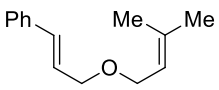
Supporting Information

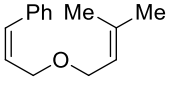
I. General information

$Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$ was prepared as described by Malliaras and Bernhard.[1] MeCN, ether, THF, and CH_2Cl_2 were purified by elution through alumina as described by Grubbs.[2] A 23W (1380 lumen) compact fluorescent lamp was used for all photochemical reactions. Flash column chromatography was performed with Silicycle 40-63Å silica (230-400 mesh) using the method of Still.[3] Diastereomeric ratios for all compounds were determined by GC or ^{1}H NMR analysis of the unpurified reaction mixture. ^{1}H and ^{13}C NMR data for all previously uncharacterized compounds were obtained using Varian Inova-500 and Varian Unity-500 spectrometers and are referenced to TMS (0.0 ppm) and $CDCl_3$ (77.0 ppm), respectively. IR spectral data were obtained using a Bruker Vector 22 spectrometer (thin film on NaCl). Melting points were obtained using a Mel-Temp II (Laboratory Devices, Inc., USA) melting point apparatus. Mass spectrometry was performed with a Waters (Micromass) AutoSpec®. These facilities are funded by the NSF (CHE-9974839, CHE-9304546) and the University of Wisconsin.

II. Synthesis of cycloaddition subtrates

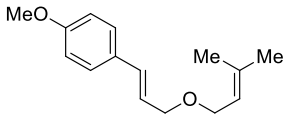


[(*E*)-3-(3-Methyl-but-2-enyloxy)-propenyl]-benzene: A flame-dried 50 mL round-bottomed flask was charged with 60% NaH (240 mg, 6.0 mmol) and dry THF (5 mL). (*E*)-Cinnamyl alcohol (0.67 g, 5.0 mmol) in THF (4 mL) was added dropwise, and the reaction was stirred for an additional 30 min at room temperature. The flask was then cooled to 0 °C, and a solution of 3,3-dimethylallyl bromide (1.0 g, 90% purity, 6.0 mmol) in 6 mL THF was added dropwise. The mixture was allowed to warm slowly to room temperature. After stirring for 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted two times with Et_2O. The combined organic phases were then washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by flash-column chromatography using 40:1 hexanes/ethyl acetate as the eluent to afford 0.901 g (4.5 mmol, 89% yield) of a colorless oil. IR(neat) 3026, 2972, 2915, 2852, 1600, 1496, 1449, 1073 cm^{-1}. ^{1}H NMR: (500.2 MHz, $CDCl_3$) δ 7.39 (d, J = 7.4 Hz, 2H), 7.31 (t, J = 7.8 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 6.61 (d, J = 15.7 Hz, 1H), 6.31 (dt, J = 15.7, 6.3 Hz, 1H), 5.42-5.37 (m, 1H), 4.14 (dd, J = 6.1, 1.4 Hz, 2H), 4.02 (d, J = 6.9 Hz, 2H), 1.76 (s, 3H), 1.69 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 137.2, 136.8, 132.3, 128.5, 127.6, 126.45, 126.39, 121.0, 70.6, 66.6, 25.8, 18.0. HRMS (EI) calculated for $[C_{14}H_{18}O]^{+}(M^{+})$ requires *m/z* 202.1353, found *m/z* 202.1345.

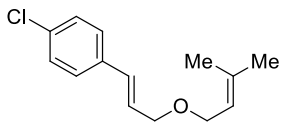


[(*Z*)-3-(3-Methyl-but-2-enyloxy)-propenyl]-benzene: A flame-dried 50 mL round-bottomed flask was charged with (*Z*)-cinnamyl alcohol[4] (670 mg, 5.0 mmol), 3,3-dimethylallyl bromide (1.0 g, 90% purity, 6.0 mmol) and DMF (5 mL). The flask was then cooled to 0 °C, and 60% NaH (240 mg, 6 mmol) was added. The mixture was warmed to room temperature, and the reaction was monitored by TLC. After stirring for 4 h, the reaction was quenched by the slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted two times with Et_2O. The combined organic phases were then washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The crude mixture could

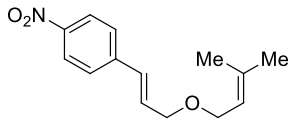
then be purified by flash-column chromatography using 40:1 hexanes/ethyl acetate as the eluent to afford 821 mg (4.1 mmol, 81%) of a colorless oil. IR(neat) 3024, 2972, 2914, 2957, 1676, 1495, 1448, 1085 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H), 7.27-7.23 (m, 1H), 7.23-7.20 (m, 2H), 6.59 (d, J = 11.9 Hz, 1H), 5.87 (dt, J = 11.9, 6.4 Hz, 1H), 5.39-5.34 (m, 1H), 4.24 (dd, J = 6.4, 1.8 Hz, 2H), 3.97 (d, J = 7.0 Hz, 2H), 1.73 (s, 3H), 1.65 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 137.3, 136.7, 131.4, 129.3, 128.8, 128.1, 127.1, 120.9, 66.74, 66.69, 25.8, 17.9. HRMS (EI) calculated for $[C_{14}H_{18}O]^+(M^+)$ requires *m/z* 202.1353, found *m/z* 202.1348.



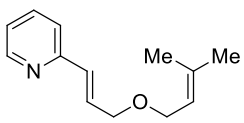
1-Methoxy-4-[(*E*)-3-(3-Methyl-but-2-enyloxy)-propenyl]-benzene: A flame-dried 50 mL round-bottomed flask was charged with 60% NaH (144 mg, 3.6 mmol) and dry THF (5 mL). (*E*)-4-Methoxycinnamyl alcohol[5] (492 mg, 3.0 mmol) in THF (4 mL) was added dropwise, and the reaction was stirred for an additional 30 min at room temperature. The flask was then cooled to 0 °C, and a solution of 3,3-dimethylallyl bromide (546 mg, 90% purity, 3.3 mmol) in 6 mL THF was added dropwise. The mixture was allowed to warm slowly to room temperature. After stirring for 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted two times with Et_2O. The combined organic phases were then washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by flash-column chromatography using 40:1 hexanes/ethyl acetate as the eluent to afford 571 mg (2.5 mmol, 82%) of a colorless oil. IR(neat) 2915, 2836, 1577, 1462, 1249, 1174 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.32 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.55 (d, J = 15.9 Hz, 1H), 6.17 (dt, J = 15.9, 6.4 Hz, 1H), 5.42-5.36 (m, 1H), 4.11 (dd, J = 5.0, 1.2 Hz, 2H), 4.01 (d, J = 7.1 Hz, 2H), 3.80 (s, 3H), 1.76 (s, 3H), 1.69 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 159.2, 137.1, 132.0, 129.6, 127.6, 124.1, 121.1, 113.9, 70.8, 66.5, 55.2, 25.8, 18.0. HRMS (EI) calculated for $[C_{15}H_{20}O_2]^+(M^+)$ requires *m/z* 232.1458, found *m/z* 232.1462.



1-Chloro-4-[(*E*)-3-(3-Methyl-but-2-enyloxy)-propenyl]-benzene: A flame-dried 50 mL round-bottomed flask was charged with (*E*)-4-chlorocinnamyl alcohol[6] (843 mg, 5.0 mmol), 3,3-dimethylallyl bromide (1.0g, purity: 90%, 6.0 mmol), and dry DMF (5 mL). The mixture was cooled to 0 °C and added with 60% NaH (240 mg, 6.0 mmol), then allowed to warm slowly to room temperature. After stirring for 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted two times with Et_2O. The combined organic phases were then washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by flash-column chromatography using 40:1 hexanes/ethyl acetate as the eluent to afford 1.072 g (4.5 mmol, 91%) of a colorless oil. IR(neat) 2972, 2915, 2864, 1675, 1594, 1491, 1448, 1090 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.32-7.25 (m, 4H), 6.56 (d, J = 15.9 Hz, 1H), 6.28 (dt, J = 15.9, 6.0 Hz, 1H), 5.41-5.36 (m, 1H), 4.12 (dd, J = 5.9, 1.5 Hz, 2H), 4.02 (d, J = 7.1 Hz, 2H), 1.76 (s, 3H), 1.69 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 137.3, 135.3, 133.2, 130.9, 128.7, 127.6, 127.1, 121.0, 70.4, 66.7, 25.8, 18.0. HRMS (EI) calculated for $[C_{14}H_{17}ClO]^+(M^+)$ requires *m/z* 236.0963, found *m/z* 236.0954.

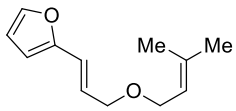


1-Nitro-4-[(*E*)-3-(3-Methyl-but-2-enyloxy)-propenyl]-benzene: A flame-dried 50 mL round-bottomed flask was charged with (*E*)-4-nitrocinnamyl alcohol (895 mg, 5.0 mmol), 3,3-dimethylallyl bromide (1.0g, purity: 90%, 6.0 mmol), and dry DMF (5 mL). The mixture was cooled to 0 °C and added with 60% NaH (240 mg, 6.0 mmol), then allowed to warm slowly to room temperature. After stirring for 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted two times with Et_2O. The combined organic phases were then washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by flash-column chromatography using 10:1 hexanes/ethyl acetate as the eluent to afford 986 mg (4.0 mmol, 80%) of a yellow oil. IR(neat) 2972, 2915, 2851, 1596, 1517, 1342 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 8.17 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 6.69 (d, J = 16.0 Hz, 1H), 6.49 (dt, J = 16.0, 5.4 Hz, 1H), 5.42-5.37 (m, 1H), 4.18 (dd, J = 5.4, 1.5 Hz, 2H), 4.05 (d, J = 7.1 Hz, 2H), 1.77 (s, 3H), 1.70 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 146.9, 143.3, 137.6, 131.6, 129.4, 126.9, 124.0, 120.7, 69.9, 67.1, 25.8, 18.0; HRMS (EI) calculated for $[C_{14}H_{17}NO_3]^+$ (M^+) requires *m/z* 247.1203, found *m/z* 247.1213.

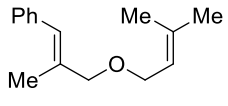


2-[(*E*)-3-(3-Methyl-but-2-enyloxy)-propenyl]-pyridine: A flame-dried 50 mL round-bottomed flask was charged with (*E*)-3-(2'-pyridinyl)allyl alcohol[7] (675 mg, 5.0 mmol), 3,3-dimethylallyl bromide (1.0g, purity: 90%, 6.0 mmol), and dry DMF (5 mL). The mixture was cooled to 0 °C and added with 60% NaH (240 mg, 6.0 mmol), then allowed to

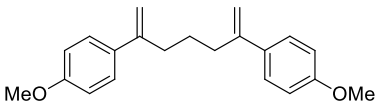
warm slowly to room temperature. After stirring for 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted two times with Et_2O. The combined organic phases were then washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by flash-column chromatography using 2:1 hexanes/ethyl acetate as the eluent to afford 701 mg (3.5 mmol, 69%) of a colorless oil. IR(neat) 2972, 2914, 2853, 1659, 1587, 1565, 1470, 1431, 1115 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 8.55 (d, J = 4.6 Hz, 1H), 7.64-7.59 (m, 1H), 7.29 (d, J = 7.9 Hz, 1H), 7.14-7.09 (m, 1H), 6.79 (dt, J = 16.0, 5.4 Hz, 1H), 6.72 (d, J = 16.0 Hz, 1H), 5.42-5.37 (m, 1H), 4.20 (dd, J = 5.4, 1.4 Hz, 2H), 4.04 (d, J = 7.1 Hz, 2H), 1.76 (s, 3H), 1.69 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 155.3, 149.4, 137.1, 136.4, 131.2, 131.1, 122.0, 121.4, 121.0, 69.9, 66.8, 25.7, 18.0. HRMS (EI) calculated for $[C_{13}H_{17}NO]^+(M^+)$ requires *m/z* 203.1305, found *m/z* 203.1311.



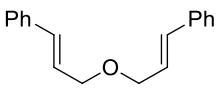
2-[(*E*)-3-(3-Methyl-but-2-enyloxy)-propenyl]-furan: : A flame-dried 50 mL round-bottomed flask was charged with (*E*)-3-(2'-furyl)allyl alcohol[8] (620 mg, 5.0 mmol), 3,3-dimethylallyl bromide (1.0g, purity: 90%, 6.0 mmol), and dry DMF (5 mL). The mixture was cooled to 0 °C and added with 60% NaH (240 mg, 6.0 mmol), then allowed to warm slowly to room temperature. After stirring for 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted two times with Et_2O. The combined organic phases were then washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by flash-column chromatography using 40:1 hexanes/ethyl acetate as the eluent to afford 654 mg (3.4 mmol, 68%) of a colorless oil. IR(neat) 2972, 2916, 2854, 1675, 1490, 1377, 1113 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.34 (d, J = 1.4 Hz, 1H), 6.43 (d, J = 15.9 Hz, 1H), 6.36-6.34 (m, 1H), 6.26-6.20 (m, 2H), 5.41-5.36 (m, 1H), 4.10 (dd, J = 5.9, 1.5 Hz, 2H), 4.00 (d, J = 7.1 Hz, 2H), 1.76 (s, 3H), 1.68 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 152.5, 141.9, 137.1, 125.1, 121.0, 120.3, 111.2, 107.7, 70.0, 66.6, 25.8, 18.0. HRMS (EI) calculated for $[C_{12}H_{16}O_2]^+(M^+)$ requires *m/z* 192.1145, found *m/z* 192.1146.



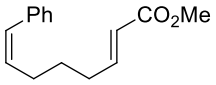
[(*E*)-2-Methyl-3-(3-methyl-but-2-enyloxy)-propenyl]-benzene: A flame-dried 50 mL round-bottomed flask was charged with (*E*)-2-methylcinnamyl alcohol (740 mg, 5.0 mmol), 3,3-dimethylallyl bromide (1.0g, purity: 90%, 6.0 mmol), and dry DMF (5 mL). The mixture was cooled to 0 °C and added with 60% NaH (240 mg, 6.0 mmol), then allowed to warm slowly to room temperature. After stirring for 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted two times with Et_2O. The combined organic phases were then washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by flash-column chromatography using 40:1 hexanes/ethyl acetate as the eluent to afford 807 mg (3.7 mmol, 75%) of a colorless oil. IR(neat) 2972, 2915, 2855, 1676, 1600, 1491, 1445, 1073 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.33 (t, J = 7.9 Hz, 2H), 7.30-7.27 (m, 2H), 7.21 (t, J = 7.1 Hz, 1H), 6.51 (s, 1H), 5.43-5.38 (m, 1H), 4.02 (s, 2H), 3.99 (d, J = 7.1 Hz, 2H), 1.90 (d, J = 1.2 Hz, 3H), 1.77 (s, 3H), 1.69 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 137.6, 137.0, 135.5, 128.9, 128.1, 126.8, 126.3, 121.2, 76.2, 66.3, 25.8, 18.0, 15.5. HRMS (EI) calculated for $[C_{14}H_{17}O]^+([M\text{-}CH_3]^+)$ requires *m/z* 201.1274, found *m/z* 201.1265.



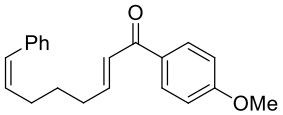
2,6-Di(4-methoxyphenyl)-1,6-heptdiene: [9] A solution of methyltriphenyl-phosphonium bromide (5.36 mg, 15 mmol) in dry THF (20 mL) was placed in a flame-dried 50 mL round-bottomed flask. *n*-Butyllithium (6 mL, 2.5 M in hexanes, 15 mmol) was then added dropwise at 0 °C, and the reaction was stirred for an additional 30 min. 1,5-Bis-(4-methoxy-phenyl)-pentane-1,5-dione[10] (1.56 g, 5 mmol) was added to the reaction mixture, and the reaction was stirred for an additional 4 h at room temperature. The reaction was cooled to 0 °C, quenched with 1 mL water, and eluted through a plug of silica gel with diethyl ether. The filtrate was concentrated by rotary evaporation. The crude mixture was then purified by flash-column chromatography using 20:1 hexanes/EtOAc as the eluent to give 1.070 g (3.5 mmol, 69%) of a white solid. Mp: 48-50 °C (hexane/EtOAc). IR(neat) 2955, 2935, 2837, 1607, 1513, 1248 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.29 (d, J = 8.8 Hz, 4H), 6.83 (d, J = 8.8 Hz, 4H), 5.20 (d, J = 1.4 Hz, 2H), 4.96 (d, J = 1.4 Hz, 2H), 3.80 (s, 6H), 2.50 (t, J = 7.9 Hz, 4H), 1.64-1.57 (m, 2H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 158.9, 147.5, 133.5, 127.2, 113.6, 110.9, 55.2, 34.8, 26.7. HRMS (EI) calculated for $[C_{21}H_{24}O_2]^+(M^+)$ requires *m/z* 308.1771, found *m/z* 308.1773.



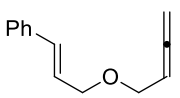
(*E*,*E'*)-Dicinnamyl ether: A flame-dried 50 mL round-bottomed flask was charged with 60% NaH (480 mg, 12 mmol) and dry THF (10 mL). (*E*)-Cinnamyl alcohol (1.34 g, 10 mmol) in THF (8 mL) was added dropwise, and the reaction was stirred for an additional 30 min at room temperature. The flask was then cooled to 0 °C, and a solution of (*E*)-cinnamyl bromide (2.17 g, 11 mmol) in THF (12 mL) was added dropwise. The mixture was allowed to warm slowly to room temperature. After stirring for 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted two times with Et_2O. The combined organic phases were then washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by flash-column chromatography using 40:1 hexanes/ethyl acetate as the eluent to afford 2.07 g (8.3 mmol, 83% yield) of a white solid. Mp: 40-41 ^oC (hexane/EtOAc). All analytical data were consistent with previously reported values.[11]



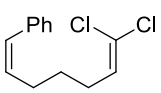
(2*E*,7*Z*)-8-Phenyl-octa-2,7-dienoic acid methyl ester: A solution of (*Z*)-6-phenylhex-5-enal (528 mg, 3.0 mmol) and (methoxycarbonylmethylene)triphenylphosphorane[12] (1.20 g, 3.6 mmol) in CH_2Cl_2 (5 mL) was placed in a round-bottomed flask. The mixture was stirred 12 h and then concentrated *in vacuo*. The crude residue was purified by flash column chromatography (20:1 hexanes/EtOAc) to afford 0.61 g (2.7 mmol, 88% yield) of the title compound as an oil. IR(neat) 3009, 2948, 2858, 1725, 1658, 1436, 1271 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.35-7.30 (m, 2H), 7.26-7.20 (m, 3H), 6.95 (dt, J = 15.6, 7.3 Hz, 1H), 6.45 (d, J = 11.6 Hz, 1H), 5.79 (dt, J = 15.6, 1.7 Hz, 1H), 5.63 (dt, J = 11.6, 7.3 Hz, 1H), 3.71 (s, 3H), 2.36 (2, J = 7.3, 1.7 Hz, 2H), 2.22 (qd, J = 7.3, 1.4 Hz, 2H), 1.65-1.58 (m, 2H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 167.0, 149.0, 137.5, 131.8, 129.6, 128.7, 128.1, 126.6, 121.2, 51.4, 31.7, 28.2, 27.9. HRMS (EI) calculated for $[C_{15}H_{18}O_2]^+(M^+)$ requires *m/z* 230.1302, found *m/z* 230.1290.



(2*E*,7*Z*)-1-(4-Methoxy-phenyl)-8-phenyl-octa-2,7-dien-1-one: A solution of (*Z*)-6-phenylhex-5-enal[18] (528 mg, 3.0 mmol) and ((4-methoxyphenyl)carbonylmethylene) triphenylphosphorane[13] (1.48 g, 3.6 mmol), in CH_2Cl_2 (5 mL) was placed in a round-bottomed flask. The mixture was stirred 4 days and then concentrated *in vacuo*. The crude residue was purified by flash column chromatography (30:1 hexanes/EtOAc) to afford 0.704 g (2.3 mmol, 77% yield) of the title compound as an oil. IR(neat) 3007, 2932, 2839, 1664, 1617, 1597, 1509, 1258 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.90 (d, J = 9.1 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.28-7.24 (m, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.01 (dt, J = 15.3, 6.9 Hz, 1H), 6.92 (d, J = 9.1 Hz, 2H), 6.84 (dt, J = 15.3, 1.6 Hz, 1H), 6.46 (d, J = 11.7 Hz, 1H), 5.66 (dt, J = 11.7, 7.4 Hz, 1H), 3.86 (s, 3H), 2.40 (qd, J = 7.5, 1.7 Hz, 2H), 2.33 (qt, J = 7.0, 1.3 Hz, 2H), 1.72-1.64 (m, 2H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 189.0, 163.2, 148.1, 137.5, 132.0, 130.8, 129.5, 128.7, 128.1, 126.6, 125.8, 113.7, 55.4, 32.2, 28.4, 28.0. HRMS (EI) calculated for $[C_{21}H_{22}O_2]^+(M^+)$ requires *m/z* 306.1615, found *m/z* 306.1619.

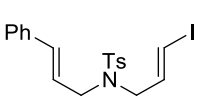


((*E*)-3-Buta-2,3-dienyloxy-propenyl)-benzene: A flame-dried 50 mL round-bottomed flask was charged with 60% NaH (240 mg, 6.0 mmol) and dry THF (5 mL). Allenol[14] (350 mg, 5.0 mmol) in THF (4 mL) was added dropwise, and the reaction was stirred for an additional 30 min at room temperature. The flask was then cooled to 0 °C, and a solution of (*E*)-cinnamyl bromide (1.2 g, 6.0 mmol) in THF (6 mL) was added dropwise. The mixture was allowed to warm slowly to room temperature. After stirring for 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted two times with Et_2O. The combined organic phases were then washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by flash-column chromatography using 40:1 hexanes/ethyl acetate as the eluent to afford 594 mg (3.2 mmol, 64% yield) of a colorless oil. IR(neat) 3026, 2852, 1955, 1599, 1495, 1449, 1360, 1114, 1080 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.26-7.21 (m, 1H), 6.61 (d, J = 16.0 Hz, 1H), 6.29 (dt, J = 16.0, 6.0 Hz, 1H), 5.28 (dt, J = 13.5, 6.7 Hz, 1H), 4.80 (dt, J = 6.4, 2.5 Hz, 2H), 4.17 (dd, J = 6.2, 1.6 Hz, 2H), 4.07 (dt, J = 6.7, 2.5 Hz, 2H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 209.4, 136.7, 132.7, 128.5, 127.7, 126.5, 125.9, 87.7, 75.7, 70.4, 67.8. HRMS (EI) calculated for $[C_{13}H_{13}O]^+([M-H]^+)$ requires *m/z* 185.0961, found *m/z* 185.0962.

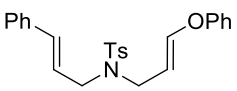


((*Z*)-7,7-Dichloro-hepta-1,6-dienyl)-benzene: A flame-dried 50 mL round-bottomed flask was charged with triphenylphosphine (1.044 g, 4 mmol), magnesium turnings (48 mg, 2 mmol), and dry THF (10 mL). Carbon tetrachloride (616 mg, 4 mmol) was then added dropwise and the reaction was stirred for an additional 30 min. A solution of (*Z*)-6-phenylhex-5-enal (352 mg, 2.0 mmol) in THF (2 mL) was added to the reaction mixture, and the reaction was stirred for an additional 4 h at room temperature. The reaction was cooled to 0 °C, quenched with water (1 mL), and filtered through a plug of silica gel

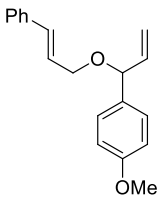
with diethyl ether. The filtrate was concentrated by rotary evaporation. The crude mixture was then purified by flash-column chromatography using 100:1 hexanes/EtOAc as the eluent to give 341 mg (1.42 mmol, 71% yield) of an oil. IR(neat) 3010, 2927, 2859, 1621, 1494, 1447 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.34 (t, J = 7.3 Hz, 2H), 7.28-7.20 (m, 3H), 6.45 (d, J = 11.5 Hz, 1H), 5.83 (t, J = 7.3 Hz, 1H), 5.63 (dt, J = 11.5, 7.3 Hz, 1H), 2.36 (qd, J = 7.6, 1.7 Hz, 2H), 2.19 (q, J = 7.6 Hz, 2H), 1.61-1.53 (m, 2H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 137.5, 131.8, 129.6, 129.5, 128.7, 128.2, 126.6, 120.2, 29.2, 28.4, 28.0. HRMS (EI) calculated for $[C_{13}H_{14}Cl_2]^+(M^+)$ requires *m/z* 240.0468, found *m/z* 240.0457.



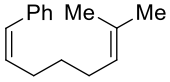
***N*-((*E*)-3-Iodo-allyl)-4-methyl-*N*-((*E*)-3-phenyl-allyl)-benzenesulfonamide**: A flame-dried 50 mL round-bottomed flask was charged 60% NaH (96 mg, 2.4 mmol) and dry THF (3 mL). (*E*)-Cinnamyl *p*-tosylamide[15] (574 mg, 2.0 mmol) in THF (4 mL) was added dropwise, and the reaction was stirred for an additional 30 min at room temperature. The flask was then cooled to 0 °C, and a solution of (*E*)-3-iodolallyl bromide[16] (590 mg, 2.4 mmol) in THF (3 mL) was added dropwise. The mixture was allowed to warm slowly to room temperature. After stirring for 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted two times with Et_2O. The combined organic phases were then washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by flash-column chromatography using 10:1 hexanes/ethyl acetate as the eluent to afford 674.0 mg (1.5 mmol, 74% yield) of a white solid. Mp: 94-95 °C (hexane/EtOAc). IR(neat) 3056, 3026, 2920, 2854, 1598, 1495, 1447, 1338, 1156 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H), 7.33-7.22 (m, 7H), 6.41 (d, J = 16.1 Hz, 1H), 6.35 (dt, J = 14.7 Hz, 1H), 6.27 (dt, J = 14.9, 1.0 Hz, 1H), 5.92 (dt, J = 15.5, 6.5 Hz, 1H), 3.94 (d, J = 6.5 Hz, 2H), 3.78 (d, J = 6.5 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 143.5, 140.1, 136.9, 135.9, 134.3, 129.7, 128.5, 128.0, 127.1, 126.4, 123.3, 80.2, 50.6, 49.4, 21.5. HRMS (ESI) calculated for $[C_{19}H_{24}IN_2O_2S]^+([M+NH_4]^+)$ requires *m/z* 471.0598, found *m/z* 471.0600.



***N*-((*E*)-3-phenoxy-allyl)-*N*-((*E*)-3-phenyl-allyl)-p-toluenesulfonamide**: *N*-((*E*)-3-Iodo-allyl)-4-methyl-*N*-((*E*)-3-phenyl-allyl)-benzenesulfonamide (906 mmol, 2.0 mmol), PhOH (310 mg, 2.5 mmol), CuCl (198 mg, 2 mmol), *N*-methylmorphine (252 mg, 2.5 mmol), Cs_2CO_3 (815 mg, 2.5 mmol), and toluene (2 mL) were placed in a round-bottomed flask equipped with a reflux condenser. The mixture was stirred and refluxed 12 h and then concentrated *in vacuo*. The crude residue was purified by flash column chromatography (10:1 to 5:1 hexanes/EtOAc) to afford 0.381 g (0.9 mmol, 45% yield) of the title compound as an oil. IR(neat) 3028, 2922, 2858, 1672, 1595, 1490, 1339, 1229, 1160 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.74 (d, J = 8.3 Hz, 2H), 7.31-7.19 (m, 9H), 7.06 (t, J = 7.3 Hz, 1H), 6.91-6.87 (m, 2H), 6.52 (d, J = 12.2 Hz, 1H), 6.48 (d, J = 15.9 Hz, 1H), 6.01 (dt, J = 15.9, 6.6 Hz, 1H), 5.09 (dt, J = 12.2, 7.6 Hz, 1H), 4.01 (d, J = 6.6 Hz, 2H), 3.88 (d, J = 7.6 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 156.5, 146.4, 143.3, 137.4, 136.1, 133.8, 129.7, 129.6, 128.6, 127.9, 127.2, 126.4, 124.1, 123.3, 116.9, 105.6, 48.6, 44.6, 21.5. HRMS (ESI) calculated for $[C_{25}H_{26}NO_3S]^+([M+H]^+)$ requires *m/z* 420.1628, found *m/z* 420.1616.

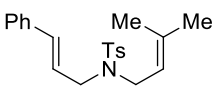


1-Methoxy-4-[1-((*E*)-3-phenyl-allyloxy)-allyl]-benzene: A flame-dried 50 mL round-bottomed flask was charged with 1-(4'-methoxyphenyl)allyl alcohol[17] (324 mg, 2.0 mmol), and (*E*)-cinnamyl bromide (0.50 g, 2.4 mmol), and dry DMF (5 mL). The mixture was cooled to 0 °C and treated with 60% NaH (96 mg, 2.4 mmol), then allowed to warm slowly to room temperature. After stirring for 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted two times with Et_2O. The combined organic phases were then washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by flash-column chromatography using 20:1 hexanes/ethyl acetate as the eluent to afford 0.440 mg (1.6 mmol, 79% yield) of a colorless oil. IR(neat) 3026, 2836, 1610, 1511, 1247 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.39-7.36 (m, 2H), 7.33-7.27 (m, 4H), 7.25-7.21 (m, 1H), 6.90 (d, J = 8.6 Hz, 2H), 6.58 (d, J = 15.9 Hz, 1H), 6.30 (dt, J = 15.9, 6.1 Hz, 1H), 5.98 (ddd, J = 16.9, 10.4, 6.7 Hz, 1H), 5.27 (d, J = 16.9 Hz, 1H), 5.20 (d, J = 10.4 Hz, 1H), 4.82 (d, J = 6.7 Hz, 1H), 4.17-4.08 (m, 2H), 3.81 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 159.2, 139.0, 136.8, 133.0, 132.2, 128.5, 128.2, 127.6, 126.4, 126.3, 116.0, 113.9, 81.6, 68.7, 55.3. HRMS (EI) calculated for $[C_{19}H_{20}O_2]^+(M^+)$ requires *m/z* 280.1458, found *m/z* 280.1454.

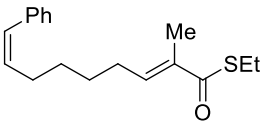


((*Z*)-7-Methyl-octa-1,6-dienyl)-benzene: A flame-dried 50 mL round-bottomed flask was charged with isopropyl(triphenyl)phosphonium iodide (1.30 g, 3.0 mmol) and dry THF (10 mL). *n*-Butyllithium (1.2 mL, 2.5 M in hexanes, 3.0 mmol) was then added dropwise at 0 °C, and the reaction was stirred for an additional 30 min. (*Z*)-6-Phenylhex-5-enal[18] (352 mmol, 2.0mmol) in

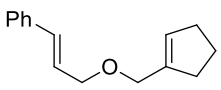
THF (2 mL) was added to the reaction mixture and the reaction was stirred for an additional 3 h at room temperature. The reaction was cooled to 0 °C, quenched with water (1 mL), and filtered through a plug of silica gel with diethyl ether. The filtrate was concentrated by rotary evaporation. The crude mixture was then purified by flash-column chromatography using hexanes as the eluent to give 354 mg (1.77 mmol, 89% yield) of a colorless oil. IR(neat) 2966, 2925, 2856, 1600, 1494, 1447, 1376 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.32 (t, J = 7.1 Hz, 2H), 7.29-7.26 (m, 2H), 7.23-7.18 (m, 1H), 6.40 (d, J = 11.5 Hz, 1H), 5.66 (dt, J = 11.5, 7.3 Hz, 1H), 5.13-5.08 (m, 1H), 2.33 (qd, J = 7.3, 1.9 Hz, 2H), 2.01 (q, J = 7.3 Hz, 2H), 1.67 (s, 3H), 1.57 (s, 3H), 1.52-1.45 (m, 2H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 137.8, 133.0, 131.7, 128.8, 128.7, 128.1, 126.4, 124.3, 30.1, 28.2, 27.7, 25.7, 17.6. HRMS (EI) calculated for $[C_{15}H_{20}]^+(M^+)$ requires *m/z* 200.1560, found *m/z* 200.1562.



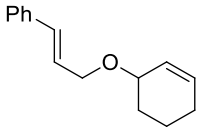
4-Methyl-*N*-(3-methyl-but-2-enyl)-*N*-((*E*)-3-phenyl-allyl)-benzenesulfonamide: A flame-dried 50 mL round-bottomed flask was charged with 60% NaH (96 mg, 2.4 mmol) and dry THF (3 mL). (*E*)-Cinnamyl *p*-tosylamide[15] (574 mg, 2.0 mmol) in THF (4 mL) was added dropwise, and the reaction was stirred for an additional 30 min at room temperature. The flask was then cooled to 0 °C, and a solution of 3,3-dimethylallyl bromide (400 g, 90% purity, 2.4 mmol) in 3 mL THF was added dropwise. The mixture was allowed to warm slowly to room temperature. After stirring for 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted two times with Et_2O. The combined organic phases were then washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by flash-column chromatography using 10:1 hexanes/ethyl acetate as the eluent to afford 497 mg (1.4 mmol, 70% yield) of a white solid. Mp: 69-70 ^oC(hexane/EtOAc). IR(neat) 2971, 2919, 1598, 1495, 1449, 1341, 1159 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.72 (d, J = 8.5 Hz, 2H), 7.31-7.27 (m, 4H), 7.27-7.21 (m, 3H), 6.40 (d, J = 15.8 Hz, 1H), 5.97 (dt, J = 15.8, 6.8 Hz, 1H), 5.05-5.00 (m, 1H), 3.93 (d, J = 6.8 Hz, 2H), 3.82 (d, J = 7.1 Hz, 2H), 2.43 (s, 3H), 1.66 (s, 3H), 1.57 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 143.1, 137.7, 136.9, 136.4, 133.5, 129.6, 128.5, 127.8, 127.3, 126.4, 124.4, 119.0, 48.8, 44.6, 25.7, 21.4, 17.9. HRMS (ESI) calculated for $[C_{21}H_{26}NO_2S]^+([M+H]^+)$ requires *m/z* 356.1679, found *m/z* 356.1671.



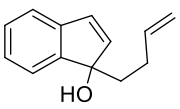
(2*E*,8*E*)-2-Methyl-9-phenyl-nona-2,8-dienethioic acid *S*-ethyl ester: To a stirred solution of *S*-ethyl 2-(diethoxyphosphoryl)propanethioate[19] (0.635 g, 2.5 mmol) in dimethoxyethane (6 mL) under an atmosphere of N_2 was added 60% NaH (80 mg, 2.0 mmol). After 30 min, the reaction was cooled to 0 °C, (*Z*)-6-phenylhept-5-enal[18, 20] (0.38 g, 2.0 mmol) was added, and the mixture was stirred at room temperature for an additional 3 h. The reaction was cooled to 0 °C, quenched with water (10 ml), and extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was purified by column chromatography (50:1 hexanes/EtOAc) to afford 0.402 g (1.4 mmol, 70% yield) of the title compound as a colorless oil. IR(neat) 2929, 2857, 1654, 1623, 1447 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.33 (t, J = 7.2 Hz, 2H), 7.28-7.24 (m, 2H), 7.24-7.19 (m, 1H), 6.70 (tq, J = 7.3, 1.3 Hz, 1H), 6.43 (d, J = 11.7 Hz, 1H), 5.64 (dt, J = 11.7, 7.3 Hz, 1H), 2.91 (q, J = 7.3 Hz, 2H), 2.38-2.32 (m, 2H), 2.20-2.15 (m, 2H), 1.83 (d, J = 1.3 Hz, 3H), 1.52-1.47 (m, 4H), 1.26 (t, J = 7.4 Hz, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 193.8, 140.5, 137.6, 136.1, 132.5, 129.1, 128.7, 128.1, 126.5, 29.5, 28.4, 28.2, 28.1, 23.2, 14.7, 12.4. HRMS (EI) calculated for $[C_{18}H_{24}OS]^+(M^+)$ requires *m/z* 288.1543, found *m/z* 288.1533.



[(*E*)-3-(Cyclopent-1-enylmethoxy)-propenyl]-benzene: A flame-dried 50 mL round-bottomed flask was charged with cyclopent-1-enyl-methanol[21] (490 mg, 5.0 mmol), (*E*)-cinnamyl bromide (1.18 g, 6.0 mmol), and dry DMF (5 mL). The mixture was cooled to 0 ^oC and treated with 60% NaH (240 mg, 6.0 mmol), and then allowed to warm slowly to room temperature. After stirring for 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted two times with Et_2O. The combined organic phases were then washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by flash-column chromatography using 40:1 hexanes/ethyl acetate as the eluent to afford 744 mg (3.5 mmol, 70% yield) of a colorless oil. IR(neat) 3026, 2926, 2846, 1599, 1495, 1448, 1357, 1074 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.40-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.25-7.21 (m, 1H), 6.61 (d, J = 15.9 Hz, 1H), 6.30 (dt, J = 15.9, 5.9 Hz, 1H), 5.68-5.65 (m, 1H), 4.14 (dd, J = 6.1, 1.4 Hz, 2H), 4.09-4.07 (m, 2H), 2.39-2.32 (m, 4H), 1.95-1.88 (m, 2H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 141.5, 136.8, 132.2, 128.5, 127.7, 127.6, 126.5, 126.3, 70.7, 69.0, 33.0, 32.4, 23.3. HRMS (EI) calculated for $[C_{15}H_{18}O]^+(M^+)$ requires *m/z* 214.1353, found *m/z* 214.1353.



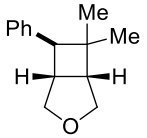
[(*E*)-3-(Cyclohex-2-enyloxy)-propenyl]-benzene: A flame-dried 50 mL round-bottomed flask was charged with 2-cyclohexen-1-ol (490 mg, 5.0 mmol), (*E*)-cinnamyl bromide (1.18 g, 6.0 mmol), and dry DMF (5 mL). The mixture was cooled to 0 °C and treated with 60% NaH (240 mg, 6.0 mmol), then allowed to warm slowly to room temperature. After stirring for 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted two times with Et_2O. The combined organic phases were then washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by flash-column chromatography using 40:1 hexanes/ethyl acetate as the eluent to afford 647 mg (3.0 mmol, 60% yield) of a colorless oil. IR(neat) 3026, 2935, 2862, 1653, 1599, 1496, 1449, 1073 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.38 (d, J = 7.1 Hz, 2H), 7.30 (t, J = 7.1 Hz, 2H), 7.22 (t, J = 7.1 Hz, 1H), 6.61 (d, J = 16.1 Hz, 1H), 6.32 (dt, J = 16.1, 6.1 Hz, 1H), 5.88 (dtd, J = 10.0, 3.4, 0.9 Hz, 1H), 5.81 (ddd, J = 10.0, 4.9, 1.9 Hz, 1H), 4.24 (ddd, J = 12.7, 6.1, 1.5 Hz, 1H), 4.18 (ddd, J = 12.7, 6.1, 1.5 Hz, 1H), 3.99-3.94 (m, 1H), 2.11-2.02 (m, 1H), 2.00-1.92 (m, 1H), 1.89-1.68 (m, 3H), 1.61-1.52 (m, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 136.8, 131.8, 131.0, 128.5, 127.7, 127.5, 126.9, 126.4, 72.2, 68.7, 28.4, 25.2, 19.2. HRMS (EI) calculated for $[C_{15}H_{18}O]^+(M^+)$ requires *m/z* 214.1353, found *m/z* 214.1344.



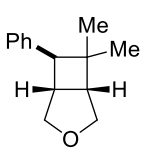
1-But-3-enyl-1*H*-inden-1-ol: Inden-1-one[22] (650 mg, 5.0 mmol) and THF (10 mL) were placed in a round-bottomed flask. A solution of homoallylmagnesium bromide in THF (10 mL, 1M, 10 mmol) was added dropwise at 0 °C. After 30 min, the mixture was quenched with water (5 mL), the phases were separated, and the aqueous phase was extracted an additional two times with Et_2O. The combined organics were then washed with brine, dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The crude mixture could then be purified by flash-column chromatography using 10:1 hexanes/ethyl acetate as the eluent to afford 0.417 g (2.2 mmol, 45% yield) of the title compound as a white solid. Mp: 51-52 °C (hexane/Et_2O). IR(neat) 3363, 3069, 2926, 2855, 1640, 1457, 1067 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.37 (d, J = 7.0 Hz, 1H), 7.27-7.22 (m, 1H), 7.22-7.17 (m, 2H), 6.63 (d, J = 5.8 Hz, 1H), 6.31 (d, J = 5.5 Hz, 1H), 5.84-5.74 (m, 1H), 5.02-4.90 (m, 2H), 2.23-2.06 (m, 2H), 1.96-1.83 (m, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 148.4, 141.9, 141.2, 138.4, 131.4, 128.5, 126.3, 121.9, 121.5, 114.4, 84.8, 36.6, 28.8. HRMS (EI) calculated for $[C_{13}H_{14}O]^+$ (M^+) requires *m/z* 186.1040, found *m/z* 186.1042.

III. [2+2] Photocycloadditions

General Procedure: A solution of 1 mol% of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$ and 1 equiv of styrene substrate in DMSO (0.01 M) was placed in a test tube (20 x 150 mm). The reaction was stirred in front of a 23 W (1380 lumen) compact fluorescent lamp at a distance of 10 cm. Upon consumption of starting material, the reaction mixture was diluted with Et_2O (60 mL) and water (10 mL). The aqueous layer was separated and extracted with ether (60 mL x 2). The combined organic layers were washed with water (10 mL x 2), brine (20 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel.

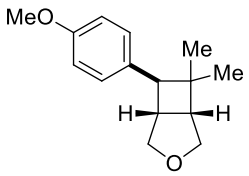


(1*R,5*R**,7*S**)-6,6-Dimethyl-7-phenyl-3-oxa-bicyclo[3.2.0]heptane (4)**, from (*E*)-**3**. Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 60.6 mg (0.3 mmol) of [(*E*)-3-(3-methyl-but-2-enyloxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. After 15 h, the reaction mixture was worked up and purified by flash column chromatography using 40:1 hexanes/EtOAc as the eluent to give 48.6 mg (0.24 mmol, 81% yield, dr: >10:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 60.6 mg (0.3 mmol) of [(*E*)-3-(3-methyl-but-2-enyloxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. Isolated 50.7 mg (0.25 mmol, 84% yield, dr: >10:1). IR(neat) 2955, 2846, 1497, 1457, 1076 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.20 (d, J = 7.3 Hz, 1H), 7.16-7.12 (m, 2H), 4.17 (d, J = 10.0 Hz, 1H), 3.79 (d, J = 9.1 Hz, 1H), 3.51 (dd, J = 10.0, 6.6 Hz, 1H), 3.44 (dd, J = 9.1, 4.5 Hz, 1H), 3.27 (td, J = 7.8, 4.5 Hz, 1H), 2.99 (d, J = 7.2 Hz, 1H), 2.40 (dd, J = 7.8, 7.2 Hz, 1H), 1.11 (s, 3H), 0.74 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 140.6, 128.0, 127.6, 125.9, 72.1, 69.1, 51.9, 46.6, 38.0, 37.2, 26.2, 24.2. HRMS (EI) calculated for $[C_{14}H_{18}O]^+(M^+)$ requires *m/z* 202.1353, found *m/z* 202.1364.

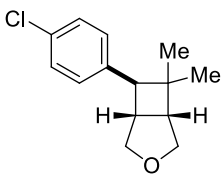


(1*R,5*R**,7*S**)-6,6-Dimethyl-7-phenyl-3-oxa-bicyclo[3.2.0]heptane (4)**, from (*Z*)-**3**. Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 60.6 mg (0.3 mmol) of [(*Z*)-3-(3-methyl-but-2-enyloxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. After 15 h, the reaction mixture was worked up and purified by flash column chromatography using 40:1 hexanes/EtOAc as the eluent to give 52.1 mg (0.26 mmol, 86% yield, dr: >10:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of

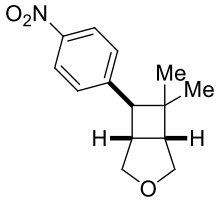
$Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 61.4 mg (0.3 mmol) of [(*Z*)-3-(3-Methyl-but-2-enyloxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. Isolated 50.6 mg (0.25 mmol, 82% yield, dr: >10:1). All spectroscopic properties were identical to those of the product from the (*E*) alkene.



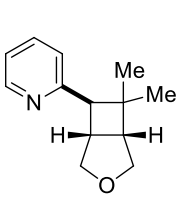
(1*R,5*R**,7*S**)-7-(4-Methoxyphenyl)-6,6-dimethyl-3-oxa-bicyclo[3.2.0]heptane (8)**: Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 70.4 mg (0.3 mmol) of 1-methoxy-4-[(*E*)-3-(3-methyl-but-2-enyloxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. After 15 h, the reaction mixture was worked up and purified by flash column chromatography using 40:1 hexanes/EtOAc as the eluent to give 61.5 mg (0.27 mmol, 87% yield, dr: >10:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 69.6 mg (0.3 mmol) of 1-methoxy-4-[(*E*)-3-(3-methyl-but-2-enyloxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. Isolated 62.4 mg (0.27 mmol, 90% yield, dr: >10:1). IR(neat) 2954, 2838, 1611, 1582, 1513, 1458, 1247 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.06 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 4.16 (d, J = 10.1 Hz, 1H), 3.80 (s, 3H), 3.78 (d, J = 9.1 Hz, 1H), 3.50 (dd, J = 10.1, 7.0 Hz, 1H), 3.43 (dd, J = 9.1, 4.3 Hz, 1H), 3.24-3.18 (m, 1H), 2.91 (d, J = 7.4 Hz, 1H), 2.39 (t, J = 7.5 Hz, 1H), 1.08 (s, 3H), 0.73 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 157.9, 132.7, 128.6, 113.4, 72.0, 69.1, 55.2, 51.2, 46.5, 38.4, 37.2, 26.2, 24.1. HRMS (EI) calculated for $[C_{15}H_{20}O_2]^+(M^+)$ requires *m/z* 232.1458, found *m/z* 232.1462.



(1*R,5*R**,7*S**)-7-(4-Chlorophenyl)-6,6-dimethyl-3-oxa-bicyclo[3.2.0]heptane (9)**: Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 71.8 mg (0.3 mmol) of 1-chloro-4-[(*E*)-3-(3-methyl-but-2-enyloxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. After 10 h, the reaction mixture was worked up and purified by flash column chromatography using 60:1 hexanes/EtOAc as the eluent to give 58.9 mg (0.25 mmol, 87% yield, dr: >10:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 71.8 mg (0.3 mmol) of 1-chloro-4-[(*E*)-3-(3-methyl-but-2-enyloxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. Isolated 58.5 mg (0.25 mmol, 82% yield, dr: >10:1). IR(neat) 2955, 2848, 1493, 1458, 1081 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.27 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 4.16 (d, J = 10.1 Hz, 1H), 3.77 (d, J = 9.1 Hz, 1H), 3.50 (dd, J = 10.1, 6.8 Hz, 1H), 3.43 (dd, J = 9.1, 4.5 Hz, 1H), 3.24-3.18 (m, 1H), 2.95 (d, J = 7.5 Hz, 1H), 2.40 (t, J = 7.5 Hz, 1H), 1.09 (s, 3H), 0.73 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 139.1, 131.6, 128.9, 128.1, 71.9, 69.0, 51.3, 46.5, 38.1, 37.2, 26.1, 24.1. HRMS (EI) calculated for $[C_{14}H_{17}ClO]^+(M^+)$ requires *m/z* 236.0953, found *m/z* 236.0956.

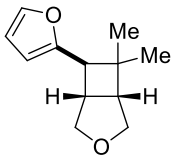


(1*R,5*R**,7*S**)-6,6-Dimethyl-7-(4-nitrophenyl)-3-oxa-bicyclo[3.2.0]heptane (10)**: Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 74.1 mg (0.3 mmol) of 1-nitro-4-[(*E*)-3-(3-methyl-but-2-enyloxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. After 12 h, the reaction mixture was worked up and purified by flash column chromatography using 20:1 to 10:1 to 5:1 hexanes/Et_2O as the gradient to give 52.6 mg (0.21 mmol, 71% yield, dr: >10:1) of cycloadduct as a white solid. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 74.1 mg (0.3 mmol) of 1-nitro-4-[(*E*)-3-(3-methyl-but-2-enyloxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. Isolated 51.7 mg (0.21 mmol, 70% yield, dr: >10:1). Mp: 87-88 °C (Hexane/$CHCl_3$). IR(neat) 2945, 2872, 1596, 1510, 1346 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 8.17 (d, J = 8.9 Hz, 2H), 7.29 (d, J = 8.9 Hz, 2H), 4.19 (d, J = 10.2 Hz, 1H), 3.81 (d, J = 9.1 Hz, 1H), 3.53 (d, J = 10.2, 6.7 Hz, 1H), 3.47 (d, J = 9.1, 4.5 Hz, 1H), 3.31 (td, J = 7.7, 4.5 Hz, 1H), 3.10 (d, J = 7.3 Hz, 1H), 2.48-2.43 (m, 1H), 1.16 (s, 3H), 0.75 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 148.6, 146.3, 128.2, 123.3, 71.8, 69.0, 51.8, 46.6, 37.98, 37.96, 38.0, 26.2, 24.2. HRMS (EI) calculated for $[C_{14}H_{17}NO_3]^+(M^+)$ requires *m/z* 247.1203, found *m/z* 247.1196.

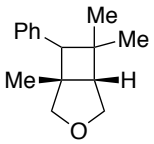


2-((1*R,5*R**,6*R**)-7,7-Dimethyl-3-oxa-bicyclo[3.2.0]hept-6-yl)-pyridine (11)**: Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 60.9 mg (0.3 mmol) of 2-[(*E*)-3-(3-methyl-but-2-enyloxy)-propenyl]-pyridine, and 30 mL (0.01 M) of DMSO. After 12 h, the reaction mixture was worked up and purified by flash column chromatography using 2:1 hexanes/EtOAc as the eluent to give 42.7 mg (0.21 mmol, 70% yield, dr: 10:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 61.3 mg (0.3 mmol) of 2-[(*E*)-3-(3-methyl-but-2-enyloxy)-propenyl]-pyridine, and 30 mL (0.01 M) of DMSO. Isolated 43.6 mg (0.21 mmol, 71% yield, dr: 10:1).

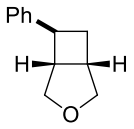
IR(neat) 2952, 2845, 1590, 1567, 1473, 1433, 1080 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 8.58 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.57 (td, J = 7.6, 1.8 Hz, 1H), 7.10 (ddd, J = 7.4, 4.9, 0.9 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 4.17 (d, J = 10.1 Hz, 1H), 3.81 (d, J = 9.2 Hz, 1H), 3.67 (ddd, J = 7.9, 7.3, 4.6 Hz, 1H), 3.51 (dd, J = 10.1, 6.4 Hz, 1H), 3.46 (dd, J = 9.2, 4.6 Hz, 1H), 3.06 (d, J = 6.8 Hz, 1H), 2.43 (dd, J = 7.6, 7.0 Hz, 1H), 1.16 (s, 3H), 0.74 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 160.3, 148.9, 135.5, 122.9, 120.9, 72.2, 69.1, 53.5, 46.5, 37.5, 36.5, 25.8, 24.1. HRMS (EI) calculated for $[C_{13}H_{17}NO]^+(M^+)$ requires *m/z* 203.1305, found *m/z* 203.1315.



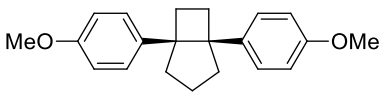
(1*S,5*R**,7*R**)-7-Furan-2-yl-6,6-dimethyl-3-oxa-bicyclo[3.2.0]heptane (12)**: Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 59.1 mg (0.3 mmol) of 2-[(*E*)-3-(3-methyl-but-2-enyloxy)-propenyl]-furan, and 30 mL (0.01 M) of DMSO. After 10 h, the reaction mixture was worked up and purified by flash column chromatography using 60:1 hexanes/EtOAc as the eluent to give 38.7 mg (0.20 mmol, 65% yield, dr: 8:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 58.0 mg (0.3 mmol) of 2-[(*E*)-3-(3-methyl-but-2-enyloxy)-propenyl]-furan, and 30 mL (0.01 M) of DMSO. Isolated 36.5 mg (0.19 mmol, 63% yield, dr: 8:1). IR(neat) 2956, 2848, 1592, 1506, 1458, 1076 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.33 (dd, J = 1.8, 0.6 Hz, 1H), 6.31 (dd, J = 3.2, 1.8 Hz, 1H), 6.03 (dt, J = 3.2, 0.9 Hz, 1H), 4.11 (d, J = 10.0 Hz, 1H), 3.79 (d, J = 9.1 Hz, 1H), 3.45 (dd, J = 10.0, 6.7 Hz, 1H), 3.40 (dd, J = 9.1, 4.4 Hz, 1H), 3.18-3.13 (m, 1H), 2.86 (d, J = 7.0 Hz, 1H), 2.40 (dd, J = 7.6, 7.0 Hz, 1H), 1.06 (s, 3H), 0.88 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 156.1, 141.2, 109.9, 105.6, 71.9, 69.1, 46.5, 45.8, 38.4, 37.6, 25.9, 23.6. HRMS (EI) calculated for $[C_{12}H_{16}O_2]^+(M^+)$ requires *m/z* 192.1145, found *m/z* 192.1140.



1,6,6-Trimethyl-7-phenyl-3-oxa-bicyclo[3.2.0]heptane (**13**) Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 65.3 mg (0.3 mmol) of [(*E*)-2-methyl-3-(3-methyl-but-2-enyloxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. After 72 h, the reaction mixture was worked up and purified by flash column chromatography using 40:1 hexanes/EtOAc as the eluent to give 51.2 mg (0.24 mmol, 78% yield, dr: 1:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 65.7 mg (0.3 mmol) of [(*E*)-2-methyl-3-(3-methyl-but-2-enyloxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. Isolated 48.5 mg (0.22 mmol, 74% yield, dr: 1:1). **(1*R**,5*S**,7*S**) Diastereomer**: IR(neat) 2954, 2926, 2866, 2841, 1603, 1496, 1456, 1064 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.30-7.24 (m, 4H), 7.23-7.18 (m, 1H), 4.14 (d, J = 10.1 Hz, 1H), 3.74 (d, J = 8.8 Hz, 1H), 3.61 (dd, J = 10.1, 6.7 Hz, 1H), 3.15 (s, 1H), 3.06 (d, J = 8.8 Hz, 1H), 2.01 (d, J = 6.7 Hz, 1H), 1.39 (s, 3H), 1.20 (s, 3H), 1.08 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 139.6, 129.4, 127.8, 125.9, 79.2, 69.6, 54.5, 53.5, 47.2, 36.9, 27.1, 24.9, 19.0. HRMS (EI) calculated for $[C_{15}H_{20}O]^+(M^+)$ requires *m/z* 216.1509, found *m/z* 216.1499. **(1*R**,5*S**,7*R**) Diastereomer**: IR(neat) 2949, 2862, 1602, 1495, 1451, 1068 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.30-7.25 (m, 4H), 7.23-7.18 (m, 1H), 4.11 (d, J = 9.8 Hz, 1H), 4.10 (d, J = 9.8 Hz, 1H), 3.65 (dd, J = 9.8, 5.6 Hz, 1H), 3.14 (d, J = 9.8 Hz, 1H), 3.10 (s, 1H), 2.18 (d, J = 5.6 Hz, 1H), 1.40 (s, 3H), 1.31 (s, 3H), 0.94 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 139.2, 130.0, 127.9, 126.1, 74.3, 69.9, 59.2, 54.0, 45.6, 35.6, 34.9, 26.2, 18.9. HRMS (EI) calculated for $[C_{15}H_{20}O]^+(M^+)$ requires *m/z* 216.1509, found *m/z* 216.1506.

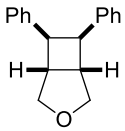


(1*S,5*R**,6*S**)-6-Phenyl-3-oxa-bicyclo[3.2.0]heptane** (**14**): Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 52.4 mg (0.3 mmol) of [(*E*)-3-(prop-2-enyloxy)-propenyl]-benzene[23], and 30 mL (0.01 M) of DMSO. After 28 h, the reaction mixture was worked up and purified by flash column chromatography using 50:1 hexanes/EtOAc as the eluent to give 43.3 mg (0.25 mmol, 83% yield, dr: 7:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 52.0 mg (0.3 mmol) of [(*E*)-3-(prop-2-enyloxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. Isolated 40.1 mg (0.23 mmol, 77% yield, dr: 7:1). All analytical data data were consistent with previously reported values.[23]

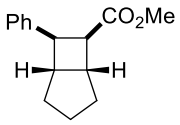


(1*R,5*S**)-1,5-Bis-(4-methoxy-phenyl)-bicyclo[3.2.0]heptane (16)**: Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 92.4 mg (0.3 mmol) of 2,6-di(4-methoxyphenyl)-1,6-heptdiene, and 30 mL (0.01 M) of DMSO. After 20 h, the reaction mixture was worked up and purified by flash column chromatography using 30:1 hexanes/EtOAc as the eluent to give 82.5 mg (0.27 mmol, 89% yield, dr: >10:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 92.4 mg (0.3 mmol) of 2,6-di(4-methoxyphenyl)-1,6-heptdiene, and 30 mL

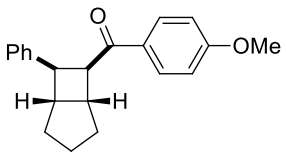
(0.01 M) of DMSO. Isolated 84.5 mg (0.27 mmol, 91% yield, dr: >10:1). All analytical data data were consistent with previously reported values. [9]



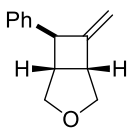
6,7-Diphenyl-3-oxabicyclo[3.2.0]heptane (**17**): Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 75.0 mg (0.3 mmol) of (*E*,*E'*)-dicinnamyl ether, and 30 mL (0.01 M) of DMSO. After 4 h, the reaction mixture was worked up and purified by flash column chromatography using 40:1 hexanes/EtOAc as the eluent to give 63.8 mg (0.26 mmol, 85% yield, dr: 3:1) of cycloadduct. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 75.0 mg (0.3 mmol) of (*E*,*E'*)-dicinnamyl ether, and 30 mL (0.01 M) of DMSO. Isolated 65.4 mg (0.27 mmol, 87% yield, dr: 3:1). **(1*R**,5*S**,6*R**,7*S**) Diastereomer** (major): solid. Mp: 73-75 ^oC (hexane/EtOAc). IR(neat) 3027, 2958, 2846, 1602, 1496, 1453, 1072 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.09-7.05 (m, 4H), 7.01-6.97 (m, 2H), 6.95-6.92 (m, 4H), 4.10 (d, J = 9.4 Hz, 2H), 3.75 (d, J = 4.1 Hz, 2H), 3.73-3.69 (m, 2H), 3.33-3.28 (m, 2H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 140.8, 128.1, 127.7, 125.6, 74.0, 47.2, 42.1. HRMS (EI) calculated for $[C_{18}H_{18}O]^+(M^+)$ requires *m/z* 250.1353, found *m/z* 250.1354. **(1*R**,5*S**,6*S**,7*S**) Diastereomer** (minor): Oil. IR(neat) 3026, 2961, 2849, 1602, 1495, 1447, 1082 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.35-7.28 (m, 4H), 7.28-7.24 (m, 4H), 7.23-7.17 (m, 2H), 4.04 (d, J = 9.2 Hz, 1H), 3.85-3.78 (m, 2H), 3.67 (dd, J = 9.6, 6.6 Hz, 1H), 3.54 (dd, J = 9.2, 4.1 Hz, 1H), 3.48 (dd, J = 10.1, 7.0 Hz, 1H), 3.28-3.22 (m, 1H), 3.12 (td, J = 7.0, 4.4 Hz, 1H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 144.4, 140.3, 128.5, 128.4, 127.7, 126.4, 126.3, 126.2, 72.9, 68.4, 45.9, 45.5, 44.1, 40.7. HRMS (EI) calculated for $[C_{18}H_{18}O]^+(M^+)$ requires *m/z* 250.1353, found *m/z* 250.1349.



(1*S,5*R**,6*S**,7*R**)-7-Phenyl-bicyclo[3.2.0]heptane-6-carboxylic acid methyl ester** (**18**): Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 70.1 mg (0.3 mmol) of (2*E*,7*Z*)-8-phenyl-octa-2,7-dienoic acid methyl ester, and 30 mL (0.01 M) of DMSO. After 11 h, the reaction mixture was worked up and purified by flash column chromatography using 100:1 hexanes/EtOAc as the eluent to give 60.2 mg (0.26 mmol, 86% yield, dr: 4:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 69.0 mg (0.3 mmol) of (2*E*,7*Z*)-8-phenyl-octa-2,7-dienoic acid methyl ester, and 30 mL (0.01 M) of DMSO. Isolated 61.4 mg (0.27 mmol, 89% yield, dr: 4:1). IR(neat) 2948, 2855, 1733, 1494, 1434, 1172 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.24-7.20 (m, 2H), 7.19-7.15 (m, 1H), 3.30 (dd, J = 10.6, 5.5 Hz, 1H), 3.27-3.21 (m, 1H), 3.15 (s, 3H), 3.06-3.01 (m, 2H), 1.95-1.88 (m, 2H), 1.72-1.57 (m, 4H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 173.3, 141.6, 128.0, 127.7, 126.3, 50.9, 47.3, 45.9, 42.1, 36.8, 32.8, 32.1, 25.4. HRMS (EI) calculated for $[C_{15}H_{18}O_2]^+(M^+)$ requires *m/z* 230.1302, found *m/z* 230.1295.

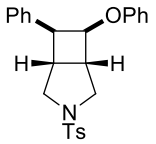


(4-Methoxy-phenyl)-((1*S,5*R**,6*S**,7*R**)-7-phenyl-bicyclo[3.2.0]hept-6-yl)-methanone** (**19**): Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 92.0 mg (0.3 mmol) of (2*E*,7*Z*)-1-(4-methoxy-phenyl)-8-phenyl-octa-2,7-dien-1-one, and 30 mL (0.01 M) of DMSO. After 11 h, the reaction mixture was worked up and purified by flash column chromatography using 40:1 hexanes/EtOAc as the eluent to give 66.1 mg (0.22 mmol, 72% yield, dr: 6:1) of cycloadduct as a white solid. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 91.8 mg (0.3 mmol) of (2*E*,7*Z*)-1-(4-methoxy-phenyl)-8-phenyl-octa-2,7-dien-1-one, and 30 mL (0.01 M) of DMSO. Isolated 70.2 mg (0.23 mmol, 76% yield, dr: 6:1). Mp: 110-111 ^oC (hexane/$CHCl_3$). IR(neat) 2946, 2853, 1666, 1601, 1510, 1245, 1169 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.52 (d, J = 8.9 Hz, 2H), 7.06-7.00 (m, 4H), 6.95-6.91 (m, 1H), 6.69 (d, J = 8.9 Hz, 2H), 3.83 (ddd, J = 10.8, 5.7, 1.0 Hz, 1H), 3.75 (s, 3H), 3.69-3.63 (m, 1H), 3.42 (dd, J = 10.9, 4.8 Hz, 1H), 2.87 (td, J = 7.6, 4.8 Hz, 1H), 2.09-1.93 (m, 2H), 1.77 (dd, J = 12.9, 6.5 Hz, 1H), 1.74-1.61 (m, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 197.8, 162.6, 141.5, 130.11, 130.05, 128.1, 127.7, 126.0, 113.0, 55.2, 49.8, 48.9, 43.5, 35.6, 32.9, 32.6, 25.5. HRMS (EI) calculated for $[C_{21}H_{22}O]^+(M^+)$ requires *m/z* 306.1615, found *m/z* 306.1609.

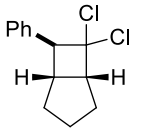


(1*R,5*R**,7*S**)-6-Methylene-7-phenyl-3-oxa-bicyclo[3.2.0]heptane** (**20**): Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 56.0 mg (0.3 mmol) of ((*E*)-3-buta-2,3-dienyloxy-propenyl)-benzene, and 30 mL (0.01 M) of DMSO. After 20 h, the reaction mixture was worked up and purified by flash column chromatography using 50:1 hexanes/EtOAc as the eluent to give 44.5 mg (0.24 mmol, 80% yield, dr: 7:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 55.8 mg (0.3 mmol) of ((*E*)-3-buta-2,3-dienyloxy-propenyl)-benzene, and 30 mL (0.01 M) of DMSO. Isolated 41.7 mg (0.22 mmol, 75% yield, dr: 7:1).

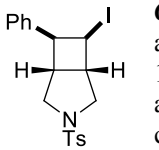
IR(neat) 2962, 2846, 1672, 1602, 1494, 1451, 1072 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2H), 7.29-7.25 (m, 2H), 7.24-7.20 (m, 1H), 5.00 (t, J = 2.4 Hz, 1H), 4.83 (t, J = 2.4 Hz, 1H), 4.10 (t, J = 9.2 Hz, 2H), 3.81-3.77 (m, 1H), 3.63 (dd, J = 8.6, 5.9 Hz, 1H), 3.59-3.52 (m, 2H), 2.97 (dt, J = 7.6, 5.1 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 153.1, 142.8, 128.5, 127.2, 126.4, 108.6, 74.0, 73.6, 52.8, 46.7, 45.3. HRMS (EI) calculated for $[C_{13}H_{14}O]^+(M^+)$ requires *m/z* 186.1040, found *m/z* 186.1043.



6-Phenoxy-7-phenyl-3-(toluene-4-sulfonyl)-3-aza-bicyclo[3.2.0]heptane (**21**): Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 125.7 mg (0.3 mmol) of 4-methyl-*N*-((*E*)-3-phenoxy-allyl)-*N*-((*E*)-3-phenyl-allyl)-benzenesulfonamide, and 30 mL (0.01 M) of DMSO. After 4 h, the reaction mixture was worked up and purified by flash column chromatography using 9:1 hexanes/EtOAc as the eluent to give 102.2 mg (0.24 mmol, 81% yield, dr: 2:1) of cycloadduct as a white solid. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 125.7 mg (0.3 mmol) of 4-methyl-*N*-((*E*)-3-phenoxy-allyl)-*N*-((*E*)-3-phenyl-allyl)-benzenesulfonamide, and 30 mL (0.01 M) of DMSO. Isolated 91.7 mg (0.22 mmol, 73% yield, dr: 2:1). **(1*R**,5*S**,6*R**,7*S**) Diastereomer** (major): Mp: 162-165 °C (hexane/EtOAc). IR(neat) 3061, 3029, 2976, 2918, 2855, 1599, 1495, 1346, 1240, 1170 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 7.26-7.17 (m, 4H), 7.14-7.06 (m, 3H), 6.80 (t, J = 7.2 Hz, 1H), 6.56 (d, J = 8.3 Hz, 2H), 4.82 (dd, J = 7.5, 2.4 Hz, 1H), 3.78 (d, J = 10.1 Hz, 1H), 3.70 (dd, J = 7.5, 3.7 Hz, 1H), 3.63 (d, J = 10.1 Hz, 1H), 3.07-3.01 (m, 2H), 2.76-2.66 (m, 2H), 2.45 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 156.7, 143.9, 137.9, 131.4, 129.7, 129.05, 129.04, 128.1, 127.8, 126.5, 120.7, 115.1, 75.6, 53.6, 52.4, 49.0, 43.9, 41.3, 21.5. HRMS (ESI) calculated for $[C_{25}H_{25}NO_3SNa]^+([M+Na]^+)$ requires *m/z* 442.1453, found *m/z* 442.1454. **(1*R**,5*S**,6*S**,7*S**)-Diastereomer** (minor): Mp: 139-140 °C (hexane/EtOAc). IR(neat) 3028, 2973, 2922, 2857, 1597, 1495, 13444, 1233, 1169 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.74 (d, J = 8.3 Hz, 2H), 7.35-7.30 (m, 4H), 7.26-7.18 (m, 5H), 6.92 (t, J = 7.2 Hz, 1H), 6.75-6.71 (m, 2H), 4.64 (t, J = 7.3 Hz, 1H), 3.82 (dd, J = 10.5, 2.1 Hz, 1H), 3.62 (d, J = 9.8 Hz, 1H), 3.51 (t, J = 7.3 Hz, 1H), 3.29-3.22 (m, 1H), 2.90 (dd, J = 9.8, 5.2 Hz, 1H), 2.87 (dd, J = 10.5, 8.8 Hz, 1H), 2.72 (td, J = 7.3, 5.2 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 156.9, 143.6, 141.4, 132.7, 129.6, 129.5, 128.6, 127.9, 126.9, 126.7, 121.1, 115.1, 73.7, 53.4, 50.1, 46.3, 40.9, 39.2, 21.5. HRMS (ESI) calculated for $[C_{25}H_{25}NO_3SNa]^+([M+Na]^+)$ requires *m/z* 442.1453, found *m/z* 442.1447.

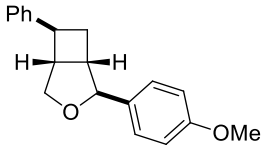


(1*S,5*R**,7*S**)-6,6-Dichloro-7-phenyl-bicyclo[3.2.0]heptane** (**22**): Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 72.0 mg (0.3 mmol) of ((*Z*)-7,7-dichloro-hepta-1,6-dienyl)-benzene, and 30 mL (0.01 M) of DMSO. After 20 h, the reaction mixture was worked up and purified by flash column chromatography using hexanes as the eluent to give 64.6 mg (0.27 mmol, 90% yield, dr: >10:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 72.0 mg (0.3 mmol) of ((*Z*)-7,7-dichloro-hepta-1,6-dienyl)-benzene, and 30 mL (0.01 M) of DMSO. Isolated 63.1 mg (0.26 mmol, 88% yield, dr: >10:1). IR(neat) 3030, 2957, 2856, 1606, 1497, 1448 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H), 7.34-7.28 (m, 3H), 3.75 (d, J = 7.5 Hz, 1H), 3.36-3.26 (m, 2H), 2.32-2.25 (m, 1H), 1.99-1.91 (m, 2H), 1.85-1.76 (m, 1H), 1.76-1.70 (m, 1H), 1.70-1.60 (m, 1H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 137.3, 128.2, 128.0, 127.4, 90.2, 61.1, 57.6, 39.2, 31.0, 29.4, 25.6. HRMS (EI) calculated for $[C_{13}H_{14}Cl_2]^+(M^+)$ requires *m/z* 240.0468, found *m/z* 240.0459.

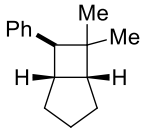


6-Iodo-7-phenyl-3-(toluene-4-sulfonyl)-3-aza-bicyclo[3.2.0]heptane (**23**): Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 136.7 mg (0.3 mmol) of *N*-((*E*)-3-iodo-allyl)-4-methyl-*N*-((*E*)-3-phenyl-allyl)-benzenesulfonamide, and 30 mL (0.01 M) of DMSO. After 15 h, the reaction mixture was worked up and purified by flash column chromatography using 15:1 to 10:1 to 5:1 hexanes/EtOAc as the gradient to give 123.0 mg (0.27 mmol, 90% yield, dr: 2:1) of cycloadduct as a white solid. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 135.1 mg (0.3 mmol) of *N*-((*E*)-3-iodo-allyl)-4-methyl-*N*-((*E*)-3-phenyl-allyl)-benzenesulfonamide, and 30 mL (0.01 M) of DMSO. Isolated 121.5 mg (0.27 mmol, 90% yield, dr: 2:1). **(1*R**,5*S**,6*R**,7*S**) Diastereomer** (major): Mp: 170-172°C (hexane/EtOAc). IR(neat) 3028, 2984, 2876, 1598, 1496, 1450, 1342, 1165 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 2H), 7.39-7.33 (m, 4H), 7.32-7.27 (m, 1H), 7.17-7.13 (m, 2H), 4.91 (dd, J = 9.0, 4.6 Hz, 1H), 3.66 (d, J = 10.23 Hz, 1H), 3.61-3.56 (m, 2H), 3.36-3.31 (m, 1H), 3.27 (dt, J = 8.2, 6.0 Hz, 1H), 2.70 (dd, J = 10.2, 6.4 Hz, 1H), 2.59 (dd, J = 10.2, 6.4 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 144.0, 142.8, 131.5, 129.7, 128.12, 128.05, 128.0, 127.3, 53.4, 53.2, 49.0, 48.4, 42.2, 29.2, 21.5. HRMS (ESI) calculated for $[C_{19}H_{21}INO_2S]^+([M+H]^+)$ requires *m/z* 454.0333, found *m/z* 454.0331. **(1*R**,5*S**,6*S**,7*S**) Diastereomer** (minor): Mp: 158-160°C (hexane/$CHCl_3$). IR(neat) 3028, 2972, 2922,

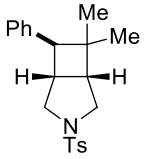
2854, 1598, 1497, 1467, 1453, 1345, 1168 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.79 (d, J = 8.3 Hz, 2H), 7.38-7.32 (m, 4H), 7.29-7.25 (m, 1H), 7.23-7.20 (m, 2H), 4.73 (t, J = 8.8 Hz, 1H), 3.93 (dd, J = 10.7, 1.4 Hz, 1H), 3.76-3.71 (m, 1H), 3.58 (d, J = 9.8 Hz, 1H), 3.19 (td, J = 6.9, 5.1 Hz, 1H), 3.07 (dd, J = 10.7, 8.1 Hz, 1H), 3.00-2.93 (m, 1H), 2.78 (dd, J = 9.8, 5.1 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 143.8, 140.6, 132.4, 129.7, 128.8, 128.1, 127.3, 126.0, 54.9, 54.7, 54.1, 45.1, 41.2, 27.2, 21.6. HRMS (ESI) calculated for $[C_{19}H_{24}IN_2O_2S]^+$($[M+NH_4]^+$) requires *m/z* 471.0598, found *m/z* 471.0595.



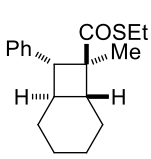
(1*S,2*S**,5*R**,6*S**)-2-(4-Methoxy-phenyl)-6-phenyl-3-oxa-bicyclo[3.2.0]heptane** (**24**): Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 84.0 mg (0.3 mmol) of 1-methoxy-4-[1-((*E*)-3-phenyl-allyloxy)-allyl]-benzene, and 30 mL (0.01 M) of DMSO. After 36 h, the reaction mixture was worked up and purified by flash column chromatography using 30:1 hexanes/EtOAc as the eluent to give 67.2 mg (0.24 mmol, 80% yield, dr: 9:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 83.4 mg (0.3 mmol) of 1-methoxy-4-[1-((*E*)-3-phenyl-allyloxy)-allyl]-benzene, and 30 mL (0.01 M) of DMSO. Isolated 67.5 mg (0.24 mmol, 81% yield, dr: 9:1). IR(neat) 2957, 2931, 2855, 1611, 1511, 1246 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H), 7.30-7.27 (m, 2H), 7.25-7.18 (m, 3H), 6.87 (d, J = 8.4 Hz, 2H), 5.09 (s, 1H), 4.01 (d, J = 9.2 Hz, 1H), 3.90 (dd, J = 9.5, 5.5 Hz, 1H), 3.79 (s, 3H), 3.41 (td, J = 8.4, 5.5 Hz, 1H), 3.21-3.15 (m, 1H), 3.13-3.08 (m, 1H), 2.45-2.41 (m, 2H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 158.7, 145.8, 134.3, 128.5, 127.1, 126.4, 126.0, 113.7, 86.3, 72.8, 55.3, 48.1, 42.4, 41.8, 31.6. HRMS (EI) calculated for $[C_{19}H_{20}O_2]^+$(M^+) requires *m/z* 280.1458, found *m/z* 280.1462.



(1*S,5*R**,7*S**)-6,6-Dimethyl-7-phenyl-bicyclo[3.2.0]heptane** (**25**): Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 59.5 mg (0.3 mmol) of ((*Z*)-7-methyl-octa-1,6-dienyl)-benzene, and 30 mL (0.01 M) of DMSO. After 38 h, the reaction mixture was worked up and purified by flash column chromatography using hexanes as the eluent to give 49.6 mg (0.25 mmol, 83% yield, dr: >10:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 61.2 mg (0.3 mmol) of ((*Z*)-7-methyl-octa-1,6-dienyl)-benzene, and 30 mL (0.01 M) of DMSO. Isolated 55.0 mg (0.28 mmol, 90% yield, dr: >10:1). IR(neat) 2950, 2859, 1602, 1497, 1447 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.19-7.13 (m, 3H), 3.14-3.08 (m, 1H), 2.74 (d, J = 7.8 Hz, 1H), 2.17 (dd, J = 8.8, 8.1 Hz, 1H), 1.87-1.79 (m, 3H), 1.57-1.43 (m, 3H), 1.02 (s, 3H), 0.71 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 141.8, 127.8, 127.7, 125.5, 51.8, 46.0, 37.5, 37.4, 31.1, 27.2, 27.0, 26.8, 24.3. HRMS (EI) calculated for $[C_{15}H_{20}]^+$(M^+) requires *m/z* 200.1560, found *m/z* 200.1561.

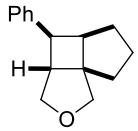


(1R,5R,7S)-6,6-Dimethyl-7-phenyl-3-(toluene-4-sulfonyl)-3-aza-bicyclo[3.2.0]heptane (**26**) Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 105.0 mg (0.3 mmol) of 4-methyl-*N*-(3-methyl-but-2-enyl)-*N*-((*E*)-3-phenyl-allyl)-benzenesulfonamide, and 30 mL (0.01 M) of DMSO. After 12 h, the reaction mixture was worked up and purified by flash column chromatography using 10:1 hexanes/EtOAc as the eluent to give 94.6 mg (0.27 mmol, 90% yield, dr: >10:1) of cycloadduct as a white solid. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 106.5 mg (0.3 mmol) of 4-methyl-*N*-(3-methyl-but-2-enyl)-*N*-((*E*)-3-phenyl-allyl)-benzenesulfonamide, and 30 mL (0.01 M) of DMSO. Isolated 90.3 mg (0.25 mmol, 85% yield, dr: >10:1).Mp: 172-174 ^oC (hexane/$CHCl_3$). IR(neat) 2951, 2863, 1599, 1495, 1338, 1161 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.19 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 7.2 Hz, 2H), 3.72 (d, J = 10.5 Hz, 1H), 3.42 (d, J = 9.6 Hz, 1H), 3.21 (d, J = 7.2 Hz, 1H), 3.15 (td, J = 7.9, 5.5 Hz, 1H), 2.64 (dd, J = 10.5, 7.9 Hz, 1H), 2.61 (dd, J = 9.6, 5.5 Hz, 1H), 2.44 (s, 3H), 2.28 (t, J = 7.9 Hz, 1H), 1.17 (s, 3H), 0.70 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 143.5, 139.9, 132.0, 129.5, 128.1, 128.0, 127.5, 126.1, 52.9, 51.7, 48.9, 45.0, 37.7, 36.3, 26.1, 24.2, 21.5. HRMS (ESI) calculated for $[C_{21}H_{26}NO_2S]^+$($[M+H]^+$) requires *m/z* 356.1679, found *m/z* 356.1684.

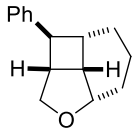


7-Methyl-8-phenyl-bicyclo[4.2.0]octane-7-carbothioic acid S-ethyl ester (**27**): Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 86.4 mg (0.3 mmol) of (2*E*,8*E*)-2-methyl-9-phenyl-nona-2,8-dienethioic acid S-ethyl ester, and 30 mL (0.01 M) of DMSO. After 36 h, the reaction mixture was worked up and purified by flash column chromatography using 100:1 hexanes/EtOAc as the eluent to give 67.5 mg (0.23 mmol, 78% yield, dr: 3:1) of cycloadduct as a colorless oil. Experiment 2: 3.3 mg (0.003

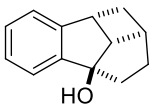
mmol) of Ir(dF(CF_3)ppy)$_2$(dtbbpy)(PF_6), 86.4 mg (0.3 mmol) of (2*E*,8*E*)-2-methyl-9-phenyl-nona-2,8-dienethioic acid S-ethyl ester, and 30 mL (0.01 M) of DMSO. Isolated 70.7 mg (0.25 mmol, 82% yield, dr: 3:1). **(1*R**,6*R**,7*S**,8*S**) Diastereomer** (major): IR(neat) 2967, 2928, 2855, 1676, 1448, 967 cm^{-1}. ^{1}H NMR: (500.2 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H), 7.25-7.22 (m, 2H), 7.22-7.18 (m, 1H), 3.64 (d, J = 10.0 Hz, 1H), 2.91 (qd, J = 7.4, 1.2 Hz, 2H), 2.00-1.90 (m, 3H), 1.90-1.81 (m, 2H), 1.78-1.73 (m, 1H), 1.48-1.34 (m, 4H), 1.28 (t, J = 7.4 Hz, 3H), 1.02 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 205.0, 139.4, 128.0, 127.9, 126.2, 60.4, 52.2, 48.1, 41.1, 31.0, 26.7, 26.5, 26.2, 23.0, 14.8, 13.0. HRMS (EI) calculated for $[C_{18}H_{24}OS]^+(M^+)$ requires *m/z* 288.1543, found *m/z* 288.1537. **(1*S**,6*R**,7*S**,8*R**) Diastereomer** (minor): IR(neat) 2930, 2854, 1667, 1449, 955 cm^{-1}. ^{1}H NMR: (500.2 MHz, $CDCl_3$) δ 7.26 (t, J = 7.5 Hz, 2H), 7.17 (t, J = 7.5 Hz, 1H), 7.14-7.11 (m, 2H), 3.41 (d, J = 11.3 Hz, 1H), 3.12-3.04 (m, 1H), 2.79 (dt, J = 10.9, 8.2 Hz, 1H), 2.59 (qq, J = 13.3, 7.4 Hz, 2H), 1.81-1.73 (m, 1H), 1.73-1.67 (m, 1H), 1.67-1.46 (m, 7H), 1.42-1.33 (m, 1H), 1.25-1.16 (m, 1H), 0.92 (t, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 203.8, 139.2, 128.0, 127.5, 126.4, 59.3, 53.1, 36.5, 31.7, 24.8, 23.7, 23.0, 22.8, 21.8, 19.5, 14.4. HRMS (EI) calculated for $[C_{18}H_{24}OS]^+(M^+)$ requires *m/z* 288.1543, found *m/z* 288.1542.



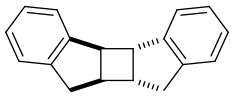
(3a*R,4*S**,4a*R**,7a*S**)-4-Phenyl-hexahydro-2-oxa-cyclobuta[1,2:1,4]dicyclopentene** (**28**): Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of Ir(dF(CF_3)ppy)$_2$(dtbbpy)(PF_6), 64.2 mg (0.3 mmol) of [(*E*)-3-(cyclopent-1-enylmethoxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. After 21 h, the reaction mixture was worked up and purified by flash column chromatography using 30:1 hexanes/EtOAc as the eluent to give 47.6 mg (0.22 mmol, 73% yield, dr: 6:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of Ir(dF(CF_3)ppy)$_2$(dtbbpy)(PF_6), 64.8 mg (0.3 mmol) of [(*E*)-3-(cyclopent-1-enylmethoxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. Isolated 51.7 mg (0.24 mmol, 79% yield, dr: 5:1). IR(neat) 2950, 2842, 1604, 1497, 1447, 1346, 1033 cm^{-1}. ^{1}H NMR: (500.2 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.18 (t, J = 7.4 Hz, 1H), 7.14-7.11 (m, 2H), 4.03 (d, J = 9.3 Hz, 1H), 3.87 (d, J = 9.3 Hz, 1H), 3.66 (dd, J = 9.3, 5.1 Hz, 1H), 3.53 (d, J = 9.3 Hz, 1H), 3.44 (dd, J = 9.5, 6.8 Hz, 1H), 2.76 (t, J = 5.7 Hz, 1H), 2.71 (t, J = 8.8 Hz, 1H), 1.70-1.61 (m, 2H), 1.55-1.40 (m, 3H), 1.36-1.30 (m, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 140.2, 128.1, 127.5, 125.6, 75.1, 73.9, 54.3, 44.8, 44.6, 41.4, 32.9, 27.5, 26.6. HRMS (EI) calculated for $[C_{15}H_{18}O]^+(M^+)$ requires *m/z* 214.1353, found *m/z* 214.1354.



(1*S,1a*R**,3a*S**,6a*S**,6b*S**)-1-Phenyl-octahydro-3-oxa-cyclobut[cd]indene** (**29**): Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of Ir(dF(CF_3)ppy)$_2$(dtbbpy)(PF_6), 64.2 mg (0.3 mmol) of [(*E*)-3-(cyclohex-2-enyloxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. After 24 h, the reaction mixture was worked up and purified by flash column chromatography using 30:1 hexanes/EtOAc as the eluent to give 48.7 mg (0.23 mmol, 76% yield, dr: 9:1) of cycloadduct as an oil. Experiment 2: 3.3 mg (0.003 mmol) of Ir(dF(CF_3)ppy)$_2$(dtbbpy)(PF_6), 64.1 mg (0.3 mmol) of [(*E*)-3-(cyclohex-2-enyloxy)-propenyl]-benzene, and 30 mL (0.01 M) of DMSO. Isolated 47.4 mg (0.22 mmol, 74% yield, dr: 9:1). IR(neat) 2935, 2841, 1601, 1497, 1452, 1069, 1035 cm^{-1}. ^{1}H NMR: (500.2 MHz, $CDCl_3$) δ 7.33-7.28 (m, 2H), 7.24-7.21 (m, 2H), 7.21-7.16 (m, 1H), 4.02 (dt, J = 7.1, 2.1 Hz, 1H), 3.95 (d, J = 9.1 Hz, 1H), 3.58 (dd, J = 9.1, 3.9 Hz, 1H), 3.25 (t, J = 8.1 Hz, 1H), 2.92 (td, J = 7.1, 3.9 Hz, 1H), 2.67 (q, J = 7.7 Hz, 1H), 2.54-2.47 (m, 1H), 2.13-2.06 (m, 1H), 2.04-1.92 (m, 1H), 1.62-1.56 (m, 1H), 1.53-1.35 (m, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 145.3, 128.3, 126.6, 125.9, 75.5, 72.8, 45.2, 43.5, 35.2, 35.0, 27.4, 25.8, 14.7. HRMS (EI) calculated for $[C_{15}H_{18}O]^+(M^+)$ requires *m/z* 214.1353, found *m/z* 214.1360.

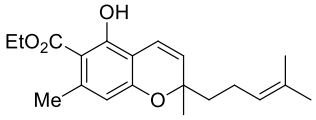


(3aR*,7bR*,7cS*)-1,1a,2,3,7b,7c-Hexahydro-benzo[a]cyclobuta[cd]pentalen-3a-ol (**30**): Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of Ir(dF(CF_3)ppy)$_2$(dtbbpy)(PF_6), 55.8 mg (0.3 mmol) of 1-but-3-enyl-1*H*-inden-1-ol, and 30 mL (0.01 M) of DMSO. After 3 h, the reaction mixture was worked up and purified by flash column chromatography using 10:1 hexanes/EtOAc as the eluent to give 50.3 mg (0.27 mmol, 90% yield, dr: >10:1) of cycloadduct as a white solid. Experiment 2: 3.3 mg (0.003 mmol) of Ir(dF(CF_3)ppy)$_2$(dtbbpy)(PF_6), 55.8 mg (0.3 mmol) of 1-but-3-enyl-1*H*-inden-1-ol, and 30 mL (0.01 M) of DMSO. Isolated 49.7 mg (0.27 mmol, 89% yield, dr: >10:1). Mp: 96-97 °C. IR(neat) 3254, 2959, 2924, 2862, 1477, 1456, 1442, 1312, 1059 cm^{-1}. ^{1}H NMR: (500.2 MHz, $CDCl_3$) δ 7.46-7.42 (m, 1H), 7.31-7.26 (m, 2H), 7.16-7.12 (m, 1H), 3.77-3.72 (m, 1H), 3.08 (dd, J = 8.9, 6.9 Hz, 1H), 2.90-2.81 (m, 1H), 2.76 (dt, J = 11.7, 9.1 Hz, 1H), 2.20-2.09 (m, 3H), 2.06-1.99 (m, 1H), 1.35 (dt, J = 11.7, 2.9 Hz, 1H), 1.12-1.03 (m, 1H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 148.4, 148.3, 128.9, 127.3, 123.9, 123.7, 93.0, 54.9, 42.2, 41.0, 35.4, 34.8, 31.9. HRMS (EI) calculated for $[C_{13}H_{14}O]^+(M^+)$ requires *m/z* 186.1040, found *m/z* 186.1044.

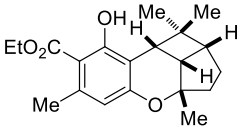


(4b*R,4c*R**,9a*R**,9b*R**)-4b,4c,9,9a,9b,10-hexahydrocyclobuta[1,2-a:4,3-a']diindene** (**31**): Experiment 1: Prepared according to the general procedure using 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 69.6 mg (0.6 mmol) of indene, and 30 mL (0.02 M) of DMSO. After 40 h, the reaction mixture was worked up and purified by flash column chromatography using 60:1 hexanes/EtOAc as the eluent to give 48.7 mg (0.21 mmol, 70% yield, dr: 4:1 (ratio of major isomer to all other isomers, as determined by ^{1}H NMR)) of cycloadduct as a white solid. Experiment 2: 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$, 70.0 mg (0.3 mmol) of indene, and 30 mL (0.02 M) of DMSO. Isolated 49.1 mg (0.21 mmol, 70% yield, dr: 4:1). Mp: 110-111 ^{o}C (hexane) (lit.[24] 110-112 ^{o}C). IR(neat) 2940, 2906, 2835, 1476, 1456 cm^{-1}. ^{1}H NMR: (500.2 MHz, $CDCl_3$) δ 7.41 (d, J = 6.9 Hz, 2H), 7.31 (d, J = 7.4 Hz, 2H), 7.29-7.21 (m, 4H), 3.70 (d, J = 5.6 Hz, 2H), 3.19 (dd, J = 16.5, 7.6 Hz, 2H), 2.94 (d, J = 16.5 Hz, 2H), 2.80-2.74 (m, 2H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 146.6, 144.0, 126.79, 126.76, 125.4, 125.2, 54.0, 43.1, 39.4. HRMS (EI) calculated for $[C_{18}H_{16}]^+(M^+)$ requires *m/z* 232.1247, found *m/z* 232.1238.

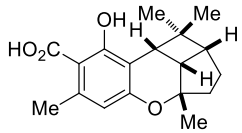
IV. Synthesis of (±)-cannabiorcicylolic acid



(±)-Ethyl cannabiorcichromenic ester (**35**): A mixture of ethyl 2,4-dihydroxy-6-methylbenzoate (50 mg, 0.25 mmol), citral (0.42 mL, 10 eq), and $Ca(OH)_2$ (185 mg, 10 eq) in *i*PrOH (1 mL) was placed in a sealed tube and heated at 140 ^{o}C for 48 h, then allowed to cool to room temperature. The reaction mixture was diluted with dichloromethane (100 mL), washed with aq. HCl (1 M) and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (100:1 hexanes/Et_2O) to afford 45.8 mg (0.14 mmol, 54% yield) of the title compound as a white solid. All analytical data data were consistent with previously reported values.[25]

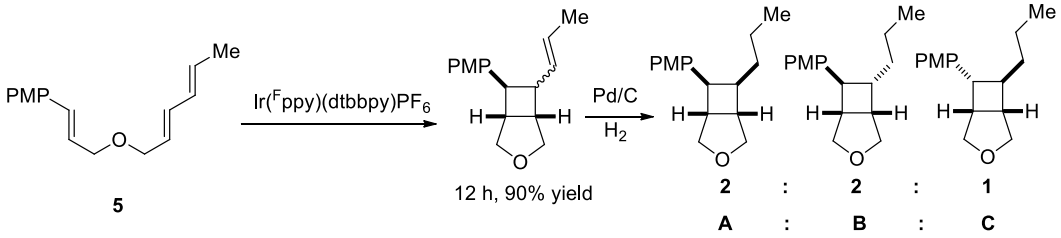


(±)-Ethyl cannabiorcicyclolic ester (**36**): A solution of 2.2 mg (0.002 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$ and 66.0 mg (0.2 mmol) of ethyl cannabiorcichromenic ester in DMSO (20 mL, 0.01 M) was placed in a test tube (20 x 150 mm). The reaction was stirred in front of a 23 W (1380 lumen) compact fluorescent lamp at a distance of 10 cm. After 8 h, the reaction mixture was diluted with Et_2O (60 mL) and water (10 mL). The aqueous layer was separated and extracted with ether (60 mL x 2). The combined organic layers were washed with water (10 mL x 2), brine (20 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified flash column chromatography using 100:1 hexanes/Et_2O as the eluent to give 56.7 mg (86% yield) of cycloadduct as a white solid. Mp: 118-119 ^{o}C (hexane/EtOAc). IR(neat) 2951, 2863, 1636, 1570, 1261 cm^{-1}. ^{1}H NMR: (500.2 MHz, $CDCl_3$) δ 11.90 (s, 1H), 6.25 (s, 1H), 4.38 (q, J = 7.3 Hz, 2H), 3.12 (d, J = 9.5 Hz, 1H), 2.57 (dd, J = 9.6, 7.3 Hz, 1H), 2.47 (s, 3H), 2.41 (t, J = 7.3 Hz, 1H), 1.92 (td, J = 13.1, 8.0 Hz, 1H), 1.71-1.63 (m, 2H), 1.63-1.56 (m, 1H), 1.42-1.37 (m, 9H), 0.78 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 172.2, 163.4, 157.8, 140.1, 113.1, 109.7, 104.6, 84.1, 61.0, 46.5, 39.1, 38.5, 37.5, 36.0, 33.6, 27.6, 25.7, 24.2, 17.7, 14.3. HRMS (ESI) calculated for $[C_{20}H_{27}O_4]^+([M+H]^+)$ requires *m/z* 331.1904, found *m/z* 331.1911.

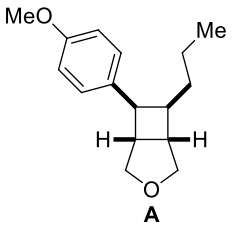


(±)-Cannabiorcicyclolic acid (**37**): To a solution of ethyl cannabiorcicyclolic ester (33.0 mg, 0.1 mmol) in methanol (0.2 mL) and THF (0.5 mL) was added 5 M aq. LiOH (2 mL). The reaction mixture was stirred at 60 °C for 8 h before it was acidified with 1 M aq. HCl, and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (1:1 hexanes/EtOAc) to afford 29.3 mg (0.1 mmol, 97% yield) of the title compound as a white solid. Mp: 174-176 ^{o}C (hexane/$CHCl_3$). IR(neat) 3060, 2942, 2861, 1618, 1576, 1453, 1257 cm^{-1}. ^{1}H NMR: (500.2 MHz, CDCl3) δ 11.64 (bs, 1H), 6.29 (s, 1H), 3.12 (d, J = 9.5 Hz, 1H), 2.58 (dd, J = 9.5, 7.5 Hz, 1H), 2.53 (s, 3H), 2.42 (t, J = 7.5 Hz, 1H), 1.92 (td, J = 12.8, 7.4 Hz, 1H), 1.69 (dd, J = 12.8, 7.4 Hz, 2H), 1.64-1.54 (m, 1H), 1.41 (s, 3H), 1.39 (s, 3H), 0.79 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 176.0, 164.4, 159.0, 141.6, 113.6, 109.7, 103.1, 84.4, 46.5, 39.1, 38.7, 37.5, 35.9, 33.6, 27.6, 25.7, 24.1, 17.7; HRMS (ESI) calculated for $[C_{18}H_{21}O_4]^+([M-H]^+)$ requires *m/z* 301.1445, found *m/z* 301.1438. ^{1}H and ^{13}C NMR spectral data obtained for this compound were identical to values reported for the natural product.[26]

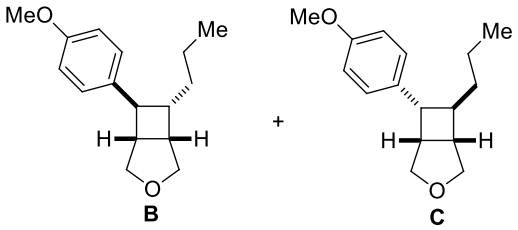
V. Photosensitized [2+2] Cycloaddition of 5



Procedure. A solution of 3.3 mg (0.003 mmol) of $Ir(dF(CF_3)ppy)_2(dtbbpy)(PF_6)$ and 73.2 mg (0.3 mmol) of 1-{(*E*)-3-[((2*E*,4*E*)-hexa-2,4-dienyl)oxy]-propenyl}-3-methoxy-benzene[27] in DMSO (30 mL, 0.01 M) was placed in a test tube (20 x 150 mm). The reaction was stirred in front of a 23 W (1380 lumen) compact fluorescent lamp at a distance of 10 cm. After 12 h, the reaction mixture was diluted with Et_2O (60 mL) and water (10 mL). The aqueous layer was separated and extracted with ether (60 mL x 2). The combined organic layers were washed with water (10 mL x 2), brine (20 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography using 20:1 hexanes/EtOAc as the eluent to give an inseparable mixture of diastereomers. This oily mixture was placed in a round-bottomed flask with Pd/C (5%Pd, 95.4 mg, 5 mol%), and ethyl acetate (5 mL) equipped with a balloon of H_2. The mixture was stirred 4 h at room temperature and then filtered. The filtrate was concentrated and purified by flash column chromatography (20:1 hexanes/EtOAc) to afford 65.0 mg (0.26 mmol, 87% yield, two steps) of the hydrogenation products as a colorless oil.



(1*S,5*R**,6*S**,7*R**)-6-(4-Methoxy-phenyl)-7-propyl-3-oxa-bicyclo[3.2.0]heptane**: IR(neat) 2955, 2920, 2842, 1611, 1513, 1248 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.13 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.95 (d, J = 9.4 Hz, 1H), 3.92 (d, J = 9.2 Hz, 1H), 3.81 (s, 3H), 3.60-3.55 (m, 2H), 3.30 (dd, J = 9.4, 5.3 Hz, 1H), 3.08 (dt, J = 8.1, 5.4 Hz, 1H), 2.58-2.53 (m, 1H), 2.30-2.22 (m, 1H), 1.16-1.07 (m, 1H), 1.07-0.91 (m, 3H), 0.72 (t, J = 7.4 Hz, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 157.8, 133.6, 129.3, 113.3, 74.2, 74.0, 55.2, 44.6, 43.1, 42.1, 41.5, 33.5, 19.8, 14.1. HRMS (EI) calculated for $[C_{16}H_{22}O_2]^+(M^+)$ requires *m/z* 246.1615, found *m/z* 246.1610.



(1*S,5*R**,6*S**,7*S**)-6-(4-Methoxy-phenyl)-7-propyl-3-oxa-bicyclo[3.2.0]heptane (major) and (1*S**,5*R**,6*R**,7*R**)-6-(4-methoxy-phenyl)-7-propyl-3-oxa-bicyclo[3.2.0]heptane (minor)**: IR(neat) 2956, 2921, 2844, 1611, 1513, 1247 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.16 (d, J = 8.5 Hz, 1.46H), 7.13 (d, J = 8.5 Hz, 0.54H), 6.85 (d, J = 8.5 Hz, 2H), 4.13 (d, J = 9.7 Hz, 0.73H), 3.85 (d, J = 8.8 Hz, 0.27H), 3.84 (d, J = 9.1 Hz, 0.73H), 3.79 (s, 3H), 3.69 (d, J = 9.9 Hz, 0.27H), 3.50 (dd, J = 10.1, 6.7 Hz, 0.73H), 3.43 (dd, J = 8.7, 4.3 Hz, 0.27H), 3.40 (dd, J = 9.1, 4.5 Hz, 0.73H), 3.33 (dd, J = 9.7, 6.7 Hz, 0.27H), 3.13 (t, J = 8.9 Hz, 0.27H), 3.08-3.02 (m, 0.27H), 2.95-2.89 (m, 0.73H), 2.89-2.84 (m, 0.73H), 2.70-2.65 (m, 0.73H), 2.57-2.52 (m, 0.27H), 2.42-2.34 (m, 0.73H), 2.34-2.37 (m, 0.27H), 1.55-1.37 (m, 2H), 1.28-1.09 (m, 2H), 0.85 (t, J = 7.4 Hz, 0.81H), 0.83 (t, J = 7.4 Hz, 2.19H). HRMS (EI) calculated for $[C_{16}H_{22}O_2]^+(M^+)$ requires *m/z* 246.1615, found *m/z* 246.1606.

VI. Time course study of [2+2] cycloaddition of 3.

A solution of 3.3 mg (0.003 mmol) of Ir(dF(CF_3)ppy)$_2$(dtbbpy)(PF_6), 60.6 mg (0.3 mmol) of [(*E*)-3-(3-methyl-but-2-enyloxy)-propenyl]-benzene, and 23.2 mg of decane as an internal standard in DMSO (30 mL, 0.01 M) was placed in a test tube (20 x 150 mm). The reaction was stirred in front of a 23 W (1380 lumen) compact fluorescent lamp at a distance of 10 cm. Yields were determined by GC analysis of aliquots sampled at 1 h intervals and are plotted below.

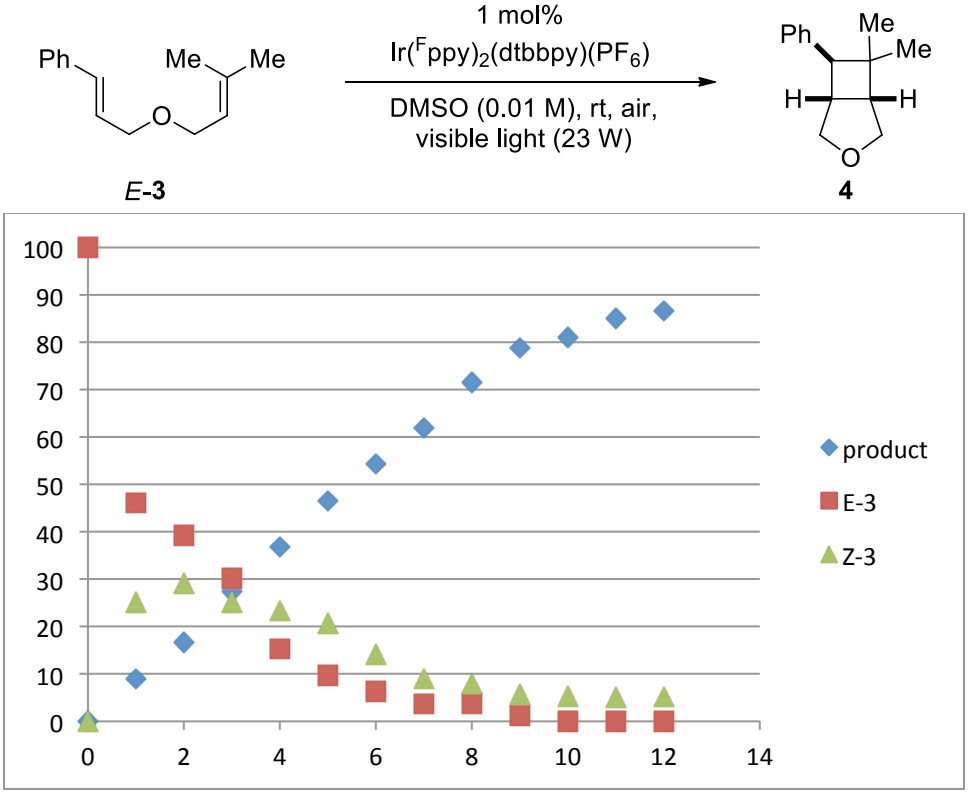
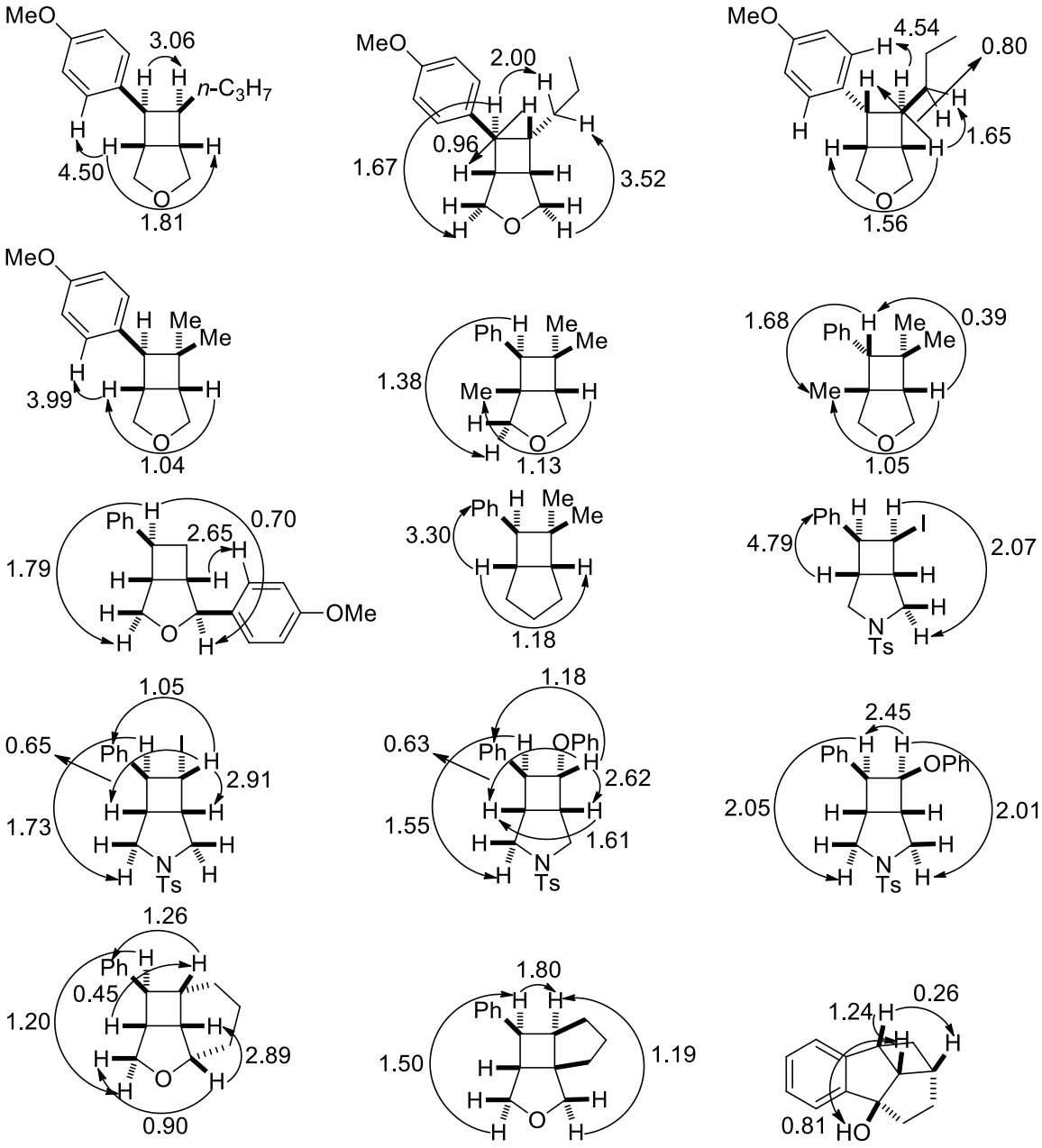


Figure S1 Time course studies.

VI. Representative NOE data



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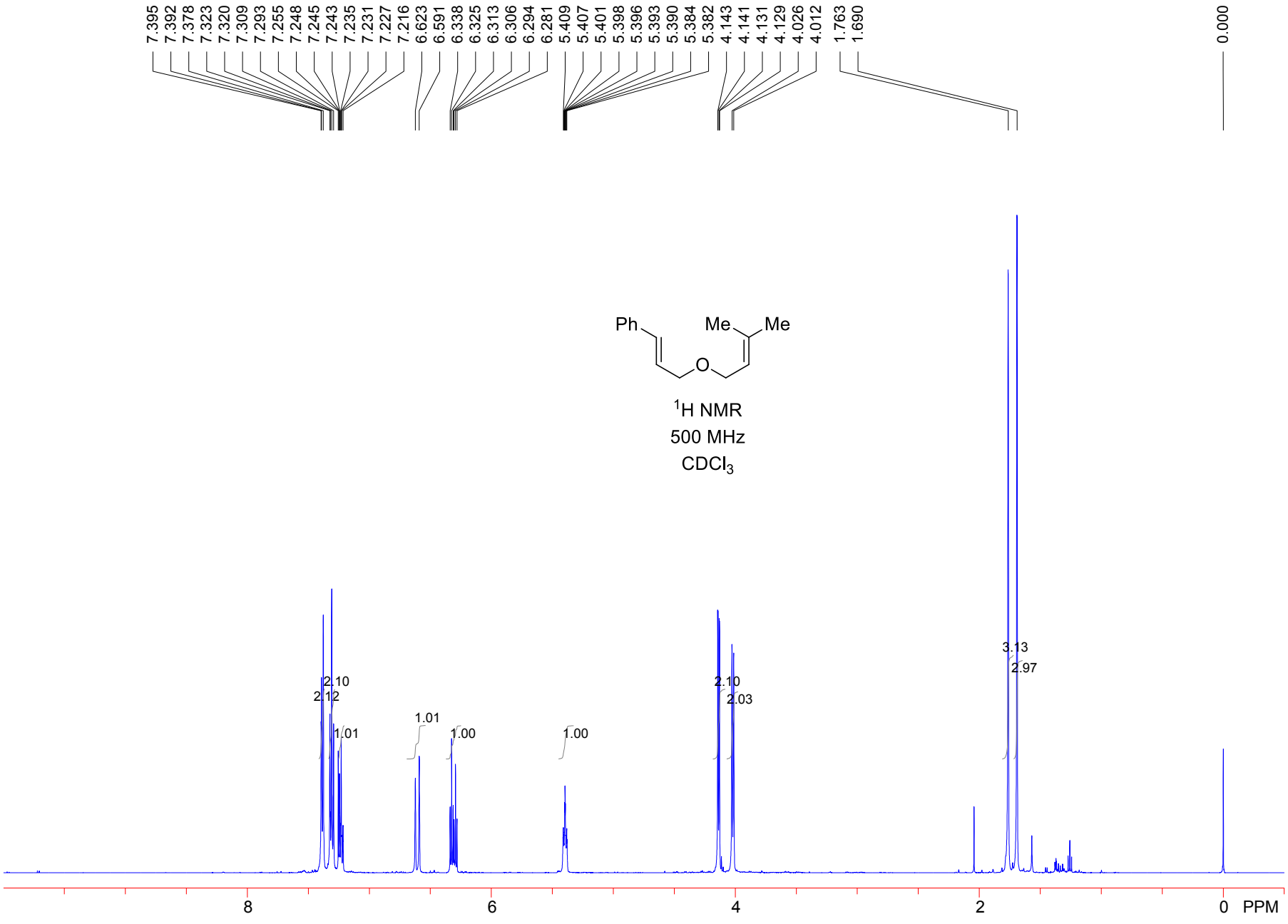
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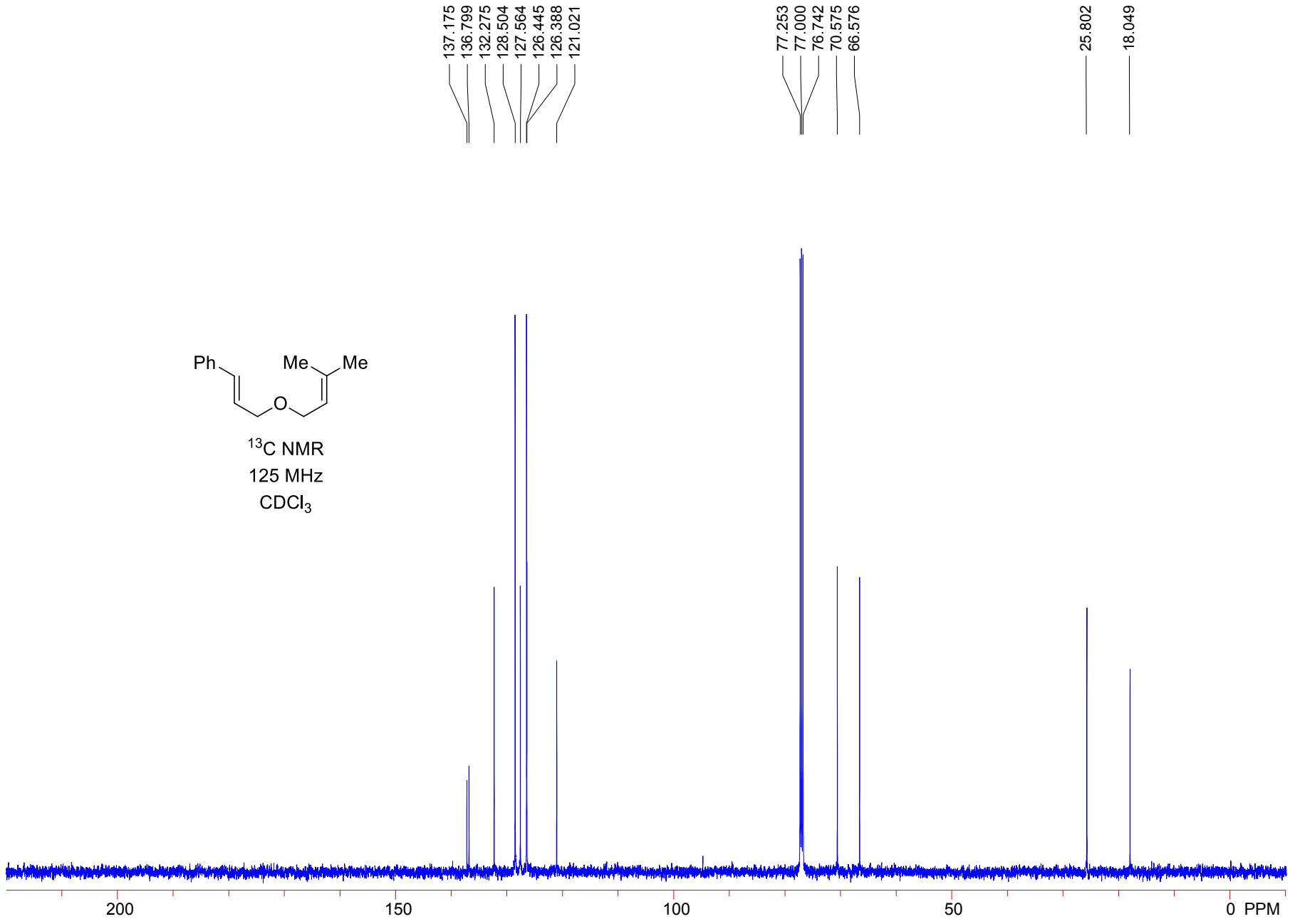
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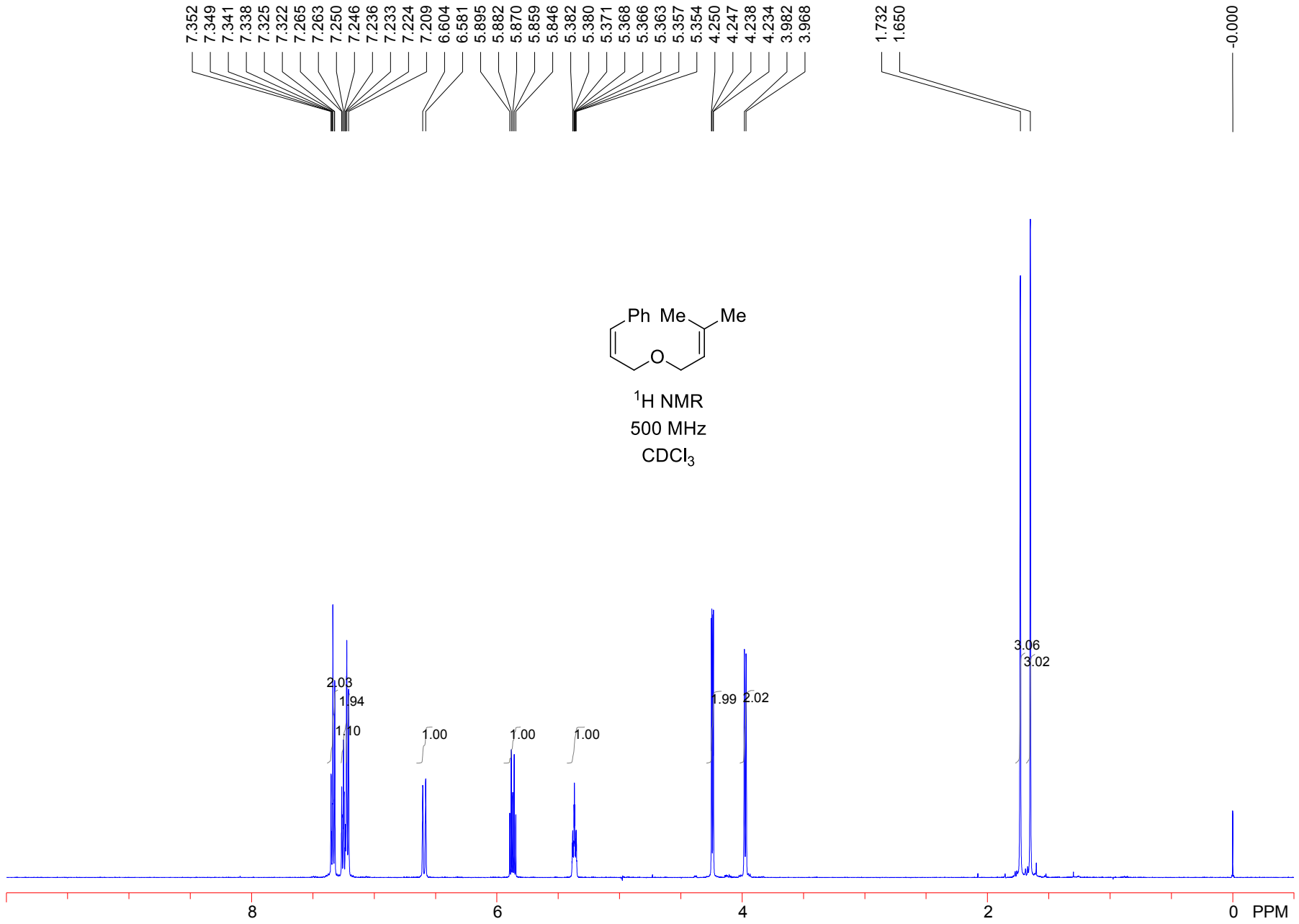
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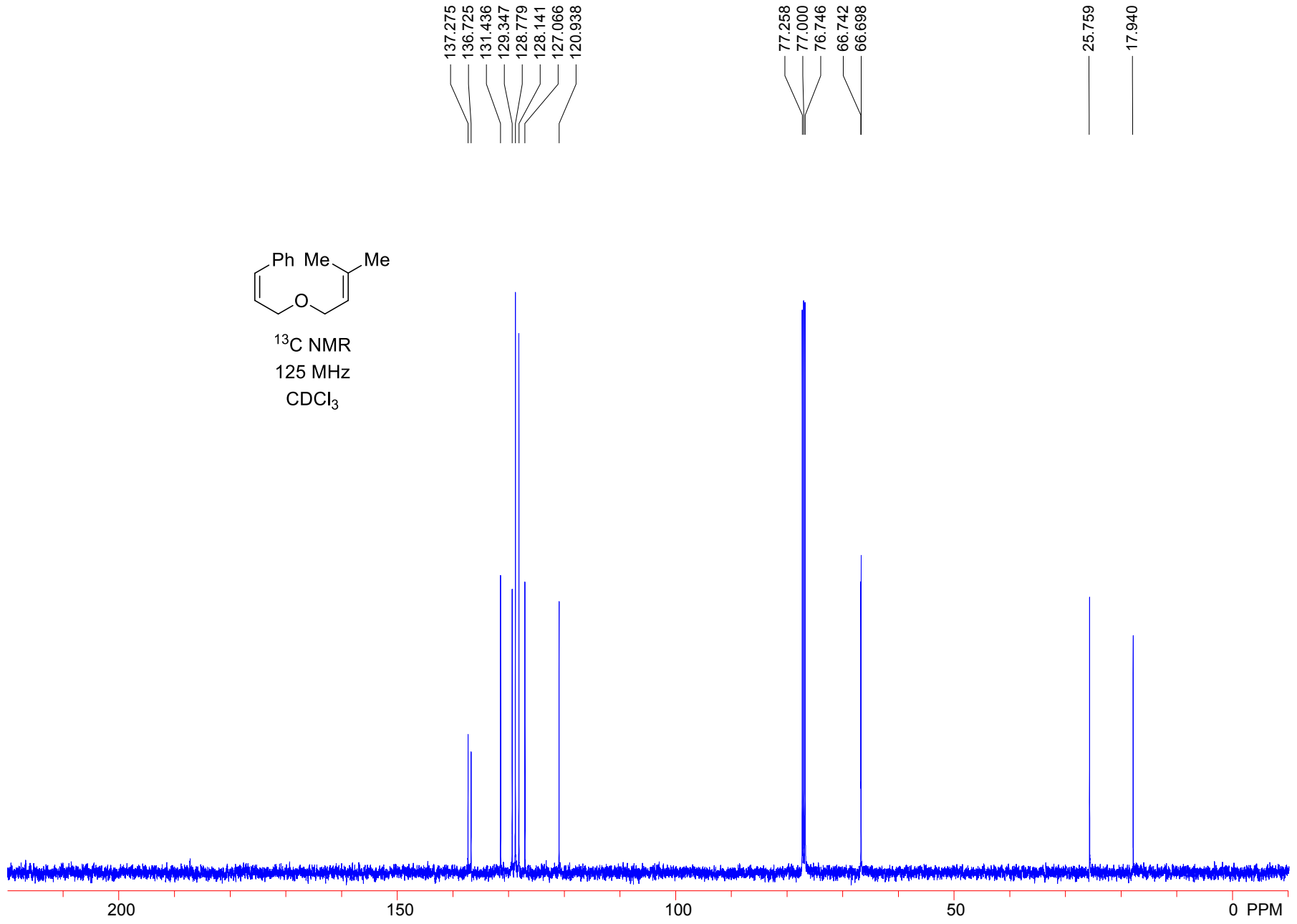
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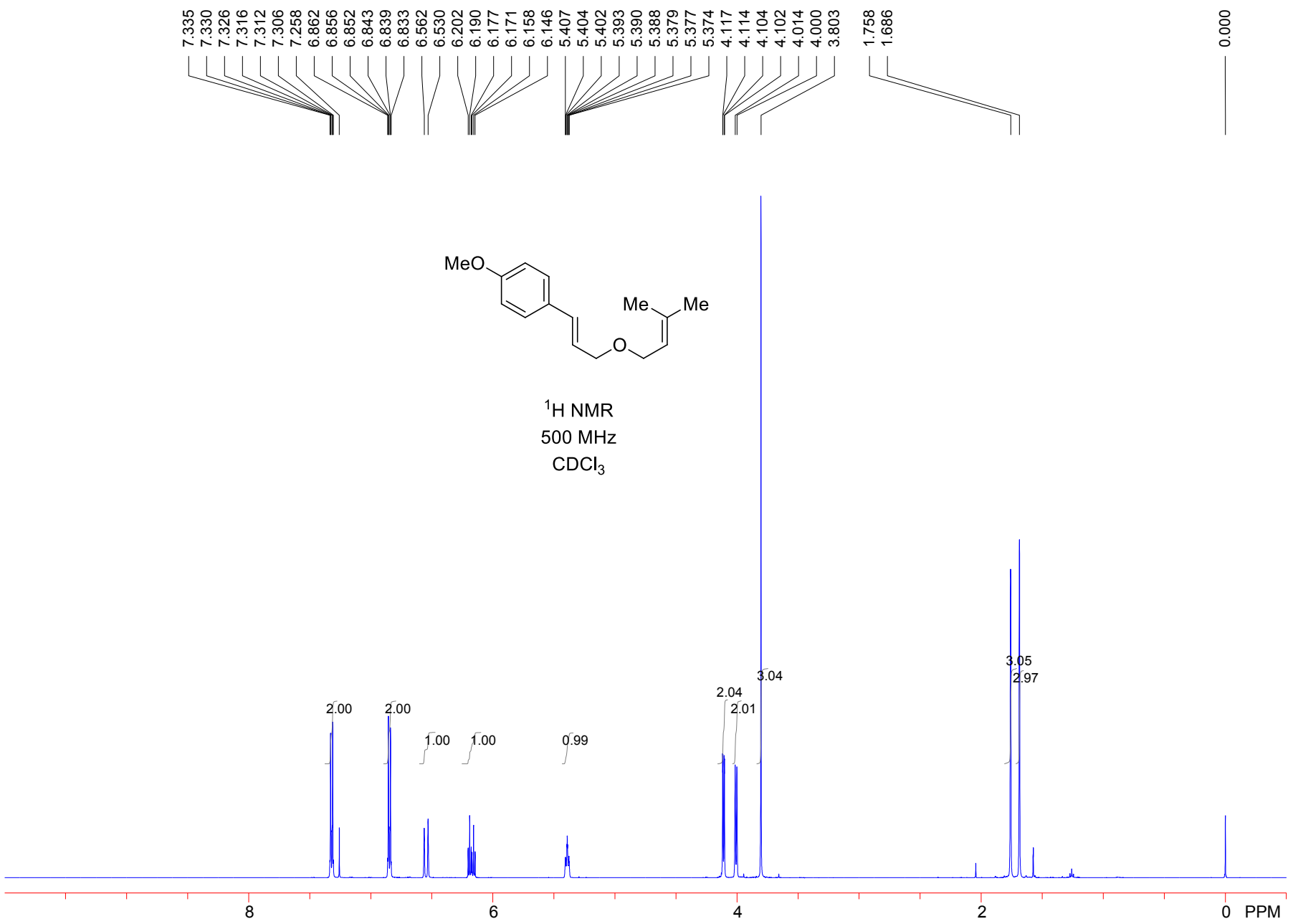
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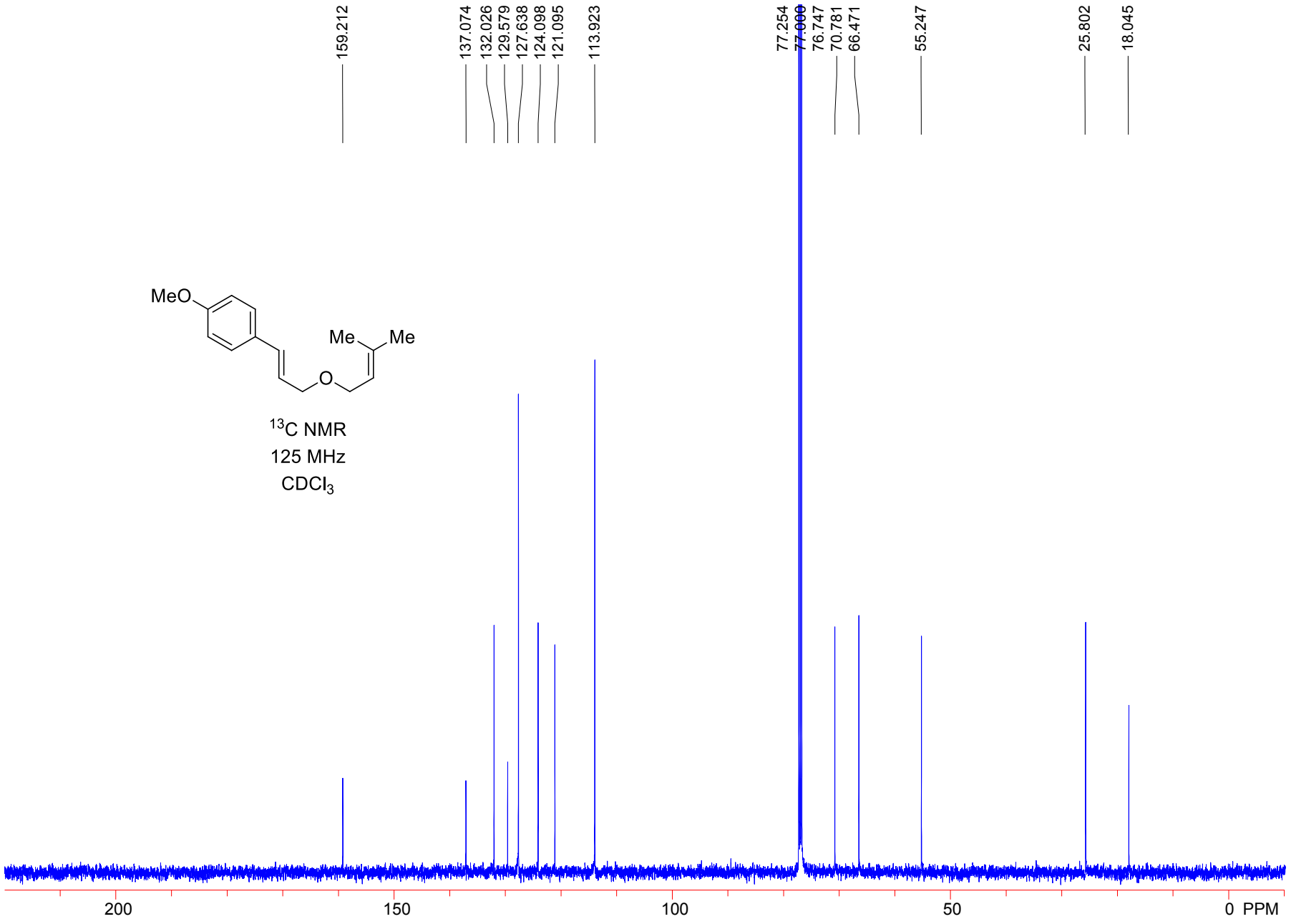
7.326
7.316
7.312
7.306
7.258
6.862
6.856
6.852
6.843
6.839
6.833
6.562
6.530
6.202
6.190
6.177
6.171
6.158
6.146
5.407
5.404
5.402
5.393
5.390
5.388
5.379
5.377
5.374
4.117
4.114
4.104
4.102
4.014
4.000
3.803
1.758
1.686
0.000
MeO
Me
Me
O
1H NMR
500 MHz
CDCl3
2.00
2.00
1.00
1.00
0.99
2.04
2.01
3.04
3.05
2.97
8
6
4
2
0
PPM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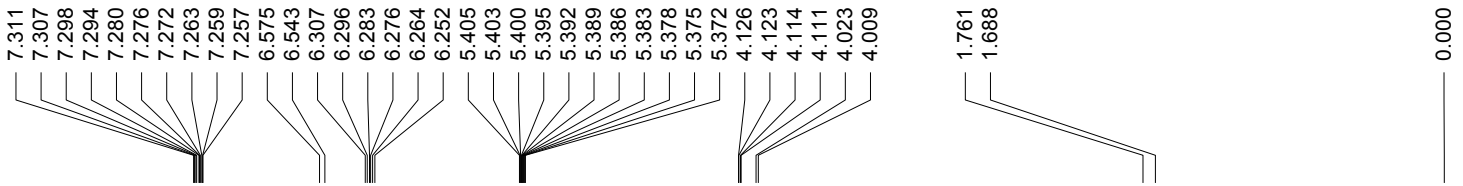
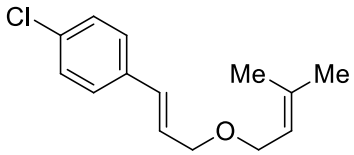
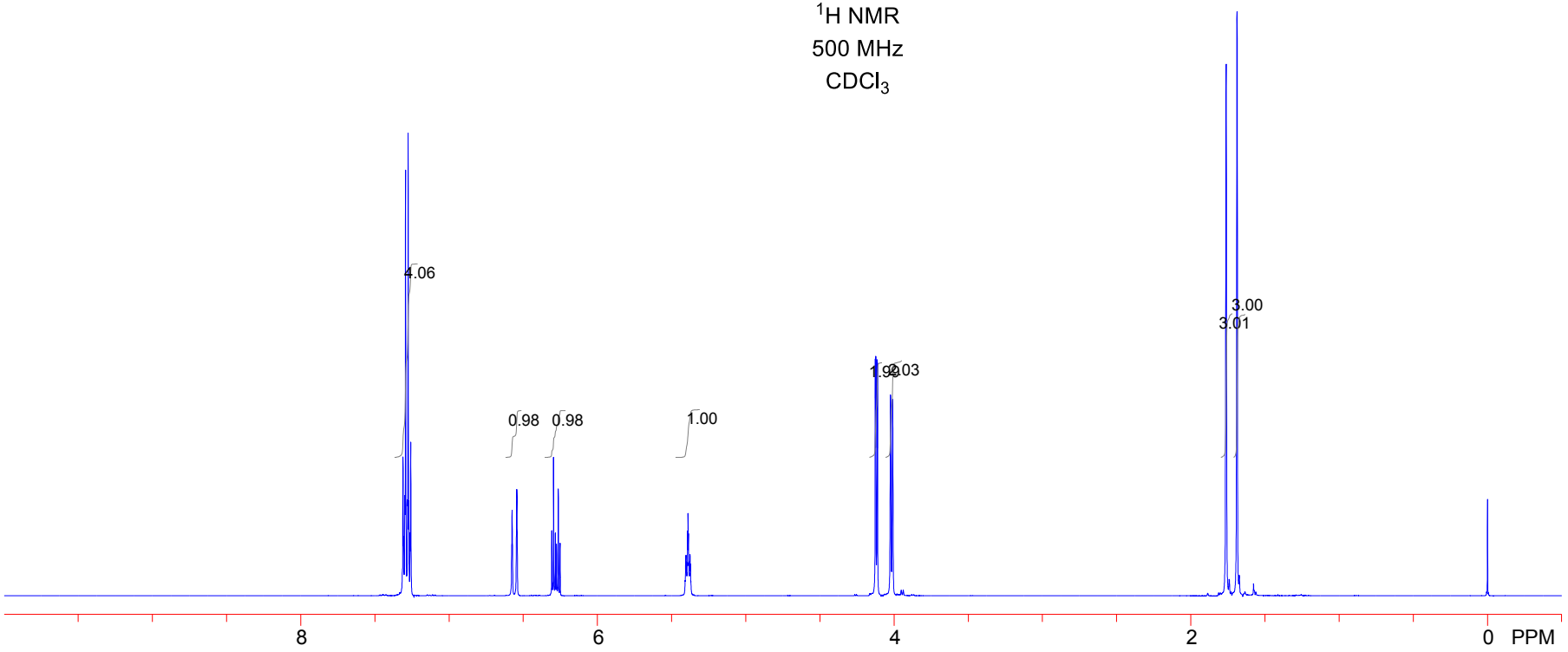
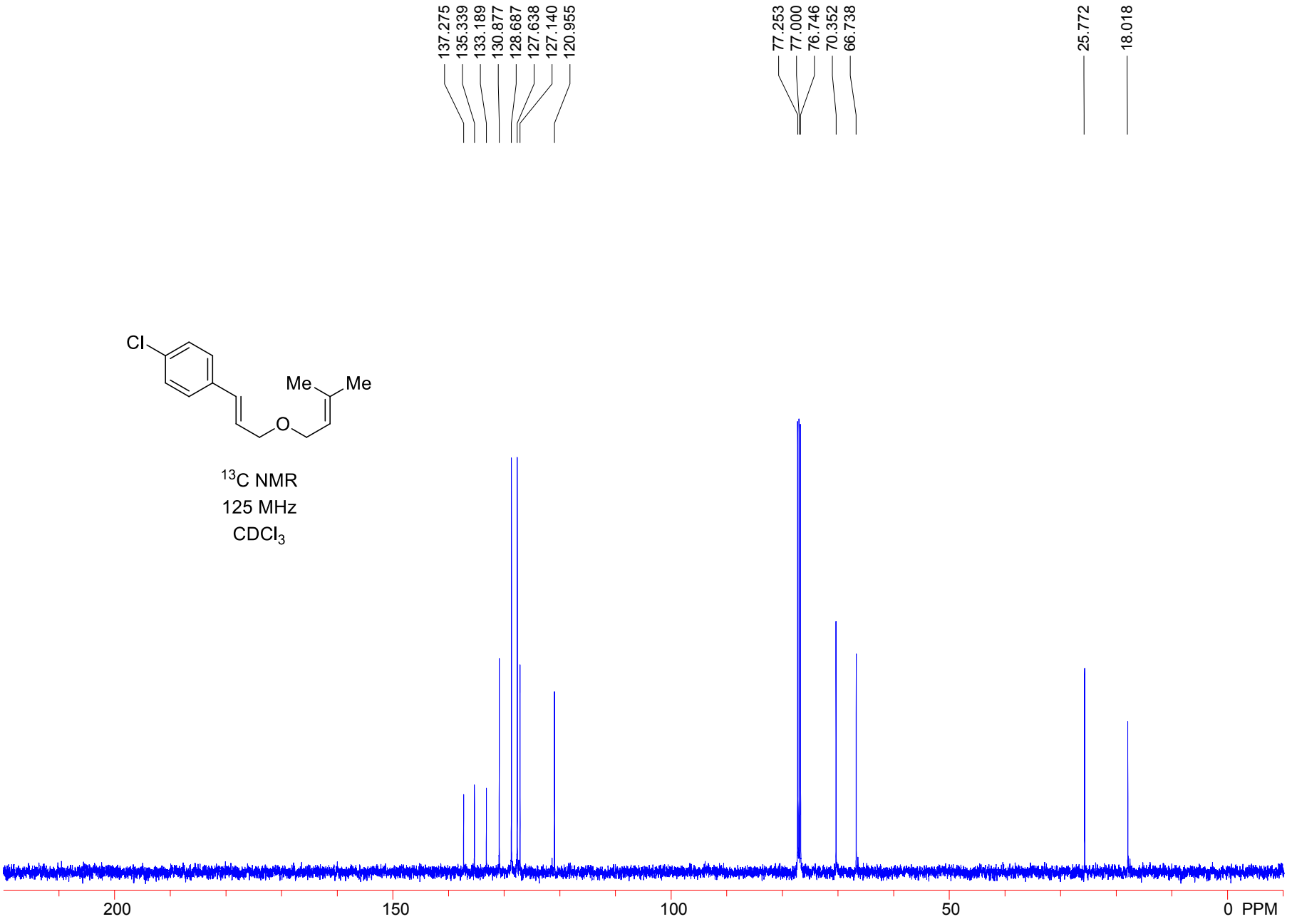
137.074
132.026
129.579
127.638
124.098
121.095
113.923
77.254
77.000
76.747
70.781
66.471
55.247
25.802
18.045
MeO
Me
Me
O
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM





^{1}H NMR
500 MHz
$CDCl_3$

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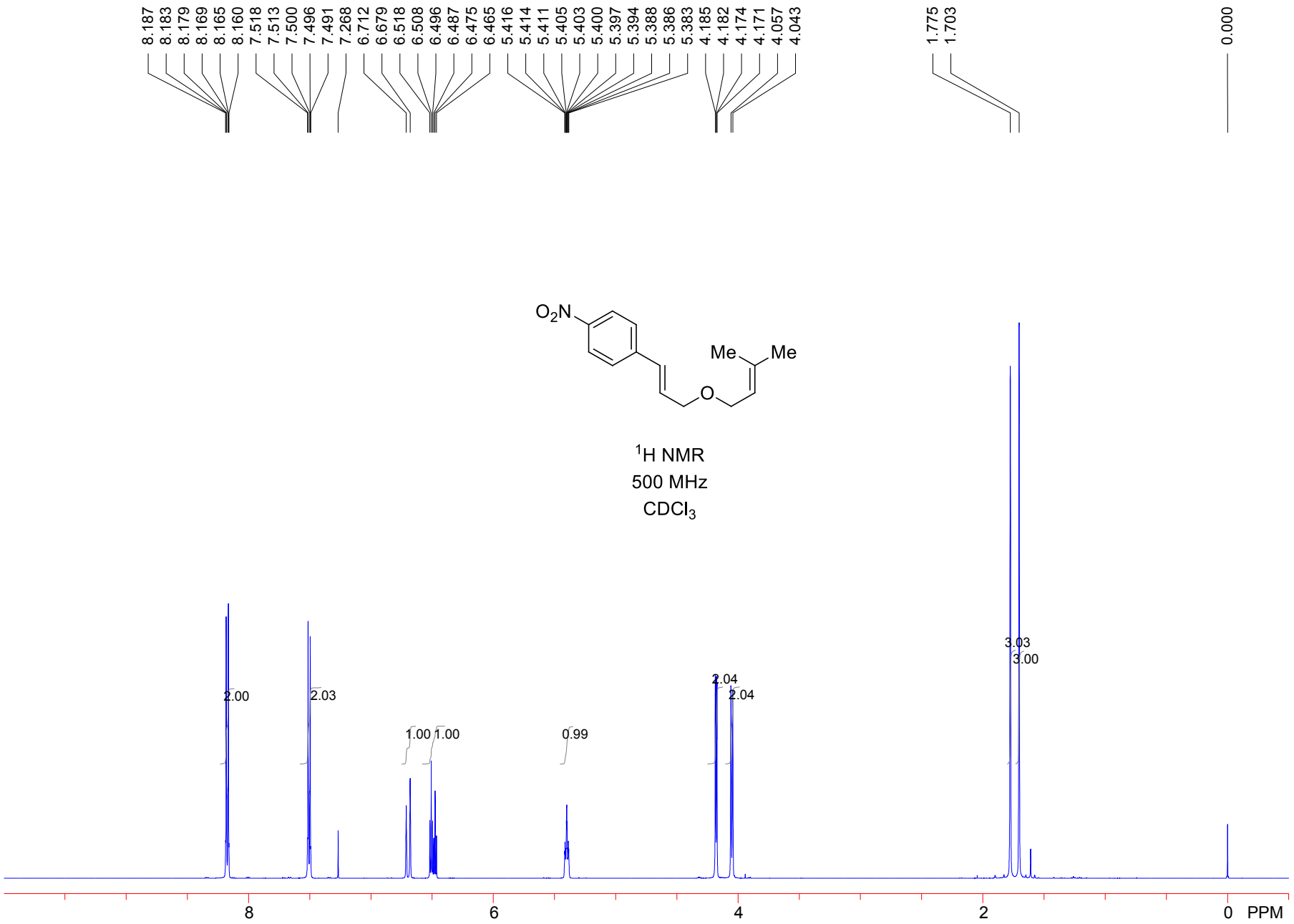
135.339
133.189
130.877
128.687
127.638
127.140
120.955
77.253
77.000
76.746
70.352
66.738
25.772
18.018
Cl
Me
Me
O
^{13}C NMR
125 MHz
$CDCl_3$
200
150
100
50
0 PPM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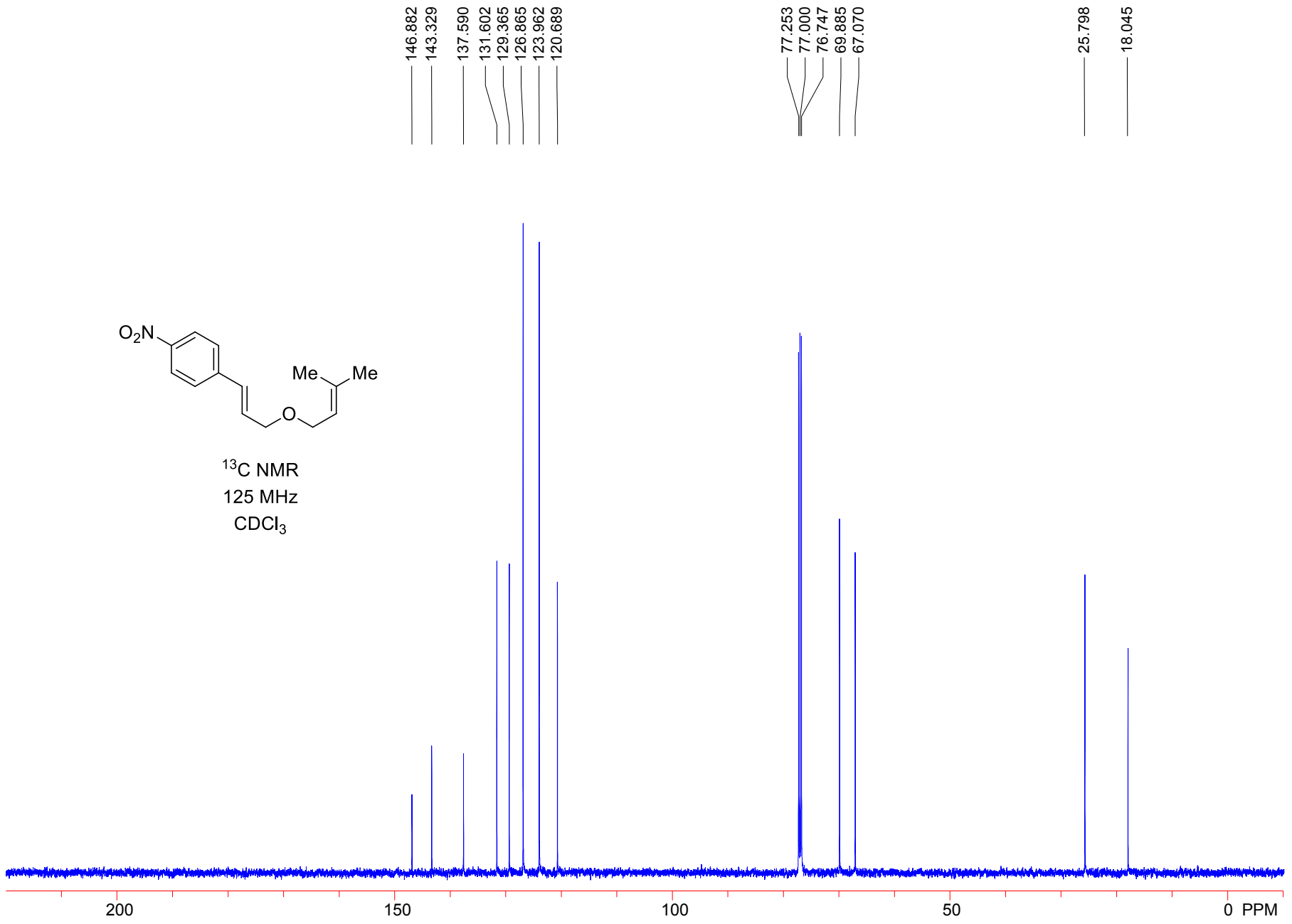
8.183
8.179
8.169
8.165
8.160
7.518
7.513
7.500
7.496
7.491
7.268
6.712
6.679
6.518
6.508
6.496
6.487
6.475
6.465
5.416
5.414
5.411
5.405
5.403
5.400
5.397
5.394
5.388
5.386
5.383
4.185
4.182
4.174
4.171
4.057
4.043
1.775
1.703
0.000
O2N
Me
Me
O
1H NMR
500 MHz
CDCl3
2.00
2.03
1.00
1.00
0.99
2.04
2.04
3.03
3.00
8
6
4
2
0
PPM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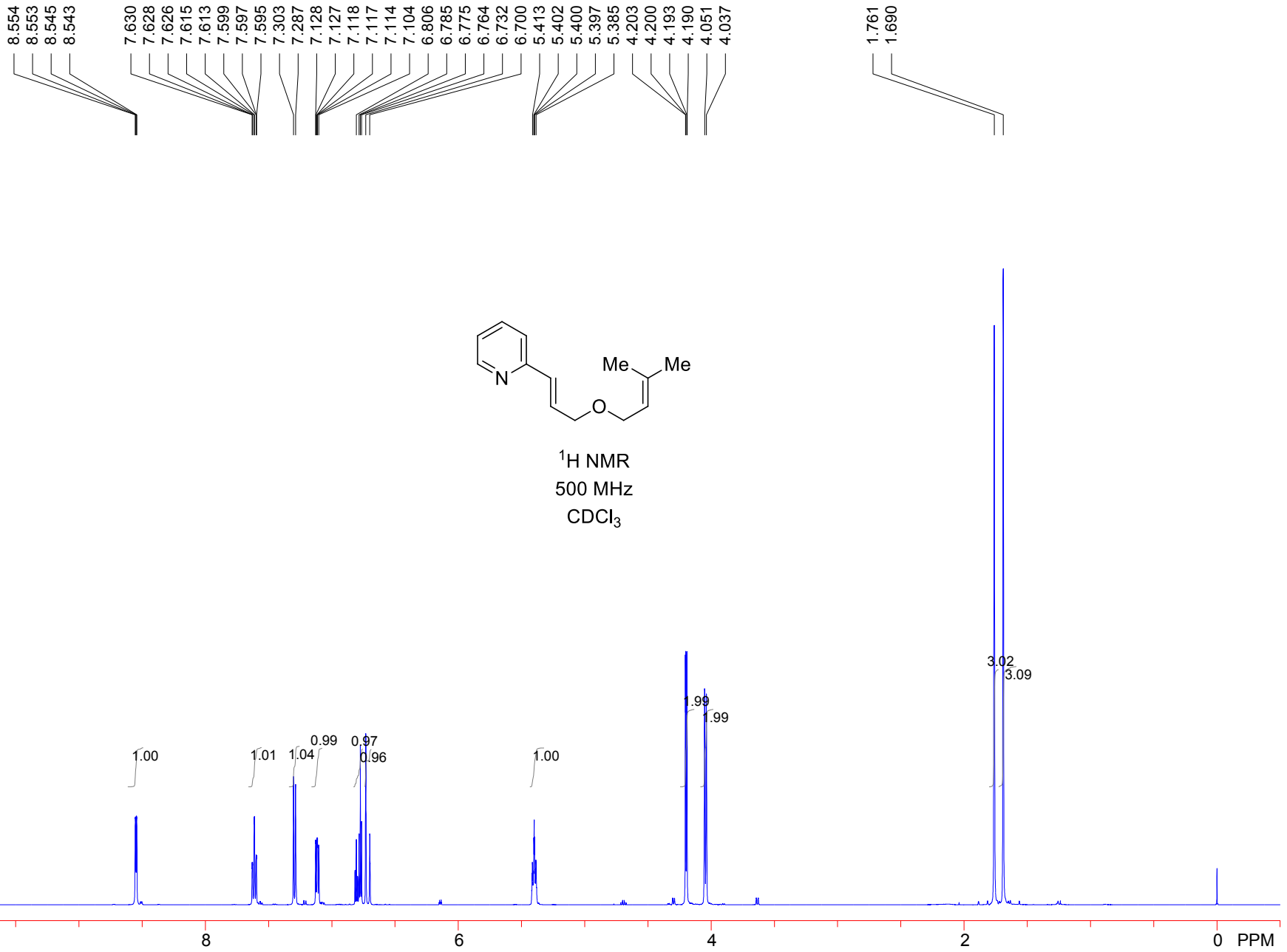
143.329
137.590
131.602
129.365
126.865
123.962
120.689
77.253
77.000
76.747
69.885
67.070
25.798
18.045
O2N
Me
Me
O
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM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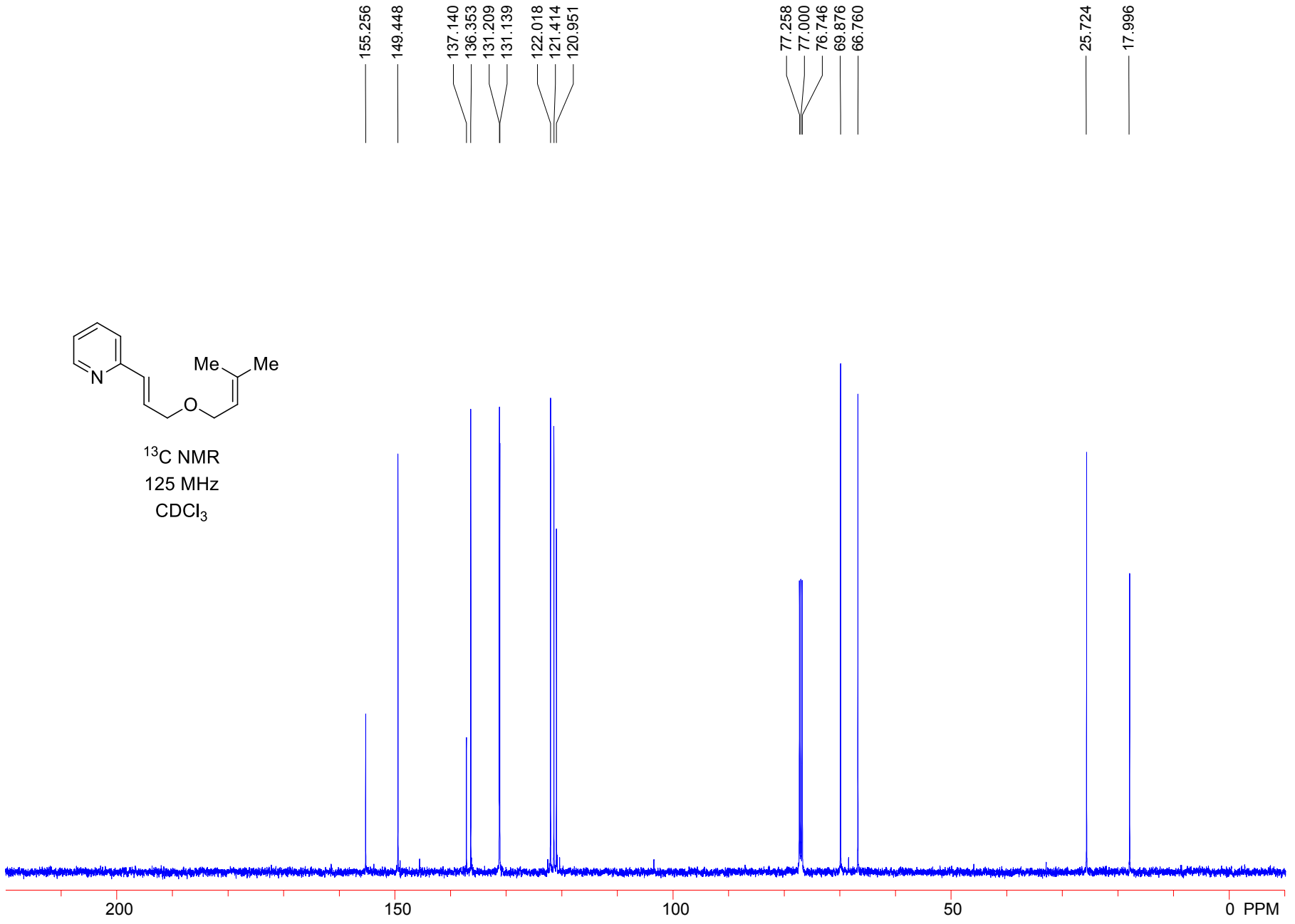
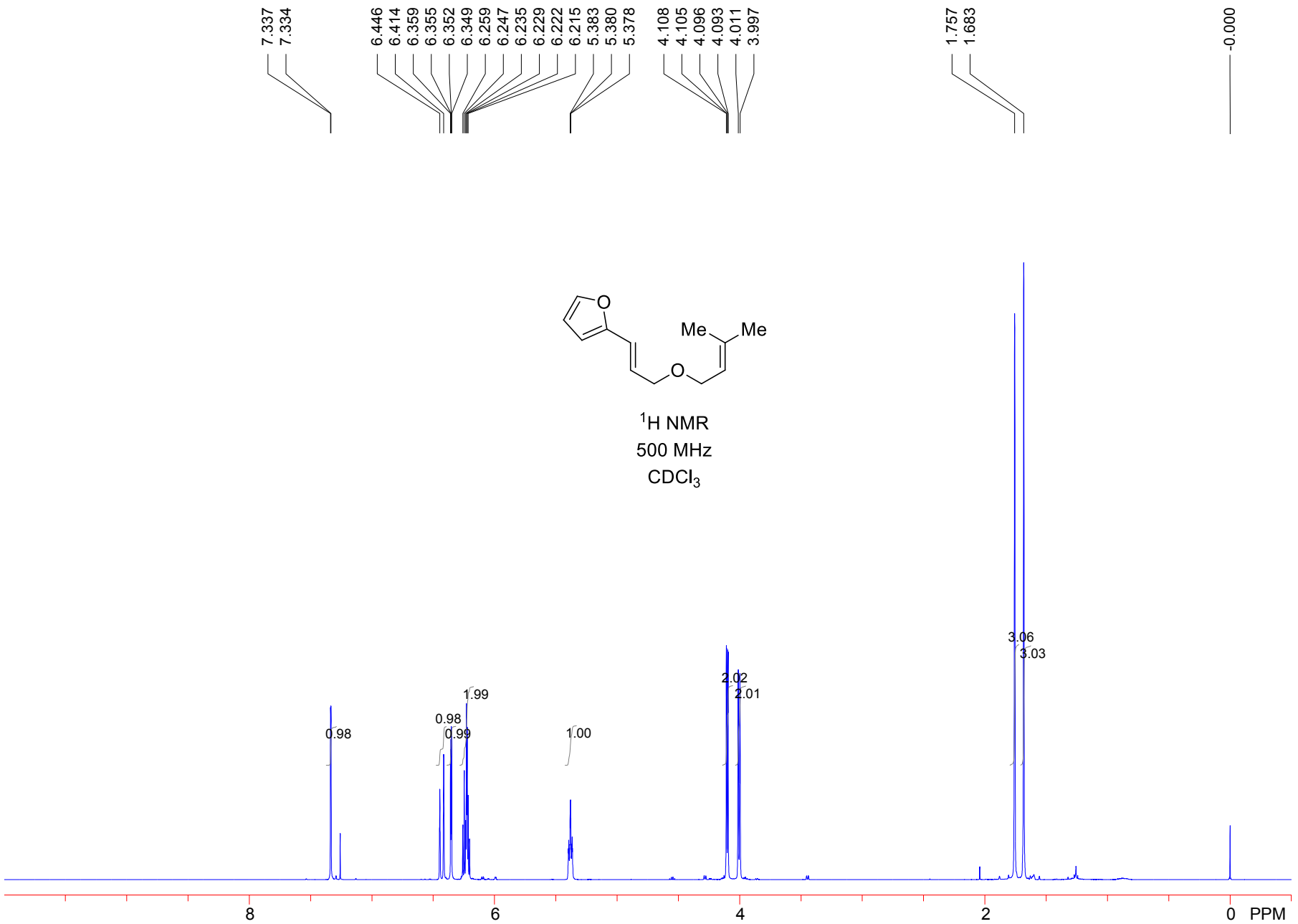
8.553
8.545
8.543
7.630
7.628
7.626
7.615
7.613
7.599
7.597
7.595
7.303
7.287
7.128
7.127
7.118
7.117
7.114
7.104
6.806
6.785
6.775
6.764
6.732
6.700
5.413
5.402
5.400
5.397
5.385
4.203
4.200
4.193
4.190
4.051
4.037
1.761
1.690
N
Me
Me
O
1H NMR
500 MHz
CDCl3
1.00
1.01
1.04
0.99
0.97
0.96
1.00
1.99
1.99
3.02
3.09
8
6
4
2
0
PPM


155.256
149.448
137.140
136.353
131.209
131.139
122.018
121.414
120.951
77.258
77.000
76.746
69.876
66.760
25.724
17.996
N
O
Me
Me
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM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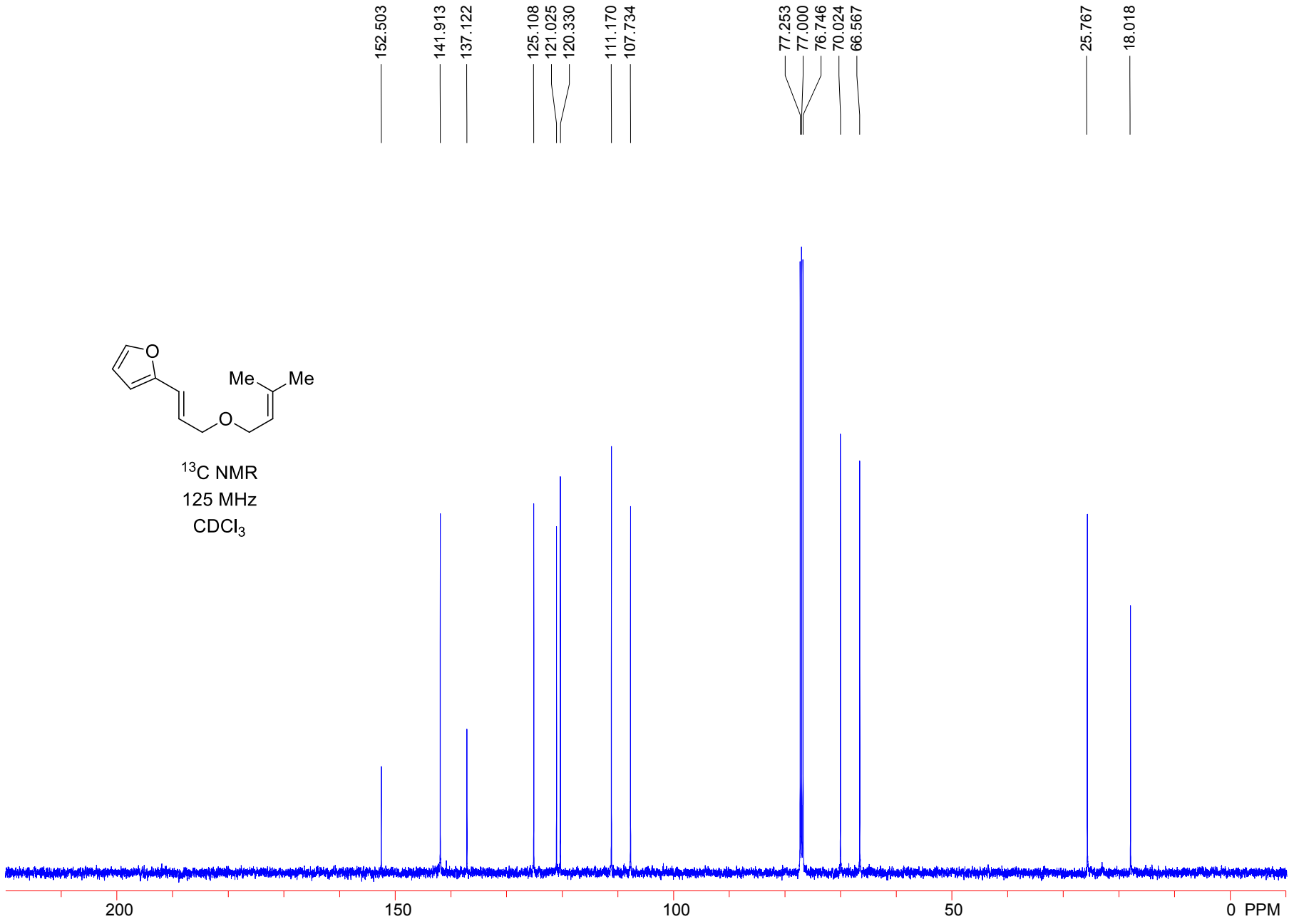
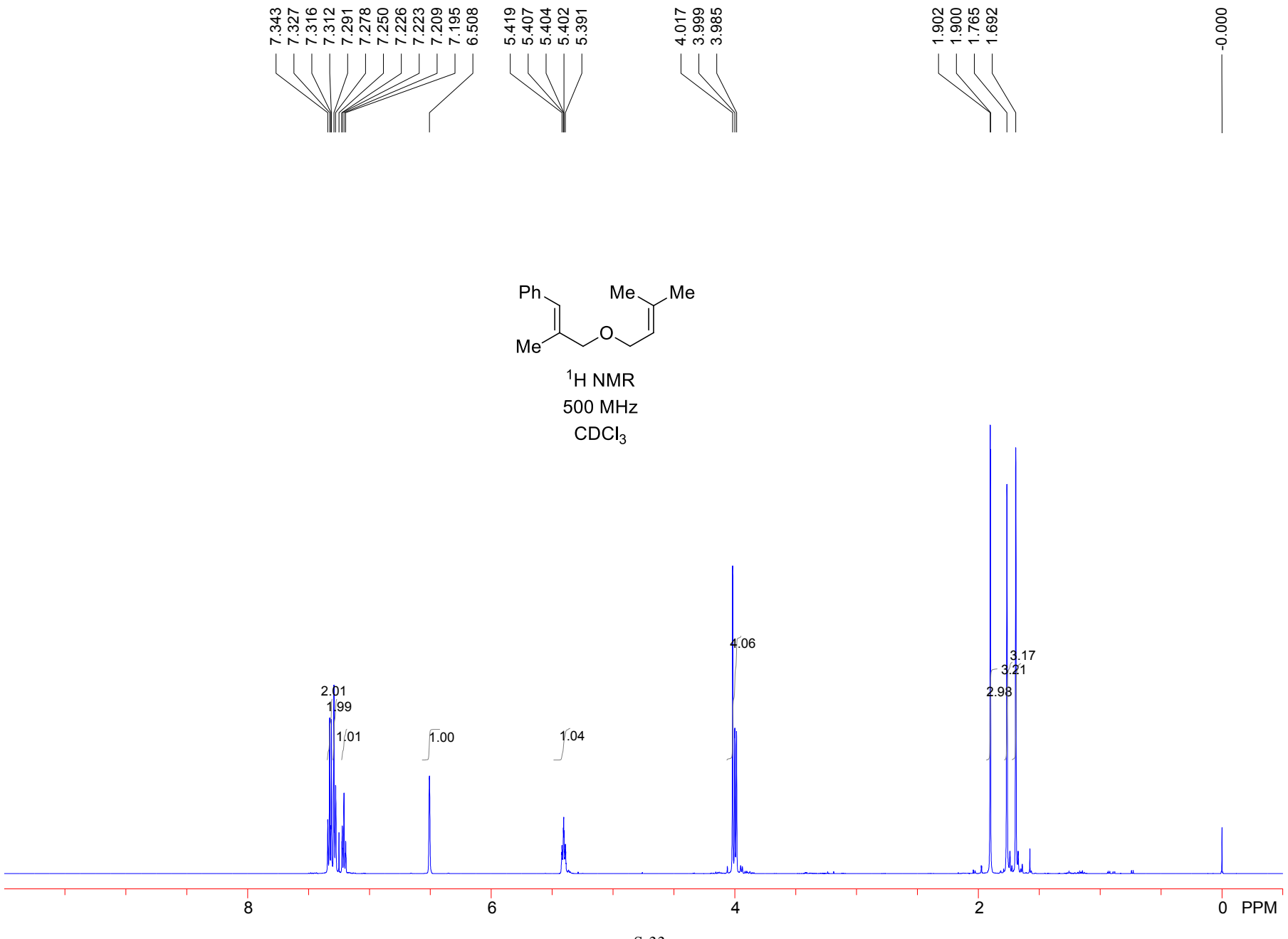
7.334
6.446
6.414
6.359
6.355
6.352
6.349
6.259
6.247
6.235
6.229
6.222
6.215
5.383
5.380
5.378
4.108
4.105
4.096
4.093
4.011
3.997
1.757
1.683
-0.000
O
Me
Me
O
1H NMR
500 MHz
CDCl3
0.98
0.98
0.99
1.99
1.00
2.02
2.01
3.06
3.03
8
6
4
2
0
PPM


152.503
141.913
137.122
125.108
121.025
120.330
111.170
107.734
77.253
77.000
76.746
70.024
66.567
25.767
18.018
O
Me
Me
O
^{13}C NMR
125 MHz
$CDCl_3$
200
150
100
50
0 PPM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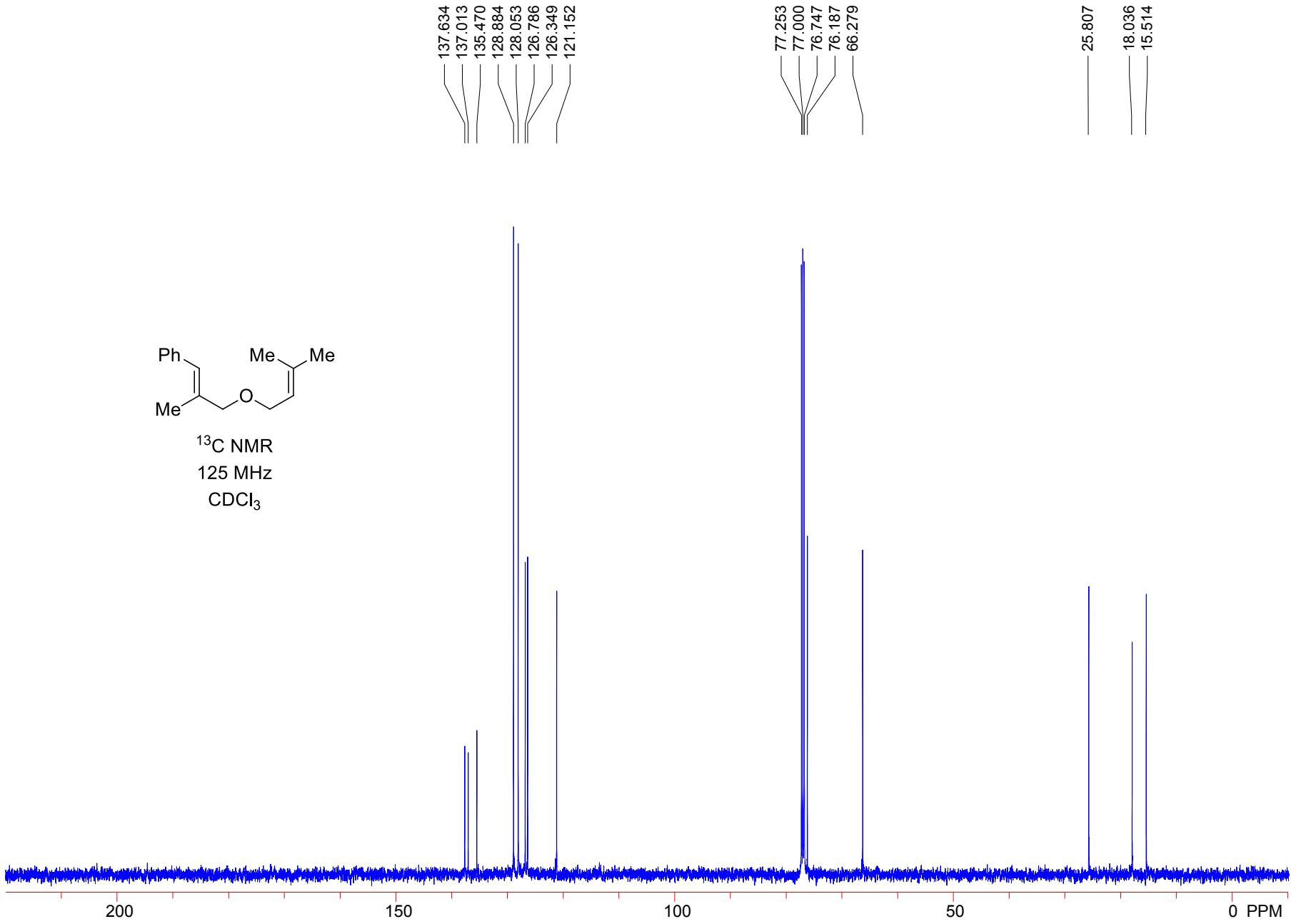
7.327
7.316
7.312
7.291
7.278
7.250
7.226
7.223
7.209
7.195
6.508
5.419
5.407
5.404
5.402
5.391
4.017
3.999
3.985
1.902
1.900
1.765
1.692
-0.000
Ph
Me
Me
Me
O
1H NMR
500 MHz
CDCl3
2.01
1.99
1.01
1.00
1.04
4.06
3.17
3.21
2.98
8
6
4
2
0
PPM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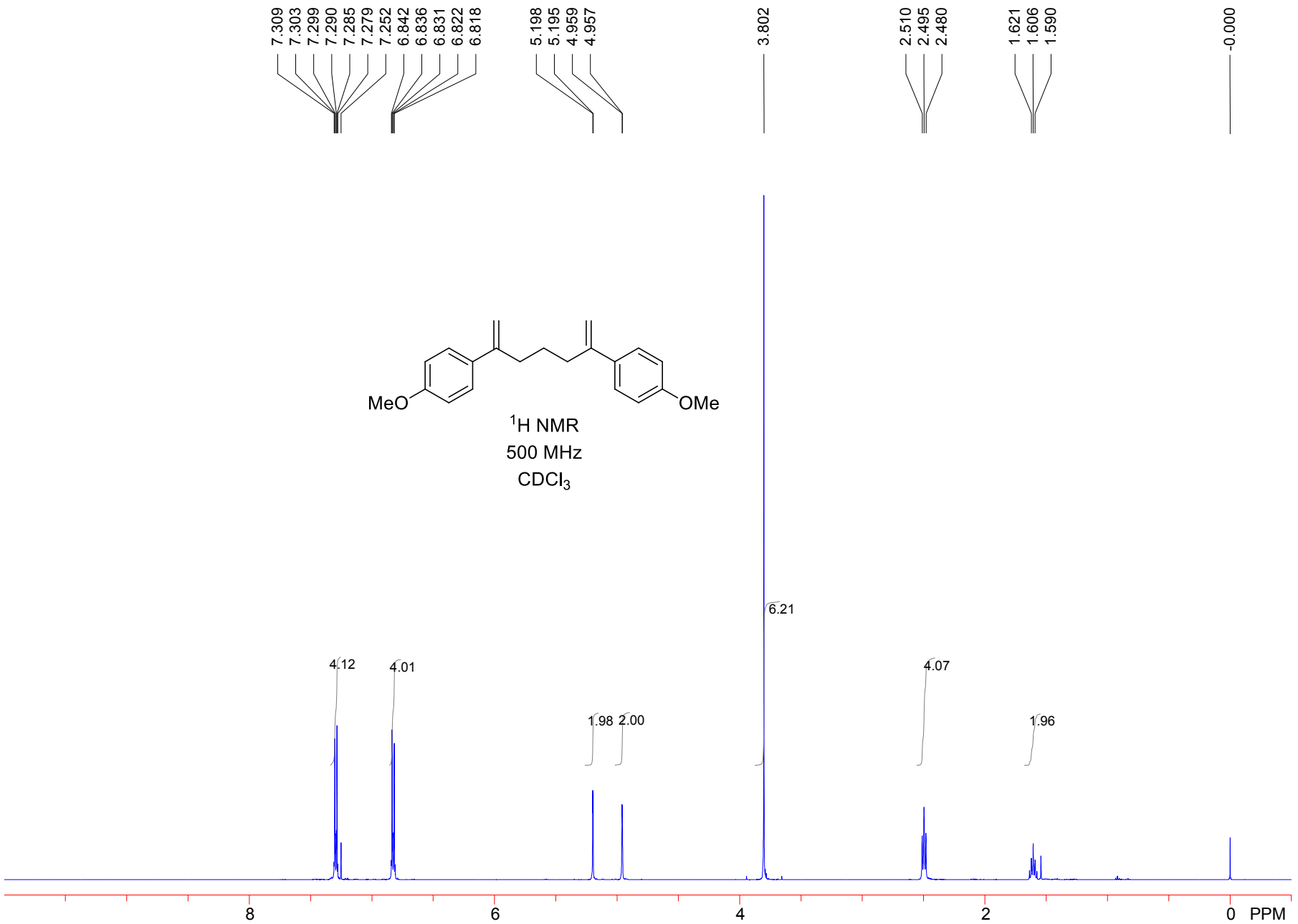
137.013
135.470
128.884
128.053
126.786
126.349
121.152
77.253
77.000
76.747
76.187
66.279
25.807
18.036
15.514
Ph
Me
Me
Me
O
^{13}C NMR
125 MHz
$CDCl_3$
200
150
100
50
0 PPM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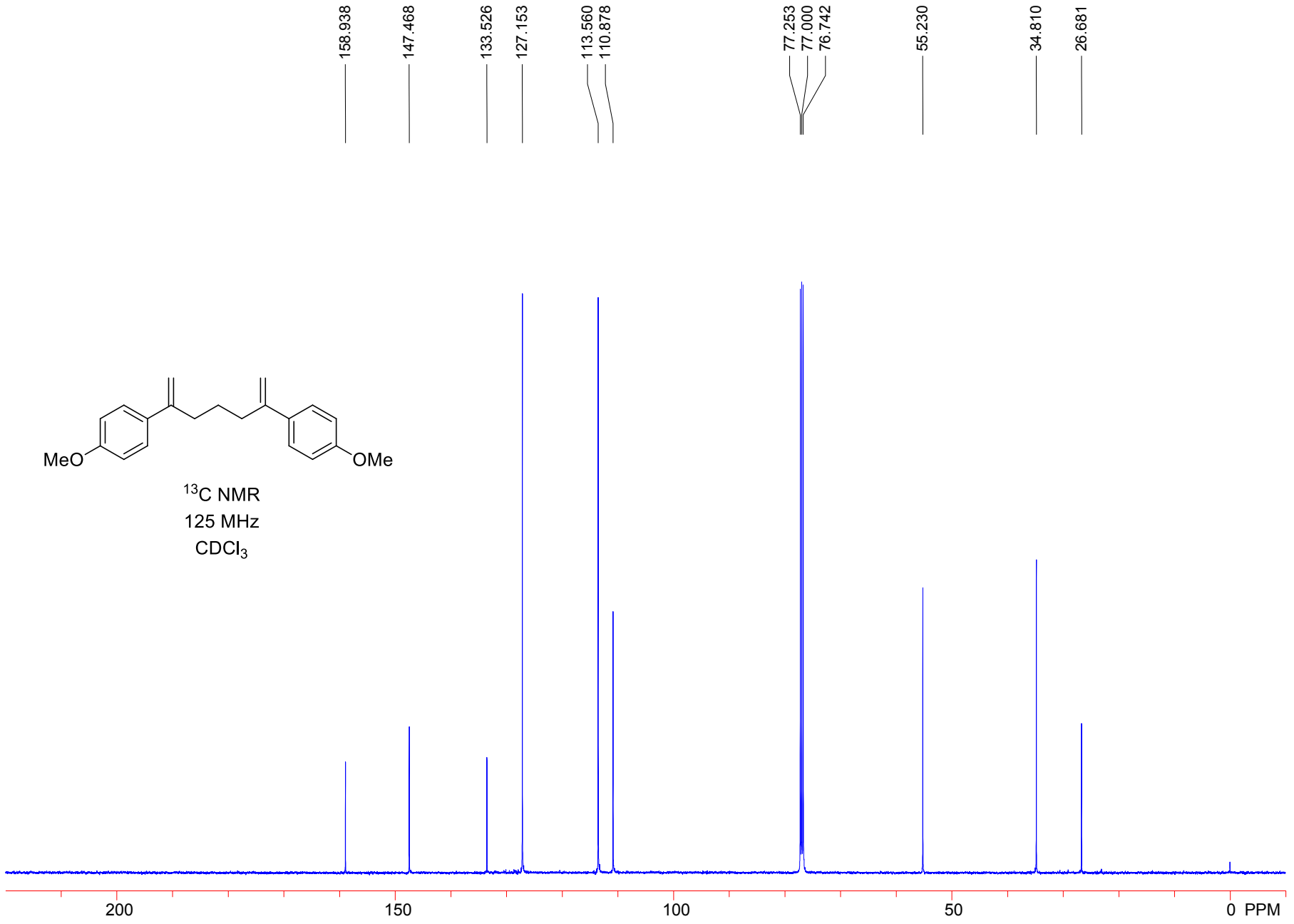
7.303
7.299
7.290
7.285
7.279
7.252
6.842
6.836
6.831
6.822
6.818
5.198
5.195
4.959
4.957
3.802
2.510
2.495
2.480
1.621
1.606
1.590
-0.000
MeO
OMe
1H NMR
500 MHz
CDCl3
6.21
4.12
4.01
4.07
1.98
2.00
1.96
8
6
4
2
0
PPM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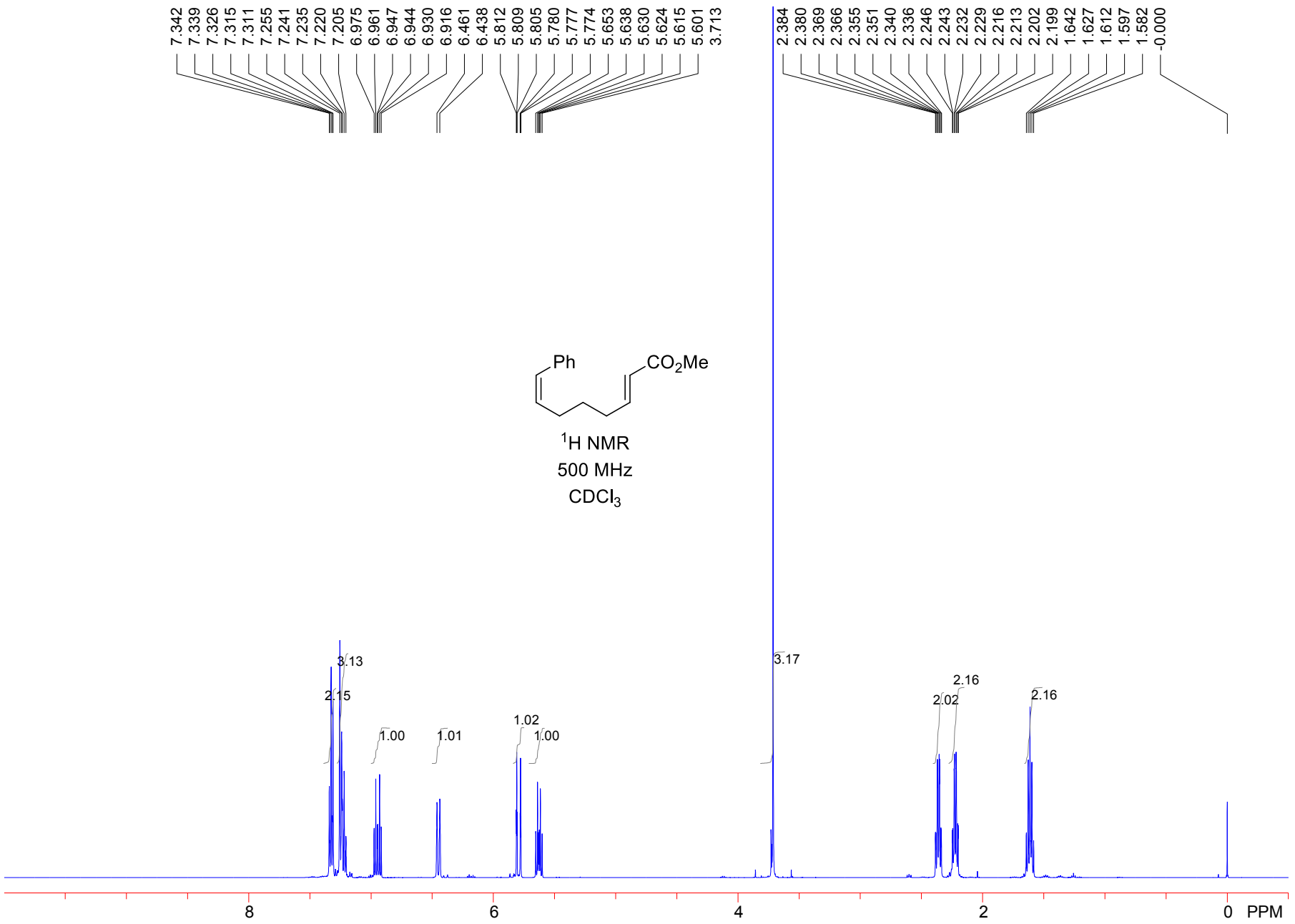
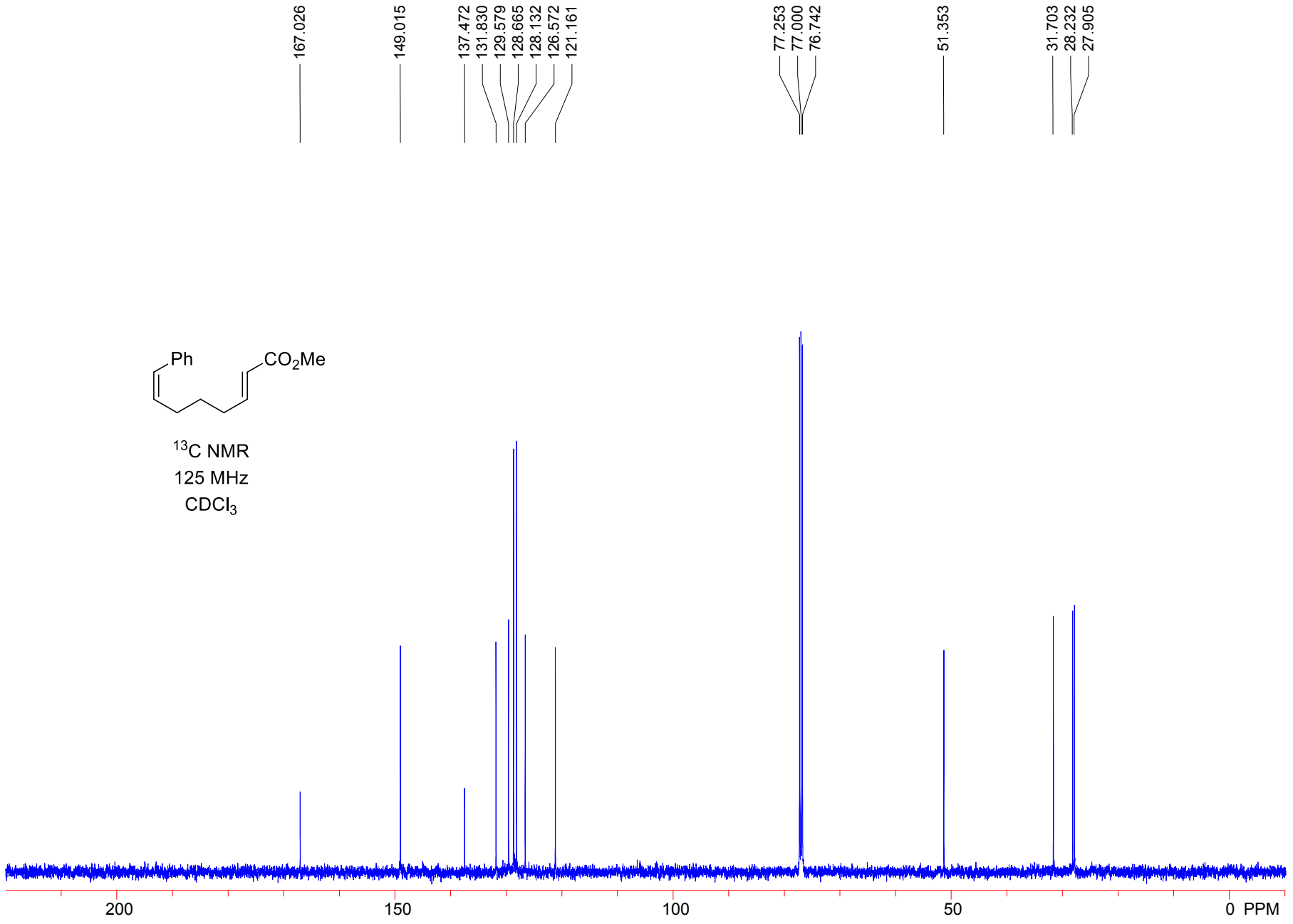
147.468
133.526
127.153
113.560
110.878
77.253
77.000
76.742
55.230
34.810
26.681
MeO
OMe
^{13}C NMR
125 MHz
$CDCl_3$
200
150
100
50
0 PPM


7.342
7.339
7.326
7.315
7.311
7.255
7.241
7.235
7.220
7.205
6.975
6.961
6.947
6.944
6.930
6.916
6.461
6.438
5.812
5.809
5.805
5.780
5.777
5.774
5.653
5.638
5.630
5.624
5.615
5.601
3.713
2.384
2.380
2.369
2.366
2.355
2.351
2.340
2.336
2.246
2.243
2.232
2.229
2.216
2.213
2.202
2.199
1.642
1.627
1.612
1.597
1.582
-0.000
Ph
CO2Me
1H NMR
500 MHz
CDCl3
3.13
2.15
1.00
1.01
1.02
1.00
3.17
2.16
2.02
2.16
8
6
4
2
0
PPM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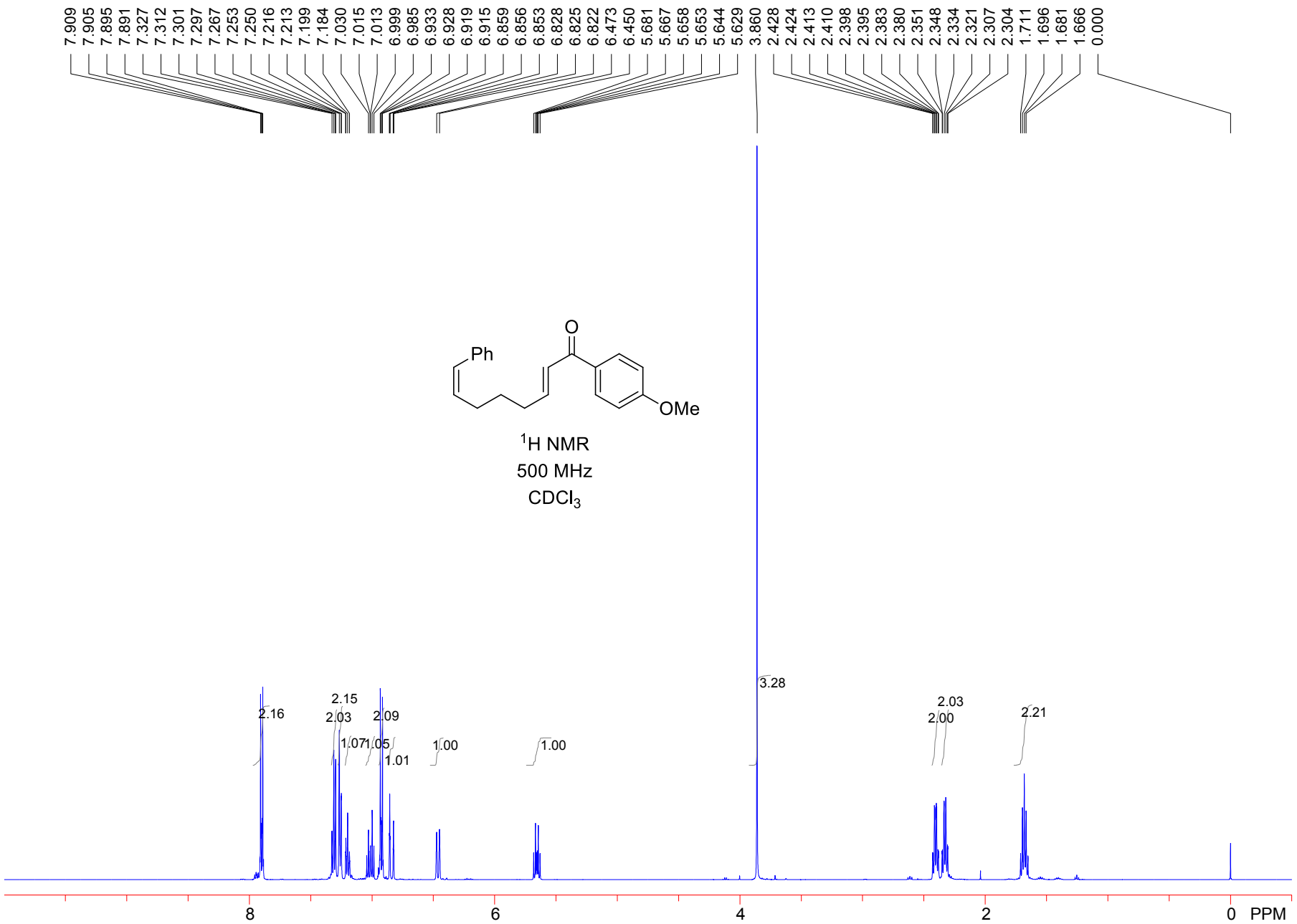
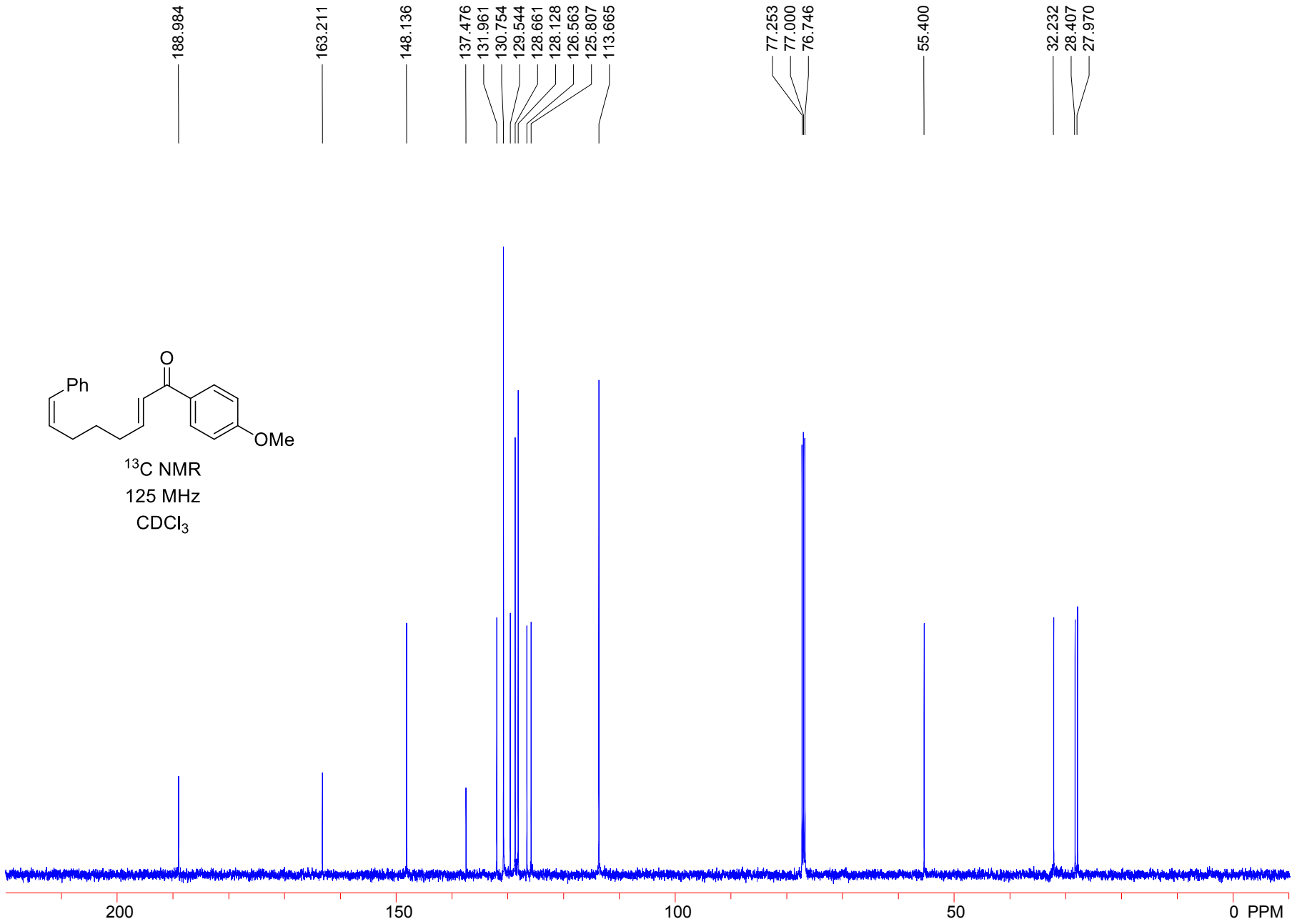
131.830
129.579
128.665
128.132
126.572
121.161
77.253
77.000
76.742
51.353
31.703
28.232
27.905
Ph
CO2Me
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM


7.909
7.905
7.895
7.891
7.327
7.312
7.301
7.297
7.267
7.253
7.250
7.216
7.213
7.199
7.184
7.030
7.015
7.013
6.999
6.985
6.933
6.928
6.919
6.915
6.859
6.856
6.853
6.828
6.825
6.822
6.473
6.450
5.681
5.667
5.658
5.653
5.644
5.629
3.860
2.428
2.424
2.413
2.410
2.398
2.395
2.383
2.380
2.351
2.348
2.334
2.321
2.307
2.304
1.711
1.696
1.681
1.666
0.000
O
Ph
OMe
1H NMR
500 MHz
CDCl3
2.16
2.15
2.03
2.09
1.07
1.05
1.01
1.00
1.00
3.28
2.03
2.00
2.21
8
6
4
2
0
PPM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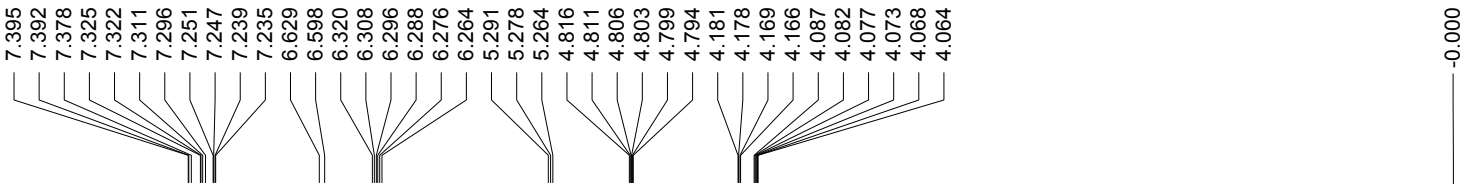
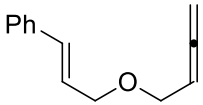
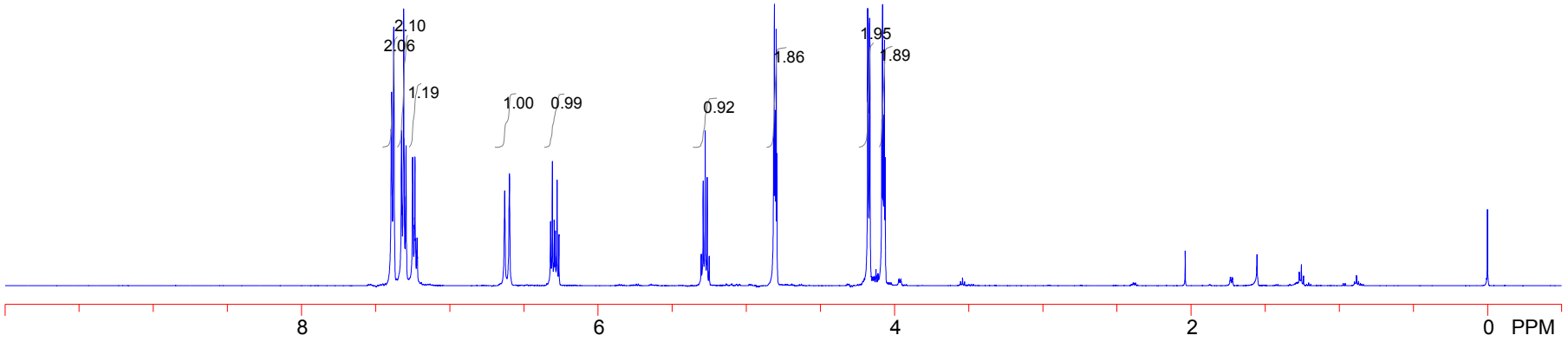
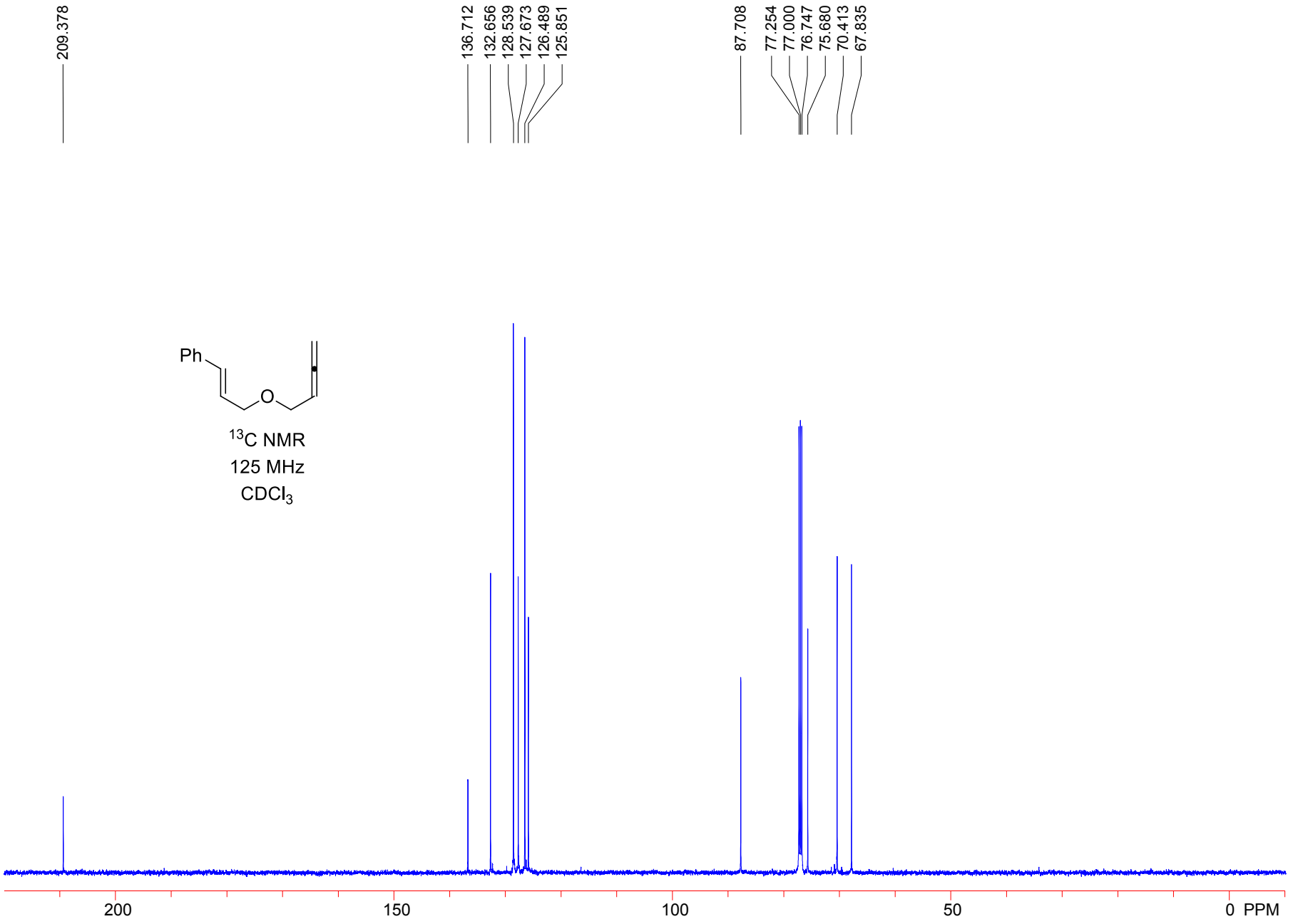
148.136
137.476
131.961
130.754
129.544
128.661
128.128
126.563
125.807
113.665
77.253
77.000
76.746
55.400
32.232
28.407
27.970
O
Ph
OMe
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM

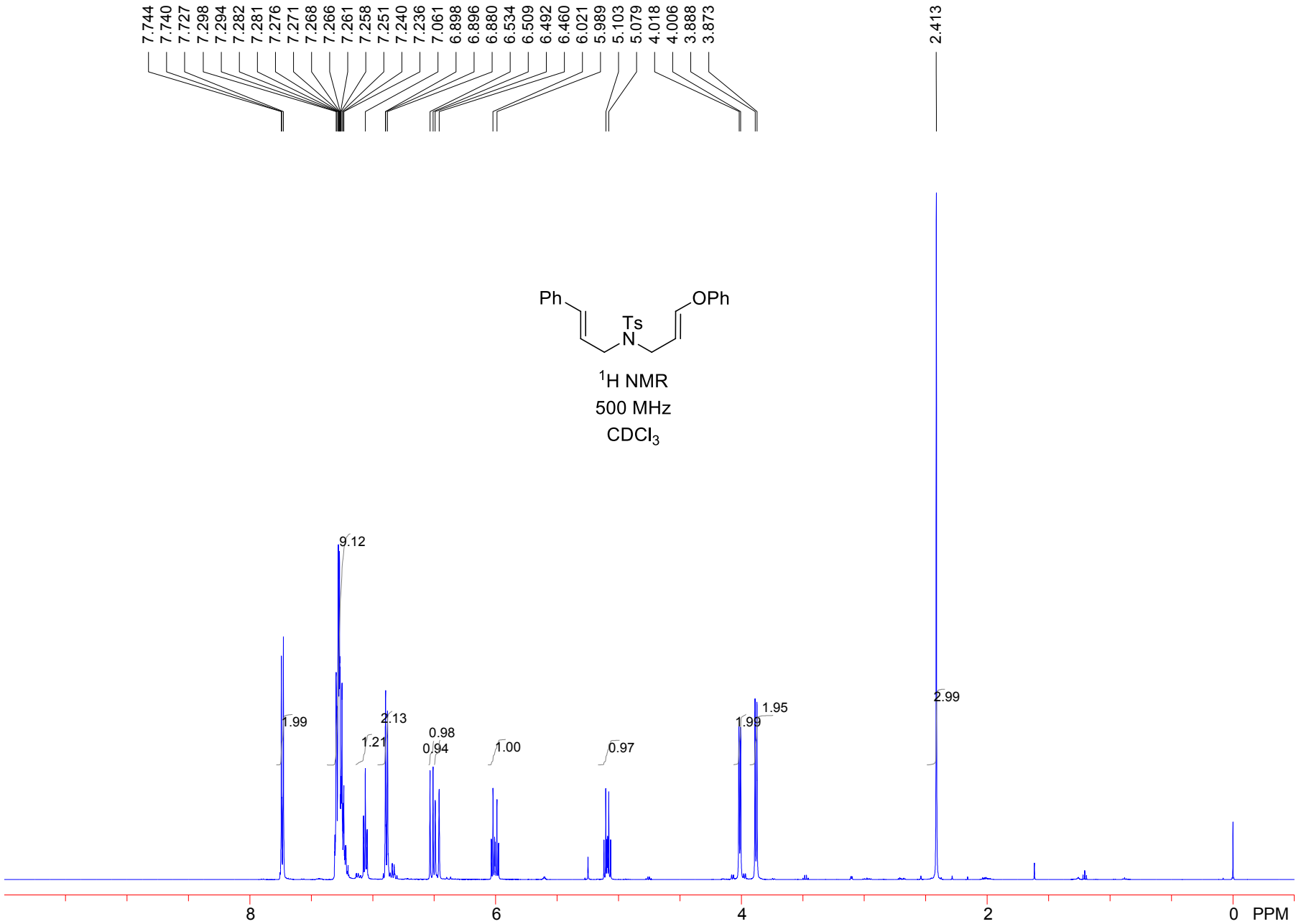




^{1}H NMR
500 MHz
$CDCl_3$




209.378
136.712
132.656
128.539
127.673
126.489
125.851
87.708
77.254
77.000
76.747
75.680
70.413
67.835
Ph
O
^{13}C NMR
125 MHz
$CDCl_3$
200
150
100
50
0 PPM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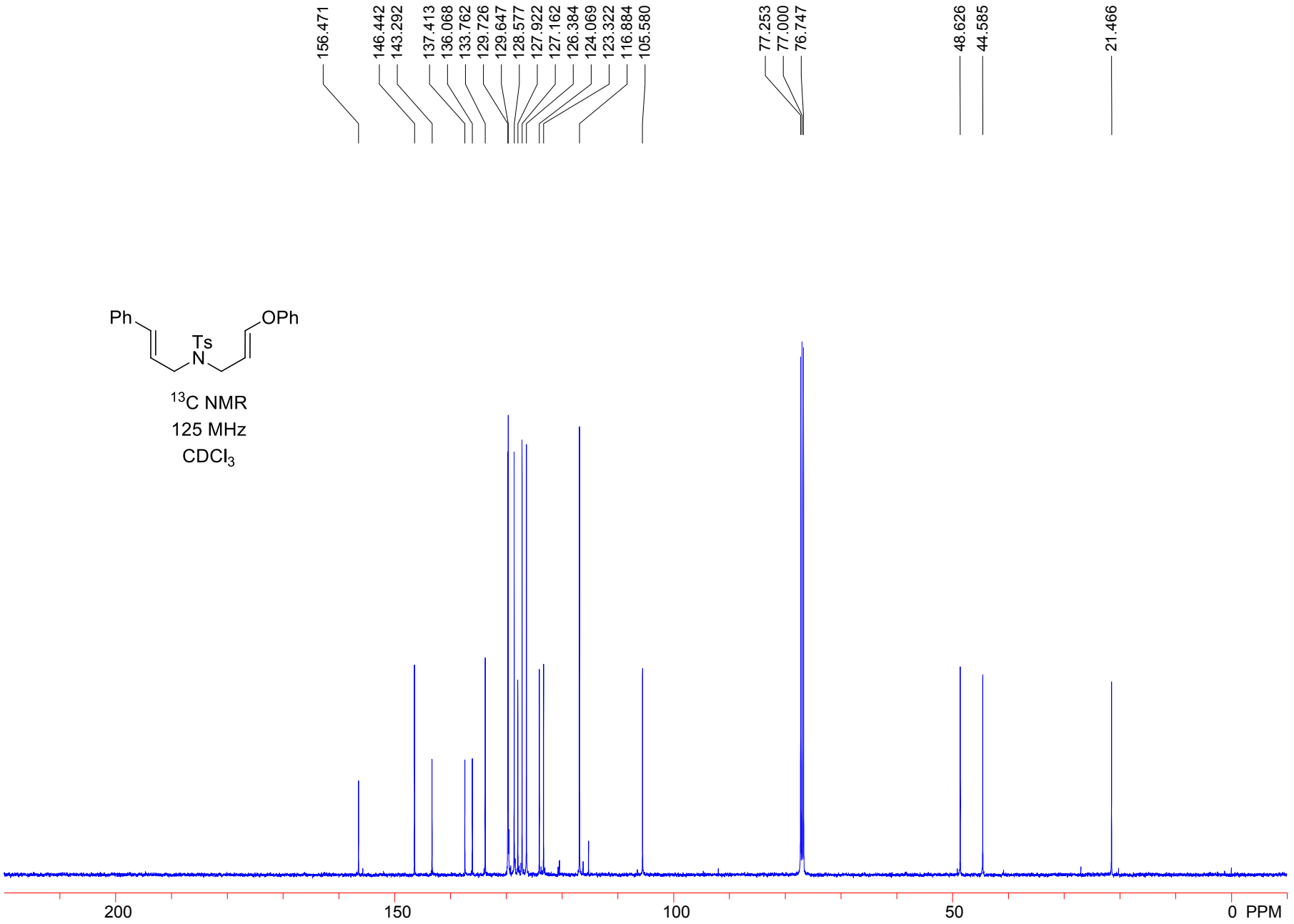
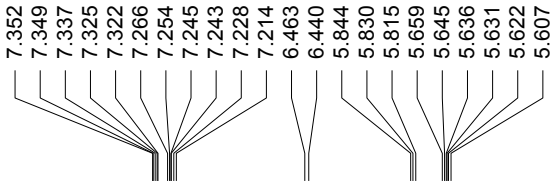
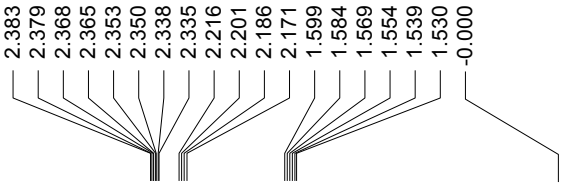
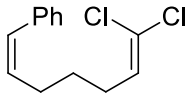
7.294
7.282
7.281
7.276
7.271
7.268
7.266
7.261
7.258
7.251
7.240
7.236
7.061
6.898
6.896
6.880
6.534
6.509
6.492
6.460
6.021
5.989
5.103
5.079
4.018
4.006
3.888
3.873
2.413
Ph
OPh
Ts
N
1H NMR
500 MHz
CDCl3
9.12
1.99
2.13
1.21
0.98
0.94
1.00
0.97
1.99
1.95
2.99
8
6
4
2
0
PPM

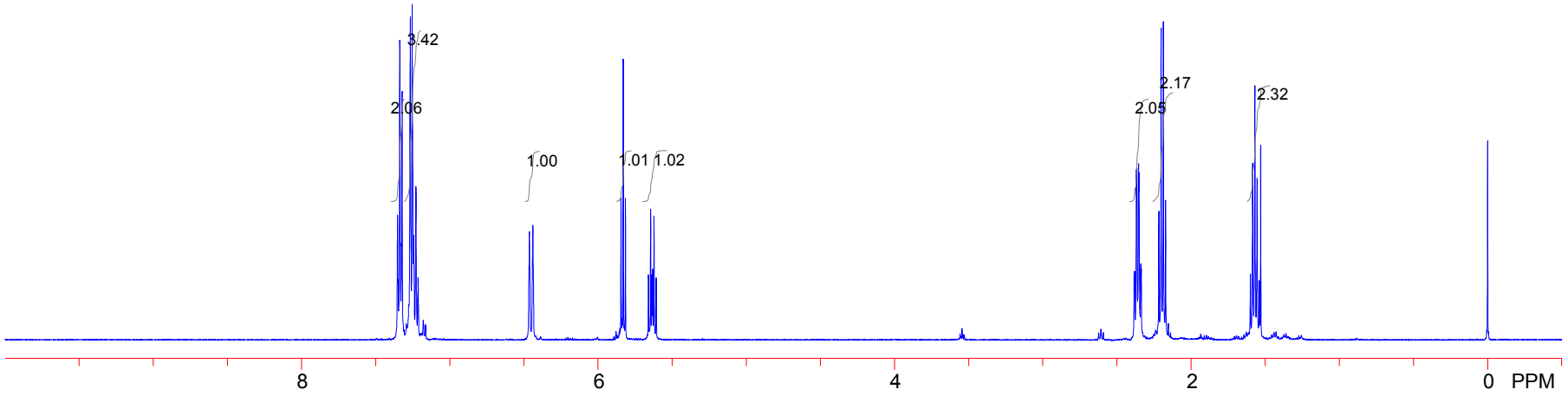

156.471
146.442
143.292
137.413
136.068
133.762
129.726
129.647
128.577
127.922
127.162
126.384
124.069
123.322
116.884
105.580
77.253
77.000
76.747
48.626
44.585
21.466
Ph
OPh
Ts
N
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM

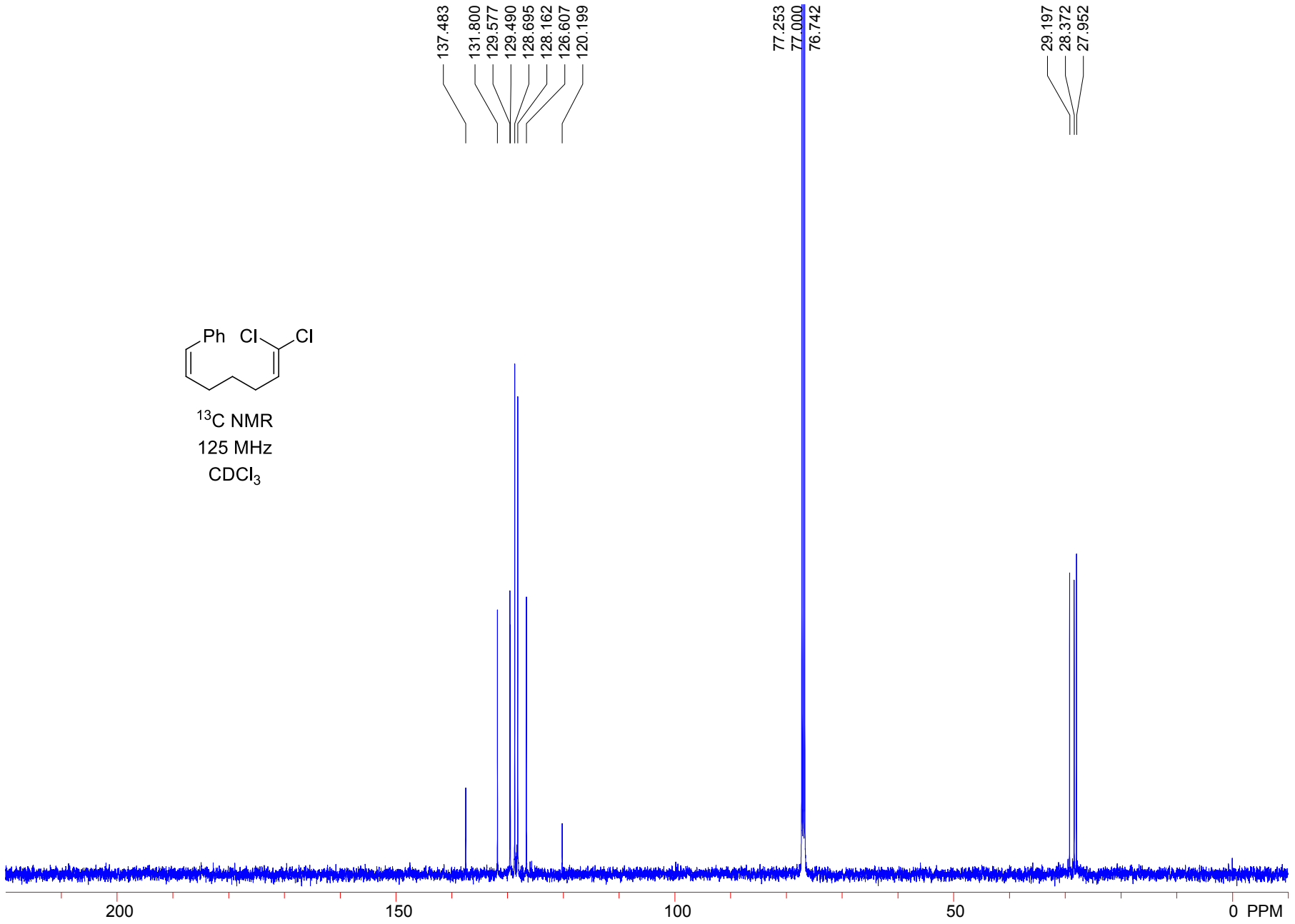


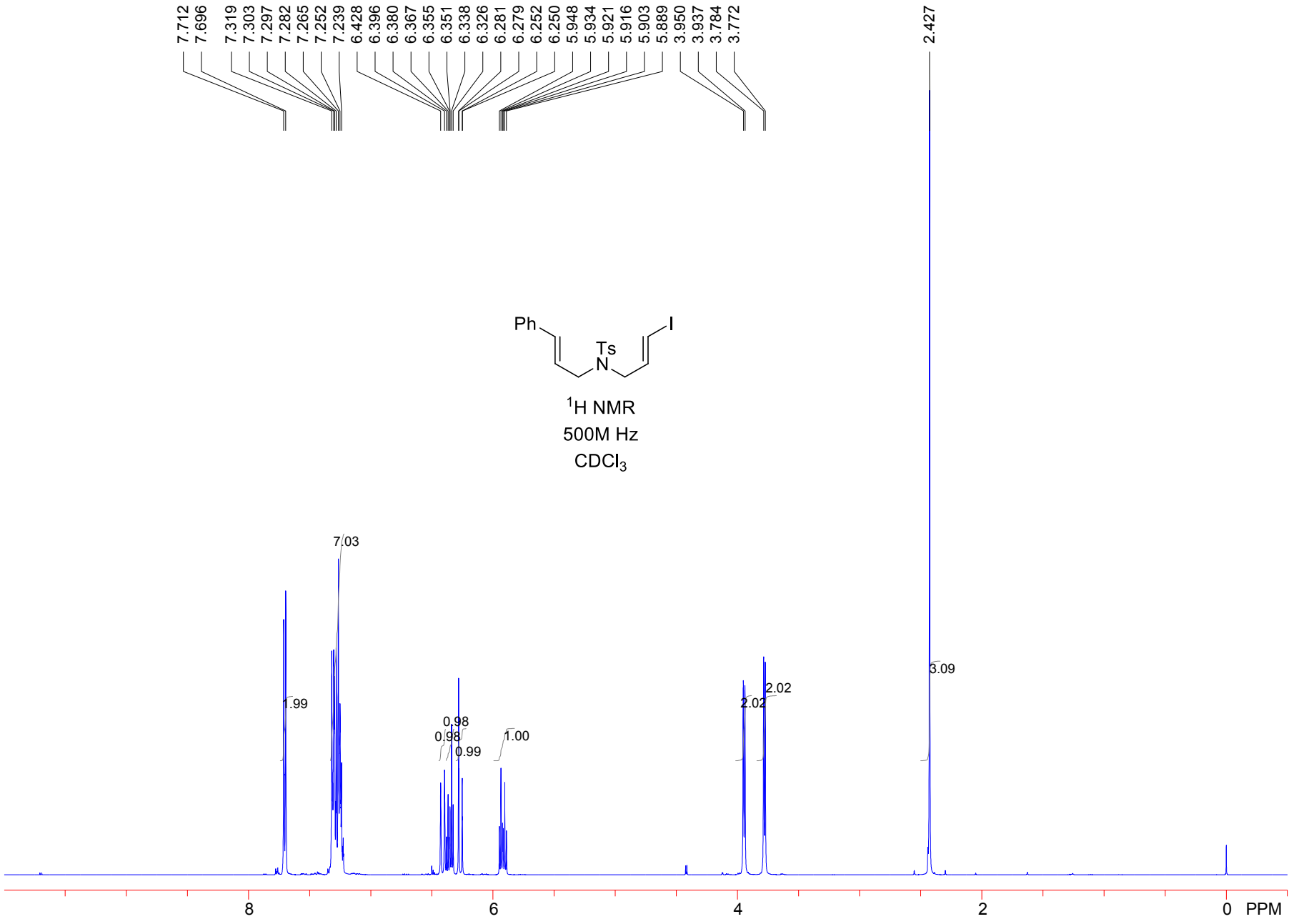




^{1}H NMR
500 MHz
$CDCl_3$




137.483
131.800
129.577
129.490
128.695
128.162
126.607
120.199
77.253
77.000
76.742
29.197
28.372
27.952
Ph
Cl
Cl
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM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7.319
7.303
7.297
7.282
7.265
7.252
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6.428
6.396
6.380
6.367
6.355
6.351
6.338
6.326
6.281
6.279
6.252
6.250
5.948
5.934
5.921
5.916
5.903
5.889
3.950
3.937
3.784
3.772
2.427
Ph
Ts
N
I
1H NMR
500M Hz
CDCl3
7.03
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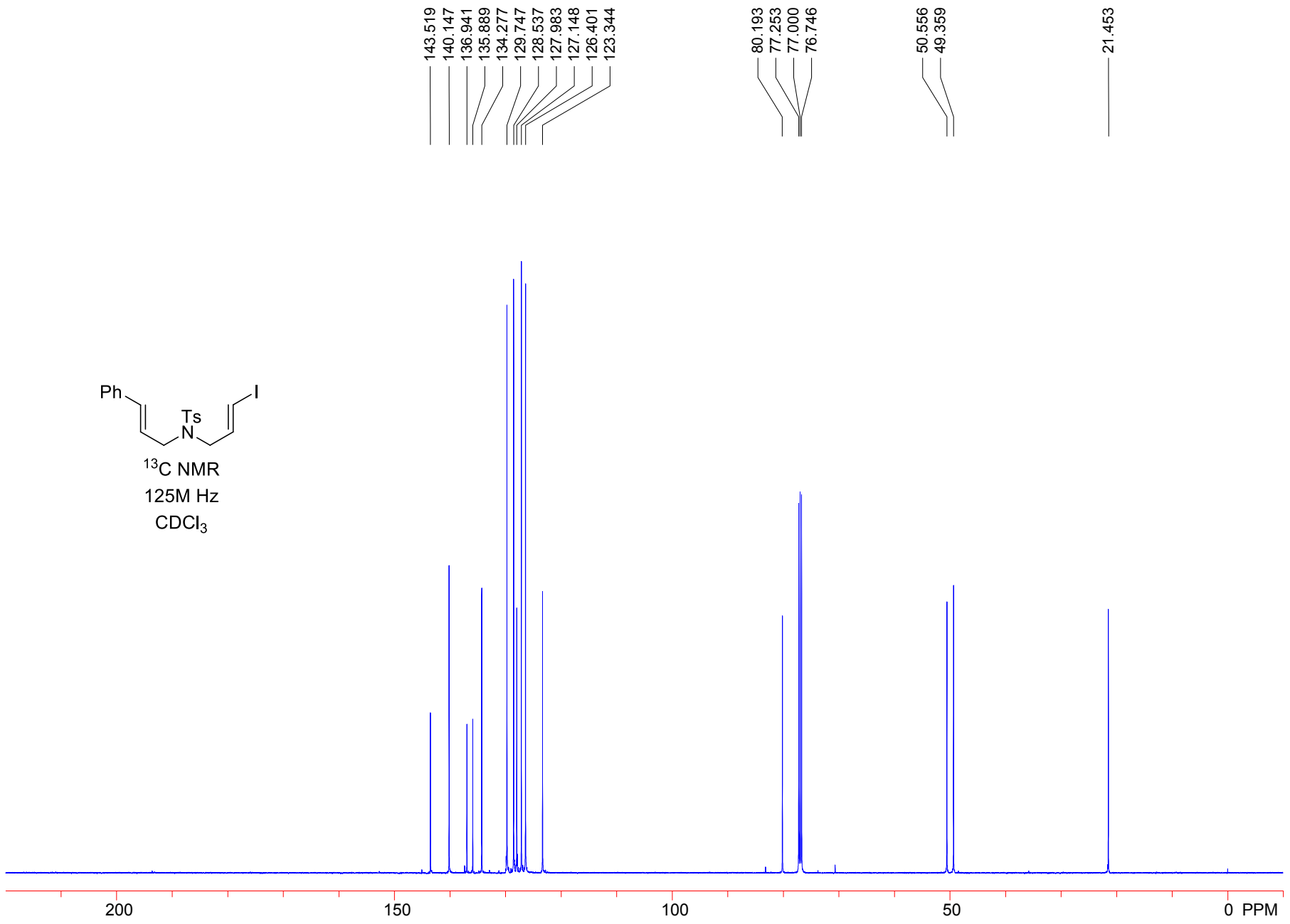
0.98
0.98
0.99
1.00
2.02
2.02
3.09
8
6
4
2
0
PPM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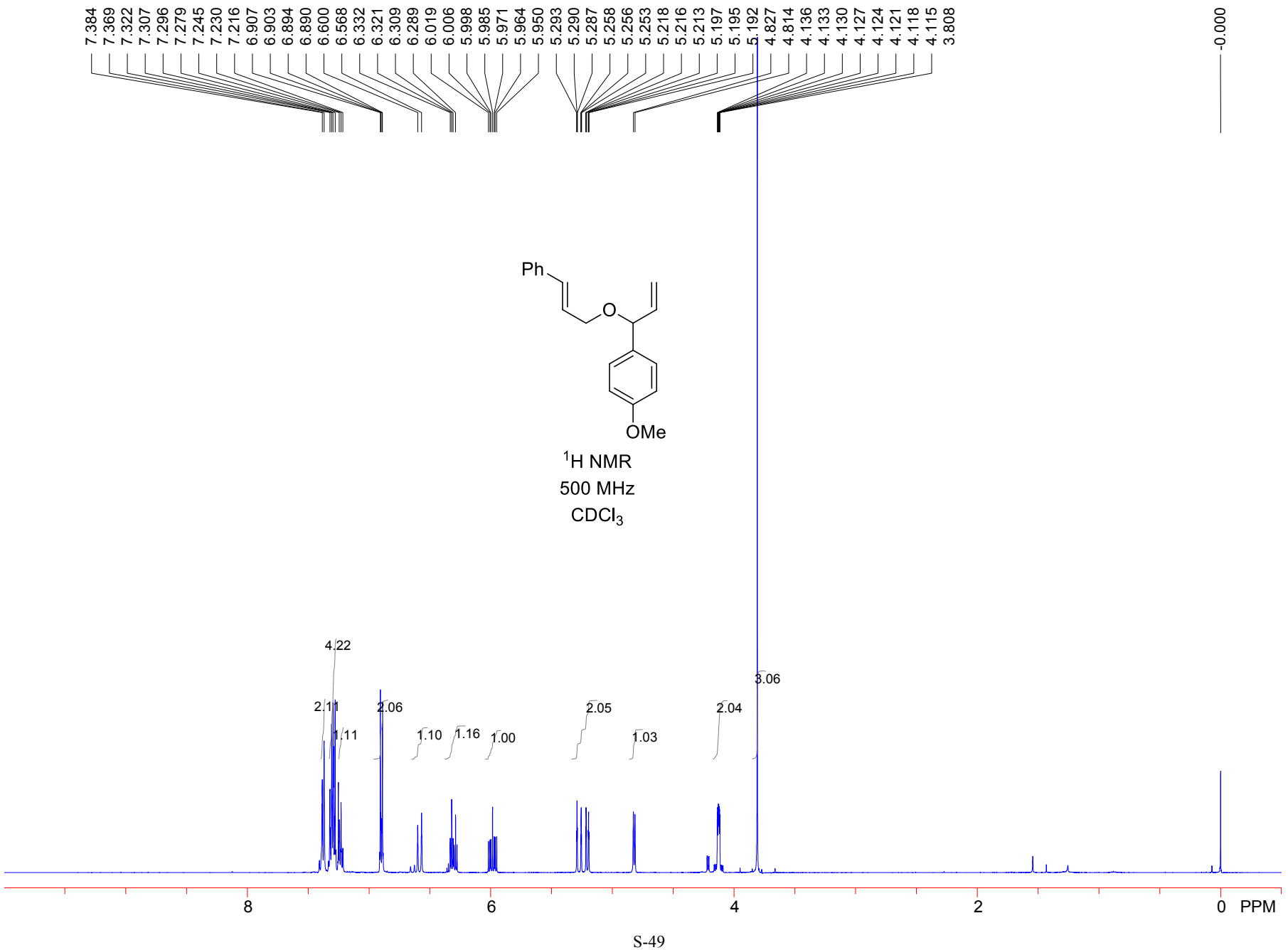
140.147
136.941
135.889
134.277
129.747
128.537
127.983
127.148
126.401
123.344
80.193
77.253
77.000
76.746
50.556
49.359
21.453
Ph
Ts
N
I
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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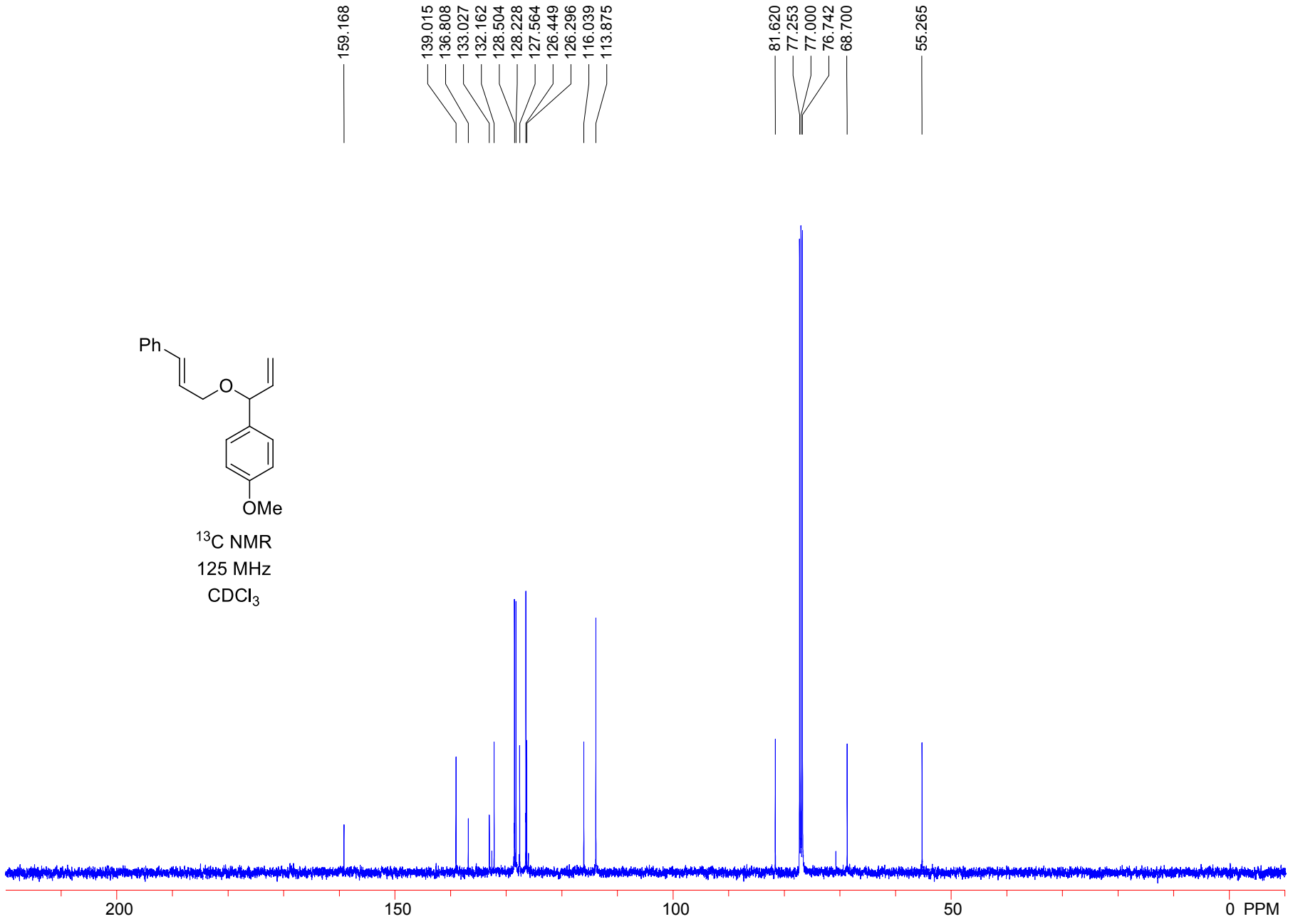
7.369
7.322
7.307
7.296
7.279
7.245
7.230
7.216
6.907
6.903
6.894
6.890
6.600
6.568
6.332
6.321
6.309
6.289
6.019
6.006
5.998
5.985
5.971
5.964
5.950
5.293
5.290
5.287
5.258
5.256
5.253
5.218
5.216
5.213
5.197
5.195
5.192
4.827
4.814
4.136
4.133
4.130
4.127
4.124
4.121
4.118
4.115
3.808
-0.000
Ph
O
OMe
1H NMR
500 MHz
CDCl3
4.22
2.11
1.11
2.06
1.10
1.16
1.00
2.05
1.03
2.04
3.06
8
6
4
2
0
PPM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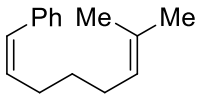
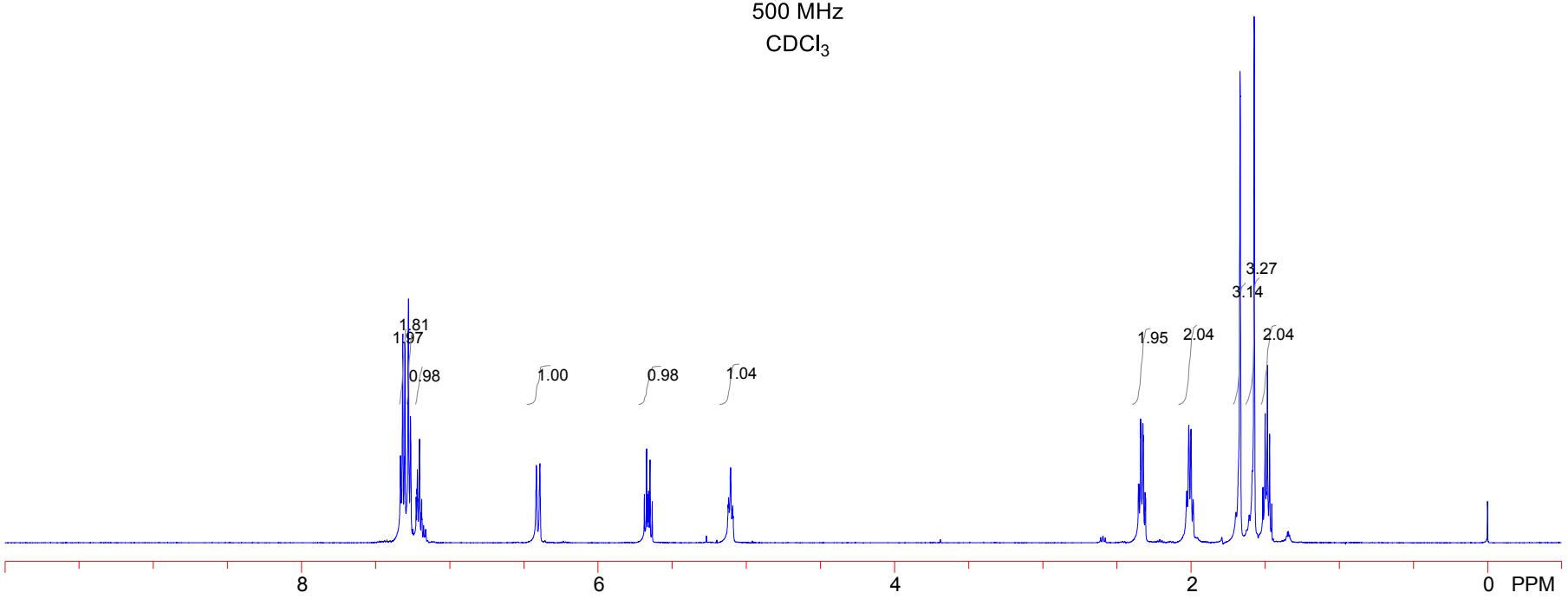
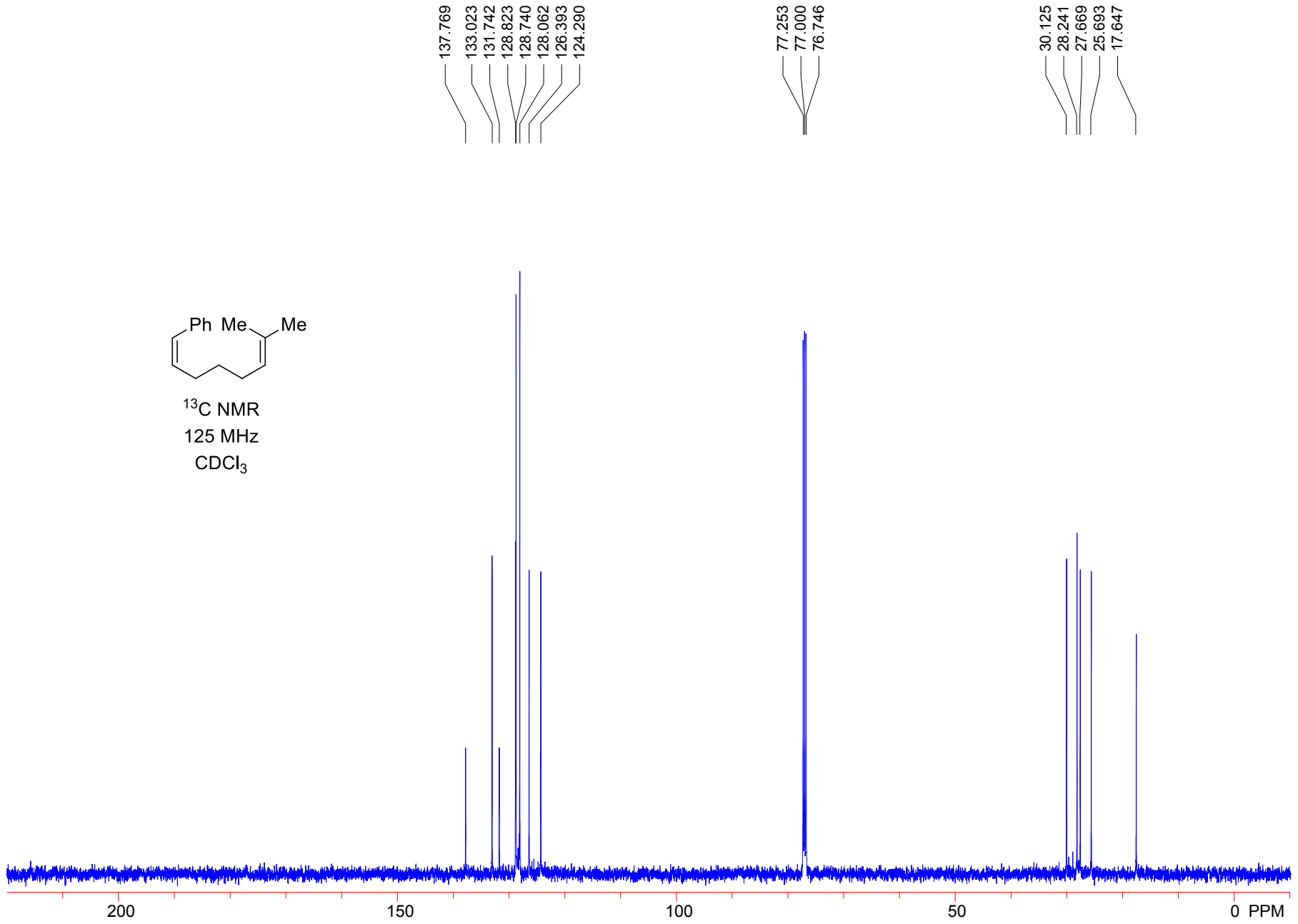
139.015
136.808
133.027
132.162
128.504
128.228
127.564
126.449
126.296
116.039
113.875
81.620
77.253
77.000
76.742
68.700
55.265
Ph
O
OMe
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM



^{1}H NMR
500 MHz
$CDCl_3$

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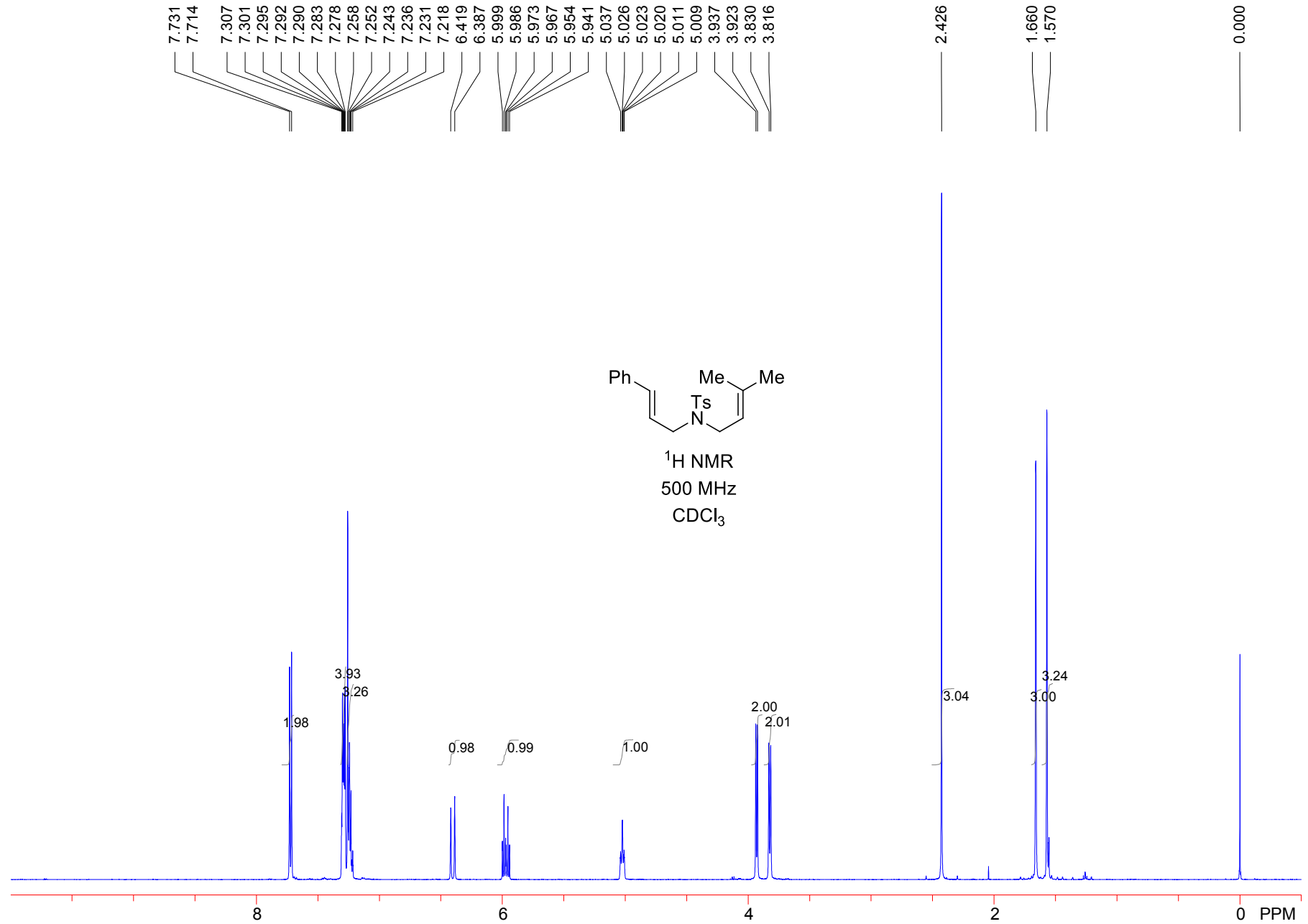
133.023
131.742
128.823
128.740
128.062
126.393
124.290
77.253
77.000
76.746
30.125
28.241
27.669
25.693
17.647
Ph
Me
Me
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM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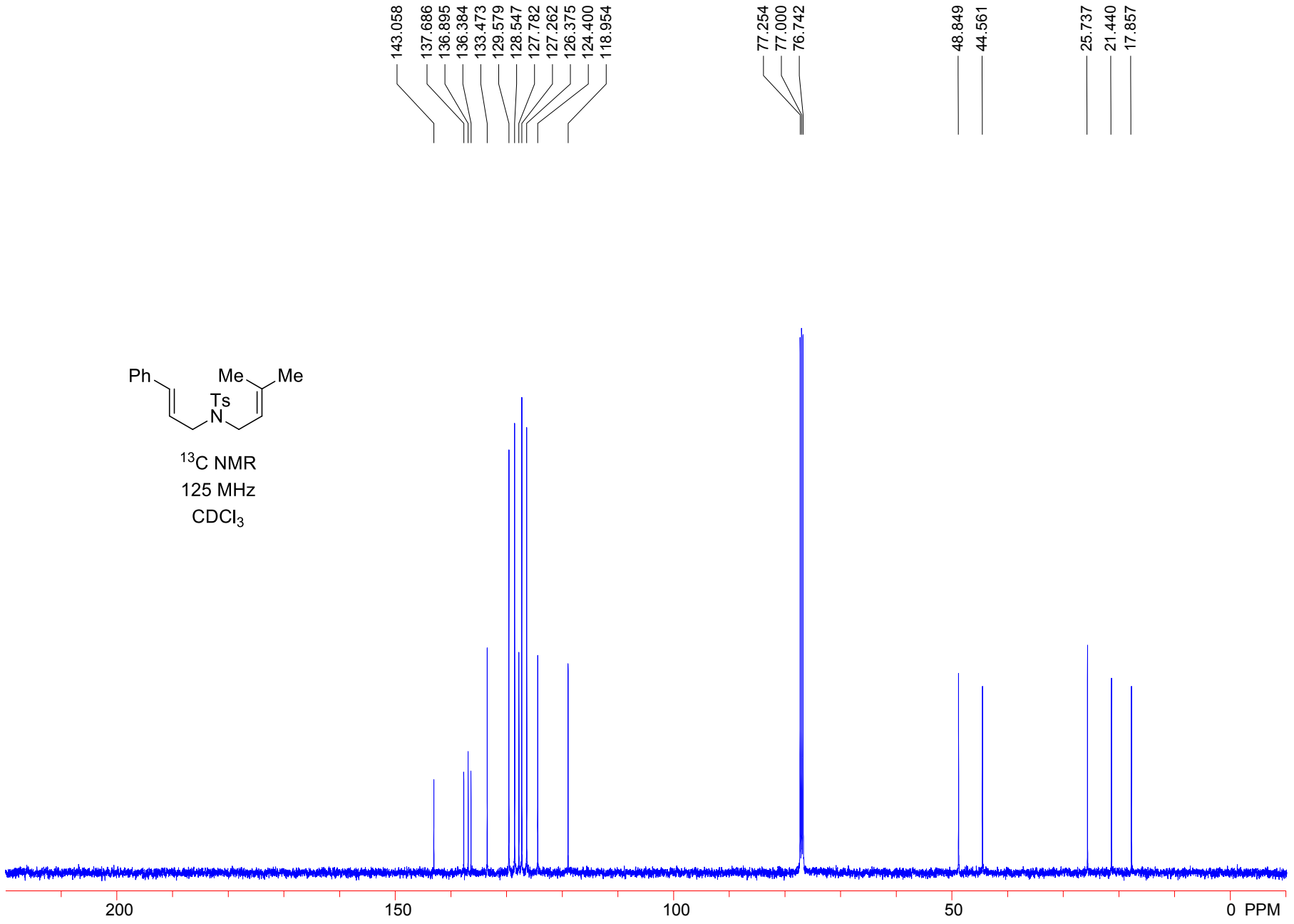
7.714
7.307
7.301
7.295
7.292
7.290
7.283
7.278
7.258
7.252
7.243
7.236
7.231
7.218
6.419
6.387
5.999
5.986
5.973
5.967
5.954
5.941
5.037
5.026
5.023
5.020
5.011
5.009
3.937
3.923
3.830
3.816
2.426
1.660
1.570
0.000
Ph
Me
Me
Ts
N
1H NMR
500 MHz
CDCl3
1.98
3.93
3.26
0.98
0.99
1.00
2.00
2.01
3.04
3.24
3.00
8
6
4
2
0
PPM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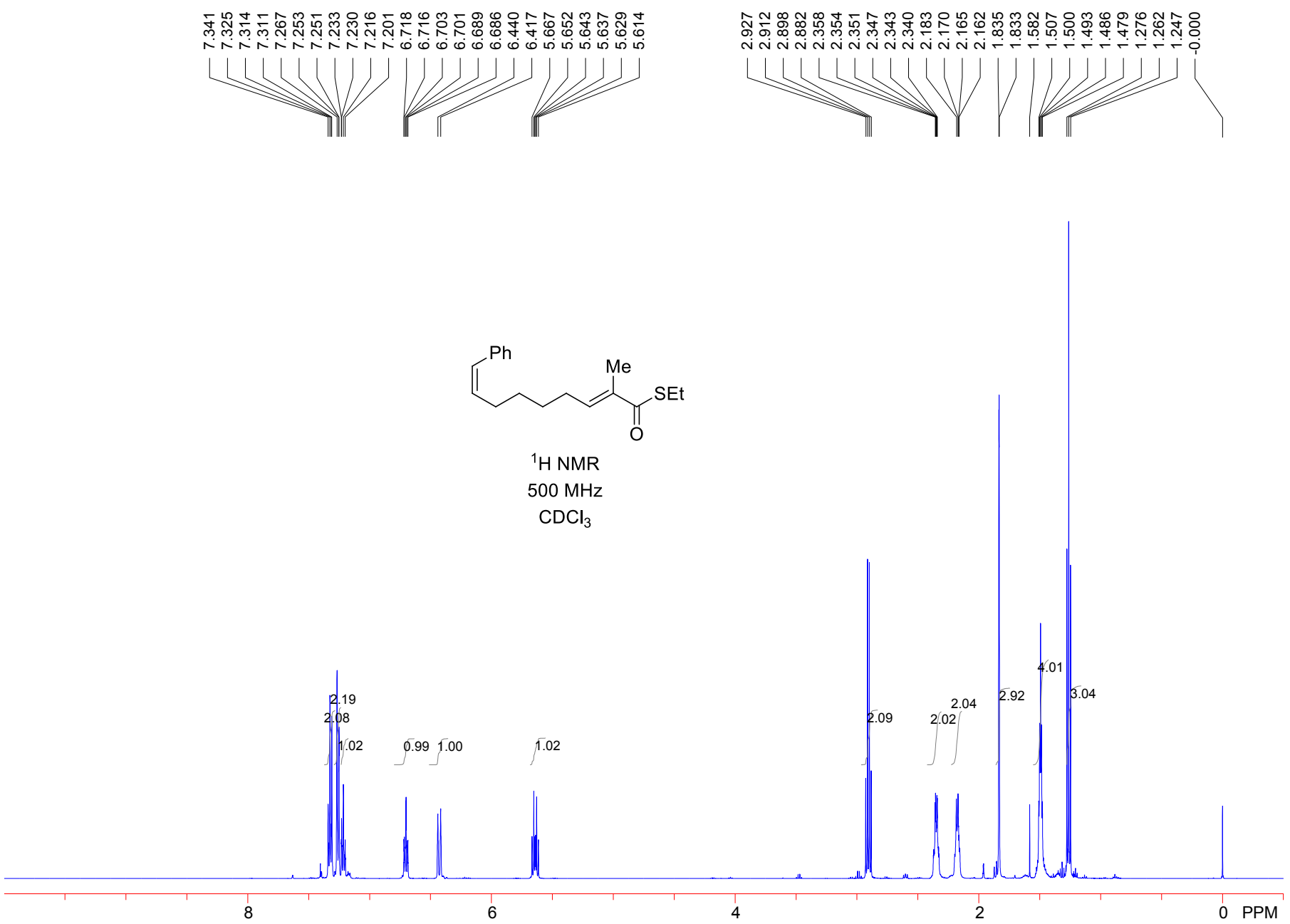
136.895
136.384
133.473
129.579
128.547
127.782
127.262
126.375
124.400
118.954
77.254
77.000
76.742
48.849
44.561
25.737
21.440
17.857
Ph
Me
Me
Ts
N
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM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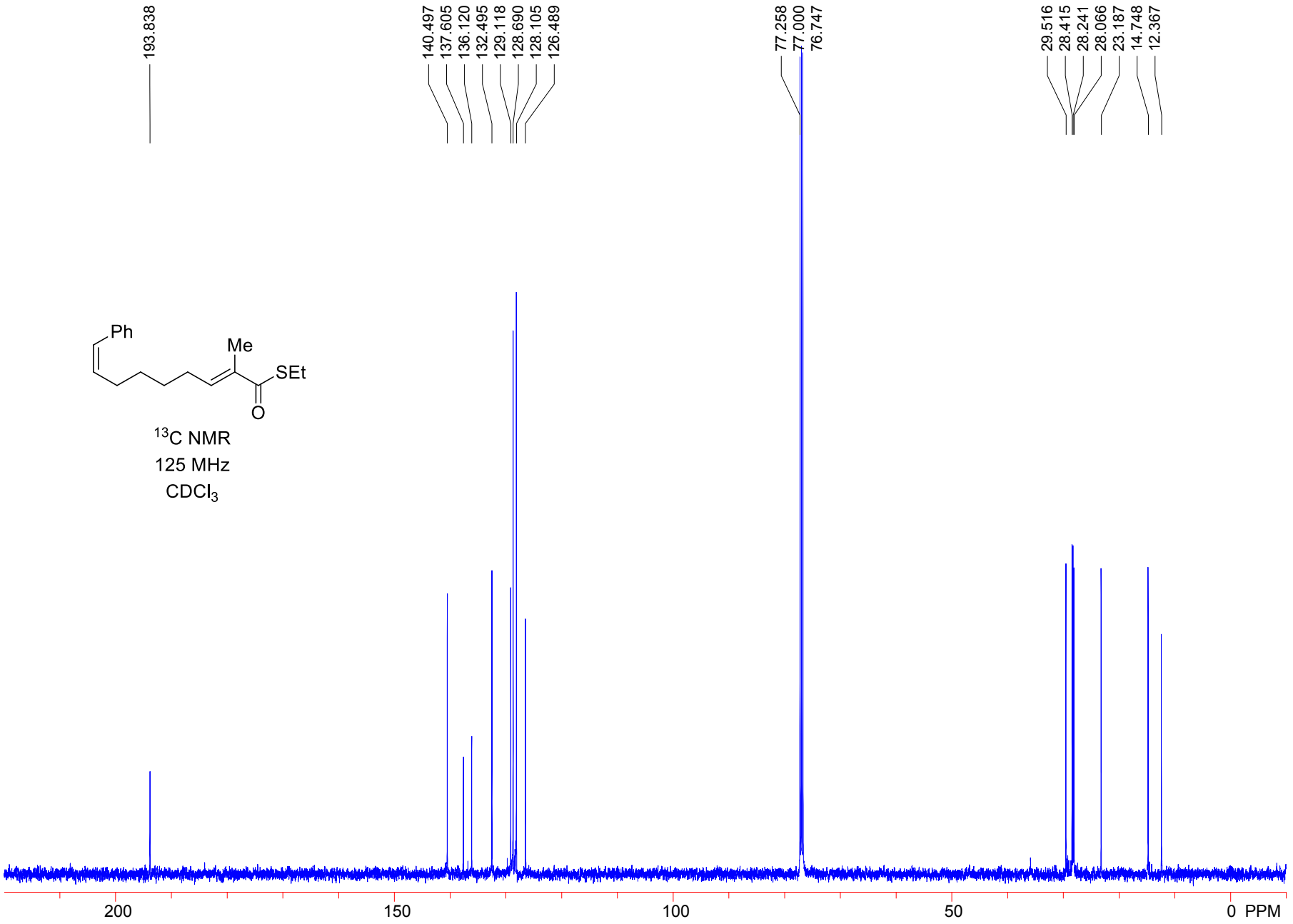
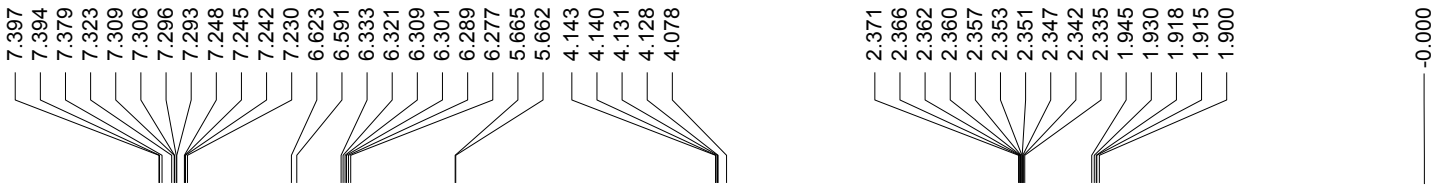
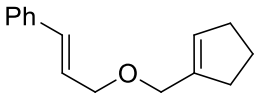
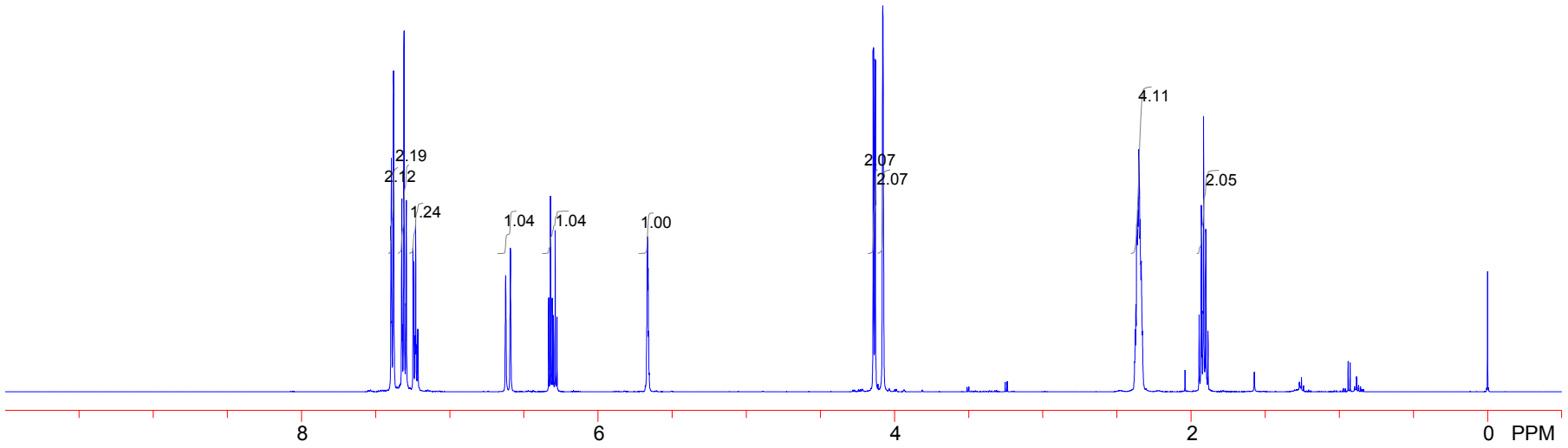
7.325
7.314
7.311
7.267
7.253
7.251
7.233
7.230
7.216
7.201
6.718
6.716
6.703
6.701
6.689
6.686
6.440
6.417
5.667
5.652
5.643
5.637
5.629
5.614
2.927
2.912
2.898
2.882
2.358
2.354
2.351
2.347
2.343
2.340
2.183
2.170
2.165
2.162
1.835
1.833
1.582
1.507
1.500
1.493
1.486
1.479
1.276
1.262
1.247
-0.000
Ph
Me
SEt
O
1H NMR
500 MHz
CDCl3
2.19
2.08
1.02
0.99
1.00
1.02
2.09
2.02
2.04
2.92
4.01
3.04
8
6
4
2
0
PPM

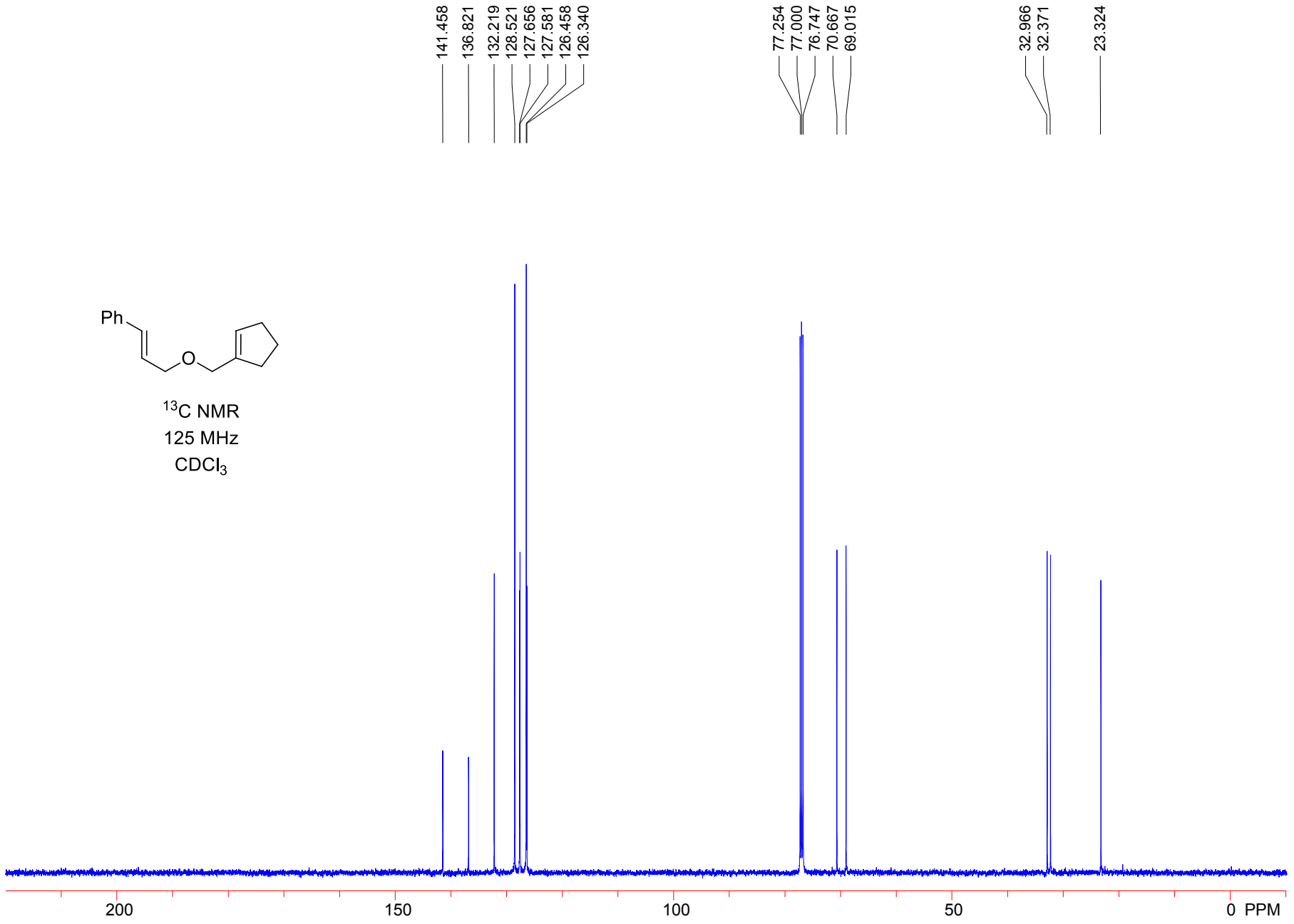

193.838
140.497
137.605
136.120
132.495
129.118
128.690
128.105
126.489
77.258
77.000
76.747
29.516
28.415
28.241
28.066
23.187
14.748
12.367
Ph
Me
SEt
O
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM

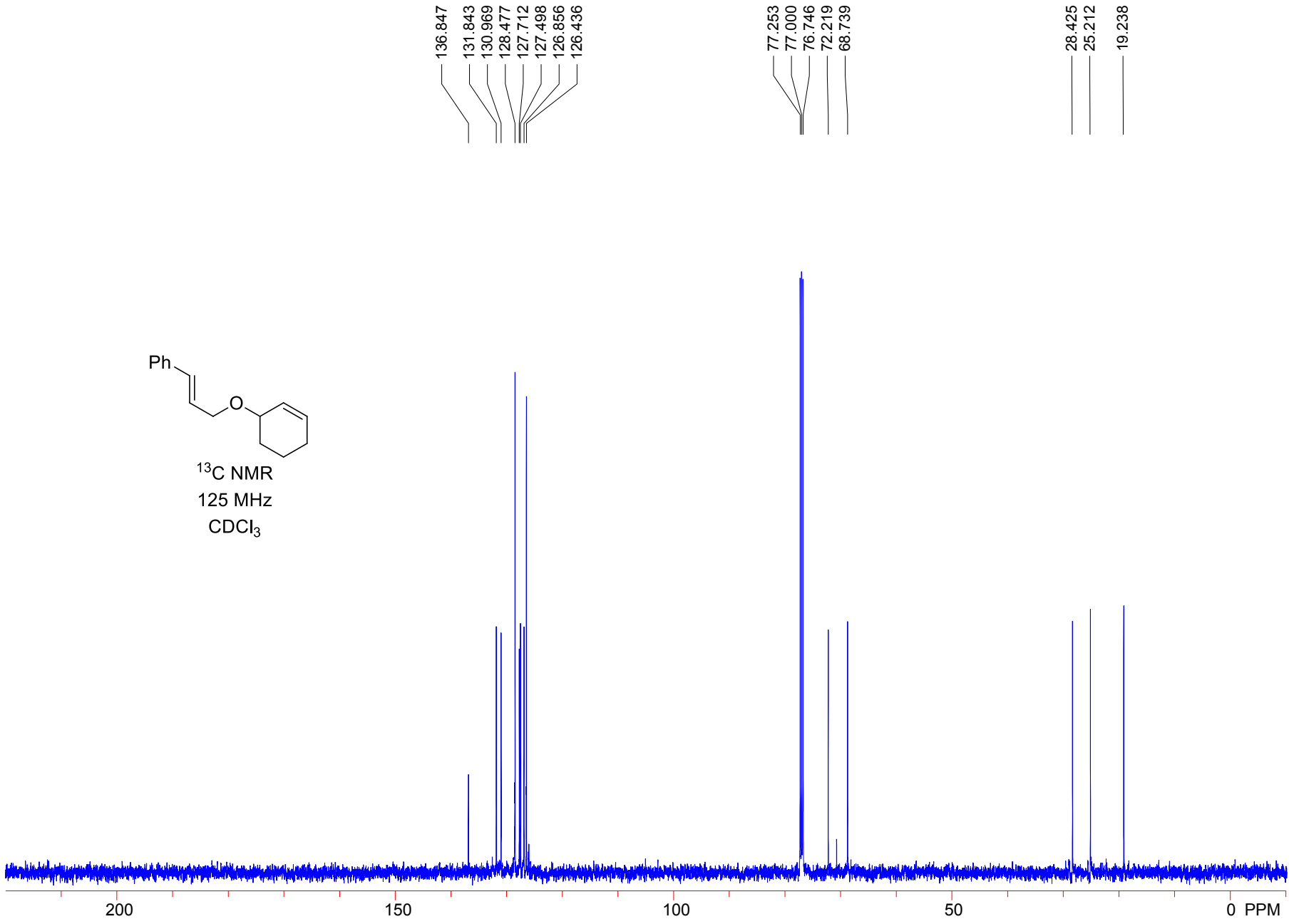


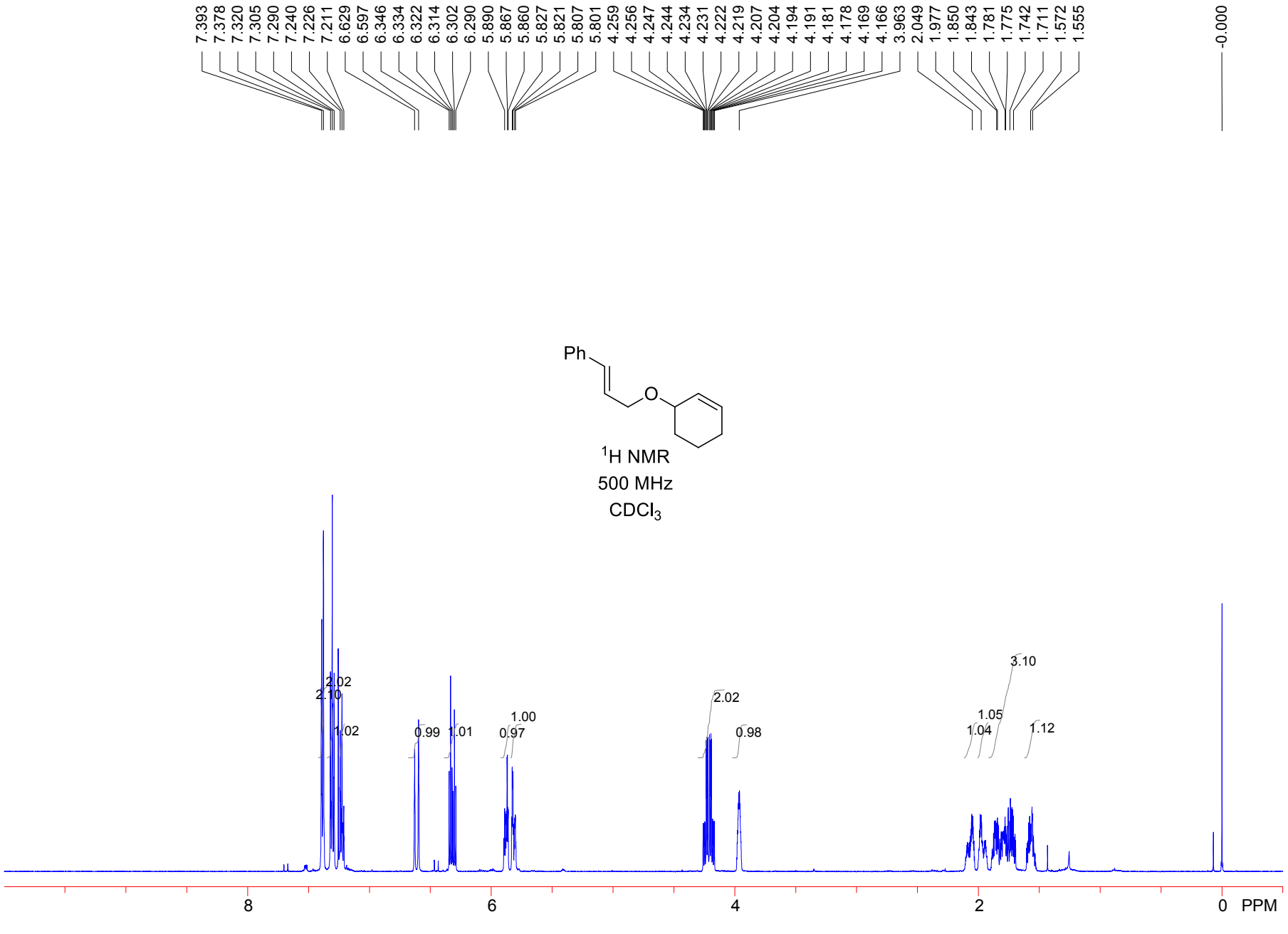


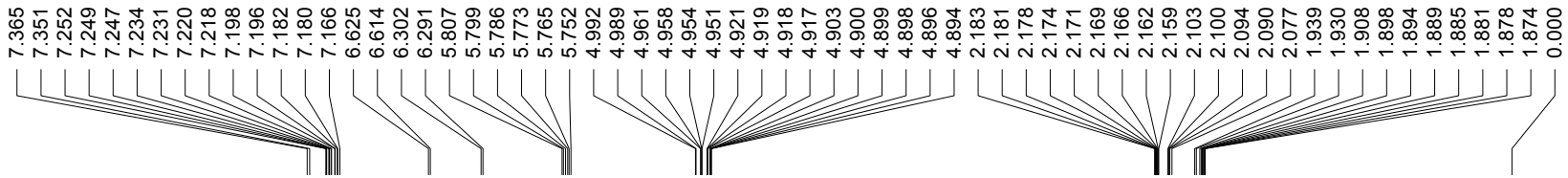
^{1}H NMR
500 MHz
$CDCl_3$

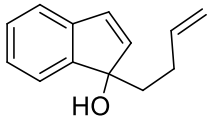



141.458
136.821
132.219
128.521
127.656
127.581
126.458
126.340
77.254
77.000
76.747
70.667
69.015
32.966
32.371
23.324
Ph
O
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM

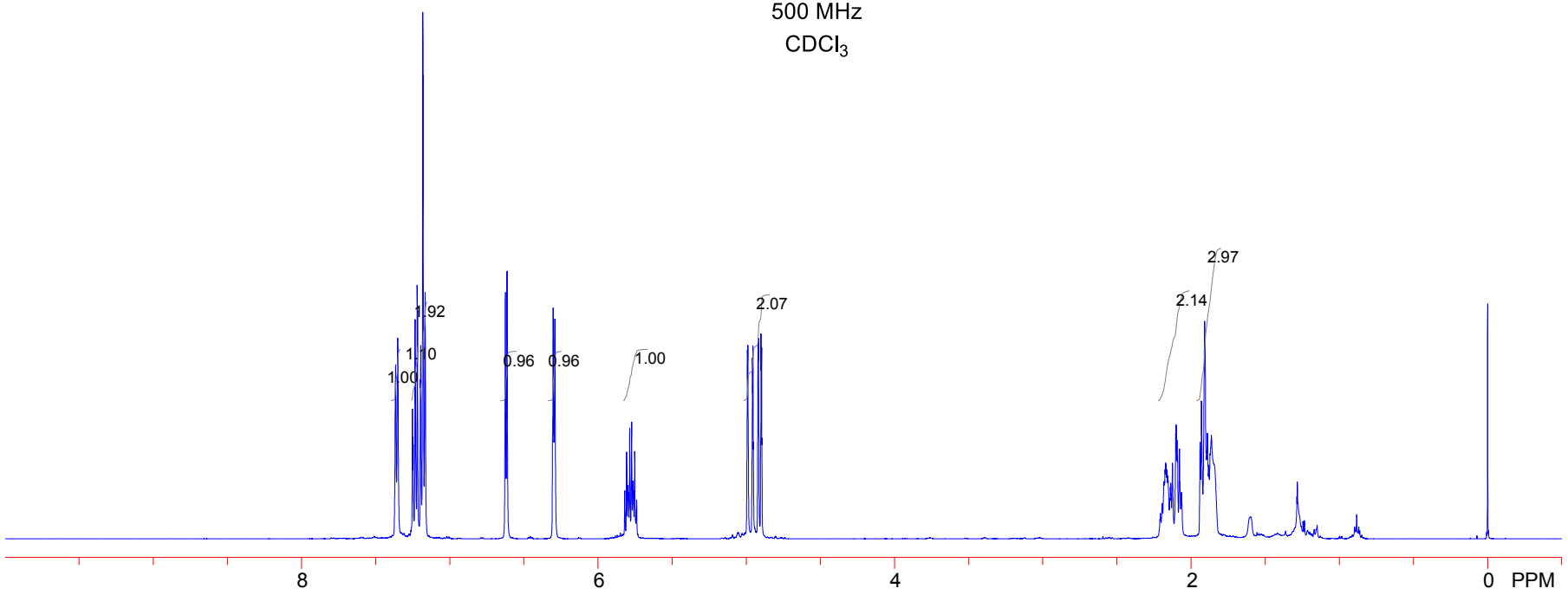

136.847
131.843
130.969
128.477
127.712
127.498
126.856
126.436
77.253
77.000
76.746
72.219
68.739
28.425
25.212
19.238
Ph
O
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM

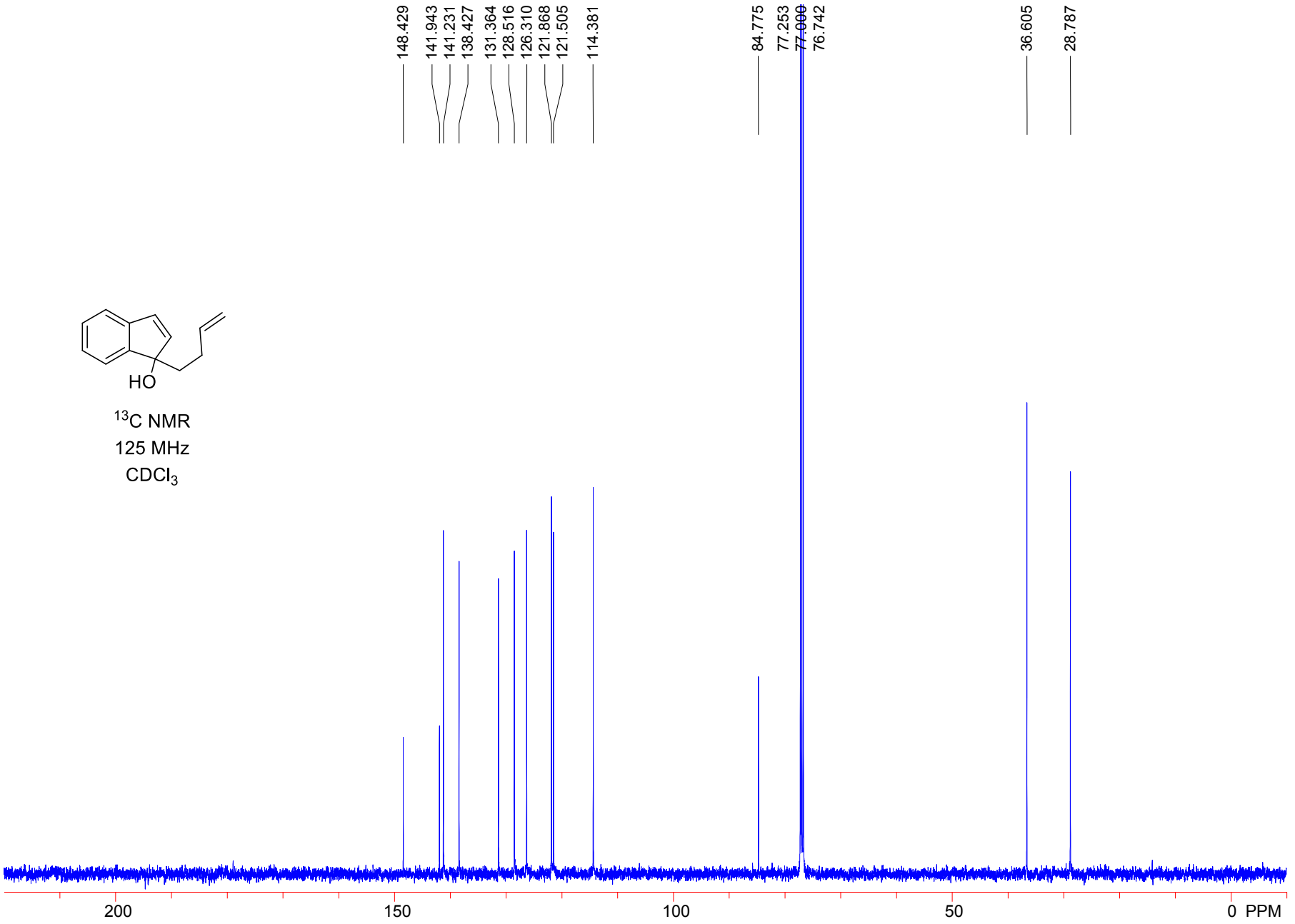

7.393
7.378
7.320
7.305
7.290
7.240
7.226
7.211
6.629
6.597
6.346
6.334
6.322
6.314
6.302
6.290
5.890
5.867
5.860
5.827
5.821
5.807
5.801
4.259
4.256
4.247
4.244
4.234
4.231
4.222
4.219
4.207
4.204
4.194
4.191
4.181
4.178
4.169
4.166
3.963
2.049
1.977
1.850
1.843
1.781
1.775
1.742
1.711
1.572
1.555
-0.000
Ph
O
1H NMR
500 MHz
CDCl3
2.10
2.02
1.02
0.99
1.01
0.97
1.00
2.02
0.98
1.04
1.05
3.10
1.12
8
6
4
2
0
PPM





^{1}H NMR
500 MHz
$CDCl_3$

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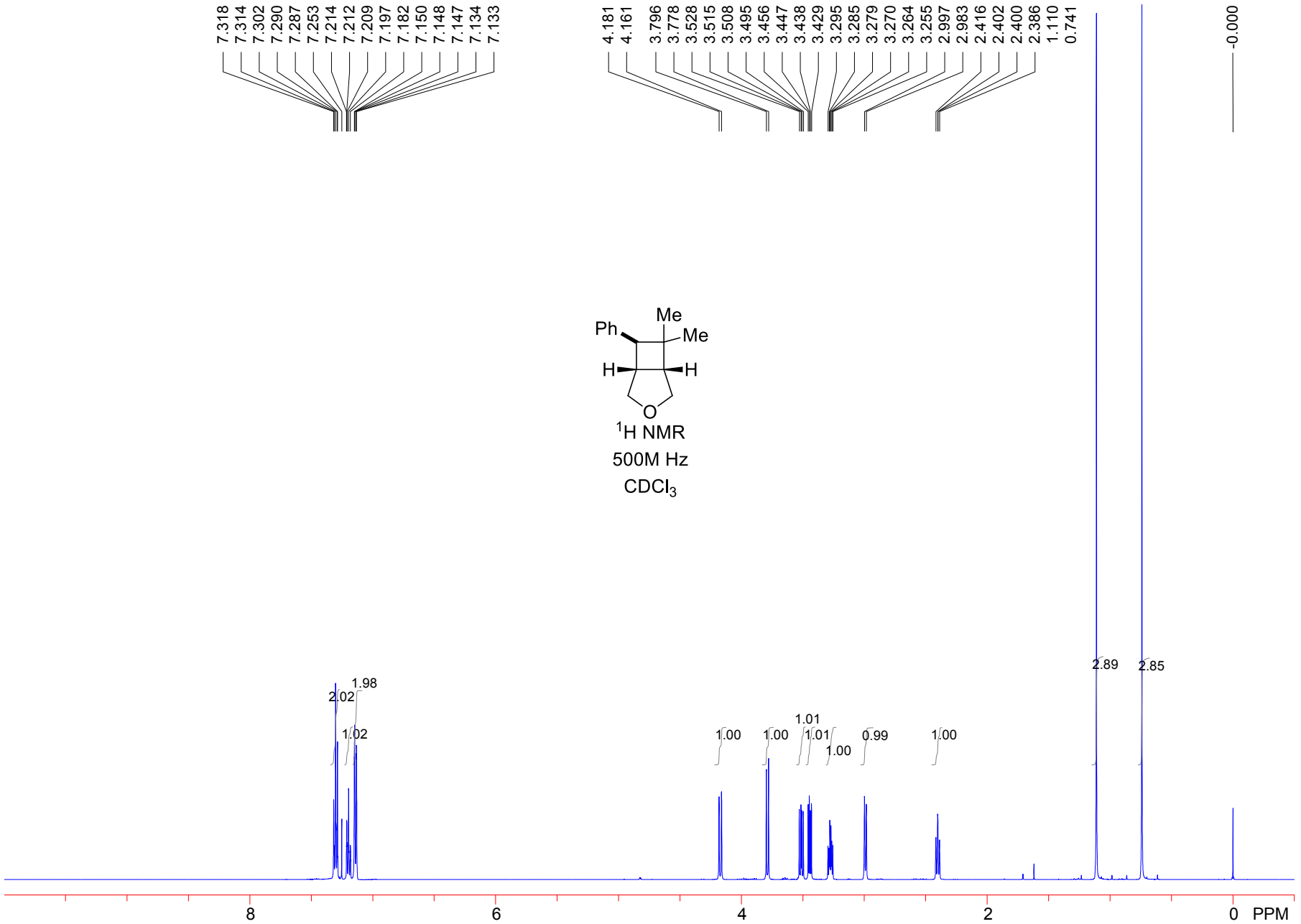
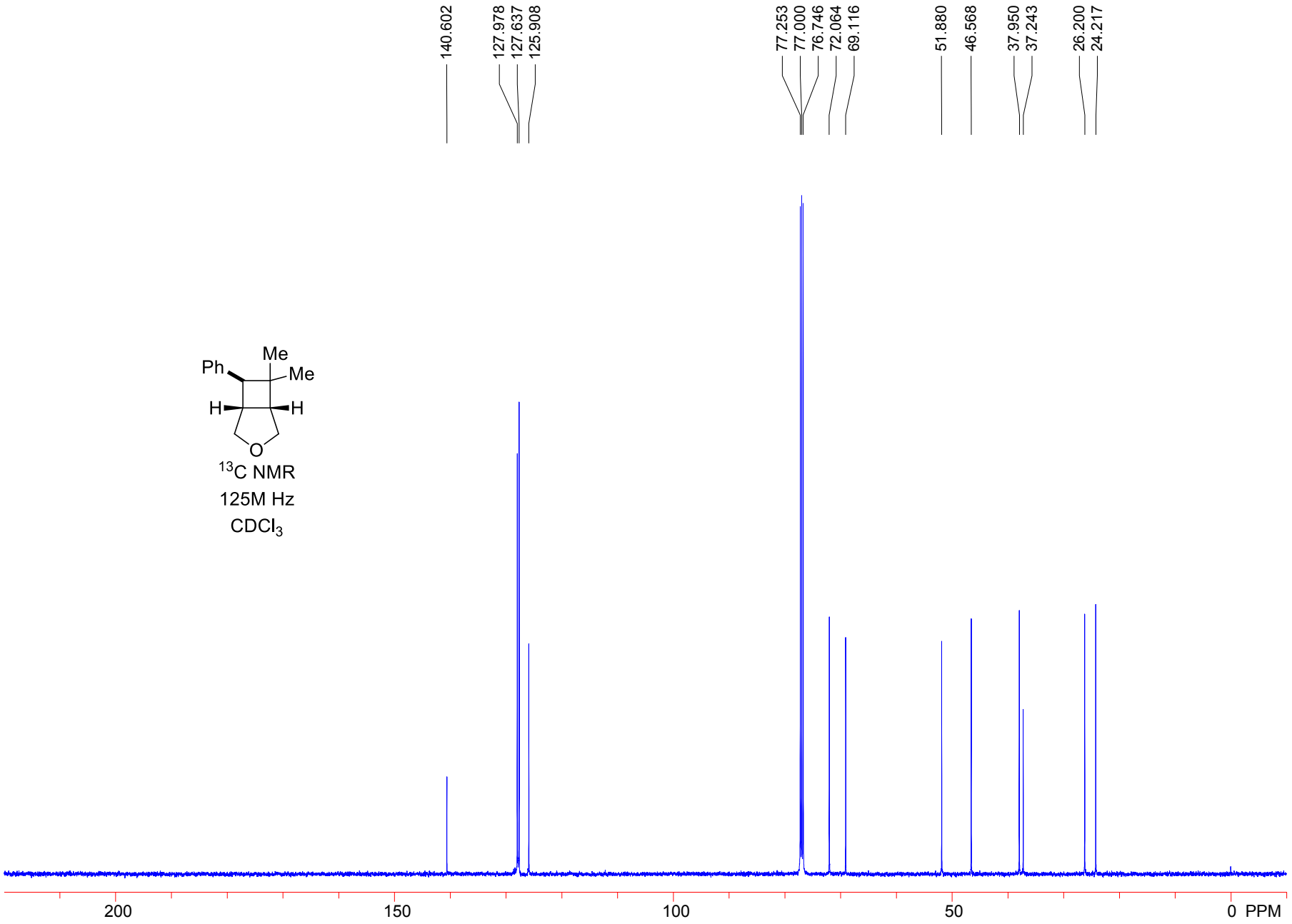
141.943
141.231
138.427
131.364
128.516
126.310
121.868
121.505
114.381
84.775
77.253
77.000
76.742
36.605
28.787
HO
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM


7.318
7.314
7.302
7.290
7.287
7.253
7.214
7.212
7.209
7.197
7.182
7.150
7.148
7.147
7.134
7.133
4.181
4.161
3.796
3.778
3.528
3.515
3.508
3.495
3.456
3.447
3.438
3.429
3.295
3.285
3.279
3.270
3.264
3.255
2.997
2.983
2.416
2.402
2.400
2.386
1.110
0.741
-0.000
Me
Ph
Me
H
H
O
1H NMR
500M Hz
CDCl3
2.02
1.98
1.02
1.00
1.00
1.01
1.01
1.00
0.99
1.00
2.89
2.85
8
6
4
2
0
PPM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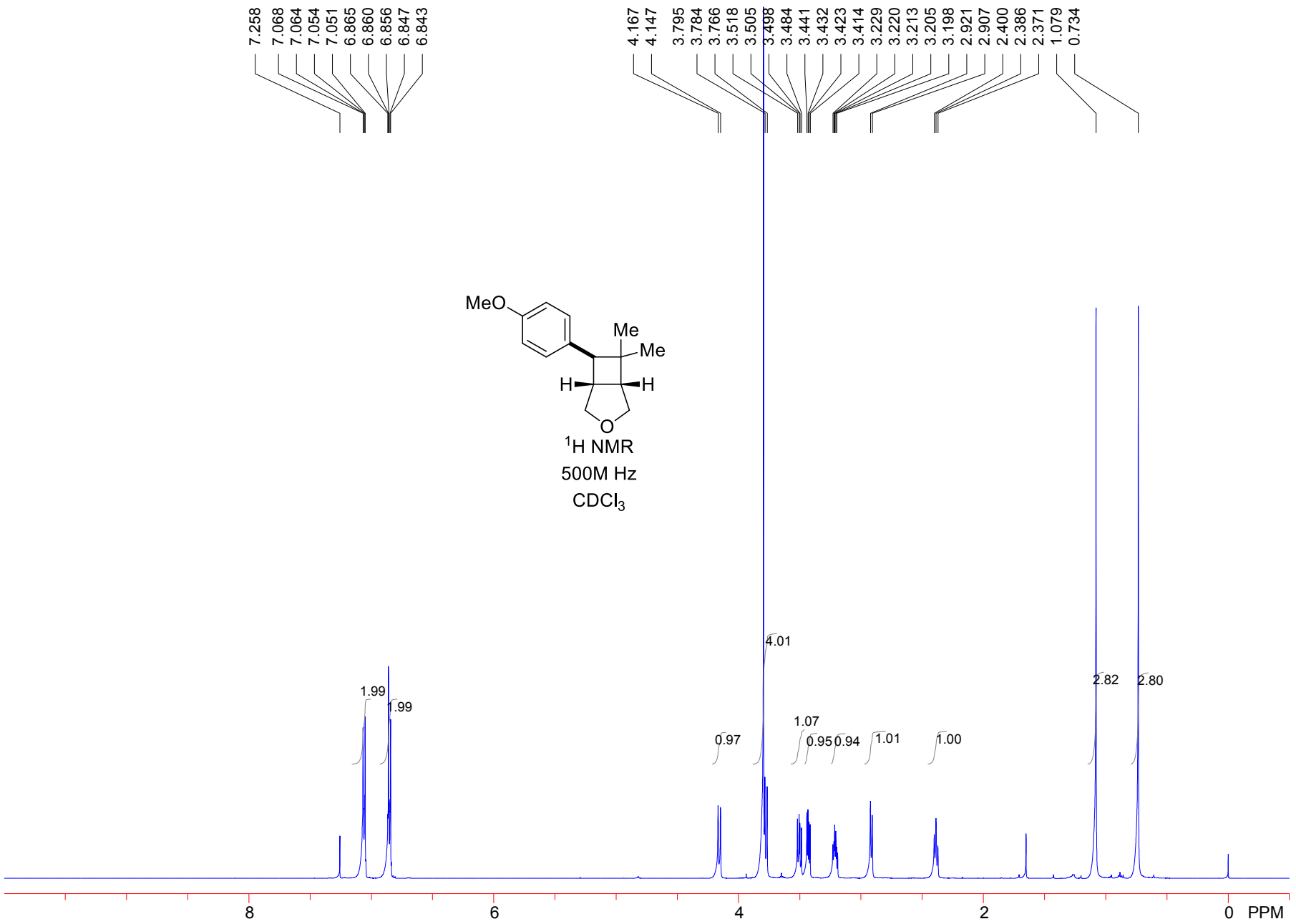
127.637
125.908
77.253
77.000
76.746
72.064
69.116
51.880
46.568
37.950
37.243
26.200
24.217
Ph
Me
Me
H
H
O
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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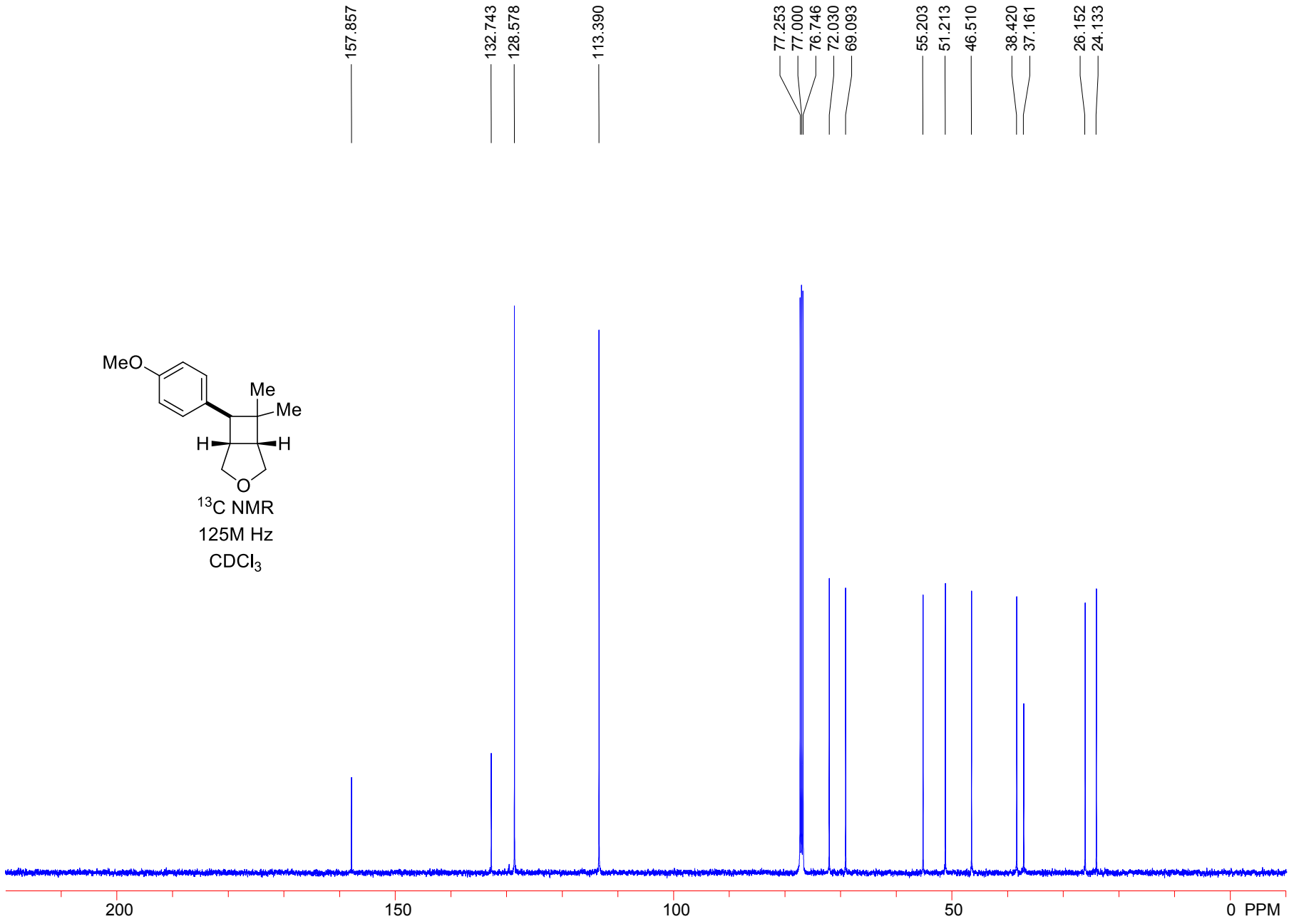
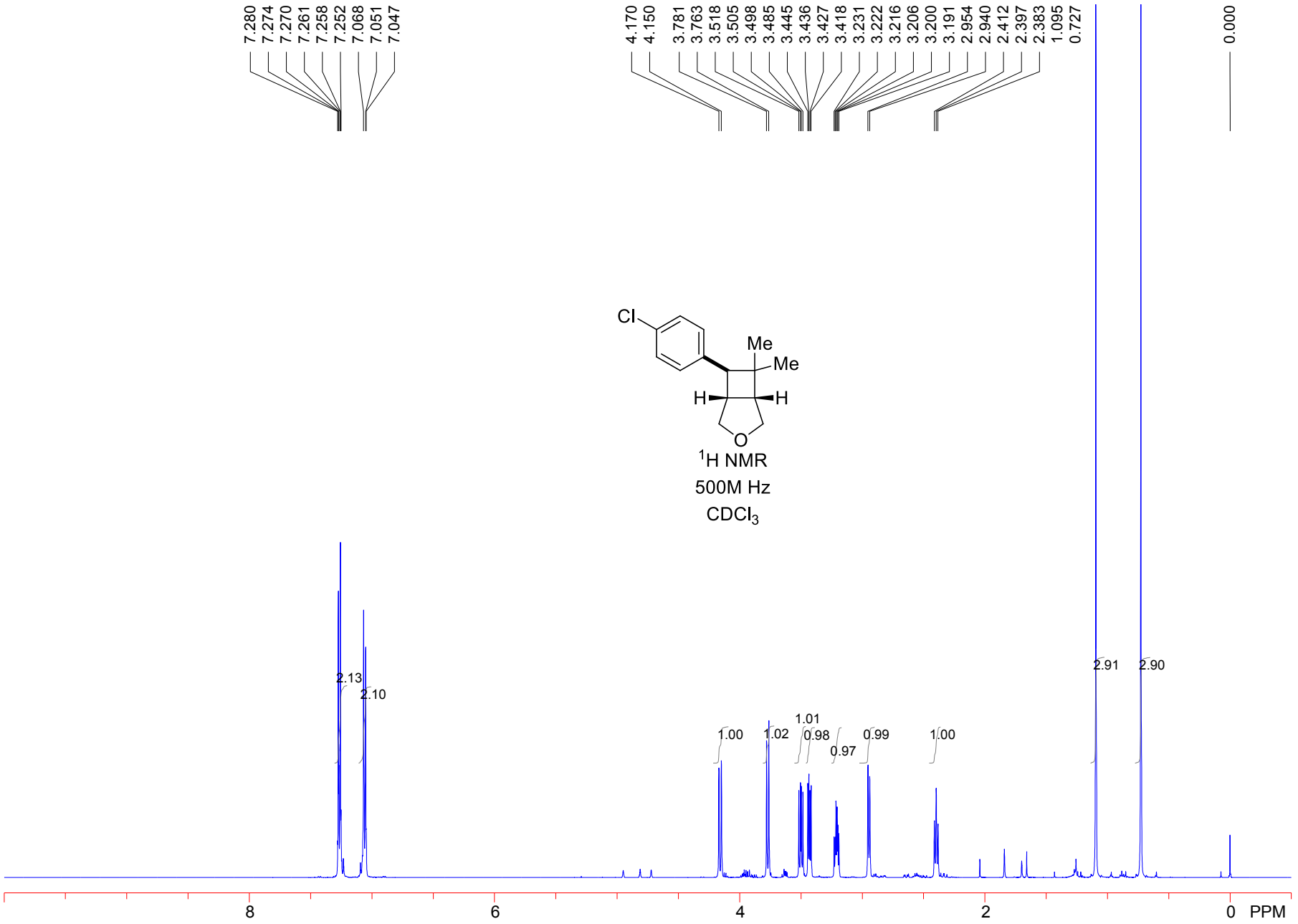
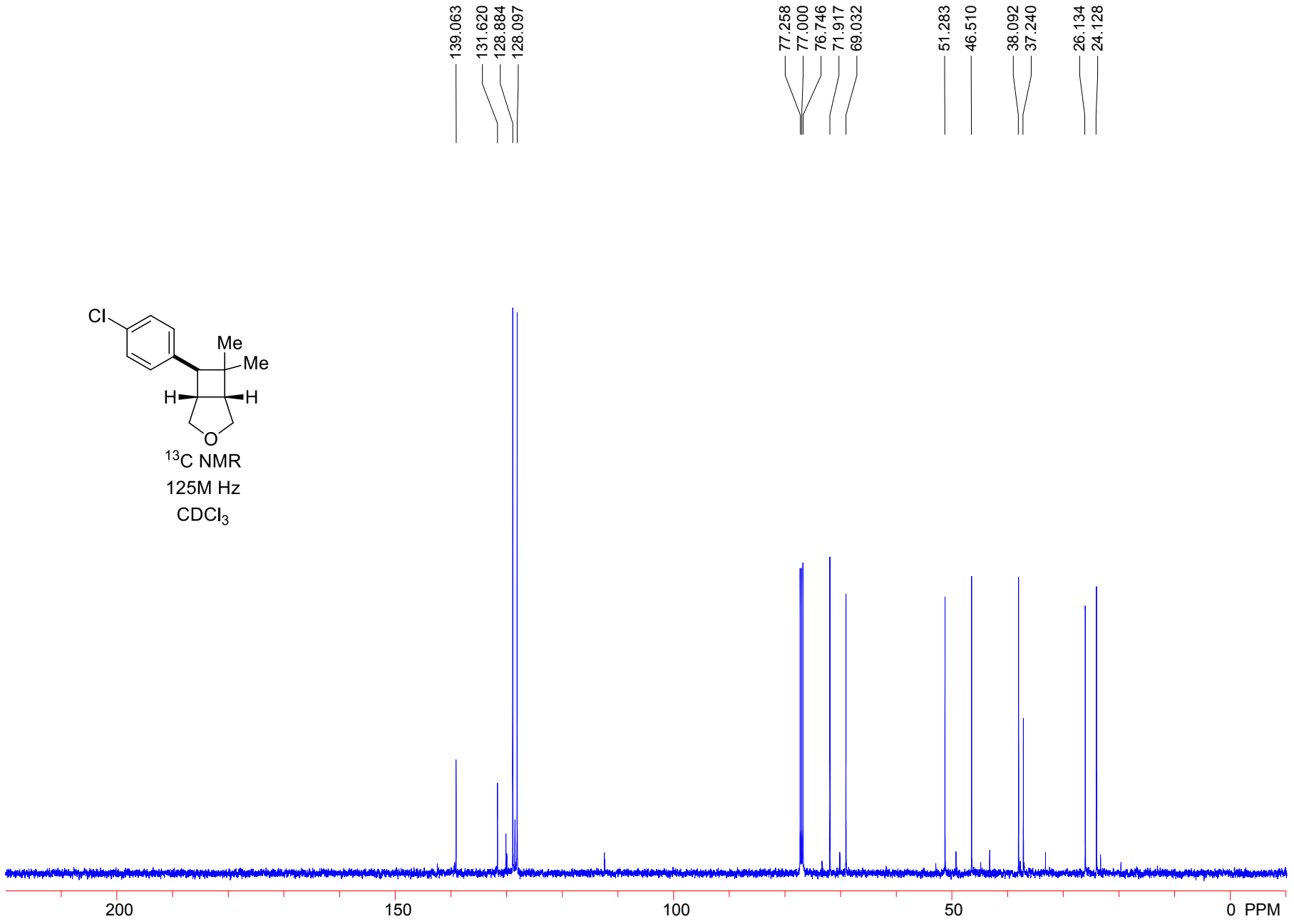
7.068
7.064
7.054
7.051
6.865
6.860
6.856
6.847
6.843
4.167
4.147
3.795
3.784
3.766
3.518
3.505
3.498
3.484
3.441
3.432
3.423
3.414
3.229
3.220
3.213
3.205
3.198
2.921
2.907
2.400
2.386
2.371
1.079
0.734
MeO
Me
Me
H
H
O
1H NMR
500M Hz
CDCl3
1.99
1.99
0.97
4.01
1.07
0.95
0.94
1.01
1.00
2.82
2.80
8
6
4
2
0
PPM


157.857
132.743
128.578
113.390
77.253
77.000
76.746
72.030
69.093
55.203
51.213
46.510
38.420
37.161
26.152
24.133
MeO
Me
Me
H
H
O
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM


7.280
7.274
7.270
7.261
7.258
7.252
7.068
7.051
7.047
4.170
4.150
3.781
3.763
3.518
3.505
3.498
3.485
3.445
3.436
3.427
3.418
3.231
3.222
3.216
3.206
3.200
3.191
2.954
2.940
2.412
2.397
2.383
1.095
0.727
0.000
Cl
Me
Me
H
H
O
1H NMR
500M Hz
CDCl3
2.13
2.10
1.00
1.02
1.01
0.98
0.97
0.99
1.00
2.91
2.90
8
6
4
2
0
PPM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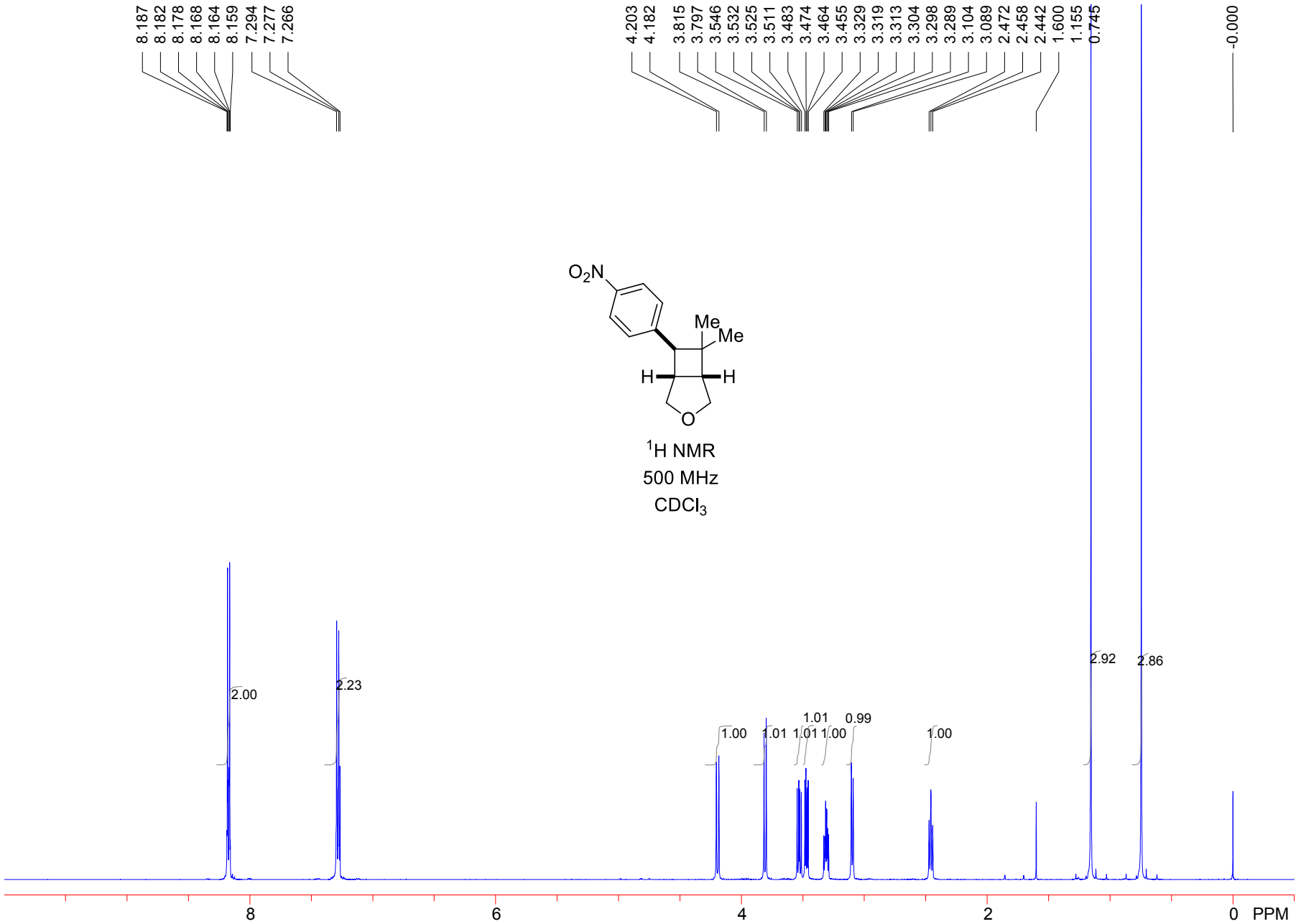
131.620
128.884
128.097
77.258
77.000
76.746
71.917
69.032
51.283
46.510
38.092
37.240
26.134
24.128
Cl
Me
Me
H
H
O
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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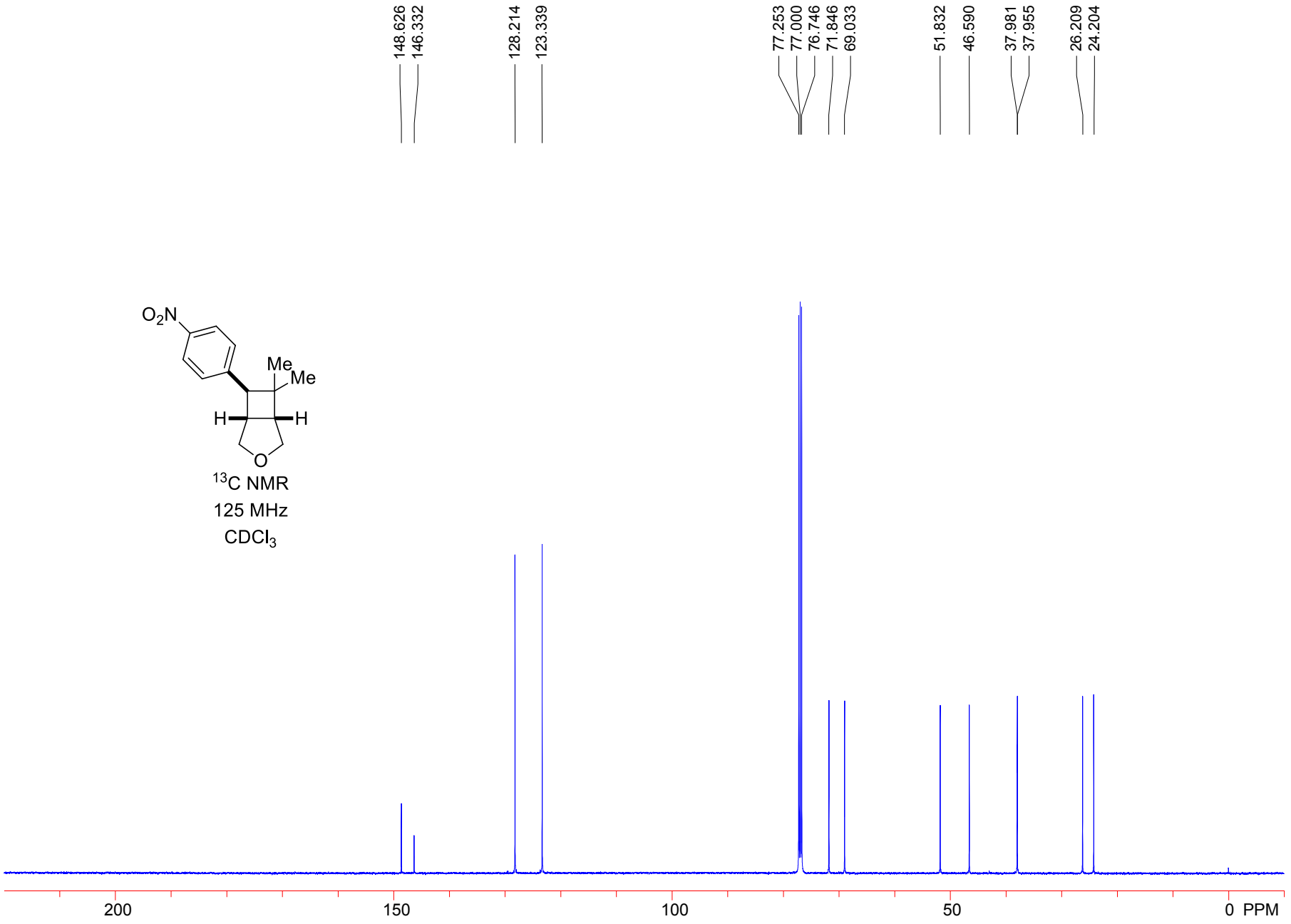
8.182
8.178
8.168
8.164
8.159
7.294
7.277
7.266
4.203
4.182
3.815
3.797
3.546
3.532
3.525
3.511
3.483
3.474
3.464
3.455
3.329
3.319
3.313
3.304
3.298
3.289
3.104
3.089
2.472
2.458
2.442
1.600
1.155
0.745
-0.000
O2N
Me
Me
H
H
O
1H NMR
500 MHz
CDCl3
2.00
2.23
1.00
1.01
1.01
1.01
1.00
0.99
1.00
2.92
2.86
8
6
4
2
0
PPM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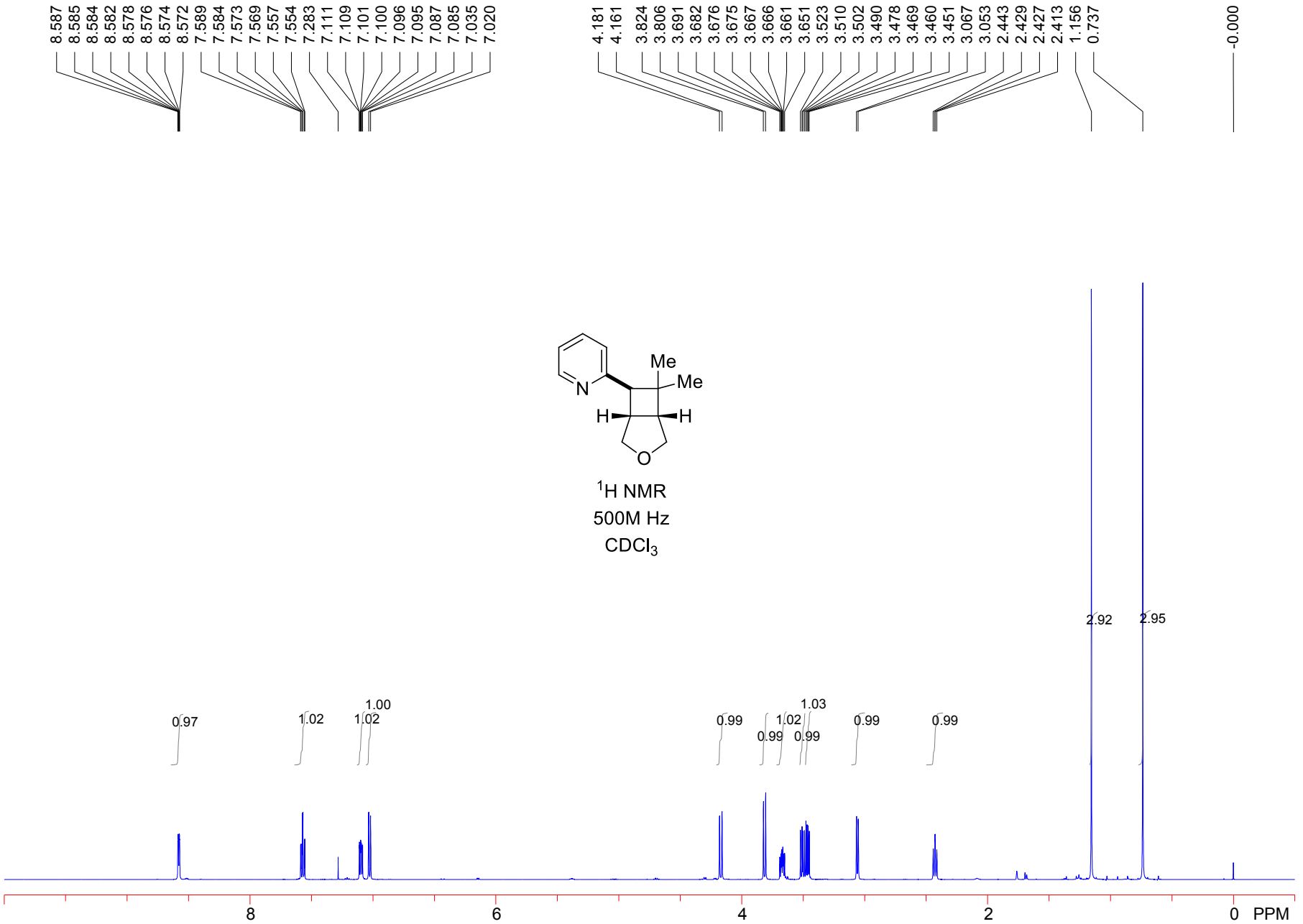
146.332
128.214
123.339
77.253
77.000
76.746
71.846
69.033
51.832
46.590
37.981
37.955
26.209
24.204
O2N
Me
Me
H
H
O
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM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8.585
8.584
8.582
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8.576
8.574
8.572
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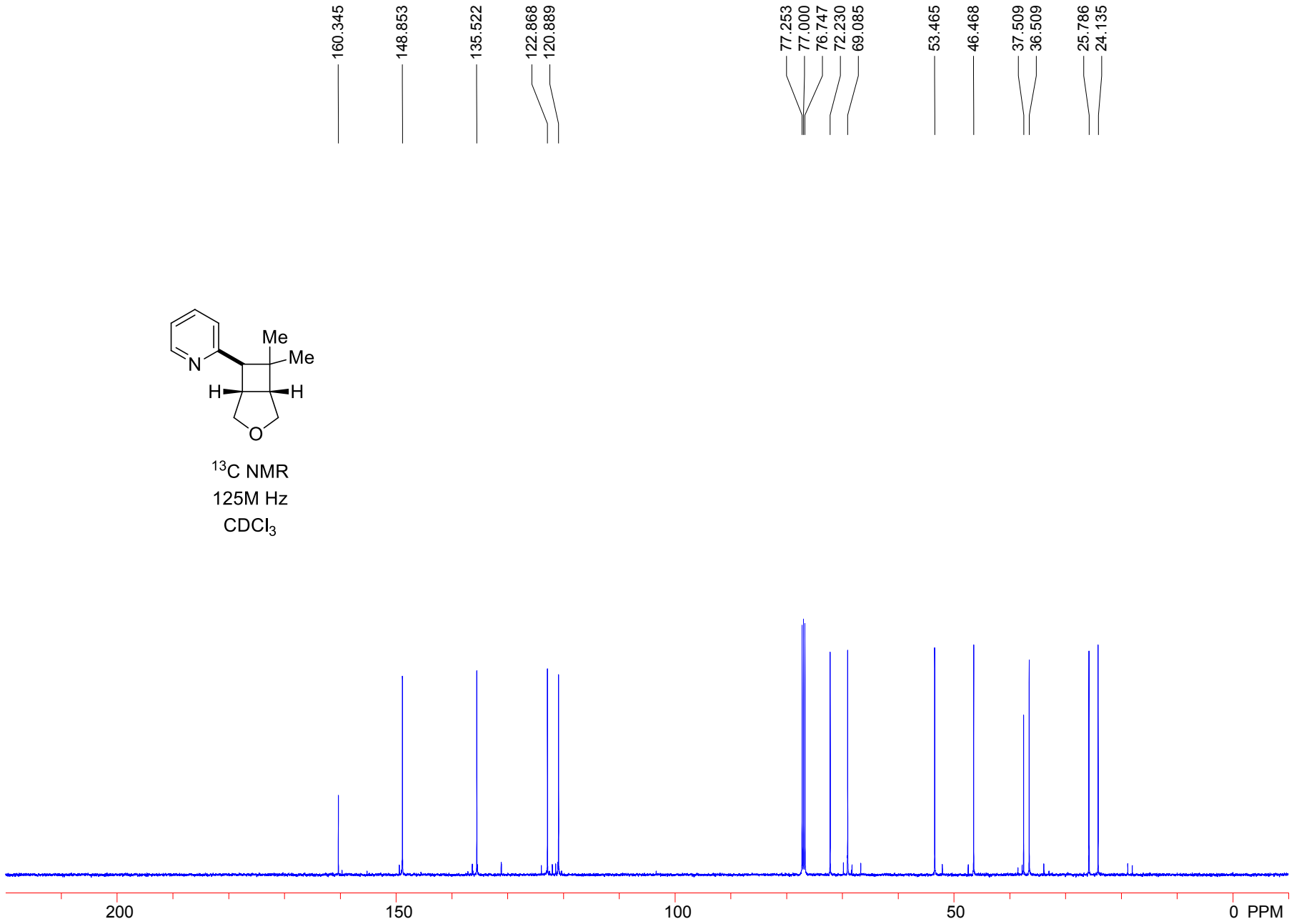
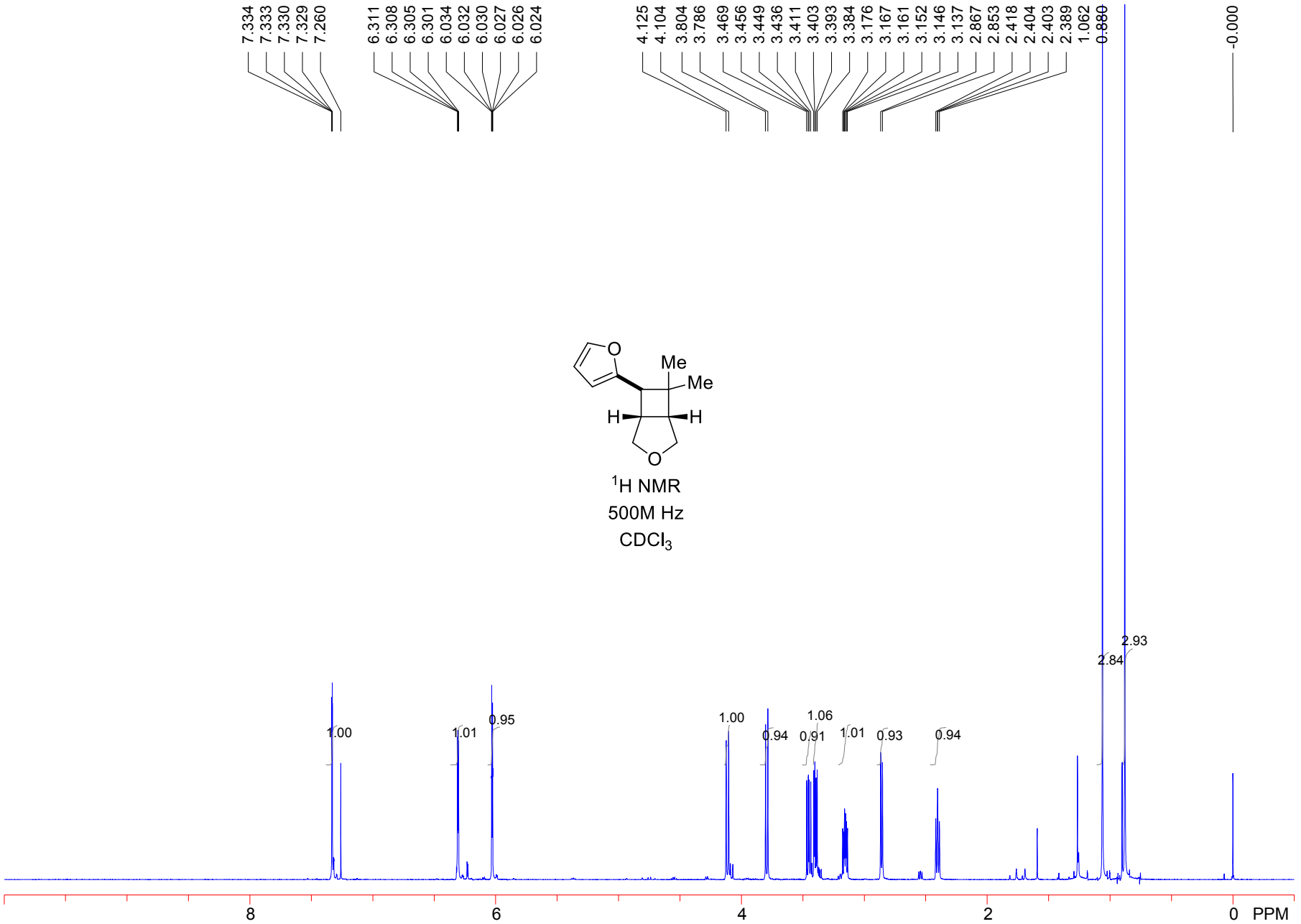
7.573
7.569
7.557
7.554
7.283
7.111
7.109
7.101
7.100
7.096
7.095
7.087
7.085
7.035
7.020
4.181
4.161
3.824
3.806
3.691
3.682
3.676
3.675
3.667
3.666
3.661
3.651
3.523
3.510
3.502
3.490
3.478
3.469
3.460
3.451
3.067
3.053
2.443
2.429
2.427
2.413
1.156
0.737
-0.000
Me
Me
N
H
H
O
1H NMR
500M Hz
CDCl3
0.97
1.02
1.02
1.00
0.99
0.99
1.02
0.99
1.03
0.99
0.99
2.92
2.95
8
6
4
2
0
PPM



^{13}C NMR

125M Hz

$CDCl_3$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7.333
7.330
7.329
7.260
6.311
6.308
6.305
6.301
6.034
6.032
6.030
6.027
6.026
6.024
4.125
4.104
3.804
3.786
3.469
3.456
3.449
3.436
3.411
3.403
3.393
3.384
3.176
3.167
3.161
3.152
3.146
3.137
2.867
2.853
2.418
2.404
2.403
2.389
1.062
0.880
-0.000
O
Me
Me
H
H
O
1H NMR
500M Hz
CDCl3
1.00
1.01
0.95
1.00
0.94
1.06
0.91
1.01
0.93
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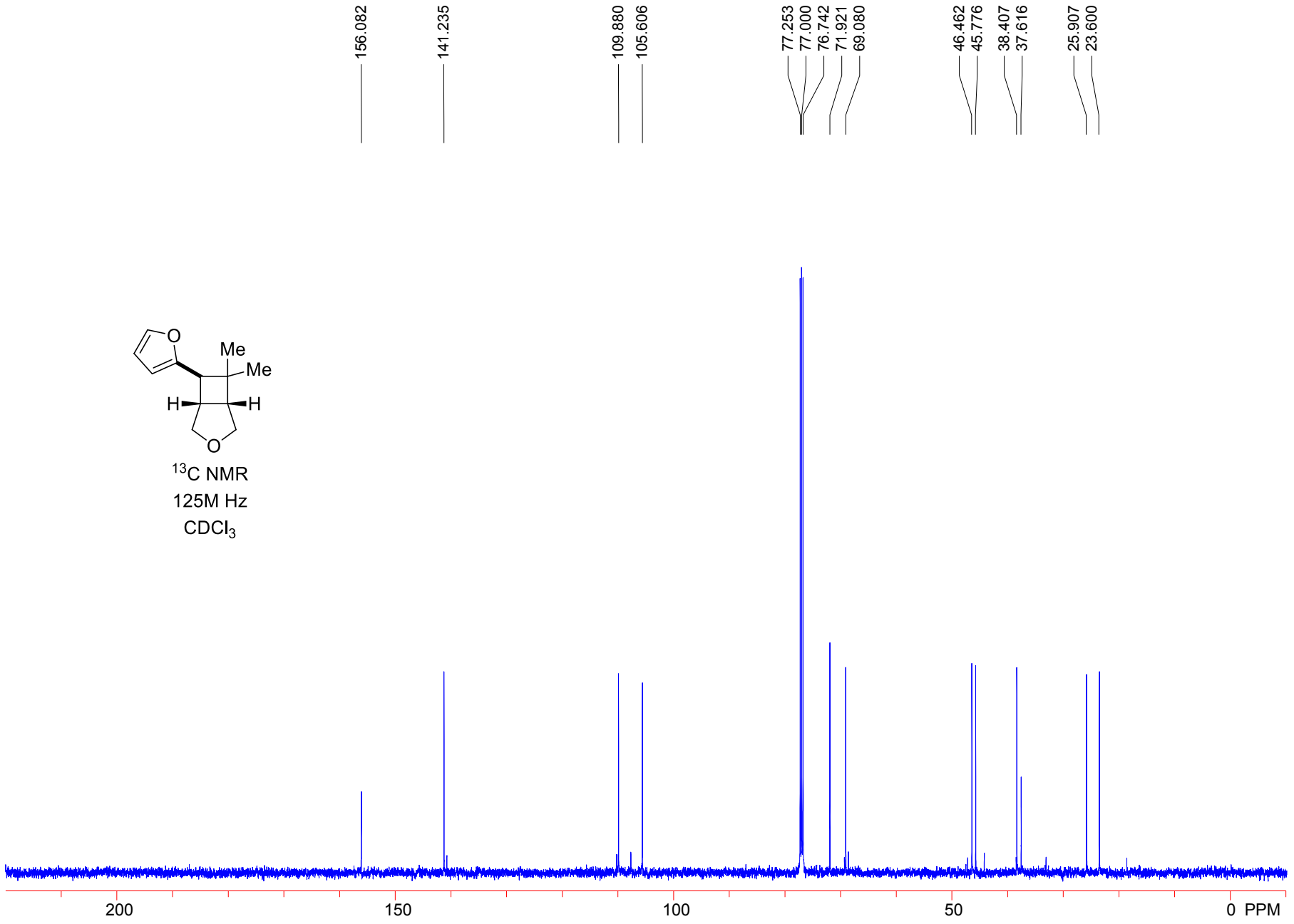
2.84
2.93
8
6
4
2
0
PPM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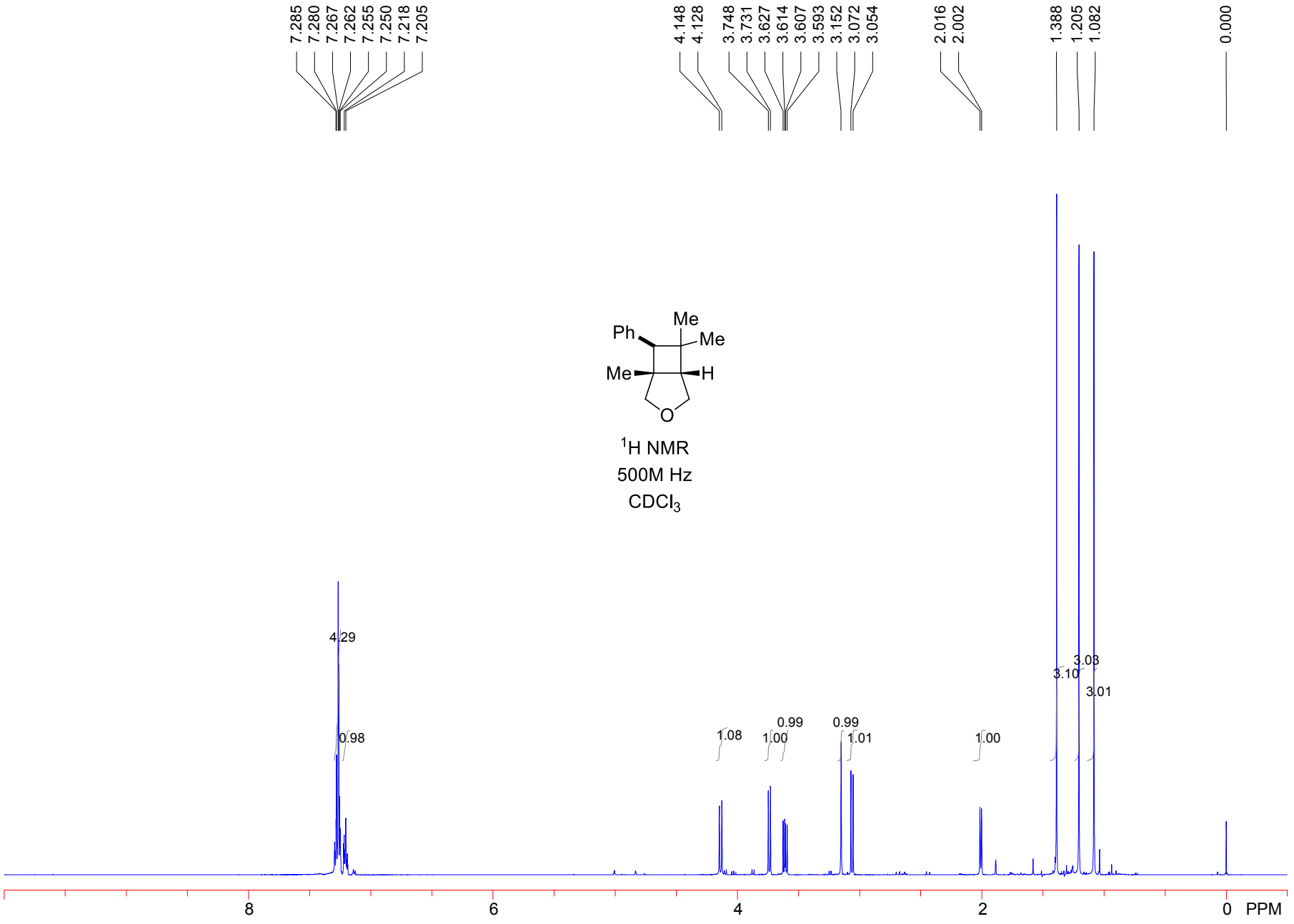
141.235
109.880
105.606
77.253
77.000
76.742
71.921
69.080
46.462
45.776
38.407
37.616
25.907
23.600
O
Me
Me
H
H
O
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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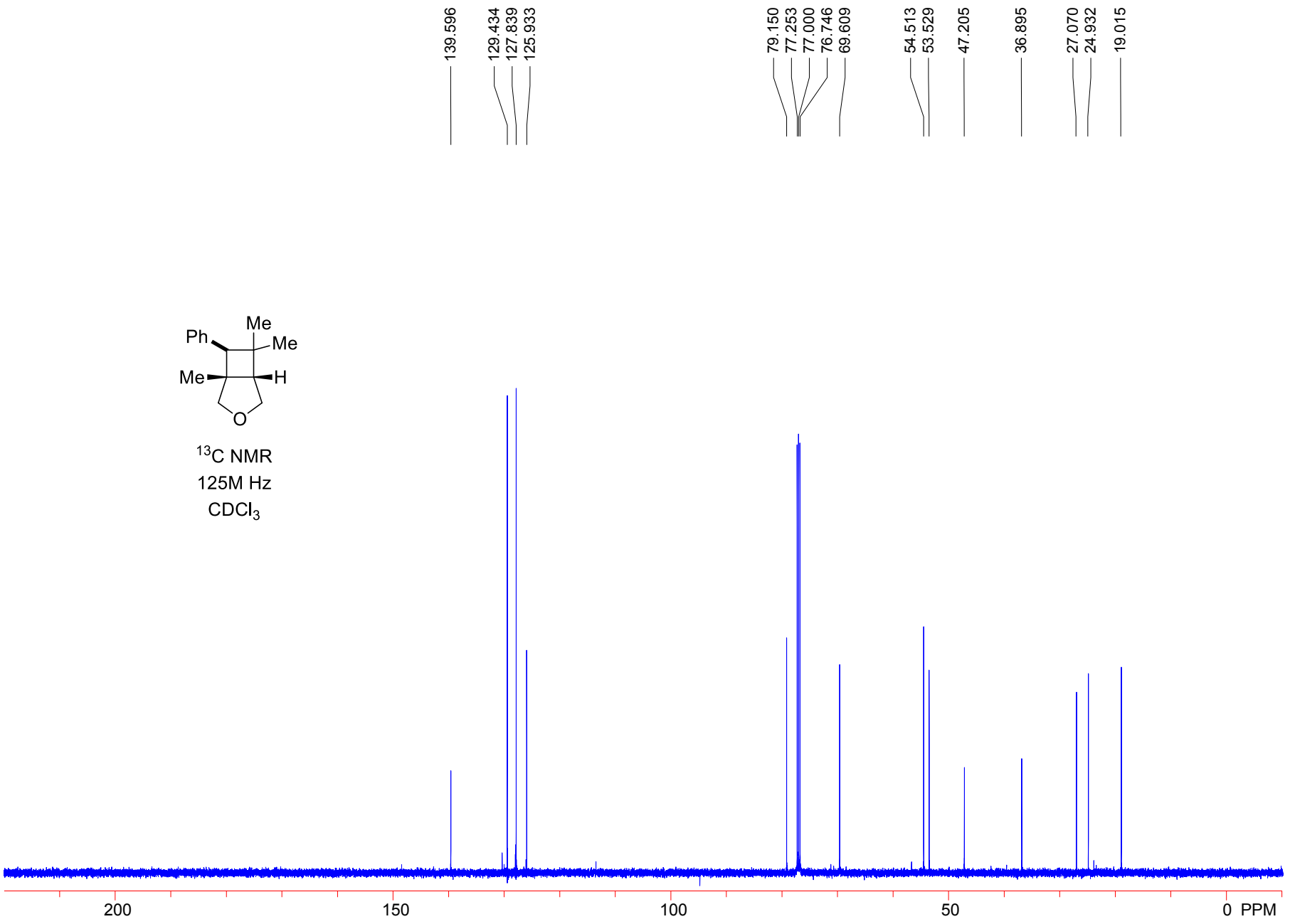
7.280
7.267
7.262
7.255
7.250
7.218
7.205
4.148
4.128
3.748
3.731
3.627
3.614
3.607
3.593
3.152
3.072
3.054
2.016
2.002
1.388
1.205
1.082
0.000
Me
Ph
Me
Me
H
O
1H NMR
500M Hz
CDCl3
4.29
0.98
1.08
1.00
0.99
0.99
1.01
1.00
3.10
3.03
3.01
8
6
4
2
0
PPM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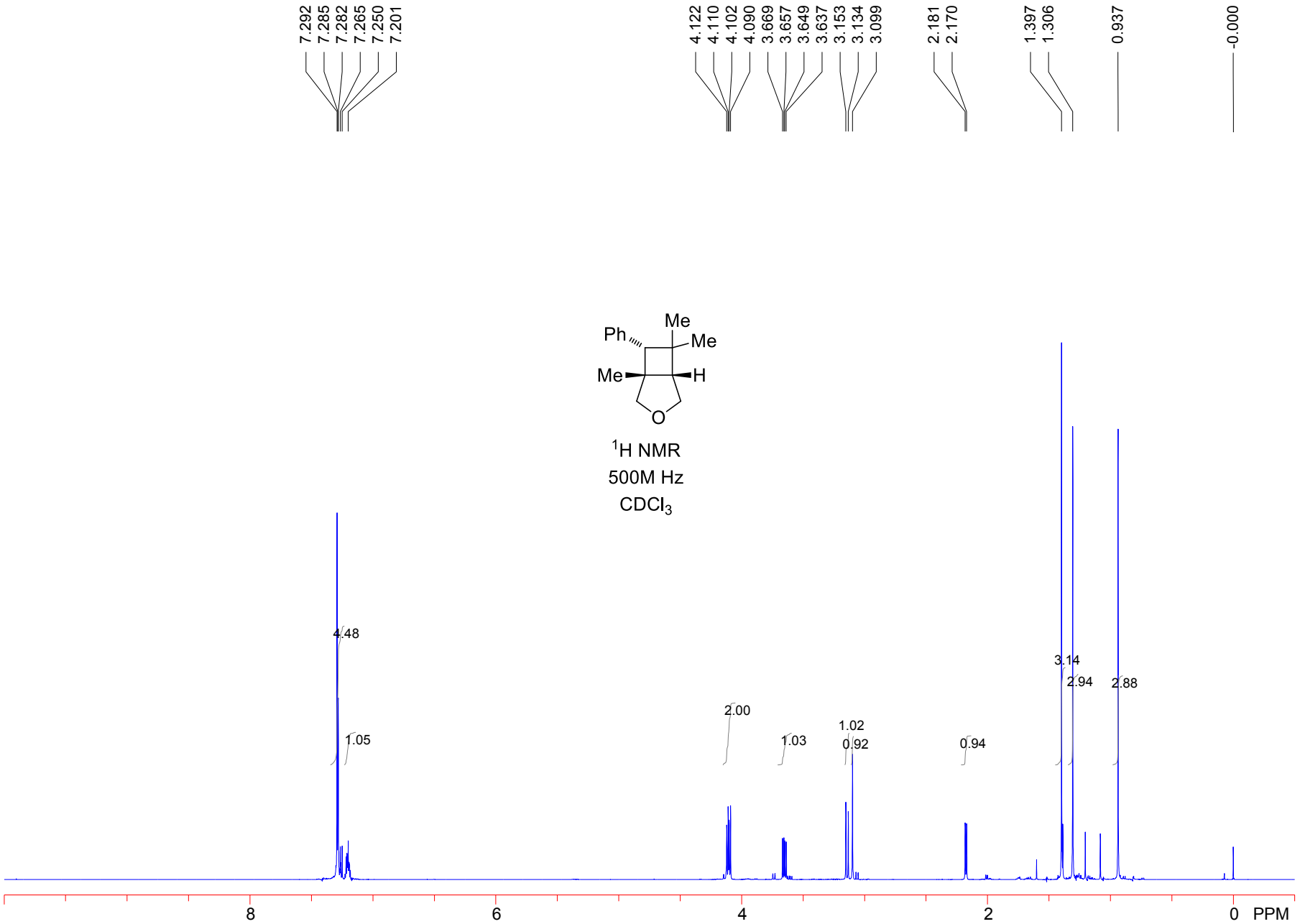
129.434
127.839
125.933
79.150
77.253
77.000
76.746
69.609
54.513
53.529
47.205
36.895
27.070
24.932
19.015
Me
Ph
Me
Me
H
O
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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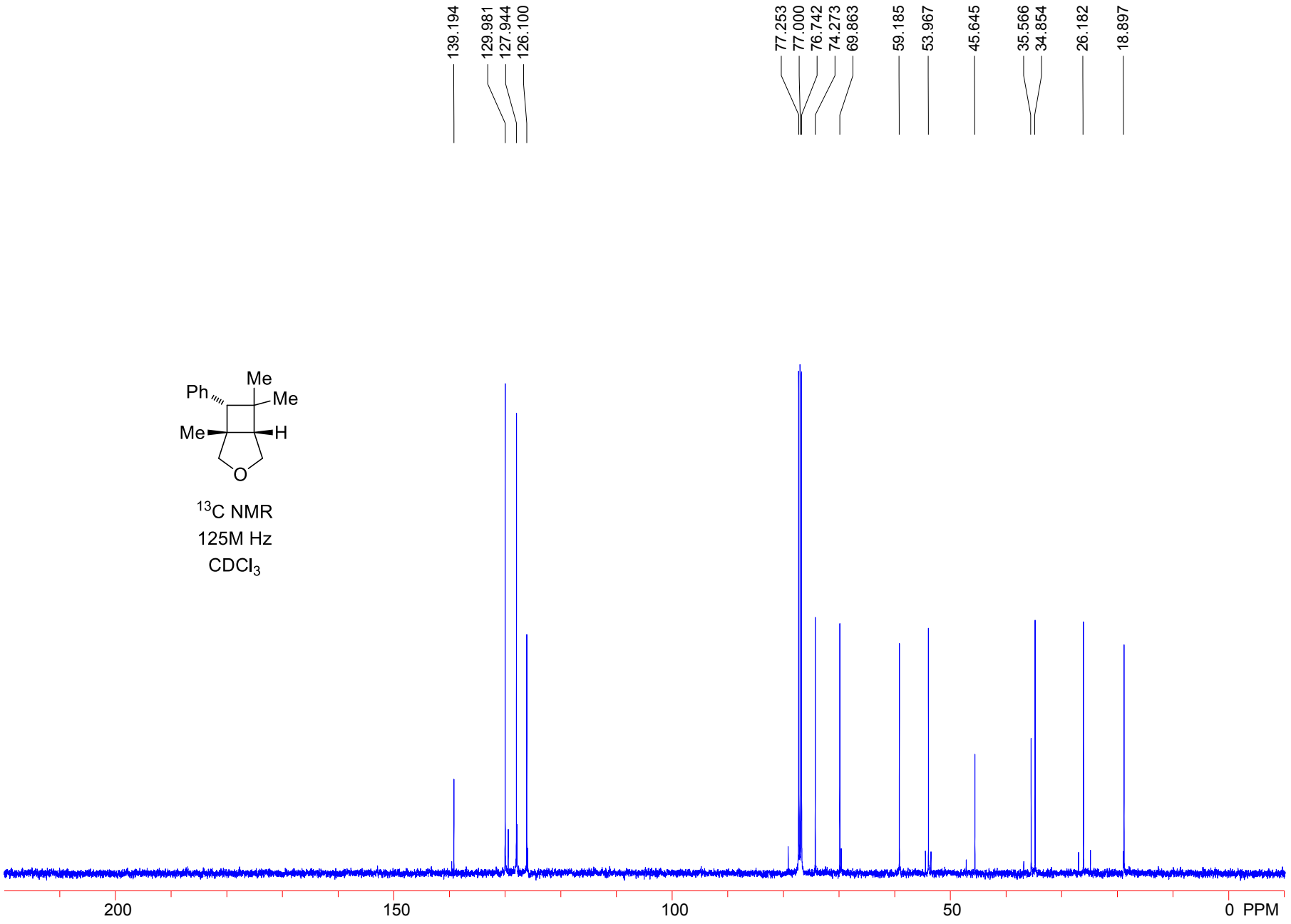
7.285
7.282
7.265
7.250
7.201
4.122
4.110
4.102
4.090
3.669
3.657
3.649
3.637
3.153
3.134
3.099
2.181
2.170
1.397
1.306
0.937
-0.000
Me
Ph
Me
Me
H
O
1H NMR
500M Hz
CDCl3
4.48
1.05
2.00
1.03
1.02
0.92
0.94
3.14
2.94
2.88
8
6
4
2
0
PPM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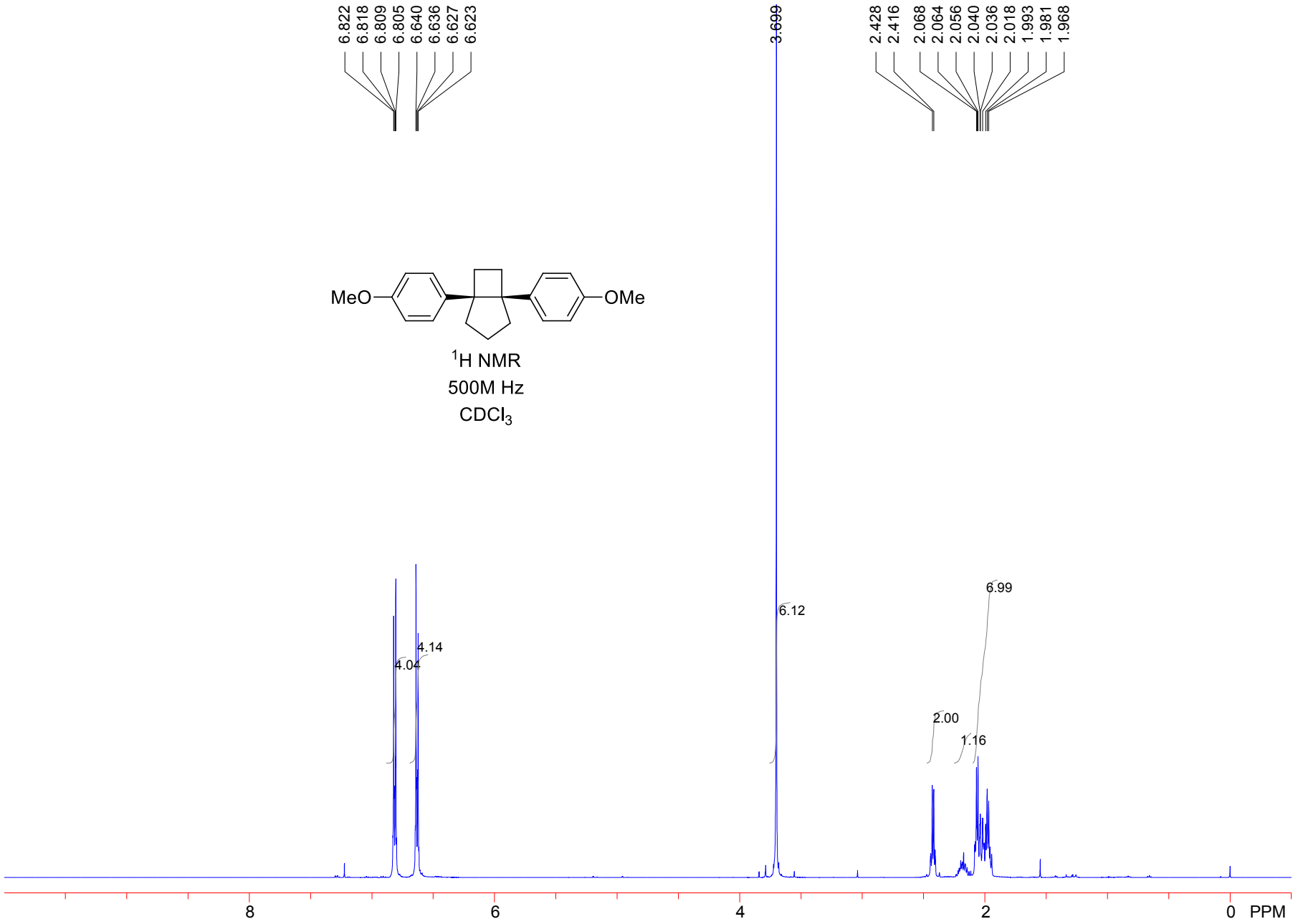
129.981
127.944
126.100
77.253
77.000
76.742
74.273
69.863
59.185
53.967
45.645
35.566
34.854
26.182
18.897
Ph
Me
Me
Me
H
O
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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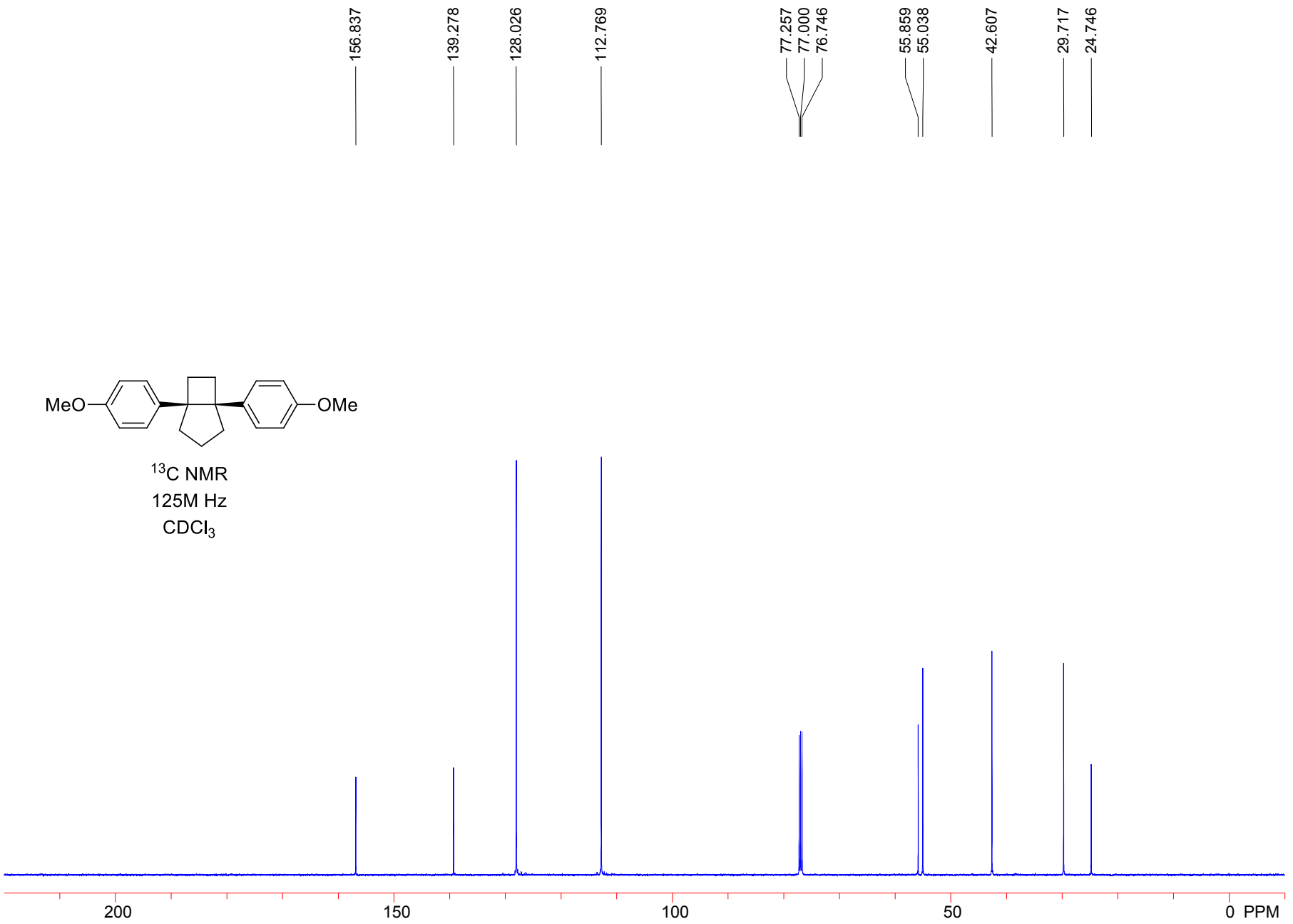
6.818
6.809
6.805
6.640
6.636
6.627
6.623
3.699
2.428
2.416
2.068
2.064
2.056
2.040
2.036
2.018
1.993
1.981
1.968
MeO
OMe
1H NMR
500M Hz
CDCl3
4.04
4.14
6.12
2.00
1.16
6.99
8
6
4
2
0
PPM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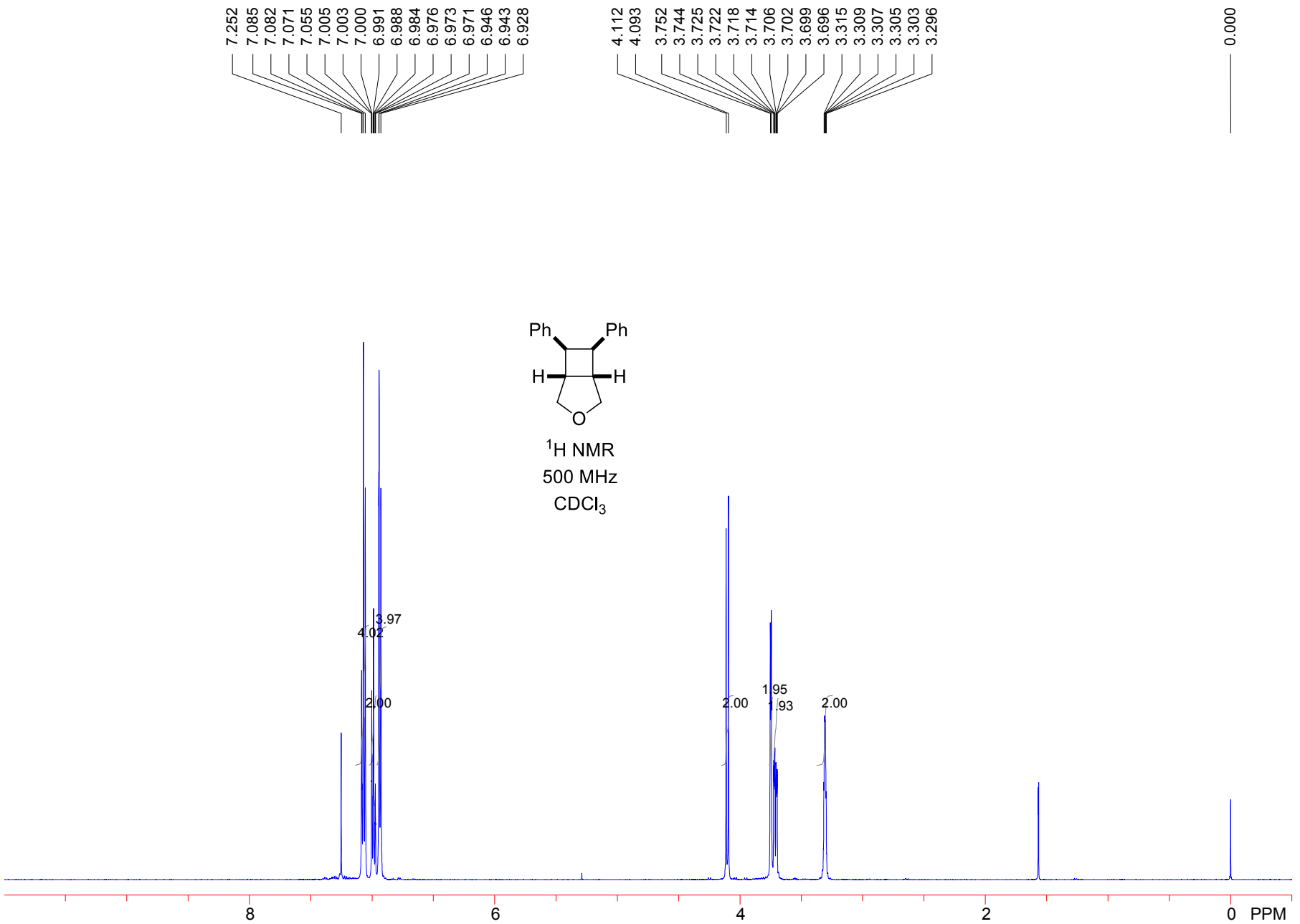
128.026
112.769
77.257
77.000
76.746
55.859
55.038
42.607
29.717
24.746
MeO
OMe
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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7.085
7.082
7.071
7.055
7.005
7.003
7.000
6.991
6.988
6.984
6.976
6.973
6.971
6.946
6.943
6.928
4.112
4.093
3.752
3.744
3.725
3.722
3.718
3.714
3.706
3.702
3.699
3.696
3.315
3.309
3.307
3.305
3.303
3.296
0.000
Ph
Ph
H
H
O
1H NMR
500 MHz
CDCl3
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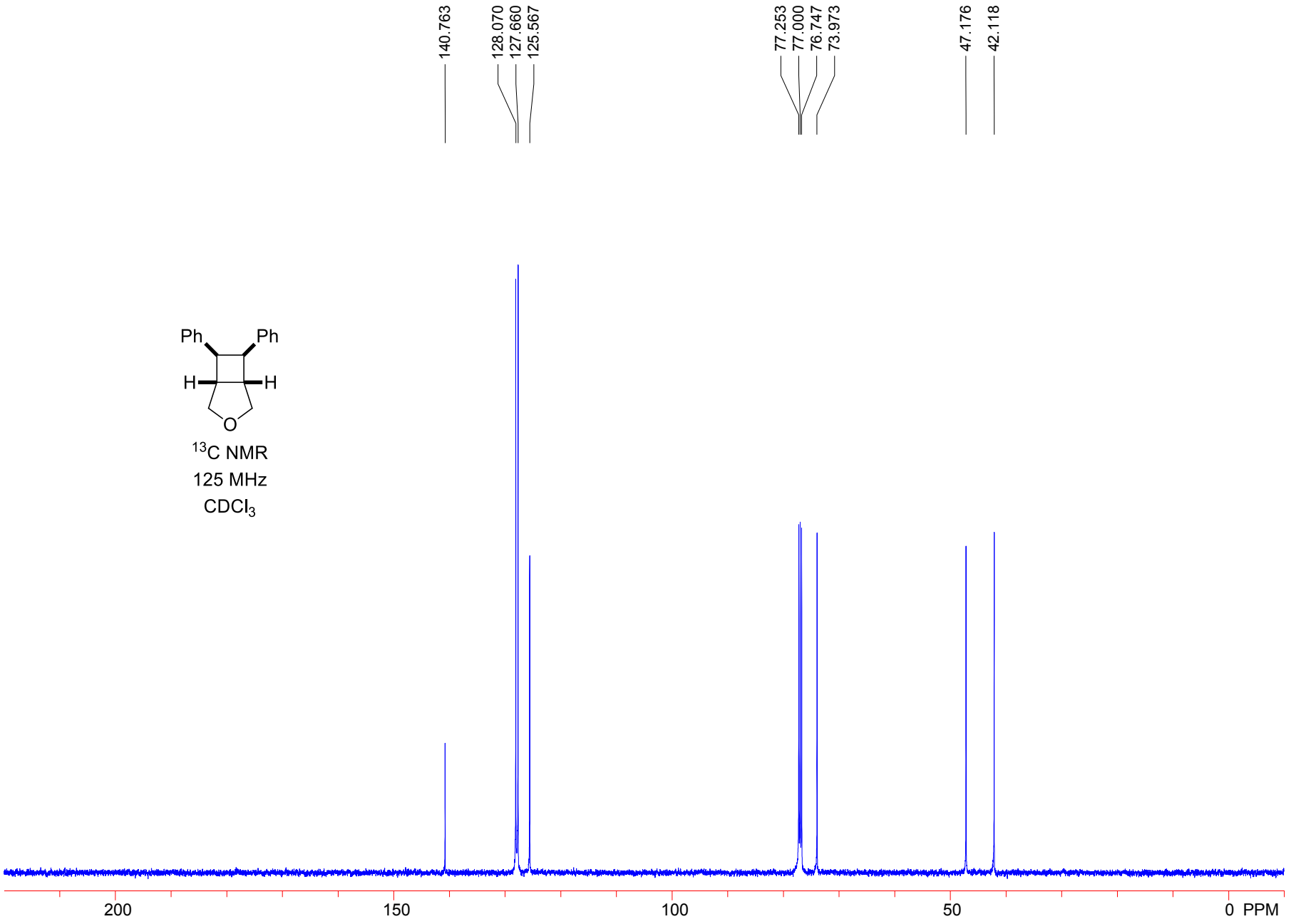
4.02
2.00
2.00
1.95
1.93
2.00
8
6
4
2
0
PPM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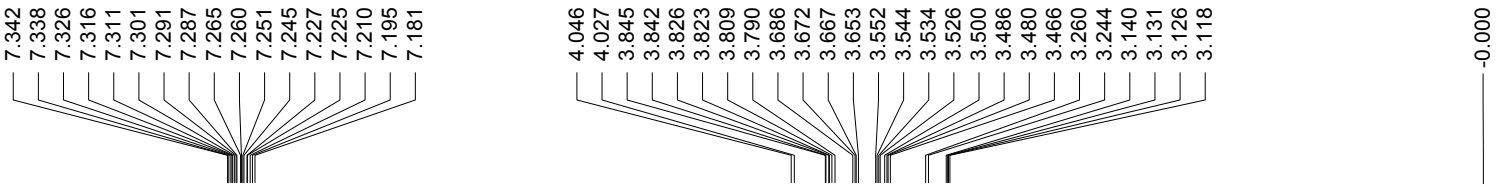
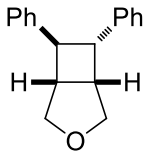
127.660
125.567
77.253
77.000
76.747
73.973
47.176
42.118
Ph
Ph
H
H
O
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM

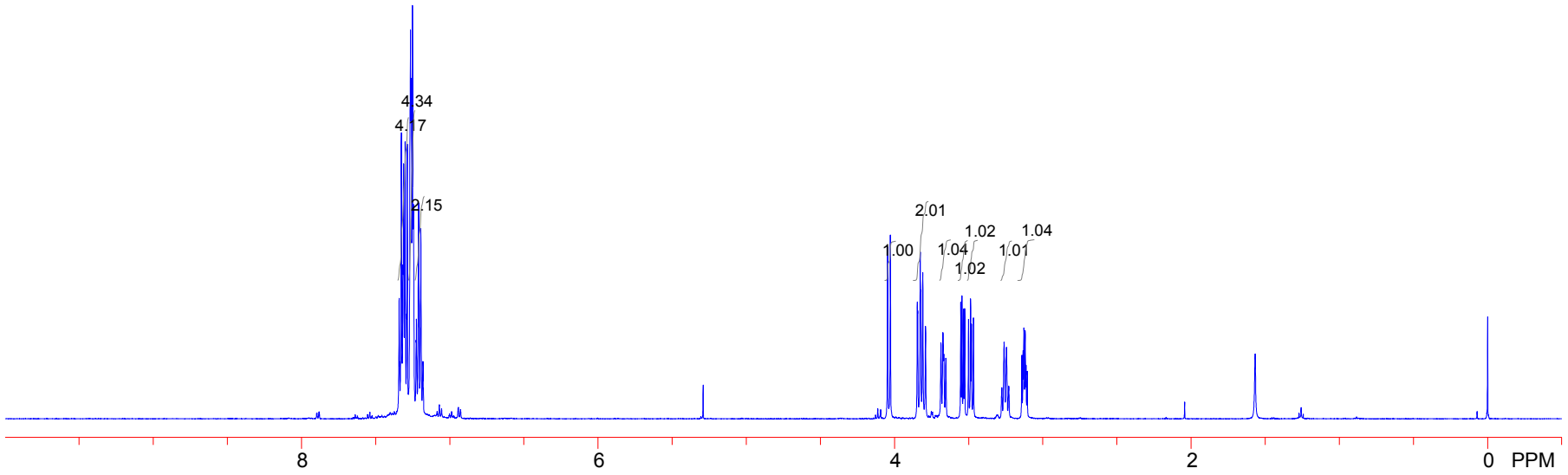


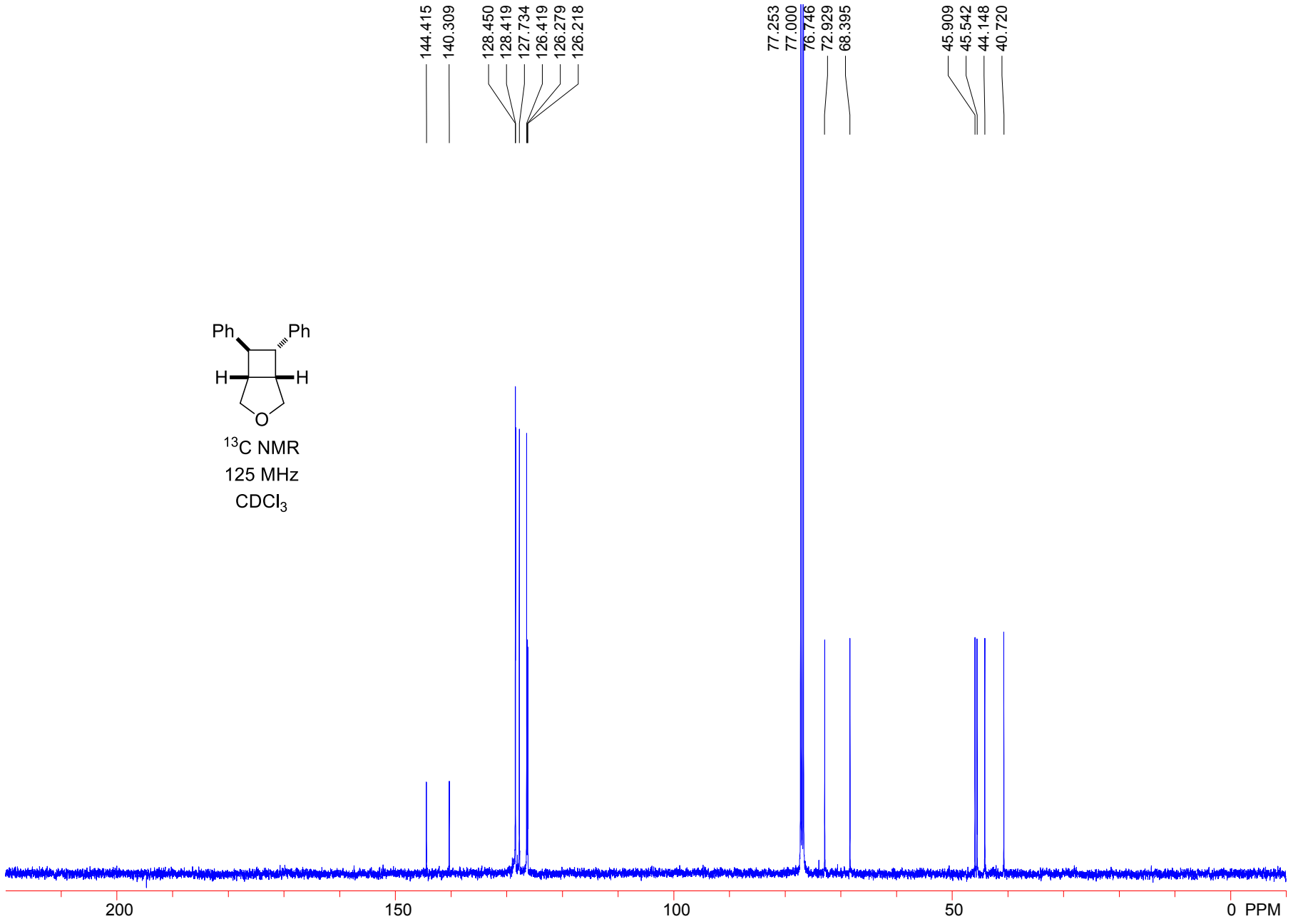


^{1}H NMR

500 MHz

$CDCl_3$

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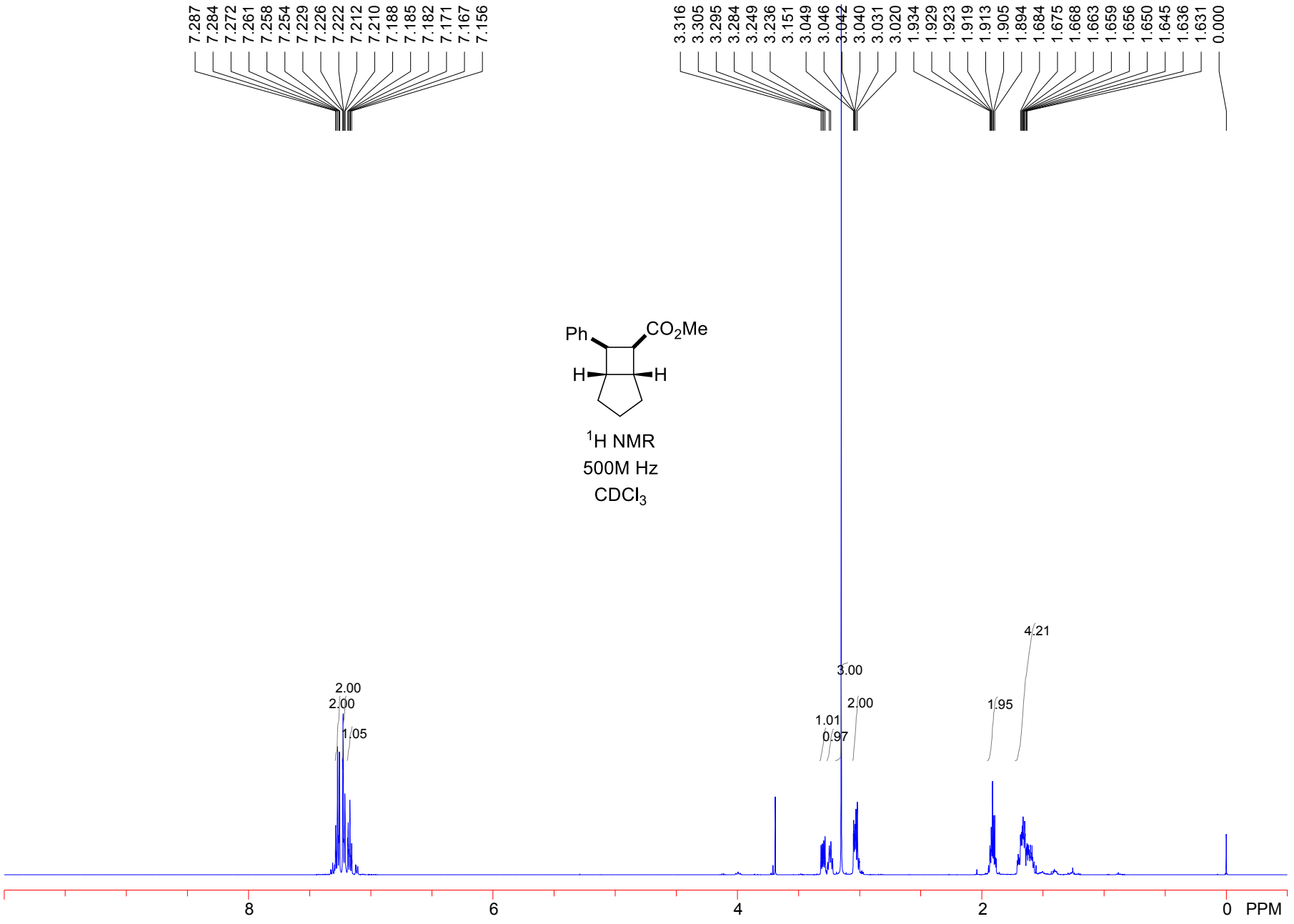
128.419
127.734
126.419
126.279
126.218
77.253
77.000
76.746
72.929
68.395
45.909
45.542
44.148
40.720
Ph
Ph
H
H
O
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM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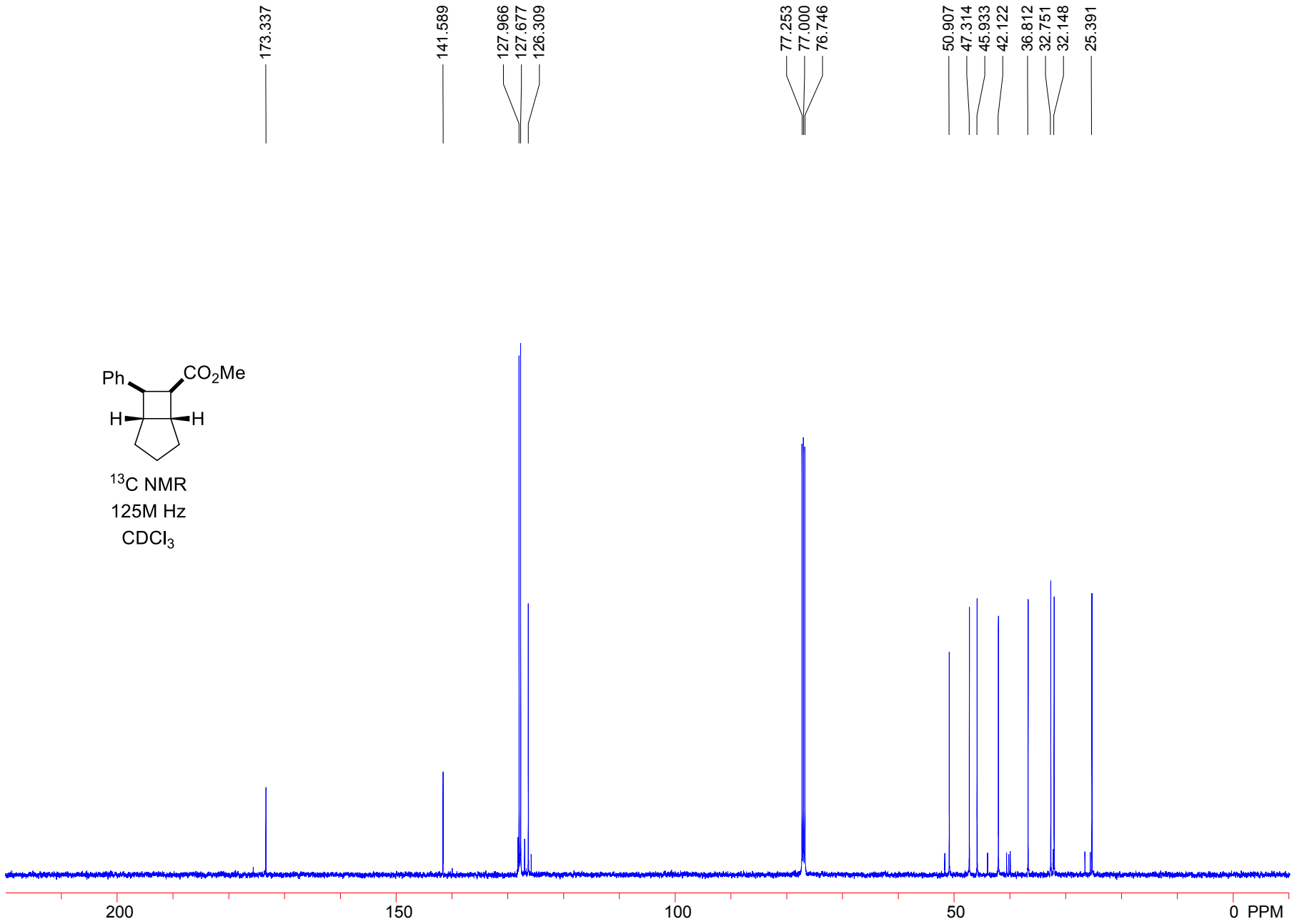
7.272
7.261
7.258
7.254
7.229
7.226
7.222
7.212
7.210
7.188
7.185
7.182
7.171
7.167
7.156
3.316
3.305
3.295
3.284
3.249
3.236
3.151
3.049
3.046
3.042
3.040
3.031
3.020
1.934
1.929
1.923
1.919
1.913
1.905
1.894
1.684
1.675
1.668
1.663
1.659
1.656
1.650
1.645
1.636
1.631
0.000
Ph
CO2Me
H
H
1H NMR
500M Hz
CDCl3
2.00
2.00
1.05
3.00
2.00
1.01
0.97
1.95
4.21
8
6
4
2
0
PPM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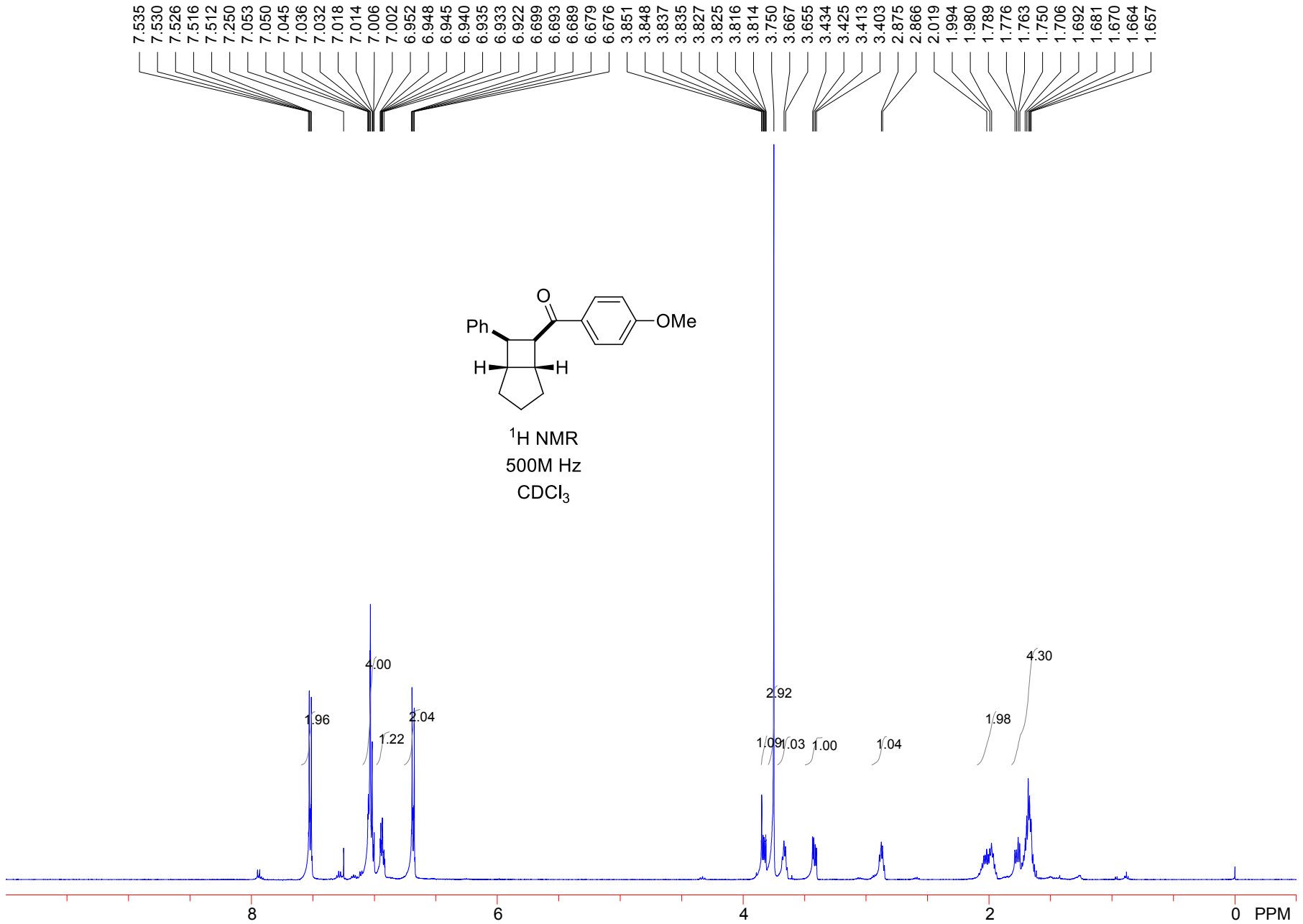
77.000
76.746
50.907
47.314
45.933
42.122
36.812
32.751
32.148
25.391
Ph
CO2Me
H
H
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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7.250
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7.050
7.045
7.036
7.032
7.018
7.014
7.006
7.002
6.952
6.948
6.945
6.940
6.935
6.933
6.922
6.699
6.693
6.689
6.679
6.676
3.851
3.848
3.837
3.835
3.827
3.825
3.816
3.814
3.750
3.667
3.655
3.434
3.425
3.413
3.403
2.875
2.866
2.019
1.994
1.980
1.789
1.776
1.763
1.750
1.706
1.692
1.681
1.670
1.664
1.657
O
Ph
OMe
H
H
1H NMR
500M Hz
CDCl3
4.00
1.96
1.22
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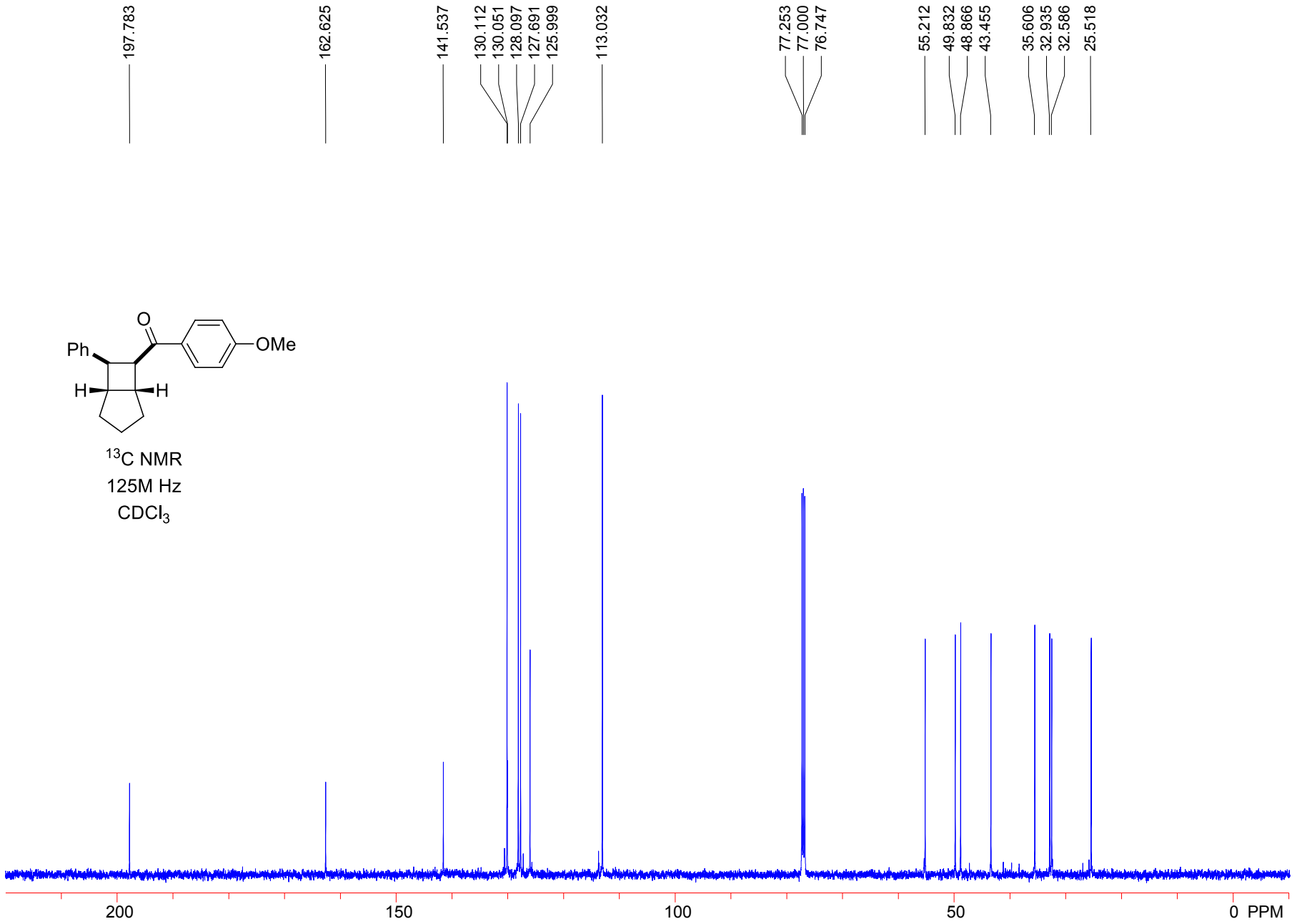
2.92
1.09
1.03
1.00
1.04
1.98
4.30
8
6
4
2
0
PPM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128.097
127.691
125.999
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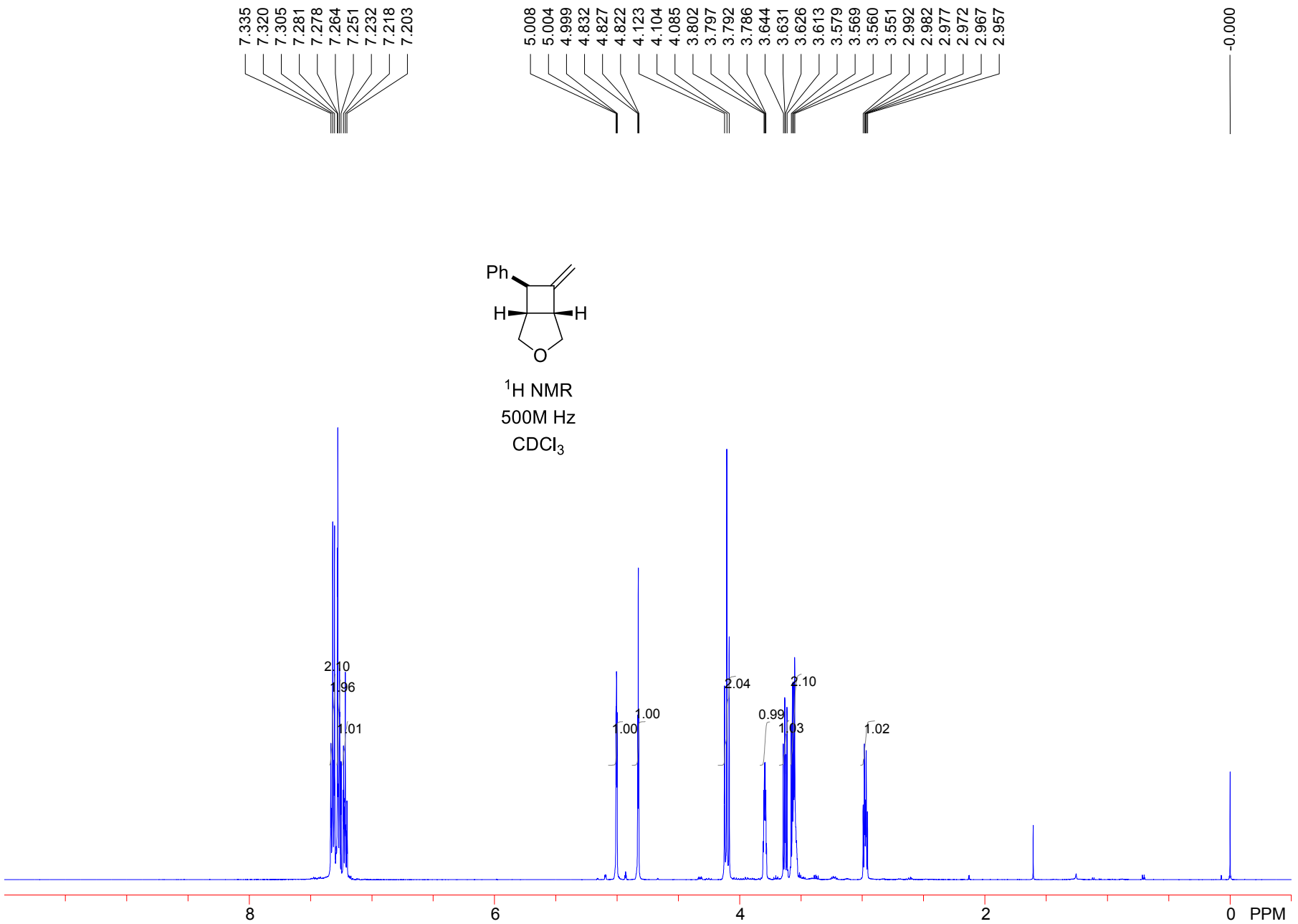
77.253
77.000
76.747
55.212
49.832
48.866
43.455
35.606
32.935
32.586
25.518
O
Ph
OMe
H
H
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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7.305
7.281
7.278
7.264
7.251
7.232
7.218
7.203
5.008
5.004
4.999
4.832
4.827
4.822
4.123
4.104
4.085
3.802
3.797
3.792
3.786
3.644
3.631
3.626
3.613
3.579
3.569
3.560
3.551
2.992
2.982
2.977
2.972
2.967
2.957
-0.000
Ph
H
H
O
1H NMR
500M Hz
CDCl3
2.10
1.96
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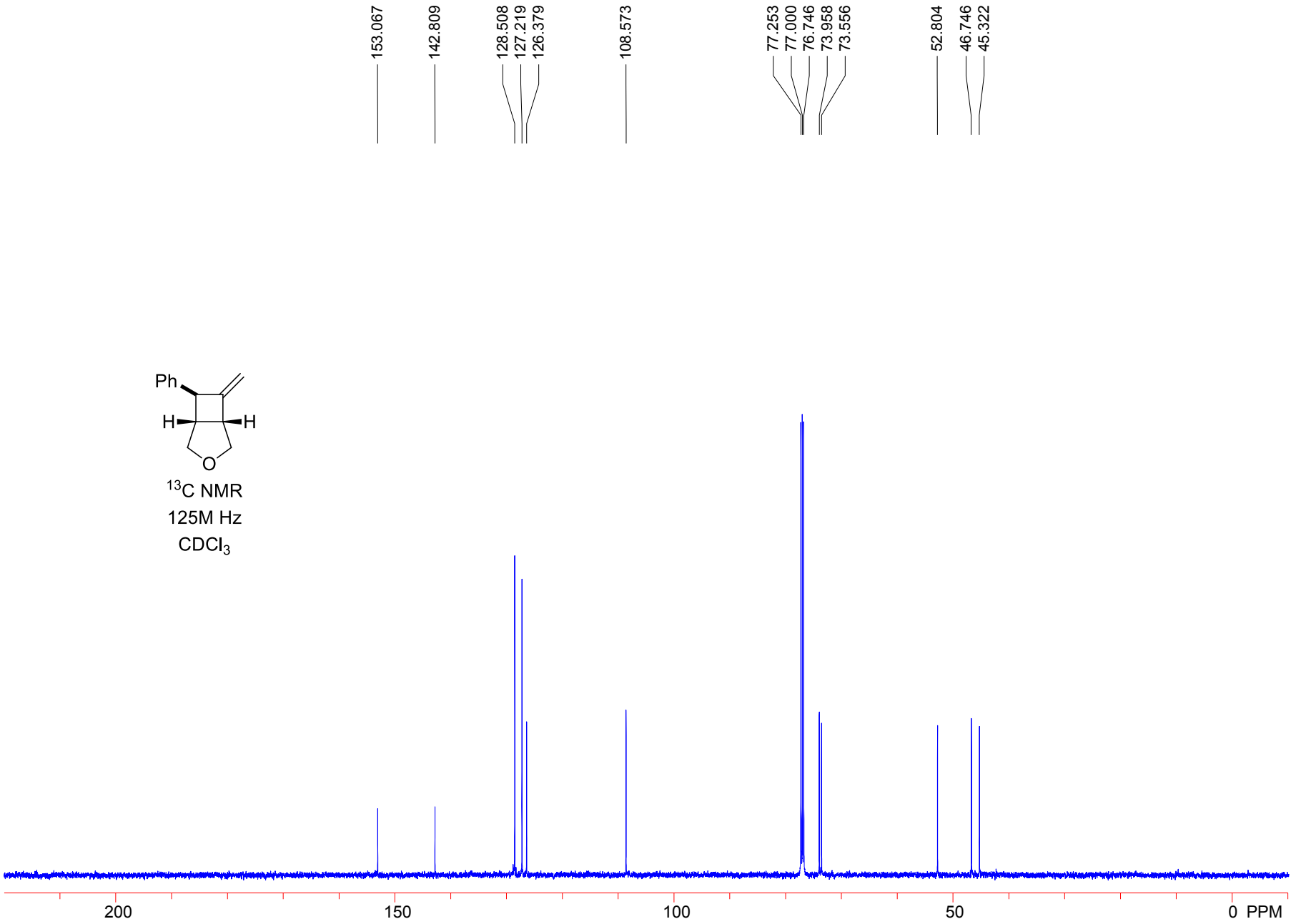
1.00
1.00
2.04
0.99
1.03
2.10
1.02
8
6
4
2
0
PPM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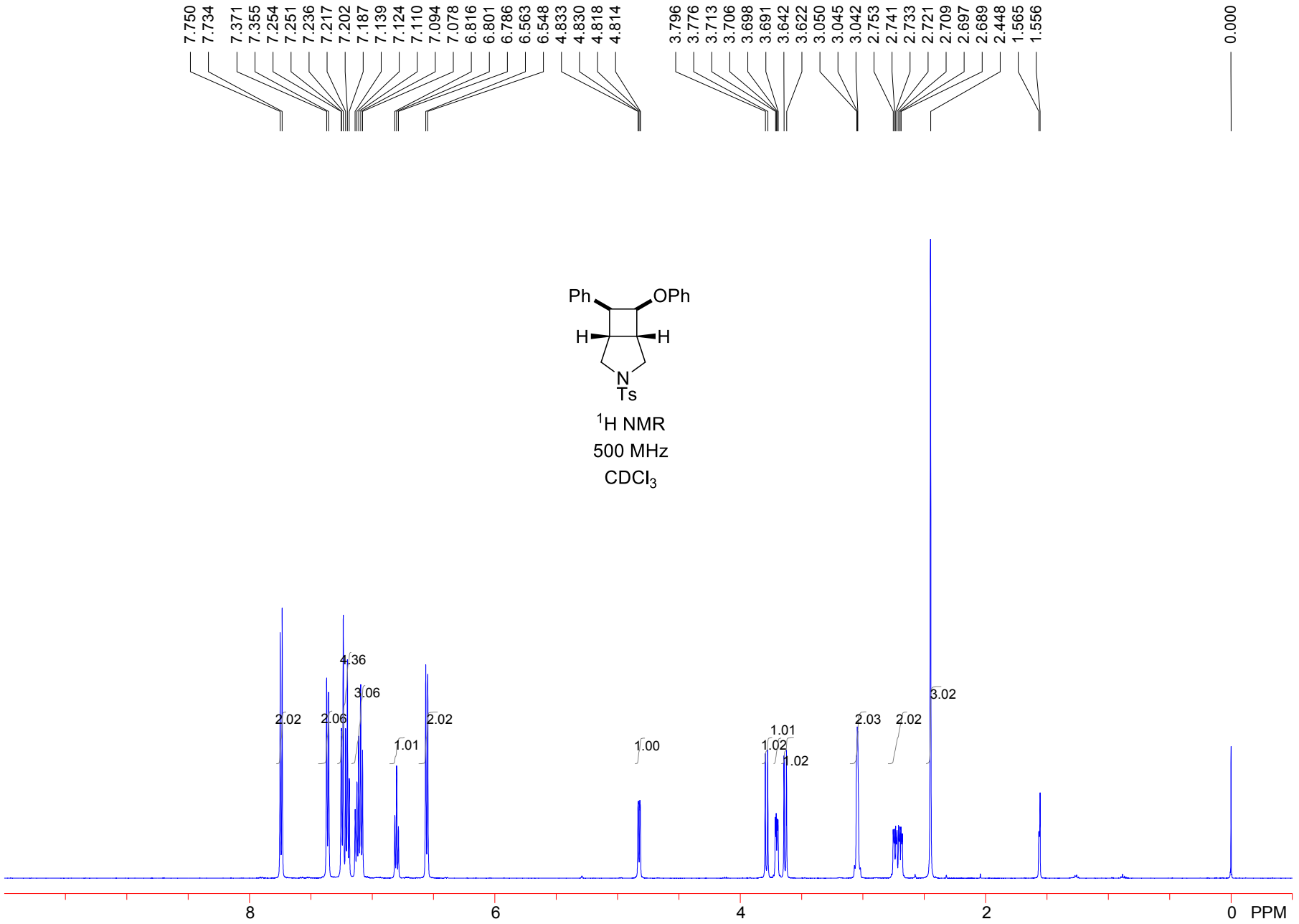
142.809
128.508
127.219
126.379
108.573
77.253
77.000
76.746
73.958
73.556
52.804
46.746
45.322
Ph
H
H
O
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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7.355
7.254
7.251
7.236
7.217
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7.187
7.139
7.124
7.110
7.094
7.078
6.816
6.801
6.786
6.563
6.548
4.833
4.830
4.818
4.814
3.796
3.776
3.713
3.706
3.698
3.691
3.642
3.622
3.050
3.045
3.042
2.753
2.741
2.733
2.721
2.709
2.697
2.689
2.448
1.565
1.556
0.000
Ph
OPh
H
H
N
Ts
1H NMR
500 MHz
CDCl3
2.02
2.06
4.36
3.06
1.01
2.02
1.00
1.02
1.01
1.02
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2.02
3.02
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6
4
2
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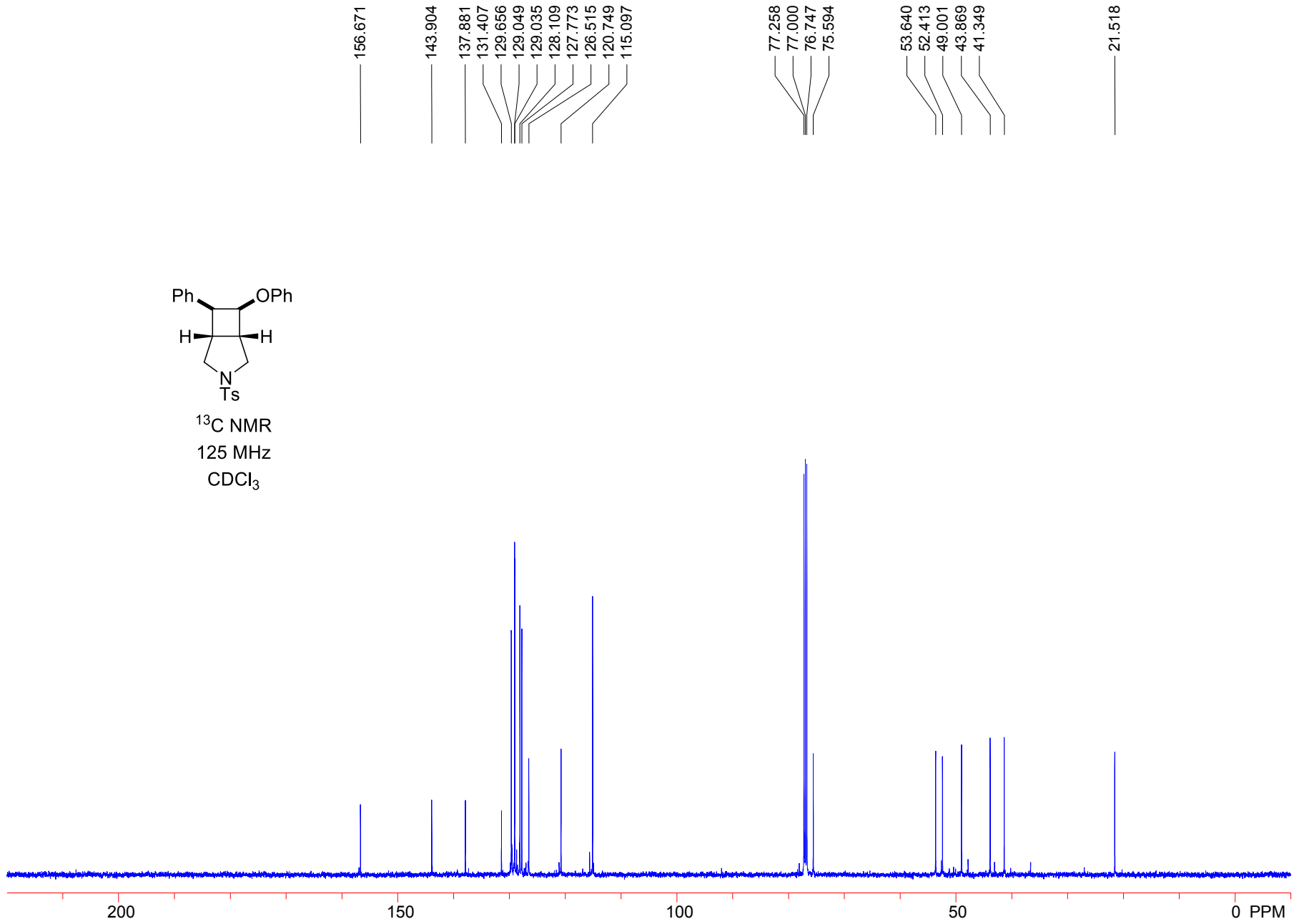
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129.035
128.109
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126.515
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77.258
77.000
76.747
75.594
53.640
52.413
49.001
43.869
41.349
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Ph
OPh
H
H
N
Ts
13C NMR
125 MHz
CDCl3
200
150
100
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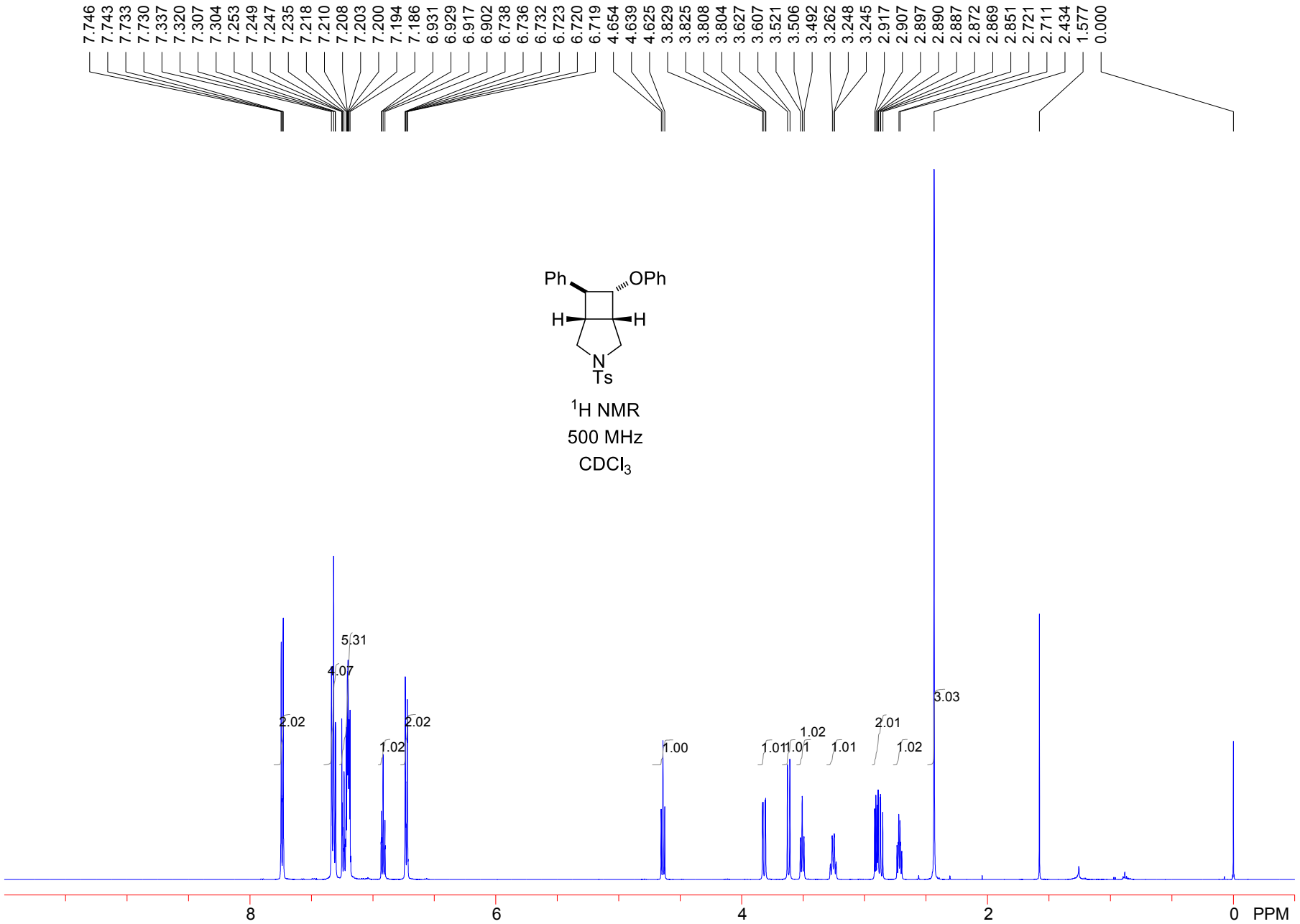
0 PPM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7.733
7.730
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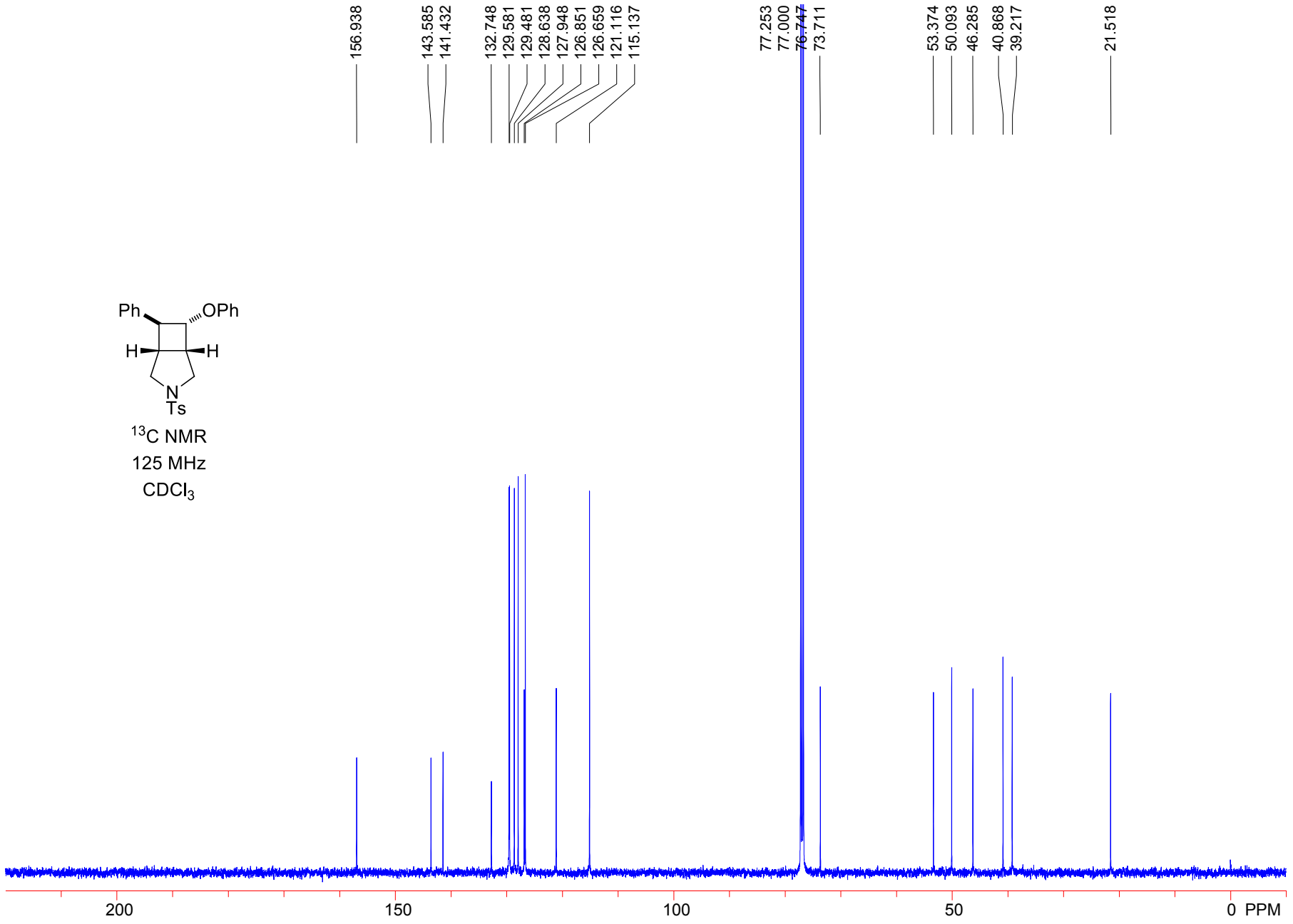
7.320
7.307
7.304
7.253
7.249
7.247
7.235
7.218
7.210
7.208
7.203
7.200
7.194
7.186
6.931
6.929
6.917
6.902
6.738
6.736
6.732
6.723
6.720
6.719
4.654
4.639
4.625
3.829
3.825
3.808
3.804
3.627
3.607
3.521
3.506
3.492
3.262
3.248
3.245
2.917
2.907
2.897
2.890
2.887
2.872
2.869
2.851
2.721
2.711
2.434
1.577
0.000
Ph
OPh
H
H
N
Ts
1H NMR
500 MHz
CDCl3
2.02
5.31
4.07
1.02
2.02
1.00
1.01
1.01
1.02
1.01
2.01
1.02
3.03
8
6
4
2
0
PPM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115.137
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77.000
76.747
73.711
53.374
50.093
46.285
40.868
39.217
21.518
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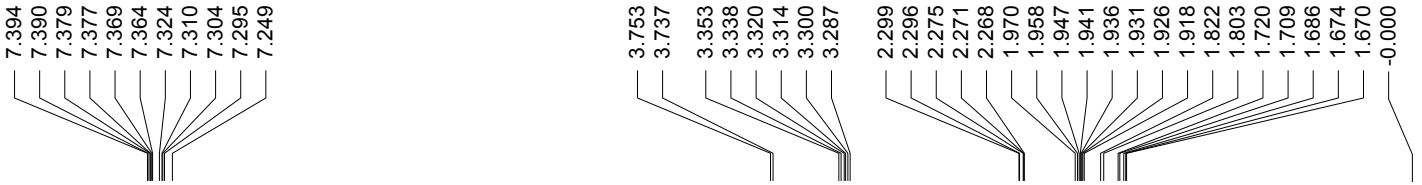
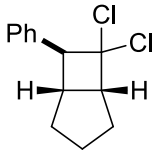
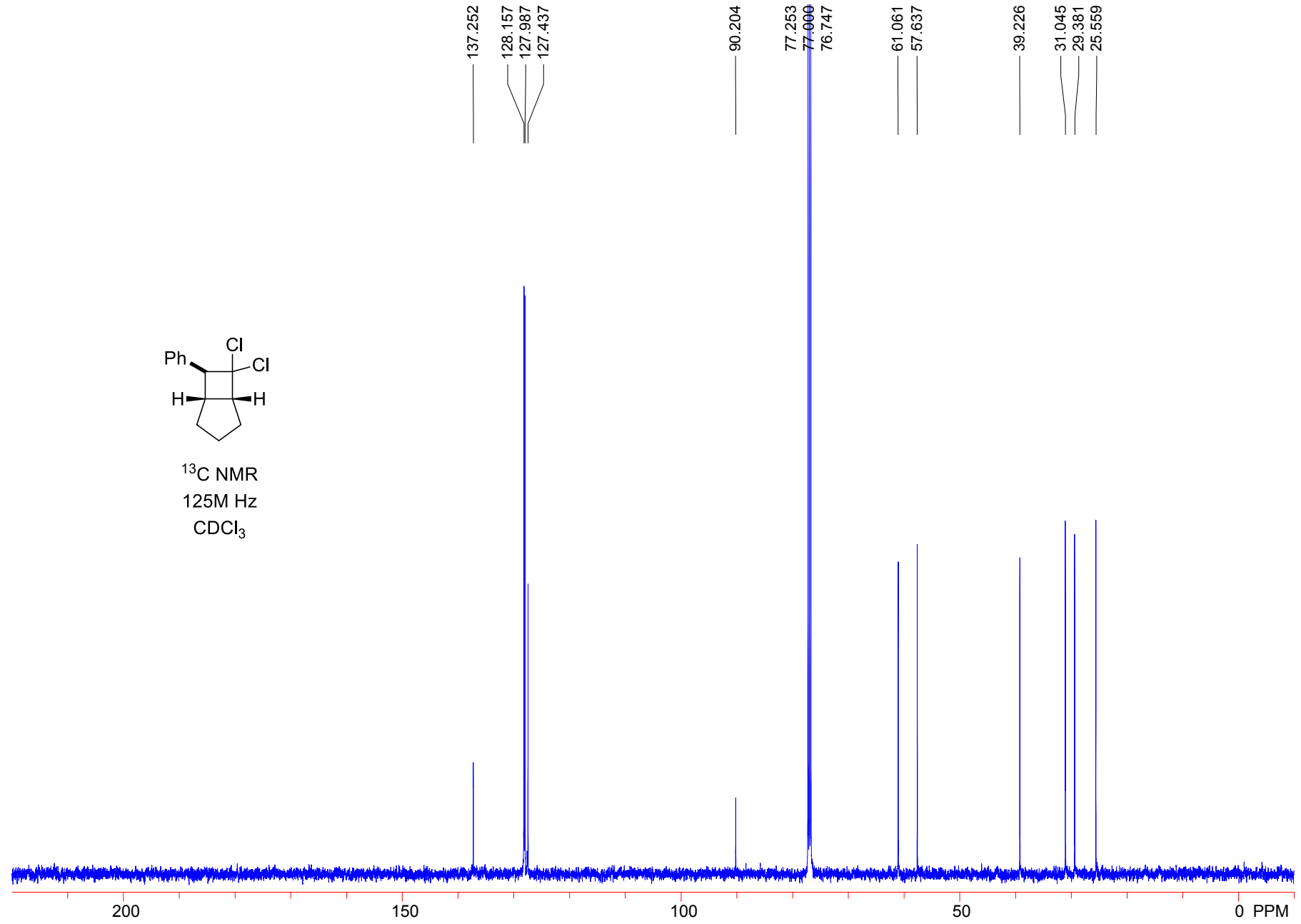
OPh
H
H
N
Ts
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM





^{1}H NMR
500M Hz
$CDCl_3$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77.000
76.747
61.061
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39.226
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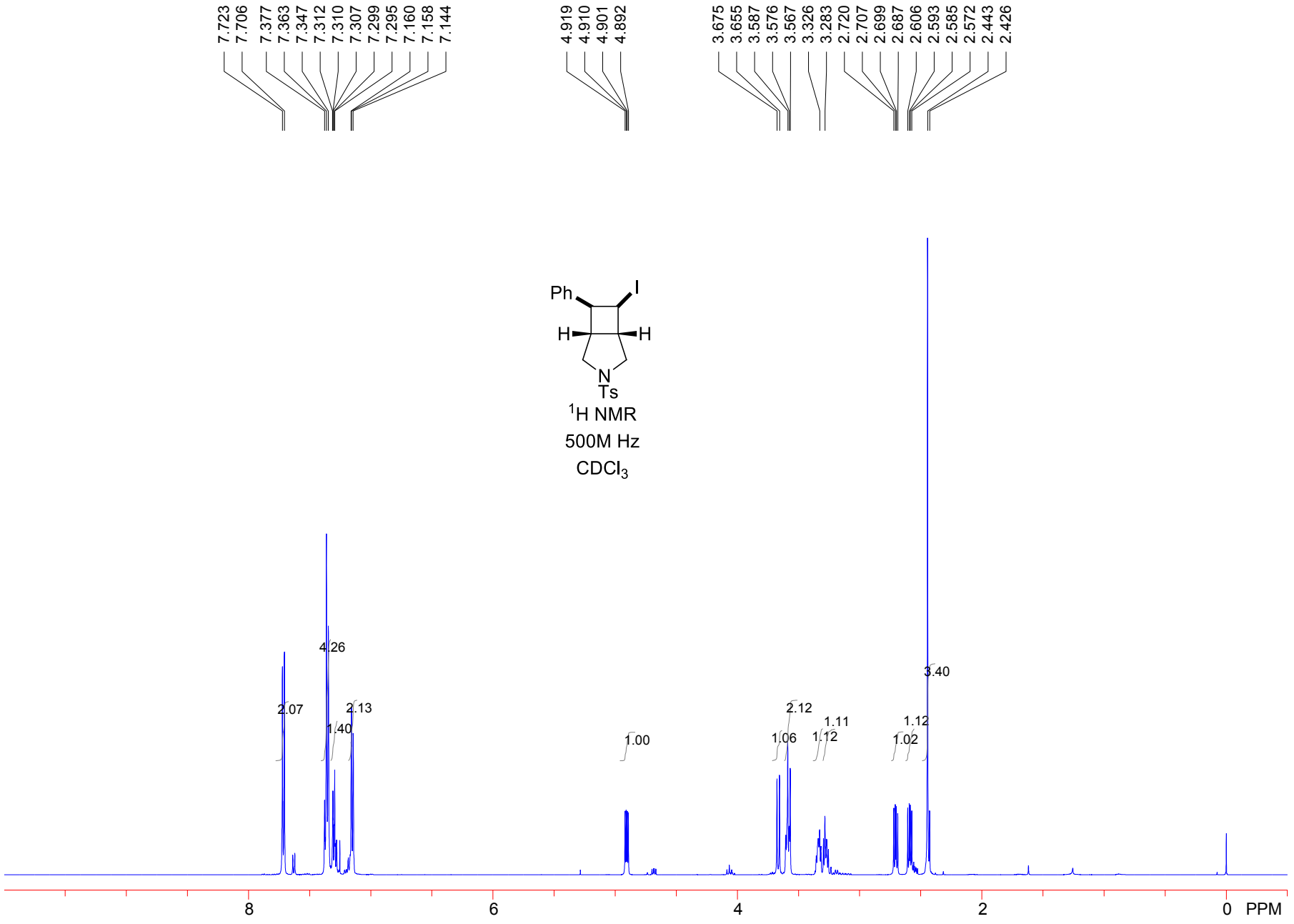
29.381
25.559
Cl
Ph
Cl
H
H
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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7.377
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7.310
7.307
7.299
7.295
7.160
7.158
7.144
4.919
4.910
4.901
4.892
3.675
3.655
3.587
3.576
3.567
3.326
3.283
2.720
2.707
2.699
2.687
2.606
2.593
2.585
2.572
2.443
2.426
Ph
I
H
H
N
Ts
1H NMR
500M Hz
CDCl3
4.26
2.07
2.13
1.40
1.00
2.12
1.06
1.11
1.12
1.12
1.02
3.40
8
6
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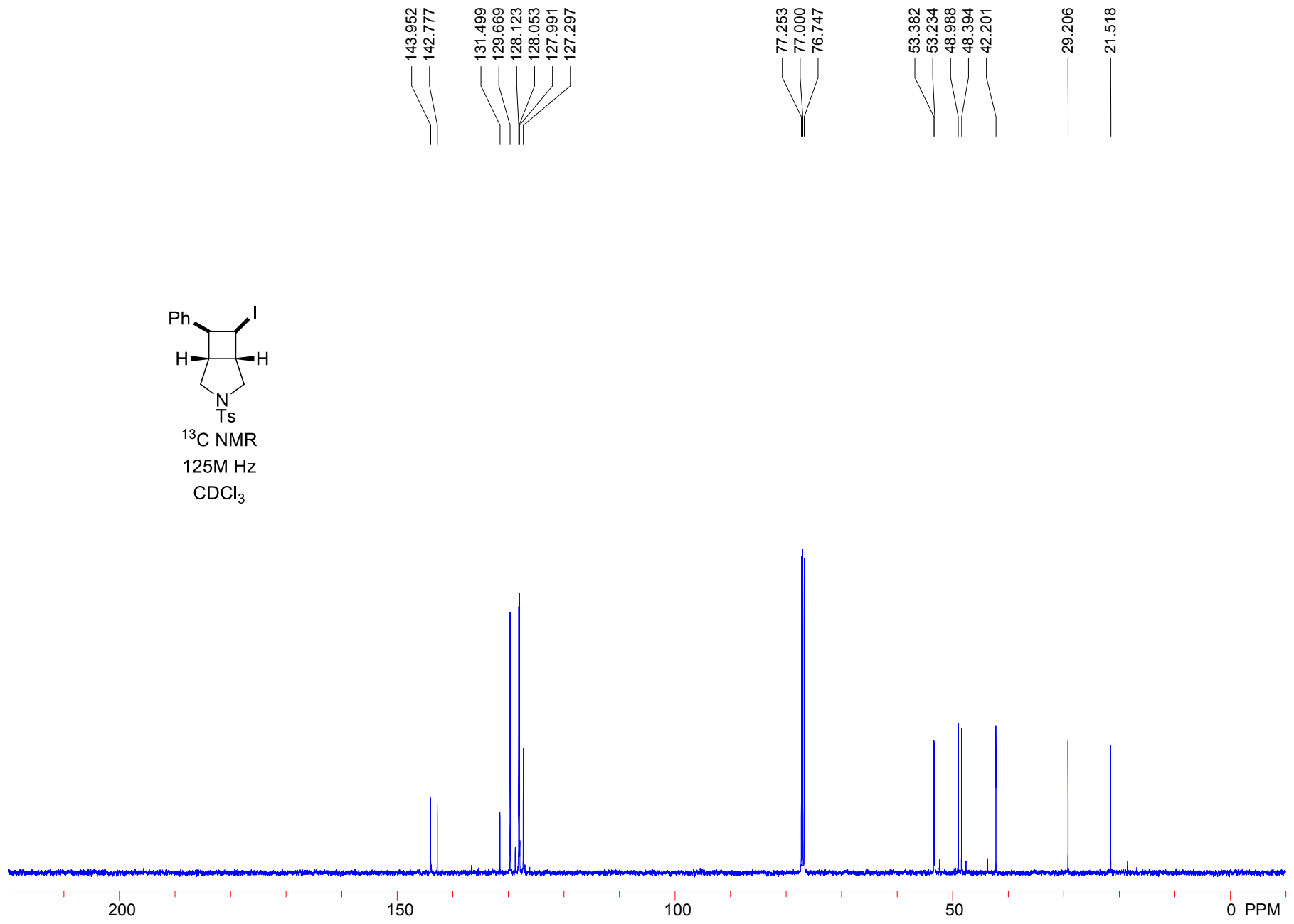
0
PPM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127.297
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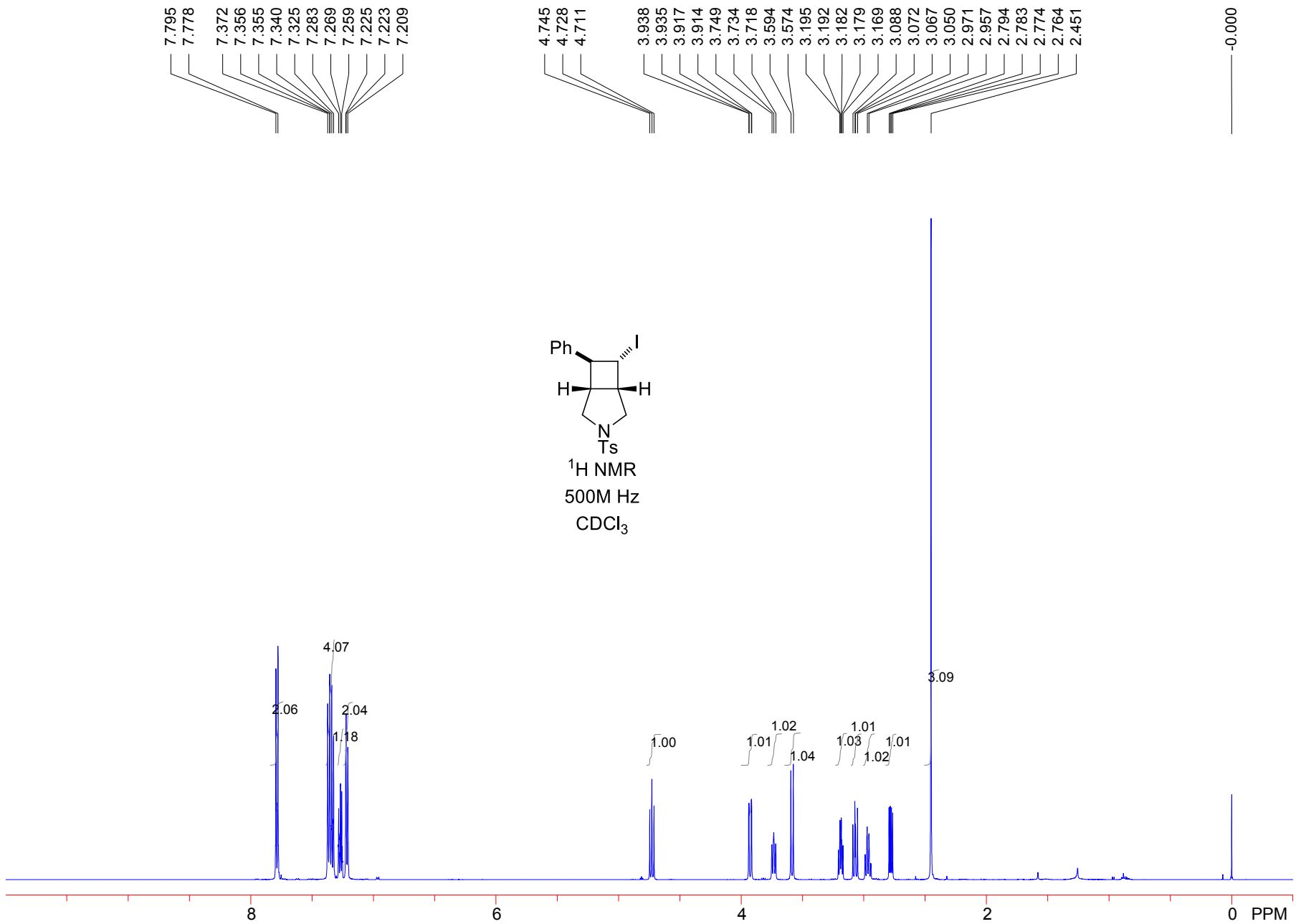
77.000
76.747
53.382
53.234
48.988
48.394
42.201
29.206
21.518
Ph
I
H
H
N
Ts
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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7.372
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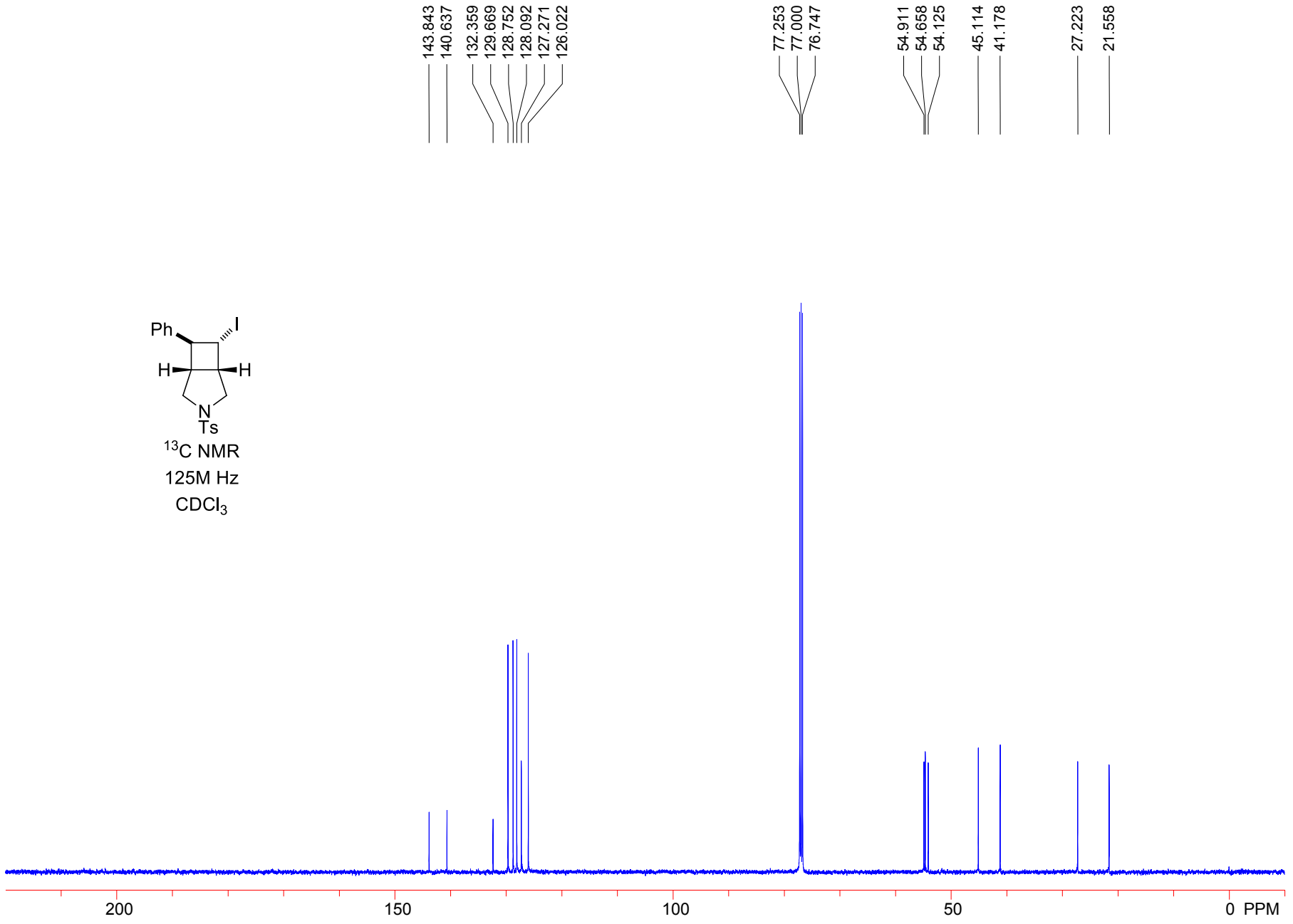
7.283
7.269
7.259
7.225
7.223
7.209
4.745
4.728
4.711
3.938
3.935
3.917
3.914
3.749
3.734
3.718
3.594
3.574
3.195
3.192
3.182
3.179
3.169
3.088
3.072
3.067
3.050
2.971
2.957
2.794
2.783
2.774
2.764
2.451
-0.000
Ph
I
H
H
N
Ts
1H NMR
500M Hz
CDCl3
4.07
2.06
2.04
1.18
1.00
1.01
1.02
1.04
1.03
1.01
1.02
1.01
3.09
8
6
4
2
0
PPM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128.752
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127.271
126.022
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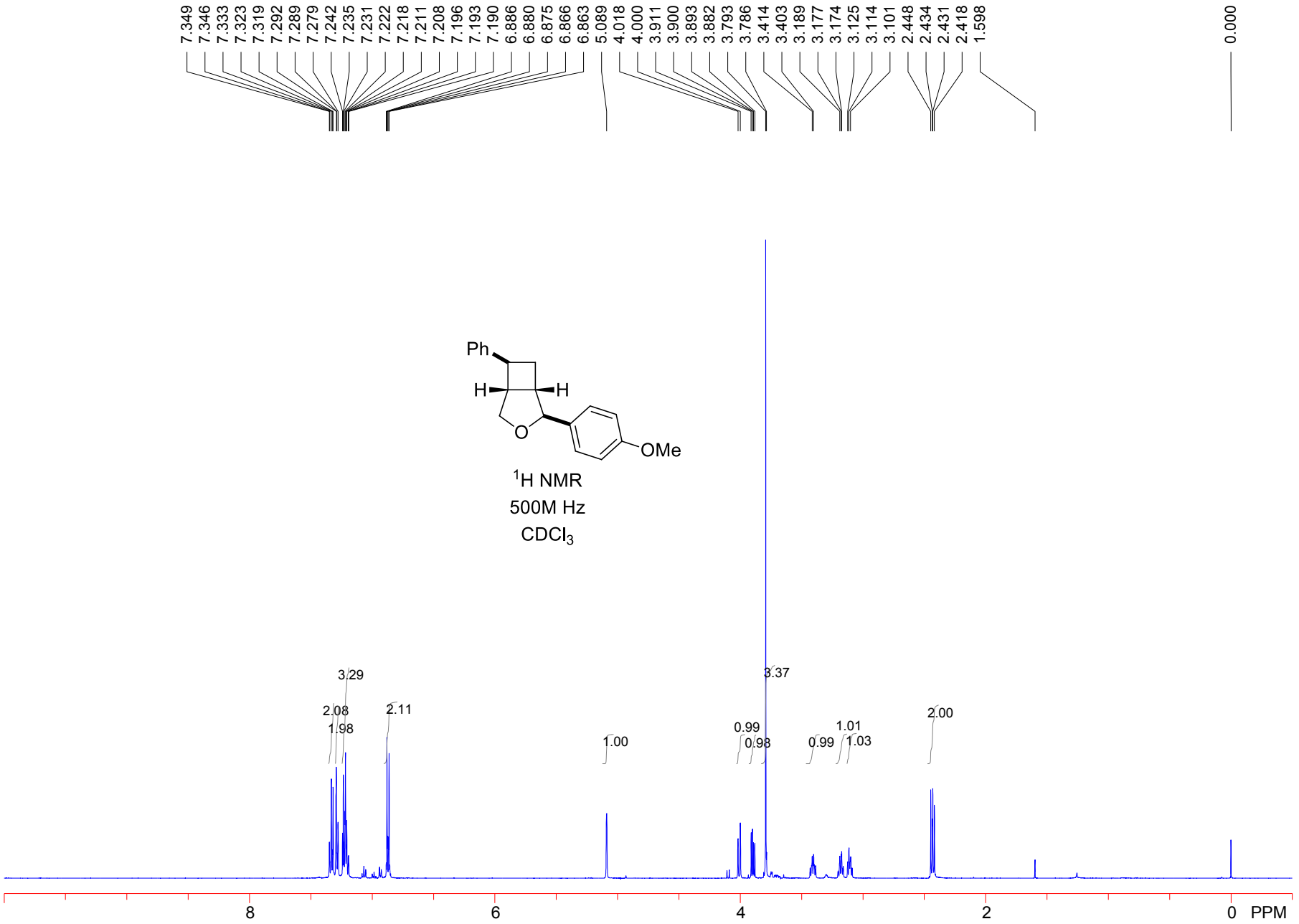
77.000
76.747
54.911
54.658
54.125
45.114
41.178
27.223
21.558
Ph
I
H
H
N
Ts
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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7.346
7.333
7.323
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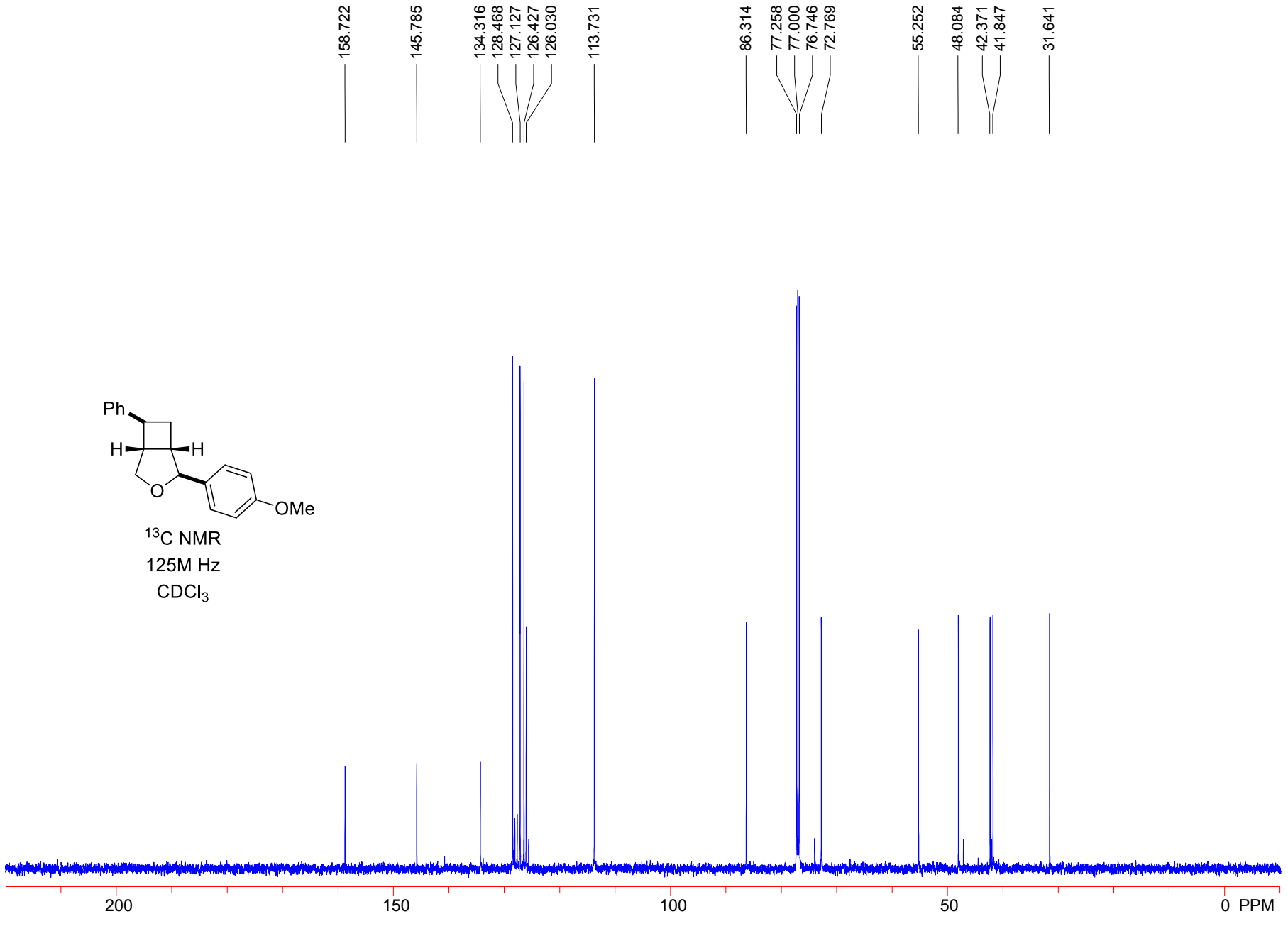
7.292
7.289
7.279
7.242
7.235
7.231
7.222
7.218
7.211
7.208
7.196
7.193
7.190
6.886
6.880
6.875
6.866
6.863
5.089
4.018
4.000
3.911
3.900
3.893
3.882
3.793
3.786
3.414
3.403
3.189
3.177
3.174
3.125
3.114
3.101
2.448
2.434
2.431
2.418
1.598
0.000
Ph
H
H
O
OMe
1H NMR
500M Hz
CDCl3
3.29
2.08
1.98
2.11
1.00
3.37
0.99
0.98
0.99
1.01
1.03
2.00
8
6
4
2
0
PPM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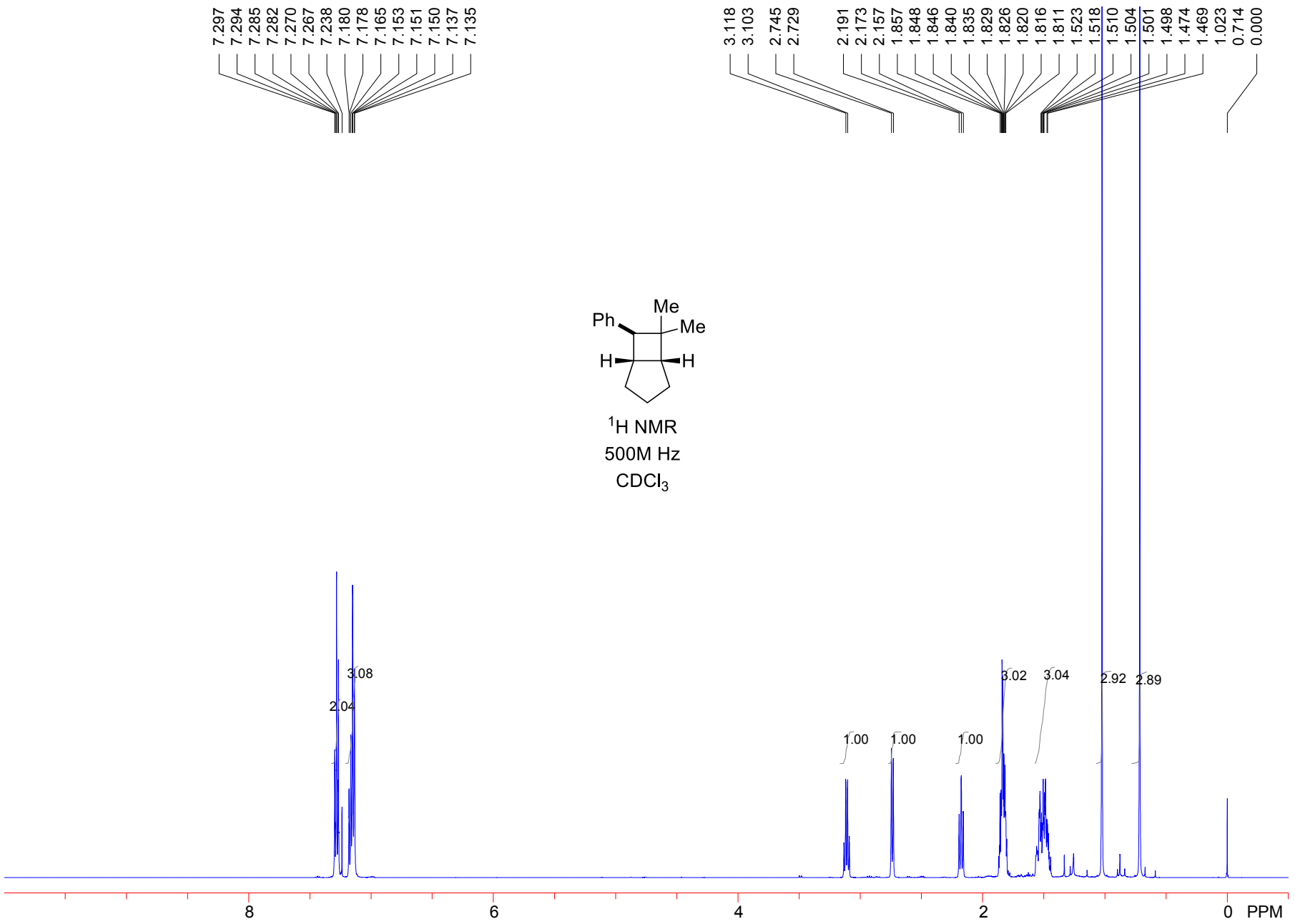
126.427
126.030
113.731
86.314
77.258
77.000
76.746
72.769
55.252
48.084
42.371
41.847
31.641
Ph
H
H
O
OMe
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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7.285
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7.270
7.267
7.238
7.180
7.178
7.165
7.153
7.151
7.150
7.137
7.135
3.118
3.103
2.745
2.729
2.191
2.173
2.157
1.857
1.848
1.846
1.840
1.835
1.829
1.826
1.820
1.816
1.811
1.523
1.518
1.510
1.504
1.501
1.498
1.474
1.469
1.023
0.714
0.000
Ph
Me
Me
H
H
1H NMR
500M Hz
CDCl3
3.08
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1.00
1.00
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3.04
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2.89
8
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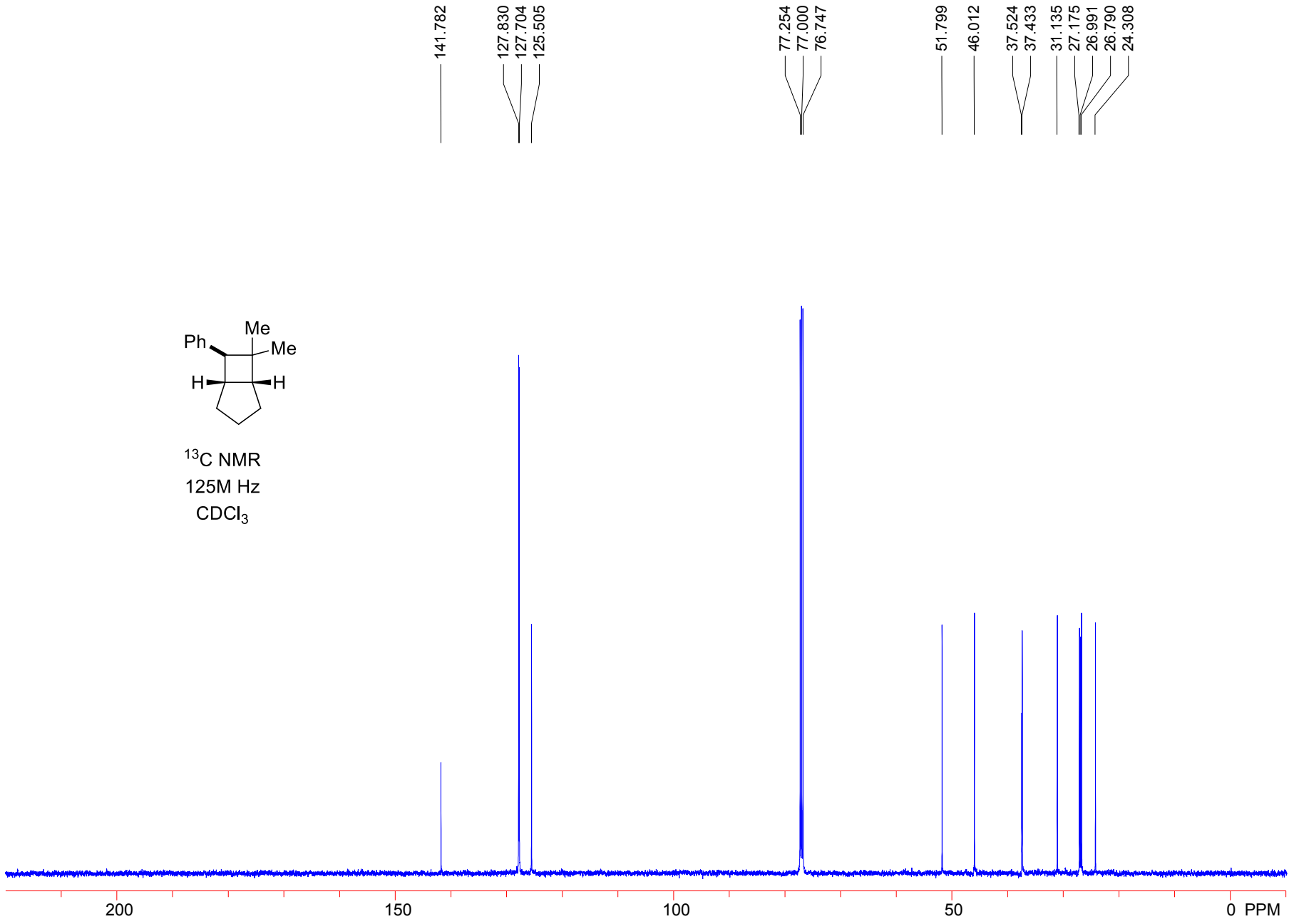
PPM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51.799
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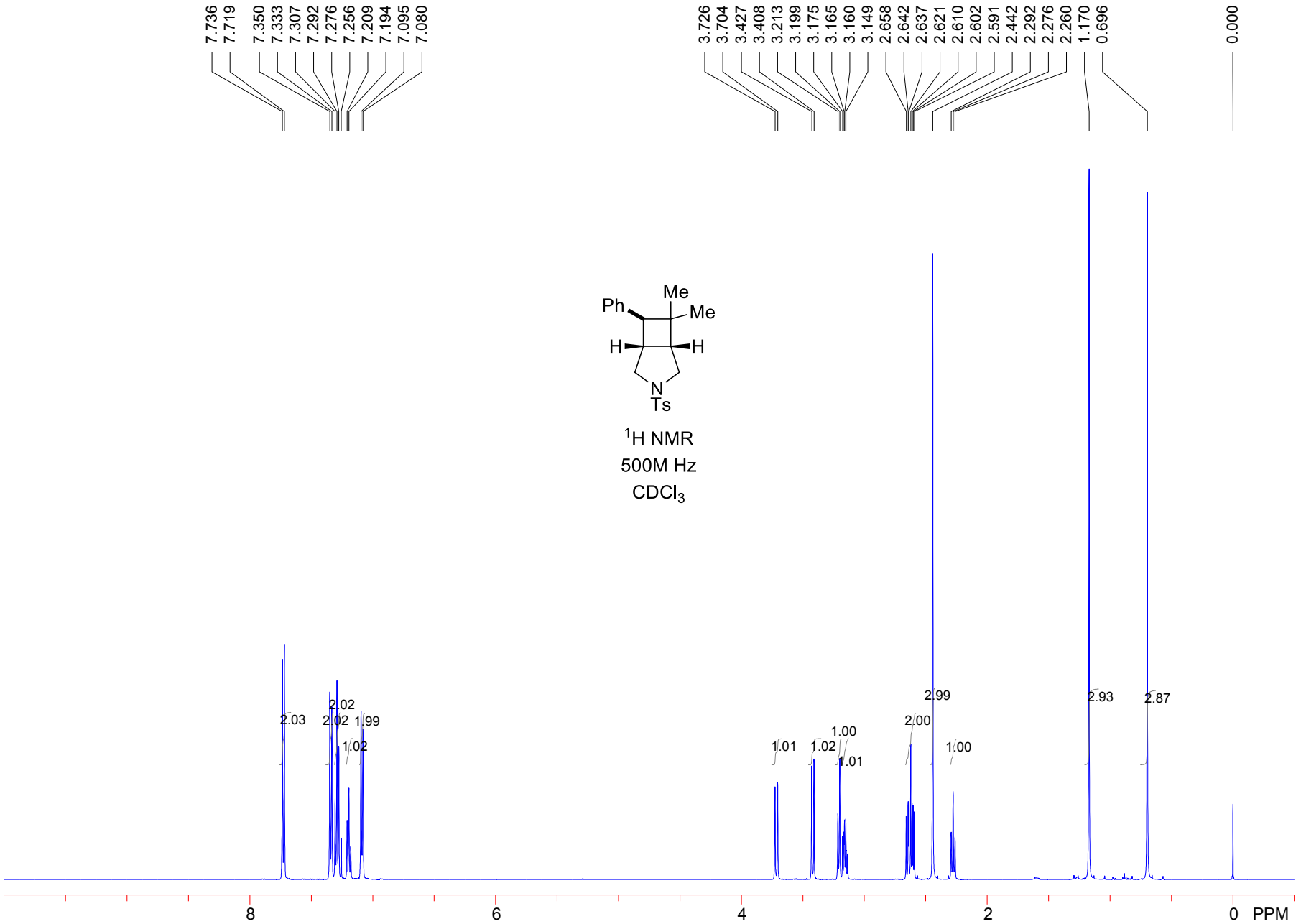
37.433
31.135
27.175
26.991
26.790
24.308
Me
Ph
Me
H
H
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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7.276
7.256
7.209
7.194
7.095
7.080
3.726
3.704
3.427
3.408
3.213
3.199
3.175
3.165
3.160
3.149
2.658
2.642
2.637
2.621
2.610
2.602
2.591
2.442
2.292
2.276
2.260
1.170
0.696
0.000
Me
Ph
Me
H
H
N
Ts
1H NMR
500M Hz
CDCl3
2.03
2.02
2.02
1.99
1.02
1.01
1.02
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1.01
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6
4
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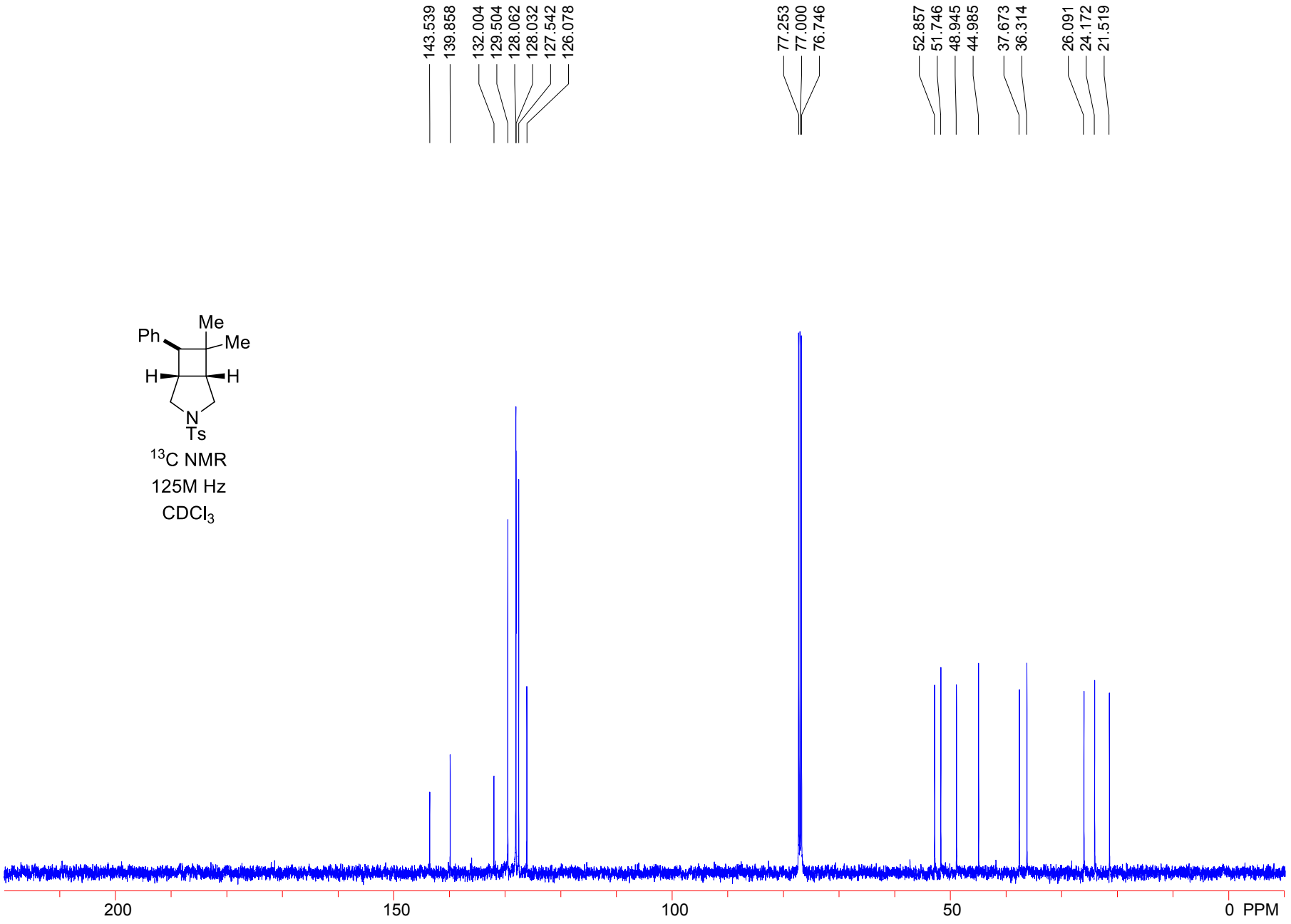
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129.504
128.062
128.032
127.542
126.078
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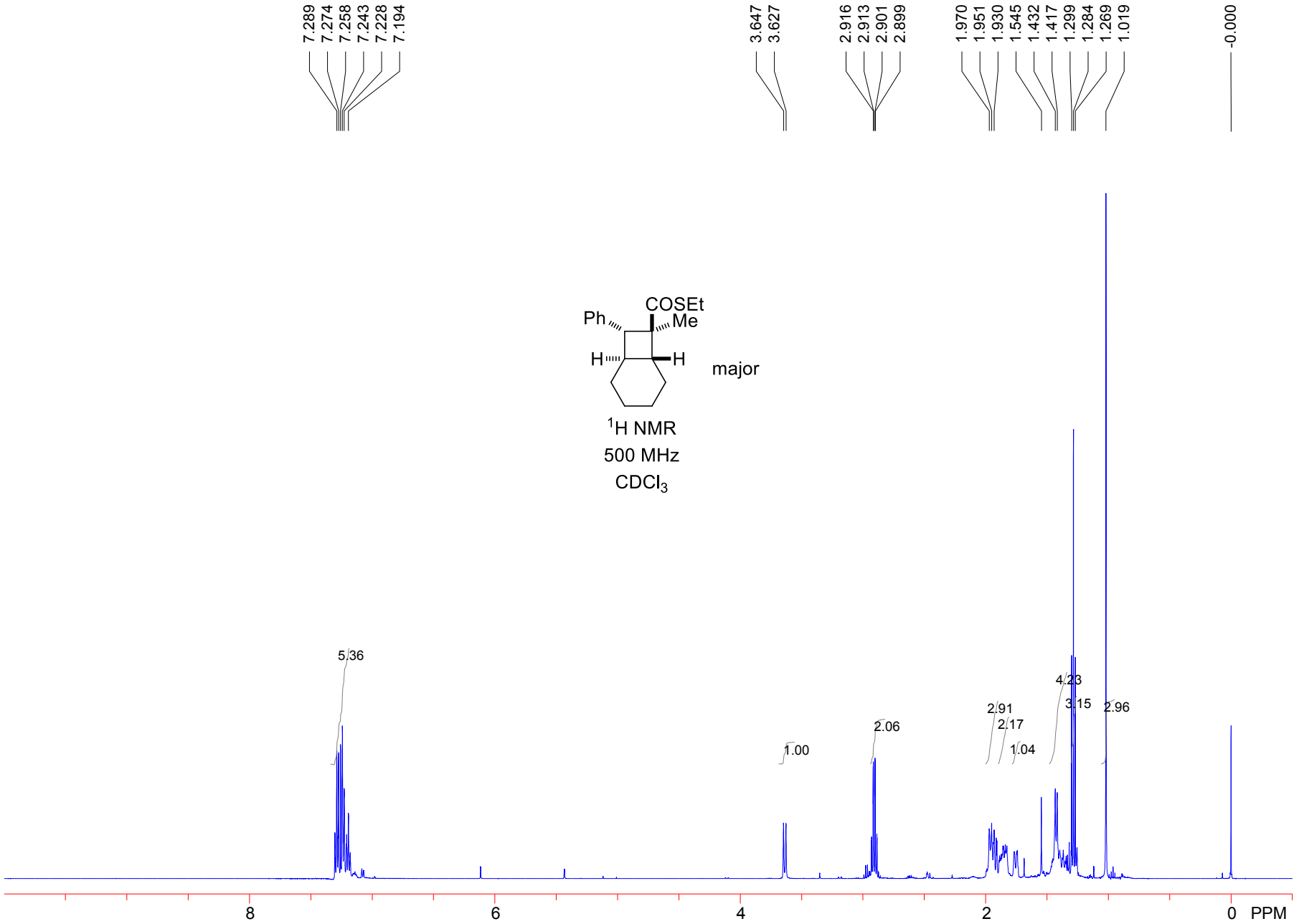
77.000
76.746
52.857
51.746
48.945
44.985
37.673
36.314
26.091
24.172
21.519
Me
Ph
Me
H
H
N
Ts
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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7.258
7.243
7.228
7.194
3.647
3.627
2.916
2.913
2.901
2.899
1.970
1.951
1.930
1.545
1.432
1.417
1.299
1.284
1.269
1.019
-0.000
COSEt
Ph
Me
H
H
major
1H NMR
500 MHz
CDCl3
5.36
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2.17
1.04
4.23
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2.96
8
6
4
2
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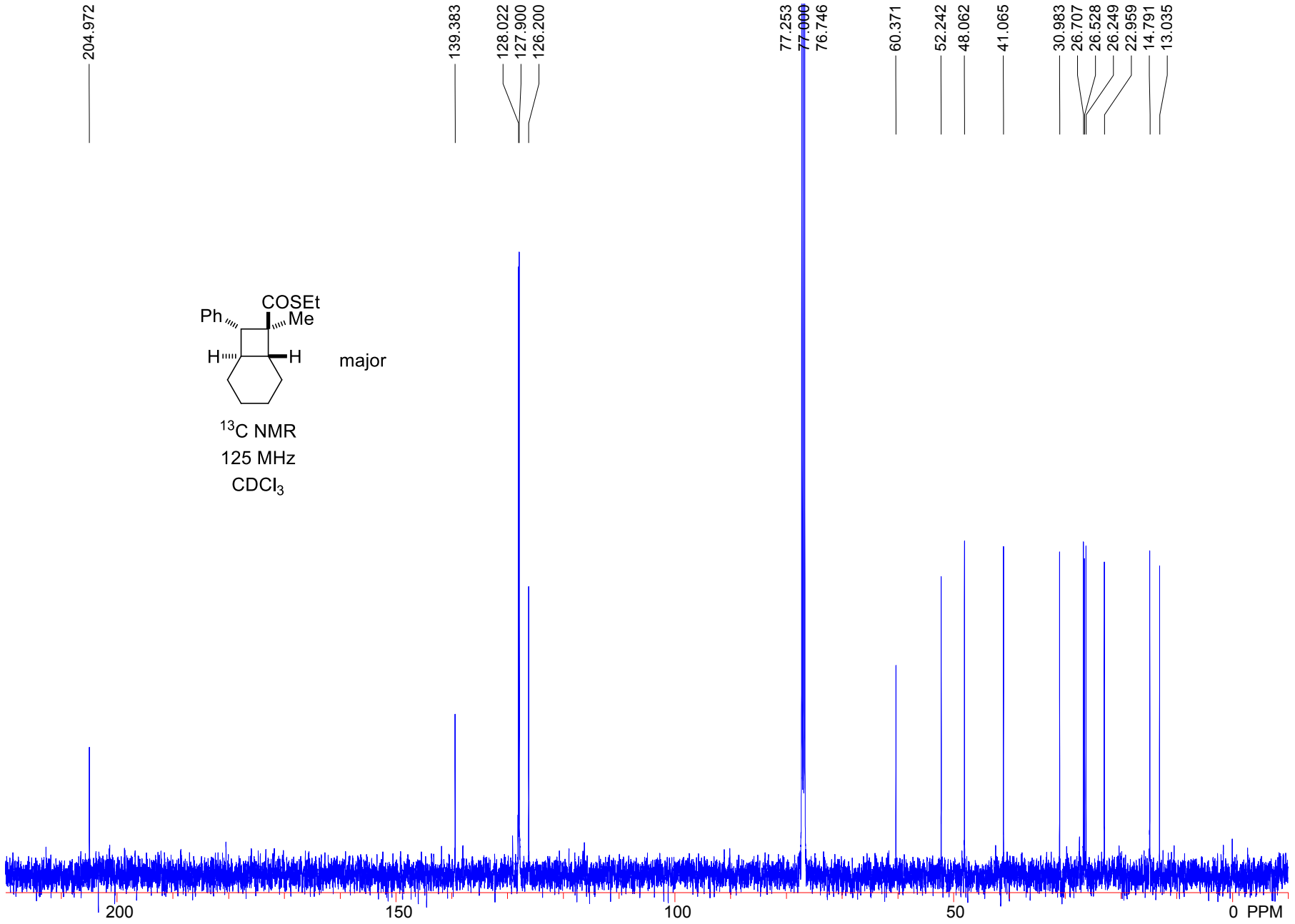
PPM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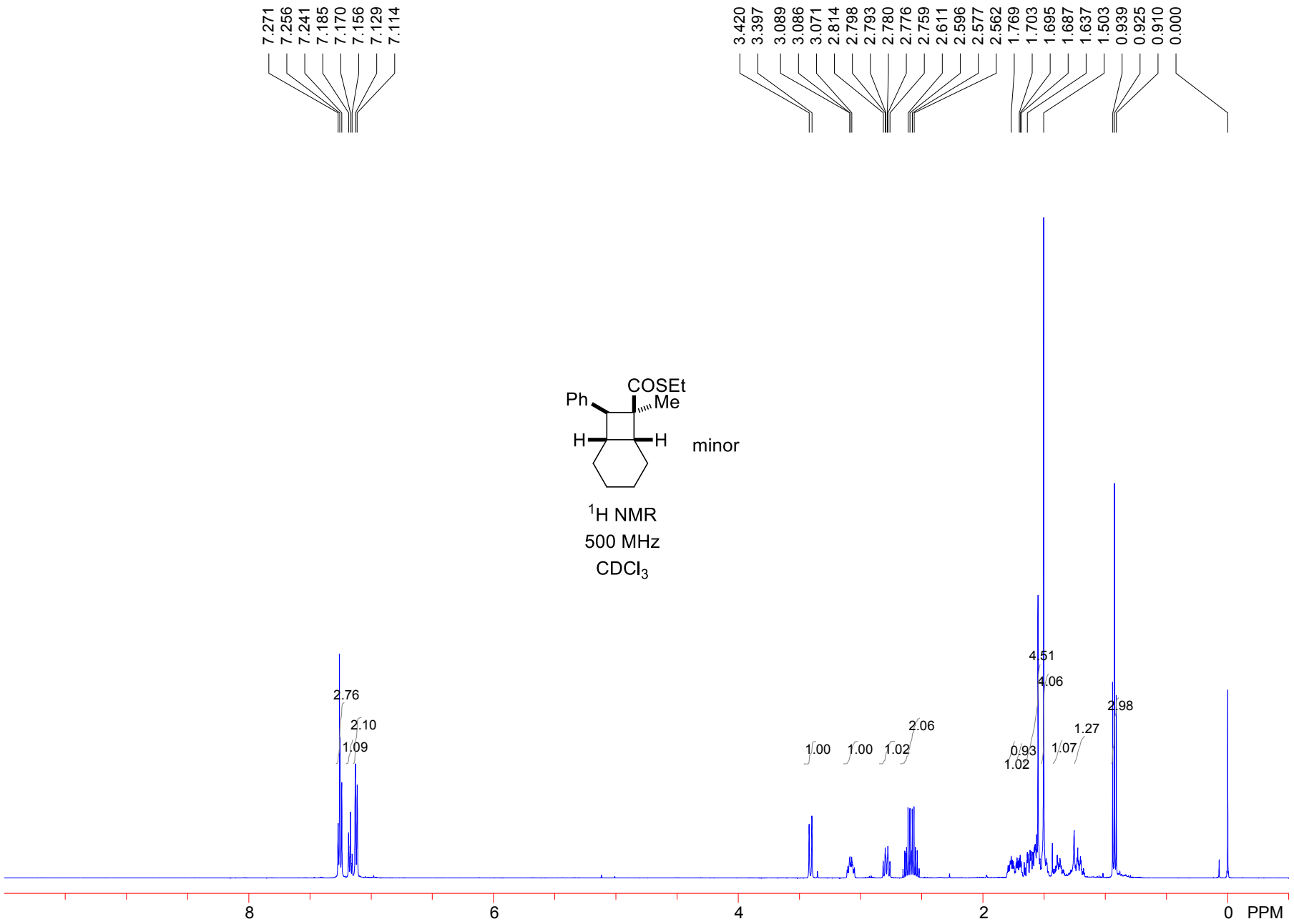
77.000
76.746
60.371
52.242
48.062
41.065
30.983
26.707
26.528
26.249
22.959
14.791
13.035
COSEt
Ph
Me
H
H
major
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM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7.256
7.241
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7.170
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7.114
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3.397
3.089
3.086
3.071
2.814
2.798
2.793
2.780
2.776
2.759
2.611
2.596
2.577
2.562
1.769
1.703
1.695
1.687
1.637
1.503
0.939
0.925
0.910
0.000
COSEt
Ph
Me
H
H
minor
1H NMR
500 MHz
CDCl3
2.76
2.10
1.09
1.00
1.00
1.02
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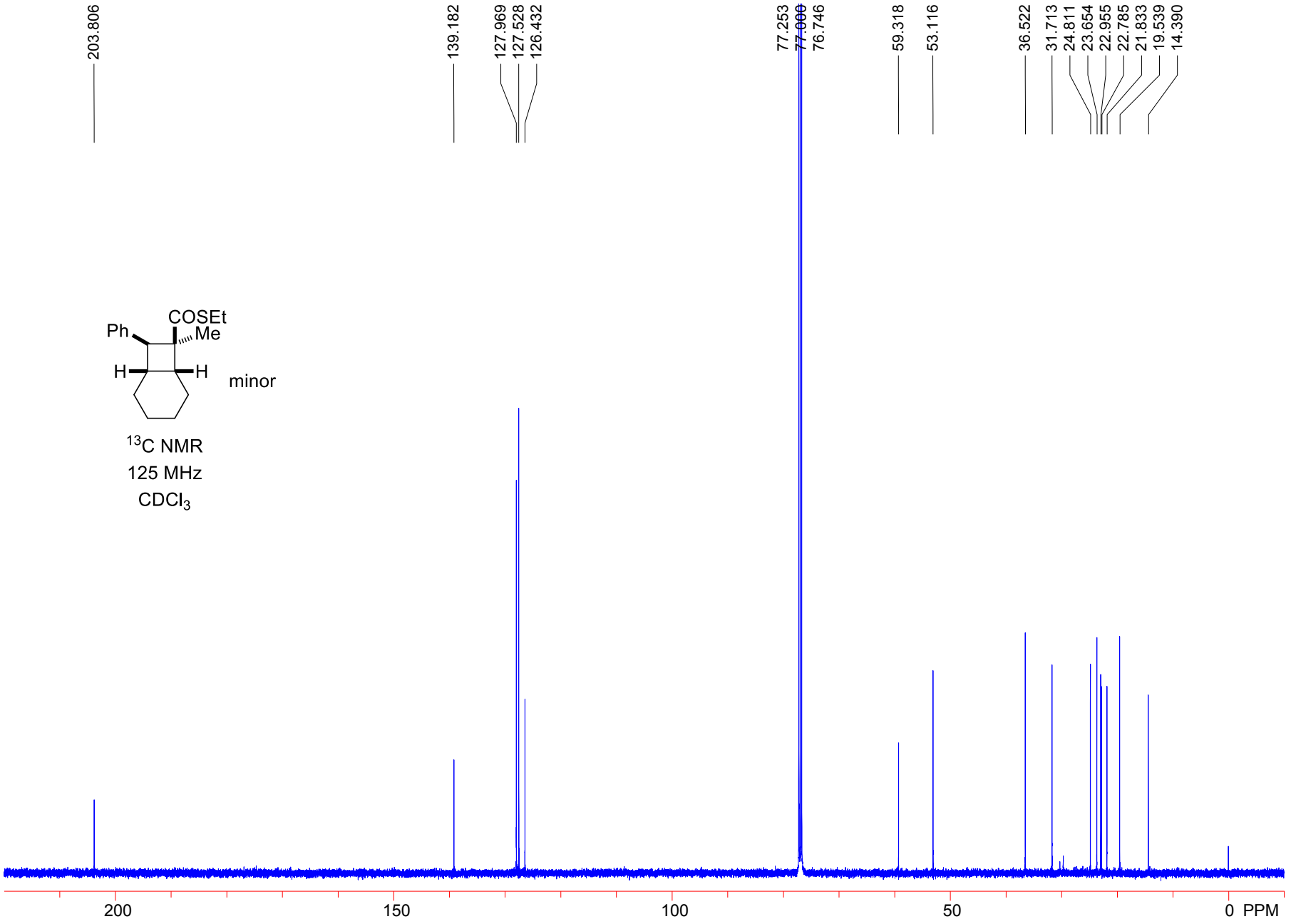
2.98
8
6
4
2
0
PPM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24.811
23.654
22.955
22.785
21.833
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Ph
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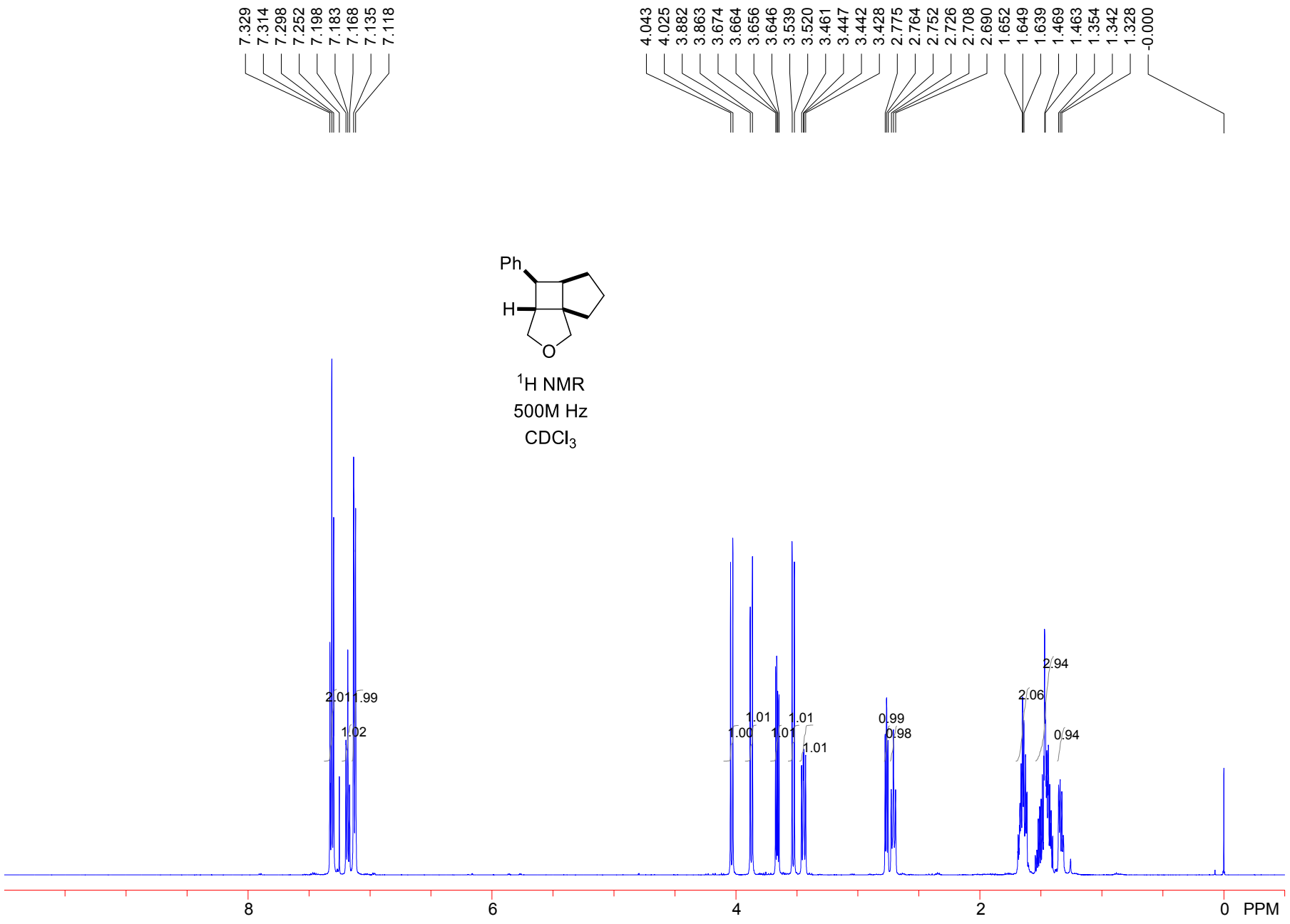
minor
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM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7.168
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4.025
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3.863
3.674
3.664
3.656
3.646
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3.520
3.461
3.447
3.442
3.428
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2.764
2.752
2.726
2.708
2.690
1.652
1.649
1.639
1.469
1.463
1.354
1.342
1.328
-0.000
Ph
H
O
1H NMR
500M Hz
CDCl3
2.01
1.99
1.02
1.00
1.01
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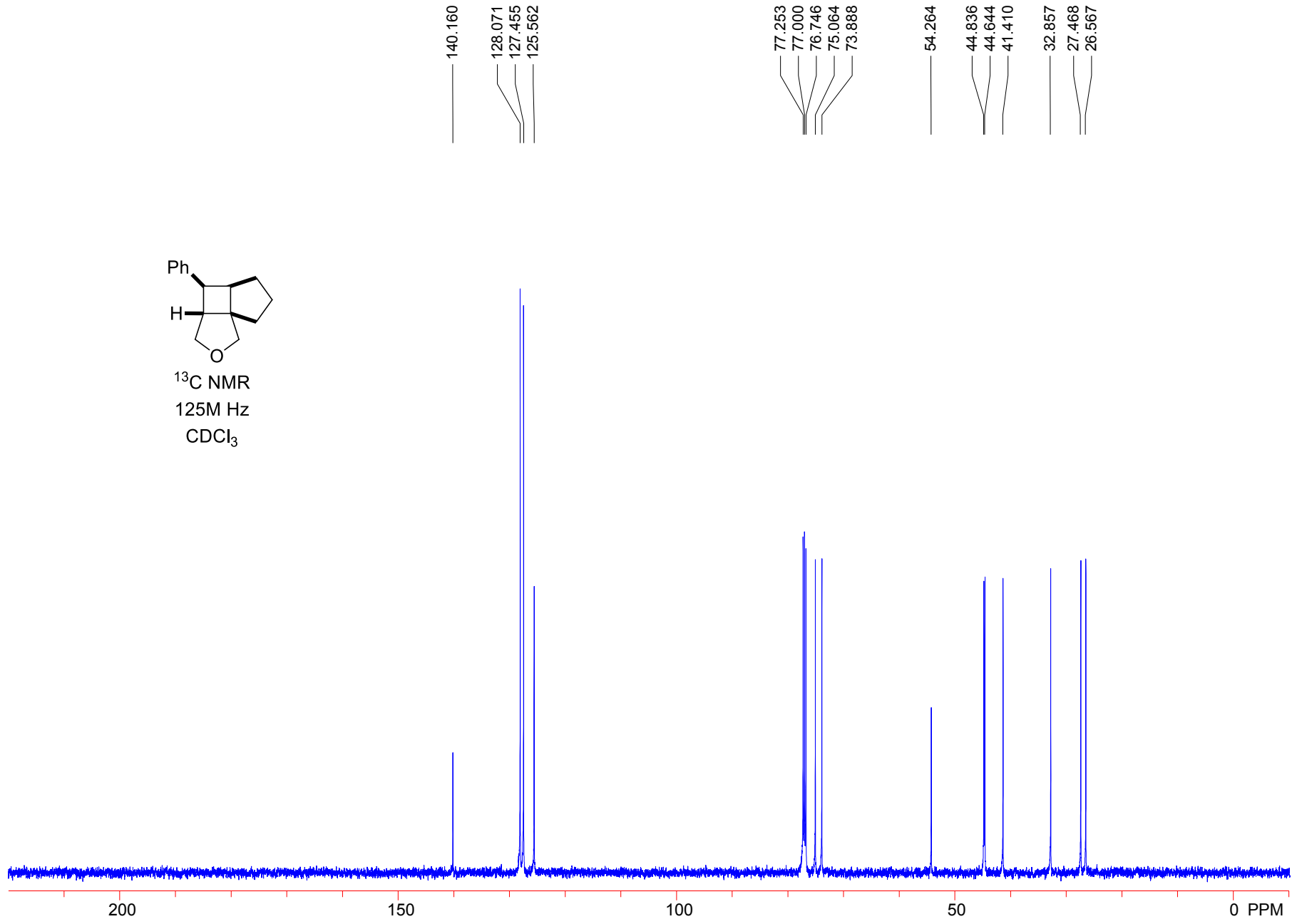
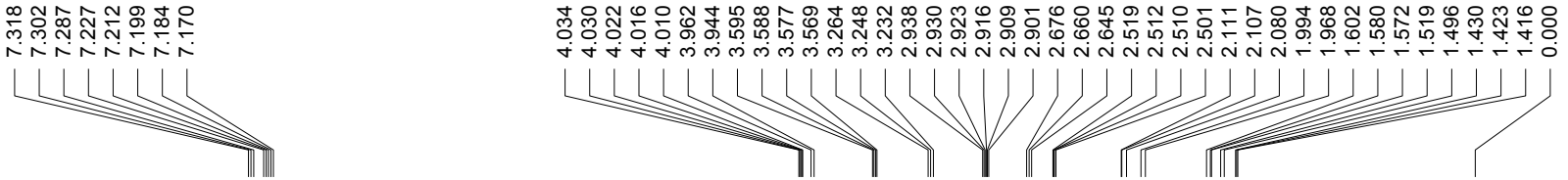
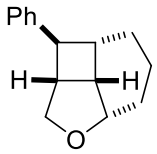
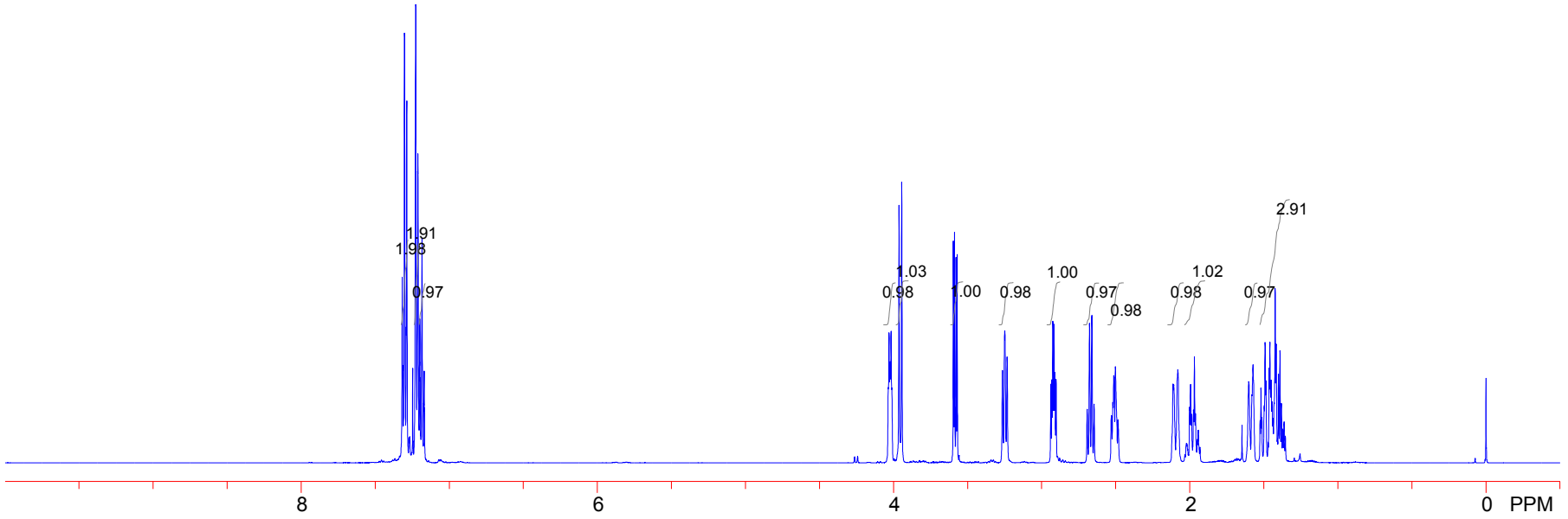
PPM

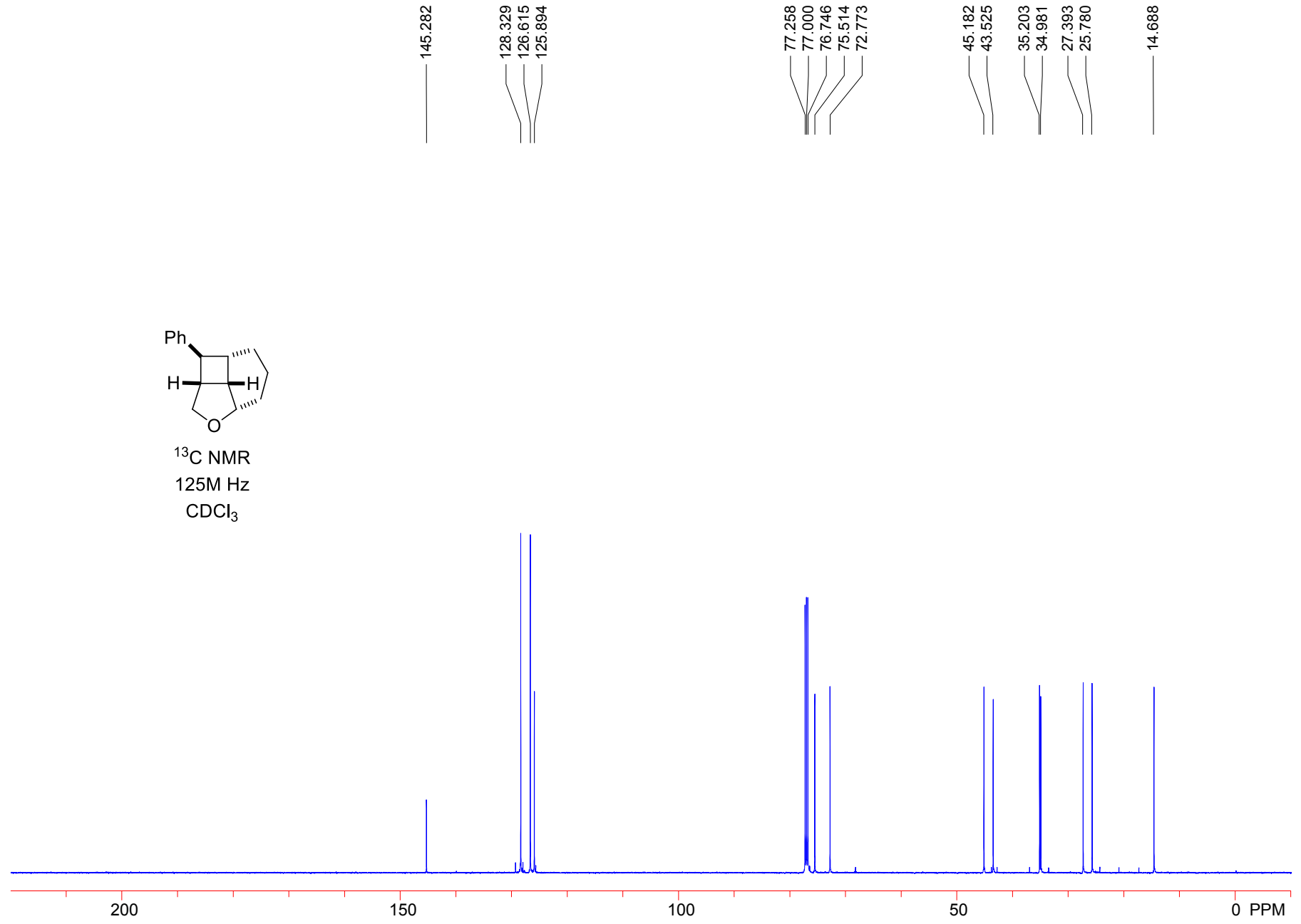

140.160
128.071
127.455
125.562
77.253
77.000
76.746
75.064
73.888
54.264
44.836
44.644
41.410
32.857
27.468
26.567
Ph
H
O
^{13}C NMR
125M Hz
$CDCl_3$
200
150
100
50
0 PPM





^{1}H NMR
500M Hz
$CDCl_3$

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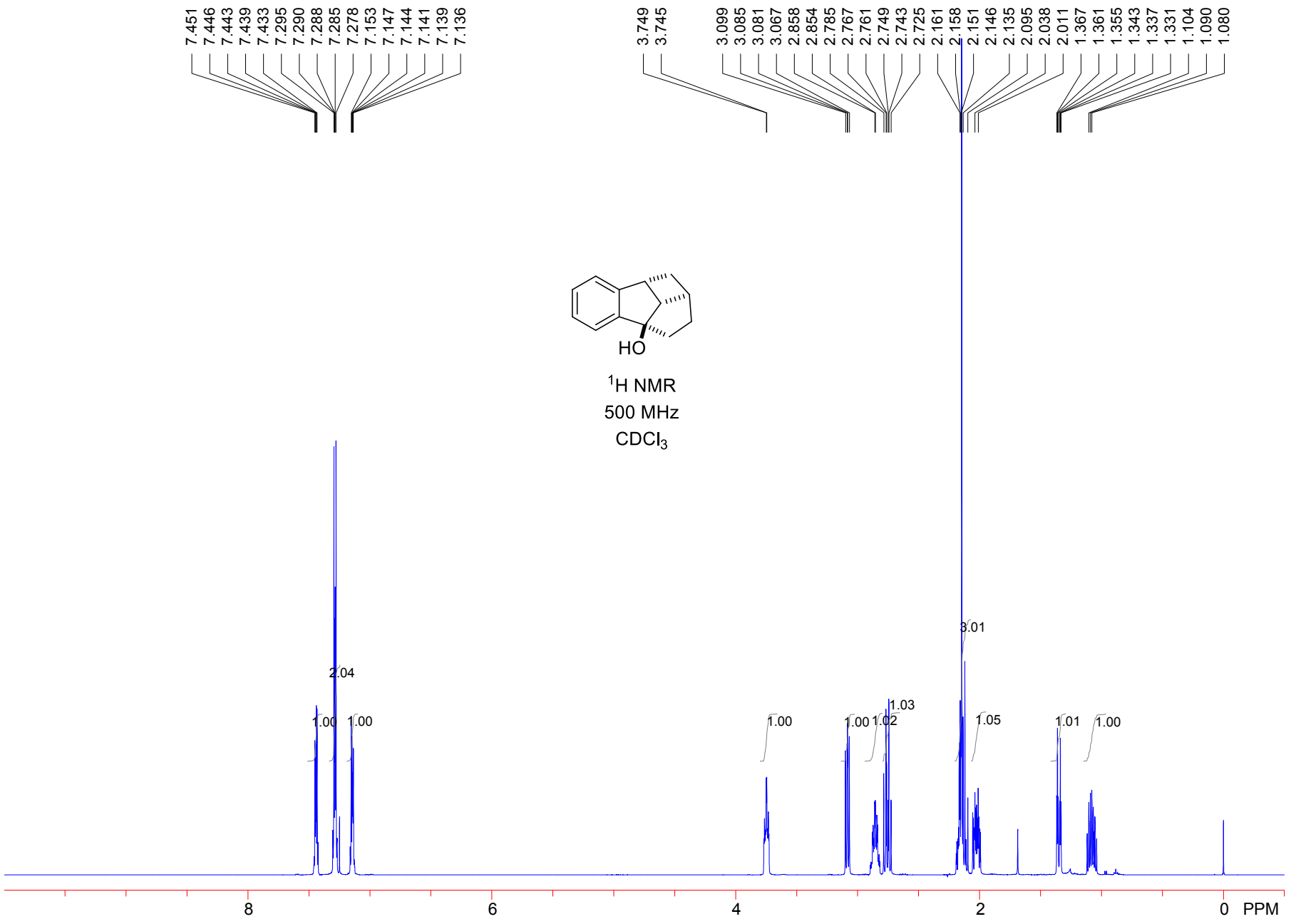
125.894
77.258
77.000
76.746
75.514
72.773
45.182
43.525
35.203
34.981
27.393
25.780
14.688
Ph
H
H
O
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM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7.144
7.141
7.139
7.136
3.749
3.745
3.099
3.085
3.081
3.067
2.858
2.854
2.785
2.767
2.761
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2.725
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2.038
2.011
1.367
1.361
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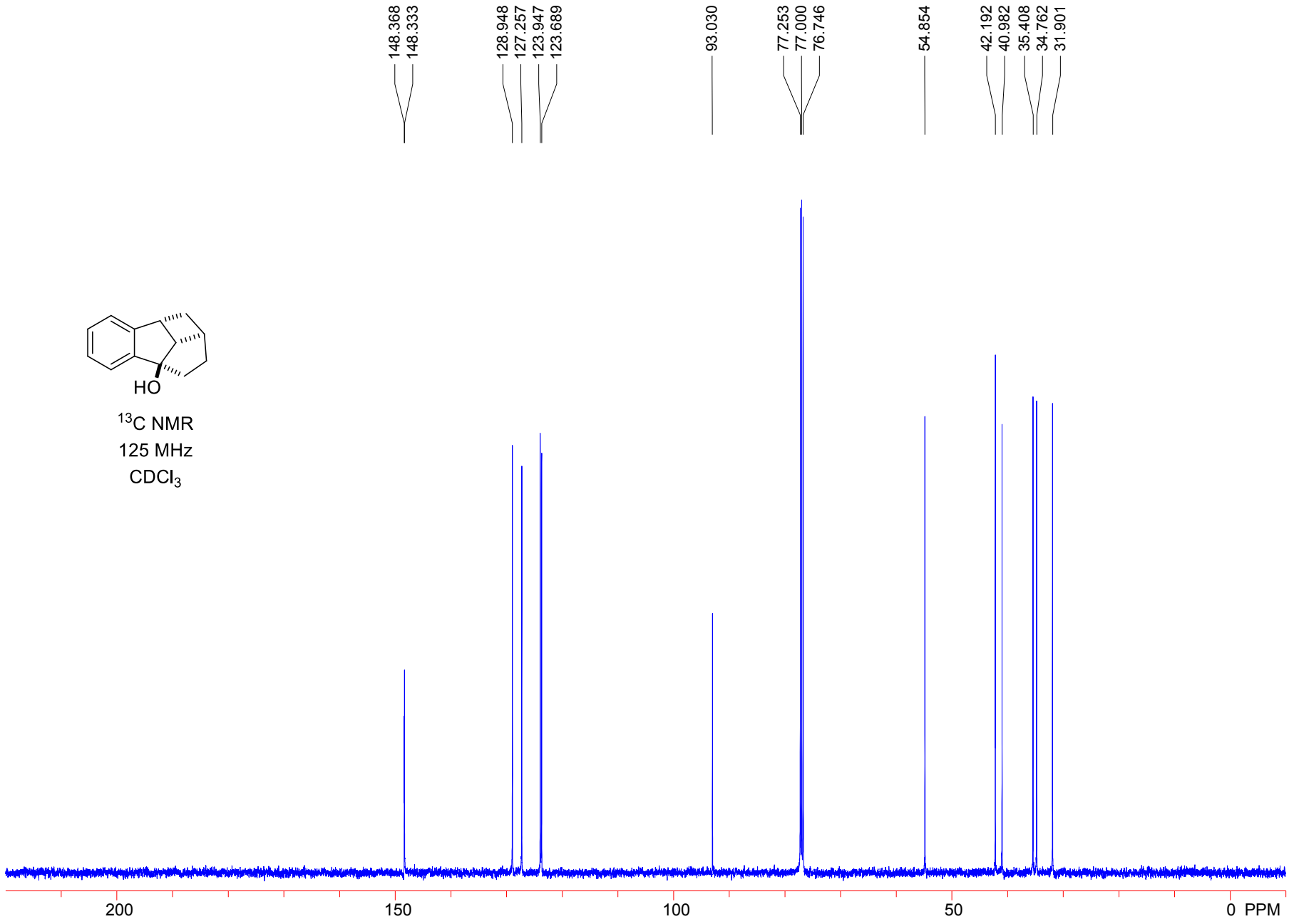
1.343
1.337
1.331
1.104
1.090
1.080
HO
1H NMR
500 MHz
CDCl3
2.04
1.00
1.00
1.00
1.00
1.02
1.03
3.01
1.05
1.01
1.00
8
6
4
2
0
PPM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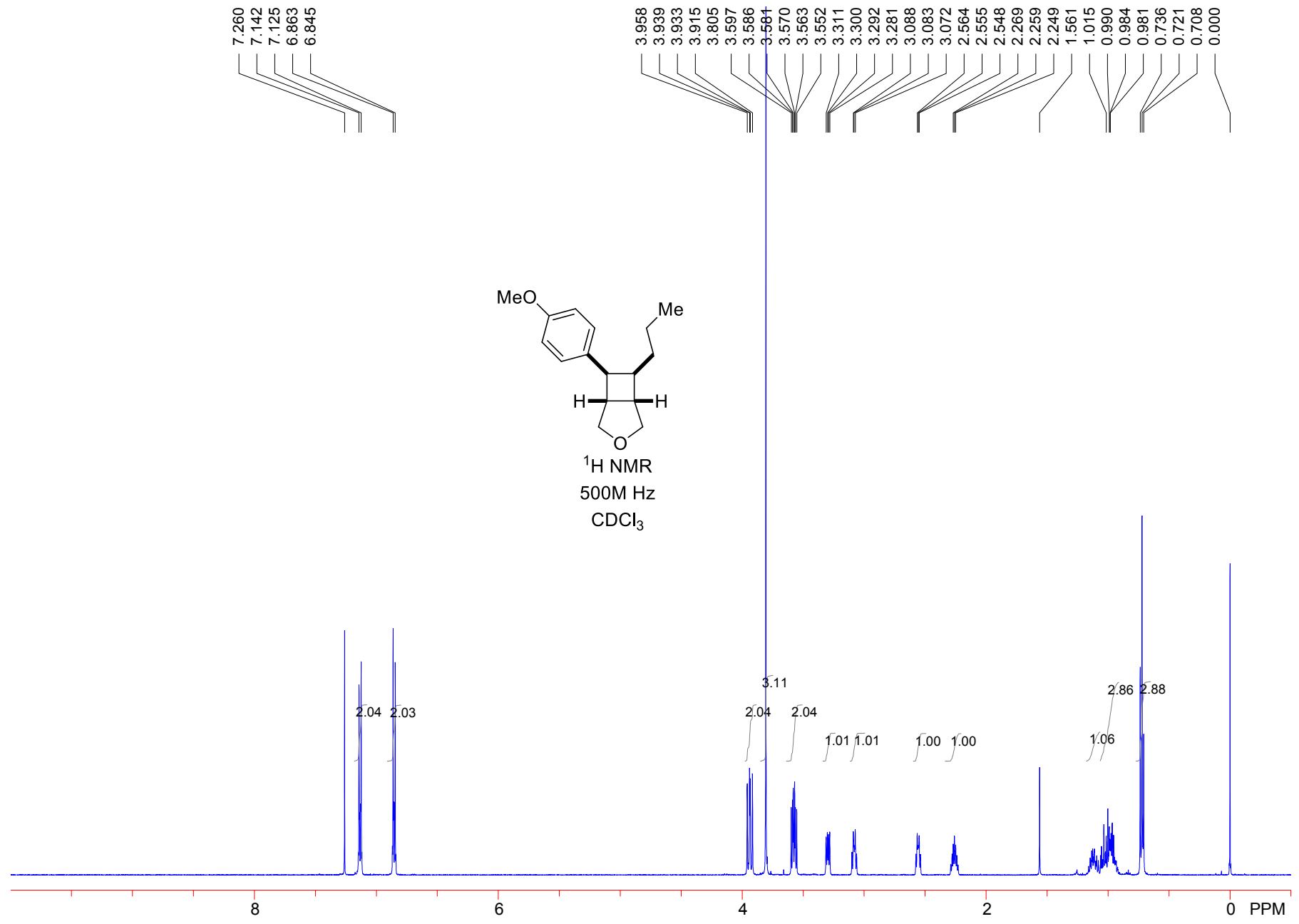
148.333
128.948
127.257
123.947
123.689
93.030
77.253
77.000
76.746
54.854
42.192
40.982
35.408
34.762
31.901
HO
^{13}C NMR
125 MHz
$CDCl_3$
200
150
100
50
0 PPM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7.142
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6.863
6.845
3.958
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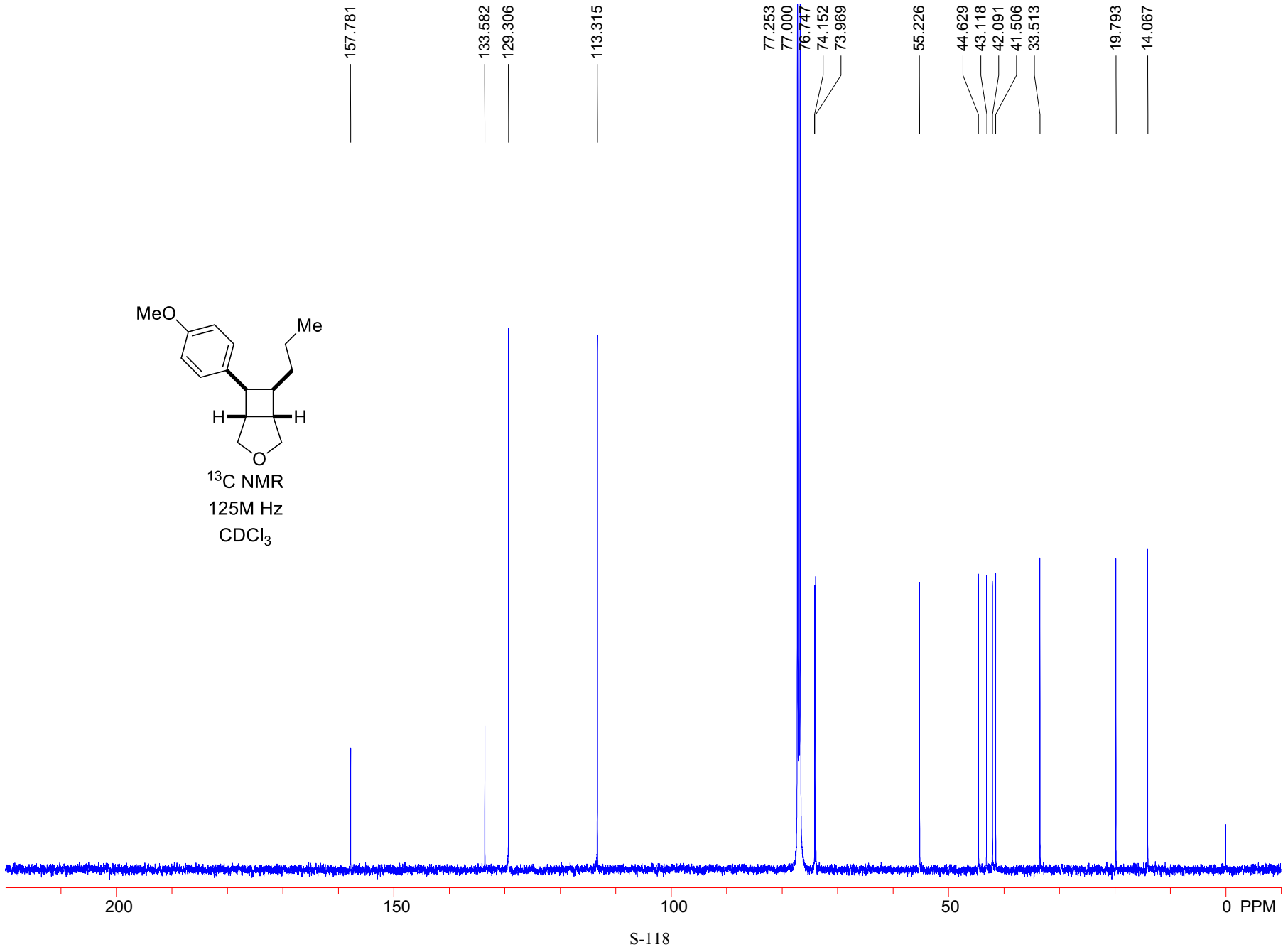
3.586
3.581
3.570
3.563
3.552
3.311
3.300
3.292
3.281
3.088
3.083
3.072
2.564
2.555
2.548
2.269
2.259
2.249
1.561
1.015
0.990
0.984
0.981
0.736
0.721
0.708
0.000
MeO
Me
H
H
O
1H NMR
500M Hz
CDCl3
2.04
2.03
3.11
2.04
2.04
1.01
1.01
1.00
1.00
1.06
2.86
2.88
8
6
4
2
0
PPM


157.781
133.582
129.306
113.315
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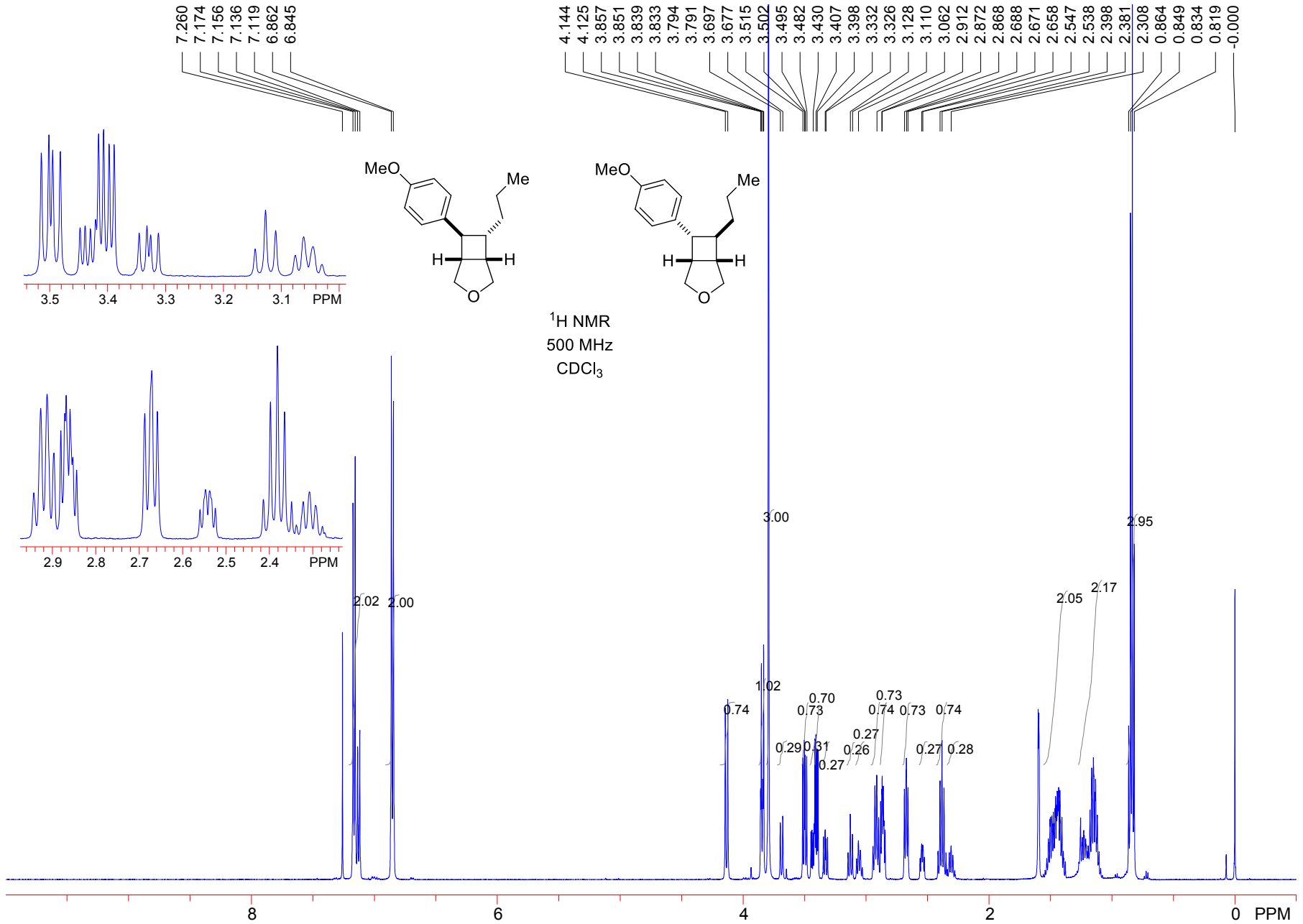
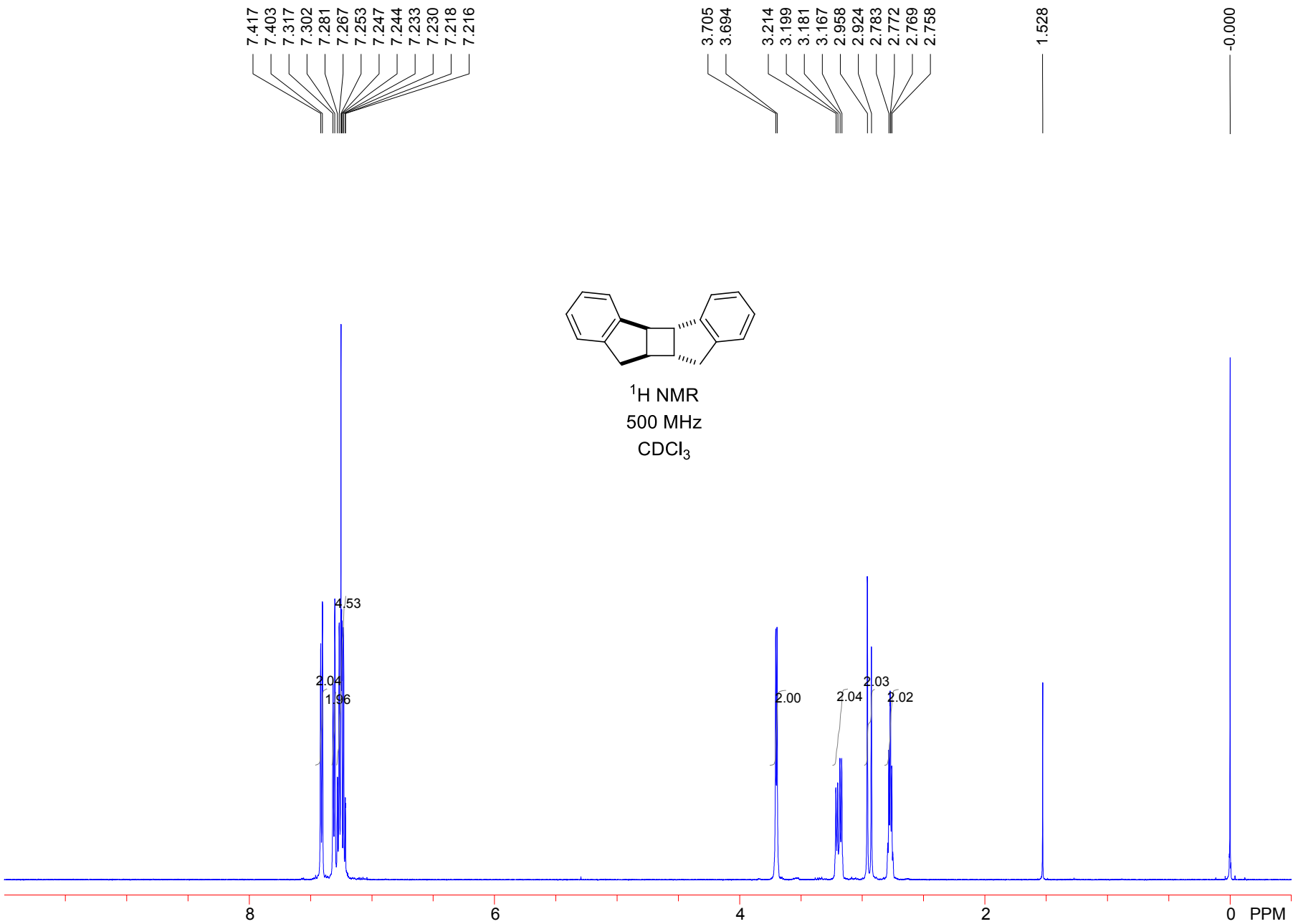
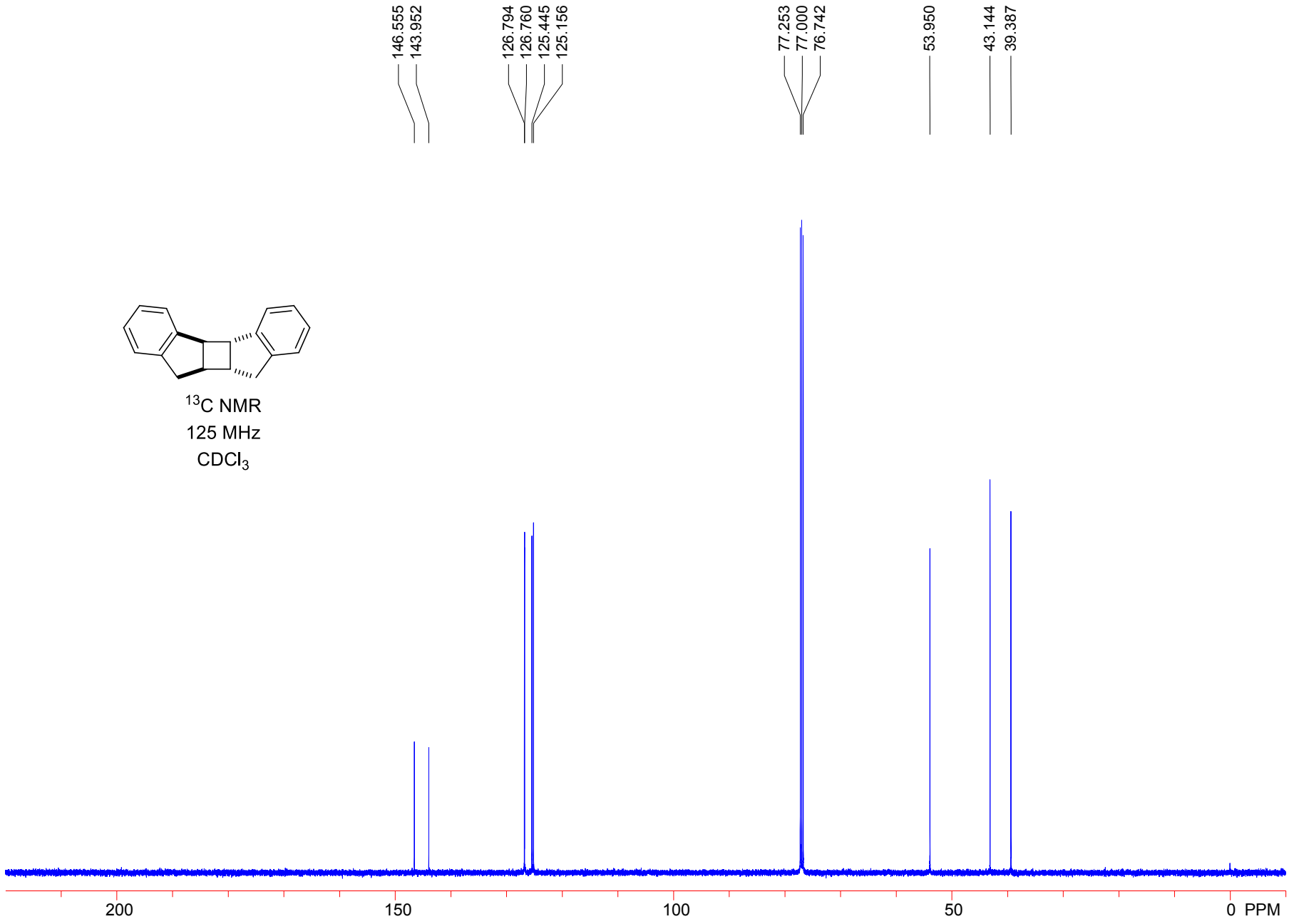
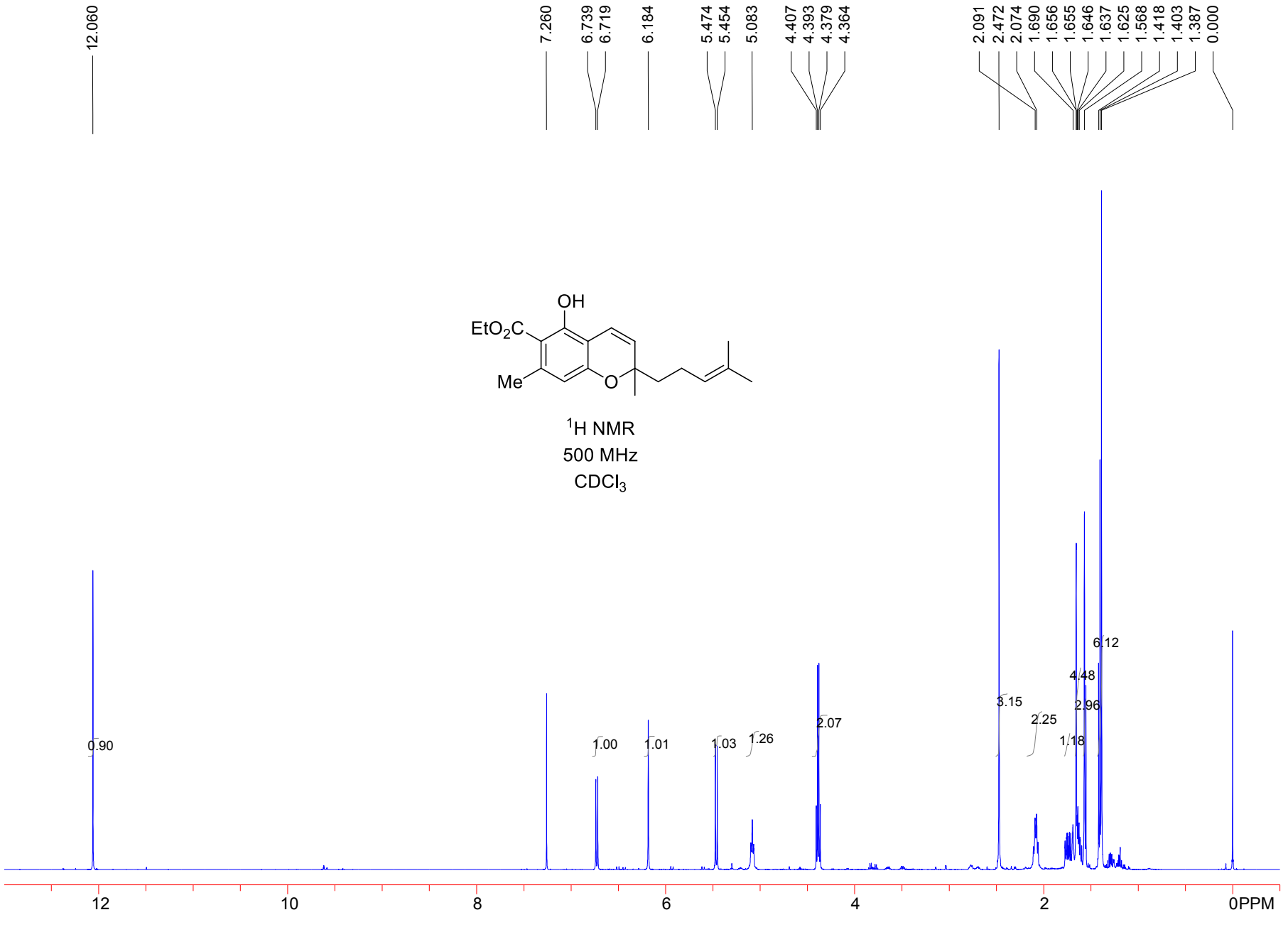
77.000
76.747
74.152
73.969
55.226
44.629
43.118
42.091
41.506
33.513
19.793
14.067
MeO
Me
H
H
O
13C NMR
125M Hz
CDCl3
200
150
100
50
0 PPM


7.260
7.174
7.156
7.136
7.119
6.862
6.845
4.144
4.125
3.857
3.851
3.839
3.833
3.794
3.791
3.697
3.677
3.515
3.502
3.495
3.482
3.430
3.407
3.398
3.332
3.326
3.128
3.110
3.062
2.912
2.872
2.868
2.688
2.671
2.658
2.547
2.538
2.398
2.381
2.308
0.864
0.849
0.834
0.819
-0.000
MeO
Me
H
H
O
MeO
Me
H
H
O
3.5 3.4 3.3 3.2 3.1 PPM
2.9 2.8 2.7 2.6 2.5 2.4 PPM
1H NMR
500 MHz
CDCl3
2.02
2.00
3.00
2.95
2.05
2.17
1.02
0.74
0.70
0.73
0.29
0.31
0.27
0.27
0.26
0.73
0.74
0.73
0.74
0.27
0.28
8
6
4
2
0 PPM


7.417
7.403
7.317
7.302
7.281
7.267
7.253
7.247
7.244
7.233
7.230
7.218
7.216
3.705
3.694
3.214
3.199
3.181
3.167
2.958
2.924
2.783
2.772
2.769
2.758
1.528
-0.000
1H NMR
500 MHz
CDCl3
4.53
2.04
1.96
2.00
2.04
2.03
2.02
8
6
4
2
0
PPM


146.555
143.952
126.794
126.760
125.445
125.156
77.253
77.000
76.742
53.950
43.144
39.387
^{13}C NMR
125 MHz
$CDCl_3$
200
150
100
50
0 PPM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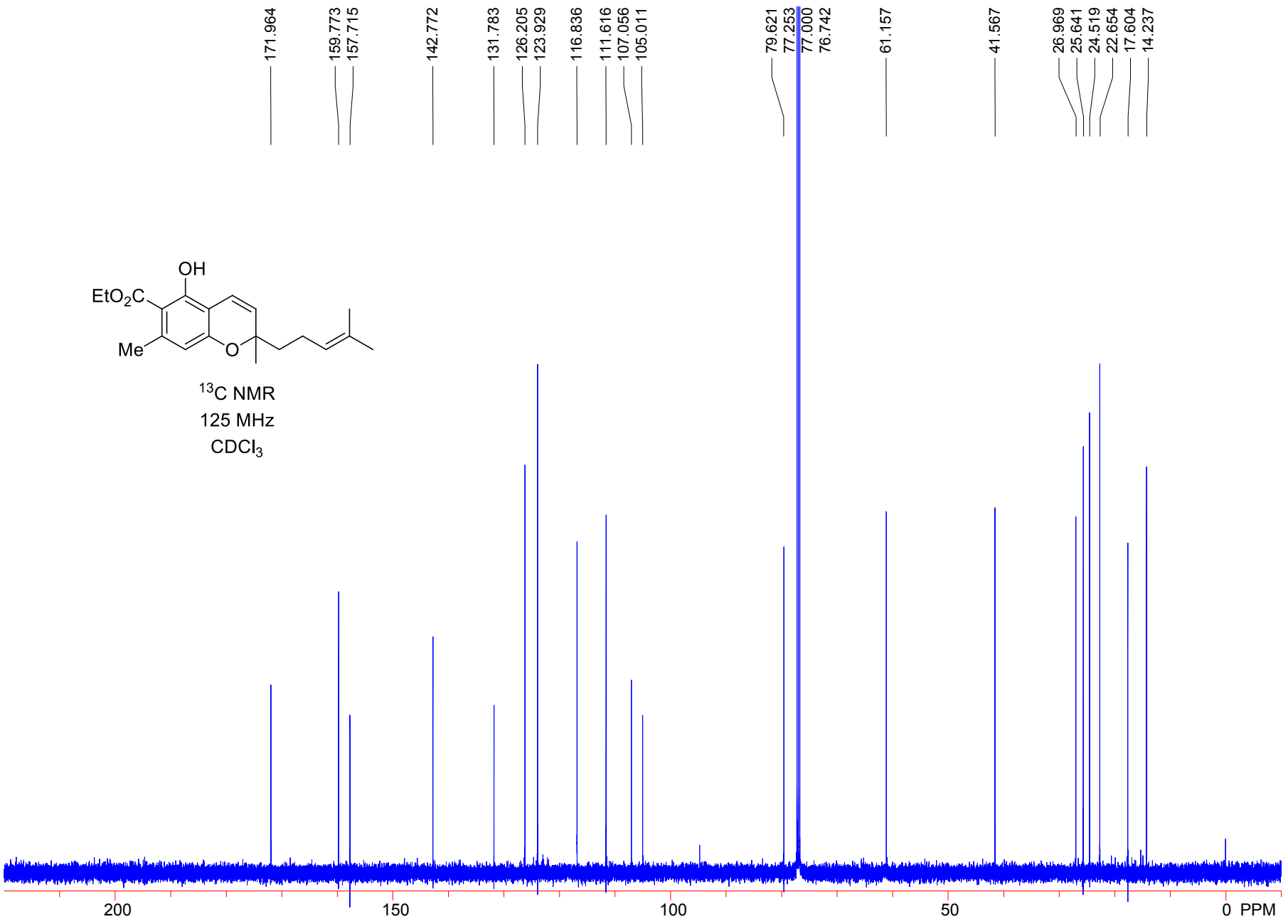
7.260
6.739
6.719
6.184
5.474
5.454
5.083
4.407
4.393
4.379
4.364
2.091
2.472
2.074
1.690
1.656
1.655
1.646
1.637
1.625
1.568
1.418
1.403
1.387
0.000
OH
EtO2C
Me
O
1H NMR
500 MHz
CDCl3
0.90
1.00
1.01
1.03
1.26
2.07
3.15
2.25
1.18
2.96
4.48
6.12
12
10
8
6
4
2
0PPM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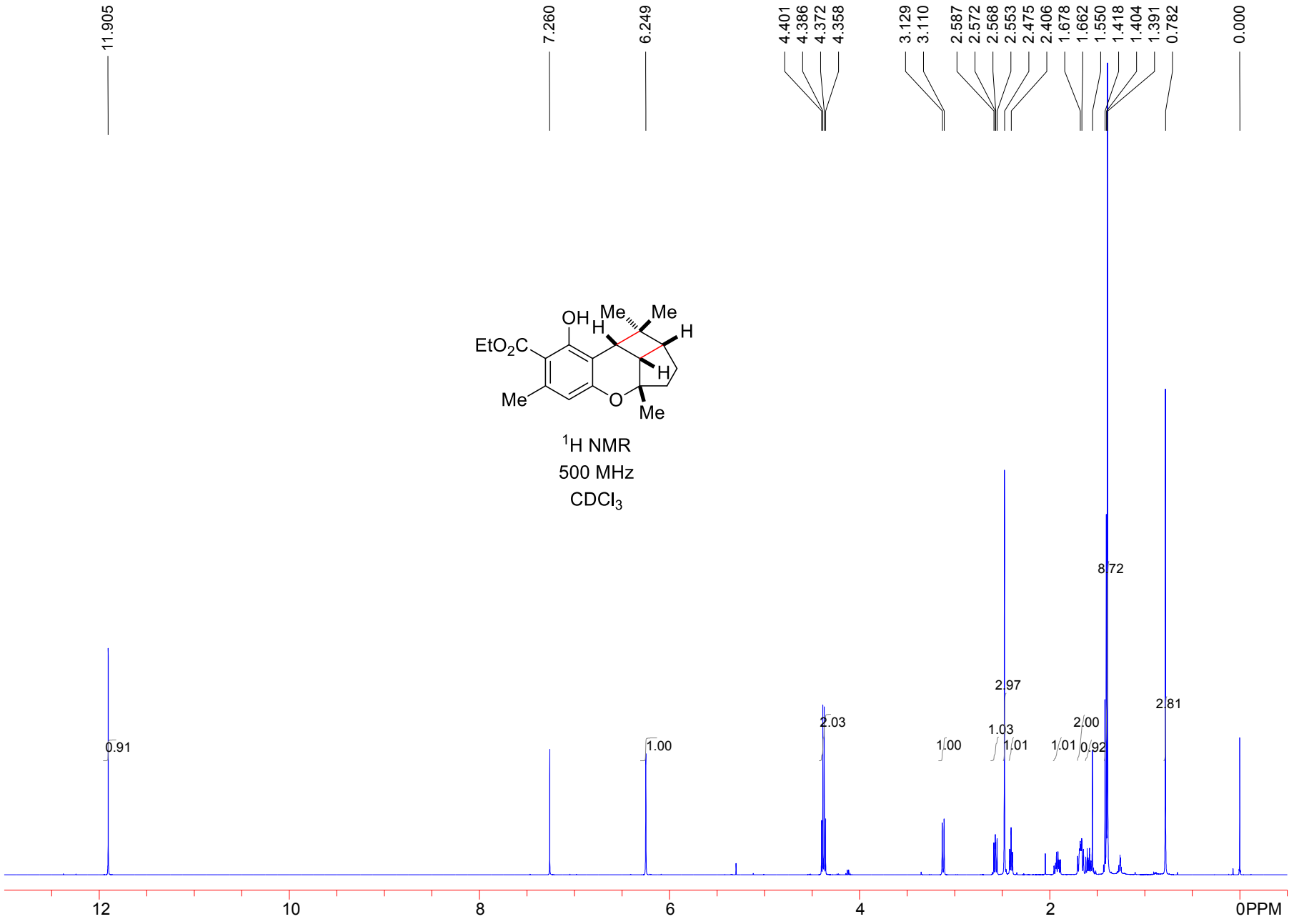
159.773
157.715
142.772
131.783
126.205
123.929
116.836
111.616
107.056
105.011
79.621
77.253
77.000
76.742
61.157
41.567
26.969
25.641
24.519
22.654
17.604
14.237
OH
EtO2C
Me
O
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM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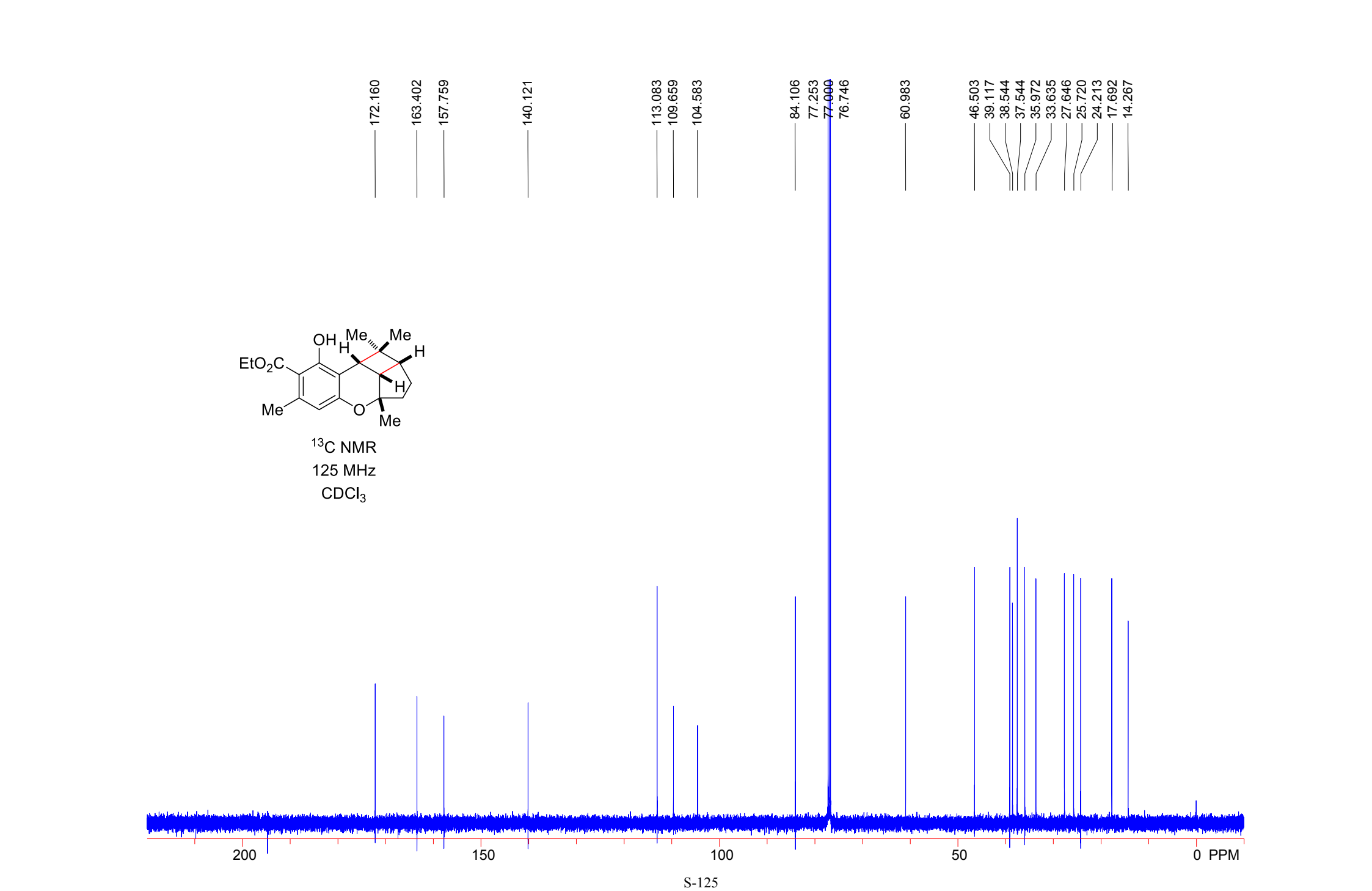
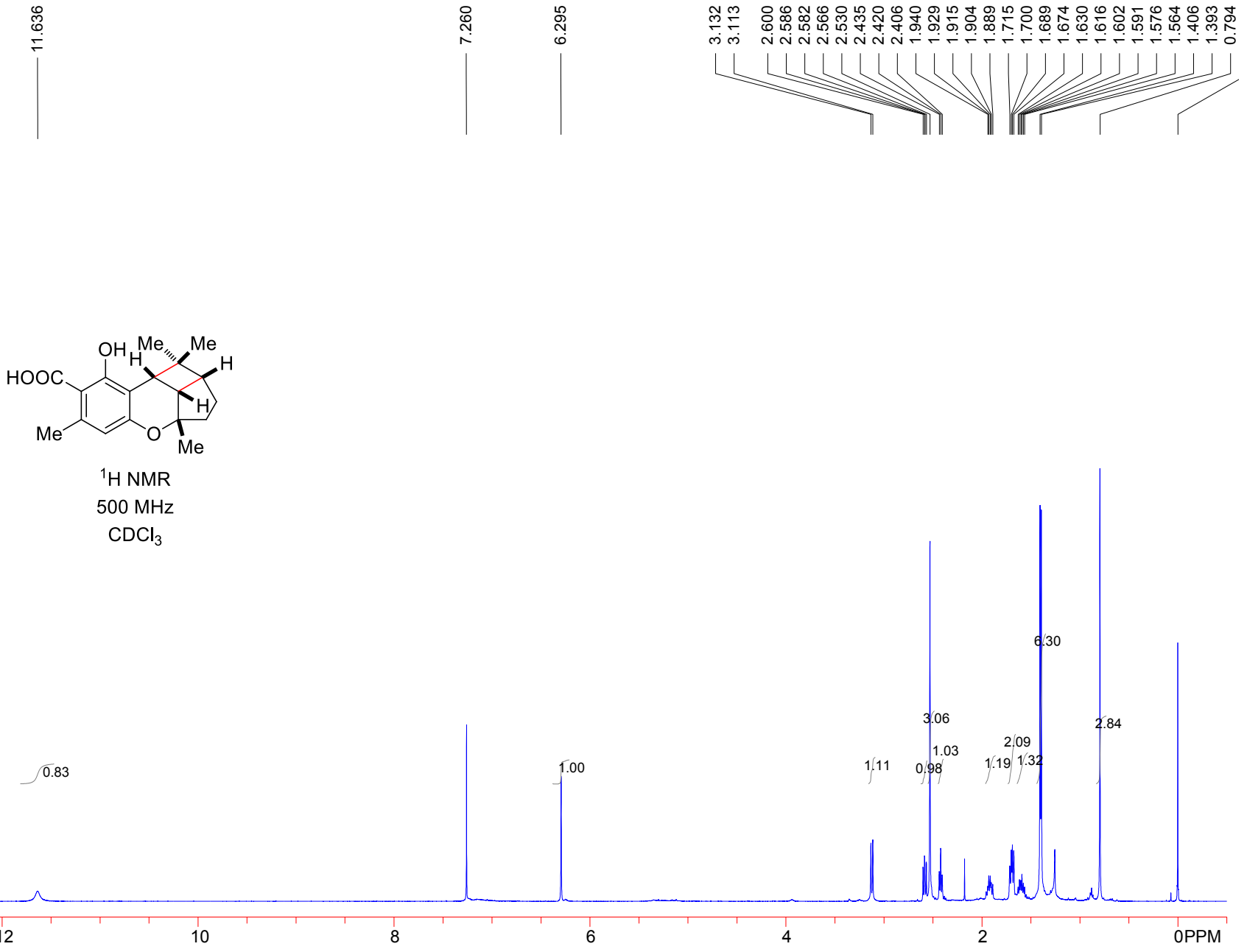
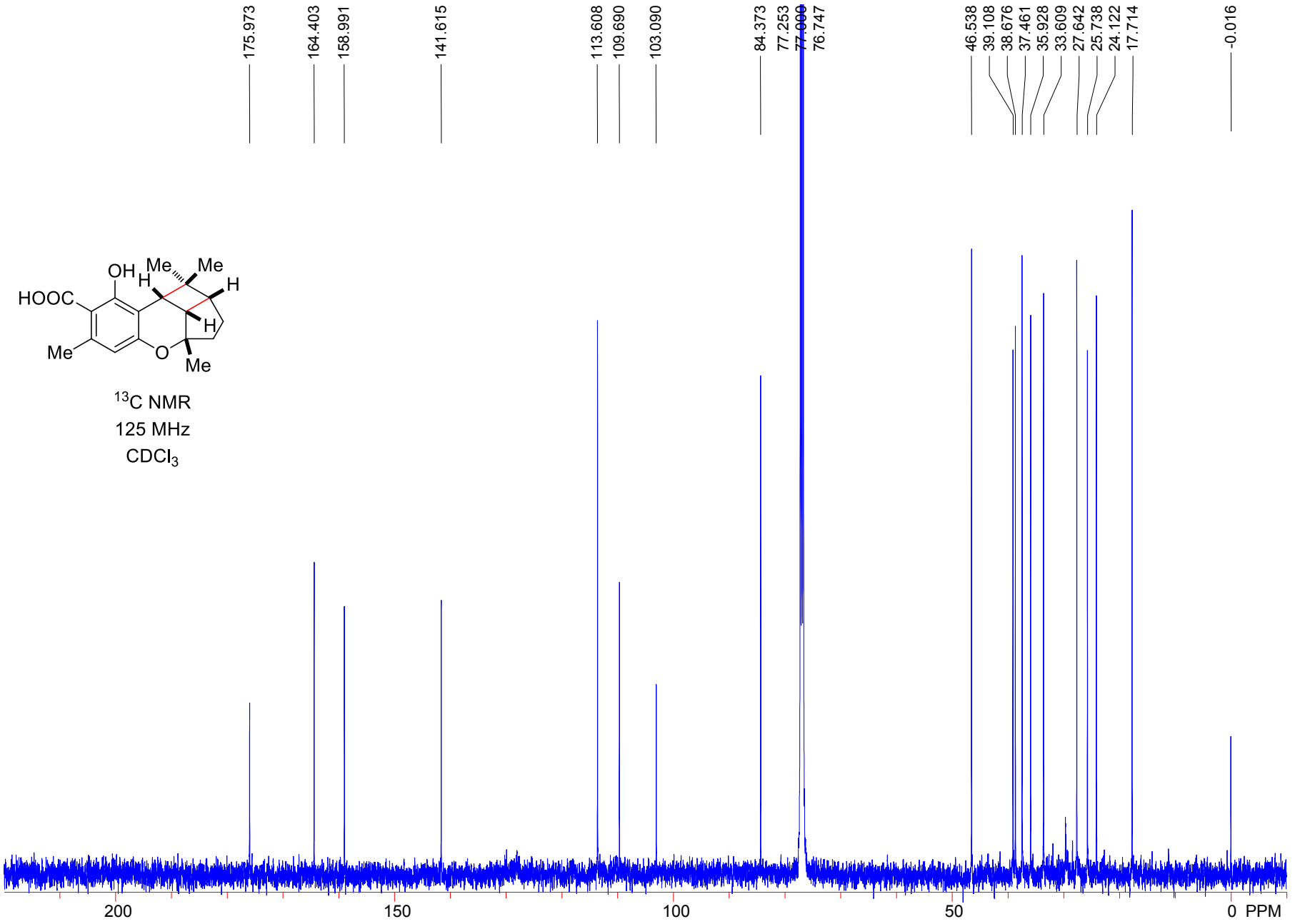
7.260
6.249
4.401
4.386
4.372
4.358
3.129
3.110
2.587
2.572
2.568
2.553
2.475
2.406
1.678
1.662
1.550
1.418
1.404
1.391
0.782
0.000
OH
Me
Me
H
H
EtO2C
Me
O
Me
1H NMR
500 MHz
CDCl3
8.72
2.97
2.81
2.03
2.00
1.03
0.91
1.00
1.00
1.01
1.01
0.92
12
10
8
6
4
2
0PPM


172.160
163.402
157.759
140.121
113.083
109.659
104.583
84.106
77.253
77.000
76.746
60.983
46.503
39.117
38.544
37.544
35.972
33.635
27.646
25.720
24.213
17.692
14.267
OH
Me
Me
H
H
EtO2C
H
Me
O
Me
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM


11.636
7.260
6.295
3.132
3.113
2.600
2.586
2.582
2.566
2.530
2.435
2.420
2.406
1.940
1.929
1.915
1.904
1.889
1.715
1.700
1.689
1.674
1.630
1.616
1.602
1.591
1.576
1.564
1.406
1.393
0.794
OH
Me
Me
H
HOOC
H
H
Me
O
Me
1H NMR
500 MHz
CDCl3
0.83
1.00
1.11
0.98
3.06
1.03
1.19
2.09
1.32
6.30
2.84
12
10
8
6
4
2
0PPM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164.403
158.991
141.615
113.608
109.690
103.090
84.373
77.253
77.000
76.747
46.538
39.108
38.676
37.461
35.928
33.609
27.642
25.738
24.122
17.714
-0.016
OH
H
Me
Me
H
HOOC
H
Me
O
Me
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM