Supporting Information for:

Crossed Intermolecular [2+2] Cycloaddition of Styrenes by Visible Light Photocatalysis

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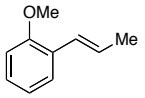
I. General Information

MeCN, THF, and CH_2Cl_2 were purified by elution through alumina as described by Grubbs.[1] A 20 W (1200 lumens) compact fluorescent light bulb (CFL) was used for all photochemical reactions. Constant reaction temperature was maintained by a cryocooled iPrOH bath. Flash-column chromatography was performed with Silicycle 40-63Å silica (230-400 mesh) using the method of Still.[2] $Ru(bpm)_3(BArF)_2$ was purified on Al_2O_3 (Sigma-Aldrich, 11028). Diastereomer ratios were determined by ^1H NMR analysis of the unpurified reaction mixture. ^1H 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® (electron impact) or with a Waters (Micromass) LCT® (electrospray ionization). These facilities are funded by the NSF (CHE-9974839, CHE-9304546) and the University of Wisconsin.

II. Synthesis of the Catalyst

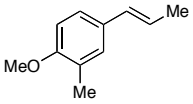
Tris(bipyrimidine)ruthenium(II) bis(tetrakis[(3,5-trifluoromethyl)phenyl]borate) [$Ru(bpm)_3(BArF)_2$]: The 2,2'-bipyrimidine ligand was synthesized according to a procedure described by Michl and coworkers.[3] $Ru(bpm)_3Cl_2$ was prepared using a procedure reported by Rillema.[4] $Ru(bpm)_3(BArF)_2$ was prepared from $Ru(bpm)_3Cl_2$ via anion metathesis[5,6] as follows: A solution of $Ru(bpm)_3Cl_2$ (239 mg, 0.37 mmol) in 1 mL deionized water was placed in 12 mL reaction vial. A separate vial was charged with NaBArF[7] (2.1 equiv, 688 mg, 0.77 mmol), which was transferred to the vial containing $Ru(bpm)_3Cl_2$ using 2 mL of a 3:1 mixture of MeOH/H_2O. The resulting bright orange precipitate was collected by vacuum filtration and purified by gravity elution through Al_2O_3 using CH_2Cl_2. The resulting solution was concentrated by rotary evaporation, and the residue was precipitated from CH_2Cl_2 by addition of hexanes. Isolated 617 mg (0.27 mmol, 72% yield) of $Ru(bpm)_3(BArF)_2$ as bright orange needles. IR(neat, ATR) 2160, 1579, 1547, 1408, 1356, 1274, 1113 cm^{-1}. ^1H NMR: (500 MHz, DMSO) δ 9.21 (dd, J = 4.8, 1.9 Hz, 6H), 8.35 (dd, J = 5.8, 1.9 Hz, 6H), 7.71 (dd, J = 5.8, 4.8 Hz, 6H), 7.67 (m, 8H), 7.61 (m, 16H). ^{13}C NMR: (125 MHz, DMSO) δ 162.3, 160.9 (q, J = 50.0 Hz), 160.5, 158.4, 134.1, 128.5 (q, J = 31.1 Hz), 124.4, 124.2 (q, J = 273.5 Hz.), 117.6.

III. Synthesis of Substrates

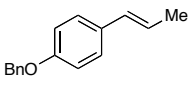


(*E*)-1-Methoxy-2-(1-propenyl)benzene: A solution of 2-methoxybenzaldehyde (2.02 g, 14.7 mmol) and ethyltriphenylphosphonium iodide (6.75 g, 16.2 mmol) in 74 mL of anhydrous Et_2O was placed in a 200 mL round-bottomed flask and cooled to 0 °C. KO^tBu (2.01 g, 17.9 mmol) was added in one portion, and the reaction was warmed to room temperature and stirred overnight. The reaction was quenched with H_2O and extracted with anhydrous Et_2O (3 x 75 mL). The combined organics were washed with brine (1 x 75 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash-column chromatography (15:1 Hexanes/EtOAc) to afford 1.80 g (12.1 mmol, 83% yield) of the desired product as a colorless oil (E/Z = 1:3). To improve the isomer ratio, the mixture of E/Z isomers was dissolved in benzene (48 mL), AIBN (296 mg, 1.80 mmol) and PhSH (672 mg, 6.10 mmol) were added, and the reaction was heated at reflux for 1 h. Upon cooling to room temperature, the mixture was washed with 1 M NaOH (3 × 25 mL) and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash-column chromatography (15:1 hexanes/EtOAc) to afford the desired product as a single isomer (1.56 g, 10.5 mmol, 87% yield). IR(neat) 2958, 1597, 1489, 1243 cm^{-1}. ^1H NMR: (500

MHz, $CDCl_3$) δ 7.39 (dd, J = 7.6, 1.6 Hz, 1H), 7.18 (td, J = 8.2, 1.7 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H), 6.72 (dq, J = 15.9, 1.7 Hz, 1H), 6.22 (dq, J = 15.9, 6.6 Hz, 1H), 3.84 (s, 3H), 1.90 (dd, J = 6.6, 1.7 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 156.2, 127.7, 127.1, 126.5, 126.4, 125.6, 120.6, 110.7, 55.4, 18.9. HRMS (EI) calculated for $[C_{10}H_{12}O]^+$ requires *m/z* 148.0883, found *m/z* 148.0882.

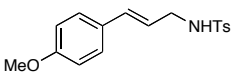


(*E*)-1-Methoxy-2-methyl-4-(1-propenyl)benzene: A solution of 4-methoxy-3-methyl-benzaledehyde (1.26 g, 8.4 mmol) and ethyltriphenylphosphonium iodide (3.8 g, 9.2 mmol) in 42 mL of anhydrous Et_2O was placed in a 100 mL round-bottomed flask and cooled to 0 ºC. KO^tBu (1.13 g, 10.1 mmol) was added in one portion, and the reaction was warmed to room temperature and stirred overnight. The crude reaction mixture was passed through a short column of SiO_2 with Et_2O, and the eluent was concentrated *in vacuo*. The residue was purified by flash-column chromatography (6:1 hexane/CH_2Cl_2) to afford the product as a mixture of isomers (1.1 g, 6.8 mmol, 81% yield, E/Z = 1:2.9). To the mixture of E/Z isomers in benzene (27 mL) was added AIBN (167 mg, 1.02 mmol) and PhSH (350 µL, 3.4 mmol), and the reaction was heated at reflux for 1 h. Upon cooling to room temperature, the mixture was washed with 1 M NaOH (3 × 25 mL) and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash-column chromatography (5:1 hexanes/CH_2Cl_2) to afford the desired product as a single isomer (743 mg, 4.6 mmol, 68% yield). IR(neat) 2915, 1507, 1253, 1154 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.12 (s, 1H), 7.09 (d, J = 8.6 Hz, 1H), 6.72 (d, J = 8.6 Hz, 1H), 6.30 (dq, J = 15.7, 1.6 Hz, 1H), 6.06 (dq, J = 15.7, 6.6 Hz, 1H), 3.78 (s, 3H), 2.19 (s, 3H), 1.83 (dd, J = 6.7, 1.6 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 156.8, 130.5, 130.3, 128.0, 126.5, 124.3, 123.1, 109.8, 77.3, 77.0, 76.7, 55.3, 18.4, 16.2. HRMS (EI) calculated for $[C_{11}H_{14}O]^+$ requires *m/z* 162.1040, found *m/z* 162.1036.



(*E*)-1-Benzyloxy-4-(1-propenyl)benzene: A flame-dried 25 mL round-bottomed flask was charged with 187 mg (7.8 mmol) of NaH (washed previously with hexanes). The flask was evacuated and backfilled with dry N_2 three times. Anhydrous DMF (3 mL) was added, and the mixture was cooled to 0 ºC. A solution of (*E*)-4-(propenyl)-1-phenol[8] (521 mg, 3.9 mmol) in 4.8 mL of anhydrous DMF was added dropwise, and the mixture was warmed to room temperature. After 10 min, 700 µL (5.9 mmol) of benzyl bromide was added and the mixture was stirred for an additional 30 min. The reaction was quenched with saturated NH_4Cl and diluted with Et_2O. The layers were separated, and the aqueous phase was extracted an additional time with 25

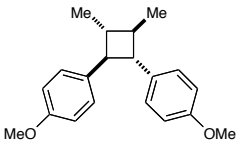
mL of Et_2O. The combined organics were washed with water (3 × 25 mL), brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude oil was purified by flash-column chromatography (5:1 hexanes/CH_2Cl_2) to afford 649 mg (2.89 mmol, 74% yield) of the desired product as a colorless solid (mp = 76–78 ºC). IR(neat) 2924, 1472, 1038, 974 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.41 (m, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.30 (m, 1H), 7.24 (AA' of AA'BB', J = 8.6 Hz, 2H), 6.89 (BB' of AA'BB', J = 8.6 Hz, 2H), 6.33 (d, J = 15.6 Hz, 1H), 6.08 (dq, J = 15.8, 6.5 Hz, 1H), 5.03 (s, 2H), 1.84 (d, J = 6.5 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 157.8, 137.1, 131.1, 130.3, 128.6, 127.9, 127.4, 126.9, 123.6, 114.9, 70.0, 18.4. HRMS (EI) calculated for $[C_{16}H_{16}O]^+$ requires *m/z* 224.1196, found *m/z* 224.1201.



***N-(E)*-3-(4-Methoxyphenyl)-2-propen-1-(4-methyl-benzenesulfonamide)**. To a solution of (*E*)-3-(*p*-methoxyphenyl)-2-propen-1-amine[9] (976 mg, 5.99 mmol) in CH_2Cl_2 (12 mL) was added 2.1 mL (14.98 mmol) of NEt_3 and 1.2 g (5.99 mmol) of TsCl. The reaction was warmed to room temperature and stirred until the starting material had been consumed (1 h). The reaction mixture was poured onto 150 mL of water and extracted with CH_2Cl_2 (3 × 100 mL). The combined organics were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude solid was purified by flash-column chromatography (6:1 to 1:1 hexanes/EtOAc) to afford 1.49 g (4.7 mmol, 78% yield) of the desired product as a white solid (mp = 112–114 ºC). IR(neat) 3278(br), 2920, 1607, 1512, 1249, 1158 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.77 (AA' of AA'BB', J = 8.3 Hz, 2H), 7.31 (BB' of AA'BB', J = 8.3 Hz, 2H), 7.19 (AA' of AA'BB', J = 8.6 Hz, 2H), 6.82 (BB' of AA'BB', J = 8.6 Hz, 2H), 6.38 (d, J = 16.0 Hz, 1H), 5.88 (dt, J = 16.0, 6.5 Hz, 1H), 4.39 (t, J = 5.9 Hz, 1H), 3.80 (s, 3H), 3.73 (td, J = 6.5, 1.4 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 159.5, 143.5, 137.1, 132.8, 129.7, 128.8, 127.6, 127.2, 121.7, 114.0, 77.3, 77.0, 76.7, 55.3, 45.7, 21.5. HRMS (ESI) calculated for $[C_{17}H_{19}NO_3S + Na]^+$ requires *m/z* 340.0978, found *m/z* 340.0971.

IV. [2+2] Cycloaddition Reactions

A. Homodimerization of anethole (1)



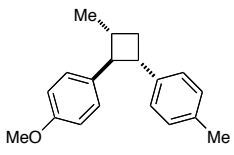
(**Table 1, entry 6, 2**). An oven-dried 25 mL borosilicate test tube equipped with a magnetic stir bar was charged with anethole (204.5 mg, 1.38 mmol) and $Ru(bpm)_3(BArF)_2$

(6.9 mg, 0.003 mmol) and cooled to 0 ºC. Anhydrous CH_2Cl_2 (6.7 mL) was added, and the test tube was sealed with a septum. The reaction mixture was vigorously stirred in front of a 20 W CFL. Upon >95% consumption of starting material as judged by gas chromatography (2 h), the reaction was filtered through short pad of SiO_2 with 100 mL of Et_2O and concentrated *in vacuo*. The crude oil was purified by flash-column chromatography (13:1 to 10:1 hexanes/EtOAc) to afford 165 mg (0.56 mmol, 81% yield) of the title compound as a colorless oil. Spectral properties matched those previously reported:[10] ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.12 (AA' of AA'BB', J = 8.6 Hz, 4H), 6.82 (BB' of AA'BB', J = 8.6 Hz, 4H), 3.76 (s, 6H), 2.80 (inverted d, 2H), 1.82 (m, 2H), 1.18 (d, J = 6.1 Hz, 6H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 157.9, 135.9, 127.7, 113.7, 55.2, 52.5, 43.2, 18.9.

B. Crossed-[2+2] cycloaddition reactions

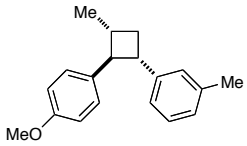
General Procedure A: An oven-dried 25 mL borosilicate test tube was charged with 0.67 mmol of **1**, 1.34 mmol of **7a**, and 0.25 mol% $Ru(bpm)_3(BArF)_2$. The test tube was cooled to –15 ºC using a controlled-temperature cooling bath and 6.7 mL of anhydrous CH_2Cl_2 was added. The reaction mixture was vigorously stirred under air in front of a 20 W CFL. Upon consumption of **1**, the reaction was passed through a short pad of silica using EtOAc or Et_2O. The solvent was removed by rotary evaporation, and the residue was purified by flash-column chromatography to afford the cycloadduct.

General Procedure B: An oven-dried 25 mL borosilicate test tube was was charged with 1.34 mmol of **7b**, 0.25 mol% $Ru(bpm)_3(BArF)_2$, and 1.7 mL of anhydrous CH_2Cl_2. The test tube was cooled to –15 ºC using a controlled-temperature cooling bath. The solution was vigorously stirred under air infront of a 20 W CFL. 5 mL of a 0.135 M solution of **1** in anhydrous CH_2Cl_2 was added dropwise over 1 h. Upon consumption of **1**, the reaction was passed through a short pad of silica using EtOAc or Et_2O. The solvent was removed by rotary evaporation, and the residue was purified by flash-column chromatography to afford the cycloadduct.

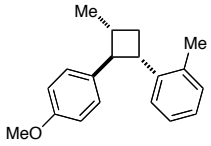


(**Table 3, entry 1, 8a**). Experiment 1: Set up according to General Procedure A with anethole (99.2 mg, 0.67 mmol), 4-methyl styrene (158 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), and 6.7 mL of anhydrous CH_2Cl_2 (1 h reaction time, >10:1 crossed/homodimer). Purification by flash-column chromatography (gradient, 6:1 to 2:1 hexanes/CH_2Cl_2) afforded

153 mg (0.57 mmol, 86% yield) of the cycloadduct as a colorless oil. Experiment 2: 98 mg (0.66 mmol) of anethole, 158 mg (1.34 mmol) of 4-methyl styrene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mL of CH_2Cl_2. Isolated 151 mg (0.57 mmol 86% yield). IR (neat) 2951, 1611, 1513, 1249, 1038 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.15 (AA' of AA'BB', J = 8.4 Hz, 2H), 7.08 (s, 4H), 6.83 (BB' of AA'BB', J = 8.8 Hz, 2H), 3.77 (s, 3H), 3.33 (td, J = 10.0, 8.1 Hz, 1H), 2.91 (t, J = 9.4 Hz, 1H), 2.48 (dt, J = 10.2, 7.9 Hz, 1H), 2.31 (m, 1H), 2.30 (s, 3H), 1.66 (q, J = 10.2 Hz, 1H), 1.17 (d, J = 6.6 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 158.0, 141.6, 135.9, 135.4, 128.9, 127.7, 126.5, 113.7, 55.6, 55.2, 43.8, 35.4, 34.1, 21.0, 20.5. HRMS (EI) calculated for $[C_{19}H_{22}O - H]^+$ requires *m/z* 265.1587, found *m/z* 265.1582.

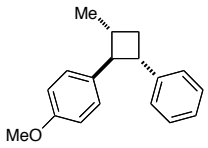


(Table 3, entry 2). Experiment 1: Set up according to General Procedure B with 3-methyl styrene (158 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), 1.67 mL of dry CH_2Cl_2 with a 2 h addition time of anethole (5 mL of a 0.135 M stock solution in CH_2Cl_2) and a total irradiation time of 2.5 h (>10:1 crossed/homodimer). Purification of the crude mixture by flash-column chromatography (gradient, 6:1 to 2:1 hexanes/CH_2Cl_2) afforded 157 mg (0.59 mmol, 88% yield) of the cycloadduct as a colorless oil. Experiment 2: 100 mg (0.67 mmol) of anethole, 158 mg (1.34 mmol) of 3-methyl styrene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of CH_2Cl_2. Isolated 150 mg (0.56 mmol, 84% yield). IR(neat) 2951, 1653, 1513, 1291 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.15 (m, 3H), 6.98 (m, 3H), 6.83 (BB' of AA'BB', J = 8.7 Hz, 2H), 3.76 (s, 3H), 3.34 (q, J = 9.4 Hz, 1H), 2.94 (t, J = 9.4 Hz, 1H), 2.48 (dt, J = 10.1, 7.8 Hz, 1H), 2.31 (m, 1H), 2.30 (s, 3H), 1.68 (q, J = 10.0 Hz, 1H), 1.17 (d, J = 6.5 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 158.0, 144.6, 137.7, 135.9, 128.1, 127.7, 127.4, 126.7, 123.7, 113.7, 55.4, 55.2, 44.0, 35.5, 34.1, 21.4, 20.5. HRMS (EI) calculated for $[C_{19}H_{22}O$ – propene$]^+$ requires *m/z* 224.1196, found *m/z* 224.1189.

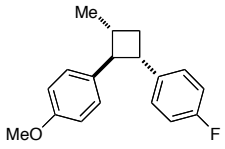


(Table 3, entry 3). Experiment 1: Set up according to General Procedure A with anethole (100.3 mg, 0.68 mmol), 2-methyl styrene (158 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), and 6.7 mL anhydrous CH_2Cl_2 (1 h irradiation time, >10:1 crossed/homodimer). Purification by flash-column chromatography (gradient, 6:1 to 2:1 hexanes/CH_2Cl_2) afforded 140 mg (0.53 mmol, 79% yield) of the cycloadduct as a colorless oil. Experiment 2: 105.9 mg (0.71 mmol) of anethole, 159 mg (1.34 mmol) of 2-methyl styrene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of

CH_2Cl_2. Isolated 155 mg (0.58 mmol, 82% yield). IR(neat) 2950, 1611, 1513, 1249, 1038 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.30 (d, J = 7.9 Hz, 1H), 7.18 (AA' of AA'BB', J = 8.7 Hz, 2H), 7.15 (m, 1H), 7.08 (m, 2H), 6.83 (BB' of AA'BB', J = 8.7 Hz, 2H), 3.77 (s, 3H), 3.52 (td, J = 10.1, 8.2 Hz, 1H), 3.12 (t, J = 9.5 Hz, 1H), 2.59 (dt, J = 10.1, 7.9 Hz, 1H), 2.33 (m, 1H), 2.18 (s, 3H), 1.54 (q, J = 10.1 Hz, 1H), 1.19 (d, J = 6.4 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 158.0, 142.3, 136.0, 135.9, 129.9, 127.7, 125.9, 125.8, 125.7, 113.7, 77.3, 77.0, 76.7, 55.2, 53.3, 41.7, 35.7, 34.7, 20.6, 19.8. HRMS (EI) calculated for $[C_{19}H_{22}O]^+$ requires *m/z* 266.1666, found *m/z* 266.1652.

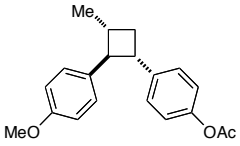


(Table 3, entry 4, 8b). Experiment 1: Set up according to General Procedure B with styrene (140 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), 1.67 mL of dry CH_2Cl_2 with a 1 h addition time of anethole (5 mL of a 0.135 M stock solution in CH_2Cl_2) and a total irradiation time of 1.5 h (>10:1 crossed/homodimer). Purification of the crude mixture by flash-column chromatography (gradient, 6:1 to 2:1 hexanes/CH_2Cl_2) afforded 130.8 mg (0.52 mmol, 78% yield) of the cycloadduct as a colorless oil. Experiment 2: 100 mg (0.67 mmol) of anethole, 140 mg (1.34 mmol) of styrene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of CH_2Cl_2. Isolated 133 mg (0.53 mmol, 79% yield). IR(neat) 2951, 1611, 1513, 1249, 1038 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.26 (m, 2H), 7.18 (m, 5H), 6.85 (BB' of AA'BB', J = 8.2 Hz, 2H), 3.79 (s, 3H), 3.39 (td, J = 10.1, 8.4 Hz, 1H), 2.94 (t, J = 9.2 Hz, 1H), 2.51 (dt, J = 10.2, 7.9 Hz, 1H), 2.33 (m, 1H), 1.75 (q, J = 9.8 Hz, 1H), 1.18 (d, J = 6.8 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 158.0, 144.6, 135.8, 128.2, 127.8, 126.6, 125.9, 113.7, 55.5, 55.2, 44.1, 35.5, 33.9, 20.4. HRMS (EI) calculated for $[C_{18}H_{20}O]^+$ requires *m/z* 252.1509, found *m/z* 252.1517.

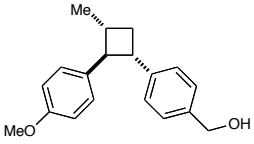


(Table 3, entry 5). Experiment 1: Set up according to General Procedure B using 4-fluorostyrene (164 mg, 1.34 mmol) and $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol) and 1.67 mL of dry CH_2Cl_2 with a 2 h addition time of anethole (5 mL of a 0.135 M stock solution in CH_2Cl_2) and a total irradiation time of 2 h (>10:1 crossed/homodimer). Purification by flash-column chromatography (gradient, 6:1 to 2:1 hexanes/CH_2Cl_2) afforded 141.5 mg (0.52 mmol, 78% yield) of the cycloadduct as a white solid (mp = 56–58 ºC). Experiment 2: 100 mg (0.67 mmol) of anethole, 164 mg (1.34 mmol) of 4-fluorostyrene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of CH_2Cl_2. Isolated 141 mg (0.52 mmol, 78% yield). IR (neat) 2952, 1610, 1511, 1250 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.13 (m, 4H), 6.93 (t, J =

8.6 Hz, 3H), 6.84 (BB' of AA'BB', J = 8.7 Hz, 2H), 3.77 (s, 3H), 3.33 (td, J = 10.1, 8.2 Hz, 1H), 2.87 (t, J = 9.4 Hz, 1H), 2.49 (dt, J = 10.2, 8.0 Hz, 1H), 2.31 (m, 1H), 1.64 (q, J = 10.0 Hz, 1H), 1.17 (d, J = 6.4 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 161.3 ($^1J_{CF}$ = 243.2 Hz), 158.1, 140.3 ($^1J_{CF}$ = 2.8 Hz), 135.5, 128 ($^3J_{CF}$ = 7.7 Hz), 127.7, 114.9 ($^2J_{CF}$ = 22.2 Hz), 113.8, 55.9, 55.2, 43.5, 35.4, 34.0, 20.4. HRMS (EI) calculated for $[C_{18}H_{19}FO]^+$ requires *m/z* 270.1415, found *m/z* 270.1412.

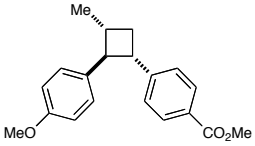


(Table 3, entry 6). Experiment 1: Set up according to General Procedure B using 4-acetoxystyrene (217 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), 1.67 mL of dry CH_2Cl_2 with a 2 h addition time of anethole (5 mL of a 0.135 M stock solution in CH_2Cl_2) and a total irradiation time of 3 h (>10:1 crossed/homodimer). Purification of the crude mixture by flash-column chromatography (gradient, 10:1 to 5:1 hexanes/Et_2O) afforded 162 mg (0.52 mmol, 78% yield) of the title cycloadduct as a colorless oil. Experiment 2: 100 mg (0.67 mmol) of anethole, 217 mg (1.34 mmol) of 4-acetoxystyrene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of CH_2Cl_2. Isolated 161 mg (0.52 mmol, 78% yield) of the cycloadduct as a colorless oil. IR(neat) 2952, 1757, 1512, 1197 cm^{-1}. ^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.17 (AA' of AA'BB', J = 8.6 Hz, 2H), 7.15 (AA' of AA'BB', J = 8.4 Hz, 2H), 6.96 (BB' of AA'BB', J = 8.5 Hz, 2H), 6.84 (BB' of AA'BB', J = 8.6 Hz, 2H), 3.76 (s, 3H), 3.37 (td, J = 9.9, 8.2 Hz, 1H), 2.90 (t, J = 9.4 Hz, 1H), 2.49 (dt, J = 10.1, 7.8 Hz, 1H), 2.31 (m, 1H), 2.25 (s, 3H), 1.66 (q, J = 10.2 Hz, 1H), 1.17 (d, J = 6.9 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 169.6, 158.1, 148.8, 142.2, 135.5, 127.8, 127.5, 121.2, 113.8, 77.3, 77.1, 76.8, 55.6, 55.2, 43.5, 35.5, 33.9, 21.1, 20.4. HRMS (EI) calculated for $[C_{20}H_{22}O_3]^+$ required *m/z* 310.1564, found *m/z* 310.1553.

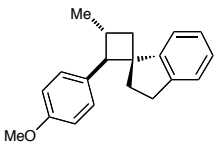


(Table 3, entry 7). Experiment 1: Set up according to General Procedure B using 4-vinyl benzylalcohol[11] (180 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), and 1.67 mL of dry CH_2Cl_2 with a 2 h addition time of anethole (5 mL of a 0.135 M stock solution in CH_2Cl_2) and a total irradiation time of 2.5 h (>10:1 crossed/homodimer). Upon filtering the reaction mixture through SiO_2 with EtOAc, the crude residue was then dissolved in 4 mL of CH_2Cl_2 and cooled 0 ºC. Excess unreacted alkene was consumed by addition of 99% *m*-CPBA (284 mg, 1.65 mmol) and the reaction warmed to room temperature. After 3 h, the mixture was poured onto saturated $NaHSO_3$ and extracted with CH_2Cl_2 (3 × 20

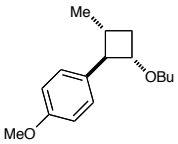
mL). The combined organic extracts were washed with $NaHCO_3$, brine, and dried over $NaSO_4$. The solvent was removed *in vacuo* and the crude oil was purified by flash-column chromatography (3:1 hexanes/EtOAc) to afford 108 mg (0.38 mmol, 57% yield) of the title compound as a colorless oil. Experiment 2: 100 mg (0.67 mmol) of anethole, 186 mg (1.34 mmol) of 4-vinyl benzylalcohol, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of CH_2Cl_2. Isolated 104 mg (0.37 mmol, 55% yield) of the cycloadduct as a colorless oil. IR(neat) 3355(br), 2951, 1611, 1513, 1249, 1037 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.25 (AA' of AA'BB', J = 7.9 Hz, 2H), 7.17 (BB' of AA'BB', J = 8.0 Hz, 2H), 7.15 (AA' of AA'BB', J = 8.6 Hz, 2H), 6.83 (BB' of AA'BB', J = 8.7 Hz, 2H), 4.61 (s, 2H), 3.77 (s, 3H), 3.41 (td, J = 9.5, 8.0 Hz, 1H), 2.92 (t, J = 9.5 Hz, 1H), 2.50 (dt, J = 10.4, 7.8 Hz, 1H), 2.33 (m, 1H), 1.80 (br s, 1H), 1.68 (q, J = 10.6 Hz, 1H), 1.18 (d, J = 7.2 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 158.1, 144.2, 138.5, 135.7, 127.7, 127.1, 126.8, 113.8, 65.2, 55.6, 55.2, 43.9, 35.4, 34.0, 20.5. HRMS (EI) calculated for $[C_{19}H_{22}O_2]^+$ requires *m/z* 282.1615, found *m/z* 282.1605.



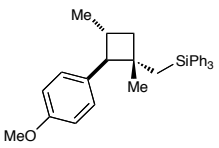
(Table 3, entry 8). Experiment 1: Set up according to General Procedure B using methyl 4-vinylbenzoate[12] (217 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), 1.67 mL of dry CH_2Cl_2 with a 4 h addition time of anethole (5 mL of a 0.135 M stock solution in CH_2Cl_2) and a total irradiation time of 4.5 h (1:1.6 crossed/homodimer). Purification by flash-column chromatography (gradient, 6:1 to 2:1 hexanes/CH_2Cl_2) afforded to afford 64 mg (0.21 mmol, 31% yield) of the title compound as a colorless oil. Experiment 2: 100 mg (0.67 mmol) of anethole, 219 mg (1.34 mmol) of methyl 4-vinylbenzoate, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of CH_2Cl_2. Isolated 65 mg (0.21 mmol, 31% yield). IR(neat) 2951, 1722, 1610, 1513, 1279, 1250 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (AA' of AA'BB', 8.6 Hz, 2H), 7.23 (BB' of AA'BB', 8.6 Hz, 2H), 7.15 (AA' of AA'BB', 8.8 Hz, 2H), 6.85 (BB' of AA'BB', 8.8 Hz, 2H), 3.89 (s, 3H), 3.79 (s, 3H), 3.42 (dt, 10, 8.2 Hz, 1H), 2.94 (t, 9.4 Hz, 1 H), 2.53 (dt, 10.1, 7.9 Hz, 1H) 2.37 (m, 1H), 1.71 (q, 10.1 Hz, 1H), 1.18 (d, 6.5 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 167.1, 158.2, 150.0, 135.3, 129.6, 127.8, 127.8, 126.6, 113.8, 55.6, 55.2, 51.9, 44.2, 35.5, 33.6, 20.4. HRMS (EI) calculated for $[C_{19}H_{22}O_3$ – propene$]^+$ requires *m/z* 268.1094, found *m/z* 268.1102.



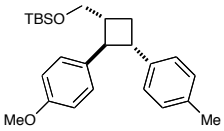
(Table 3, entry 9). Set up according to General Procedure A using anethole (102.1 mg, 0.69 mmol), 1-methylene-2,3-dihydro-1*H*-indene[13] (174 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), and 6.7 mL of anhydrous CH_2Cl_2 (2 h irradiation time, >10:1 crossed/homodimer). Purification by flash-column chromatography (gradient, 6:1 to 2:1 hexanes/CH_2Cl_2) afforded 167 mg (0.60 mmol, dr = 8.6:1, 87% yield) of the title compound as a colorless oil. Experiment 2: 102 mg (0.69 mmol) of anethole, 178 mg (1.34 mmol) of 1-methylene-2,3-dihydro-1*H*-indene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of CH_2Cl_2. Isolated 163 mg (0.59 mmol, dr = 8.6:1, 86% yield) of the cycloadduct as a colorless oil. IR(neat) 2951, 1581, 1281, 1251, 1054 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.43 (d, J = 7.5 Hz, 1H), 7.26 (t, J = 7.2 Hz, 1H), 7.16 (t, J = 7.2 Hz, 1H), 7.13 (t, J = 6.9 Hz, 1H), 6.88 (AA', J = 8.4 Hz, 2H), 6.76 (BB', J = 8.4 Hz, 2H), 3.75 (s, 3H), 3.24 (d, J = 10.6 Hz, 1H), 2.68 (m, 2H), 2.36 (dd, J = 15.4, 7.2 Hz, 1H), 2.16 (dd, J = 10.3, 7.8 Hz, 1H), 2.00 (ddd, J = 13.1, 8.3, 5.7 Hz, 1H), 1.86 (m, 2H), 1.22 (d, J = 6.5 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 158.0, 149.3, 144.0, 132.7, 128.1, 126.5, 126.5, 124.2, 122.4, 113.5, 57.3, 55.2, 53.2, 40.5, 33.7, 30.3, 29.1, 20.4. HRMS (EI) calculated for $[C_{20}H_{22}O]^+$ requires *m/z* 278.1666, found *m/z* 278.1662.



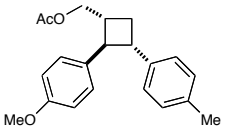
(Table 3, entry 11). Experiment 1: Set up according to General Procedure A with anethole (103 mg, 0.70 mmol), *n*-butyl vinyl ether (134 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), and 6.7 mL of anhydrous CH_2Cl_2 (3.5 h reaction time, >10:1 crossed/homodimer). Purification by flash-column chromatography (gradient, 15:1 to 10:1 hexanes/EtOAc) afforded 116 mg (0.47 mmol, 67% yield) of the cycloadduct as a colorless oil. Experiment 2: 105 mg (0.71 mmol) of anethole, 135 mg (1.34 mmol) of n-butyl vinyl ether, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of CH_2Cl_2. Isolated 116 mg (0.47 mmol, 66% yield) of the cycloadduct as a colorless oil. IR(neat) 2956, 2933, 2867, 1513, 1248 cm^{-1}.^1H NMR: (500 MHz, $CDCl_3$) δ 7.16 (AA' of AA'BB', J = 8.7 Hz, 2H), 6.85 (BB' of AA'BB', J = 8.7 Hz, 2H), 3.79 (s, 3H), 3.78 (m, 1H), 3.30 (m, 2H), 2.75 (dd, J = 8.9, 7.9 Hz, 1H), 2.41 (dt, J = 10.4, 7.2 Hz, 1H), 1.81 (m, 1H), 1.47 (m, 3H), 1.32 (m, 2H), 1.15 (d, J = 6.6 Hz, 3H), 0.87 (t, J = 7.3 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 158.1, 135.1, 127.8, 113.7, 76.4, 68.2, 56.4, 55.2, 35.0, 31.9, 29.4, 20.4, 19.3, 13.9. HRMS (ESI) calculated for $[C_{16}H_{24}O_2 + Na]^+$ requires *m/z* 271.1669, found *m/z* 271.1663.



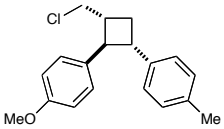
(Table 3, entry 12). Experiment 1: Set up according to General Procedure B using (2-methyl-allyl)-triphenylsilane[14] (421 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), 1.67 mL of dry CH_2Cl_2 with a 2 h addition time of anethole (5 mL of a 0.135 M stock solution in CH_2Cl_2) and a total irradiation time of 2.5 h (8.2:1 crossed/homodimer). Purification by flash-column chromatography (gradient, 6:1 to 2:1 hexanes/CH_2Cl_2) afforded to afford 145 mg (0.31 mmol, dr = 3:1, 47% yield) of the title compound as a colorless oil. Experiment 2: 100 mg (0.67 mmol) of anethole, 421 mg (1.34 mmol) of (2-methyl-allyl)-triphenylsilane, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of CH_2Cl_2. Isolated 151 mg (0.33 mmol, dr = 3:1, 49% yield). Major diastereomer: IR(neat) 2954, 1511, 1428, 1251, 1108 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) d 7.57 (m, 6H), 7.33 (m, 9H), 7.06 (AA' of AA'BB', J = 8.7 Hz, 2H), 6.84 (BB' of AA'BB', J = 8.7 Hz, 2H), 3.78 (s, 3H), 2.73 (d, J = 10.0 Hz, 1H), 2.40 (m, 1H), 2.00 (AB q, J = 14.9 Hz, 1H), 1.80 (AB q, J = 14.9 Hz, 1H), 1.37 (dd, J = 10.8, 8.1 Hz, 1H), 1.21 (dd, J = 10.8, 9.6 Hz, 1H), 0.93 (d, J = 6.8 Hz, 3H), 0.72 (s, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) d 158.0, 135.9, 135.8, 132.7, 129.2, 128.3, 127.7, 113.4, 61.0, 55.2, 41.4, 39.6, 29.9, 28.8, 24.1, 20.3. HRMS (EI) calculated for $[C_{32}H_{34}OSi]^+$ requires m/z 462.2374, found m/z 462.2381.



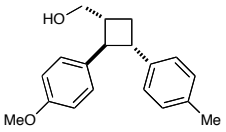
(Table 4, entry 1). Experiment 1: Set up according to General Procedure A with (*E*)-1-(*tert*-butyldimethylsilyloxy)-3-(4-methoxyphenyl)-2-propene[15] (186 mg, 0.67 mmol), 4-methyl styrene (158 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), and 6.7 mL of anhydrous CH_2Cl_2 (2.5 h irradiation time, >10:1 crossed/homodimer). Purification by flash-column chromatography (gradient, 6:1 to 1:1 hexanes/CH_2Cl_2) afforded 171 mg (0.43 mmol, 64% yield) of the cycloadduct as a colorless oil. Experiment 2: 187 mg (0.67 mmol) of (*E*)-1-(*tert*-butyldimethylsilyloxy)-3-(4-methoxyphenyl)-2-propene, 158 mg (1.34 mmol) of 4-methyl styrene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of CH_2Cl_2. Isolated 162 mg (0.41 mmol, 61% yield) of the cycloadduct as a colorless oil. IR(neat) 2954, 2929, 1513, 1249 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.17 (AA' of AA'BB', J = 8.6 Hz, 2H), 7.13 (AA' of AA'BB', J = 8.1 Hz, 2H), 7.08 (BB' of AA'BB', J = 8.1 Hz, 2H), 6.81 (BB' of AA'BB', J = 8.6 Hz, 2H), 3.77 (s, 3H), 3.69 (m, 2H), 3.34 (td, J = 9.6, 7.9 Hz, 1H), 3.30 (q, J = 9.1 Hz, 1H), 2.48 (m, 1H), 2.34 (dt, J = 10.6, 7.1 Hz, 1H), 2.31 (s, 3H), 1.94 (q, J = 9.7 Hz, 1H), 0.90 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 157.9, 141.7, 136.0, 135.5, 128.9, 127.9, 126.7, 113.6, 65.3, 55.2, 49.4, 43.9, 41.5, 28.5, 25.9, 21.0, 18.3, -5.3. HRMS (EI) calculated for $[C_{25}H_{36}O_2Si - C_4H_9]^+$ required *m/z* 339.1775, found *m/z* 339.1768.



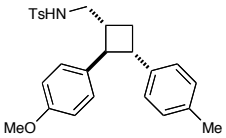
(Table 4, entry 2). Experiment 1: Set up according to General Procedure A with (*E*)-3-(4-methoxyphenyl) allyl acetate[16] (138 mg, 0.67 mmol), 4-methyl styrene (158 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), and 6.7 mL of anhydrous CH_2Cl_2 (4 h irradiation time, >10:1 crossed/homodimer). Purification by flash-column chromatography (5:1 hexanes/EtOAc) afforded 197 mg (0.61 mmol, 91% yield) of the cycloadduct as a colorless oil. Experiment 2: 136 mg (0.66 mmol) of (*E*)-3-(4-methoxyphenyl) allyl acetate, 158 mg (1.34 mmol) of 4-methyl styrene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of CH_2Cl_2. Isolated 195 mg (0.60 mmol, 91% yield) of the cycloadduct as a colorless oil. IR(neat) 2939, 1740, 1513, 1247, 1034 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.16 (AA', J = 8.4 Hz, 2H), 7.09 (s, 4H), 6.83 (BB', J = 8.6 Hz, 2H), 4.21 (dd, J = 11.4, 5.9 Hz, 1H), 4.17 (dd, J = 11.2, 5.9 Hz, 1H), 3.78 (s, 3H), 3.41 (td, J = 10.0, 8.3 Hz, 1H), 3.21 (t, J = 9.7 Hz, 1H), 2.63 (m, 1H), 2.44 (dt, J = 10.3, 7.8 Hz, 1H), 2.31 (s, 3H), 2.01 (s, 3H), 1.89 (q, J = 10.2 Hz, 1H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 171.2, 158.2, 140.9, 135.7, 134.9, 129.0, 127.8, 126.5, 113.8, 67.0, 55.2, 50.6, 43.9, 38.4, 29.0, 21.0, 20.9. HRMS (EI) calculated for $[C_{21}H_{24}O_3]^+$ requires *m/z* 324.1720, found *m/z* 324.1712.



(Table 4, entry 3). Experiment 1: Set up according to General Procedure A using (*E*)-1-(3-chloroprop-1-en-1-yl)-4-methoxybenzene[17] (125 mg, 0.68 mmol), 4-methyl styrene (154 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), and 6.7 mL of CH_2Cl_2 (3 h irradiation time, >10:1 crossed/homodimer). Purification by flash-column chromatography (gradient, 6:1 to 1:1 hexanes/CH_2Cl_2) afforded 74 mg (0.25 mmol, 37% yield) of the cycloadduct as a colorless oil. Experiment 2: (*E*)-1-(3-chloroprop-1-en-1-yl)-4-methoxybenzene (122 mg, 0.67 mmol), 4-methyl styrene (154 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), and 6.7 mL of CH_2Cl_2. Isolated 72 mg (0.24 mmol, 36% yield). IR(neat) 2941, 1612, 1513, 1249, 1037 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.16 (AA', J = 8.4 Hz, 2H), 7.09 (s, 4H), 6.84 (BB', J = 8.7 Hz, 2H), 3.78 (s, 3H), 3.71 (dd, J = 11.4, 5.0 Hz, 1H), 3.62 (dd, J = 11.1, 7.1 Hz, 1H), 3.39 (td, J = 9.9, 8.1 Hz, 1H), 3.22 (t, J = 9.6 Hz, 1H), 2.69 (m, 1H), 2.51 (dt, J = 10.7, 8.1 Hz, 1H), 2.31 (s, 3H), 1.96 (q, J = 10.3 Hz, 1H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 158.3, 140.7, 135.8, 134.5, 129.0, 127.9, 126.5, 113.8, 77.3, 77.0, 76.8, 55.2, 51.5, 48.3, 43.3, 41.3, 29.9, 21.0. HRMS (EI) calculated for $[C_{19}H_{21}ClO]^+$ requires *m/z* 300.1276, found *m/z* 300.1266.

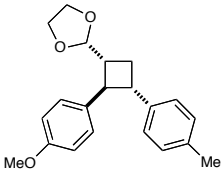


(Table 4, entry 4). Experiment 1: Set up according to General Procedure A with (*E*)-3-(4-methoxyphenyl)prop-2-en-1-ol (109 mg, 0.66 mmol), 4-methyl styrene (158 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), and 6.7 mL of anhydrous CH_2Cl_2 (3 h irradiation time, >10:1 crossed/homodimer). Purification by flash-column chromatography (2:1 hexanes/EtOAc) afforded 137 mg (0.74 mmol, 74% yield) of the cycloadduct as a colorless oil. Experiment 2: 115.5 mg (0.70 mmol) of (*E*)-3-(4-methoxyphenyl)prop-2-en-1-ol, 158 mg (1.34 mmol) of 4-methyl styrene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of CH_2Cl_2. Isolated 143 mg (0.51 mmol, 73% yield) of the cycloadduct as a colorless oil. IR(neat) 3356(br), 2933, 1611, 1513, 1248, 1036 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.17 (AA', J = 8.3 Hz, 2H), 7.09 (m, 4H), 6.82 (BB', J = 8.3 Hz, 2H), 3.76 (s, 3H), 3.74 (dd, J = 11.2, 5.5 Hz, 1H), 3.69 (dd, J = 11.0, 6.1 Hz, 1H), 3.38 (td, J = 9.9, 8.2 Hz, 1H), 3.20 (t, J = 9.6 Hz, 1H), 2.53 (m, 1H), 2.42 (dt, J = 10.4, 8.1 Hz, 1H), 2.30 (s, 3H), 1.87 (q, J = 10.2 Hz, 1H), 1.58 (br s, 1H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 158.1, 141.2, 135.6, 135.5, 129.0, 127.9, 126.5, 113.8, 66.0, 55.2, 50.1, 43.9, 41.6, 28.6, 21.0. HRMS (EI) calculated for $[C_{19}H_{22}O_2$ – allyl alcohol$]^+$ requires *m/z* 224.1196, found *m/z* 224.1191.

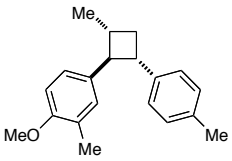


(Table 4, entry 5). Experiment 1: Set up according to General Procedure A with *N-(E)*-3-(4-methoxyphenyl)-2-propen-1-(4-methyl-benzenesulfonamide) (212 mg, 0.67 mmol), 4-methyl styrene (158 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), and 6.7 mL of anhydrous CH_2Cl_2 (24 h irradiation time, >10:1 crossed/homodimer). Purification by flash-column chromatography (5:1 hexanes/EtOAc) afforded 215 mg (0.49 mmol, 73% yield) of the cycloadduct as a colorless oil. Experiment 2: 212 mg (0.67 mmol) of *N-(E)*-3-(4-methoxyphenyl)-2-propen-1-(4-methyl-benzenesulfonamide), 158 mg (1.34 mmol) of 4-methyl styrene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of CH_2Cl_2. Isolated 217 mg (0.50 mmol, 75% yield) of the cycloadduct as a colorless oil. IR(neat) 3279, 2923, 1513, 1305, 1160 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.70 (AA' of AA'BB', J = 8.3 Hz, 2H), 7.26 (BB' of AA'BB', J = 8.3 Hz, 2H), 7.07 (AA' of AA'BB', J = 8.7 Hz, 2H), 7.04 (AA' of AA'BB', J = 8.0 Hz, 2H), 6.99 (BB' of AA'BB', J = 8.0 Hz, 2H), 6.80 (BB' of AA'BB', J = 8.7 Hz, 2H), 4.73 (t, J = 6.1 Hz, 1H), 3.76 (s, 3H), 3.30 (m, 1H), 3.07 (m, 2H), 2.98 (t, J = 9.2 Hz, 1H), 2.40 (s, 3H), 2.37 (m, 2H), 2.28 (s, 3H), 1.71 (m, 1H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 158.3, 143.4, 140.6,

136.9, 135.7, 134.4, 129.7, 129.0, 127.9, 127.1, 126.4, 113.9, 77.3, 77.1, 76.8, 55.2, 51.7, 47.5, 44.0, 39.0, 29.6, 21.5, 21.0. HRMS (ESI) calculated for $[C_{26}H_{29}NO_3S]^+$ required *m/z* 324.1720, found *m/z* 324.1724.

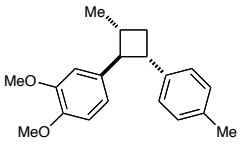


(Table 4, entry 6). Experiment 1: Set up according to General Procedure A with 2-[2-(4-methoxyphenyl)ethenyl]-1,3-dioxolane[18] (140 mg, 0.68 mmol), 4-methyl styrene (158 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), and 6.7 mL of anhydrous CH_2Cl_2 (24 h irradiation time, >10:1 crossed/homodimer). Purification by flash-column chromatography (8:1 hexanes/EtOAc) afforded 169 mg (0.52 mmol, 76% yield) of the cycloadduct as a colorless oil. Experiment 2: 142 mg (0.69 mmol) of 2-[2-(4-methoxyphenyl)ethenyl]-1,3-dioxolane, 158 mg (1.34 mmol) of 4-methyl styrene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of CH_2Cl_2. Isolated 181 mg (0.56 mmol, 81% yield) of the cycloadduct as a colorless oil. IR(neat) 2945, 1513, 1248, 1035 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.19 (J = 8.8 Hz, 2H), 7.15 (J = 8.0 Hz, 2H), 7.09 (J = 8.0 Hz, 2H), 6.82 (J = 8.8 Hz, 2H), 4.98 (d, J = 4.0 Hz, 1H), 3.97 (m, 2H), 3.87 (m, 2H), 3.76 (s, 3H), 3.48 (t, J = 9.6 Hz, 1H), 3.36 (q, J = 9.6 Hz, 1H), 2.67 (qd, J = 9.6, 4.0 Hz, 1H), 2.37 (dt, J = 10.6, 8.5 Hz, 1H), 2.31 (s, 3H), 2.08 (q, 1H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 158.0, 141.3, 135.7, 135.6, 129.0, 127.8, 126.7, 113.7, 105.2, 65.2, 65.0, 55.2, 47.9, 44.1, 41.2, 26.4, 21.0. HRMS (EI) calculated for $[C_{21}H_{24}O_3]^+$ required *m/z* 324.1720, found *m/z* 324.1724.

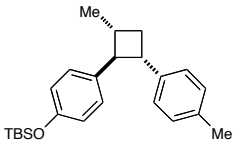


(Table 4, entry 7). Experiment 1: Set up according to General Procedure A using (*E*)-4-methoxy-3-methyl-propenyl benzene (106.4 mg, 0.66 mmol), 4-methyl styrene (158 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), and 6.7 mL of anhydrous CH_2Cl_2 (1.5 h irradiation time, 8:1 crossed/homodimer). Purification by flash-column chromatography (6:1 hexanes/CH_2Cl_2) afforded 110 mg (0.39 mmol, 59% yield) of the cycloadduct as a colorless oil. Experiment 2: 112.5 mg (0.69 mmol) of (*E*)-4-methoxy-3-methyl-propenyl benzene, 158 mg (1.34 mmol) of 4-methyl styrene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mL of CH_2Cl_2. Isolated 116 mg (0.41 mmol 59% yield). IR(neat) 2949, 1505, 1254, 1161 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.11 (m, 4H), 7.06 (m, 2H), 6.78 (d, J = 8.8 Hz, 1H), 3.83 (s, 3H), 3.38 (td, J = 9.9, 8.2 Hz, 1H), 2.91 (t, J = 9.5 Hz, 1H), 2.51 (dt, J = 9.9, 7.8 Hz, 1H), 2.34 (m, 1H), 2.33 (s, 3H), 2.23 (s, 3H), 1.68 (q, J = 10.0 Hz, 1H), 1.20 (d, J = 6.5 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 156.2, 141.8, 135.5, 135.3,

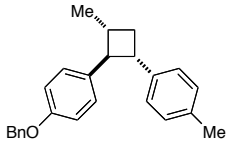
129.2, 128.9, 126.5, 126.3, 125.0, 109.8, 55.6, 55.3, 43.7, 35.5, 34.1, 21.0, 20.5, 16.3. HRMS (EI) calculated for $[C_{20}H_{24}O]^+$ requires *m/z* 280.1822, found *m/z* 280.1828.



(Table 4, entry 8). Experiment 1: Set up according to General Procedure A with methoxyisoeugenol (122 mg, 0.68 mmol), 4-methyl styrene (158 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), and 6.7 mL of anhydrous CH_2Cl_2 (24 h irradiation time, >10:1 crossed/homodimer). Purification by flash-column chromatography (8:1 hexanes/EtOAc) afforded 57 mg (0.19 mmol, 28% yield) of the cycloadduct as a colorless oil. Experiment 2: 123.5 mg (0.69 mmol) of methylisoeugenol, 158 mg (1.34 mmol) of 4-methyl styrene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mmol of CH_2Cl_2. Isolated 56 mg (0.19 mmol, 28% yield) of the cycloadduct as a colorless oil. IR(neat) 2950, 1516, 1464, 1243 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.09 (m, 4H), 6.80 (m, 2H), 6.75 (m, 1H), 3.85 (s, 3H), 3.85 (s, 3H), 3.35 (q, J = 9.4 Hz, 1, H), 2.90 (t, J = 9.4 Hz, 1H), 2.49 (dt, J = 10.4, 7.9 Hz, 1H), 2.33 (m, 1H), 2.31 (s, 3H), 1.69 (q, J = 10.1 Hz, 1H), 1.19 (d, J = 6.5 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 148.8, 147.4, 141.6, 136.5, 135.4, 128.9, 126.5, 118.6, 111.1, 110.2, 77.3, 77.0, 76.8, 56.1, 55.9, 55.8, 43.8, 35.4, 33.8, 21.0, 20.5. HRMS (EI) calculated for $[C_{20}H_{24}O_2]^+$ required *m/z* 296.1771, found *m/z* 296.1757.



(Table 4, entry 10). Set up according to General Procedure A with 165.6 mg (0.667 mmol) (*E*)-*tert*-butyldimethyl(4-(prop-1-enyl)phenoxy)silane[8], 161.4 mg (1.36 mmol) 4-methyl styrene, and 4.1 mg (0.0018 mmol) $Ru(bpm)_3(BArF)_2$, and 6.7 mL of anhydrous CH_2Cl_2 (2.5 h irradiation time, >10:1 crossed/homodimer). Purification by flash-column chromatography (15:1 to 10:1 Hexanes:CH_2Cl_2) led to 214.8 mg (0.586 mmol, 88% yield) of the desired cyclobutane as a colorless oil. Experiment 2: 169 mg (0.68 mmol) of (*E*)-*tert*-butyldimethyl(4-(prop-1-enyl)phenoxy)silane, 158 mg (1.34 mmol) of 4-methyl styrene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mL of CH_2Cl_2. Isolated 217 mg (0.59 mmol, 87% yield). IR(neat) 2956, 2929, 2859, 1510, 1262 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.08 (m, 6H), 6.75 (BB' of AA'BB', J = 8.5 Hz, 2H), 3.32 (q, J = 9.0 Hz, 1H), 2.91 (t, J = 9.0 Hz, 1H), 2.48 (dt, J = 9.3, 7.5 Hz, 1H), 2.31 (m, 1H), 2.30 (s, 3H), 1.65 (q, J = 10.2 Hz, 1H), 1.17 (d, J = 6.5 Hz, 3H), 0.97 (s, 9H), 0.18 (s, 6H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 153.9, 141.7, 136.5, 135.3, 128.9, 127.6, 126.6, 119.7, 55.5, 43.8, 35.3, 34.2, 25.7, 21.0, 20.5, 18.1, –4.4. HRMS (EI) calculated for $[C_{24}H_{34}OSi]^+$ requires *m/z* 366.2374, found *m/z* 366.2370.



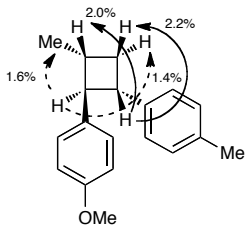
(Table 4, entry 11). Experiment 1: Set up according to General Procedure A using (*E*)-1-benzyloxy-4-(1-propenyl)benzene (149 mg, 0.66 mmol), 4-methyl styrene (158 mg, 1.34 mmol), $Ru(bpm)_3(BArF)_2$ (4 mg, 0.0017 mmol), and 6.7 mL of anhydrous CH_2Cl_2 (1.5 h irradiation time, >10:1 crossed/homodimer). Purification by flash-column chromatography (3:1 hexanes/CH_2Cl_2) afforded 177 mg (0.52 mmol, 79% yield) of the cycloadduct as a white solid (39–40 ºC). Experiment 2: 152.4 mg (0.68 mmol) of (*E*)-1-benzyloxy-4-(1-propenyl)benzene, 154 mg (1.34 mmol) of 4-methyl styrene, 4 mg (0.0017 mmol) of $Ru(bpm)_3(BArF)_2$, and 6.7 mL of CH_2Cl_2. Isolated 182 mg (0.53 mmol 78% yield). IR(neat) 2949, 1627 cm^{-1}. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.41 (d, J = 7.3 Hz, 2H), 7.35 (t, J = 7.3 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 7.14 (AA' of AA'BB', J = 8.6 Hz, 2H), 7.07 (m, 4H), 6.90 (BB' of AA'BB', J = 8.6 Hz, 2H), 5.01 (s, 2H), 3.32 (td, J = 9.8, 8.2 Hz, 1H), 2.91 (t, J = 9.4 Hz, 1H), 2.47 (dt, J = 10.2, 7.9 Hz, 1H), 2.31 (m, 1H), 2.29 (s, 3H), 1.66 (q, J = 10.2 Hz, 1H), 1.17 (d, J = 6.5 Hz, 3H). ^{13}C NMR: (125 MHz, $CDCl_3$) δ 157.3, 141.6, 137.2, 136.2, 135.4, 128.9, 128.5, 127.9, 127.7, 127.5, 126.5, 114.6, 77.3, 77.0, 76.8, 70.0, 55.5, 43.8, 35.3, 34.1, 21.0, 20.5. HRMS (EI) calculated for $[C_{25}H_{36}O]^+$ requires *m/z* 342.1979, found *m/z* 342.1980.

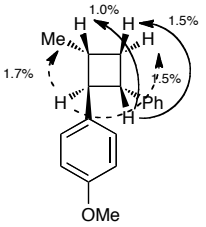
C. Large-scale synthesis of 8a (eq 1**).** A 250 mL round-bottomed flask was charged with 1.0 g **1** (6.7 mmol), 1.6 g **7a** (13.4 mmol) and 4 mg $Ru(bpm)_3(BArF)_2$ (1.7 μmol) The flask was cooled to –15 ºC using a controlled-temperature cooling bath and 67 mL of anhydrous CH_2Cl_2 was added. The reaction mixture was vigorously stirred under air in front of a 20 W CFL. After 2 h, the reaction was passed through a short pad of silica using 250 mL Et_2O. The solvent was removed by rotary evaporation, and the residue was purified by flash-column chromatography (2.5:1 hexanes:CH_2Cl_2) to afford 1.45 g (5.4 mmol, 81% yield) of the pure cycloadduct as a colorless oil.

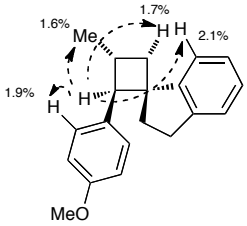
V. Typical Experimental Setup

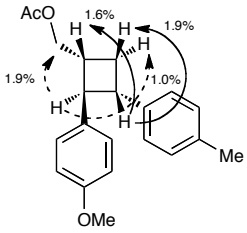
A photograph of the experimental setup for a typical cycloaddition is shown below. The reaction vessel is a standard borosilicate test tube immersed in an acetone bath cooled to –15 °C using a Neslab immersion cooler. The light source is a 20 W GE Reveal CFL bulb installed in a clamp light.

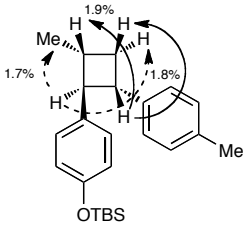
VI. Representative nOe Relationships

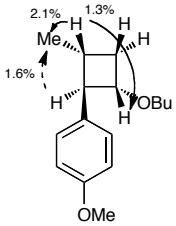


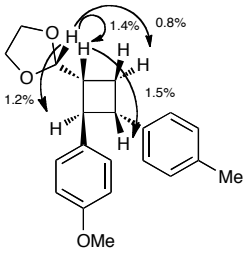


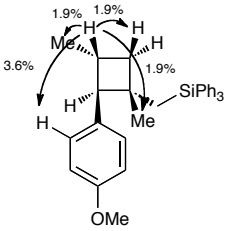












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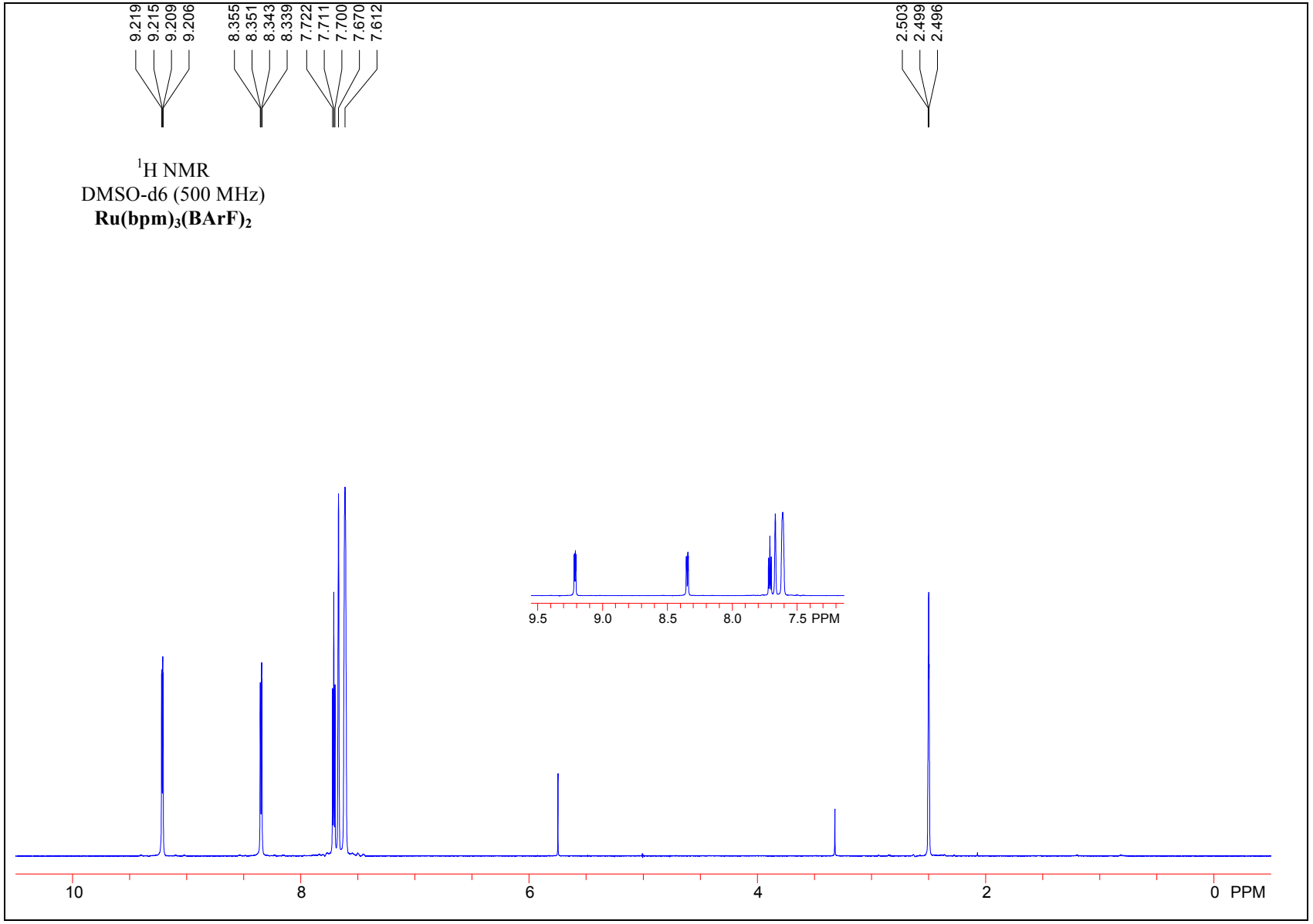
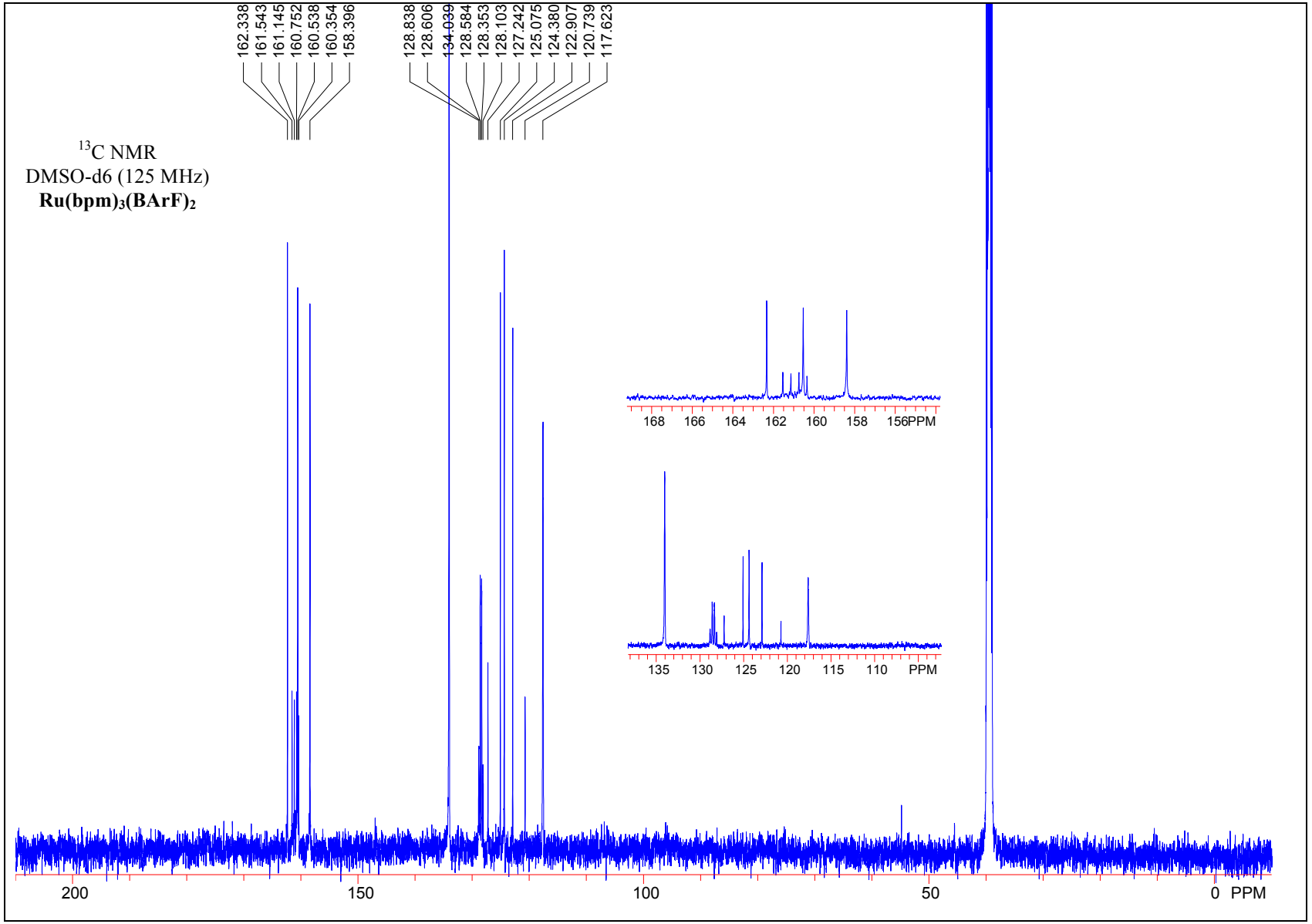
18 Xu, W.; Chen, Q.-Y. *Org. Biomol. Chem.* **2003**, *1*, 1151-1156.

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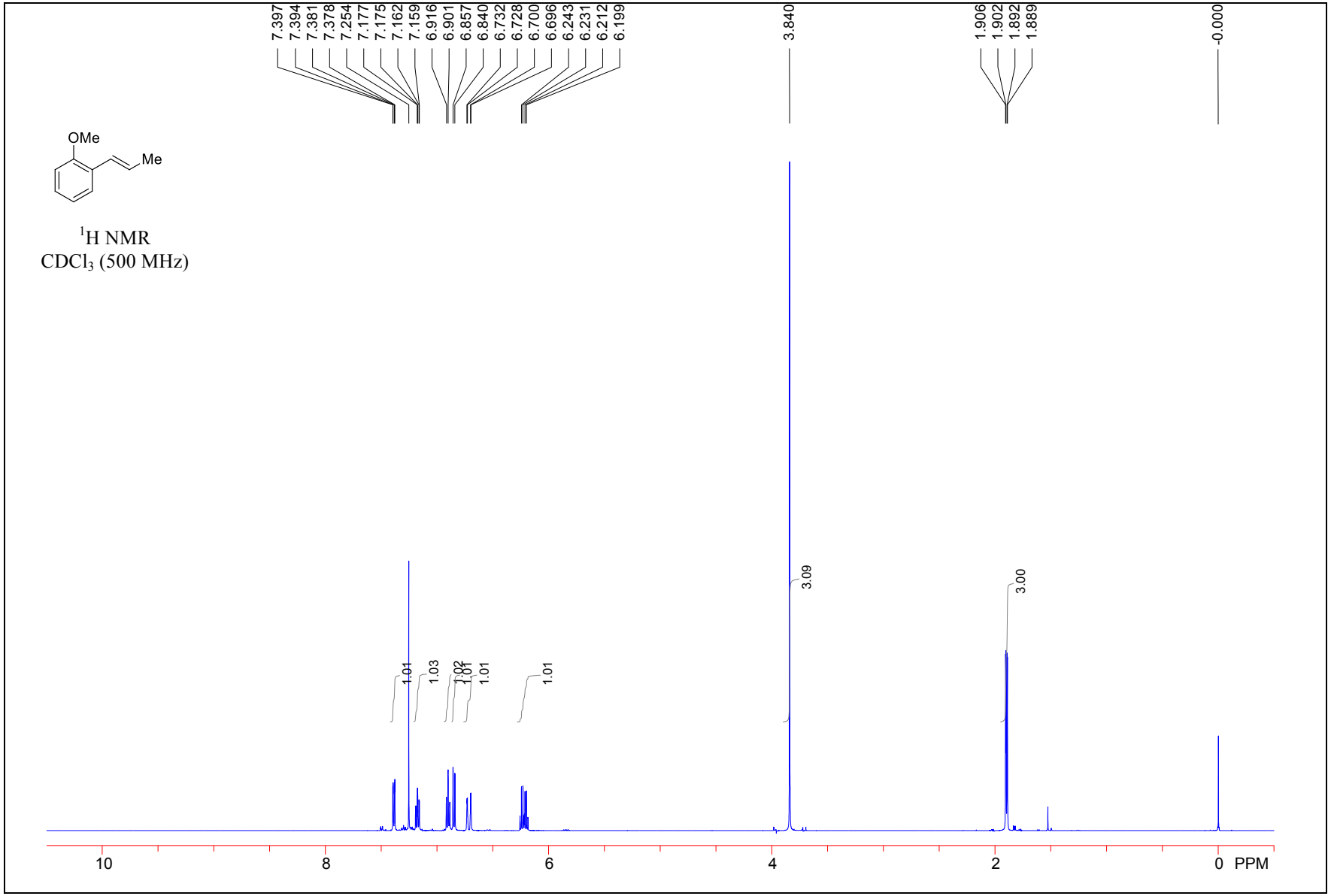
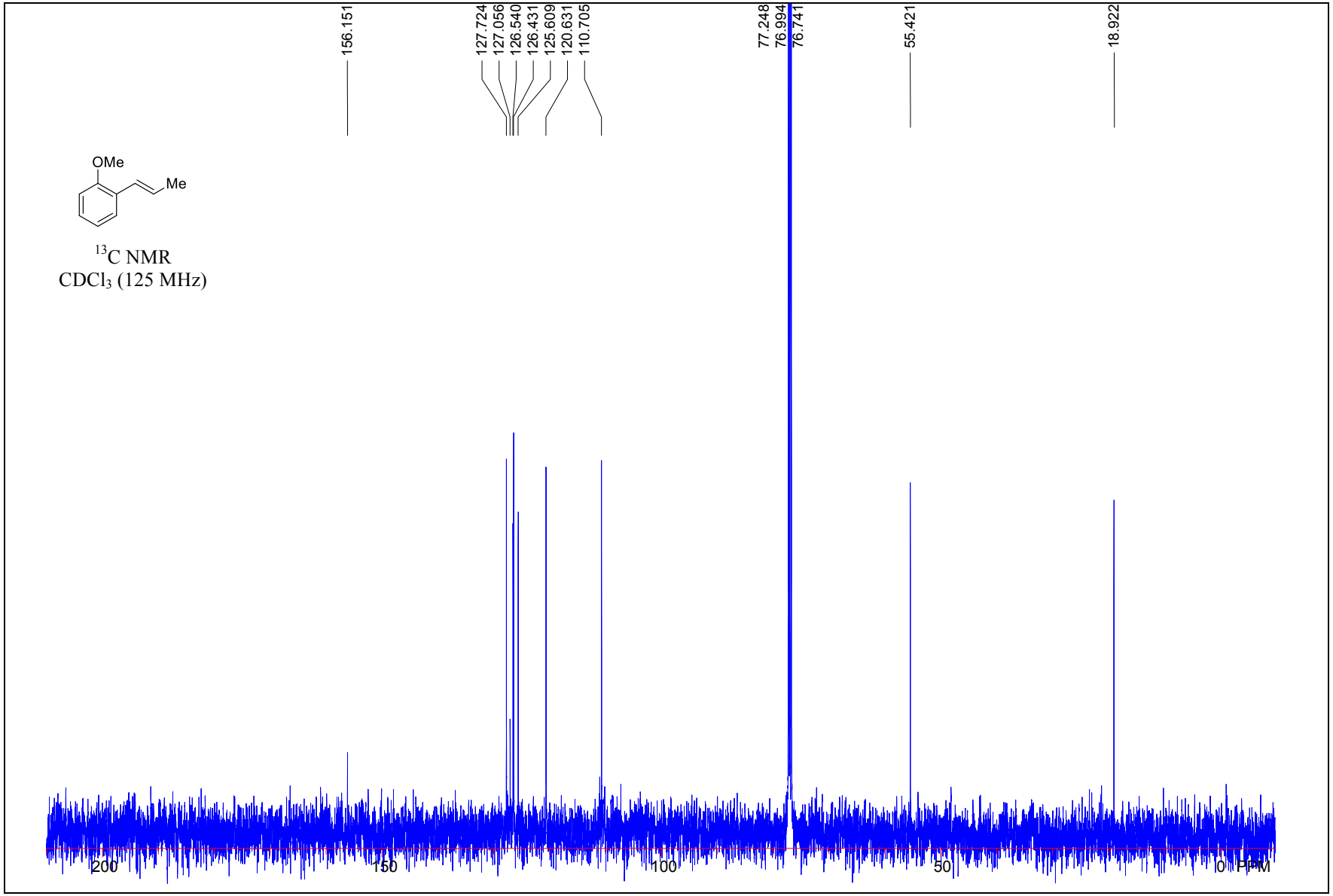
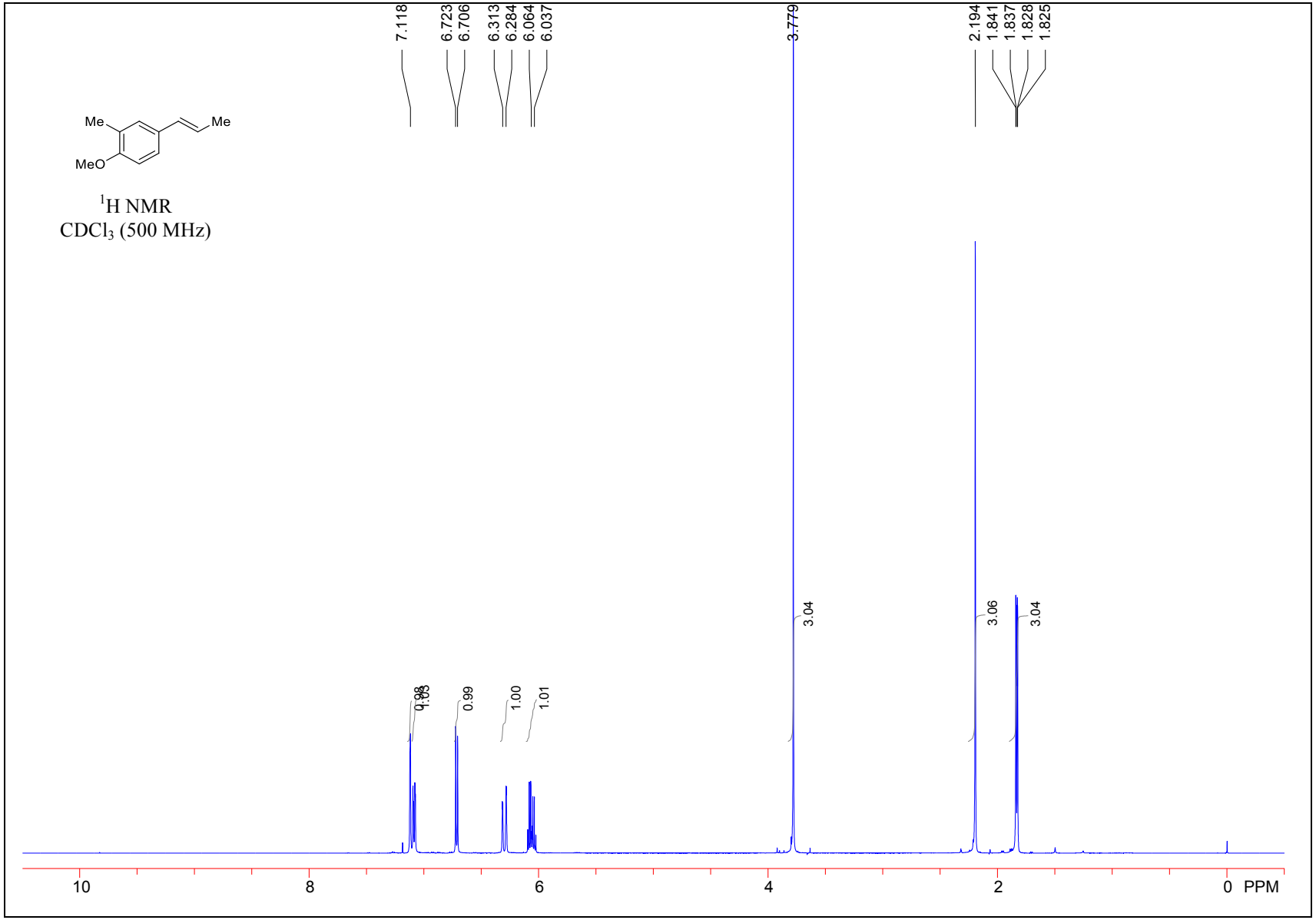
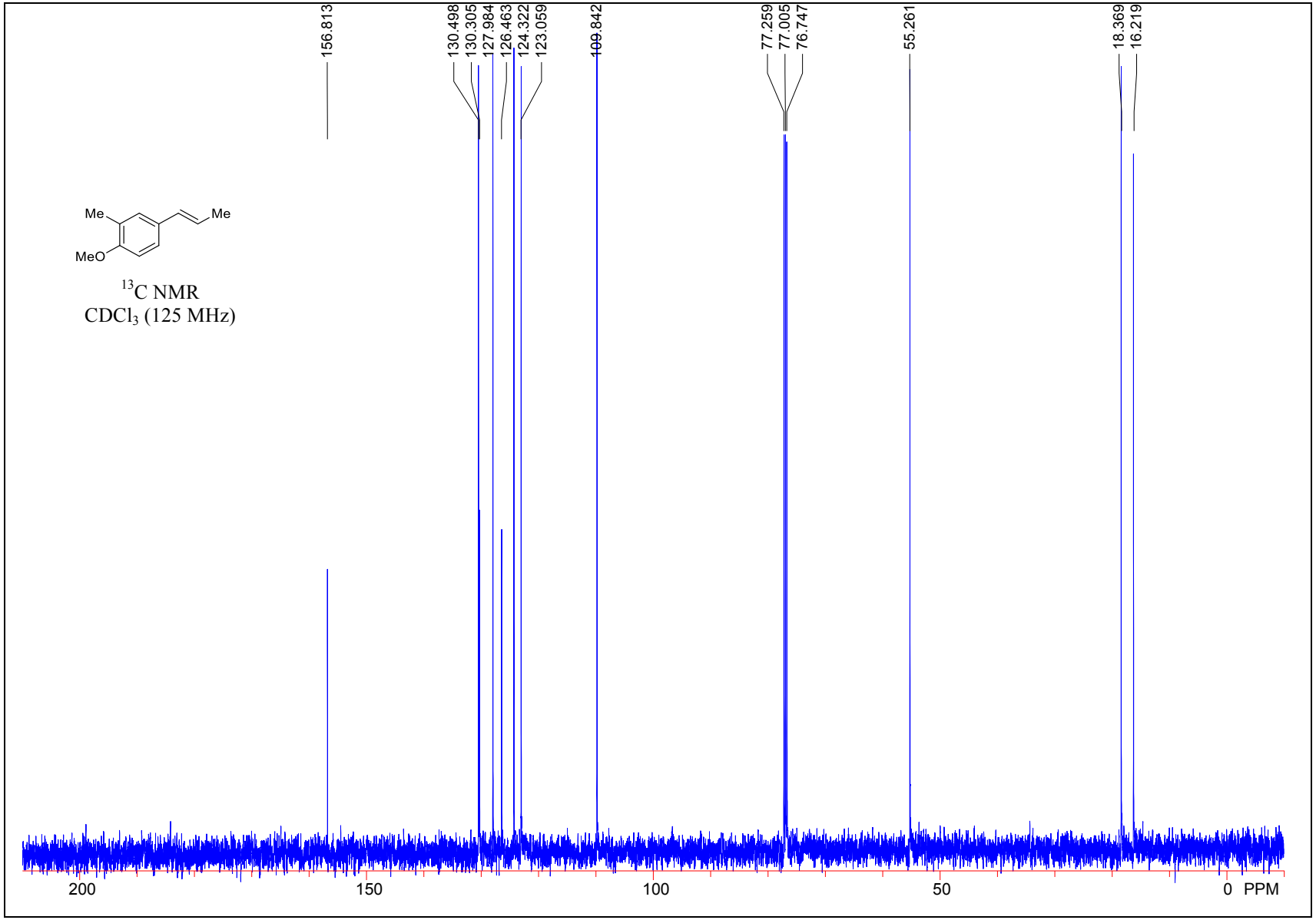
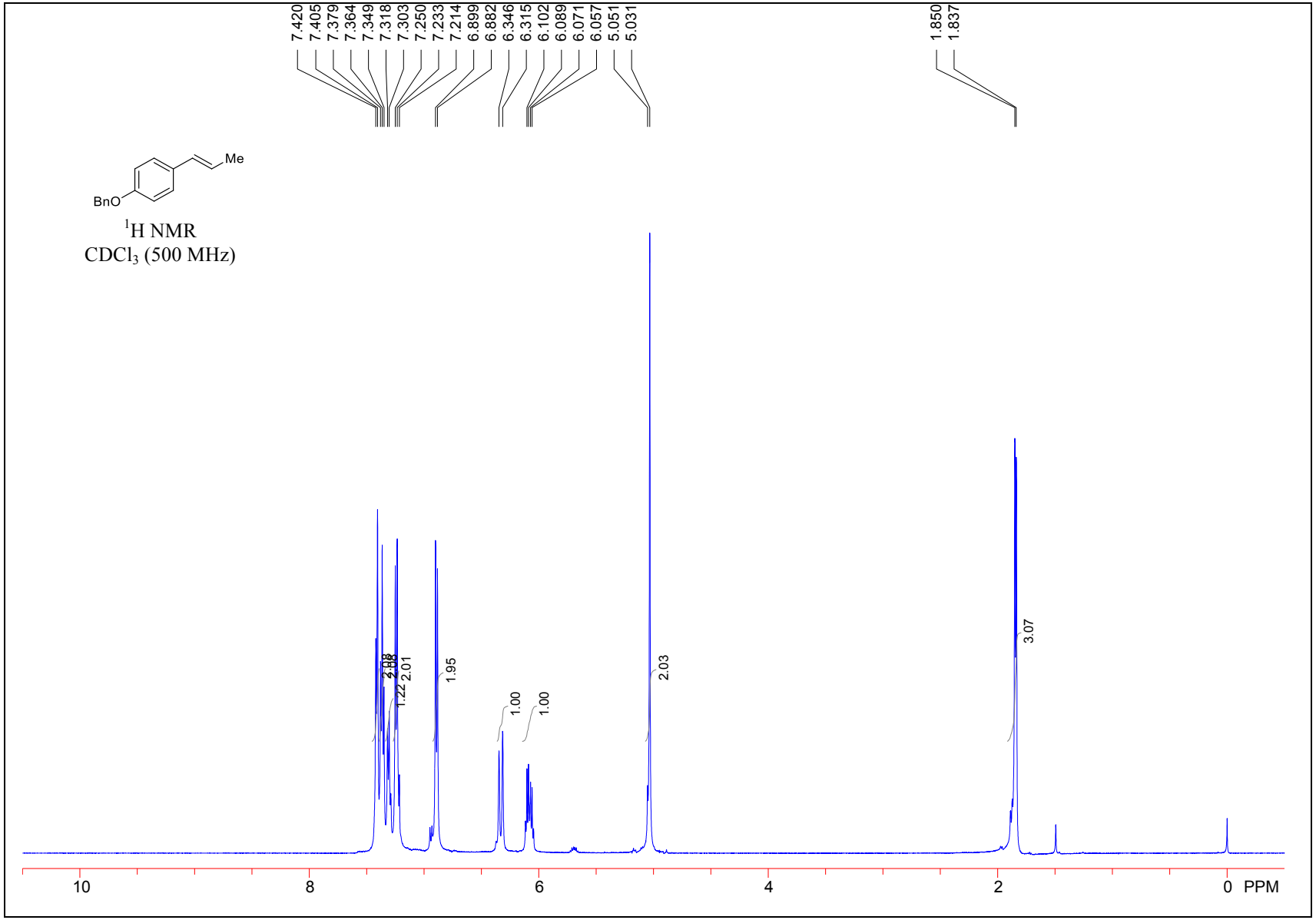
161.543
161.145
160.752
160.538
160.354
158.396
128.838
128.606
134.039
128.584
128.353
128.103
127.242
125.075
124.380
122.907
120.739
117.623
^{13}C NMR
DMSO-d6 (125 MHz)
Ru(bpm)$_3$(BArF)$_2$
168 166 164 162 160 158 156PPM
135 130 125 120 115 110 PPM
200 150 100 50 0 PPM

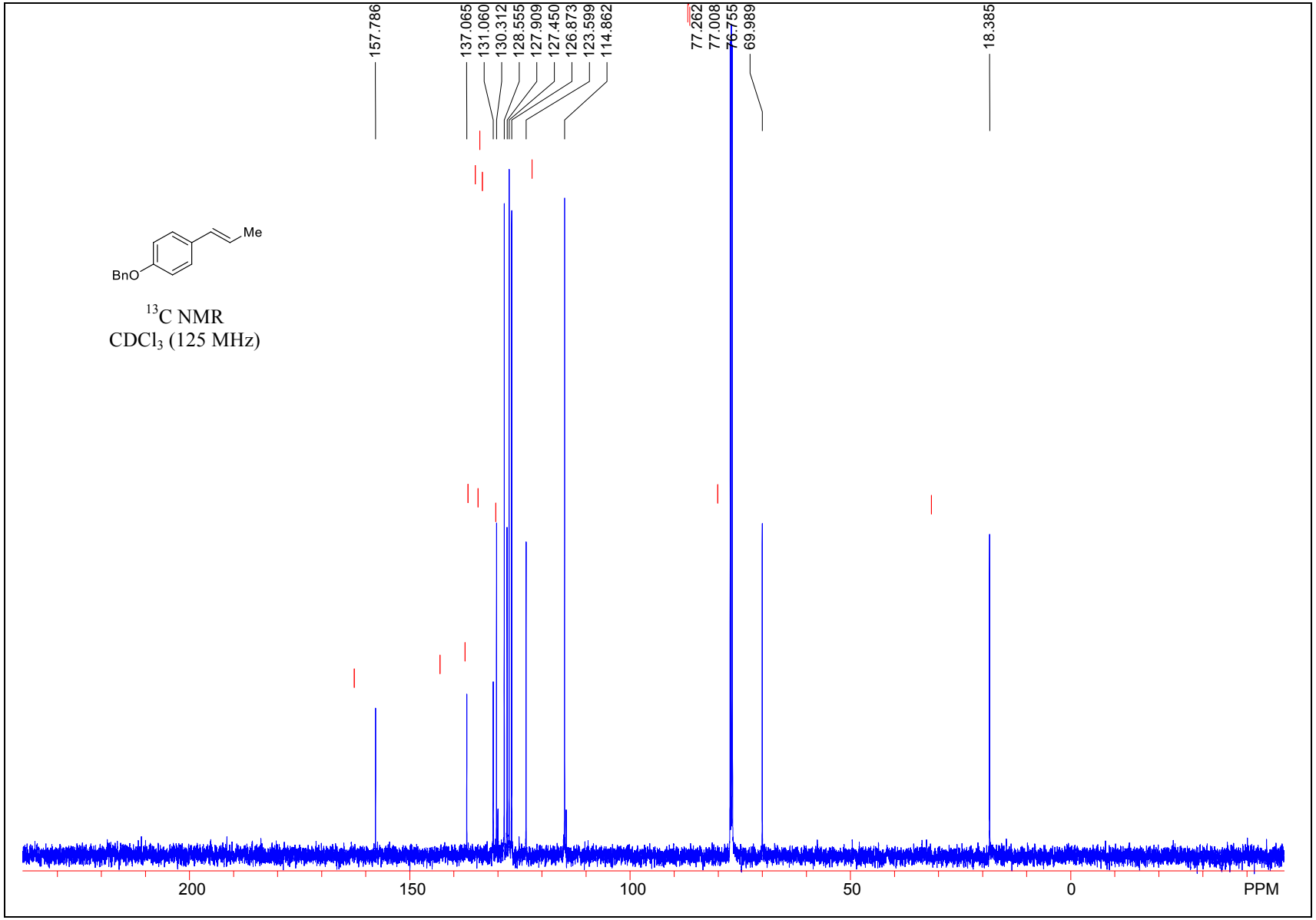


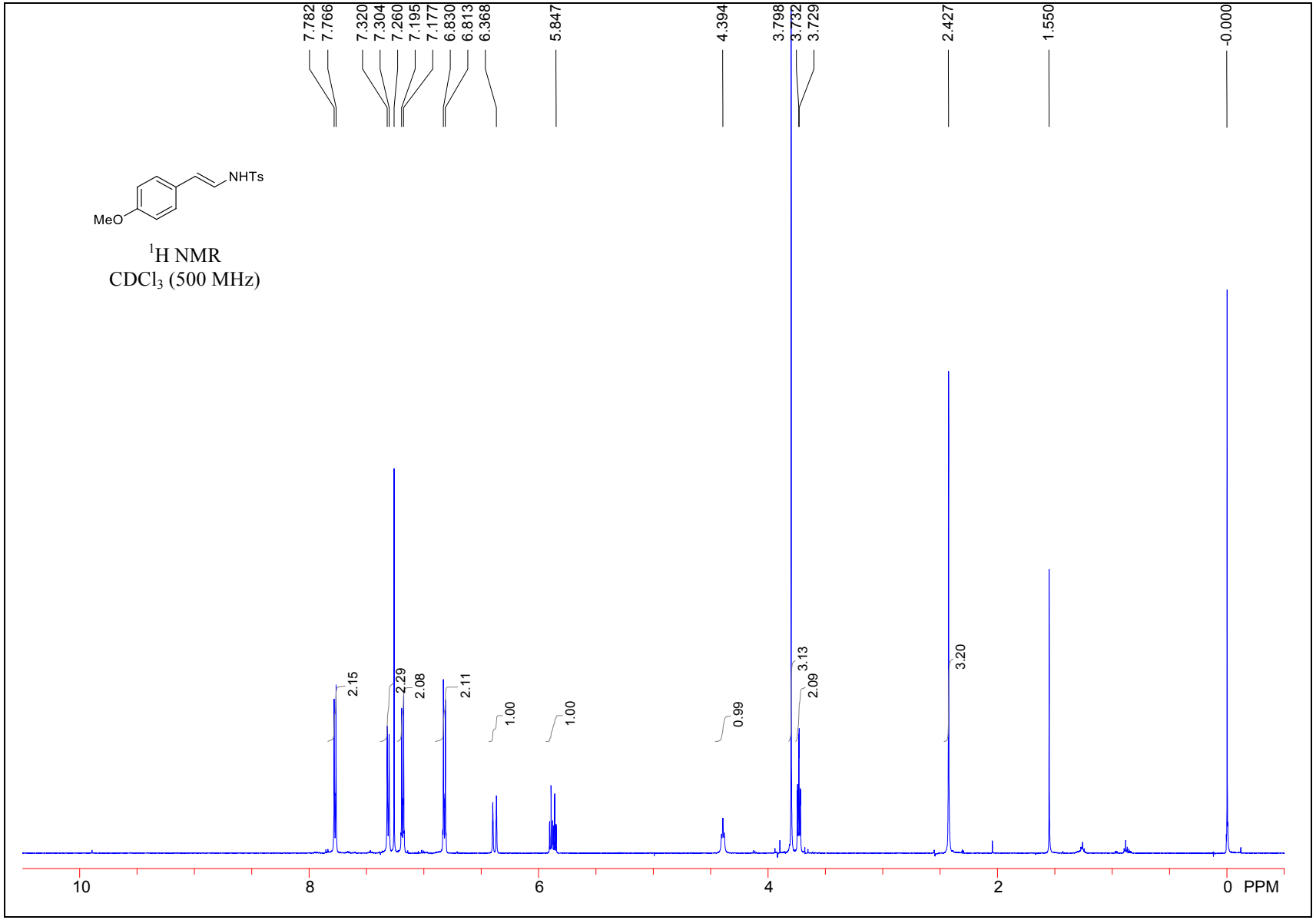


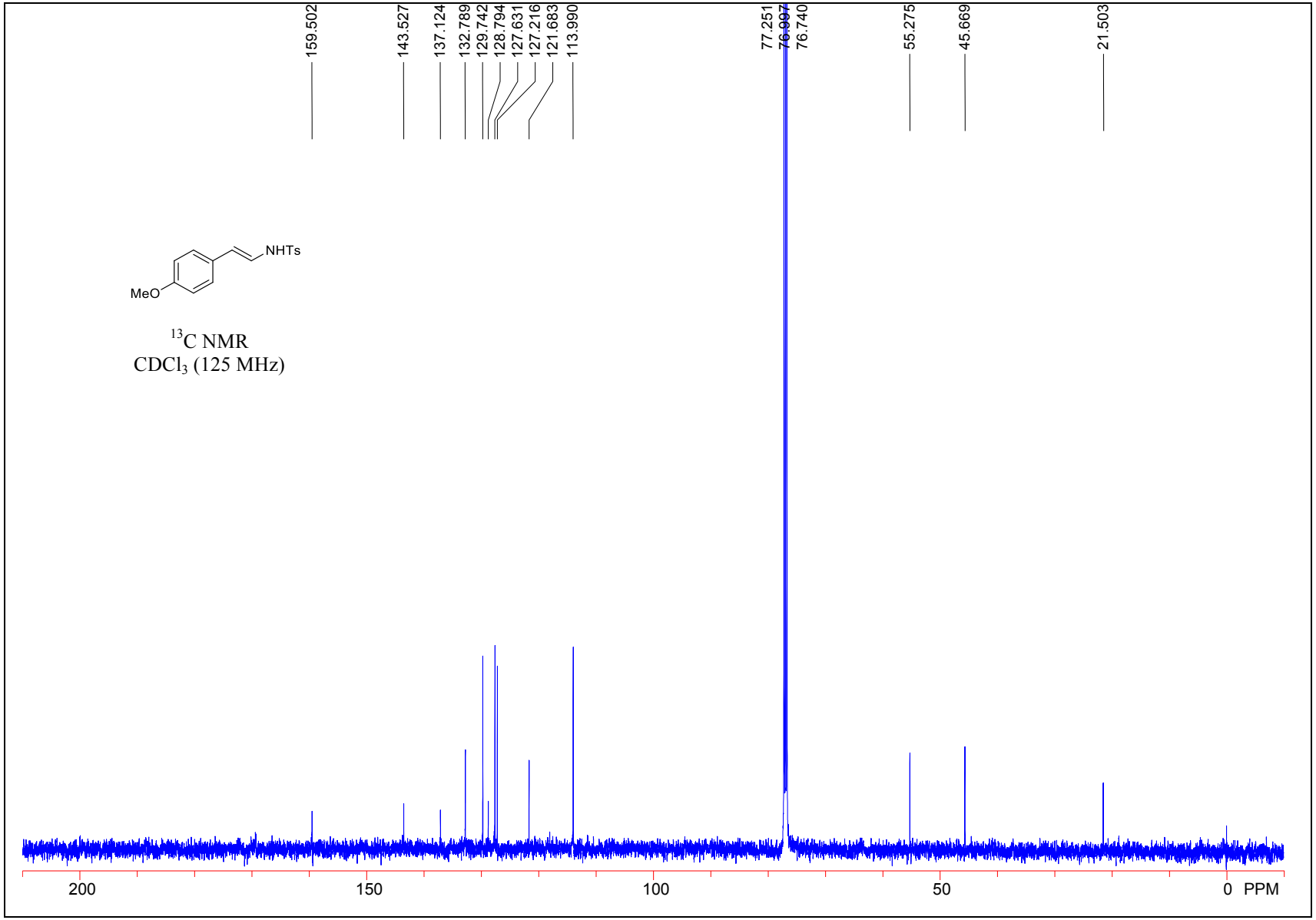

7.118
6.723
6.706
6.313
6.284
6.064
6.037
3.779
2.194
1.841
1.837
1.828
1.825
Me
Me
MeO
^{1}H NMR
$CDCl_3$ (500 MHz)
3.04
3.06
3.04
0.98
1.03
0.99
1.00
1.01
10
8
6
4
2
0 PPM

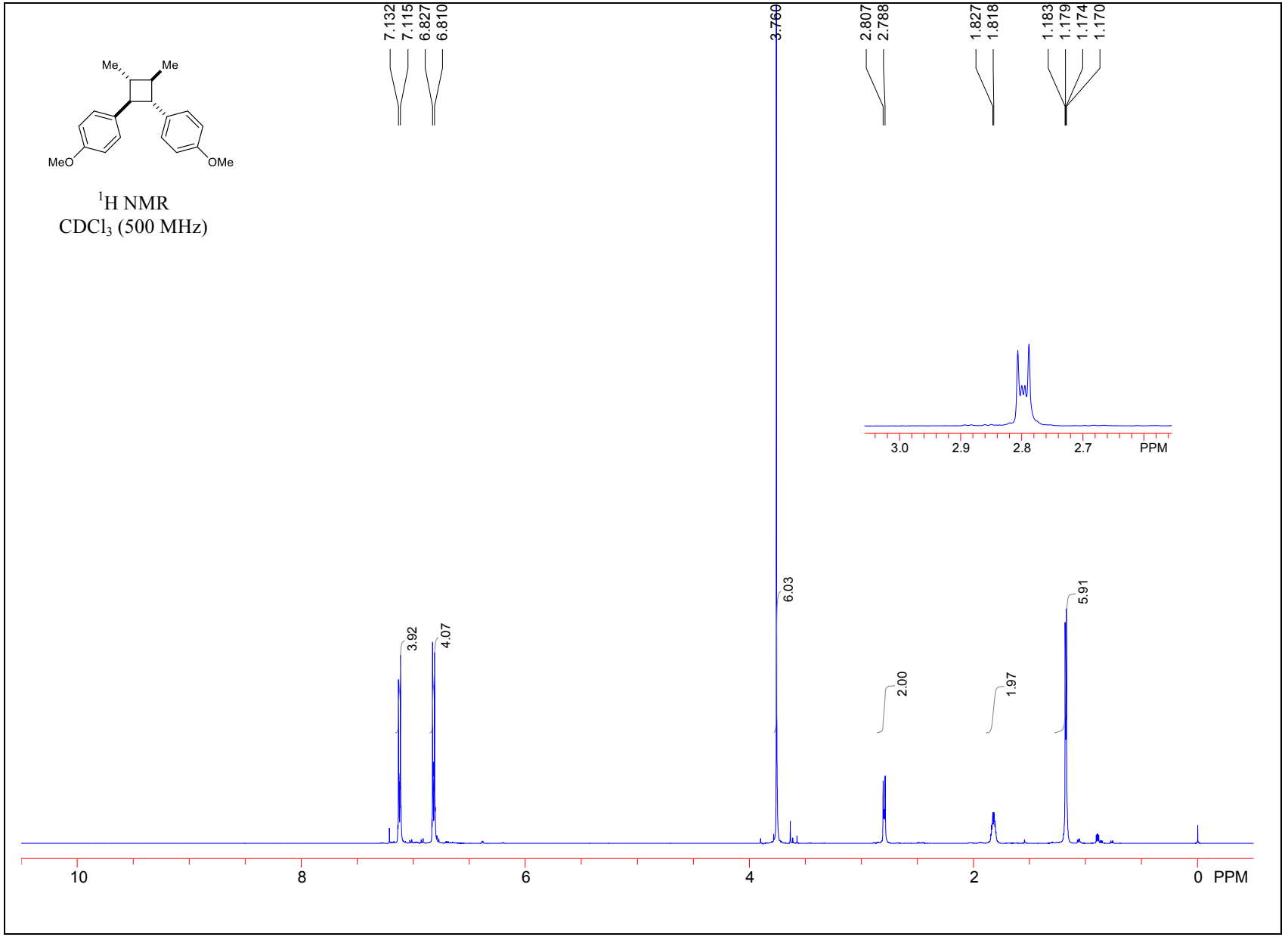


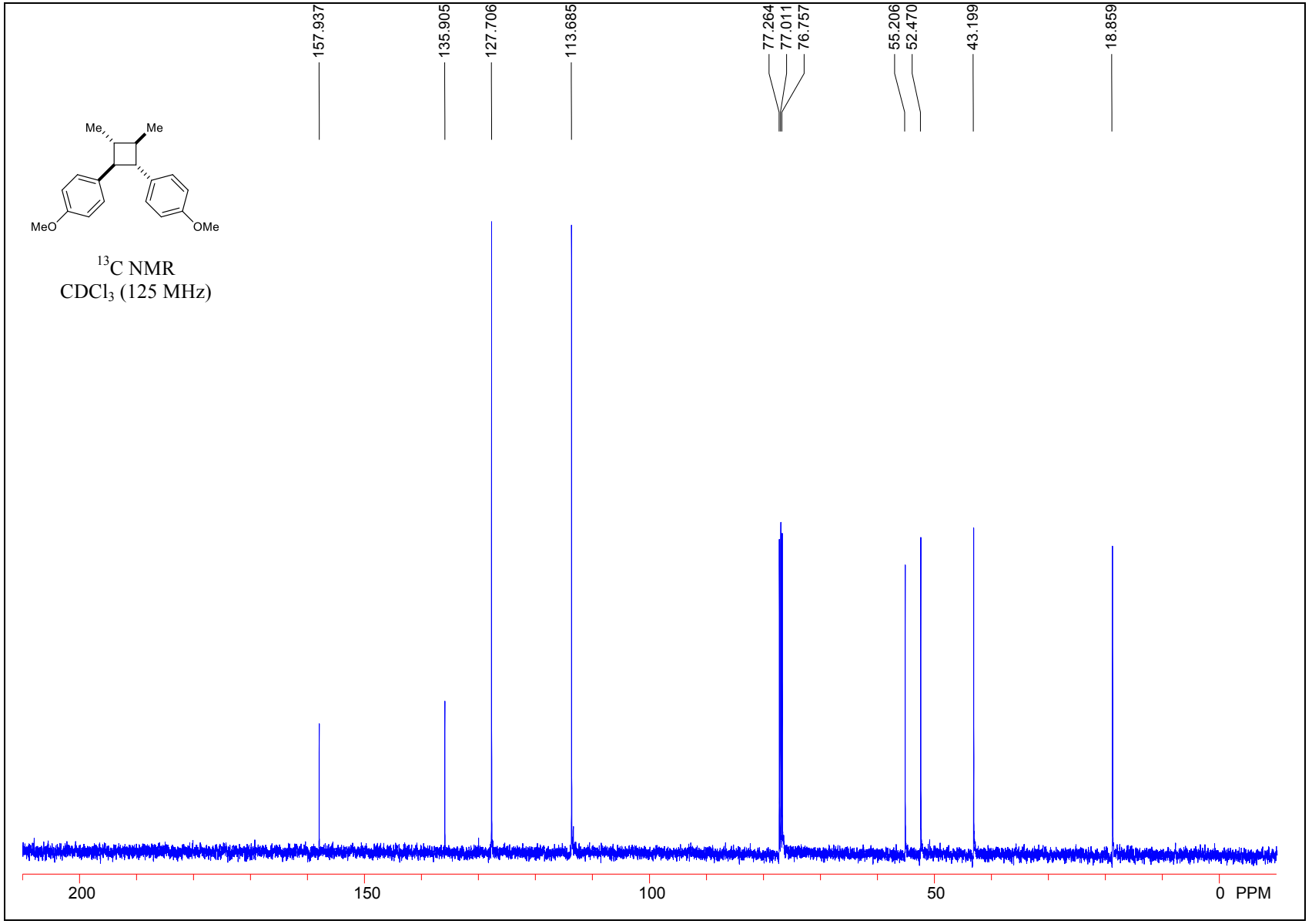








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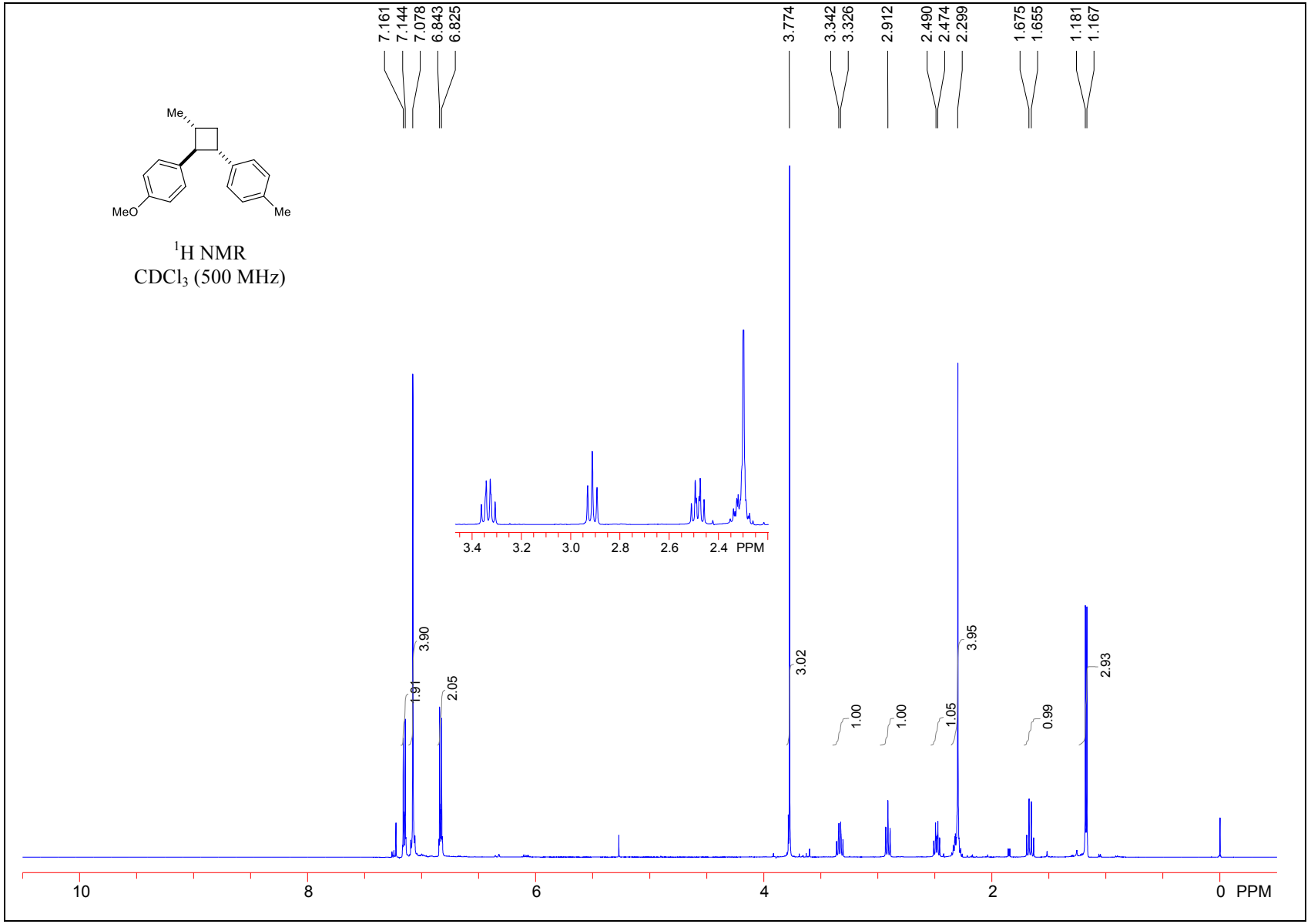
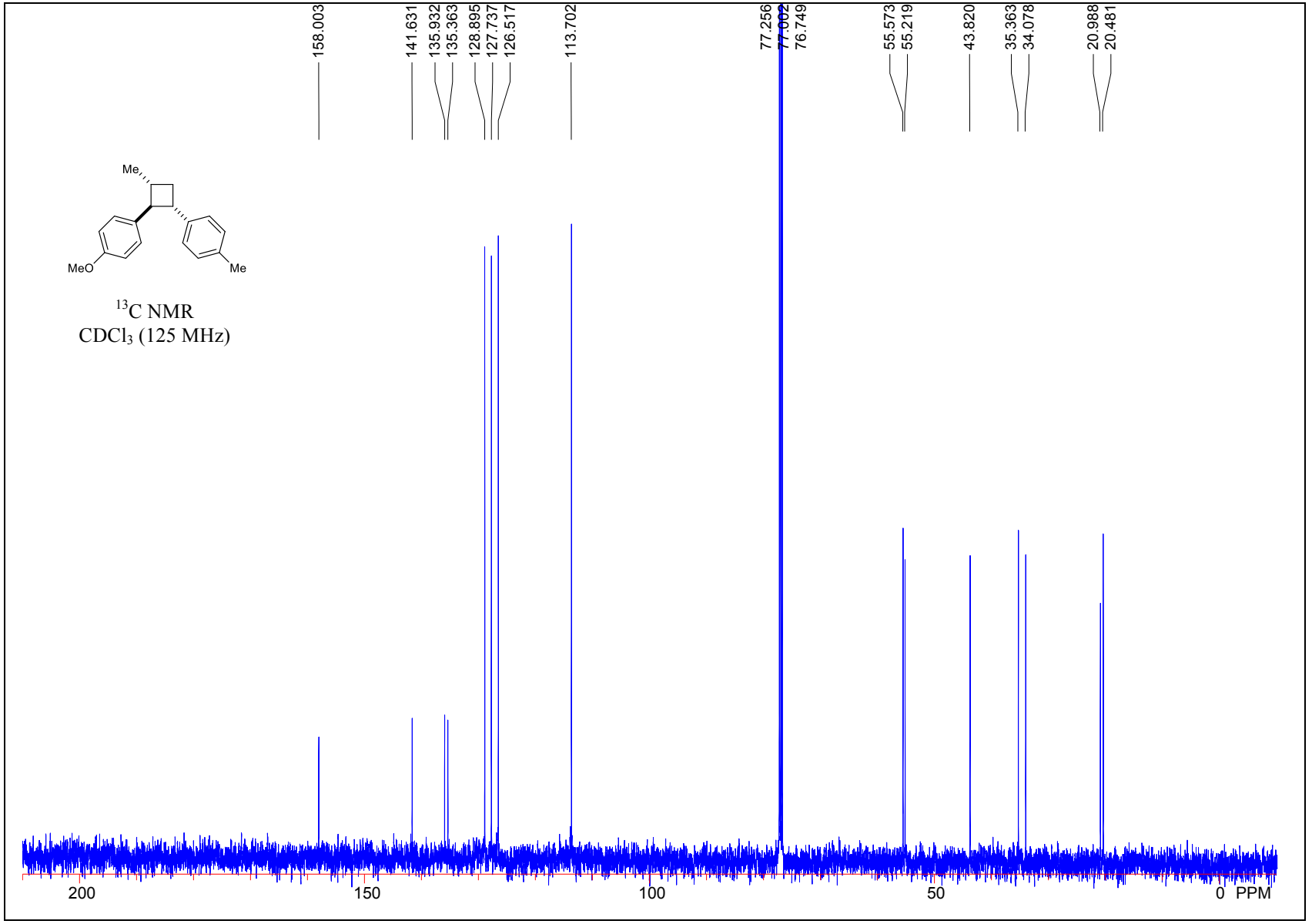
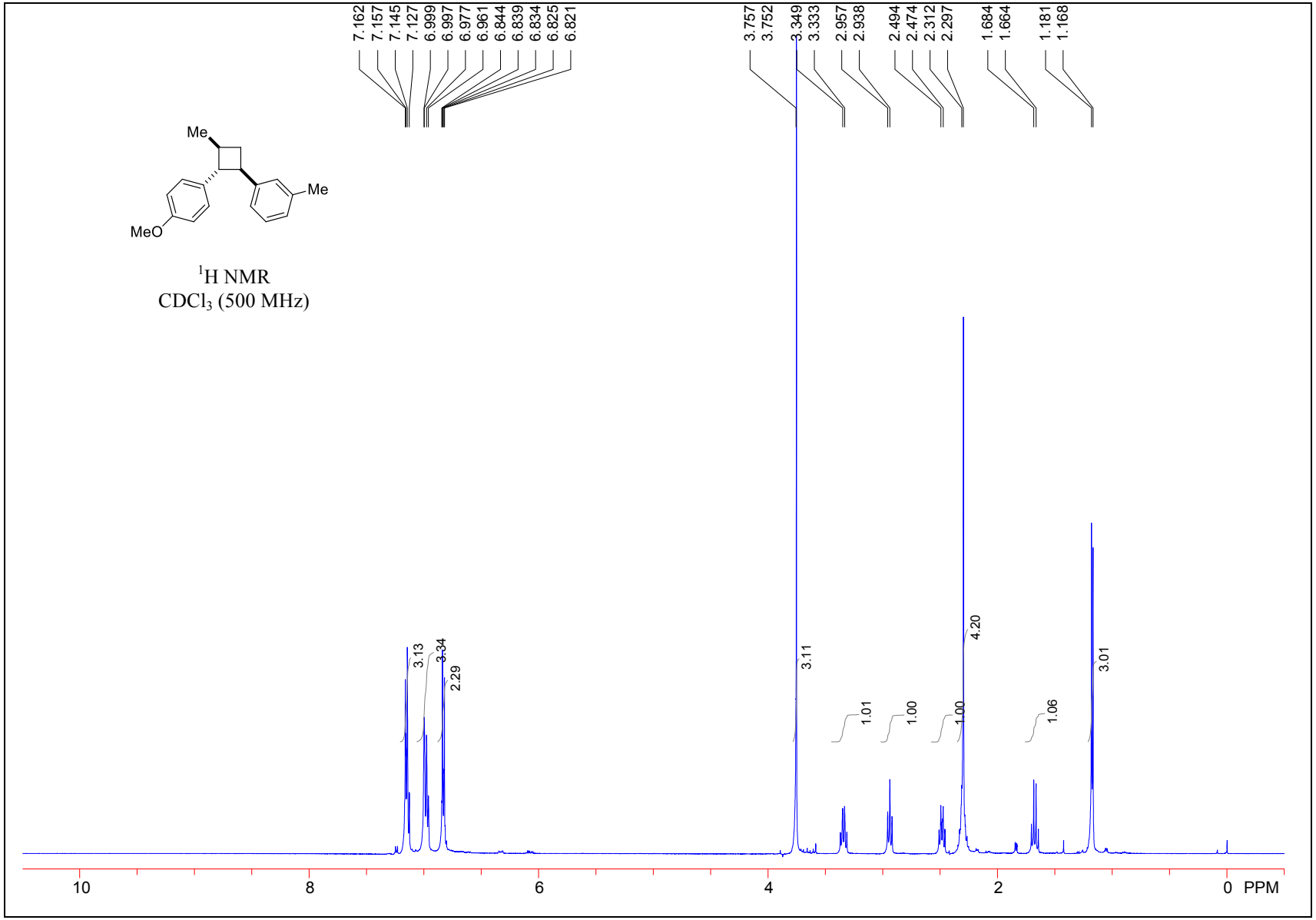
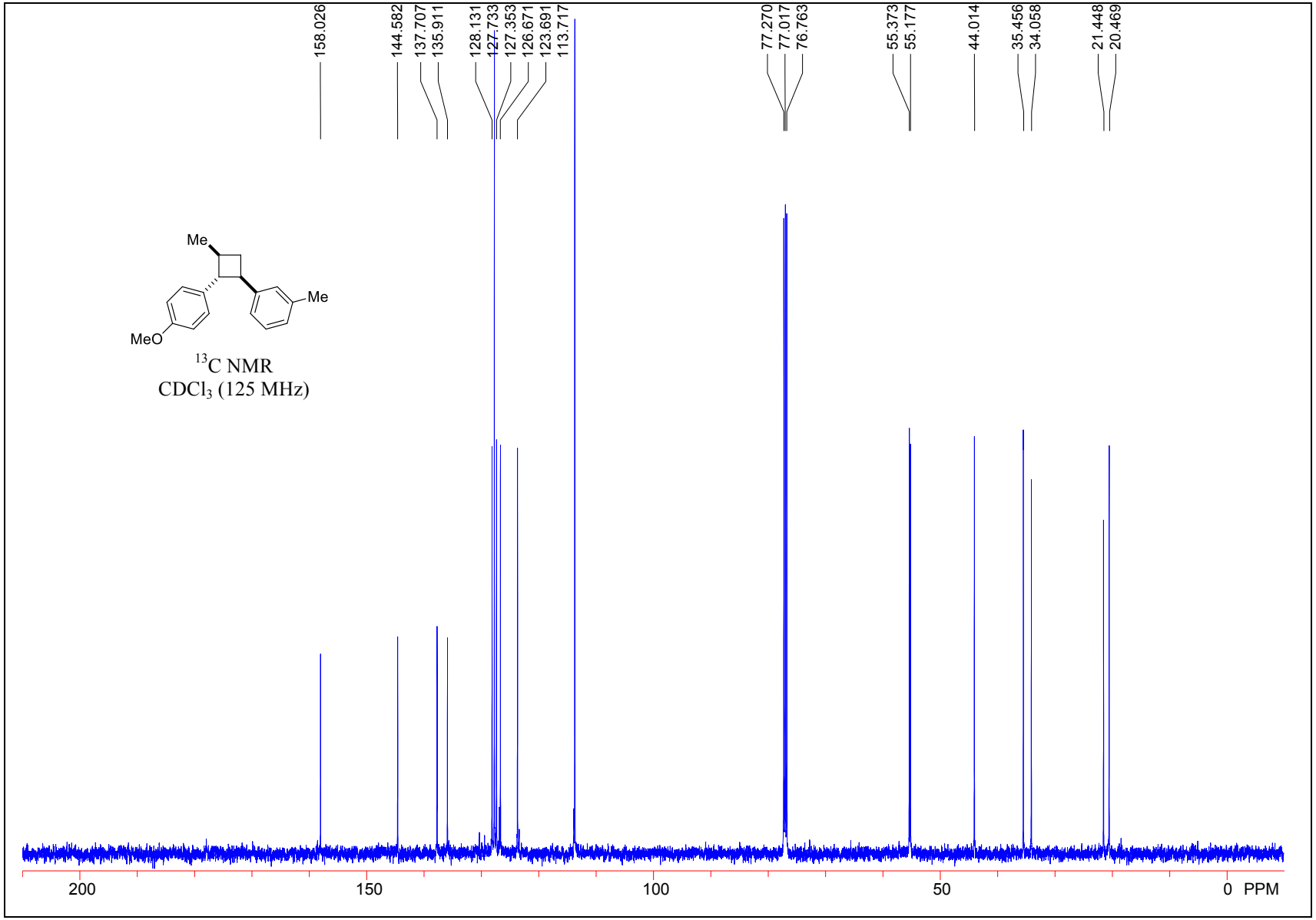
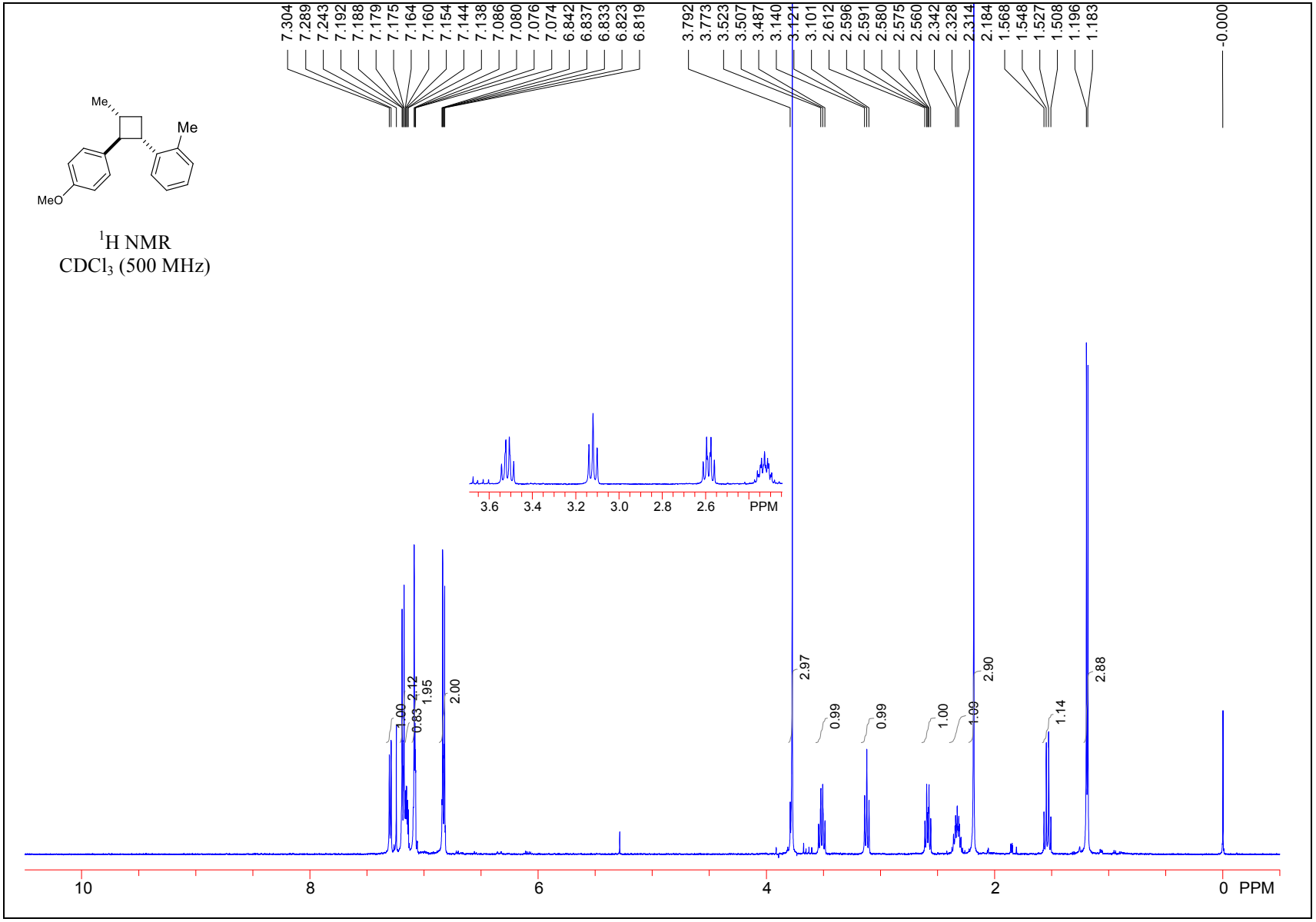
135.905
127.706
113.685
77.264
77.011
76.757
55.206
52.470
43.199
18.859
Me
Me
MeO
OMe
^{13}C NMR
$CDCl_3$ (125 MHz)
200
150
100
50
0 PPM

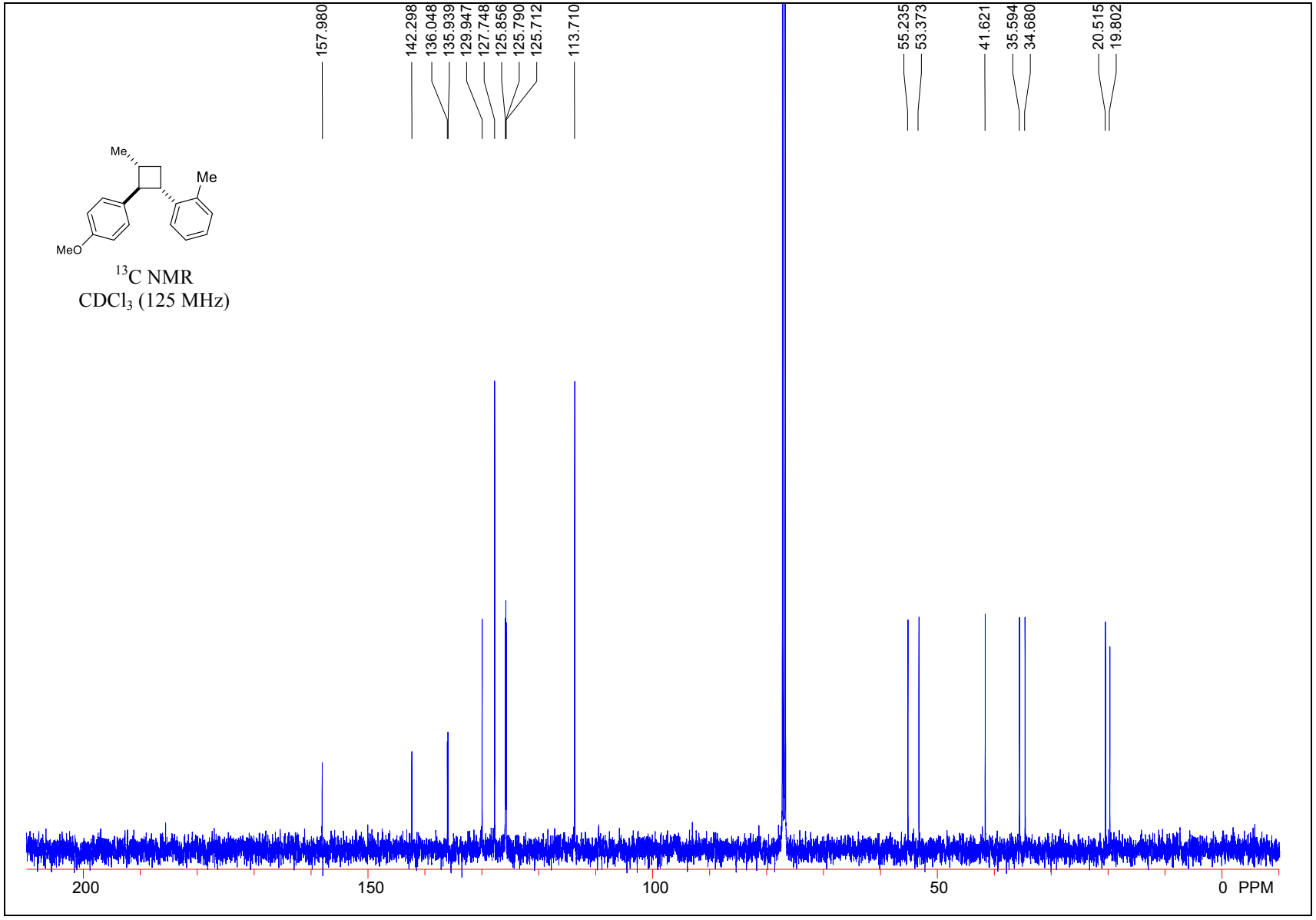


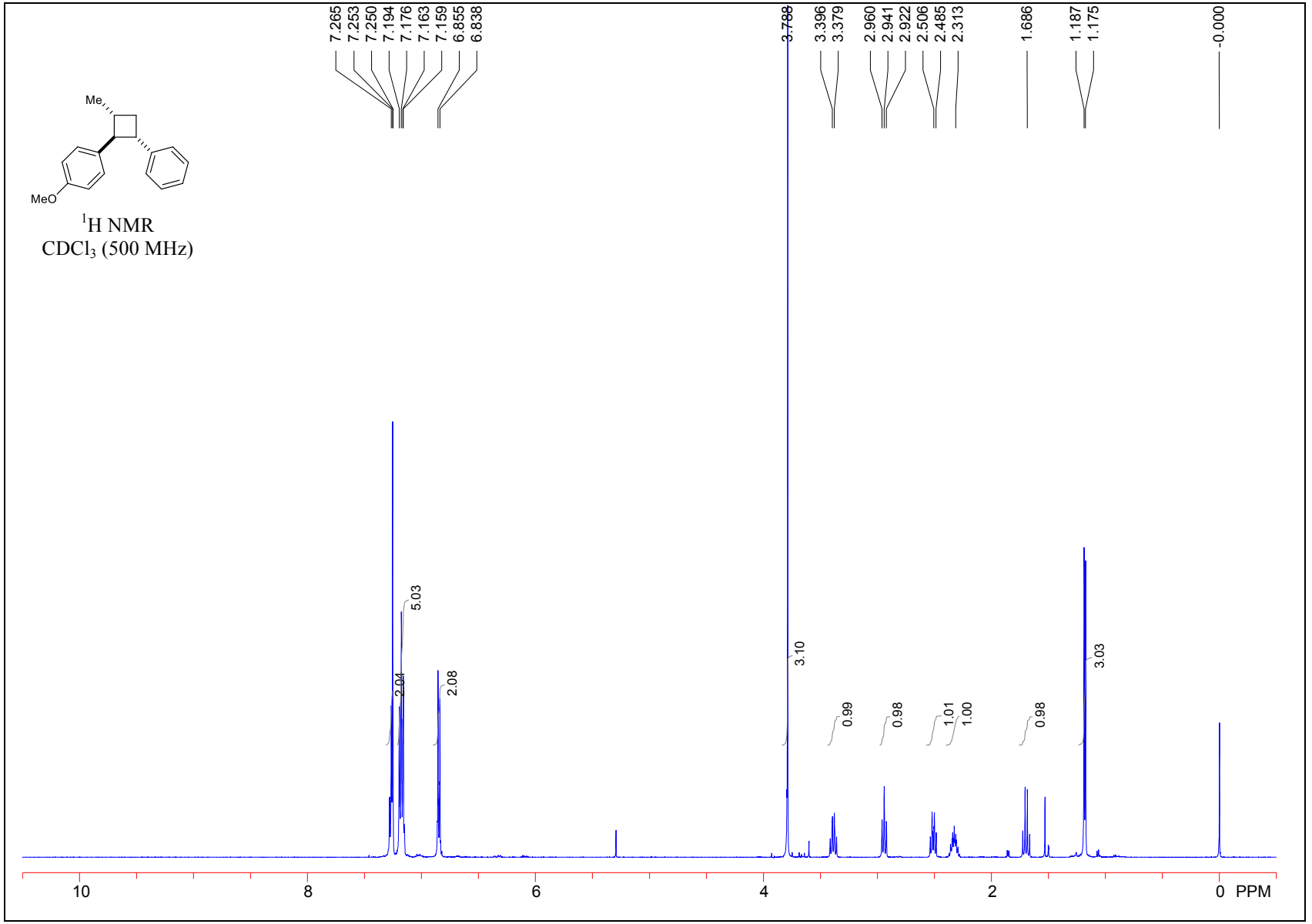


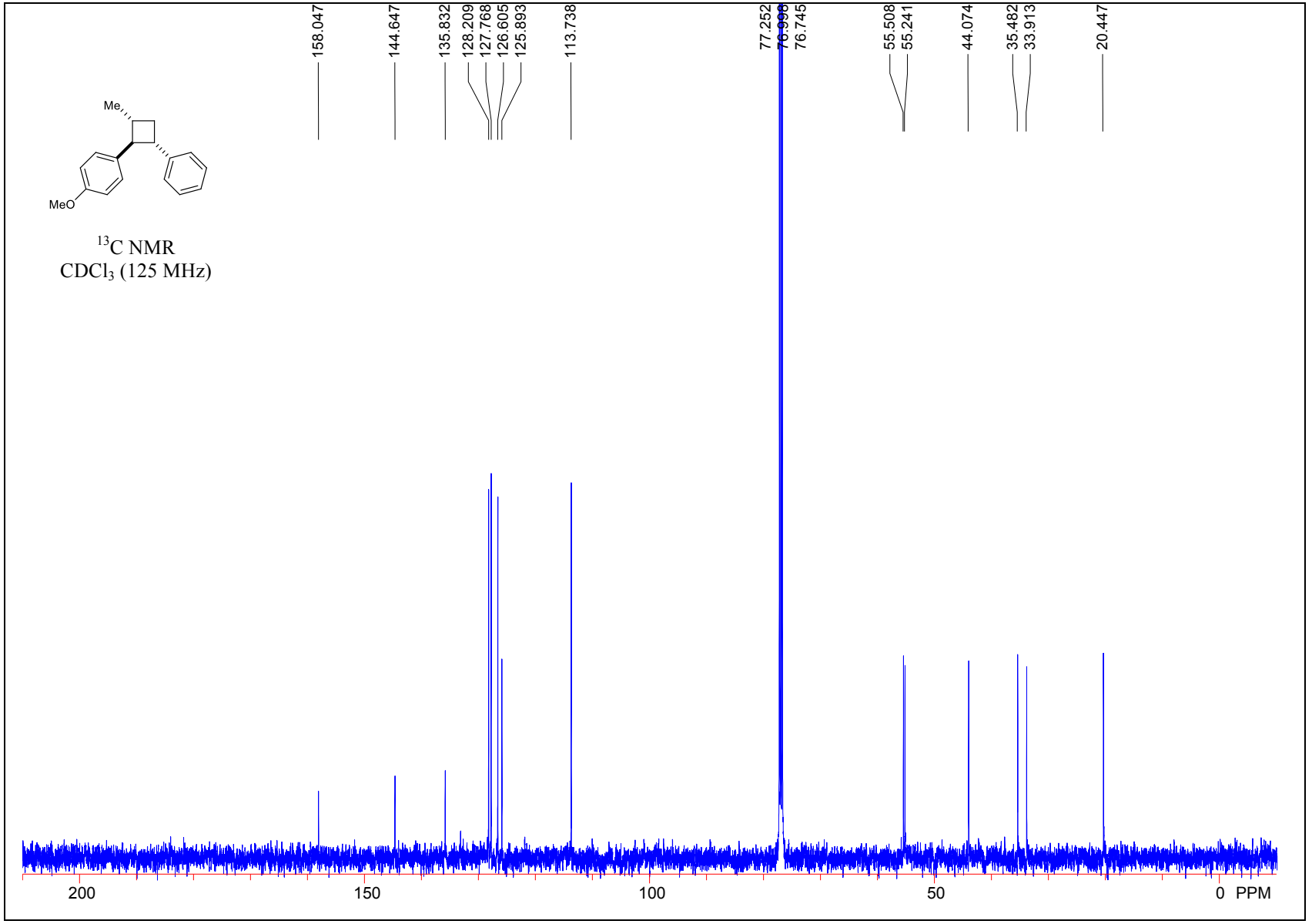




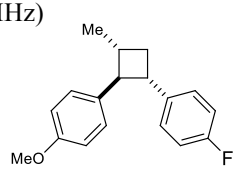

Me
Me
MeO
^{1}H NMR
$CDCl_3$ (500 MHz)
7.304 7.289 7.243 7.192 7.188 7.179 7.175 7.164 7.160 7.154 7.144 7.138 7.086 7.080 7.076 7.074 6.842 6.837 6.833 6.823 6.819
3.792 3.773 3.523 3.507 3.487 3.140 3.121 3.101 2.612 2.596 2.591 2.580 2.575 2.560 2.342 2.328 2.314 2.184 1.568 1.548 1.527 1.508 1.196 1.183
-0.000
1.00 0.83 2.12 1.95 2.00 2.97 0.99 0.99 1.00 1.00 2.90 1.14 2.88
3.6 3.4 3.2 3.0 2.8 2.6 PPM
10 8 6 4 2 0 PPM



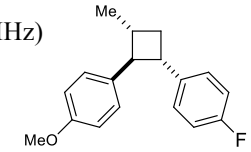


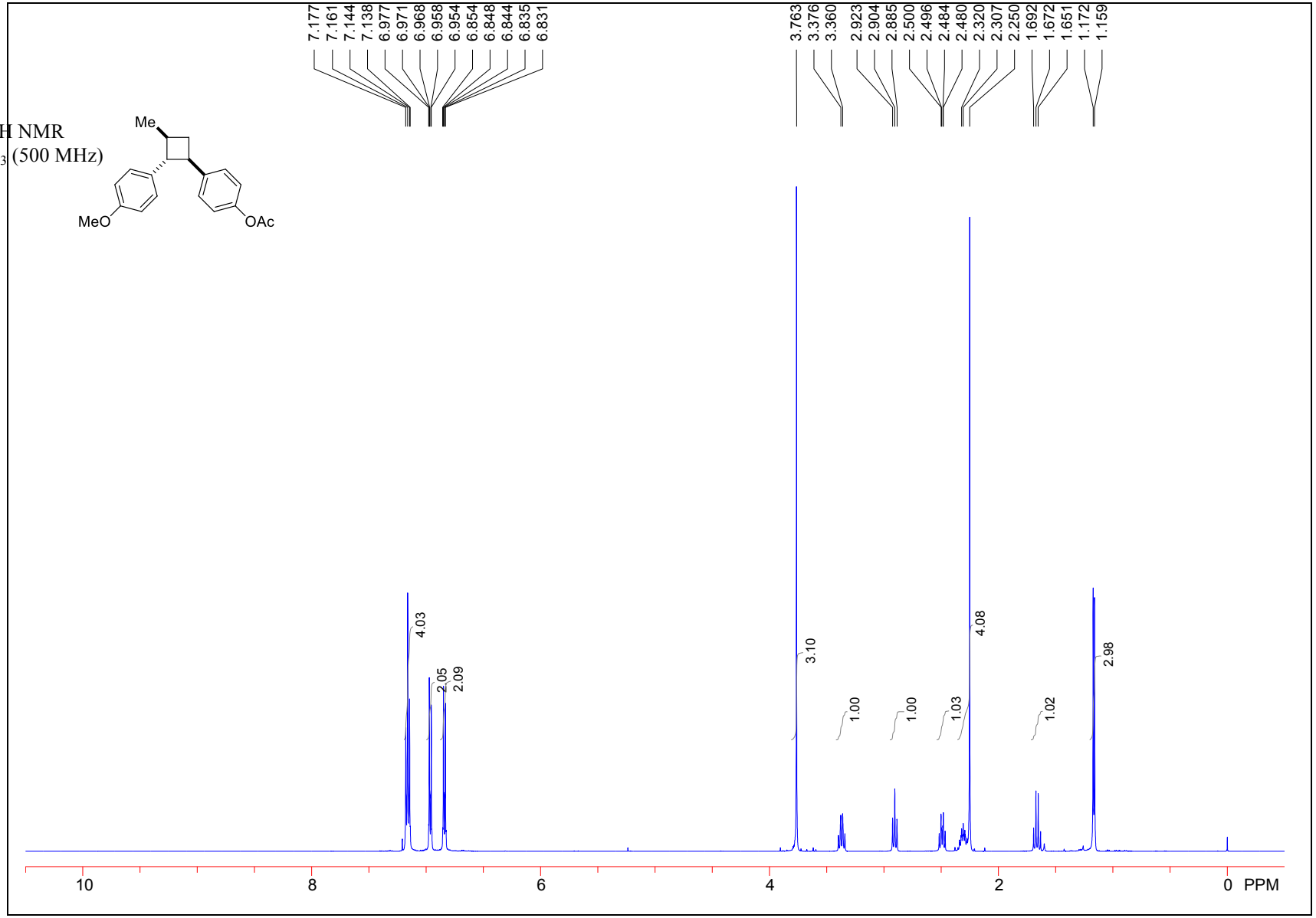


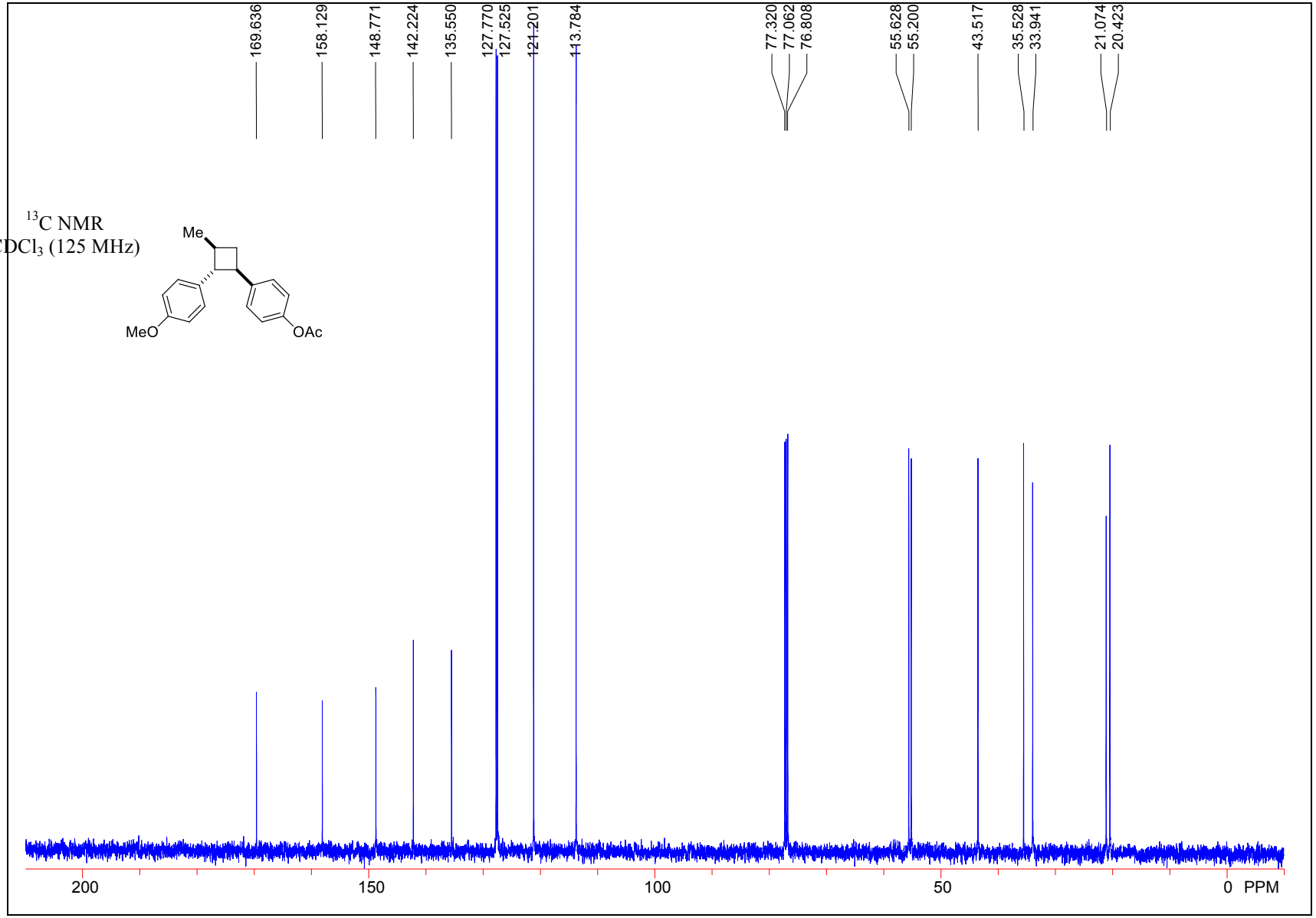
^{1}H NMR
$CDCl_3$ (500 MHz)

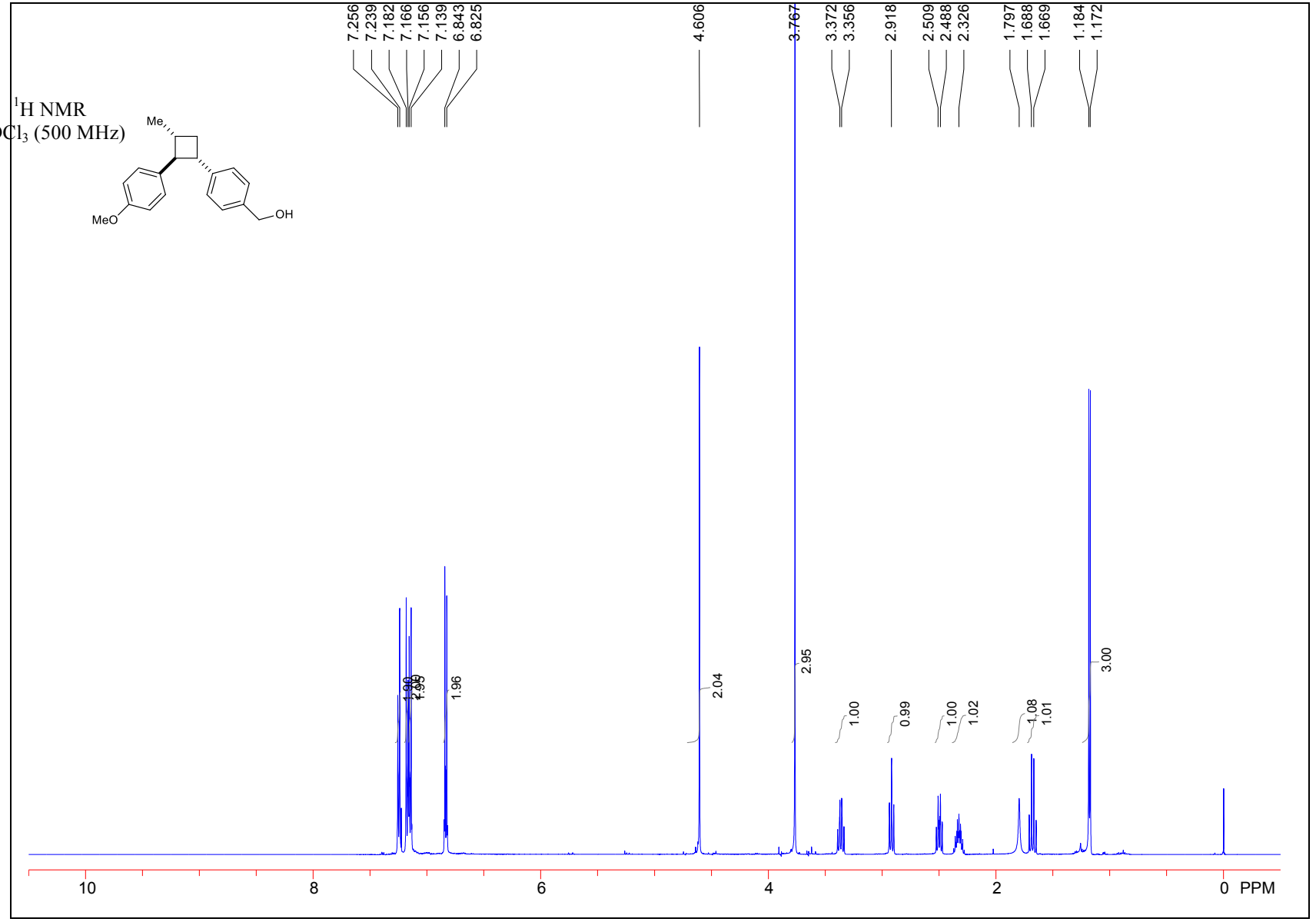


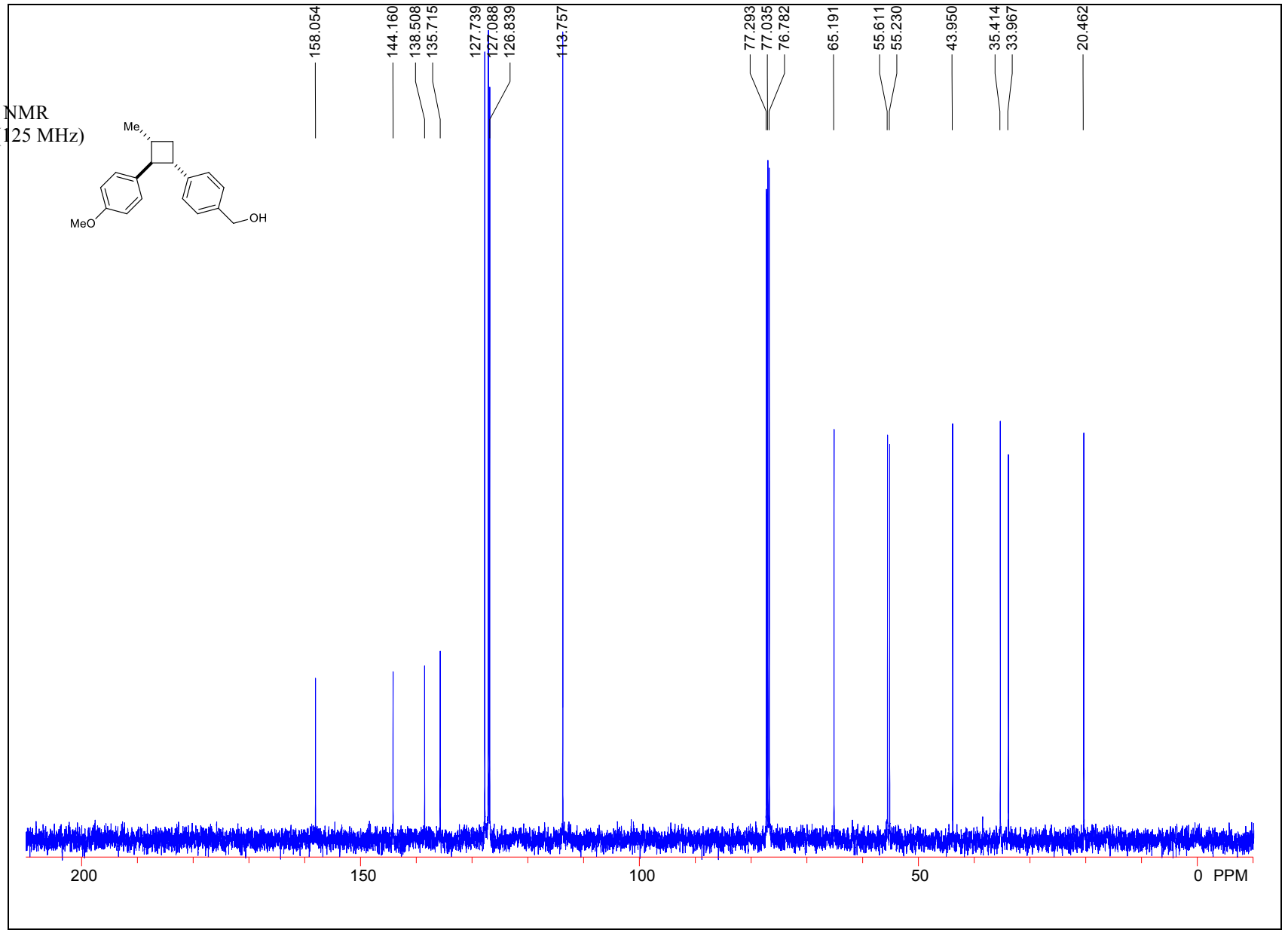
^{13}C NMR
$CDCl_3$ (125 MHz)



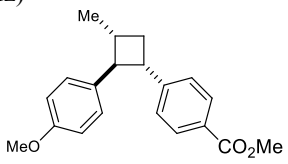




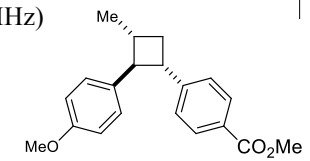



158.054
144.160
138.508
135.715
127.739
127.088
126.839
113.757
77.293
77.035
76.782
65.191
55.611
55.230
43.950
35.414
33.967
20.462
^{13}C NMR
$CDCl_3$ (125 MHz)
Me
MeO
OH
200
150
100
50
0 PPM

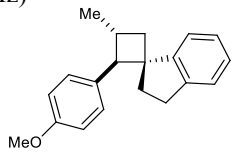
^{1}H NMR
$CDCl_3$ (500 MHz)

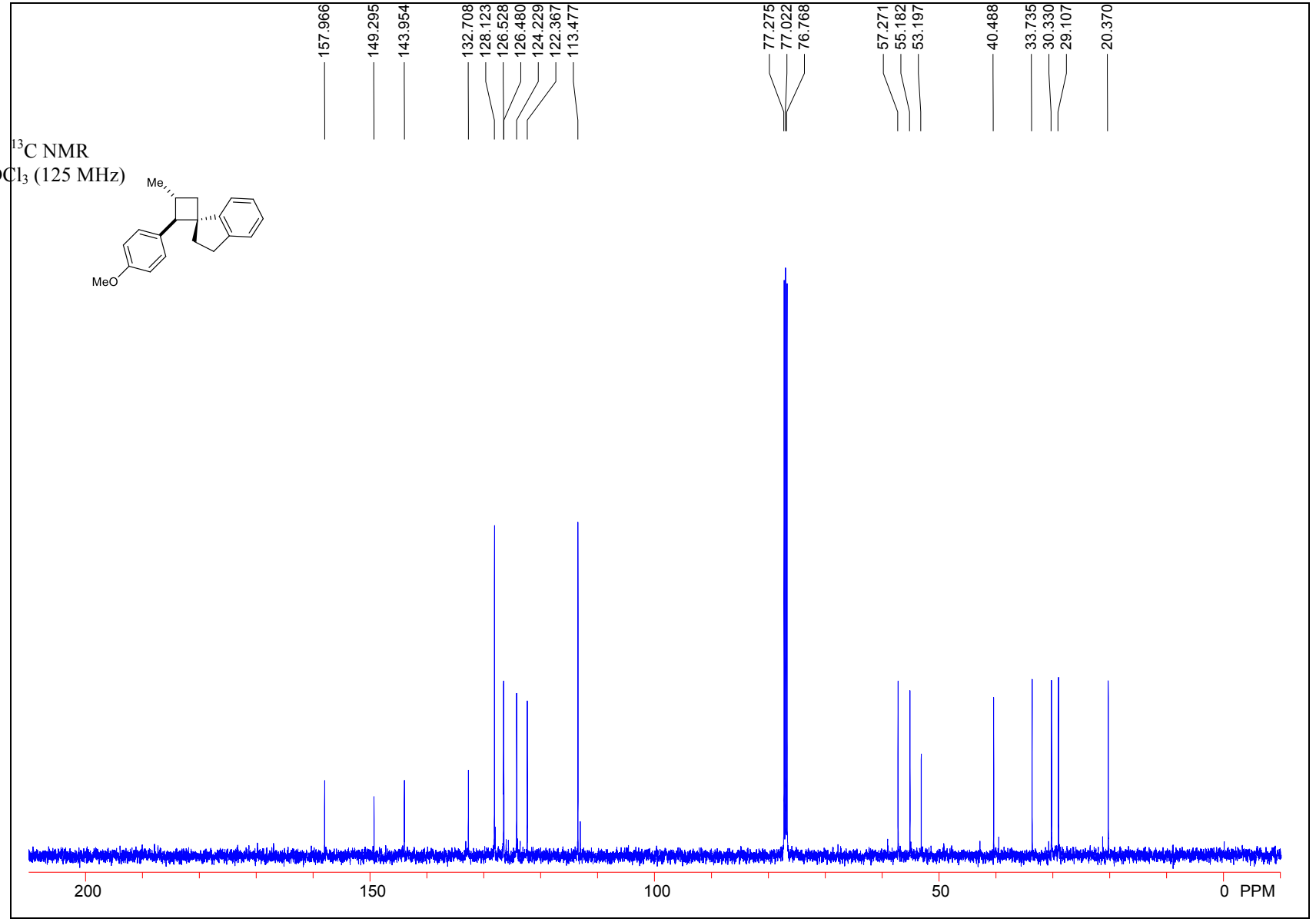


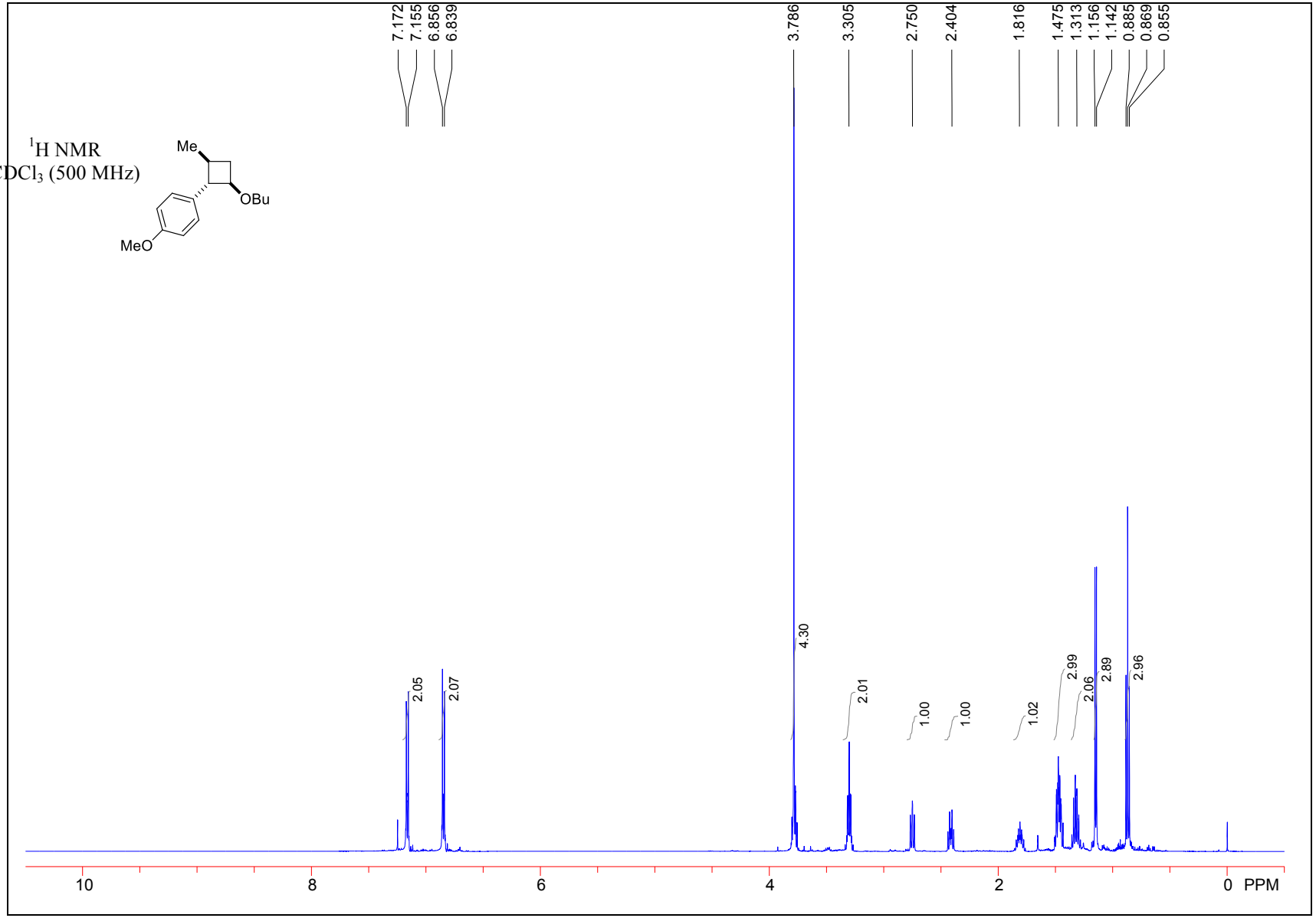
^{13}C NMR
$CDCl_3$ (125 MHz)

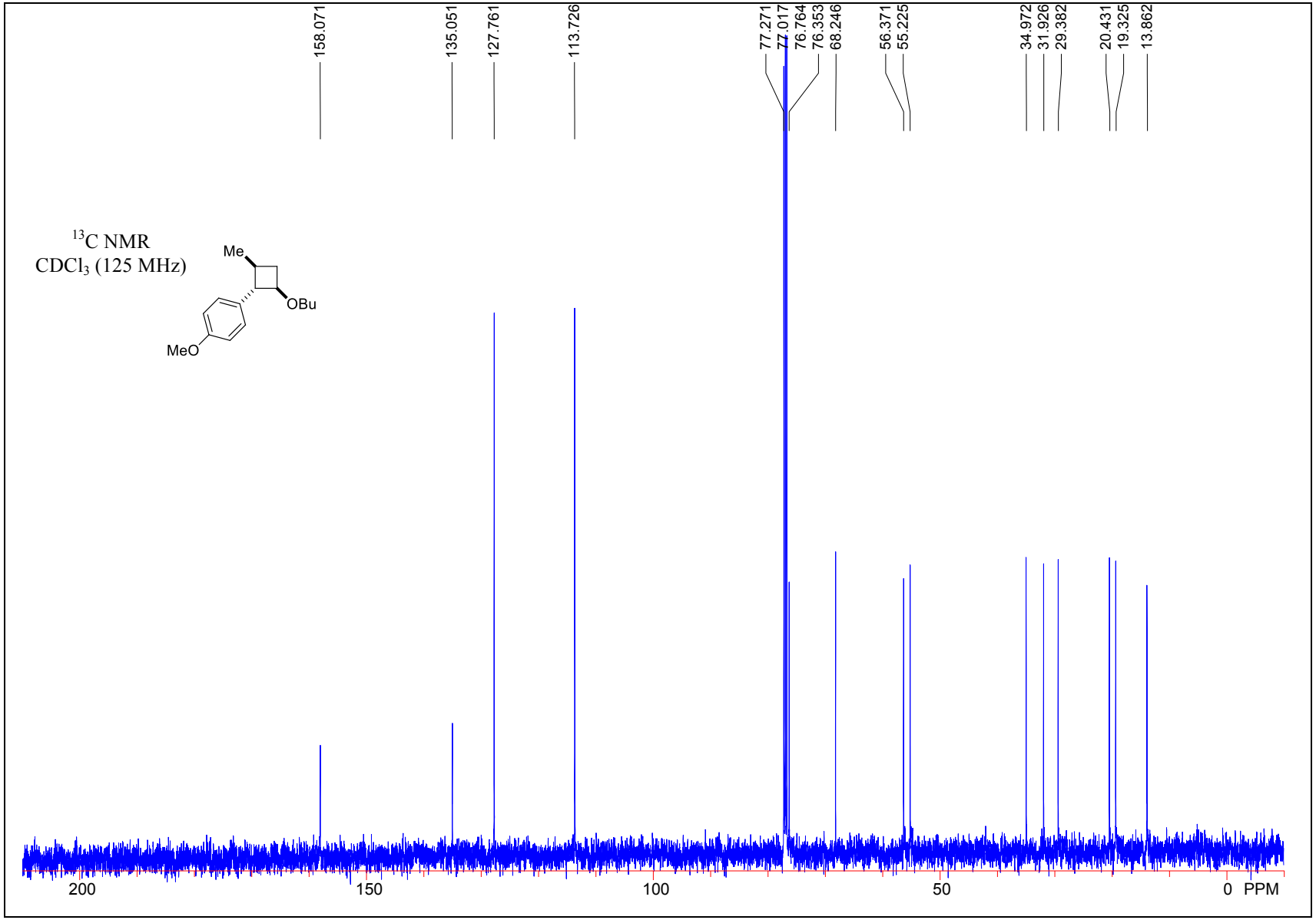


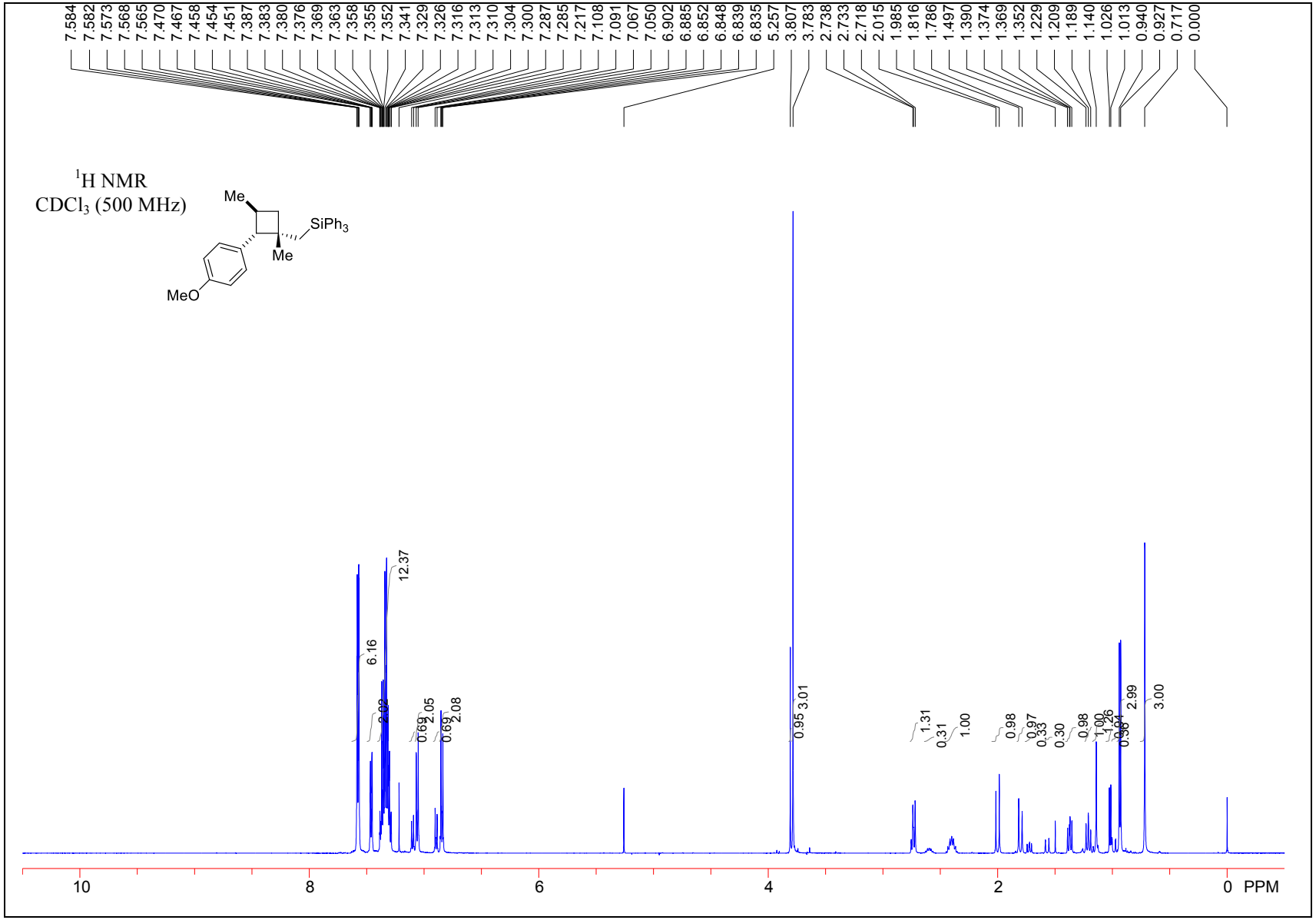
^{1}H NMR
$CDCl_3$ (500 MHz)

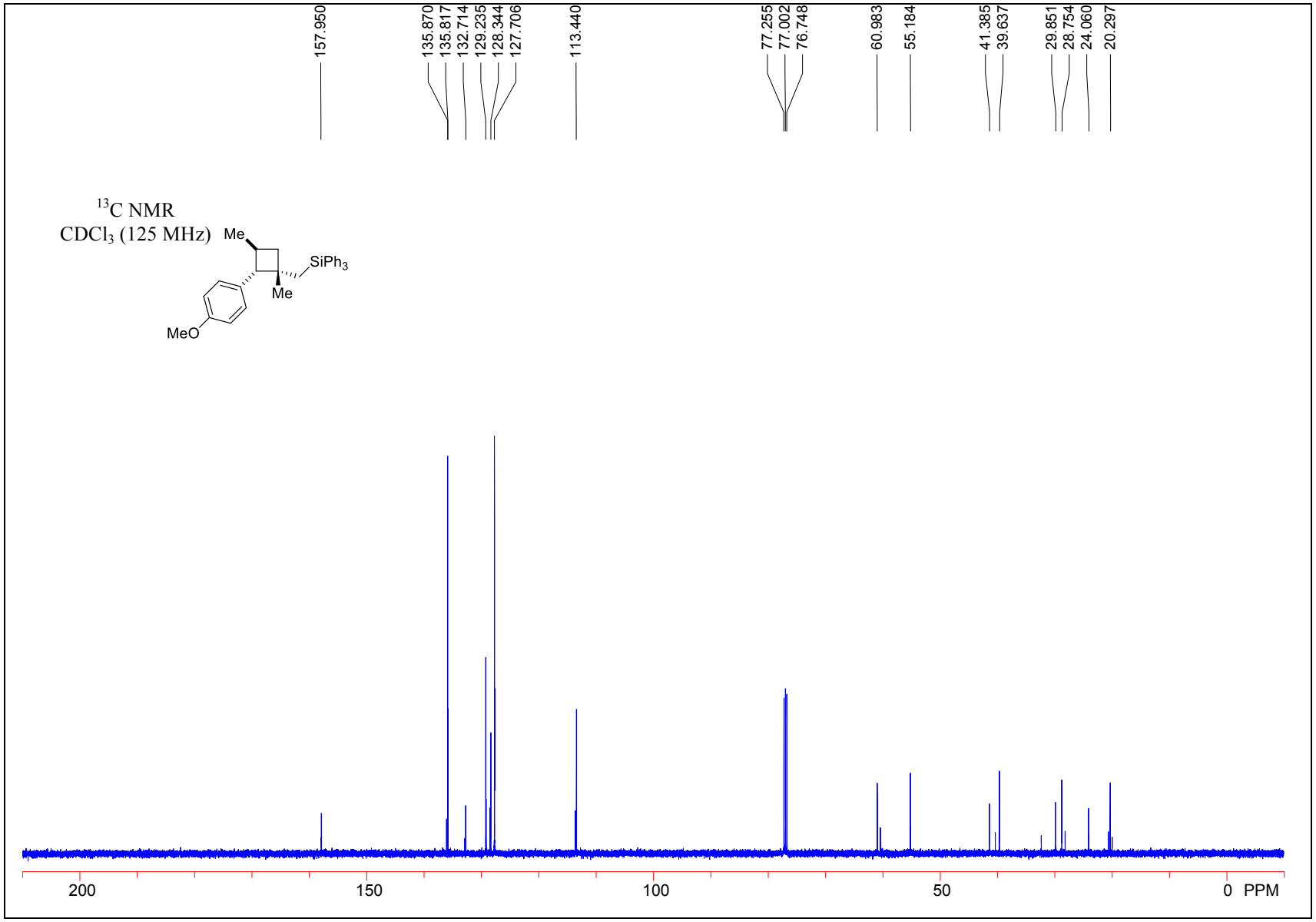


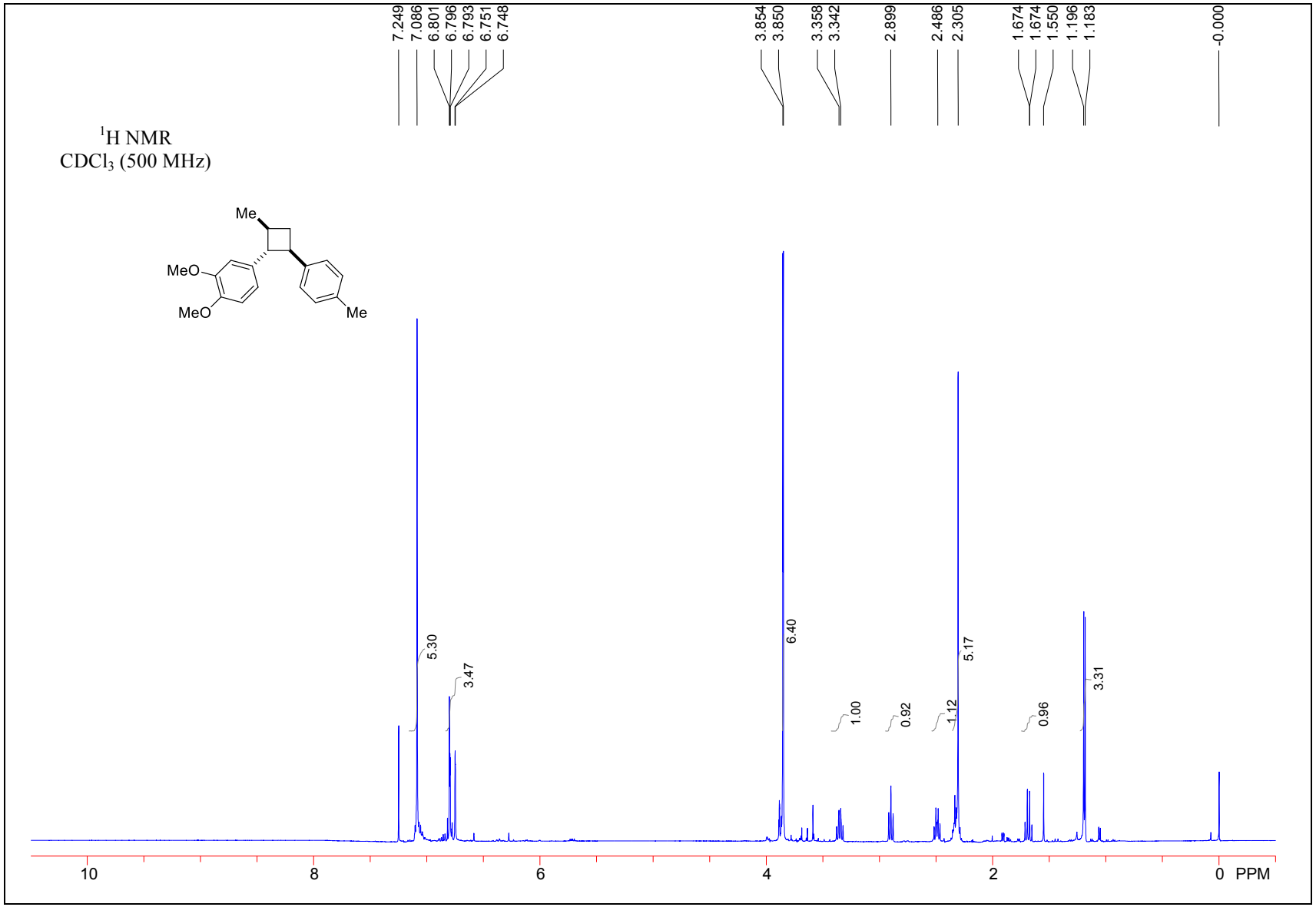


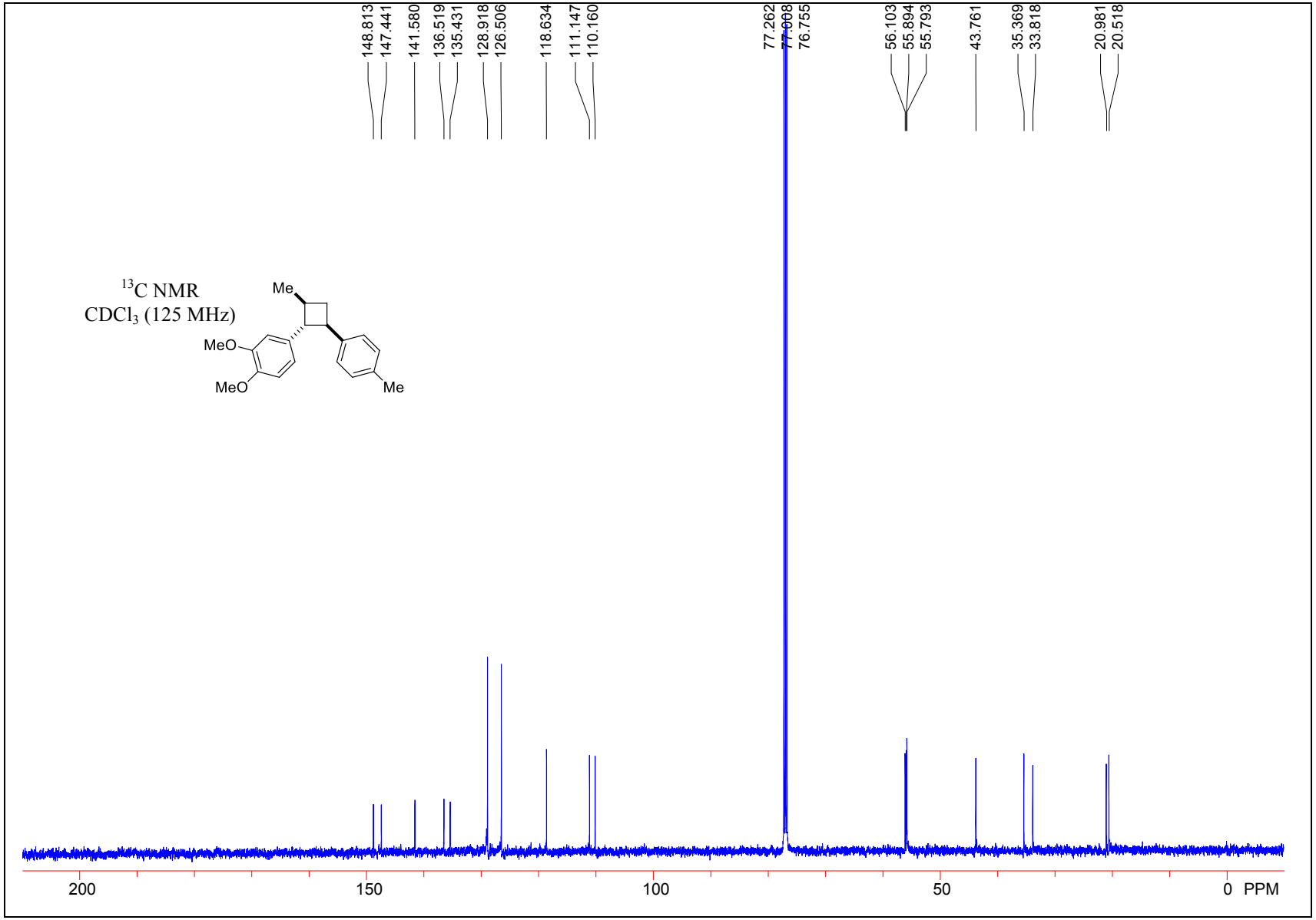


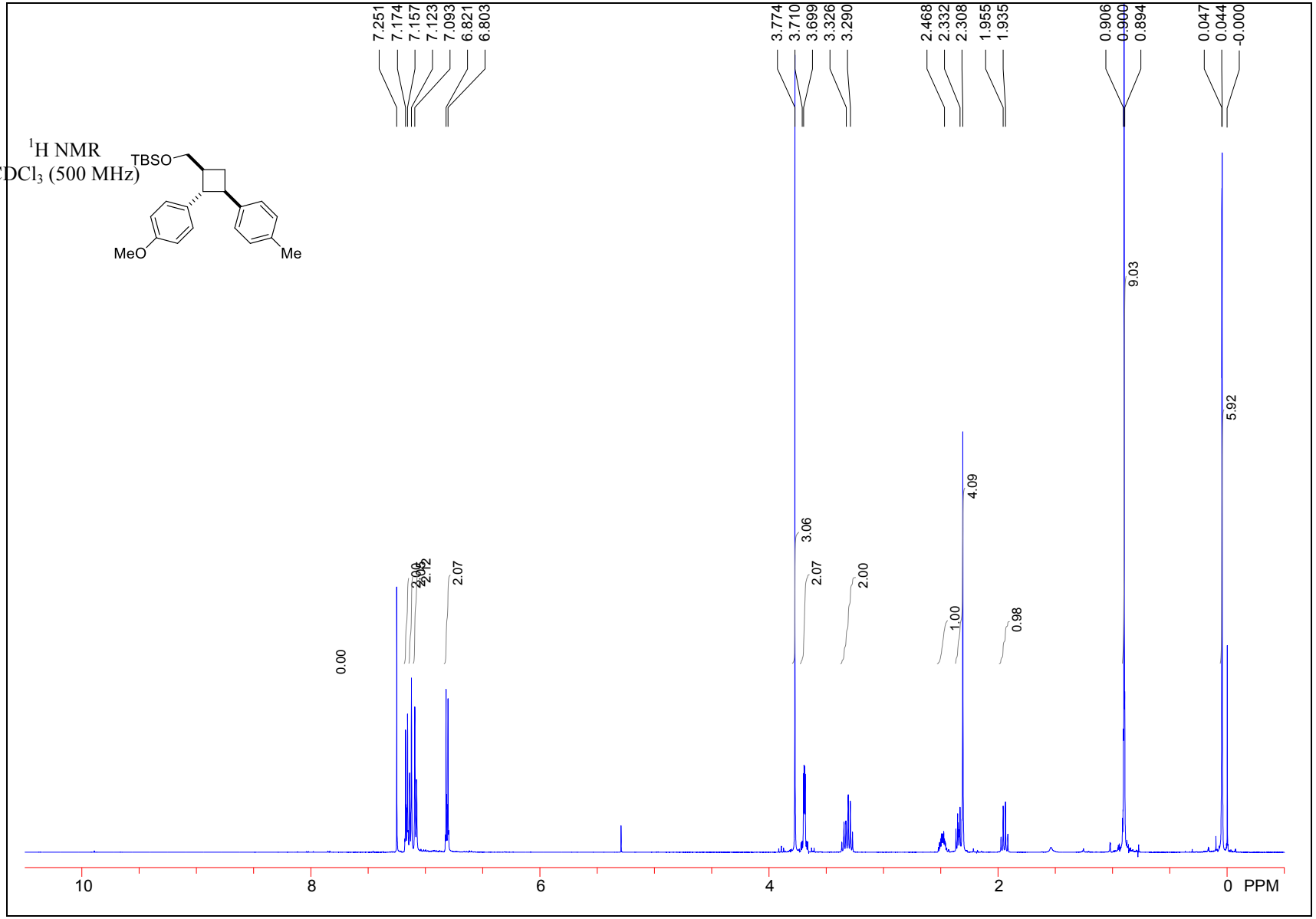


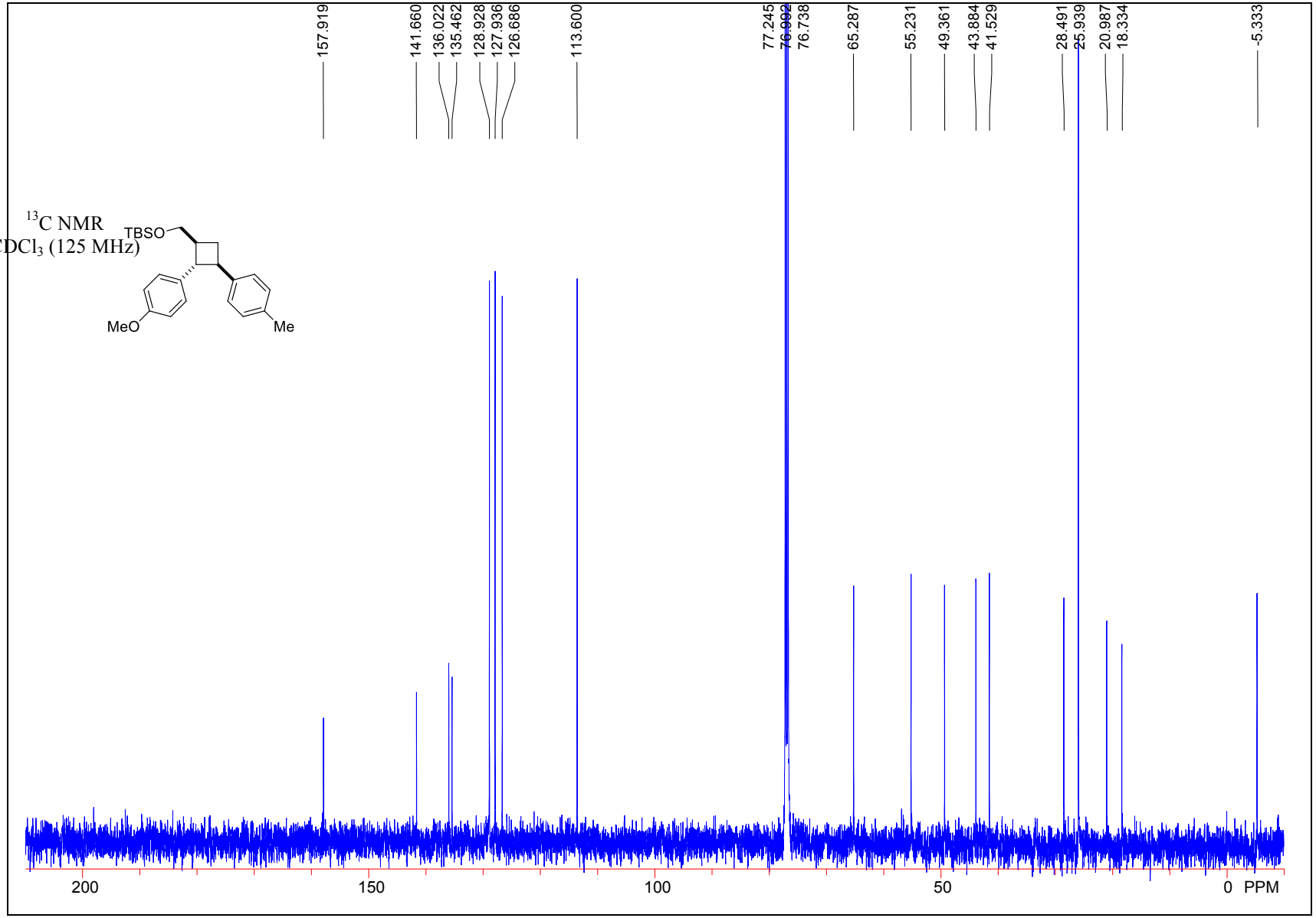




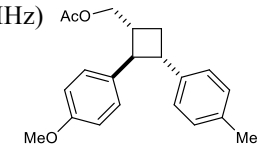

7.249
7.086
6.801
6.796
6.793
6.751
6.748
3.854
3.850
3.358
3.342
2.899
2.486
2.305
1.674
1.674
1.550
1.196
1.183
-0.000
^{1}H NMR
$CDCl_3$ (500 MHz)
Me
MeO
MeO
Me
5.30
3.47
6.40
1.00
0.92
1.12
5.17
0.96
3.31
10
8
6
4
2
0
PPM



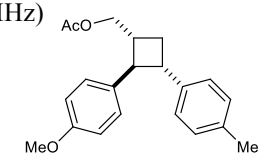




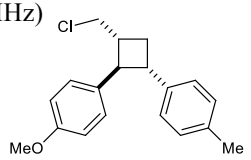
^{1}H NMR
$CDCl_3$ (500 MHz)



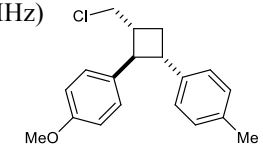
^{13}C NMR
$CDCl_3$ (125 MHz)

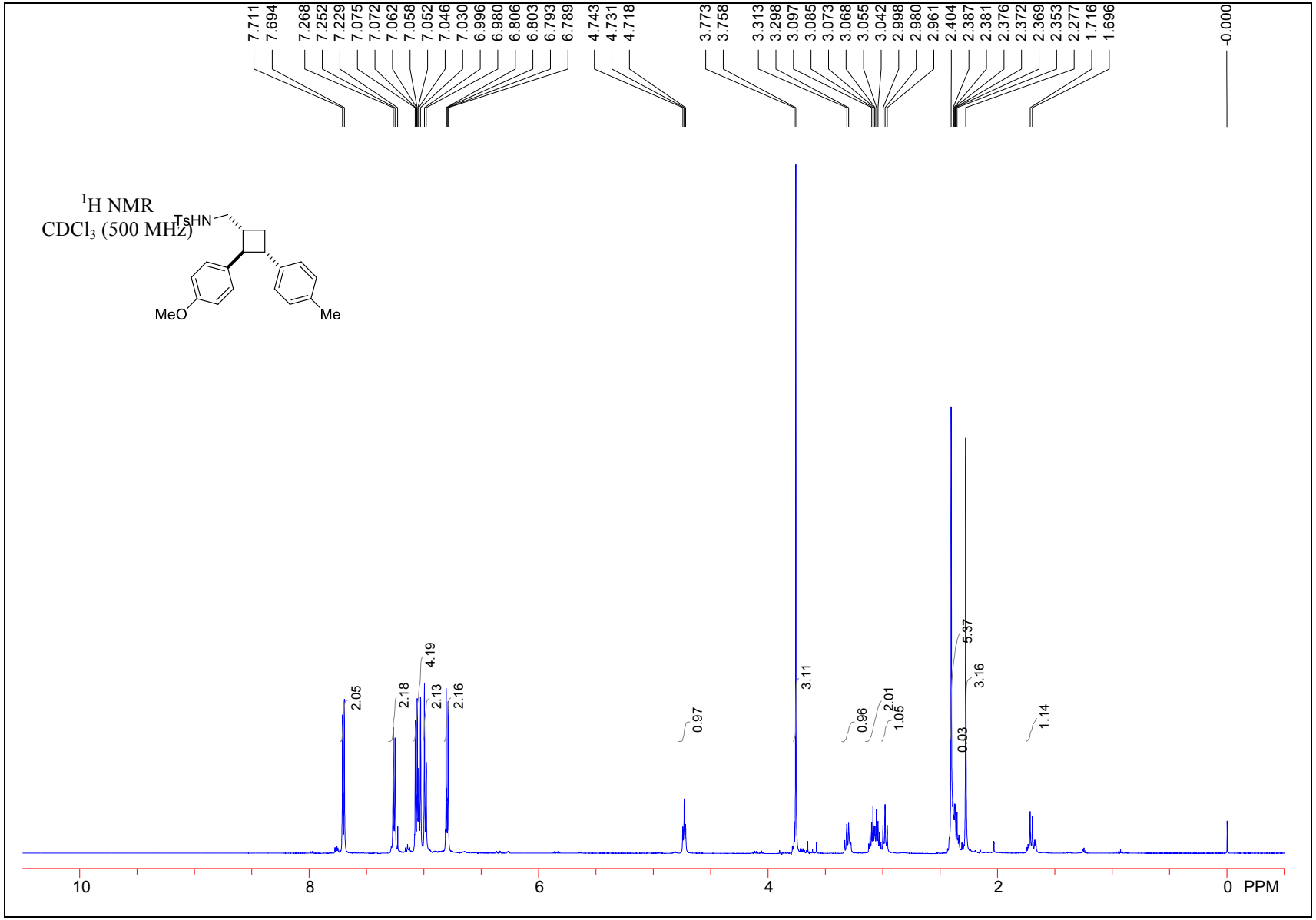


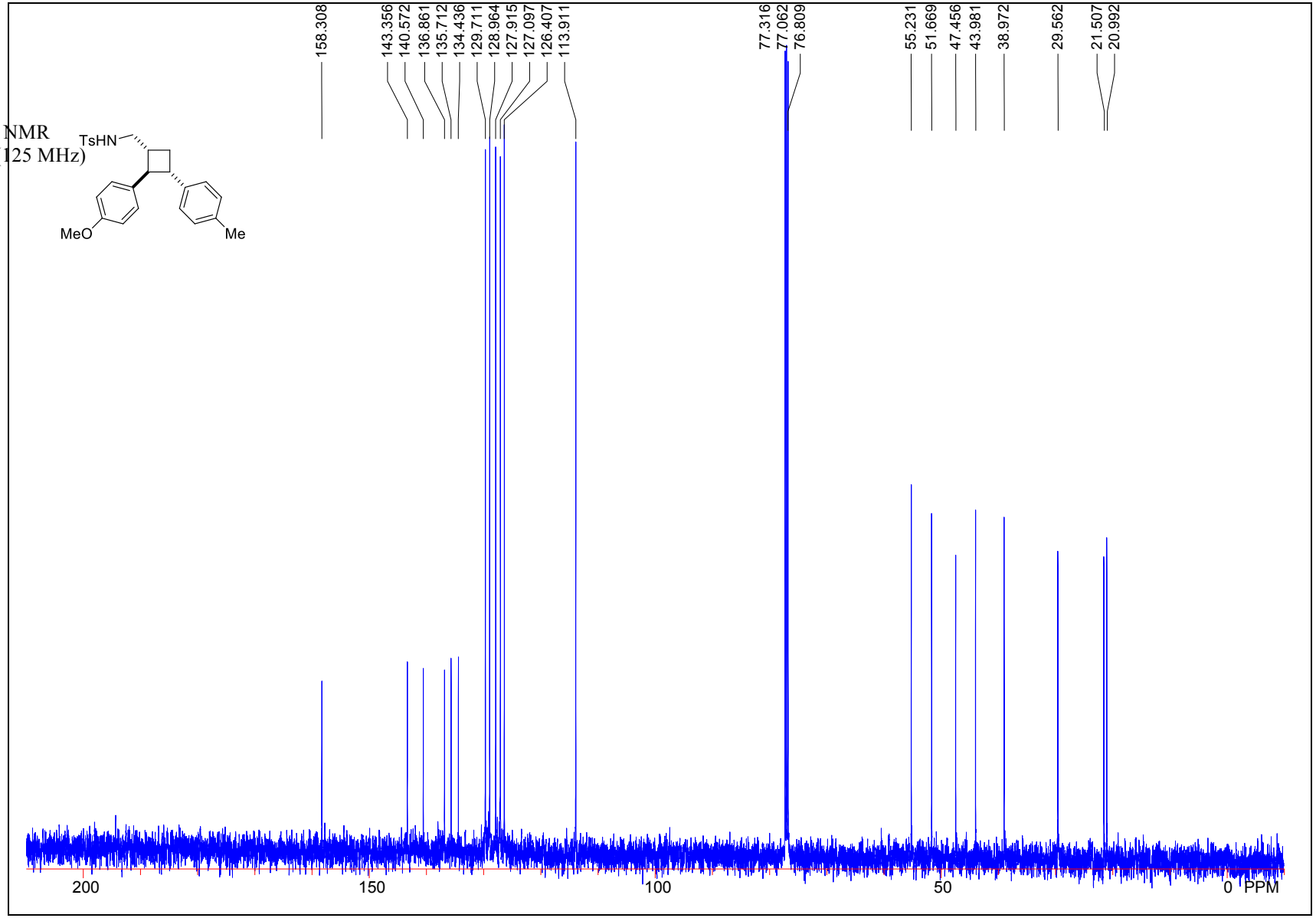
^{1}H NMR
$CDCl_3$ (500 MHz)



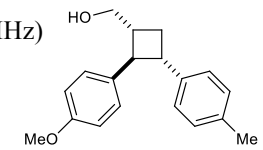
^{13}C NMR
$CDCl_3$ (125 MHz)



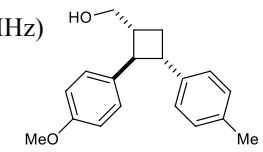

7.711
7.694
7.268
7.252
7.229
7.075
7.072
7.062
7.058
7.052
7.046
7.030
6.996
6.980
6.806
6.803
6.793
6.789
4.743
4.731
4.718
3.773
3.758
3.313
3.298
3.097
3.085
3.073
3.068
3.055
3.042
2.998
2.980
2.961
2.404
2.387
2.381
2.376
2.372
2.369
2.353
2.277
1.716
1.696
-0.000
1H NMR
CDCl3 (500 MHz)
TsHN
MeO
Me
2.05
2.18
4.19
2.13
2.16
0.97
3.11
0.96
2.01
1.05
5.37
3.16
0.03
1.14
10
8
6
4
2
0 PPM

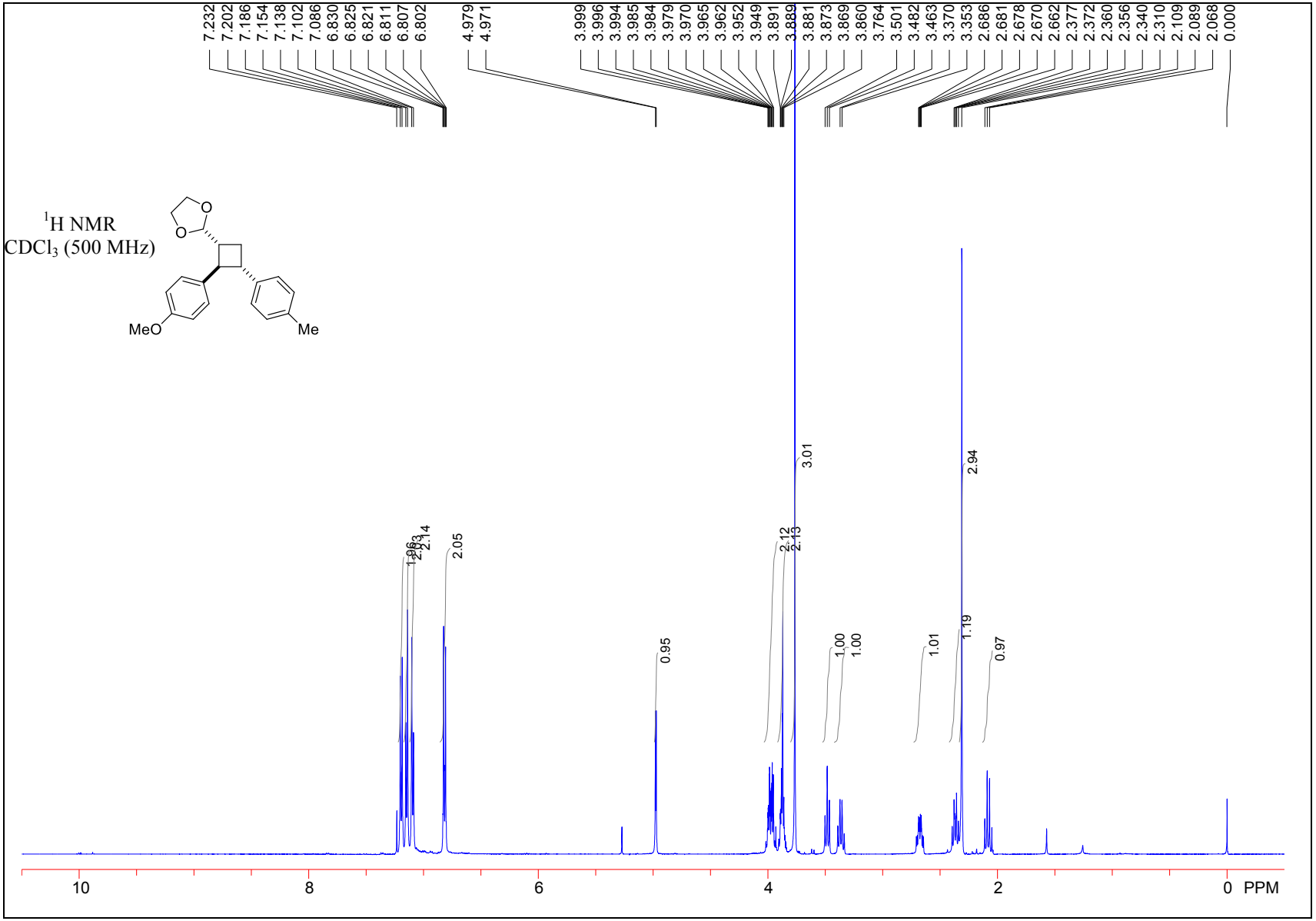


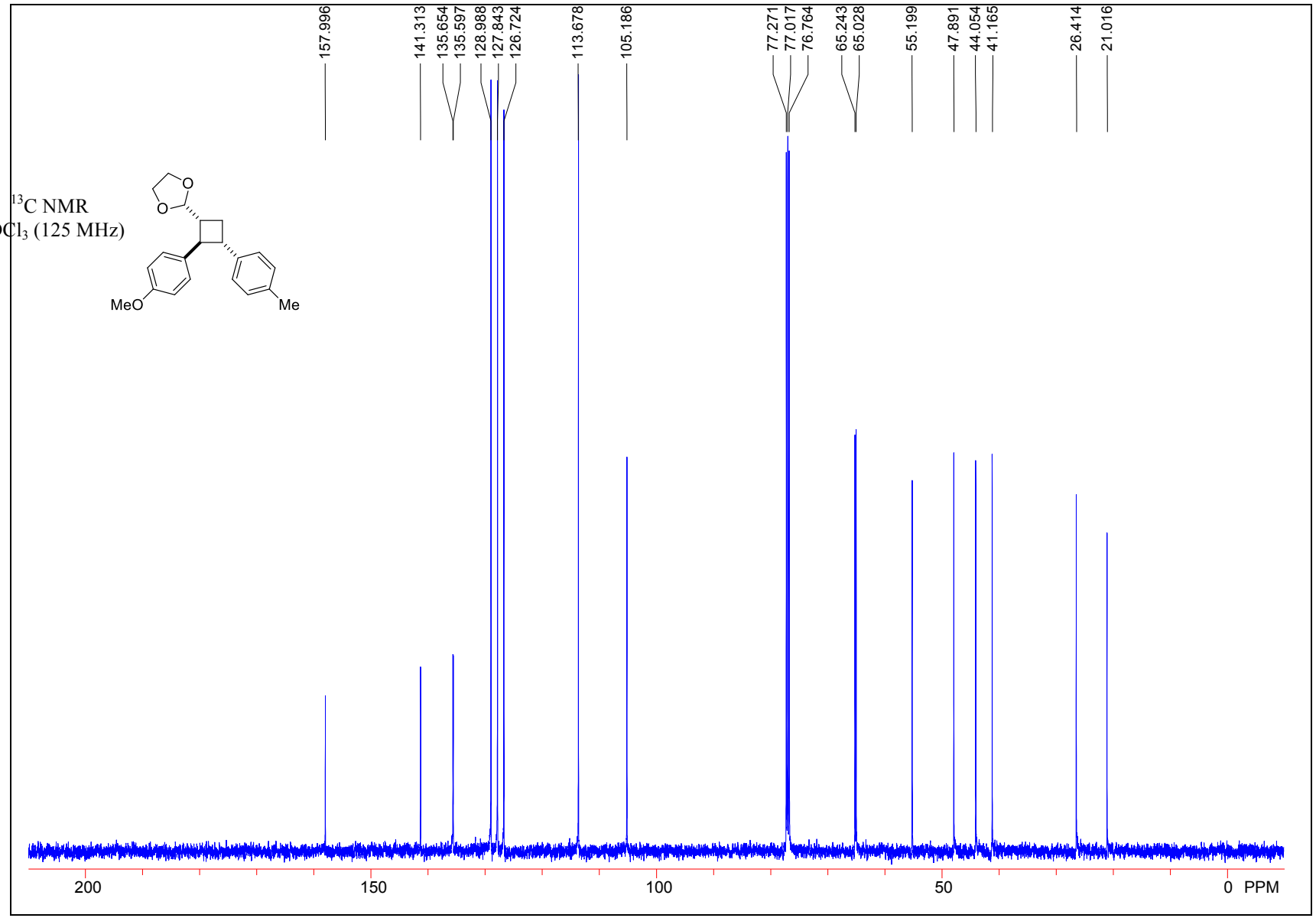
^{1}H NMR
$CDCl_3$ (500 MHz)



^{13}C NMR
$CDCl_3$ (125 MHz)







^{1}H NMR
$CDCl_3$ (500 MHz)