Supporting Information for

Copper-Catalyzed Silylation of Propargyl Carbonates: A General Entry to Allenylsilanes

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General Methods.

Unless noted, all reactions were carried out using standard Schlenk technique under an argon atmosphere or a dry box technique under a nitrogen atmosphere. THF was distilled from sodium and benzophenone or purified using Innovative Technology Solvent Purifier (for the synthesis of substrates). 1,4-Dioxane was distilled from sodium and benzophenone. CuCl, $NaHCO_3$ and PPh_3 were purchased from J&K Chemical Company. PCy_3 was purchased from Alfa Chemical Company. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources. Triethyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (Et_3Si-Bpin) was prepared according to published method.[1]

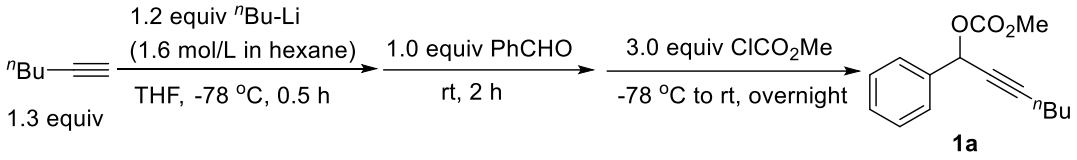
^{1}H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ (containing 0.03% TMS) solutions on Varian XL-400 MHz spectrometer, Agilent XL-400 MHz spectrometer or Bruker Avance III HD 400MHz spectrometer. ^{1}H NMR spectra was recorded with tetramethylsilane (0.00 ppm) or solvent residual peak ($CDCl_3$: 7.26 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (77.00 ppm) as internal reference. High-resolution mass spectra were obtained by using JEOL AccuTOF GCv4G GCT MS spectrometer, Agilent Technologies 7250 GCQTOF spectrometer, Thermo Scientific Q Exactive HF Orbitrap-FTMS and Thermo Fisher Scientific LTQ FTICR-MS. The IR spectra were measured on a ThermoFisher Nicolet FT-IR spectrometer.

Synthesis and characterization of propargyl carbonates 1.

The propargyl carbonates were prepared from the corresponding propargyl alcohols.

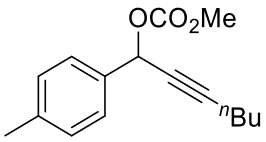
For the synthesis of propargyl carbonates 1a-1w, see the following:

Typical procedure for the synthesis of 1a.



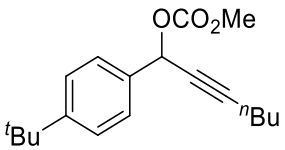
Methyl (1-phenylhept-2-yn-1-yl) carbonate (1a). 1-Hexyne (0.75 mL, 534.0 mg, 6.5 mmol) was deprotonated in dry THF (10 mL) by *n*-BuLi solution (1.6 M in hexane, 3.8 mL, 6 mmol) slowly at -78 °C (using a dry ice/acetone bath) under argon. After the slow addition, the mixture was stirred at the same temperature for 30 minutes at -78 °C. Then the dry ice/acetone bath was removed. To the mixture, benzaldehyde (0.51 mL, 530.6 mg, 5 mmol) was added. After the reaction was complete (2 h), the mixture was cooled to -78 °C, and $ClCO_2Me$ (1.42 g, 15 mmol) was slowly added. Then the dry ice/acetone bath was removed. The reaction was stirred overnight at room temperature until the reaction was complete as monitored by TLC. The mixture was quenched with saturated NH_4Cl solution and extracted with ethyl acetate. The combined organic layers were washed with water and brine and dried over anhydrous Na_2SO_4. Then the solvent was evaporated under the reduced pressure. Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 15: 1) to afford the title product **1a** in 79% yield (970 mg) as

a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 6.4 Hz, 2H), 7.38-7.35 (m, 3H), 6.29 (s, 1H), 3.77 (s, 3H), 2.26 (t, J = 6.8 Hz, 2H), 1.55-1.37 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 137.0, 128.9, 128.5, 127.6, 89.4, 76.0, 70.1, 54.8, 30.3, 21.8, 18.4, 13.5. The spectroscopic data are in agreement with that previously reported.[2]



1b

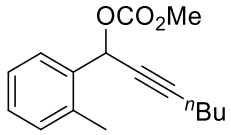
Methyl (1-(*p*-tolyl)hept-2-yn-1-yl) carbonate (1b). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1b** in 88% yield (1.15 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 6.25 (s, 1H), 3.77 (s, 3H), 2.34 (s, 3H), 2.26 (td, J = 7.0, 2.0 Hz, 2H), 1.53-1.50 (m, 2H), 1.45-1.39 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 138.9, 134.2, 129.2, 127.7, 89.1, 76.2, 70.1, 54.8, 30.4, 21.9, 21.1, 18.5, 13.5. IR (neat): 2957, 2234, 1746, 1515, 1440, 1321, 1248, 1181, 1143, 946, 917, 816, 789, 740, 723 cm^{-1}. HRMS (FI) m/z : $[M]^+$ Calcd for $C_{16}H_{20}O_3$ 260.1407; Found 260.1403.



1c

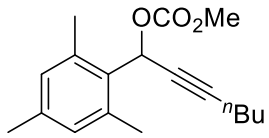
1-(4-(*tert*-Butyl)phenyl)hept-2-yn-1-yl methyl carbonate (1c). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1c** in 66% yield (1.0 g) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 7.6 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 6.28 (s, 1H), 3.78 (s, 3H), 2.27 (t, J = 7.2 Hz, 2H), 1.54-1.50 (m, 2H), 1.44-1.38 (m, 2H), 1.31 (s, 9H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 152.1, 134.0,

127.5, 125.5, 89.2, 76.2, 70.1, 54.9, 34.6, 31.2, 30.4, 21.9, 18.5, 13.6. IR (neat): 2958, 2871, 2236, 1747, 1440, 1321, 1250, 1146, 1107, 948, 919, 839, 788, 682 cm^{-1}. HRMS (FI) m/z : $[M]^+$ Calcd for $C_{19}H_{26}O_3$ 302.1876; Found 302.1881.



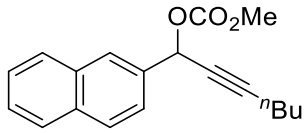
1d

Methyl (1-(*o*-tolyl)hept-2-yn-1-yl) carbonate (1d). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1d** in 88% yield (1.15 g) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 6.8 Hz, 1H), 7.25-7.16 (m, 3H), 6.41 (s, 1H), 3.79 (s, 3H), 2.43 (s, 3H), 2.25 (td, *J* = 6.8, 1.6 Hz, 2H), 1.54-1.49 (m, 2H), 1.42-1.35 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 136.1, 135.1, 130.7, 128.9, 127.9, 126.1, 89.2, 75.9, 68.2, 54.9, 30.4, 21.9, 19.0, 18.5, 13.5. The spectroscopic data are in agreement with that previously reported.[3]



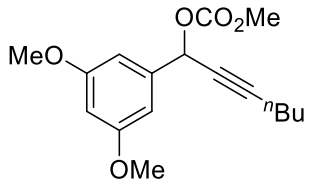
1e

1-Mesitylhept-2-yn-1-yl methyl carbonate (1e). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1e** in 72% yield (1.04 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (s, 2H), 6.69 (s, 1H), 3.73 (s, 3H), 2.51 (s, 6H), 2.24 (s, 3H), 2.20 (td, *J* = 7.2, 2.0 Hz, 2H), 1.49-1.34 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 138.2, 137.0, 130.8, 129.7, 88.3, 75.7, 66.2, 54.7, 30.3, 21.9, 20.8, 20.0, 18.5, 13.5. IR (neat): 2957, 1746, 1611, 1440, 1319, 1256, 1159, 1129, 1034, 920, 851, 793, 739, 695 cm^{-1}. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{18}H_{24}O_3$ 288.1720; Found 288.1724.



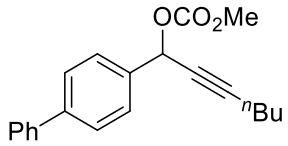
1f

Methyl (1-(naphthalen-2-yl)hept-2-yn-1-yl) carbonate (1f). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1f** in 72% yield (1.06 g) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.86-7.81 (m, 3H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.49-7.47 (m, 2H), 6.46 (s, 1H) , 3.79 (s, 3H), 2.29 (t, *J* = 6.8 Hz, 2H), 1.56-1.37 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 134.3, 133.4, 132.9, 128.5, 128.2, 127.6, 127.0, 126.6, 126.3, 125.0, 89.7, 76.1, 70.3, 54.9, 30.3, 21.9, 18.5, 13.5. IR (neat): 2956, 2871, 2235, 1746, 1440, 1325, 1249, 1140, 1121, 925, 892, 859, 789, 746 cm^{-1}. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{19}H_{20}O_3$ 296.1407; Found 296.1410.



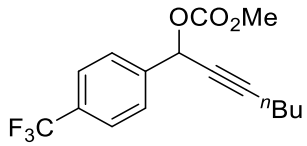
1g

1-(3,5-Dimethoxyphenyl)hept-2-yn-1-yl methyl carbonate (1g). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10: 1) to afford the title product **1g** in 89% yield (1.36 g) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.69 (s, 2H), 6.44 (s, 1H), 6.22 (s, 1H), 3.79 (s, 9H), 2.27 (t, *J* = 6.8 Hz, 2H), 1.52-1.50 (m, 2H), 1.44-1.39 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 154.8, 139.1, 105.4, 101.0, 89.2, 75.9, 69.9, 55.2, 54.8, 30.2, 21.8, 18.4, 13.4. IR (neat): 2957, 2237, 1747, 1598, 1459, 1431, 1329, 1252, 1204, 1154, 1066, 916, 837, 788, 689 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{22}O_5$ 306.1462; Found 306.1458.



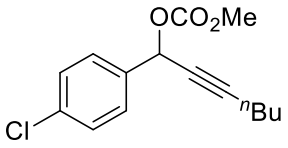
1h

1-([1,1'-Biphenyl]-4-yl)hept-2-yn-1-yl methyl carbonate (1h). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10: 1) to afford the title product **1h** in 68% yield (1.10 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.57 (m, 6H), 7.43 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.6 Hz, 1H), 6.34 (s, 1H), 3.80 (s, 3H), 2.29 (t, J = 6.8 Hz, 2H), 1.56-1.39 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 141.9, 140.5, 136.0, 128.8, 128.2, 127.5, 127.3, 127.1, 89.6, 76.0, 70.0, 54.9, 30.4, 21.9, 18.5, 13.5. The spectroscopic data are in agreement with that previously reported.[3]



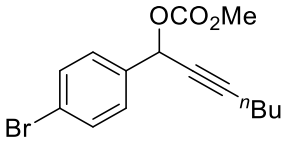
1i

Methyl (1-(4-(trifluoromethyl)phenyl)hept-2-yn-1-yl) carbonate (1i). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1i** in 85% yield (1.33 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (t, J = 9.2 Hz, 4H), 6.33 (s, 1H), 3.81 (s, 3H), 2.28 (t, J = 6.8 Hz, 2H), 1.54-1.50 (m, 2H), 1.43-1.39 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 140.9, 131.0 (q, $^{2}J_{C\text{-}F}$ = 32.3 Hz), 127.9, 125.6 (q, $^{4}J_{C\text{-}F}$ = 3.6 Hz), 123.9 (d, $^{1}J_{C\text{-}F}$ = 270.7 Hz), 90.2, 75.4, 69.2, 55.1, 30.3, 21.9, 18.5, 13.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8. IR (neat): 2960, 2236, 1750, 1622, 1442, 1323, 1252, 1165, 1125, 1110, 1066, 929, 836, 788 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{17}F_3O_3$ 314.1124; Found 314.1123.



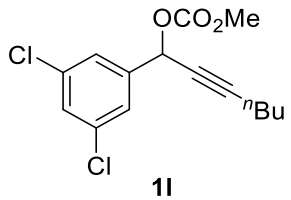
1j

1-(4-Chlorophenyl)hept-2-yn-1-yl methyl carbonate (1j). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1j** in 84% yield (1.18 g) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.25 (s, 1H), 3.79 (s, 3H), 2.27 (td, *J* = 7.0, 2.0 Hz, 2H), 1.53-1.48 (m, 2H), 1.42-1.39 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 135.6, 134.9, 129.1, 128.7, 89.8, 75.6, 69.3, 54.9, 30.3, 21.9, 18.4, 13.5. IR (neat): 2957, 2873, 2236, 1747, 1492, 1440, 1321, 1248, 1145, 1089, 1017, 946, 922, 825, 788 cm^{-1}. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{15}H_{17}O_3Cl$ 280.0861; Found 280.0862.



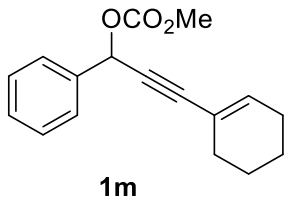
1k

1-(4-Bromophenyl)hept-2-yn-1-yl methyl carbonate (1k). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1k** in 87% yield (1.42 g) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 6.23 (s, 1H) , 3.79 (s, 3H), 2.26 (td, *J* = 7.0, 1.2 Hz, 2H), 1.53-1.49 (m, 2H), 1.40-1.37 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 136.1, 131.7, 129.3, 123.1, 89.8, 75.6, 69.4, 54.9, 30.2, 21.8, 18.4, 13.5. IR (neat): 2957, 2872, 2232, 1747, 1440, 1322, 1247, 1144, 1070, 1013, 946, 921, 819, 788, 741 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{17}BrO_3$ 324.0356; Found 324.0347.



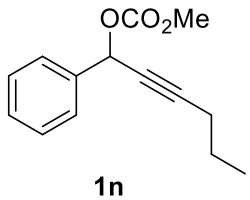
1l

1-(3,5-Dichlorophenyl)hept-2-yn-1-yl methyl carbonate (1l). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1l** in 88% yield (1.38 g) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (s, 2H), 7.34 (s, 1H), 6.21 (s, 1H), 3.82 (s, 3H), 2.28 (td, *J* = 7.6, 1.6 Hz, 2H), 1.55-1.51 (m, 2H), 1.45-1.38 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 140.2, 135.1, 129.0, 126.1, 90.5, 74.9, 68.5, 55.2, 30.2, 21.9, 18.4, 13.5. IR (neat): 2958, 2873, 2236, 1749, 1591, 1572, 1439, 1253, 1201, 1148, 942, 914, 861, 788, 680 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{16}Cl_2O_3$ 314.0471; Found 314.0465.



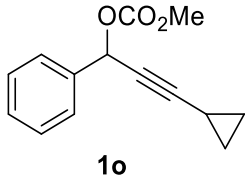
1m

3-(Cyclohex-1-en-1-yl)-1-phenylprop-2-yn-1-yl methyl carbonate (1m). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1m** in 83% yield (1.12 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.6 Hz, 2H), 7.38-7.35 (m, 3H), 6.42 (s, 1H), 6.19 (s, 1H), 3.79 (s, 3H), 2.13-2.09 (m, 4H), 1.61-1.57(m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 136.8, 136.6, 129.0, 128.6, 127.7, 119.7, 89.9, 82.1, 70.3, 54.9, 28.8, 25.6, 22.1, 21.3. IR (neat): 2930, 2223, 1746, 1439, 1322, 1249, 1211, 1189, 1049, 939, 907, 842, 788, 767, 695 cm^{-1}. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{17}H_{18}O_3$ 270.1250; Found 270.1252.



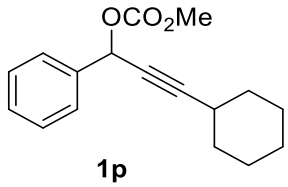
1n

Methyl (1-phenylhex-2-yn-1-yl) carbonate (1n). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1n** in 95% yield (1.10 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.37-7.36 (m, 3H), 6.30 (s, 1H), 3.78 (s, 3H), 2.25 (t, *J* = 5.2 Hz, 2H), 1.58-1.53 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 137.0, 128.9, 128.5, 127.6, 89.3, 76.2, 70.1, 54.9, 21.7, 20.7, 13.4. IR (neat): 2962, 2236, 1746, 1496, 1440, 1322, 1248, 1143, 1029, 931, 909, 788, 762, 695 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{16}O_3$ 232.1094; Found 232.1090.



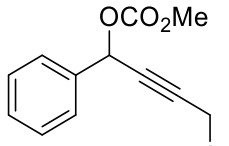
1o

3-Cyclopropyl-1-phenylprop-2-yn-1-yl methyl carbonate (1o). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1o** in 58% yield (668.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.50 (m, 2H), 7.37-7.35 (m, 3H), 6.26 (s, 1H), 3.78 (s, 3H), 1.32-1.28 (m, 1H), 0.80-0.73 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 137.0, 128.9, 128.5, 127.6, 92.4, 71.2, 70.2, 54.9, 8.3, -0.5. IR (neat): 3011, 2240, 1745, 1496, 1440, 1320, 1248, 1158, 1048, 930, 907, 893, 788, 768, 696 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{14}O_3$ 230.0937; Found 230.0933.



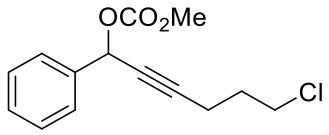
1p

3-Cyclohexyl-1-phenylprop-2-yn-1-yl methyl carbonate (1p). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1p** in 76% yield (831.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.2 Hz, 2H), 7.37-7.35 (m, 3H), 6.32 (s, 1H), 3.77 (s, 3H), 2.46 (m, 1H), 1.80-1.78 (m, 2H), 1.69 (bs, 2H), 1.49-1.43 (m, 3H), 1.32-1.30 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 137.1, 128.9, 128.5, 127.7, 93.3, 76.0, 70.2, 54.8, 32.2, 29.0, 25.7, 24.7. IR (neat): 2929, 2854, 2235, 1746, 1440, 1323, 1249, 1151, 931, 909, 890, 788, 762, 713, 695 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{20}O_3$ 272.1407; Found 272.1401.



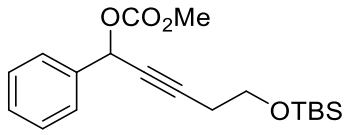
1q

4-Chloro-1-phenylbut-2-yn-1-yl methyl carbonate (1q). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1q** in 64% yield (763.0 mg) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 4.8 Hz, 2H), 7.38 (d, *J* = 5.2 Hz, 3H), 6.33 (s, 1H), 4.18 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 135.7, 129.3, 128.7, 127.6, 82.9, 82.1, 69.3, 55.1, 29.9. IR (neat): 2957, 1747, 1440, 1323, 1245, 1148, 936, 913, 860, 787, 763, 695 cm^{-1}. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{12}H_{11}O_3Cl$ 238.0391; Found 238.0395.



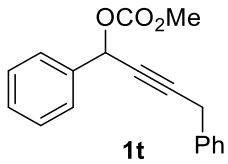
1r

6-Chloro-1-phenylhex-2-yn-1-yl methyl carbonate (1r). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10: 1) to afford the title product **1r** in 91% yield (1.22 g) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 6.8 Hz, 2H), 7.38-7.36 (m, 3H), 6.28 (s, 1H), 3.78 (s, 3H), 3.61 (t, J = 6.4 Hz, 2H), 2.46 (t, J = 6.8 Hz, 2H), 2.00-1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 136.6, 129.0, 128.5, 127.5, 87.2, 77.2, 69.8, 54.9, 43.4, 30.9, 16.2. IR (neat): 2957, 2235, 1746, 1440, 1322, 1248, 1197, 1138, 931, 910, 788, 762, 695 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{15}ClO_3$ 266.0704; Found 266.0705.



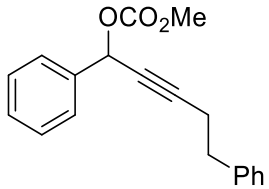
1s

5-((*tert*-Butyldimethylsilyl)oxy)-1-phenylpent-2-yn-1-yl methyl carbonate (1s). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1s** in 41% yield (361.0 mg) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 7.6 Hz, 2H), 7.37-7.36 (m, 3H), 6.29 (s, 1H), 3.79 (s, 3H), 3.74 (t, J = 7.2 Hz, 2H), 2.49 (t, J = 8.4 Hz, 2H), 0.88 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 136.8, 129.0, 128.5, 127.7, 86.3, 77.1, 70.0, 61.4, 54.9, 25.8, 23.2, 18.2, -5.4. IR (neat): 2954, 2929, 2856, 1749, 1440, 1323, 1250, 1144, 1103, 1057, 932, 910, 834, 776, 695 cm^{-1} HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{28}O_4Si$ 348.1751; Found 348.1750.



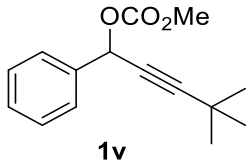
1t

1,4-Diphenylbut-2-yn-1-yl methyl carbonate (1t). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1t** in 88% yield (491.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.37-7.30 (m, 7H), 7.24-7.21 (m, 1H), 6.36 (s, 1H), 3.78 (s, 3H), 3.69 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 136.7, 135.8, 129.1, 128.6, 128.5, 127.8, 127.7, 126.7, 86.6, 78.3, 70.0, 54.9, 25.1. IR (neat): 3031, 2956, 1746, 1495, 1454, 1440, 1322, 1249, 1197, 1139, 933, 910, 787, 731, 694 cm^{-1}. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{18}H_{16}O_3$ 280.1094; Found 280.1100.



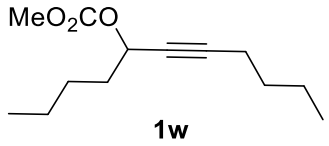
1u

1,5-Diphenylpent-2-yn-1-yl methyl carbonate (1u). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1u** in 89% yield (521.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.45 (m, 2H), 7.34-7.33 (m, 3H), 7.28-7.25 (m, 2H), 7.22-7.17 (m, 3H), 6.27 (s, 1H), 3.77 (s, 3H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 140.2, 136.7, 128.9, 128.5, 128.4, 128.3, 127.6, 126.3, 88.4, 76.9, 70.0, 54.9, 34.5, 21.0. The spectroscopic data are in agreement with that previously reported.[4]



1v

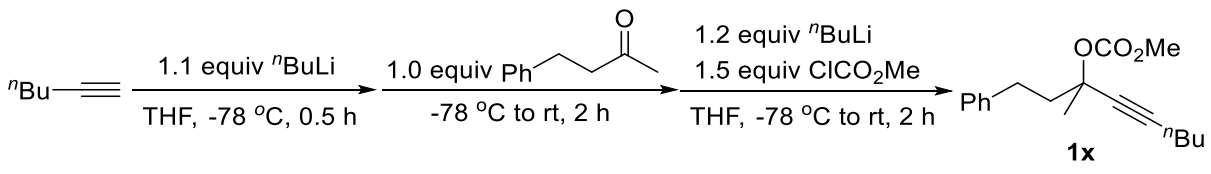
4,4-Dimethyl-1-phenylpent-2-yn-1-yl methyl carbonate (1v). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1v** in 92% yield (1.13 g) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 6.0 Hz, 2H), 7.37-7.35 (m, 3H), 6.31 (s, 1H), 3.77 (s, 3H), 1.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 137.1, 128.9, 128.5, 127.7, 97.2, 74.5, 70.1, 54.8, 30.6, 27.5. IR (neat): 2970, 2242, 1739, 1456, 1438, 1265, 1247, 1194, 956, 933, 908, 857, 790, 770, 703 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{18}O_3$ 246.1250; Found 246.1245.



1w

Methyl undec-6-yn-5-yl carbonate (1w). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30: 1) to afford the title product **1w** in 87% yield (984.0 mg) as a colorless oil.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.20 (t, *J* = 6.4 Hz, 1H), 3.79 (s, 3H), 2.22 (t, *J* = 6.8 Hz, 2H), 1.80-1.76 (m, 2H), 1.51-1.36 (m, 8H), 0.92-0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 87.0, 76.9, 68.7, 54.7, 34.8, 30.4, 27.0, 22.1, 21.8, 18.3, 13.8, 13.5. The spectroscopic data are in agreement with that previously reported.[5]

For the synthesis of propargyl carbonate 1x, see the following:



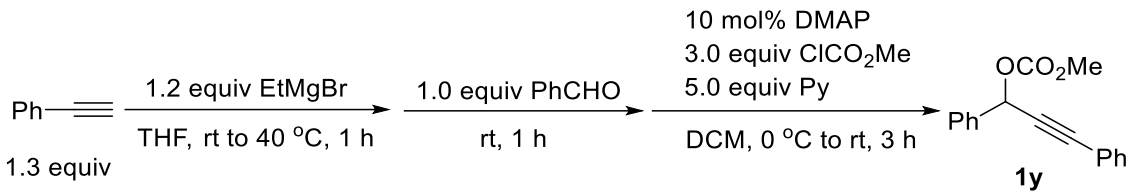
1x

Methyl (3-methyl-1-phenylnon-4-yn-3-yl) carbonate (1x). 1-Hexyne (985.8 mg, 12 mmol) was deprotonated in dry THF (10 mL) by *n*-BuLi solution (1.6 M in hexane, 6.9 mL, 11 mmol) slowly at -78 ºC (using a dry ice/acetone bath) under argon. After the slow addition, the mixture was stirred for 30 minutes at -78 ºC. Then to the mixture, 4-phenylbutan-2-one (1.48 g, 10 mmol) was added, and then the dry ice/acetone bath was removed. The mixture was stirred at room temperature for 2 h. The resulting reaction mixture was quenched with saturated NH_4Cl solution and extracted with ethyl acetate. The combined organic extracts were washed with brine, then dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure to afford the product of alcohol, which was used directly without further purification for the next step.

The above crude alcohol was deprotonated in dry THF (26 mL) by *n*-BuLi solution (1.6 M in hexane, 7.5 mL, 12 mmol) slowly at -78 ºC (using a dry ice/acetone bath) under argon. After the slow addition, the mixture was stirred for 30 minutes at -78 ºC. Then to the mixture, $ClCO_2Me$ (1.42 g, 15 mmol) was added, and then the dry ice/acetone bath was removed. The reaction mixture was stirred at room temperature until the reaction was complete as monitored by TLC (2 h). The resulting reaction mixture was quenched with water and extracted with ethyl acetate. The combined organic extracts were washed with brine, then dried over anhydrous Na_2SO_4.The mixture was concentrated and the solvent was evaporated under the reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20: 1) to afford the title product **1x** in 90% overall yield (2.6 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (q, J = 7.6 Hz, 2H), 7.22-7.17 (m, 3 H), 3.76 (s, 3H), 2.83 (t, J = 8.4 Hz, 2H), 2.30-2.23 (m, 3H), 2.11-2.04 (m, 1H), 1.74 (s, 3H), 1.54-1.40 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 141.6, 128.40, 128.38, 125.9, 86.8, 79.4, 77.7, 54.2, 43.7, 30.8, 30.6, 26.7, 21.9, 18.4, 13.6. The spectroscopic data are in agreement with that previously reported.[6]

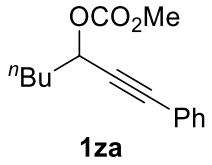
For the synthesis of new propargyl carbonates 1y and 1za, see the following:

Typical procedure for the synthesis of 1y:



1,3-Diphenylprop-2-yn-1-yl methyl carbonate (1y). To a solution of phenylacetylene (3.98 g, 39.0 mmol) in THF (60 mL) was added dropwise EtMgBr (3.0 M solution in Et_2O, 12.0 mL, 36.0 mmol) at room temperature under argon. Then the mixture was warmed up to 40 °C and stirred for 1 h. After cooling to room temperature, benzaldehyde (3.18 g, 30 mmol) was added and the reaction mixture was stirred until the reaction was complete as monitored by TLC (1 h). The resulting reaction mixture was quenched with saturated NH_4Cl solution and extracted with ethyl acetate. The combined organic extracts were washed with water and brine, then dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure to afford the product of alcohol, which was used directly without further purification for the next step.

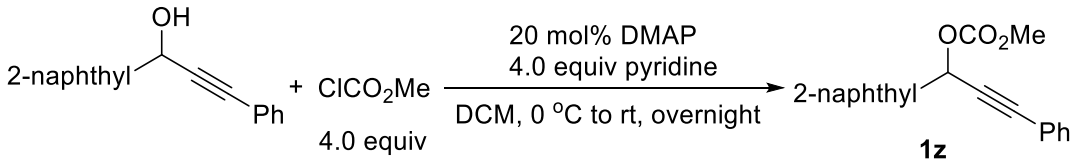
To a solution of the above crude alcohol in DCM (60 mL) were added pyridine (12.1 mL, 150.0 mmol) and DMAP (366.5 mg, 3.0 mmol) under air. The solution was cooled to 0 °C, $ClCO_2Me$ (7.0 mL, 90.0 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 3 h. The mixture was quenched with water and extracted with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4. The mixture was concentrated and the solvent was evaporated under the reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10: 1) to afford the title product **1y** in 75% overall yield (6.0 g) as a light-yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63-7.61 (m, 2H), 7.48-7.46 (m, 2H), 7.41-7.37 (m, 3H), 7.32-7.29 (m, 3H), 6.53 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 136.5, 131.9, 129.2, 128.9, 128.7, 128.2, 127.8, 121.9, 88.0, 84.8, 70.2, 55.0. The spectroscopic data are in agreement with that previously reported.[7]



Methyl (1-phenylhept-1-yn-3-yl) carbonate (1za). First step: phenylacetylene (1.99 g, 19.5

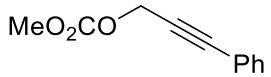
mmol) and EtMgBr (3.0 M solution in Et_2O, 6.0 mL, 18.0 mmol) in THF (30 mL) was stirred at 40 °C for 1 h, and after valeraldehyde (1.29 g, 15.0 mmol) was added, the reaction mixture was stirred at room temperature for 1 h. Second step: To a solution of the above crude alcohol in DCM (30 mL) were added pyridine (6.0 mL, 75.0 mmol) and DMAP (183.3 mg, 1.5 mmol), $ClCO_2Me$ (3.5 mL, 45.0 mmol) was added at 0 °C and then stirred at room temperature. Then saturated ammonium chloride solution and $CuSO_4 \cdot 5H_2O$ were added to the reaction mixture. The mixture was filtered and extracted with dichloromethane, washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 15: 1) to afford the title product **1za** in 54% overall yield (2.0 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.43 (m, 2H), 7.31-7.26 (m, 3H), 5.46 (t, *J* = 6.4 Hz, 1H), 3.82 (s, 3H), 1.94-1.86 (m, 2H), 1.55-1.47 (m, 2H), 1.42-1.36 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 131.8, 128.6, 128.2, 122.2, 86.0, 85.8, 68.7, 54.8, 34.6, 27.0, 22.2, 13.9. The spectroscopic data are in agreement with that previously reported.[5]

For the synthesis of new propargyl carbonates 1z, 1zb, 1zc, see the following:



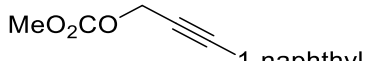
Methyl (1-(naphthalen-2-yl)-3-phenylprop-2-yn-1-yl) carbonate (1z). Methyl chloroformate (755.9 mg, 8.0 mmol) was added to a solution of 1-(naphthalen-2-yl)-3-phenylprop-2-yn-1-ol (516.6 mg, 2.0 mmol), pyridine (632.8 mg, 8.0 mmol), and DMAP (48.9 mg, 0.4 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The resulting mixture was stirred overnight at room temperature. The resulting solution was quenched with a saturated aqueous $CuSO_4 \cdot 5H_2O$ solution, washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10: 1) to afford the title product **1z** in 55% yield (346.2 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.88-7.80 (m, 3H), 7.72 (d, *J*= 8.4 Hz, 1H), 7.49-7.47 (m, 4H), 7.30-7.29 (m, 3H), 6.71 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 133.7, 133.5, 132.9, 131.8, 128.9, 128.7, 128.3, 128.2, 127.6, 127.2, 126.7, 126.4,

124.9, 121.8, 88.2, 84.8, 70.3, 55.0. IR (neat): 3058, 2228, 1746, 1490, 1440, 1326, 1248, 1165, 1125, 1033, 923, 859, 788, 754, 690 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{16}O_3Na$ 339.0992; Found 330.0993.



1zb

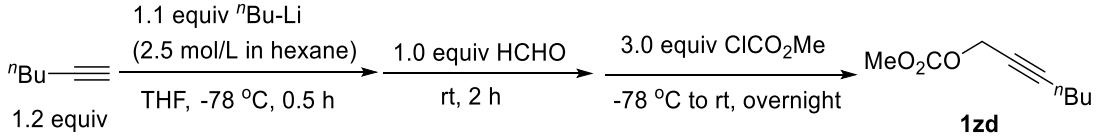
Methyl (3-phenylprop-2-yn-1-yl) carbonate (1zb). The residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30: 1) to afford the title product **1zb** in 85% yield (812.0 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (dd, *J*= 7.6, 2.0 Hz, 2H), 7.33-7.30 (m, 3H), 4.96 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 131.8, 128.8, 128.2, 121.9, 87.1, 82.2, 56.1, 55.0. The spectroscopic data are in agreement with that previously reported.[8]



1zc

Methyl (3-(naphthalen-1-yl)prop-2-yn-1-yl) carbonate (1zc). The residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10: 1) to afford the title product **1zc** in 85% yield (407.8 mg) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J*= 8.4 Hz, 1H), 7.82 (d, *J*= 8.0 Hz, 1H), 7.69 (d, *J*= 7.2 Hz, 1H), 7.57 (t, *J*= 6.8 Hz, 1H), 7.50 (t, *J*= 7.6 Hz, 1H), 7.40 (t, *J*= 8.4 Hz, 1H), 5.11 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 133.2, 133.0, 131.0, 129.3, 128.2, 126.9, 126.4, 125.9, 125.0, 119.5, 87.0, 85.2, 56.3, 55.1. IR (neat): 3058, 2961, 2226, 1744, 1449, 1431, 1367, 1274, 1253, 1104, 958, 932, 901, 799, 772 cm^{-1}. HRMS (EI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{13}O_3$ 241.0859; Found 241.0860.

For the synthesis of propargyl carbonate 1zd, see the following:



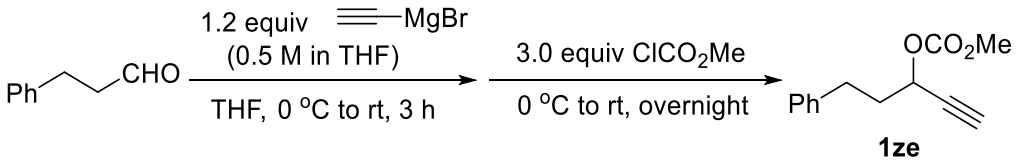
1zd

Hept-2-yn-1-yl methyl carbonate (1zd). 1-Hexyne (1.4 mL, 985.8 mg, 12 mmol) was

deprotonated in dry THF (20 mL) by *n*-BuLi solution (2.5 M in hexane, 4.4 mL, 11 mmol) slowly at -78 °C under argon. After the slow addition, the mixture was stirred for 30 minutes. To the mixture, HCHO (300.0 mg, 10 mmol) was added under nitrogen, and then the mixture was stirred at room temperature for 2 h. After the reaction was complete, $ClCO_2Me$ (2.84 g, 30 mmol) was slowly added at -78 °C under argon. The reaction mixture was stirred overnight at room temperature until the reaction was complete as monitored by TLC. The mixture was quenched with saturated NH_4Cl solution and extracted with ethyl acetate. The combined organic layers were washed with water and brine and dried over anhydrous Na_2SO_4. The mixture was concentrated and the solvent was evaporated under the reduced pressure. Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 30: 1) to afford the title product **1zd** in 79% yield (1.34 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.72 (t, *J* = 2.0 Hz, 2H), 3.81 (s, 3H), 2.22 (t, *J* = 6.8 Hz, 2 H), 1.53-1.37 (m, 4H), 0.91 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 88.5, 73.3, 56.2, 54.9, 30.3, 21.8, 18.4, 13.5. The spectroscopic data are in agreement with that previously reported.[4]

For the synthesis of propargyl carbonates 1ze – 1zf, 1zh – 1zj, and 1zm, see the following:

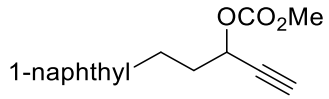
Typical procedure for the synthesis of 1ze.



1ze

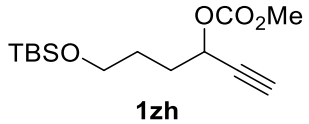
Methyl (5-phenylpent-1-yn-3-yl) carbonate (1ze). To a schlenk tube were added 3-phenylpropanal (0.66 mL, 670.9 mg, 5 mmol), THF (10 mL), then the solution was cooled to 0 °C and ethynylmagnesium bromide was added (0.5 M in THF, 12 mL, 6 mmol). After the reaction was stirred at room temperature for 3 h, $ClCO_2Me$ (1.42 g, 15 mmol) was slowly added at 0 °C under argon. The reaction mixture was stirred overnight at room temperature until the reaction was complete as monitored by TLC. The mixture was quenched with saturated NH_4Cl solution and extracted with ethyl acetate. The combined organic layers were washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced

pressure. Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10: 1) to afford the title product **1ze** in 57% yield (622.0 mg) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.28 (m, 2H), 7.25-7.19 (m, 3H), 5.20 (td, *J* = 6.6, 2.0 Hz, 1H), 3.82 (s, 3H), 2.81 (t, *J* = 6.8 Hz, 2H), 2.57 (d, *J* = 2.0 Hz, 1H), 2.19-2.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 140.3, 128.5, 128.4, 126.2, 80.2, 74.9, 67.1, 55.0, 36.1, 30.9. The spectroscopic data are in agreement with that previously reported.[9]



1zf

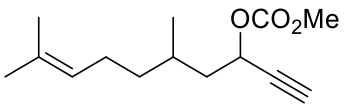
Methyl (5-(naphthalen-1-yl)pent-1-yn-3-yl) carbonate (1zf). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5: 1) to afford the title product **1zf** in 61% yield (812.0 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.54-7.46 (m, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 6.4 Hz, 1H), 5.29 (td, *J* = 6.4, 2.0 Hz, 1H), 3.82 (s, 3H), 3.30-3.24 (m, 2H), 2.61 (d, *J* = 2.0 Hz, 1H), 2.31-2.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 136.4, 133.9, 131.6, 128.8, 127.1, 126.1, 126.0, 125.54, 125.52, 123.4, 80.2, 75.0, 67.4, 55.0, 35.3, 28.0. IR (neat): 3286, 2956, 1747, 1597, 1510, 1441, 1396, 1344, 1257, 1180, 1031, 1004, 944, 777 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{16}O_3$ 268.1094; Found 268.1083.



1zh

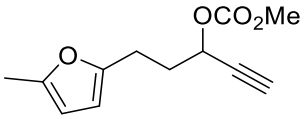
6-((*tert*-Butyldimethylsilyl)oxy)hex-1-yn-3-yl methyl carbonate (1zh). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent:

petroleum ether: ethyl acetate = 20: 1) to afford the title product **1zh** in 52% yield (506.0 mg) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.26 (td, *J* = 6.8, 2.0 Hz, 1H), 3.81 (s, 3H), 3.65 (t, *J* = 6.0 Hz, 2H), 2.52 (d, *J* = 2.0 Hz, 1H), 1.93-1.88 (m, 2H), 1.73-1.68 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 80.5, 74.4, 67.7, 62.2, 54.8, 31.3, 27.9, 25.9, 18.2, -5.4. The spectroscopic data are in agreement with that previously reported.[10]



1zi

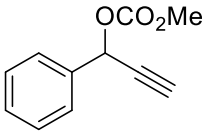
5,9-Dimethyldec-8-en-1-yn-3-yl methyl carbonate (1zi). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10: 1) to afford the title product **1zi** in 28% yield (338.0 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.27 (m, 1H), 5.08 (t, *J* = 6.8Hz, 1H), 3.81 (s, 3H), 2.52 (s, 1H), 2.03-1.83 (m, 3H), 1.68 (m, 5H), 1.60 (m, 3H), 1.41-1.35 (m, 1H), 1.24-1.19 (m, 1H), 0.95 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 154.9, 131.4, 124.3, 80.9, 80.6, 74.49, 74.48, 74.20. 74.19, 66.8, 66.3, 54.91, 54.88, 41.8, 41.4, 36.8, 36.7, 29.0, 28.7, 25.6, 25.2, 25.1, 19.3, 19.2, 17.59, 17.58. IR (neat): 3294, 2959, 2917, 1749, 1442, 1379, 1342, 1259, 1109, 962, 925, 790, 667 cm^{-1}. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{14}H_{22}O_3$ 238.1563; Found 238.1562.



1zj

Methyl (5-(5-methylfuran-2-yl)pent-1-yn-3-yl) carbonate (1zj). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5: 1) to afford the title product **1zj** in 73% yield (811.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 (s, 1H), 5.84 (s, 1H), 5.23 (t, *J* = 6.8 Hz, 1H), 3.81 (s, 3H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.54 (s, 1H), 2.24 (s, 3H), 2.17-2.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 152.0, 150.7, 106.1, 105.9, 80.1, 74.8, 66.9, 55.0, 33.1, 23.4,

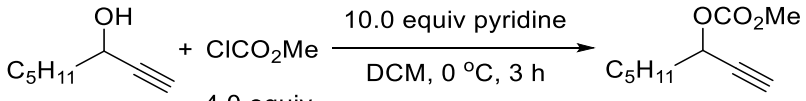
13.4. IR (neat): 3288, 2957, 1749, 1570, 1442, 1258, 1018, 942, 784 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_{14}O_4$ 222.0887; Found 222.0883.



1zm

Methyl (1-phenylprop-2-yn-1-yl) carbonate (1zm). Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10: 1) to afford the title product **1zm** in 73% yield (1.39 g) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.55 (m, 2H), 7.40-7.39 (m, 3H), 6.29 (d, *J* = 2.0 Hz, 1H), 3.81 (s, 3H), 2.73 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 135.7, 129.3, 128.7, 127.6, 79.5, 76.4, 69.2, 55.1. The spectroscopic data are in agreement with that previously reported.[11]

For the synthesis of propargyl carbonate 1zg, see the following:

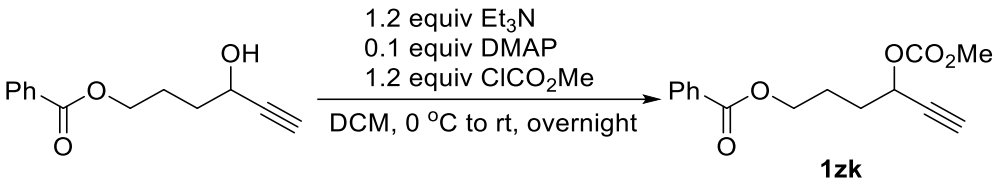


1zg

Methyl oct-1-yn-3-yl carbonate (1zg). To a stirred solution of propargyl alcohol (0.73 mL, 631.0 mg, 5 mmol) and pyridine (4.5 mL, 3.96 g, 50 mmol) in dichloromethane (50 mL) was added dropwise $ClCO_2Me$ (1.89 g, 20 mmol) at 0 °C. Then the mixture was stirred for 3 h at room temperature. The mixture was quenched with saturated NH_4Cl solution and extracted with DCM. The combined organic layers were washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10: 1) to afford the title product **1zg** in 91% yield (834.0 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.20 (t, *J* = 6.8 Hz, 1H), 3.81 (s, 3H), 2.52 (s, 1H), 1.85-1.79 (m, 2H), 1.51-1.44 (m, 2H), 1.34-1.32 (m, 4H), 0,90 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 80.5, 74.3, 67.8, 54.8, 34.5, 31.1, 24.3, 22.3, 13.8. The spectroscopic data are in agreement with that

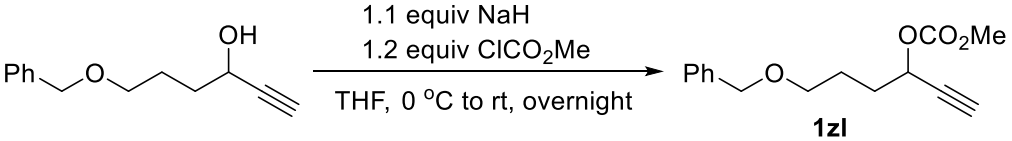
previously reported.[12]

For the synthesis of propargyl carbonate 1zk, see the following:



4-((Methoxycarbonyl)oxy)hex-5-yn-1-yl benzoate (1zk). Under an argon atmosphere, to a dried Schlenk tube equipped with a stirring bar were added 4-hydroxyhex-5-yn-1-yl benzoate (589.0 mg, 2.7 mmol), DCM (6 mL) and Et_3N (0.45 mL, 327.9 mg, 3.24 mmol). Then DMAP (33.0 mg, 0.27 mmol) was added at 0 °C. The reaction mixture was stirred at 0 °C for 2 h, then $ClCO_2Me$ (306.2 mg, 3.24 mmol) was added. The reaction mixture was stirred at room temperature overnight. Then the mixture was quenched with saturated NH_4Cl aqueous solution, extracted with ethyl acetate. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5: 1) to afford the title product **1zk** in 34% yield (253.6 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 8.06-8.03 (m, 2H), 7.58-7.55 (m, 1H), 7.45 (t, J = 7.6 Hz, 2H), 5.33-5.30 (m, 1H), 4.37 (t, J = 5.6 Hz, 2H), 3.81 (s, 3H), 2.57 (d, J = 2.4 Hz, 1H), 2.01-2.00 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 154.8, 132.9, 130.1, 129.5, 128.3, 79.9, 74.9, 67.2, 64.1, 55.0, 31.3, 24.2. The spectroscopic data are in agreement with that previously reported.[10]

For the synthesis of propargyl carbonate 1zl, see the following:



6-(Benzyloxy)hex-1-yn-3-yl methyl carbonate (1zl). Under an argon atmosphere, to dried Schlenk tube equipped with a stirring bar was added 6-(benzyloxy)hex-1-yn-3-ol (572.0 mg, 2.8 mmol) and THF (6 mL). After the mixture was cooled down to 0 °C, NaH (60% dispersion

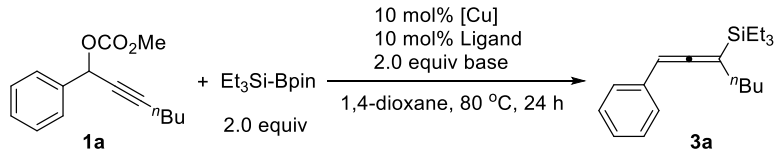
in mineral oil) (123.2 mg, 3.08 mmol) was added in portions. The reaction mixture was stirred at same temperature for 30 min. Then $ClCO_2Me$ (317.5 mg, 3.36 mmol) was added. The reaction mixture was stirred at room temperature overnight. Then the mixture was quenched with saturated NH_4Cl aqueous solution, extracted with ethyl acetate. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Before the column chromatography, the column was alkalified using petroleum ether: triethylamine = 20: 1 as the eluent. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5: 1) to afford the title product **1zl** in 72% yield (531.9 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.28 (m, 5H), 5.25 (td, *J* = 6.6, 2.0 Hz, 1H), 4.50 (s, 2H), 3.80 (s, 3H), 3.51 (t, *J* = 6.0 Hz, 2H), 2.52 (d, *J* = 1.6 Hz, 1H), 1.98-1.92 (m, 2H), 1.84-1.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ154.9, 138.3, 128.3, 127.6, 127.5, 80.3, 74.6, 72.8, 69.3, 67.6, 54.9, 31.5, 25.0. The spectroscopic data are in agreement with that previously reported.[10]

Optimization studies for the formation of 3a.

General procedure for optimization studies.

The reaction was conducted in an oven-dried screw-cap vial (volume: 4 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, Cu catalyst (0.02 mmol), ligand (0.02 mmol), base, Et_3Si-Bpin (0.4 mmol, 96.9 mg), solvent (1 mL) were added sequentially to a screw-cap vial. The mixture was stirred for 1 minute, and **1a** (0.2 mmol, 49.3 mg) was added. The vial cap was then securely fitted and taken outside the glove box. After the reaction mixture was stirred at 80 ºC in an oil bath for 24 h, the mixture was cooled down to room temperature, filtered through a pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the yields were determined by ^{1}H NMR using 1,3,5-trimethylbenzene (1.0 equiv., 24.0 mg) in $CDCl_3$ as the internal standard.

Table S1. Optimization studies for the formation of 3a.

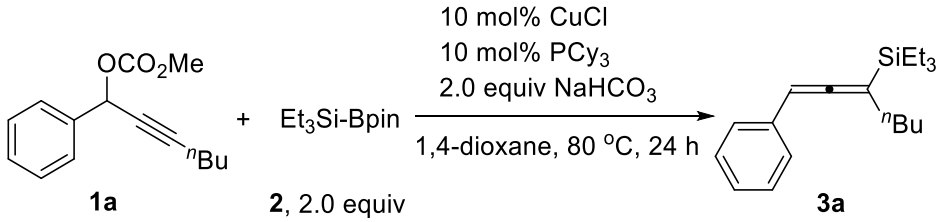


entry	[Cu]	ligand	base	solvent	Temp (°C)	time (h)	NMR yield (%)[a]
1	CuCl	PPh_3	$NaHCO_3$	1,4-dioxane	80	24	88
2	CuCl	$PPhCy_2$	$NaHCO_3$	1,4-dioxane	80	24	90
3	**CuCl**	**PCy_3**	**$NaHCO_3$**	**1,4-dioxane**	80	24	**91**
4	CuCl	P(*p*-tol)$_3$	$NaHCO_3$	1,4-dioxane	80	24	70
5	CuCl	^{t}BuXphos	$NaHCO_3$	1,4-dioxane	80	24	13
6	CuCl	dppe	$NaHCO_3$	1,4-dioxane	80	24	63
7	CuCl	dppf	$NaHCO_3$	1,4-dioxane	80	24	67
8	CuCl	DPEphos	$NaHCO_3$	1,4-dioxane	80	24	25
9	CuCl	Xantphos	$NaHCO_3$	1,4-dioxane	80	24	68
10	CuCl	DCype	$NaHCO_3$	1,4-dioxane	80	24	68
11	CuCl	IMes	$NaHCO_3$	1,4-dioxane	80	24	50
12	CuCl	IPr	$NaHCO_3$	1,4-dioxane	80	24	46
13	CuCl	PCy_3	KO^tBu	1,4-dioxane	80	24	0
14	CuCl	PCy_3	NaO^tBu	1,4-dioxane	80	24	0
15	CuCl	PCy_3	LiO^tBu	1,4-dioxane	80	24	82
16	CuCl	PCy_3	NaOMe	1,4-dioxane	80	24	74
17	CuCl	PCy_3	K_3PO_4	1,4-dioxane	80	24	87
18	CuCl	PCy_3	Na_2CO_3	1,4-dioxane	80	24	79
19	$[Cu(MeCN)_4]^+[PF_6]^-$	PCy_3	$NaHCO_3$	1,4-dioxane	80	24	77
20	$Cu(OAc)_2$	PCy_3	$NaHCO_3$	1,4-dioxane	80	24	81
21	$Cu(OTf)_2$	PCy_3	$NaHCO_3$	1,4-dioxane	80	24	64
22	CuCl	PCy_3	$NaHCO_3$	THF	80	24	80
23	CuCl	PCy_3	$NaHCO_3$	toluene	80	24	75
24	CuCl	PCy_3	$NaHCO_3$	MeCN	80	24	49
25	CuCl	PCy_3	$NaHCO_3$	DMF	80	24	13
26	-	PCy_3	$NaHCO_3$	1,4-dioxane	80	24	0
27	CuCl	-	$NaHCO_3$	1,4-dioxane	80	24	0
28	CuCl	PCy_3	-	1,4-dioxane	80	24	13
29	CuCl	PCy_3	$NaHCO_3$	1,4-dioxane	50	24	trace
30	CuCl	PCy_3	$NaHCO_3$	1,4-dioxane	rt	24	0
31	CuCl	PCy_3	$NaHCO_3$[b]	1,4-dioxane	80	24	77
32	CuCl	PCy_3	$NaHCO_3$[c]	1,4-dioxane	80	24	79
33[d]	CuCl	PCy_3	$NaHCO_3$	1,4-dioxane	80	24	63

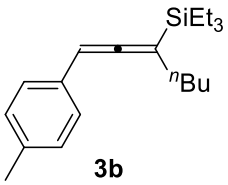
[a]0.2 mmol scale. NMR yields. [b]1.5 equiv of base was used. [c]1.0 equiv of base was used. [d]1.5 equiv Et_3Si-Bpin was used.

Synthesis of allenylsilanes 3.

Typical procedure for the synthesis of 3a.

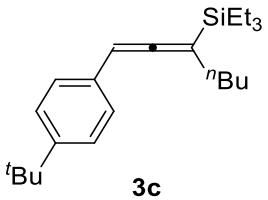


Triethyl(1-phenylhepta-1,2-dien-3-yl)silane (3a). In the nitrogen-filled glove box, CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), $Et_3SiBpin$ (0.6 mmol, 145.3 mg), 1,4-dioxane (1.5 mL) was added to screw-cap vial (4 mL). The solvent stirred at ambient temperature for 1 minute. Then **1a** (0.3 mmol, 73.9 mg) was added. The vial was sealed with a screw cap featuring a PTFE/silicone septum and taken outside the glove box. The vial was immersed into an oil bath preheated at 80 °C. After the reaction mixture was stirred at 80 °C for 24 h. The mixture was filtered over a silica gel pad and washed with ethyl acetate. The solvent was evaporated under the reduced pressure. Purification by silica gel plate (eluent: petroleum ether) afforded the titile product **3a** in 80% yield (69.0 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.21 (m, 4H), 7.10 (t, J = 6.8 Hz, 1H), 5.85 (bs, 1H), 2.09-2.05 (m, 2H), 1.54-1.47 (m, 2H), 1.37-1.32 (m, 2H), 0.96 (t, J = 7.6 Hz, 9H), 0.87 (t, J = 8.4 Hz, 3H), 0.64 (q, J = 8.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.8, 136.4, 128.4, 125.8, 125.6, 98.3, 89.7, 31.3, 29.4, 22.6, 13.9, 7.4, 3.2. IR (neat): 2954, 2931, 2873, 1917, 1598, 1496, 1457, 1414, 1377, 1238, 1007, 973, 905, 798. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{30}Si$ 286.2111; Found 286.2115.



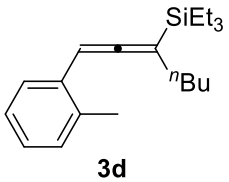
Triethyl(1-(*p*-tolyl)hepta-1,2-dien-3-yl)silane (3b). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1b** (0.3 mmol, 78.1 mg) were stirred at 80 °C for 24 h. Purification by silica gel column (eluent: petroleum ether) afforded the title product **3b** in 73% yield (66.0 mg) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz,

2H), 5.83 (t, J = 2.8 Hz, 1H), 2.30 (s, 3H), 2.06-2.04 (m, 2H), 1.52-1.48 (m, 2H), 1.37-1.34 (m, 2H), 0.96 (t, J = 8.0 Hz, 9H), 0.87 (t, J = 7.2 Hz, 3H), 0.64 (q, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.9, 135.2, 133.3, 129.2, 125.7, 98.2, 89.5, 31.3, 29.5, 22.6, 21.1, 13.9, 7.4, 3.3. IR (neat): 2953, 2930, 2873, 1917, 1512, 1457, 1415, 1377, 1237, 1107, 1008, 973, 826. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{32}Si$ 300.2268; Found 300.2274.



3c

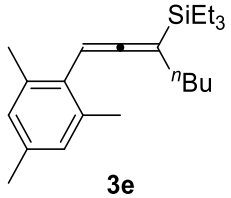
(1-(4-(*tert*-Butyl)phenyl)hepta-1,2-dien-3-yl)triethylsilane (3c). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1c** (0.3 mmol, 90.7 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **3c** in 86% yield (88.4 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 5.84 (t, J = 2.4 Hz, 1H), 2.05-2.01 (m, 2H), 1.50-1.46 (m, 2H), 1.37-1.33 (m, 2H), 1.30 (s, 9H), 0.97 (t, J = 8.0 Hz, 9H), 0.87 (t, J = 7.6 Hz, 3H), 0.65 (q, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.0, 148.5, 133.3, 125.5, 125.4, 98.1, 89.4, 34.4, 31.4, 29.5, 22.7, 14.0, 7.4, 3.2. IR (neat): 2954, 2932, 2873, 1917, 1514, 1459, 1420, 1377, 1362, 1269, 1237, 1008, 973, 839, 715. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{23}H_{38}Si$ 342.2737; Found 342.2749.



3d

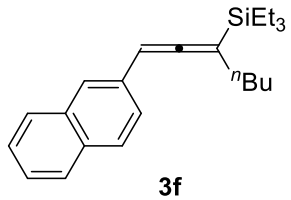
Triethyl(1-(*o*-tolyl)hepta-1,2-dien-3-yl)silane (3d). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1d** (0.3 mmol, 78.1mg) were stirred at 80 °C for 24 h. Purification by silica gel column (eluent: petroleum ether) afforded the title product **3d** in 77% yield (69.3 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 7.6 Hz, 1H), 7.11 (t, J = 8.0 Hz, 2H),

7.02 (t, J = 6.8 Hz, 1H), 6.02 (t, J = 2.8 Hz, 1H), 2.32 (s, 3H), 2.07-2.06 (m, 2H), 1.52-1.47 (m, 2H), 1.38-1.33 (m, 2H), 0.96 (t, J = 7.6 Hz, 9H), 0.88 (t, J = 7.2 Hz, 3H), 0.65 (q, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.4, 134.4, 133.8, 130.3, 126.1, 125.9, 125.4, 97.1, 86.6, 31.4, 29.4, 22.7, 19.8, 13.9, 7.4, 3.2. IR (neat): 2954, 2931, 2874, 1915, 1600, 1489, 1463, 1414, 1377, 1237, 1006, 973, 795. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{32}Si$ 300.2268; Found 300.2271.



3e

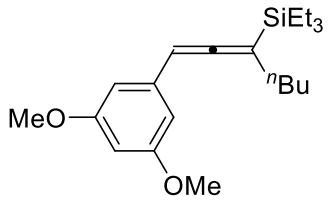
Triethyl(1-mesitylhepta-1,2-dien-3-yl)silane (3e). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1e** (0.3 mmol, 86.5 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **3e** in 45% yield (44.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (s, 2H), 5.99 (s, 1H), 2.32 (s, 6H), 2.25 (s, 3H), 2.14-2.08 (m, 1H), 2.00-1.93 (m, 1H), 1.56-1.53 (m, 2H), 1.40-1.34 (m, 2H), 0.94-0.90 (m, 12H), 0.65-0.58 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.7, 135.7, 134.8, 129.6, 129.0, 93.4, 84.7, 31.5, 29.5, 22.7, 21.7, 20.8, 14.0, 7.4, 3.3. IR (neat): 2953, 2931, 2873, 1919, 1480, 1458, 1414, 1376, 1237, 1010, 974, 851, 803, 718 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{22}H_{36}Si$ 328.2581; Found 328.2587.



3f

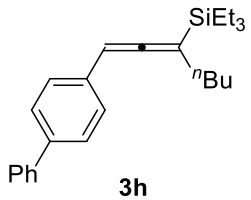
Triethyl(1-(naphthalen-2-yl)hepta-1,2-dien-3-yl)silane (3f). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1f** (0.3 mmol, 88.9 mg) were stirred at 80 °C for 24 h. Purification

by silica gel plate (eluent: petroleum ether) afforded the title product **3f** in 76% yield (76.5 mg) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (t, *J* = 8.8 Hz, 3H), 7.57 (s, 1H), 7.45-7.35 (m, 3H), 6.04 (s, 1H), 2.11-2.09 (m, 2H), 1.56-1.51 (m, 2H), 1.38-1.34 (m, 2H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.88 (t, *J* = 7.6 Hz, 3H), 0.67 (q, *J* = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.3, 133.95, 133.88, 132.1, 128.0, 127.6, 127.4, 126.0, 124.9, 124.4, 123.8, 98.5, 90.1, 31.3, 29.4, 22.6, 14.0, 7.4, 3.2. IR (neat): 2953, 2930, 2873, 1916, 1628, 1598, 1508, 1457, 1317, 1237, 1006, 886, 855, 817, 716 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{23}H_{32}Si$ 336.2268; Found 336.2272.



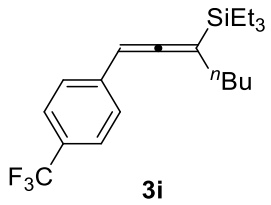
3g

(1-(3,5-Dimethoxyphenyl)hepta-1,2-dien-3-yl)triethylsilane (3g). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1g** (0.3 mmol, 91.9 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **3g** in 93% yield (97.1 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.42 (d, *J* = 2.0 Hz, 2H), 6.26 (t, *J* = 2.4 Hz, 1H), 5.80 (t, *J* = 2.8 Hz, 1H), 3.76 (s, 6H), 2.08-2.04 (m, 2H), 1.54-1.48 (m, 2H), 1.40-1.33 (m, 2H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.64 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.8, 160.8, 138.6, 103.7, 98.41, 98.35, 89.9, 55.1, 31.3, 29.4, 22.6, 13.9, 7.4, 3.2. IR (neat): 2953, 2873, 1917, 1591, 1460, 1428, 1377, 1306, 1290, 1204, 1139, 1066, 1009, 972, 928, 848, 830, 715, 682 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{34}O_2Si$ 346.2323; Found 346.2332.



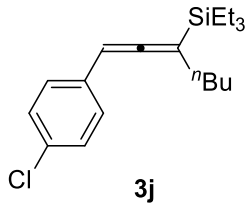
3h

(1-([1,1'-Biphenyl]-4-yl)hepta-1,2-dien-3-yl)triethylsilane (3h). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1h** (0.3 mmol, 96.7 mg) were stirred at 80 °C for 24 h. Purification by silica gel column (eluent: petroleum ether) afforded the title product **3h** in 76% yield (82.9 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 3H), 5.90 (s, 1H), 2.09 (m, 2H), 1.54-1.50 (m, 2H), 1.39-1.32 (m, 2H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.89 (t, *J* = 7.6 Hz, 3H), 0.66 (q, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.0, 141.0, 138.5, 135.5, 128.7, 127.2, 126.9, 126.8, 126.2, 98.4, 89.4, 31.4, 29.4, 22.6, 13.9, 7.4, 3.3. IR (neat): 3028, 2953, 2930, 2872, 1915, 1600, 1486, 1457, 1417, 1237, 1007, 844, 781, 758, 695cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{25}H_{34}Si$ 362.2424; Found 362.2437.



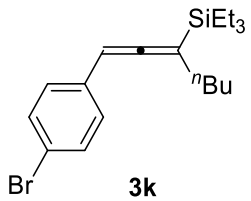
3i

Triethyl(1-(4-(trifluoromethyl)phenyl)hepta-1,2-dien-3-yl)silane (3i). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1i** (0.3 mmol, 94.3 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **3i** in 90% yield (95.6 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 5.88 (s, 1H), 2.09 (m, 2H), 1.51-1.47 (m, 2H), 1.37-1.35 (m, 2H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.66 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.8, 140.6, 127.5 (q, $^2J_{C\text{-}F}$ = 31.9 Hz), 125.8, 125.4 (q, $^4J_{C\text{-}F}$ = 3.7 Hz), 124.4 (d, $^1J_{C\text{-}F}$ = 269.9 Hz), 99.0, 89.0, 31.3, 29.2, 22.6, 13.9, 7.3, 3.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3. IR (neat): 2956, 2875, 1916, 1615, 1458, 1426, 1322, 1237, 1162, 1106, 1066, 1016, 973, 847, 716 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{29}F_3Si$ 354.1985; Found 354.1980.



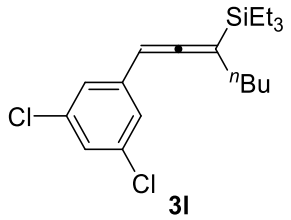
3j

(1-(4-Chlorophenyl)hepta-1,2-dien-3-yl)triethylsilane (3j). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1j** (0.3 mmol, 84.2 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **3j** in 82% yield (78.9 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J = 8.8 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 5.81 (t, J = 2.8 Hz, 1H), 2.09-2.04 (m, 2H), 1.51-1.47 (m, 2H), 1.35-1.34 (m, 2H), 0.95 (t, J = 8.0 Hz, 9H), 0.88 (t, J = 7.6 Hz, 3H), 0.64 (q, J = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.7, 135.0, 131.0, 128.6, 126.9, 98.8, 88.9, 31.3, 29.3, 22.6, 13.9, 7.4, 3.2. IR (neat): 2954, 2931, 2873, 1916, 1490, 1457, 1418, 1237, 1194, 1090, 1011, 974, 835, 716 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{29}ClSi$ 320.1722; Found 320.1730.



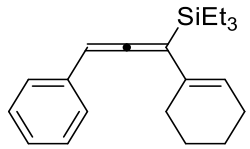
3k

(1-(4-Bromophenyl)hepta-1,2-dien-3-yl)triethylsilane (3k). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1k** (0.3 mmol, 97.6 mg) were stirred at 80 °C for 24 h. Purification by silica gel column (eluent: petroleum ether) afforded the title product **3k** in 80% yield (88.2 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 5.80 (bs, 1H), 2.08-2.03 (m, 2H), 1.51-1.45 (m, 2H), 1.35-1.33 (m, 2H), 0.95 (t, J = 8.0 Hz, 9H), 0.87 (t, J = 7.2 Hz, 3H), 0.64 (q, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.6, 135.5, 131.5, 127.3, 118.9, 98.9, 88.9, 31.3, 29.3, 22.6, 13.9, 7.4, 3.2. IR (neat): 2954, 2932, 2873, 1916, 1741, 1488, 1457, 1417, 1238, 1070, 1047, 1008, 974, 833 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{29}BrSi$ 364.1216; Found 364.1222.



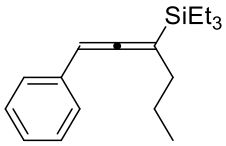
3l

(1-(3,5-Dichlorophenyl)hepta-1,2-dien-3-yl)triethylsilane (3l). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1l** (0.3 mmol, 94.6 mg) were stirred at 80 ºC for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **3l** in 85% yield (90.6 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (s, 3H), 5.74 (s, 1H), 2.08-2.04 (m, 2H), 1.49-1.33 (m, 4H), 0.96 (t, J = 8.0 Hz, 9H), 0.89 (t, J = 7.2 Hz, 3H), 0.65 (q, J = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.3, 140.2, 134.9, 125.3, 123.9, 99.6, 88.2, 31.2, 29.2, 22.6, 13.9, 7.3, 3.1. IR (neat): 2954, 2874, 1916, 1583, 1561, 1427, 1377, 1238, 1112, 1006, 909, 871, 847, 800, 671 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{28}Cl_2Si$ 354.1332; Found 354.1335.



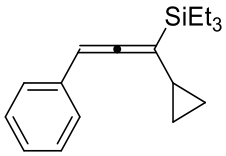
3m

(1-(Cyclohex-1-en-1-yl)-3-phenylpropa-1,2-dien-1-yl)triethylsilane (3m). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1m** (0.3 mmol, 81.1 mg) were stirred at 80 ºC for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **3m** in 65% yield (61.0 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.22 (m, 4H), 7.12 (t, J = 6.8 Hz, 1H), 6.03 (s, 1H), 5.74 (bs, 1H), 2.17-2.11 (m, 4H), 1.63-1.58 (m, 4H), 0.95 (t, J = 8.0 Hz, 9H), 0.74-0.66 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.9, 135.8, 133.4, 128.5, 125.93, 125.87, 125.3, 103.3, 91.0, 28.4, 26.1, 23.0, 22.2, 7.5, 4.1. IR (neat): 2932, 2873, 1900, 1598, 1495, 1455, 1376, 1238, 1116, 1003, 976, 875, 797, 729, 692 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{30}Si$ 310.2111; Found 310.2109.



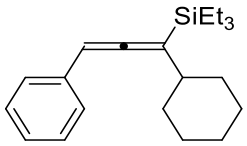
3n

Triethyl(1-phenylhexa-1,2-dien-3-yl)silane (3n). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1n** (0.3 mmol, 69.7 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **3n** in 92% yield (75.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.22 (m, 4H), 7.12-7.09 (m, 1H), 5.86 (t, *J* = 2.4 Hz, 1H), 2.07-2.02 (m, 2H), 1.57-1.50 (m, 2H), 0.98-0.91 (m, 12H), 0.64 (q, *J* = 8.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.9, 136.3, 128.5, 125.8, 125.6, 98.1, 89.7, 31.9, 22.4, 14.1, 7.4, 3.2. IR (neat): 2953, 2873, 1917, 1598, 1496, 1456, 1413, 1237, 1072, 1001, 905, 796, 715, 691 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{28}Si$ 272.1955; Found 272.1958.



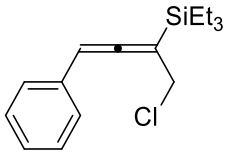
3o

(1-Cyclopropyl-3-phenylpropa-1,2-dien-1-yl)triethylsilane (3o). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1o** (0.3 mmol, 69.1 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **3o** in 86% yield (69.5 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.23 (m, 2H), 7.19-7.17 (m, 2H), 7.12-7.09 (m, 1H), 5.91 (s, 1H), 1.15 (bs, 1H), 0.99 (t, *J* = 7.2 Hz, 9H), 0.71-0.69 (m, 8H), 0.49 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.0, 136.0, 128.5, 125.9, 125.8, 102.7, 91.5, 9.8, 8.6, 8.0, 7.4, 3.4. IR (neat): 2952, 2909, 2874, 1917, 1596, 1495, 1456, 1414, 1237, 1000, 847, 800, 733, 717, 691 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{26}Si$ 270.1798; Found 270.1798.



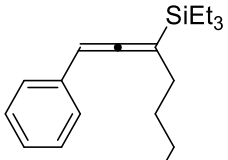
3p

(1-Cyclohexyl-3-phenylpropa-1,2-dien-1-yl)triethylsilane (3p). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1p** (0.3 mmol, 81.7 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **3p** in 79% yield (74.1 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.22 (m, 4H), 7.12-7.10 (m, 1H), 5.88 (s, 1H), 1.90 (m, 2H), 1.82 (d, J = 11.2 Hz, 1H), 1.71 (m, 2H), 1.62 (d, J = 12.0 Hz, 1H), 1.28-1.15 (m, 5H), 0.96 (t, J = 7.6 Hz, 9H), 0.65 (q, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.1, 136.3, 128.5, 125.64, 125.59, 104.2, 90.5, 39.6, 34.7, 34.1, 26.82, 26.78, 26.0, 7.5, 3.5. IR (neat): 2923, 2873, 1911, 1598, 1495, 1456, 1448, 1237, 1005, 978, 905, 796, 731, 715, 691 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{32}Si$ 312.2268; Found 312.2274.



3q

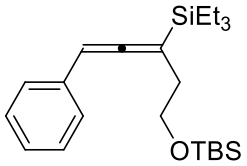
(1-Chloro-4-phenylbuta-2,3-dien-2-yl)triethylsilane (3q). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1q** (0.3 mmol, 71.6 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded trace product **3q**.



3r

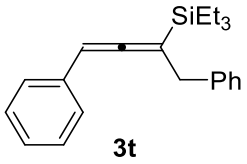
(6-Chloro-1-phenylhexa-1,2-dien-3-yl)triethylsilane (3r). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1r** (0.3 mmol, 80.0 mg) were stirred at 80 °C for 24 h. Purification by silica

gel plate (eluent: petroleum ether) afforded the title product **3r** in 78% yield (71.8 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 2H), 7.13 (t, *J* = 6.8 Hz, 1H), 5.90 (s, 1H), 3.57 (t, *J* = 6.0 Hz, 2H), 2.24-2.21 (m, 2H), 2.02-1.98 (m, 2H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.66 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.5, 135.7, 128.6, 125.9, 125.8, 97.2, 90.5, 44.7, 31.6, 26.5, 7.4, 3.1. IR (neat): 2953, 2874, 1917, 1597, 1496, 1456, 1414, 1237, 1002, 973, 907, 800, 766, 733, 716, 692 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{27}ClSi$ 306.1565; Found 306.1567.



3s

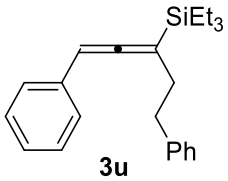
***tert*-Butyldimethyl((5-phenyl-3-(triethylsilyl)penta-3,4-dien-1-yl)oxy)silane (3s).** CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1s** (0.3 mmol, 104.6 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **3s** in 84% yield (98.0 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.33 (m, 4H), 7.24 (t, *J* = 6.8 Hz, 1H), 5.97 (t, *J* = 2.4 Hz, 1H), 3.88 (t, *J* = 7.6 Hz, 2H), 2.46-2.38 (m, 2H), 1.09 (t, *J* = 8.0 Hz, 9H), 1.01 (s, 9H), 0.77 (q, *J* = 8.4 Hz, 6H), 0.16 (d, *J* = 4.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.0, 136.0, 128.5, 125.9, 125.7, 94.5, 89.6, 62.8, 32.7, 25.9, 18.3, 7.4, 3.1, -5.28, -5.29. IR (neat): 2952, 2929, 2874, 1917, 1599, 1496, 1457, 1254, 1095, 1004, 975, 834, 798, 774, 734, 715, 692 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{23}H_{40}OSi_2$ 388.2612; Found 388.2604.



3t

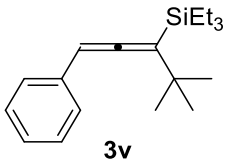
(1,4-Diphenylbuta-2,3-dien-2-yl)triethylsilane (3t). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-

dioxane (1.5 mL), **1t** (0.3 mmol, 84.1 mg) were stirred at 80 ºC for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **3t** in 80% yield (77.3 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.22 (m, 6H), 7.18-7.16 (m, 3H), 7.12-7.10 (m, 1H), 5.84 (m, 1H), 3.48-3.38 (m, 2H), 0.91 (t, *J* = 10.0 Hz, 9H), 0.60 (q, *J* = 5.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.8, 140.2, 135.7, 128.9, 128.4, 128.1, 126.1, 125.9, 125.8, 98.1, 89.7, 36.9, 7.3, 3.3. IR (neat): 2952, 2908, 2873, 1917, 1598, 1495, 1454, 1413, 1237, 1072, 1004, 793, 735, 715, 691 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{22}H_{28}Si$ 320.1955; Found 320.1957.



3u

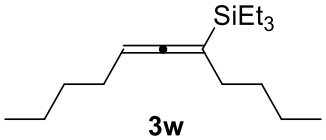
(1,5-Diphenylpenta-1,2-dien-3-yl)triethylsilane (3u). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1u** (0.3 mmol, 88.3 mg) were stirred at 80 ºC for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **3u** in 91% yield (91.0 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.10 (m, 10H), 5.91 (bs, 1H), 2.87-2.76 (m, 2H), 2.41-2.32 (m, 2H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.65 (q, *J* = 9.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.9, 142.2, 136.0, 128.5, 128.4, 128.3, 125.9, 125.77, 125.76, 98.0, 90.4, 35.4, 31.6, 7.4, 3.2. IR (neat): 2951, 2908, 2873, 1919, 1598, 1495, 1455, 1413, 1237, 1004, 963, 905, 799, 734, 716, 692 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{23}H_{30}Si$ 334.2111; Found 334.2114.



3v

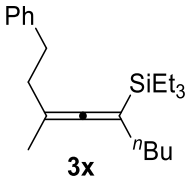
(4,4-Dimethyl-1-phenylpenta-1,2-dien-3-yl)triethylsilane (3v). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1v** (0.3 mmol, 73.9 mg) were stirred at 80 ºC for 24 h. Purification

by silica gel column (eluent: petroleum ether) afforded the title product **3v** in 41% yield (35.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.22 (m, 4H), 7.13-7.09 (m, 1H), 5.87 (s, 1H), 1.18 (s, 9H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.72-0.67 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.1, 136.3, 128.5, 125.7, 125.6, 108.5, 90.4, 36.0, 31.5, 7.5, 4.8. IR (neat): 2955, 2874, 1918, 1600, 1495, 1455, 1361, 1225, 1002, 905, 798, 731, 716, 692 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{30}Si$ 286.2111; Found 286.2116.



3w

Triethyl(undeca-5,6-dien-5-yl)silane (3w). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1w** (0.3 mmol, 67.9 mg) were stirred at 80 °C for 24 h. Purification by silica gel column (eluent: petroleum ether) afforded the title product **3w** in 84% yield (67.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.76-4.73 (m, 1H), 1.96-1.87 (m, 4H), 1.46-1.30 (m, 8H), 0.95-0.88 (m, 15H), 0.58 (q, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.2, 93.0, 85.3, 32.2, 31.3, 29.4, 28.6, 22.5, 22.3, 14.01, 13.97, 7.4, 3.2. IR (neat): 2954, 2927, 2873, 1932, 1458, 1414, 1378, 1237, 1008, 974, 714 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{34}Si$ 266.2424; Found 266.2417.

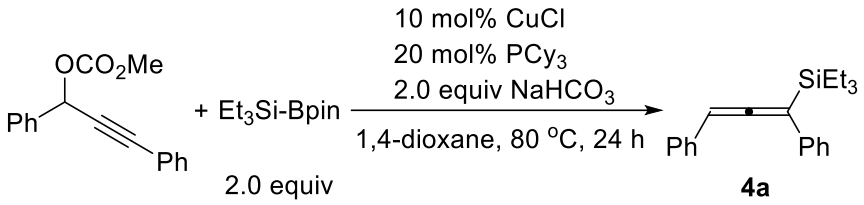


3x

Triethyl(3-methyl-1-phenylnona-3,4-dien-5-yl)silane (3x). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1x** (0.3 mmol, 86.5 mg) were stirred at 80 °C for 24 h. Purification by silica gel column (eluent: petroleum ether) afforded the title product **3x** in 84% yield (82.9 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, *J* = 7.6 Hz, 2H), 7.19-7.14 (m, 3H), 2.71 (t, *J* = 8.0 Hz, 2H), 2.21 (t, *J* = 8.4 Hz, 2H), 1.86 (t, *J* = 6.8 Hz, 2H), 1.68 (s, 3H), 1.36-1.30

(m, 4H), 0.94 (t, J = 8.0 Hz, 9H), 0.88 (t, J = 7.2 Hz, 3H), 0.57 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.8, 142.6, 128.3, 128.2, 125.6, 93.4, 93.0, 35.8, 34.6, 31.4, 29.7, 22.5, 18.8, 14.1, 7.4, 3.3. IR (neat): 2952, 2873, 1936, 1496, 1454, 1375, 1237, 1008, 731, 715, 696 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{22}H_{36}Si$ 328.2581; Found 328.2592.

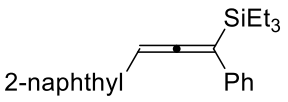
Synthesis of allenylsilanes 4a-4b.



4a

(1,3-Diphenylpropa-1,2-dien-1-yl)triethylsilane (4a). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.06 mmol, 16.8 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1y** (0.3 mmol, 79.9 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **4a** in 72% yield (65.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.26 (m, 8H), 7.20-7.14 (m, 2H), 6.18 (s, 1H), 0.98 (t, J = 7.6 Hz, 9H), 0.81-0.77 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.2, 137.1, 134.8, 128.6, 128.5, 127.6, 126.5, 126.3, 126.2, 101.6, 90.7, 7.4, 3.9. IR (neat): 2952, 2909, 2873, 1910, 1595, 1490, 1456, 1238, 1002, 803, 760, 734, 691, 672 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{26}Si$ 306.1798; Found 306.1798.

When the reaction was carried out using CuCl (10 mol%, 0.03 mmol, 3.0 mg), PCy_3 (10 mol%, 0.03 mmol, 8.4 mg), $NaHCO_3$ (2.0 equiv, 0.6 mmol, 50.4 mg), Et_3Si-Bpin (2.0 equiv, 0.6 mmol, 145.3 mg), 1,4-dioxane (1.5 mL), and **1y** (0.3 mmol, 79.9 mg) at 80 °C for 24 h, the product **4a** was obtained in 53% yield (49.0 mg) as a colorless oil.



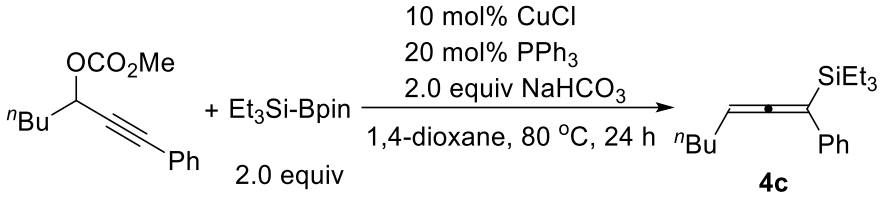
4b

Triethyl(3-(naphthalen-2-yl)-1-phenylpropa-1,2-dien-1-yl)silane (4b). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.06 mmol, 16.8 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1z** (0.3 mmol, 94.4 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **4b** in 60%

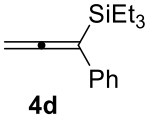
yield (64.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.26 (m, 8H), 7.77-7.73 (m, 3H), 7.65 (s, 1H), 7.50 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.43-7.36 (m, 4H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.36 (s, 1H), 0.99 (t, *J* = 7.6 Hz, 9H), 0.83-0.76 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.6, 137.0, 133.8, 132.4, 132.4, 128.6, 128.3, 127.7, 127.5, 126.6, 126.2, 125.3, 124.6, 124.4, 101.9, 91.1, 7.5, 4.0. IR (neat): 2952, 2873, 1908, 1628, 1595, 1508, 1490, 1377, 1238, 1111, 1002, 908, 888, 731, 694 cm-1. HRMS (EI) m/z: [M]+ Calcd for $C_{25}H_{28}Si$ 356.1955; Found 356.1955.

Synthesis of allenylsilanes 4c-4f.

Typical procedure for the synthesis of 4c:



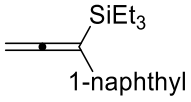
Triethyl(1-phenylhepta-1,2-dien-1-yl)silane (4c). CuCl (0.03 mmol, 3.0 mg), PPh_3 (0.06 mmol, 15.7 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1za** (0.3 mmol, 73.9 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **4c** in 70% yield (60.1 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 2.8 Hz, 4H), 7.16-7.15 (m ,1H), 5.10 (t, *J* = 6.0 Hz, 1H), 2.07 (q, *J* = 6.8 Hz, 2H), 1.46-1.34 (m, 4H), 0.97-0.88 (m, 12H), 0.72 (q, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.3, 138.7, 128.3, 127.5, 125.8, 96.7, 86.5, 31.9, 28.2, 22.4, 13.9, 7.4, 4.0. IR (neat): 2954, 2931, 2873, 1925, 1596, 1490, 1457, 1415, 1238, 1002, 732, 718, 693 cm^{-1}.HRMS (EI) m/z: $[M-C_2H_5]^+$ Calcd for $C_{17}H_{25}Si$ 257.1720; Found 257.1715.



4d

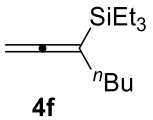
Triethyl(1-phenylpropa-1,2-dien-1-yl)silane (4d). CuCl (0.03 mmol, 3.0 mg), PPh_3 (0.06 mmol, 15.7 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1zb** (0.3 mmol, 57.1 mg) were stirred at 80 °C for 24 h. Purification by silica

gel plate (eluent: petroleum ether) afforded the title product **4d** in 71% yield (49.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, J = 4.8 Hz, 4H), 7.19-7.14 (m ,1H), 4.64 (s, 2H), 0.96 (t, J = 7.6 Hz, 9H), 0.74 (q, J = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 137.6, 128.4, 127.6, 126.0, 95.6, 69.7, 7.3, 3.9. IR (neat): 2953, 2874, 1916, 1596, 1490, 1415, 1238, 1003, 974, 812, 760, 732, 718, 695 cm^{-1}. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{15}H_{22}Si$ 230.1485; Found 230.1487.



4e

Triethyl(1-(naphthalen-1-yl)propa-1,2-dien-1-yl)silane (4e). CuCl (0.03 mmol, 3.0 mg), PPh_3 (0.06 mmol, 15.7 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1zc** (0.3 mmol, 72.1 mg) were stirred at 80 ºC for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **4e** in 72% yield (60.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 8.8 Hz, 1H), 7.82-7.80 (m, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.48-7.37 (m, 3H), 7.21 (d, J = 7.2 Hz, 1H), 4.52 (s, 2H), 0.93 (t, J = 7.6 Hz, 9H), 0.66 (q, J = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.9,135.5, 134.0, 131.6, 128.3, 126.4, 125.9, 125.6, 125.5, 125.3, 124.9, 93.5, 67.7, 7.3, 3.5. IR (neat): 2952, 2874, 1923, 1576, 1457, 1389, 1237, 1138, 1005, 908, 800, 781, 718, 699 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{24}Si$ 280.1642; Found 280.1640.



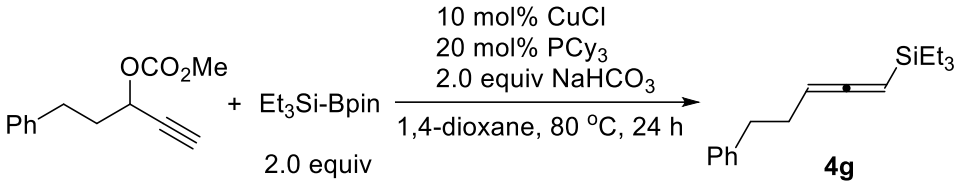
4f

Triethyl(hepta-1,2-dien-3-yl)silane (4f). CuCl (0.03 mmol, 3.0 mg), PPh_3 (0.06 mmol, 15.7 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1zd** (0.3 mmol, 51.1 mg) were stirred at 80 ºC for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **4f** in 62% yield (39.1 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.31 (t, J = 3.2 Hz, 2H), 1.93-1.88 (m, 2H), 1.49-1.31 (m, 4H), 0.96-0.88 (m, 12H), 0.61 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.0, 91.5, 68.5,

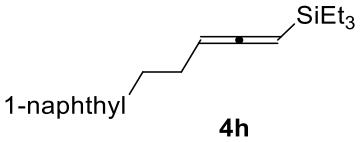
31.1, 28.7, 22.5, 14.0, 7.3, 3.1. IR (neat): 2954, 2931, 2874, 1925, 1458, 1415, 1378, 1238, 1005, 807, 716 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{13}H_{26}Si$ 210.1798; Found 210.1794.

Synthesis of allenylsilanes 4g-4n.

Typical procedure for the synthesis of 4g.

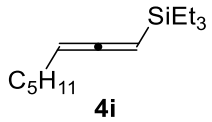


Triethyl(5-phenylpenta-1,2-dien-1-yl)silane (4g). CuCl (0.02 mmol, 2.0 mg), PCy_3 (0.04 mmol, 11.2 mg), $NaHCO_3$ (0.4 mmol, 33.6 mg), Et_3Si-Bpin (0.4 mmol, 96.9 mg) and 1,4-dioxane (1.0 mL), **1ze** (0.2 mmol, 43.7 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **4g** in 75% yield (38.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.20-7.16 (m, 3H), 4.85 (dt, *J* = 10.8, 3.6 Hz, 1H), 4.78 (q, *J* = 6.8 Hz, 1H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.31-2.26 (m, 2H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.57 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.6, 142.0, 128.5, 128.3, 125.8, 82.3, 78.8, 36.1, 30.0, 7.3, 3.8. The spectroscopic data are in agreement with that previously reported.[13]



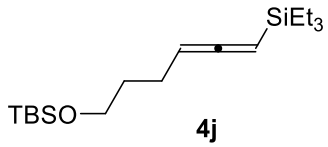
Triethyl(5-(naphthalen-1-yl)penta-1,2-dien-1-yl)silane (4h). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.06 mmol, 16.8 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1zf** (0.3 mmol, 80.5 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **4h** in 72% yield (67.1 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (q, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.47 (dt, *J* = 16.8, 6.4 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 6.8 Hz, 1H), 4.91-4.84 (m, 2H), 3.17 (t, *J* = 6.8 Hz, 2H), 2.45-2.39 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 9H), 0.57 (q, *J*= 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.6, 138.0, 133.9, 131.9, 128.7, 126.6, 126.0, 125.7, 125.5, 125.4, 123.7, 82.5, 79.0, 33.2, 29.3, 7.3, 3.8. IR (neat): 2952,

2909, 2873, 1935, 1597, 1510, 1457, 1413, 1395, 1376, 1236, 1007, 854, 775, 720 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{28}Si$ 308.1955; Found 308.1958.



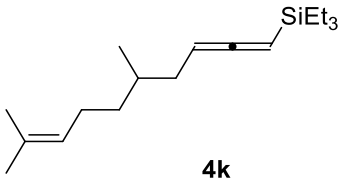
4i

Triethyl(octa-1,2-dien-1-yl)silane (4i). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.06 mmol, 16.8 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1zg** (0.3 mmol, 55.3 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **4i** in 74% yield (50.0 mg) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 4.82 (dt, *J* = 6.8, 4.0 Hz, 1H), 4.73 (q, *J* = 6.8 Hz, 1H), 1.99-1.93 (m, 2H), 1.43-1.29 (m, 6H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.89 (t, *J* = 7.2 Hz , 3H), 0.58 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.8, 82.9, 78.2, 31.4, 29.5, 28.0, 22.5, 14.1, 7.3, 3.9. IR (neat): 2954, 2932, 2874, 2173, 1936, 1458, 1415, 1378, 1339, 1236, 1132, 1016, 974, 856, 722 cm^{-1}. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{14}H_{28}Si$ 224,1955; Found 224.1957.



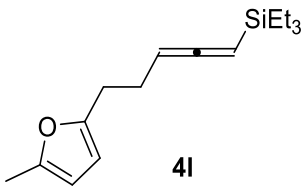
4j

***tert*-Butyldimethyl((6-(triethylsilyl)hexa-4,5-dien-1-yl)oxy)silane (4j).** CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.06 mmol, 16.8 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1zh** (0.3 mmol, 85.9 mg) were stirred at 80 °C for 24 h. Purification by silica gel column (eluent: petroleum ether: ethyl acetate = 50: 1) afforded the title product **4j** in 88% yield (86.4 mg) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 4.84 (dt, *J* = 7.2, 3.6 Hz, 1H), 4.74 (q, *J* = 7.2 Hz, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.05-2.00 (m, 2H), 1.65-1.59 (m, 2H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.89 (s, 9H), 0.58 (q, *J* = 8.0 Hz, 6H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.8, 82.5, 78.5, 62.6, 32.8, 25.9, 24.3, 18.3, 7.3, 3.8, -5.3. IR (neat): 2954, 2930, 2876, 1936, 1463, 1413, 1386, 1361, 1254, 1099, 1005, 834, 813, 775, 722 cm^{-1}. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{18}H_{38}OSi_2$ 326.2456; Found 326.2450.



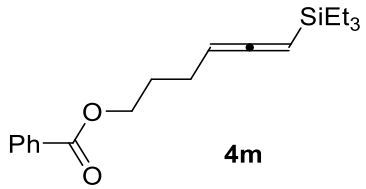
4k

(5,9-Dimethyldeca-1,2,8-trien-1-yl)triethylsilane (4k). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.06 mmol, 16.8 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1zi** (0.3 mmol, 71.5 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **4k** in 95% yield (79.5 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.10 (t, *J* = 6.8 Hz, 1H), 4.81-4.78 (m, 1H), 4.69 (q, *J* = 7.2 Hz, 1H), 2.03-1.81 (m, 4H), 1.68 (s, 3H), 1.60 (s, 3H), 1.52-1.35 (m, 2H), 1.92-1.11 (m, 1H), 0.95 (t, *J* = 8.0 Hz, 9H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.58 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.3, 131.0, 124.9, 81.2, 81.0, 77.42, 77.36, 36.59, 36.56, 35.8, 35.7, 33.34, 33.28, 25.70, 25.65, 25.6, 19.43, 19.40, 17.6, 7.3, 3.9. IR (neat): 2954, 2912, 2875, 1935, 1457, 1415, 1377, 1236, 1016, 974, 857, 722 cm^{-1}. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{18}H_{34}Si$ 278.2424; Found 278.2431.



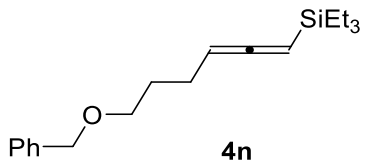
4l

Triethyl(5-(5-methylfuran-2-yl)penta-1,2-dien-1-yl)silane (4l). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.06 mmol, 16.8 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1zj** (0.3 mmol, 66.7 mg) were stirred at 80 °C for 24 h. Purification by silica gel column (eluent: petroleum ether) afforded the title product **4l** in 91% yield (72.0 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85 (d, *J* = 8.0 Hz, 2H), 4.86 (dt, *J* = 6.8, 3.6 Hz, 1H), 4.78 (q, *J* = 6.4 Hz, 1H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.31-2.27 (m, 2H), 2.24 (s, 3H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.58 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.5, 153.8, 150.2, 105.8, 105.5, 82.0, 78.9 , 28.3, 26.7, 13.5, 7.3, 3.8. IR (neat): 2953, 2911, 2875, 1936, 1699, 1570, 1457, 1414, 1377, 1237, 1017, 963, 856, 778, 720 cm^{-1}. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{16}H_{26}OSi$ 262.1747; Found 262.1751.



4m

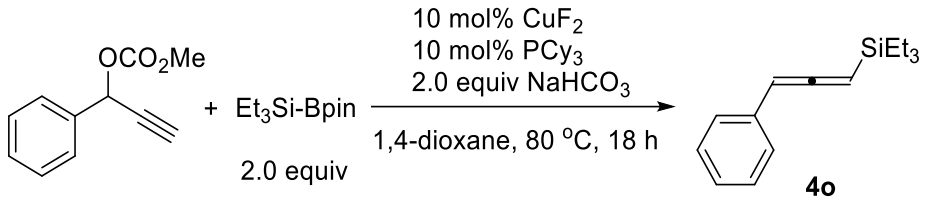
6-(Triethylsilyl)hexa-4,5-dien-1-yl benzoate (4m). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.06 mmol, 16.8 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1zk** (0.3 mmol, 82.9 mg) were stirred at 80 °C for 24 h. Purification by silica gel column (eluent: petroleum ether to petroleum ether: ethyl acetate = 100: 1) afforded the title product **4m** in 76% yield (72.4 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J*= 8.4 Hz, 2H), 7.54 (t, *J*= 8.8 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 4.89 (dt, *J* = 7.2, 3.6 Hz, 1H), 4.79 (q, *J* = 6.8 Hz, 1H), 4.38-4.35 (m, 2H), 2.17-2.12 (m, 2H), 1.92-1.85 (m, 2H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.58 (q, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.6, 166.6, 132.7, 130.4, 129.5, 128.2, 81.7, 79.0, 64.3, 28.6, 24.5, 7.2, 3.8 cm^{-1}. IR (neat): 2952, 2910, 2874, 1936, 1720, 1451, 1269, 1114, 855, 708, 687 cm^{-1}. HRMS (EI) m/z: $[M-H]^+$ Calcd for $C_{19}H_{27}O_2Si$ 315.1775; Found 315.1780.



4n

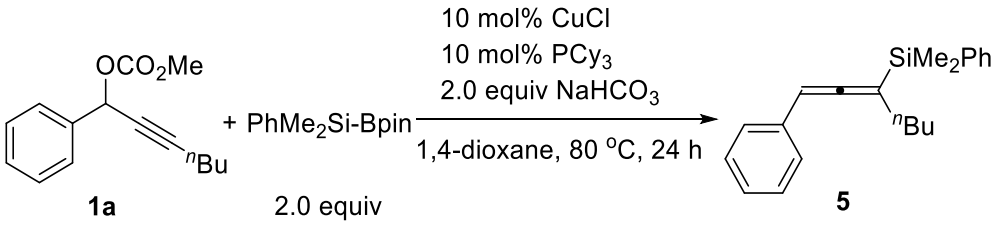
(6-(Benzyloxy)hexa-1,2-dien-1-yl)triethylsilane (4n). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.06 mmol, 16.8 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1zl** (0.3 mmol, 78.7 mg) were stirred at 80 °C for 24 h. Purification by silica gel column (eluent: petroleum ether to petroleum ether: ethyl acetate = 100: 1) afforded the title product **4n** in 73% yield (66.6 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 4.4 Hz, 4H), 7.29-7.25 (m, 1H), 4.84 (dt, *J* = 6.8, 3.6 Hz, 1H), 4.74 (q, *J* = 6.8 Hz, 1H), 4.50 (s, 2H), 3.51 (t, *J* = 6.4 Hz, 2H), 2.10-2.04 (m, 2H), 1.76-1.69 (m, 2H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.58 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.7, 138.6, 128.3, 127.6, 127.5, 82.3, 78.7, 72.9, 69.8, 29.7, 24.7, 7.3, 3.8 cm^{-1}. IR (neat): 2950, 2910, 2873, 1935, 1454, 1377, 1363, 1237, 1102, 1016, 854, 720, 696 cm^{-1}. HRMS (EI) m/z: $[M-C_2H_7]^+$ Calcd for $C_{17}H_{23}OSi$ 271.1513; Found 271.1508.

Synthesis of allenylsilane 4o.



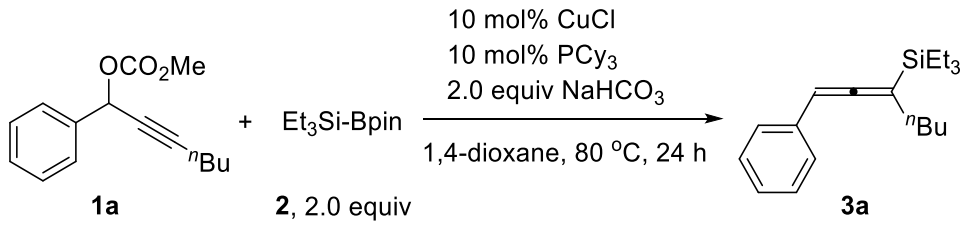
Triethyl(3-phenylpenta-1,2-dien-1-yl)silane (4o). CuF_2 (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), Et_3Si-Bpin (0.6 mmol, 145.3 mg) and 1,4-dioxane (1.5 mL), **1zm** (0.3 mmol, 57.1 mg) were stirred at 80 °C for 18 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **4o** in 41% yield (28.6 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.22 (m, 4H), 7.13 (t, *J* = 7.2 Hz, 1H), 5.84 (d, *J* = 6.8 Hz, 1H), 5.37 (d, *J* = 7.2 Hz, 1H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.65 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.8, 135.1, 128.5, 126.0, 125.8, 87.5, 83.2, 7.3, 3.9. IR (neat): 2953, 2909, 2874, 1921, 1596, 1495, 1456, 1413, 1237, 1179, 1016, 858, 765, 720, 695 cm^{-1}. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{22}Si$ 230.1485; Found 230.1480.

Synthesis of allenylsilane 5.



Dimethyl(phenyl)(1-phenylhepta-1,2-dien-3-yl)silane (5). CuCl (0.03 mmol, 3.0 mg), PCy_3 (0.03 mmol, 8.4 mg), $NaHCO_3$ (0.6 mmol, 50.4 mg), $PhMe_2Si$-Bpin (0.6 mmol, 157.3 mg) and 1,4-dioxane (1.5 mL), **1a** (0.3 mmol, 73.9 mg) were stirred at 80 °C for 24 h. Purification by silica gel plate (eluent: petroleum ether) afforded the title product **5** in 87% yield (79.6 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.56 (m, 2H), 7.36-7.35 (m, 3H), 7.29-7.22 (m, 4H), 7.15-7.11 (m, 1H), 5.94 (t, *J* = 2.8 Hz, 1H), 2.08-2.01 (m, 2H), 1.47-1.40 (m, 2H), 1.30-1.24 (m, 2H), 0.80 (t, *J* = 7.2 Hz, 3H), 0.40 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.4, 137.8, 136.0, 133.8, 129.2, 128.5, 127.8, 125.9, 125.8, 100.0, 90.4, 31.3, 29.4, 22.4, 13.9, -2.86, -2.94 The spectroscopic data are in agreement with that previously reported.[2]

1 mmol Scale reaction of 1a.



Triethyl(1-phenylhepta-1,2-dien-3-yl)silane (3a). In the nitrogen-filled glove box, CuCl (0.1 mmol, 9.9 mg), PCy_3 (0.1 mmol, 28.0 mg), $NaHCO_3$ (2.0 mmol, 168.0 mg), $Et_3SiBpin$ (2.0 mmol, 484.5 mg), 1,4-dioxane (5 mL) was added to the sealing tube. The solvent stirred at ambient temperature for 1 minute. Then **1a** (1.0 mmol, 246.3 mg) was added. The tube was sealed and taken outside the glove box. The tube was immersed into an oil bath preheated at 80 °C. After the reaction mixture was stirred at 80 °C for 24 h. The mixture was filtered over a silica gel pad and washed with ethyl acetate. The solvent was evaporated under the reduced pressure. Purification by silica gel column (eluent: petroleum ether) afforded the titile product **3a** in 86% yield (246.7 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.22 (m, 4H), 7.12 (t, J = 6.8 Hz, 1H), 5.85 (bs, 1H), 2.10-2.03 (m, 2H), 1.52-1.45 (m, 2H), 1.38-1.32 (m, 2H), 0.96 (t, J = 8.0 Hz, 9H), 0.88 (t, J = 7.2 Hz, 3H), 0.65 (q, J = 8.0 Hz, 6H).

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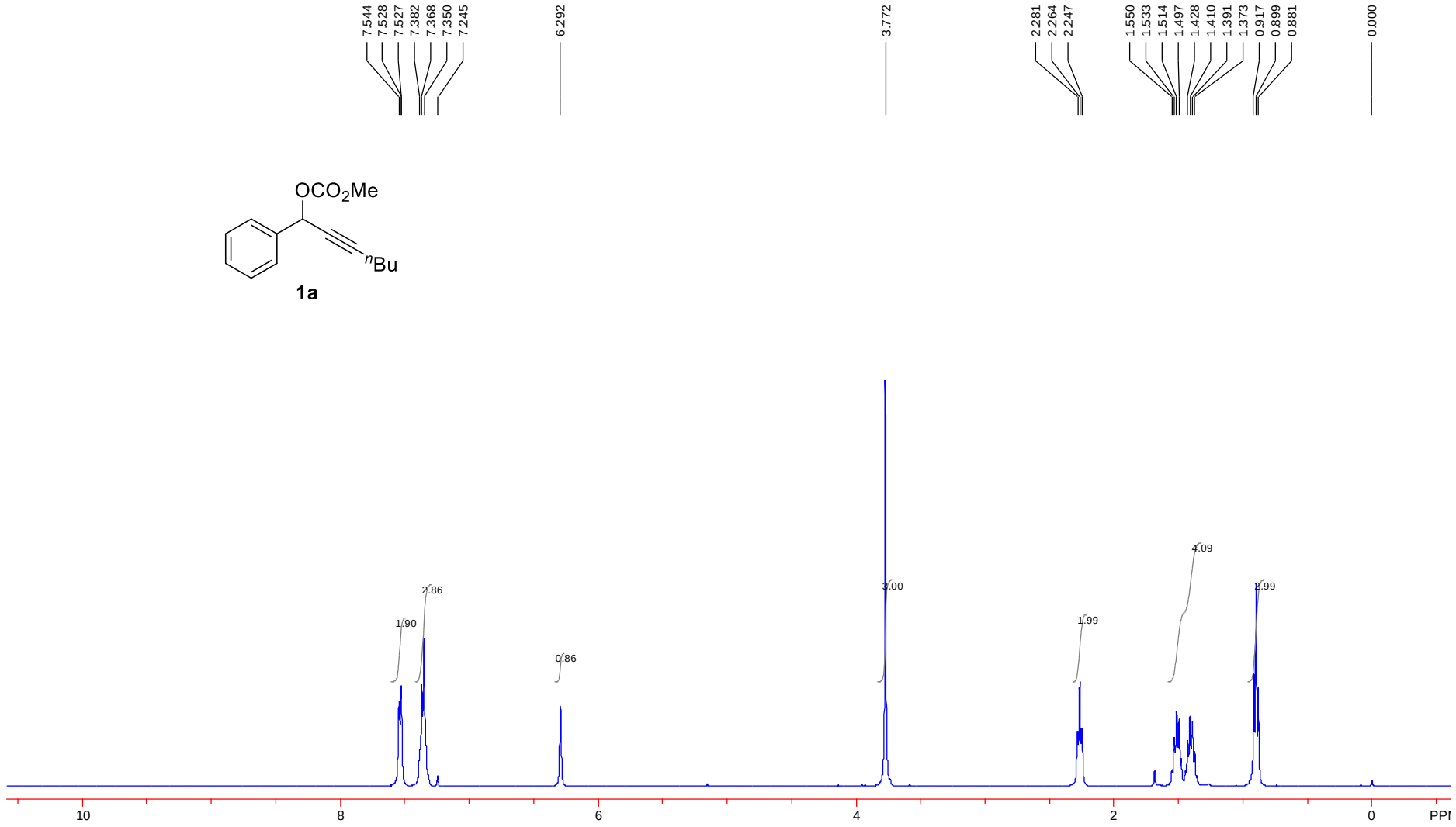
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1.497
1.428
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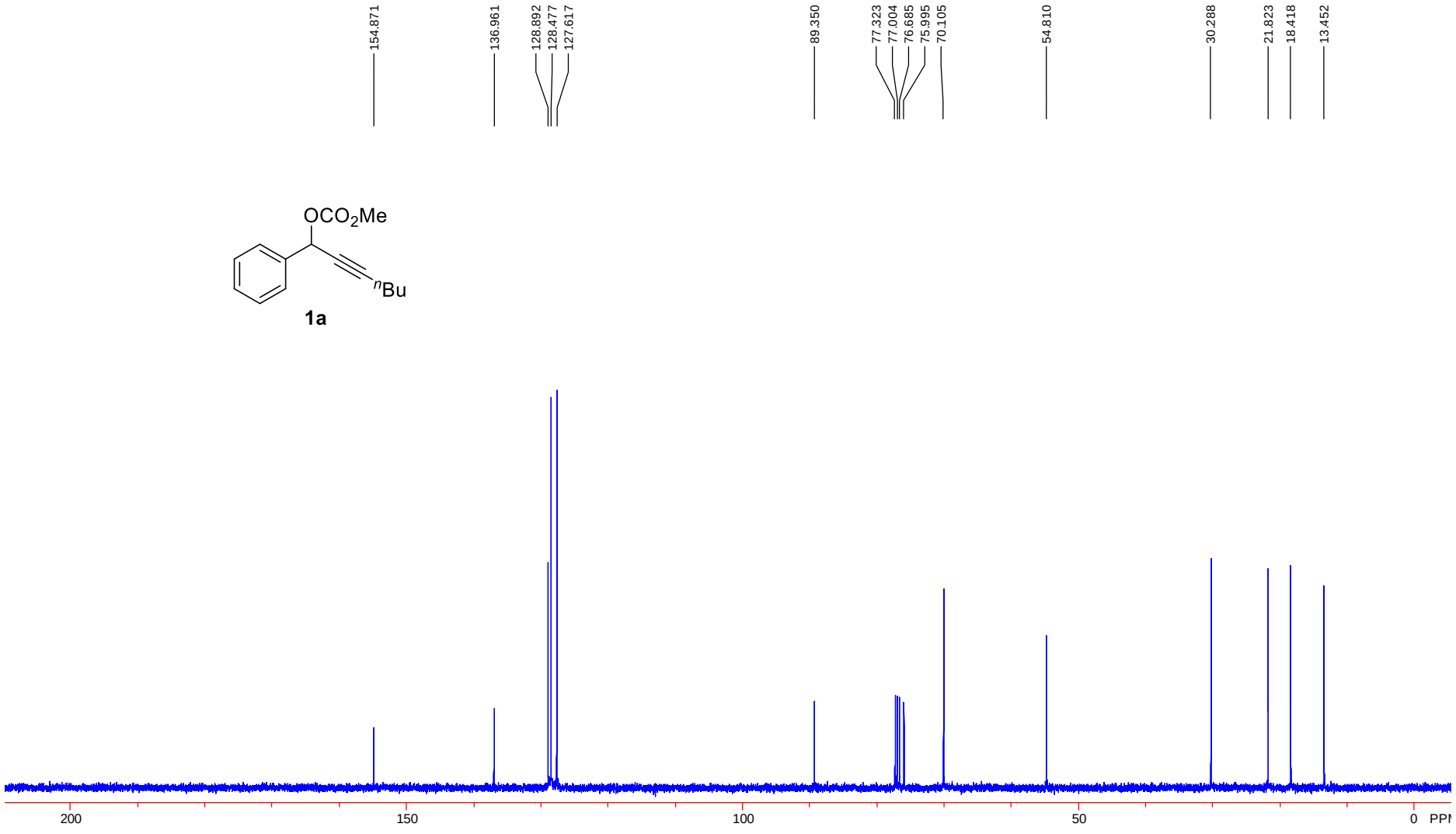
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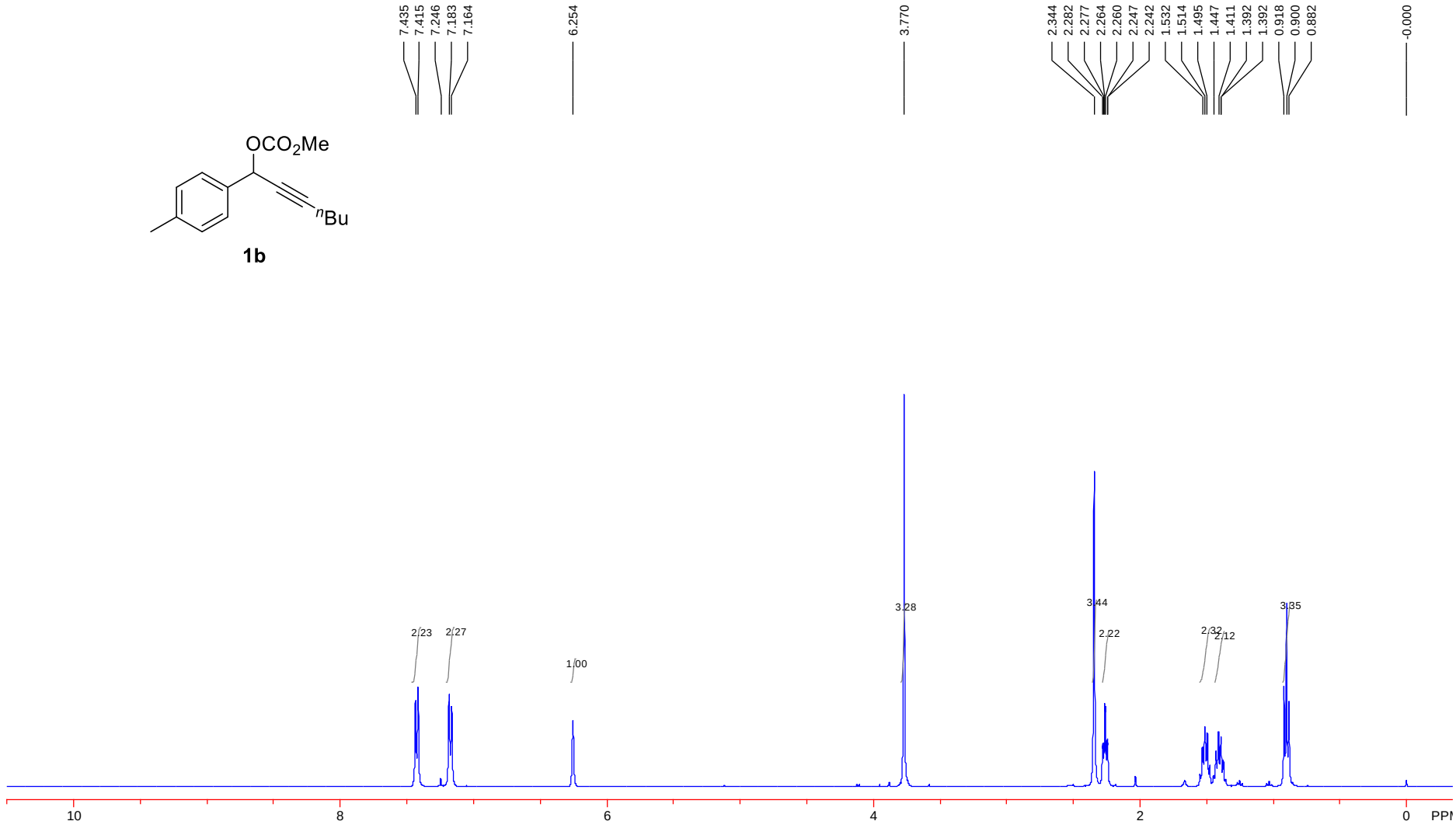
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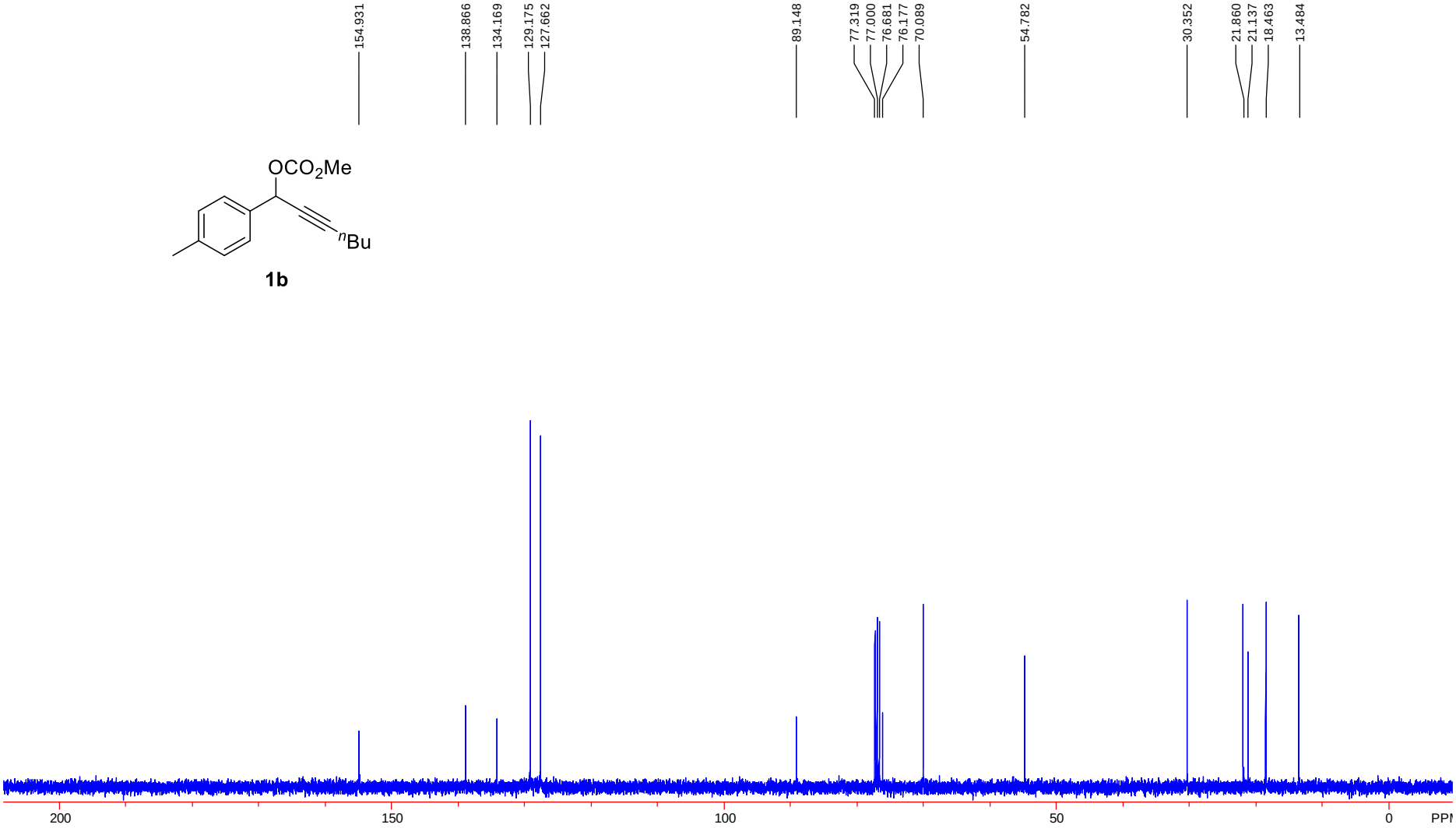
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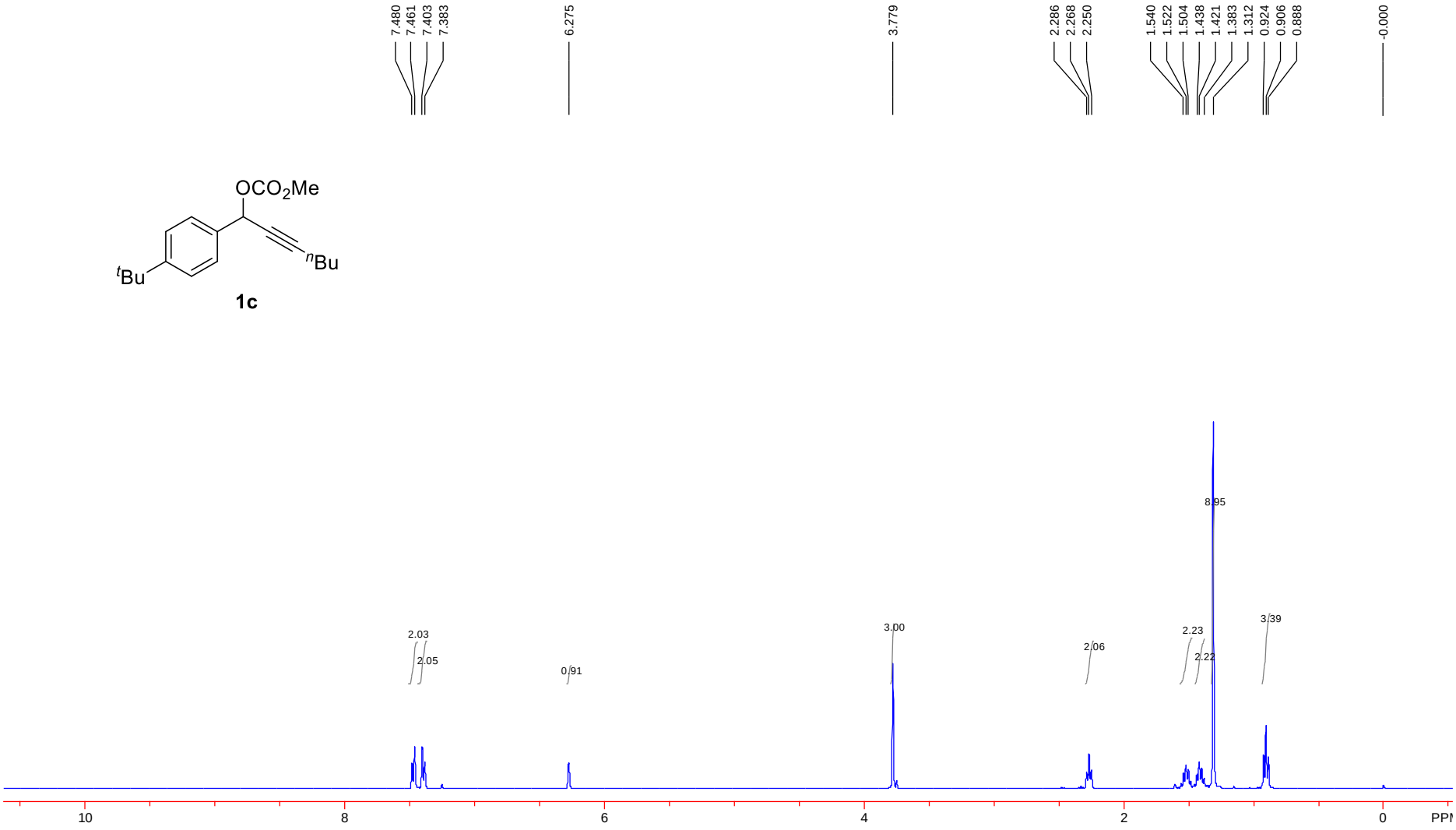
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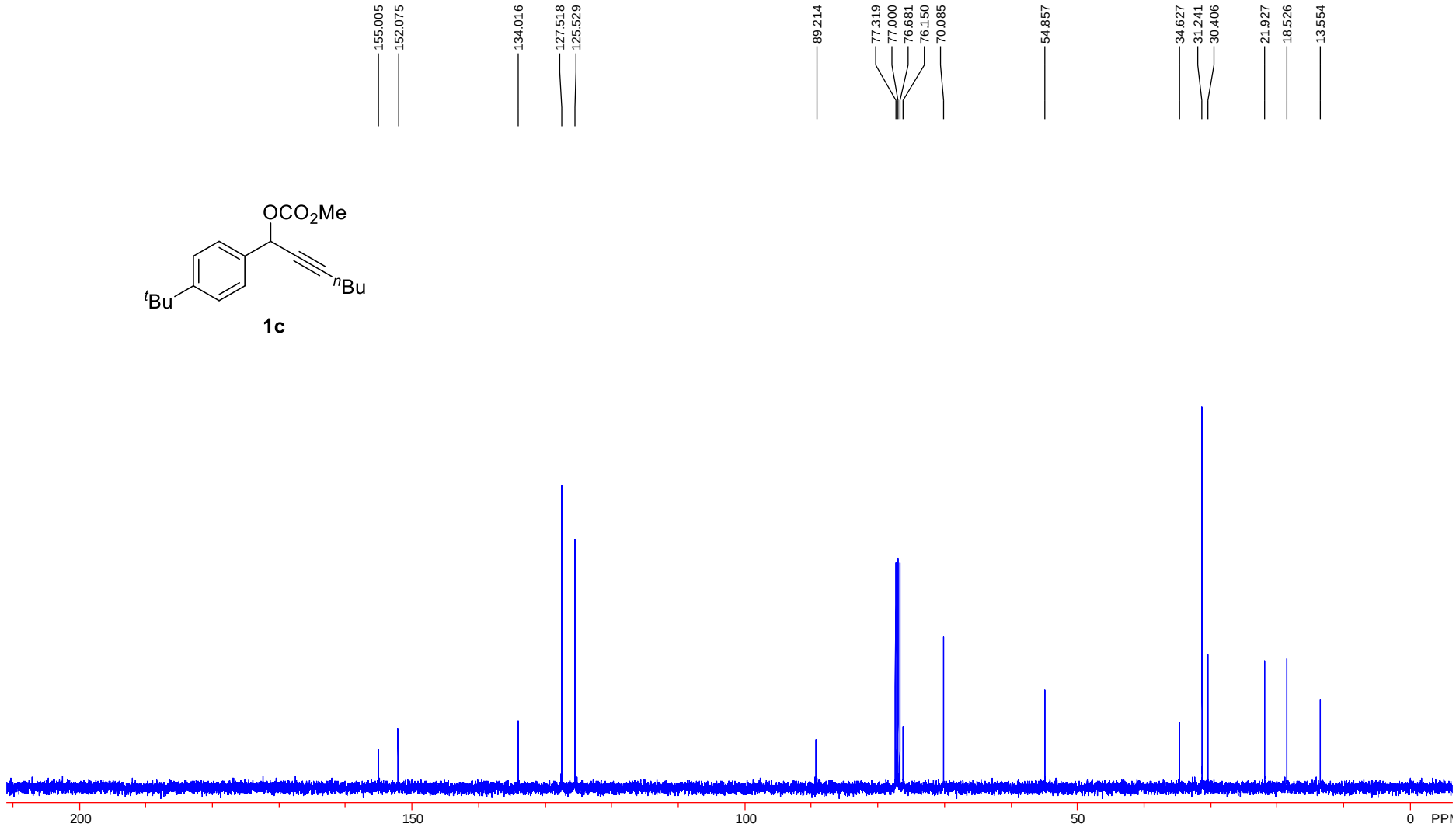
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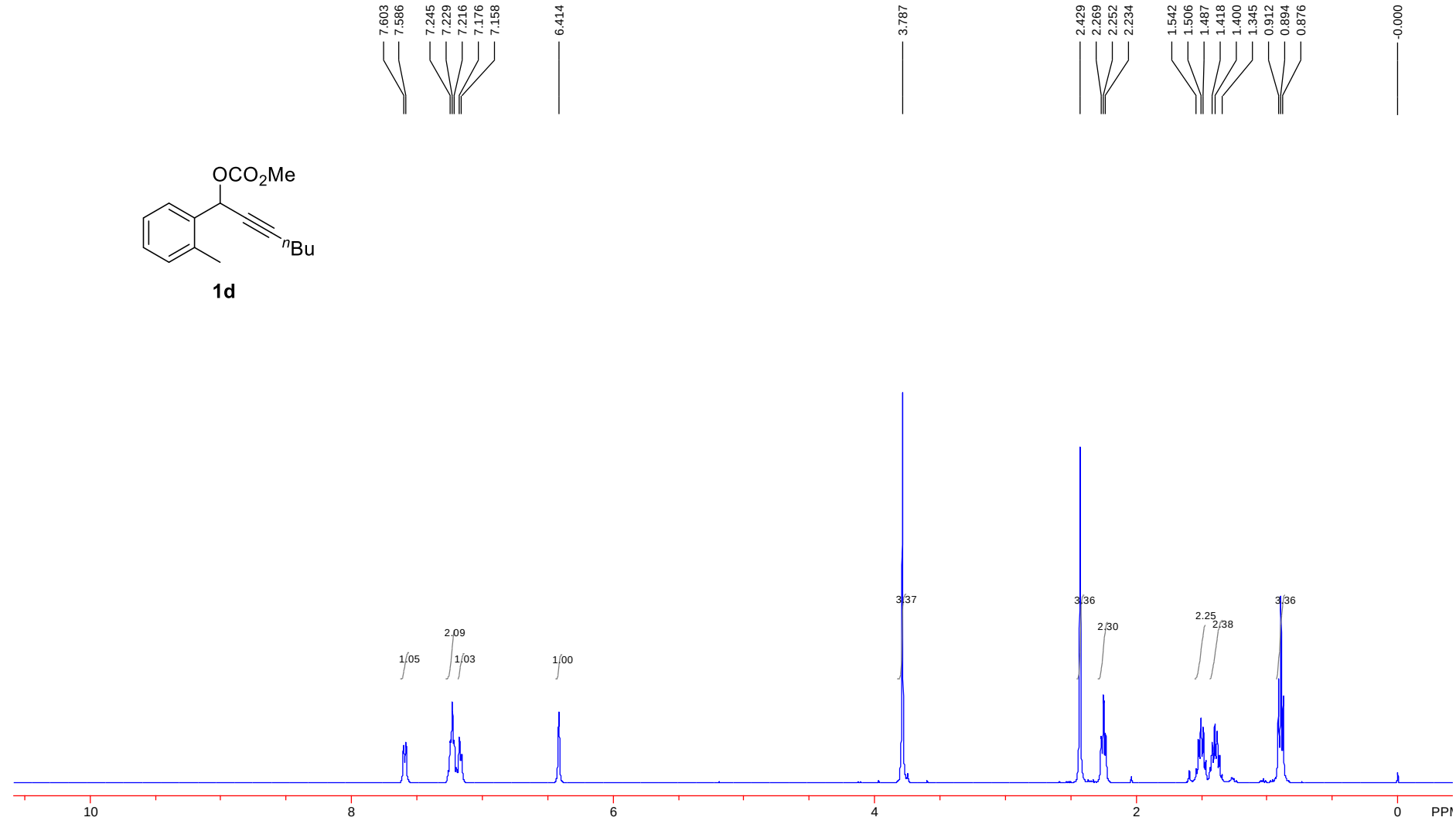
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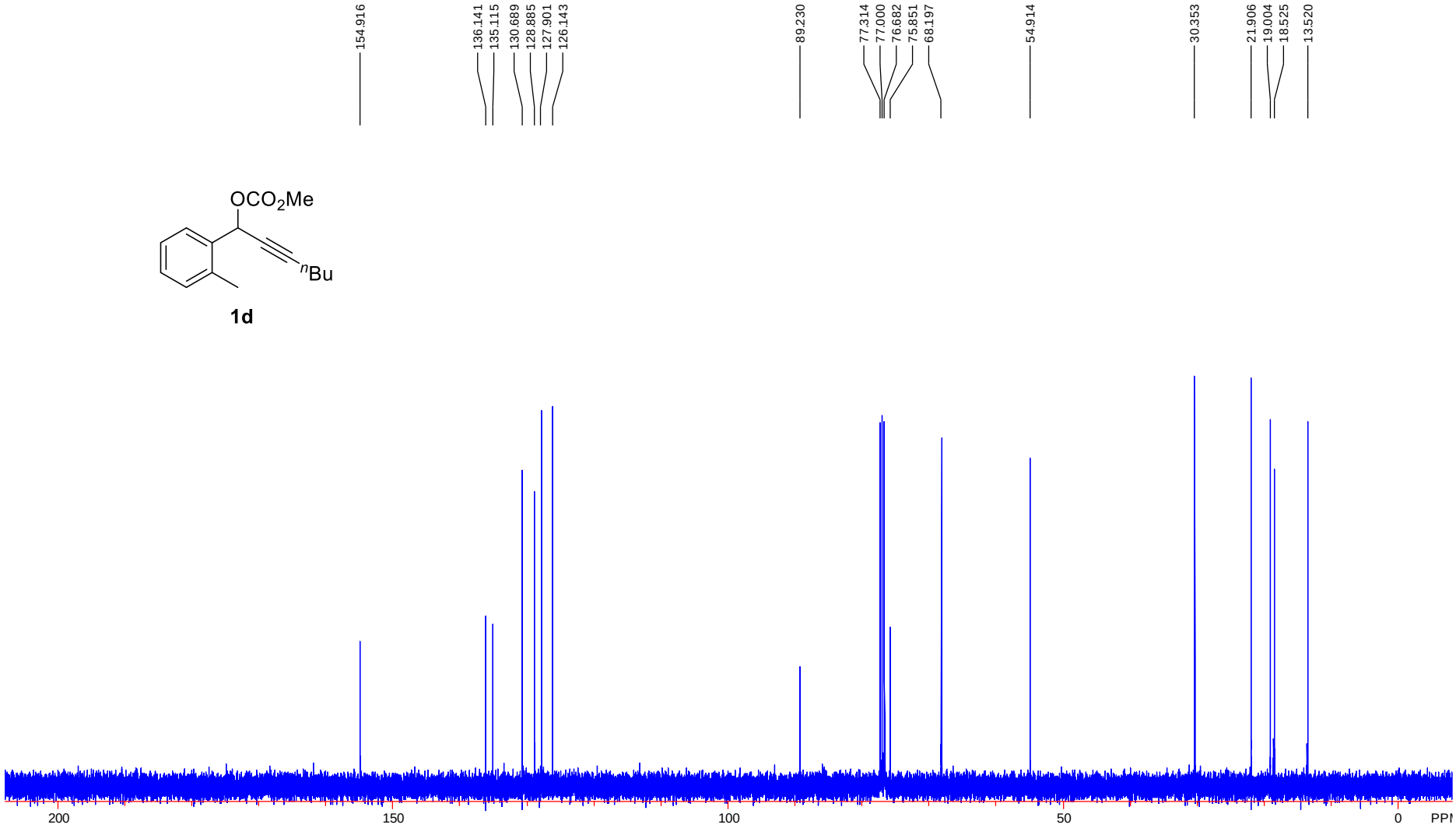
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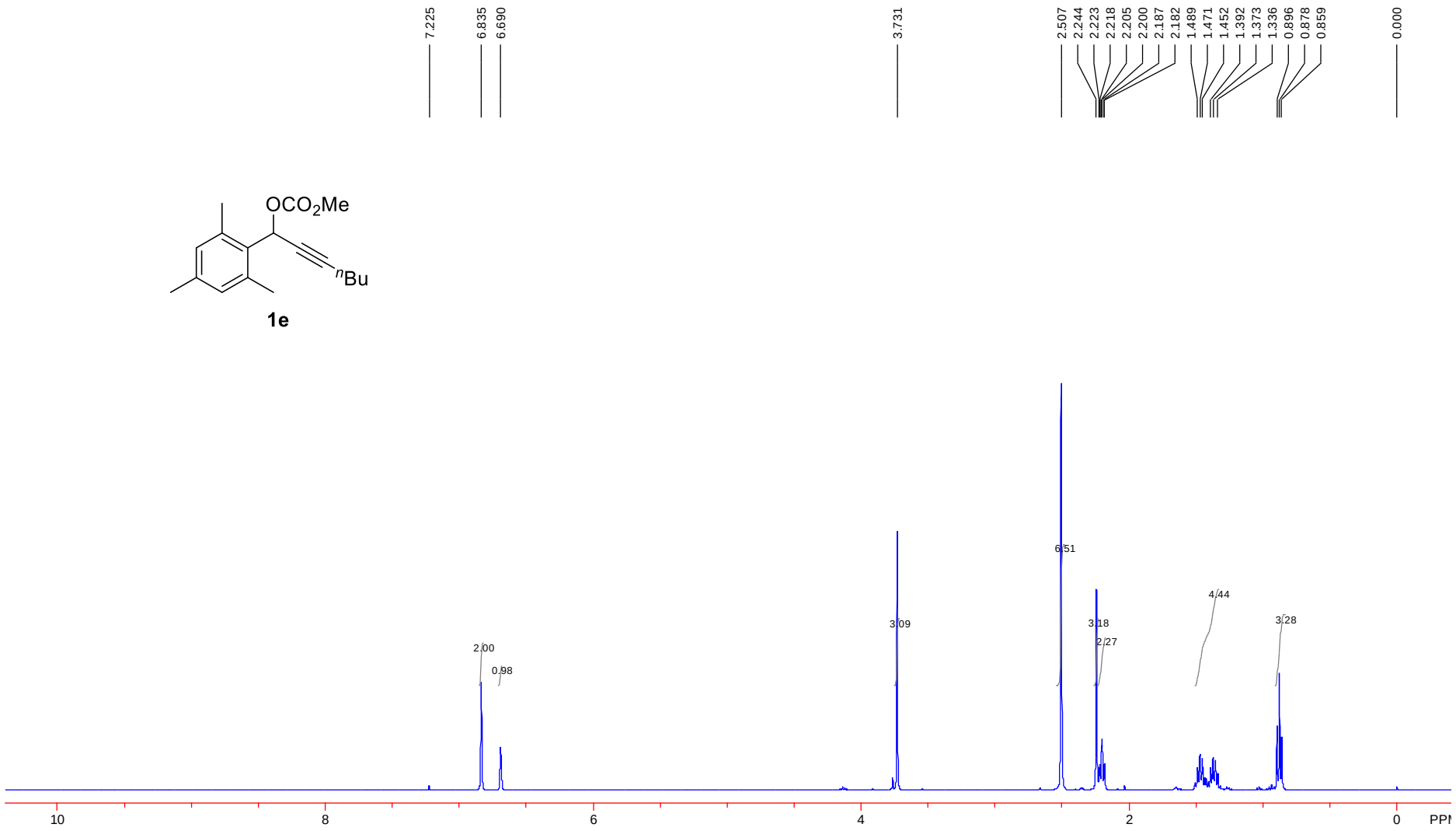
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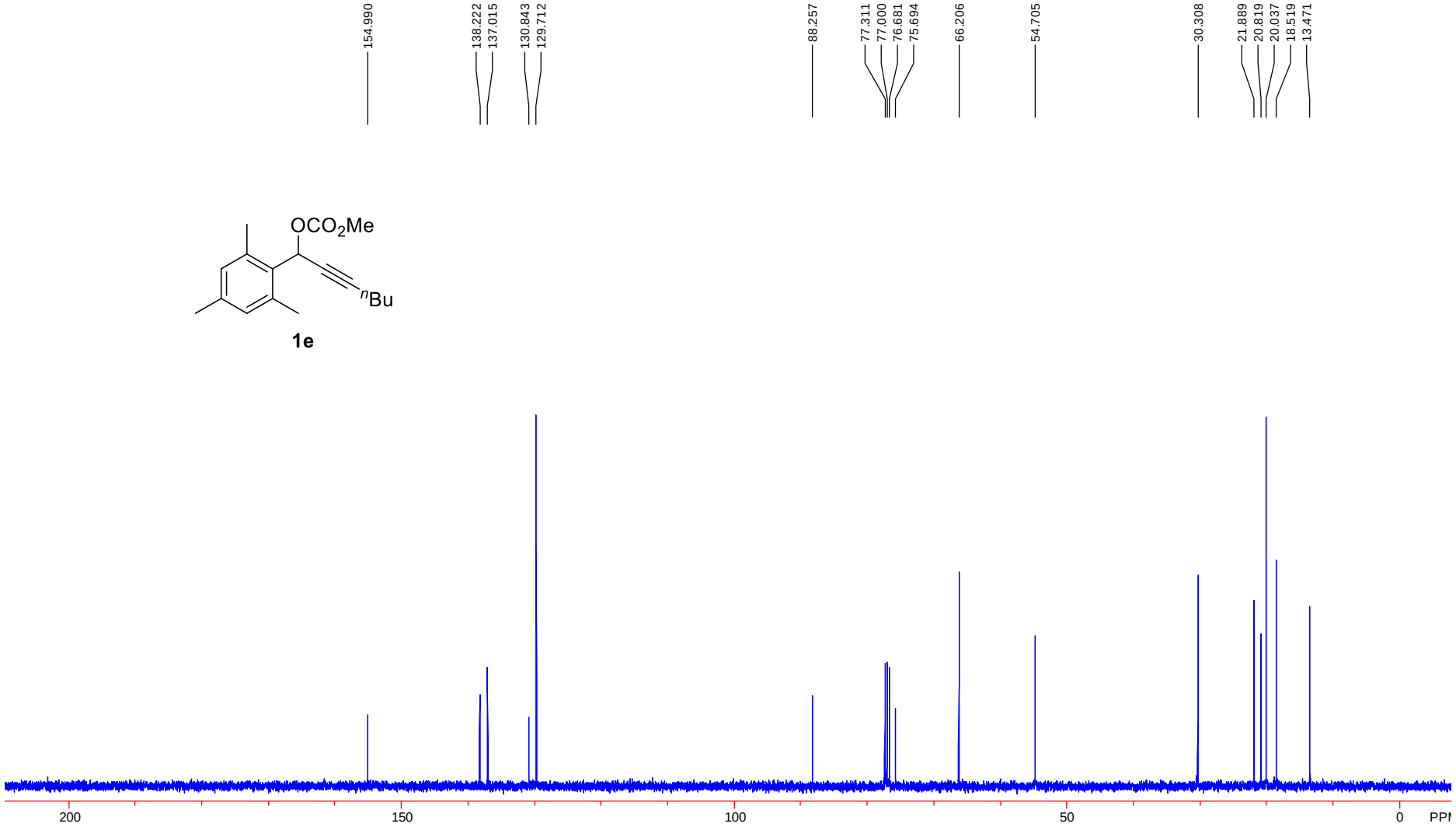
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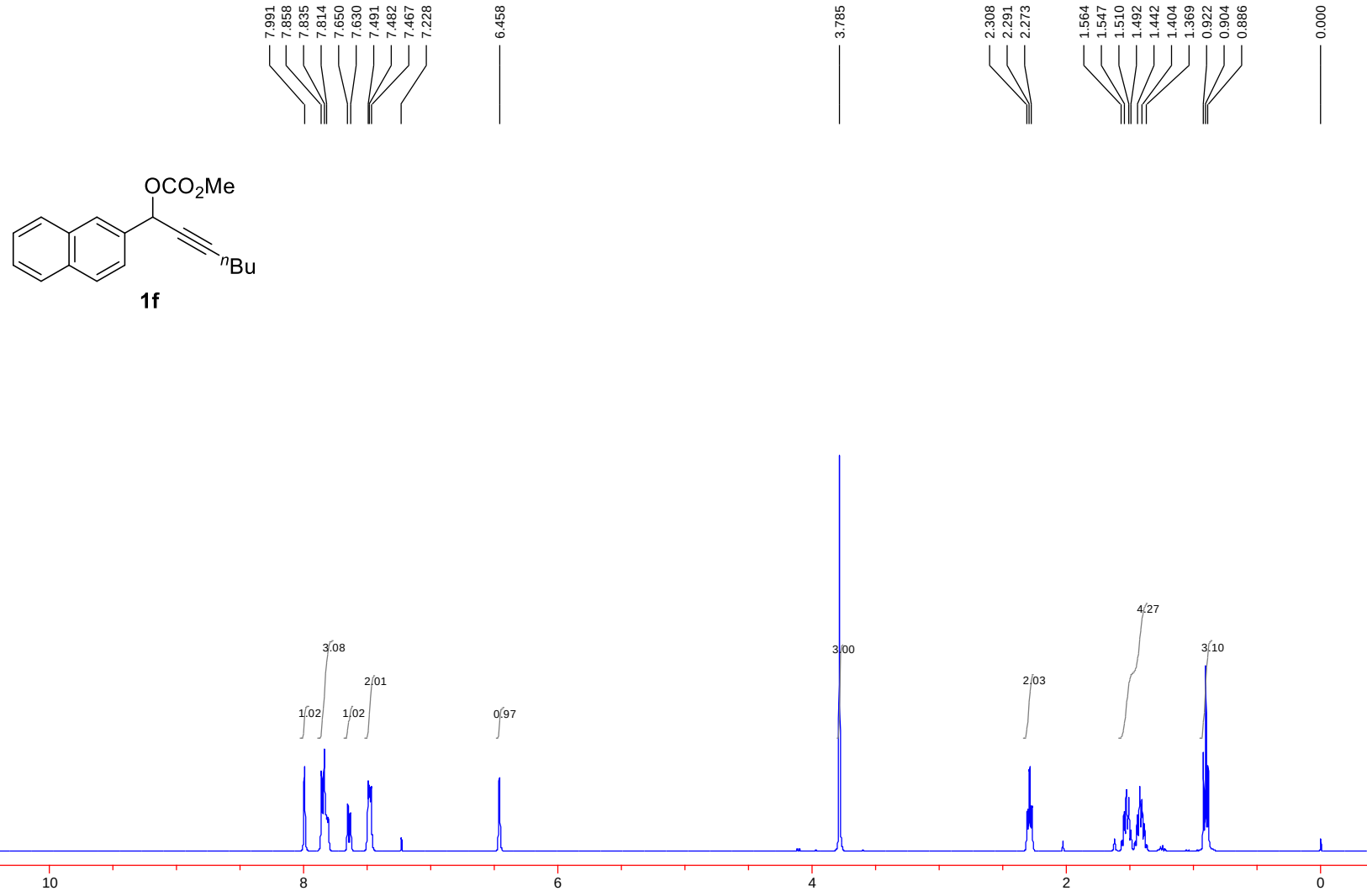
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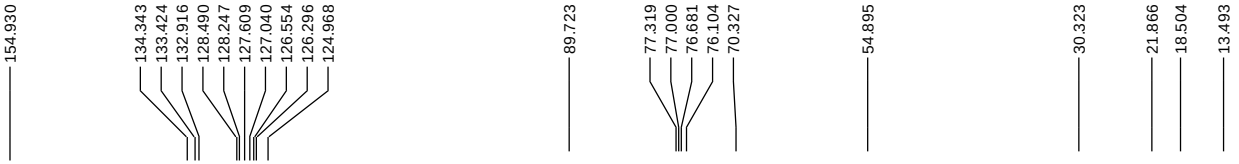
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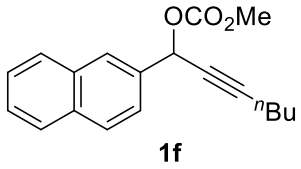
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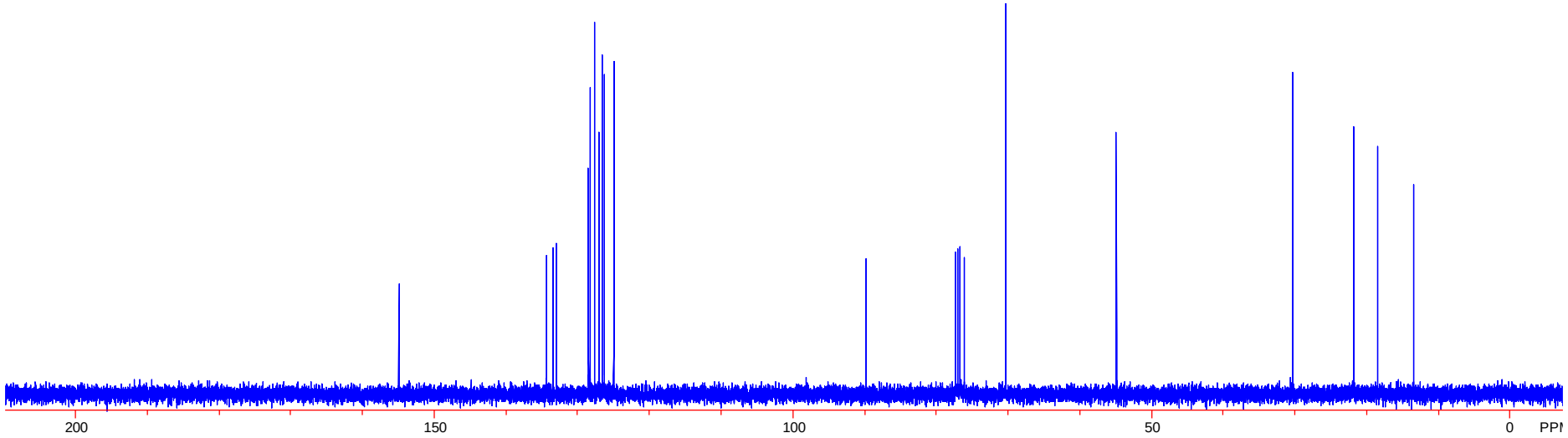
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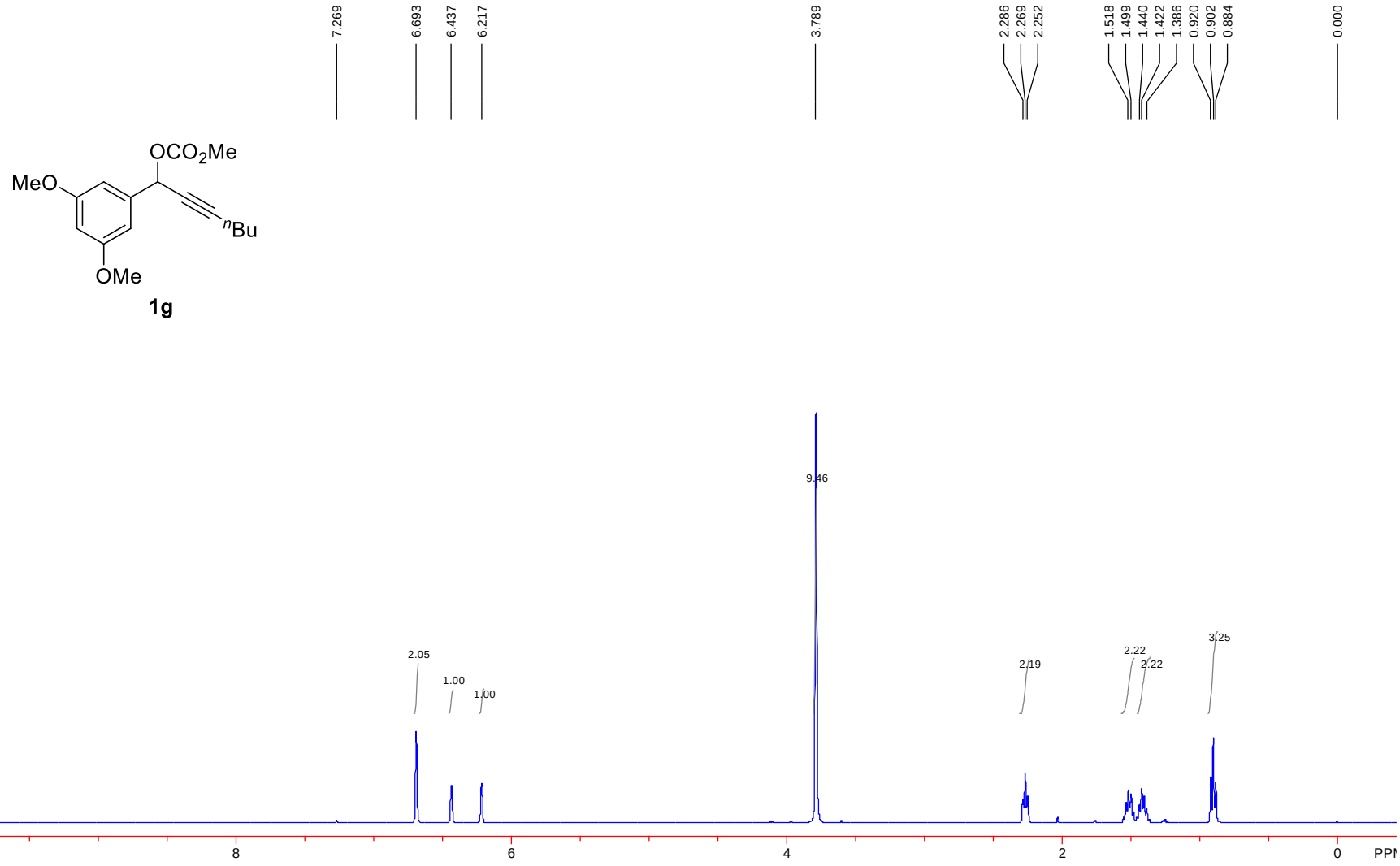
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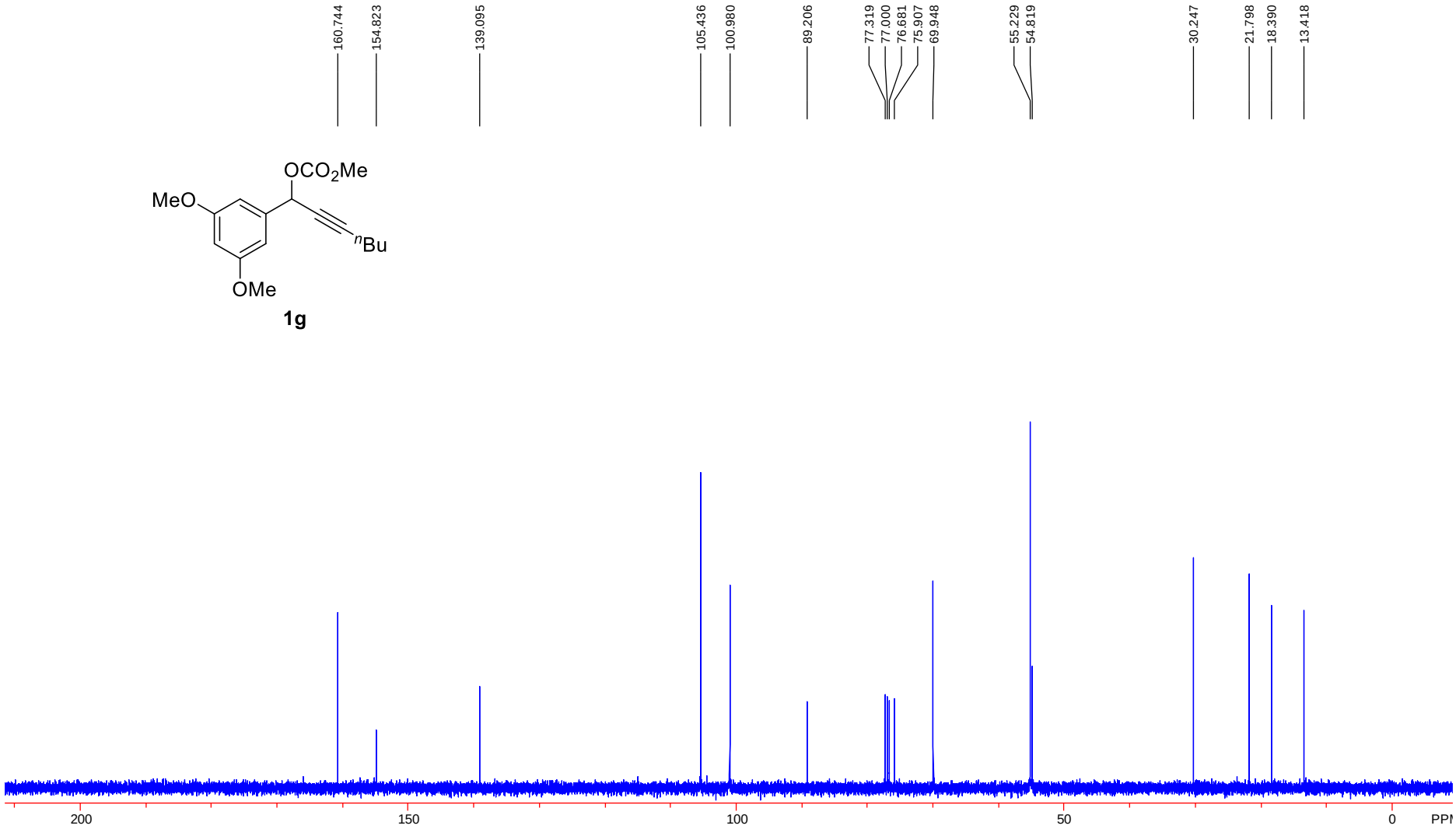
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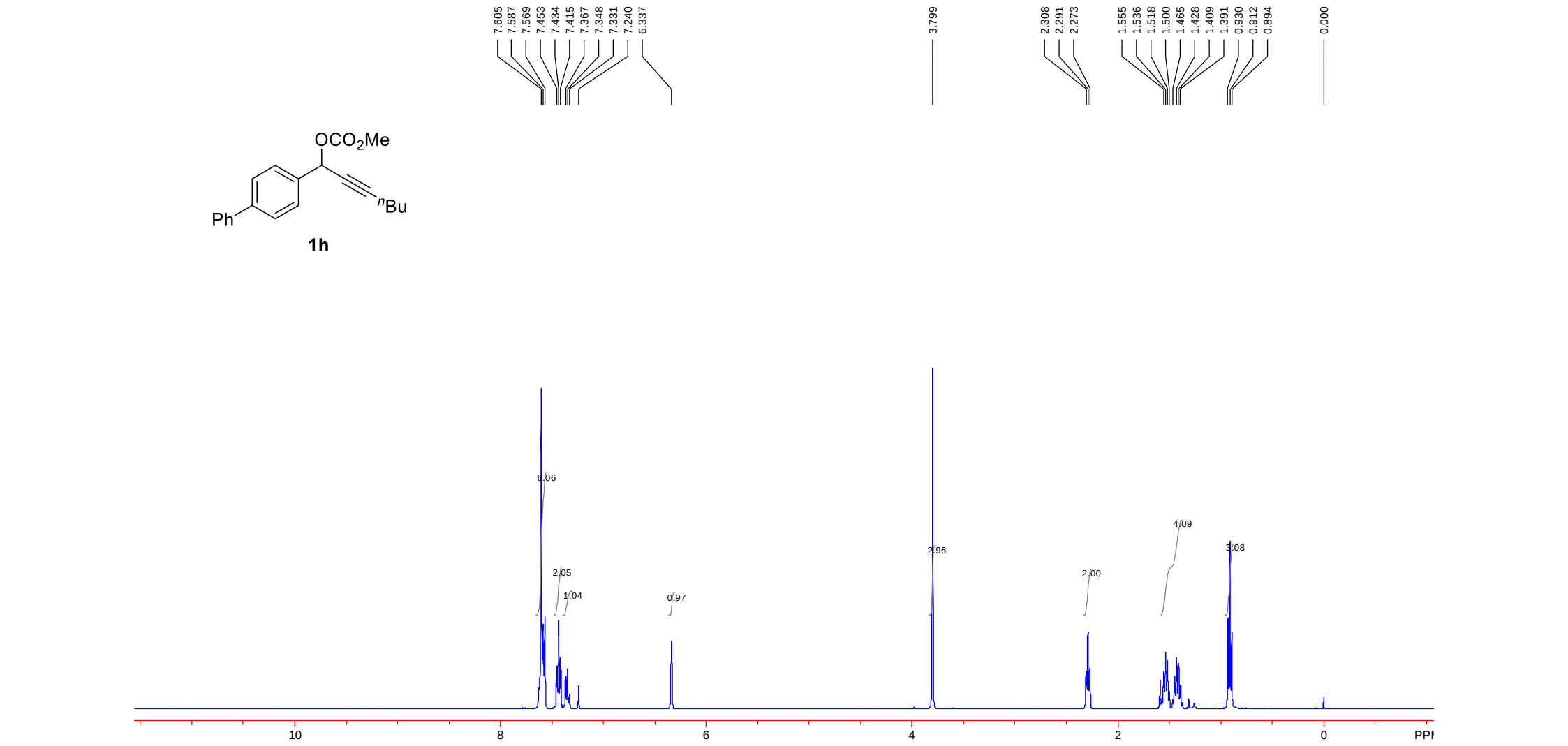
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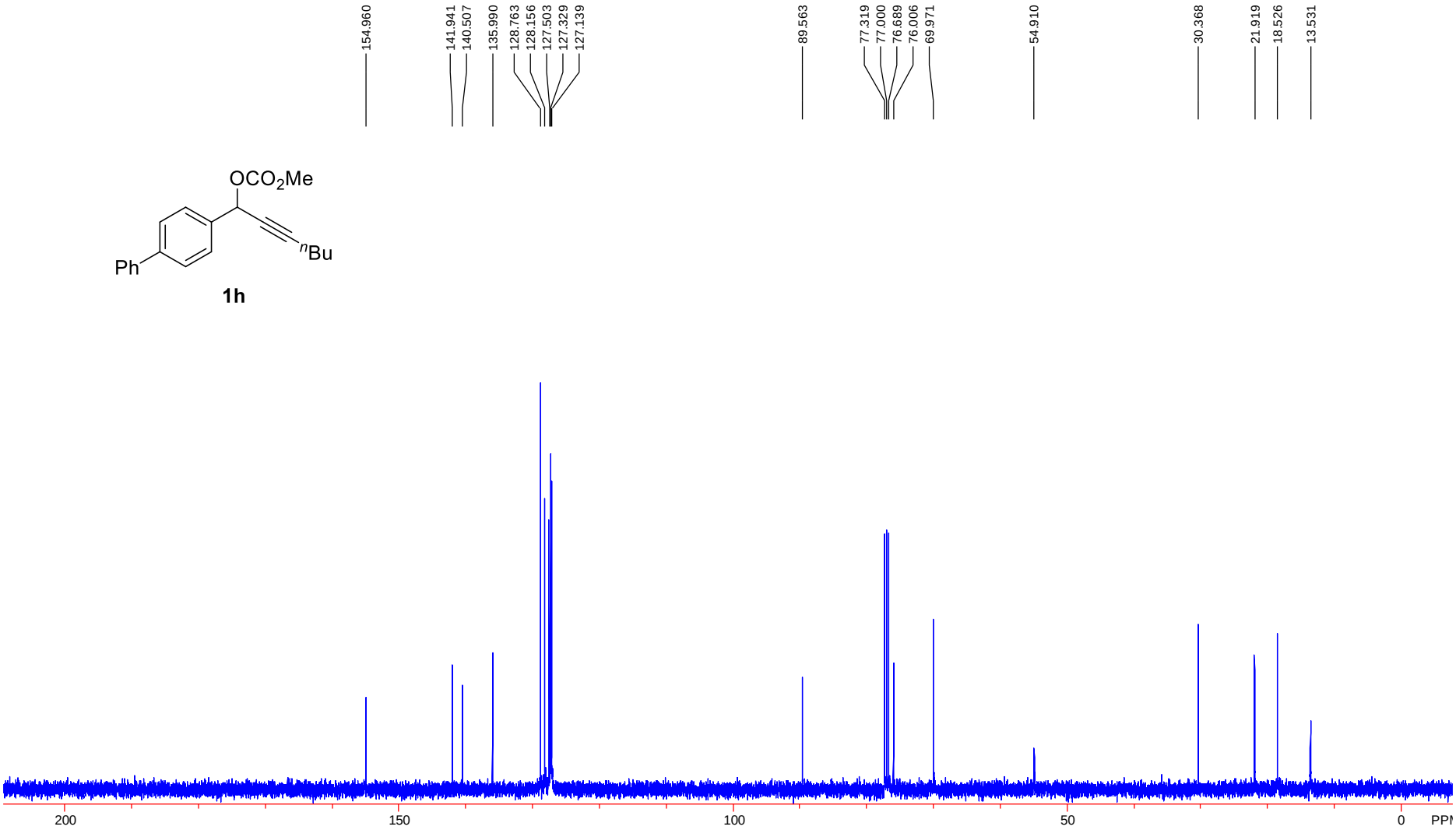
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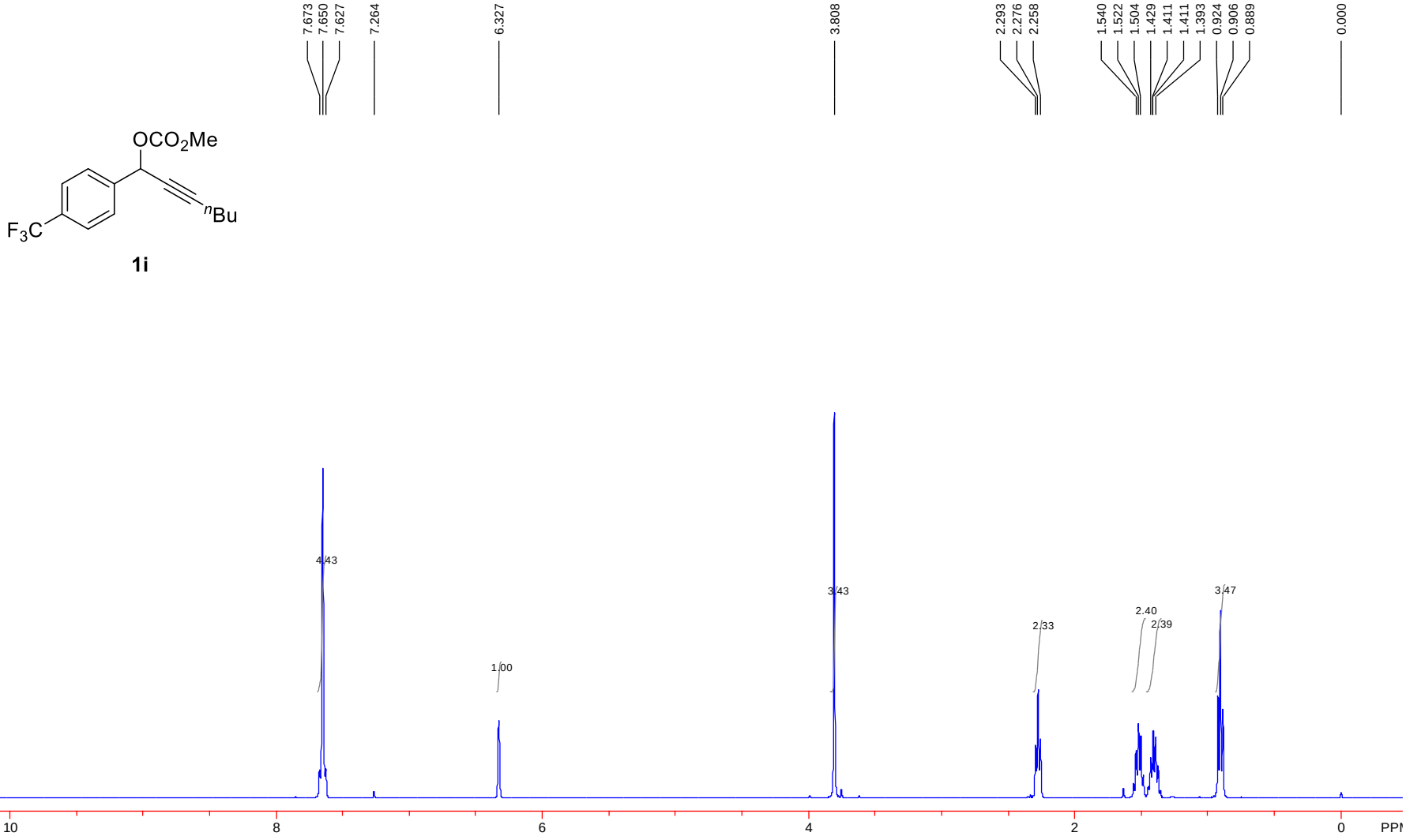
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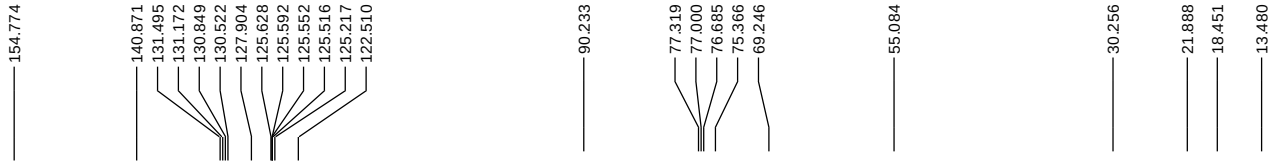
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75.366
69.246
55.084
30.256
21.888
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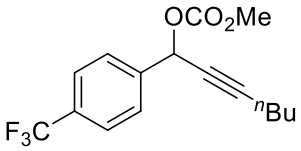
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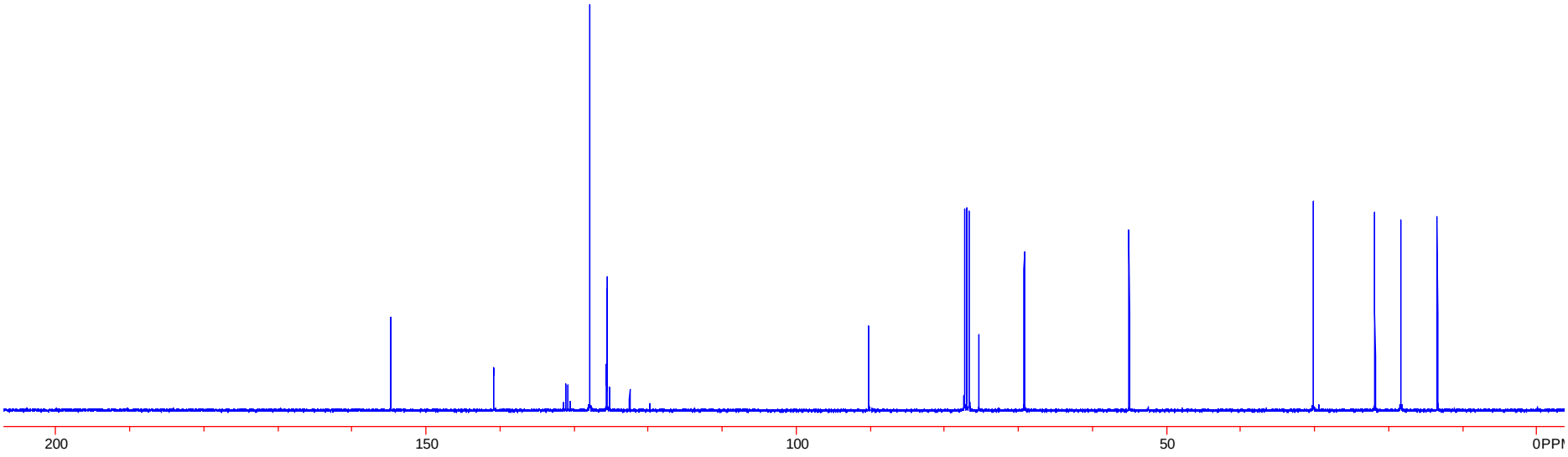
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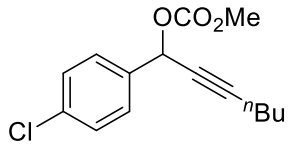
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Cl
nBu

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2.252
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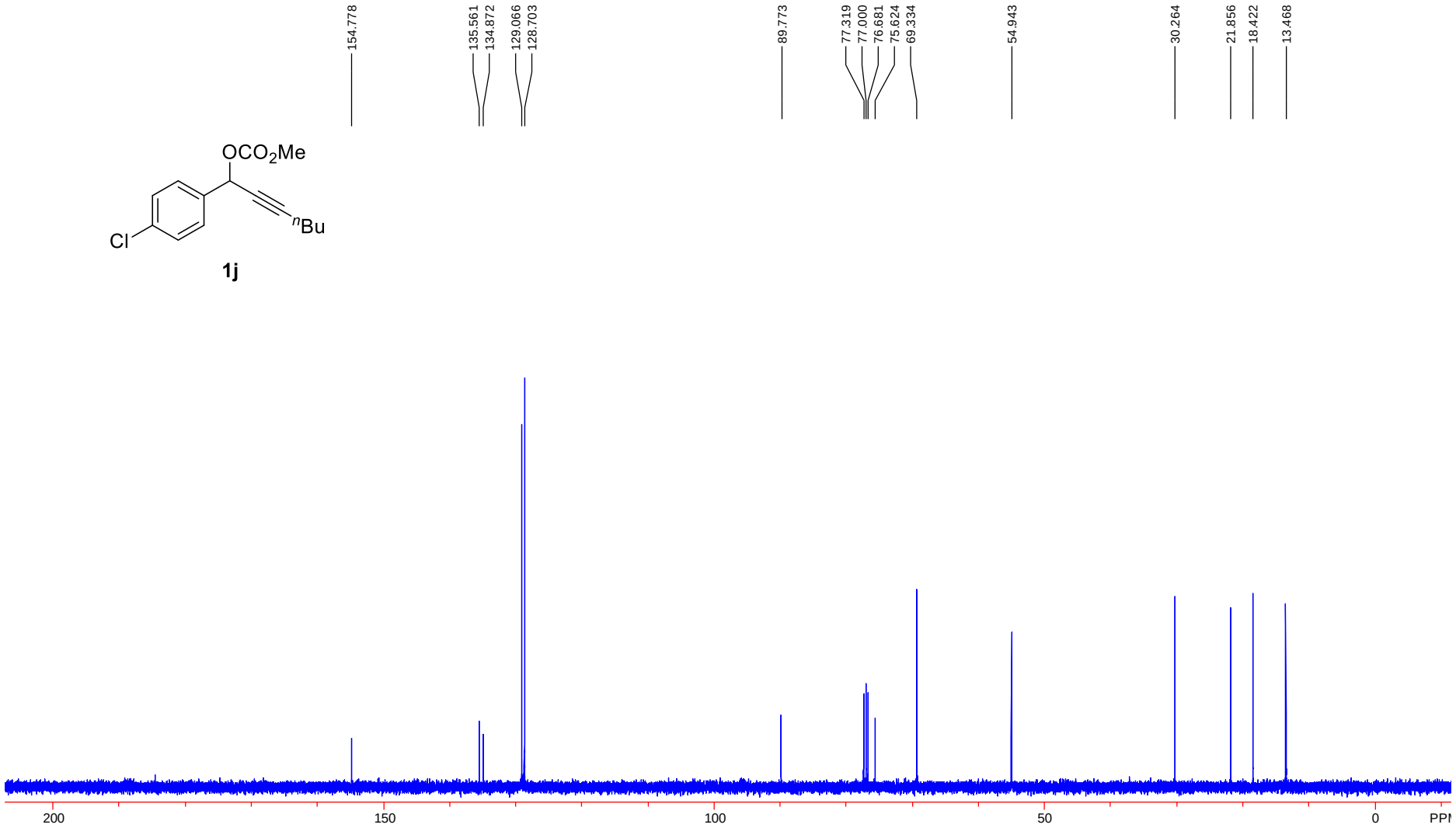
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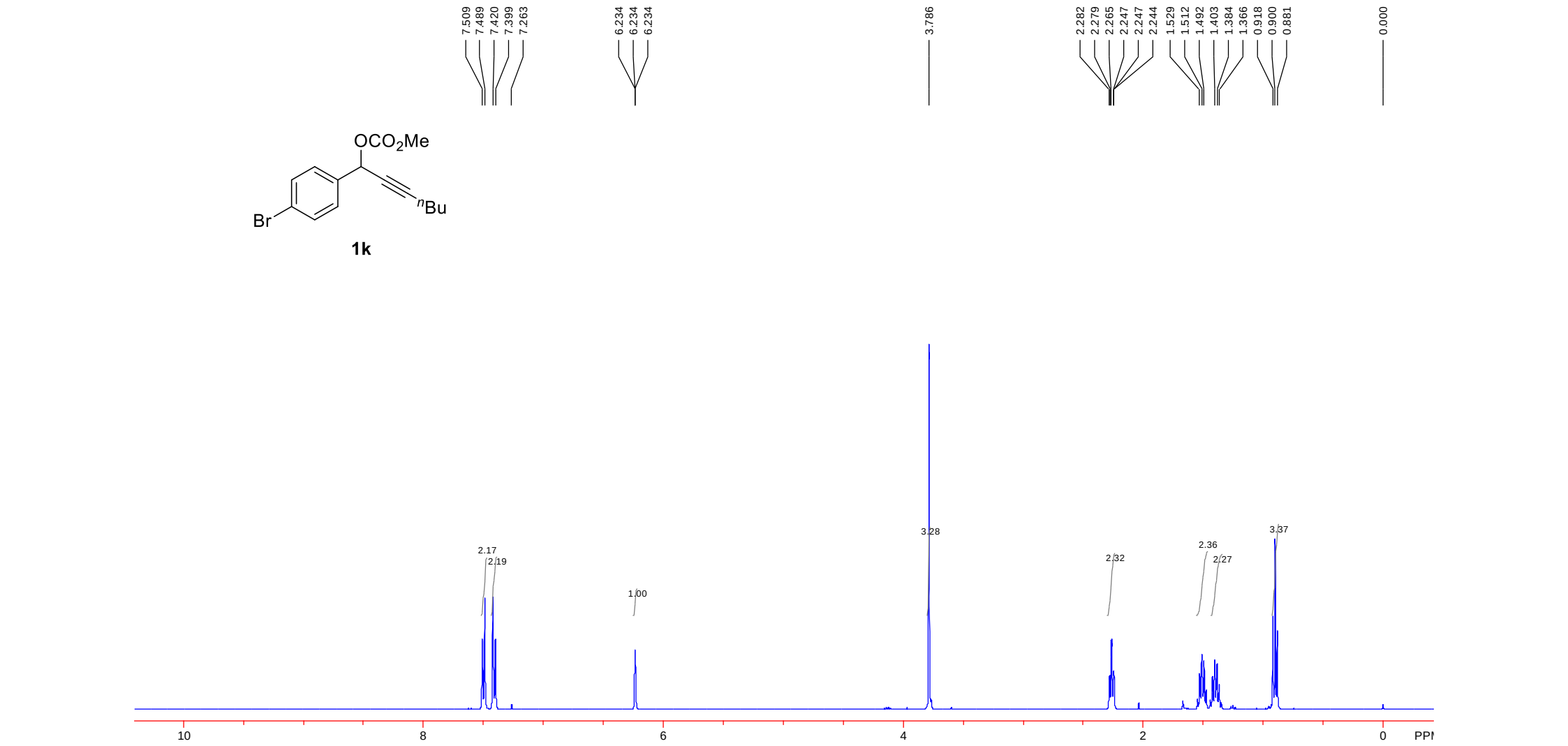
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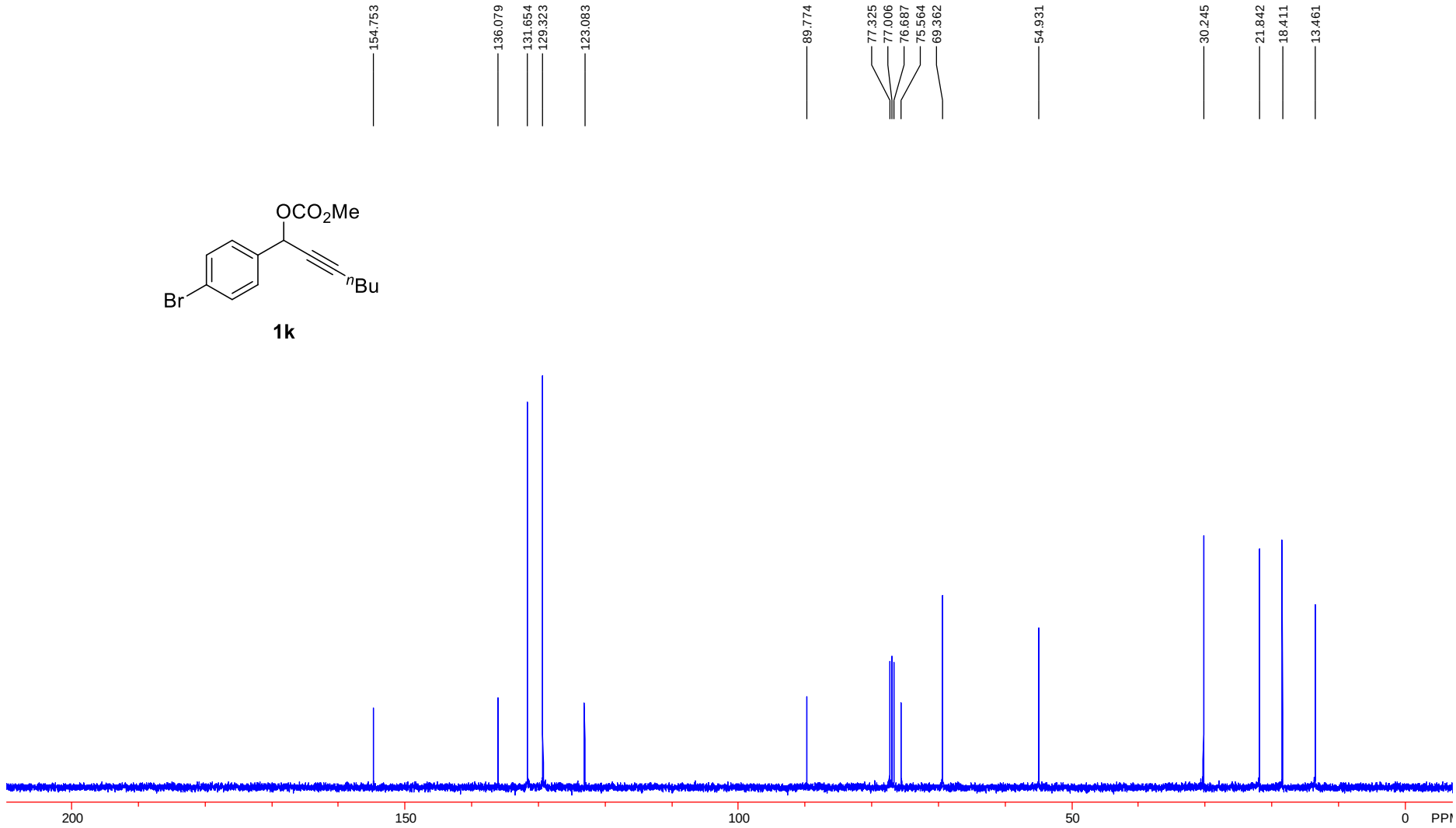
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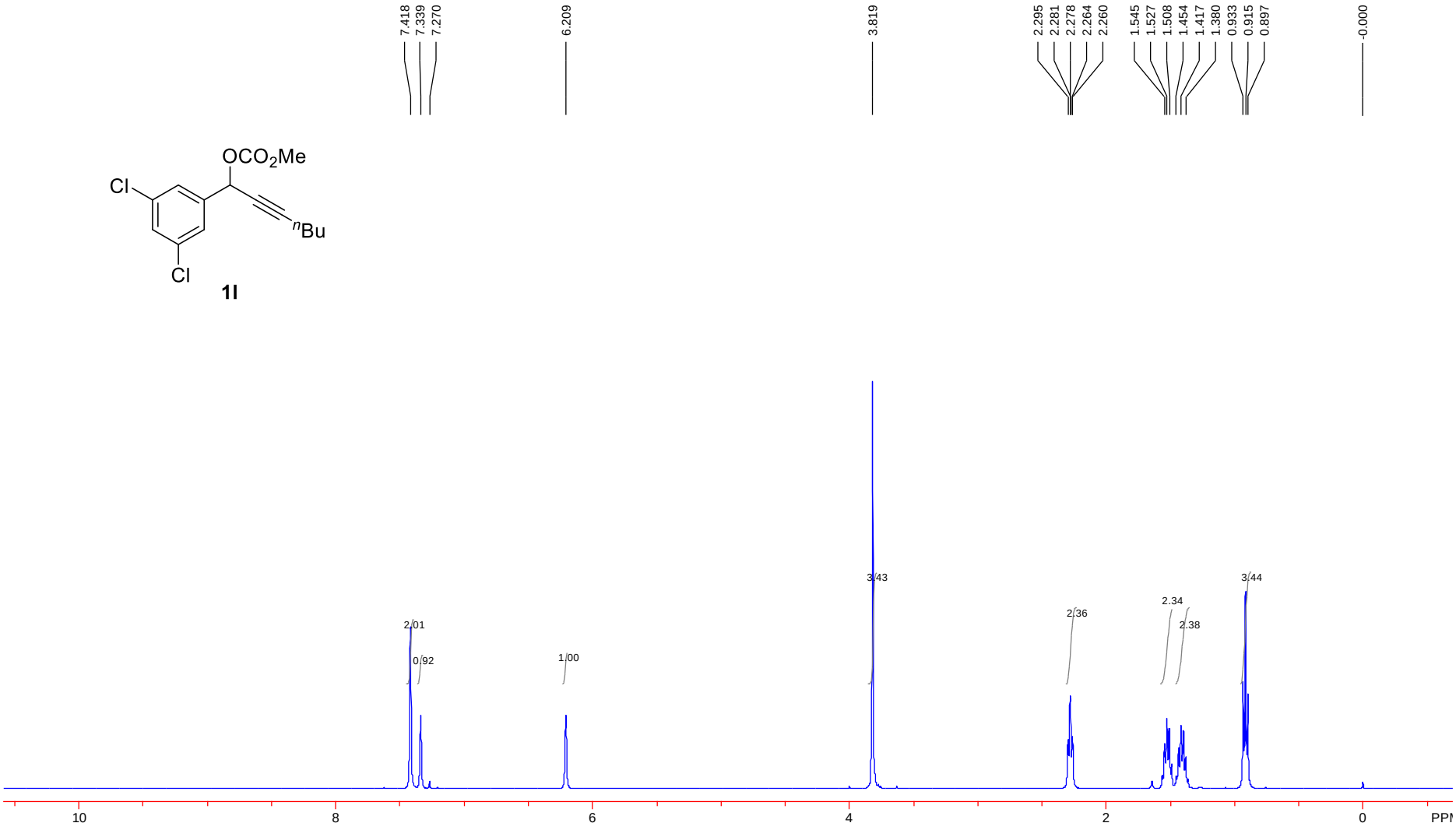
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1.508
1.454
1.417
1.380
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0.915
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Cl
nBu
Cl
1l
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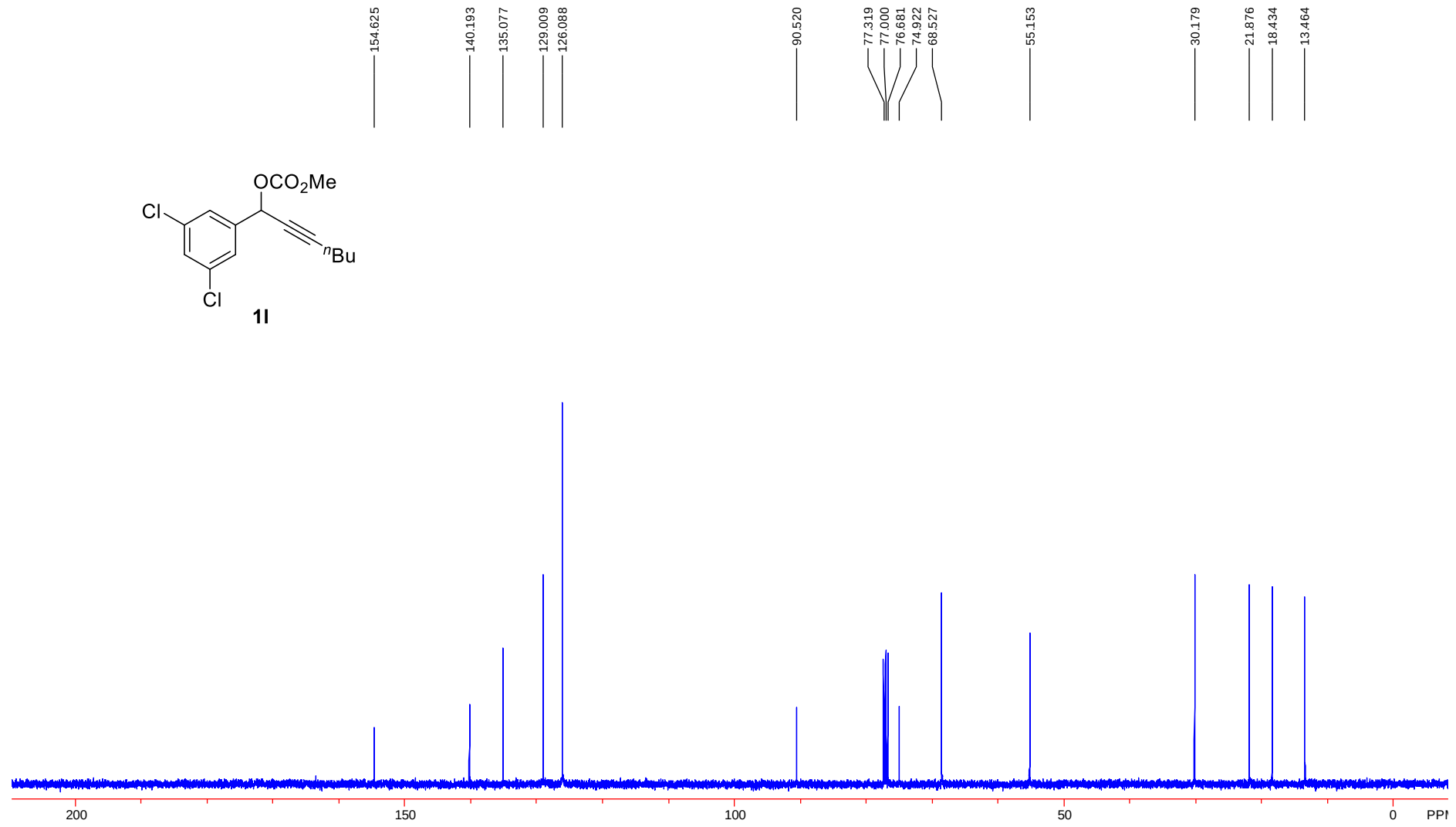
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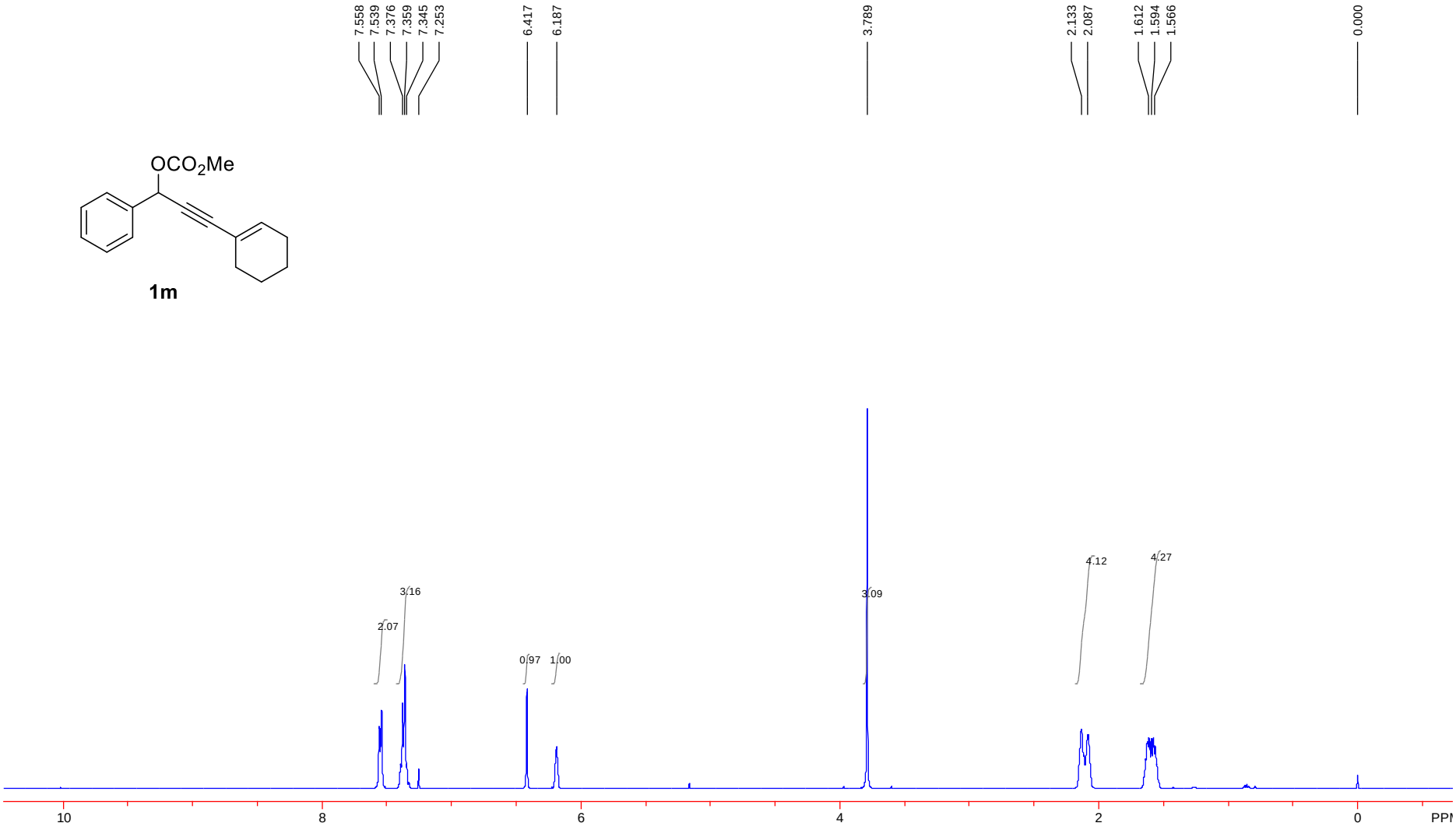
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1.594
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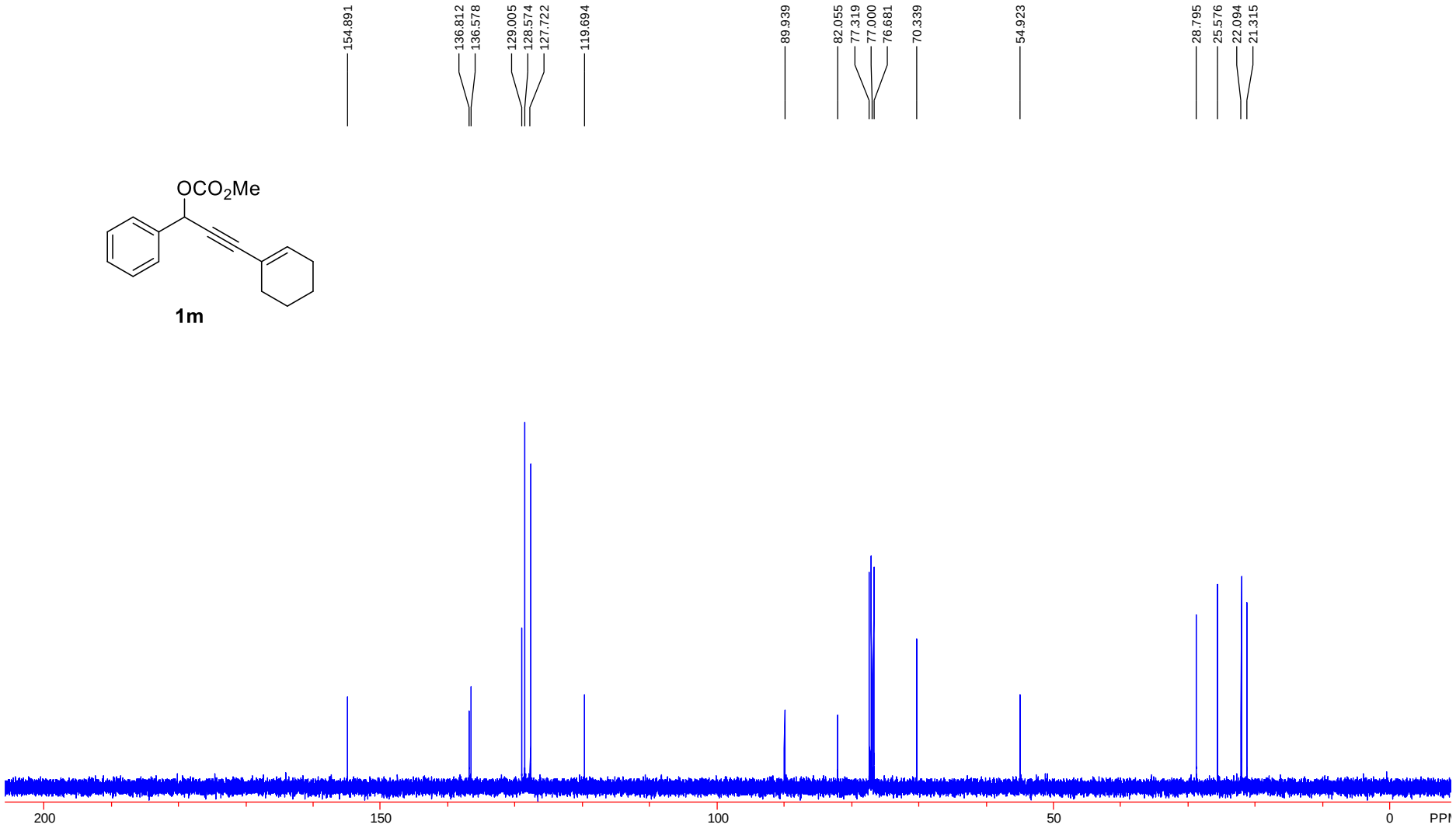
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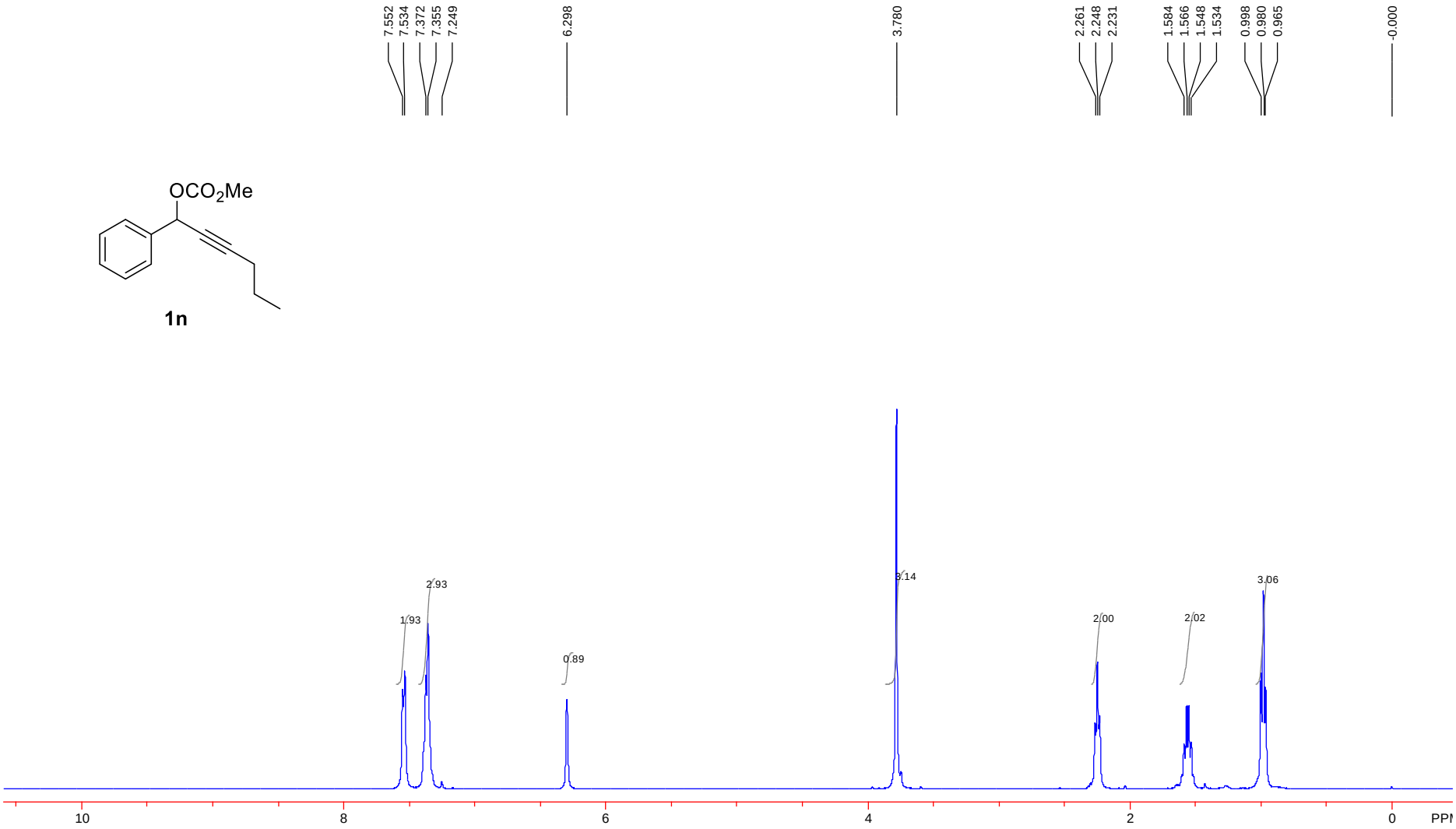
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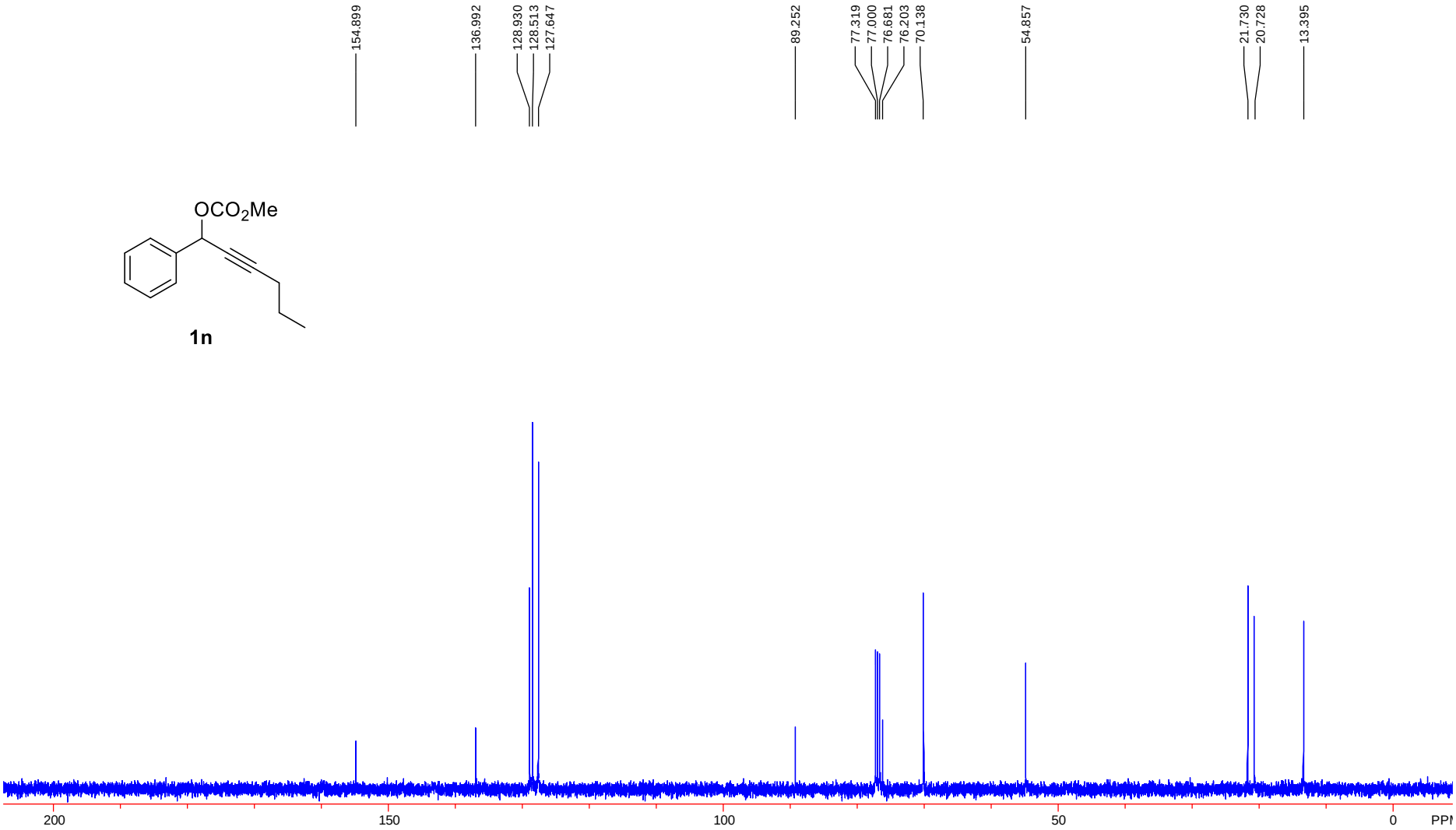
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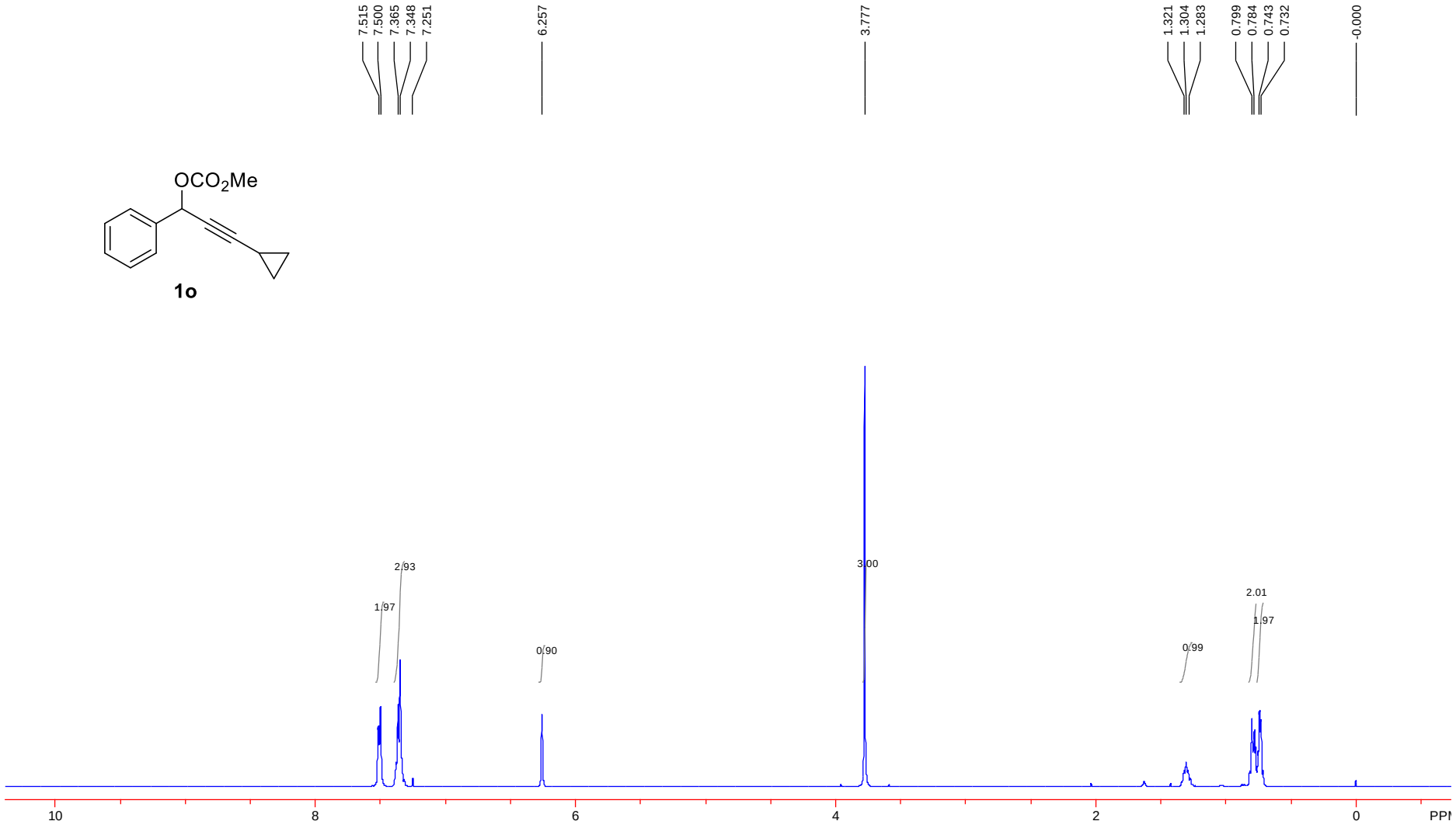
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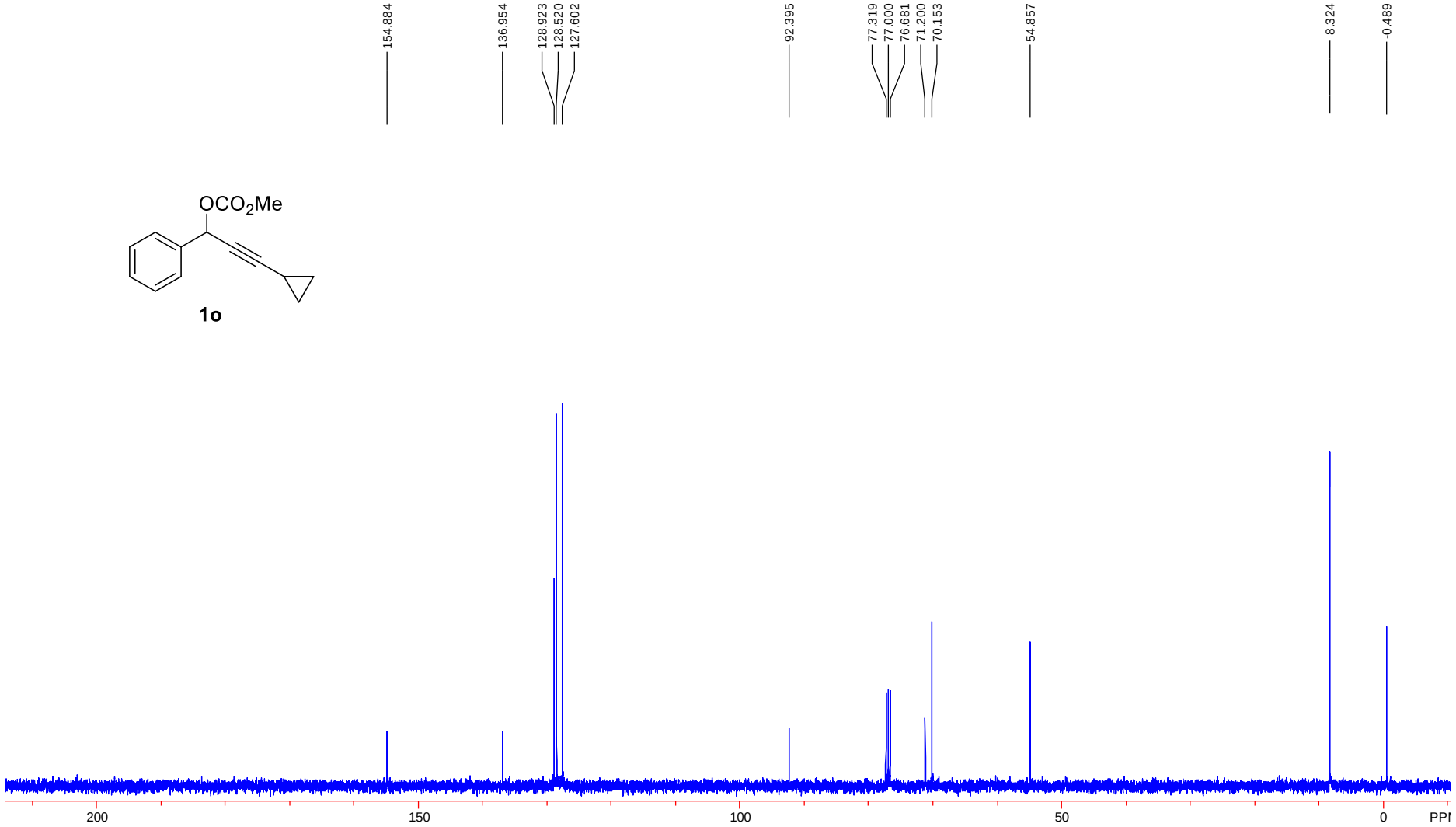
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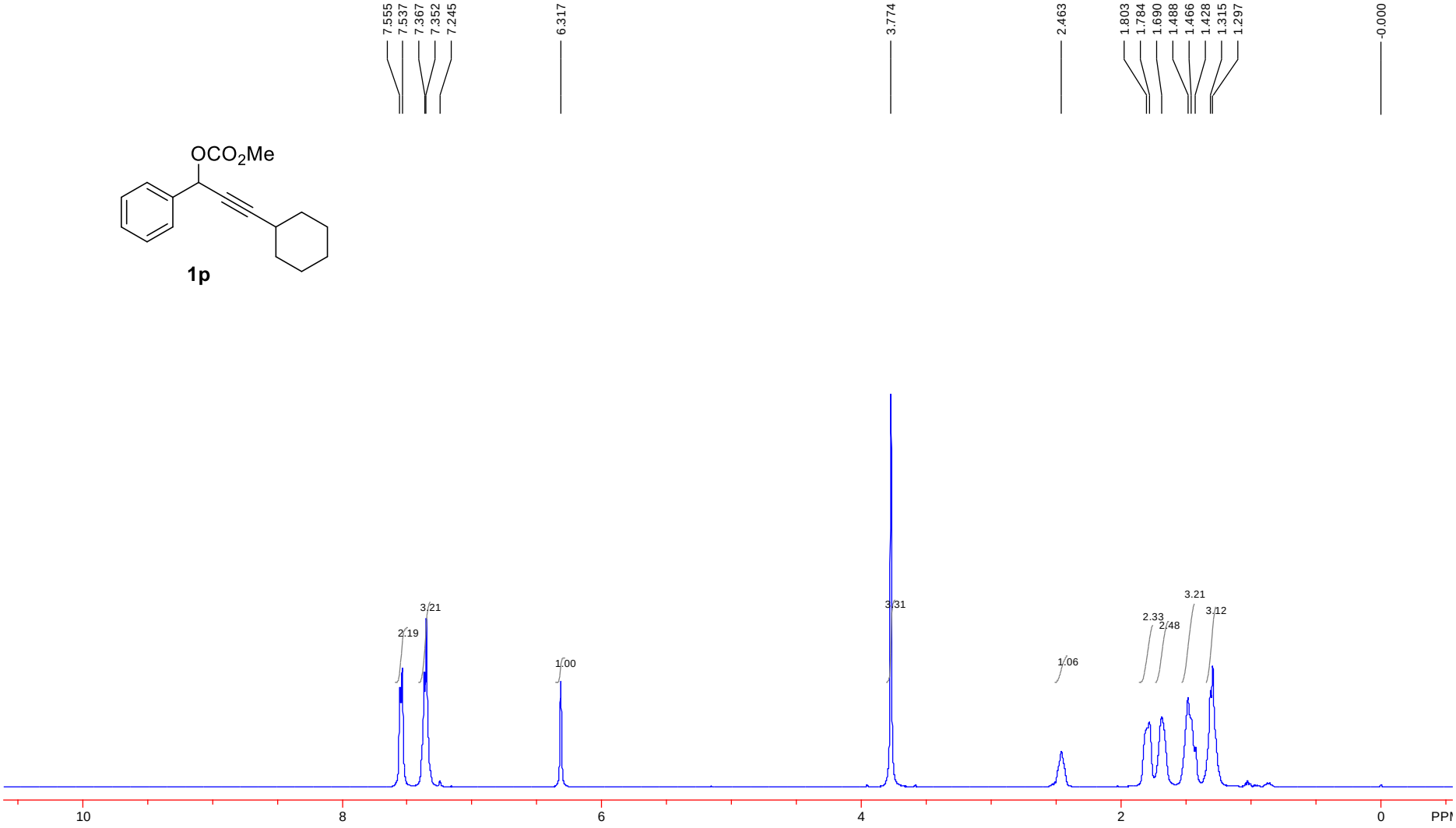
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1.466
1.428
1.315
1.297
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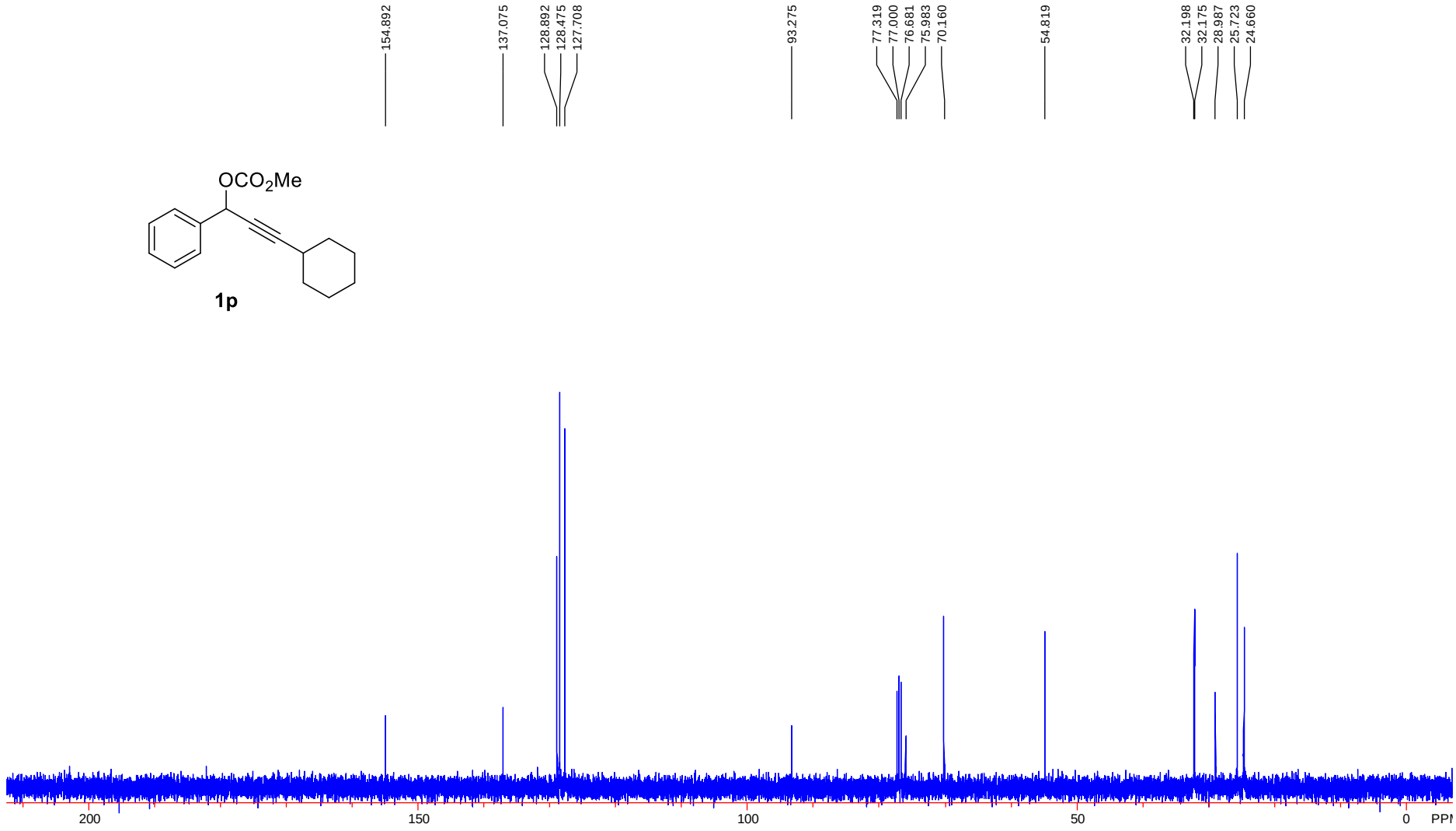
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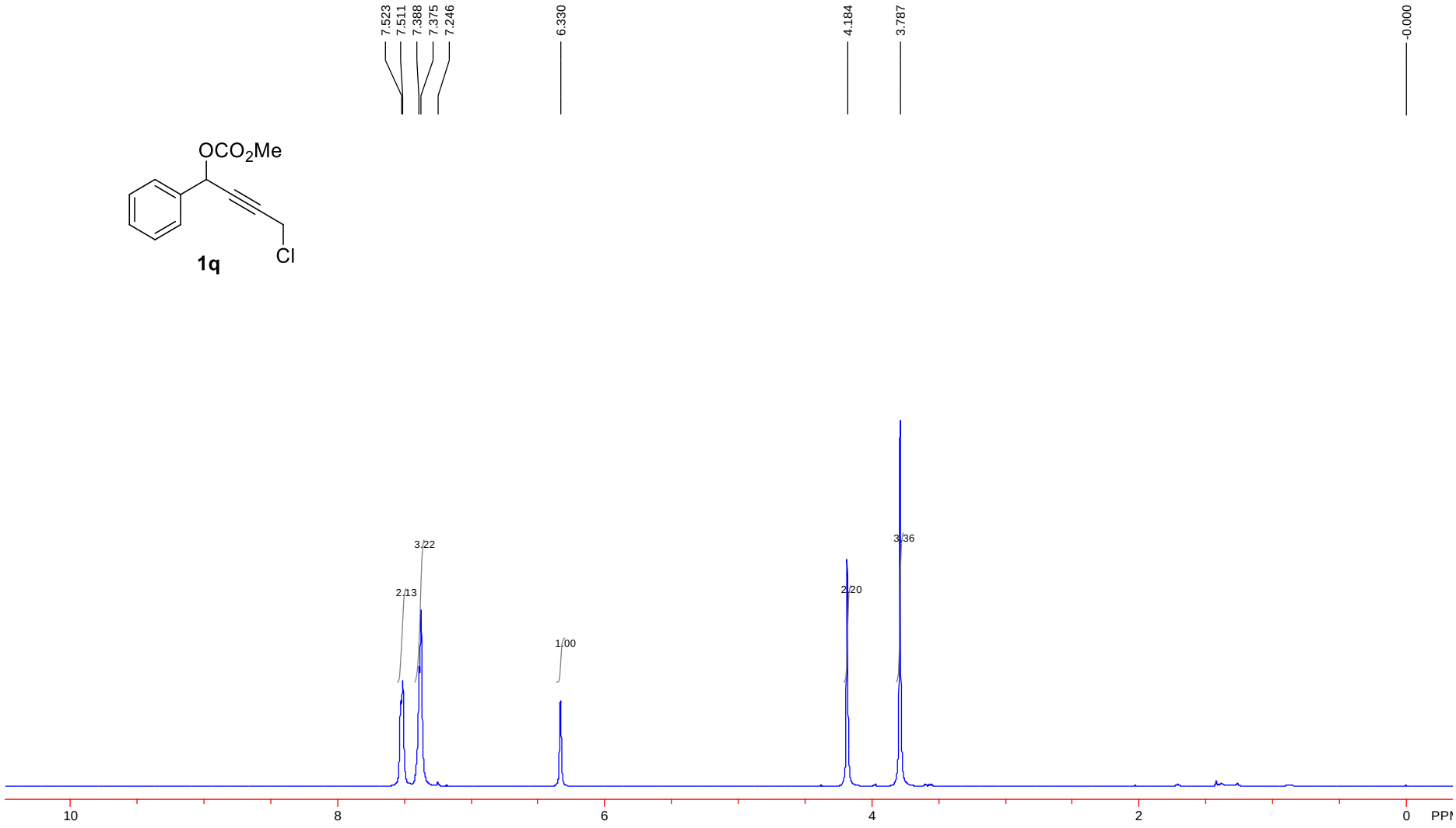
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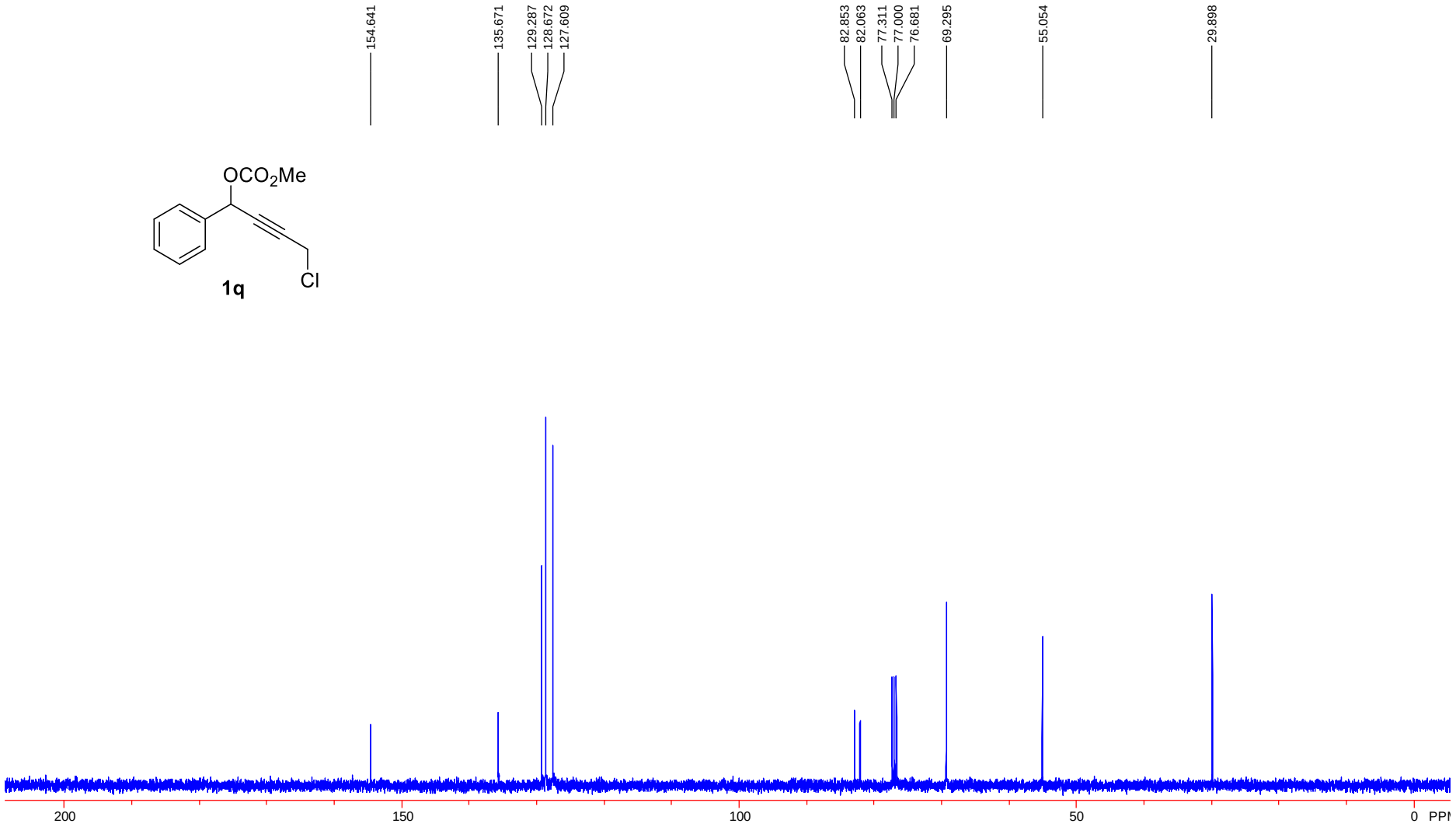
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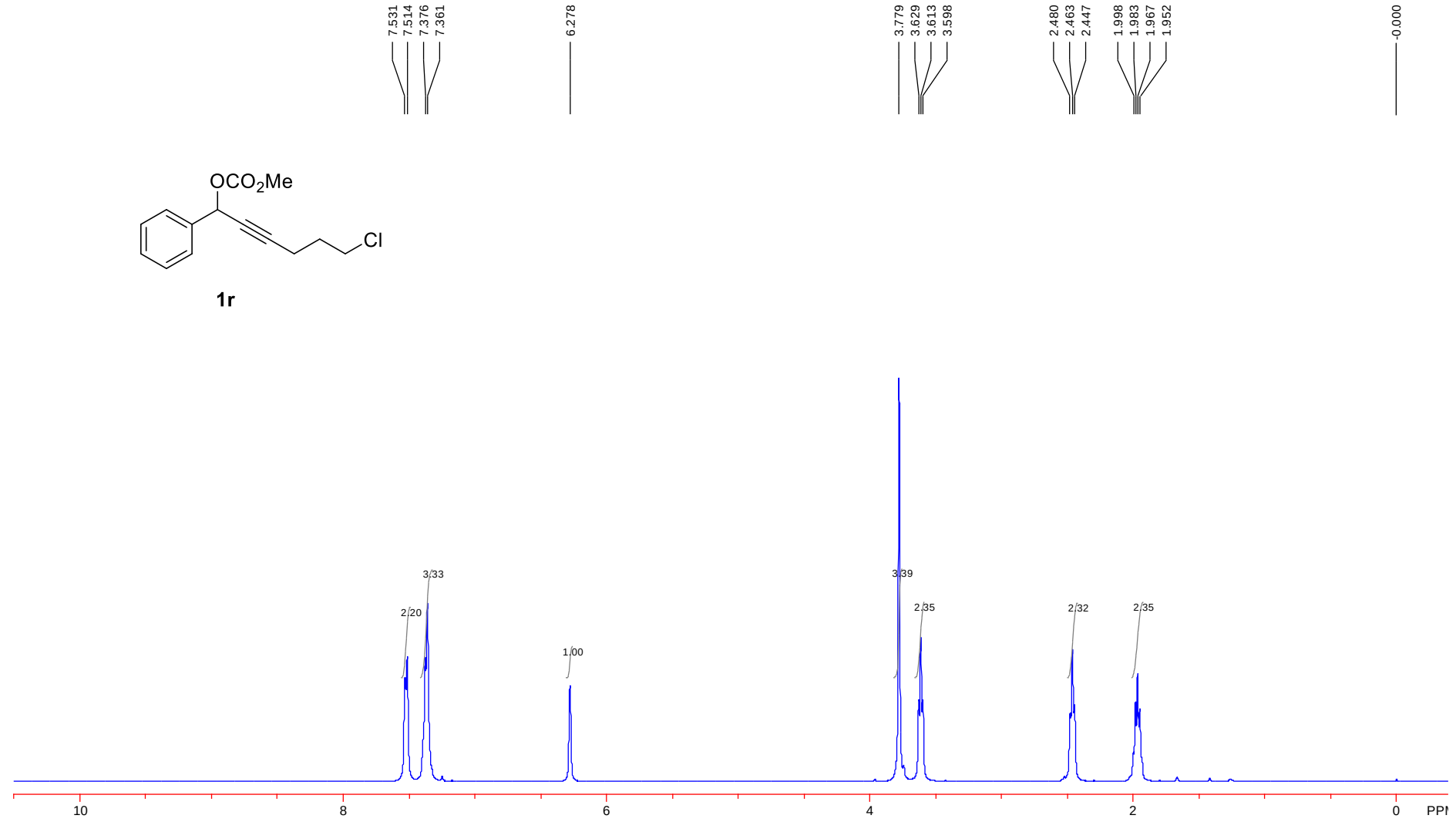
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Cl
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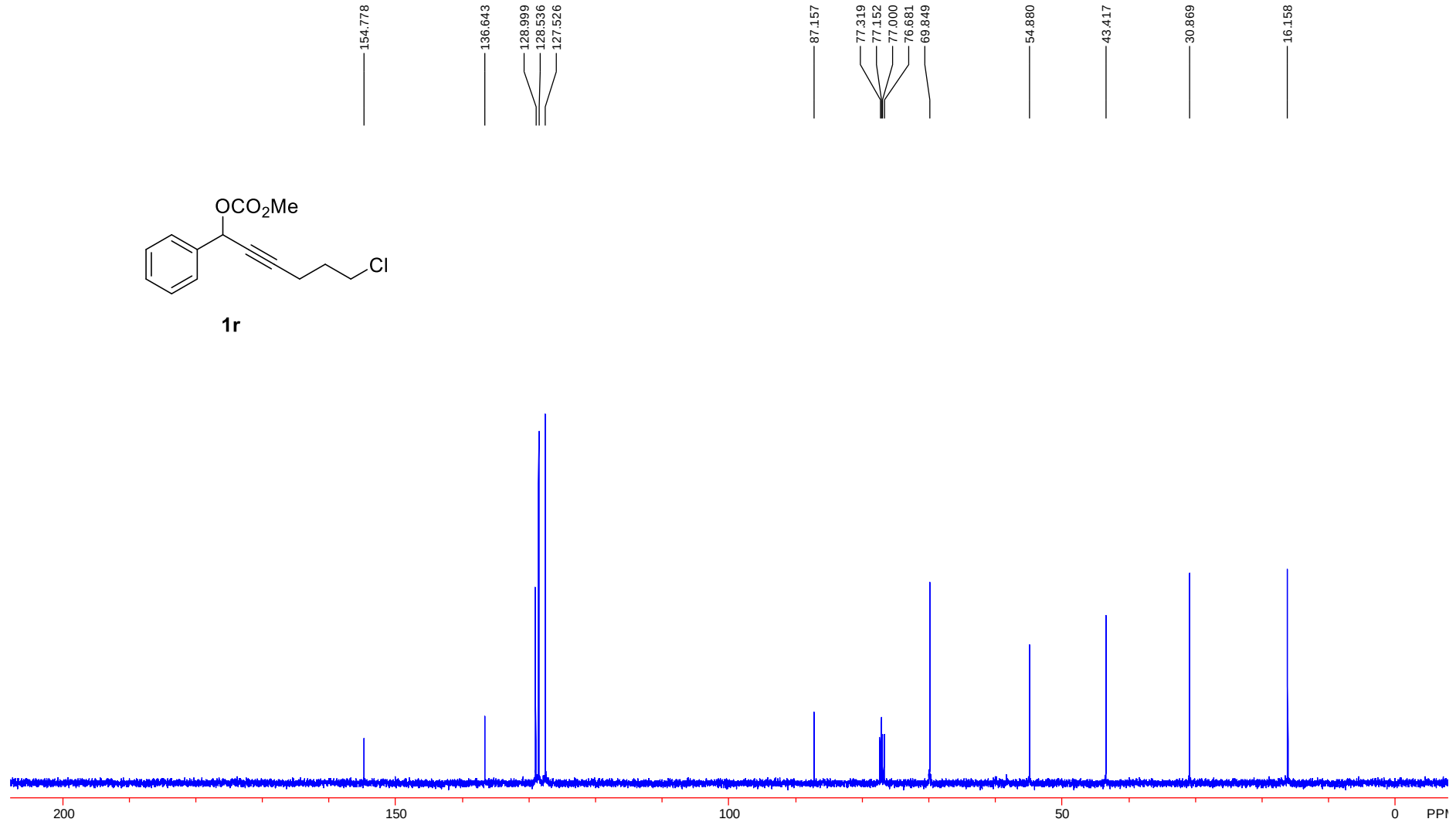
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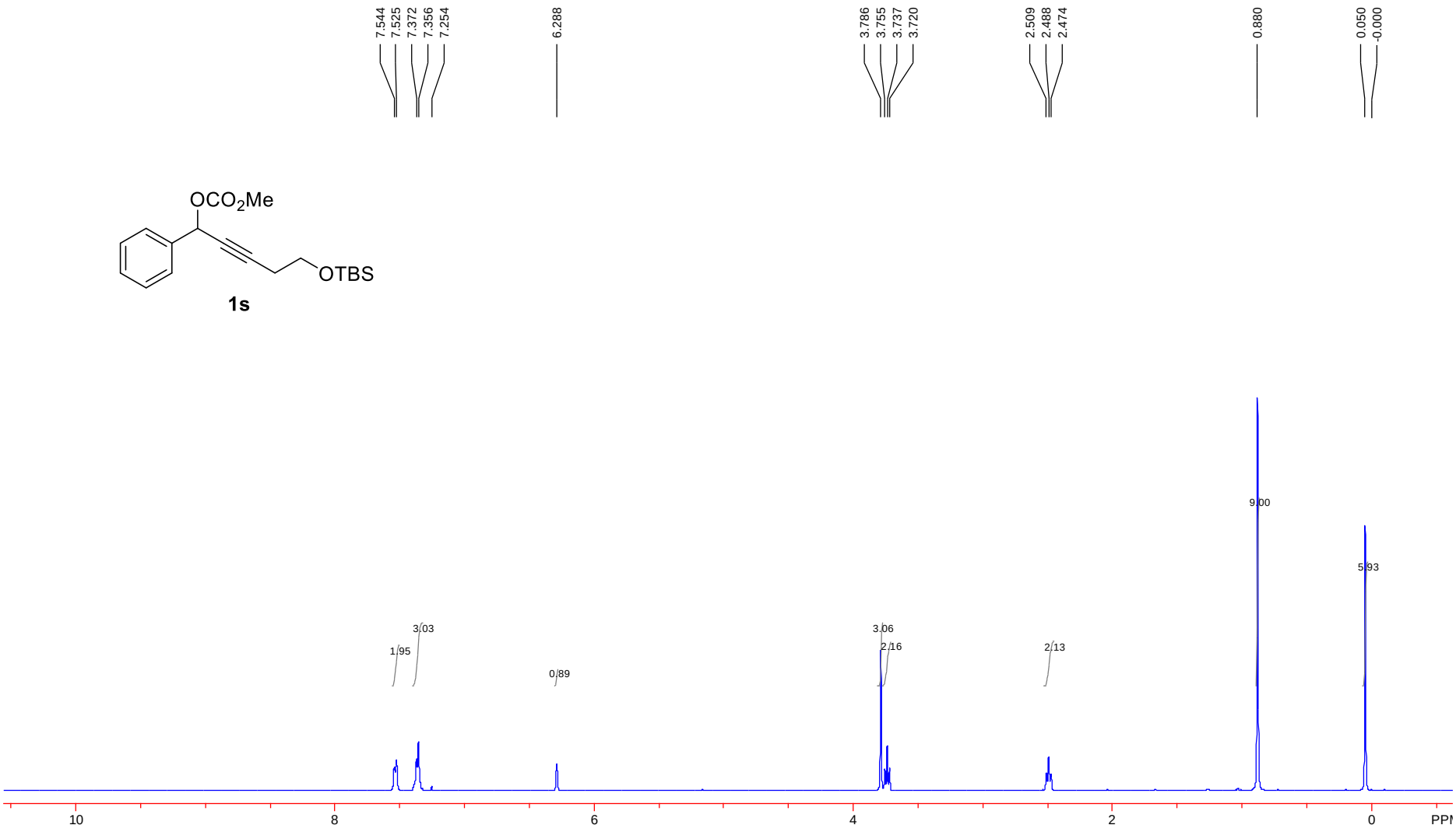
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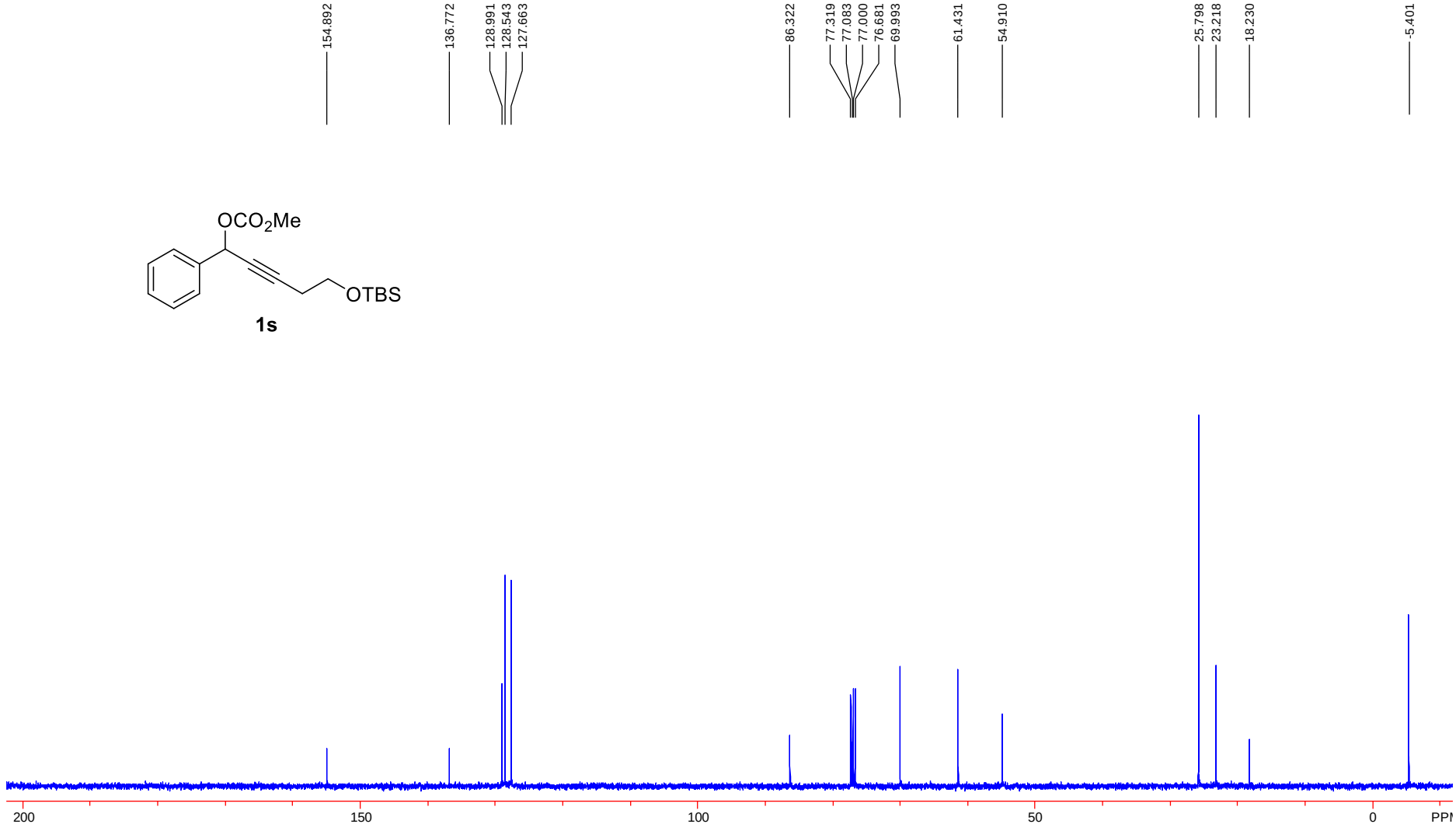
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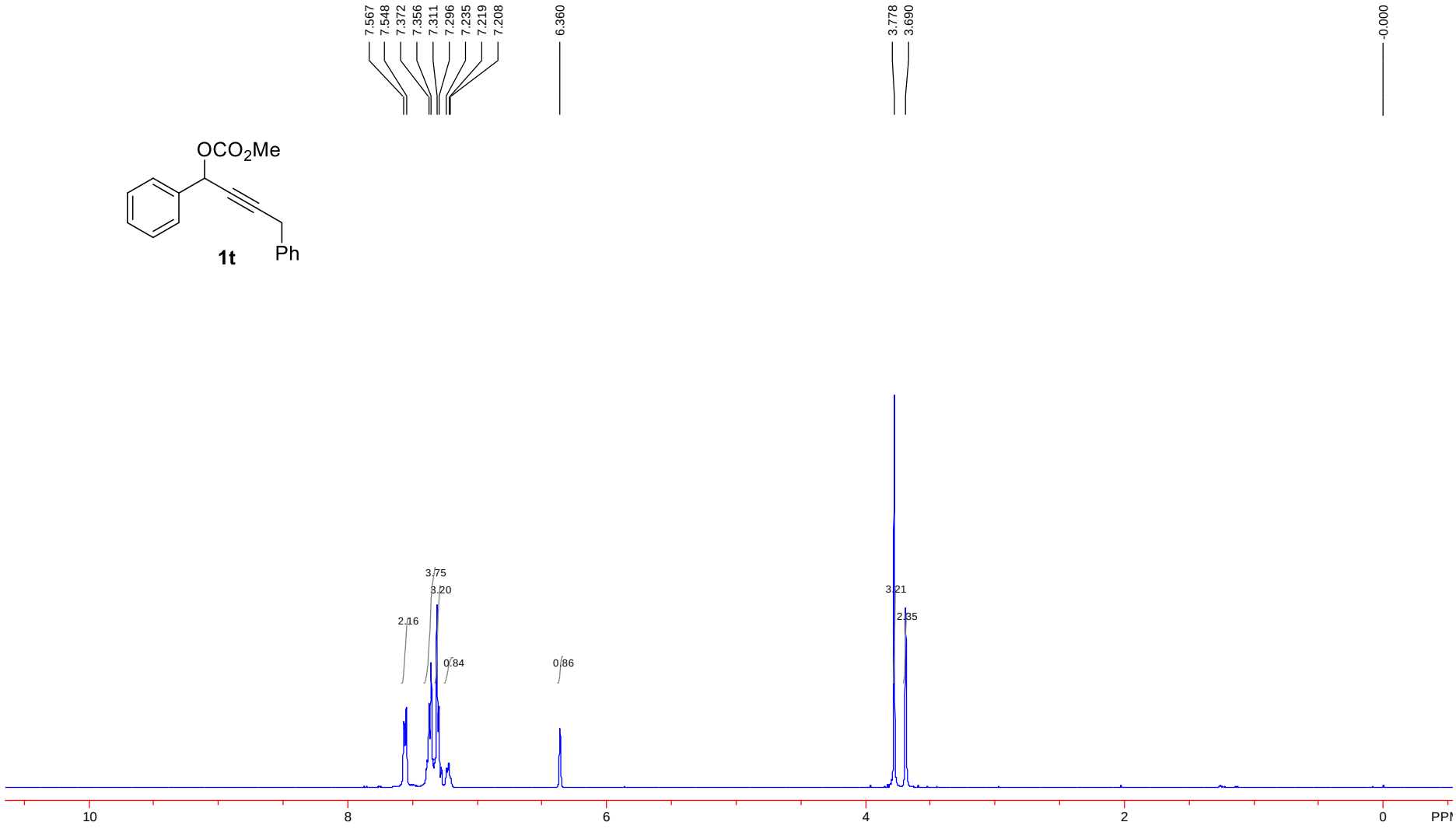
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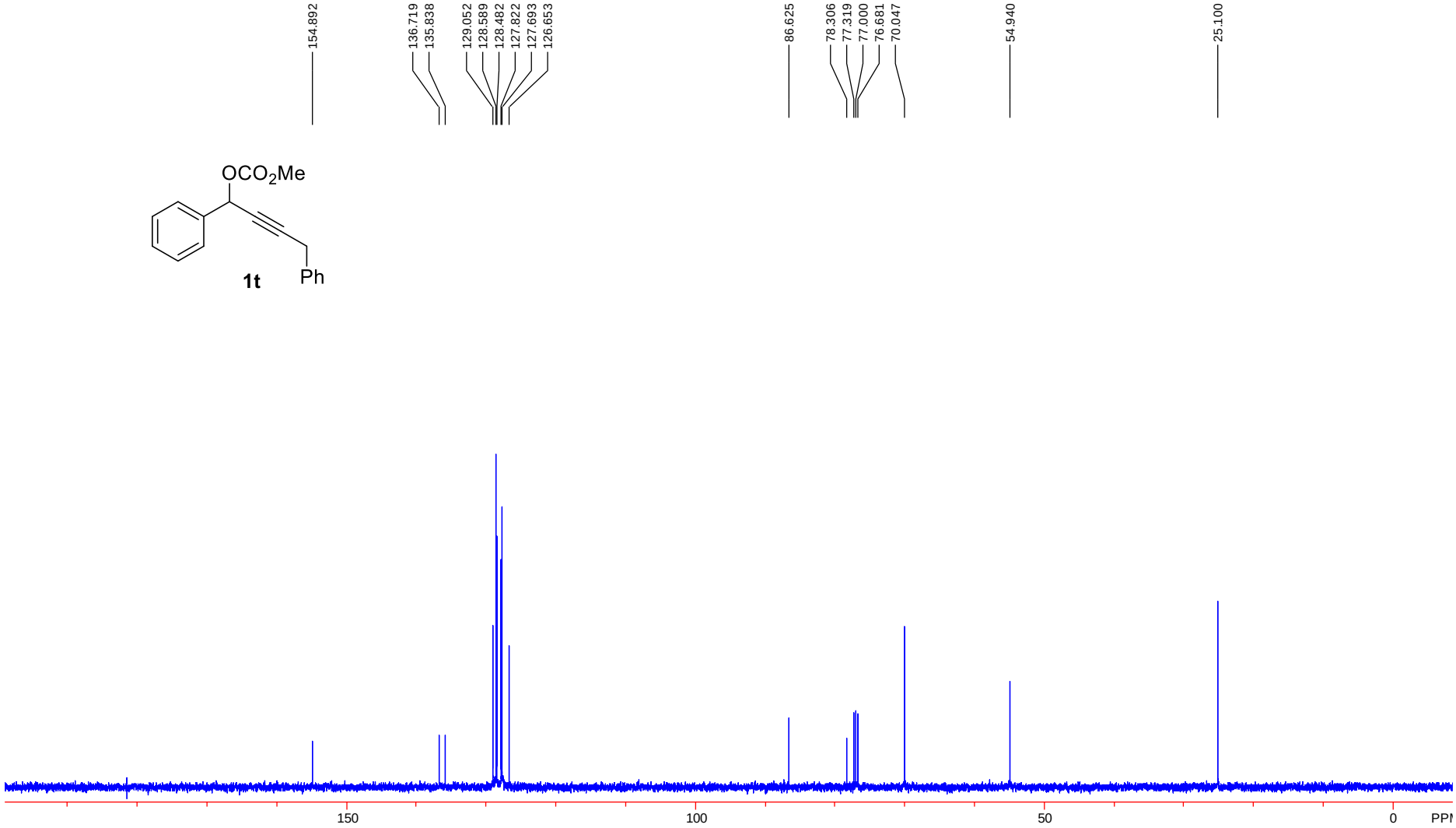
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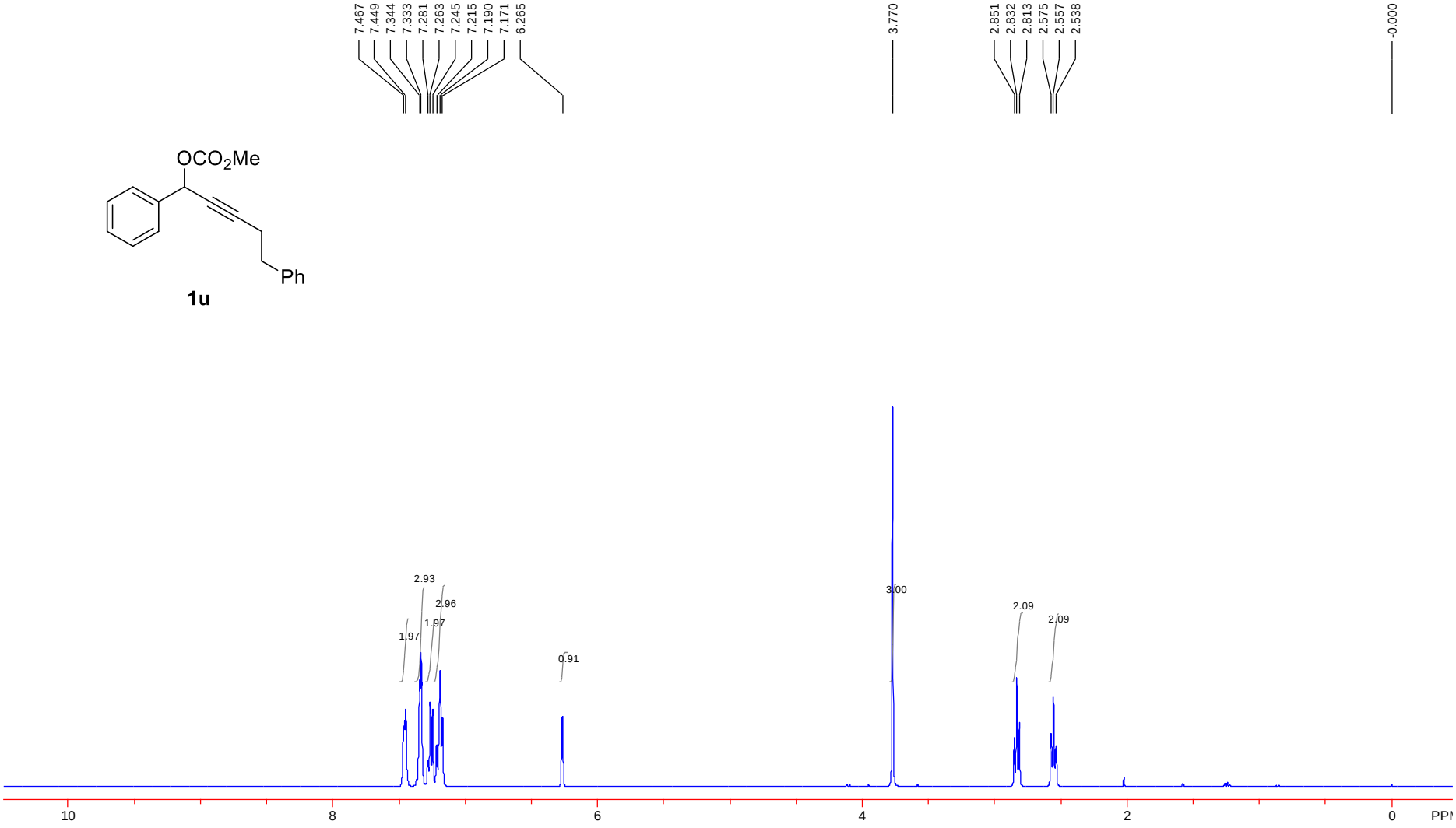
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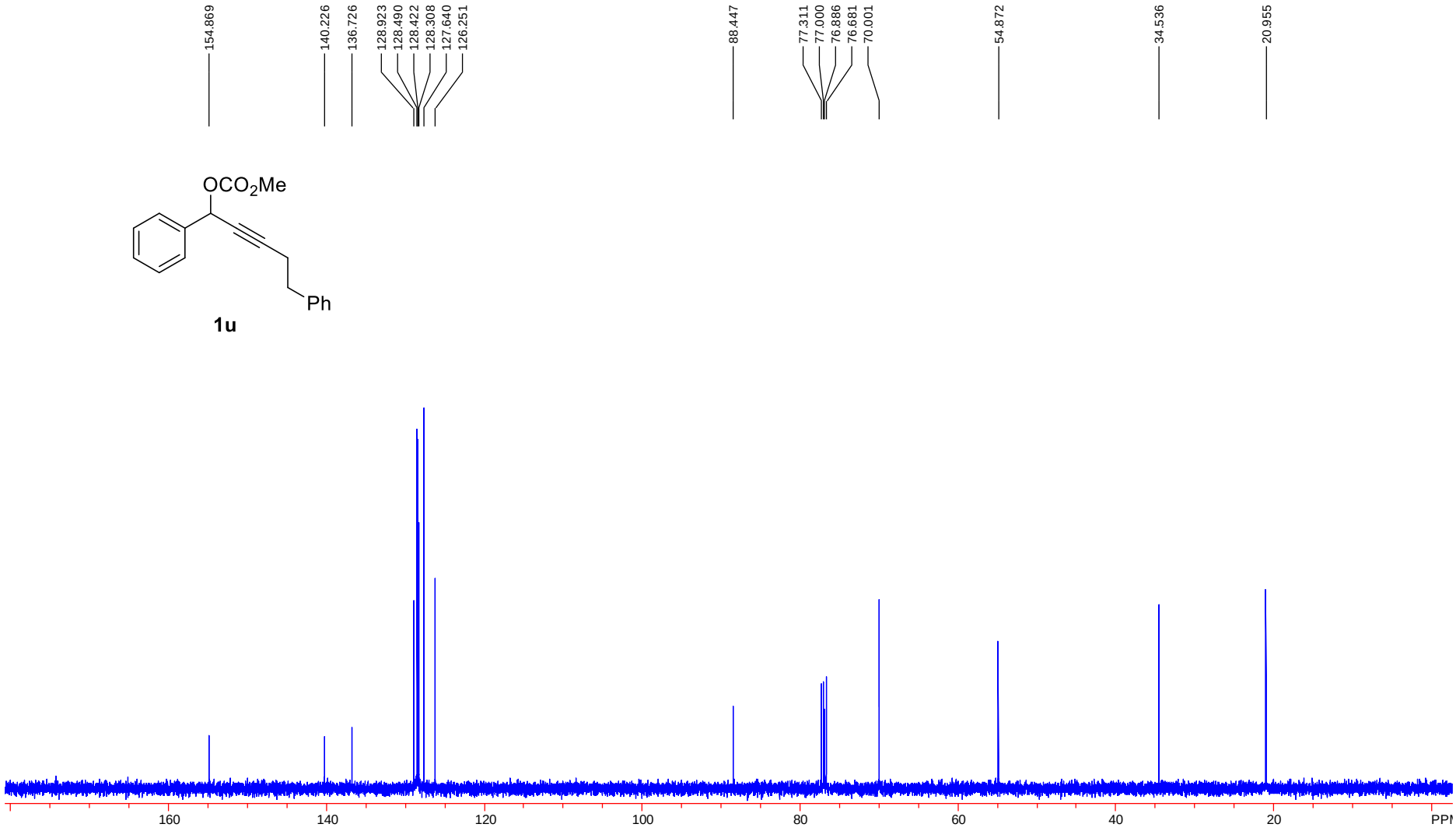
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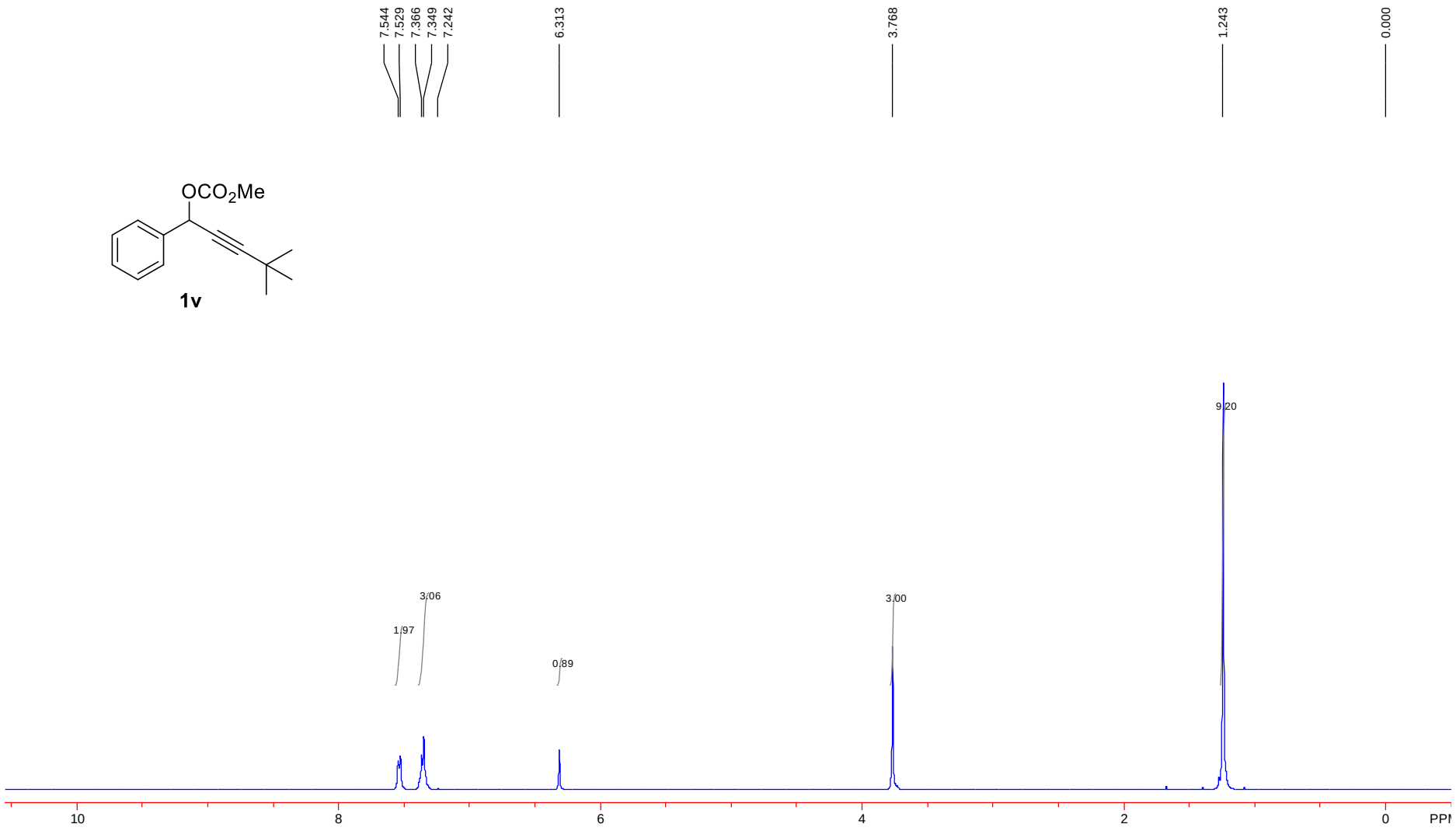
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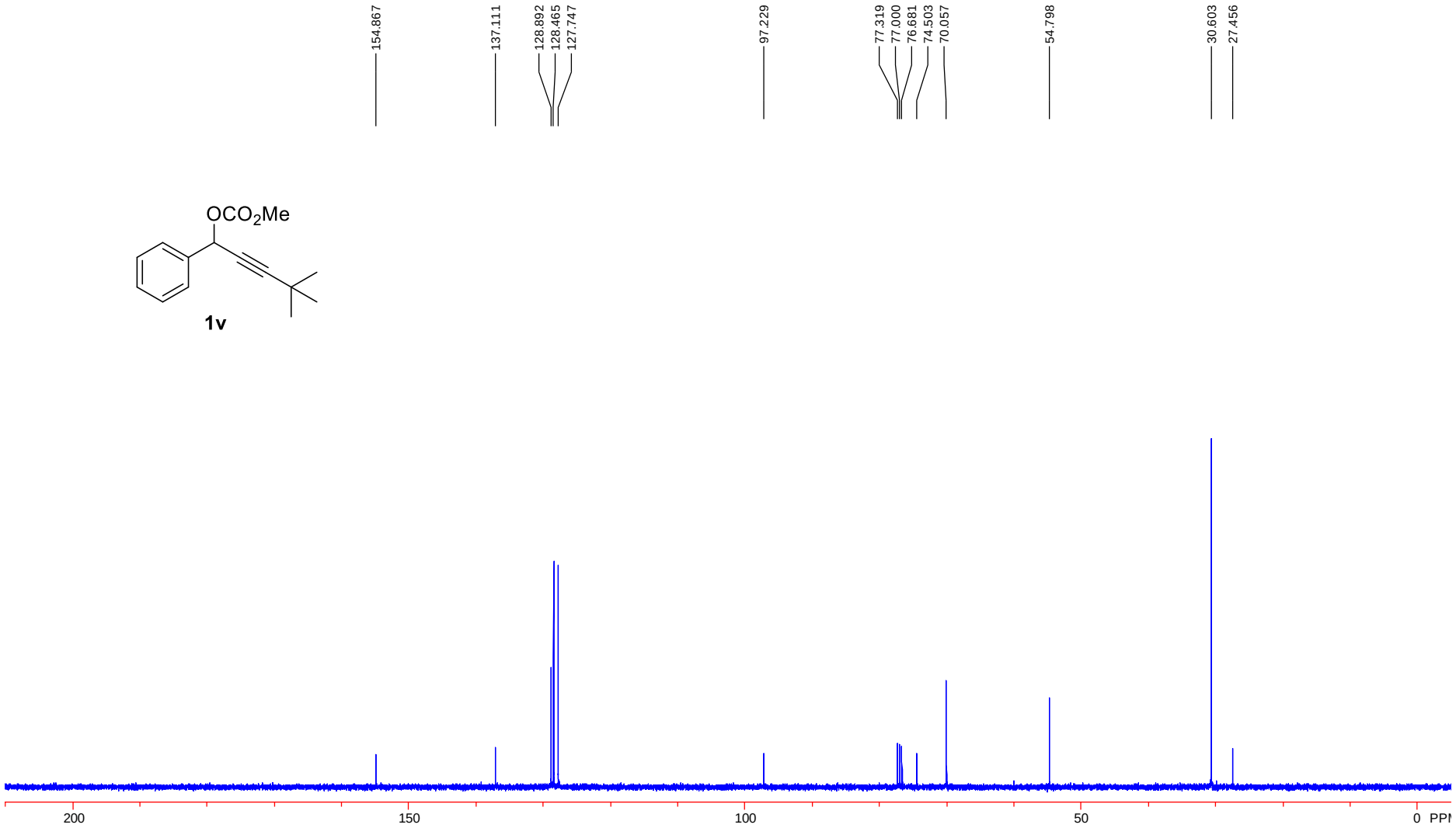
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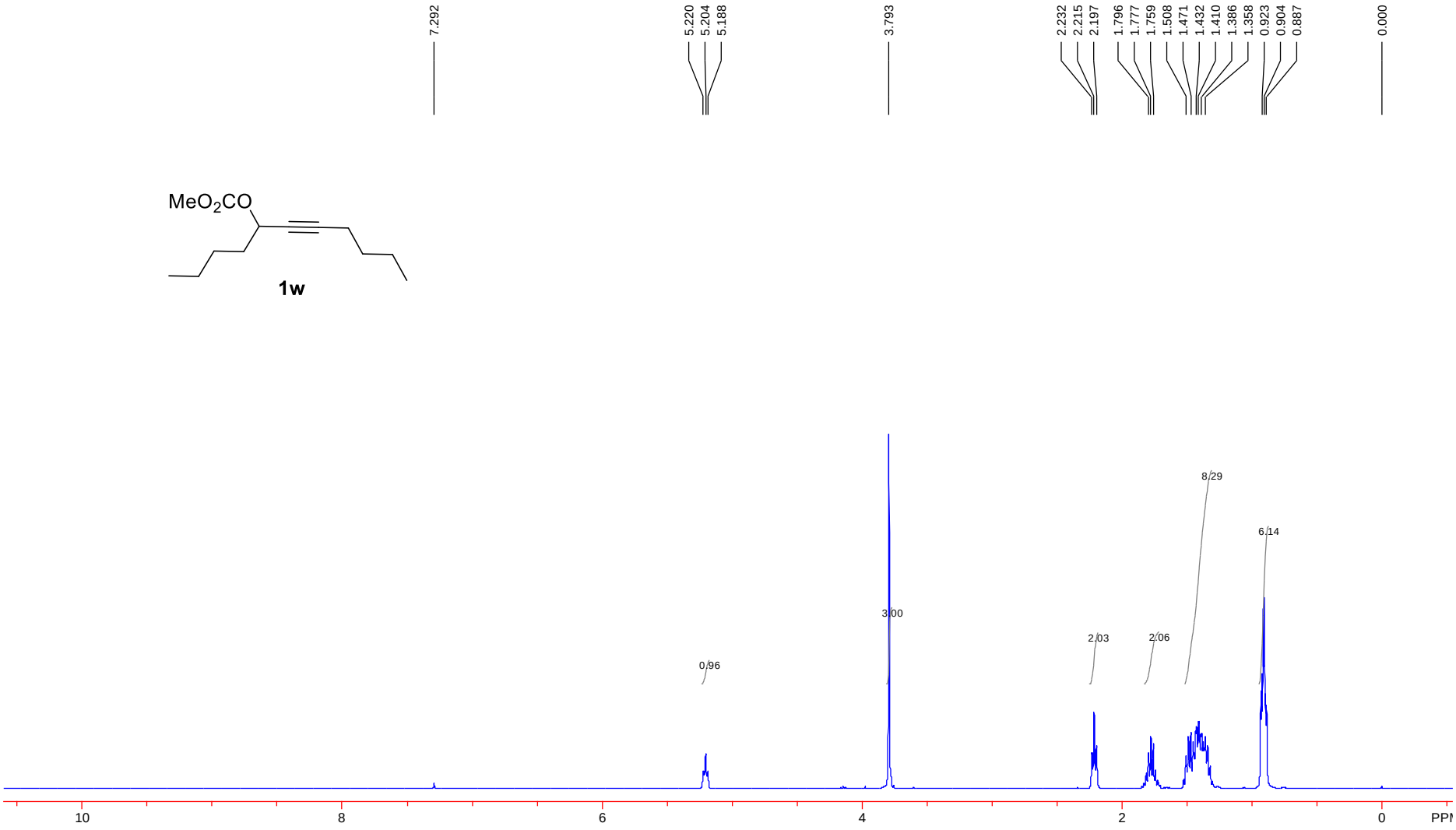
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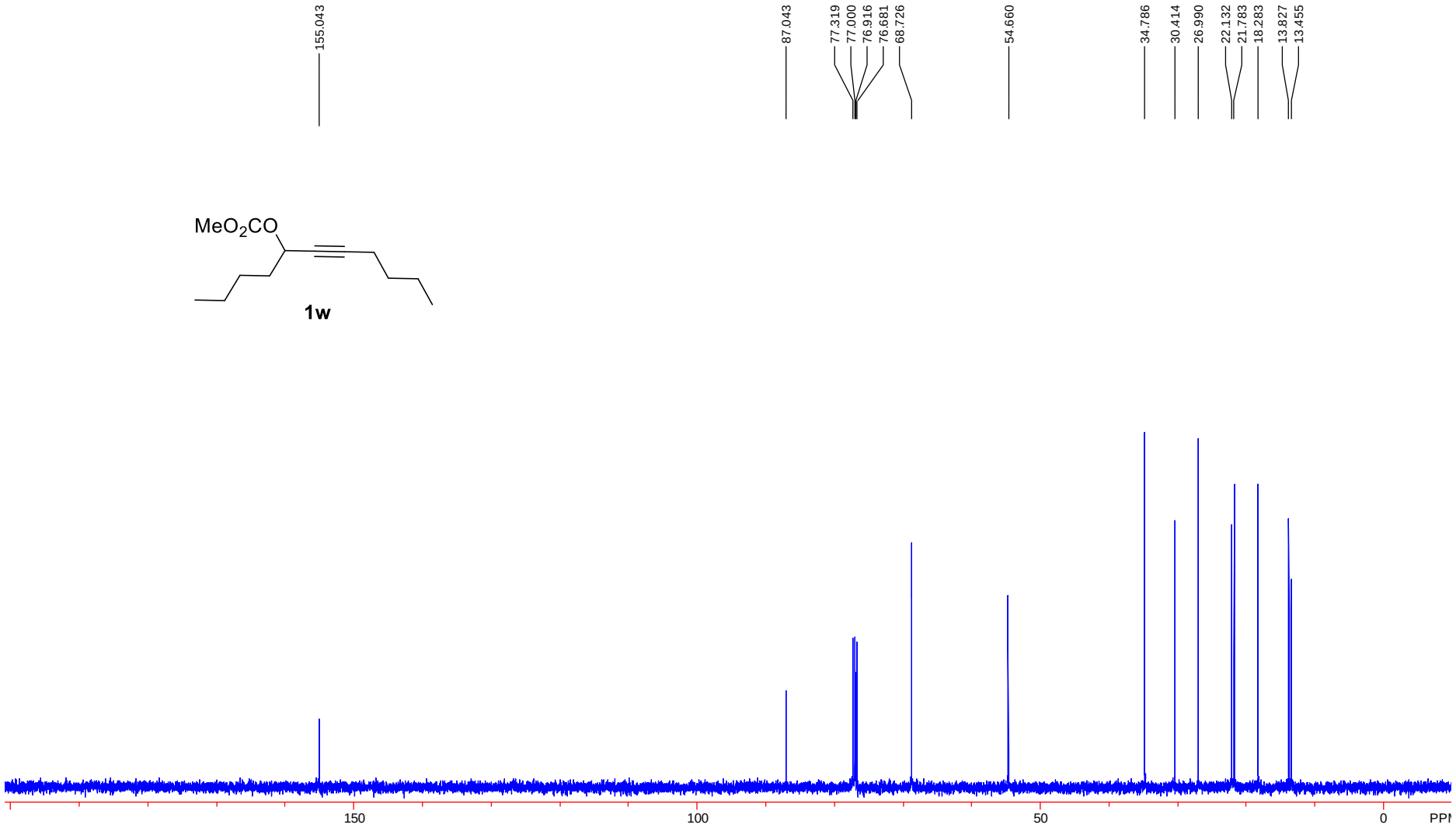
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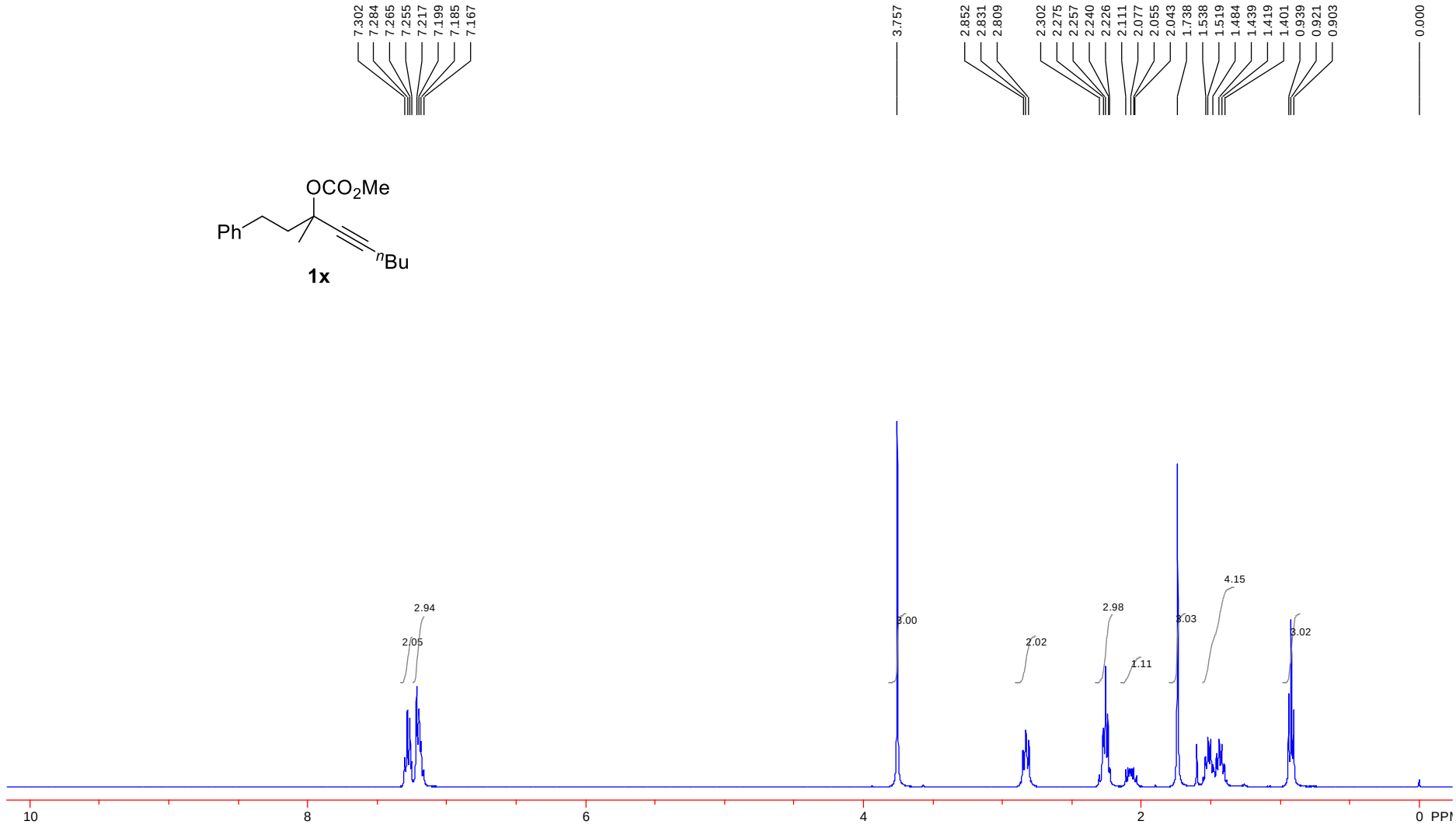
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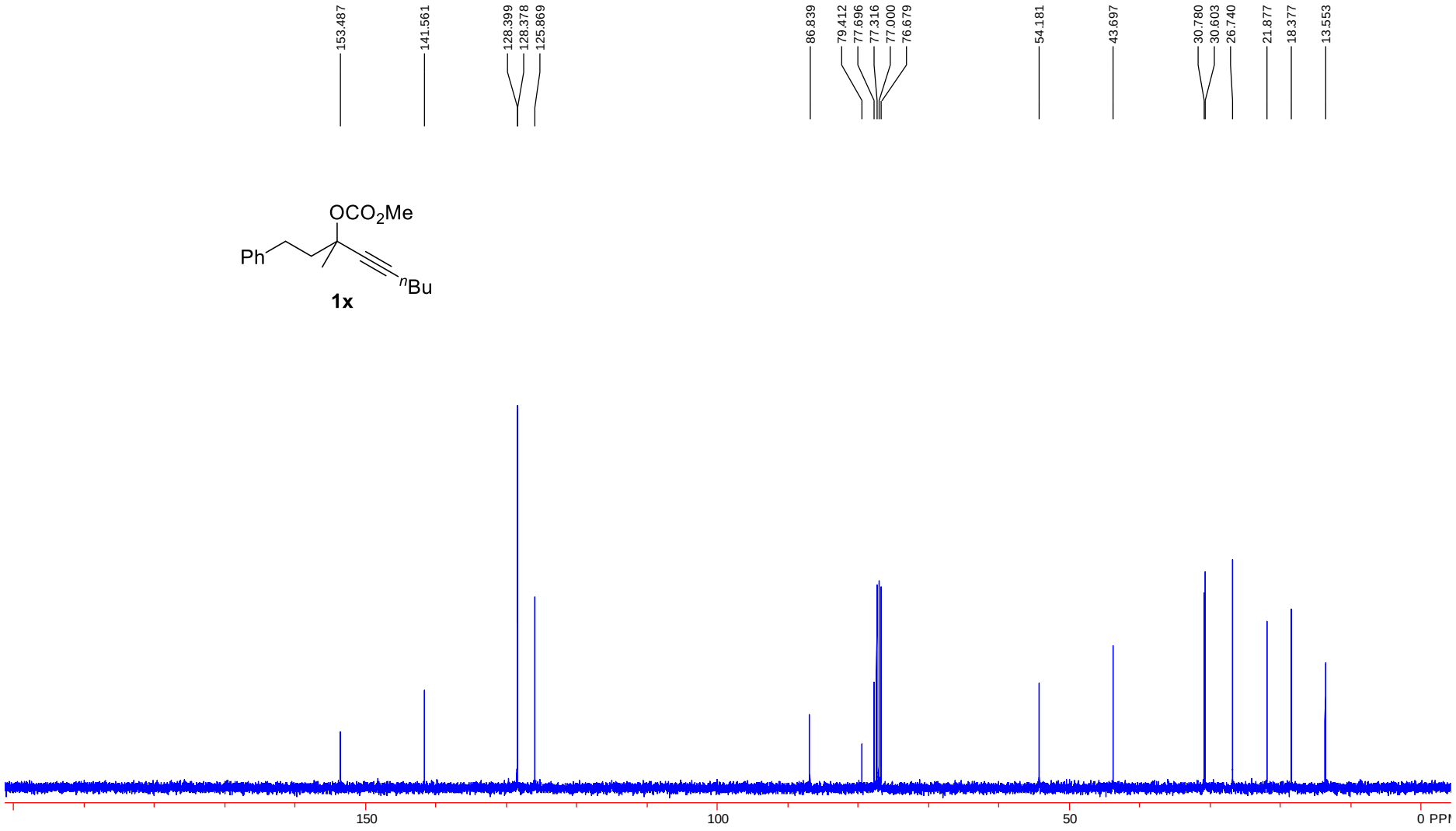
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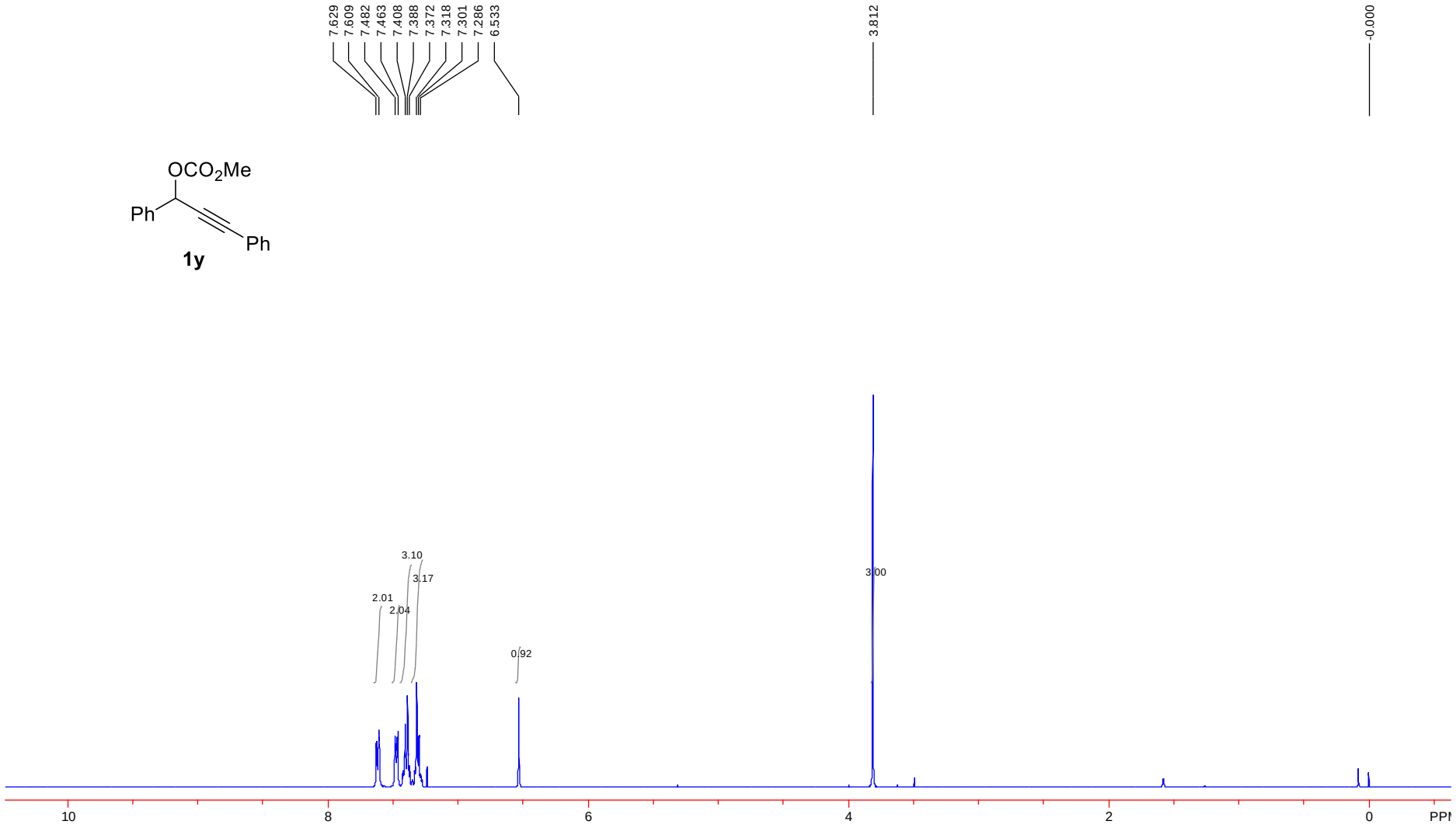
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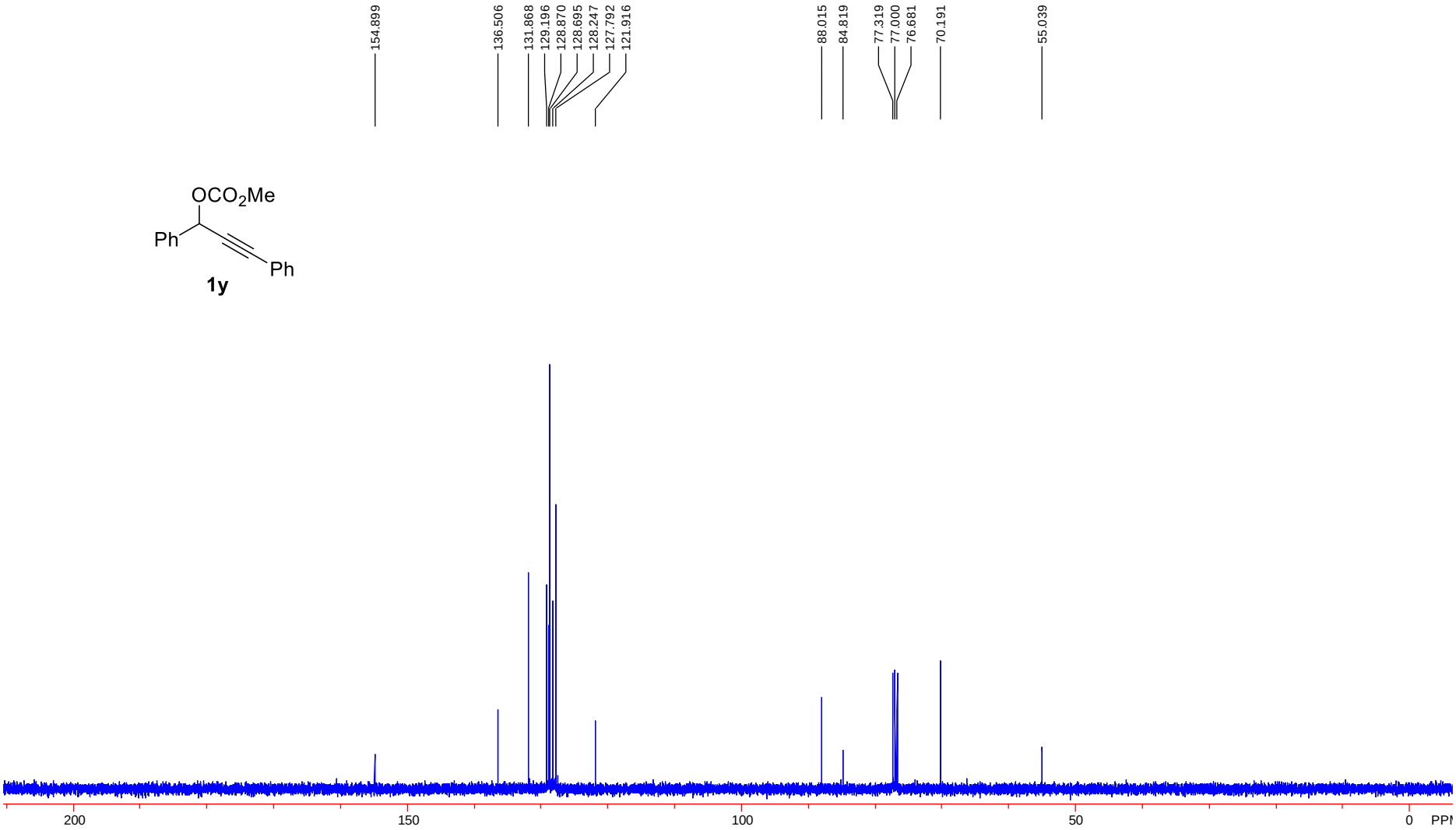
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Ph
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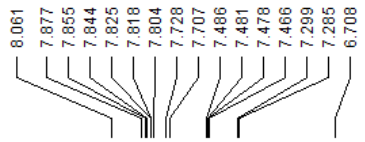
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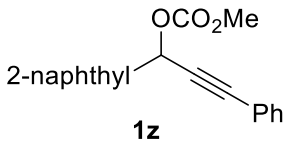
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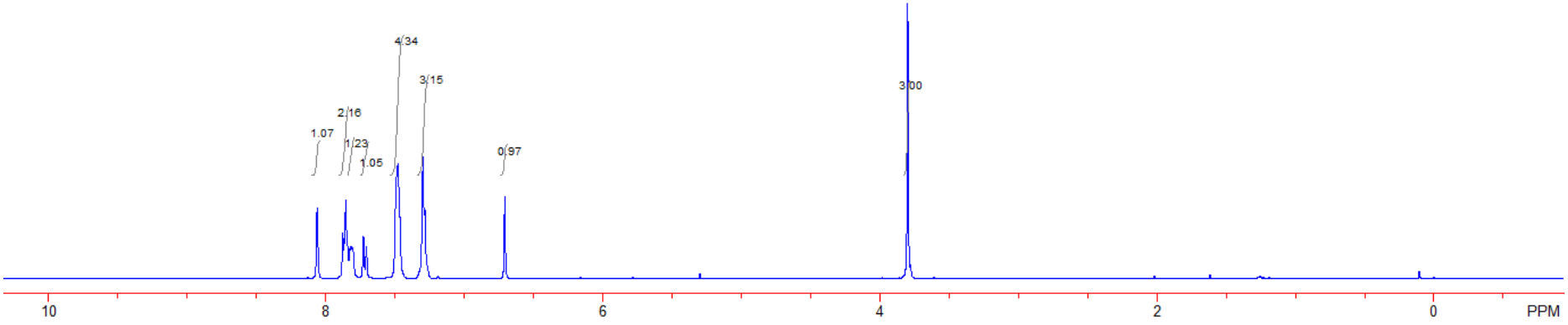
Ph

1z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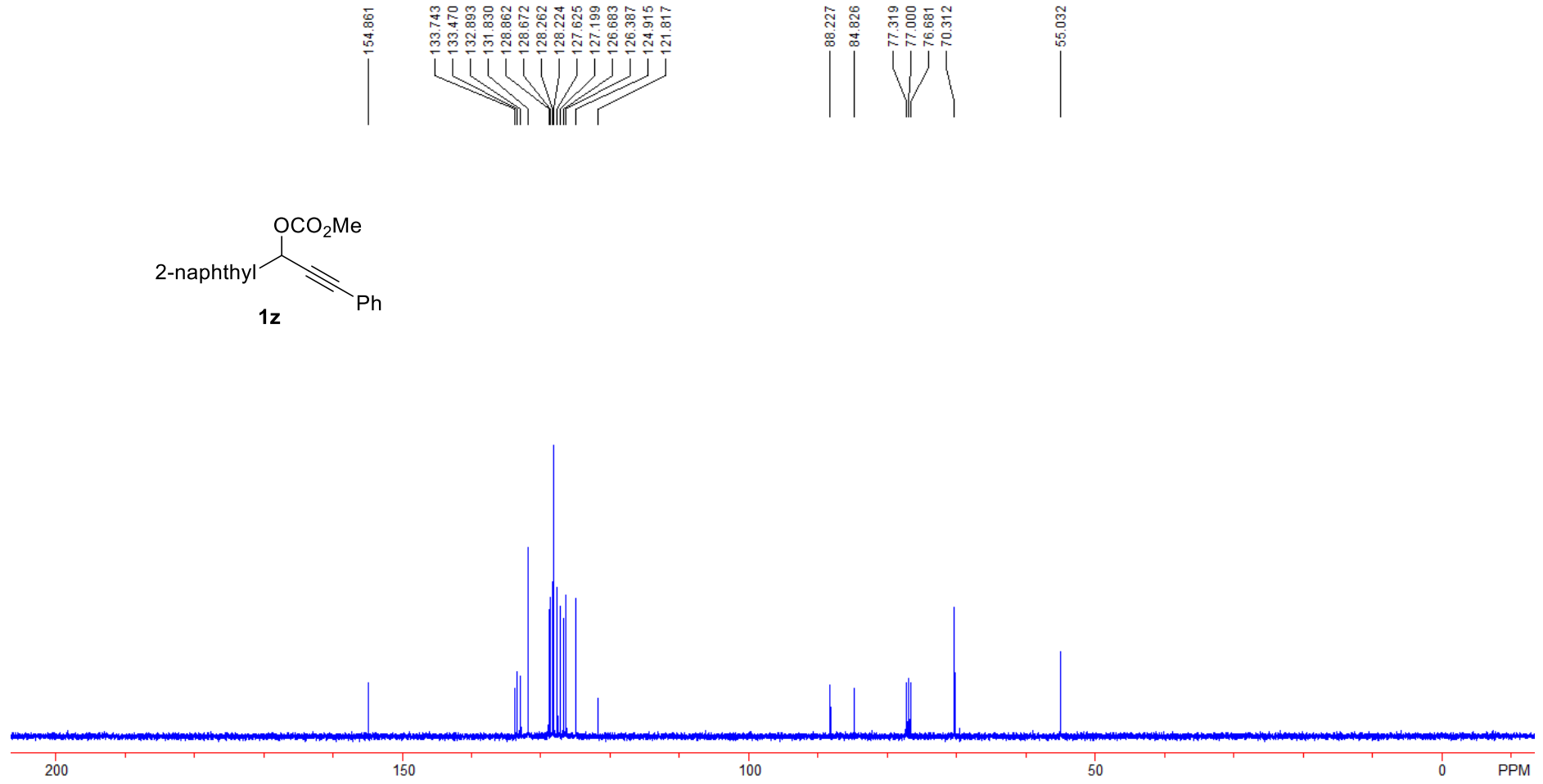
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Ph
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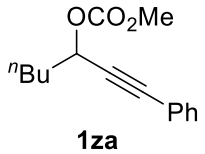
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nBu
Ph

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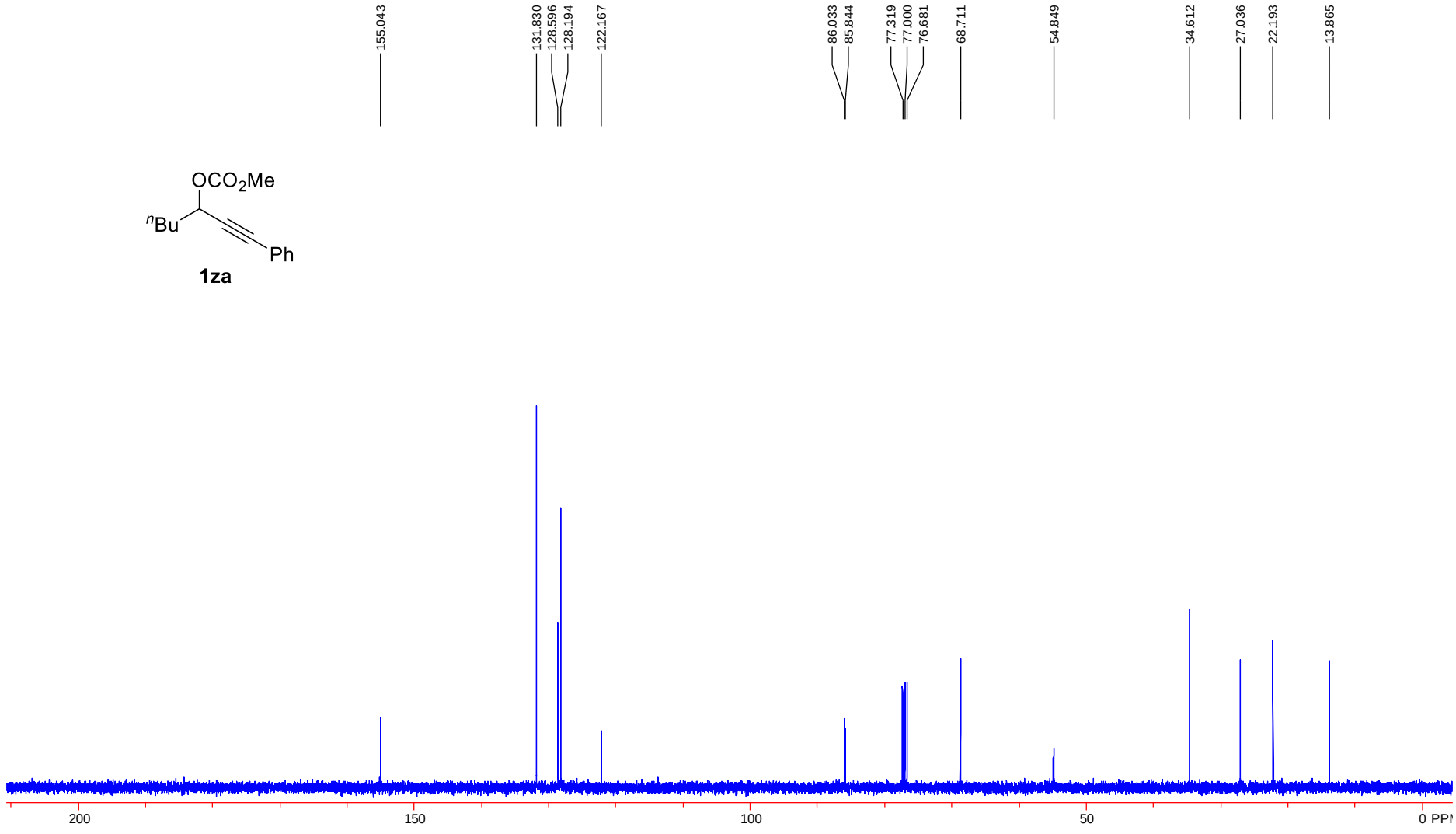
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Ph
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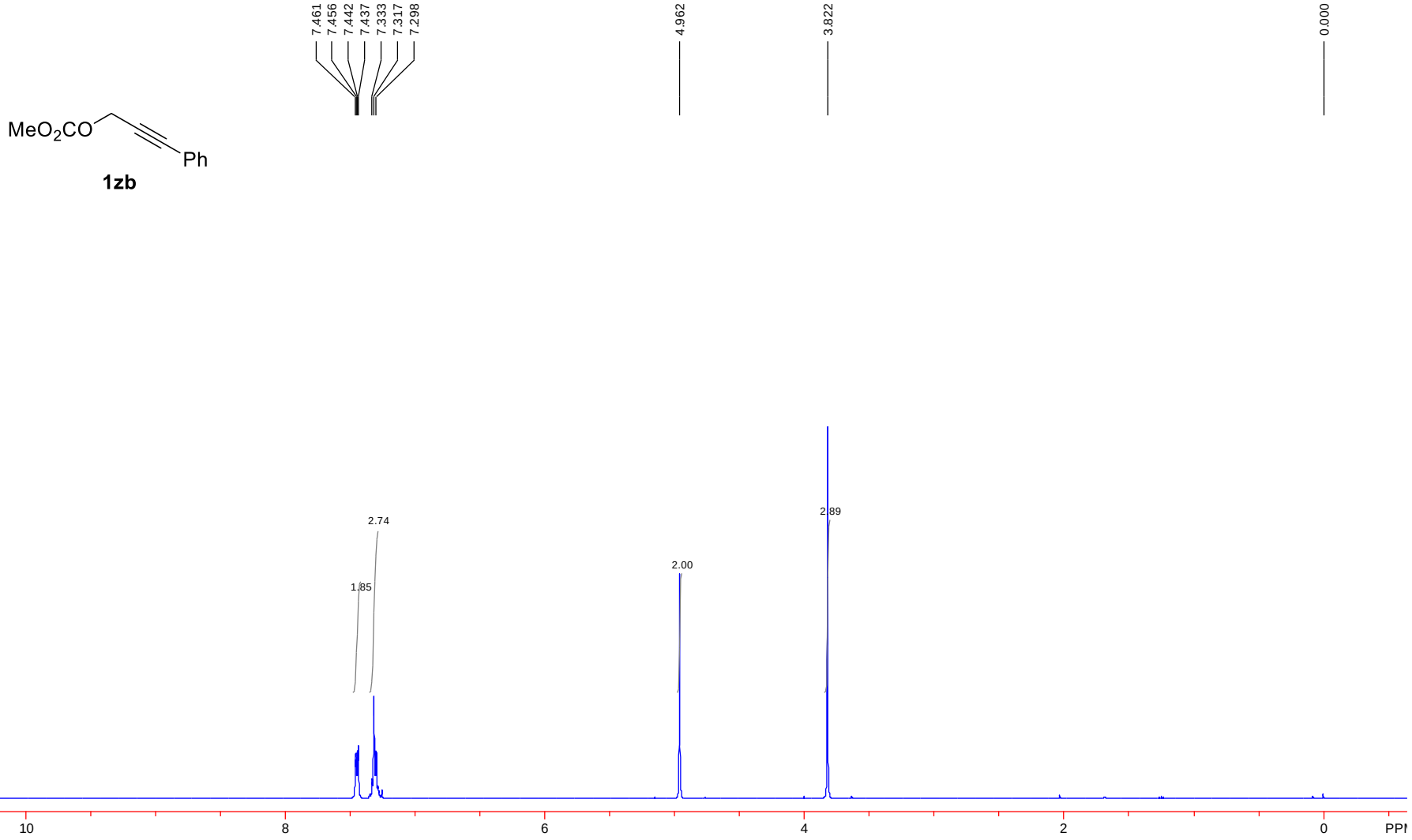
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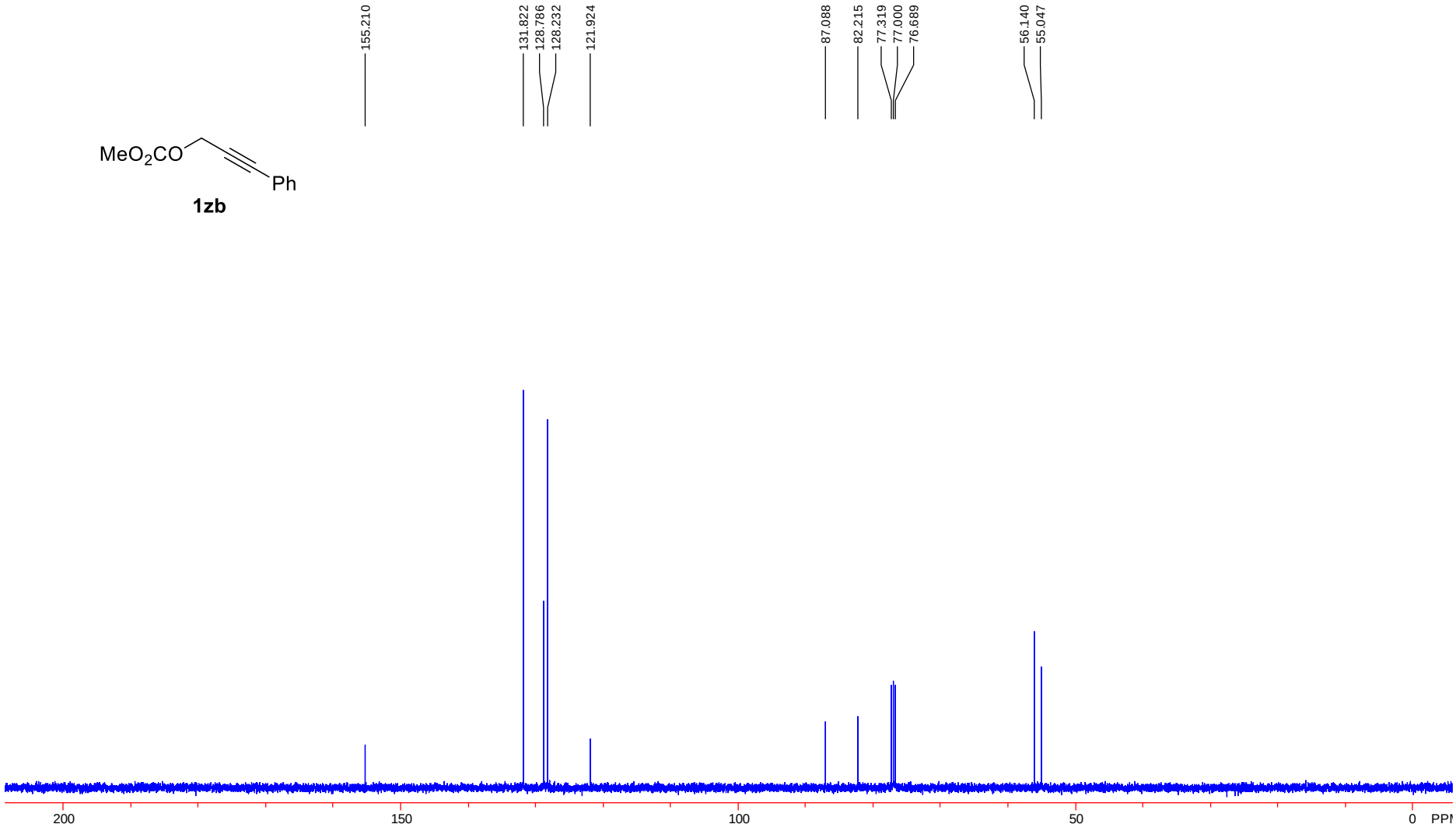
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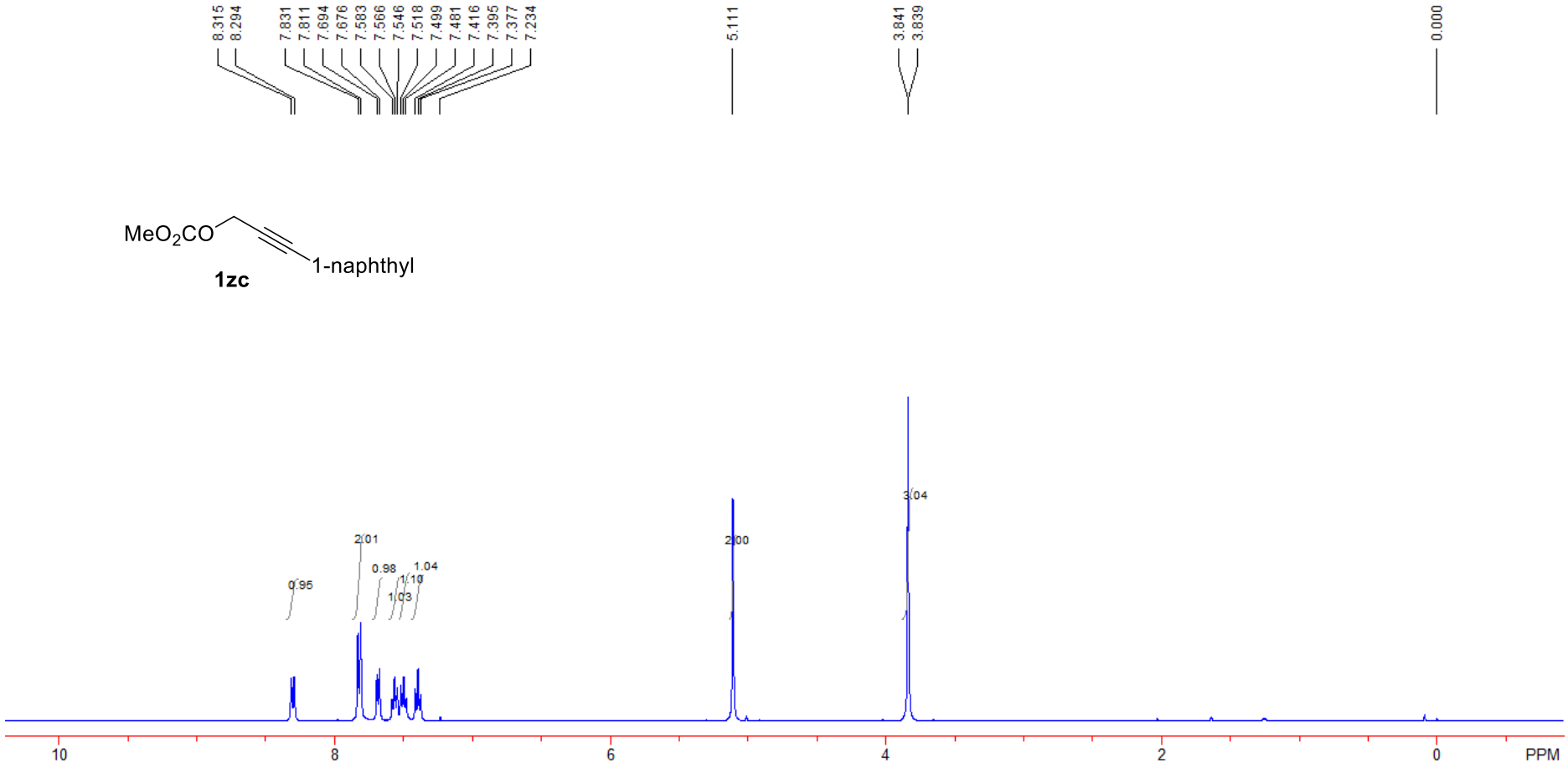
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7.395
7.377
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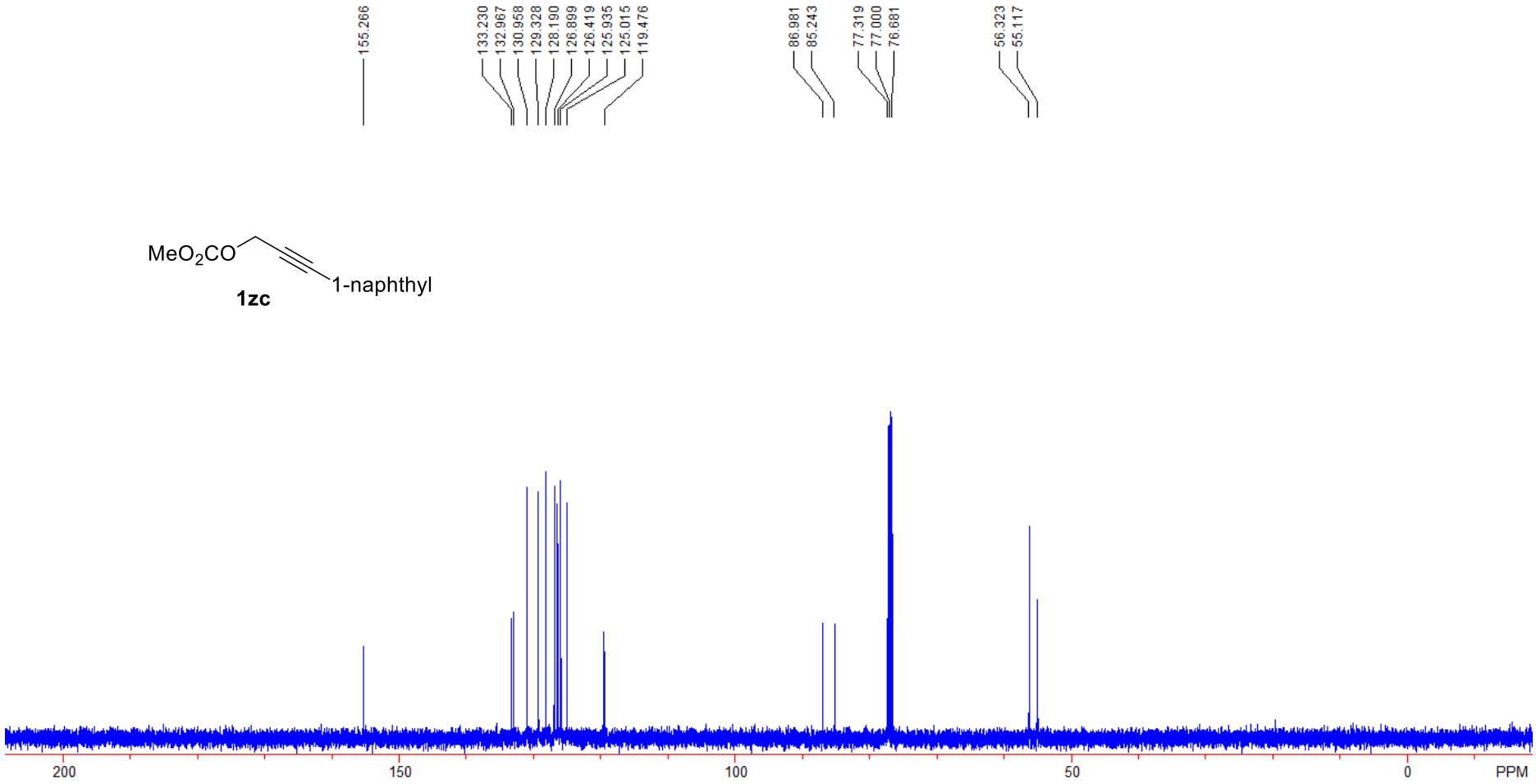
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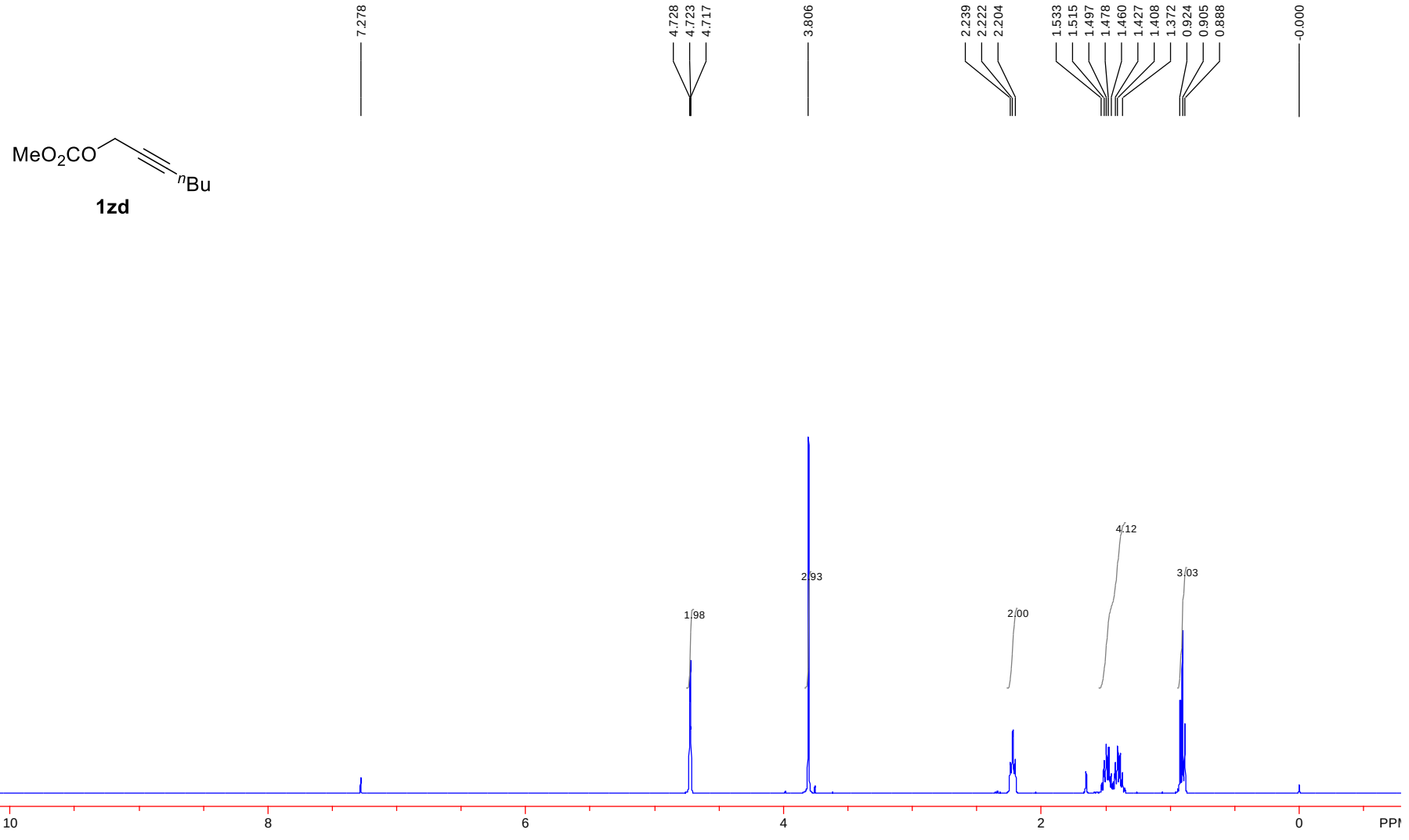
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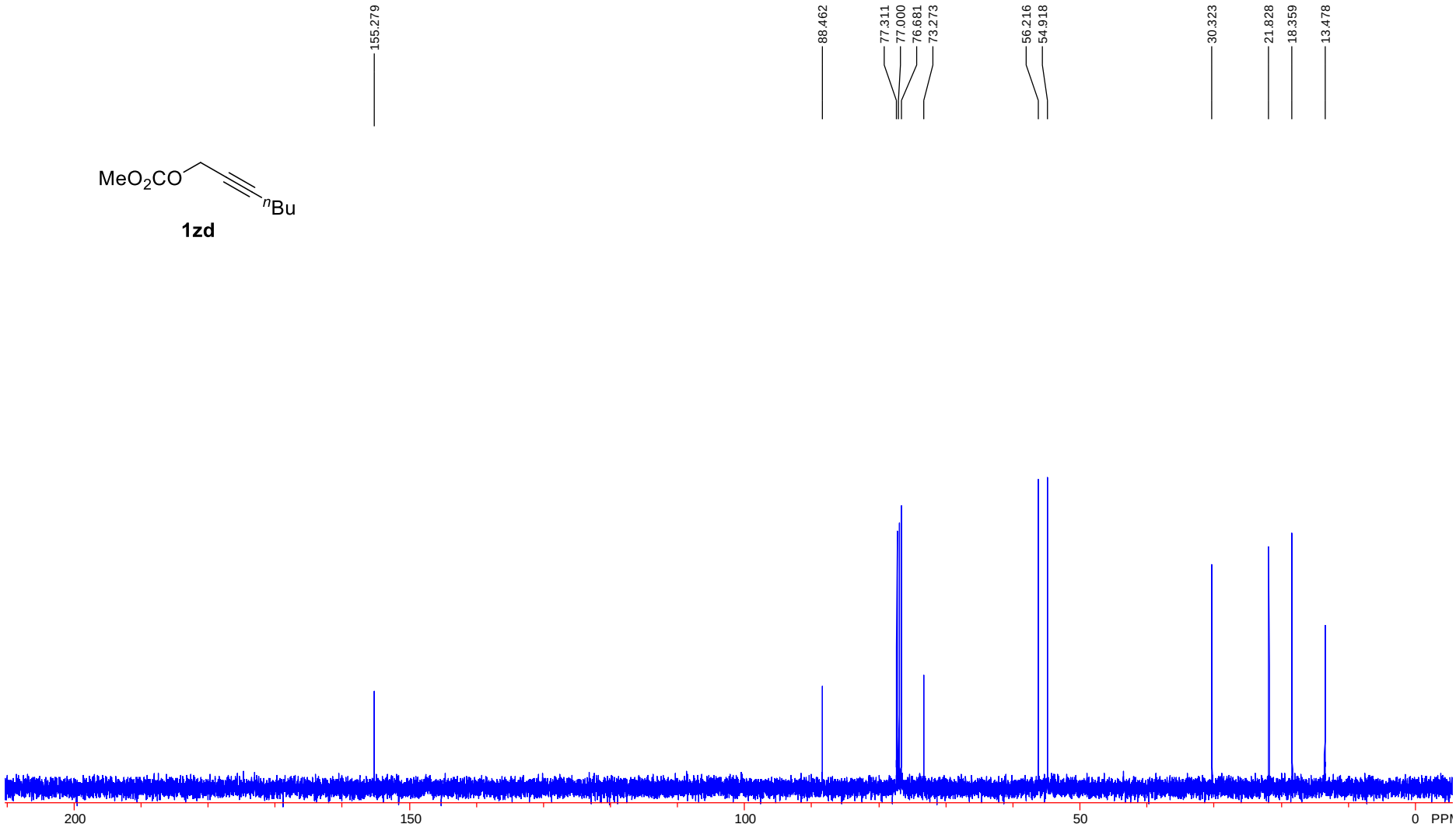
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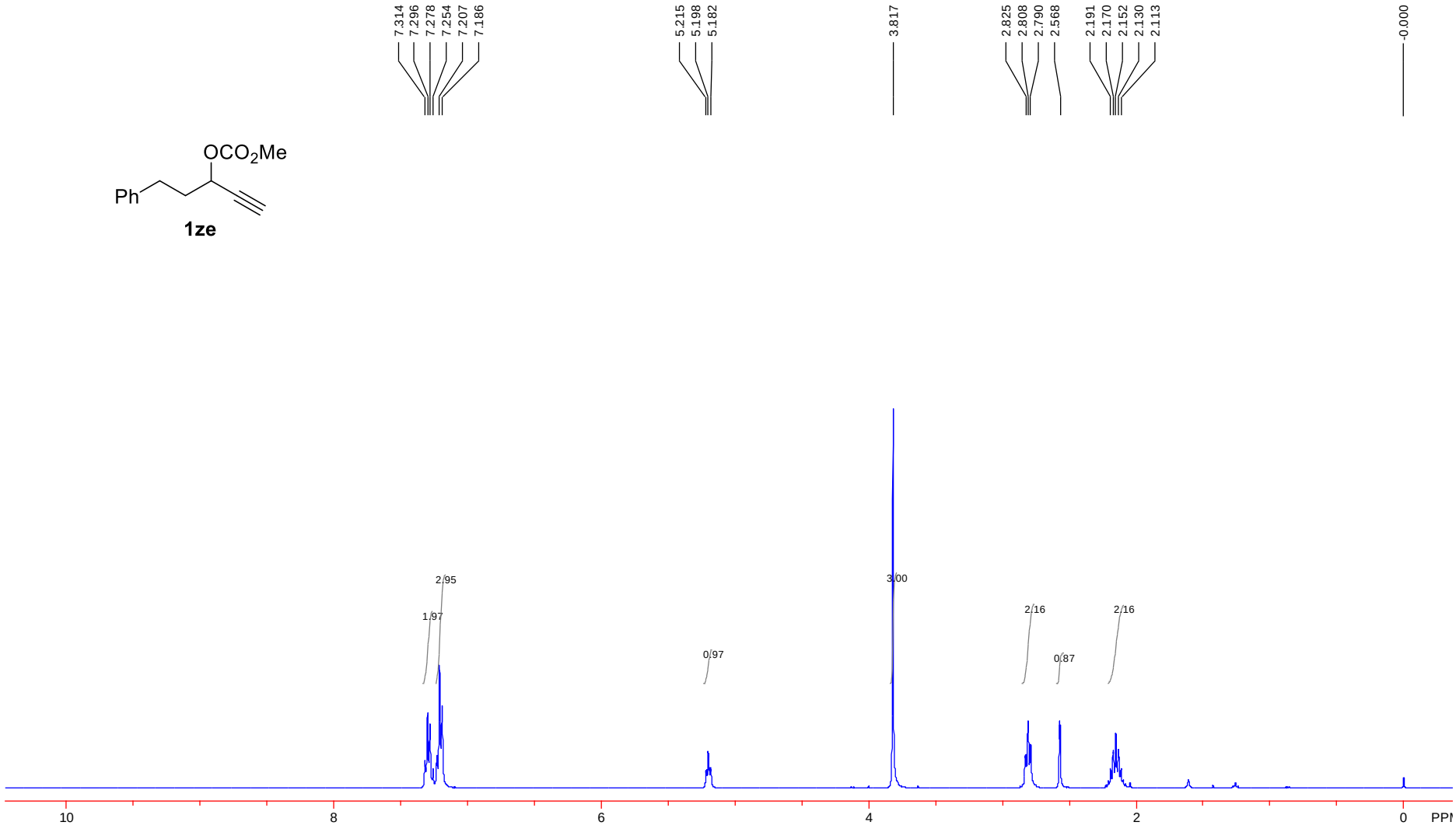
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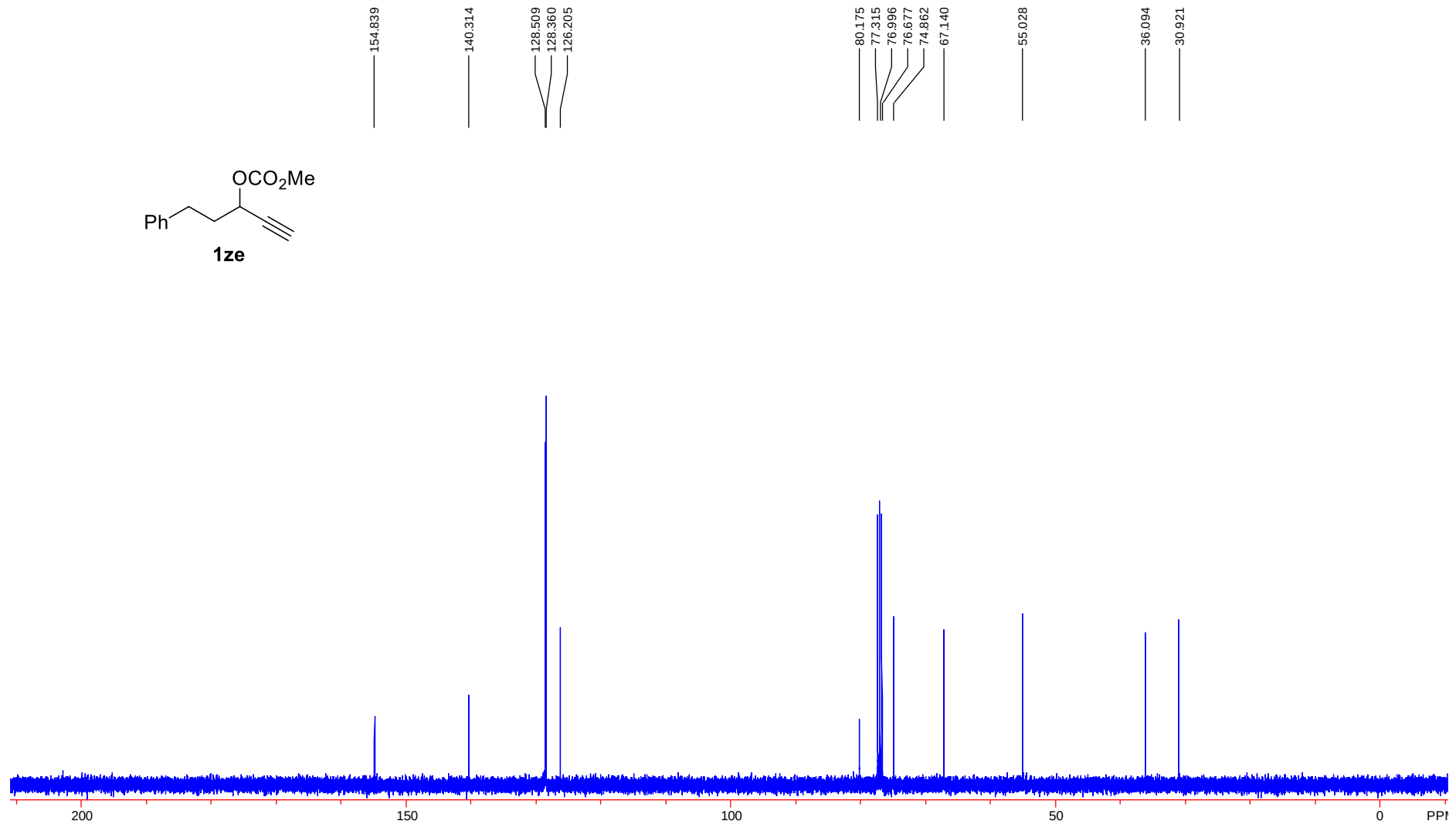
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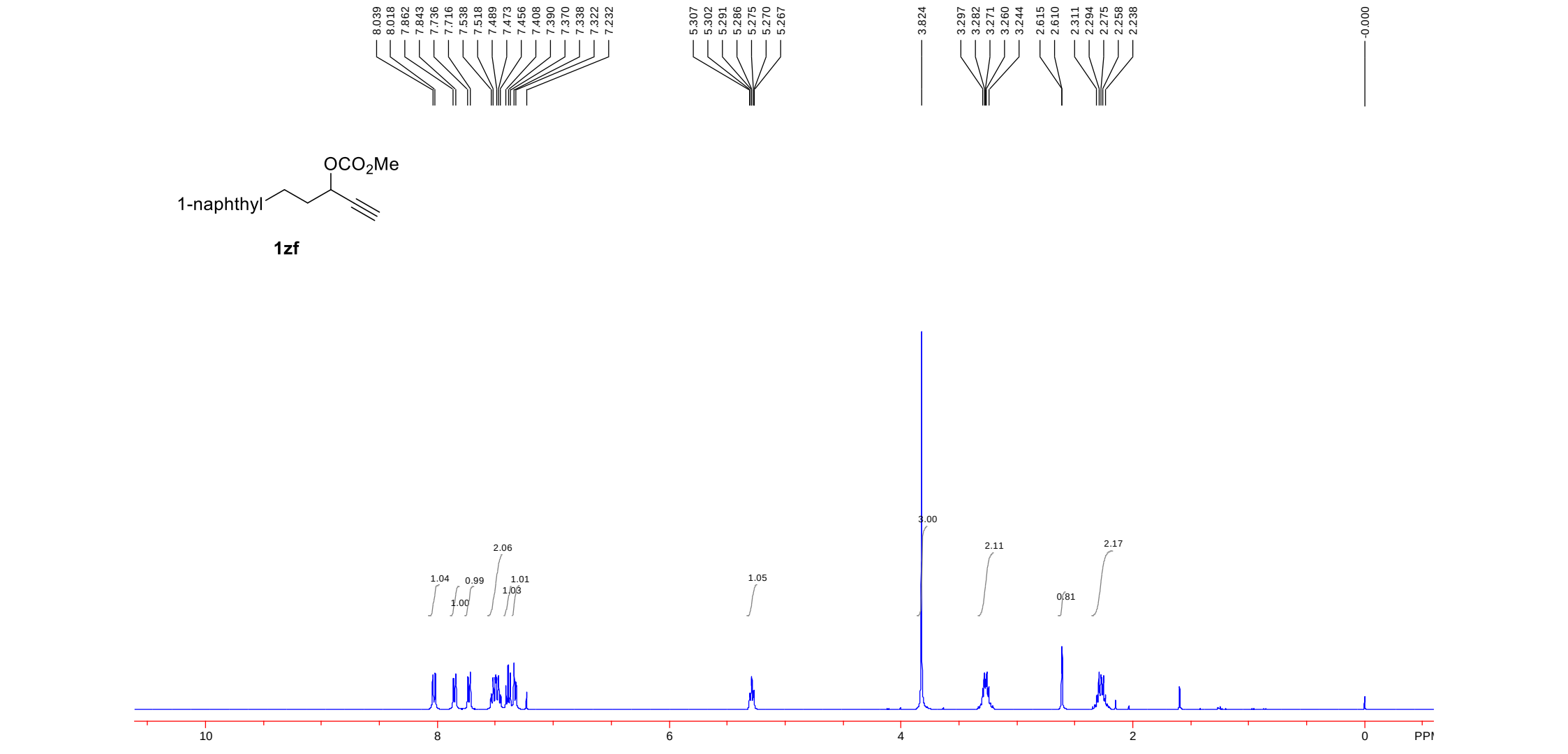
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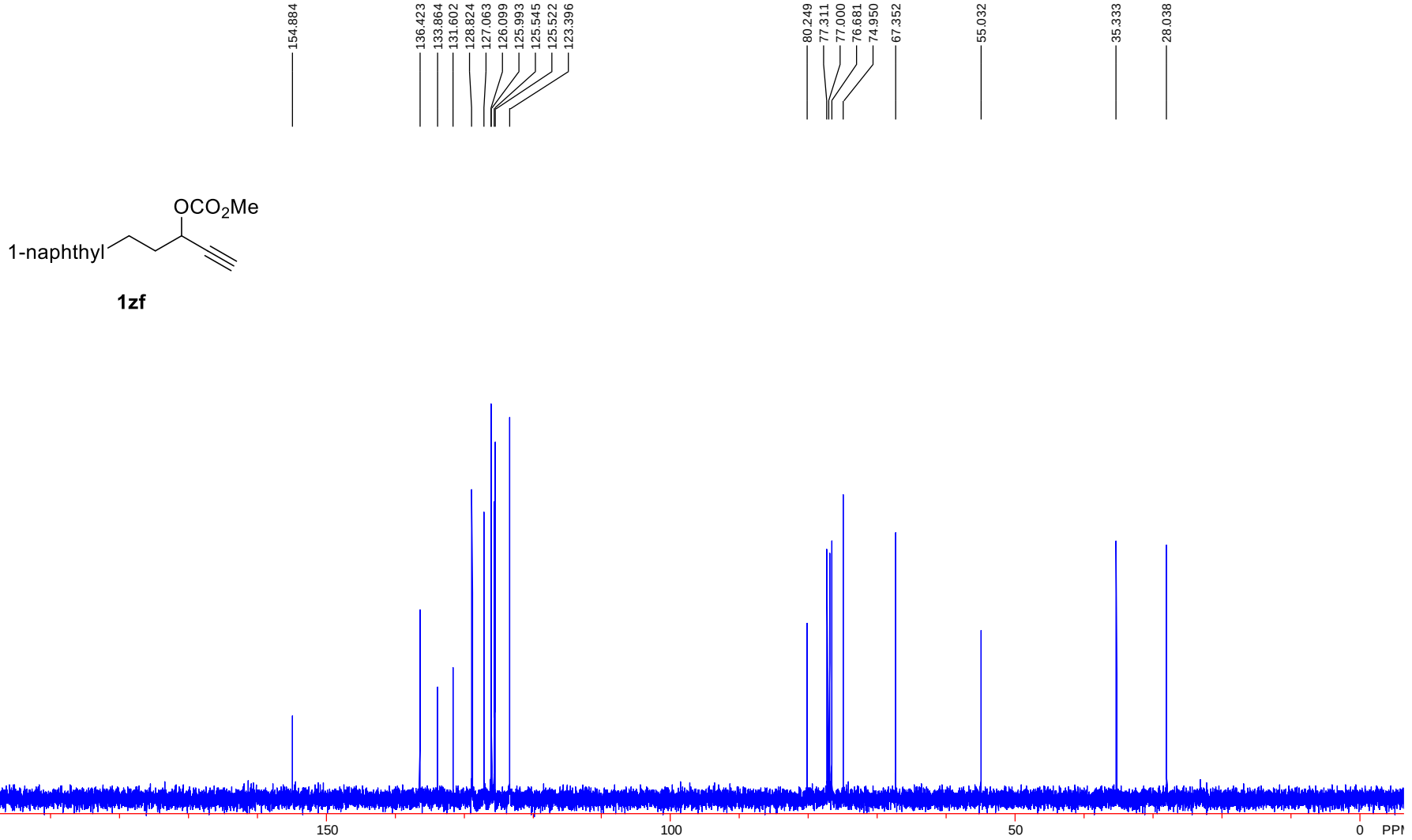
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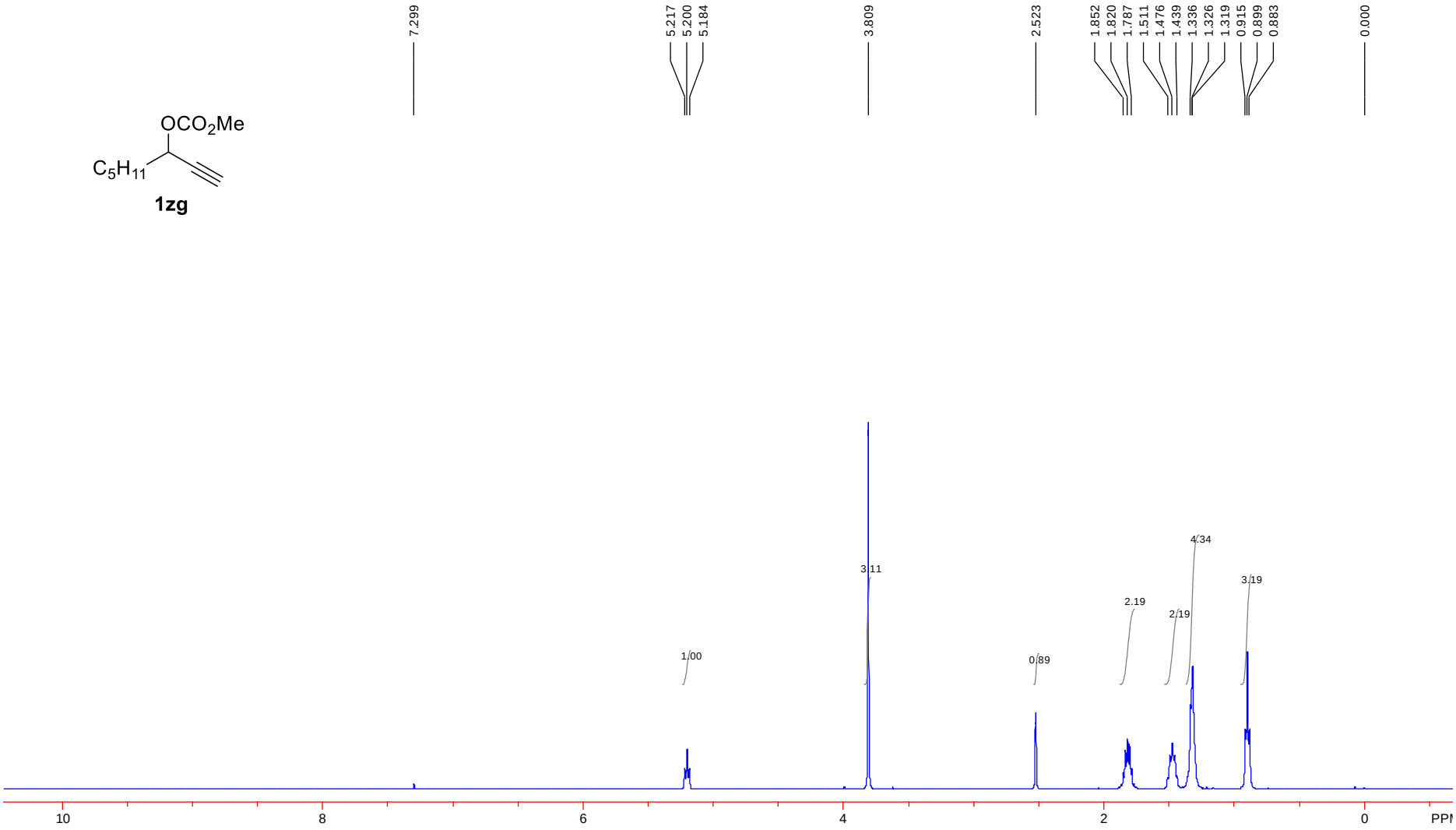
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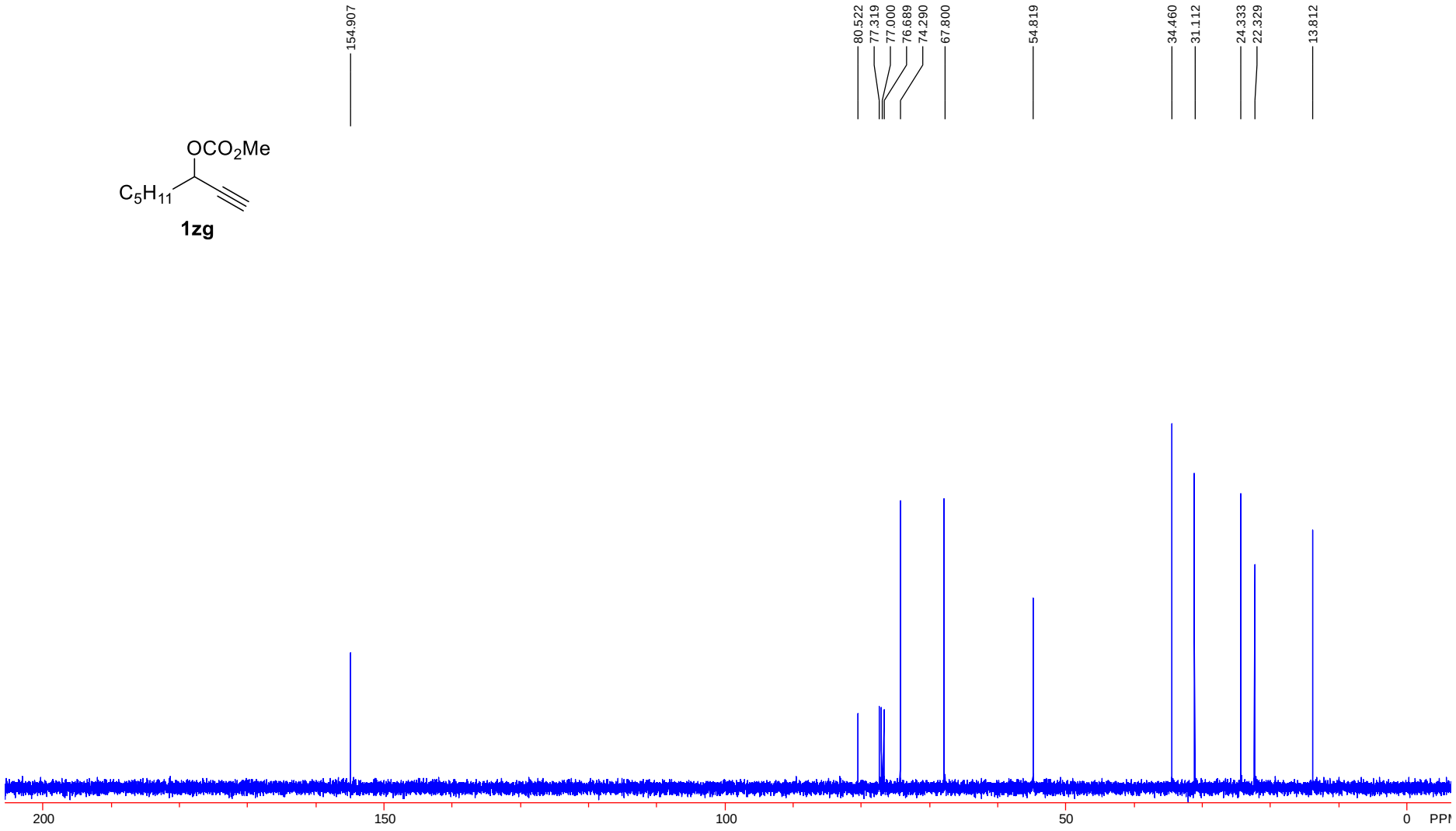
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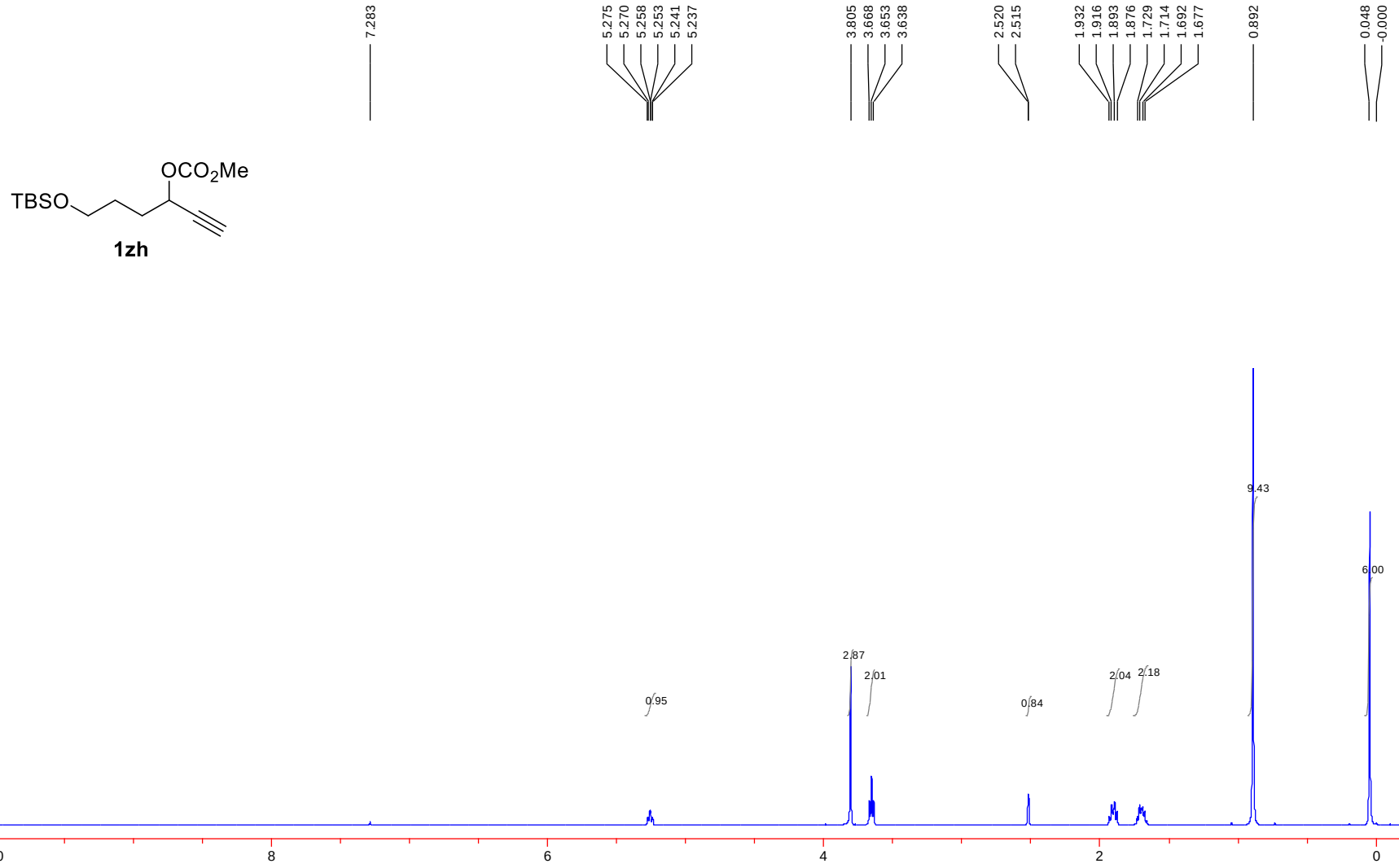
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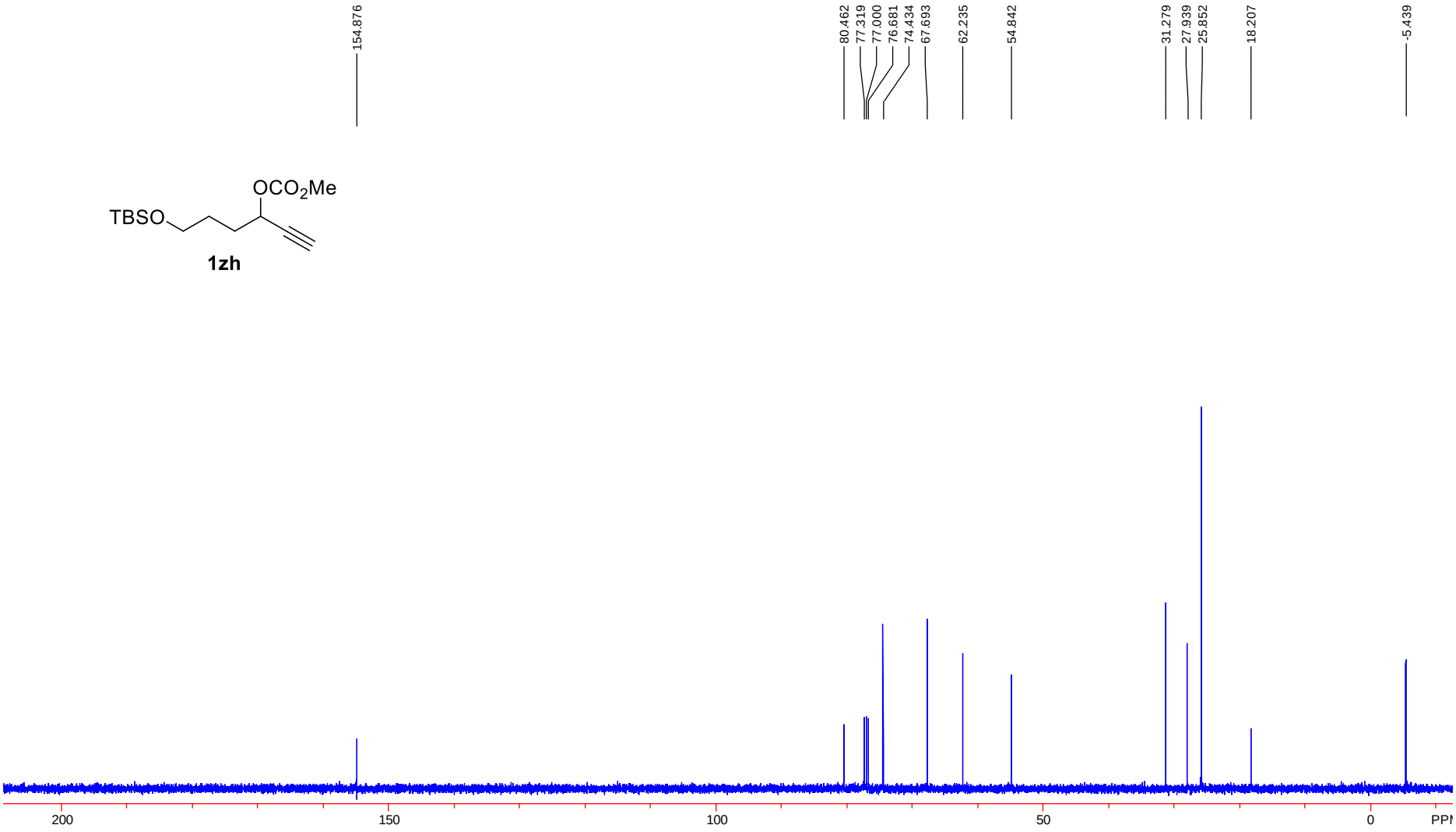
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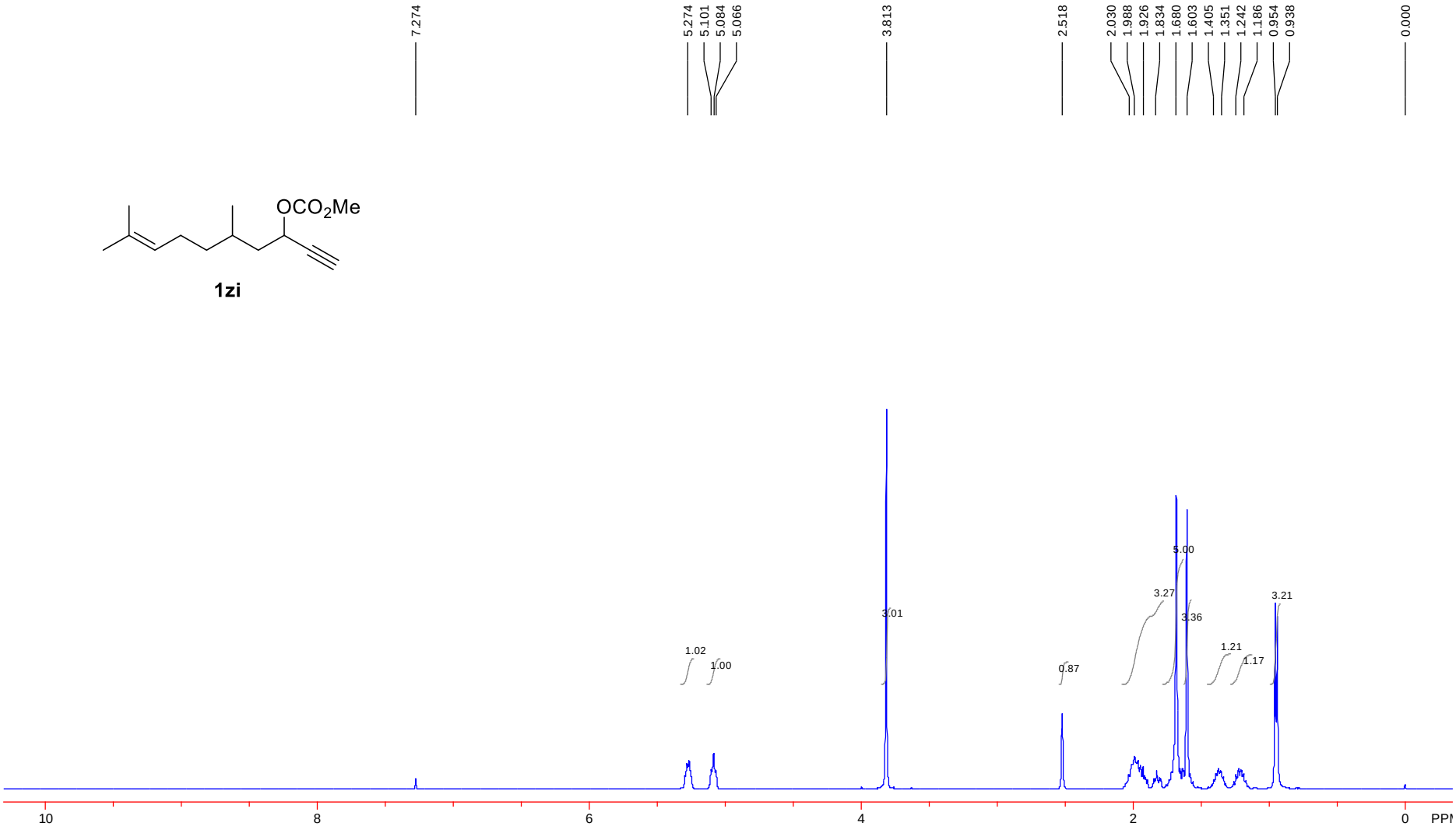
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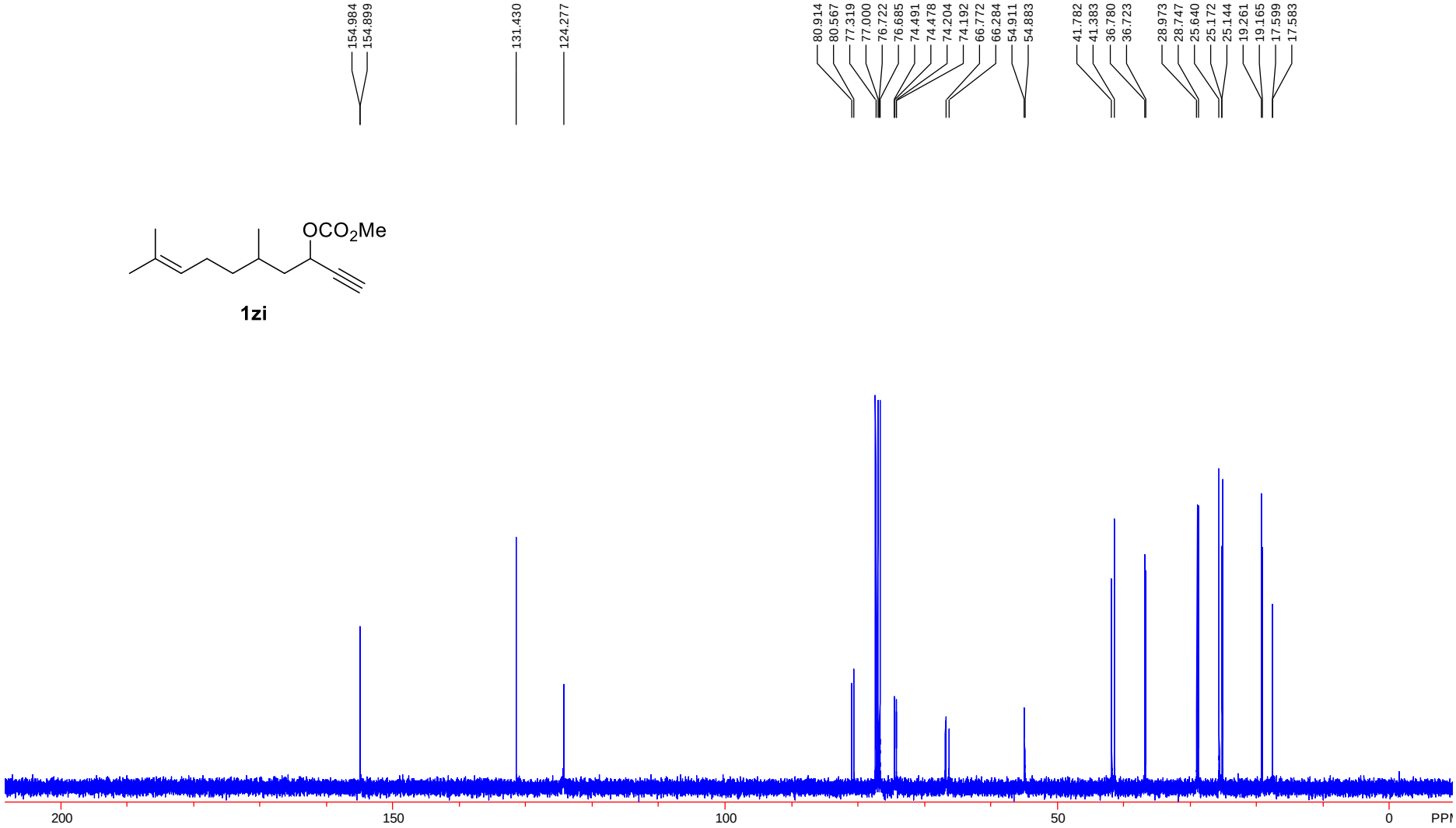
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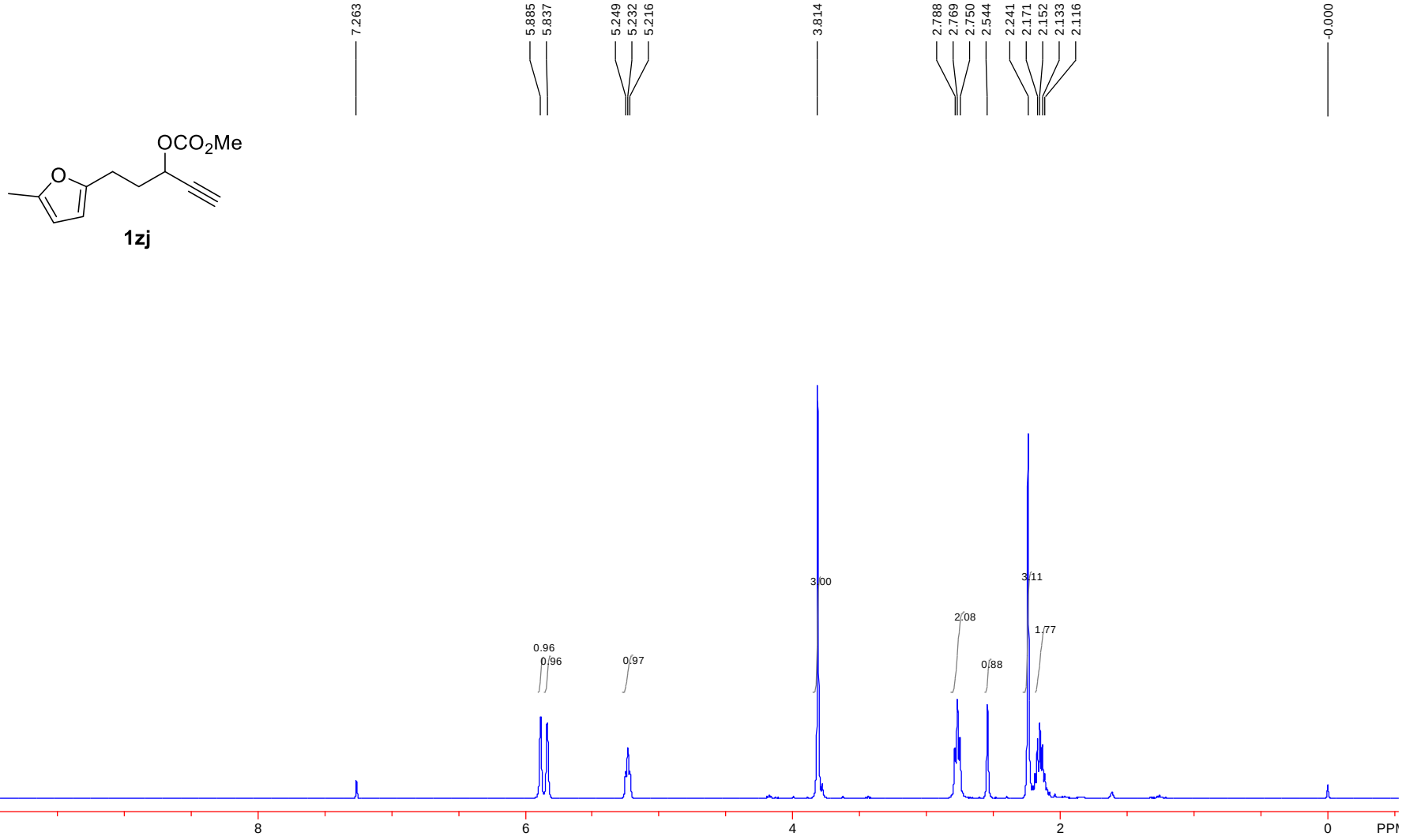
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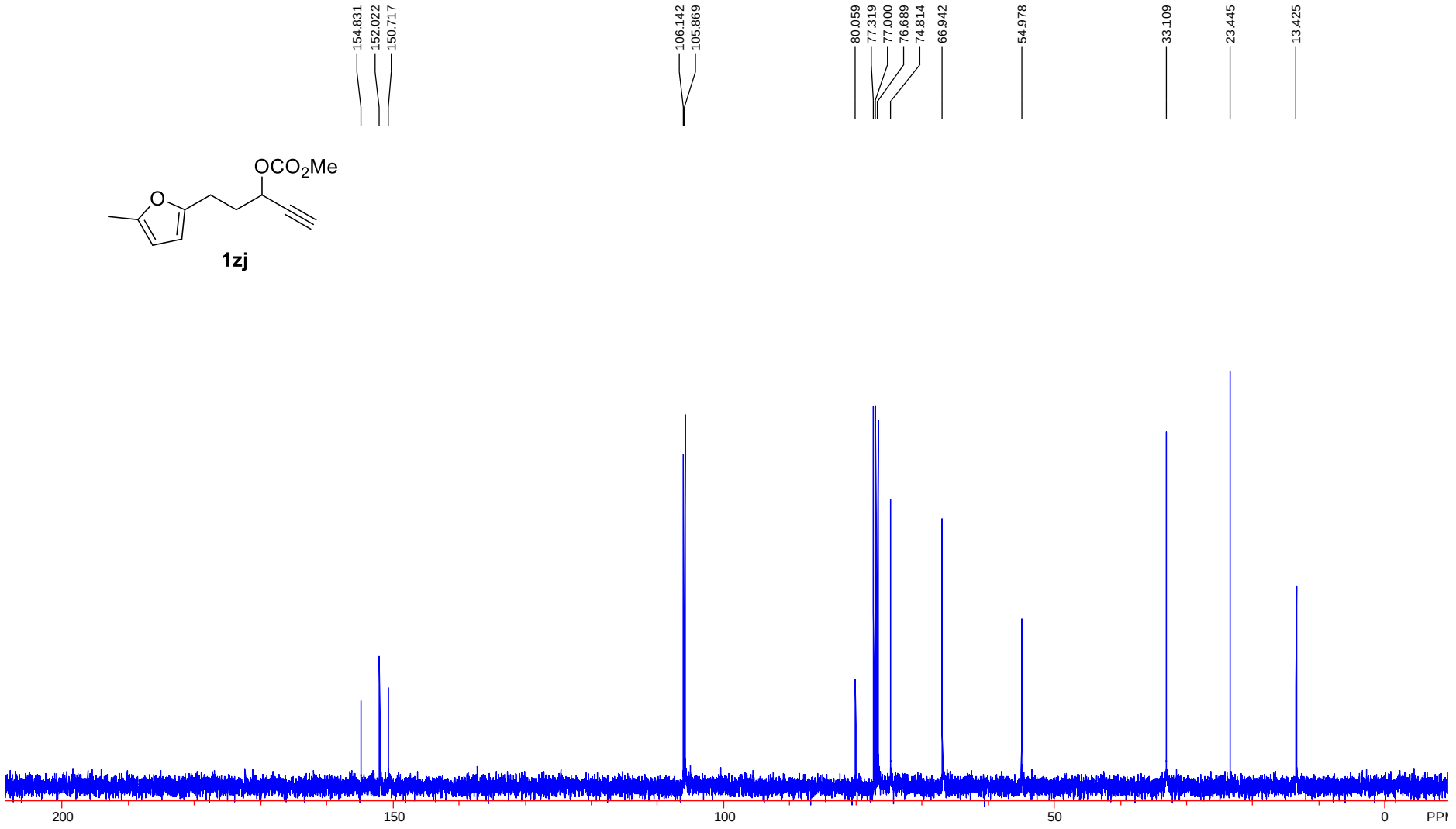
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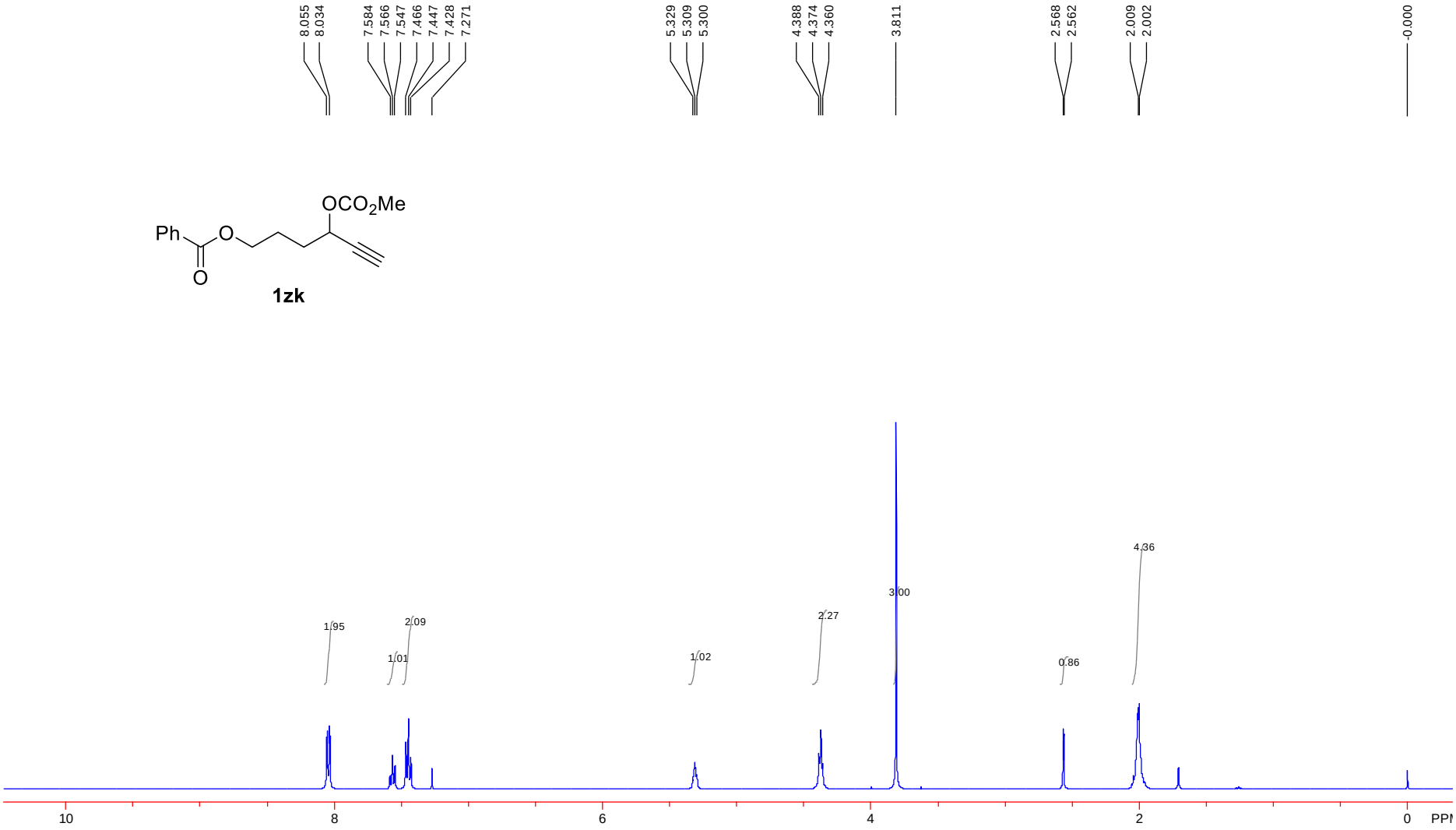
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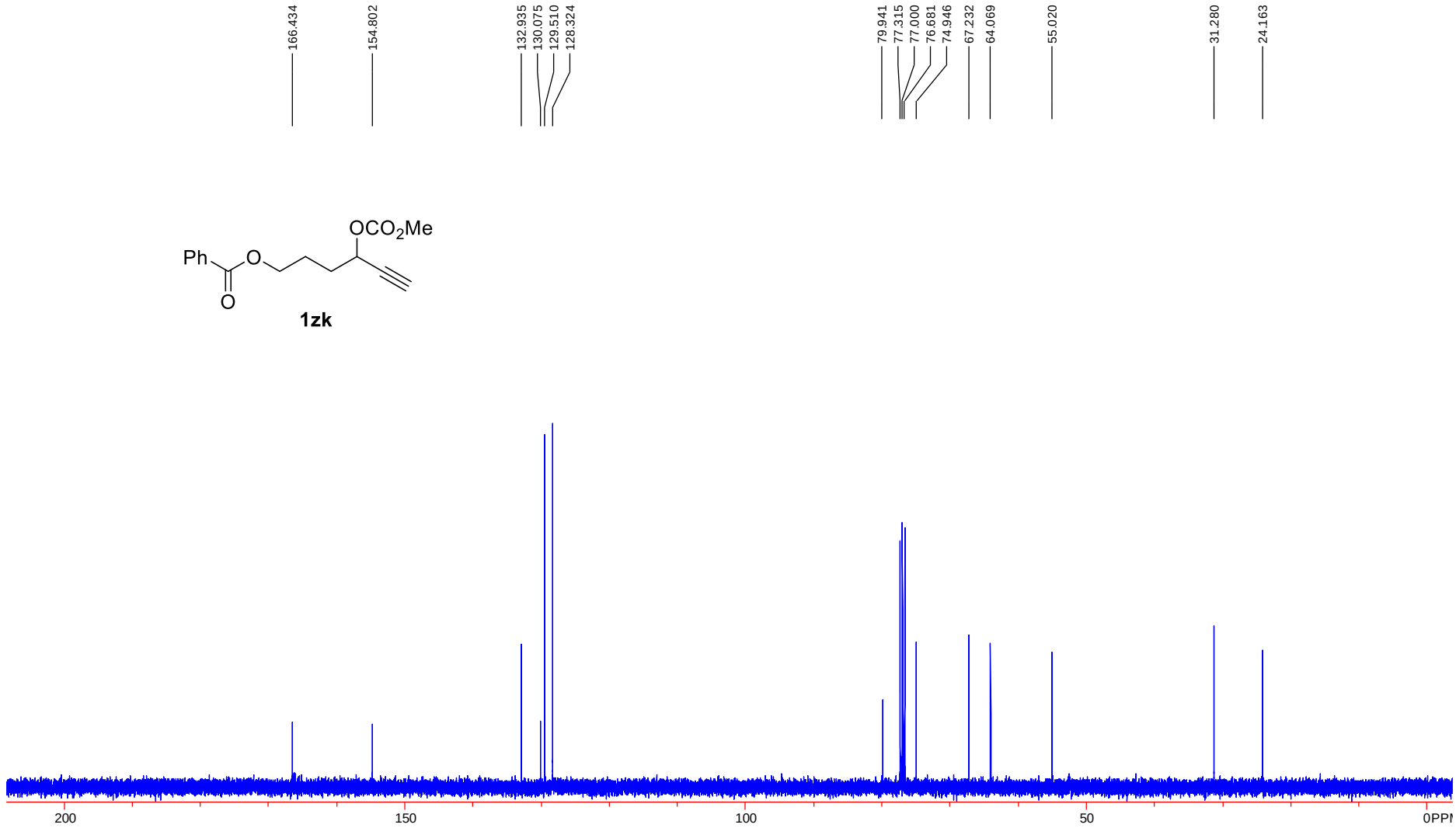
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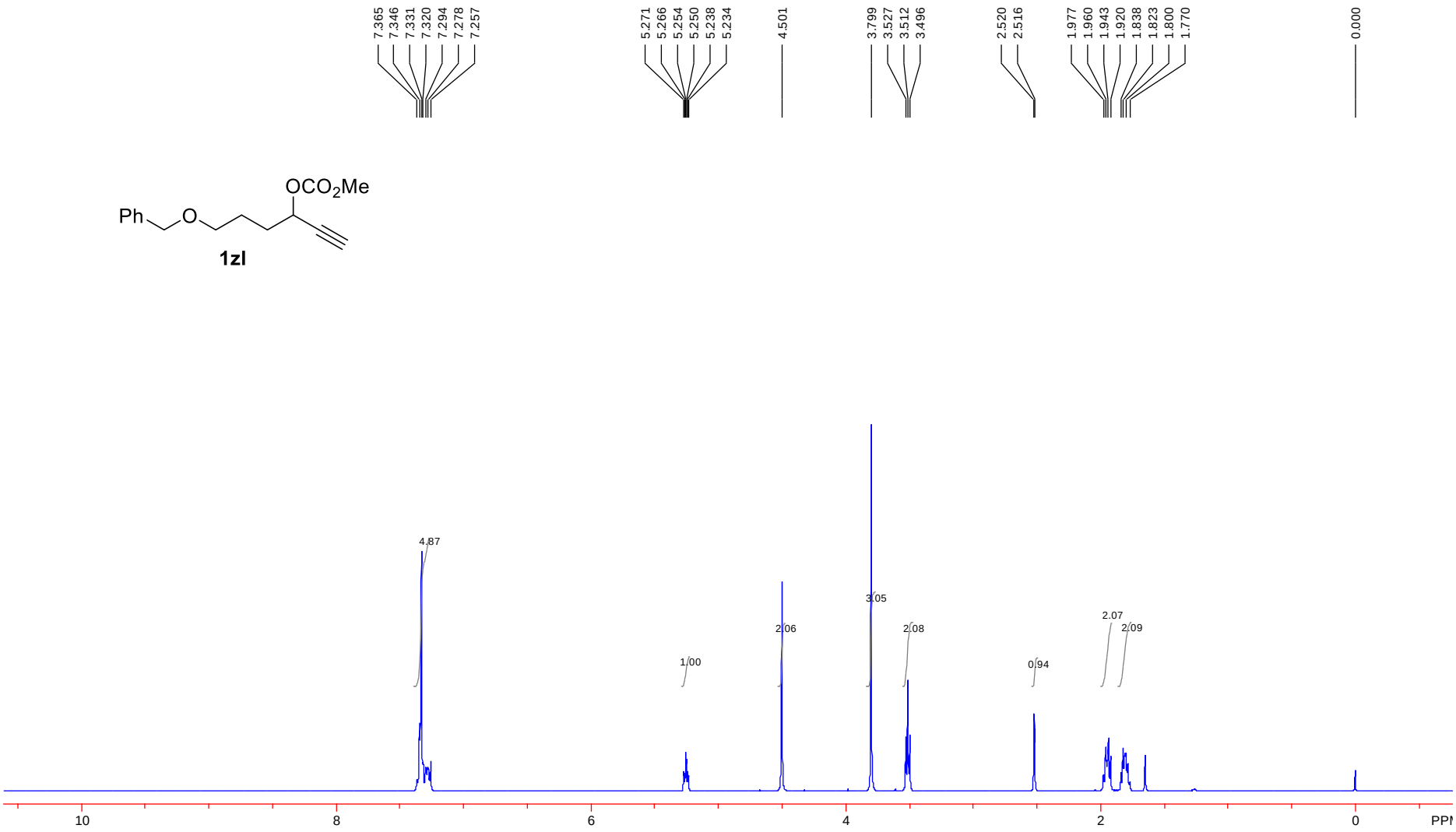
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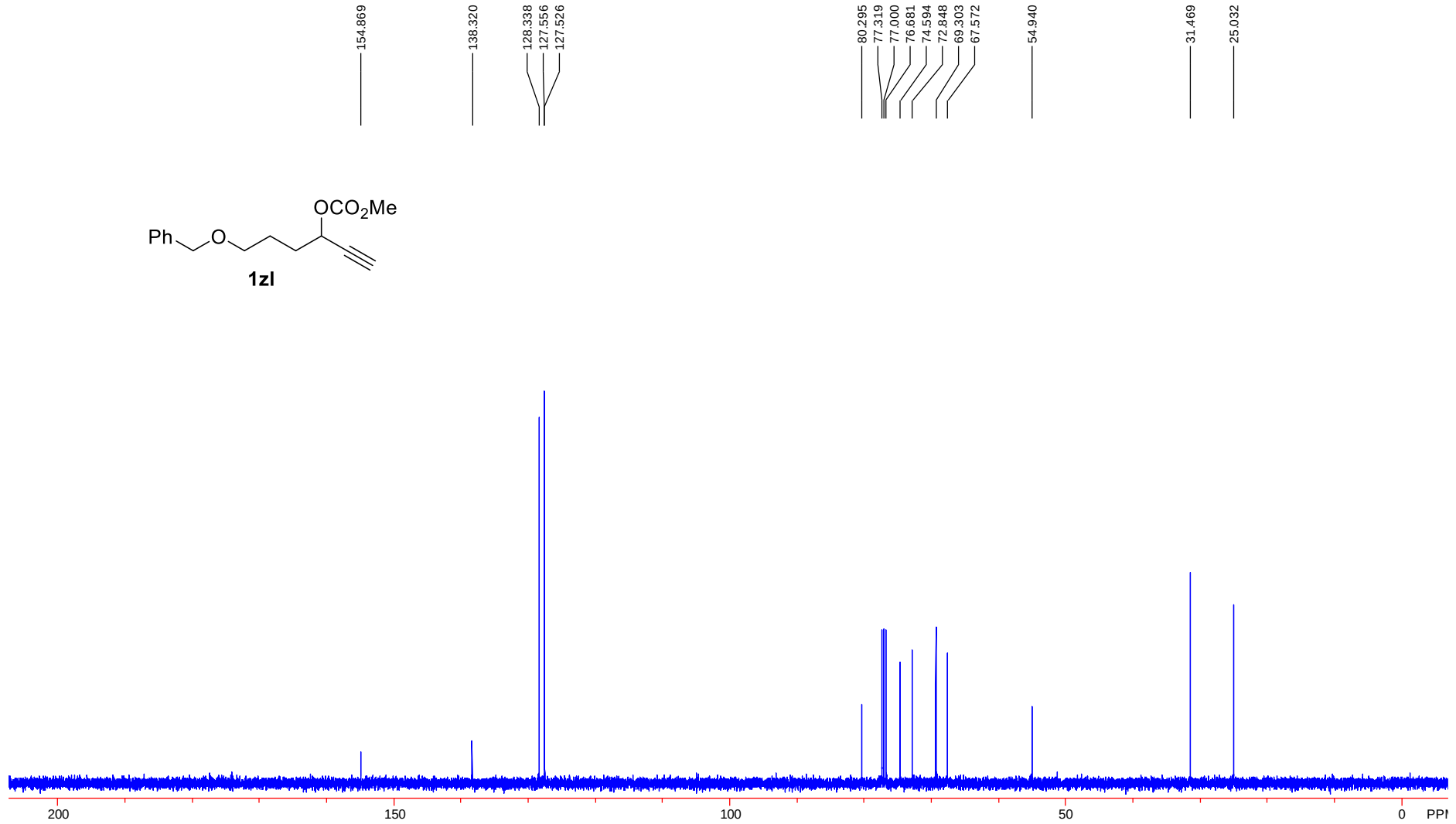
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Ph
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1zl
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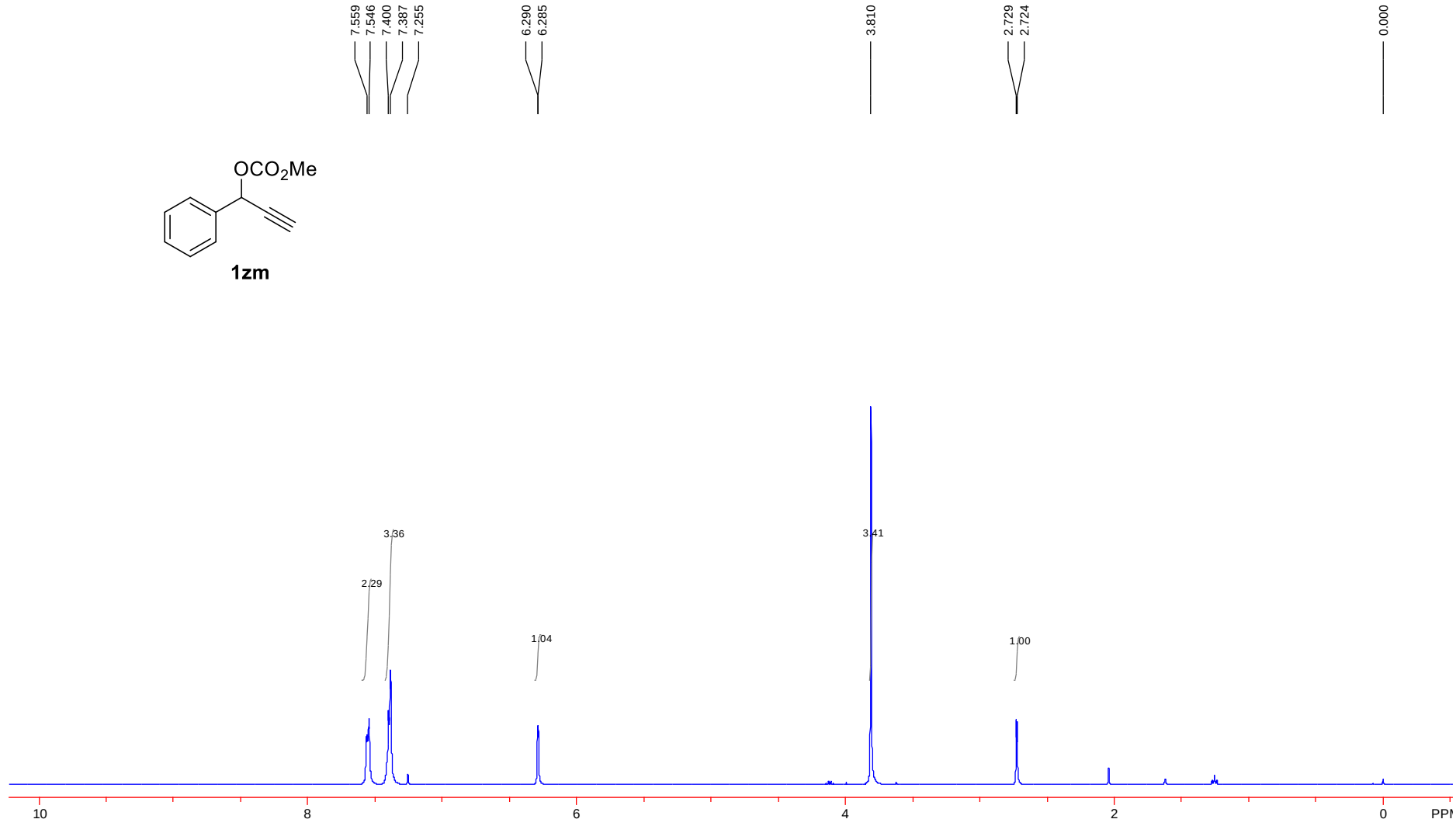
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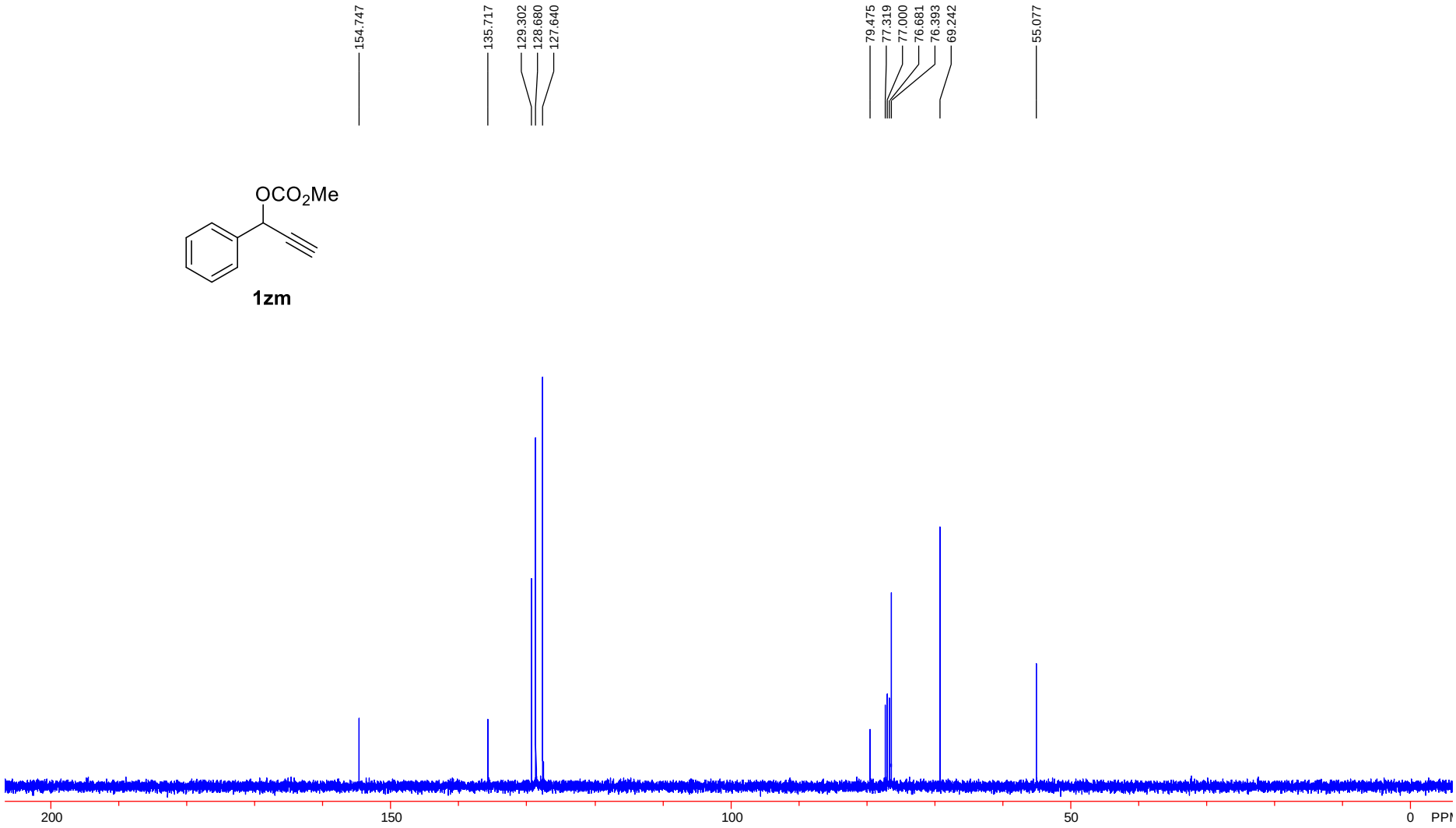
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OCO2Me
1zm
200
150
100
50
0
PPM


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7.251
7.231
7.213
7.118
7.101
7.085
5.853
2.086
2.057
2.051
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1.486
1.471
1.374
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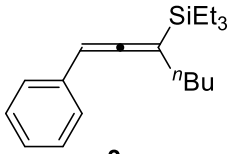
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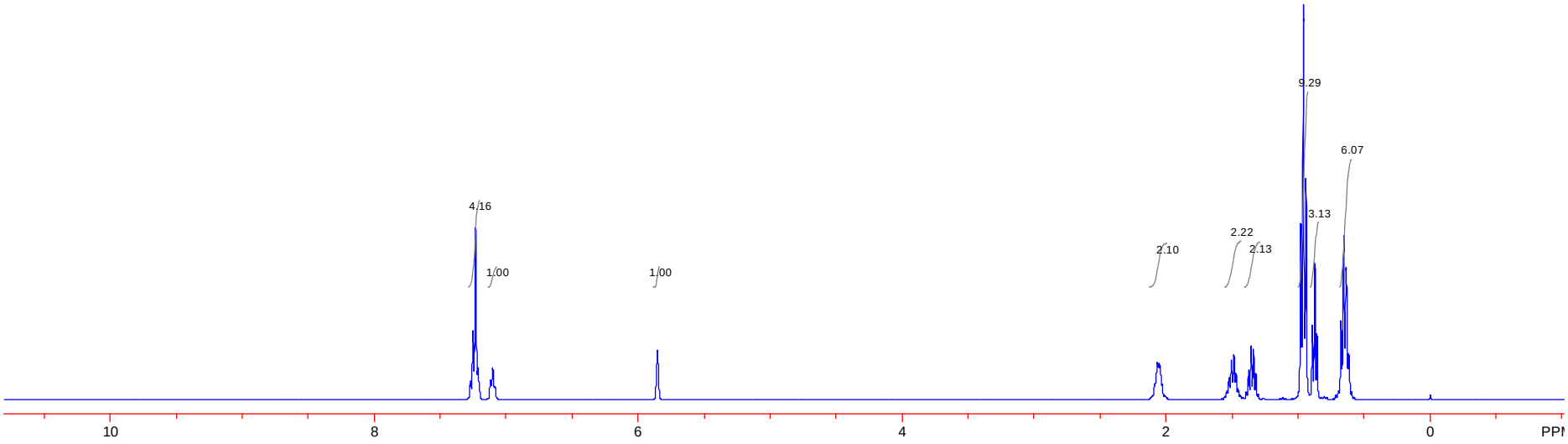
nBu

3a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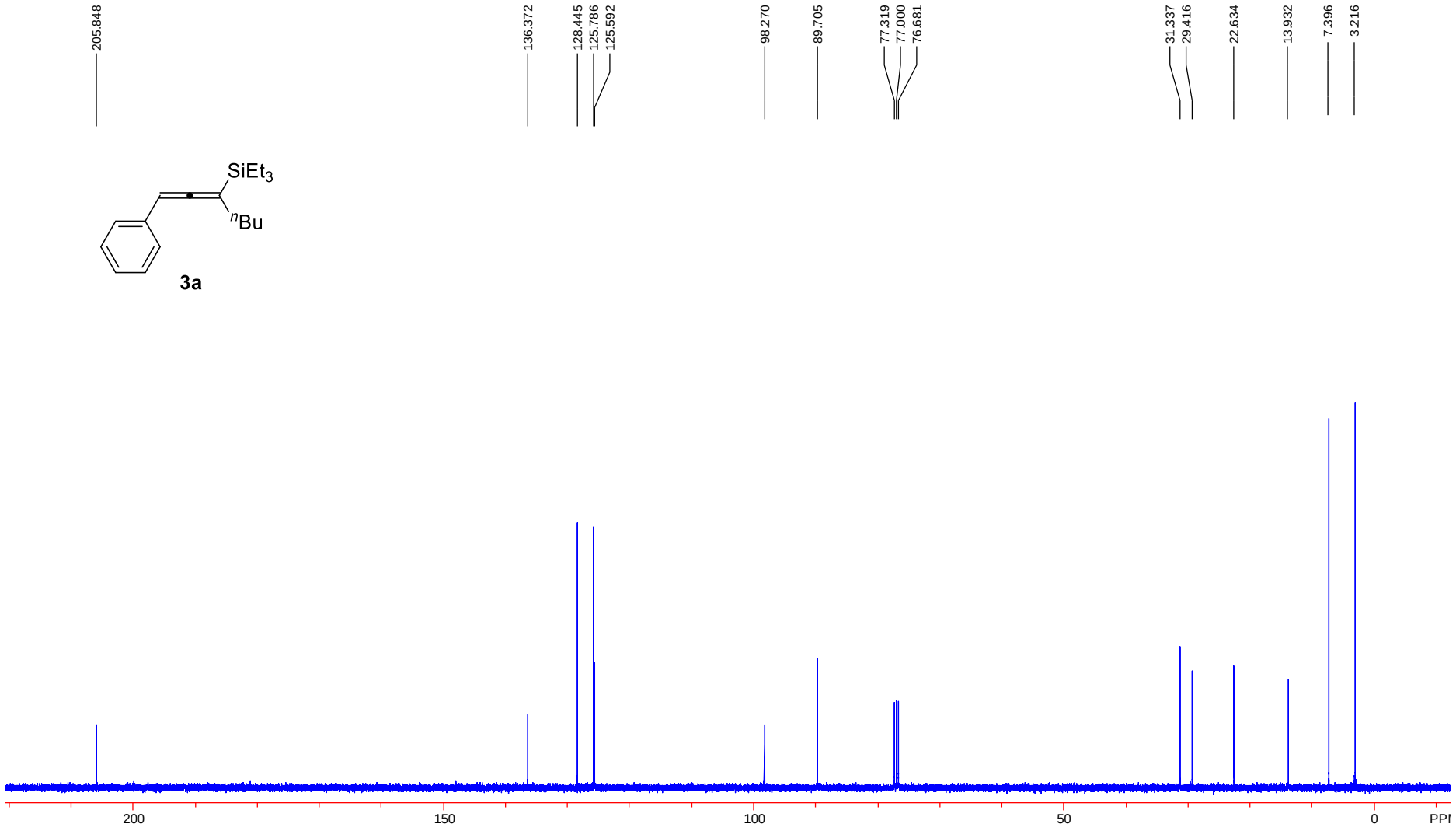
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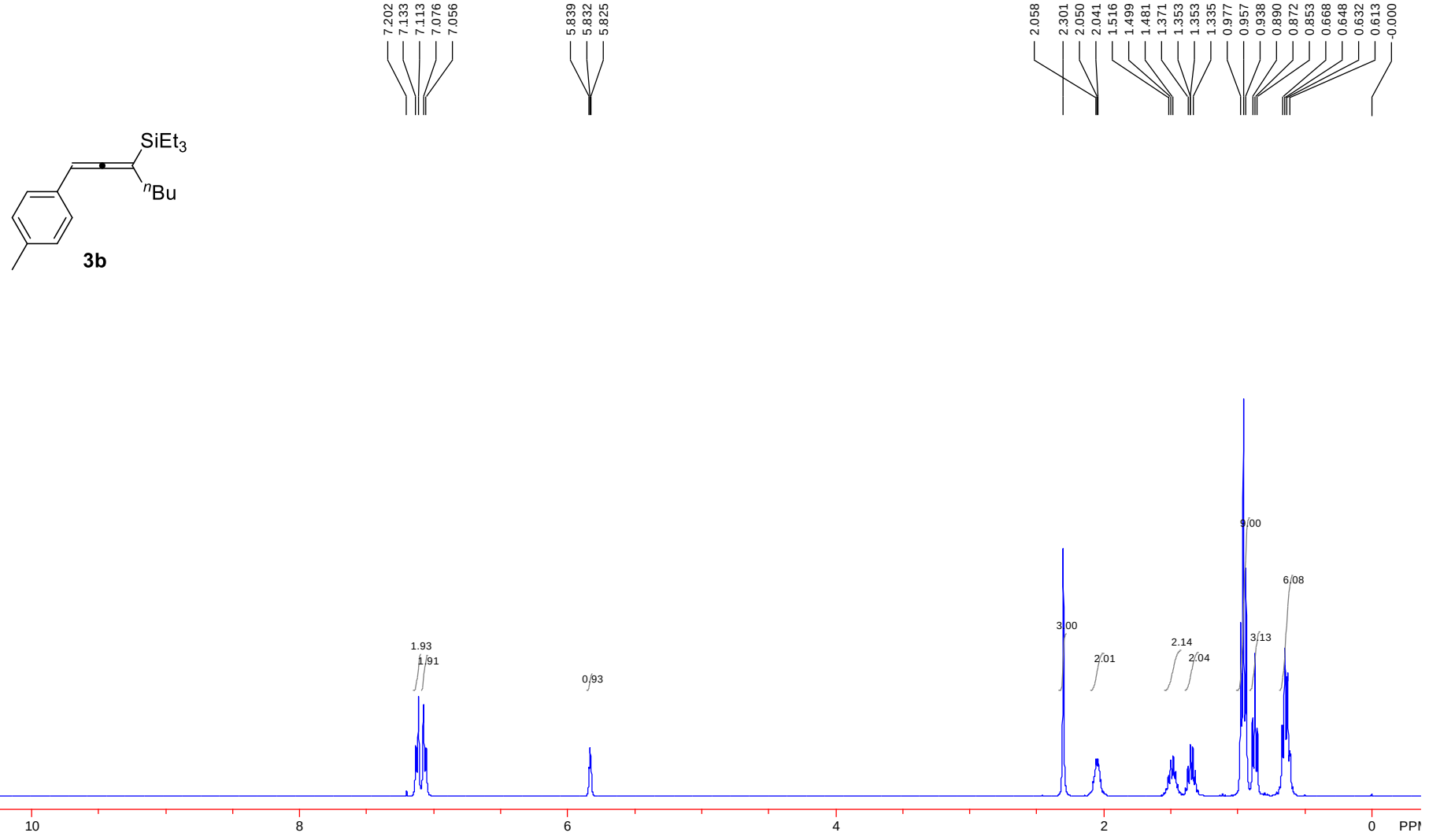
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2.050
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1.499
1.481
1.371
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1.335
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0.890
0.872
0.853
0.668
0.648
0.632
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nBu
3b
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1.91
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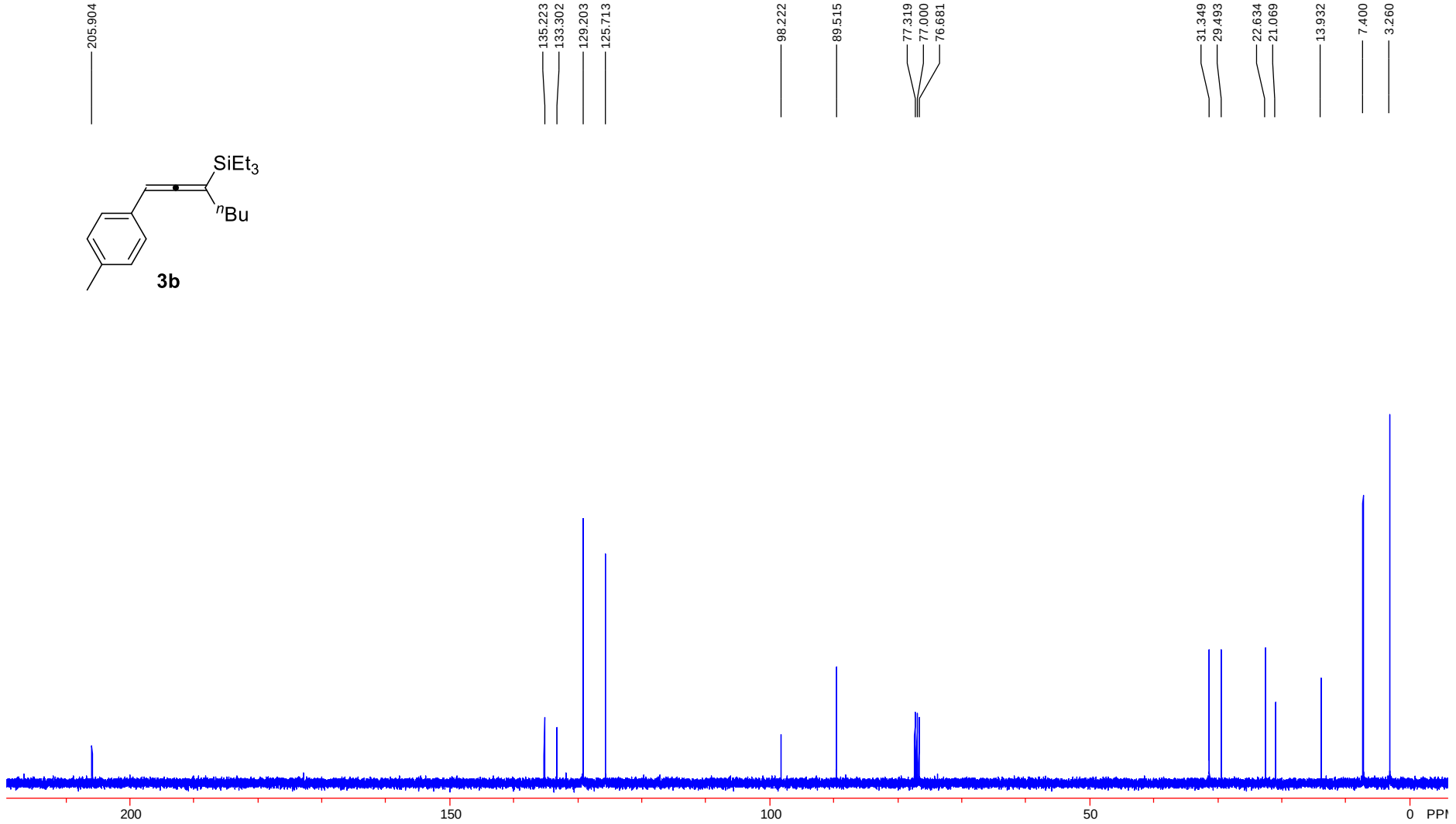
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22.634
21.069
13.932
7.400
3.260
SiEt3
nBu
3b
200
150
100
50
0
PPM


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7.156
5.849
5.843
5.836
2.053
2.037
2.014
1.497
1.481
1.462
1.369
1.351
1.332
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0.872
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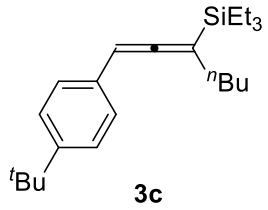
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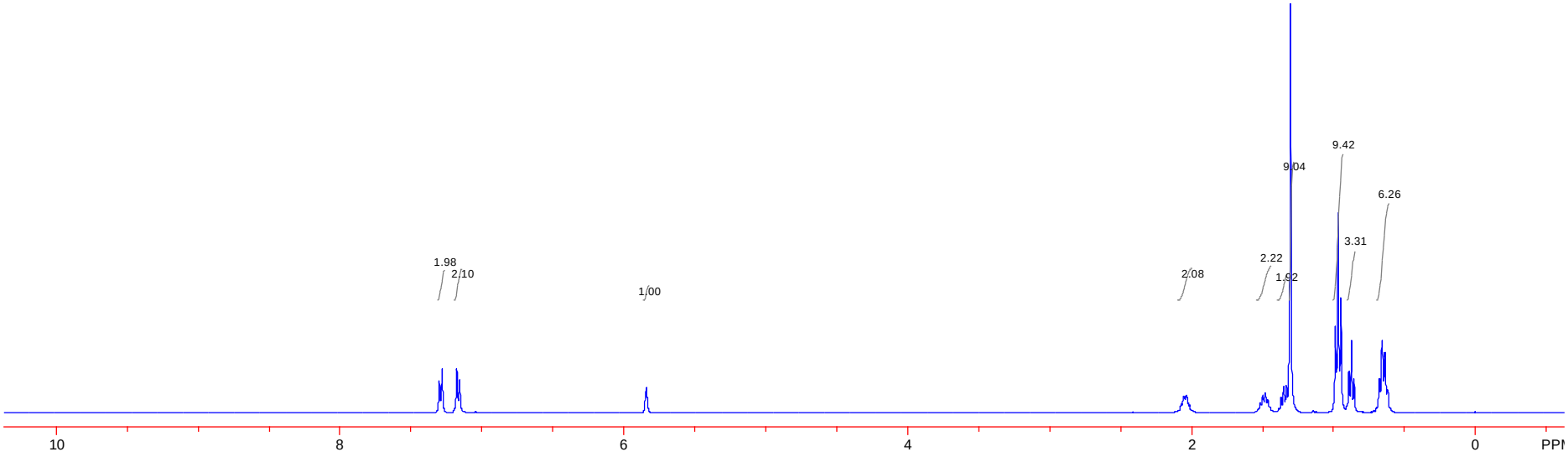
nBu
tBu

3c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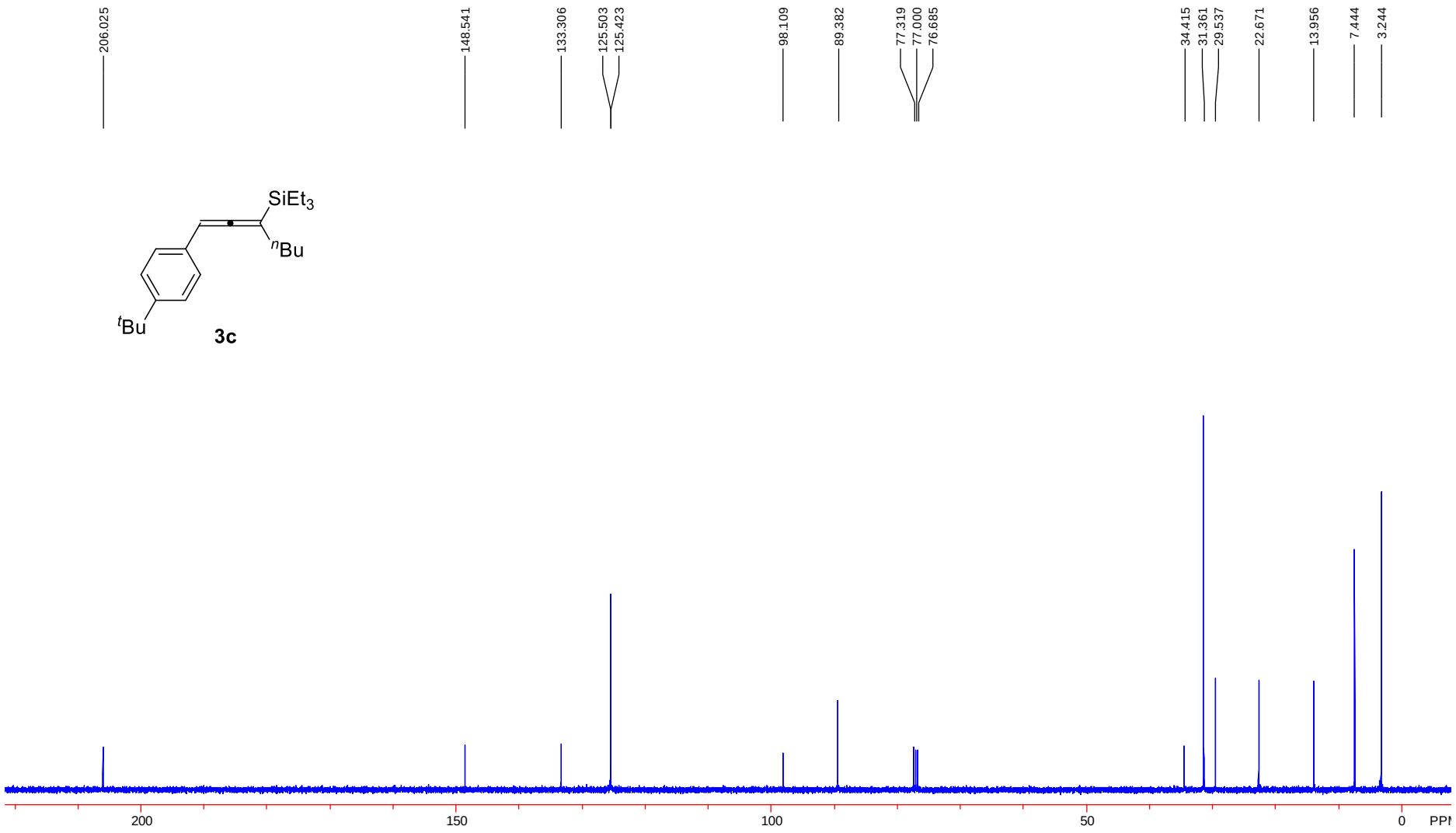
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tBu
3c
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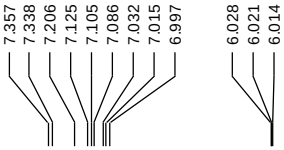
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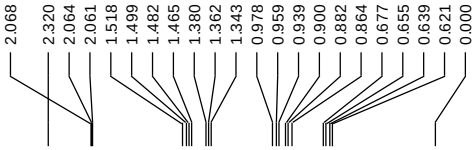
6.028
6.021
6.014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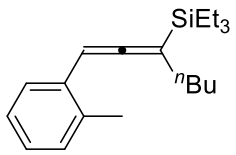
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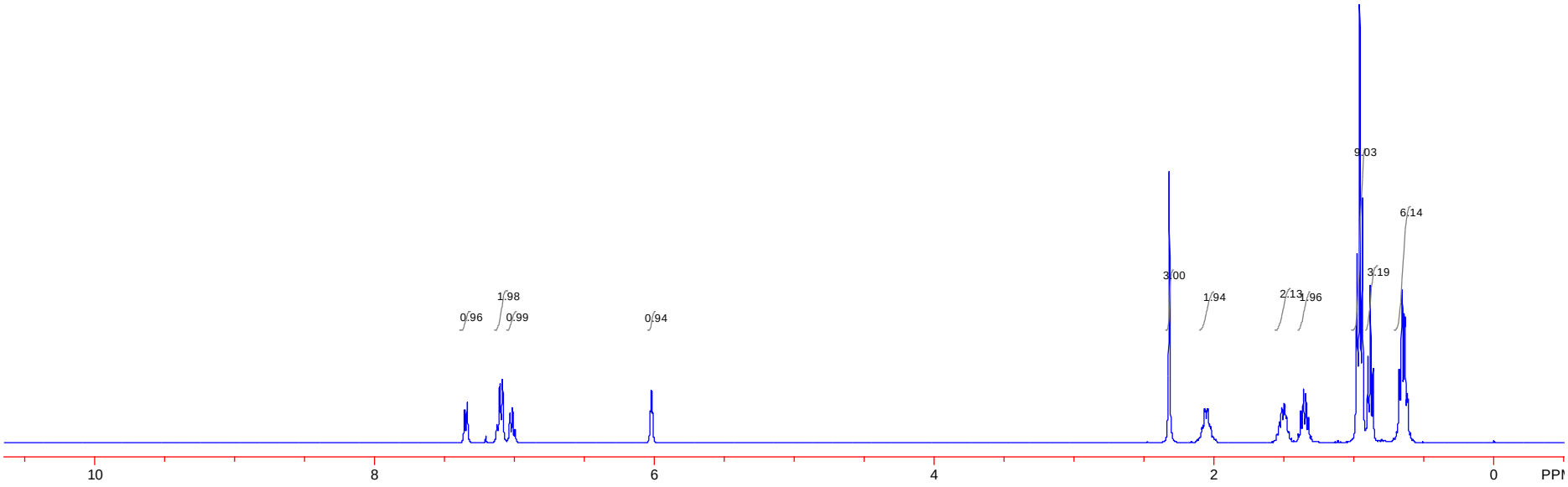
nBu

3d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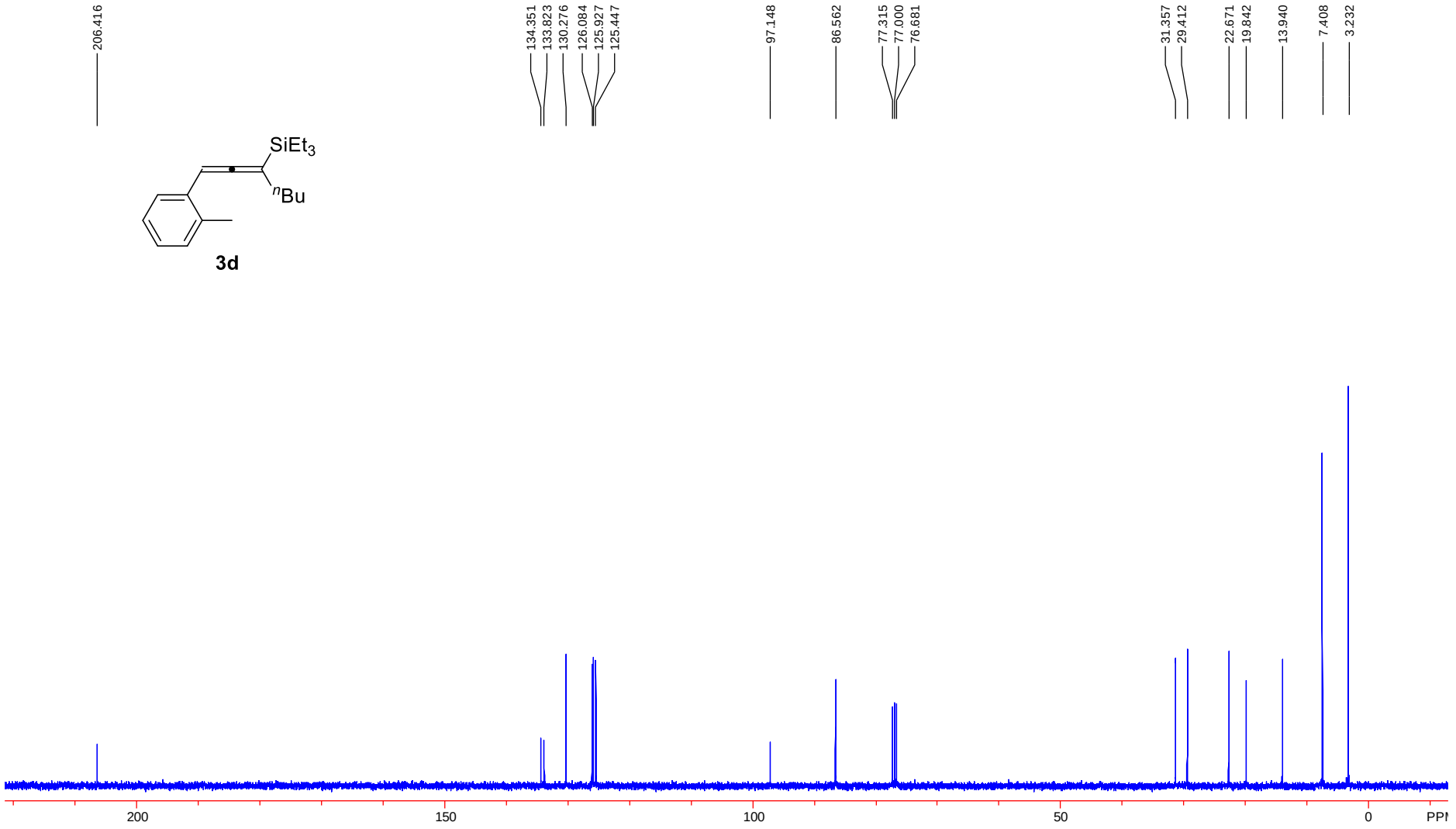
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3d
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100
50
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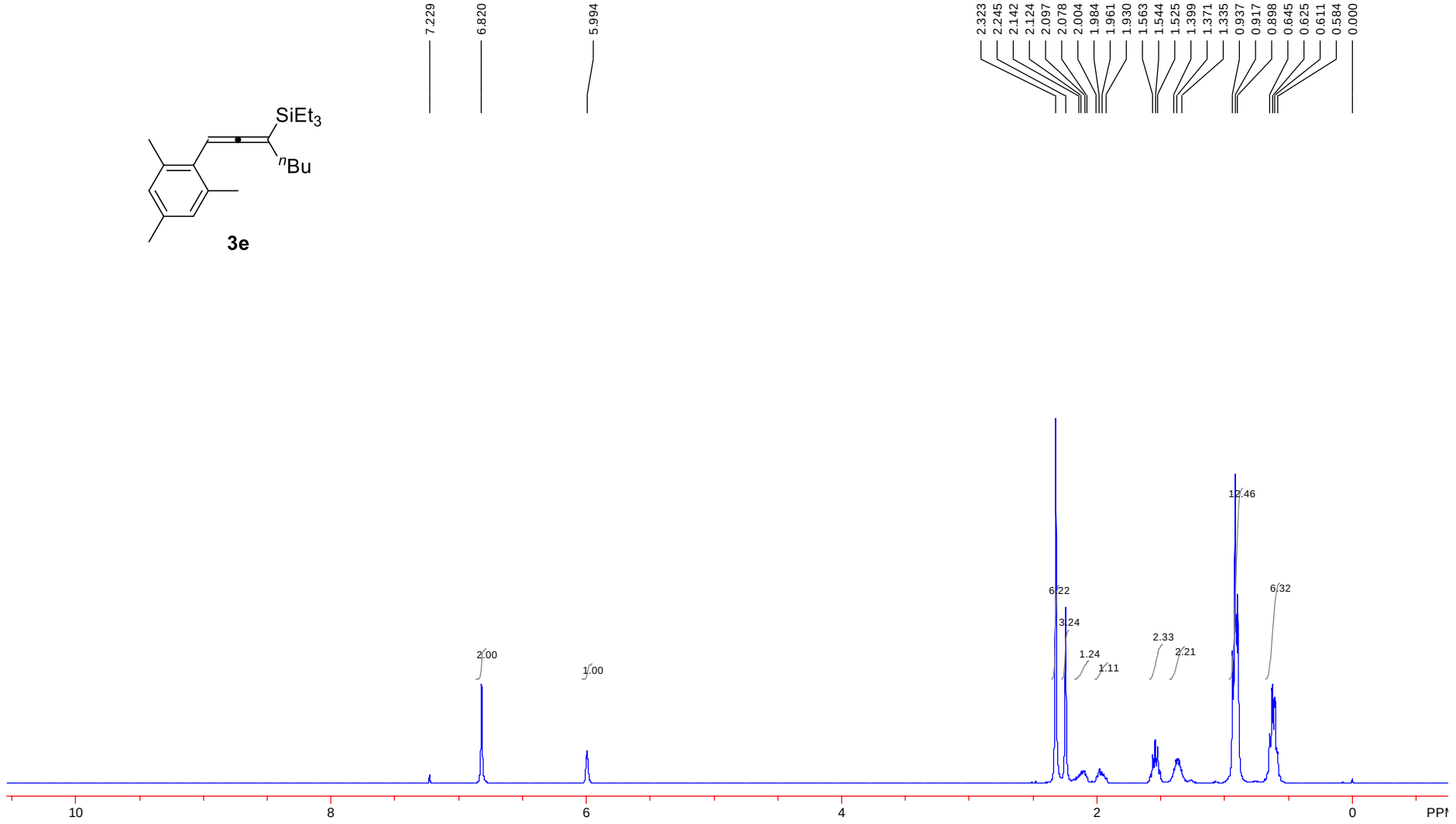
PPM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1.961
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1.399
1.371
1.335
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0.645
0.625
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0.584
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1.00
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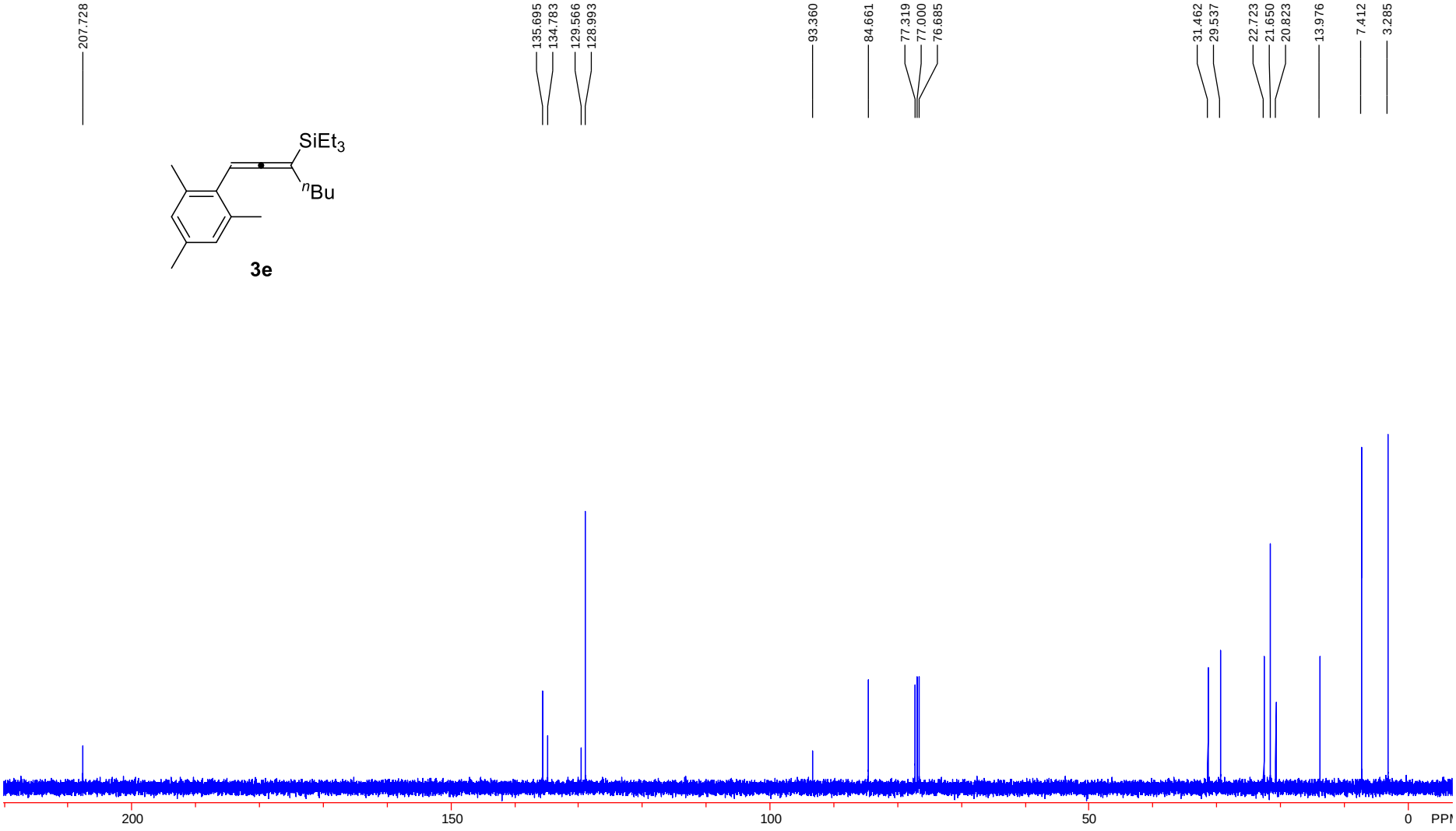
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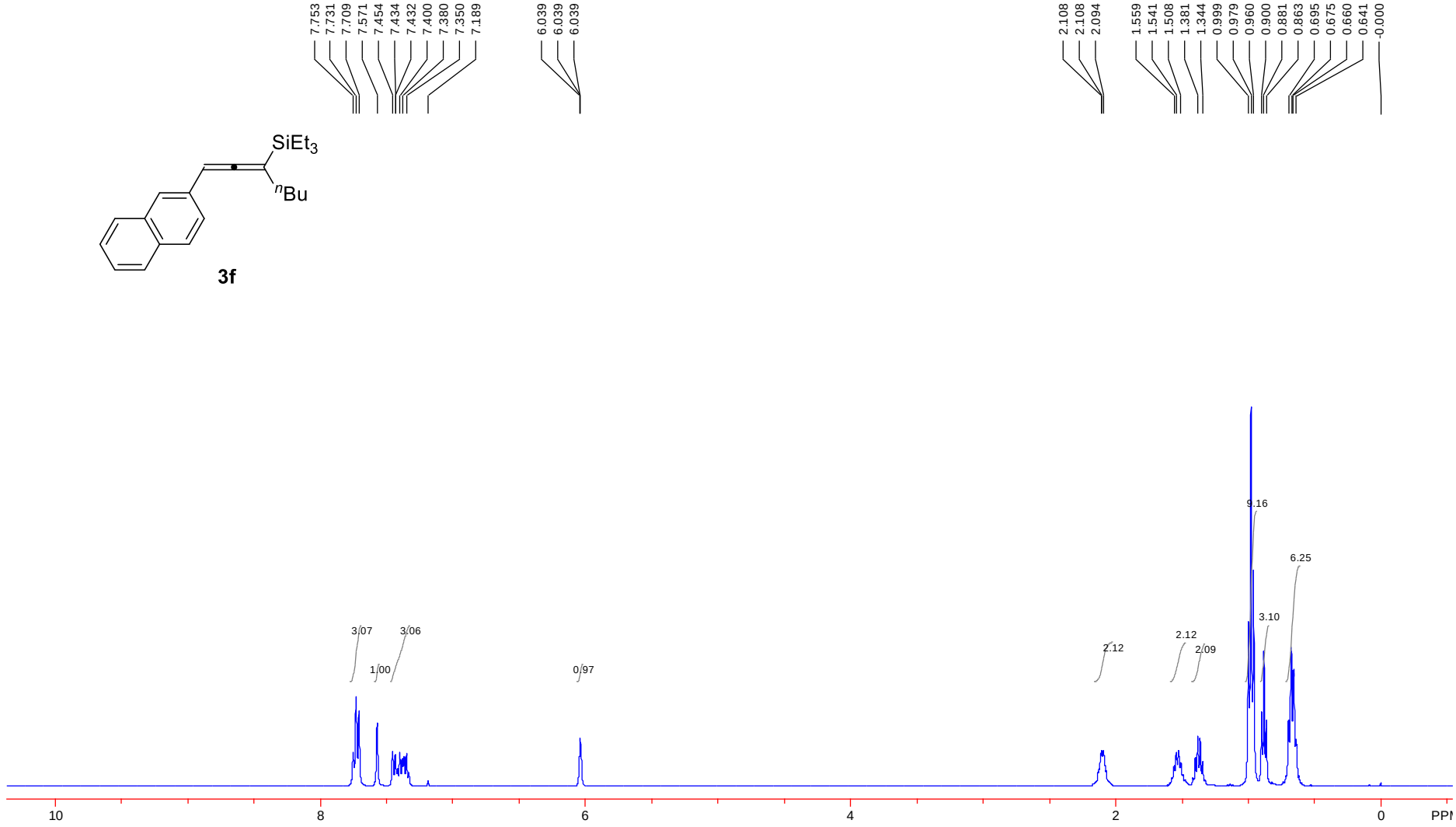
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6.039
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2.108
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1.508
1.381
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0.960
0.900
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0.863
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0.675
0.660
0.641
-0.000
SiEt3
nBu
3f
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3.06
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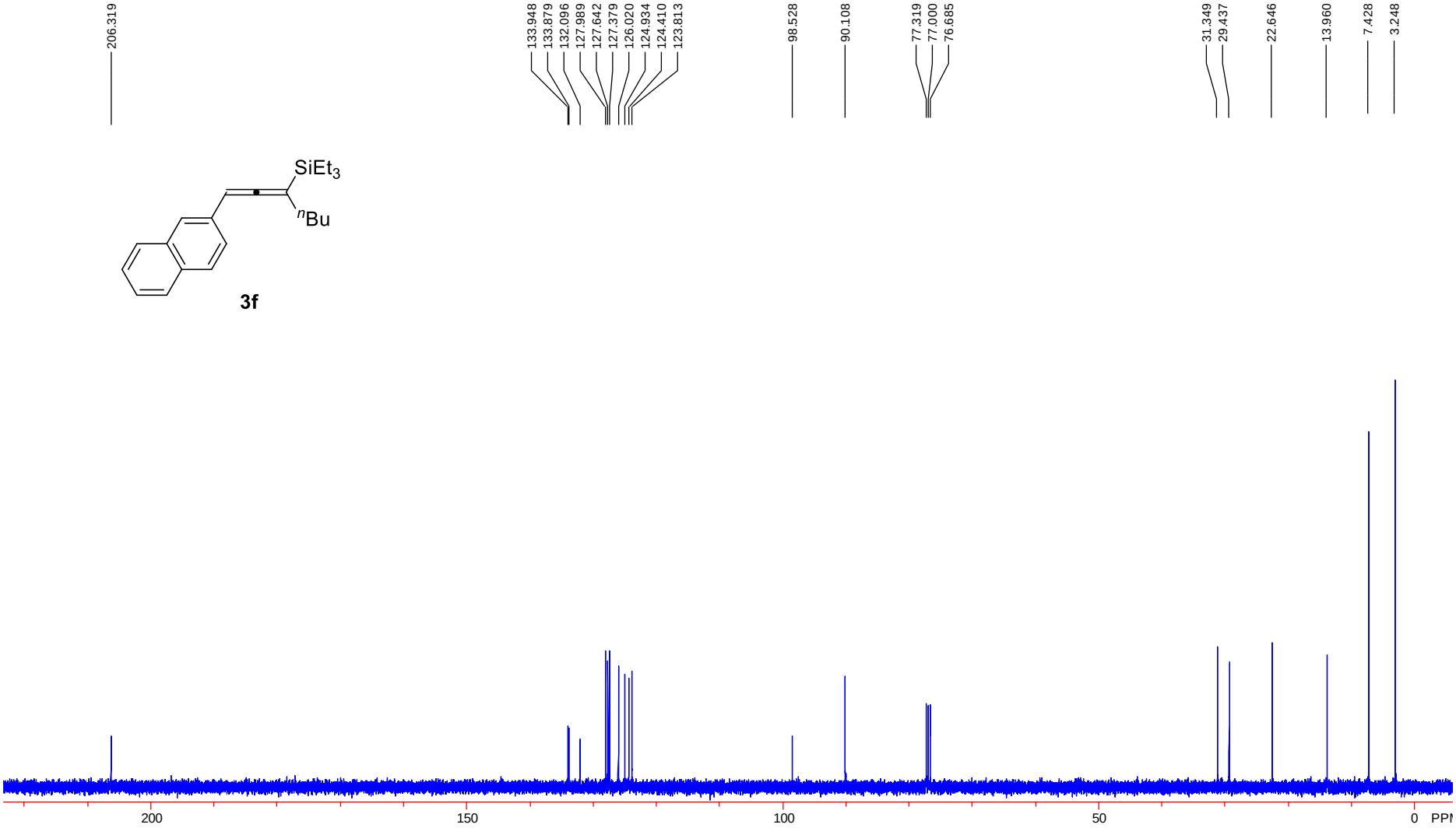
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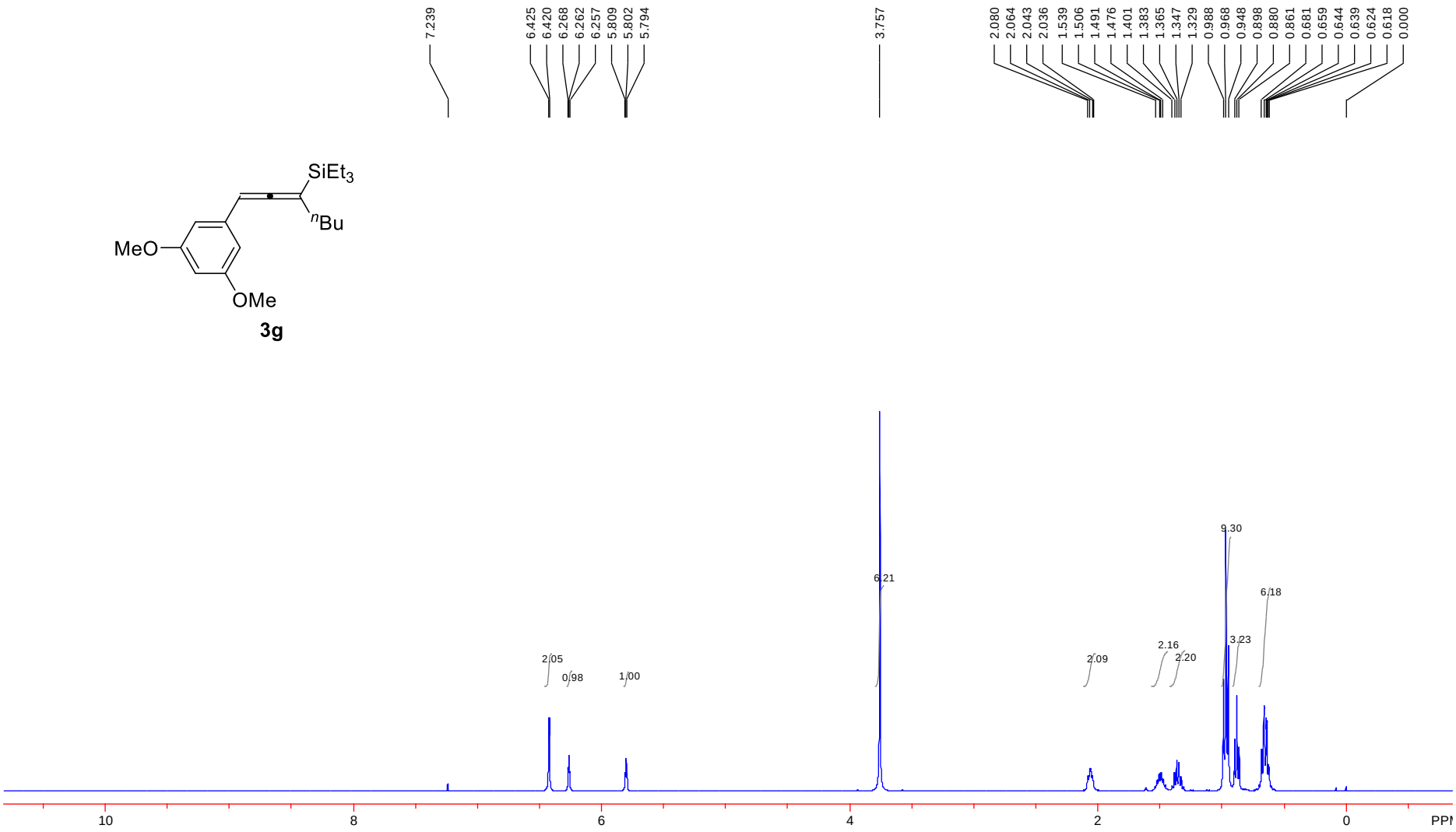
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1.383
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0.948
0.898
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OMe
3g
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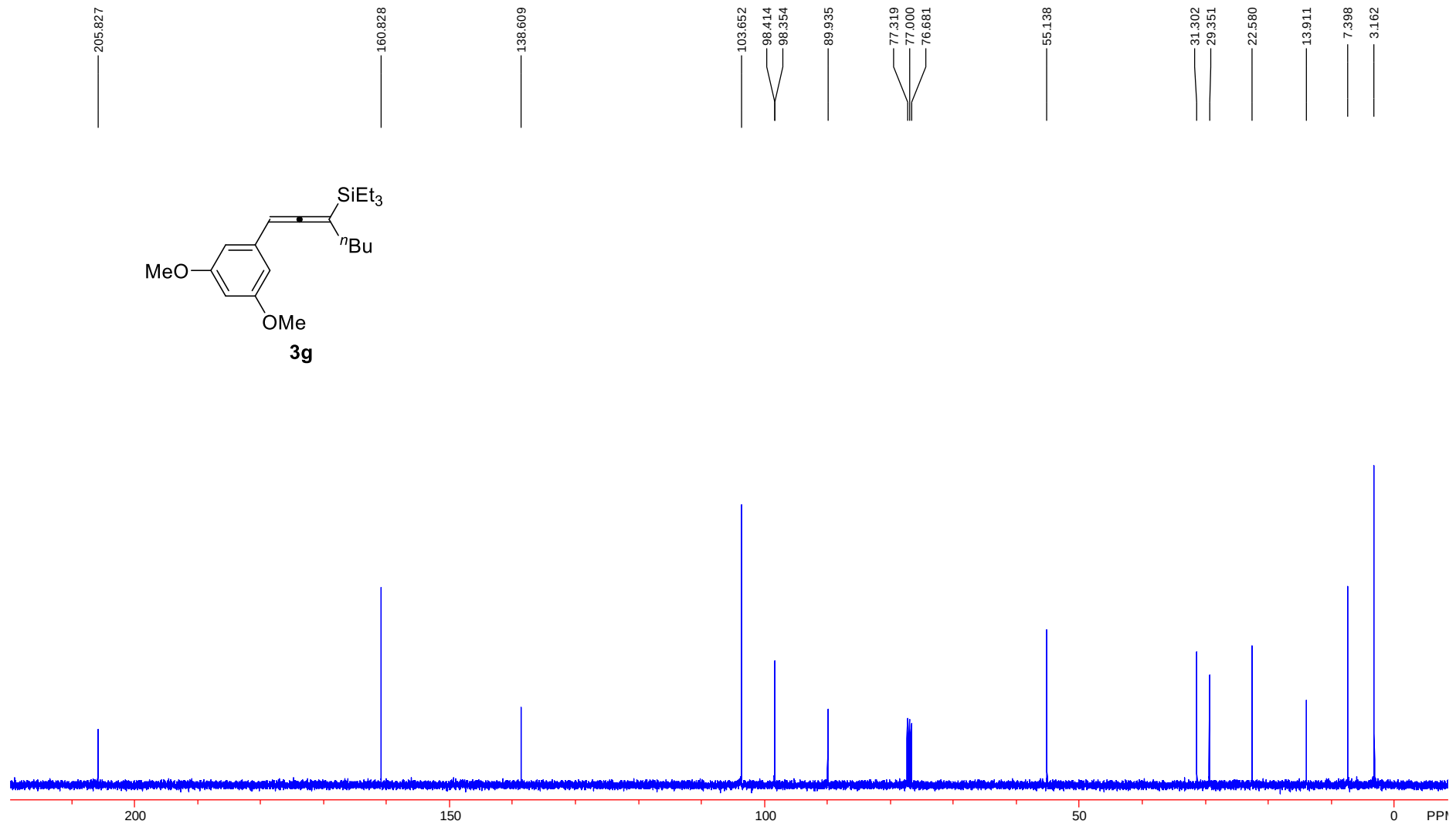
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OMe
3g
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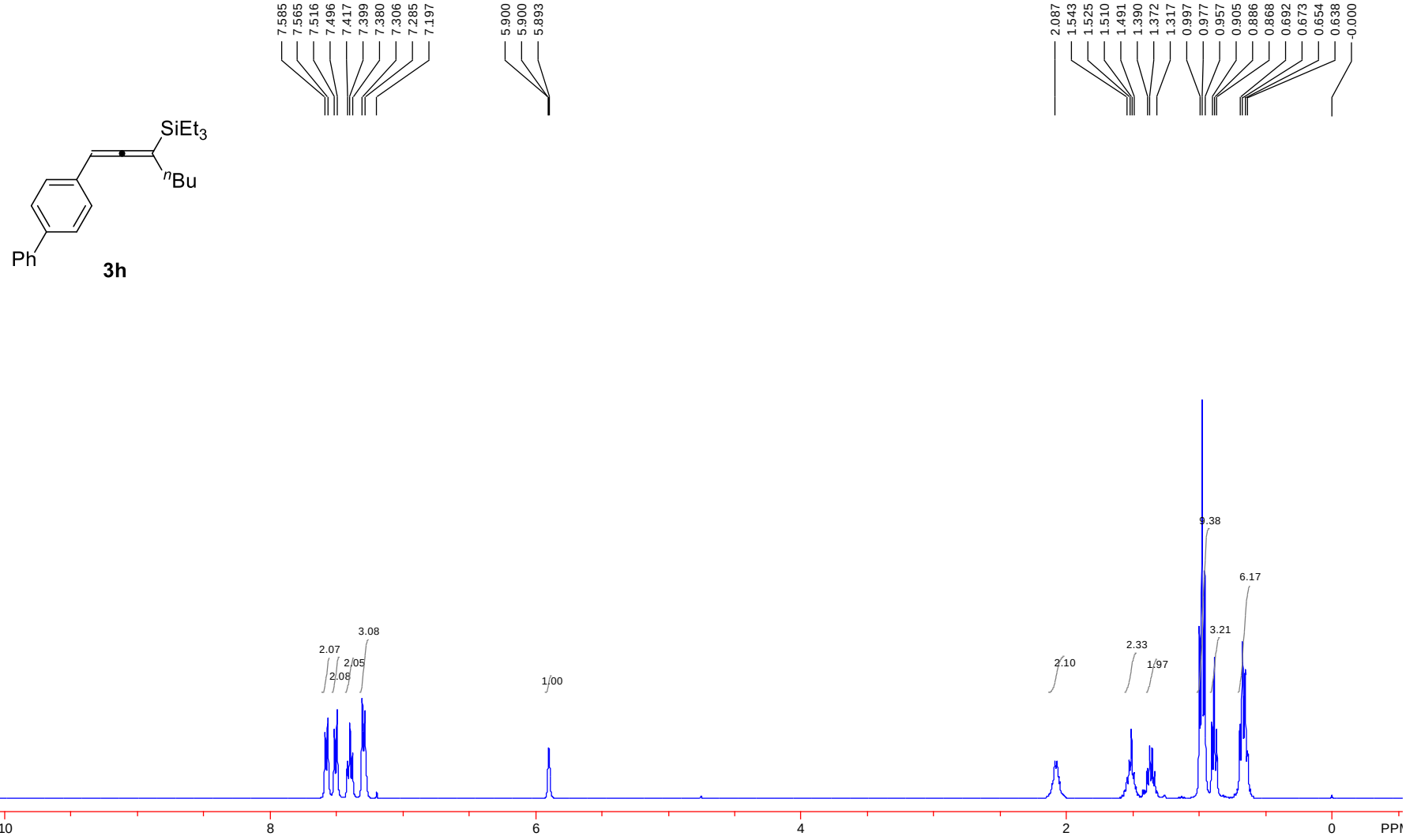
PPM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nBu
Ph
3h
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2.08
2.05
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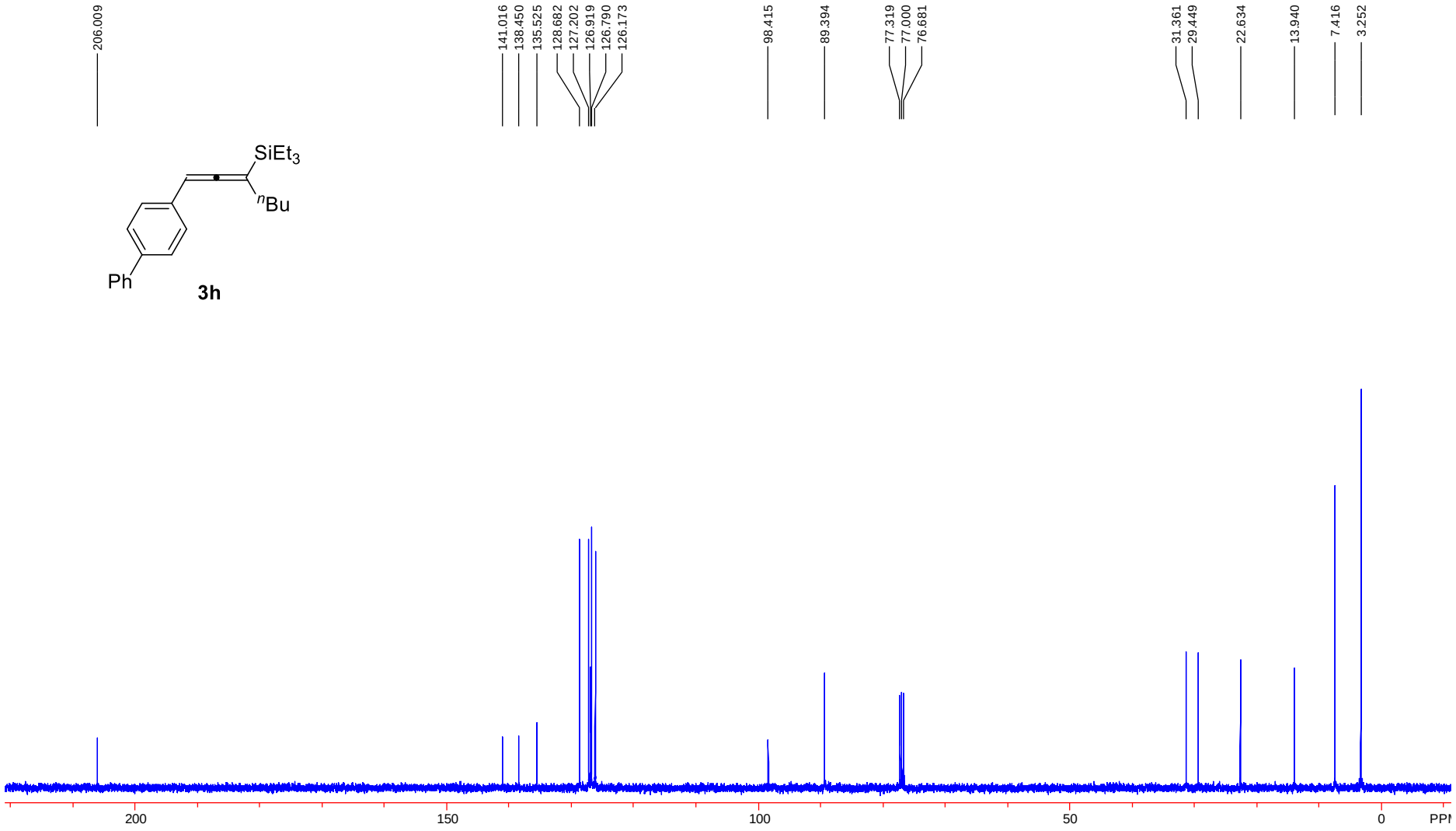
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29.449
22.634
13.940
7.416
3.252
SiEt3
nBu
Ph
3h
200
150
100
50
0
PPM


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2.086
2.086
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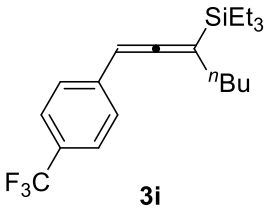
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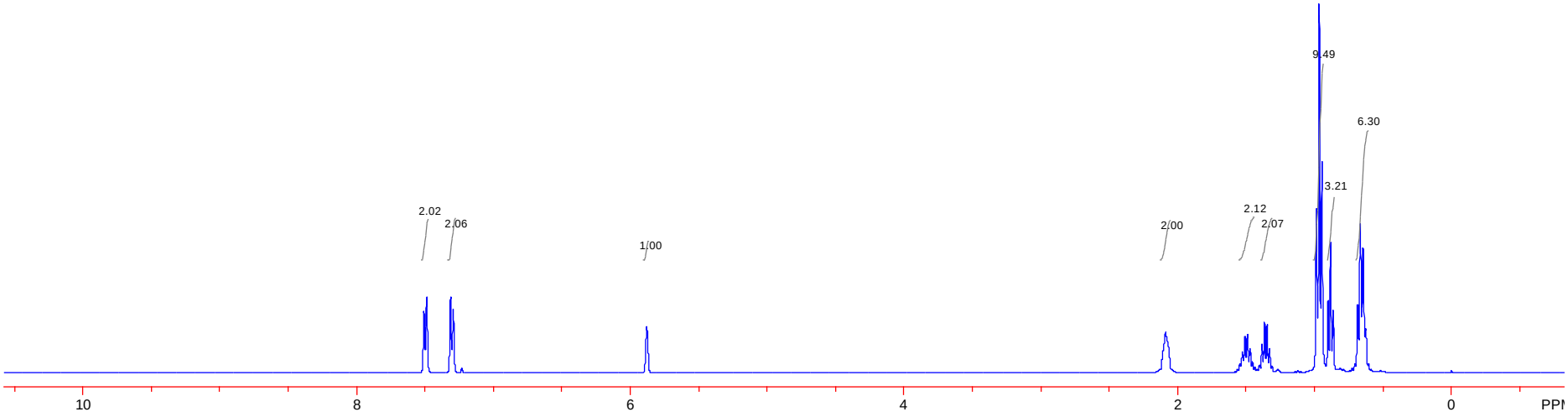
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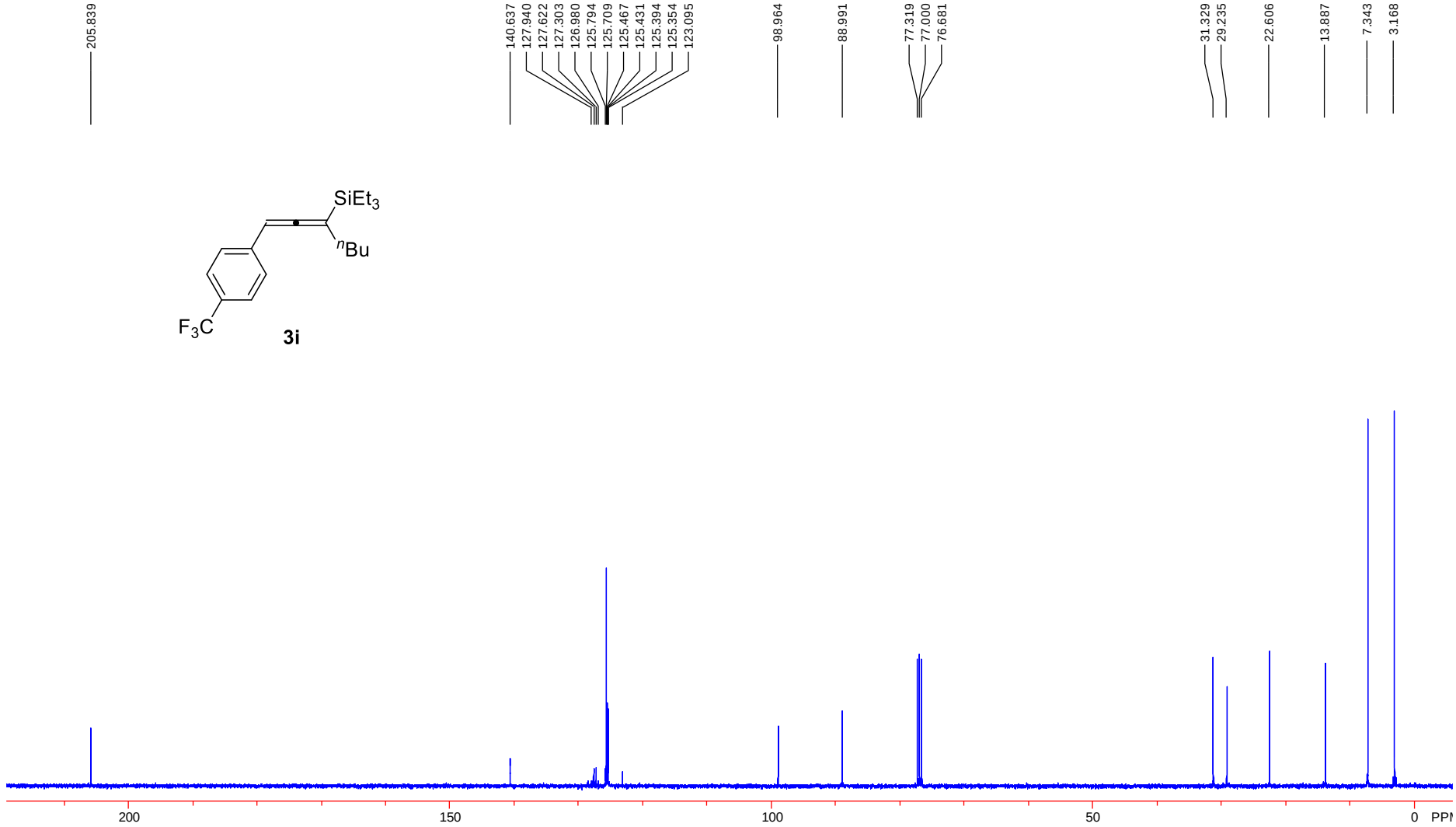
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3i
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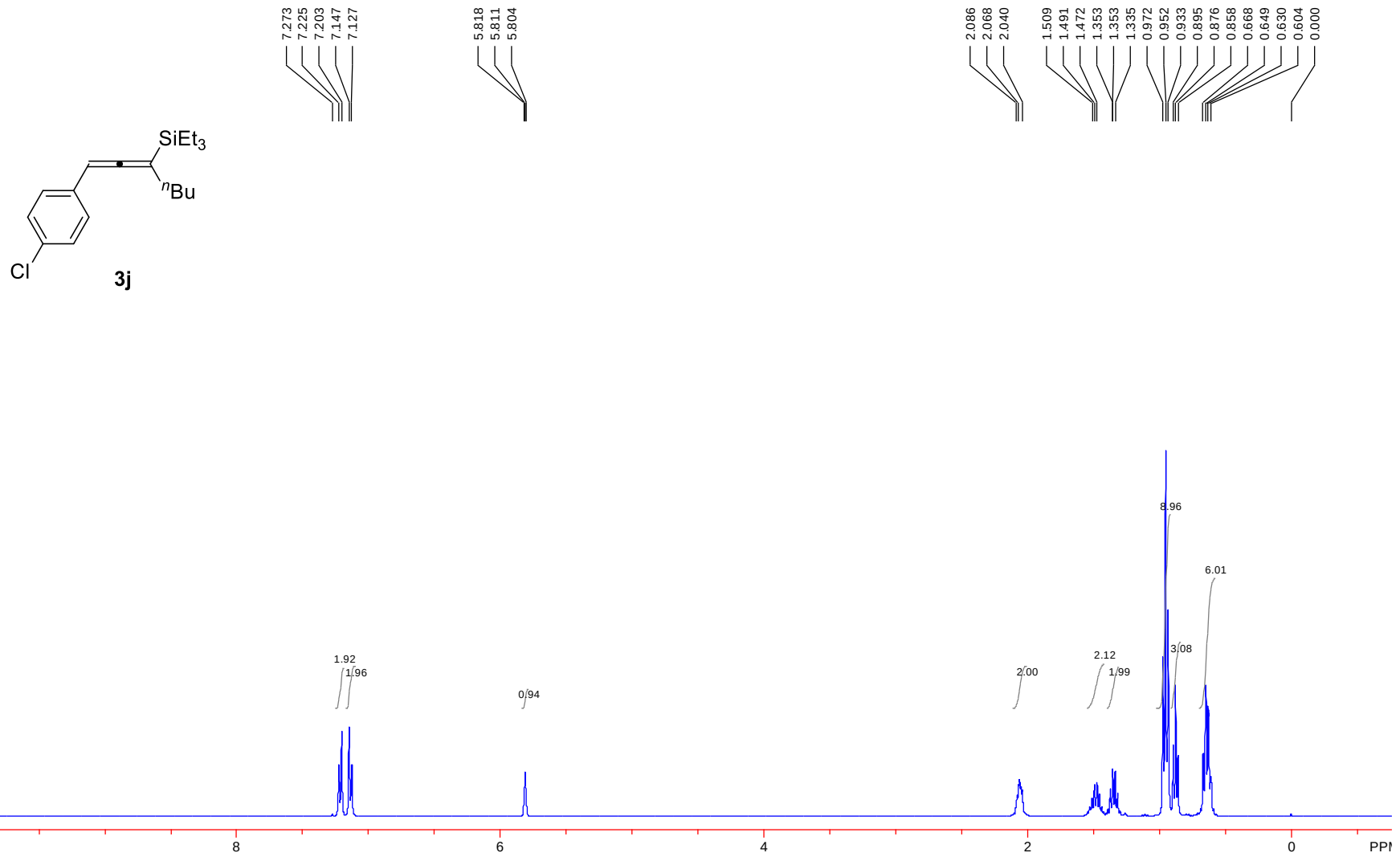
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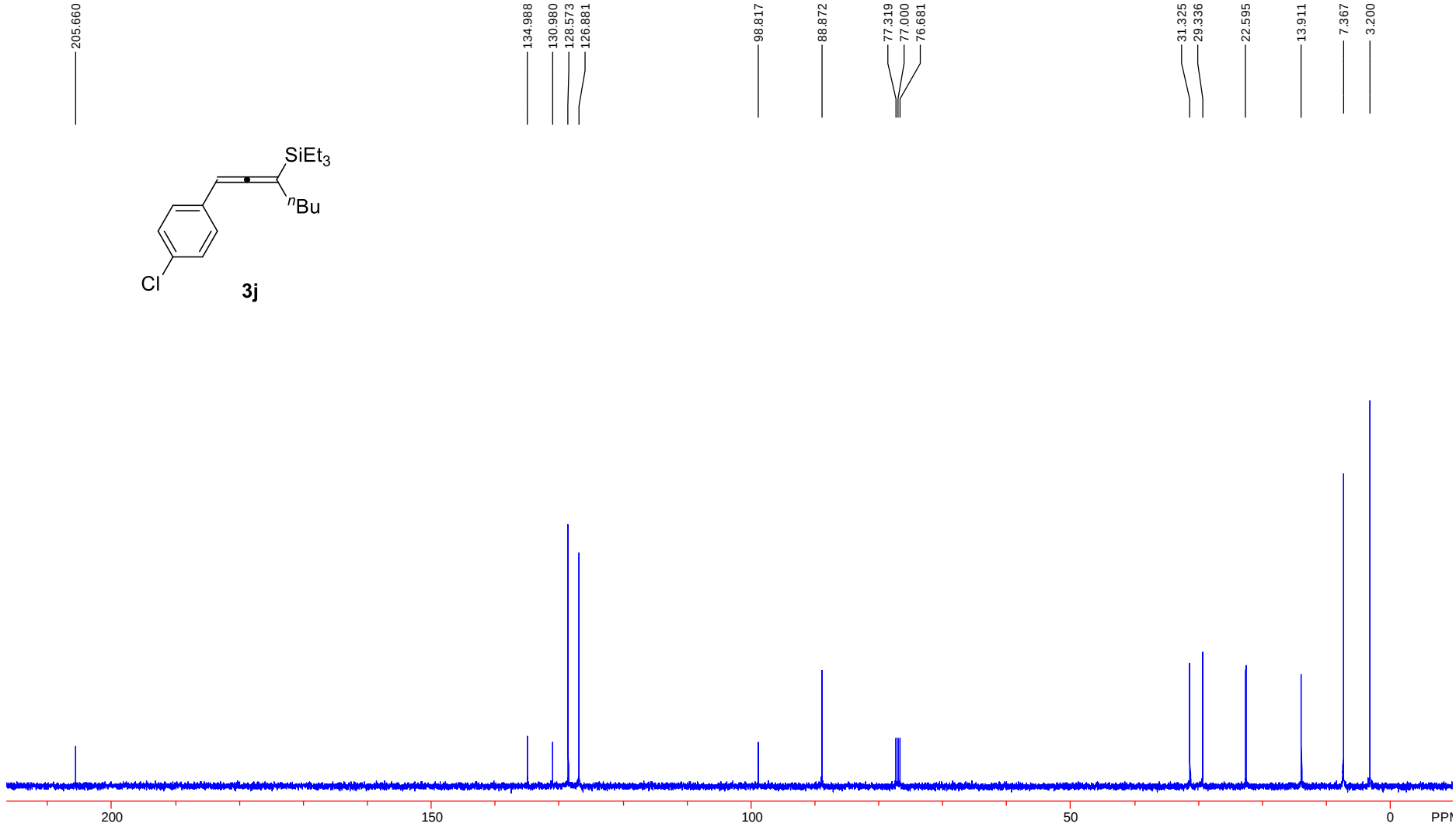
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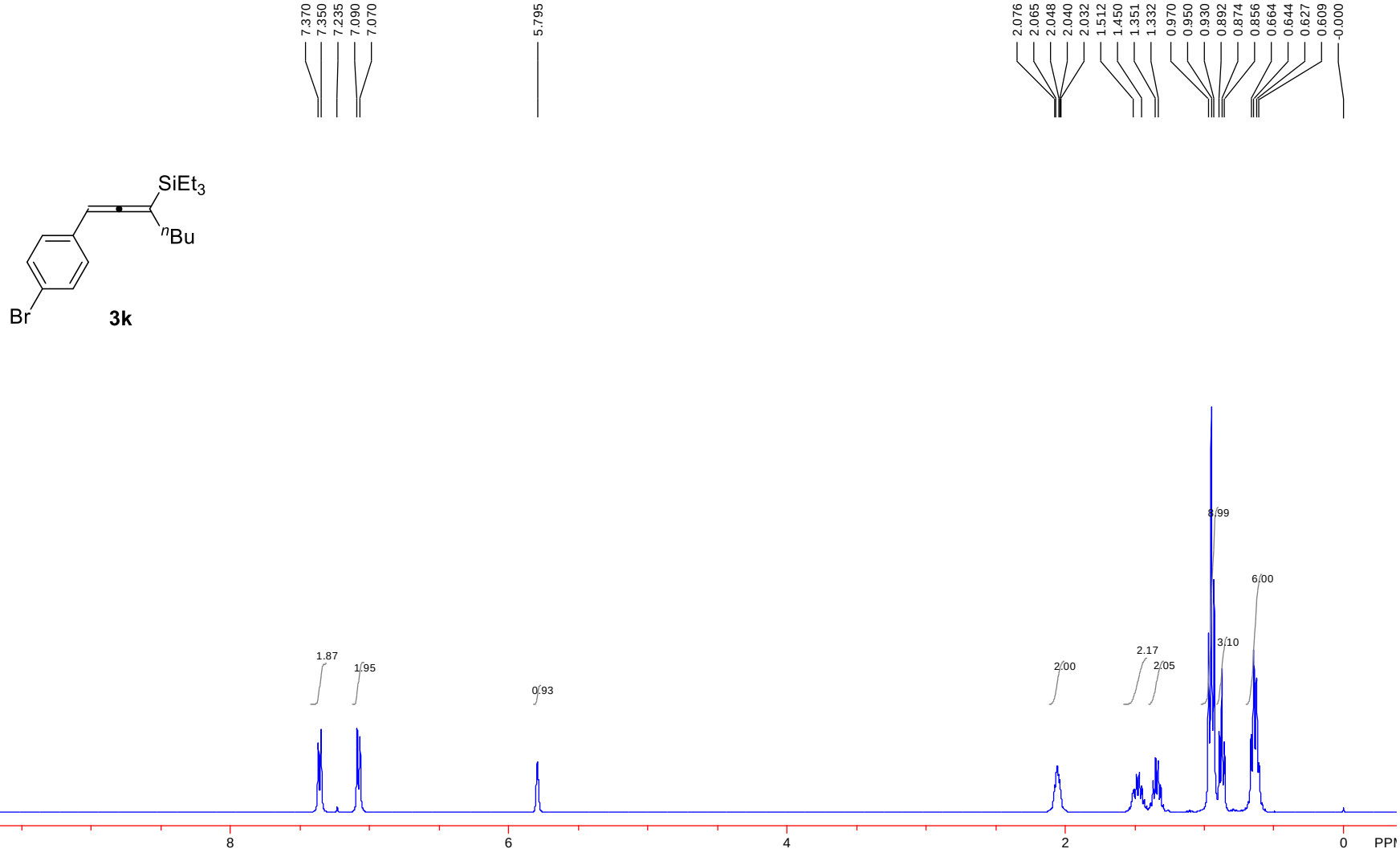
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0.856
0.664
0.644
0.627
0.609
-0.000
SiEt3
nBu
Br
3k
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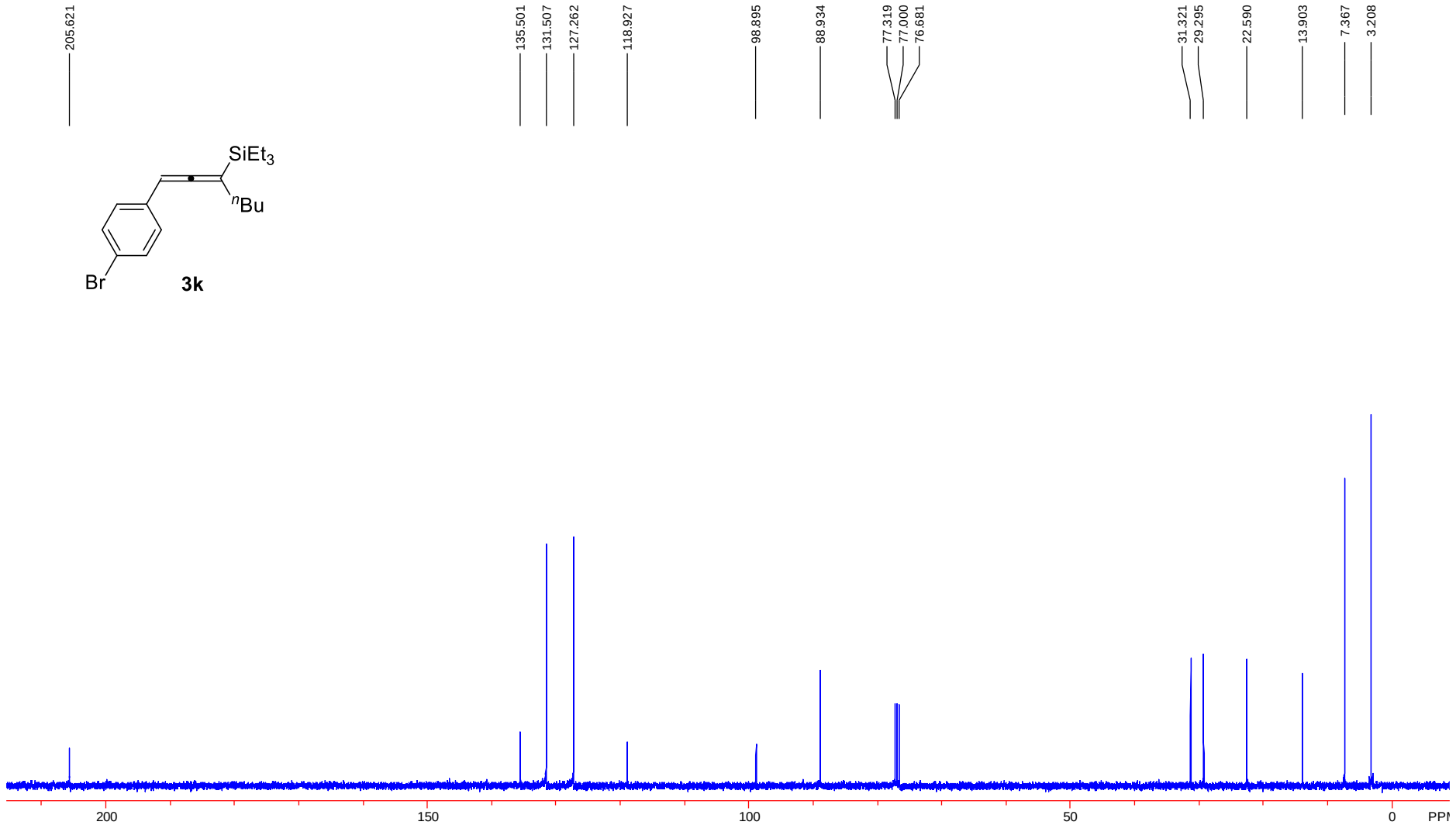
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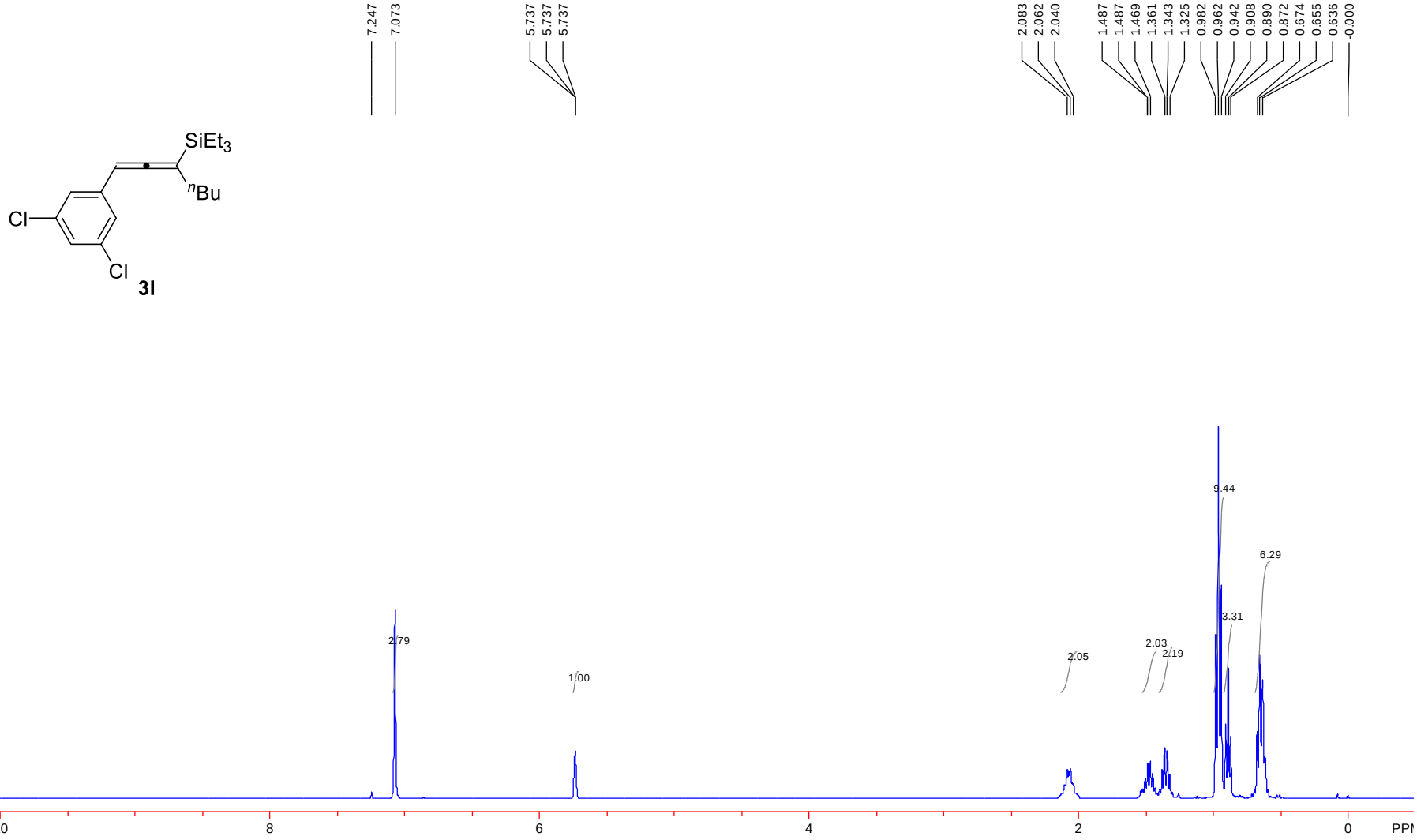
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1.325
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0.962
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nBu
Cl
Cl
3l
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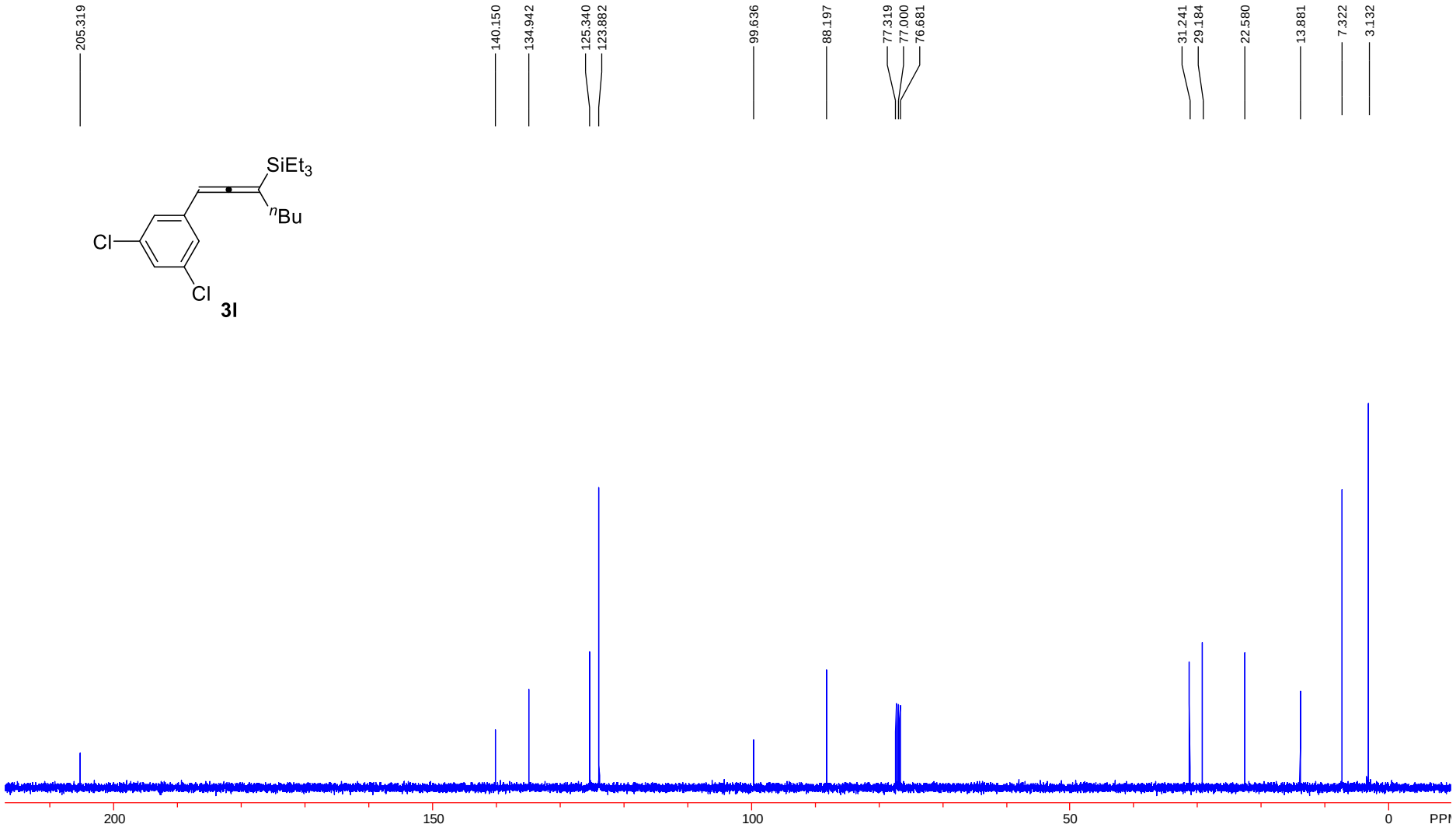
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Cl
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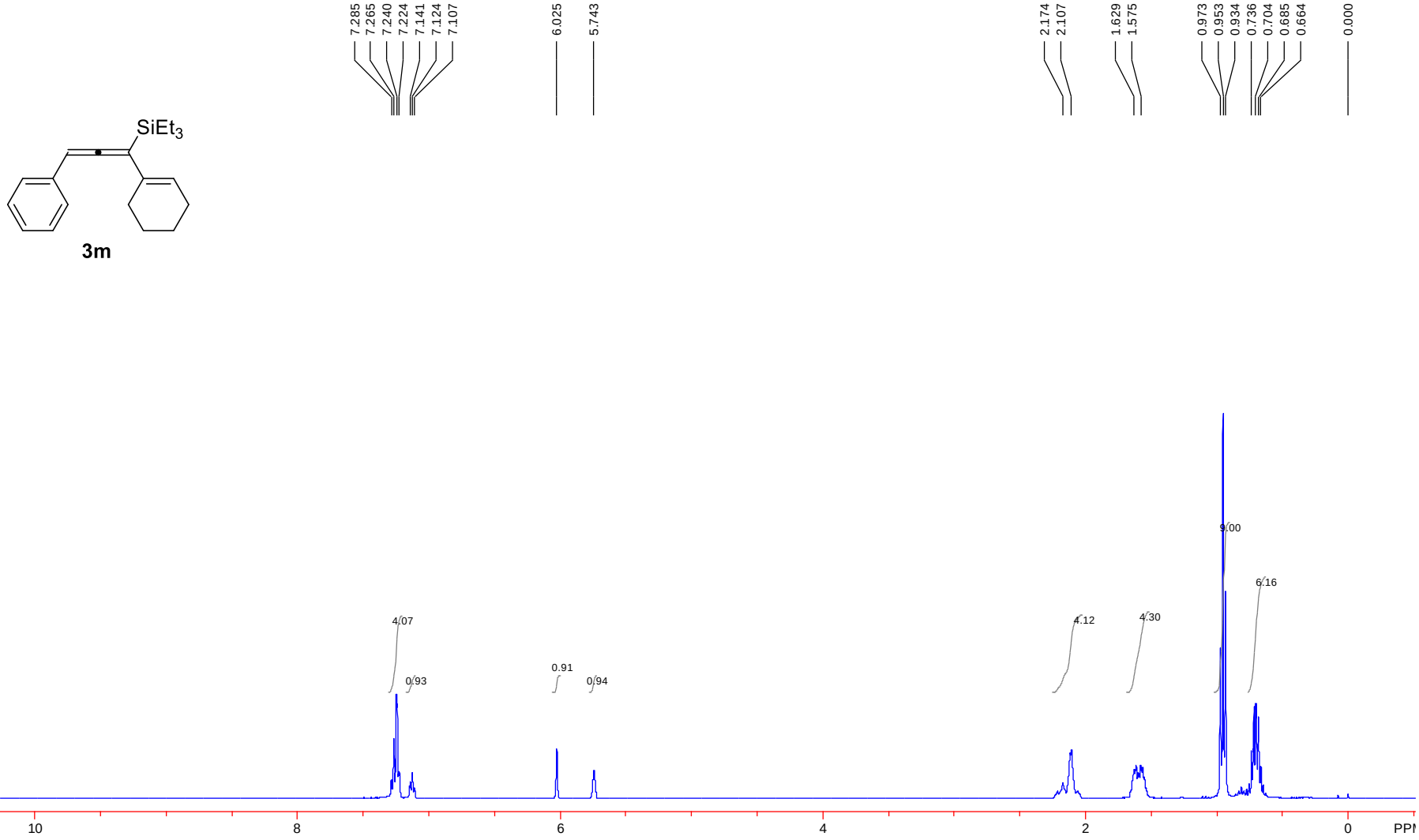
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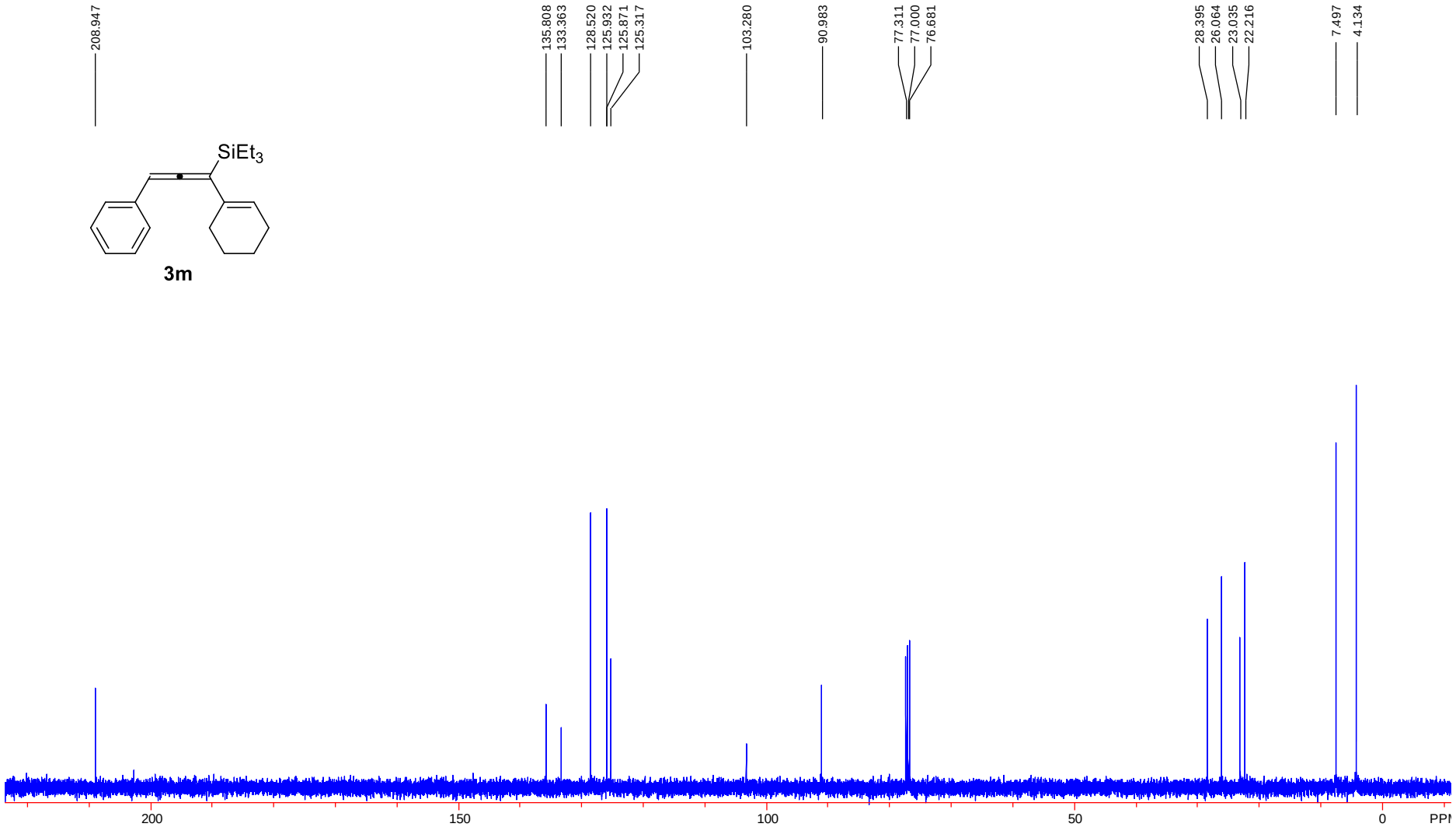
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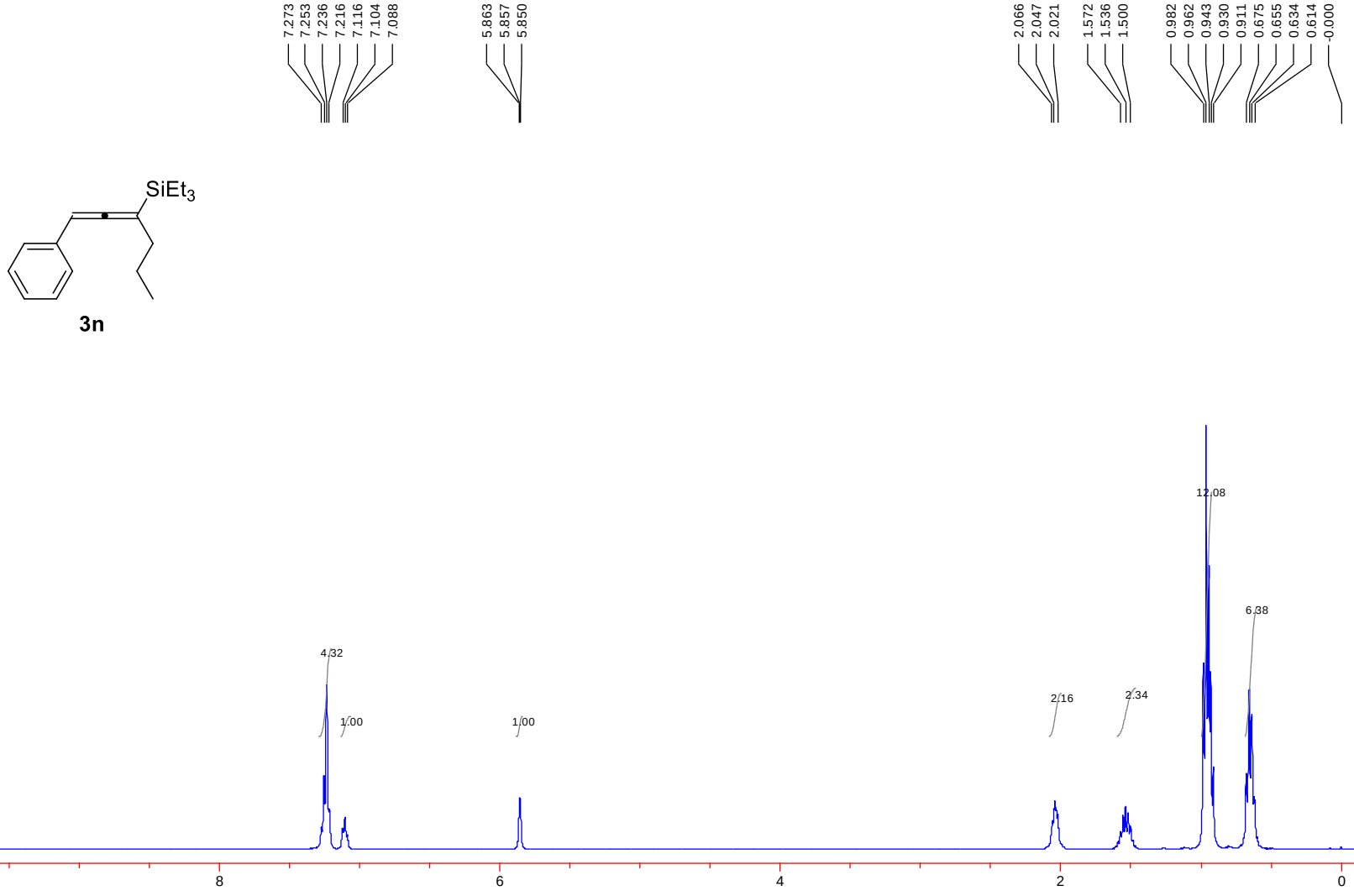
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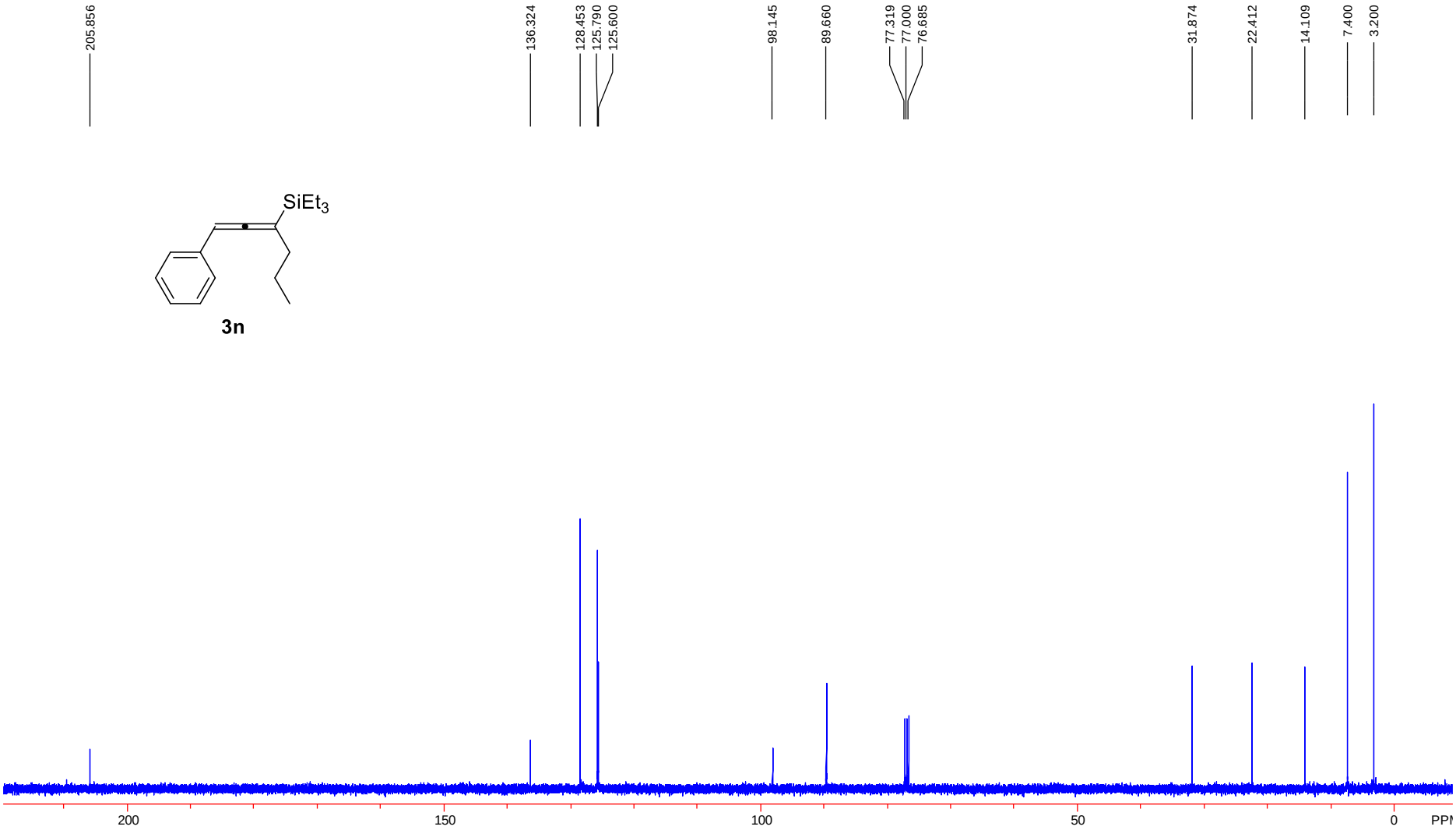
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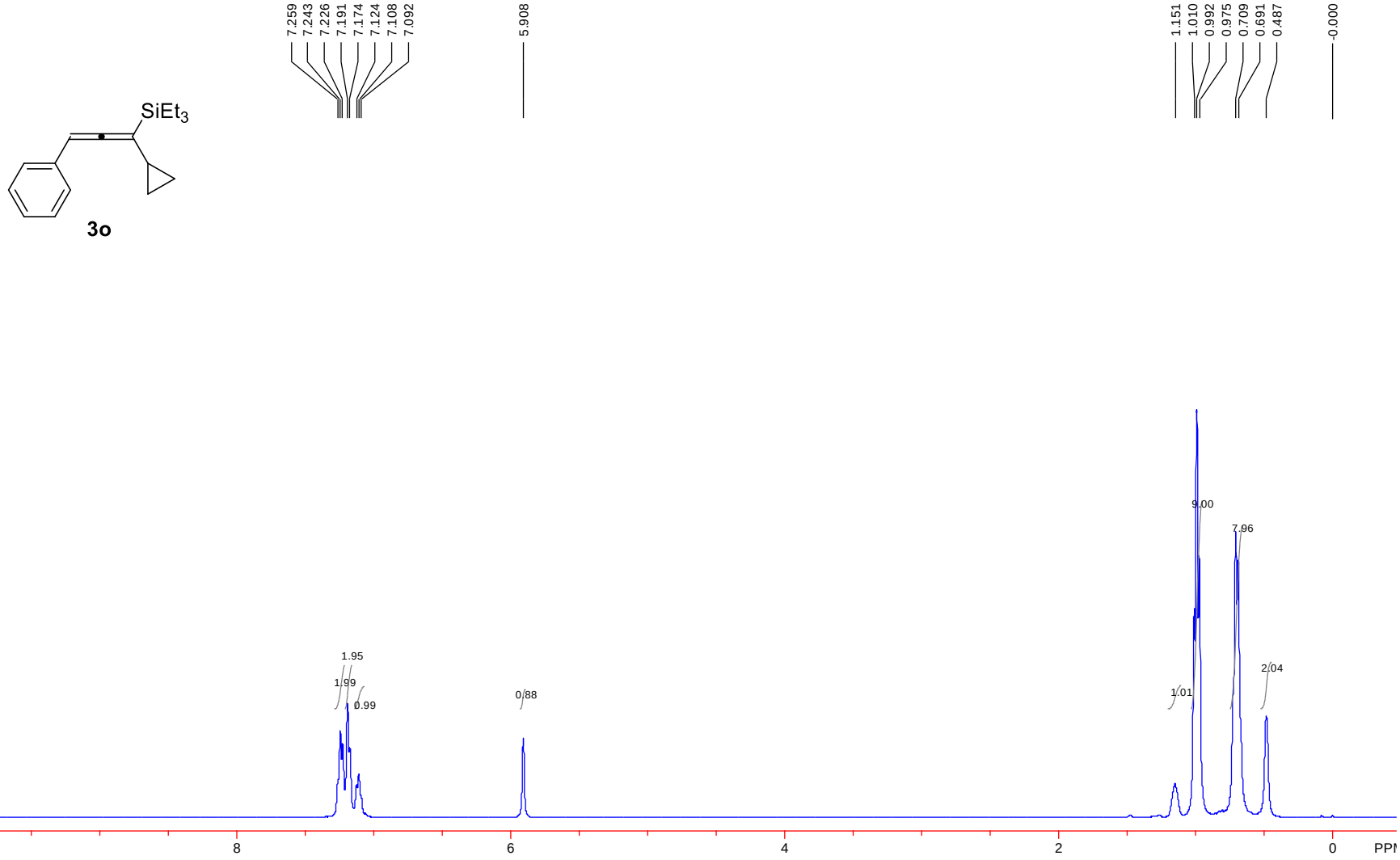
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0.709
0.691
0.487
-0.000
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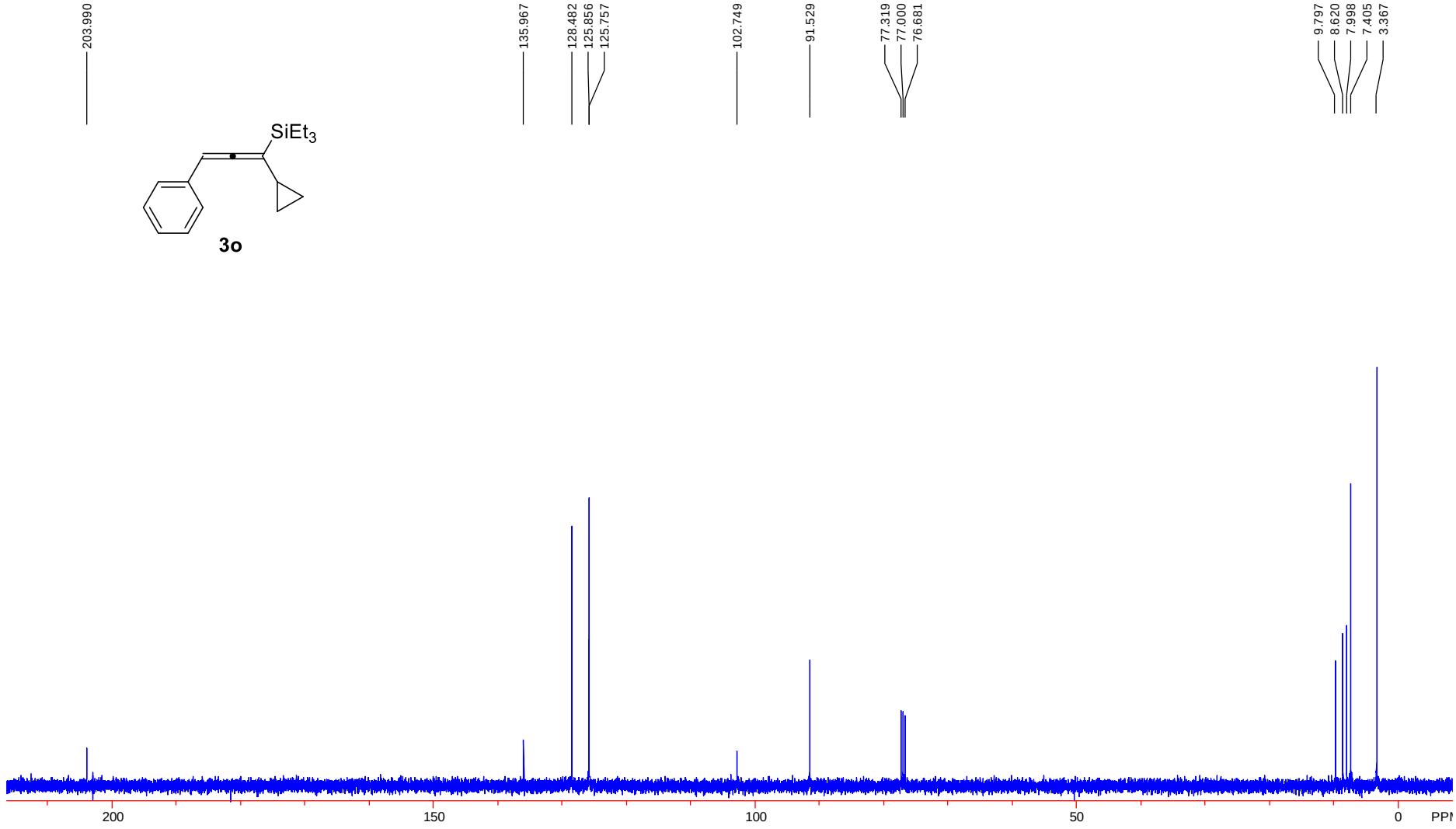
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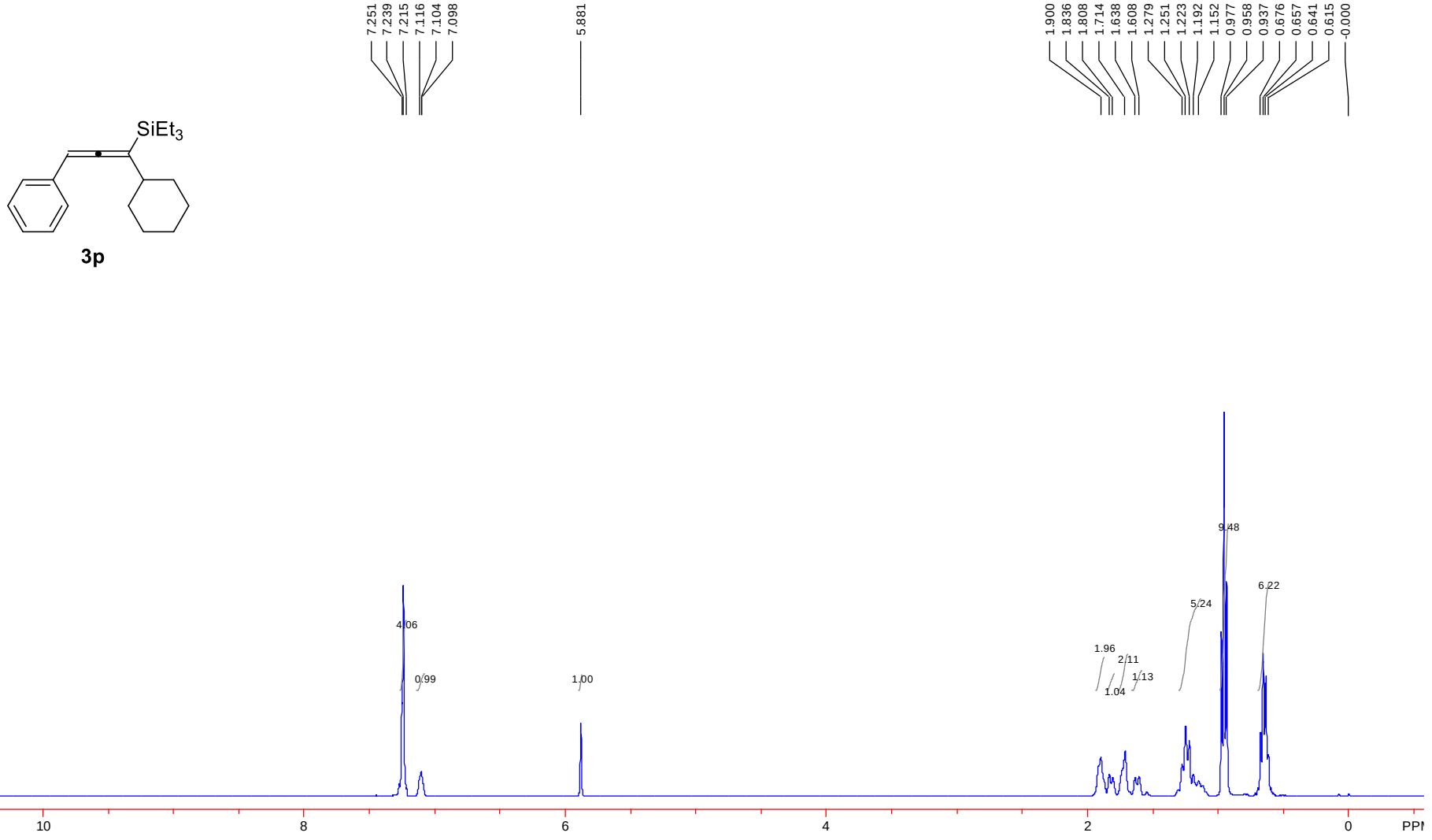
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0.615
-0.000
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3p
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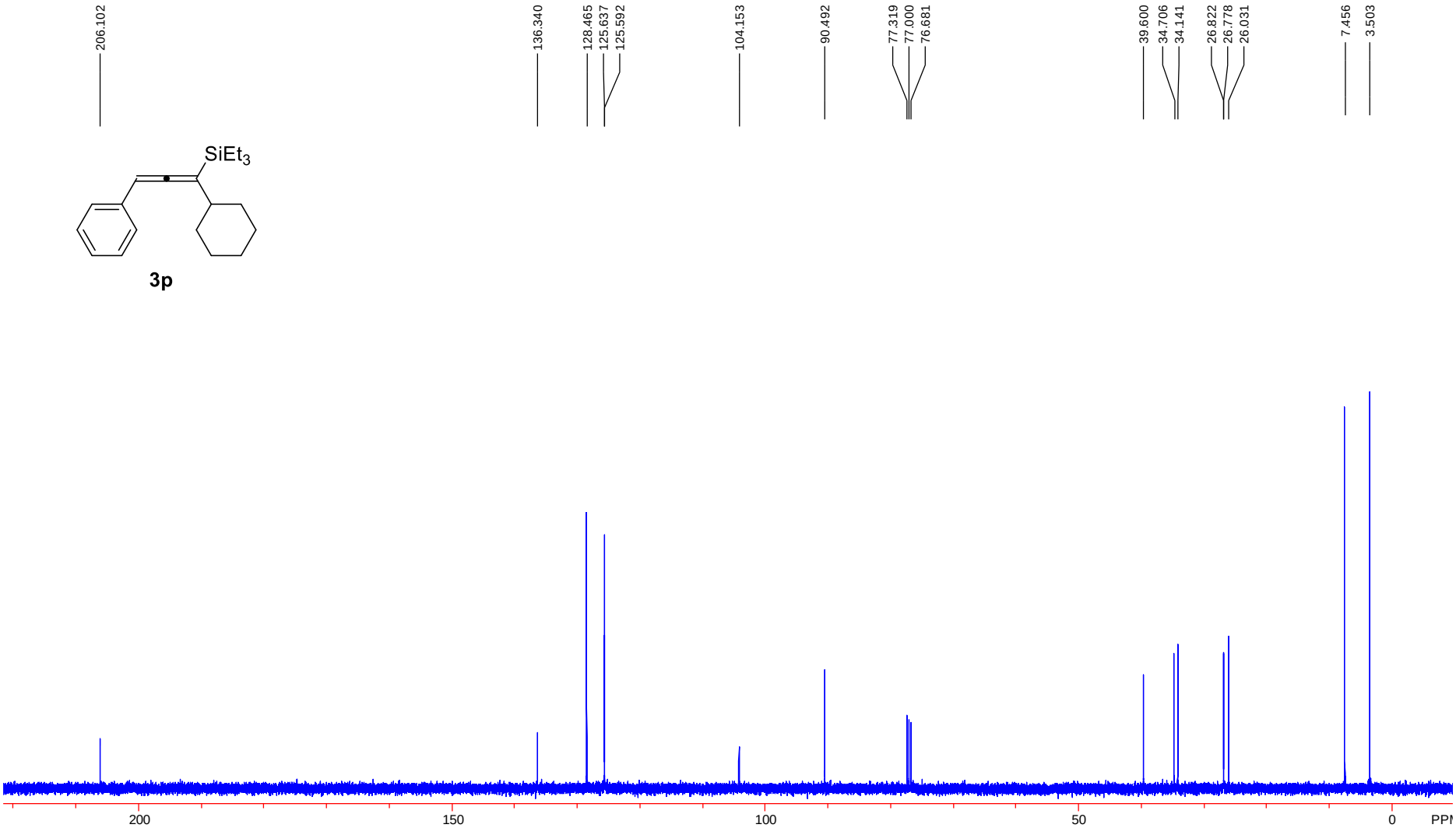
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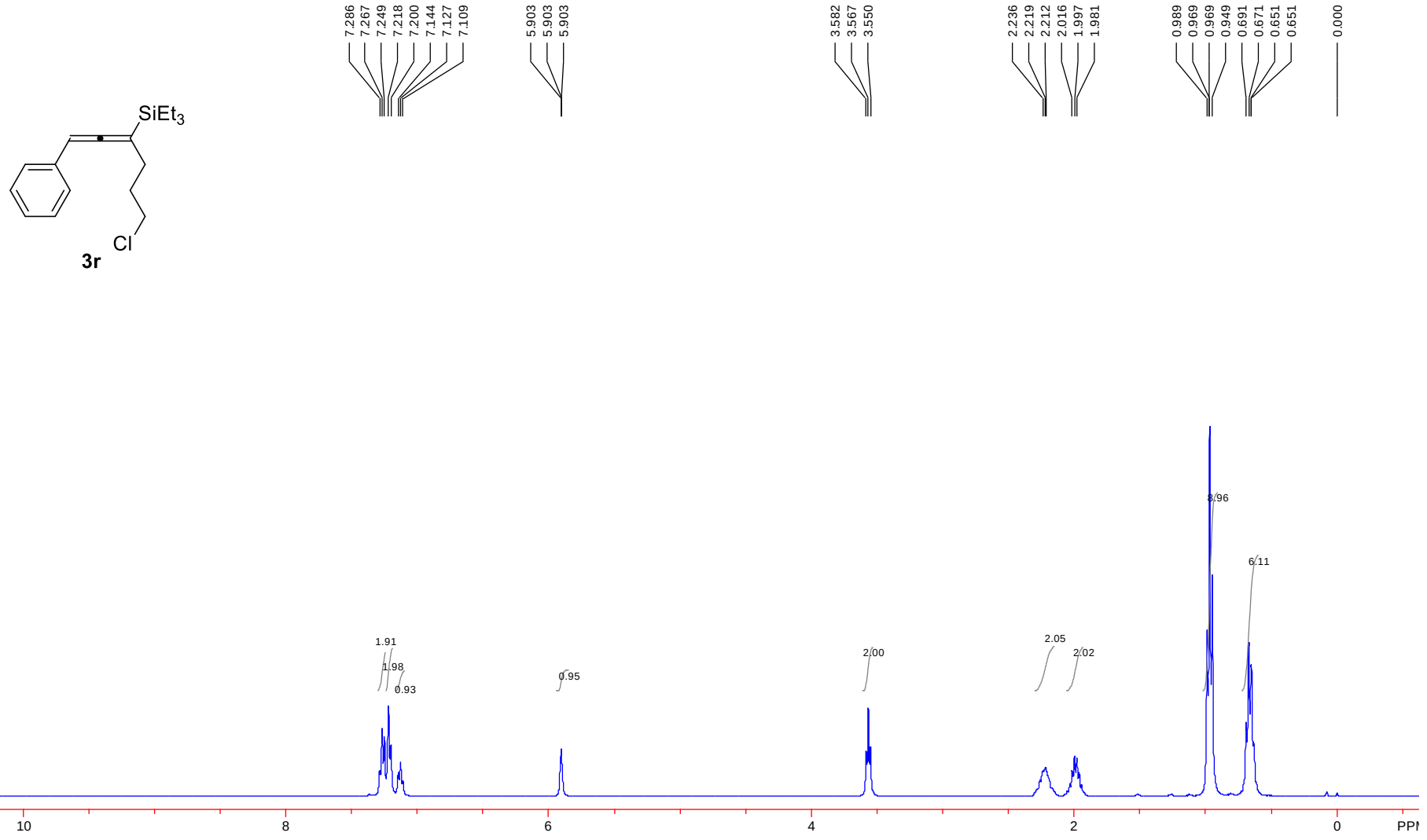
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3.550
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2.219
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0.969
0.949
0.691
0.671
0.651
0.651
0.000
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Cl
3r
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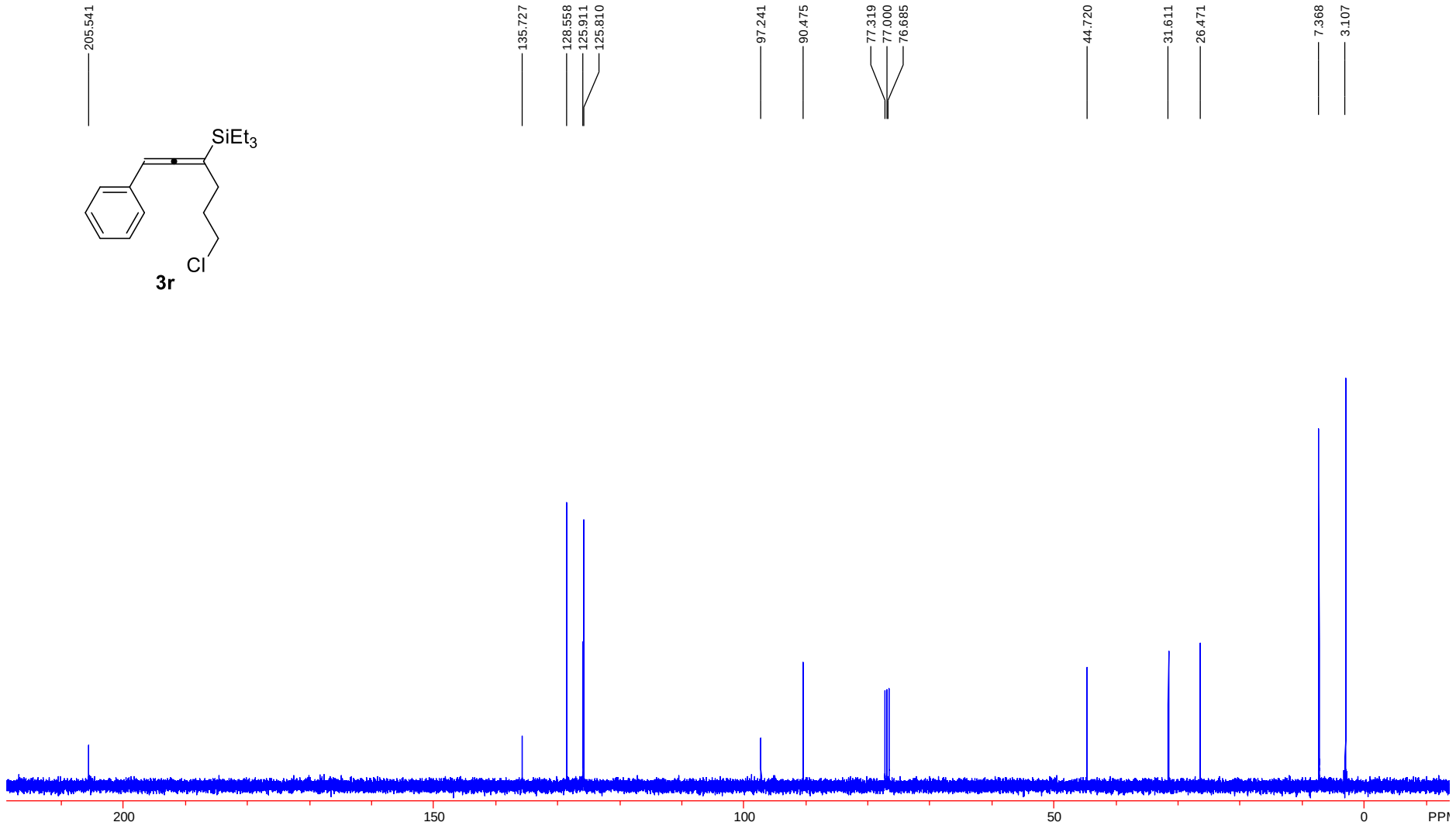
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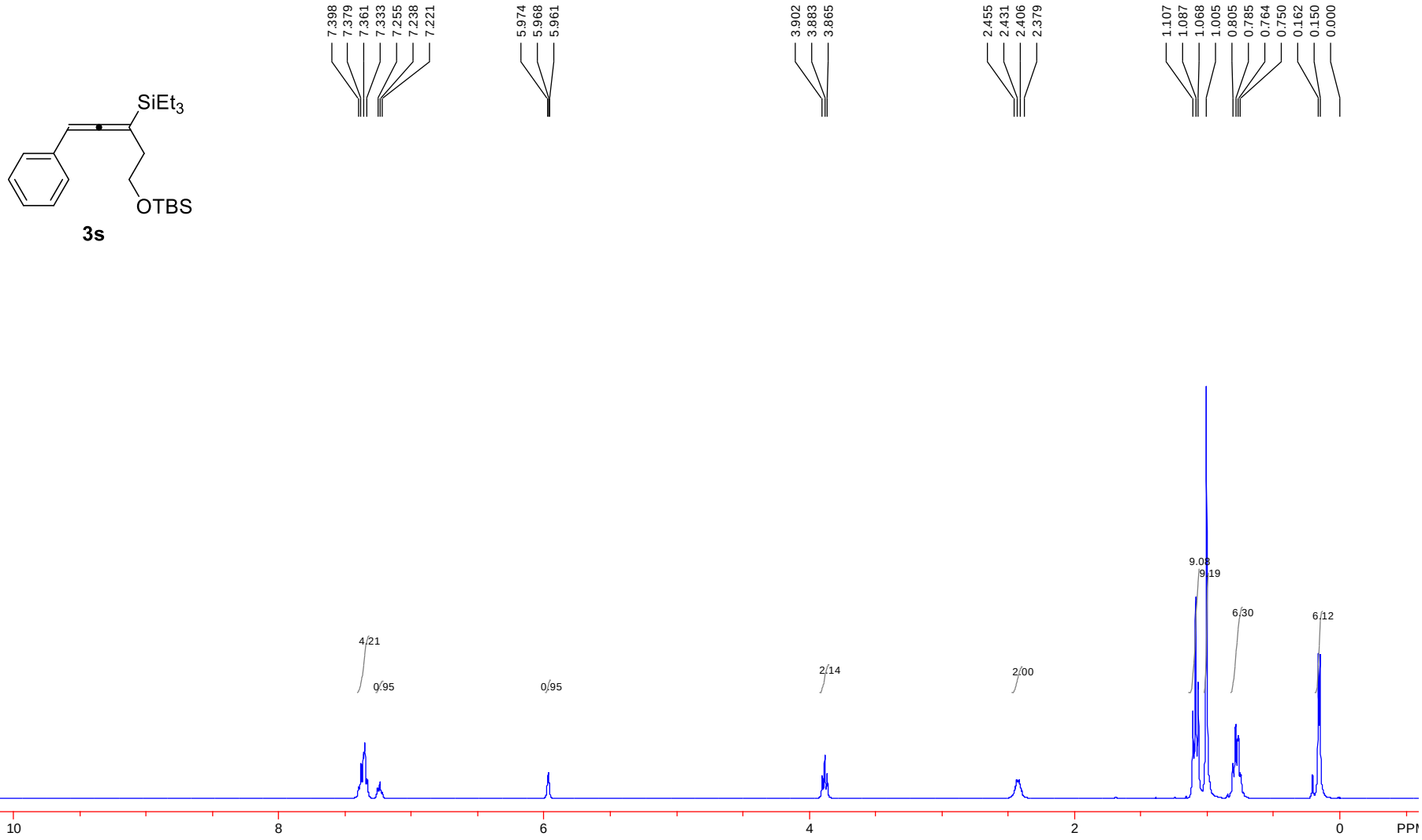
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2.431
2.406
2.379
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1.087
1.068
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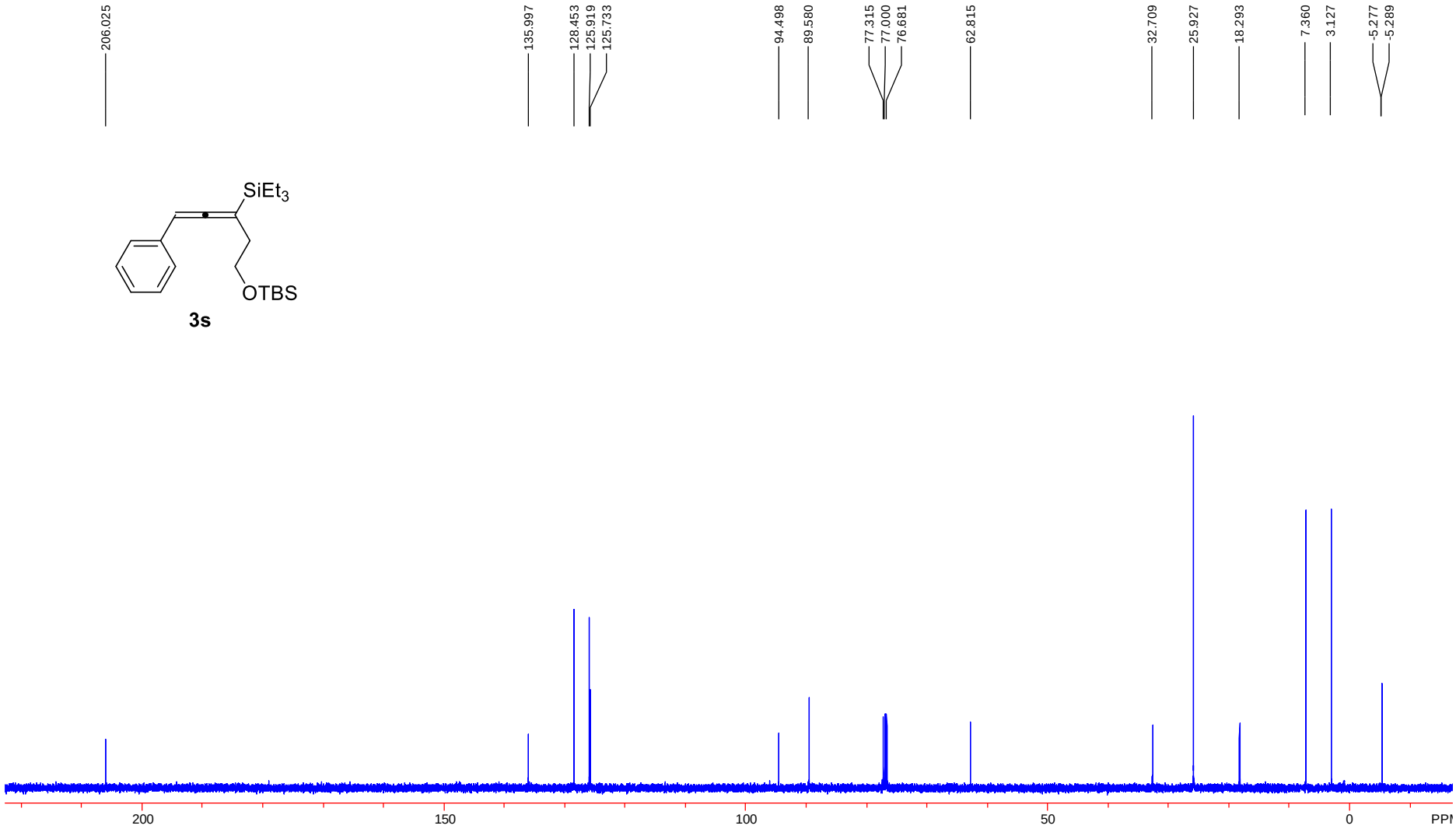
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3s
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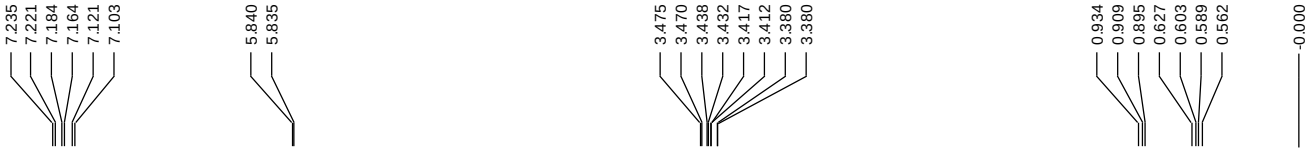
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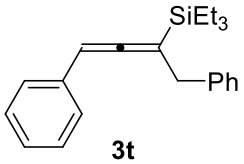
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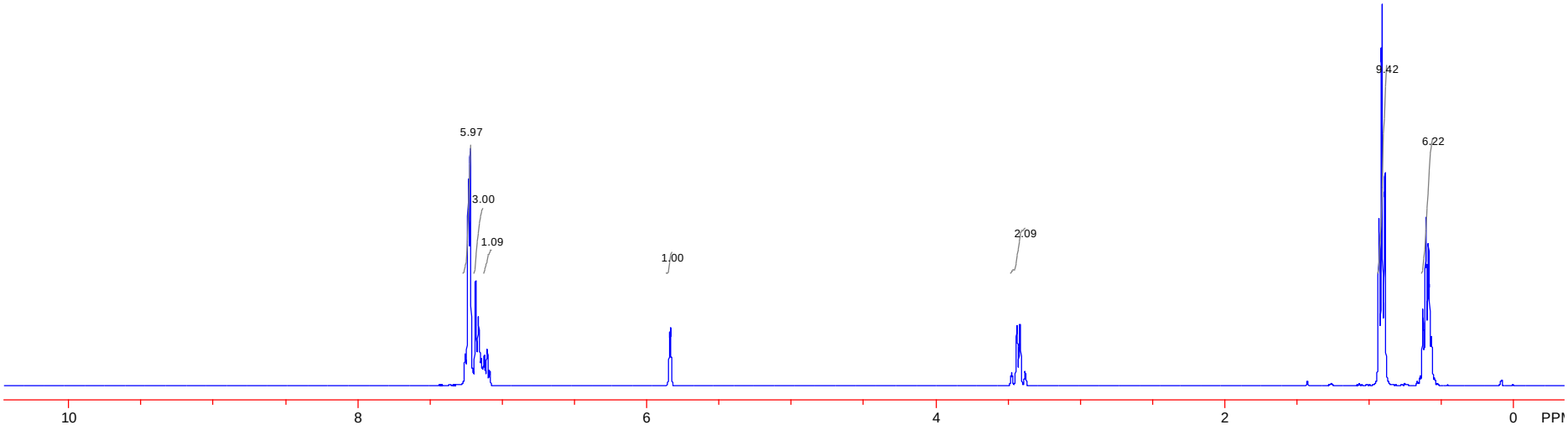
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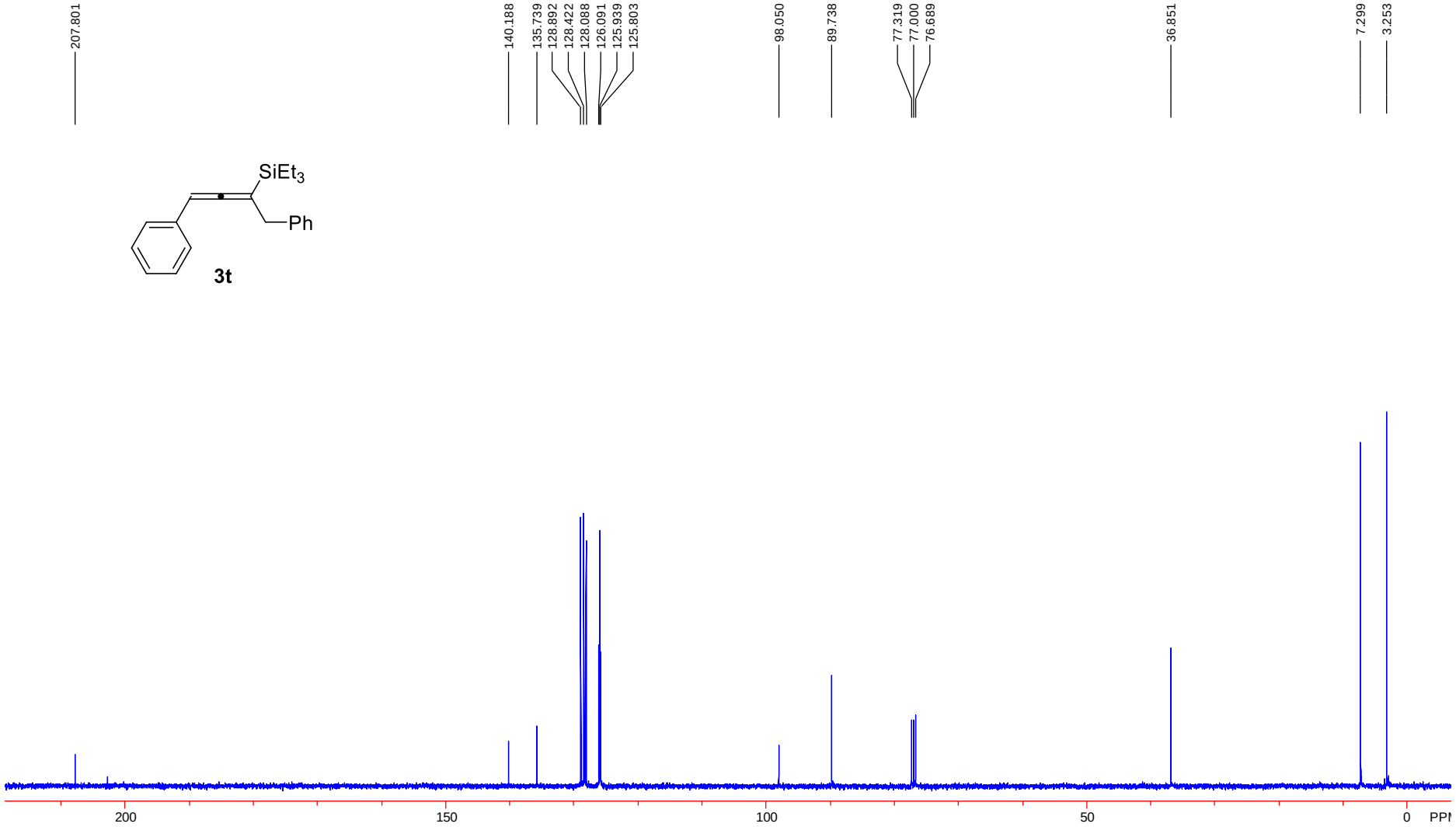
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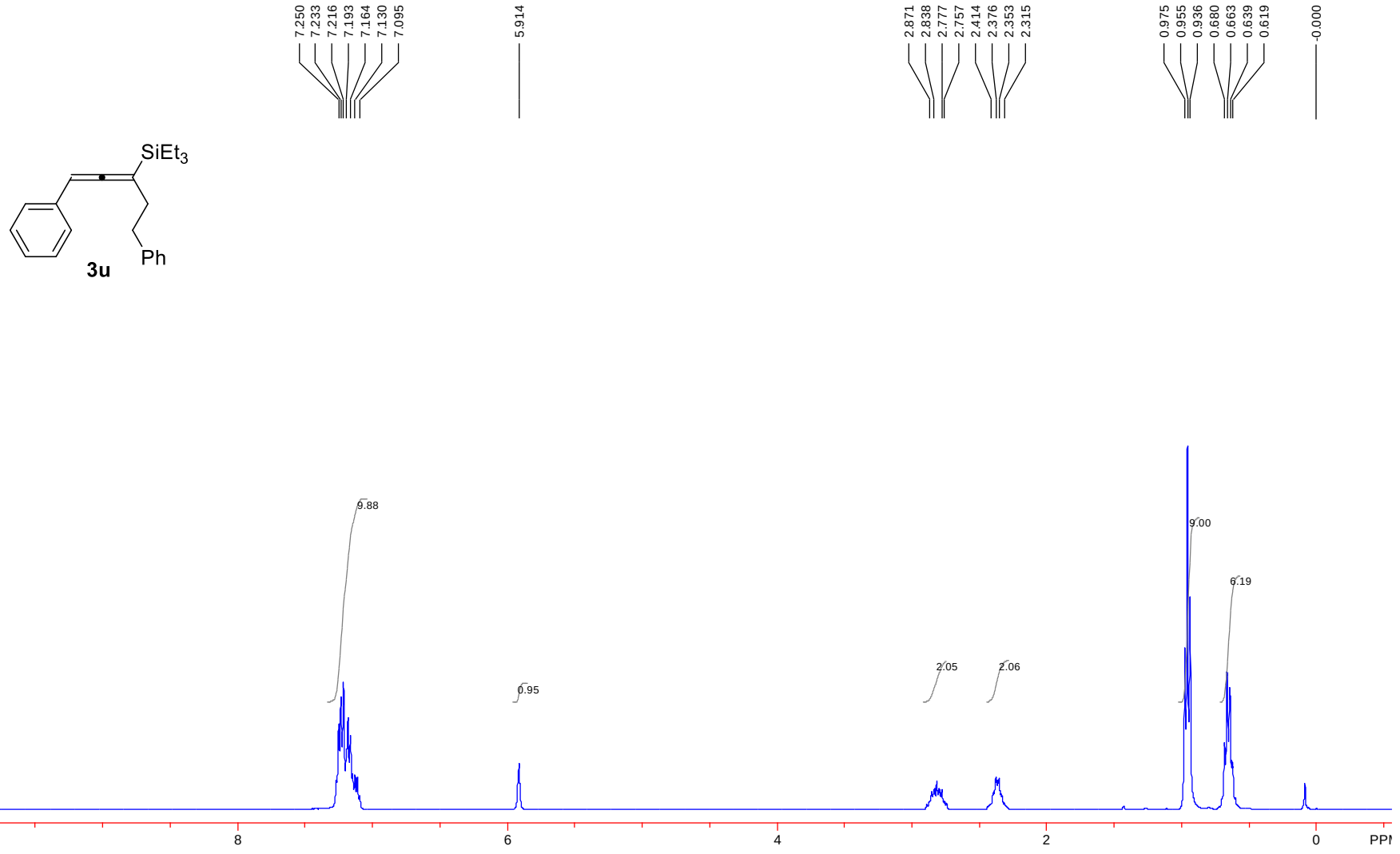
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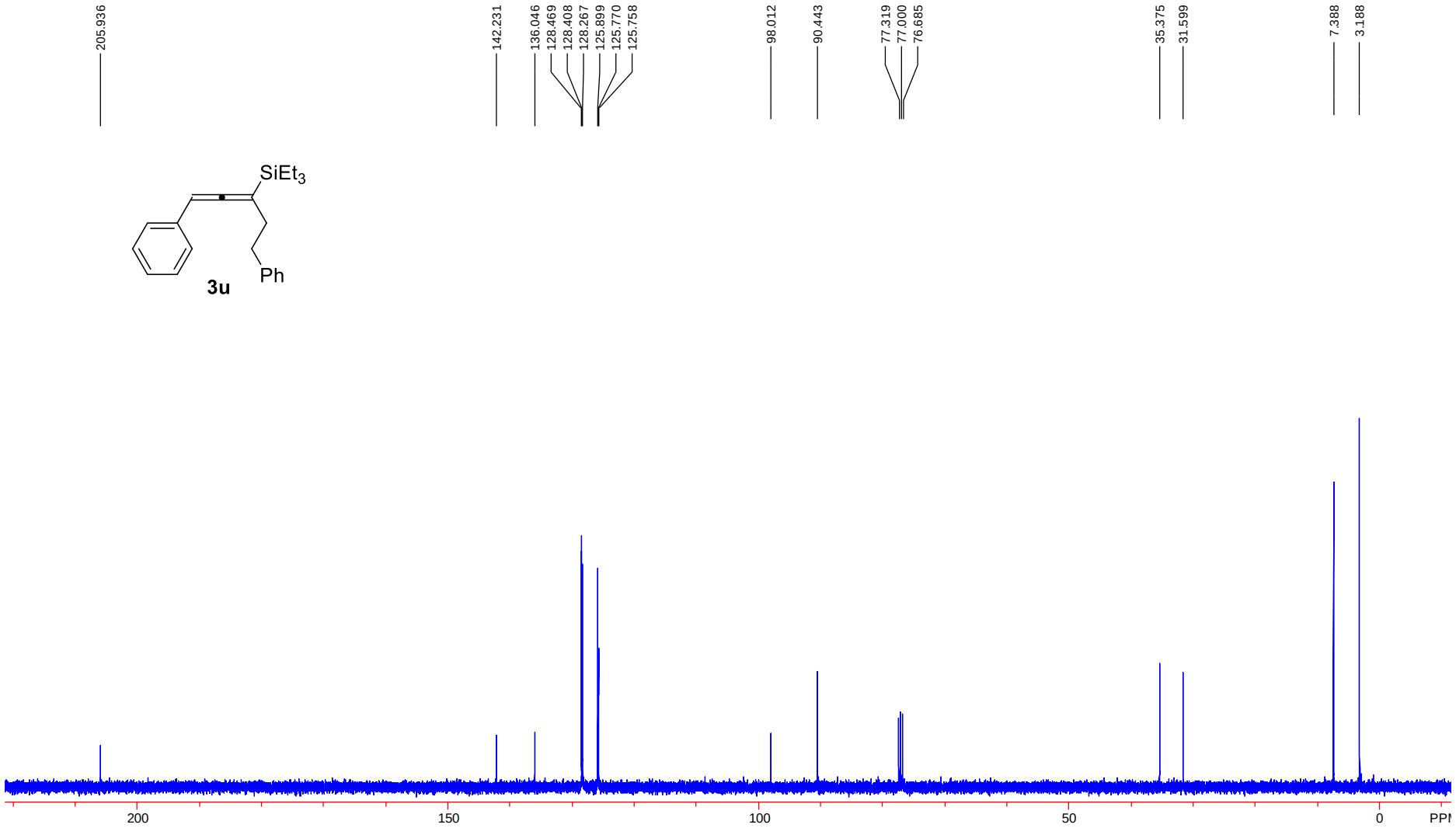
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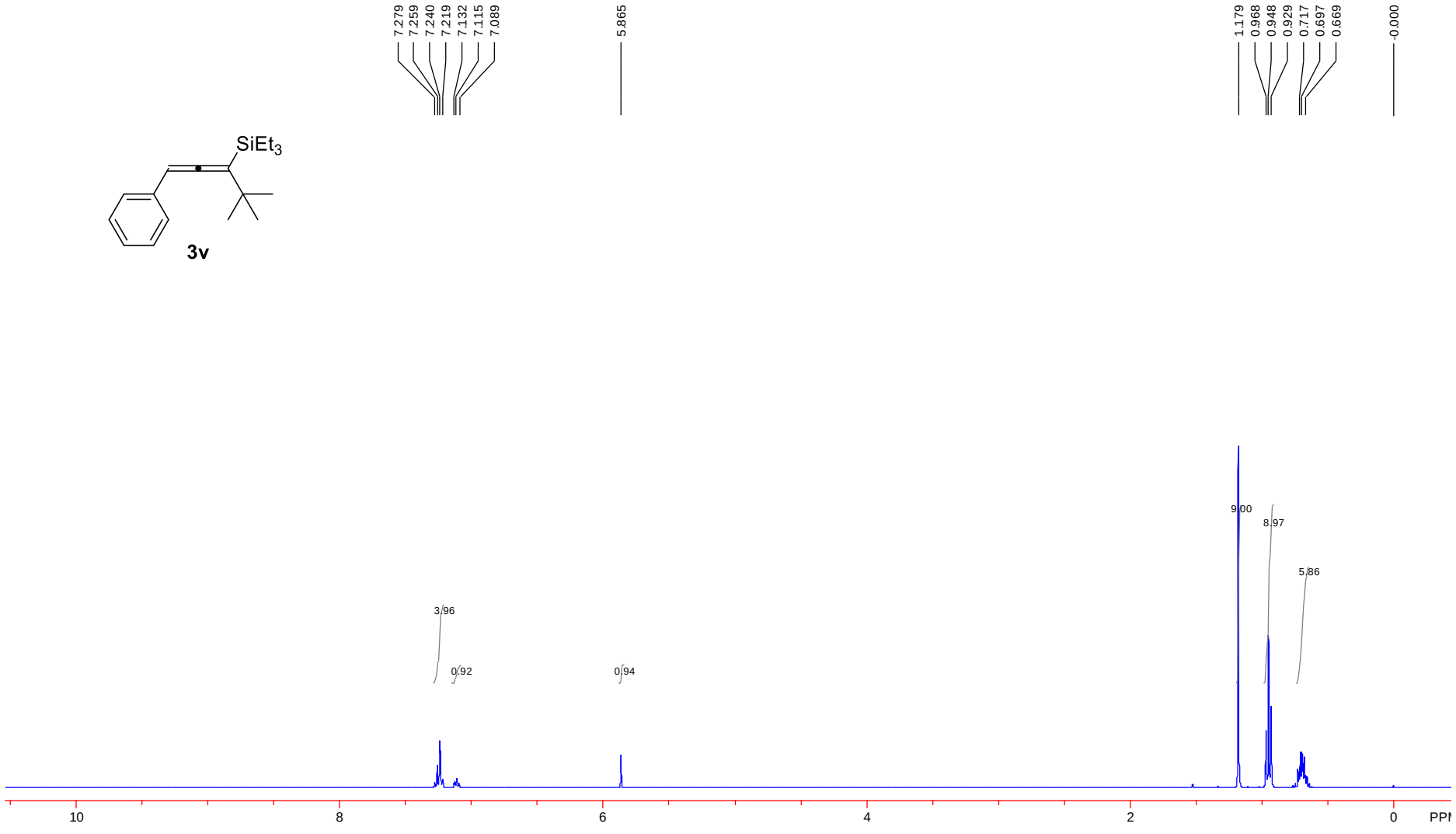
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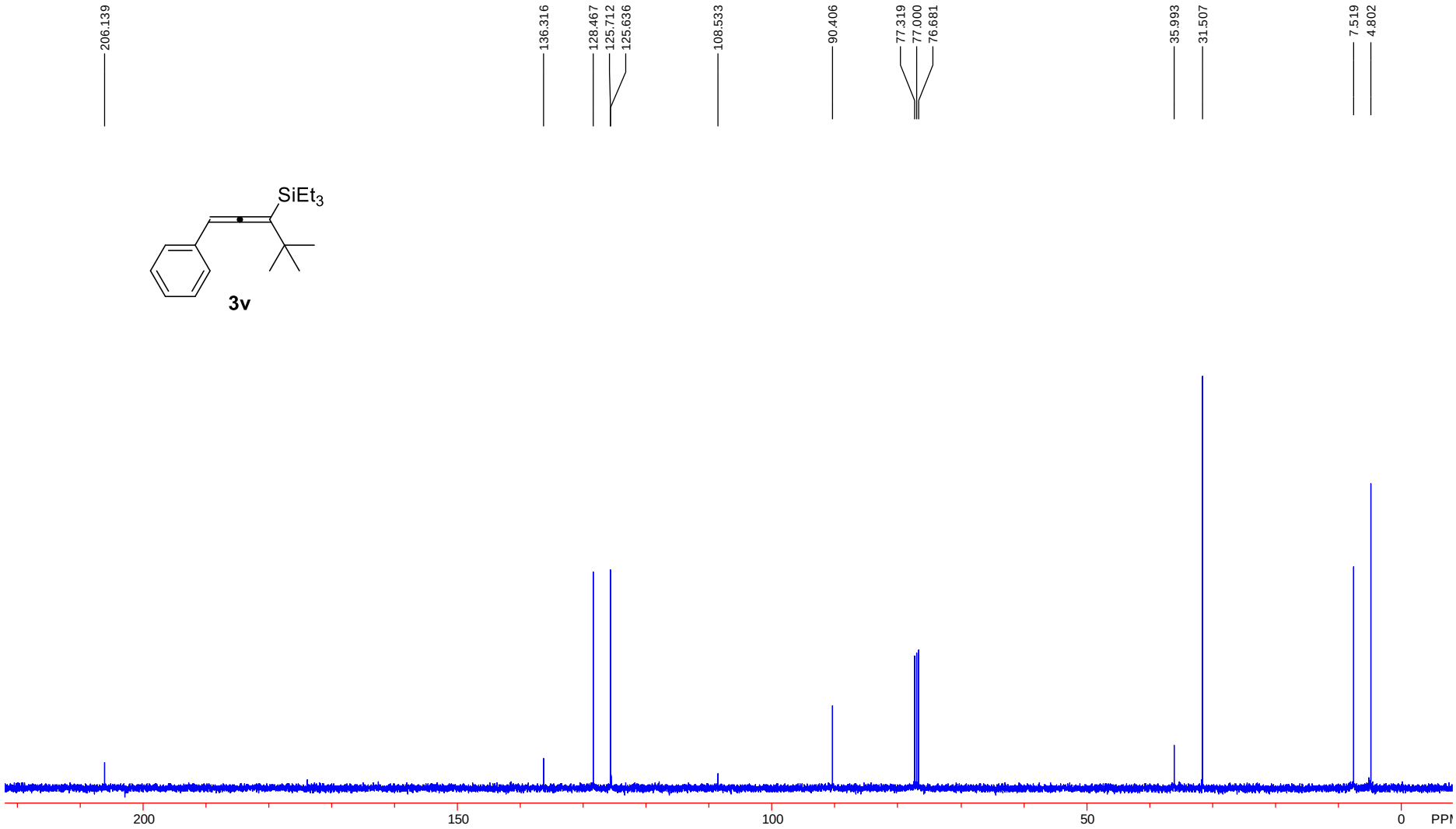
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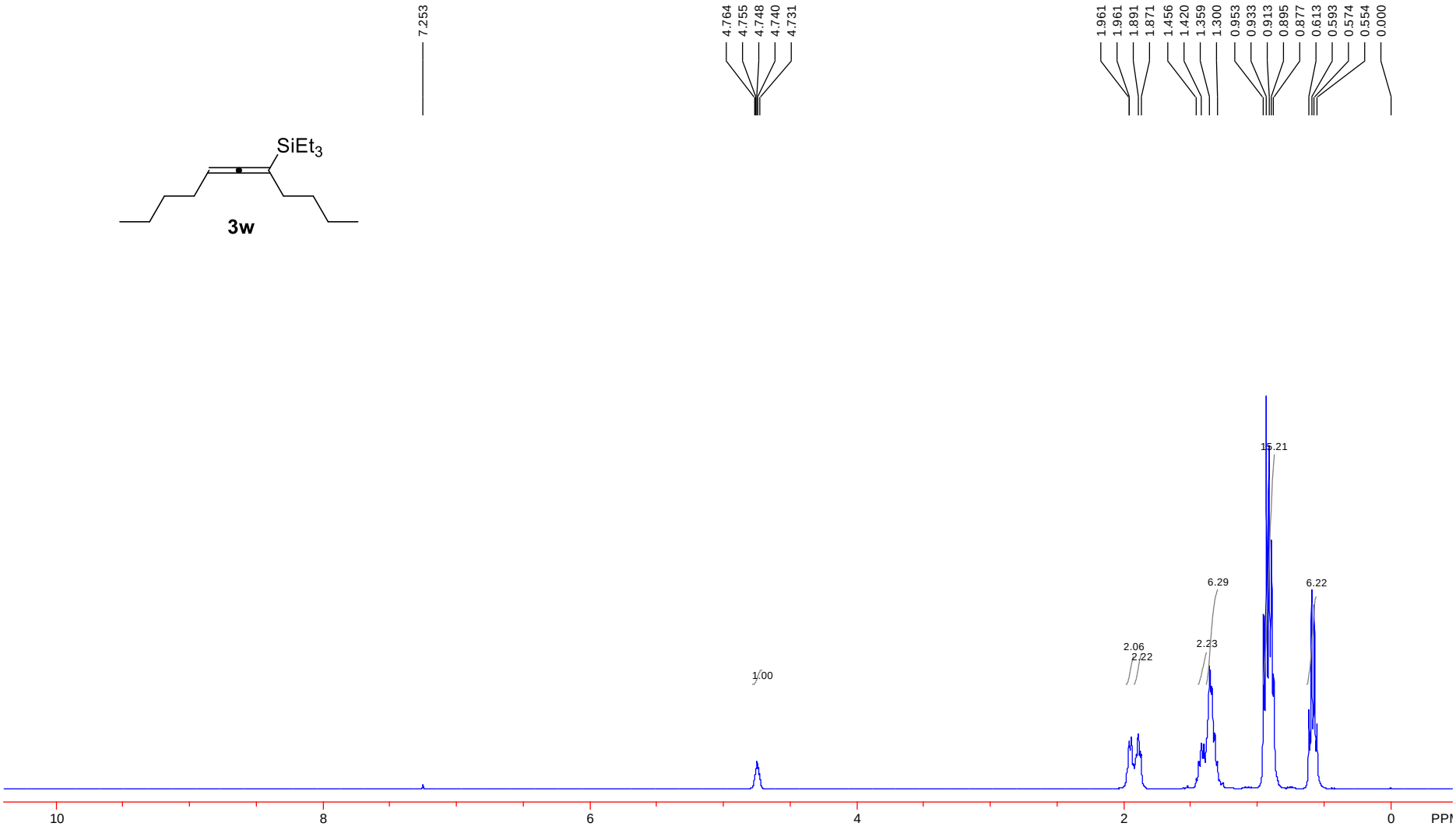
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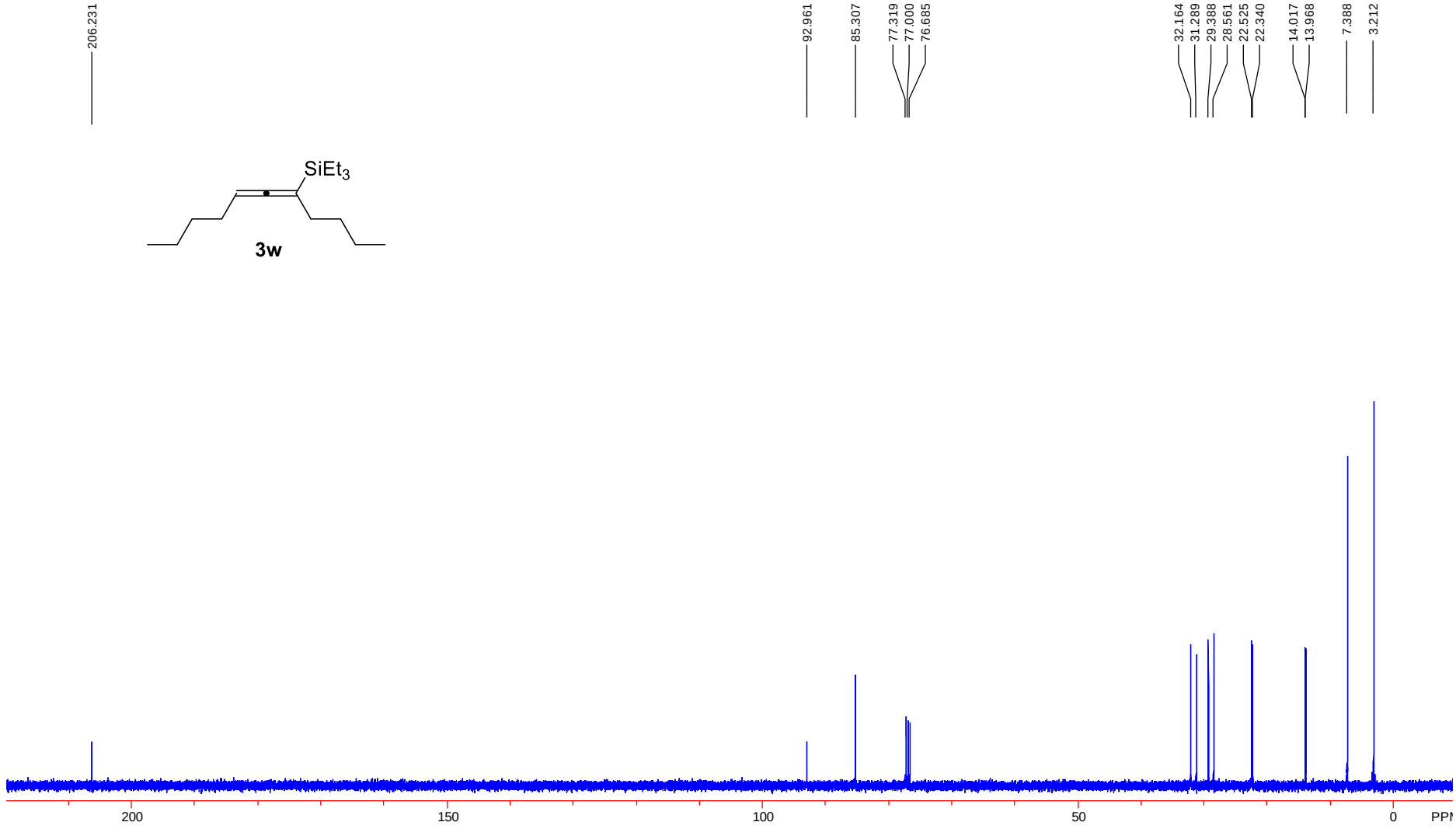
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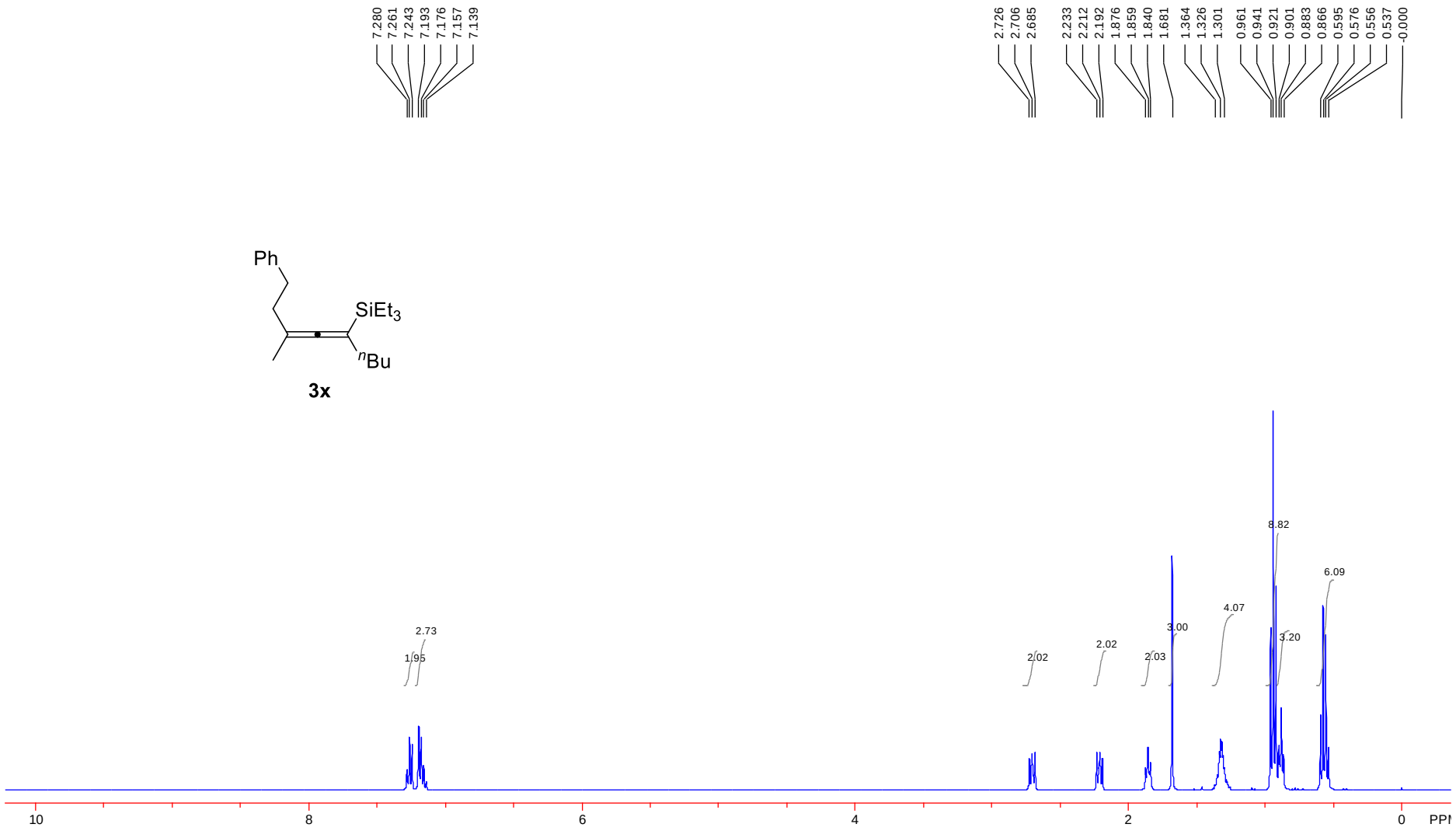
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0.883
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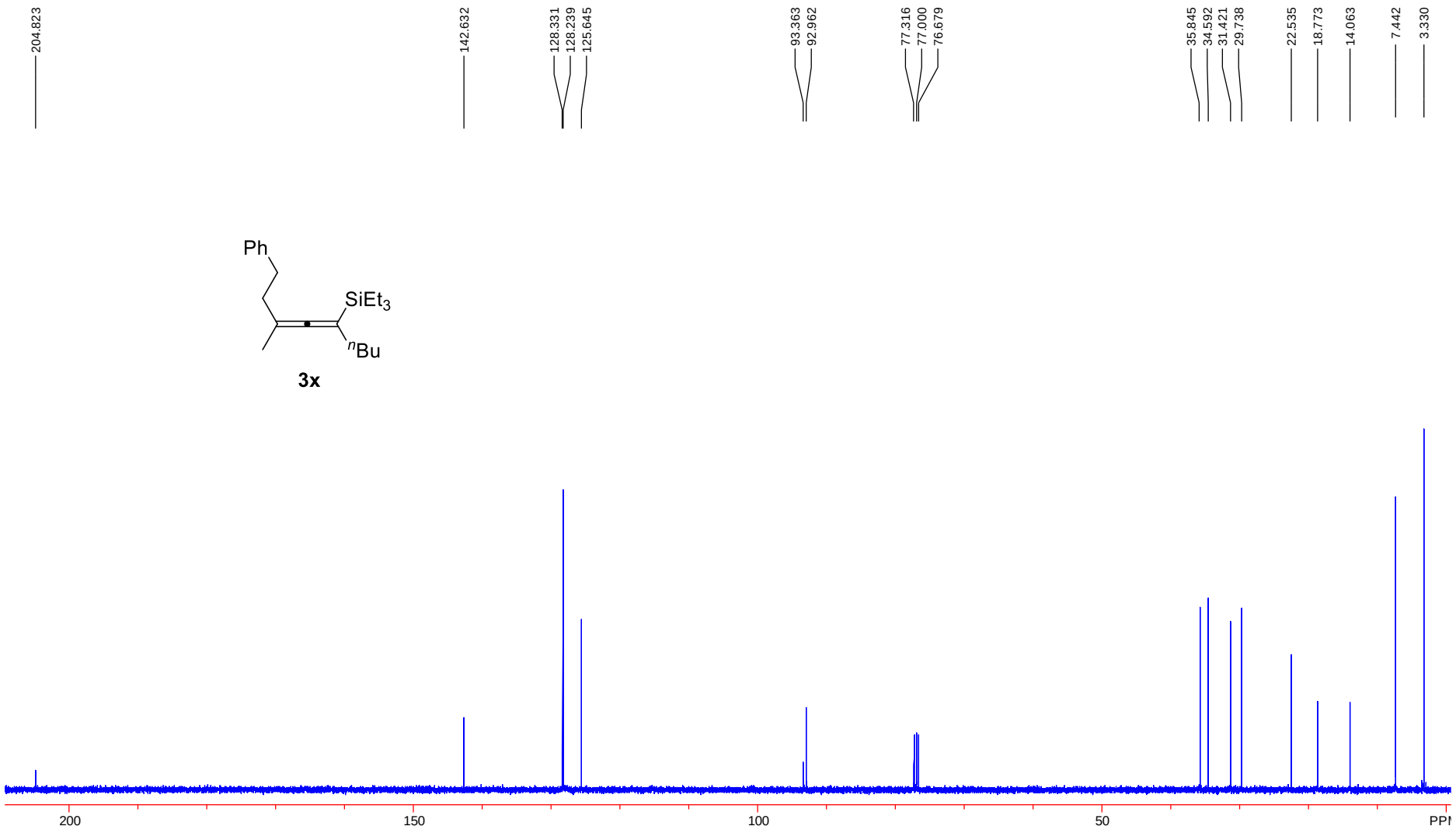
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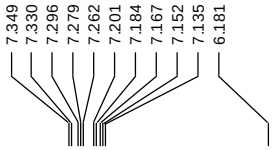
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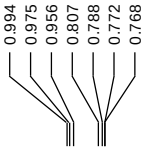
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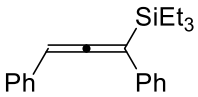
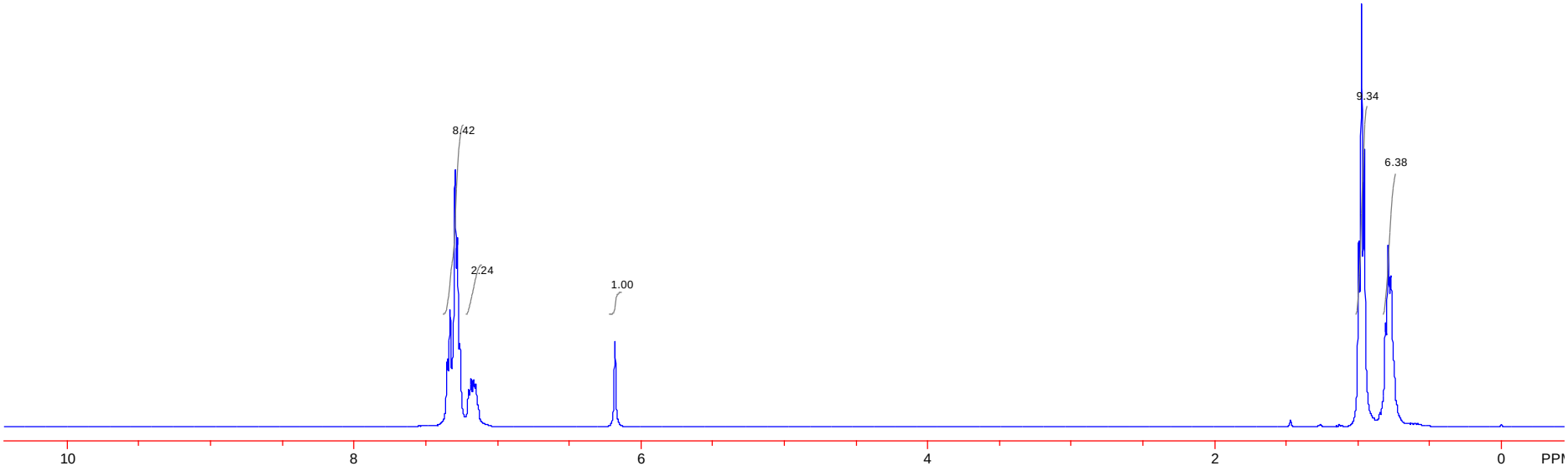

SiEt3
Ph
Ph

4a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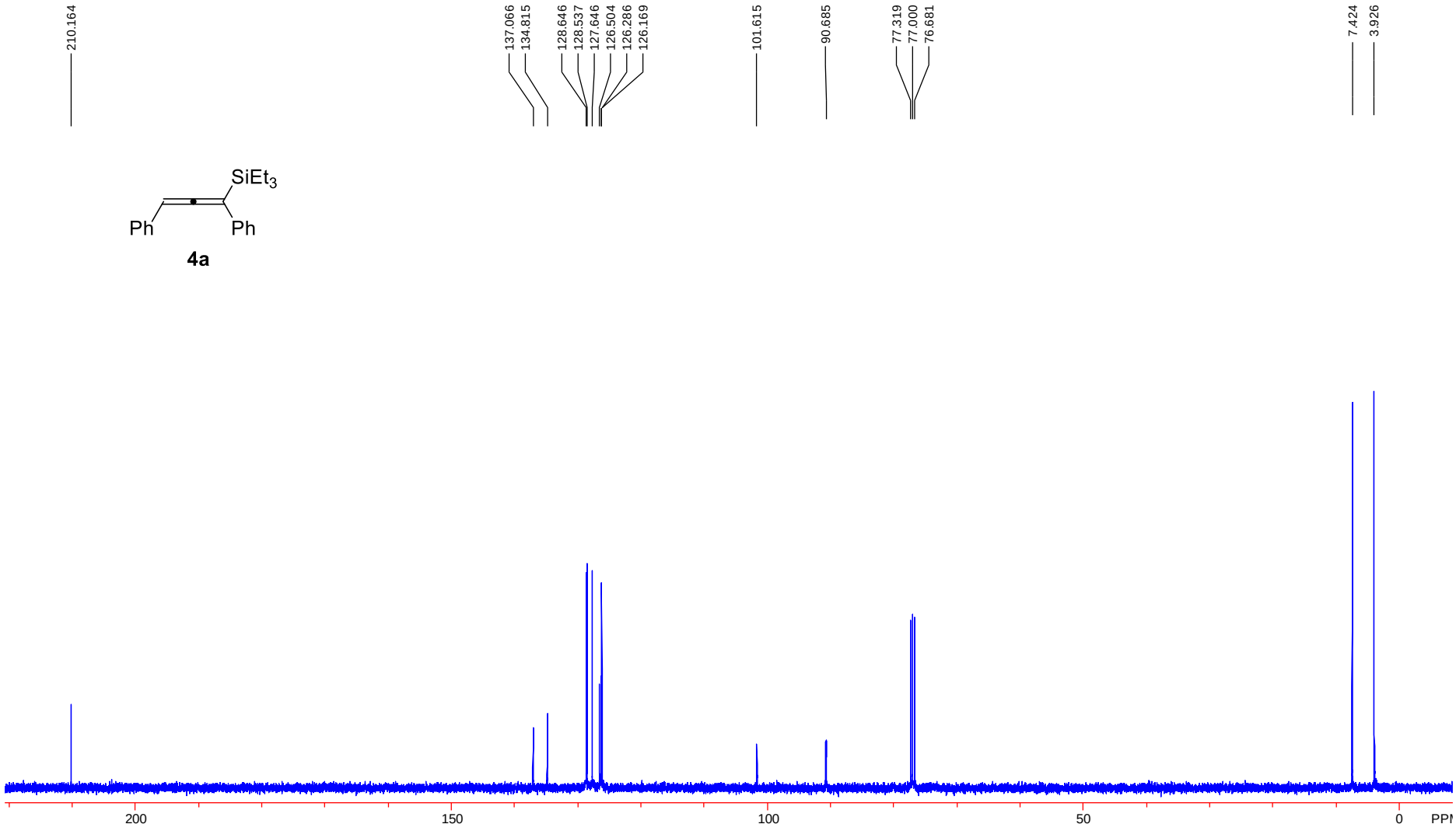
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126.286
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SiEt3
Ph
Ph
4a
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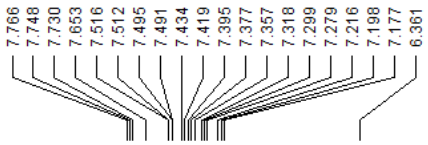
PPM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7.491
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7.395
7.377
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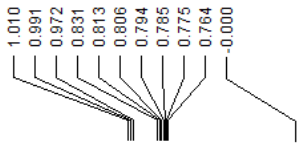
7.299
7.279
7.216
7.198
7.177
6.361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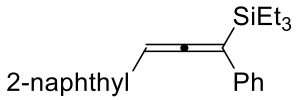
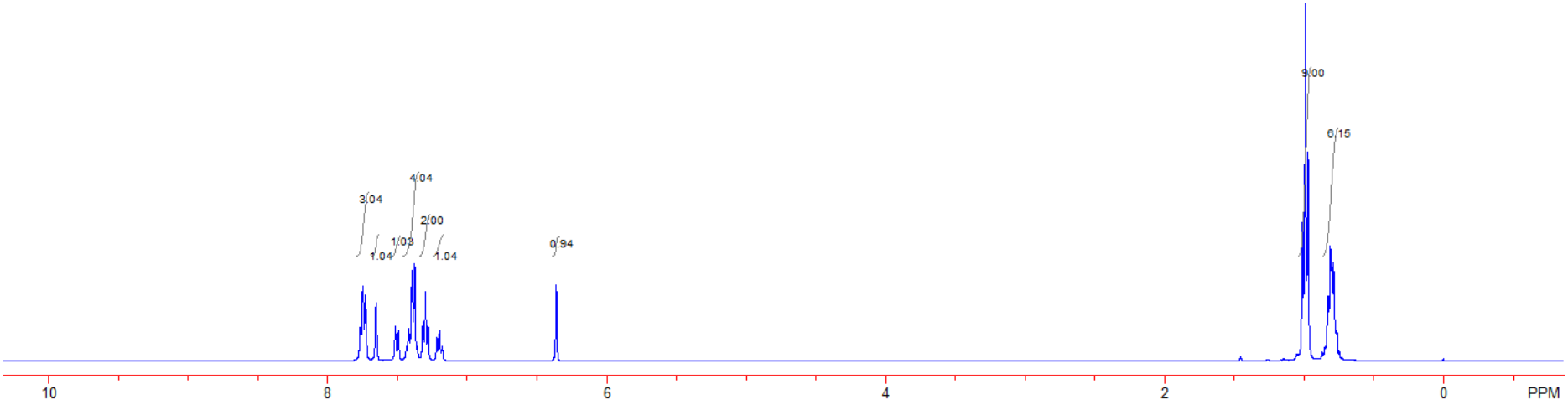
0.785
0.775
0.764
-0.000


SiEt3
2-naphthyl
Ph

4b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1.04
1.04
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10
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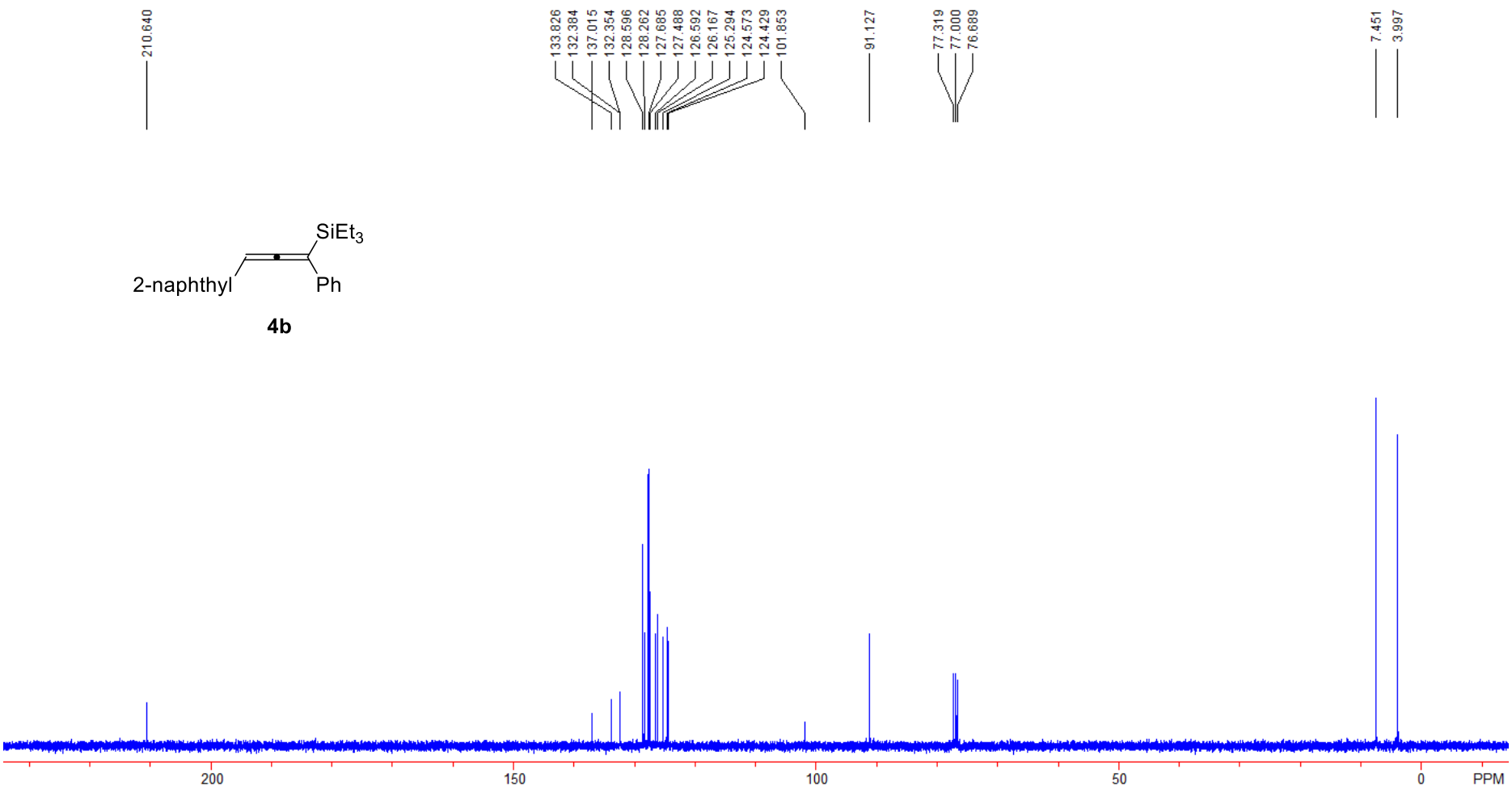
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127.685
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126.592
126.167
125.294
124.573
124.429
101.853
91.127
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7.451
3.997
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2-naphthyl
Ph
200
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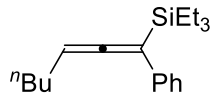
50
0
PPM

4b


SiEt3
nBu
Ph

4c

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5.078
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2.081
2.064
2.047
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1.439
1.421
1.404
1.391
1.373
1.356
1.338
0.966
0.947
0.928
0.898
0.881
0.746
0.728
0.709
0.689
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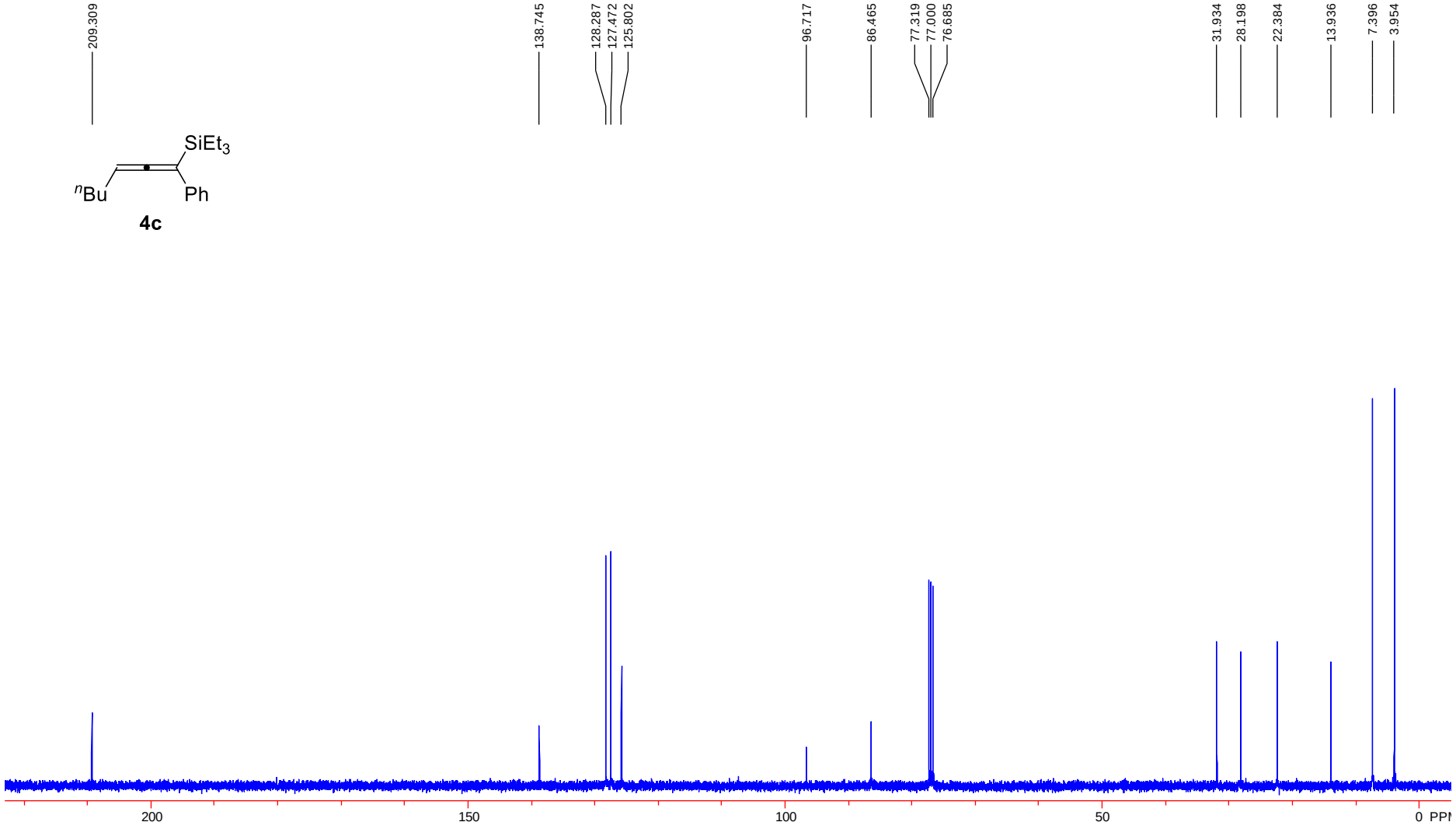
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nBu
Ph
200
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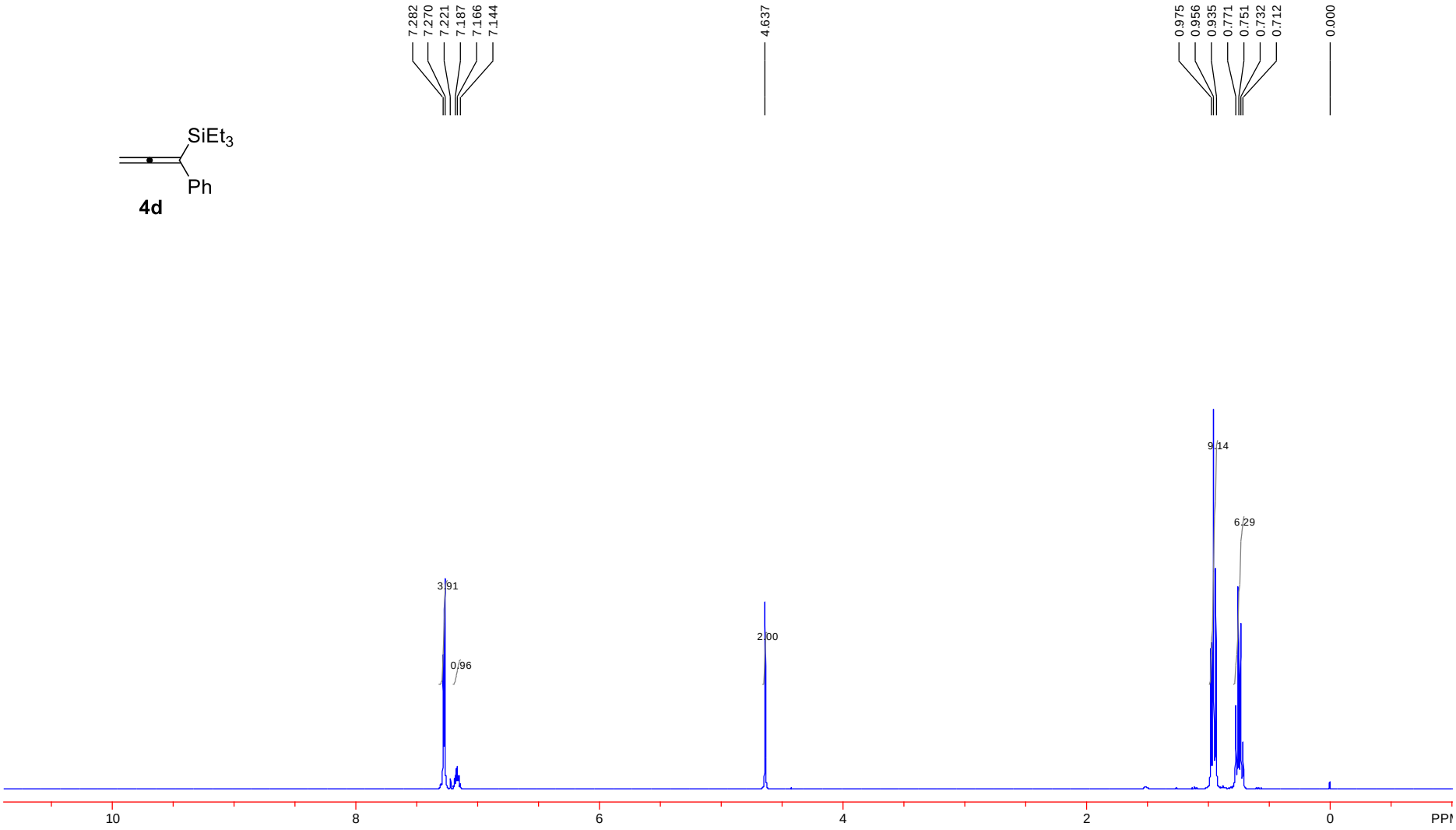
100
50
0 PPM

4c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0.732
0.712
0.000
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Ph
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2.00
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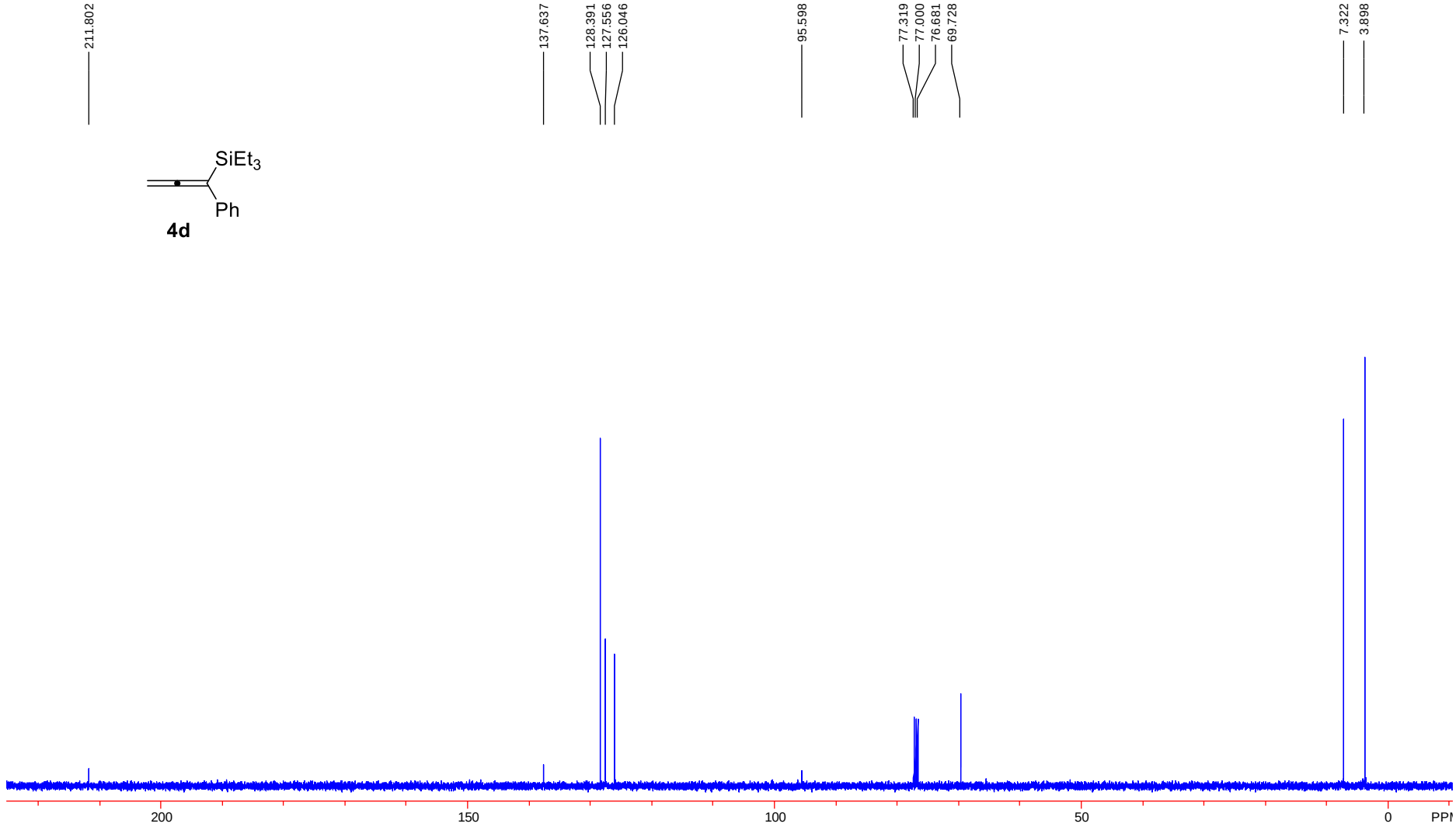
10
8
6
4
2
0
PPM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77.000
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3.898
SiEt3
Ph
4d
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100
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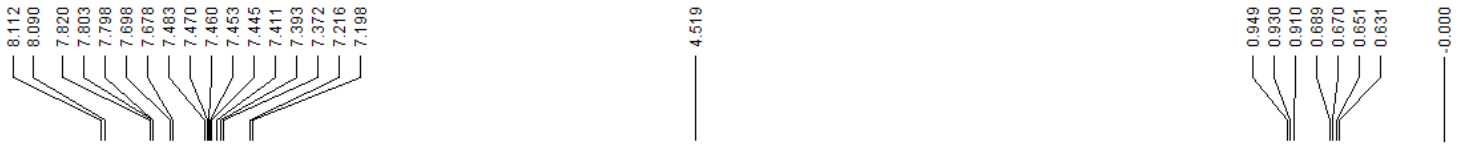
PPM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7.798
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7.483
7.470
7.460
7.453
7.445
7.411
7.393
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0.930
0.910
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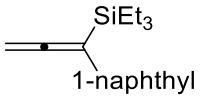
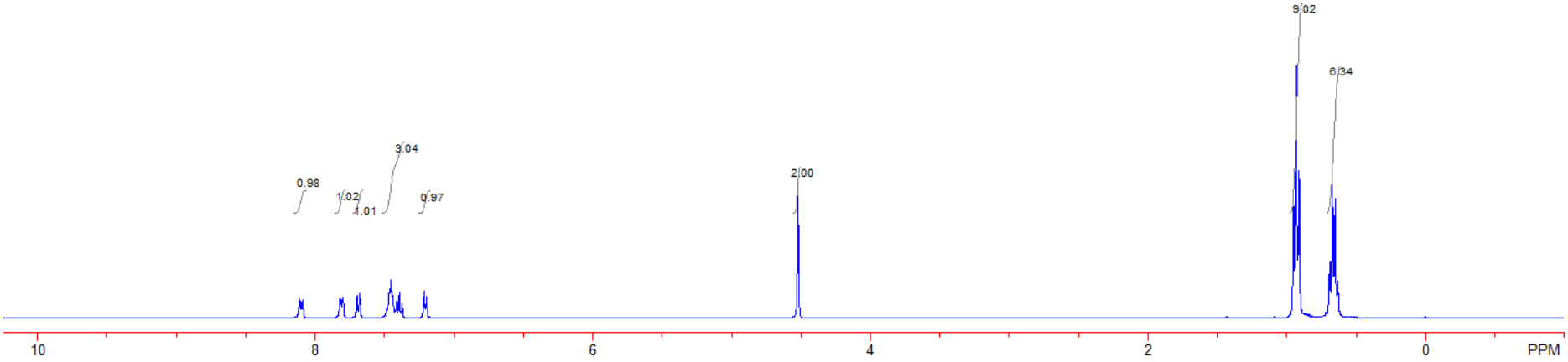
0.670
0.651
0.631
-0.000


SiEt3
1-naphthyl

4e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6.34
10
8
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4
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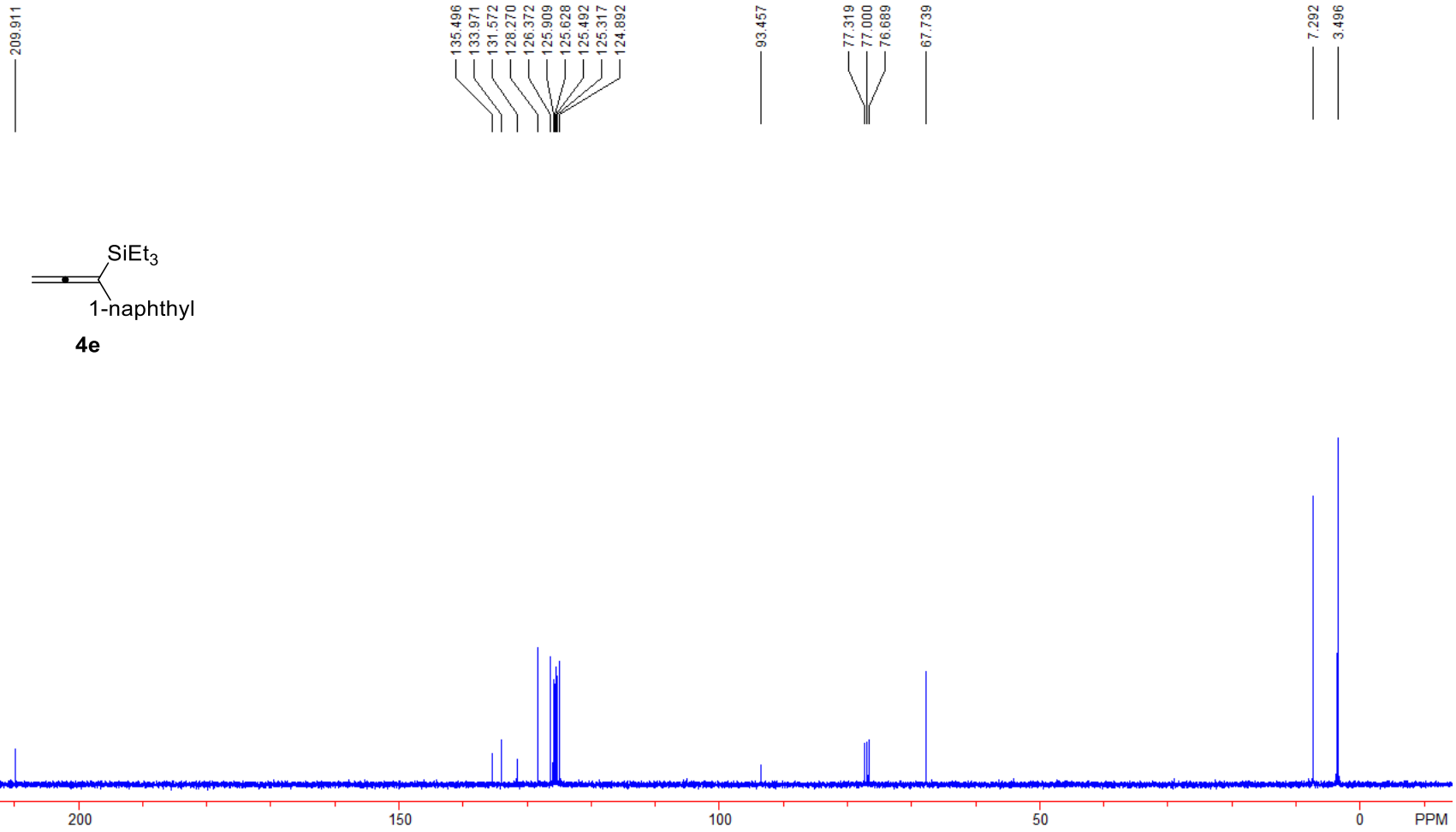
PPM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125.628
125.492
125.317
124.892
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77.319
77.000
76.689
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7.292
3.496
SiEt3
1-naphthyl
4e
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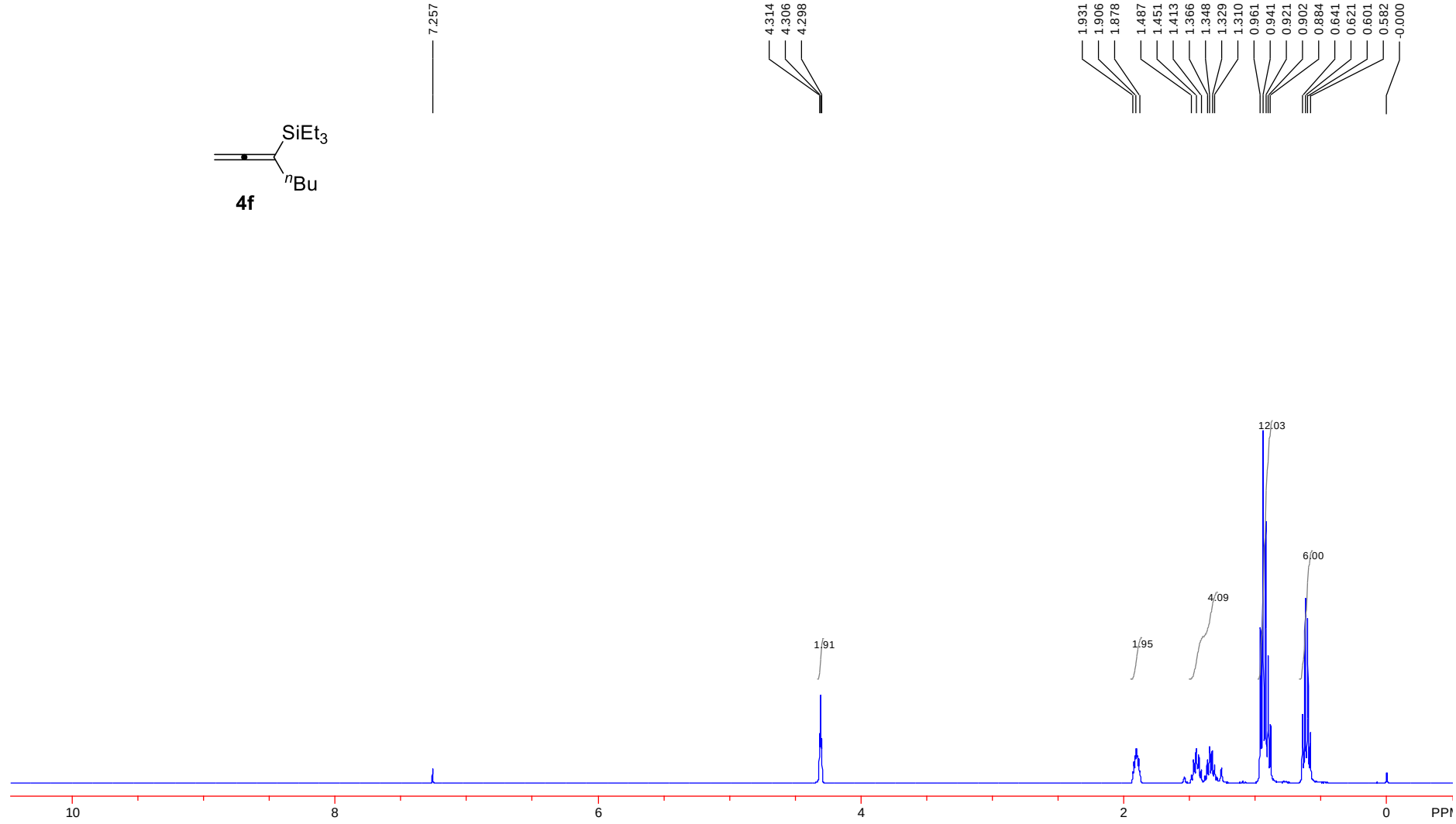
150
100
50
0
PPM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1.348
1.329
1.310
0.961
0.941
0.921
0.902
0.884
0.641
0.621
0.601
0.582
-0.000
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nBu
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4.09
1.91
1.95
10
8
6
4
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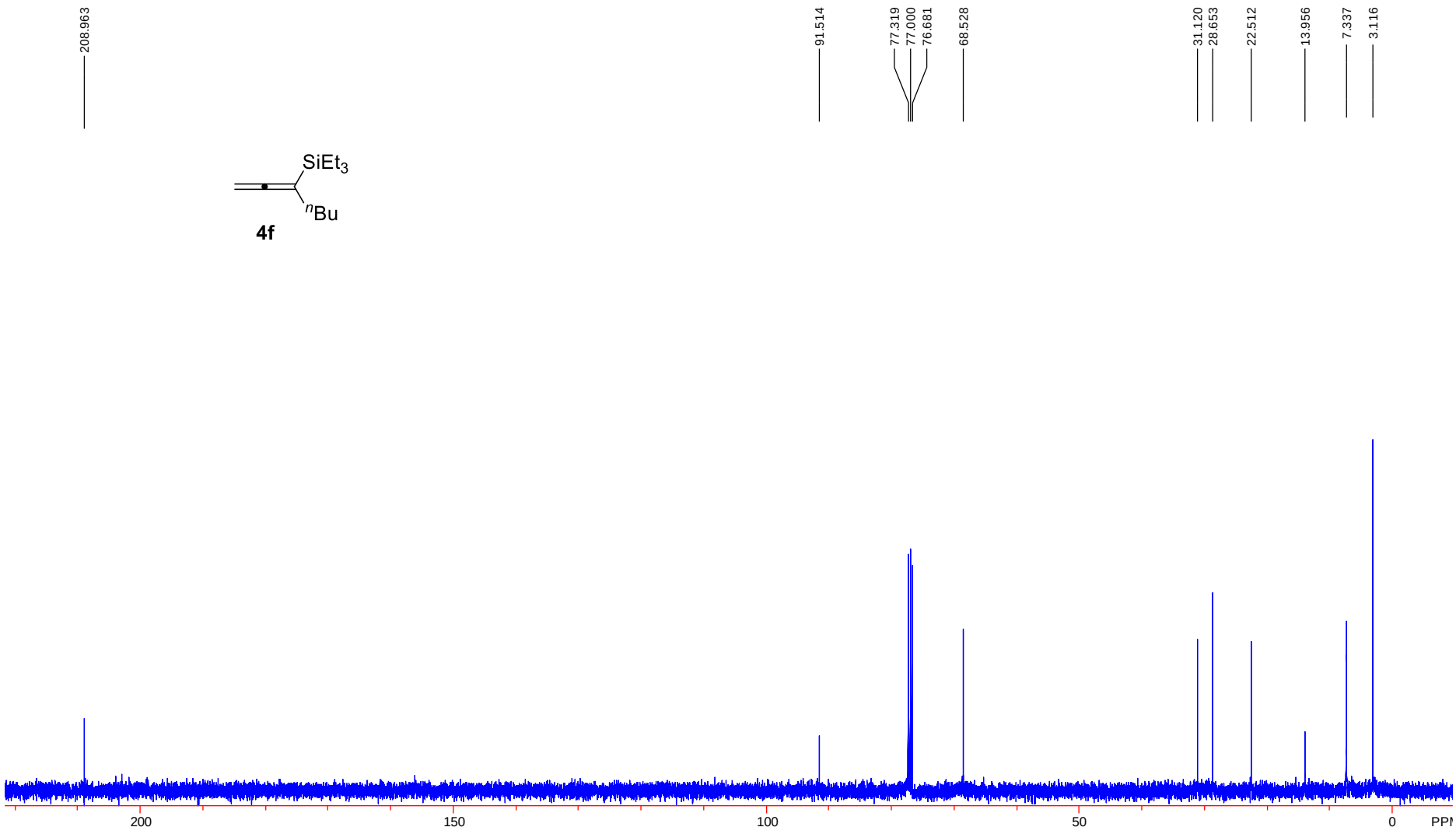
0
PPM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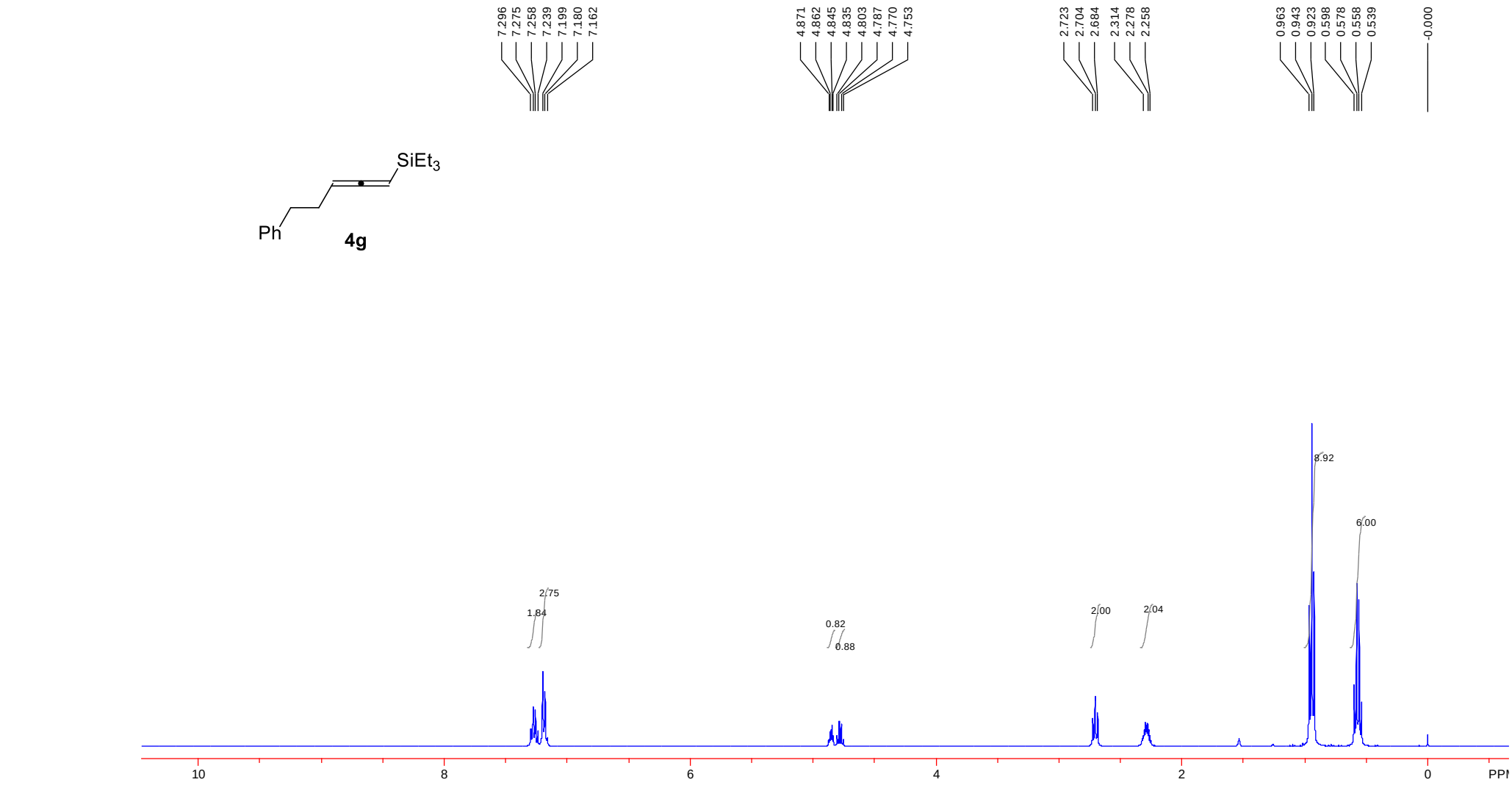
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4.787
4.770
4.753
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2.704
2.684
2.314
2.278
2.258
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0.943
0.923
0.598
0.578
0.558
0.539
-0.000
SiEt3
Ph
4g
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4
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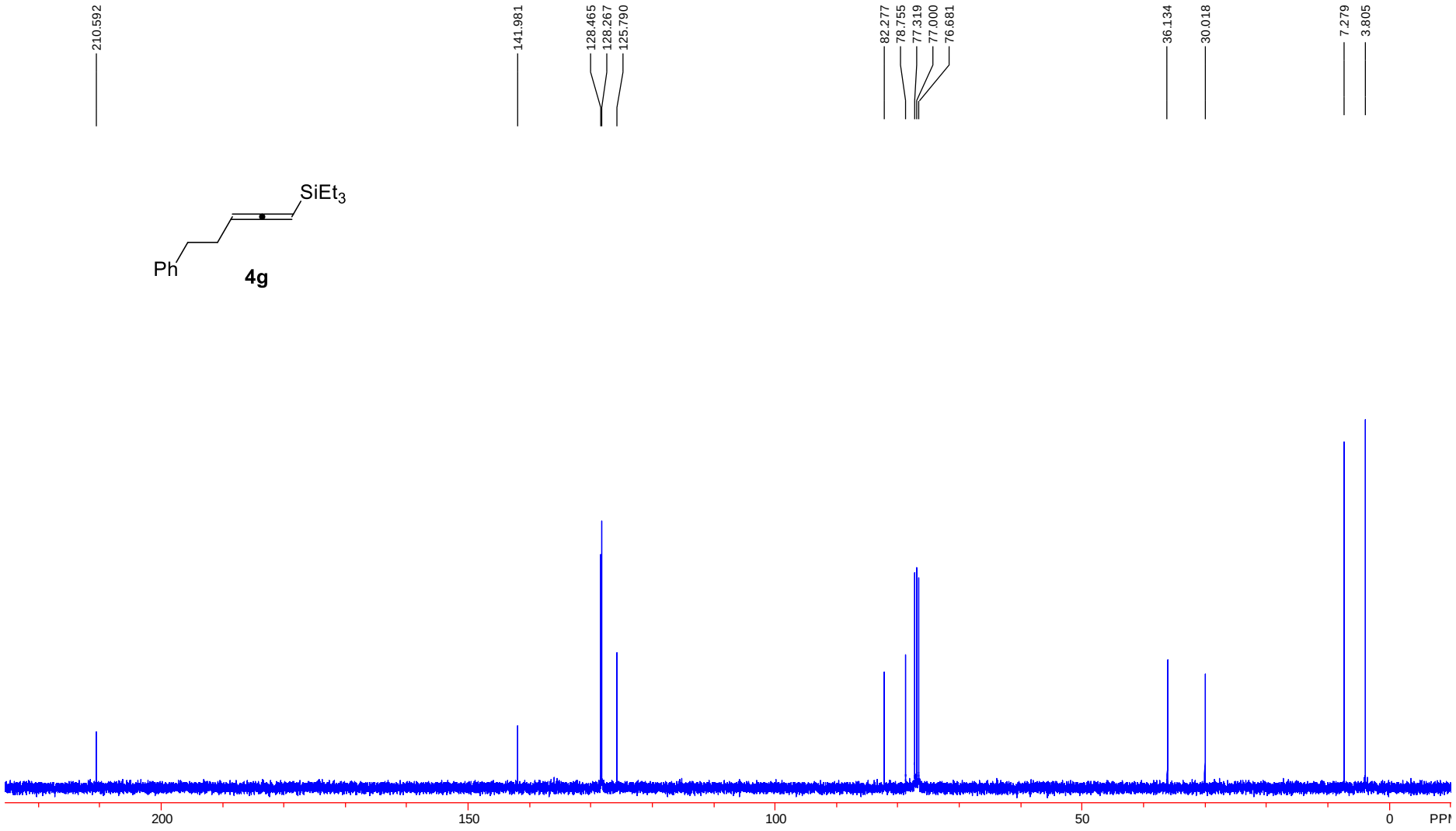
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4g
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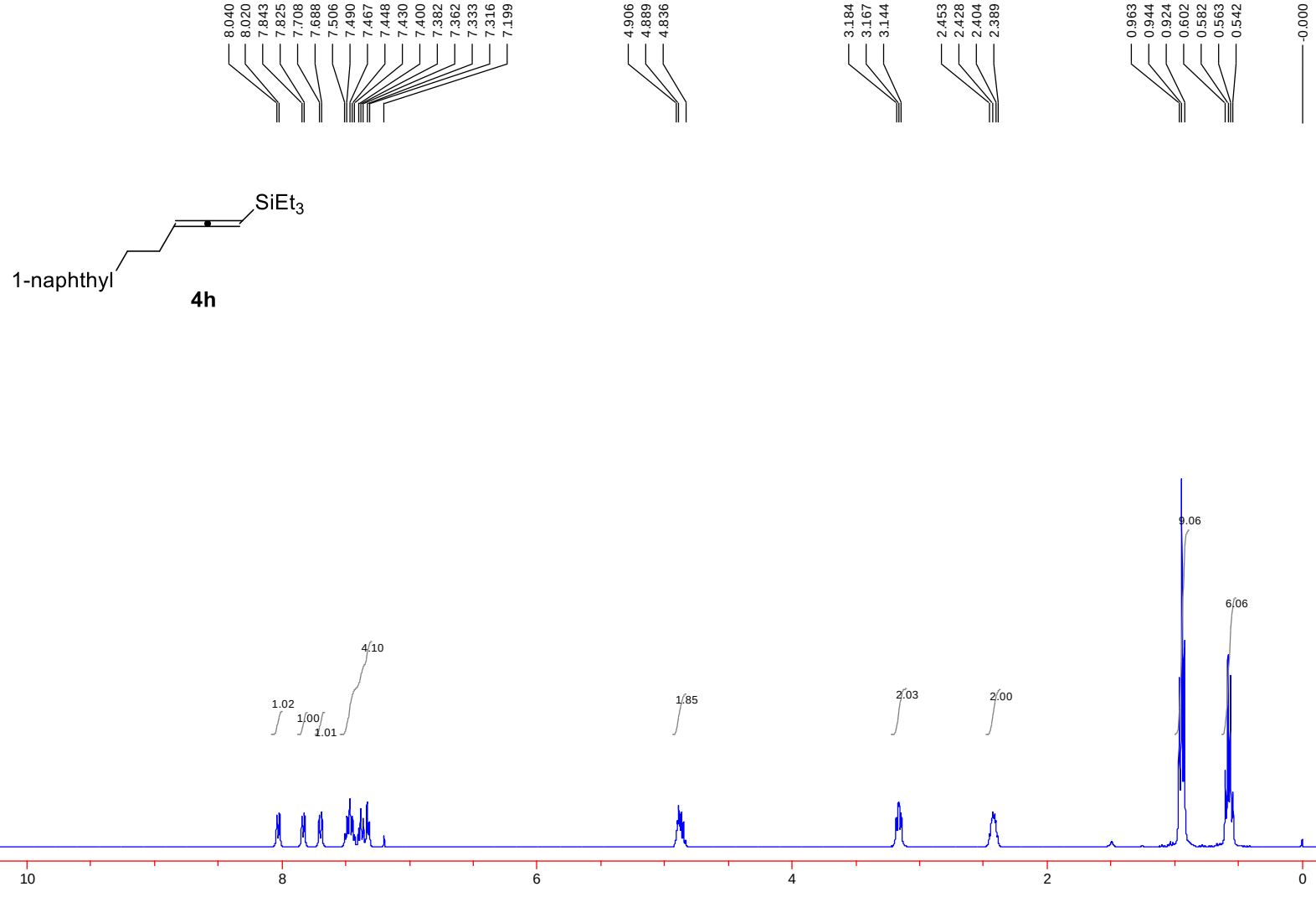
PPM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7.448
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7.382
7.362
7.333
7.316
7.199
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4.889
4.836
3.184
3.167
3.144
2.453
2.428
2.404
2.389
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0.944
0.924
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0.563
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SiEt3
1-naphthyl
4h
1.02
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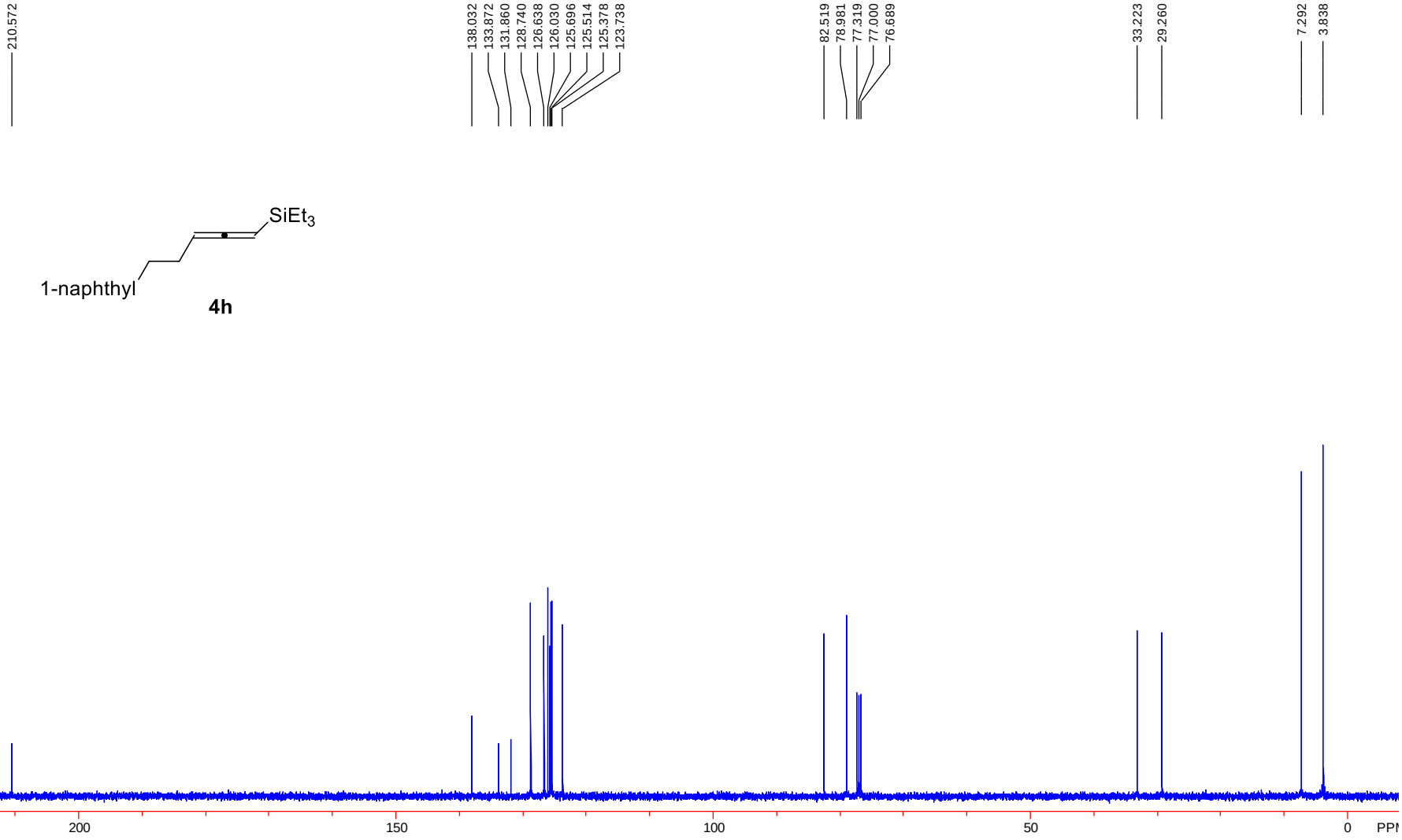
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4h
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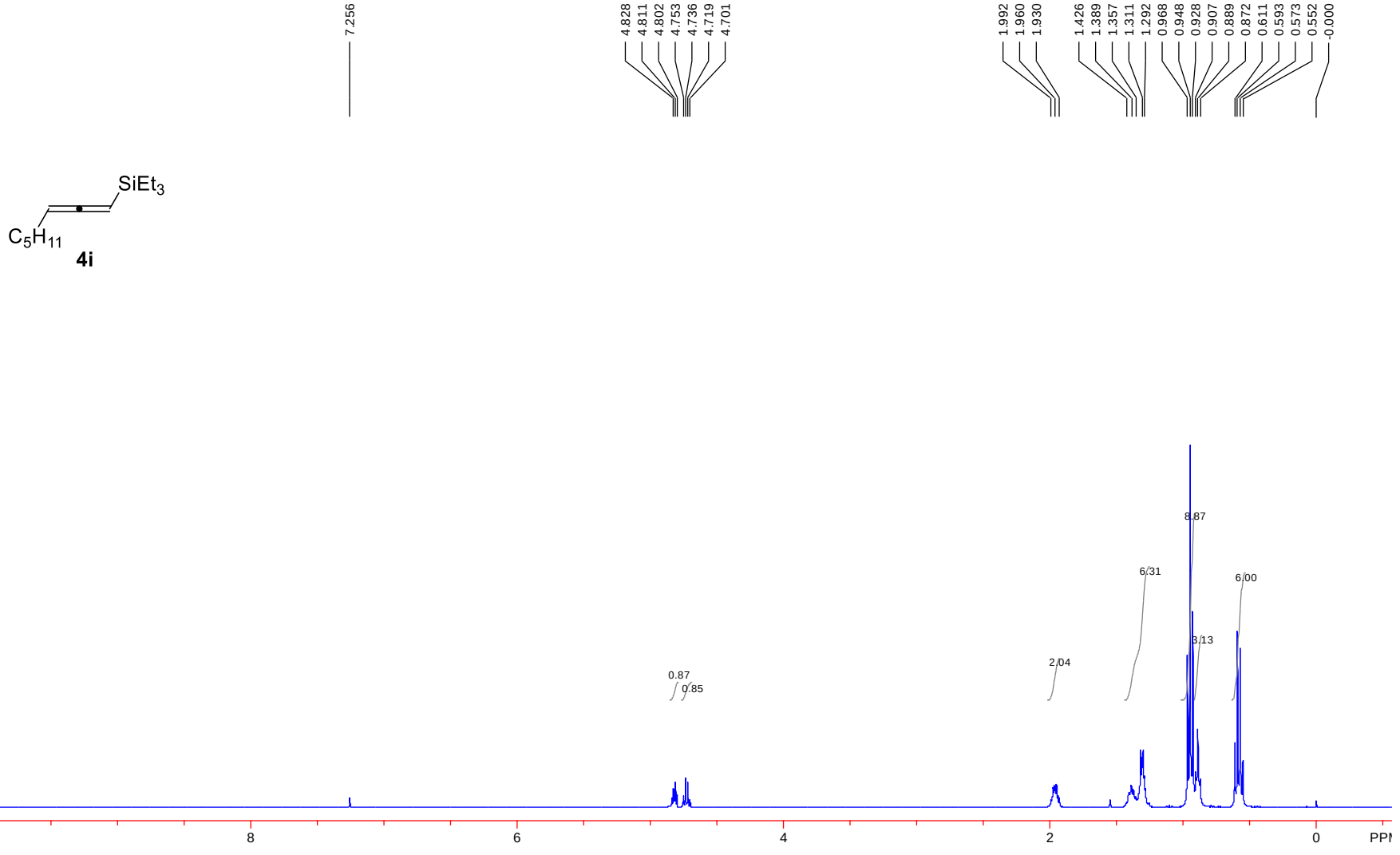
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0.889
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C5H11
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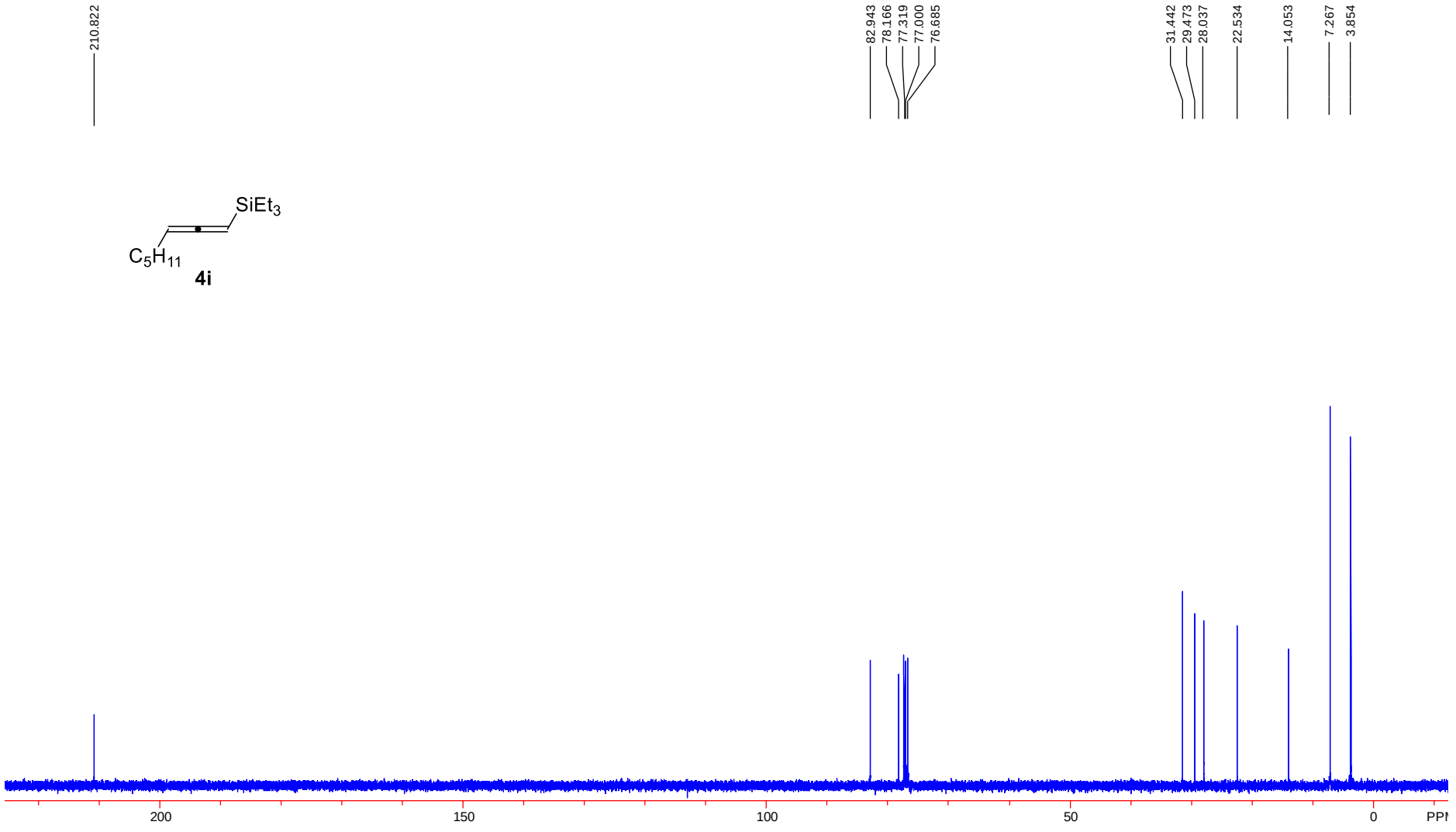
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29.473
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C5H11
4i
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150
100
50
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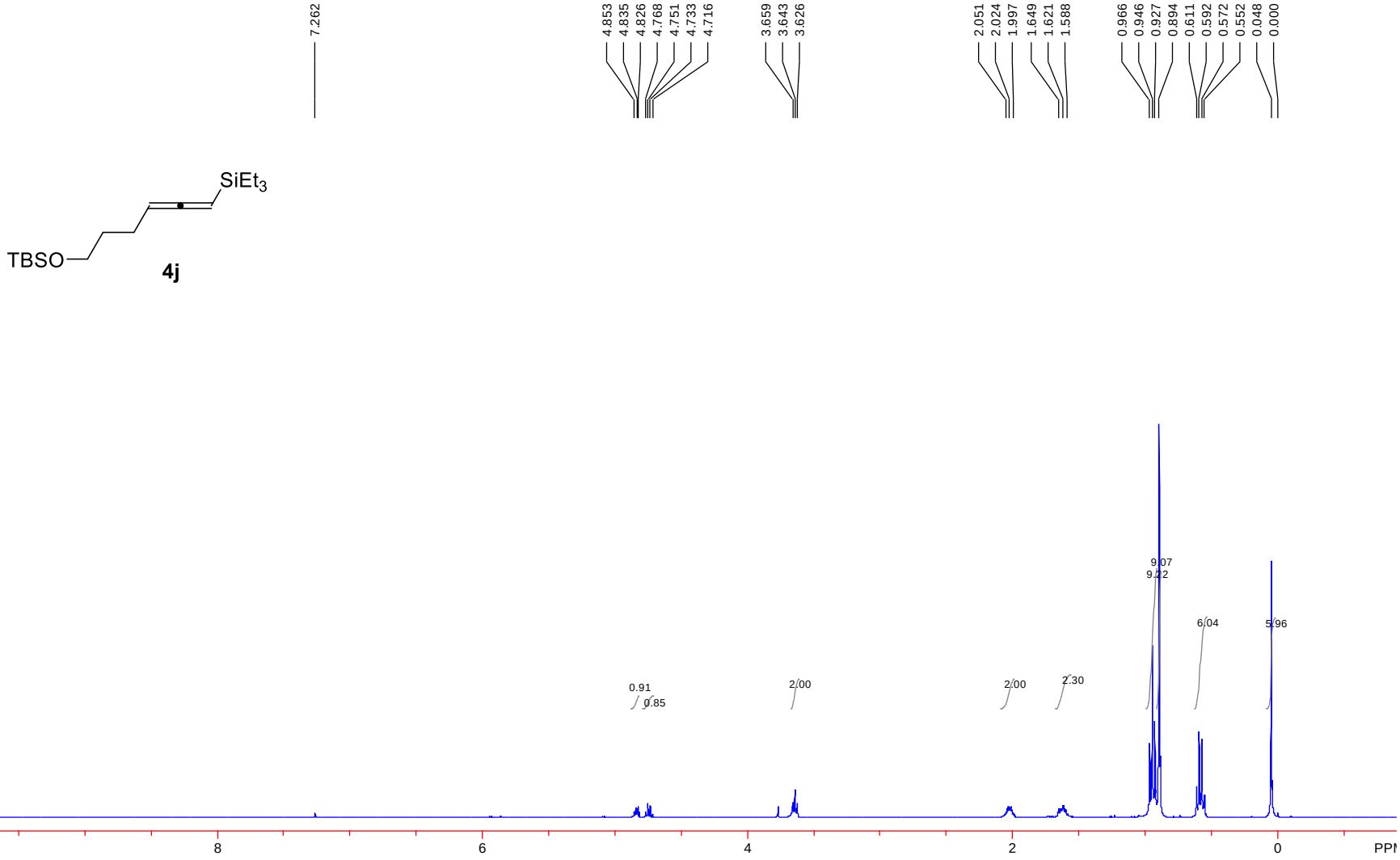
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4.716
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3.643
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2.024
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1.649
1.621
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0.946
0.927
0.894
0.611
0.592
0.572
0.552
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0.000
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TBSO
4j
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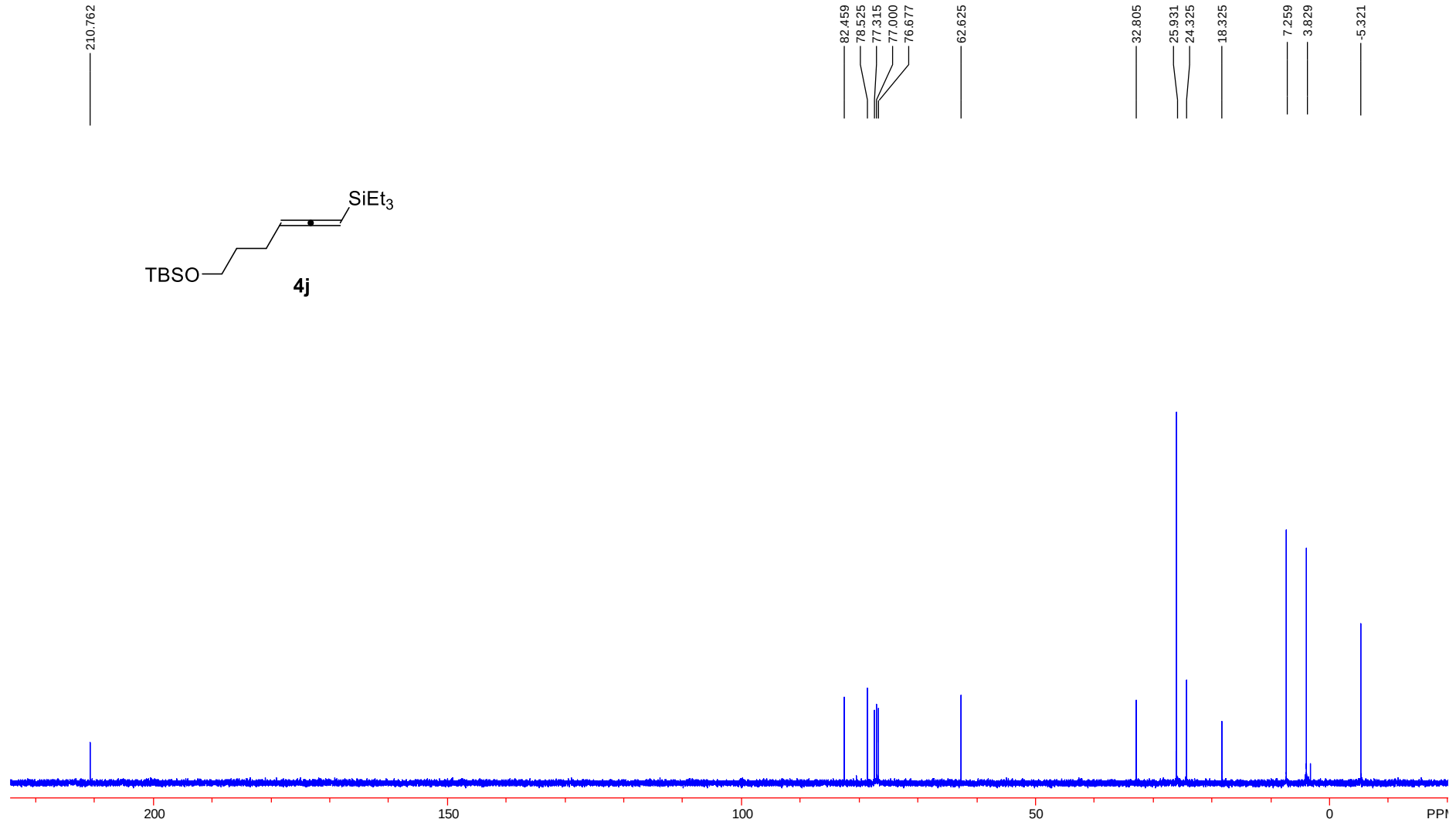
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TBSO
4j
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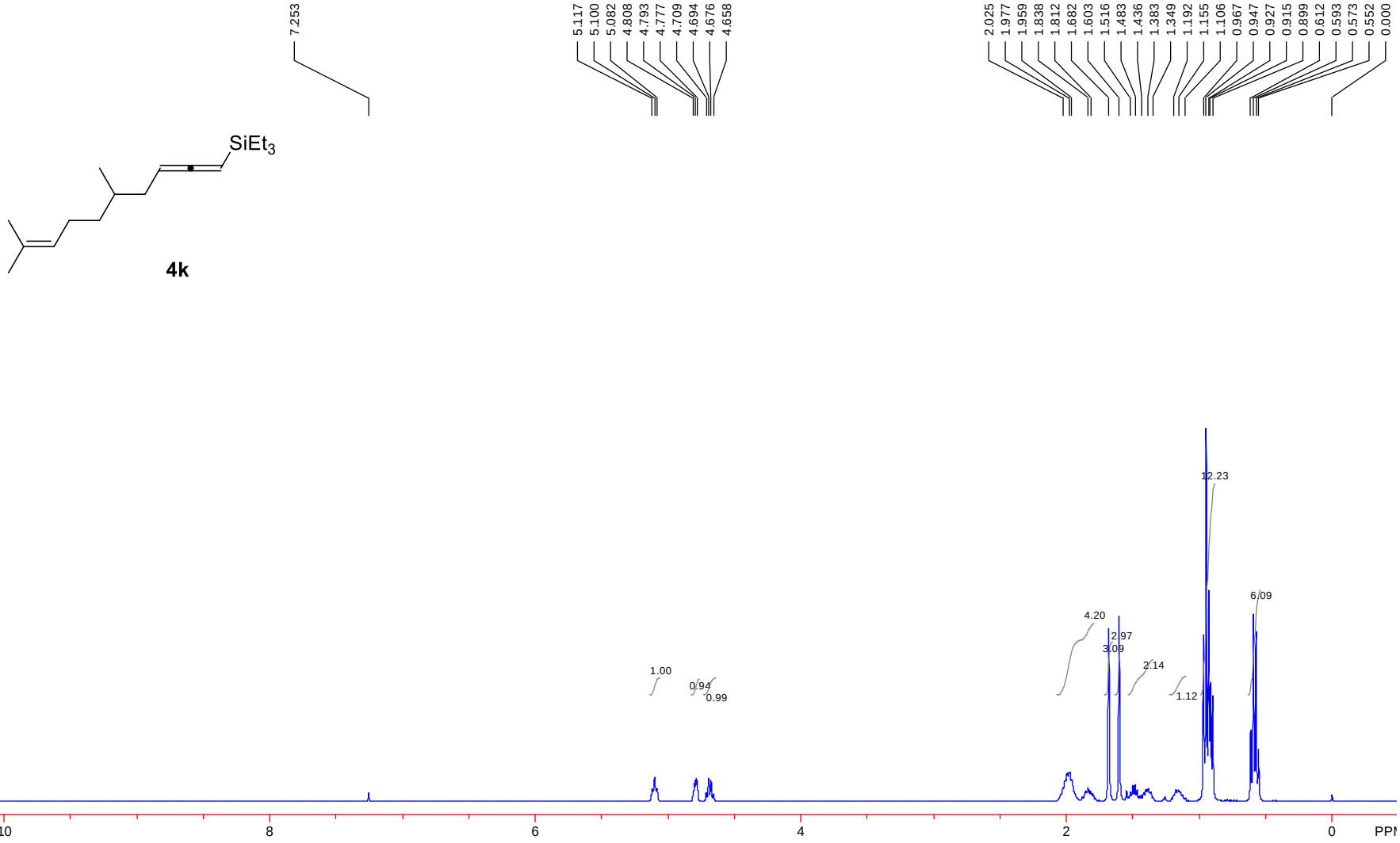
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1.959
1.838
1.812
1.682
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1.436
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1.349
1.192
1.155
1.106
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0.927
0.915
0.899
0.612
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0.573
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SiEt3
4k
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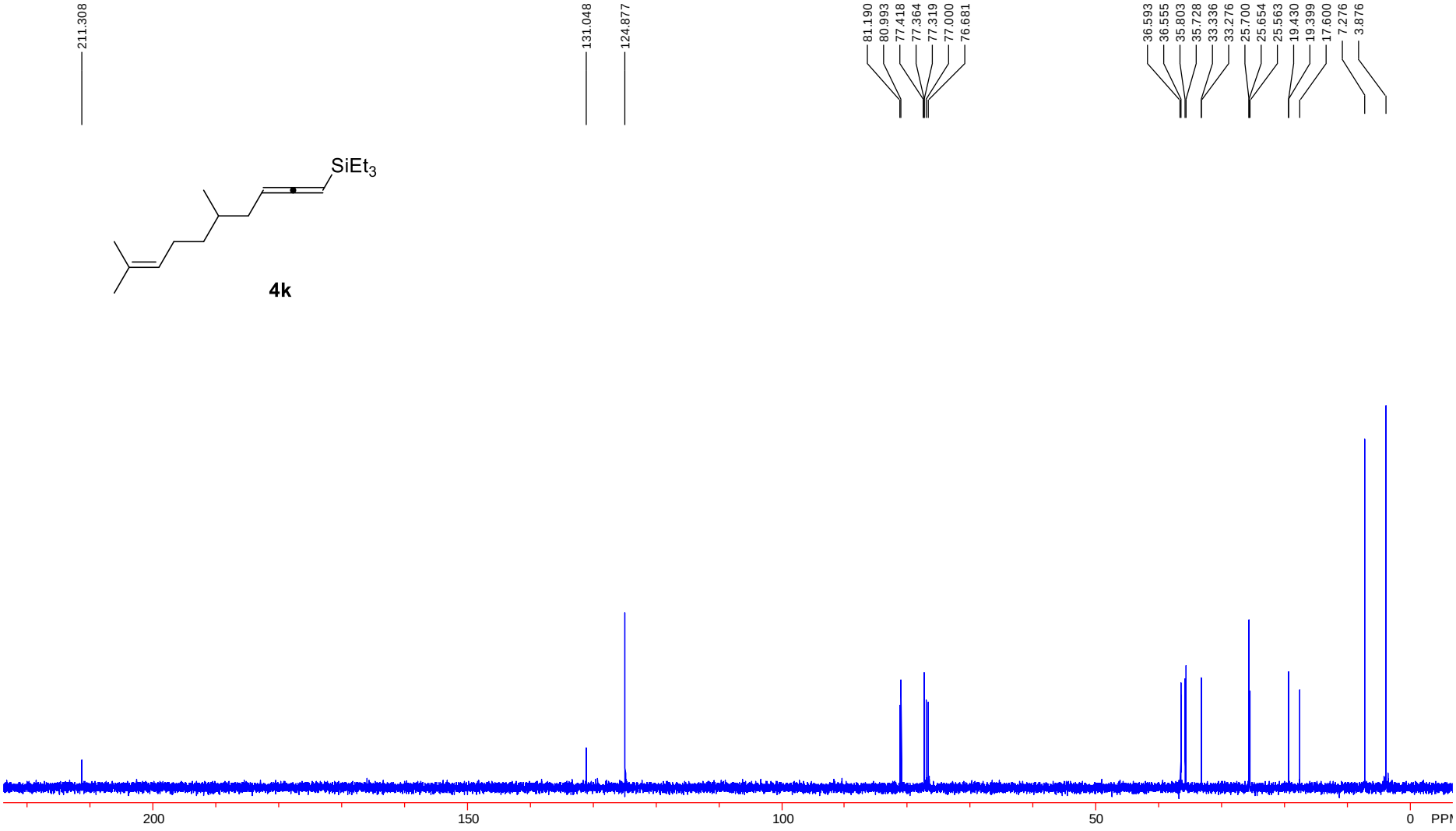
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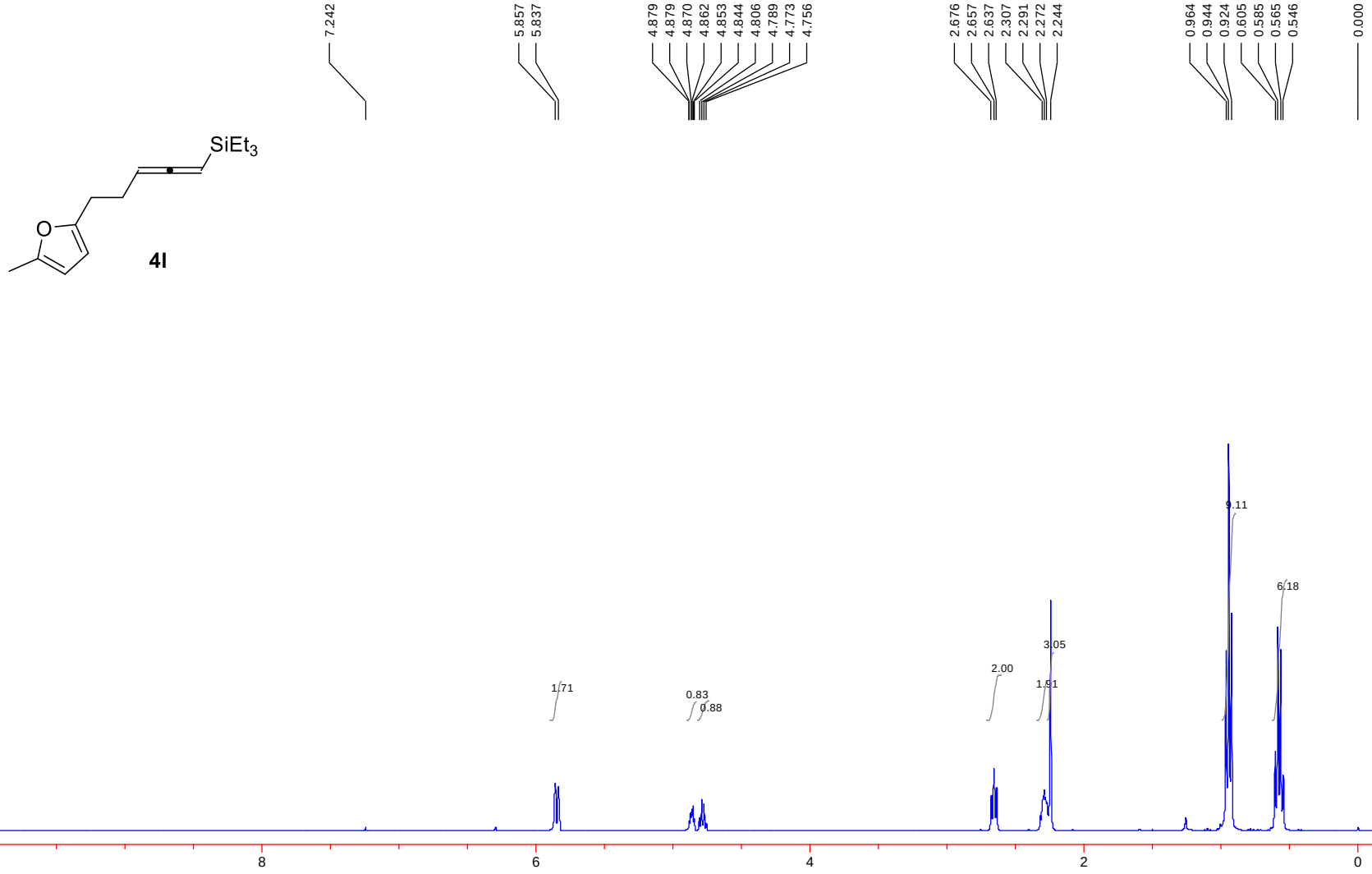
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0.924
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0.546
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SiEt3
O
4l
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10
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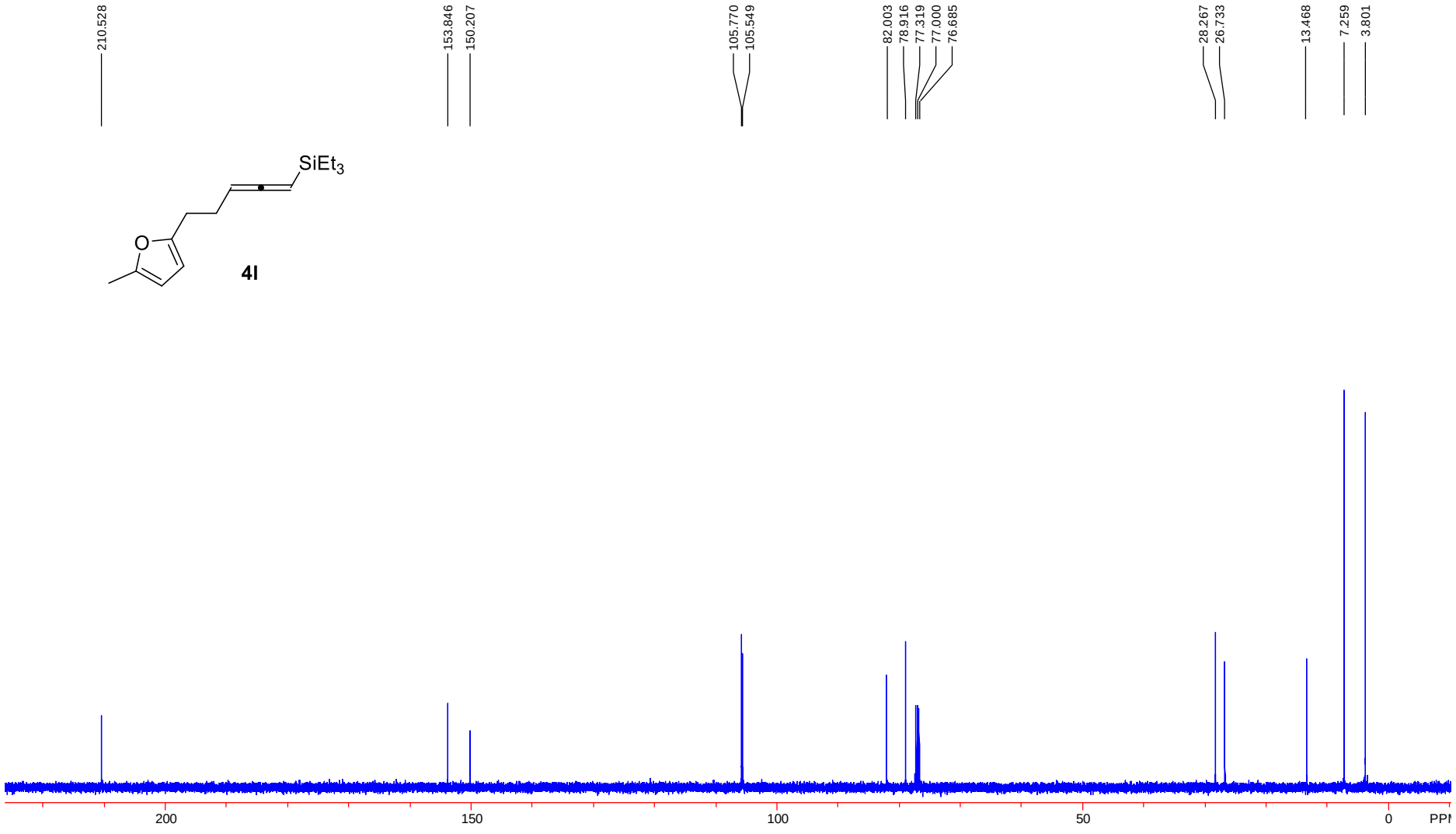
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13.468
7.259
3.801
SiEt3
O
4l
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100
50
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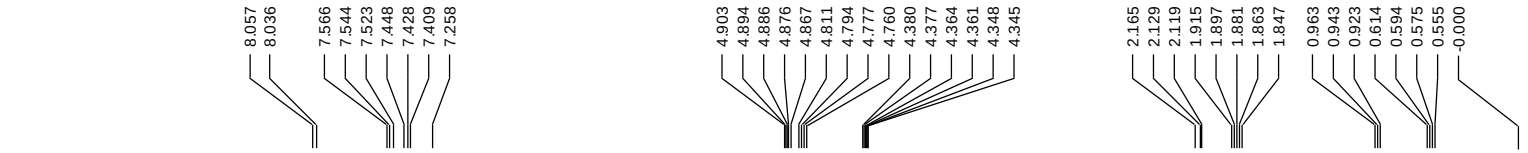
PPM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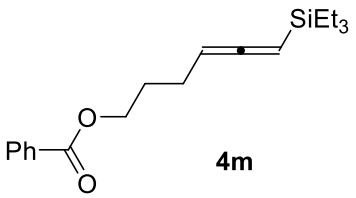
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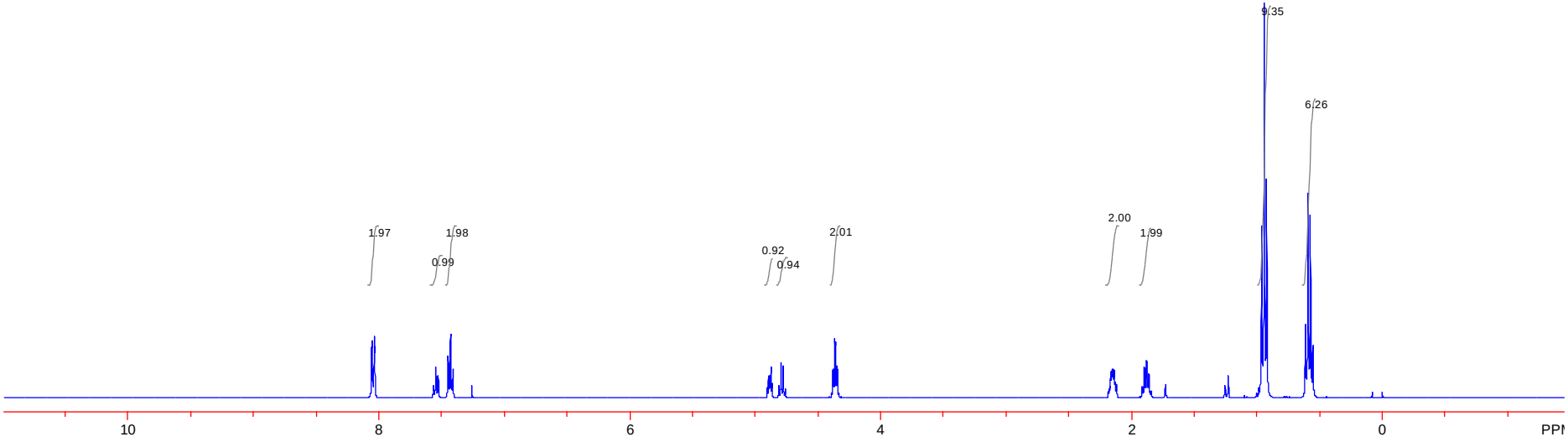
O
Ph
O

4m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0.92
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1.99
10
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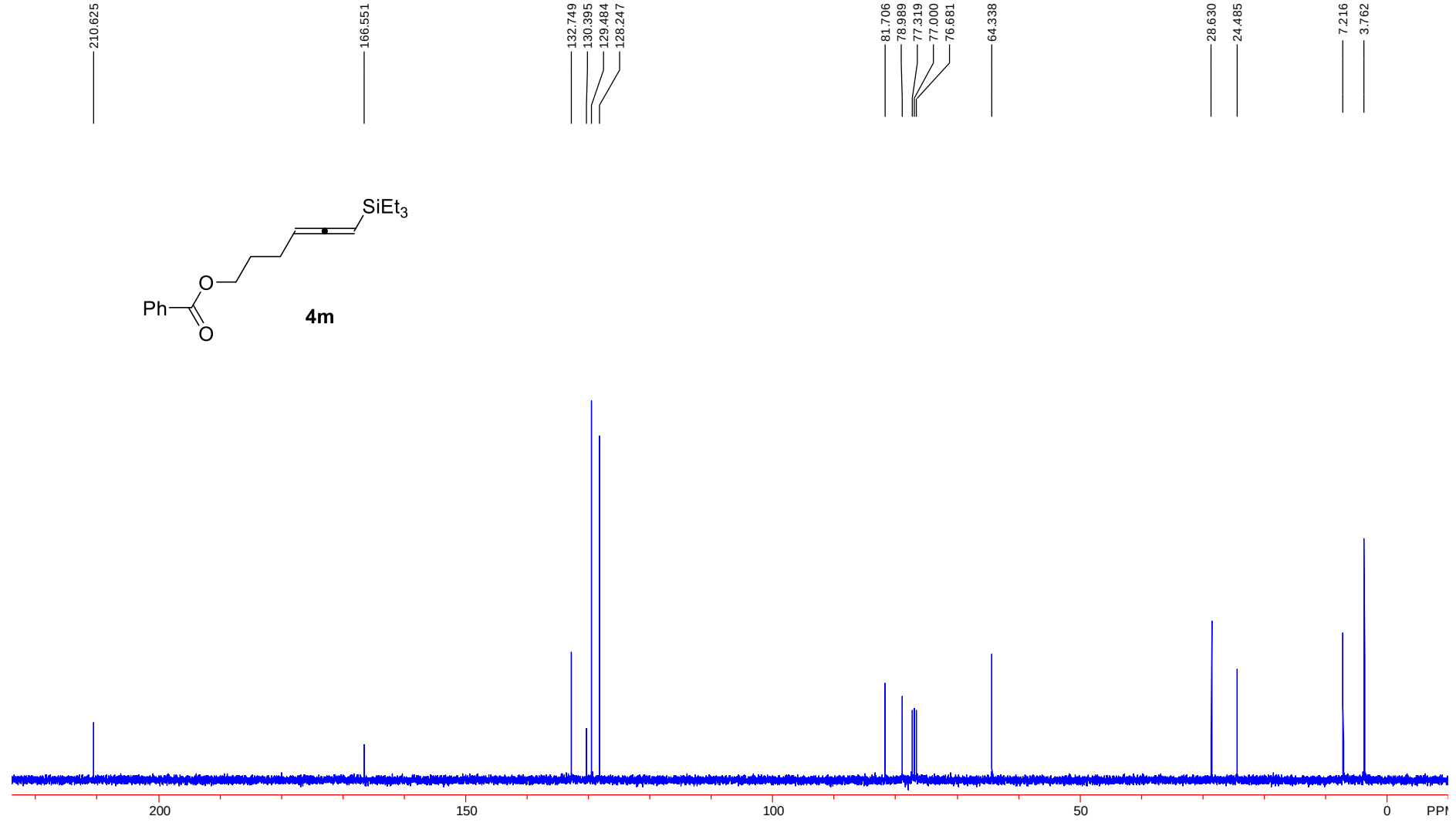
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3.762
SiEt3
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Ph
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4m
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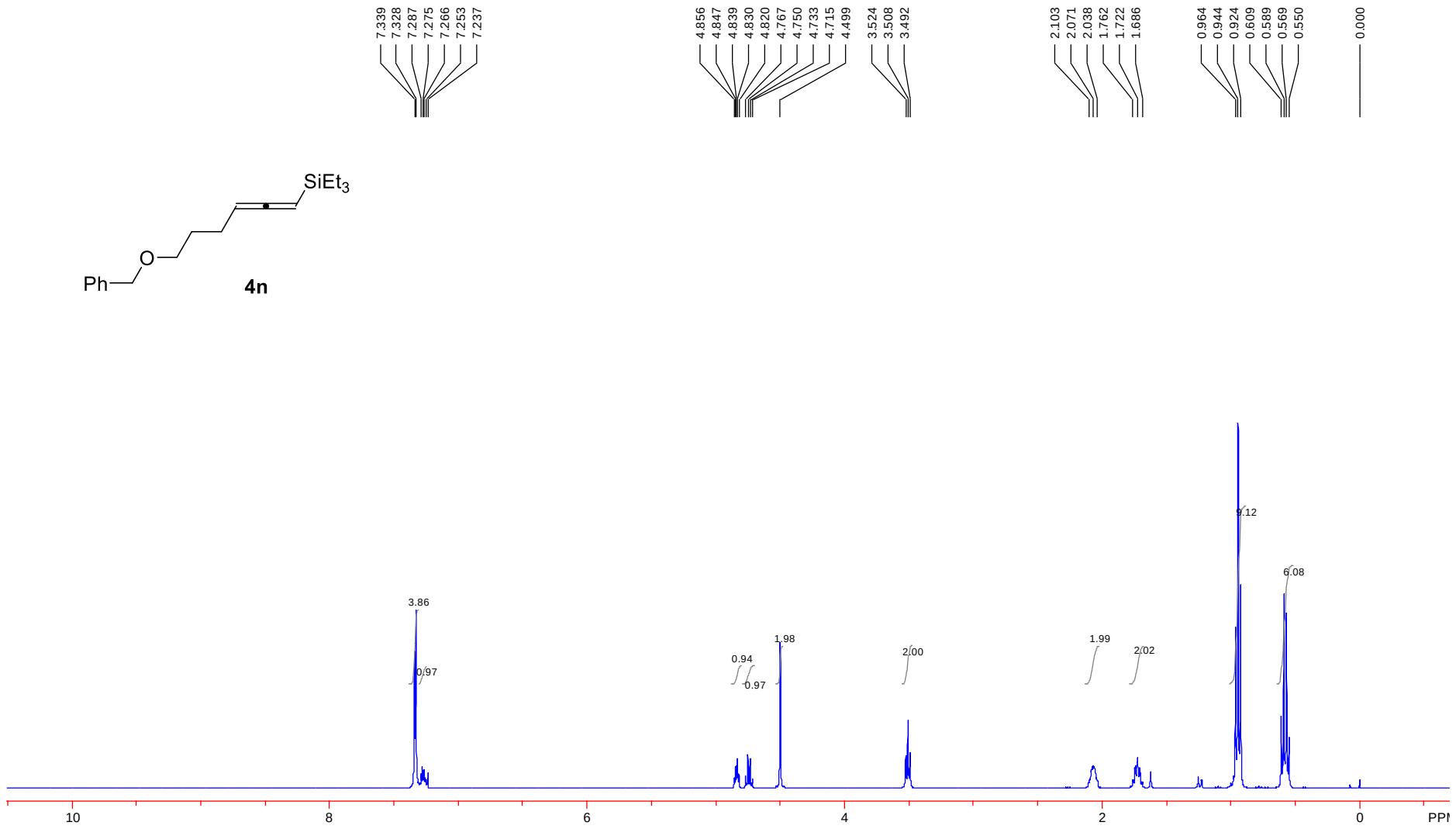
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4.767
4.750
4.733
4.715
4.499
3.524
3.508
3.492
2.103
2.071
2.038
1.762
1.722
1.686
0.964
0.944
0.924
0.609
0.589
0.569
0.550
0.000
SiEt3
O
Ph
4n
3.86
0.97
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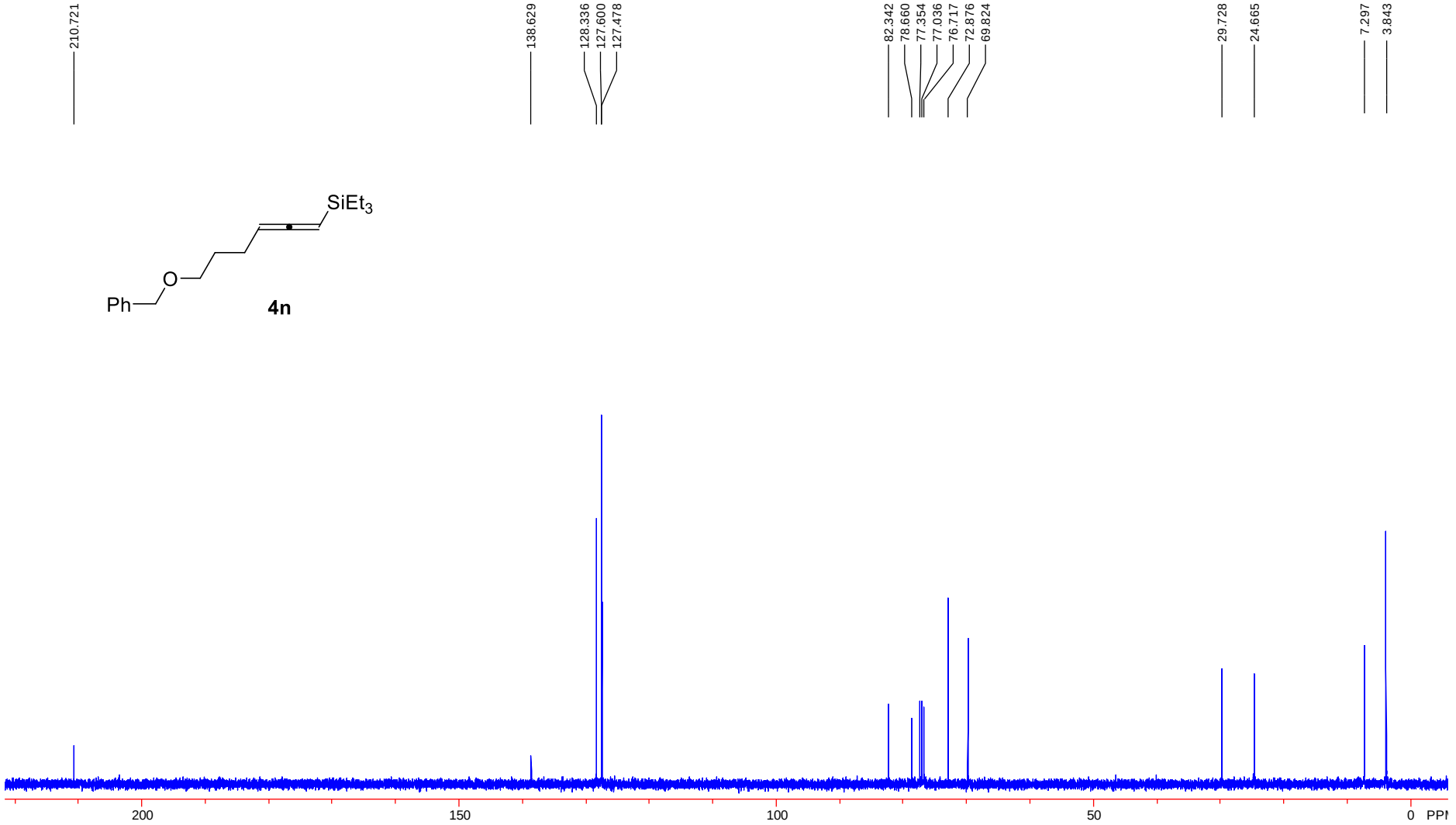
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7.297
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SiEt3
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Ph
4n
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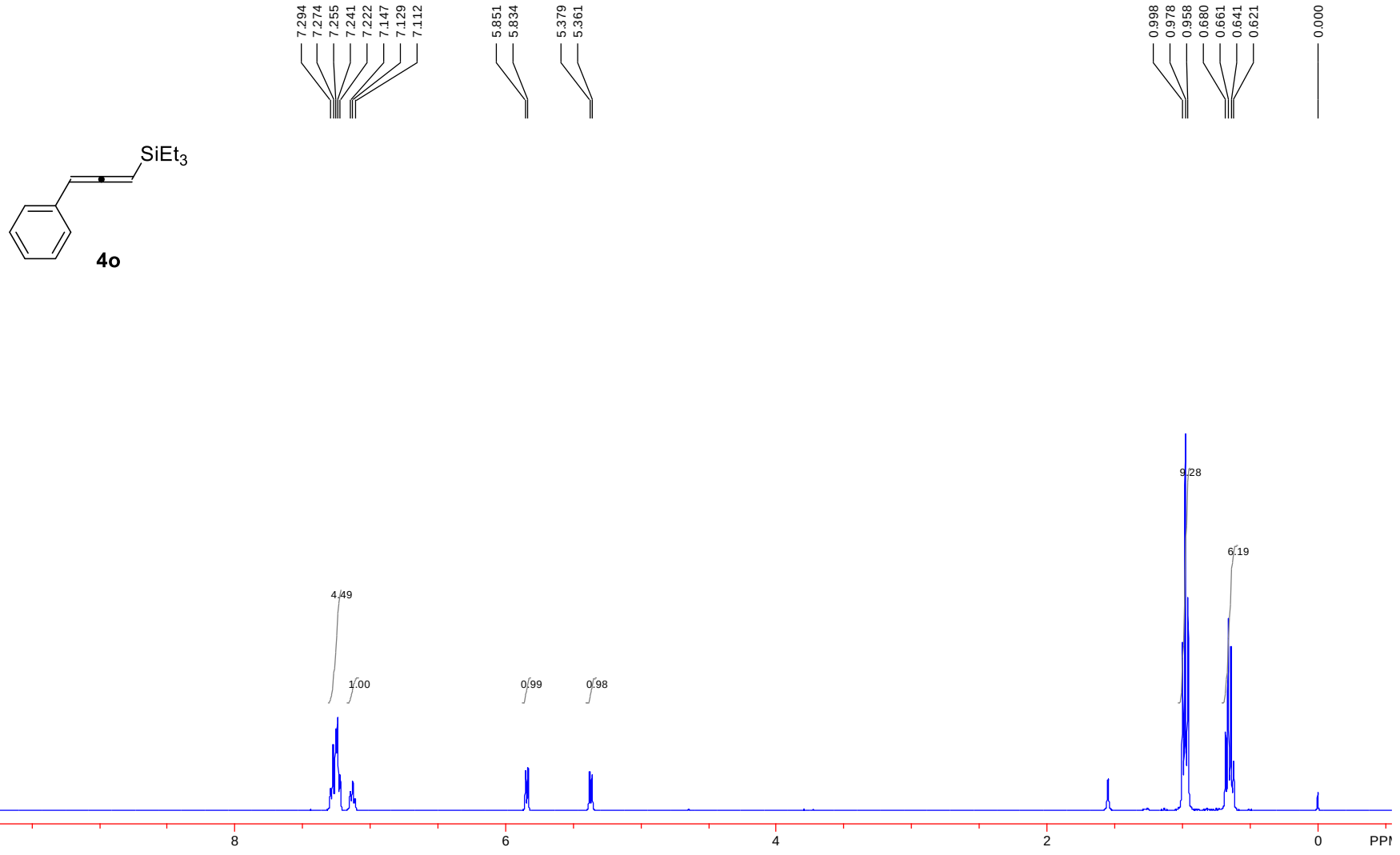
100
50
0
PPM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7.255
7.241
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7.147
7.129
7.112
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0.998
0.978
0.958
0.680
0.661
0.641
0.621
0.000
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1.00
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10
8
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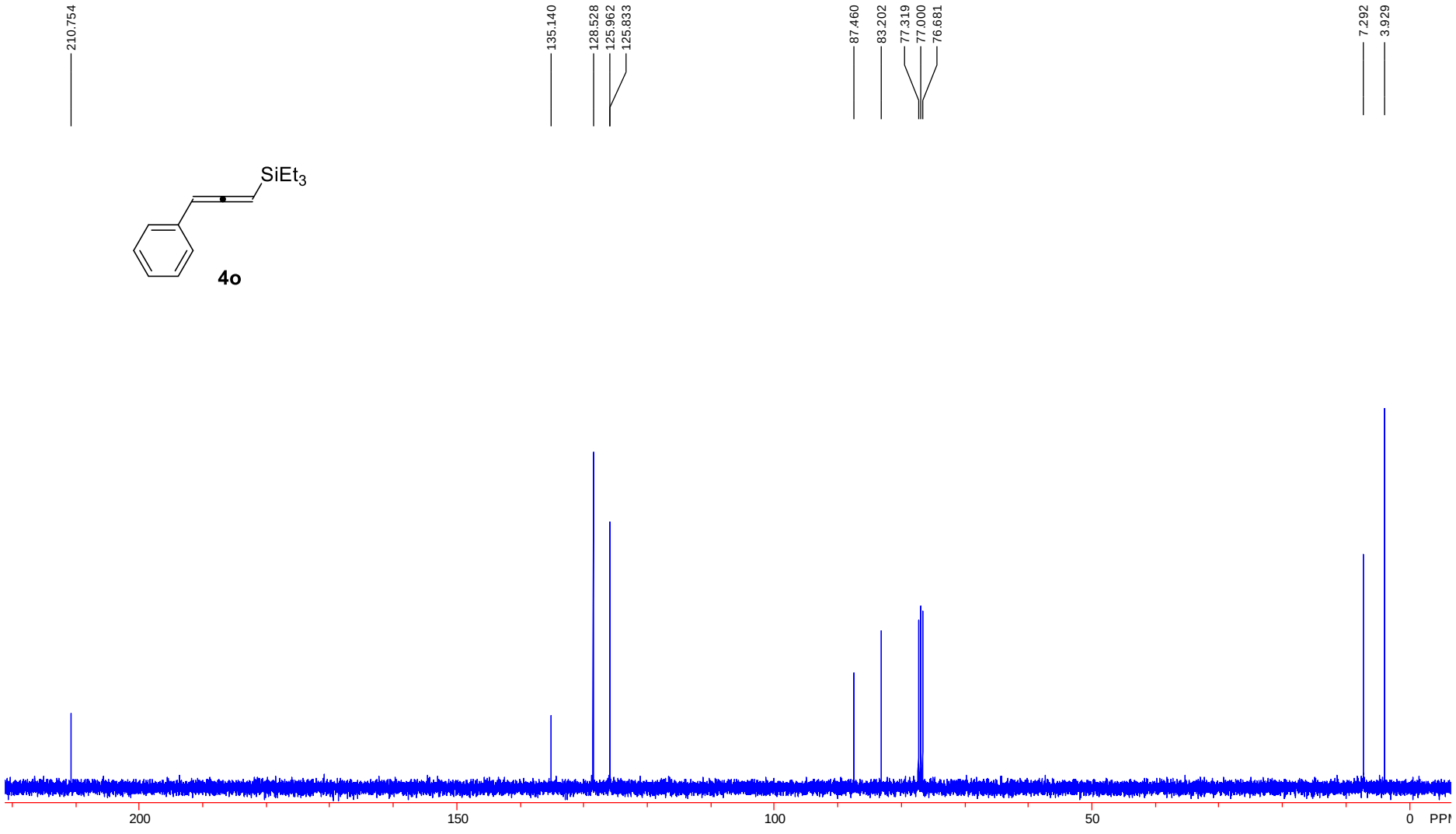
PPM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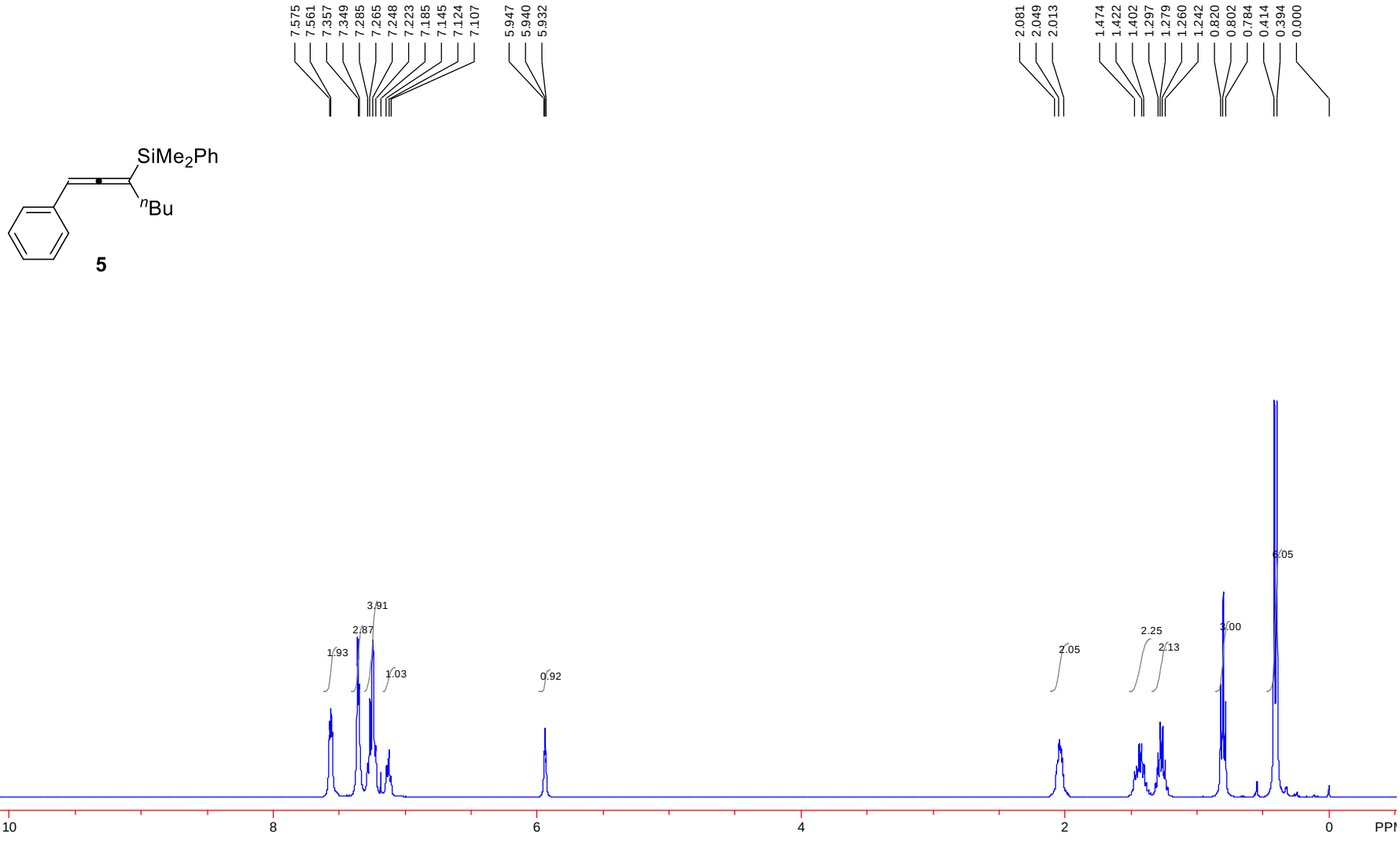
SiEt3
4o
200
150
100
50
0
PPM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5.940
5.932
2.081
2.049
2.013
1.474
1.422
1.402
1.297
1.279
1.260
1.242
0.820
0.802
0.784
0.414
0.394
0.000
SiMe2Ph
nBu
5
1.93
2.87
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10
8
6
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0
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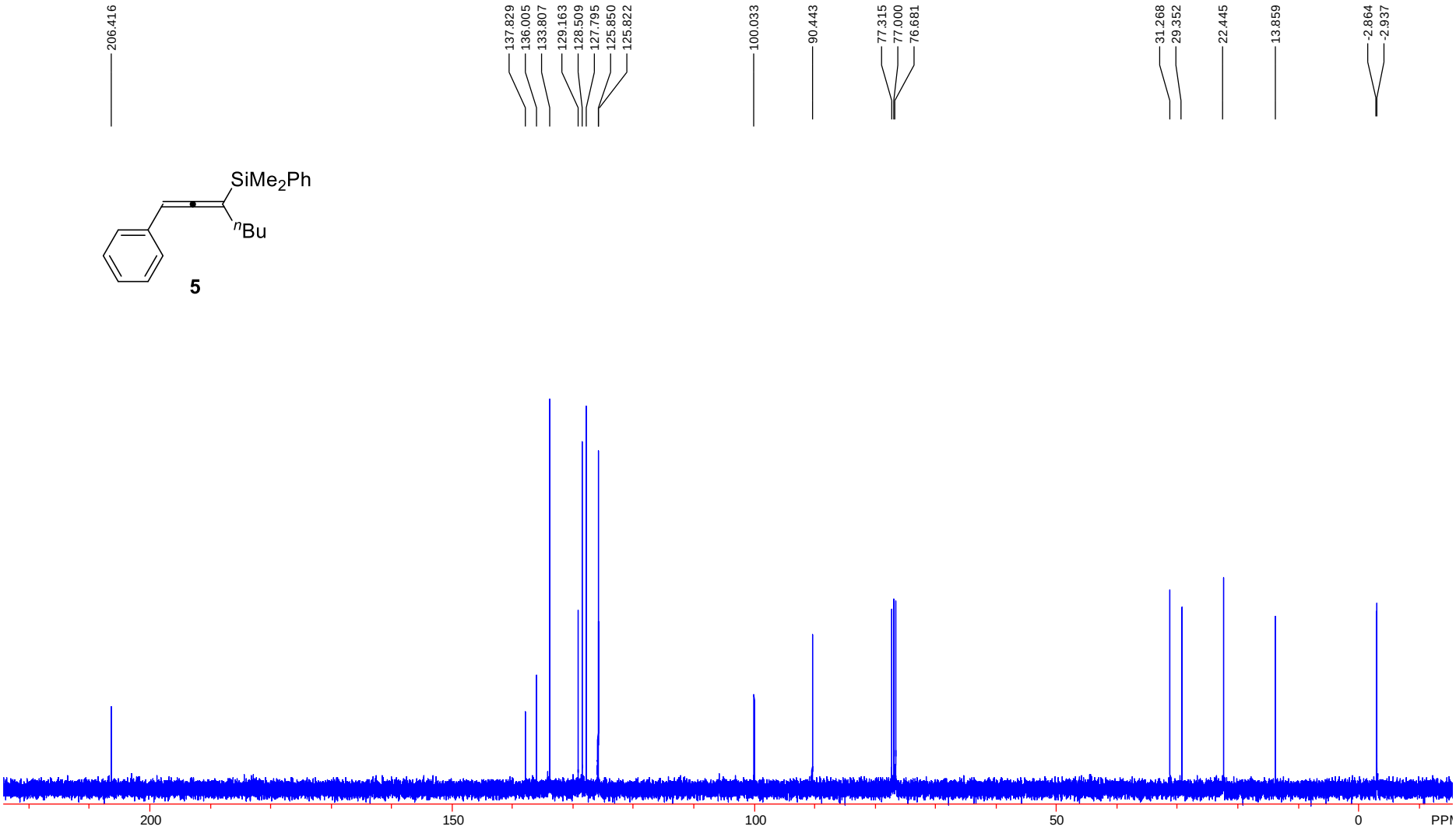
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76.681
31.268
29.352
22.445
13.859
-2.864
-2.937
SiMe2Ph
nBu
5
200
150
100
50
0
PPM