Supporting Information for:

Radical Cation Diels–Alder Cycloadditions by Visible Light Photocatalysis

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I. General Information

Methyl viologen bis(hexafluorophosphate) ($MV(PF_6)_2$)[1], tris(bipyridyl)ruthenium(II) bis(hexafluorophosphate) ($Ru(bpy)_3(PF_6)_2$)[1] and tris(bipyrizyl)ruthenium(II) bis(hexafluorophosphate) ($Ru(bpz)_3(PF_6)_2$) [2] were prepared as previously described. *trans*-1-Phenyl-1,3-butadiene,[3] methyl 2,4-pentadienoate,[4] 1-(4-methoxyphenyl)cyclohexene,[5] 1-acetoxy-4-propenylbenzene,[6] (*E*)-1-(*tert*-butyldimethylsilyloxy)-3-(4-methoxyphenyl)-2-propene[7], (Z)-1-(4-methoxyphenyl)propene[8], (*E*)-4-methoxystyryl acetate[9] and (*E*)-(1-propenyloxy)benzene[10] were synthesized as previously described, and all spectroscopic data were consistent with those reported for these compounds. 1-(4-Methoxyphenyl)cyclopentene was synthesized using the same method as 1-(4-methoxyphenyl)cyclohexene, and its spectroscopic data were consistent with reported values.[11] (*E*)-*tert*-Butyldimethyl(4-(prop-1-en-1-yl)phenoxy)silane is a new compound and its synthesis is reported below. All dienes were purified prior to use. MeCN, THF, Et_2O and CH_2Cl_2 were purified by elution through alumina as described by Grubbs.[12] A 23 W (1200 lumens) SLI Lighting Mini-Lynx compact fluorescent light bulb was used for all photochemical reactions unless otherwise stated. Flash column chromatography was performed with Silicycle 40-63Å silica (230-400 mesh). Diastereomer ratios for all compounds were determined by ^{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 unless otherwise stated. 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.

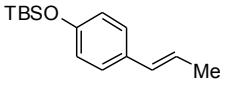
II. Catalyst synthesis.

2,2'-Bipyrazine (bpz). Chloropyrazine (5.0 g, 43.7 mmol), $Pd(PPh_3)_4$ (1.5 g, 1.3 mmol), tetrabutylammonium bromide (14.0 g, 43.4 mmol), K_2CO_3 (20.5 g, 148.3 mmol) and DMF (42 mL) were placed together in a 250 mL round-bottomed flask. The reaction was heated to 140 °C, open to the atmosphere. After 16 h, the reaction was cooled to ambient temperature and filtered through celite. The filter pad was rinsed with CH_2Cl_2, and the filtrate was washed with water (400 mL). The aqueous phase was extracted 3 times with CH_2Cl_2. The combined organic layers were washed 3 times with water, dried over $MgSO_4$ and concentrated by rotary evaporation. Flash column chromatography (1:1 hexanes/ethyl acetate) gave the crude product,

which was triturated with MeOH to afford 1.46 g (9.23 mmol, 42 % yield) of a pale yellow solid. All spectroscopic data were consistent with previously reported values.[13]

$Ru(bpz)_3(BArF)_2$. A solution of tris(bipyrizyl)ruthenium(II) dichloride[14] (450 mg, 0.70 mmol) in 30 mL water was placed in a 100 mL round-bottomed flask. Sodium (tetrakis[(3,5-trifluoromethyl)phenyl]borate)[15] (1.36 g, 1.53 mmol) dissolved in methanol (10 mL) was added to the reaction mixture followed by water (10 mL). The resulting heterogeneous suspension was filtered through a fritted glass funnel. The collected solids were dissolved in 1:1 acetone:CH_2Cl_2 and purified by alumina flash column chromatography using CH_2Cl_2 as the eluent. Upon concentration by rotary evaporation, the crude product was recrystallized from CH_2Cl_2:benzene to afford 820 mg (0.356 mmol, 51 % yield) of an orange solid. IR (neat) 3000, 2090, 1653, 1265 cm^{-1}. ^1H NMR: (500 MHz, CD_3CN) δ 9.8 (d, J = 1.3 Hz, 6H), 8.6 (d, J = 3.2 Hz, 6H), 7.8 (dd, J = 3.2, 1.3 Hz, 6H), 7.7 (m, 16H), 7.7 (s, 8H). ^{13}C NMR: (125 MHz, CD_3CN) δ 162.7 (q, J = 50.5 Hz), 151.3, 149.8, 148.1, 146.5, 135.7, 130.0 (q, J = 31.6 Hz), 125.5 (q, J = 124.44 Hz), 118.7.

III. Synthesis of cyclization substrates



(*E*)-*tert*-Butyldimethyl(4-(prop-1-en-1-yl)phenoxy)silane. A solution of ethyl triphenylphosphonium iodide (4.18 g, 10.0 mmol) in 50 mL dry THF was placed in a flame-dried 100 mL round-bottomed flask. The solution was cooled to 0 °C, and *n*-BuLi (1.6 M in hexanes, 10.0 mmol) was added dropwise. After stirring at 0 °C for 30 minutes, *p*-hydroxybenzaldehyde (611 mg, 5.0 mmol) was added. The reaction mixture was gradually warmed to room temperature. After 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted twice with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. Flash column chromatography (gradient, 15:1 to 5:1 hexanes/EtOAc) afforded 472 mg (3.6 mmol, 70% yield) of (*E*)-4-(prop-1-en-1-yl)phenol. The phenol (150 mg, 1.1 mmol) was dissolved in 0.5 mL DMF in a 10 mL round-bottom flask, to which imidazole (152 mg, 2.2 mmol) and TBSCl (253 mg, 1.7 mmol) were added. After 8 h, flash column chromatography (gradient, 50:1 to 30:1 hexanes/EtOAc) afforded 245 mg (1.0 mmol, 88% yield) of a clear oil. IR (neat) 3026, 2959, 2253, 1508, 1261, 907 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.19 (d, J = 8.5 Hz, 2H), 6.76 (d, J = 8.5 Hz, 2H), 6.33 (dd, J = 15.4, 1.5 Hz, 1H), 6.08 (dq, J = 15.4, 6.4 Hz, 1H), 1.85 (dd, J = 6.6, 1.5 Hz, 3H), 0.97 (s, 9H), 0.18 (s, 6H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 154.6, 131.3, 130.4, 126.8, 123.6, 120.1, 25.7, 18.4, 18.2, -4.4. HRMS (ESI) calculated for $[C_{15}H_{24}OSi]^+$ requires *m/z* 248.1591, found *m/z* 248.1595.

IV. Photocycloadditions

General Procedure: A solution of the dienophile in CH_2Cl_2 (0.08 M) was placed in a 25 mL round-bottomed flask. In a dark hood, the diene (2–3 equiv) and $Ru(bpz)_3(BArF)_2$ (0.005– 0.03 equiv) were added to the flask.. The reaction was stirred at ambient temperature in front of a 23 W CFL bulb. Upon consumption of the dienophile, the reaction was eluted through a short pad of silica using EtOAc. After concentration by rotary evaporation, the pure cycloadduct was isolated by flash column chromatography.

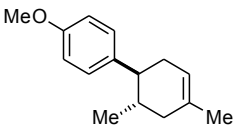


Chart 1, compound 3. Experiment 1: Prepared according to the General Procedure using 100.2 mg (0.676 mmol) *trans*-anethole, 202 μL (2.02 mmol) isoprene, 7.8 mg (0.0034 mmol) $Ru(bpz)_3(BArF)_2$, 8.4 mL CH_2Cl_2 and an irradiation time of 1.0 h. Elution through a pad of silica using EtOAc and concentration by rotary evaporation afforded 145 mg (0.670 mmol, 99%) of analytically pure cycloadduct as a clear oil. Experiment 2: 100.6 mg (0.679 mmol) *trans*-anethole, 202 μL (2.02 mmol) isoprene, 7.8 mg (0.0034 mmol) $Ru(bpz)_3(BArF)_2$ and 8.4 mL CH_2Cl_2. Isolated 142 mg (0.656 mmol, 97% yield, dr: >10:1). IR (neat) 2951, 2834, 1512, 1038 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.12 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 5.48 (bs, 1H), 3.82 (s, 3H), 2.33 (td, J = 11.3, 5.1 Hz, 1H), 2.25 (m, 1H), 2.19 (m,1H), 2.12 (dd, J = 17.6, 4.0 Hz, 1H), 1.92 (qd, J = 5.7, 1.7 Hz, 1H), 1.83 (m, 1H), 1.72 (s, 3H), 0.74 (d, J = 6.2 Hz, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 157.8, 138.2, 133.8, 128.5, 120.9, 113.7, 55.2, 47.0, 39.9, 35.3, 34.0, 23.4, 20.3. HRMS (EI) calculated for $[C_{15}H_{20}O]^+$ requires *m/z* 216.1509, found *m/z* 216.1511.

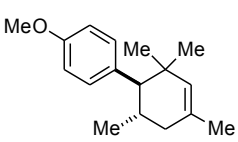


Chart 1, compound 7. Experiment 1: Prepared according to the General Procedure using 100.4 mg (0.677 mmol) *trans*-anethole, 262 μL (2.02 mmol) 2,4-dimethyl-1,3-pentadiene, 7.8 mg (0.0034 mmol) $Ru(bpz)_3(BArF)_2$, 8.4 mL CH_2Cl_2 and an irradiation time of 2.0 h. Purification by flash column chromatography (50:1 hexanes/EtOAc) afforded 149 mg (0.610 mmol, 90 %) of a clear oil. Experiment 2: 100.1 mg (0.675 mmol) *trans*-anethole, 262 μL (2.02 mmol) 2,4-dimethyl-1,3-

pentadiene, 7.8 mg (0.0034 mmol) $Ru(bpz)_3(BArF)_2$ and 8.4 mL CH_2Cl_2. Isolated 152 mg (0.622 mmol, 92 % yield, dr: >10:1). IR (neat) 2956, 1512, 907, 733 cm^{-1}. ^1H NMR: (500 MHz, C_6D_6) δ 6.96 (dd, J = 20.3, 7.5 Hz, 2H), 6.81 (dd, J = 46.7, 7.5 Hz, 2H), 5.28 (s, 1H), 3.36 (s, 3H), 2.20 (d, J = 12.1 Hz, 1H), 2.12 (m, 1H), 1.97 (dd, J = 17.6, 4.9 Hz, 1H), 1.69 (d, J = 10.4 Hz, 1H), 1.66 (s, 3H), 0.94 (s, 1H), 0.90 (s, 1H), 0.77 (d, J = 6.4 Hz, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 157.8, 133.1, 130.3, 129.3, 113.2, 112.1, 57.5, 55.0, 40.3, 36.0, 29.9, 28.7, 24.4, 23.0, 20.6. HRMS (EI) calculated for $[C_{17}H_{24}O]^+$ requires *m/z* 244.1822, found *m/z* 244.1815.

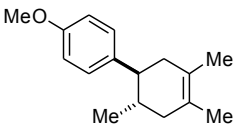


Chart 1, compound 8. Experiment 1: Prepared according to the General Procedure using 99.6 mg (0.672 mmol) *trans*-anethole, 230 μL (2.03 mmol) 2,3-dimethyl-1,3-butadiene, 7.8 mg (0.0034 mmol) $Ru(bpz)_3(BArF)_2$, 8.4 mL CH_2Cl_2 and an irradiation time of 1.0 h. Elution through a pad of silica using EtOAc and concentration by rotary evaporation afforded 154 mg (0.669 mmol, 99%) of analytically pure cycloadduct as a clear oil. Experiment 2: 100.7 mg (0.679 mmol) *trans*-anethole, 230 μL (2.03 mmol) 2,3-dimethyl-1,3-butadiene, 7.8 mg (0.0034 mmol) $Ru(bpz)_3(BArF)_2$ and 8.4 mL CH_2Cl_2. Isolated 150 mg (0.651 mmol, 96% yield, dr: >10:1). IR (neat) 3032, 2888, 1456, 1246 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.07 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 3.77 (s, 3H), 2.33 (td, J = 10.8, 5.2 Hz, 1H), 2.16 (m, 1H), 2.08 (m, 2H), 1.84 (m, 2H), 1.64 (s, 3H), 1.61 (s, 3H), 0.70 (d, J = 6.1 Hz, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 157.8, 138.2, 128.5, 125.5, 125.3, 113.7, 55.2, 47.9, 41.9, 41.7, 34.3, 20.1, 18.8, 18.7. HRMS (EI) calculated for $[C_{16}H_{22}O]^+$ requires *m/z* 230.1666, found *m/z* 230.1665.

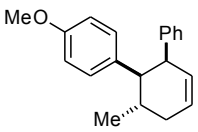


Chart 1, compound 9. Experiment 1: Prepared according to the General Procedure using 99.8 mg (0.673 mmol) *trans*-anethole, 176 mg (1.35 mmol) 1-phenyl-1,3-butadiene, 7.8 mg (0.0034 mmol) $Ru(bpz)_3(BArF)_2$, 8.4 mL CH_2Cl_2 and an irradiation time of 20 h. Purification by flash column chromatography (50:1 hexanes/EtOAc) afforded 134 mg (0.481 mmol, 72%) of a clear oil. Experiment 2: 100.2 mg (0.676 mmol) *trans*-anethole, 176 mg (1.35 mmol) 1-phenyl-1,3-butadiene, 7.8 mg (0.0034 mmol) $Ru(bpz)_3(BArF)_2$ and 8.4 mL CH_2Cl_2. Isolated 136 mg (0.489 mmol, 72% yield, dr: >10:1). IR (neat) 3017, 2966, 2873, 1497, 1055 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.09 (m, 3H), 6.74 (d, J = 8.0 Hz, 2H), 6.60 (d, J = 9.0 Hz, 2H), 6.47 (d, J = 8.0 Hz, 2H), 5.98 (m, 1H), 5.83 (m, 1H), 3.74 (s, 3H), 3.49 (m, 1H), 2.88 (dd, J = 11.8, 5.9 Hz, 1H), 2.45 (dt, J = 18.1, 5.6 Hz, 1H), 2.16 (m, 1H), 1.94 (m, 1H), 0.71 (d, J = 6.6 Hz, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 157.5, 140.7, 134.3, 130.6, 130.1, 129.5, 127.5, 127.1, 126.0, 112.7, 55.1, 51.8, 48.7, 35.3, 26.3, 20.3. HRMS (EI) calculated for $[C_{20}H_{22}O]^+$ requires *m/z* 278.1666, found *m/z* 278.1666.

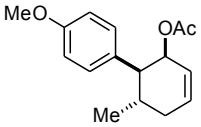


Chart 1, compound 10. Experiment 1: Prepared according to the General Procedure using 100.3 mg (0.677 mmol) *trans*-anethole, 227 mg (2.02 mmol) 1-acetoxy-1,3-butadiene, 47 mg (0.0202 mmol) $Ru(bpz)_3(BArF)_2$, 8.4 mL CH_2Cl_2 and an irradiation time of 18 h. Purification by flash column chromatography (gradient, 25:1 to 15:1 to 10:1 to 5:1 hexanes/EtOAc) afforded 117 mg (0.449 mmol, 66%) of a white solid. Experiment 2: 100.1 mg (0.675 mmol) *trans*-anethole, 230 mg (2.05 mmol) 1-acetoxy-1,3-butadiene, 47 mg (0.0202 mmol) $Ru(bpz)_3(BArF)_2$ and 8.4 mL CH_2Cl_2. Isolated 120 mg (0.461 mmol, 68% yield, dr: >10:1). IR (neat) 3034, 2952, 1730, 1514, 1179 cm^{-1}. ^1H NMR: (500 MHz, C_6D_6) δ 7.02 (dd, J = 8.7, 2.0 Hz, 2H), 6.79 (dd, J = 8.7, 1.8 Hz, 2H), 6.03 (m, 1H), 5.78 (ddd, J = 9.8, 5.1, 2.2 Hz, 1H), 5.44 (t, J = 4.2 Hz, 1H), 3.33 (s, 1H), 2.41 (dd, J = 12.0, 3.7 Hz, 1H), 2.28 (m, 1H), 2.08 (dtd, J = 18.5, 5.0, 1.0 Hz, 1H), 1.60 (s, 3H), 1.55 (m, 1H), 0.72 (d, J = 6.5 Hz, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 170.1, 158.3, 132.8, 130.1, 124.9, 113.3, 69.9, 55.1, 50.9, 35.0, 26.7, 21.3, 19.7. HRMS (EI) calculated for $[C_{16}H_{20}O_3]^+$ requires *m/z* 260.1407, found *m/z* 260.1411.

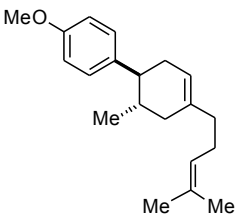


Chart 1, compound 11. Experiment 1: Prepared according to the General Procedure using 100.8 mg (0.680 mmol) *trans*-anethole, 350 μL (2.03 mmol) myrcene, 7.8 mg (0.0034 mmol) $Ru(bpz)_3(BArF)_2$, 8.4 mL CH_2Cl_2 and an irradiation time of 1.5 h. Purification by flash column chromatography (60:1 hexanes/EtOAc) afforded 170 mg (0.598 mmol, 88%) of a clear oil. Experiment 2: 100.5 mg (0.678 mmol) *trans*-anethole, 350 μL (2.03 mmol) myrcene, 7.8 mg (0.0034 mmol) $Ru(bpz)_3(BArF)_2$ and 8.4 mL CH_2Cl_2. Isolated 168 mg (0.591 mmol, 87% yield, dr: >10:1). IR (neat) 2966, 2834, 1513, 1247 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.08 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 5.46 (s, 1H), 5.14 (m, 1H), 3.78 (s, 3H), 2.31 (m, 1H), 2.20 (m, 2H), 2.09 (m, 3H), 1.99 (m, 2H), 1.88 (m, 1H), 1.80 (m, 1H), 1.70 (s, 3H), 1.62 (s, 3H), 0.71 (d, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 157.8, 138.2, 137.5, 131.4, 128.5, 124.4, 120.4, 113.7, 55.1, 47.0, 38.1, 37.5, 35.1, 33.9, 26.4, 25.7, 20.2, 17.7. HRMS (EI) calculated for $[C_{20}H_{28}O]^+$ requires *m/z* 284.2135, found *m/z* 284.2140.

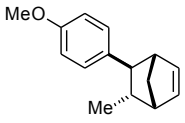


Chart 1, compound 12. Experiment 1: Prepared according to the General Procedure using 100.5 mg (0.678 mmol) *trans*-anethole, 170 μL (2.02 mmol) 1,3-cyclopentadiene, 7.8 mg (0.0034 mmol) $Ru(bpz)_3(BArF)_2$, 8.4 mL CH_2Cl_2 and an irradiation time of 1.5 h. Purification by flash column chromatography (55:1 hexanes/EtOAc) afforded 134 mg (0.625 mmol, 92%) of a colorless oil. Experiment 2: 100.2 mg (0.676 mmol) of *trans*-anethole, 170 μL (2.02 mmol) of 1,3-cyclopentadiene, 7.8 mg (0.0034 mmol) of $Ru(bpz)_3(BArF)_2$ and 8.4 mL of CH_2Cl_2. Isolated 131 mg (0.611 mmol, 90% yield, dr: 6:1). All spectroscopic data were consistent with previously reported values.[16]

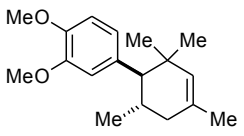


Chart 1, compound 13. Experiment 1: Prepared according to the General Procedure using 100.3 mg (0.563 mmol) 1,2-dimethoxy-4-propenylbenzene, 217 μL (1.68 mmol) 2,4-dimethyl-1,3-pentadiene, 6.5 mg (0.0028 mmol) $Ru(bpz)_3(BArF)_2$, 7.0 mL CH_2Cl_2 and an irradiation time of 1.0 h. Purification by flash column chromatography (gradient, 40:1 to 20:1 to 10:1 hexanes/EtOAc) afforded 117 mg (0.426 mmol, 76%) of a clear oil. Experiment 2: 100.1 mg (0.562 mmol) of 1,2-dimethoxy-4-propenylbenzene, 217 μL (1.68 mmol) 2,4-dimethyl-1,3-pentadiene, 6.5 mg (0.0028 mmol) $Ru(bpz)_3(BArF)_2$ and 7.0 mL CH_2Cl_2. Isolated 123 mg (0.448 mmol, 80% yield, dr: >10:1). IR (neat) 2953, 1518, 1255, 1031 cm^{-1}. ^1H NMR: (500 MHz, DMSO) δ 6.87 (d, J = 8.2 Hz, 1H), 6.73 (d, J = 2.1 Hz, 1H), 6.68 (dd, J = 8.2, 2.1 Hz, 1H), 5.21 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 2.19 (m, 2H), 2.11 (m, 1H), 1.74 (dd, J = 17.4, 8.4 Hz, 1H), 1.65 (s, 3H), 0.84 (s, 3H), 0.80 (s, 3H), 0.70 (d, J = 5.7 Hz, 3H); ^{13}C NMR: (125 MHz, DMSO) δ 149.1, 148.4, 134.4, 133.7, 130.0, 123.4, 116.6, 113.1, 58.0, 56.9, 56.6, 40.6, 36.4, 30.4, 28.9, 25.2, 23.1, 20.9. HRMS (EI) calculated for $[C_{18}H_{26}O_2]^+$ requires *m/z* 274.1928, found *m/z* 274.1928.

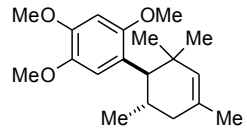


Chart 1, compound 14. Experiment 1: Prepared according to the General Procedure using 100.4 mg (0.482 mmol) *trans*-1,2,4-trimethoxy-5-(1-propenyl)benzene, 186 μL (1.44 mmol) 2,4-dimethyl-1,3-pentadiene, 5.5 mg (0.0024 mmol) $Ru(bpz)_3(BArF)_2$, 6.0 mL CH_2Cl_2 and an irradiation time of 8.0 h. Purification by flash column chromatography (gradient, 40:1 to 20:1 to 10:1 hexanes/EtOAc) afforded 107 mg (0.351 mmol, 73%) of a clear oil. Experiment 2: 100.3 mg (0.482 mmol) *trans*-1,2,4-trimethoxy-5-(1-propenyl)benzene, 186 μL (1.44 mmol) 2,4-dimethyl-1,3-pentadiene, 5.5 mg (0.0024 mmol) $Ru(bpz)_3(BArF)_2$ and 6.0 mL CH_2Cl_2. Isolated 104 mg (0.342 mmol, 71% yield, dr: >10:1). IR (neat) 2928, 1512, 1249, 834 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 6.645 (s, 1H), 6.534 (s, 1H), 5.208 (bs, 1H), 3.888 (s, 3H), 3.819 (s, 3H), 3.757 (s, 3H), 2.924 (d, J = 11.4 Hz, 1H), 2.098 (m, 2H), 1.788 (dd, J = 18.4, 11.4 Hz, 1H), 1.667 (s, 3H), 0.832 (s, 3H), 0.793 (s, 3H), 0.690 (d, J = 6.0 Hz, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 153.1, 147.4, 142.3, 133.6, 130.2, 121.7, 114.5, 97.7, 56.8, 56.8, 55.9, 46.9, 40.6, 36.8, 29.6, 28.8, 25.1, 23.3, 20.5. HRMS (EI) calculated for $[C_{19}H_{28}O_3]^+$ requires *m/z* 304.2033, found *m/z* 304.2039.

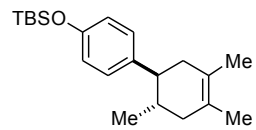


Chart 1, compound 15. Experiment 1: Prepared according to the General Procedure using 100.7 mg (0.405 mmol) (*E*)-*tert*-butyldimethyl(4-(prop-1-en-1-yl)phenoxy)silane, 137 μL (1.21 mmol) 2,3-dimethyl-1,3-butadiene, 4.6 mg (0.0020 mmol) $Ru(bpz)_3(BArF)_2$, 5.0 mL CH_2Cl_2 and an irradiation time of 4 h. Purification by flash column chromatography (gradient, 50:1 to 40:1 hexanes/EtOAc) afforded 101 mg (0.306 mmol, 75%) of a clear oil. Experiment 2: 100.1 mg (0.403 mmol) (*E*)-*tert*-butyldimethyl(4-(prop-1-en-1-yl)phenoxy)silane, 137 μL (1.21 mmol) 2,3-dimethyl-1,3-butadiene, 4.6 mg (0.0020 mmol) $Ru(bpz)_3(BArF)_2$, 5.0 mL CH_2Cl_2. Isolated 104 mg (0.315 mmol, 78 % yield, dr: >10:1). IR (neat) 2958, 2254, 1510, 1255, 908 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.00 (d, J = 8.5 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 2.31 (td, J = 10.8, 5.6 Hz, 1H), 2.15 (m, 1H), 2.07 (m, 2H), 1.82 (m, 2H), 1.64 (s, 3H), 1.61 (s, 3H), 0.98 (s, 9H), 0.67 (d, J = 6.2 Hz, 3H), 0.19 (s, 6H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 153.6, 138.7, 128.3, 125.5, 125.3, 119.7, 47.9, 41.7, 41.6, 34.3, 25.7, 20.0, 18.7, 18.6, 18.2, -4.4. HRMS (ESI) calculated for $[C_{21}H_{34}OSi]^+$ requires *m/z* 330.2374, found *m/z* 330.2375.

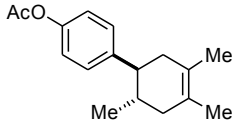


Chart 1, compound 16. Experiment 1: Prepared according to the General Procedure using 100.2 mg (0.569 mmol) 1-acetoxy-4-propenylbenzene, 193 μL (1.71 mmol) 2,3-dimethyl-1,3-butadiene, 39 mg (0.0170 mmol) $Ru(bpz)_3(BArF)_2$, 7.1 mL CH_2Cl_2 and an irradiation time of 3 h. Purification by flash column chromatography (50:1 hexanes/EtOAc) afforded 83 mg (0.321 mmol, 56%) of a clear oil. Experiment 2: 99.8 mg (0.566 mmol) 1-acetoxy-4-propenylbenzene, 193 μL (1.71 mmol) 2,3-dimethyl-1,3-butadiene, 39 mg (0.0170 mmol) $Ru(bpz)_3(BArF)_2$ and 7.1 mL CH_2Cl_2. Isolated 86 mg (0.333, 59% yield, dr: >10:1). IR (neat) 2925, 1756, 1506, 1201 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.16 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 8.5 Hz, 2H), 2.39 (td, J = 10.1, 5.8 Hz, 1H), 2.29 (s, 3H), 2.12 (m, 3H), 1.88 (m, 1H), 1.80 (m, 1H), 1.64 (s, 3H), 1.61 (s, 3H), 0.70

(d, J = 6.2 Hz, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 169.6, 148.7, 143.6, 128.5, 125.3, 125.3, 121.2, 48.1, 41.5, 41.4, 34.1, 21.2, 20.0, 18.7, 18.6. HRMS (EI) calculated for $[C_{17}H_{22}O_2]^+$ requires *m/z* 258.1615, found *m/z* 258.1613.

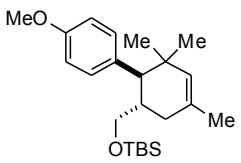


Chart 1, compound 17. Experiment 1: Prepared according to the General Procedure using 100.2 mg (0.360 mmol) (*E*)-1-(*tert*-butyldimethylsilyloxy)-3-(4-methoxyphenyl)-2-propene, 140 μL (1.08 mmol) 2,4-dimethyl-1,3-pentadiene, 4.1 mg (0.0018 mmol) $Ru(bpz)_3(BArF)_2$, 4.5 mL CH_2Cl_2 and an irradiation time of 2.0 h. Purification by flash column chromatography (gradient, 50:1 to 40:1 to 30:1 hexanes/EtOAc) afforded 125 mg (0.334 mmol, 93%) of a clear oil. Experiment 2: 100.6 mg (0.361 mmol) (*E*)-*tert*-butyl(3-(4-methoxyphenyl)allyloxy)dimethylsilane, 140 μL (1.08 mmol) 2,4-dimethyl-1,3-pentadiene, 4.1 mg (0.0018 mmol) $Ru(bpz)_3(BArF)_2$ and 4.5 mL CH_2Cl_2. Isolated 122 mg (0.326 mmol, 90% yield, dr: >10:1). IR (neat) 2955, 2856, 1512, 1250, 835 cm^{-1}. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.014 (m, 2H), 6.808 (m, 2H), 5.182 (s, 1H), 3.803 (s, 1H), 3.399 (dd, J = 9.7, 3.0 Hz, 1H), 3.176 (dd, J = 9.7, 6.4 Hz, 1H), 2.393 (d, J = 11.9 Hz, 1H), 2.221 (m, 1H), 2.139 (dd, J = 17.4, 5.5 Hz, 1H), 2.040 (dd, J = 17.4, 11.3 Hz, 1H), 1.728 (s, 3H), 0.814 (s, 9H), 0.814 (s, 3H), 0.782 (s, 3H), -0.137 (s, 3H), -0.200 (s, 3H); ^{13}C NMR: (125 MHz, CDCl) δ 157.8, 133.3, 132.9, 132.4, 130.4, 129.1, 112.9, 112.3, 77.2, 77.0, 76.7, 65.7, 55.2, 51.9, 36.2, 36.0, 34.9, 29.7, 25.9, 24.8, 23.5, 18.3, -5.7, -5.7. HRMS (EI) calculated for $[C_{23}H_{38}O_2SiH]^+$ requires *m/z* 375.2714, found *m/z* 375.2703.

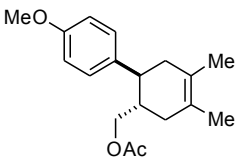


Chart 1, compound 18. Experiment 1: Prepared according to the General Procedure using 100.9 mg (0.489 mmol) (*E*)-4-methoxystyryl acetate, 165 μL (1.46 mmol) 2,3-dimethyl-1,3-butadiene, 5.6 mg (0.0024 mmol) $Ru(bpz)_3(BArF)_2$, 6.1 mL CH_2Cl_2 and an irradiation time of 4 h. Purification by flash column chromatography (gradient, 50:1 to 10:1 hexanes/EtOAc) afforded 122 mg (0.423 mmol, 87%) of a clear oil. Experiment 2: 100.5 mg (0.487 mmol) (*E*)-4-methoxystyryl acetate, 165 μL (1.46 mmol) 2,3-dimethyl-1,3-butadiene, 5.6 mg (0.0024 mmol) $Ru(bpz)_3(BArF)_2$, 6.1 mL CH_2Cl_2. Isolated 125 mg (0.433 mmol, 89% yield, dr: >10:1). IR (neat) 2901, 2254, 1731, 1513, 1303, 1037 cm^{-1}. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 1H NMR: 7.08 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 3.89 (dd, J = 11.1, 3.7 Hz, 1H), 3.78 (s, 3H), 3.65 (dd, J = 11.1, 7.3 Hz, 1H), 2.60 (td, J = 10.5, 5.9 Hz, 1H), 2.20 (m, 1H), 2.13 (m, 3H), 1.98 (m, 1H), 1.97 (s, 3H), 1.66 (s, 3H), 1.63 (s, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 171.1, 158.1, 136.4, 128.3, 125.3, 124.4, 113.9, 67.4, 55.2, 42.7, 41.0, 38.7, 35.7, 20.8, 18.8, 18.6. HRMS (EI) calculated for $[C_{18}H_{24}O_3]^+$ requires *m/z* 288.1720, found *m/z* 288.1728.

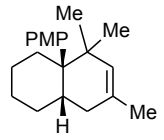


Chart 1, compound 19. Experiment 1: Prepared according to the General Procedure using 100.3 mg (0.533 mmol) 1-(4-methoxyphenyl)cyclohexene, 206 μL (1.59 mmol) 2,4-dimethyl-1,3-pentadiene, 6.1 mg (0.0027 mmol) $Ru(bpz)_3(BArF)_2$, 6.6 mL CH_2Cl_2 and an irradiation time of 20 h. Purification by flash column chromatography (gradient, 50:1 to 40:1 hexanes/EtOAc) afforded 140 mg (0.492 mmol, 92%) of a clear oil. Experiment 2: 100.5 mg (0.534 mmol) 1-(4-methoxyphenyl)cyclohexene, 206 μL (1.59 mmol) 2,4-dimethyl-1,3-pentadiene, 6.1 mg (0.0027 mmol) $Ru(bpz)_3(BArF)_2$ and 6.6 mL CH_2Cl_2. Isolated 138 mg (0.485 mmol, 91% yield, dr: >10:1). IR (neat) 2945, 2834, 1514, 1251, 1040 cm^{-1}. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.274 (d, J = 8.2 Hz, 1H), 7.233 (d, J = 9.3 Hz, 1H), 6.850 (d, J = 8.2 Hz, 2H), 5.099 (s, 1H), 3.805 (s, 3H), 2.790 (m, 1H), 2.293 (dd, J = 18.0, 10.3 Hz, 1H), 2.083 (d, J = 13.9 Hz, 1H), 1.935 (dd, J = 18.0, 6.7 Hz, 1H), 1.679 (s, 3H), 1.645 (m, 1H), 1.553 (m, 2H), 1.426 (m, 1H), 1.236 (m, 3H), 0.787 (s, 1H), 0.511 (s, 1H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 157.0, 134.1, 132.2, 130.6, 130.2, 128.4, 112.5, 112.3, 55.0, 45.1, 38.7, 32.2, 30.3, 28.4, 26.0, 24.6, 24.1, 23.1, 21.7, 19.5. HRMS (EI) calculated for $[C_{20}H_{28}O_2]^+$ requires *m/z* 284.2135, found *m/z* 284.2124.

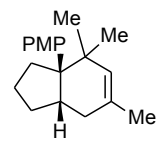


Chart 1, compound 20. Prepared according to the General Procedure using 100.6 mg (0.577 mmol) 1-(4-methoxyphenyl)cyclopentene, 223 μL (1.73 mmol) 2,4-dimethyl-1,3-pentadiene, 6.6 mg (0.0029 mmol) $Ru(bpz)_3(BArF)_2$, 7.2 mL CH_2Cl_2 and an irradiation time of 1.5 h. Purification by flash column chromatography (gradient, 50:1 to 40:1 hexanes/EtOAc) afforded 131 mg (0.484 mmol, 84%) of a clear oil. Experiment 2: 100.2 mg (0.575 mmol) 1-(4-methoxyphenyl)cyclopentene, 223 μL (1.73 mmol) 2,4-dimethyl-1,3-pentadiene, 6.6 mg (0.0029 mmol) $Ru(bpz)_3(BArF)_2$ and 7.2 mL CH_2Cl_2. Isolated 132 mg (0.488 mmol, 85% yield, dr: >10:1). IR(neat) 2958, 287, 1513, 1251 cm^{-1}. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.34 (d, J = 9.2 Hz, 2H), 6.83 (d, J = 9.2 Hz, 2H), 5.13 (m, 1H), 3.80 (s, 3H), 2.75 (dd, J = 13.9, 6.4 Hz, 1H), 2.14 (m, 2H), 1.73 (m, 1H), 1.68 (m, 2H), 1.65 (s, 3H), 1.46 (m, 1H), 1.28 (m, 1H), 1.24 (m, 1H), 0.88 (s, 3H), 0.57 (s, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 157.3, 135.5, 132.2, 129.3, 127.9, 112.5, 55.1, 54.9, 37.0, 37.0, 35.2, 30.3, 30.1, 29.8, 26.0, 23.2, 19.8. HRMS (EI) calculated for $[C_{19}H_{26}O]^+$ requires *m/z* 270.1979, found *m/z* 270.1970.

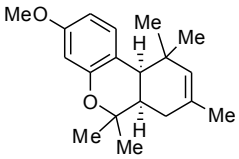


Chart 1, compound 21. Experiment 1: Prepared according to the General Procedure using 101.2 mg (0.532 mmol) precocene I, 204 μL (1.58 mmol) 2,4-dimethyl-1,3-pentadiene, 36 mg (0.0158 mmol) $Ru(bpz)_3(BArF)_2$, 6.6 mL of CH_2Cl_2 and an irradiation time of 48 h. Purification by flash column chromatography (2:1 hexanes/CH_2Cl_2) yielded 60% of cycloadduct as determined by ^1H NMR using CH_2Br_2 as a calibrated internal standard. Experiment 2: Prepared according to the General Procedure using 106.1 mg (0.558 mmol) precocene I, 204 μL (1.58 mmol) 2,4-dimethyl-1,3-pentadiene, 36 mg (0.0158 mmol) $Ru(bpz)_3(BArF)_2$ and 6.6 mL of CH_2Cl_2. Yielded 64% of cycloadduct as determined by ^1H NMR, dr: >10:1. IR (neat) 3039, 2975, 2836, 1504, 1159 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.26 (d, J = 8.2 Hz, 1H), 6.41 (m, 2H), 5.18 (m, 1H), 3.75 (s, 3H), 2.74 (d, J = 4.9 Hz, 1H), 2.23 (td, J = 6.9, 5.2 Hz, 1H), 2.02 (dd, J = 17.5, 6.9 Hz, 1H), 1.78 (dd, J = 17.5, 6.7 Hz, 1H), 1.60 (s, 3H), 1.36 (s, 3H), 1.31 (s, 3H), 1.17 (s, 3H), 1.14 (s, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 158.8, 155.7, 130.8, 130.1, 129.6, 118.9, 106.2, 102.7, 78.6, 55.1, 42.0, 40.2, 35.5, 33.5, 29.6, 29.3, 27.5, 25.4, 23.5. HRMS (EI) calculated for $[C_{21}H_{30}O_2]^+$ requires *m/z* 286.1928, found *m/z* 286.1938.

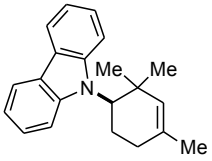


Chart 1, compound 22. Experiment 1: Prepared according to the General Procedure using 100.2 mg (0.519 mmol) 9-vinylcarbazole, 201 μL (1.55 mmol) 2,4-dimethyl-1,3-pentadiene, 36 mg (0.0155 mmol) $Ru(bpz)_3(BArF)_2$, 6.5 mL CH_2Cl_2 and an irradiation time of 24 h. Purification by flash column chromatography (50:1 hexanes/EtOAc) afforded 96 mg (0.332 mmol, 64%) of a clear oil. Experiment 2: 100.8 mg (0.522 mmol) of *trans*-anethole, 201 μL (1.55 mmol) 2,4-dimethyl-1,3-pentadiene, 36 mg (0.0155 mmol) $Ru(bpz)_3(BArF)_2$ and 6.5 mL CH_2Cl_2. Isolated 100 mg (0.346 mmol, 66% yield, dr: >10:1. IR (neat) 3060, 2963, 1451, 1195, 909 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 8.08 (dd, J = 7.6, 6.4 Hz, 2H), 7.67 (d, J = 8.8 Hz, 1H), 7.48 (d, J = 8.8 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.19 (m, 2H), 5.27 (s, 1H), 4.60 (dd, J = 13.5, 2.0 Hz, 1H), 2.97 (qd, J = 12.7, 5.6 Hz, 1H), 2.27 (m, 1H), 2.17 (m, 1H), 1.91 (m, 1H), 1.75 (s, 3H), 1.17 (s, 3H), 1.06 (s, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 142.6, 140.6, 132.8, 131.3, 125.4, 124.9, 124.0, 122.9, 119.9, 119.7, 118.7, 118.5, 113.6, 110.2, 62.4, 40.2, 32.2, 29.9, 25.9, 25.3, 23.3. HRMS (EI) calculated for $[C_{21}H_{23}N]^+$ requires *m/z* 289.1825, found *m/z* 189.1828.

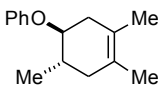
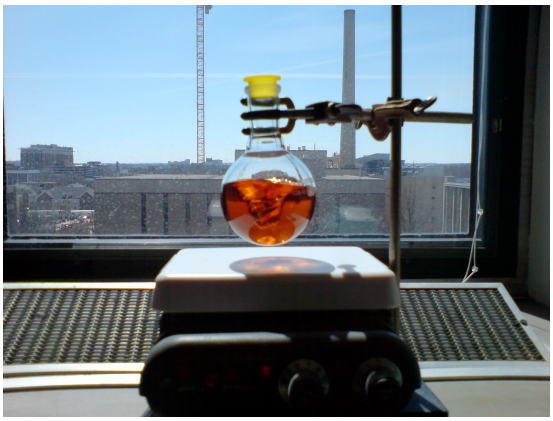


Chart 1, compound 23. Experiment 1: Prepared according to the General Procedure using 100.4 mg (0.748 mmol) (*E*)-(1-propenyloxy)benzene, 253 μL (2.24 mmol) 2,3-dimethyl-1,3-butadiene, 8.6 mg (0.0037 mmol) $Ru(bpz)_3(BArF)_2$, 9.3 mL CH_2Cl_2 and an irradiation time of 20 h. Purification by flash column chromatography (40:1 hexanes/EtOAc) yielded 43% of cycloadduct as determined by ^1H NMR using CH_2Br_2 as a calibrated internal standard. Experiment 2: 100.1 mg (0.746 mmol) (*E*)-(1-propenyloxy)benzene, 253 μL (2.24 mmol) 2,3-dimethyl-1,3-butadiene, 8.6 mg (0.0037 mmol) $Ru(bpz)_3(BArF)_2$ and 9.3 mL CH_2Cl_2. Yielded 41 % of cycloadduct as determined by ^1H NMR, dr: >10:1. IR (neat) 2956, 2909, 1494, 1245 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.26 (m, 2H), 6.93 (d, J = 8.1 Hz, 3H), 4.10 (td, J = 8.1, 5.4 Hz, 1H), 2.41 (dd, J = 16.8, 4.3 Hz, 1H), 2.19 (dd, J = 16.8, 4.3 Hz, 1H), 2.09 (m, 1H), 2.01 (m, 1H), 1.80 (m, 1H), 1.62 (s, 3H), 1.60 (s, 3H), 1.04 (d, J = 6.4 Hz, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 158.6, 129.4, 124.9, 122.7, 120.5, 116.2, 116.0, 78.8, 39.3, 36.8, 34.0, 18.8, 18.5, 17.8. HRMS (EI) calculated for $[C_{15}H_{20}O]^+$ requires *m/z* 216.1509, found *m/z* 216.1515.

Large-scale solar cycloaddition (Table 2, entry 4). A 250 mL round-bottom flask was charged with 2.01 g (13.6 mmol) *trans*-anethole, 31 mg (0.013 mmol) $Ru(bpz)_3(BArF)_2$, 4.1 mL (41.0 mmol) isoprene, and 250 mL CH_2Cl_2. The reaction was stirred in a laboratory window for 2 h. The reaction mixture was concentrated and passed through a short pad of silica with EtOAc. The solvent was removed by rotary evaporation to afford 2.79 g (12.9 mmol, 95% yield, dr >10:1) of analytically pure cycloadduct.



V. Studies on the synthesis of heitziamide A

Thermal cycloaddition of fagaramide and myrcene. Fagaramide (500 mg, 2.02 mmol) and myrcene (7.0 mL, 40.6 mmol) were placed together in a sealed tube and heated to 150 °C. After 72 h, the reaction mixture was passed through a plug of SiO_2 eluting with 10:1 hexanes:ethyl acetate. The solvent was removed by rotary evaporation, and the residue was purified by flash column chromatography (gradient, 10:1 to 3:1 hexanes/EtOAc) to afford 465 mg (1.21 mmol, 60% yield) of the "thermal" regioisomer (**32**) as a 2:1 mixture of *trans*:*cis* diastereomers.

Trans diastereomer: IR (neat) 3053, 2986, 2914, 1723, 1520, 1265 cm^{-1}. ^1H NMR: (600 MHz, C_6D_6) δ 6.88 (d, J = 1.5 Hz, 1H), 6.74 (dd, J = 8.2, 1.5 Hz, 1H), 6.71 (d, J = 8.2 Hz, 1H), 5.79 (t, J = 5.8 Hz, 1H), 5.50 (s, 1H), 5.40 (dd, J = 7.6, 1.5 Hz, 2H), 5.25 (t, J = 7.1 Hz, 1H), 3.17 (dt, J = 11.3, 8.9 Hz, 1H), 3.11 (m, 1H), 2.77 (m, 1H), 2.61 (ddd, J = 12.5, 7.1, 5.3 Hz, 1H), 2.35 (m, 1H), 2.30 (dt, J = 17.2, 5.1 Hz, 1H), 2.18 (m, 4H), 2.04 (m, 2H), 1.69 (s, 3H), 1.58 (s, 3H), 1.42 (m, J = 6.5 Hz, 1H), 0.63 (d, J = 6.5 Hz, 3H), 0.61 (d, J = 6.5 Hz, 3H); ^{13}C NMR: (150 MHz, C_6D_6) δ 173.9, 147.8, 146.3, 138.8, 136.8, 131.1, 128.0, 127.9, 121.2, 119.4, 108.1, 108.1, 100.5, 48.0, 46.5, 43.2, 37.5, 37.3, 30.2, 28.5, 26.5, 25.5, 19.7, 17.5. HRMS (ESI) calculated for $[C_{24}H_{33}NO_3]^+$ requires *m/z* 383.2455, found *m/z* 383.2471.

Cis diastereomer: IR (neat) 3053, 2966, 2915, 1666, 1519, 1268 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 6.71 (m, 2H), 6.68 (dd, J = 8.0, 1.6 Hz, 1H), 5.90 (d, J = 1.5 Hz, 1H), 5.89 (d, J = 1.5 Hz, 1H), 5.47 (s, 1H), 5.19 (t, J = 5.18 Hz, 1H), 5.11 (m, 1H), 2.93 (m, 2H), 2.71 (ddd, J = 13.2, 7.0, 5.5 Hz, 1H), 2.52 (m, 1H), 2.40 (td, J = 10.9, 4.8 Hz, 1H), 2.31 (dt, J = 17.4, 4.8 Hz, 1H), 2.16 (m, 4H), 2.01 (m, 2H), 1.70 (s, 3H), 1.61 (s, 3H), 1.41 (m, J = 6.7 Hz, 1H), 0.66 (d, J = 6.7 Hz, 3H), 0.64 (d, J = 6.7 Hz, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 174.4, 147.6, 146.0, 138.3, 136.4, 131.7, 124.1, 120.8, 119.8, 108.3, 107.6, 100.8, 49.4, 46.6, 42.7, 37.4, 33.6, 32.7, 28.3, 26.3, 25.7, 19.8, 17.7. HRMS (ESI) calculated for $[C_{24}H_{33}NO_3]^+$ requires *m/z* 383.2455, found *m/z* 383.2438.

Additional NMR experimental notes for compound 32

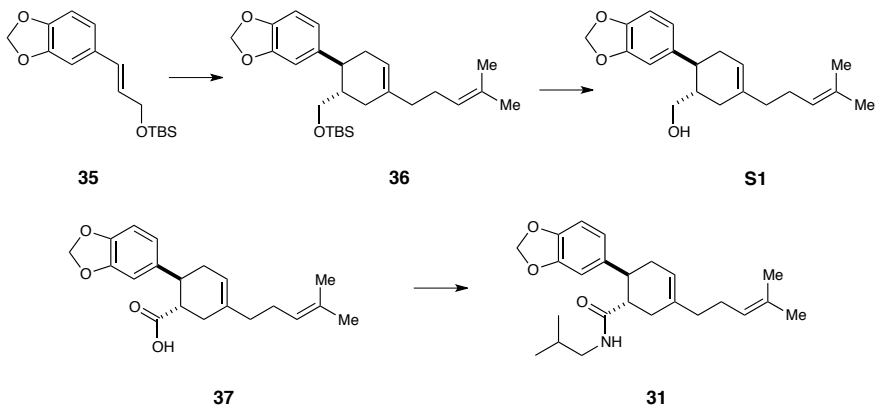
a) NOESY1D spectra (summarized on S-60) – Varian's standard NOESY1D Chempack sequence was used with a typical setup as follows: mix=0.7×T_1(shortest)~0.5s, d1=3×T_1(longest)~5.4s, nt=16, ss=-2, selective pulse using a seduce shape. The numbers shown are % enhancements measured as ratios of integrals, normalized by number of protons involved, of the enhanced to selected protons ×(-1).

b) gcosy spectrum (S-61) – 90°-90° gradient cosy with: d1=1.8 nt=2 np=2048 ni=512 fn=fn1=4096, referenced to TMS, sinebell apodization, symmetrized.

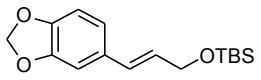
c) HSQC spectrum (S-62) – Varian's standard HSQC Chempack sequence setup as follows: nt=2 ss=128 np=2048 at=0.198 ni=512 j1xh=140 fn=fn1=4096, 4× linear prediction applied in F1; cosine-squared apodization. The experiment was run in multiplicity-edited mode (mult=2) with red contours denoting –CH_2– correlations.

d) HMBC spectrum (S-63) – Varian's standard gHMBC Chempack sequence setup as follows: nt=8 ss=128 np=2048 ni=800 j1xh=140 jnxh=8.0 fn=4096 fn1=8192, sinebell apodization, 2× linear prediction in F1.

Scheme S1



Compound 35. A 25 mL round-bottomed flask was charged with trans-3,4-methylenedioxycinnamyl alcohol[17] (1.5 g, 8.42 mmol), *tert*-butyldimethylsilyl chloride (1.91 g, 12.7 mmol), imidazole (1.15 g, 16.9 mmol) and 4.5 mL DMF. After 5 h, the reaction was diluted with water and Et_2O. The phases were separated, and the aqueous phase was extracted two additional times with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. Flash column chromatography (gradient, 50:1 to 20:1 hexanes/EtOAc) afforded 2.36 g (8.07 mmol, 96% yield) a white solid. All spectroscopic data were consistent with reported values.[18]

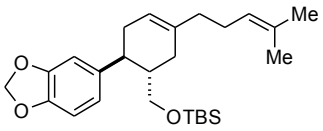


Comparison study using aminium cation initiator $[(4\text{-}BrPh)_3N]SbCl_6$.

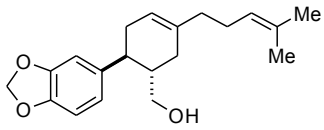
A 25 mL round-bottomed flask was charged with 100.5 mg (0.344 mmol) of **35**, 300 μL (1.74 mmol) of myrcene, 6.0 mg (0.0068 mmol) of $[(4\text{-}BrPh)_3N]SbCl_6$ and 6.8 mL of CH_2Cl_2. After 15 h, the reaction was passed through a short pad of silica using EtOAc as eluent. The solvent was removed by rotary evaporation. No cycloadduct could be detected by ^1H NMR analysis of the reaction mixture using CH_2Br_2 as a calibrated internal standard.

Comparison study using triphenylpyrrilium tetrafloroborate.

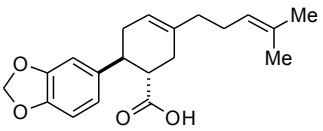
A solution of **35** (100.7 mg, 0.344 mmol) in 6.8 mL $MeNO_2$ was placed in a 25 mL round-bottomed flask. In a dark hood, myrcene (300 μL, 1.74 mmol), AcOH (40 μL, 0.699 mmol), $MgSO_4$ (200 mg) and triphenylpyrrilium tetrafloroborate (4.2 mg, 0.0068 mmol) were added to the flask. The reaction was stirred at ambient temperature in front of a 23 W CFL bulb. After 15 h, the reaction was eluted through a short pad of silica using EtOAc. The solvent was removed by rotary evaporation. ^1H NMR analysis of the reaction mixture showed 8% conversion to the cycloadduct using CH_2Br_2 as a calibrated internal standard.



Compound 36. A solution of **35** (100.3 mg, 0.343 mmol) in 6.8 mL $MeNO_2$ was placed in a 25 mL round-bottomed flask. In a dark hood, myrcene (300 μL, 1.74 mmol), AcOH (40 μL, 0.699 mmol) and $Ru(bpz)_3(PF)_2$ (5.9 mg, 0.0068 mmol) were added to the flask. The reaction was stirred at ambient temperature in front of a 23 W CFL bulb. After 15 h, the reaction was eluted through a short pad of silica using EtOAc, and the filtrate was concentrated by rotary evaporation. Purification by flash column chromatography (gradient, 50:1 to 10:1 hexanes/EtOAc) afforded 118 mg (0.275 mmol, 80%) of a clear oil. IR (neat) 2957, 2857, 2253, 1472, 1250 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 6.65 (d, J = 7.8 Hz, 1H), 6.62 (d, J = 1.6 Hz, 1H), 6.57 (dd, J = 7.8, 1.6 Hz, 1H), 5.85 (d, J = 1.4 Hz, 1H), 5.84 (d, J = 1.4 Hz, 1H), 5.36 (s, 1H), 5.06 (t, J = 7.1 Hz, 1H), 3.30 (dd, J = 10.1, 3.5 Hz, 1H), 3.16 (dd, J = 10.1, 6.4 Hz, 1H), 2.53 (td, J = 10.6, 5.5 Hz, 1H), 2.13 (m, 1H), 2.05 (m, 5H), 1.95 (m, 2H), 1.81 (m, 1H), 1.63 (s, 3H), 1.55 (s, 3H), 0.79 (s, 9H), -0.13 (s, 3H), -0.16 (s, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 147.4, 145.5, 139.4, 137.4, 131.3, 124.3, 120.7, 119.7, 107.9, 107.7, 100.6, 65.0, 41.9, 41.4, 37.6, 34.4, 32.0, 26.4, 25.8, 25.6, 18.2, 17.6, 0.9, -5.6. HRMS (EI) calculated for $[C_{26}H_{40}O_3Si]^+$ requires *m/z* 428.2742, found *m/z* 428.2751.



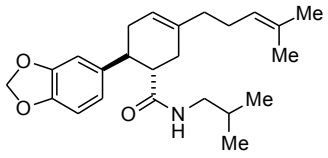
Compound S1. A solution of **36** (640 mg, 1.49 mmol) in dry THF (7.5 mL) was placed in a 25 mL round-bottomed flask. The vessel was cooled to 0 °C, TBAF (1.17 g, 4.47 mmol) was added, and the reaction mixture was gradually warmed to room temperature. After 2 h, the reaction was concentrated by rotary evaporation. Flash column chromatography (gradient, 30:1 to 3:1 hexanes/EtOAc) afforded 360 mg (1.14 mmol, 76% yield) of a clear oil. IR (neat) 3436, 2899, 1505, 1245, 909 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 6.74 (d, J = 7.7 Hz, 1H), 6.71 (d, J = 1.7 Hz, 1H), 6.67 (dd, J = 7.7, 1.7 Hz, 1H), 5.93 (s, 2H), 5.46 (bs, 1H), 5.13 (t, J = 7.1 Hz, 1H), 3.46 (dd, J = 10.8, 3.9 Hz, 1H), 3.34 (dd, J = 10.8, 5.8 Hz, 1H), 2.55 (td, J = 10.8, 6.0 Hz, 1H), 2.26 (m, 1H), 2.15 (m, 4H), 2.02 (m, 3H), 1.96 (m, 1H), 1.70 (s, 3H), 1.62 (s, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 147.8, 145.9, 138.9, 137.0, 131.5, 124.2, 120.5, 120.0, 108.3, 107.6, 100.8, 65.9, 42.9, 41.5, 37.5, 34.6, 32.2, 26.4, 25.7, 17.7. HRMS (ESI) calculated for $[C_{20}H_{26}O_3]^+$ requires *m/z* 314.1877, found *m/z* 314.1875.



Compound 37. A mixture of **S1** (360 mg, 1.14 mmol), *N*-methylmorpholine *N*-oxide (200 mg, 1.71 mmol), tetrapropylammonium perruthenate (41 mg, 0.117 mmol), 4 Å molecular sieves (576 mg), and 4.6 mL dry CH_2Cl_2 was placed in a 25 mL round-bottomed flask. After 1 h, the reaction mixture was poured directly onto a silica gel column and eluted with CH_2Cl_2. The filtrates were combined and solvent removed to afford 286 mg (0.92 mmol,

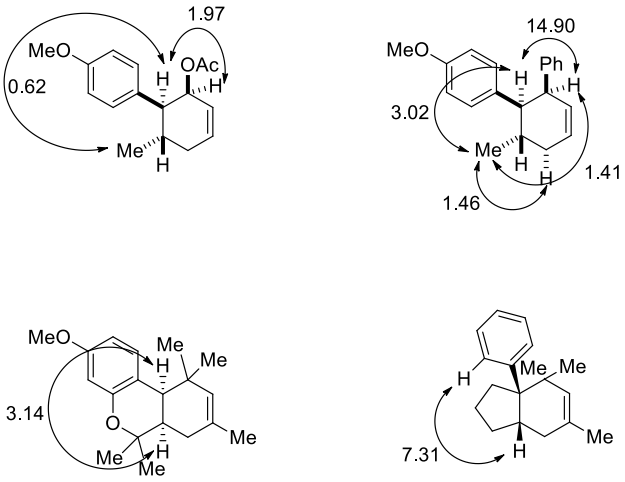
80% yield) of (1*S*,6*S*)-6-(benzo[*d*][1,3]dioxol-5-yl)-3-(4-methylpent-3-en-1-yl)cyclohex-3-enecarbaldehyde as a clear oil, which was used in the next step without any further purification.

The aldehyde (250 mg, 0.80 mmol), 6.8 mL *t*-butanol, and 2-methyl-2-butene (4.1 mL, 38.7 mmol) were placed in a 10 mL round-bottomed flask. The flask was cooled to 0 °C, and a solution of $NaClO_2$ (681 mg, 7.53 mmol) and NaH_2PO_4 (658 mg, 5.48 mmol) dissolved in 1.8 mL H_2O was added. After 2 h, the volatile solvents were removed and mixture dissolved in 25 mL H_2O, which was acidified to pH 3 with aqueous 1 M HCl. The acidified aqueous phase was then extracted three times with Et_2O. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated by rotary evaporation. Flash column chromatography (gradient, 30:1 to 1:1 hexanes/EtOAc) afforded 200 mg (0.61 mmol, 76% yield) of the carboxylic acid **37** as a clear oil. IR (neat) 3583, 3154, 2903, 1706, 1379 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 6.71 (d, J = 4.8 Hz, 1H), 6.70 (d, J = 1.4 Hz, 1H), 6.66 (dd, J = 8.1, 1.4 Hz, 1H), 5.93 (d, J = 1.2 Hz, 1H), 5.91 (d, J = 1.2 Hz, 1H), 5.47 (s, 1H), 5.10 (tt, J = 6.6, 1.2 Hz, 1H), 2.92 (td, J = 10.7, 5.6 Hz, 1H), 2.80 (td, J = 10.7, 5.6 Hz, 1H), 2.32 (m, 3H), 2.13 (m, 3H), 2.01 (t, J = 7.0 Hz, 2H), 1.70 (s, 3H), 1.61 (s, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 179.7, 147.7, 146.1, 137.7, 135.6, 131.7, 123.9, 120.4, 120.1, 108.1, 107.7, 100.9, 46.1, 42.0, 37.2, 33.7, 32.2, 26.3, 25.7, 17.7. HRMS (ESI) calculated for $[C_{20}H_{23}O_4]^-$ requires *m/z* 327.1591, found *m/z* 327.1587.



Heitziamide A (31) A solution of **37** (100.6 mg, 0.306 mmol), EDC•HCl (60 mg, 0.313 mmol), DMAP (4 mg, 0.033 mmol), and isobutylamine (90 µL, 0.91 mmol) in 2.0 mL CH_2Cl_2 was placed in a 10 mL round-bottomed flask. After 12 h, the solvent was removed by rotary evaporation. Flash column chromatography (gradient, 30:1 to 4:1 hexanes/EtOAc) afforded 95 mg (0.25 mmol, 81% yield) of a white solid. All spectroscopic data were consistent with values reported in the isolation report for heitziamide A.[19] ^1H NMR: (500 MHz, $CDCl_3$) δ 6.72 (d, J = 1.6 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 6.68 (dd, J = 8.0, 1.6 Hz, 1H), 5.89 (d, J = 1.3 Hz, 1H), 5.88 (d, J = 1.3 Hz, 1H), 5.47 (s, 1H), 5.32 (t, J = 5.7 Hz, 1H), 5.11 (t, J = 6.9 Hz, 1H), 2.96 (m, 1H), 2.91 (td, J = 11.1, 5.7 Hz, 1H), 2.70 (m, 1H), 2.52 (m, 1H), 2.43 (td, J = 17.0, 5.0 Hz, 1H), 2.30 (m, 1H), 2.22 (m, 1H), 2.11 (m, 3H), 2.01 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.41 (m, 1H), 0.66 (d, J = 6.6 Hz, 3H), 0.64 (d, J = 6.6 Hz, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 174.4, 147.6, 146.0, 138.3, 136.3, 131.7, 124.1, 120.8, 119.8, 108.3, 107.7, 100.8, 49.3, 46.6, 42.7, 37.4, 33.7, 32.7, 28.3, 26.3, 25.7, 19.8, 17.7. HRMS (ESI) calculated for $[C_{24}H_{33}NO_3Na]^+$ requires *m/z* 406.2353, found *m/z* 406.2357.

VI. Representative NOEs



VII. References

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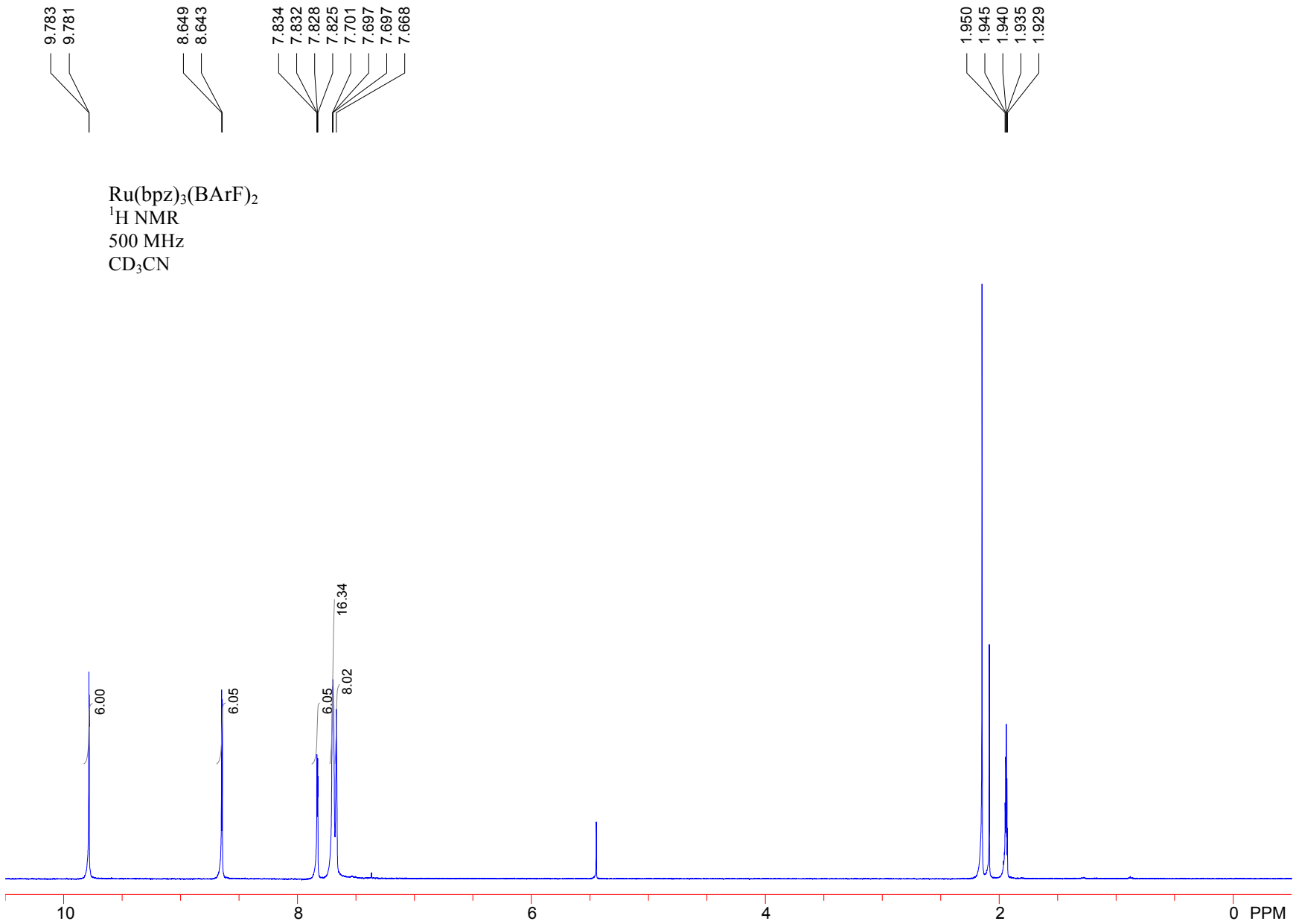
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1.945
1.940
1.935
1.929
Ru(bpz)3(BArF)2
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6.00
6.05
6.05
10
8
6
4
2
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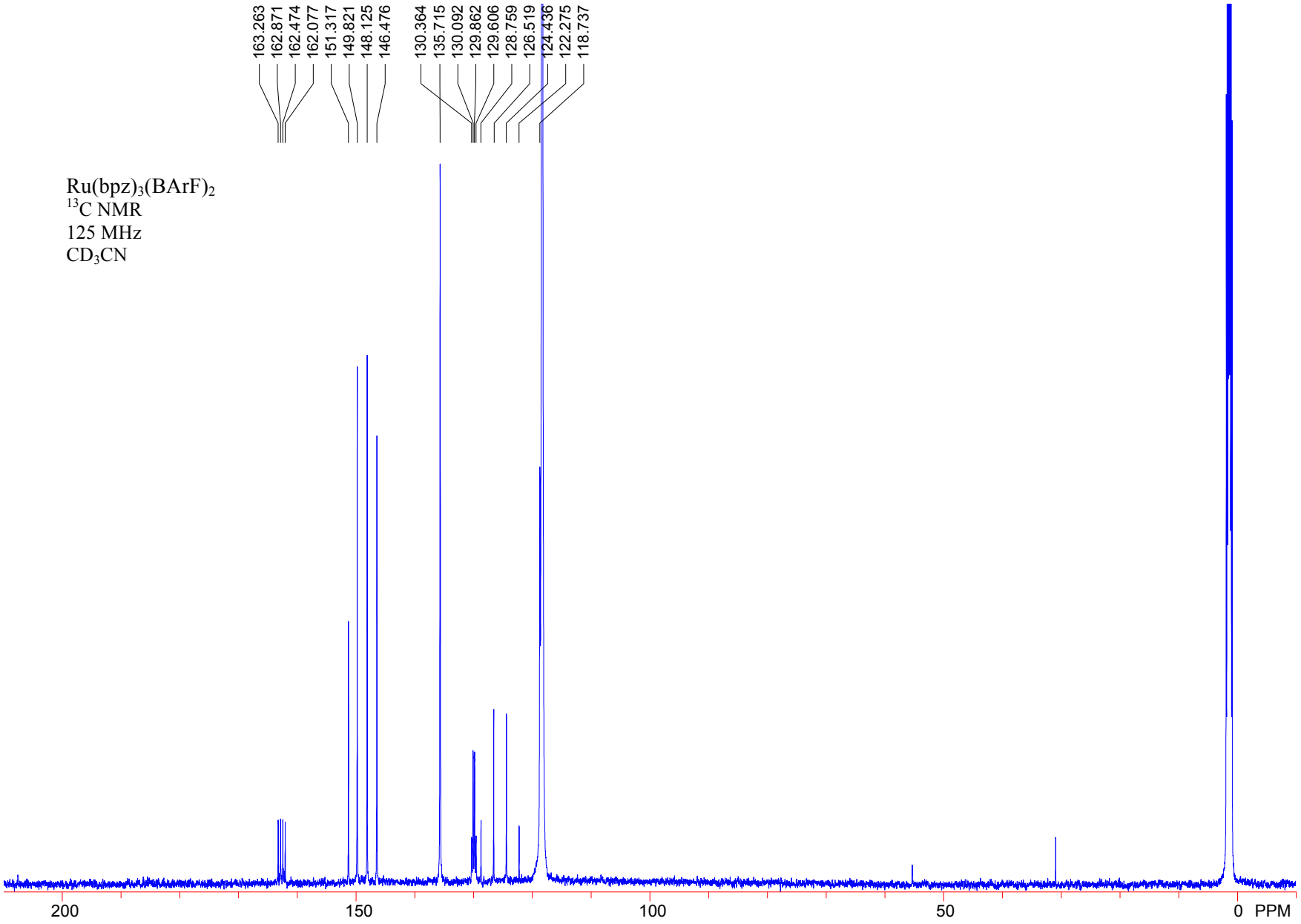
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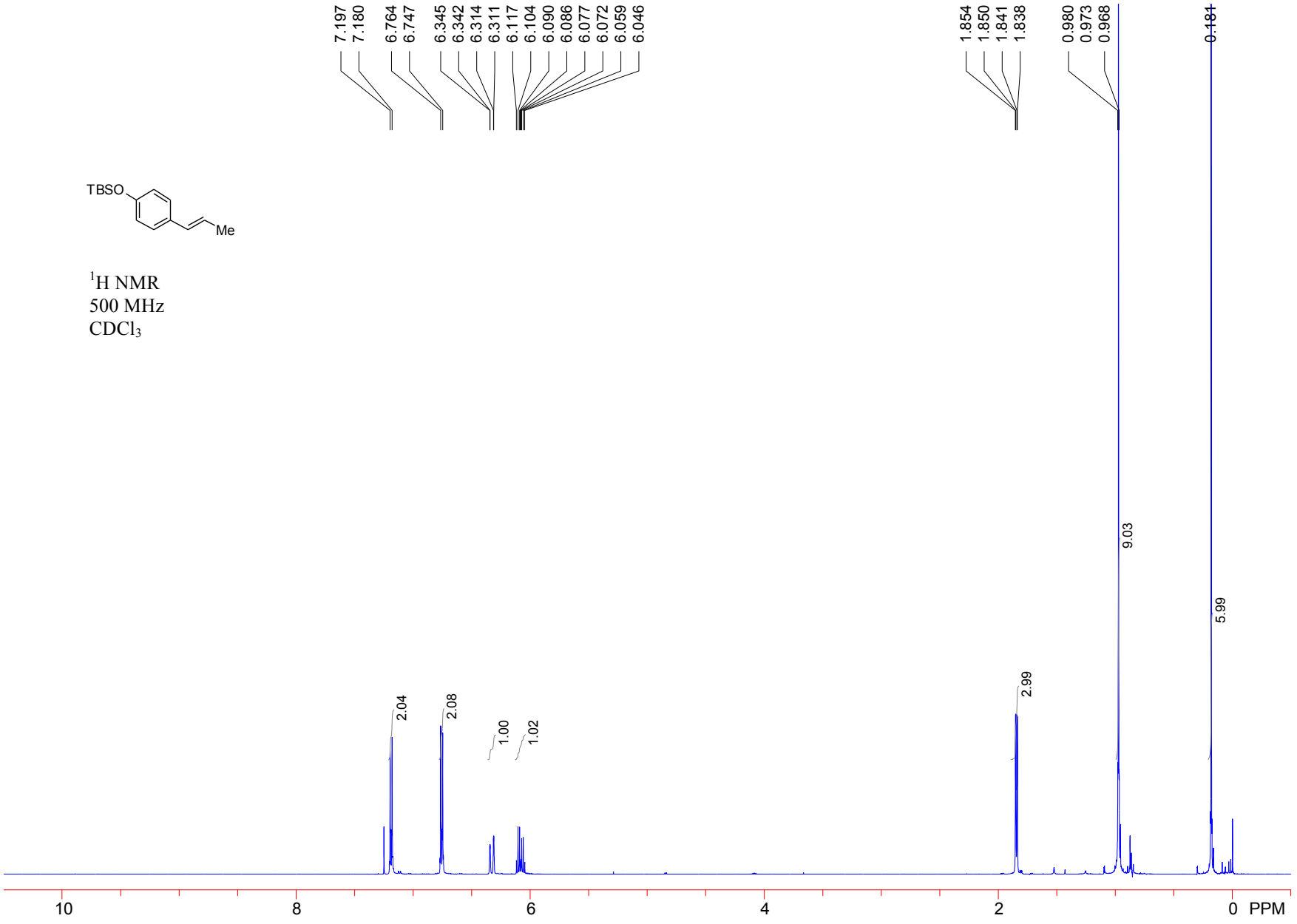

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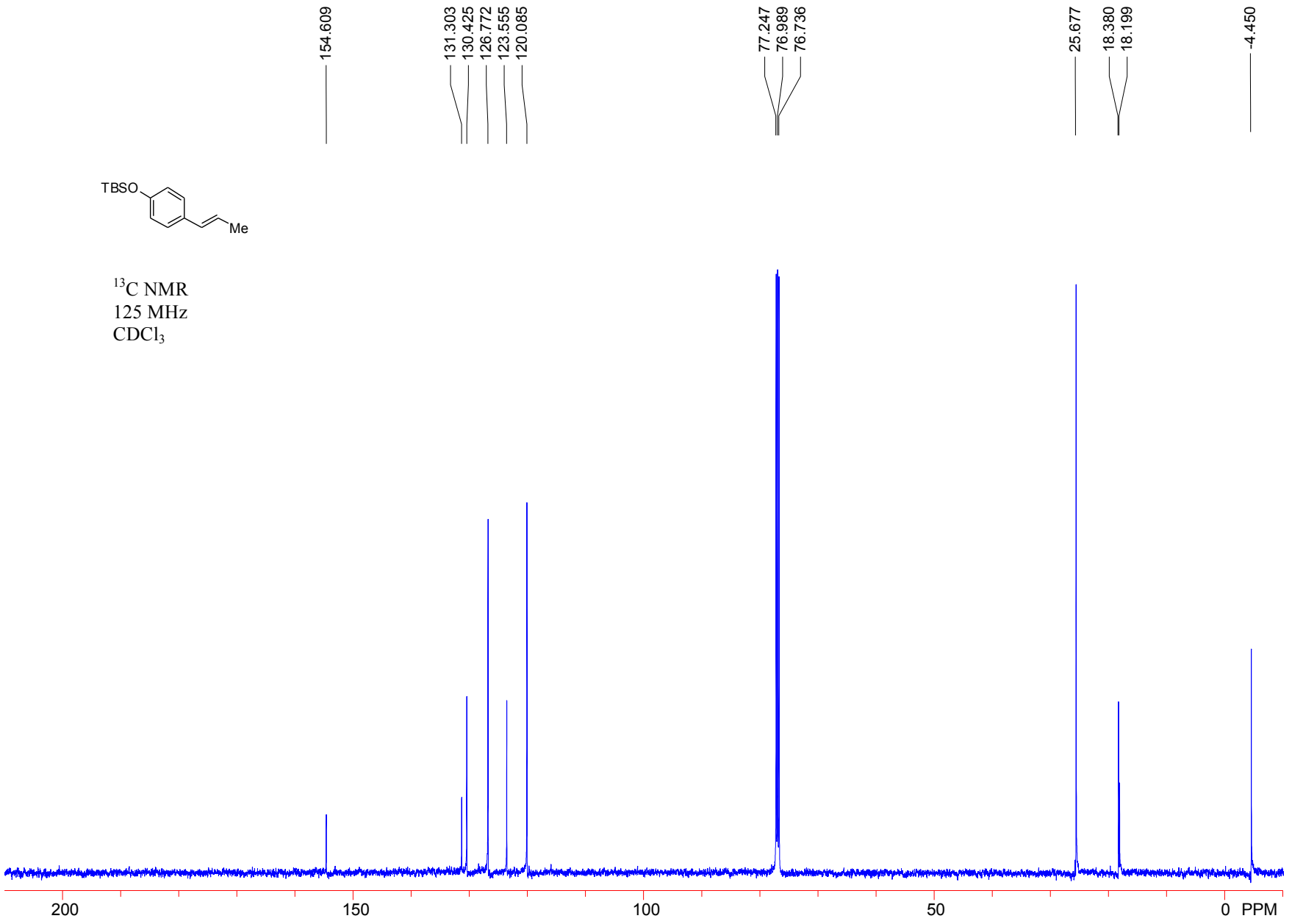
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100
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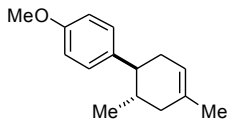

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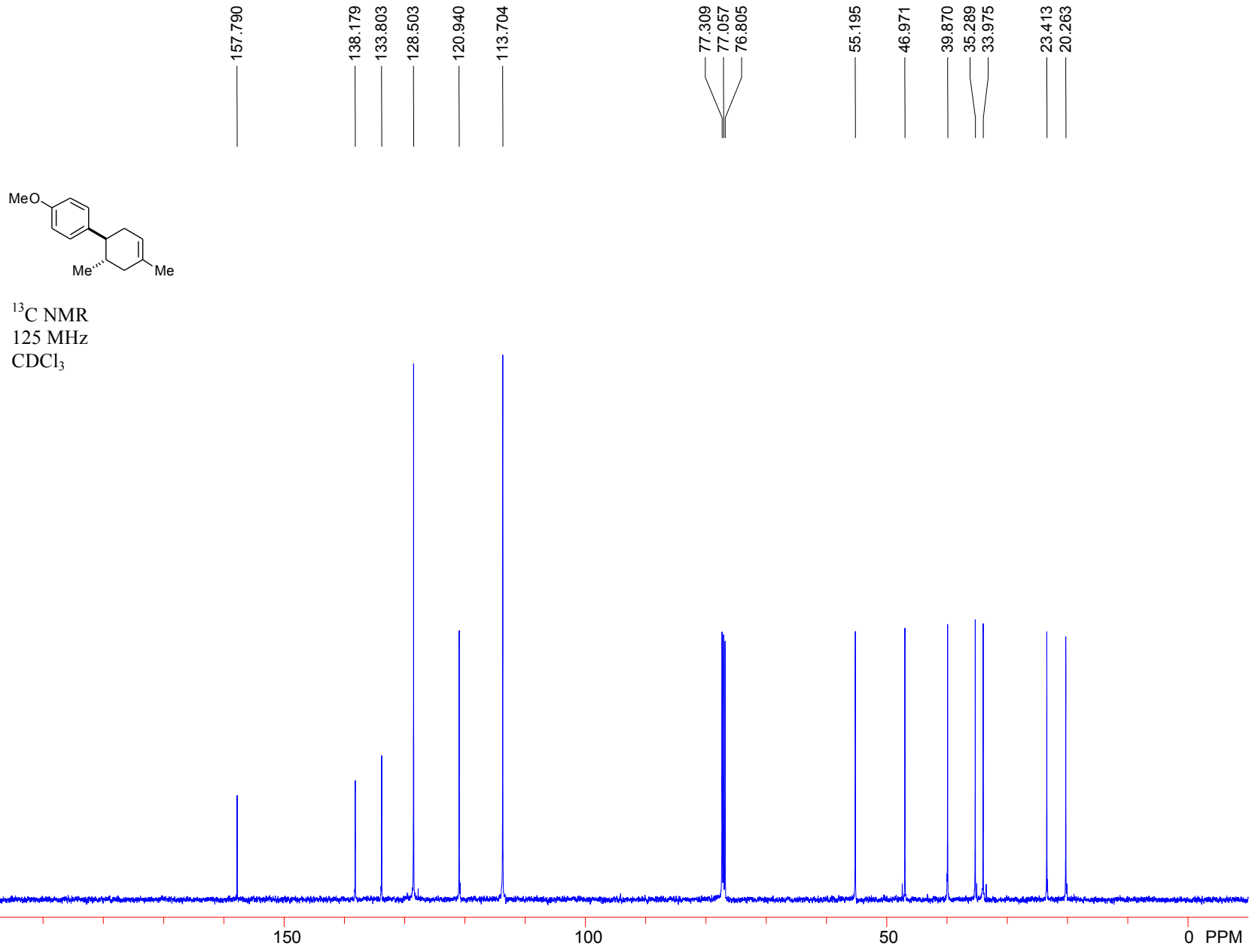
500 MHz
$CDCl_3$



^{13}C NMR
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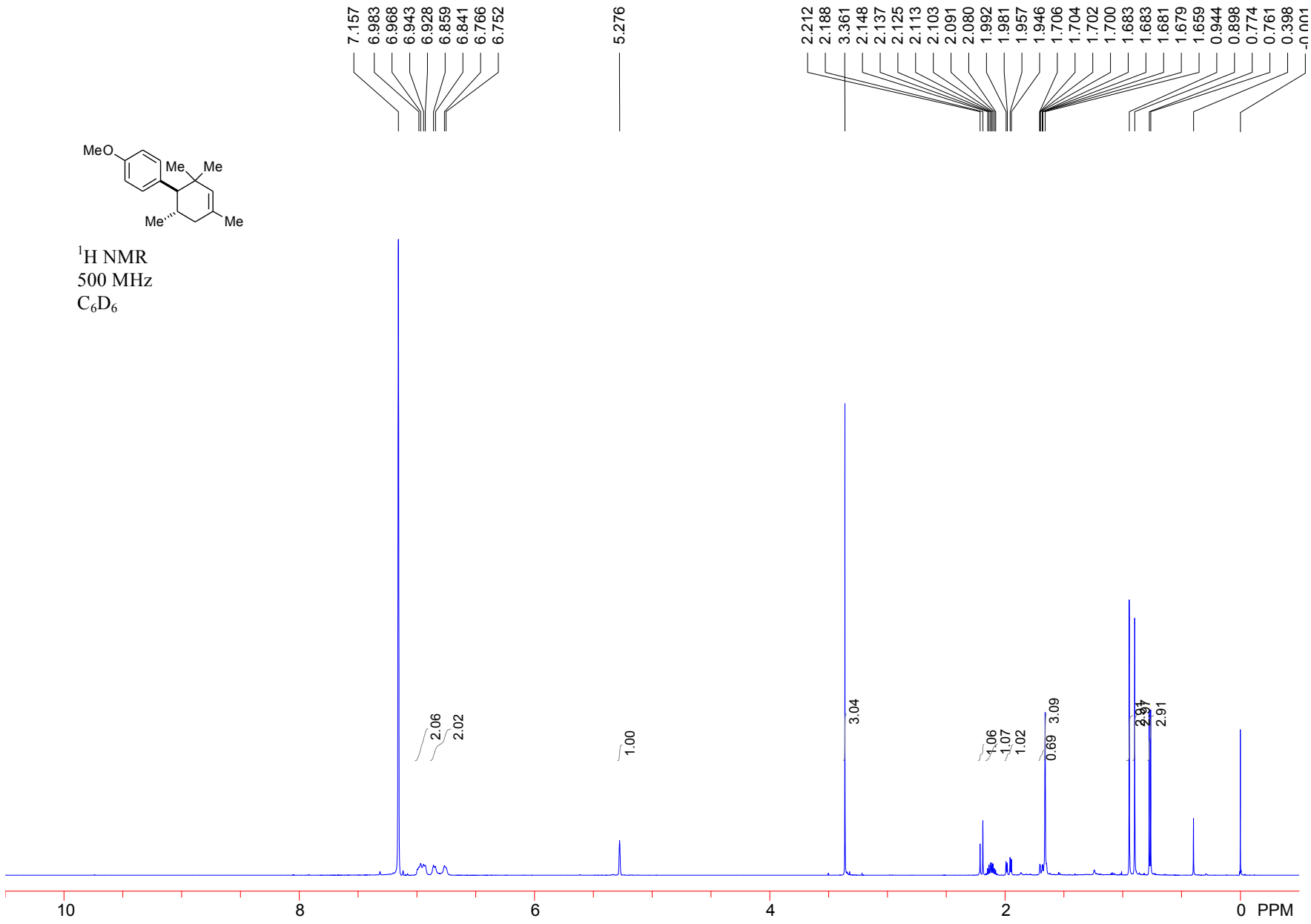
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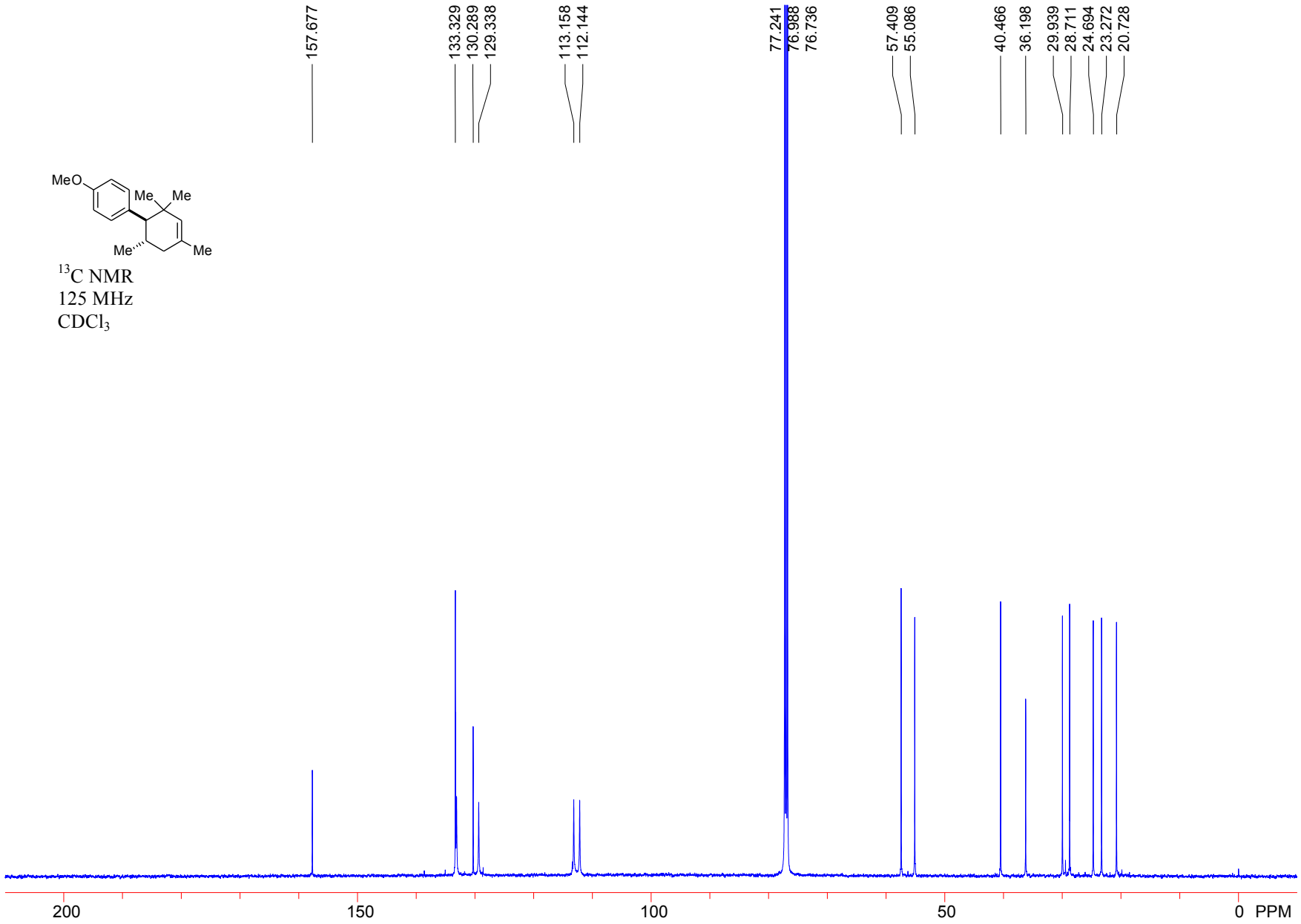
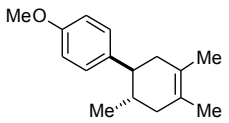
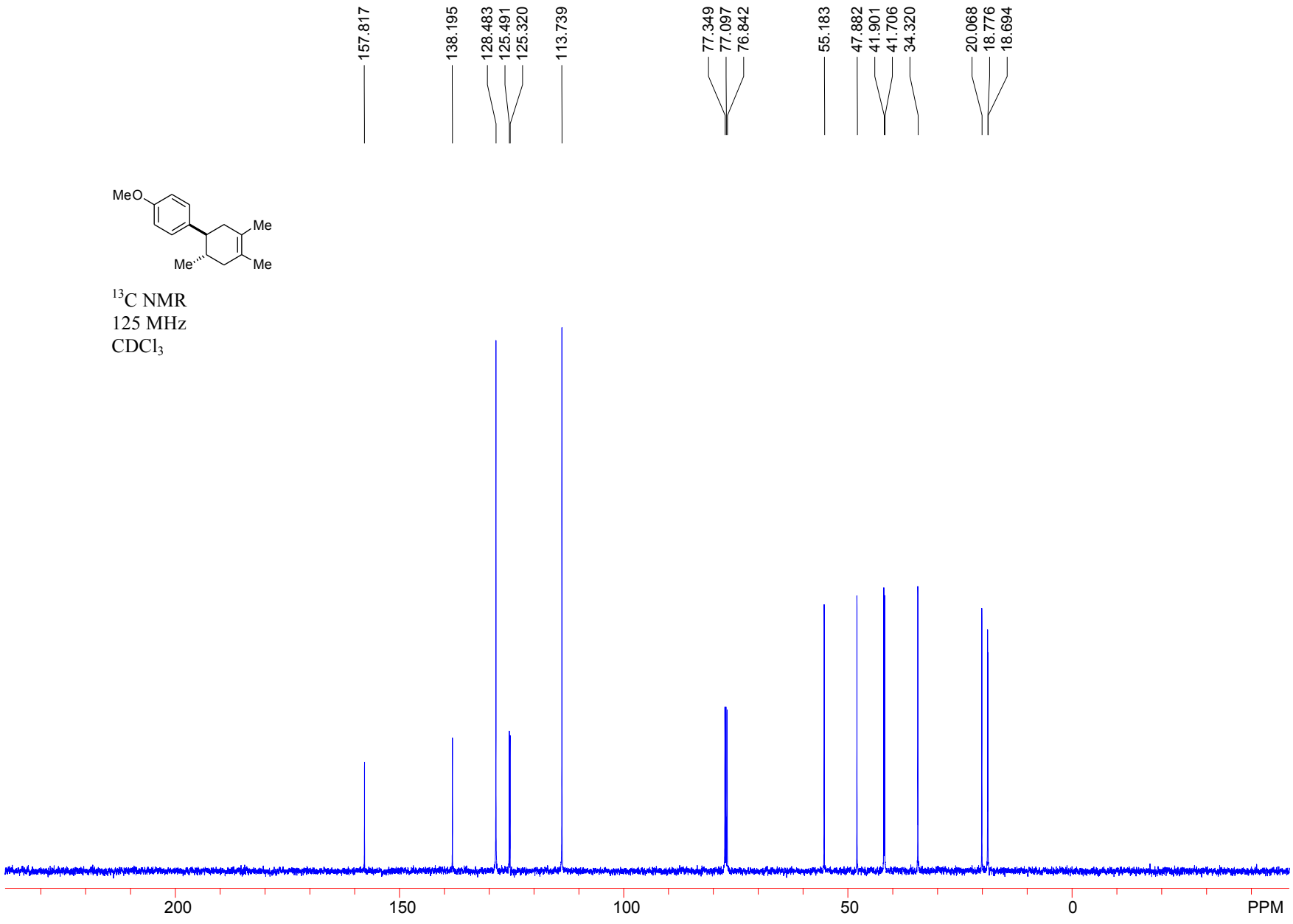
4
2
0 PPM

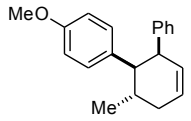


^{13}C NMR
125 MHz
$CDCl_3$

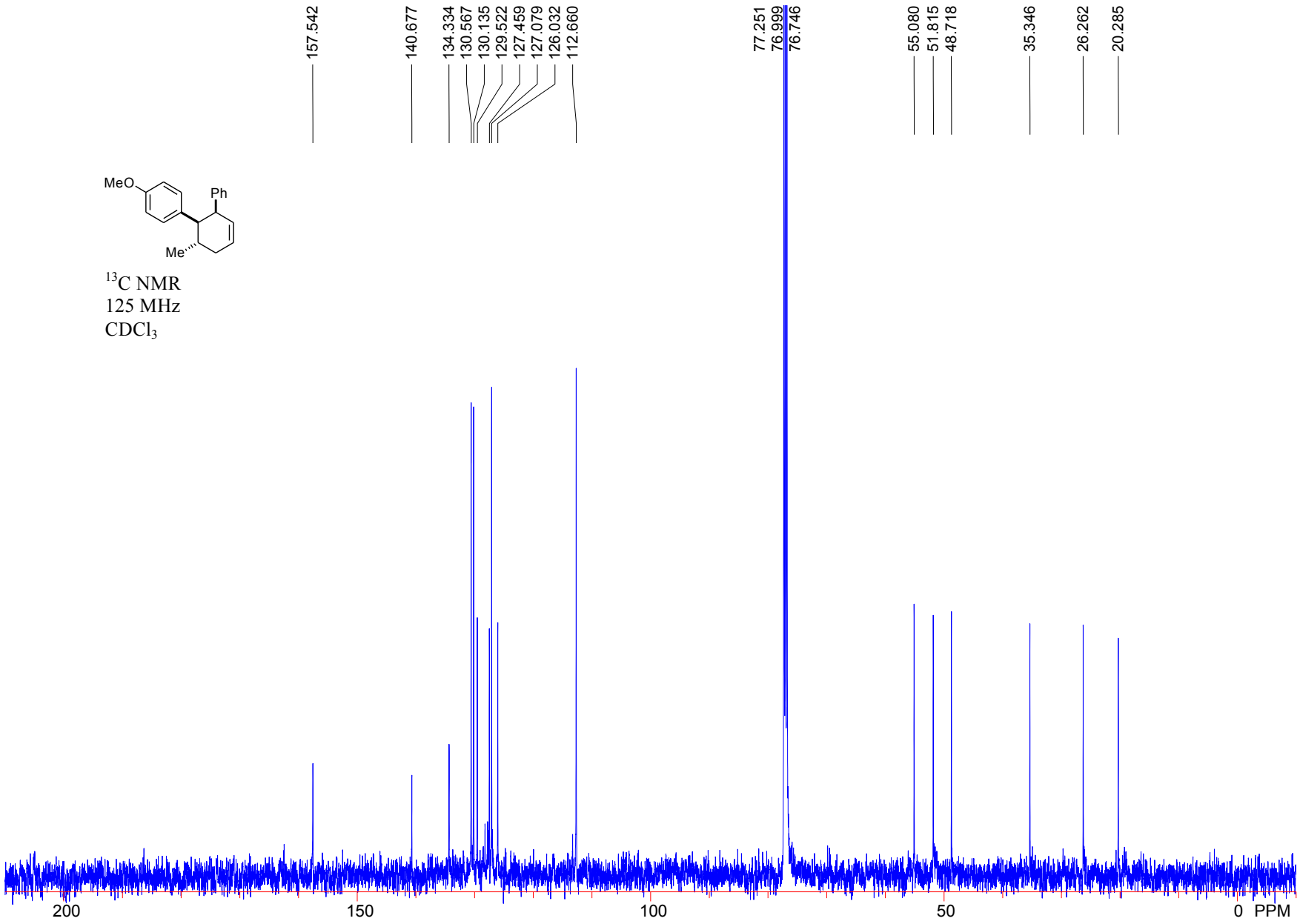


^{1}H NMR
500 MHz
$CDCl_3$

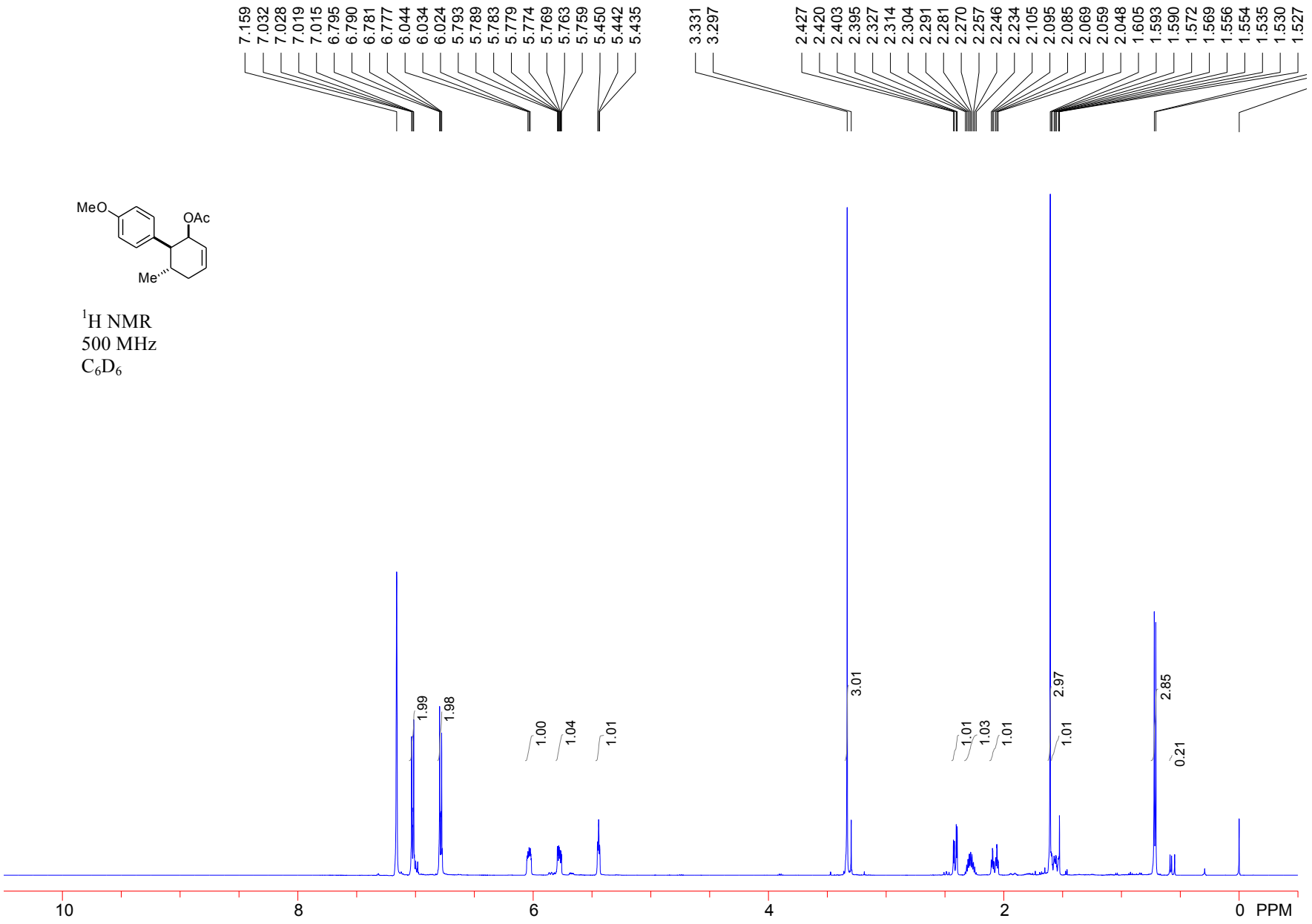

157.817
138.195
128.483
125.491
125.320
113.739
77.349
77.097
76.842
55.183
47.882
41.901
41.706
34.320
20.068
18.776
18.694
MeO
Me
Me
Me
^{13}C NMR
125 MHz
$CDCl_3$
200
150
100
50
0
PPM



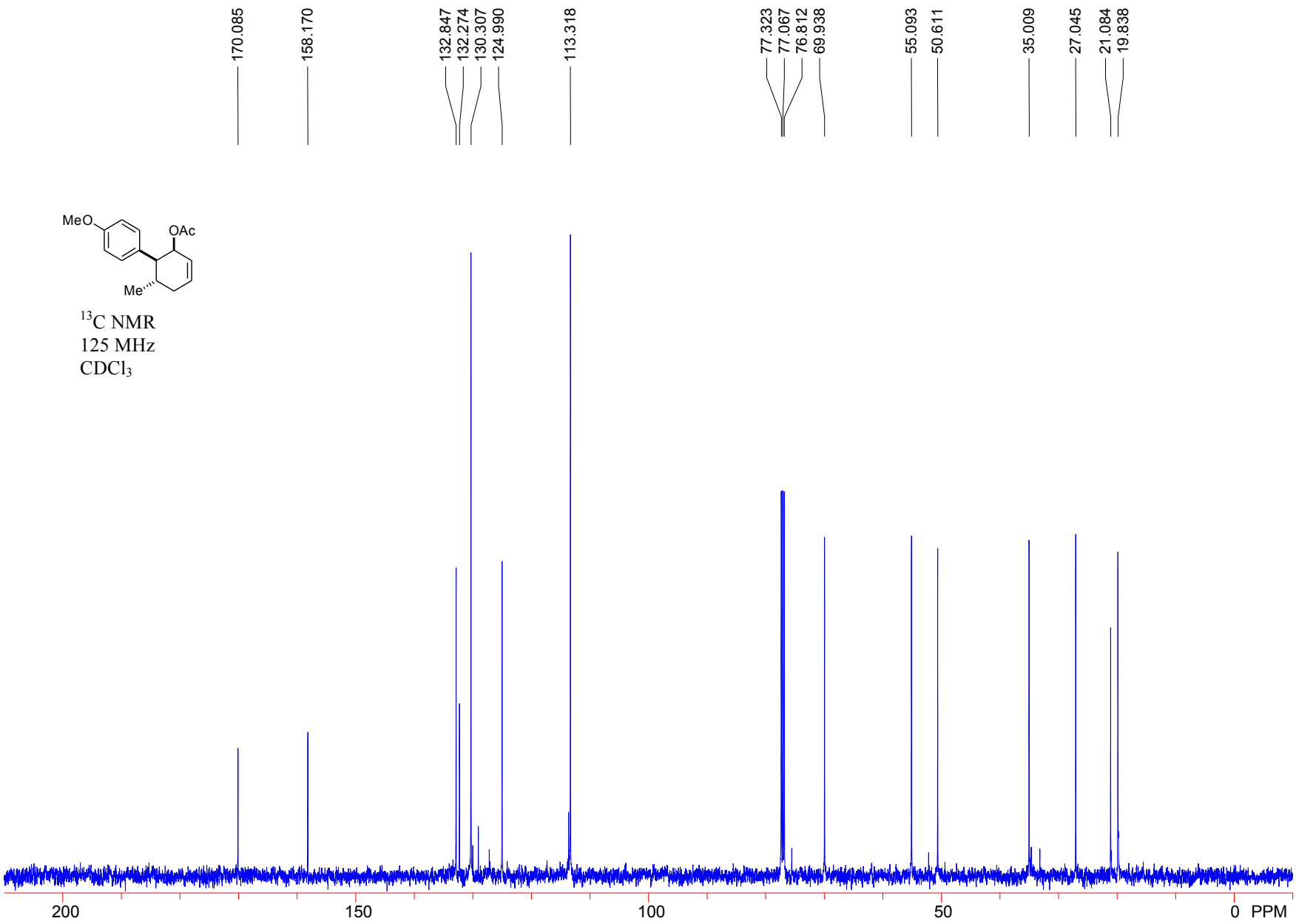
^{1}H NMR
500 MHz
$CDCl_3$

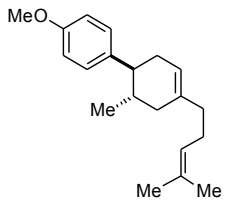


^{13}C NMR
125 MHz
$CDCl_3$

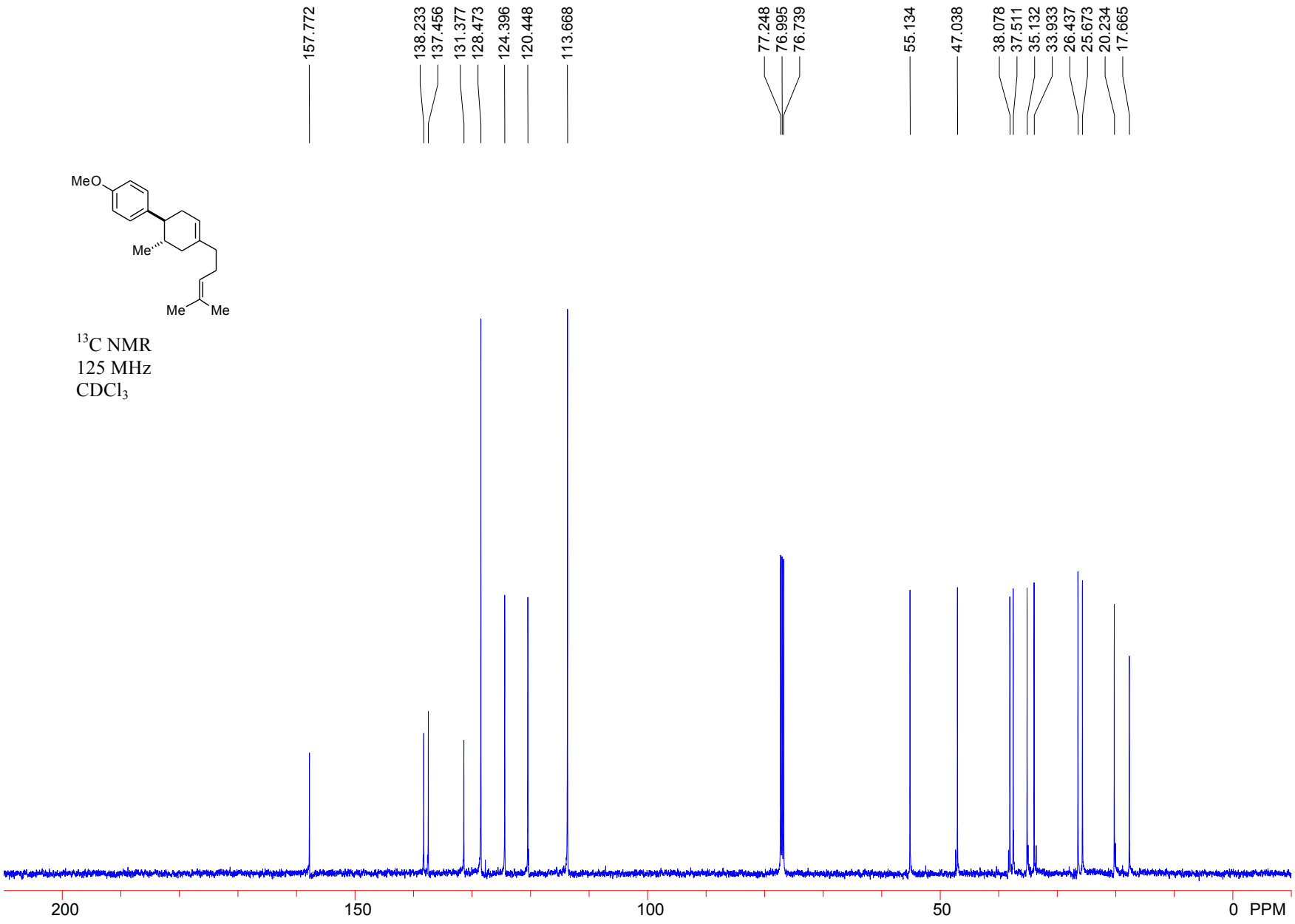


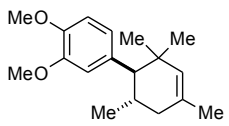
^{1}H NMR
500 MHz
C_6D_6


170.085
158.170
132.847
132.274
130.307
124.990
113.318
77.323
77.067
76.812
69.938
55.093
50.611
35.009
27.045
21.084
19.838
MeO
OAc
Me
13C NMR
125 MHz
CDCl3
200
150
100
50
0 PPM

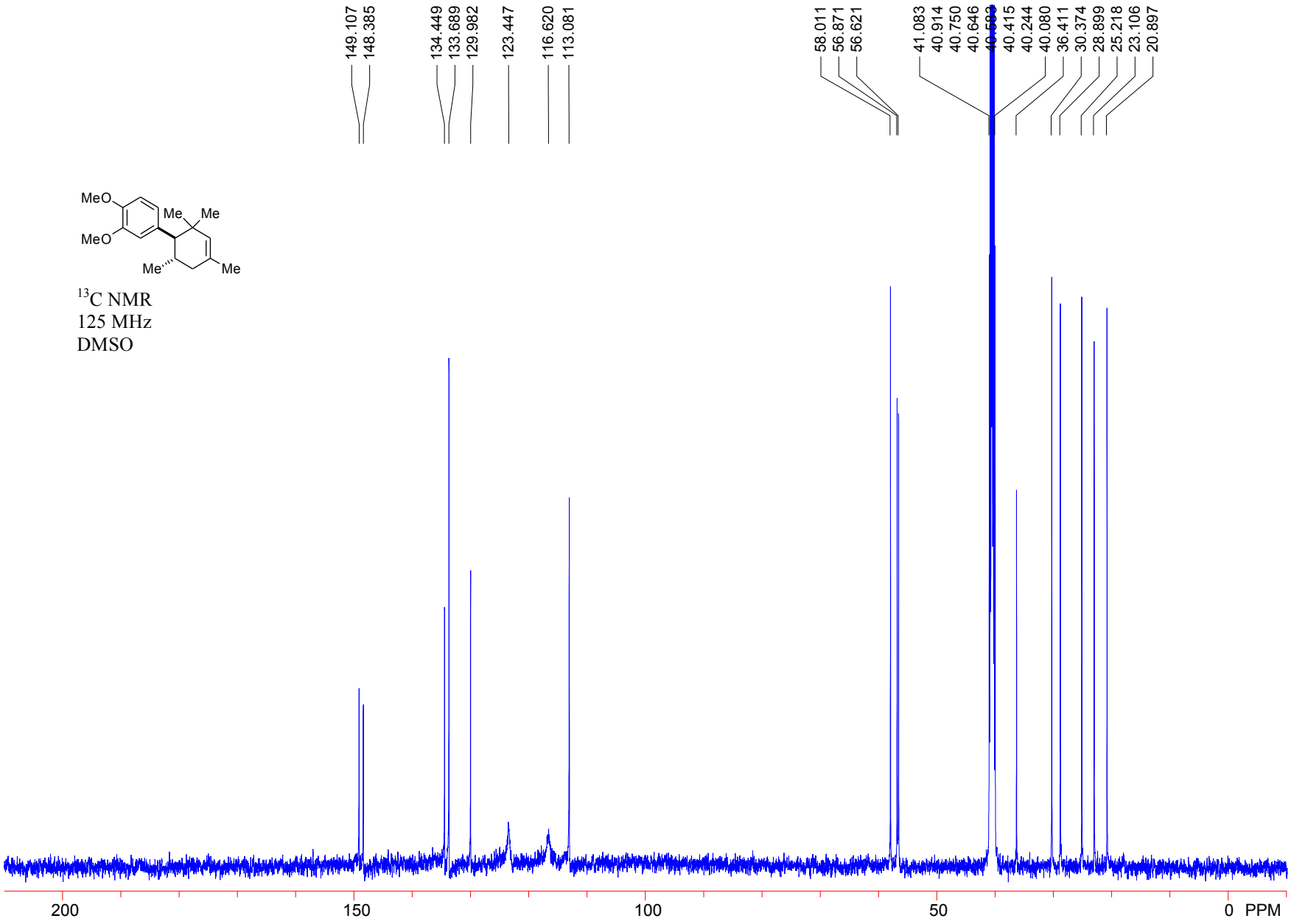


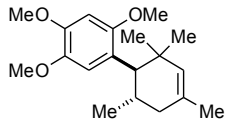
^{1}H NMR
500 MHz
$CDCl_3$


157.772
138.233
137.456
131.377
128.473
124.396
120.448
113.668
77.248
76.995
76.739
55.134
47.038
38.078
37.511
35.132
33.933
26.437
25.673
20.234
17.665
MeO
Me
Me
Me
^{13}C NMR
125 MHz
$CDCl_3$
200
150
100
50
0
PPM

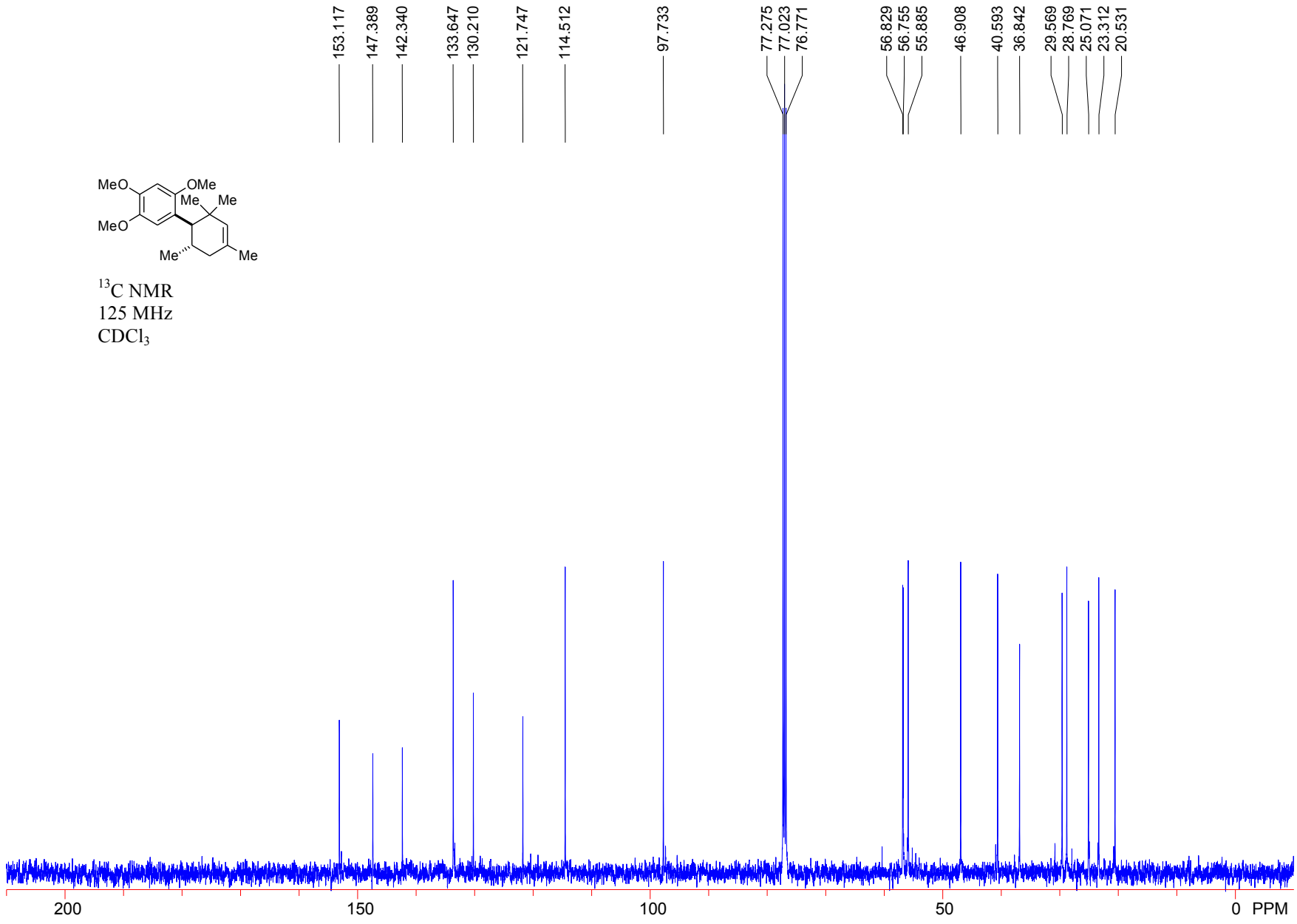


^{1}H NMR
500 MHz
DMSO

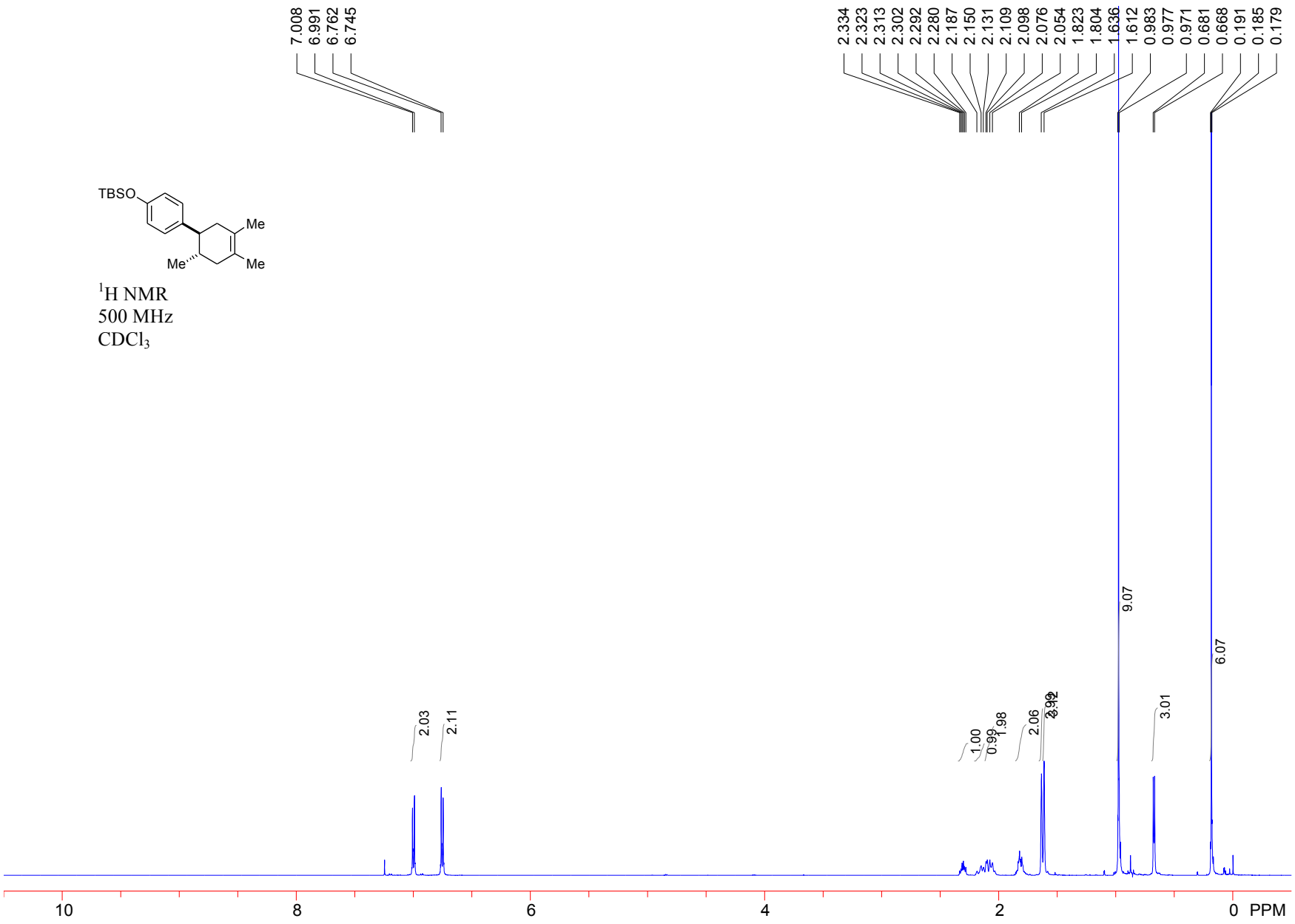

149.107
148.385
134.449
133.689
129.982
123.447
116.620
113.081
58.011
56.871
56.621
41.083
40.914
40.750
40.646
40.583
40.415
40.244
40.080
36.411
30.374
28.899
25.218
23.106
20.897
MeO
MeO
Me
Me
Me
Me
13C NMR
125 MHz
DMSO
200
150
100
50
0 PPM



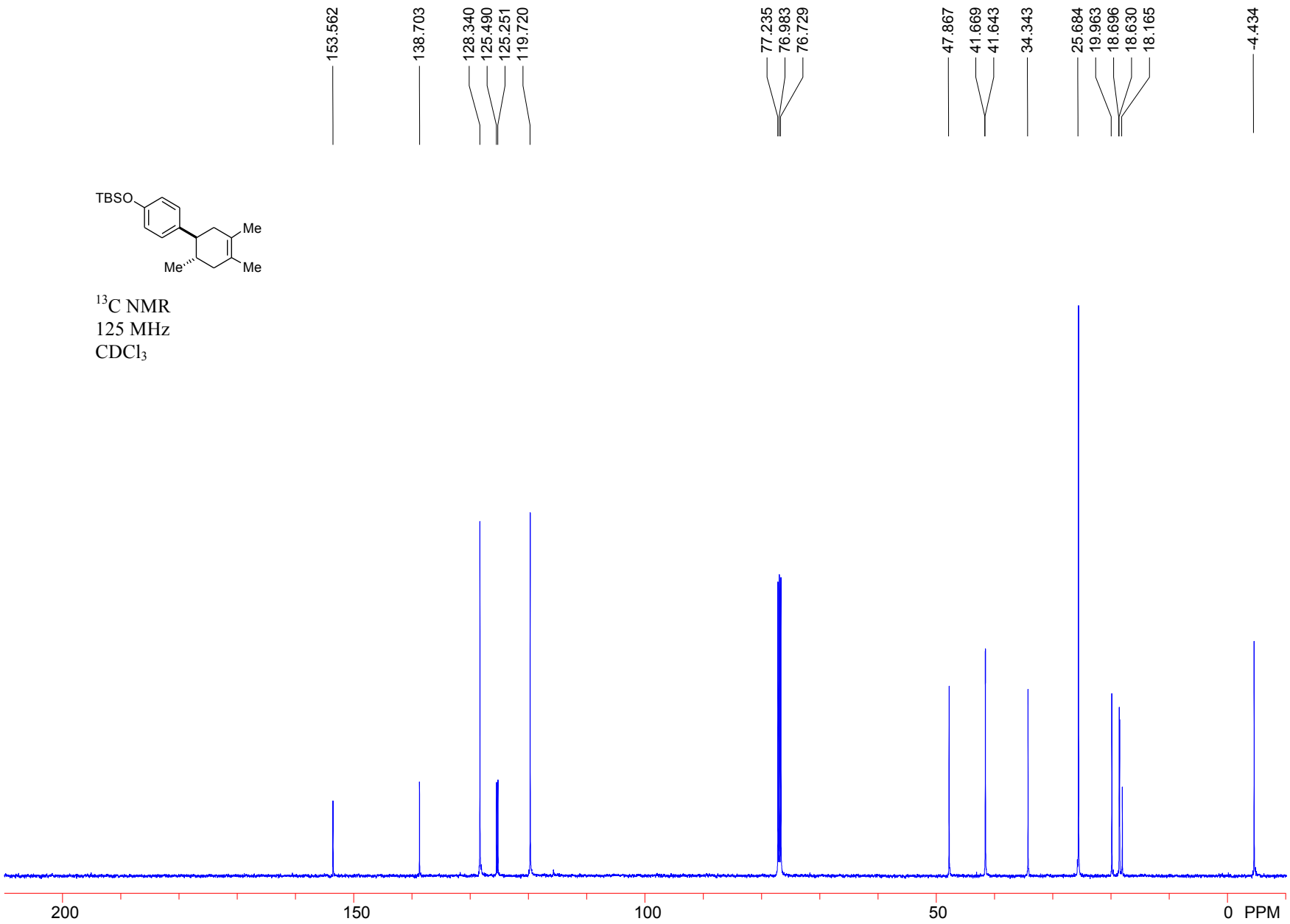
^{1}H NMR
500 MHz
$CDCl_3$



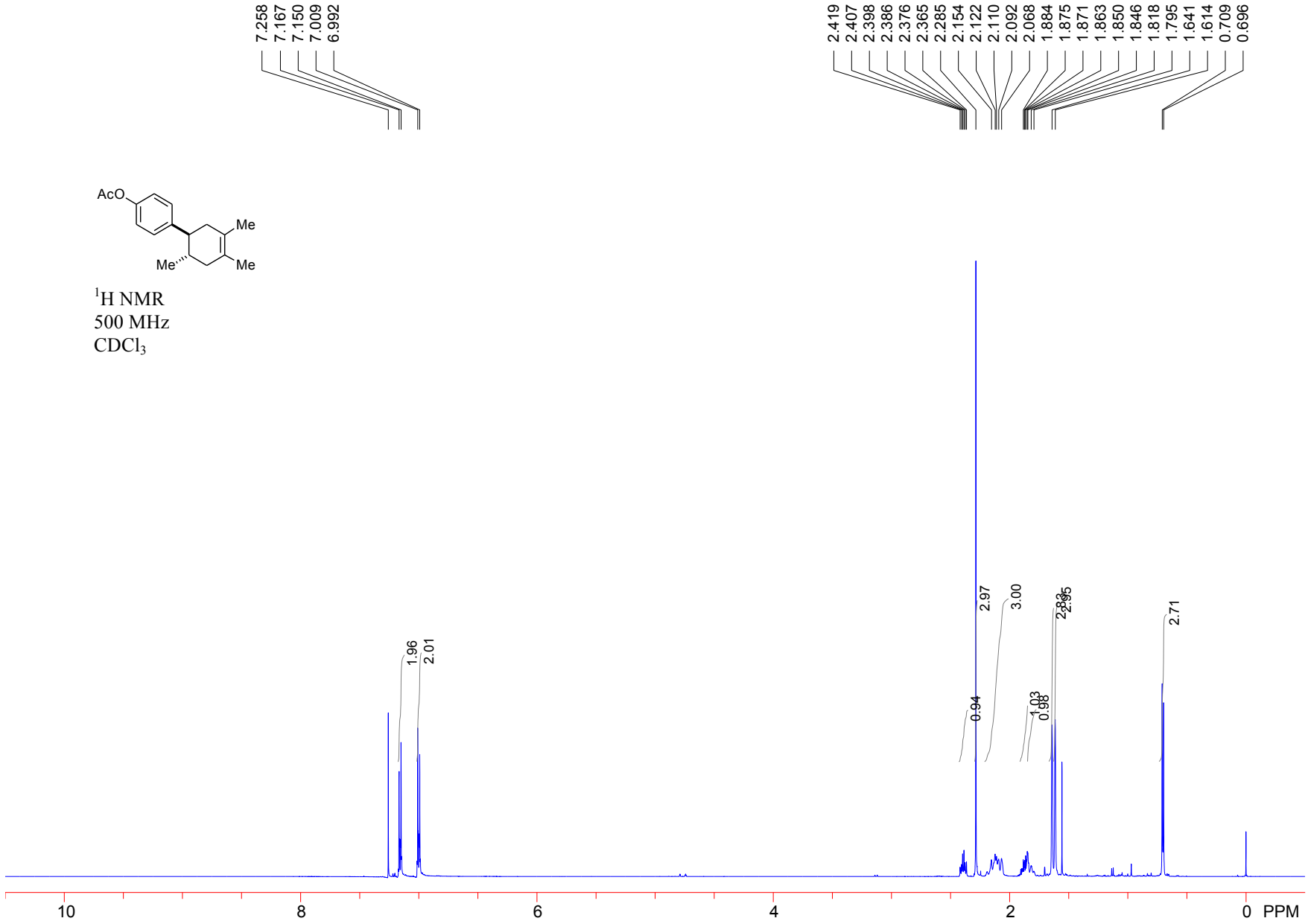
^{13}C NMR
125 MHz
$CDCl_3$

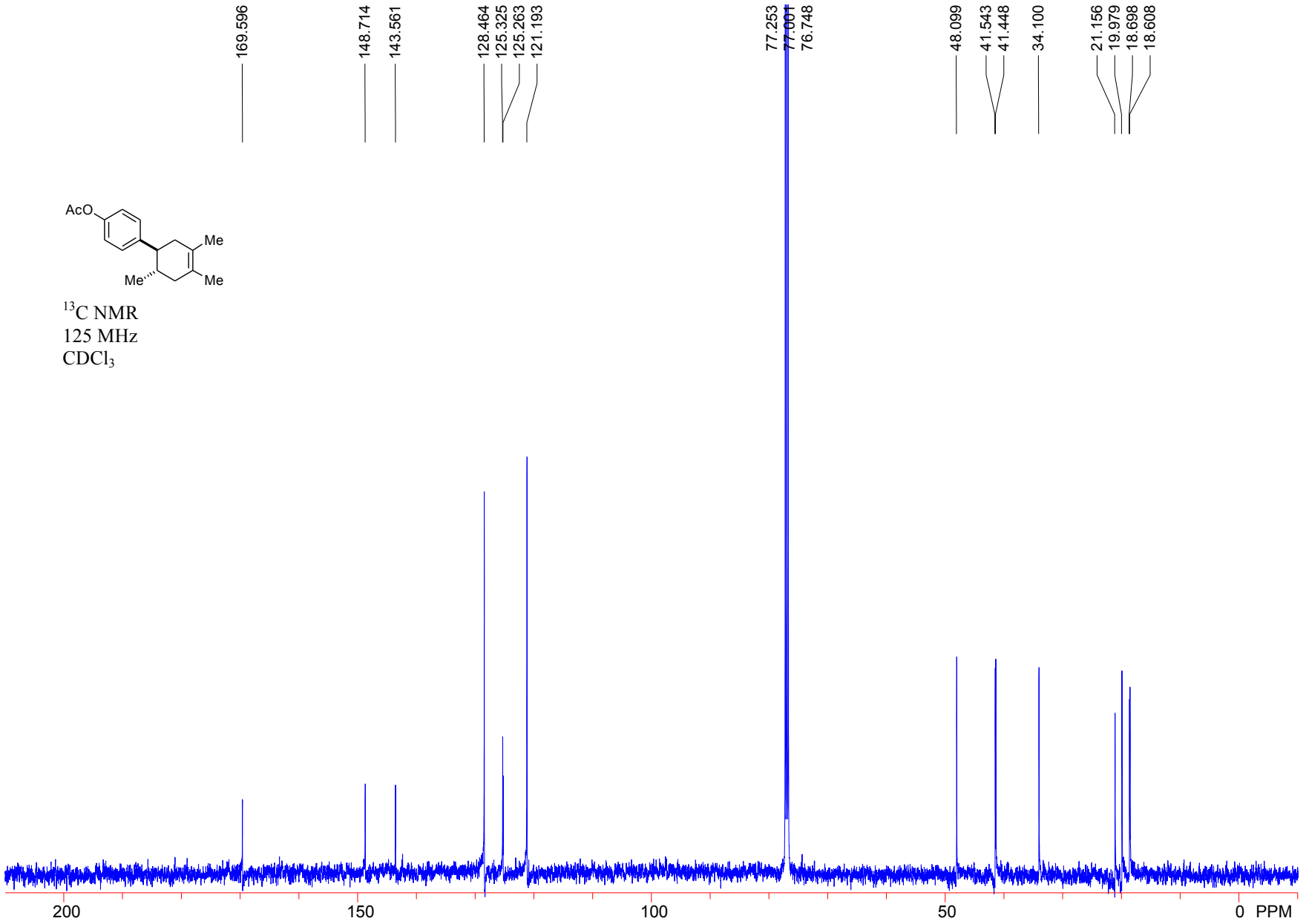


^{1}H NMR
500 MHz
$CDCl_3$

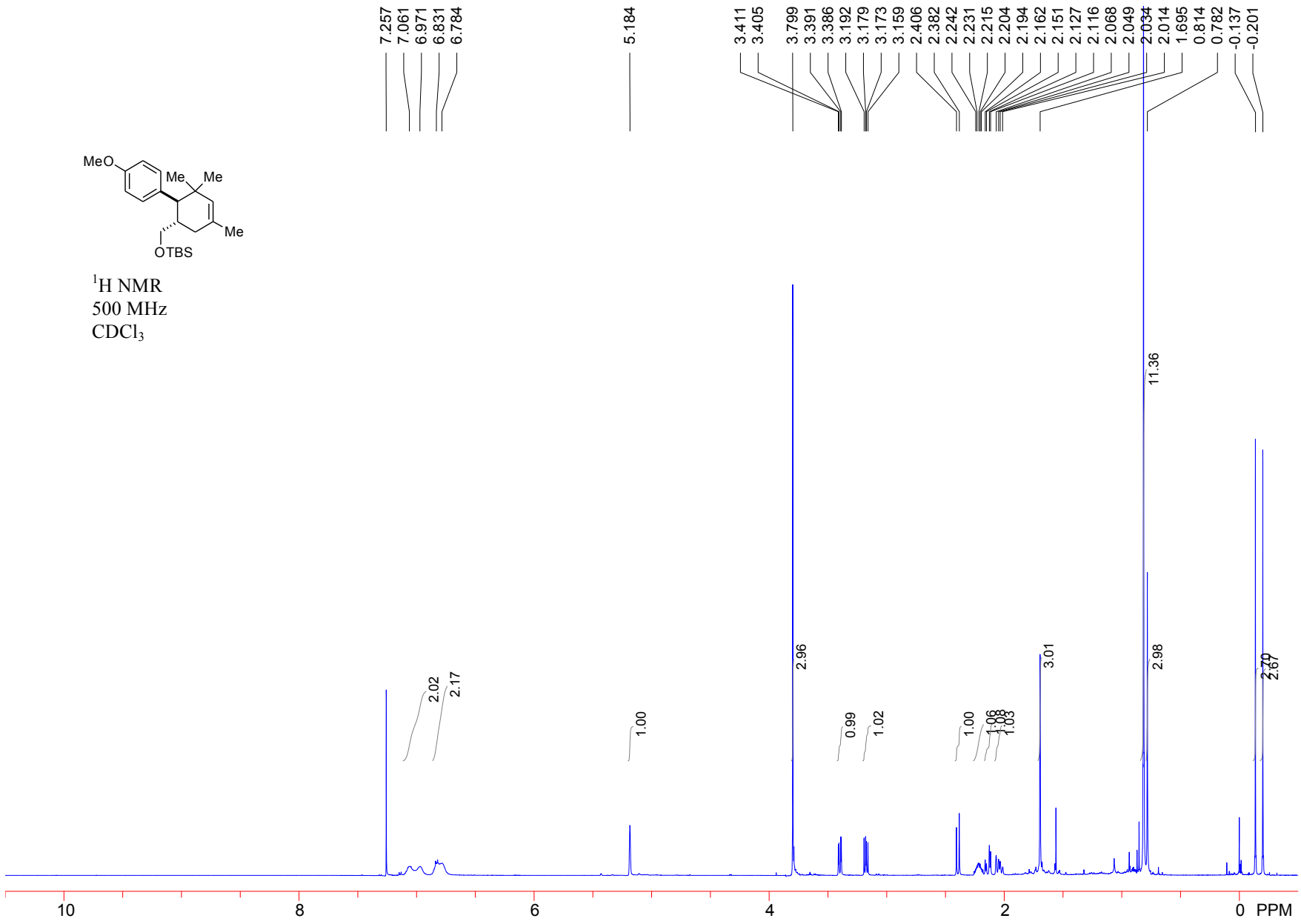


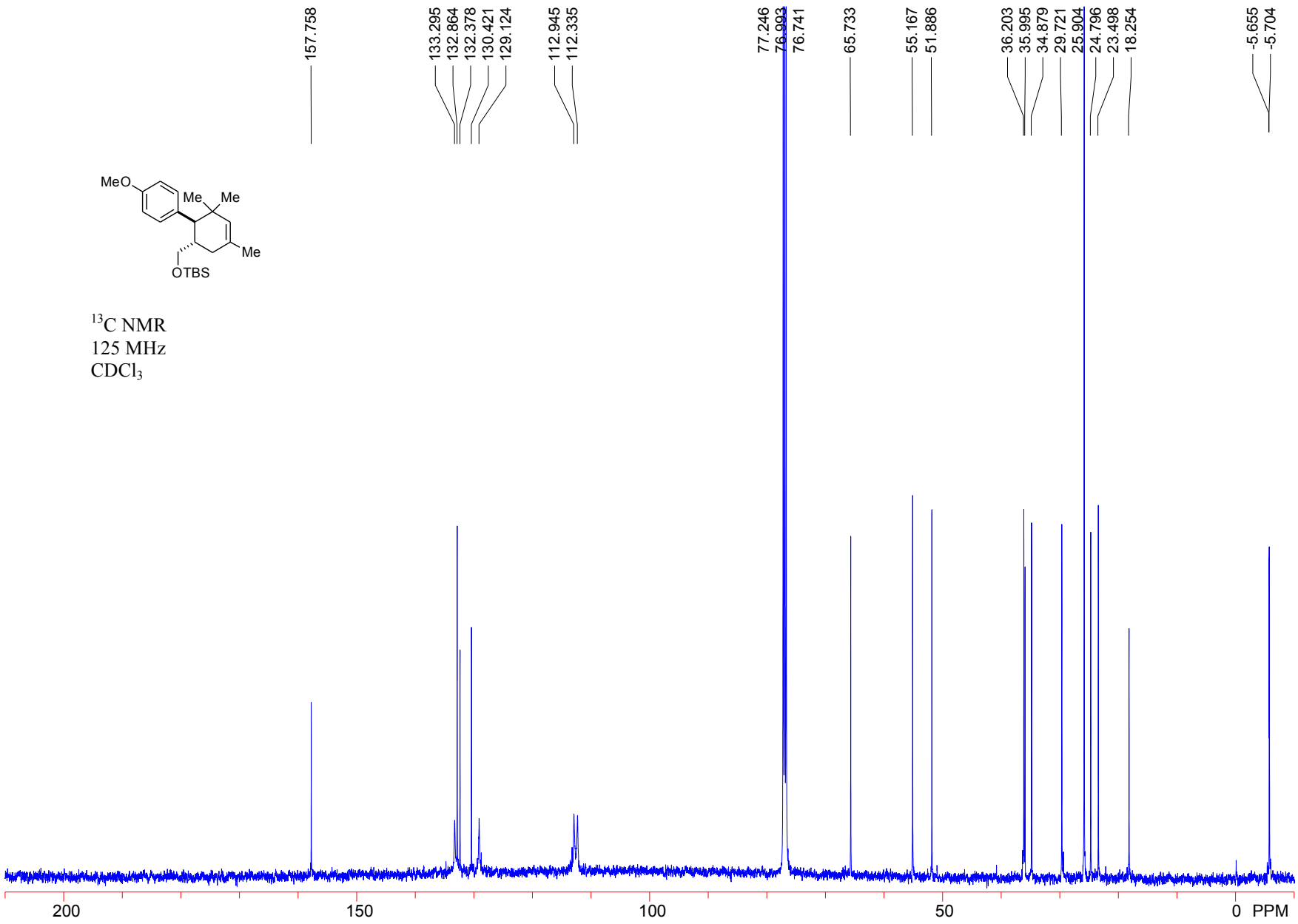
^{13}C NMR
125 MHz
$CDCl_3$


7.258
7.167
7.150
7.009
6.992
2.419
2.407
2.398
2.386
2.376
2.365
2.285
2.154
2.122
2.110
2.092
2.068
1.884
1.875
1.871
1.863
1.850
1.846
1.818
1.795
1.641
1.614
0.709
0.696
AcO
Me
Me
Me
1H NMR
500 MHz
CDCl3
1.96
2.01
0.94
2.97
1.03
0.98
3.00
2.83
2.95
2.71
10
8
6
4
2
0 PPM

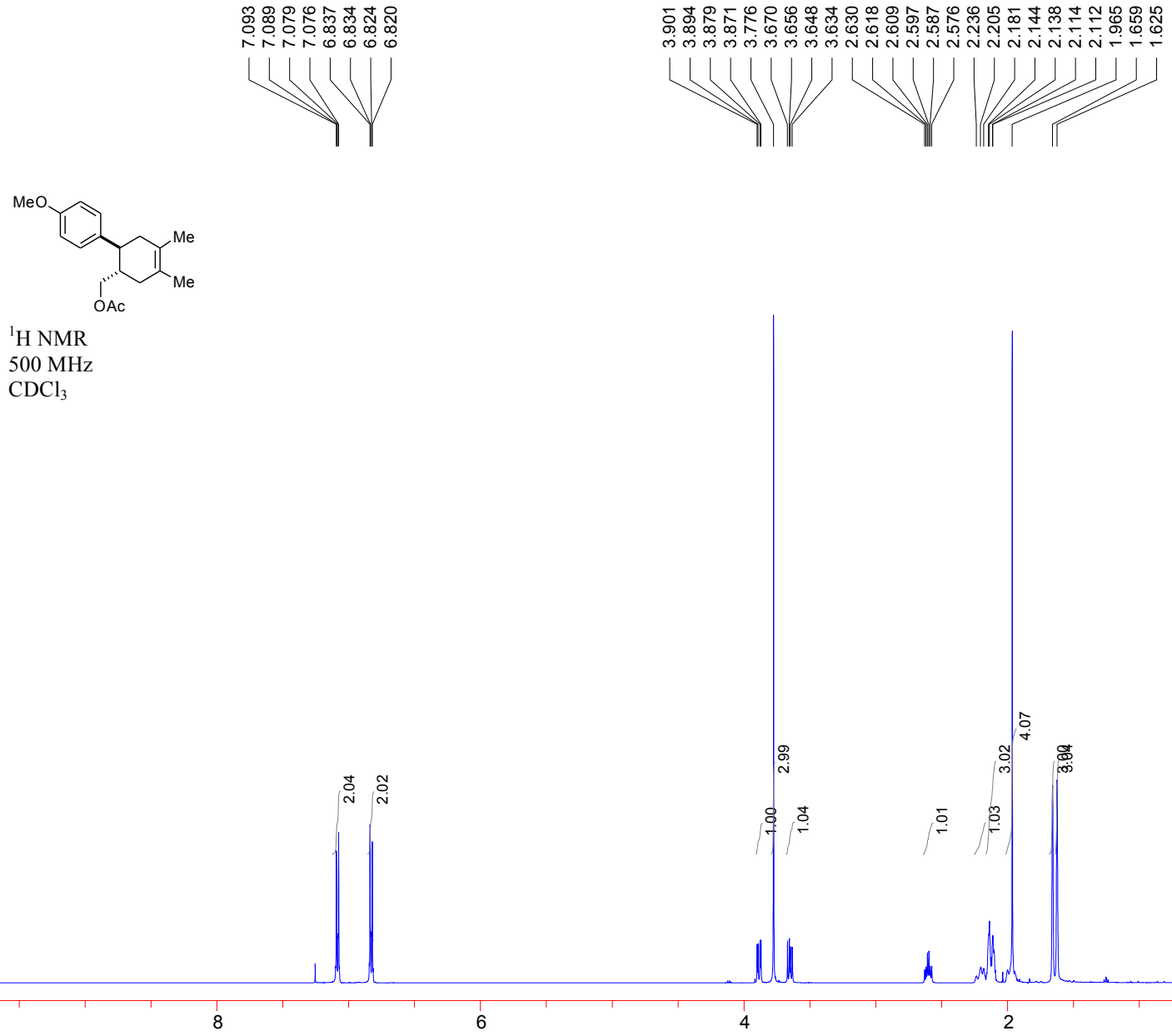


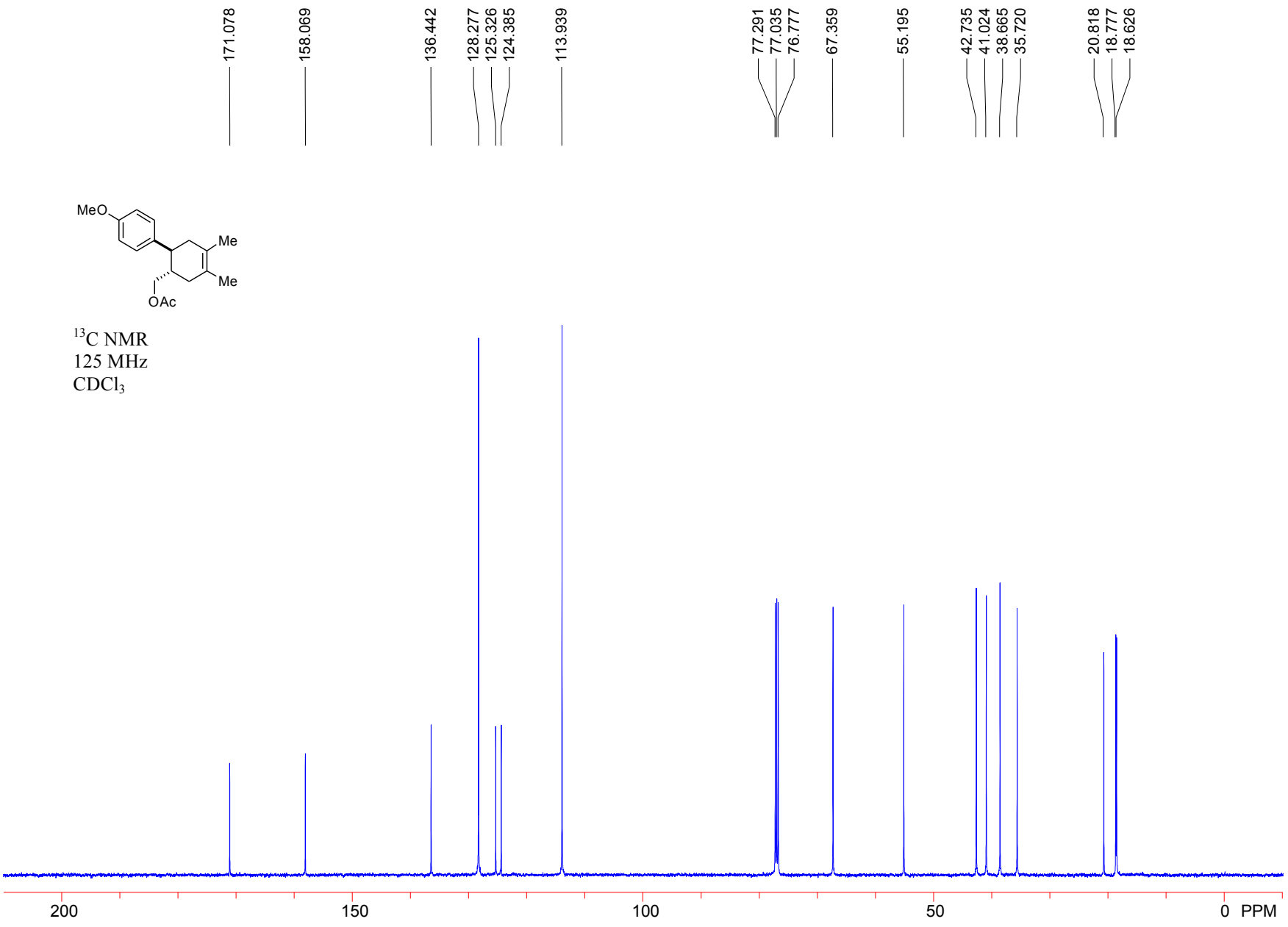
^{13}C NMR
125 MHz
$CDCl_3$


MeO
Me
Me
Me
OTBS
^{1}H NMR
500 MHz
$CDCl_3$
7.257
7.061
6.971
6.831
6.784
5.184
3.411
3.405
3.799
3.391
3.386
3.192
3.179
3.173
3.159
2.406
2.382
2.242
2.231
2.215
2.204
2.194
2.162
2.151
2.127
2.116
2.068
2.049
2.034
2.014
1.695
0.814
0.782
-0.137
-0.201
11.36
2.96
3.01
2.98
2.70
2.67
2.02
2.17
1.00
0.99
1.02
1.00
1.06
1.08
1.03
10
8
6
4
2
0 PPM

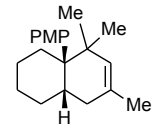


^{13}C NMR
125 MHz
$CDCl_3$

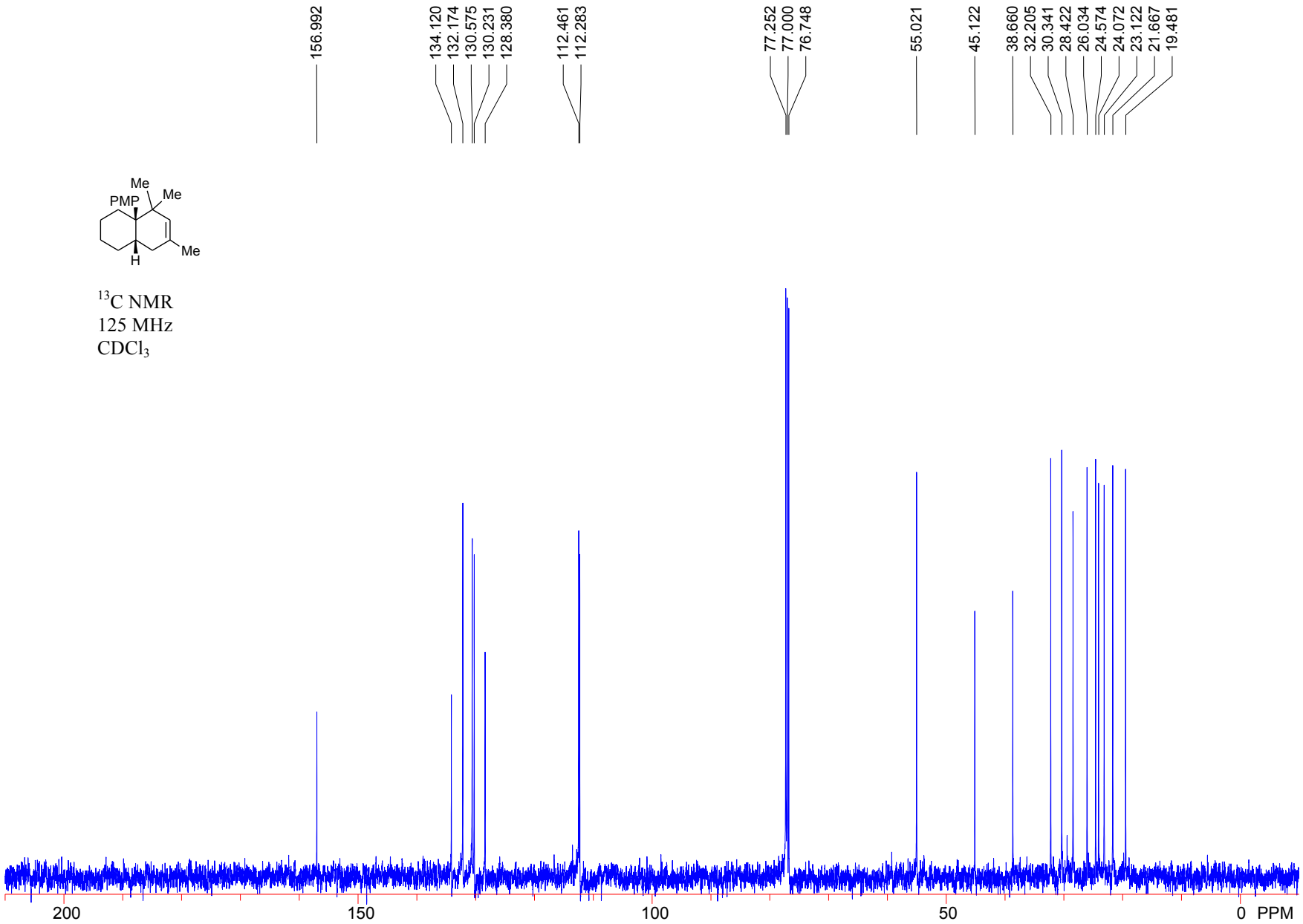

7.093
7.089
7.079
7.076
6.837
6.834
6.824
6.820
3.901
3.894
3.879
3.871
3.776
3.670
3.656
3.648
3.634
2.630
2.618
2.609
2.597
2.587
2.576
2.236
2.205
2.181
2.144
2.138
2.114
2.112
1.965
1.659
1.625
MeO
Me
Me
OAc
1H NMR
500 MHz
CDCl3
2.04
2.02
1.00
2.99
1.04
1.01
1.03
3.02
4.07
10
8
6
4
2
0 PPM

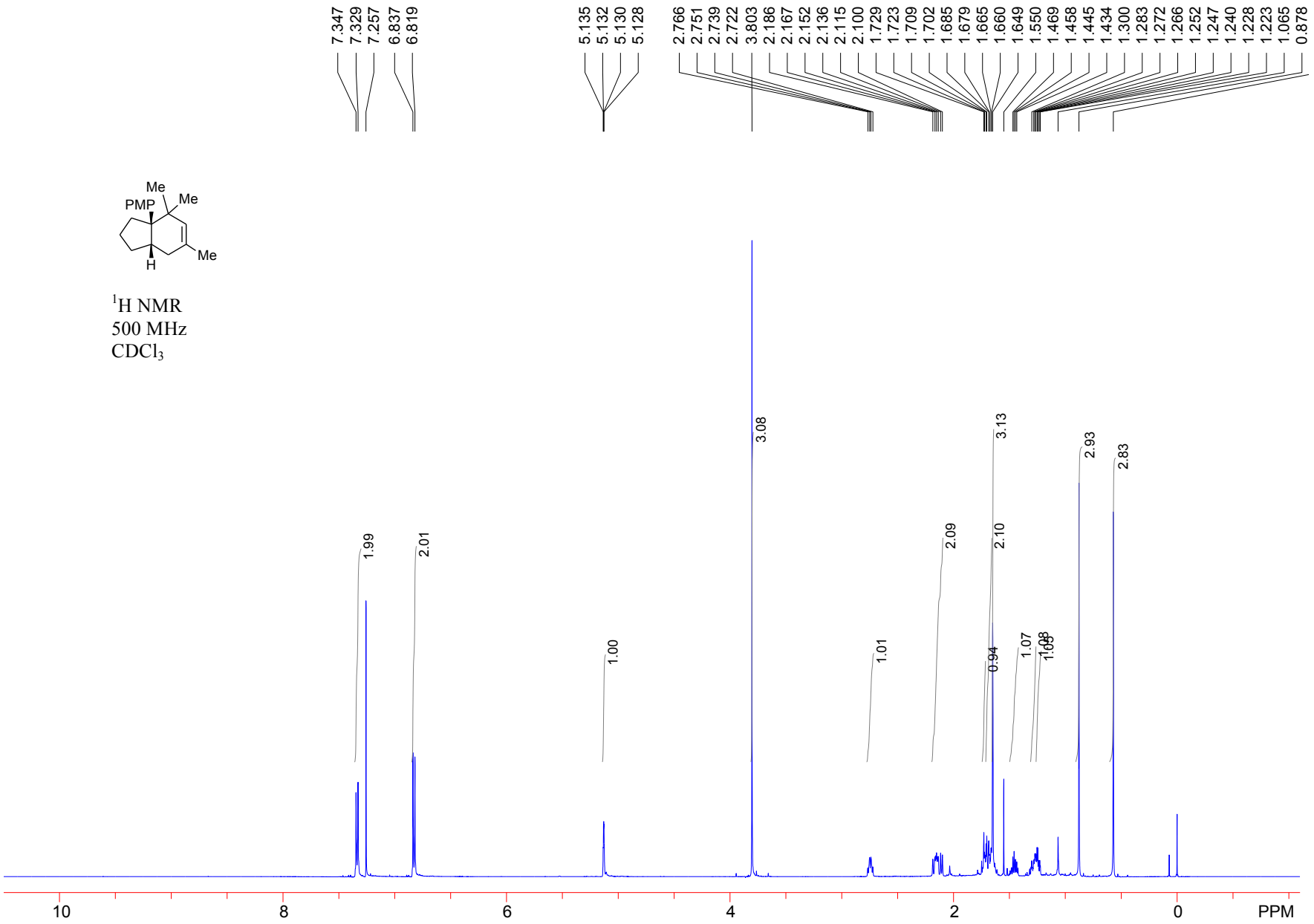


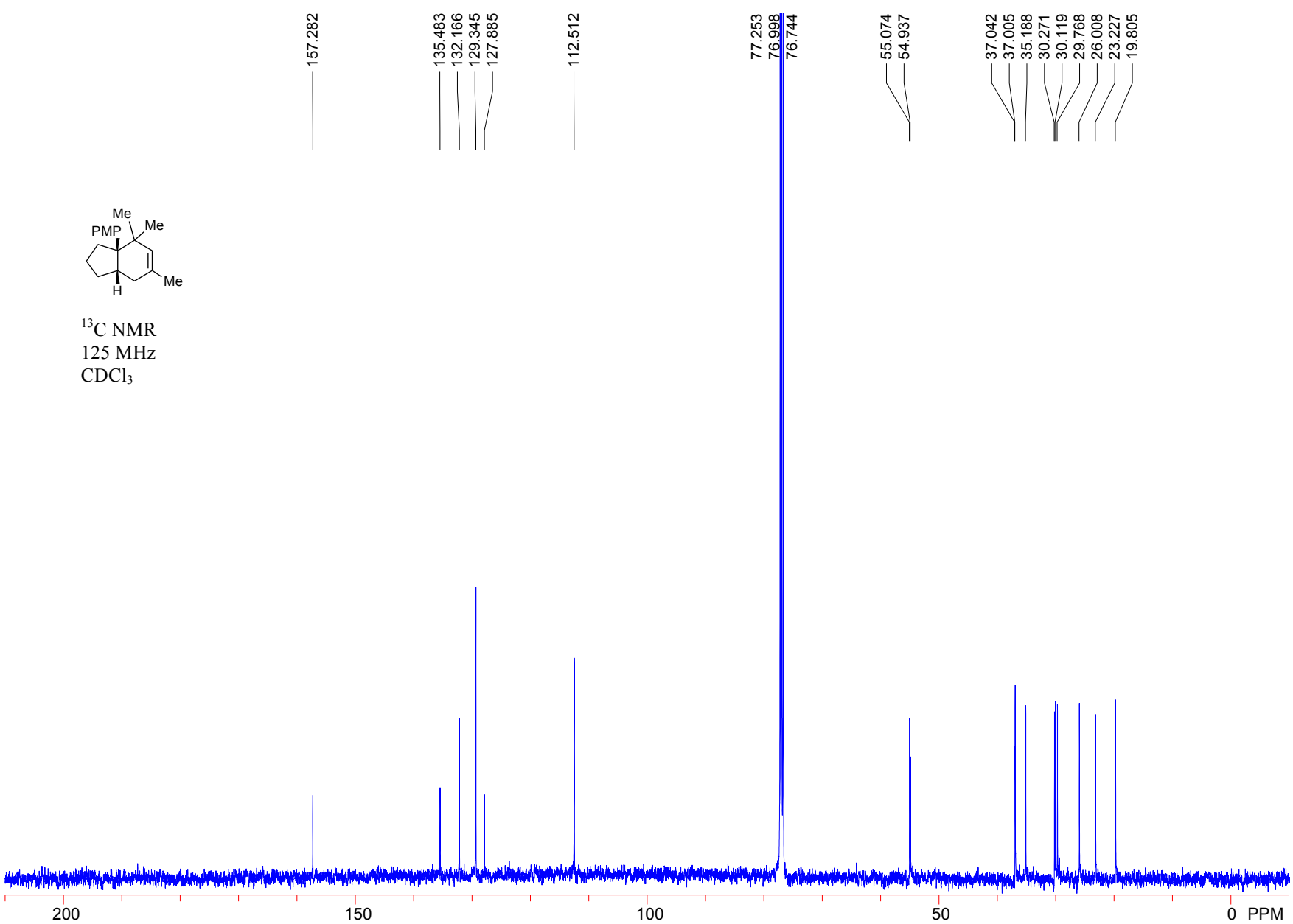
^{13}C NMR
125 MHz
$CDCl_3$



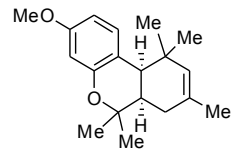
^{1}H NMR
500 MHz
$CDCl_3$


156.992
134.120
132.174
130.575
130.231
128.380
112.461
112.283
77.252
77.000
76.748
55.021
45.122
38.660
32.205
30.341
28.422
26.034
24.574
24.072
23.122
21.667
19.481
Me
PMP
Me
Me
H
^{13}C NMR
125 MHz
$CDCl_3$
200
150
100
50
0 PPM

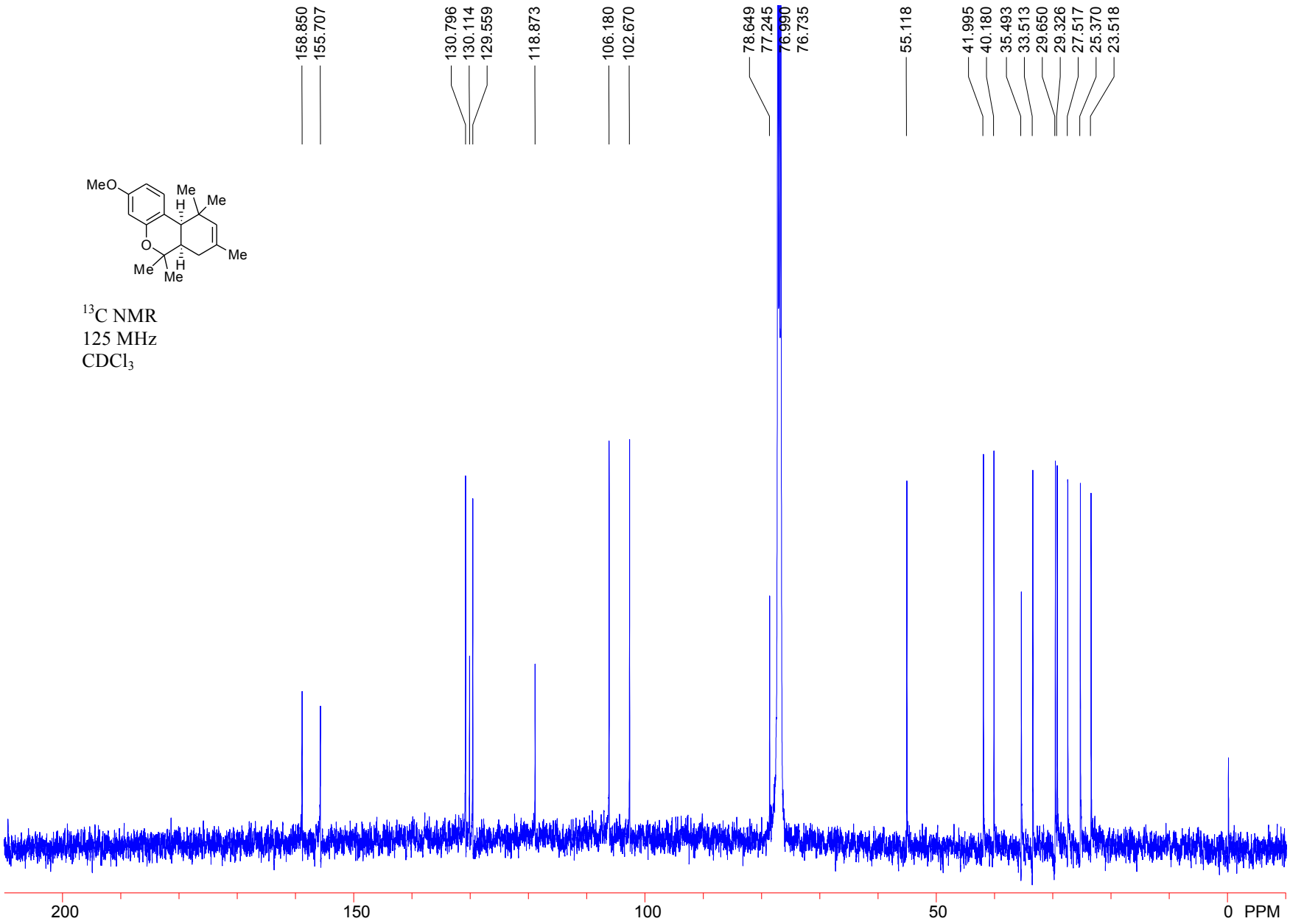

7.347
7.329
7.257
6.837
6.819
5.135
5.132
5.130
5.128
2.766
2.751
2.739
2.722
3.803
2.186
2.167
2.152
2.136
2.115
2.100
1.729
1.723
1.709
1.702
1.685
1.679
1.665
1.660
1.649
1.550
1.469
1.458
1.445
1.434
1.300
1.283
1.272
1.266
1.252
1.247
1.240
1.228
1.223
1.065
0.878
Me
PMP
Me
Me
H
1H NMR
500 MHz
CDCl3
1.99
2.01
1.00
3.08
1.01
2.09
3.13
2.10
0.94
1.07
2.93
2.83
10
8
6
4
2
0
PPM

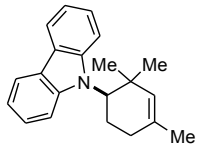


^{13}C NMR
125 MHz
$CDCl_3$

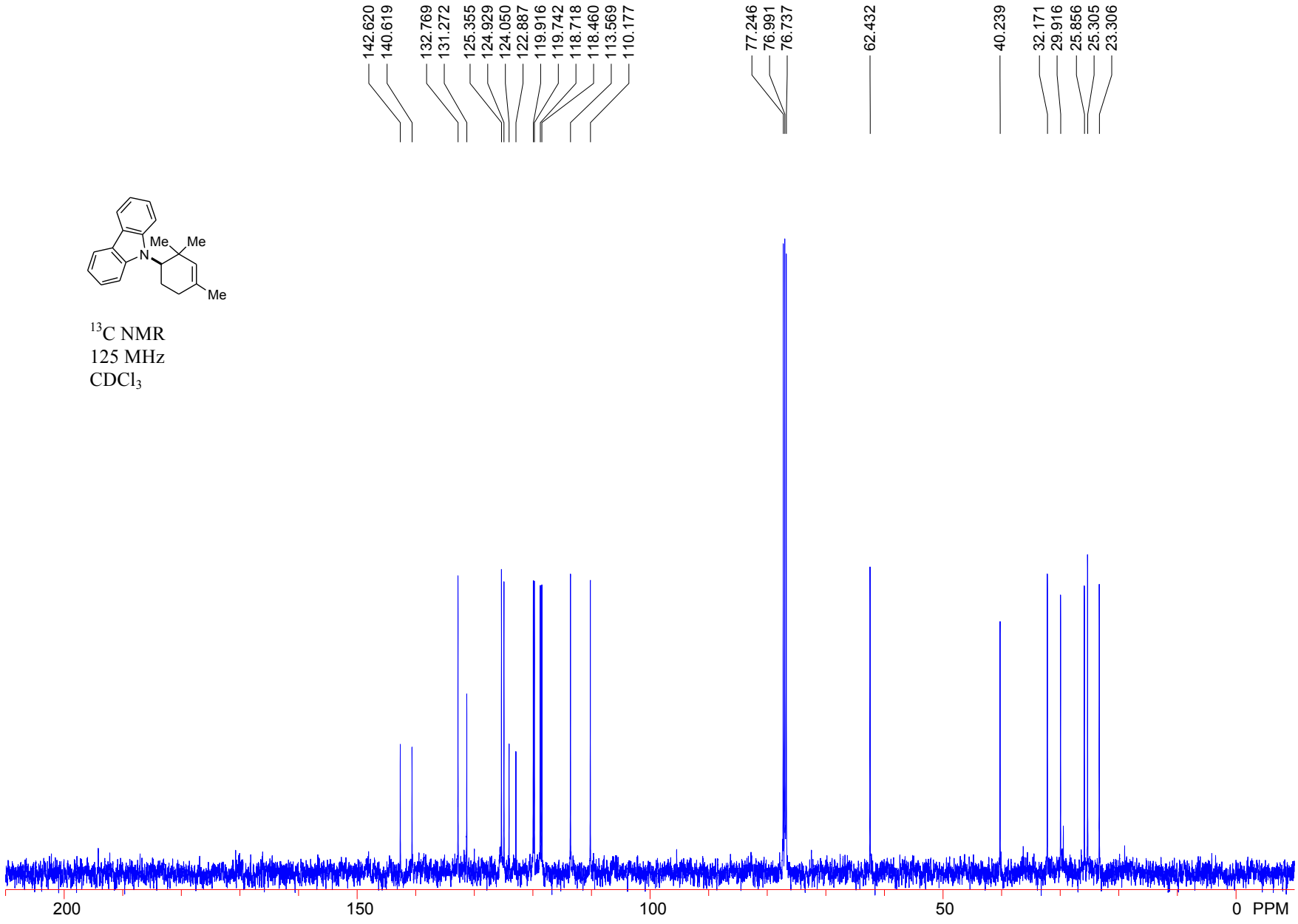


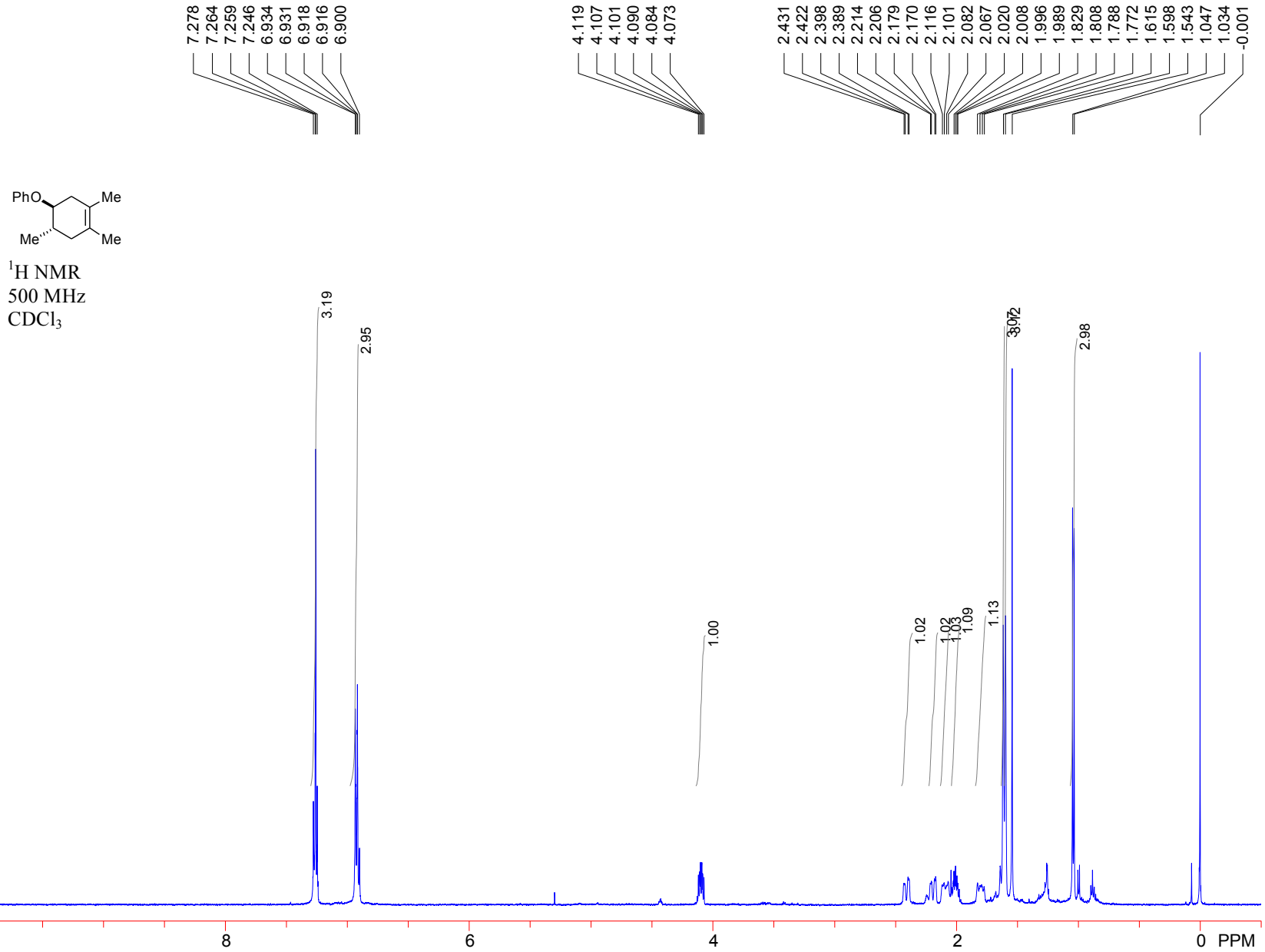
^{1}H NMR
500 MHz
$CDCl_3$

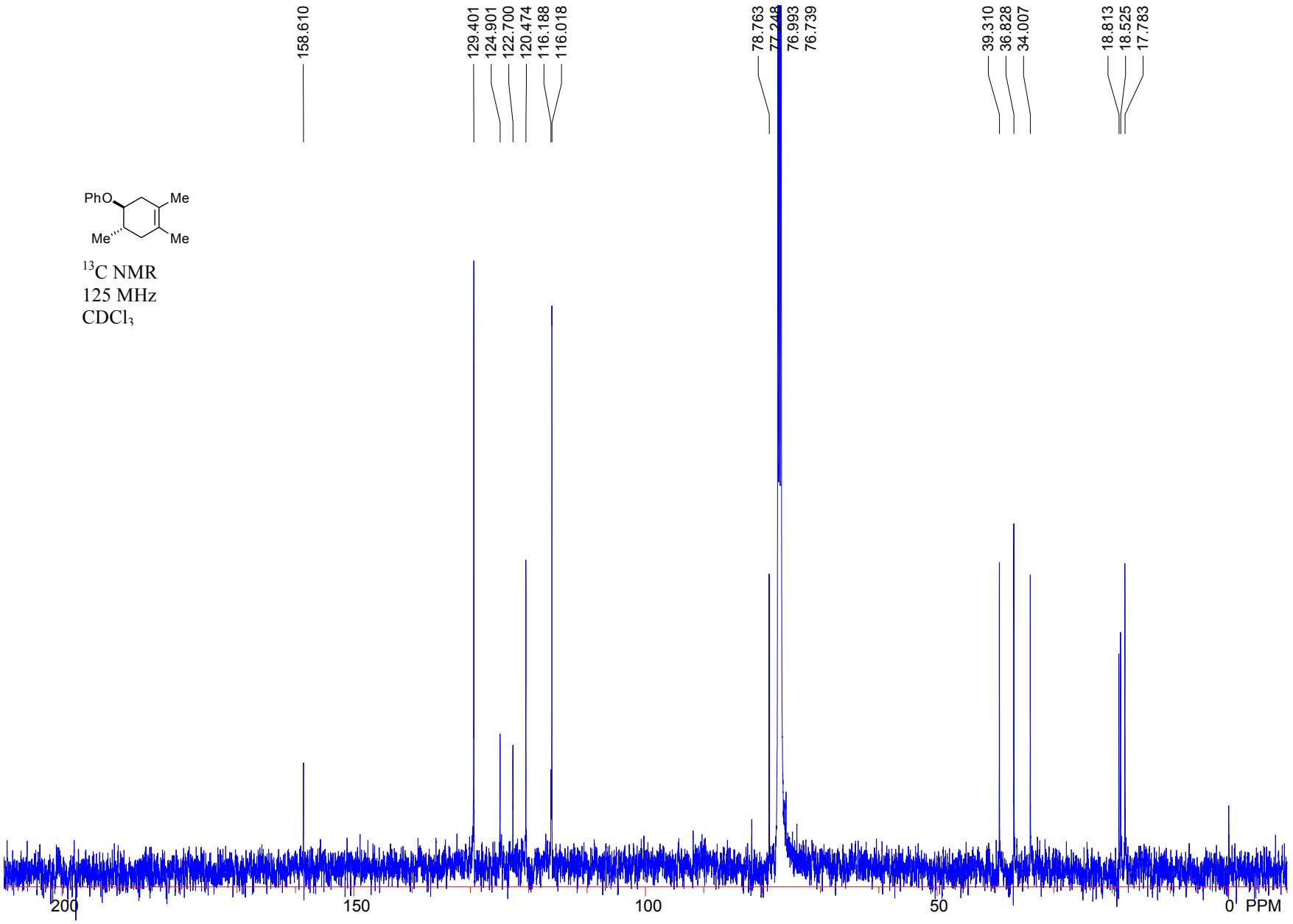

158.850
155.707
130.796
130.114
129.559
118.873
106.180
102.670
78.649
77.245
76.990
76.735
55.118
41.995
40.180
35.493
33.513
29.650
29.326
27.517
25.370
23.518
MeO
Me
H
Me
O
Me
Me
H
Me
^{13}C NMR
125 MHz
$CDCl_3$
200
150
100
50
0 PPM

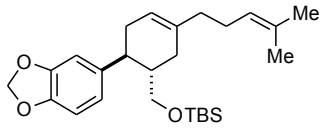


^{1}H NMR
500 MHz
$CDCl_3$

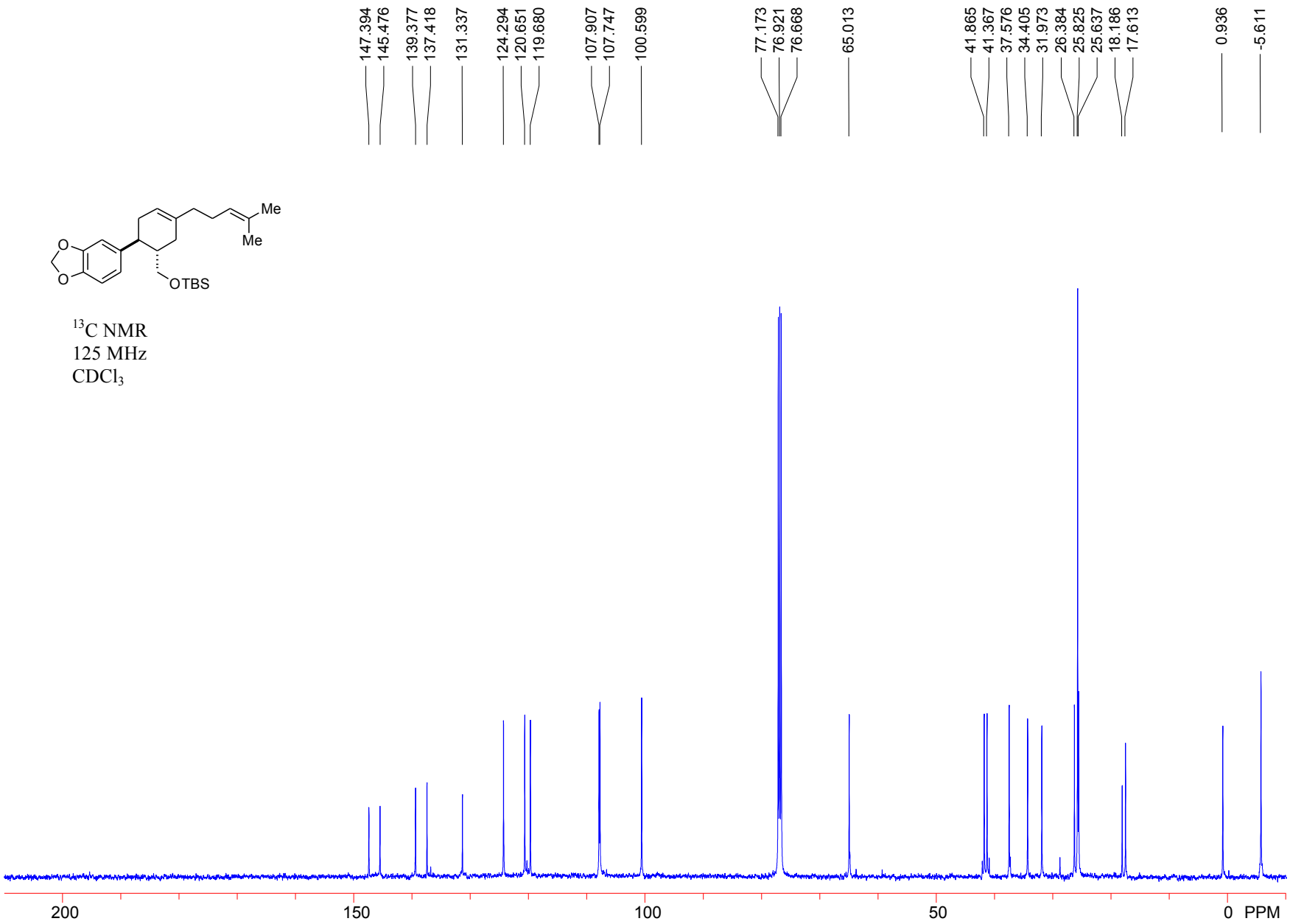

142.620
140.619
132.769
131.272
125.355
124.929
124.050
122.887
119.916
119.742
118.718
118.460
113.569
110.177
77.246
76.991
76.737
62.432
40.239
32.171
29.916
25.856
25.305
23.306
Me
Me
N
Me
^{13}C NMR
125 MHz
$CDCl_3$
200
150
100
50
0 PPM


7.278
7.264
7.259
7.246
6.934
6.931
6.918
6.916
6.900
4.119
4.107
4.101
4.090
4.084
4.073
2.431
2.422
2.398
2.389
2.214
2.206
2.179
2.170
2.116
2.101
2.082
2.067
2.020
2.008
1.996
1.989
1.829
1.808
1.788
1.772
1.615
1.598
1.543
1.047
1.034
-0.001
PhO
Me
Me
Me
1H NMR
500 MHz
CDCl3
3.19
2.95
1.00
1.02
1.02
1.03
1.09
1.13
3.07
3.02
2.98
10
8
6
4
2
0 PPM

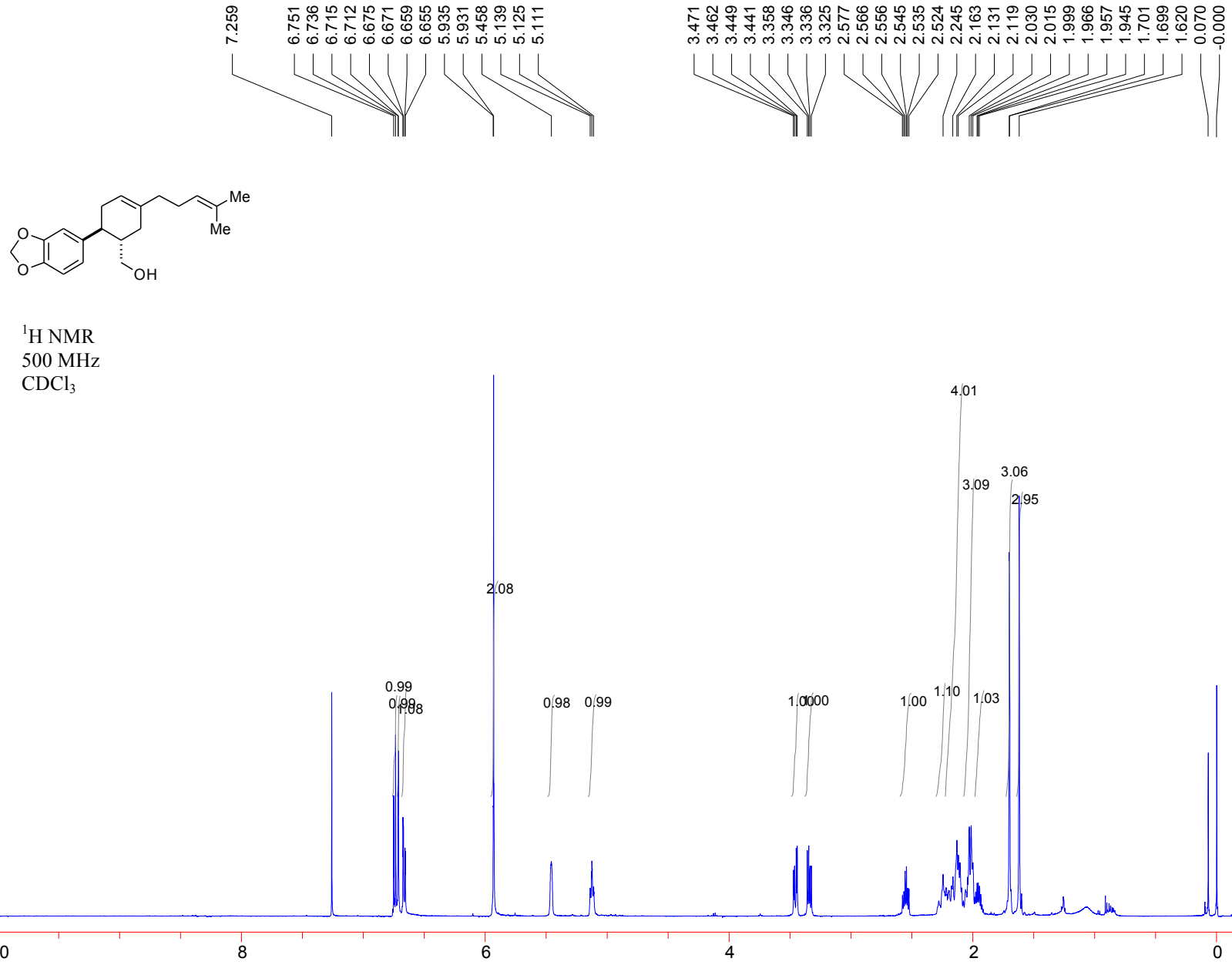

158.610
129.401
124.901
122.700
120.474
116.188
116.018
78.763
77.248
76.993
76.739
39.310
36.828
34.007
18.813
18.525
17.783
PhO
Me
Me
Me
13C NMR
125 MHz
CDCl3
200
150
100
50
0
PPM

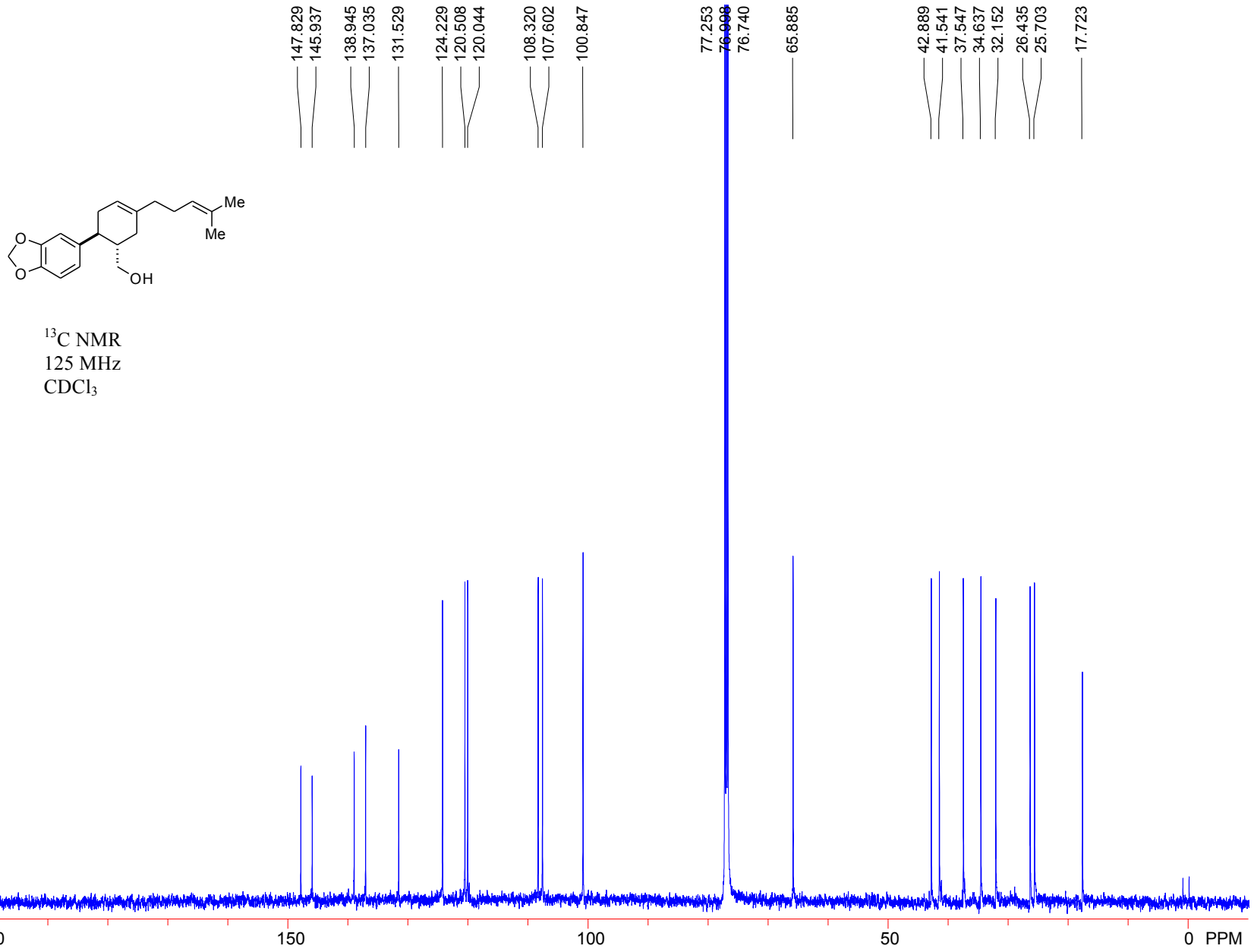


^{1}H NMR
500 MHz
$CDCl_3$

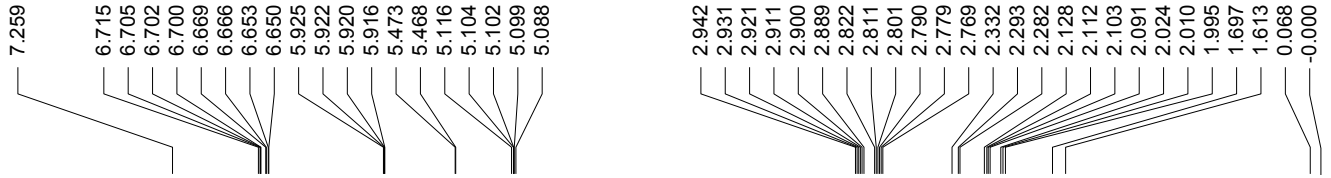


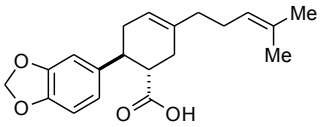
^{13}C NMR
125 MHz
$CDCl_3$


7.259
6.751
6.736
6.715
6.712
6.675
6.671
6.659
6.655
5.935
5.931
5.458
5.139
5.125
5.111
3.471
3.462
3.449
3.441
3.358
3.346
3.336
3.325
2.577
2.566
2.556
2.545
2.535
2.524
2.245
2.163
2.131
2.119
2.030
2.015
1.999
1.966
1.957
1.945
1.701
1.699
1.620
0.070
-0.000
Me
Me
O
O
OH
1H NMR
500 MHz
CDCl3
4.01
3.09
3.06
2.95
2.08
0.99
0.99
1.08
0.98
0.99
1.00
1.00
1.00
1.10
1.03
10
8
6
4
2
0
PPM

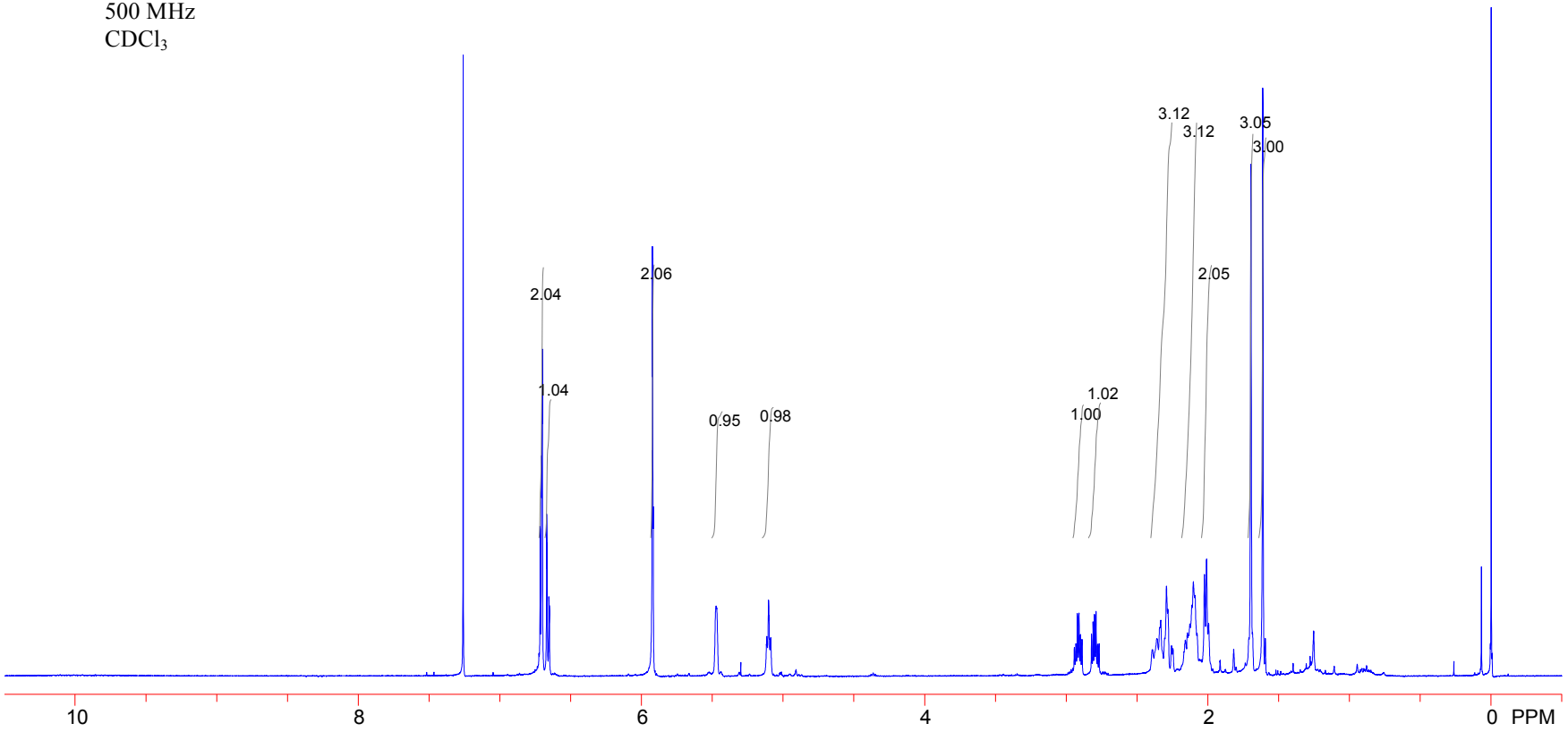


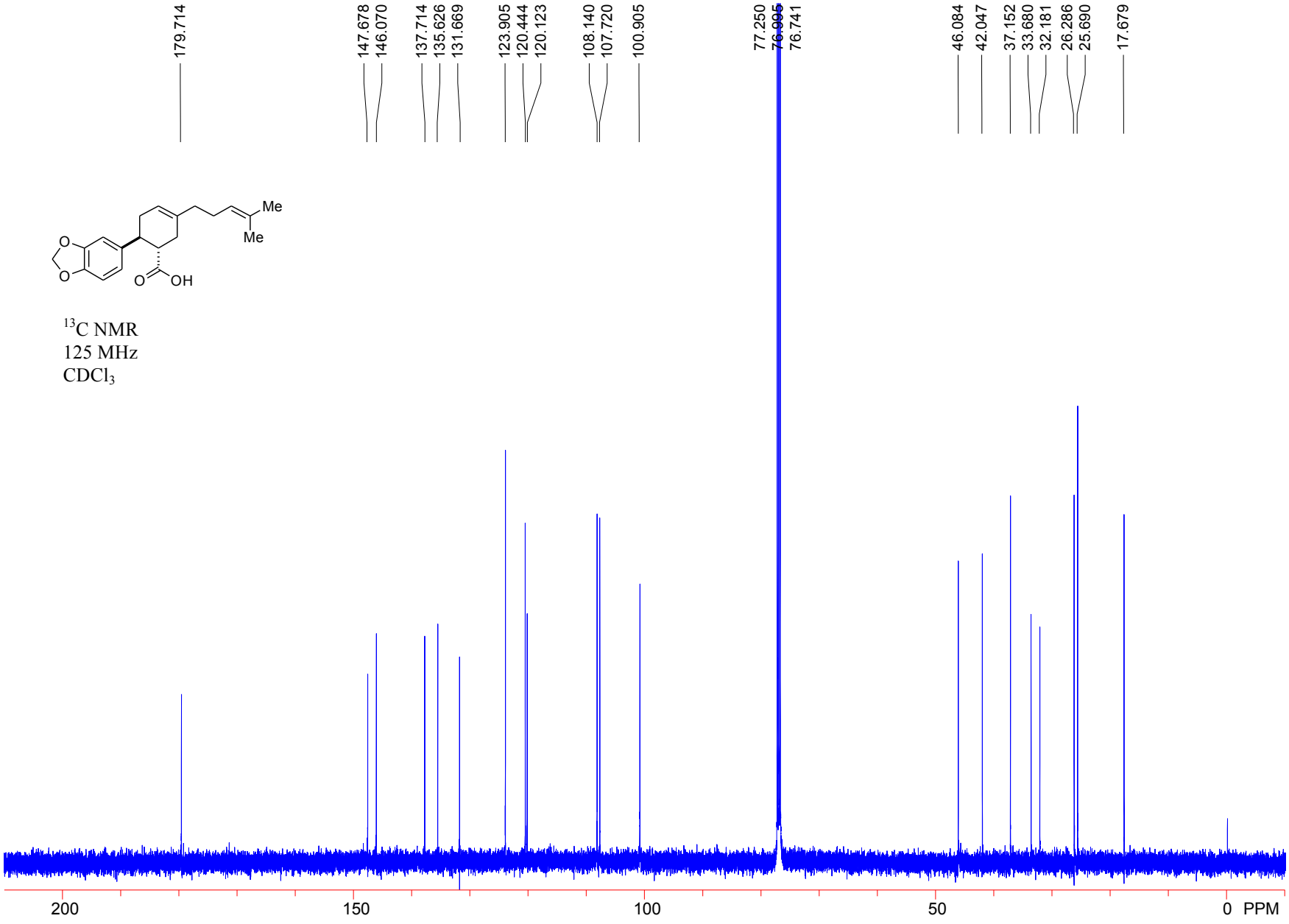
^{13}C NMR
125 MHz
$CDCl_3$



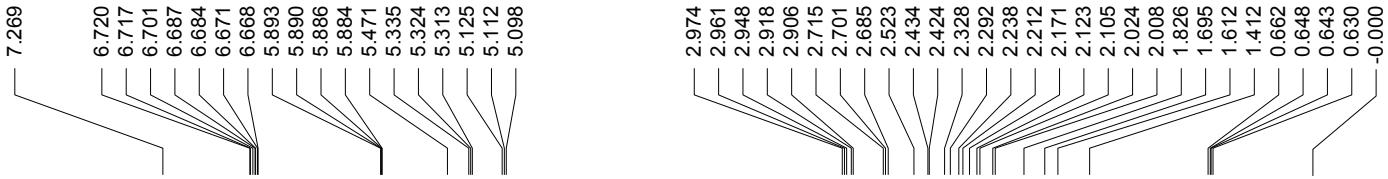


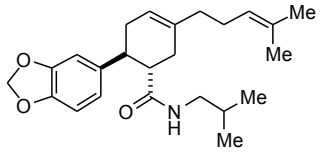
^{1}H NMR
500 MHz
$CDCl_3$



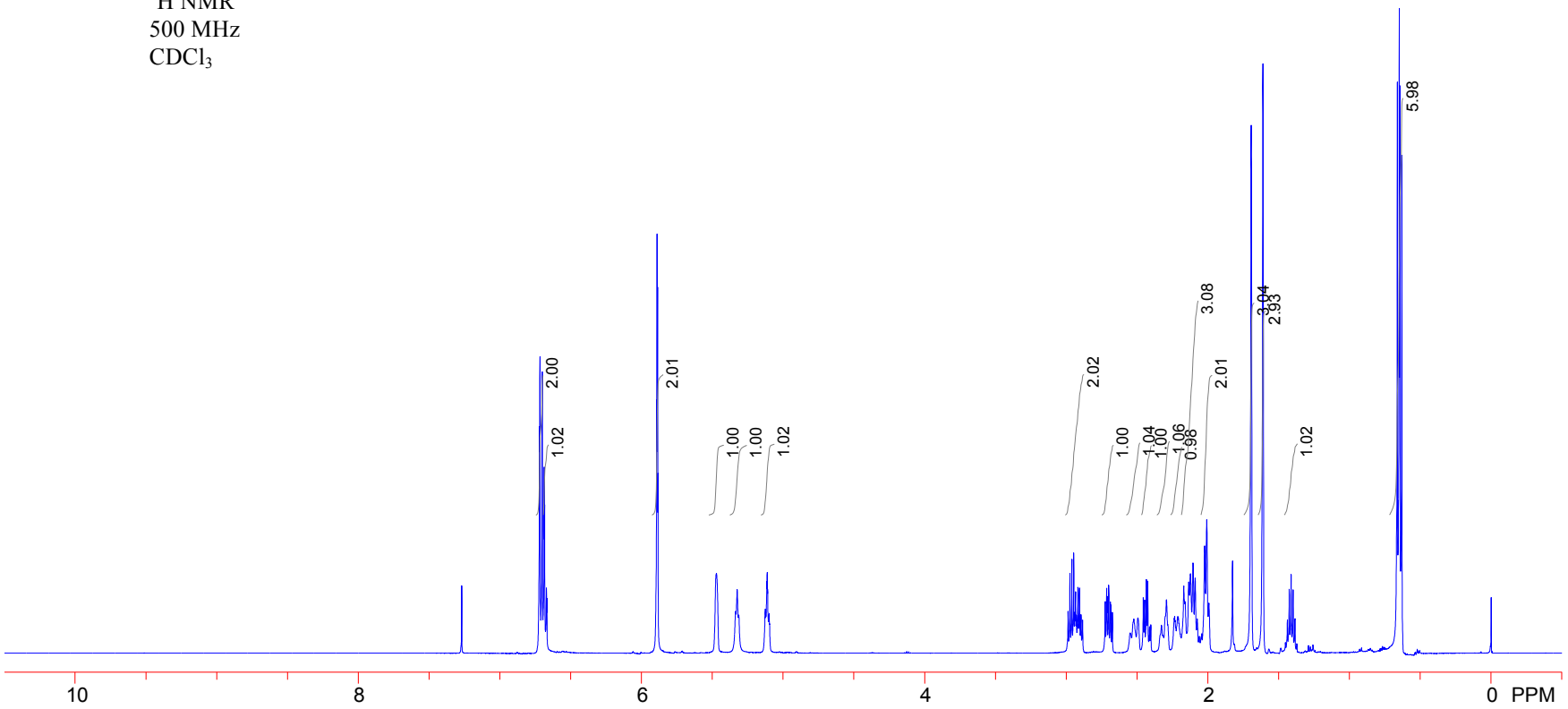


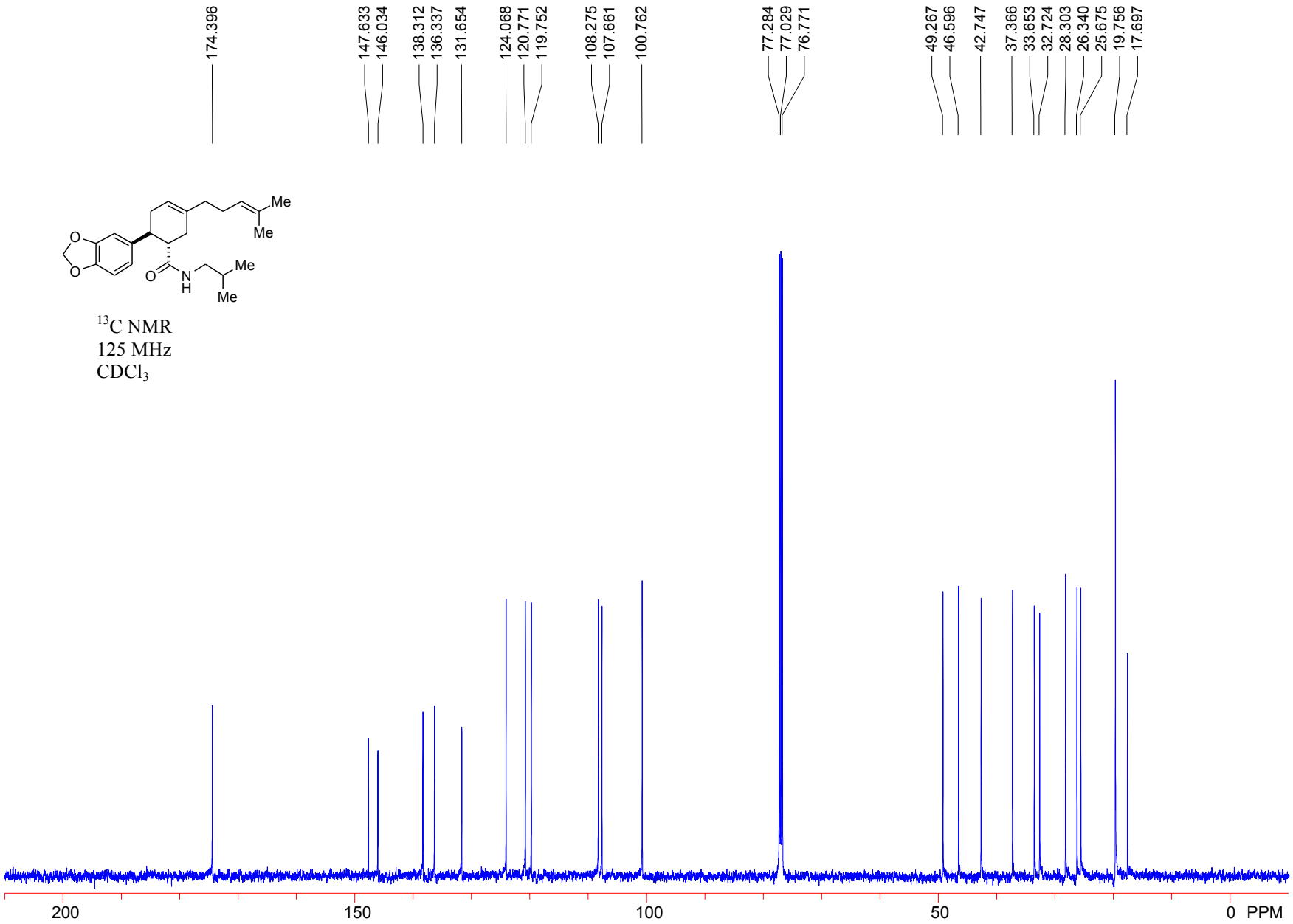
^{13}C NMR
125 MHz
$CDCl_3$



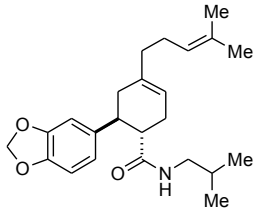


^{1}H NMR
500 MHz
$CDCl_3$

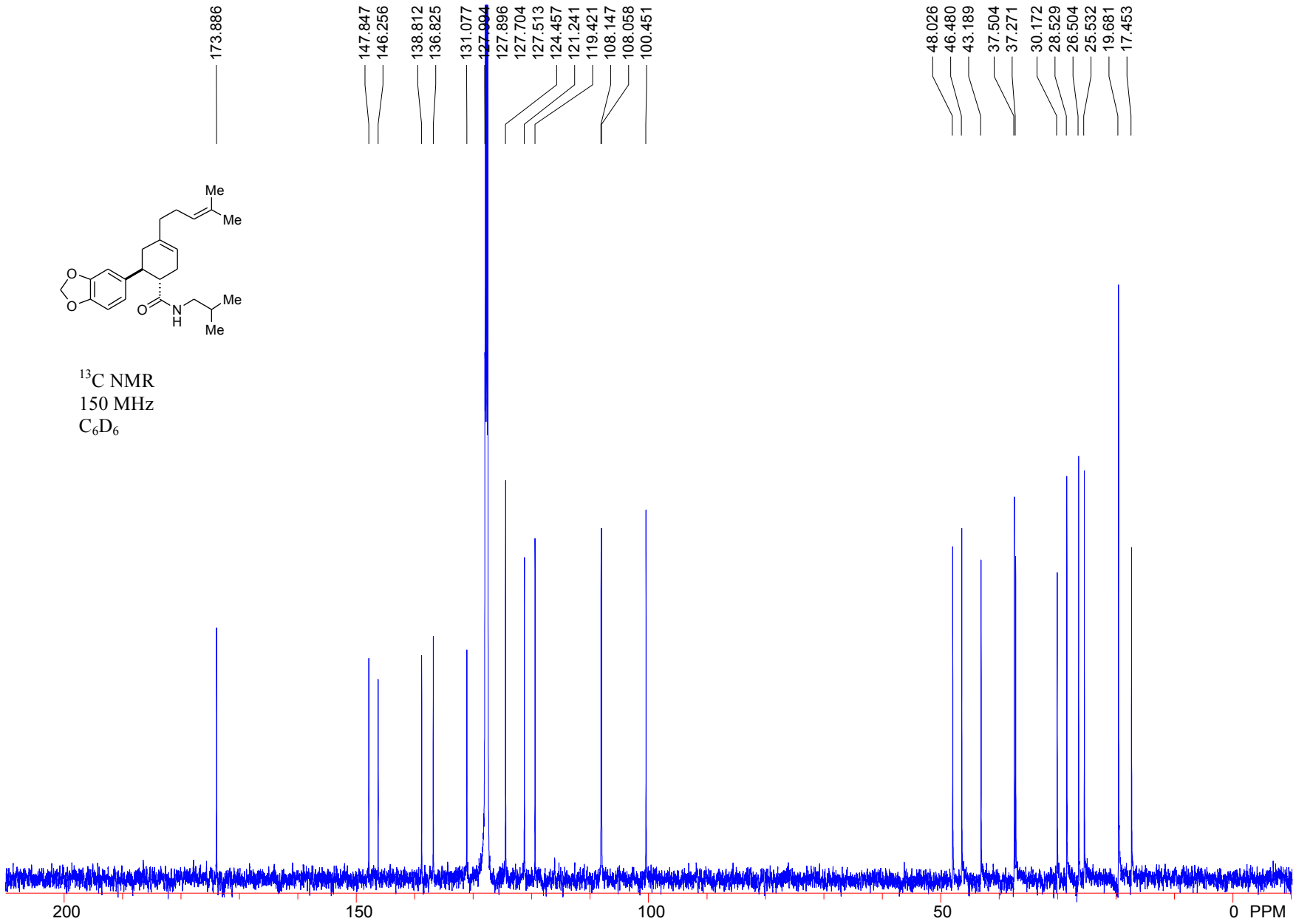




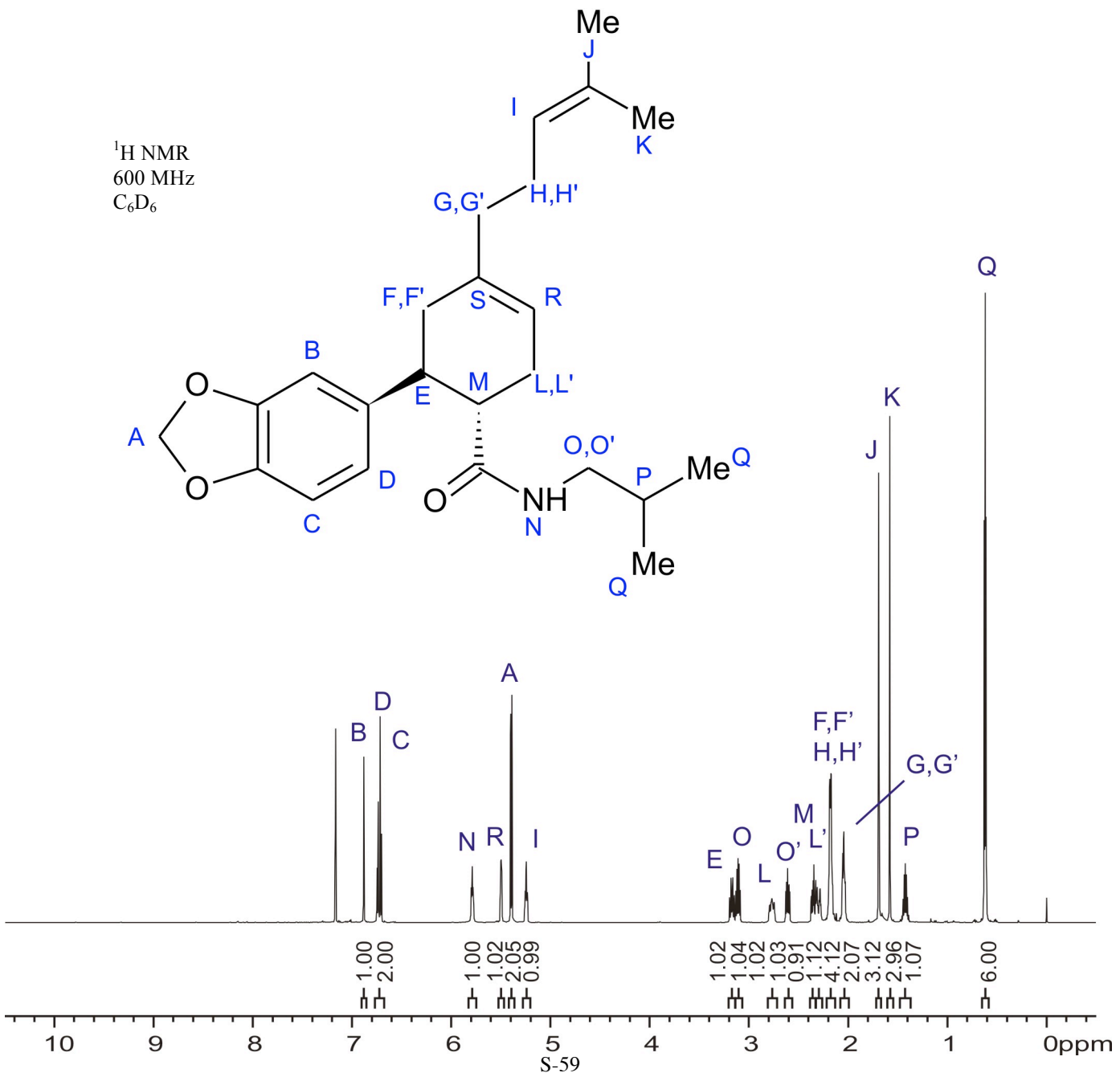
^{13}C NMR
125 MHz
$CDCl_3$



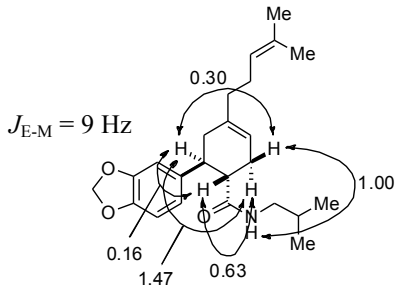
^{1}H NMR
600 MHz
C_6D_6

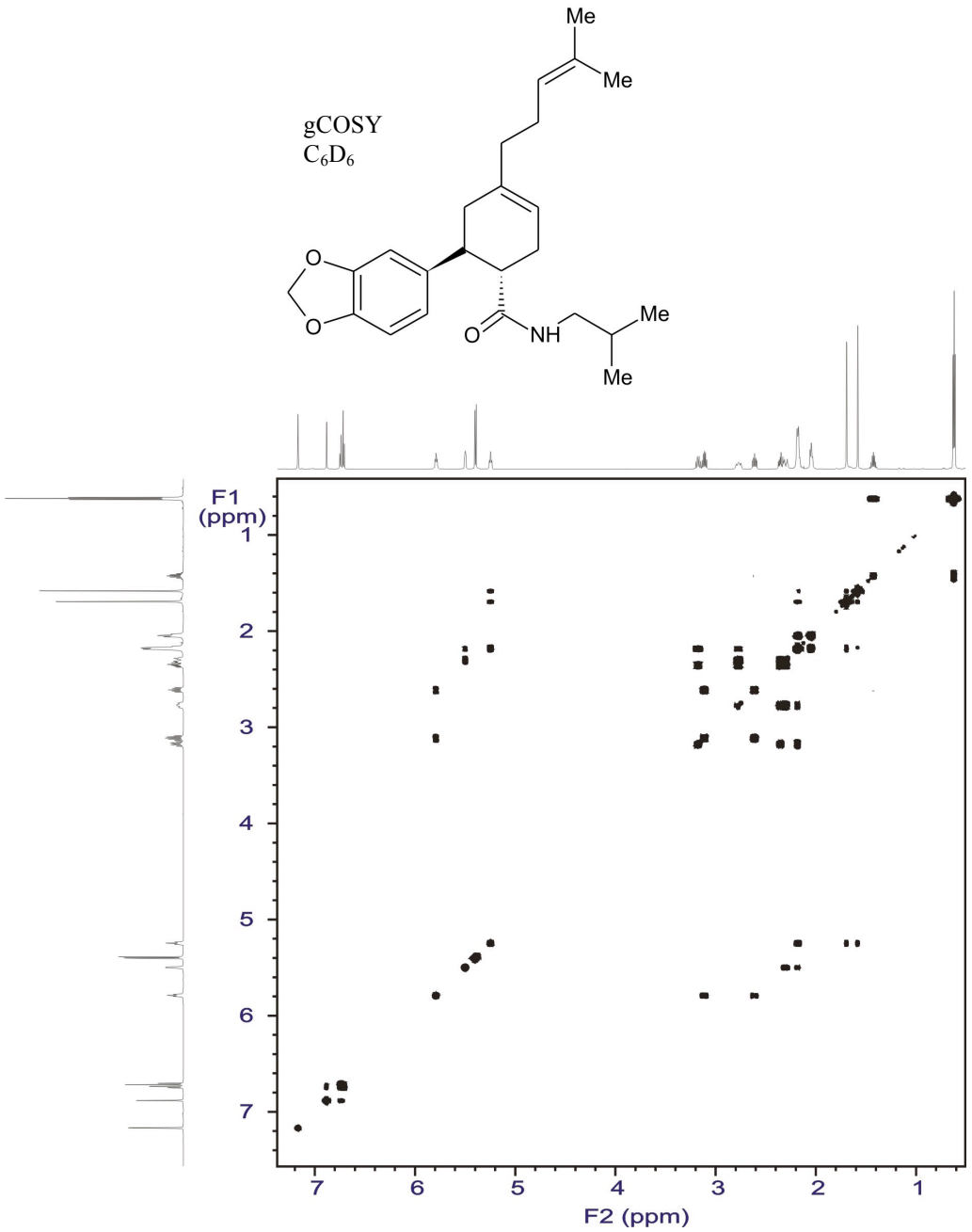


^{13}C NMR
150 MHz
C_6D_6

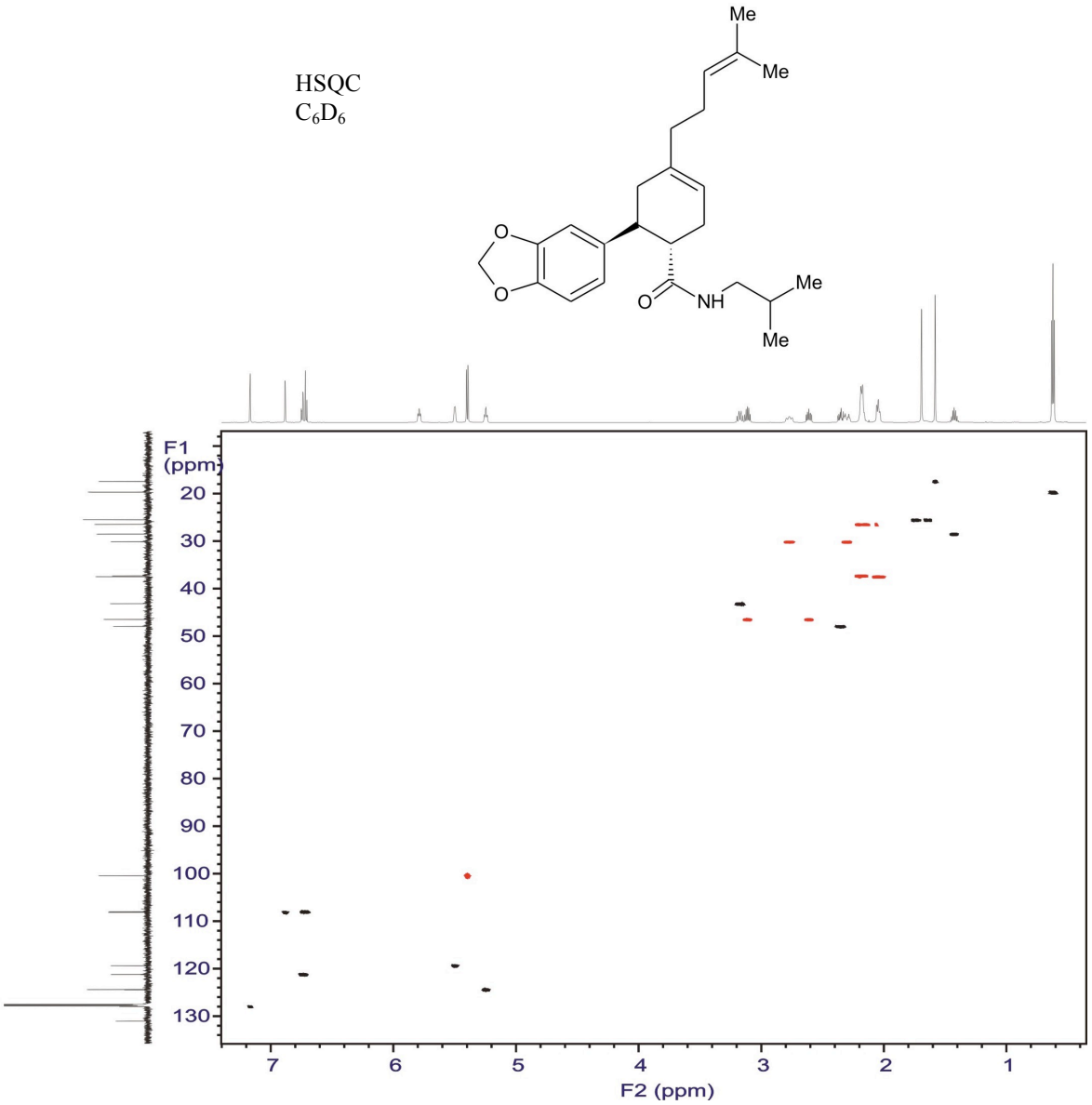

^{1}H NMR
600 MHz
C_6D_6
Me
J
I
Me
K
G,G'
H,H'
F,F'
S
R
B
O
A
O
E
M
L,L'
O,O'
P
Me
Q
D
O
NH
N
C
Me
Q
A
D
B
C
N
R
I
E
O
L
O'
M
L'
F,F'
H,H'
G,G'
P
Q
K
J
1.00
2.00
1.00
1.02
2.05
0.99
1.02
1.04
1.02
1.03
0.91
1.12
4.12
2.07
3.12
2.96
1.07
6.00
10
9
8
7
6
5
4
3
2
1
0ppm

NOE Effect

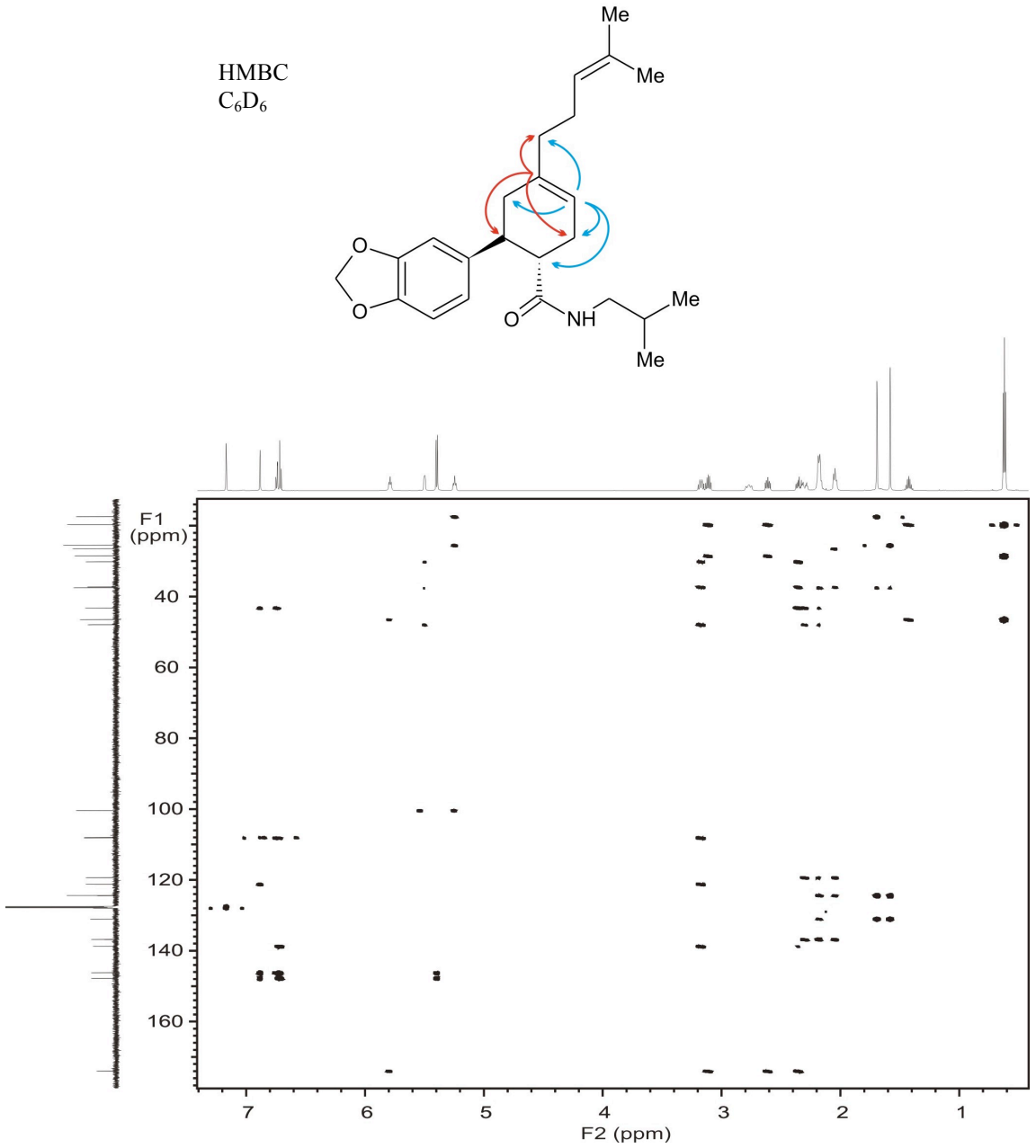


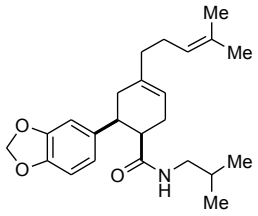

gCOSY
C6D6
Me
Me
O
O
O
NH
Me
Me
F1 (ppm)
1
2
3
4
5
6
7
F2 (ppm)
7
6
5
4
3
2
1

HSQC
C_6D_6

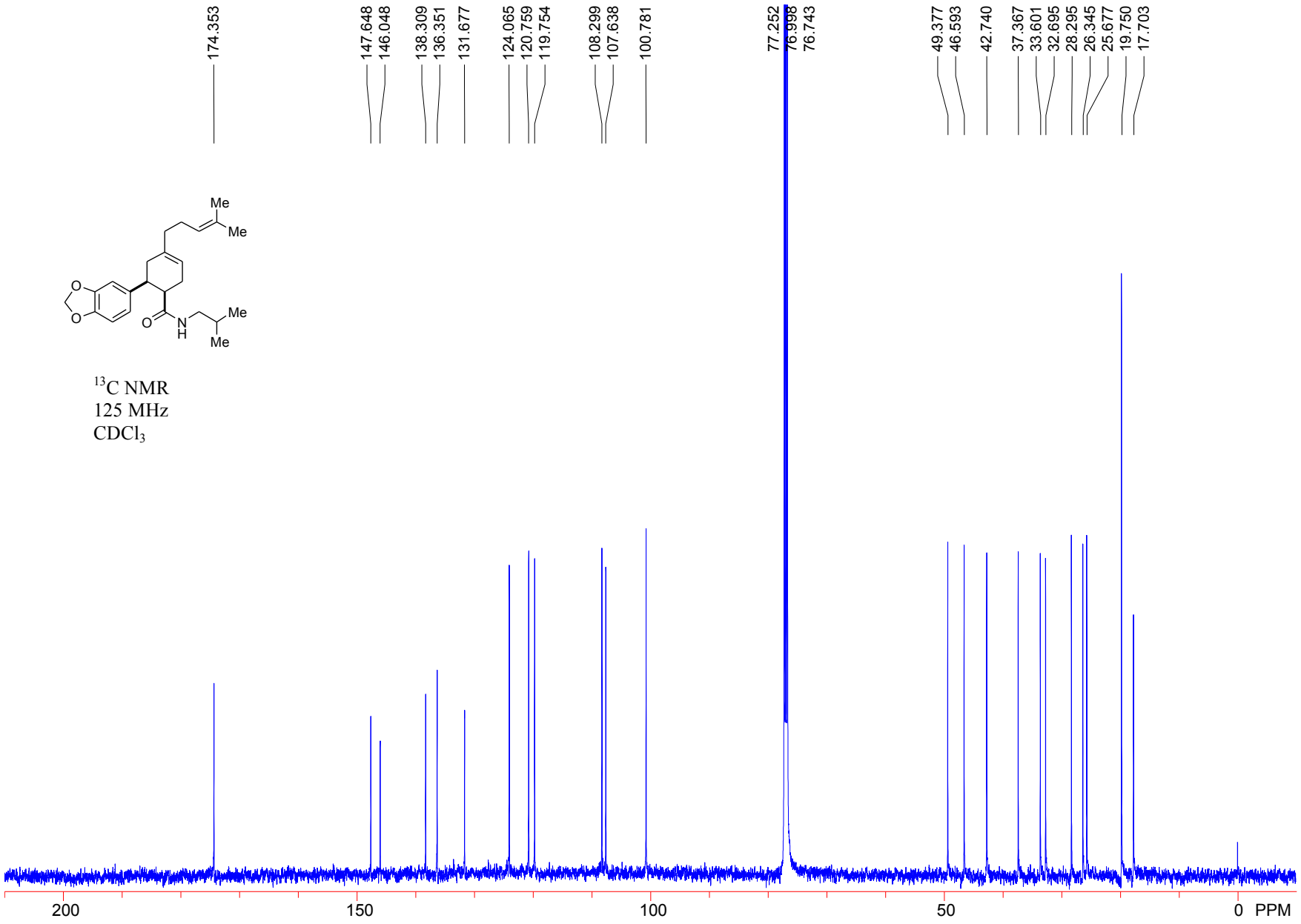

Me
Me
O
O
O
NH
Me
Me
F1 (ppm)
20
30
40
50
60
70
80
90
100
110
120
130
7
6
5
4
3
2
1
F2 (ppm)

HMBC
C_6D_6





^{1}H NMR
500 MHz
$CDCl_3$



^{13}C NMR
125 MHz
$CDCl_3$