Supporting Information

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1. General Considerations

TLC analysis was performed (fluorescence quenching or $KMnO_4$ stain) with silica gel HL TLC plates with UV254 purchased from Sorbent Technologies.

Silica gel used for column chromatography (60 Å porosity, 230 x 400 mesh, standard grade) was purchased from Sorbent Technologies (catalog # 30930M-25).

$Pd(PPh_3)_4$ and (R,R)-ANDEN-Phenyl Trost ligand were purchased from Sigma Aldrich and stored in an Ar filled glovebox. Pd_2dba_3 was purchased from Strem Chemicals and stored in a glovebox.

The photocatalyst $[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$ was either synthesized according to a literature procedure[1] or purchased from Sigma Aldrich and stored in a glove box.

Anhydrous DMSO and Toluene were purchased from Sigma Aldrich and stored in a glove box.

GC/MS data was obtained on a Shimadzu GCMS-QP2010 SE. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker ADVANCE 500 DRX equipped with a QNP cryoprobe. ^{1}H and ^{13}C NMR spectra were referenced to residual protio solvent signals. HRMS data was obtained on a ESI LC-TOF Micromass LCT (Waters).

Final decarboxylative allylation reactions were run in screw threaded tubes from Chemglass (CLS-4208). Two different blue LED light baths were employed. Room temperature reactions were run in a beaker wrapped with blue LED strips which was then covered in aluminum foil. A fan was placed directly above the beaker (photo 1). Reactions performed at elevated temperatures were done in a glass crystallization dish with the outside walls wrapped in blue LED strips. The dish was covered in aluminum foil and filled with water, which was heated to a preset temperature while stirring using a stir plate. The reaction tubes were held in place by a cardboard lid (photo 2).

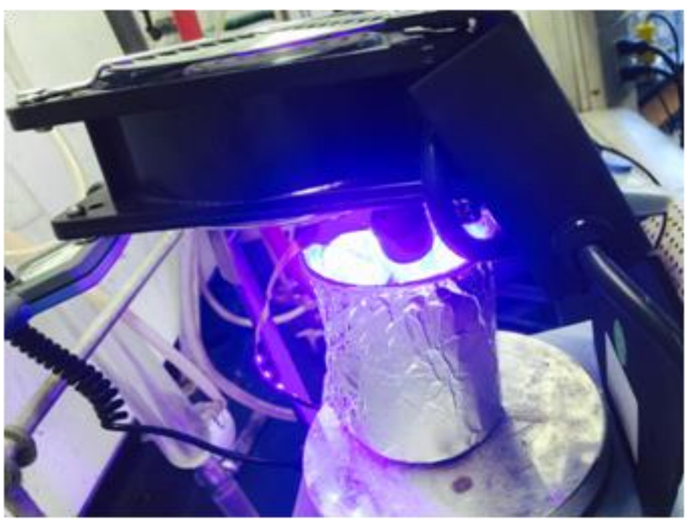


Photo 1

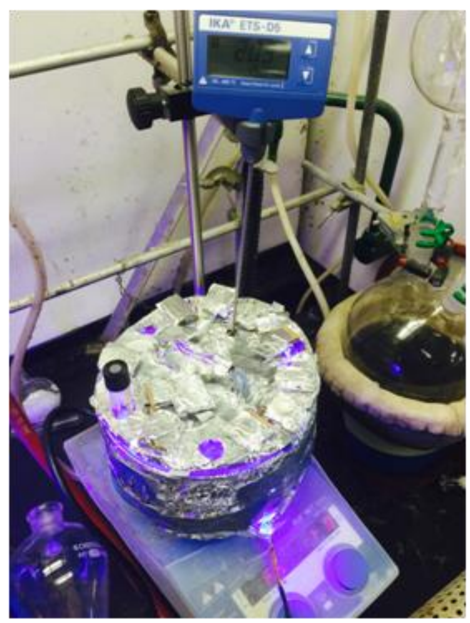
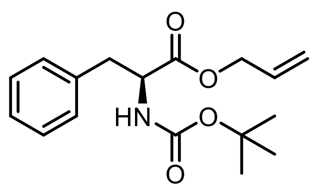


Photo 2

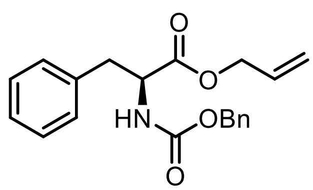
2. Synthesis and Characterization of Allylic Esters

The allylic esters corresponding to products **1a** – **1i** have been previously described by our group.[2]

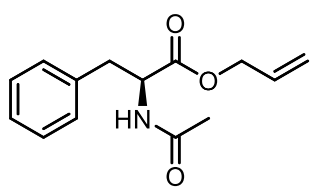
Representative procedure for the synthesis of allylic esters: The N-protected amino acid (5.0 mmol) was added to DMF (15 mL) and the solution cooled to 0 °C (ice bath). Hunig's base (6.5 mmol) was added followed by allyl bromide (6.5 mmol) and the solution was allowed to warm to room temperature and stir overnight. The solution was diluted with EtOAc (40 mL) and then washed with water (2 x 30 mL) and brine (30 mL). The organic phase was dried with $MgSO_4$, concentrated *in vacuo*, and purified via flash column chromatography.



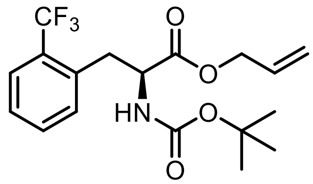
Prepared according to the representative procedure (7.5 mmol scale, 98% yield). The spectroscopic data matched that already reported in the literature.[3]



Prepared according to the representative procedure (6.7 mmol scale, 99% yield). The spectroscopic data matched that already reported in the literature.[4]



Prepared according to the representative procedure (9.7 mmol scale, 81% yield). The spectroscopic data matched that already reported in the literature.[5]



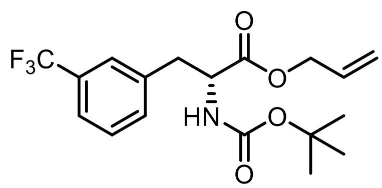
Prepared according to the representative procedure (3 mmol scale, 69% yield). A mixture of rotamers. Major resonances reported.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 7.95 Hz, 1H), 7.48 (t, J = 7.52 Hz, 1H), 7.36 (m, 2H), 5.81 (ddt, J = 16.5, 10.9, 5.70, 1H), 5.23 (m, 2H), 5.07 (d, J = 8.75 Hz, 1H), 4.61 (m, 3H), 3.34 (dd, J = 14.5, 5.95 Hz, 1H), 3.09 (dd, J = 14.4, 9.01 Hz, 1H), 1.36 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 155.1, 135.4, 131.9, 131.7, 131.4, 129.2 (q, J = 29.6 Hz), 127.1, 126.2 (q, J = 5.59 Hz), 124.6 (q, J = 273.7 Hz), 118.8, 80.1, 66.1, 54.6, 35.6, 28.3.

IR (film) 3367, 2980, 2935, 1745, 1715, 1504, 1454, 1367, 1315, 1251, 1171, 1120, 1060, 1039, 989, 935, 767 cm^{-1}.

HRMS: Calc'd $C_{18}H_{22}F_3NO_4Na$ (M+Na) = 396.1399, found 396.1389.



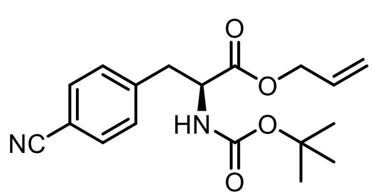
Prepared according to the representative procedure (3 mmol scale, 61% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 7.77 Hz, 1H), 7.38 (m, 3H), 5.85 (ddt, J = 16.5, 10.4, 5.95 Hz, 1H), 5.28 (m, 2H), 5.04 (d, J = 7.90 Hz, 1H), 4.60 (m, 3H), 3.22 (dd, J = 13.8, 5.95 Hz, 1H), 3.12 (dd, J = 13.9, 6.07 Hz, 1H), 1.42 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 155.1, 137.2, 132.9, 131.3, 130.9 (q, J = 32.3 Hz), 129.1, 126.3 (q, J = 3.36 Hz), 124.1 (q, J = 273 Hz), 124.0 (q, J = 3.61 Hz), 119.6, 80.3, 66.3, 54.4, 38.3, 28.4.

IR (film) 3365, 2979, 2935, 1745, 1714, 1504, 1454, 1367, 1328, 1251, 1164, 1126, 1074, 991, 937, 794, 703, 659 cm^{-1}.

HRMS: Calc'd $C_{18}H_{22}F_3NO_4Na$ $(M+Na)^+$ = 396.1399, found = 396.1397.



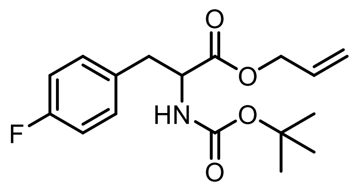
Prepared according to the representative procedure (3.4 mmol scale, 59% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 7.91 Hz, 2H), 7.26 (d, J = 7.99 Hz, 2H), 5.85 (ddt, J = 16.6, 11.1, 5.91 Hz, 1H), 5.28 (m, 2H), 5.04 (d, J = 8.05 Hz, 1H), 4.61 (m, 3H), 3.22 (dd, J = 13.8, 5.86 Hz, 1H), 3.08 (dd, J = 13.8, 6.51 Hz, 1H), 1.40 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 155.0, 142.0, 132.3, 131.3, 130.4, 119.5, 118.9, 111.1, 80.4, 66.4, 54.2, 38.8, 28.4.

IR (film) 3367, 2977, 2933, 2227, 1743, 1714, 1650, 1608, 1504, 1454, 1367, 1274, 1251, 1166, 1054, 1022, 991, 937, 825, 748, 557 cm^{-1}.

HRMS: Calc'd $C_{18}H_{22}N_2O_4Na$ $(M+Na)^+$ = 353.1477, found = 353.1474.



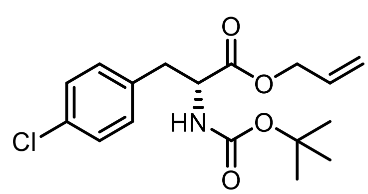
The free amino acid (5.5 mmol) was added to a 1:1 mixture of THF/H_2O (15 mL each) and the mixture was cooled to 0 °C (ice bath). Triethylamine (9.0 mmol) was added to the reaction mixture followed by Boc_2O (7.0 mmol). The reaction was allowed to warm to room temperature and stirred overnight. Next, the volatiles were removed *in vaccuo*, the pH was adjusted to 3 with 1M HCl and the reaction mixture extracted with EtOAc (40 mL). The organic phase was washed with brine (20 mL), dried with $MgSO_4$ and concentrated *in vacuo*. The crude product was subjected to the representative procedure to yield the desired allyl ester after flash column chromatography (66% yield over two steps).

^1H NMR (500 MHz, $CDCl_3$) δ 7.10 (m, 2H), 6.97 (t, *J* = 8.67 Hz, 2H), 5.86 (ddt, *J* = 17.2, 10.3, 5.85 Hz, 1H), 5.29 (m, 2H), 4.98 (d, *J* = 8.31 Hz, 1H), 4.60 (m, 3H), 3.11 (dd, *J* = 14.0, 5.86 Hz, 1H), 3.03 (dd, *J* = 14.0, 6.19 Hz, 1H), 1.42 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 162.1 (d, *J* = 245 Hz), 155.1, 131.8 (d, *J* = 3.12 Hz), 131.5, 131.0 (d, *J* = 7.95 Hz), 119.2, 115.5 (d, *J* = 21.3 Hz), 80.2, 66.2, 55.6, 37.8, 28.4.

IR (film) 3434, 3365, 2977, 2933, 1745, 1714, 1602, 1510, 1446, 1367, 1222, 1168, 1097, 1056, 1016, 991, 935, 825, 748 cm^{-1}.

HRMS: Calc'd $C_{17}H_{22}FNO_4Na$ $(M+Na)^+$ = 346.1431, found = 346.1412.



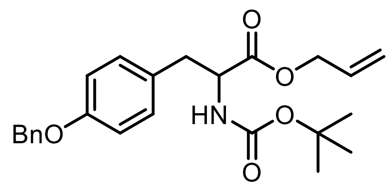
Prepared according to the representative procedure (2.2 mmol scale, 95% yield).

^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 2H), 7.07 (d, *J* = 8.38 Hz, 2H), 5.86 (ddt, *J* = 17.2, 10.4, 5.90 Hz, 1H), 5.29 (m, 2H), 4.97 (d, *J* = 8.27 Hz, 1H), 4.60 (m, 3H), 3.11 (dd, *J* = 13.9, 5.80 Hz, 1H), 3.03 (dd, *J* = 13.9, 6.10 Hz, 1H), 1.42 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 155.1, 134.6, 133.1, 131.5, 130.9, 128.8, 119.3, 80.2, 66.2, 54.5, 37.9, 28.4.

IR (film) 3355, 2977, 2933, 1741, 1714, 1492, 1454, 1367, 1253, 1166, 1091, 1056, 1016, 989, 933, 748 cm^{-1}.

HRMS: Calc'd $C_{17}H_{22}ClNO_4Na$ $(M+Na)^+$ = 362.1135, found = 362.1128.



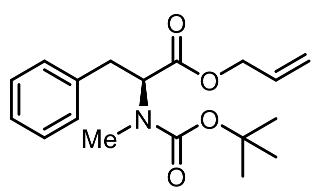
Prepared according to the representative procedure (6.5 mmol scale, 32% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (m, 4H), 7.33 (m, 1H), 7.05 (d, *J* = 8.59 Hz, 2H), 6.90 (m, 2H), 5.87 (ddt, *J* = 17.2, 10.4, 5.84 Hz, 1H), 5.31 (dq, *J* = 17.2, 1.49 Hz, 1H), 5.24 (dd, *J* = 10.4, 1.31 Hz, 1H), 5.04 (s, 2H), 4.96 (d, *J* = 8.35 Hz, 1H), 4.58 (m, 3H), 3.04 (m, 2H), 1.42 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 158.0, 155.2, 137.1, 131.7, 130.5, 128.7, 128.3, 128.1, 127.6, 119.1, 115.0, 80.0, 70.1, 66.1, 54.7, 37.6, 28.5.

IR (film) 3367, 3031, 2977, 2931, 1741, 1714, 1610, 1583, 1512, 1454, 1367, 1244, 1174, 1056, 1018, 991, 931, 862, 821, 738, 696 cm^{-1}.

HRMS: Calc'd $C_{24}H_{29}NO_5Na$ $(M+Na)^+$ = 434.1943, found = 434.1940.



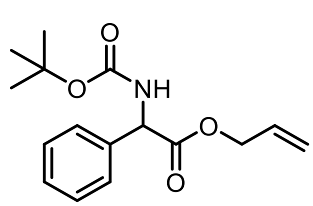
Prepared according to the representative procedure (3.6 mmol scale, 51% yield). A mixture of rotamers.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 2H), 7.19 (m, 3H), 5.91 (dtt, *J* = 16.4, 10.8, 5.65 Hz, 1H), 5.29 (m, 2H), 4.92 (dd, *J* = 10.7, 5.33 Hz, 0.5H), 4.63 (m, 2.5H), 3.31 (m, 1H), 3.03 (m, 1H), 2.74 (s, 1.6 H), 2.71 (s, 1.4H), 1.37 (s, 3.8H), 1.33 (s, 5.2H).

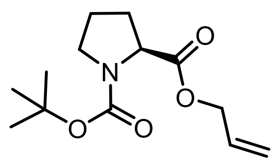
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1 (br s), 155.5 (br s), 137.7 (br s), 131.9 (br s), 129.1 (br s), 128.6 (br s), 126.7 (br s), 118.6 (br s), 80.3 (br s), 65.9 (br s), 60.8 (br s), 35.4 (br s), 32.4 (br s), 28.3 (br s).

IR (film) 3064, 3028, 2975, 2931, 1745, 1697, 1479, 1454, 1392, 1367, 1326, 1274, 1257, 1218, 1170, 1143, 1080, 1029, 987, 933, 869, 750, 700 cm^{-1}.

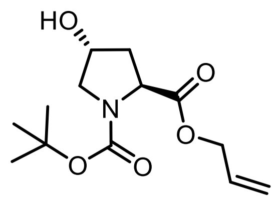
HRMS: Calc'd $C_{18}H_{25}NO_4Na$ $(M+Na)^+$ = 342.1681, found = 342.1678.



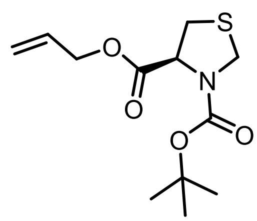
The free amino acid (25.3 mmol) was added to 1M NaOH (35.0 mL). To this solution was added Boc_2O (28.1 mmol) in $^{t}BuOH$ (20.0 mL) and the mixture was stirred for 1 h. After removing volatiles *in vaccuo* the pH was adjusted to 3 with 1M HCl and the solution was extracted with DCM (3 x 50 mL) which was dried with $MgSO_4$, and concentrated *in vaccuo*. The crude material was subjected to the representative reaction conditions to furnish the desired allyl ester after flash column chromatography (76% yield over two steps). The spectroscopic data matched that already reported in the literature.[6]



Prepared according to the representative procedure (3 mmol scale, 95% yield). The spectroscopic data matched that already reported in the literature.[7]



Prepared according to a literature procedure with matching spectroscopic data.[8]



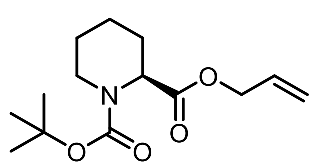
Prepared according to the representative procedure (2 mmol scale, 82% yield). A mixture of rotamers.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91 (m, 1H), 5.31 (m, 2H), 4.91 (m, 0.5H), 4.63 (m, 3H), 4.50 (m, 1.5H), 3.32 (m, 1H), 3.20 (m, 1H), 1.47 (s, 4.5H), 1.43 (s, 4.5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5 (br s), 153.3 (br s), 131.6 (br s), 118.8 (br s), 81.4, 66.2, 61.7 (br s), 48.7 (br s), 34.2 (br s), 28.4 (br s).

IR (film) 3429, 2977, 2935, 1749, 1697, 1650, 1456, 1384, 1367, 1336, 1274, 1257, 1163, 1108, 985, 914, 889, 864, 763, 748 cm^{-1}.

HRMS: Calc'd $C_{12}H_{19}NO_4SNa$ $(M+Na)^+$ = 296.0933, found = 296.0919.



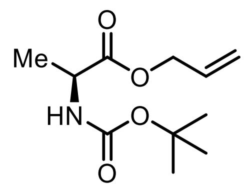
Prepared according to the representative procedure (2.2 mmol scale, 96% yield). A mixture of rotamers.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (ddt, *J* = 16.6, 10.8, 5.54 Hz, 1H), 5.32 (d, *J* = 17.0 Hz, 1H), 5.23 (d, *J* = 10.5 Hz, 1H), 4.91 (s, 0.5H), 4.73 (s, 0.5H), 4.63 (m, 2H), 4.02 (d, *J* = 11.9 Hz, 0.5H), 3.91 (d, *J* = 11.9 Hz, 0.5H), 2.98 (t, *J* = 13.2 Hz, 0.5H), 2.87 (t, *J* = 13.3 Hz, 0.5H), 2.22 (t, *J* = 13.8 Hz, 1H), 1.67 (m, 3H), 1.44 (m, 10H), 1.22 (q, *J* = 14.0 Hz, 1H).

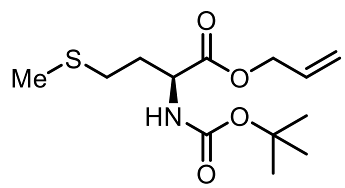
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8 (br s), 155.8 (br s), 132.0 (br s), 118.4 (br s), 80.1, 65.6, 54.5 (br s), 41.7 (br s), 28.5, 26.9, 24.8 (br s), 20.8 (br s).

IR (film) 2974, 2941, 2862, 1743, 1693, 1650, 1475, 1448, 1392, 1365, 1338, 1323, 1269, 1247, 1186, 1157, 1124, 1091, 1043, 1000, 977, 931, 871, 771, 559 cm^{-1}.

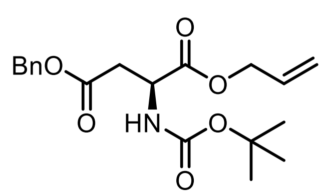
HRMS: Calc'd $C_{14}H_{23}NO_4Na$ $(M+Na)^+$ = 292.1525, found = 292.1523.



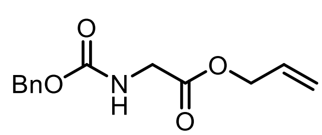
Prepared according to the representative procedure (5 mmol scale, 99% yield). The spectroscopic data matched that already reported in the literature.[6]



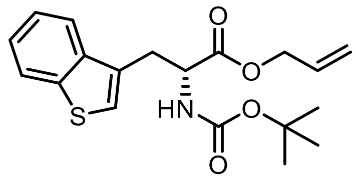
The free amino acid (16.8 mmol) was added to a solution of 1M NaOH (16.0 mL) and dioxane (20.0 mL). The solution was cooled to 0 °C (ice bath) and Boc_2O (17.6 mmol) was added and allowed to stir at room temperature overnight. Next, the volatiles were removed *in vaccuo*, the pH was adjusted to 3 with 1M HCl, and the solution was extracted with EtOAc (2 x 20 mL). The organic phase was washed with brine (15 mL), dried with $MgSO_4$, and concentrated *in vaccuo*. The crude product was subjected to the representative reaction conditions to provide the desired product after flash column chromatography (63% yield over two steps). The spectroscopic data matched that already reported in the literature.[4]



Prepared according to the representative procedure (6.2 mmol scale, 99% yield). The spectroscopic data matched that already reported in the literature.[9]



Prepared according to the representative procedure (5 mmol scale, 86% yield). The spectroscopic data matched that already reported in the literature.[10]



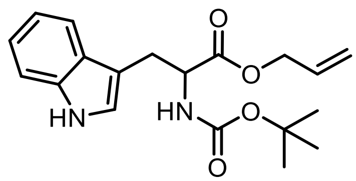
Prepared according to the representative procedure (3.1 mmol scale, 41% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.52 Hz, 1H), 7.76 (m, 1H), 7.36 (m, 2H), 7.17 (s, 1H), 5.80 (ddt, *J* = 16.4, 11.1, 5.82 Hz, 1H), 5.24 (m, 2H), 5.10 (d, *J* = 8.20 Hz, 1H), 4.73 (q, *J* = 6.13 Hz, 1H), 4.56 (m, 2H), 3.41 (dd, *J* = 14.7, 5.89 Hz, 1H), 3.34 (dd, *J* = 14.7, 6.12 Hz, 1H), 1.43 (s, 7.5H, Boc), 1.25 (s, 1.5H, Boc).

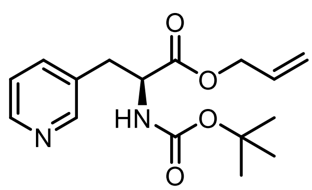
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 155.2, 140.4, 139.1, 131.5, 131.0, 124.5, 124.2, 124.0, 123.0, 121.8, 119.2, 80.2, 66.3, 53.8, 31.4, 28.3 (br s).

IR (film) 3357, 2977, 2931, 1739, 1712, 1504, 1458, 1365, 1274, 1251, 1166, 1058, 1020, 989, 933, 854, 761, 732 cm^{-1}.

HRMS: Calc'd $C_{19}H_{23}NO_4SNa$ $(M+Na)^+$ = 384.1246, found = 384.1241.



The free amino acid (7.3 mmol) was added to a solution of H_2O (15 mL) and THF (15 mL). NaOH (8.0 mmol) was added followed by Boc_2O (8.0 mmol). After stirring overnight the THF was removed *in vaccuo* and the pH adjusted to 4 using 1M HCl. The aqueous phase was extracted with DCM (2 x 20 mL) which was dried with $MgSO_4$ and concentrated *in vaccuo*. The crude material was subjected to the representative reaction conditions to furnish the desired allyl ester after flash column chromatography in a 16% yield. The spectroscopic data matched that already reported in the literature.[11,12]



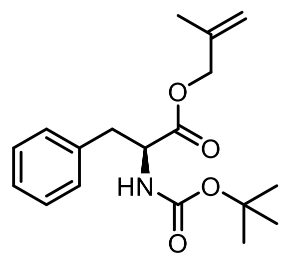
Prepared according to the representative procedure (3.8 mmol scale, 34% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.64 Hz, 1H), 8.39 (br s, 1H), 7.48 (dt, *J* = 7.78, 1.99 Hz, 1H), 7.22 (dd, *J* = 7.84, 4.81 Hz, 1H), 5.86 (m, 1H), 5.30 (m, 2H), 5.06 (br s, 1H), 4.62 (m, 3H), 3.17 (dd, *J* = 14.0, 5.72 Hz, 1H), 3.05 (dd, *J* = 14.0, 6.17 Hz, 1H), 1.41 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 155.1, 150.8, 148.6, 137.0, 131.8, 131.4, 123.5, 119.6, 80.3, 66.4, 54.3, 35.8, 28.4.

IR (film) 3350, 3217, 2977, 2933, 1743, 1712, 1649, 1577, 1519, 1481, 1446, 1425, 1367, 1276, 1253, 1168, 1054, 1027, 991, 935, 750, 713 cm^{-1}.

HRMS: Calc'd $C_{16}H_{23}N_2O_4$ $(M+H)^+$ = 307.1658, found = 307.1664.



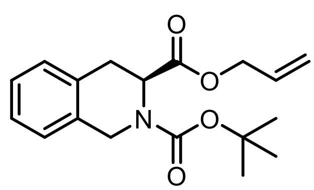
Boc-Phe-OH (5.7 mmol) was added to 20 mL DCM under Ar. The solution was cooled to 0 ^{o}C (ice bath) and β-Methallyl alcohol (7.3 mmol) and triethylamine (14 mmol) were added. After stirring for 5 mins, PyBOP (7.3 mmol) was added and the solution was allowed to warm to room temperature and stir overnight. Next, the reaction mixture was washed with water (1 x 10 mL), brine (1 x 10 mL), concentrated *in vaccuo*, and purified via flash column chromatography to provide the desired allyl ester in a 96% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.25 (m, 1H), 7.14 (d, *J* = 7.03 Hz, 2H), 4.95 (m, 3H), 4.63 (q, *J* = 6.18 Hz, 1H), 4.52 (s, 2H), 3.14 (dd, *J* = 13.8, 5.88 Hz, 1H), 3.07 (dd, *J* = 13.9, 6.28 Hz, 1H), 1.71 (s, 3H), 1.41 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 155.2, 139.4, 136.1, 129.5, 128.7, 127.2, 113.9, 80.0, 68.7, 54.6, 38.5, 28.4, 19.7.

IR (film) 3369, 3064, 3029, 2977, 2931, 1745, 1693, 1604, 1487, 1454, 1367, 1251, 1164, 1054, 1022, 960, 912, 860, 744, 700, 568 cm^{-1}.

HRMS: Calc'd $C_{18}H_{25}NO_4Na$ (M+Na)+ = 342.1681, found = 342.1670.



The free amino acid (14.1 mmol) was added to a solution of 1,4 dioxane (30 mL) and 1M NaOH (18 mL). The solution was cooled to 0^{o}C (ice bath), and Boc_2O (18.0 mmol) was added. The solution was allowed to warm to room temperature and stirred overnight. Next, the dioxane was removed *in vacuo*, the pH was adjusted to 3 with 1 M HCl and the reaction mixture extracted with EtOAc (50 mL). The organic phase was washed with brine (30 mL), dried with $MgSO_4$, and concentrated *in vacuo*. The crude product was subjected to the representative procedure to yield the desired allyl ester after flash column chromatography (58% yield over two steps) as a mixture of rotamers.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (m, 4H), 5.76 (dddd, *J* = 18.0, 12.9, 6.31, 3.70 Hz, 1H), 5.14 (m, 2.5H), 4.81 (t, *J* = 5.40 Hz, 0.5H), 4.70 (dd, *J* = 16.3, 9.82 Hz, 1H), 4.51 (m, 3H), 3.27 (dd, *J* = 15.8, 3.11 Hz, 0.5H), 3.18 (m, 1.5H), 1.53 (s, 4.5H), 1.45 (s, 4.5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5 (br s), 155.3 (br s), 134.1, 133.0, 132.1(br s), 131.8 (br s), 128.3 (br s), 127.0 (br s), 126.8 (br s), 126.4 (br s), 118.2 (br s), 80.7, 65.7 (br s), 53.6 (br s), 44.5 (br s), 31.6 (br s), 28.5 (br s).

IR (film) 3336, 2975, 2931, 1737, 1697, 1456, 1392, 1367, 1357, 1332, 1251, 1220, 1164, 1122, 997, 923, 757 cm^{-1}.

HRMS: Calc'd $C_{18}H_{23}NO_4Na$ $(M+Na)^+$ = 340.1525, found = 340.1517.

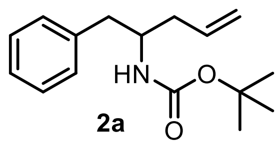
3. General Experimental Procedures

For conversion of allylic esters to homoallylic amines: An oven dried 16 x 125 mm threaded glass tube charged with a stirbar was taken into the glovebox. $Pd(PPh_3)_4$ and $[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$ (5.0 and 1.0 mol %, respectively) were added to the vial. If the starting material was a solid, 0.25 mmol was added at this time. 2.0 mL DMSO was added to the vial which was then capped and removed from the glovebox. If the starting material was a liquid, it was added via syringe at this time. The reaction was placed in a room temperature blue LED light bath (photo 1, S-2) and analyzed by GC/MS. The crude reaction mixture was directly loaded onto a silica gel column and purified using EtOAc/Hexanes as the eluant.

For conversion of carboxylic acids to homoallylic amines: An oven dried 16 x 125 mm threaded glass tube charged with a stirbar was taken into the glovebox. $Pd(PPh_3)_4$ and $[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$ (5.0 and 1.0 mol %, respectively) were added to the vial followed by the carboxylic acid (0.25 mmol), and 2.0 mL DMSO. The vial was capped, removed from the glovebox, and 0.25 mmol of allyl methyl carbonate was added via syringe. The reaction was placed in a room temperature blue LED light bath (photo 1, S-2) and analyzed by GC/MS. The crude reaction mixture was directly loaded onto a silica gel column and purified using EtOAc/Hexanes as the eluant.

4. Characterization of Allylated Products

The products **1a** – **1i** have been previously described by our group.[2]



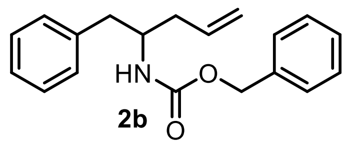
2a

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.21 (m, 3H), 5.80 (ddt, *J* = 17.3, 10.5, 7.04 Hz, 1H), 5.10 (m, 2H), 4.40 (s, 1H), 3.91 (s, 1H), 2.78 (m, 2H), 2.26 (m, 1H), 2.11 (m, 1H), 1.41 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5, 138.3, 134.6, 129.6, 128.5, 126.5, 118.1, 79.3, 51.2, 40.6, 38.2, 28.5.

IR (film) 3348, 3076, 2977, 2927, 1697, 1641, 1523, 1496, 1454, 1438, 1388, 1363, 1272, 1251, 1230, 1172, 1045, 1024, 910, 856, 742, 698 cm^{-1}.

HRMS: Calc'd $C_{16}H_{23}NO_2Na$ $(M+Na)^+$ = 284.1626, found = 284.1616.



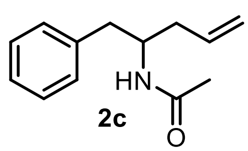
2b

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 7H), 7.19 (m, 3H), 5.79 (ddt, *J* = 17.3, 10.4, 7.04 Hz, 1H), 5.09 (m, 4H), 4.63 (d, *J* = 8.34 Hz, 1H), 3.99 (m, 1H), 2.81 (m, 2H), 2.29 (dt, *J* = 12.7, 6.09 Hz, 1H), 2.14 (dt, *J* = 14.2, 7.13 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 137.9, 136.7, 134.3, 129.6, 128.6, 128.5, 128.2, 128.1, 126.6, 118.4, 66.7, 51.7, 40.5, 38.2.

IR (film) 3325, 3062, 3029, 2943, 1697, 1531, 1514, 1454, 1440, 1342, 1257, 1222, 1041, 1027, 993, 914, 746, 698 cm^{-1}.

HRMS: Calc'd $C_{19}H_{21}NO_2Na$ $(M+Na)^+$ = 318.1470, found = 318.1469.



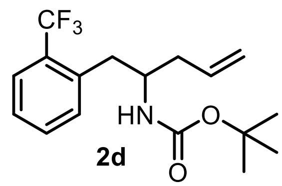
2c

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.20 (m, 3H), 5.79 (ddt, *J* = 17.3, 10.3, 7.07 Hz, 1H), 5.30 (d, *J* = 7.47 Hz, 1H), 5.10 (m, 2H), 4.26 (m, 1H), 2.79 (dd, *J* = 14.0, 6.27 Hz, 2H), 2.28 (m, 1H), 2.13 (m, 1H), 1.92 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 137.9, 134.5, 129.5, 128.6, 126.6, 118.2, 49.6, 40.1, 37.9, 23.6.

IR (film) 3274, 3076, 2927, 1645, 1556, 1496, 1438, 1373, 1298, 991, 748, 700 cm^{-1}.

HRMS: Calc'd $C_{13}H_{17}NONa$ $(M+Na)^+$ = 226.1208, found = 226.1187.



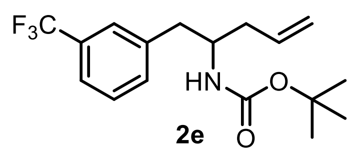
2d

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.83 Hz, 1H), 7.46 (m, 2H), 7.30 (m, 1H), 5.81 (ddt, *J* = 17.7, 9.66, 7.10 Hz, 1H), 5.12 (m, 2H), 4.42 (d, *J* = 9.23 Hz, 1H), 4.00 (m, 1H), 2.96 (m, 2H), 2.28 (m, 2H), 1.33 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4, 137.5, 134.3, 131.8, 131.6, 129.0 (q, *J* = 29.7 Hz), 126.5, 126.0 (q, *J* = 6.32 Hz), 124.8 (q, *J* = 274 Hz), 118.3, 79.3, 51.3, 39.6, 37.4, 28.4.

IR (film) 3363, 2981, 2931, 1681, 1606, 1523, 1454, 1367, 1307, 1271, 1251, 1163, 1107, 1049, 914, 767 cm^{-1}.

HRMS: Calc'd $C_{17}H_{22}F_3NO_2Na$ $(M+Na)^+$ = 352.1500, found = 352.1505.



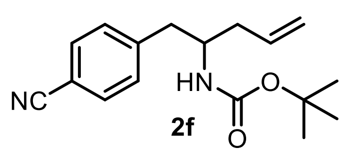
2e

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (m, 1H), 7.41 (m, 3H), 5.79 (ddt, *J* = 17.3, 10.3, 7.05 Hz, 1H), 5.11 (m, 2H), 4.39 (m, 1H), 3.91 (m, 1H), 2.85 (d, *J* = 6.65 Hz, 2H), 2.26 (m, 1H), 2.13 (m, 1H), 1.39 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4, 139.3, 134.2, 133.0, 130.7 (q, *J* = 30.9 Hz), 128.9, 126.3, 124.4 (q, *J* = 272 Hz), 123.4 (q, *J* = 3.65 Hz), 118.5, 79.5, 51.1, 40.4, 38.3, 28.4.

IR (film) 3363, 2979, 2935, 1681, 1523, 1446, 1392, 1367, 1332, 1159, 1116, 1074, 918, 800, 750, 703 cm^{-1}.

HRMS: Calc'd $C_{17}H_{22}F_3NO_2Na$ $(M+Na)^+$ = 352.1500, found = 352.1470.



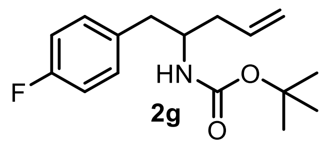
2f

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (m, 2H), 7.31 (d, *J* = 8.07 Hz, 2H), 5.77 (ddt, *J* = 17.2, 10.3, 7.04 Hz, 1H), 5.13 (m, 2H), 4.38 (d, *J* = 8.68 Hz, 1H), 3.91 (m, 1H), 2.84 (d, *J* = 6.74 Hz, 2H), 2.25 (m, 1H), 2.14 (m, 1H), 1.38 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3, 144.2, 133.9, 132.3, 130.3, 119.1, 118.7, 110.4, 79.6, 51.0, 41.0, 38.5, 28.5.

IR (film) 3363, 2979, 2962, 2929, 2225, 1681, 1645, 1608, 1523, 1461, 1442, 1390, 1367, 1350, 1272, 1251, 1174, 1049, 1029, 919, 842, 823, 750, 655, 567 cm^{-1}.

HRMS: Calc'd $C_{17}H_{22}N_2O_2Na$ $(M+Na)^+$ = 309.1579, found = 309.1585.



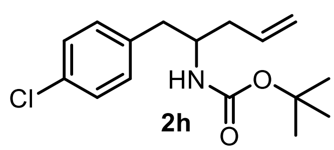
2g

^1H NMR (500 MHz, $CDCl_3$) δ 7.14 (m, 2H), 6.97 (m, 2H), 5.78 (ddt, *J* = 17.3, 10.4, 7.07 Hz, 1H), 5.10 (m, 2H), 4.37 (s, 1H), 3.86 (s, 1H), 2.73 (m, 2H), 2.24 (m, 1H), 2.10 (m, 1H), 1.40 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6 (d, *J* = 244 Hz), 155.4, 134.4, 134.0 (d, *J* = 3.03 Hz), 130.9 (d, *J* = 7.65 Hz), 118.2, 115.3 (d, *J* = 21.1 Hz), 79.4, 51.2, 39.9, 38.2, 28.5.

IR (film) 3342, 2979, 2929, 1687, 1600, 1504, 1454, 1365, 1271, 1253, 1218, 1172, 1045, 914, 831, 750 cm^{-1}.

HRMS: Calc'd $C_{16}H_{22}FNO_2Na$ $(M+Na)^+$ = 302.1532, found = 302.1546.



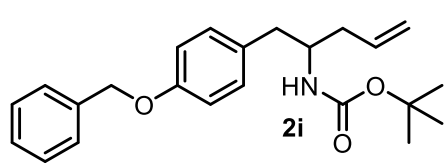
2h

^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 2H), 7.13 (d, *J* =8.26 Hz, 2H), 5.79 (ddt, *J* = 17.2, 10.3, 7.06 Hz, 1H), 5.11 (m, 2H), 4.38 (s, 1H), 3.88 (s, 1H), 2.76 (m, 2H), 2.25 (m, 1H), 2.11 (m, 1H), 1.41 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4, 136.8, 134.3, 132.3, 130.9, 128.6, 118.3, 79.4, 51.1, 40.0, 38.2, 28.5.

IR (film) 3344, 2977, 2929, 1687, 1643, 1519, 1492, 1444, 1390, 1365, 1269, 1251, 1170, 1091, 1043, 1016, 667 cm^{-1}.

HRMS: Calc'd $C_{16}H_{22}ClNO_2Na$ $(M+Na)^+$ = 318.1237, found = 318.1220.



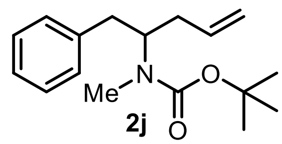
2i

^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.39 (ddd, *J* = 7.65, 6.80, 1.29 Hz, 2H), 7.33 (m, 1H), 7.11 (d, *J* = 8.35 Hz, 2H), 6.91 (m, 2H), 5.79 (ddt, *J* = 17.5, 10.5, 7.02 Hz, 1H), 5.09 (m, 2H), 5.04 (s, 2H), 4.39 (s, 1H), 3.87 (s, 1H), 2.72 (m, 2H), 2.45 (m, 1H), 2.10 (m, 1H), 1.41 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6, 155.5, 137.2, 134.6, 130.6, 128.7, 128.1, 127.6, 118.0, 114.9, 79.2, 70.2, 51.3, 39.7, 38.1, 28.5.

IR (film) 3365, 2977, 2929, 1687, 1610, 1510, 1454, 1390, 1365, 1242, 1170, 1024, 914, 742, 696, 667 cm^{-1}.

HRMS: Calc'd $C_{23}H_{29}NO_3Na$ $(M+Na)^+$ = 390.2045, found = 390.2039.



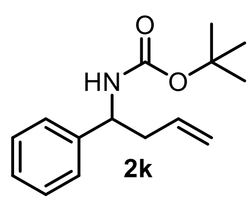
2j

A mixture of rotamers.
^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 2H), 7.17 (m, 3H), 5.73 (br m, 1H), 5.06 (br m, 2H), 4.47 (br m, 0.4H), 4.29 (br m, 0.6H) 2.77 (d, *J* = 7.76 Hz, 1H), 2.71 (t, *J* = 3.39 Hz, 3H), 2.62 (s, 1H), 2.27 (br m, 2H), 1.36 (s, 4H), 1.28 (s, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 139.0 (br s), 135.2 (br s), 129.1 (br s), 128.4 (br s), 126.3 (br s), 116.9 (br s), 79.2 (br s), 56.5 (br s), 38.9 (br s), 36.9 (br s), 29.5 (br s), 28.4 (br s).

IR (film) 3028, 2975, 2927, 1693, 1643, 1479, 1454, 1392, 1365, 1298, 1253, 1224, 1172, 1143, 991, 914, 873, 769, 746, 700 cm^{-1}.

HRMS: Calc'd $C_{17}H_{25}NO_2Na$ $(M+Na)^+$ = 298.1783, found = 298.1772.



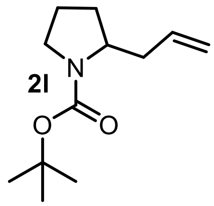
2k

^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (m, 2H), 7.26 (m, 3H), 5.68 (ddt, *J* = 17.2, 10.2, 7.05 Hz, 1H), 5.09 (m, 2H), 4.87 (s, 1H), 4.74 (s, 1H), 2.52 (m, 2H), 1.42 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3, 142.5, 134.1, 128.6, 127.3, 126.4, 118.3, 79.6, 54.1, 41.4, 28.5.

IR (film) 3338, 3064, 2977, 2931, 1693, 1519, 1494, 1454, 1367, 1251, 1170, 1018, 916, 756, 700 cm^{-1}.

HRMS: Calc'd $C_{15}H_{21}NO_2Na$ $(M+Na)^+$ = 270.1470, found = 270.1468.



2l

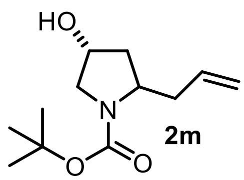
A mixture of rotamers.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (br m, 1H), 5.04 (m, 2H), 3.80 (br m, 1H), 3.35 (br m, 2H), 2.45 (br m, 1H), 2.11 (br m, 1H), 1.80 (br m, 4H), 1.46 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7, 135.4, 117.1, 79.1 (br s), 56.9, 46.6 (br s), 38.8 (br s), 29.8 (br s), 28.70, 23.4(br s).

IR (film) 3076, 2974, 2875, 1693, 1641, 1479, 1454, 1392, 1365, 1253, 1172, 1108, 995, 914, 771 cm^{-1}.

HRMS: Calc'd $C_{12}H_{21}NO_2Na$ $(M+Na)^+$ = 234.1470, found = 234.1452.



2m

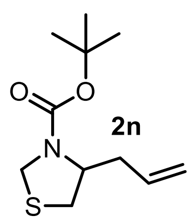
A mixture of diastereomers and rotamers.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (br m, 1H), 5.07 (br m, 2H), 4.38 (br m, 1H), 3.43 (br m, 3H), 2.34 (br m, 2H), 2.09 (br m, 2H), 1.84 (br m, 1H), 1.46 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$, major resonances reported) δ 154.6, 135.4, 117.6, 79.6, 70.1 (br s), 56.6, 55.4 (br s), 39.4 (br s), 38.2 (br s), 28.6.

IR (film) 3419, 2975, 2931, 1693, 1668, 1407, 1365, 1255, 1166, 1118, 1080, 914, 765 cm^{-1}.

HRMS: Calc'd $C_{12}H_{21}NO_3Na$ $(M+Na)^+$ = 250.1419, found = 250.1411.



2n

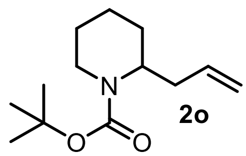
A mixture of rotamers.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (ddt, J = 17.1, 10.1, 7.01 Hz, 1H), 5.09 (m, 2H), 4.62 (br s, 1H), 4.22 (br m, 2H), 3.07 (m, 1H), 2.80 (dd, J = 11.2, 2.53 Hz, 1H), 2.46 (br s, 1H), 2.33 (m, 1H), 1.47 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 134.7, 118.0, 80.6, 59.2, 48.0 (br s), 37.7 (br s), 34.6 (br s), 28.5.

IR (film) 3367, 2977, 2931, 1735, 1693, 1384, 1369, 1330, 1255, 1151, 1041, 918, 852, 767, 667 cm $^{-1}$.

HRMS: [M – isobutylene + H]$^+$ = 174.0589, found = 174.0581. GC/MS: [M]$^+$ = 229.1, found = 229.2.



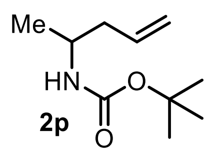
2o

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (ddt, *J* = 17.2, 10.1, 7.15 Hz, 1H), 5.01 (m, 2H), 4.27 (s, 1H), 3.96 (d, *J* = 12.3 Hz, 1H), 2.75 (m, 1H), 2.39 (m, 1H), 2.22 (dt, *J* = 14.1, 7.19 Hz, 1H), 1.57 (m, 5H), 1.44 (s, 9H), 1.39 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 115.2, 135.8, 116.7, 79.2, 50.2, 39.0, 34.6, 28.6, 27.8, 25.6, 19.0.

IR (film) 3076, 2975, 2933, 2858, 1693, 1643, 1446, 1409, 1365, 1319, 1267, 1170, 1147, 1068, 1033, 995, 912, 869, 806, 767 cm^{-1}.

HRMS: Calc'd $C_{13}H_{23}NO_2Na$ (M+Na)$^+$ = 248.1626, found = 248.1615.



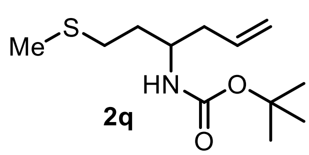
2p

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 (m, 1H), 5.08 (m, 2H), 4.38 (s, 1H), 3.73 (m, 1H), 2.19 (m, 2H), 1.43 (s, 9H), 1.12 (d, *J* = 6.63 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4, 134.6, 117.8, 79.2, 46.0, 41.4, 28.6, 20.7.

IR (film) 3338, 3078, 2977, 2931, 1693, 1643, 1519, 1454, 1390, 1365, 1251, 1174, 1056, 993, 914, 781, 634 cm^{-1}.

HRMS: Calc'd $C_{10}H_{19}NO_2Na$ (M+Na)$^+$ = 208.1313, found = 208.1293.



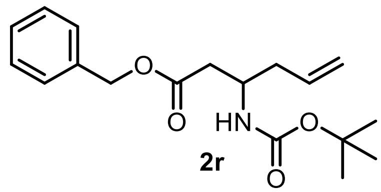
2q

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (ddt, *J* = 17.6, 9.55, 7.13 Hz, 1H), 5.09 (m, 2H), 4.39 (d, *J* = 9.23 Hz, 1H), 3.74 (m, 1H), 2.52 (m, 2H), 2.23 (m, 2H), 2.10 (s, 3H), 1.79 (m, 1H), 1.63 (m, 1H), 1.43 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 134.2, 118.2, 79.3, 49.7, 39.7, 34.6, 30.9, 28.5, 15.8.

IR (film) 3336, 3076, 2977, 2918, 1693, 1641, 1519, 1442, 1390, 1365, 1290, 1251, 1170, 1049, 1020, 993, 914, 856, 779, 748, 649 cm^{-1}.

HRMS: Calc'd $C_{12}H_{23}NO_2SNa$ $(M+Na)^+$ = 268.1347, found = 268.1338.



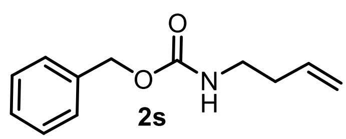
2r

^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 5H), 5.74 (ddt, *J* = 17.4, 10.5, 7.15 Hz, 1H), 5.08 (m, 4H), 4.95 (m, 1H), 4.01 (m, 1H), 2.58 (d, *J* = 5.73 Hz, 2H), 2.29 (m, 2H), 1.42 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 155.3, 135.8, 134.1, 128.8, 128.5, 128.4, 118.4, 79.5, 66.6, 47.3, 38.9, 38.5, 28.5.

IR (film) 3359, 3066, 2977, 1714, 1697, 1643, 1504, 1456, 1390, 1365, 1249, 1170, 1047, 1026, 993, 918, 750, 698 cm^{-1}.

HRMS: Calc'd $C_{18}H_{25}NO_4Na$ $(M+Na)^+$ = 342.1681, found = 342.1674.

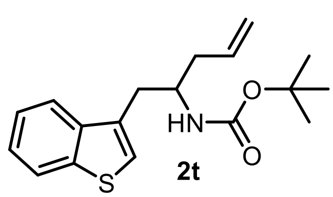


2s

^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 5H), 5.75 (ddt, *J* = 17.2, 10.4, 6.82 Hz, 1H), 5.09 (m, 4H), 4.79 (s, 1H), 3.28 (q, *J* = 6.48 Hz, 2H), 2.27 (q, *J* = 6.92 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 136.7, 135.2, 128.6, 128.3, 128.2, 117.5, 66.8, 40.2, 34.2.
IR (film) 3330, 3074, 3031, 2935, 1697, 1641, 1523, 1454, 1253, 1217, 1134, 1026, 914, 748, 695 cm^{-1}.

HRMS: Calc'd $C_{12}H_{15}NO_2Na$ $(M+Na)^+$ = 228.1000, found = 228.0989.



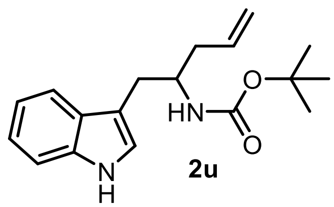
2t

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (m, 2H), 7.38 (m, 2H), 7.17 (s, 1H), 5.82 (ddt, *J* = 17.3, 10.4, 7.02 Hz, 1H), 5.12 (m, 2H), 4.48 (d, *J* = 8.89 Hz, 1H), 4.08 (m, 1H), 3.10 (m, 1H), 3.00 (dd, *J* = 14.3, 6.99 Hz, 1H), 2.32 (m, 1H), 2.18 (m, 1H), 1.43 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5, 140.4, 139.3, 134.4, 132.9, 124.4, 124.2, 123.3, 122.9, 122.2, 118.3, 79.4, 49.8, 38.5, 33.6, 28.5.

IR (film) 3425, 3340, 3074, 2975, 2929, 1697, 1641, 1502, 1458, 1429, 1390, 1365, 1251, 1168, 1047, 1020, 914, 852, 759, 732 cm^{-1}.

HRMS: Calc'd $C_{18}H_{23}NO_2SNa$ (M+Na) = 340.1347, found 340.1330.



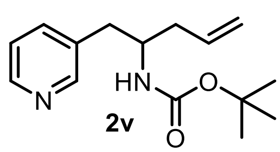
2u

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.65 (d, *J* = 7.92 Hz, 1H), 7.36 (dt, *J* = 8.16, 0.96 Hz, 1H), 7.20 (ddd, *J* = 8.14, 6.97, 1.20 Hz, 1H), 7.13 (ddd, *J* = 8.04, 7.03, 1.06 Hz, 1H), 7.03 (s, 1H), 5.83 (m, 1H), 5.09 (m, 2H), 4.48 (s, 1H), 4.02 (m, 1H), 2.95 (m, 2H), 2.32 (m, 1H), 2.15 (m, 1H), 1.43 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 136.3, 134.9, 128.1, 122.8, 122.1, 119.6, 119.3, 117.8, 112.3, 111.1, 79.2, 50.5, 38.6, 30.1, 28.6.

IR (film) 3411, 3325, 3056, 2975, 2929, 1693, 1641, 1504, 1438, 1392, 1365, 1249, 1168, 1099, 1060, 1010, 914, 742 cm^{-1}.

HRMS: Calc'd $C_{18}H_{24}N_2O_2Na$ $(M+Na)^+$ = 323.1735, found = 323.1725.



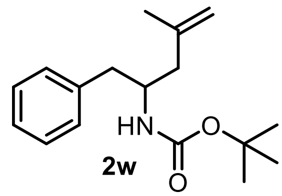
2v

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 4.89, 1.67 Hz, 1H), 8.43 (s, 1H), 7.54 (m, 1H), 7.22 (dd, *J* = 7.63, 4.92 Hz, 1H), 5.78 (ddt, *J* = 17.2, 10.3, 7.05 Hz, 1H), 5.12 (m, 2H), 4.42 (m, 1H), 3.90 (m, 1H), 2.80 (m, 2H), 2.25 (m, 1H), 2.13 (m, 1H), 1.38 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4, 150.8, 148.0, 137.0, 134.0, 133.8, 123.4, 118.5, 79.5, 50.9, 38.4, 37.8, 28.5.

IR (film) 3336, 3240, 2977, 2929, 1693, 1519, 1440, 1425, 1390, 1365, 1249, 1170, 1045, 1027, 914, 844, 715 cm^{-1}.

HRMS: Calc'd $C_{15}H_{23}N_2O_2$ (M+H)$^+$ = 263.1760, found = 263.1764.



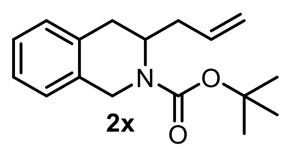
2w

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.21 (m, 3H), 4.81 (s, 1H), 4.73 (s, 1H), 4.32 (s, 1H), 3.99 (s, 1H), 2.79 (m, 2H), 2.18 (dd, *J* = 14.3, 5.57 Hz, 1H), 2.06 (dd, *J* = 14.2, 8.97 Hz, 1H), 1.72 (s, 3H), 1.40 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.5, 142.6, 138.3, 129.7, 128.4, 126.4, 113.3, 79.2, 49.6, 42.8, 41.1, 28.5, 22.2.

IR (film) 3350, 3072, 3028, 2975, 2929, 1701, 1496, 1454, 1390, 1365, 1247, 1170, 1049, 1016, 889, 746, 700, 667 cm^{-1}.

HRMS: Calc'd $C_{17}H_{25}NO_2Na$ (M+Na)$^+$ = 298.1783, found = 298.1786.



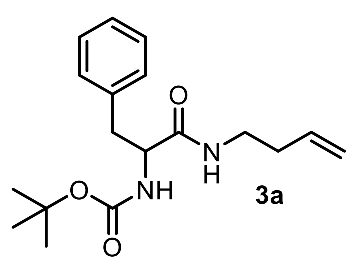
2x

A mixture of rotamers.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (m, 2H), 7.11 (m, 2H), 5.78 (m, 1H), 5.00 (m, 2H), 4.48 (br m, 1H), 4.54 (br m, 1H), 4.26 (s, 0.5H), 4.23 (s, 0.5H), 3.03 (dd, *J* = 15.9, 5.93 Hz, 1H), 2.69 (d, *J* = 15.3 Hz, 1H), 2.24 (m, 1H), 2.06 (m, 1H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1, 135.2 (br s), 133.2 (br s), 132.9 (br s), 129.4 (br s), 126.7, 126.3 (br s), 117.3 (br s), 79.9, 49.2 (br s), 42.9 (br s), 36.7 (br s), 32.6 (br s), 28.6.

IR (film) 3350, 2975, 2931, 1697, 1456, 1392, 1367, 1245, 1168, 1124, 1010, 993, 914, 862, 753, 648 cm^{-1}.

HRMS: Calc'd $C_{17}H_{23}NO_2Na$ (M+Na)$^+$ = 296.1626, found = 296.1620.



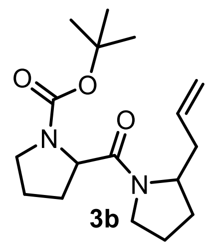
3a

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (tt, *J* = 6.98, 1.11 Hz, 2H), 7.24 (m, 1H), 7.20 (m, 2H), 5.72 (br s, 1H), 5.61 (ddt, *J* = 17.1, 10.6, 6.89 Hz, 1H), 5.08 (br s, 1H), 4.97 (m, 2H), 4.26 (q, *J* = 7.51 Hz, 1H), 3.22 (m, 2H), 3.04 (m, 2H), 2.09 (m, 2H), 1.41 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 155.5, 137.0, 135.0, 129.4, 128.8, 127.0, 117.4, 80.2, 56.2, 38.9, 38.4, 33.5, 28.4.

IR (film) 3415, 2256, 2129, 1650, 1519, 1496, 1454, 1365, 1249, 1170, 1049, 1026, 1000, 825, 763, 700, 632 cm^{-1}.

HRMS: Calc'd $C_{18}H_{26}N_2O_3Na$ $(M+Na)^+$ = 341.1841, found = 341.1835.



3b

A mixture of diastereomers and rotamers.

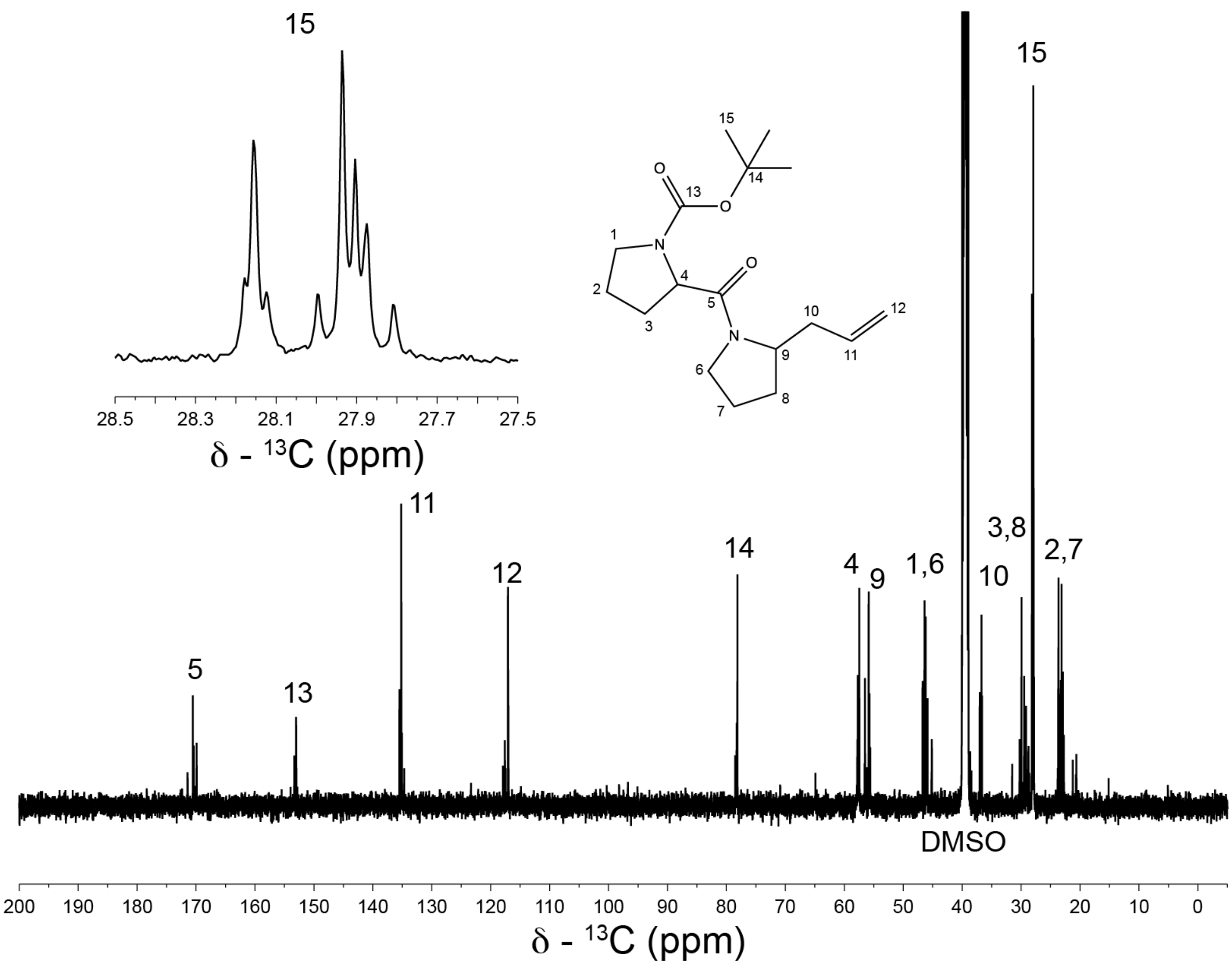
^{1}H NMR (500 MHz, DMSO-d_6) δ 5.86 – 5.68 (m, 1H), 5.18 – 4.98 (m, 2H), 4.43 – 4.29 (m, 1H), 4.09 – 3.79 (m, 1H), 3.60 – 3.22 (m, 4H), 2.47 – 2.29 (m, 1H), 2.29 – 1.95 (m, 2H), 1.94 – 1.61 (m, 7H), 1.48 – 1.22 (m, 9H).

In the 1D 13C spectrum of **3b**, there are 8 peaks for each carbon, corresponding to 2 diastereomers and 4 rotamers for each diastereomer (see below).

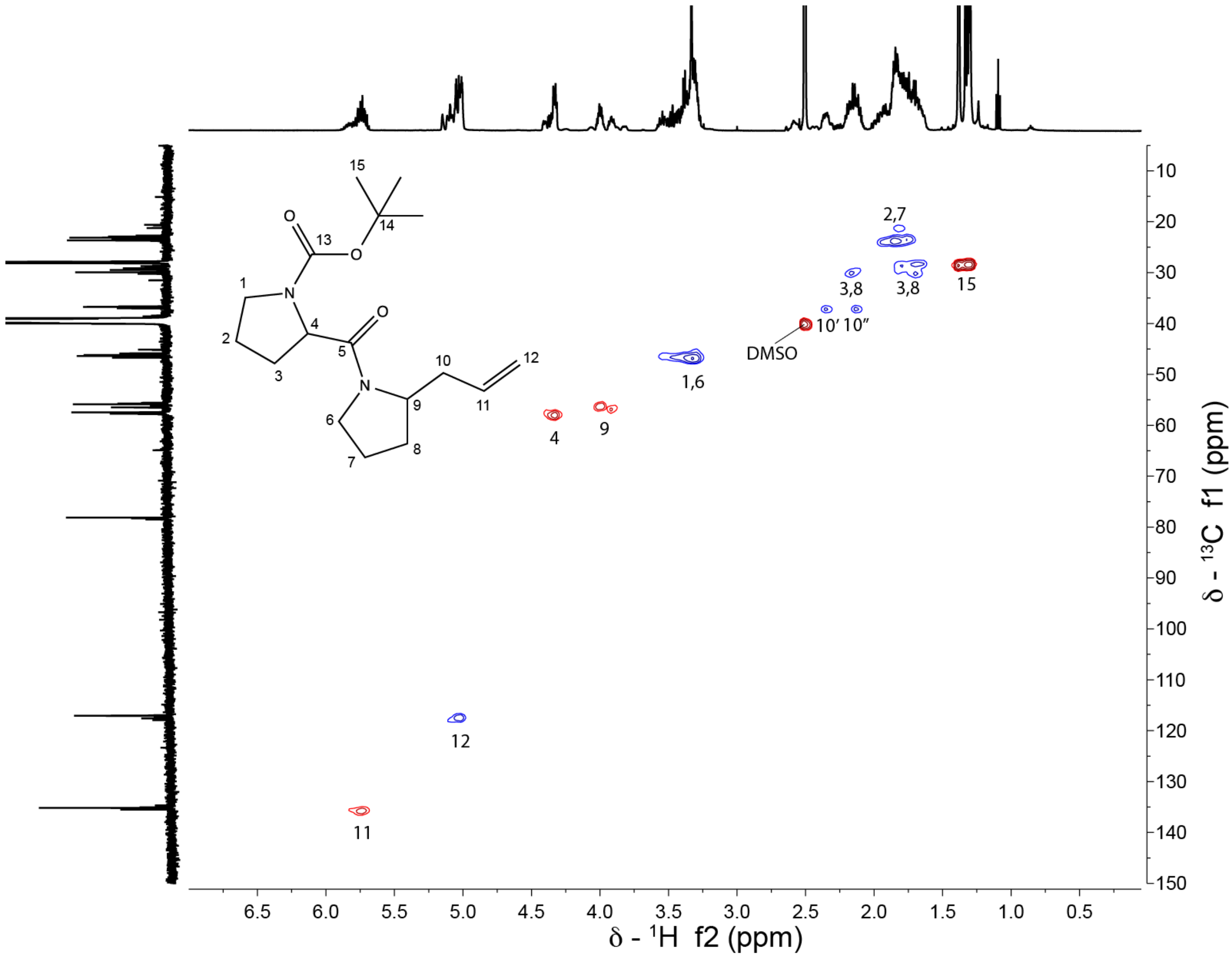
^{13}C NMR (126 MHz, DMSO-d_6) δ 171.4, 170.5, 170.4, 169.9, 153.3, 153.0, 153.0, 135.5, 135.5, 135.2, 135.1, 134.7, 117.9, 117.6, 117.5, 117.1, 117.0, 117.0, 78.5, 78.3, 78.3, 78.1, 64.9, 57.8, 57.7, 57.7, 57.6, 57.5, 57.5, 56.6, 56.5, 56.2, 55.9, 55.7, 55.7, 55.6, 46.7, 46.6, 46.5, 46.4, 46.4, 46.2, 46.1, 46.1, 46.0, 45.9, 45.2, 45.1, 40.1, 40.0, 39.9, 39.8, 39.7, 39.6, 39.6, 39.5, 39.4, 39.3, 39.1, 39.0, 38.6, 38.4, 37.0, 36.7, 36.6, 31.5, 30.3, 29.9, 29.5, 29.4, 29.1, 29.0, 28.7, 28.6, 28.2, 28.2, 28.1, 28.0, 27.9, 27.9, 27.9, 27.8, 23.8, 23.7, 23.7, 23.6, 23.6, 23.4, 23.3, 23.2, 23.1, 22.9, 22.7, 21.2, 20.7, 20.6, 15.1.

IR (film) 3456, 2974, 2875, 1693, 1645, 1427, 1398, 1259, 1163, 1120, 1085, 997, 912, 748 cm^{-1}.

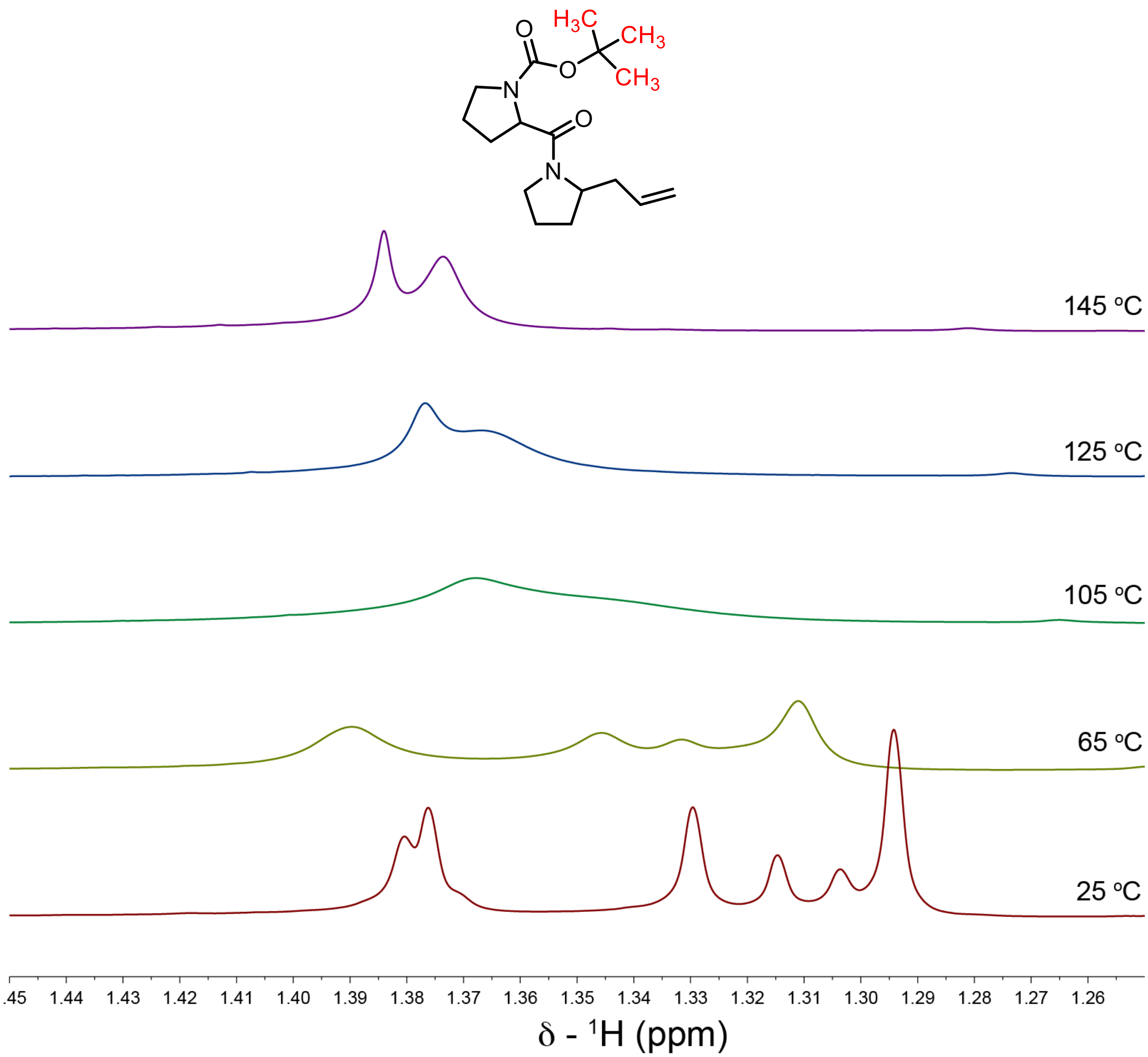
HRMS: Calc'd $C_{17}H_{29}N_2O_3$ $(M+H)^+$ = 309.2178, found = 309.2163.

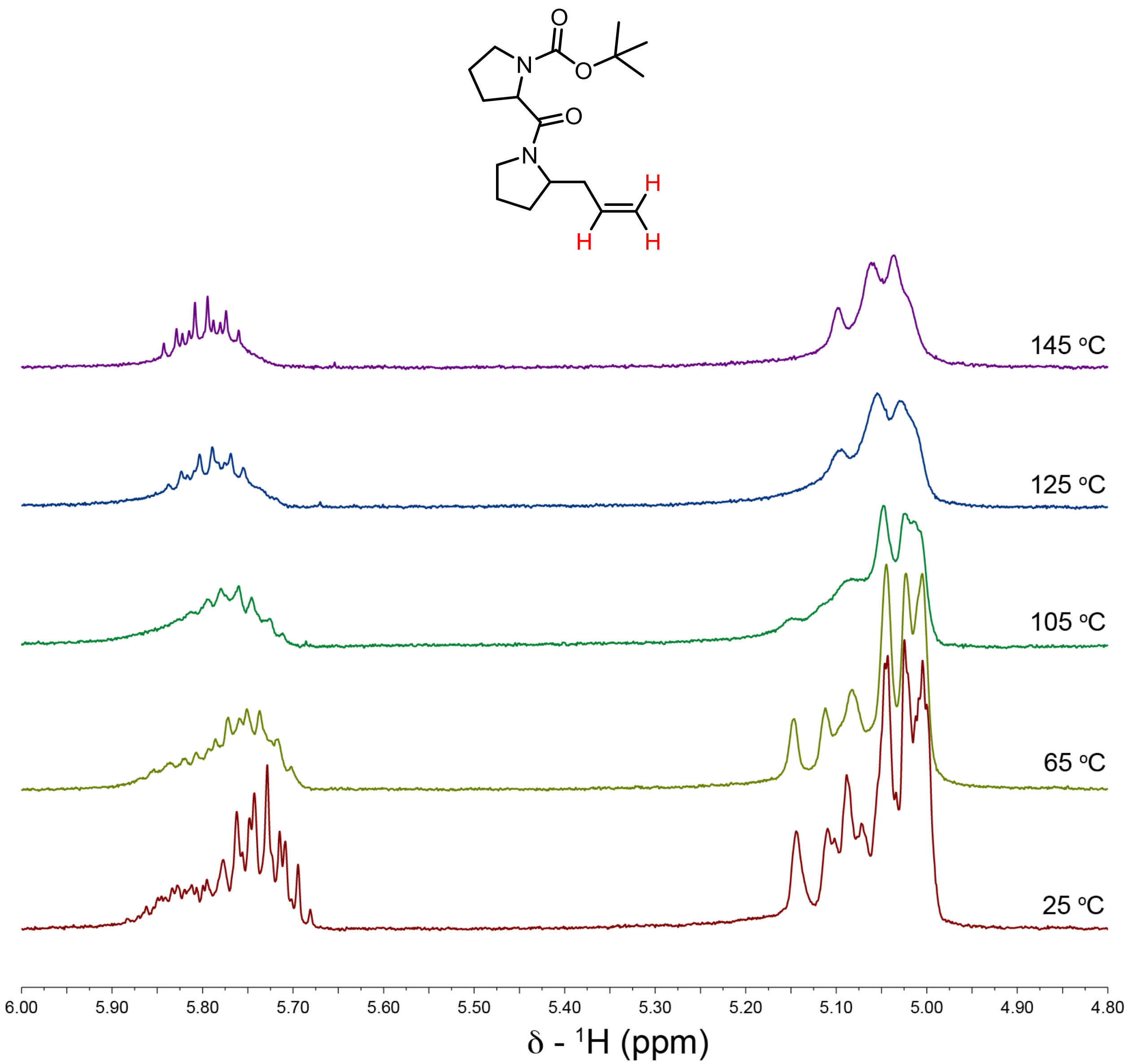


To assign this spectrum, we used a combination of 1D and 2D homo- and heteronuclear NMR (see 2D ^{1}H-^{13}C HSQC spectrum below).

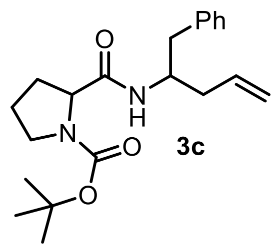

15
O
13
14
O
1
N
4
O
2
5
3
10
12
N
9
11
6
8
7
2,7
3,8
3,8
15
10′ 10″
DMSO
1,6
4
9
12
11
δ - ¹H f2 (ppm)
δ - ¹³C f1 (ppm)

To confirm the presence of rotamers, variable temperature NMR was performed. At 145 °C the rotamers coalesce and only two peaks are present in 1D ^{1}H and 1D ^{13}C spectra.





O
N
O
O
N
H
H
H
145 °C
125 °C
105 °C
65 °C
25 °C
6.00
5.90
5.80
5.70
5.60
5.50
5.40
5.30
5.20
5.10
5.00
4.90
4.80
δ - 1H (ppm)



3c

Mixture of diastereomers and rotamers

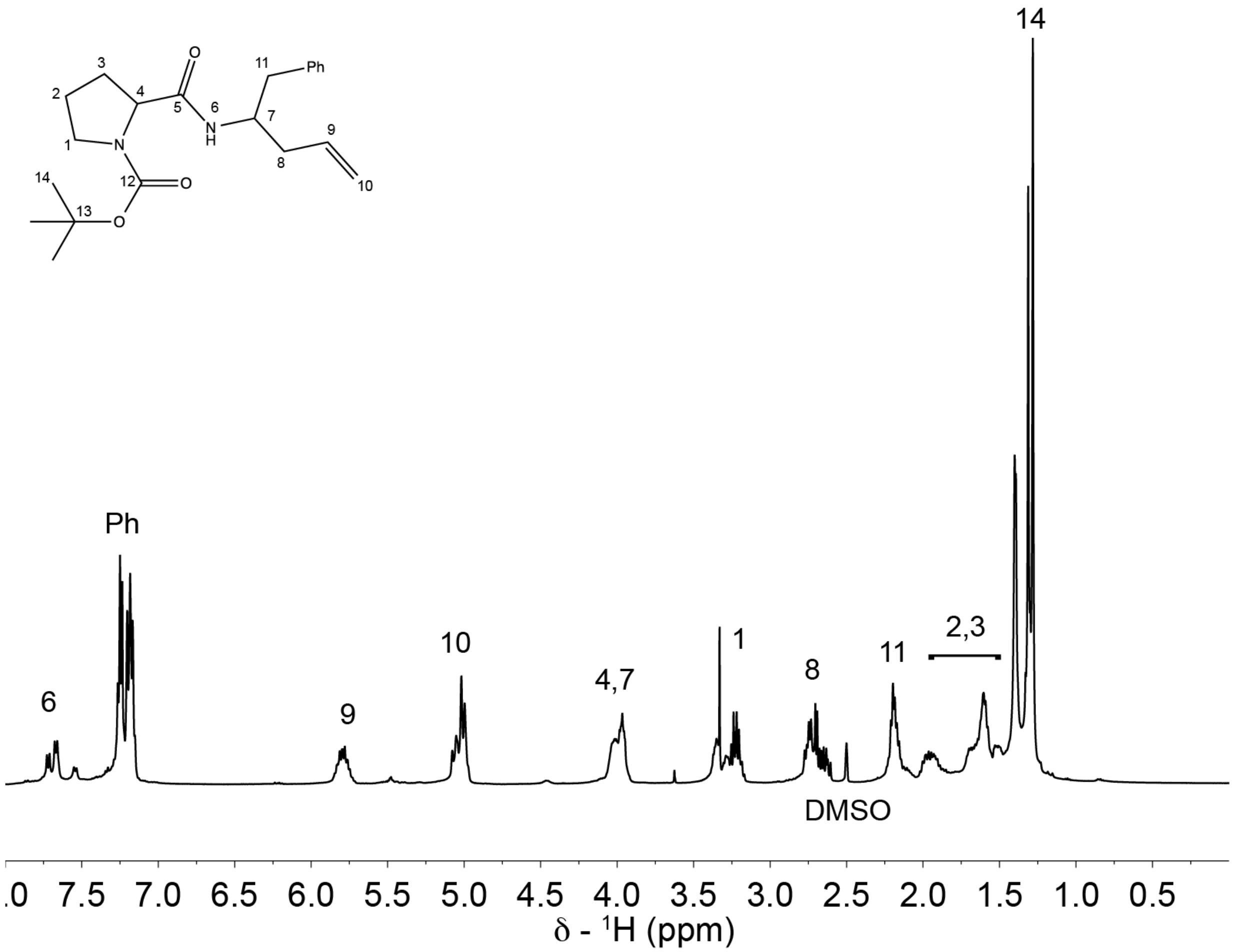
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.78 – 7.49 (m, 1H), 7.36 – 7.11 (m, 5H), 5.90 – 5.69 (m, 1H), 5.13 – 4.92 (m, 2H), 4.12 – 3.88 (m, 2H), 3.41 – 3.16 (m, 2H), 2.82 – 2.58 (m, 2H), 2.30 – 2.08 (m, 2H), 2.05 – 1.84 (m, 1H), 1.78 – 1.47 (m, 3H), 1.45 – 1.24 (m, 9H).

^{13}C NMR at 105 ^{o}C (126 MHz, DMSO-d_6) δ 172.0, 154.2, 139.4, 139.4, 135.9, 135.8, 129.5, 129.5, 128.5, 128.4, 126.4, 126.3, 117.0, 117.0, 79.6, 79.0, 78.9, 60.5, 60.3, 50.1, 50.0, 47.0, 47.0, 40.4, 40.3, 38.9, 38.6, 31.0, 28.6, 28.6, 23.6.

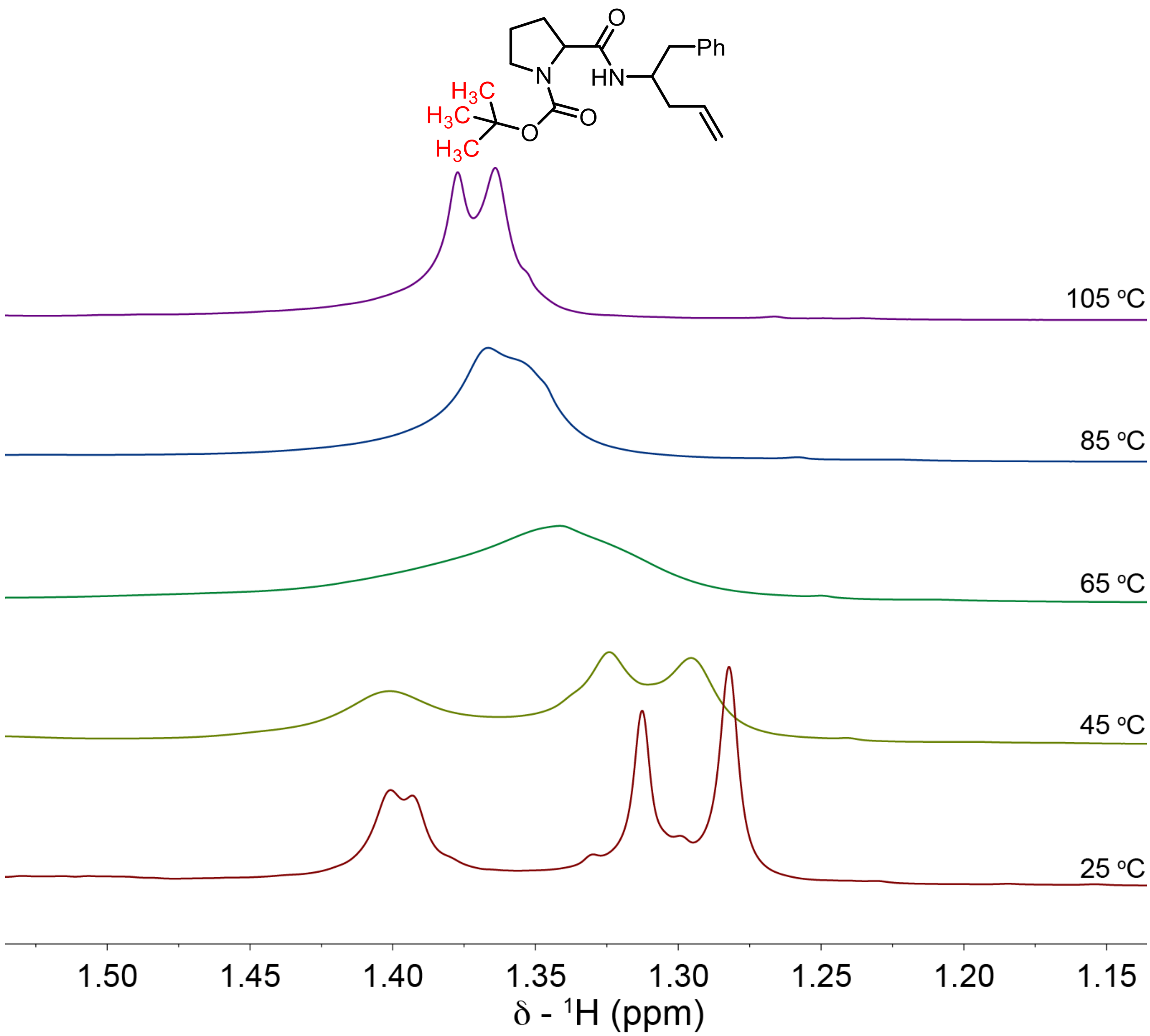
IR (film) 3303, 3074, 2975, 2877, 1697, 1660, 1552, 1454, 1392, 1365, 1257, 1163, 1122, 912, 748 cm^{-1}.

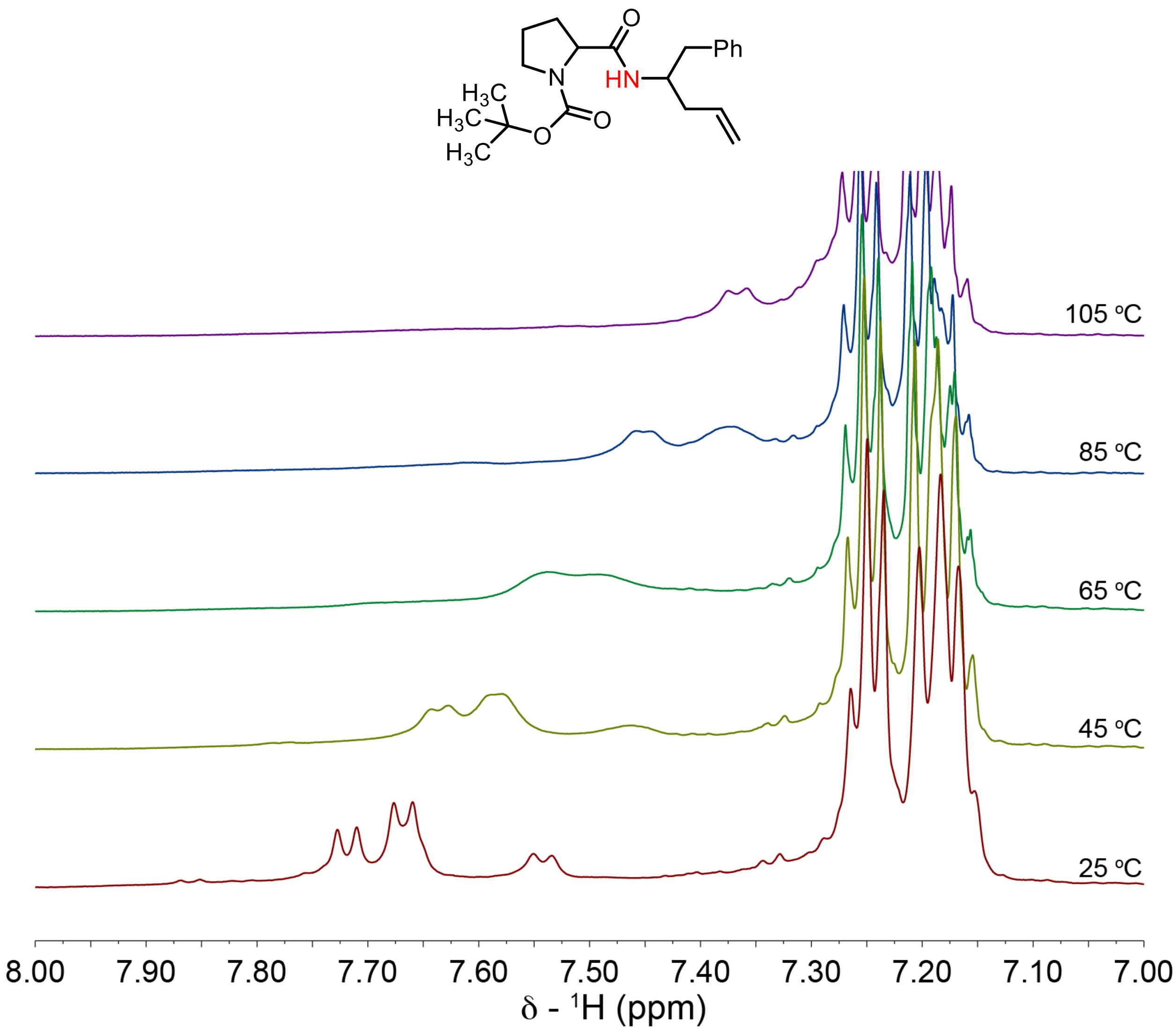
HRMS: Calc'd $C_{21}H_{30}N_2O_3Na$ $(M+Na)^+$ = 381.2154, found = 381.2149.

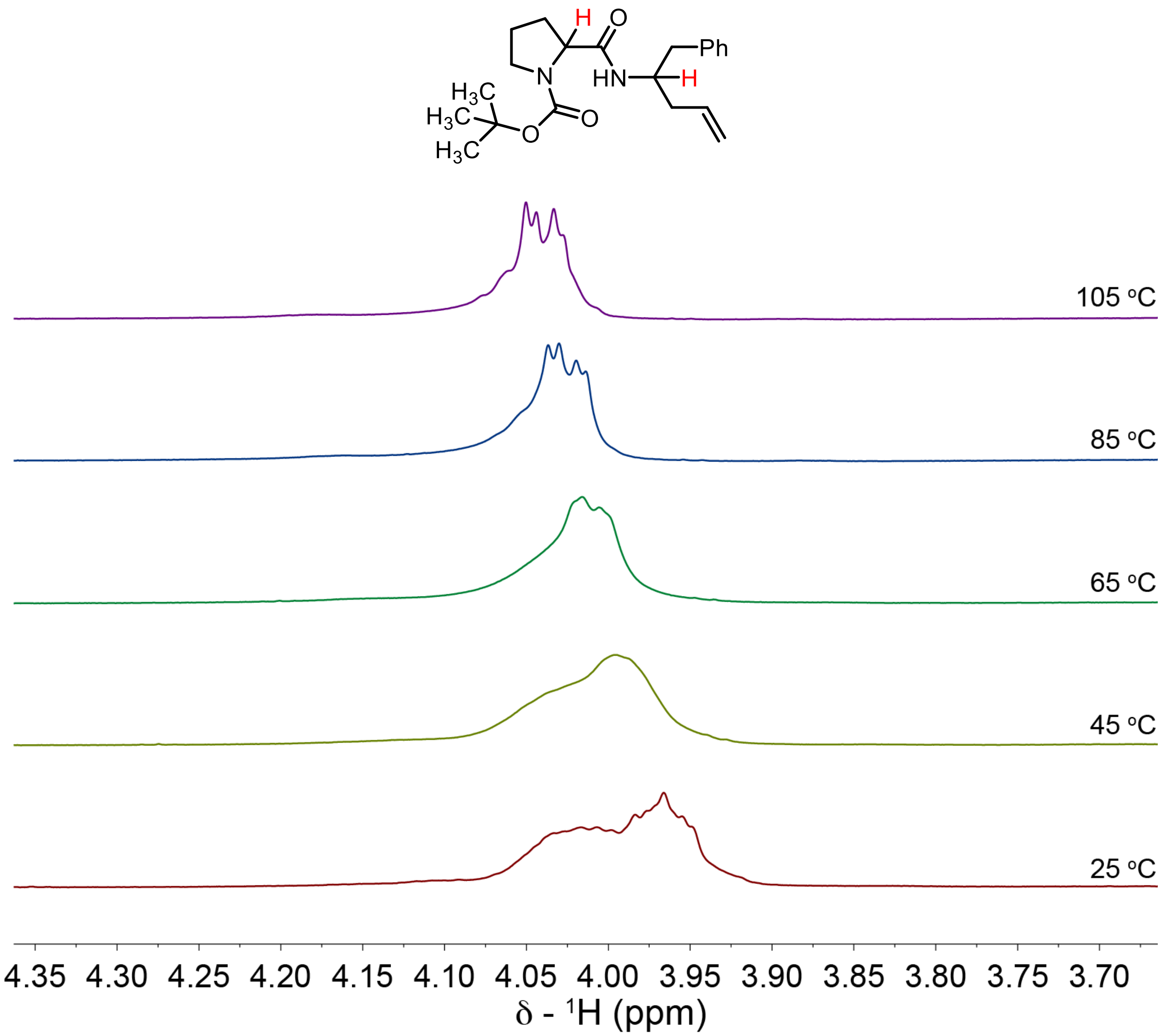
At room temperature the 1D 1H of **3c** includes a mixture of diastereomers and rotamers. Upon raising the temperature to 105 °C, these peaks coalesce into discernable signals in the 1D 1H and 1D 13C spectra (see below)



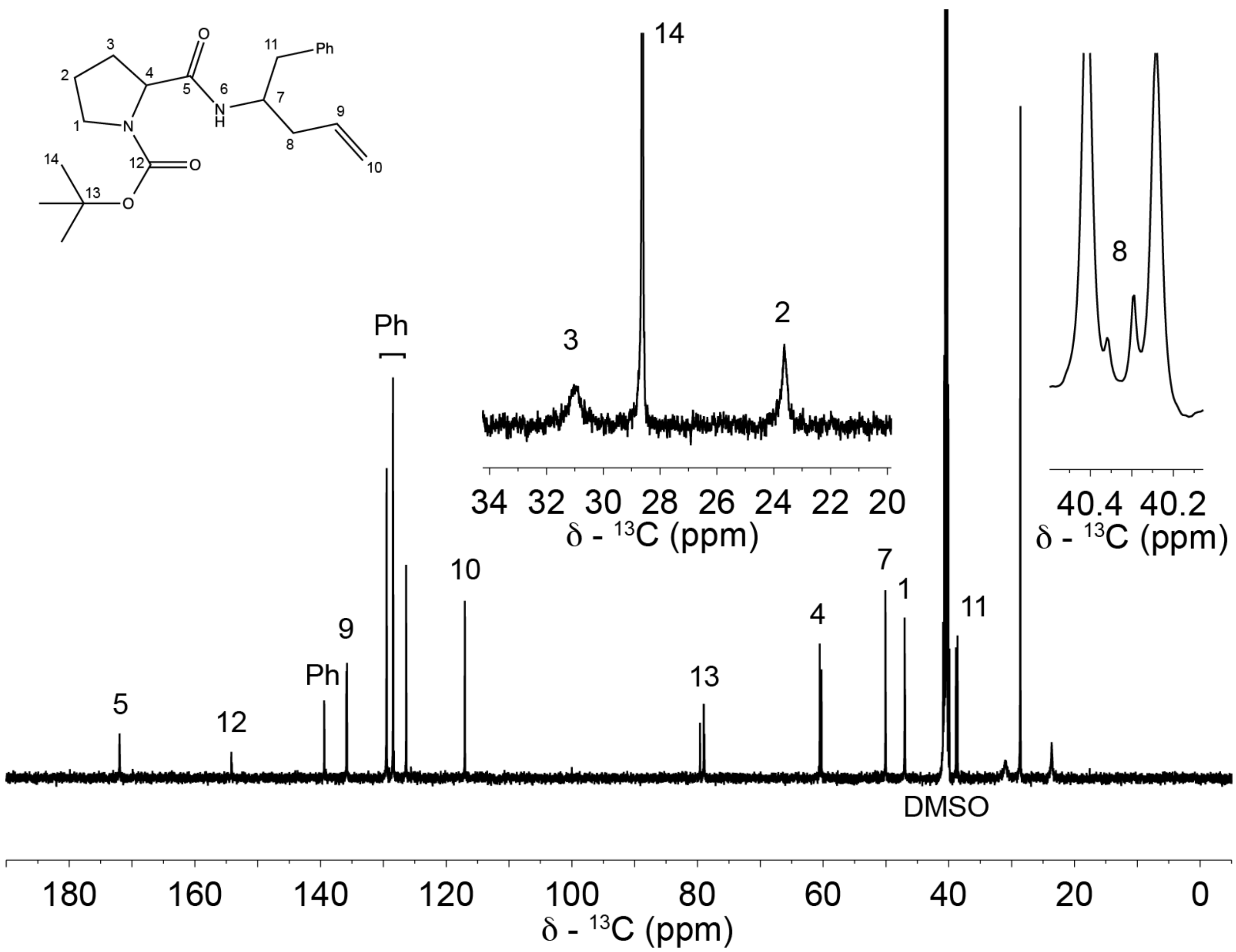
Room Temperature 1D 1H


H3C
H3C
H3C
O
N
O
HN
O
Ph
105 ºC
85 ºC
65 ºC
45 ºC
25 ºC
1.50
1.45
1.40
1.35
1.30
1.25
1.20
1.15
δ - 1H (ppm)


O
Ph
HN
N
H_3C
H_3C
O
O
H_3C
105 °C
85 °C
65 °C
45 °C
25 °C
8.00 7.90 7.80 7.70 7.60 7.50 7.40 7.30 7.20 7.10 7.00
δ - ¹H (ppm)



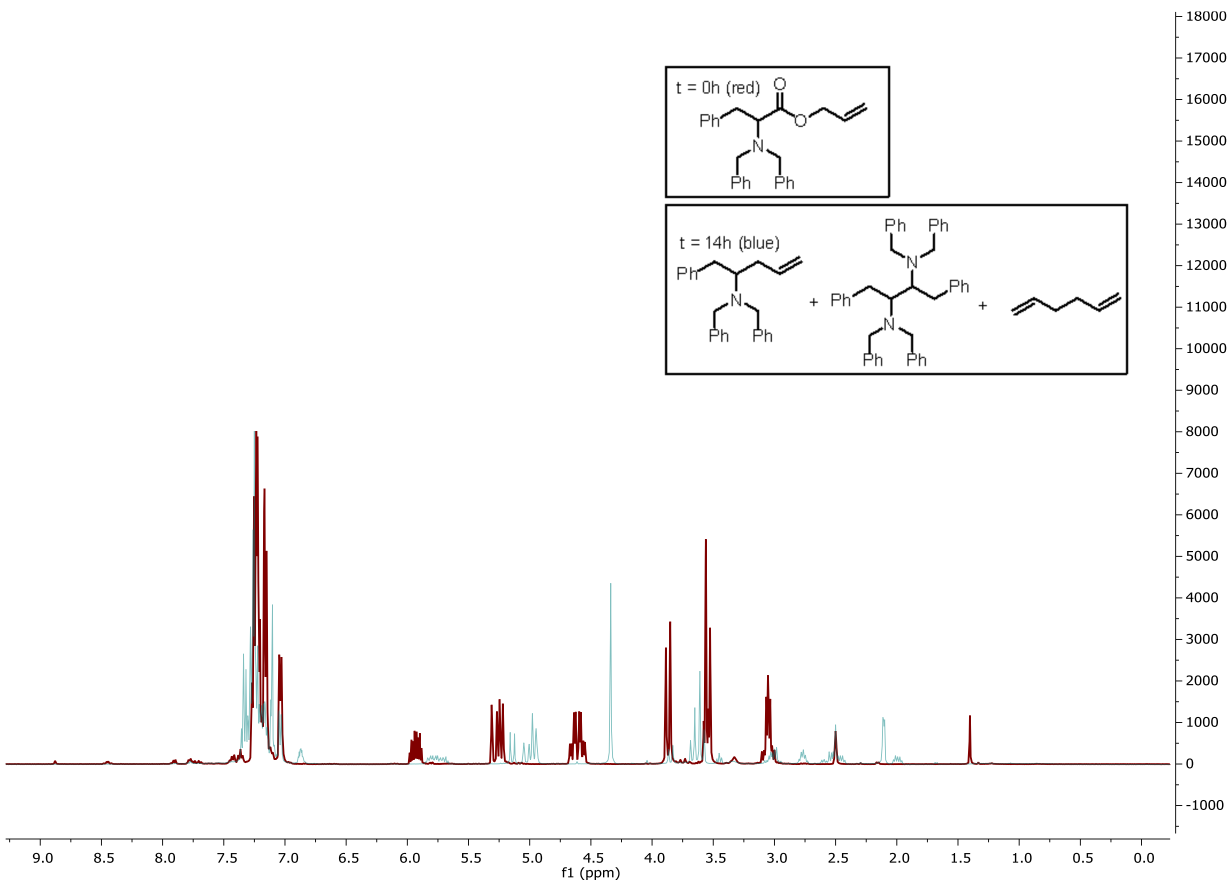
H
O
Ph
N
HN
H
H3C
H3C
H3C
O
O
105 °C
85 °C
65 °C
45 °C
25 °C
4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 3.80 3.75 3.70
δ - 1H (ppm)

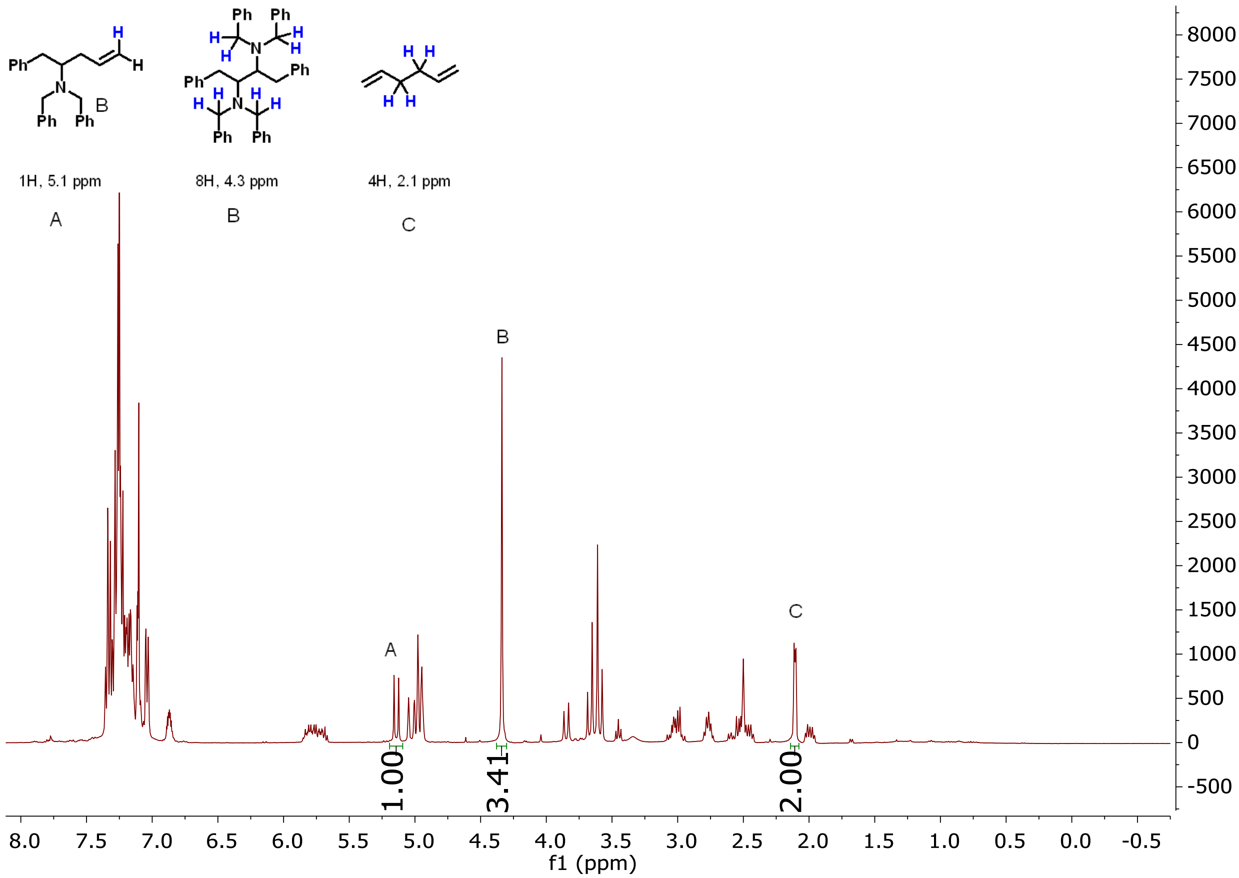


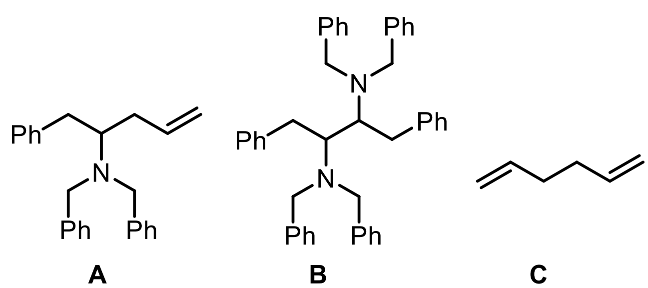
1D 13C at 105 °C

5. ^{1}H NMR Spectroscopy Experiments

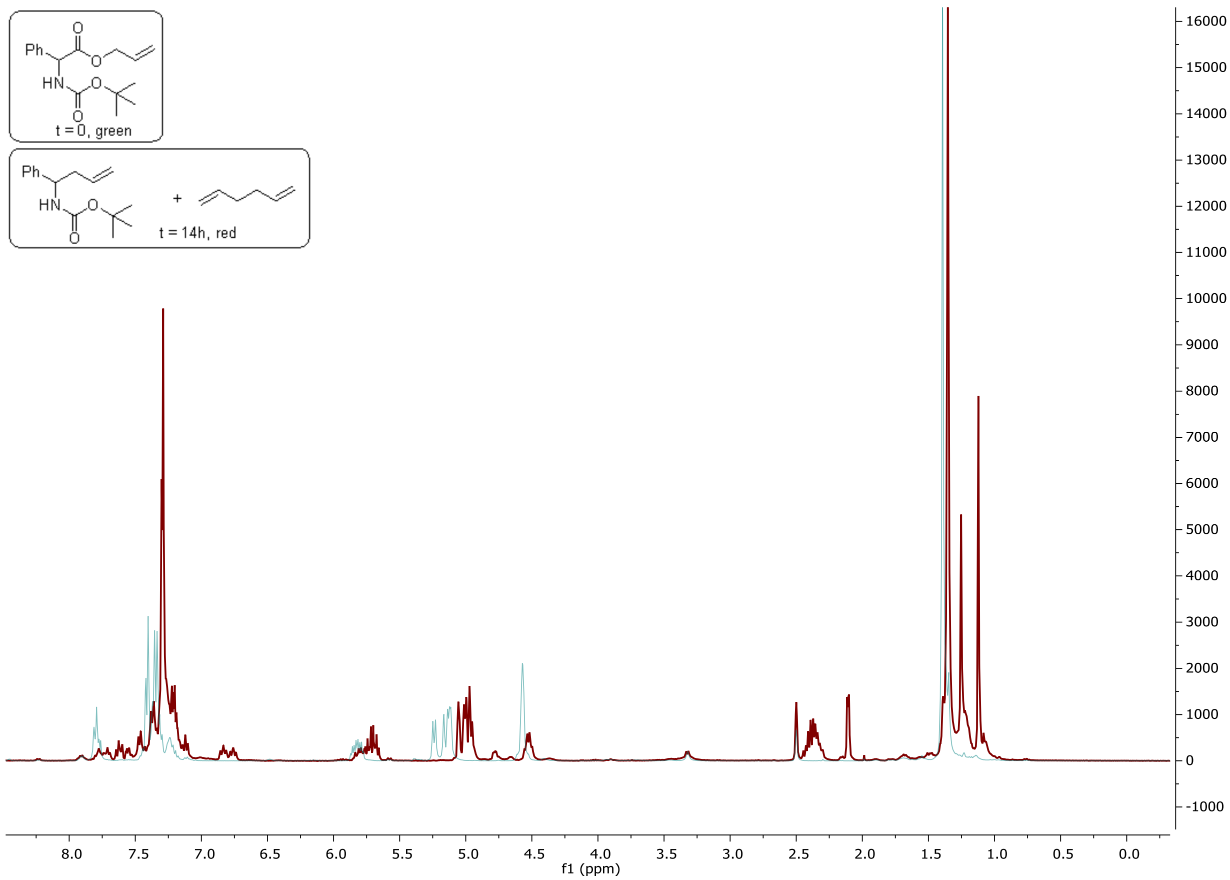
General Procedure: An oven dried 16 x 125 mm threaded glass tube and an oven dried NMR tube were taken into a glovebox. Allyl ester (0.25 mmol), was added to the threaded glass tube followed by $Pd(PPh_3)_4$ and $[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$ (5.0 and 1.0 mol %, respectively). DMSO-d6 (2.0 mL) was added to the glass tube and the reaction mixture was gently shaken for 5 mins. After this time, approximately 0.8 mL of the reaction mixture was transferred via syringe to the NMR tube, which was then capped and removed from the glovebox. A t = 0h ^{1}H NMR spectrum was recorded and the tube was placed in a blue LED light bath at rt for 14h (photo 1). A t = 14h ^{1}H NMR spectrum was then recorded.

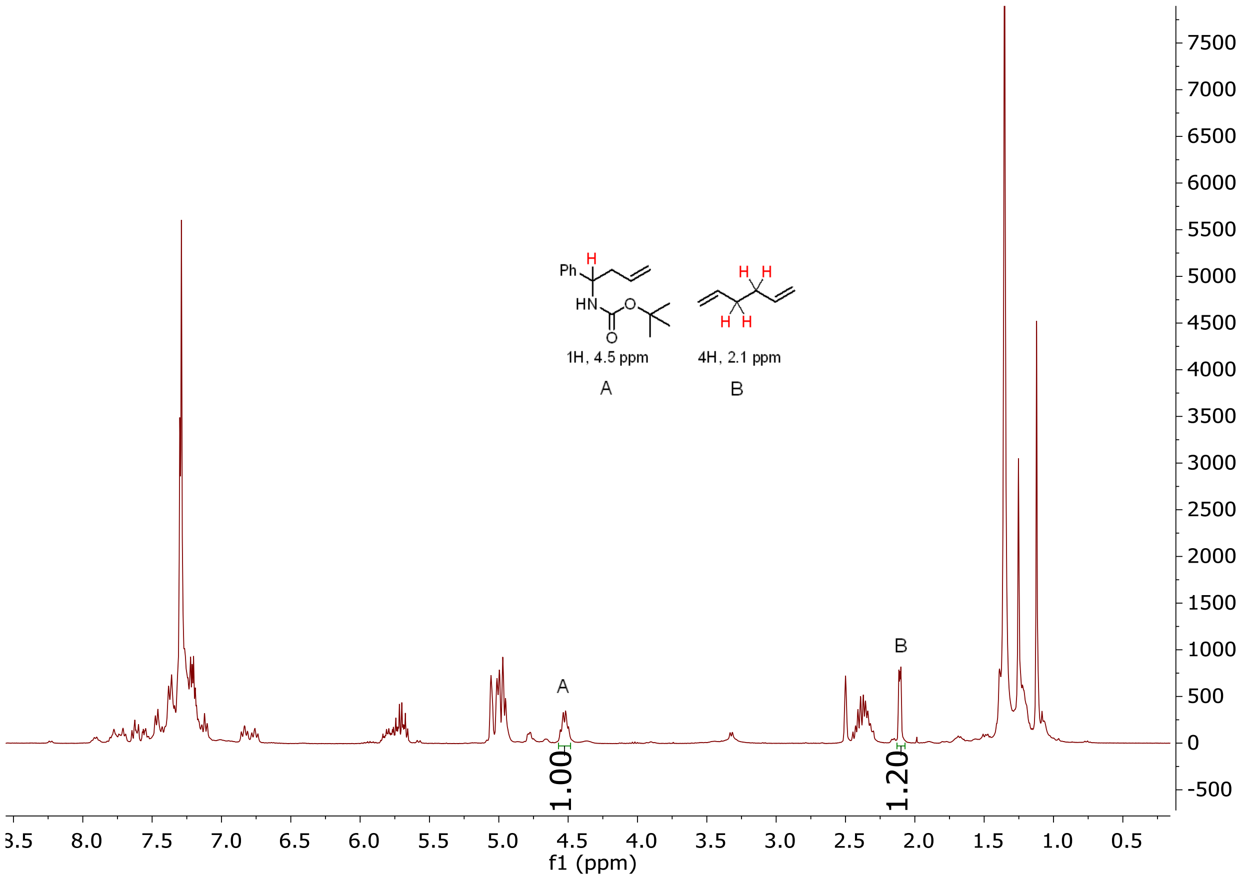


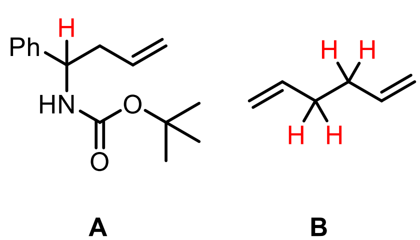




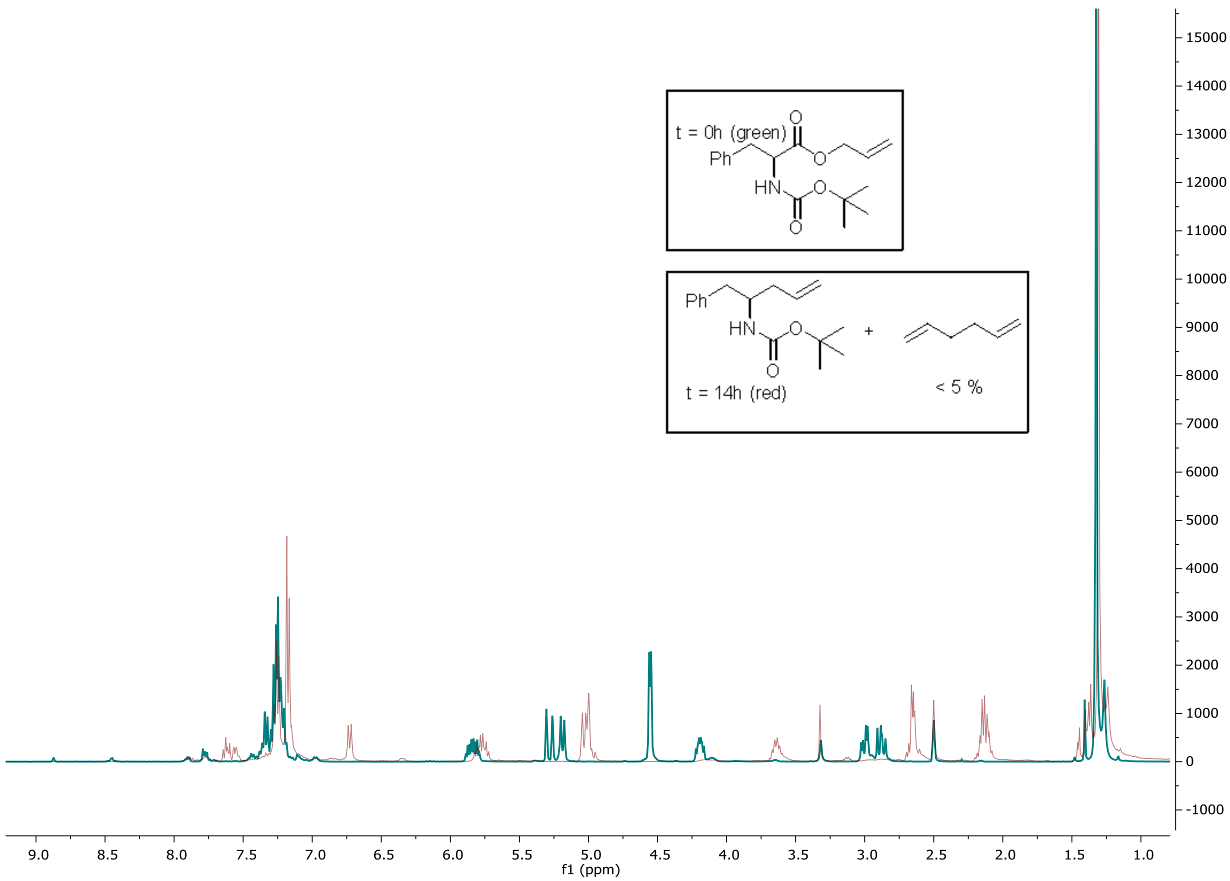
A:B:C = 1.0 : 0.43 : 0.50


Ph
HN
O
O
t = 0, green
Ph
HN
O
+
t = 14h, red
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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)

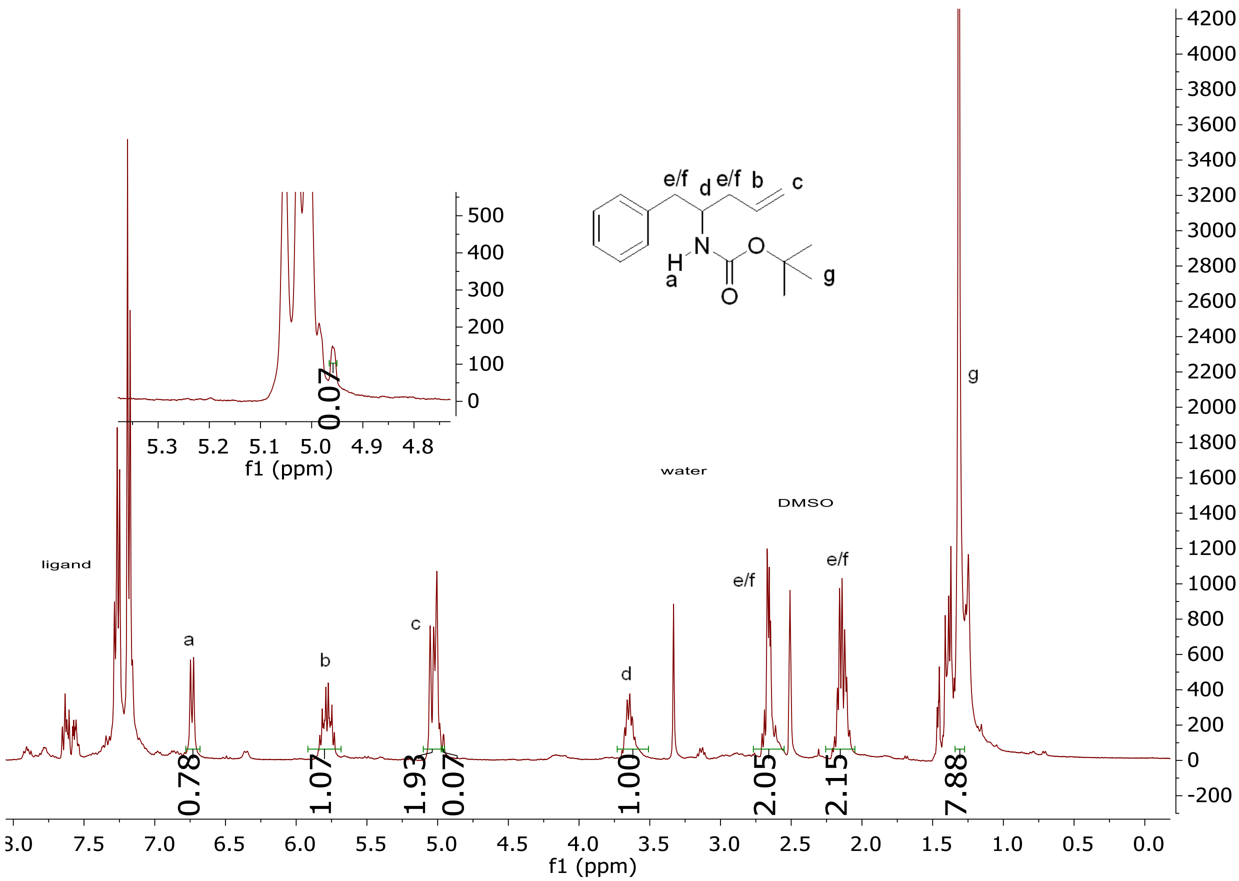




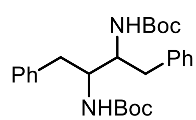
A:B = 1 : 0.30



t = 0h (green)
Ph
HN
O
t = 14h (red)
+
< 5 %
f1 (ppm)

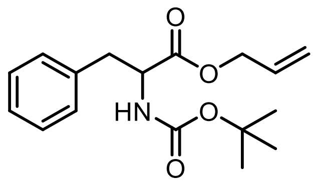


No significant amount of dibenzyl dicarbamate dimer was detected. ~ 7% 1,5 hexadiene was detected.

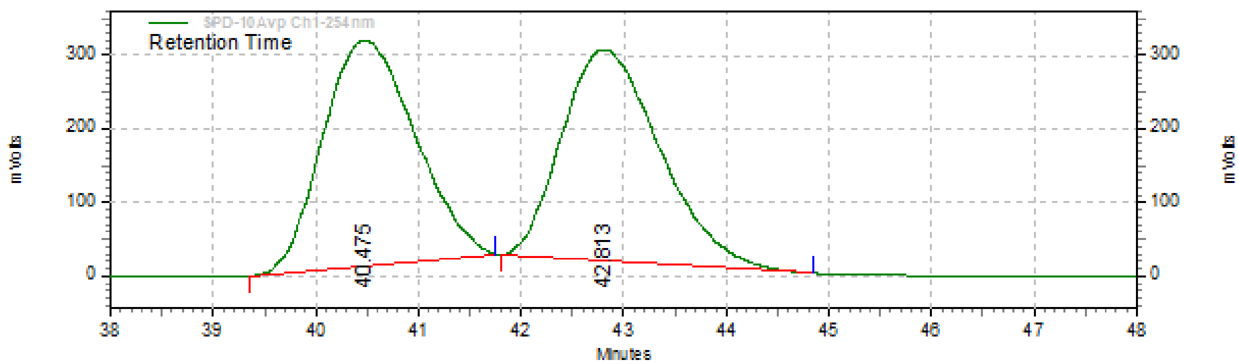


not detected

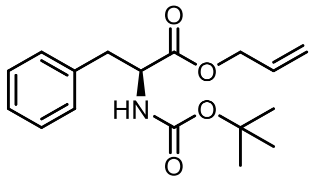
6. Chiral HPLC Analysis



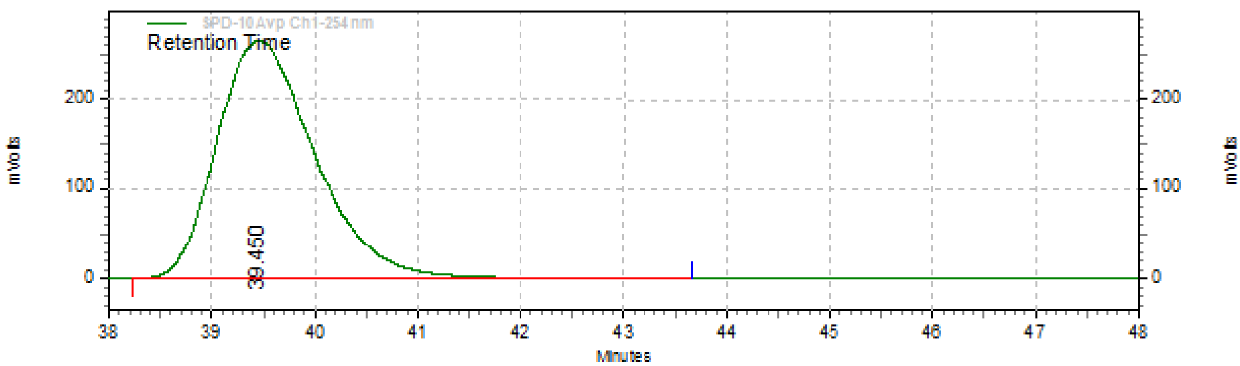
Racemic, ADH column, 30:70 ^{i}PrOH:hexanes, 0.38 mL/min



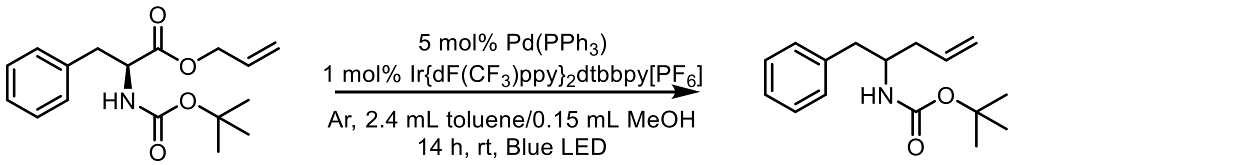
SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
40.475	19100552	50.01	306410	51.65
42.813	19095979	49.99	286811	48.35
Totals				
	38196531	100.00	593221	100.00



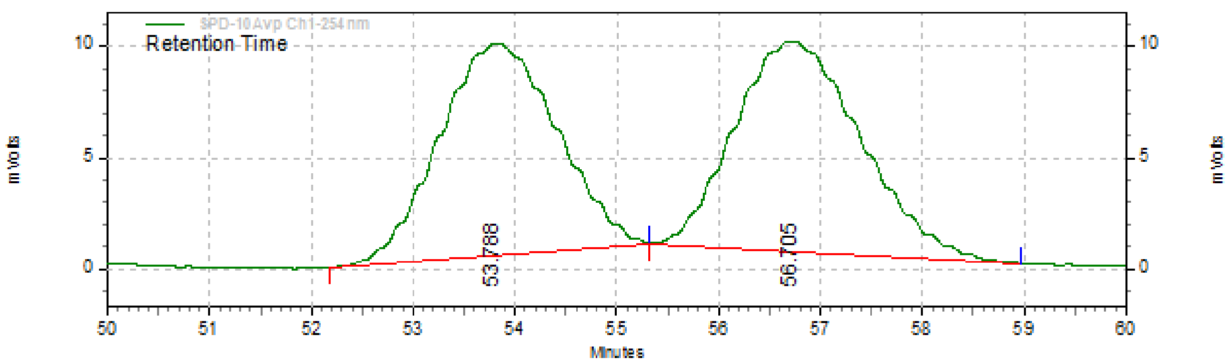
Enantioenriched, ADH column, 30:70 ^{i}PrOH:hexanes, 0.38 mL/min



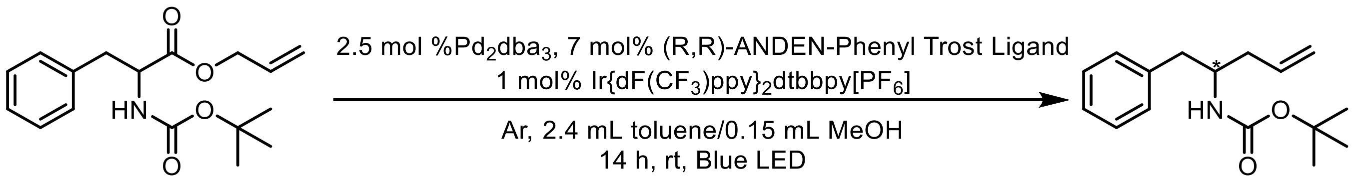
SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
39.450	17593284	100.00	265087	100.00
Totals				
	17593284	100.00	265087	100.00



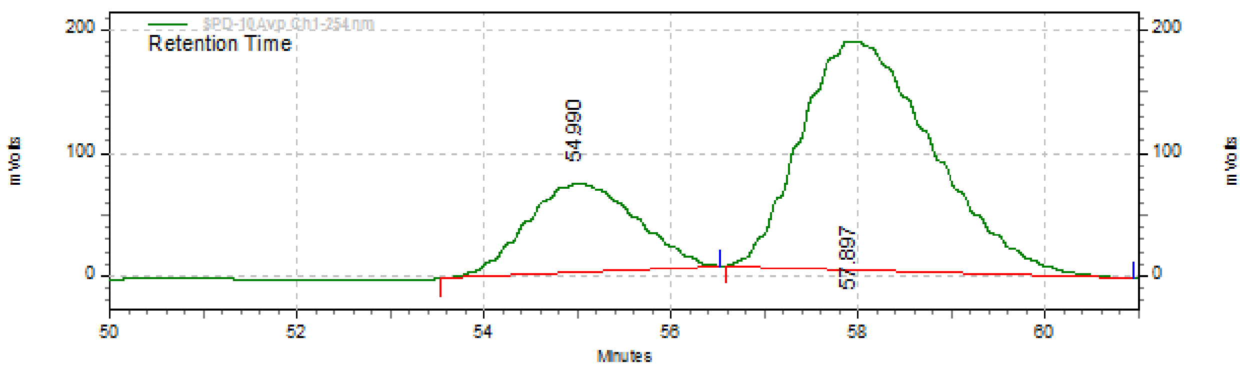
Racemic, OD column, 1:99 ^{i}PrOH:hexanes, 0.25 mL/min



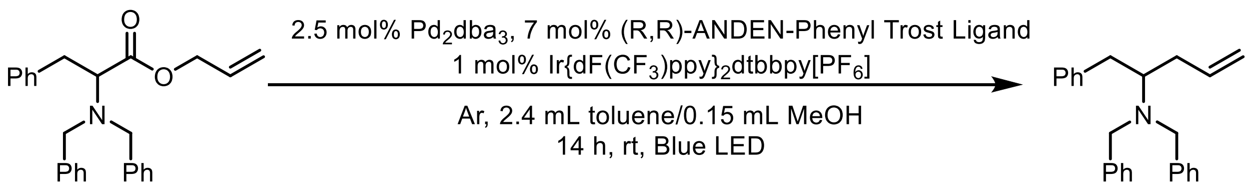
SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
53.788	760590	48.35	9481	50.18
56.705	812548	51.65	9414	49.82
Totals				
	1573138	100.00	18895	100.00



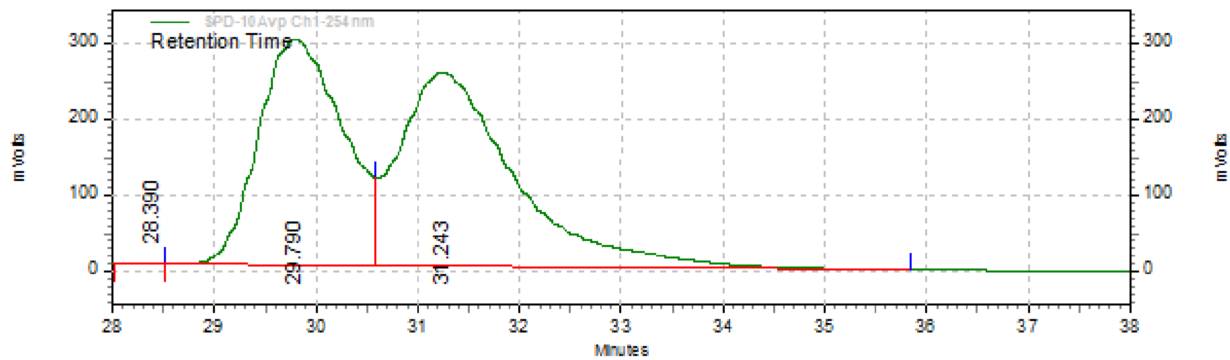
Enantioenriched, OD column, 1:99 ^{i}PrOH:hexanes, 0.25 mL/min



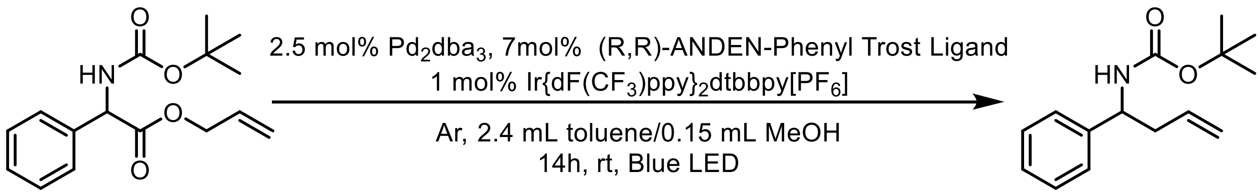
SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
54.990	5916249	24.54	72540	28.10
57.897	18195938	75.46	185612	71.90
Totals				
	24112187	100.00	258152	100.00



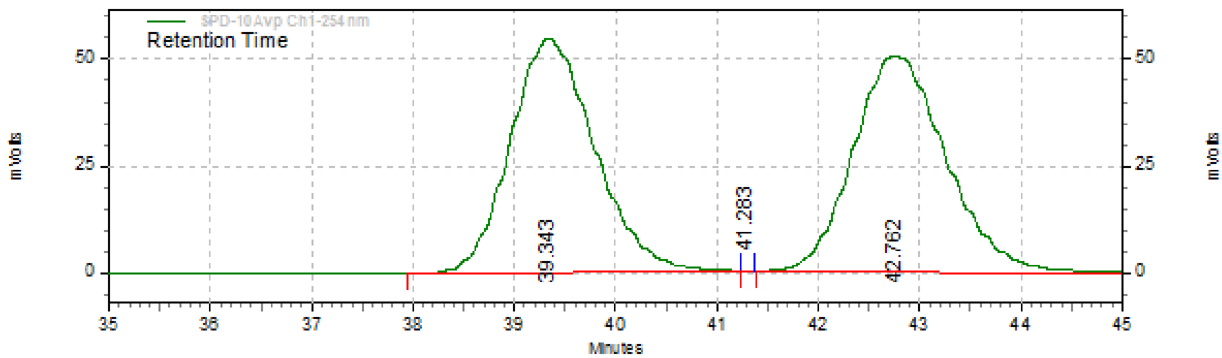
ADH column, 0.1:99.9 ^{i}PrOH:hexanes, 0.30 mL/min



SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
28.390	13335	0.04	656	0.12
29.790	17275395	46.03	298344	53.78
31.243	20238562	53.93	255717	46.10
Totals				
	37527292	100.00	554717	100.00



ADH column, 0.1:99.9 ^{i}PrOH:hexanes, 0.30 mL/min



SPD-10Avp Ch1-254nm Results				
Retention Time	Area	Area %	Height	Height %
39.343	3146874	49.67	54437	52.09
41.283	380	0.01	70	0.07
42.762	3187722	50.32	49991	47.84
Totals				
	6334976	100.00	104498	100.00

7. References

(1) Singh, A.; Teegardin, K.; Kelly, M.; Prasad, K. S.; Krishnan, S.; Weaver, J. D. *J. Organomet. Chem.* **2015**, *776*, 51.

(2) Lang, S. B.; O'Nele, K. M.; Tunge, J. A. *J. Am. Chem. Soc.* **2014**, *136*, 13606.

(3) Enholm, E.; Low, T. *J. Org. Chem.* **2006**, *71*, 2272.

(4) Konnert, L.; Lamaty, F.; Martinez, J.; Colacino, E. *J. Org. Chem.* **2014**, *79*, 4008.

(5) da Silva, M. R.; de Mattos, M. C.; de Oliveira, M. da C. F.; de Lemos, T. L. G.; Ricardo, N. M. P. S.; de Gonzalo, G.; Lavandera, I.; Gotor-Fernández, V. Gotor, V. *Tetrahedron*. **2014**, *70*, 2264.

(6) Hupp, C. D.; Tepe, J. J. *J. Org. Chem.* **2009**, *74*, 3406.

(7) Bugde, S.; Majik, M.; Mandrekar, V.; Nadkarni, V.; Tilve, S. *Synth. Commun.* **2013**, 2536.

(8) Xie, N.; Taylor, C. M. *Org. Lett*. **2010**, *12*, 4968.

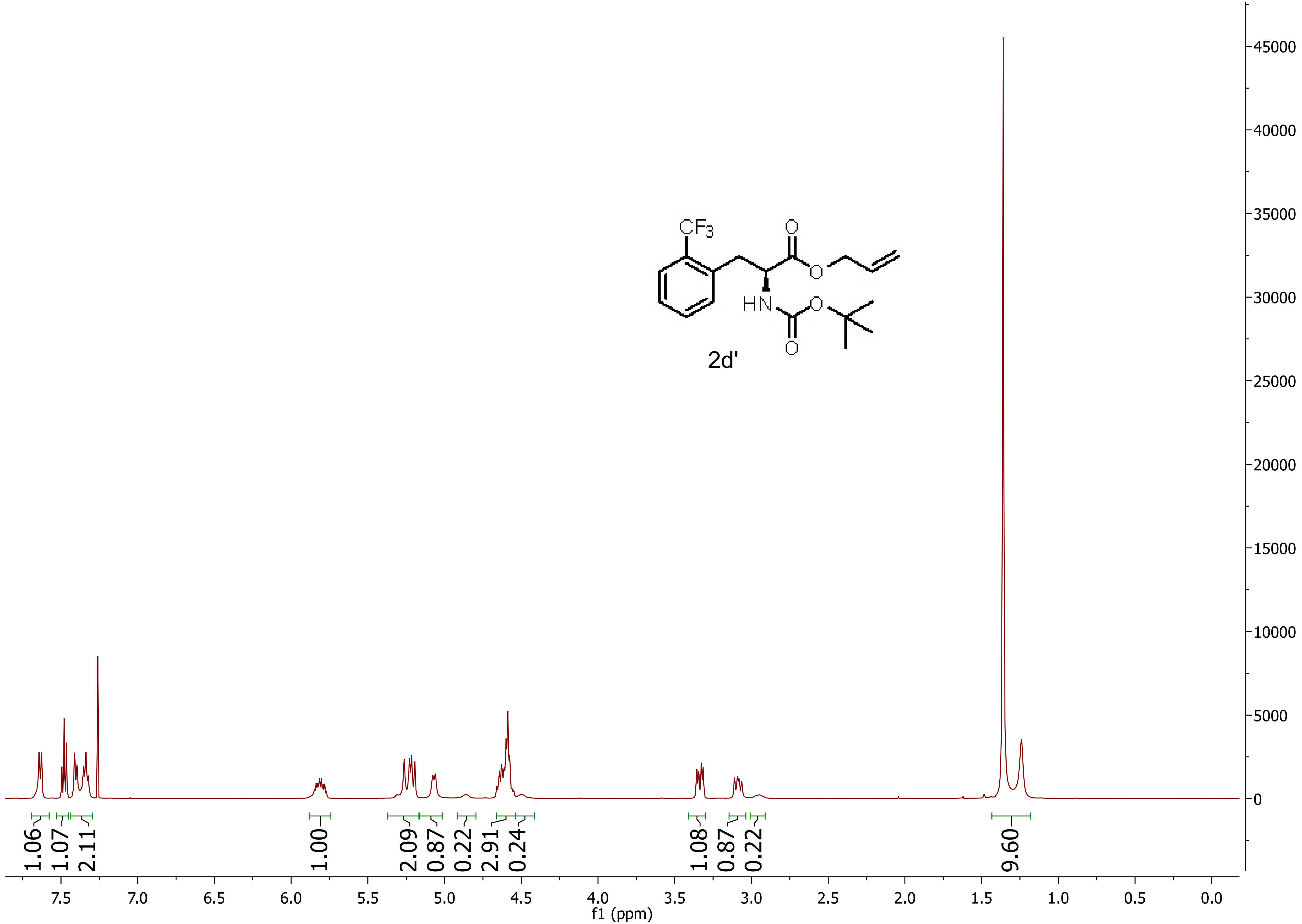
(9) Arnaud, O.; Koubeissi, A.; Ettouati, L.; Terreux, R.; Alamé, G.; Grenot, C.; Dumontet, C.; Di Pietro, A.; Paris, J.; Flason, P. *J. Med. Chem.* **2010**, *53*, 6720.

(10) Maegawa, Y.; Agura, K.; Hayashi, Y.; Ohshima, T.; Mashima, K. *Synlett.* **2012**, *23*, 137.

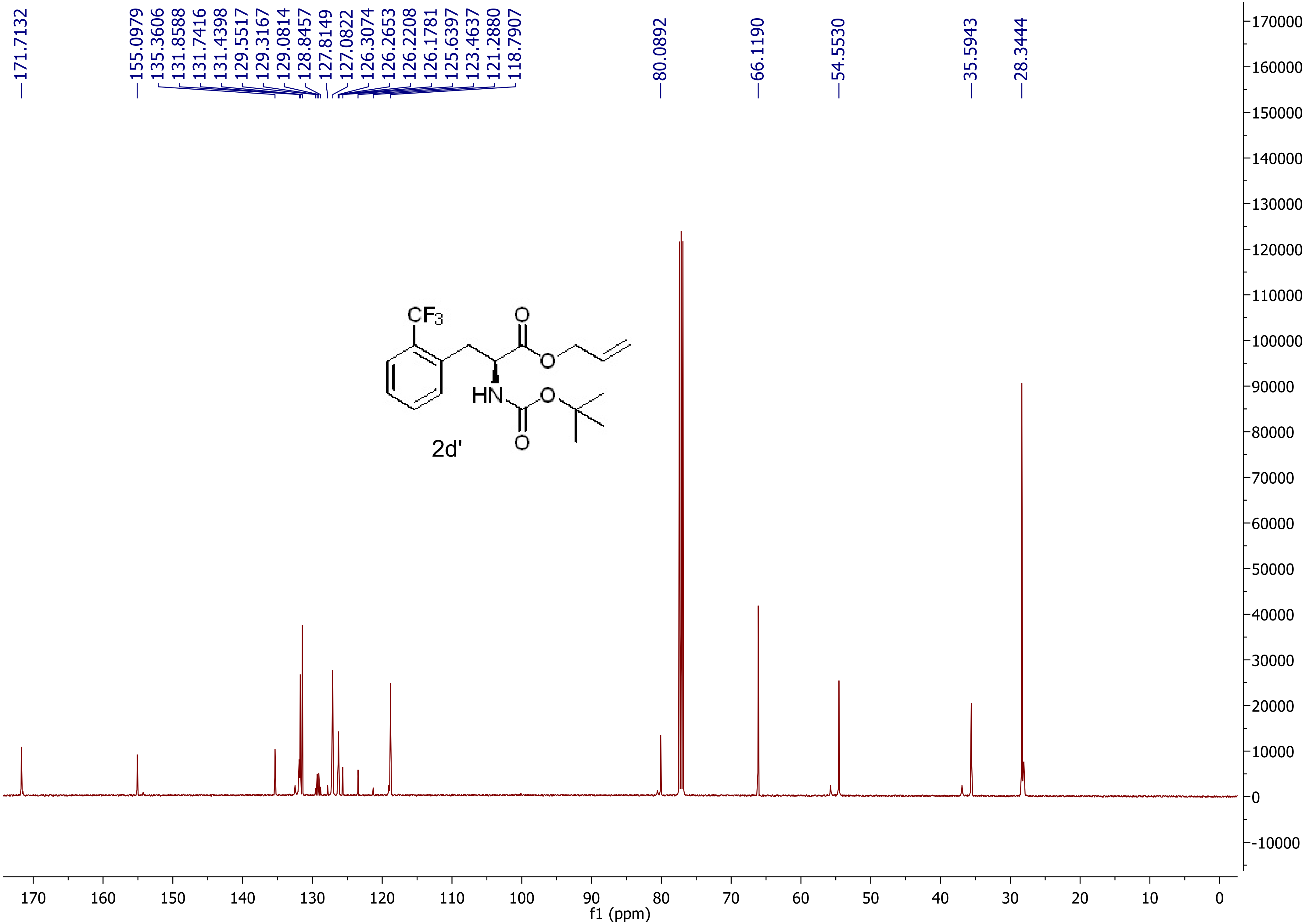
(11) Crosignani, S.; Gonzalez, J.; Swinnen, D. *Org. Lett.* **2004**, *6*, 4579.

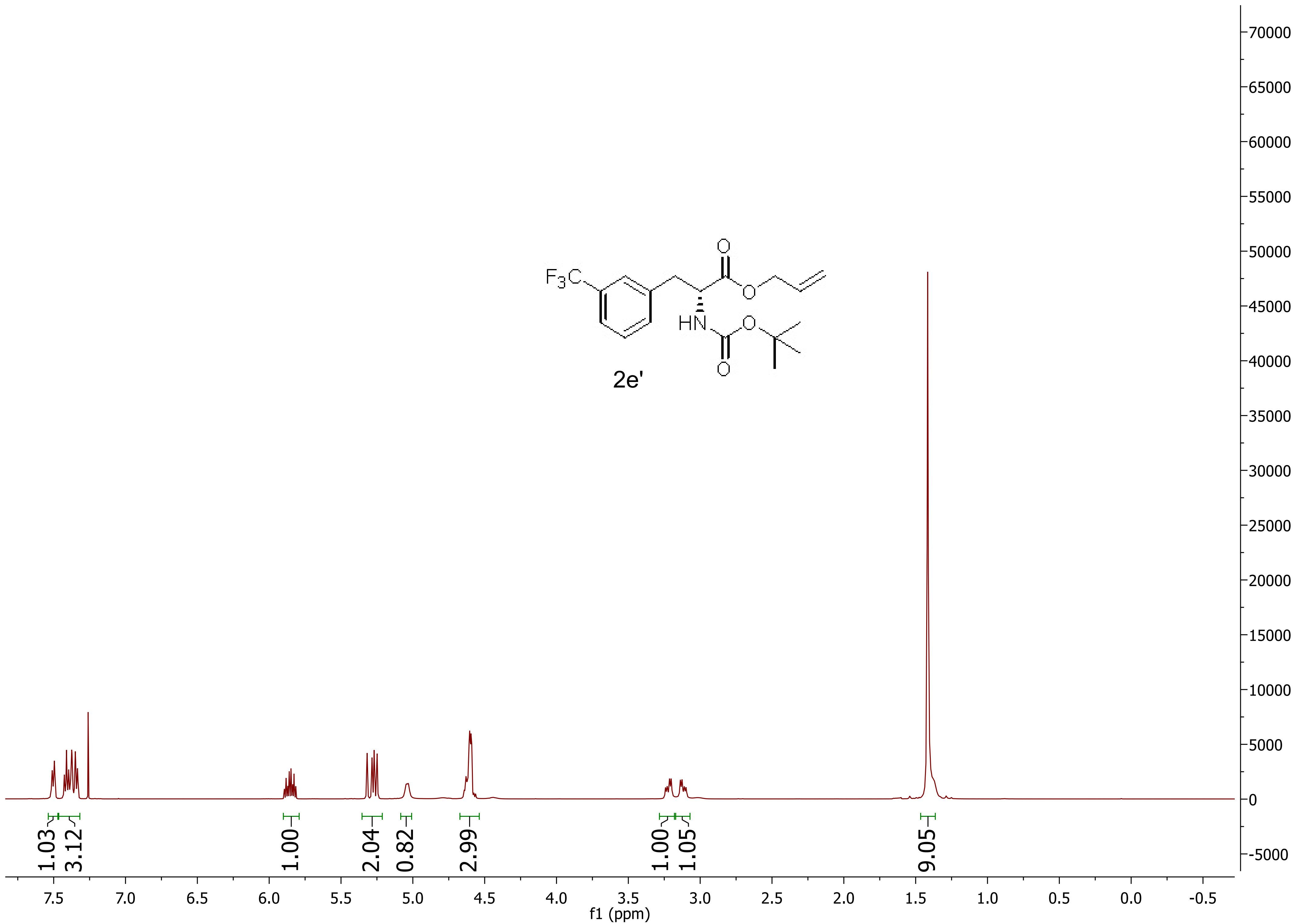
(12) Crosignani, S.; White, P. D.; Linclau, B. *J. Org. Chem.* **2004**, *69*, 5897.

8. ^{1}H and ^{13}C NMR Spectra

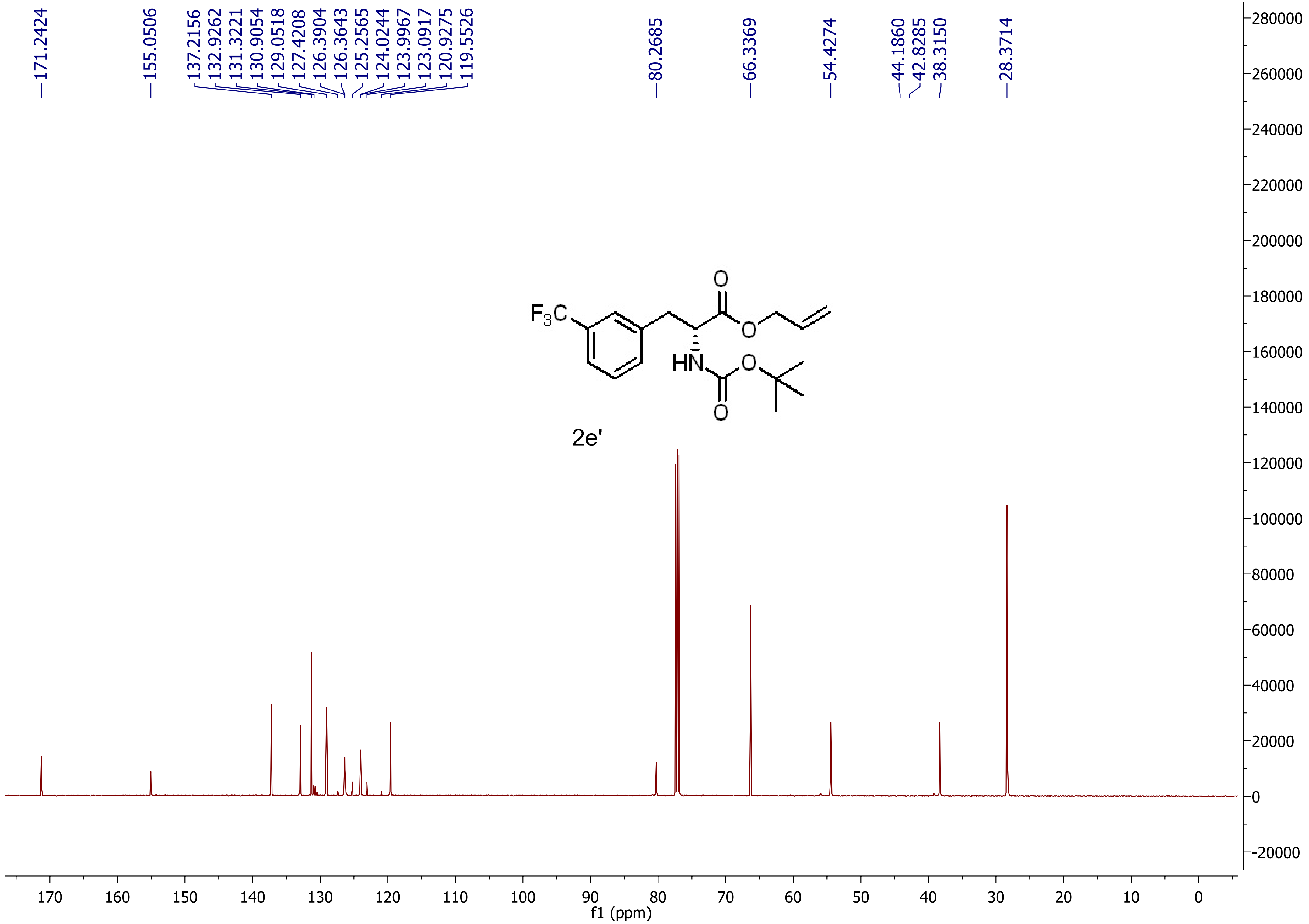


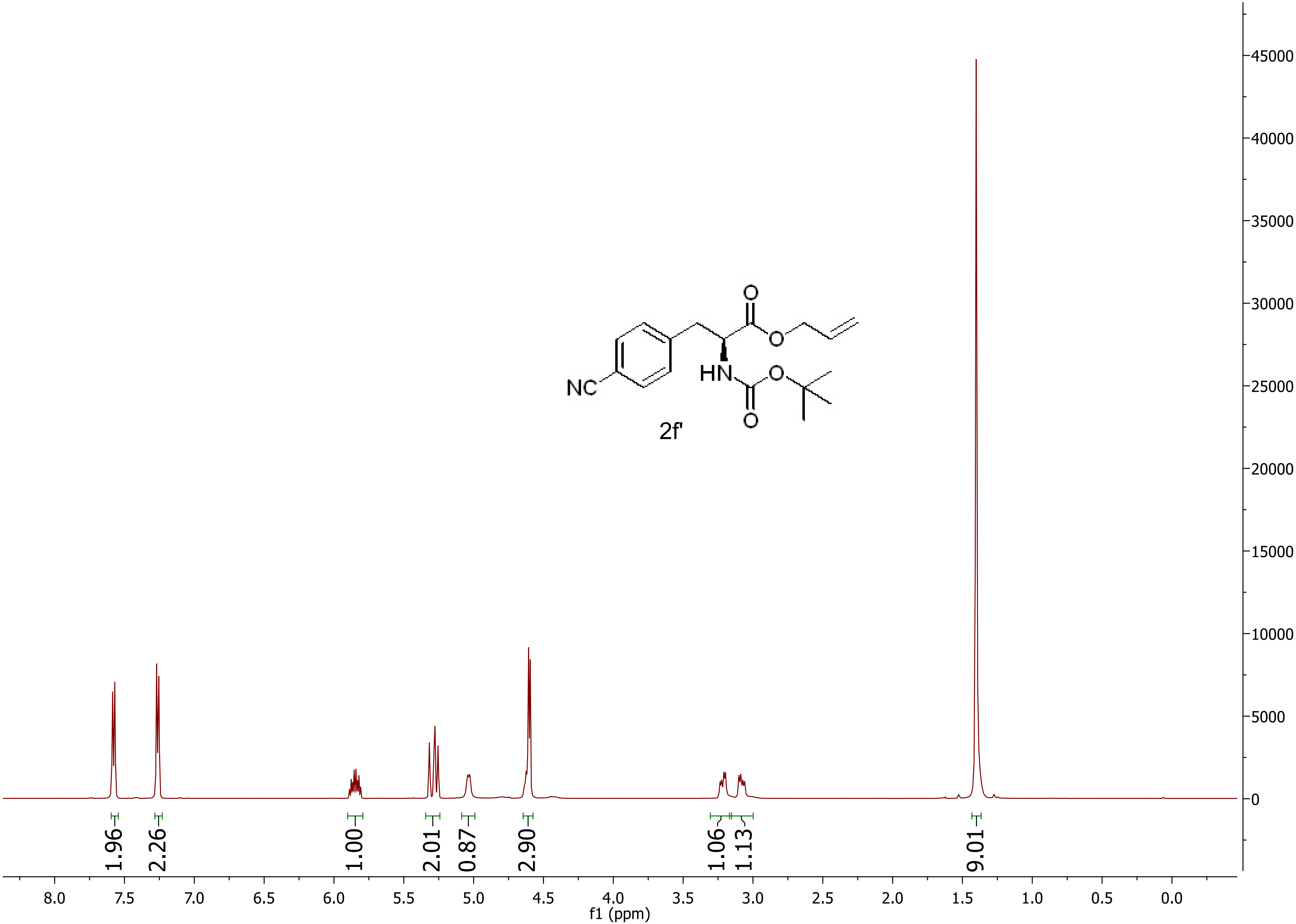
CF3
O
O
HN
O
O
2d'
1.06
1.07
2.11
1.00
2.09
0.87
0.22
2.91
0.24
1.08
0.87
0.22
9.60
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
45000
40000
35000
30000
25000
20000
15000
10000
5000
0


171.7132
155.0979
135.3606
131.8588
131.7416
131.4398
129.5517
129.3167
129.0814
128.8457
127.8149
127.0822
126.3074
126.2653
126.2208
126.1781
125.6397
123.4637
121.2880
118.7907
80.0892
66.1190
54.5530
35.5943
28.3444
CF3
O
O
HN
O
O
2d'
f1 (ppm)

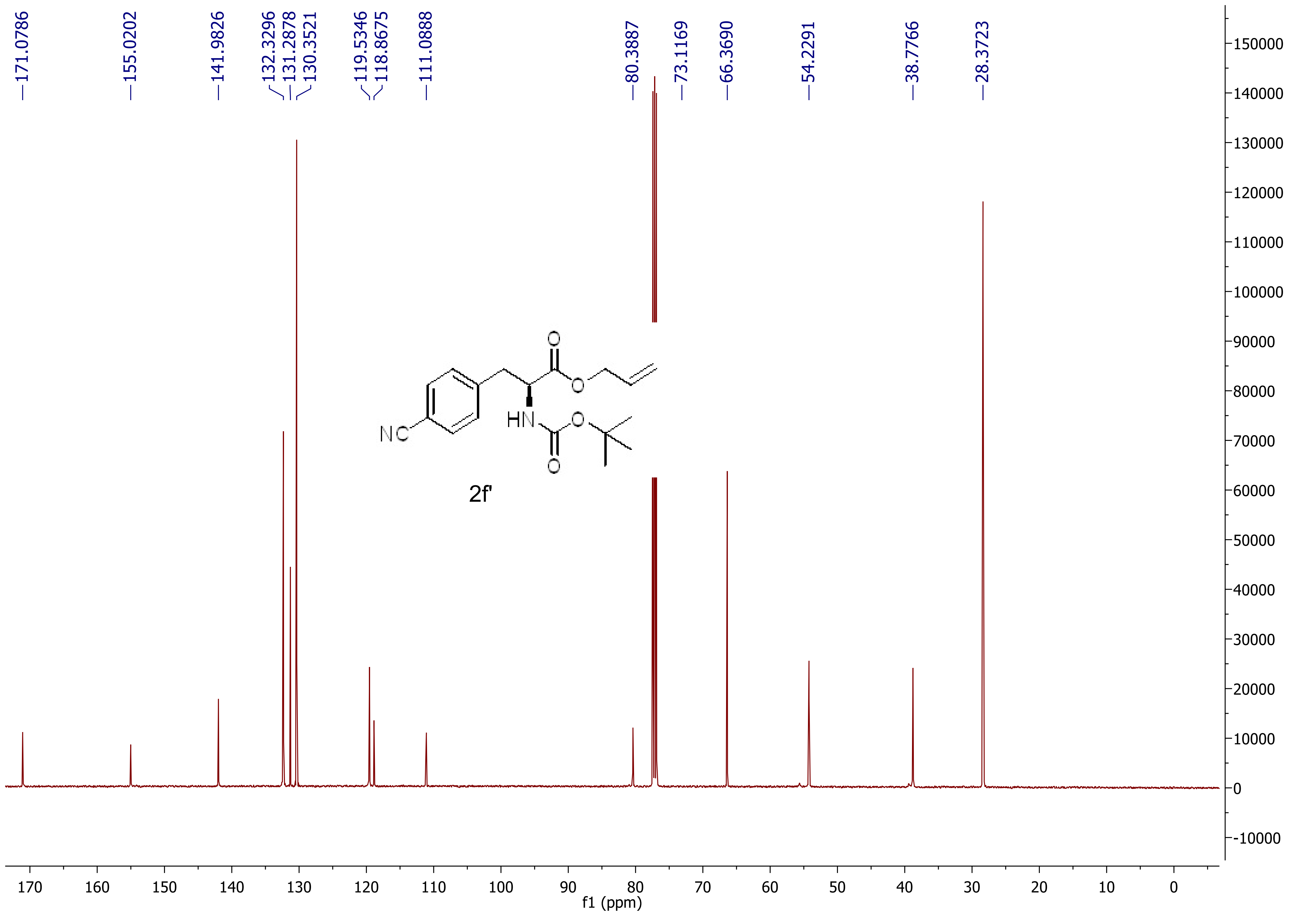


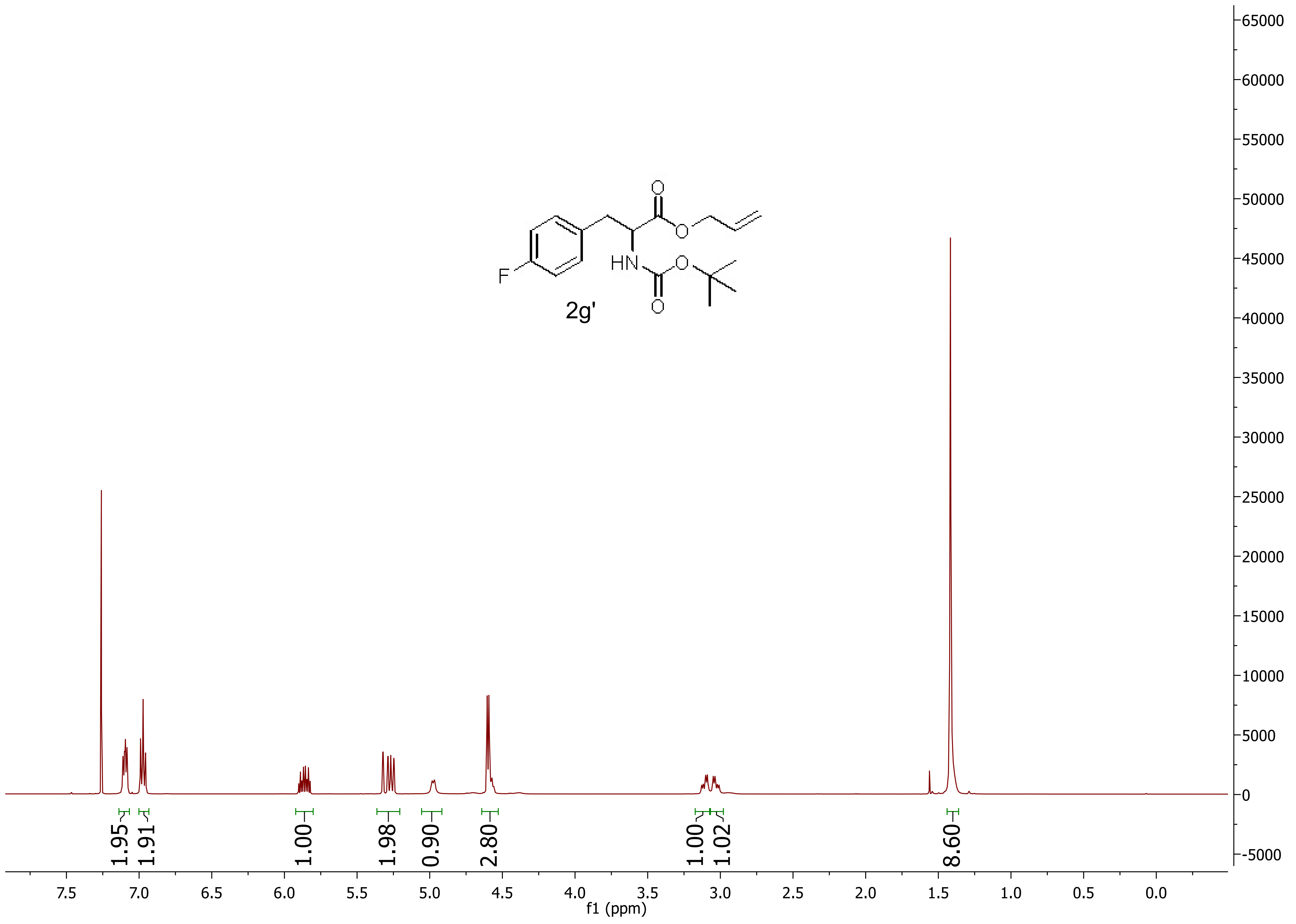
F3C
O
O
HN
O
O
2e'
1.03
3.12
1.00
2.04
0.82
2.99
1.00
1.05
9.05
f1 (ppm)

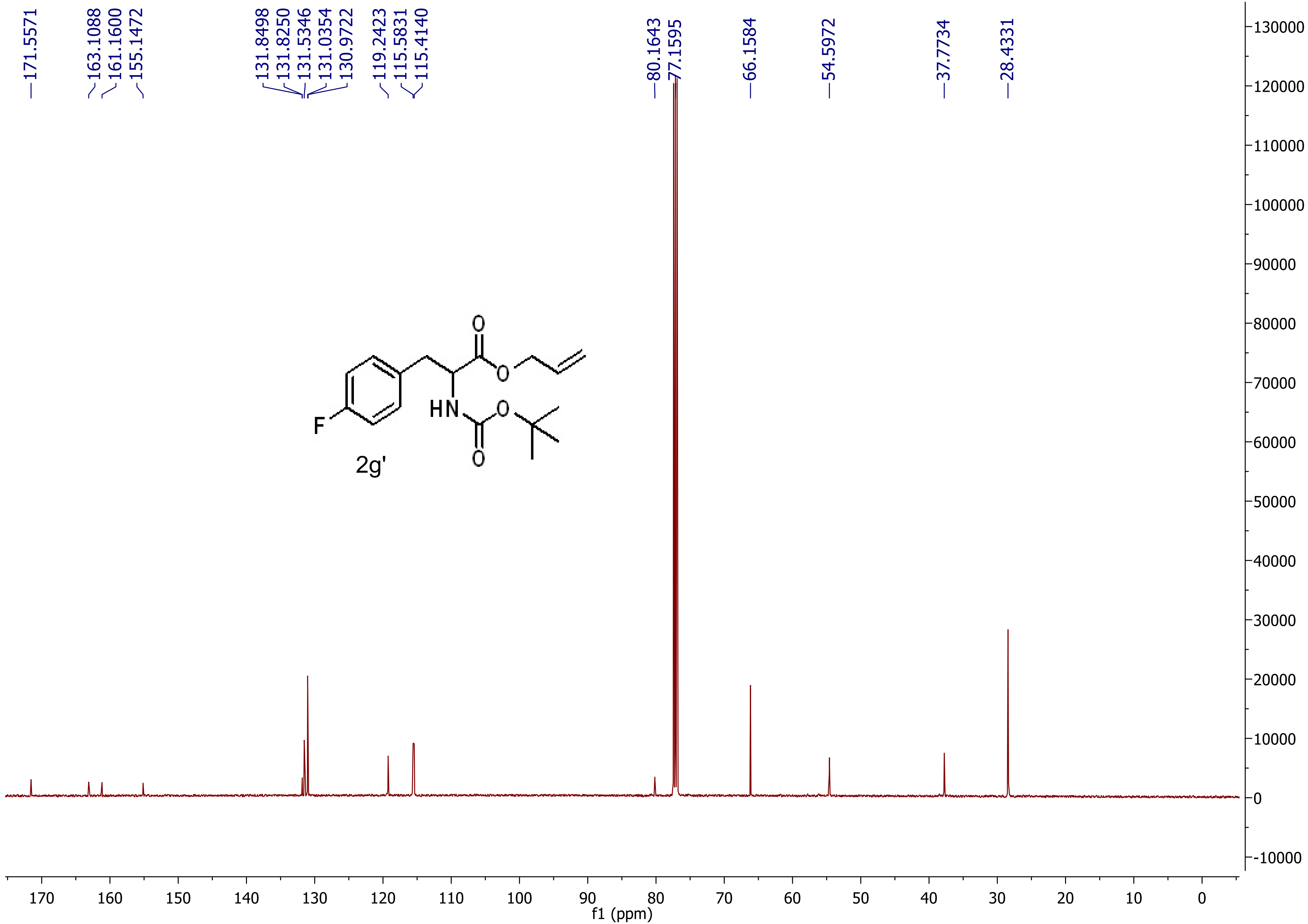

171.2424
155.0506
137.2156
132.9262
131.3221
130.9054
129.0518
127.4208
126.3904
126.3643
125.2565
124.0244
123.9967
123.0917
120.9275
119.5526
80.2685
66.3369
54.4274
44.1860
42.8285
38.3150
28.3714
F3C
O
O
HN
O
O
2e'
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



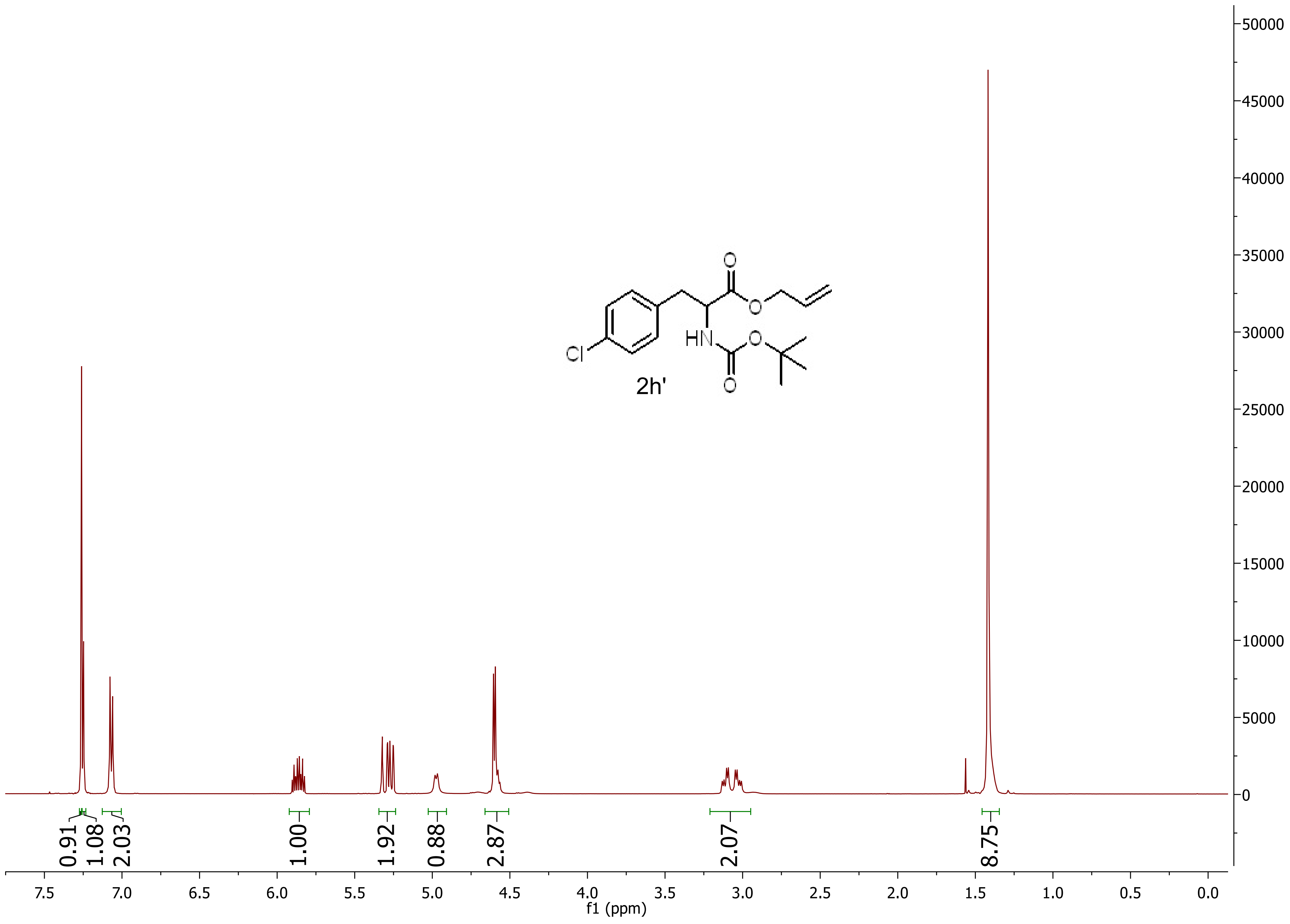
NC
HN
O
2f'
1.96
2.26
1.00
2.01
0.87
2.90
1.06
1.13
9.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
45000
40000
35000
30000
25000
20000
15000
10000
5000
0


171.0786
155.0202
141.9826
132.3296
131.2878
130.3521
119.5346
118.8675
111.0888
80.3887
73.1169
66.3690
54.2291
38.7766
28.3723
NC
HN
O
2f'
f1 (ppm)

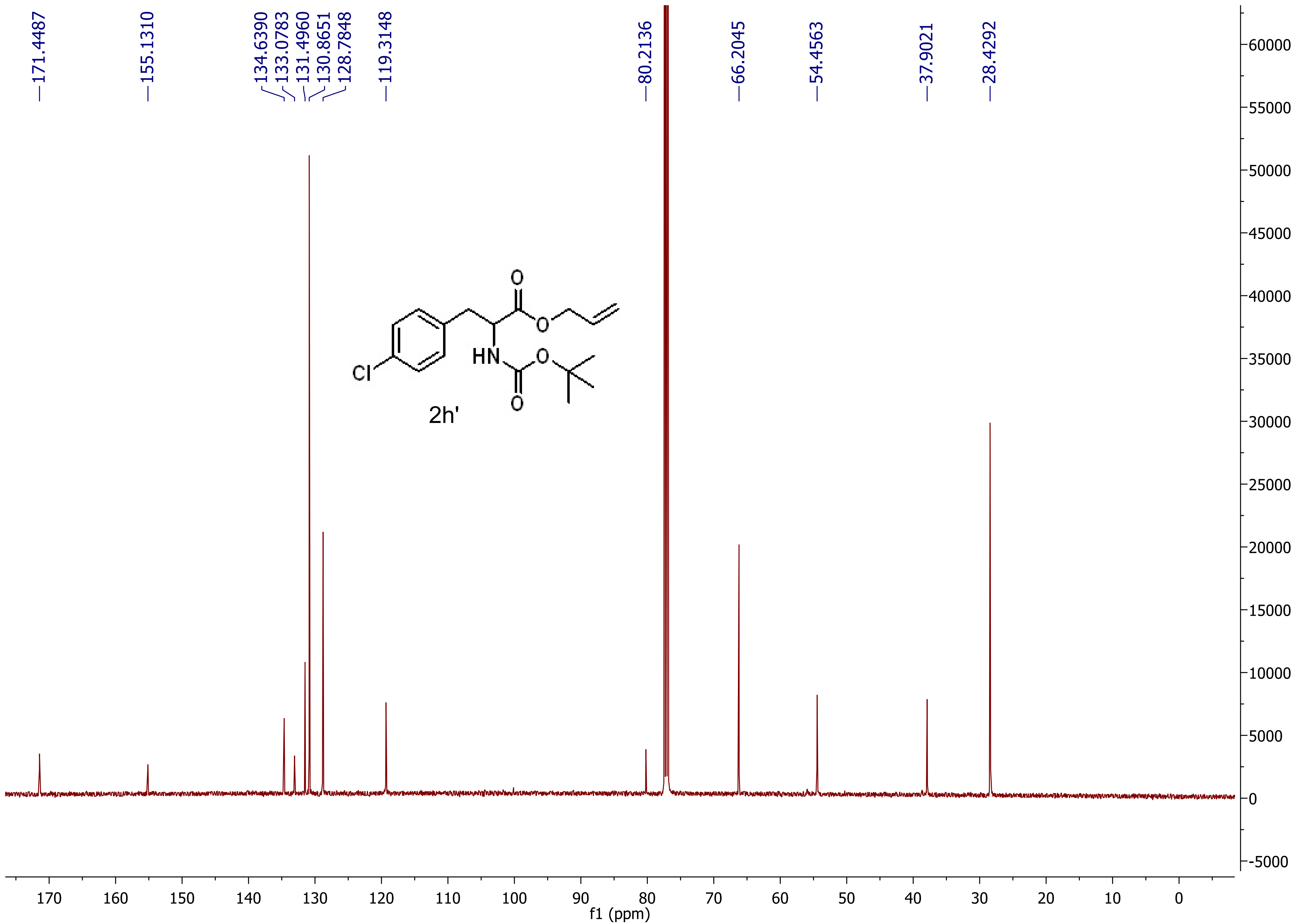

2g'
f1 (ppm)
1.95
1.91
1.00
1.98
0.90
2.80
1.00
1.02
8.60

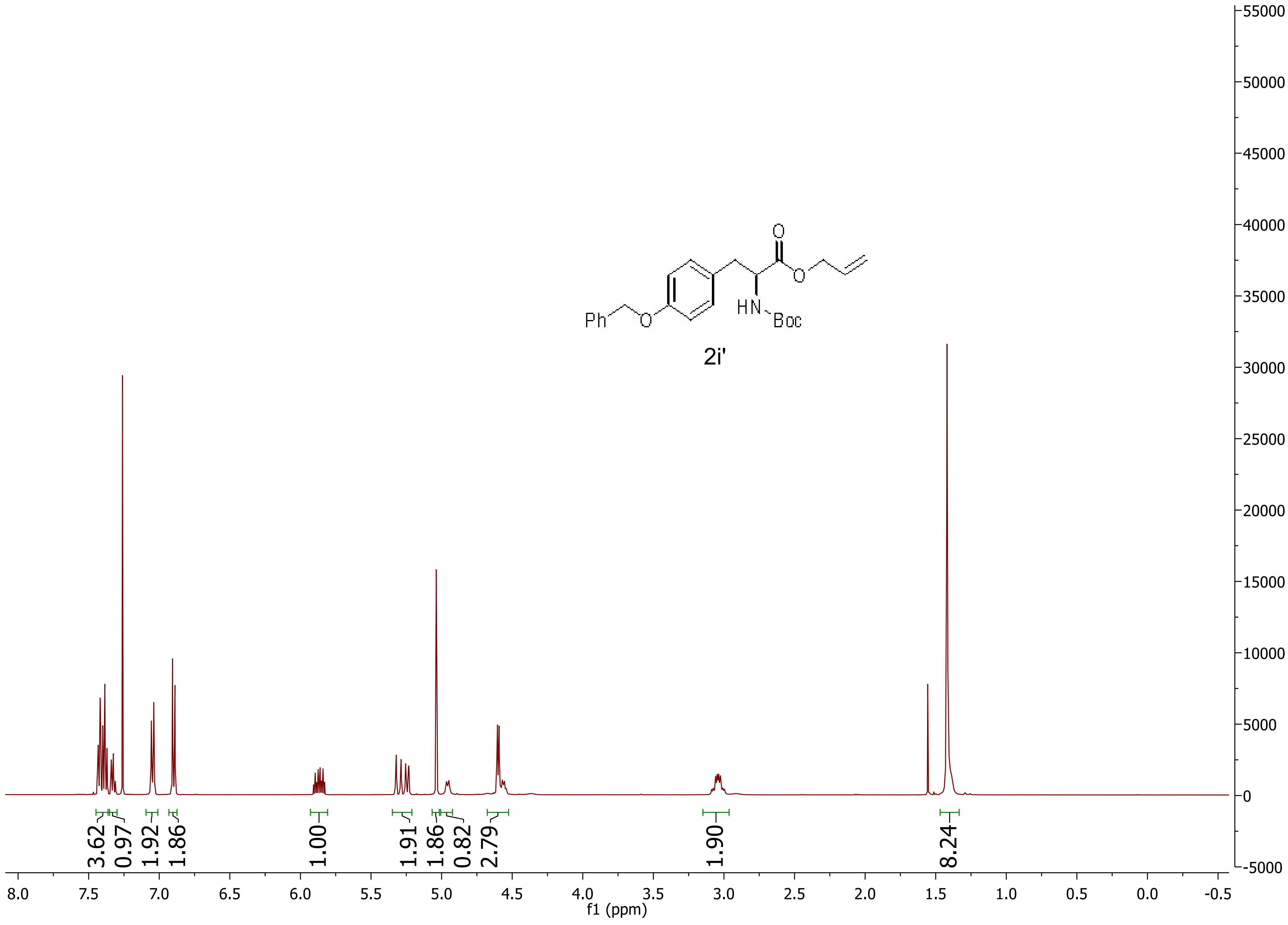


171.5571
163.1088
161.1600
155.1472
131.8498
131.8250
131.5346
131.0354
130.9722
119.2423
115.5831
115.4140
80.1643
77.1595
66.1584
54.5972
37.7734
28.4331
F
HN
O
2g'
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

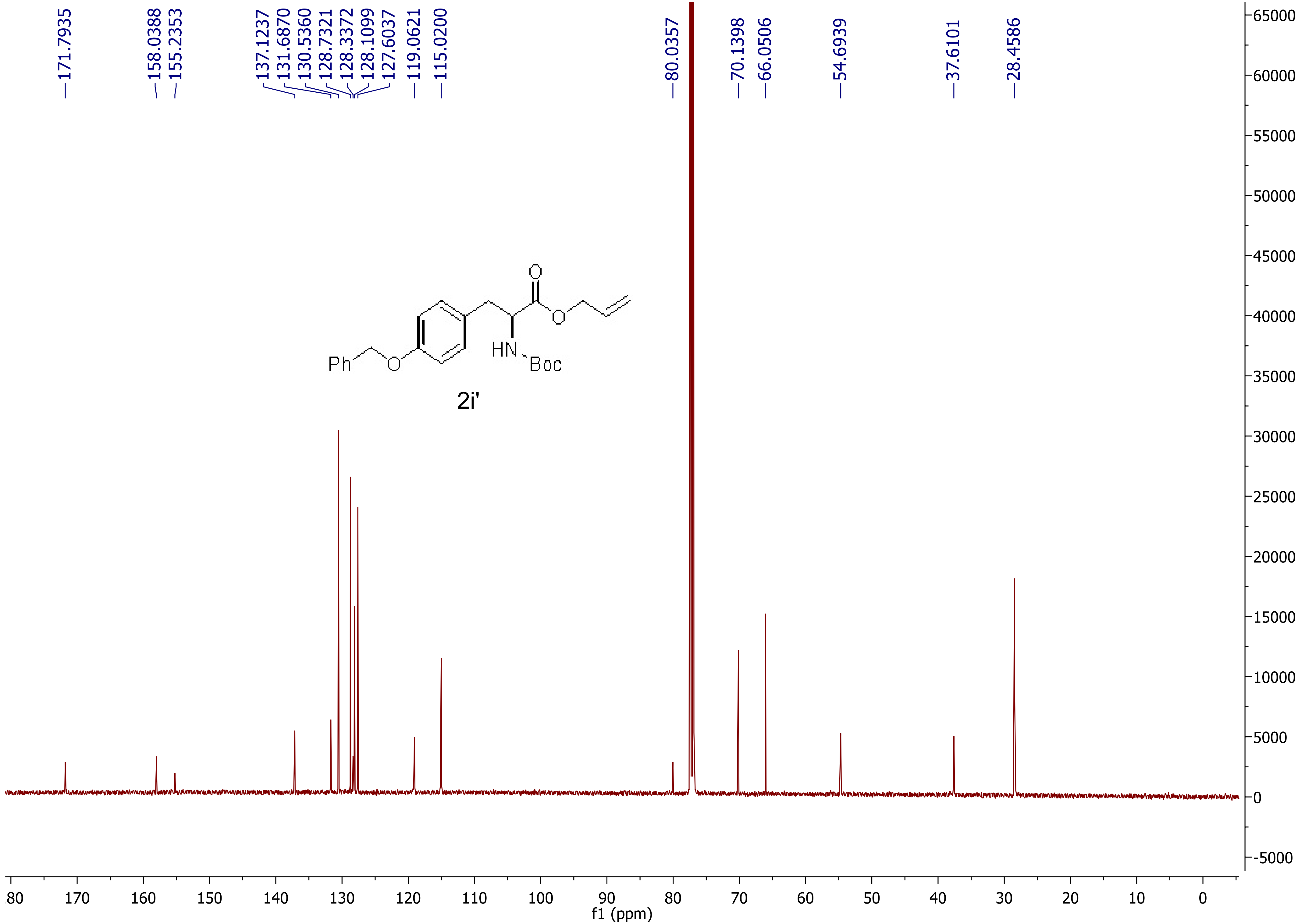


2h'
0.91
1.08
2.03
1.00
1.92
0.88
2.87
2.07
8.75
f1 (ppm)

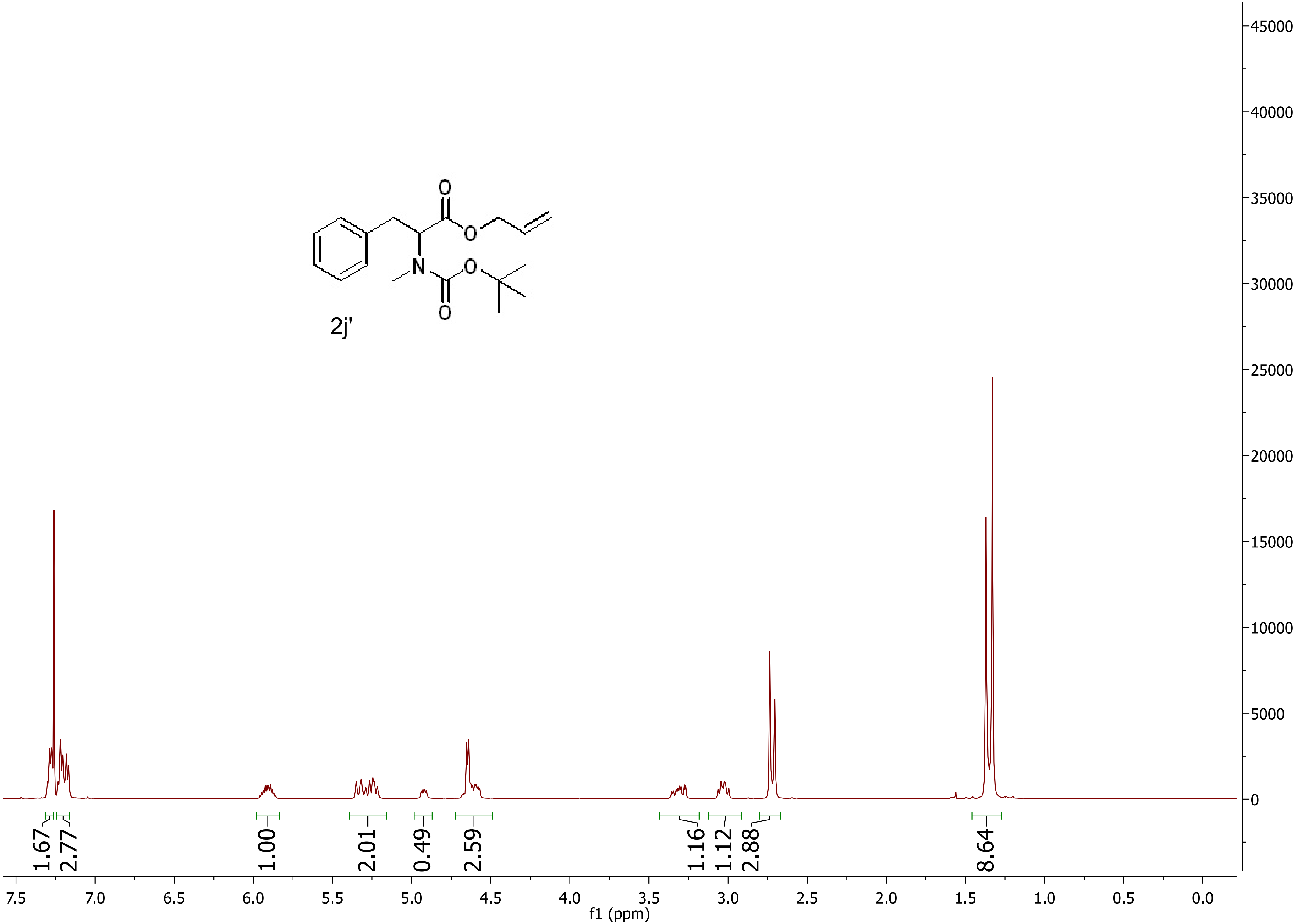

171.4487
155.1310
134.6390
133.0783
131.4960
130.8651
128.7848
119.3148
80.2136
66.2045
54.4563
37.9021
28.4292
Cl
HN
O
2h'
f1 (ppm)



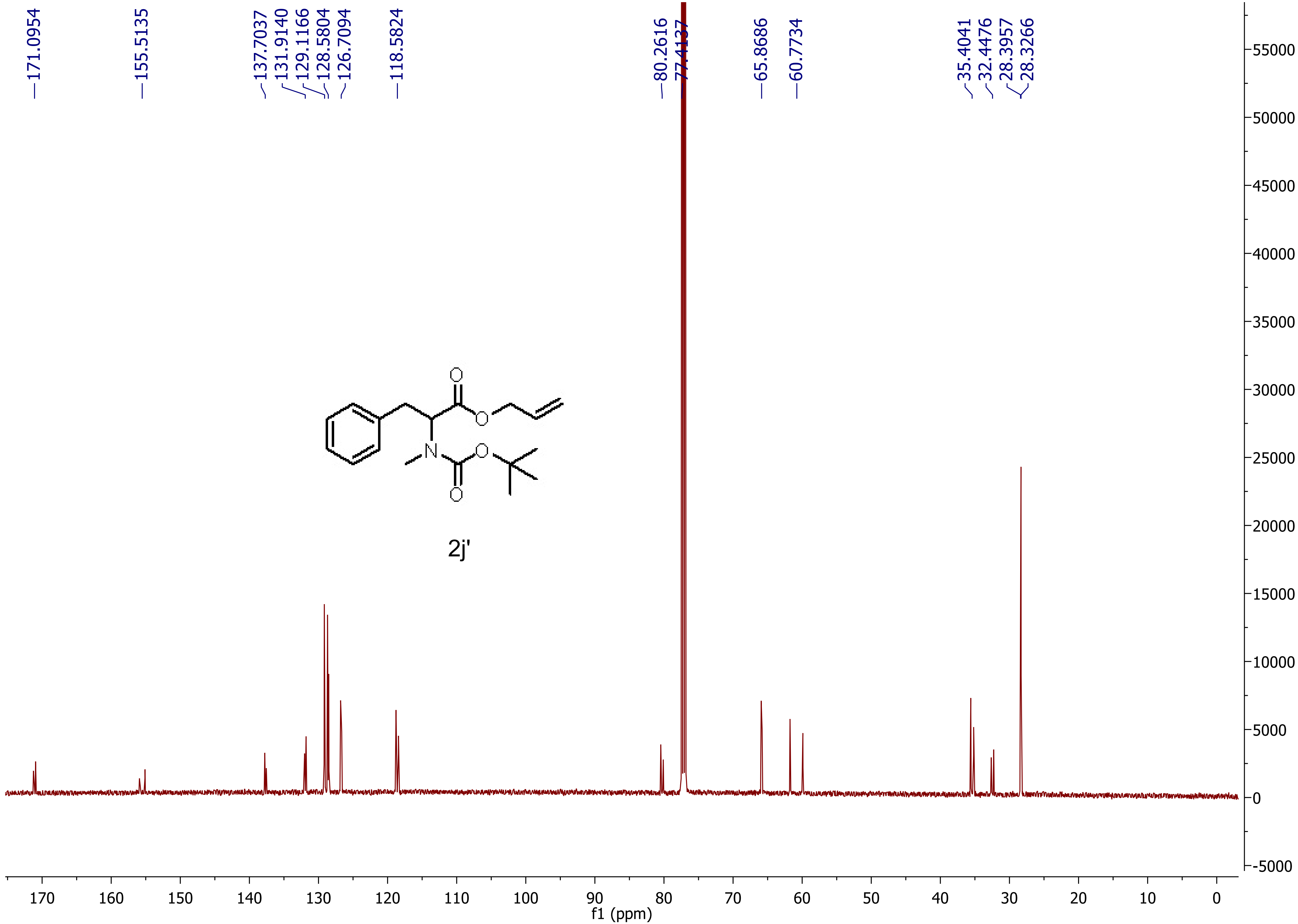
Ph
O
O
O
HN
Boc
2i'
3.62
0.97
1.92
1.86
1.00
1.91
1.86
0.82
2.79
1.90
8.24
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

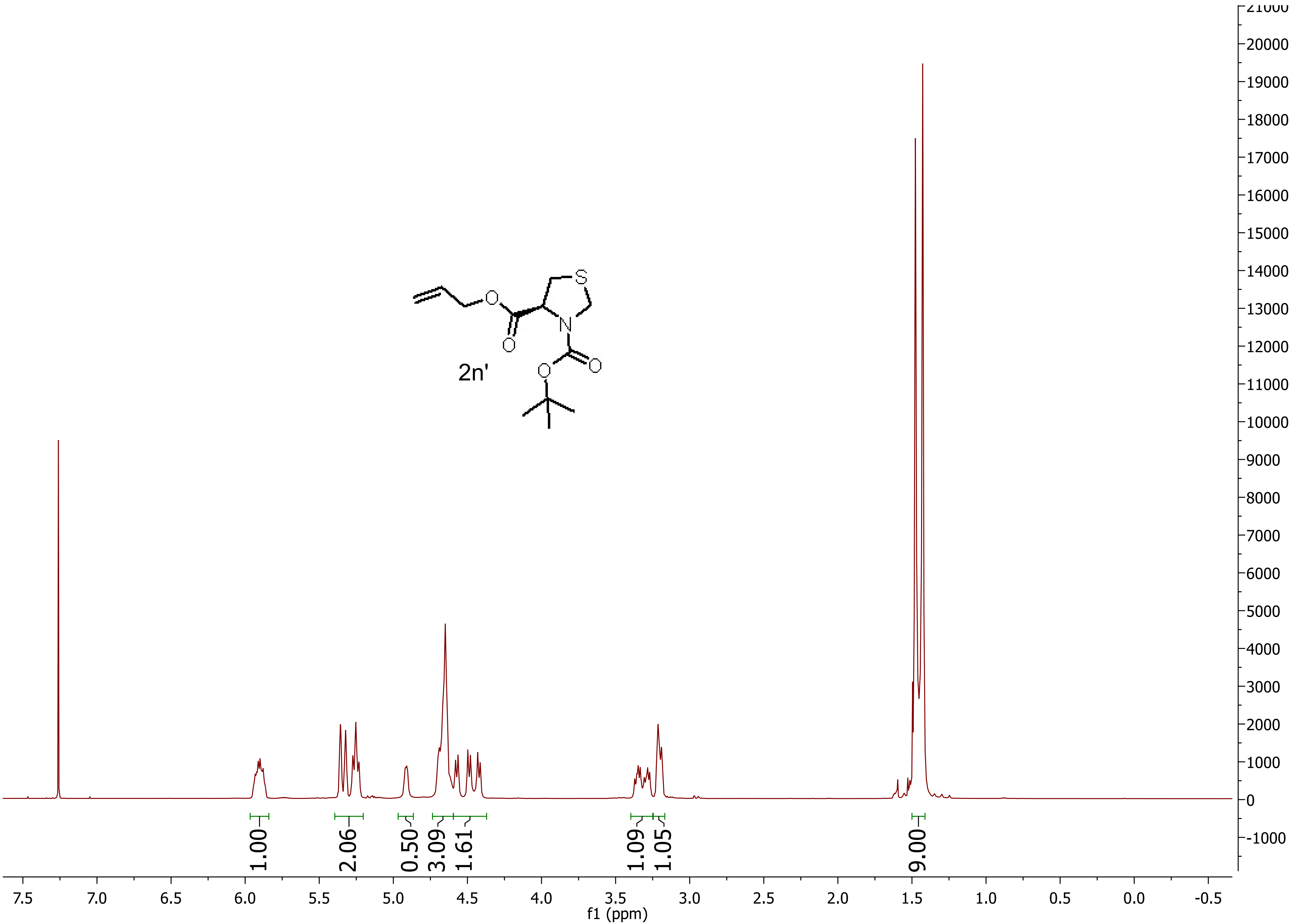


171.7935
158.0388
155.2353
137.1237
131.6870
130.5360
128.7321
128.3372
128.1099
127.6037
119.0621
115.0200
80.0357
70.1398
66.0506
54.6939
37.6101
28.4586
Ph
O
O
O
HN
Boc
2i'
f1 (ppm)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
65000 60000 55000 50000 45000 40000 35000 30000 25000 20000 15000 10000 5000 0 -5000

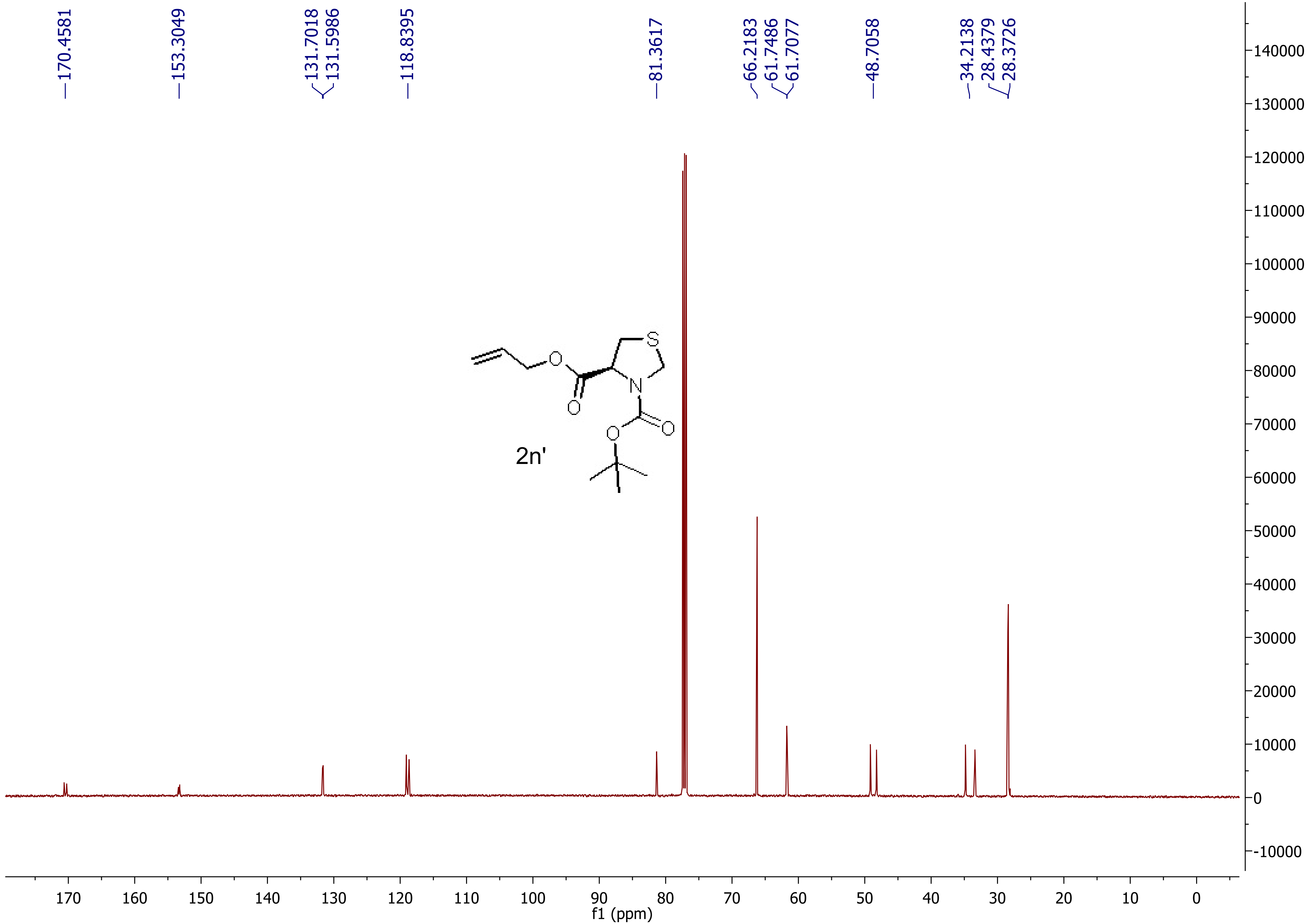


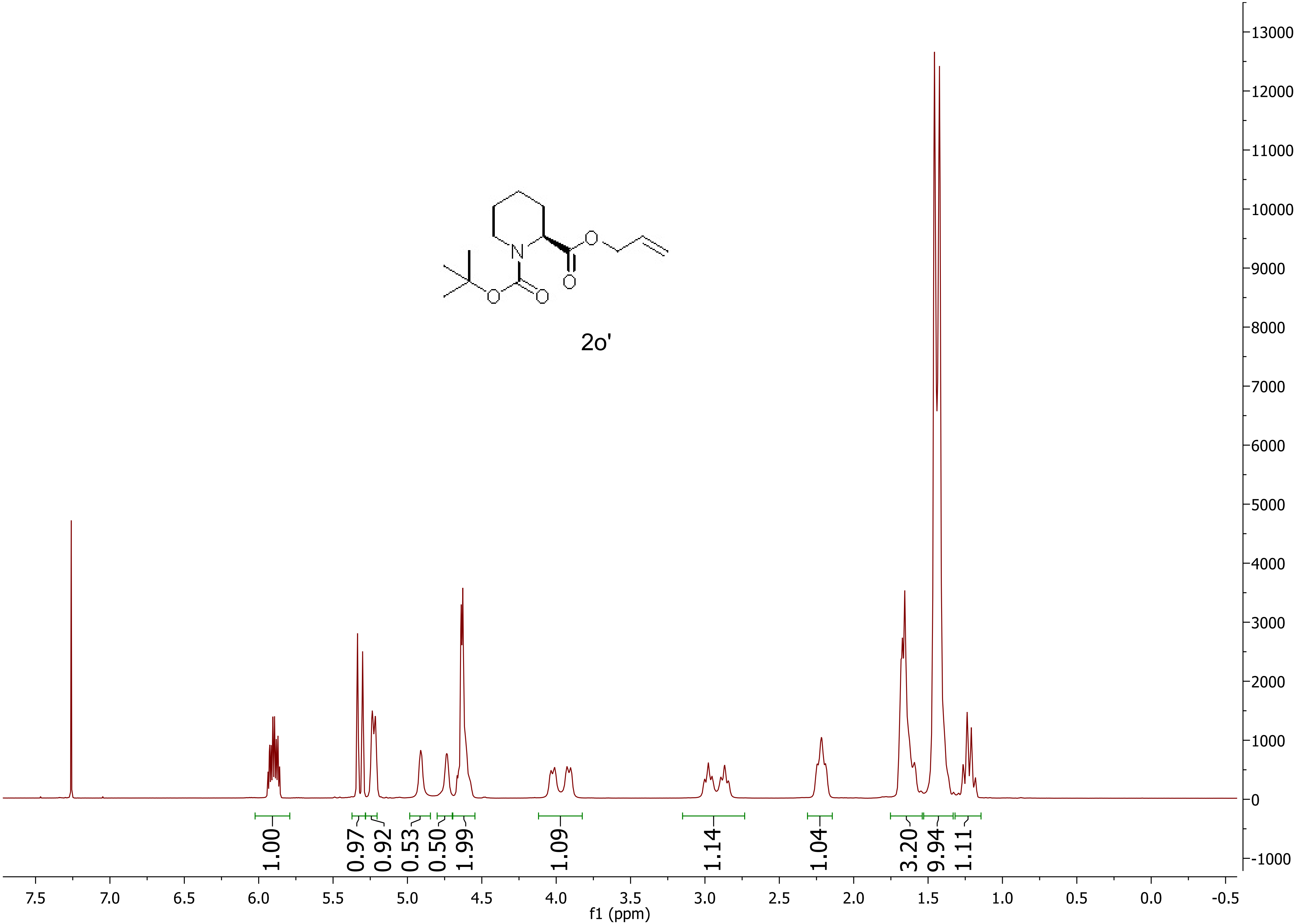
2j'
1.67
2.77
1.00
2.01
0.49
2.59
1.16
1.12
2.88
8.64
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
45000
40000
35000
30000
25000
20000
15000
10000
5000
0

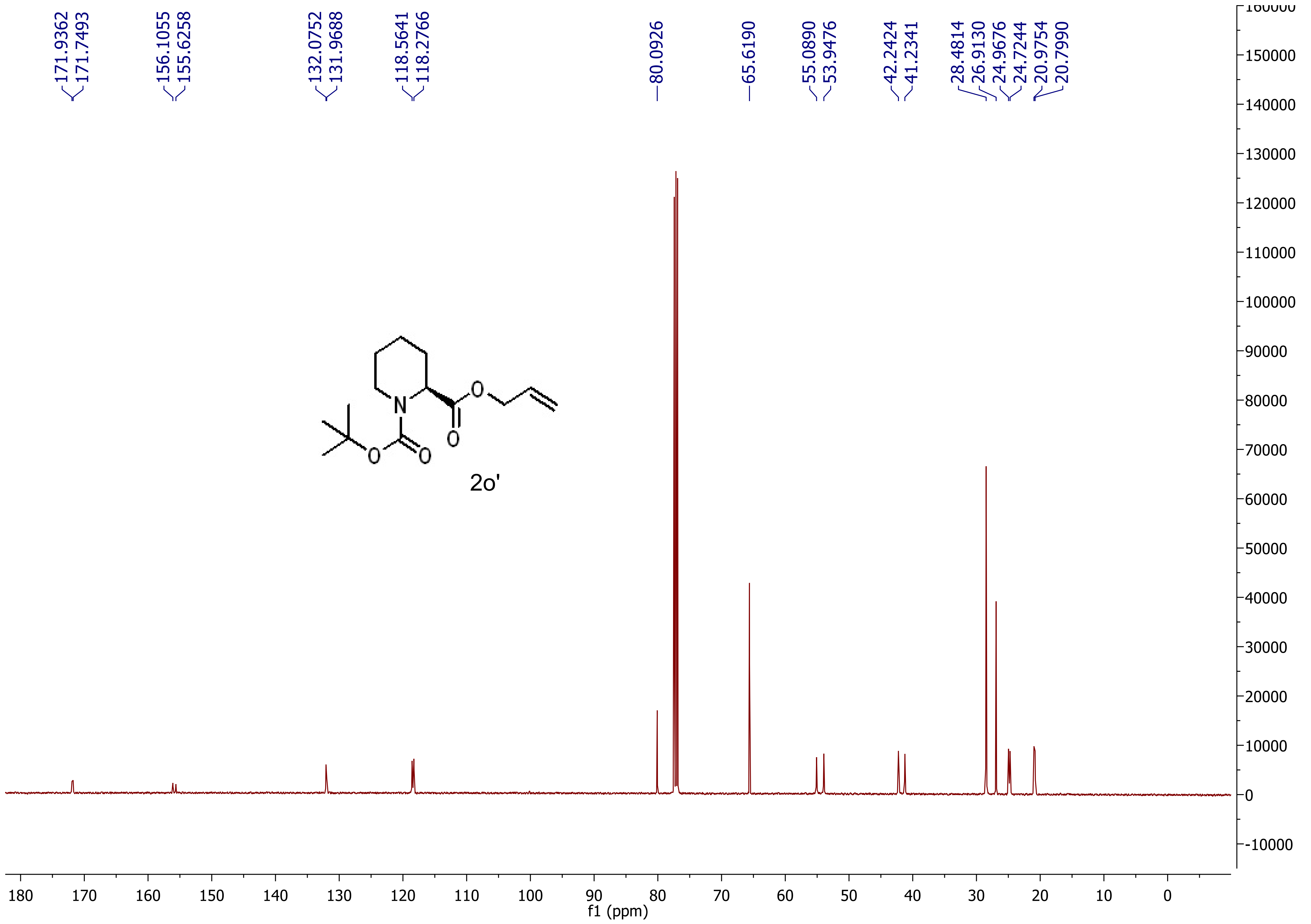

171.0954
155.5135
137.7037
131.9140
129.1166
128.5804
126.7094
118.5824
80.2616
77.4137
65.8686
60.7734
35.4041
32.4476
28.3957
28.3266
2j'
f1 (ppm)

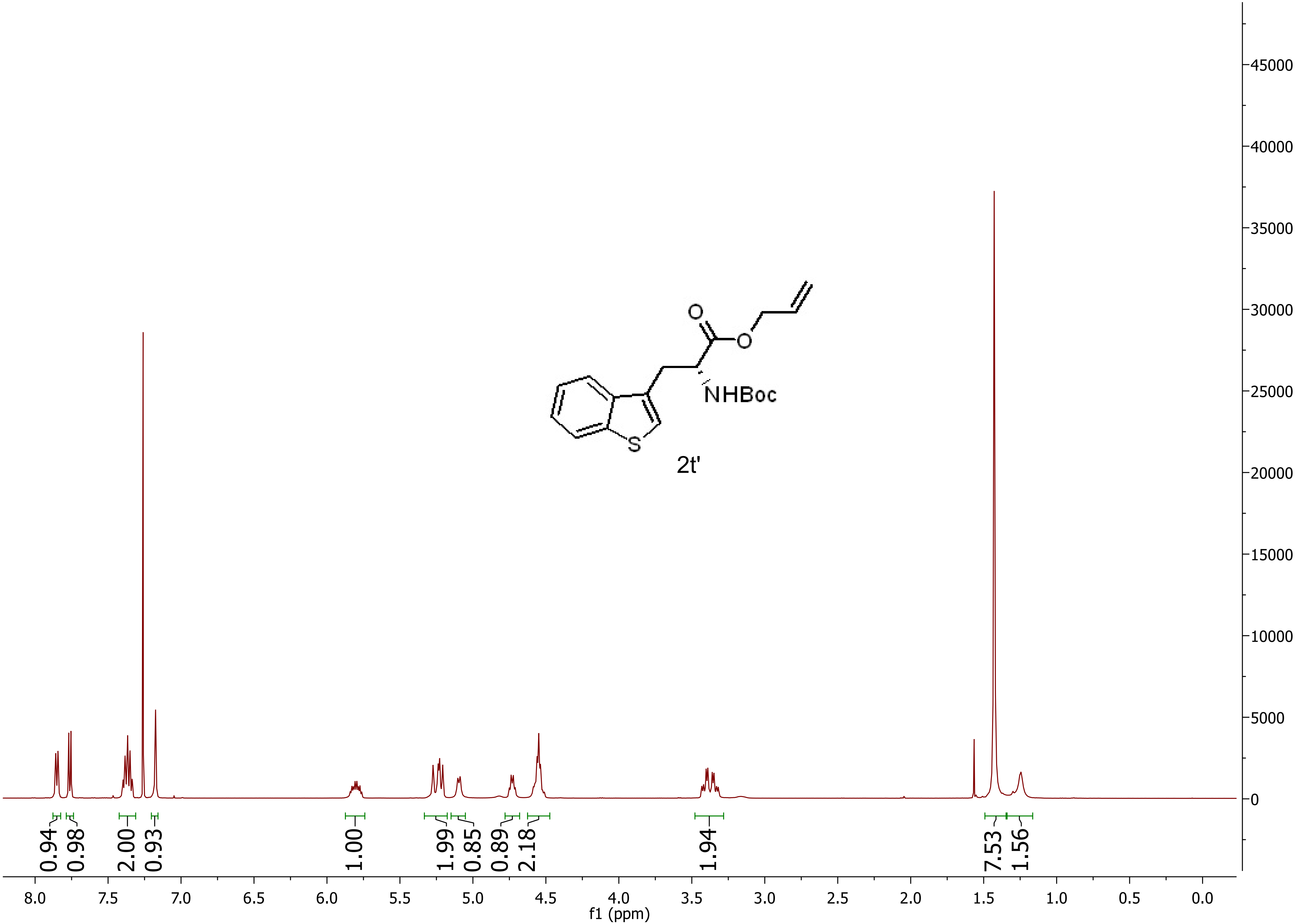


2n'
1.00
2.06
0.50
3.09
1.61
1.09
1.05
9.00
f1 (ppm)

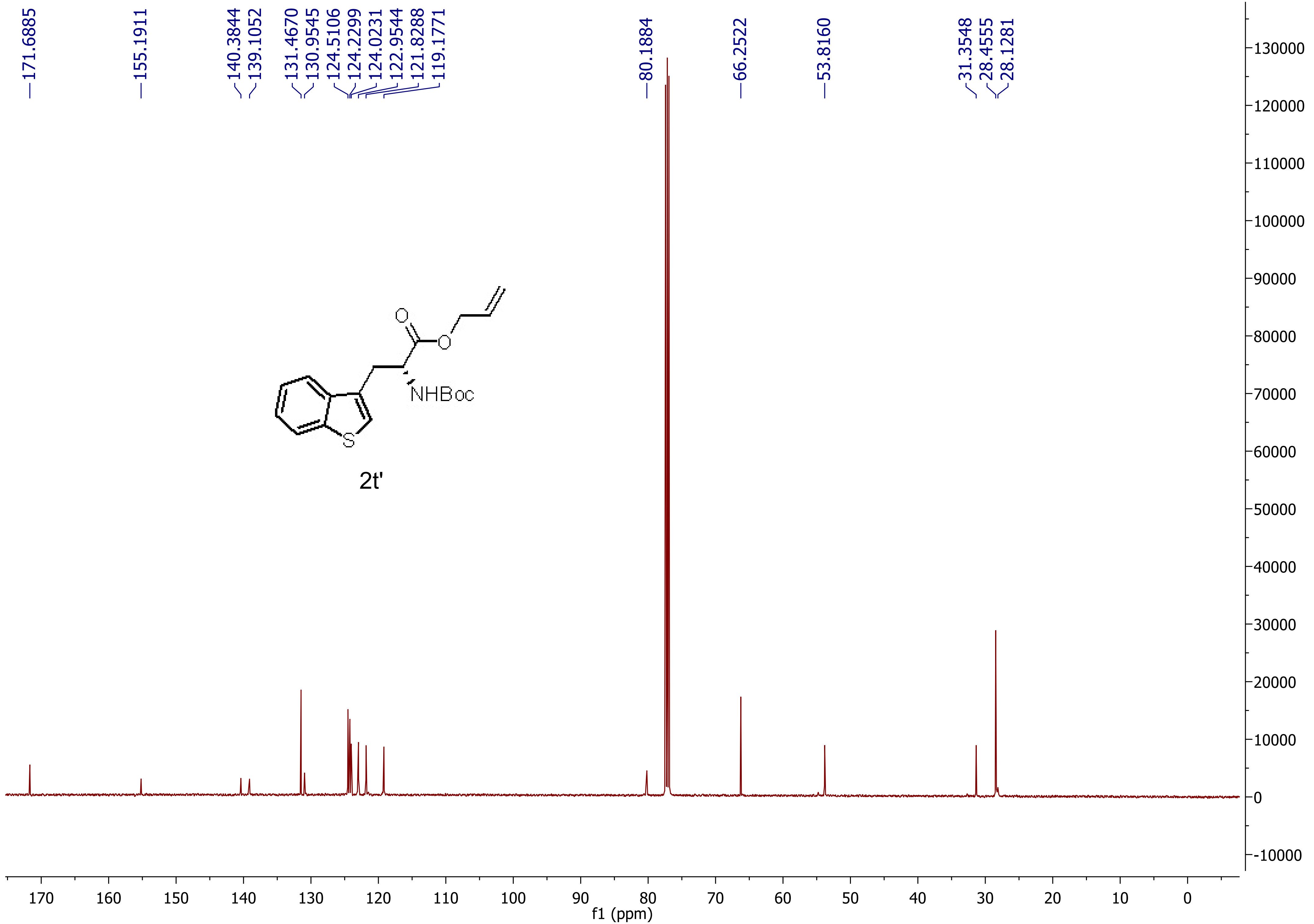

170.4581
153.3049
131.7018
131.5986
118.8395
81.3617
66.2183
61.7486
61.7077
48.7058
34.2138
28.4379
28.3726
2n'
f1 (ppm)


2o'
1.00
0.97
0.92
0.53
0.50
1.99
1.09
1.14
1.04
3.20
9.94
1.11
f1 (ppm)
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 -0.5
13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000

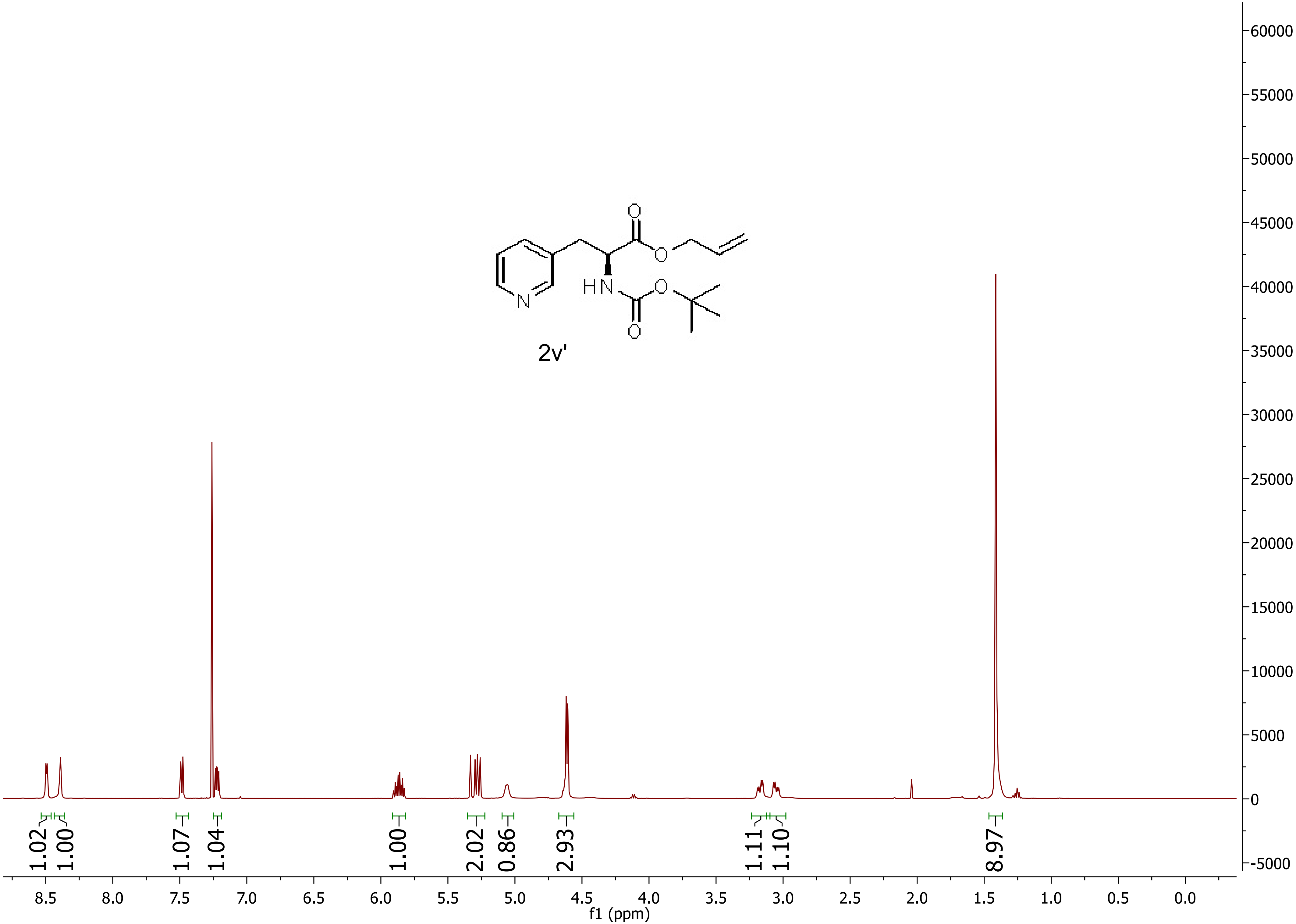

171.9362
171.7493
156.1055
155.6258
132.0752
131.9688
118.5641
118.2766
80.0926
65.6190
55.0890
53.9476
42.2424
41.2341
28.4814
26.9130
24.9676
24.7244
20.9754
20.7990
2o'
f1 (ppm)

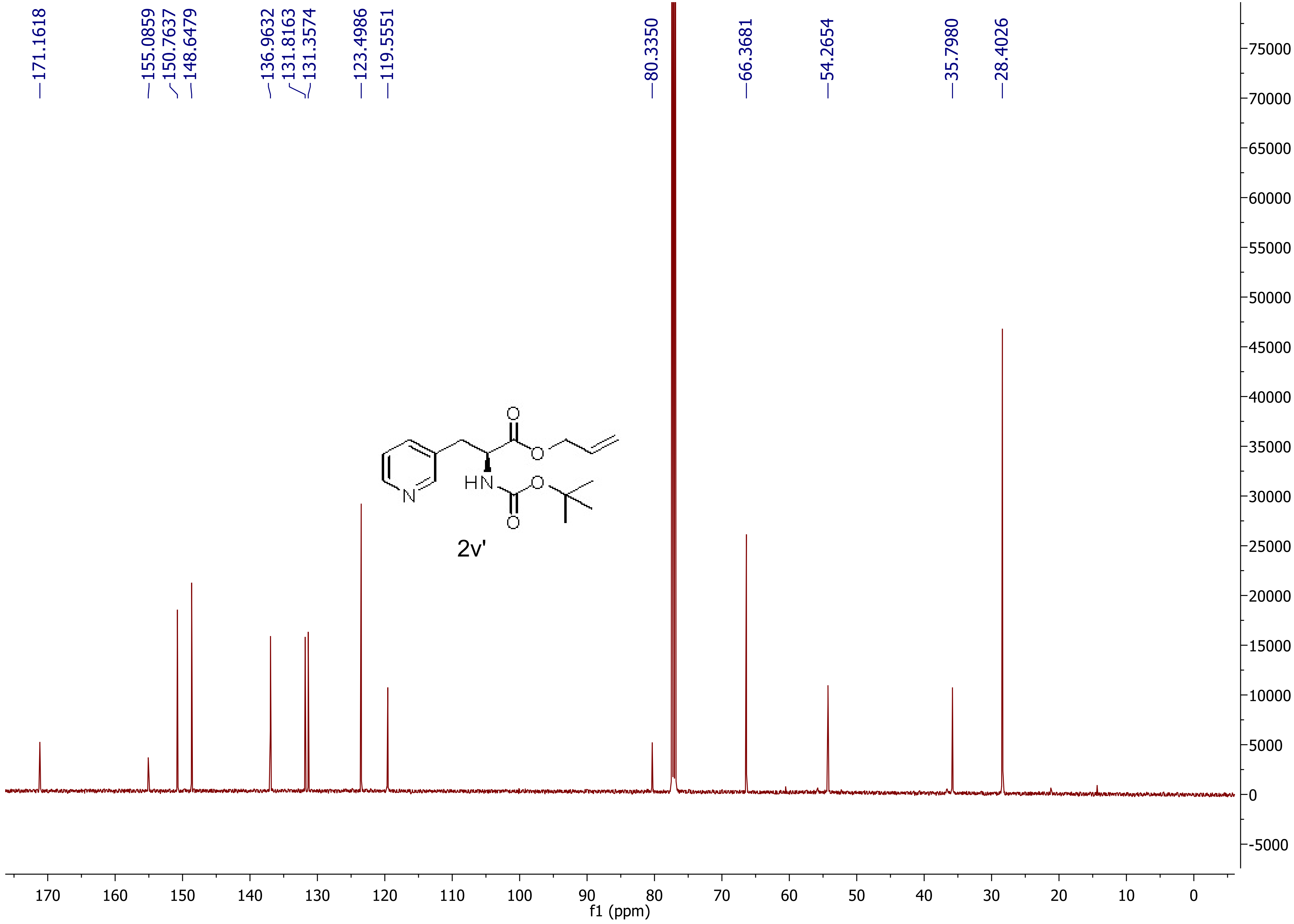


NHBoc
O
O
S
2t'
0.94
0.98
2.00
0.93
1.00
1.99
0.85
0.89
2.18
1.94
7.53
1.56
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
45000
40000
35000
30000
25000
20000
15000
10000
5000
0

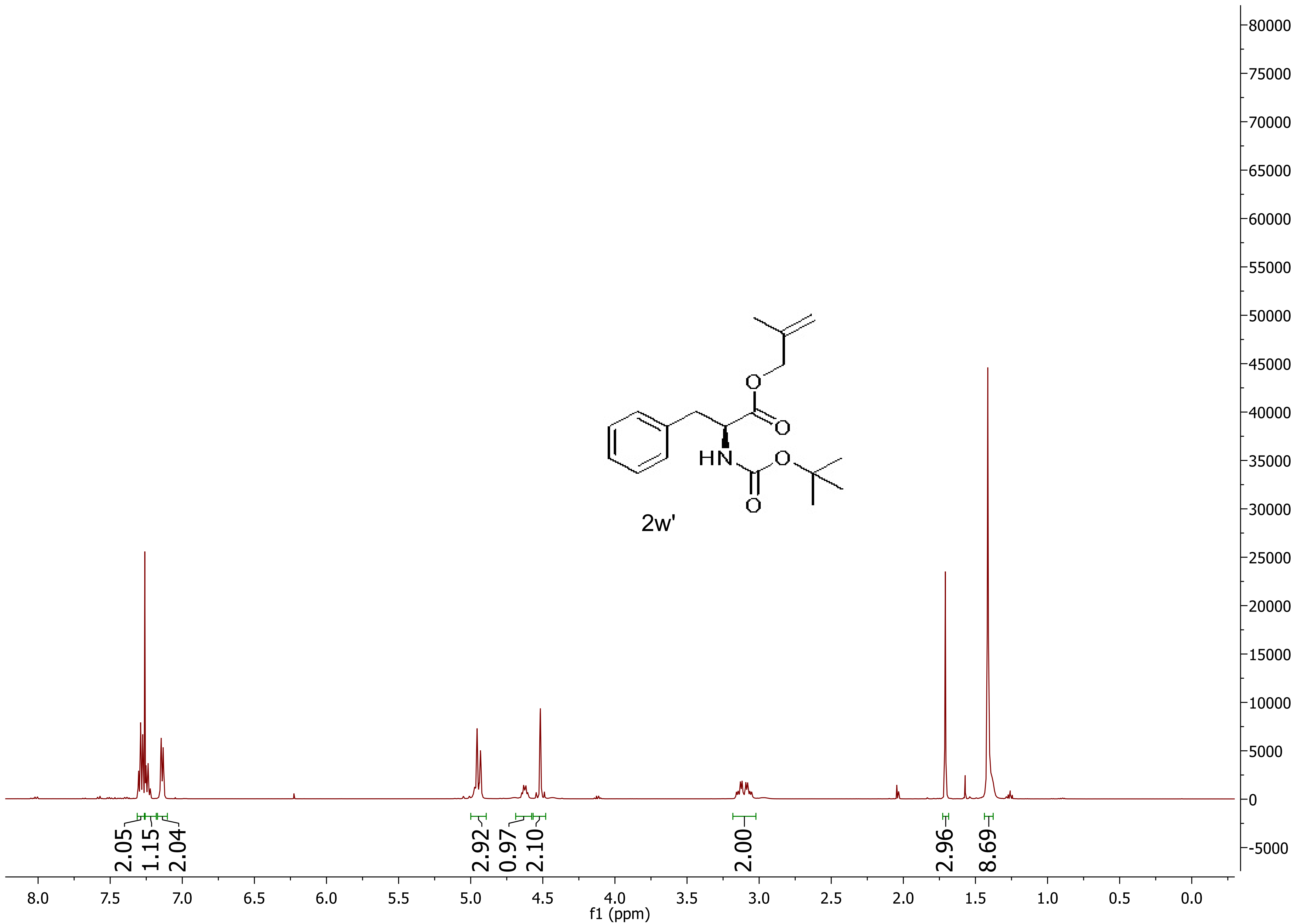

171.6885
155.1911
140.3844
139.1052
131.4670
130.9545
124.5106
124.2299
124.0231
122.9544
121.8288
119.1771
80.1884
66.2522
53.8160
31.3548
28.4555
28.1281
O
O
NHBoc
S
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

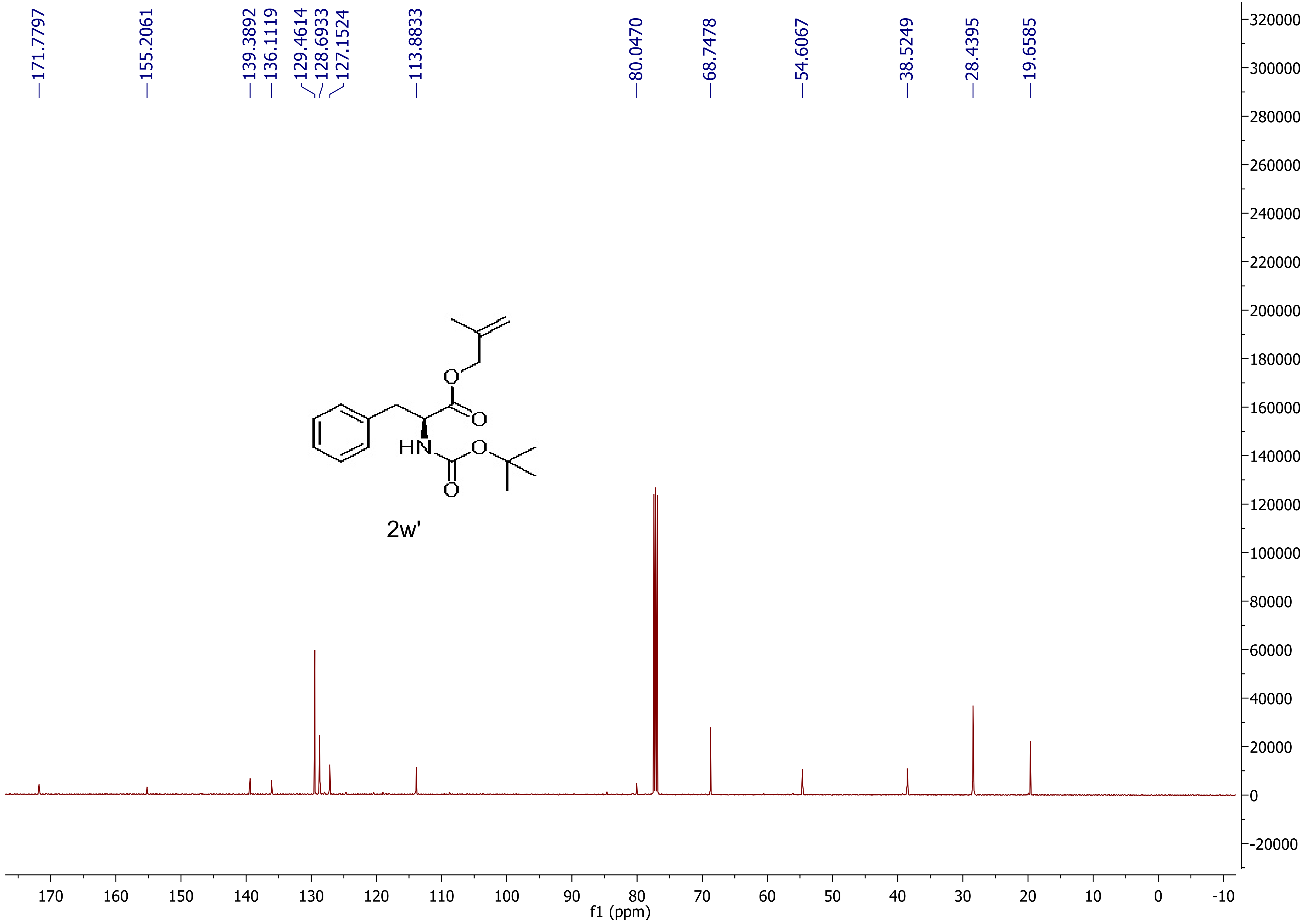
2t'

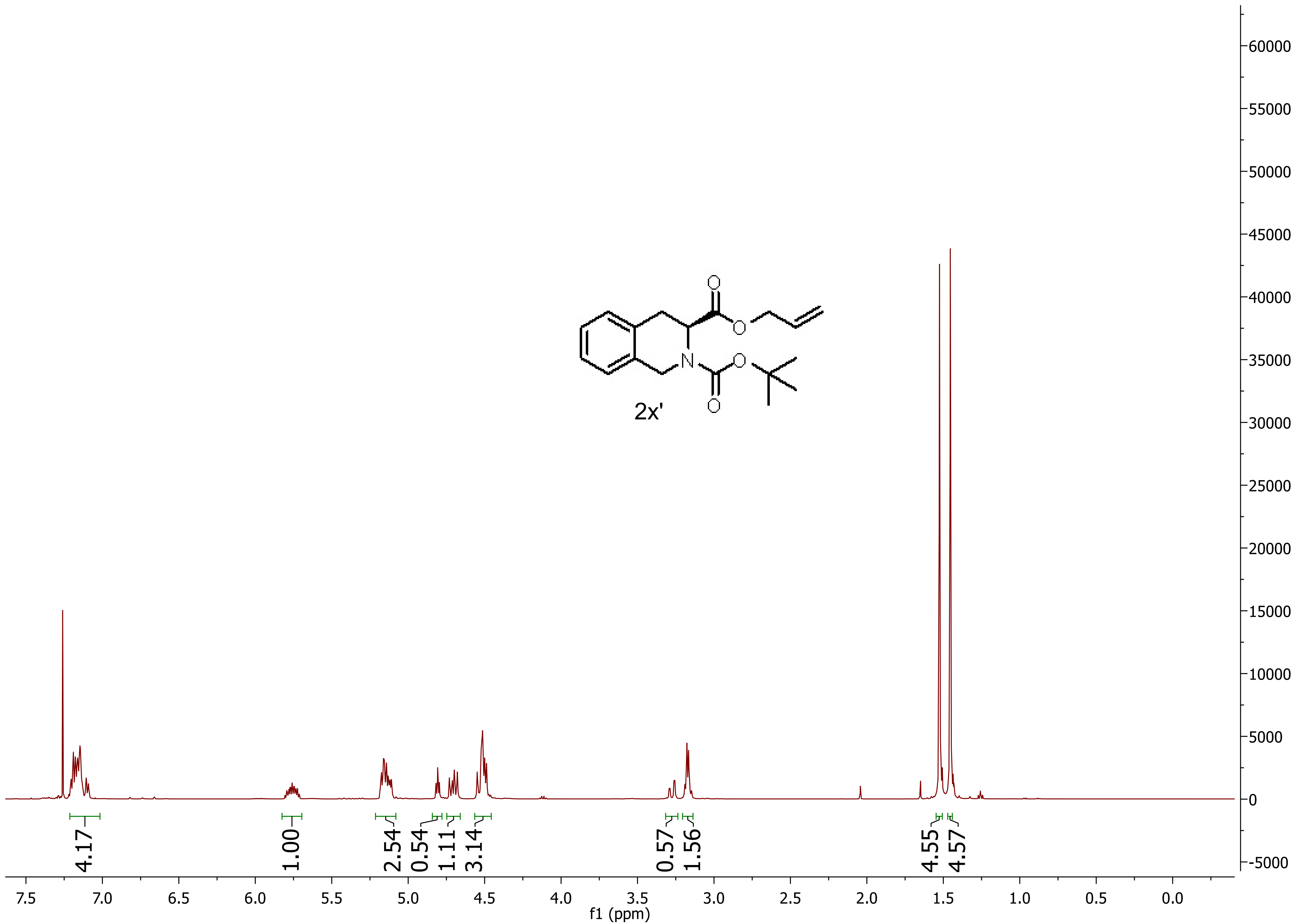

2v'
O
O
HN
N
1.02
1.00
1.07
1.04
1.00
2.02
0.86
2.93
1.11
1.10
8.97
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

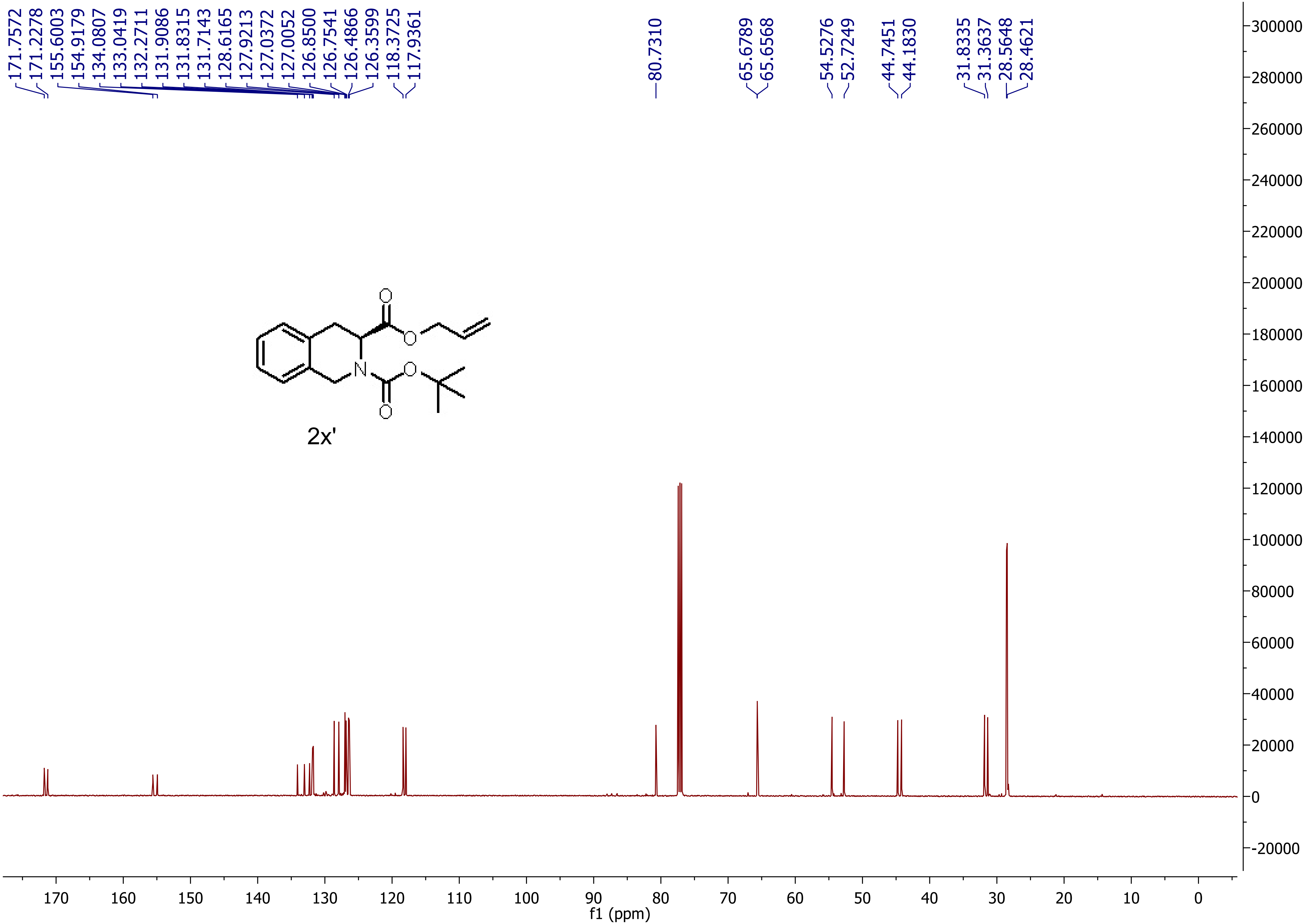


171.1618
155.0859
150.7637
148.6479
136.9632
131.8163
131.3574
123.4986
119.5551
80.3350
66.3681
54.2654
35.7980
28.4026
2v'
f1 (ppm)

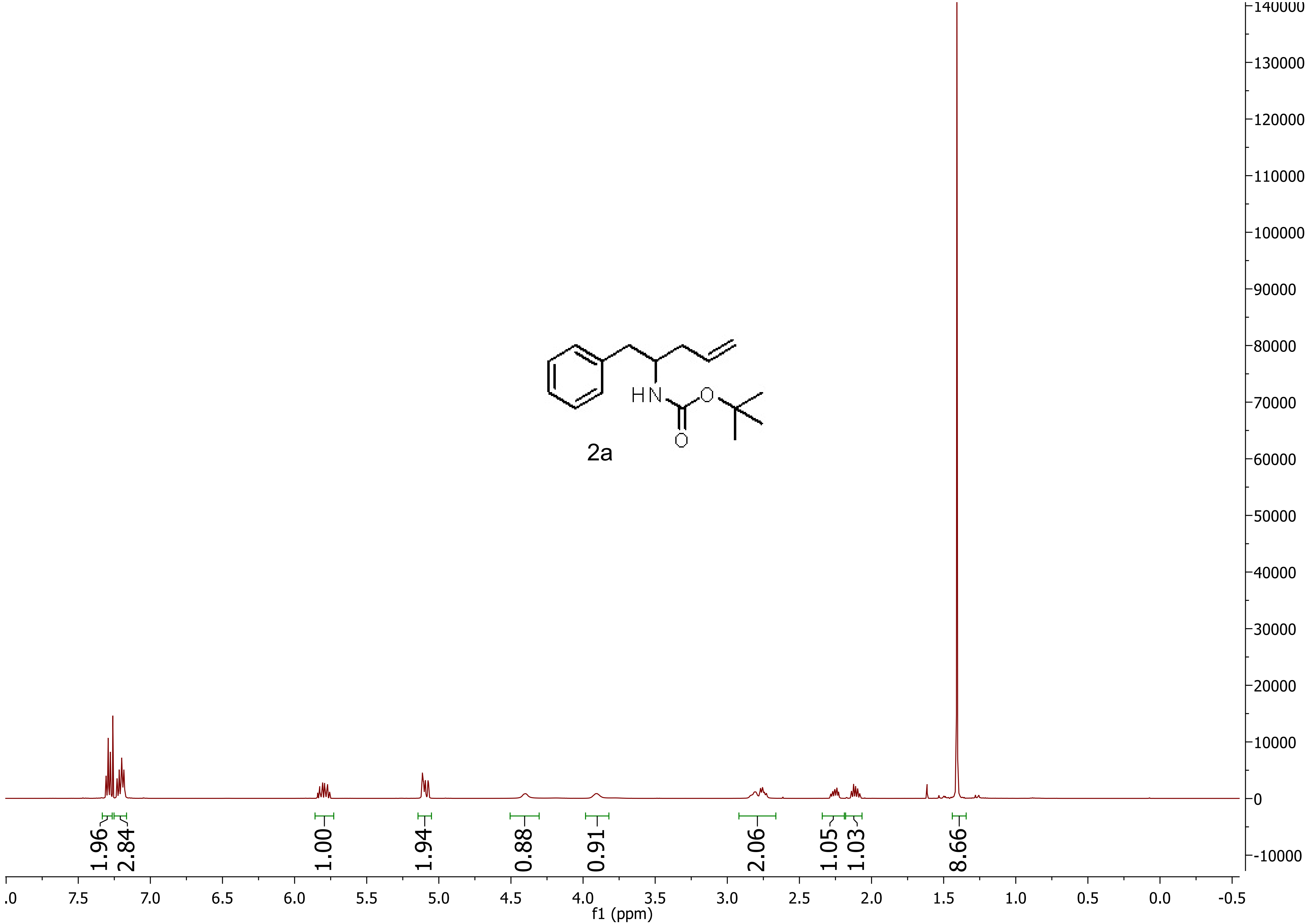

2w'
HN
O
2.05
1.15
2.04
2.92
0.97
2.10
2.00
2.96
8.69
f1 (ppm)


171.7797
155.2061
139.3892
136.1119
129.4614
128.6933
127.1524
113.8833
80.0470
68.7478
54.6067
38.5249
28.4395
19.6585
2w'
HN
O
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
320000 300000 280000 260000 240000 220000 200000 180000 160000 140000 120000 100000 80000 60000 40000 20000 0 -20000

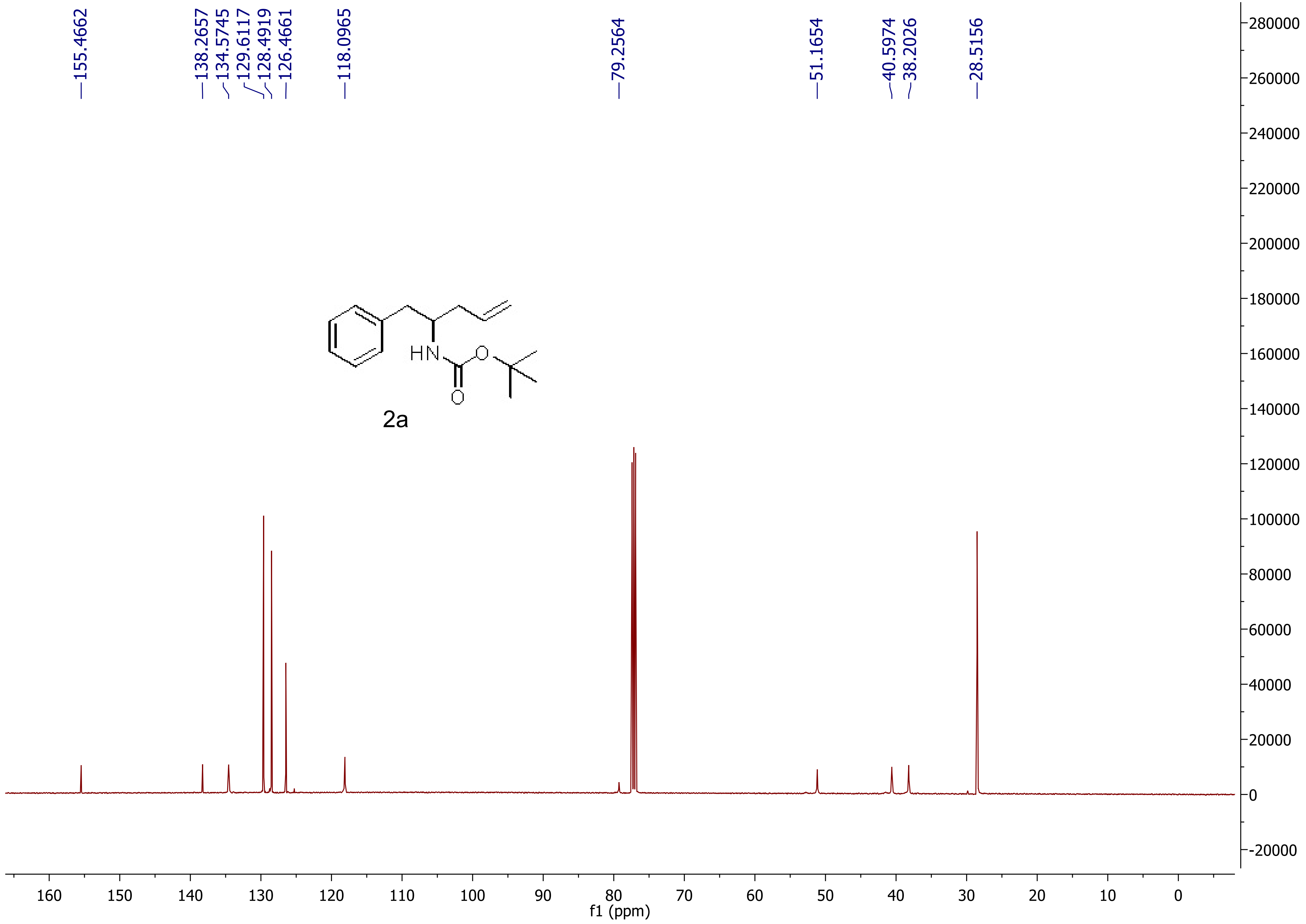

2x'
4.17
1.00
2.54
0.54
1.11
3.14
0.57
1.56
4.55
4.57
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

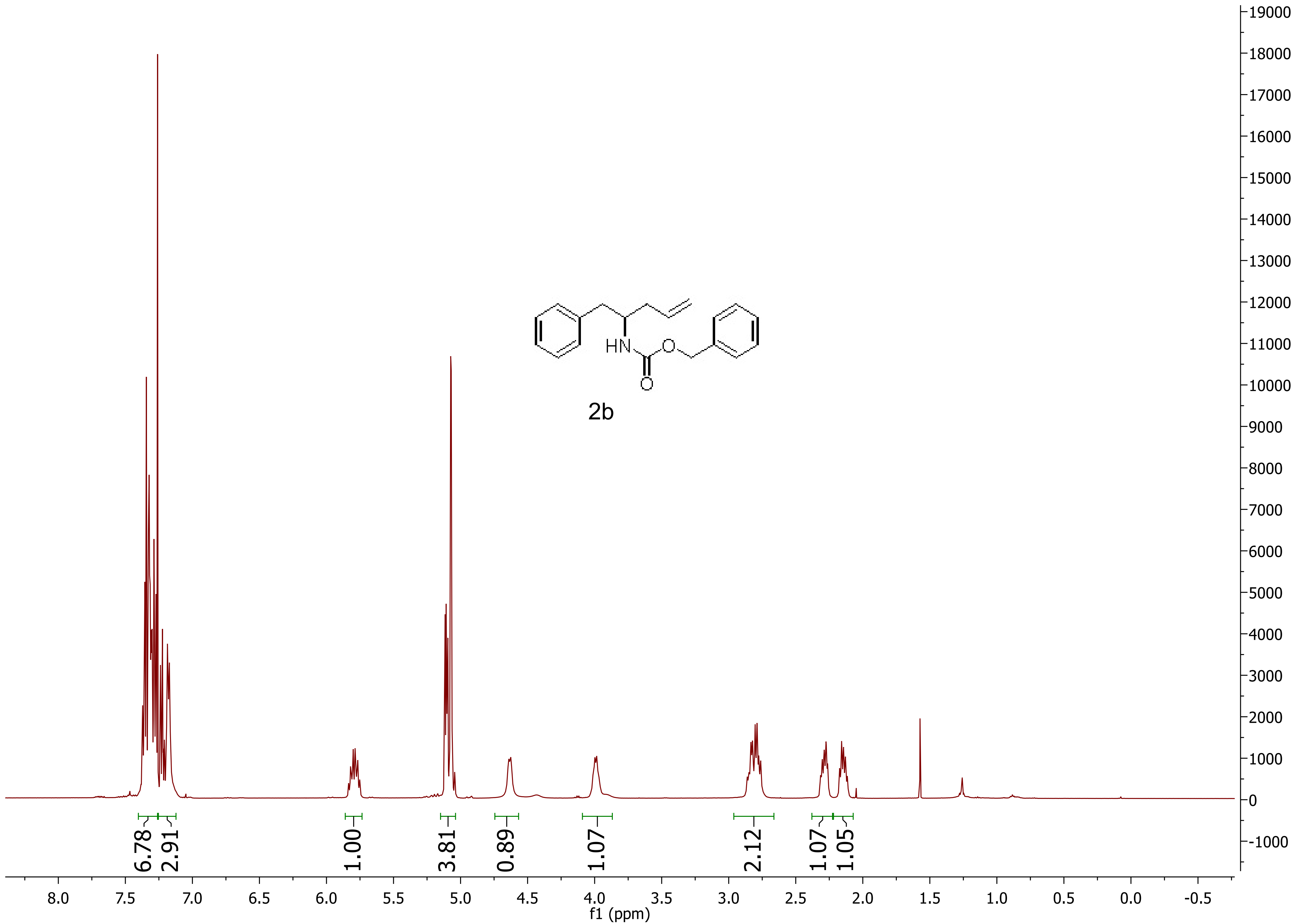

171.7572
171.2278
155.6003
154.9179
134.0807
133.0419
132.2711
131.9086
131.8315
131.7143
128.6165
127.9213
127.0372
127.0052
126.8500
126.7541
126.4866
126.3599
118.3725
117.9361
80.7310
65.6789
65.6568
54.5276
52.7249
44.7451
44.1830
31.8335
31.3637
28.5648
28.4621
2x'
f1 (ppm)

Product NMRs

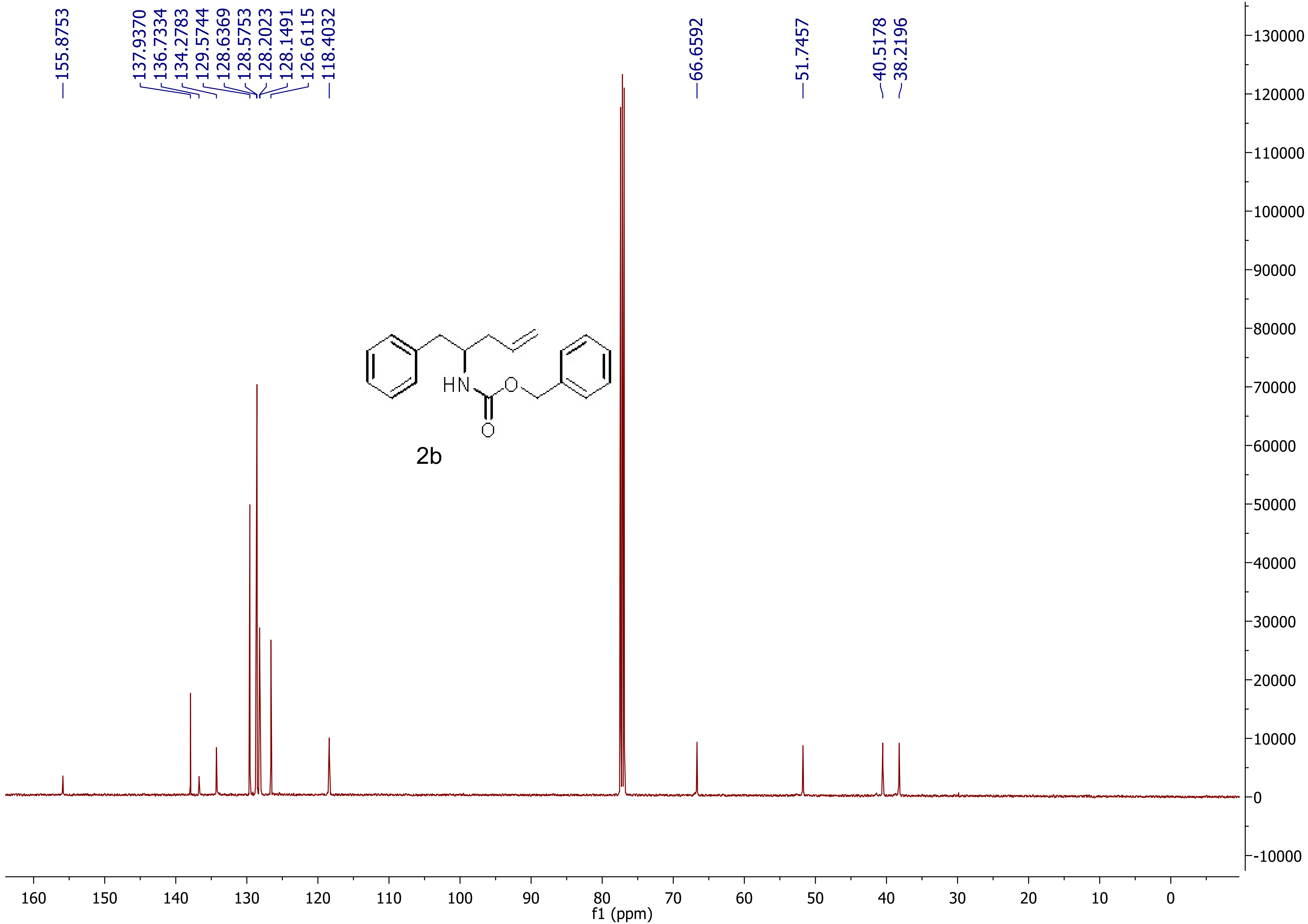


2a
HN
O
O
1.96
2.84
1.00
1.94
0.88
0.91
2.06
1.05
1.03
8.66
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000

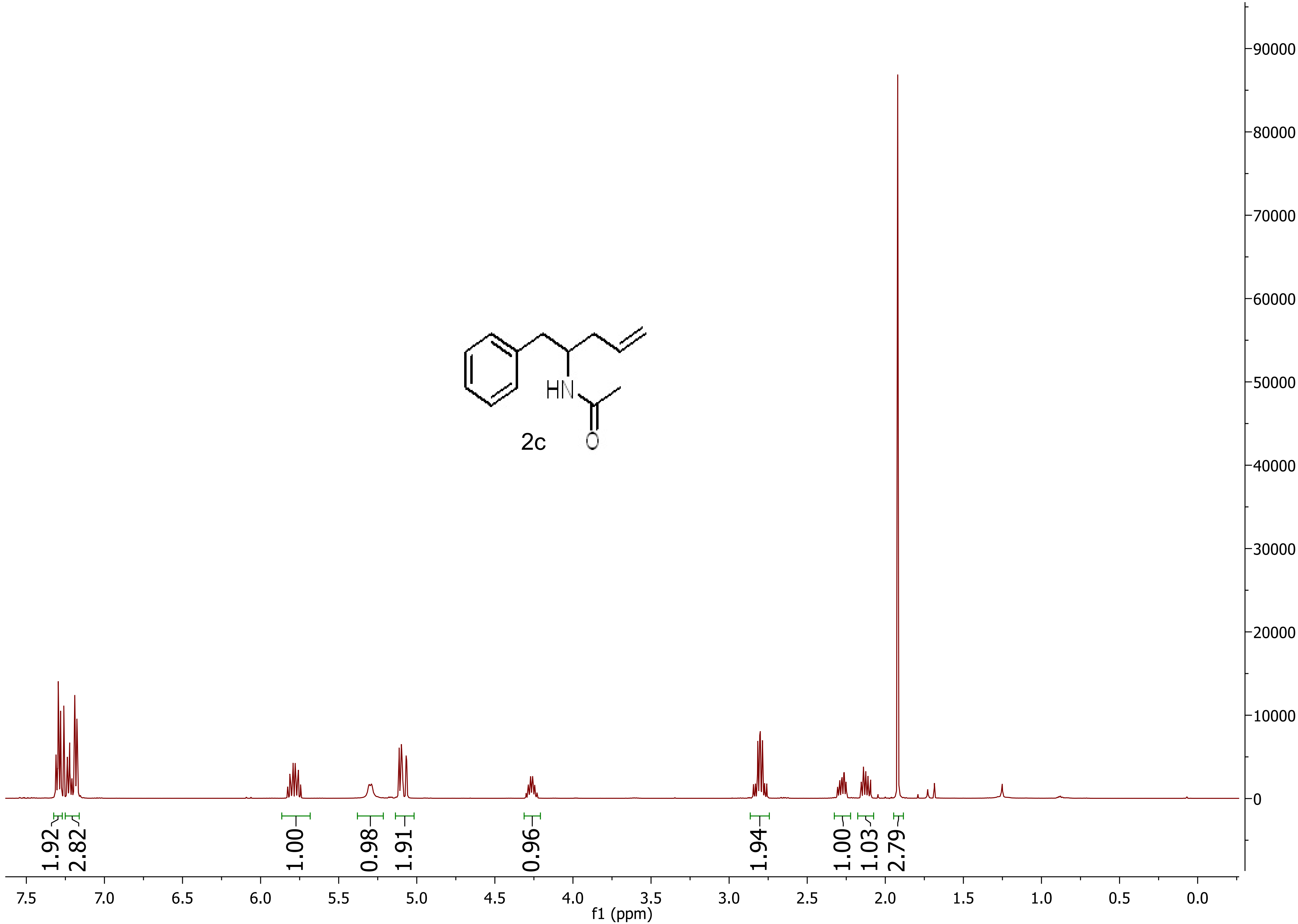

155.4662
138.2657
134.5745
129.6117
128.4919
126.4661
118.0965
79.2564
51.1654
40.5974
38.2026
28.5156
HN
O
O
2a
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



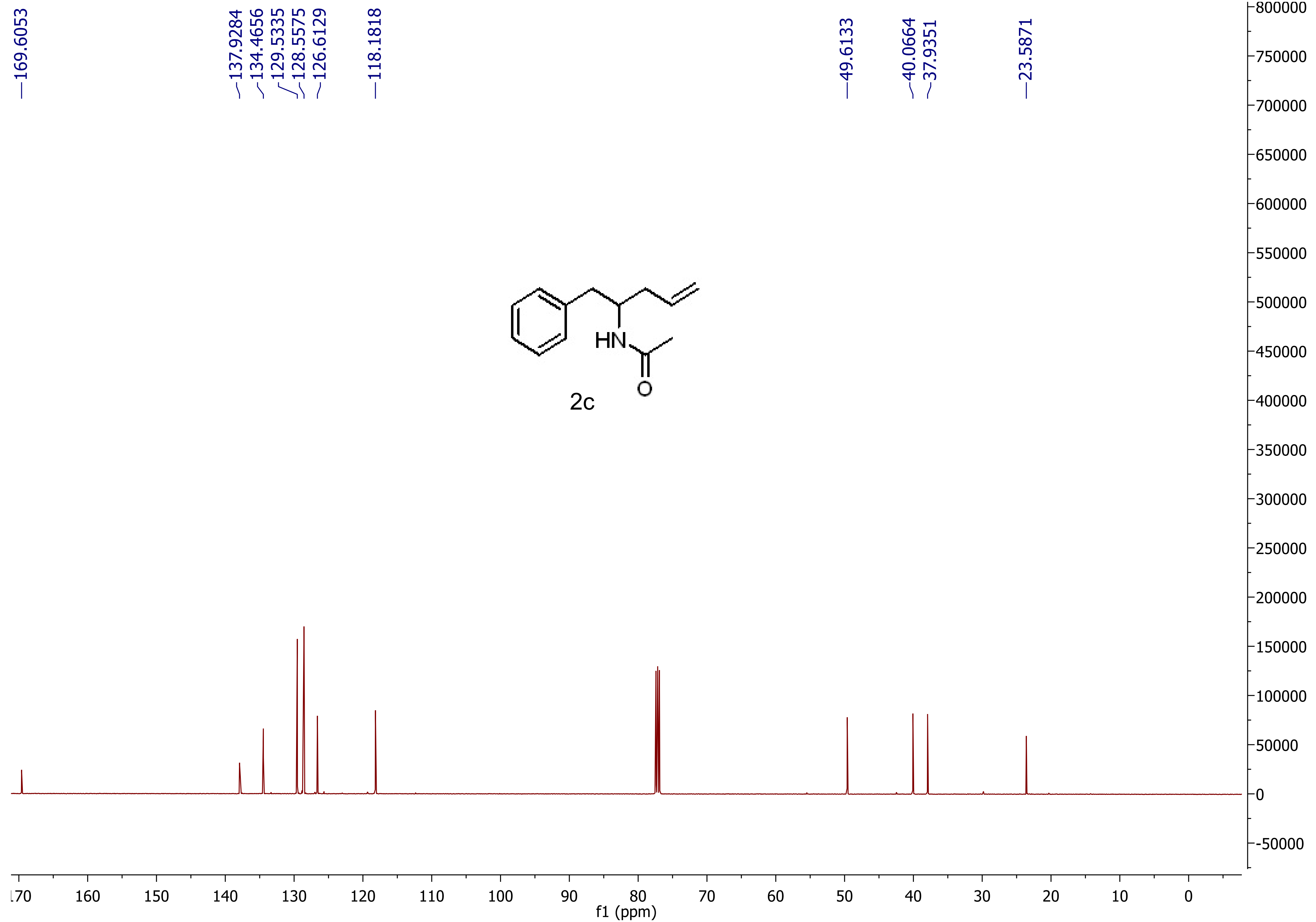
2b
HN
O
O
6.78
2.91
1.00
3.81
0.89
1.07
2.12
1.07
1.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

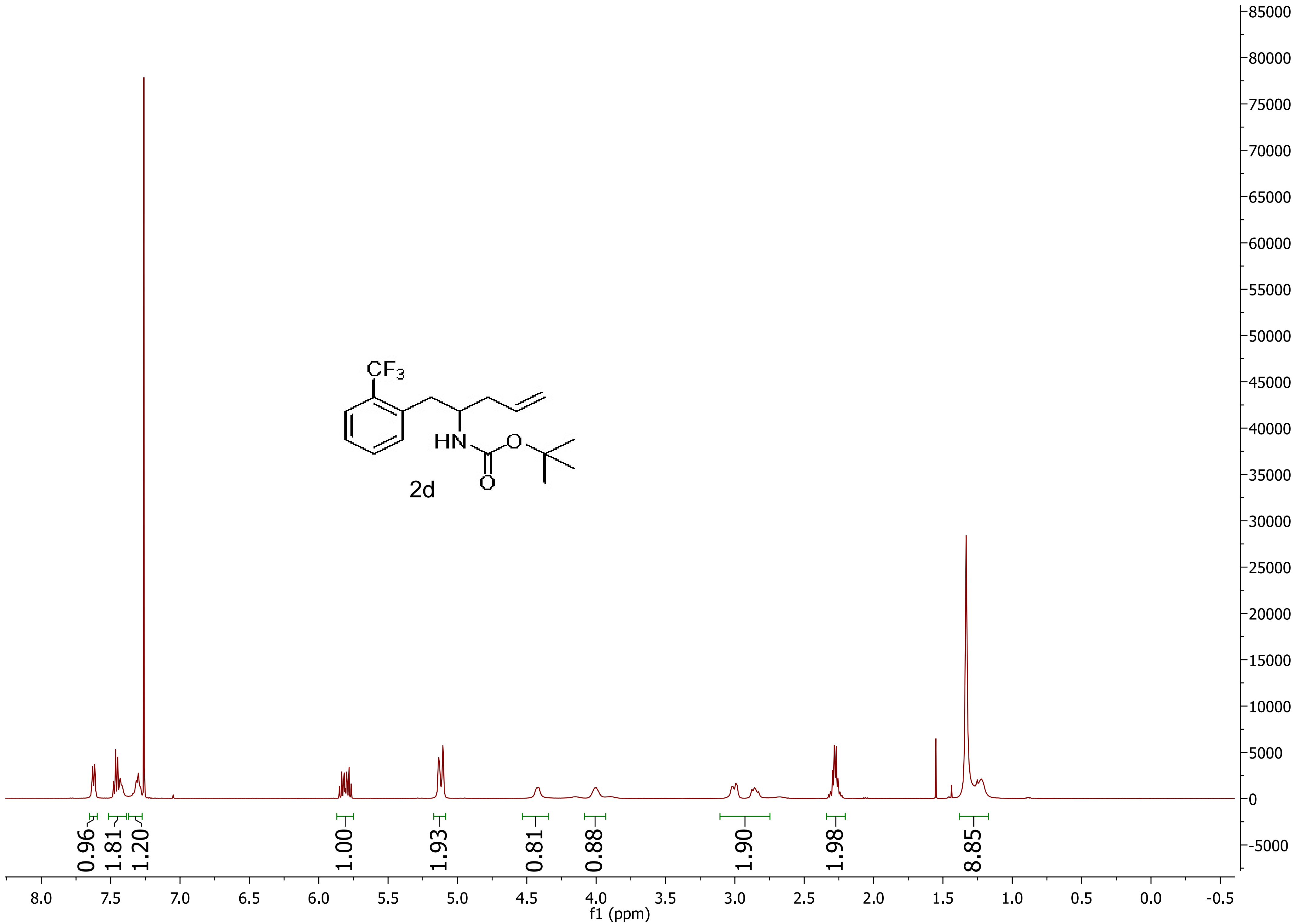


155.8753
137.9370
136.7334
134.2783
129.5744
128.6369
128.5753
128.2023
128.1491
126.6115
118.4032
66.6592
51.7457
40.5178
38.2196
HN
O
O
2b
f1 (ppm)

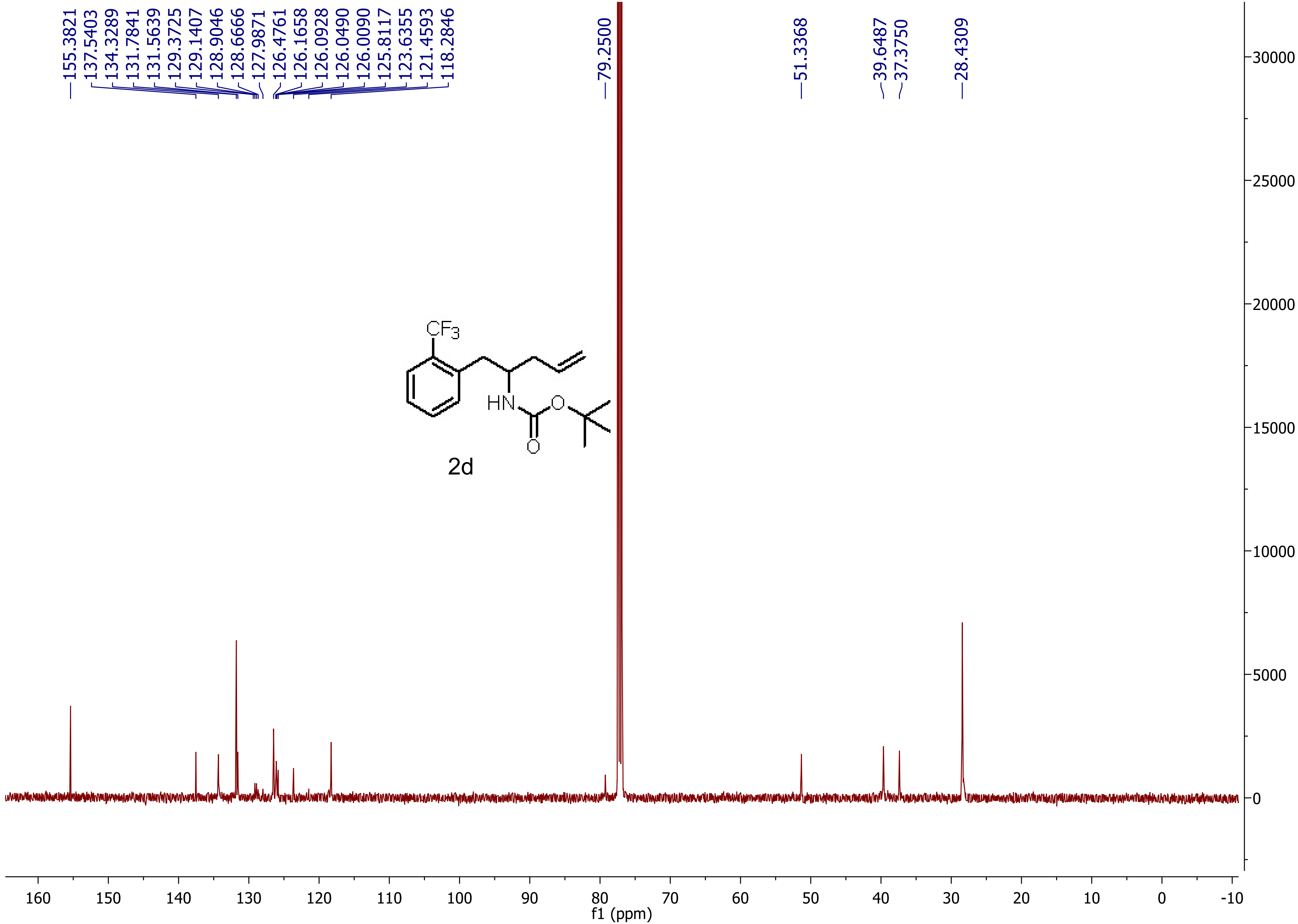


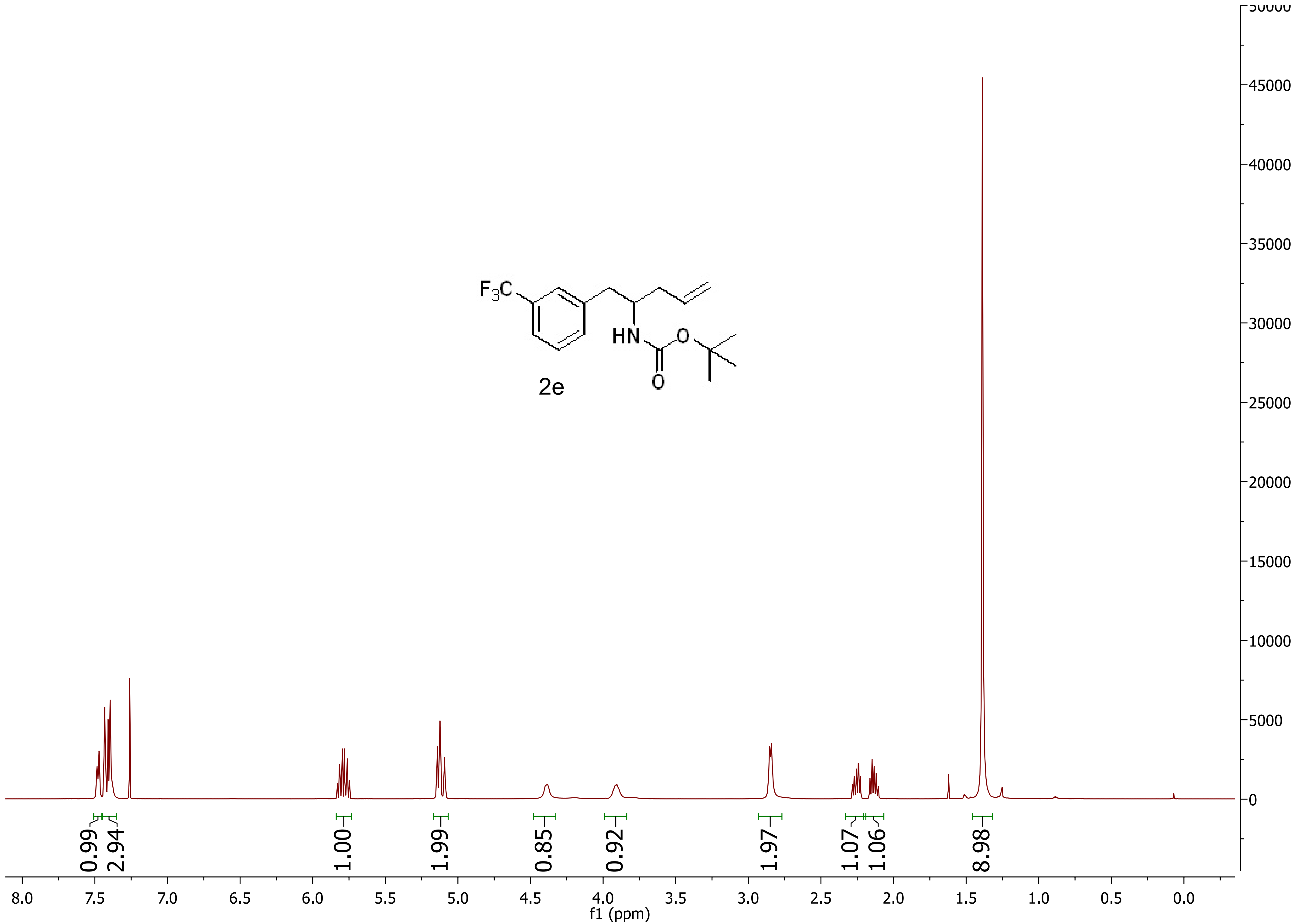
2c
HN
O
1.92
2.82
1.00
0.98
1.91
0.96
1.94
1.00
1.03
2.79
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
90000
80000
70000
60000
50000
40000
30000
20000
10000
0


169.6053
137.9284
134.4656
129.5335
128.5575
126.6129
118.1818
49.6133
40.0664
37.9351
23.5871
HN
O
2c
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

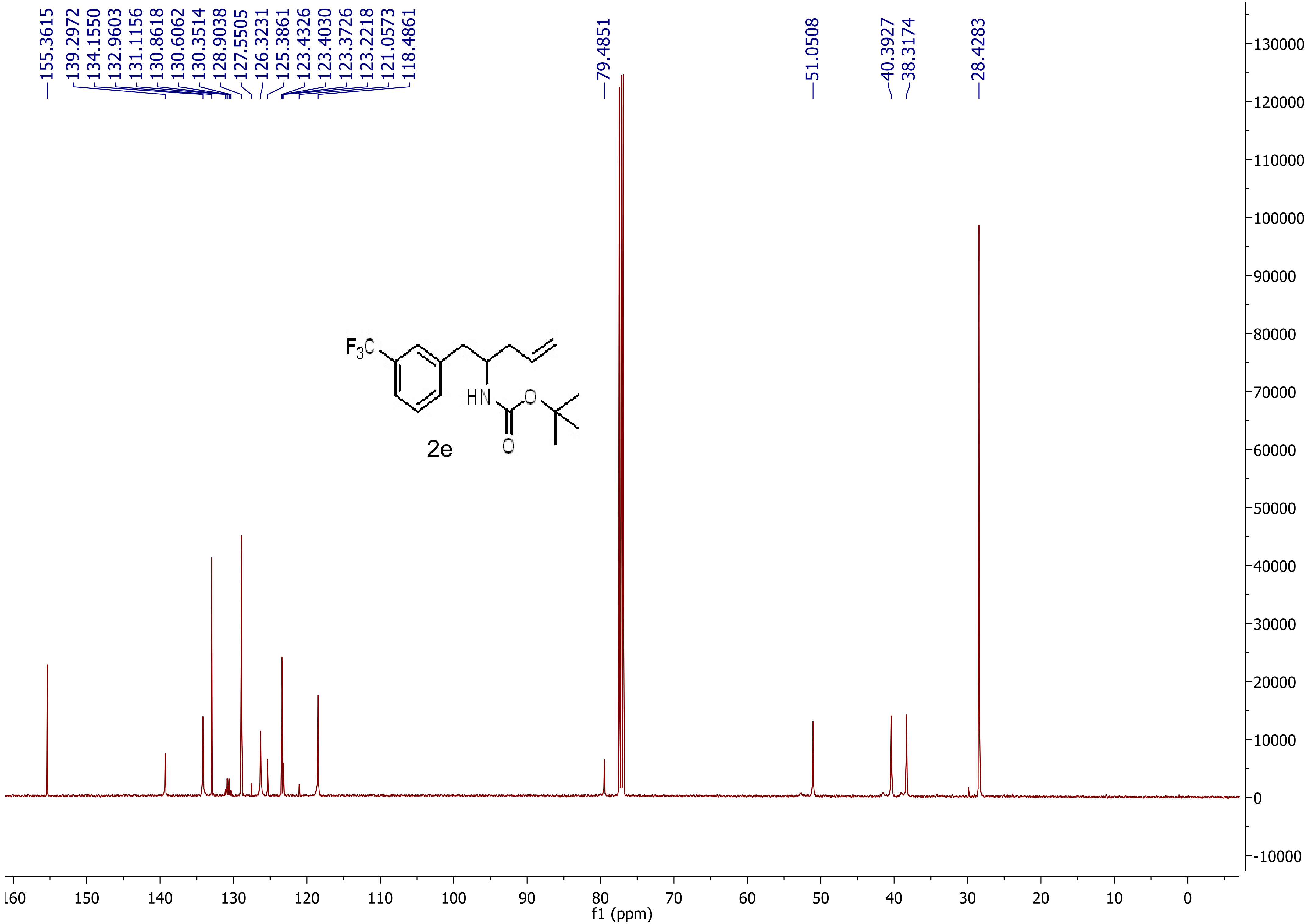


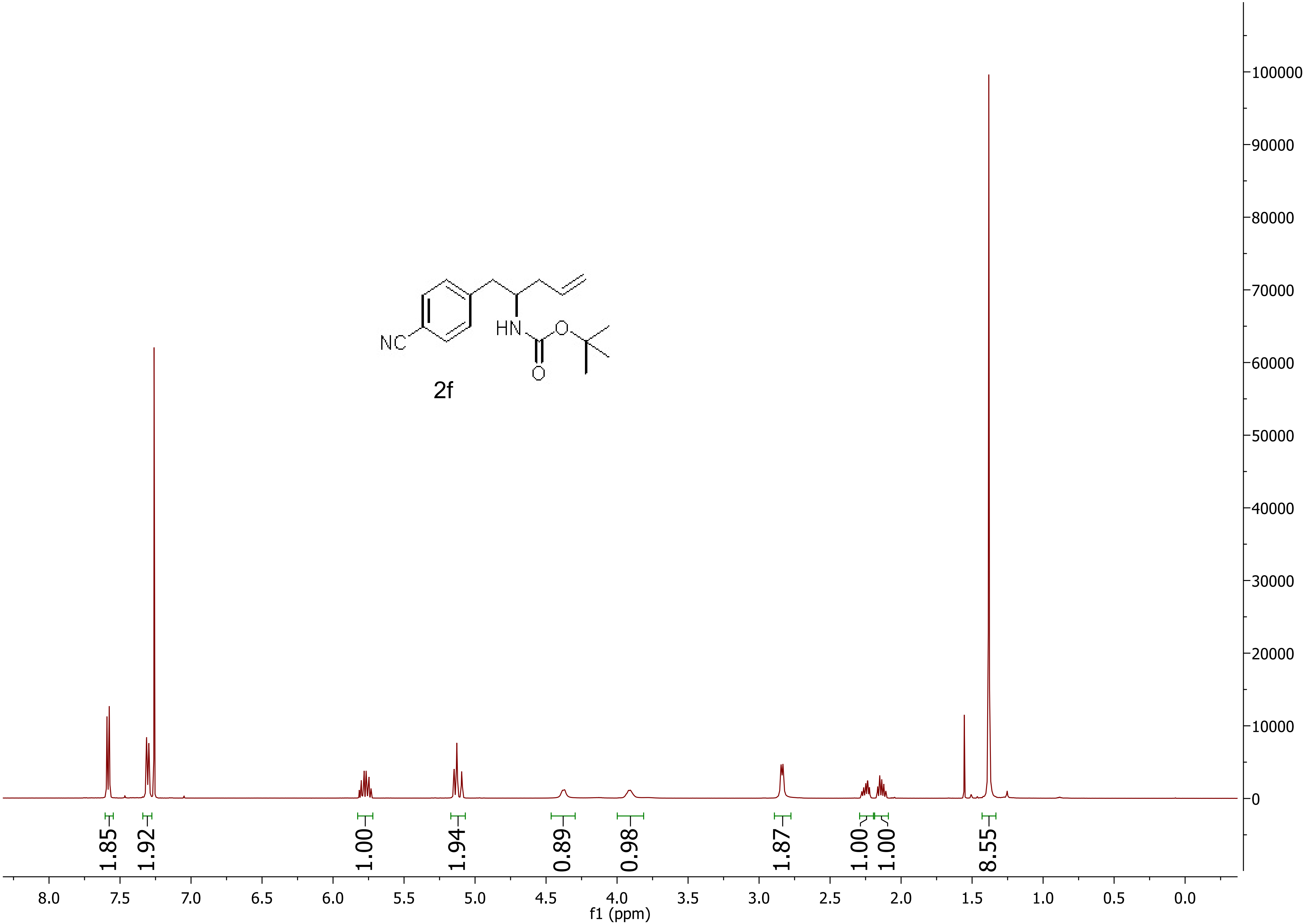
CF3
HN
O
O
2d
0.96
1.81
1.20
1.00
1.93
0.81
0.88
1.90
1.98
8.85
f1 (ppm)

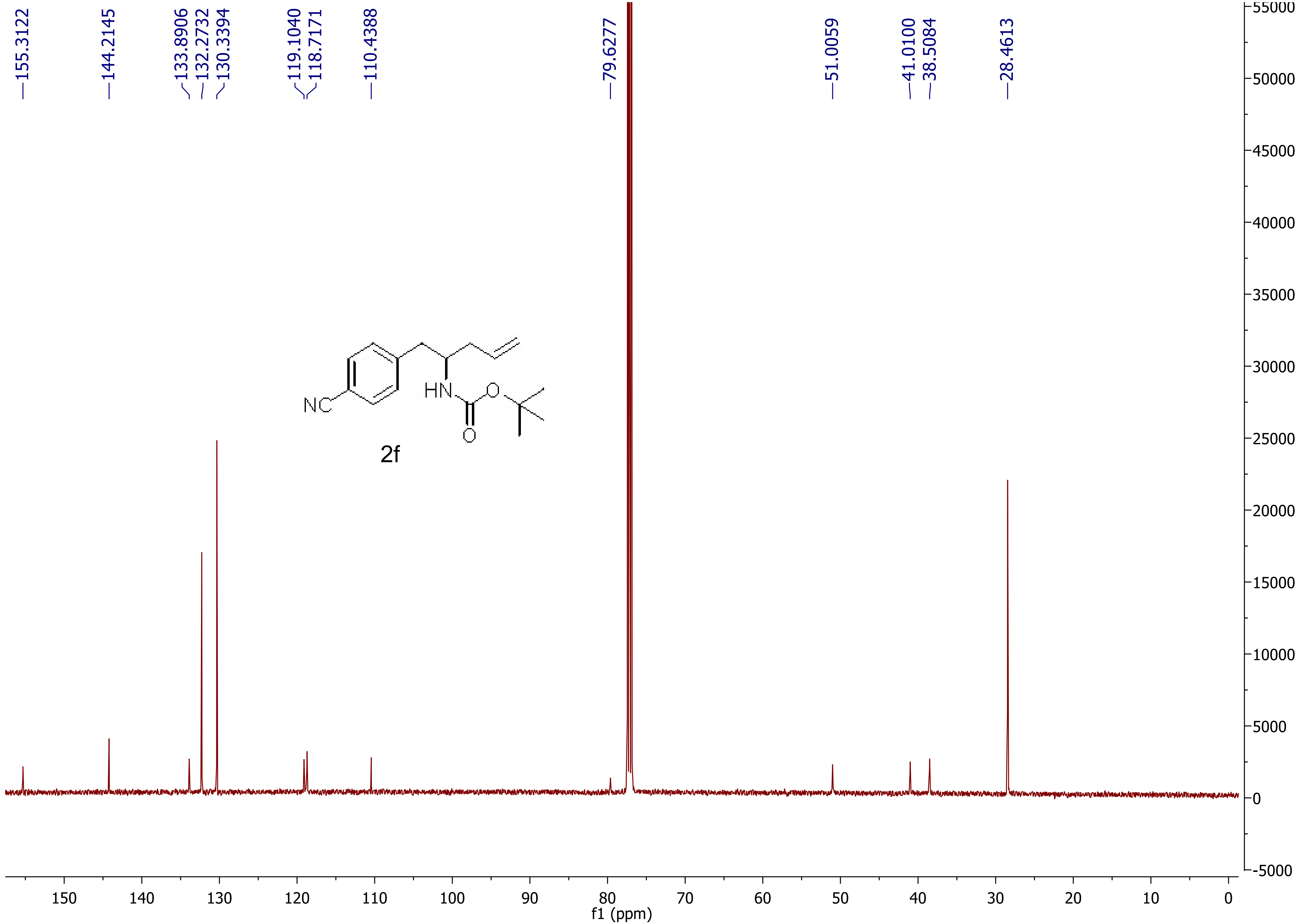

155.3821
137.5403
134.3289
131.7841
131.5639
129.3725
129.1407
128.9046
128.6666
127.9871
126.4761
126.1658
126.0928
126.0490
126.0090
125.8117
123.6355
121.4593
118.2846
79.2500
51.3368
39.6487
37.3750
28.4309
CF3
HN
O
O
2d
30000
25000
20000
15000
10000
5000
0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



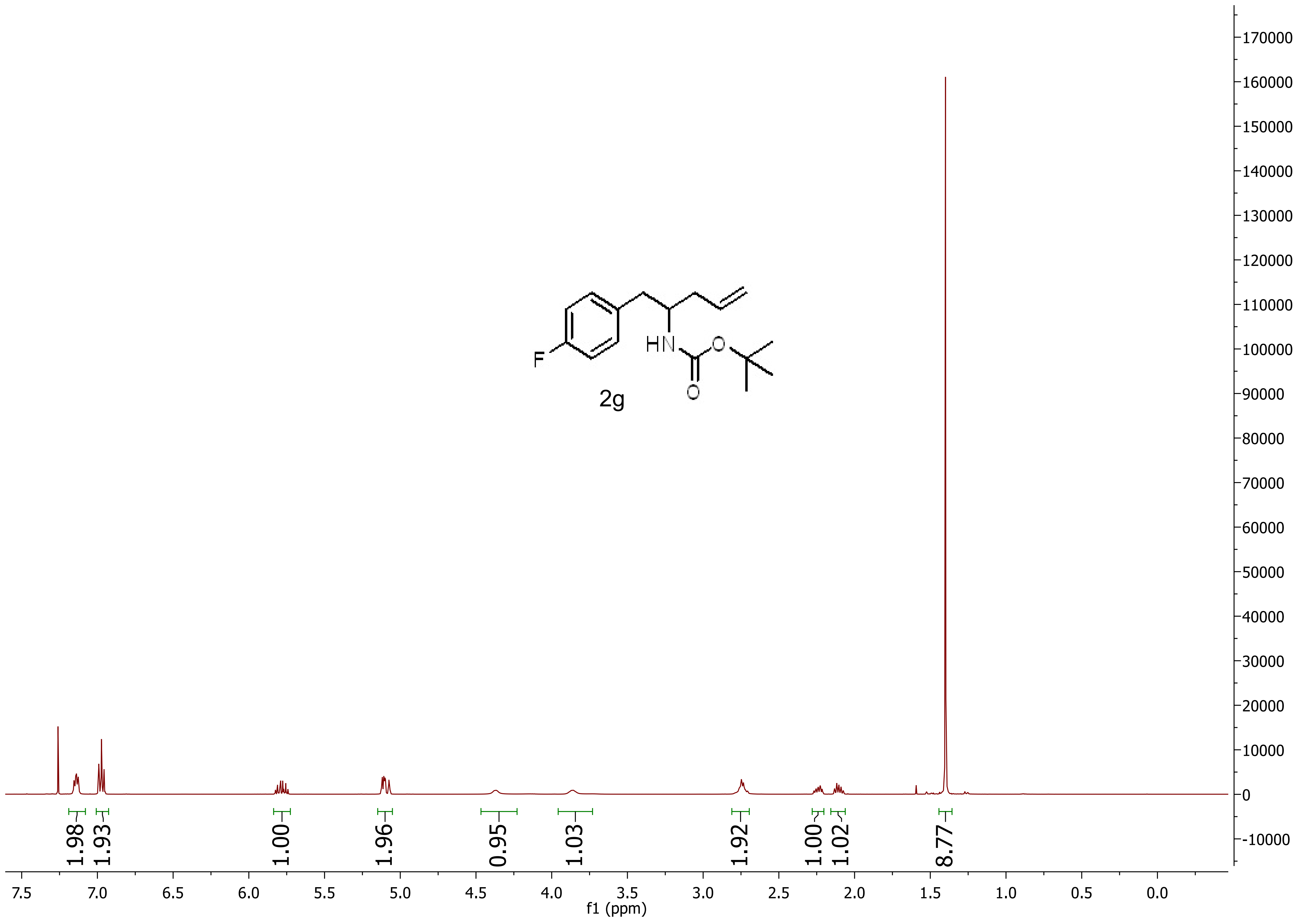
F3C
HN
O
O
2e
0.99
2.94
1.00
1.99
0.85
0.92
1.97
1.07
1.06
8.98
f1 (ppm)

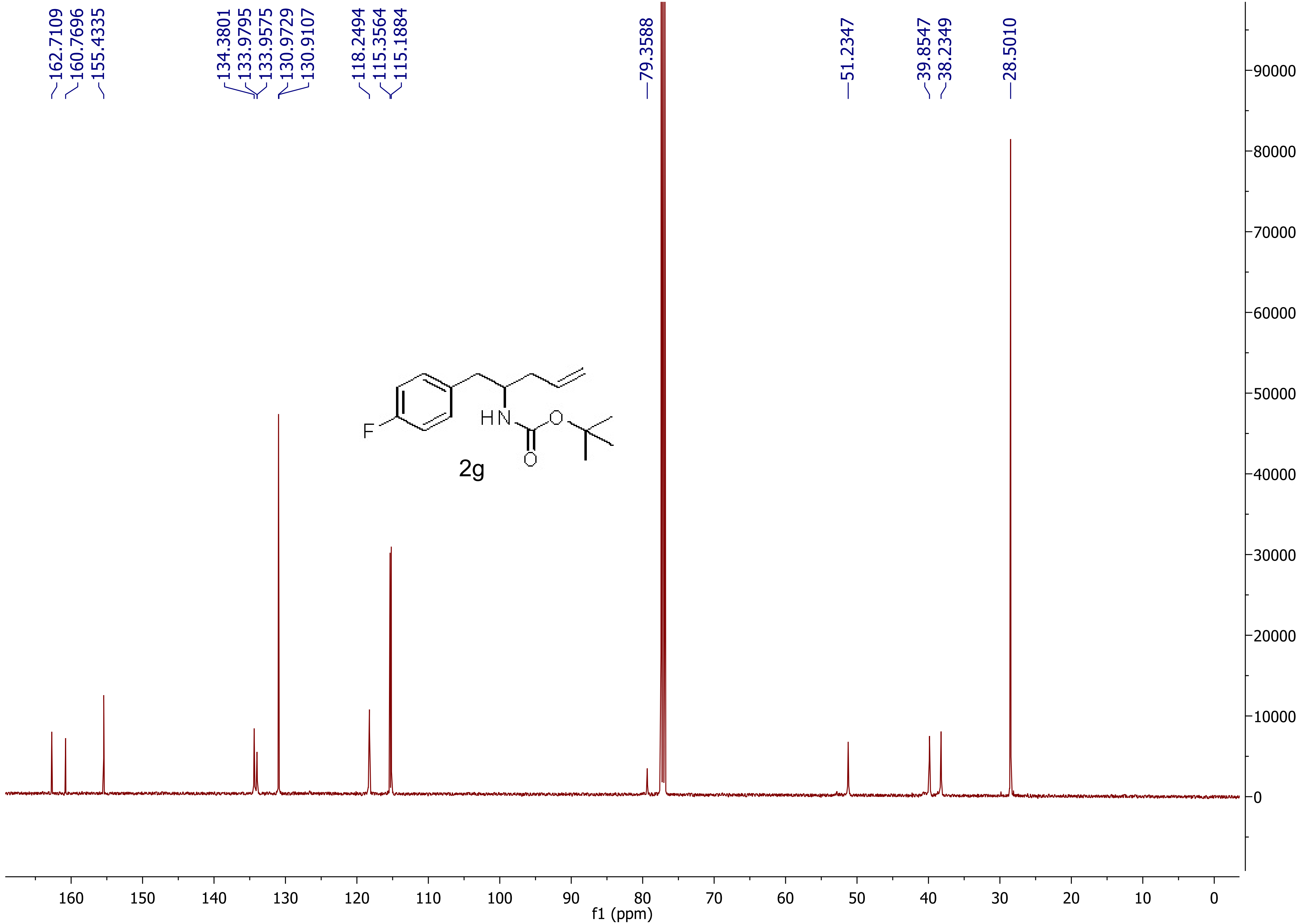

155.3615
139.2972
134.1550
132.9603
131.1156
130.8618
130.6062
130.3514
128.9038
127.5505
126.3231
125.3861
123.4326
123.4030
123.3726
123.2218
121.0573
118.4861
79.4851
51.0508
40.3927
38.3174
28.4283
F3C
HN
O
O
2e
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

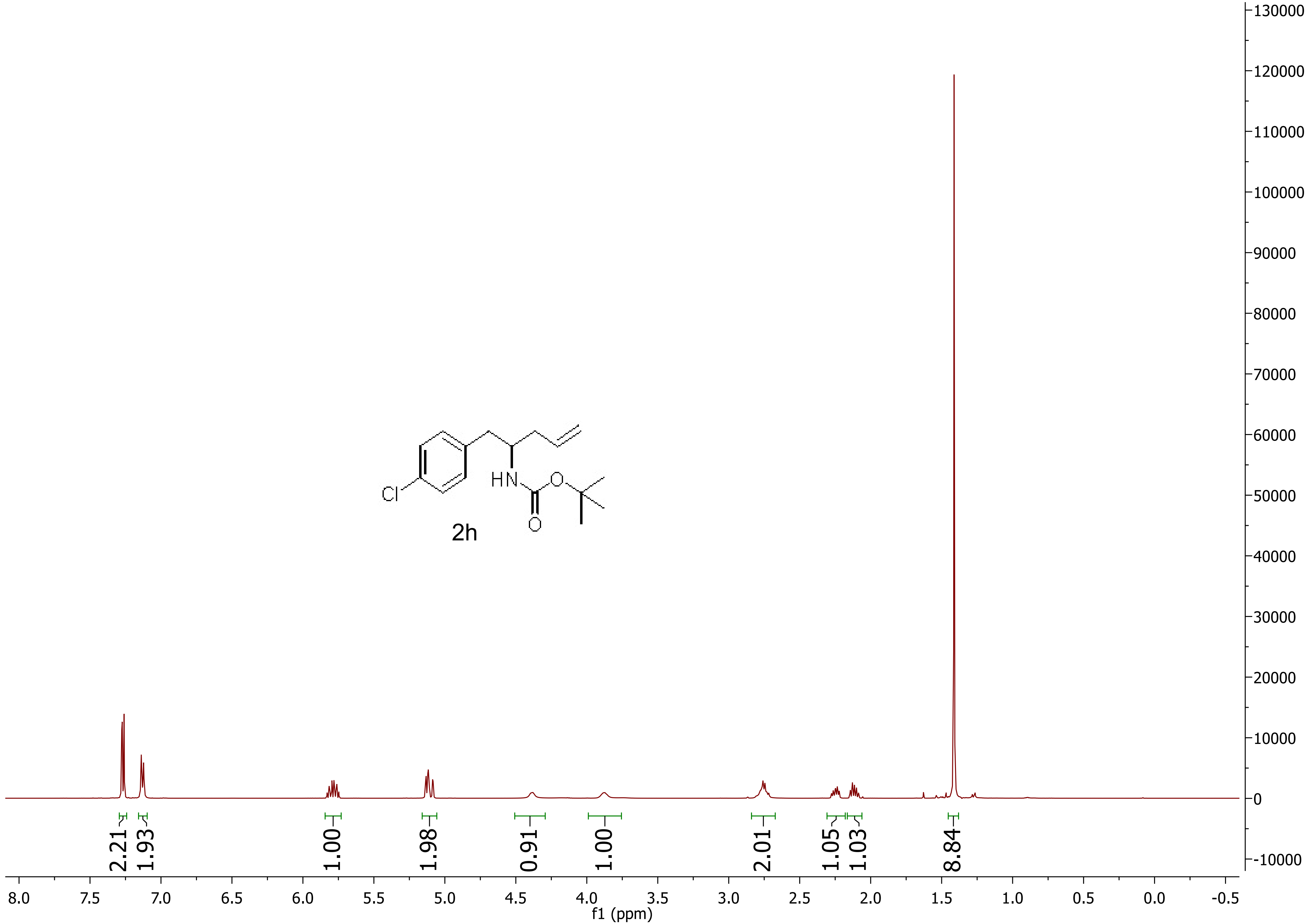

NC
HN
O
O
2f
1.85
1.92
1.00
1.94
0.89
0.98
1.87
1.00
1.00
8.55
f1 (ppm)

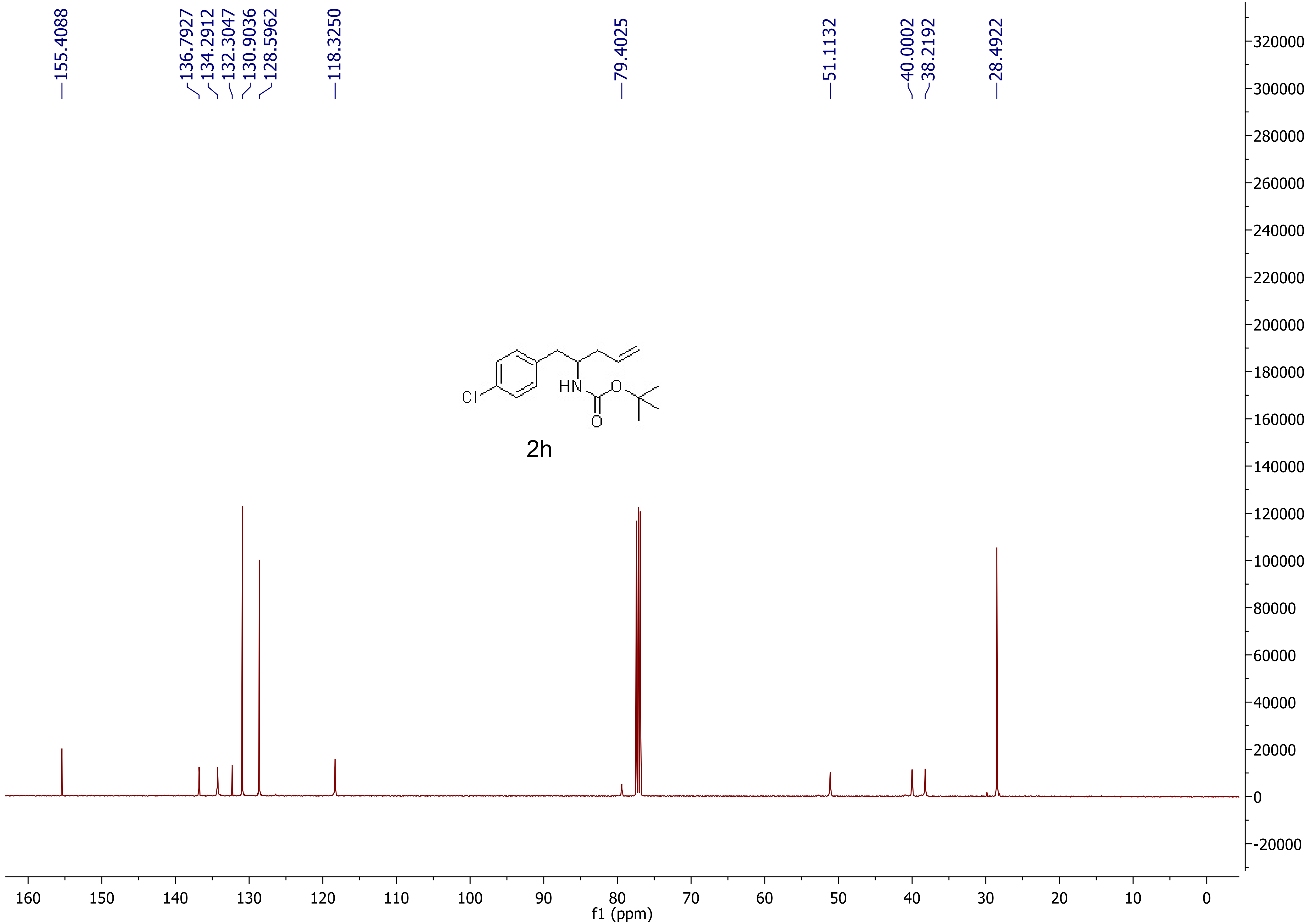


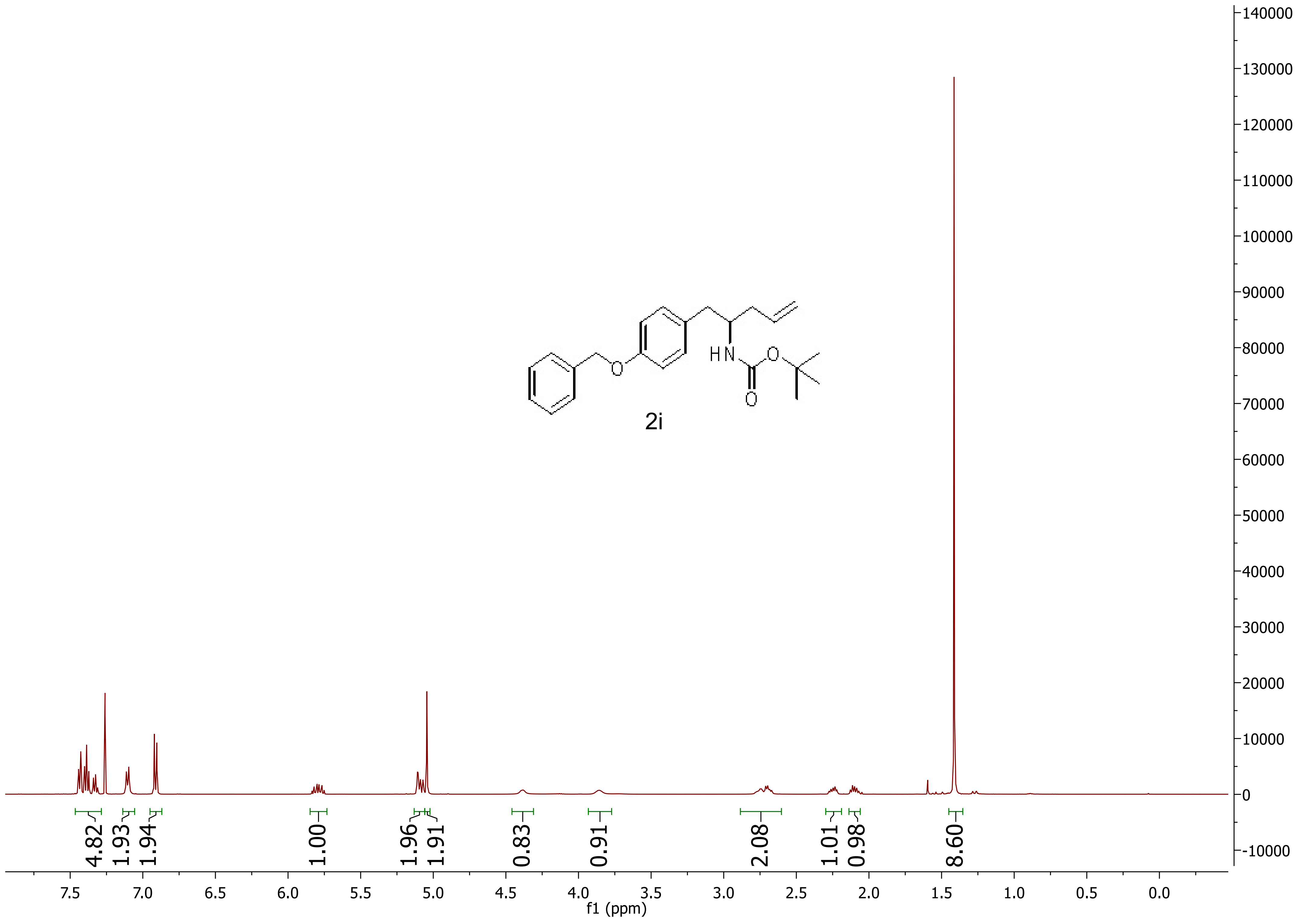
155.3122
144.2145
133.8906
132.2732
130.3394
119.1040
118.7171
110.4388
79.6277
51.0059
41.0100
38.5084
28.4613
NC
HN
O
O
2f
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

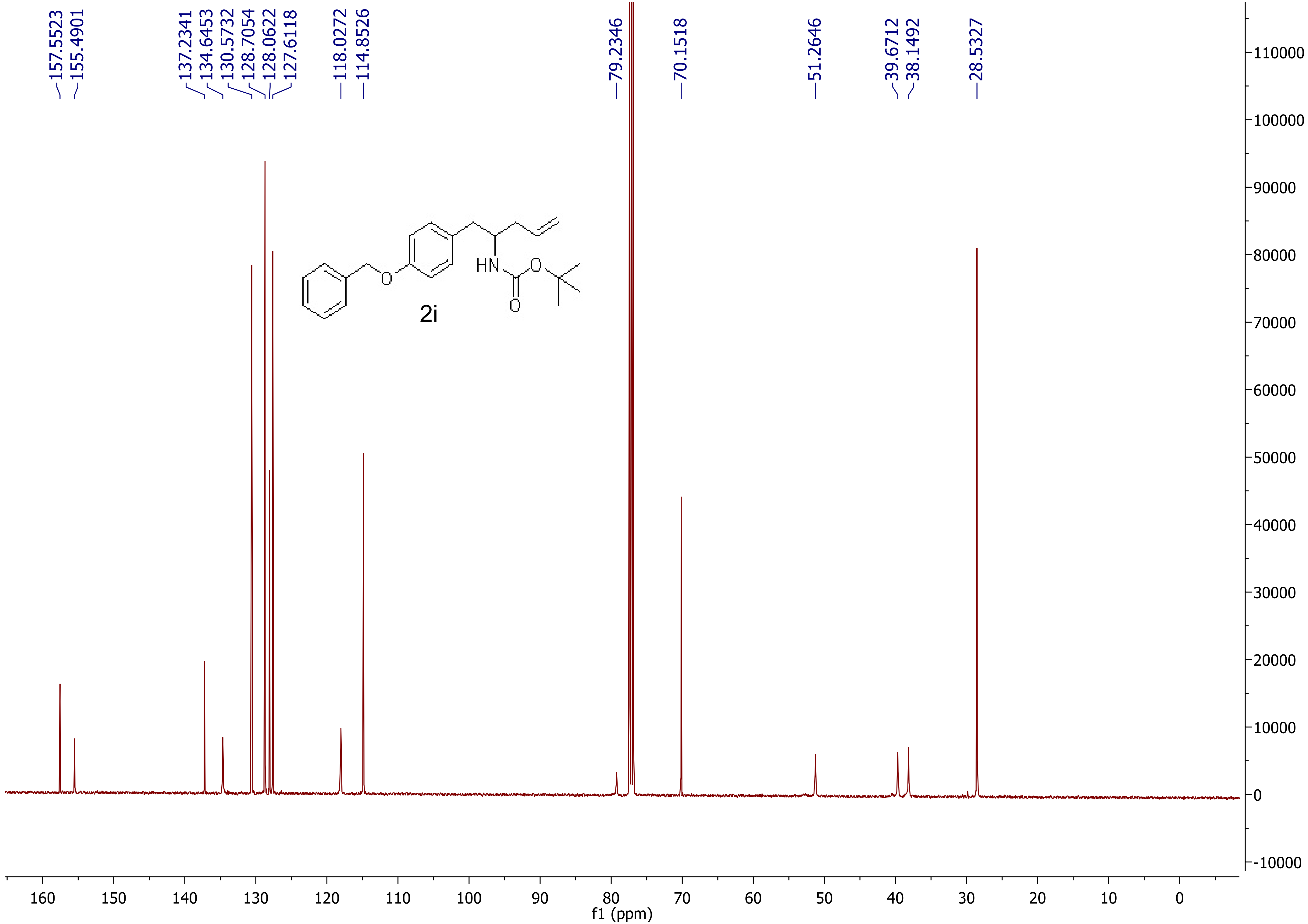

2g
F
HN
O
O
1.98
1.93
1.00
1.96
0.95
1.03
1.92
1.00
1.02
8.77
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000

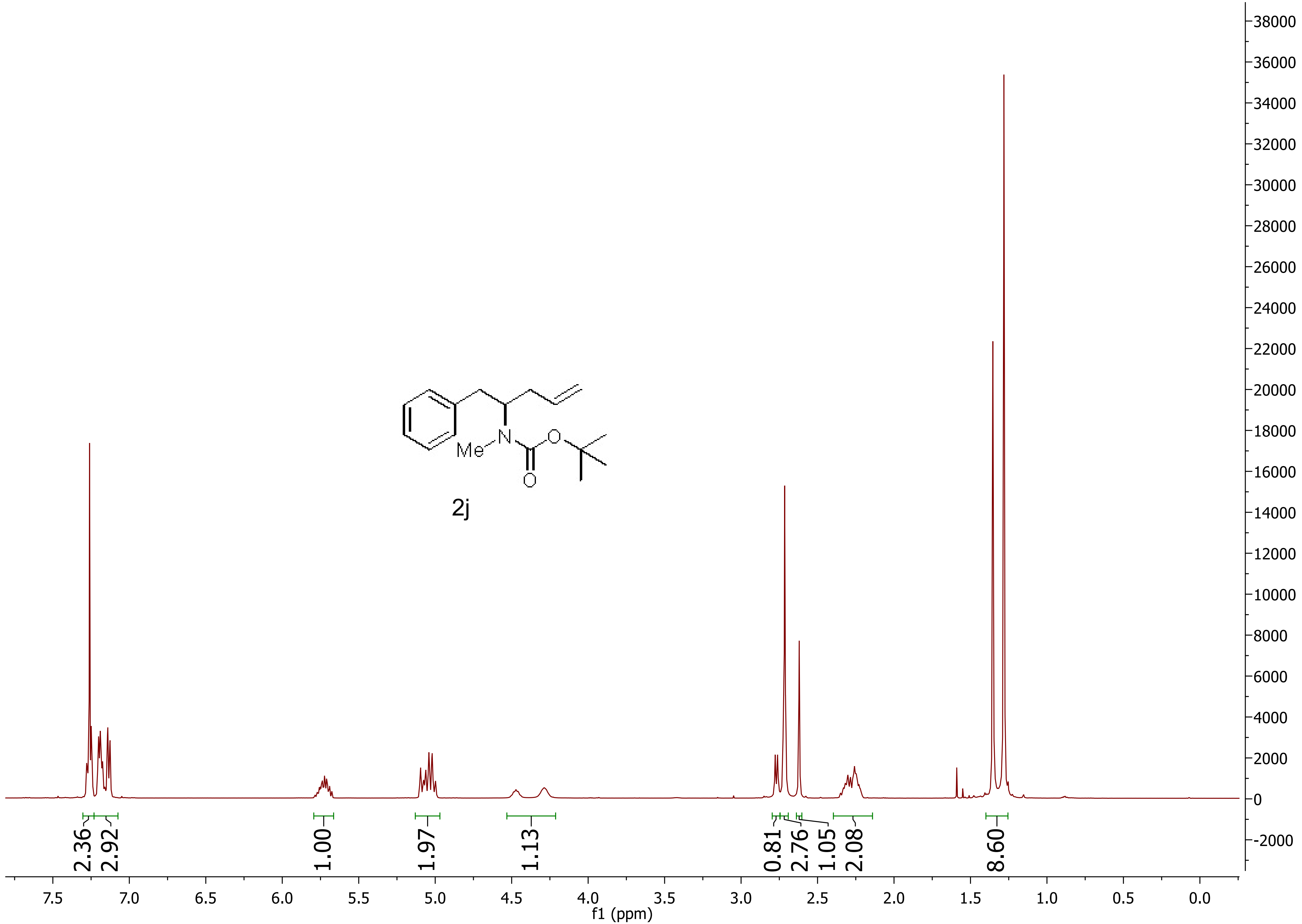

162.7109
160.7696
155.4335
134.3801
133.9795
133.9575
130.9729
130.9107
118.2494
115.3564
115.1884
79.3588
51.2347
39.8547
38.2349
28.5010
F
HN
O
O
2g
f1 (ppm)


Cl
HN
O
O
2h
2.21
1.93
1.00
1.98
0.91
1.00
2.01
1.05
1.03
8.84
f1 (ppm)

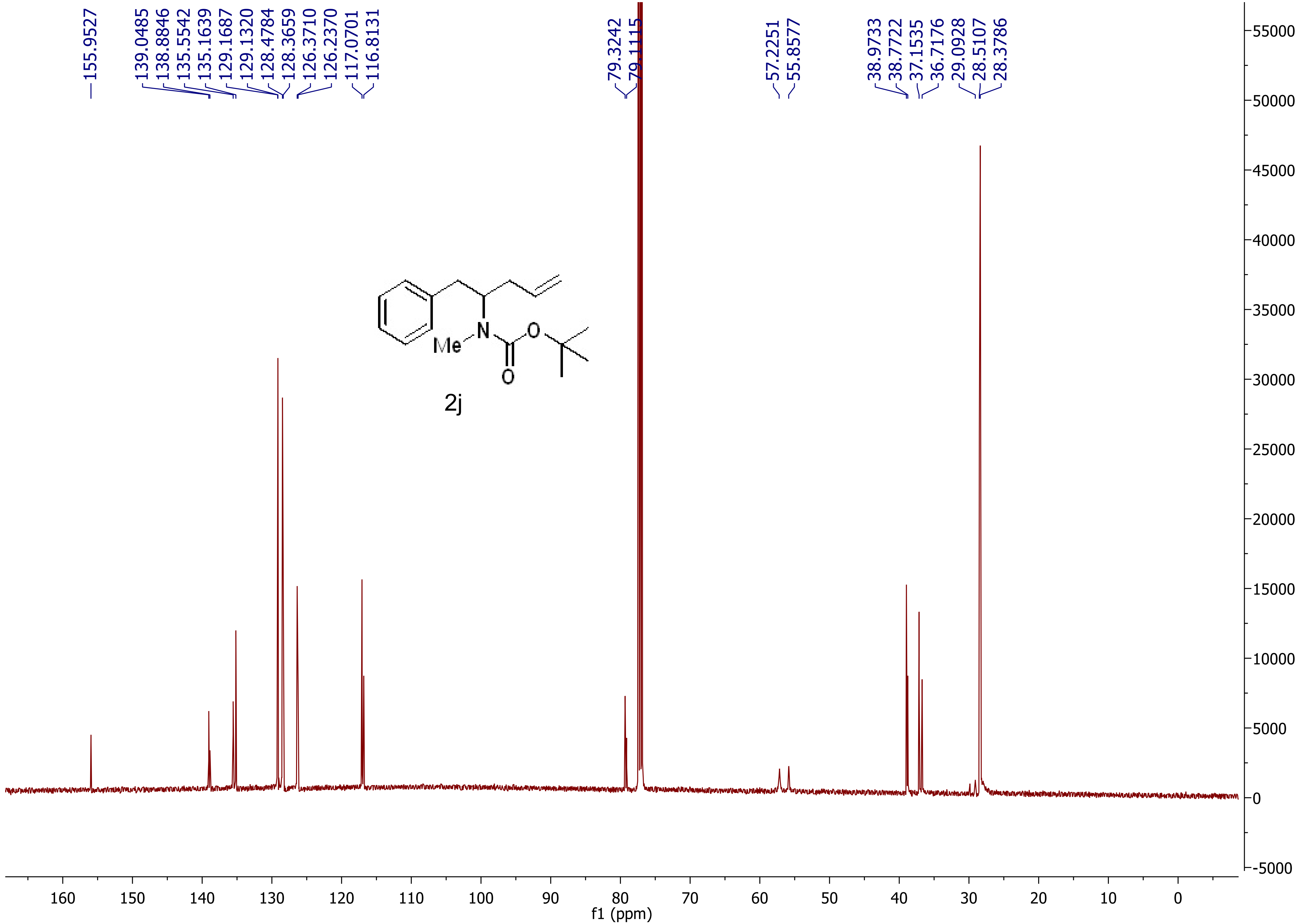

155.4088
136.7927
134.2912
132.3047
130.9036
128.5962
118.3250
79.4025
51.1132
40.0002
38.2192
28.4922
Cl
HN
O
O
2h
f1 (ppm)

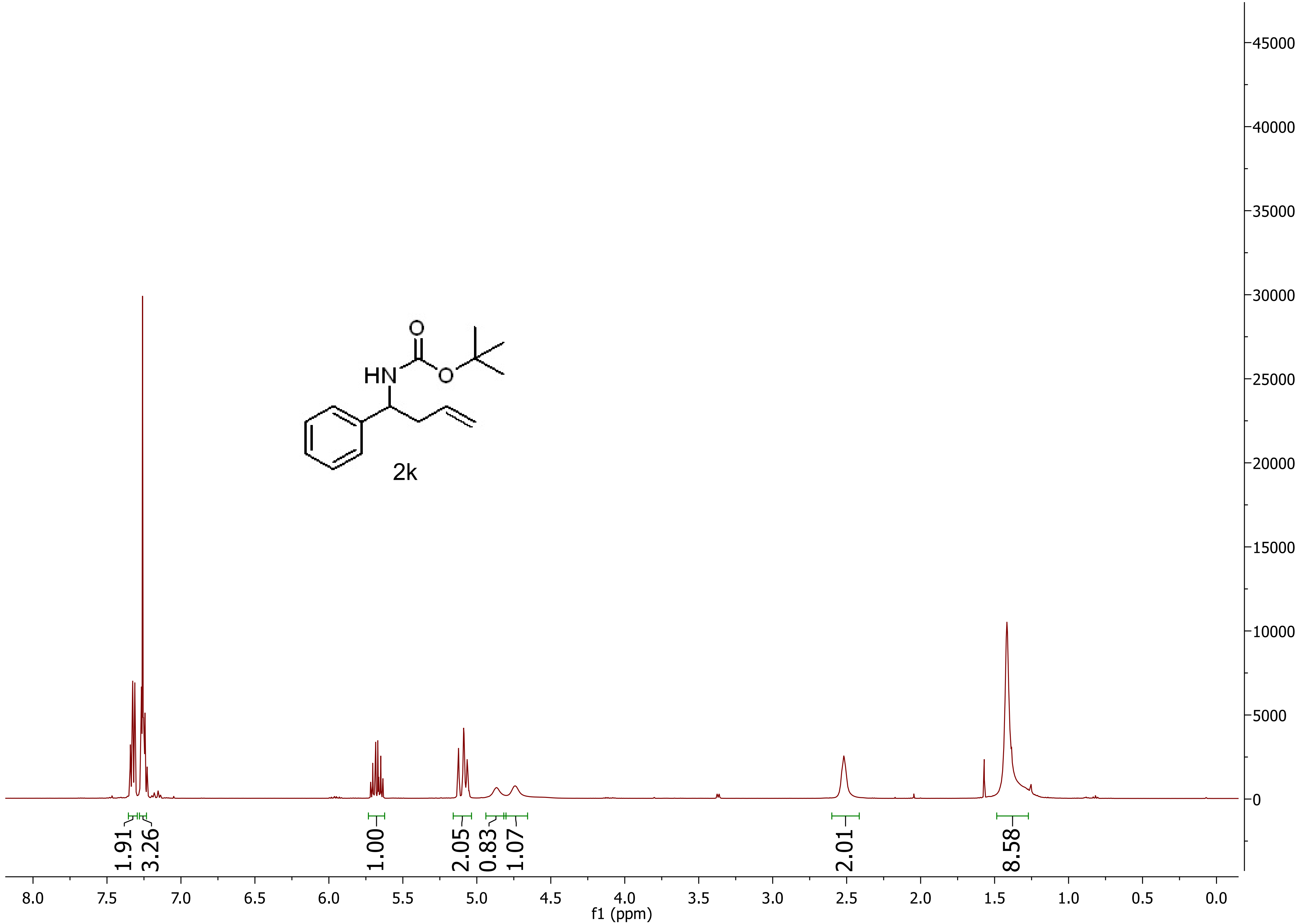



157.5523
155.4901
137.2341
134.6453
130.5732
128.7054
128.0622
127.6118
118.0272
114.8526
79.2346
70.1518
51.2646
39.6712
38.1492
28.5327
HN
O
O
O
2i
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

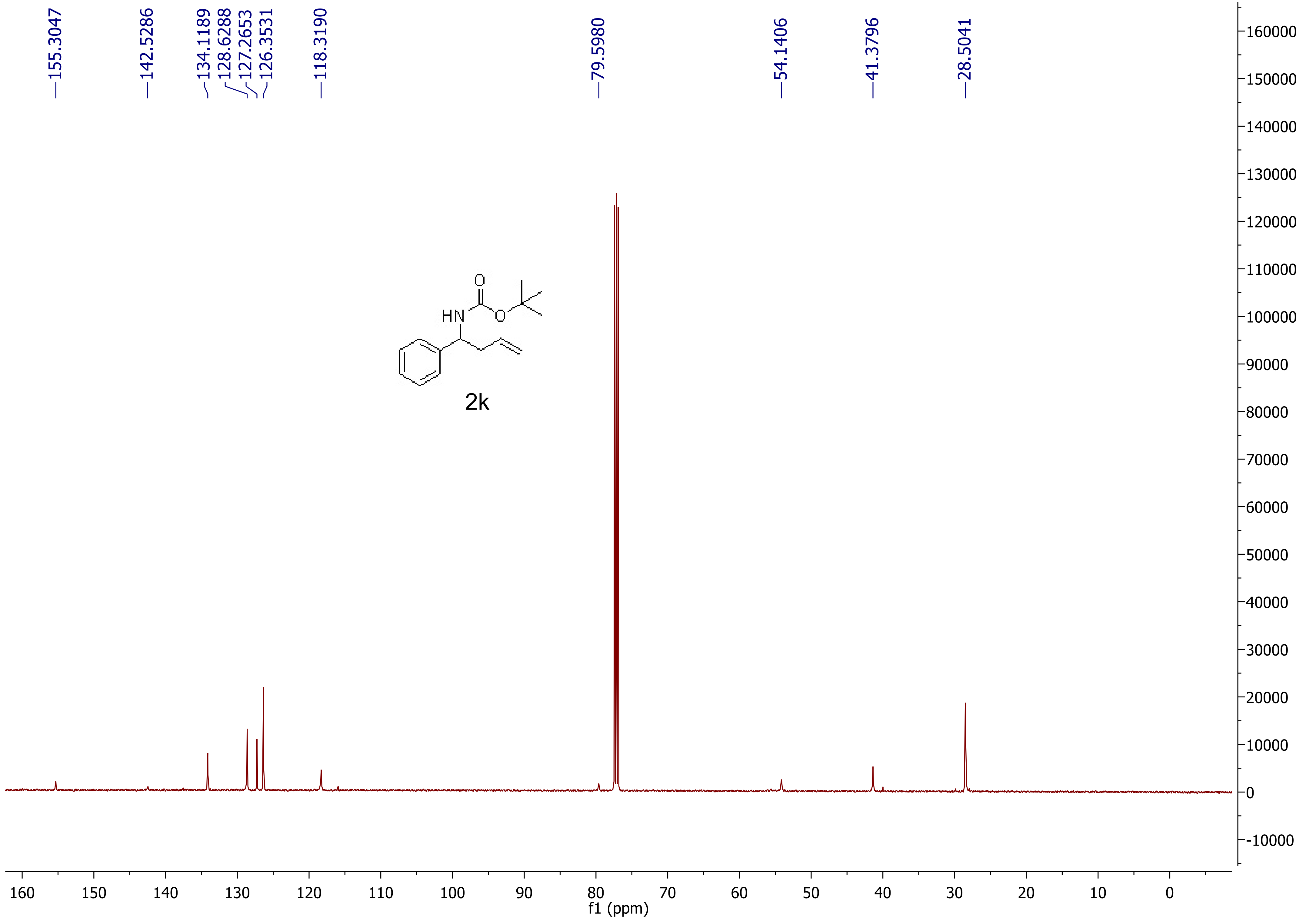


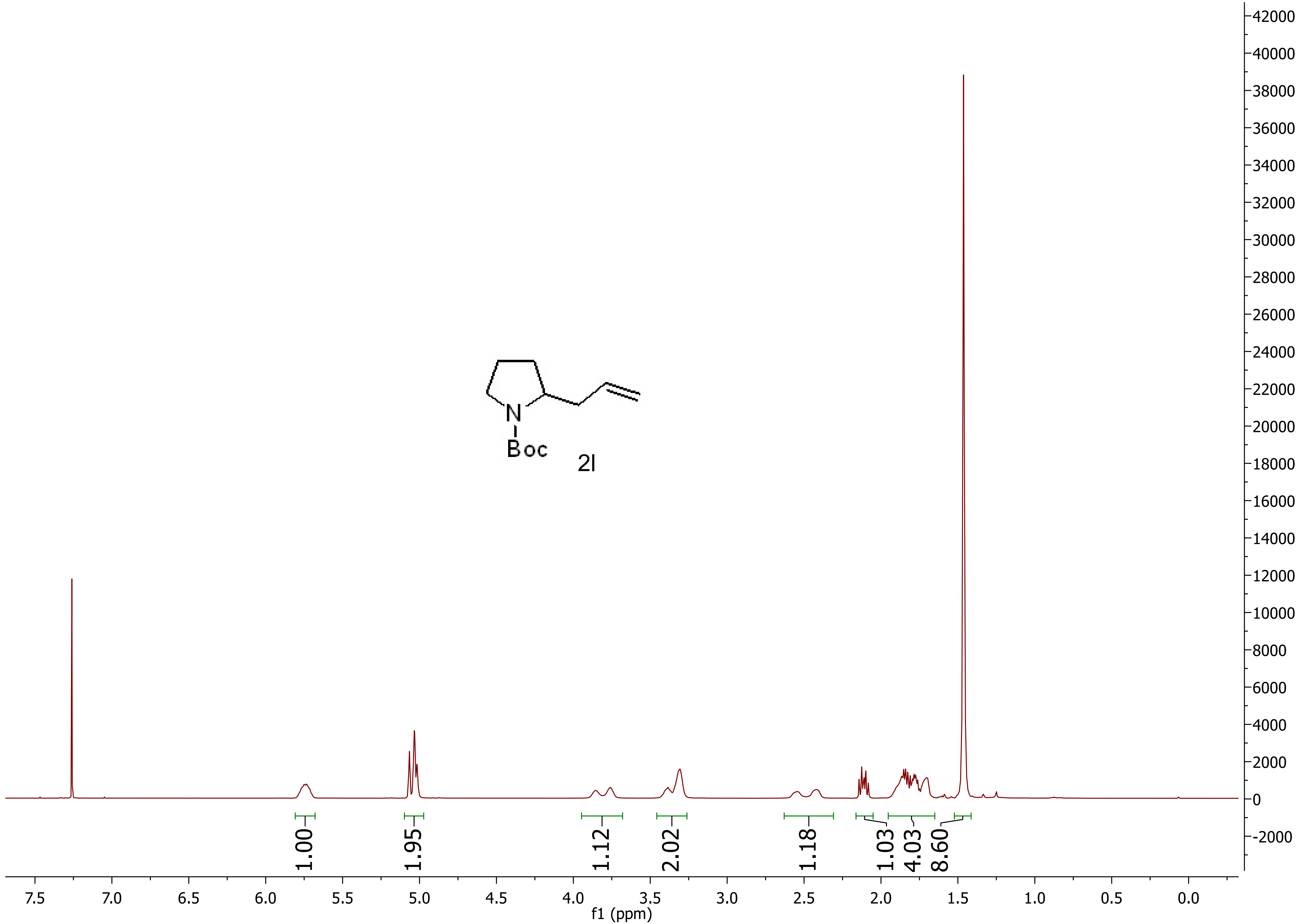
Me
N
O
O
2j
2.36
2.92
1.00
1.97
1.13
0.81
2.76
1.05
2.08
8.60
f1 (ppm)

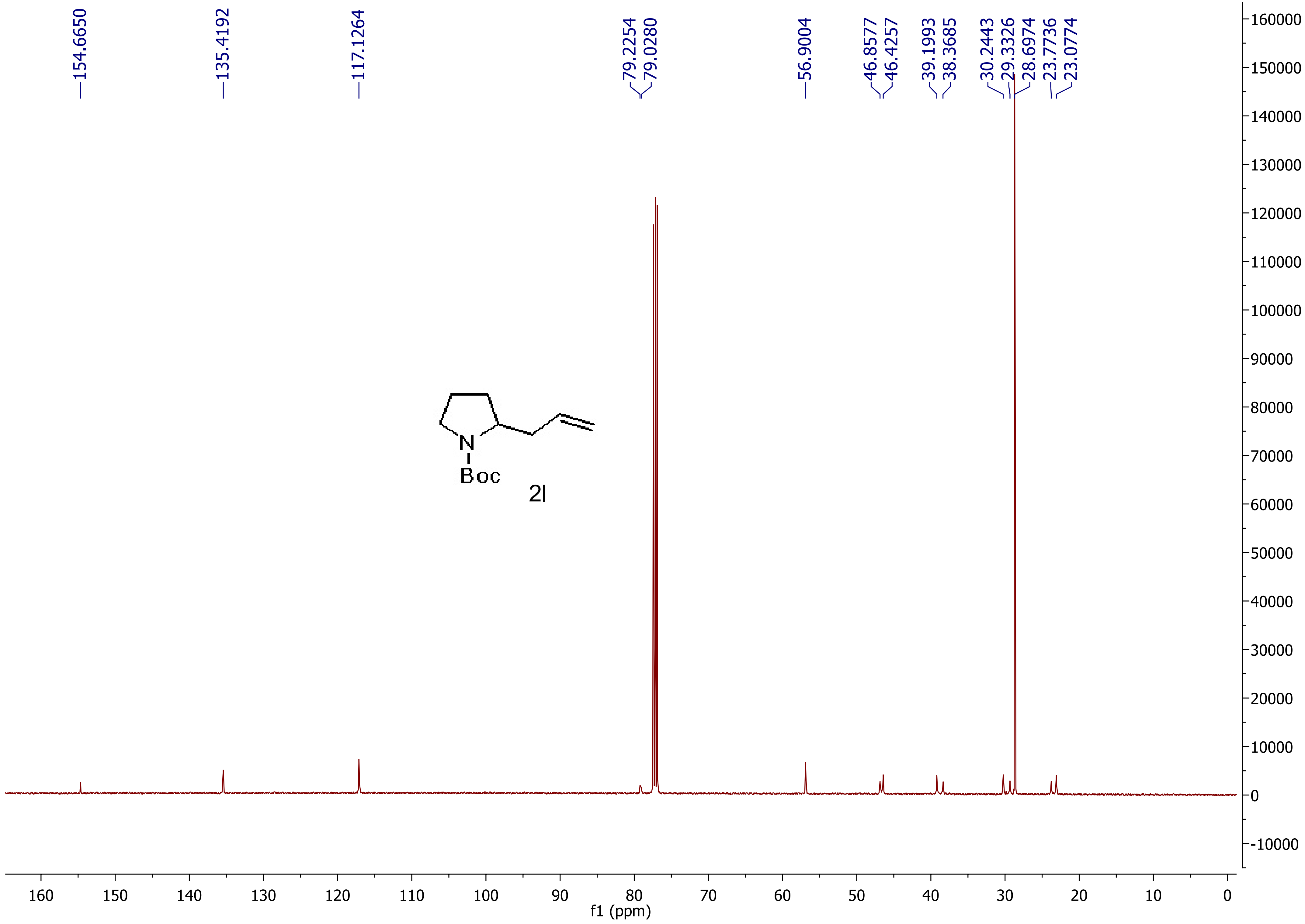

155.9527
139.0485
138.8846
135.5542
135.1639
129.1687
129.1320
128.4784
128.3659
126.3710
126.2370
117.0701
116.8131
79.3242
79.1115
57.2251
55.8577
38.9733
38.7722
37.1535
36.7176
29.0928
28.5107
28.3786
Me
N
O
O
2j
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



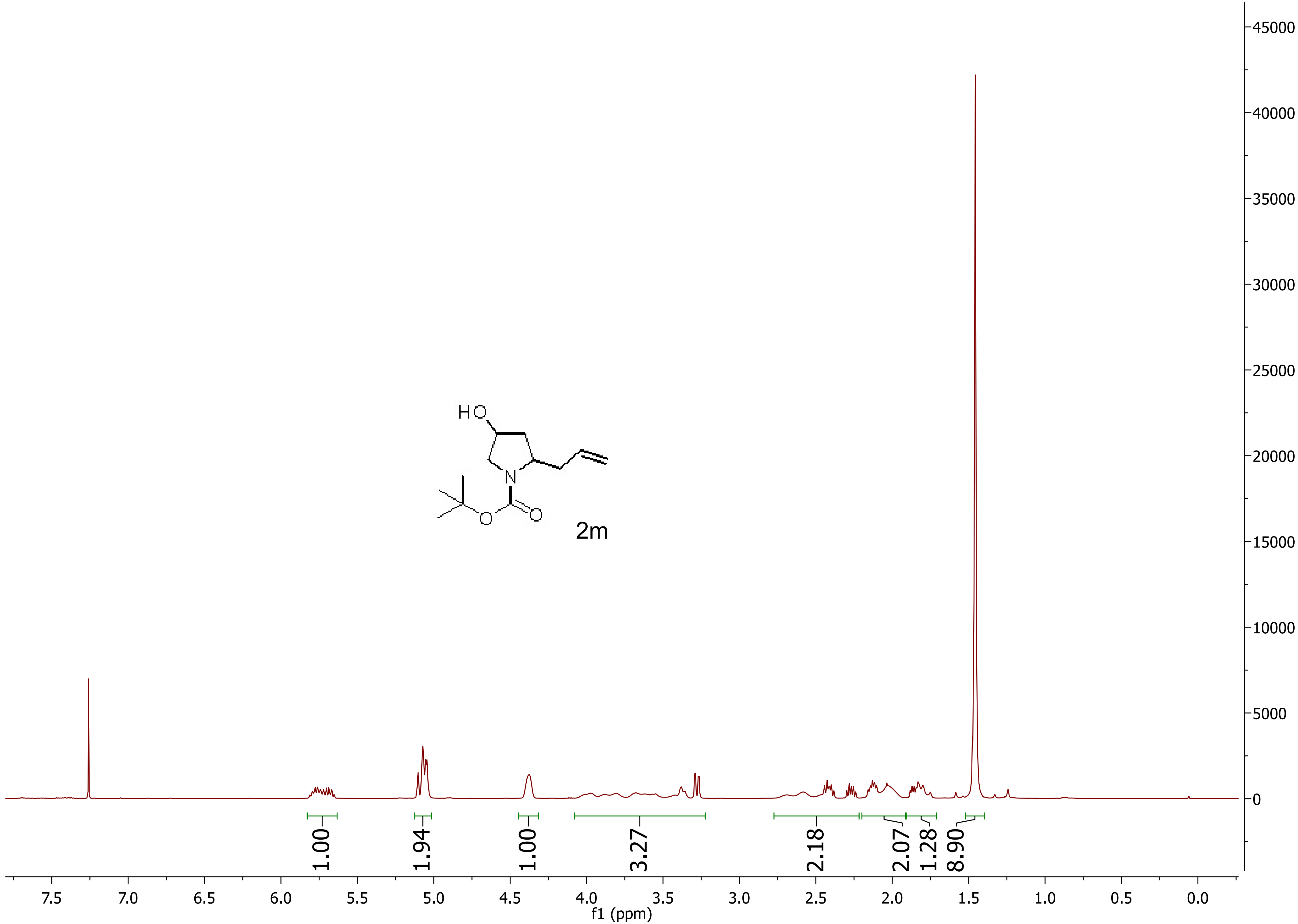
2k
HN
O
O
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
1.91
3.26
1.00
2.05
0.83
1.07
2.01
8.58
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

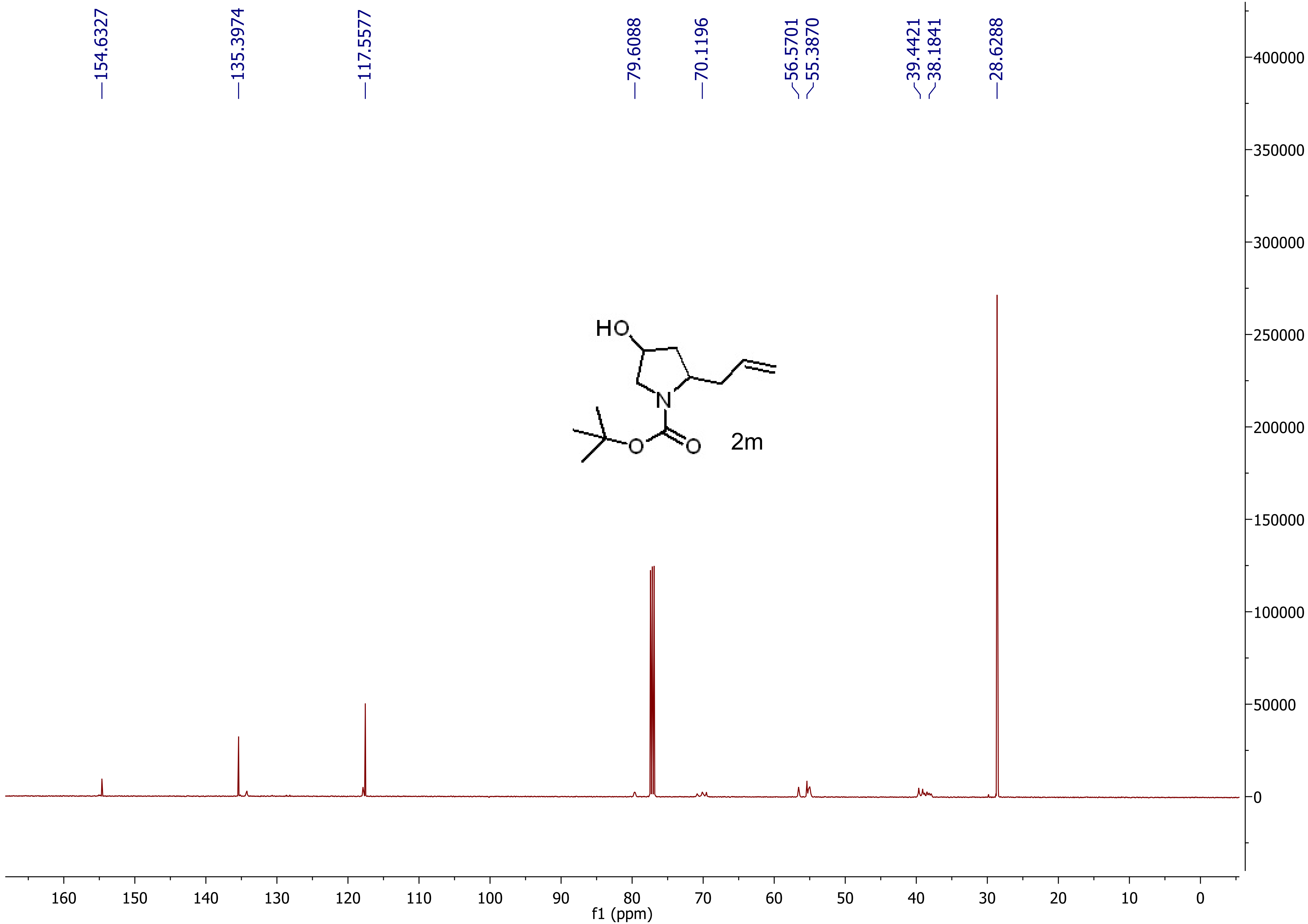

155.3047
142.5286
134.1189
128.6288
127.2653
126.3531
118.3190
79.5980
54.1406
41.3796
28.5041
HN
O
O
2k
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

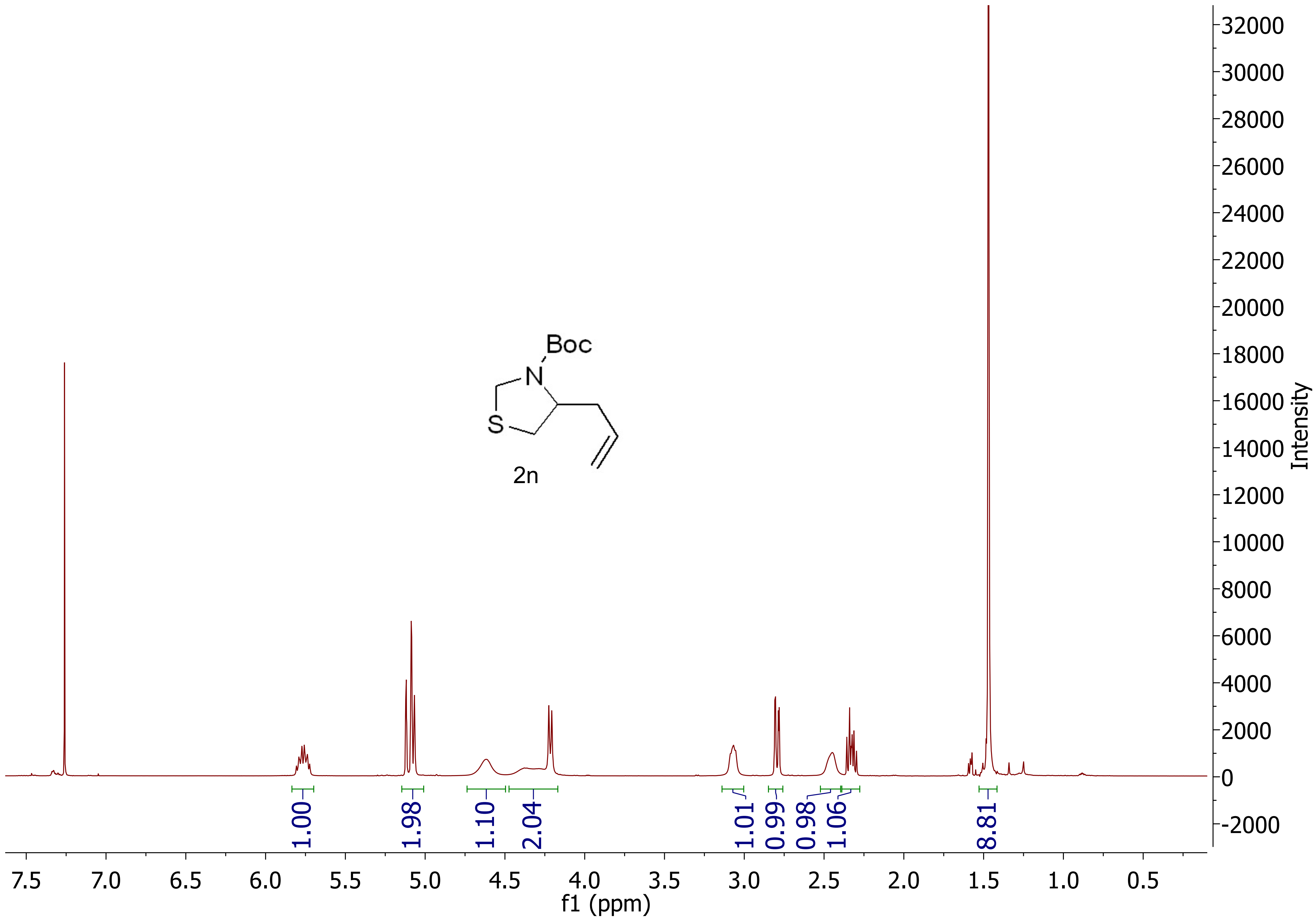

N
Boc
2l
1.00
1.95
1.12
2.02
1.18
1.03
4.03
8.60
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
42000 40000 38000 36000 34000 32000 30000 28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 -2000

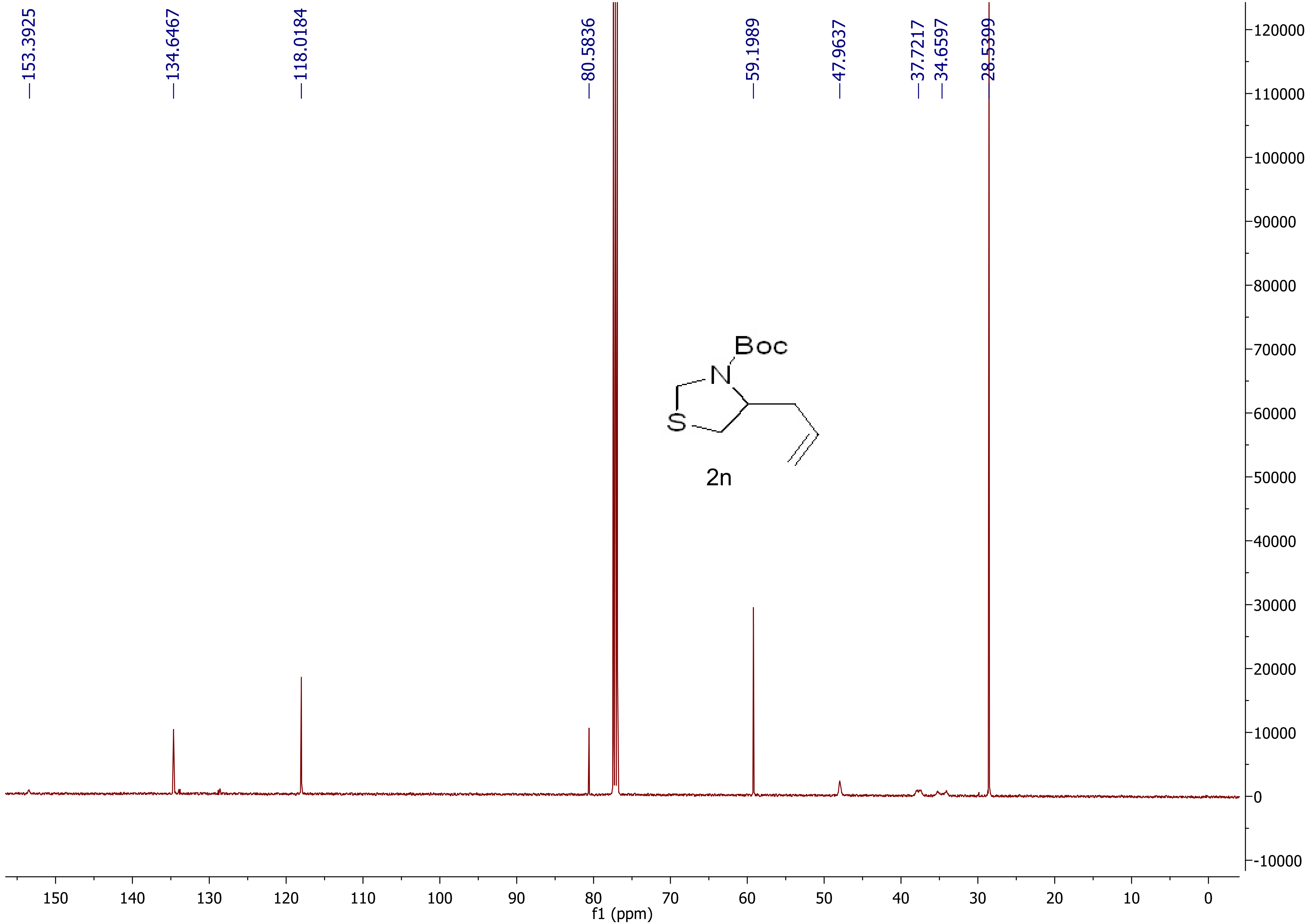


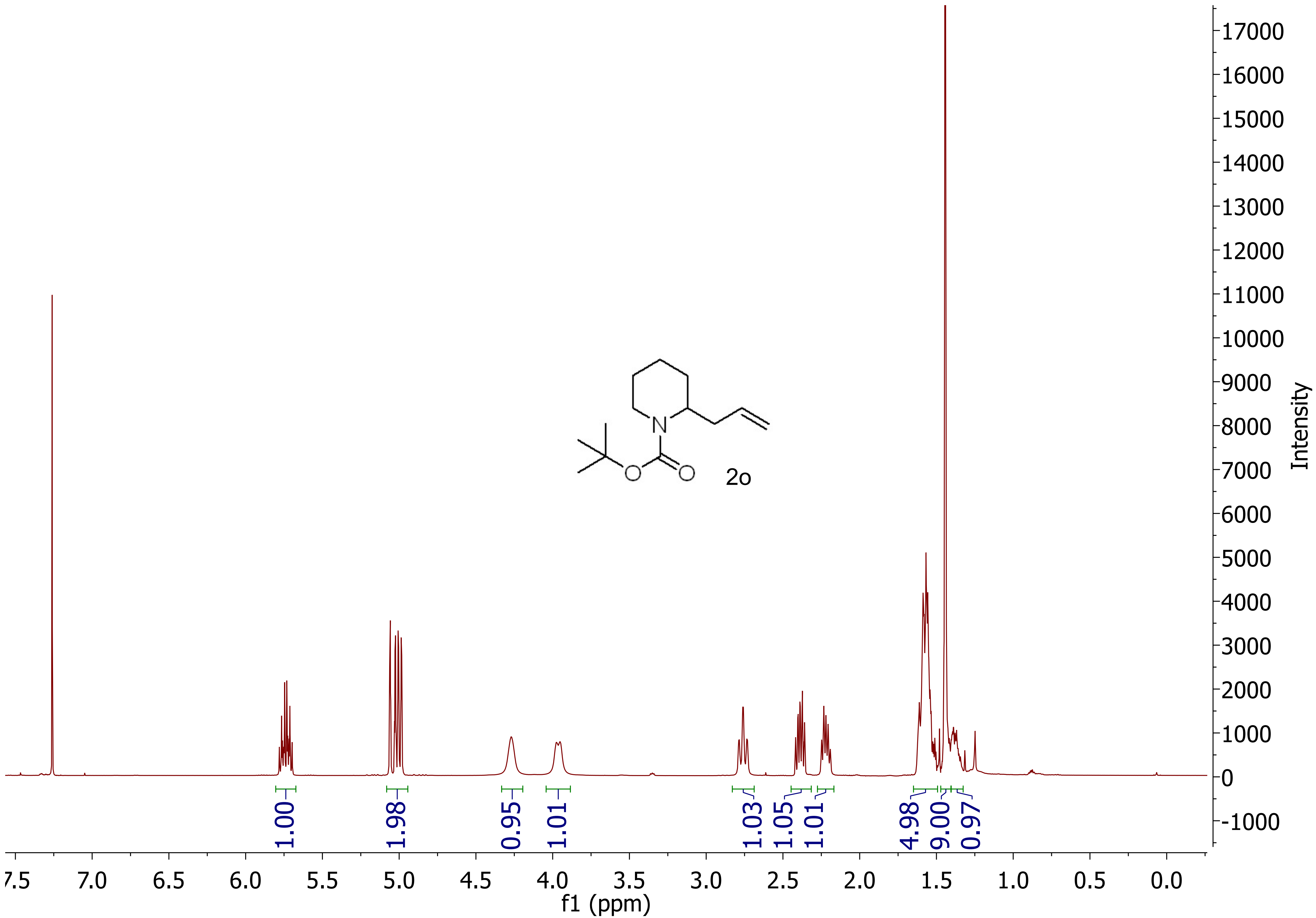
154.6650
135.4192
117.1264
79.2254
79.0280
56.9004
46.8577
46.4257
39.1993
38.3685
30.2443
29.3326
28.6974
23.7736
23.0774
N
Boc
2l
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
160000 150000 140000 130000 120000 110000 100000 90000 80000 70000 60000 50000 40000 30000 20000 10000 0 -10000


HO
N
O
O
2m
1.00
1.94
1.00
3.27
2.18
2.07
1.28
8.90
45000
40000
35000
30000
25000
20000
15000
10000
5000
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)

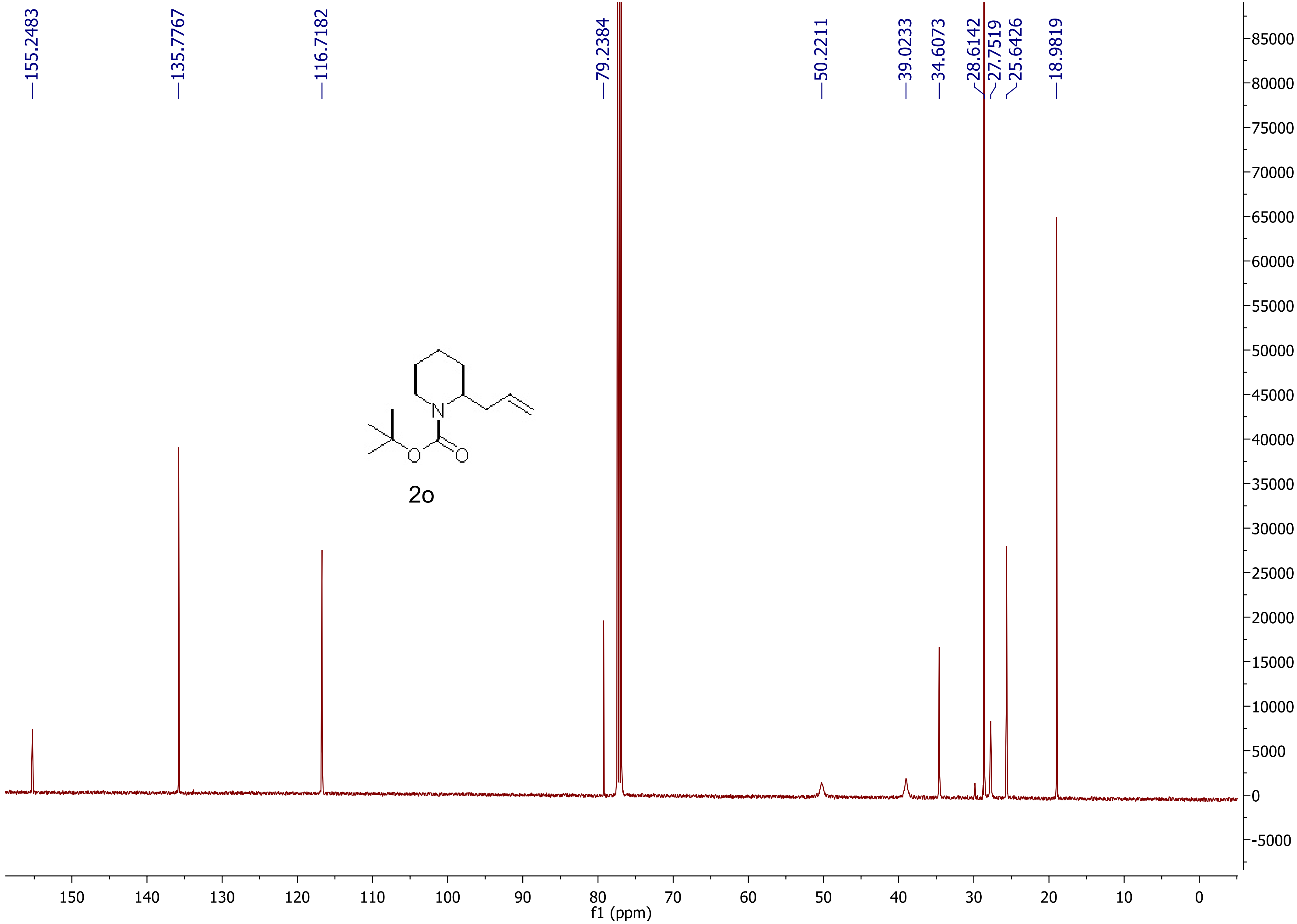

154.6327
135.3974
117.5577
79.6088
70.1196
56.5701
55.3870
39.4421
38.1841
28.6288
HO
N
O
O
2m
400000
350000
300000
250000
200000
150000
100000
50000
0
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

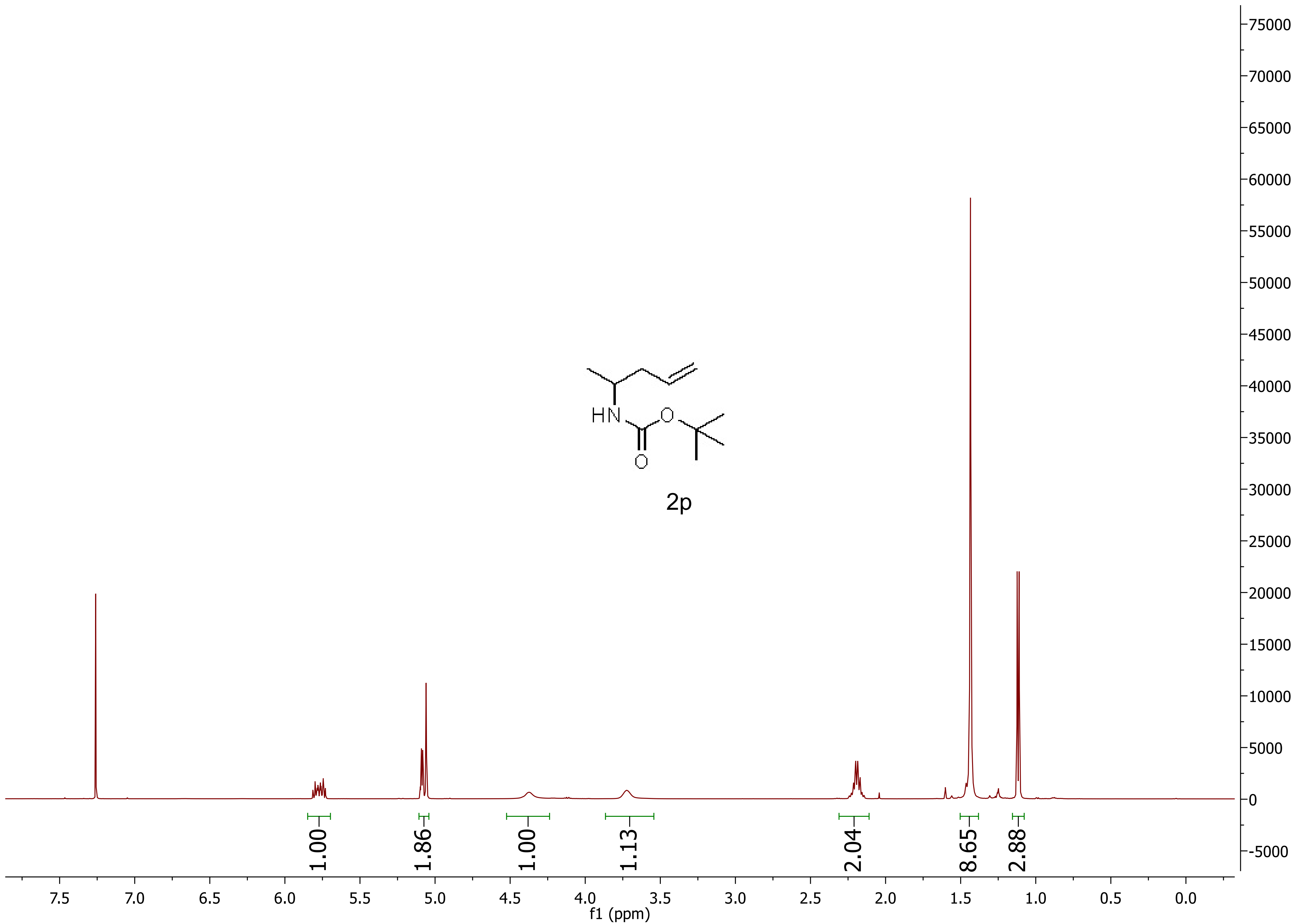

Boc
N
S
2n
Intensity
f1 (ppm)
1.00
1.98
1.10
2.04
1.01
0.99
0.98
1.06
8.81


153.3925
134.6467
118.0184
80.5836
59.1989
47.9637
37.7217
34.6597
28.5399
Boc
N
S
2n
f1 (ppm)

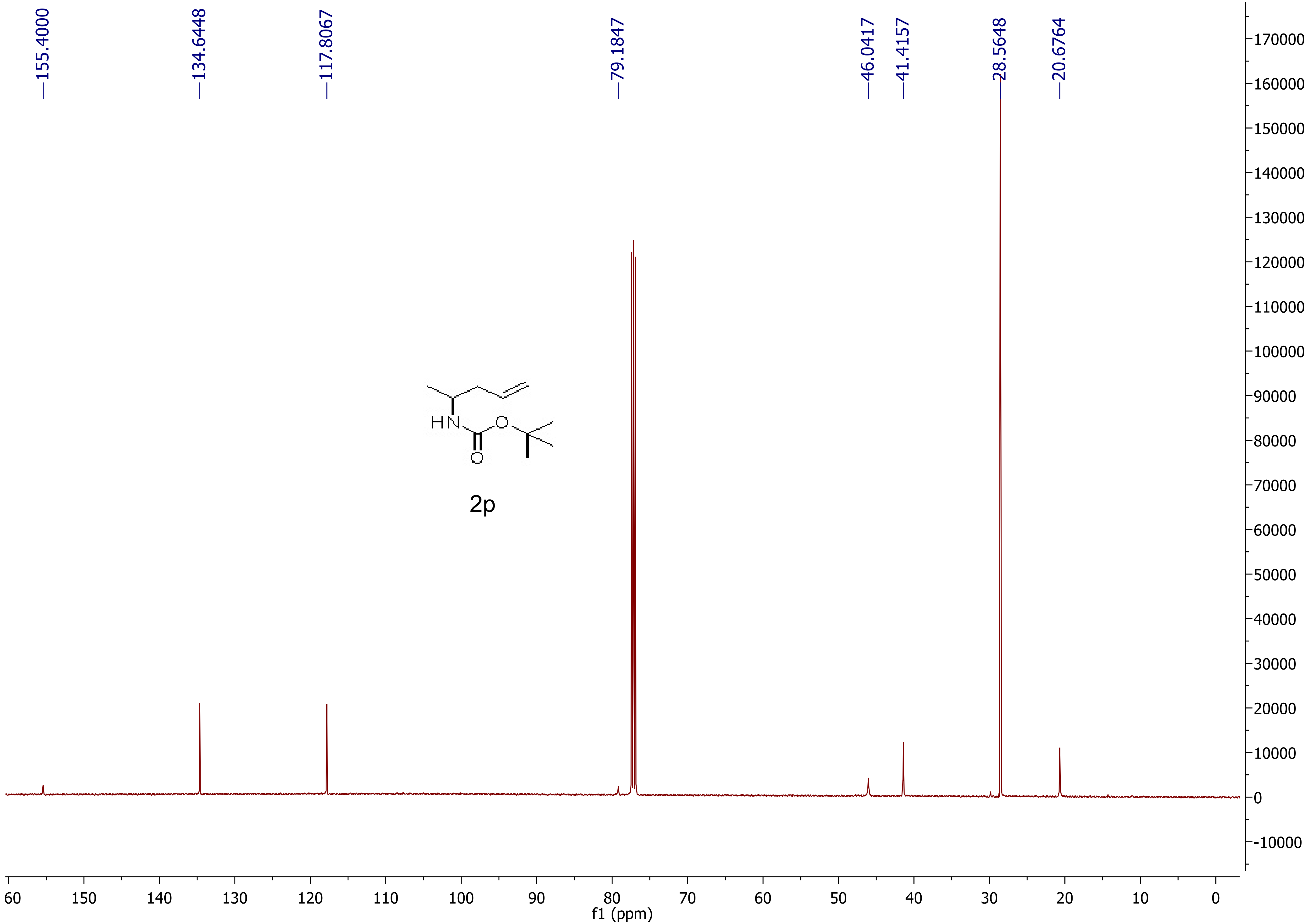


2o
1.00
1.98
0.95
1.01
1.03
1.05
1.01
4.98
9.00
0.97
f1 (ppm)
Intensity

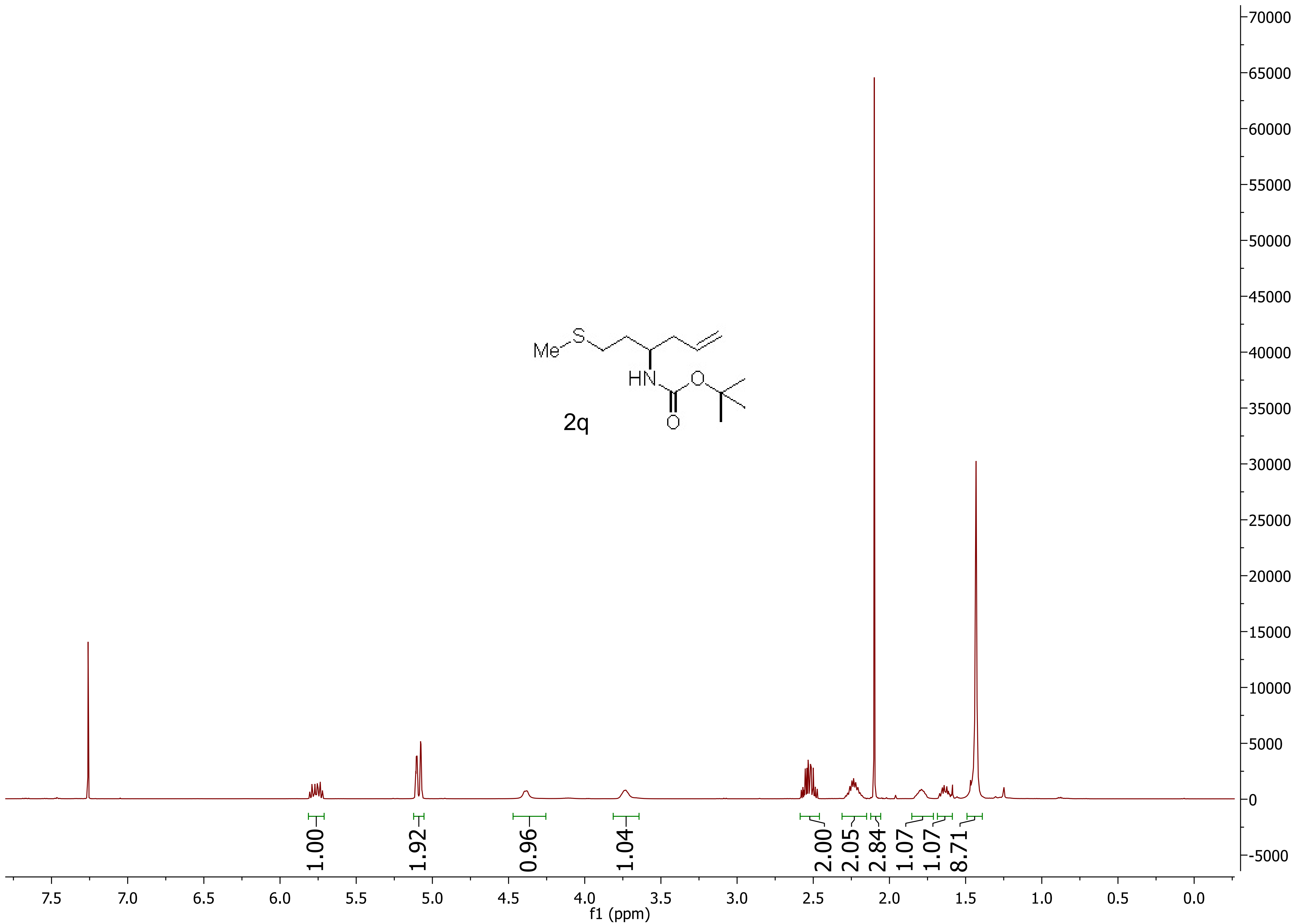

155.2483
135.7767
116.7182
79.2384
50.2211
39.0233
34.6073
28.6142
27.7519
25.6426
18.9819
N
O
O
2o
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



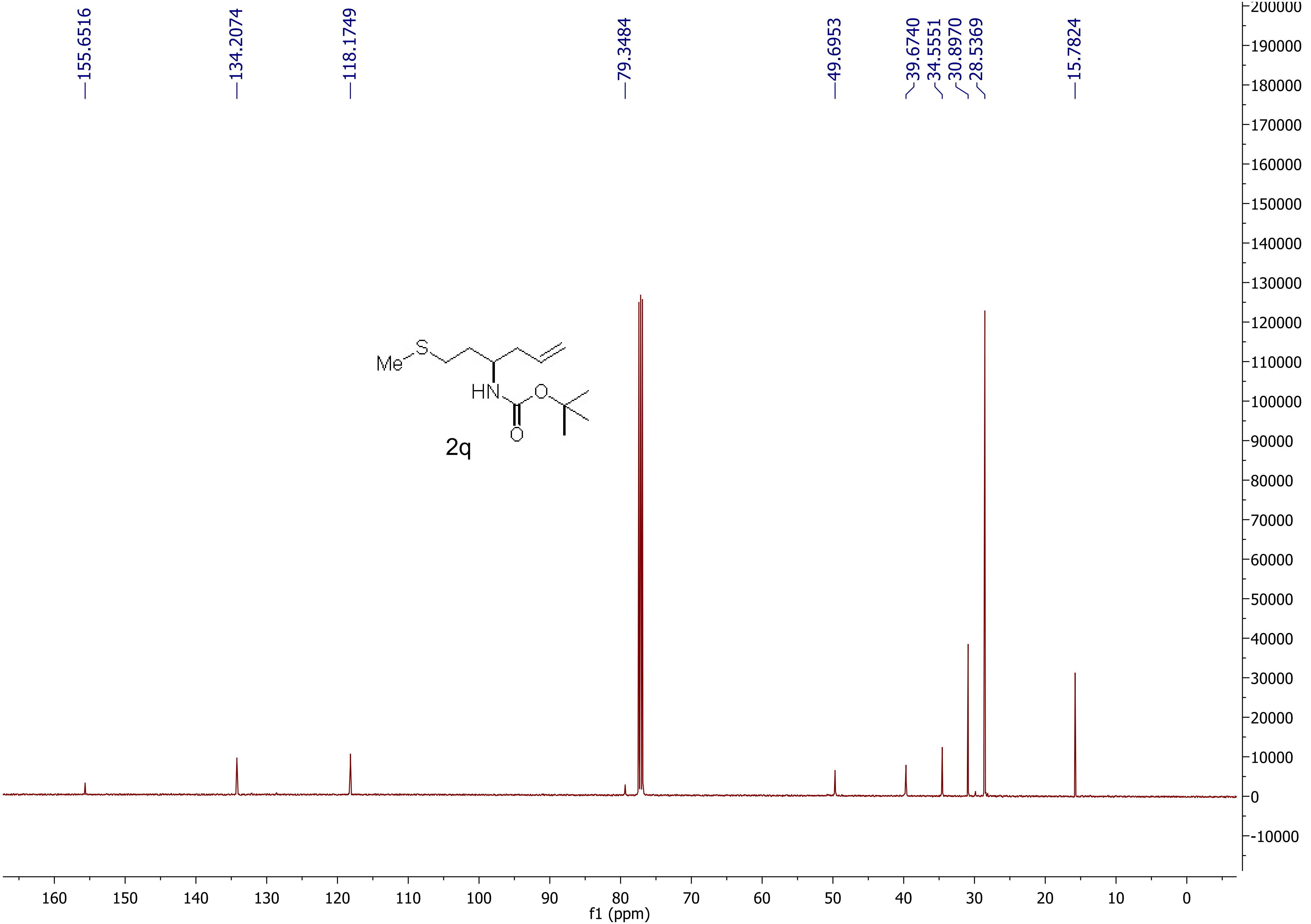
HN
O
O
2p
1.00
1.86
1.00
1.13
2.04
8.65
2.88
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

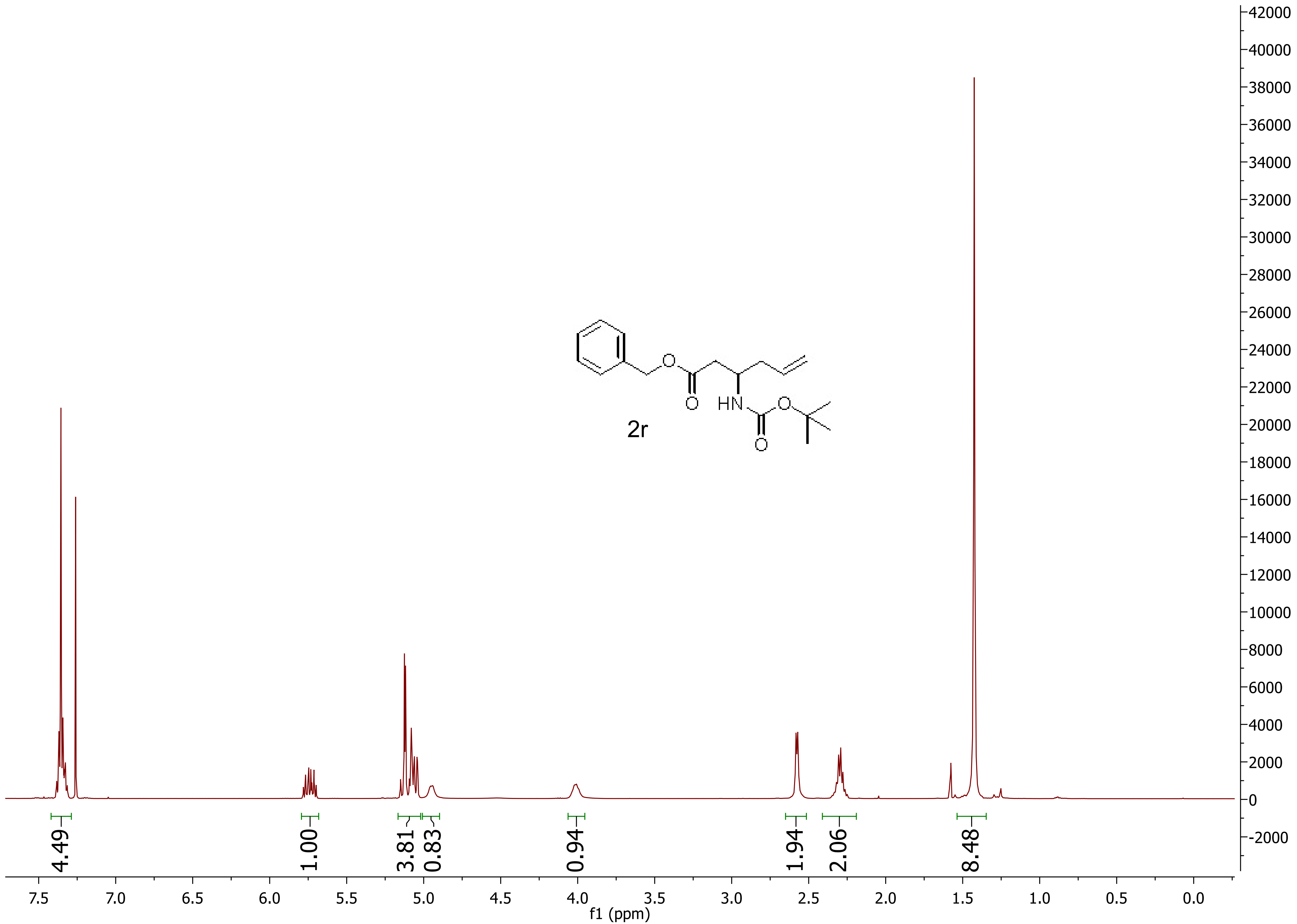


155.4000
134.6448
117.8067
79.1847
46.0417
41.4157
28.5648
20.6764
HN
O
O
2p
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

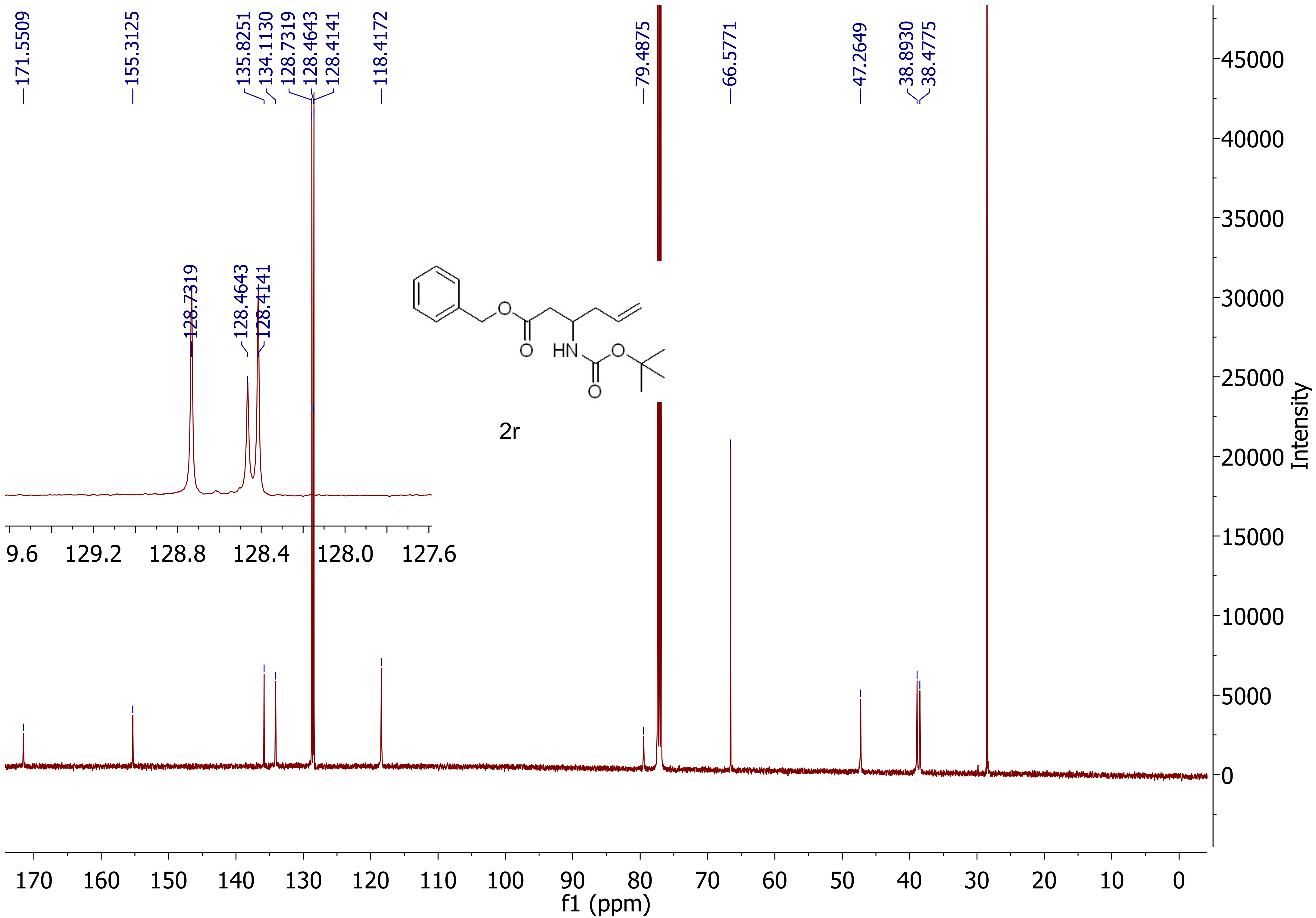


Me
S
HN
O
O
2q
1.00
1.92
0.96
1.04
2.00
2.05
2.84
1.07
1.07
8.71
f1 (ppm)

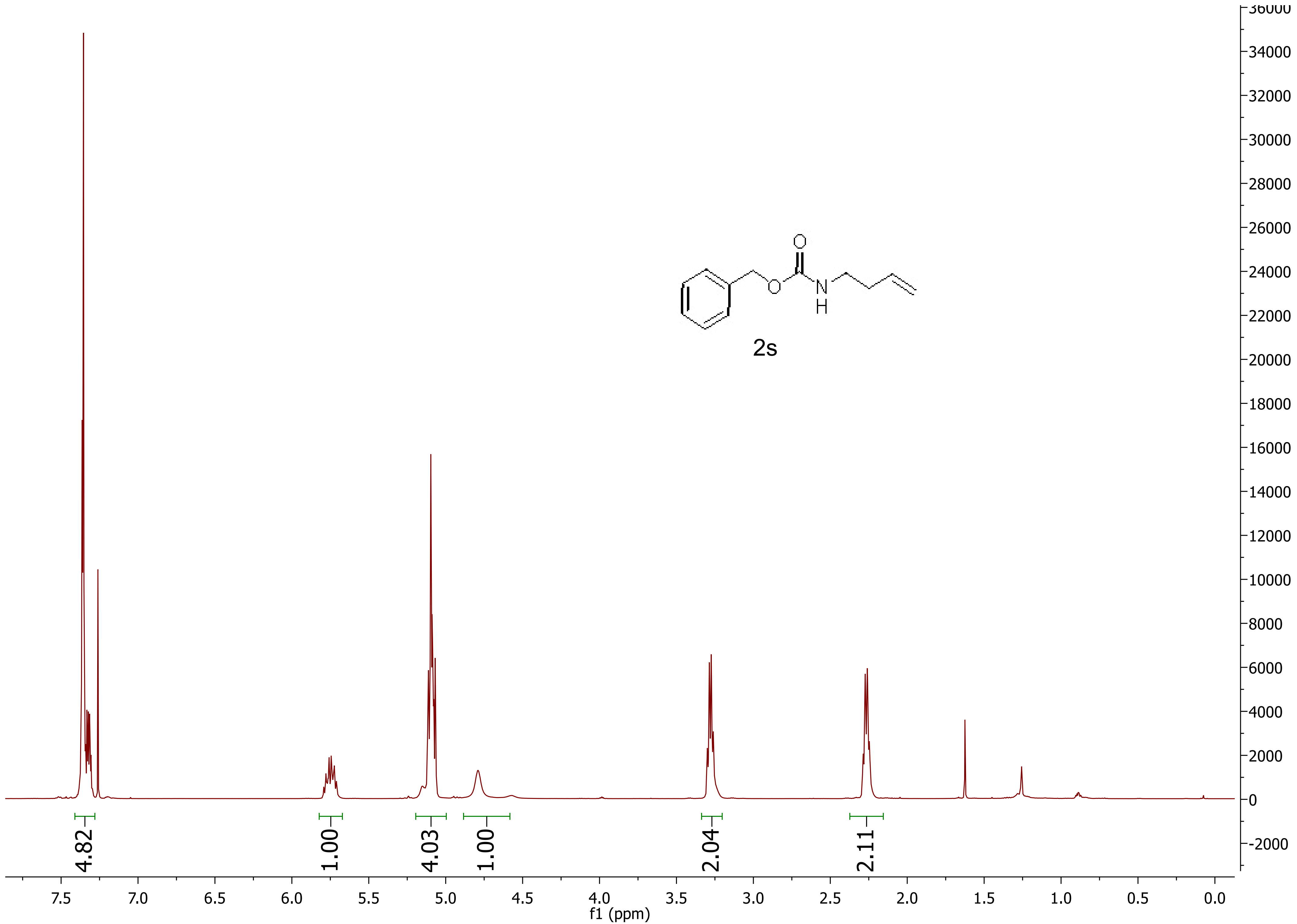

155.6516
134.2074
118.1749
79.3484
49.6953
39.6740
34.5551
30.8970
28.5369
15.7824
Me
S
HN
O
O
2q
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000



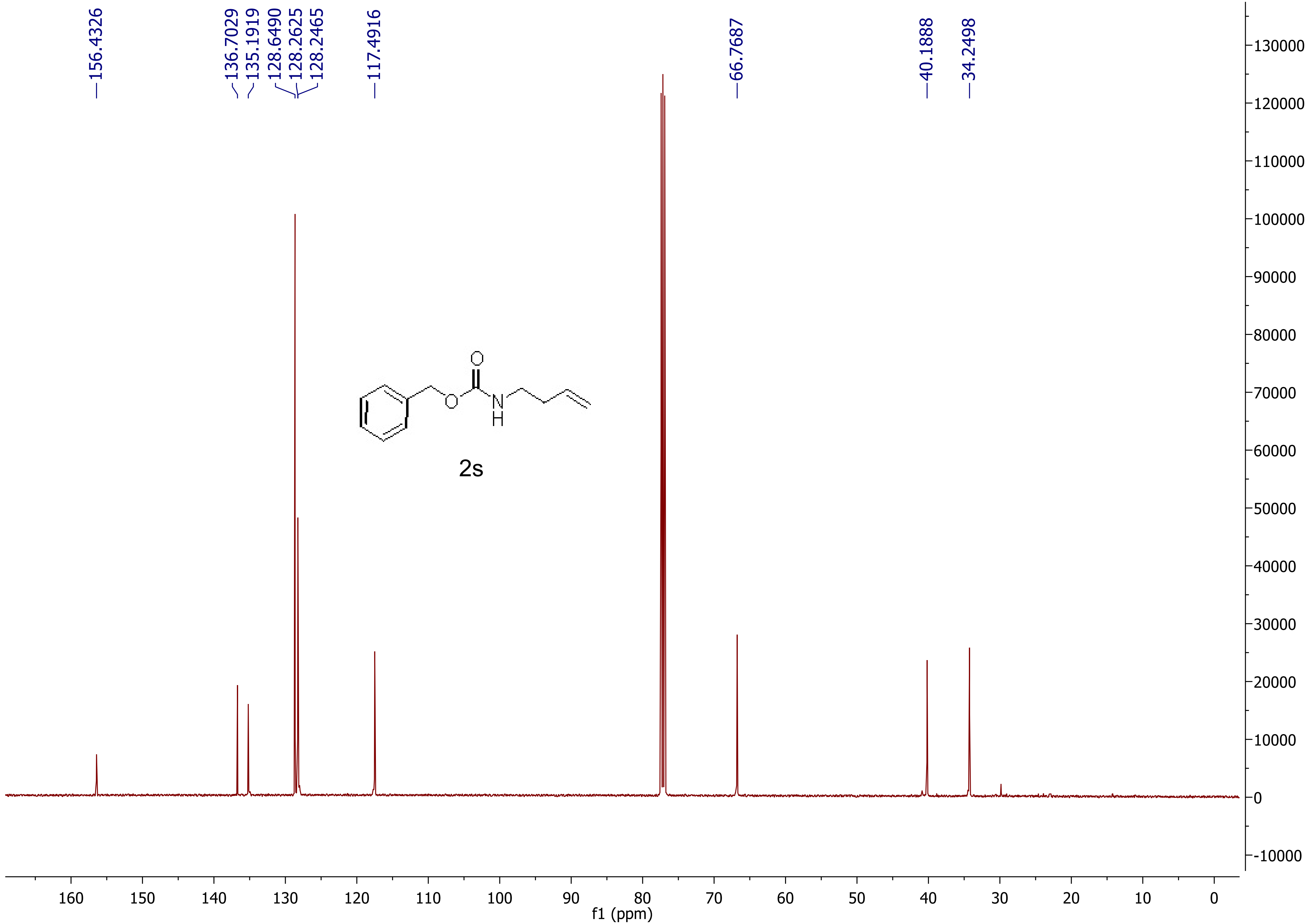
2r
HN
4.49
1.00
3.81
0.83
0.94
1.94
2.06
8.48
f1 (ppm)



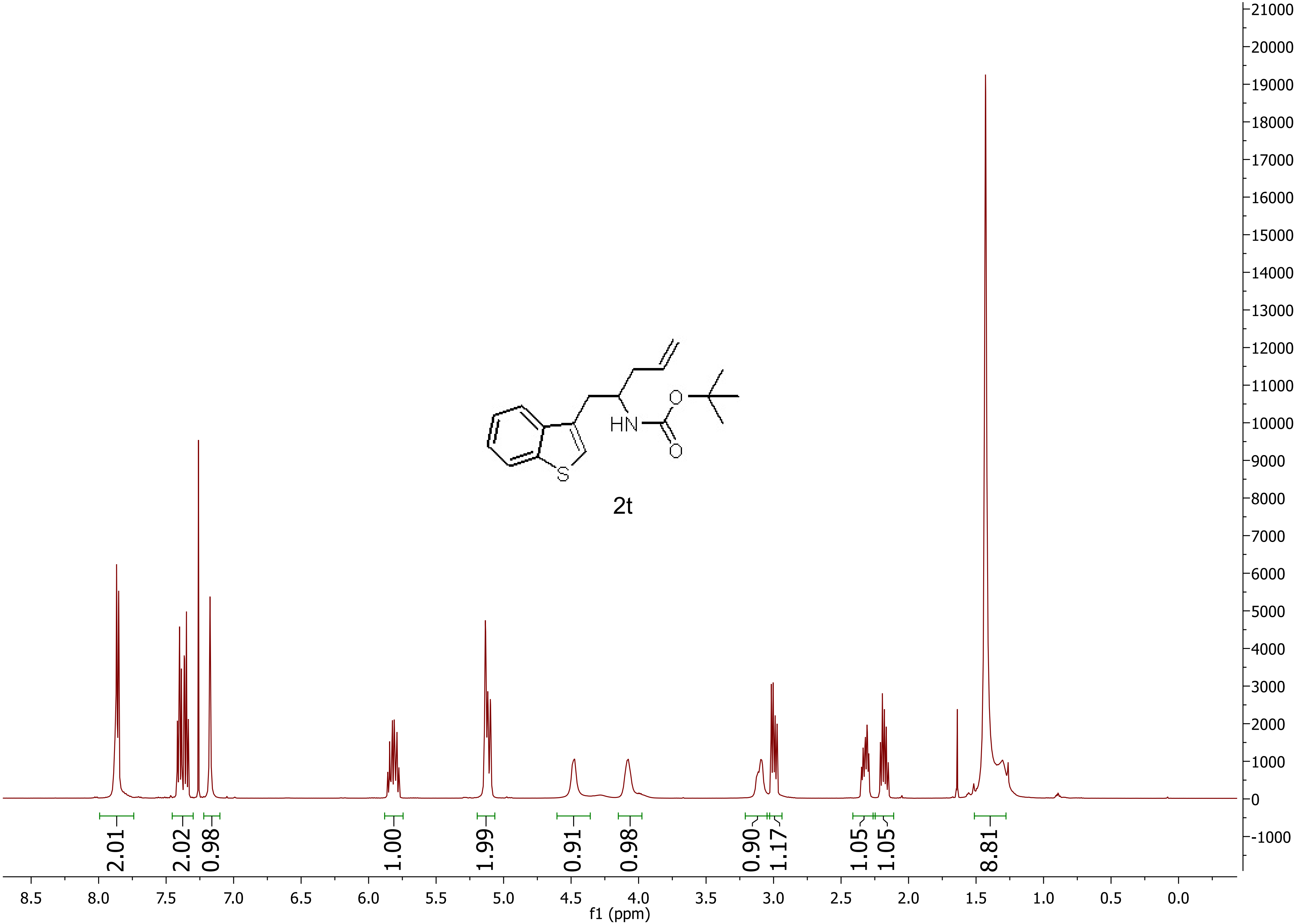
171.5509
155.3125
135.8251
134.1130
128.7319
128.4643
128.4141
118.4172
79.4875
66.5771
47.2649
38.8930
38.4775
2r
f1 (ppm)
Intensity



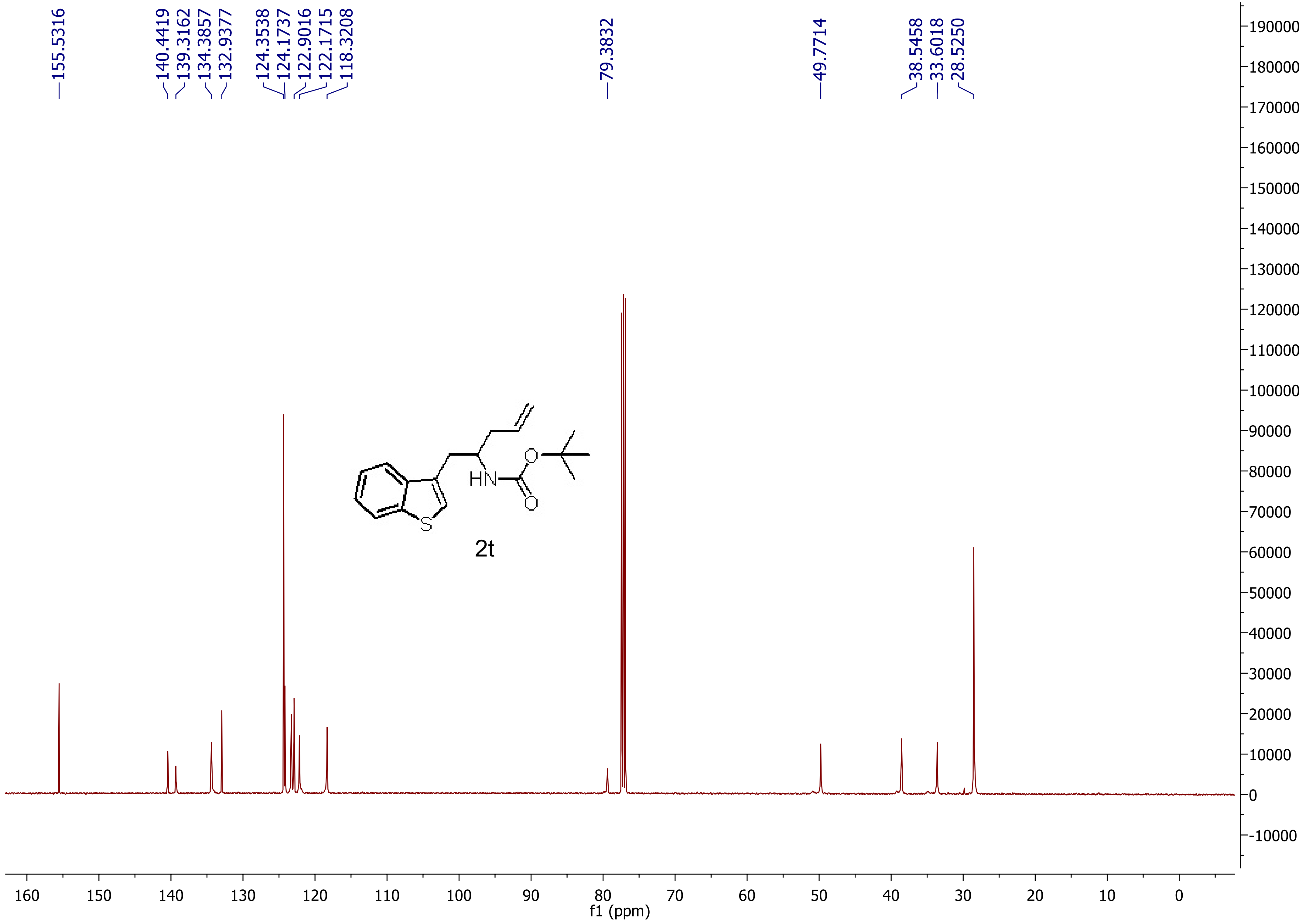
O
N
H
2s
4.82
1.00
4.03
1.00
2.04
2.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

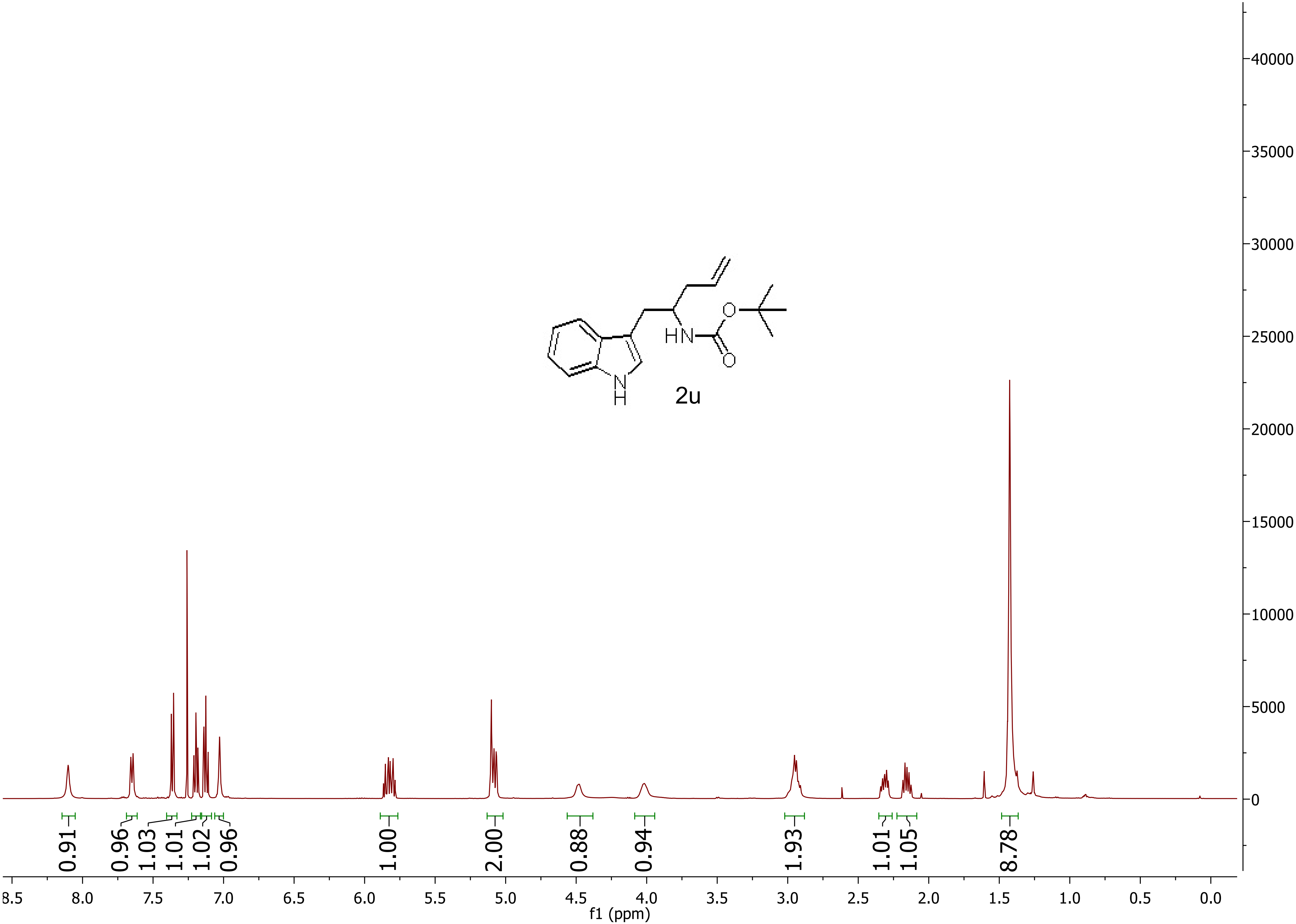


156.4326
136.7029
135.1919
128.6490
128.2625
128.2465
117.4916
66.7687
40.1888
34.2498
O
O
N
H
2s
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000

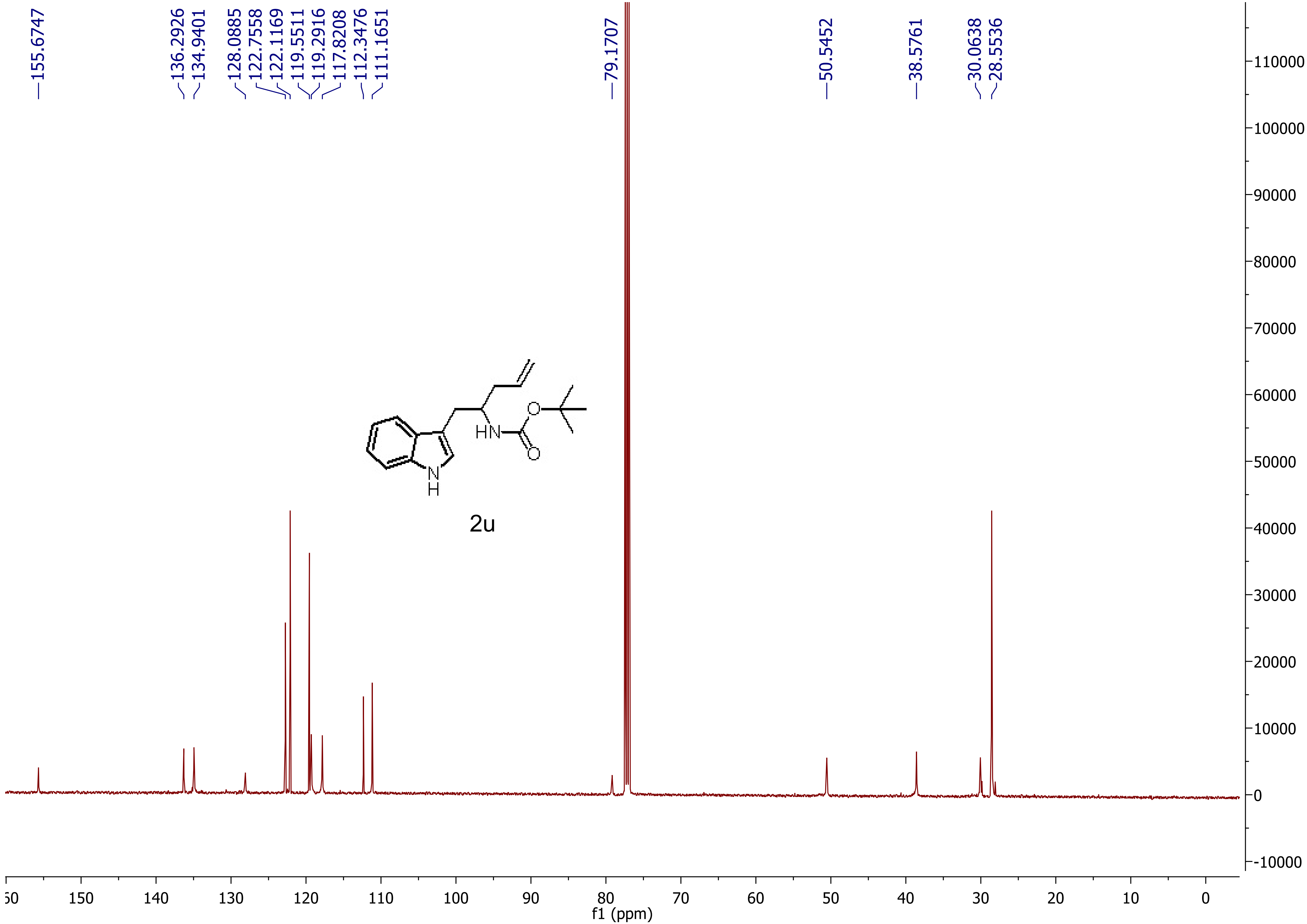


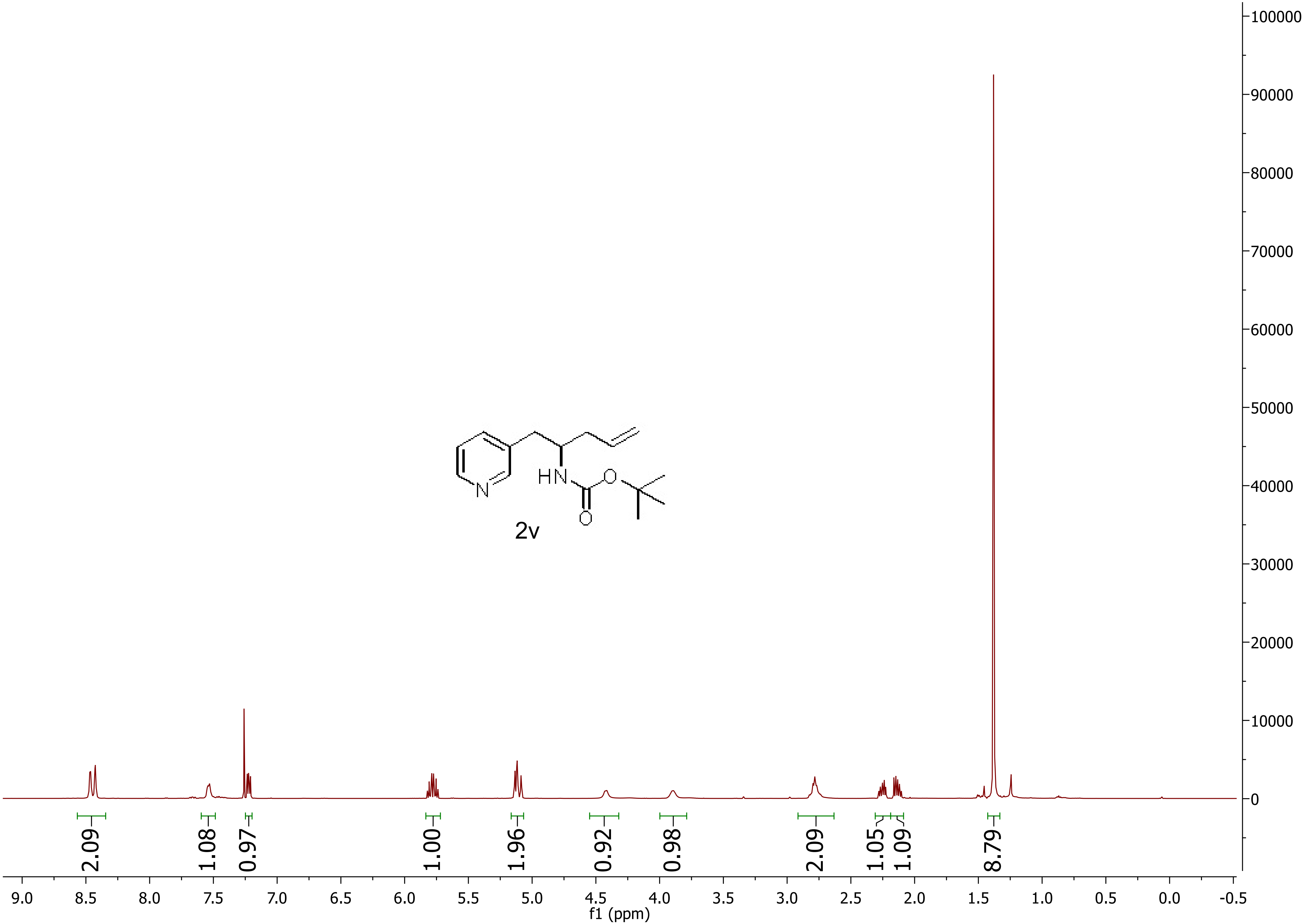
HN
O
O
S
2t
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
2.01
2.02
0.98
1.00
1.99
0.91
0.98
0.90
1.17
1.05
1.05
8.81
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.5316
140.4419
139.3162
134.3857
132.9377
124.3538
124.1737
122.9016
122.1715
118.3208
79.3832
49.7714
38.5458
33.6018
28.5250
2t
f1 (ppm)

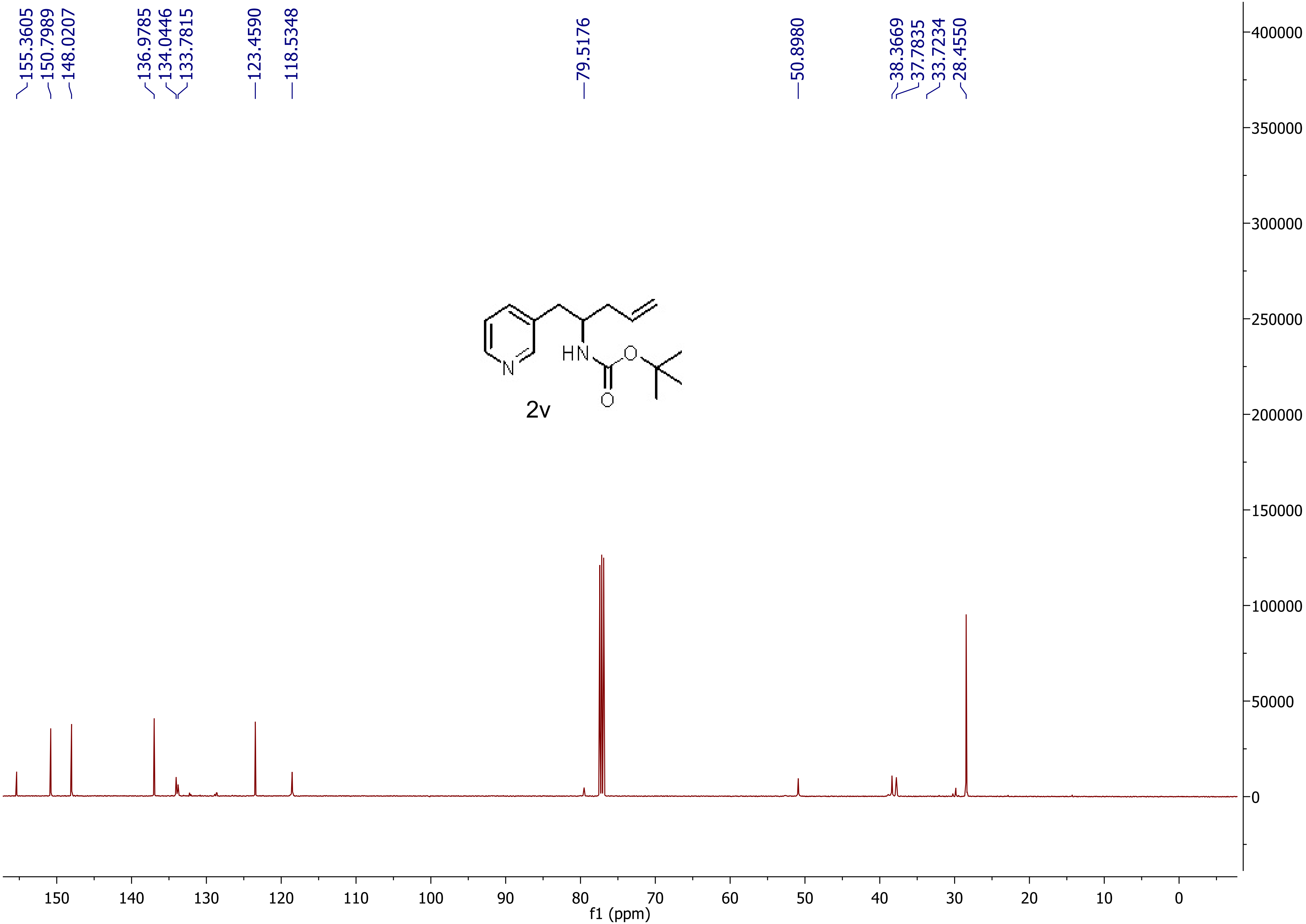


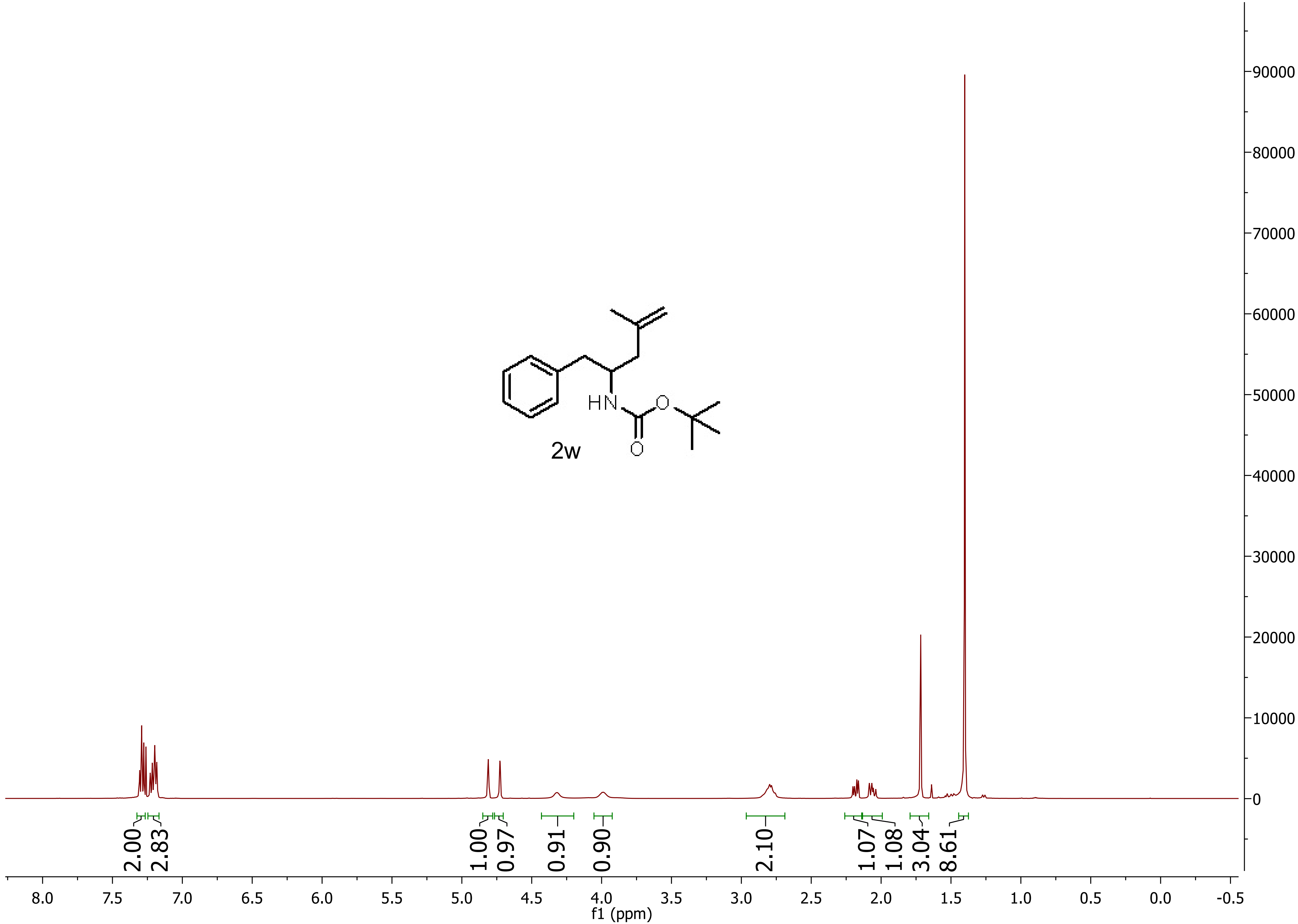
HN
O
O
N
H
2u
0.91
0.96
1.03
1.01
1.02
0.96
1.00
2.00
0.88
0.94
1.93
1.01
1.05
8.78
f1 (ppm)


155.6747
136.2926
134.9401
128.0885
122.7558
122.1169
119.5511
119.2916
117.8208
112.3476
111.1651
79.1707
50.5452
38.5761
30.0638
28.5536
HN
O
O
N
H
2u
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
50
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

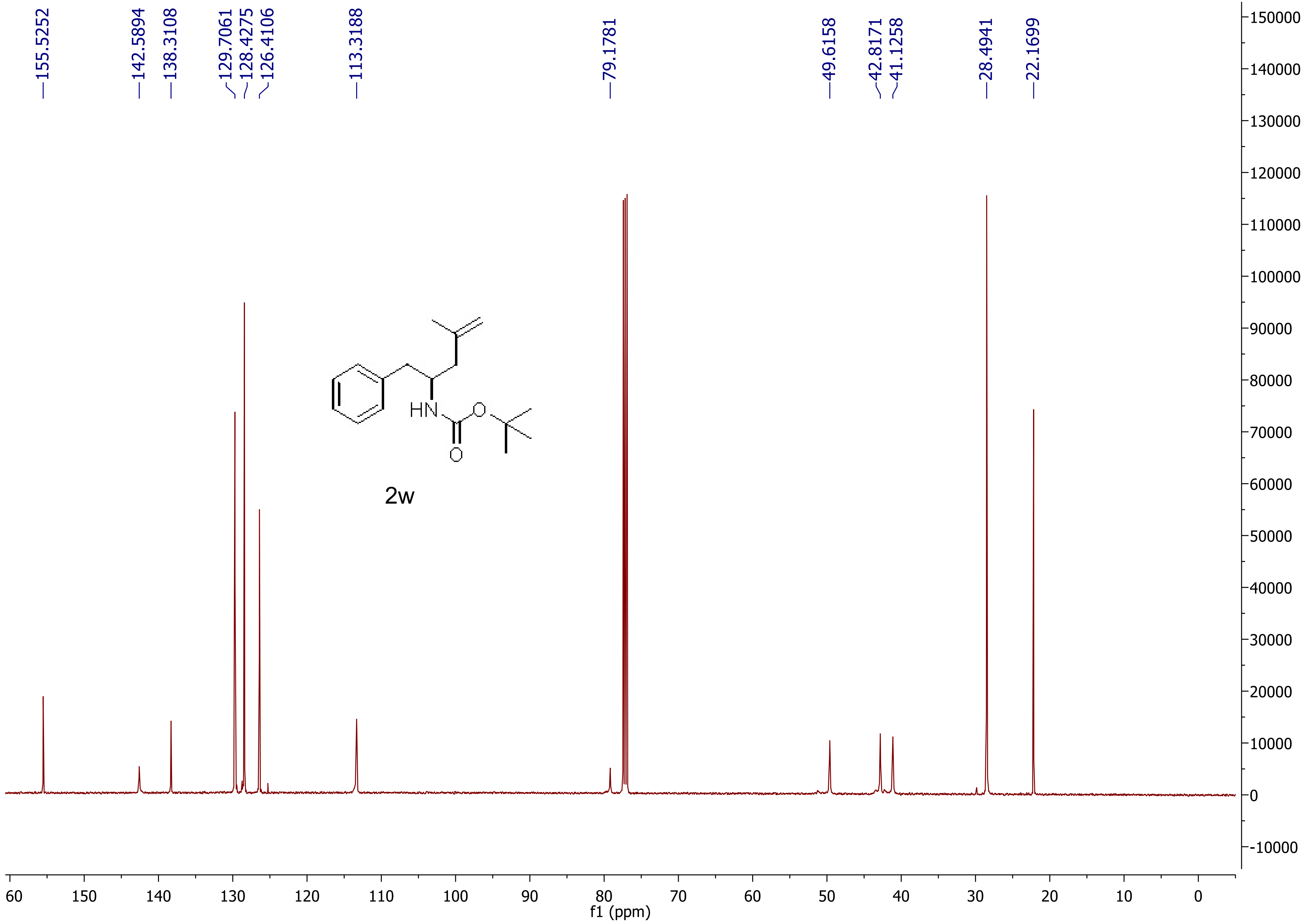


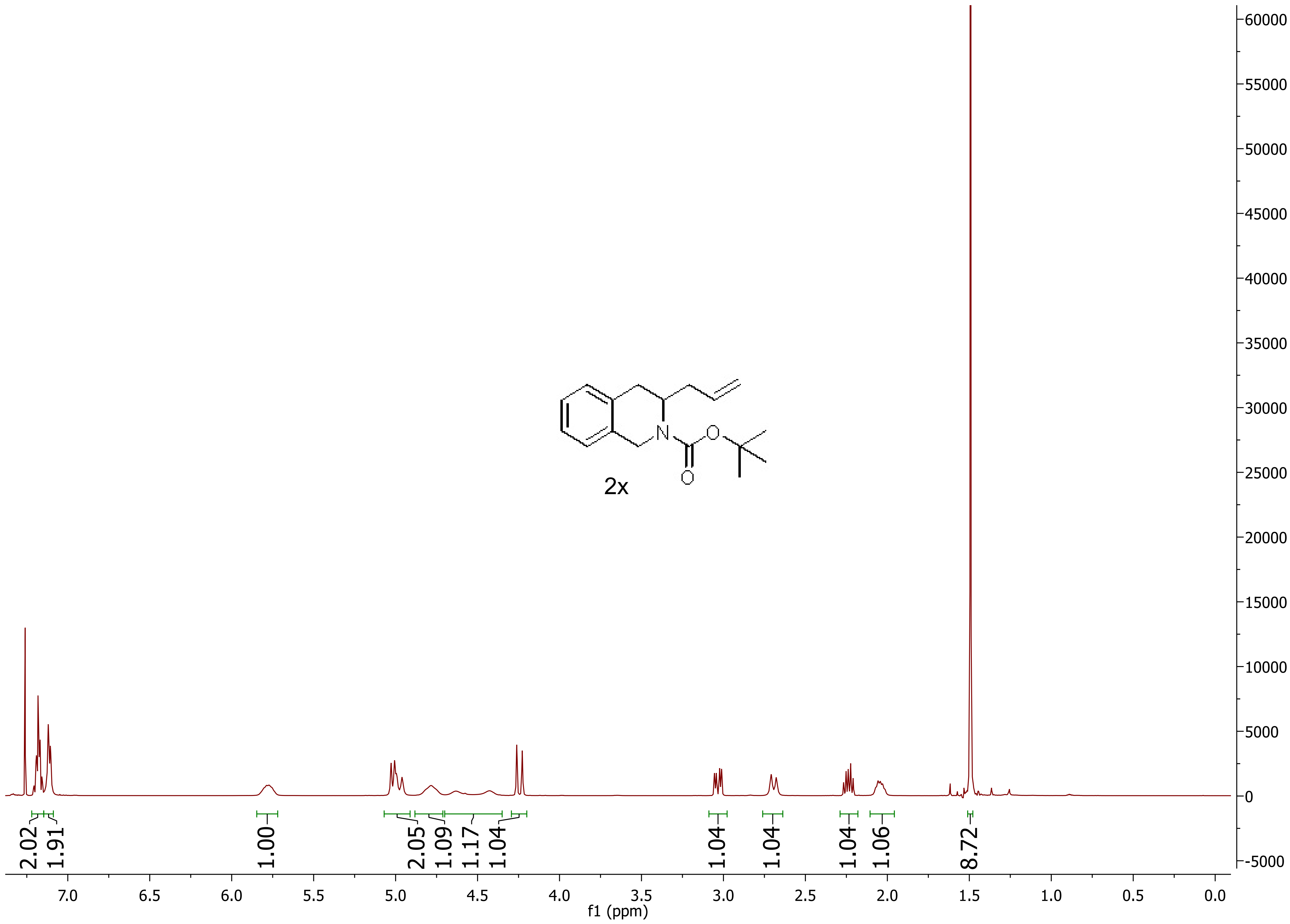
HN
O
N
O
2v
2.09
1.08
0.97
1.00
1.96
0.92
0.98
2.09
1.05
1.09
8.79
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
100000 90000 80000 70000 60000 50000 40000 30000 20000 10000 0


155.3605
150.7989
148.0207
136.9785
134.0446
133.7815
123.4590
118.5348
79.5176
50.8980
38.3669
37.7835
33.7234
28.4550
2v
HN
N
O
O
400000
350000
300000
250000
200000
150000
100000
50000
0
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

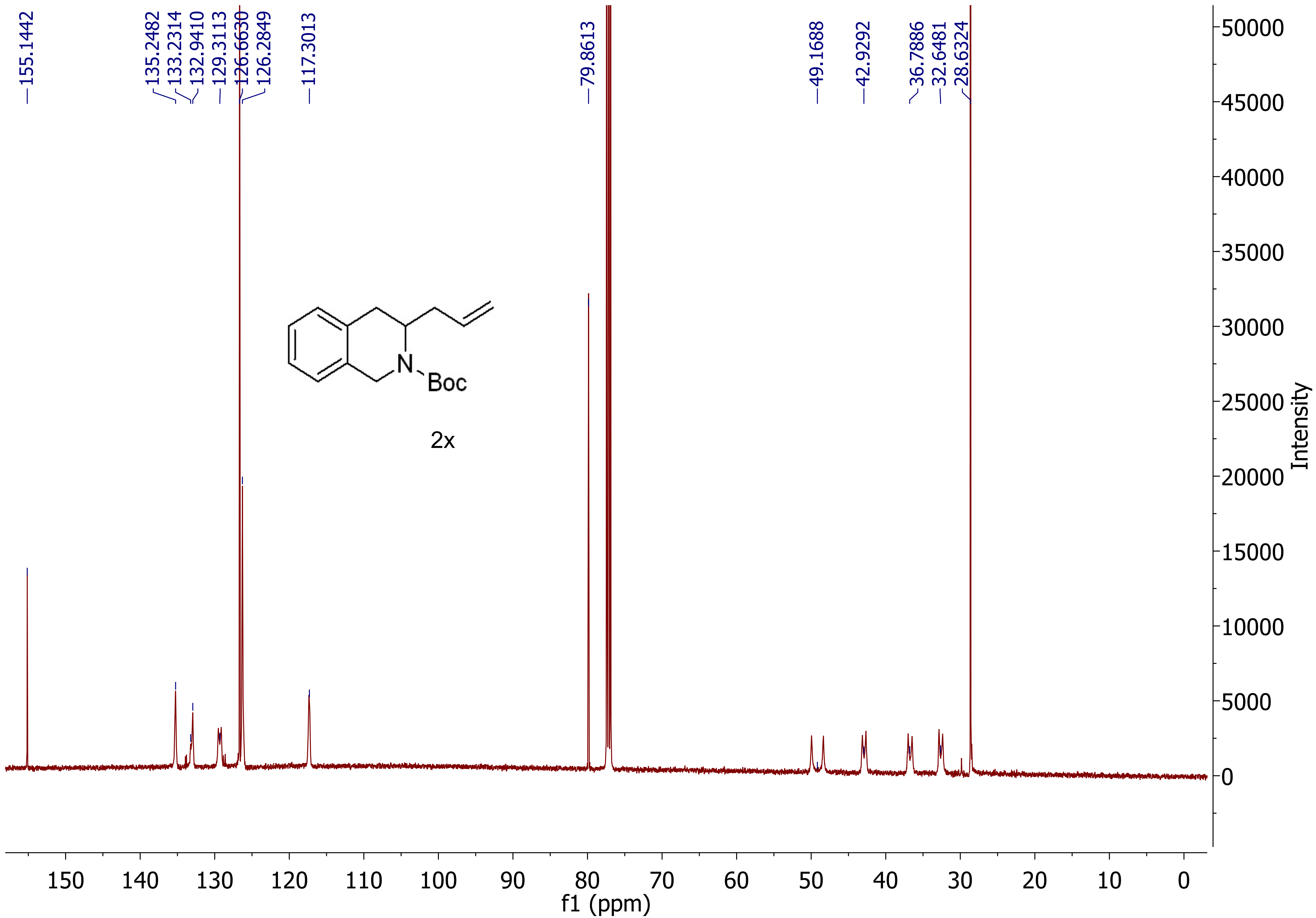


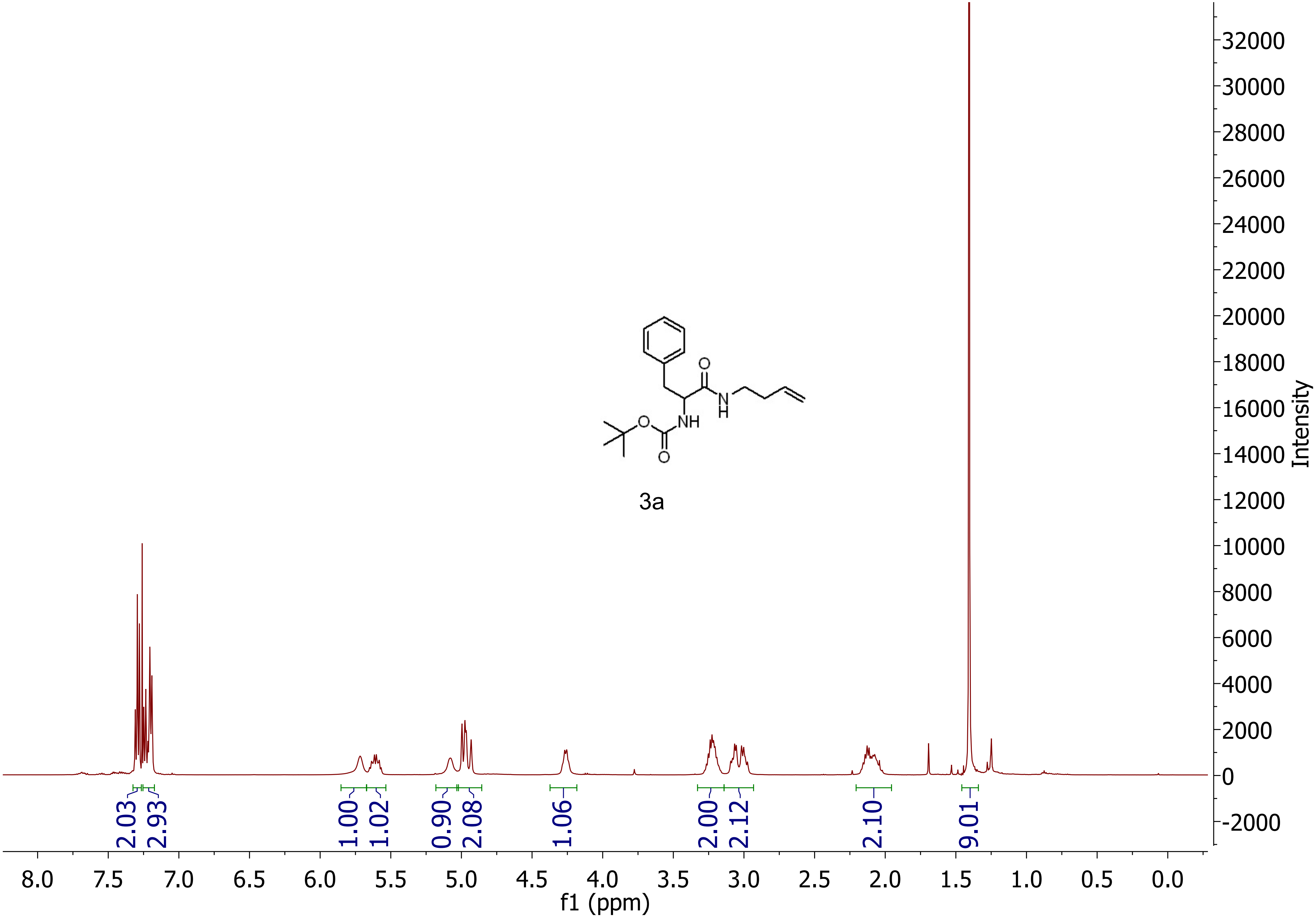
2w
HN
O
O
2.00
2.83
1.00
0.97
0.91
0.90
2.10
1.07
1.08
3.04
8.61
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
90000
80000
70000
60000
50000
40000
30000
20000
10000
0


155.5252
142.5894
138.3108
129.7061
128.4275
126.4106
113.3188
79.1781
49.6158
42.8171
41.1258
28.4941
22.1699
HN
O
O
2w
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

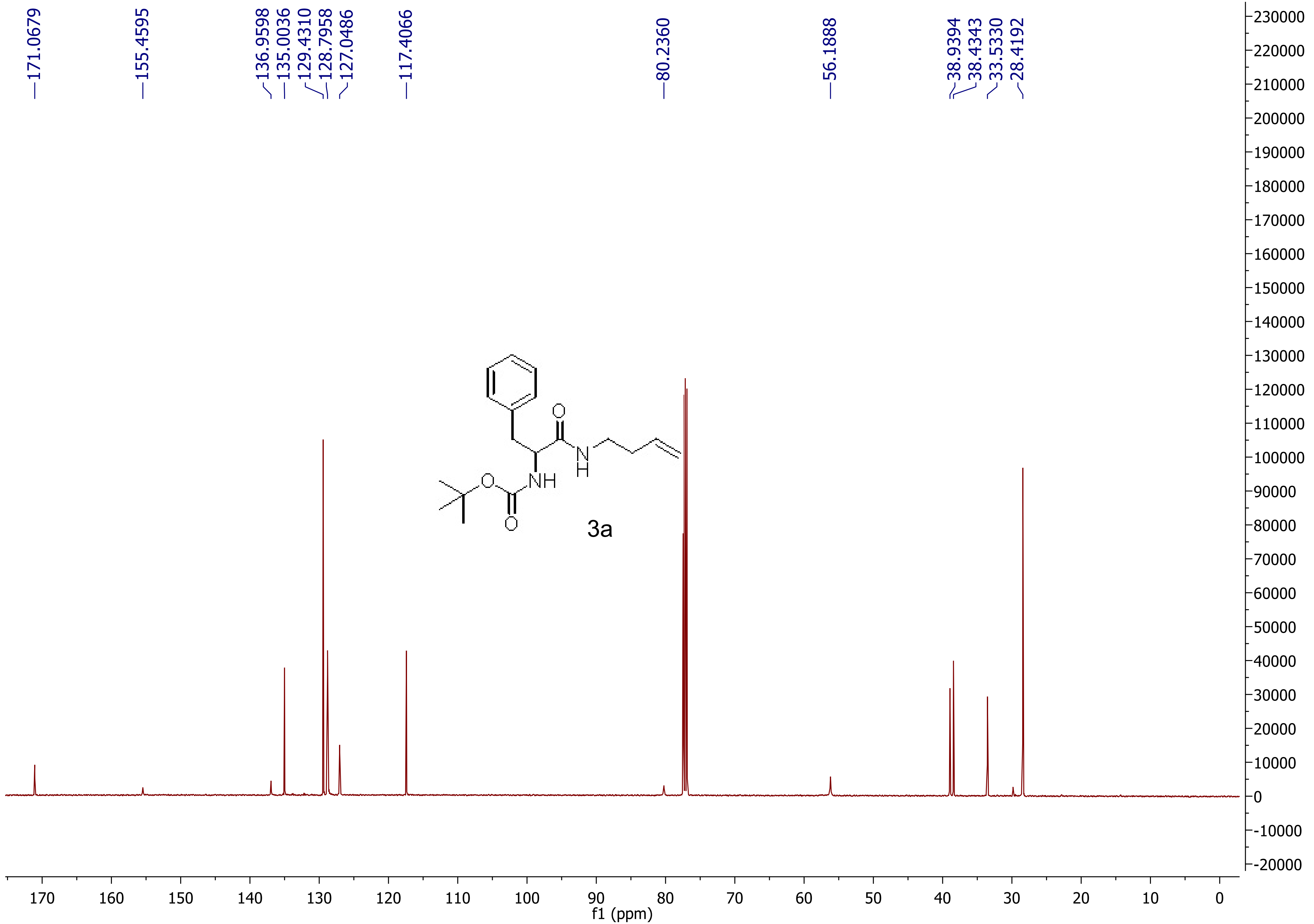


2x
N
O
O
2.02
1.91
1.00
2.05
1.09
1.17
1.04
1.04
1.04
1.04
1.06
8.72
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000


155.1442
135.2482
133.2314
132.9410
129.3113
126.6630
126.2849
117.3013
79.8613
49.1688
42.9292
36.7886
32.6481
28.6324
N
Boc
2x
Intensity
f1 (ppm)



O
NH
N
H
3a
2.03
2.93
1.00
1.02
0.90
2.08
1.06
2.00
2.12
2.10
9.01
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)
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity


171.0679
155.4595
136.9598
135.0036
129.4310
128.7958
127.0486
117.4066
80.2360
56.1888
38.9394
38.4343
33.5330
28.4192
O
N
H
O
NH
O
3a
f1 (ppm)