Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

Alkynedicobalt Mediated Vinylogous Nazarov Reactions

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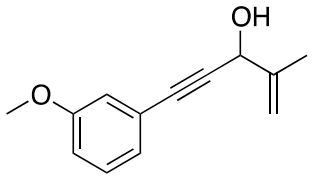
General Considerations. Reagents were obtained from commercial sources otherwise stated. Reactions were conducted under inert atmosphere (N_2) using glassware dried in an oven (110 °C, > 1h). The solvent for each reaction was acquired from a solvent purification system (Innovative Technologies). Flash chromatography was performed according to the method of Still.[1] High-Resolution Mass Spectrometry (HRMS) results were obtained via a Direct Insertion Probe-Electron Ionization method (70 eV), on a GCT Time of Flight (Tof) Mass Spectrometer at the McMaster Regional Centre for Mass Spectrometry, and in the University of Windsor Mass Spectrometry lab with a Tof mass spectrometer using the Atmospheric Solids Analysis Probe (ASAP) and a corona discharge to facilitate ionization. ^{1}H NMR spectra were obtained on 300 or 500 MHz spectrometers. Chemical shifts (δ) are reported in parts per million (ppm), relative to the 7.27 ppm resonance for the residual $CHCl_3$ in $CDCl_3$, unless otherwise indicated. Coupling constants are reported in Hertz (Hz). ^{13}C NMR data were obtained at either 75 or 125 MHz. Infrared spectra (IR) were recorded neat on a FT-IR spectrophotometer using an ATR attachment.

Experimental Procedures for New Compounds

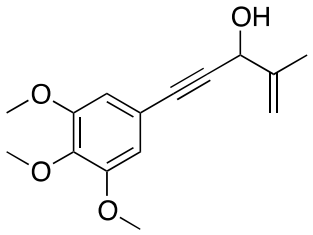
5-(3-Methoxyphenyl)-2-methylpent-1-en-4-yn-3-ol (6a):



General procedure A: In a round bottom flask, 1-ethynyl-3-methoxybenzene (0.2738 g, 2.07 mmol) was dissolved in dry THF (10 mL). The flask was cooled to -78 ^{o}C under N_2, at which point ^{n}BuLi (2.5 M in hexanes, 1.2 mL, 3.1 mmol, 1.5 equiv) was added dropwise at -78 ^{o}C and allowed to stir. After 45 minutes, the reaction mixture was allowed to warm to 0 ^{o}C. At this point was added a solution of **methacrolein** (2.0 equiv, 0.34 mL, 4.1 mmol) dissolved in THF (3 mL) and allowed to stir for 30 minutes. After this time, the reaction mixture was allowed to warm to room temperature and then NH_4Cl (aq., sat.) was added. This was extracted with Et_2O (3 x 100 mL), then dried with $MgSO_4$, filtered, and the solvent removed under reduced pressure.

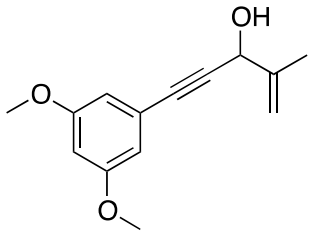
The crude material was obtained and purified by radial chromatography (1:1 hexanes : Et_2O) to yield the product **6a**, as a yellow viscous oil (0.3232 g, 1.60 mmol, 77 % yield); IR ν_{max} 3388 (broad), 3075, 2943, 2837, 2225, 1702, 1655, 1598, 1576 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 (apparent t, J = 7.9 Hz, 1H), 7.05 (apparent dt, J = 7.6, 1.2 Hz, 1H), 6.98 (m, 1H), 6.89 (ddd, J = 8.4, 2.7, 0.9 Hz, 1H), 5.26 (s, 1H), 5.03 (s, 1H), 4.99 (s, 1H), 3.80 (s, 3H), 2.19 (br s, 1H), 1.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 159.3, 144.0, 129.4, 124.3, 123.5, 116.6, 115.2, 112.6, 87.9, 85.8, 66.7, 55.3, 18.2; **HRMS** *m/e* for $C_{13}H_{14}O_2$ [$M\text{-}H^+$] calculated 201.0916, found 201.0915.

2-Methyl-5-(3,4,5-trimethoxyphenyl)pent-1-en-4-yn-3-ol (6b):



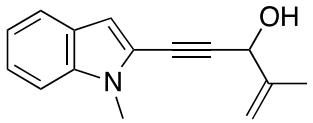
Compound **6b** was prepared according to **General Procedure A**, using 5-ethynyl-1,2,3-trimethoxybenzene as starting material (0.7147 g, 3.718 mmol) and **methacrolein** (2 equiv, 0.52 g, 0.62 mL, 7.4 mmol). Compound **6b** was isolated following column chromatography (2:1 hexane : Et_2O) as a colourless solid (0.794 g, 3.031 mmol, 56 % yield), m.p. 103-106 ^oC; IR ν_{max} 3434 (broad), 3010, 2971, 2945, 2876, 2842, 1577, 1501 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.67 (s, 2H), 5.24 (s, 1H), 5.01 (d, J = 5.4 Hz, 1H), 4.98 (s, 1H), 3.84 (s, 3H), 3.83 (s, 6H), 2.26 (br s, 1H), 1.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 152.9, 143.9, 138.8, 117.4, 112.5, 108.8, 87.0, 85.7, 66.6, 60.9, 56.1, 18.2; **HRMS** *m/e* for $C_{15}H_{18}O_4$ [M^+] calculated 262.1205, found 262.1207.

5-(3,5-Dimethoxyphenyl)-2-methylpent-1-en-4-yn-3-ol (6c):



Compound **6c** was prepared according to **General Procedure A**, using of 1-ethynyl-3,5-dimethoxybenzene as starting material (0.2951 g, 1.818 mmol) and **methacrolein** (2 equiv, 0.2500 g, 0.30 mL, 3.600 mmol). Compound **6c** was isolated following column chromatography (1:1 petroleum ether : Et_2O) as a yellow oil (0.2677 g, 1.152 mmol, 64 % yield). IR ν_{max} 3405 (broad), 3083, 2941, 2840, 2225, 1586 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.59 (d, J = 2.4 Hz, 2H), 6.44 (t, J = 2.4 Hz, 1H), 5.24 (d, J = 0.9 Hz, 1H), 5.01 (s, 1H), 4.98 (apparent t, J = 1.5 Hz, 1H), 3.77 (s, 6H), 2.10 (br s, 1H), 1.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 160.2, 143.7, 123.4, 112.4, 109.2, 101.7, 87.3, 85.6, 66.4, 55.1, 17.9; **HRMS(EI)** *m/e* for $C_{14}H_{16}O_3$ [M^+] calculated 232.1099, found 232.1090.

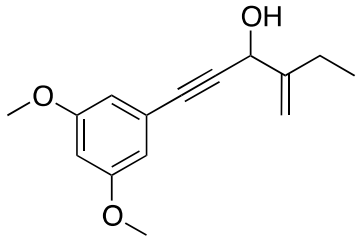
2-Methyl-5-(1-methyl-1*H*-indol-2-yl)pent-1-en-4-yn-3-ol (6d):



General Procedure G: Compound **6d** was prepared using a Sonogashira coupling reaction. In a two nicked round bottom flask, 2-iodo-1-methyl-1*H*-indole (0.5637g, 2.193 mmol) and 5-(trimethylsilyl)pent-1-en-4-yn-3-ol[2] (1.02 equiv, 0.3764 g, 2.443 mmol) were dissolved in degassed THF (3.5 mL). Triethylamine (Et_3N) (10 mL). $Pd(PPh_3)_4$ (0.0800 g, 0.066 mmol, 3 mol%) and CuI (0.0250 g, 0.109 mmol, 5 mol%) were added under N_2. TBAF (1.15 equiv, 2.5 mL) was added dropwise to the reaction flask. The reaction was allowed to stir for 14 hours at room temperature. After this time, the reaction was filtered through Celite®, dissolved in Et_2O (60 mL), and extracted with NH_4Cl (aq., sat., 2 X 60 mL), followed by brine (1 X 60 mL). The organic fraction was dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure. Column chromatography (2:1 hexane : Et_2O) eluted the product **6d** (0.4303 g, 1.909 mmol, 87 % yield), as a dark yellow solid, m.p. 70-72 ^oC; IR ν_{max} 3360 (broad), 3056, 2974,

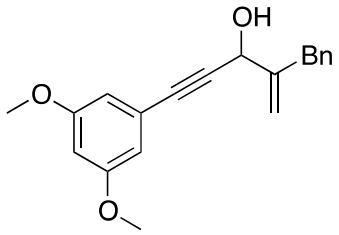
2942, 2918, 2878, 2225, 2061, 2027 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, J = 8.0, 0.7 Hz, 1H), 7.29 (d, J = 4.2 Hz, 2H), 7.14 (m, 1H), 6.80 (s, 1H), 5.31 (s, 1H), 5.13 (d, J = 5.8 Hz, 1H), 5.05 (s, 1H), 3.81 (s, 3H), 2.19 (m, 1H), 1.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 143.6, 137.1, 127.0, 123.1, 121.1, 121.0, 120.1, 112.9, 109.4, 107.8, 94.0, 77.7, 66.9, 30.6, 18.2; **HRMS** *m/e* for $C_{15}H_{15}NO$ $[M+H^+]$ calculated 226.1232, found 226.1232.

1-(3,5-Dimethoxyphenyl)-4-methylenehex-1-yn-3-ol (6e):



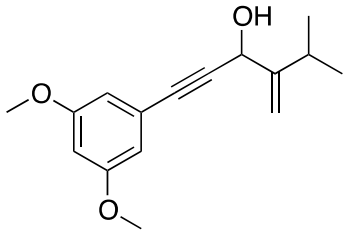
Following **General Procedure A,** 1-ethynyl-3,5-dimethoxybenzene (0.1217 g, 0.750 mmol) was used with **2-methylenebutanal** (2 equiv, 0.15 mL, 1.5 mmol). Compound **6e** was isolated following preparative chromatography (2:1 hexane : Et_2O) as a colourless viscous oil (0.0886 g, 0.360 mmol, 48 % yield). IR ν_{max} 3413, 2963, 2937, 2876, 2840, 1589 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.59 (d, J = 2.3 Hz, 2H), 6.44 (t, J = 2.3 Hz, 1H), 5.33 (apparent t, J = 1.2 Hz, 1H), 5.05 (s, 1H), 5.00 (s, 1H), 3.77 (s, 6H), 2.30 (q, J = 7.5 Hz, 2H), 1.98 (br s, 1H), 1.15 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 160.5, 149.7, 123.8, 110.4, 109.5, 101.9, 87.8, 85.8, 66.2, 55.4, 24.5, 12.2; **HRMS** *m/e* for $C_{15}H_{18}O_3$ $[M-H^+]$ calculated 245.1178, found 245.1175.

2-Benzyl-5-(3,5-dimethoxyphenyl)pent-1-en-4-yn-3-ol (6f):



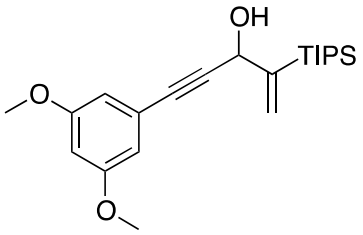
Following **General Procedure A:** 1-ethynyl-3,5-dimethoxybenzene (0.1087 g, 0.670 mmol) was used with **2-benzylacrylaldehyde** (2 equiv, 0.1958 g, 1.340 mmol). Compund **6f** was isolated following column chromatography (3:1 Hexane : Et_2O) as a viscous yellow oil (0.1590 g, 0.515 mmol, 77 % yield). IR ν_{max} 3372 (broad), 2924, 2842, 1587, 1452 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.18-7.36 (m, 5H), 6.59 (d, J = 2.4 Hz, 2H), 6.46 (t, J = 2.4 Hz, 1H), 5.46 (s, 1H), 5.00 (br s, 1H), 4.95 (s, 1H), 3.78 (s, 6H), 3.62 (s, 2H), 2.15 (d, J = 5.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 160.4, 147.4, 138.8, 129.2, 128.4, 126.3, 123.7, 113.7, 109.5, 101.9, 87.5, 86.3, 65.2, 55.4, 38.8; **HRMS** *m/e* for $C_{20}H_{20}O_3$ [M^+] calculated 308.1412, found 308.1417.

1-(3,5-Dimethoxyphenyl)-5-methyl-4-methylenehex-1-yn-3-ol (6g):



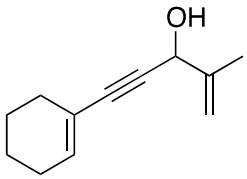
Following **General Procedure A,** 1-ethynyl-3,5-dimethoxybenzene (0.5407 g, 3.333 mmol) was used with **3-methyl-2-methylidenebutanal** (2 equiv, 0.6500 g, 0.80 mL, 6.700 mmol). Compound **6g** was isolated following column chromatography (5:1 petroleum ether : Et_2O) as a yellow viscous oil (0.7118 g, 2.734 mmol, 82 % yield). IR ν_{max} 3436 (broad), 2962, 2873, 2841, 2250, 1588 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.60 (d, J = 2.4 Hz, 2H), 6.45 (t, J = 2.4 Hz, 1H), 5.40 (s, 1H), 5.10 (s, 1H), 5.05 (s, 1H), 3.77 (s, 6H), 2.60 (septet, J = 6.9 Hz, 1H), 2.24 (br, 1H), 1.16 (d, J = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 160.4, 154.6, 123.8, 109.5, 101.8, 88.1, 85.7, 65.3, 55.3, 30.1, 22.6; **HRMS** *m/e* for $C_{16}H_{20}O_3$ [M^+] calculated 260.1412, found 260.1414.

5-(3,5-Dimethoxyphenyl)-2-(triisopropylsilyl)pent-1-en-4-yn-3-ol (6h):



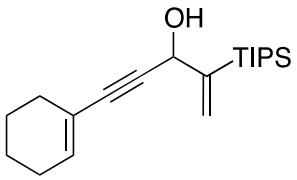
Compound **6g** was prepared according to **General Procedure A**. 1-ethynyl-3,5-dimethoxybenzene as starting material (0.0707 g, 0.692 mmol) was used with **2-(triisopropylsilyl)acrylaldehyde** (2 equiv, 6.516 g, 1.384 mmol). Compound **6h** was isolated following column chromatography (5:1 Hexane : Et_2O) as a yellow oil (0.0553 g, 0.148 mmol, 34 % yield). IR ν_{max} 3420 (broad), 2941, 2864, 1588, 1458, 1419, 1383 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.60 (d, J = 2.4 Hz, 2H), 6.42-6.47 (m, 2H), 5.63 (dd, J = 1.9, 0.7 Hz, 1H), 5.21 (s, 1H), 3.78 (s, 6H), 2.03 (br s, 1H), 1.29 (m, 3H), 1.12 (d, J = 6.9 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) 160.4, 146.5, 129.0, 124.0, 109.4, 101.8, 88.8, 86.4, 65.5, 55.4, 18.8, 11.3; **HRMS** *m/e* for $C_{22}H_{34}O_3Si$ [$M+H^+$] calculated 375.2355, found 375.2344.

5-(Cyclohex-1-en-1-yl)-2-methylpent-1-en-4-yn-3-ol (6i):



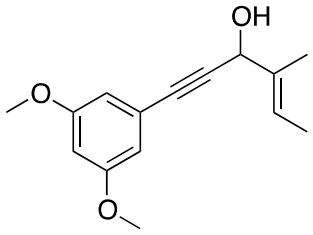
Compound **6i** was prepared according to **General Procedure A**. 1-ethynylcyclohex-1-ene as starting material (0.60 g, 0.66 mL, 5.6 mmol) was used with **methacrolein** (2 equiv, 0.79 g, 0.93 mL, 11 mmol). Compound **6i** was isolated following column chromatography (5:1 Hexane : Et_2O) as a clear to yellowish oil (0.4881 g, 2.769 mmol, 49 % yield). IR ν_{max} 3348 (broad), 3080, 2931, 2863, 2186, 1711, 1647, 1614 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.12 (m, 1H), 5.15 (s, 1H), 4.87-4.93 (m, 2H), 2.03-2.16 (m, 4H), 1.87 (s, 3H), 1.52-1.68 (m, 4H); ^{13}C NMR (300 MHz, $CDCl_3$) 144.3, 135.5, 120.0, 112.1, 111.1, 87.7, 85.3, 66.6, 29.0, 25.6, 22.2, 21.4, 18.0; **HRMS** *m/e* for $C_{12}H_{16}O$ [M^+-H^+] calculated 175.1123, found 175.1126.

5-(Cyclohex-1-en-1-yl)-2-(triisopropylsilyl)pent-1-en-4-yn-3-ol (6j):



Following **General Procedure A:** 1-ethynylcyclohexene (3 equiv, 0.18 mL, 1.5 mmol) was used with **2-triisopropylsilylacrolein** (0.0986 g, 0.464 mmol). Preparative TLC (20:1 hexane : Et_2O) afforded compound **6j** as a colourless viscous liquid (0.0597 g, 0.187 mmol, 40 % yield). IR ν_{max} 3401 (broad), 2930, 2864, 2214, 1698, 1459 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.36 (apparen t, J = 1.5 , 1H), 6.11 (m, 1H), 5.56 (dd, J = 3.5, 1.4 Hz, 1H), 5.09 (s, 1H), 2.05-2.16 (m, 4H), 1.82 (br s, 1H), 1.52-1.70 (m, 4H), 1.19-1.35 (m, 3H), 1.09 (d, J = 6.9 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) 146.8, 135.1, 128.6, 120.2, 88.4, 86.5, 65.5, 29.0, 25.6, 22.2, 21.4, 18.8, 11.2; **HRMS** *m/e* for $C_{20}H_{34}OSi$ [M^+-H^+] calculated 317.2301, found 317.2292.

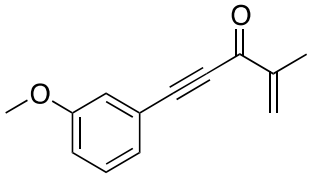
(*E*)-1-(3,5-dimethoxyphenyl)-4-methylhex-4-en-1-yn-3-ol (6k):



Following **General Procedure A:** 1-ethynyl-3,5-dimethoxybenzene (0.1148 g, 0.708 mmol) was used with tiglic aldehyde ((*E*)-2-methylbut-2-enal) (2 equiv, 0.12 g, 0.14 mL, 1.0 mmol). The crude yellow oil was obtained and purified by radial chromatography (5:1 hexanes : Et_2O) to yield **6k**, as a yellow viscous oil (0.1521 g, 0.617 mmol, 87 % yield); IR ν_{max} 3414 (broad), 2959, 2935, 2200, 1690, 1647, 1589, 1454, 1420 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.60 (d, J = 2.3 Hz, 2H), 6.44 (t, J = 2.3 Hz, 1H), 5.77 (m, 1H), 4.97 (s, 1H), 3.77 (s, 6H), 2.32 (br, 1H), 1.82 (s, 3H), 1.68 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 160.6, 135.0,

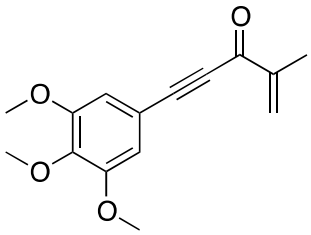
124.0, 123.0, 109.6, 102.0, 88.1, 86.0, 68.7, 55.5, 13.4, 12.2; **HRMS** *m/e* for $C_{15}H_{18}O_3$ [M^+] calculated 246.1256, found 246.1247.

5-(3-Methoxyphenyl)-2-methylpent-1-en-4-yn-3-one (7a):



General procedure B: In a round bottom flask, alkynol **6a** (0.0500 g, 0.247 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL). To this flask, pyridinium dichromate (PDC) powder (1.5 equiv, 0.1391 g, 0.370 mmol) was added in one portion, and the mixture allowed to stir at room temperature. Following stirring for overnight, the solution was filtered through a silica gel plug to remove the excess solid. The filtrate was concentrated under reduced pressure and purified by column chromatography (15:1 hexane : Et_2O) to obtain the dienynone, **7a** (0.0426 g, 0.212 mmol, 86 % yield), as a yellow oil; IR ν_{max} 3073, 2926, 2839, 2196, 1637, 1598, 1576 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.29 (apparent t, J = 7.7 Hz, 1H), 7.19 (dt, J = 7.6, 2.5 Hz, 1H), 7.11 (m, 1H), 7.00 (ddd, J = 8.3, 2.5, 1.8 Hz, 1H), 6.56 (s, 1H), 6.10 (s, 1H), 3.83 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (75 MHZ, $CDCl_3$) 180.1, 159.4, 145.3, 130.8, 129.7, 125.4, 121.2, 117.3, 91.3, 85.7, 55.4, 16.2; **HRMS** *m/e* for $C_{13}H_{12}O_2$ [$M+H^+$] calculated 201.0916, found 201.0915.

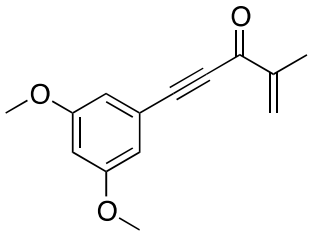
2-Methyl-5-(3,4,5-trimethoxyphenyl)pent-1-en-4-yn-3-one (7b):



Compound **7b** was prepared according to **General Procedure B,** using compound **6b** as starting material (0.1531 g, 0.583 mmol) with PDC powder (1.5 equiv, 0.3289 g, 0.874 mmol).

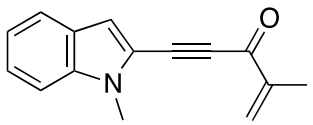
Compound **7b** was isolated following column chromatography (1:1 petroleum ether : Et_2O) as a yellow solid (0.1289 g, 0.495 mmol, 85 % yield), m.p. 99-101 ^oC; IR ν_{max} 3002, 2934, 2837, 2195, 1639, 1623, 1573, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.81 (s, 2H), 6.51 (d, J = 0.9 Hz, 1H), 6.06 (d, J = 0.9 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 6H), 1.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 180.2, 153.3, 145.3, 140.9, 130.8, 115.0, 110.3, 91.9, 85.5, 61.1, 56.4, 16.3; **HRMS** *m/e* for $C_{15}H_{16}O_4$ $[M+H^+]$ calculated 261.1127, found 261.1133.

5-(3,5-Dimethoxyphenyl)-2-methylpent-1-en-4-yn-3-one (7c):



Compound **7c** was prepared according to **General Procedure B**, using compound **6c** as starting material (0.0446 g, 0.191 mmol) with pyridinium dichromate (PDC) powder (1.5 equiv, 0.1077 g, 0.286 mmol). Compound **7c** was isolated following column chromatography (15:1 petroleum ether : Et_2O) as a yellow oil (0.0381 g, 0.165 mmol, 87 % yield). IR ν_{max} 2930, 2842, 2198, 1678, 1636, 1587 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.99 (d, J = 2.3 Hz, 2H), 6.51-6,56 (m, 2H), 6.08 (s, 1H), 3.78 (s, 6H), 1.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 180.3, 160.6, 145.2, 130.7, 121.4, 110.5, 103.9, 91.3, 85.3, 55.5, 16.1; **HRMS** *m/e* for $C_{14}H_{14}O_3$ $[M^+]$ calculated 231.1021, found 231.1025.

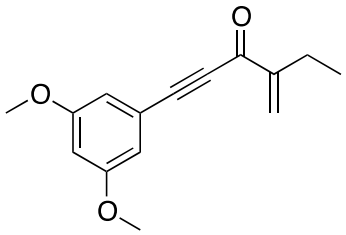
2-Methyl-5-(1-methyl-1*H*-indol-2-yl)pent-1-en-4-yn-3-one (7d):



Compound **7d** was prepared according to **General Procedure B**, by the reaction of compound **6d** as starting material (0.2201 g, 0.976 mmol) and PDC powder (1.5 equiv, 0.5507 g,

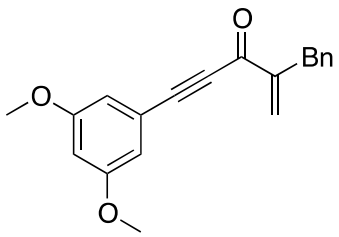
1.464 mmol). Compound **7d** was isolated following column chromatography (1:1 petroleum ether : Et_2O) as a yellow oil (0.1307 g, 0.585 mmol, 60 % yield). IR ν_{max} 2954, 2920, 2852, 2181, 1622, 1516 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 1H), 7.32 (m, 2H), 7.15 (m, 1H), 7.05 (s, 1H), 6.53 (s, 1H), 6.10 (s, 1H), 3.88 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 179.4, 145.2, 138.2, 130.1, 126.8, 124.8, 121.7, 120.7, 118.8, 112.5, 109.8, 93.3, 84.0, 30.9, 16.3; **HRMS** *m/e* for $C_{15}H_{13}NO$ [$M^+ + H^+$] calculated 224.1075, found 224.1081.

1-(3,5-Dimethoxyphenyl)-4-methylenehex-1-yn-3-one (7e):



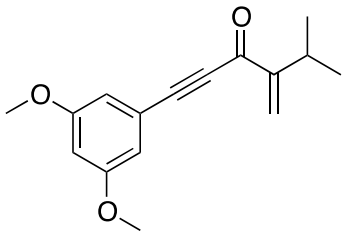
Compound **7e** was prepared according to **General Procedure B**, using compound **6e** as starting material (0.0992 g, 0.375 mmol) and the oxidation reagent PDC powder (1.5 equiv, 0.2116 g, 0.562 mmol). After 12 h, compound **7e** was isolated following column chromatography (5:1 petroleum ether : Et_2O) as a yellow oil (0.0839 g, 0.352 mmol, 94 % yield). IR ν_{max} 2964, 2936, 2876, 2841, 2197, 1636 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.73 (d, J = 2.4 Hz, 2H), 6.57 (s, 1H), 6.55 (t, J = 2.4 Hz, 1H), 6.04 (s, 1H), 3.79 (s, 6H), 2.38 (q, J = 7.5 Hz, 2H), 1.09 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 179.9, 160.7, 151.0, 129.3, 121.5, 110.5, 104.0, 91.1, 85.6, 55.5, 22.6, 12.4; **HRMS** *m/e* for $C_{15}H_{16}O_3$ [$M+H^+$] calculated 245.1178, found 245.1185.

2-Benzyl-5-(3,5-dimethoxyphenyl)pent-1-en-4-yn-3-one (6f):



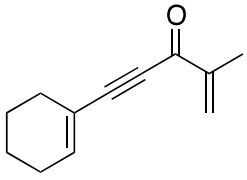
Compound **7f** was prepared according to **General Procedure B**, using compound **6f** as starting material (0.1341 g, 0.434 mmol) and the oxidation reagent PDC powder (1.5 equiv, 0.2449 g, 0.651 mmol). After 12 h, compound **7f** was isolated following column chromatography (5:1 hexane : Et_2O) as a tan oil (0.0864 g, 0.282 mmol, 65 % yield). IR ν_{max} 2964, 2936, 2876, 2841, 2197, 1636 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.17-7.35 (m, 5H), 6.72 (d, J = 2.4 Hz, 2H), 6.65 (s, 1H), 6.55 (t, J = 2.4 Hz, 1H), 5.90 (s, 1H), 3.79 (s, 6H), 3.69 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 179.4, 160.8, 149.1, 138.5, 131.8, 129.3, 128.6, 126.5, 121.4, 110.6, 104.1, 91.7, 85.6, 55.6, 35.8; **HRMS** *m/e* for $C_{20}H_{18}O_3$ [M^+] calculated 306.1256, found 306.1257.

1-(3,5-Dimethoxyphenyl)-5-methyl-4-methylenehex-1-yn-3-one (7g):



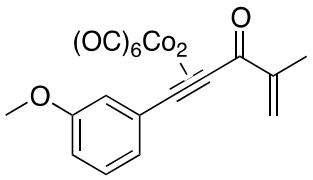
Compound **7g** was prepared according to **General Procedure B,** by the reaction of compound **6g** as starting material (0.1264 g, 0.485 mmol) with PDC powder (1.5 equiv, 0.2738 g, 0.728 mmol). After 12 h, compound **7g** was isolated following column chromatography (5:1 petroleum ether : Et_2O) as a yellow oil (0.1170 g, 0.453 mmol, 93 % yield). IR ν_{max} 2962, 2873, 2841, 2197, 1637, 1586 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$) δ 6.73 (d, J = 2.1 Hz, 2H), 6.59 (s, 1H), 6.55 (t, J = 2.1 Hz, 1H), 6.04 (s, 1H), 3.79 (s, 6H), 2.98 (septet, J = 6.9 Hz, 1H), 1.10 (d, J = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 179.8, 160.6, 155.6, 128.1, 121.4, 110.4, 103.8, 90.8, 85.8, 55.5, 27.0, 21.7; **HRMS** *m/e* for $C_{16}H_{18}O_3$ [M^++H^+] calculated 259.1334, found 259.1334.

5-(Cyclohex-1-en-1-yl)-2-methylpent-1-en-4-yn-3-one (7i):



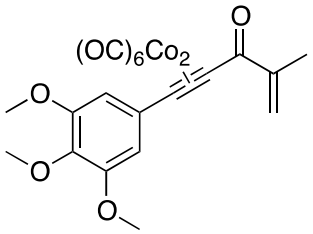
Compound **7i** was prepared according to **General Procedure B**, using compound **6i** as starting material (0.4440 g, 2.521 mmol) and PDC powder (1.5 equiv, 1.4226 g, 3.781 mmol). After 12 h, compound **7i** was isolated following column chromatography (5:1 hexane : Et_2O) as a yellow oil (0.3134 g, 1.789 mmol, 71 % yield). IR ν_{max} 2930, 2865, 2184, 1635, 1617 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.45 (m, 1H), 6.39 (s, 1H), 5.97 (s, 1H), 2.10-2.23 (m, 4H), 1.90 (s, 3H), 1.55-1.71 (m, 4H);^{13}C NMR (75 MHz, $CDCl_3$) 180.2, 145.2, 141.7, 130.0, 119.0, 93.8, 84.2, 28.3, 26.0, 21.9, 21.1, 16.1; **HRMS** *m/e* for $C_{12}H_{14}O$ [$M+H^+$] calculated 175.1123, found 175.1124.

Hexacarbonyl[μ-η^4 (5-(3-methoxyphenyl)-2-methylpent-1-en-4-yn-3-one)]dicobalt (Co-Co) (4a):



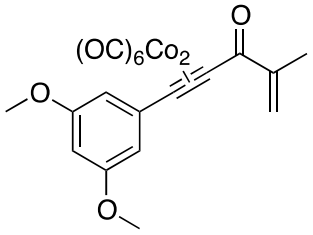
General procedure D: Dienynone **7a** (0.1551 g, 0.771 mmol) was dissolved in anhydrous CH_2Cl_2 and cooled to 0 ºC using an ice bath. An excess amount of dicobalt octacarbonyl ($Co_2(CO)_8$) was added to this solution and the reaction was stirred while maintaining the temperature at 0 ºC. After 2 h, the mixture was concentrated under reduced pressure in a cold water bath, obtaining the crude product as a dark red material. This crude material was purified on a plug of silica, first washing with 100% petroleum ether to remove the remaining $Co_2(CO)_8$, followed by a second washing with 100% Et_2O to obtain product **4a** (0.2750 g, 0.639 mmol, 83 % yield), as a dark red solid, m.p. 58-60 ºC; UV-vis ($CHCl_3$) λ_{max} = 545 nm, ε = 221 $M^{-1}cm^{-1}$; IR ν_{max} 3081, 2935, 2842, 2093, 2057, 2008, 1626 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (apparent t, J = 7.8 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.05 (s, 1H), 6.90 (dd, J = 8.1, 1.8 Hz, 1H), 5.86 (s, 1H), 5.81 (s, 1H), 3.83 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 198.3 (broad), 194.8, 159.9, 144.0, 138.2, 130.1, 126.1, 122.4, 115.3, 113.9, 91.7, 85.7, 55.3, 18.4; **HRMS(EI)** *m/e* for $C_{19}H_{12}Co_2O_8$ [M^+-2CO] calculated 429.9297, found 429.9298.

Hexacarbonyl[μ-η^4 (2-methyl-5-(3,4,5-trimethoxyphenyl)pent-1-en-4-yn-3-one)]dicobalt (Co-Co) (4b):



Compound **4b** was prepared according to **General Procedure D**, using compound **7b** as starting material (0.0900 g, 0.346 mmol) with an excess amount of $Co_2(CO)_8$. Compound **4b** was isolated following column chromatography (1:1 petroleum ether : Et_2O) as a red solid (0.1570 g, 0.287 mmol, 83 % yield), m.p. 65-68 ^oC; IR ν_{max} 3012, 2954, 2932, 2831, 2094, 2067, 2016, 1620, 1573 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.77 (s, 2H), 5.94 (s, 1H), 5.84 (s, 1H), 3.90 (s, 3H), 3.85 (s, 6H), 2.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 198.4 (broad), 194.9, 153.4, 144.3, 138.3, 132.0, 125.9, 107.1, 92.7, 85.2, 60.9, 56.1, 18.5; **HRMS** *m/e* for $C_{21}H_{16}Co_2O_{10}$ [$M+H^+$] calculated 546.9485, found 546.9489.

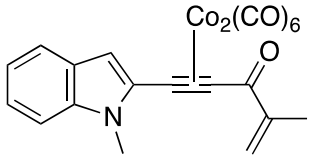
Hexacarbonyl[μ-η^4 (5-(3,5-dimethoxyphenyl)-2-methylpent-1-en-4-yn-3-one)]dicobalt (Co-Co) (8c):



Compound **4c** was prepared according to **General Procedure D**, using compound **7c** as starting material (0.0700 g, 0.304 mmol) with an excess amount of $Co_2(CO)_8$. Compound **4c** was isolated following column chromatography (15:1 petroleum ether : Et_2O) as a red solid (0.1091 g, 0.212 mmol, 70 % yield), m.p. 64-66 ^oC; IR ν_{max} 3006, 2962, 2924, 2840, 2099, 2008, 1630, 1580 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.67 (d, J = 2.1 Hz, 2H), 6.47 (t, J = 2.1 Hz, 1H), 5.88

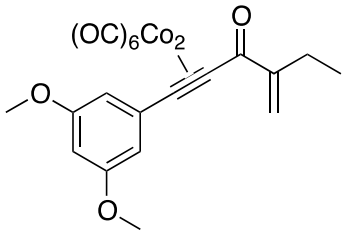
(s, 1H), 5.82 (s, 1H), 3.80 (s, 6H), 2.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 198.4 (broad), 194.9, 161.1, 144.1, 139.0, 126.4, 108.1, 100.6, 92.0, 85.8, 55.5, 18.6; **HRMS** *m/e* for $C_{20}H_{14}Co_2O_9$ [M+H$^+$] calculated 516.9380, found 516.9380.

Hexacarbonyl[μ-η^4 (2-methyl-5-(1-methyl-1*H*-indol-2-yl)pent-1-en-4-yn-3-one)]dicobalt (Co-Co) (4d):



Compound **4d** was prepared according to **General Procedure D**, using compound **7d** (0.1210 g, 0.542 mmol) with an excess amount of $Co_2(CO)_8$. Compound **4d** was isolated following column chromatography (1:1 petroleum ether : Et_2O) as a dark green solid (0.2590 g, 0.508 mmol, 94 % yield), m.p. 134-137 ºC; UV-vis ($CHCl_3$) λ_{max} = 598 nm, ε = 1199 $M^{-1}cm^{-1}$; IR ν_{max} 2934, 2512, 2194, 2142, 2094, 2059, 2019, 1617 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 7.8 Hz, 1H), 7.27-7.35 (m, 2H), 7.15 (m, 1H), 6.86 (s, 1H), 5.82 (s, 2H), 3.72 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 198.5 (broad), 195.0, 144.4, 139.0, 134.2, 128.0, 126.3, 123.4, 120.9, 120.7, 109.6, 108.0, 78.1, 77.3, 30.7, 18.6; **HRMS** *m/e* for $C_{21}H_{13}Co_2NO_7$ [M+H$^+$] calculated 509.9434, found 509.9436.

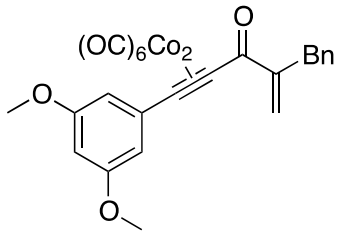
Hexacarbonyl[μ-η^4 (1-(3,5-dimethoxyphenyl)-4-methylenehex-1-yn-3-one)]dicobalt (Co-Co) (4e):



Compound **4e** was prepared according to **General Procedure D**, using compound **7e** as starting material (0.0446 g, 0.183 mmol) and an excess amount of $Co_2(CO)_8$. Compound **4e** was

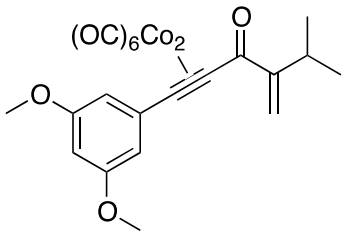
isolated as a dark red viscous oil (0.0737 g, 0.139 mmol, 76 % yield). IR ν_{max} 2966, 2937, 2838, 2096, 2057, 2012, 1635, 1583 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.65 (d, J = 2.2 Hz, 2H), 6.46 (t, J = 2.2 Hz, 1H), 5.85 (s, 1H), 5.72 (s, 1H), 3.79 (s, 6H), 2.47 (q, J = 7.4 Hz, 2H), 1.09 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 198.3 (broad), 194.9, 161.0, 150.3, 138.9, 123.8, 108.0, 100.5, 92.1, 86.6, 55.4, 24.9, 12.6; **HRMS** *m/e* for $C_{21}H_{16}Co_2O_9$ [$M+H^+$] calculated 530.9537, found 530.9537.

Hexacarbonyl[μ-η^4 (2-benzyl-5-(3,5-dimethoxyphenyl)pent-1-en-4-yn-3-one)]dicobalt (Co-Co) (4f):



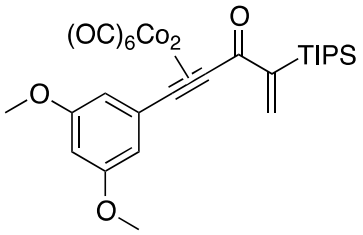
Compound **4f** was prepared according to **General Procedure D**, using compound **7f** as starting material (0.0751 g, 0.245 mmol) and an excess amount of $Co_2(CO)_8$. Compound **4f** was isolated following column chromatography (10:1 petroleum ether : Et_2O) as a dark red solid (0.1132 g, 0.191 mmol, 78 % yield), m.p. 58-60 ^oC; IR ν_{max} 3062, 3021, 2967, 2921, 2840, 2094, 2058, 2037, 2005, 1637, 1623 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 5H), 6.62 (d, J = 2.2 Hz, 2H), 6.44 (t, J = 2.2 Hz, 1H), 5.91 (s, 1H), 5.68 (s, 1H), 3.78 (s, 2H), 3.77 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 198.2 (broad), 194.3, 161.1, 148.5, 139.0, 138.6, 129.2, 128.6, 126.5, 125.8, 108.0, 100.7, 92.3, 86.3, 55.5, 38.3; **HRMS** *m/e* for $C_{26}H_{18}Co_2O_9$ [$M+H^+$] calculated 592.9693, found 592.9694.

Hexacarbonyl[μ-η^4 (1-(3,5-dimethoxyphenyl)-5-methyl-4-methylenehex-1-yn-3-one)]dicobalt (Co-Co) (4g):



Compound **4g** was prepared according to **General Procedure D**, using compound **7g** as starting material (0.1091 g, 0.422 mmol) and an excess amount of $Co_2(CO)_8$. Compound **4g** was isolated as a dark red viscous oil (0.2036 g, 0.374 mmol, 89 % yield). IR ν_{max} 2962, 2096, 2057, 2017, 1585 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.67 (d, J = 2.4 Hz, 2H), 6.47 (t, J = 2.1 Hz, 1H), 5.83 (s, 1H), 5.66 (d, J = 1.2 Hz, 1H), 3.80 (s, 6H), 3.09 (septet, J = 6.9 Hz, 1H), 1.11 (d, J=6.9, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 198.3 (broad), 195.4, 161.0, 155.3, 138.9, 121.2, 107.9, 100.6, 92.3, 87.6, 55.4, 29.1, 21.4; **HRMS** *m/e* for $C_{22}H_{18}Co_2O_9$ [$M+H^+$] calculated 544.9693, found 544.9693.

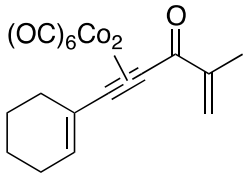
Hexacarbonyl[μ-η^4 (5-(3,5-dimethoxyphenyl)-2-(triisopropylsilyl)pent-1-en-4-yn-3-one)]dicobalt (Co-Co) (4h):



To a solution of alcohol **6h** (0.0823 g, 0.219 mmol) in anhydrous CH_2Cl_2 at room temperature was added PDC powder (1.5 equiv, 0.1234 g, 0.328 mmol), and allowed the reaction was stirred for 16 h. After this time, an excess amount of $Co_2(CO)_8$ at 0 ^oC and allowed to stir for 10 h. The mixture was treated following **General Procedure D**. Compound **4h** was isolated following preparative chromatography (25:1 Hexane : Et_2O) as a dark red solid (0.0833 g, 0.126 mmol, 69 % yield), m.p. 108-110 ^oC; IR ν_{max} 2937, 2864, 2092, 2053, 2020, 1621, 1575 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.67 (d, J = 2.2 Hz, 2H), 6.53 (d, J = 1.6 Hz, 1H), 6.47 (t, J = 2.2 Hz, 1H), 6.20 (d, J = 1.6 Hz, 1H), 3.79 (s, 6H), 1.38 (septet, J = 7.5 Hz, 3H), 1.10 (d, J = 7.5 Hz,

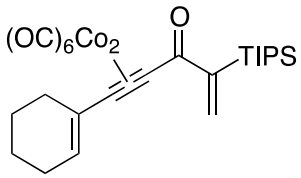
18H); ^{13}C NMR (75 MHz, $CDCl_3$) 199.5, 198.4 (broad), 161.0, 149.4, 139.2, 138.9, 107.7, 100.6, 93.3, 88.0, 55.3, 18.7, 11.2; **HRMS** *m/e* for $C_{28}H_{32}Co_2O_9Si$ [$M+H^+$] calculated 659.0558, found 659.0549.

Hexacarbonyl[μ-η^4 (5-(cyclohex-1-en-1-yl)-2-methylpent-1-en-4-yn-3-one)]dicobalt (Co-Co) (4i):



Compound **4i** was prepared according to **General Procedure D**, using compound **7i** as starting material (0.0820 g, 0.470 mmol) and an excess amount of $Co_2(CO)_8$. Compound **4i** was isolated following column chromatography (10:1 petroleum ether : Et_2O) as a dark red solid (0.1732 g, 0.376 mmol, 80 % yield), m.p. 76-78 ^oC; IR ν_{max} 2931, 2861, 2091, 2003, 1765, 1625, 1579 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.23 (m, 1H), 5.88 (s, 1H), 5.84 (m, 1H), 2.26 (m, 2H), 2.16 (m, 2H), 2.02 (dd, J = 1.5, 0.9 Hz , 3H), 1.62-1.80 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) 198.7 (broad), 194.8, 144.6, 133.9, 131.7, 125.3, 96.6, 86.5, 30.7, 26.4, 22.9, 21.9, 18.4; **HRMS** *m/e* for $C_{18}H_{14}Co_2O_7$ [$M+H^+$] calculated 460.9482, found 460.9482.

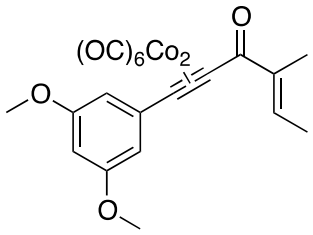
Hexacarbonyl[μ-η^4 (5-(cyclohex-1-en-1-yl)-2-(triisopropylsilyl)pent-1-en-4-yn-3-one)]-dicobalt (Co-Co) (4j):



Alcohol **6j** (0.0492 g, 0.154 mmol) was dissolved in anhydrous CH_2Cl_2 and (1.5 equiv, 0.0869 g, 0.231 mmol) of PDC was added and allowed to stir overnight, the solution was stirred for overnight. Then an excess amount of $Co_2(CO)_8$ was added to this solution. The reaction was stirred while maintaining the temperature at 0 ^oC. After 2 h, the mixture was treated following

General Procedure D. Preparative chromatography (15:1 hexane : Et_2O) gave **4j** (0.0558 g, 0.093 mmol, 60 % yield) as dark red solid, m.p. 58-60 ^oC; IR ν_{max} 2928, 2865, 2093, 2055, 2019 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.53 (d, J = 1.7 Hz, 1H), 6.20-6.24 (m, 2H), 2.27 (m, 2H), 2.17 (m, 2H), 1.76 (m, 2H), 1.69 (m, 2H), 1.37 (septet, J = 7.5 Hz, 3H), 1.10 (d, J = 7.5 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) 199.4, 198.9 (broad), 150.1, 137.9, 134.1, 131.3, 97.9, 88.8, 30.8, 26.4, 23.0, 21.9, 18.7, 11.2; **HRMS** *m/e* for $C_{26}H_{32}Co_2O_7Si$ [$M+H^+$] calculated 603.0660, found 603.0665.

Synthesis of hexacarbonyl[μ-η^4 ((*E*)-1-(3,5-dimethoxyphenyl)-4-methylhex-4-en-1-yn-3-one)]dicobalt (Co-Co) (4k):



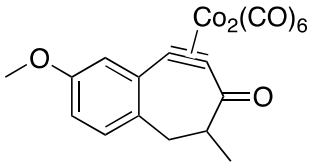
According to **General Procedure B**, alcohol **6k** (0.2051 g, 0.948 mmol) was dissolved in anhydrous CH_2Cl_2 (30 mL) and (1.5 equiv, 0.5351 g, 1.422 mmol) of PDC was added. Afterward, the crude material was dissolved in anhydrous CH_2Cl_2 (20 mL) and an excess amount of $Co_2(CO)_8$ was added to this solution following **General Procedure D**. The reaction was stirred while maintaining the temperature at 0 ^oC. After 2 h, the mixture was concentrated under reduced pressure in a cold water bath, obtaining a dark red material. This crude material was purified first on a plug of silica, first washing with 100% petroleum ether to remove the remaining $Co_2(CO)_8$, followed by a second washing with 100% Et_2O to obtain the product complexes. Column chromatography (1:1 petroleum ether : Et_2O) gave **4k** (0.1421 g, 0.674 mmol, 48 % yield) as a dark red viscous oil. IR ν_{max} 3005, 2938, 2838, 2095, 2054, 2009, 1625, 1583 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.75 (qd, J = 7.0, 1.2 Hz, 1H), 6.67 (d, J = 2.2 Hz, 2H), 6.47 (t, J = 2.2 Hz, 1H), 3.80 (s, 6H), 1.97 (s, 3H), 1.77 (d, J=6.9 Hz, 3H); NOESY-2D NMR (300 MHz, $CDCl_3$): an off diagonal cross peak correlating the δ 1.77 and δ 1.97

resonances; ^{13}C NMR (75 MHz, $CDCl_3$) 198.4 (broad), 194.4, 161.0, 139.7, 139.1, 137.5, 108.0, 100.6, 91.8, 86.6, 55.4, 14.5, 12.0; **HRMS** *m/e* for $C_{21}H_{16}Co_2O_9$ [M^+] calculated 530.9537, found 530.9531.

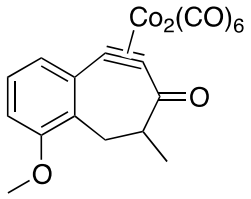
Hexacarbonyl[μ-η^4-(2-methoxy-6-methyl-5,6-dihydro-8,9-dehydro-5*H*-benzo[7]annulen-7(6*H*)-one)]dicobalt (Co-Co) (9a) *para-*:

Hexacarbonyl[μ-η^4-(1-methoxy-8-methyl-8,9-dihydro-5,6-dehydro-5*H*-benzo[7]annulen-7(6*H*)-one)]dicobalt (Co-Co) (9a′) *ortho-:*

General procedure E: In a round bottom flask, the complexed dienynone, **4a** (0.1120 g, 0.230 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL) under N_2. Later, a 1.0 M solution of tin tetrachloride ($SnCl_4$) in CH_2Cl_2 (3 equiv, 0.70 mL, 0.70 mmol), was added dropwise to the reaction mixture at 0 ºC. The reaction mixture was monitored under TLC (20:1 petroleum ether : Et_2O) and was allowed to warm to room temperature. After complete disappearance of the starting material (24 h), the solution was treated with NH_4Cl (aq., sat.) and extracted with Et_2O (3 x 100 mL). the combined ether layers were with $MgSO_4$, filtered, and the solvent removed under reduced pressure. This crude material was subjected column chromatography (20:1 petroleum ether : Et_2O) to obtain major and minor products, *para-* **9a (major)** (elute first) and *ortho-* **9a′ (minor),** each as a red-maroon solid.

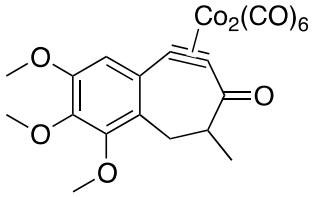


***Para-* 9a** (0.0589 g, 0.121 mmol, 53 % yield), m.p. 68-71 ºC; IR ν_{max} 2926, 2201, 2099, 2062, 2016, 1675, 1606 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (obscured d, J = 2.7 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 6.87 (dd, J = 8.4, 2.7 Hz, 1H), 3.86 (s, 3H), 2.73-2.95 (m, 3H), 1.25 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 204.6, 198.0 (broad), 159.4, 136.8, 131.5, 131.4, 118.1, 114.4, 86.9, 78.2, 55.3, 45.8, 38.3, 16.3; **HRMS** *m/e* for $C_{19}H_{12}Co_2O_8$ [$M+H^+$] calculated 486.9274, found 486.9260.



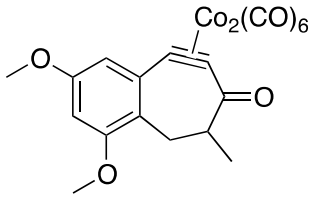
***Ortho*- 9a′** (0.0268 g, 0.055 mmol, 24 % yield), m.p. 64-68 ºC; IR ν_{max} 2960, 2921, 2852, 2098, 2061, 2007, 1677, 1565 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 7.3 Hz, 1H), 7.31 (apparent t, J = 7.9 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 3.87 (s, 3H), 3.30 (d, J = 16.1 Hz, 1H), 2.83 (m, 1H), 2.72 (dd, J = 16.0, 10.1 Hz, 2H), 1.27 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 205.1 (broad), 198.3, 156.8, 137.2, 128.3, 127.7, 125.4, 111.2, 87.6, 78.0, 55.9, 45.5, 28.4, 16.3; **HRMS** *m/e* for $C_{19}H_{12}Co_2O_8$ $[M+H^+]$ calculated 486.9274, found 486.9277.

Hexacarbonyl[μ-η^4-(1,2,3-trimethoxy-8-methyl-8,9-dihydro-5,6-dehydro-5*H*-benzo[7]annulen-7(6*H*)-one)]dicobalt (Co-Co) (9b):



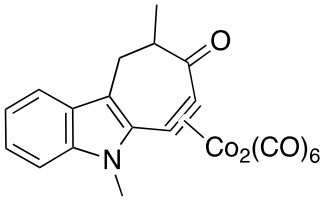
Compound **9b** was prepared according to **General Procedure E**, using compound **4b** as starting material (0.0651 g, 0.119 mmol). After stirring 12 h, compound **9b** was isolated following column chromatography (1:1 petroleum ether : Et_2O) as a red solid (0.0454 g, 0.083 mmol, 70 % yield), m.p. 77-80 ºC; IR ν_{max} 2968, 2936, 2096, 2057, 2010, 1680, 1578, 1557 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (s, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.90 (s, 3H), 3.13 (d, J = 15.9 Hz, 1H), 2.82 (m, 1H), 2.69 (dd, J = 15.9, 9.9 Hz, 2H), 1.27 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 204.9, 198.4 (broad), 153.0, 151.6, 143.4, 131.4, 126.1, 111.9, 88.0, 78.2, 61.5, 61.0, 56.0, 45.8, 29.1, 16.5; **HRMS** *m/e* for $C_{21}H_{16}Co_2O_{10}$ $[M+H^+]$ calculated 546.9485, found 546.9495.

Hexacarbonyl[μ-η^4-(2,4-dimethoxy-6-methyl-5,6-dihydro-8,9-dehydro-5*H*-benzo[7]annulen-7(6*H*)-one)]dicobalt (Co-Co) (9c):



Compound **9c** was prepared according to **General Procedure E**, using compound **4c** as starting material (0.0671 g, 0.130 mmol). After 24 h, compound **9c** was isolated following column chromatography (20:1 petroleum ether : Et_2O) as a red solid (0.0374 g, 0.072 mmol, 56 % yield), m.p. 67-70 ^oC; IR ν_{max} 3003, 2924, 2850, 2097, 2025, 2004, 1727, 1677, 1605, 1567 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.88 (s, 1H), 6.52 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.21 (d, J = 15.9 Hz, 1H), 2.80 (m, 1H), 2.64 (dd, J = 15.9, 10.0 Hz, 1H), 1.26 (d, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 205.2, 198.1 (broad), 159.7, 157.9, 137.6, 120.4, 108.7, 99.4, 88.1, 78.0, 55.9, 55.3, 45.7, 28.1, 16.3; **HRMS** *m/e* for $C_{20}H_{14}Co_2O_9$ [M+H$^+$] calculated 516.9380, found 516.9373.

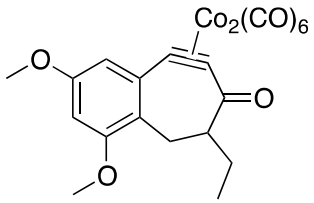
Hexacarbonyl[μ-η^4-(5,9-dimethyl-9,10-dihydro-6,7-dehydrocyclohepta[b]indole-8(5*H*)-one)]dicobalt (Co-Co) (9d):



Compound **9d** was prepared according to **General Procedure E**, using compound **4d** (0.0789 g, 0.155 mmol). After 48 h, compound **9d** was isolated following column chromatography (20:1 petroleum ether : Et_2O) as a dark green solid (0.0513 g, 0.101 mmol, 65 % yield), m.p. >150 ^oC (dec); IR ν_{max} 2924, 2859, 2094, 2046, 2009, 1664 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 1H), 7.30-7.29 (m, 2H), 7.15 (apparent dt, J = 1.1, 7.4 Hz, 1H), 3.94 (s, 3H), 3.16 (dd, J=16.5, 2.1 Hz, 1H), 3.04 (m, 1H), 2.81 (dd, J = 16.5, 11.1 Hz, 1H),

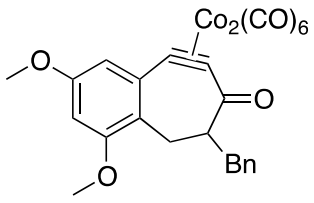
1.39 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 204.8, 198.0 (broad), 138.8, 132.6, 126.6, 123.6, 120.1, 119.2, 115.3, 109.5, 86.5, 72.4, 43.9, 29.9, 29.5, 16.4; **HRMS** *m/e* for $C_{21}H_{13}Co_2NO_7$ [M+H$^+$] calculated 509.9434, found 509.9428.

Hexacarbonyl[μ-η^4-(6-ethyl-2,4-dimethoxy-5,6-dihydro-8,9-dehydro-5*H*-benzo[7]annulen-7(6*H*)-one)]dicobalt (Co-Co) (9e):



Compound **9e** was prepared according to **General Procedure E**, using compound **4e** as starting material (0.1035 g, 0.195 mmol). After 12 h, compound **9e** was isolated following column chromatography (10:1 petroleum ether : Et_2O) as a dark red solid (0.0775 g, 0.146 mmol, 75 % yield), m.p. 87-90 ºC; IR ν_{max} 2963, 2938, 2877, 2840, 2096, 2056, 2011, 1674, 1601 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (d, J = 2.4 Hz, 1H), 6.52 (d, J = 2.4 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.03 (dd, J = 16.2, 1.7 Hz), 2.93 (dd, J = 16.2, 13.7 Hz, 1H), 2.63 (m, 1H), 1.74 (m, 1H), 1.42 (m, 1H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 205.4, 198.3 (broad), 159.8, 158.1, 138.0, 119.8, 108.7, 99.4, 87.5, 77.9, 56.0, 55.4, 53.2, 25.2, 23.5, 11.8; **HRMS** *m/e* for $C_{21}H_{16}Co_2O_9$ [M+H$^+$] calculated 530.9537, found 530.9540.

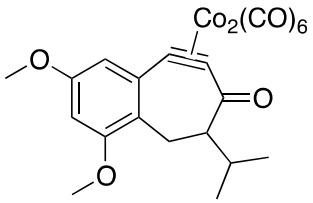
Hexacarbonyl[μ-η^4-(6-benzyl-2,4-dimethoxy-5,6-dihydro-8,9-dehydro-5*H*-benzo[7]annulen-7(6*H*)-one)]dicobalt (Co-Co) (9f):



Compound **9f** was prepared according to **General Procedure E**, using compound **4f** as starting material (0.0481 g, 0.081 mmol). After 20 h, compound **9f** was isolated following

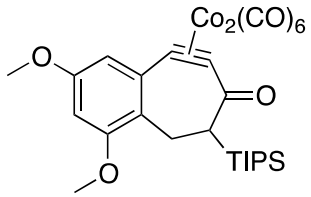
column chromatography (5:1 petroleum ether : Et_2O) as a dark red solid (0.0351 g, 0.059 mmol, 73 % yield), m.p. 63-66 ^oC; IR ν_{max} 2922, 2850, 2097, 2058, 2017, 1728, 1680, 1600 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.13-7.32 (m, 5H), 6.87 (d, J = 2.4 Hz, 1H), 6.44 (d, J = 2.4 Hz, 1H), 3.85 (s, 3H), 3.59 (s, 3H), 3.20-3.33 (m, 2H), 3.00 (m, 1H), 2.52-2.72 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 204.2, 198.1 (broad), 159.7, 157.8, 139.3, 137.7, 129.1, 128.1, 126.0, 120.2, 108.5, 99.4, 87.8, 78.0, 55.7, 55.2, 52.7, 36.0, 24.9; **HRMS** *m/e* for $C_{26}H_{18}Co_2O_9$ $[M+H^+]$ calculated 592.9693, found 592.9695.

Hexacarbonyl[μ-η^4-(6-isopropyl-2,4-dimethoxy-5,6-dihydro-8,9-dehydro-5*H*-benzo[7]annulen-7(6*H*)-one)]dicobalt (Co-Co) (9g):



Compound **9g** was prepared according to **General Procedure E**, using compound **4g** as starting material (0.1142 g, 0.209 mmol). After 4 h at 0 ^oC, compound **9g** was isolated following column chromatography (10:1 petroleum ether : Et_2O) as a dark red solid (0.0978 g, 0.179 mmol, 86 % yield), m.p. 85-88 ^oC; IR ν_{max} 2960, 2871, 2838, 2095, 2056, 2011, 1672 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.86 (d, J = 2.4 Hz, 1H), 6.53 (d, J = 2.4 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.18 (dd, J = 16.2, 7.8 Hz, 1H), 2.81 (d, J = 16.2 Hz, 1H), 2.48 (apparent t, J = 8.2 Hz, 1H), 1.80 (m, 1H), 0.94 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 204.9, 198.3 (broad), 159.7, 158.1, 138.1, 119.2, 108.6, 99.4, 87.0, 77.7, 58.7, 55.9, 55.3, 27.5, 22.8, 20.8, 19.6; **HRMS** *m/e* for $C_{22}H_{18}Co_2O_9$ $[M+H^+]$ calculated 544.9693, found 544.9694.

Hexacarbonyl[μ-η^4-(6-(triisopropylsilyl)-2,4-dimethoxy-5,6-dihydro-8,9-dehydro-5*H*-benzo[7]annulen-7(6*H*)-one)]dicobalt (Co-Co) (9h):



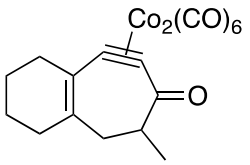
Compound **9h** was prepared according to **General Procedure E**, using compound **4h** as starting material (0.0710 g, 0.108 mmol). After 5 minutes at 0 °C, the product **9h** was isolated following column chromatography (40:1 petroleum ether : Et_2O) as a dark red solid (0.0639 g, 0.0970 mmol, 90 % yield), m.p. 112-114 °C; IR ν_{max} 2942, 2866, 2096, 2057, 2016, 1673, 1600 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.87 (d, J = 2.4, 1H), 6.51 (d, J = 2.4 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.72 (d, J = 15.0 Hz, 1H), 2.49 (1/2 AB, J = 11.5 Hz, 1H), 2.40 (d of ½ AB, J = 15.0, 11.5 Hz, 1H), 1.44 (apparent septet, J = 7.5 Hz, 3H), 1.14 (d, J = 7.5 Hz, 9H), 1.13 (d, J = 7.5 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) 205.4, 198.4 (broad), 159.6, 157.2, 138.1, 122.5, 108.5, 99.0, 87.9, 83.4, 55.6, 55.3, 40.7, 22.5, 19.2, 19.1, 11.7; **HRMS** *m/e* for $C_{28}H_{32}Co_2O_9Si$ $[M+H^+]$ calculated 659.0558, found 659.0562.

Compound **9h** was prepared according to **General Procedure E**, using compound **4h** as starting material (0.0831 g, 0.126 mmol), except that 50 mol% $SnCl_4$ (0.007 mL, 0.06 mmol) was added. After 30 minutes at 0 °C, the product was isolated following column chromatography (40:1 petroleum ether : Et_2O) as a dark red solid (0.0736 g, 0.112 mmol, 89 % yield).

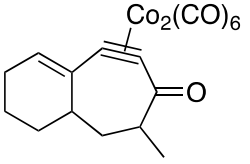
To a solution of compound **4h** (0.0690 g, 0.105 mmol) in CH_2Cl_2 at 0 °C was added $SnCl_4$ (10 μL of a 1.0 M solution, 10 mol%). The ice bath was removed after 1 h and the solution allowed to stir for 12 h. The solution was re-cooled 0 °C and $SnCl_4$ (10 μL of a 1.0 M solution, 10 mol%) was added. The ice bath was removed and the solution allowed to stir for 8 h. to except that 50 mol% $SnCl_4$ (0.007 mL, 0.06 mmol) was added. After addition of NH_4Cl (aq) and a conventional extractive workup, flash chromatography (40:1 petroleum ether : Et_2O) afforded 0.0625 g of a 73.5:26.5 mixture of **9h** (67% yield, 88% yield based on recovered starting material) and starting **4h** (24% recovery).

Hexacarbonyl[μ-η^4-(6-methyl-3,4,5,6-tetrahydro-8,9-dehydro-1*H*-benzo[7]annulen-7(2*H*)-one)]dicobalt (Co-Co) (9i, 9i′):

Compound **9i** and **9i′** were prepared according to **General Procedure E**, using **4i** as starting material (0.1004 g, 0.218 mmol). After 12 h, the product was isolated following column chromatography (50:1 hexane : Et_2O) as dark red viscous oil (0.0442 g, 0.0958 mmol) 44 % yield as a 66:34 ratio of **9i** (29%) and **9i'** (15%). Subsequent preparative TLC (50:1 hexanes : Et_2O) afforded the separated isomers, with **9i′** eluting first.

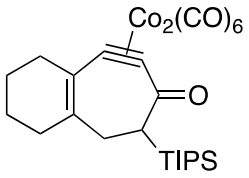


9i: dark red viscous oil. IR ν_{max} 2924, 2094, 2035, 2014, 1679 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.78 (m, 1H), 2.30-2.45 (m, 3H), 2.19 (m, 1H), 1.96-2.14 (m, 2H), 1.60-1.81 (m, 4H), 1.20 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 204.6, 198.6 (broad), 140.5, 128.8, 91.7, 78.0, 44.0, 39.9, 33.9, 29.8, 22.9, 22.6, 16.1; **HRMS** *m/e* for $C_{18}H_{14}Co_2O_7$ [M^++H^+] calculated 460.9482, found 460.9482.



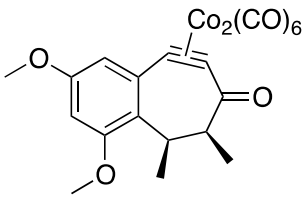
9i': dark red viscous oil. IR ν_{max} 2956, 2922, 2854, 2094, 2057, 2024, 1726 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.44 ((br s), 1H), 2.88 (m, 1H), 2.63 (m, 1H), 2.09-2.21 (m, 2H), 1.96 (m, 1H), 1.83 (m, 1H), 1.54-1.70 (m, 3H), 1.40 (m, 1H), 1.23 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 204.3, 198.7 (broad), 143.8, 137.8, 136.7, 91.8, 82.0, 48.5, 42.2, 41.0, 32.4, 26.9, 21.8, 17.5; **HRMS** *m/e* for $C_{18}H_{14}Co_2O_7$ [M^++H^+] calculated 460.9482, found 460.9480.

Hexacarbonyl[μ-η^4-(6-(triisopropylsilyl)-3,4,5,6-tetrahydro-8,9-dehydro-1*H*-benzo[7]annulen-7(2*H*)-one)]dicobalt (Co-Co) (9j, 9j′):



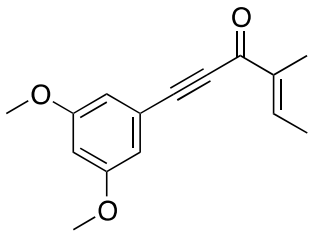
Compound **9j** + **j′** were prepared according to **General Procedure E**, using **4j** as starting material (0.0438 g, 0.0727 mmol). After 7 h at 0 °C, the product was isolated following column chromatography (50:1 hexane : Et_2O) as dark red viscous oil (0.0366 g, 84 % yield, as a 78:22 mixture of **9j:9j'**. IR ν_{max} 2940, 2891, 2864, 2094, 2050, 2008 cm^{-1}; **9j** ^1H NMR (500 MHz, $CDCl_3$) δ 2.50 (d, J = 11.7 Hz, 1H), 2.31 (d, J = 16.2 Hz, 1H), 2.27-2.54 (m, 3H), 2.08-2.27 (m, 2H), 1.77 (m, 2H), 1.72 (m, 4H), 1.33 (septet, J = 6.9 Hz, 3H), 1.10 (d, J = 6.9 Hz, 18H); peaks from minor isomer **9j'** could be observed at 6.46 (m, 1H), 2.72 (d, J = 10.7 Hz, 1H), 1.95 (m, 1H), 1.91 (d, J = 15.3 Hz, 1H), 1.84 (m, 1H), 1.60 (m, 1H), 1.11 (d, obscured, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) 204.8, 198.8 (broad), 143.0, 129.3, 91.7, 82.3, 38.2, 33.8, 33.6, 29.8, 22.9, 22.6, 19.3, 11.5; peaks from the minor isomer could be observed at 204.9, 138.4, 136.7, 44.1, 43.7, 34.1, 32.4, 26.9, 21.9; **HRMS** *m/e* for $C_{26}H_{32}Co_2O_7Si$ $[M^+ + H^+]$ calculated 603.0660, found 603.0653.

cis-Hexacarbonyl[μ-η^4-(2,4-dimethoxy-5,6-dimethyl-5,6-dihydro-8,9-dehydro-5_H_-benzo[7]annulen-7(6_H_)-one)]dicobalt (Co-Co) (9k):



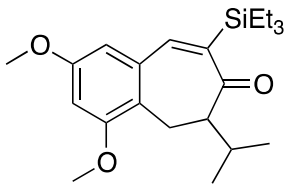
Compound **9k** was prepared according to **General Procedure E**, using *E*- **4k** as starting material (0.2425 g, 0.457 mmol). After 48 h, preparative (7:1 petroleum ether : Et_2O) resulted in the isolation an 89:11 mixture of **9k** and **4k** (0.0850 g, 31% **9k**, 4% recovered **4k**)., followed by **7k** (0.0305 g, 27% yield). Repeated preparative TLC (7:1 petroleum ether : Et_2O) of the first fraction resulted in the isolation of **9k** uncontaminated by **4k** as dark red viscous oil. **9k:** IR ν_{max}

= 2923, 2853, 2201, 2095, 2060, 2030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 6.91 (d, J=2.4, 1H), 6.51 (d, J=2.4, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.60 (qd, J = 7.4, 1.8 Hz, 1H), 3.13 (qd, J = 6.9, 1.8 Hz 1H), 1.32 (d, J = 6.9 Hz, 3H), 0.94 (d, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 203.1, 198.4 (broad), 159.3, 157.2, 135.4, 126.5, 109.3, 99.7, 89.9, 80.1, 55.8, 55.2, 48.1, 34.4, 18.2, 15.0, 14.4; **HRMS** *m/e* for $C_{21}H_{16}Co_2O_9$ [M^+] calculated 530.9537, found 530.9539.



7k: IR ν_{max} = 2926, 2844, 2199, 1623, 1591cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.33 (q, J = 6.9 Hz, 1H), 6.73 (d, J = 2.0 Hz, 2H), 6.54 (t, J = 2.0 Hz, 1H), 3.80 (s, 6H), 1.99 (d, J = 6.9 Hz, 3H), 1.86 (s, 3H); NOESY-2D NMR (500 MHz, $CDCl_3$): an off diagonal cross peak correlating the δ 1.86 and δ 1.99 resonances; ^{13}C NMR (125 MHz, $CDCl_3$) 180.1, 160.6, 145.3, 139.5, 121.7, 110.3, 103.6, 90.8, 85.4, 55.5, 15.2, 10.2; **HRMS** *m/e* for $C_{15}H_{16}O_3$ [M^++H^+] calculated 245.1178, found 245.1179.

6-Isopropyl-2,4-dimethoxy-8-(triethylsilyl)-5*H*-benzo[7]annulen-7(6*H*)-one (10)



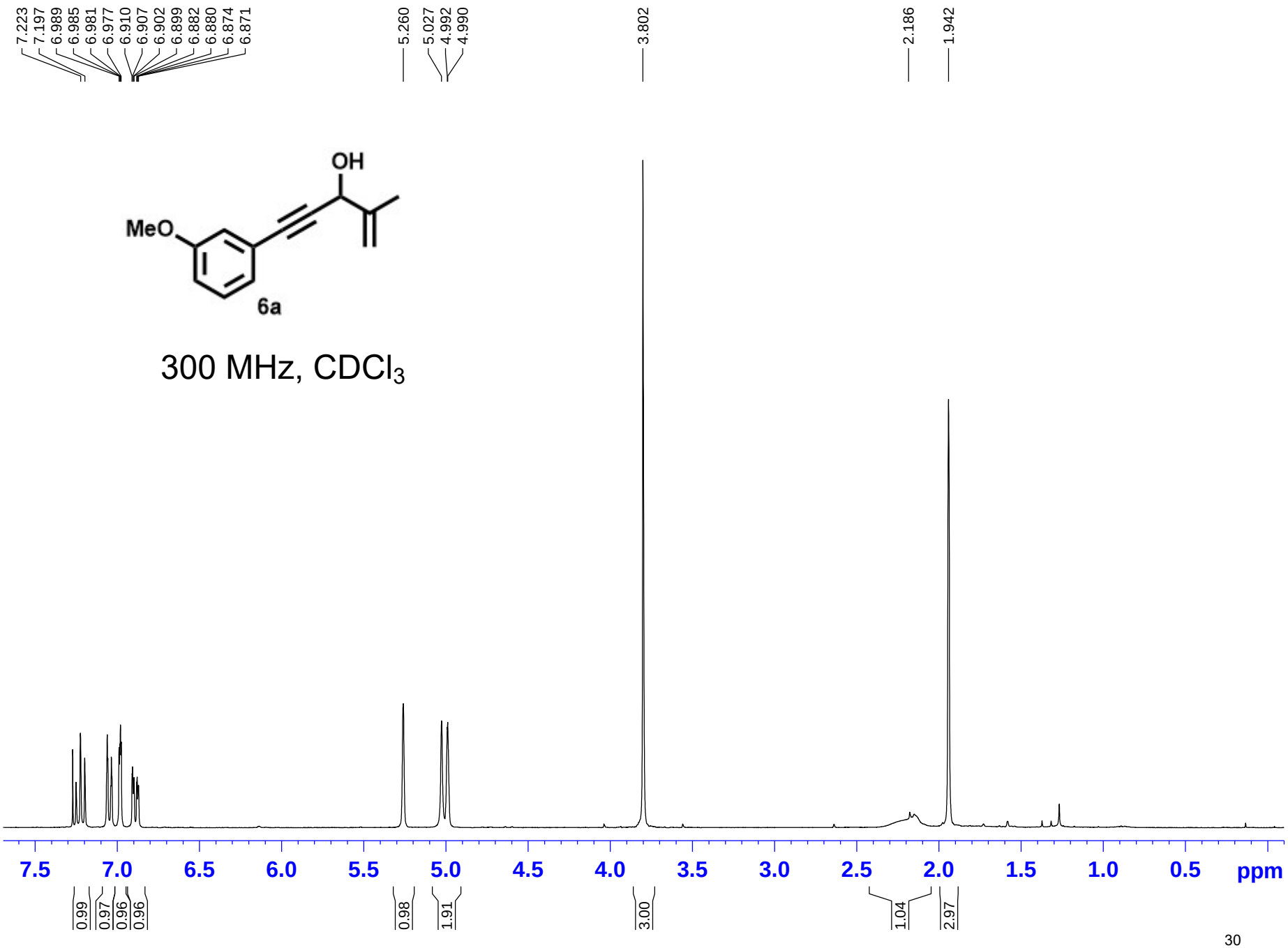
Compound **9g** (0.1019 g, 0.187 mmol) was dissolved in degassed 1,2-dichloroethane (3 mL). To this stirred solution, bis(trimethylsilyl)acetylene (0.088 mL, 0.374 mmol) and triethylsilane (0.14 mL, 0.898 mmol) were added. The reaction was placed in an oil bath set at 65 ^oC for 4 h under N_2. After this time, the mixture was allowed to cool down, dissolved in Et_2O (60 mL) and extracted with H_2O (3 X 60 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. Preparative TLC (5:1 petroleum ether : Et_2O)

provided compound **10** as a yellow liquid (0.0609 g, 0.163 mmol, 87%). IR ν_{max} = 2953, 2875, 2841, 2250, 1641, 1595, 1565 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.08 (s, 1H), 6.49 (d, J = 2.4 Hz, 1H), 6.44 (d, J = 2.4 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.03 (dd, J = 15.1, 2.4 Hz, 1H), 2.90 (dd, J = 15.1, 10.0 Hz, 1H), 2.30 (m, 1H), 2.07 (m, 1H), 0.98 (t, J = 7.9 Hz, 9H), 0.94 (d, J = 6.8 Hz, 3H), 0.85 (d, J = 6.7 Hz, 3H), 0.70-0.83 (m, 6H); NOESY-2D NMR (300 MHz, $CDCl_3$): an off diagonal cross peak correlating the δ 6.44 and δ 7.08 resonances; ^{13}C NMR (125 MHz, $CDCl_3$) 208.6, 158.6, 157.7, 147.5, 142.4, 137.9, 121.0, 107.1, 99.8, 60.8, 55.9, 55.3, 28.5, 21.6, 21.1, 19.1, 7.5, 3.5; **HRMS** *m/e* for $C_{22}H_{34}O_3Si$ [$M+H^+$] calculated 375.2355, found 375.2373.

References

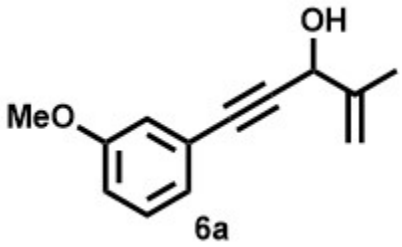
1. W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.* 1978, **43**, 2923.
2. Z.-Y. Li, M. Wang, Q.-H. Bian, B. Zheng, J.-Y. Mao, S.-N. Li, S.-Z. Liu, M. A. Wang, J.-C. Zhong, and H.-C. Guo, *Chem-Eur. J.* 2011, **17**, 5782.

jrg.1447 4, 3-MeOPh-CC-H + BuLi/methacroein, 7/7/21



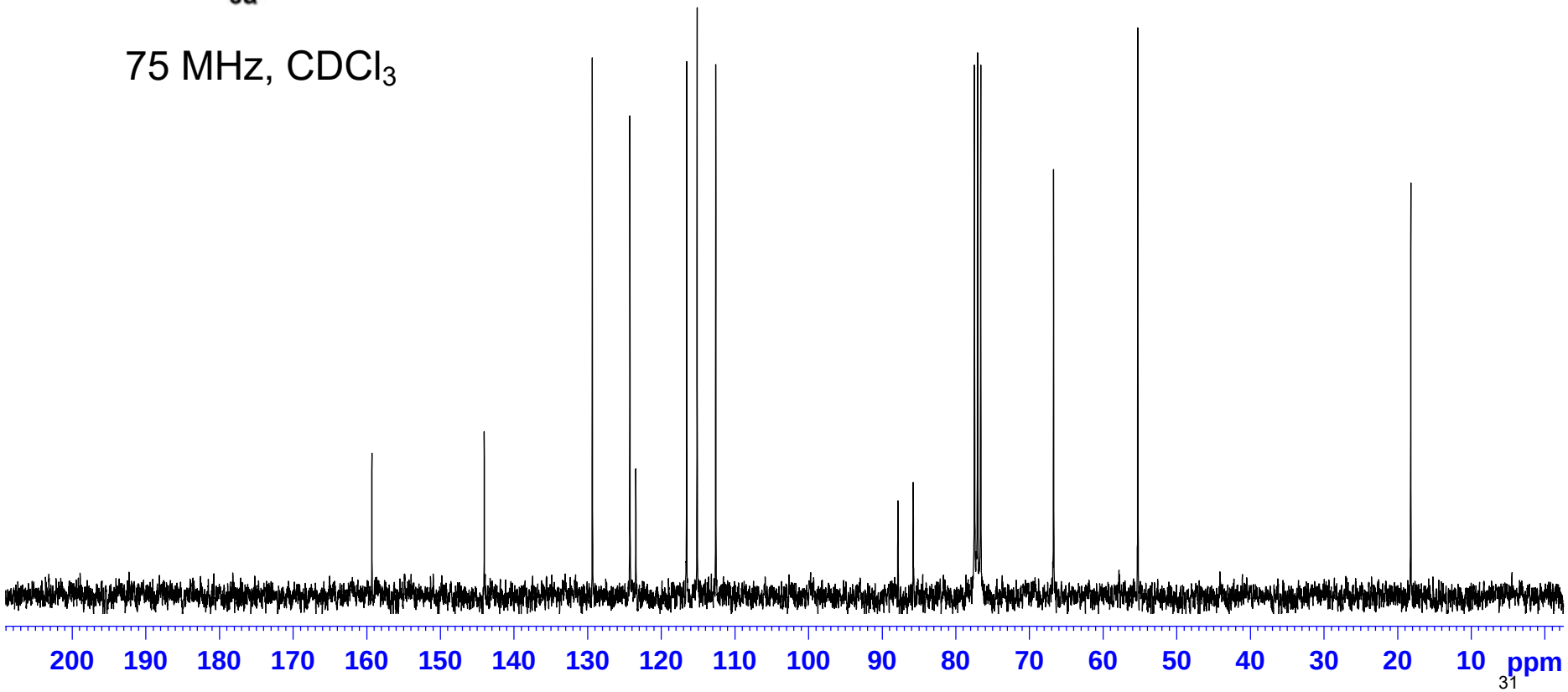
jrg.1447 5 13C 3-MeOPh-CC-methacol OH, 7/8/21

159.292
144.029
129.390
124.289
123.481
116.581
115.161
112.624
87.875
85.801
77.483
77.059
76.638
66.744
55.303
18.224

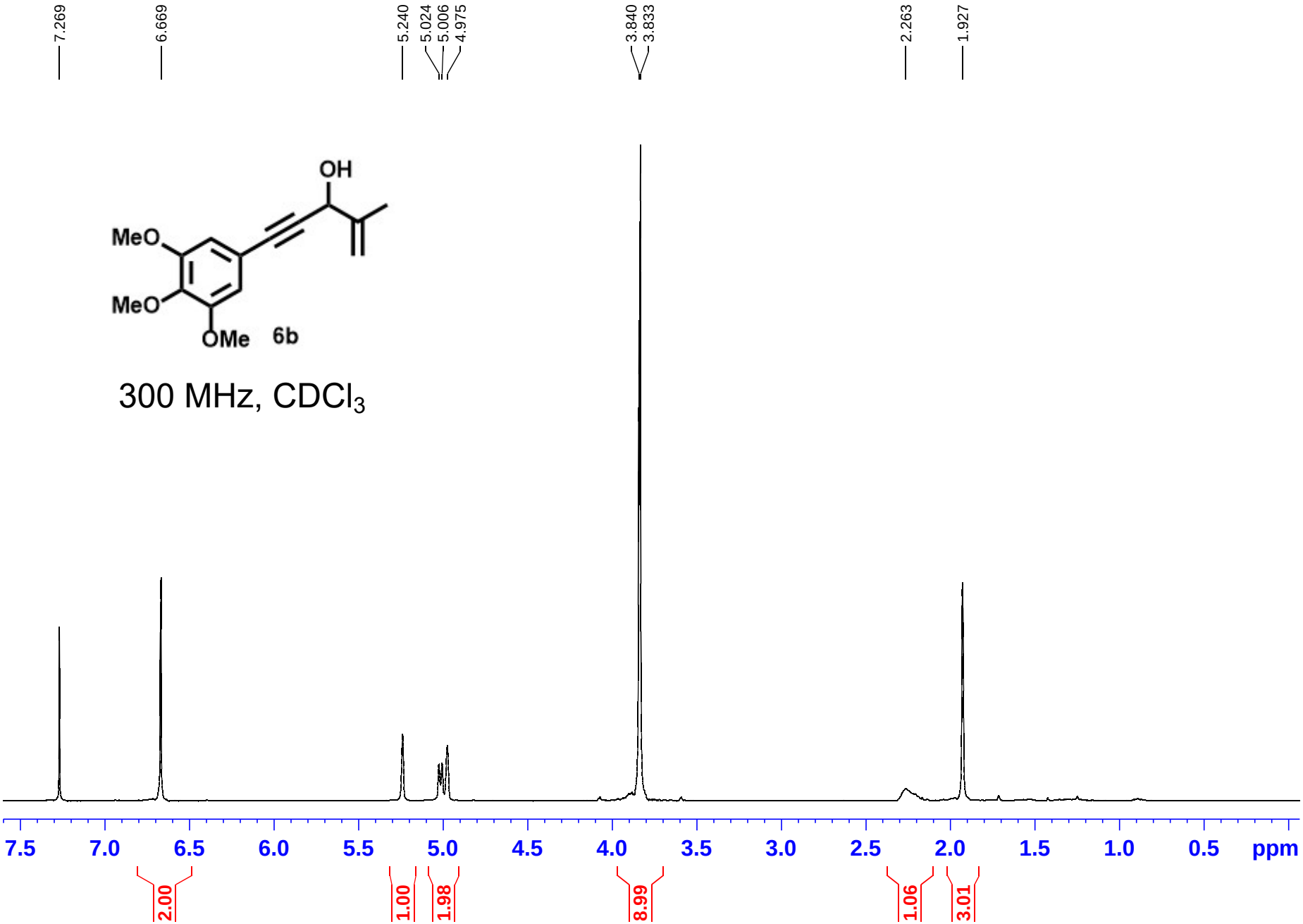


6a

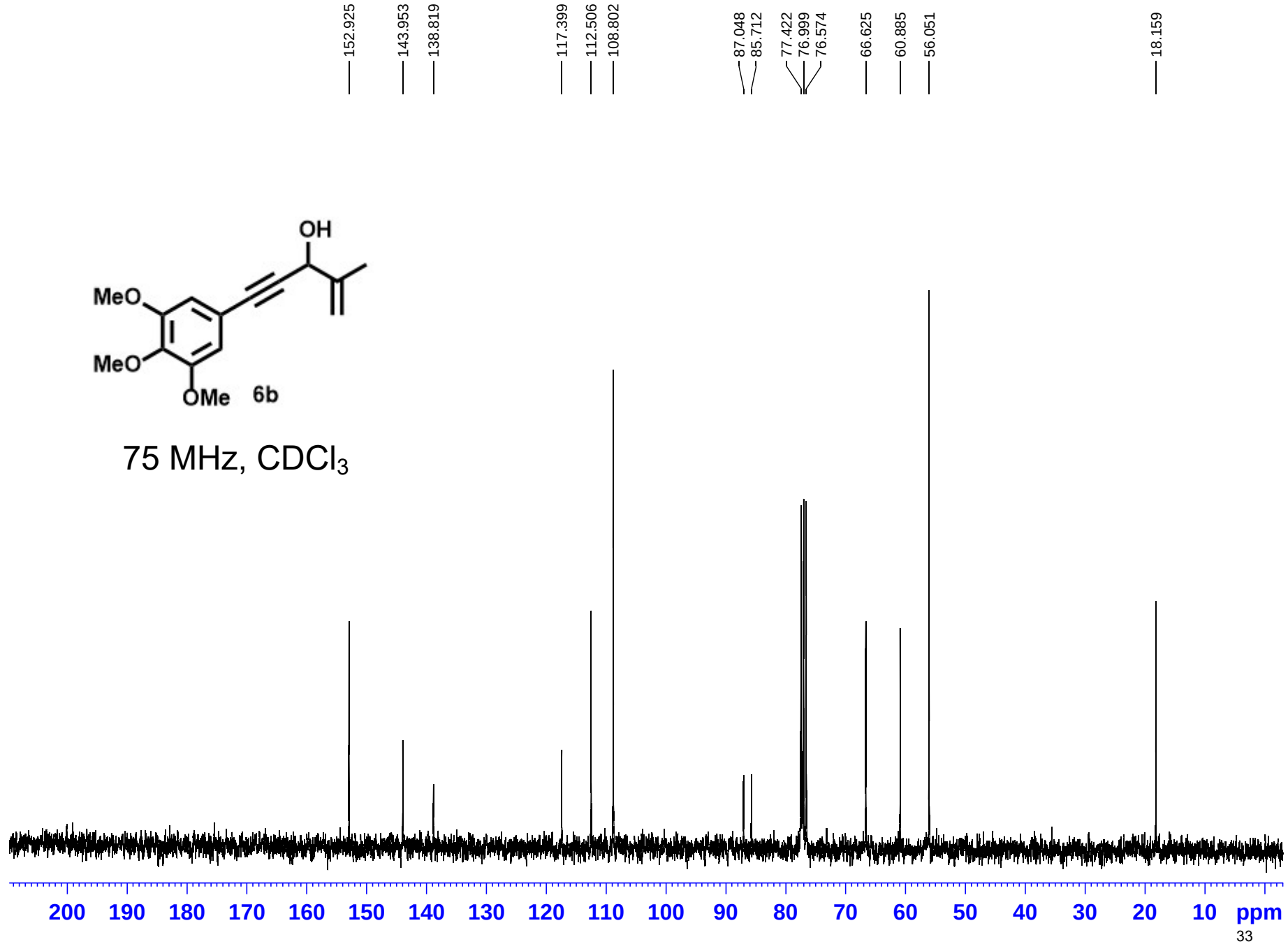
75 MHz, $CDCl_3$



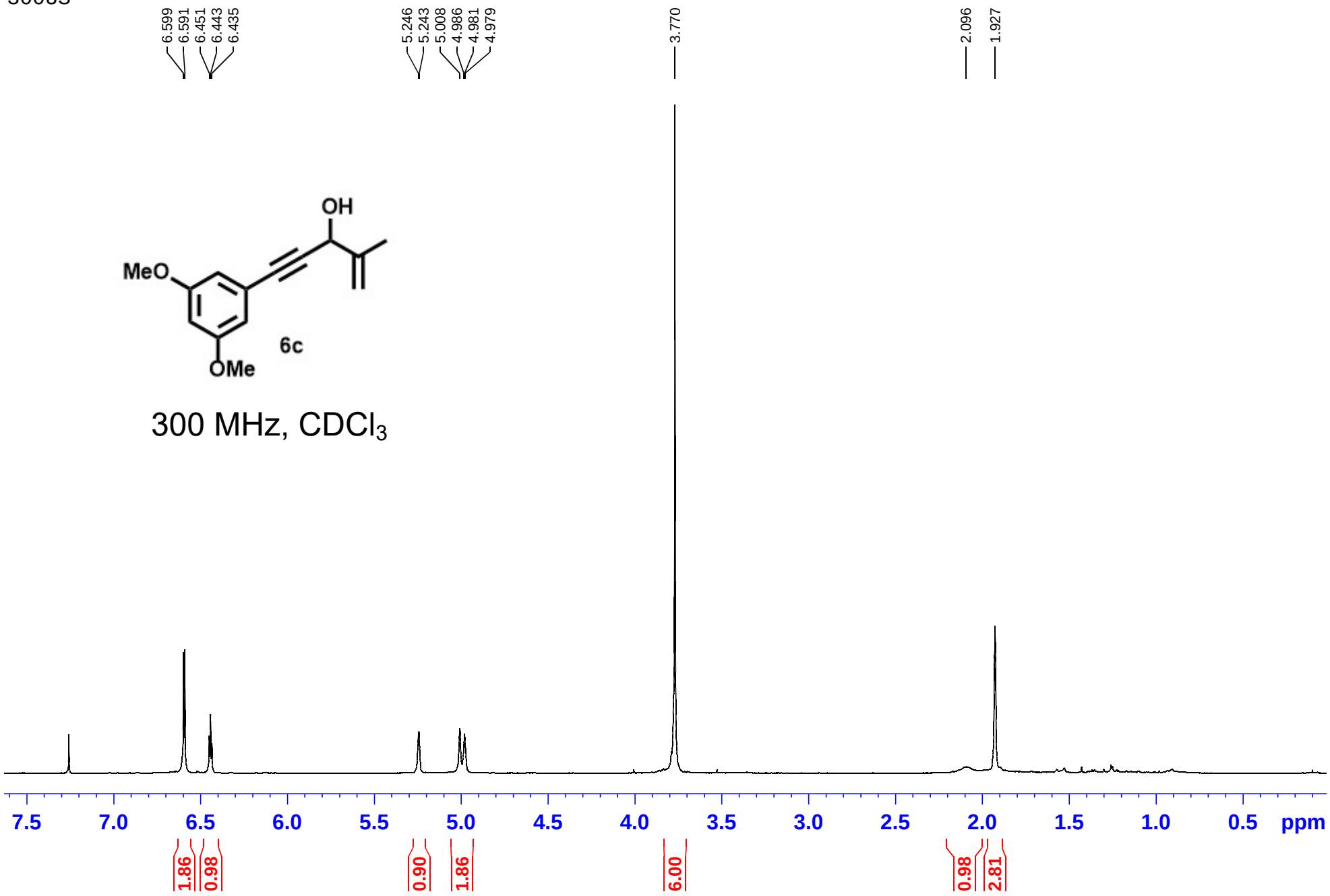
jrg.1240 8, low Rf fr, 345-MeO3Ph-CC-CH(OH)-C(Me)=CH2 prep, 1/11/16



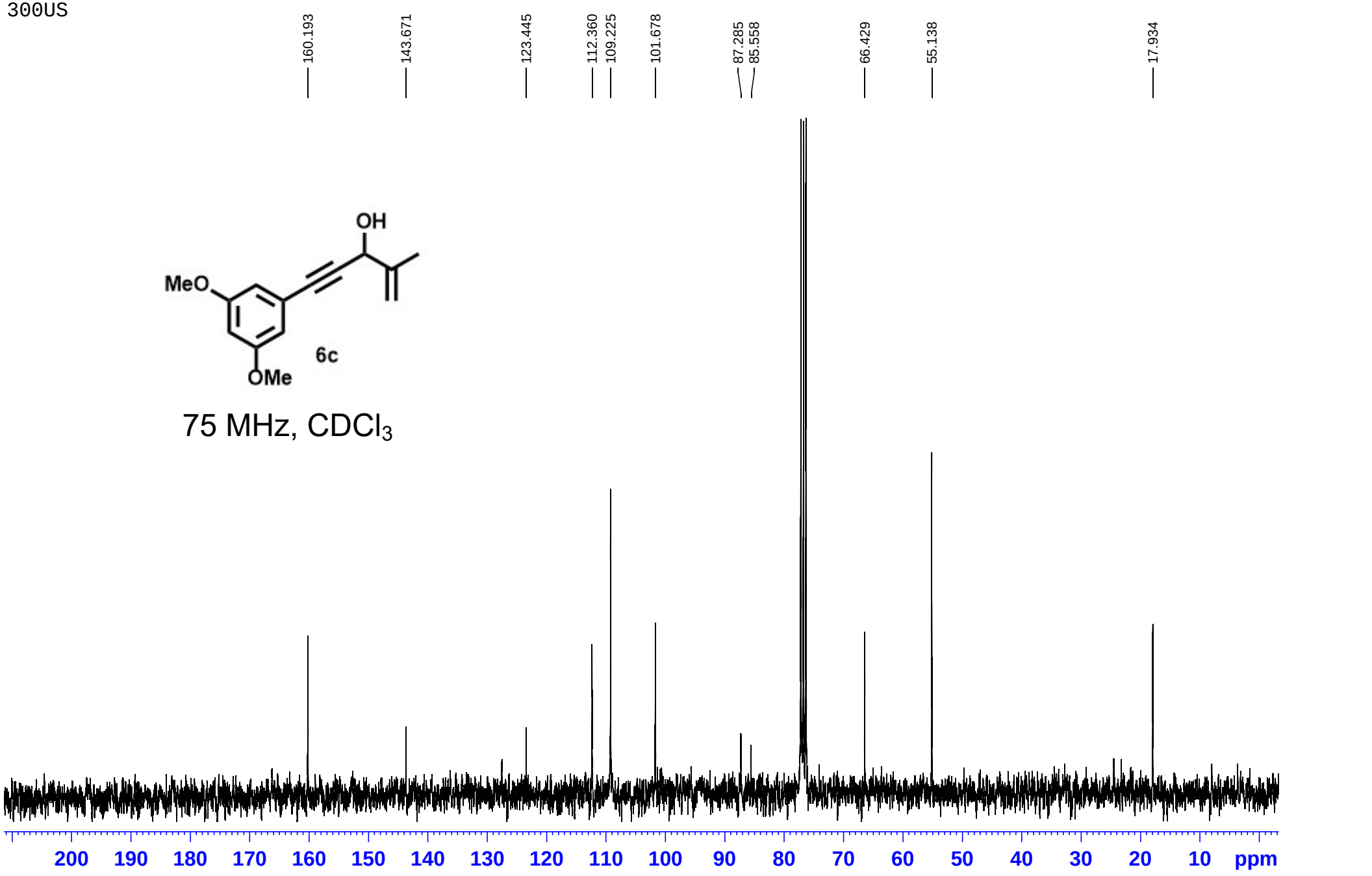
jrg.1240 9, 13C, (300US) 345-MeO3Ph-CC-CH(OH)-C(Me)=CH2, 1/11/16



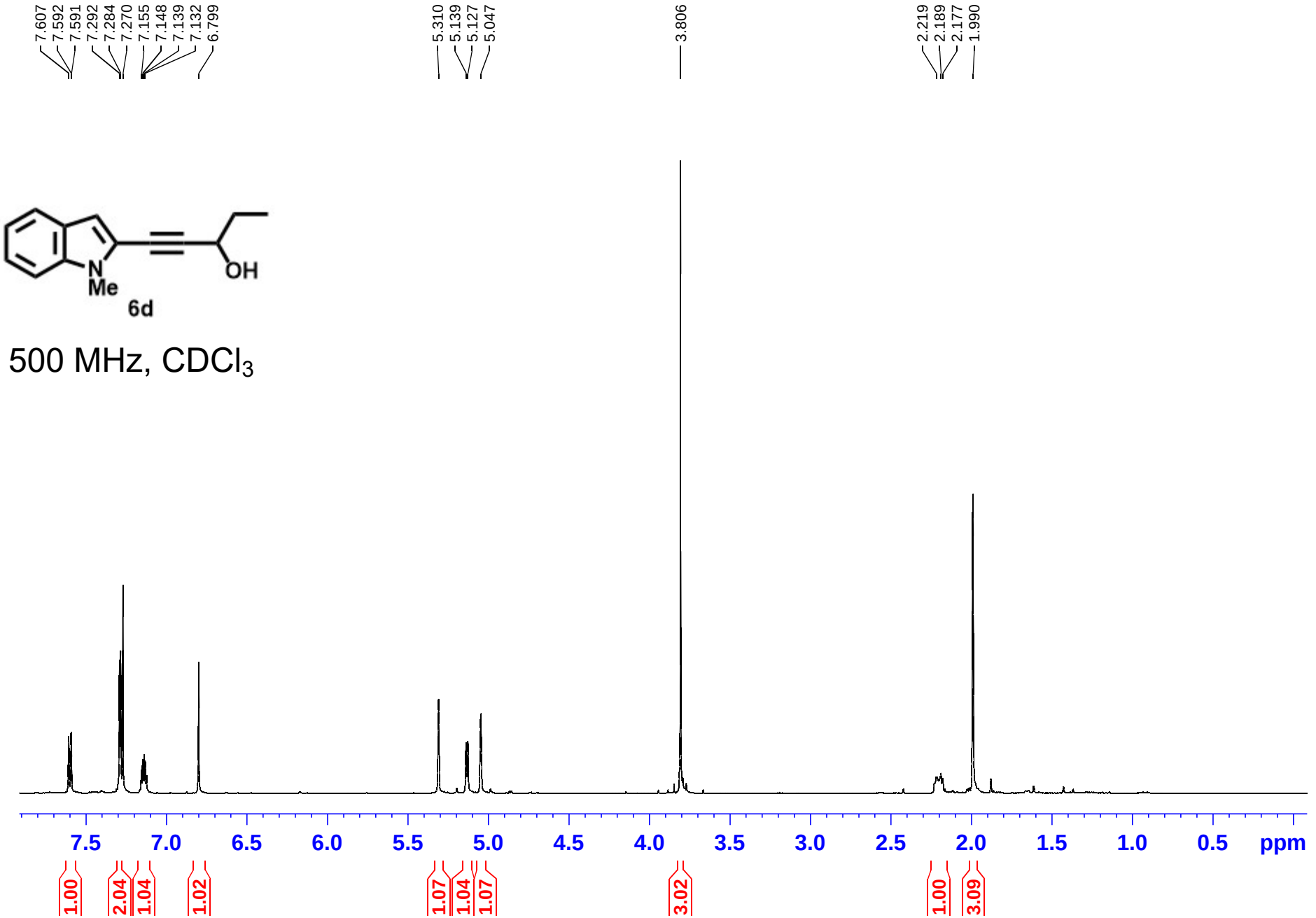
project2_dimethoxy_Metha_OH_H1
300US



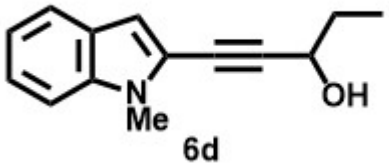
project2_dimethoxy_Metha_OH_C13
300US



jrg.1238 12, N-Me -2-CC-CH(OH)-C(Me)=CH2 indole, 1/3/16



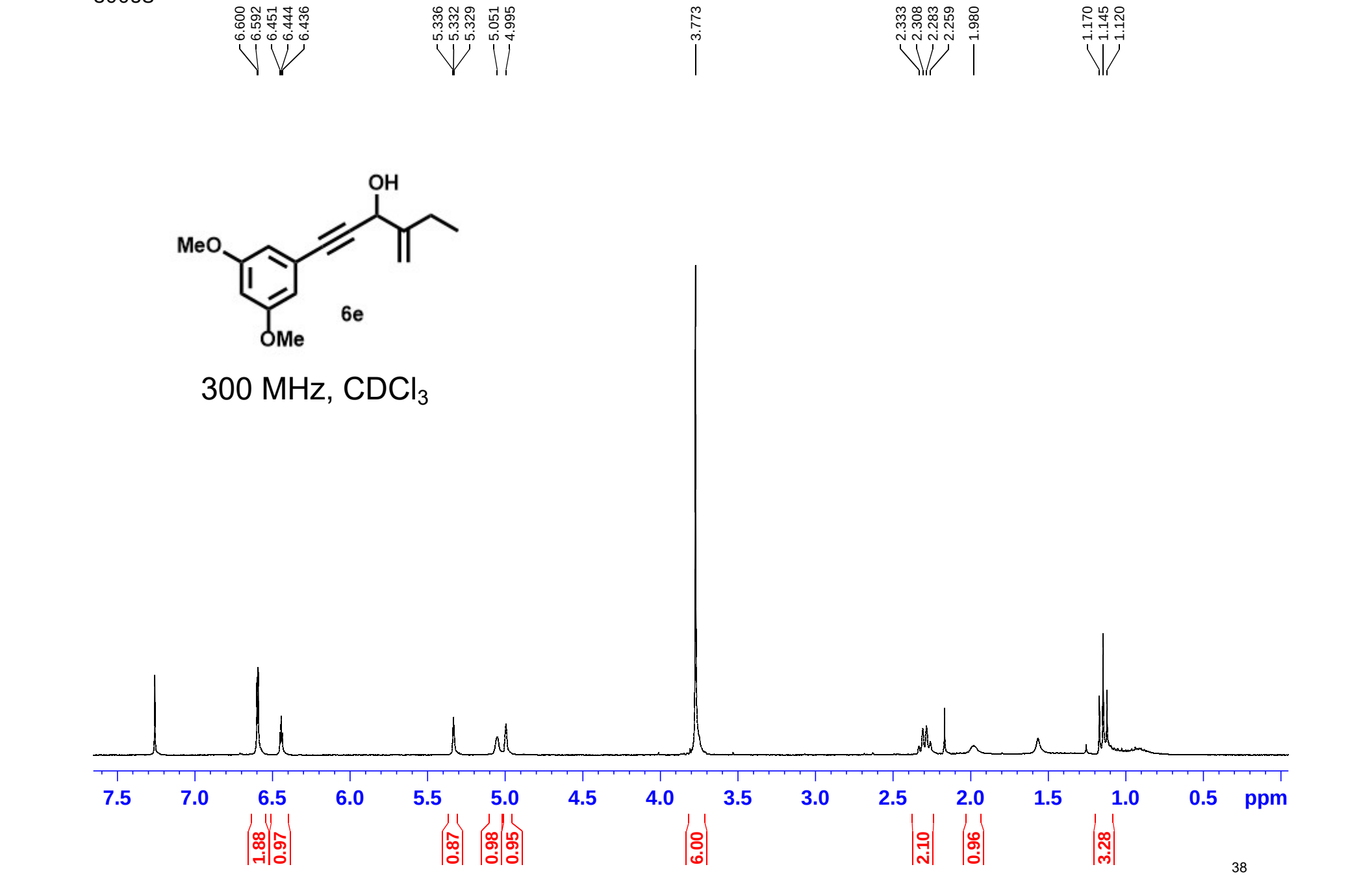
jrg.1238 14, 13C, N-Me , 2-CC-CH(OH)-C(Me)=CH2 indole, 1/3/16



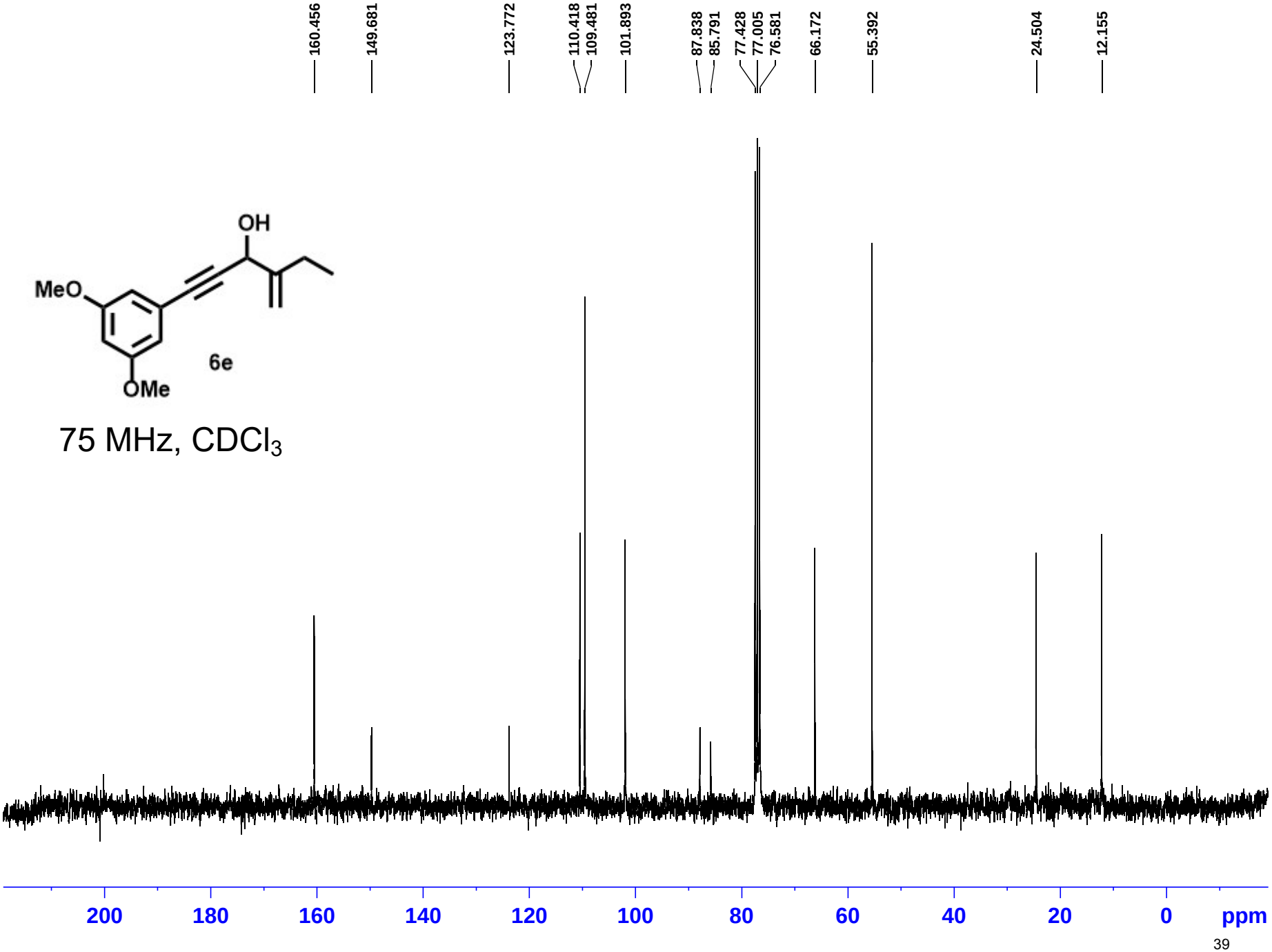
6d

125 MHz, $CDCl_3$

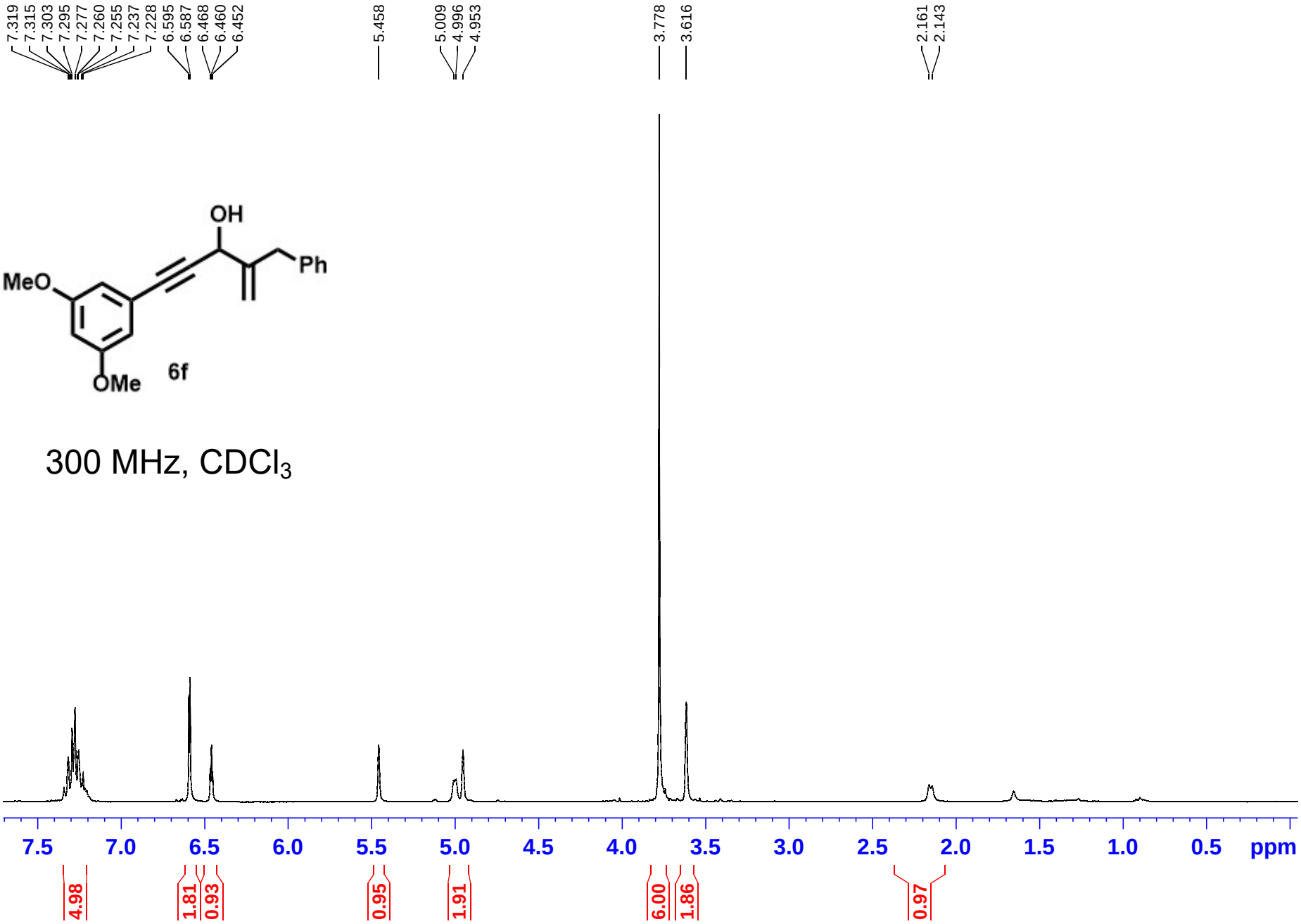
2MeO_cc_OH_ch2ch3_f2_2
300US



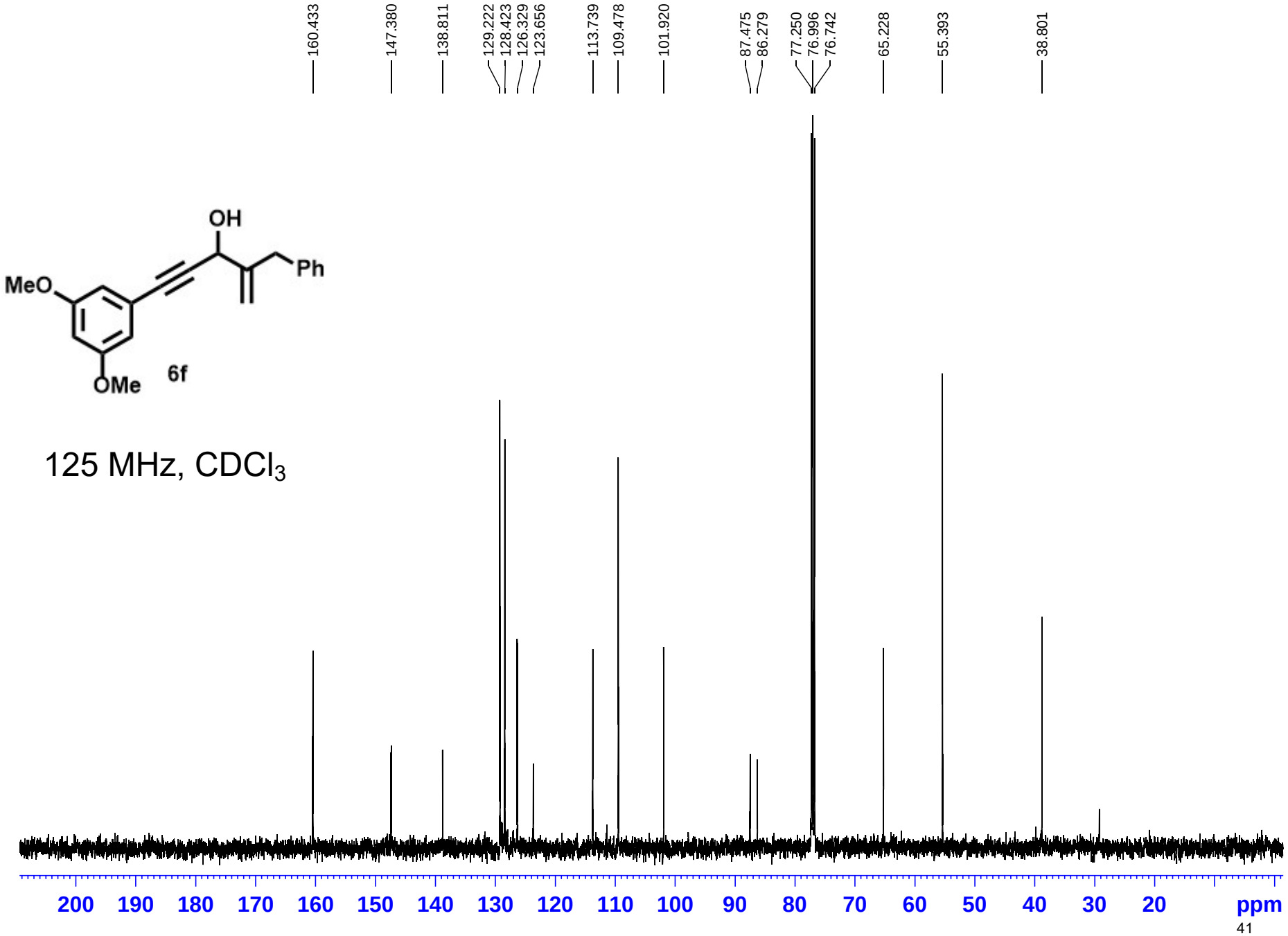
jrg.1283 10, 13C, 3,5-MeO)2Ph-CC-CH(OH)(Et)=CH2, 7/18/17



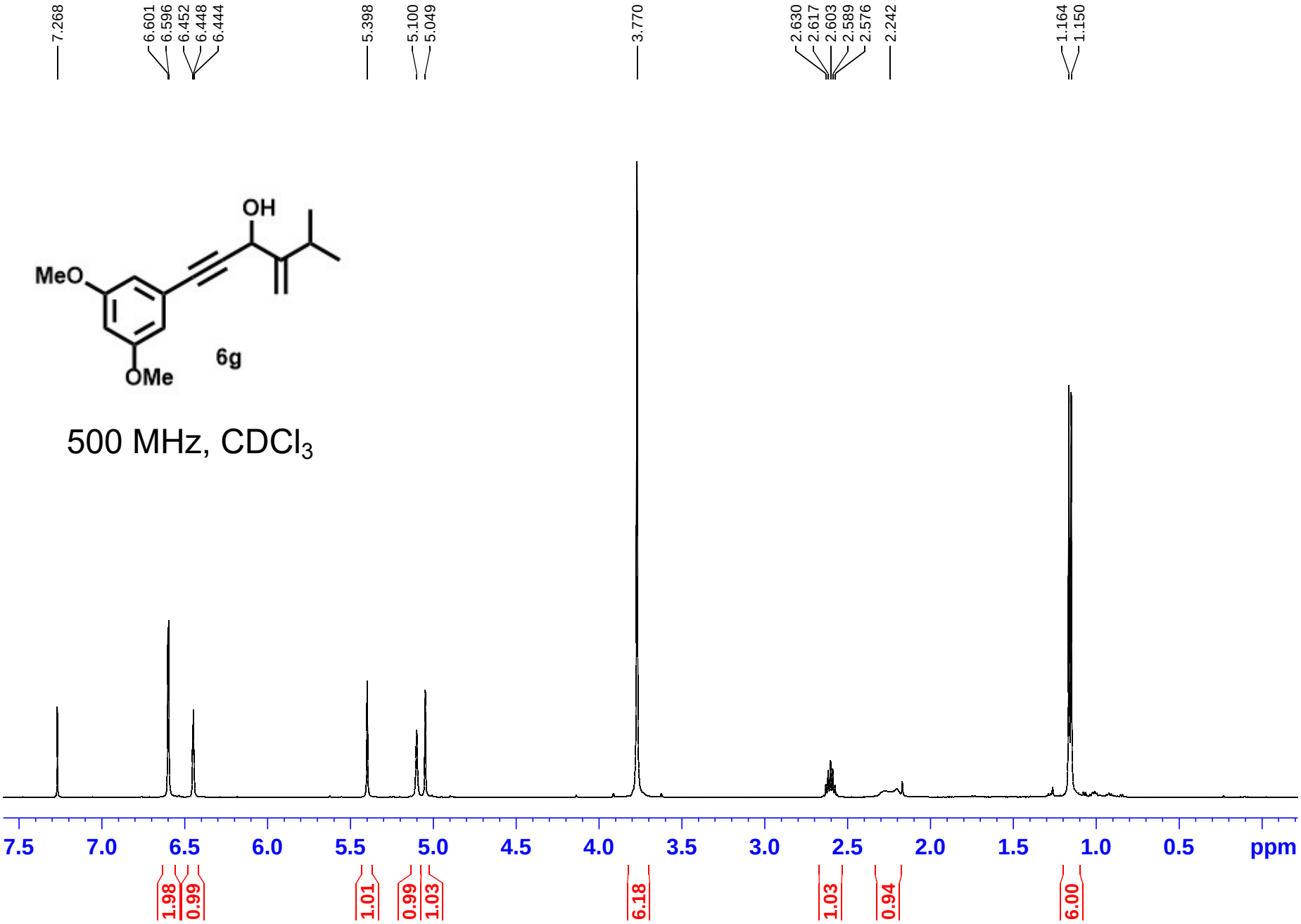
2MeO_cc_OH_Bn_H1 1D 1H DPX300



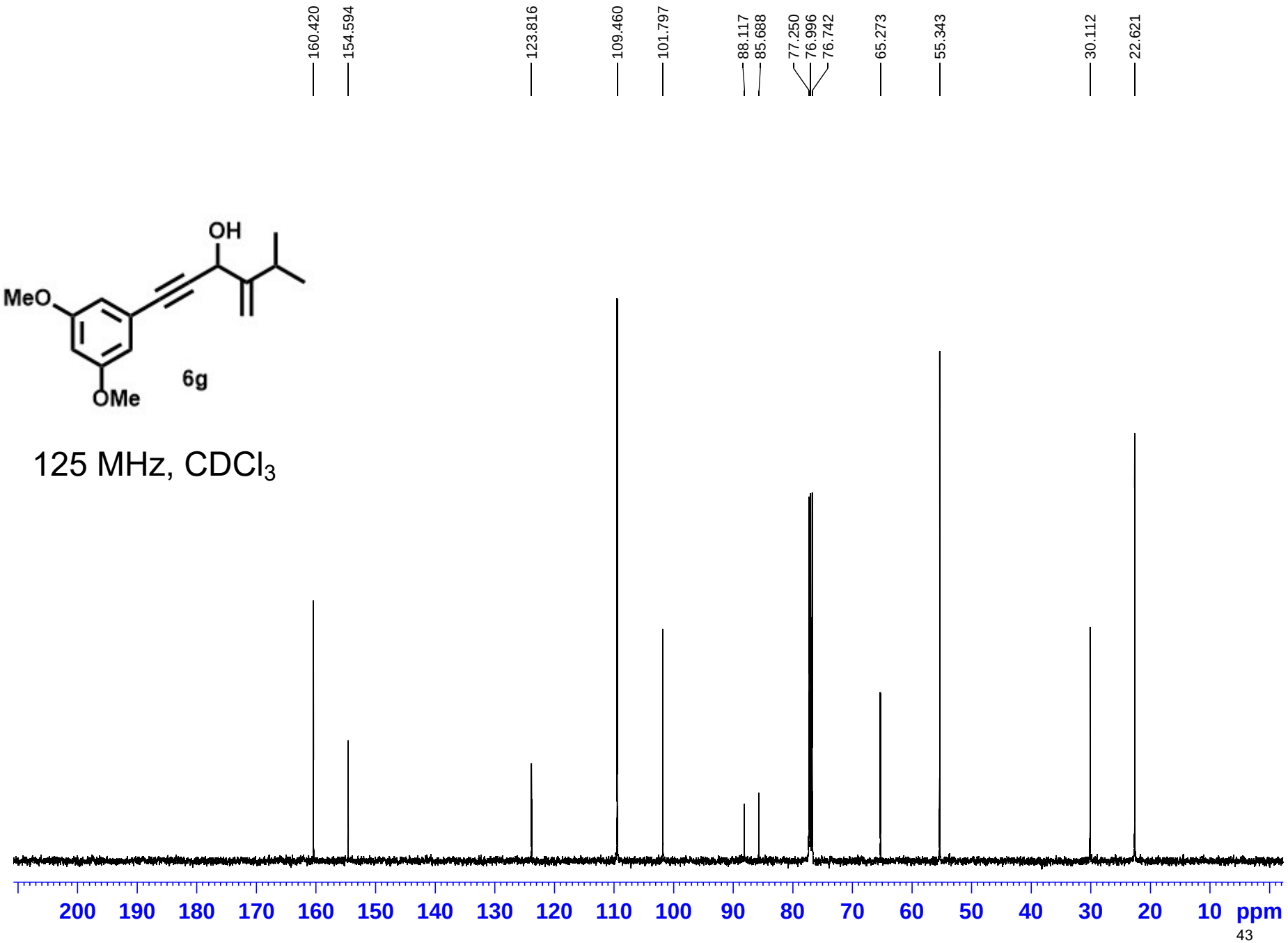
jrg.1281 7, 13C, 3,5-di(OMe)Ph-CC-CH(OH)-C(Bn)=CH2



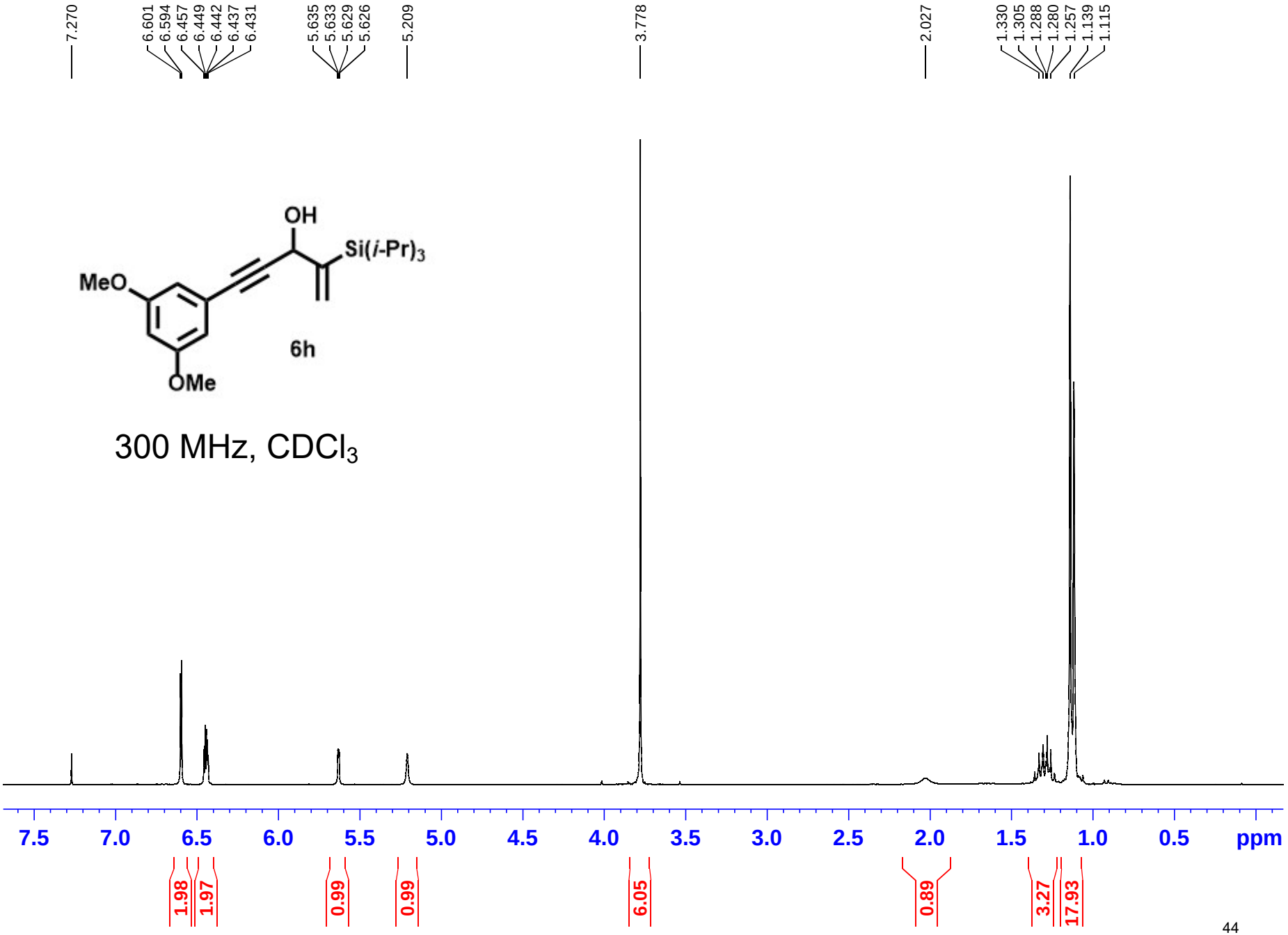
som.06f 1 1H, (MeO)2Ph-CC-CH(OH)-C(iPr)=CH2, 9/2/21



som.06f 2 13C, (MeO)2Ph-CC-CH(OH)-C(iPr)=CH2, 9/2/21

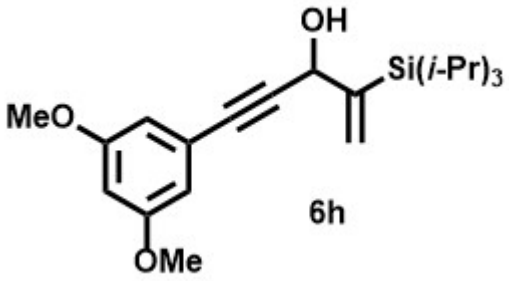


jrg.1457 9, (MeO)2Ph-CC-CH(OH)-C(TIPS)=CH2, 9/17/21



jrg.1457 8, 13C, (MeO)2Ph-CC-CH(OH)-C(TIPS)=CH2, B82, 9/17/21

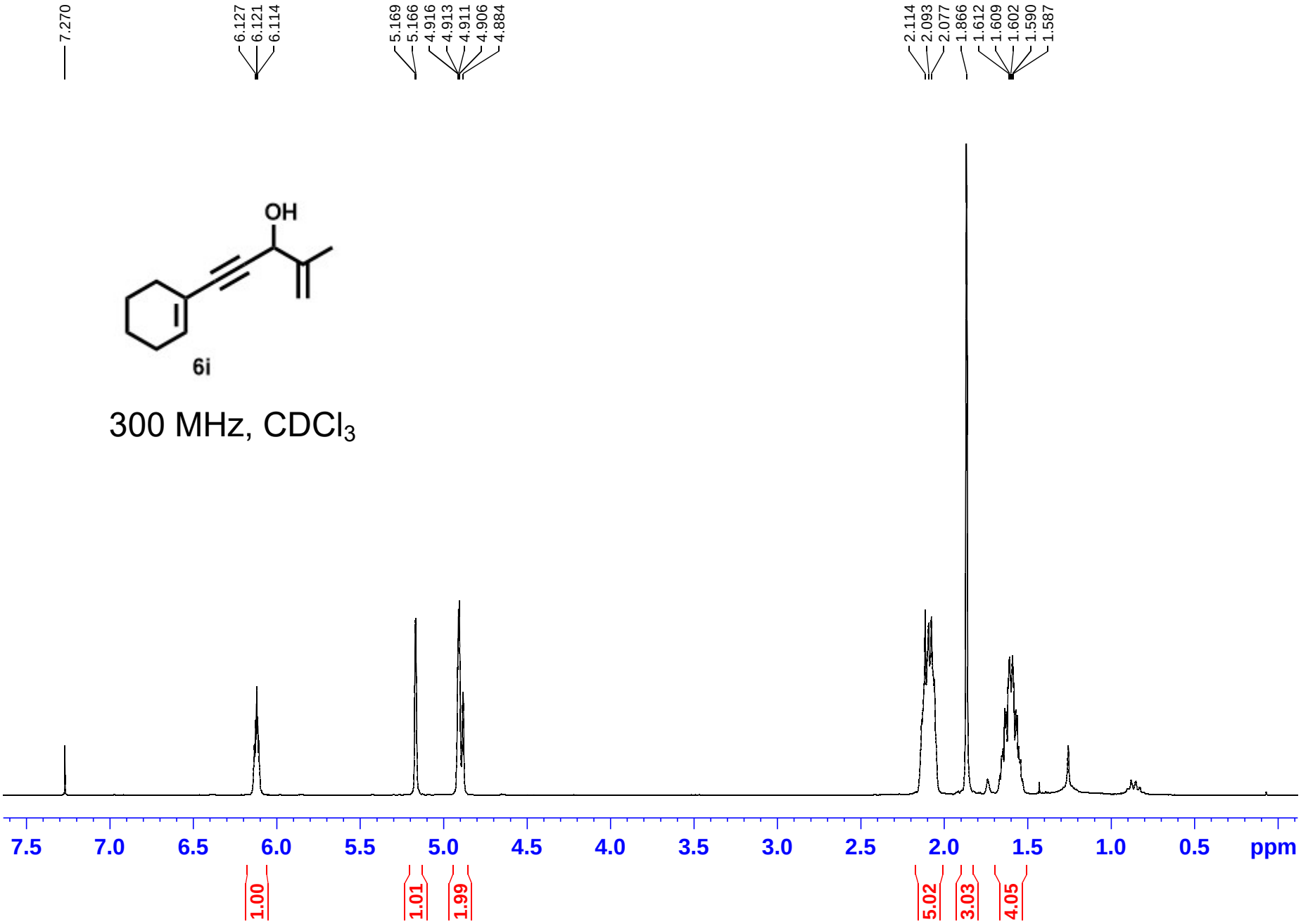
160.446
146.500
128.993
124.019
109.392
101.755
88.833
86.434
77.430
77.007
76.583
65.493
55.358
18.783
11.274



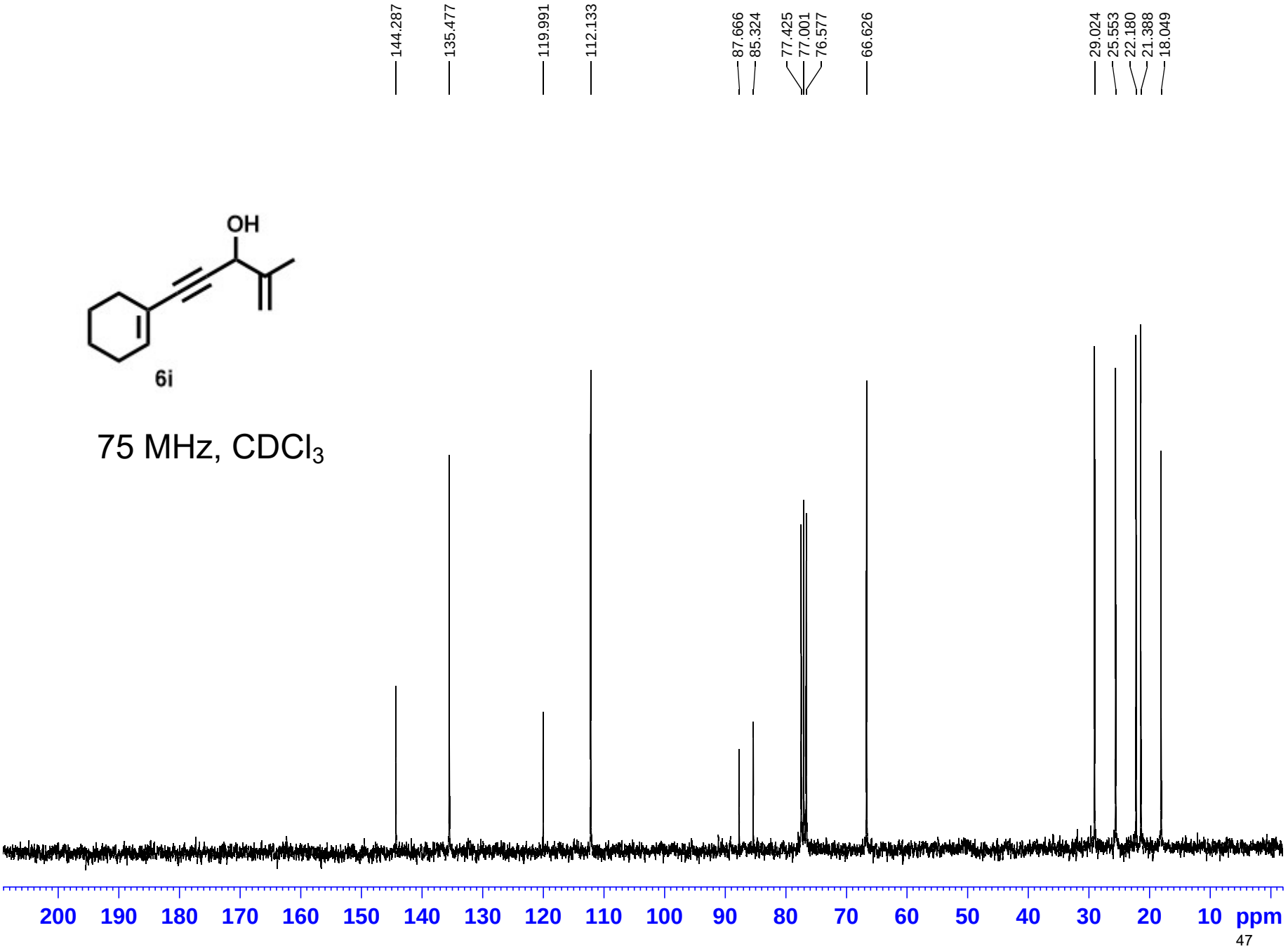
6h

75 MHz, $CDCl_3$

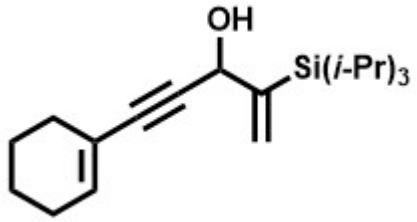
som.06i 2, cyclohexenyl-CC-C(OH)-C(Me)=CH2, B82, 8/16/21



som.06i 3, 13C, cyclohexenyl-CC-C(OH)-C(Me)=CH2, B82, 8/16/21



som.06j 1, cyclohexenyl-CC-C(OH)-C(TIPS)=CH2, B82 8/10/21

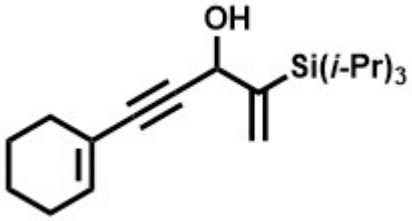


6j

300 MHz, $CDCl_3$

som.06j 2 13C, cyclohexenyl-CC-C(OH)-C(TIPS)=CH2, B82, 8/10/21

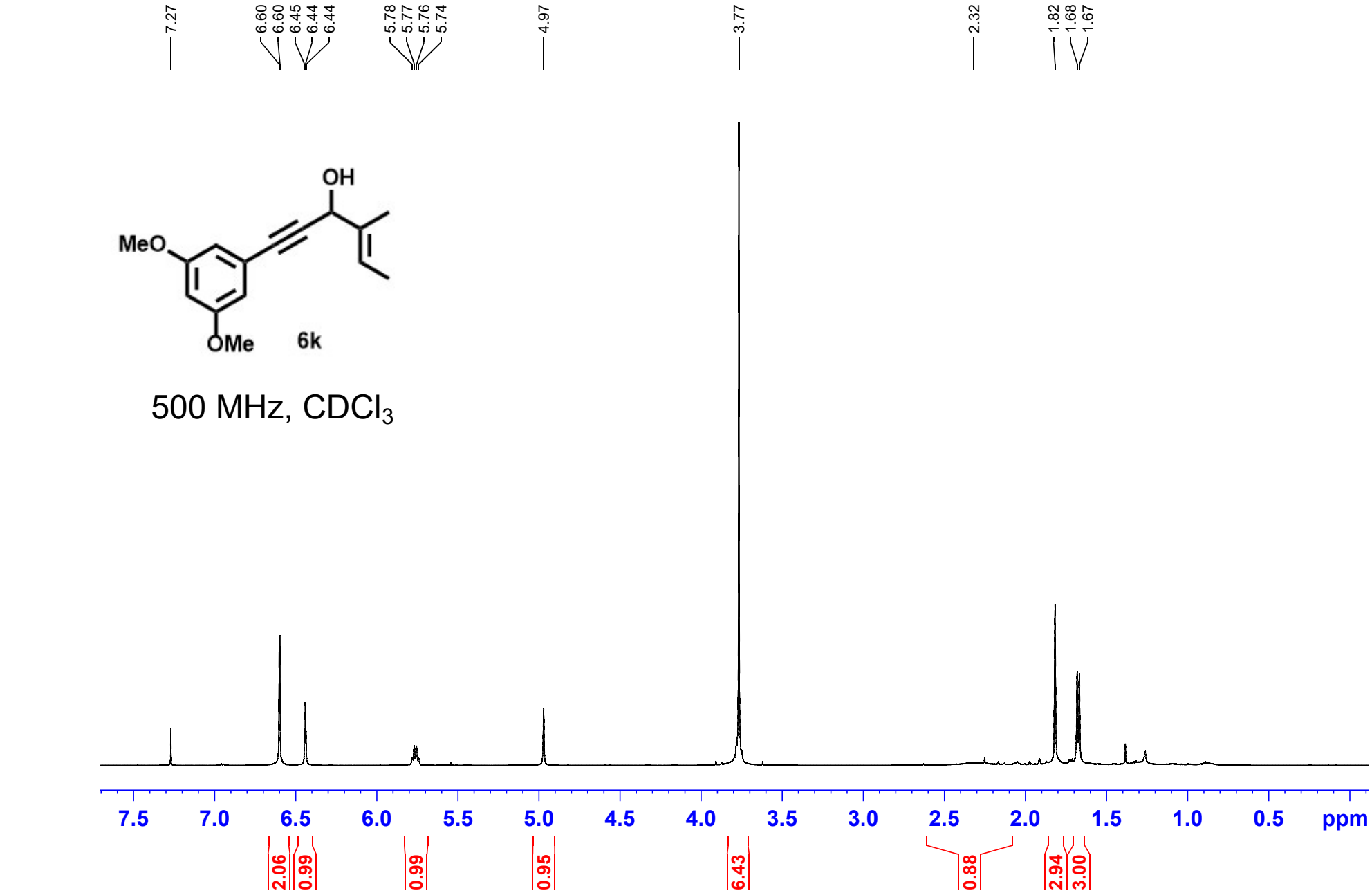
146.761
135.051
128.624
120.211
88.386
86.450
77.414
76.993
76.569
65.503
29.024
25.587
22.237
21.443
18.766
11.244



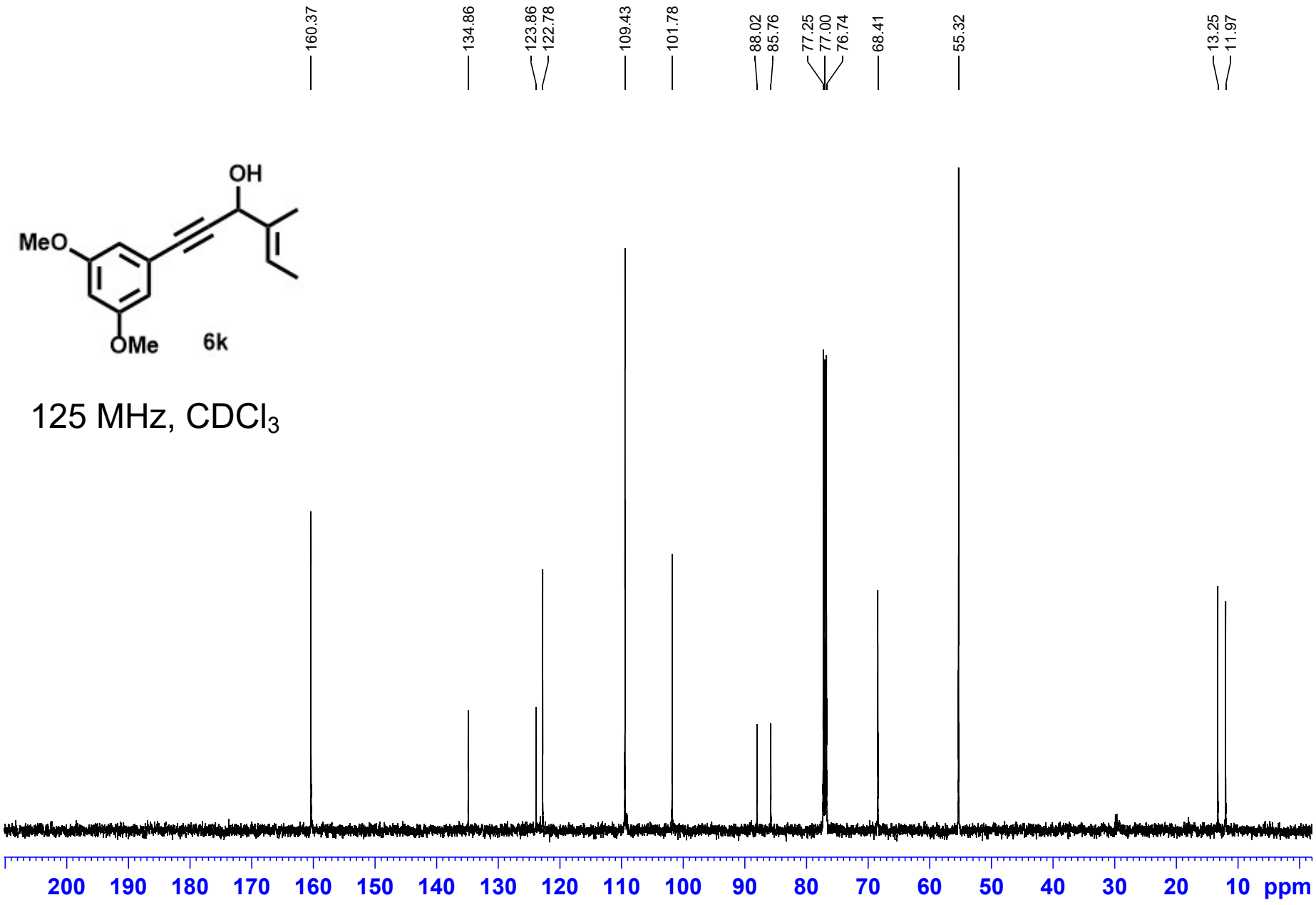
6j

75 MHz, $CDCl_3$

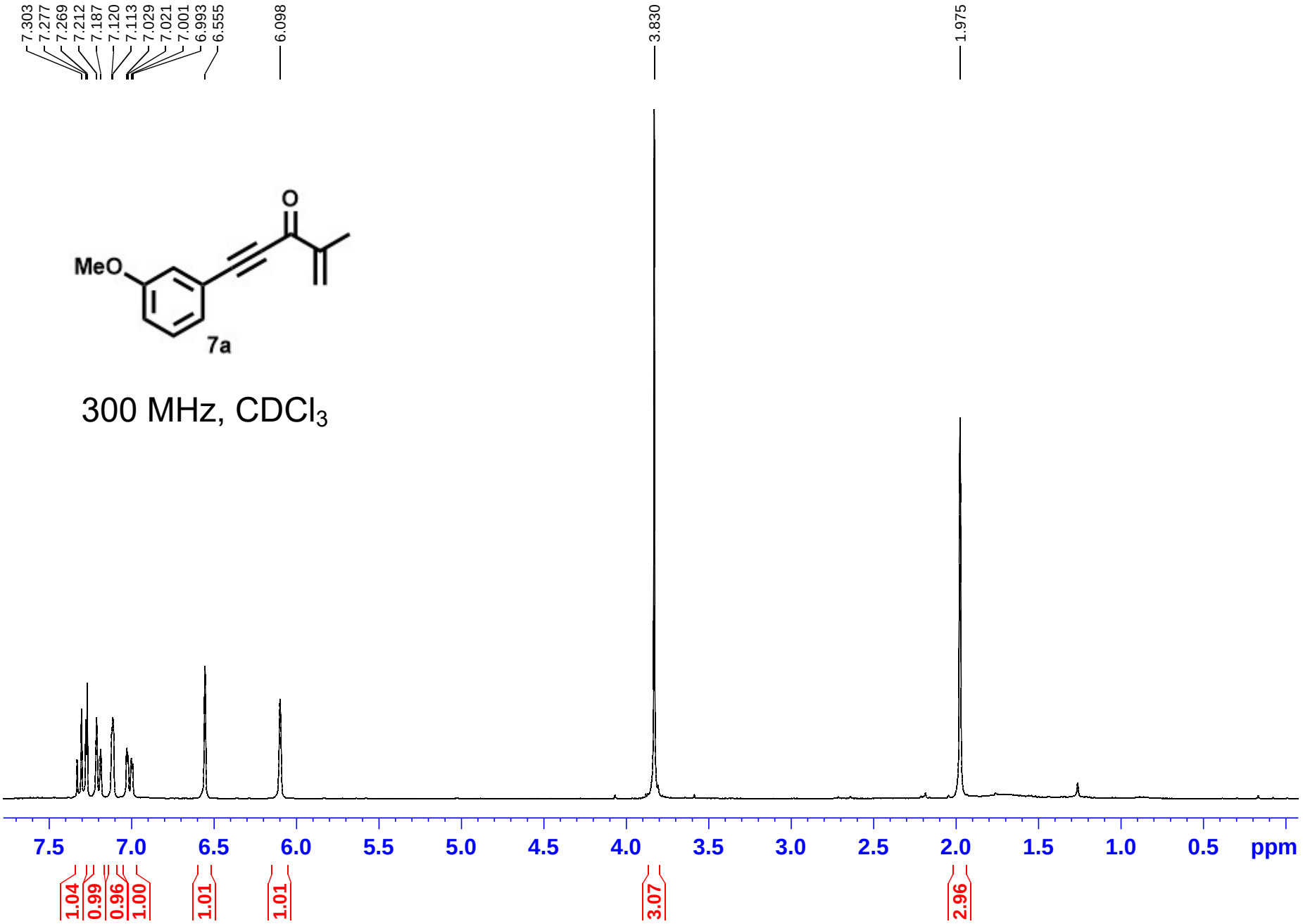
jrg.1459 1, (MeO)2Ph-CC-CH(OH)-C(Me)=CHMe, 9/18/21



jrg.1459 2, 13C, (MeO)2Ph-CC-CH(OH)-C(Me)=CH(Me), 9/18/21

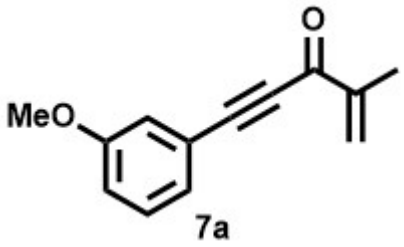


jrg.1448 July 8, 2021 300US



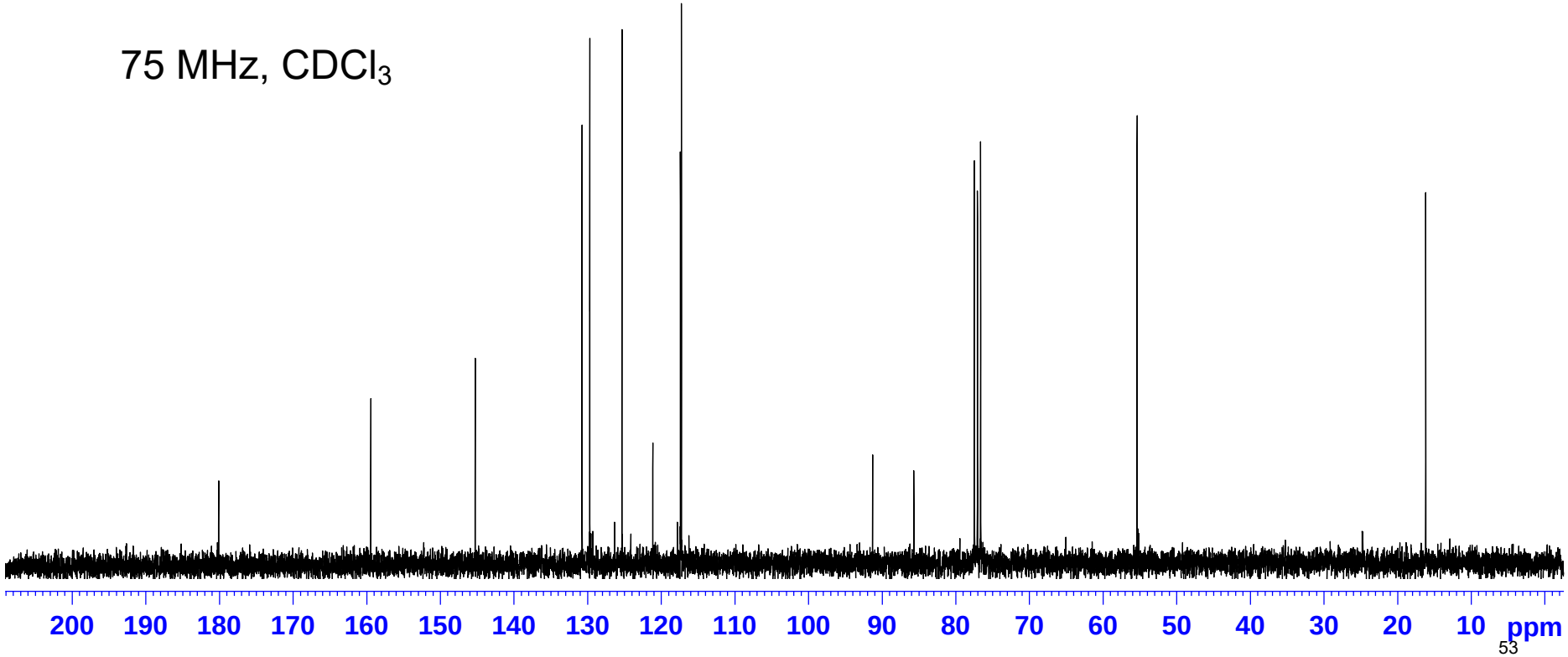
jrg.1448 2, 13C, 3-MeOPh-CC-methacol ketone, 300 B82, 7/8/21

180.096
159.437
145.263
130.795
129.739
125.365
121.171
117.290
91.311
85.716
77.498
77.076
76.653
16.199

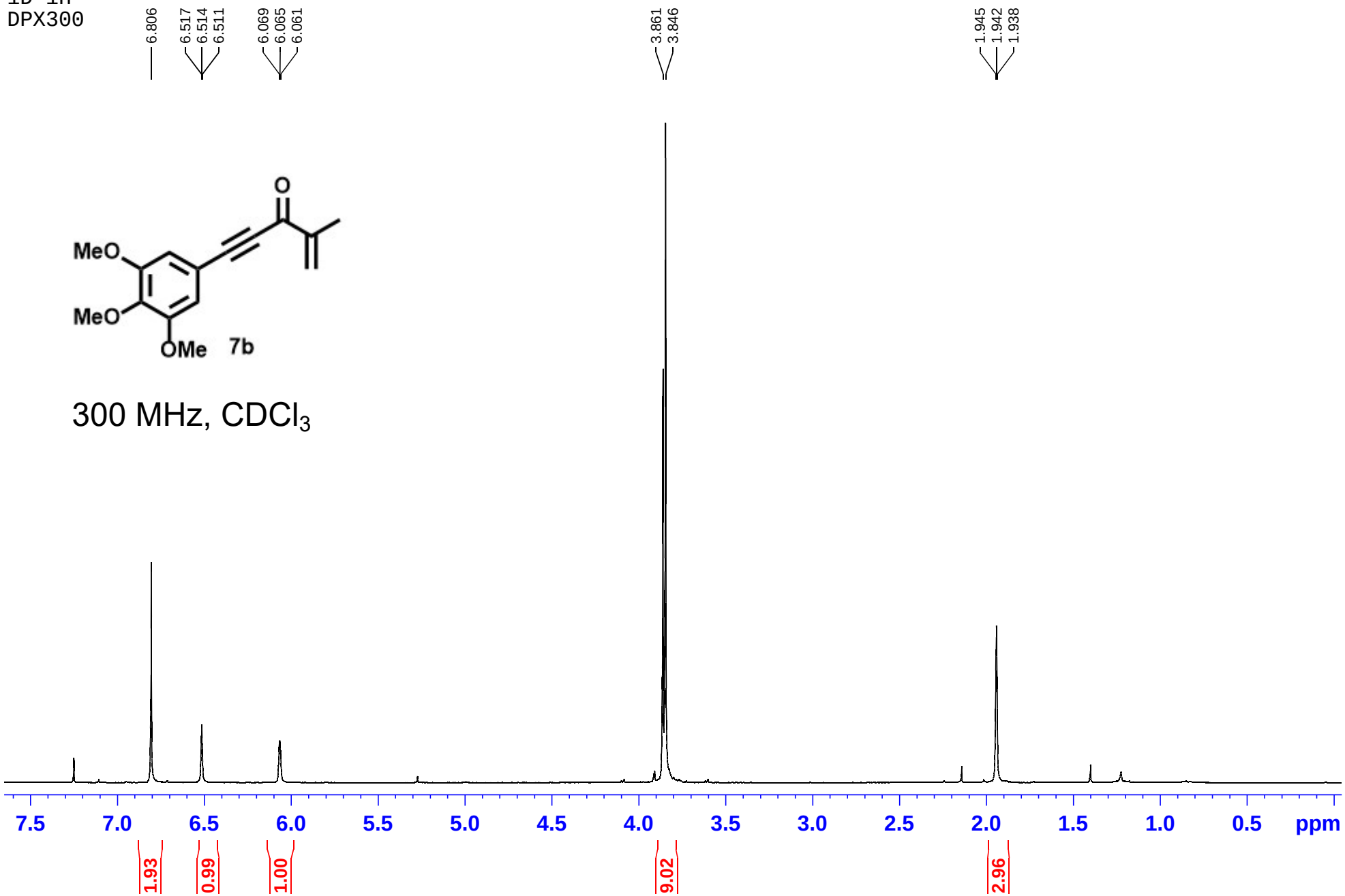


7a

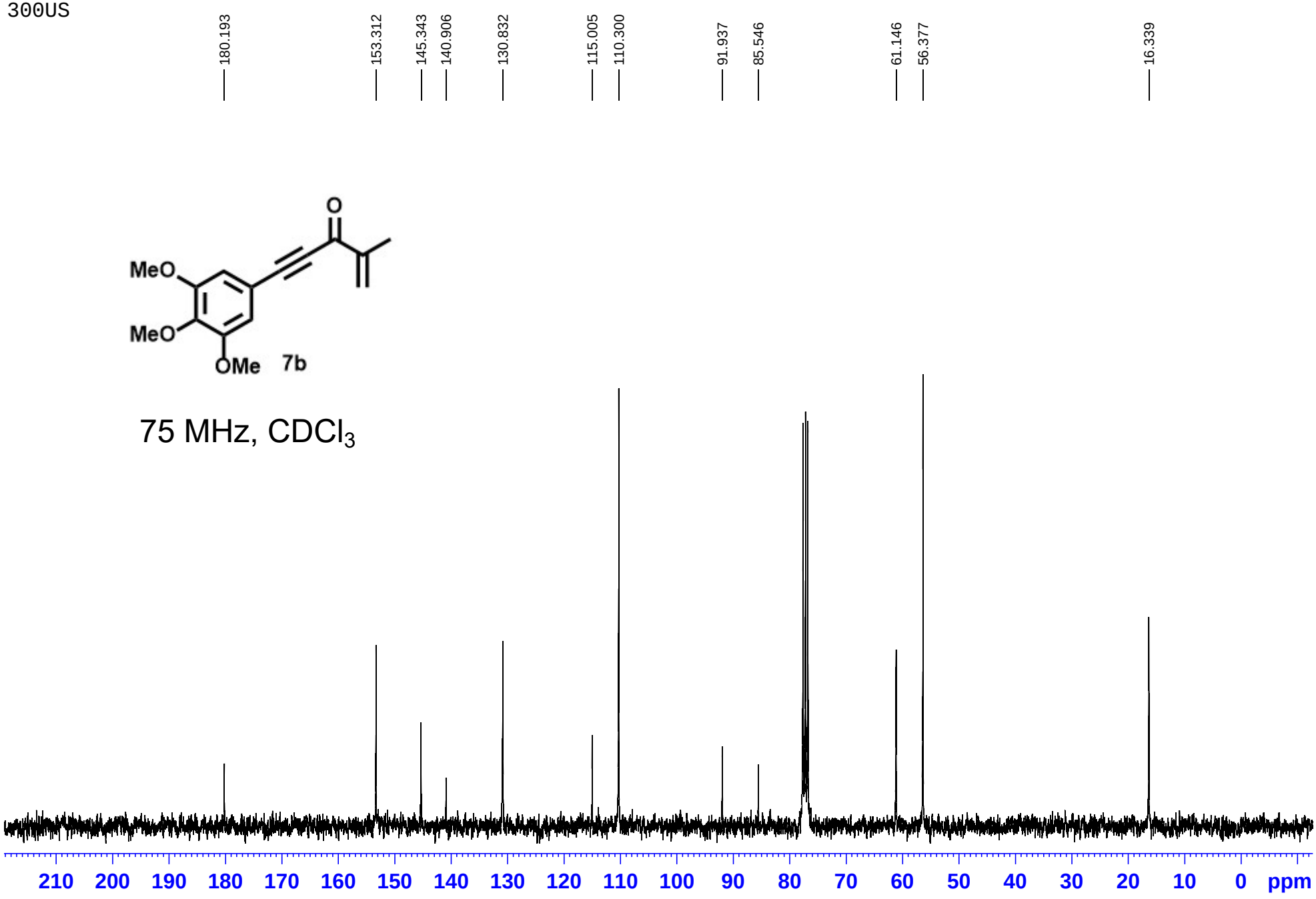
75 MHz, $CDCl_3$



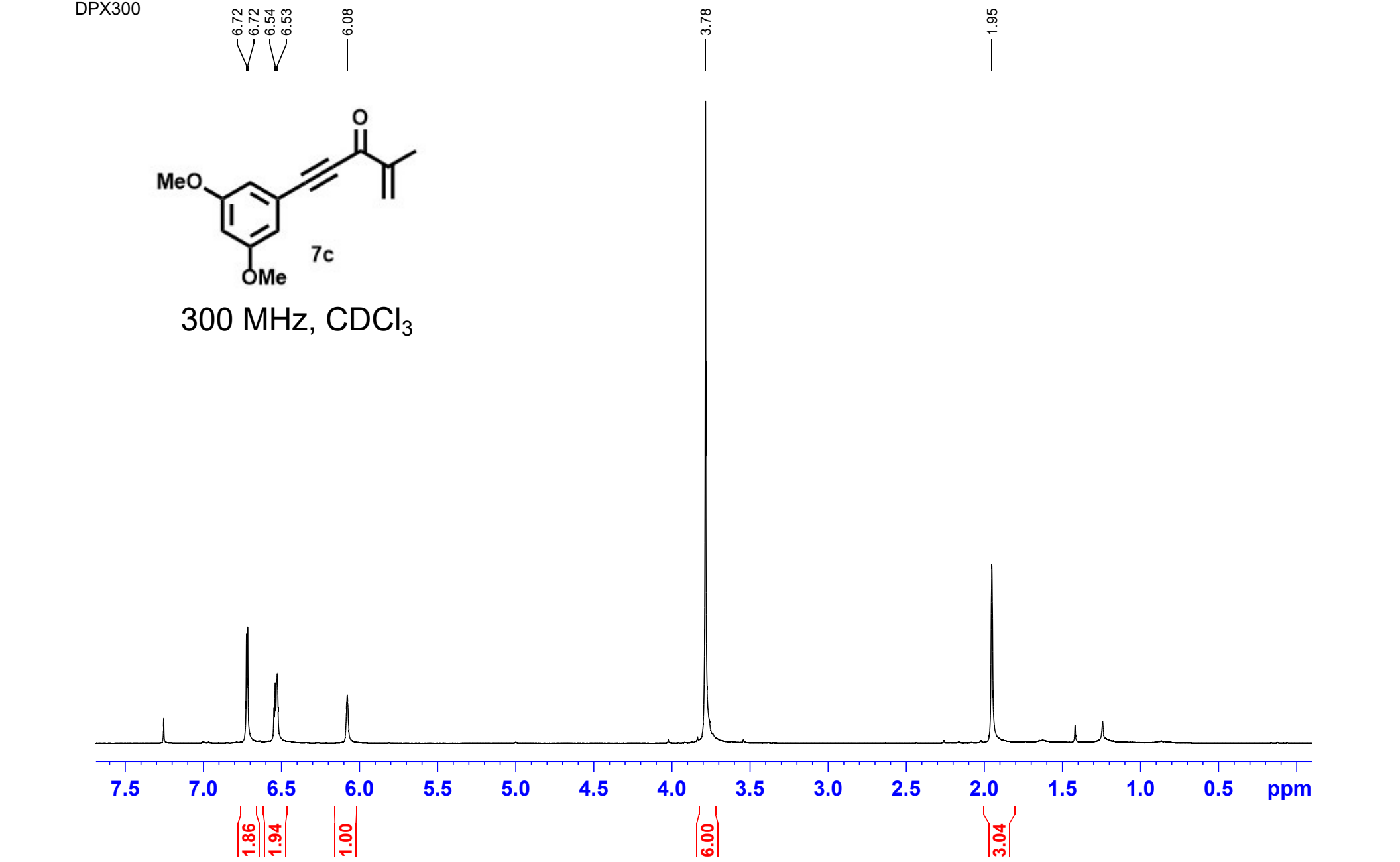
project4_trimethoxy_PDC_ox_crude
1D 1H
DPX300



project4_trimethoxy_PDC_ox_C13
300US

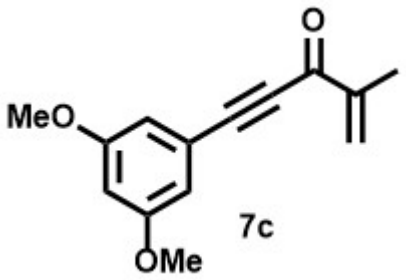


Project2_P4_PDC_PURE
1D 1H
DPX300



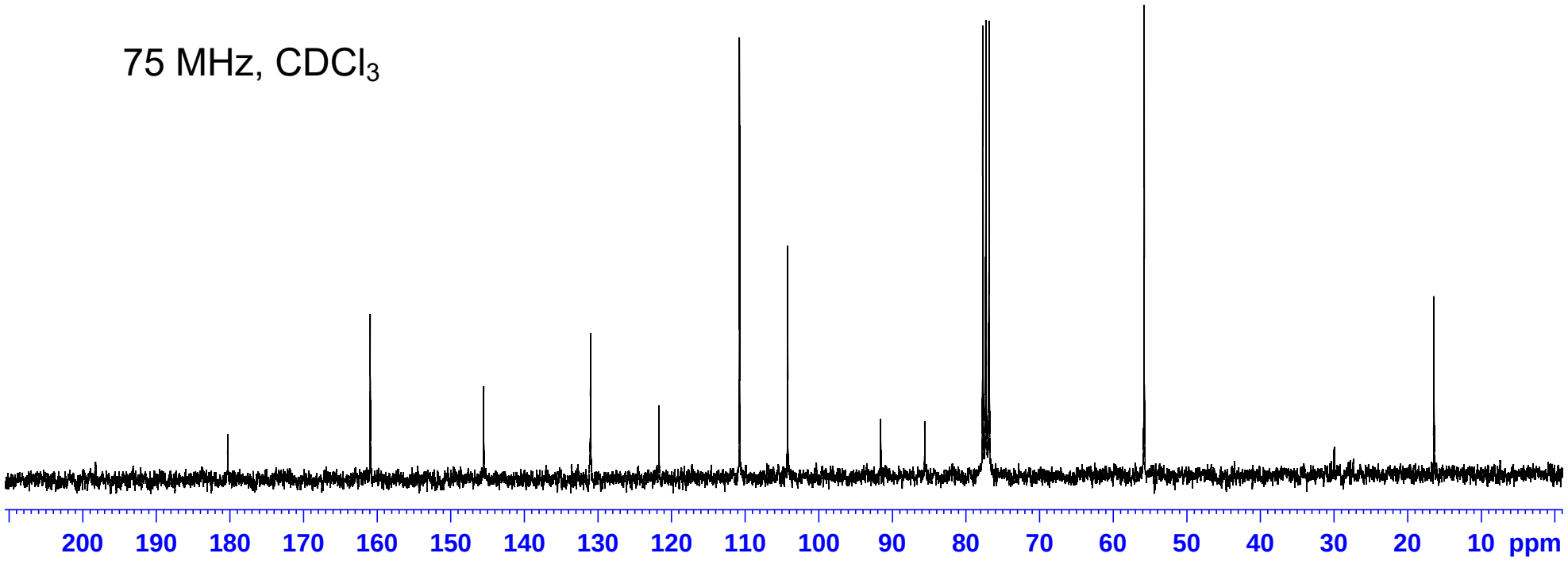
Project2_P4_PDC_C13
standard 1D 13C experiment
DPX300

180.283
160.932
145.513
130.987
121.702
110.764
104.219
91.587
85.604
55.786
16.413

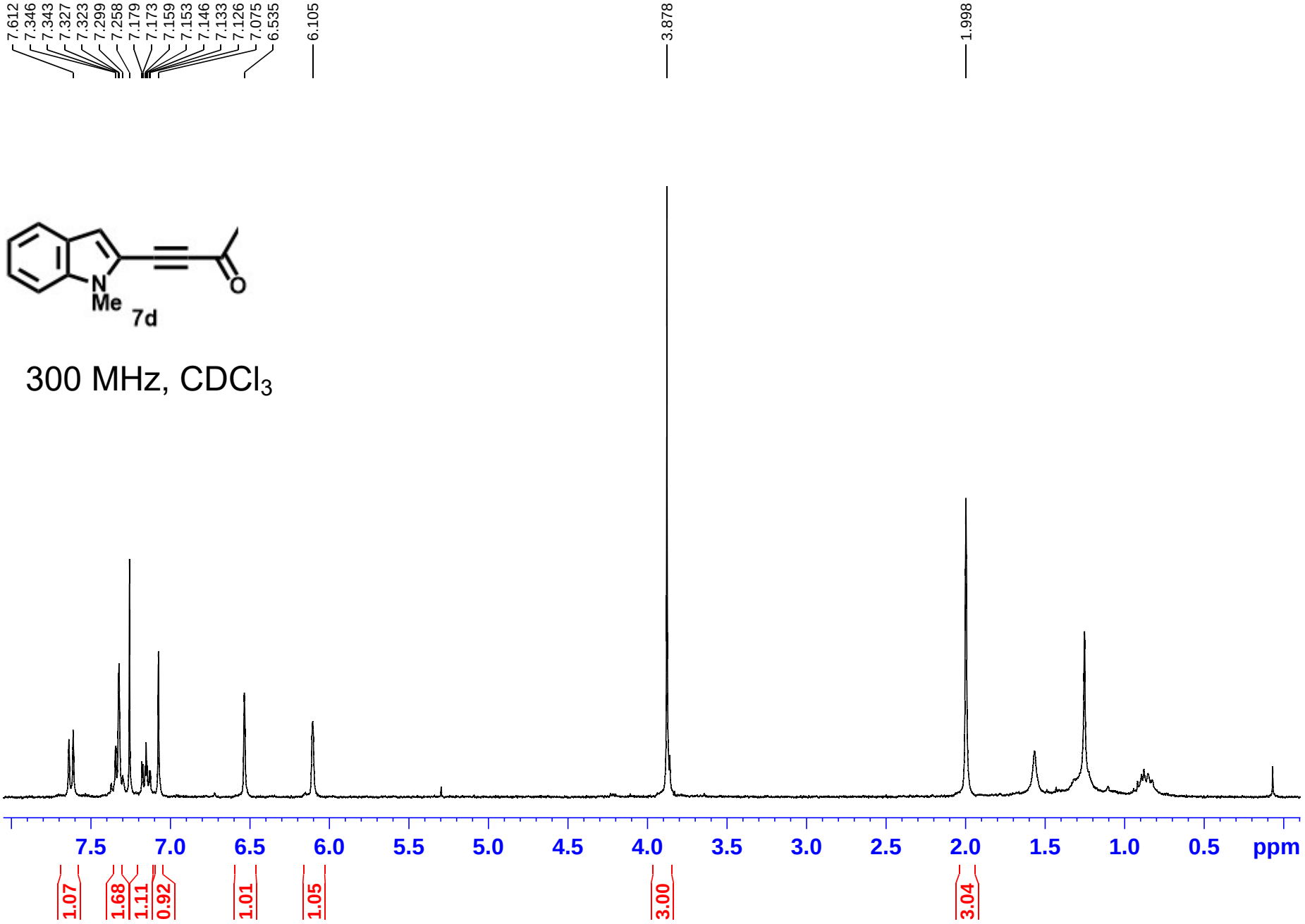


7c

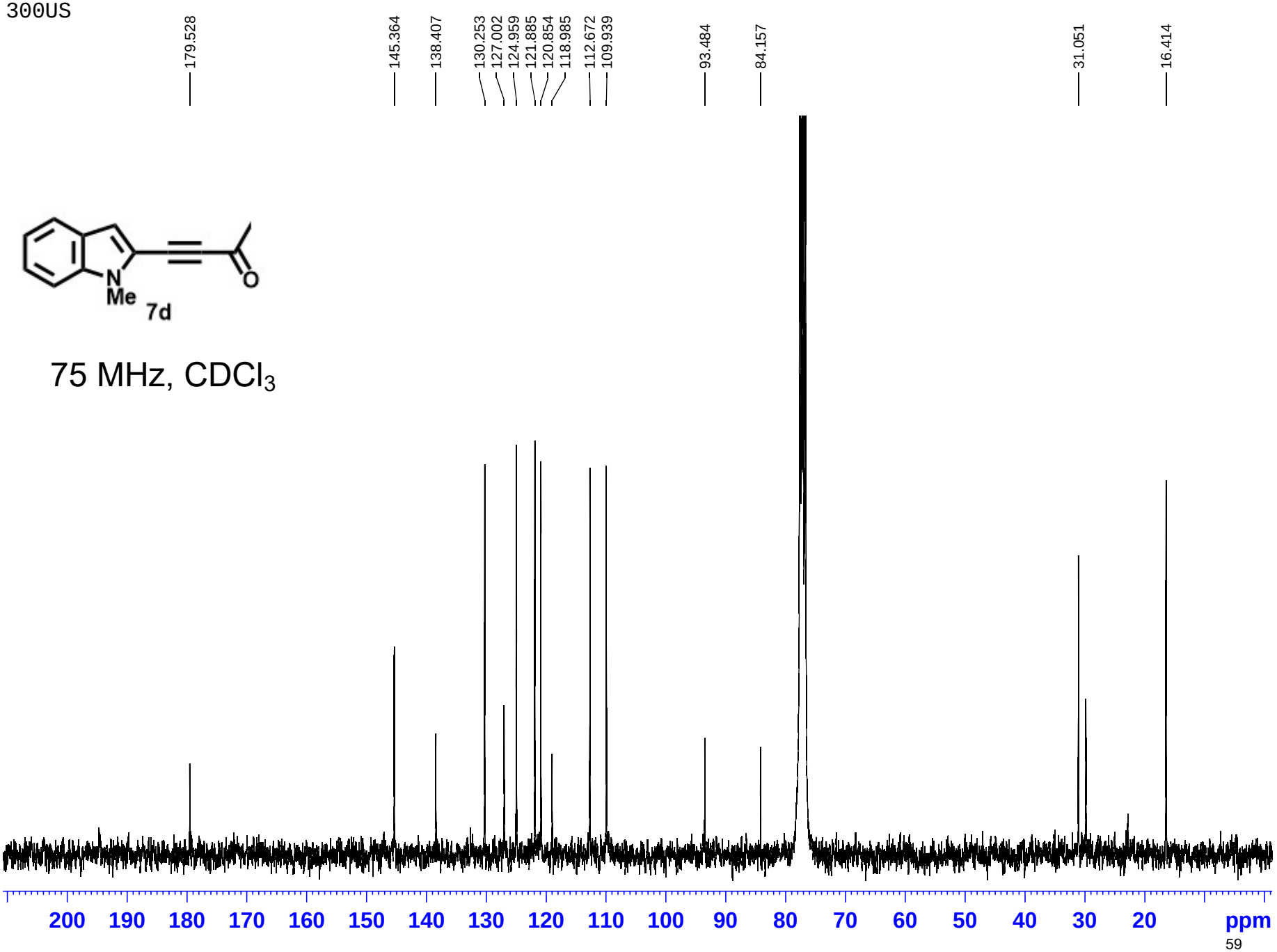
75 MHz, $CDCl_3$



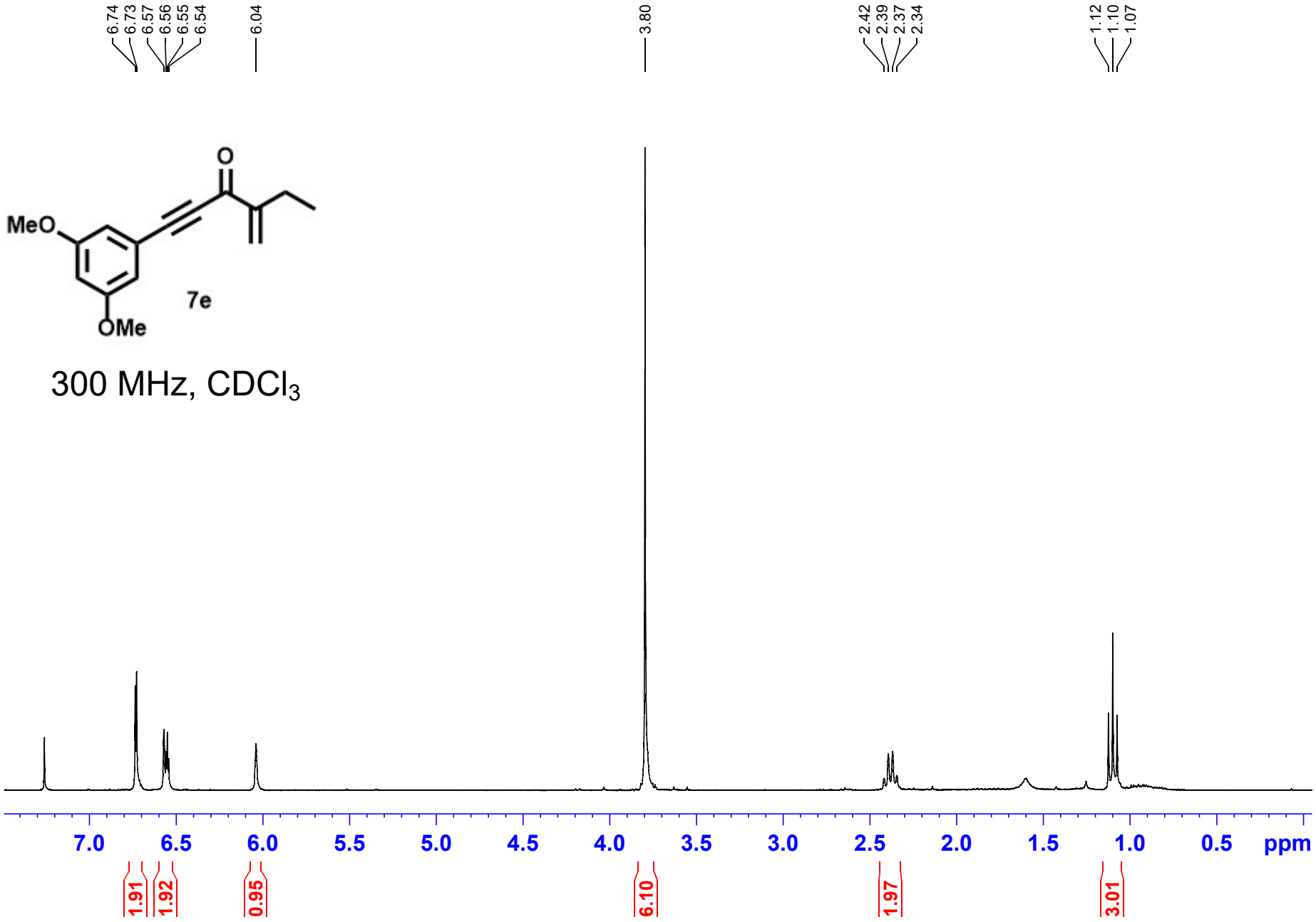
project4_pyrrol_ox_PDC_H1
300US



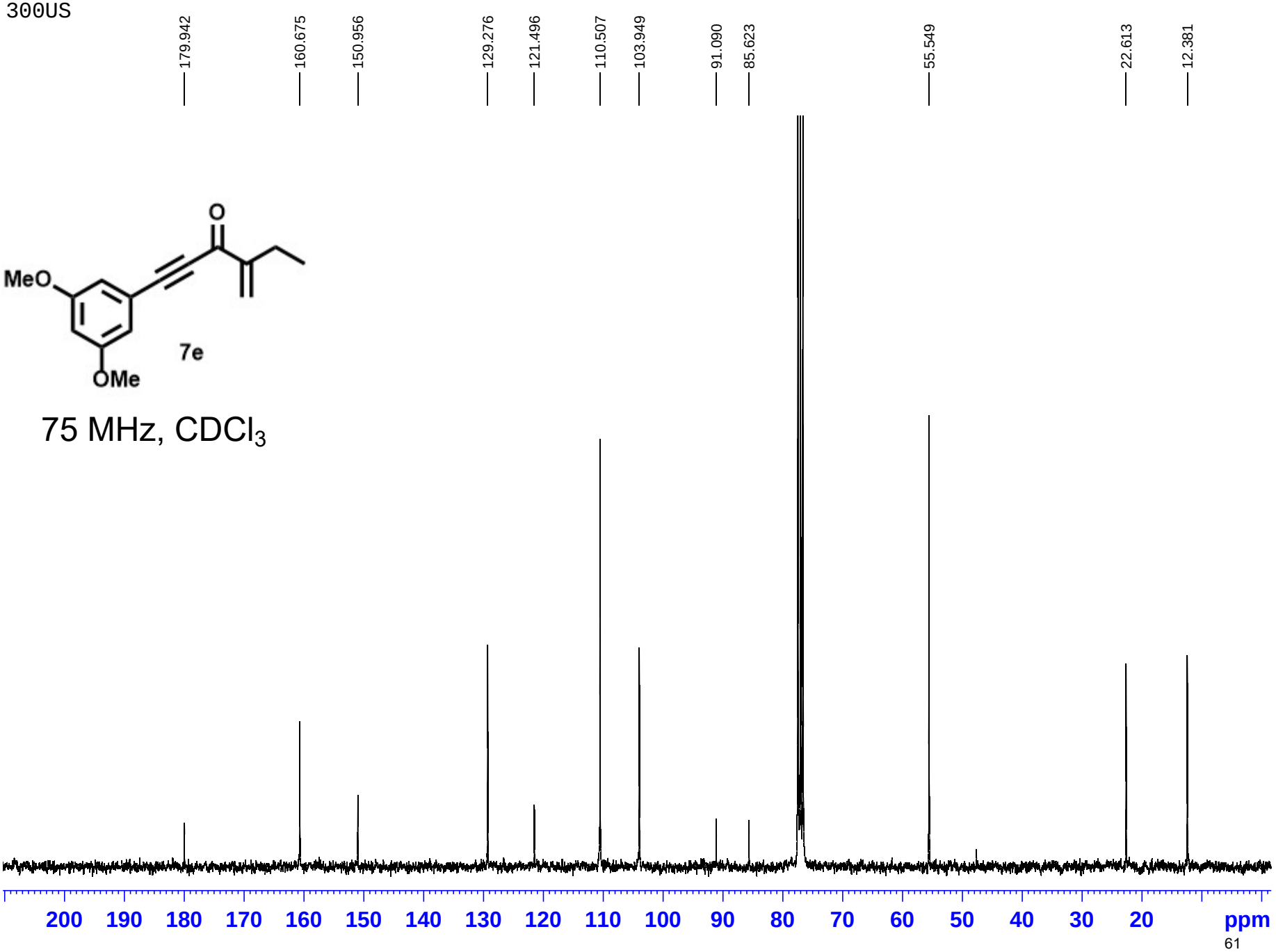
indole_cc_CO_ox_metha_c13
300US



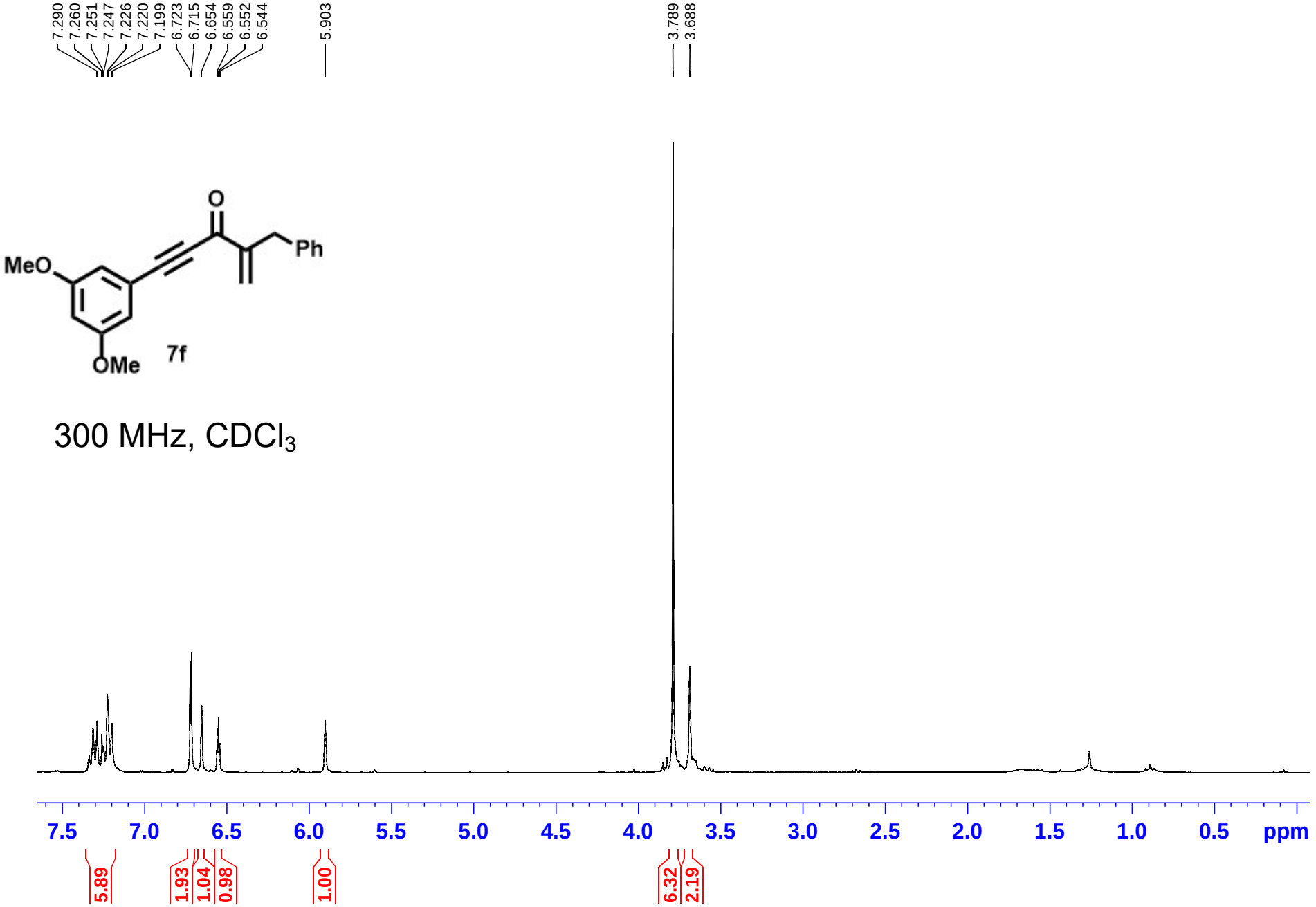
2MeO_cc_ketone_ethyl
300US



2MeO_cc_ketone_ethyl_c13
300US

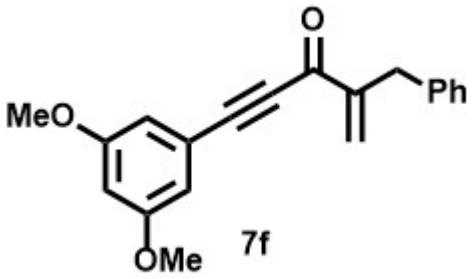


2MeO_cc_Ox_Bn_H1_proton 1D 1H DPX300



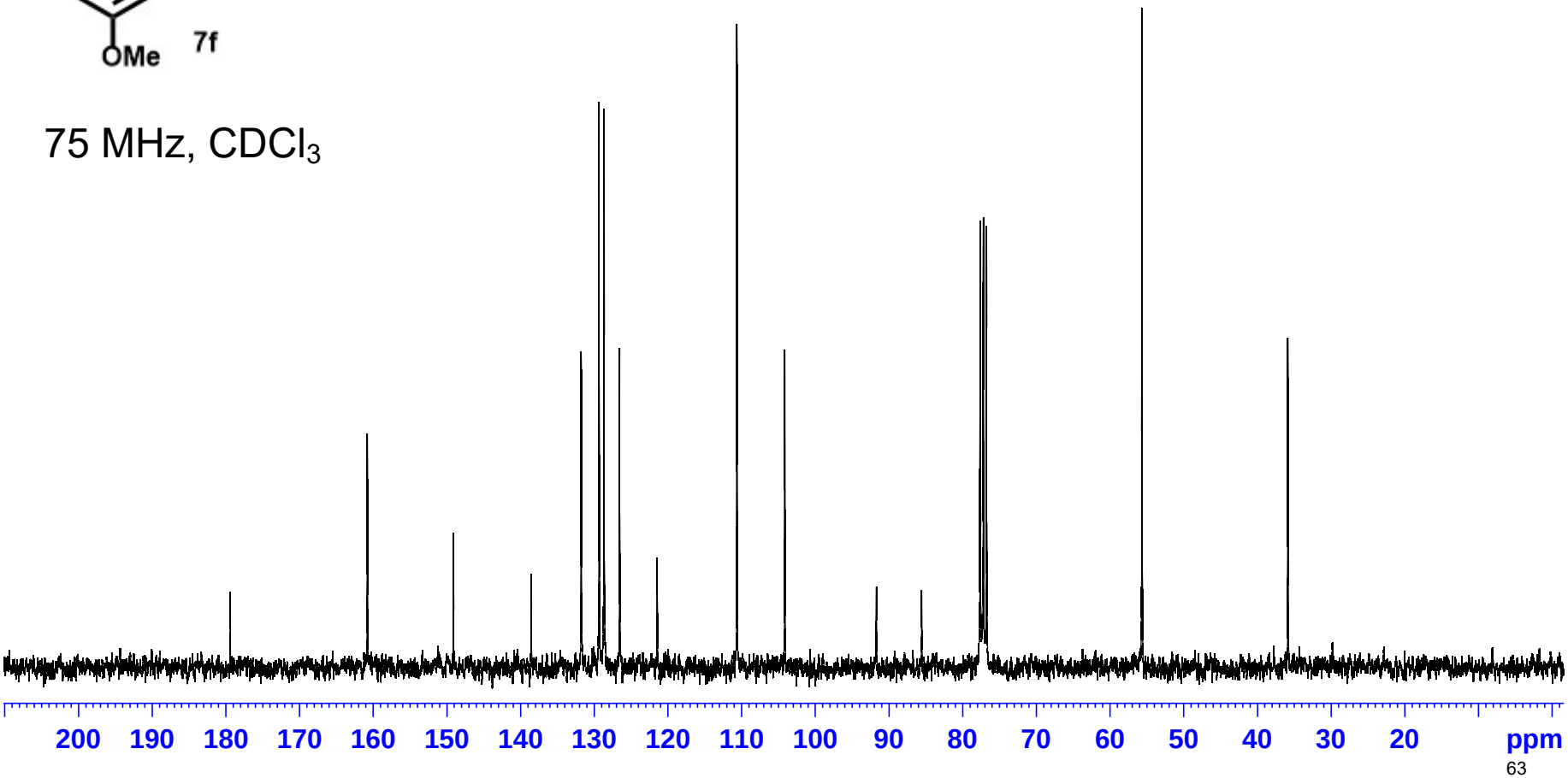
2MeO_cc_Ox_CO_Bn_c13
300US

179.401
160.777
149.088
138.536
131.760
129.332
128.652
126.548
121.449
110.617
104.133
91.692
85.557
55.650
35.838

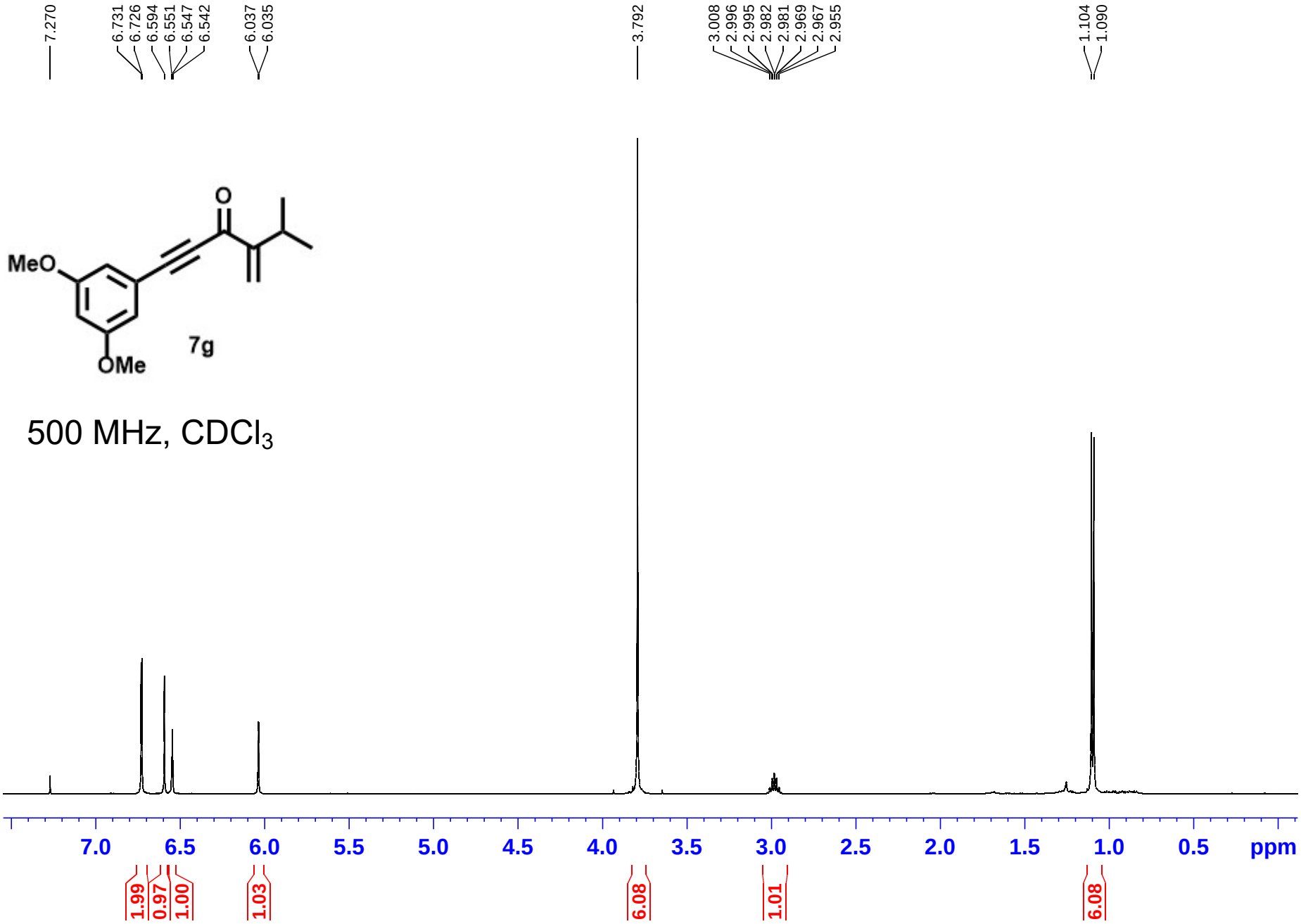


7f

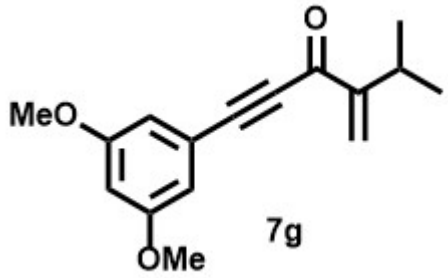
75 MHz, $CDCl_3$



som.07f 3 1H, (MeO)2Ph-CC-CH(O)-C(iPr)=CH2, 9/3/21



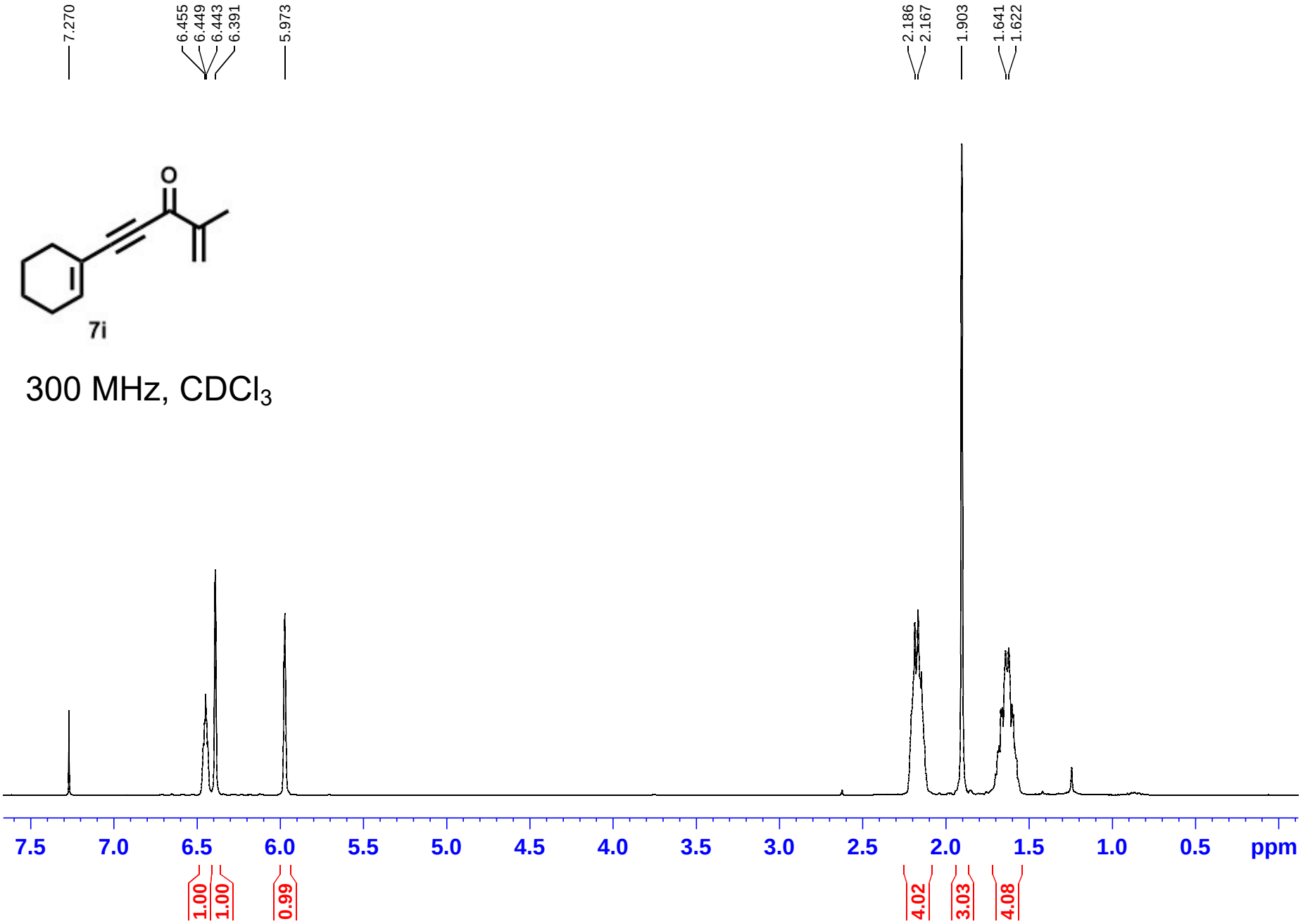
som.07f 4 13C, (MeO)2Ph-CC-C(O)-C(iPr)=CH2, 9/4/21



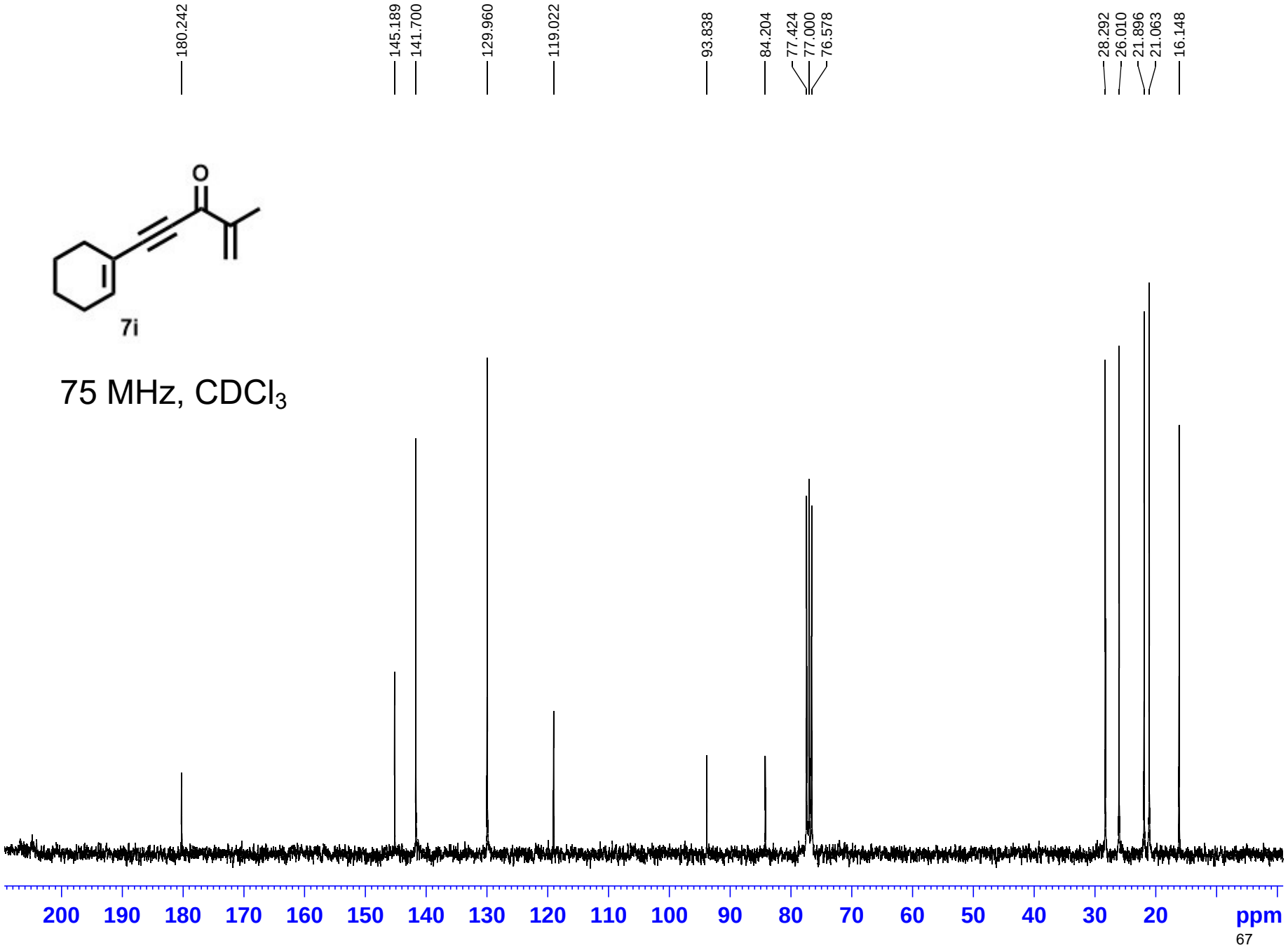
7g

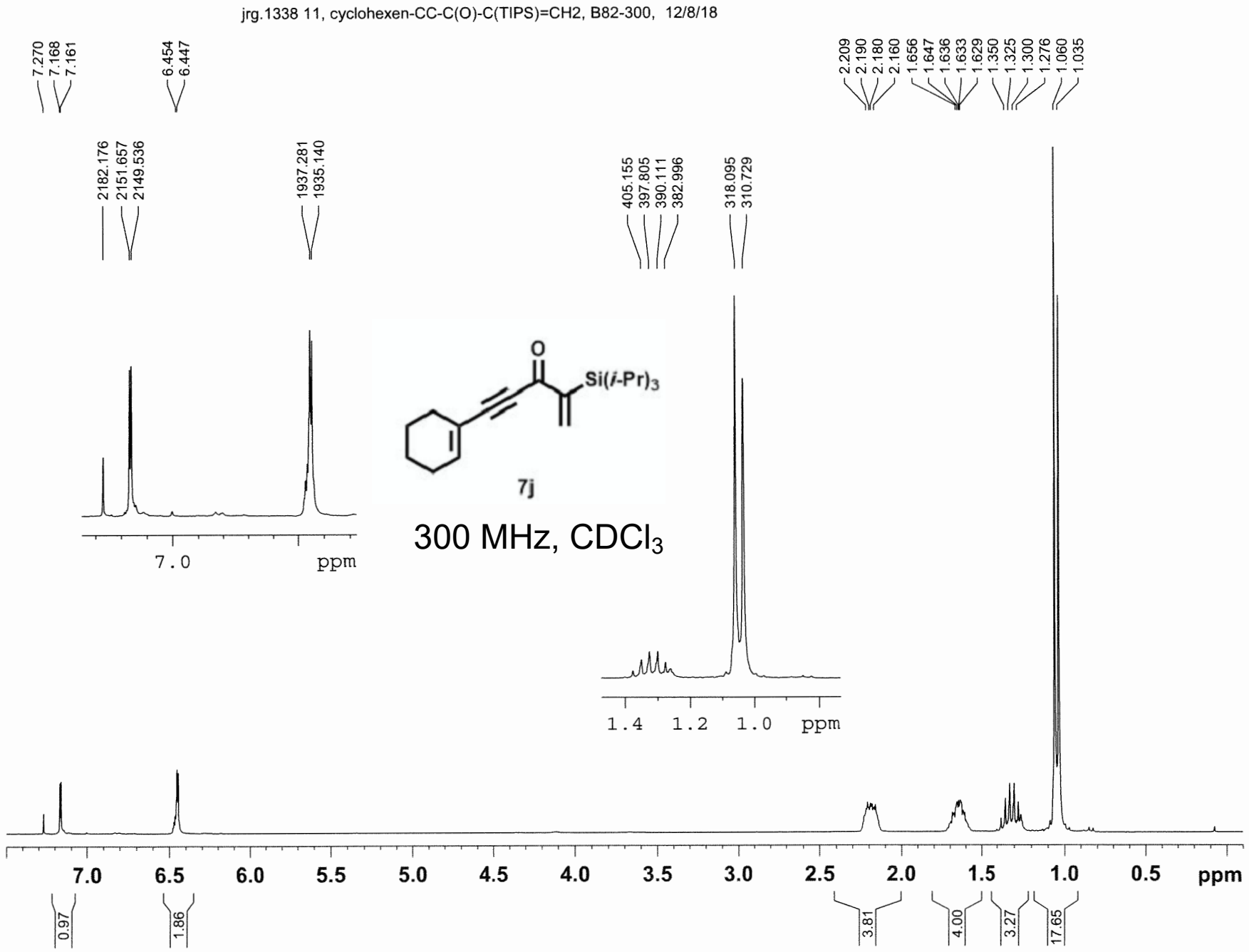
125 MHz, $CDCl_3$

som.07i 2, cyclohexenyl-CC-C(O)-C(Me)=CH2, B82, 8/17/21



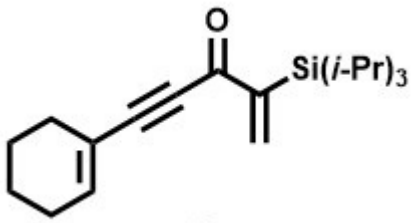
som.07i 3 13C, cyclohexenyl-CC-C(O)-C(Me)=Ch2, 8/17/21




jrg.1338 11, cyclohexen-CC-C(O)-C(TIPS)=CH2, B82-300, 12/8/18
7.270
7.168
7.161
6.454
6.447
2182.176
2151.657
2149.536
1937.281
1935.140
405.155
397.805
390.111
382.996
318.095
310.729
2.209
2.190
2.180
2.160
1.656
1.647
1.636
1.633
1.629
1.350
1.325
1.300
1.276
1.060
1.035
O
Si(i-Pr)3
7j
300 MHz, CDCl3
7.0
ppm
1.4
1.2
1.0
ppm
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.97
1.86
3.81
4.00
3.27
17.65

jrg.1338.12, 13C, cyclohexen-CC-C(O)-C(TIPS)=CH2, B82-300, 12/8/18

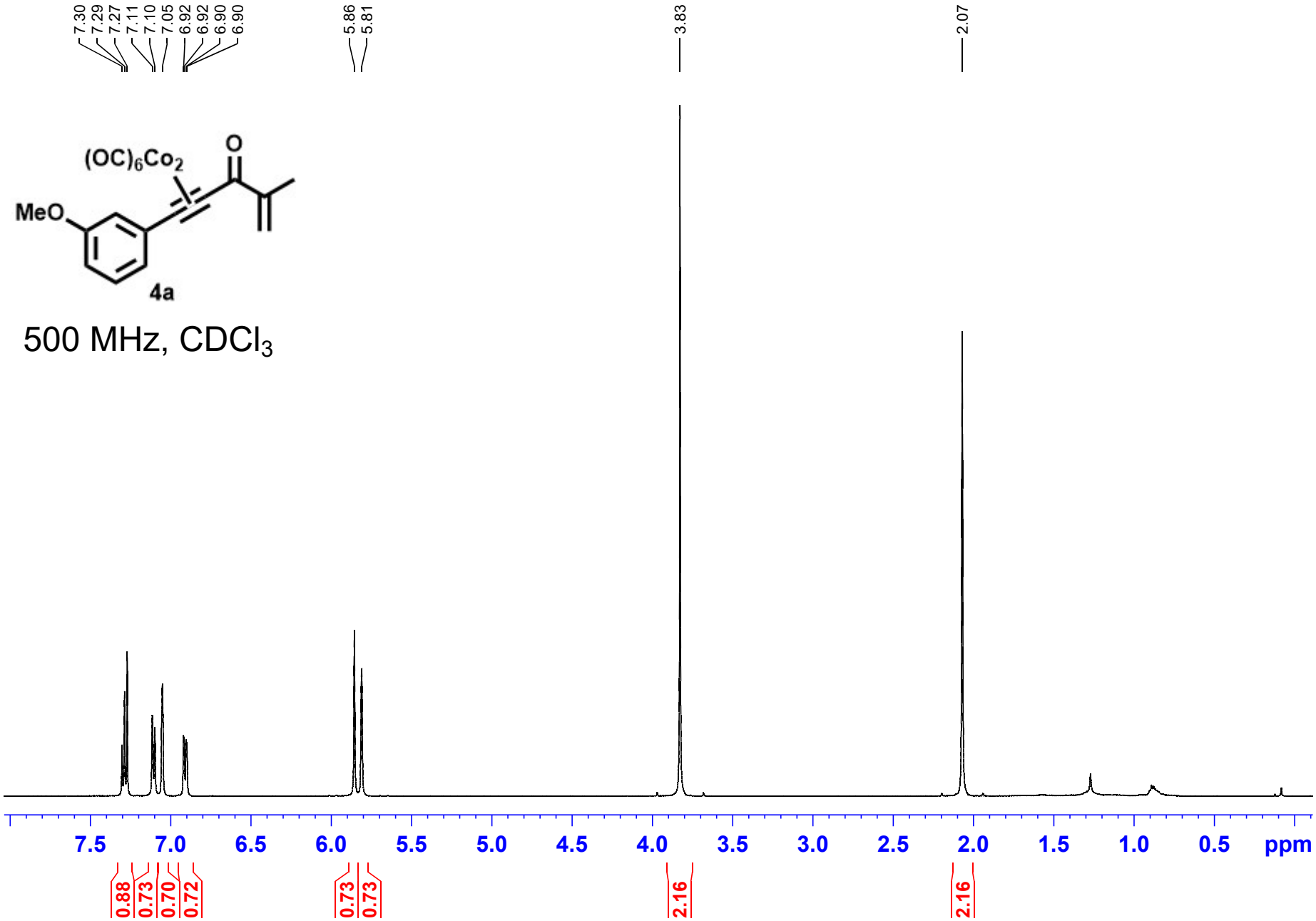
184.503
149.232
144.625
141.487
119.207
93.760
84.619
77.432
77.008
76.585
28.456
26.064
21.988
21.146
18.660
11.077



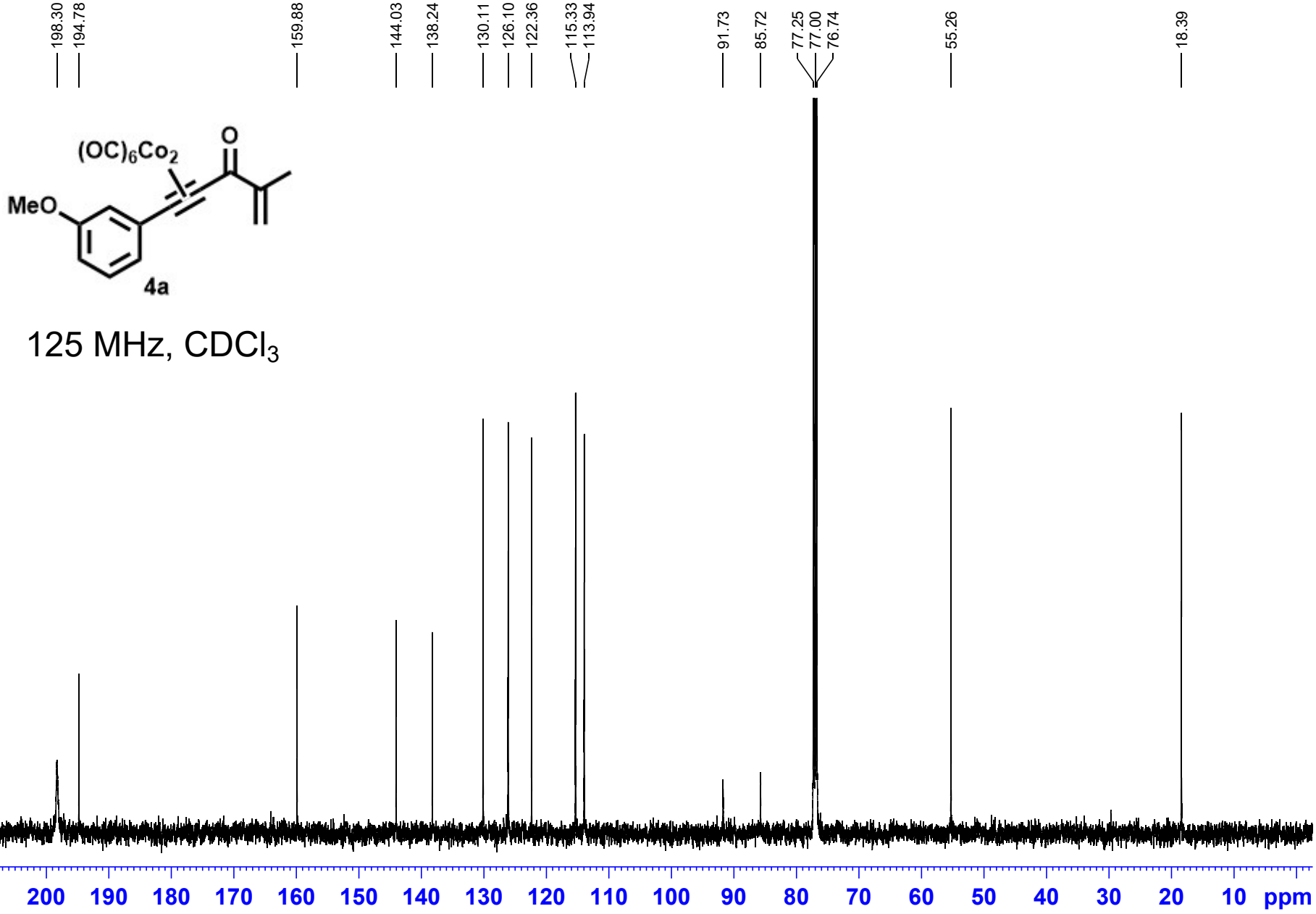
7j

75 MHz, $CDCl_3$

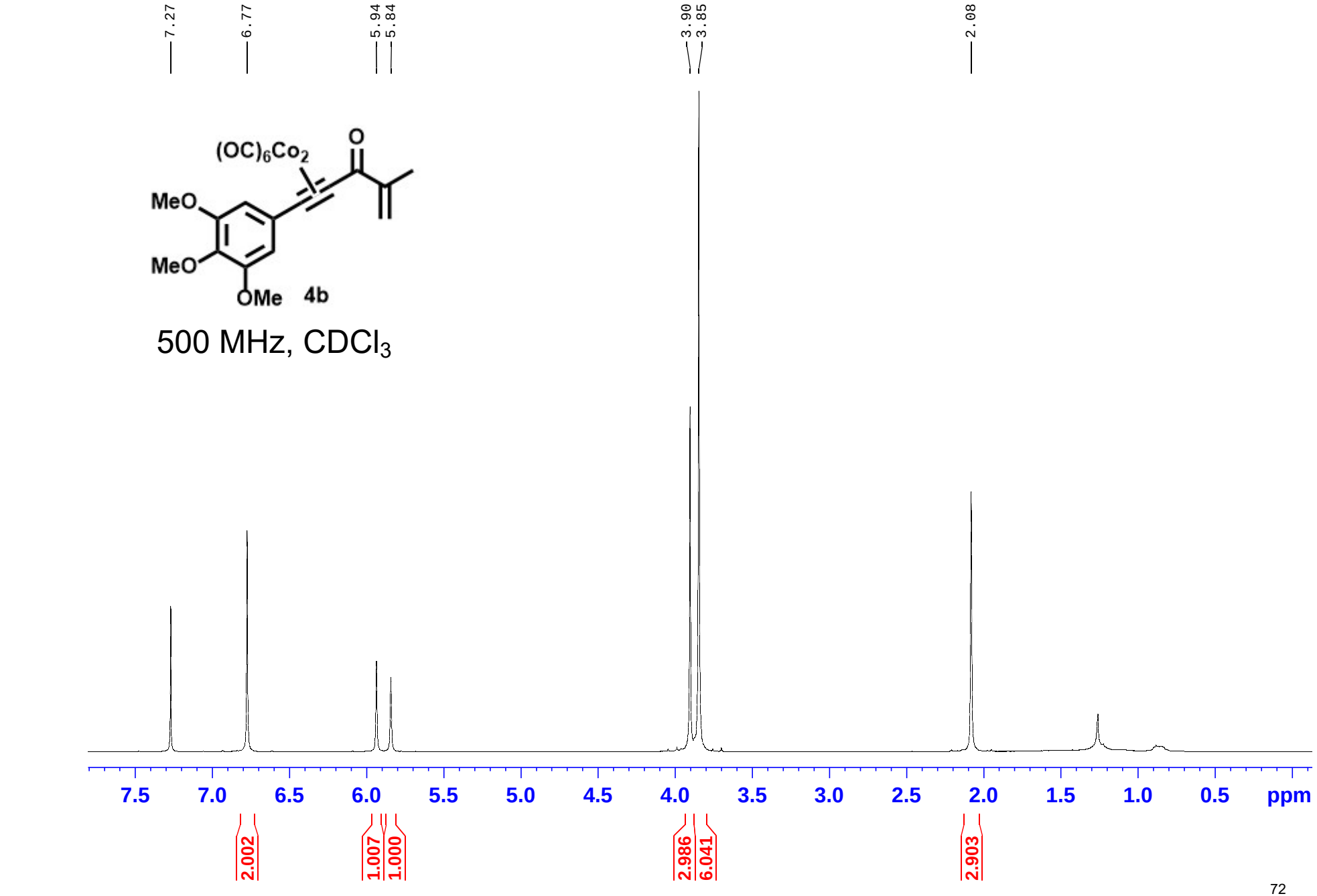
jrg.1448 3, 1H, 3-MeOPh-CC-C(O)-C(Me)=CH2]-Co2, 7/10/21



jrg.1449 4, 13C, 3-MeOPh-CC-C(O)-C(Me)=CH2]-Co2, 7/10/21

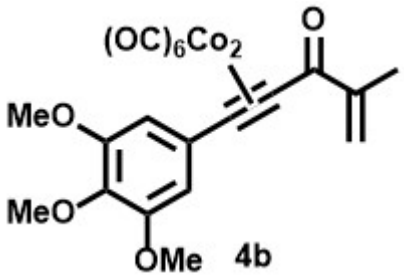


som.04b 1, (MeO)3Ph-CC-C(O)-C(Me)=CH2]-Co2, 1H, 10/13/21



som.08b 2, 13C, (MeO)3Ph-CC-C(O)-C(Me)=Ch2]-Co2, 10/6/21

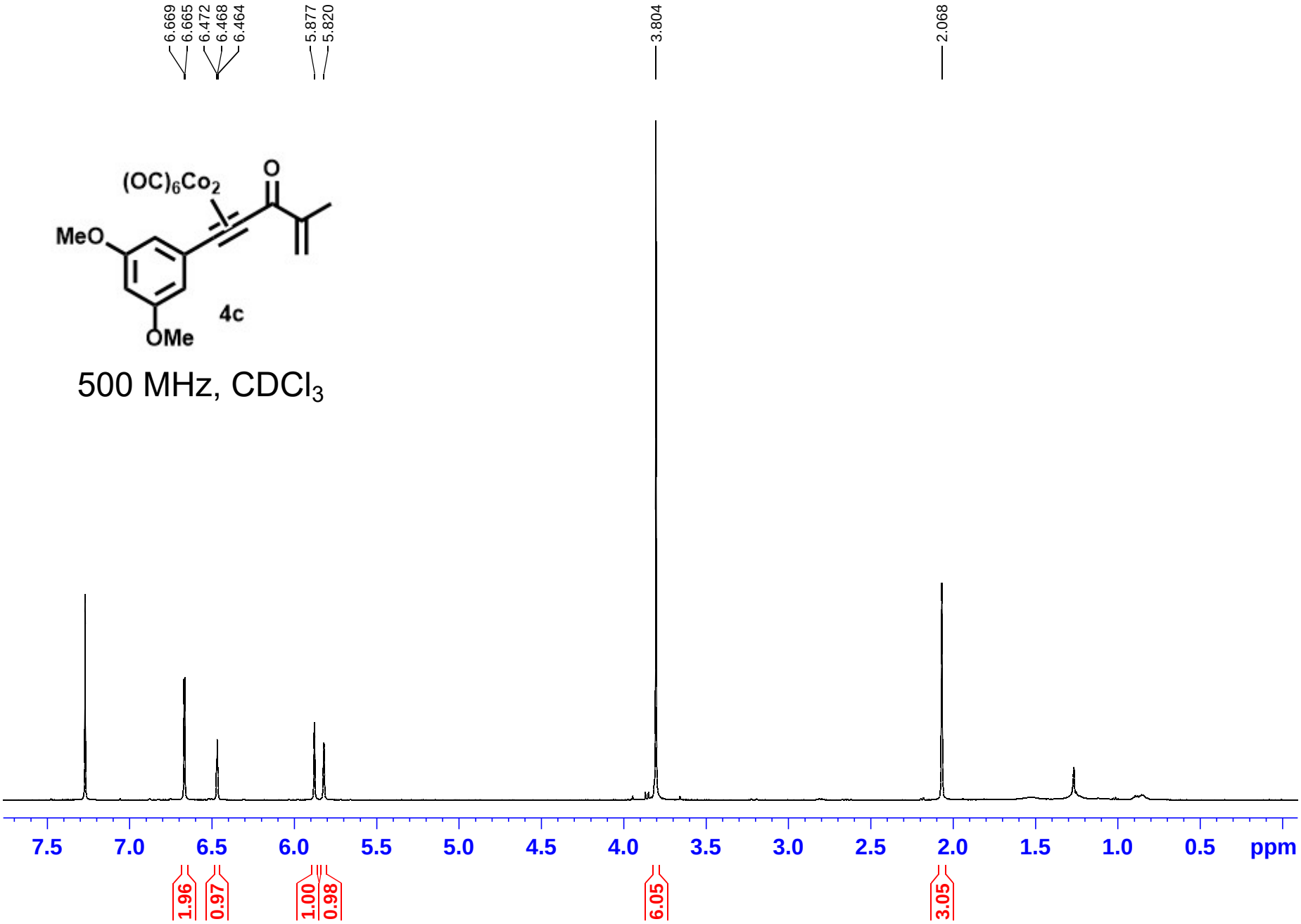
198.352
194.917
153.413
144.327
138.384
131.977
125.880
107.066
92.665
85.197
77.430
77.008
76.584
60.861
56.102
18.474



4b

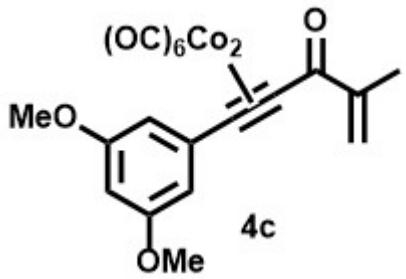
75 MHz, $CDCl_3$

som.04c 2, (MeO)2Ph-CC-C(O)-C(Me)=CH2]-Co2, 1H, 10/13/21



dimethoxy_cc_cobalt_methyl_carbon_c13
300US

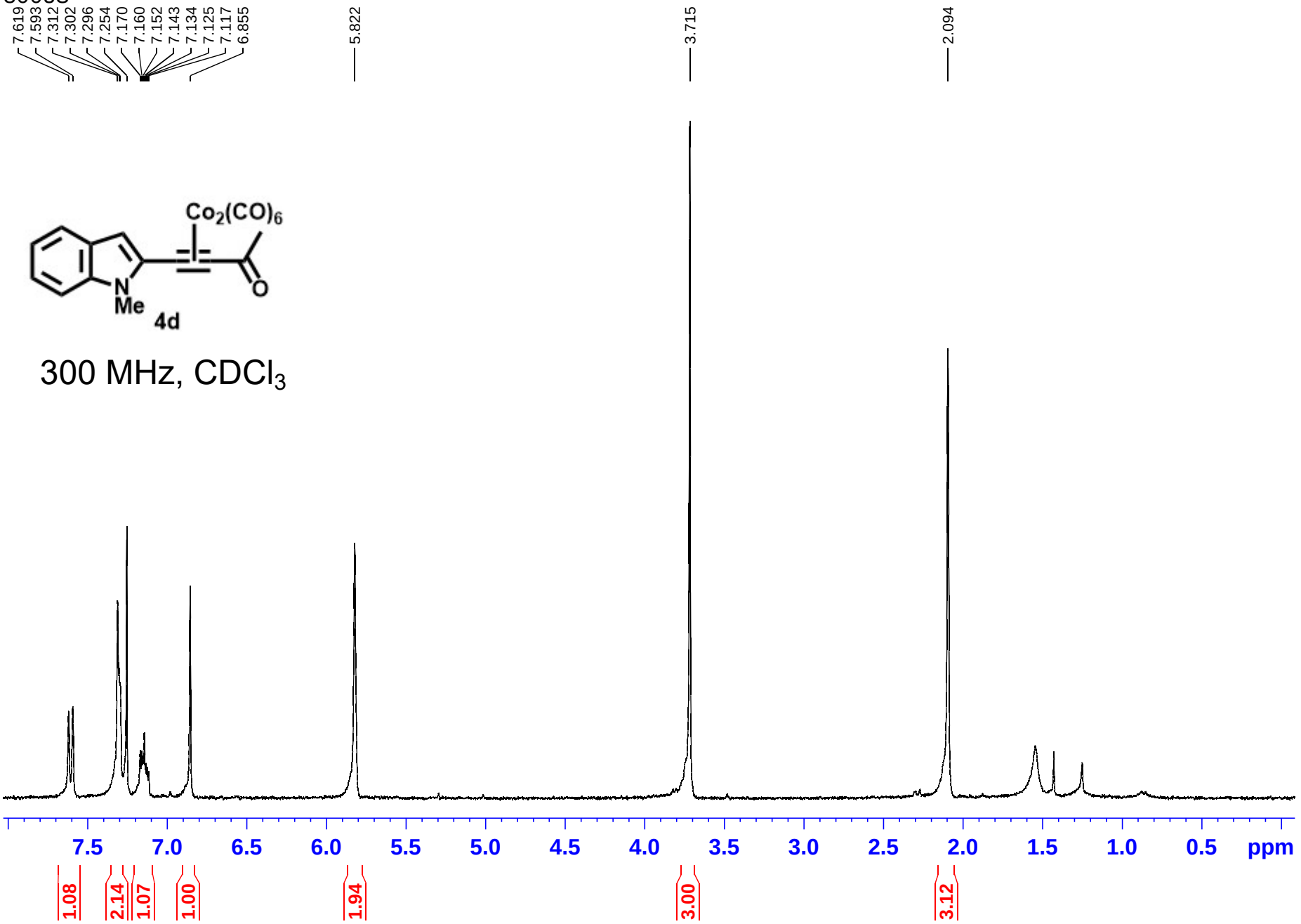
198.361
194.929
161.096
144.132
138.987
126.367
108.113
100.587
92.049
85.763
55.535
18.566



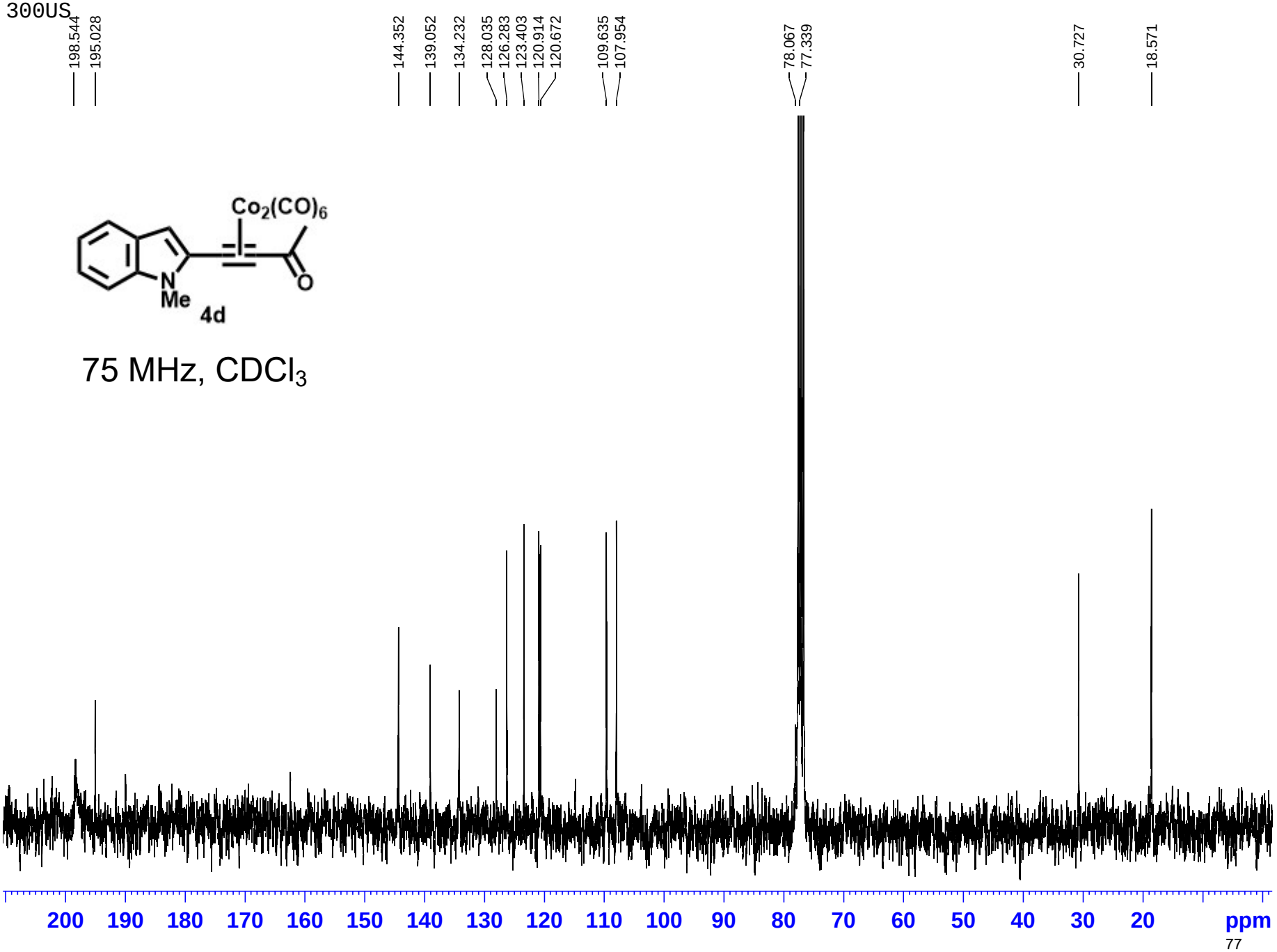
4c

75 MHz, $CDCl_3$

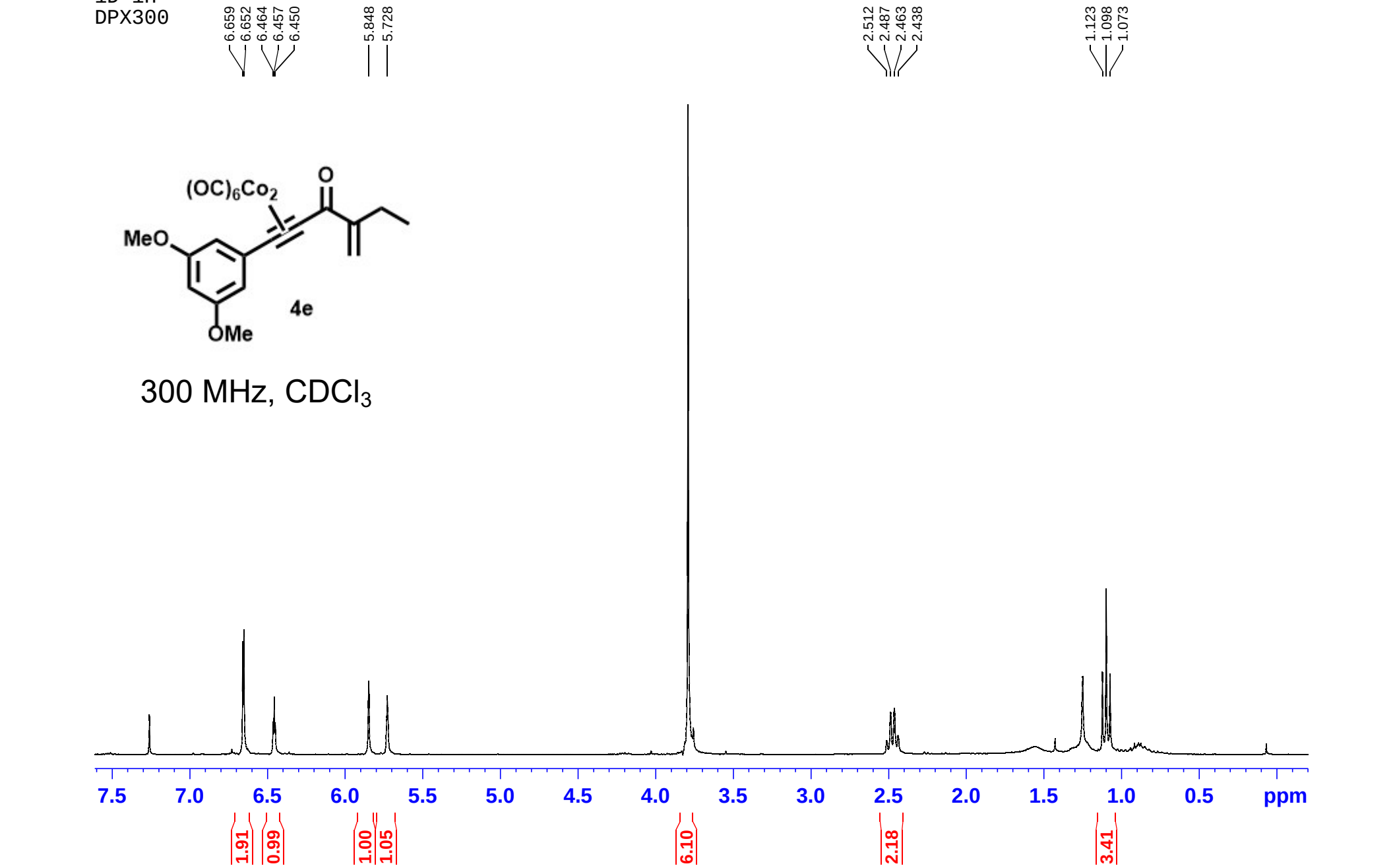
project3_pyrrole_H1_cobalt_clean
300US



indole_cc_keton_cobalt_C13
300US

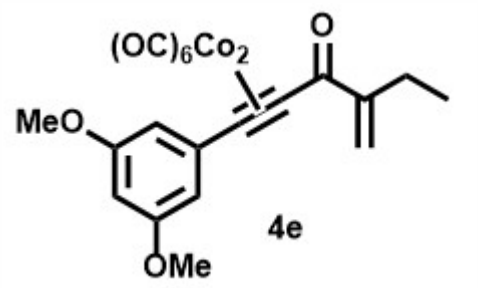


dimethoxy_cc_cobalt_ethyl
1D 1H
DPX300



dimethoxy_cc_cobalt_ethyl_c13

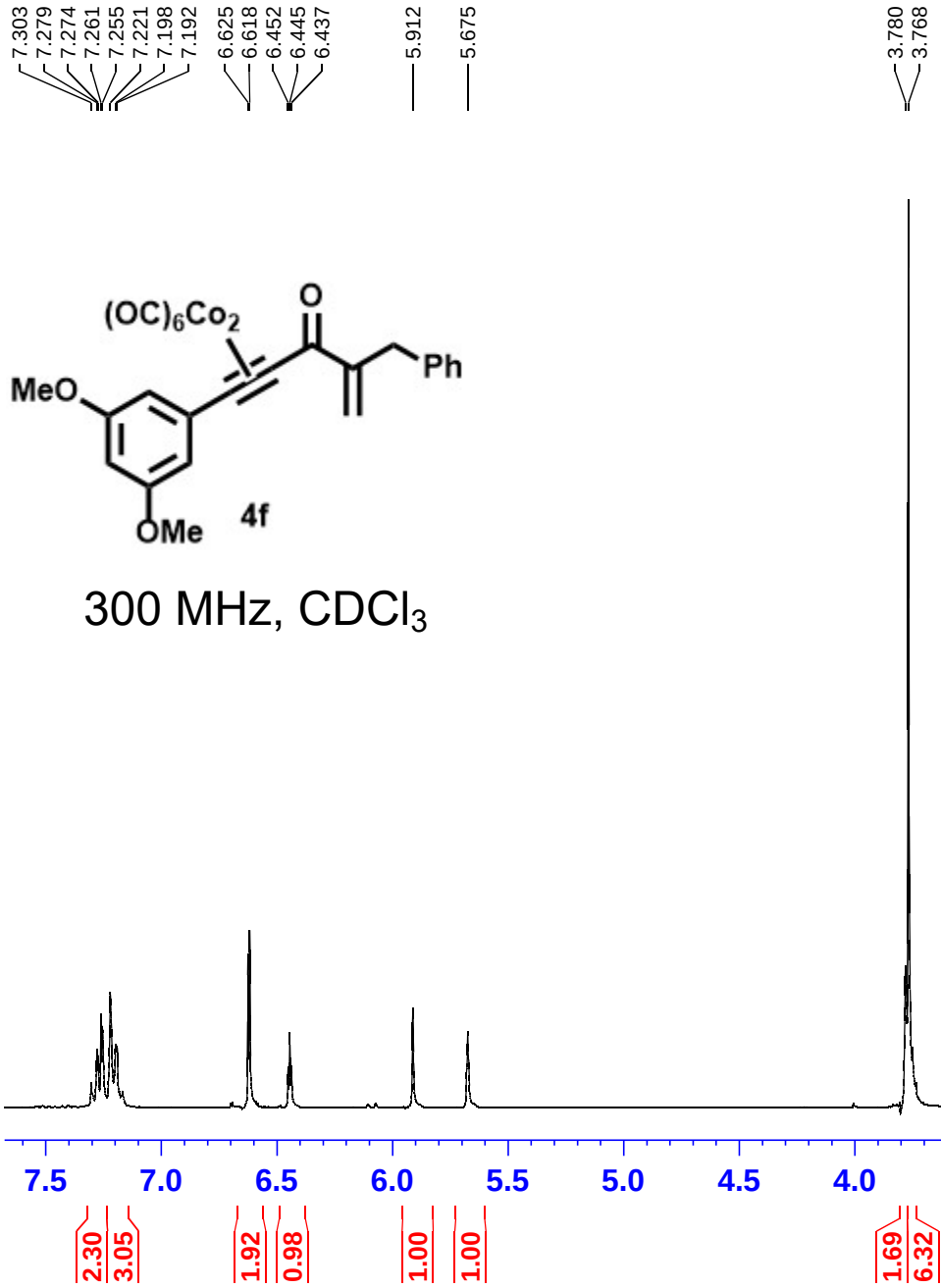
198.325
194.913
160.995
150.281
138.907
123.769
107.962
100.553
92.054
86.624
55.404
29.709
24.932
12.567



4e

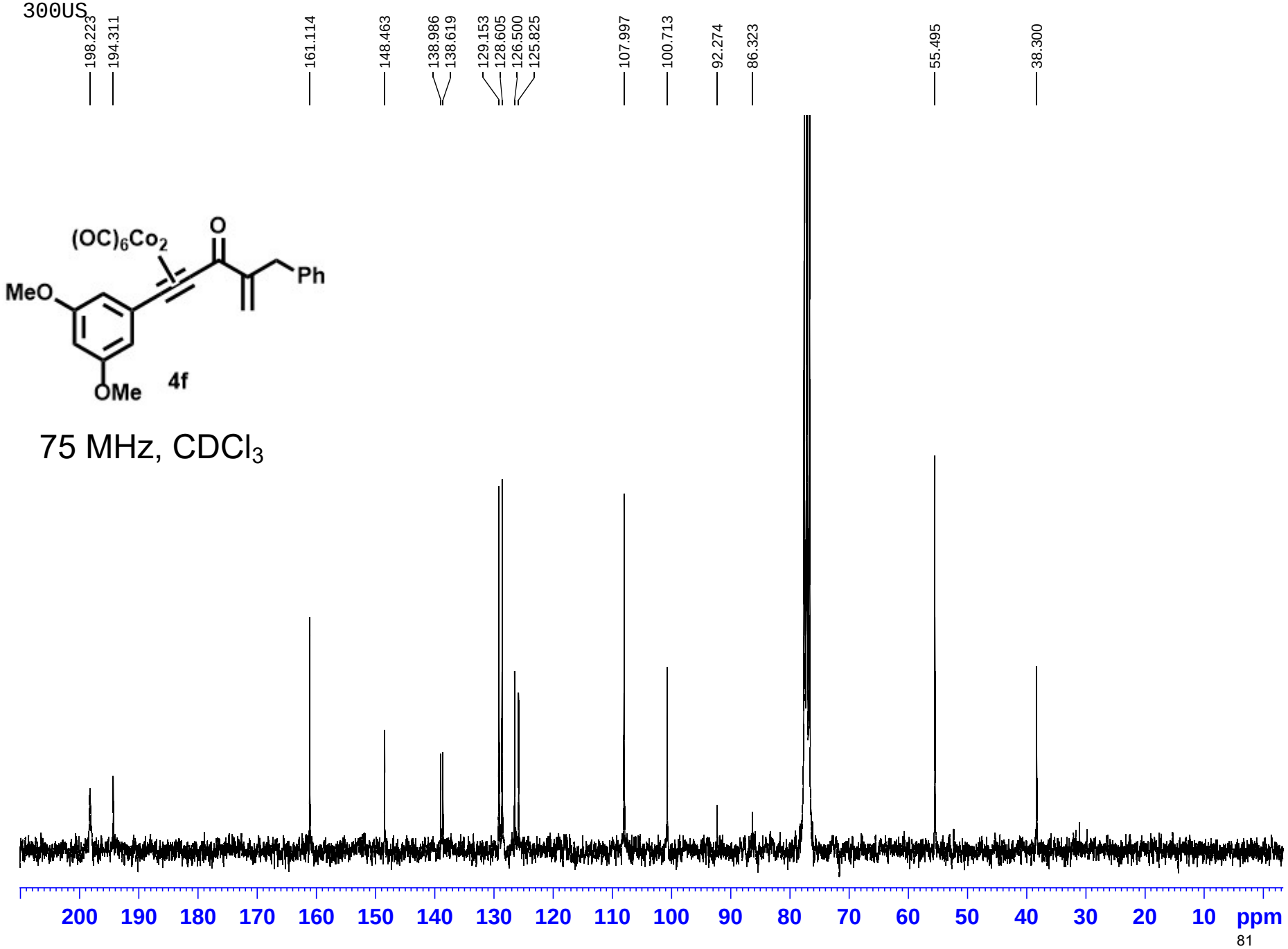
75 MHz, $CDCl_3$

dimethoxy_cc_cobalt_benzyl_f1 1D 1H DPX300

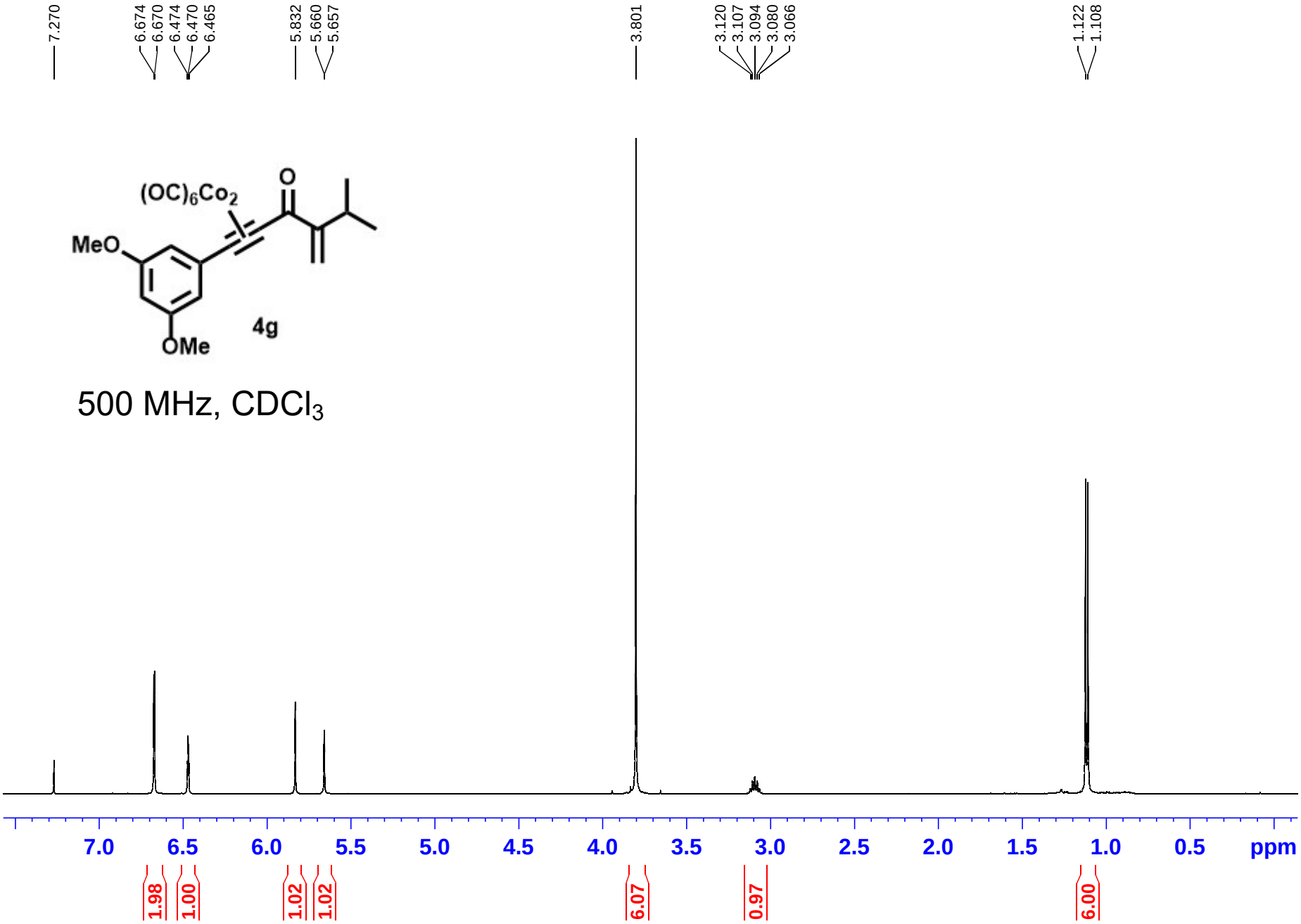


300 MHz, $CDCl_3$

dimethoxy_cc_cobalt_benzyl_f1_C13_1
300US

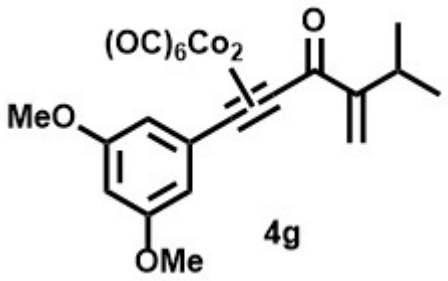


som.08f 1 1H, (MeO)2Ph-CC-CH(O)-C(iPr)=CH2]-Co2, 9/4/21



som.08f 2, 13C, (MeO)2Ph-CC-C(O)-C(iPr)=CH2]-Co2, 9/4/21

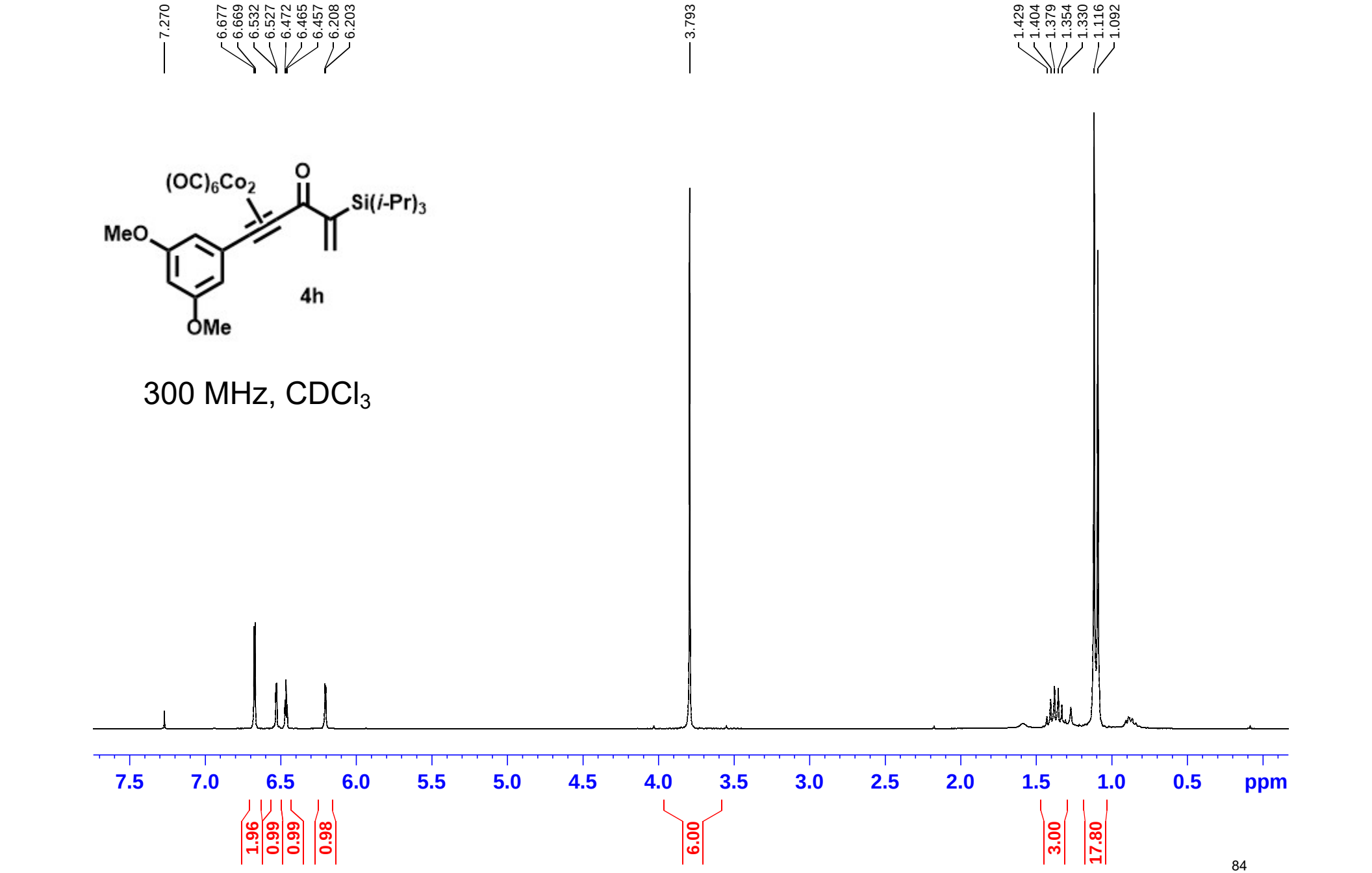
198.275
195.399
160.990
155.340
138.915
121.239
107.888
100.585
92.280
87.608
77.250
76.996
76.742
55.368
29.070
21.431



4g

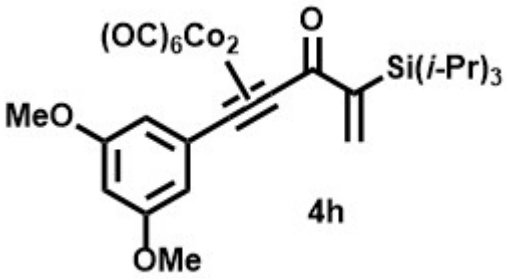
125 MHz, $CDCl_3$

som.08g 1, 1H, (MeO)2Ph-CC-C(O)-C(TIPS)=Ch2]-Co2, B82, 9/26/21



som.08g 2, 13C, (MeO)2Ph-CC-C(O)-C(TIPS)=CH2]-Co2, B82, 9/26/21

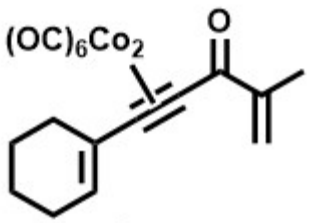
199.525
198.368
160.973
149.375
139.177
138.876
107.704
100.602
93.266
88.044
77.430
77.007
76.584
55.326
18.722
11.198



4h

75 MHz, $CDCl_3$

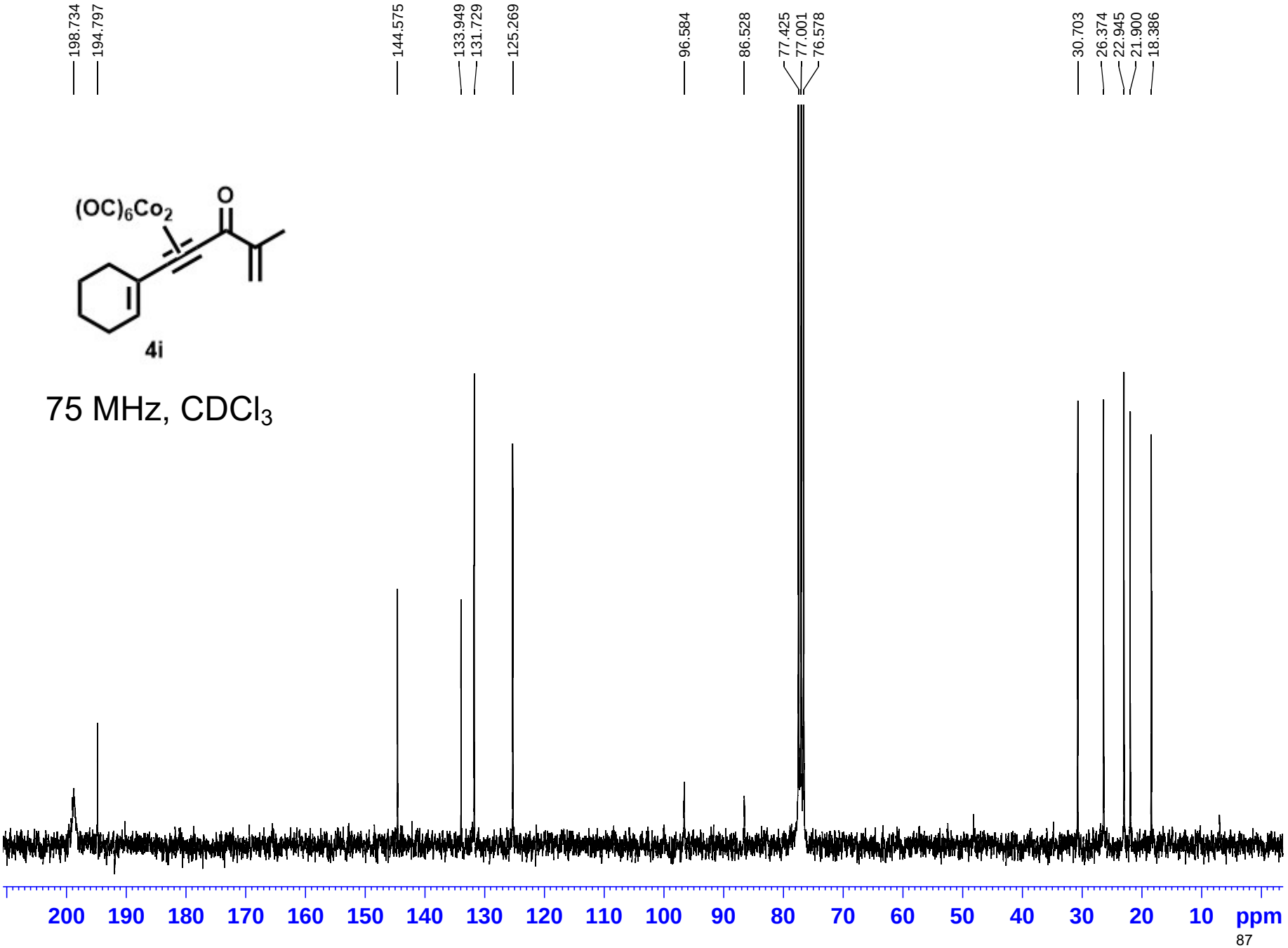
som.08i 1, cyclohexenyl-CC-C(O)-C(Me)=CH2]-Co2, B82, 8/18/21



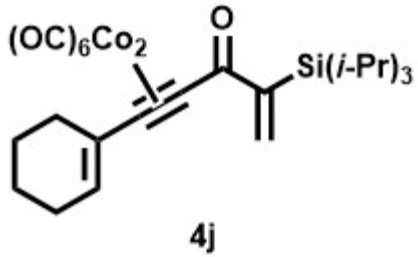
4i

300 MHz, $CDCl_3$

som.08i 2, 13C, cyclohexenyl-CC-C(O)-C(Me)=CH2]-Co2, B82, 8/18/21



som.08j, 1H, cyclohexenyl-CC-C(O)-C(TIPS)=CH2]- Co2, 500, 8/13/21

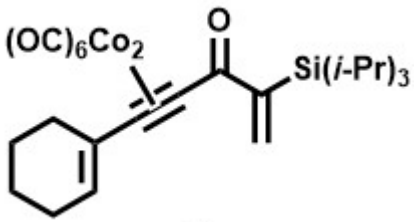


4j

500 MHz, $CDCl_3$

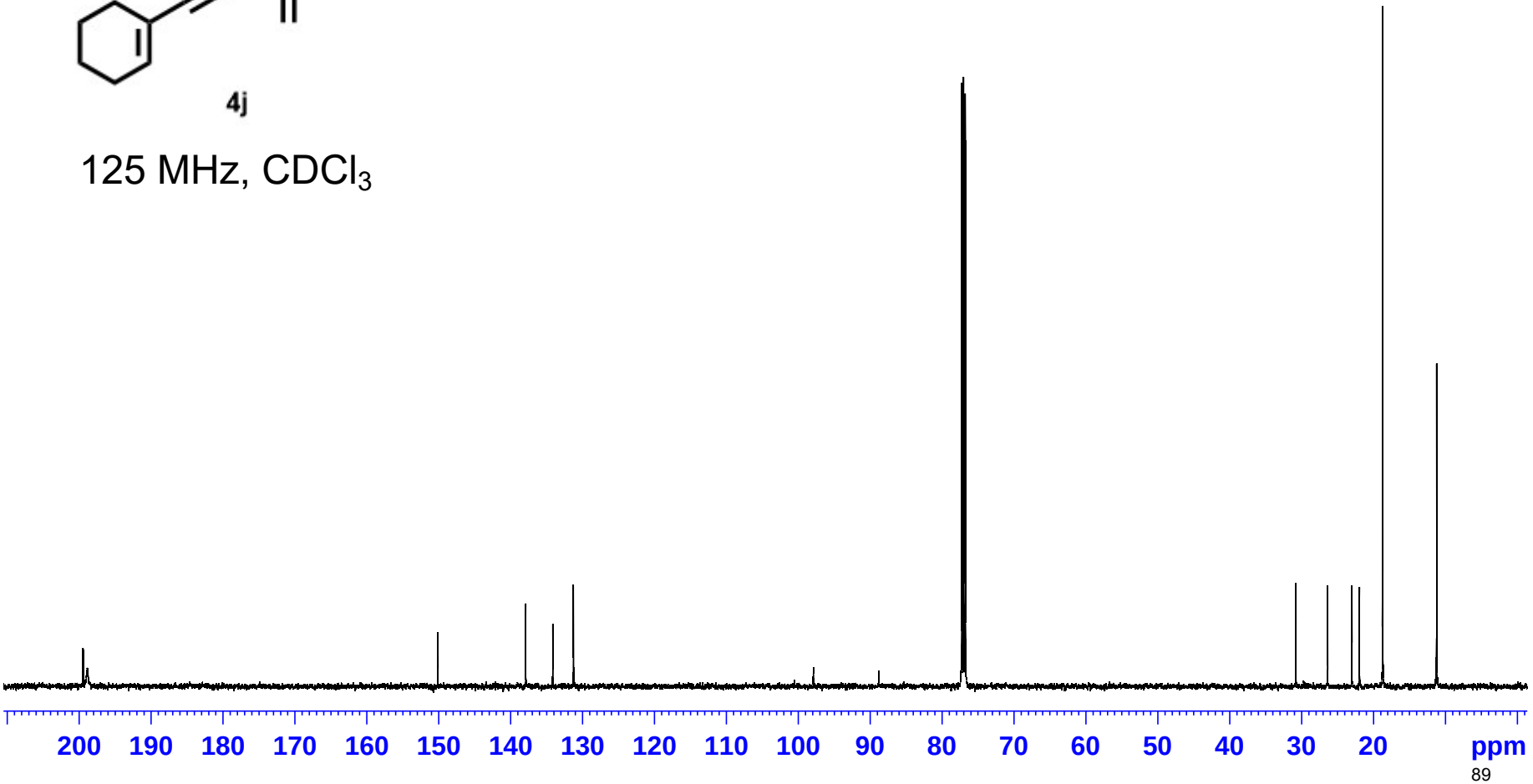
som.08j 3, 13C, cyclohexenyl-CC-C(O)-C(TIPS)=CH2]-Co2, 500, 8/12/21

199.441
198.908
150.110
137.899
134.127
131.268
97.875
88.795
77.250
76.997
76.743
30.783
26.373
22.984
21.927
18.712
11.198

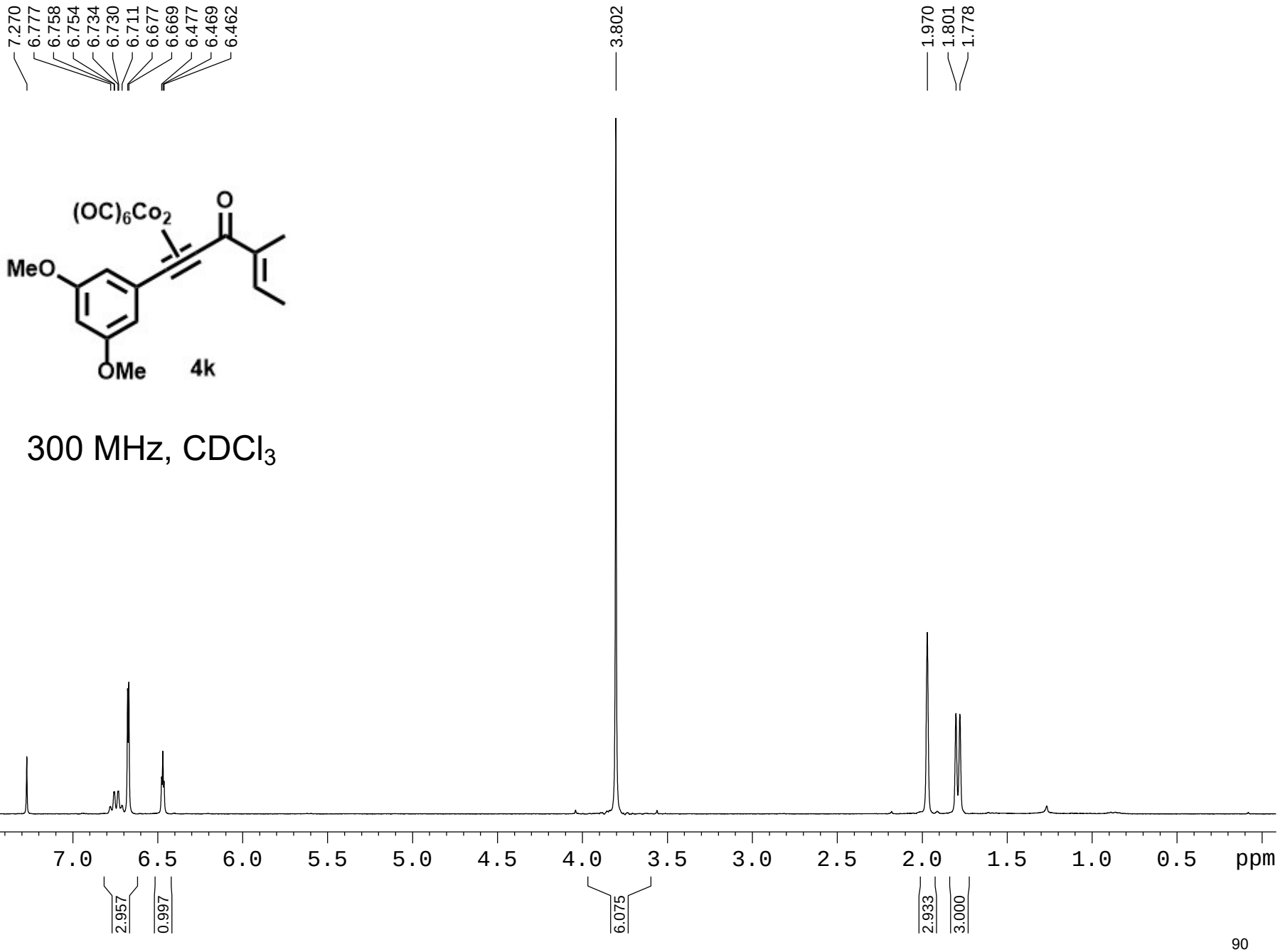


4j

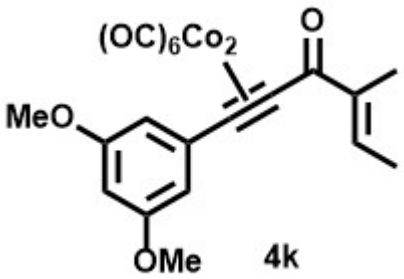
125 MHz, $CDCl_3$



som.04k 1, 1H, (MeO)2Ph-CC-C(O)-C(Me)=CHMe]-Co2, B82, 9/27/21



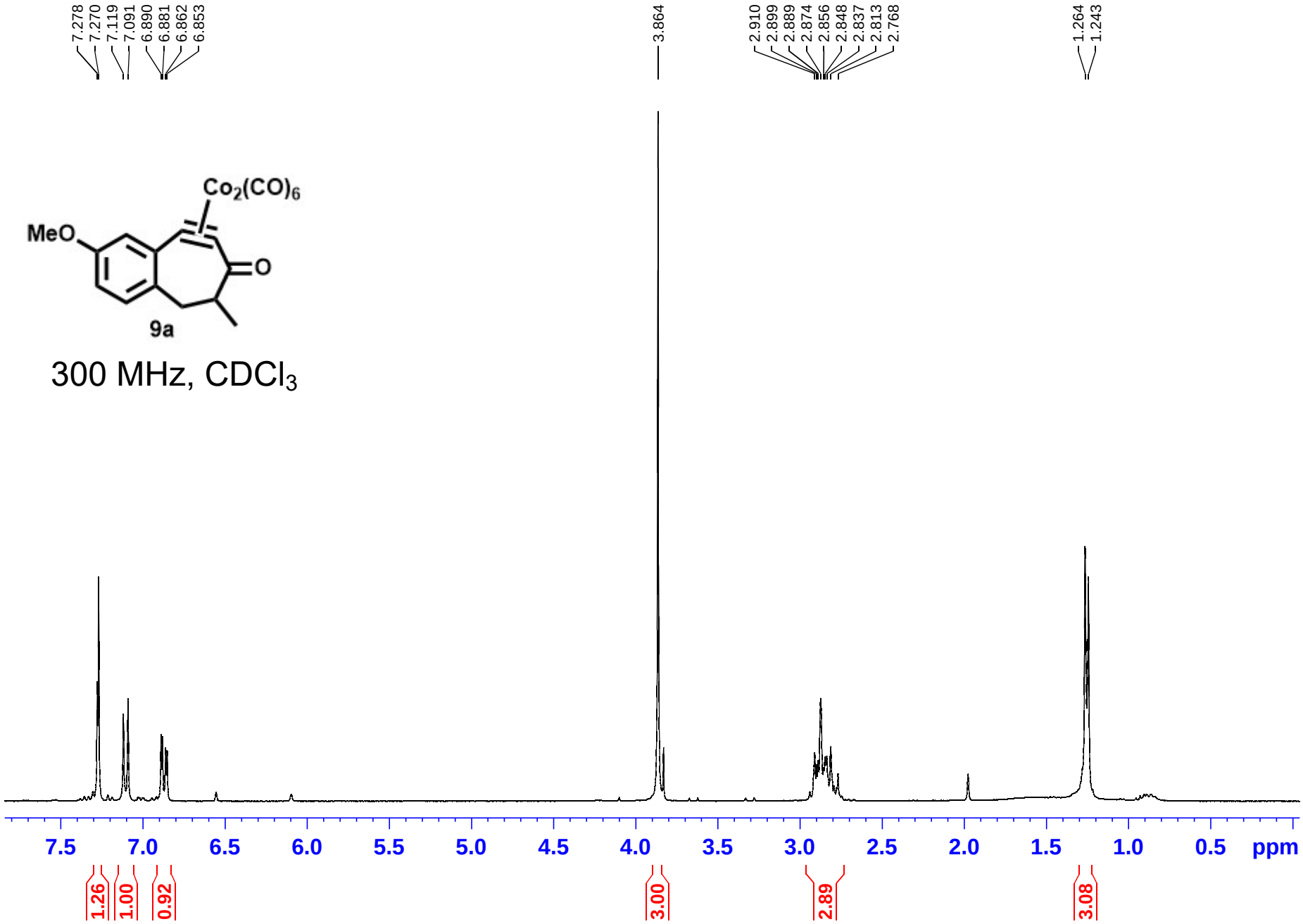
som.04k 2, 13C, (MeO)2Ph-CC-C(O)-C(Me)=CHMe]-Co2, B82, 9/27/21



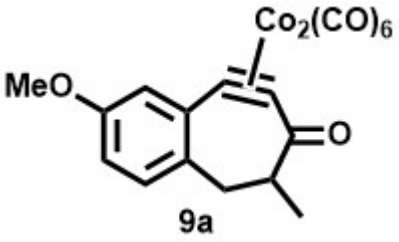
4k

75 MHz, $CDCl_3$

som.0727 3, MeOPh-CC-C(O)-C(Me)=CH2]-Co2 cyclizn, maj fr, 300 B82, 7/27/21



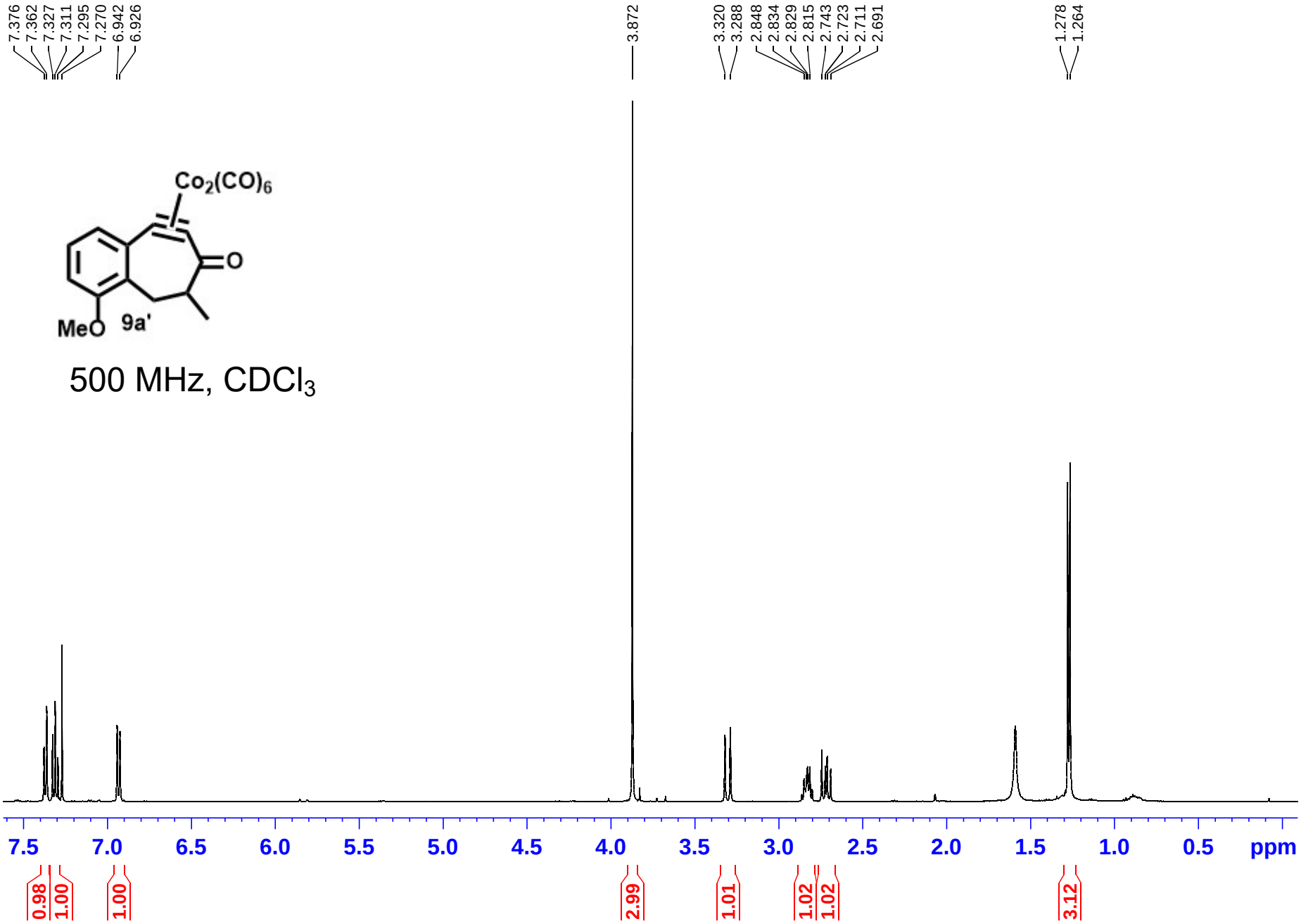
som.0727 2, 13C, p-cyclizn prod, mono OMe, 7/27/21



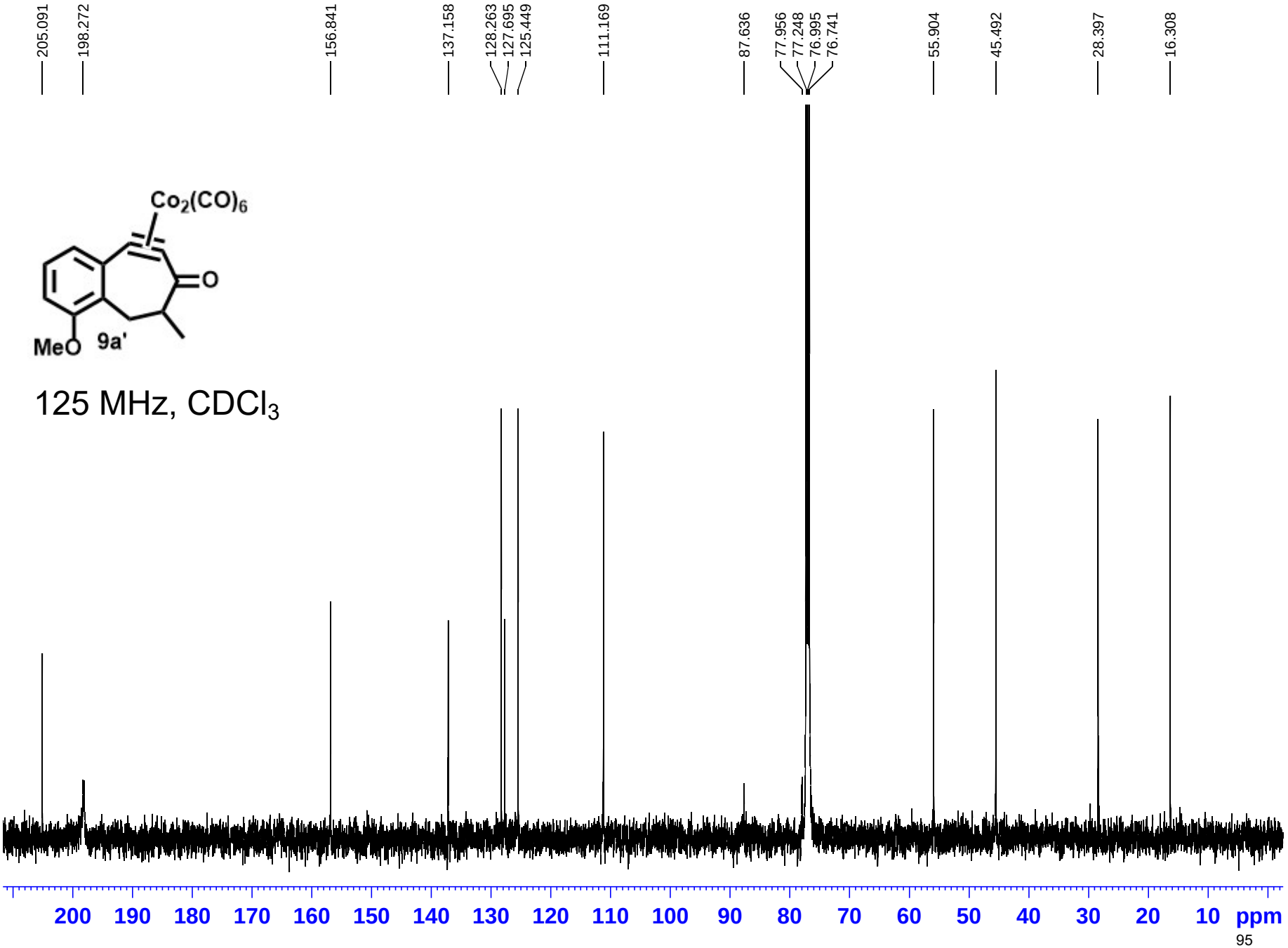
9a

75 MHz, $CDCl_3$

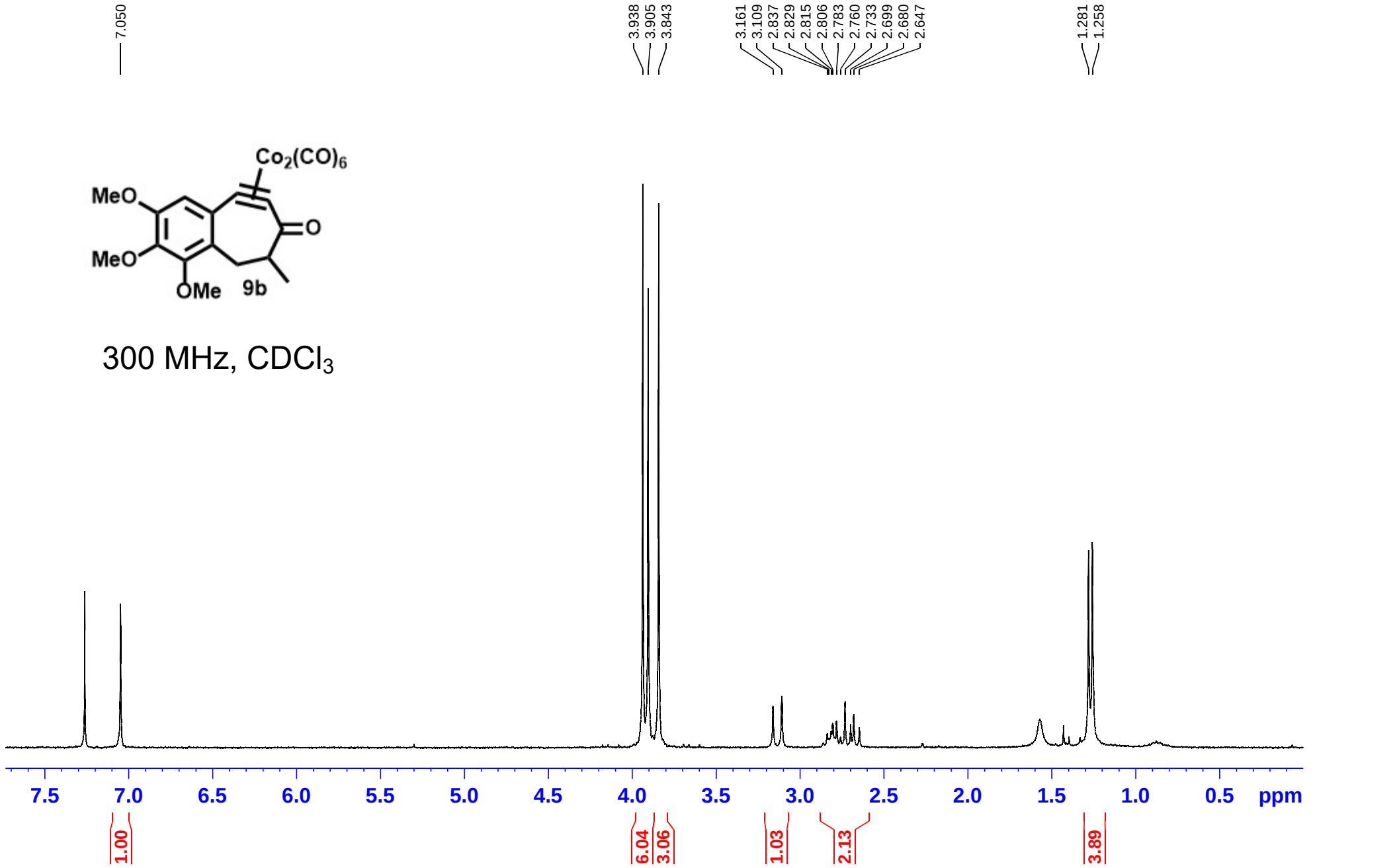
som.0728 1, minor prod, monoOMe Nazarov, 1H 500, 7/28/21



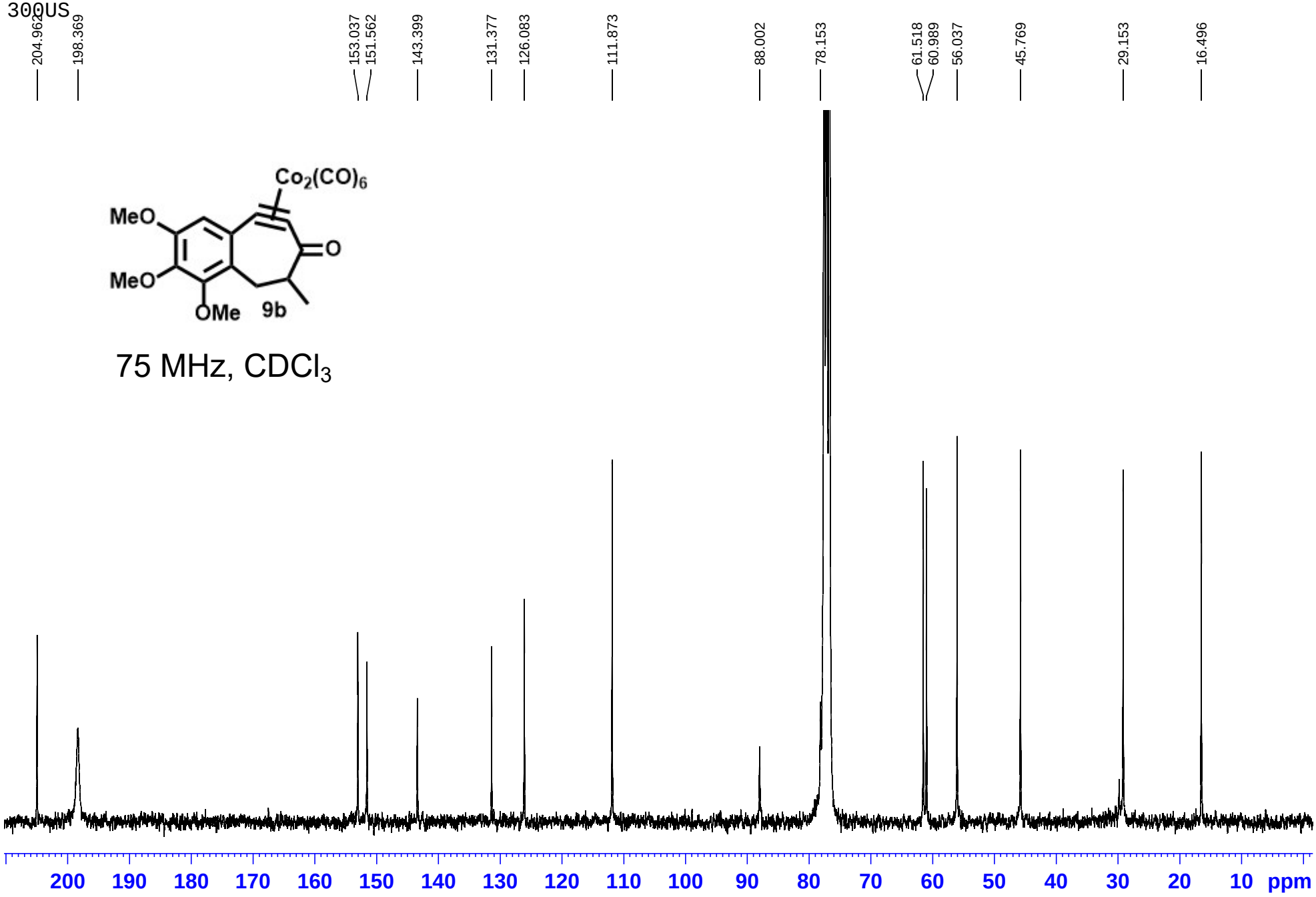
som.0728 2, 13C, mono OMe Nazarov, minor prod, 500, 7/28/21



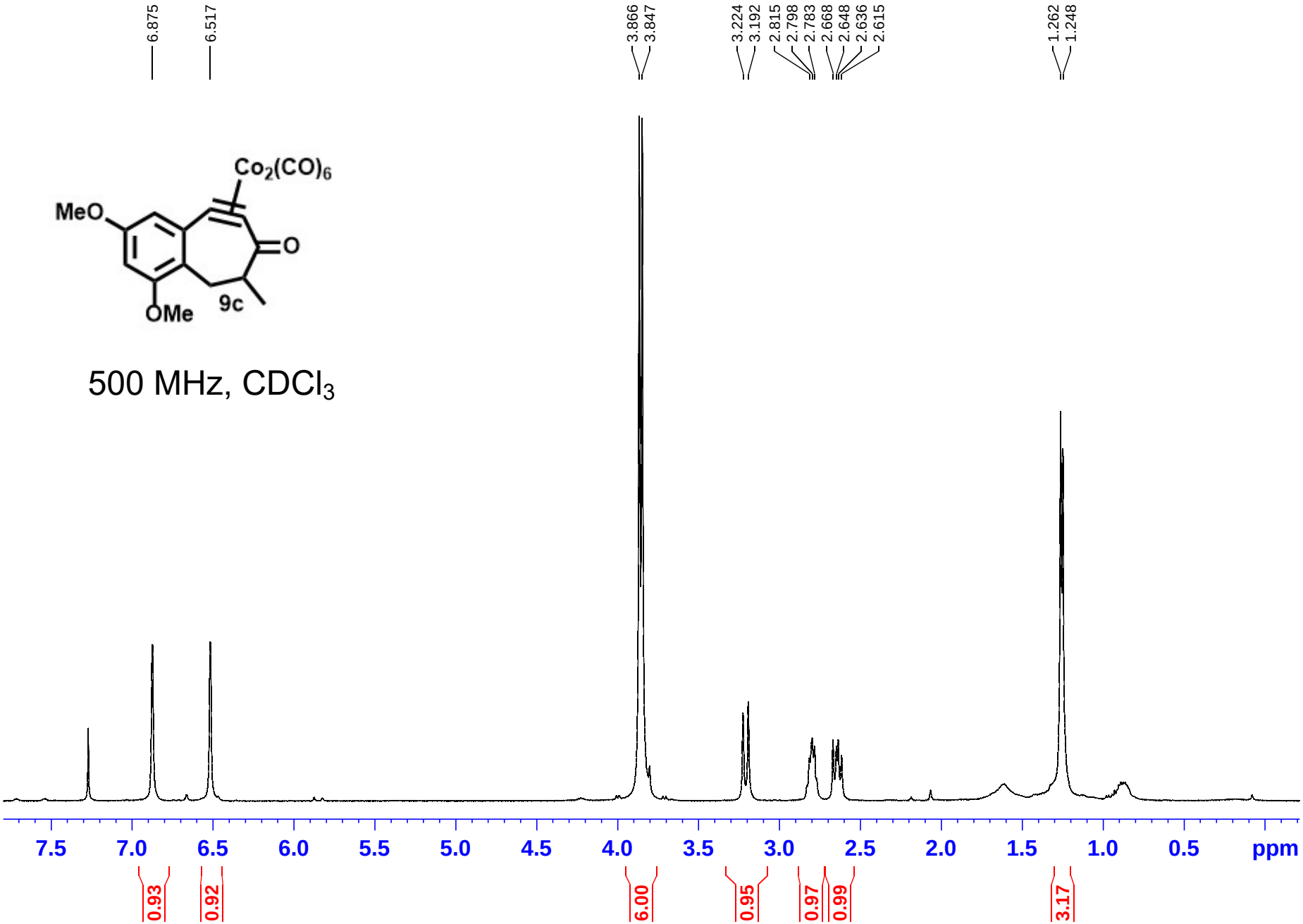
project3_trimethoxy_metha_SnCl4_cycli_H1
300US



3MeO_cc_cobalt_cycl_metha_c13
300US

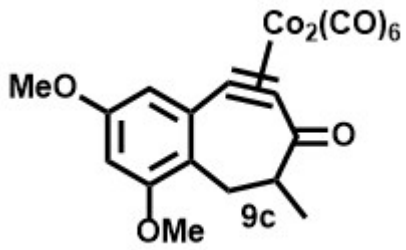


jrg.1099 2, main fr, 3,5-MeO2Ph-CC-CH(O)-C(Me)=CH2]-|Co2 cyclizn



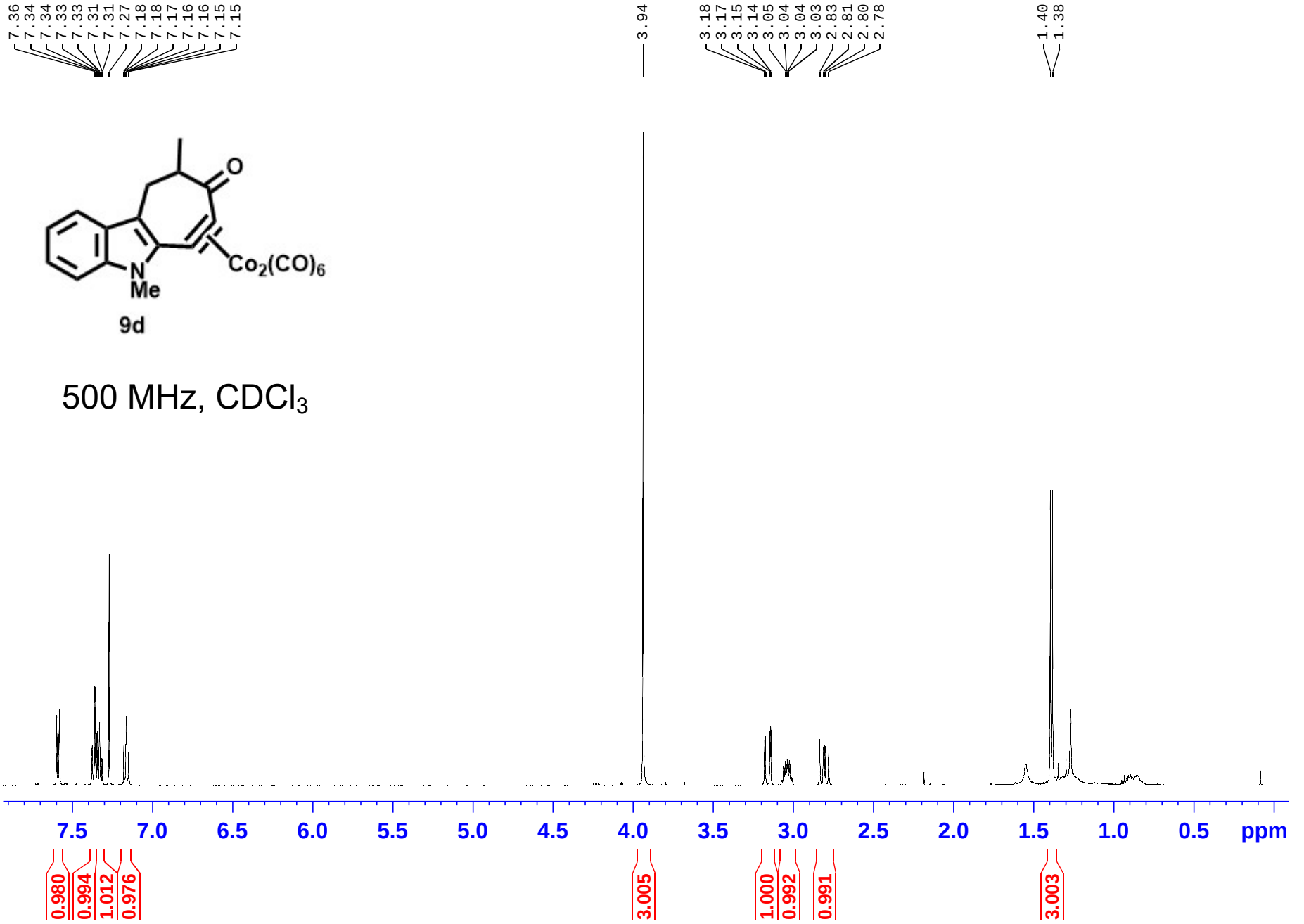
2MeO_CC_CYCL_ME_C13
300US

205.225
198.131
159.709
157.851
137.642
120.356
108.653
99.372
88.085
78.041
55.929
55.331
45.662
28.098
16.286

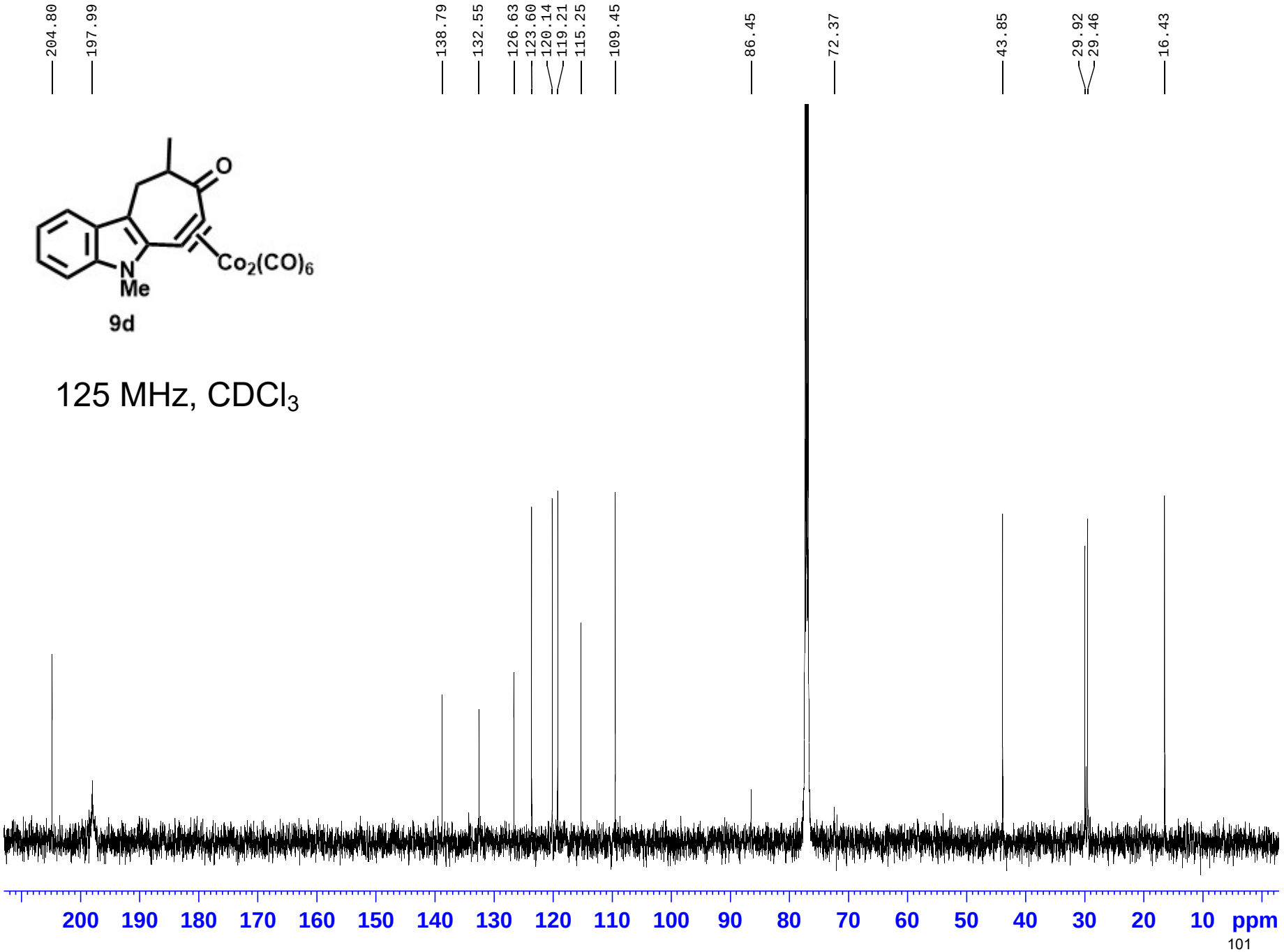


75 MHz, $CDCl_3$

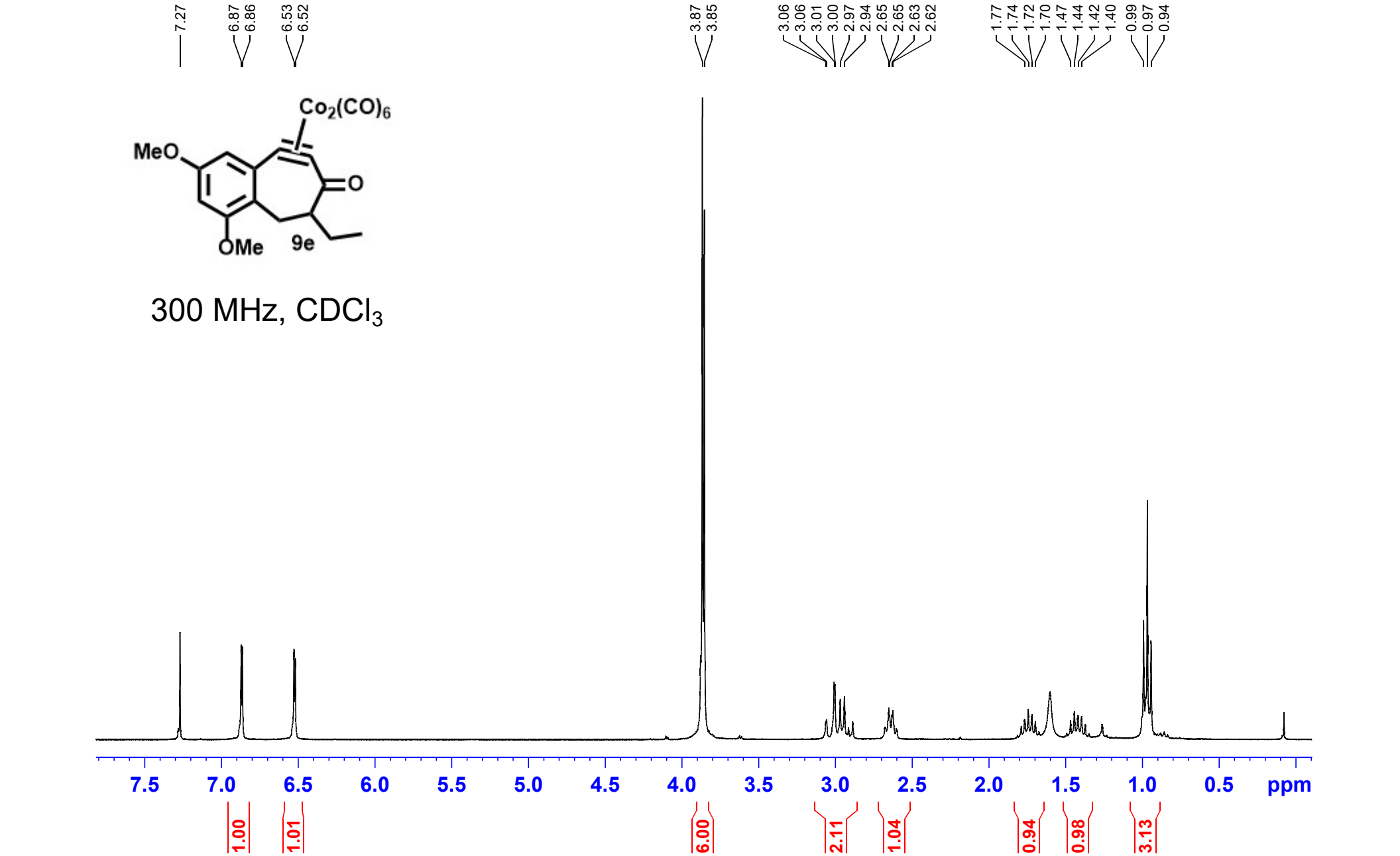
som.0704 1, indolyl cyclizn, 7/4/21



som.0704 2, 13C indolyl cyclizn, 7/4/21

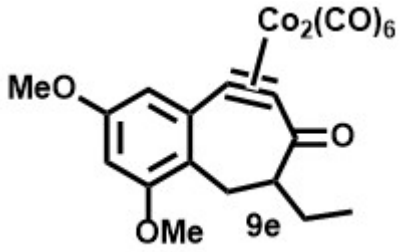


dimethoxy_cc_cobalt_cyclization_ethyl_H1
300US



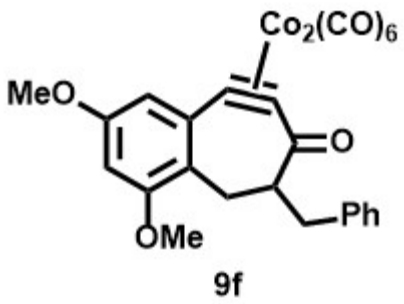
dimethoxy_cc_cobalt_cyclization_ethyl_C13_overnight
300US

205.371
198.308
159.794
158.134
138.033
119.764
108.668
99.440
87.531
56.041
55.443
53.189
25.242
23.538
11.820



75 MHz, $CDCl_3$

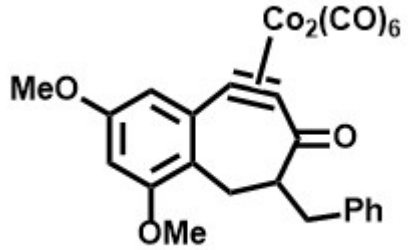
som.09e 1, cycliz prod, benzyl, 8/4/21



9f

300 MHz, $CDCl_3$

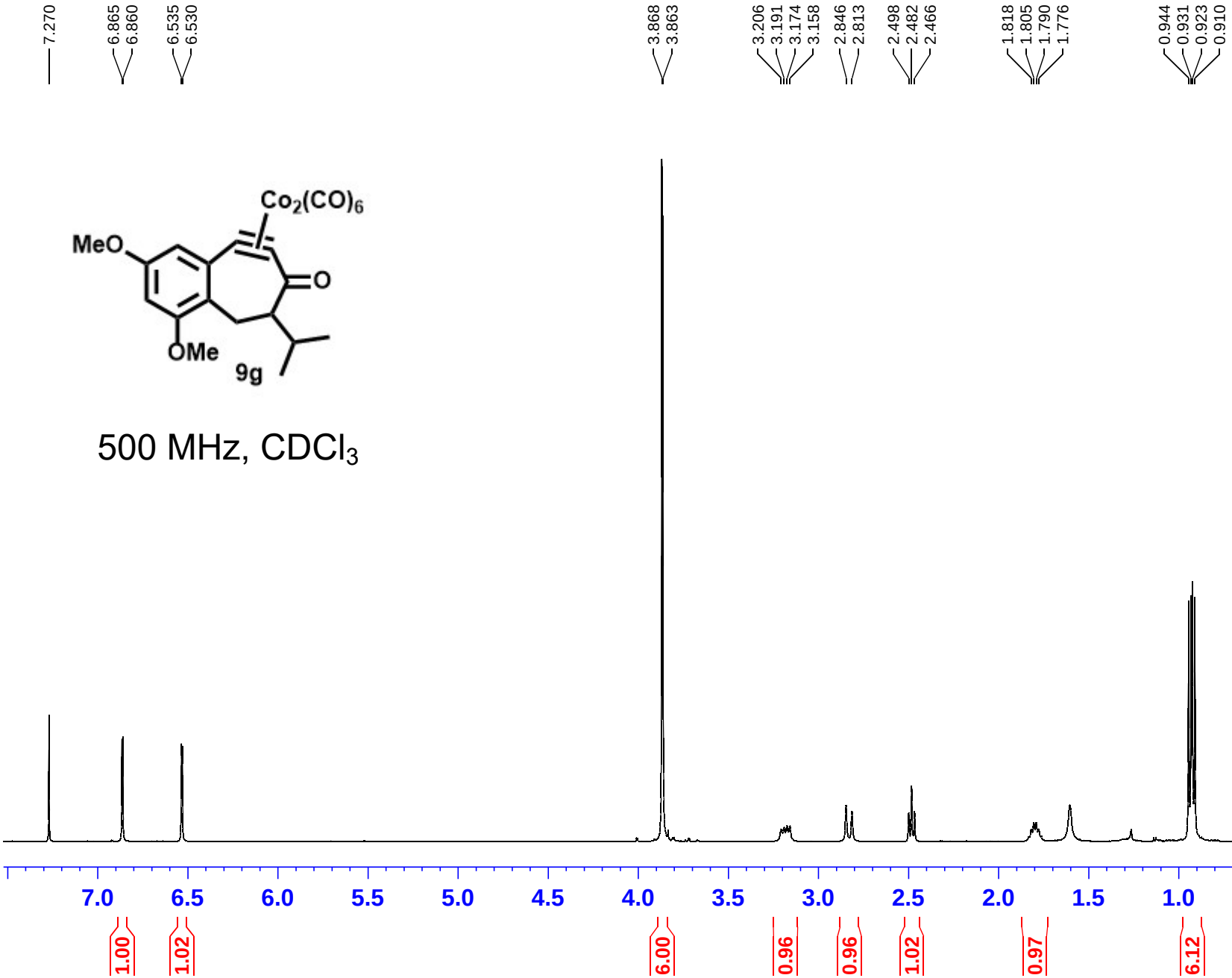
2MeO_Bn_cycl_c13
300US



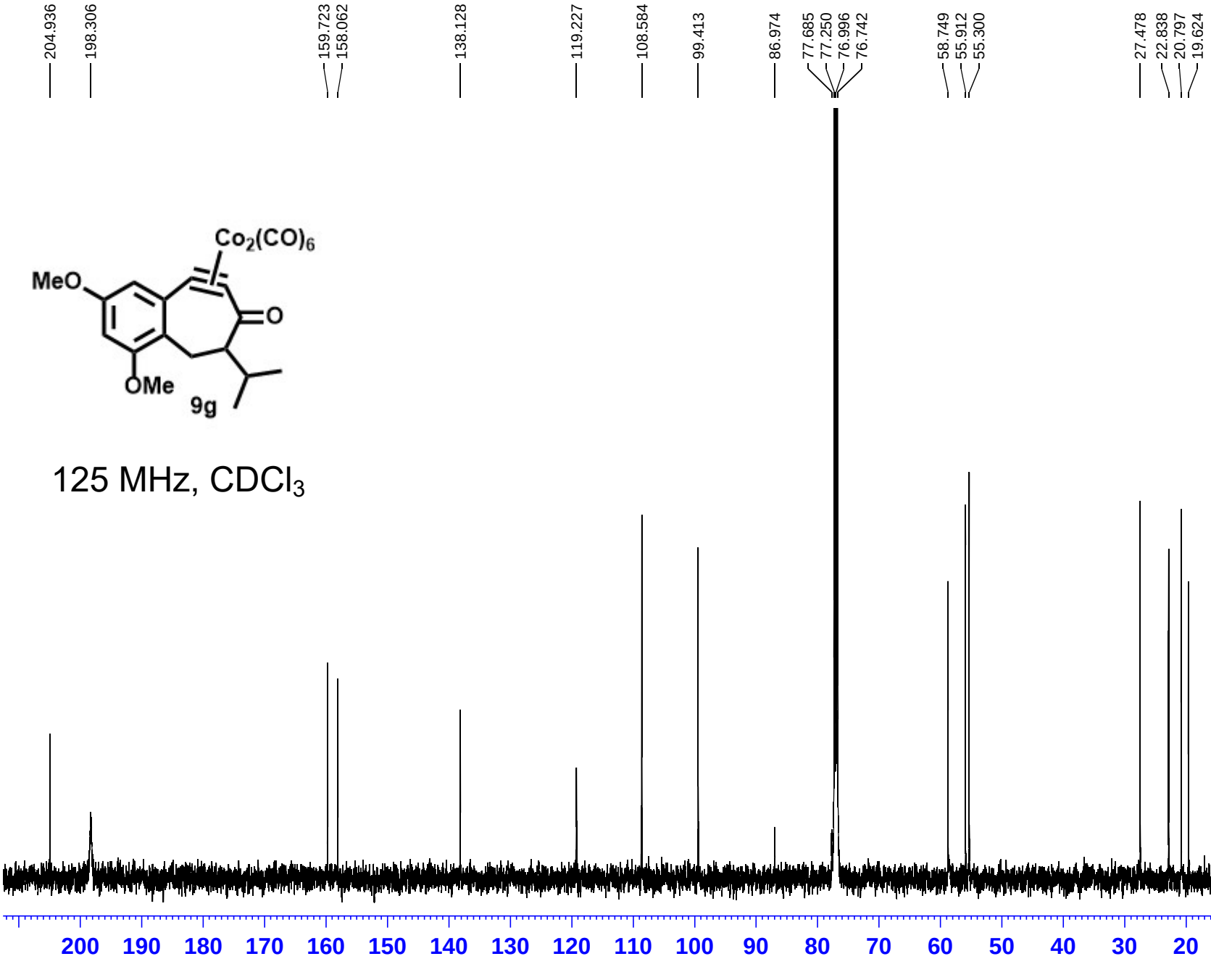
9f

75 MHz, $CDCl_3$

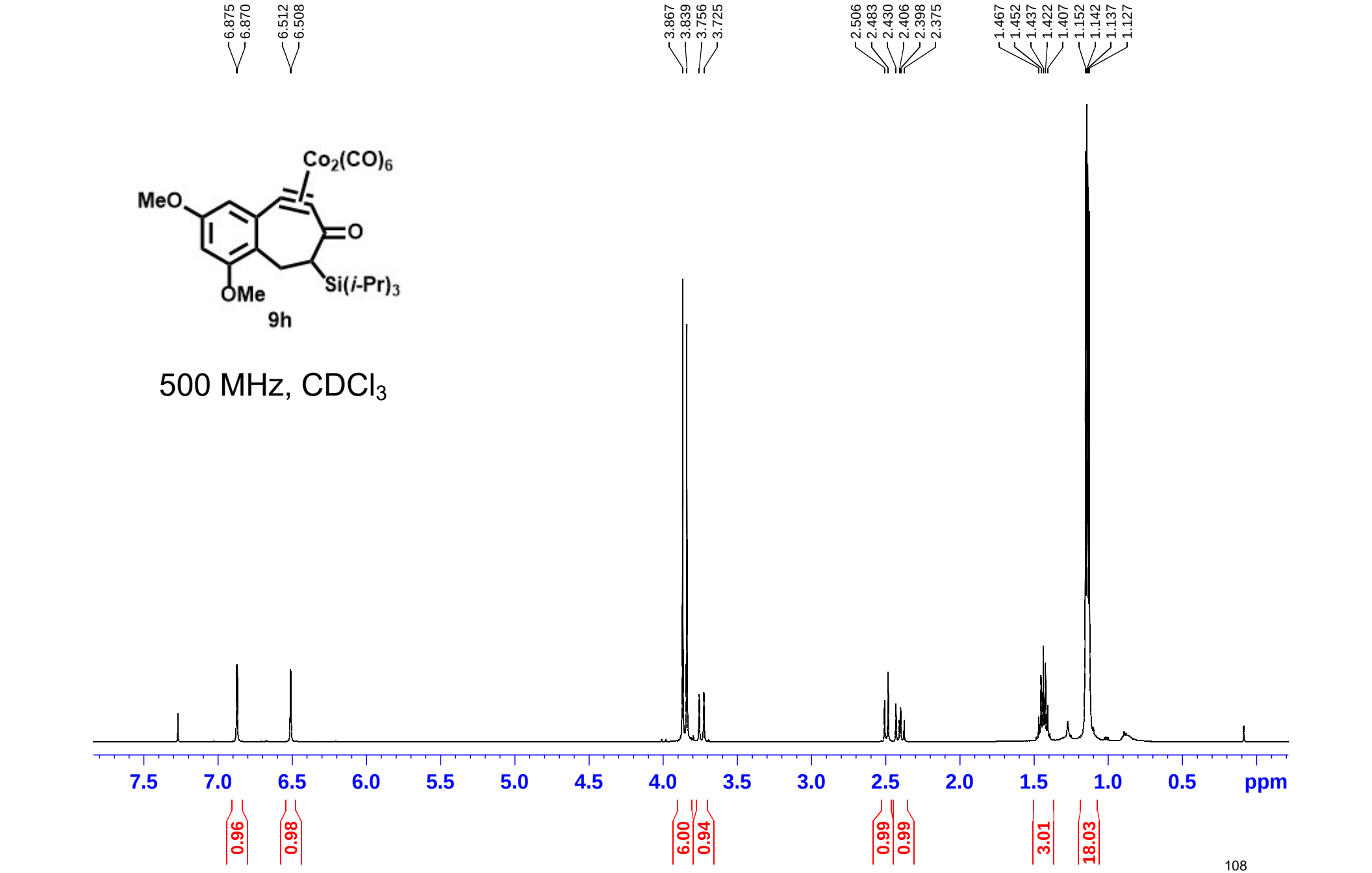
som.09f 1 1H, cyclized, di(OMe)-isopropyl, 9/5/21



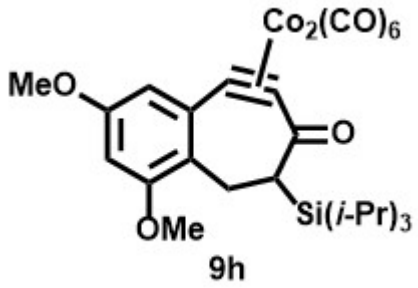
som.09f 2 13C, (MeO)2-isopropyl cyclizn, 9/5/21



som.09g 1H, (MeO)2Ph-cyclizn, TIPS, 9/23/21



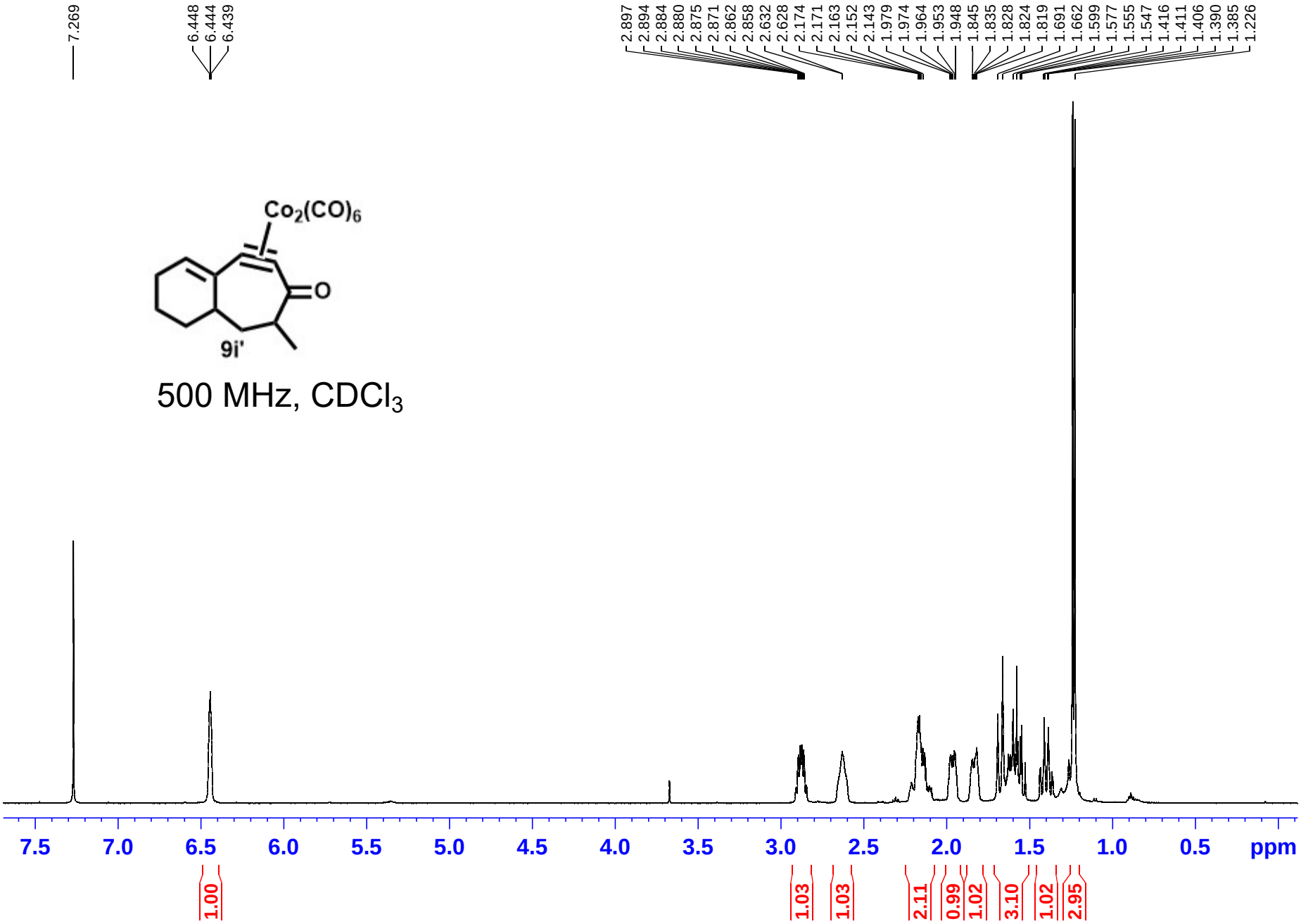
som.09g, 13C, (MeO)2Ph cyclizn, TIPS, 9/23/21



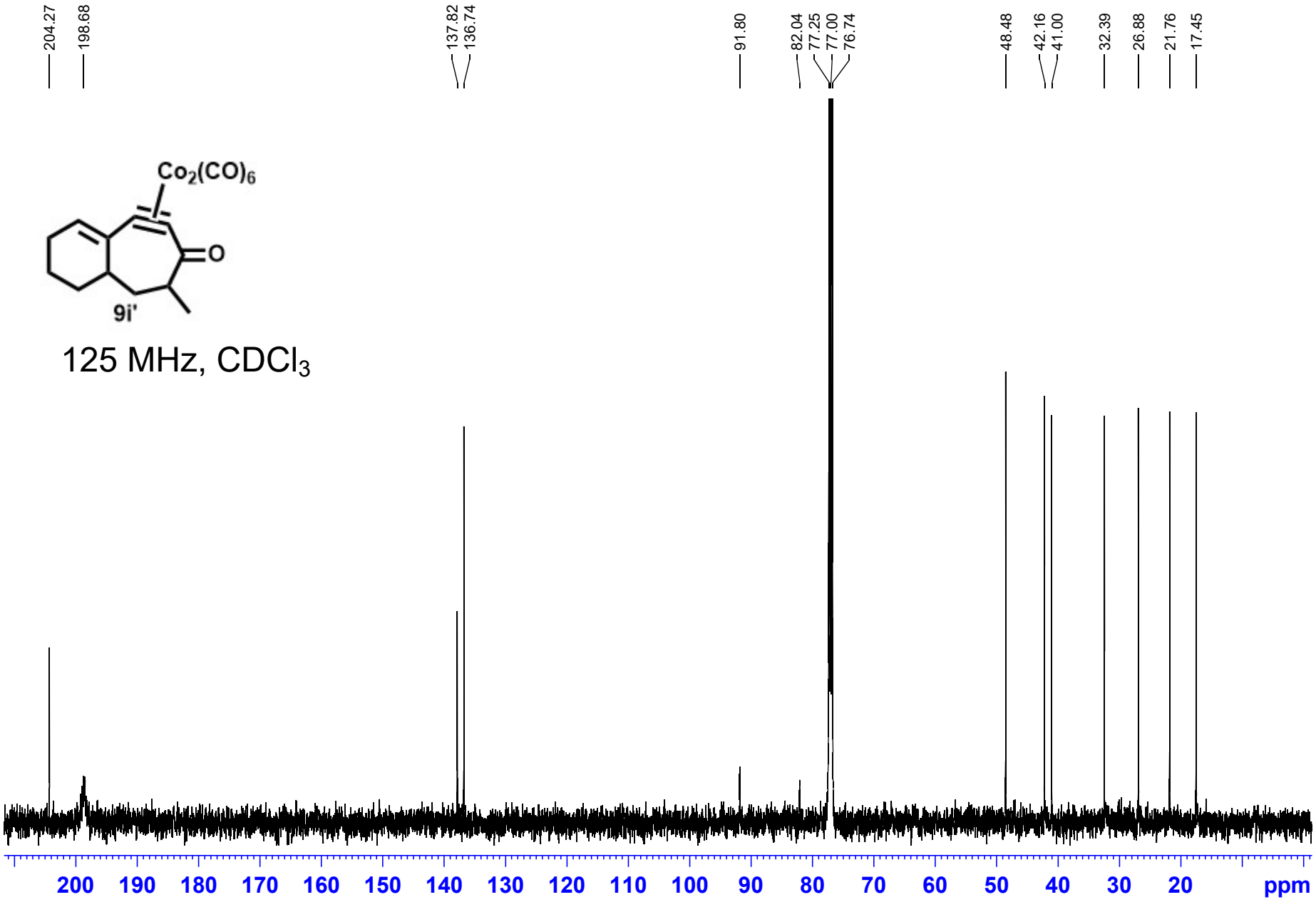
9h

125 MHz, $CDCl_3$

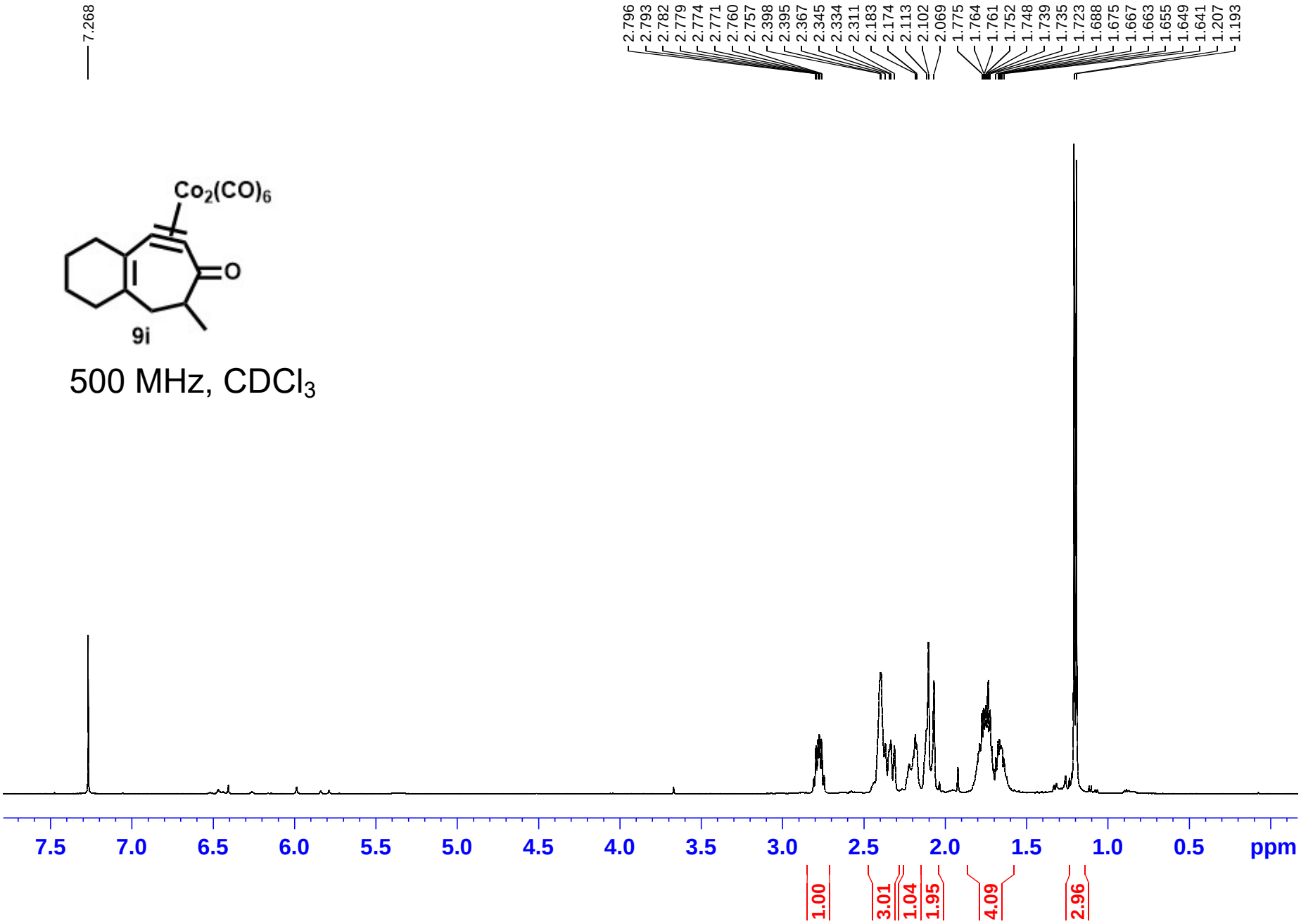
som.09i 11, cps 9i, 1st min fr 8/23/21



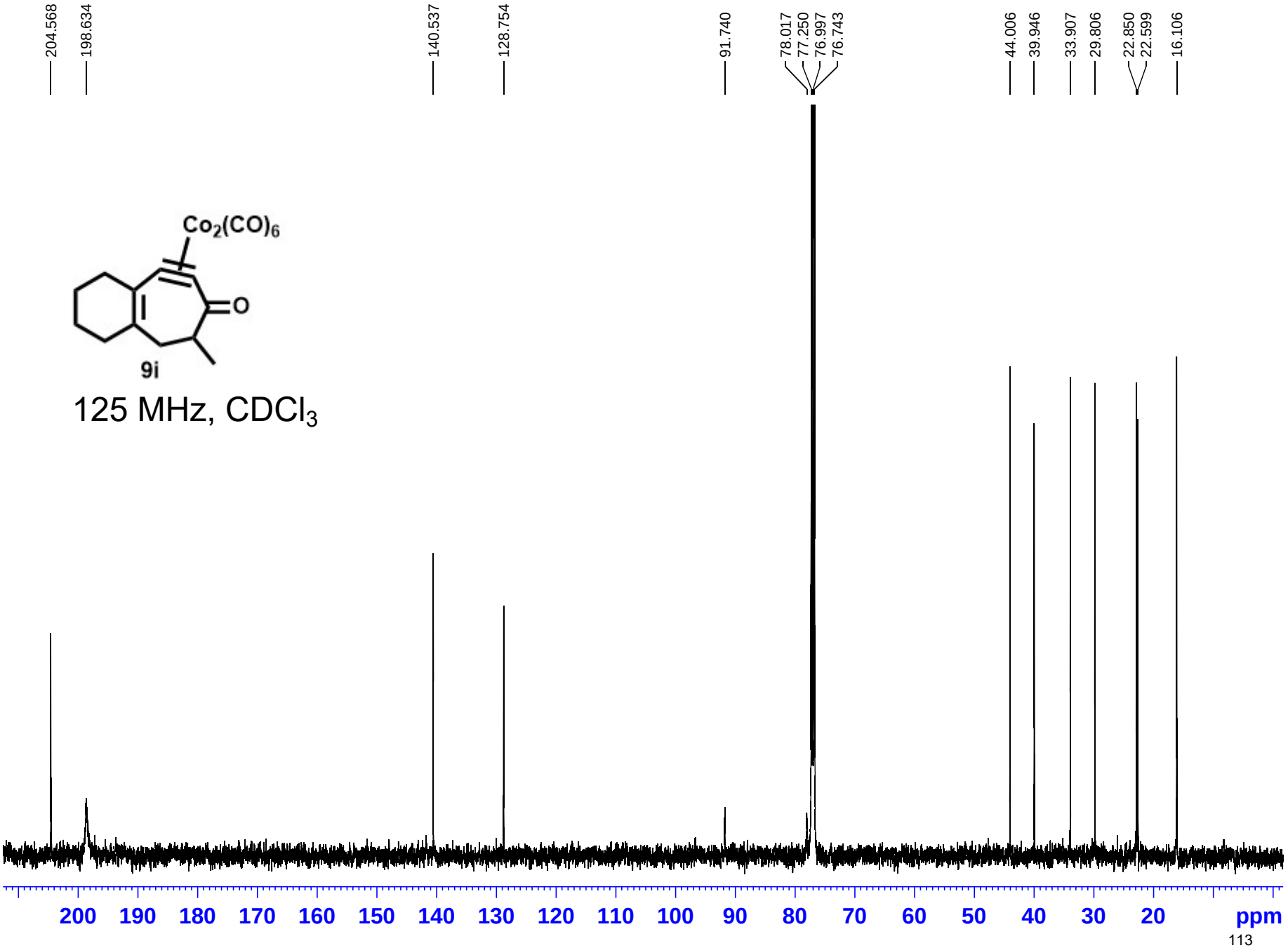
som.09i 1, fr1 (min), cyclohexene-Nazarov prod, 8/22/21



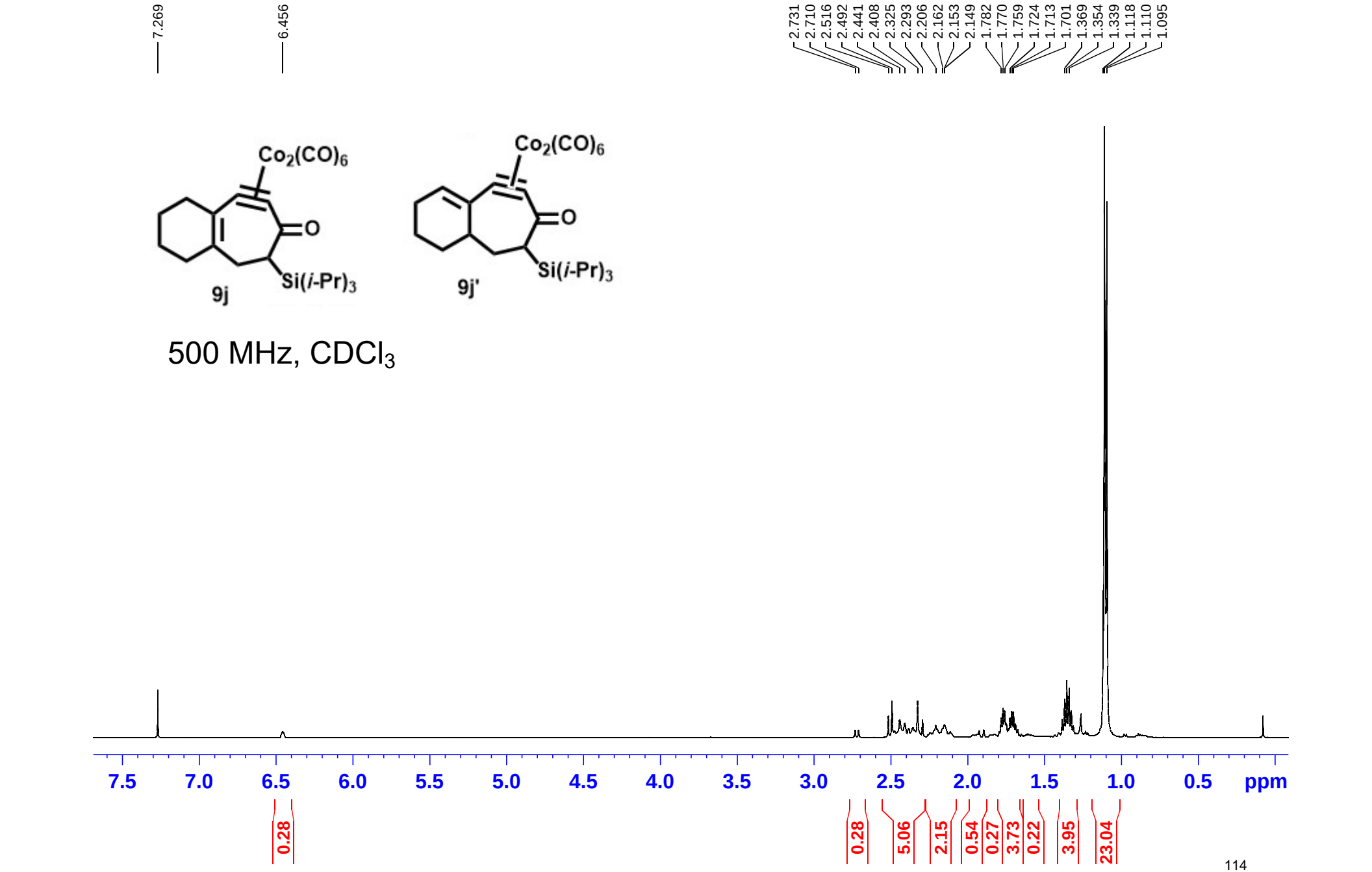
som.09i 5, cps 9i, 2nd maj fr 8/23/21



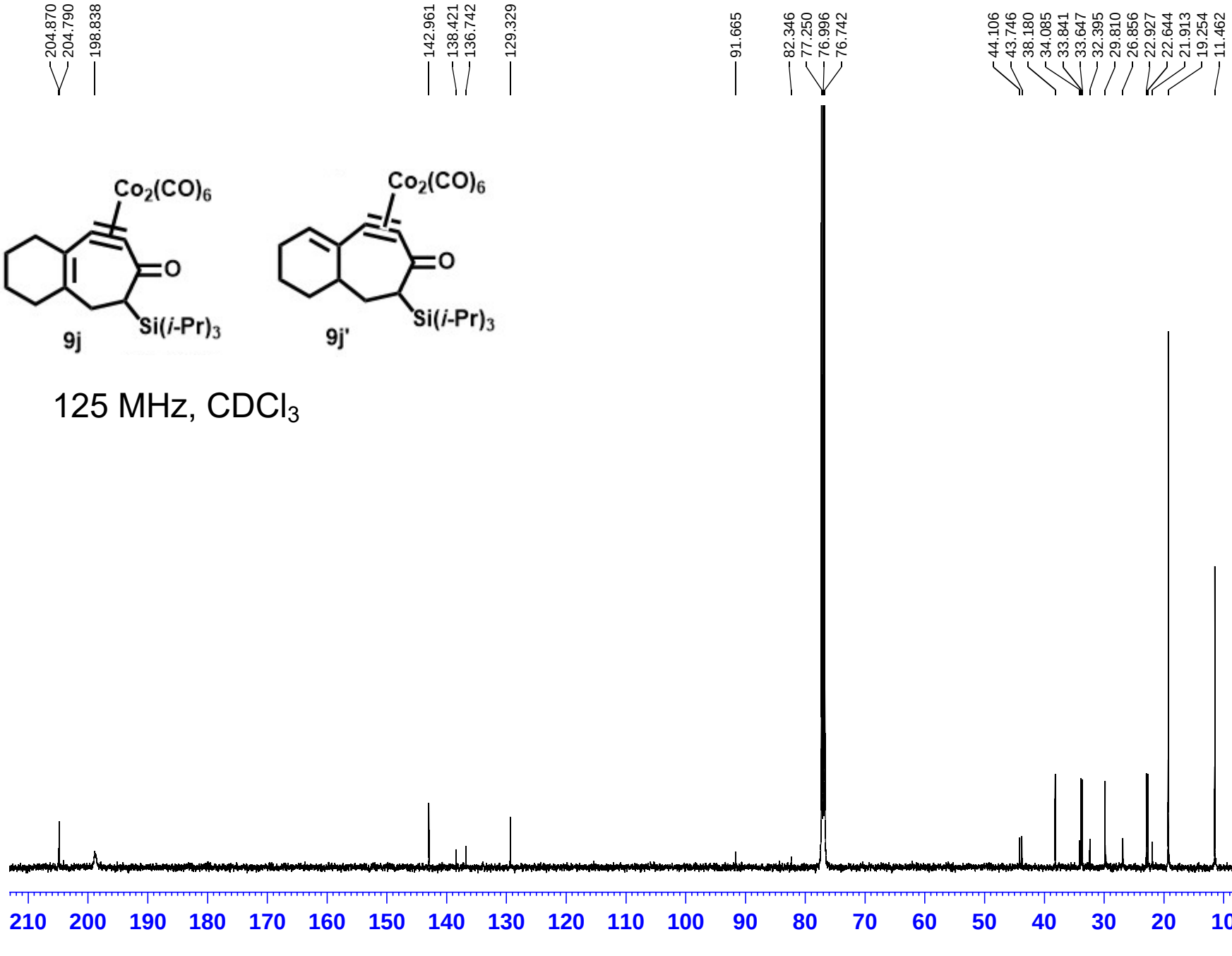
som.09i 6, 13C, maj/2nd fr, cpd 9i-b, 8/23/21



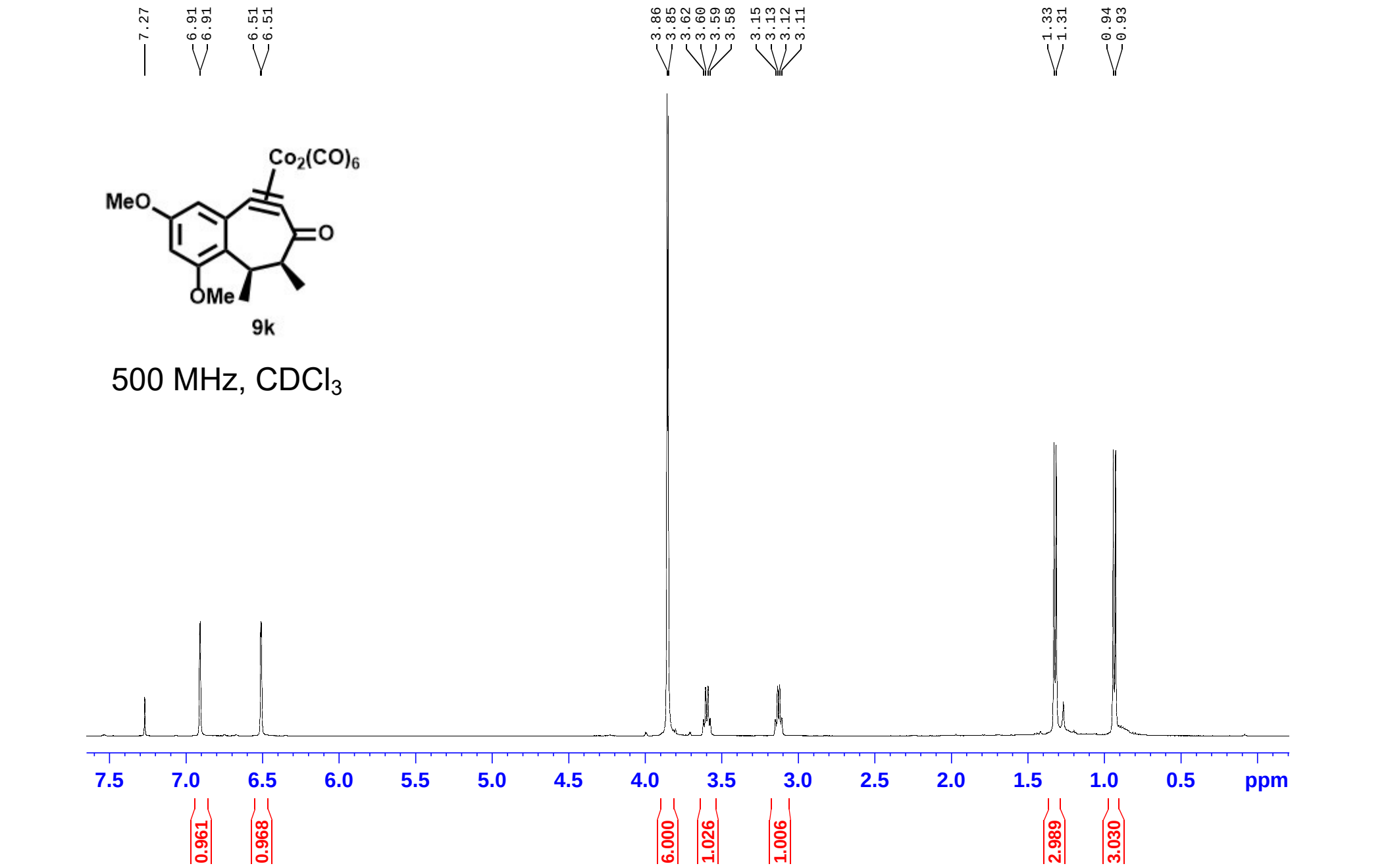
som.09j 3, 1H cyclohexenyl TIPS cycliz prod, 8/29/21



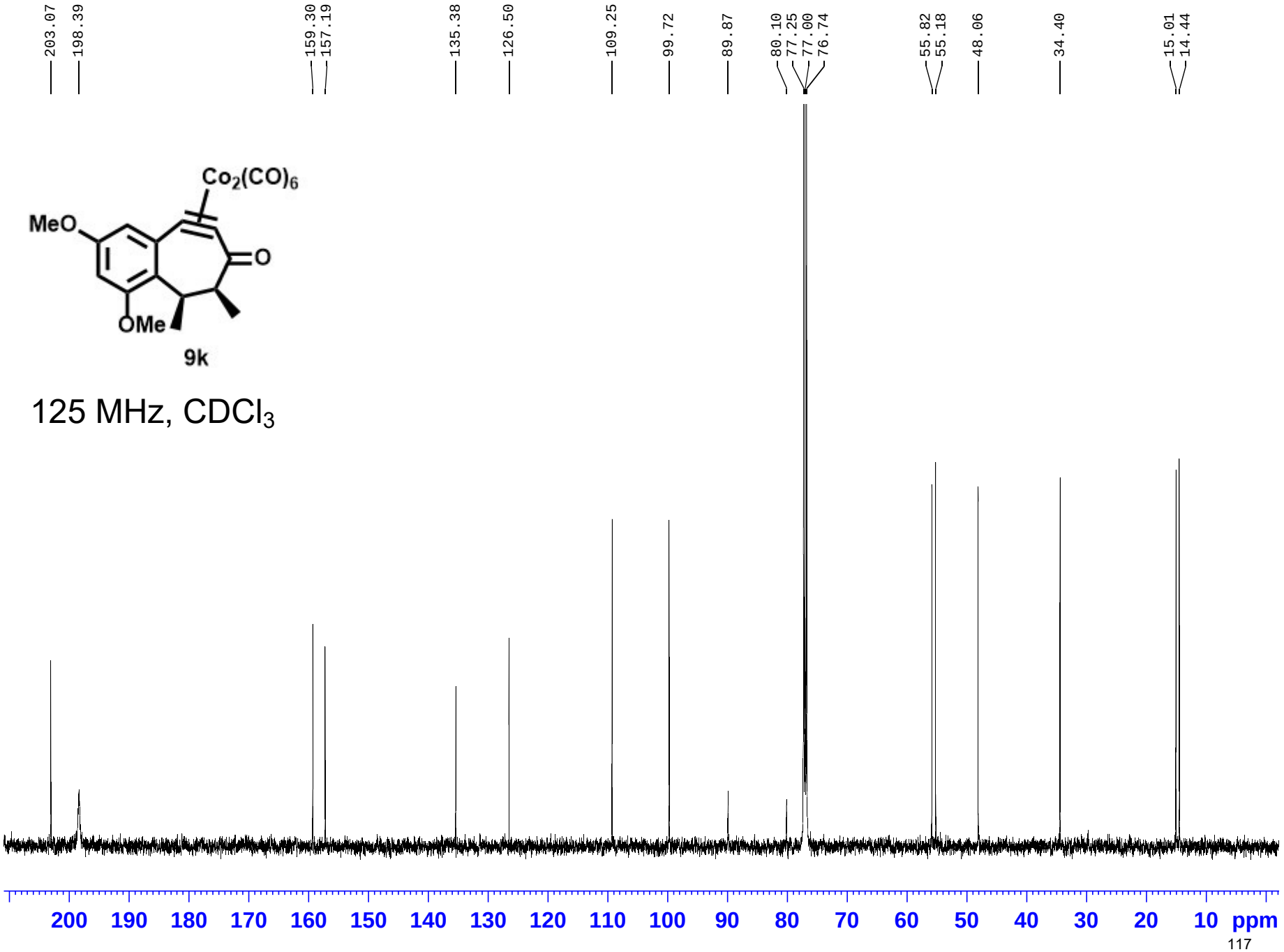
som.09j 4, 13C, cyclohexenyl cyclization TIPS, cpd 9j, 8/29/21



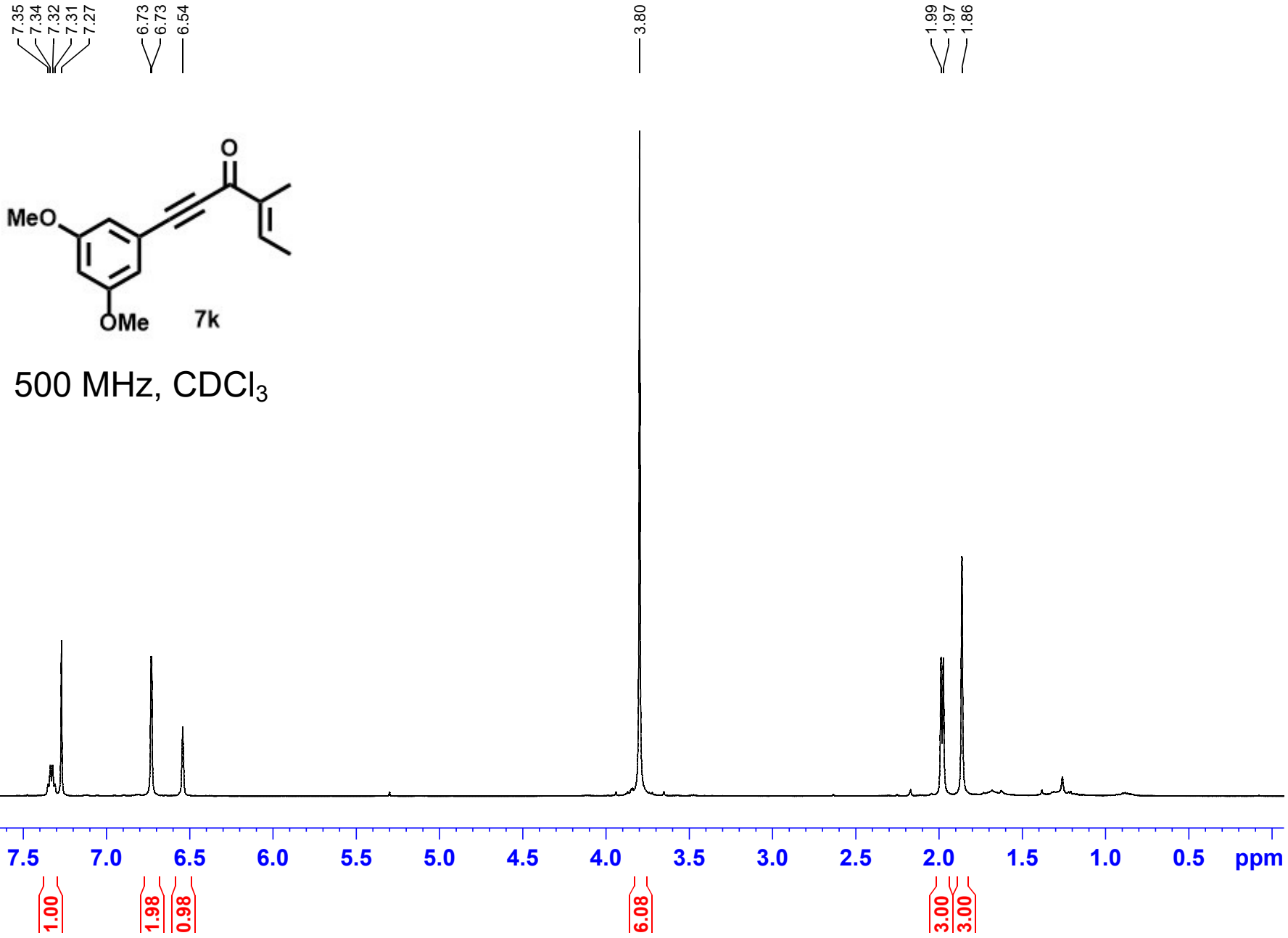
som.09k 16, , som 8k + SnCl4, 2days, fr1a 10/11/21



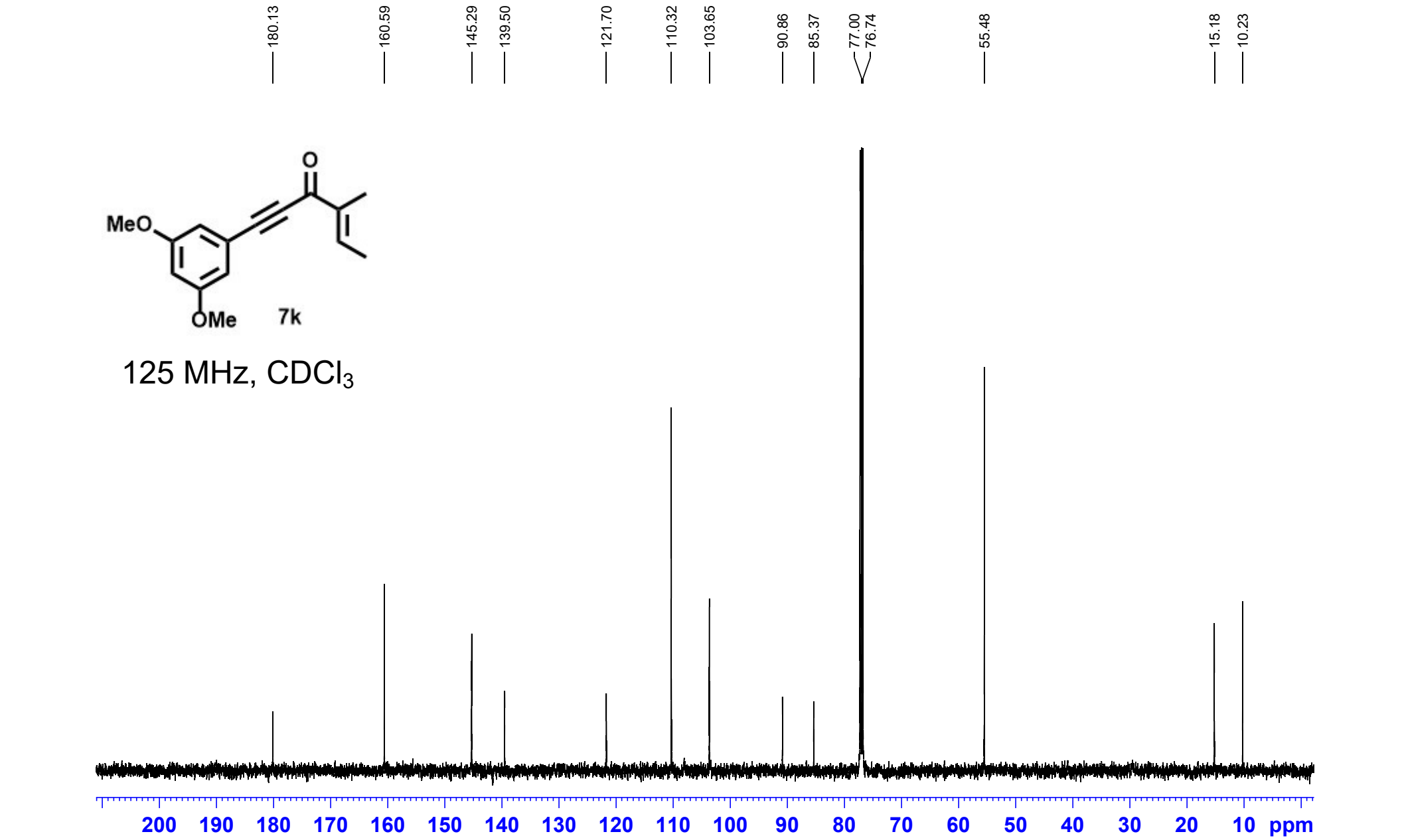
som.09k 17, 13C, tiglic cyclizn prod, 10/11/21



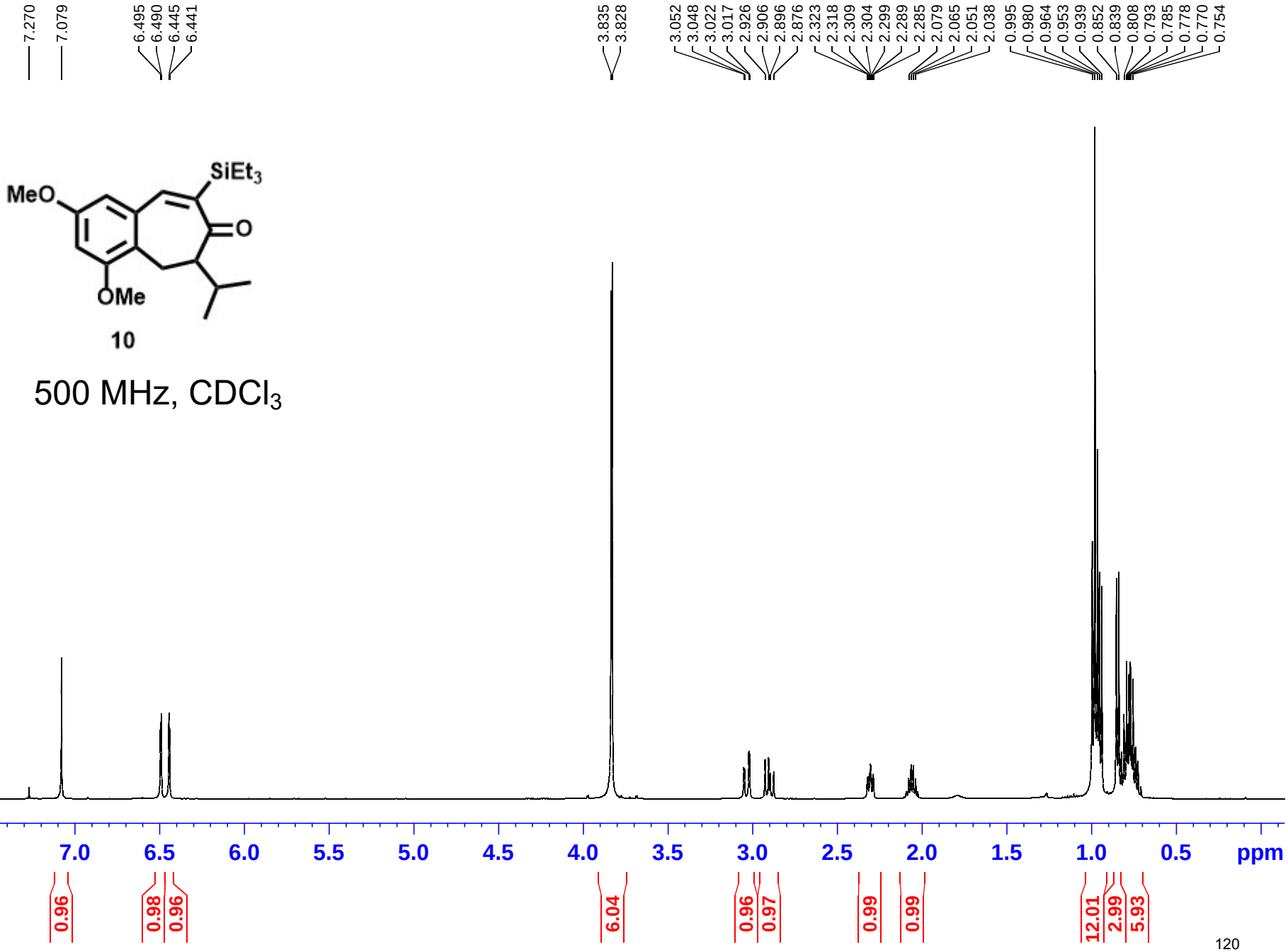
som.09k 13, , som 8k + SnCl4, 2days, fr2 10/9/21



som.09k 14, 13C fr2, decomp SM, 10/9/21

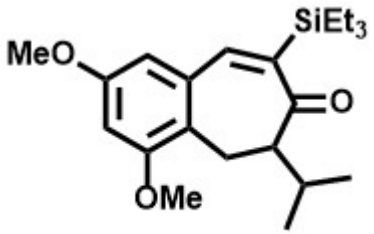


som.010 1, hydrosil of iPr prod, 9/7/21



som.010 2 13C, hydrosilylation, iPr cycliz prod, 9/7/21

208.563
158.594
157.656
147.541
142.394
137.910
120.997
107.079
99.767
77.251
76.997
76.742
60.762
55.888
55.340
28.507
21.559
21.068
19.131
7.453
3.503



10

125 MHz, $CDCl_3$