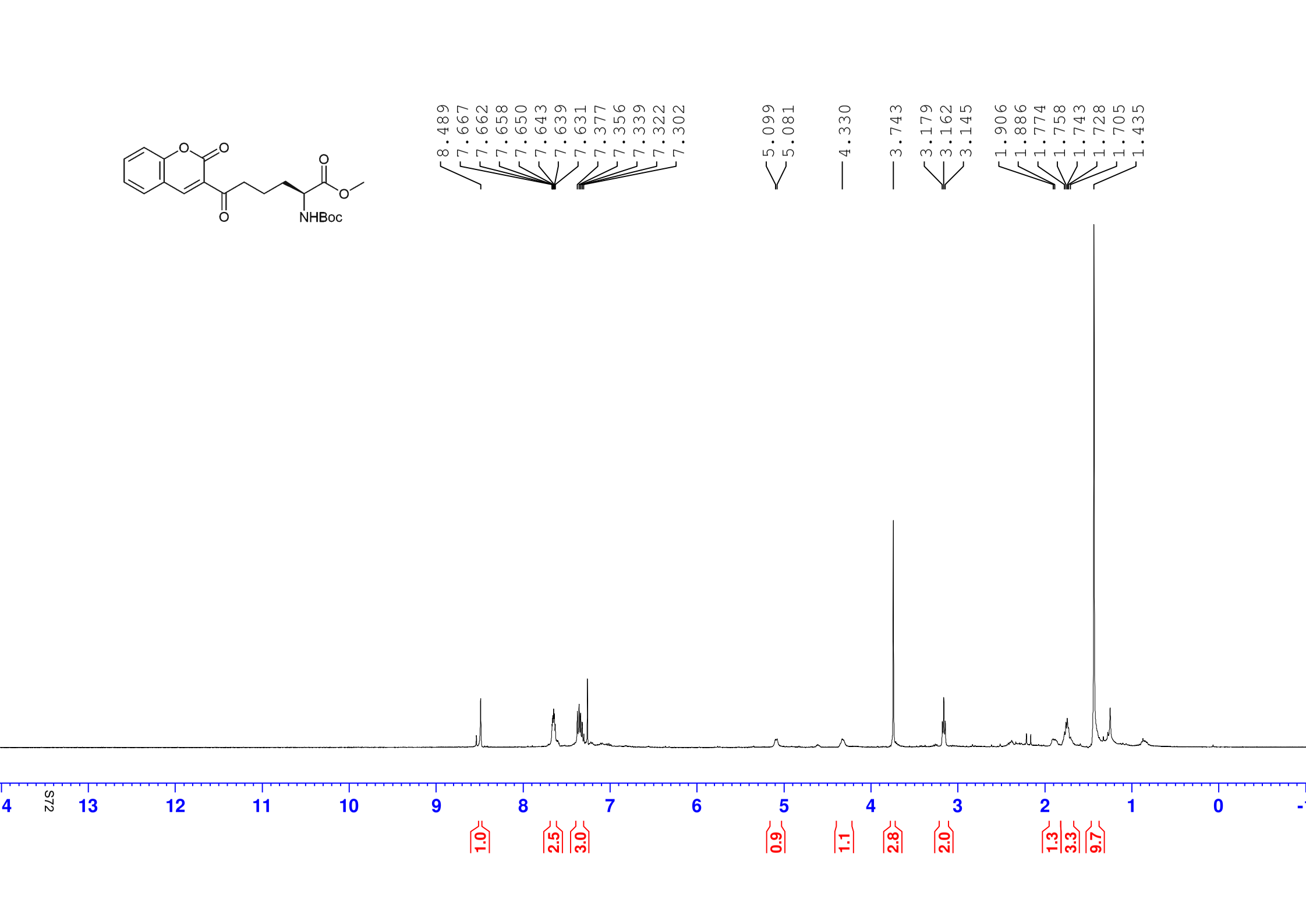
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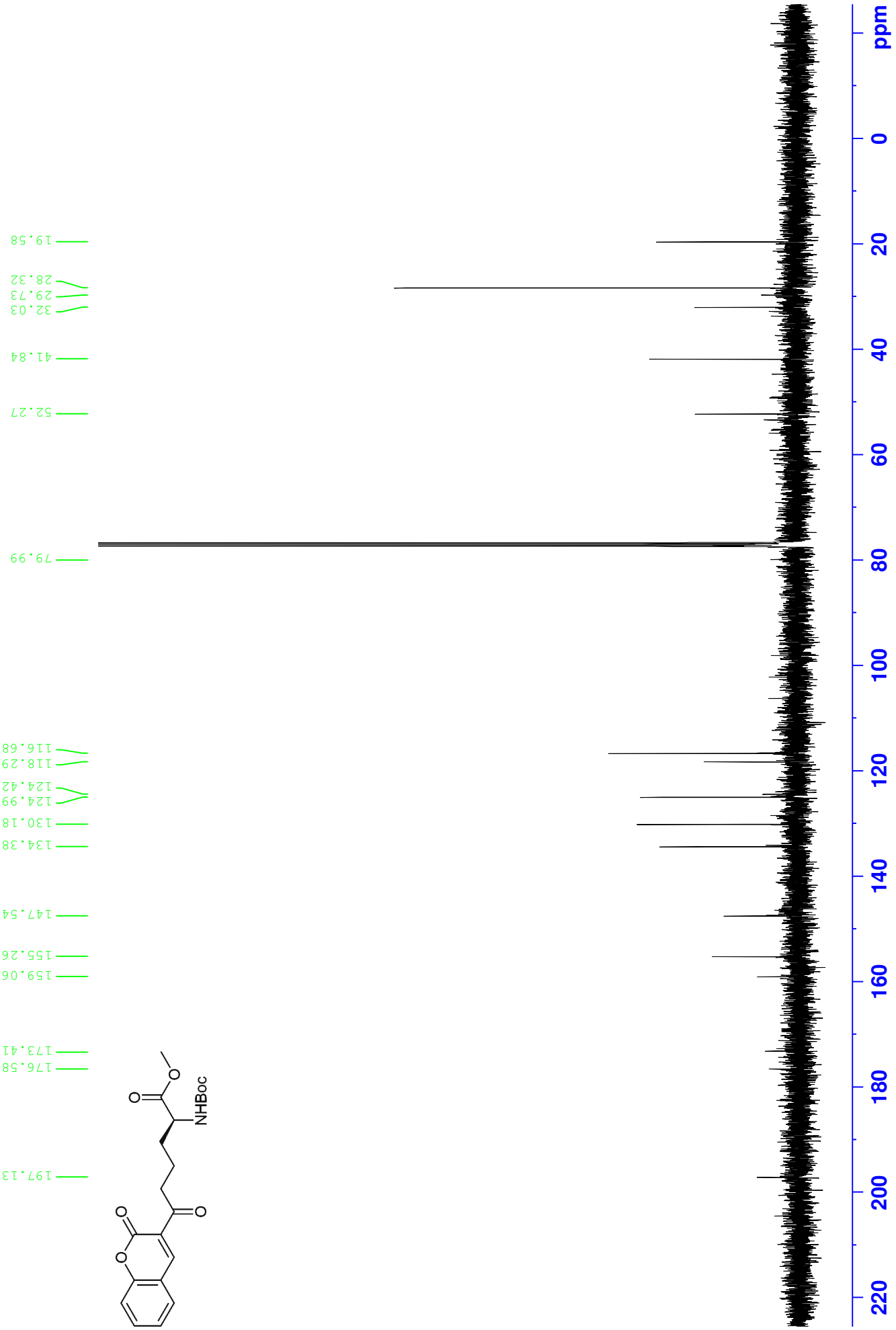
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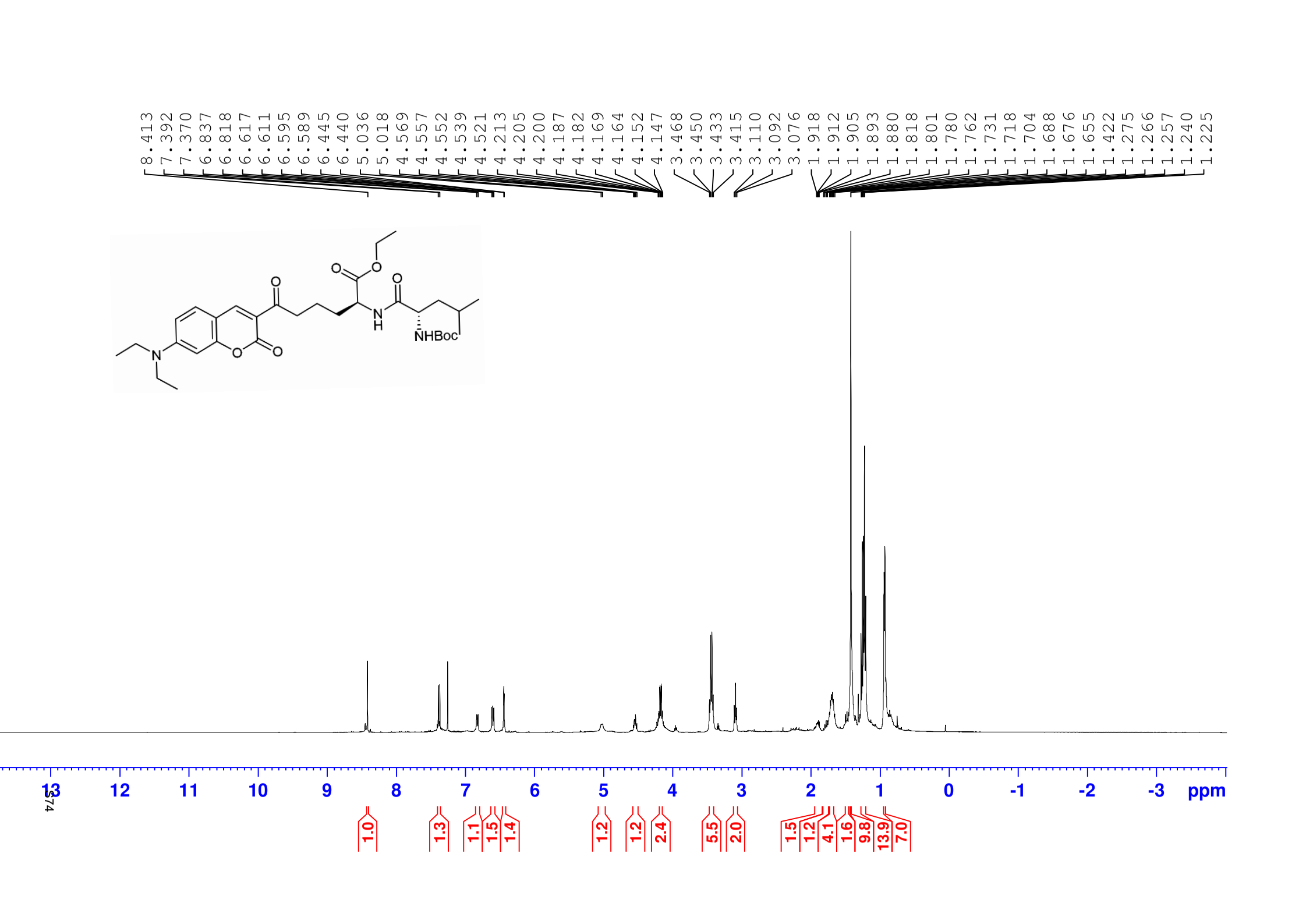
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4.164
4.152
4.147
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O
O
N
H
NHBoc
N
O
O
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12
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10
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8
7
6
5
4
3
2
1
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-1
-2
-3
ppm
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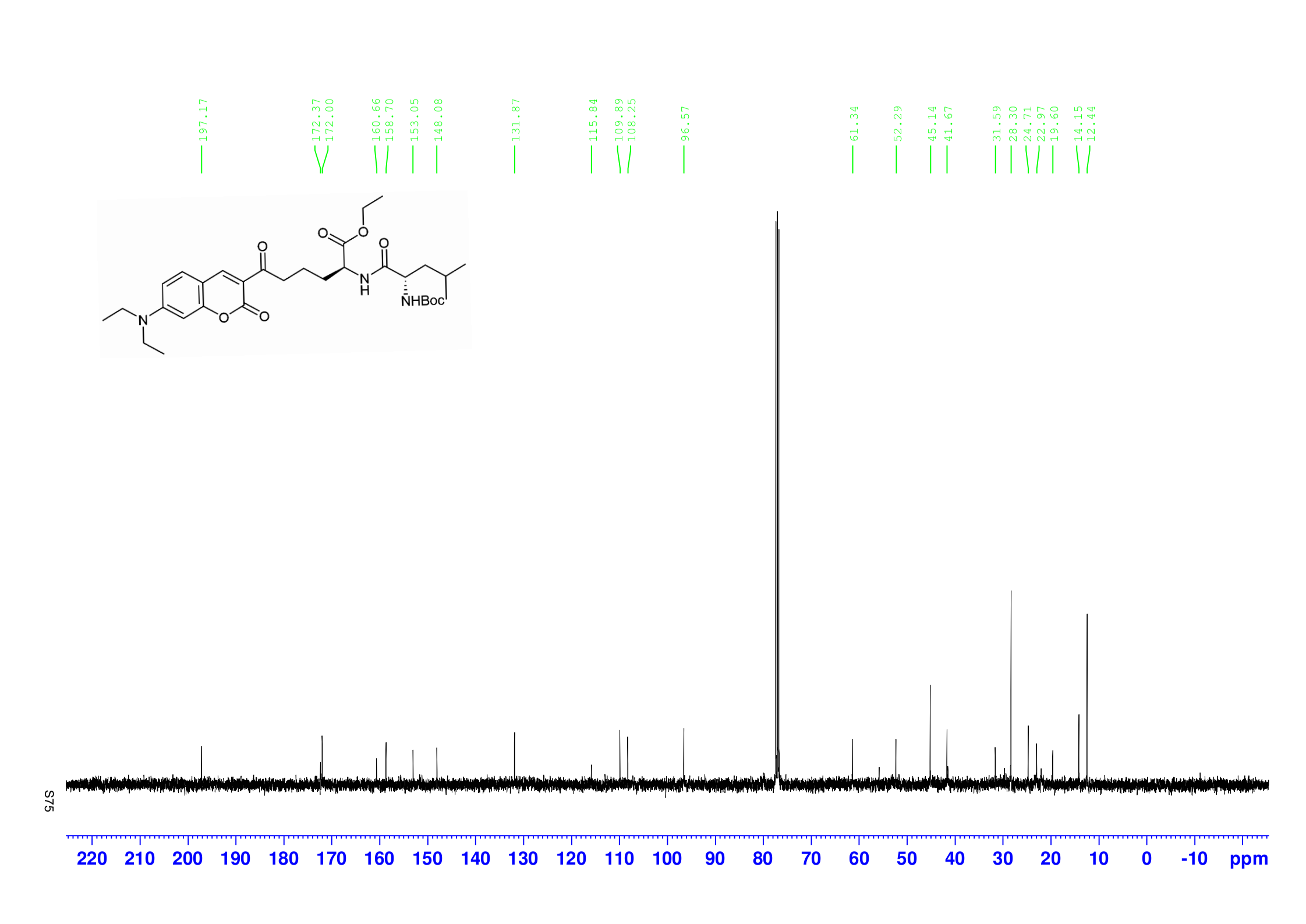
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14.15
12.44
O
O
O
N
H
NHBoc
N
O
O
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200
190
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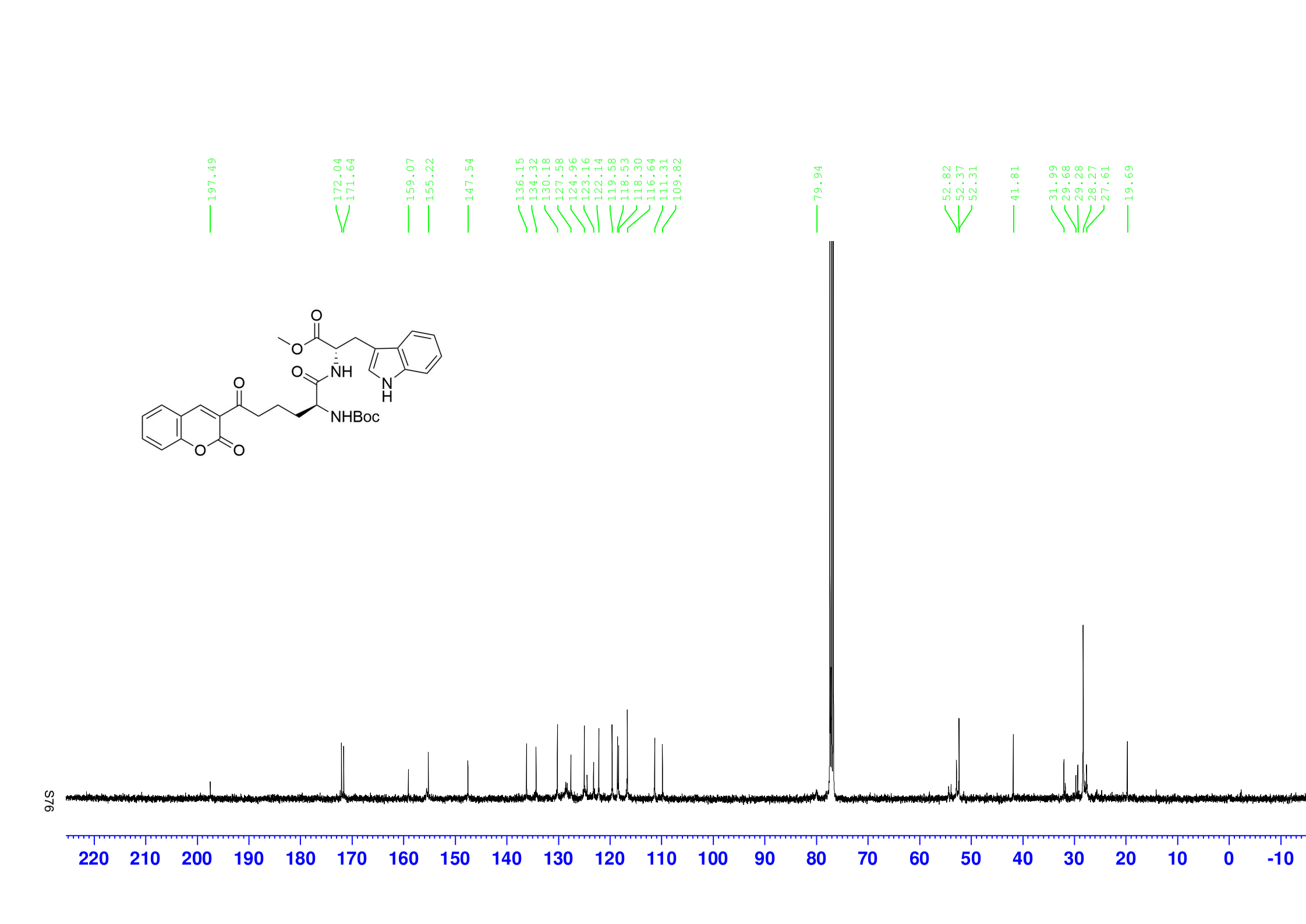
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79.94
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52.31
41.81
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29.68
29.28
28.27
27.61
19.69
O
O
NH
O
N
H
O
NHBoc
O
O
220
210
200
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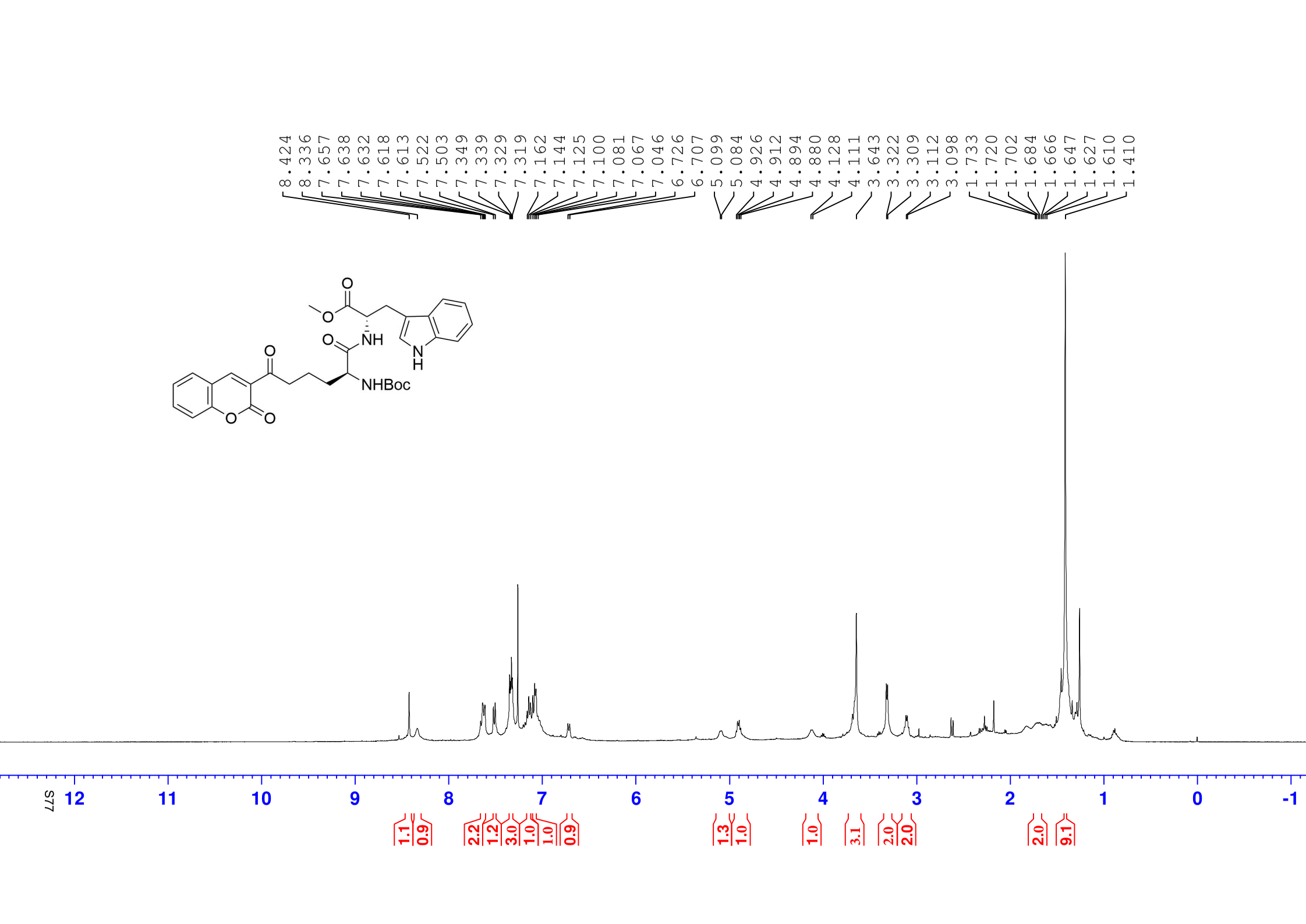
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3.112
3.098
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1.666
1.647
1.627
1.610
1.410
O
O
NH
O
N
H
O
NHBoc
O
O
S77
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8
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5
4
3
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-1
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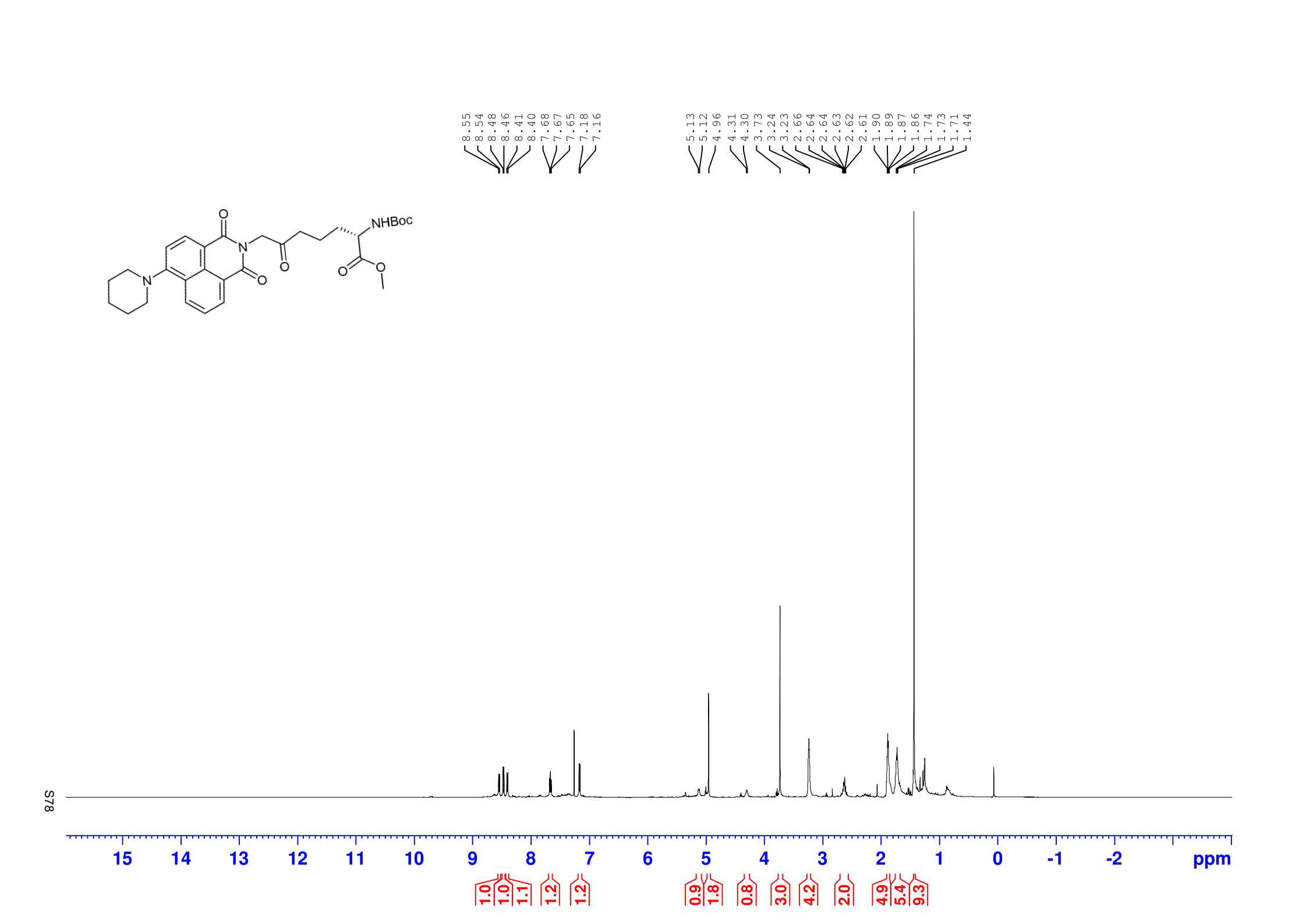
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3.23
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2.63
2.62
2.61
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1.89
1.87
1.86
1.74
1.73
1.71
1.44
NHBoc
O
N
O
O
O
O
N
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm
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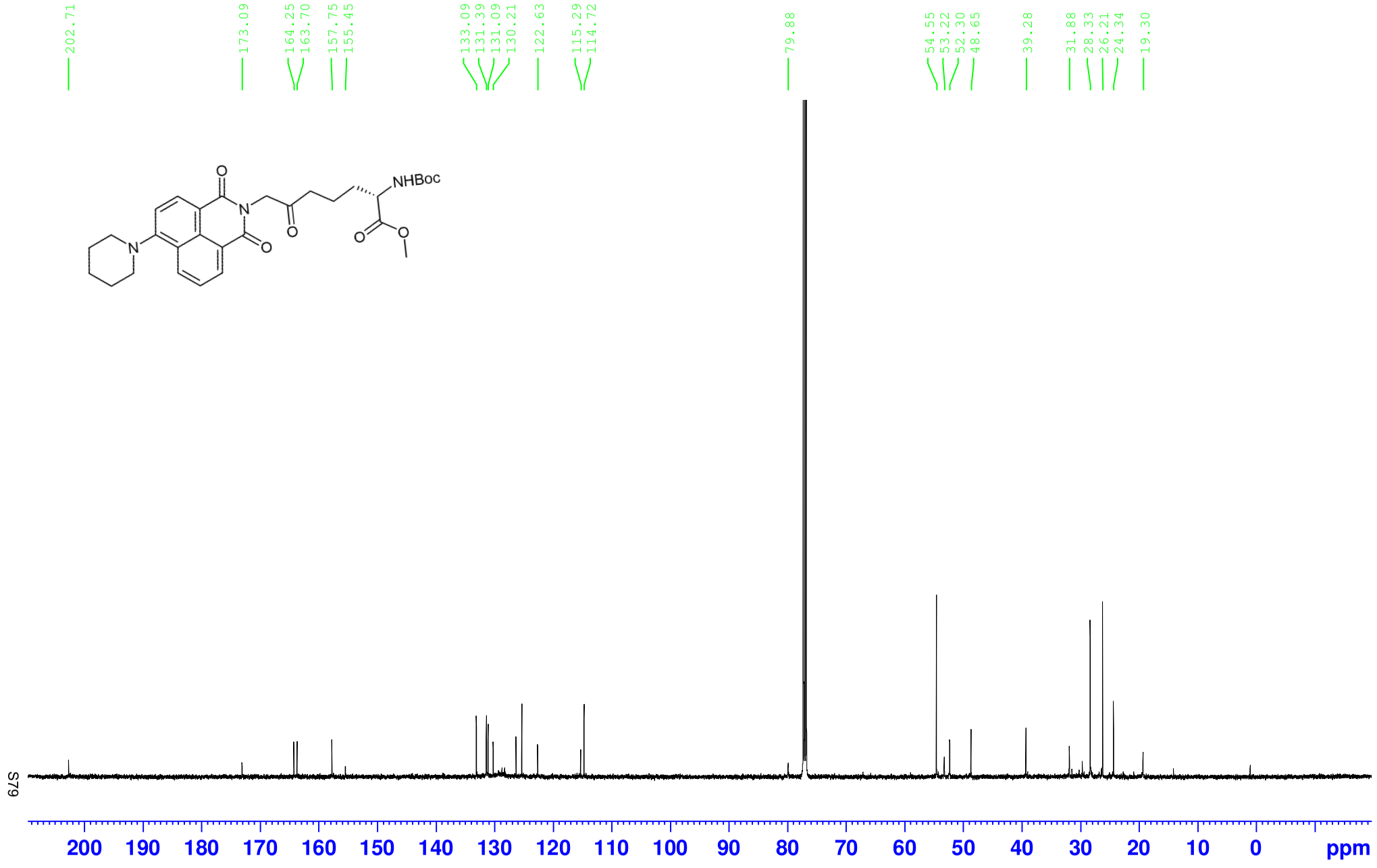
9.3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122.63
115.29
114.72
79.88
54.55
53.22
52.30
48.65
39.28
31.88
28.33
26.21
24.34
19.30
NHBoc
O
N
O
O
O
O
N
200
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140
130
120
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100
90
80
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60
50
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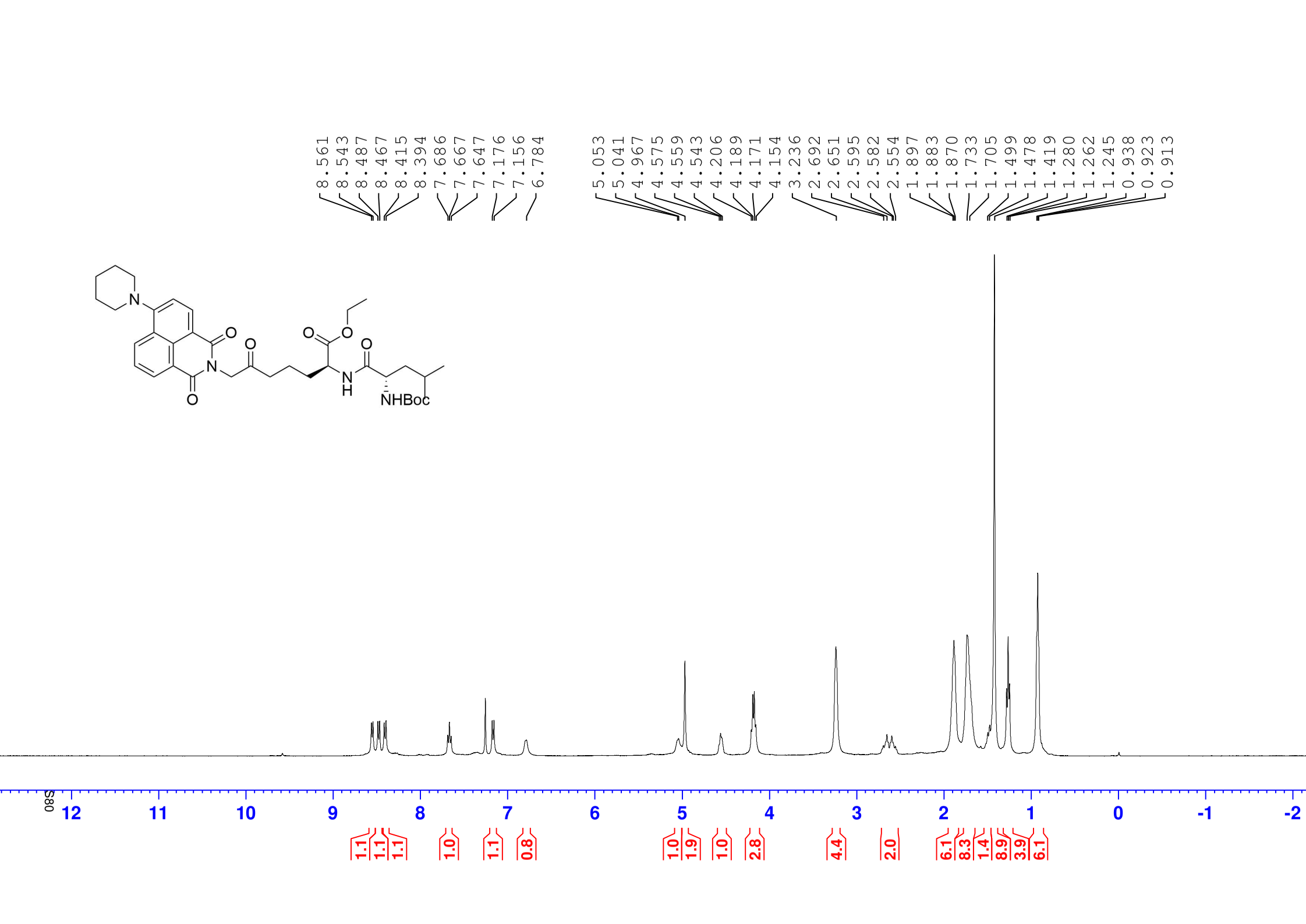
10
0
ppm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4.543
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1.499
1.478
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0.913
N
O
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O
O
O
N
O
N
H
O
NHBoc
S80
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11
10
9
8
7
6
5
4
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2
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0
-1
-2
1.1
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1.0
1.1
0.8
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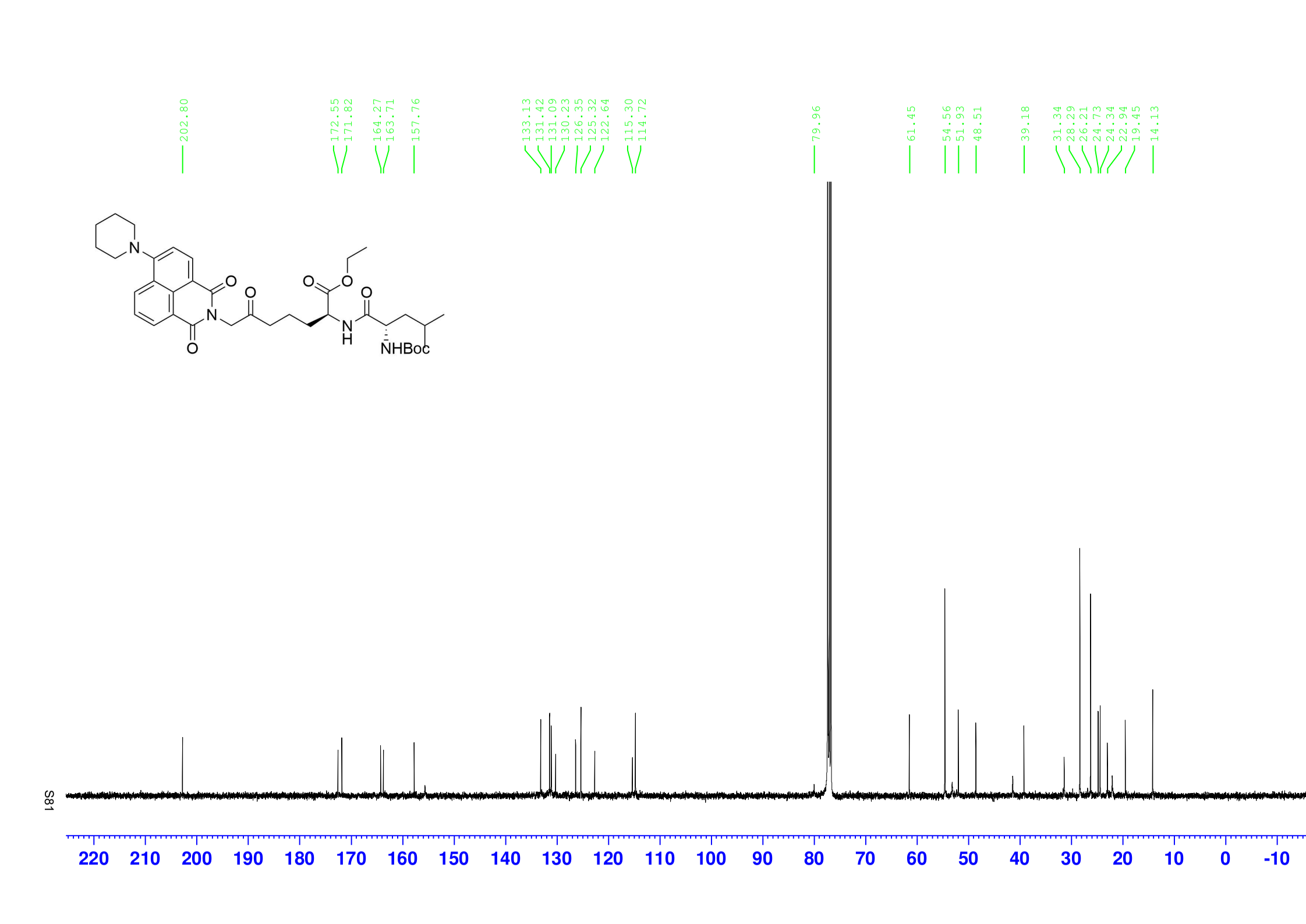
3.9
6.1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51.93
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31.34
28.29
26.21
24.73
24.34
22.94
19.45
14.13
N
O
O
O
N
O
O
O
N
H
NHBoc
220
210
200
190
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120
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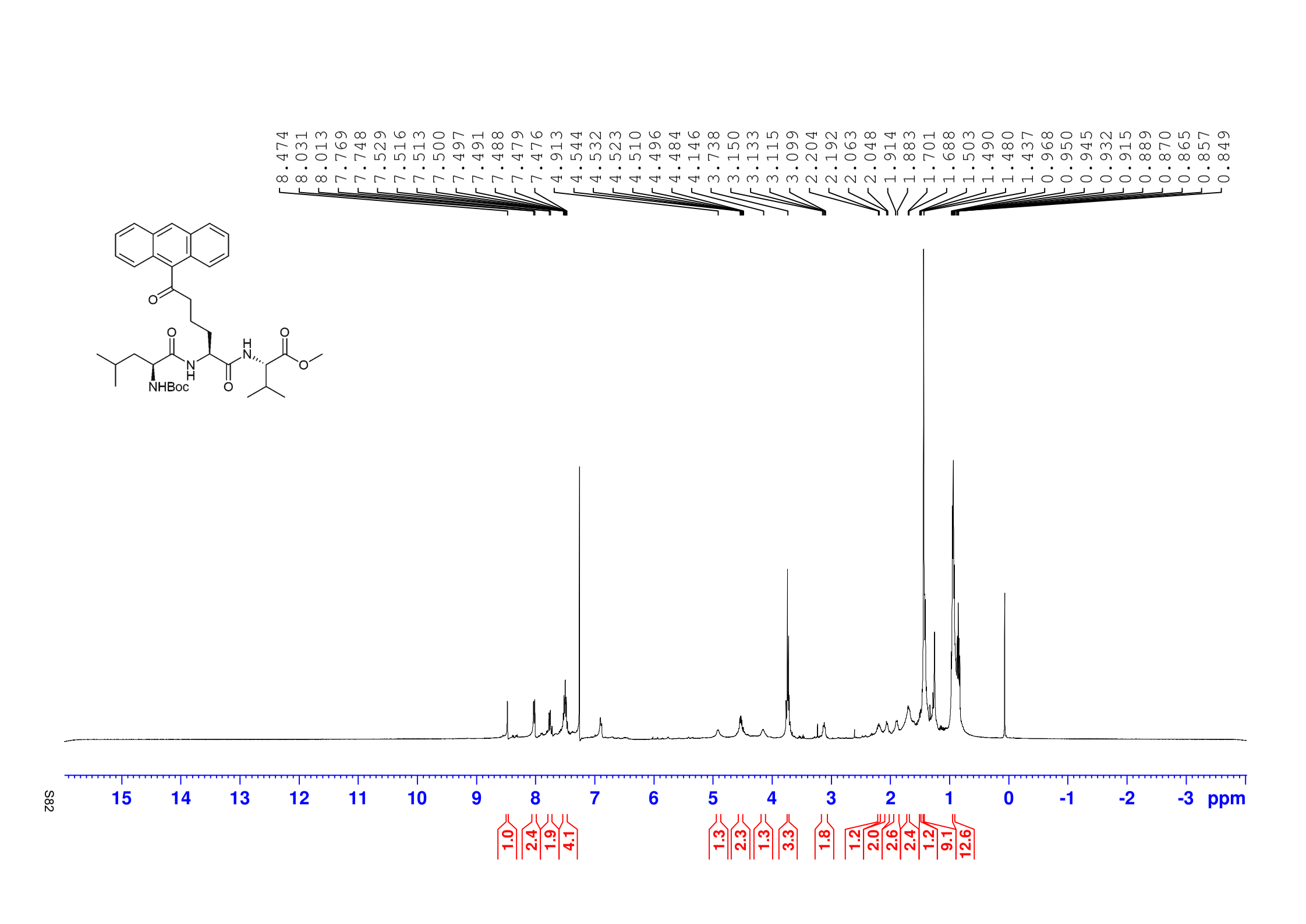
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0.932
0.915
0.889
0.870
0.865
0.857
0.849
NHBoc
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm
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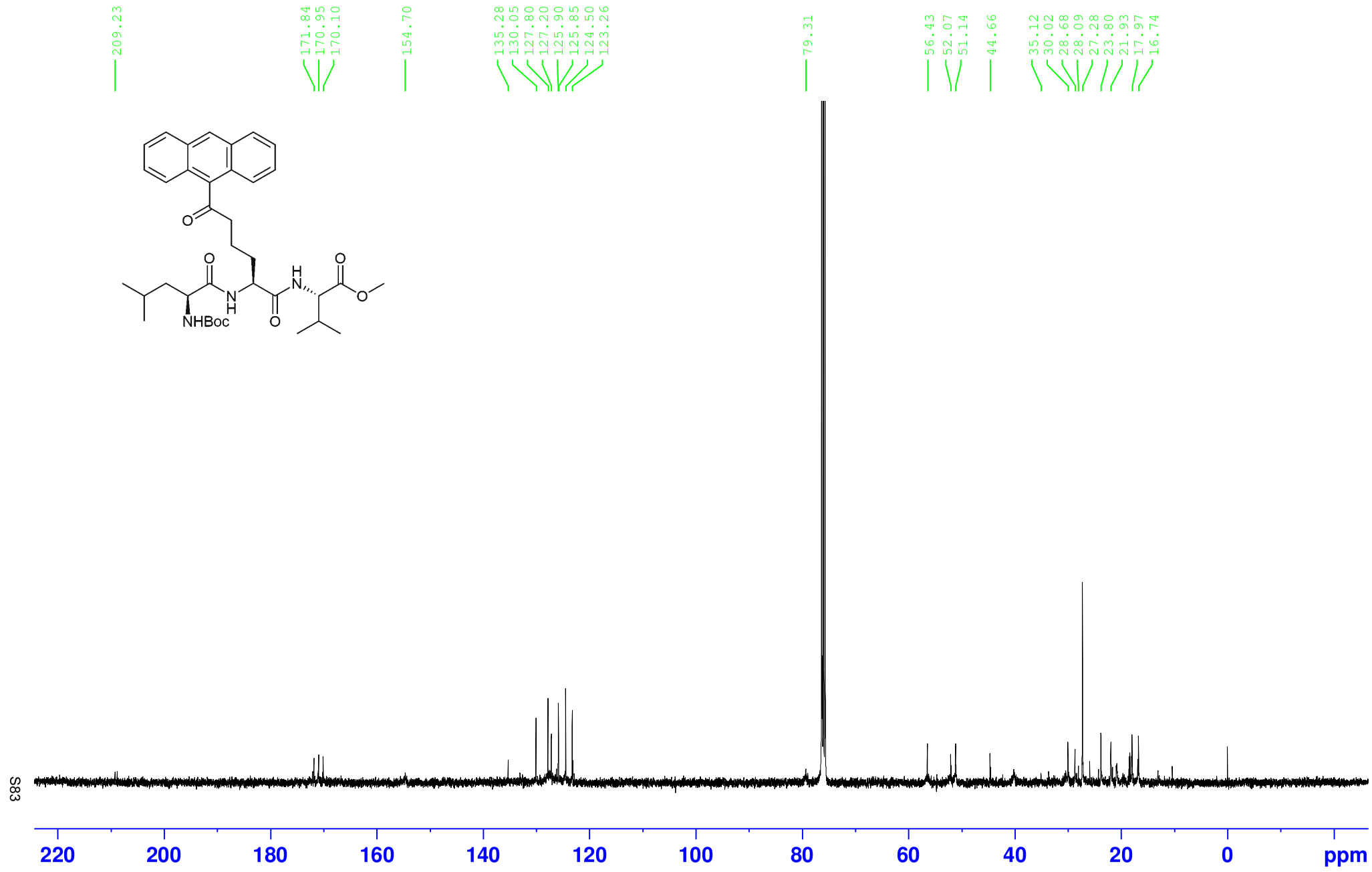
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52.07
51.14
44.66
35.12
30.02
28.68
28.09
27.28
23.80
21.93
17.97
16.74
O
O
N
H
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H
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O
NHBoc
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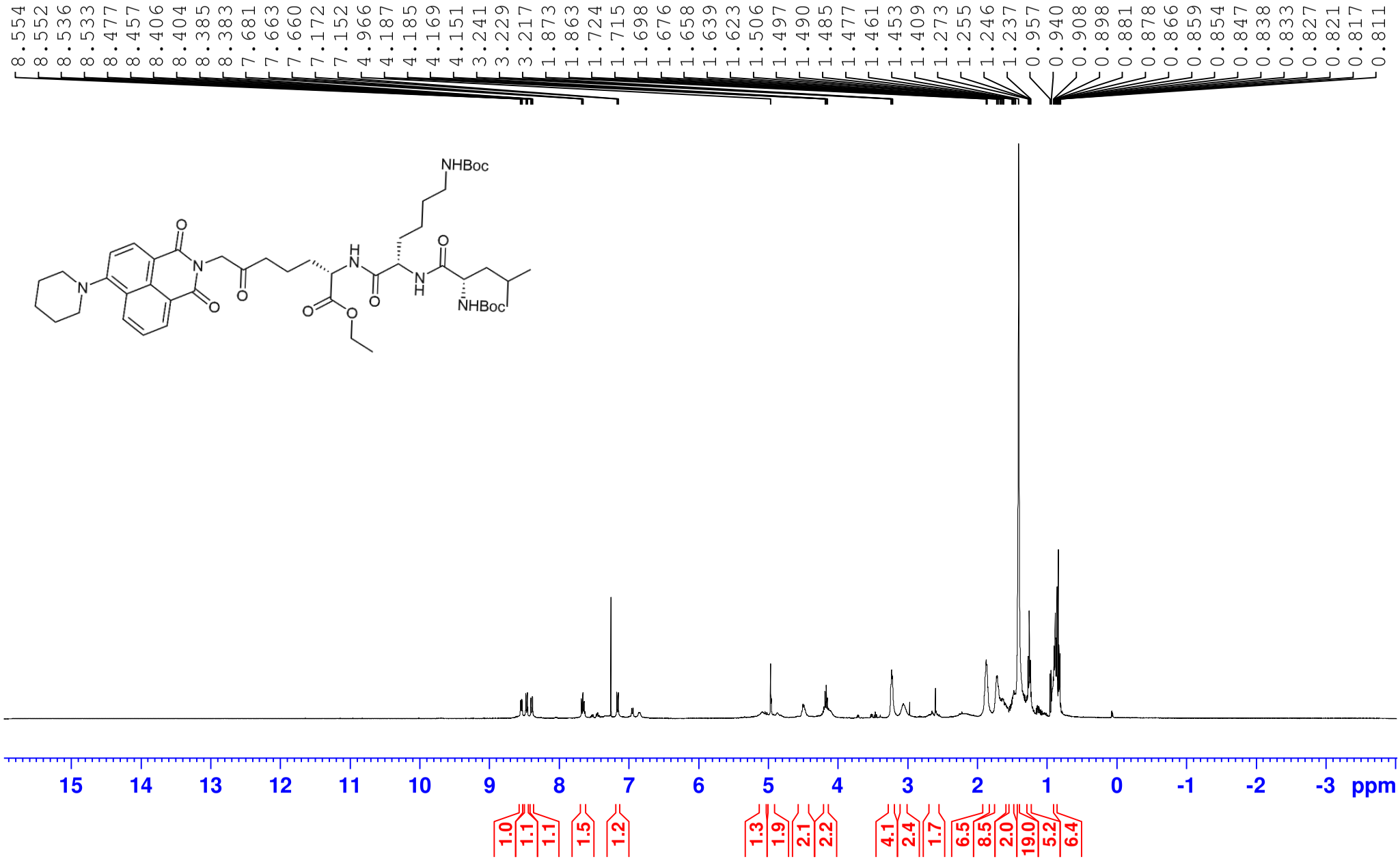
ppm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1.237
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0.881
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0.859
0.854
0.847
0.838
0.833
0.827
0.821
0.817
0.811
NHBoc
NHBoc
15
14
13
12
11
10
9
8
7
6
5
4
3
2
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0
-1
-2
-3
ppm
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1.5
1.2
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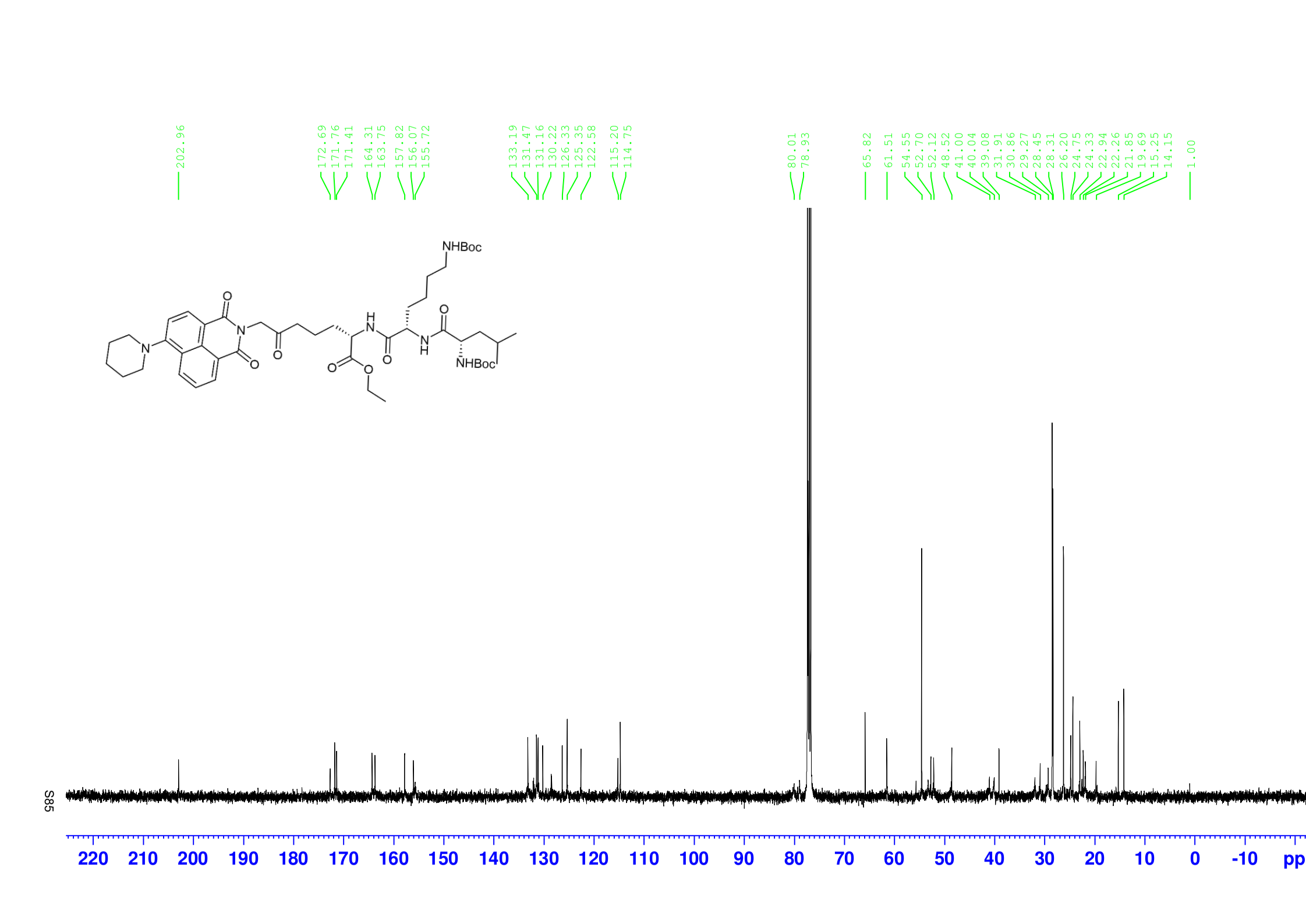
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26.20
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24.33
22.94
22.26
21.85
19.69
15.25
14.15
1.00
NHBoc
NHBoc
220
210
200
190
180
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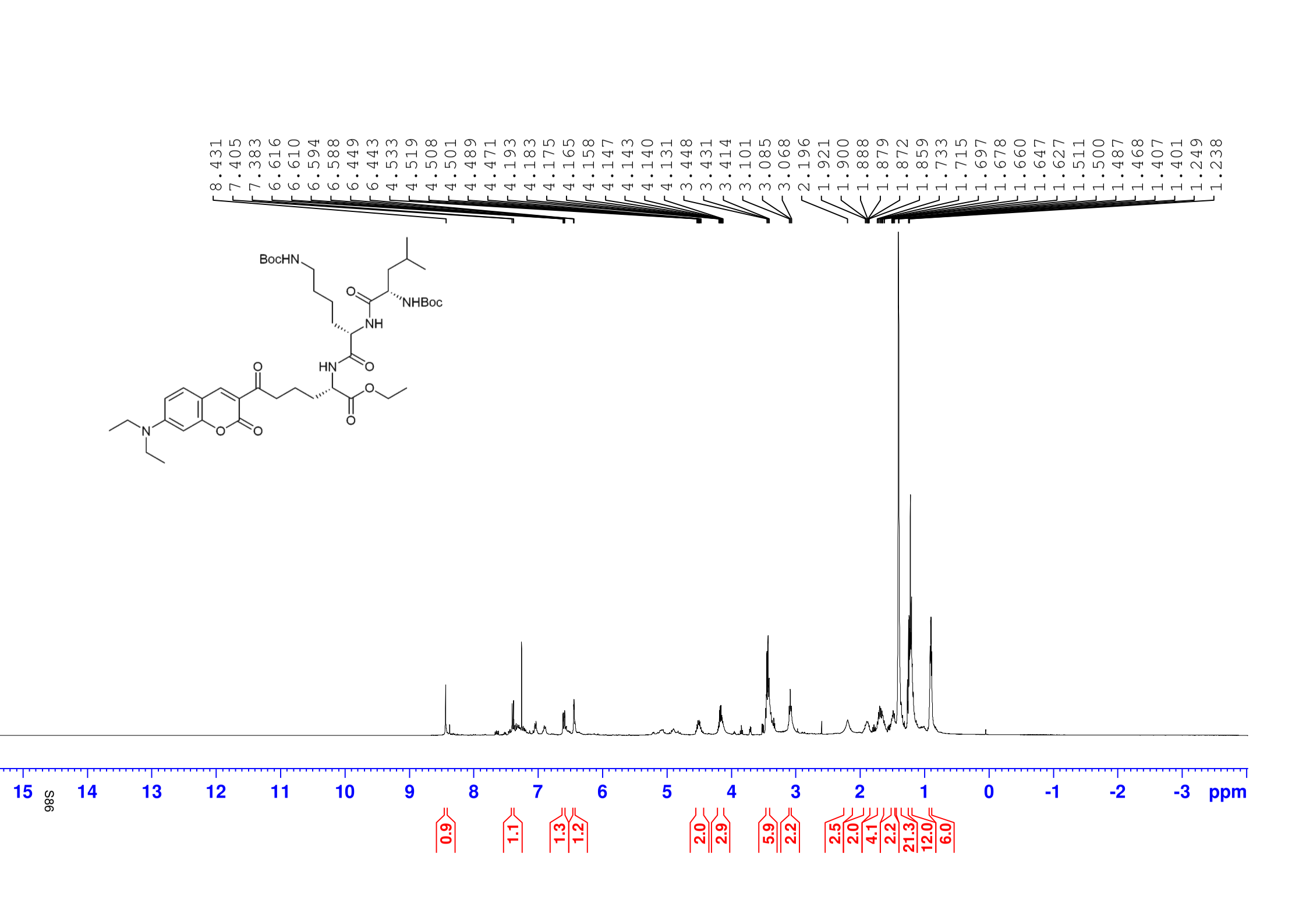
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1.468
1.407
1.401
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1.238
BocHN
NHBoc
NH
HN
O
N
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm
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1.3
1.2
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2.2
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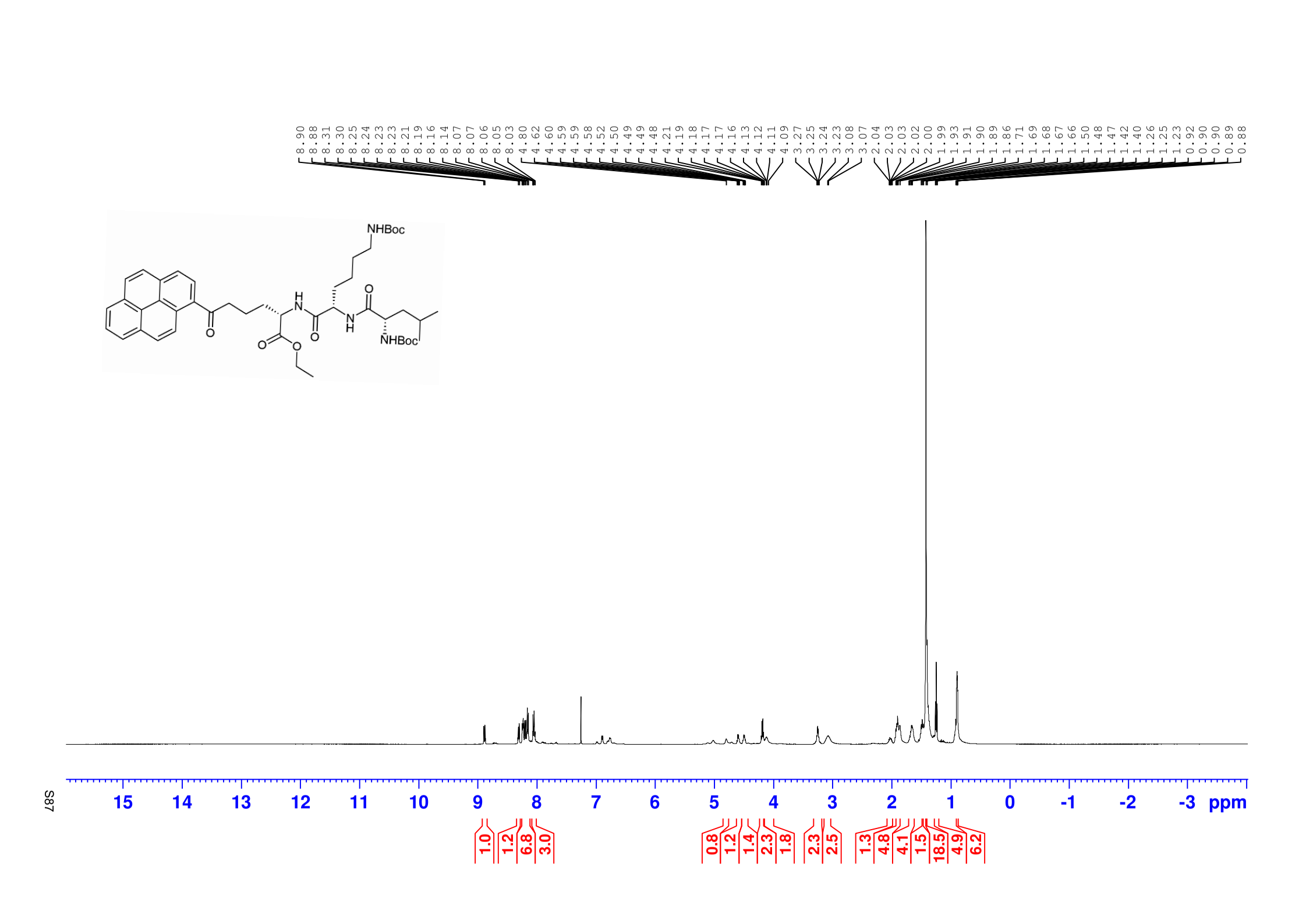
12.0
6.0

S86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4.18
4.17
4.17
4.16
4.13
4.12
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3.24
3.23
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2.03
2.02
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NHBoc
NHBoc
15
14
13
12
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9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm
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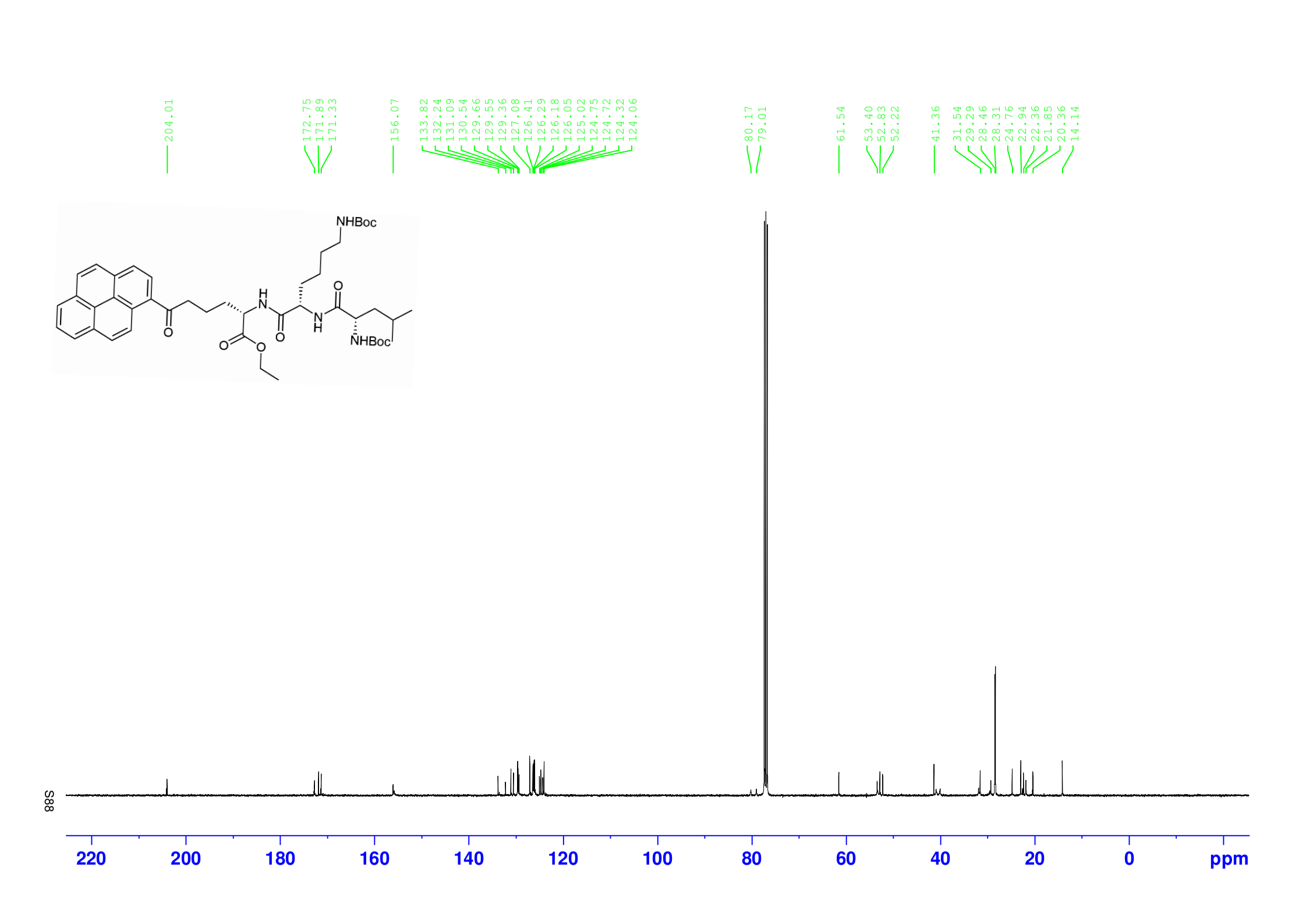
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126.05
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124.32
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31.54
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28.46
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20.36
14.14
NHBoc
NHBoc
S88
220
200
180
160
140
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100
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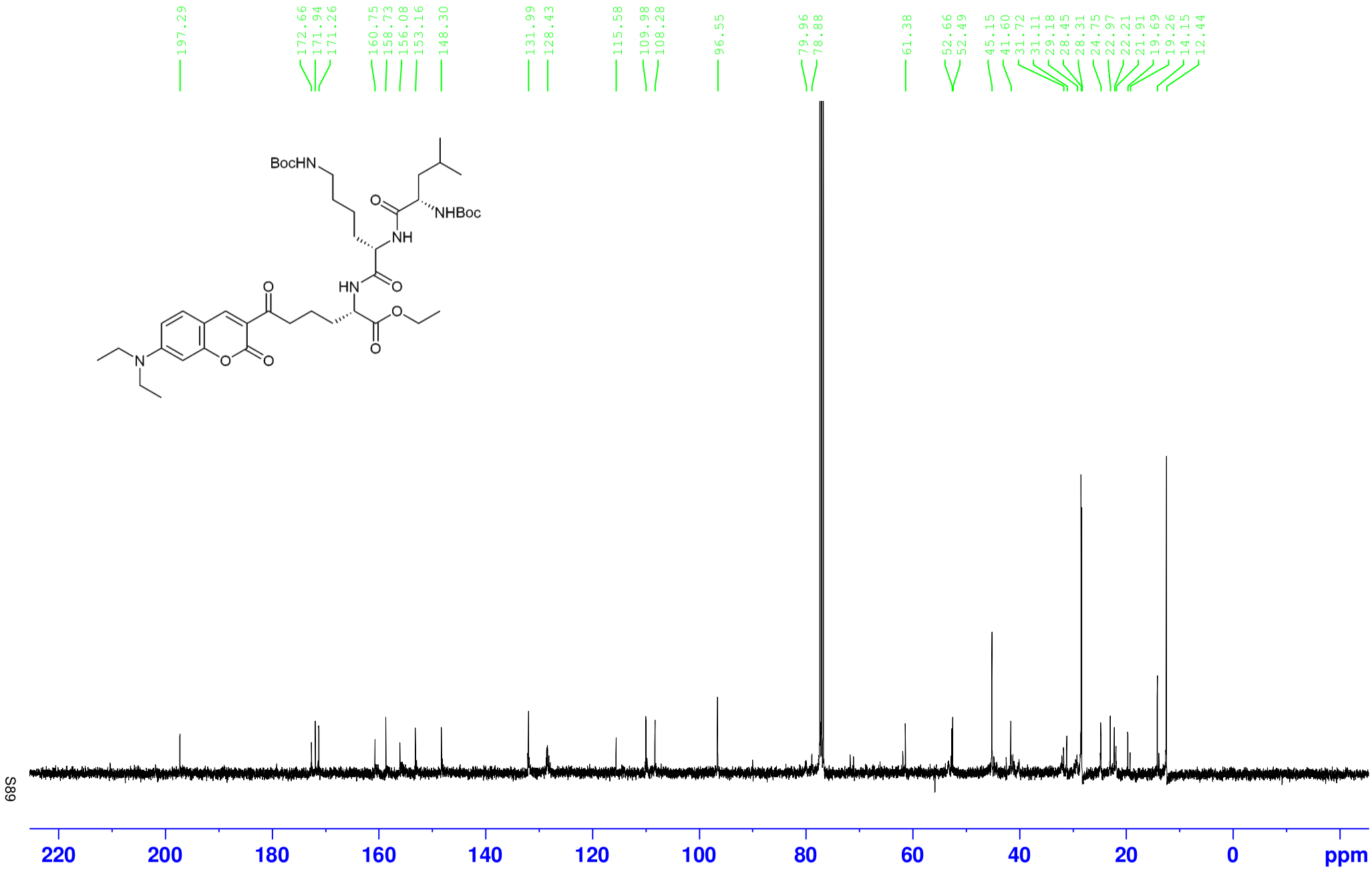
60
40
20
0
ppm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172.66
171.94
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108.28
96.55
79.96
78.88
61.38
52.66
52.49
45.15
41.60
31.72
31.11
29.18
28.45
28.31
24.75
22.97
22.21
21.91
19.69
19.26
14.15
12.44
BocHN
NHBoc
NH
HN
O
N
O
O
O
O
O
O
S89
220
200
180
160
140
120
100
80
60
40
20
0
ppm