Supporting Information on

Carbon-Nitrogen Bond Formation via the Vanadium Oxo Catalyzed Sigmatropic Functionalization of Allenols.

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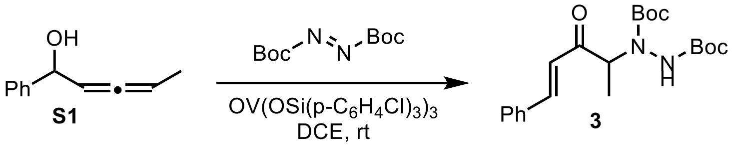
I. General Information

All reactions were carried out in oven- or flame-dried glassware under a nitrogen atmosphere. All solvents were freshly distilled from a nitrogen or argon environment or dried by passing through an Alumina column under argon. Flash chromatography was performed with 0.035-0.070 μm Silica Gel (Acros). ^{1}H and ^{13}C NMR spectroscopy was performed at ambient temperature with $CDCl_3$ as the solvent on a Mercury NMR at 400 (^{1}H) or 100 (^{13}C) MHz, an Inova NMR at 500 (^{1}H) or 125 (^{13}C) MHz, and an Inova NMR at 600 (^{1}H) MHz unless otherwise indicated. Chemical shifts are reported in ppm relative to tetramethylsilane or residual protiated solvent. All ^{13}C NMR spectra are proton decoupled. Infrared spectroscopy data was recorded on sodium chloride plates as thin films on a Thermo Scientific Nicolet IR100 FT-IR spectrometer. Analytical thin layer chromatography was performed using silica gel 60-F_{254} plates (Millipore). High-resolution mass spectra were obtained in the Vincent Coates Foundation Mass Spectrometry Laboratory, Stanford University Mass Spectrometry (http://mass-spec.stanford.edu).

II. Experimental Procedures and Compound Characterization

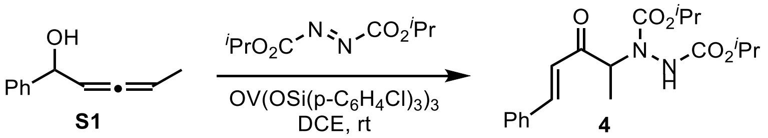
di-tert-butyl (E)-1-(3-oxo-5-phenylpent-4-en-2-yl)hydrazine-1,2-dicarboxylate (**3**)



$OV(OSi(p\text{-}ClC_6H_4)_3)_3$ (12 mg, 0.010 mmol) and di-*tert*-butyl azodicarboxylate (129 mg, 0.560 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.4 mL) was added followed by allenol **S1** (63.5 mg, 0.396 mmol) neat via syringe. The vial was immediately capped and stirred at room temperature for 15 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 5.5:1) to afford 146.1 mg (94%) of a clear oil.

IR(C_6D_6) 3302, 2970, 2920, 1700, 1600, 1470, 1440, 1360, 1240, 1150, 1050 cm^{-1}. ^1H NMR (400 MHz, 75 °C Benzene-d_6) δ 7.69 (d, *J* = 15.9 Hz, 1H), 7.26 (d, *J* = 6.1 Hz, 2H), 7.04 (p, *J* = 3.3, 2.7 Hz, 2H), 6.91 (s (broad), 1H), 6.53 – 6.34 (m, 1H), 5.02 (s (broad), 1H), 1.60 – 1.23 (series of obscured peaks, 21H total). ^{13}C NMR (101 MHz, 75 °C Benzene-d_6) δ 197.30, 155.90, 155.42, 143.29, 135.46, 130.31, 128.99, 128.70, 123.51, 81.58, 80.56, 61.63 (broad), 28.38, 28.31, 13.61. HRMS (EI) calculated for $C_{21}H_{30}N_2O_5$ (Na^+) 413.2052, found: 413.2055. R_f (petroleum ether / EtOAc 5.5:1) = 0.22.

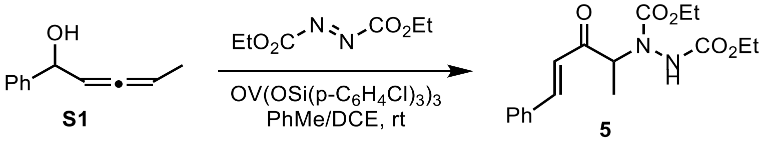
diisopropyl (E)-1-(3-oxo-5-phenylpent-4-en-2-yl)hydrazine-1,2-dicarboxylate (**4**)



$OV(OSi(p\text{-}ClC_6H_4)_3)_3$ (12 mg, 0.010 mmol) and di-isopropyl azodicarboxylate (110 µL, 0.560 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.4 mL) was added followed by allenol **S1** (63.6 mg, 0.397 mmol) neat via syringe. The vial was immediately capped and stirred at room temperature for 16 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 3:1) to afford 129.4 mg (90 %) of a white oily foam.

IR(C_6D_6) 3250, 2940, 2900, 1690, 1590, 1450, 1430, 1370, 1280, 1220, 1090, 1040 cm^{-1}. ^1H NMR (500 MHz, 75°C, Benzene-d_6) δ 7.68 (d, *J* = 15.9 Hz, 1H), 7.32 – 7.23 (m, 2H), 7.10 – 7.01 (m, 3H), 6.89 (d, *J* = 15.9 Hz, 1H), 6.66 (s, 1H), 5.05 (s, 1H), 4.95 (m, 2H), 1.40 (d, *J* = 7.2 Hz, 3H), 1.13 – 1.06 (m, 12H). ^{13}C NMR (126 MHz, 75°C, Benzene-d_6) δ 197.20, 156.50, 156.17, 143.54, 135.48, 130.37, 129.01, 128.72, 123.49, 70.63, 69.53, 62.19 (broad), 22.02, 22.00, 21.95, 21.92, 13.58. HRMS (EI) calculated for $C_{19}H_{26}N_2O_5$ (Na^+) 385.1740, found: 385.1736. R_f (petroleum ether / EtOAc 3:1) = 0.27.

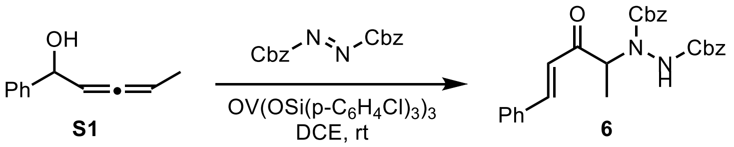
diethyl (E)-1-(3-oxo-5-phenylpent-4-en-2-yl)hydrazine-1,2-dicarboxylate (**5**)



$OV(OSi(p\text{-}ClC_6H_4)_3)_3$ (24 mg, 0.020 mmol) and diethyl azodicarboxylate (40% weight in PhMe, 0.44 mL, 0.56 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.4 mL) was added followed by allenol **S1** (64.2 mg, 0.401 mmol) neat via syringe. The vial was immediately capped and stirred at room temperature for 16.5 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 2:1) to afford 131.6 mg (90%) of a pale-yellow foam.

IR(C_6D_6) 3240, 2940, 1690, 1590, 1430, 1390,1320, 1210, 1040 cm^{-1}. ^{1}H NMR (500 MHz, 75°C, Benzene-*d*$_6$) δ 7.69 (d, *J* = 15.9 Hz, 1H), 7.34 – 7.24 (m, 2H), 7.11 – 7.03 (m, 3H), 6.90 (s, 1H), 6.87 (s, 1H), 5.06 (s, 1H), 4.33 – 3.66 (m, 4H), 1.40 (d, *J* = 7.2 Hz, 3H), 1.01 (2 obscured triplets d, *J* = 7.1, 6H total). ^{13}C NMR (126 MHz, 75°C, Benzene-*d*$_6$) δ 197.27, 156.83, 156.60, 143.71, 135.43, 130.44, 129.03, 128.75, 123.39, 62.76, 62.29, 61.86, 14.45, 14.43, 13.57. HRMS (EI) calculated for $C_{17}H_{22}N_2O_5$ (Na^+) 357.1426, found: 357.1420. R_f (petroleum ether / EtOAc 2:1) = 0.28.

dibenzyl (E)-1-(3-oxo-5-phenylpent-4-en-2-yl)hydrazine-1,2-dicarboxylate (**6**)

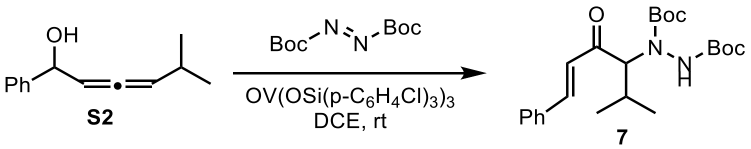


$OV(OSi(p\text{-}ClC_6H_4)_3)_3$ (12 mg, 0.010 mmol) and dibenzyl azodicarboxylate (167 mg, 0.560 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.4 mL) was added followed by allenol **S1** (63.6 mg, 0.397 mmol) neat via syringe. The vial was immediately capped and stirred at room temperature for 18 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 2.5:1) to afford 168 mg (91%) of a pale-yellow oil.

For 2 mmol scale: $OV(OSi(p\text{-}ClC_6H_4)_3)_3$ (60 mg, 0.05 mmol) and dibenzyl azodicarboxylate (835 mg, 2.80 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (2.0 mL) was added followed by allenol **S1** (319 mg, 1.99 mmol) neat via syringe. The vial was immediately capped and stirred at room temperature for 18 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 2.5:1) to afford 805 mg (88%) of a pale-yellow oil.

IR(C_6D_6) 3250, 3020, 2990, 2900, 1700, 1590, 1480, 1430, 1390, 1320, 1280, 1200, 1110, 1040, 990, 730, 690 cm^{-1}. 1H NMR (500 MHz, 75 °C Benzene-*d*$_6$) δ 7.61 (d, *J* = 15.9 Hz, 1H), 7.21 – 7.12 (series of m, 6H total), 7.10 – 6.97 (series of m, 9H total), 6.74 (d, *J* = 16.0 Hz, 1H), 6.74 (s, 1H), 5.11 – 4.95 (series of m, 5H total), 1.32 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, 75 °C Benzene-*d*$_6$) δ 197.05, 156.69, 156.48, 143.85, 136.82, 136.74, 135.36, 130.42, 128.98, 128.77, 128.67, 128.34, 128.27, 128.27, 128.22, 128.20, 123.26, 68.58, 67.78, 62.29 (broad), 13.55. HRMS (EI) calculated for $C_{27}H_{26}N_2O_5$ (Na^+) 481.1740, found: 481.1729. R_f (petroleum ether / EtOAc 2.5:1) = 0.24.

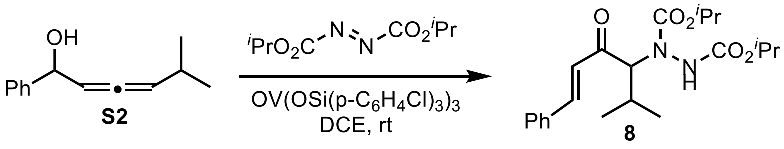
diethyl (E)-1-(2-methyl-4-oxo-6-phenylhex-5-en-3-yl)hydrazine-1,2-dicarboxylate (**7**)



$OV(OSi(p\text{-}ClC_6H_4)_3)_3$ (12 mg, 0.010 mmol) and di-*tert*-butyl azodicarboxylate (129 mg, 0.560 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.4 mL) was added followed by allenol **S2** (74.9 mg, 0.398 mmol) neat via syringe. The vial was immediately capped and stirred at room temperature for 17 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 6.5:1) to afford 125.3 mg (75 %) of a pale-yellow foam in a 12.2/1 E/Z ratio.

IR(C_6D_6) 3250, 2940, 2890, 1670, 1590, 1430, 1370, 1350, 1140 cm^{-1}. ^1H NMR (500 MHz, 75°C, Benzene-d_6) δ 7.75 (d, *J* = 16.0 Hz, 1H), 7.34 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.11 – 6.98 (m, 3H), 6.42 (s, 1H), 4.80 (s, 1H), 2.55 – 2.32 (m, 1H), 1.42 – 1.40 (m due to rotomers, 9H), 1.40 – 1.39 (m due to rotomers, 9H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.99 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, 75°C, Benzene-d_6) δ 196.22, 155.81, 155.35, 142.79, 135.81, 130.17, 129.01, 128.68, 126.51, 81.73, 80.77, 70.05 (very broad), 28.44, 28.34, 27.79, 20.04, 19.70. HRMS (EI) calculated for $C_{23}H_{34}N_2O_5$ (Na^+) 441.2365, found: 441.2366. R_f (petroleum ether / EtOAc 7:1) = 0.21.

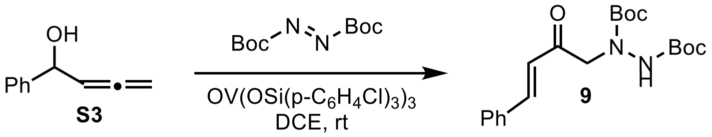
diisopropyl (E)-1-(2-methyl-4-oxo-6-phenylhex-5-en-3-yl)hydrazine-1,2-dicarboxylate (**8**)



$OV(OSi(p\text{-}ClC_6H_4)_3)_3$ (12 mg, 0.010 mmol) and di-isopropyl azodicarboxylate (110 μL, 0.560 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.4 mL) was added followed by allenol **S2** (75.2 mg, 0.400 mmol) neat via syringe. The vial was immediately capped and stirred at room temperature for 16 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 4.5:1) to afford 129.1 mg (83 %) of a clear oil in a 17.5/1 E/Z ratio.

IR(C_6D_6) 3250, 2940, 2890, 2840, 1690, 1590, 1450, 1430, 1370, 1270, 1210, 1160, 1090, 1020, 960, 750, 680 cm^{-1}. ^1H NMR (500 MHz, 75°C, Benzene-d_6) δ 7.76 (d, *J* = 16.0 Hz, 1H), 7.33 (apparent s, 2H), 7.04 (apparent s, 4H), 6.61 (s, 1H), 4.94 (tt, *J* = 12.2, 6.2 Hz, 2H), 4.91 – 4.75 (s (broad), 1H), 2.47 (dq, *J* = 15.9, 7.1 Hz, 1H), 1.11 (d, *J* = 6.5 Hz, 3H), 1.09 – 1.06 (m, 9H), 1.04 (d, *J* = 6.2 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, 75°C, Benzene-d_6) δ 196.38, 156.55, 155.97, 143.08, 135.65, 130.28, 129.02, 128.72, 126.31, 70.78, 70.17 (broad), 69.60, 27.74, 21.98, 21.96, 21.93, 19.97, 19.73. HRMS (EI) calculated for $C_{21}H_{30}N_2O_5$ (Na^+) 413.2052, found: 413.2034. R_f (petroleum ether / EtOAc 4.5:1) = 0.20.

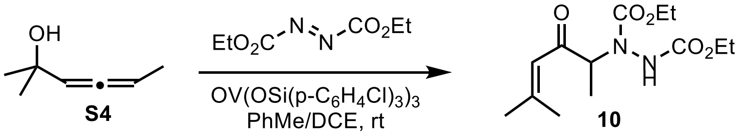
di-tert-butyl (E)-1-(2-oxo-4-phenylbut-3-en-1-yl)hydrazine-1,2-dicarboxylate (**9**)



OV(OSi(p-ClC$_6$H$_4$)$_3$)$_3$ (12 mg, 0.010 mmol) and di-*tert*-butyl azodicarboxylate (129 mg, 0.560 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.4 mL) was added followed by allenol **S3** (53.0 mg, 0.363 mmol) neat via syringe. The vial was immediately capped and stirred at room temperature for 23 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO$_2$; Petroleum ether / EtOAc 6:1) to afford 135.8 mg (99 %) of a pale-yellow oil.

IR(C$_6$D$_6$) 3270, 2940, 2890, 1690, 1590, 1460, 1430, 1370, 1350, 1240, 1210, 1140, 1080, 1040, 1010, 960, 840, 740, 680, 660 cm^{-1}. ^{1}H NMR (500 MHz, 75°C, Benzene-*d*$_6$) δ 7.42 (d, *J* = 16.2 Hz, 1H), 7.16 (apparent s, 2H), 7.11 – 6.95 (m, 3H), 6.72 (s, 1H), 6.52 (d, *J* = 16.7 Hz, 1H), 4.86 – 3.84 (m, 2H), 1.43 (s, 9H), 1.41 (s, 9H). ^{13}C NMR (126 MHz, 75°C, Benzene-*d*$_6$) δ 194.22, 155.72, 155.25, 143.20, 135.20, 130.42, 128.96, 128.62, 123.97, 81.50, 80.69, 58.60 (broad), 28.42, 28.32. HRMS (EI) calculated for C$_{20}$H$_{28}$N$_2$O$_5$ (Na$^+$) 399.1896, found: 399.1907. R$_f$ (petroleum ether / EtOAc 5:1) = 0.33.

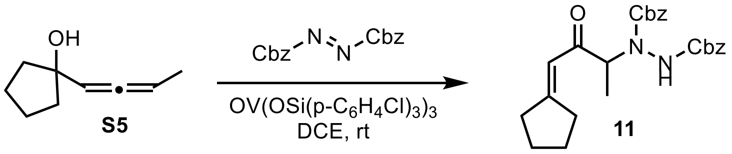
diethyl 1-(5-methyl-3-oxohex-4-en-2-yl)hydrazine-1,2-dicarboxylate (**10**)



OV(OSi(p-ClC$_6$H$_4$)$_3$)$_3$ (24 mg, 0.020 mmol) and diethyl azodicarboxylate (40% weight in PhMe, 0.44 mL, 0.56 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.4 mL) was added followed by allenol **S4** (45.6 mg, 0.407 mmol) neat via syringe. The vial was immediately capped and stirred at room temperature for 17 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO$_2$; Petroleum ether / EtOAc 2.2:1) to afford 104.4 mg (90%) of a clear oil.

IR(C$_6$D$_6$) 3240, 2940, 2900, 1690, 1600, 1390, 1360, 1280, 1210, 1050 cm^{-1}. ^{1}H NMR (500 MHz, 75°C, Benzene-*d*$_6$) δ 6.77 (s, 1H), 5.96 (s, 1H), 4.84 (s, 1H), 4.09 – 3.94 (m, 4H), 2.02 (s, 3H), 1.53 (d, *J* = 1.3 Hz, 3H), 1.33 (d, *J* = 7.3 Hz, 3H), 1.03 – 0.97 (m, 6H). ^{13}C NMR (126 MHz, 75°C, Benzene-*d*$_6$) δ 198.15, 157.02, 156.73, 121.21, 63.39, 62.54, 61.69, 27.29, 20.81, 14.46, 14.43, 13.50 (one carbamate carbonyl or the β-enone sp^2 is carbon is obscured by another peak). LRMS (EI) calculated for C$_{13}$H$_{22}$N$_2$O$_5$ (Na$^+$) 309.1, found: 309.1 R$_f$ (petroleum ether / EtOAc 2.5:1) = 0.21.

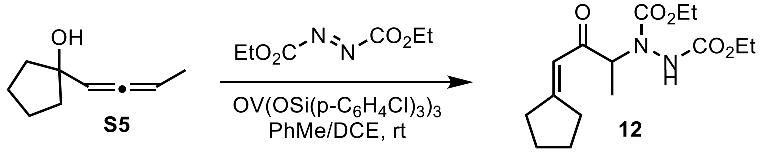
dibenzyl 1-(4-cyclopentylidene-3-oxobutan-2-yl)hydrazine-1,2-dicarboxylate (**11**)



OV(OSi(p-ClC$_6$H$_4$)$_3$)$_3$ (12 mg, 0.010 mmol) and dibenzyl azodicarboxylate (167 mg, 0.560 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.4 mL) was added followed by allenol **S5** (55.6 mg, 0.402 mmol) neat via syringe. The vial was immediately capped and stirred at room temperature for 16.5 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 3.5:1) to afford 150.2 mg (86%) of a clear oil.

IR(C_6D_6) 3250, 2920, 1700, 1600, 1480, 1430, 1390, 1280, 1200, 1040 cm^{-1}. ^1H NMR (500 MHz, 75°C, Benzene-d_6) δ 7.21 – 7.11 (m, 4H), 7.11 – 6.98 (m, 6H), 6.90 (s, 1H), 6.04 (s, 1H), 5.11 – 4.94 (m, 4H), 4.94 – 4.80 (m, 1H), 2.71 (t, *J* = 6.6 Hz, 2H), 2.04 (t, *J* = 7.4 Hz, 2H), 1.41 (p, *J* = 7.0 Hz, 2H), 1.33 – 1.26 (m, 5H). ^{13}C NMR (126 MHz, 75°C, Benzene-d_6) δ 197.37, 170.54, 156.72, 156.67, 136.95, 128.65, 128.62, 128.30, 128.20, 128.10, 116.40, 68.37, 67.62, 63.25, 36.37, 33.75, 26.62, 25.37, 13.59 (one aromatic peak was obscured). HRMS (EI) calculated for $C_{25}H_{28}N_2O_5$ (Na^+) 459.1896, found: 459.1890. R_f (petroleum ether / EtOAc 3.5:1) = 0.25.

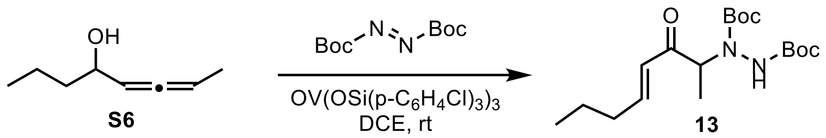
diethyl 1-(4-cyclopentylidene-3-oxobutan-2-yl)hydrazine-1,2-dicarboxylate (**12**)



OV(OSi(p-ClC_6H_4)$_3$)$_3$ (24 mg, 0.020 mmol) and diethyl azodicarboxylate (40% weight in PhMe, 0.44 mL, 0.56 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.4 mL) was added followed by allenol **S5** (55.3 mg, 0.400 mmol) neat via syringe. The vial was immediately capped and stirred at room temperature for 17 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 2.5:1) to afford 91.9 mg (74 %) of a clear oil.

IR(C_6D_6) 3250, 2940, 1690, 1600, 1390, 1360, 1280, 1210, 1160, 1040 cm^{-1}. ^1H NMR (500 MHz, 75°C, Benzene-d_6) δ 6.74 (s, 1H), 6.11 (s, 1H), 4.93 (s, 1H), 4.13 – 3.91 (m, 4H), 2.81 – 2.72 (m, 2H), 2.10 (t, *J* = 7.0 Hz, 2H), 1.49 – 1.41 (m, 2H), 1.36 (d, *J* = 7.5 Hz, 3H), 1.35 – 1.29 (m, 2H), 1.00 (2 overlapping triplets, *J* = 7.1, 6H total). ^{13}C NMR (126 MHz, Benzene) δ 197.58, 170.22, 156.82, 156.68, 116.49, 63.12, 62.53, 61.67, 36.37, 33.73, 26.63, 25.38, 14.47, 14.44, 13.61. HRMS (EI) calculated for $C_{15}H_{24}N_2O_5$ (Na^+) 335.1583, found: 335.1588. R_f (petroleum ether / EtOAc 2:1) = 0.31.

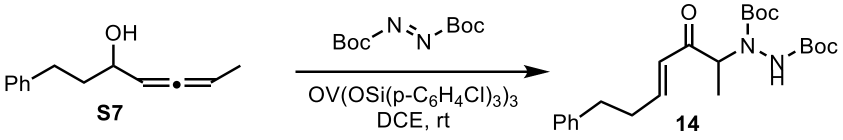
di-tert-butyl (E)-1-(3-oxooct-4-en-2-yl)hydrazine-1,2-dicarboxylate (**13**)



OV(OSi(p-ClC_6H_4)$_3$)$_3$ (12 mg, 0.010 mmol) and di-*tert*-butyl azodicarboxylate (184 mg, 0.800 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.4 mL) was added followed by allenol **S6** (50.5 mg, 0.396 mmol) neat via syringe. The vial was immediately capped and stirred at 45°C for 15 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 6.5:1) to afford 95 mg (67%) of a pale-yellow oil.

IR(C_6D_6) 3300, 2940, 2890, 1680, 1610, 1440, 1370, 1350, 1230, 1140 cm^{-1}. ^{1}H NMR (500 MHz, 75°C, Benzene-d_6) δ 6.84 (dt, J = 15.7, 6.9 Hz, 1H), 6.37 (s, 1H), 6.15 (d, J = 15.7 Hz, 1H), 4.97 (s, 1H), 1.84 (qd, J = 7.1, 1.6 Hz, 2H), 1.42 (s, 9H), 1.40 (s, 9H), 1.34 (d, J = 7.2 Hz, 3H), 1.21 (h, J = 7.4 Hz, 2H), 0.73 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, 75°C, Benzene-d_6) δ 197.40, 155.79, 155.47, 147.55, 127.41, 81.41, 80.45, 60.98 (very broad), 34.58, 28.37 (broad), 21.55, 13.65, 13.50. HRMS (EI) calculated for $C_{18}H_{32}N_2O_5$ (Na^+) 379.2209, found: 379.2196. R_f (petroleum ether / EtOAc 6.5:1) = 0.23.

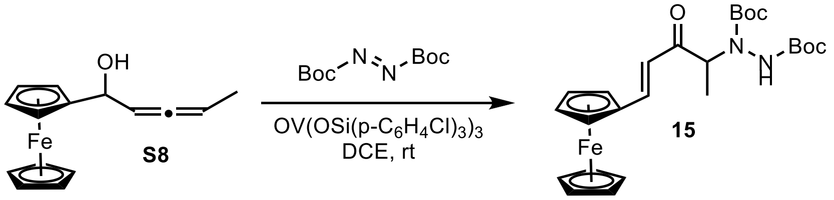
di-tert-butyl (E)-1-(3-oxo-7-phenylhept-4-en-2-yl)hydrazine-1,2-dicarboxylate (**14**)



$OV(OSi(p\text{-}ClC_6H_4)_3)_3$ (12 mg, 0.010 mmol) and di-*tert*-butyl azodicarboxylate (184 mg, 0.800 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.4 mL) was added followed by allenol **S7** (76.0 mg, 0.404 mmol) neat via syringe. The vial was immediately capped and stirred at 45°C for 19 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 6:1) to afford 99.2 mg (59%) of a pale-yellow oil.

IR(C_6D_6) 3280, 2940, 2890, 1680, 1610, 1440, 1370, 1350, 1230, 1140, 1040, 740, 690 cm^{-1}. ^{1}H NMR (500 MHz, 75°C, Benzene-d_6) δ 7.15 – 7.08 (m, 2H), 7.08 – 7.01 (m, 1H), 6.95 (d, J = 7.8 Hz, 2H), 6.83 (dt, J = 15.8, 6.8 Hz, 1H), 6.32 (s, 1H), 6.11 (d, J = 16.2 Hz, 1H), 4.92 (s, 1H), 2.47 (t, J = 7.6 Hz, 2H), 2.17 (q, J = 7.2 Hz, 2H), 1.41 (s, 9H), 1.40 (s, 9H), 1.31 (d, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, 75°C, Benzene-d_6) δ 197.26, 155.79, 155.43, 146.54, 141.20, 128.74, 128.64, 127.74, 126.46, 81.44, 80.48, 61.27 (broad), 34.65, 34.11, 28.40, 28.35, 13.60. HRMS (EI) calculated for $C_{23}H_{34}N_2O_5$ (Na^+) 441.2365, found: 441.2357. R_f (petroleum ether / EtOAc 6:1) = 0.24.

di-tert-butyl (E)-1-(3-oxo-5-ferrocenylpent-4-en-2-yl)hydrazine-1,2-dicarboxylate (**15**)

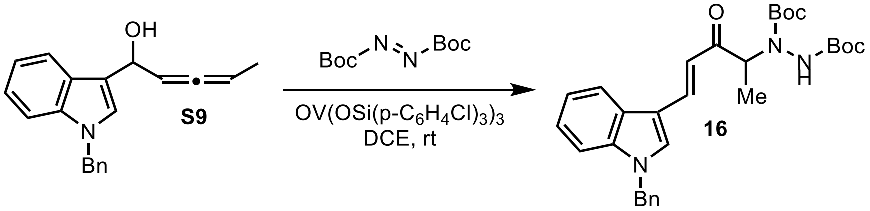


$OV(OSi(p\text{-}ClC_6H_4)_3)_3$ (12 mg, 0.010 mmol) and di-*tert*-butyl azodicarboxylate (129 mg, 0.560 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.4 mL) was added followed by allenol **S8** (107 mg, 0.400 mmol) neat via syringe. The vial was immediately capped and stirred at room temperature for 8 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 5:1) to afford 111.7 mg (56 %) of a yellow oil.

IR(C_6D_6) 3260, 3050, 2940, 2890, 2250, 1720, 1690, 1580, 1460, 1440, 1370, 1350, 1290, 1230, 1140, 1090, 1030, 990, 900, 810, 750, 660 cm^{-1}. ^{1}H NMR (500 MHz, 75°C, Benzene-d_6) δ 7.64 (d, J = 15.7 Hz, 1H), 6.59 (d, J = 15.7 Hz, 1H), 6.43 (s, 1H), 5.08 (s, 1H), 4.27 (m, 2H), 4.12 (t, J = 1.9 Hz, 2H), 3.94 (m, 5H), 1.45 (s, 9H), 1.42 (s, 9H), 1.41 (d, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, 75°C, Benzene-d_6) δ

196.71, 155.83, 155.57, 144.65, 121.17, 81.43, 80.45, 79.75, 71.20, 70.05, 69.29, 69.22, 61.35 (broad), 28.43, 28.42, 13.86. HRMS (EI) calculated for $C_{25}H_{34}FeN_2O_5$ (Na^+) 521.1715, found: 521.1708. R_f (petroleum ether / Et_2O 3:1) = 0.16.

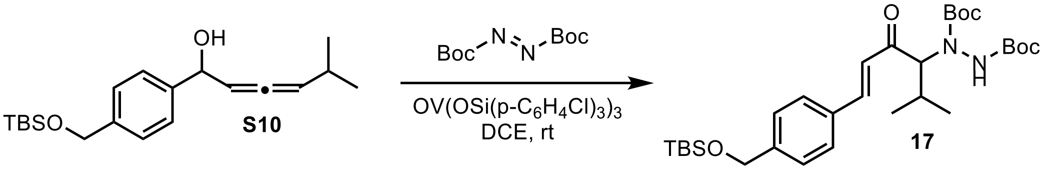
<u>di-tert-butyl (E)-1-(5-(1-benzyl-1H-indol-3-yl)-3-oxopent-4-en-2-yl)hydrazine-1,2-dicarboxylate</u> (**16**)



$OV(OSi(p\text{-}ClC_6H_4)_3)_3$ (17.4 mg, 0.0145 mmol) and di-*tert*-butyl azodicarboxylate (93.4 mg, 0.406 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.3 mL) was added followed by a slow addition of allenol **S9** (84.5 mg, 0.290 mmol) in DCE (0.3 mL) over two hours. The vial was immediately capped and stirred at room temperature for an additional 4 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 3:1) to afford 46.9 mg (31 %) of a pale-yellow oil.

IR(C_6D_6) 3350, 2940, 2880, 1690, 1570, 1510, 1450, 1370, 1350, 1230, 1140, 1030 cm^{-1}. ^1H NMR (500 MHz, 75°C, Benzene-d_6) δ 8.06 (d, *J* = 15.8 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.10 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 2H), 7.05 – 6.97 (m, 4H), 6.83 (s, 1H), 6.81 – 6.74 (m, 2H), 6.49 (d, *J* = 19.0 Hz, 1H), 5.18 (s, 1H), 4.63 (s, 2H), 1.50 (d, *J* = 7.3 Hz, 3H), 1.45 (s, 9H), 1.42 (s, 9H). ^{13}C NMR (126 MHz, Benzene) δ 197.42, 155.92, 155.71, 138.46, 136.86, 136.86, 133.17, 129.07, 127.36, 127.18, 123.43, 121.94, 121.51, 119.27, 114.03, 110.65, 81.36, 80.37, 61.67 (broad), 50.37, 28.45, 28.43, 13.98. HRMS (EI) calculated for $C_{30}H_{37}N_3O_5$ (Na^+) 542.2631, found: 542.2642. R_f (petroleum ether / EtOAc 3:1) = 0.33.

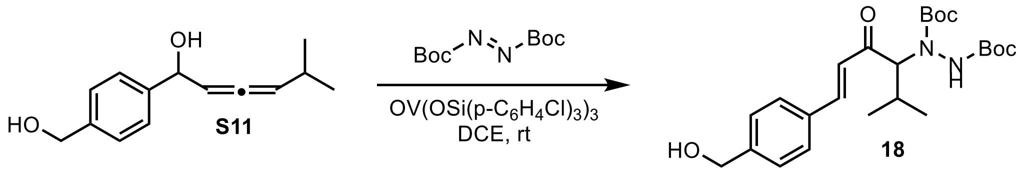
<u>di-tert-butyl (E)-1-(6-(4-(((tert-butyldimethylsilyl)oxy)methyl)phenyl)-2-methyl-4-oxohex-5-en-3-yl)hydrazine-1,2-dicarboxylate</u> (**17**)



$OV(OSi(p\text{-}ClC_6H_4)_3)_3$ (9.0 mg, 0.0075 mmol) and di-*tert*-butyl azodicarboxylate (96.7 mg, 0.420 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.3 mL) was added followed by allenol **S10** (99.2 mg, 0.298 mmol) neat via syringe. The vial was immediately capped and stirred at room temperature for 17 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 12:1 then 10:1) to afford 133 mg (79 %) of a clear oil in a 7.7/1 E/Z ratio.

IR(CH_2Cl_2) 3260, 2920, 2900, 2820, 1690, 1580, 1450, 1370, 1350, 1280, 1240, 1280, 1240, 1140, 1080, 930, 770 cm^{-1}. ^1H NMR (500 MHz, 75 °C Benzene-d_6) δ 7.79 (d, *J* = 16.0 Hz, 1H), 7.35 (dd, *J* = 6.7, 4.9 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.13 – 7.01 (m, 1H), 6.39 (s, 1H), 4.84 (s, 1H), 4.57 (s, 2H), 2.53 – 2.39 (m, 1H), 1.42 (s, 9H), 1.40 (s, 9H), 1.04 (d, *J* = 6.7 Hz, 3H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.96 (s, 9H), 0.05 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (126 MHz, 75 °C Benzene-d_6) δ 196.41, 155.84, 155.31, 144.24, 142.74, 134.57, 128.74, 126.94, 126.09, 81.70, 80.73, 70.08, 65.20, 28.44, 28.34, 27.86, 26.17, 20.06, 19.72, 18.61, -5.11. HRMS (EI) calculated for $C_{30}H_{50}N_2O_6Si$ (Na^+) 585.3336, found: 585.3322. R_f (petroleum ether / EtOAc 10:1) = 0.25.

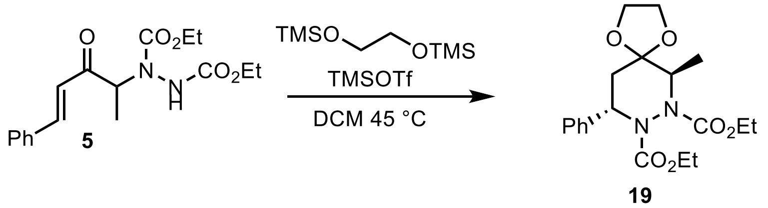
di-tert-butyl (E)-1-(6-(4-(hydroxymethyl)phenyl)-2-methyl-4-oxohex-5-en-3-yl)hydrazine-1,2-dicarboxylate (**18**)



OV(OSi(p-ClC$_6$H$_4$)$_3$)$_3$ (9.0 mg, 0.0075 mmol) and di-*tert*-butyl azodicarboxylate (96.8 mg, 0.420 mmol) were placed in a flame-dried vial along with magnetic stir bar under a nitrogen atmosphere at room temperature. DCE (0.36 mL) was added followed by allenol **S11** (67.8 mg, 0.311 mmol) neat via syringe. The vial was immediately capped and stirred at 35 °C for 15 hr. The reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 2.2:1) to afford 102 mg (73 %) of a clear oil in an 8.7/1 E/Z ratio.

IR(CH_2Cl_2) 3380, 3250, 2930, 2890, 2840, 1670, 1580, 1450, 1370, 1350, 1310, 1280, 1240, 1140, 1040, 1000 cm^{-1}. ^{1}H NMR (500 MHz, 75 °C Benzene-*d*$_6$) δ 7.78 (d, *J* = 16.0 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.44 (s, 1H), 4.82 (s, 1H), 4.33 (s, 2H), 2.46 (dp, *J* = 8.8, 6.8 Hz, 1H), 1.42 (s, 9H), 1.41 (s, 9H), 1.03 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, 75 °C Benzene-*d*$_6$) δ 196.54, 155.86, 155.38, 144.35, 142.73, 134.70, 128.79, 127.33, 126.16, 81.79, 80.83, 69.96, 64.70, 28.43, 28.33, 27.83, 20.05, 19.71. HRMS (EI) calculated for $C_{24}H_{36}N_2O_6$ (Na^+) 471.2471, found: 471.2466. R_f (petroleum ether / EtOAc 2.5:1) = 0.21.

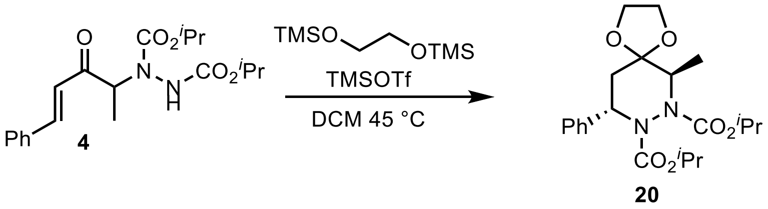
diethyl-6-methyl-9-phenyl-1,4-dioxa-7,8-diazaspiro[4.5]decane-7,8-dicarboxylate (**19**)



To a sealed pointed microwave vial equipped with a stir bar containing protected hydrazine **5** (37.4 mg, 0.112 mmol) under a nitrogen atmosphere was added dichloromethane (0.56 mL). To this mixture was added 1,2-bis(trimethylsiloxy)ethane (55 µL, 0.22 mmol) followed by trimethylsilyl trifluoromethanesulfonate (2 µL, 0.011 mmol). The sealed vial was placed in a 45 °C oil bath and stirred. After 15 hours of stirring at 45 °C, the reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 1.5:1) to afford 39.3 mg (93%) of a pale-yellow oil in >20:1 d.r.

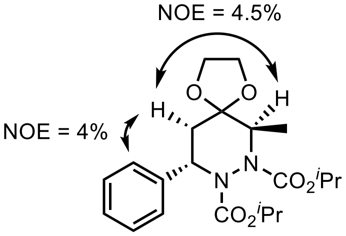
IR(C_6D_6) 2940, 2890, 1680, 1430, 1390, 1360, 1300, 1220, 1160, 1120, 1050, 750, 690, 660 cm^{-1}. ^{1}H NMR (500 MHz, 110 °C, DMSO-*d*$_6$) δ 7.48 (d, *J* = 7.4 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.26 – 7.21 (m, 1H), 5.23 (dd, *J* = 10.0, 6.8 Hz, 1H), 4.27 (q, *J* = 6.7 Hz, 1H), 4.18 – 4.04 (m, 5H), 4.02 – 3.88 (m, 3H), 2.35 (dd, *J* = 13.5, 6.8 Hz, 1H), 1.88 (dd, *J* = 13.6, 10.0 Hz, 1H), 1.20 (t, *J* = 4.4 Hz, 3H), 1.19 (d, *J* = 2.9 Hz, 3H), 1.15 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, 110 °C, DMSO-*d*$_6$) δ 154.80, 153.58, 140.18, 127.08, 126.12, 125.85, 106.24, 64.66, 63.33, 60.89, 60.68, 58.67, 57.01, 35.32, 13.35, 13.32, 10.82. HRMS (EI) calculated for $C_{19}H_{26}N_2O_6$ (Na^+) 401.1689, found: 401.1696. R_f (petroleum ether / EtOAc 2:1) = 0.28.

diisopropyl-6-methyl-9-phenyl-1,4-dioxa-7,8-diazaspiro[4.5]decane-7,8-dicarboxylate (**20**)

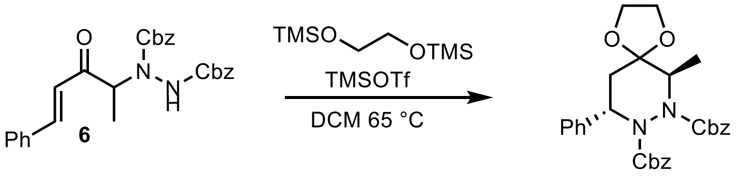


To a sealed pointed microwave vial equipped with a stir bar containing protected hydrazine **4** (74.4 mg, 0.205 mmol) under a nitrogen atmosphere was added dichloromethane (1.0 mL). To this mixture was added 1,2-bis(trimethylsiloxy)ethane (101 µL, 0.411 mmol) followed by trimethylsilyl trifluoromethanesulfonate (4.6 µL, 0.021 mmol). The sealed vial was placed in a 45 °C oil bath and stirred. After 19 hours of stirring at 45 °C, the reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 3:1) to afford 79.9 mg (96%) of a white solid in >20:1 d.r.

Melting point: 80-82 °C. IR(C_6D_6) 2940, 2900, 2850, 1680, 1480, 1450, 1430, 1390, 1370, 1290, 1220, 1160, 1130, 1100, 1070, 1050, 960, 940, 900, 880, 750, 690, 660 cm^{-1}. ^1H NMR (500 MHz, 115 °C, DMSO-d_6) δ 7.48 (d, J = 7.9 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.25 – 7.20 (m, 1H), 5.22 (t, J = 8.5 Hz, 1H), 4.92 – 4.75 (m, 2H), 4.25 (q, J = 6.7 Hz, 1H), 4.13 – 4.04 (m, 1H), 4.01 – 3.89 (m, 3H), 2.34 (dd, J = 13.5, 6.7 Hz, 1H), 1.85 (dd, J = 13.5, 10.0 Hz, 1H), 1.22 (d, J = 6.2 Hz, 3H), 1.19 (dd, J = 6.4, 4.8 Hz, 9H), 1.13 (s, 3H). ^{13}C NMR (126 MHz, 115 °C, DMSO-d_6) δ 154.39, 153.08, 140.33, 127.00, 126.04, 125.87, 106.29, 68.59, 68.36, 64.63, 63.30, 58.45, 56.81, 35.36 (broad), 20.95, 20.93, 20.77, 20.74, 10.83. HRMS (EI) calculated for $C_{21}H_{30}N_2O_6$ (Na^+) 429.2002, found: 429.1999. R_f (petroleum ether / EtOAc 3:1) = 0.25.



dibenzyl-6-methyl-9-phenyl-1,4-dioxa-7,8-diazaspiro[4.5]decane-7,8-dicarboxylate (**21**)

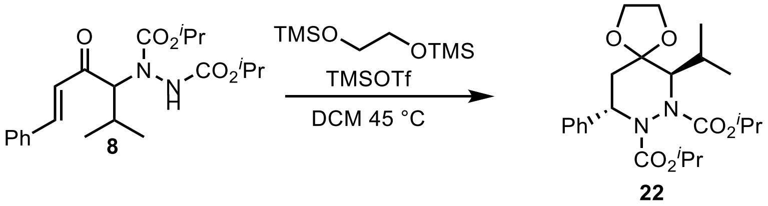


To a sealed pointed microwave vial equipped with a stir bar containing protected hydrazine **6** (53.4 mg, 0.116 mmol) under a nitrogen atmosphere was added toluene (0.60 mL). To this mixture was added 1,2-

bis(trimethylsiloxy)ethane (57 µL, 0.232 mmol) followed by trimethylsilyl trifluoromethanesulfonate (2.1 µL, 0.012 mmol). The sealed vial was placed in a 65 °C oil bath and stirred. After 15 hours of stirring at 65 °C, the reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 3.5:1) to afford 43 mg (74%) of a pale-yellow oil in >20:1 d.r.

IR(C_6D_6) 3020, 2990, 2940, 2850, 1680, 1440, 1390, 1300, 1120, 1070, 1050, 1020, 740, 690 cm^{-1}. ^1H NMR (500 MHz, 110 °C, DMSO-d_6) δ 7.54 – 7.38 (m, 3H), 7.38 – 7.14 (m, 12H), 5.33 – 5.23 (m, 1H), 5.21 – 4.89 (m, 4H), 4.36 – 4.23 (m, 1H), 4.15 – 4.03 (m, 1H), 4.01 – 3.82 (m, 3H), 2.36 (dd, *J* = 13.5, 6.7 Hz, 1H), 1.90 (dd, *J* = 13.5, 10.0 Hz, 1H), 1.15 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, 110 °C, DMSO-d_6) δ 154.70, 153.48, 139.86, 135.51, 135.50, 127.44, 127.41, 127.11, 127.00, 126.98, 126.75, 126.57, 126.15, 125.80, 106.15, 66.59, 66.49, 64.68, 63.35, 59.01, 57.38, 35.39, 10.88. HRMS (EI) calculated for $C_{29}H_{30}N_2O_6$ (Na^+) 525.2001, found: 525.2003. R_f (petroleum ether / EtOAc 3.5:1) = 0.18.

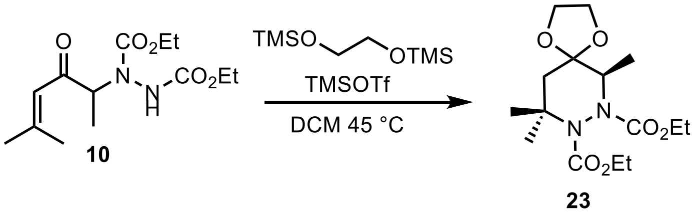
diisopropyl-6-isopropyl-9-phenyl-1,4-dioxa-7,8-diazaspiro[4.5]decane-7,8-dicarboxylate (**22**)



To a sealed pointed microwave vial equipped with a stir bar containing protected hydrazine **8** (23.1 mg, 0.0592 mmol) under a nitrogen atmosphere was added dichloromethane (0.3 mL). To this mixture was added 1,2-bis(trimethylsiloxy)ethane (29 µL, 0.12 mmol) followed by trimethylsilyl trifluoromethanesulfonate (1.1 µL, 0.0059 mmol). The sealed vial was placed in a 45 °C oil bath and stirred. After 16 hours of stirring at 45 °C, the reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 5:1) to afford 23.5 mg (96%) of a white solid in >20:1 d.r.

Melting point: 99-100 °C. IR(C_6D_6) 2940, 2880, 1680, 1440, 1380, 1370, 1300, 1270, 1160, 1130, 1090, 1030, 750 cm^{-1}. ^1H NMR (500 MHz, 115 °C, DMSO-d_6) δ 7.52 – 7.44 (m, 2H), 7.33 – 7.25 (m, 2H), 7.25 – 7.19 (m, 1H), 5.08 (dd, *J* = 11.8, 5.9 Hz, 1H), 4.90 – 4.76 (m, 2H), 4.16 – 4.04 (m, 3H), 3.95 (t, *J* = 6.9 Hz, 2H), 2.31 (dd, *J* = 13.7, 5.8 Hz, 1H), 2.16 – 2.04 (m, 1H), 1.70 (dd, *J* = 13.6, 11.5 Hz, 1H), 1.20 (t, *J* = 5.9 Hz, 6H), 1.15 (s, 3H), 1.10 (d, *J* = 6.3 Hz, 3H), 1.07 (d, *J* = 6.8 Hz, 3H), 0.99 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, 115 °C, DMSO-d_6) δ 154.76, 153.76, 140.13, 126.84, 126.27, 126.03, 107.11, 68.79, 68.43, 67.10, 63.94, 61.89, 57.42, 35.27, 26.53, 20.97, 20.89, 20.66, 20.52, 19.71, 19.30. HRMS (EI) calculated for $C_{23}H_{34}N_2O_6$ (Na^+) 457.2314, found: 457.2301. R_f (petroleum ether / EtOAc 5:1) = 0.25.

diethyl 6,9,9-trimethyl-1,4-dioxa-7,8-diazaspiro[4.5]decane-7,8-dicarboxylate (**23**)

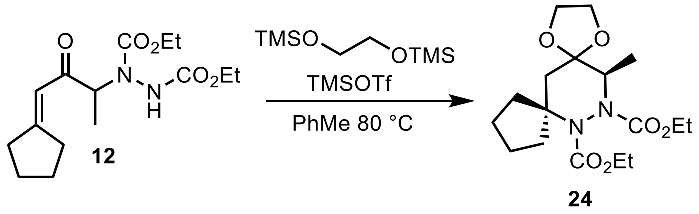


10 → **23**

To a sealed pointed microwave vial equipped with a stir bar containing protected hydrazine **10** (16.5 mg, 0.0576 mmol) under a nitrogen atmosphere was added dichloromethane (0.30 mL). To this mixture was added 1,2-bis(trimethylsiloxy)ethane (28 µL, 0.12 mmol) followed by trimethylsilyl trifluoromethanesulfonate (1 µL, 0.006 mmol). The sealed vial was placed in a 45 °C oil bath and stirred. After 13 hours of stirring at 45 °C, the reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 4:1) to afford 14 mg (74%) of a pale-yellow oil.

IR(neat) 2940, 2900, 1690, 1450, 1430, 1390, 1360, 1310, 1290, 1230, 1200, 1180, 1160, 1100, 1080, 740 cm^{-1}. ^{1}H NMR (500 MHz, 110 °C, DMSO-*d*$_6$) δ 4.29 (s, 1H), 4.17 – 4.08 (m, 2H), 4.08 – 3.99 (m, 1H), 3.96 – 3.87 (m, 4H), 1.89 (d, *J* = 14.0 Hz, 1H), 1.58 (s, 3H), 1.55 (d, *J* = 13.9 Hz, 1H), 1.32 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.0 Hz, 3H), 1.13 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, 110 °C, DMSO-*d*$_6$) δ 153.67, 153.15, 106.45, 63.67, 62.99, 60.66, 59.91, 58.43, 55.10 (broad), 43.39, 27.68, 24.80, 13.46, 13.40, 11.26. HRMS (EI) calculated for $C_{15}H_{26}N_2O_6$ (Na$^+$) 353.1689, found: 353.1695. R$_f$ (petroleum ether / EtOAc 4:1) = 0.19

diethyl (R)-14-methyl-1,4-dioxa-12,13-diazadispiro[4.1.4^7.3^5]tetradecane-12,13-dicarboxylate (**24**)

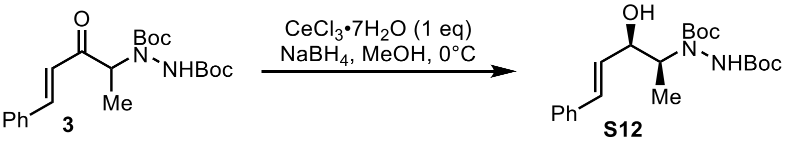


12 → **24**

To a sealed pointed microwave vial equipped with a stir bar containing protected hydrazine **12** (28.3 mg, 0.0906 mmol) under a nitrogen atmosphere was added toluene (0.45 mL). To this mixture was added 1,2-bis(trimethylsiloxy)ethane (44 µL, 0.18 mmol) followed by trimethylsilyl trifluoromethanesulfonate (3.3 µL, 0.018 mmol). The sealed vial was placed in an 80 °C oil bath and stirred. After 14 hours of stirring at 80 °C, the reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 3.5:1) to afford 22 mg (68%) of a pale-yellow oil.

IR(neat) 2940, 1680, 1430, 1400, 1350, 1130, 1190, 1090, 1040 cm^{-1}. ^{1}H NMR (500 MHz, 110 °C, DMSO-*d*$_6$) δ 4.31 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.98 – 3.85 (m, 4H), 2.78 – 2.69 (m, 1H), 2.18 – 2.10 (m, 1H), 2.06 (d, *J* = 13.9 Hz, 1H), 1.89 – 1.80 (m, 1H), 1.75 (q, *J* = 9.0 Hz, 1H), 1.70 – 1.49 (m, 5H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.20 (s, 3H), 1.12 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, 110 °C, DMSO-*d*$_6$) δ 153.50, 153.49, 106.30, 69.50, 63.56, 63.15, 60.58, 60.03, 54.71 (very broad), 36.20, 35.93, 22.62, 22.49, 13.47, 13.34, 11.34. HRMS (EI) calculated for $C_{17}H28N_2O6$ (Na$^+$) 379.1845, found: 379.1847. R$_f$ (petroleum ether / EtOAc 3.5:1) = 0.23.

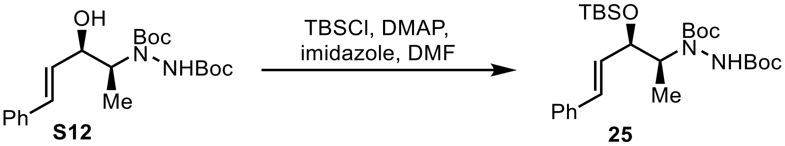
di-tert-butyl (E)-1-(3-hydroxy-5-phenylpent-4-en-2-yl)hydrazine-1,2-dicarboxylate (**S12**)



To a flask containing enone **3** (218 mg, 0.558 mmol), $CeCl_3{\cdot}7H_2O$ (208 mg, 0.558 mmol) and a magnetic stir bar under nitrogen was added MeOH (2.8 mL). The reaction mixture was cooled to 0°C at which point $NaBH_4$ (43.3 mg, 1.12 mmol) was added. The reaction was allowed to stir at 0°C for 10 minutes at which point the raction was diluted with water (10 mL) and 0.5M $NaHSO_4$ (5 mL). The reaction mixture was extracted with Et_2O (2 x 15 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The resulting residue was purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 2:1) to afford 181.6 mg (83%) of a clear oil as an inseparable 5.7:1 mixture of diastereomers.

IR($CHCl_3$) 3330, 2940, 2890, 1690, 1430, 1370, 1350, 1240, 1150, 960, 720 cm^{-1}. ^{1}H NMR (500 MHz, 55°C, Chloroform-*d*) δ 7.38 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.26 – 7.19 (m, 1H), 6.70 (dd, *J* = 15.9, 1.7 Hz, 1H), 6.28 (s, 1H), 6.26 – 6.19 (m, 1H), 4.63 (s, 1H), 4.42 – 4.22 (m, 1H), 1.53 – 1.47 (m, 18H), 1.20 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.09, 137.39, 130.77, 129.34, 128.59, 127.51, 126.61, 82.12, 81.81, 73.81, 58.53, 28.40, 28.40, 28.35, 11.21. HRMS (EI), calculated for $C_{21}H_{32}N_2O_5$ (Na^+) 415.2209, found: 415.2208. R_f (petroleum ether / EtOAc 2:1) = 0.57.

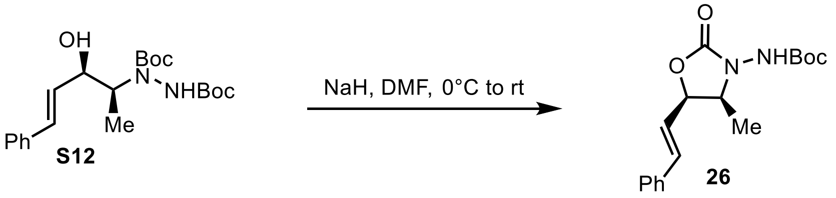
di-tert-butyl (E)-1-(3-((tert-butyldimethylsilyl)oxy)-5-phenylpent-4-en-2-yl)hydrazine-1,2-dicarboxylate (**25**)



To a flask equipped with a stir bar and containing free alcohol **S12** (182 mg, 0.493 mmol) under a nitrogen atmosphere was added DMF (1.0 mL). Imidazole (94 mg, 1.38 mmol), TBSCl (139 mg, 0.920 mmol), and DMAP (56.2 mg, 0.460 mmol) were added and the reaction was allowed to stir at room temperature for 17 hours at which point TLC revealed the reaction to be complete. The reaction mixture was diluted with water (5.0 mL) and washed with diethyl ether (15 mL). The organic layer was separated and washed with water (2 x 5.0 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting residue was purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 10:1) to afford 220 mg (94%) of a clear oil contaminated with Bis[*tert*-butyl(dimethyl)]siloxane.

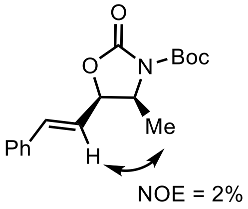
IR($CHCl_3$) 2890, 2820, 1680, 1370, 1350, 1240, 1150, 1050, 820, 770 cm^{-1}. ^{1}H NMR (500 MHz, 55 °C, Chloroform-*d*) δ 7.34 (d, *J* = 7.5 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.21 (td, *J* = 7.2, 1.5 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 15.9, 7.2 Hz, 1H), 5.99 (s, 1H), 4.31 (s, 2H), 1.47 (s, 9H), 1.41 (s, 9H), 1.29 – 1.22 (d, J = 6.1 Hz, 3H), 0.96 – 0.89 (m, 9H), 0.11 – 0.08 (m, 6H). ^{13}C NMR (126 MHz, 55 °C, $CDCl_3$) δ 155.83, 154.95, 137.10, 131.31, 131.25, 128.66, 127.72, 126.65, 81.04, 80.96, 76.31, 58.12 (very broad), 28.39, 28.37, 26.04, 18.23,18.10, -3.84, -4.61. HRMS (EI) calculated for $C_{27}H_{46}N_2O_5Si$ (Na^+) 529.3074, found: 529.3062.. R_f (petroleum ether / EtOAc 10:1) = 0.37.

tert-butyl-4-methyl-2-oxo-5-((E)-styryl)oxazolidin-3-yl)carbamate (**26**)

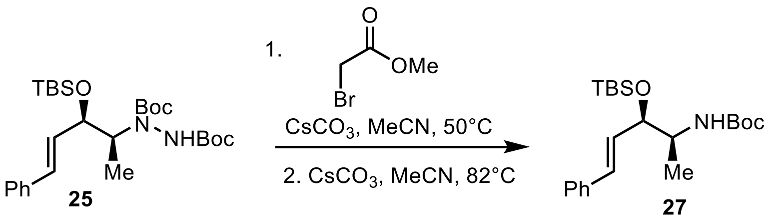


To an oven dried flask containing alcohol **S12** (43.4 mg, 0.111 mmol) under nitrogen was added dimethylformamide (0.55 mL). The reaction mixture was cooled to 0 °C and NaH (60% suspension in mineral oil, 6.7 mg, 0.17 mmol) was added. The reaction was allowed to warm to room temperature over one hour. Incomplete reaction was observed via TLC analysis. The reaction mixture was once again cooled to 0 °C and additional NaH (60% suspension in mineral oil, 6.0 mg, 0.15 mmol) was added. The reaction mixture was warmed up to room temperature over 30 minutes at which point complete conversion was observed. At this point the reaction was diluted with saturated aqueous ammonium chloride (5 mL) and extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated via rotary evaporation. The crude mixture was purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 2:1) to afford 26.9 mg (76%) of a clear oil as a 5.2:1 mixture of diastereomers.

IR($CHCl_3$) 3250, 2940, 2890, 1760, 1700, 1480, 1430, 1370, 1350, 1230, 1140, 1100, 1030, 1010, 950 cm^{-1}. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 2H), 7.36 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 6.72 (d, J = 15.7 Hz, 1H), 6.61 (s, 1H), 6.20 (dd, J = 15.9, 8.0 Hz, 1H), 5.17 (t, J = 8.1 Hz, 1H), 4.26 (s, 1H), 1.50 (s, 9H), 1.20 (d, J = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.91, 154.57, 135.77, 135.54, 128.83, 128.73, 126.95, 121.51, 82.49, 78.37, 56.17, 28.26, 13.56. HRMS (EI) calculated for $C_{17}H_{22}N_2O_4$ (Na^+) 341.1477, found: 341.1479. R_f (petroleum ether / EtOAc 2:1) = 0.26.



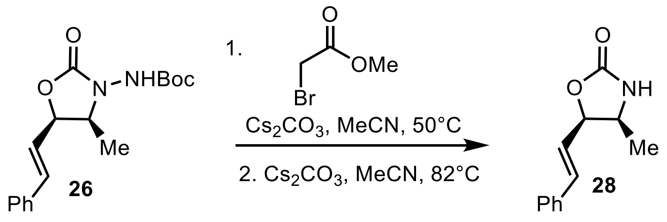
tert-butyl (E)-(3-((tert-butyldimethylsilyl)oxy)-5-phenylpent-4-en-2-yl)carbamate (**27**)



To a microwave vial equipped with a stir bar and containing hydrazine **25** (24.6 mg, 0.0485 mmol) under a nitrogen atmosphere was added MeCN (0.3 mL). Methyl bromoacetate (12 μL, 0.12 mmol) was added followed by $CsCO_3$ (47.4 mg, 0.146 mmol). The vial was sealed and placed in a 50 °C oil bath and stirred for 12.5 hrs until NMR analysis revealed no starting material. The reaction mixture was diluted with an aqueous solution of saturated ammonium chloride (5 mL) and washed with DCM (3 x 5 mL). The combined organic layers were combined, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The material was purified via flash chromatography (SiO_2; petroleum ether / EtOAc 12:1). The purified material was not characterized due to the larger number of rotomers present. The isolated material was dissolved in MeCN (0.4 mL) under nitrogen in a microwave vial. $CsCO_3$ was added (47.4 mg, 0.146 mol) and the vial was sealed. The reaction mixture was stirred at 85 °C for 60 hrs at which point the reaction mixture was diluted with an aqueous solution of saturated ammonium chloride (5 mL) and washed with DCM (3 x 5 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The resulting residue was purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 12:1) to afford 146.0mg (84% over two steps) of a clear oil.

IR($CHCl_3$) 3440, 2940, 2920, 2840, 1710, 1490, 1350, 1250, 1170, 1050, 830, 770 cm^{-1}. ^1H NMR (500 MHz, 55 °C, Chloroform-*d*) δ 7.37 – 7.33 (m, 2H), 7.31 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.25 – 7.20 (m, 1H), 6.59 (dd, *J* = 16.0, 1.2 Hz, 1H), 6.13 (dd, *J* = 16.0, 6.2 Hz, 1H), 4.55 (s, 1H), 4.43 (ddd, *J* = 6.2, 3.6, 1.4 Hz, 1H), 3.74 (s, 1H), 1.45 (s, 9H), 1.12 (d, *J* = 6.8 Hz, 3H), 0.96 (m, 9H), 0.11 (s, 3H), 0.07 (s, 3H). ^{13}C NMR (126 MHz, 55 °C, $CDCl_3$) δ 155.45, 137.27, 131.20, 130.43, 128.74, 127.71, 126.66, 75.91, 51.82, 28.68, 26.13, 18.46, 14.65, -4.07, -4.69. HRMS (EI) calculated for $C_{22}H_{37}NO_3Si$ (Na^+) 414.2440, found: 414.2444. R_f (petroleum ether / EtOAc 12:1) = 0.35.

4-methyl-5-((E)-styryl)oxazolidin-2-one (**28**)

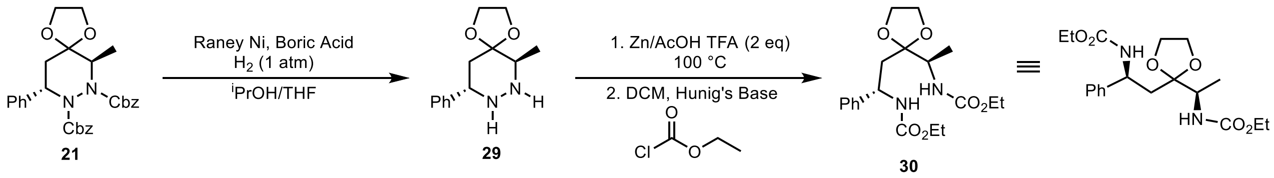


Oxazolidinone **26** (26.9 mg, 0.0838 mmol) was dissolved in MeCN (0.42 mL) in a microwave vial equipped with a magnetic stir bar under a nitrogen atmosphere. Methyl bromoacetate (19.8 μL, 0.209 mmol) was added followed by cesium carbonate (82 mg, 0.251 mmol). The microwave vial was sealed and stirred in a 50 °C oil bath for 16 hours. At this point, the reaction mixture was diluted with 5 mL of saturated aqueous ammonium chloride and extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated by rotary evaporation. The crude mixture was purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 3:1) to afford a mixture of products of products that have at least three distinct R_f values on a silica TLC plate using a petroleum ether / ethyl acetate 2:1 eluent. This complicated mixture of products was used immediately in the next step without further characterization.

The mixture of alkylated oxazolidinone products was dissolved in MeCN (0.42 mL) in a microwave vial equipped with a magnetic stir bar under a nitrogen atmosphere. Cesium carbonate (82 mg, 0.25 mmol) was added and the microwave vial was sealed and stirred in an 80 °C oil bath for 66 hours. At this point, the reaction mixture was diluted with 5 mL of saturated aqueous ammonium chloride and extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated by rotary evaporation. The crude mixture was purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 1:1.5) to afford 10.7 mg (63% over two steps) of a clear oil in a 5.2:1 mixture of diastereomers. Additional careful chromatography allowed for isolation of the major diastereomer for characterization purposes.

IR($CHCl_3$) 3230, 2940, 2880, 1730, 1630, 1470, 1430, 1360, 1210, 1090, 960, 740, 680, 660 cm^{-1}. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.49 – 7.39 (m, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.27 (m, 1H), 6.75 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.9, 7.6 Hz, 1H), 5.66 (s, 1H), 5.23 (td, *J* = 7.7, 1.1 Hz, 1H), 4.15 – 4.01 (m, 1H), 1.21 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.17, 135.70, 135.24, 128.87, 128.68, 126.93, 121.71, 80.80, 52.03, 17.29. Characterization data matched that reported in the literature.[1] R_f (petroleum ether / EtOAc 1:1.5) = 0.24.

ethyl (2-(2-(1-((ethoxycarbonyl)amino)ethyl)-1,3-dioxolan-2-yl)-1-phenylethyl)carbamate (**30**)



Protected hydrazine **21** (33.1 mg, 0.0659 mmol) was dissolved in THF (0.21 mL) and isopropanol (0.43 mL) in a microwave vial equipped with a stir bar under nitrogen. Boric acid (20.4 mg, 0.329 mmol) was added followed by a large spatula tip of Raney-nickel. The reaction mixture was sparged for 10 minutes with a hydrogen balloon and then allowed to stir overnight at room temperature under a 1 atm hydrogen atmosphere. Once complete, the reaction mixture was filtered with methanol though a plug of mixed celite and freshly ground potassium carbonate. The filtrate was concentrated under reduced pressure using a rotary evaporator and characterized as a white solid (m.p 92-94) without further purification (16.4 mg, 91%).

IR($CDCl_3$) 3310, 2950, 2920, 2880, 1590, 1450, 1430, 1370, 1320, 1300, 1180, 1150, 1100, 1070, 1030, 1010, 950, 930, 760, 700 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.31 (m, 4H), 7.30 – 7.27 (m, 1H), 4.11 – 3.89 (m, 6H), 3.10 (q, *J* = 6.6 Hz, 1H), 2.02 (dd, *J* = 12.8, 2.8 Hz, 1H), 1.91 – 1.83 (m, 1H), 1.02 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.10, 128.71, 127.88, 127.15, 106.88, 65.64, 65.41, 62.99, 59.27, 42.82, 11.71. HRMS (EI) calculated for $C_{13}H_{18}N_2O_2$ (H^+) 235.1441, found: 235.1442.

The above residue was transferred into a microwave vial equipped with a stir bar under nitrogen and dissolved in acetic acid (1 mL) and trifluoroacetic acid (0.15 mL). Freshly activated zinc powder (260 mg, 3.95 mmol) was added and the microwave vial was sealed and stirred in a 90 °C oil bath for 18 hours. At this point, the reaction mixture was filtered with methanol through a cotton plug and concentrated under reduced pressure using a rotary evaporator. The crude residue was utilized directly in the next step without further purification. (To activate the zinc, 1 gram of zinc dust was added to 3 mL of diethyl ether. Trimethylsilyl chloride (0.5 mL) was added and the mixture was sonicated for 2 minutes. The solvent was removed via trituration and the zinc residue was washed with diethyl ether (2 x 2 mL) and then placed under high vacuum to remove any residual solvents.)

The above crude residue was transferred into a round-bottom flask equipped with a magnetic stir bar and placed under an atmosphere of nitrogen. Dichloromethane (0.6 mL) was added followed by Hünig's base (N,N-Diisopropylethylamine, 80 μL, 0.198 mmol) and then ethyl chloroformate (19 μL, 0.198 mmol). The reaction mixture was stirred at room temperature for 15 hours at which point the reaction mixture was loaded directly onto a silica column and purified via flash chromatography (SiO_2; Petroleum ether / EtOAc 1.2:1) to afford 12.5 mg (50% over three steps) of a clear colorless oil.

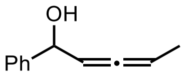
IR($CDCl_3$) 3290, 2940, 2860, 1670, 1520, 1430, 1410, 1360, 1300, 1230, 1160, 1050, 940, 770 cm^{-1}. ^{1}H NMR (500 MHz, 115 °C, DMSO-d_6) δ 7.40 – 7.22 (m, 4H), 7.22 – 7.13 (m, 1H), 6.61 (s, 1H), 5.95 (d, *J* = 8.9 Hz, 1H), 4.80 (td, *J* = 8.4, 3.8 Hz, 1H), 4.09 – 3.95 (m, 5H), 3.94 – 3.80 (m, 4H), 1.19 (t, *J* = 7.4 Hz, 3H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.08 (d, *J* = 7.0 Hz, 3H). 13C NMR (126 MHz, 115 °C, DMSO-d_6) δ

155.09, 154.70, 144.22, 127.15, 125.52, 125.49, 110.15, 64.39, 64.36, 58.90, 58.77, 50.69, 50.18, 39.23, 14.72, 13.66. HRMS (EI) calculated for $C_{19}H_{28}N_2O_6$ (Na^+) 403.1840, found: 403.1834.

Allenols

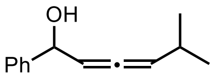
All of the allenic alcohols were prepared according to the general procedure of Tamaru from commercially available propargyl alcohols and are used as a mixture of diastereomers (when diastereomers are possible) in an approximate 1:1 ratio.[2] In this procedure, it is important to utilize fresh lithium aluminum hydride to ensure consistently high yields

1-phenylpenta-2,3-dien-1-ol (**S1**)



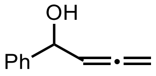
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.47 – 7.27 (m, 5H), 5.47 – 5.29 (m, 2H), 5.24 (dt, *J* = 5.3, 3.0 Hz, 1H), 2.16 (d, *J* = 3.6 Hz, 1H), 1.72 (ddd, *J* = 8.1, 6.8, 3.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.10, 203.00, 143.22, 143.17, 128.58, 128.57, 127.82, 127.79, 126.24, 126.20, 95.64, 89.91, 89.80, 72.35, 72.26, 14.53, 14.40. Spectroscopic data matched that reported in the literature.[3]

5-methyl-1-phenylhexa-2,3-dien-1-ol (**S2**)



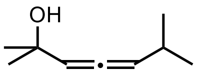
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 5.48 (dtd, *J* = 8.1, 6.1, 3.0 Hz, 1H), 5.40 (qd, *J* = 6.1, 2.4 Hz, 1H), 5.23 (dddd, *J* = 7.9, 5.9, 4.0, 2.5 Hz, 1H), 2.34 (dqdd, *J* = 13.6, 6.8, 5.8, 3.0 Hz, 1H), 2.14 (dd, *J* = 4.2, 1.4 Hz, 1H), 1.01 (ddd, *J* = 10.5, 6.8, 1.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.01, 200.60, 143.35, 143.20, 128.55, 128.54, 127.80, 127.73, 126.35, 126.18, 103.05, 102.49, 97.66, 97.51, 72.63, 72.22, 28.14, 28.10, 22.60, 22.58, 22.52, 22.51. IR($CDCl_3$) 3300, 2920, 1930, 1430, 1020, 860, 730, 690 cm^{-1}. Spectroscopic data matched that reported in the literature.[4]

1-phenylbuta-2,3-dien-1-ol (**S3**)



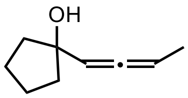
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.27 (m, 5H), 5.46 (q, *J* = 6.5 Hz, 1H), 5.29 (ddt, *J* = 6.5, 4.3, 2.4 Hz, 1H), 4.94 (dh, *J* = 6.5, 2.3 Hz, 2H), 2.20 – 2.00 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.16, 142.90, 128.61, 127.93, 126.19, 95.28, 78.36, 72.06. Spectroscopic data matched that reported in the literature.[5]

2,6-dimethylhepta-3,4-dien-2-ol (**S4**)



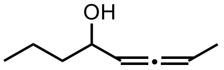
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.48 – 5.22 (m, 2H), 2.39 – 2.26 (m, 1H), 1.63 (d, *J* = 0.9 Hz, 1H), 1.34 (s, 6H), 1.02 (dd, *J* = 6.8, 1.8 Hz, 6H). ^{13}C NMR (101 MHz, $cdcl_3$) δ 199.02, 102.68, 102.63, 69.74, 30.25, 30.16, 28.14, 22.68, 22.57. Spectroscopic data matched that reported in the literature.[4]

1-(buta-1,2-dien-1-yl)cyclopentan-1-ol (**S5**)



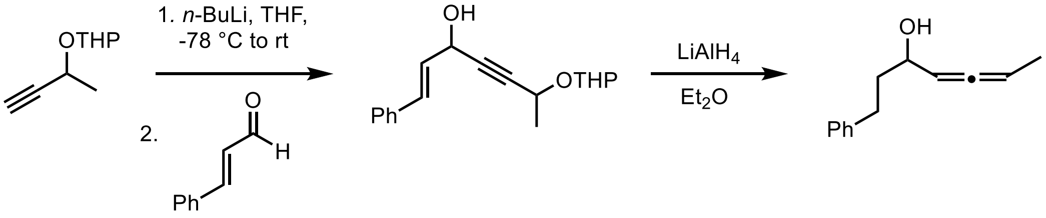
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.25 (dq, *J* = 6.5, 3.2 Hz, 1H), 5.22 – 5.11 (m, 1H), 2.19 (dt, *J* = 6.2, 2.2 Hz, 1H), 1.83 – 1.70 (m, 2H), 1.68 – 1.63 (m, 4H), 1.63 – 1.59 (m, 3H), 1.58 – 1.44 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.54, 98.77, 89.00, 80.01, 40.24, 40.15, 23.57, 23.54, 14.40. Spectroscopic data matched that reported in the literature.[6]

octa-5,6-dien-4-ol (**S6**)



^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.32 – 5.21 (m, 1H), 5.21 – 5.11 (m, 1H), 4.22 – 4.04 (m, 1H), 1.69 (app dt, *J* = 6.9, 3.1 Hz, 3H), 1.60 (s, 1H), 1.59 – 1.48 (m, 2H), 1.48 – 1.31 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.11, 203.02, 95.29, 95.22, 88.86, 88.66, 70.03, 69.75, 39.74, 39.69, 18.76, 18.74, 14.54, 14.53, 14.11, 14.07. Spectroscopic data matched that reported in the literature.[6]

1-phenylhepta-4,5-dien-3-ol (**S7**)

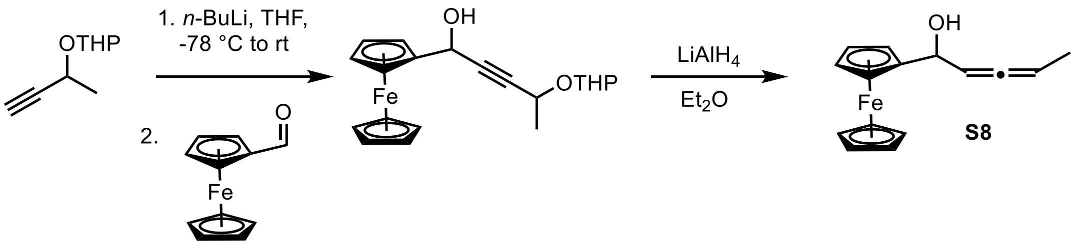


In a flame-dried round bottom flask equipped with a magnetic stir bar under nitrogen, the THP protected propargyl alcohol (1.54 g, 10.0 mmol) was dissolved in THF (10 mL) and cooled to -78 °C. BuLi (2.35 M in hexanes, 4.67 mL, 11.0 mmol) was added dropwise and the reaction mixture was allowed to stir for thirty minutes at -78 °C. Cinnamaldehyde (1.45 g, 11.5 mmol) was added neat and the reaction was allowed to warm slowly to rt overnight. At this point, the reaction mixture was diluted with 10 mL of an aqeous solution of saturated NH_4Cl and extracted with Et_2O (15 mL x 3). The combined organic layers were washed with brine (10 mL), dried with magnesium sulfate, filtered and concentrated using the rotary evaporator. The resulting residue was purified via flash chromatography (SiO_2; Petroleum ether / Et_2O 4:3) and carried directly into the next step.

The above purified residue was dissolved in dry Et_2O (10 mL) and added dropwise to a flame-dried round bottom flask equipped with a reflux condenser and a magnetic stir bar containing a solution of lithium aluminum hydride in Et_2O (1.0 M, 9.9 mL, 9.9 mmol) at 0 °C under an atmosphere of nitrogen. After stirring for 4 hours at reflux, excess hydride was quenched through the sequential addition of 0.4 mL water, 0.8 mL 1 M aqueous NaOH, and 0.8 mL water. After stirring for 15 minutes, magnesium sulfate was added and stirred for an additional 15 minutes at which point the aluminum salts and magnesium sulfate were filtered off. The resulting solution was concentrated using the rotary evaporator and the resulting residue was purified via flash chromatography (SiO_2; Petroleum ether / Et_2O 3:1) to afford 1.07 g of the desired product contaminated with 10 % of the styrenyl product. This mixture was re-subjected to the above reaction conditions and purification to yield 548 mg (29% over two steps) of a clear oil as a mixture of diastereomers.

IR($CDCl_3$) 3330, 2920, 2850, 1600, 1500, 1450, 1030, 870, 750, 700 cm^{-1}. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.24 – 7.16 (m, 3H), 5.38 – 5.26 (m, 1H), 5.23 (dtq, *J* = 7.9, 6.3, 3.2 Hz, 1H), 4.23 – 4.08 (m, 1H), 2.84 – 2.65 (m, 2H), 1.93 – 1.82 (m, 2H), 1.74 – 1.69 (m, 3H), 1.66 (two s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.19, 203.14, 142.09, 142.07, 128.62, 128.62, 128.51, 128.51, 125.96, 125.95, 95.13, 95.12, 89.30, 89.16, 69.41, 69.22, 39.22, 39.19, 31.87, 31.87, 14.58, 14.57. HRMS (EI)c alculated for $C_{15}H_{16}FeO$ (Na^+) 211.1099, found: 211.1094. R_f (petroleum ether / Et_2O 3:1) = 0.30.

1- ferrocenylpenta-2,3-dien-1-ol (**S8**)

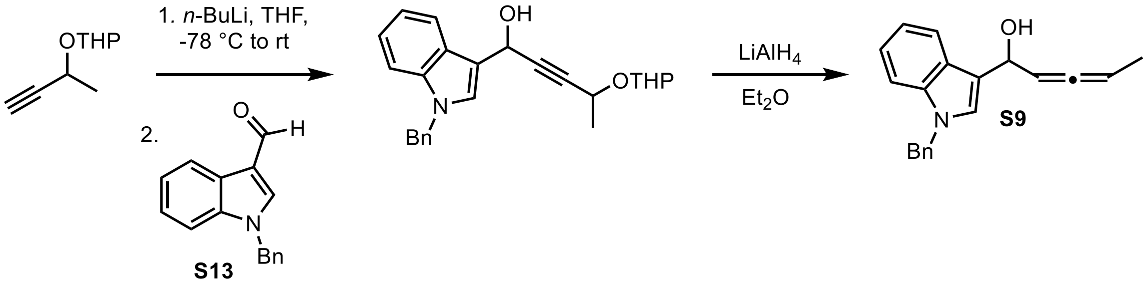


In a flame-dried round bottom flask equipped with a magnetic stir bar under nitrogen, the tetrahydropyran (THP) protected propargyl alcohol (763 mg, 4.96 mmol) was dissolved in THF (5 mL) and cooled to -78 °C. BuLi (2.35 M in hexanes, 2.32 mL, 5.45 mmol) was added dropwise and the reaction mixture was allowed to stir for thirty minutes at -78 °C. A solution of ferrocenecarboxaldehyde (1.22 g, 5.70 mmol) in THF (1 mL) was added and the reaction was allowed to warm slowly to rt overnight. At this point, the reaction mixture was diluted with 5 mL of an aqeous solution of saturated NH_4Cl and extracted with Et_2O (8 mL x 3). The combined organic layers were washed with brine (10 mL), dried with magnesium sulfate, filtered and concentrated using the rotary evaporator. The resulting residue was purified via flash chromatography (SiO_2; Petroleum ether / Et_2O 4:3) and carried directly into the next step.

The above purified residue was dissolved in dry Et_2O (5 mL) and added dropwise to a flame-dried round bottom flask equipped with a magnetic stir bar containing a solution of lithium aluminum hydride in Et_2O (1.0 M, 5.46 mL, 5.46 mmol) at 0 °C under an atmosphere of nitrogen. After stirring for 4 hours at room temperature, excess hydride was quenched through the sequential addition of 0.2 mL water, 0.4 mL 1 M aqueous NaOH, and 0.4 mL water. After stirring for 15 minutes, magnesium sulfate was added and stirred for an additional 15 minutes at which point the aluminum salts and magnesium sulfate were filtered off. The resulting solution was concentrated using the rotary evaporator and the resulting residue was purified via flash chromatography (SiO_2; Petroleum ether / Et_2O 3:1) to afford 637 mg (48 % over two steps) of a thick yellow oil that decomposes slowly on silica as a mixture of diastereomers.

IR($CDCl_3$) 3370, 3050, 2880, 2810, 1390, 1090, 1030, 1010, 990, 860, 810 cm^{-1}. ^1H NMR (400 MHz, Chloroform-*d*) δ 5.49 – 5.38 (m, 1H), 5.36 – 5.26 (m, 1H), 4.97 – 4.84 (m, 1H), 4.27 – 4.11 (m, 9H), 2.05 (s, 1H), 1.84 – 1.67 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.67, 203.58, 94.50, 94.43, 92.36, 92.27, 88.98, 88.84, 68.59, 68.57, 68.49, 68.35, 68.32, 68.30, 68.28, 67.17, 67.15, 66.52, 66.50, 14.54, 14.51. HRMS (EI)c alculated for $C_{15}H_{16}FeO$ (Na^+) 291.0448, found: 291.0443. R_f (petroleum ether / Et_2O 3:1) = 0.29.

1-(1-benzyl-1H-indol-3-yl)penta-2,3-dien-1-ol (**S9**)

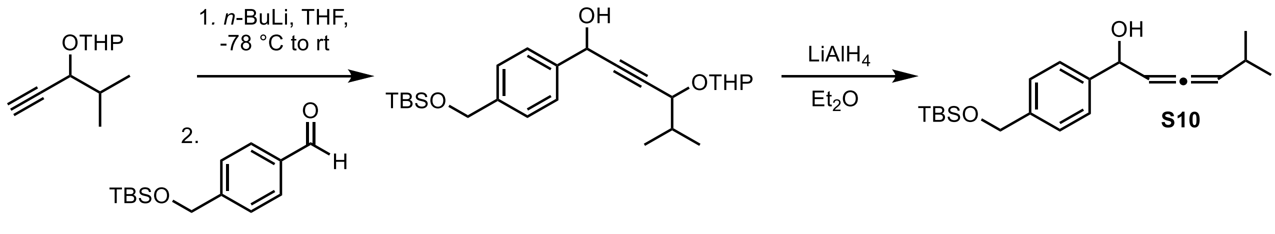


In a flame-dried round bottom flask equipped with a magnetic stir bar under nitrogen, the THP protected propargyl alcohol (1.32 g, 8.70 mmol) was dissolved in THF (10 mL) and cooled to -78 °C. BuLi (2.50 M in hexanes, 3.65 mL, 9.14 mmol) was added dropwise and the reaction mixture was allowed to stir for thirty minutes at -78 °C. A solution of indole **S13** (1.45 g, 11.5 mmol) in THF (10 mL) was added and the reaction was allowed to warm slowly to rt overnight. At this point, the reaction mixture was diluted with 10 mL of an aqeous solution of saturated NH_4Cl and extracted with Et_2O (15 mL x 3). The combined organic layers were washed with brine (15 mL), dried with magnesium sulfate, filtered and concentrated using the rotary evaporator. The resulting residue was purified via flash chromatography (SiO_2; Petroleum ether / Et_2O 2:1) and carried directly into the next step.

The above purified residue was dissolved in dry Et_2O (10 mL) and added dropwise to a flame-dried round bottom flask equipped with a reflux condenser and a magnetic stir bar containing a solution of lithium aluminum hydride in Et_2O (1.0 M, 8.9 mL, 8.9 mmol) at 0 °C under an atmosphere of nitrogen. After stirring for 4 hours at reflux, excess hydride was quenched through the sequential addition of 0.35 mL water, 0.70 mL 1 M aqueous NaOH, and 0.70 mL water. After stirring for 15 minutes, magnesium sulfate was added and stirred for an additional 15 minutes at which point the aluminum salts and magnesium sulfate were filtered off. The resulting solution was concentrated using the rotary evaporator and the resulting residue was purified twice via flash chromatography (SiO_2; Petroleum ether / Et_2O 2:1) to afford 160 mg (6% over two steps) of a brown oil that decomposes on silica and could only be isolated in approximately 80% purity as a mixture of diastereomers.

IR($CDCl_3$) 3370, 3010, 2990, 2810, 1450, 1430, 1370, 1340, 1320, 1150, 1010, 730, 690 cm^{-1}. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.79 (t, *J* = 8.5 Hz, 1H), 7.36 – 7.24 (m, 4H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.18 – 7.10 (m, 3H), 5.61 – 5.46 (m, 2H), 5.42 – 5.31 (m, 1H), 5.29 (s, 2H), 2.12 (2 s, 1H), 1.74 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.36, 203.30, 137.41, 137.40, 137.18, 137.15, 128.88, 127.78, 127.00, 126.52, 125.89, 125.85, 122.24, 122.23, 120.12, 120.02, 119.65, 119.65, 117.88, 117.83, 110.00, 95.07, 89.47, 89.42, 66.63, 50.18, 14.55. HRMS (EI) calculated for $C_{20}H_{19}NO$ (Na^+) 312.1362, found: 312.1368. R_f (petroleum ether / Et_2O 2:1) = 0.21.

<u>1-(4-(((tert-butyldimethylsilyl)oxy)methyl)phenyl)penta-2,3-dien-1-ol</u> (**S10**)



In a flame-dried round bottom flask equipped with a magnetic stir bar under nitrogen, the THP protected propargyl alcohol (1.1 g, 6.0 mmol) was dissolved in THF (10 mL) and cooled to -78 °C. BuLi (2.50 M in hexanes, 2.4 mL, 6.0 mmol) was added dropwise and the reaction mixture was allowed to stir for thirty minutes at -78 °C. A solution of the aldehyde (1.5 g, 6.0 mmol) in THF (10 mL) was added and the reaction was allowed to warm slowly to rt overnight. At this point, the reaction mixture was diluted with 10 mL of an aqeous solution of saturated NH_4Cl and extracted with Et_2O (15 mL x 3). The combined organic layers were washed with brine (15 mL), dried with magnesium sulfate, filtered and concentrated using the rotary evaporator. The resulting residue was purified via flash chromatography (SiO_2; Petroleum ether / Et_2O 2:1) and carried directly into the next step.

The above purified residue was dissolved in dry Et_2O (10 mL) and added dropwise to a flame-dried round bottom flask equipped with a reflux condenser and a magnetic stir bar containing a solution of lithium aluminum hydride in Et_2O (1.0 M, 3.8 mL, 3.8 mmol) under an atmosphere of nitrogen. After stirring for 1 hour at room temperature and 40 minutes at reflux, excess hydride was quenched through the sequential addition of 0.20 mL water, 0.40 mL 1 M aqueous NaOH, and 0.40 mL water. After stirring for 15 minutes, magnesium sulfate was added and stirred for an additional 15 minutes at which point the aluminum salts and magnesium sulfate were filtered off. The resulting solution was concentrated using the rotary evaporator and the resulting residue was purified twice via flash chromatography (SiO_2; Petroleum ether / Et_2O 4:1) to afford 899 mg (45% over two steps) of a clear oil as a mixture of diastereomers.

IR($CDCl_3$) 3370, 2920, 2890, 2850, 2820, 1440, 1400, 1360, 1240, 1200, 1080, 1000, 830, 770, 660 cm^{-1}. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.29 (m, 2H), 5.51 – 5.43 (m, 1H), 5.43 – 5.35 (m, 1H), 5.27 – 5.17 (m, 1H), 4.74 (s, 2H), 2.41 – 2.25 (m, 1H), 2.09 (s, 1H), 1.07 – 0.97 (m, 6H), 0.94 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.93, 200.45, 141.98, 141.84, 141.07, 141.00, 126.26, 126.26, 126.10, 103.07, 102.48, 97.70, 97.52, 72.50, 72.05, 64.90, 28.14, 28.11, 26.10, 22.61, 22.58, 22.56, 22.53, 18.58, -5.09. HRMS (EI) Sample did not ionize. HRMS of the free alcohol obtained, *vide infra*. R_f (petroleum ether / Et_2O 2:1) = 0.46.

1-(4-(hydroxymethyl)phenyl)-5-methylhexa-2,3-dien-1-ol (**S11**)

TBS- protected alcohol **S10** (434 mg, 1.35 mmol) was dissolved in THF (5 mL) in a round bottom flask equipped with a stir bar. TBAF in wet THF (1.0 M, 1.49 mL, 1.49 mmol) was added dropwise and the reaction was allowed to stir at room temperature for 2 h. At this point, the reaction mixture was diluted with with 10 mL of an aqeous solution of saturated sodium bicarbonate and extracted with ethyl acetate (20 mL x 3). The combined organic layers were dried with magnesium sulfate, filtered and concentrated using the rotary evaporator. The resulting residue was purified via flash chromatography (SiO_2; Petroleum ether / Et_2O 2:1) to yield 287 mg (quantitative) of the desired diol as a white solid (m.p. 34-36 °C).

IR($CDCl_3$) 3310, 2920, 2880, 2830, 2810, 1450, 1020 cm^{-1}. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 5.52 – 5.43 (m, 1H), 5.43 – 5.36 (m, 1H), 5.28 – 5.19 (m, 1H), 4.68 (s, 2H), 2.41 – 2.28 (m, 1H), 2.17 (s, 1H), 1.71 (s, 1H), 1.06 – 0.94 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.95, 200.47, 142.82, 142.69, 140.41, 140.35, 127.23, 126.57, 126.42, 103.17, 102.57, 97.62, 97.43, 72.42, 71.95, 65.27, 28.12, 28.09, 22.59, 22.57, 22.53, 22.52. HRMS (EI) calculated for $C_{14}H_{18}O_2$ (Na^+) 241.1205, found: 241.1202. R_f (petroleum ether / Et_2O 2:1) = 0.21.

Tris(tri (*p*-chloro phenyl) silyl)vanadate

This catalyst was prepared according to the procedure of Pauling.[7] Pale yellow solid m.p. 182-183 (Litt 181°C). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 6H), 7.25 – 7.21 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.67, 136.43, 131.29, 128.70.

III. References

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[2] Kimura, M.; Tanaka, S.; Tamaru, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1689-1705.

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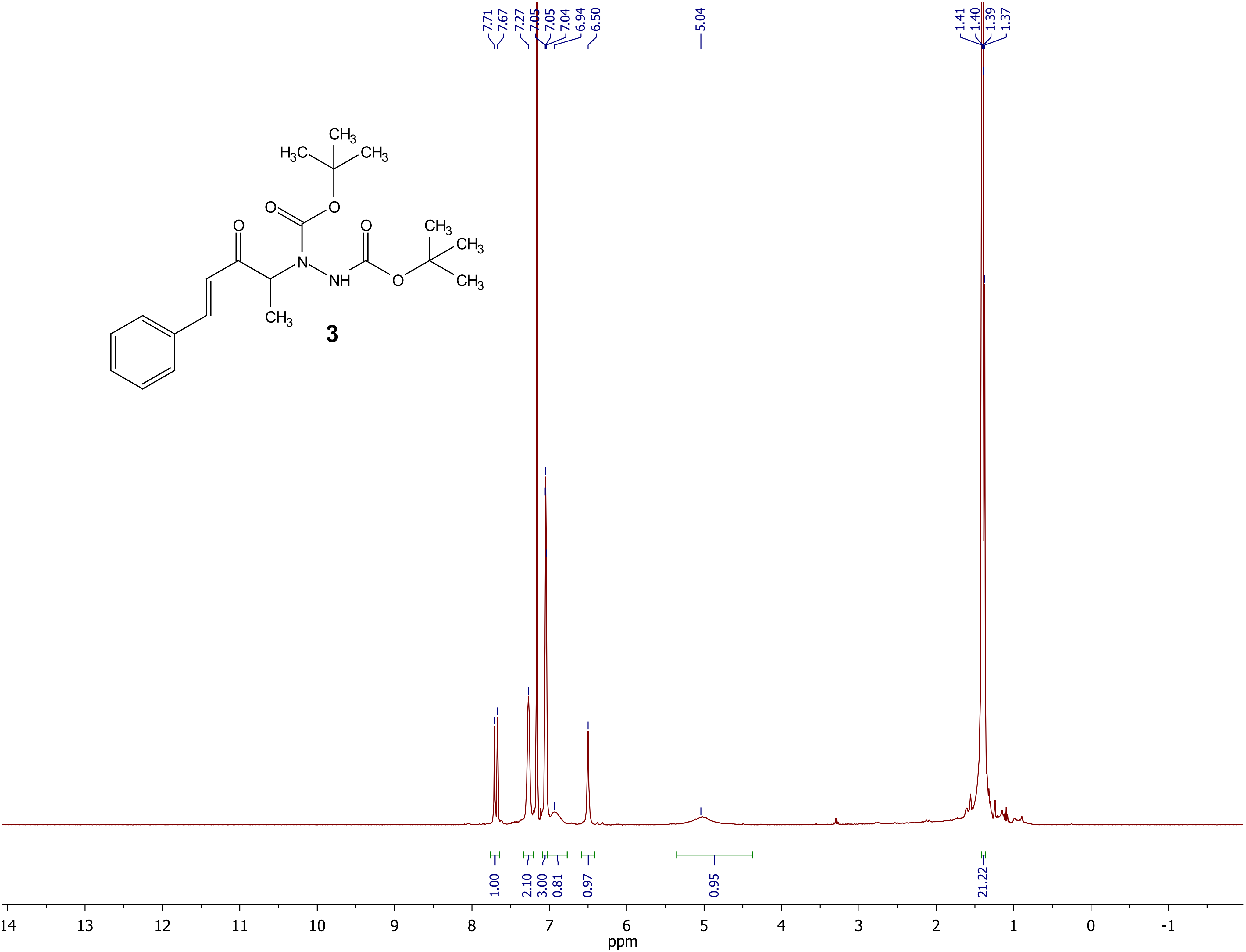
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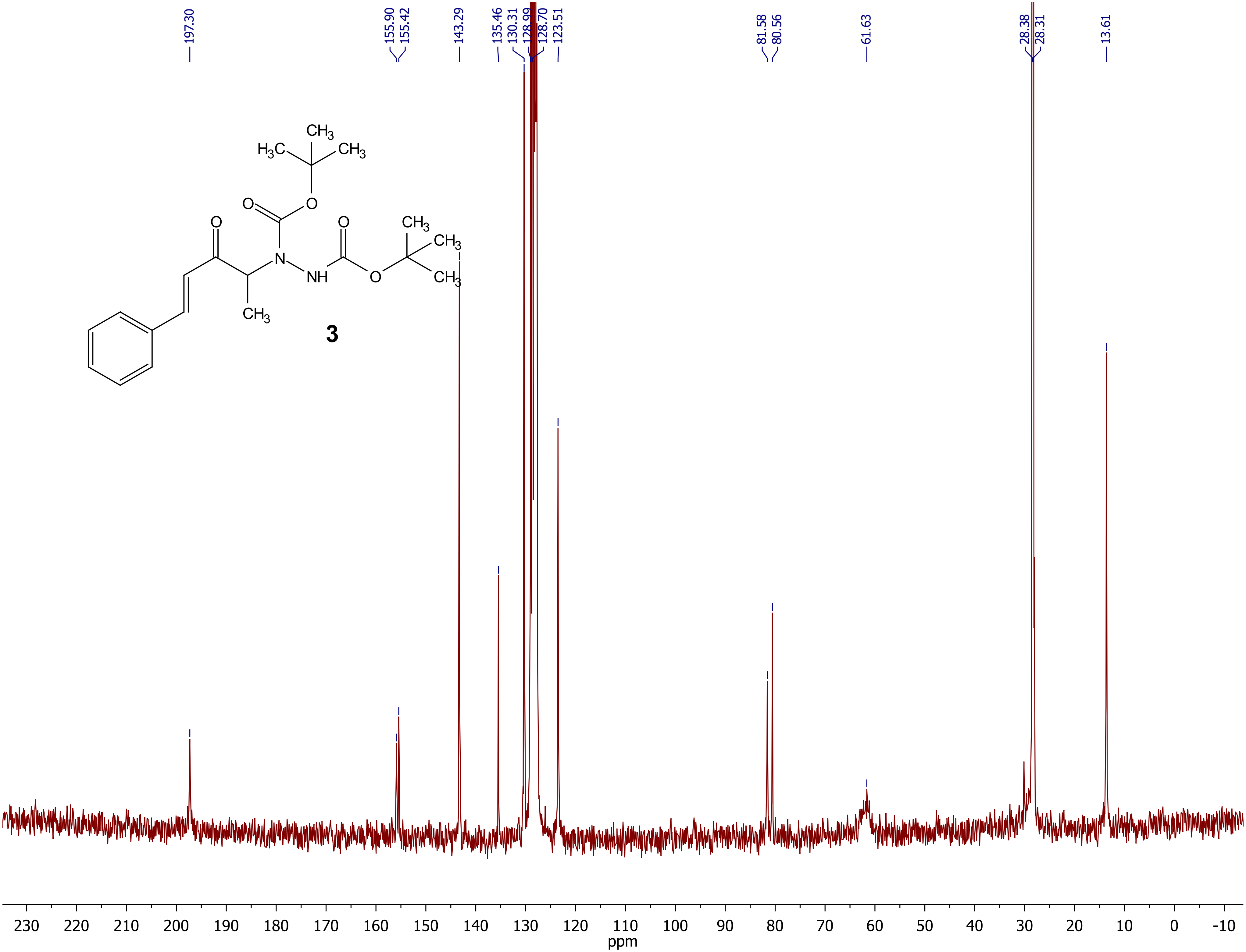
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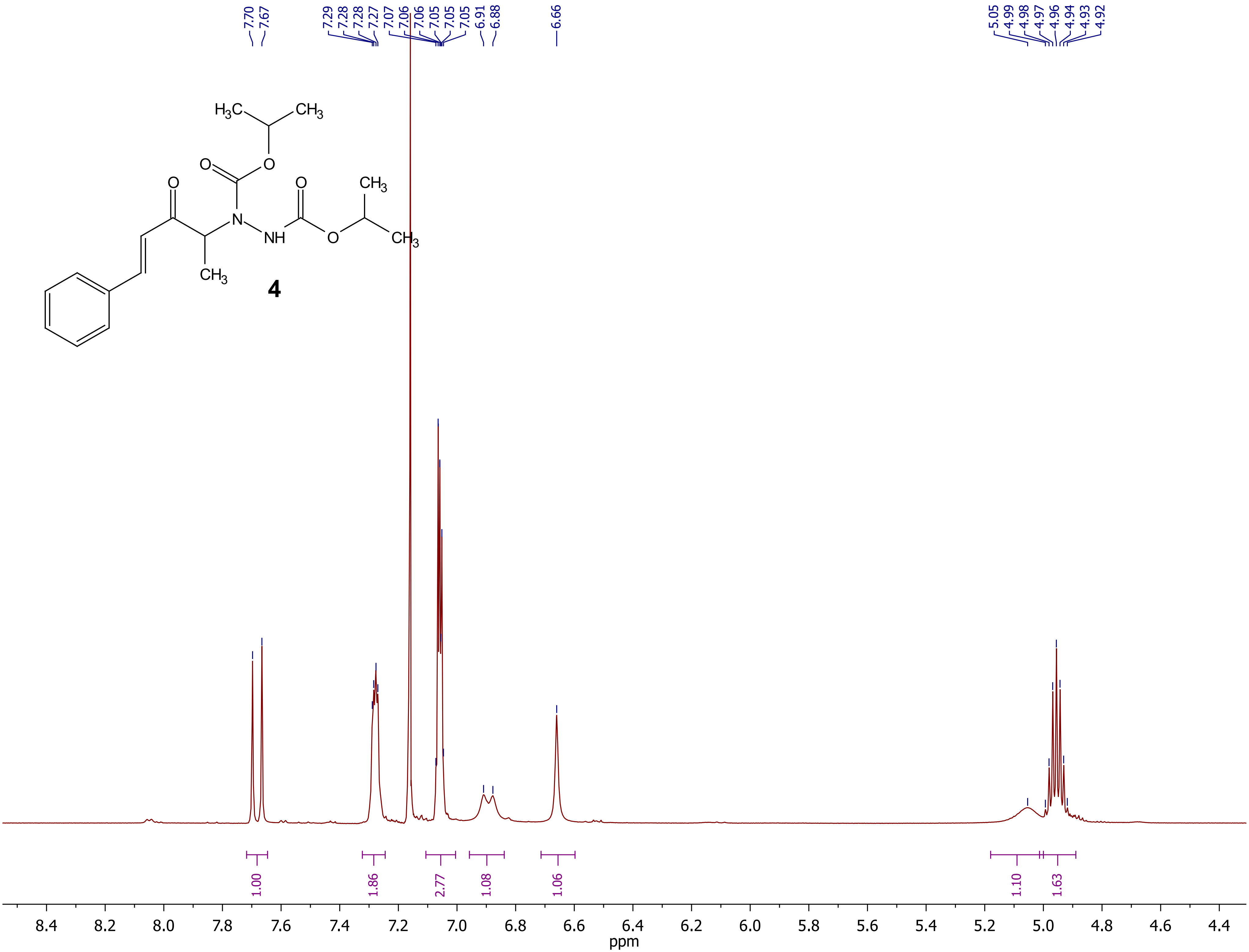
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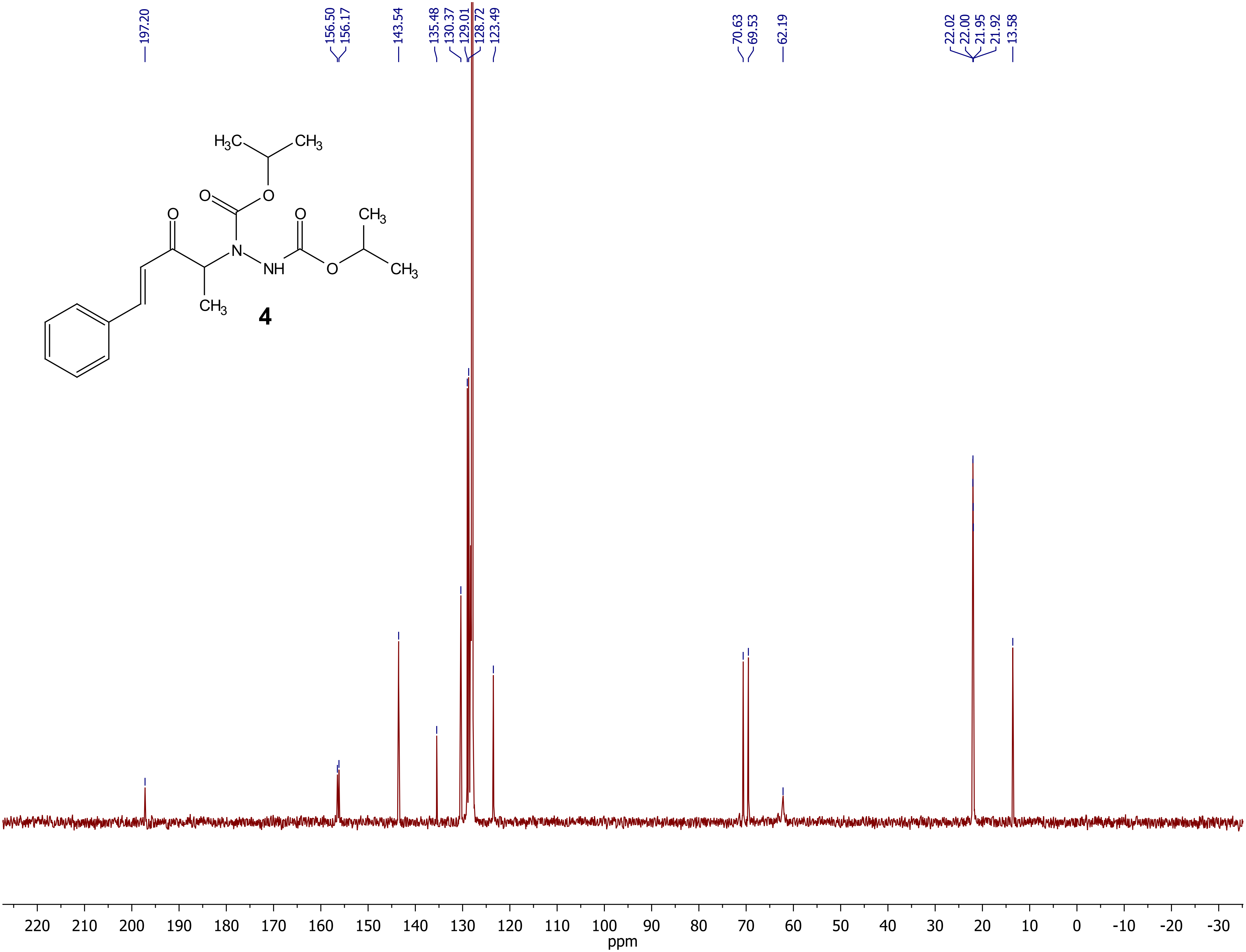
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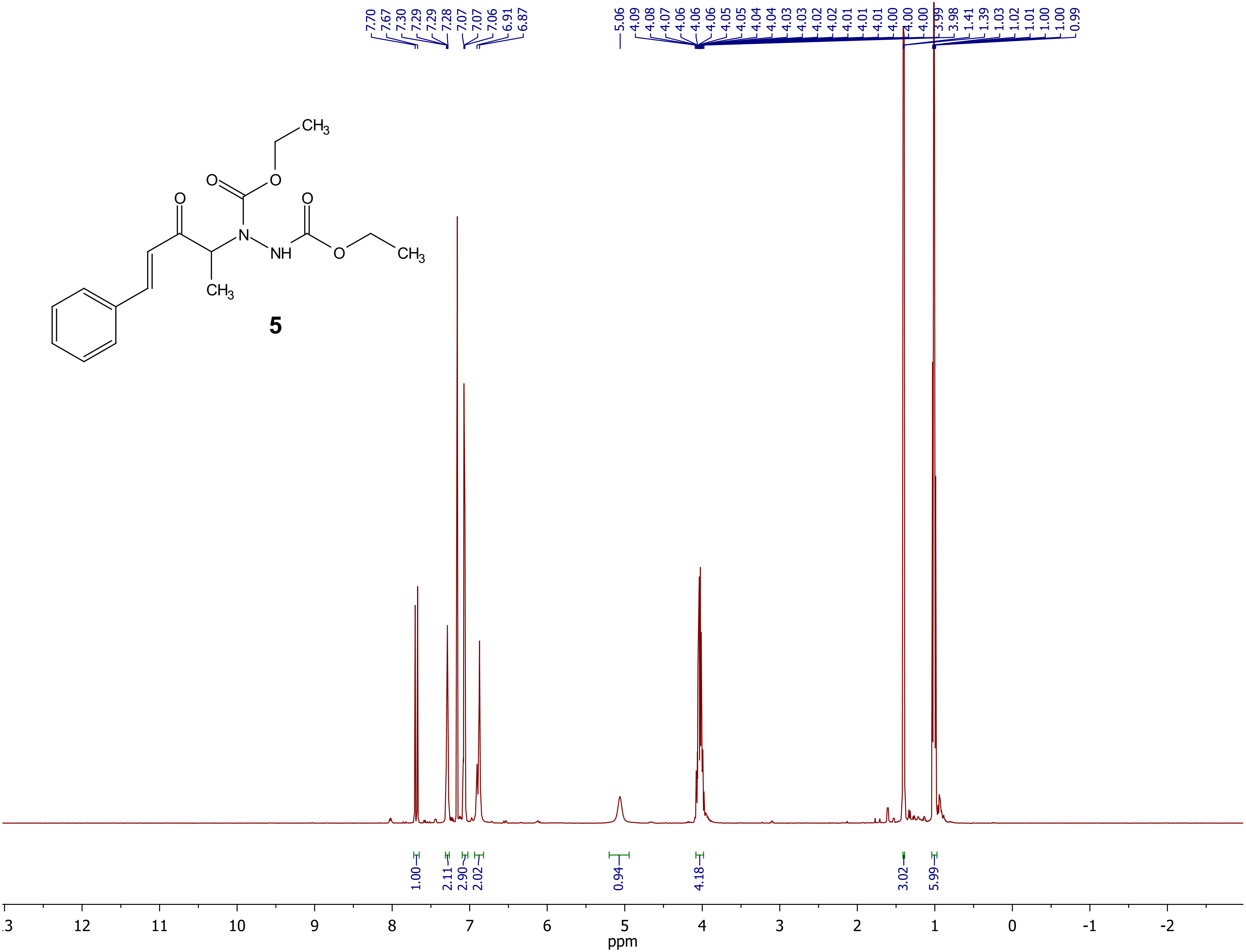
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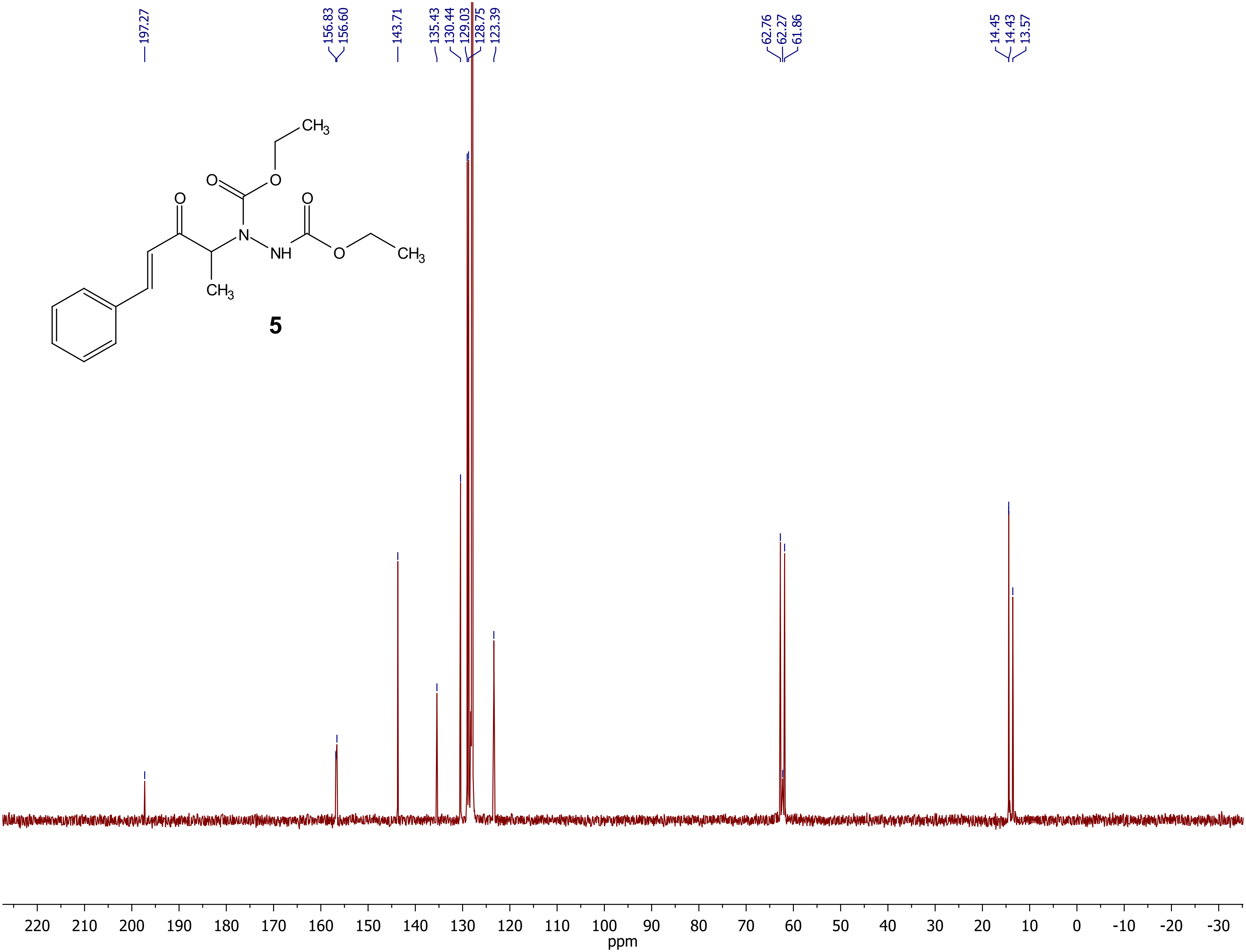
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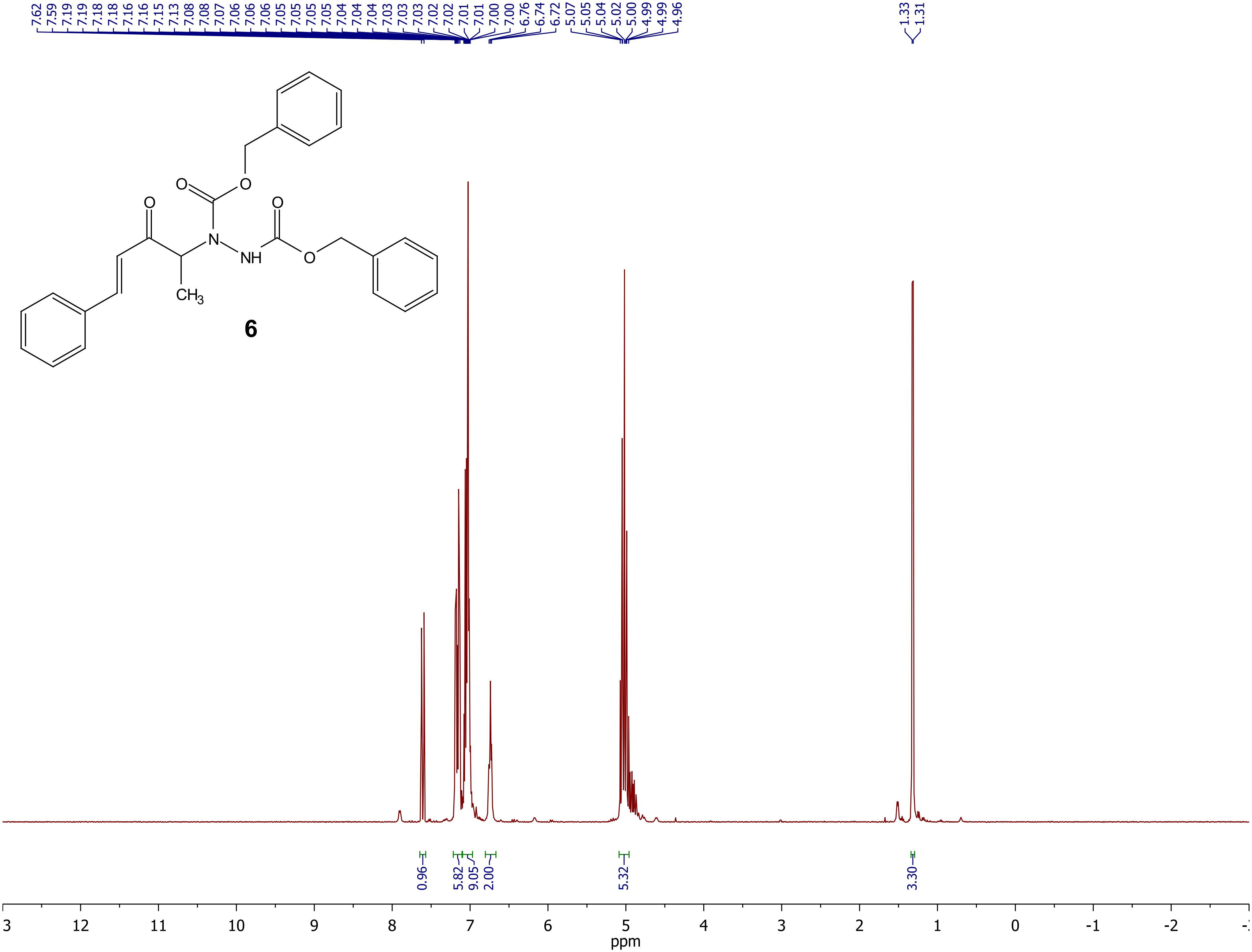
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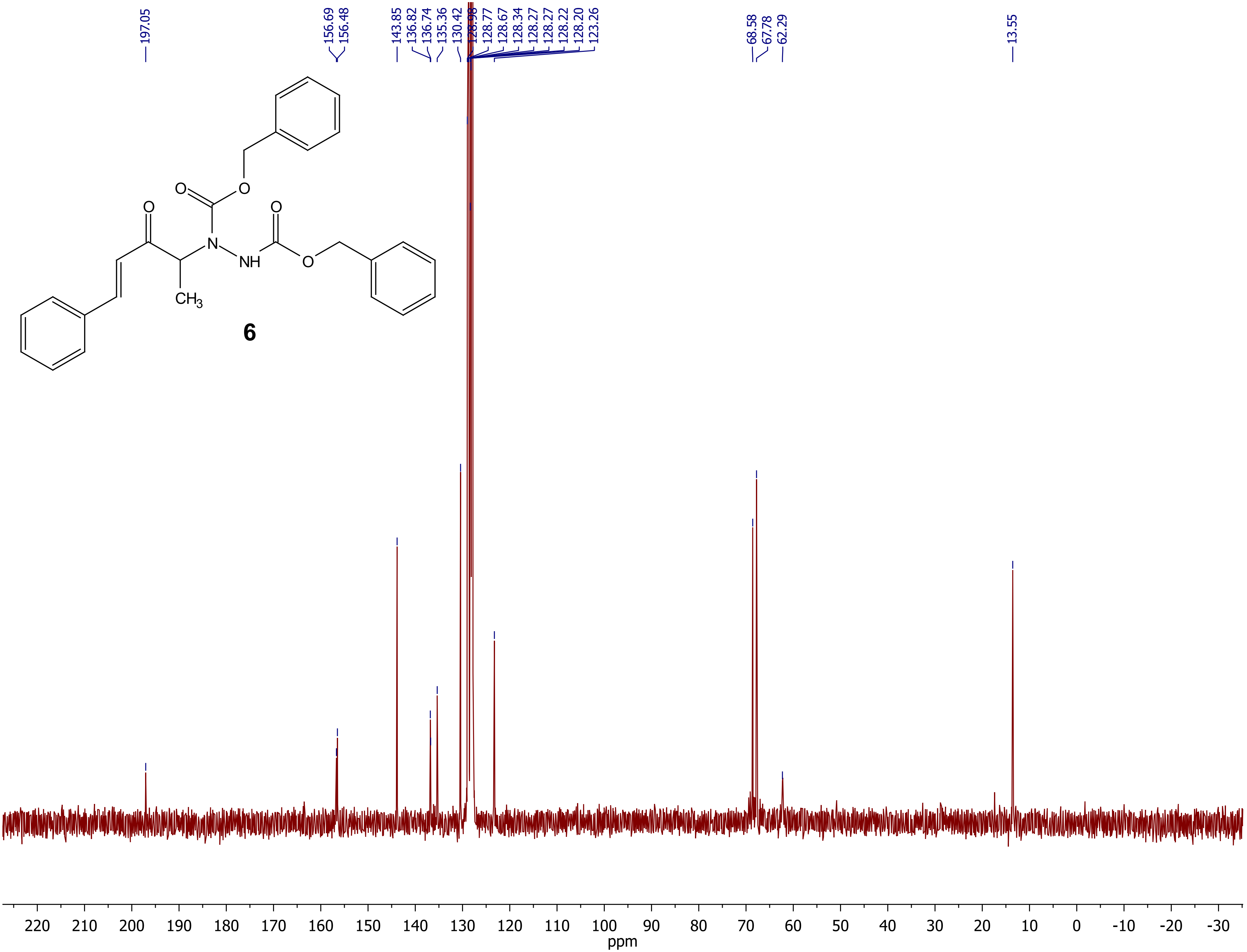
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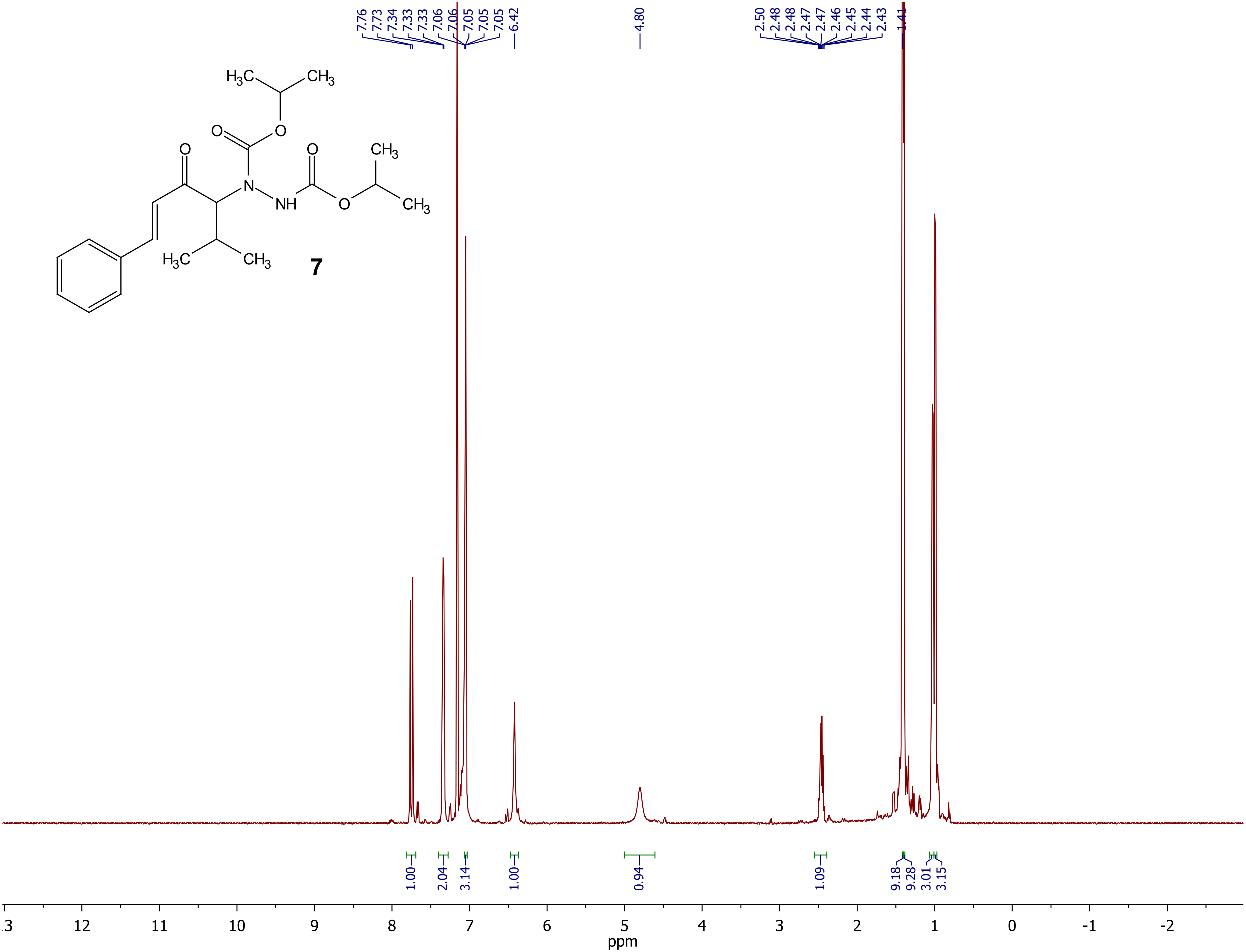
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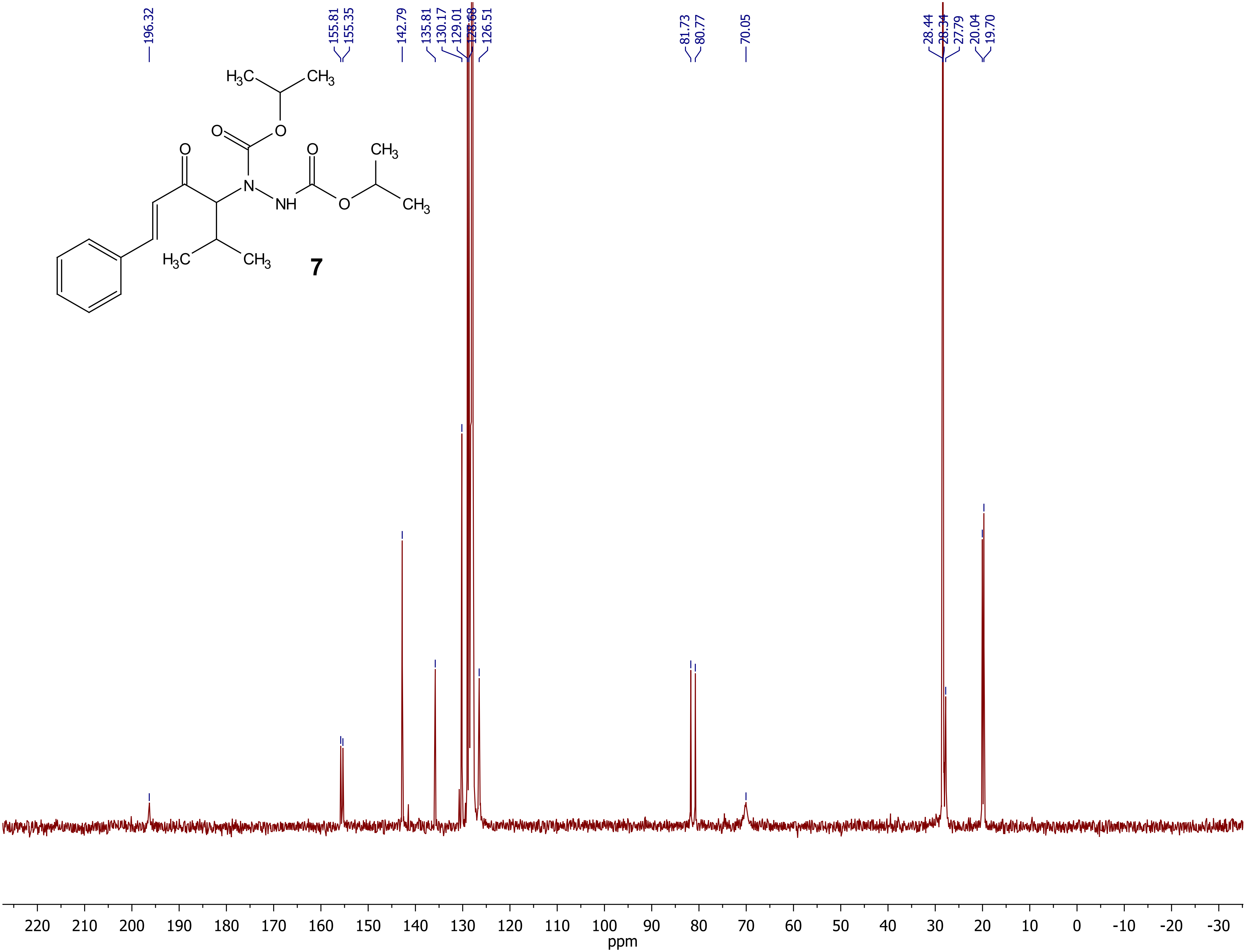
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28.34
27.79
20.04
19.70
H3C
CH3
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O
O
O
CH3
N
NH
O
CH3
H3C
CH3
220
210
200
190
180
170
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150
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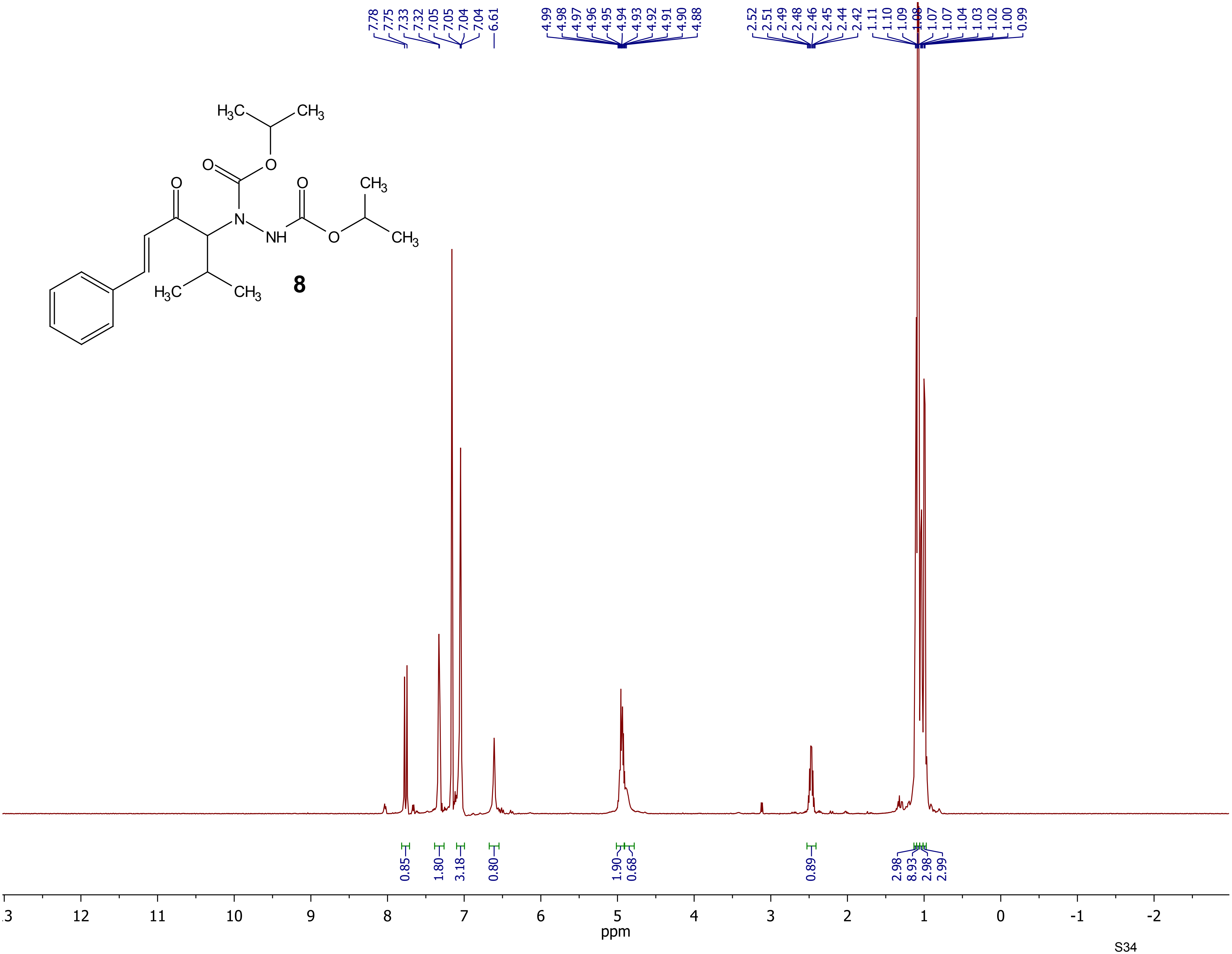
7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4.94
4.93
4.92
4.91
4.90
4.88
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2.48
2.46
2.45
2.44
2.42
1.11
1.10
1.09
1.08
1.07
1.07
1.04
1.03
1.02
1.00
0.99
H_3C
CH_3
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O
O
CH_3
O
N
NH
O
CH_3
H_3C
CH_3
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3.18
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8.93
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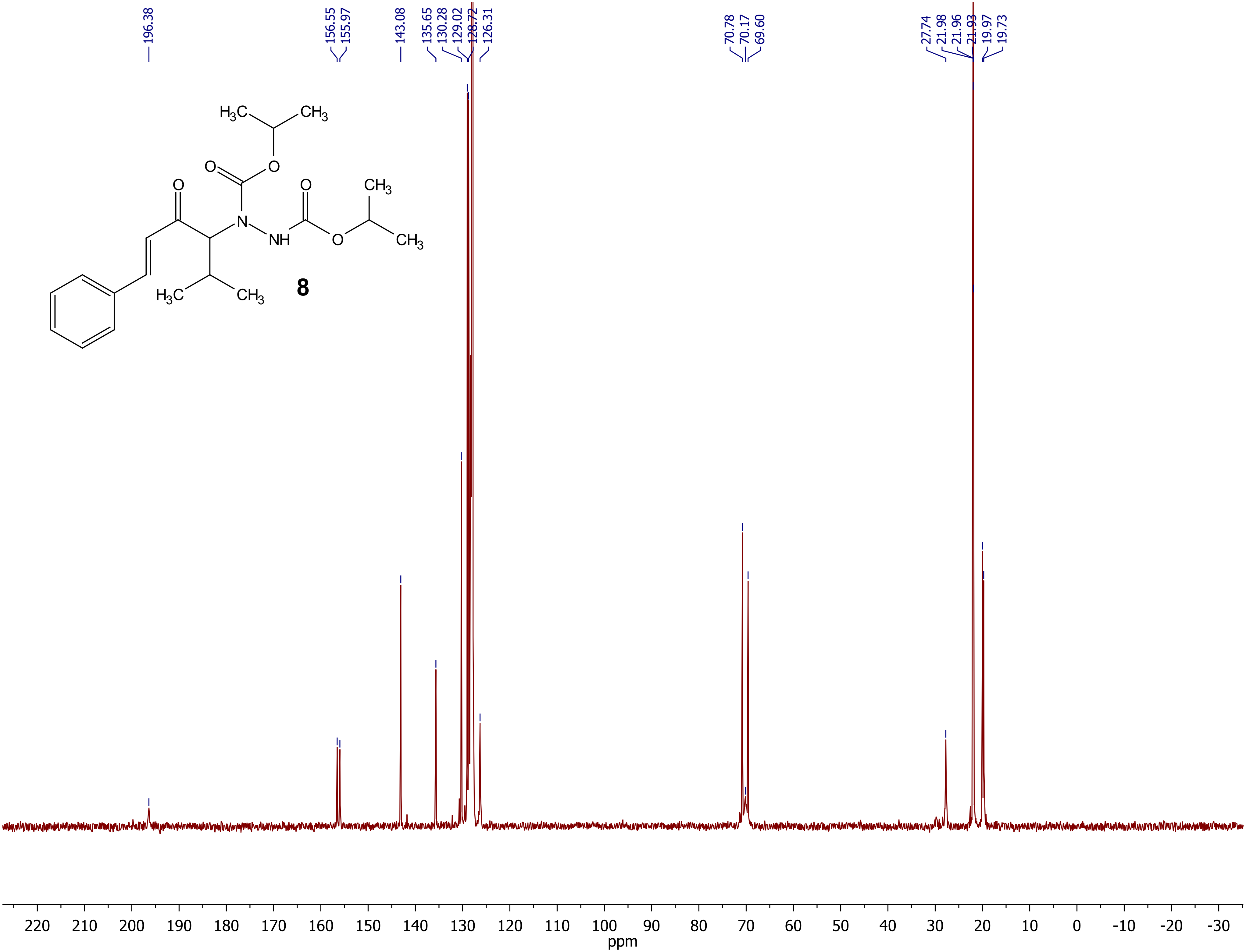
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21.98
21.96
21.93
19.97
19.73
H3C
CH3
O
O
O
O
CH3
N
NH
O
CH3
H3C
CH3
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180
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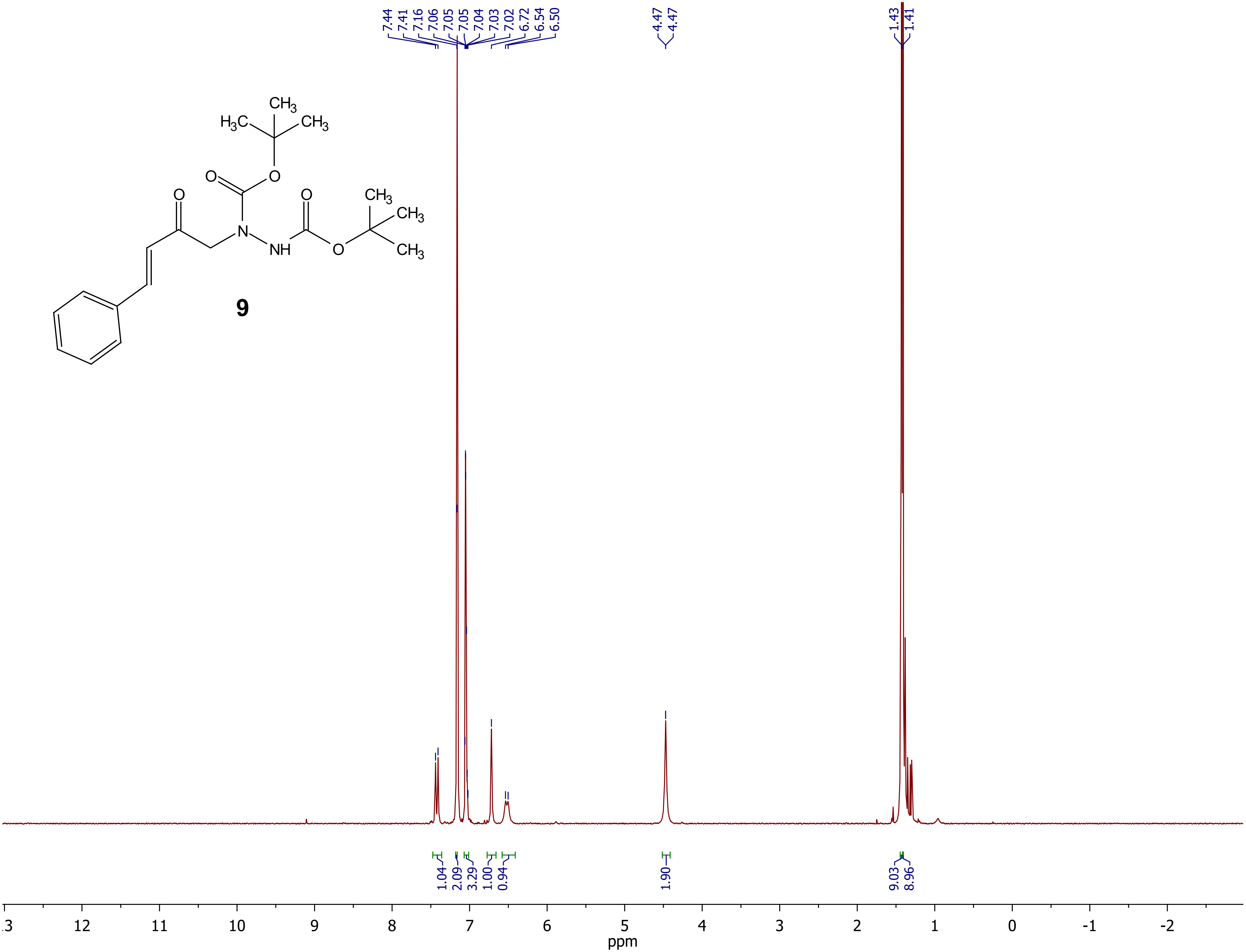

9

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4.47
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CH3
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N
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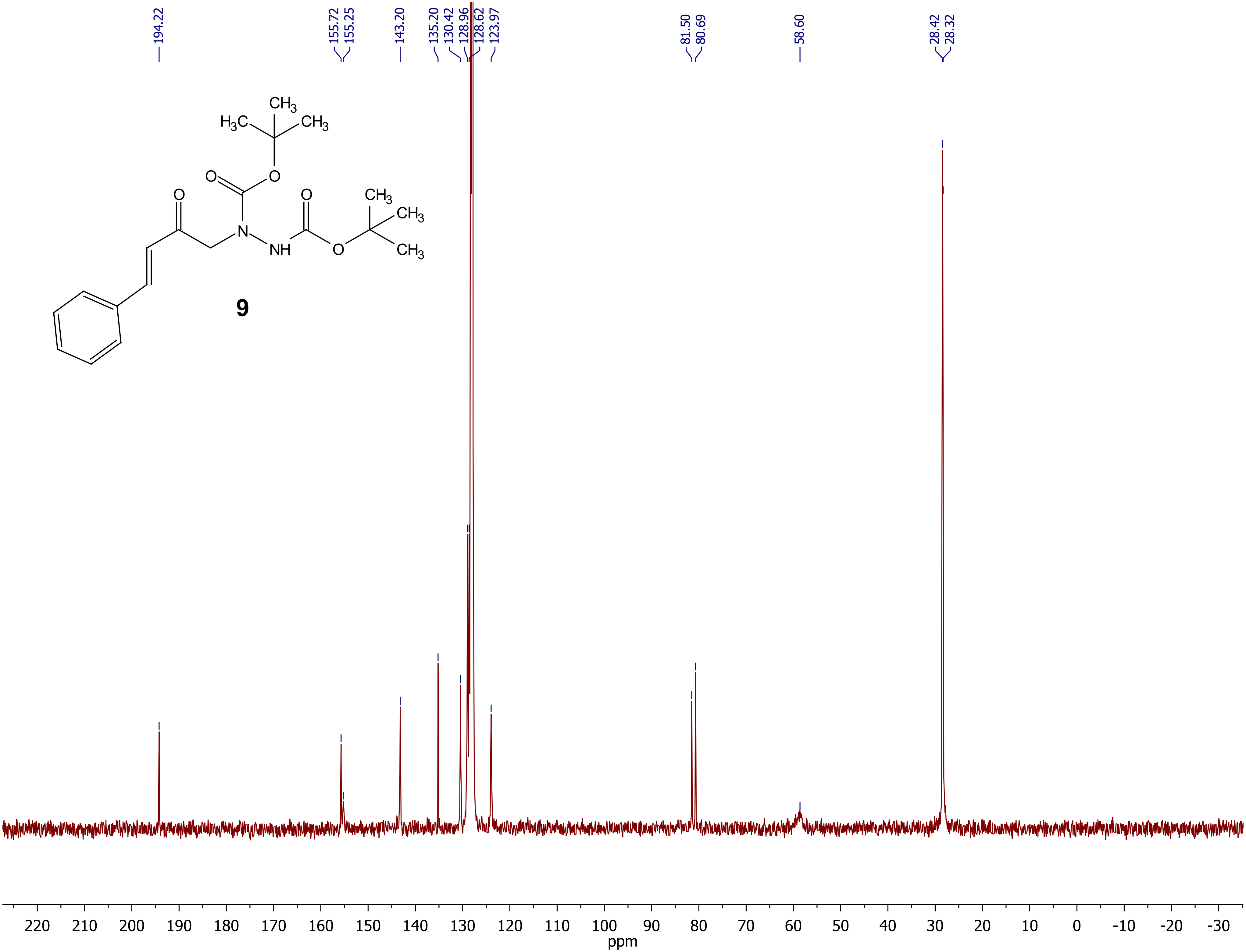
CH3
CH3
CH3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28.32
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H3C
CH3
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O
CH3
CH3
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NH
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CH3
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210
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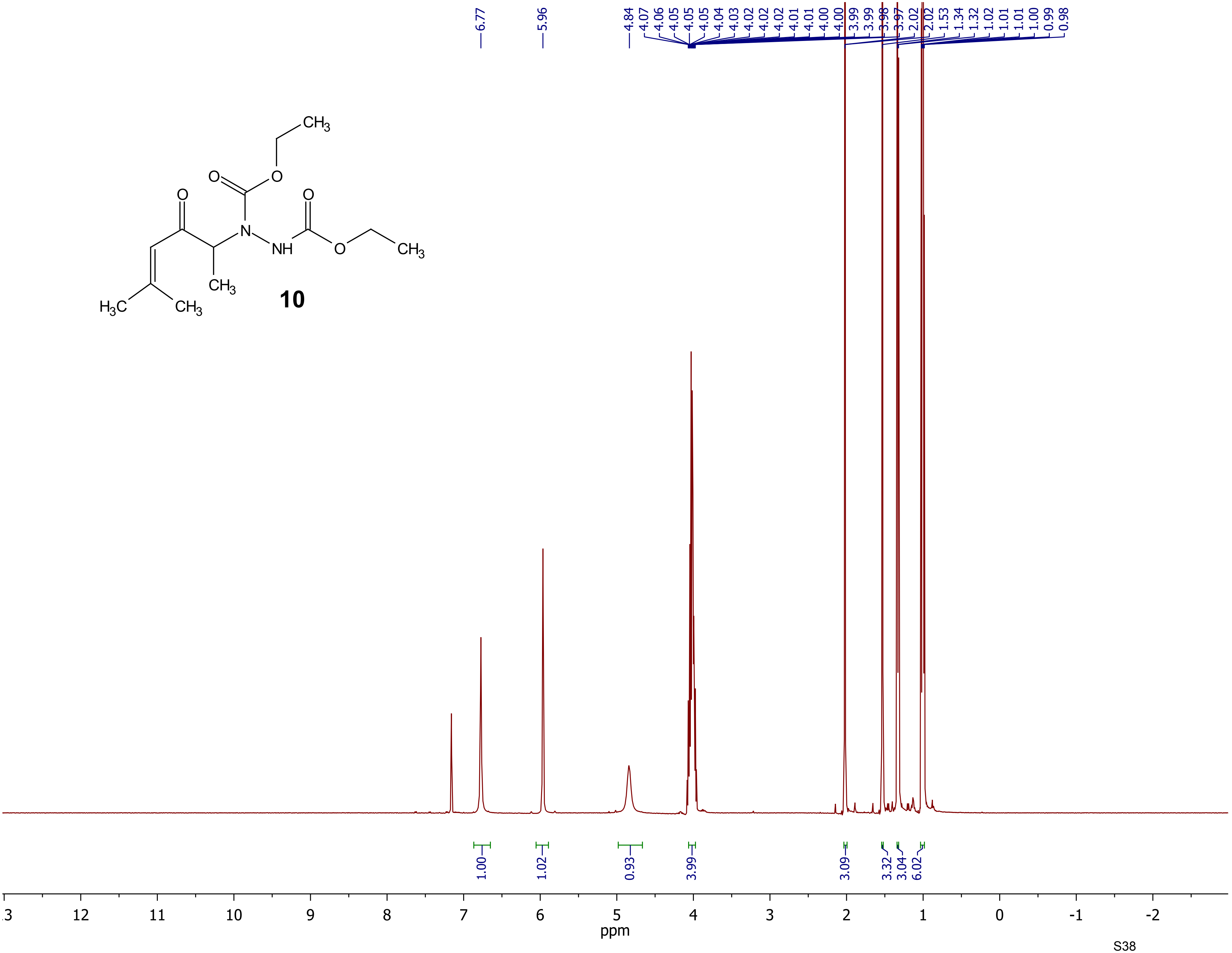6.77
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4.01
4.01
4.00
4.00
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3.99
3.98
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2.02
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1.02
1.01
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1.00
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0.98
CH3
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O
O
N
NH
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CH3
CH3
H3C
CH3
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1.02
0.93
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3.32
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-2
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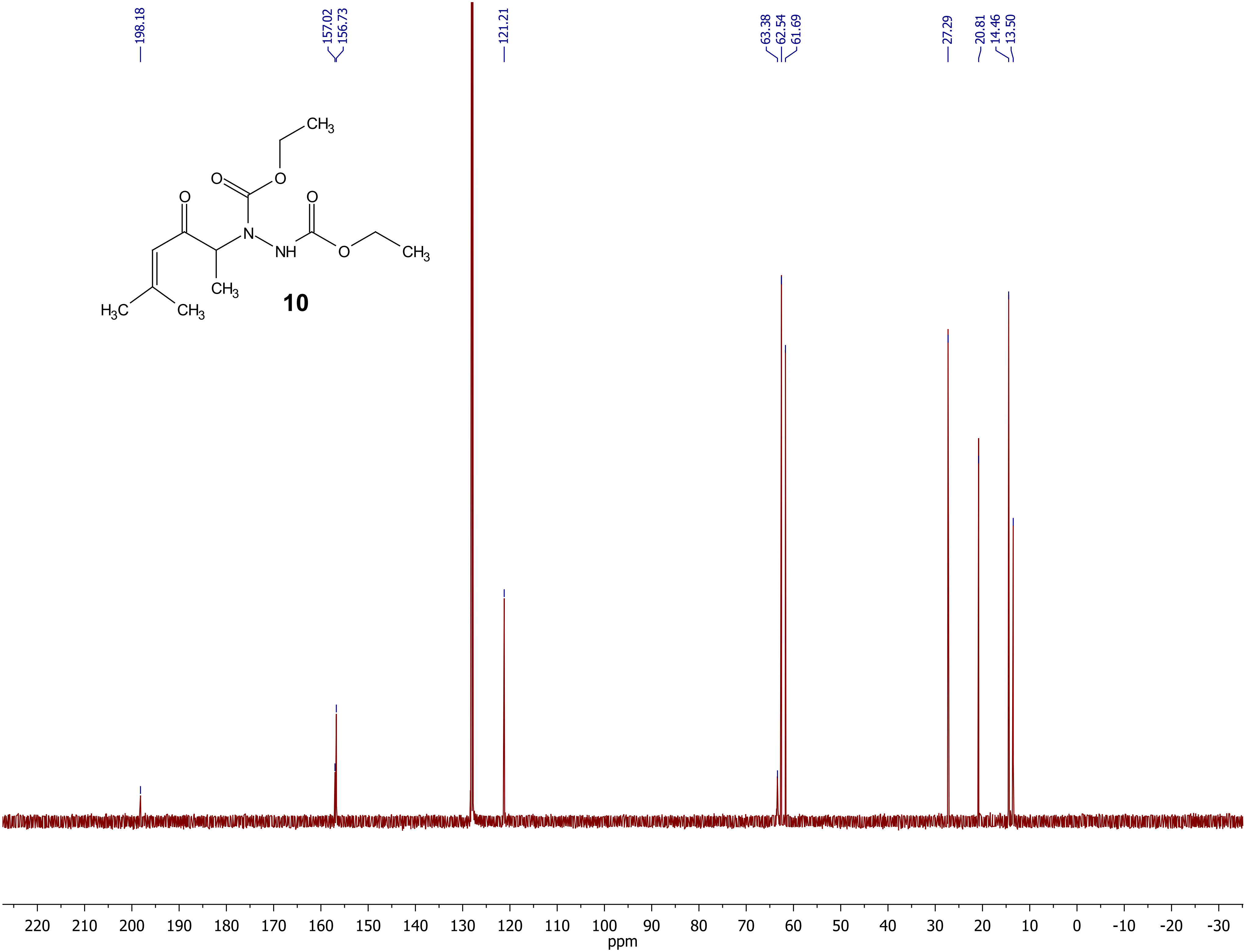
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14.46
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O
N
NH
O
CH3
CH3
H3C
CH3
10
220
210
200
190
180
170
160
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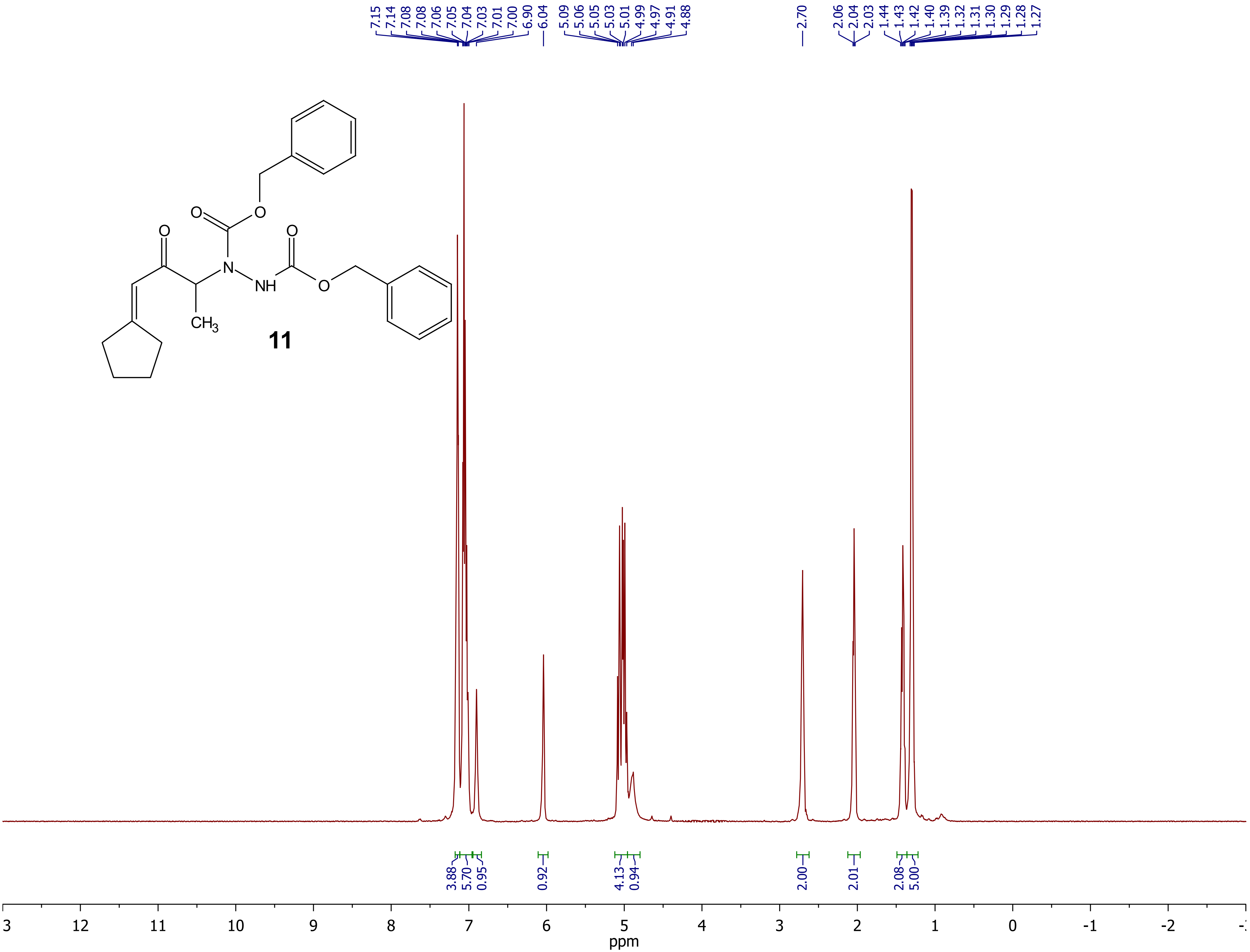
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5.06
5.05
5.03
5.01
4.99
4.97
4.91
4.88
2.70
2.06
2.04
2.03
1.44
1.43
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1.32
1.31
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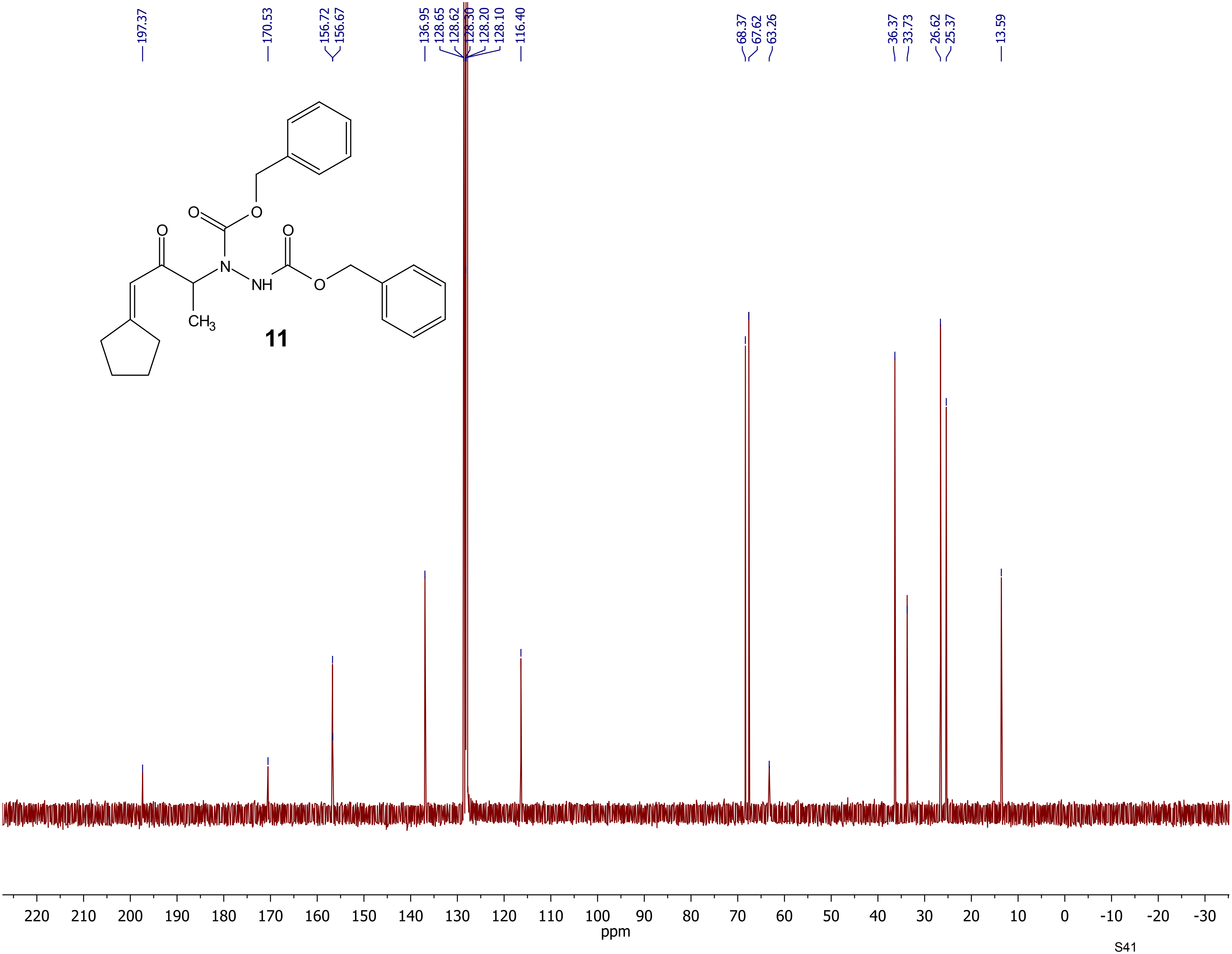
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63.26
36.37
33.73
26.62
25.37
13.59
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NH
O
CH3
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ppm

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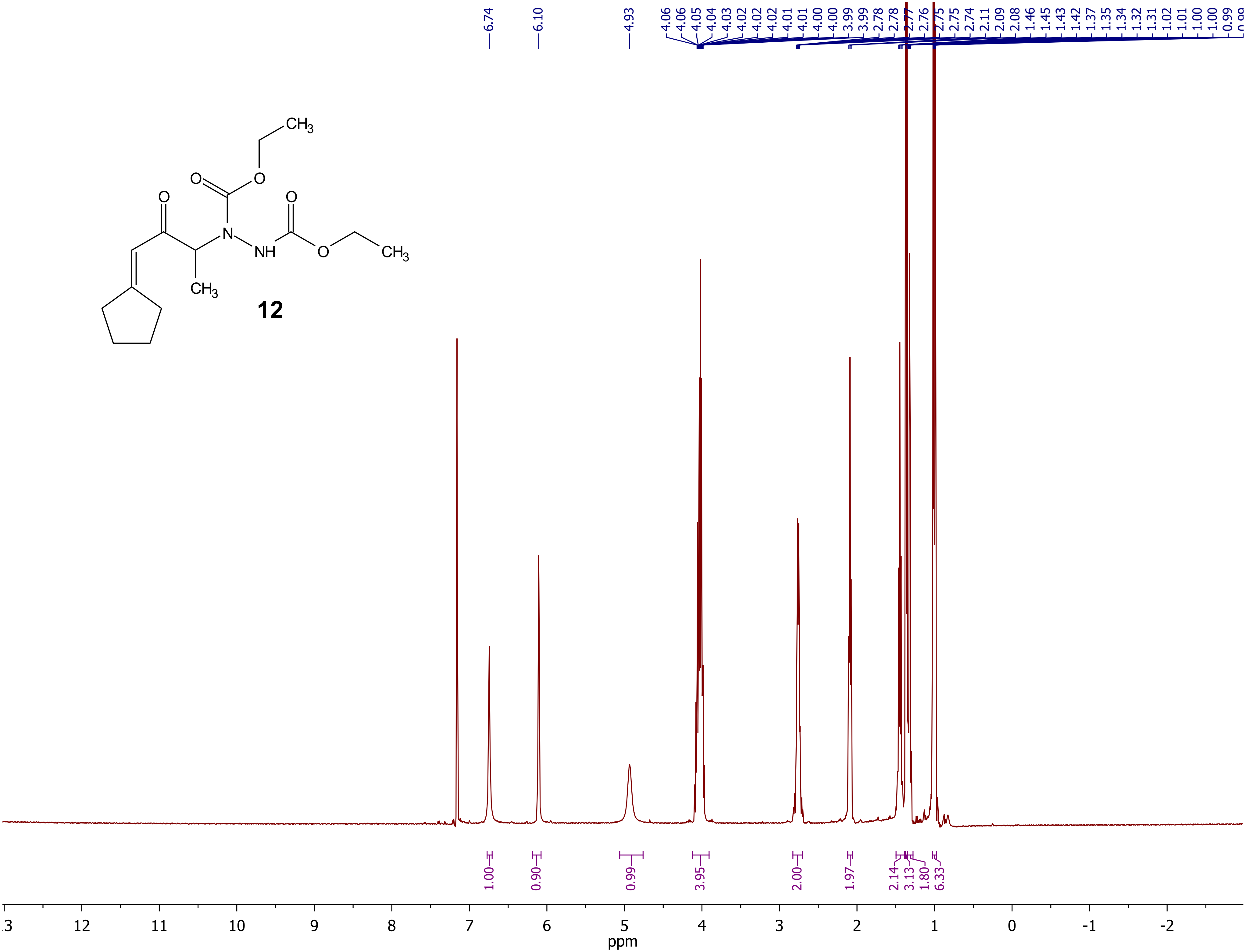
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2.78
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2.08
1.46
1.45
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1.42
1.37
1.35
1.34
1.32
1.31
1.02
1.01
1.00
1.00
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O
O
N
NH
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CH3
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0.99
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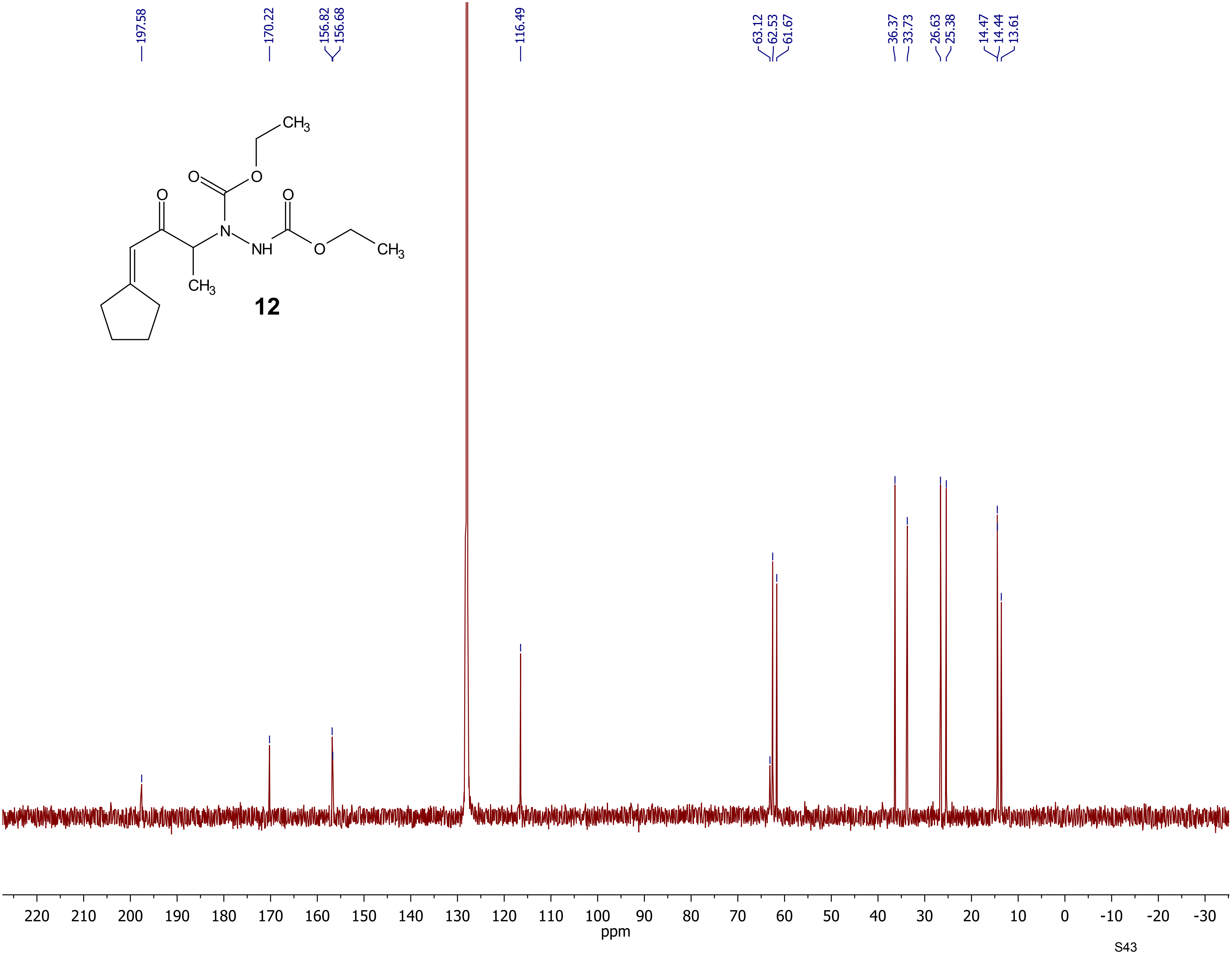
-2
ppm

12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14.44
13.61
CH3
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O
O
O
N
NH
O
CH3
CH3
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200
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160
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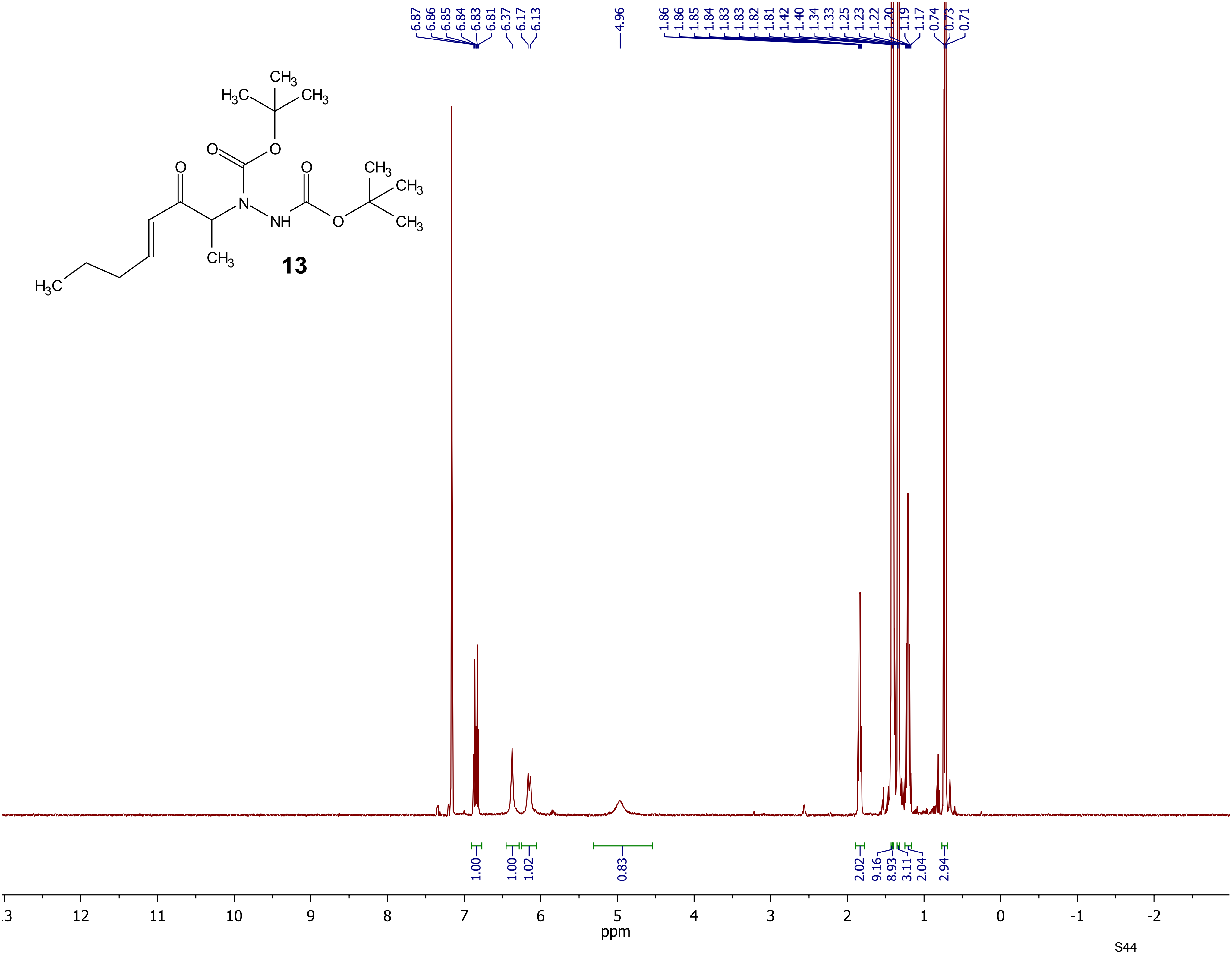
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1.81
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1.23
1.22
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1.17
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CH3
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CH3
H3C
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1.00
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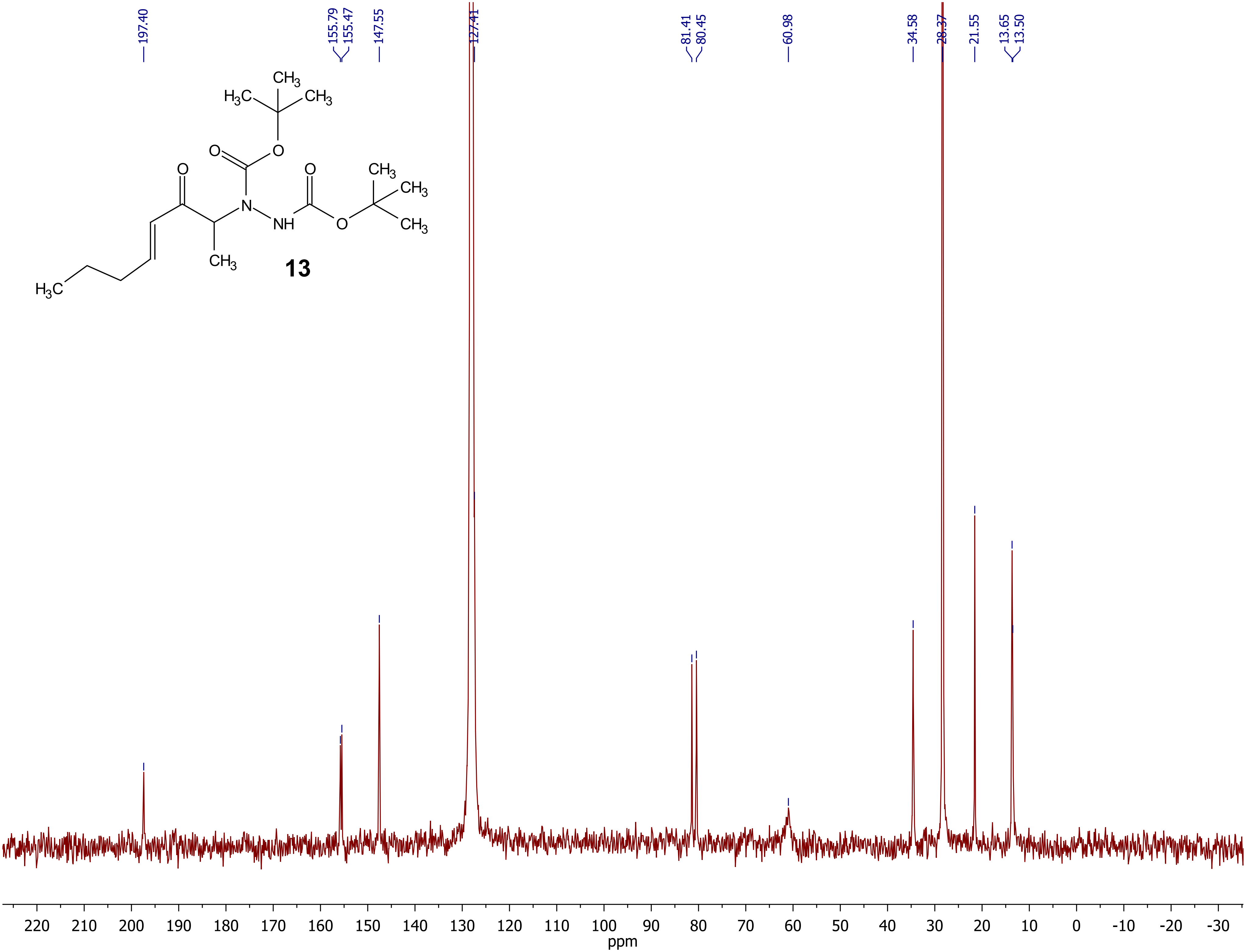
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CH3
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O
O
CH3
CH3
N
NH
O
CH3
CH3
H3C
13
220
210
200
190
180
170
160
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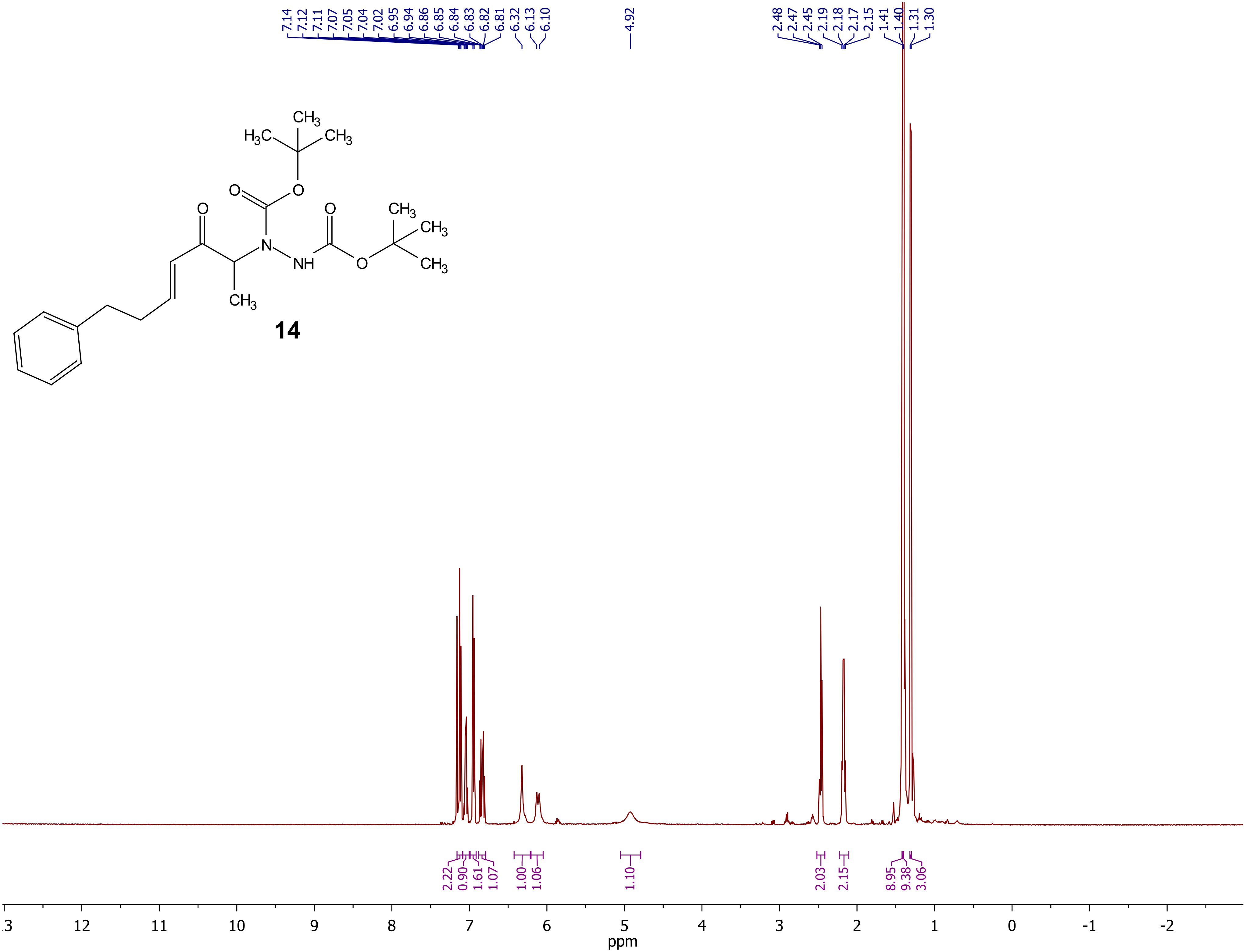
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6.81
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2.18
2.17
2.15
1.41
1.40
1.31
1.30
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1.06
1.10
2.03
2.15
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9
8
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5
4
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0
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CH3
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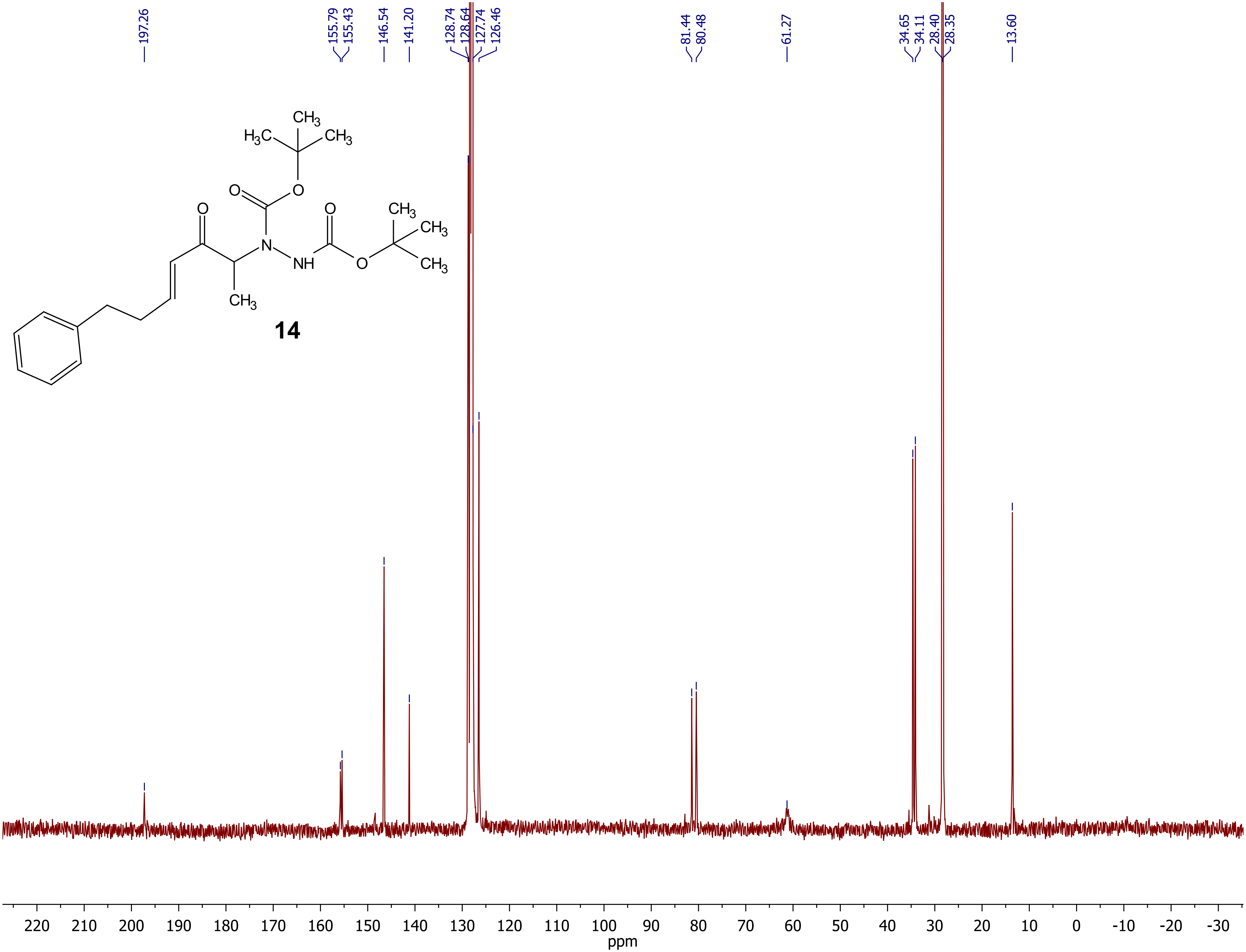
CH3
CH3
CH3

14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200
190
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170
160
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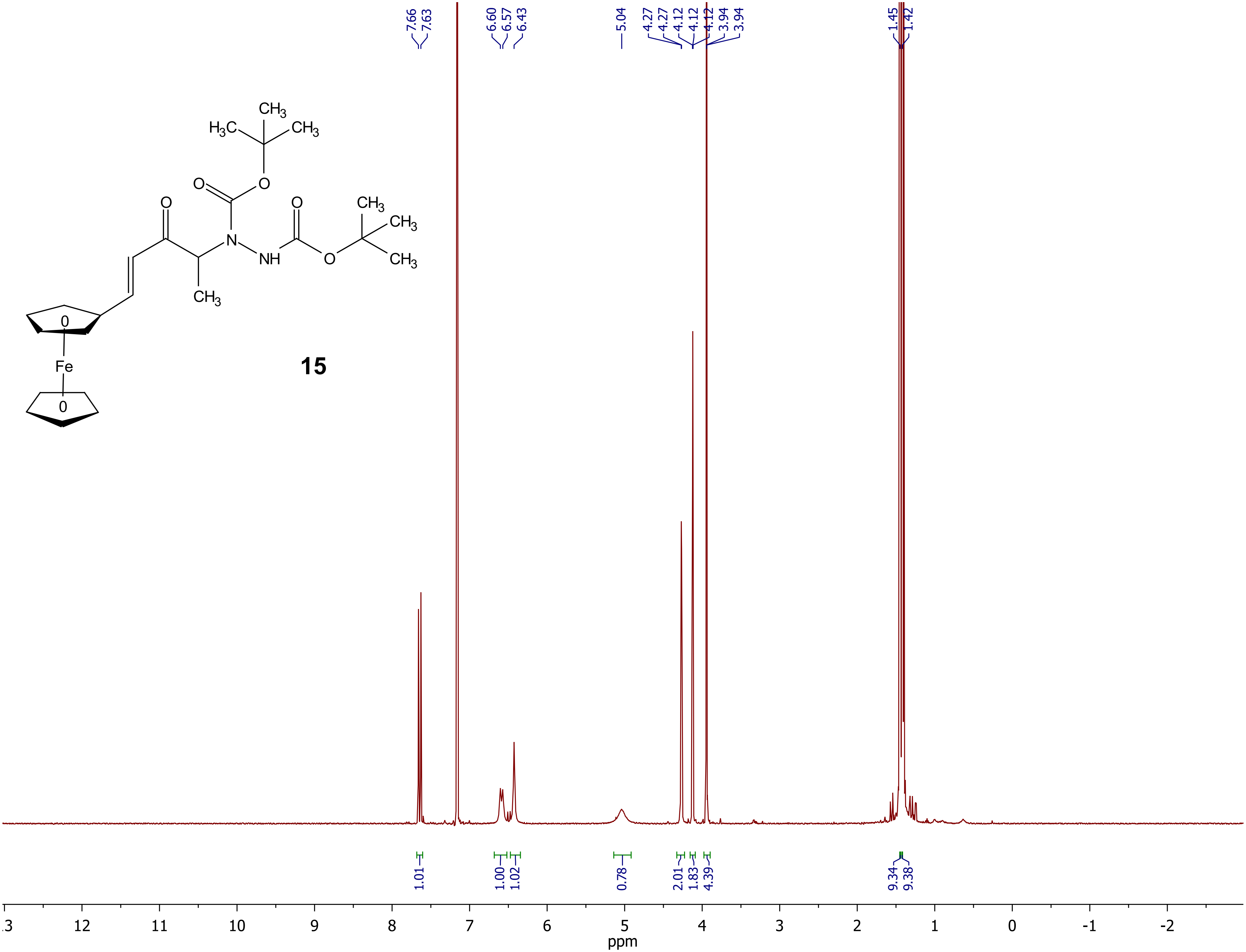
ppm

14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9
8
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5
4
3
2
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-2
ppm
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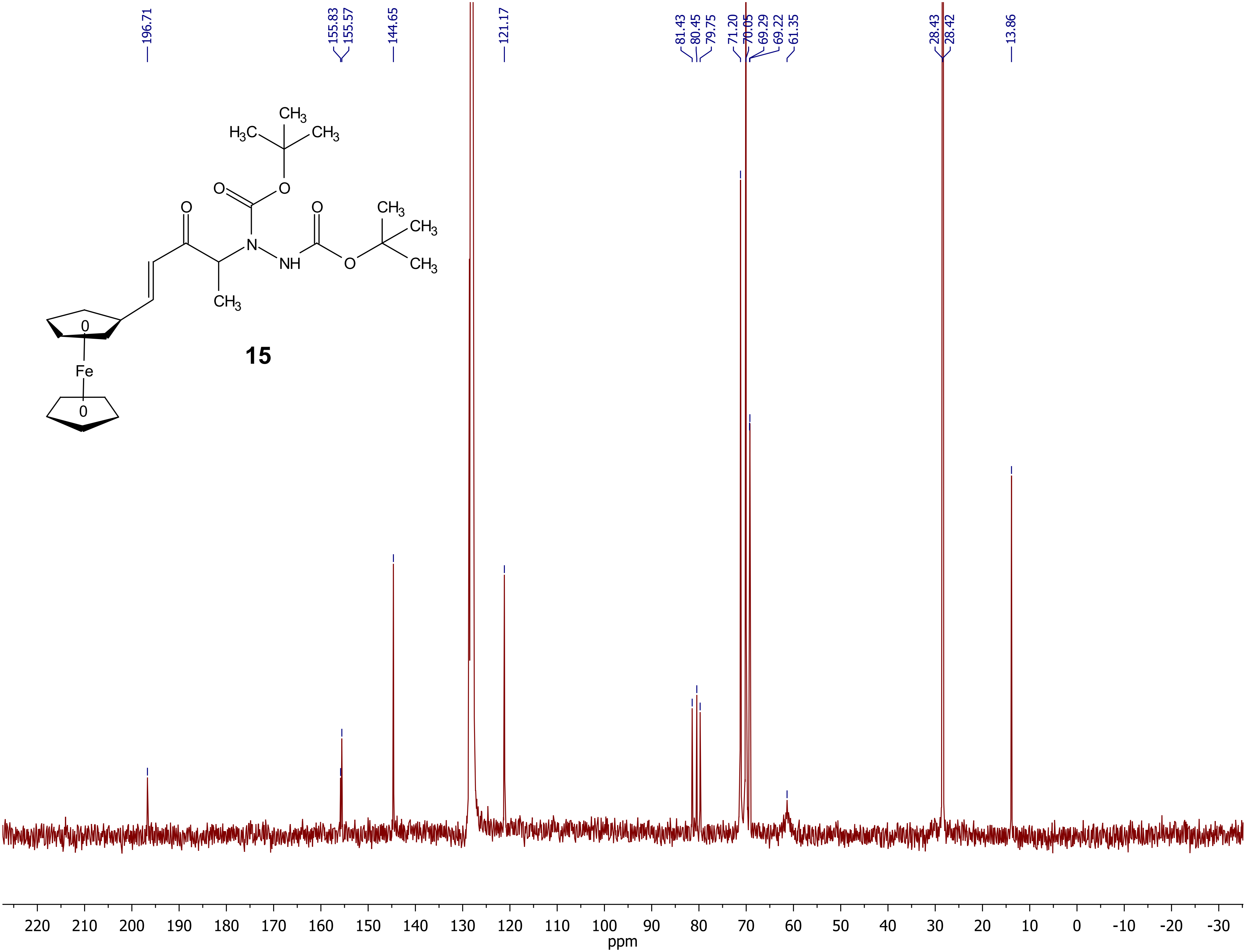
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28.42
13.86
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CH3
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O
O
N
NH
O
CH3
CH3
CH3
O
CH3
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Fe
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200
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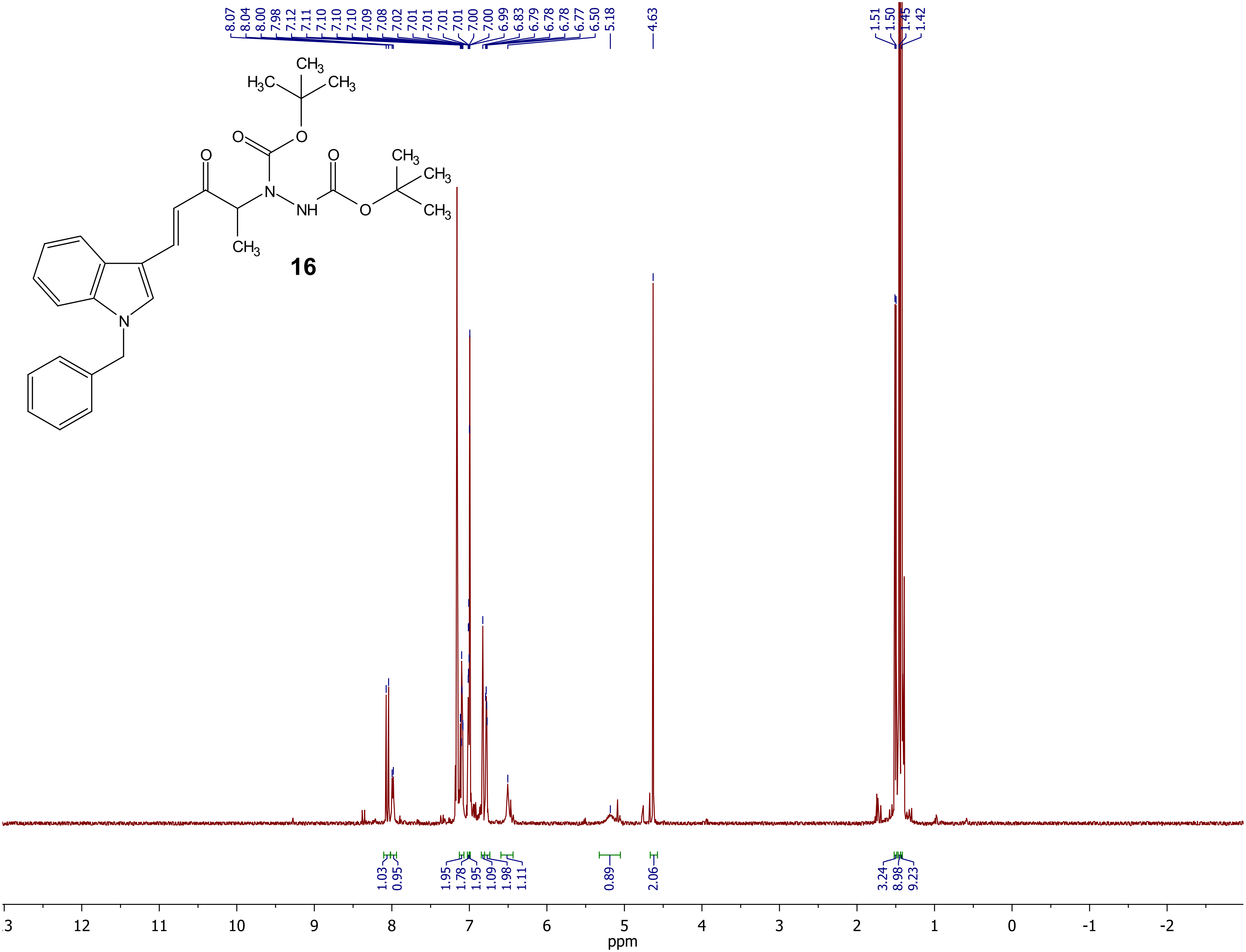
15



16

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6.50
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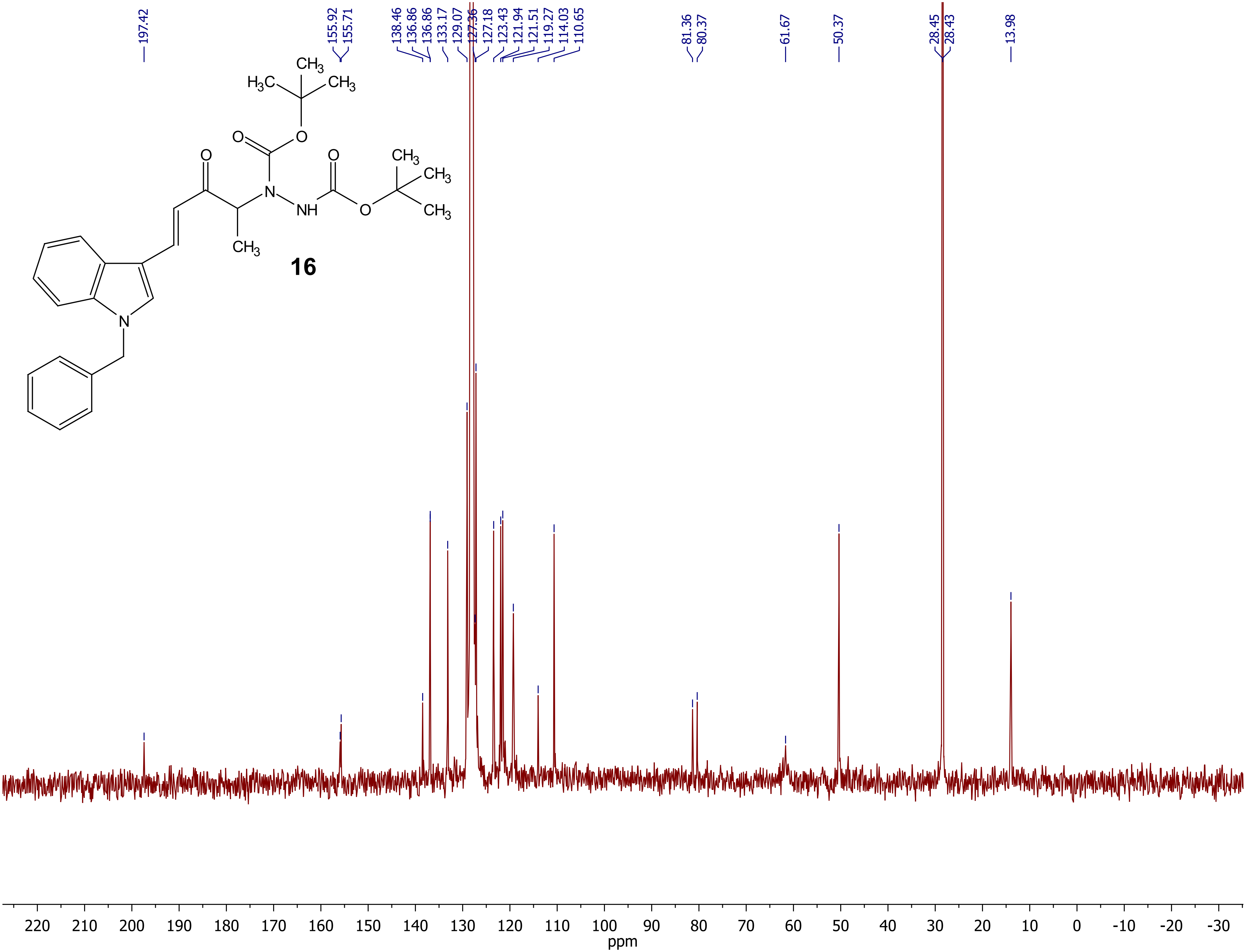
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61.67
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28.43
13.98
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H3C
CH3
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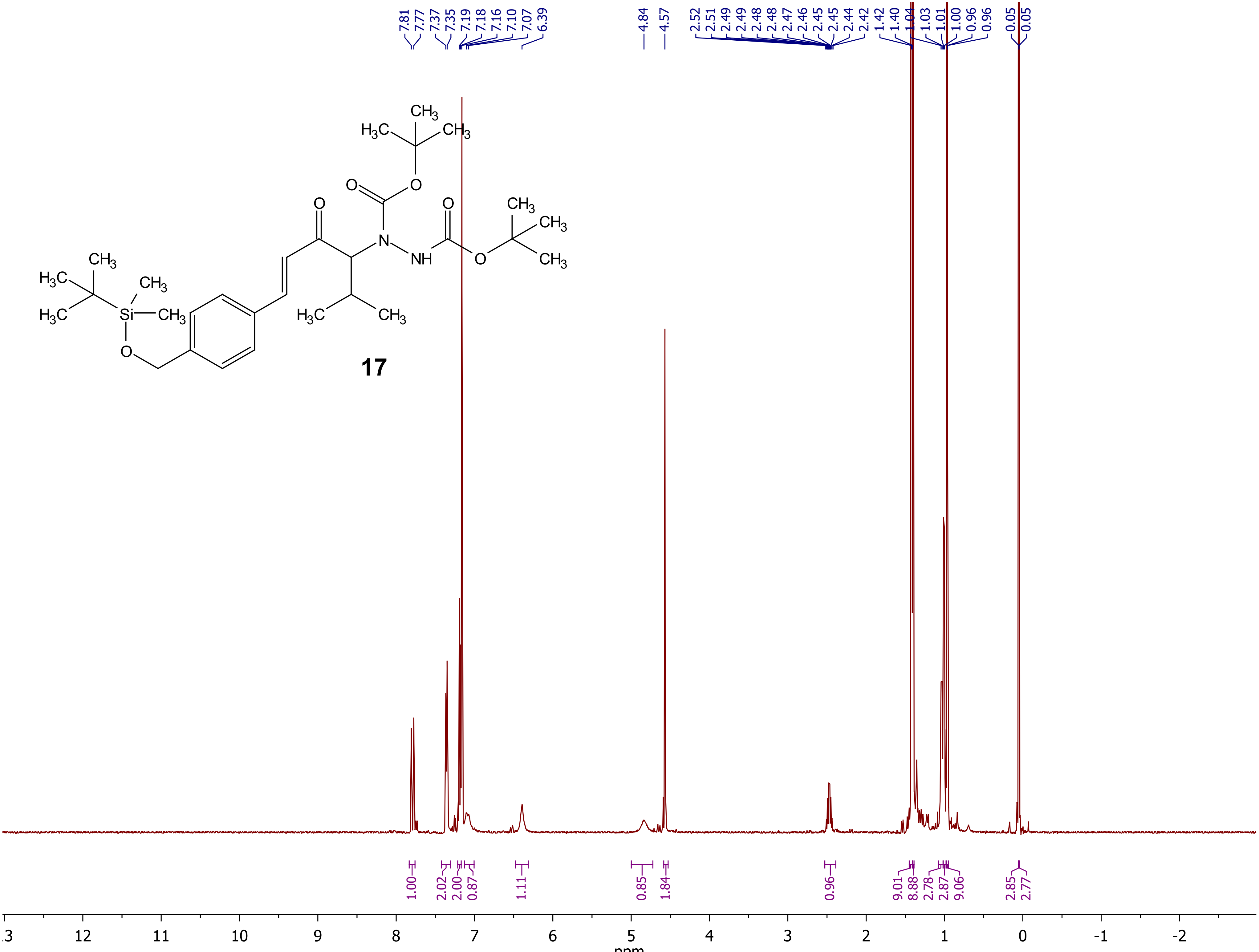
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2.48
2.48
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CH3
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NH
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CH3
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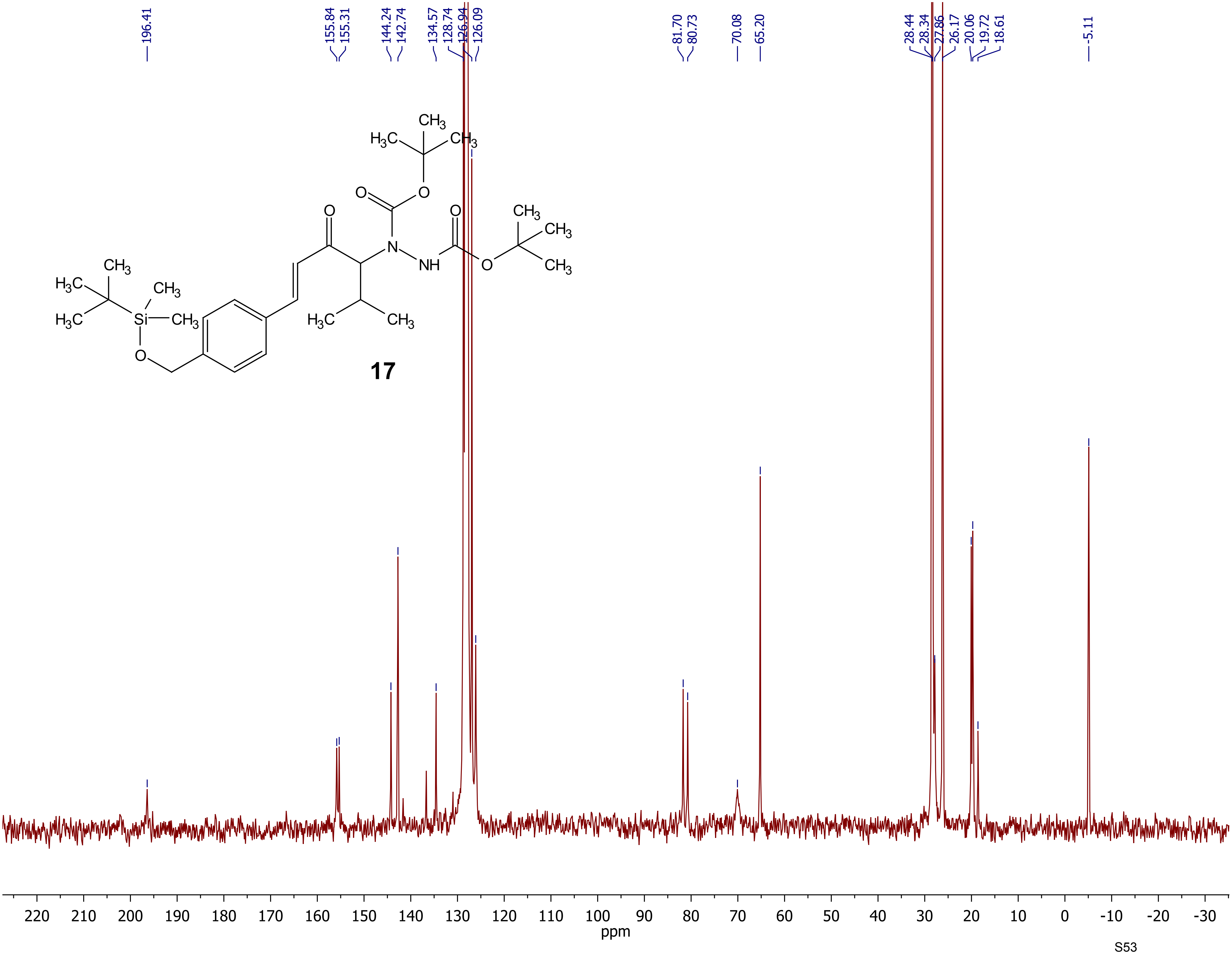
17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28.34
27.86
26.17
20.06
19.72
18.61
-5.11
CH3
H3C
O
N
NH
Si
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200
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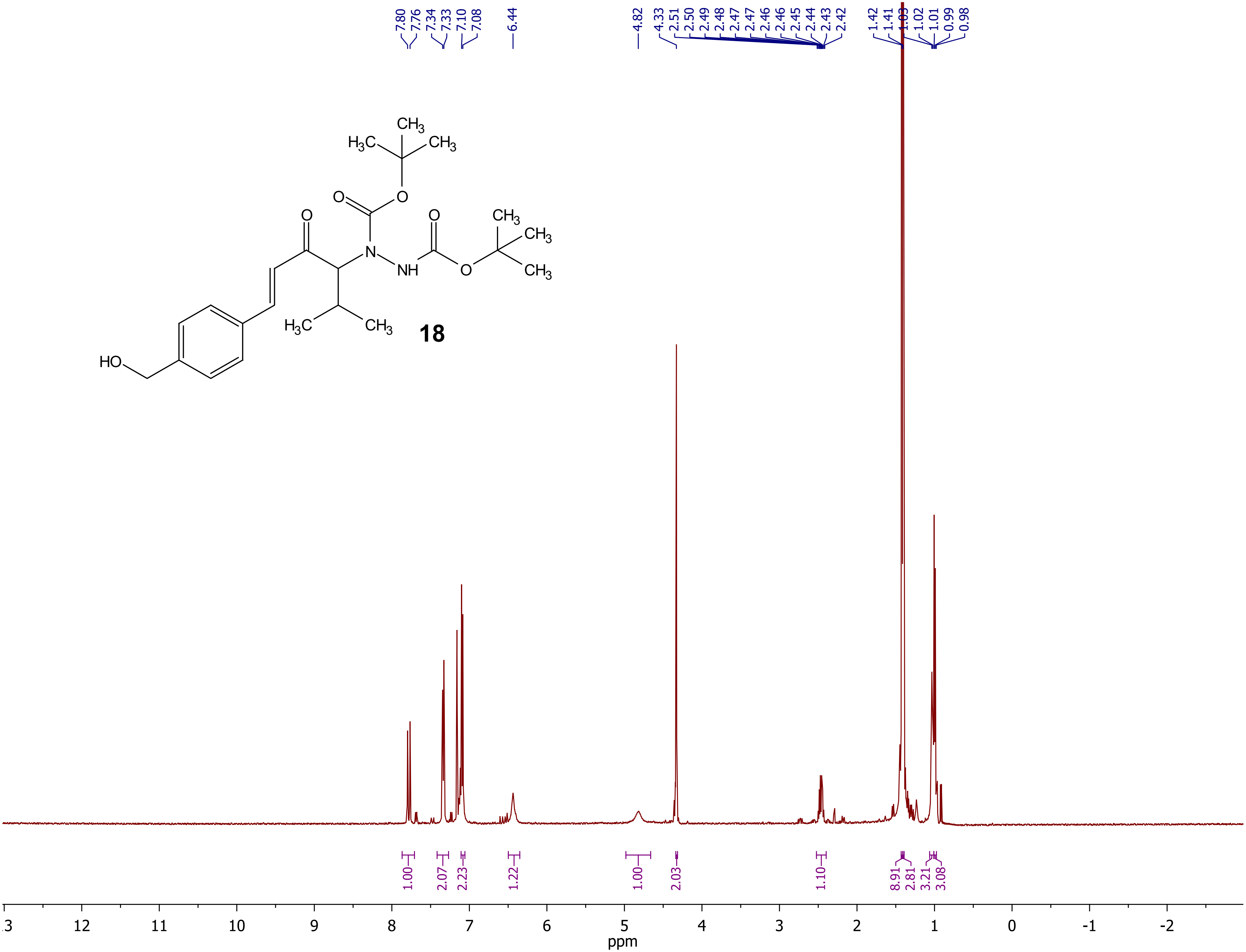
ppm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1.02
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O
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N
NH
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CH3
CH3
CH3
HO
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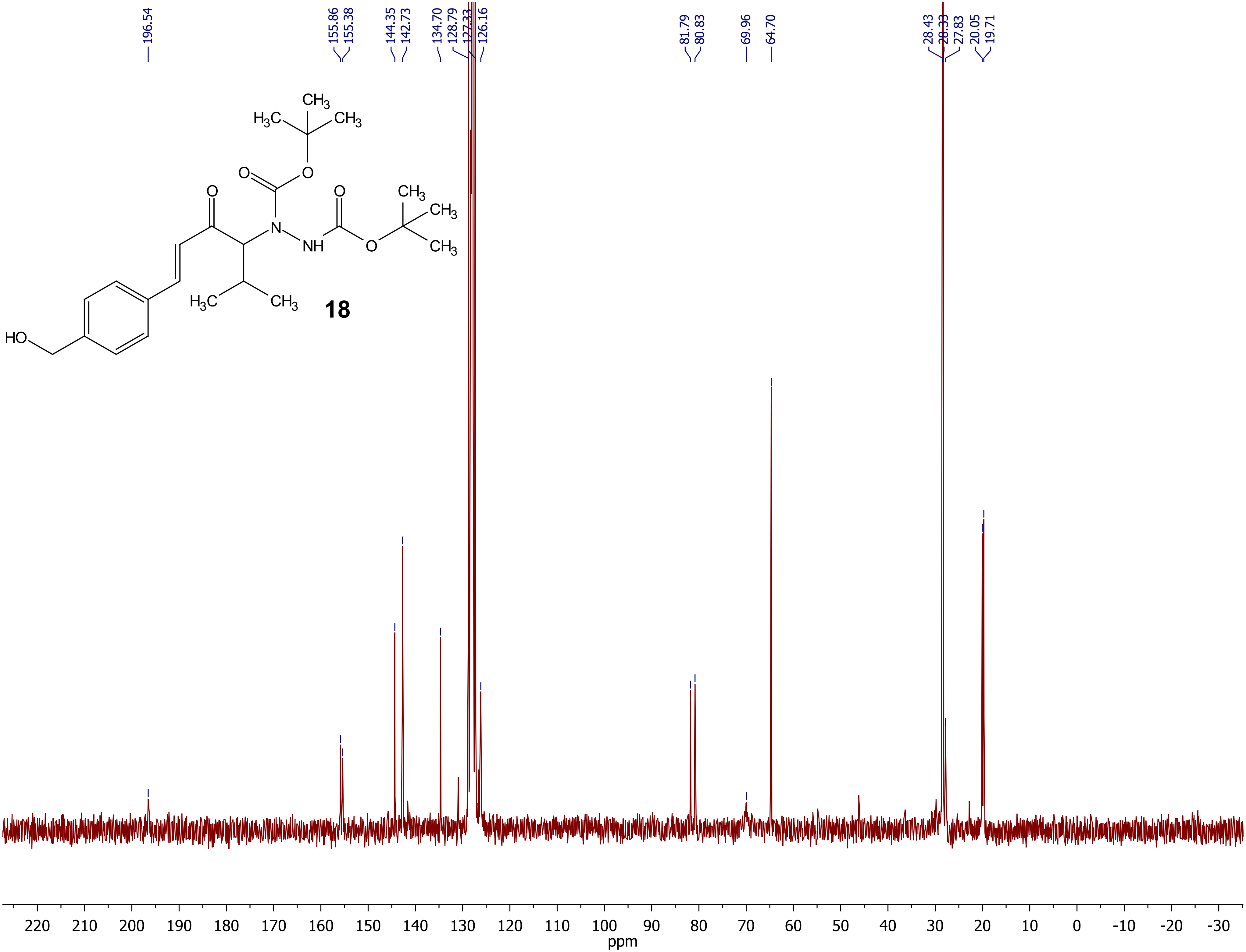

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127.33
126.16
81.79
80.83
69.96
64.70
28.43
28.33
27.83
20.05
19.71
CH3
H3C
CH3
O
O
O
N
NH
O
O
CH3
CH3
CH3
HO
H3C
CH3
18
220
210
200
190
180
170
160
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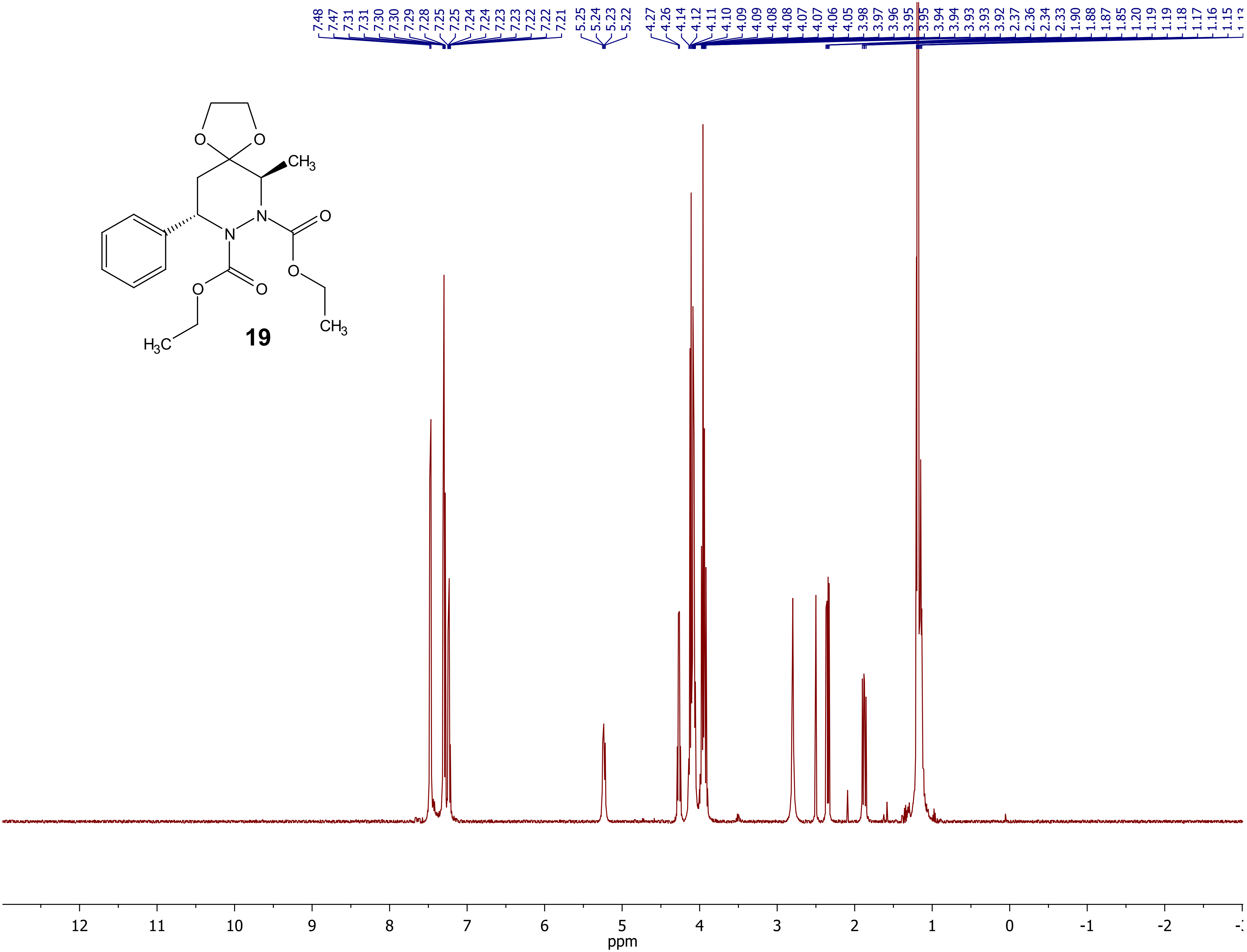
-30
ppm



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7.23
7.23
7.22
7.22
7.21
5.25
5.24
5.23
5.22
4.27
4.26
4.14
4.12
4.11
4.10
4.09
4.09
4.08
4.08
4.07
4.07
4.06
4.05
3.98
3.97
3.96
3.95
3.95
3.94
3.94
3.93
3.93
3.92
2.37
2.36
2.34
2.33
1.90
1.88
1.87
1.85
1.20
1.19
1.19
1.18
1.17
1.16
1.15
O
O
CH3
N
O
N
O
O
O
H3C
CH3
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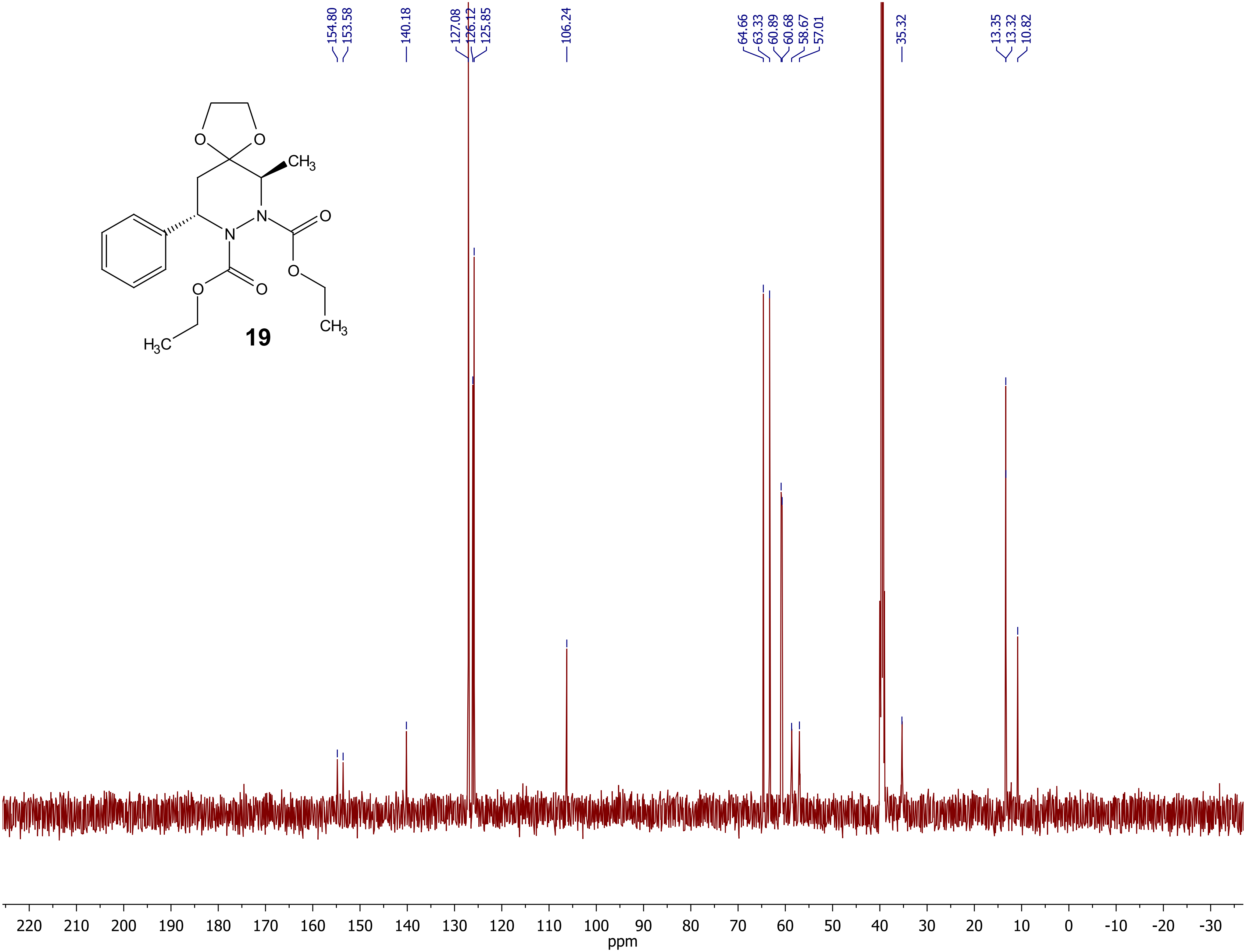
-2
ppm

19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57.01
35.32
13.35
13.32
10.82
O
O
CH3
N
N
O
O
O
O
H3C
CH3
19
220
210
200
190
180
170
160
150
140
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100
90
80
70
60
50
40
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20
10
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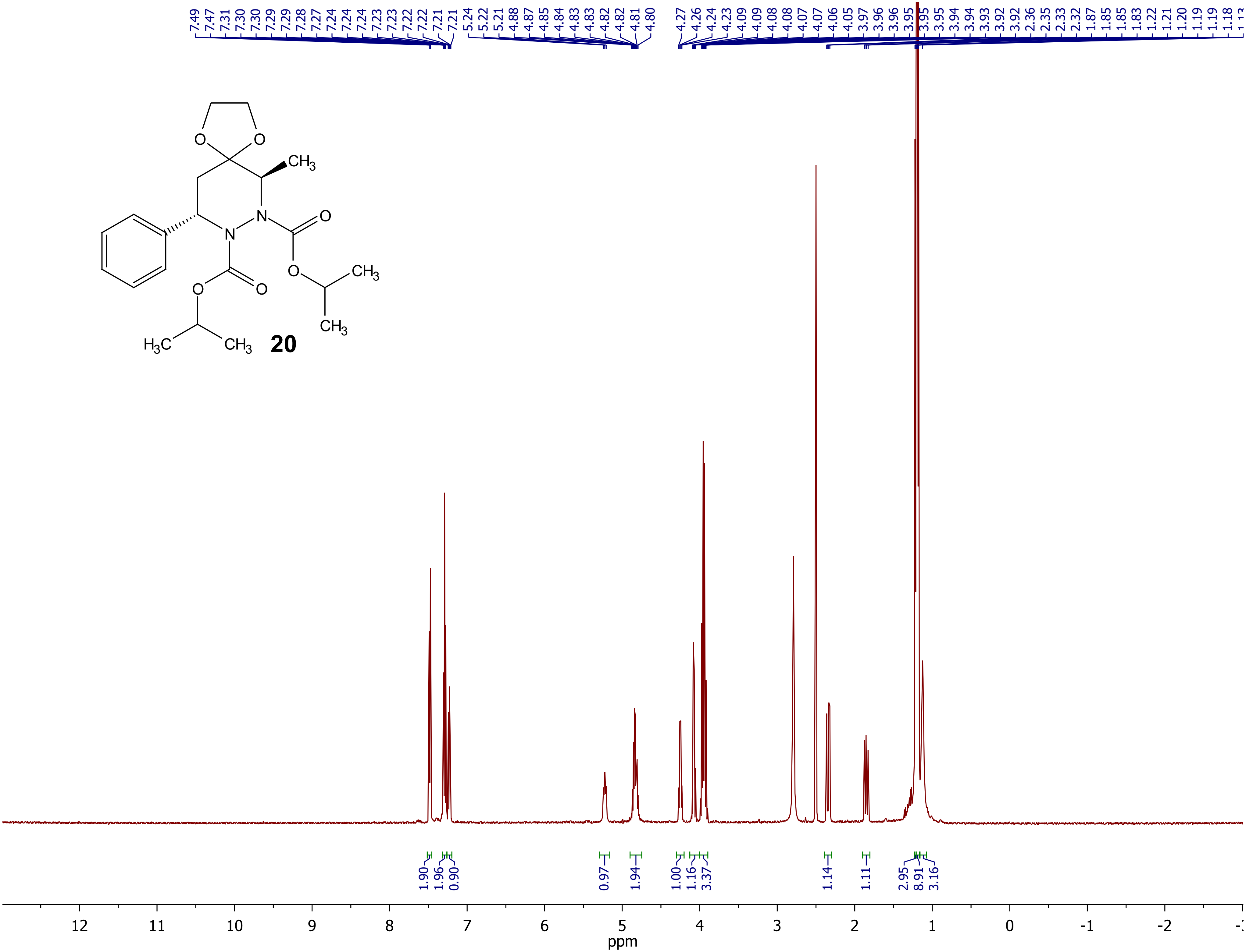
-10
-20
-30
ppm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7.24
7.23
7.23
7.22
7.22
7.21
7.21
5.24
5.22
5.21
4.88
4.87
4.85
4.84
4.83
4.83
4.82
4.82
4.81
4.80
4.27
4.26
4.24
4.23
4.09
4.09
4.08
4.08
4.07
4.07
4.06
4.05
3.97
3.96
3.96
3.95
3.95
3.95
3.94
3.94
3.93
3.92
3.92
2.36
2.35
2.33
2.32
1.87
1.85
1.85
1.83
1.22
1.21
1.20
1.19
1.19
1.18
O
O
CH3
N
N
O
O
O
O
CH3
CH3
H3C
CH3
20
1.90
1.96
0.90
0.97
1.94
1.00
1.16
3.37
1.14
1.11
2.95
8.91
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12
11
10
9
8
7
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3
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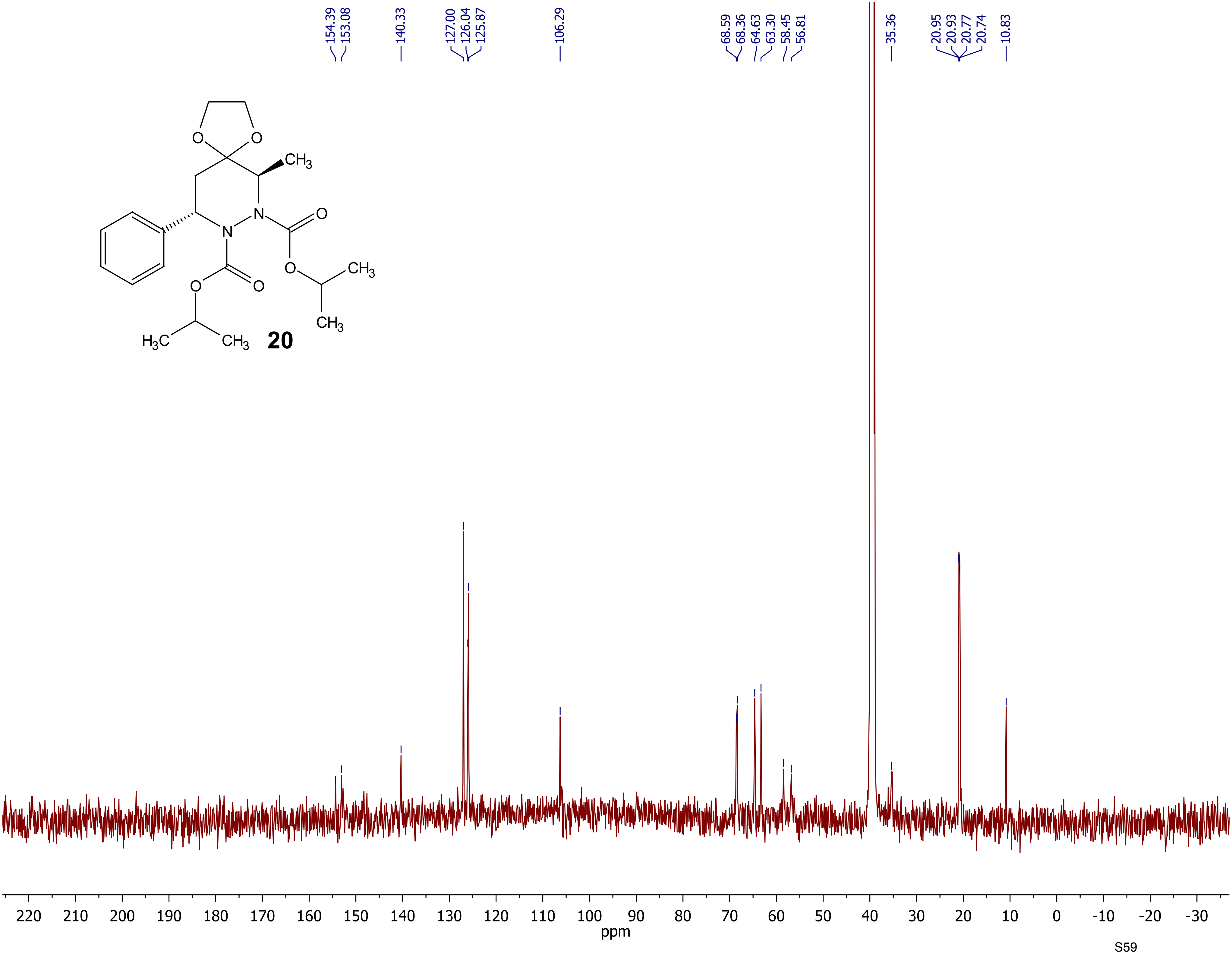
-1
-2
ppm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153.08
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126.04
125.87
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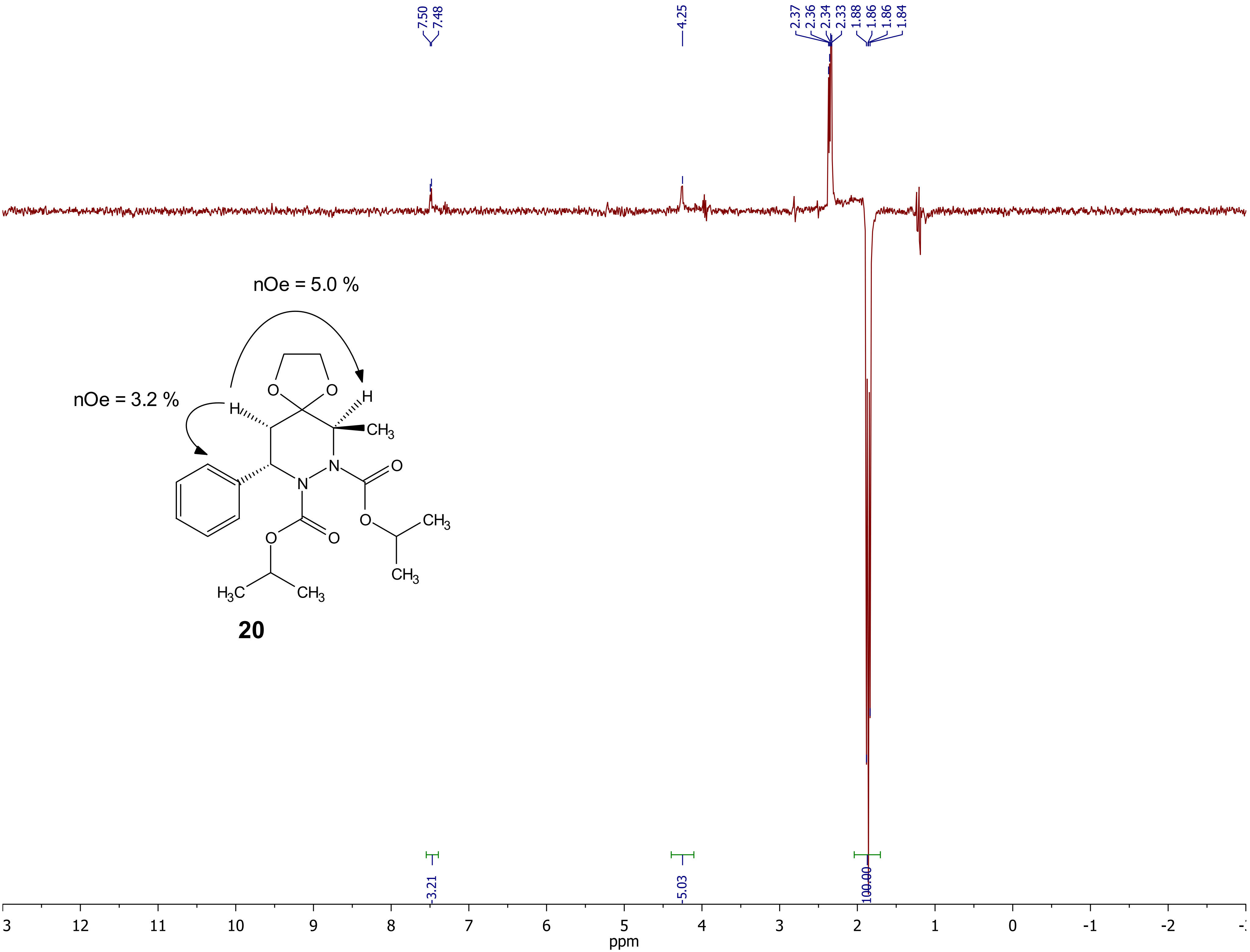
68.59
68.36
64.63
63.30
58.45
56.81
35.36
20.95
20.93
20.77
20.74
10.83
O
O
CH3
N
N
O
O
O
O
CH3
CH3
H3C
CH3
20
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm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7.48
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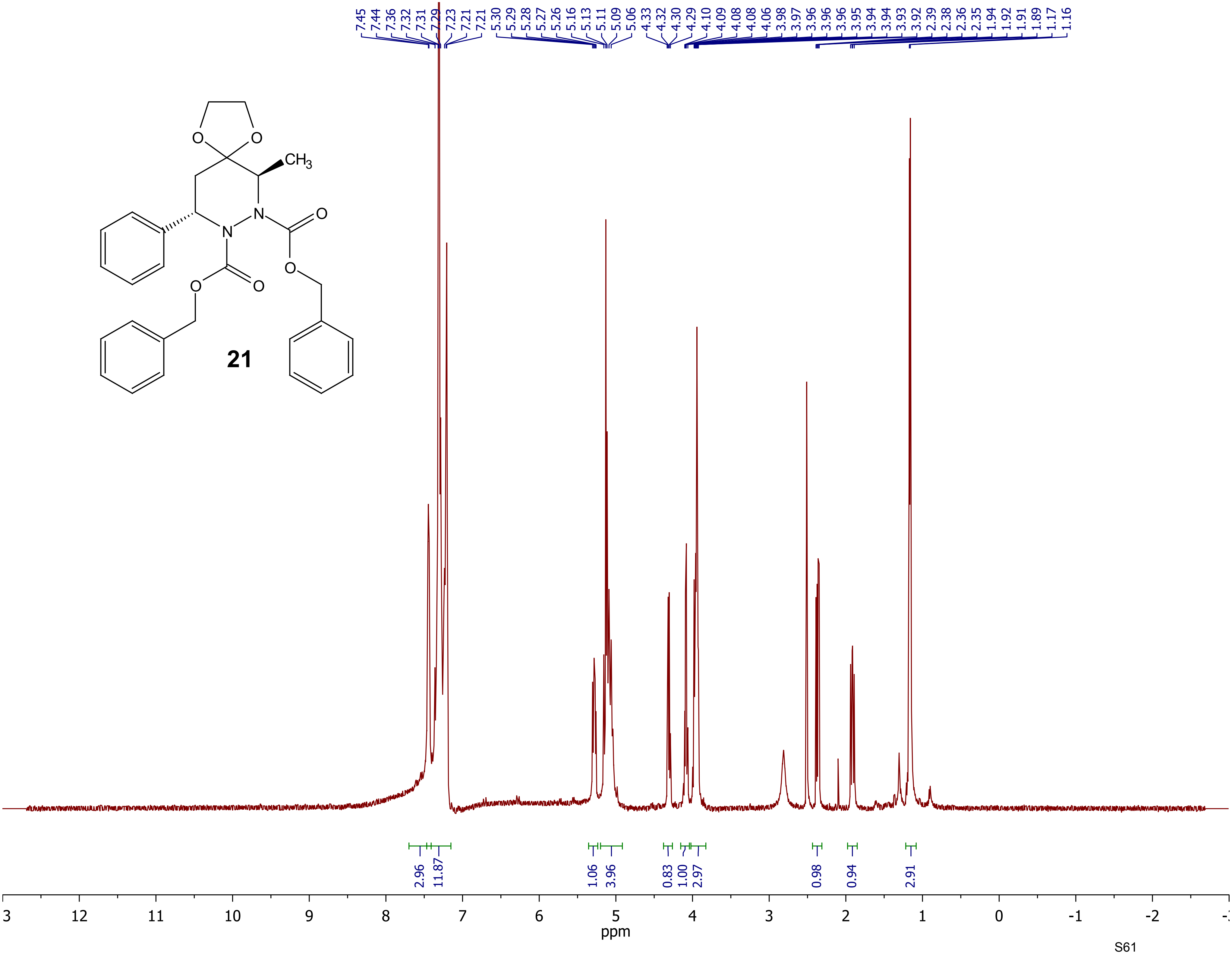
2.37
2.36
2.34
2.33
1.88
1.86
1.86
1.84
nOe = 5.0 %
nOe = 3.2 %
H
H
O
O
CH3
N
N
O
O
O
O
CH3
CH3
H3C
CH3
3.21
5.03
100.00
3
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm

20



21

O
O
CH3
N
N
O
O
O
O
7.45
7.44
7.36
7.32
7.31
7.29
7.23
7.21
7.21
5.30
5.29
5.28
5.27
5.26
5.16
5.13
5.11
5.09
5.06
4.33
4.32
4.30
4.29
4.10
4.09
4.08
4.08
4.06
3.98
3.97
3.96
3.96
3.96
3.95
3.94
3.94
3.93
3.92
2.39
2.38
2.36
2.35
1.94
1.92
1.91
1.89
1.17
1.16
2.96
11.87
1.06
3.96
0.83
1.00
2.97
0.98
0.94
2.91
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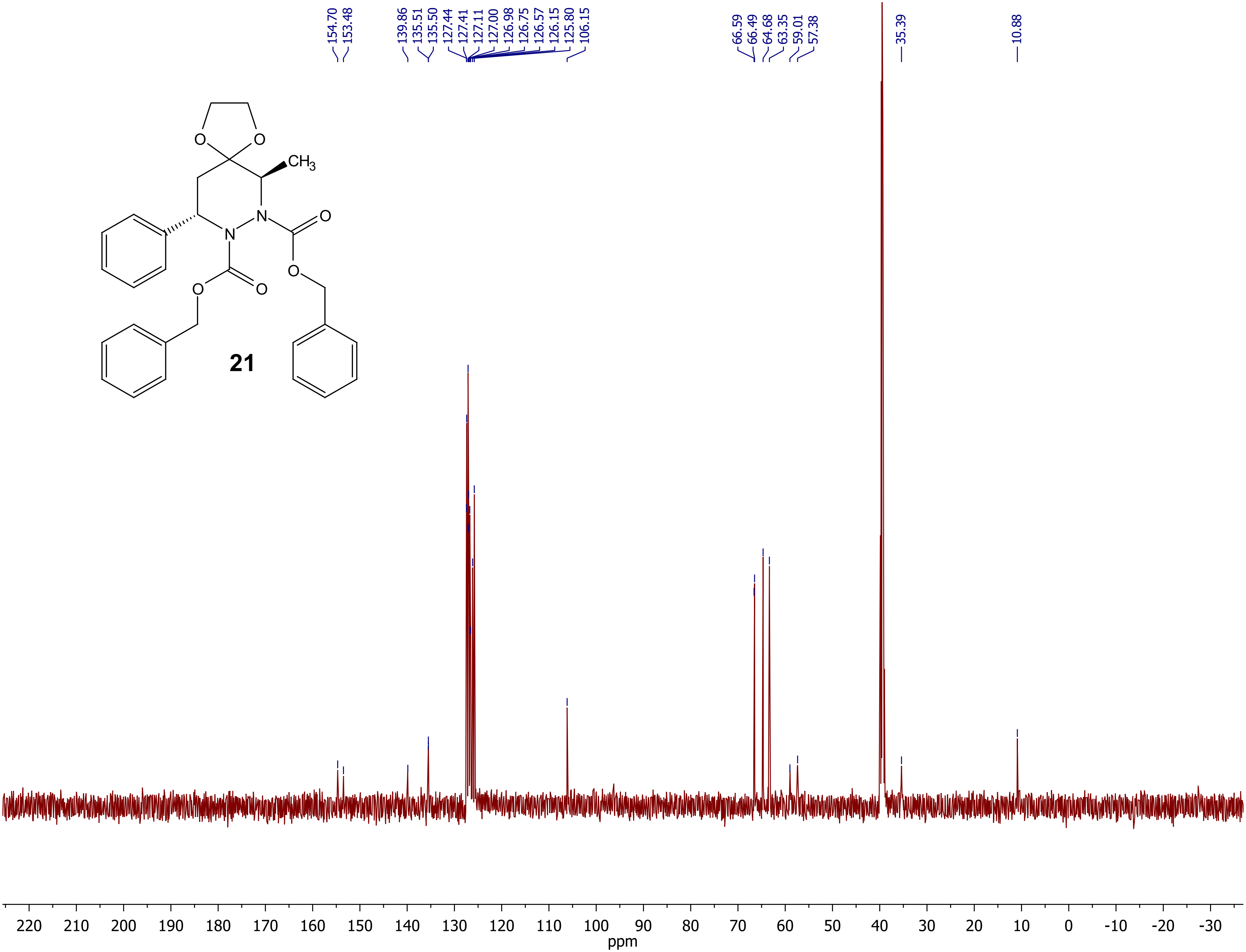
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm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135.50
127.44
127.41
127.11
127.00
126.98
126.75
126.57
126.15
125.80
106.15
66.59
66.49
64.68
63.35
59.01
57.38
35.39
10.88
O
O
CH3
N
N
O
O
O
O
220
210
200
190
180
170
160
150
140
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120
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80
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10
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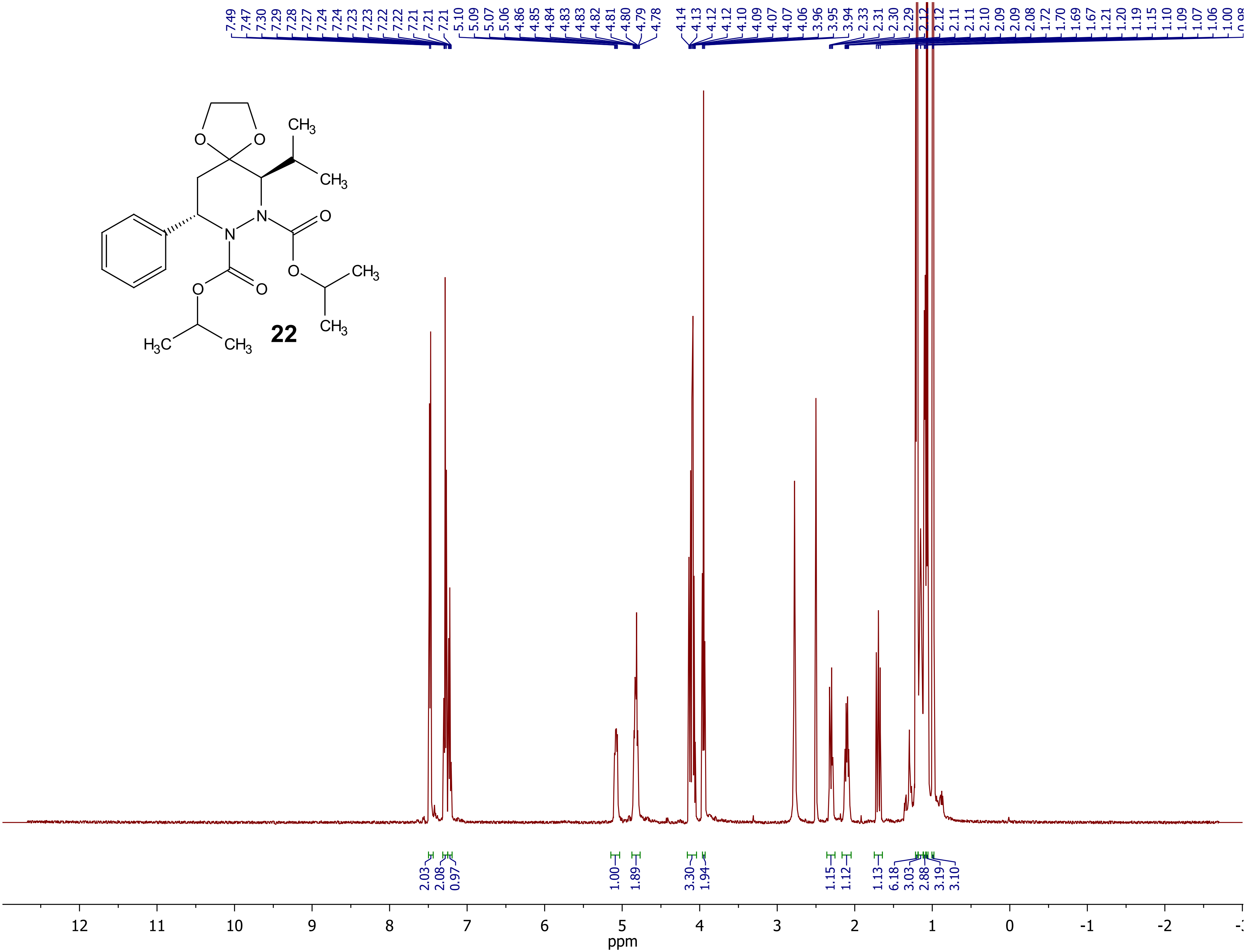
-10
-20
-30
ppm

21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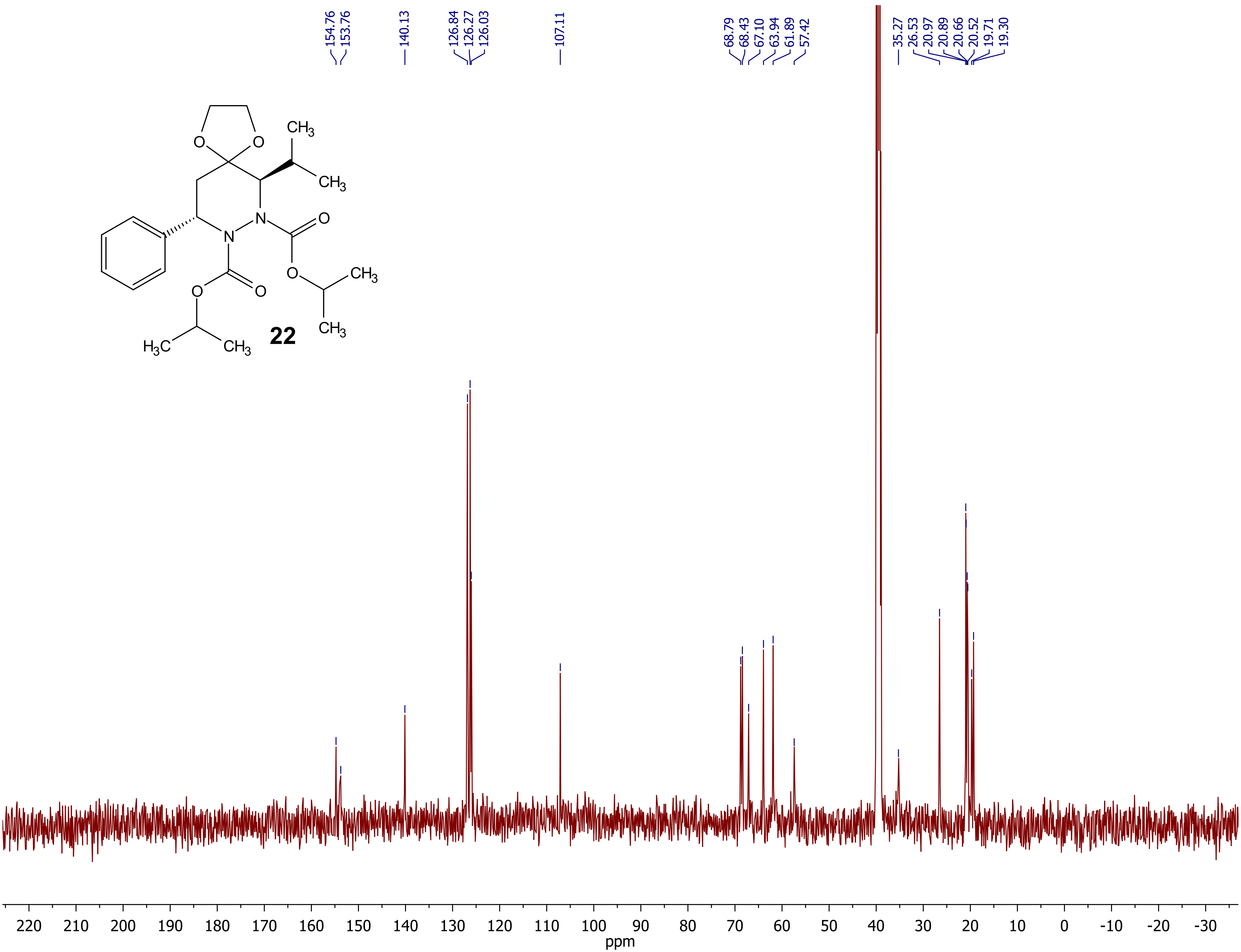
O
O
CH3
CH3
N
N
O
O
O
O
CH3
CH3
H3C
CH3
22
2.03
2.08
0.97
1.00
1.89
3.30
1.94
1.15
1.12
1.13
6.18
3.03
2.88
3.19
3.10
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm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126.03
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68.79
68.43
67.10
63.94
61.89
57.42
35.27
26.53
20.97
20.89
20.66
20.52
19.71
19.30
O
O
CH3
CH3
N
N
O
O
O
O
CH3
CH3
H3C
CH3
22
220
210
200
190
180
170
160
150
140
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120
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100
90
80
70
60
50
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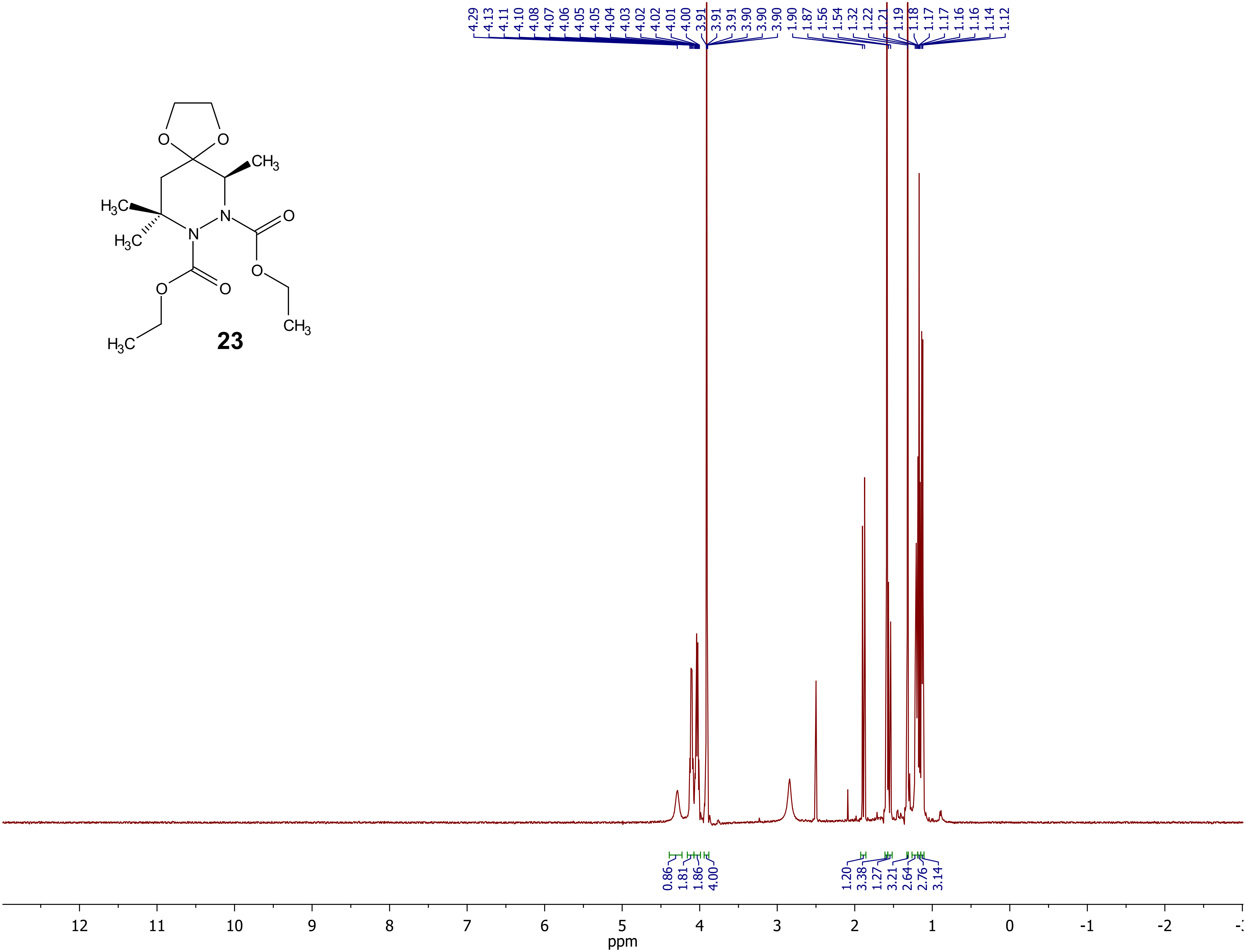
-20
-30
ppm



23

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4.06
4.05
4.05
4.04
4.03
4.02
4.02
4.01
4.00
3.91
3.91
3.91
3.90
3.90
3.90
1.90
1.87
1.56
1.54
1.32
1.22
1.21
1.19
1.18
1.17
1.17
1.16
1.16
1.14
1.12
0.86
1.81
1.86
4.00
1.20
3.38
1.27
3.21
2.64
2.76
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12
11
10
9
8
7
6
5
4
3
2
1
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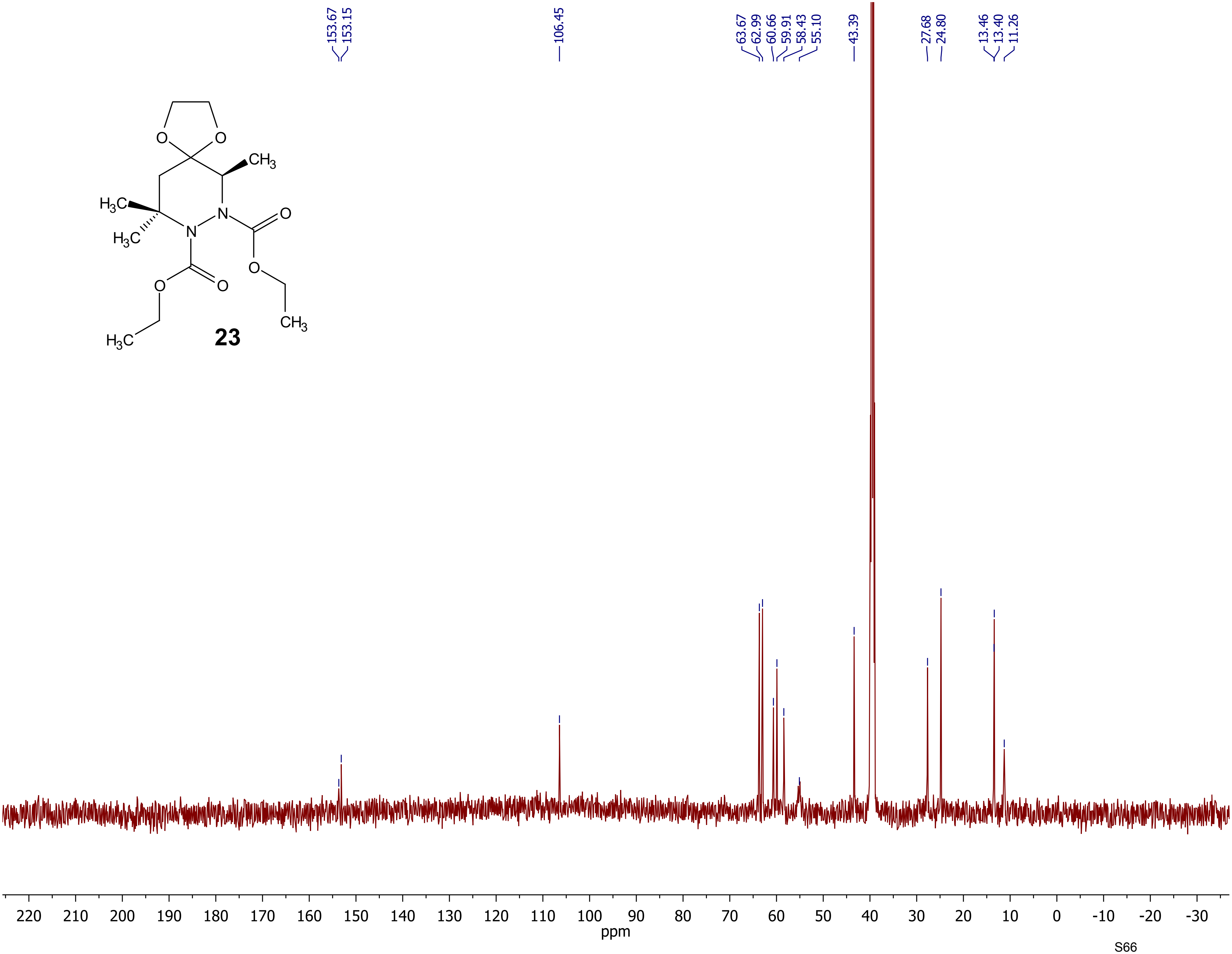
-1
-2
ppm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59.91
58.43
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43.39
27.68
24.80
13.46
13.40
11.26
O
O
CH3
H3C
H3C
N
N
O
O
O
O
CH3
H3C
23
220
210
200
190
180
170
160
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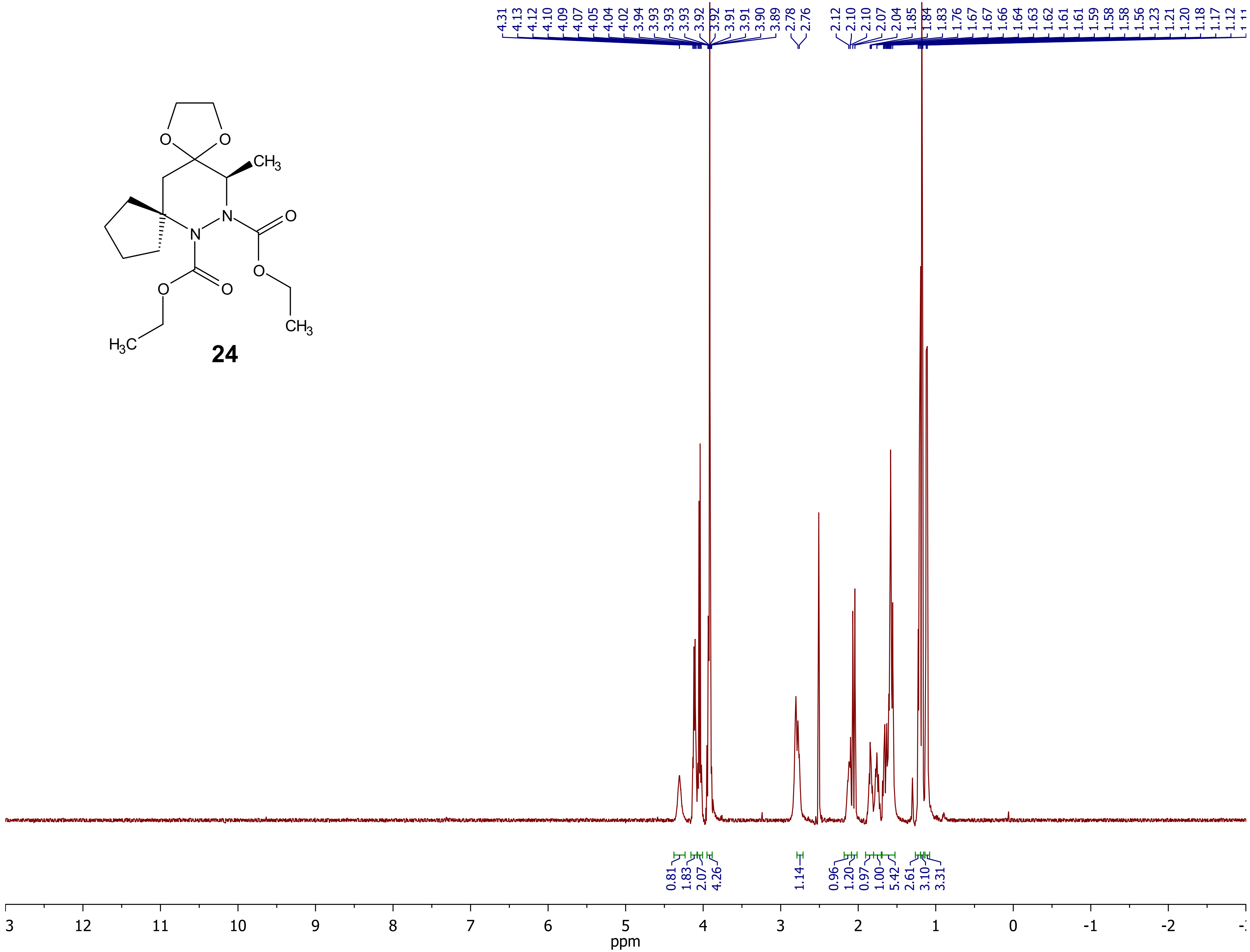
-20
-30
ppm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4.07
4.05
4.04
4.02
3.94
3.93
3.93
3.93
3.92
3.92
3.91
3.91
3.90
3.89
2.78
2.76
2.12
2.10
2.10
2.07
2.04
1.85
1.84
1.83
1.76
1.67
1.67
1.66
1.64
1.63
1.62
1.61
1.61
1.59
1.58
1.58
1.56
1.23
1.21
1.20
1.18
1.17
1.12
O
O
CH3
N
N
O
O
O
O
CH3
H3C
0.81
1.83
2.07
4.26
1.14
0.96
1.20
0.97
1.00
5.42
2.61
3.10
3.31
3
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10
9
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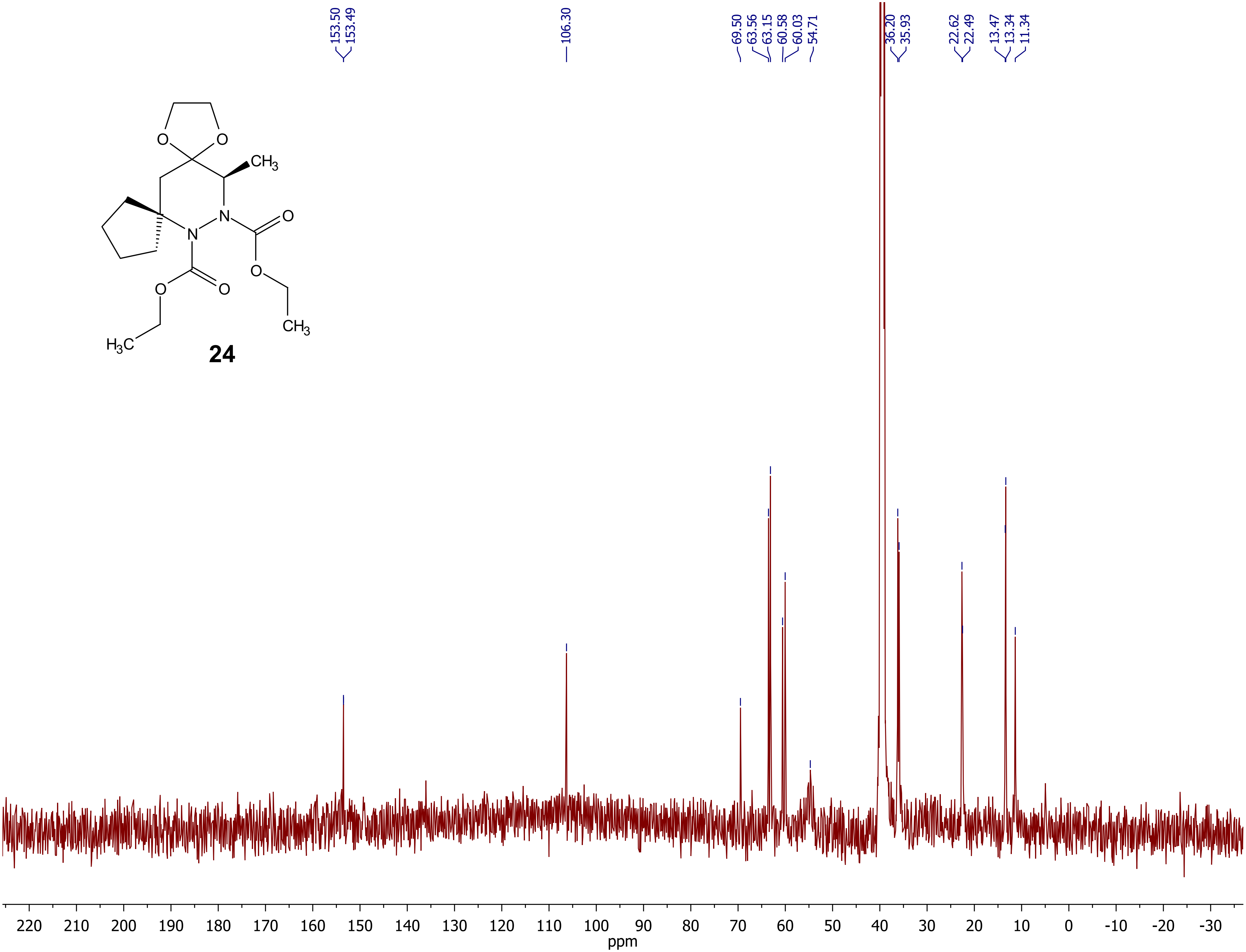
7
6
5
4
3
2
1
0
-1
-2
ppm

24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60.58
60.03
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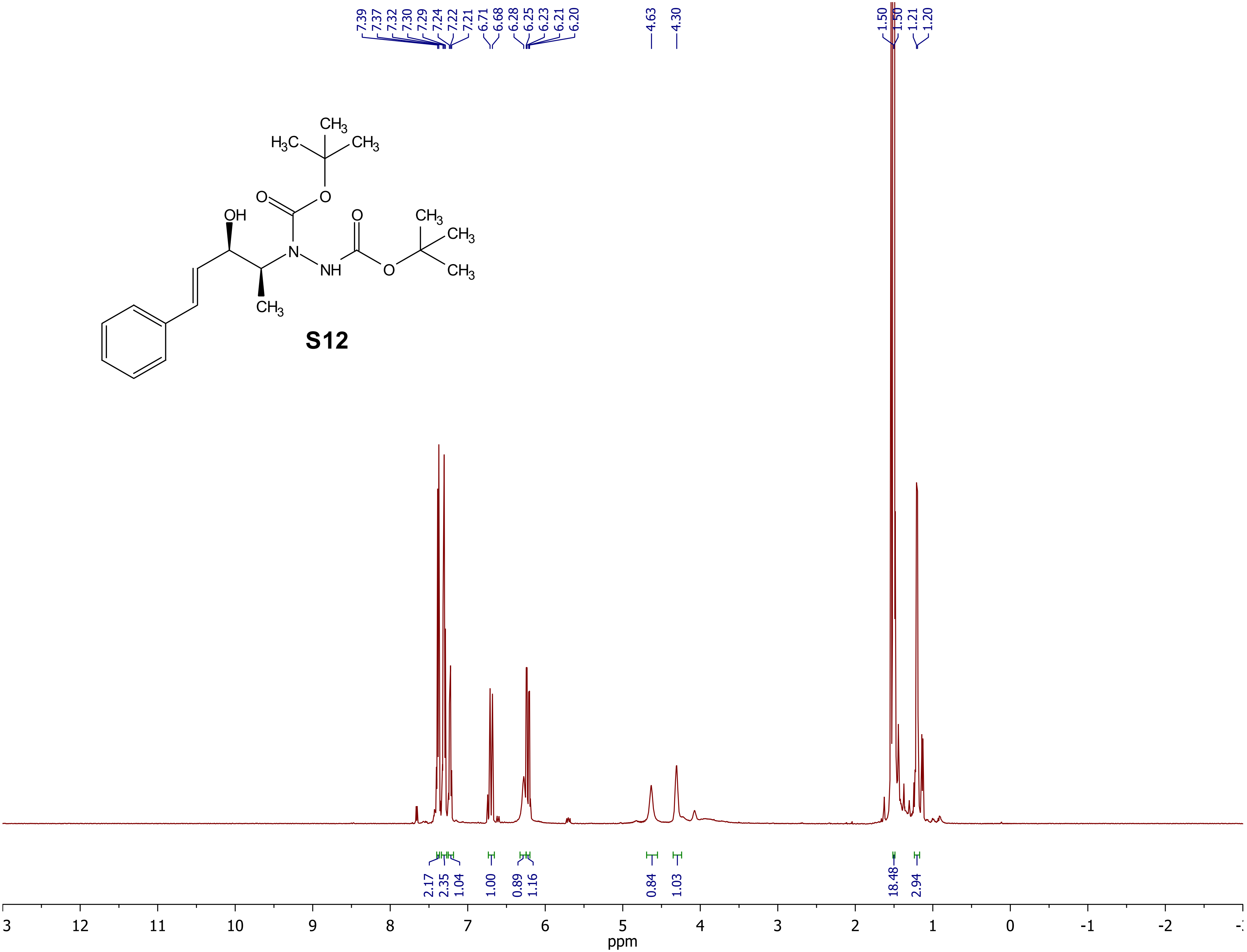
36.20
35.93
22.62
22.49
13.47
13.34
11.34
O
O
CH3
N
N
O
O
O
O
H3C
CH3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm

24



S12

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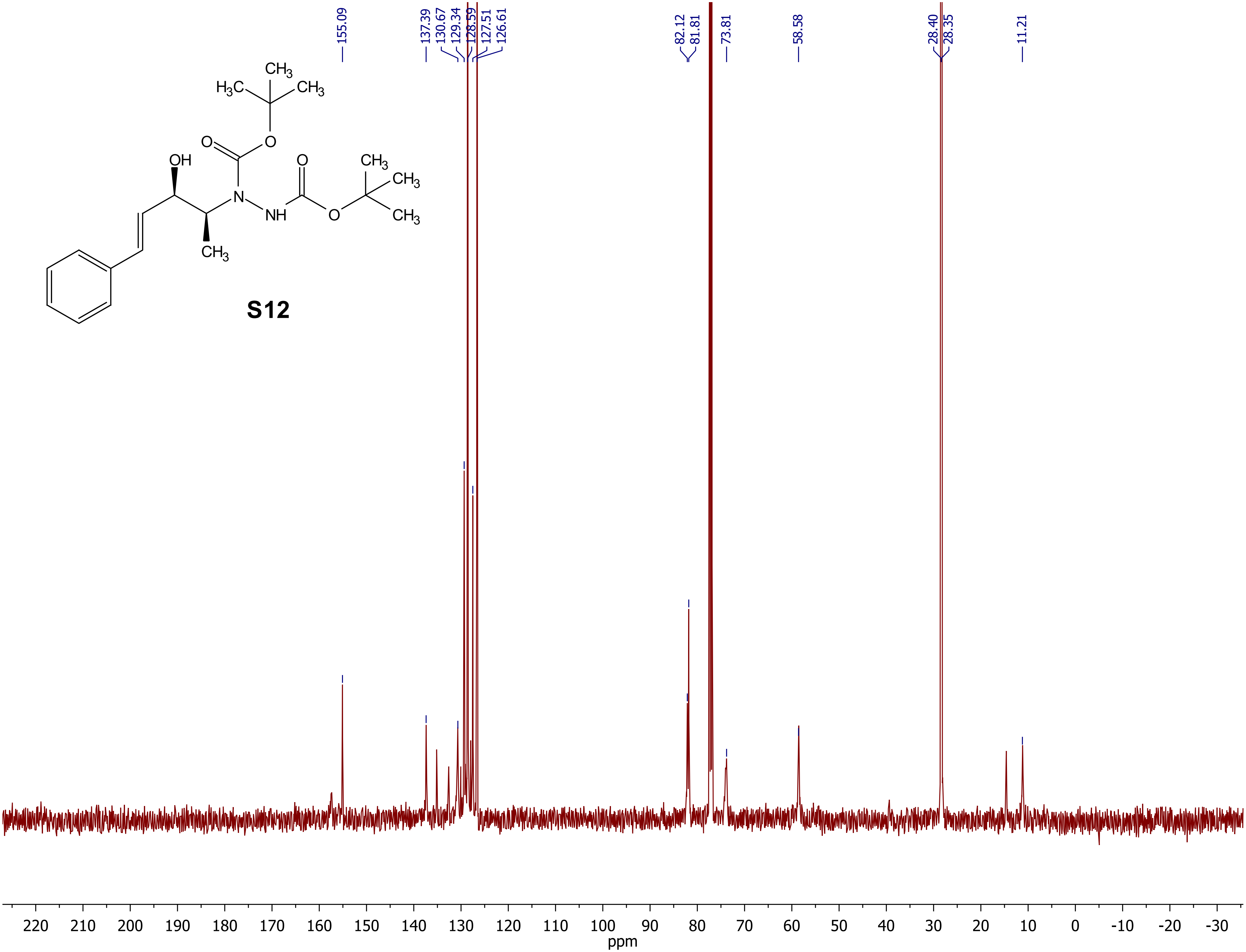
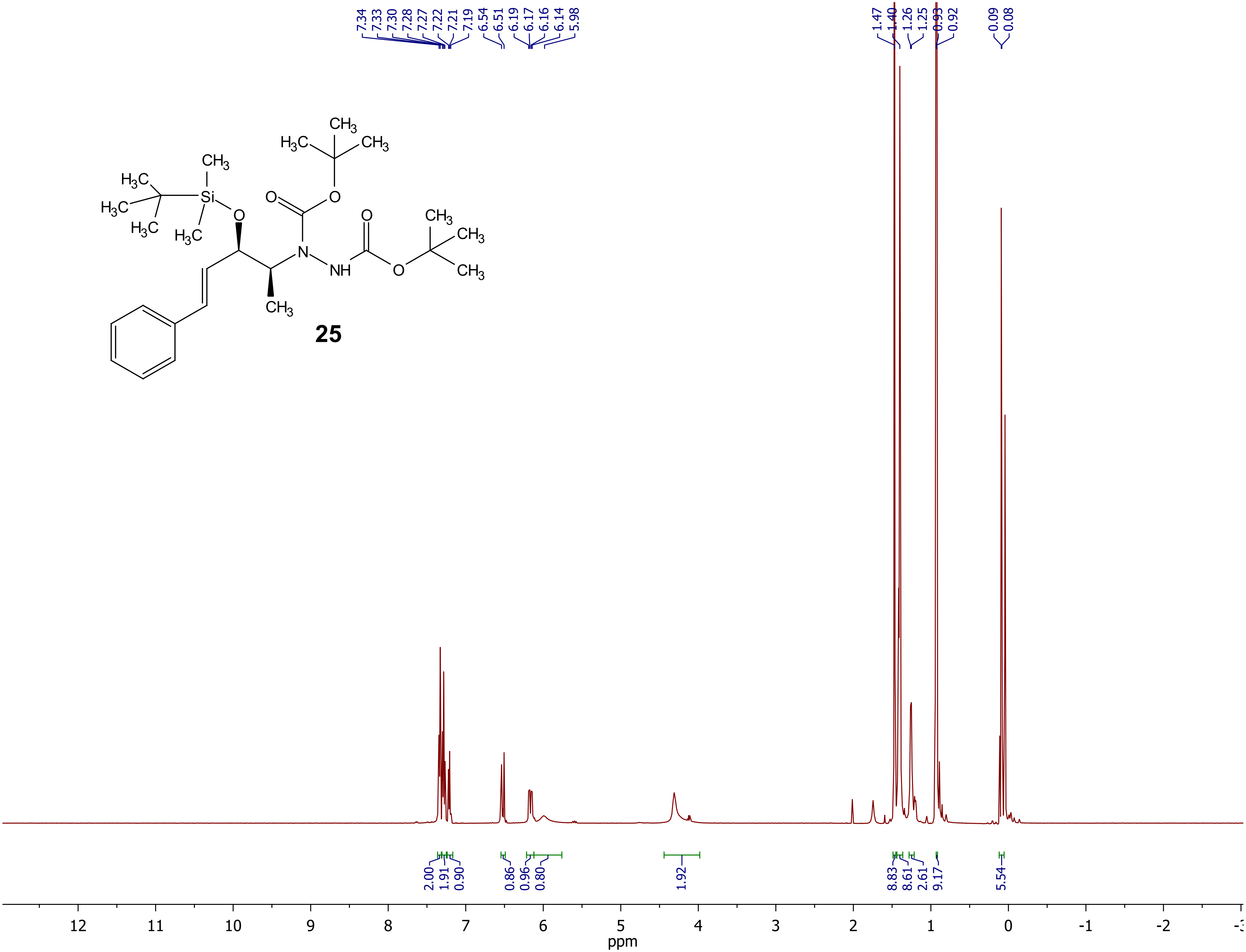
7.37
7.32
7.30
7.29
7.24
7.22
7.21
6.71
6.68
6.28
6.25
6.23
6.21
6.20
4.63
4.30
1.50
1.50
1.21
1.20
2.17
2.35
1.04
1.00
0.89
1.16
0.84
1.03
18.48
2.94
CH3
H3C
CH3
O
O
OH
O
CH3
CH3
N
NH
O
CH3
CH3
3
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm



S12

155.09
137.39
130.67
129.34
128.59
127.51
126.61
82.12
81.81
73.81
58.58
28.40
28.35
11.21
OH
O
N
NH
CH3
H3C
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm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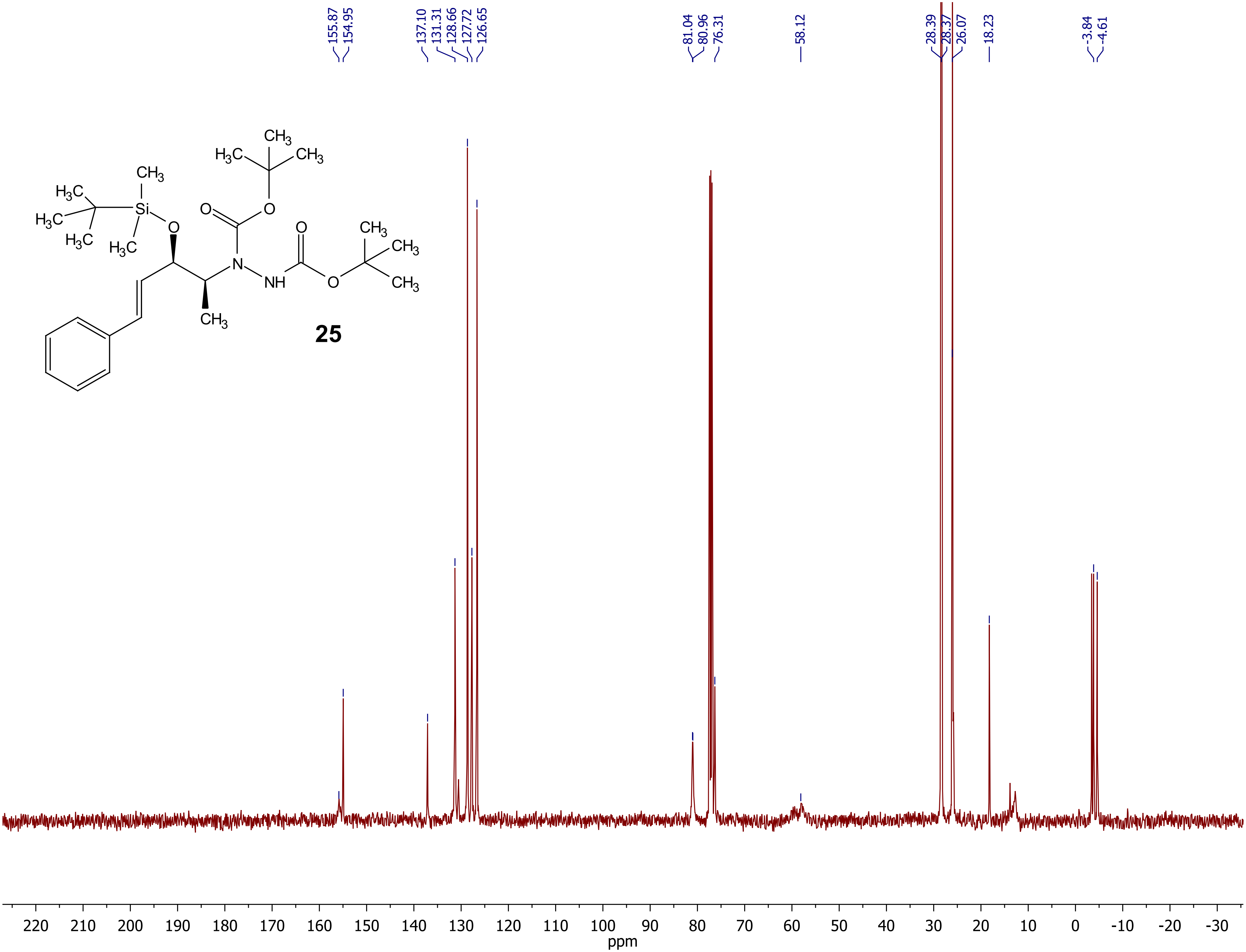
7.33
7.30
7.28
7.27
7.22
7.21
7.19
6.54
6.51
6.19
6.17
6.16
6.14
5.98
1.47
1.40
1.26
1.25
0.93
0.92
0.09
0.08
25
2.00
1.91
0.90
0.86
0.96
0.80
1.92
8.83
8.61
2.61
9.17
5.54
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm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128.66
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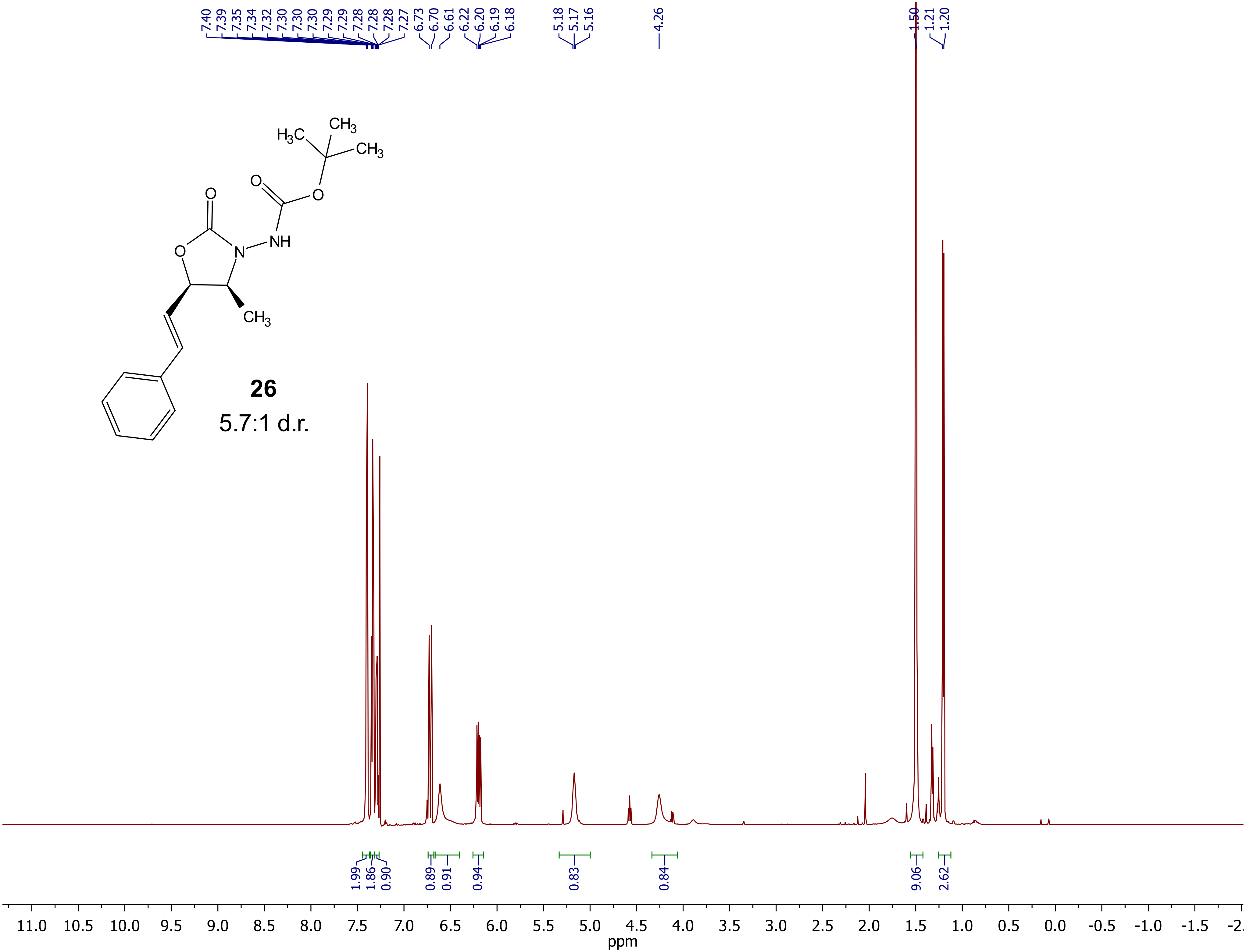
81.04
80.96
76.31
58.12
28.39
28.37
26.07
18.23
-3.84
-4.61
25
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm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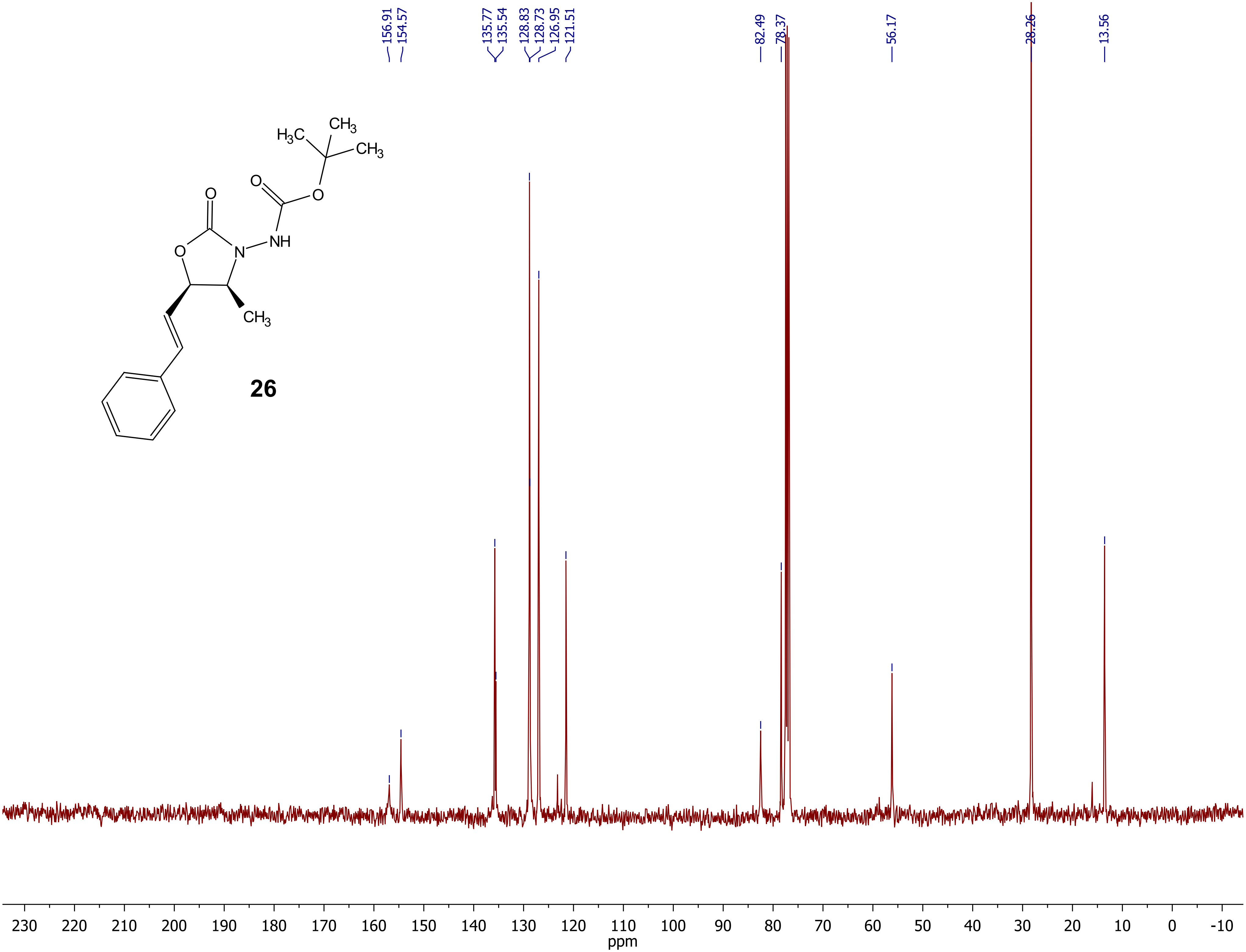
7.34
7.32
7.30
7.30
7.30
7.29
7.29
7.28
7.28
7.28
7.27
6.73
6.70
6.61
6.22
6.20
6.19
6.18
5.18
5.17
5.16
4.26
1.50
1.21
1.20
H_3C
CH_3
CH_3
O
O
O
O
N
NH
CH_3
1.99
1.86
0.90
0.89
0.91
0.94
0.83
0.84
9.06
2.62
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.
ppm

26

5.7:1 d.r.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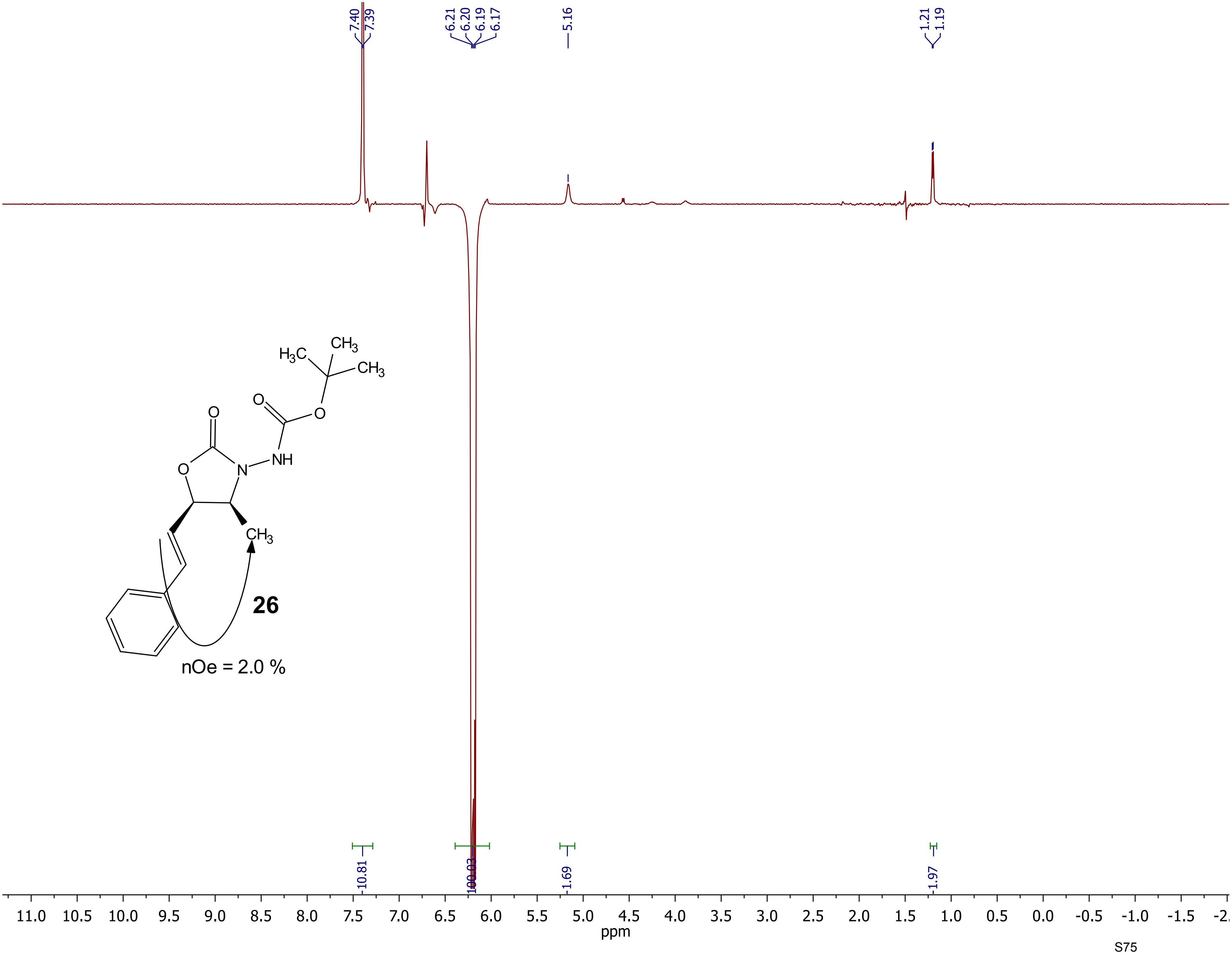
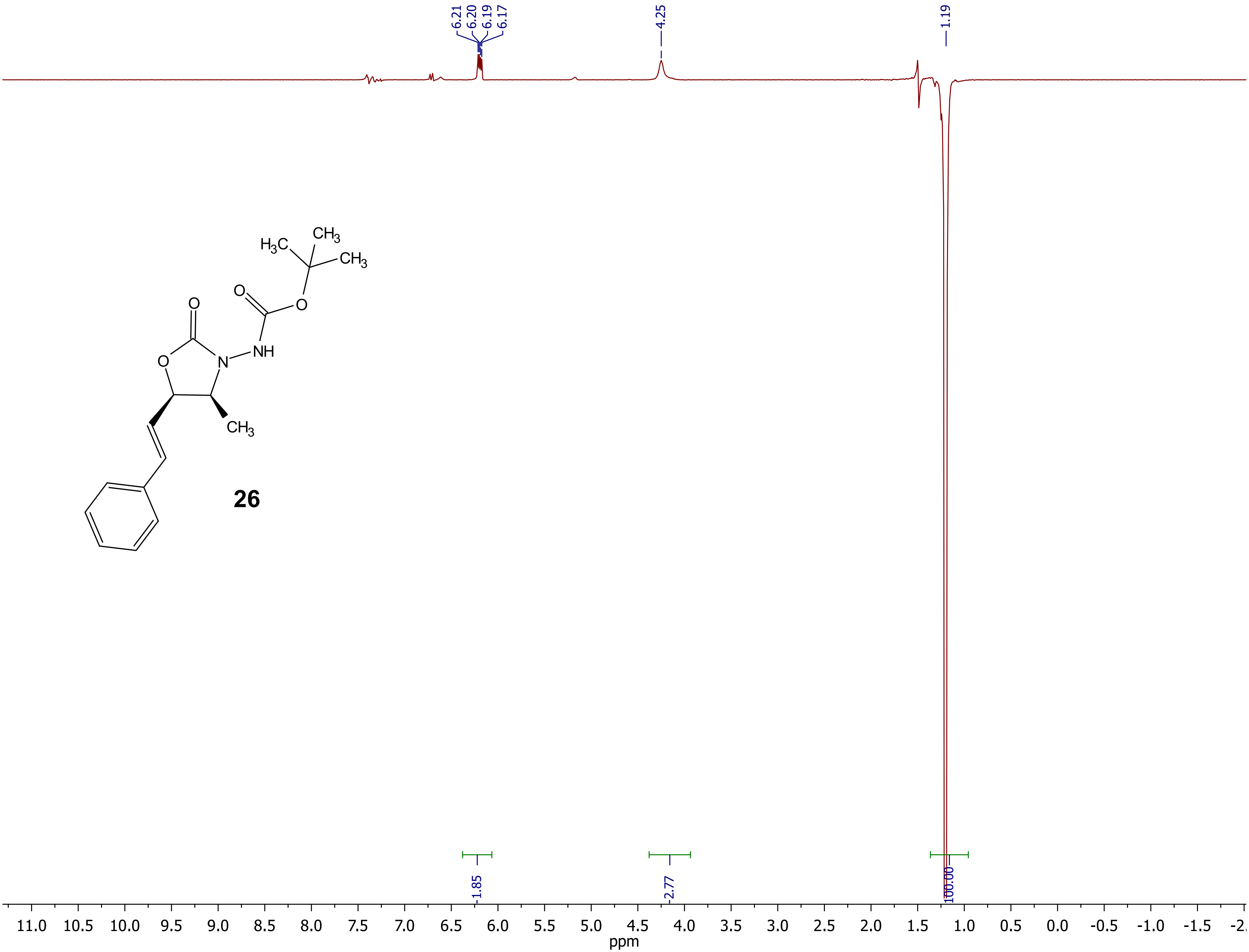
154.57
135.77
135.54
128.83
128.73
126.95
121.51
82.49
78.37
56.17
28.26
13.56
H3C
CH3
CH3
O
O
O
NH
N
O
CH3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

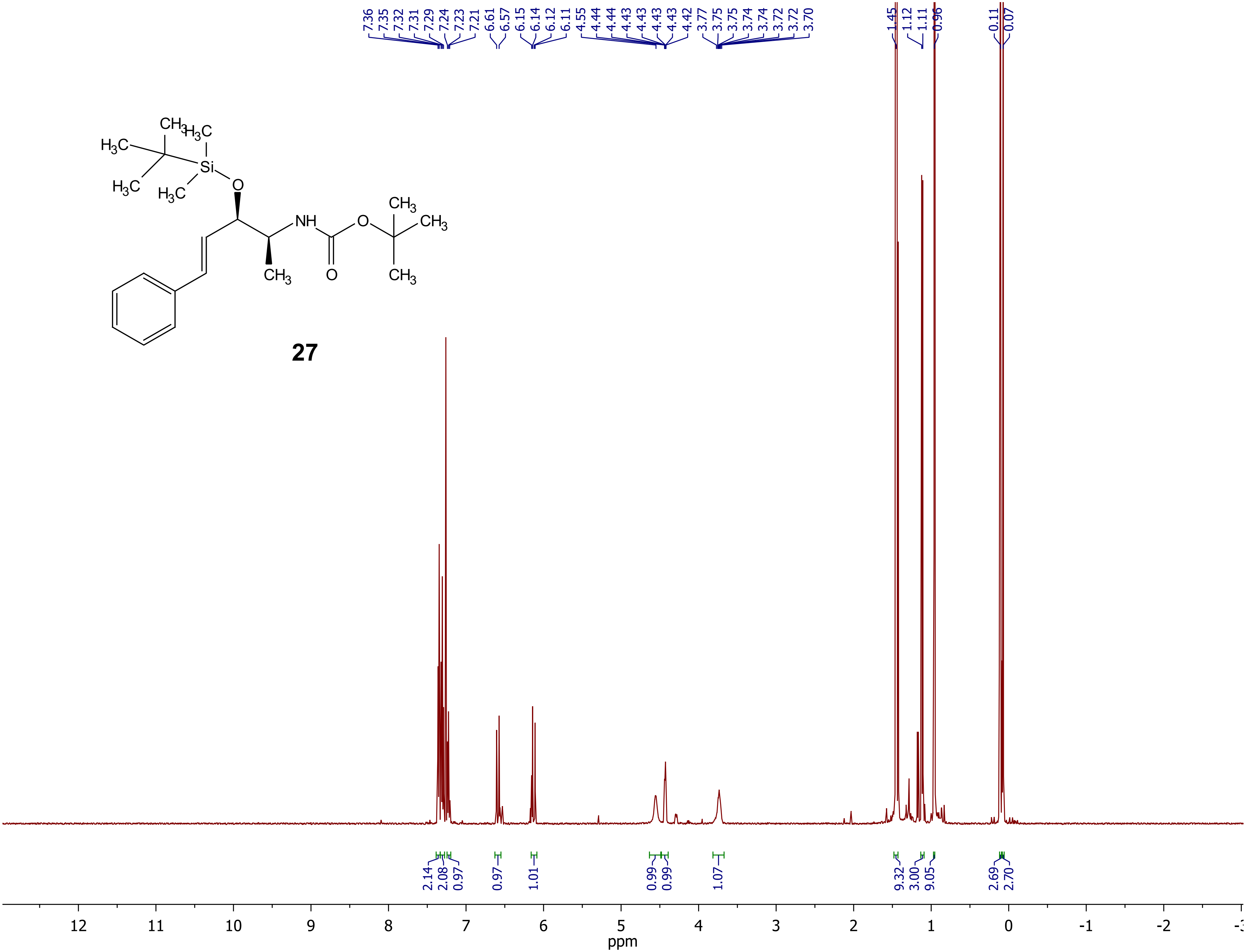
26


7.40
7.39
6.21
6.20
6.19
6.17
5.16
1.21
1.19
10.81
100.03
1.69
1.97
11.0
10.5
10.0
9.5
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
-1.0
-1.5
-2.
ppm
H3C
CH3
CH3
O
O
O
O
N
NH
CH3

26

nOe = 2.0 %


6.21
6.20
6.19
6.17
4.25
1.19
H3C
CH3
CH3
O
O
O
O
N
NH
CH3
26
1.85
2.77
100.00
11.0 10.5 10.0 9.5 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 -1.0 -1.5 -2.
ppm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6.11
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4.44
4.44
4.43
4.43
4.43
4.43
4.42
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3.75
3.74
3.74
3.72
3.72
3.70
1.45
1.12
1.11
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0.11
0.07
2.14
2.08
0.97
0.97
1.01
0.99
0.99
1.07
9.32
3.00
9.05
2.69
2.70
12
11
10
9
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7
6
5
4
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2
1
0
-1
-2
-3
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H3C
Si
O
H3C
H3C
NH
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CH3
CH3
CH3
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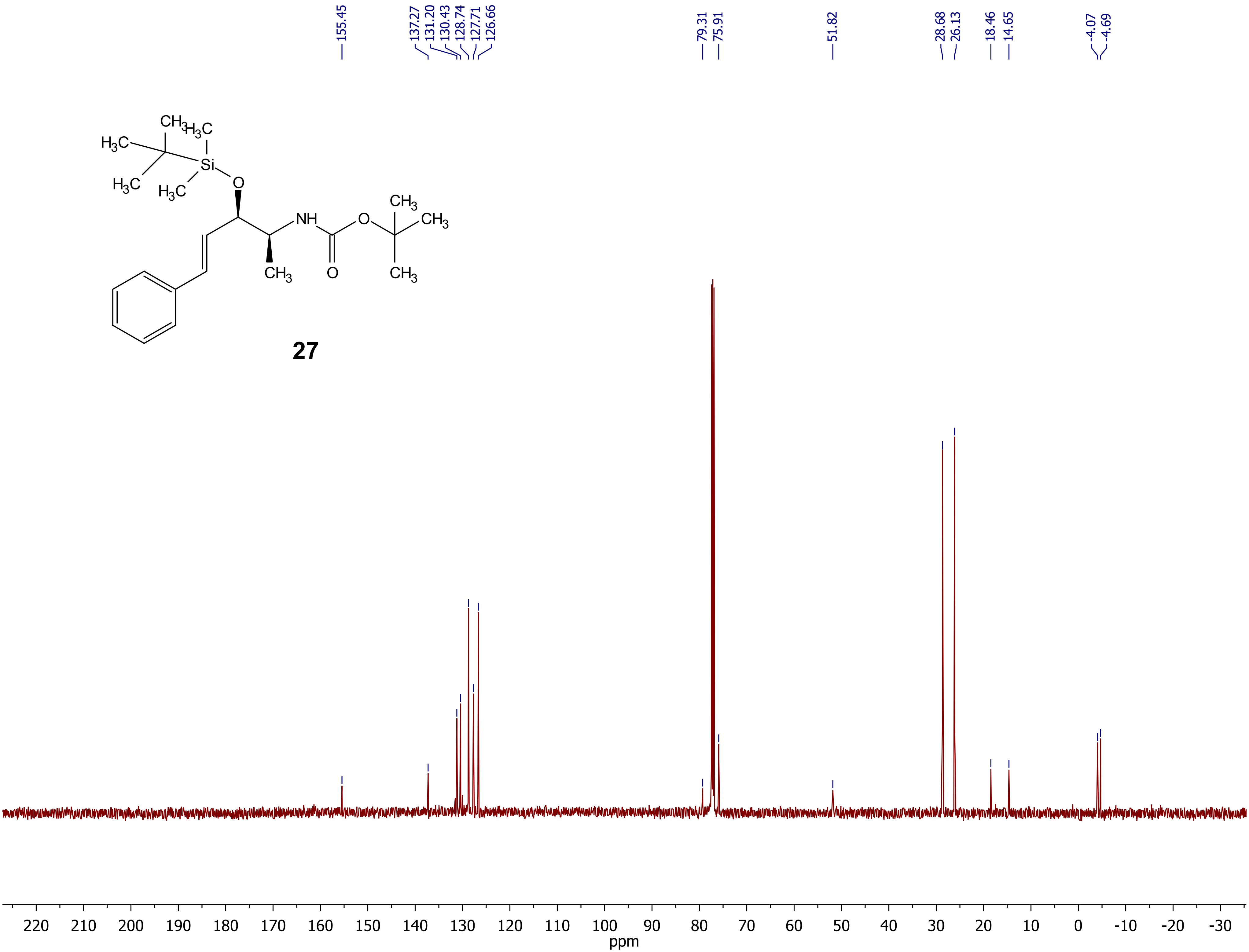
CH3
27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14.65
-4.07
-4.69
CH3
H3C
H3C
Si
O
H3C
H3C
NH
O
CH3
CH3
CH3
CH3
O
220
210
200
190
180
170
160
150
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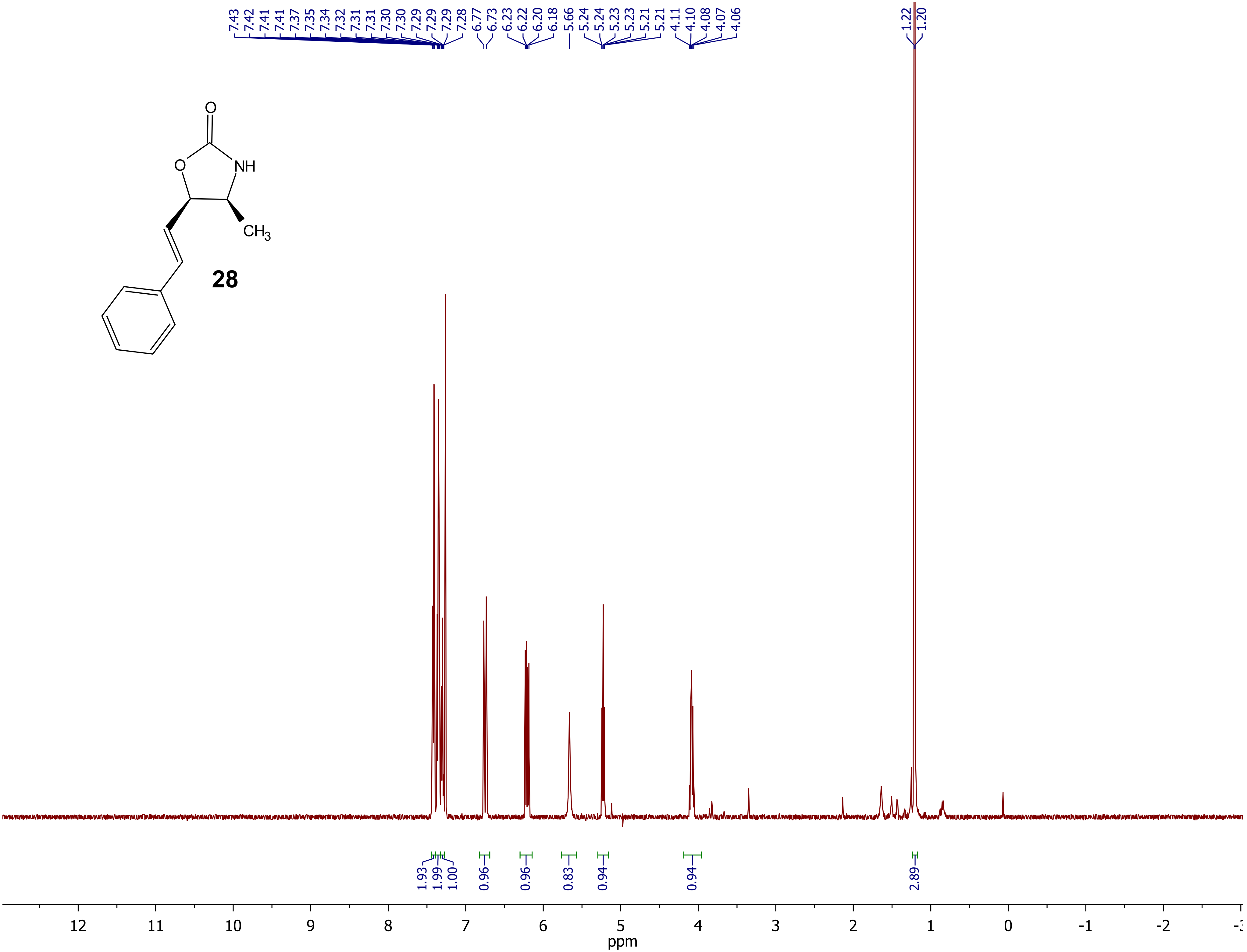
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6.22
6.20
6.18
5.66
5.24
5.24
5.23
5.23
5.21
5.21
4.11
4.10
4.08
4.07
4.06
1.22
1.20
O
O
NH
CH3
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1.99
1.00
0.96
0.96
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0.94
0.94
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-2
-3
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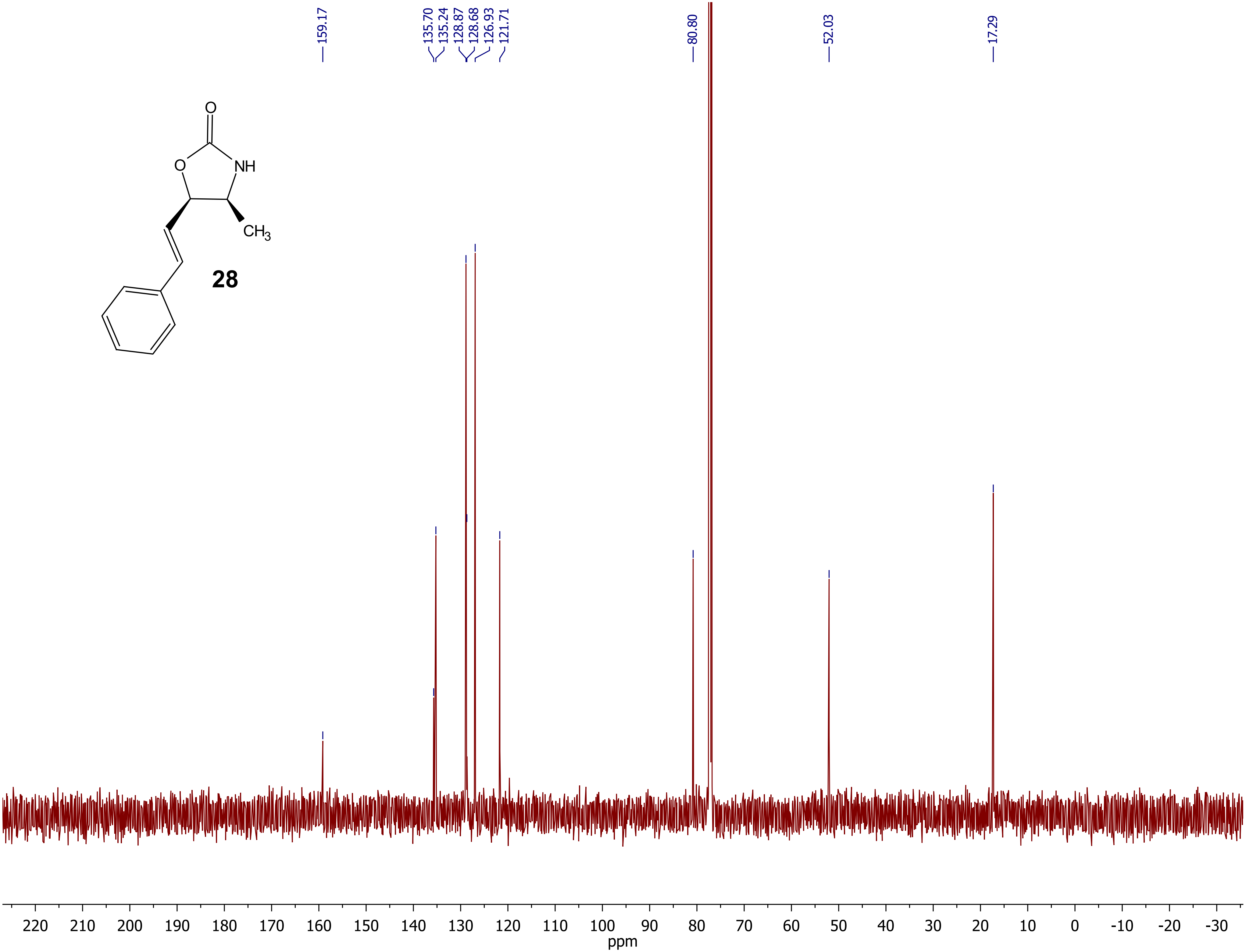
28



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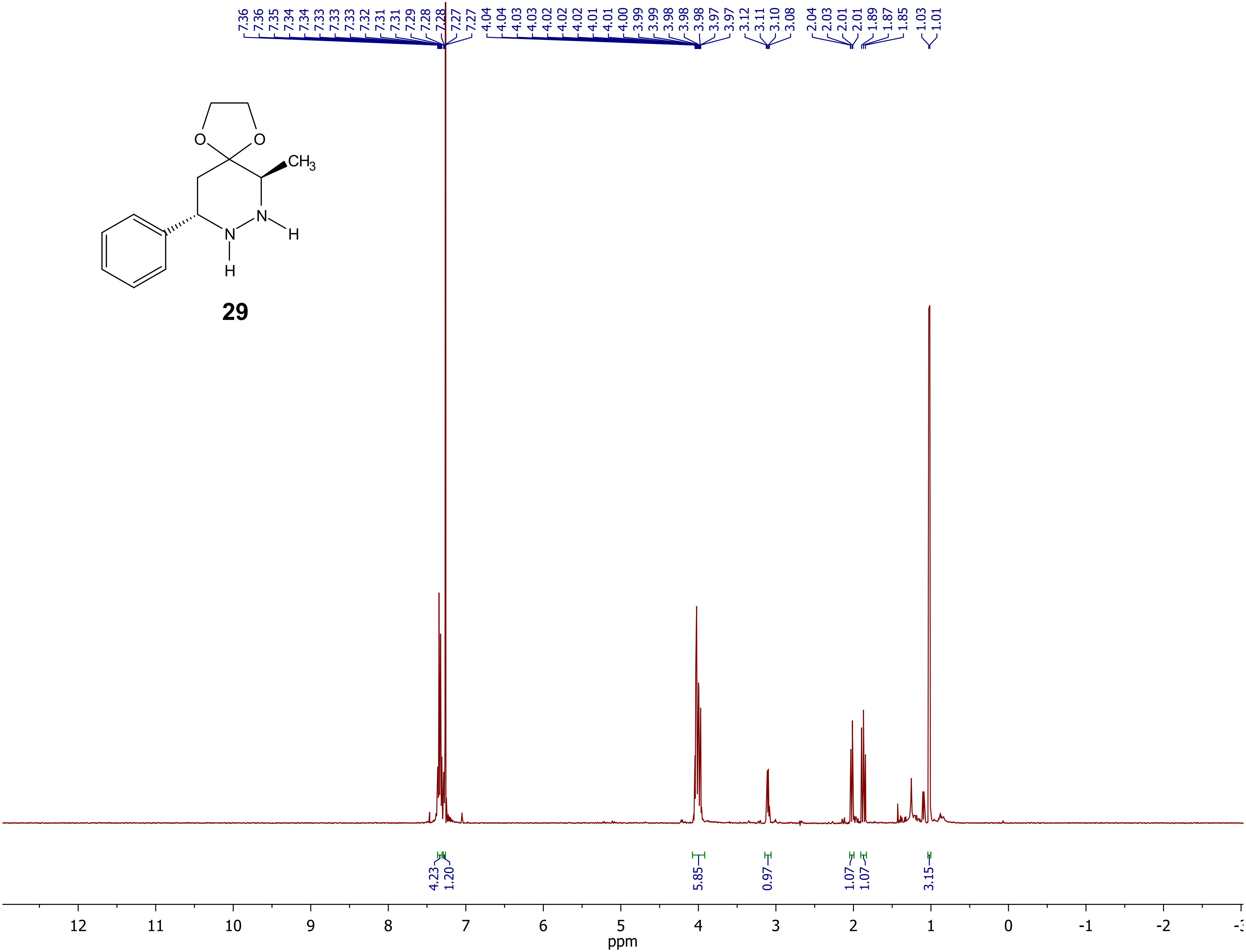
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7.28
7.28
7.27
7.27
4.04
4.04
4.03
4.03
4.02
4.02
4.02
4.01
4.01
4.00
3.99
3.99
3.98
3.98
3.98
3.97
3.97
3.12
3.11
3.10
3.08
2.04
2.03
2.01
2.01
1.89
1.87
1.85
1.03
1.01
O
O
CH3
N
H
N
H
4.23
1.20
5.85
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1.07
1.07
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-2
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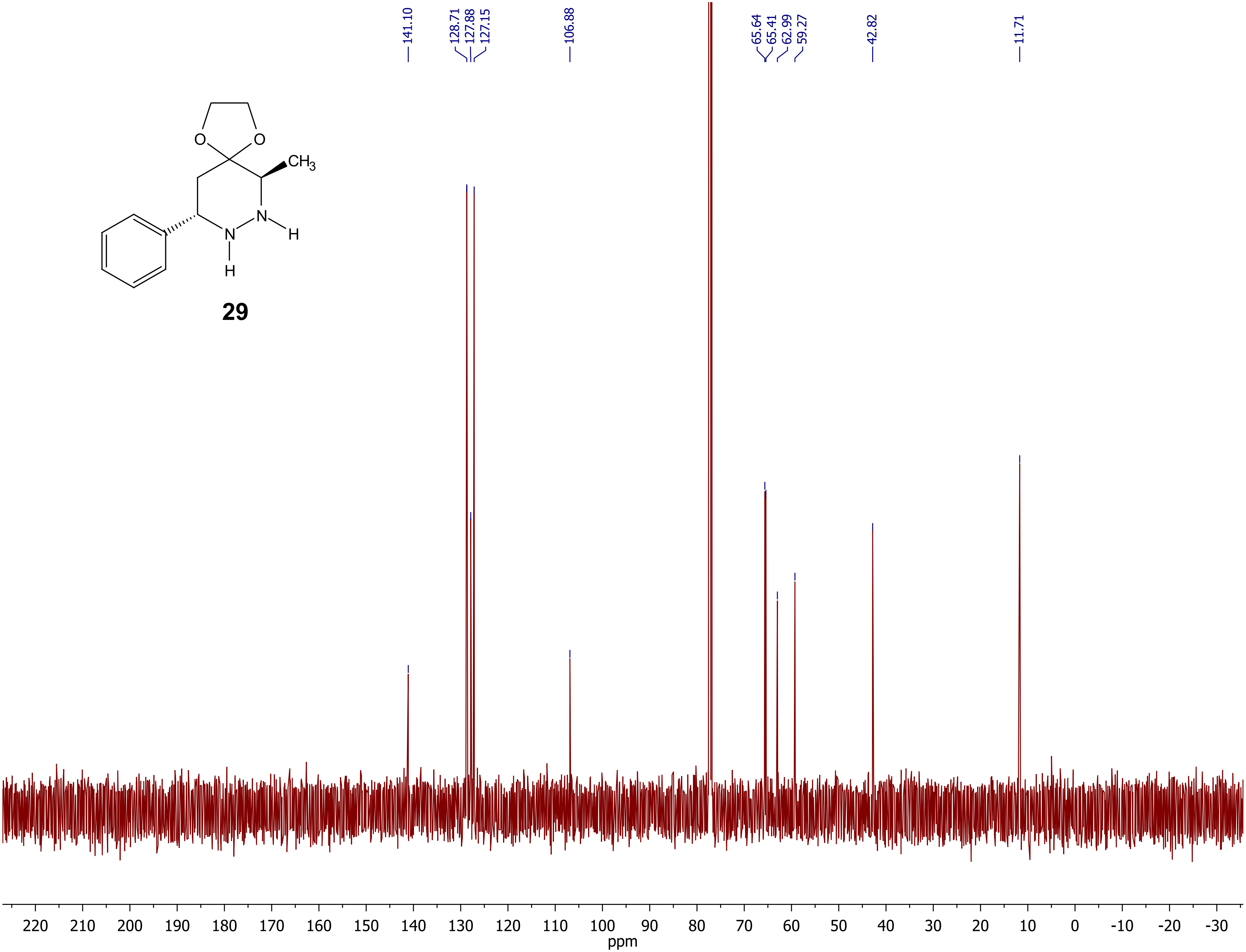
ppm

29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42.82
11.71
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O
CH3
N
H
N
H
220
210
200
190
180
170
160
150
140
130
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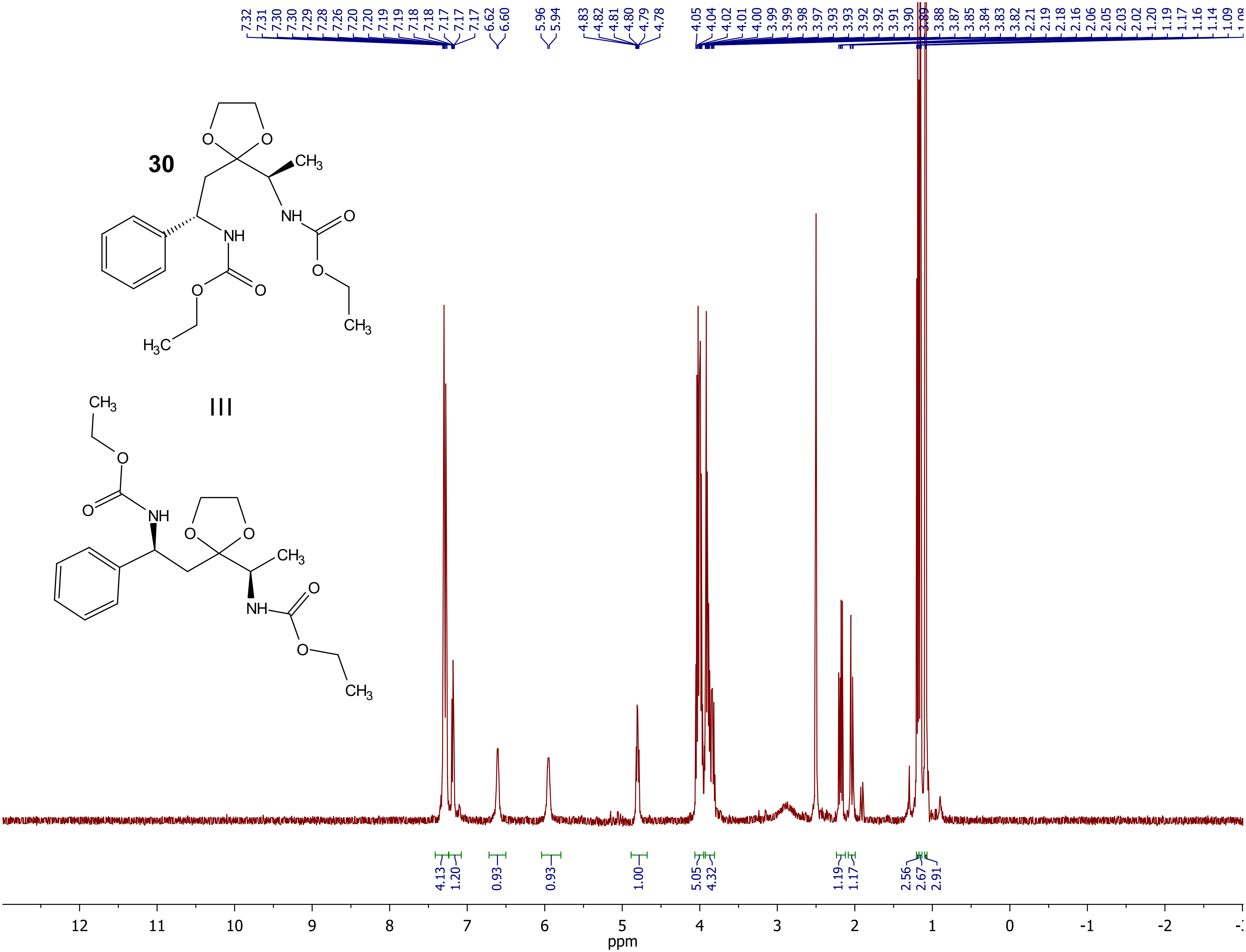
29

30

III



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NH
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NH
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H3C
CH3
CH3
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O
NH
O
O
CH3
NH
O
O
CH3
7.32
7.31
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7.28
7.26
7.20
7.20
7.19
7.19
7.18
7.18
7.17
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7.17
6.62
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5.94
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4.79
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4.04
4.02
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3.92
3.91
3.90
3.89
3.88
3.87
3.85
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2.19
2.18
2.16
2.06
2.05
2.03
2.02
1.20
1.19
1.17
1.16
1.14
1.09
1.0
4.13
1.20
0.93
0.93
1.00
5.05
4.32
1.19
1.17
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10
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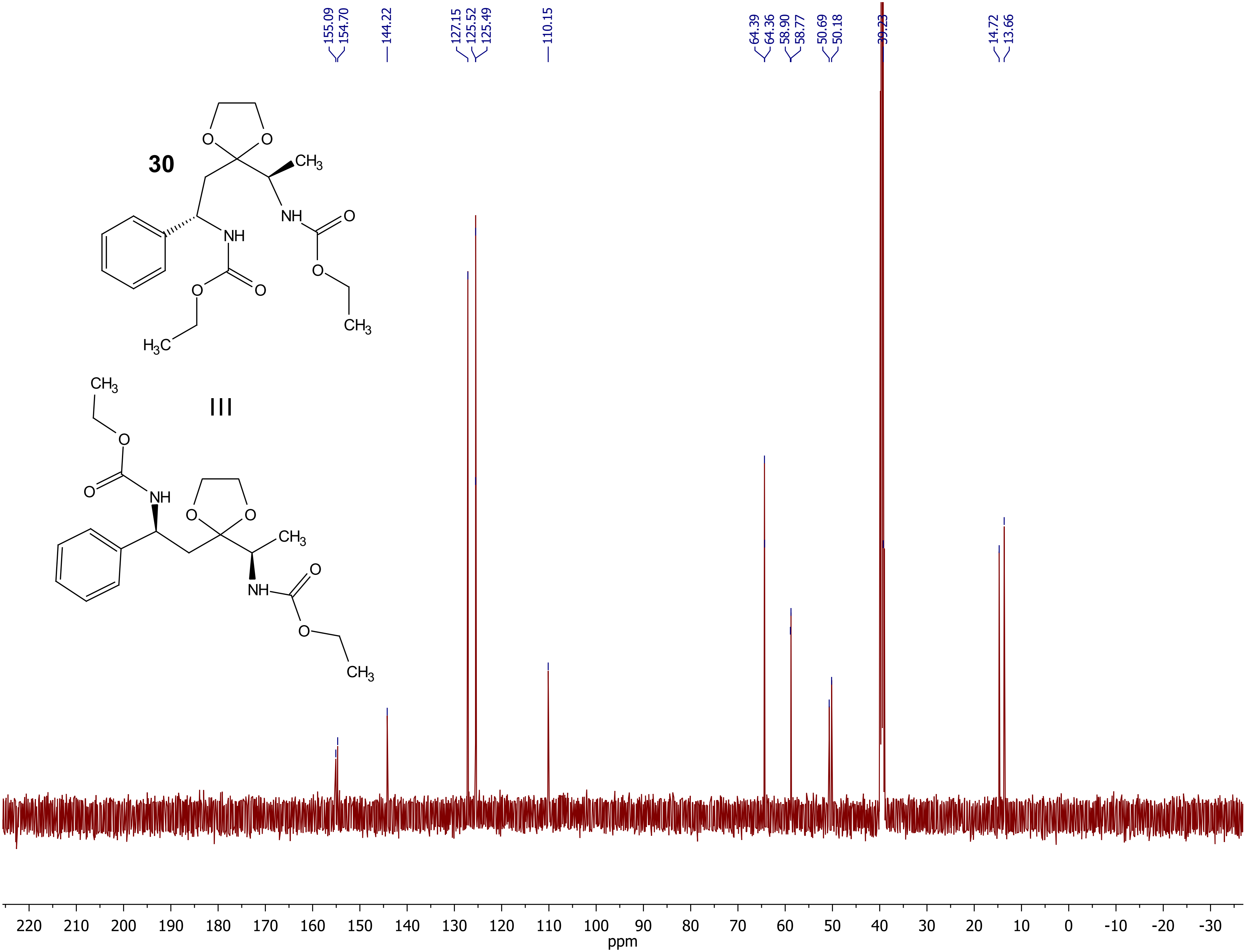
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125.49
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58.77
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50.18
39.23
14.72
13.66
30
III
CH3
NH
O
H3C
220
210
200
190
180
170
160
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120
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90
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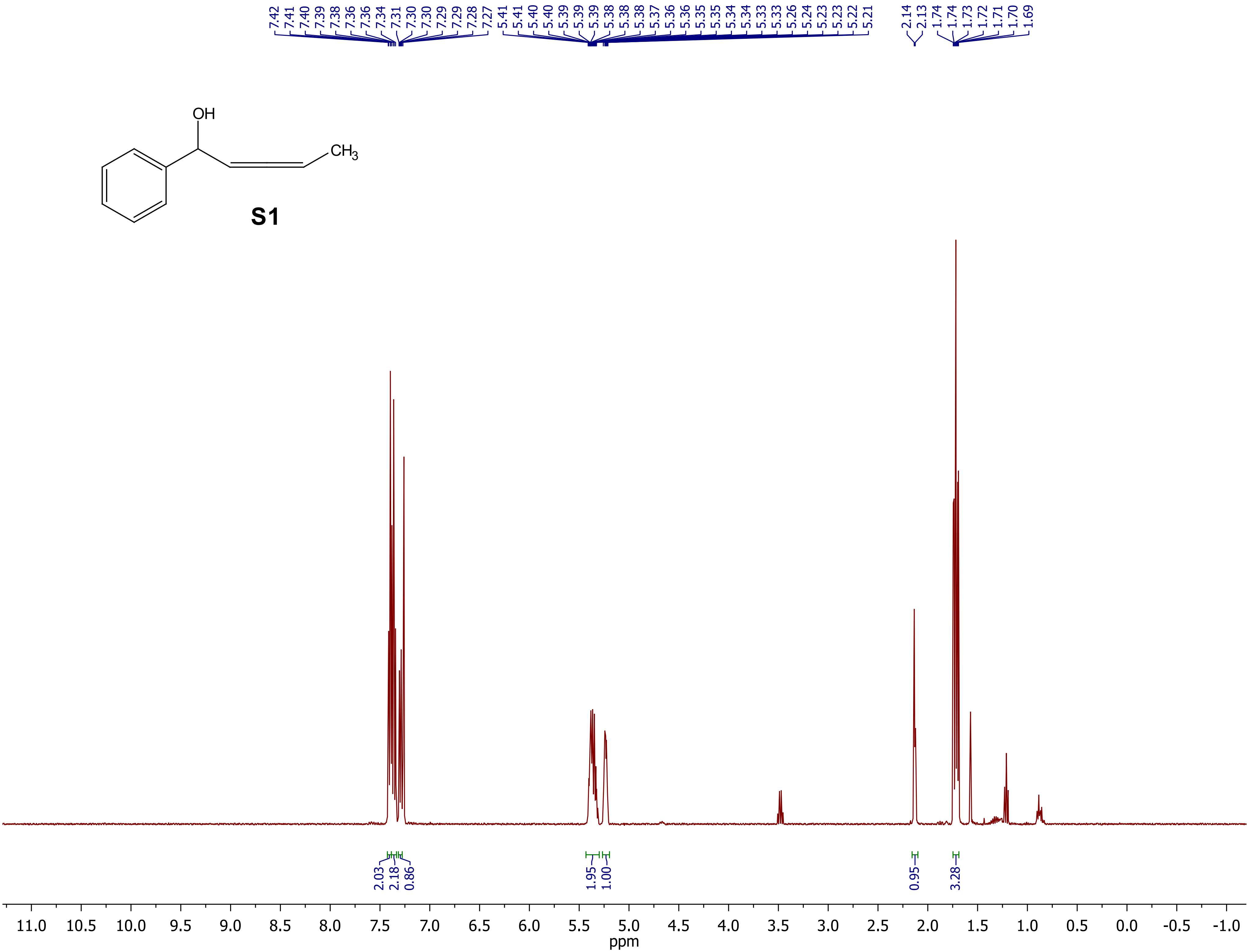
ppm



S1

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7.30
7.29
7.29
7.28
7.27
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5.41
5.40
5.40
5.39
5.39
5.39
5.38
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5.38
5.37
5.36
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5.35
5.35
5.34
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5.33
5.33
5.26
5.24
5.23
5.23
5.22
5.21
2.14
2.13
1.74
1.74
1.73
1.72
1.71
1.70
1.69
2.03
2.18
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0.95
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10.0
9.5
9.0
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7.5
7.0
6.5
6.0
5.5
5.0
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1.5
1.0
0.5
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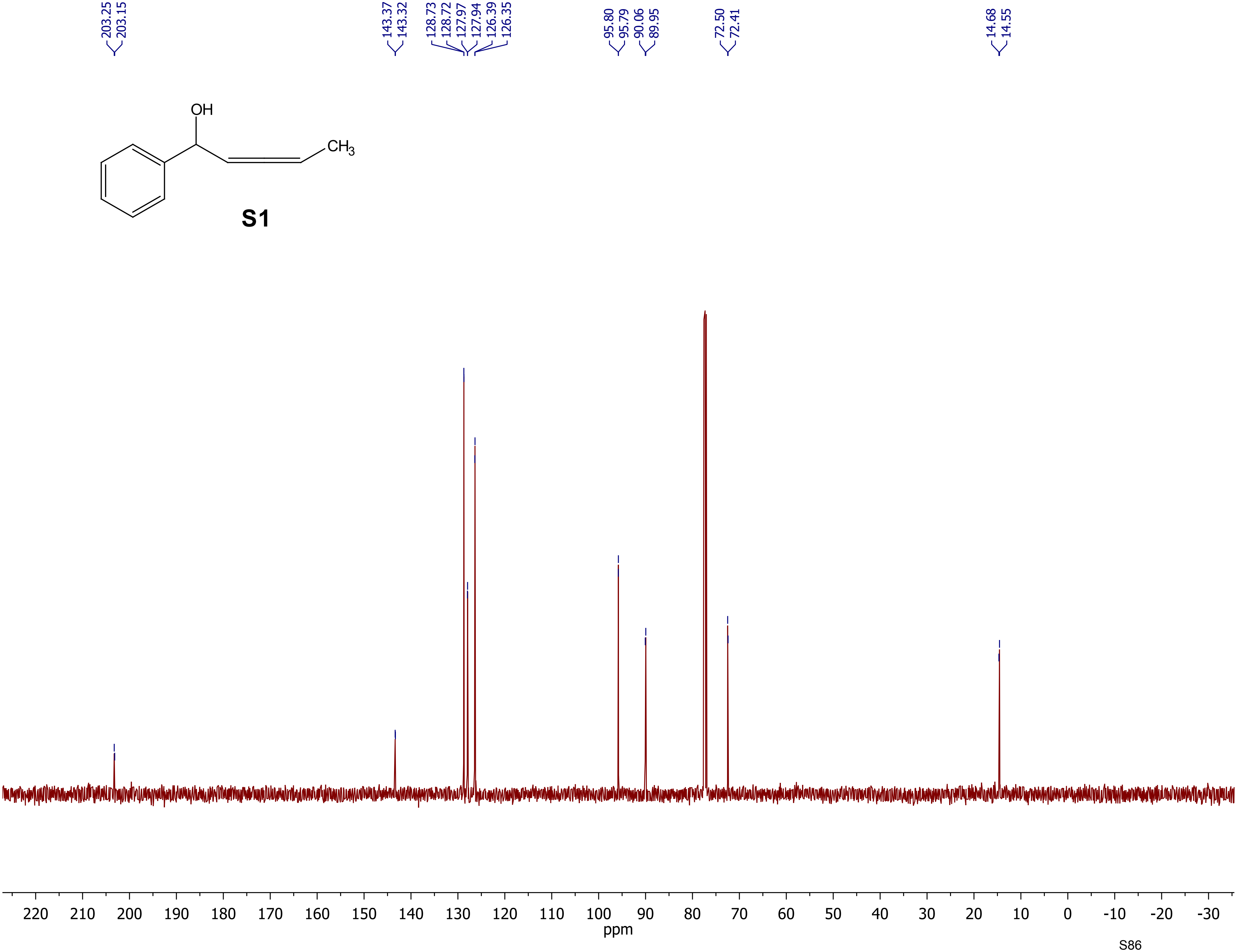
-1.0
ppm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90.06
89.95
72.50
72.41
14.68
14.55
OH
CH3
S1
220
210
200
190
180
170
160
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100
90
80
70
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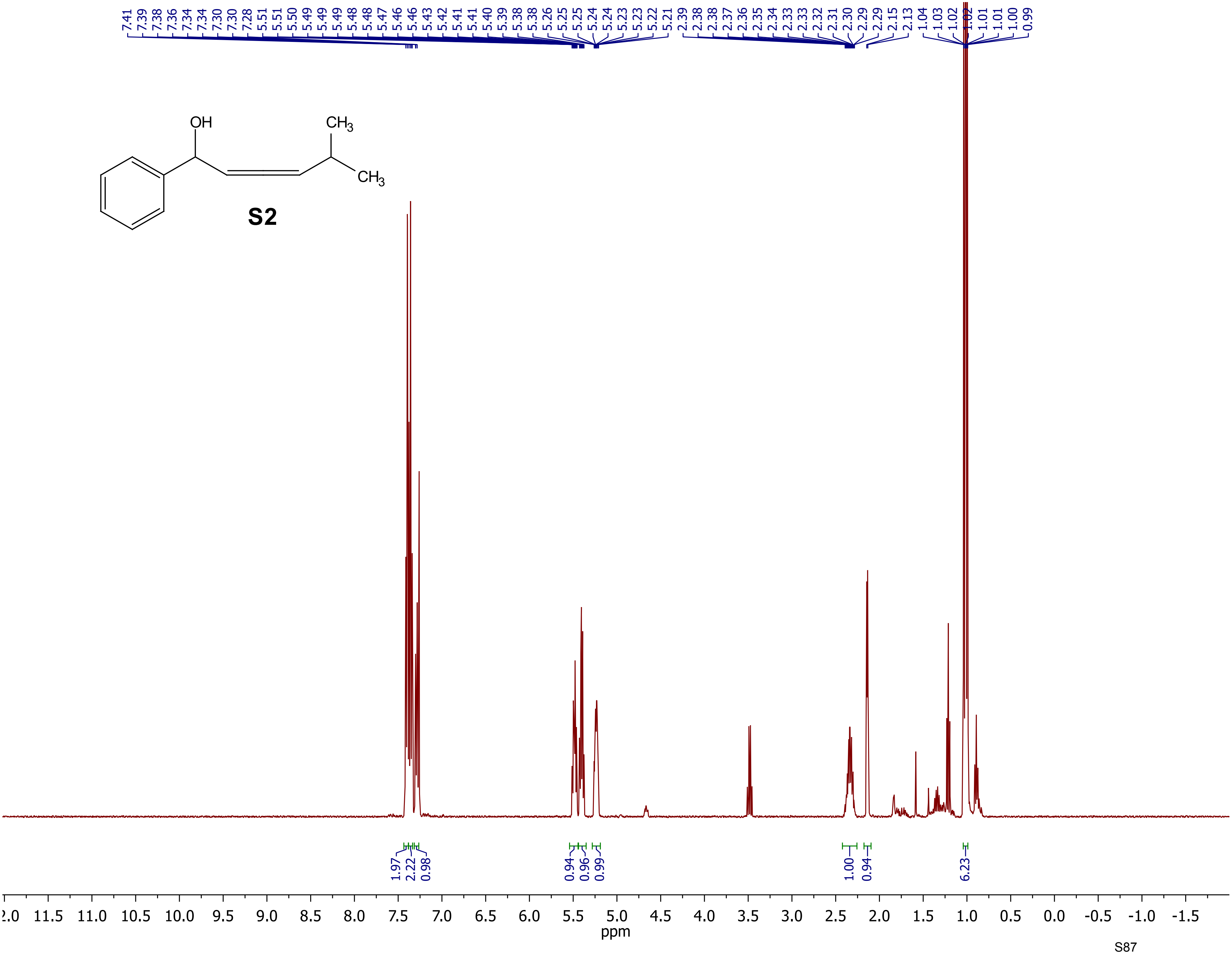
ppm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CH3
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7.30
7.28
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2.30
2.29
2.29
2.15
2.13
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1.03
1.02
1.02
1.01
1.01
1.00
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2.22
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0.94
0.96
0.99
1.00
0.94
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9.0
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6.5
6.0
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4.0
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1.0
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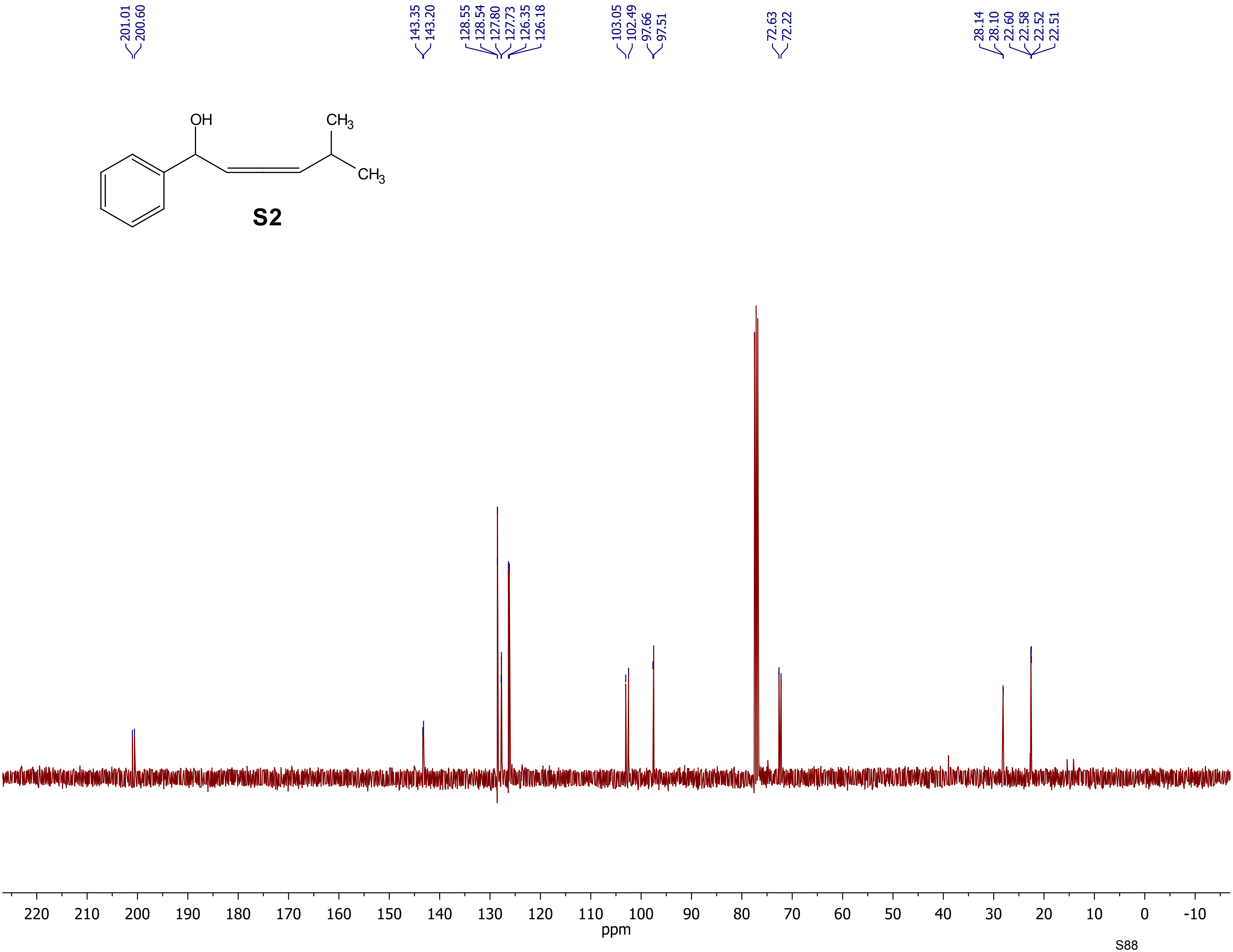
ppm


S2

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102.49
97.66
97.51
72.63
72.22
28.14
28.10
22.60
22.58
22.52
22.51
OH
CH3
CH3
220
210
200
190
180
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130
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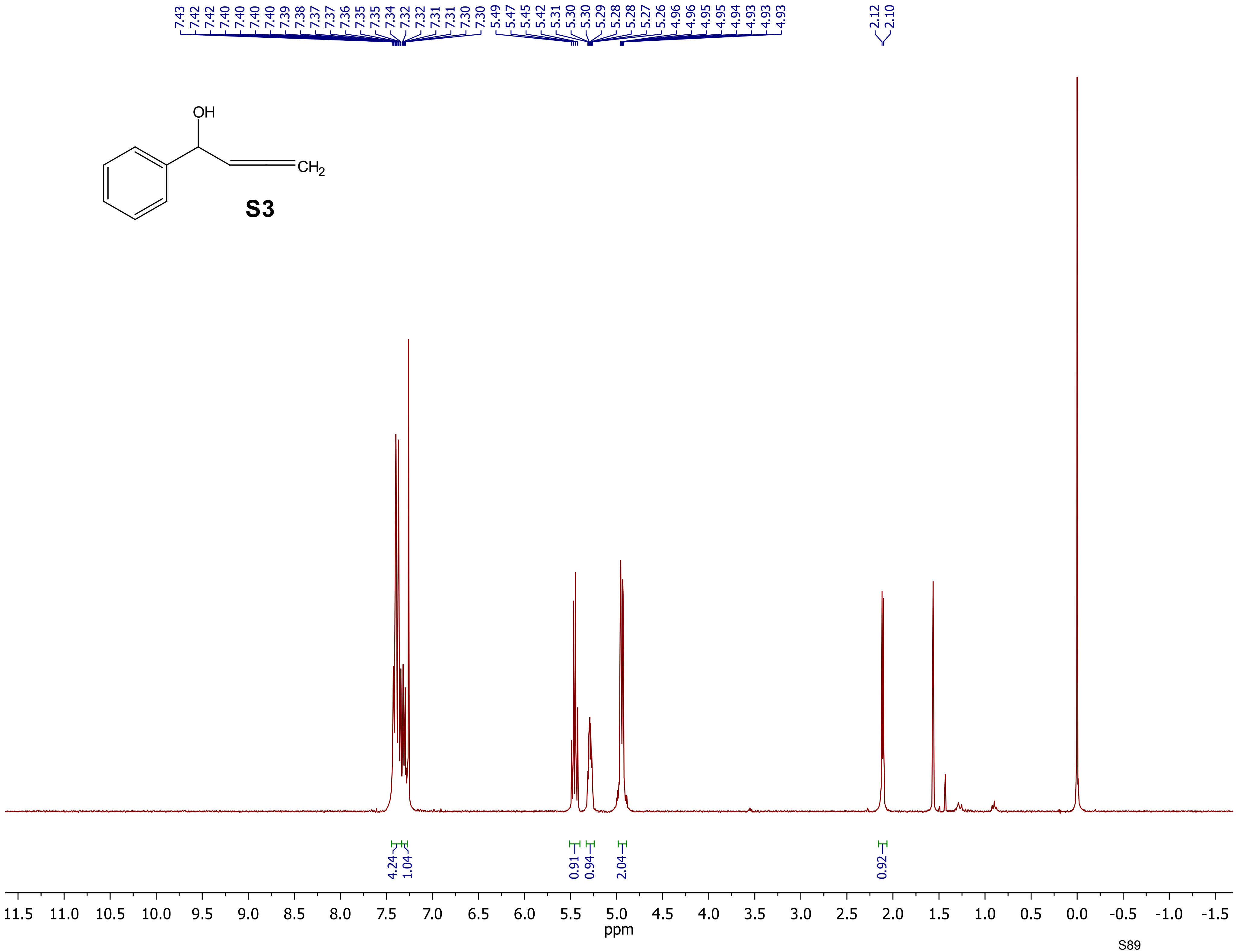
ppm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7.31
7.30
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5.31
5.30
5.30
5.29
5.28
5.28
5.27
5.26
4.96
4.96
4.95
4.95
4.94
4.93
4.93
4.93
2.12
2.10
OH
CH2
S3
4.24
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0.94
2.04
0.92
11.5
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9.0
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6.0
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4.5
4.0
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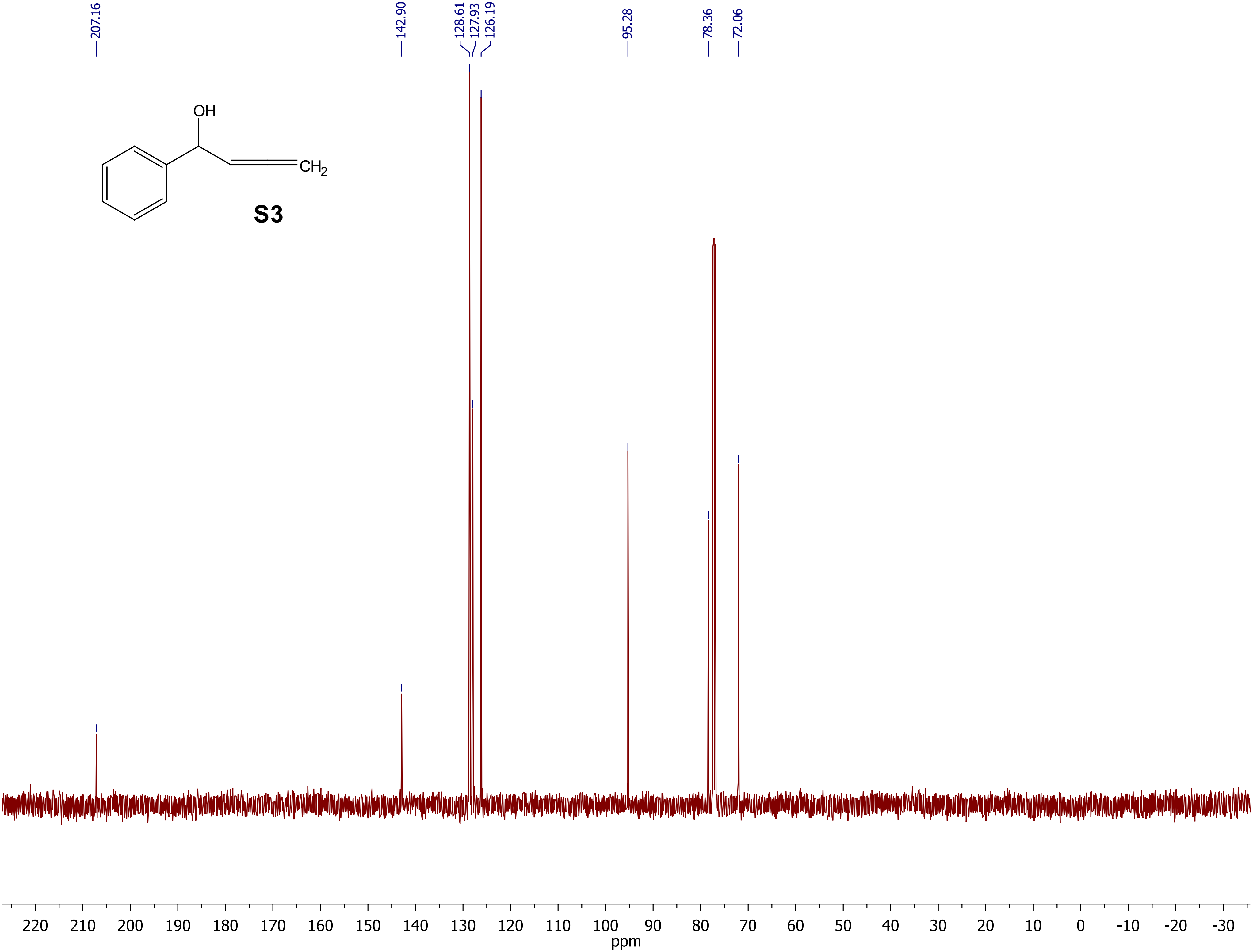
ppm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CH_2
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200
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170
160
150
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-20
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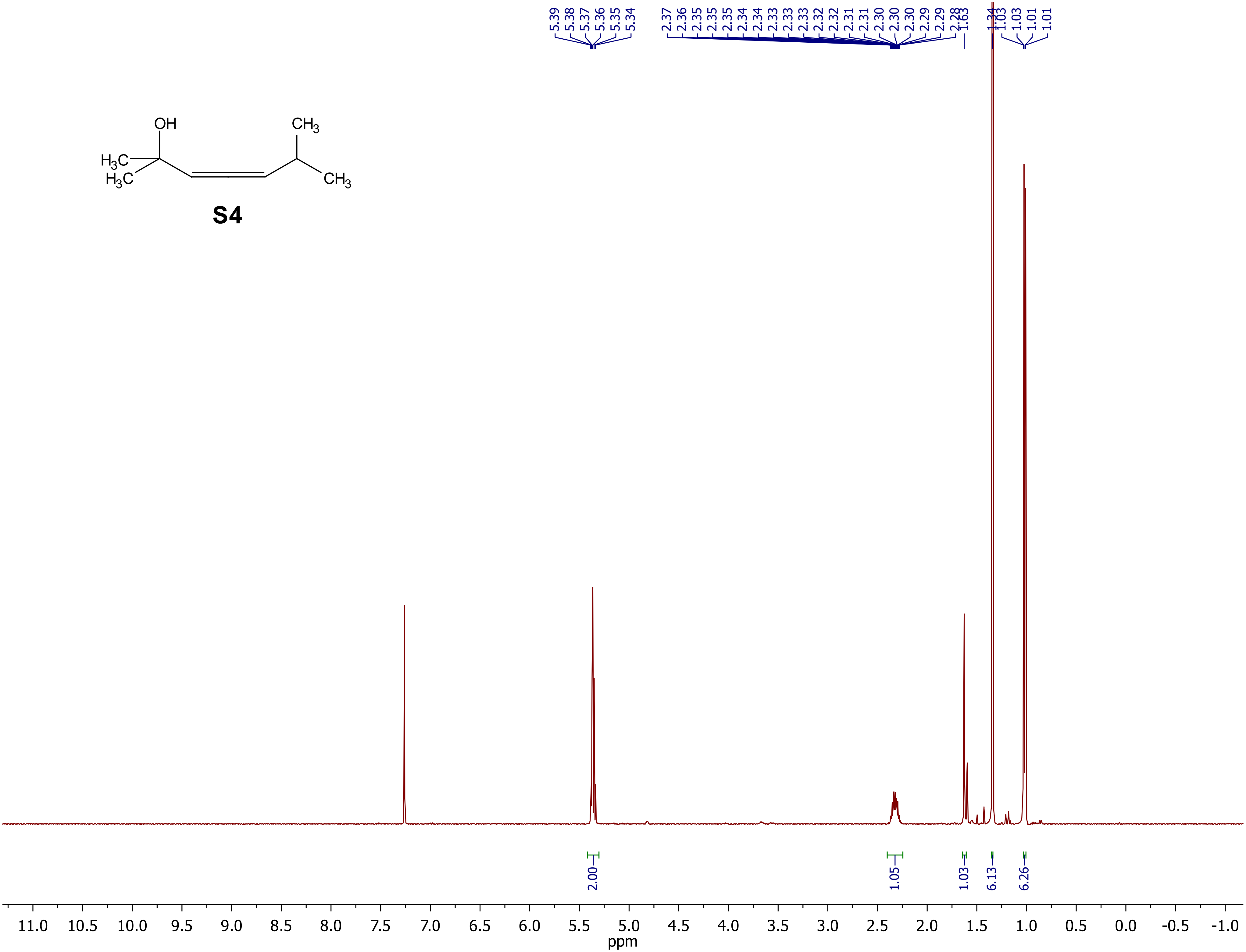
ppm

S3



S4

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H3C
H3C
CH3
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1.03
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2.00
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10.0
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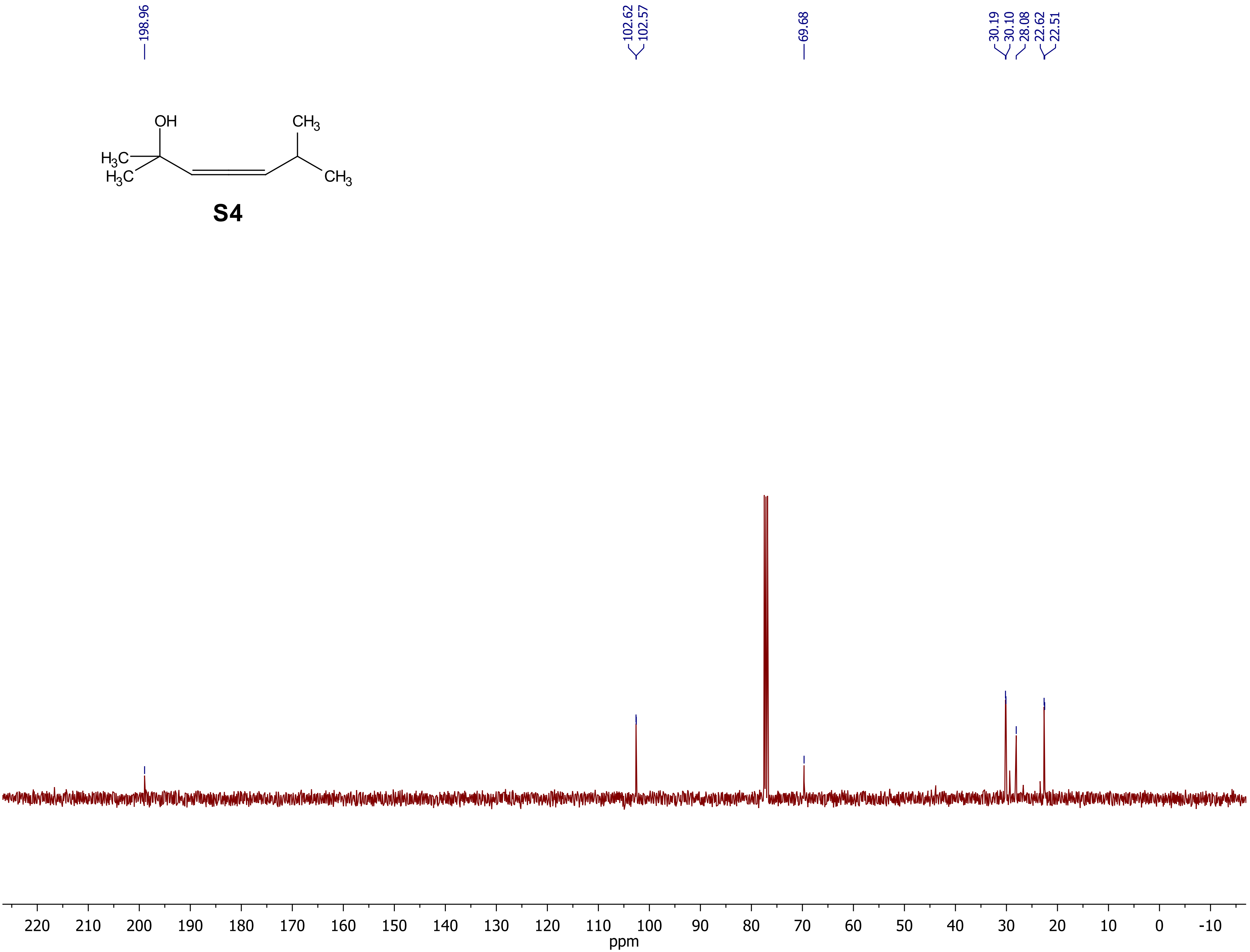
ppm



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OH
CH3
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H3C
CH3
S4
220
210
200
190
180
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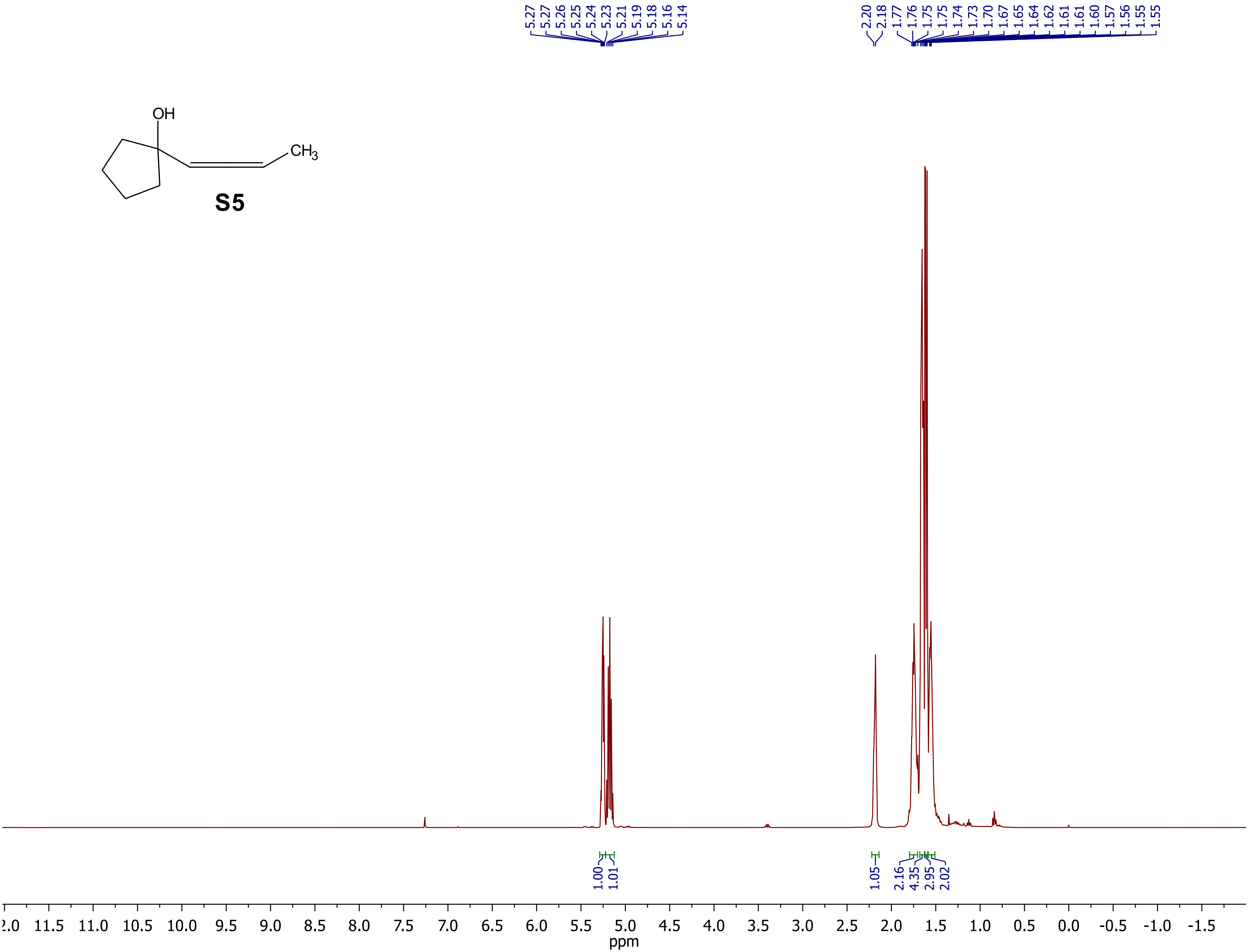
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OH
CH_3
S5
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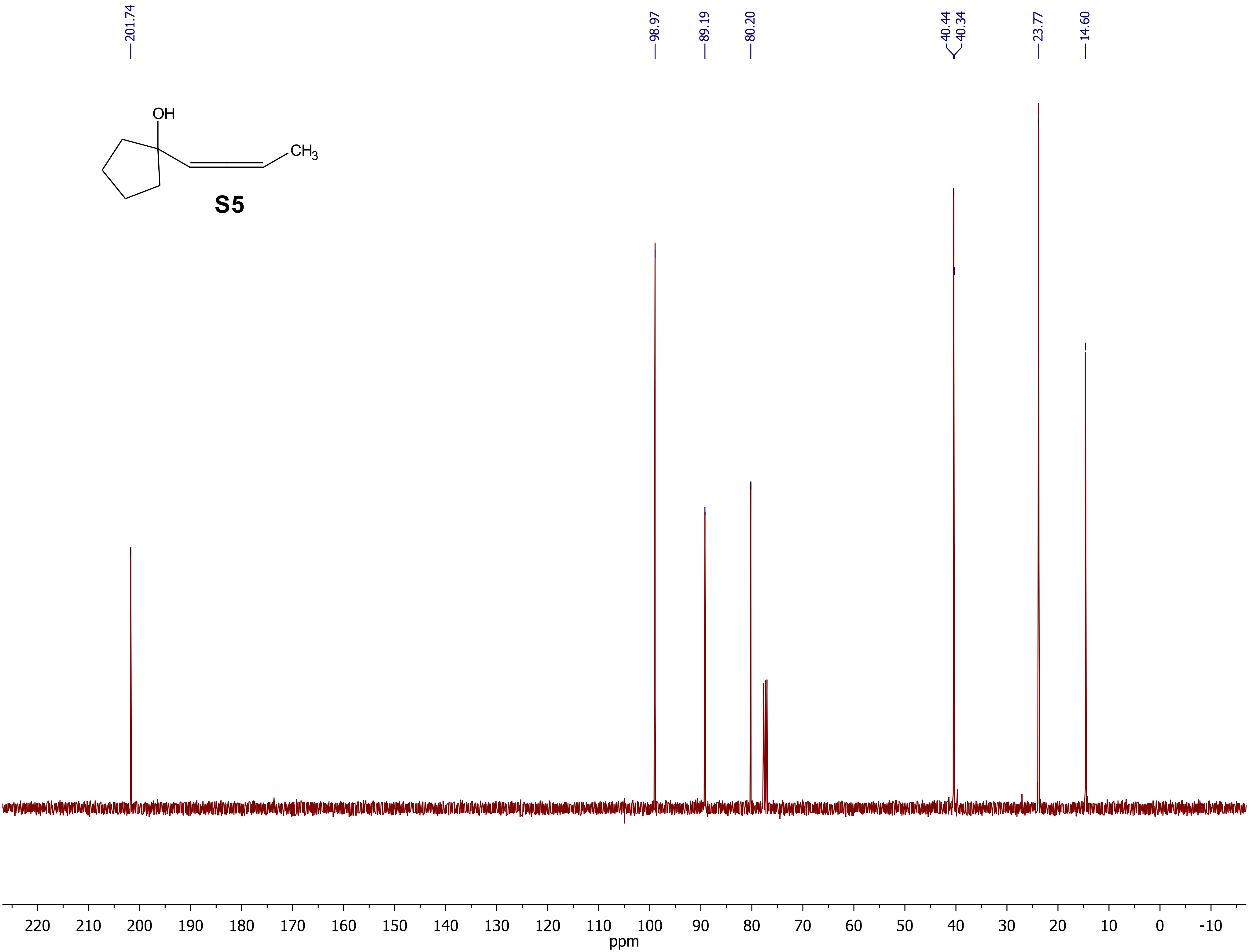
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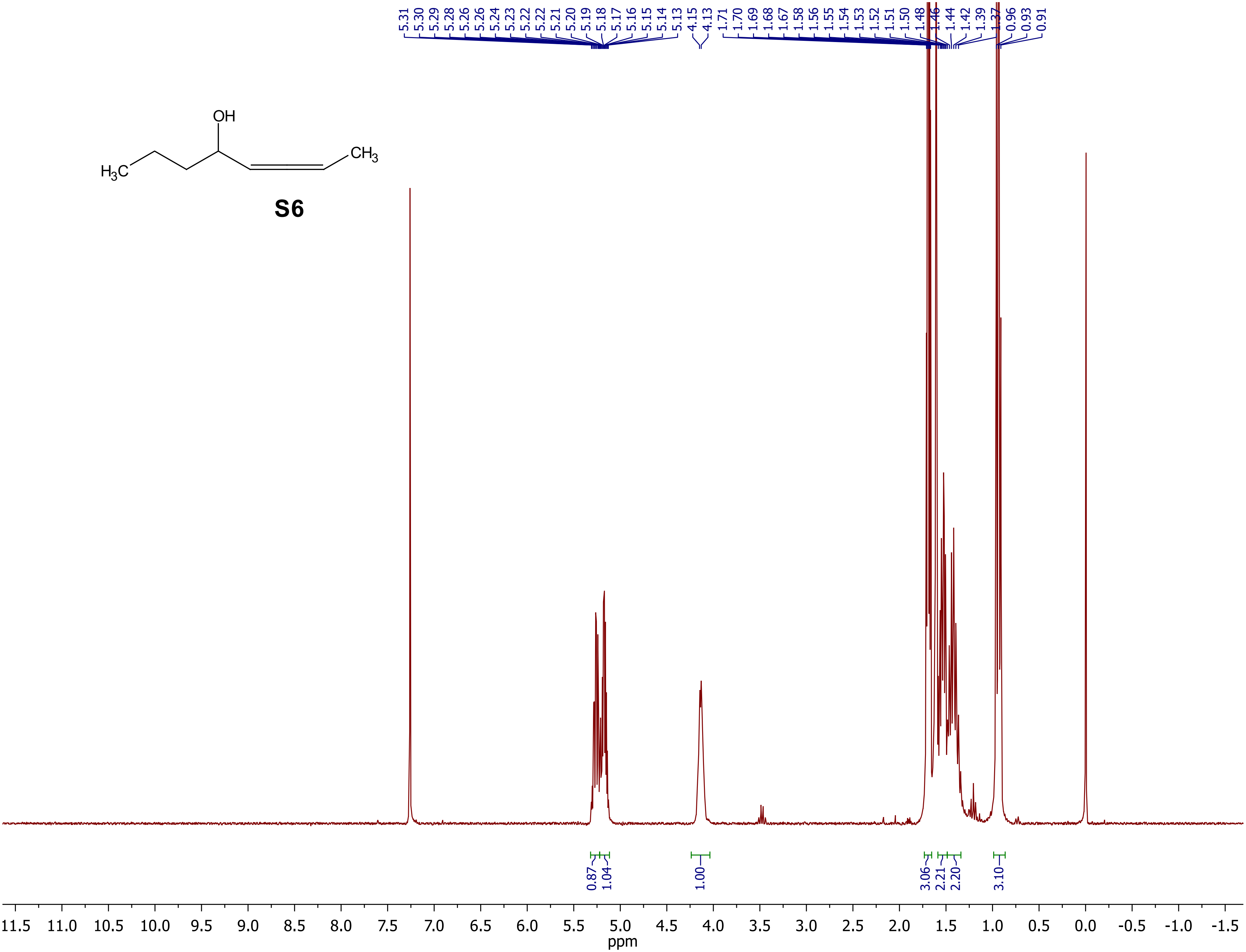

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5.14
5.13
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S6
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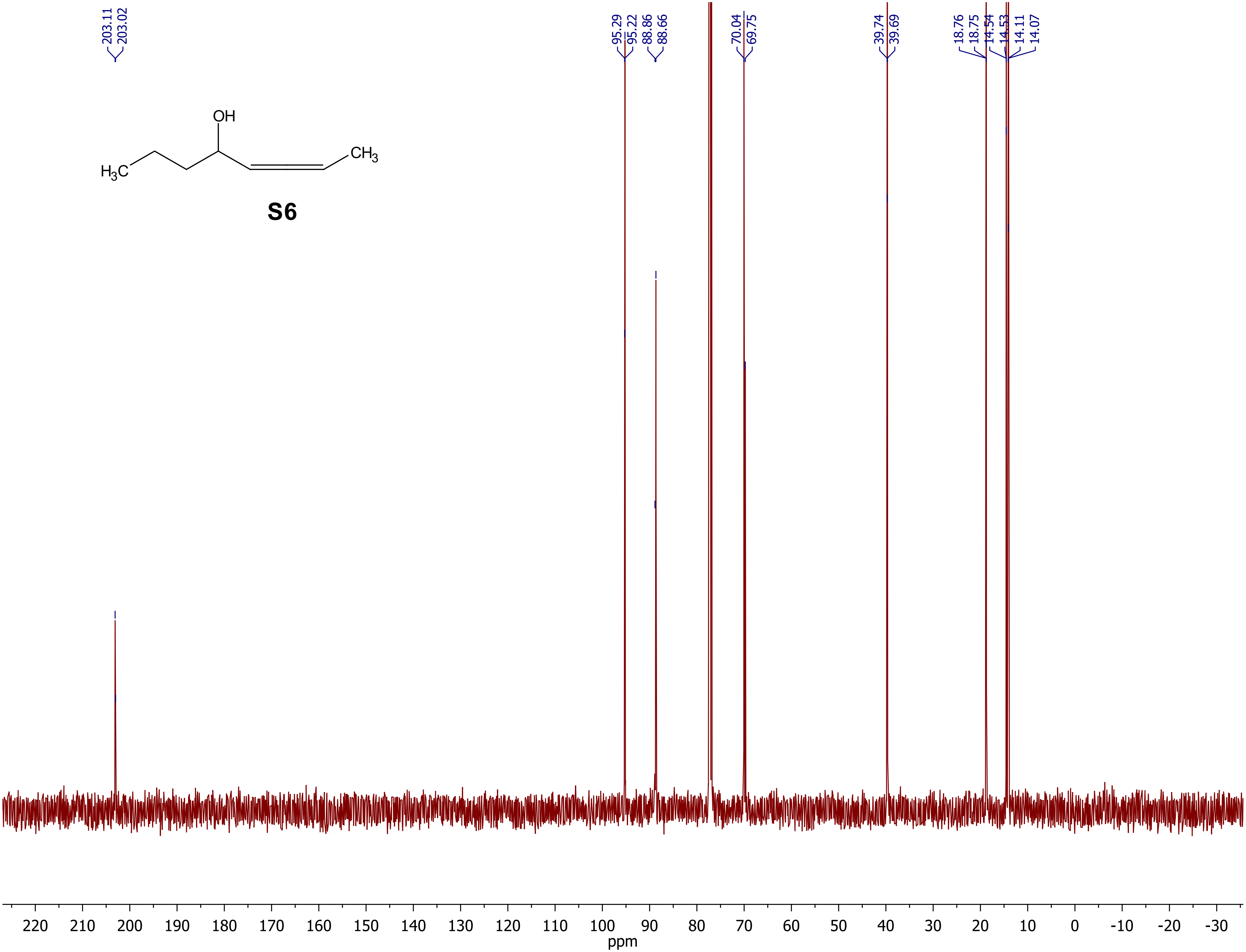
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14.53
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14.07
OH
H3C
CH3
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210
200
190
180
170
160
150
140
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50
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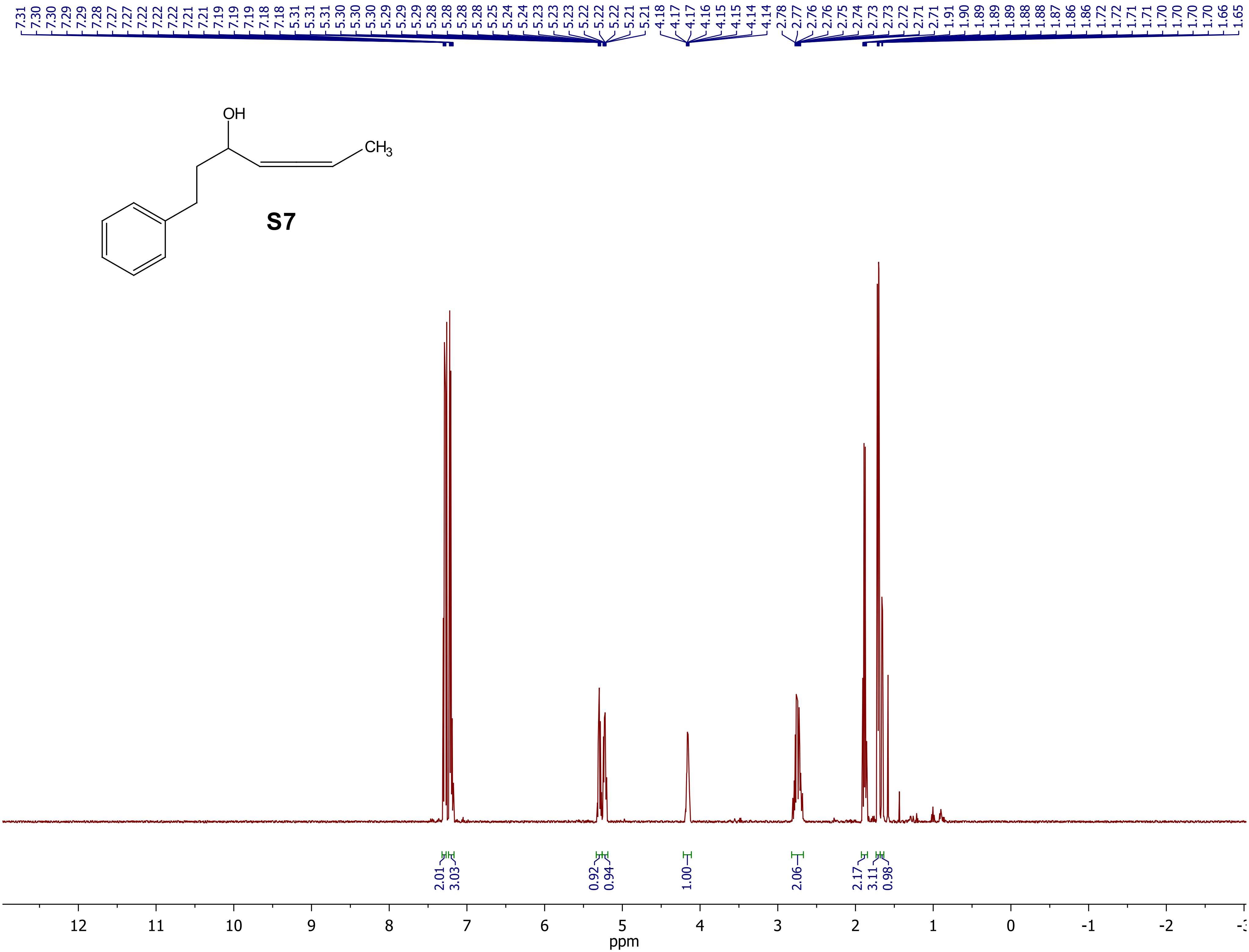
-30
ppm

S6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2.76
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2.74
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1.65
OH
CH3
S7
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3.03
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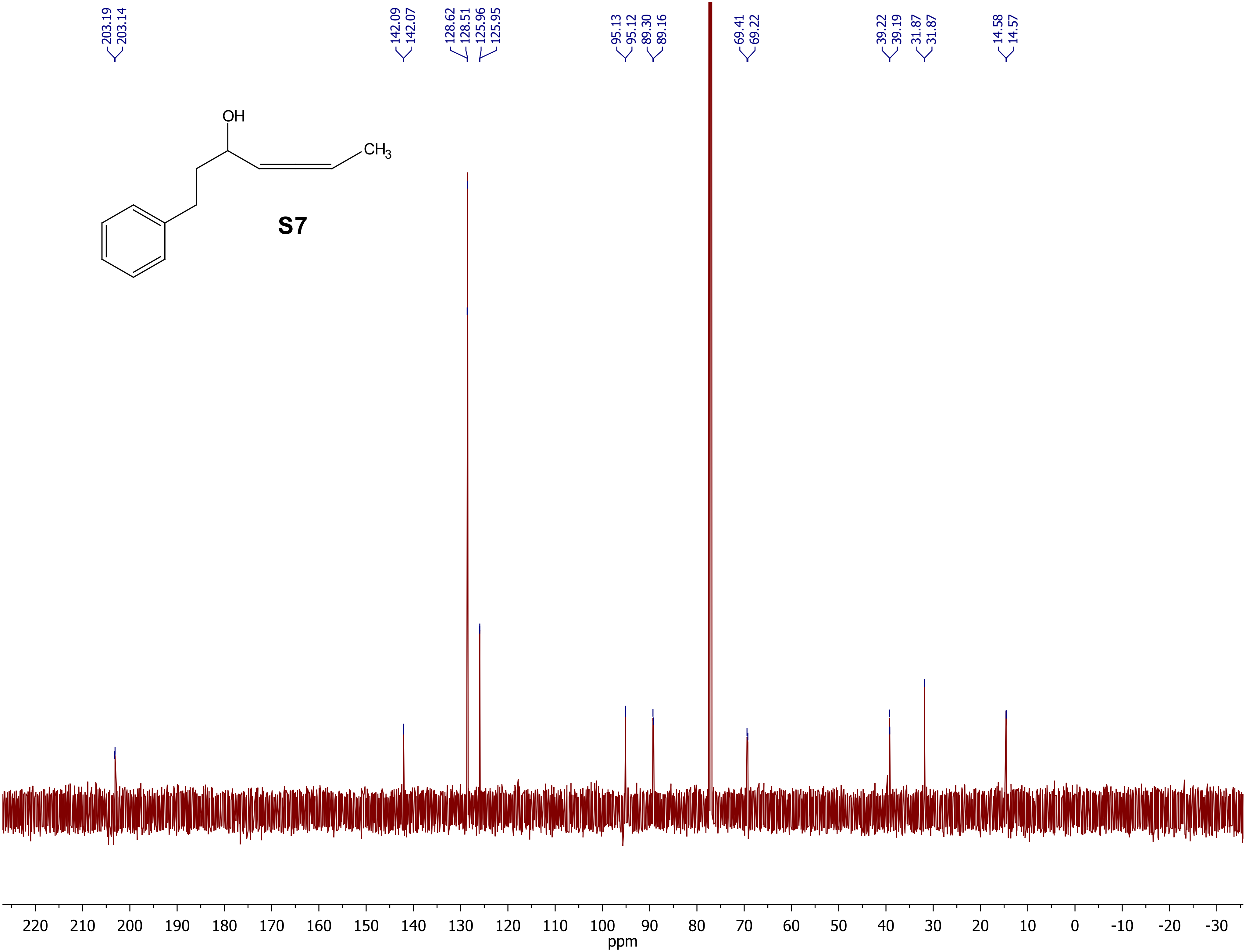
S7

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69.22
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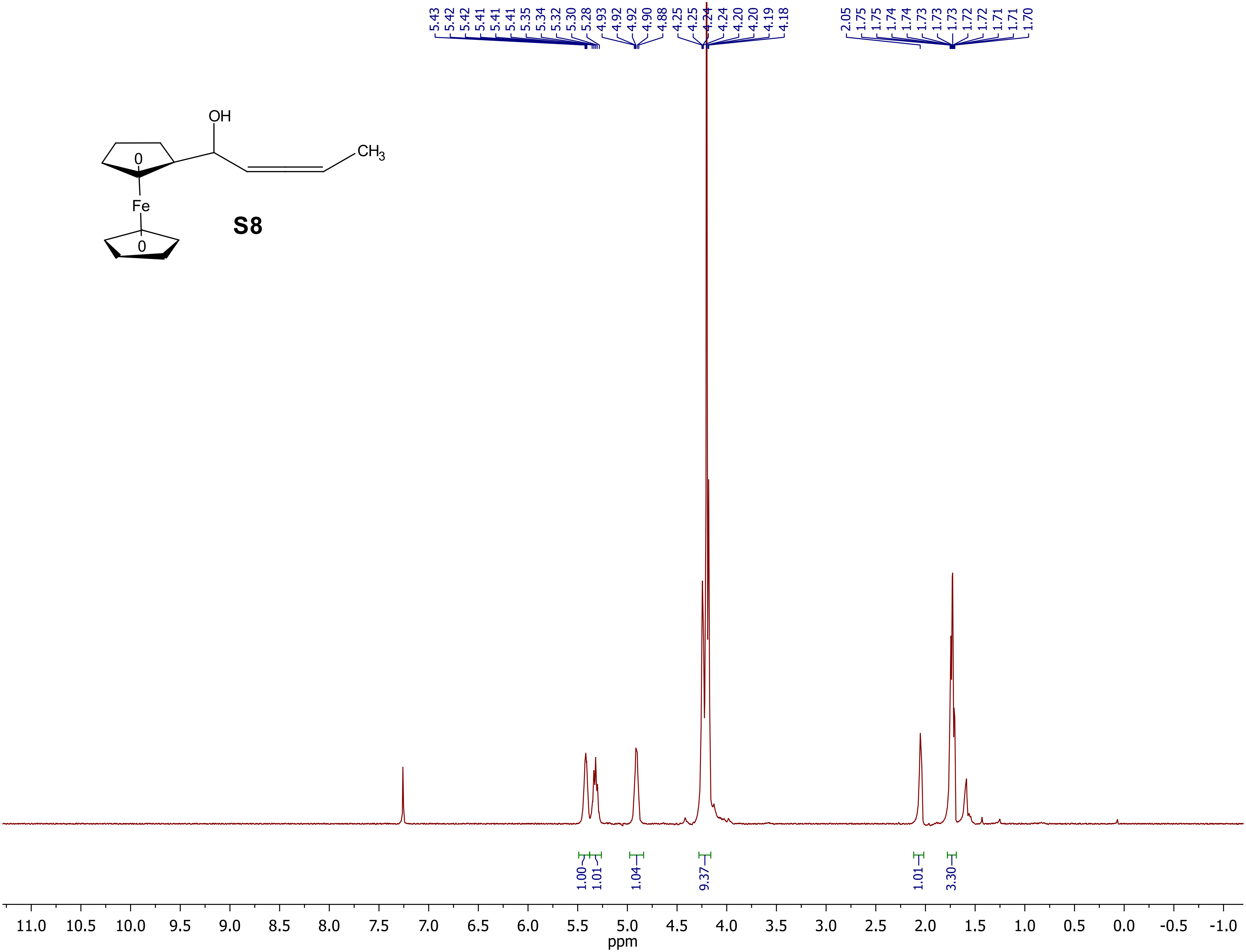
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4.90
4.88
4.25
4.25
4.24
4.24
4.20
4.20
4.19
4.18
2.05
1.75
1.75
1.74
1.74
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1.72
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1.71
1.70
OH
CH_3
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Fe
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S8
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1.01
1.04
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3.30
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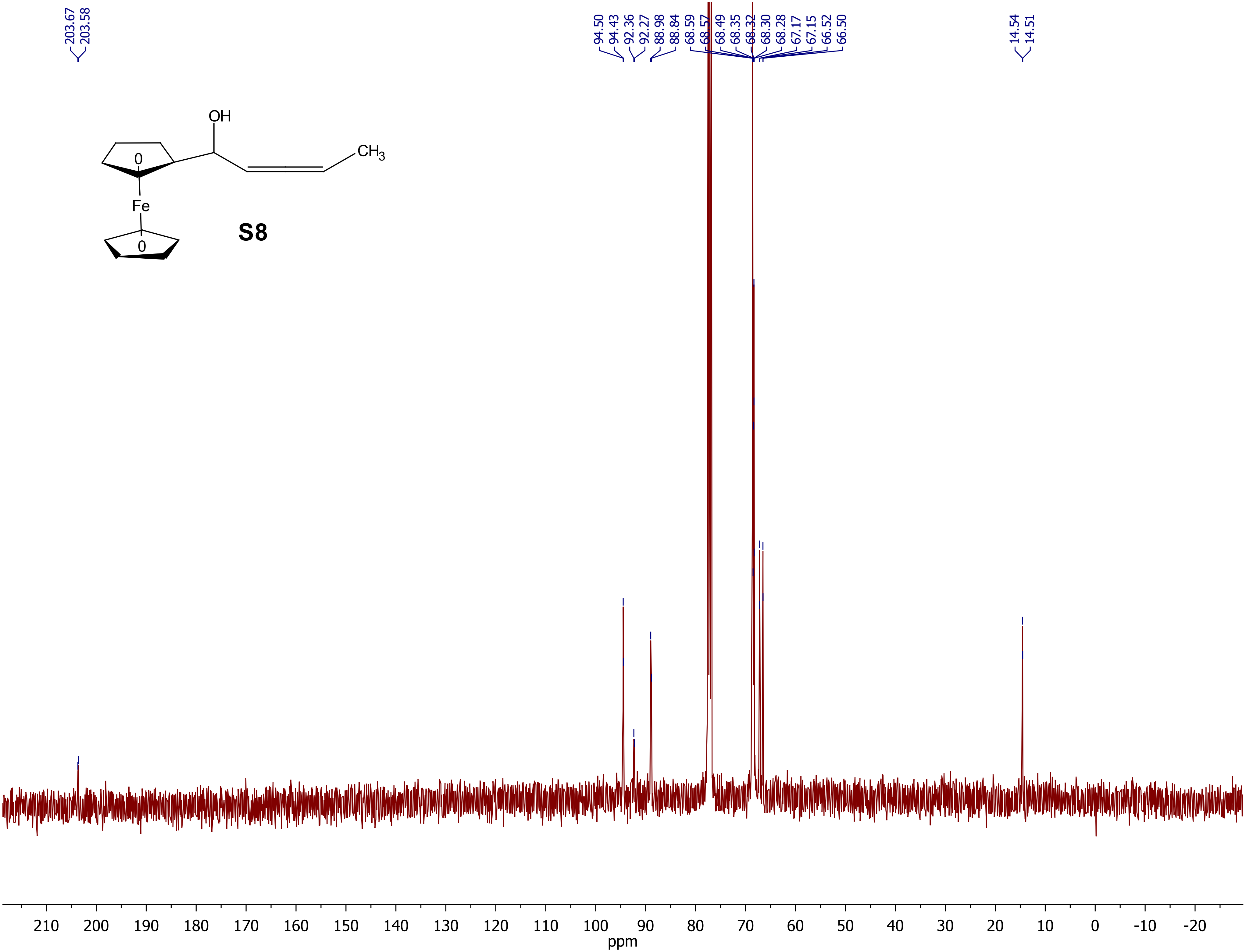
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68.30
68.28
67.17
67.15
66.52
66.50
14.54
14.51
OH
CH3
Fe
0
0
S8
210
200
190
180
170
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100
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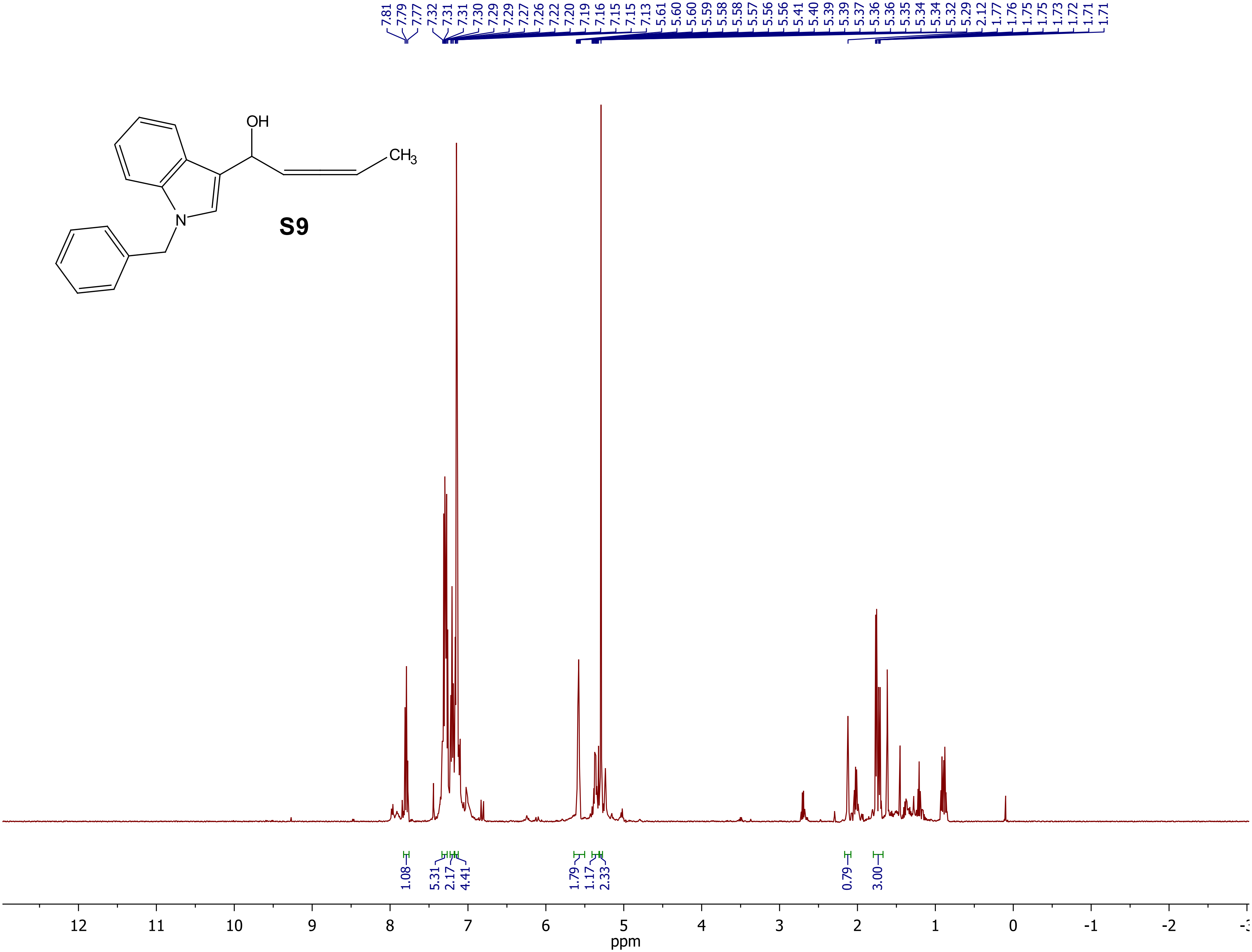
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7.15
7.13
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5.60
5.59
5.58
5.58
5.57
5.56
5.56
5.41
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5.37
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5.34
5.34
5.32
5.29
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1.77
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1.75
1.75
1.73
1.72
1.71
1.71
OH
CH_3
N
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1.17
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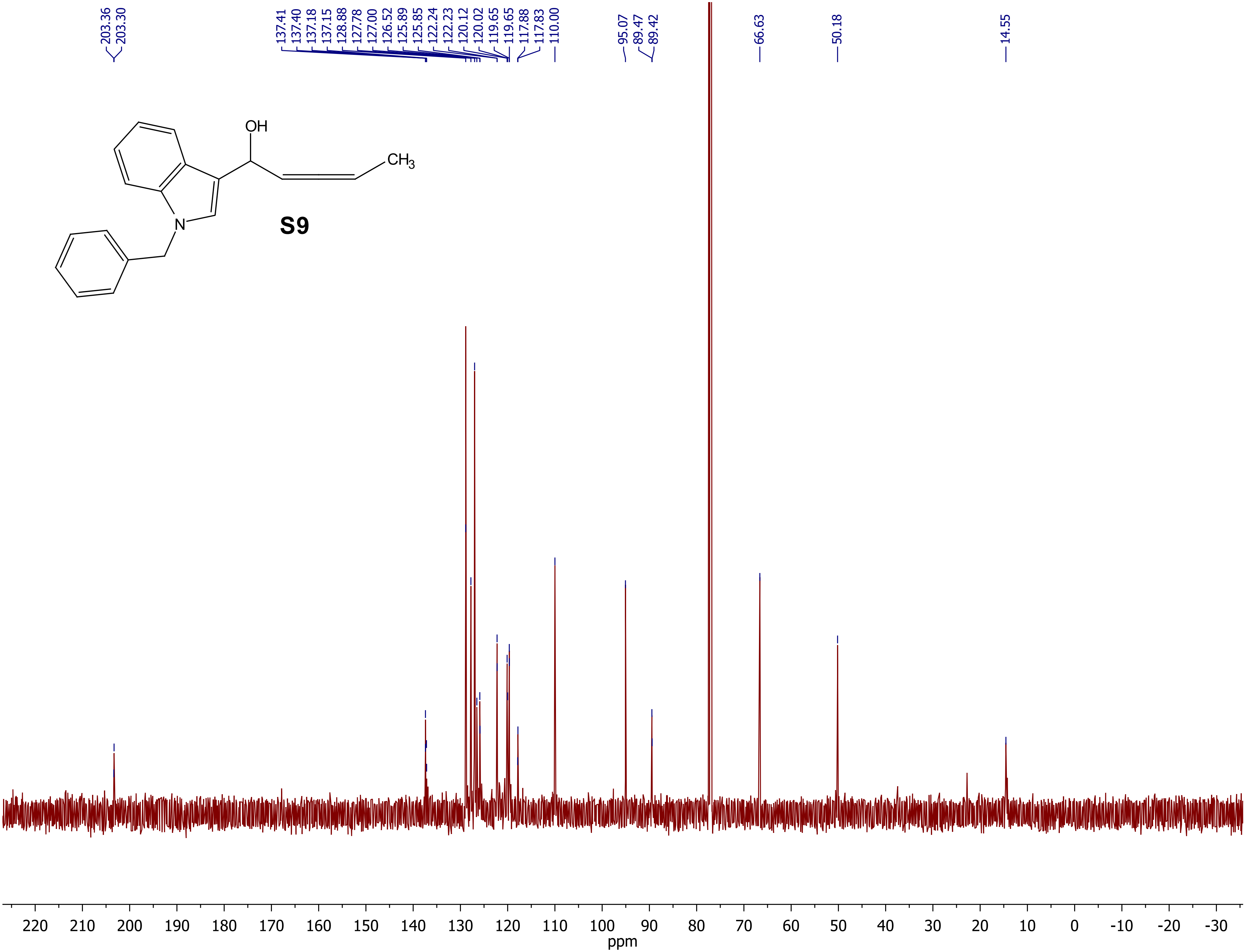
-2
ppm

S9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95.07
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89.42
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CH3
N
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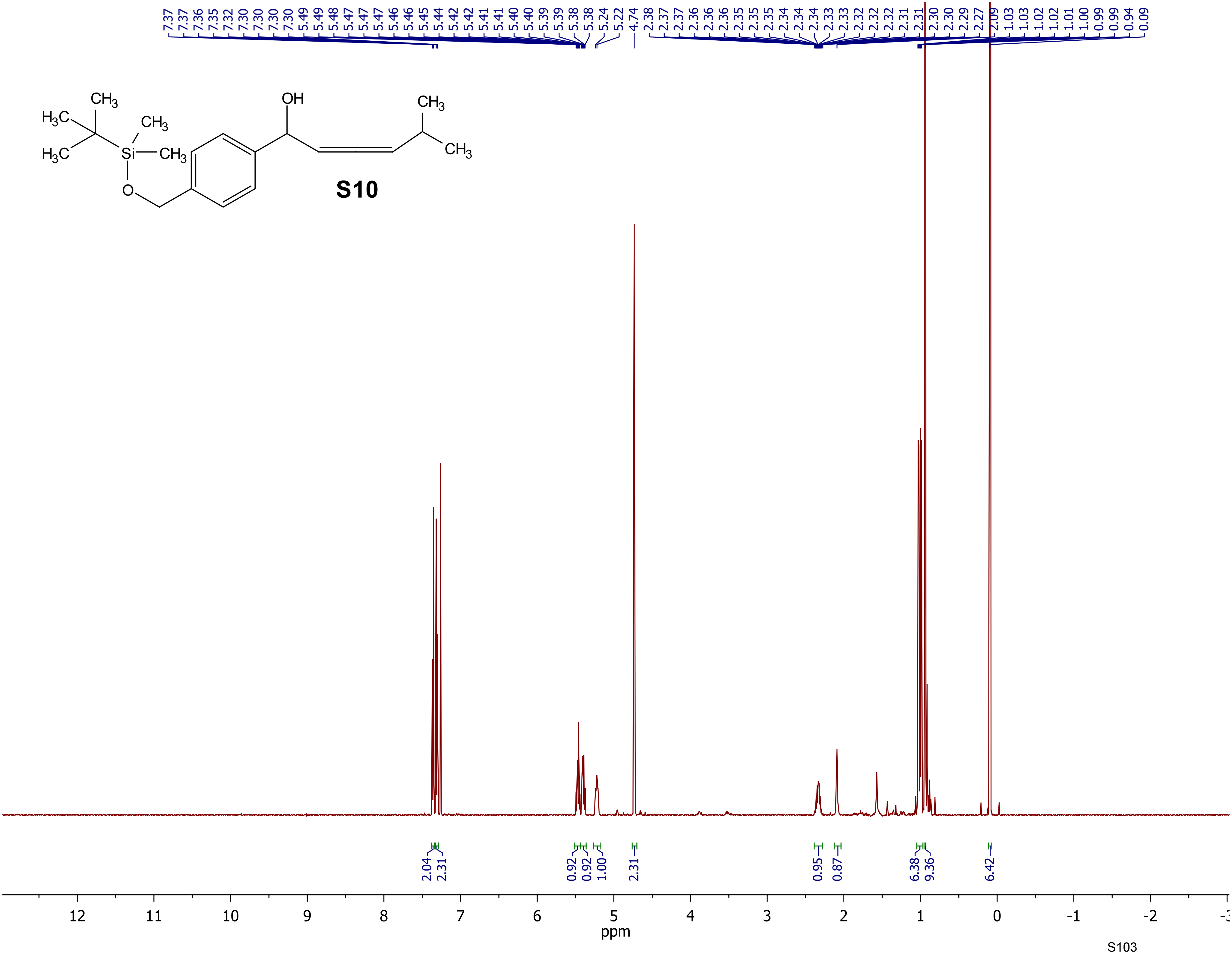
ppm

S9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5.38
5.38
5.24
5.22
4.74
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2.33
2.32
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2.30
2.30
2.29
2.27
2.09
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1.03
1.02
1.02
1.01
1.00
0.99
0.99
0.94
0.09
CH3
H3C
CH3
H3C
Si
CH3
O
OH
CH3
CH3
S10
2.04
2.31
0.92
0.92
1.00
2.31
0.95
0.87
6.38
9.36
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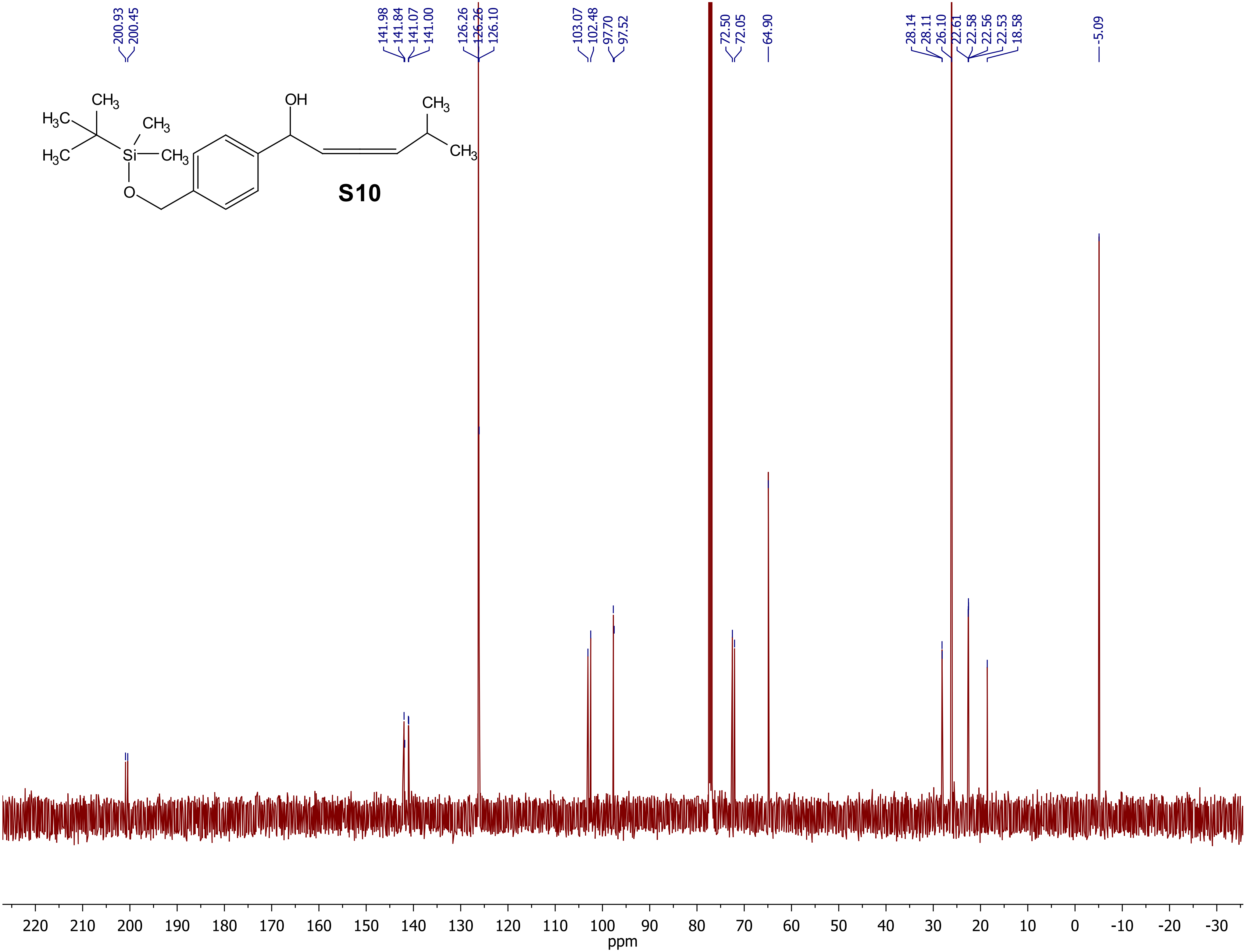
ppm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103.07
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97.52
72.50
72.05
64.90
28.14
28.11
26.10
22.61
22.58
22.56
22.53
18.58
-5.09
S10
220
210
200
190
180
170
160
150
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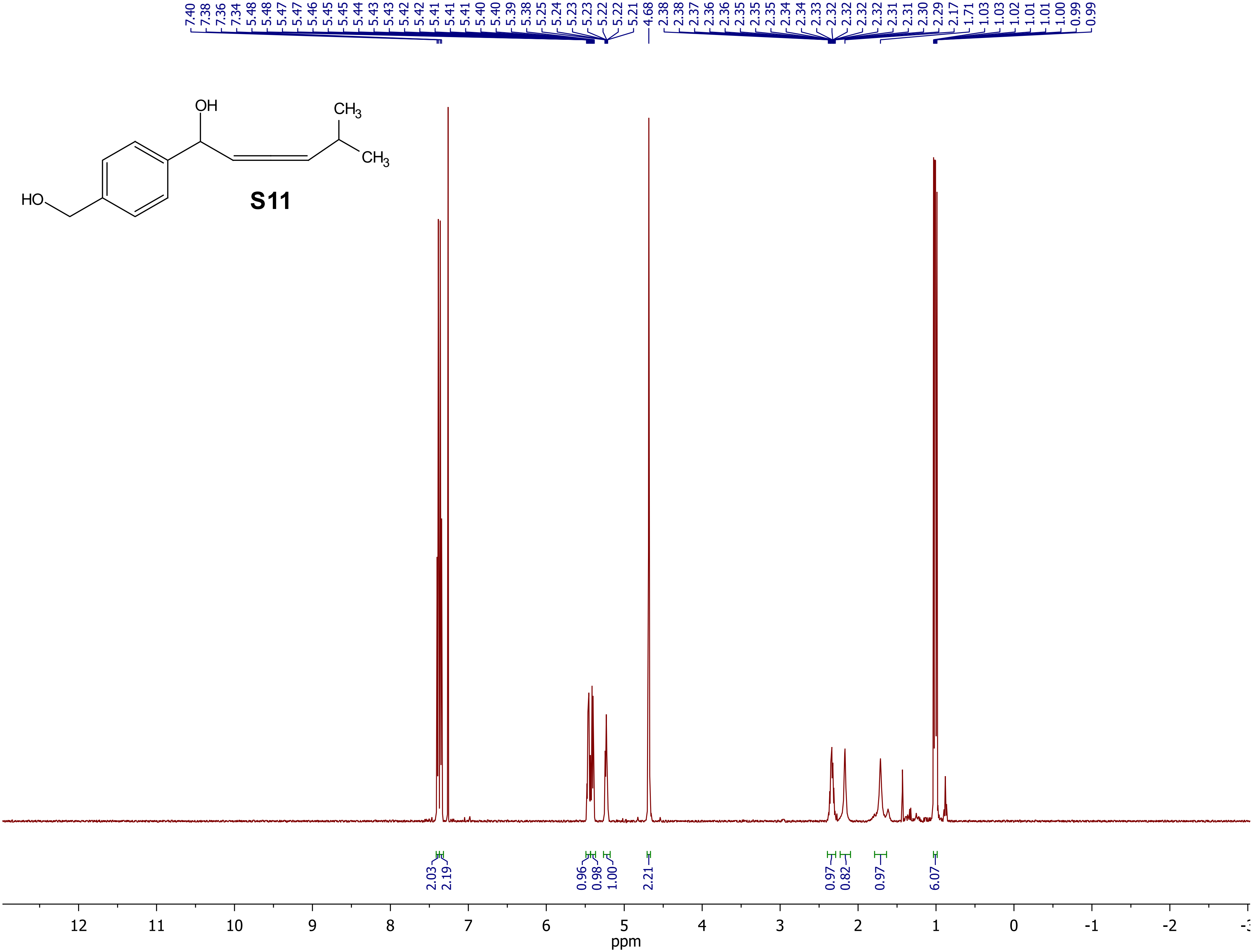
ppm



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5.42
5.42
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5.41
5.41
5.40
5.40
5.39
5.38
5.25
5.24
5.23
5.23
5.22
5.22
5.21
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2.38
2.37
2.36
2.36
2.35
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2.31
2.31
2.30
2.29
2.17
1.71
1.03
1.03
1.02
1.01
1.01
1.00
0.99
0.99
OH
CH3
CH3
HO
2.03
2.19
0.96
0.98
1.00
2.21
0.97
0.82
0.97
6.07
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9
8
7
6
5
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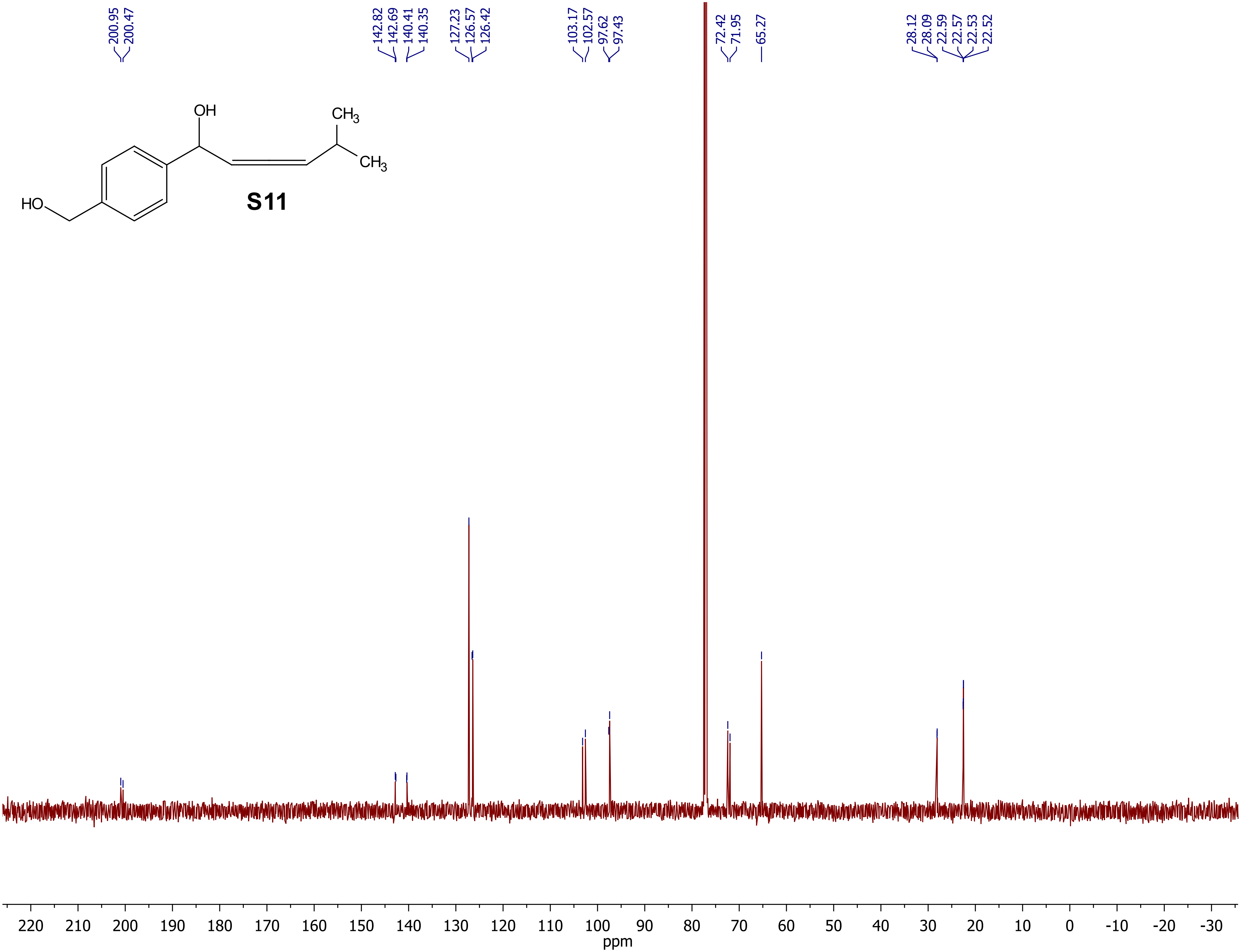
0
-1
-2
-3
ppm

S11


S11
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127.23
126.57
126.42
103.17
102.57
97.62
97.43
72.42
71.95
65.27
28.12
28.09
22.59
22.57
22.53
22.52
OH
CH3
CH3
HO
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
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20
10
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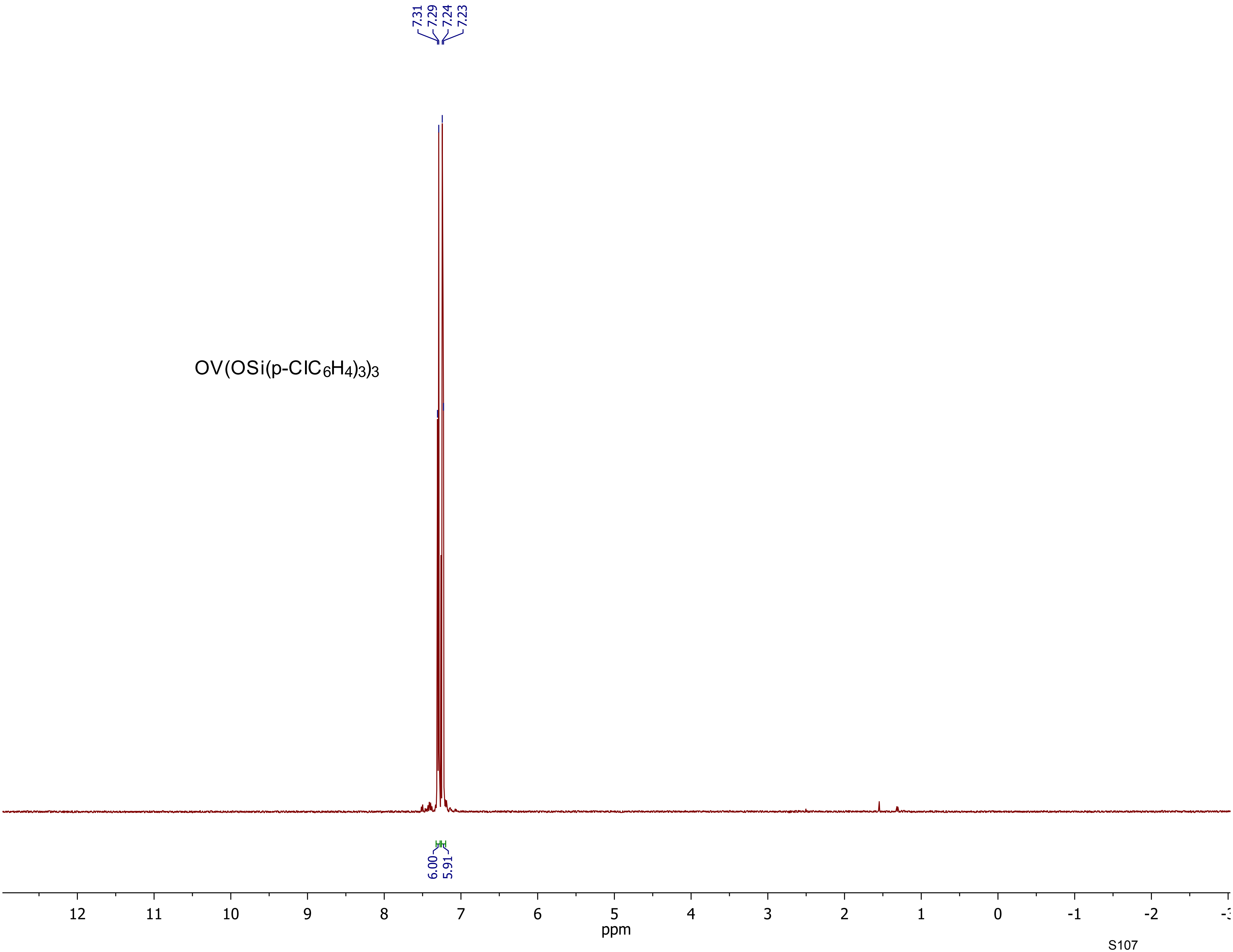
-10
-20
-30
ppm



OV(OSi(p-ClC$_6$H$_4$)$_3$)$_3$

$OV(OSi(p\text{-}ClC_6H_4)_3)_3$