Direct, Intermolecular Iridium-Catalyzed Enantioselective Allylation of Carbamates to Form Branched Allylic Amines

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Supporting Information

General Methods.

Elemental Analyses were performed by Robertson Microlit Laboratories, Inc. (Madison, NJ) or by the University of Illinois Microanalysis Laboratory. GC/MS analyses were performed on an Agilent 6890N GC equipped with a 5973 MS and an HP-5ms column (30 m x 0.25 mm ID x 0.25 μm film). GC analyses were obtained on an Agilent 6890 GC equipped with an HP-5 column (25 m x 0.20 mm ID x 0.33 μm film) and an FID detector. Optical rotations were measured as solutions in chloroform (c = g/100 mL) on a Rudolph Instruments (Denville, NJ) Autopol IV. We thank the Zimmerman group for allowing us to use this instrument. IR spectra were obtained from thin films on NaCl plates using a Perkin-Elmer Spectrum BX FT-IR instrument. NMR spectra were acquired on 400, 500, or 600 MHz Varian Unity or Innova instruments (University of Illinois VOICE NMR facility) and data were processed using the NUTS software program (Acorn NMR, Inc., Livermore, CA). Chemical shifts are reported in ppm relative to residual solvent peak ($CDCl_3$ = 7.26 ppm for ^1H, 77.0 ppm for ^{13}C) or to external standard ($CFCl_3$ = 0 for ^{19}F and 85% H_3PO_4 = 0 for ^{31}P). Coupling constants are given in Hertz. HPLC analyses were conducted on a Waters chromatography system (1525 binary pump, 717+ autosampler, 2487 dual wavelength detector). SFC analysis was conducted on a Berger SFC system. We thank the Denmark group for allowing us to use this instrument.

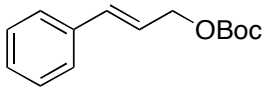
Chromatography was conducted on Silicycle Siala-P Silica gel using hexanes/ethyl acetate, hexanes/ether, or pentane/ether mixtures. While many products were visible on TLC using UV irradiation, all products were more easily identified by strong staining with $KMnO_4$ (orange). NMR yields were obtained from the unpurified isolate before chromatography by adding 50 μL of dichloroethane (Aldrich, 99.8%), diluting with a small amount of $CDCl_3$ to be sure all material is dissolved and the solution is homogeneous, and diluting a portion of this mixture in ~0.75 mL $CDCl_3$ for analysis (pulse delay of 10 s to ensure complete relaxation of protons).

Reaction progress was monitored by GC and GC/MS with dodecane as the internal standard (10 μL). Branched-to-linear ratios were determined by ^1H NMR spectroscopy (usually the olefinic protons) or by isolated yield when NMR was inconclusive. GC methods were found to be unreliable for many substrates. For example, in the case of *N*-Boc 1-heptyl allyl amine a 92:8 b:l ratio was indicated by GC analysis of the crude reaction mixture, but an 85:15 ratio was indicated by ^1H NMR analysis.

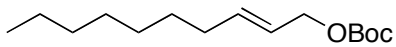
All starting materials were purchased from Aldrich except for $FmocNH_2$ (Fluka), Boc_2O (Fluka), $IrCl_3$ (Pressure Chemical or gift from Johnson Matthey), Xantphos (9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene) (Strem) and Trost's ligand [(1*S*, 2*S*)-(-)-1,2-Diaminocyclohexane-*N*,*N*'-bis(2-diphenylphosphino-1-naphthoyl)] (Strem). Propylamine was dried over calcium hydride, distilled, and stored under nitrogen. THF, pentane, benzene, ether, toluene, and CH_2Cl_2 were purified by passage of the degassed solvent (Ar) through a column of activated alumina (Solvent purification system purchased from Innovative Technologies of Newburyport, MA). Allylic alcohols were either purchased or synthesized from the corresponding aldehydes by the Roush-Masamune modification of the Horner-Wadsworth-Emmons reaction,[1] followed by DIBAL-H reduction. $[Ir(cod)Cl]_2$ was synthesized according to the procedure of Crabtree,[2] or commercial material (gift from Johnson-Matthey) was recrystallized from

CH_2Cl_2/EtOH. Unpurified commercial $[Ir(cod)Cl]_2$ produced a catalyst that was less reactive, but just as selective as the catalyst derived from purified material. The activity could be largely regained by the addition of 50 mol% K_3PO_4. Phosphoramidite ligands were synthesized according to published procedures.[3] $TeocNH_2$ was synthesized according to the published procedure.[4]

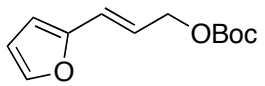
General Procedure for the Synthesis of Allylic Boc Carbonates. The procedure of Fréchet[5] was utilized with 1.4 equiv of Boc_2O, 0.03 equiv Bu_4NHSO_4, 30% aq NaOH (0.5 mL/mmol), and the allylic alcohol as limiting reagent in methylene chloride (0.26 mL/mmol). Mechanical stirring was used because the reaction mixture becomes a paste. The use of large amounts of methylene chloride in the workup prevented the formation of emulsions (15 mL/mmol). Products were generally contaminated with Boc_2O, and this impurity can be difficult to visualize by TLC or to remove by chromatography. We found that the procedure of Basel and Hassner was effective for removing unreacted Boc_2O.[6] The crude product was combined with 0.5 equiv of imidazole in absolute ethanol (0.5 M) and stirred for 5 min. The solvent was then removed, and the product was purified by column chromatography (SiO_2 with indicated solvent mixture, usually a short "plug" column was sufficient).



***tert*-Butoxy cinnamyl carbonate 2a.** The general procedure was followed on a 42 mmol scale, and the product was purified by column chromatography (98:2 EtOAc/Hexanes). The product was isolated as a turbid, viscous oil (8.2 g, 84% yield). The ^1H NMR spectrum matched the literature reports.[5,7] Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74; N, 0.0; Found: C, 72.03; H, 7.74; N, 0.02.

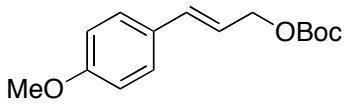


***tert*-Butoxy decenyl carbonate 2b.** The general procedure was followed on a 42 mmol scale, and the product was purified by column chromatography (TLC 30% CH_2Cl_2/70% Hexanes, product $R_f = 0.5$). The product was isolated as a clear oil (10.1 g, 94% yield). ^1H NMR ($CDCl_3$, 500 MHz) δ 0.88 (t, *J*=6.9 Hz, 3H), 1.21-1.32 (m, 8H), 1.37 (m, 2H), 1.48 (s, 9H), 2.04 (q, *J*=6.8 Hz, 2 H), 4.49 (dd, *J*=6.6,0.9 Hz, 2H), 5.57 (dtt, *J*=15.3,6.6,1.3 Hz, 1H), 5.79 (dt, *J*=15.3,6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1, 22.6, 27.8, 28.8, 29.08, 29.12, 31.8, 32.2, 67.8, 81.9, 123.4, 137.2, 153.4. IR (thin film): 2928, 1739, 1369, 1278, 1169, 970, 861 cm^{-1}. Anal. Calcd for $C_{15}H_{28}O_3$: C, 70.27; H, 11.01; N, 0.00; found: C, 70.67; H, 11.43; N, 0.02.

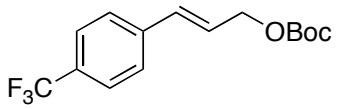


***tert*-Butoxy *E*-3-(2-furyl)-prop-2-enyl carbonate 2c.** The general procedure was followed on a 30 mmol scale, and the product was purified by column chromatography (40:1 Hexanes:Et_2O, the product is only moderately stable on silica gel). The product was isolated as a light yellow oil (5.3 g, 79% yield). ^1H NMR ($CDCl_3$, 600 MHz) δ 1.50 (s, 9H), 4.68 (dd, *J*=6.4,1.3 Hz, 2H), 6.21 (dt, *J*=15.8,6.5 Hz, 1H), 6.28 (d, *J*=3.3 Hz, 1H),

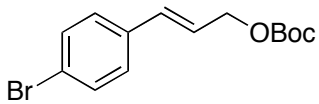
6.37 (dd, *J*=3.3,1.9 Hz, 1H), 6.47 (d, *J*=15.9 Hz, 1H), 7.35 (d, *J*=1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ 27.8, 67.0, 82.2, 108.9, 111.3, 121.4, 122.3, 142.4, 151.8, 153.3. IR (thin film): 1741, 1276, 1255, 1160 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19; N, 0.00; found: C, 63.91; H, 7.42; N, 0.02.



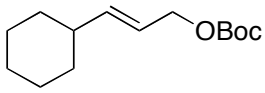
***tert*-Butoxy *E*-4-methoxycinnamyl carbonate 2d.** The general procedure was followed on a 6 mmol scale, and the product was purified by column chromatography (TLC, 70:30 CH_2Cl_2:Hexanes, R_f = 0.43). The product was isolated as a light yellow oil (0.91 g, 58% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.50 (s, 9H), 3.81 (s, 3H), 4.69 (dd, *J*=1.2, 6.7 Hz, 2H), 6.16 (dt, *J*=6.6, 15.8 Hz, 1H), 6.61 (d, *J*=15.9 Hz, 1H), 6.85 (m, 2H), 7.32 (m, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ 27.8, 55.3, 67.8, 82.1, 114.0, 120.5, 127.9, 128.9, 134.3, 153.4, 159.6. IR (thin film): 1740, 1512, 1274, 1250, 1160 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63; N, 0.00; found: C, 67.98; H, 7.37; N, 0.02.



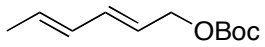
***tert*-Butoxy *E*-4-(trifluoromethyl)cinnamyl carbonate 2e.** The general procedure was followed on a 7.5 mmol scale, except that the treatment with imidazole and ethanol was omitted, and Boc_2O was removed by distillation under high-vacuum. The product was purified by column chromatography (SiO_2, 98:2 Hexanes:EtOAc) and isolated as a clear oil (2.0 g, 89% yield). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.51 (s, 9H), 4.74 (d, *J*=6.2 Hz, 2H), 6.38 (dt, *J*=6.1, 15.9 Hz, 1H), 6.70 (d, *J*=15.9 Hz, 1H), 7.48 (d, *J*=8.1 Hz, 2H), 7.57 (d, *J*=8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ 27.8, 66.9, 82.5, 122.9 (q, *J*=271.9 Hz), 125.6 (q, *J*=3.8 Hz), 125.8, 126.8, 129.3 (q, *J*=32.5), 132.5, 139.6, 153.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ -60.3. IR (thin film): 1742, 1326, 1276, 1255, 1163, 1123, 1068 cm^{-1}. Anal. Calcd for $C_{15}H_{17}F_3O_3$: C, 59.60; H, 5.67; N, 0.0; found: C, 59.75; H, 5.53; N, 0.02.



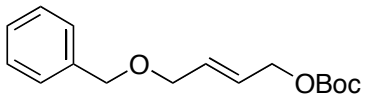
***tert*-butoxy 4-bromocinnamyl carbonate 2f.** The general procedure was followed on a 9.3 mmol scale, and the product was purified by column chromatography (90:10 pentane:Et_2O) and then recrystallized from hexanes (cooled to room temperature, then to -35 ºC overnight). The product was isolated as white crystals (2.11 g, 73% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.50 (s, 9H), 4.70 (dd, *J*=6.3,1.2 Hz, 2H), 6.28 (dt, *J*=15.9,6.4 Hz, 1H), 6.60 (d, *J*=15.9 Hz, 1H), 7.24 (m, 2H), 7.44 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.7, 67.1, 82.3, 121.9, 123.7, 128.1, 131.7, 133.0, 135.1, 153.3. IR (thin film): 1740, 1276, 1254, 1159 cm^{-1}. Anal. Calcd for $C_{14}H_{17}BrO_3$: C, 53.69; H, 5.47; N, 0.00; found: C, 53.93; H, 5.52; N, 0.02.



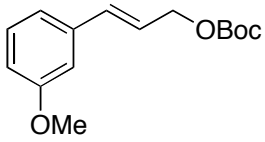
***tert*-butoxy *E*-3-cyclohexyl-2-propenyl carbonate 2g.** The general procedure was followed on a 7.5 mmol scale, except that the treatment with imidazole and ethanol was omitted, and the product was purified by column chromatography (SiO_2, 98:2 Hexanes:EtOAc). The product was isolated as a clear oil (1.39 g, 78% yield). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.01-1.32 (m, 5H), 1.48 (s, 9H), 1.61-1.73 (m, 5H), 1.97 (m, 1H), 4.49 (dt, *J*=6.7, 0.7 Hz, 2H), 5.52 (dtd, *J*=15.6, 6.6, 1.3 Hz, 1H), 5.73 (dd, *J*=15.6,6.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 25.9, 26.1, 27.8, 32.4, 40.3, 68.0, 81.9, 121.0, 142.6, 153.4. IR (thin film): 2925, 1740, 1278, 1254, 1163 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07; N, 0.00; found: C, 70.20; H, 10.16; N, 0.02.



***tert*-butoxy *E,E*-2,4-hexadienyl carbonate 2h.** The general procedure was followed except that the treatment with imidazole and ethanol was omitted, and the product was purified by column chromatography (TLC, 80:20 Hexanes:EtOAc, R_f = 0.55). The product was isolated as a light yellow oil (yield not determined). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.47 (s, 9H), 1.74 (ddd, *J*=6.8,1.0,0.4 Hz, 3H), 4.54 (d, *J*=6.6 Hz, 2H), 5.62 (dtd, *J*=15.3,6.7,0.7 Hz, 1H), 5.73 (dq, *J*=15.0,6.8 Hz, 1H), 6.03 (ddd, *J*=15.1,10.5,0.4 Hz, 1H), 6.24 (dd, *J*=15.3,10.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.1, 27.8, 67.4, 82.0, 123.3, 130.4, 131.4, 135.2, 153.4. IR (thin film): 1739, 1276, 1254, 1162 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15; N, 0.00; found: C, 66.92; H, 9.42; N, 0.02.

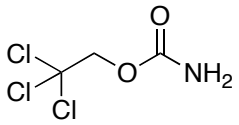


***tert*-butoxy *E*-4-benzyloxybut-2-enyl carbonate 2i.** The general procedure was followed on a 6 mmol scale, and the product was purified by column chromatography (TLC, 80:20 Hexanes:EtOAc, R_f = 0.55, column in 80:20 Hexanes:Et_2O). The product was isolated as a light yellow oil (1.44 g, 86% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.49 (s, 9H), 4.03-4.05 (m, 2H), 4.52 (s, 2H), 4.57-4.58 (m, 2H), 5.84-5.95 (m, 2H), 7.26-7.36 (m, 5H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.8, 66.7, 69.7, 72.2, 82.2, 126.4, 127.6, 127.7, 128.4, 131.4, 138.1, 153.3. IR (thin film): 1739, 1275, 1254, 1161 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97; N, 0.00; found: C, 69.02; H, 7.73; N, 0.02.

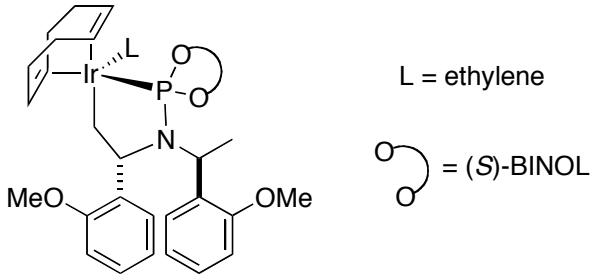


***tert*-butoxy 3-methoxycinnamyl carbonate 2j**. The general procedure was followed on a 6 mmol scale, and the product was purified by column chromatography (80:20 pentane:Et_2O). The product was isolated as a clear oil (1.38 g, 87% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.50 (s, 9H), 3.81 (s, 3H), 4.72 (dd, *J*=6.4,1.3 Hz, 2H), 6.29 (dt, *J*=15.9,6.4 Hz, 1H), 6.64 (d, *J*=15.9 Hz, 1H), 6.82 (ddd, *J*=8.2,2.6,0.7 Hz, 1H), 6.92 (t, *J*=2.0 Hz, 1H), 6.48 (d, *J*=7.7 Hz, 1H), 7.24 (t, *J*=7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.8, 55.2, 67.4, 82.3, 111.8, 113.8, 119.3, 123.2, 129.6, 134.2, 137.6, 153.3,

159.7. IR (thin film): 2979, 1733, 1599, 1580, 1368, 1271, 1156 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63; N, 0.00; found: C, 68.09; H, 7.63; N, 0.02.



2,2,2-trichloroethyl carbamate.[8] Commercially available 2,2,2-trichloroethyl chloroformate was added dropwise to an excess of ammonium hydroxide with vigorous stirring at 0 ºC. The white precipitated product was dissolved in methylene chloride, washed with water and brine, dried over Na_2SO_4, filtered, and the solvent removed. The product was isolated as a white solid in near quantitative yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.72 (s, 2H), 5.21 (br s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 74.6, 95.3, 155.1. IR (thin film): 3469, 1712, 1393, 1335, 807, 723 cm^{-1}. Anal. Calcd for $C_3H_4Cl_3NO_2$: C, 18.72; H, 2.10; N, 7.28; found: C, 18.97; H, 2.04; N, 7.32.



Ir(cod)(*P*,*C*-L2)(CH_2CH_2).[9]

Caution! Choose a vessel large enough so that the pressure inside the reaction will be close to ambient to avoid the chance of explosion!

The procedure of Markovic and Hartwig was generally followed with some modifications. A mixture of (*R*,*R*,*R*)-**L2** (346 mg, 0.576 mmol) and $[Ir(cod)Cl]_2$ (193 mg, 0.287 mmol, see general methods section) was dissolved in THF (6 mL) under N_2 and stirred (magnetic stir bar) in a sealed tube for 30 min. A heavy orange precipitate was observed. Under an inert atmosphere, 1 mL of anhydrous propylamine was added via syringe. The vessel was then attached to a vacuum line, the reaction mixture was frozen in liquid N_2, and the vessel was evacuated. Ethylene (5.76 mmol, 10 equiv, volumetric gas bulb) was then condensed into the reaction vessel. The vessel was sealed and allowed to warm to room temperature with stirring overnight. The reaction turned bright yellow and homogeneous during this time. The vessel was moved into a nitrogen filled glove box, and the reaction mixture was transferred to a 20 mL scintillation vial. To the THF solution in the vial was then added 6 mL of pentane. The vial was capped, the mixture shaken, and the resulting mixture was then cooled to -35 ºC to precipitate the $PrNH_2$•HCl salt. This solution was filtered (45 μm teflon syringe filter), and the solvent removed under vacuum. The product was isolated as a yellow/brown powder in quantitative yield. ^{1}H NMR (500 MHz, benzene-d_6) 8.73 (d, J = 6.5 Hz, 1H), 7.90-7.93 (m, 2H, ArH), 7.68 (d, J = 8.5 Hz, 1H, ArH), 7.67 (d, J = 9.0 Hz, 1H, ArH), 7.62 (d, J = 8.0 Hz, 1H, ArH), 7.59 (d, J = 8.0 Hz, 1H, ArH), 7.56 (d, J = 9.0 Hz, 1H, ArH), 7.46 (d, J = 8.5 Hz, 1H, ArH), 7.42 (d, J = 8.5 Hz, 1H, ArH), 7.17 (dt, J = 1.0, 7.5 Hz, 1H, ArH),

7.05-7.15 (m, 3H, ArH), 6.93-6.97 (m, 2H, ArH), 6.87-6.92 (m, 2H, ArH), 6.48 (dd, J = 8.0, 1.0 Hz, 1H, ArH), 6.22-6.26 (m, 1H, ArH), 5.14 (dq, J_{PH} = 9.5, J_{HH} = 7.0 Hz, 1H, C$\underline{H}$CH$_3$), 5.02 (ddd, J_{PH} = 30.0 Hz, J_{HH} = 8.0, 3.0 Hz, 1H, C$\underline{H}$CH$_2$Ir), 3.38-3.46 (m, 1H, =C$\underline{H}$ COD), 3.10-3.22 (m, 2H, 2 x =C$\underline{H}$ COD), 3.14 (s, 3H, OC$\underline{H}_3$), 2.88-2.95 (m, 1H, =C$\underline{H}_2$ ethylene), 2.78 (s, 3H, OC$\underline{H}_3$), 2.49-2.59 (m, 2H, 2 x C$\underline{H}_2$ COD), 2.33-2.40 (m, 1H, C$\underline{H}_2$ COD), 2.17-2.23 (m, 1H, =C$\underline{H}_2$ ethylene), 1.84-1.99 (m, 4H, 2 x =C$\underline{H}_2$ ethylene + 2 x C$\underline{H}_2$ COD), 1.75-1.83 (m, 2H, =C$\underline{H}$ COD + C$\underline{H}_2$ COD), 1.25-1.37 (m, 3H, Ir-C$\underline{H}_2$-CH + C$\underline{H}_2$ COD + C$\underline{H}_2$ COD), 1.19 (d, J = 7.0 Hz, 3H CH-C$\underline{H}_3$), 0.96 (dd, J= 11.5, 8.0 Hz, 1H, Ir-C$\underline{H}_2$-CH). ^{13}C NMR (125 MHz, benzene-d_6) δ 157.1 (Ar $\underline{C}$), 156.9 (Ar $\underline{C}$), 151.8 (d, J = 17 Hz, Ar $\underline{C}$), 150.3 (d, J = 5 Hz, Ar $\underline{C}$), 137.0 (Ar $\underline{C}$), 133.7 (Ar $\underline{C}$), 133.6 (Ar $\underline{C}$), 132.9 (Ar $\underline{C}$), 131.5 (Ar $\underline{C}$), 131.2 (Ar $\underline{C}$), 130.5 (Ar $\underline{C}$H), 130.0 (Ar $\underline{C}$H), 128.6 (Ar $\underline{C}$H), 128.5 (Ar $\underline{C}$H), 128.4 (Ar $\underline{C}$H), 127.8 (Ar $\underline{C}$H), 127.6 (Ar $\underline{C}$H), 127.5 (Ar $\underline{C}$H), 127.2 (Ar $\underline{C}$H), 127.1 (Ar $\underline{C}$H), 126.6 (Ar $\underline{C}$H), 126.5 (Ar $\underline{C}$H), 125.4 (Ar $\underline{C}$H), 125.0 (Ar $\underline{C}$H), 123.5 (Ar $\underline{C}$H), 122.6 (Ar $\underline{C}$H), 122.28 (Ar $\underline{C}$), 122.26 (Ar $\underline{C}$), 120.6 (Ar $\underline{C}$H), 120.0 (Ar $\underline{C}$H) 110.5 (Ar $\underline{C}$H), 110.1 (Ar $\underline{C}$H), 90.5 (COD $\underline{C}$H), 77.7 (COD $\underline{C}$H), 62.2 (d, J_{CP} = 43 Hz, $\underline{C}$H-CH$_2$), 58.6 (d, J = 8 Hz, COD CH), 58.2 (d, J_{CP} = 22 Hz, COD $\underline{C}$H), 54.6 (O$\underline{C}$H$_3$), 54.2 (O$\underline{C}$H$_3$), 52.6 (d, J = 7 Hz, COD $\underline{C}$H), 37.0 (COD $\underline{C}$H$_2$), 33.3 (=$\underline{C}$H$_2$ ethylene), 33.0 (COD $\underline{C}$H$_2$), 32.5 (COD $\underline{C}$H$_2$), 29.6 (=$\underline{C}$H$_2$ ethylene) 29.5 (COD $\underline{C}$H$_2$), 22.9, (Ir-$\underline{C}$H$_2$), 20.9 (CH-$\underline{C}$H$_3$). ^{31}P NMR ($CDCl_3$, 243 MHz) δ 154.0. Anal. Calcd for $C_{48}H_{49}IrNO_4P$: C, 62.18; H, 5.33; N, 1.51; found: C, 61.99; H, 5.46; N, 1.95.

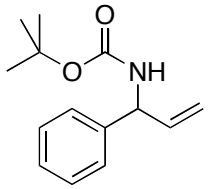
General Procedures for the Synthesis of *N*-Boc Allyl Amines.

Procedure A. In an nitrogen filled glove box, Ir(cod)(*P*,*C*-**L2**)(CH_2CH_2) (18.5 mg, 0.02 mmol, derived from (*R*,*R*,*R*)-**L2** unless otherwise noted) was added to a 1-dram vial, followed by *tert*-butoxy carbamate (82 mg, 0.7 mmol). A small stirbar and dodecane (10 μL) were then added, and 0.5 mL of THF was added. This mixture was stirred briefly to dissolve all of the catalyst (The carbamate may not completely dissolve.). Finally, the allylic *tert*-butoxy carbonate (0.5 mmol) was weighed into the vial by pipette. The vial was sealed with a PTFE faced septum in a screw-top cap, removed from the glove box, and stirred at 30 ºC for the specified time.

Procedure B. Same as procedure A except that diethyl ether was the solvent instead of THF, and the reaction was conducted at room temperature.

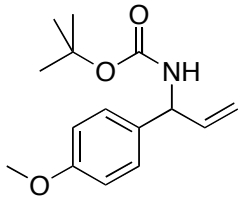
Procedure C. Same as procedure A except that diethyl ether was the solvent and 0.5 equiv of K_3PO_4 was added along with the carbamate.

Procedure D. Same as procedure A except that diethyl ether was the solvent and 0.2 equiv of DBU was added along with the carbamate.

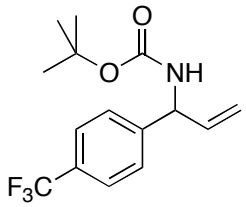


***N*-Boc 1-phenyl allylamine 3a.**[10-14] General procedure A was followed on a 0.508 mmol scale, and the reaction was judged complete by GC after 24 h. Chromatogaphy on silica gel (TLC 90:10 hexanes:EtOAc, R_f = 0.35) yielded 94.6 mg of pure branched product (80 % yield). HPLC (Daicel Chiralcel OJ-H (0.46 cm x 25 cm), hexanes/2-propanol = 99 : 1, v = 1.0 mL/min, λ = 210 nm, ~25 °C): t_R [min] = 10.2 (99.3%), 12.3 (0.7%), 99 % ee. ^{1}H

NMR ($CDCl_3$, 500 MHz) δ 1.45 (s, 9H), 4.92 (br s, 1H), 5.21 (dt, *J*=13.3,1.7 Hz, 2H), 5.27 (br s, 1H), 5.98 (m, 1H), 7.21-7.35 (m, 5H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.3, 56.6, 79.6, 115.4, 127.0, 127.5, 128.6, 137.9, 141.0, 155.0. $[\alpha]_D^{28}$ + 73.0 º (*c* 1.06, $CHCl_3$). Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00; found: C, 72.04; H, 8.47; N, 5.90. The experiment was repeated using the catalyst derived from (*S*,*S*,*S*)-**L2** on a 0.503 mmol scale, and 105 mg of product (89% yield, 99% ee) was obtained.

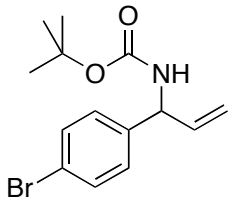


***N*-Boc 1-(4-methoxyphenyl) allylamine 3d.** General procedure B was followed on a 0.522 mmol scale, and the reaction was judged complete by GC after 3 h. Chromatogaphy on silica gel (TLC 7:3 hexanes:Et_2O, R_f = 0.36) yielded 122 mg of pure branched product (89 % yield) as a white crystalline solid. HPLC (Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99 : 1, v = 1.0 mL/min, λ = 220 nm, ~25 °C): t_R [min] = 22.8 (99.2%), 25.0 (0.8%), 98% ee. ^1H NMR ($CDCl_3$, 500 MHz) δ 1.44 (s, 9H), 3.79 (s, 3H), 4.82 (br s, 1H), 5.18-5.26 (overlapping br s and m, 3H), 5.98 (m, 1H), 6.87 (m, 2H), 7.21 (d, *J*=8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.3, 55.3, 56.0, 79.6, 114.0, 115.1, 128.2, 133.2, 138.1, 155.0, 158.9. IR (thin film): 3371, 1681, 1524, 1169, 1029 cm^{-1}. $[\alpha]_D^{28}$ + 77.3 º (*c* 0.82, $CHCl_3$). Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32; found: C, 68.23; H, 8.35; N, 5.11. The experiment was repeated using the catalyst derived from (*S*,*S*,*S*)-**L2** on 0.492 mmol scale, and 105 mg of product (81% yield) was obtained. HPLC (Daicel Chiralcel AS-H (0.46 cm x 25 cm), hexanes/2-propanol = 99 : 1, v = 1.0 mL/min, λ = 210 nm, ~25 °C): t_R [min] = 12.1 (99.5 %), 14.8 (0.5%), 99% ee.

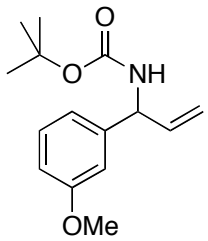


***N*-Boc 1-(4-trifluoromethylphenyl) allylamine 3e.** General procedure C was followed on a 0.483 mmol scale, and the reaction was judged complete by GC after 23 h. Chromatogaphy on silica gel (TLC 7:3 hexanes:Et_2O, $R_{f(branched)}$ = 0.36, $R_{f(linear)}$ = 0.19) yielded 106 mg of pure branched product (73 % yield). HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99 : 1, v = 1.0 mL/min, λ = 210 nm, ~25 °C): t_R [min] = 6.8 (0.4 %), 8.9 (99.6%), 99% ee. ^1H NMR ($CDCl_3$, 500 MHz) δ 1.43 (s, 9H), 4.95 (br s, 1H), 5.20 (d, *J*=17 Hz, 1H), 5.26 (d, *J*=10.4 Hz, 1H), 5.34 (br s, 1H), 5.96 (m, 1H), 7.41 (d, *J*=8.1 Hz, 2H), 7.59 (d, *J*=8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.3, 56.3, 80.0, 116.7, 124.1 (q, *J*=271 Hz), 125.6 (q, *J*=3.7 Hz), 127.2, 129.7 (q, *J*=32.6 Hz), 137.1, 145.2, 154.9. ^{19}F NMR ($CDCl_3$, 470 MHz) δ -62.8. IR (thin film): 3371, 2980, 1683, 1527, 1327, 1161, 1124, 1067 cm^{-1}. $[\alpha]_D^{28}$ + 30.7 º (*c* 2.17, $CHCl_3$). Anal. Calcd for $C_{15}H_{18}F_3NO_2$: C, 59.79; H, 6.02; N, 4.65; found: C, 60.17; H, 6.03; N, 4.47.

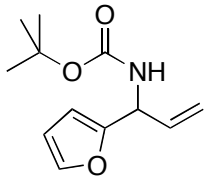
The experiment was repeated using the catalyst derived from (*S*,*S*,*S*)-**L2** on a 0.500 mmol scale for 36 h, and 86 mg of product (57% yield, 99% ee by HPLC) was obtained.



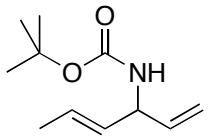
***N*-Boc 1-(4-bromophenyl) allylamine 3f.** General procedure A was followed on a 0.498 mmol scale. Chromatogaphy on silica gel (TLC 7:3 hexanes:Et_2O, R_f = 0.40) yielded 122 mg of pure branched product (79 % yield). HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99 : 1, v = 1.0 mL/min, λ = 210 nm, ~25 °C): t_R [min] = 8.2 (0.4 %), 9.8 (99.6%), 99% ee. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.42 (s, 9H), 4.91 (br s, 1H), 5.18 (d, *J*=17.2 Hz, 1H), 5.22 (d, *J*=20.4 Hz, 1H), 5.24 (br s, 1H), 5.93 (m, 1H), 7.16 (d, *J*=8.1 Hz, 2H), 7.45 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 20.3, 56.0, 79.8, 116.1, 121.3, 128.7, 131.6, 137.3, 140.1, 154.9. IR (thin film): 3377, 1682, 1514, 1168 cm^{-1}. $[\alpha]_D^{28}$ + 53.0 º (*c* 1.03, $CHCl_3$). Anal. Calcd for $C_{14}H_{18}BrNO_2$: C, 53.86; H, 5.81; N, 4.49; found: C, 54.04; H, 5.90; N, 4.30. The experiment was repeated using procedure C and the catalyst derived from (*S*,*S*,*S*)-**L2** on 0.498 mmol scale for 21 h, and 122 mg of product (79% yield, 99% ee by HPLC) was obtained.



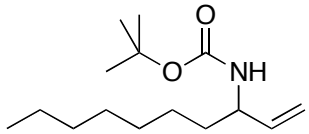
***N*-Boc 1-(3-methoxyphenyl) allylamine 3h.** General procedure B was followed on a 0.518 mmol scale, except that the catalyst derived from (*S*,*S*,*S*)-**L2** was used. The reaction was judged complete by GC after 12 h. Chromatography on silica gel (TLC 7:3 hexanes:Et_2O, R_f = 0.23) yielded 99.1 mg of pure branched product (73 % yield) as an oil. HPLC (Daicel Chiralcel OJ-H (0.46 cm x 25 cm), hexanes/2-propanol = 99 : 1, v = 1.0 mL/min, λ = 210 nm, ~25 °C): t_R [min] = 12.3 (0.7%), 15.9 (99.3%), 99% ee. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.44 (s, 9H), 3.79 (s, 3H), 4.91 (br s, 1H), 5.21 (d, *J*=2.3,1.5 Hz, 1H), 5.23 (d, *J*=10.6 Hz, 1H), 5.26 (br s, 1H), 5.97 (m, 1H), 6.80-6.83 (m, 2H), 6.88 (d, *J*=7.7 Hz, 1H), 7.25 (t, *J*=7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.3, 55.1, 56.5, 79.6, 112.7, 112.8, 115.4, 119.2, 129.6, 137.8, 142.6, 155.0, 159.8. IR (thin film): 3339, 1695, 1489, 1366, 1249, 1167, 1043 cm^{-1}. $[\alpha]_D^{28}$ – 60.3 º (*c* 1.08, $CHCl_3$). Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32; found: C, 68.68; H, 7.78; N, 5.28. The experiment was repeated on 0.492 mmol scale using the catalyst derived from (*R*,*R*,*R*)-**L2** for 12 h and 114 mg of product (88% yield, 99% ee) was obtained.



***N*-Boc 1-(2-furyl) allylamine 3c.** General procedure B was followed on a 0.513 mmol scale, except that the catalyst derived from (*S*,*S*,*S*)-**L2** was used, and the reaction was judged complete by GC after 21 h. Chromatography on silica gel (TLC 7:3 hexanes:Et_2O, R_f = 0.59) yielded 73.0 mg of pure branched product (64 % yield) as a clear oil. HPLC (Daicel Chiralcel OJ-H (0.46 cm x 25 cm), hexanes/2-propanol = 99 : 1, v = 1.0 mL/min, λ = 200 nm, ~25 °C): t_R [min] = 8.1 (0.8 %), 10.7 (99.2%), 98% ee. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.45 (s, 9H), 4.95 (br s, 1H), 5.21-5.27 (m, 2H), 5.37 (br s, 1H), 5.98 (m, 1H), 6.18 (d, *J*=3 Hz, 1H), 6.31 (dd, *J*=3.1, 1.9 Hz, 1H), 7.36 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.3, 50.6, 79.8, 106.5, 110.2, 116.0, 135.4, 142.2, 153.3, 154.9. IR (thin film): 3323, 1699, 1501, 1367, 1168 cm^{-1}. $[\alpha]_D^{28}$ – 71.2 º (*c* 0.98, $CHCl_3$). Anal. Calcd for $C_{12}H_{17}NO_2$: C, 64.55; H, 7.67; N, 6.27; found: C, 64.47; H, 7.90; N, 6.25. The experiment was repeated using the catalyst derived from (*R*,*R*,*R*)-**L2** on a 0.482 mmol scale, and 41.5 mg of product (39% yield, 97% ee) was obtained.

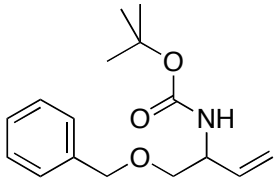


***N*-Boc 1-vinyl prop-2-enylamine 3h.** General procedure B was followed on a 0.484 mmol scale, and the reaction was judged complete by GC after 19 h. Chromatogaphy on silica gel (TLC 7:3 hexanes:Et_2O, R_f = 0.54) yielded 73.5 mg of pure branched product (77 % yield) as a light yellow oil. HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.75 : 0.25, v = 1.0 mL/min, λ = 200 nm, ~25 °C): t_R [min] = 9.2 (2.1 %), 10.5 (97.9%), 96% ee. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.45 (s, 9H), 1.70 (m, 3H), 4.54 (br s, 1H), 4.63 (br s, 1H), 5.11 (dt, *J*=10.4,1.3 Hz, 1H), 5.17 (dt, *J*=17.2,1.4 Hz, 1H), 5.42 (dd, *J*=15.3,1.7 Hz, 1H), 5.63 (dqd, *J*=15.4,6.5,1.2 Hz, 1H), 5.81 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.7, 28.4, 54.0, 79.4, 114.7, 127.1, 130.0, 138.0, 155.1. IR (thin film): 3318, 1699, 1695, 1505, 1173 cm^{-1}. $[\alpha]_D^{28}$ + 28.1 º (*c* 0.81, $CHCl_3$). Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10; found: C, 66.88; H, 9.87; N, 6.94. The experiment was repeated using the catalyst derived from (*S*,*S*,*S*)-**L2** on a 0.489 mmol scale, and 76.8 mg of product (80% yield, 94% ee) was obtained.



***N*-Boc 1-heptyl allylamine 3b.** General procedure B was followed on a 0.503 mmol scale, and the reaction was judged complete by GC after 5 h. Chromatogaphy on silica gel (97.5:2.5 EtOAc:hexanes) yielded 104 mg of pure branched product (76 % yield) as an oil. HPLC (Daicel Chiralcel AS-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.9 : 0.1, v = 1.0 mL/min, λ = 210 nm, ~25 °C): t_R [min] = 9.3 (0.7%), 10.9 (99.3%), 99% ee.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.87 (t, *J*=7.2 Hz, 3H), 1.21-1.34 (m, 10 H), 1.41-1.53 (m, 2H), 1.44 (s, 9H), 4.08 (br s, 1H), 4.43 (br s, 1H), 5.07 (d, *J*=10.3 Hz, 1H), 5.14 (d, *J*=17.3 Hz, 1H), 5.74 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1, 22.6, 25.7, 28.4, 29.2, 29.4, 31.8, 35.2, 52.7, 79.2, 114.1, 139.2, 155.4. IR (thin film): 3337, 2928, 1694, 1519, 1365, 1173 cm^{-1}. $[\alpha]_D^{28}$ + 12.0 º (*c* 1.02, $CHCl_3$). Anal. Calcd for $C_{15}H_{29}NO_2$: C, 70.54; H, 11.45; N, 5.48; found: C, 70.80; H, 11.72; N, 5.62. The experiment was repeated using the catalyst derived from (*S*,*S*,*S*)-**L2** on a 0.488 mmol scale, and 74.0 mg of product (59% yield, 94% ee) was obtained.



1-(Benzyloxy)-2-(Boc-amino)but-3-ene 3i.[15] General procedure B was followed on 0.489 mmol scale, and the reaction was judged complete by GC after 21 h. Chromatography on silica gel (85:15 to 80:20 pentane:Et_2O) yielded 77.4 mg of pure branched product (57 % yield) as an oil. HPLC (Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99 : 1, v = 1.0 mL/min, λ = 200 nm, ~25 °C): t_R [min] = 14.5 (1.25%), 16.7 (98.75%), 98% ee. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.45 (s, 9H), 3.50-3.57 (m, 2H), 4.32 (br s, 1H), 4.51 (d, *J*=11.9 Hz, 1H), 4.55 (d, *J*=12 Hz, 1H), 4.91 (br s, 1H), 5.17 (dt, *J*=10.3,1.1 Hz, 1H), 5.24 (dt, *J*=17.2,1.4 Hz, 1H), 5.86 (ddd, *J*=17.2,10.5,5.4 Hz, 1H), 7.27-7.37 (m, 5H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 28.4, 52.5, 72.1, 73.2, 79.4, 155.6, 127.6, 127.7, 128.4, 136.4, 137.9, 155.4. IR (thin film): 3437, 3333, 2976, 1716, 1495, 1365, 1248, 1169, 1104, 735, 697 cm^{-1}. $[\alpha]_D^{28}$ +30.9 º (*c* 0.62, $CHCl_3$). Anal. Calcd for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05; found: C, 69.07; H, 8.09; N, 4.94. The experiment was repeated on 0.489 mmol scale using the catalyst derived from (*S*,*S*,*S*)-**L2** and 87.8 mg of product (65% yield, 97% ee) was obtained.

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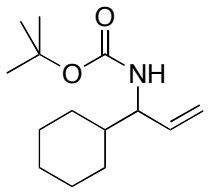
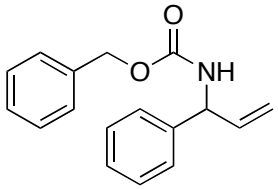
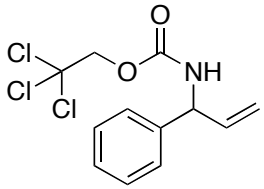


***N*-Boc 1-cyclohexyl allylamine 3g.**[15] General procedure C was followed on a 0.491 mmol scale, and the reaction was judged complete by GC after 48 h. Chromatogaphy on silica gel (TLC 9:1 hexanes:EtOAc, $R_{f(branch)}$ = 0.31, $R_{f(linear)}$ = 0.25; column in 9:1 pentane:Et_2O) yielded 31.0 mg of pure branched product (26 % yield) as a cystalline solid. HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.75 : 0.25, v = 1.0 mL/min, λ = 200 nm, ~25 °C): t_R [min] = 7.9 (0.6%), 9.3 (99.4%), 99% ee. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.93-1.25 (series of m, 5 H), 1.35-1.45 (m, 1H), 1.44 (s, 9H), 1.63-1.76 (series of m, 5H), 3.96 (br s, 1H), 4.52 (br s, 1H), 5.09-5.14 (m, 2H), 5.72 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 26.1, 26.2, 26.3, 28.4, 28.6, 29.3, 42.3, 57.5, 79.1, 114.9, 137.5, 155.5. IR (thin film): 3360, 2916, 1681, 1526 cm^{-1}. $[\alpha]_D^{28}$ + 36.0 º (*c* 0.65, $CHCl_3$). Anal. Calcd for $C_{14}H_{25}NO_2$: C, 70.25; H, 10.53; N, 5.85; found: C,

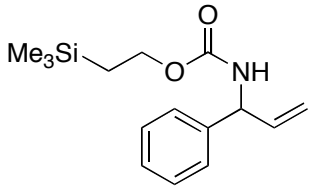
70.32; H, 10.81; N, 5.73. The experiment was repeated using 8 mol% of the catalyst derived from (*S*,*S*,*S*)-**L2** and 10 mol% K_3PO_4 on a 0.500 mmol scale for 72 h, and 31.0 mg of product (25% yield, 99% ee) was obtained.



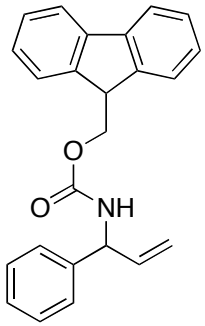
(*R*)-*N*-Cbz 1-phenyl allylamine 4.[11,16,17] General procedure C was followed on 0.512 mmol scale, and the reaction was judged complete by GC at 9 h. Chromatogaphy on silica gel (TLC 9:1 hexanes:EtOAc, R_f = 0.17) yielded 103 mg of pure branched product as a white solid (76 % yield). HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99 : 1, v = 1.0 mL/min, λ = 210 nm, ~25 °C): t_R [min] = 22.5 (1.4%), 31.5 (98.6%), 97% ee. Correlation with the reported order of elution on an OD-H column showed the product to possess the (*R*) configuration.[17] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.09-5.15 (m, 3H), 5.22-5.26 (m, 2H), 5.37 (br s, 1H), 6.01 (m, 1H), 7.27-7.36 (m, 10 H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ 57.0, 66.9, 82.5, 115.8, 127.0, 127.7, 128.1, 128.5, 128.7, 136.3, 137.5, 140.5, 155.5. IR (thin film): 3323, 1687, 1538, 1245, 698 cm^{-1}. $[\alpha]_D^{28}$ + 52.9 º (*c* 1.04, $CHCl_3$). Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24; found: C, 76.48; H, 6.61; N, 5.18. The experiment was repeated on a 0.495 mmol scale at room temperature for 24 h, and 94 mg of product (71% yield, 97% ee) was obtained.



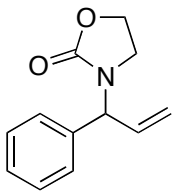
***N*-Troc 1-phenyl allylamine 5.** General procedure D was followed on a 0.482 mmol scale, and the reaction was judged complete by GC at 10 h. Chromatogaphy on silica gel (9:1 pentane:Et_2O) yielded 124 mg of pure branched product (83 % yield) as an oil. HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99 : 1, v = 1.0 mL/min, λ = 200 nm, ~25 °C): t_R [min] = 15.9 (97.6%), 30.1 (2.4%), 95% ee. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.71 (d, *J*=12.1 Hz, 1H), 4.78 (d, *J*=12.1 Hz, 1H), 5.26-5.32 (overlapping m, 3H), 5.38 (m, 1H), 6.03 (m, 1H), 7.29-7.32 (m, 3H), 7.36-7.39 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 57.3, 74.6, 95.5, 116.2, 127.1, 127.9, 128.8, 136.9, 139.9, 153.7. IR (thin film): 3326, 1719, 1517, 1232, 700 cm^{-1}. $[\alpha]_D^{28}$ + 54.2 º (*c* 1.02, $CHCl_3$). Anal. Calcd for $C_{12}H_{12}Cl_3NO_2$: C, 46.71; H, 3.92; N, 4.54; found: C, 46.86; H, 3.85; N, 4.46. The experiment was repeated on a 0.492 mmol scale using the catalyst derived from (*S*,*S*,*S*)-**L2** for 12 h, and 116 mg of product (77% yield, 95% ee) was obtained.



***N*-Teoc 1-phenyl allylamine 6.** General procedure C was followed on 0.503 mmol scale, and the reaction was judged complete by GC at 10 h. Chromatogaphy on silica gel (TLC hexanes:Et_2O, R_f = 0.4) yielded 107 mg of pure branched product (76 % yield) as an oil. HPLC (Daicel Chiralcel OJ-H (0.46 cm x 25 cm), hexanes/2-propanol = 99 : 1, v = 1.0 mL/min, λ = 210 nm, ~25 °C): t_R [min] = 15.1 (99.1%), 18.4 (0.9%), 98% ee. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.03 (s, 9H), 0.98 (dd, *J*=9.8,7.3 Hz, 2H), 4.12-4.21 (m, 2H), 4.95 (br s, 1H), 5.21-5.24 (m, 2H), 5.34 (br s, 1H), 6.00 (m, 1H), 7.27-7.30 (m, 3H), 7.33-7.37 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ -1.5, 17.7, 56.9, 63.3, 115.7, 127.0, 127.6, 128.7, 137.7, 140.8, 156.2. IR (thin film): 3314, 1685, 1534, 1247, 736 cm^{-1}. $[\alpha]_D^{28}$ + 63.0 º (*c* 0.98, $CHCl_3$). Anal. Calcd for $C_{15}H_{23}NO_2Si$: C, 64.94; H, 8.36; N, 4.76; found: C, 65.17; H, 8.13; N, 4.78. The experiment was repeated on 0.500 mmol scale using the catalyst derived from (*S*,*S*,*S*)-**L2**, and 96.7 mg of product (70% yield, 99% ee) was obtained.



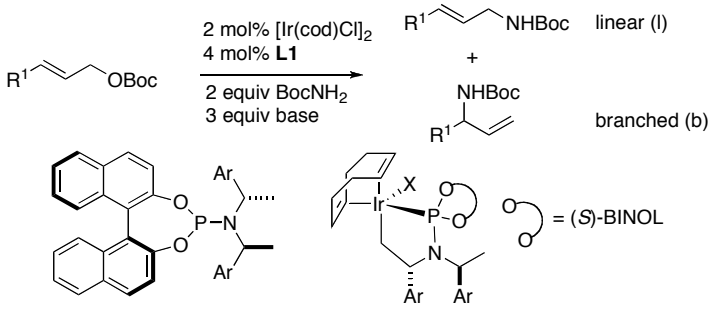
***N*-Fmoc 1-phenyl allylamine 7.** General procedure C was followed on a 0.503 mmol scale with an extra 0.5 mL of THF added, and the reaction was judged complete by GC and TLC after 21 h. Chromatogaphy on silica gel (dry-load on SiO_2 with CH_2Cl_2, elute with 85:15 pentane:Et_2O) yielded 103 mg of pure branched product (57 % yield) as a white solid. SFC analysis (Daicel Chiralcel OD (0.46 cm x 25 cm), 15% MeOH in $scCO_2$, v = 3.0 mL/min, λ = 220 nm, ~25 °C): t_R [min] = 9.3 (97.9%), 12.5 (2.1%), 96% ee. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.23 (t, *J*=6.6 Hz, 1H), 4.46 (m, 2H), 5.15 (br s, 1H), 5.22-5.27 (m, 2H), 5.38 (br s, 1H), 6.03 (m, 1H), 7.29-7.43 (m, 9H), 7.60 (d, *J*=5.9 Hz, 2H), 7.78 (d, *J*=7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 47.2, 57.0, 66.6, 115.9, 119.9, 125.0, 127.00, 127.04, 127.6, 127.7, 128.7, 137.4, 140.5, 141.3, 143.8, 155.5. IR (thin film): 3326, 1719, 1232, 1107, 700 cm^{-1}. Anal. Calcd for $C_{24}H_{21}NO_2$: C, 81.10; H, 5.96; N, 3.94; found: C, 80.95; H, 5.72; N, 3.80. $[\alpha]_D^{28}$ + 41.0 º (*c* 0.60, $CHCl_3$). The experiment was repeated on a 0.508 mmol scale using the catalyst derived from (*S*,*S*,*S*)-**L2** with 20 mol% K_3PO_4 for 60 h, and 103 mg of product (57% yield, 93% ee) was obtained.



***N*-1-phenylallyl 2-oxazolidinone 8.** General procedure D was followed on a 0.508 mmol scale, and the reaction was judged complete by GC after 10 h. Chromatogaphy on

silica gel (1:1 pentane:Et_2O to 100% Et_2O) yielded 78.5 mg of pure branched product (76 % yield) as an oil. HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 97 : 3, v = 1.0 mL/min, λ = 220 nm, ~25 °C): t_R [min] = 34.0 (0.5%), 99.5 (99.5%), 99% ee. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.16 (m, 1H), 3.51 (m, 1H), 4.25 (m, 1H), 4.32 (m, 1H), 5.33 (dt, *J*=17.2,1.3 Hz, 1H), 5.41 (dt, *J*=10.6,1.3 Hz, 1H), 5.63 (d, *J*=5.6 Hz, 1H), 6.08 (ddd, *J*=17.0,10.4,5.6 Hz, 1H), 7.28-7.32 (m, 3H), 7.35-7.38 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 40.8, 58.6, 62.0, 118.3, 127.8, 128.0, 128.7, 133.4, 137.4, 158.1. IR (thin film): 1740, 1419, 1250, 712 cm^{-1}. Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89; found: C, 70.68; H, 6.35; N, 6.78. The experiment was repeated on a 0.500 mmol scale using the catalyst derived from (*S*,*S*,*S*)-**L2**, and 68.9 mg of product (68% yield, 99% ee) was obtained. $[\alpha]_D^{28}$ – 115.8 º (*c* 1.11, $CHCl_3$).

Optimization Table S1. Survey of weak bases.



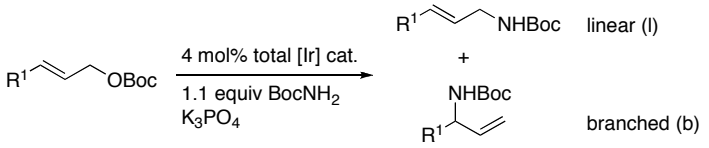
Ar = Ph **L1**
Ar = 2-anisyl **L2**

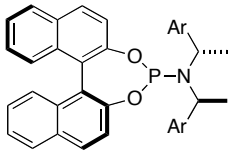
Ir(cod)(*P*,*C*-**L1**)(**L1**) **1a**
Ir(cod)(*P*,*C*-**L2**)(**L2**) **1b**
Ir(cod)(*P*,*C*-**L1**)(ethylene) **1c**
Ir(cod)(*P*,*C*-**L2**)(ethylene) **1d**

entry[a]	base	R^1	yield (%)[b]	b:l[c]
1	$CsOH•H_2O$	Ph	14	nd
2	Na_2CO_3	Ph	19	nd
3	K_2CO_3	Ph	15	nd
4	Cs_2CO_3	Ph	74	80:20
5	Cs_2CO_3	heptyl	38	54:46
6	Na_3PO_4	Ph	41	84:16
7	K_3PO_4	Ph	61	80:20
8[d]	K_3PO_4	heptyl	32	72:38
9	CsF	Ph	67	80:20
10	KF	Ph	6	nd
11[e,f]	DBU	heptyl	45	87:13
12[d,f]	DBU/PS	heptyl	34	87:13
13[d,f]	$Ba(OH)_2$	heptyl	29	84:16

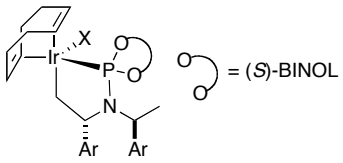
[a] General conditions: 0.5 mmol allylic carbonate, 1.0 mmol $BocNH_2$, 1.5 mmol base, pre-activated catalyst (5 mol%, activated according to the literature method[18]), in THF at 50 ºC. [b] Yields determined by GC vs. dodecane as internal standard of branched product. [c] Branched:linear ratios of products were determined by GC and are reported corrected for the difference in response factors. [d] Reaction run in toluene at rt. [e] Reaction run in toluene at 50 ºC. [f] Reaction run with 4 mol% catalyst.

Optimization Table S2. Base stoichiometry and solvent screen.





Ar = Ph **L1**
Ar = 2-anisyl **L2**



Ir(cod)(*P,C*-**L1**)(**L1**) **1a**
Ir(cod)(*P,C*-**L2**)(**L2**) **1b**
Ir(cod)(*P,C*-**L1**)(ethylene) **1c**
Ir(cod)(*P,C*-**L2**)(ethylene) **1d**

entry[a]	equiv base	R^1	solvent	catalyst	t (h)	yield (%)[b]	b:l
1	1	Ph	THF	**1b**	18	85	93:7
2	1	heptyl	THF	**1b**	18	76	84:16
3	1	Ph	THF	**1c**	>34	44	94:6
4	1	heptyl	THF	**1c**	34	62	86:14
5	1	Ph	THF	**1d**	23	73	93:7
6	1	heptyl	THF	**1d**	23	63	86:14
7	0.5	Ph	THF	**1d**	24	72	94:6
8	0.5	heptyl	THF	**1d**	24	67	85:15
9	0	heptyl	THF	**1d**	22	68	85:15
10[c,d]	0	Ph	THF	**1d**	24	95	93:7
11[c,d]	0	heptyl	THF	**1d**	7.5	72	84:16
12[c,d]	0	heptyl	dioxane	**1d**	5	74	86:14
13[c,d]	0	heptyl	DME	**1d**	5	75	85:15
14[c,d]	0	heptyl	CH_2Cl_2	**1d**	5	56	87:13
15[c,d]	0	heptyl	ether	**1d**	5	81	85:15
16[c]	0	heptyl	ether	**1d**	5	83	87:13

[a] Reactions using catalyst **1b** were conducted as in Table 1, reactions using catalysts **1c** and **1d** were conducted as in Table 1 except that no $[Ir(cod)Cl]_2$ was used. [b] Branched:linear (b:l) ratios were determined by GC analysis of the crude reaction mixture and are *uncorrected* (see methods section). Yield is of branched product as determined by GC and/or NMR analysis of the crude reaction mixture vs. internal standards. [c] 1.4 Equiv of $BocNH_2$ were used. [d] Reaction was conducted at 30 ºC.

Procedure for Palladium-Catalyzed Allylation of *tert*-Butyl Carbamate with *tert*-Butyl Cinnamyl Carbonate. In an nitrogen-filled glove box, $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (7.32 mg, 0.020 mmol) and Xantphos (23.1 mg, 0.040 mmol) were added to a 1-dram vial, followed by *tert*-butyl carbamate (70.3 mg, 0.600 mmol) and K_3PO_4 (127 mg, 0.600 mmol). A small stirbar and 1.0 mL of THF were added. This mixture was stirred briefly to dissolve all of the catalyst. Finally, the *tert*-butyl cinnamyl carbonate (117 mg, 0.499 mmol) was transferred to the vial by pipette. The vial was sealed with a cap containing a PTFE-faced septum, removed from the glove box, and stirred at room temperature for 15 h. ^1H NMR analysis of the crude reaction mixture showed a linear to branched ratio of >99:1. Chromatogaphy on silica gel (3:1 pentane:Et_2O) yielded 108 mg of pure linear product **9** (93 % yield) as an oil. ^1H and ^{13}C NMR spectra matched those previously reported.[19]

Procedure for Palladium-Catalyzed Allylation of *tert*-Butyl Carbamate with *tert*-butyl cyclohexenyl carbonate. In an nitrogen filled glove box, $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (3.66 mg, 0.010 mmol) and Trost's ligand (15.8 mg, 0.020 mmol) were added to a 1-dram vial, followed by *tert*-butyl carbamate (70.3 mg, 0.600 mmol) and K_3PO_4 (106 mg, 0.499 mmol). A small stirbar and 1.0 mL of THF were added. This mixture was stirred briefly to dissolve all of the catalyst. Finally, the *tert*-butyl cyclohexenyl carbonate (99.1 mg, 0.500 mmol) was transferred to the vial by pipette. The vial was sealed with a cap containing a PTFE-faced septum, removed from the glove box, and stirred at room temperature for 15 h. ^1H NMR analysis of the crude product mixture showed only starting materials.

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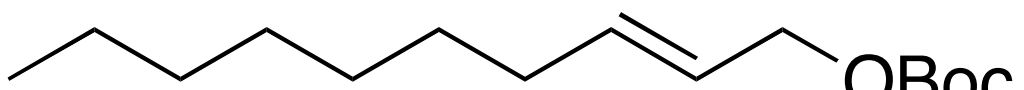
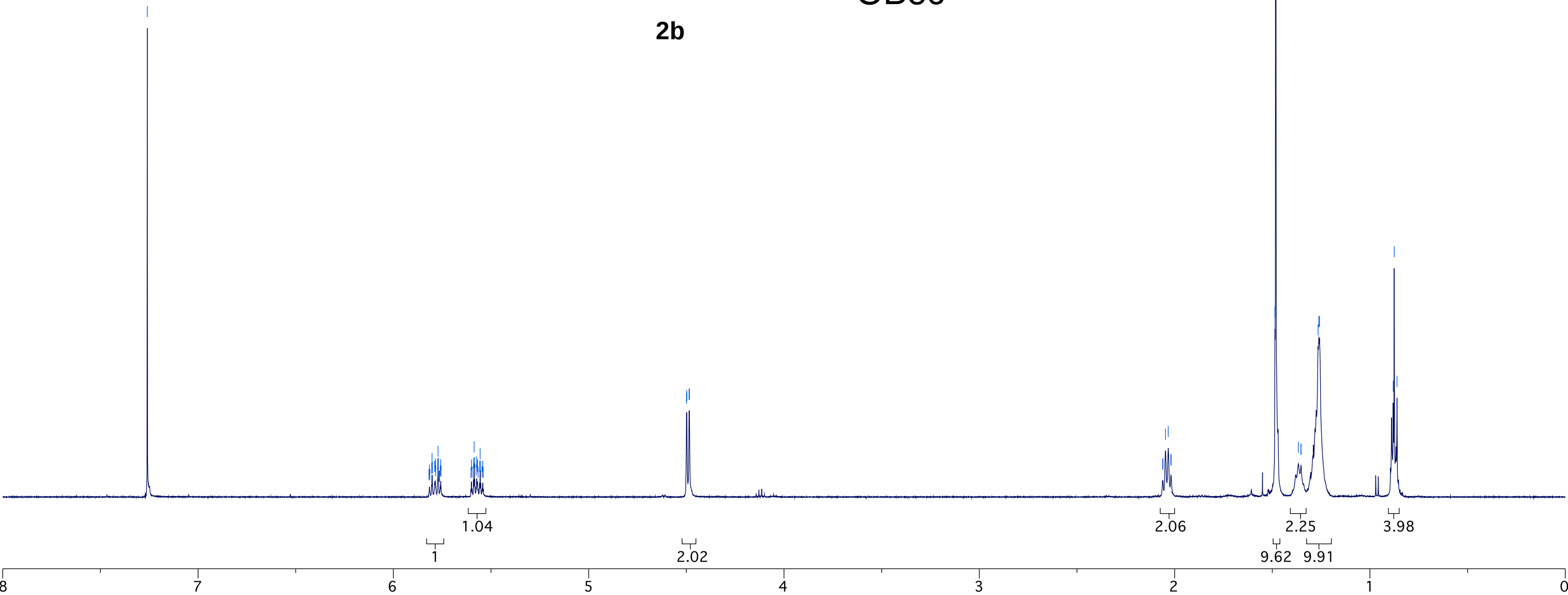

OBoc

2b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2.02
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9.91
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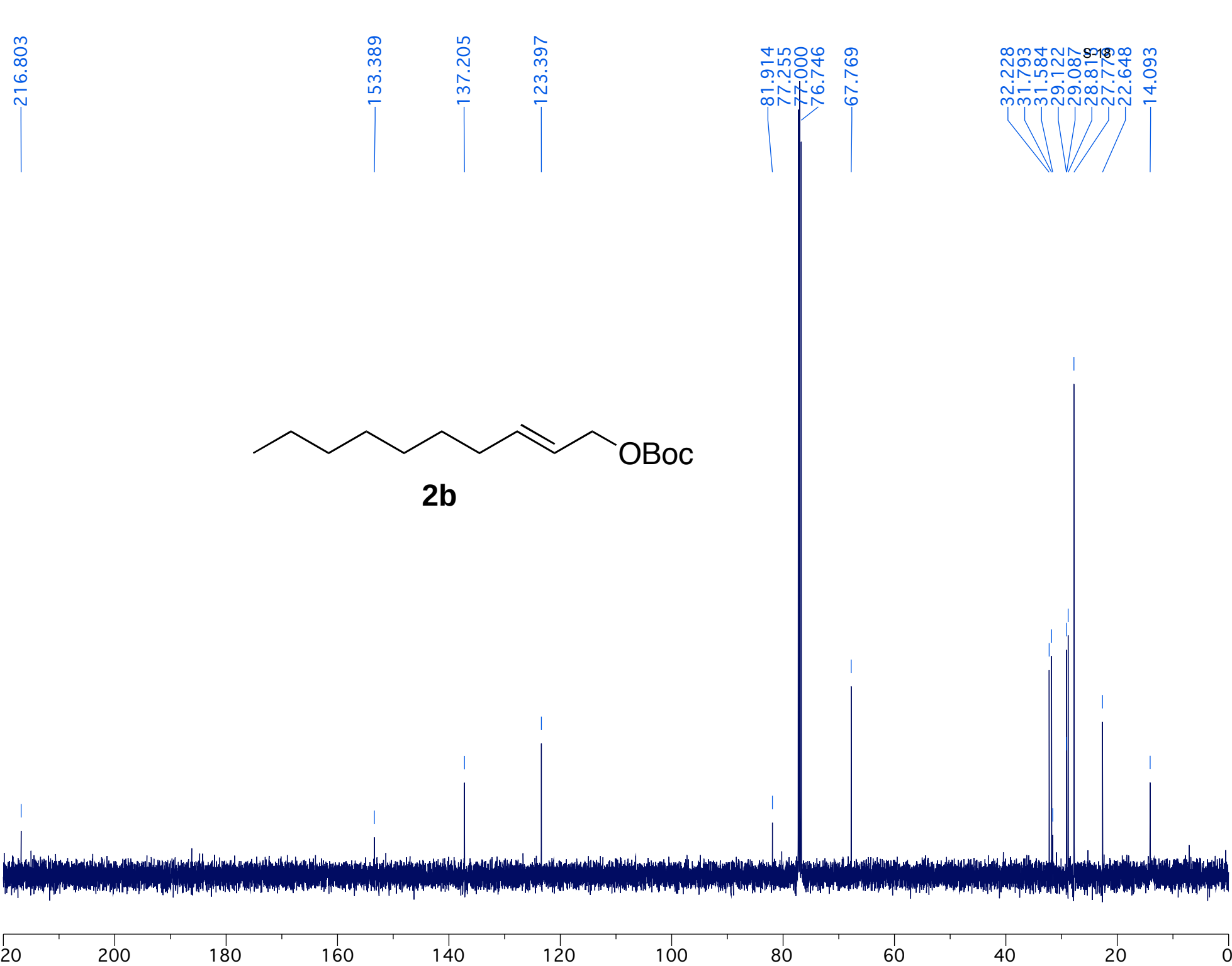
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77.000
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32.228
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31.584
29.122
29.087
28.819
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14.093
OBoc
2b
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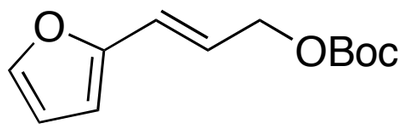

2c

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77.212
77.000
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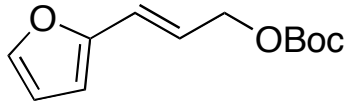
66.997
27.770



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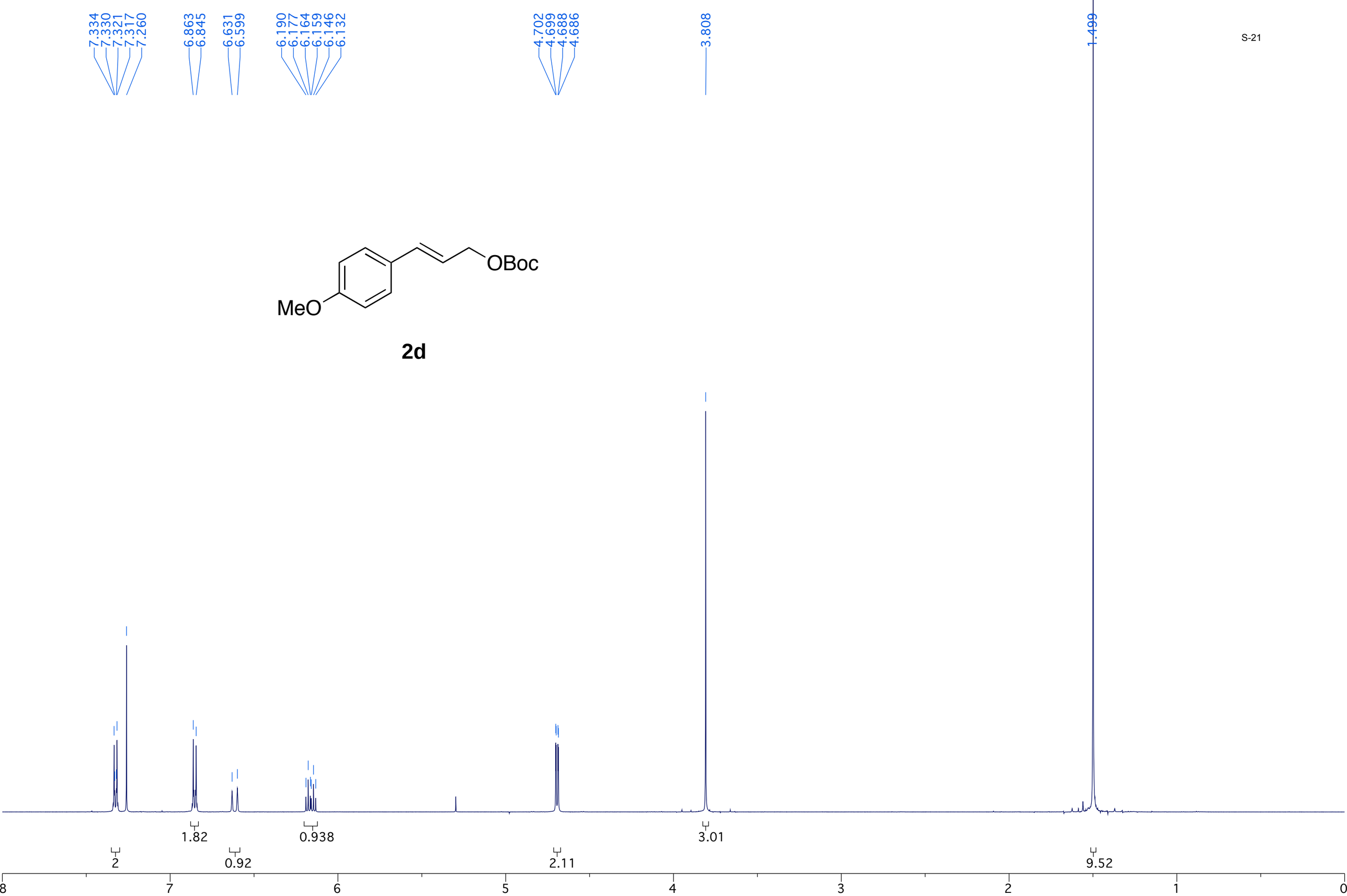
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6.190
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6.164
6.159
6.146
6.132
4.702
4.699
4.688
4.686
3.808
1.499
OBoc
MeO
1.82
0.938
3.01
2
0.92
2.11
9.52
8
7
6
5
4
3
2
1
0

2d

159.546
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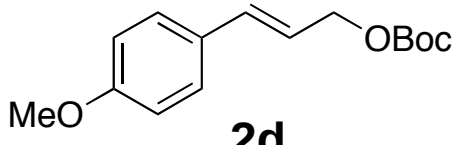
27.781



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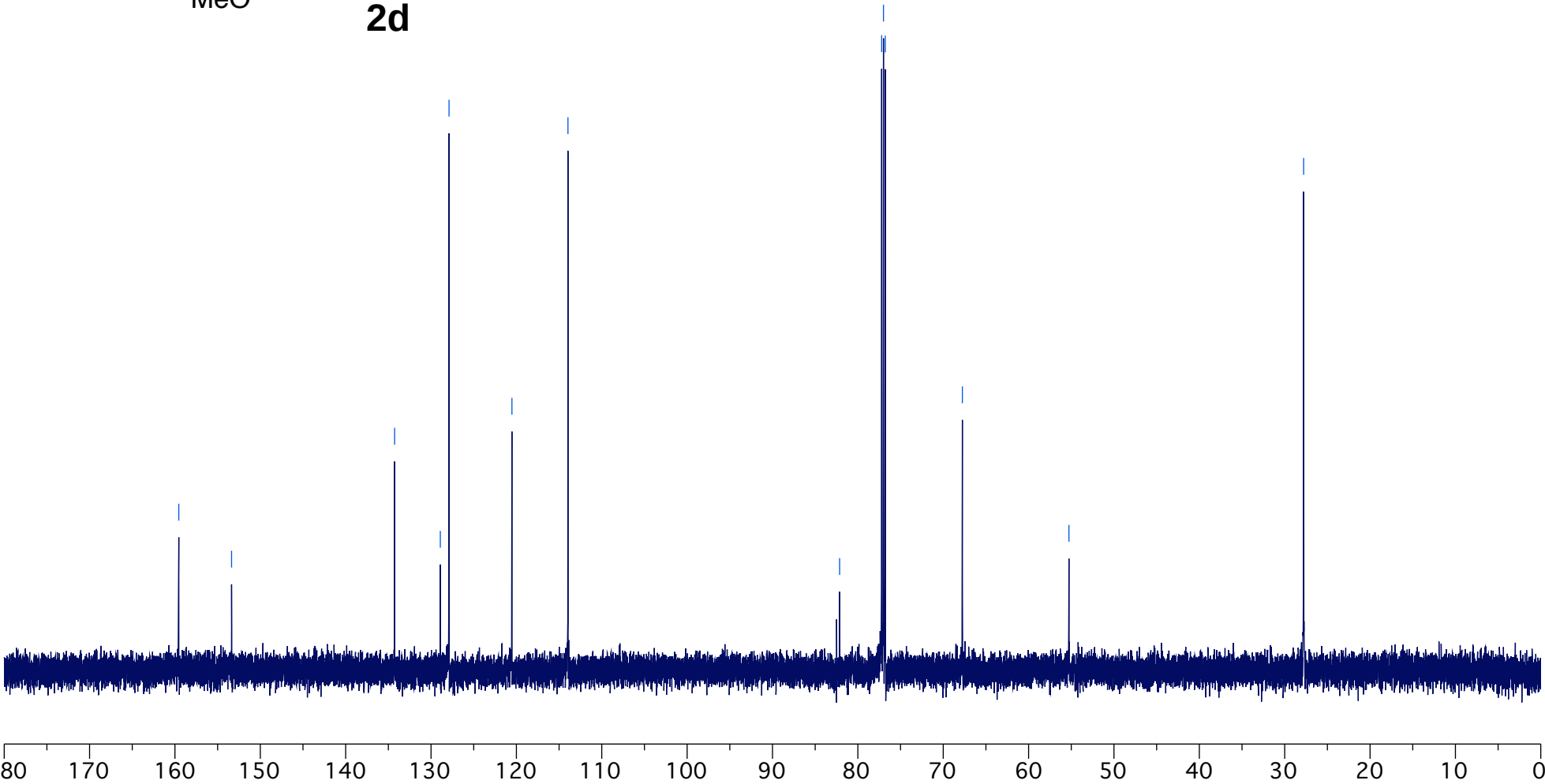

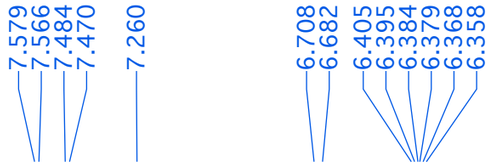
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7.260

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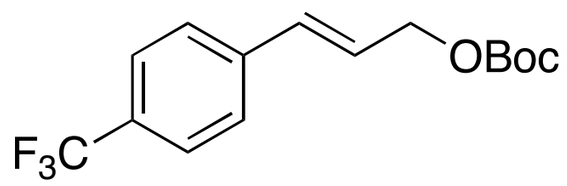
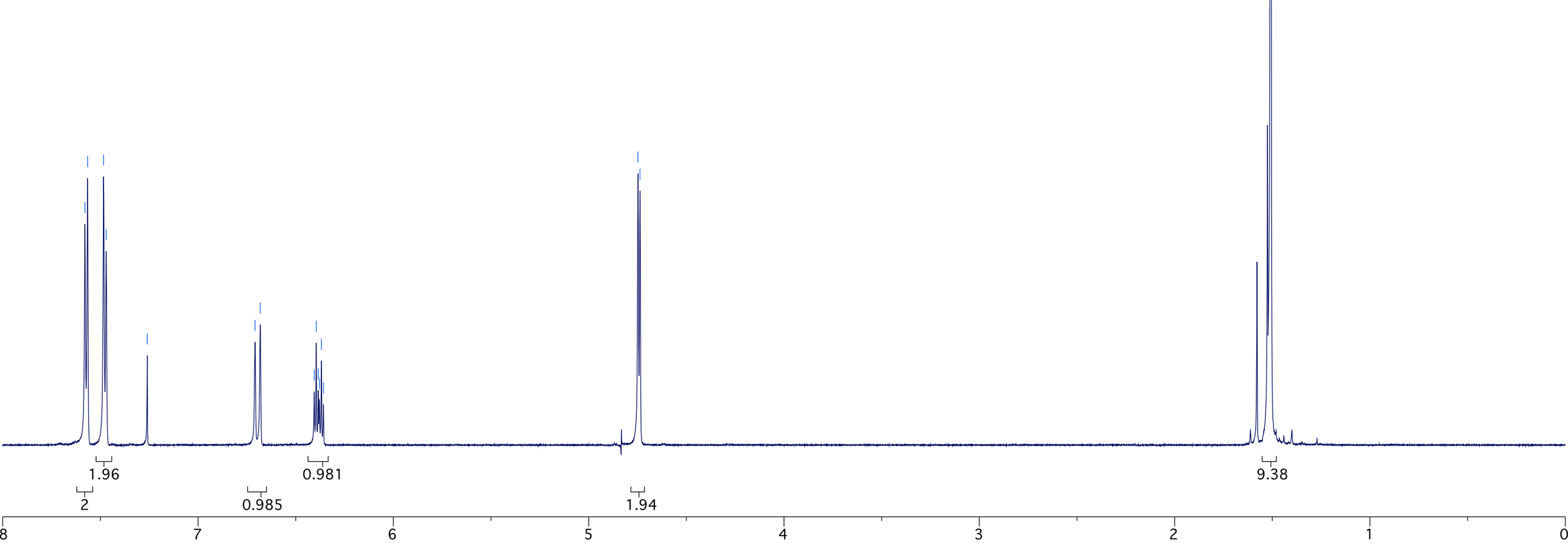
6.405
6.395
6.384
6.379
6.368
6.358


4.748
4.738


1.567


OBoc
F3C

2e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7
6
5
4
3
2
1
0

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139.629
132.481
130.116
129.903
129.687
129.470
126.753
125.665
125.587
125.562
125.537
125.512
124.967
123.164
82.476
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77.000
76.788
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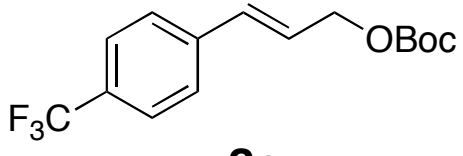
27.750
27.725
27.681



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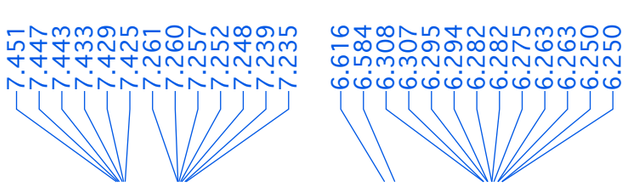
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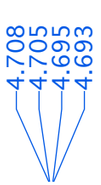
7.443
7.433
7.429
7.425
7.261
7.260
7.257
7.252
7.248
7.239
7.235

6.616
6.584
6.308
6.307
6.295
6.294
6.282
6.282
6.275
6.263
6.263
6.250
6.250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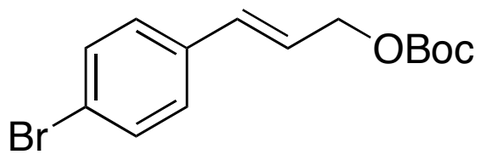
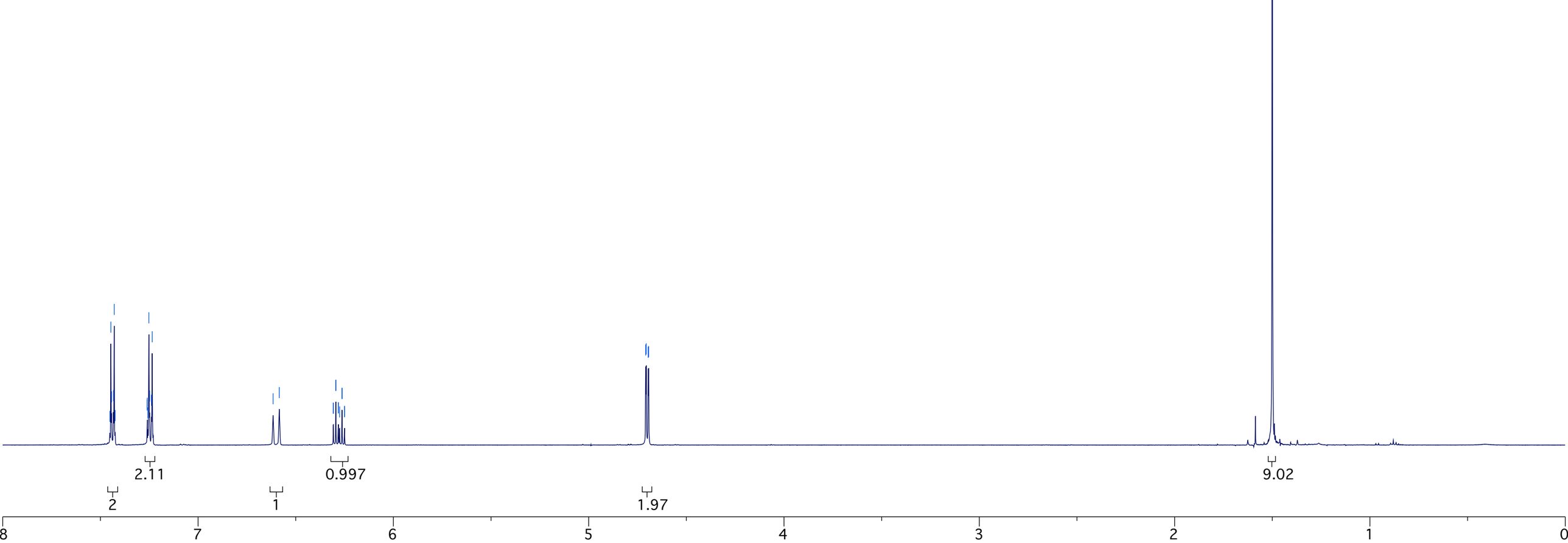
4.695
4.693


1.501


OBoc
Br

2f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1.97
8
7
6
5
4
3
2
1
0

153.252
135.096
133.004
131.693
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77.255
77.000
76.746
67.149
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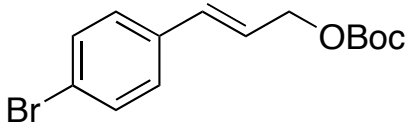
27.738
27.640



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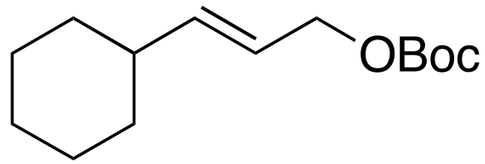
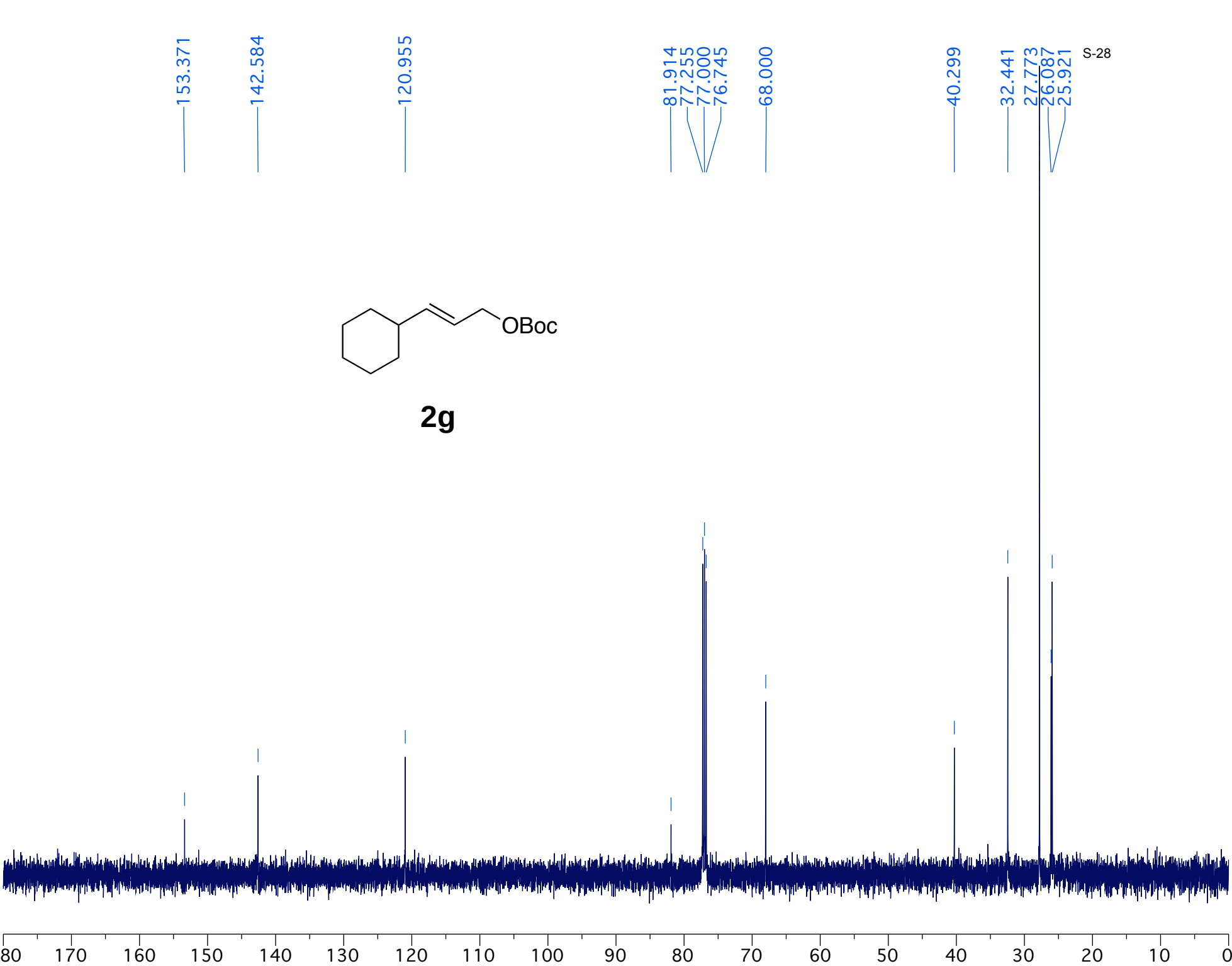


2g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81.914
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77.000
76.745
68.000
40.299
32.441
27.773
26.087
25.921
OBoc
2g
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150
140
130
120
110
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80
70
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50
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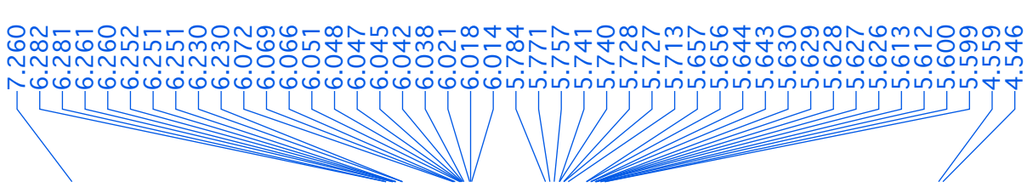
30
20
10
0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6.252
6.251
6.230
6.230
6.072
6.069
6.066
6.051
6.048
6.047
6.045
6.042
6.038
6.021
6.018
6.014
5.784
5.771
5.757
5.741
5.740
5.728
5.727
5.713
5.657
5.656
5.644
5.643
5.630
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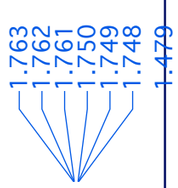
5.628
5.627
5.626
5.613
5.612
5.600
5.599
4.559
4.546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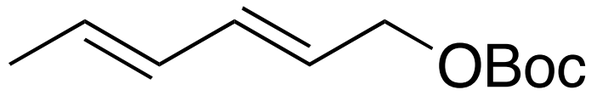
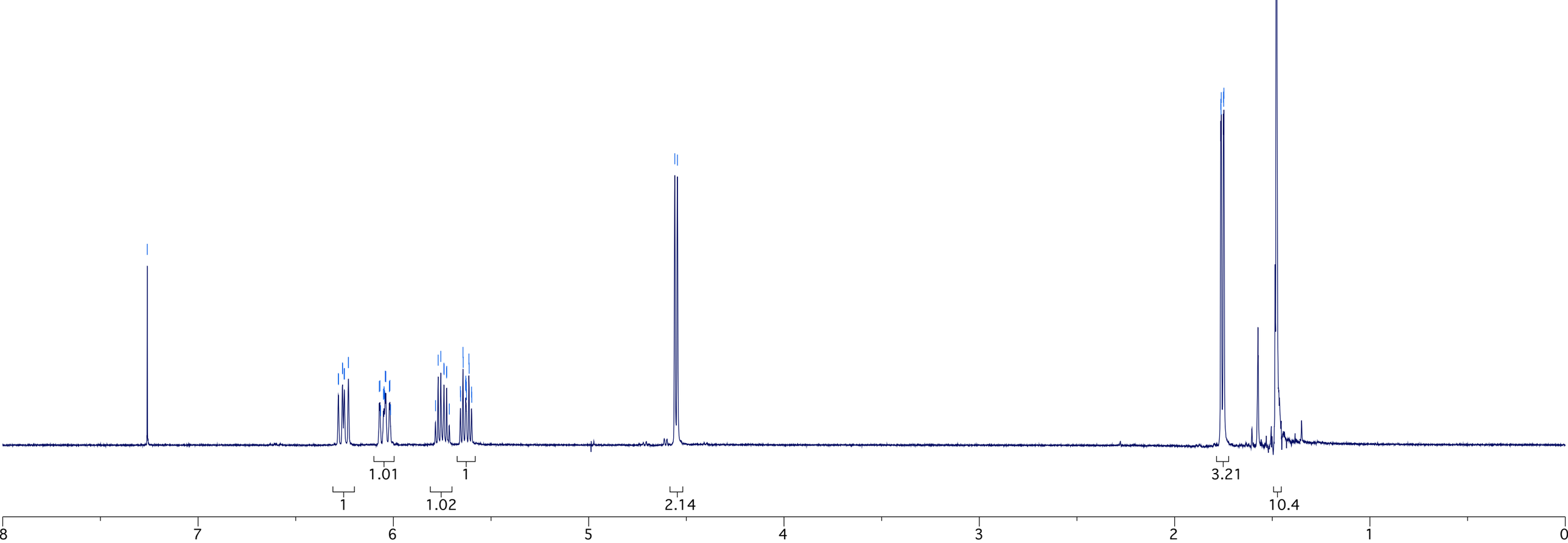
1.762
1.761
1.750
1.749
1.748
1.479


OBoc

2h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1.02
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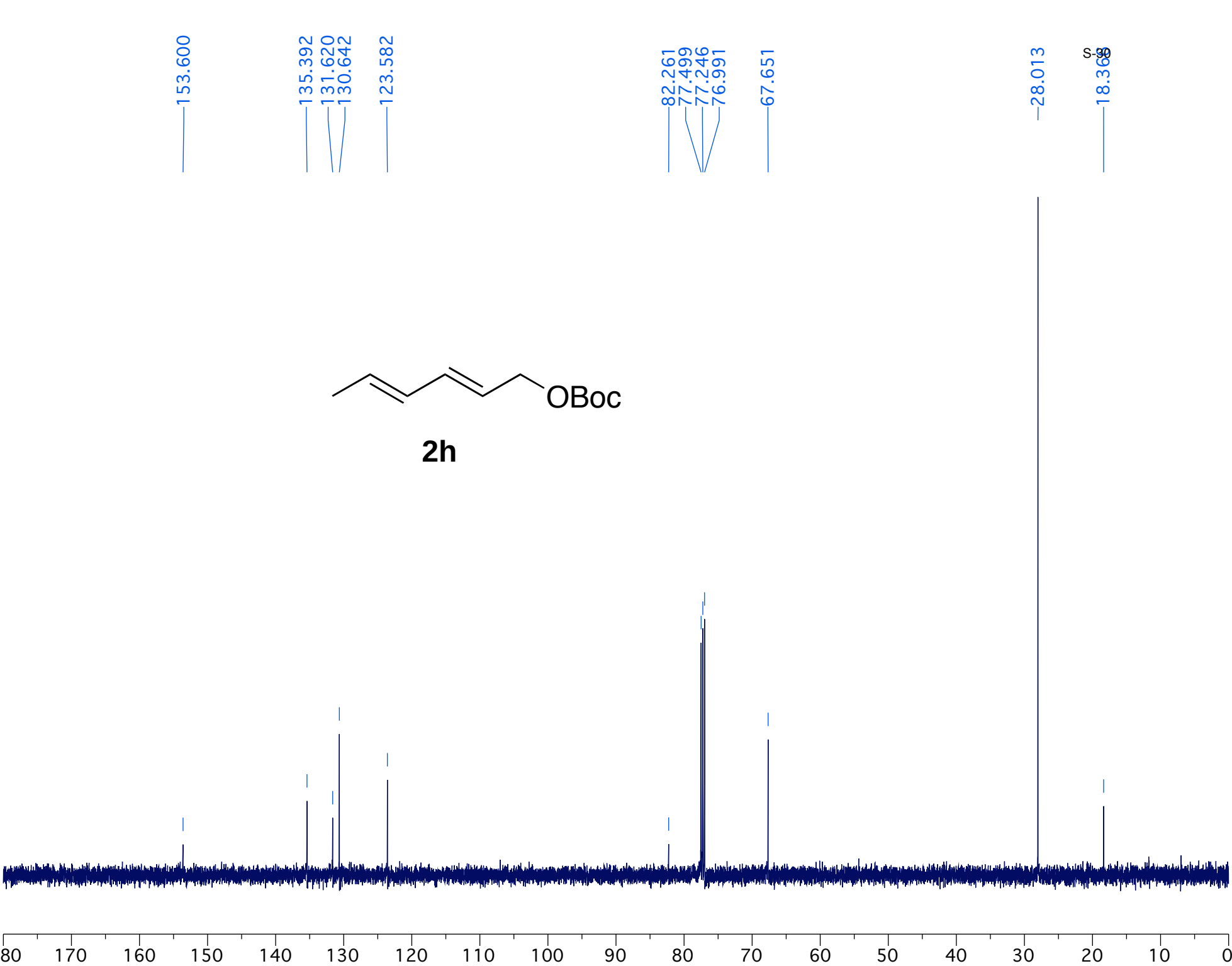
6
5
4
3
2
1
0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77.246
76.991
67.651
28.013
18.360
OBoc
2h
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170
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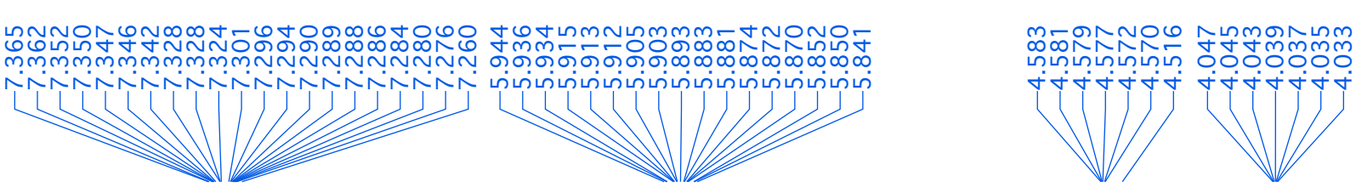
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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7.290
7.289
7.288
7.286
7.284
7.280
7.276
7.260
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5.936
5.934
5.915
5.913
5.912
5.905
5.903
5.893
5.883
5.881
5.874
5.872
5.870
5.852
5.850
5.841
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4.581
4.579
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4.516
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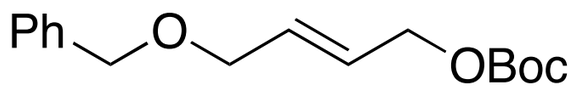
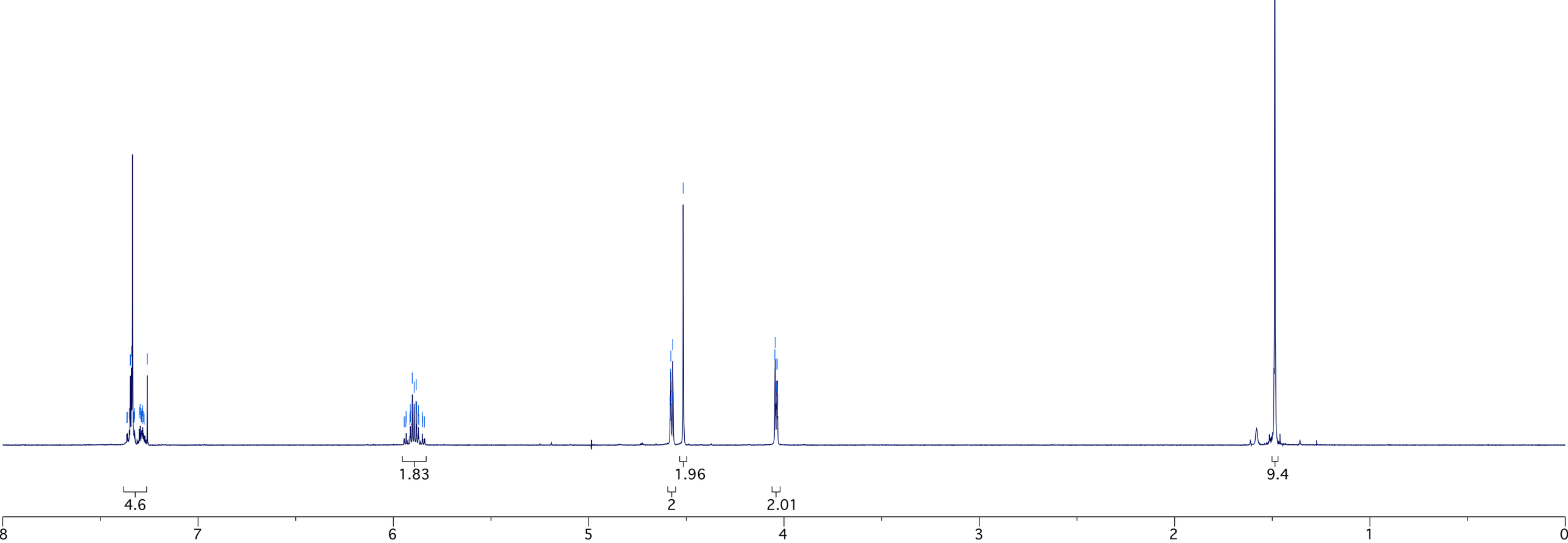
4.045
4.043
4.039
4.037
4.035
4.033
1.487


Ph
O
OBoc

2i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4.6
2
2.01
8
7
6
5
4
3
2
1
0

153.262
138.067
131.366
128.375
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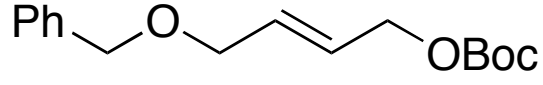
127.628
126.352
82.166
77.255
77.000
76.745
72.248
69.684
66.700
27.753



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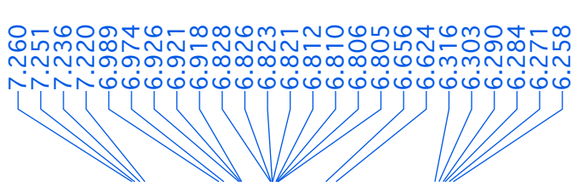
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7.236
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6.974
6.926
6.921
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6.828
6.826
6.823
6.821
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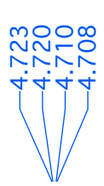
6.303
6.290
6.284
6.271
6.258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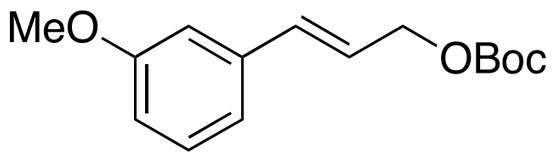
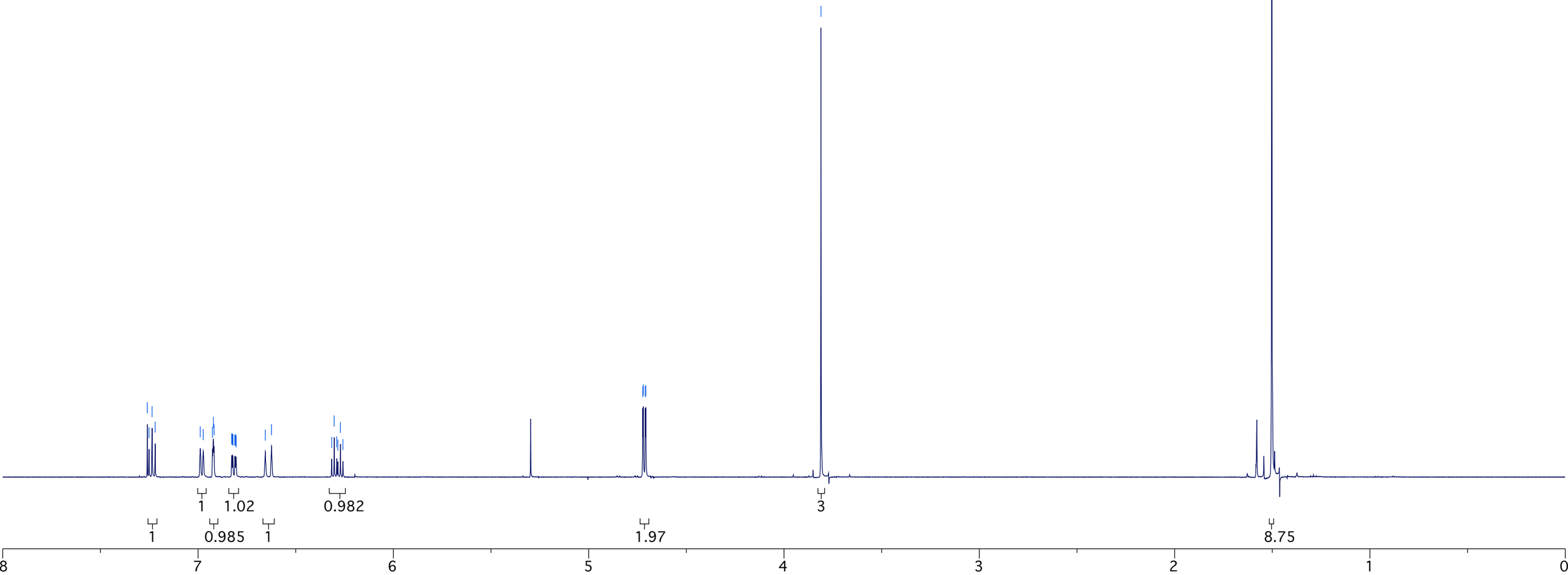
4.710
4.708

3.811

1.503


MeO
OBoc

2j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1
1.02
0.982
1.97
3
8.75
8
7
6
5
4
3
2
1
0

159.737
153.307
137.607
134.230
129.548
123.206
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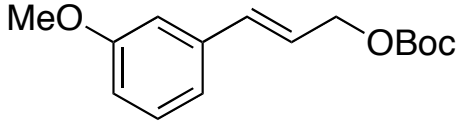
113.768
111.818
82.258
77.255
77.000
76.746
67.373
55.201
27.774



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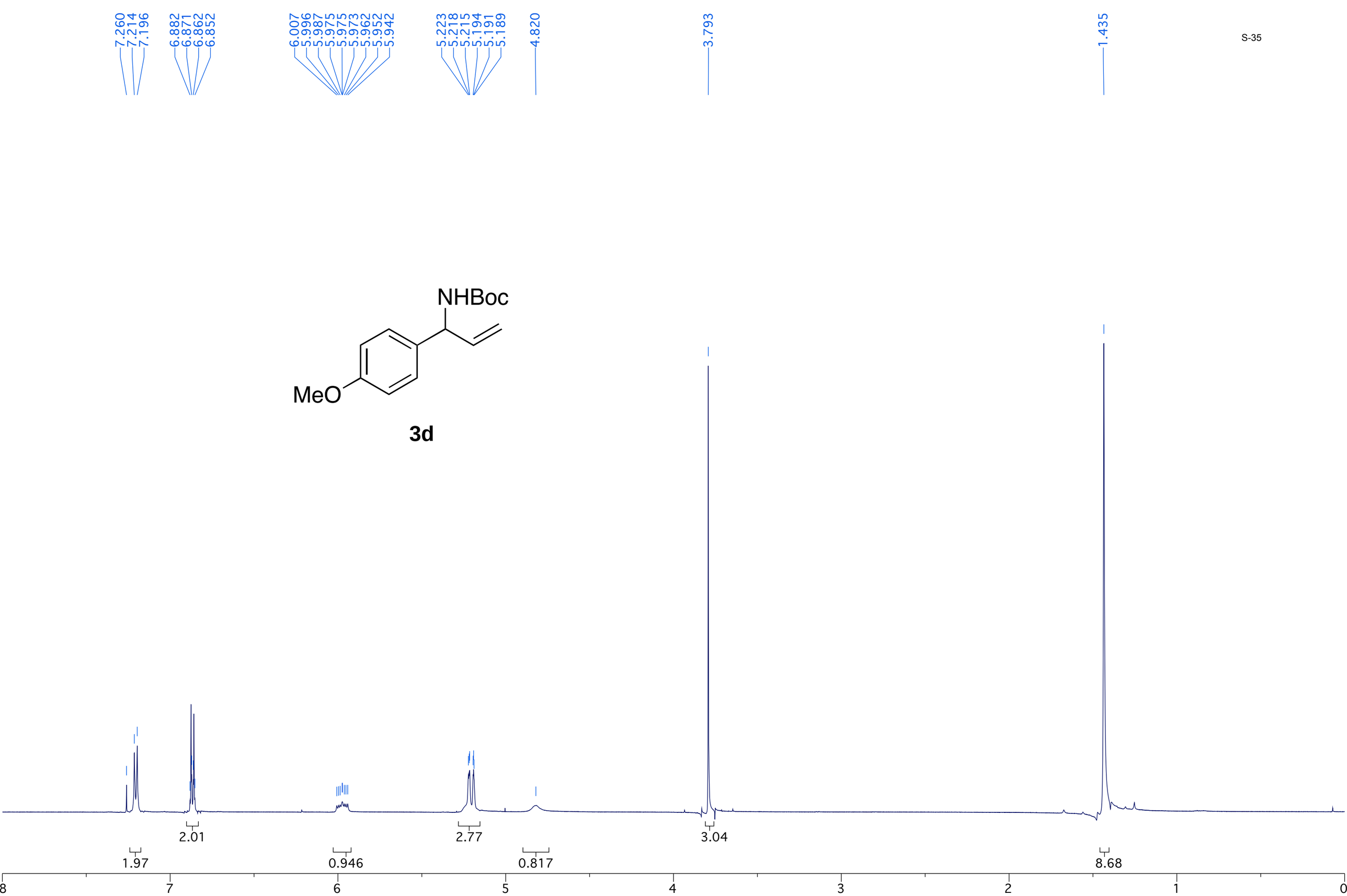
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6.007
5.996
5.987
5.975
5.973
5.962
5.952
5.942
5.223
5.218
5.215
5.194
5.191
5.189
4.820
3.793
1.435
NHBoc
MeO
3d
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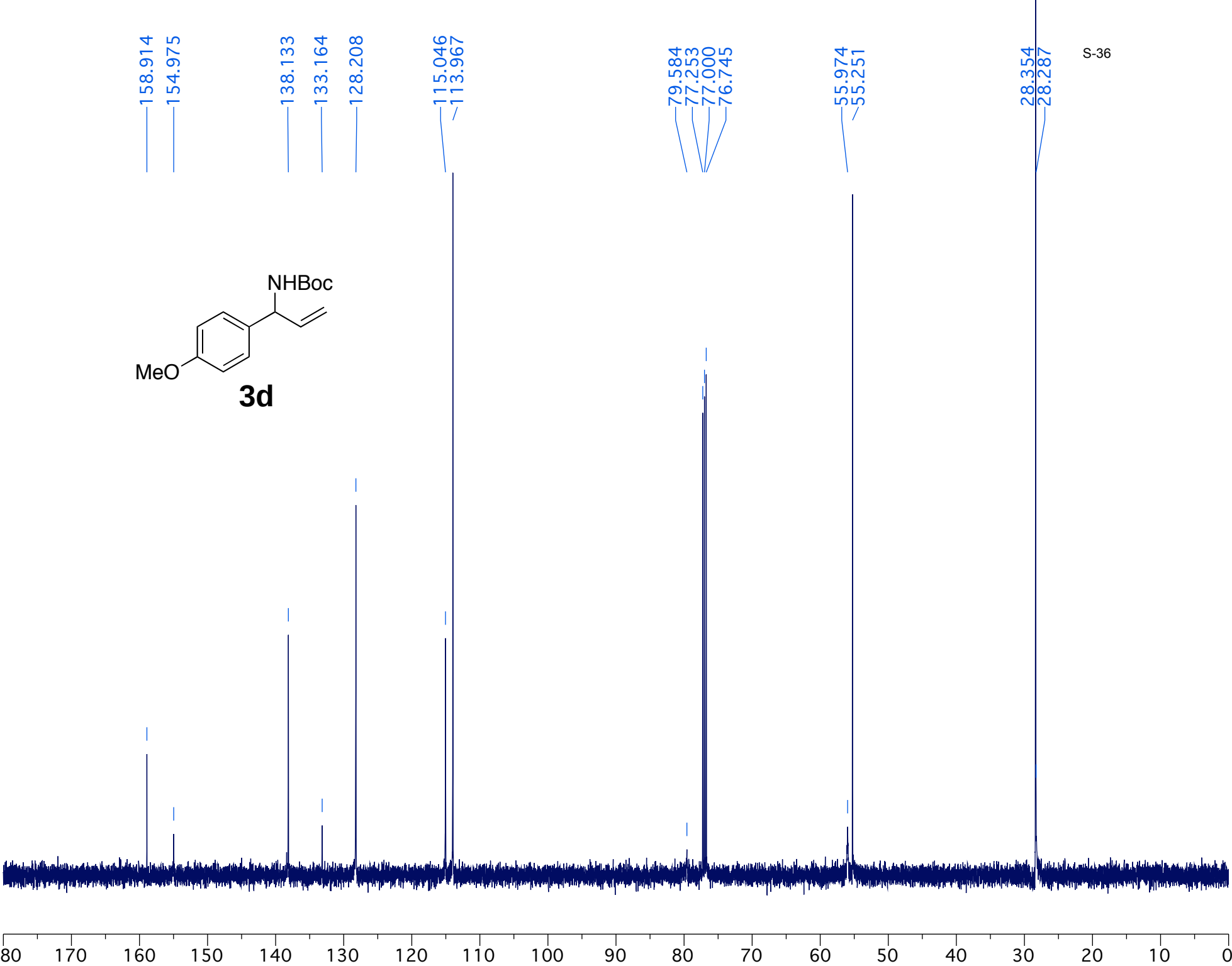
2
1
0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55.251
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28.287
NHBoc
MeO
3d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


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7.586
7.416
7.399
7.260
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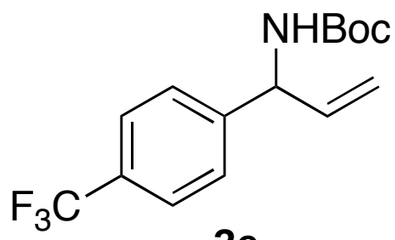
4.952
1.431


NHBoc
F3C

3e

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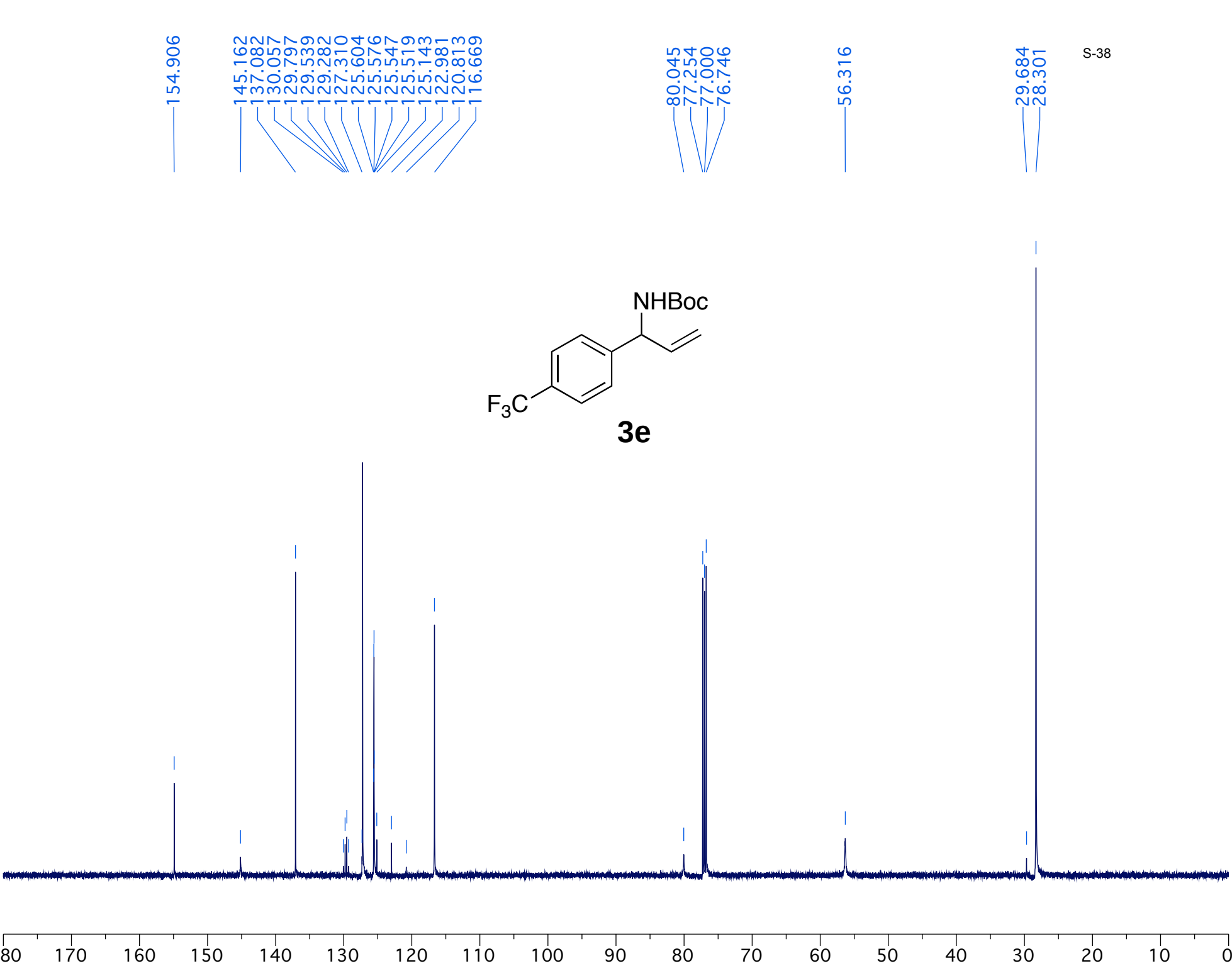
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120.813
116.669
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77.254
77.000
76.746
56.316
29.684
28.301
NHBoc
F3C
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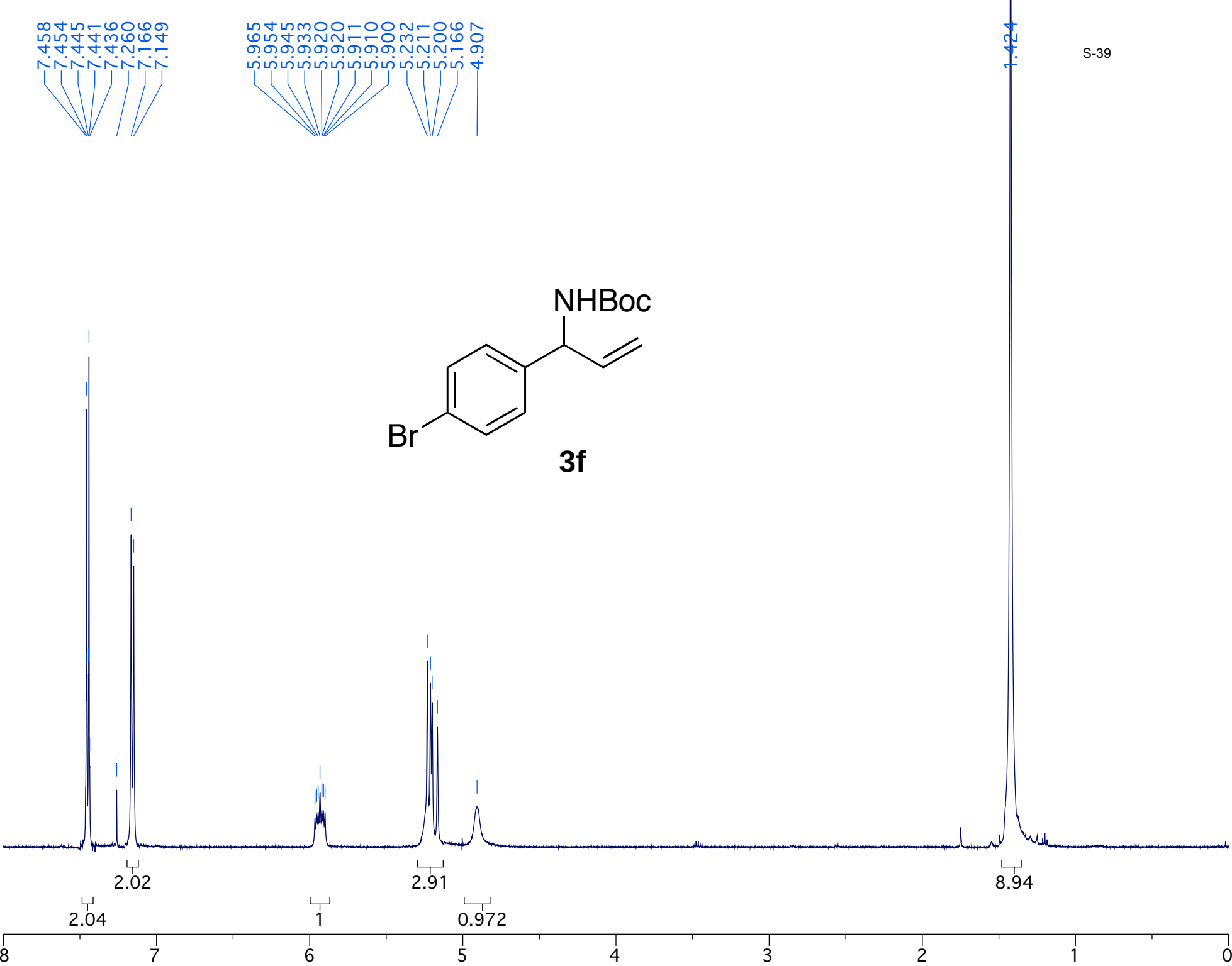
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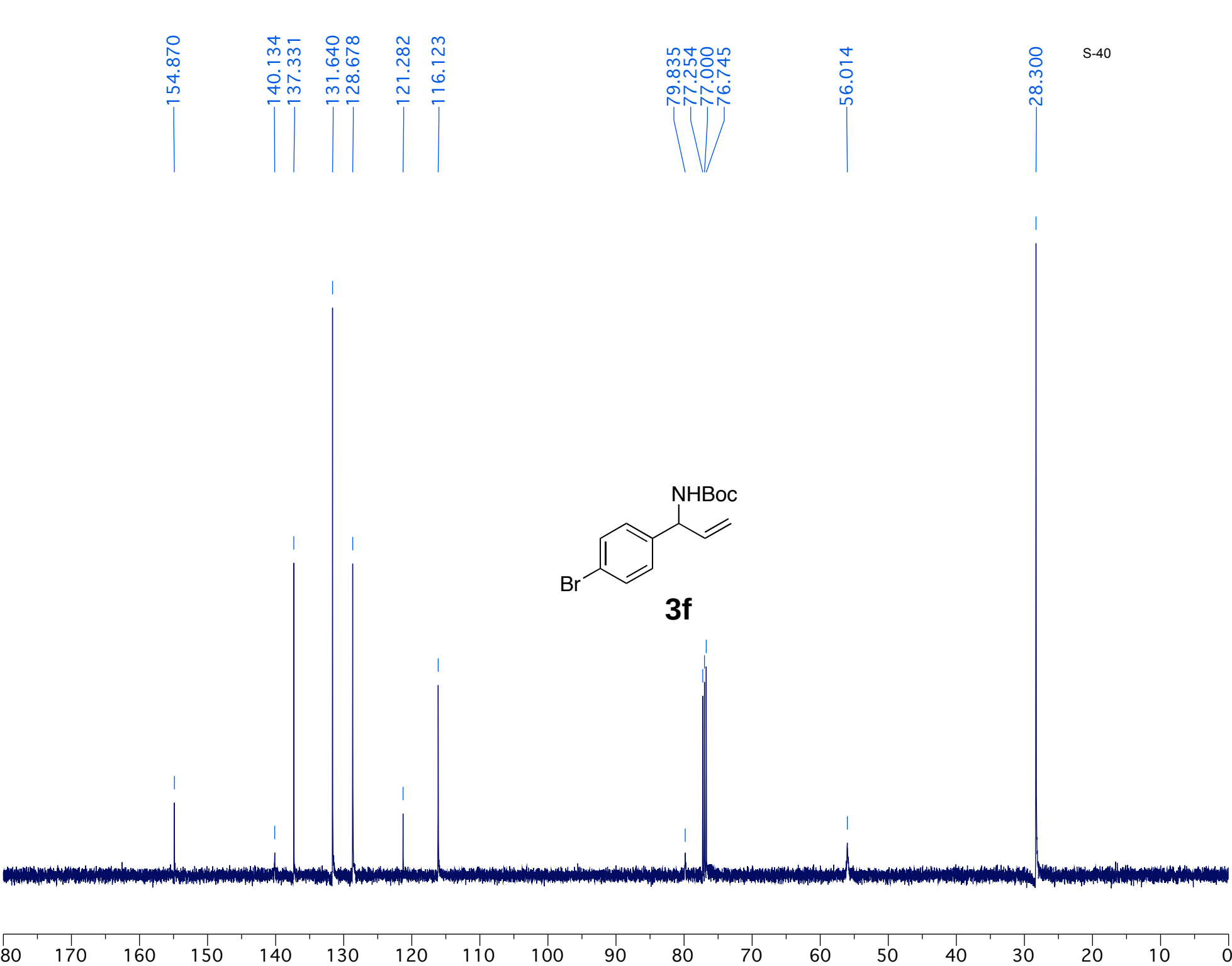
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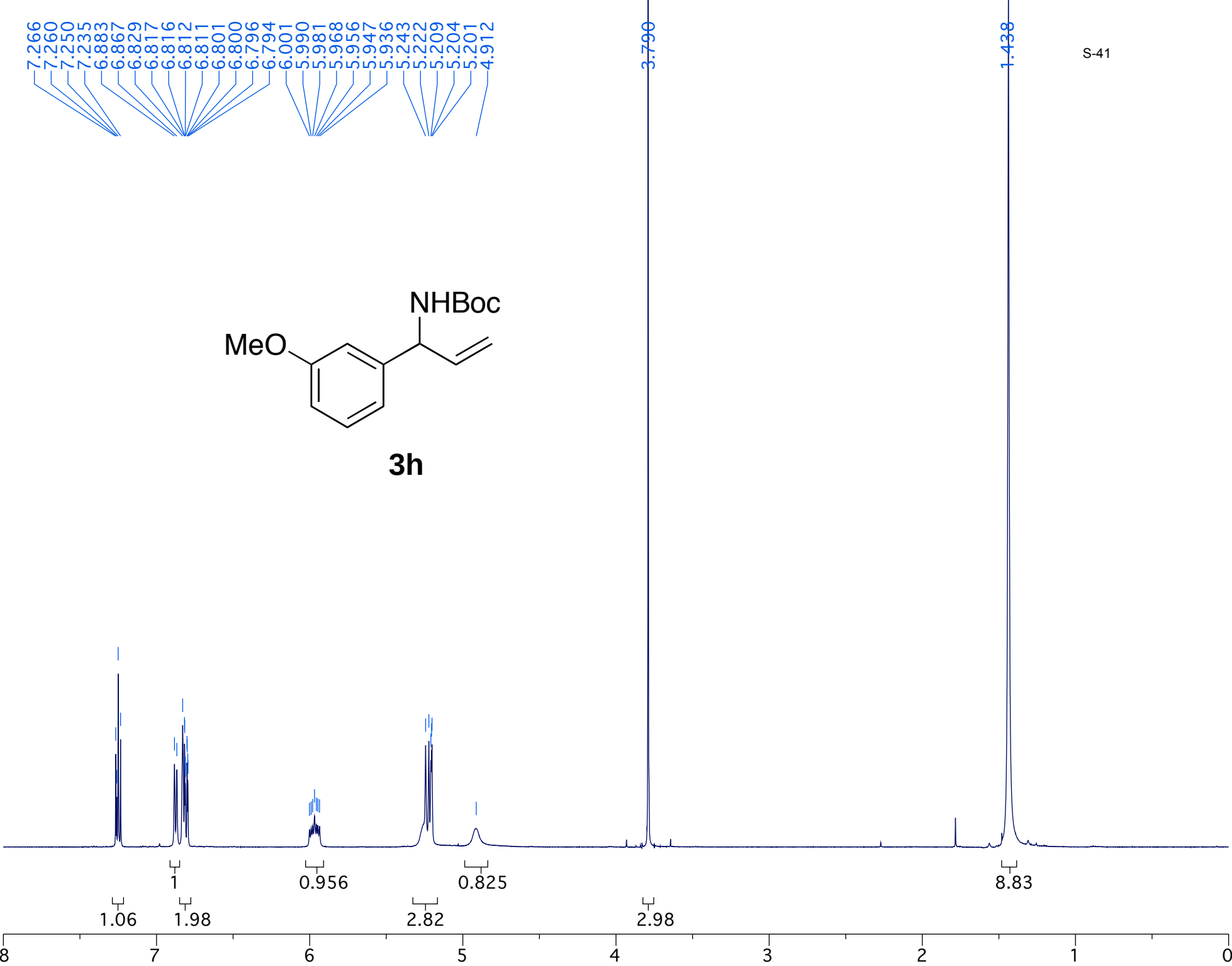
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MeO
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3h

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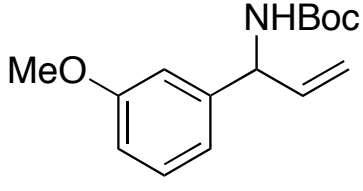

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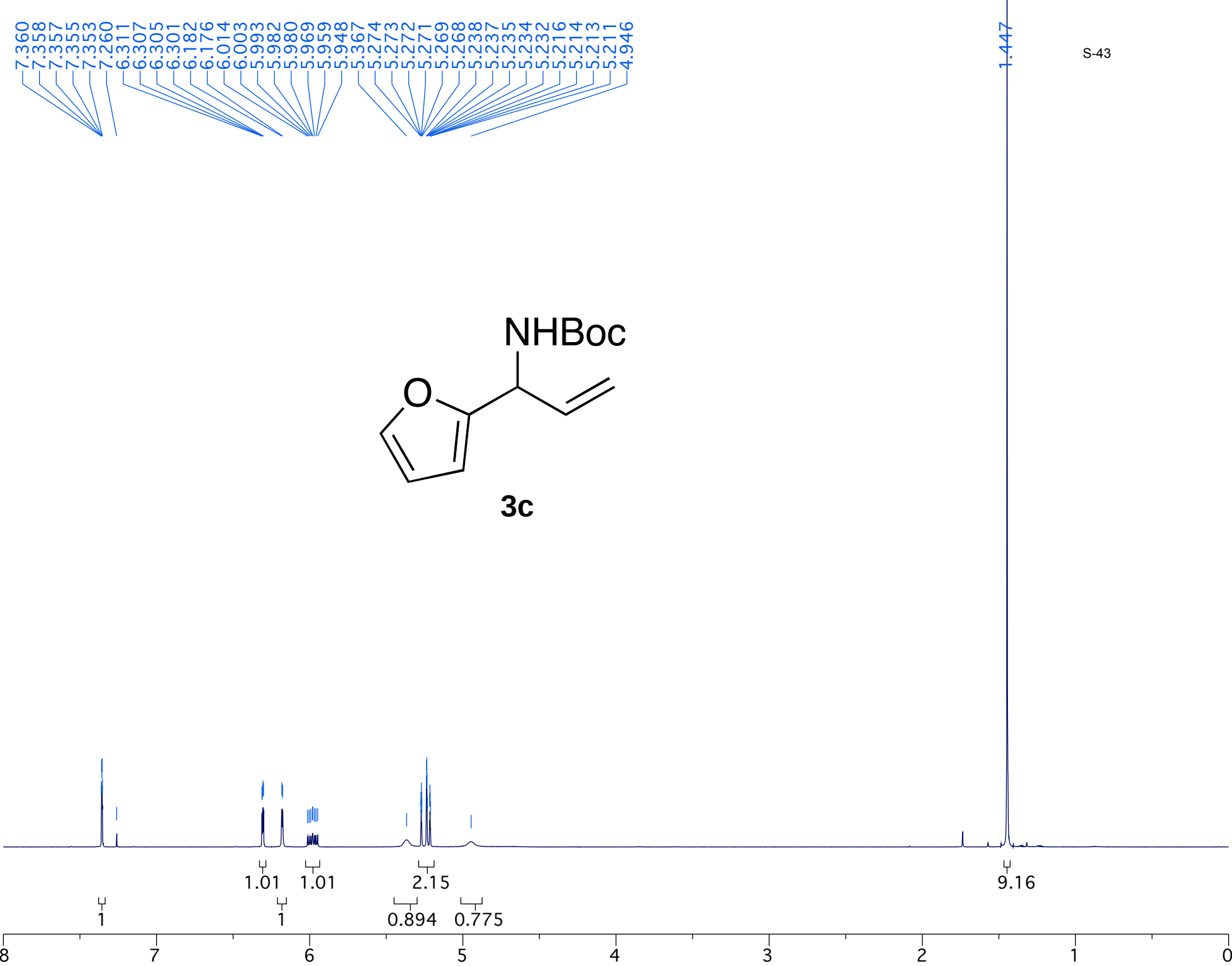
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5.232
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NHBoc
O
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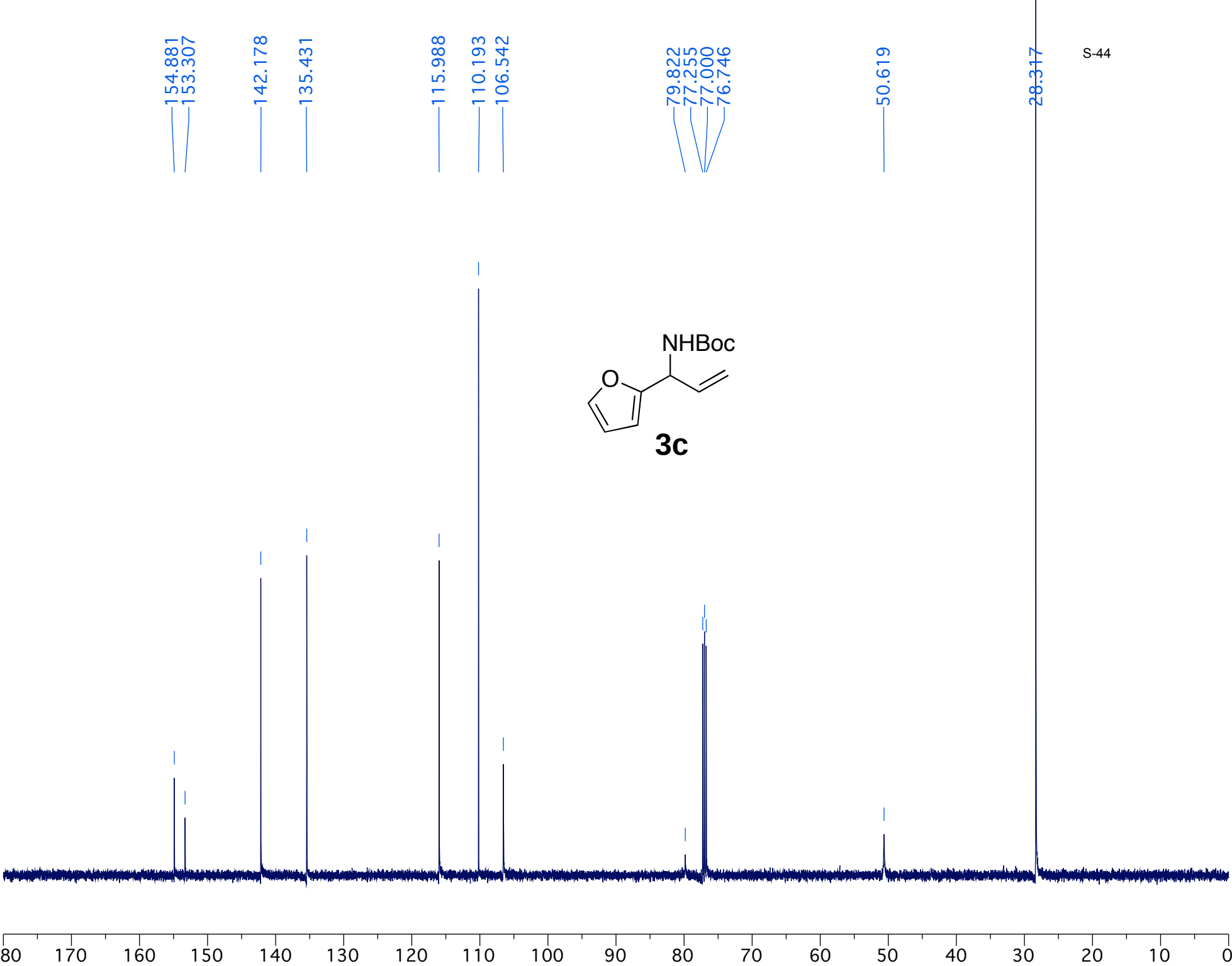
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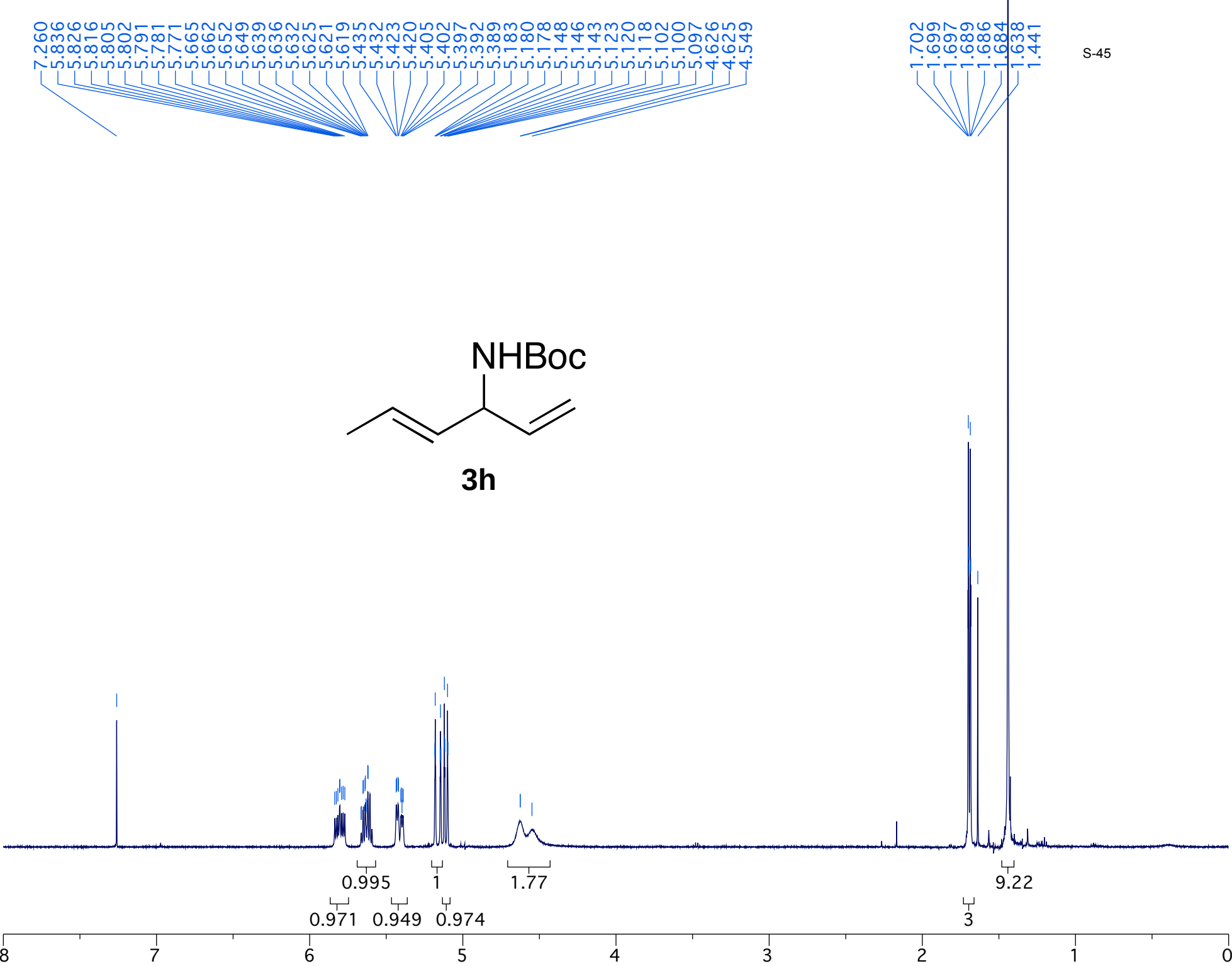
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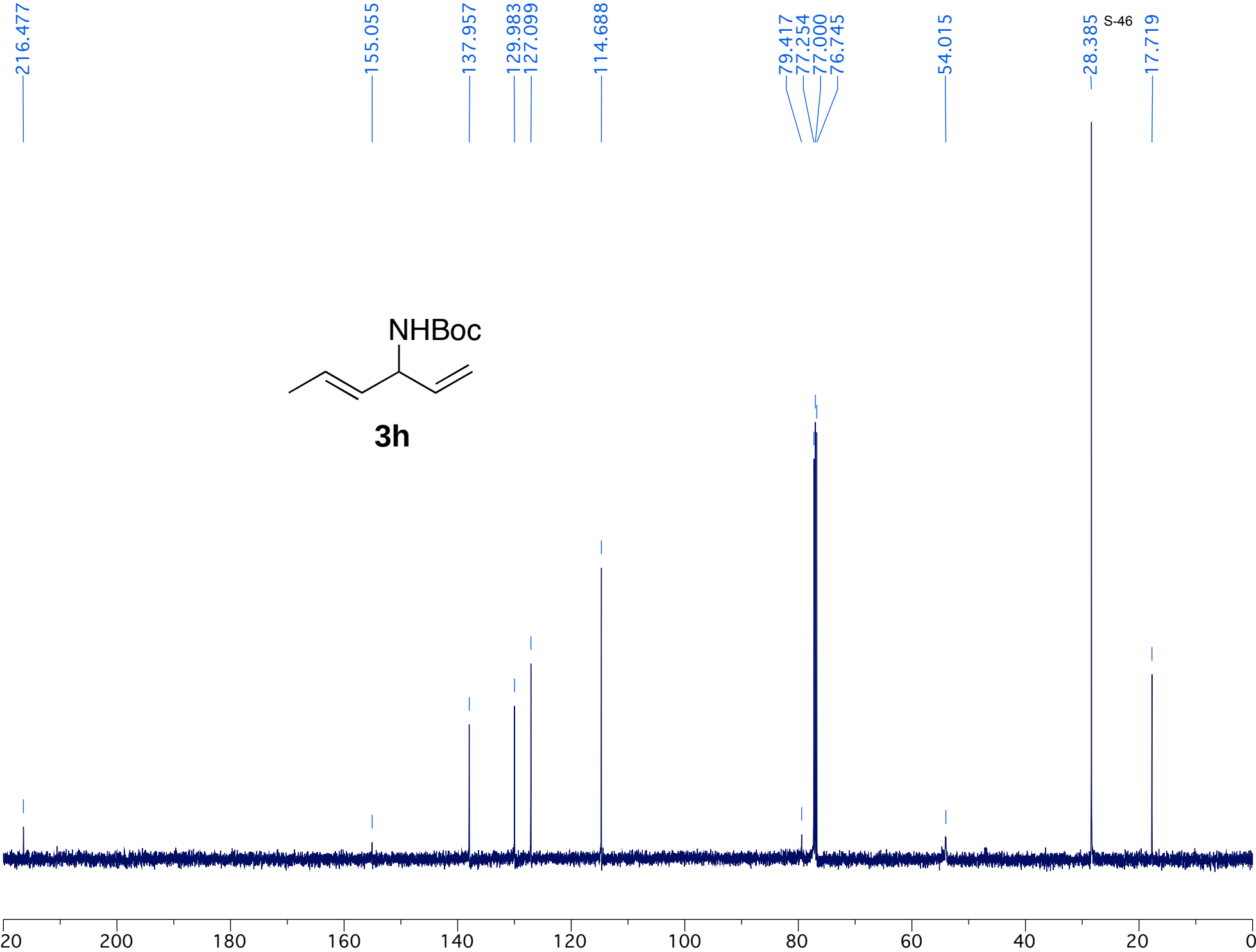
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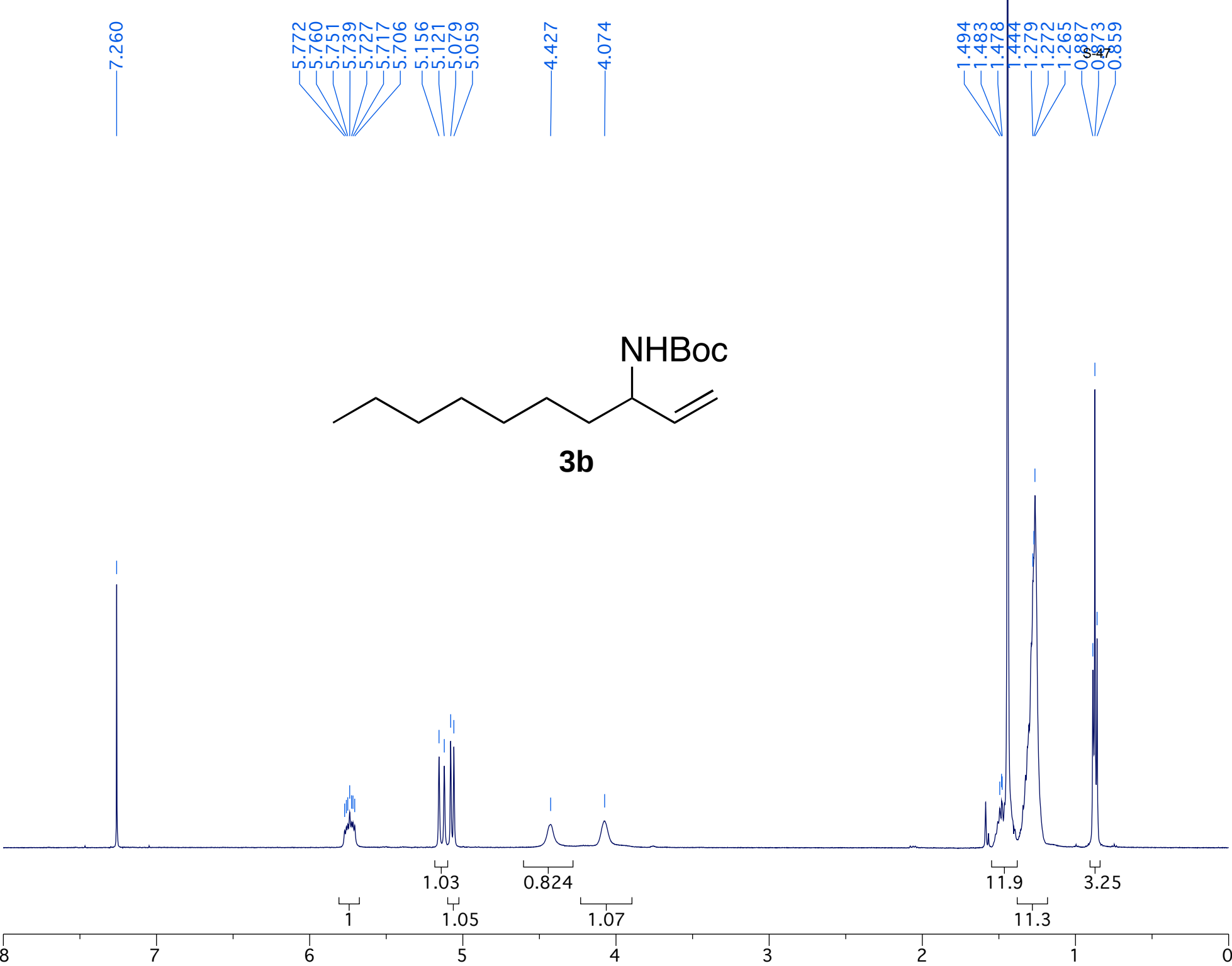
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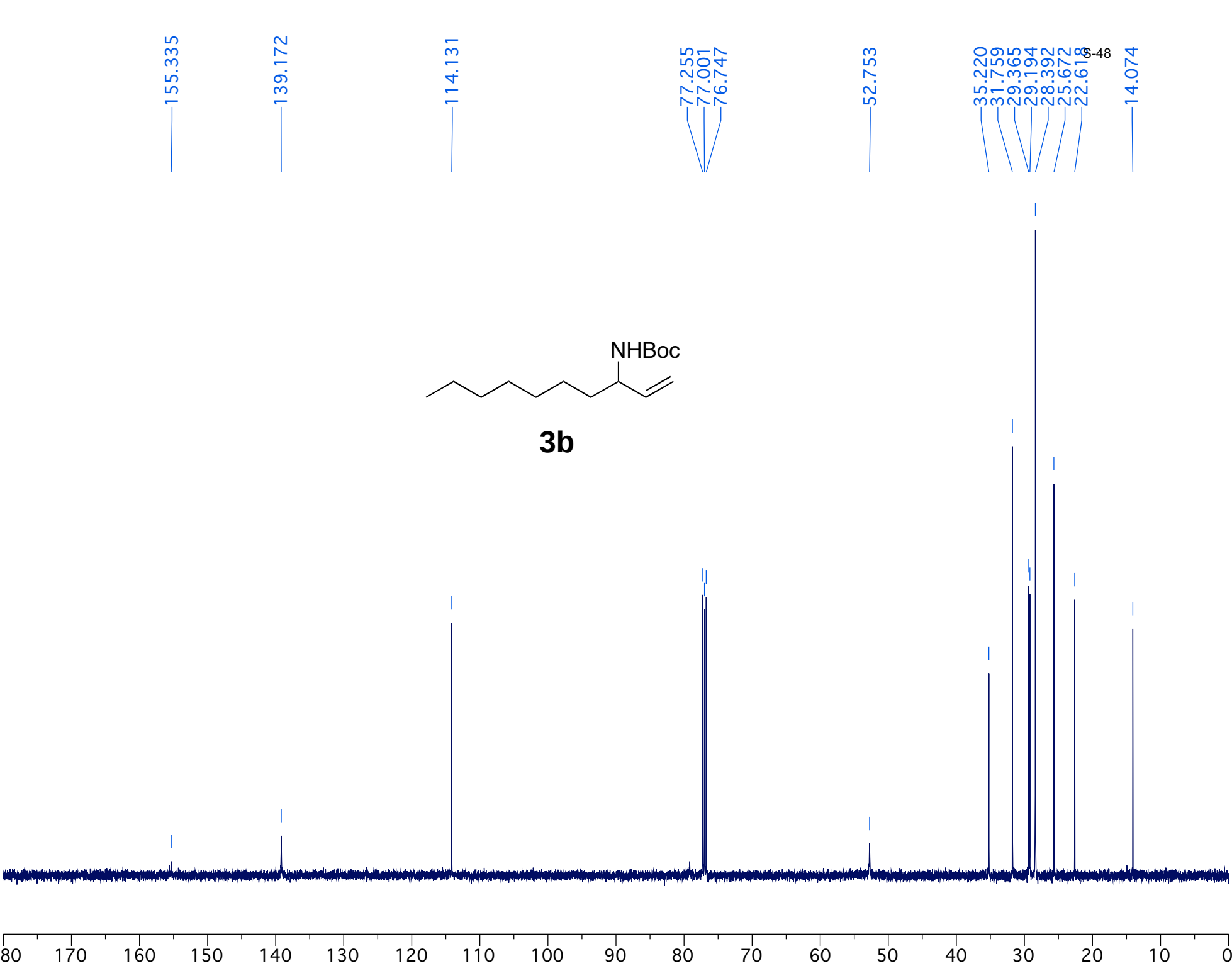
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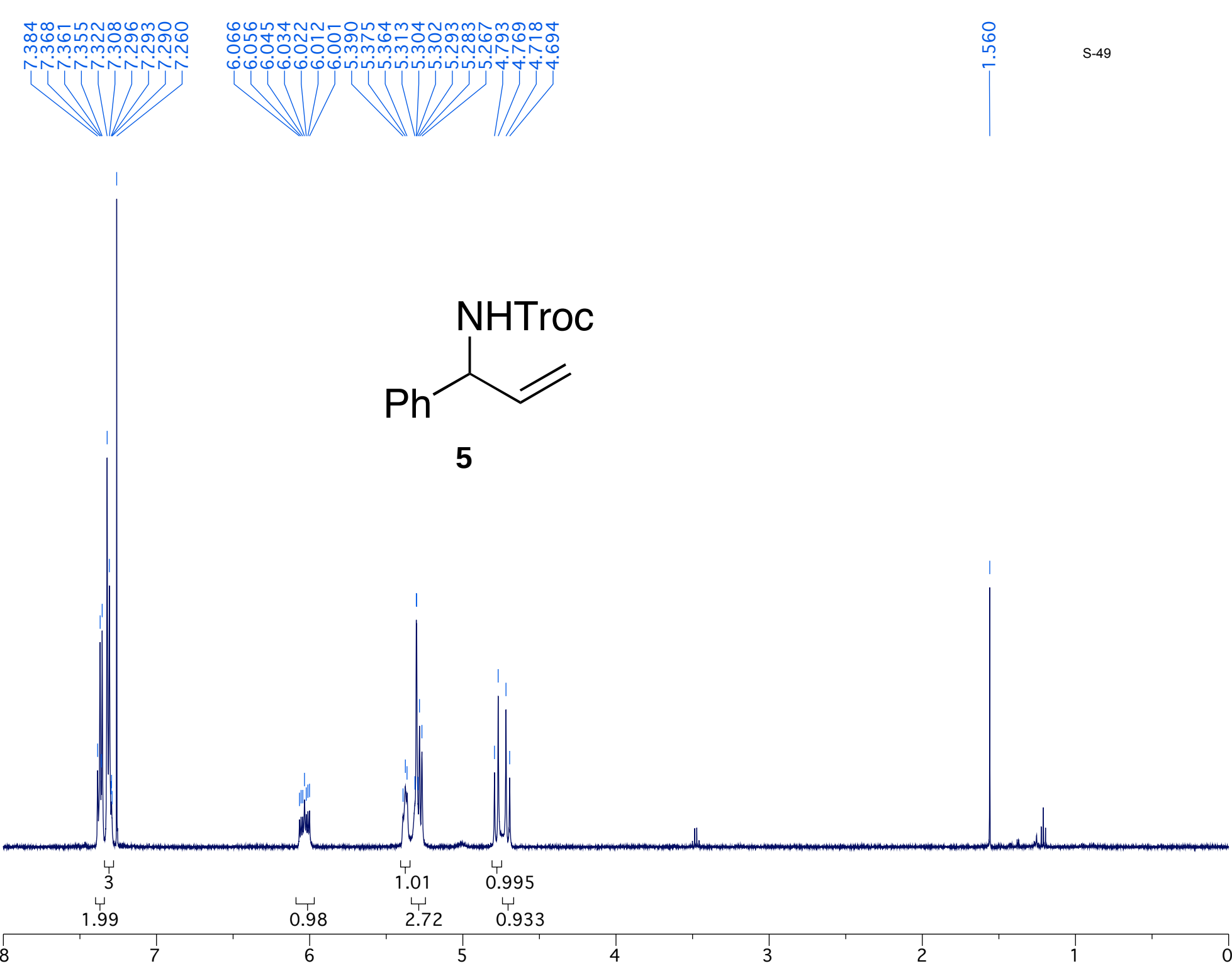
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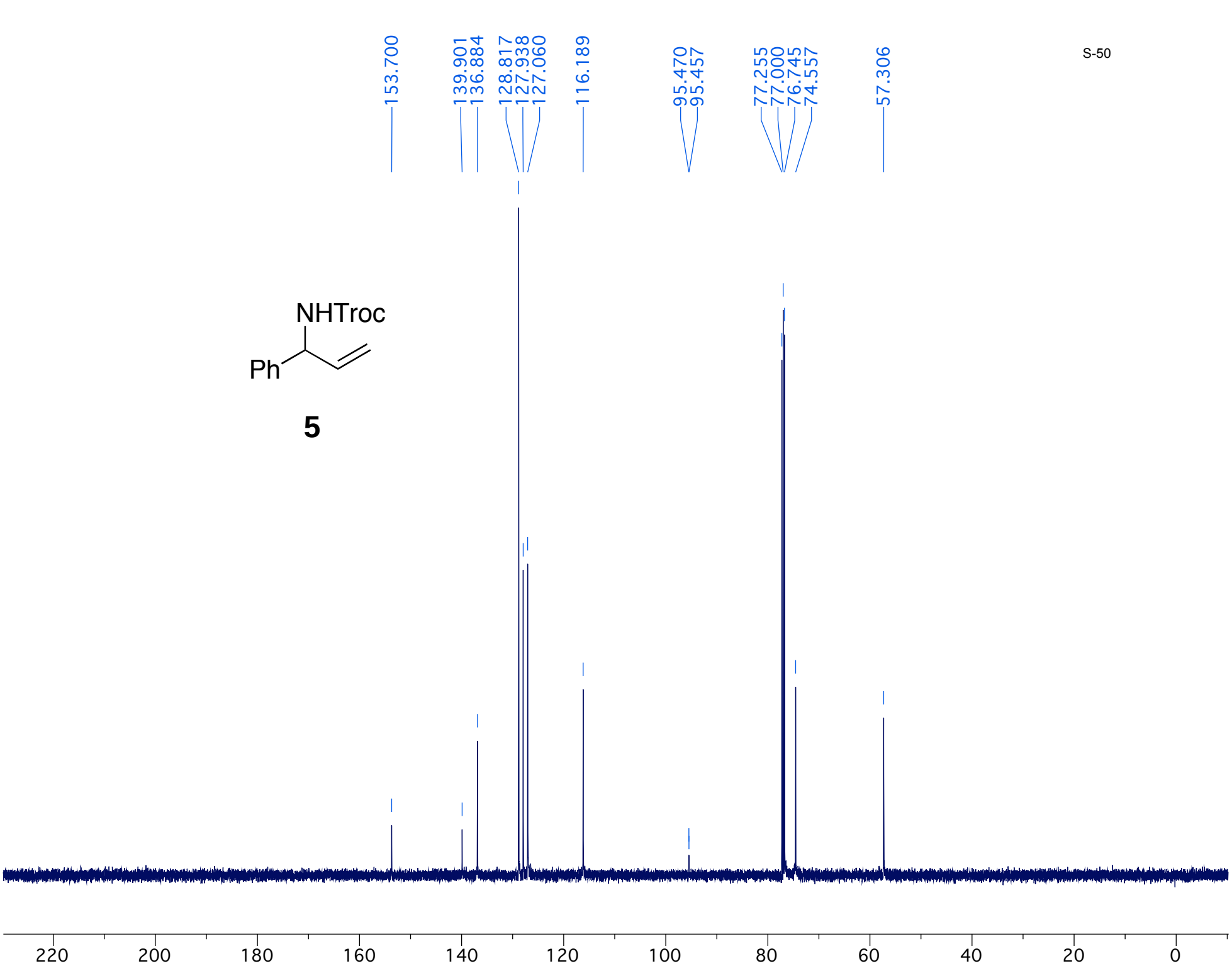
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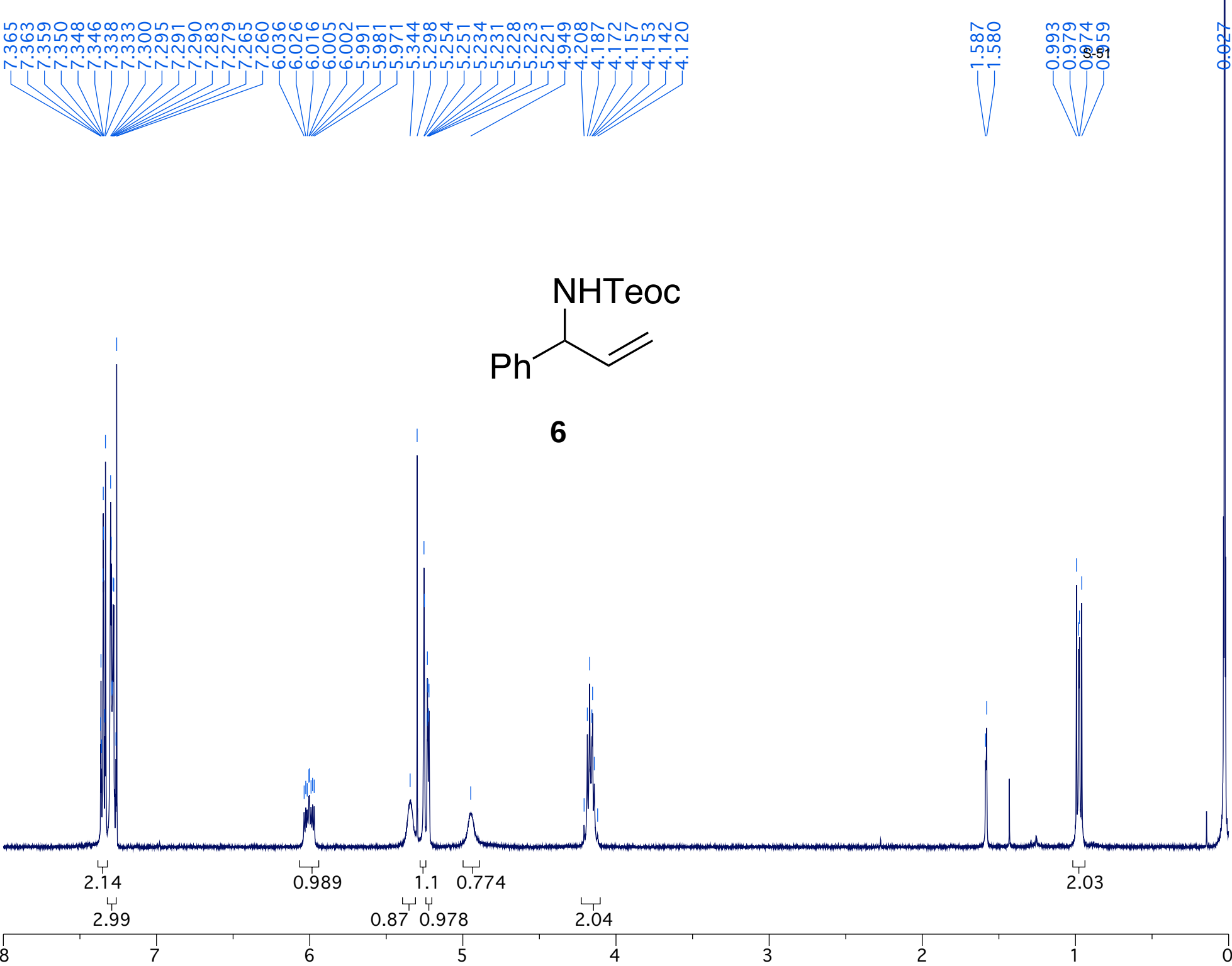
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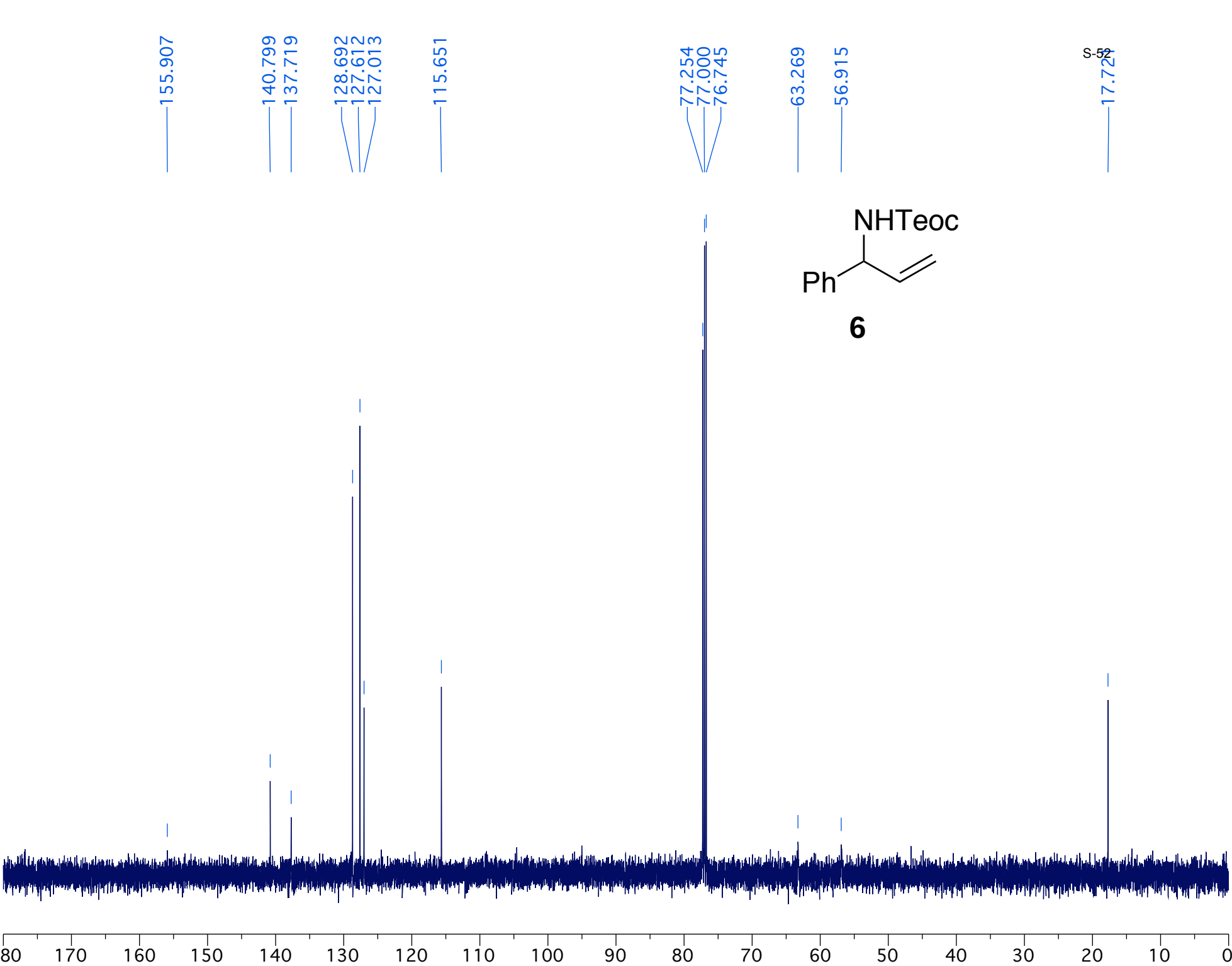
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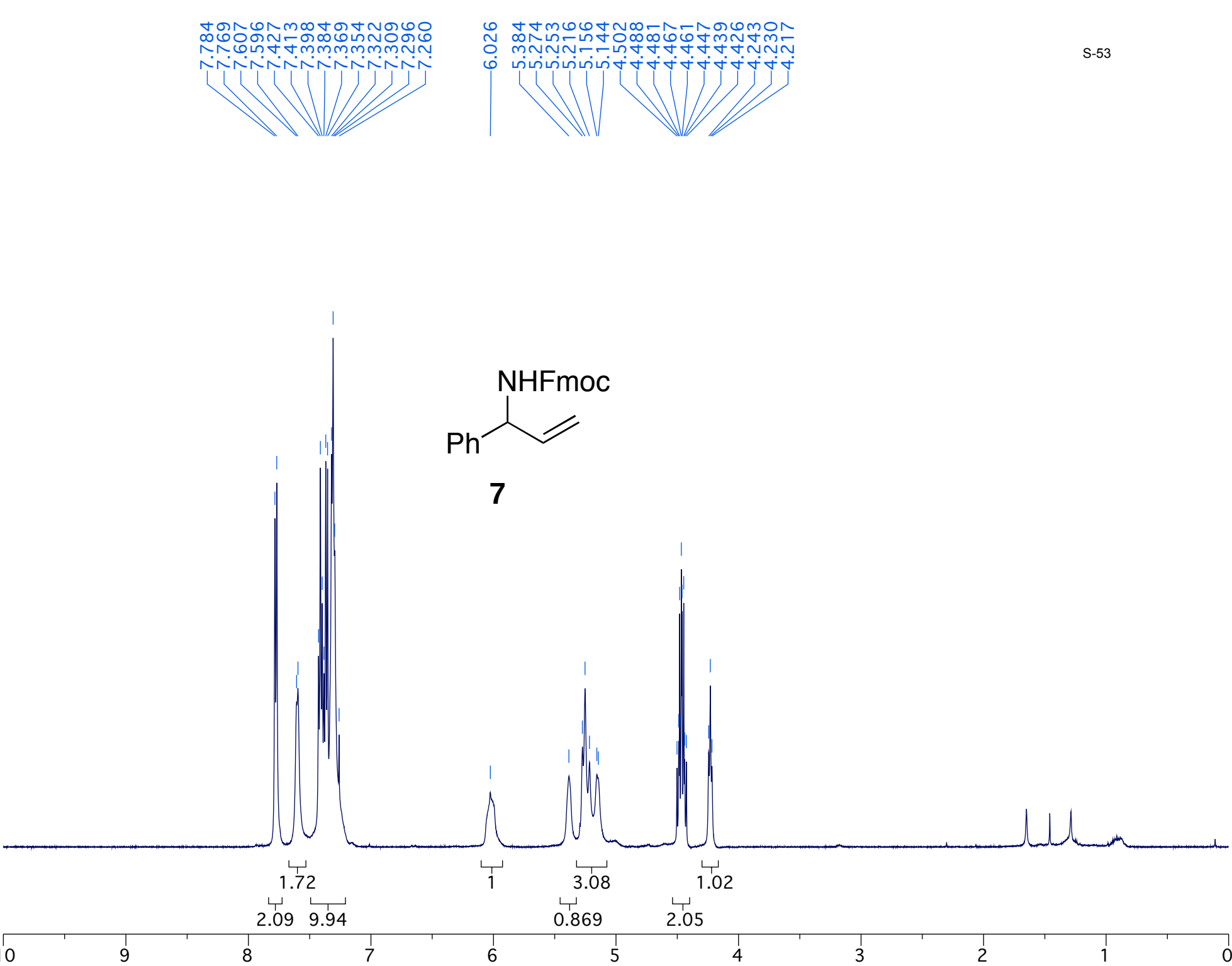
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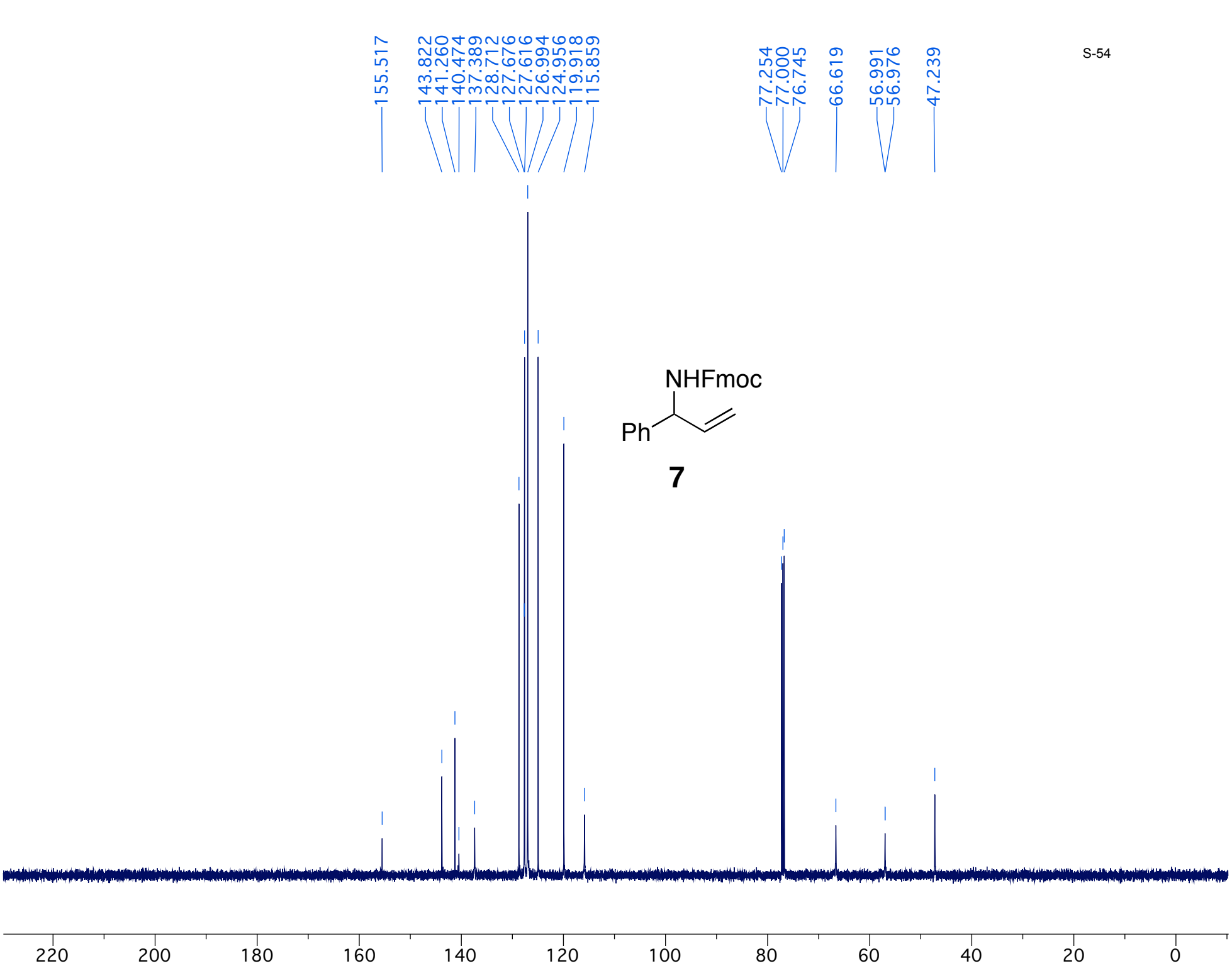
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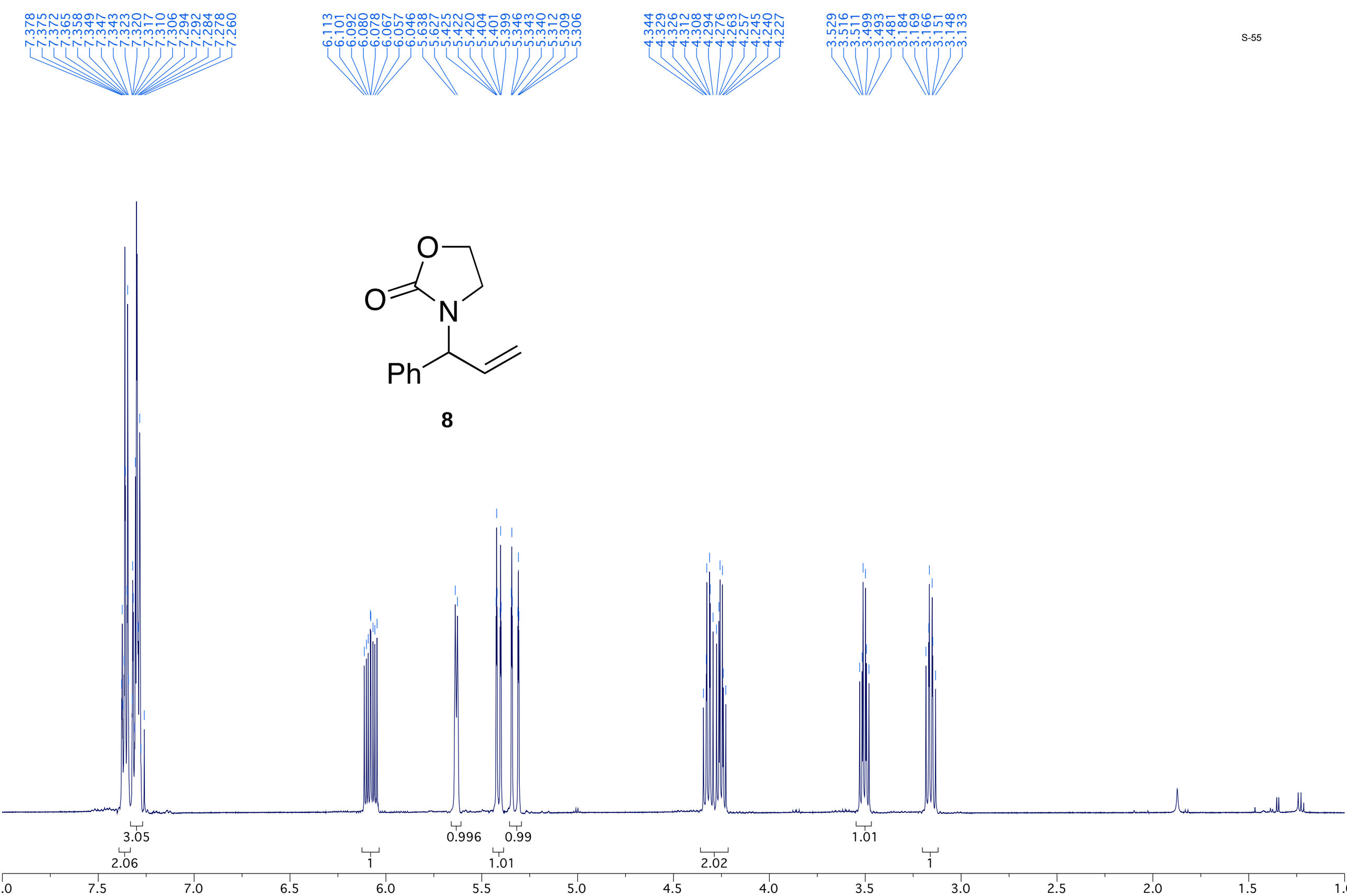
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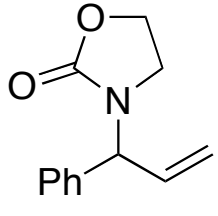

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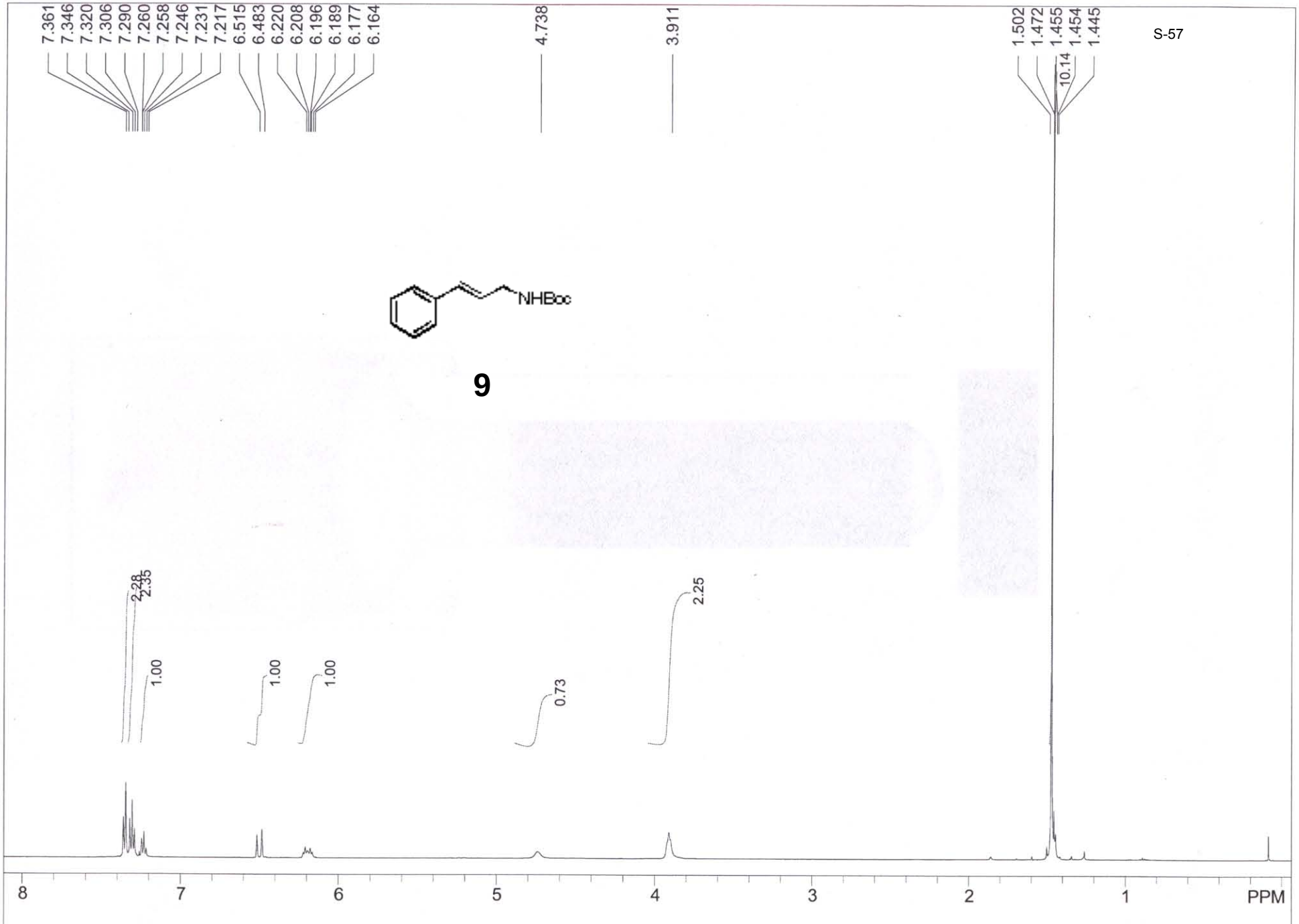
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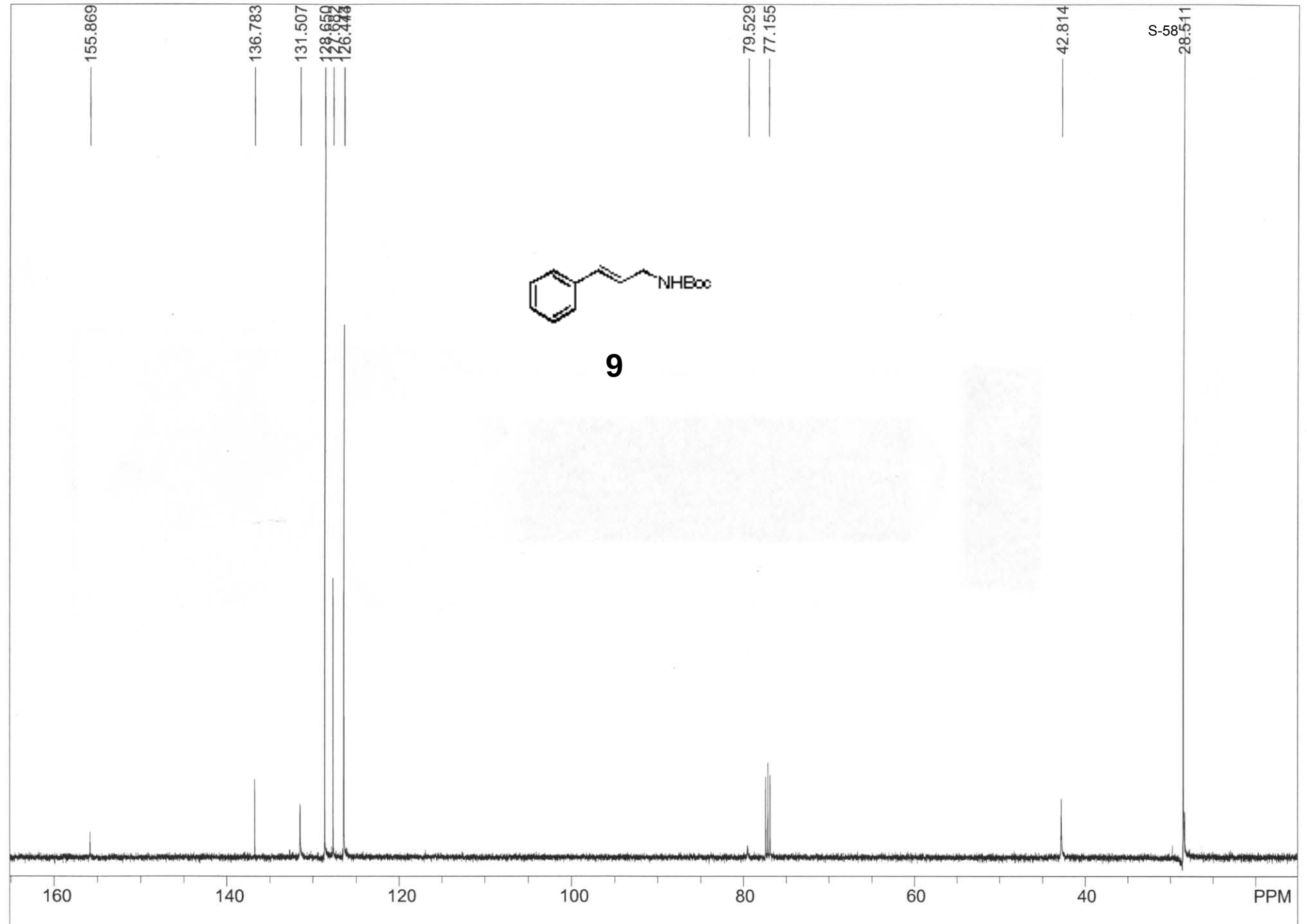
9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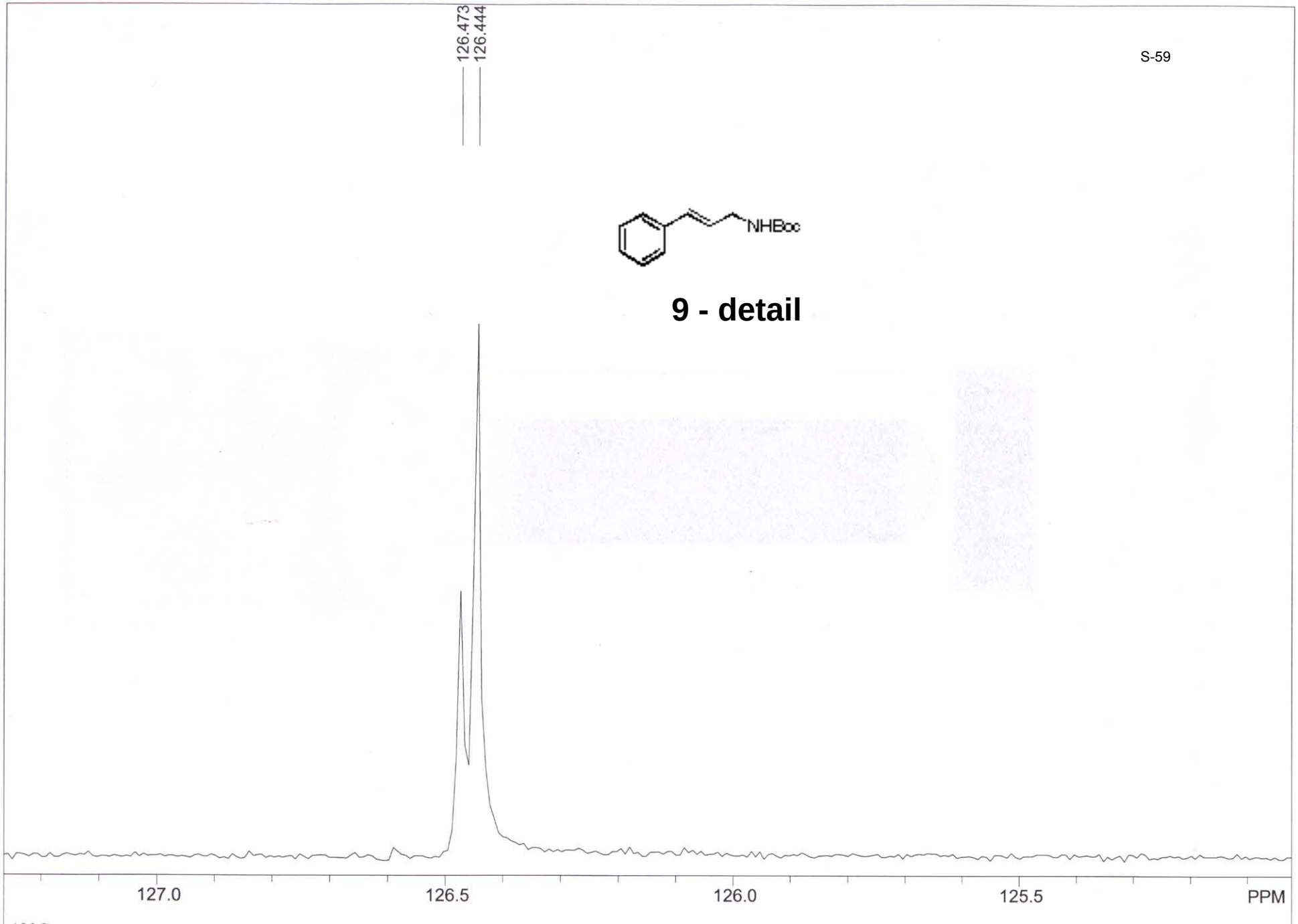
PPM

9



9 - detail