Supplementary Information

The Formation of Benzoxacin-3-ones via Intramolecular Nicholas Reactions and Synthesis of 8- Membered Heliannuols

Brent. St. Onge and James R. Green*

Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON, N9B 3P4, Canada

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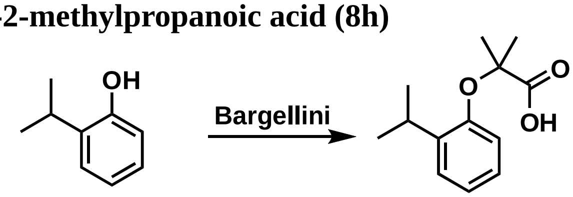
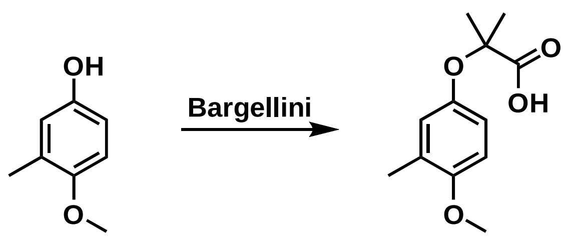
General Considerations. Reagents were obtained from commercial sources otherwise stated. Reactions were conducted under inert atmosphere (N_2) using glassware dried in an oven (110 °C, > 1h). The solvent for each reaction was acquired from a solvent purification system (Innovative Technologies). BF_3-OEt_2 was distilled prior to use and stored under an inert atmosphere (N_2). Flash chromatography was performed according to the method of Still. 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, on a GCT Time of Flight (Tof) Mass Spectrometer at Queen's University, 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 (*d*) 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. Phenolic ether carboxylic acids **8a-g,**[1] and **8i,**[2] were made by literature methods.

2-(2-Isopropylphenoxy)-2-methylpropanoic acid (8h)



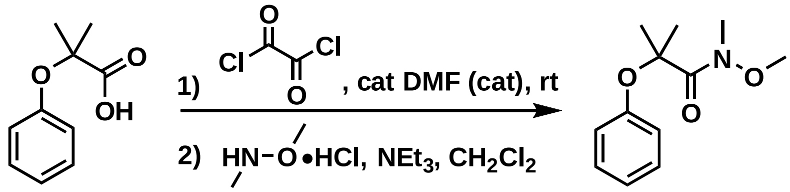
General Procedure 1 (GP1): Sodium hydroxide (1.4623 g, 36.6 mmol, 5 equiv) was added with acetone (7 mL). To the resulting suspension, a solution of 2-isopropyl phenol (0.9950 g, 7.31 mmol) in acetone (7 mL) was added. The mixture was heated to reflux for 30 min, and chloroform (0.79 mL, 8.8 mmol, 1.2 equiv) in acetone (7 mL) was added. The resulting solution was further stirred at reflux for 3.5 hours and was subsequently concentrated under vacuum. The residue was dissolved using water and extracted with dichloromethane. The aqueous phase was acidified using 1M HCl. The resulting white suspension was extracted with dichloromethane. The combined CH_2Cl_2 phases were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting **8h** was obtained as an off-white solid (1.1289 g, 70%) and of sufficient purity for subsequent use: **8h**, mp 85-86°C ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.51 (br s, 1H), 7.33 – 7.30 (m, 1H) 7.17 – 7.15 (m, 1H) 7.12 – 7.02 (m, 1H) 6.87 – 6.84 (m, 1H) 3.44 (septet, J = 6.9 Hz, 1H) 1.72 (s, 6H) 1.30 (d, J = 6.9 Hz, 6H); ^{13}C (75 MHz, $CDCl_3$) 180.6, 152.0, 139.7, 126.5, 126.0, 122.3, 116.9, 78.6, 26.9, 25.2, 22.8; IR $ν_{max}$: 3102, 3081, 2997, 2963, 1701, 1487, 1450, 1237, 1155, 754; HRMS m/e for $C_{13}H_{18}O_3$ calcd (M^+) 222.1255 found 222.1253.

2-(4-Methoxy-3-methylphenoxy)-2-methylpropanoic acid (8j)



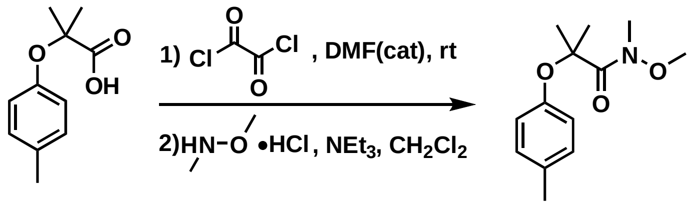
The application of **GP1** using 4-methyl-3-methoxyphenol (0.5376 g, 3.89 mmol). The resulting **8j** was obtained as a light tan oil (0.6694 g, 77%) and of sufficient purity for future use: **8j**, ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (br s, 1H), 6.80 – 6.68 (m, 3H) 3.80 (s, 3H) 2.19 (s, 3H) 1.56 (s, 6H);^{13}C (125 MHz, $CDCl_3$) 177.5, 154.3, 146.8, 127.6, 124.6, 119.5, 110.2, 80.2, 55.6, 24.8, 16.3; IR $ν_{max}$: 2983, 2940, 2835, 1708, 1497, 1465, 1256, 1142, 1033; HRMS m/e for $C_{12}H_{16}O_4$ calcd (M^+) 224.1049 found 224.1051.

N-Methoxy-N,2-dimethyl-2-(phenoxy)propenamide (9a)



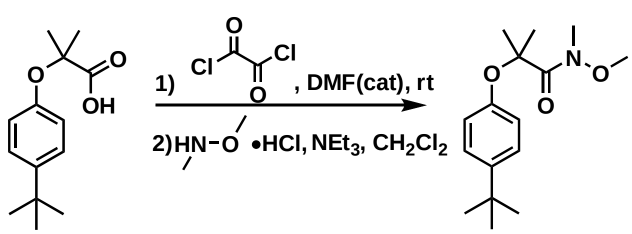
General Procedure 2 (**GP2):** To a 50mL 2-necked round bottom flask containing carboxylic acid **8a** (0.5250 g, 2.97 mmol) was added dry dichloromethane (25 mL) and a drying tube. To the resulting solution, a few drops of dimethylformamide (DMF) and oxalyl chloride (0.764 mL, 8.91 mmol, 3 equiv) was added dropwise (**HCl formation!**). The resulting solution was stirred at room temperature for 3.5 h and concentrated under reduced pressure to yield the crude acid chloride. The flask was fitted with a drying tube and dichloromethane (25 mL) was added. N,O-dimethylhydroxylamine hydrochloride was added (0.3475 g, 3.56 mmol, 1.2 equiv), followed by triethylamine (1.03 mL, 7.42 mmol, 2.5 equiv) at 0°C dropwise. Once the addition of triethylamine is complete, the resulted solution was allowed to stir overnight at room temperature. Saturated sodium bicarbonate was added and the mixture extracted with dichloromethane. The organic phase was then washed with 1M HCl (3x) and brine. The organic phase was dried using magnesium sulfate ($MgSO_4$) and concentrated under reduced pressure. The product **9a** was sufficient purity for future use as a tan oil (0.6492 g, 98%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (m, 2H) 6.97 – 6.92 (m, 1H) 6.86 (m, 2H) 3.58 (s, 3H) 3.28 (s, 3H) 1.61 (s, 6H); ^{13}C (75 MHz, $CDCl_3$) 172.8, 155.5, 129.2, 121.5, 118.1, 79.7, 60.4, 34.5, 25.0; IR ν_{max} : 2991, 2979, 1650, 1595, 1490, 1228, 1148, 753, 694; HRMS m/e for $C_{12}H_{17}NO_3$ calcd (M^++H) 224.1286 found 224.1282.

N-Methoxy-N,2-dimethyl-2-(p-tolyloxy)propenamide (9b)



GP2 was applied to carboxylic acid **8b** (0.5167 g, 2.66 mmol) employing oxalyl chloride (0.680 mL, 7.98 mmol, 3 equiv), N,O-dimethylhydroxylamine hydrochloride (0.3114 g, 3.19 mmol, 1.2 equiv) and triethylamine (0.930 mL, 6.65 mmol, 2.5 equiv). Once the addition of triethylamine was complete, the resulting solution was allowed to stir overnight at room temperature. The reaction was quenched with saturated sodium bicarbonate and extracted with dichloromethane. The organic phase was then washed with 1M HCl (3x) and brine. The organic phase was dried using magnesium sulfate ($MgSO_4$) and concentrated under reduced pressure. The product **9b** was isolated as a yellow oil (0.5921 g, 94%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (d, J = 8.4 Hz, 2H) 6.74 (d, J = 8.4 Hz, 2H) 3.59 (s, 3H) 3.27 (s, 3H) 2.24 (s, 3H) 1.57 (s, 6H); ^{13}C (75 MHz, $CDCl_3$) 172.7, 153.2, 130.9, 129.6, 118.1, 79.7, 60.4, 34.5, 24.9, 20.3; IR ν_{max} : 2974, 2924, 1652, 1611, 1583, 1506, 1227, 1150, 811; HRMS m/e for $C_{13}H_{19}NO_3$ calcd (M^++H) 238.1443 found 238.1440.

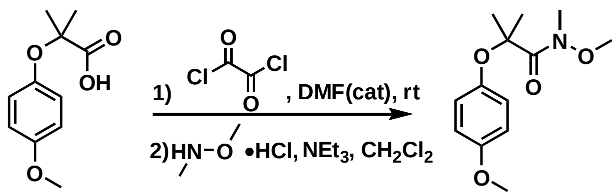
2-(4-tert-Butylphenoxy)-N-methoxy-N,2-dimethylpropanamide (9c)



GP2 was applied to carboxylic acid **8c** (0.6255 g, 2.64 mmol), using oxalyl chloride (0.680 mL, 7.94 mmol), N,O-dimethylhydroxylamine hydrochloride (0.3098 g, 3.17 mmol), and triethylamine (0.920 mL, 6.60 mmol). The product **9c** was isolated crude as a gold oil (0.6159 g, 83%); ^{1}H NMR (300 MHz, $CDCl_3$) δ7.22 (d, J = 7.5 Hz, 2H) 6.78 (d, J = 7.8 Hz, 2H), 3.60 (s, 3H) 3.29 (s, 3H)

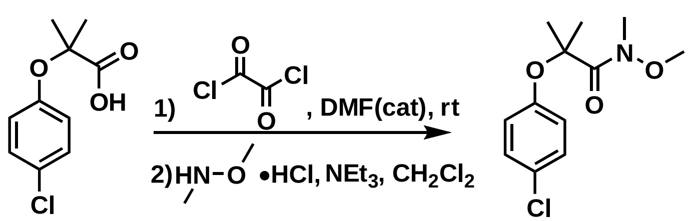
1.58 (s, 6H) 1.26 (s, 9H); ^{13}C (75 MHz, $CDCl_3$) 173.5, 153.2, 144.5, 126.1, 118.0, 79.9, 60.6, 34.8, 34.1, 31.5, 25.2; IR ν_{max} : 2961, 2903, 1652, 1607, 1509, 1461, 1290, 1176, 832; HRMS m/e for $C_{16}H_{25}NO_3$ calcd (M^++H) 280.1912 found 280.1908.

N-Methoxy-2-(4-methoxyphenoxy)-N,2-dimethylpropanamide (9d)



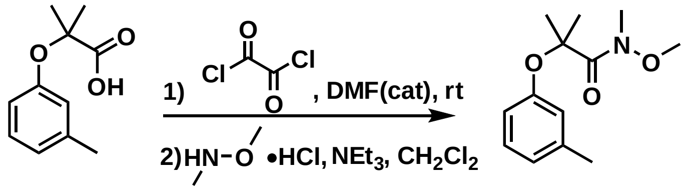
GP2 was applied to carboxylic acid **8d** (0.7593 g, 3.61 mmol), using oxalyl chloride (0.930 mL, 10.8 mmol), N,O-dimethylhydroxylamine hydrochloride (0.4228 g, 4.33 mmol), and triethylamine (1.26 mL, 9.03 mmol). The crude product subjected to flash chromatography using 5:1 petroleum ether : Et_2O, to afford **9d** as a yellow oil (0.6555 g, 72%); ^1H NMR (300 MHz, $CDCl_3$) δ 6.83 – 6.74 (m, 4H) 3.74 (s, 3H) 3.64 (s, 3H), 3.30 (br s, 3H), 1.55 (s, 6H); ^{13}C (125 MHz, $CDCl_3$) 173.5, 154.6, 149.1, 120.0, 114.3, 80.2, 60.5, 55.4, 34.6, 25.0; IR ν_{max} : 2993, 2936, 2835, 1650, 1504, 1441, 1216, 1149; HRMS m/e for $C_{13}H_{19}NO_4$ calcd (M^++H) 254.1392 found 254.1394.

2-(4-Chlorophenoxy)-N-methoxy-N,2-dimethylpropanamide (9e)



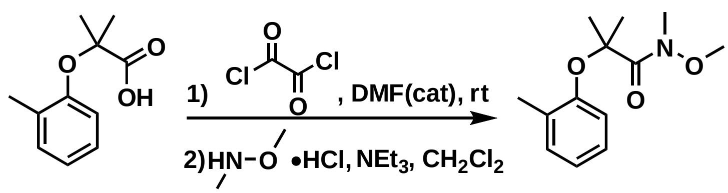
GP2 was applied to carboxylic acid derivative **8e** (0.8148 g, 3.79 mmol), using oxalyl chloride (0.980 mL, 11.3 mmol), N,O-dimethylhydroxylamine hydrochloride (0.4443 g, 4.55 mmol), and triethylamine (1.32 mL, 9.49 mmol). The crude product subjected to flash chromatography 10:1 petroleum ether : Et_2O, which gave **9e** as a yellow oil (0.6074 g, 62%); this material was spectroscopically identical to a literature report.[3]

N-Methoxy-N,2-dimethyl-2-(m-tolyloxy)propenamide (9f)



GP2 was applied to carboxylic acid derivative carboxylic acid **8f** (0.6328 g, 3.26 mmol), using oxalyl chloride (0.840 mL, 9.77 mmol), N,O-dimethylhydroxylamine hydrochloride (0.3814 g, 3.91 mmol), and triethylamine (1.14 mL, 8.14 mmol). The crude product was subjected to flash chromatography (10:1 petroleum ether : Et_2O) to afford **9f** a pale yellow oil (0.4559 g, 59%); ^1H NMR (500 MHz, $CDCl_3$) δ 7.11 (m, 1H), 6.78 (m, 1H), 6.70 – 6.64 (m, 2H), 3.61 (s, 3H), 3.30 (s, 3H), 2.29 (s, 3H), 1.61 (s, 6H);^{13}C (125 MHz, $CDCl_3$) 173.4, 155.5, 139.3, 129.0, 122.5, 119.0, 114.9, 79.7, 60.5, 34.7, 25.1, 21.4; IR ν_{max} : 2980, 2923, 2866, 1652, 1601, 1487, 1258, 1171; HRMS m/e for $C_{13}H_{19}NO_3$ calcd (M^++H) 238.1443 found 238.1444.

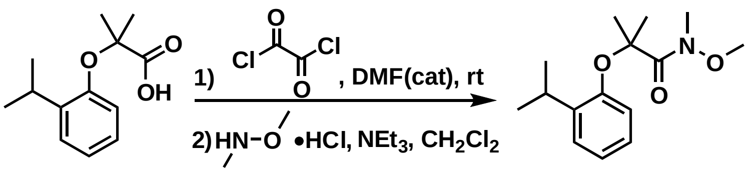
N-Methoxy-N,2-dimethyl-2-(o-tolyloxy)propenamide (9g)



GP2 was applied to carboxylic acid derivative carboxylic acid **8g** (0.7603 g, 3.91 mmol), using oxalyl chloride (1.00 mL, 11.7 mmol), N,O-dimethylhydroxylamine hydrochloride (0.4582 g, 4.70 mmol), and triethylamine (1.36 mL, 9.79 mmol). The crude product was subjected to flash chromatography (10:1 petroleum ether : Et_2O) to give **9g** as a white crystalline solid (0.6805 g, 73 %), mp 63-65°C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.13 (d, J = 7.4 Hz, 1H) 7.04 (apparent t, J = 7.8 Hz, 1H) 6.85 (apparent t, J = 7.4 Hz, 1H) 6.75 (d, J = 8.1 Hz, 1H) 3.56 (s, 3H) 3.28 (s, 3H) 2.22 (s, 3H) 1.63 (s, 6H); ^{13}C (75 MHz, $CDCl_3$) 173.0, 153.7, 130.8, 128.3, 126.3, 121.1, 115.4,

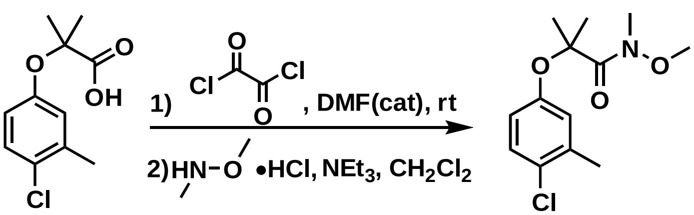
79.5, 60.2, 34.5, 25.1, 16.5; IR ν_{max} : 3005, 2992, 2818, 1644, 1599, 1488, 1454, 1201, 1154; HRMS m/e for $C_{13}H_{19}NO_3$ calcd (M^++H) 238.1443 found 238.1442.

2-(2-Isopropylphenoxy)-N-methoxy-N,2-dimethylpropanamide (9h)



GP2 was applied to carboxylic acid derivative carboxylic acid **8h** (0.5500 g, 2.47 mmol), with oxalyl chloride (0.640 mL, 7.42 mmol), N,O-dimethylhydroxylamine hydrochloride (0.2896 g, 2.97 mmol), and triethylamine (0.860 mL, 6.18 mmol). The crude product was purified using flash chromatography (15:1 hexanes : ethyl acetate) to afford **9h** as a white solid (0.5043 g, 77%), mp 52-53°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, J = 7.4 Hz, 1H) 7.02 (dd, J = 8.1, 7.4 Hz, 1H) 6.92 (dd, J = 8.1, 7.4 Hz, 1H) 6.72 (d, J = 8.1 Hz, 1H) 3.57 (s, 3H) 3.32 (septet, J = 6.9 Hz, 1H) 3.30 (s, 3H) 1.63 (s, 6H) 1.23 (d, J = 6.9 Hz, 6H) ;^{13}C (75 MHz, $CDCl_3$) 173.4, 152.7, 138.6, 126.5, 126.1, 121.4, 115.7, 79.5, 60.4, 34.5, 27.2, 25.1, 22.7; IR ν_{max} : 2965, 2949, 1650, 1597, 1583, 1487, 1442, 1236, 1152, 746; HRMS m/e for $C_{15}H_{23}NO_3$ calcd (M^++H) 266.1756 found 266.1756.

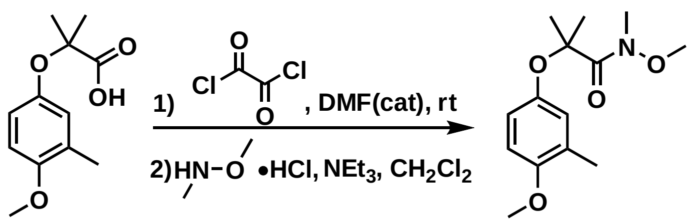
2-(4-Chloro-3-methylphenoxy)-N-methoxy-N,2-dimethylpropanamide (9i)



GP2 was applied to carboxylic acid derivative carboxylic acid **8i** (1.1940 g, 5.22 mmol), using oxalyl chloride (1.34 mL, 15.7 mmol), N,O-dimethylhydroxylamine hydrochloride (0.6112 g, 6.27 mmol), and triethylamine (1.82 mL, 13.1 mmol). The crude product was subjected to flash chromatography (10:1 petroleum ether : Et_2O) to afford **9i** a yellow oil (1.3071 g, 92%); ^{1}H NMR

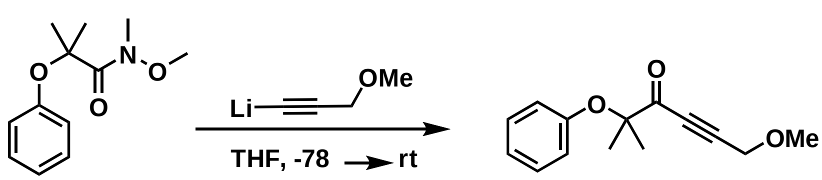
(300 MHz, $CDCl_3$) δ 7.17 (d, J = 8.7 Hz, 1H) 6.76 (d, J = 2.9 Hz, 1H) 6.64 (dd, J = 8.7, 2.9 Hz, 1H) 3.60 (s, 3H) 3.29 (s, 3H) 2.30 (s, 3H) 1.60 (s, 6H); ^{13}C (75 MHz, $CDCl_3$) 173.0, 154.1, 137.1, 129.5, 127.0, 120.9, 116.7, 80.2, 60.6, 34.6, 25.1, 20.2; IR $ν_{max}$: 2980, 2937, 2866, 1652, 1477, 1240, 1177; HRMS m/e for $C_{13}H_{18}ClNO_3$ calcd (M^++H) 272.1053 found 272.1053.

N-Methoxy-2-(4-methoxy-3-methylphenoxy)-N,2-dimethylpropanamide (9j)



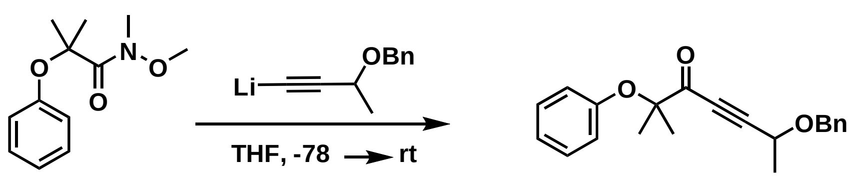
GP2 was applied to carboxylic acid derivative carboxylic acid **8j** (1.3011 g, 5.80 mmol), using oxalyl chloride (1.50 mL, 17.4 mmol), N,O-dimethylhydroxylamine hydrochloride (0.6791 g, 6.96 mmol), and triethylamine (2.00 mL, 14.5 mmol).The crude product was subjected to flash chromatography (5:1 petroleum ether : Et_2O) to afford **9j** as a pale yellow oil (1.4423 g, 93%); ^1H NMR (300 MHz, $CDCl_3$) δ 6.70 – 6.66 (m, 3H) 3.75 (s, 3H) 3.65 (s, 3H) 3.32 (s, 3H) 2.15 (s, 3H) 1.55 (s, 6H); ^{13}C (75 MHz, $CDCl_3$) 173.1, 152.9, 148.6, 127.5, 122.0, 116.3, 110.3, 80.0, 60.5, 55.5, 34.7, 25.0, 16.2; IR $ν_{max}$: 2973, 2866, 1651, 1498, 1218, 1149; HRMS m/e for $C_{14}H_{21}NO_4$ calcd (M^++H) 268.1549 found 268.1554.

6-Methoxy-2-methyl-2-phenoxyhex-4-yn-3-one (10a)



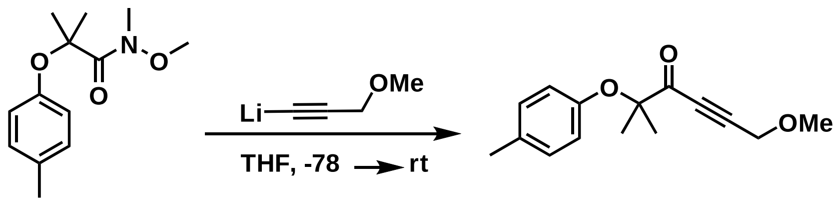
General Procedure 3 (GP3): To a solution of methyl propargyl ether (0.27 mL, 3.2 mmol) dry tetrahydrofuran (15 mL) at -78 ºC was added n-butyllithium (0.79 mL, 1.6 mmol). The solution was stirred at -78°C for 1 h. The Weinreb amide **9a** (0.1507 g, 0.67 mmol) was dissolved in dry tetrahydrofuran and injected dropwise. The resulting solution was allowed to warm to room temperature with stirring overnight. Saturated NH_4Cl(aq) was added and the mixture was extracted with diethyl ether. The organic phase was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude material was filtered through a silica plug, giving **10a** as a yellow oil (0.1489g, 95%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (t, J = 7.8 Hz, 2H), 7.03 (apparent t, J = 7.3 Hz, 1H), 6.91 (d, J = 7.9 Hz, 2H), 4.27 (s, 2H), 3.34 (s, 3H), 1.58 (s, 6H); ^{13}C (75 MHz, $CDCl_3$) 189.9, 155.1, 129.2, 122.5, 119.7, 91.7, 83.74, 83.66, 59.5, 57.8, 23.7; IR v_{max} :3064, 3039, 2989, 2935, 2897, 2206, 1677, 1589, 1490, 1462, 1227, 1125, 1100, 752, 693; HRMS m/e for $C_{14}H_{16}O_3Na$ calcd (M^+ + Na) 255.0997, found 255.0991.

6-Methoxy-2-methyl-2-phenoxyhex-4-yn-3-one (10aa)



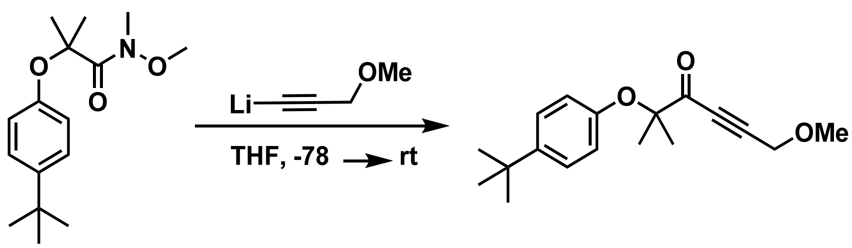
GP3 was applied to Weinreb amide **9a** (0.2081 g, 0.93 mmol) using the lithium acetylide generated from the 3-benzyloxybutyne and n-butyllithium. The crude product was subjected to column chromatography (25:1 hexane : Et_2O), to give **10aa** (0.2253 g, 75%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 7H) 7.05 (t, J = 7.4, 1H), 6.94 (m, 2H) 4.69 (d, J = 11.6 Hz, 1H) 4.40 (d, J = 11.6 Hz, 1H) 4.34 (q, J = 6.9 Hz , 1H) 1.64 (s, 3H) 1.63 (s, 3H) 1.49 (d, J = 6.9 Hz, 3H);^{13}C (75 MHz, $CDCl_3$) 190.3, 155.2, 137.1, 129.2, 128.3, 128.0, 127.8, 122.2, 119.1, 95.4, 83.7, 82.3, 70.7, 63.9, 24.2, 23.4, 21.0; IR v_{max} : 3064, 3031, 2988, 2868, 2209, 1679, 1589, 1489, 1455, 1106, 1027, 750, 694; HRMS m/e for $C_{21}H_{22}O_3$ calcd 323.1647 (M^++H), found 323.1641.

6-Methoxy-2-methyl-2-(p-tolyloxy)hex-4-yn-3-one (10b)



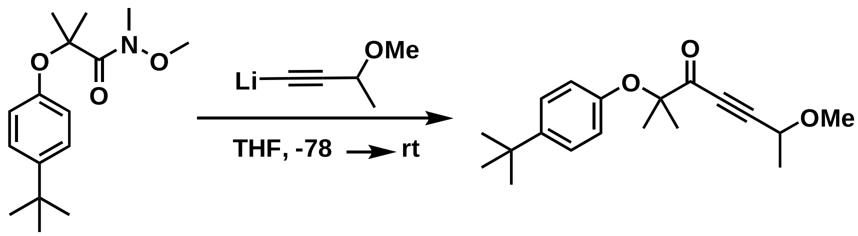
GP3 was applied to Weinreb amide **9b** (0.3909 g, 1.65 mmol) using methyl propargyl ether (0.70 mL, 8.25 mmol) and n-butyllithium (2.05 mL, 2.00 M, 4.12 mmol). Compound **10b** was isolated as a gold oil (0.3652 g, 90%) with sufficient purity for future use; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, J = 8.5 Hz, 2H), 6.78 (d, J = 8.5 Hz 2H), 4.27 (s, 2H), 3.35 (s, 3H), 2.29 (s, 3H), 1.52 (s, 6H); ^{13}C (75 MHz, $CDCl_3$) 190.1, 152.7, 132.1, 129.7, 119.9, 91.5, 83.74, 83.71, 59.6, 57.8, 23.7, 20.5; IR v_{max} : 2988, 2932, 2208, 1677, 1610, 1506, 1224, 1156, 1125, 1099, 809; HRMS m/e for $C_{15}H_{18}O_3$ calcd (M^++H) 247.1334 found 247.1336.

2-(4-tert-Butylphenoxy)-6-methoxy-2-methylhex-4-yn-3-one (10c)



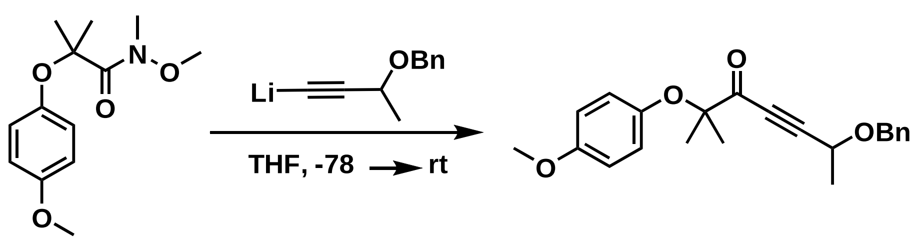
GP3 was applied to Weinreb amide **9c** (0.2212 g, 0.79 mmol) The crude product was subjected flash chromatography using (10:1 petroleum ether : Et_2O) to afford **10c** (0.0966 g, 42%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 4.25 (s, 2H), 3.30 (s, 3H), 1.54 (s, 6H), 1.28 (s, 9H); ^{13}C (75 MHz, $CDCl_3$) 190.1, 152.6, 145.2, 125.9, 119.2, 91.5, 83.7, 83.6, 59.5, 57.7, 34.1, 31.4, 23.7; IR v_{max} : 2963, 2904, 2869, 2208, 1678, 1607, 1509, 1462, 1160, 1128, 1102, 860; HRMS m/e for $C_{18}H_{24}O_3$ calcd (M^++H) 289.1804, found 289.1794.

2-(4-tert-Butylphenoxy)-6-methoxy-2-methylhept-4-yn-3-one (10cc)



GP3 was applied to Weinreb amide **9c** (0.2302 g, 0.82 mmol) using the lithium acetylide generated from the 3-methoxybutyne and n-butyllithium. Following filtration through a short silica plug using dichloromethane, **10cc** was isolated as a yellow oil (0.2472 g, 99%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 4.19 (q, J = 6.6 Hz, 1H), 3.28 (s, 3H) 1.54 (s, 6H), 1.40 (d, J = 6.9 Hz, 3H), 1.28 (s, 9H); ^{13}C (75 MHz, $CDCl_3$) 190.4, 152.8, 145.1, 125.9, 118.9, 95.2, 83.6, 82.3, 66.7, 56.5, 34.0, 31.4, 24.1, 23.6, 20.9; IR ν_{max} : 3096, 3041, 2964, 2823, 2207, 1679, 1607, 1509, 1461, 1235, 1139; HRMS m/e for $C_{19}H_{26}O_3$ calcd (M^{+}+H) 303.1960 found 303.1948.

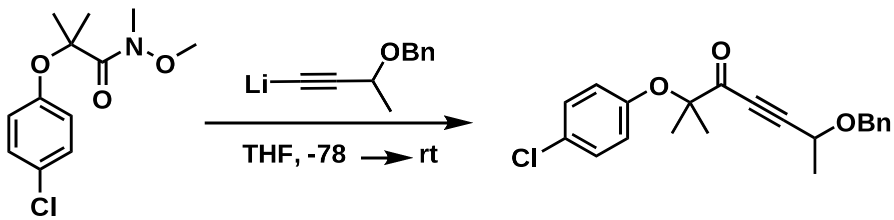
6-(Benzyloxy)-2-(4-methoxyphenoxy)-2-methylhept-4-yn-3-one (10d)



GP3 was applied to Weinreb amide **9d** (0.2187 g, 0.86 mmol) using the lithium acetylide generated from the 3-benzyloxybutyne and n-butyllithium. The crude product was subjected to column chromatography using 7.5:1 petroleum ether : Et_2O to afford **10d** as a yellow oil (0.2788 g, 92%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 6.91 (d, J = 9.2 Hz, 2H), 6.81 (d, J = 9.2 Hz, 2H), 4.75 (d, J = 11.6 Hz, 1H), 4.47 (d, J = 11.6 Hz, 1H), 4.40 (q, J = 6.7 Hz, 1H), 3.78 (s, 3H), 1.56 – 1.53 (m, 9H); ^{13}C (75 MHz, $CDCl_3$) 190.2, 155.3, 148.6, 137.1, 128.3, 128.0, 127.8, 121.5, 114.2, 95.3, 84.0, 82.4, 70.8, 64.1, 55.4, 23.9, 23.4, 21.1; IR ν_{max} :3064, 3032, 2961, 2868, 2208,

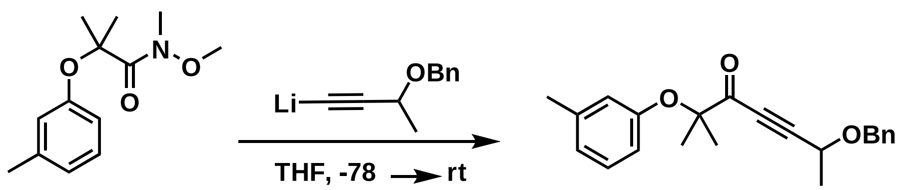
1679, 1596, 1450, 1257, 1147, 1100, 743, 698; HRMS m/e for $C_{22}H_{24}O_4$ calcd (M^+) 352.1674 found 352.1681.

6-(Benzyloxy)-2-(4-chlorophenoxy)-2-methylhept-4-yn-3-one (10e)



GP3 was applied to Weinreb amide **9e** (0.2041 g, 0.82 mmol) using the lithium acetylide generated from the 3-benzyloxybutyne and n-butyllithium. The crude product was subjected to column chromatography using 7.5:1 petroleum ether : Et_2O to afford **10e** as a yellow oil (0.2414 g, 85%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.16 (m, 7H), 6.80 (m, 2H), 4.64 (d, J = 11.7 Hz, 1H), 4.36 (d, J = 11.7 Hz, 1H), 4.31 (q, J = 6.8 Hz, 1H), 1.56 (s, 3H), 1.55 (s, 3H), 1.45 (d, J = 6.8 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) 189.6, 153.8, 137.0, 129.2, 128.4, 127.9, 127.8, 127.4, 120.6, 95.7, 84.1, 82.1, 70.8, 64.0, 24.0, 23.3, 21.0; IR ν_{max} : 3063, 3030, 2982, 2844, 2207, 1679, 1616, 1487, 1223, 1146; HRMS m/e for $C_{21}H_{21}ClO_3$ calcd (M^++H) 357.1257 found 357.1247.

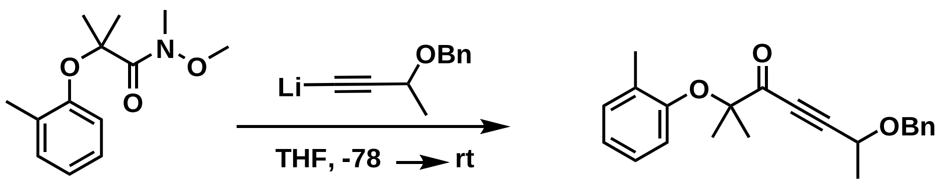
6-(Benzyloxy)-2-methyl-2-(m-tolyloxy)hept-4-yn-3-one (10f)



GP3 was applied to Weinreb amide **9f** (0.2443 g, 1.02 mmol). The crude product was subjected to column chromatography (25:1 hexane : Et_2O) to afford **10f** as a as a yellow oil (0.2761 g, 80%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 5H), 7.19 (m, 1H), 6.88 (m, 1H), 6.79 – 6.72 (m, 2H), 4.70 (d, J = 11.4 Hz, 1H), 4.40 (d, J = 11.4 Hz, 1H), 4.38 (q, J = 6.6 Hz, 1H), 2.34 (s, 3H), 1.65 (s, 3H), 1.64 (s, 3H), 1.52 (d, J = 6.9 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) 190.4, 155.2, 139.3,

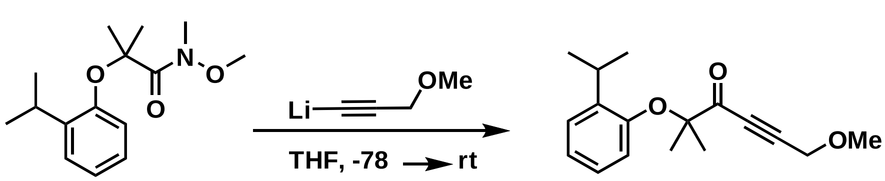
137.1, 128.9, 128.3, 128.0, 127.8, 123.1, 120.0, 115.9, 95.3, 83.6, 82.3, 70.7, 63.9, 24.2, 23.3, 21.3, 21.0; IR v_{max} : 3023, 2982, 2937, 2844, 2209, 1679, 1583, 1455, 1146, 1098; HRMS m/e for $C_{22}H_{24}O_3$ calcd 337.1803 (M^++H) found 337.1800.

6-(Benzyloxy)-2-methyl-2-(o-tolyloxy)hept-4-yn-3-one (10g)



GP3 was applied to Weinreb amide **9g** (0.2407 g, 1.01 mmol) using the lithium acetylide generated from the 3-benzyloxybutyne and n-butyllithium. The crude product was subjected to column chromatography (25:1 hexane : Et_2O) to afford **10g** (0.3156 g, 92%) as a light orange oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.17 (m, 7H), 6.91 (apparent t, J = 7.4, 1H), 6.71 (apparent d, J = 8.1, 1H), 4.64 (d, J = 11.6 Hz, 1H), 4.35 (d, J = 11.6 Hz, 1H), 4.31 (q, J = 6.7 Hz, 1H), 2.29 (s, 3H), 1.63 (s, 3H), 1.62 (s, 3H), 1.47 (d, J = 6.7 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) 190.6, 153.5, 137.1, 131.0, 129.0, 128.2, 128.0, 127.7, 126.2, 121.7, 116.4, 95.3, 83.6, 82.2, 70.6, 63.8, 24.2, 23.3, 20.9, 16.7; IR v_{max} : 3064, 3030, 2987, 2865, 2208, 1679, 1601, 1491, 1454, 1238, 1147, 1100, 777, 698; HRMS m/e for $C_{22}H_{24}O_4$ calcd 337.1804 (M^++H) found 337.1800.

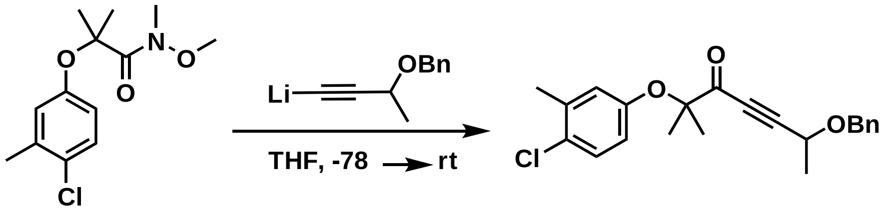
2-(2-Isopropylphenoxy)-6-methoxy-2-methylhex-4-yn-3-one (10h)



GP3 was applied to Weinreb amide **9h** (0.3350 g, 1.26 mmol). After filtration through a short silica plug, **10h** was isolated as a orange oil (0.3454 g, 99%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (dd, J = 7.5, 1.9 Hz, 1H), 7.04 (apparent dt, J = 8.0, 1.9 Hz, 1H), 6.96 (apparent dt, J = 7.4, 1.2 Hz, 1H), 6.63 (dd, J = 8.0, 1.2 Hz, 1H), 4.21 (s, 2H), 3.38 (sept, J = 6.9 Hz, 1H), 3.26 (s, 3H), 1.59 (s, 6H),

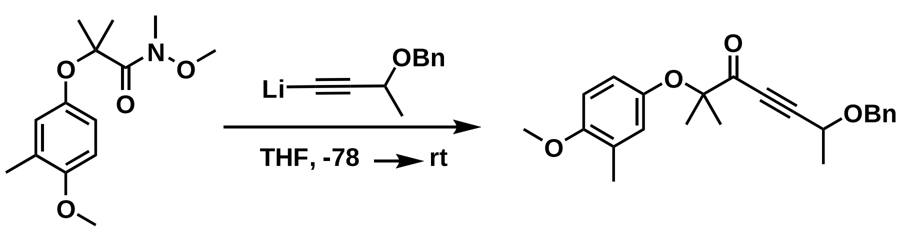
1.24 (d, J = 6.9 Hz, 6H); ^{13}C (75 MHz, $CDCl_3$) 190.6, 152.3, 139.3, 126.5, 125.9, 121.9, 116.5, 91.5, 83.7, 83.4, 59.5, 57.7, 27.0, 23.7, 22.7; IR ν_{max} : 2961, 2934, 2870, 2208, 1678, 1486, 1448 1259, 1158, 1126, 1086, 749; HRMS m/e for $C_{17}H_{22}O_3$ calcd (M^++H) 275.1647 found 275.1649.

6-(Benzyloxy)-2-(4-chloro-3-methylphenoxy)-2-methylhept-4-yn-3-one (10i)



GP3 was applied to Weinreb amide **9i** (0.1578 g, 0.58 mmol) using the lithium acetylide generated from the 3-benzyloxybutyne and n-butyllithium. The crude product was subjected to column chromatography using 30:1 petroleum ether : Et_2O to afford **10i** (0.1723 g, 80%), as a yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 6H), 6.79 (d, J = 1.9 Hz, 1H), 6.65 (dd, J = 8.6, 1.9 Hz, 1H), 4.66 (d, J =11.7 Hz, 1H), 4.40 – 4.30 (m, 2H), 2.30 (s, 3H), 1.58 (s, 6H), 1.48 (d, 6.6 Hz, 3H); ^{13}C (125 MHz, $CDCl_3$) 190.0, 153.7, 137.0, 129.4, 128.39, 128.0, 127.9, 127.7, 121.9, 117.8, 95.7, 84.0, 82.2, 70.8, 64.0, 24.1, 23.4, 21.0, 20.2; IR ν_{max} : 3087, 3064, 3031, 2987, 2936, 2865, 2208, 1679, 1596, 1478, 1159, 1098, 806, 734, 696; HRMS m/e for $C_{22}H_{23}ClO_3$ calcd 371.1414 (M^++H) 371.1411.

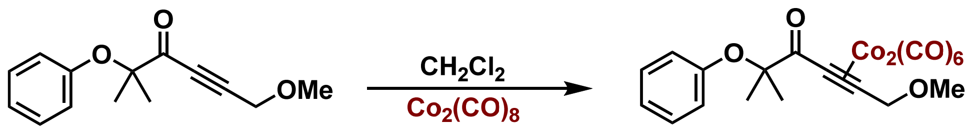
6-(Benzyloxy)-2-(4-methoxy-3-methylphenoxy)-2-methylhept-4-yn-3-one (10j)



GP3 was applied to Weinreb amide **9j** (0.1758 g, 0.65 mmol) using the lithium acetylide generated from the 3-benzyloxybutyne and n-butyllithium. The crude product was subjected to column chromatography (20:1 hexane : Et_2O) to afford **10j** (0.2104 g, 87%) as a colorless oil; ^1H NMR

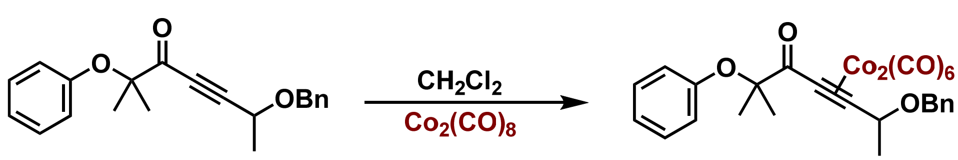
(300 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 5H), 6.86 – 6.74 (m, 3H), 4.81 (d, J = 11.7 Hz, 1H), 4.53 (d, J = 11.7 Hz, 1H), 4.46 (q, J = 6.9 Hz, 1H), 3.86 (s, 3H), 2.26 (s, 3H), 1.60 (m, 9H); ^{13}C (75 MHz, $CDCl_3$) 190.4, 153.5, 148.2, 137.2, 128.3, 128.1, 127.8, 127.4, 123.3, 117.9, 110.1, 95.2, 83.8, 82.5, 70.8, 64.1, 55.5, 24.0, 23.4, 21.1, 16.2; IR ν_{max} : 3064, 3032, 2985, 2868, 2208, 1679, 1598, 1487, 1450, 1147, 1092, 747, 697; HRMS m/e for $C_{23}H_{26}O_4$ calcd 367.1909 (M^++H) found 367.1909.

Hexacarbonyl[*μ*-*η*^{4}-(6-methoxy-2-methyl-2-phenoxyhex-4-yn-3-one)]dicobalt (6a)



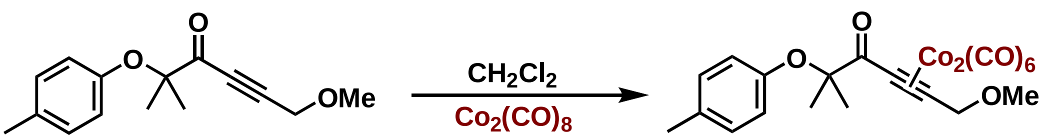
General Procedure 4 (GP4): To a solution of alkyne **10a** (0.1540 g, 0.66 mmol) in CH_2Cl_2 (15 mL) was added an unweighed amount of dicobalt octacarbonyl in portions, with monitoring by TLC. After 2 h, the deep red solution was concentrated under reduced pressure and filtered through a plug of silica using hexane, to remove excess $Co_2(CO)_8$, followed by diethyl ether. The residue of the diethyl ether washings was subjected to flash chromatography (25:1 hexanes : ethyl acetate), to afford **6a** was isolated as a dark red oil (0.2920 g, 85%); ^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (apparent t, J = 7.9 Hz, 2H), 7.06 (apparent t, J = 7.2 Hz, 1H), 6.88 (dd, J = 7.8 Hz, 2H), 4.40 (s, 2H), 3.46 (s, 3H), 1.60 (s, 6H); ^{13}C (75 MHz, $CDCl_3$) 206.8, 198.3, 154.5, 129.4, 122.9, 120.7, 96.3, 85.2, 80.3, 72.8, 59.0, 25.3; IR ν_{max} : 2987, 2876, 2098, 2057, 2012, 1740, 1588, 1492, 1455, 1220, 1158, 753, 696; HRMS m/e for $C_{20}H_{16}Co_2O_9$ calcd (M^++H) 518.9536 found 518.9539.

Hexacarbonyl[*μ*-*η*^{4}-(6-methoxy-2-methyl-2-phenoxyhex-4-yn-3-one)]dicobalt (6aa)



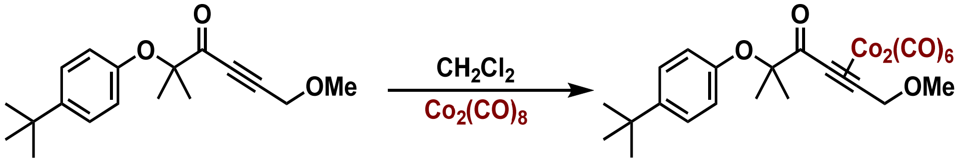
GP4 was applied to propargyl ether ketone **10aa** (0.2089 g, 0.65 mmol). Following the silica plug fitration, the compound was found to be sufficiently pure, and product **6aa** was isolated as a dark red oil (0.3660 g, 93%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.29 (m, 7H), 7.14 (apparent t, J = 7.4 Hz, 1H), 6.92 (m, 2H), 4.76 (q, J = 6.2 Hz, 1H), 4.75 (1/2 AB, J = 11.8 Hz, 1H), 4.68 (1/2 AB, J = 11.8 Hz, 3H), 1.64 (s, 3H), 1.60 (s, 3H), 1.59 (d, J = 6.2 Hz, 3H); ^{13}C (125 MHz, $CDCl_3$) 207.1, 198.6, 153.9, 138.1, 129.3, 128.3, 127.5, 123.4, 121.8, 104.3, 85.7, 81.9, 74.6, 71.0, 25.7, 25.1, 22.6; IR v_{max} : 3064, 3030, 2980, 2865, 2127, 2057, 2018, 1662, 1587, 1455, 1230, 1154; HRMS m/e for $C_{27}H_{22}Co_2O_9$ calcd (M -3CO) 524.0080 found 524.0097.

Hexacarbonyl[*μ*-*η*^{4}-(6-methoxy-2-methyl-2-phenoxyhex-4-yn-3-one)]dicobalt (6b)



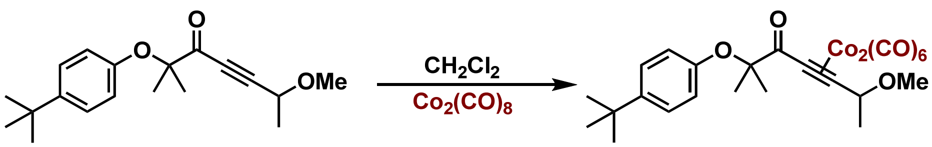
GP4 was applied to propargyl ether ketone **10b** (0.2571 g, 1.04 mmol). Following the silica plug fitration, the compound was found to be sufficiently pure and product **6b** was isolated as a dark red oil (0.3753 g, 68%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (d, J = 8.1 Hz, 2H), 6.78 (d, J = 8.1 Hz, 2H), 4.46 (s, 2H), 3.48 (s, 3H), 2.31 (s, 3H), 1.56 (s, 6H);^{13}C (75 MHz, $CDCl_3$) 206.6, 198.5, 151.9, 132.7, 129.8, 121.2, 96.3, 85.3, 80.6, 72.9, 58.9, 25.2, 20.6; IR v_{max} : 3030, 2987, 2931, 2874, 2129, 2056, 2007,1664, 1608, 1583, 1506, 1462, 1157, 1127, 1101 ; HRMS m/e for $C_{21}H_{18}Co_2O_9$ calcd (M^++H) 532.9693 found 532.9692.

Hexacarbonyl[*μ*-*η*^{4}-(2-(4-tert-butylphenoxy)-6-methoxy-2-methylhex-4-yn-3-one)]dicobalt (6c)



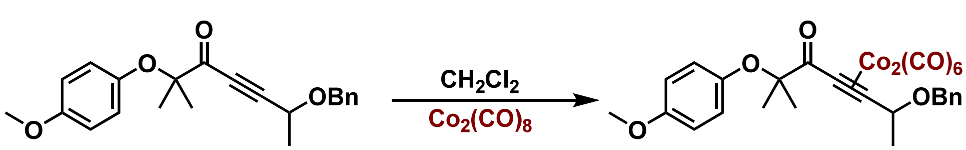
GP4 was applied to propargyl ether ketone **10c** (0.0722 g, 0.25 mmol). Subsequent flash chromatography (25:1 hexanes : ethyl acetate) afforded **6c** as a dark red oil (0.1424 g, 99%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27(m, 2H), 6.79 (m, 2H), 4.36 (s, 2H), 3.45 (s, 3H), 1.60 (s, 6H), 1.30 (s, 9H); ^{13}C (75 MHz, $CDCl_3$) 207.0, 198.5, 152.0, 145.6, 126.1, 119.9, 96.5, 85.0, 80.6, 72.7, 58.9, 34.2, 31.4, 25.3; IR v_{max} :2964, 2905, 2871, 2098,2057, 2016, 1664, 1607, 1579, 1509, 1462, 1159, 1125, 1103, 832; HRMS m/e for $C_{24}H_{24}Co_2O_9$ calcd (M^{+}+H) 575.0162 found 575.0154.

Hexacarbonyl[*μ*-*η*^{4}-(2-(4-tert-butylphenoxy)-6-methoxy-2-methylhept-4-yn-3-one)]dicobalt (6cc)



GP4 was applied to propargyl ether ketone **10cc** (0.2040 g, 0.67 mmol). Following the silica plug filtration, the compound was found to be sufficiently pure and **6cc** was isolated as a dark red oil (0.3882 g, 98%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, J = 8.7, 2H), 6.83 (d, J = 8.7, 2H), 4.45 (q, J = 6.2 Hz, 1H), 3.44 (s, 3H), 1.58 (s, 3H), 1.56 (s, 3H), 1.48 (d, J = 6.2 Hz, 3H), 1.30 (s, 9H); ^{13}C (75 MHz, $CDCl_3$) 207.3, 198.7, 151.5, 146.2, 126.1, 121.2, 103.9, 85.6, 82.5, 57.0, 34.2, 31.4, 25.6, 25.2, 22.2; IR v_{max} : 3096, 3041, 2964, 2869, 2097, 2057, 2016, 1662, 1509, 1225, 1158; HRMS m/e for $C_{25}H_{26}Co_2O_9$ calcd (M^{+}+H-3CO) 504.0416 found 504.0393.

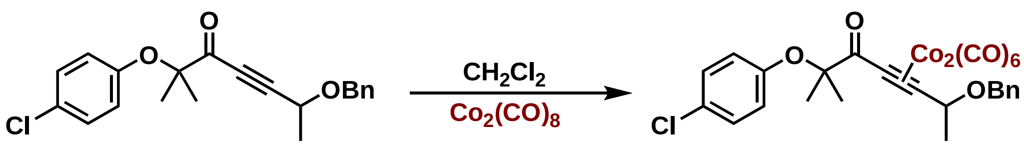
Hexacarbonyl[*μ*-*η*^{4}-(2-(6-(benzyloxy)-2-(4-methoxyphenoxy)-2-methylhept-4-yn-3-one)]dicobalt (6d)



GP4 was applied to propargyl ether ketone **6d** (0.1750 g, 0.50 mmol). Following the silica plug filtration, the compound was found to be sufficiently pure and **3d** was isolated as a dark red oil

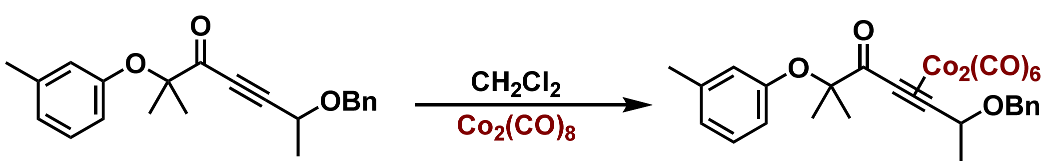
(0.3168 g, 99%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.24 (m, 5H), 6.83 – 6.78 (m, 4H), 4.78 (q, J = 6.4 Hz, 1H), 4.69 (1/2 AB, J = 11.8 Hz, 1H), 4.65 (1/2 AB, J = 11.8 Hz, 1H), 3.79 (s, 3H), 1.55 (d, J = 6.4 Hz, 3H), 1.52 (s, 3H), 1.49 (s, 3H); ^{13}C (125 MHz, $CDCl_3$) 206.8, 198.7, 156.0, 146.8, 138.1, 128.3, 127.5, 124.0, 114.2, 103.8, 86.2, 82.0, 74.7, 71.1, 55.5, 25.6, 25.1, 22.8; IR ν_{max} : 3088, 3065, 3032, 2981, 2867, 2097, 2057, 2016, 1661, 1587, 1504, 1455, 1213, 1149; HRMS m/e for $C_{28}H_{24}Co_2O_{10}$ calcd (M -3CO) 554.0186 found 554.0193.

Hexacarbonyl[*μ*-*η*^{4}-(6-(benzyloxy)-2-(4-chlorophenoxy)-2-methylhept-4-yn-3-one)]dicobalt (6e)



GP4 was applied to propargyl ether ketone **10e** (0.1548 g, 0.43 mmol). Following the silica plug filtration, the compound was found to be sufficiently pure and **6e** was isolated as a dark red oil (0.2146 g, 77%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.31 (m, 5H), 7.25 (m, 2H), 6.83 (m, 2H), 4.75 (1/2 AB, J = 11.8 Hz, 1H), 4.73 (q, J = 6.1 Hz, 1H), 4.67 (1/2 AB, J = 11.8 Hz, 1H), 1.61 (s, 3H), 1.579 (d, J = 6.1 Hz, 3H), 1.576 (s, 9H); ^{13}C (125 MHz, $CDCl_3$) 206.6, 198.5, 152.4, 138.0, 129.3, 128.8, 128.3, 127.6, 127.5, 123.1, 104.3, 86.1, 81.5, 74.4, 71.0, 25.5, 24.9, 22.5; IR ν_{max}: 3065, 3031, 2980, 2867, 2097, 2057, 2016, 1661, 1487, 1455, 1234, 1153; HRMS m/e for $C_{27}H_{21}ClCo_2O_9$ calcd (M -3CO) 557.9690 found 557.9703.

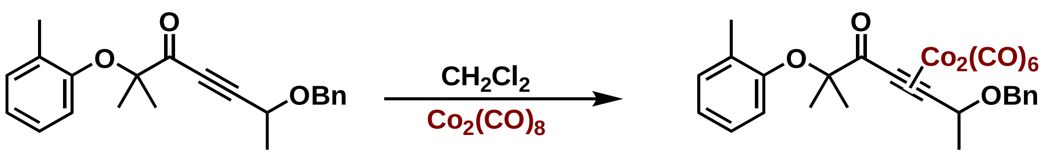
Hexacarbonyl[*μ*-*η*^{4}-(6-(benzyloxy)-2-methyl-2-(m-tolyloxy)hept-4-yn-3-one)]dicobalt (6f)



GP4 was applied to propargyl ether ketone **6f** (0.1642 g, 0.49 mmol). Following the silica plug filtration, the compound was found to be sufficiently pure and **3f** was isolated as a dark red oil

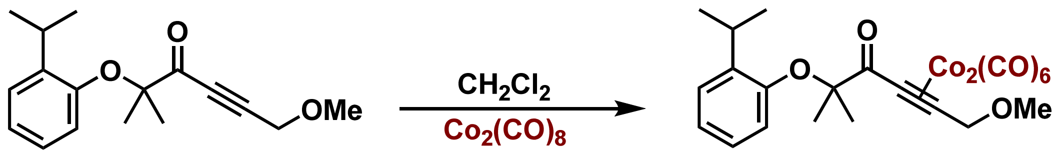
(0.2741 g, 90%); ^{1}H NMR (500 MHz, $CDCl_3$): 7.35-7.25 (m, 5H), 7.14 (dd, J = 8.6, 7.7 Hz, 1H), 6.90 (d, J = 7.5 Hz, 1H), 6.64-6.69 (m, 2H), 4.71 (q, J = 6.2 Hz, 1H), 4.69 (1/2 AB, J = 11.8 Hz, 1H), 4.64 (1/2 AB, J = 11.8 Hz, 1H), 2.30 (s, 3H), 1.58 (s, 3H), 1.55 (s, 3H), 1.54 (d, J = 6.2, 3H); ^{13}C (125 MHz, $CDCl_3$) 207.3, 198.6, 154.0, 139.3, 138.1, 129.0, 128.3, 127.5, 124.2, 122.3, 118.7, 104.3, 85.5, 82.0, 74.7, 71.0, 25.7, 25.1, 22.6, 21.4; IR ν_{max} : 3086, 3064, 2981, 2866, 2097, 2058, 2024, 1662, 1584, 1497, 1456, 1254, 1140; HRMS m/e for $C_{28}H_{24}Co_2O_9$ calcd (M-3CO) 538.0237 found 538.0251.

Hexacarbonyl[μ-η^4-(6-(benzyloxy)-2-methyl-2-(o-tolyloxy)hept-4-yn-3-one)]dicobalt (6g)



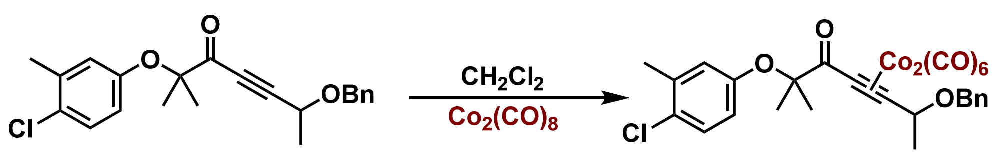
GP4 was applied to propargyl ether ketone **6g** (0.2005 g, 0.60 mmol). Following the silica plug filtration, the compound was found to be sufficiently pure and **3g** was isolated as a dark red oil (0.3639 g, 98%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 – 7.29 (m, 5H), 7.16 (d, J = 7.5 Hz, 1H), 6.99 (apparent t, J = 7.5 Hz, 1H), 6.91 (apparent t, J = 7.5 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 4.69 (1/2 AB, J = 11.8 Hz, 1H), 4.64 (q, J = 6.2 Hz, 1H), 4.61 (1/2 AB, J = 11.8 Hz, 1H) 2.22 (s, 3H) 1.63 (s, 3H) 1.60 (s, 3H) 1.50 (d, J = 6.2 Hz, 3H); ^{13}C (125 MHz, $CDCl_3$) 208.5, 198.5, 153.0, 138.1, 131.3, 129.4, 128.3, 127.6, 127.5, 126.2, 122.1, 117.8, 105.3, 84.5, 81.7, 74.4, 71.0, 25.6, 25.0, 22.3, 16.6; IR ν_{max} : 3065, 3030, 2981, 2864, 2097, 2057, 2016, 1659, 1587, 1492, 1445, 1240, 1155; HRMS m/e for $C_{28}H_{24}Co_2O_9$ calcd (M -6CO) 454.0389 found 454.0393.

Hexacarbonyl[μ-η^4-(2-(2-isopropylphenoxy)-6-methoxy-2-methylhex-4-yn-3-one)]dicobalt (6h)



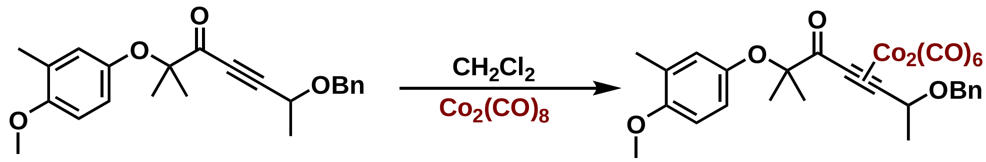
GP4 was applied to propargyl ether ketone **10h** (0.2242 g, 0.81 mmol). Subsequent flash chromatography (25:1 hexanes : ethyl acetate) afforded **6h** as a dark red solid (0.3603 g, 79%), mp 51-53°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (dd, J = 7.2, 2.4 Hz, 1H), 7.04 – 6.94 (m, 2H), 6.57 (dd, J = 7.5, 1.2 Hz, 1H), 4.25 (s, 2H), 3.43 (s, 3H), 3.39 (sept, J = 7.2 Hz, 1H), 1.65 (s, 6H), 1.23 (d, J = 7.2 Hz, 6H); ^{13}C (75 MHz, $CDCl_3$) 207.8, 198.4, 152.0, 139.3, 126.8, 125.9, 122.2, 117.0, 96.1, 84.2, 80.0, 72.6, 58.9, 26.5, 25.6, 23.0; IR $ν_{max}$: 2966, 2941, 2870, 2096, 2041, 2006, 1658, 1609, 1584, 1486, 1160, 1126, 752; HRMS m/e for $C_{23}H_{22}Co_2O_9$ calcd (M^++H) 561.0006 found 561.0001.

Hexacarbonyl[*μ*-*η*^{4}-(6-(benzyloxy)-2-(4-chloro-3-methylphenoxy)-2-methylhept-4-yn-3-one)]dicobalt (6i)



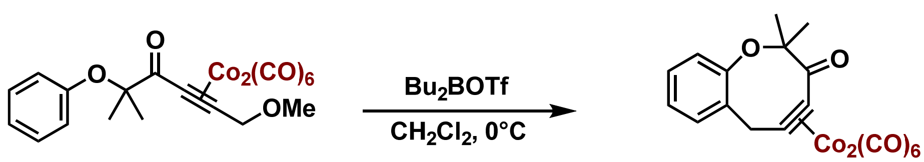
GP4 was applied to propargyl ether ketone **10i** (0.1250 g, 0. mmol). Following the silica plug filtration, the compound was found to be sufficiently pure and **6i** was isolated as a dark red oil (0.1920 g, 90%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32-7.27 (m, 5H), 7.20 (d, J = 8.7 Hz, 1H) 6.72 (d, J = 2.5 Hz, 1H), 6.63 (m, 1H), 4.72 – 4.67 (m, 2H), 4.63 (1/2 AB, J = 11.9 Hz, 1H), 2.31 (s, 3H), 1.56 (s, 6H), 1.54 (obscured d, J = 6.1 Hz, 3H), 1.52 (s, 3H) ;^{13}C: (125 MHz, $CDCl_3$) 206.8, 198.6, 152.4, 138.0, 137.0, 129.5, 128.9, 128.3, 127.6, 127.5, 124.1, 120.5, 104.3, 85.9, 81.6, 74.5, 71.0, 25.6, 25.0, 22.6, 20.2; IR $ν_{max}$: 3064, 3030, 2981, 2936, 2866, 2097, 2057, 2019, 1662, 1596, 1455, 1154, 1092, 736, 697; HRMS m/e for $C_{25}H_{23}ClCo_2O_6$ calcd (M-3CO) 571.9847 found 571.9851.

Hexacarbonyl[μ-η^4-(6-(benzyloxy)-2-(4-methoxy-3-methylphenoxy)-2-methylhept-4-yn-3-one)]dicobalt (6j)



GP4 was applied to propargyl ether ketone **10j** (0.1750 g, 0.48 mmol). Following the silica plug filtration, the compound was found to be sufficiently pure and **6j** was isolated as a dark red solid (0.2742 g, 88%), mp 52-55°C; ^{1}H NMR (500 MHz, $CDCl_3$) 7.40-7.30 (m, 5H), 6.71-6.74 (m, 3H), 4.84 (q, J = 6.2 Hz, 1H), 4.75 (1/2 AB, J = 11.8 Hz, 1H), 4.71 (1/2 AB, J = 11.8 Hz, 1H), 3.86 (s, 3H), 2.23 (s, 3H), 1.61 (d, J = 6.2 Hz, 3H), 1.57 (s, 3H), 1.54 (s, 3H); ^{13}C (125 MHz, $CDCl_3$) 207.0, 198.7, 154.2, 146.4, 138.2, 128.3, 127.5, 127.3, 125.4, 120.6, 110.1, 103.9, 86.0, 82.2, 74.8, 71.1, 55.6, 25.6, 25.2, 22.8, 16.3; IR ν_{max} : 3030, 3006, 2975, 2869, 2096, 2057, 2013, 1665, 1497, 1455, 1217, 1143; HRMS m/e for $C_{29}H_{26}Co_2O_{10}$ calcd (M -3CO) 568.0342 found 568.0344.

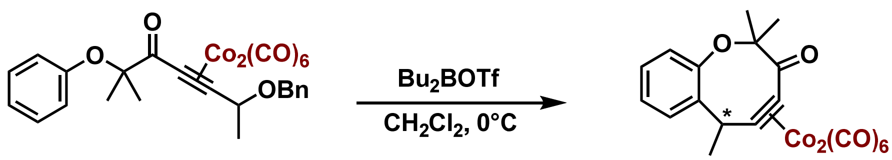
Hexacarbonyl[μ-η^4-(4,5-didehydro-2,2-dimethyl-2H-benzo[b]oxocin-3(6H)-one)]dicobalt (7a)



General Procedure 5 (GP5): To a solution of cobalt alkynyl ether complex **6a** (0.0614 g, 0.12 mmol) in dichloromethane (50 mL), at 0°C was added dibutyl boron triflate (178 uL, 1M in CH_2Cl_2, 1.5 equiv). The solution was stirred for 15 min with monitoring by TLC. Saturated aqueous ammonium chloride was added and the mixture extracted with dichloromethane. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography (25:1 hexanes : Et_2O) afforded **7a** isolated as a dark red solid (0.0365g, 63%), mp 59-61°C; ^{1}H

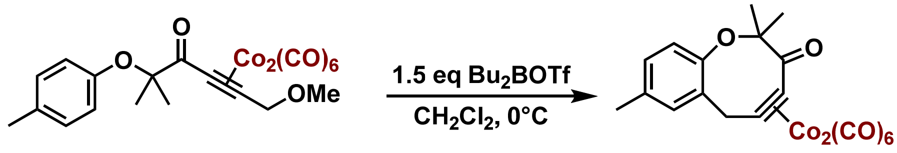
NMR (300 MHz, $CDCl_3$) δ 7.18-7.23 (m, 2H), 7.12 (dd, J = 8.4, 1.2 Hz, 1H), 7.01 (apparent dt, J = 1.2, 7.3 Hz, 1H), 4.28 (br, 2H), 1.73 (s, 6H); ^{13}C (75 MHz, $CDCl_3$) 207.2, 198.3, 154.3, 136.3, 129.3, 128.1, 125.2, 124.1, 98.3, 88.2, 78.3, 38.5, 27.8 (br); IR v_{max} : 3066, 2983, 2873, 2097, 2040, 2015, 1659, 1593, 1454, 1152, 1133; HRMS m/e for $C_{19}H_{12}Co_2O_8$ calcd (M^++H) 486.9274 found 486.9277.

Hexacarbonyl[*μ*-*η*^{4}-(4,5-didehydro-2,2,6-trimethyl-2H-benzo[b]oxocin-3(6H)-one)]docibalt (7aa)



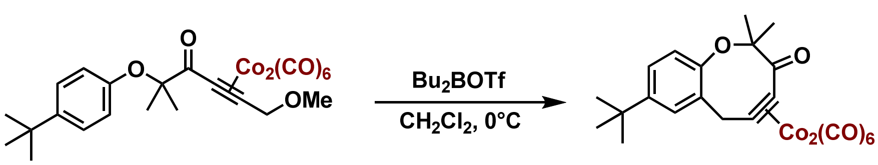
GP5 was applied to cobalt protected alkynyl ether complex **6aa** (0.0721 g, 0.12 mmol) using dibutyl boron triflate (178 uL, 1M in CH_2Cl_2, 1.5 equiv). The product **7aa** was purified using Flash chromatography (25:1 petroleum ether : Et_2O) followed by preparative TLC (25:1 petroleum ether:diethyl ether) afforded **7aa** as a dark red crystalline solid (0.0480 g, 81%), mp 84-85°C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 (m, 1H), 7.13 – 7.20 (m, 2H), 7.05 (m, 1H), 4.70 (broad s, 1H), 1.77 (s, 3H), 1.75 (obscured d, 3H); ^{13}C (125 MHz, $CDCl_3$) 207.1, 198.4, 154.1, 140.4, 127.6, 125.3, 124.7, 124.0, 107.3, 88.5, 78.6, 36.5, 29.9, 25.8, 17.8; IR v_{max} : 2986, 2877, 2095, 2052, 2006, 1665, 1594, 1481, 1456, 1138, 1067; HRMS m/e for $C_{20}H_{14}Co_2O_8$ calcd (M^++H) 500.9431 found 500.9429.

Hexacarbonyl[*μ*-*η*^{4}-(4,5-didehydro-2,2,8-trimethyl-2H-benzo[b]oxocin-3(6H)-one)]dicobalt (7b)



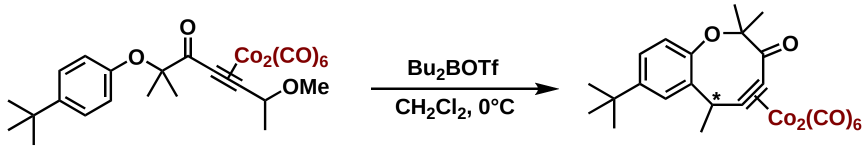
GP5 was applied to cobalt protected alkynyl ether complex **6b** (0.0601 g, 0.11 mmol) using dibutyl boron triflate (1.5 equiv, 170 uL, 1 M in CH_2Cl_2, 1.5 equiv). Flash chromatography and preparative thin-layer chromatography (25:1 hexanes : ethyl acetate) afforded **7b** as a red oil (0.0485 g, 86%); ^{1}H NMR (300 MHz, $CDCl_3$): 6.99 (m, 3H), 4.21 (br, 2H), 2.27 (s, 3H), 1.70 (s, 6H); at -30 ºC the 4.21 resonance decoalesces to 4.55 (d, J = 15.2 Hz, 1H), 3.84 (d, J = 15.2 Hz, 1H); ^{13}C (75 MHz, $CDCl_3$) 208.4, 198.1, 151.3, 135.8, 133.5, 129.7, 128.3, 124.5, 98.2, 87.8, 38.1, 29.6, 25.3, 20.6; IR v_{max} : 3020, 2995, 2928, 2098, 2060, 2027, 1661, 1601, 1527, 1493, ; HRMS m/e for $C_{20}H_{14}Co_2O_8$ calcd (M^++H) 500.9430 found 500.9423.

Hexacarbonyl[*μ*-*η*^{4}-(8-tert-butyl-4,5-didehydro-2,2-dimethyl-2H-benzo[b]oxocin-3(6H)-one)]dicobalt (7c)



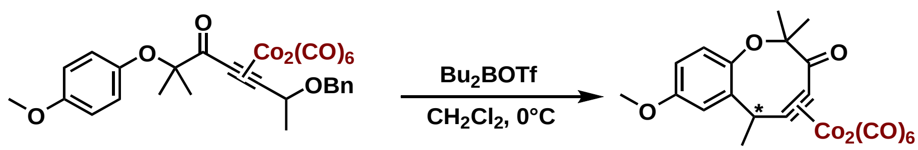
GP5 was applied to cobalt protected alkynyl ether complex **6c** (0.0627 g, 0.11 mmol) using dibutyl boron triflate (0.160 uL, 1M in CH_2Cl_2, 1.5 equiv). Flash chromatography (25:1 hexanes : ethyl acetate) afforded **7c** as a dark red solid (0.0446g, 75%), mp 59-60°C; ^{1}H NMR (300 MHz, $CDCl_3$): 7.16-7.20 (m, 2H), 7.03 (m, 1H), 4.24 (br, 2H), 1.71 (s, 6H), 1.27 (s, 9H);^{13}C (75 MHz, $CDCl_3$) 207.4, 198.2, 151.8, 147.0, 135.7, 126.3, 124.7, 124.5, 99.0, 88.0, 78.7, 38.8, 34.2, 31.3; IR v_{max} : 2961, 2932, 2869, 2093, 2047, 2006, 1653, 1605, 1494, 1461, 832; HRMS m/e for $C_{23}H_{20}Co_2O_8$ calcd (M^++H) 542.9900 found 542.9902.

Hexacarbonyl[*μ*-*η*^{4}-(8-tert-butyl-4,5-didehydro-2,2,6-trimethyl-2H-benzo[b]oxocin-3(6H)-one)]dicobalt (7cc)



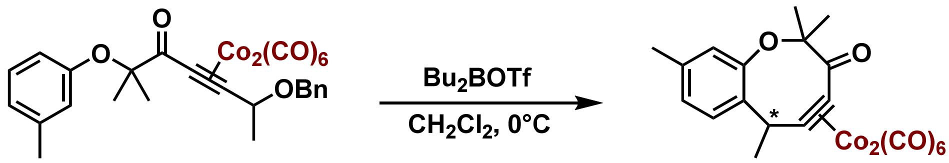
GP5 was applied to cobalt protected alkynyl ether complex **6cc** (0.1057 g, 0.18 mmol) using dibutyl boron triflate (270 uL, 1M in CH_2Cl_2, 1.5 equiv) Flash chromatography (25:1 hexanes : Et_2O) afforded **7cc** as a dark red solid (0.0748g, 75%), mp 86-87°C; ^{1}H NMR (300 MHz, $CDCl_3$): 7.27-7.15 (m, 2H), 7.04 (d, J = 8.7 Hz, 1H), 4.69 (br, 1H), 1.76 (br s, 6H), 1.72 (obscured d, 3H), 1.27 (s, 9H); ^{13}C (75 MHz, $CDCl_3$) 207.4, 198.1, 151.7, 146.6, 139.6, 128.8, 124.1, 122.0, 107.8, 88.2, 79.1, 36.6, 34.4, 31.3, 30.0, 25.8, 17.8; IR ν_{max} : 3116, 3074, 3044, 2966, 2869, 2096, 2058, 2019, 1662, 1586, 1490, 1463, 1140,1125; HRMS m/e for $C_{24}H_{22}Co_2O_8$ calcd (M^++H) 557.0057 found 557.0043.

Hexacarbonyl[*μ*-*η*^{4}-(4,5-didehydro-8-methoxy-2,2,6-trimethyl-2H-benzo[b]oxocin-3(6H)-one)]dicobalt (7d)



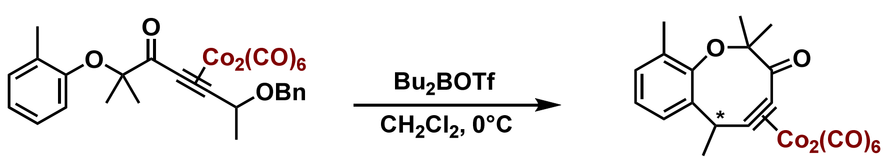
GP5 was applied to cobalt protected alkynyl ether complex **6c** (0.0614 g, 0.10 mmol) using dibutyl boron triflate (144 uL, 1M in CH_2Cl_2, 1.5 equiv) Flash chromatography (25:1 petroleum ether : Et_2O) followed by prep TLC (25:1 ether:diethyl ether) which afforded **7d** as a dark red crystalline solid (0.0405 g, 79%), mp 136-137°C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, J = 8.8 Hz, 1H), 6.79 (s, 1H), 6.68 (dd, J = 8.8, 2.9 Hz, 1H), 4.68 (br q, J = 6.2 Hz, 1H), 3.76 (s, 3H), 1.75 (s, 3H), 1.73 (s, 3H), 1.71 (br, 3H);^{13}C (125 MHz, $CDCl_3$) 207.3, 198.2, 155.7, 147.7, 141.6, 125.2, 112.1, 111.1, 107.0, 88.1, 78.9, 55.6, 36.5, 29.9, 25.7, 17.8; IR ν_{max} : 3066, 2983, 2873, 2097, 2061, 2015, 1659, 1583, 1454, 1152, 1133; HRMS m/e for $C_{21}H_{16}Co_2O_9$ calcd (M^++H) 530.5936 found 530.5942.

Hexacarbonyl[μ-η^4-(4,5-didehydro-2,2,6,9-tetramethyl-2H-benzo[b]oxocin-3(6H)-one)]dicobalt (7f)



GP5 was applied to cobalt protected alkynyl ether complex **6f** (0.0758 g, 0.12 mmol) using dibutyl boron triflate (182 uL, 1M in CH_2Cl_2, 1.5 equiv). Flash chromatography (25:1 petroleum ether : Et_2O) followed by prep TLC (25:1 ether:diethyl ether) afforded **7f** as a dark red crystalline solid (0.0385 g, 61%), mp 54-56°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, J = 7.3 Hz, 1H), 6.94 (s, 1H), 6.85 (d, J = 7.3 Hz, 1H), 4.64 (broad s, 1H), 2.29 (s, 3H), 1.77 (s, 3H), 1.72 (obscured d, 3H), 1.72 (s, 3H); ^{13}C (125 MHz, $CDCl_3$) 207.2, 198.1, 154.0, 137.6, 137.4, 125.4, 124.9, 124.6, 107.8, 88.2, 78.9, 36.3, 30.0, 25.8, 21.1, 17.9; IR ν_{max} : 2979, 2873, 2095, 2054, 2005, 1661, 1588, 1491, 1454, 1136, 1065; HRMS m/e for $C_{21}H_{16}Co_2O_8$ calcd (M^++H) 548.9207 found 548.9198.

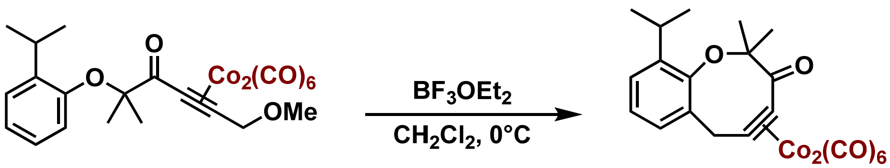
Hexacarbonyl[μ-η^4-(4,5-didehydro-2,2,6,10-tetramethyl-2H-benzo[b]oxocin-3(6H)-one)]dicobalt (7g)



GP5 was applied to cobalt protected alkynyl ether complex **6g** (0.0647 g, 0.10 mmol) using dibutyl boron triflate (155 uL, 1M in CH_2Cl_2, 1.5 equiv). Flash chromatography (25:1 petroleum ether : Et_2O) followed by prep TLC (25:1 ether:diethyl ether) which yielded **7g** as a dark red crystalline solid (0.0441 g, 82%), mp 76-77°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11-7.14 (m, 2H), 7.01 (apparent t, J = 7.5 Hz, 1H), 4.40 (q, J = 7.0 Hz, 1H), 2.37 (s, 3H), 1.71 (d, J = 7.0 Hz, 3H), 1.64 (br s, 3H), 1.56 (br s, 3H) ^{13}C (75 MHz, $CDCl_3$) 206.7, 198.5, 153.0, 139.9, 134.1, 130.6, 125.4,

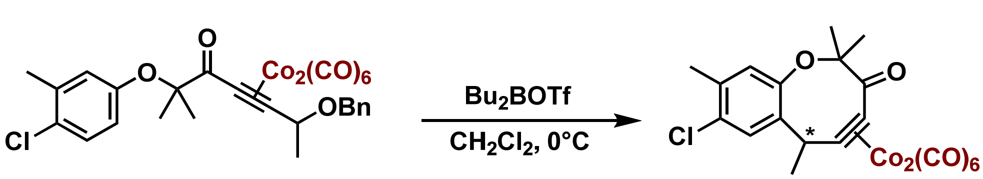
124.1, 104.4, 88.6, 77.9, 29.7, 25.6, 25.1, 22.5, 19.2; IR v_{max} : 3003, 2937, 2865, 2096, 2052, 2007, 1659, 1578, 1481, 1456, 1151, 1121; HRMS m/e for $C_{21}H_{16}Co_2O_8$ calcd (M^++H) 514.9587 found 514.9600.

Hexacarbonyl[*μ*-*η*^{4}-(4,5-didehydro-10-isopropyl-2,2-dimethyl-2H-benzo[b]oxocin-3(6H)-one)]dicobalt (7h)



A modified **GP5** was applied to cobalt protected alkynyl ether complex **6h** (0.0946 g, 0.17 mmol) using boron trifluoride diethyl etherate (0.68 mmol, 85 μL, 4.0 equiv), and allowing the reaction to progress for 1.5 h. Flash chromatography and preparative thin-layer chromatography (25:1 hexanes : ethyl acetate) afforded **7h** as a red oil (0.0512 g, 57%). Product indicated by ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22 (m, 1H), 7.08 – 7.04 (m, 2H) 4.39 (s, 2H) 3.40 (sept, J = 6.9 Hz, 1H) 1.57 (s, 6H) 1.20 (d, J = 6.9 Hz, 6H); ^{13}C (75 MHz, $CDCl_3$) 207.7, 198.5, 151.0, 145.3, 133.2, 127.8, 125.6, 124.7, 96.3, 88.9, 79.5, 39.5, 27.6, 25.3, 23.5; IR v_{max} : 2967, 2936, 2870, 2097, 2057, 2018, 1669, 1614, 1584, 1457, 1135, 777; HRMS m/e for $C_{22}H_{18}Co_2O_8$ calcd (M^++H) 528.9743 found 528.9742.

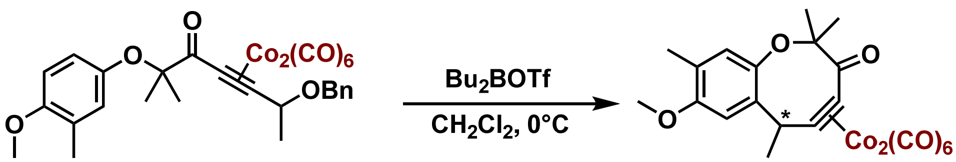
Hexacarbonyl[*μ*-*η*^{4}-(4,5-didehydro-2,2,6,8,9-pentamethyl-2H-benzo[b]oxocin-3(6H)-one)]dicobalt (7i)



GP5 was applied to cobalt protected alkynyl ether complex **6i** (0.0815 g, 0.12 mmol) using dibutyl boron triflate (186 uL, 1 M in CH_2Cl_2, 1.5 equiv). Flash chromatography (30:1 petroleum ether :

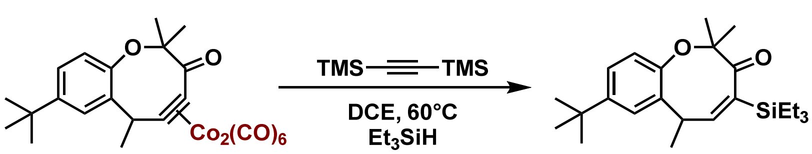
Et_2O) followed by prep TLC yielded (30:1 petroleum ether : Et_2O) **7i** as a dark red crystalline solid (0.0401 g, 59%), mp 56-57°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (s, 1H), 7.00 (s, 1H), 4.61 (br, 1H), 2.30 (s, 3H), 1.75 (s, 3H), 1.72 (d, J = 7.1 Hz, 3H), 1.71 (s, 3H); ^{13}C (125 MHz, $CDCl_3$) 206.7, 198.0, 152.4, 139.5, 135.1, 129.3, 127.0, 125.8, 106.5, 88.6, 78.6, 36.2, 29.8, 25.7, 20.0, 17.8; IR ν_{max} : 2985, 2877, 2095, 2054, 2010, 1666, 1594, 1482, 1456, 1137, 1067; HRMS m/e for $C_{21}H_{16}Co_2O_8$ calcd (M^++H) 514.9587 found 514.9581.

Hexacarbonyl[*μ*-*η*^{4}-(4,5-didehydro-8-methoxy-2,2,6,9-tetramethyl-2H-benzo[b]oxocin-3(6H)-one)]dicobalt (7j)



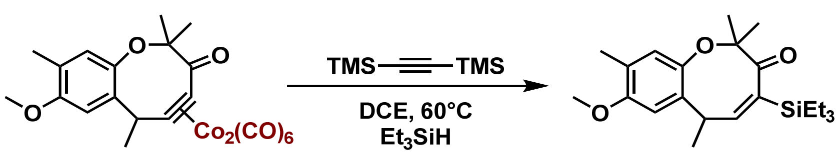
GP5 was applied to cobalt protected alkynyl ether complex **6j** (0.0647 g, 0.10 mmol) using dibutyl boron triflate (150 uL, 1 M in CH_2Cl_2, 1.5 equiv). Flash chromatography (25:1 petroleum ether : Et_2O) followed by prep TLC (25:1 petroleum ether : Et_2O) afforded **7j** as a dark red crystalline solid (0.0426 g, 79%), mp 54-56°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (s, 1H), 6.67 (s, 1H), 4.66 (br, 1H), 3.79 (s, 3H), 2.14 (s, 3H), 1.70-1.75 (m, 9H); ^{13}C (75 MHz, $CDCl_3$) 207.4, 198.2, 153.9, 147.2, 138.3, 126.94, 126.92, 125.6, 107.5, 87.8, 55.9, 36.5, 30.0, 25.8, 18.0, 16.0; IR ν_{max} :2998, 2850, 2095, 2055, 2001, 1671, 1589, 1495, 1463, 1135, 1061; HRMS m/e for $C_{22}H_{18}Co_2O_9$ calcd (M^++H) 544.9693 found 544.9692

8-tert-Butyl-2,2,6-trimethyl-4-(triethylsilyl)-2H-benzo[b]oxocin-3(6H)-one (11cc)



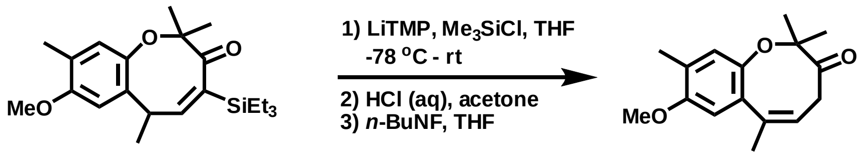
General procedure 6 (GP6): Triethylsilane (102 uL, 0.64 mmol) was added to a mixture containing cyclooctyne complex **7cc** (71.4 mg, 0.13 mmol) and bis(trimethylsilyl)acetylene (55 uL, 0.26 mmol) in degassed 1,2-dichloroethane (15 mL) at room temperature. The reaction mixture was heated to 60°C until TLC showed complete consumption of the complexed cyclooctyne (3 h). The resulting mixture was concentrated under reduced pressure and the residue was passed through a plug of silica using hexane as solvent. Preparative thin-layer chromatography (20:1 hexanes : Et_2O) afforded vinyltriethylsilane **11cc** (35.8 mg, 0.09 mmol, 72%) as an off- white solid, mp 45-47°C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.11-7.17 (m, 2H), 6.90 (d, J = 8.1 Hz, 1H), 6.07 (d, J = 6.3 Hz, 1H), 3.70 (br m, 1H), 1.48 (d, J = 6.9, 3H), 1.46 (s, 3H), 1.45 (s, 3H), 1.28 (s, 9H), 0.94 (t, J = 7.8 Hz, 9H), 0.66 (m, 6H); ^{13}C (75 MHz, $CDCl_3$) 210.8, 151.9, 147.7, 147.5, 139.4, 135.2, 124.2, 124.13, 124.10, 85.9, 40.2, 34.4, 31.5, 26.5, 23.5, 19.0, 7.1, 3.5; IR ν_{max} : 2955, 2872, 1672, 1608, 1496, 1459, 1145, 1080; HRMS m/e for $C_{24}H_{38}O_2Si$ calcd (M^++H) 387.2719 found 387.2719.

8-Methoxy-2,2,6,9-tetramethyl-4-(triethylsilyl)-2H-benzo[b]oxocin-3(6H)-one (**11j**)



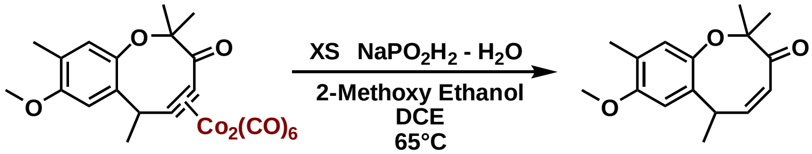
GP6 was applied to cyclic cobalt complex **7j** (41.4 mg, 0.08 mmol). The residue was passed through a plug of silica using hexane as solvent. Preparative thin-layer chromatography (20:1 hexanes : Et_2O) afforded the vinyltriethylsilane **11j** (26.2 mg, 92%) as an colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): 6.79 (s, 1H), 6.55 (s, 1H), 6.08 (d, J = 6.0 Hz, 1H), 3.79 (s, 3H), 3.71 (br m, 1H), 2.15 (s, 3H), 1.48 (d, J = 7.2 Hz, 3H), 1.46 (s, 3H), 1.43 (s, 3H), 0.93 (t, J = 7.8 Hz, 9H), 0.62 (m, 6H); ^{13}C(75 MHz, $CDCl_3$): 210.6, 154.7, 147.4, 139.6, 134.0, 128.4, 126.9, 125.5, 109.1, 85.8, 40.1, 26.1, 23.6, 19.1, 15.7, 7.2, 3.5; HRMS m/e for $C_{22}H_{34}O_3Si$ calcd (M^++H) 374.2277 found 261.1491.

8-Methoxy-2,2,6,9-tetramethyl-2H-benzo[b]oxocin-3(4H)-one (13)



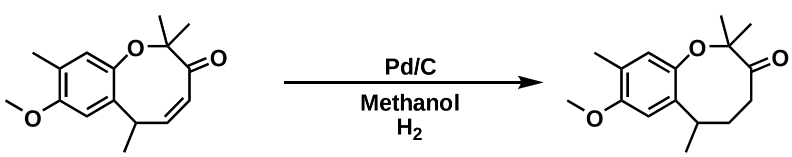
To a solution of 2,2,6,6-tetramethylpiperidine (0.16 mL, 0.94 mmol, 5 equiv) in THF (5 mL) at 0 °C was added *n*-BuLi (0.37 mL, 2.5 M, 0.93 mmol, 5 equiv). The solution was stirred at 0 °C for 30 min and added by syringe to a solution of **11j** (0.0687 g, 0.183 mmol) and chlorotrimethylsilane (0.14 mL, 1.1 mmol, 6 equiv) in THF (3 mL) at -78 °C. The solution was stirred at -78 °C for 1 h and allowed to warm to rt for 30 min. NH_4Cl (aq) was added and the mixture subjected to a conventional extractive workup. The crude material was dissolved in acetone (10 mL) and 3 M HCl (1 mL) was added. The mixture was stirred for 1 h, and $NaHCO_3$ (aq) was added. Following the removal of acetone under reduced pressure, the mixture was subjected to a conventional extractive workup. The crude product was dissolved in THF (5 mL), and NH_4Cl(aq) (7 drops) and *n*-Bu_4NF (0.27 mL, 1 M, 0.27 mmol, 1.5 equiv) was added. After 10 h, the mixture was subjected to a conventional extractive workup. Following preparative TLC (15:1 petroleum ether : Et_2O) afforded **13** (0.0350 g, 73%) as a colorless oil, which was spectroscopically identical to the literature report;[4,5] ^{1}H NMR (300 MHz, $CDCl_3$) 6.88 (s, 1H), 6.64 (s, 1H), 5.75 (dq, J = 7.7, 1.5 Hz, 1H), 3.83 (s, 3H), 2.98 (d, J = 7.7 Hz, 2H), 2.21 (s, 3H), 2.06 (m, 3H), 1.47 (s, 6H); ^{13}C (75 MHz, $CDCl_3$) 208.7, 154.6, 145.1, 137.2, 132.9, 127.5, 126.4, 119.4, 108.5, 81.7, 55.6, 41.0, 24.6, 23.8, 16.1.

8-Methoxy-2,2,6,9-tetramethyl-2H-benzo[b]oxocin-3(6H)-one (14)



Sodium hypophosphite monohydrate (112.4 mg, 1.27 mmol) was added to a mixture of the cyclooctyne complex **7j** (139.0 mg, 0.26 mmol) in 1,2-dichloroethane/2-methoxyethanol (5 mL + 15 mL) at room temperature. The reaction was heated to 65°C for 4 hours (with monitoring by TLC). The mixture was cooled to room temperature and filtered through a plug of Celite®. The resulting solution was washed with brine and extracted with ethyl acetate. The organic phase was dried using magnesium sulfate and concentrated under reduced pressure to afford an orange oil. Preparative TLC (10:1 hexanes : Et_2O) gave, in order of elution, recovered **7j** (3.8 mg, 3%) and **14** as a light yellow oil (36.3 mg, 55%, 57% BRSM); ^1H NMR (300 MHz, $CDCl_3$) 6.86 (s, 1H), 6.56 (s, 1H), 6.23 (dd, J = 12.9, 5.1 Hz, 1H), 5.77 (dd, J = 12.9, 2.1 Hz, 1H), 3.88 (br m, 1H), 3.78 (s, 3H), 2.16 (s, 3H), 1.55 (s, 3H), 1.54 (s, 3H), 1.51 (d, J = 7.5 Hz, 3H); ^{13}C (75 MHz, $CDCl_3$) 206.0, 154.8, 147.5, 144.2, 135.6, 126.8, 126.2, 125.5, 109.5, 87.3, 55.7, 38.5, 25.6, 24.7, 19.5, 15.8; $C_{16}H_{21}O_3$ calcd (M^++H) 261.1491 found 261.1491.

Heliannuol K methyl ether (**3b**)



To a round bottom flask containing the enone (36.3 mg, 0.14 mmol) in methanol (5 mL) added 5% Pd/C (10 mg) and was allowed to stir at room temperature under a hydrogen atmosphere. The reaction mixture was filtered through a glass-frit which was then concentrated under reduced pressure. The following crude product was filtered through a plug of silica to give Heliannuol K methyl ether (**3b**) (32.8 mg, 90%) as a colorless oil. Product indicated by ^1H NMR (300 MHz, $CDCl_3$): 6.74 (s, 1H), 6.58 (s, 1H), 3.80 (s, 3H), 3.12 (m, 1H), 2.40-2.55 (m, 2H), 2.16 (s, 3H), 2.02 (m, 1H), 1.71 (m, 1H), 1.50 (s, 3H), 1.47 (s, 3H), 1.33 (d, J = 7.1 Hz, 3H); ^{13}C (75 MHz,

$CDCl_3$) 213.0, 154.0, 146.0, 137.0, 127.5, 124.4, 108.8, 86.0, 55.5, 36.1, 34.7, 34.5, 24.4, 23.5, 20.5, 15.8.[5]

The following is a ^{1}H and ^{13}C NMR spectra comparison between the currently prepared **3b** and the literature report.[5]

^{1}H NMR current work	^{1}H NMR[5]	^{13}C NMR current work		^{13}C NMR[5]	
6.74 (s, 1H)	6.74 (s, 1H)	213.0	34.5	212.98	34.46
6.58 (s, 1H)	6.58 (s, 1H)	154.0	24.4	154.86	24.36
3.80 (s, 3H)	3.80 (s, 3H)	146.0	23.5	145.96	23.45
3.12 (m, 1H)	3.02-3.20 (m, 1H)	137.0	20.5	136.90	20.43
2.40-2.55 (m, 2H)	2.39-2.61 (m, 2H)	127.5	15.8	127.46	15.78
2.16 (s, 3H)	2.15 (s, 3H)	124.4		124.37	
2.02 (m, 1H)	1.90-2.07 (m, 1H)	108.8		108.71	
1.71 (m, 1H)	1.61-1.79 (m, 1H)	86.0		85.91	
1.50 (s, 3H)	1.49 (s, 3H)	55.5		55.45	
1.47 (s, 3H)	1.45 (s, 3H)	36.1		36.03	
1.33 (d, J = 7.1 Hz, 3H)	1.34 (d, J = 7.1 Hz, 3H)	34.7		34.65	

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(1) Wang, B.; Tang, C.; Han, Y.; Guo, R.; Qian, H.; Huang, W. Synthesis and Preliminary Antihyperlipidaemic Actvities Evaluation of Andrographolide Derivatives. *Med. Chem.* **2012**, 293–298.

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(3) Shimizu, T.; Osako, K.; Nakata, T. Efficient Method for Preparation of N-Methoxy-N-methyl Amides by Reaction of Lactones or Esters with Me_2AlCl-MeONHMe•HCl. *Tetrahedron Lett.* **1997**, *38*, 2685–2688.

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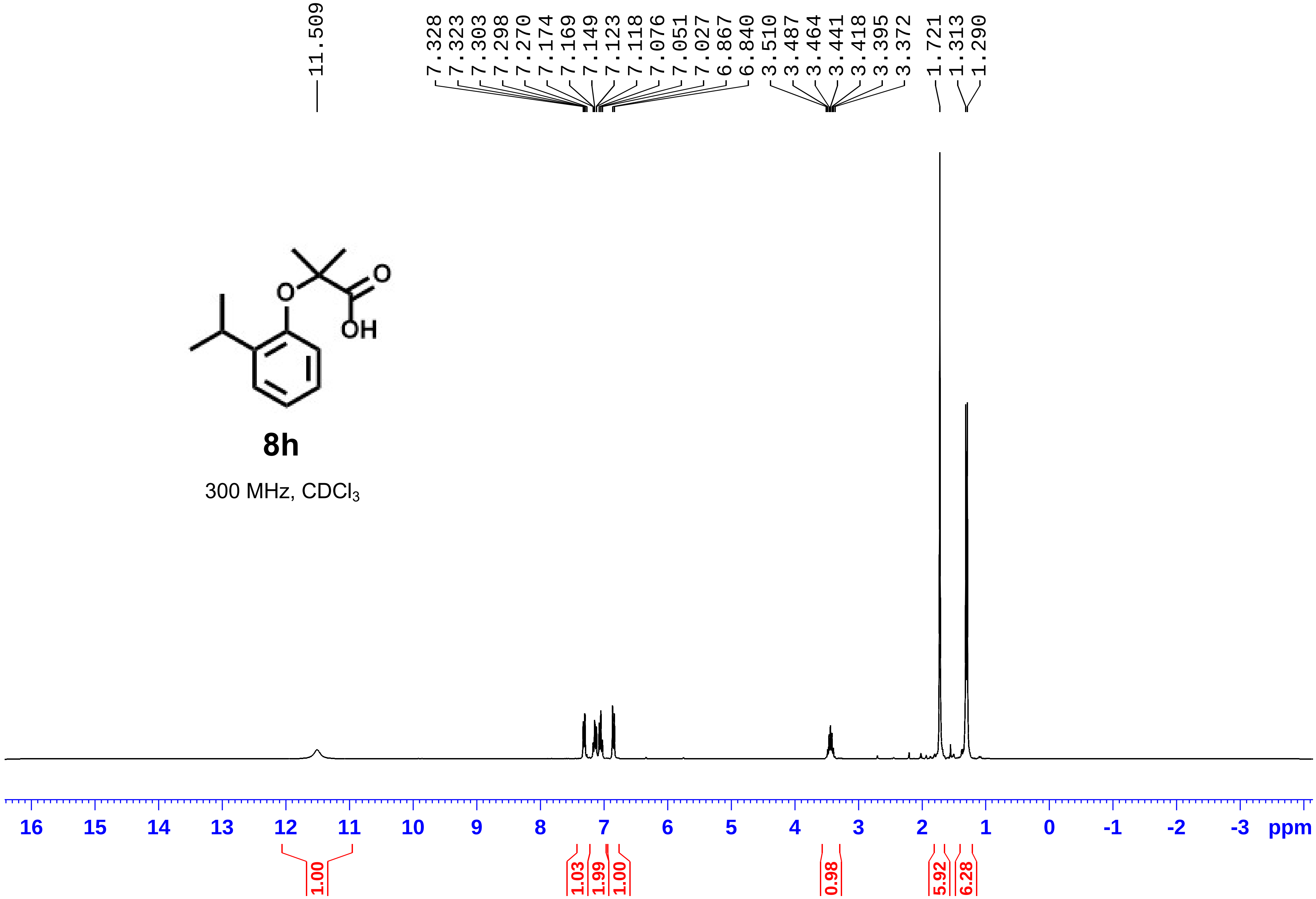
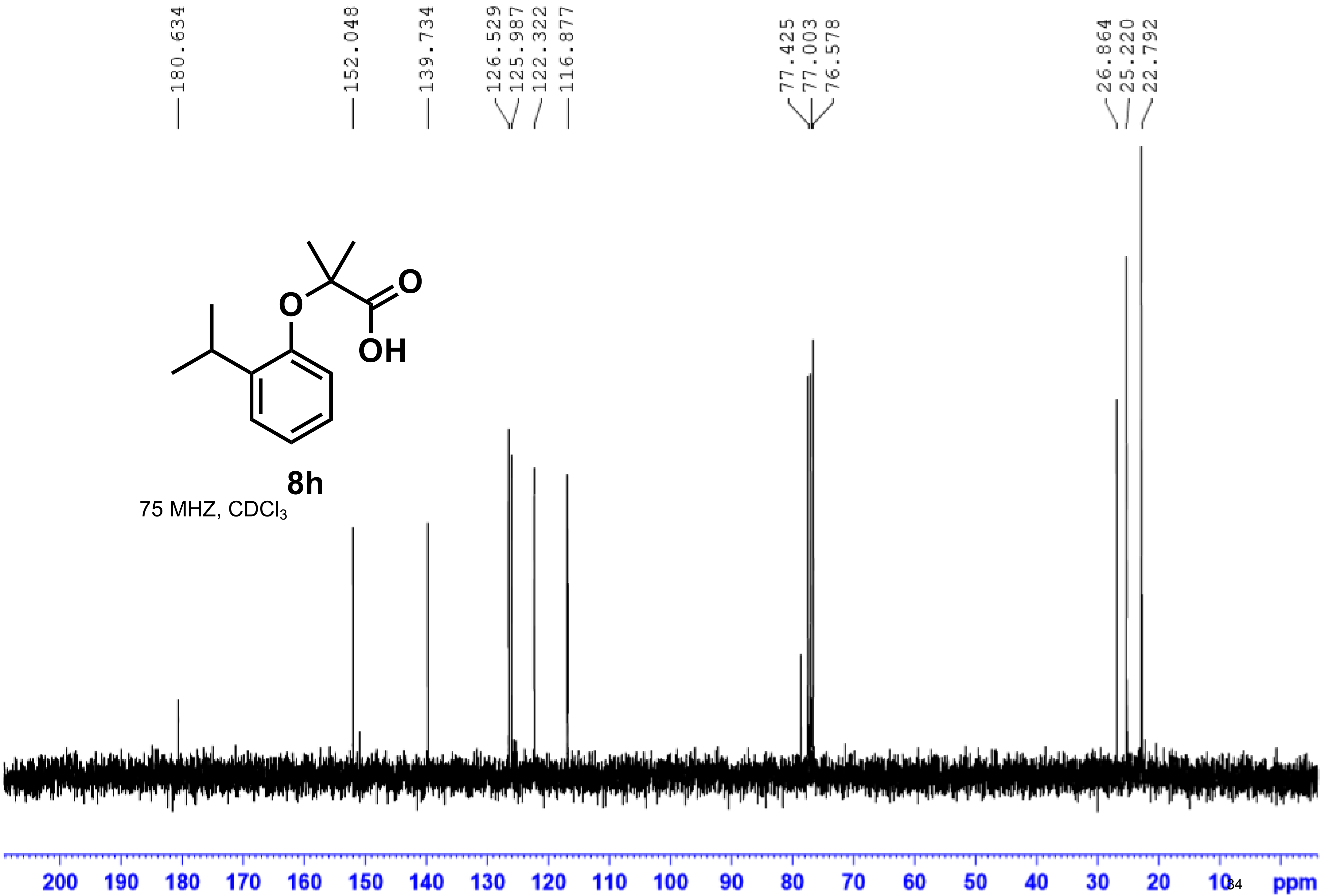
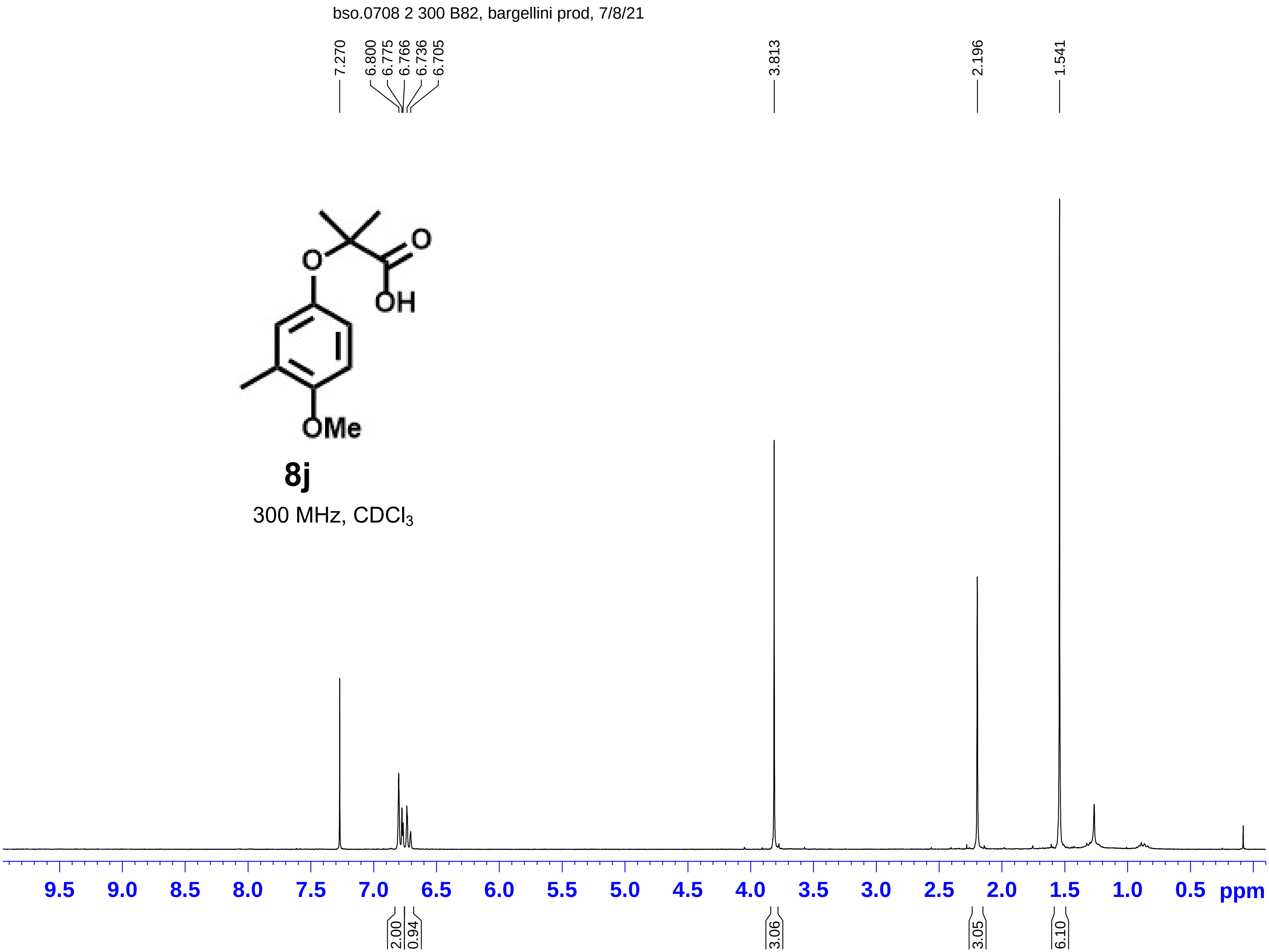
(5) Lecornue, F.; Ollivier, J. Convergent Formal Synthesis of (±)-Heliannuols A, K, and L From a Common Intermediate. *Synlett* **2004**, 1613-1615.

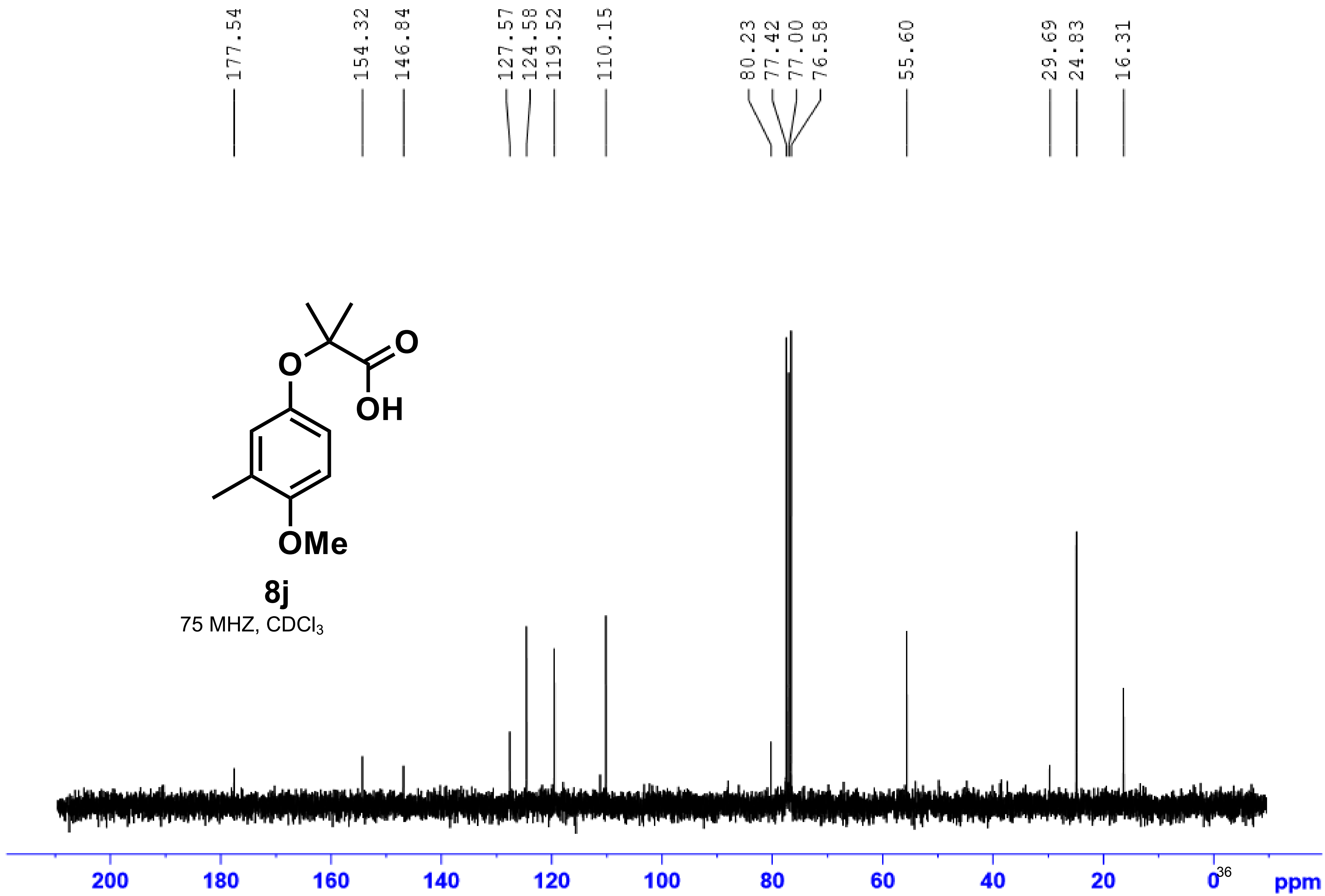


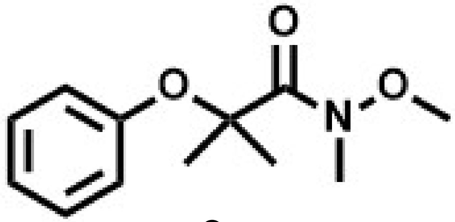
8h

300 MHz, $CDCl_3$


180.634
152.048
139.734
126.529
125.987
122.322
116.877
77.425
77.003
76.578
26.864
25.220
22.792
O
OH
8h
75 MHZ, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

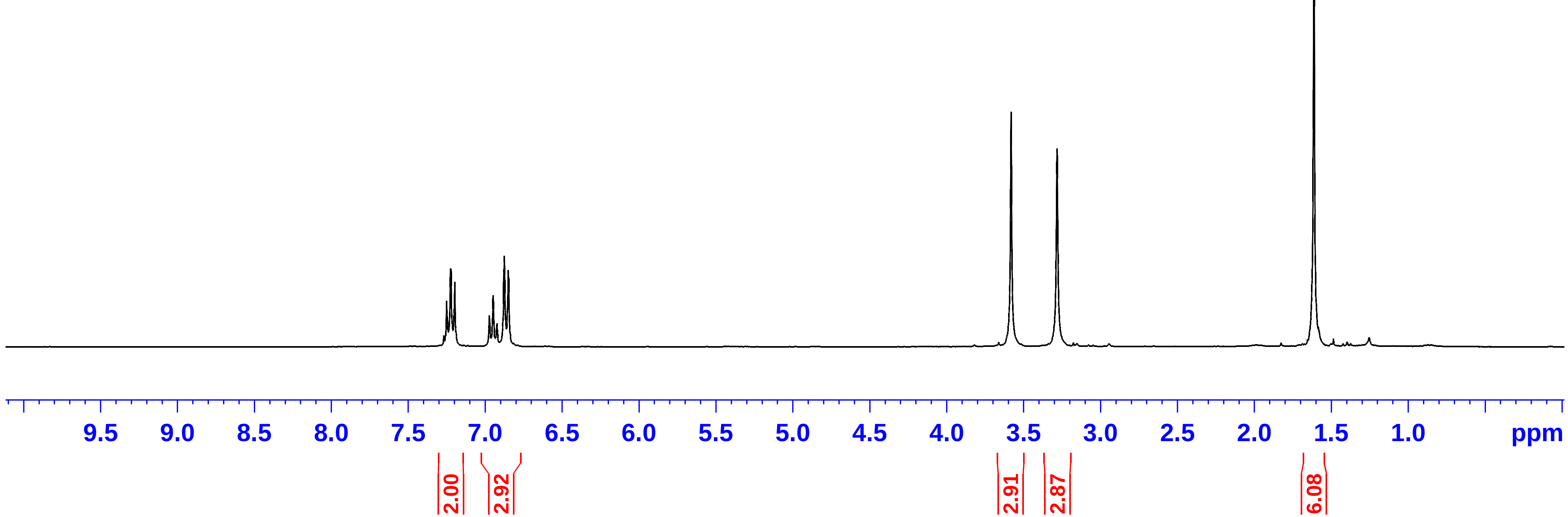

bso.0708 2 300 B82, bargellini prod, 7/8/21
7.270
6.800
6.775
6.766
6.736
6.705
3.813
2.196
1.541
O
OH
O
OMe
8j
300 MHz, $CDCl_3$
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
0.94
3.06
3.05
6.10

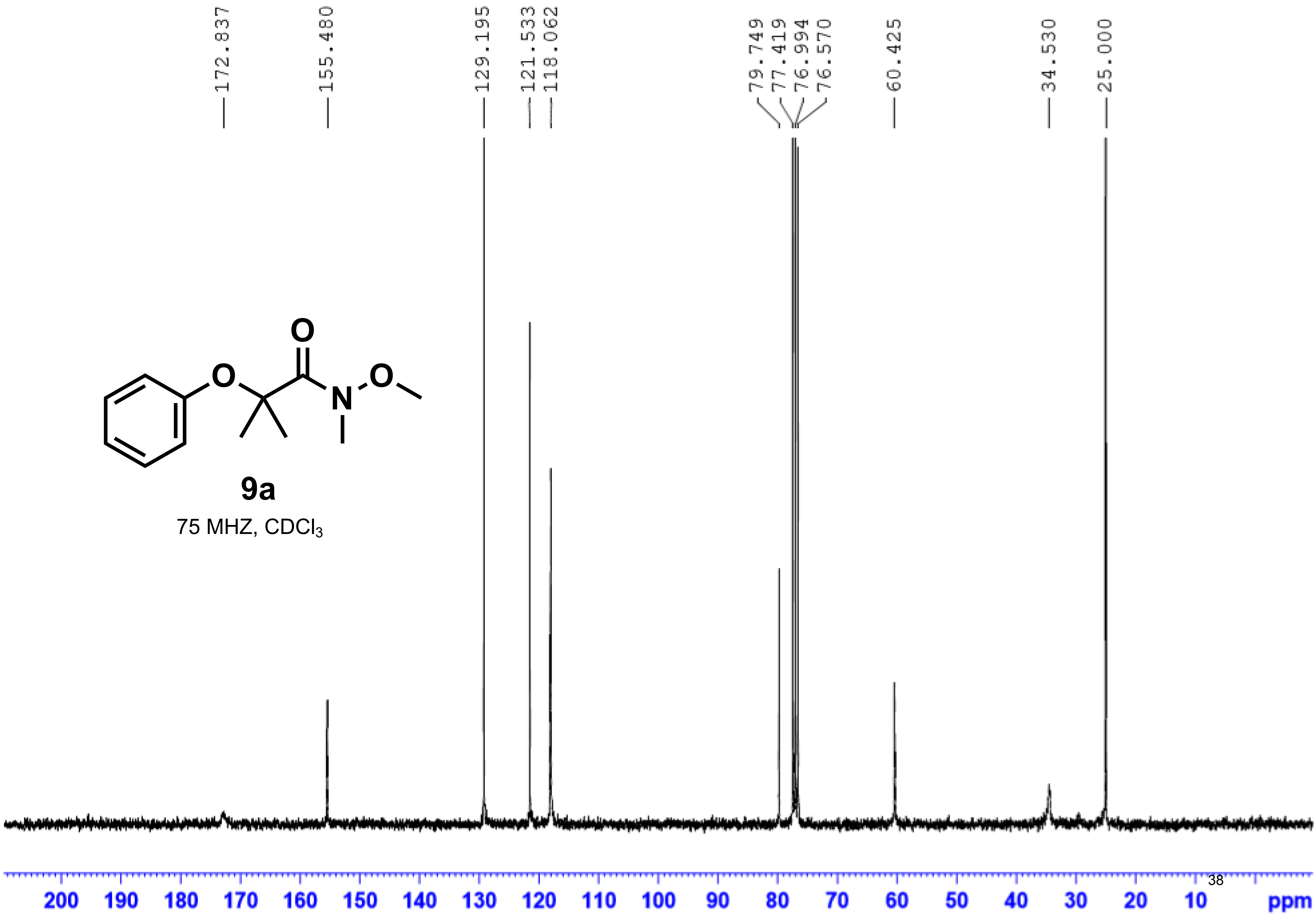

177.54
154.32
146.84
127.57
124.58
119.52
110.15
80.23
77.42
77.00
76.58
55.60
29.69
24.83
16.31
O
O
OH
OMe
8j
75 MHZ, $CDCl_3$
200 180 160 140 120 100 80 60 40 20 0 ppm



9a

300 MHz, $CDCl_3$

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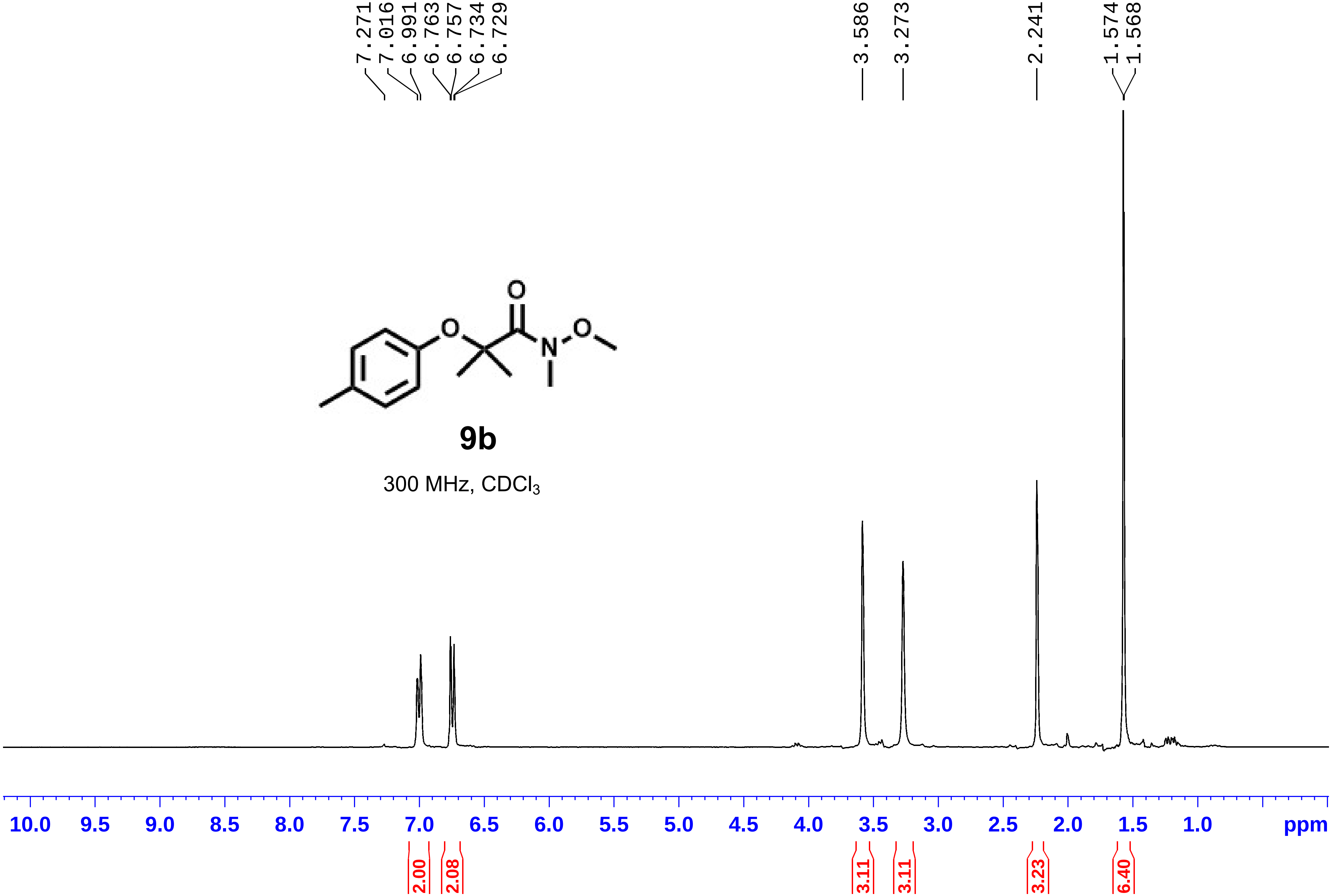
155.480
129.195
121.533
118.062
79.749
77.419
76.994
76.570
60.425
34.530
25.000
O
O
N
O
9a
75 MHZ, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.271
7.016
6.991
6.763
6.757
6.734
6.729
3.586
3.273
2.241
1.574
1.568
9b
300 MHz, $CDCl_3$
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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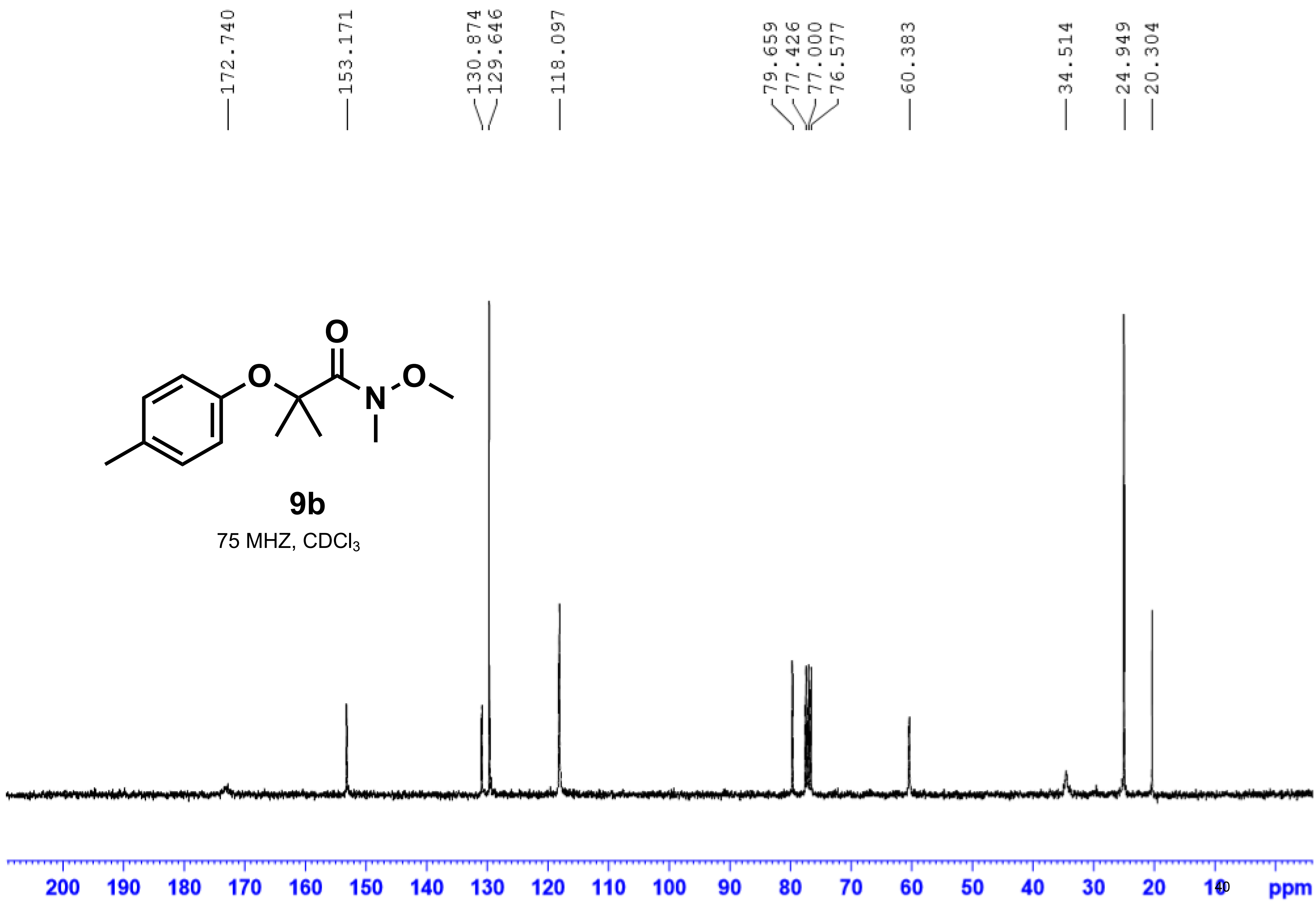
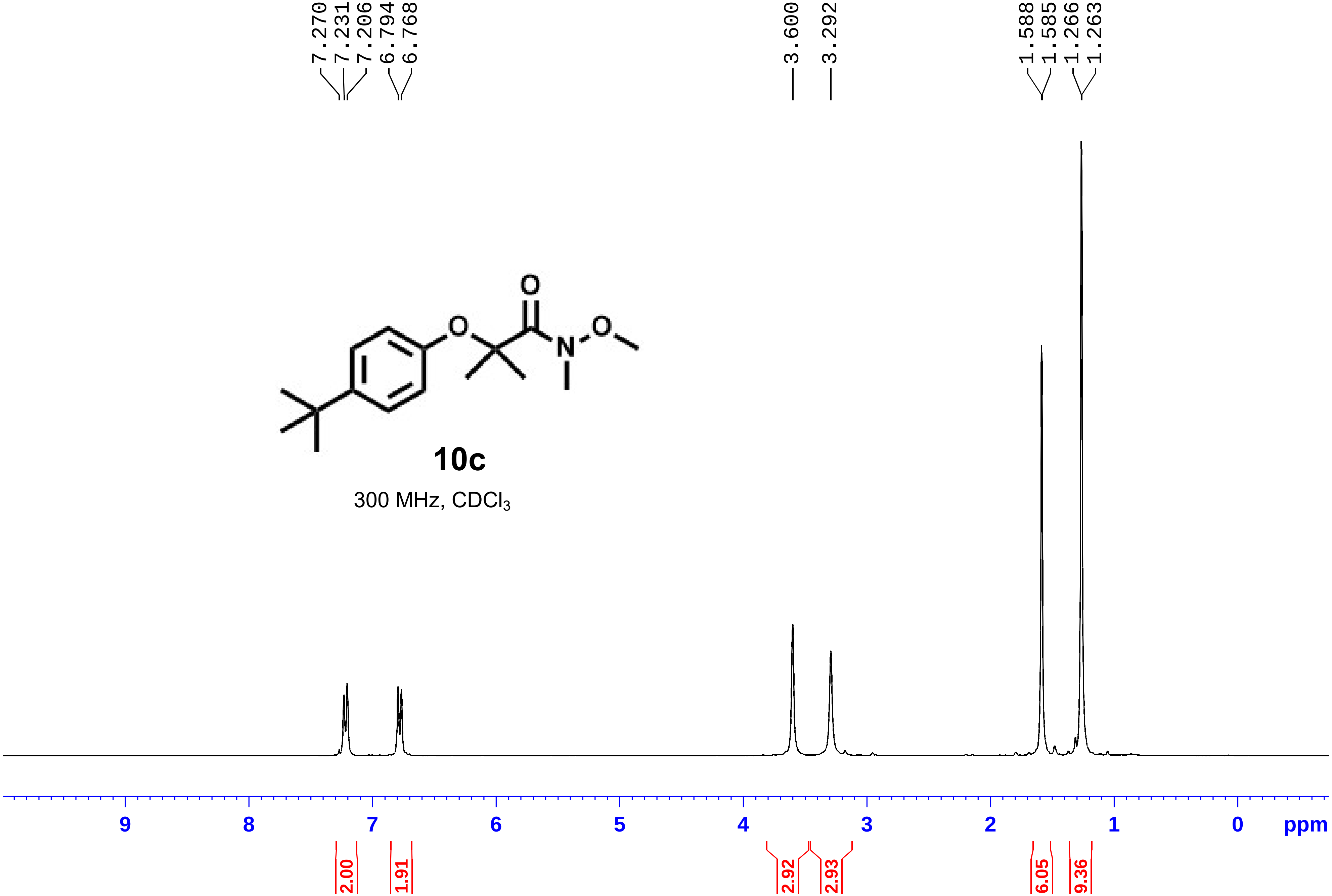
2.0
1.5
1.0
ppm
2.00
2.08
3.11
3.11
3.23
6.40

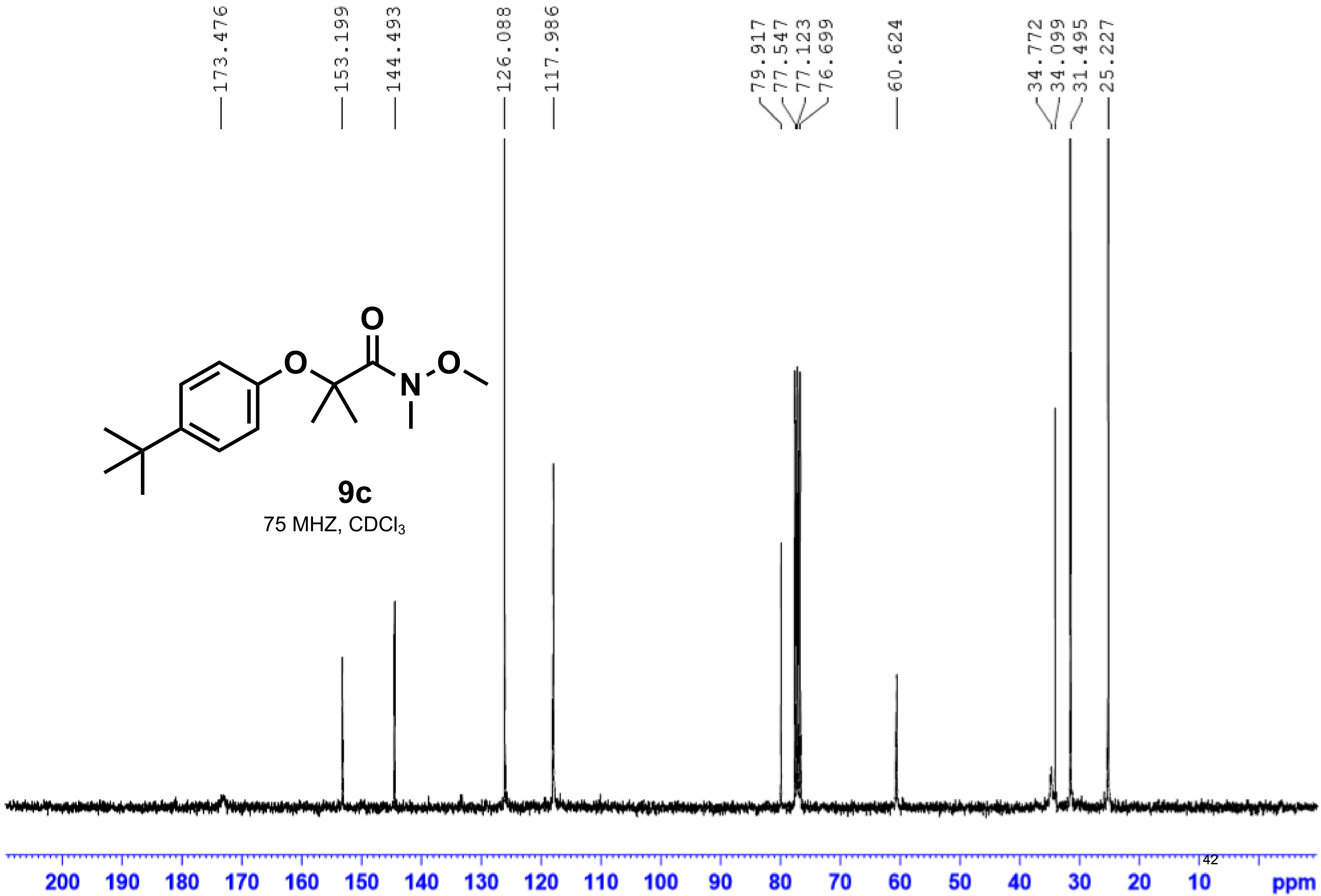


172.740
153.171
130.874
129.646
118.097
79.659
77.426
77.000
76.577
60.383
34.514
24.949
20.304
O
O
N
O
9b
75 MHZ, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



10c

300 MHz, $CDCl_3$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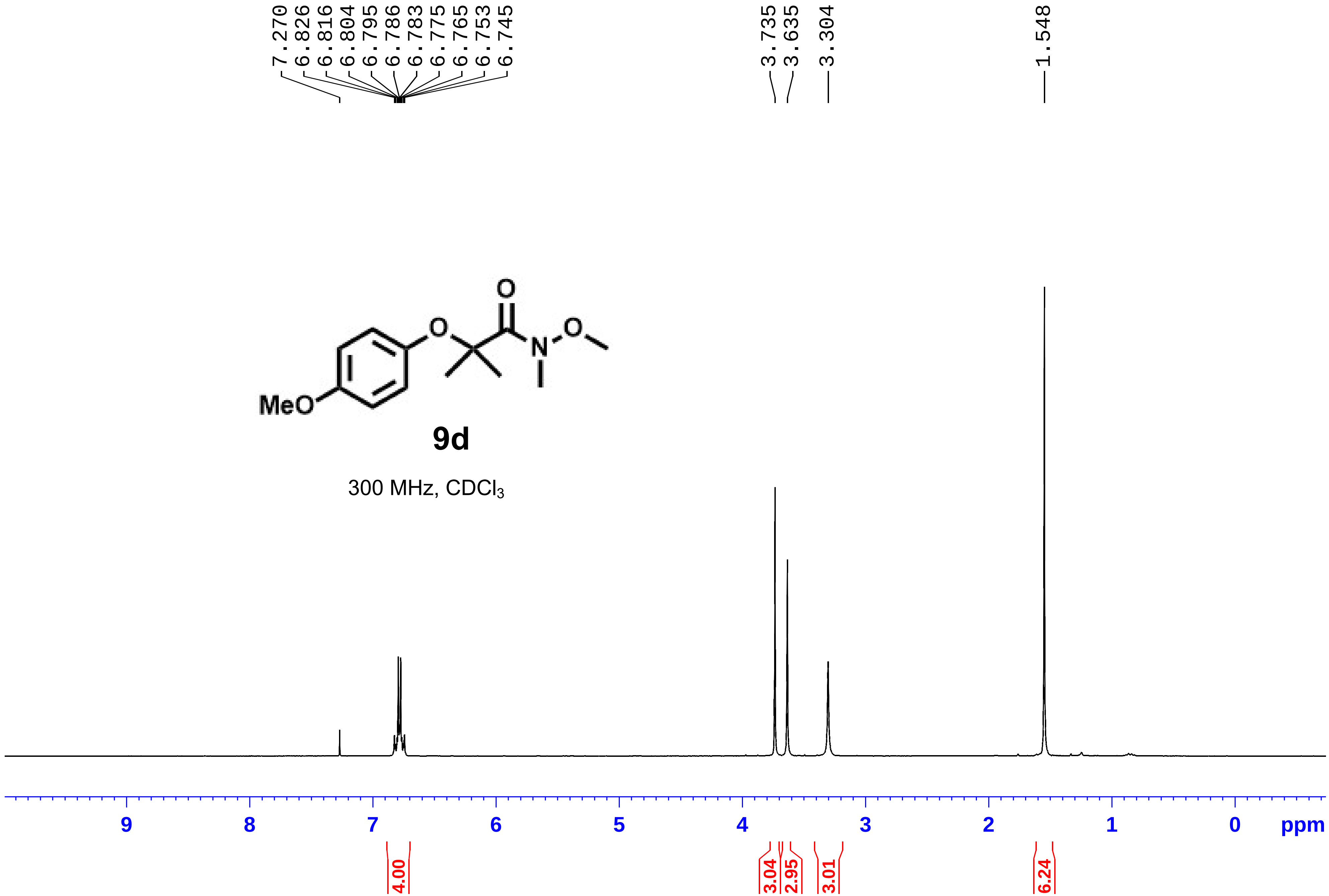
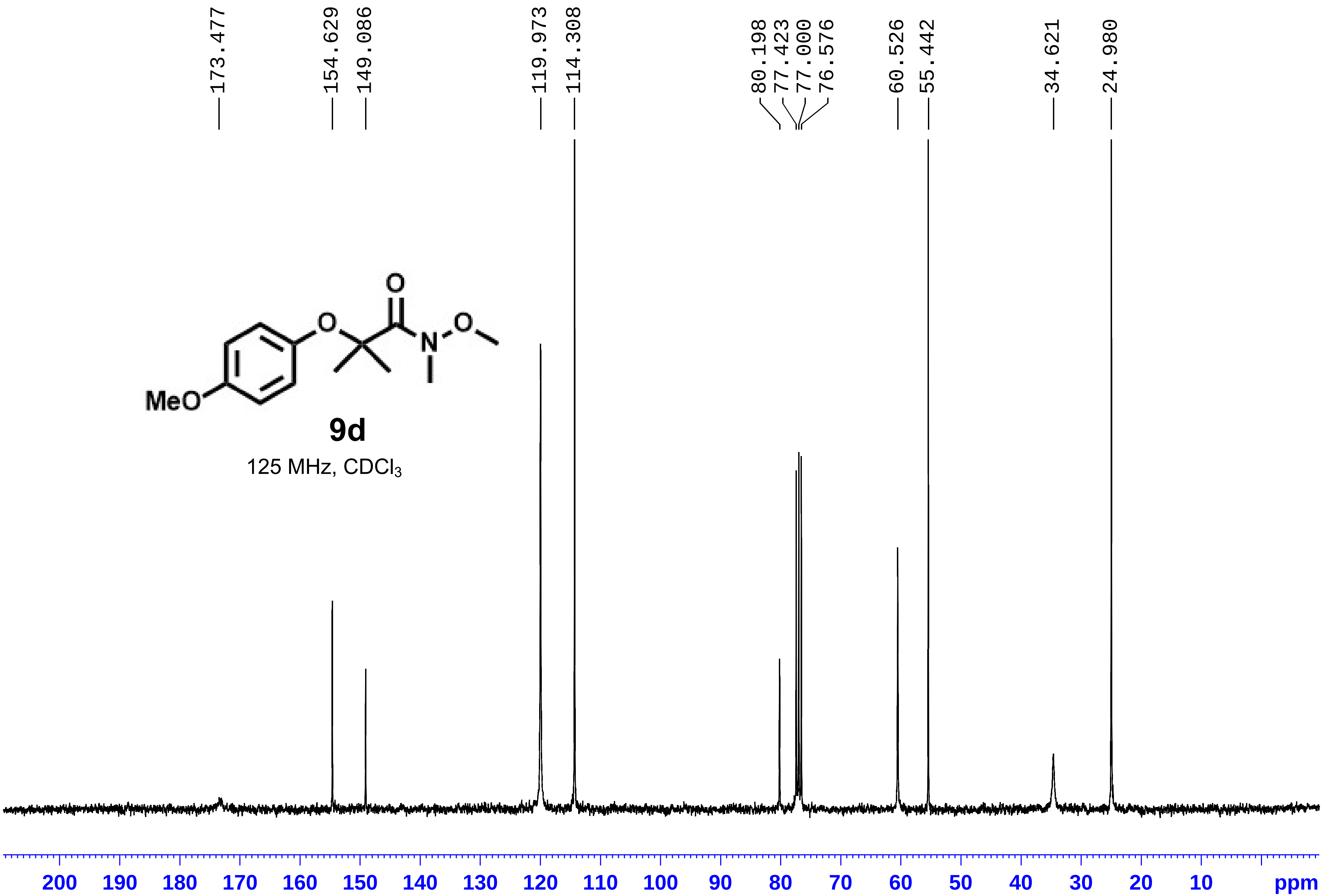
153.199
144.493
126.088
117.986
79.917
77.547
77.123
76.699
60.624
34.772
34.099
31.495
25.227
9c
75 MHZ, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.270
6.826
6.816
6.804
6.795
6.786
6.783
6.775
6.765
6.753
6.745
3.735
3.635
3.304
1.548
MeO
9d
300 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
4.00
3.04
2.95
3.01
6.24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77.000
76.576
60.526
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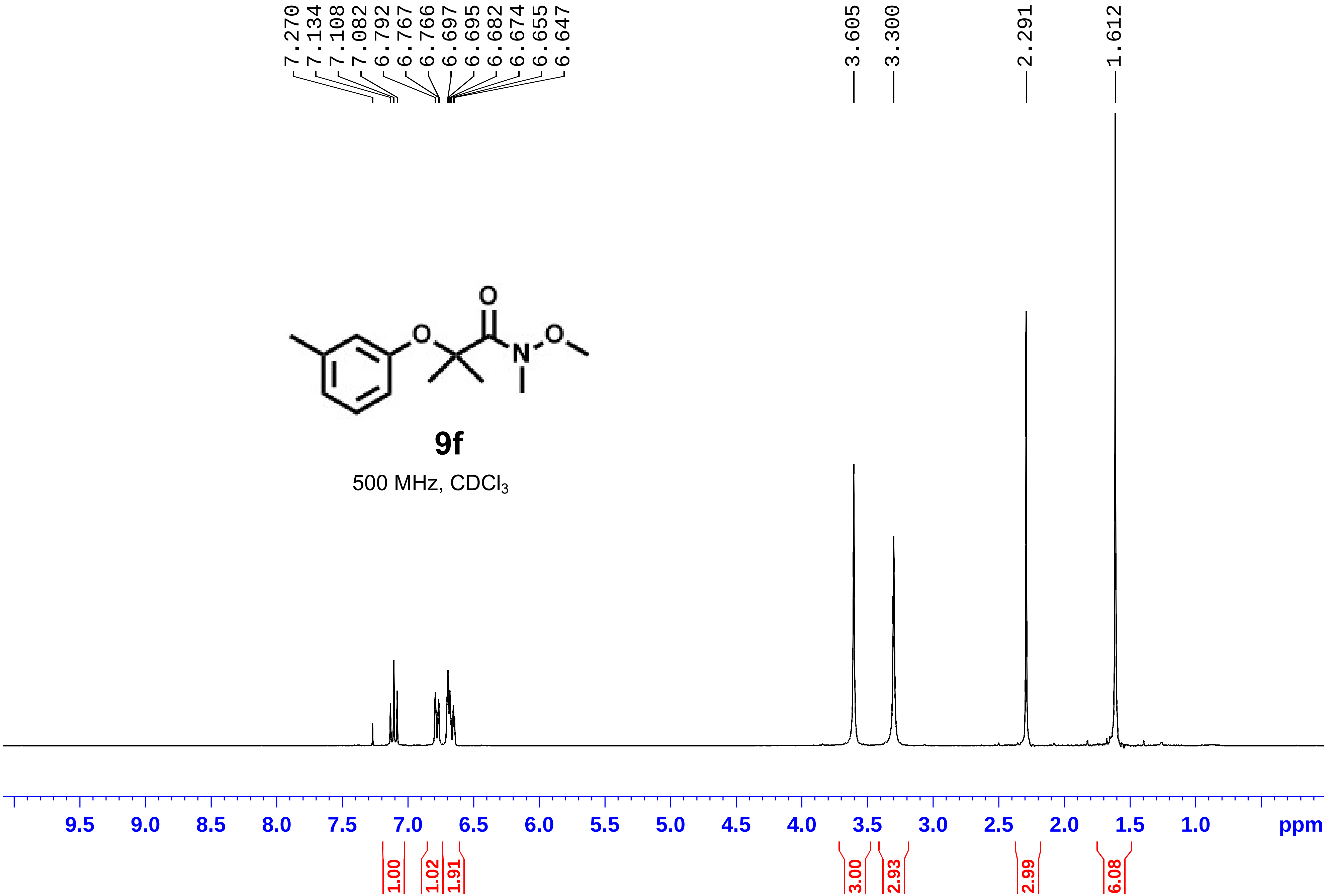
34.621
24.980
MeO
O
O
N
O
9d
125 MHz, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.134
7.108
7.082
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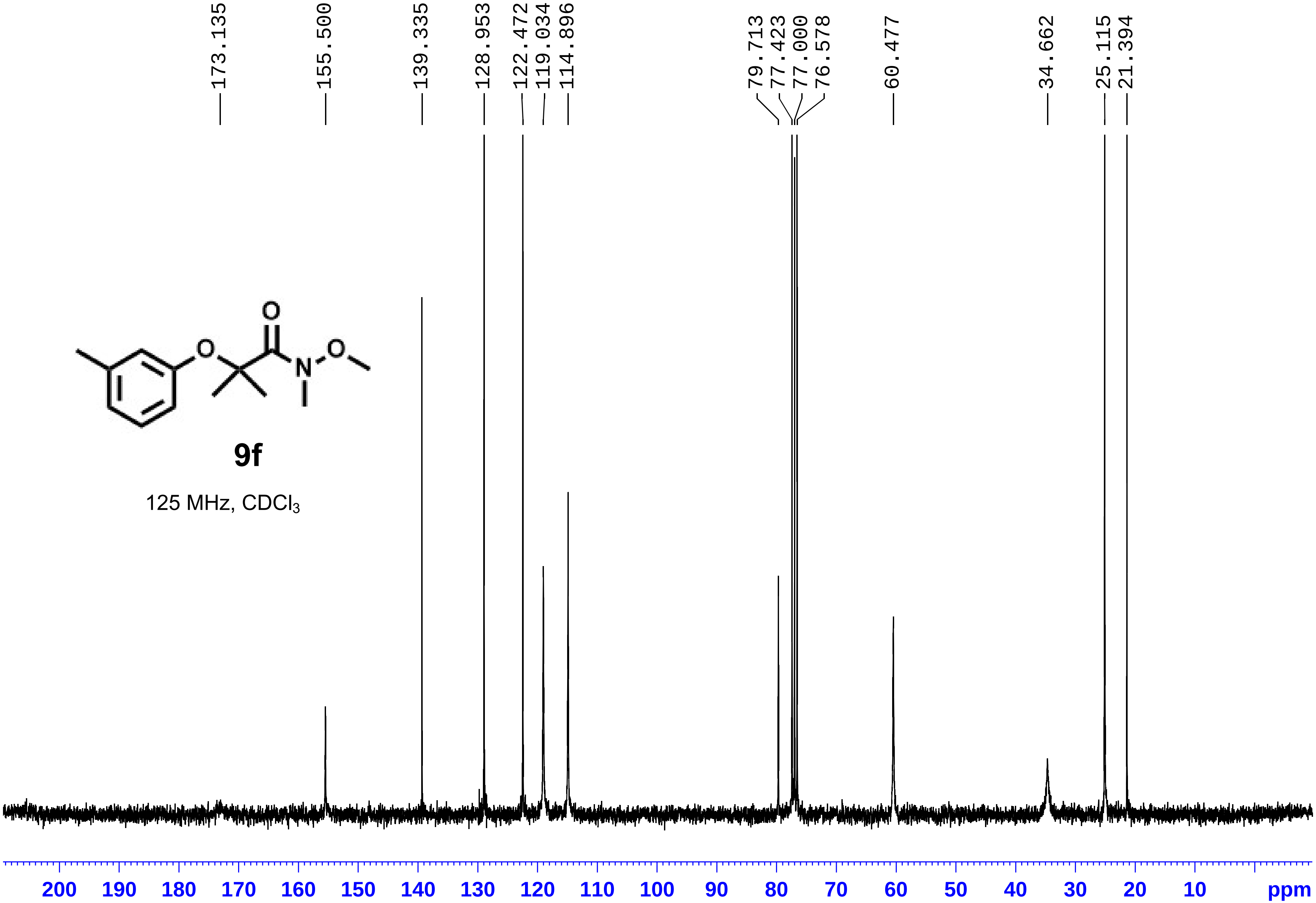
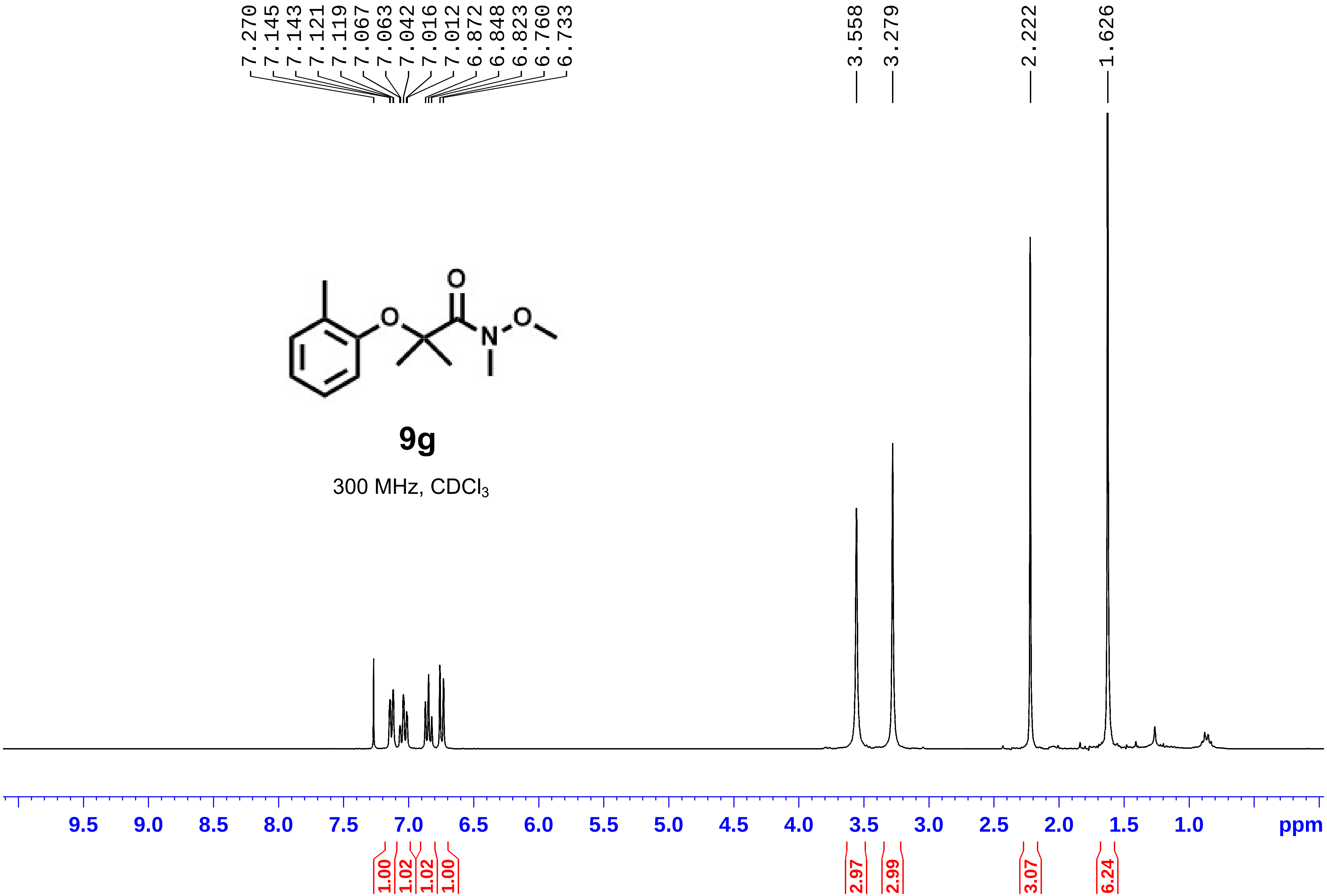
6.697
6.695
6.682
6.674
6.655
6.647
3.605
3.300
2.291
1.612
9f
500 MHz, $CDCl_3$
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.02
1.91
3.00
2.93
2.99
6.08



9f

125 MHz, $CDCl_3$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7.042
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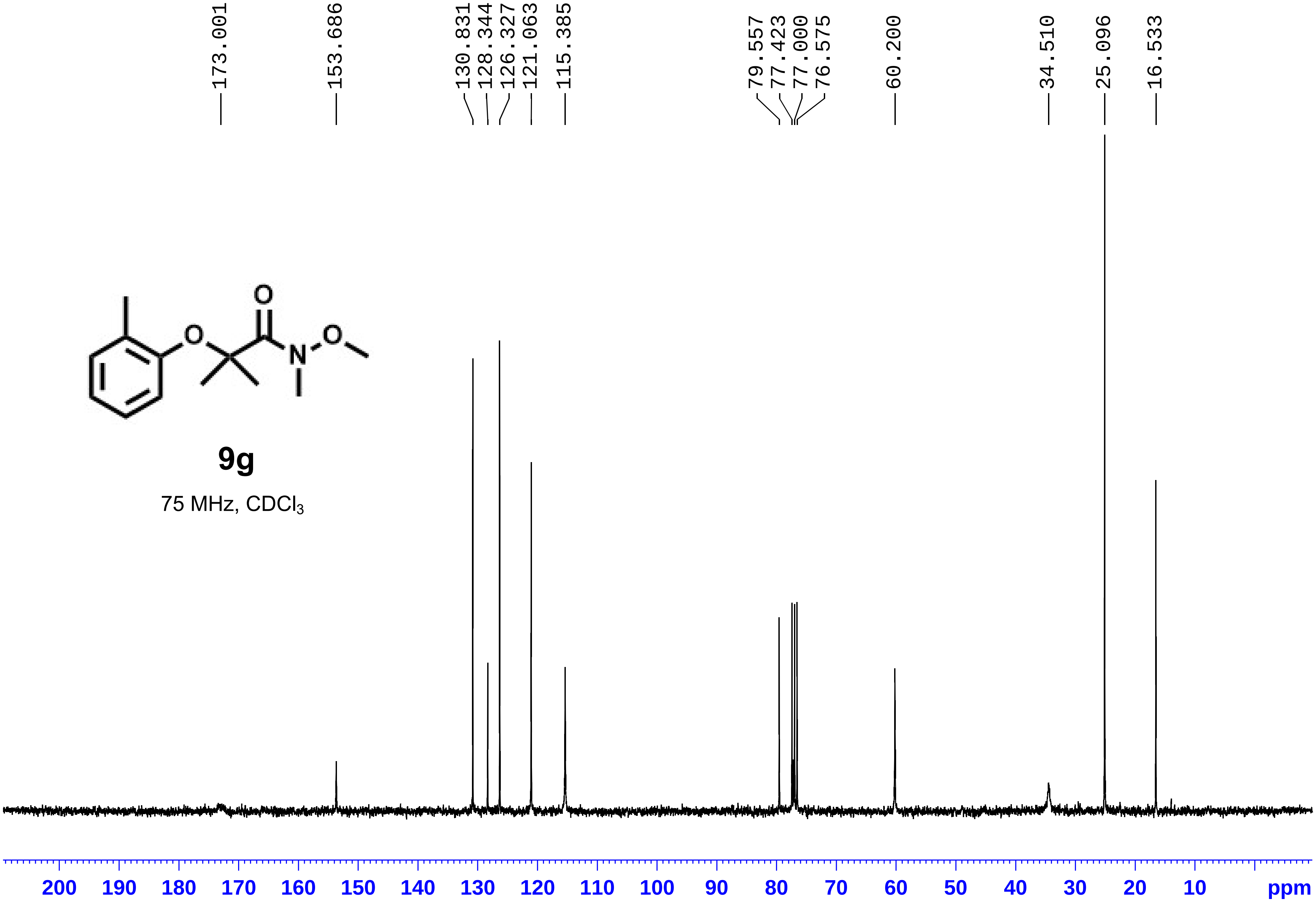
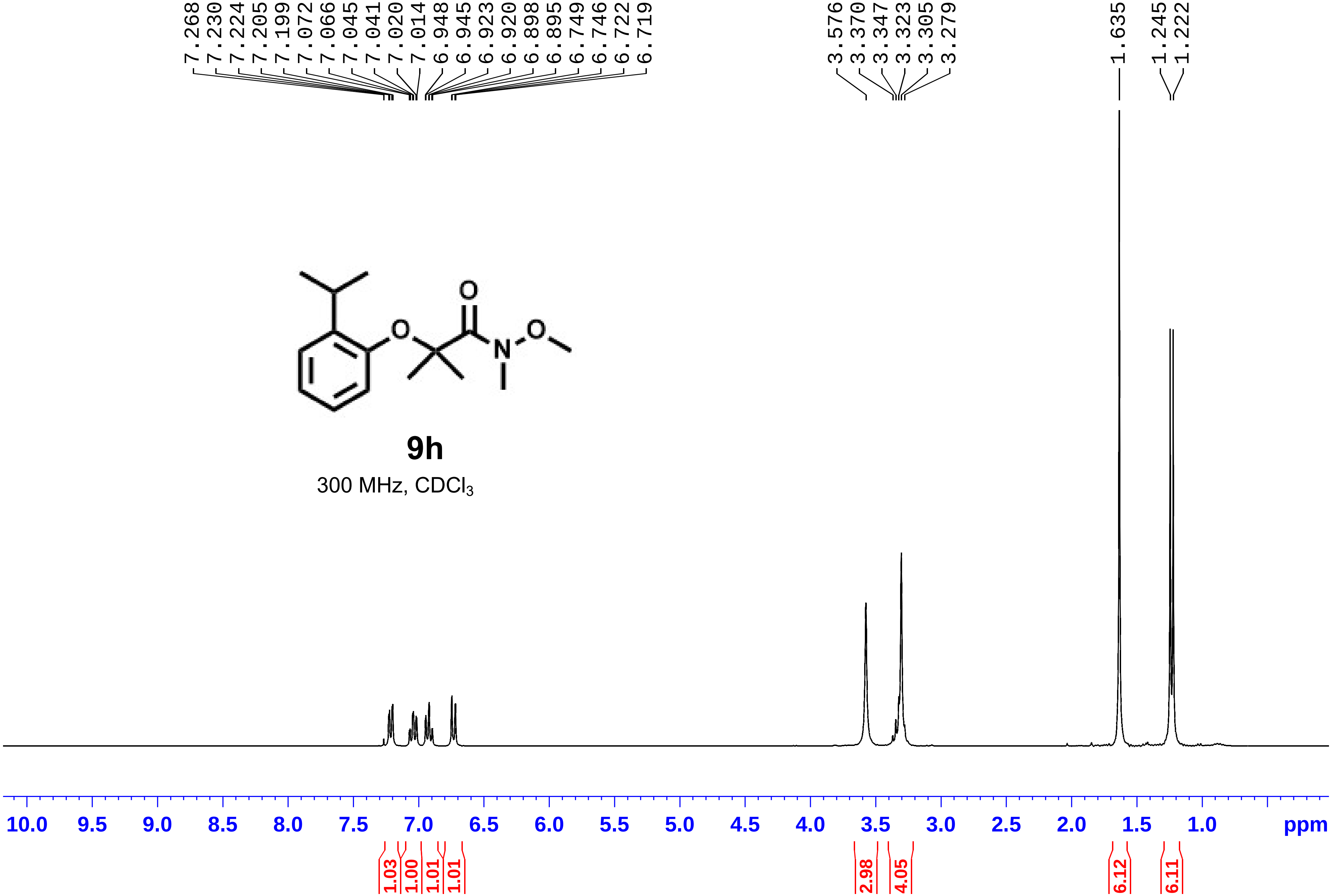
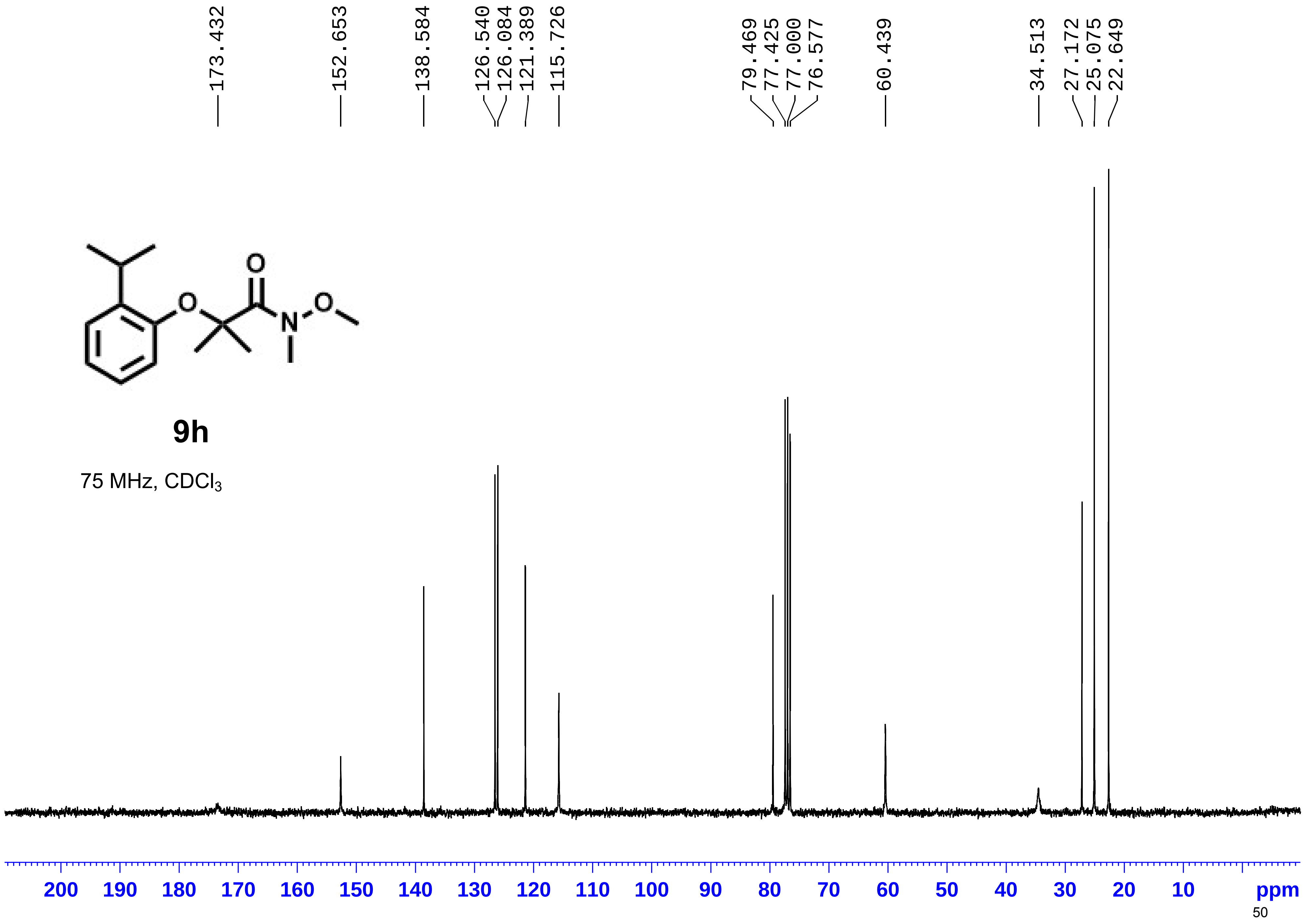
7.012
6.872
6.848
6.823
6.760
6.733
3.558
3.279
2.222
1.626
9g
300 MHz, $CDCl_3$
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.02
1.02
1.00
2.97
2.99
3.07
6.24

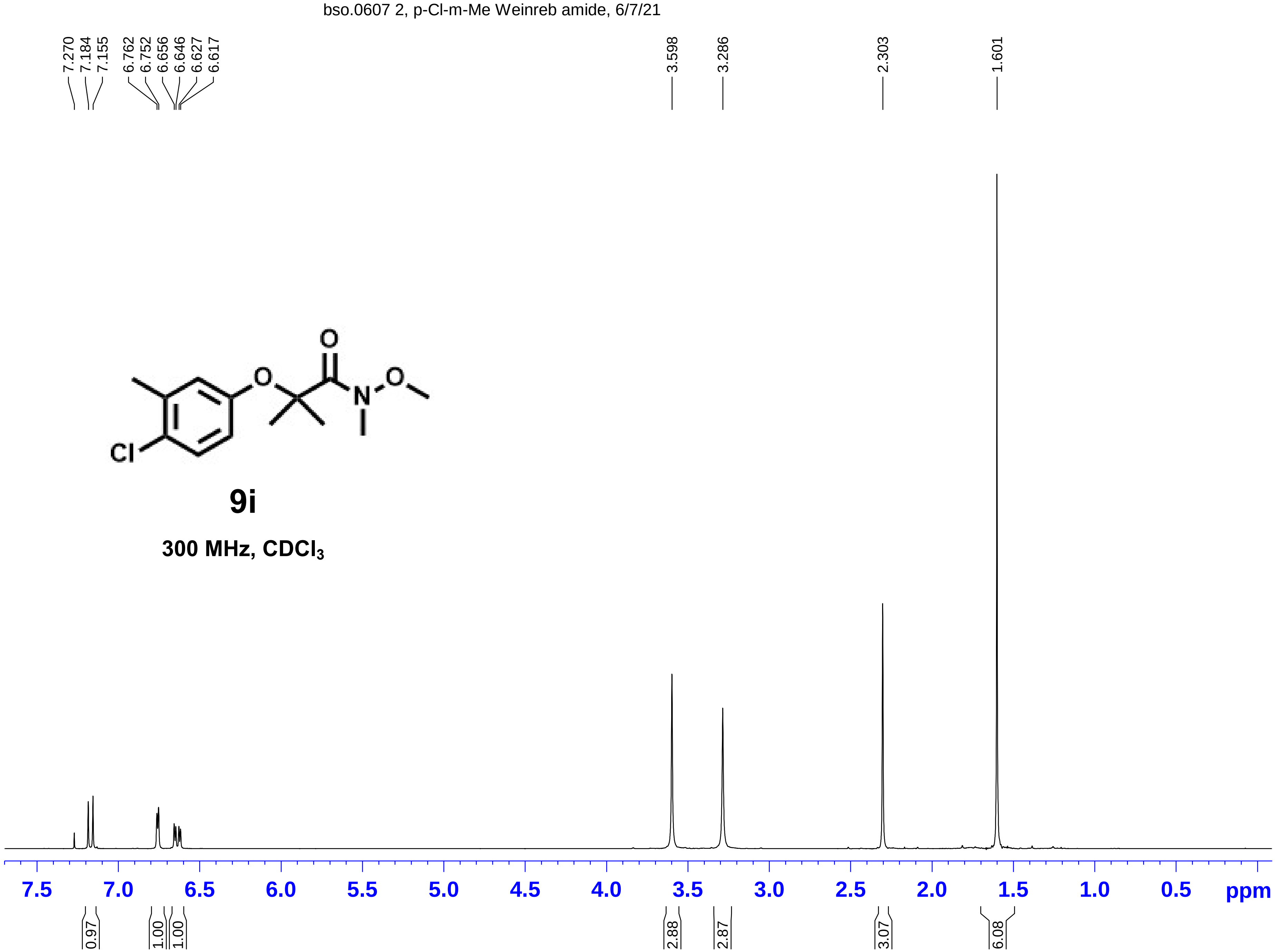


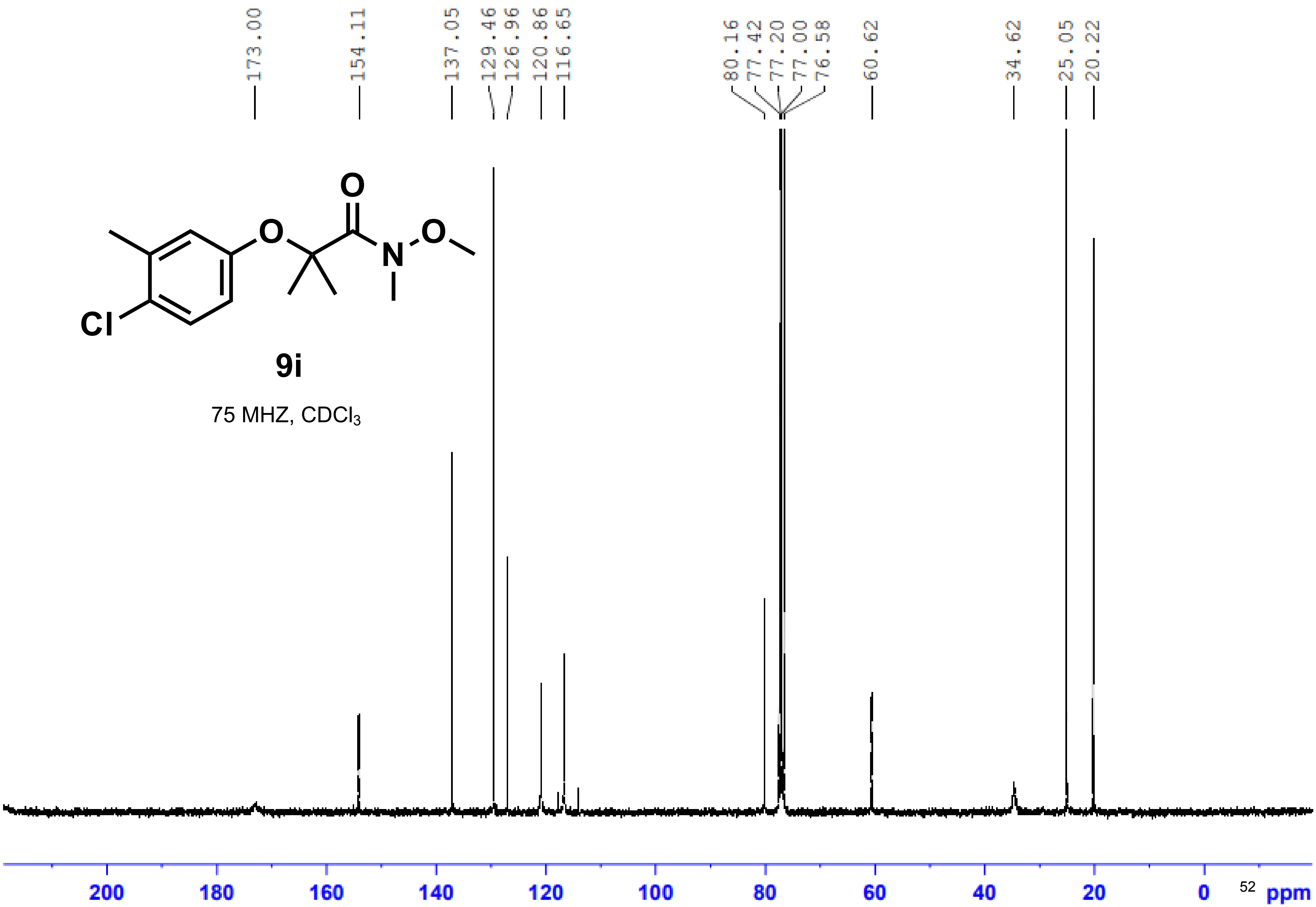
9g

75 MHz, $CDCl_3$


7.268
7.230
7.224
7.205
7.199
7.072
7.066
7.045
7.041
7.020
7.014
6.948
6.945
6.923
6.920
6.898
6.895
6.749
6.746
6.722
6.719
3.576
3.370
3.347
3.323
3.305
3.279
1.635
1.245
1.222
9h
300 MHz, $CDCl_3$
10.0 9.5 9.0 8.5 8.0 7.5 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 ppm
1.03
1.00
1.01
1.01
2.98
4.05
6.12
6.11

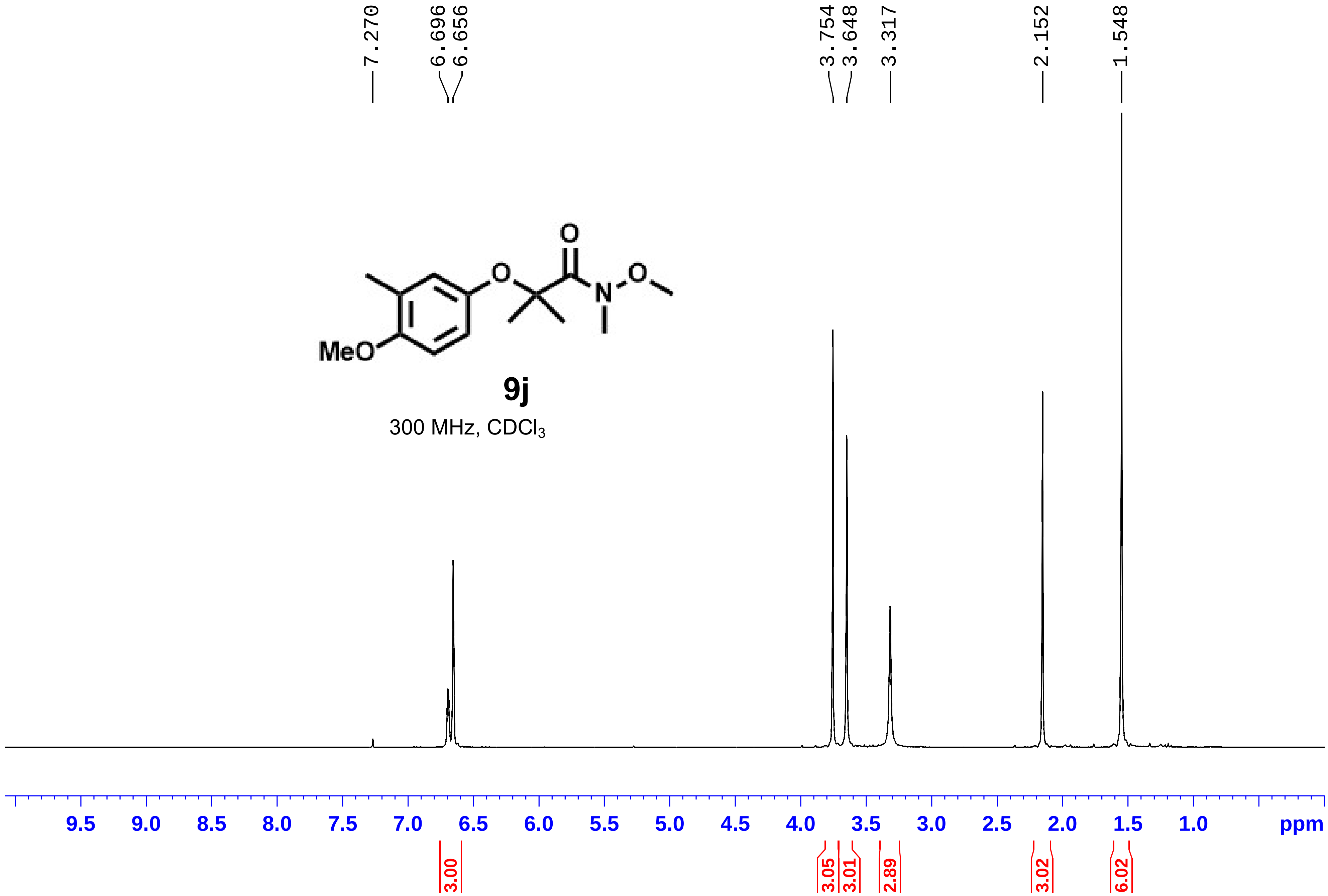

173.432
152.653
138.584
126.540
126.084
121.389
115.726
79.469
77.425
77.000
76.577
60.439
34.513
27.172
25.075
22.649
O
O
N
O
9h
75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

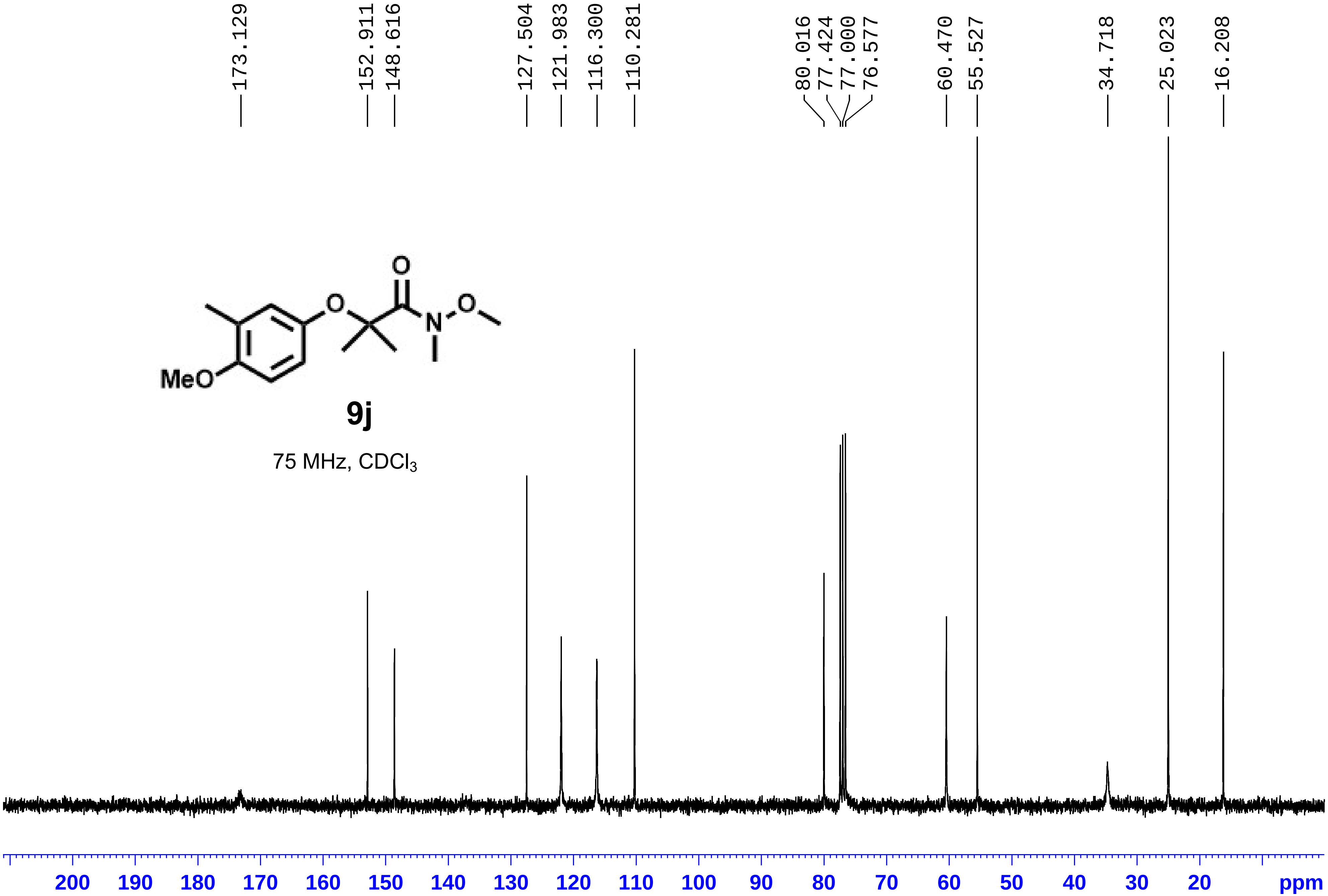

bso.0607 2, p-Cl-m-Me Weinreb amide, 6/7/21
7.270
7.184
7.155
6.762
6.752
6.656
6.646
6.627
6.617
3.598
3.286
2.303
1.601
O
O
N
O
Cl
9i
300 MHz, CDCl3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.97
1.00
1.00
2.88
2.87
3.07
6.08

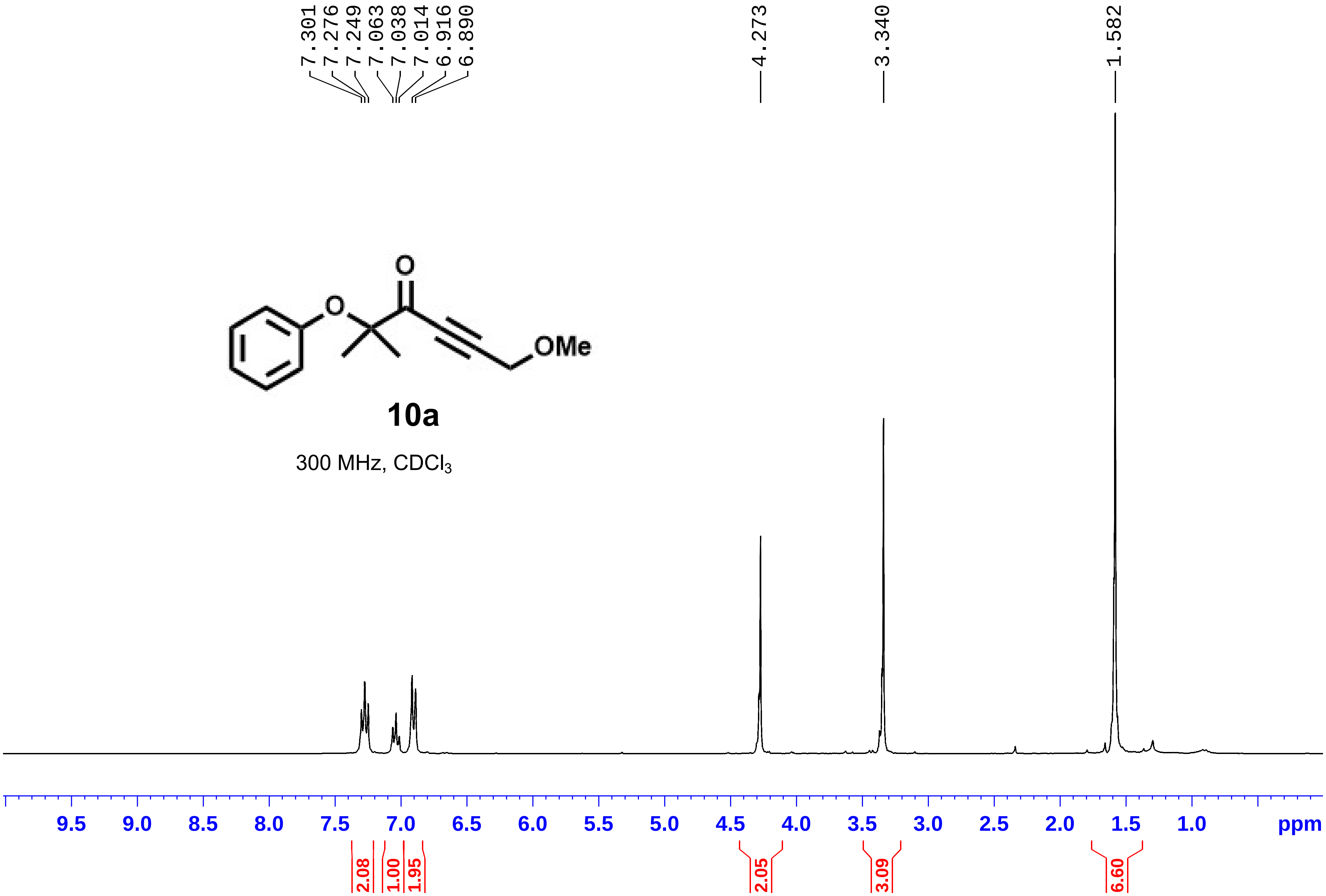


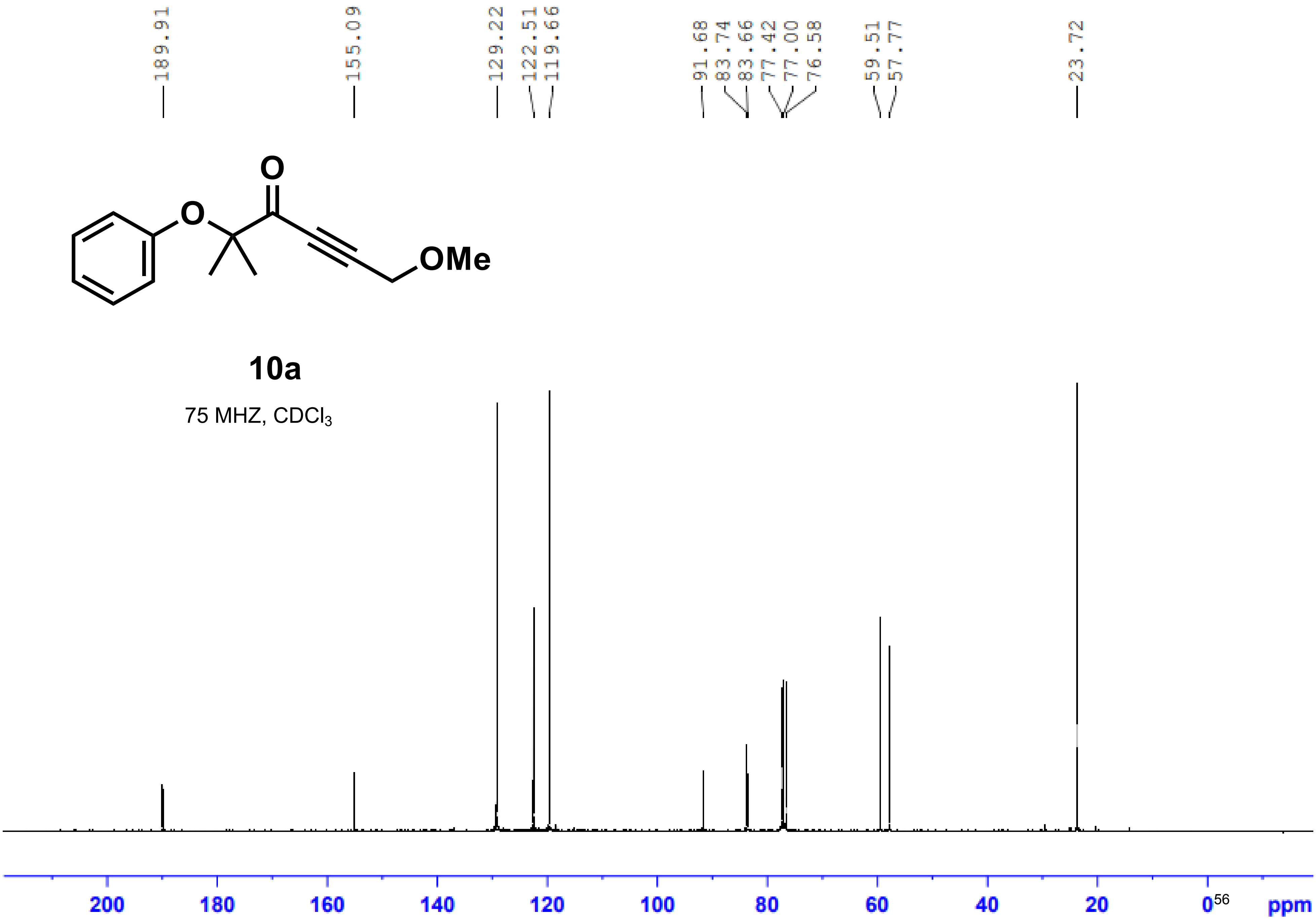
9i

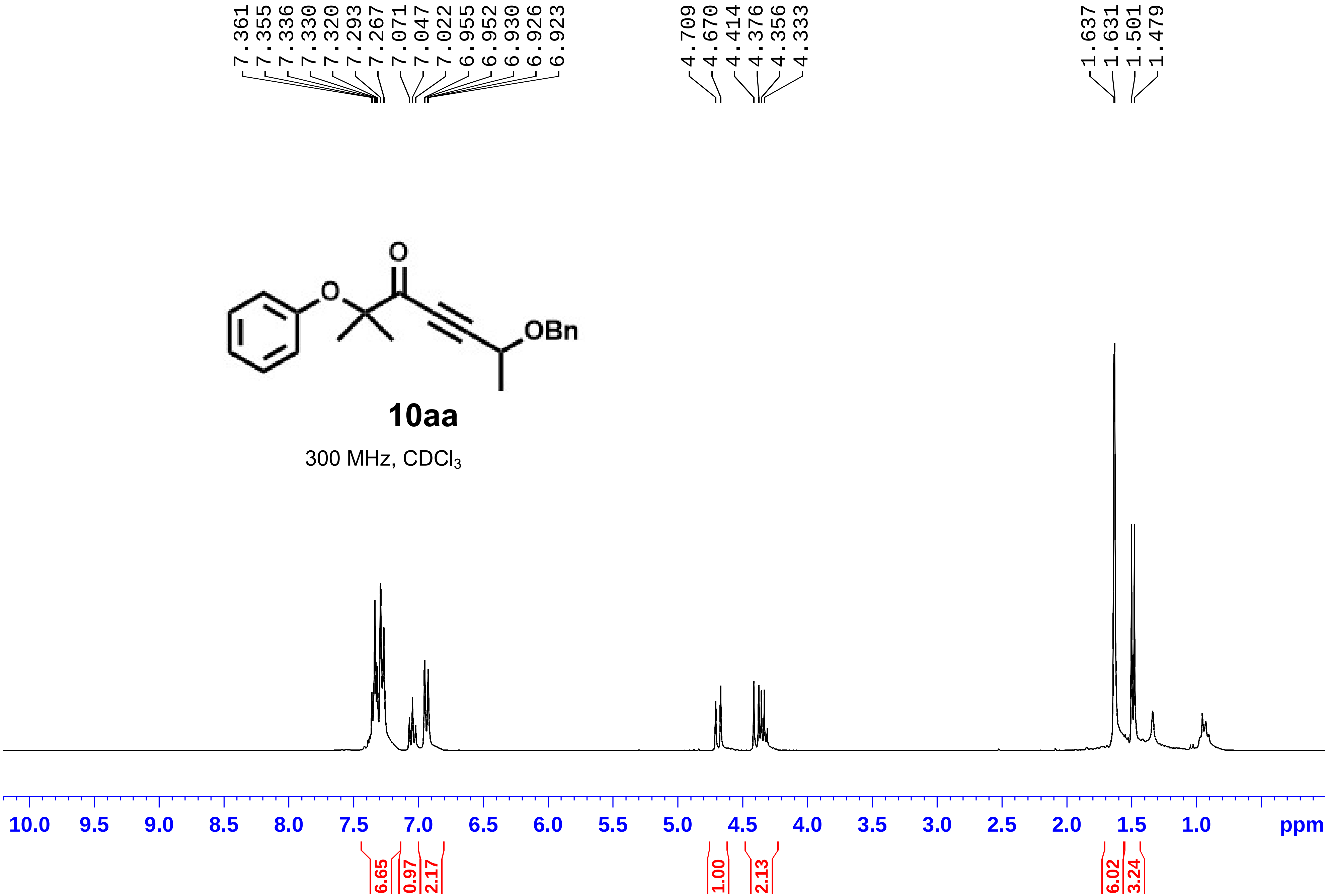
75 MHZ, $CDCl_3$

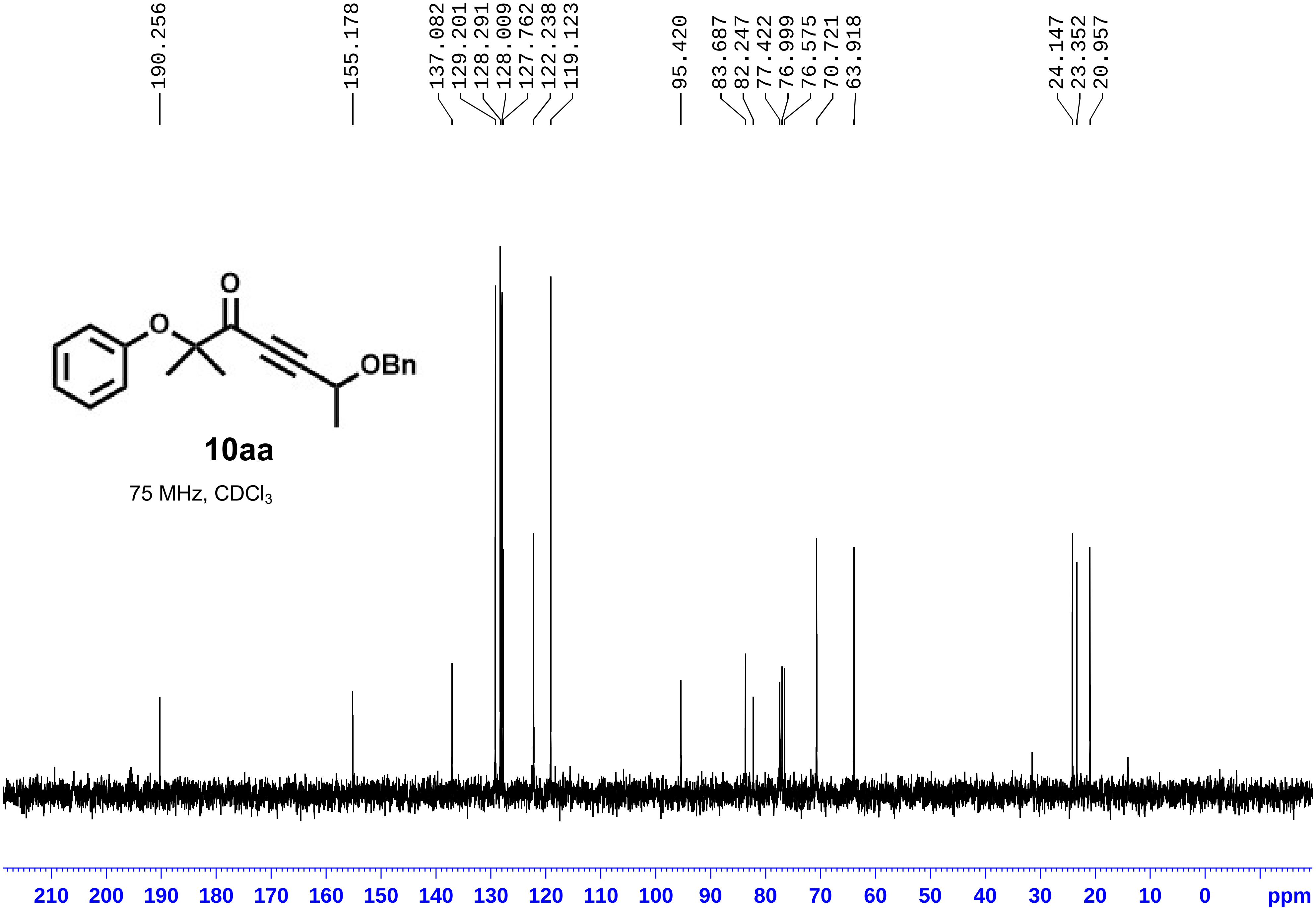

7.270
6.696
6.656
3.754
3.648
3.317
2.152
1.548
MeO
O
N
9j
300 MHz, $CDCl_3$
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
3.00
3.05
3.01
2.89
3.02
6.02

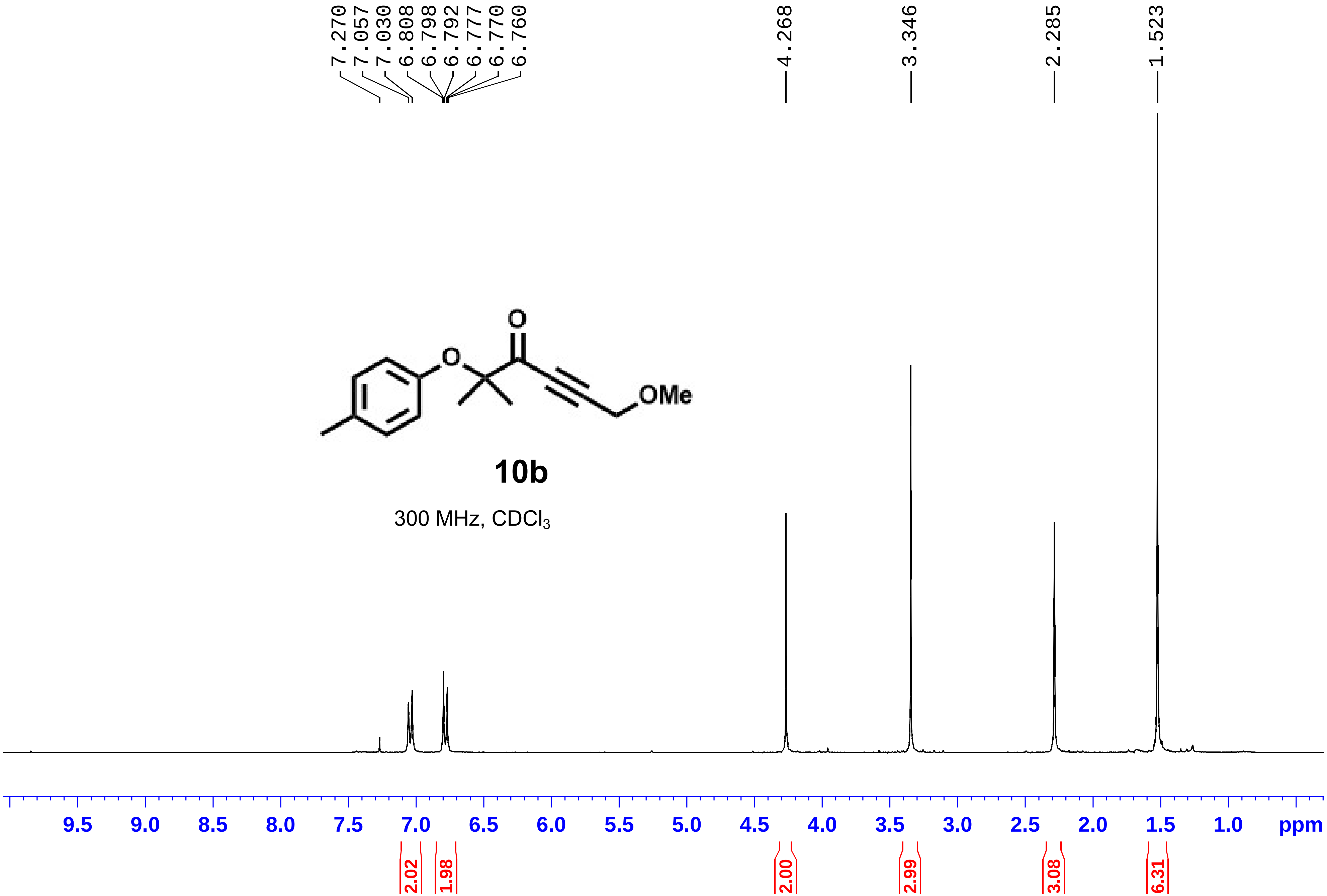

173.129
152.911
148.616
127.504
121.983
116.300
110.281
80.016
77.424
77.000
76.577
60.470
55.527
34.718
25.023
16.208
MeO
O
N
9j
75 MHz, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm

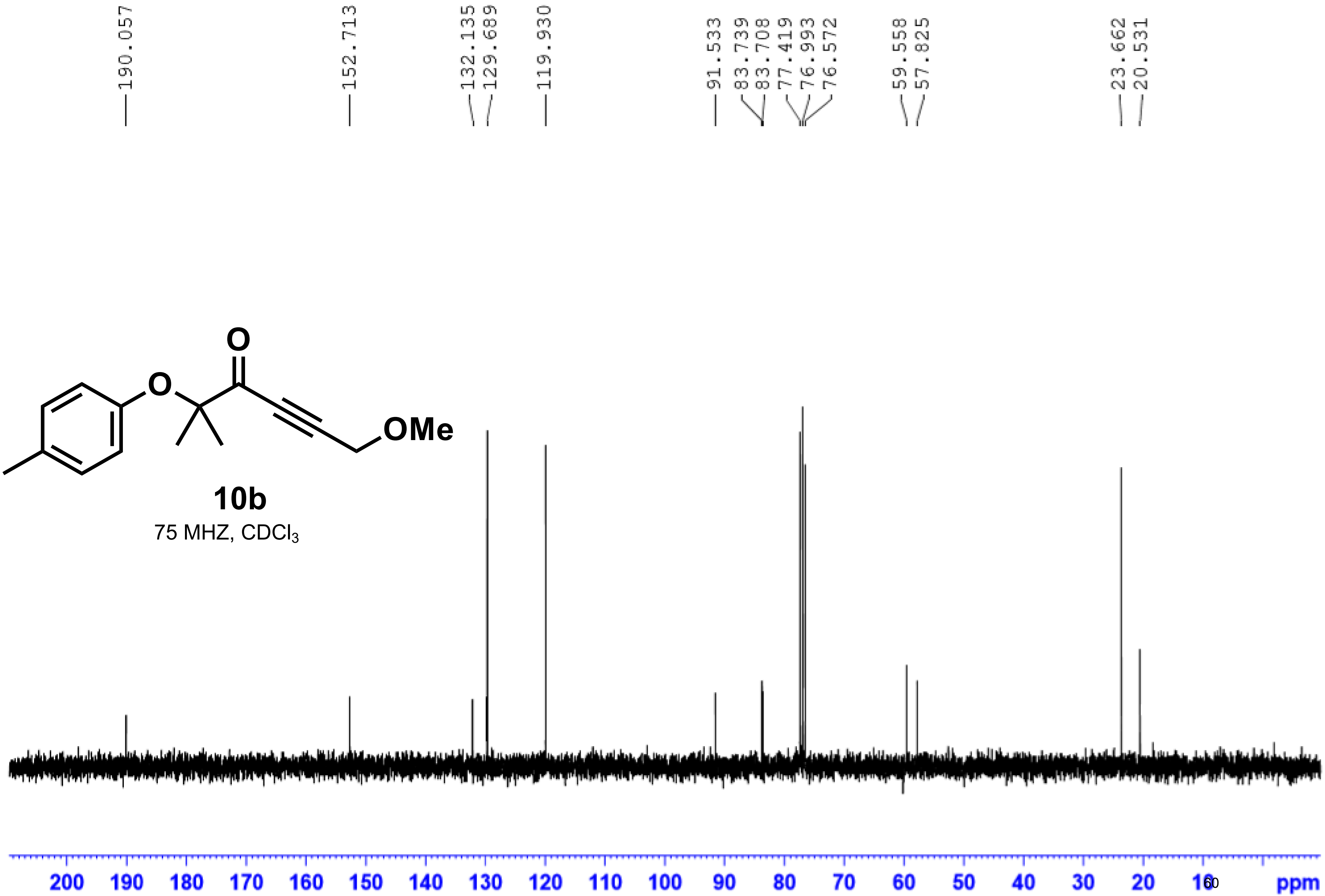

7.301
7.276
7.249
7.063
7.038
7.014
6.916
6.890
4.273
3.340
1.582
O
O
OMe
10a
300 MHz, CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.08
1.00
1.95
2.05
3.09
6.60


189.91
155.09
129.22
122.51
119.66
91.68
83.74
83.66
77.42
77.00
76.58
59.51
57.77
23.72
O
O
OMe
10a
75 MHZ, $CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
ppm

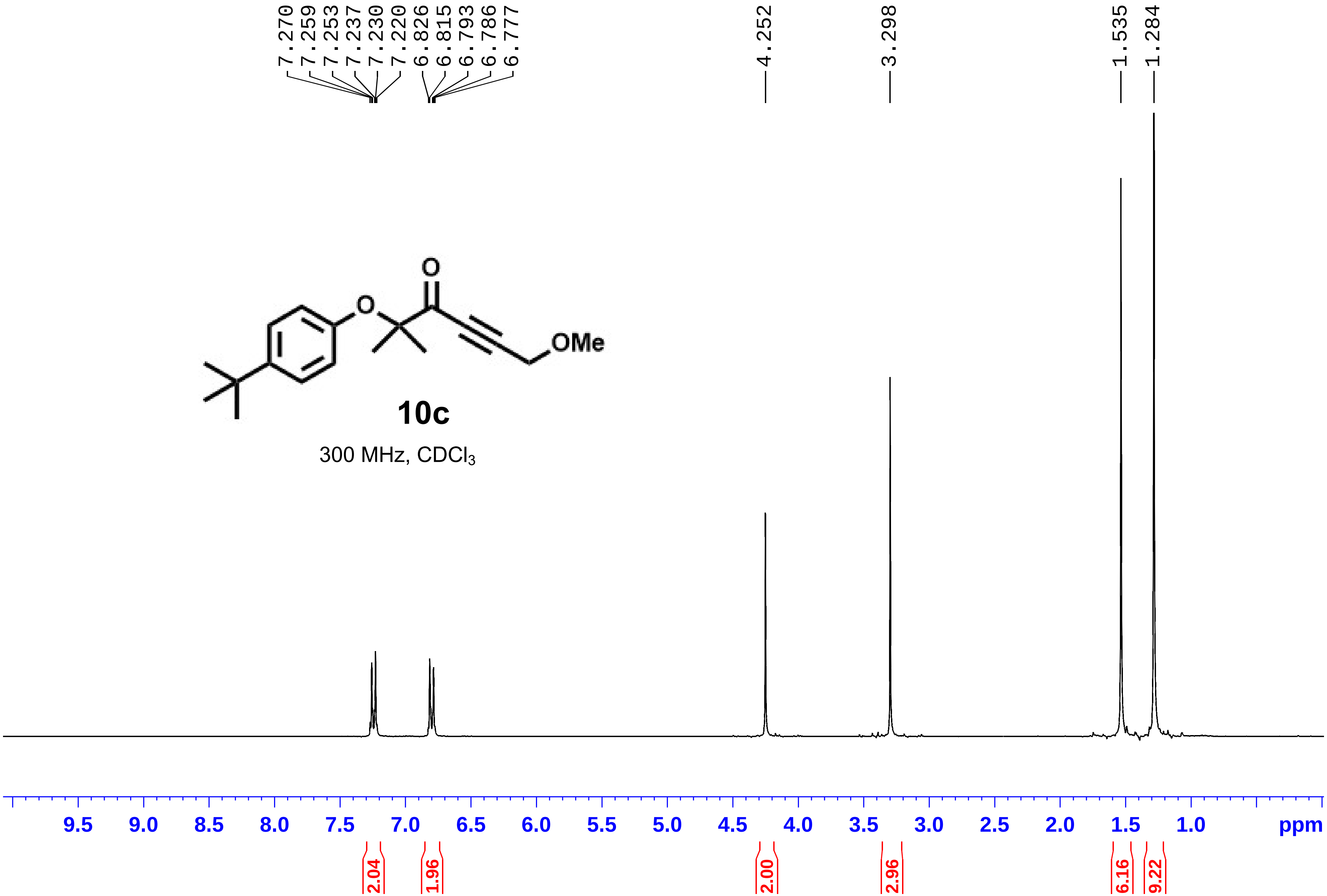

7.361
7.355
7.336
7.330
7.320
7.293
7.267
7.071
7.047
7.022
6.955
6.952
6.930
6.926
6.923
4.709
4.670
4.414
4.376
4.356
4.333
1.637
1.631
1.501
1.479
O
OBn
10aa
300 MHz, CDCl3
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
6.65
0.97
2.17
1.00
2.13
6.02
3.24


190.256
155.178
137.082
129.201
128.291
128.009
127.762
122.238
119.123
95.420
83.687
82.247
77.422
76.999
76.575
70.721
63.918
24.147
23.352
20.957
OBn
10aa
75 MHz, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.270
7.057
7.030
6.808
6.798
6.792
6.777
6.770
6.760
4.268
3.346
2.285
1.523
O
OMe
10b
300 MHz, CDCl3
9.5
9.0
8.5
8.0
7.5
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
ppm
2.02
1.98
2.00
2.99
3.08
6.31

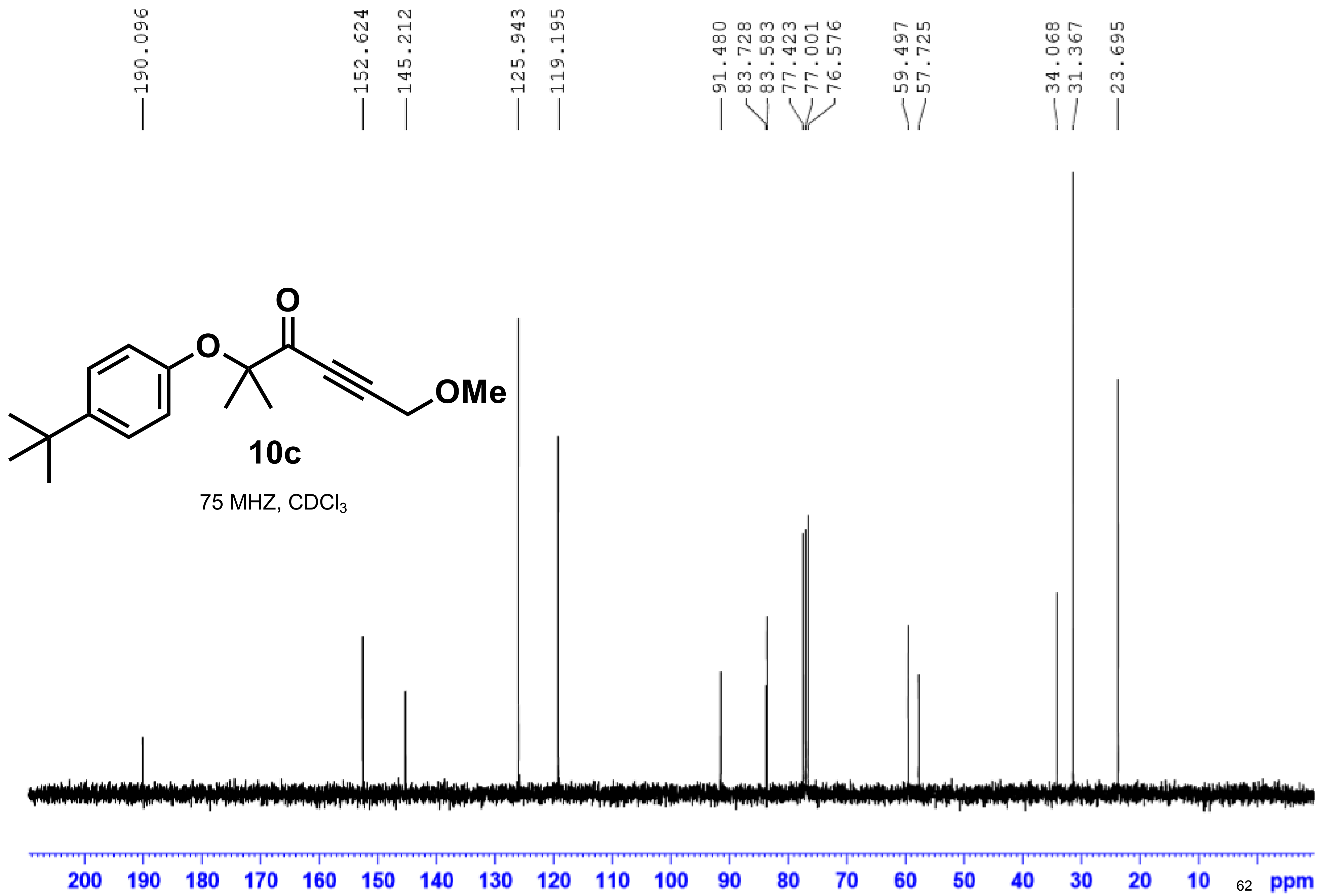


190.057
152.713
132.135
129.689
119.930
91.533
83.739
83.708
77.419
76.993
76.572
59.558
57.825
23.662
20.531
O
OMe
10b
75 MHZ, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

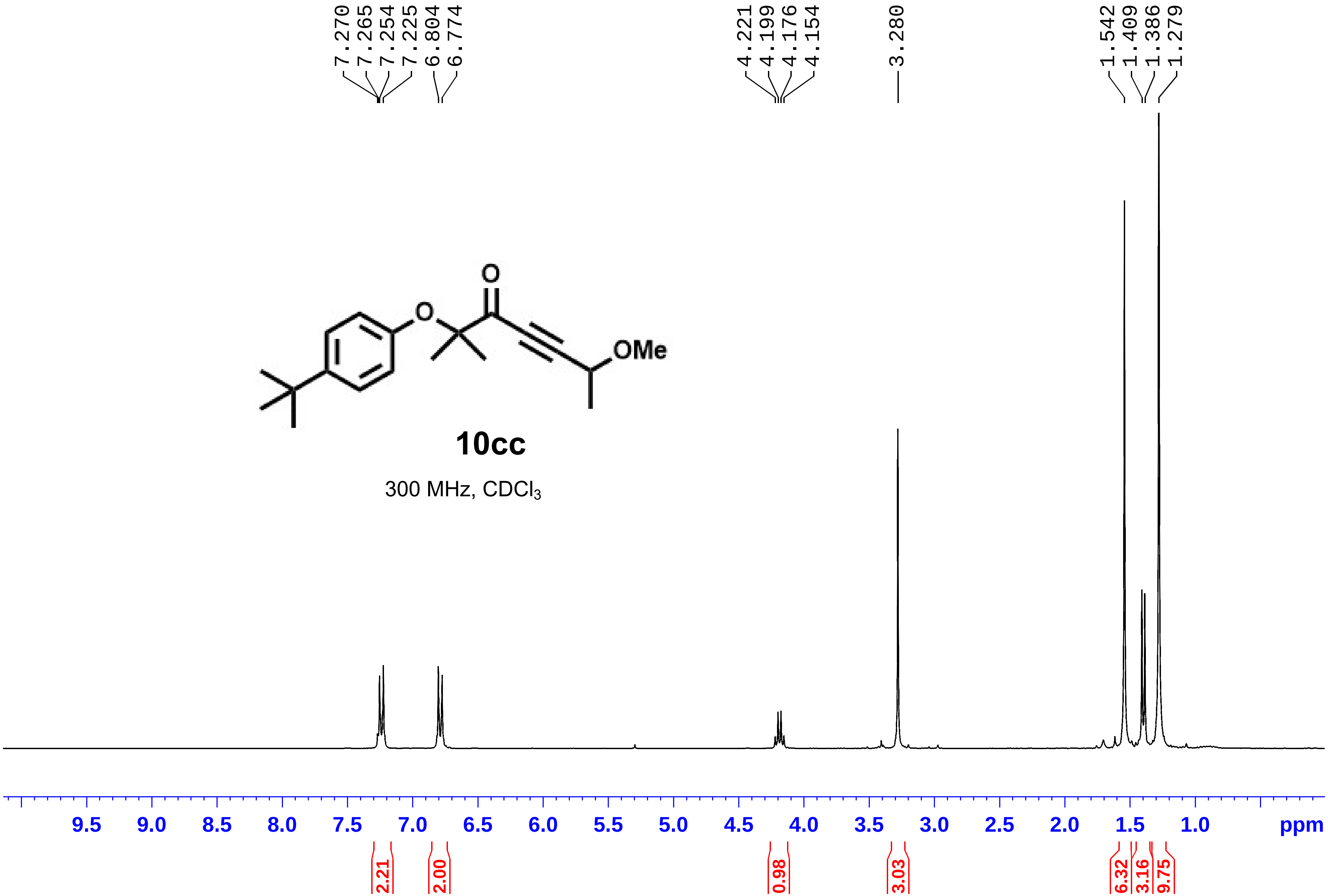


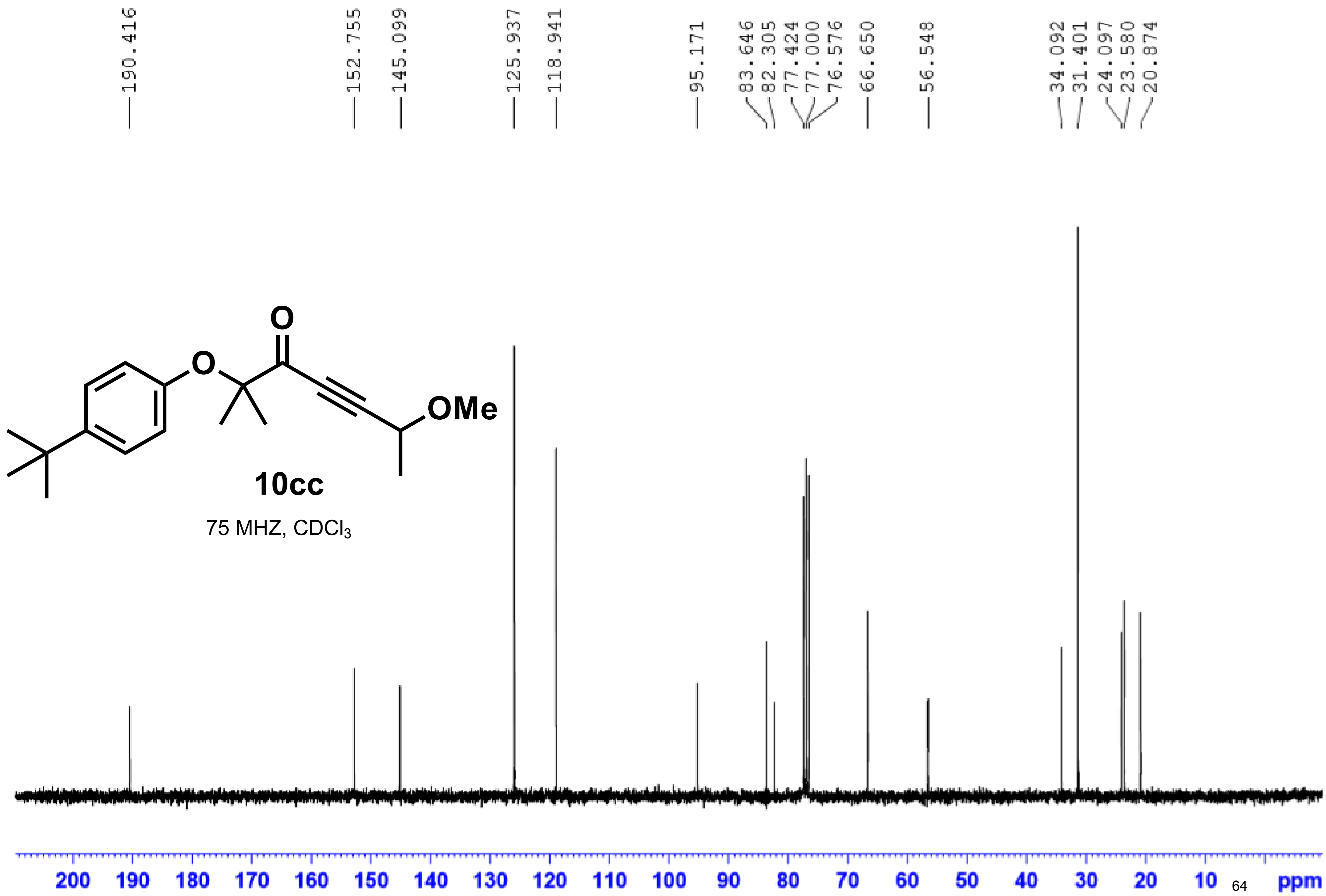
10c

300 MHz, $CDCl_3$

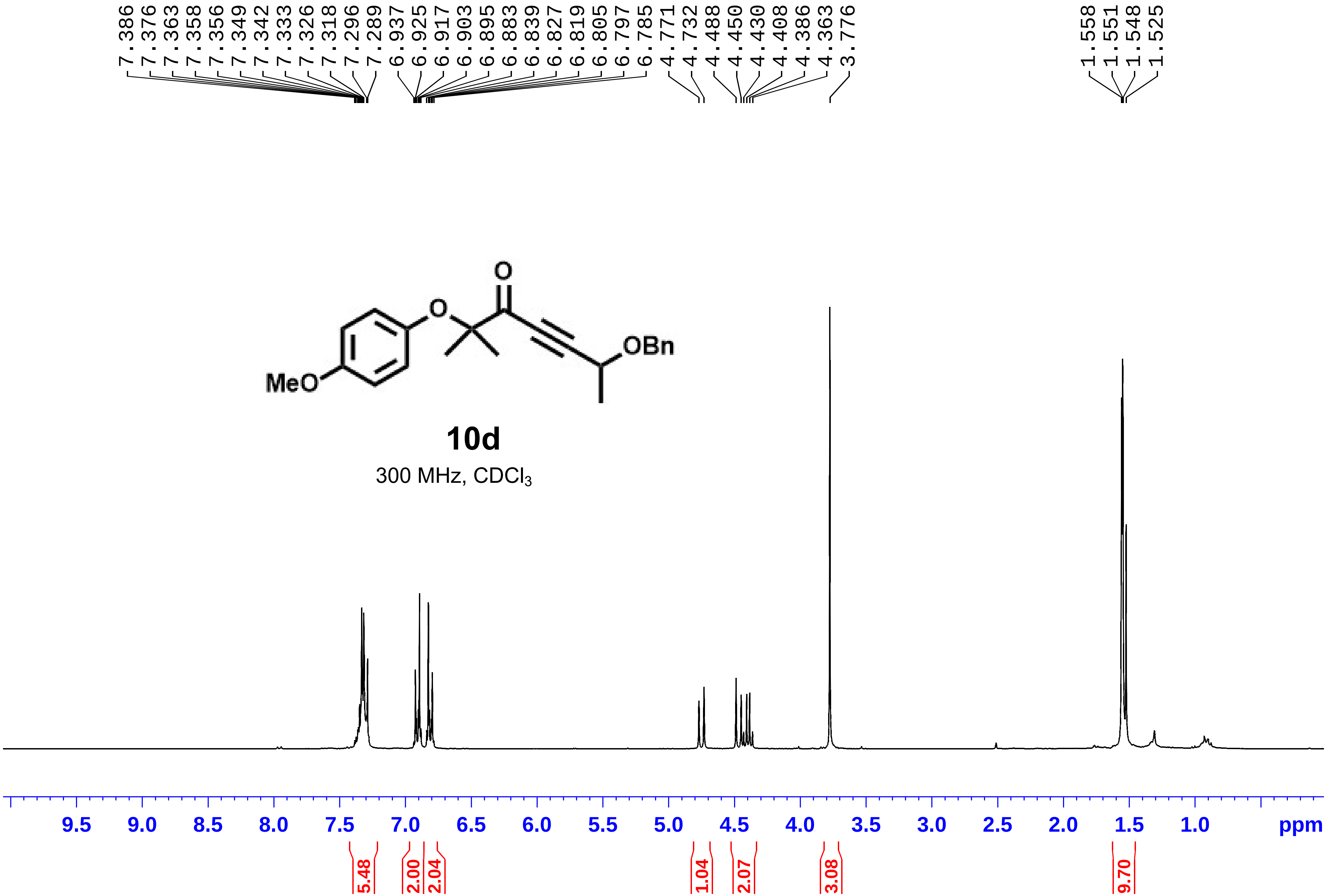


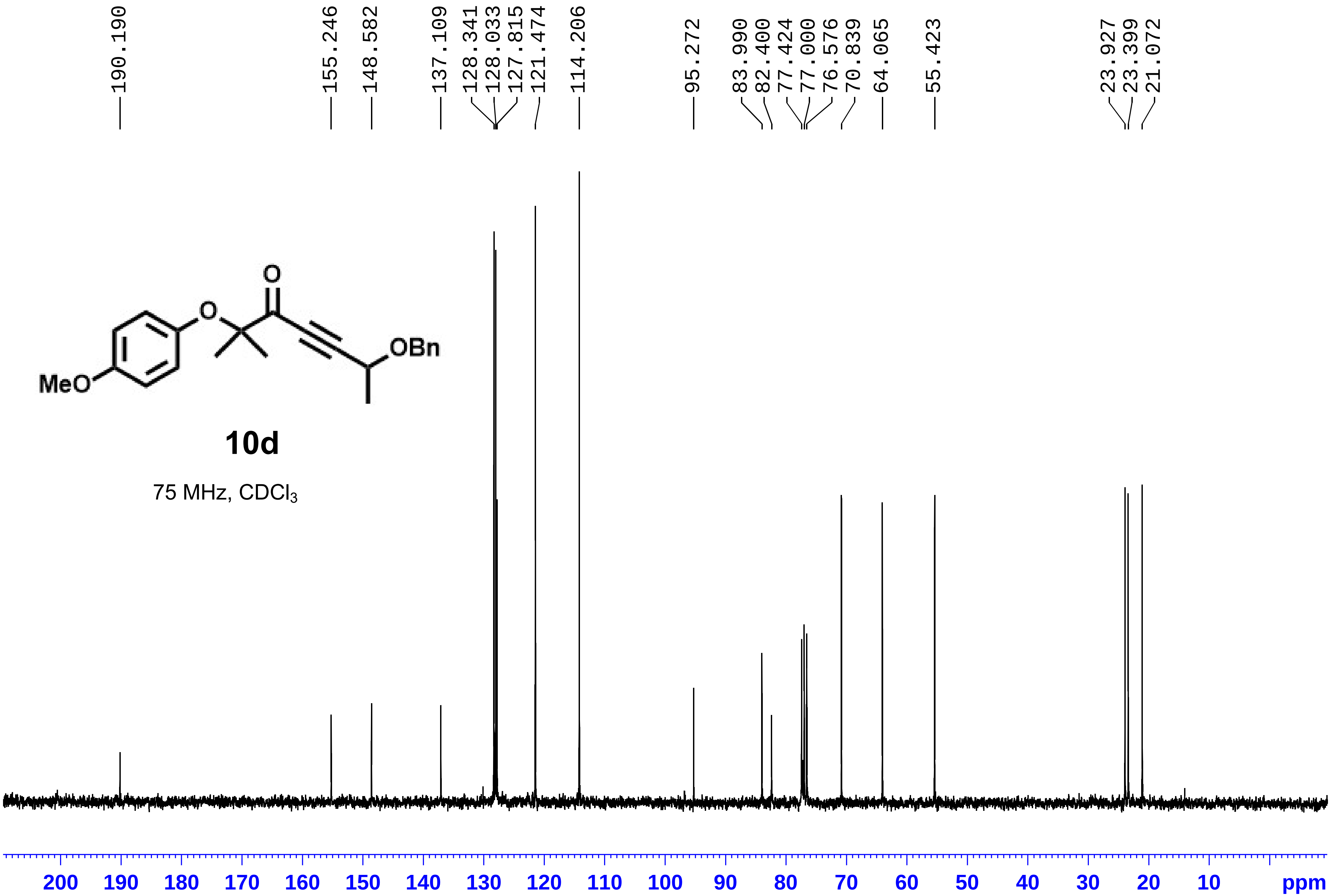
190.096
152.624
145.212
125.943
119.195
91.480
83.728
83.583
77.423
77.001
76.576
59.497
57.725
34.068
31.367
23.695
O
O
OMe
10c
75 MHZ, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

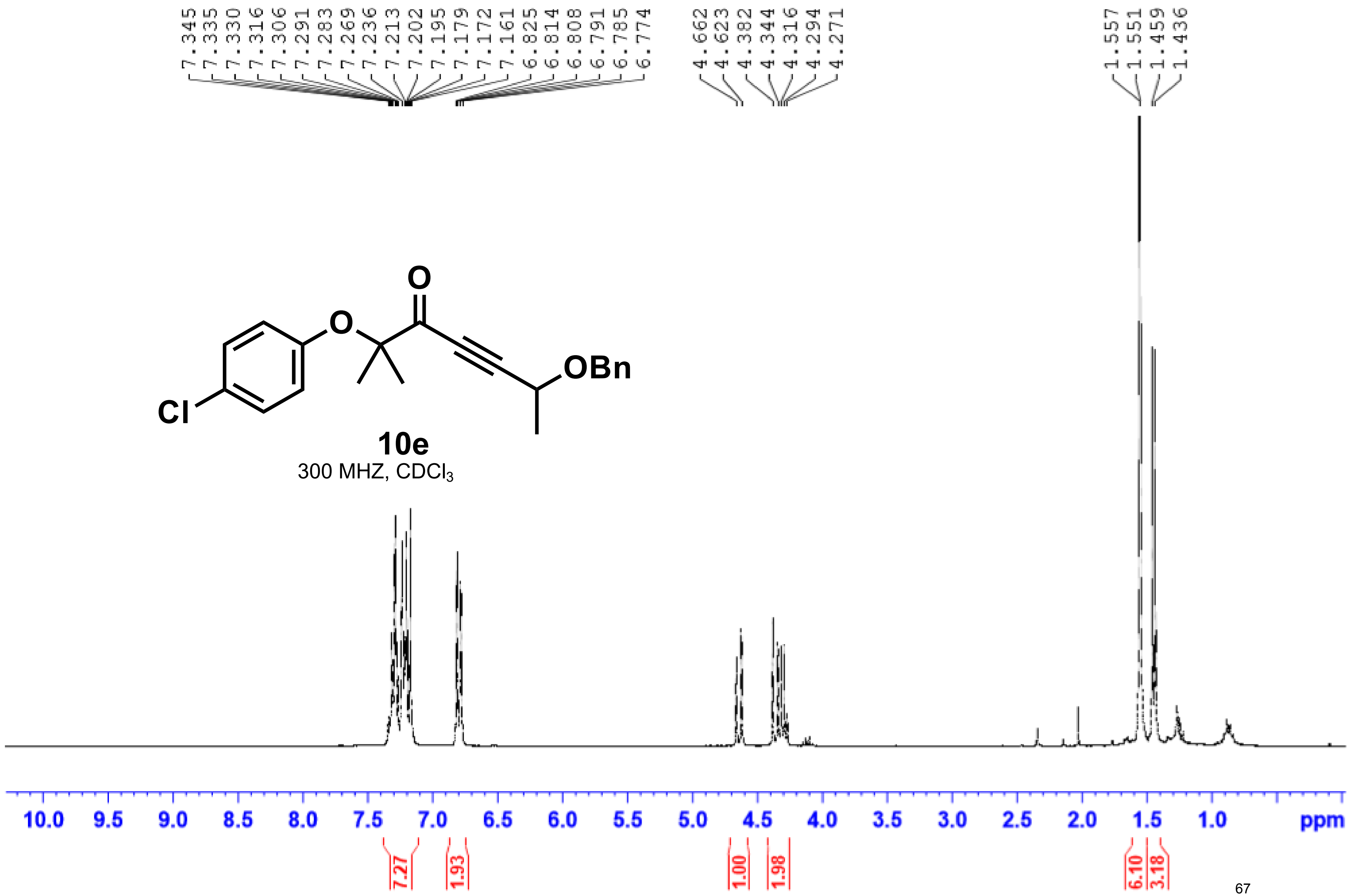

7.270
7.265
7.254
7.225
6.804
6.774
4.221
4.199
4.176
4.154
3.280
1.542
1.409
1.386
1.279
O
O
OMe
10cc
300 MHz, CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.21
2.00
0.98
3.03
6.32
3.16
9.75



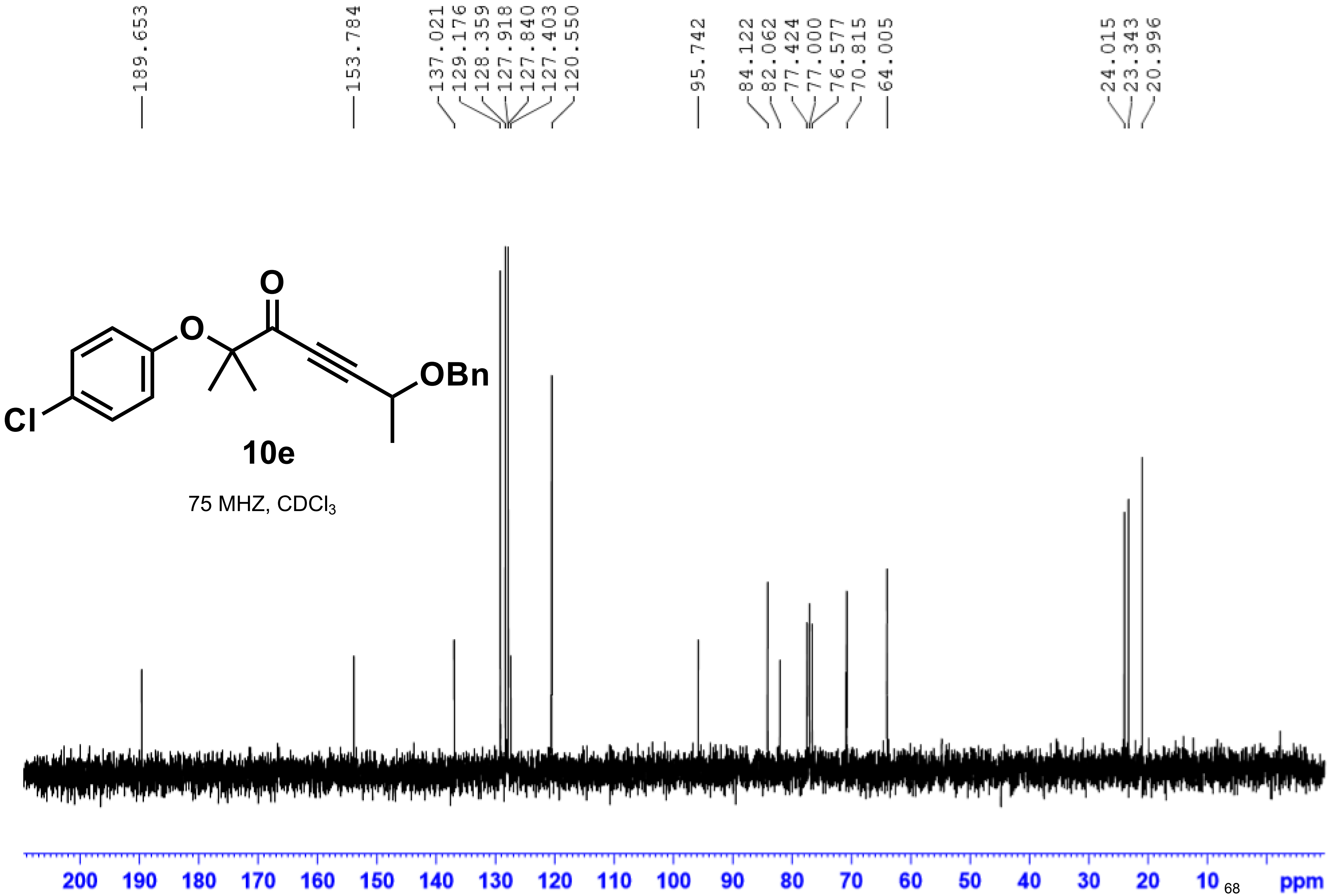
190.416
152.755
145.099
125.937
118.941
95.171
83.646
82.305
77.424
77.000
76.576
66.650
56.548
34.092
31.401
24.097
23.580
20.874
O
O
OMe
10cc
75 MHZ, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

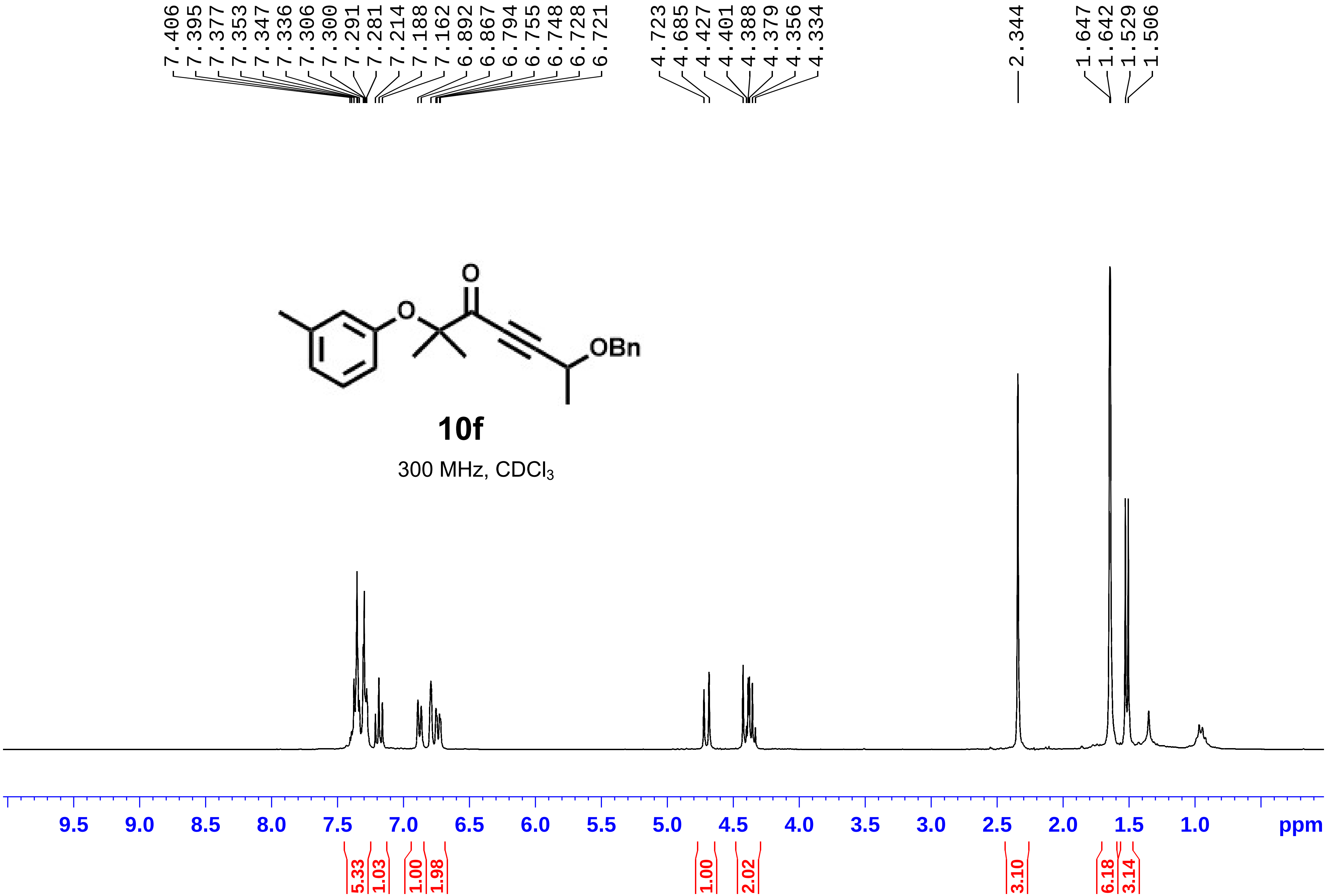

7.386
7.376
7.363
7.358
7.356
7.349
7.342
7.333
7.326
7.318
7.296
7.289
6.937
6.925
6.917
6.903
6.895
6.883
6.839
6.827
6.819
6.805
6.797
6.785
4.771
4.732
4.488
4.450
4.430
4.408
4.386
4.363
3.776
1.558
1.551
1.548
1.525
MeO
O
O
OBn
10d
300 MHz, $CDCl_3$
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
5.48
2.00
2.04
1.04
2.07
3.08
9.70

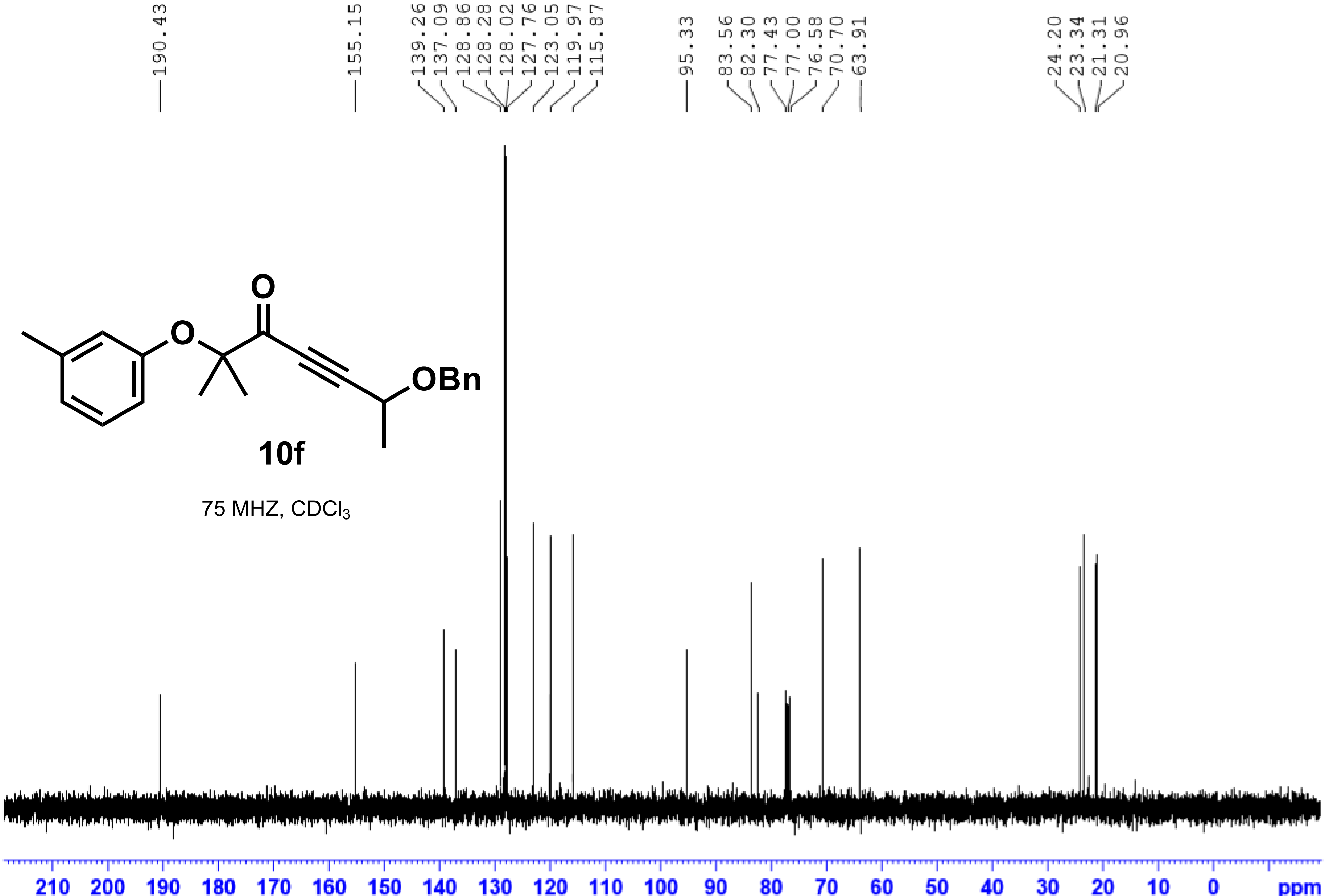

190.190
155.246
148.582
137.109
128.341
128.033
127.815
121.474
114.206
95.272
83.990
82.400
77.424
77.000
76.576
70.839
64.065
55.423
23.927
23.399
21.072
O
O
OBn
MeO
10d
75 MHz, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

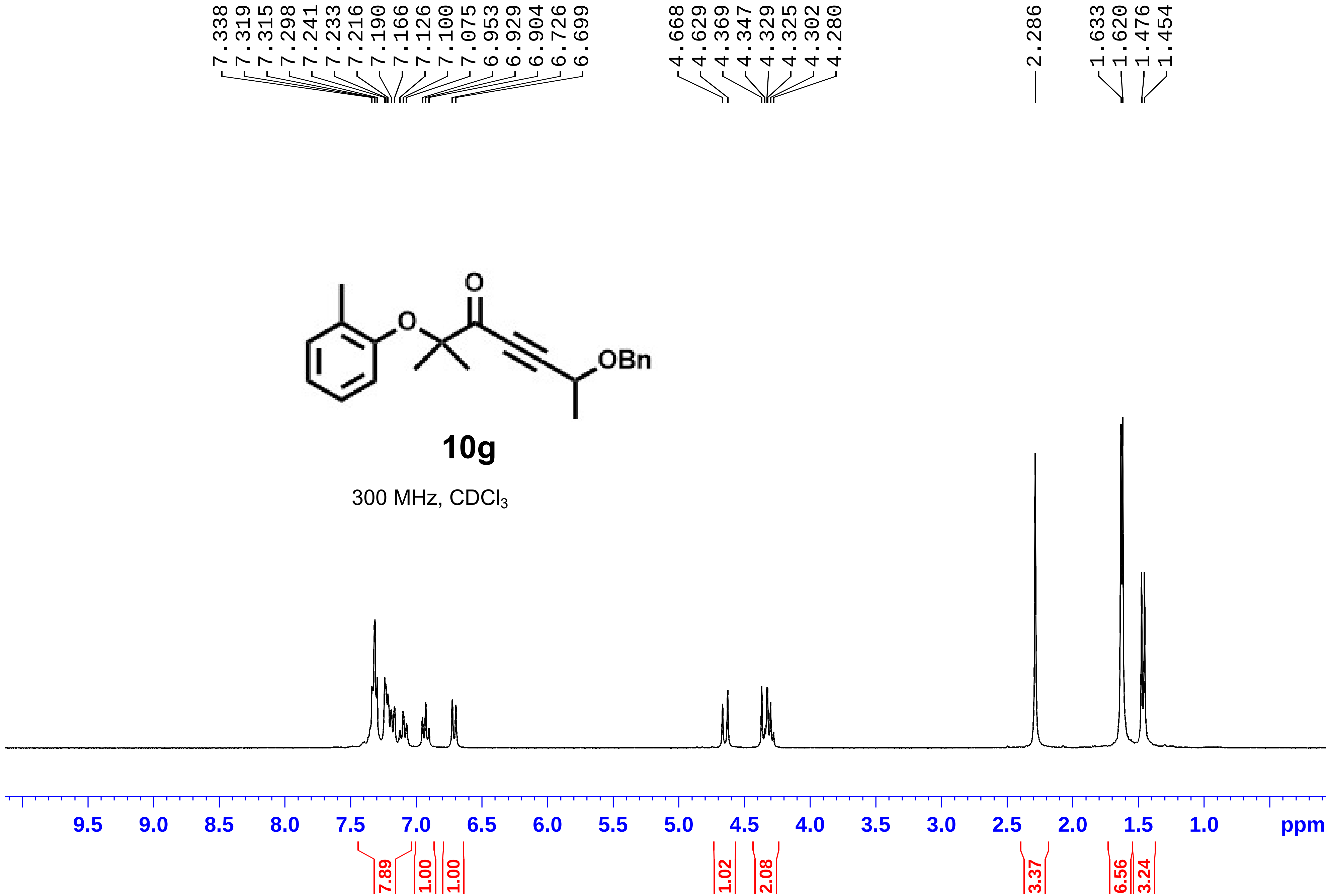


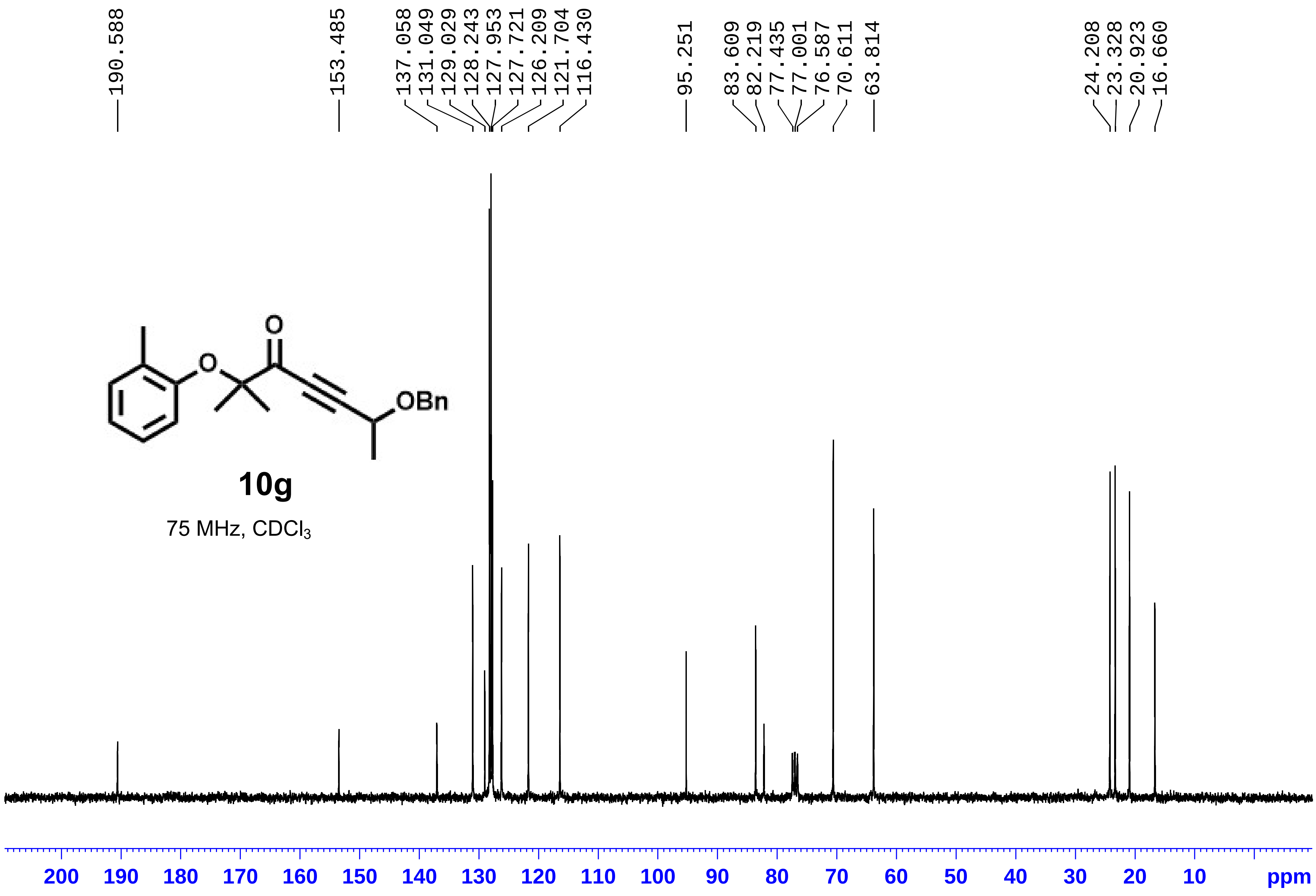
7.345 7.335 7.330 7.316 7.306 7.291 7.283 7.269 7.236 7.213 7.202 7.195 7.179 7.172 7.161 6.825 6.814 6.808 6.791 6.785 6.774
4.662 4.623 4.382 4.344 4.316 4.294 4.271
1.557 1.551 1.459 1.436
O
O
OBn
Cl
10e
300 MHZ, $CDCl_3$
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
7.27 1.93 1.00 1.98 6.10 3.18

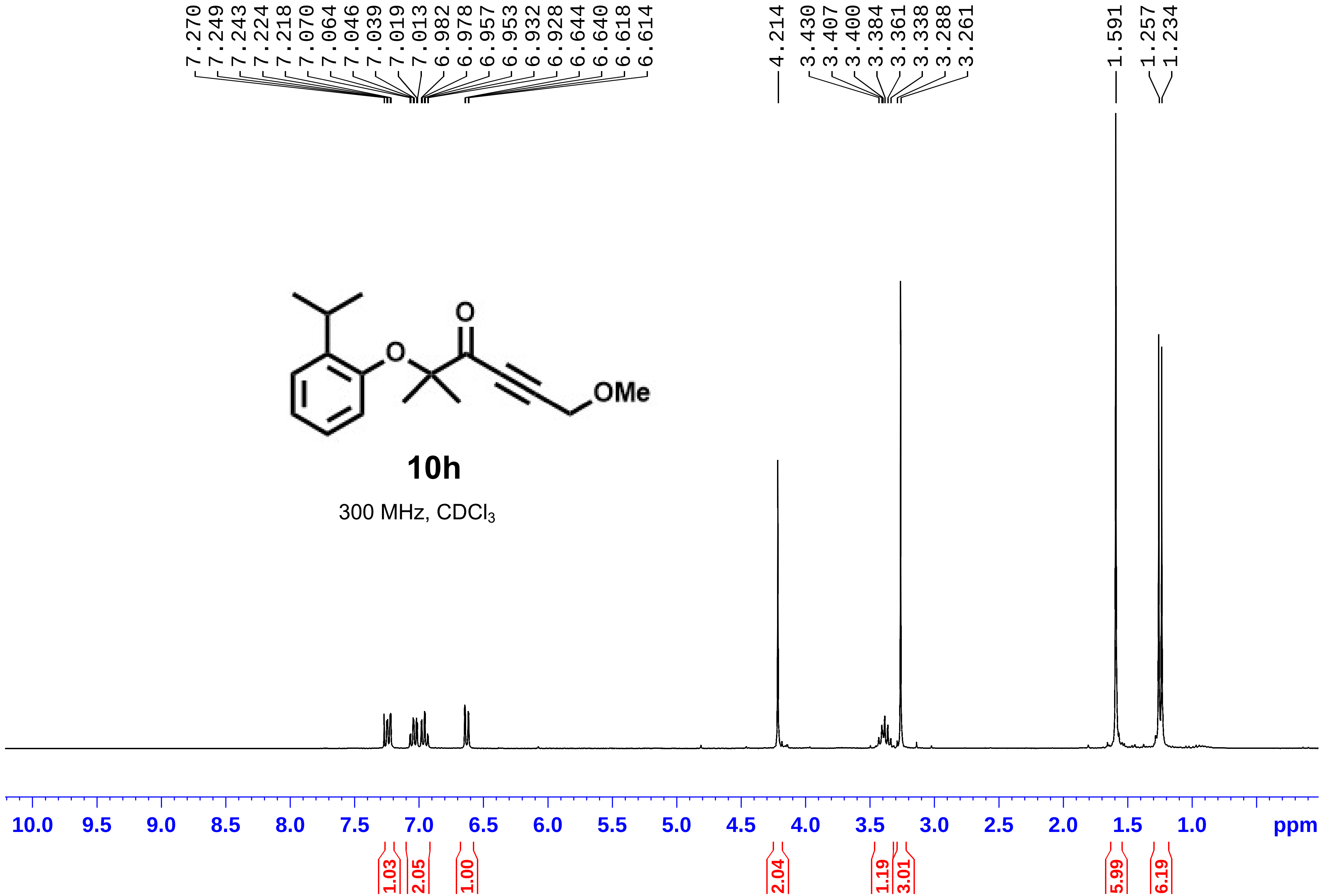

189.653
153.784
137.021
129.176
128.359
127.918
127.840
127.403
120.550
95.742
84.122
82.062
77.424
77.000
76.577
70.815
64.005
24.015
23.343
20.996
O
O
OBn
Cl
10e
75 MHZ, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

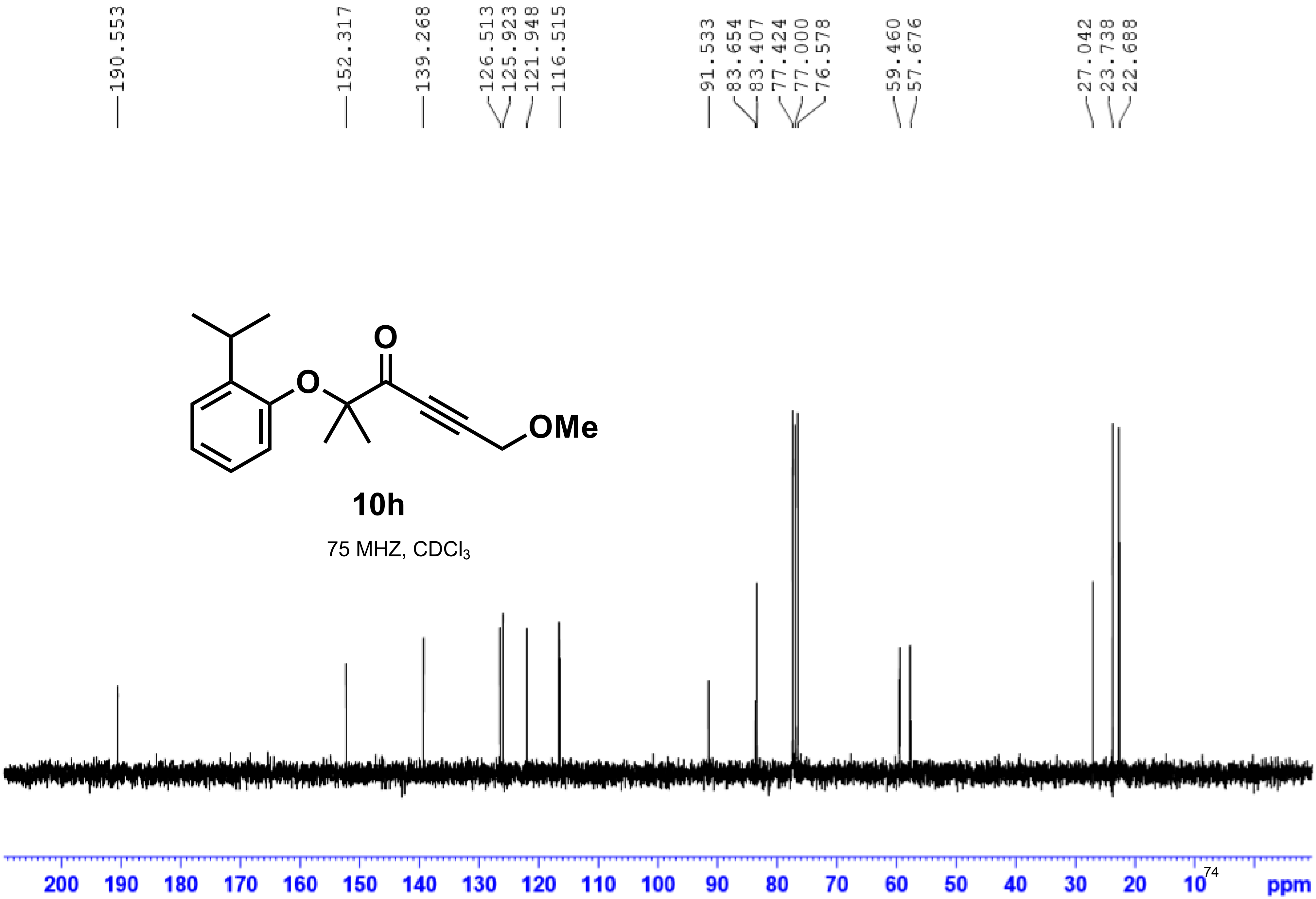

7.406 7.395 7.377 7.353 7.347 7.336 7.306 7.300 7.291 7.281 7.214 7.188 7.162 6.892 6.867 6.794 6.755 6.748 6.728 6.721
4.723 4.685 4.427 4.401 4.388 4.379 4.356 4.334
2.344
1.647 1.642 1.529 1.506
OBn
10f
300 MHz, CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
5.33 1.03 1.00 1.98 1.00 2.02 3.10 6.18 3.14

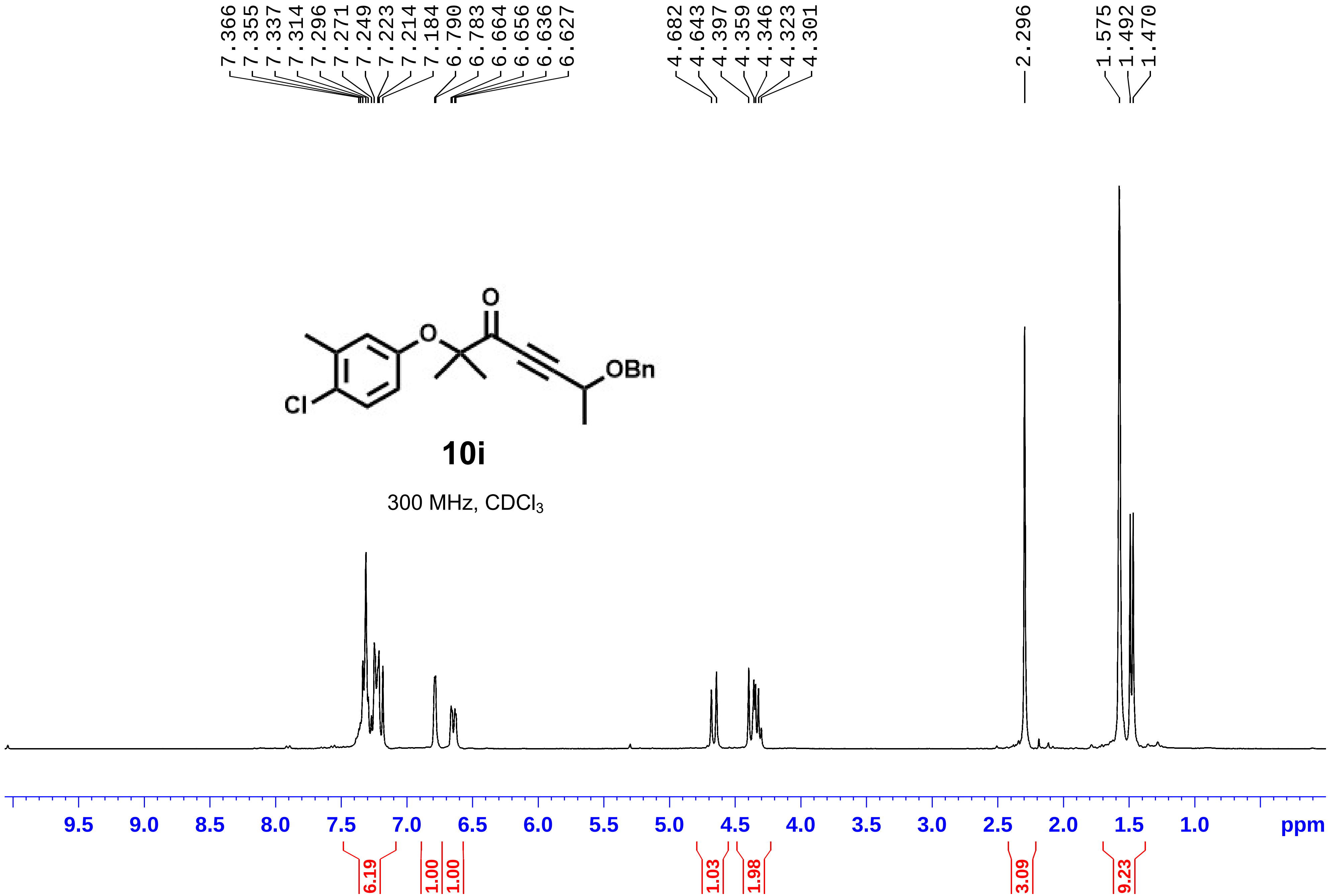

190.43
155.15
139.26
137.09
128.86
128.28
128.02
127.76
123.05
119.97
115.87
95.33
83.56
82.30
77.43
77.00
76.58
70.70
63.91
24.20
23.34
21.31
20.96
O
O
OBn
10f
75 MHZ, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

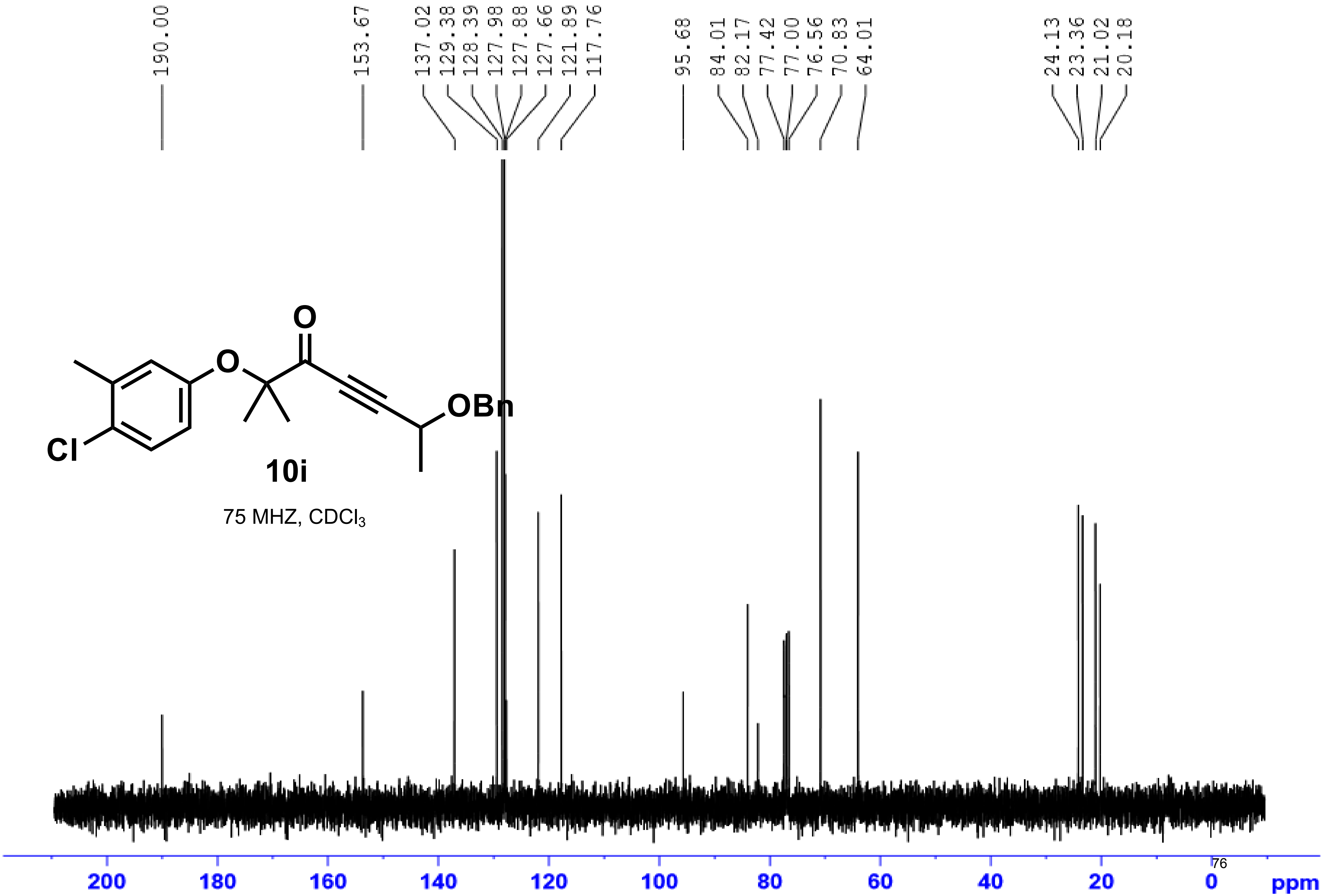

7.338
7.319
7.315
7.298
7.241
7.233
7.216
7.190
7.166
7.126
7.100
7.075
6.953
6.929
6.904
6.726
6.699
4.668
4.629
4.369
4.347
4.329
4.325
4.302
4.280
2.286
1.633
1.620
1.476
1.454
OBn
10g
300 MHz, CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
7.89
1.00
1.00
1.02
2.08
3.37
6.56
3.24

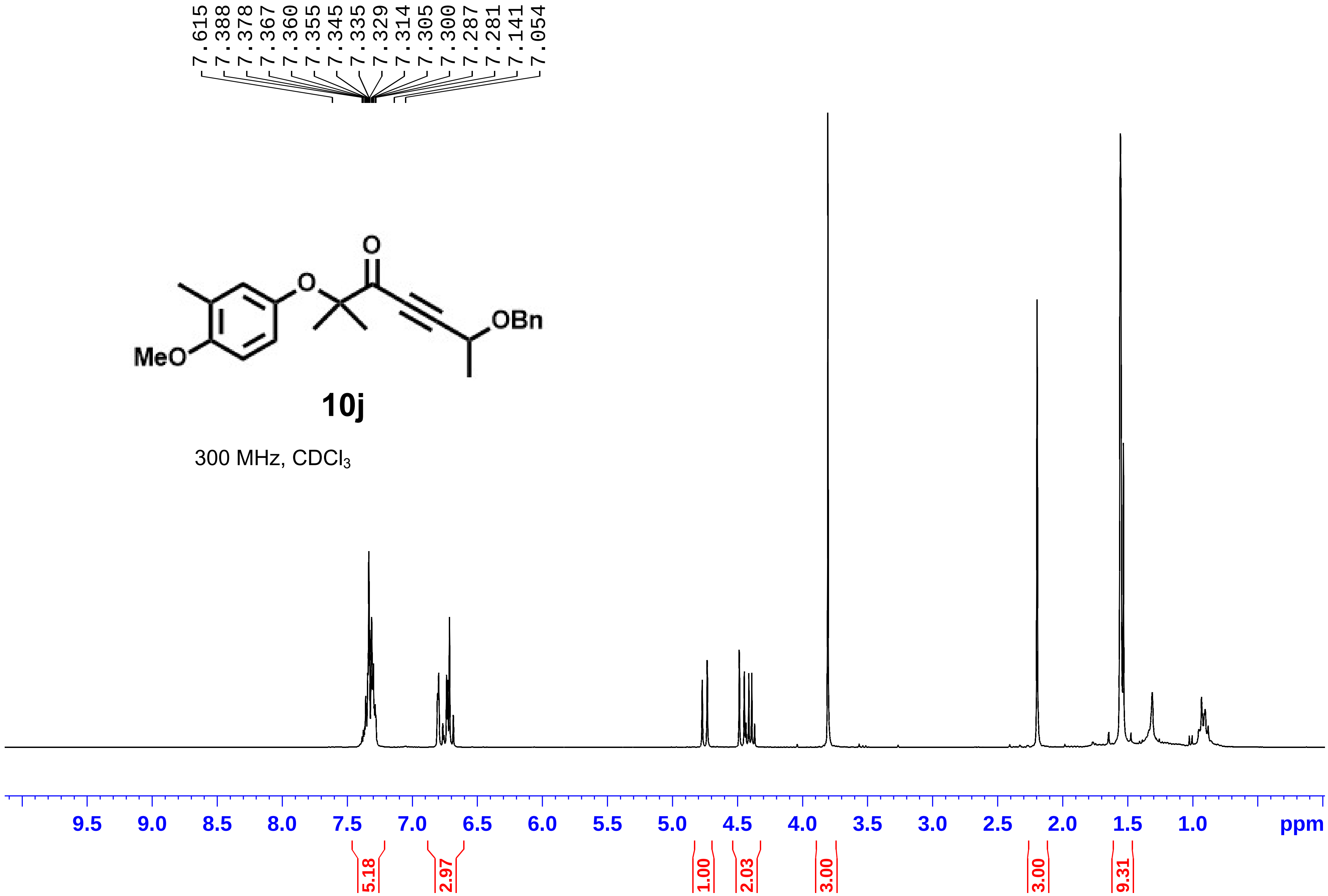

190.588
153.485
137.058
131.049
129.029
128.243
127.953
127.721
126.209
121.704
116.430
95.251
83.609
82.219
77.435
77.001
76.587
70.611
63.814
24.208
23.328
20.923
16.660
O
O
OBn
10g
75 MHz, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.270
7.249
7.243
7.224
7.218
7.070
7.064
7.046
7.039
7.019
7.013
6.982
6.978
6.957
6.953
6.932
6.928
6.644
6.640
6.618
6.614
4.214
3.430
3.407
3.400
3.384
3.361
3.338
3.288
3.261
1.591
1.257
1.234
O
O
OMe
10h
300 MHz, $CDCl_3$
10.0 9.5 9.0 8.5 8.0 7.5 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 ppm
1.03
2.05
1.00
2.04
1.19
3.01
5.99
6.19

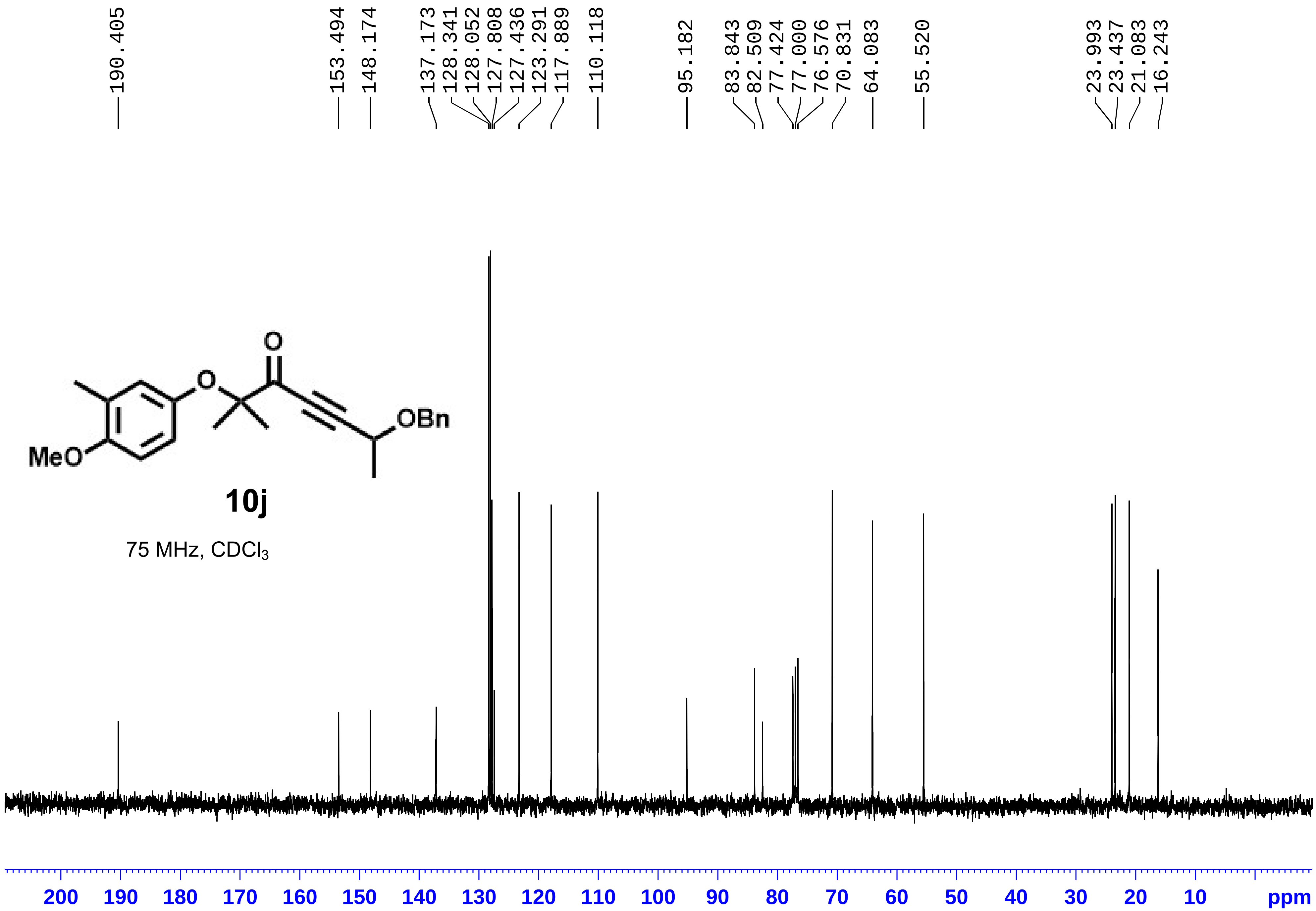

190.553
152.317
139.268
126.513
125.923
121.948
116.515
91.533
83.654
83.407
77.424
77.000
76.578
59.460
57.676
27.042
23.738
22.688
O
O
OMe
10h
75 MHZ, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

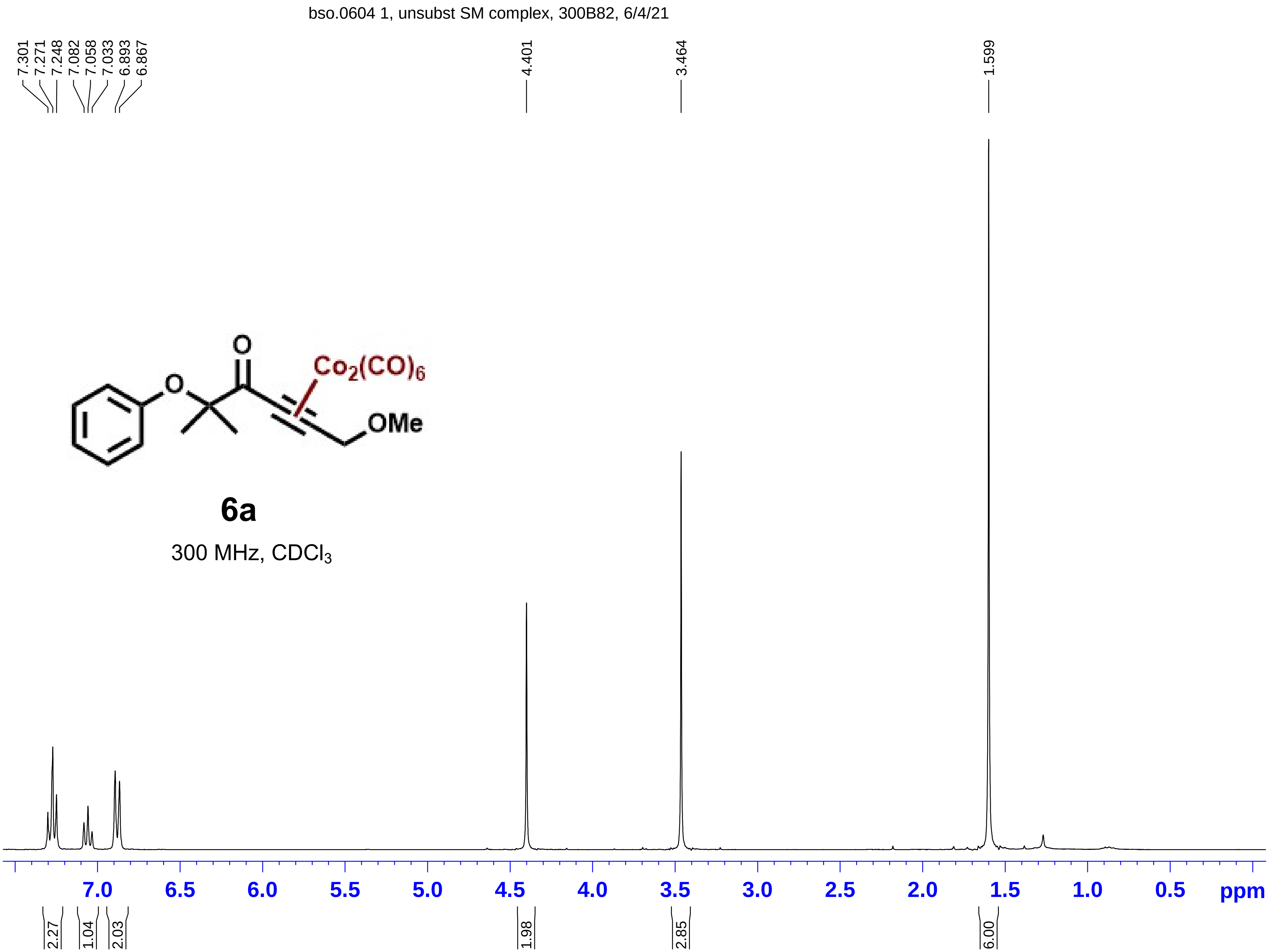

7.366
7.355
7.337
7.314
7.296
7.271
7.249
7.223
7.214
7.184
6.790
6.783
6.664
6.656
6.636
6.627
4.682
4.643
4.397
4.359
4.346
4.323
4.301
2.296
1.575
1.492
1.470
O
O
OBn
Cl
10i
300 MHz, $CDCl_3$
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
6.19
1.00
1.00
1.03
1.98
3.09
9.23


190.00
153.67
137.02
129.38
128.39
127.98
127.88
127.66
121.89
117.76
95.68
84.01
82.17
77.42
77.00
76.56
70.83
64.01
24.13
23.36
21.02
20.18
O
O
OBn
Cl
10i
75 MHZ, CDCl3
200
180
160
140
120
100
80
60
40
20
0
ppm

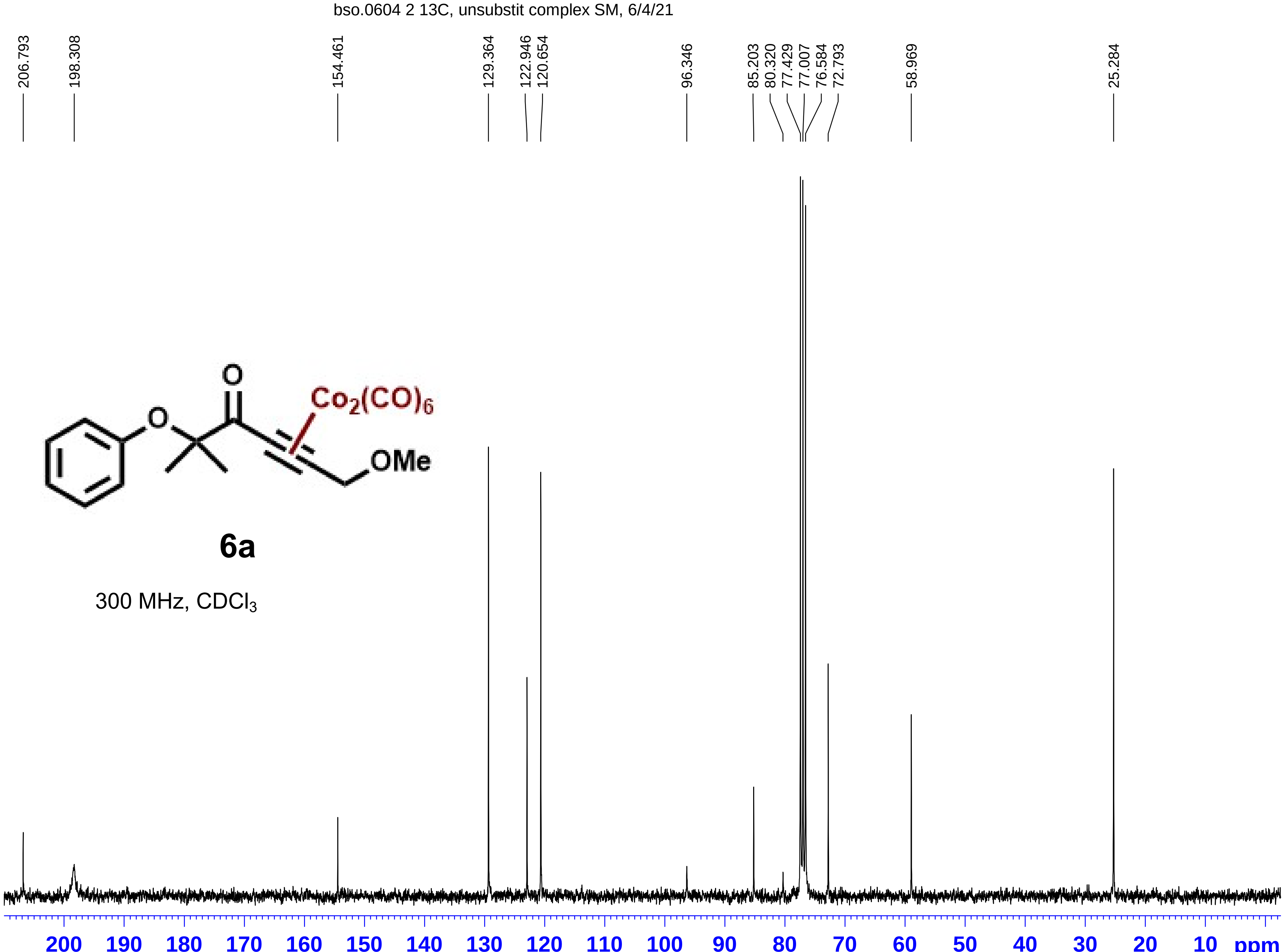


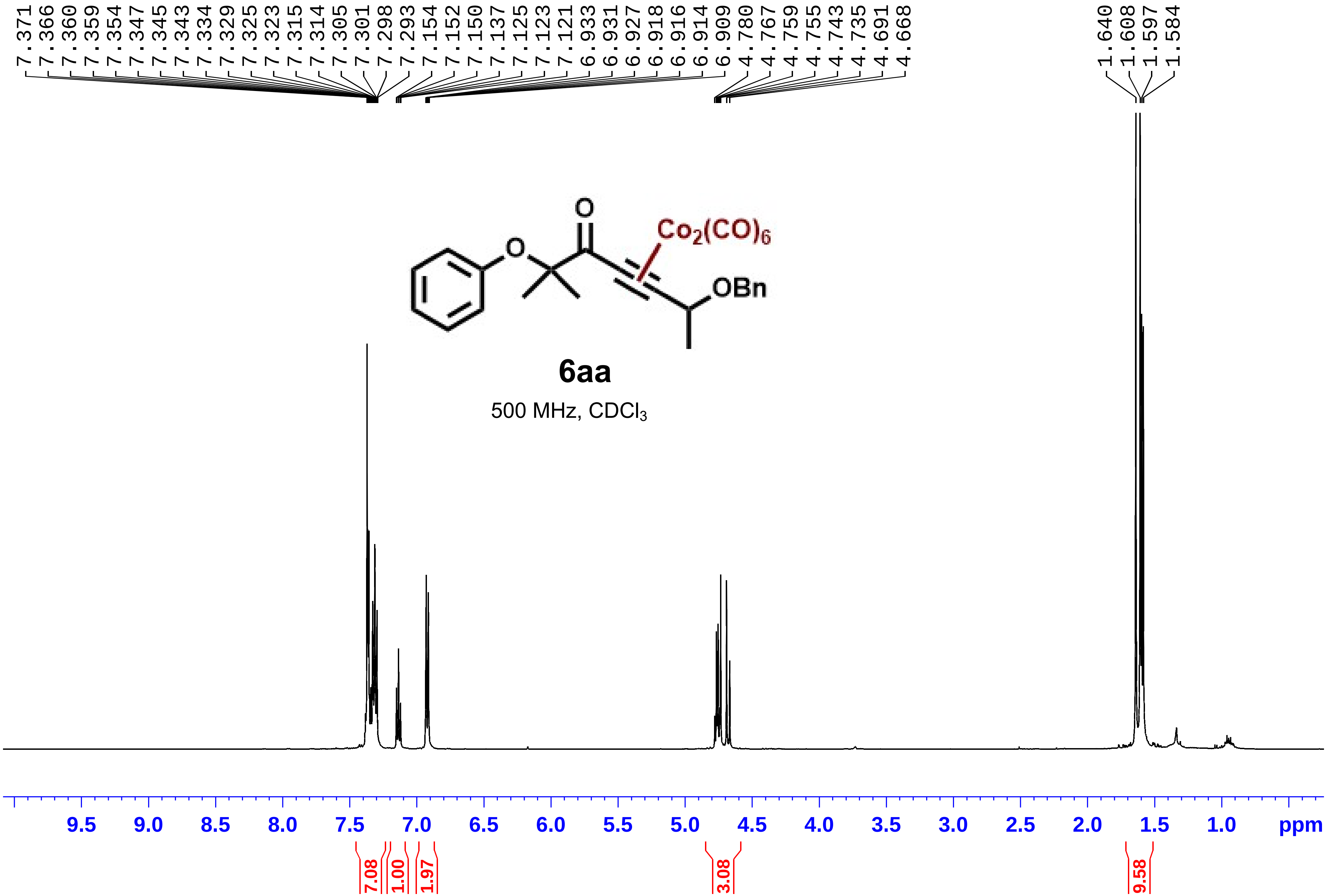
7.615
7.388
7.378
7.367
7.360
7.355
7.345
7.335
7.329
7.314
7.305
7.300
7.287
7.281
7.141
7.054
MeO
O
O
OBn
10j
300 MHz, $CDCl_3$
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
5.18
2.97
1.00
2.03
3.00
3.00
9.31

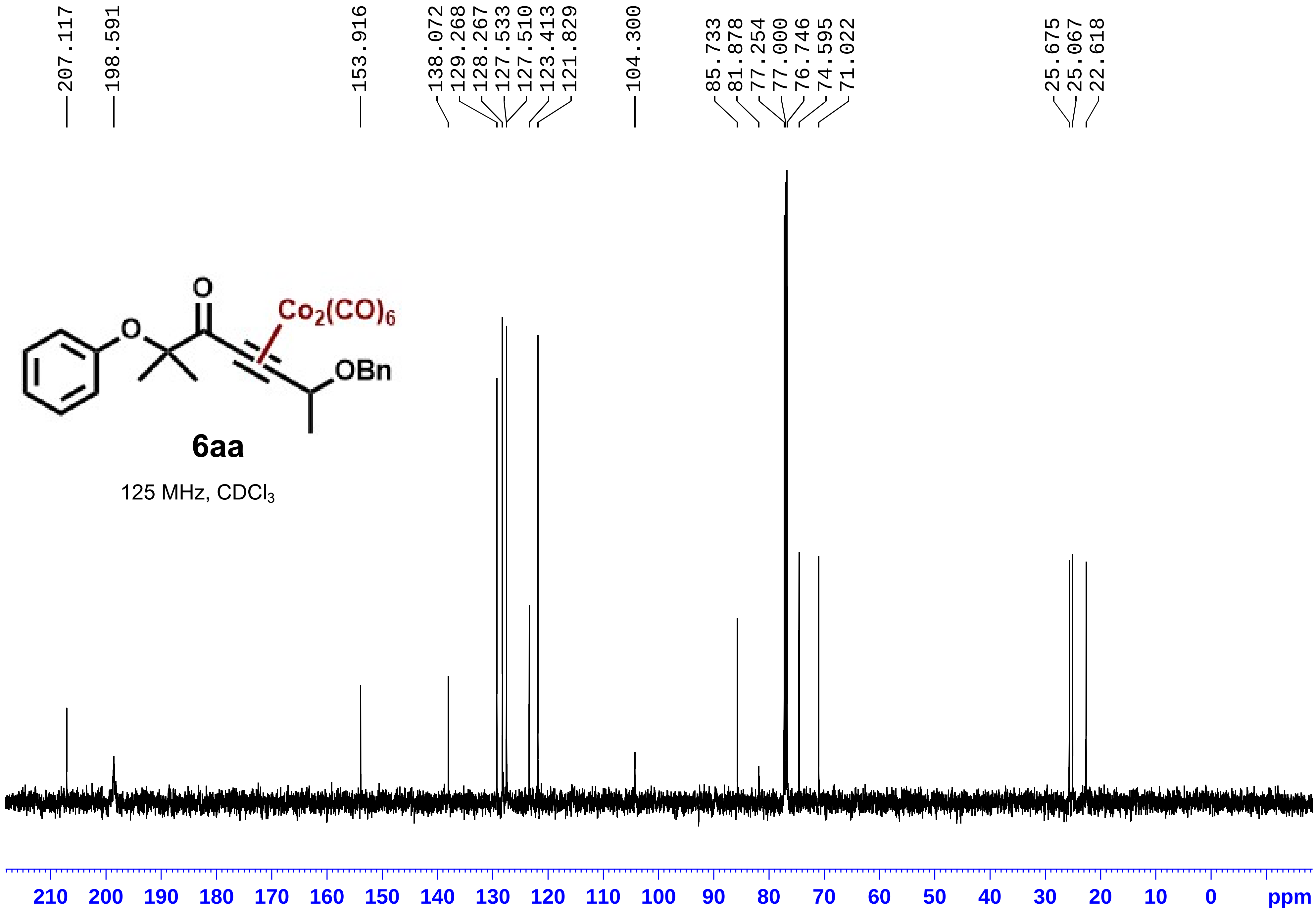

190.405
153.494
148.174
137.173
128.341
128.052
127.808
127.436
123.291
117.889
110.118
95.182
83.843
82.509
77.424
77.000
76.576
70.831
64.083
55.520
23.993
23.437
21.083
16.243
O
OBn
MeO
10j
75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

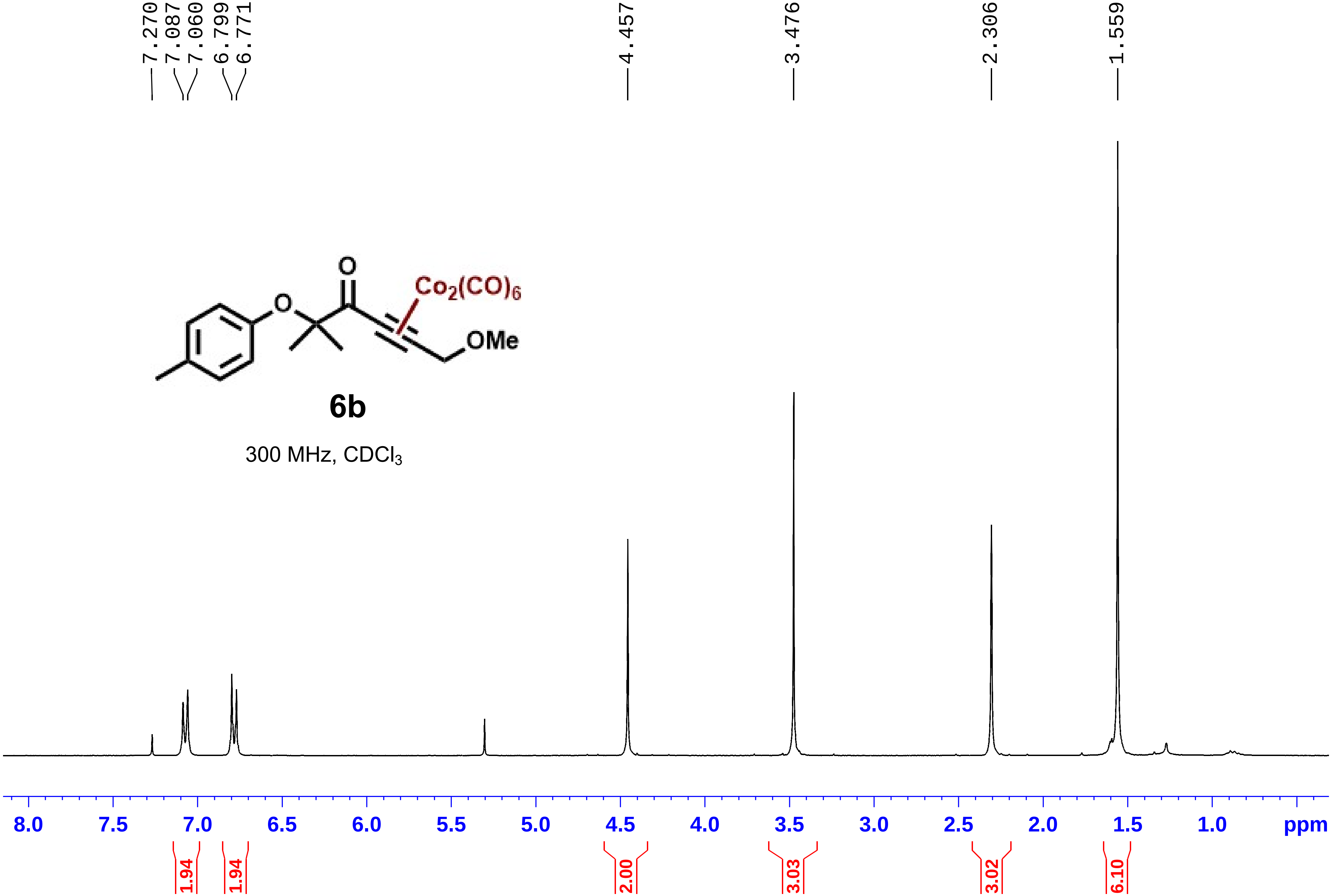


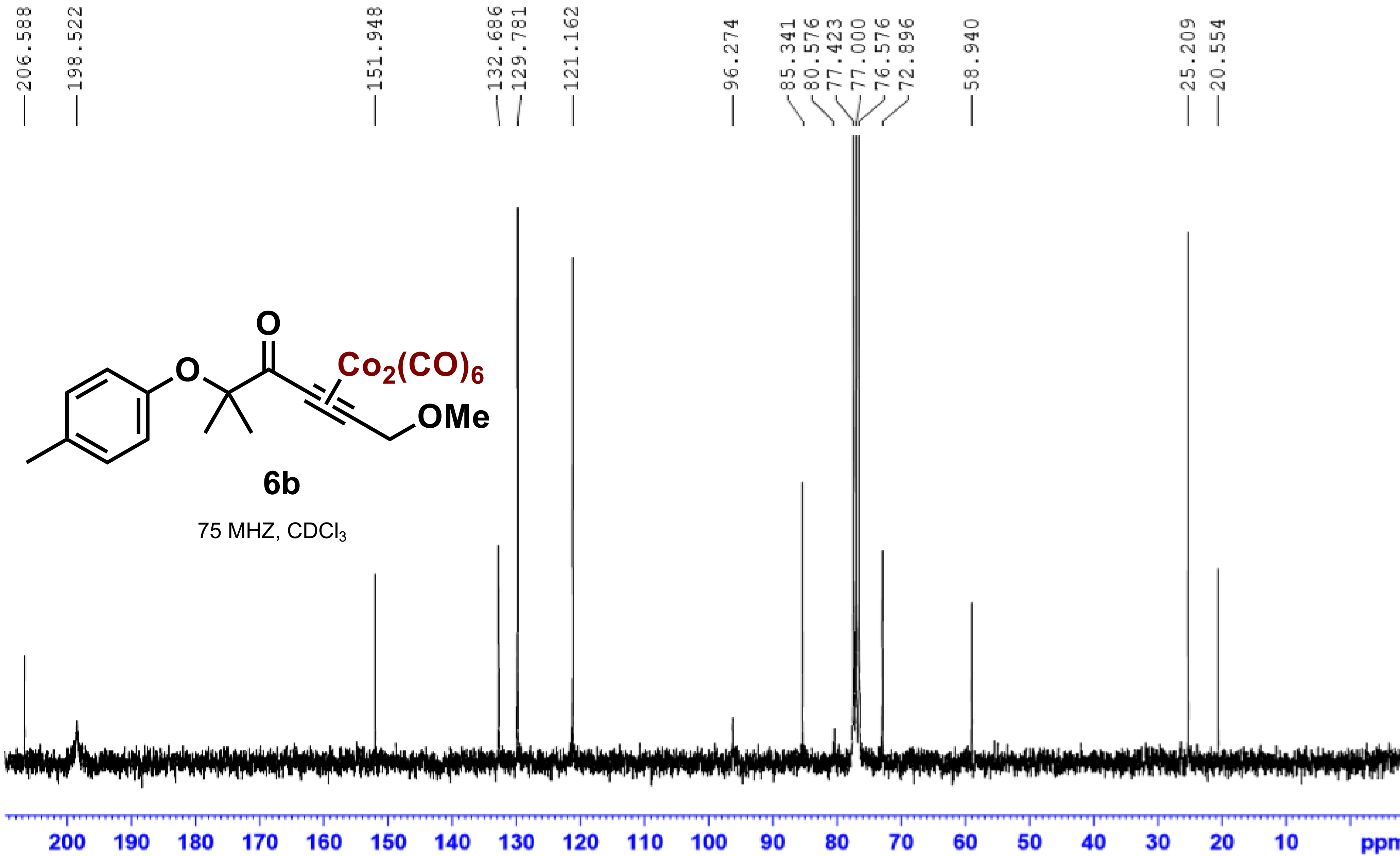
bso.0604 1, unsubst SM complex, 300B82, 6/4/21
7.301
7.271
7.248
7.082
7.058
7.033
6.893
6.867
4.401
3.464
1.599
Co2(CO)6
OMe
O
6a
300 MHz, CDCl3
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.27
1.04
2.03
1.98
2.85
6.00


bso.0604 2 13C, unsubstit complex SM, 6/4/21
206.793
198.308
154.461
129.364
122.946
120.654
96.346
85.203
80.320
77.429
77.007
76.584
72.793
58.969
25.284
O
O
$Co_2(CO)_6$
OMe
6a
300 MHz, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

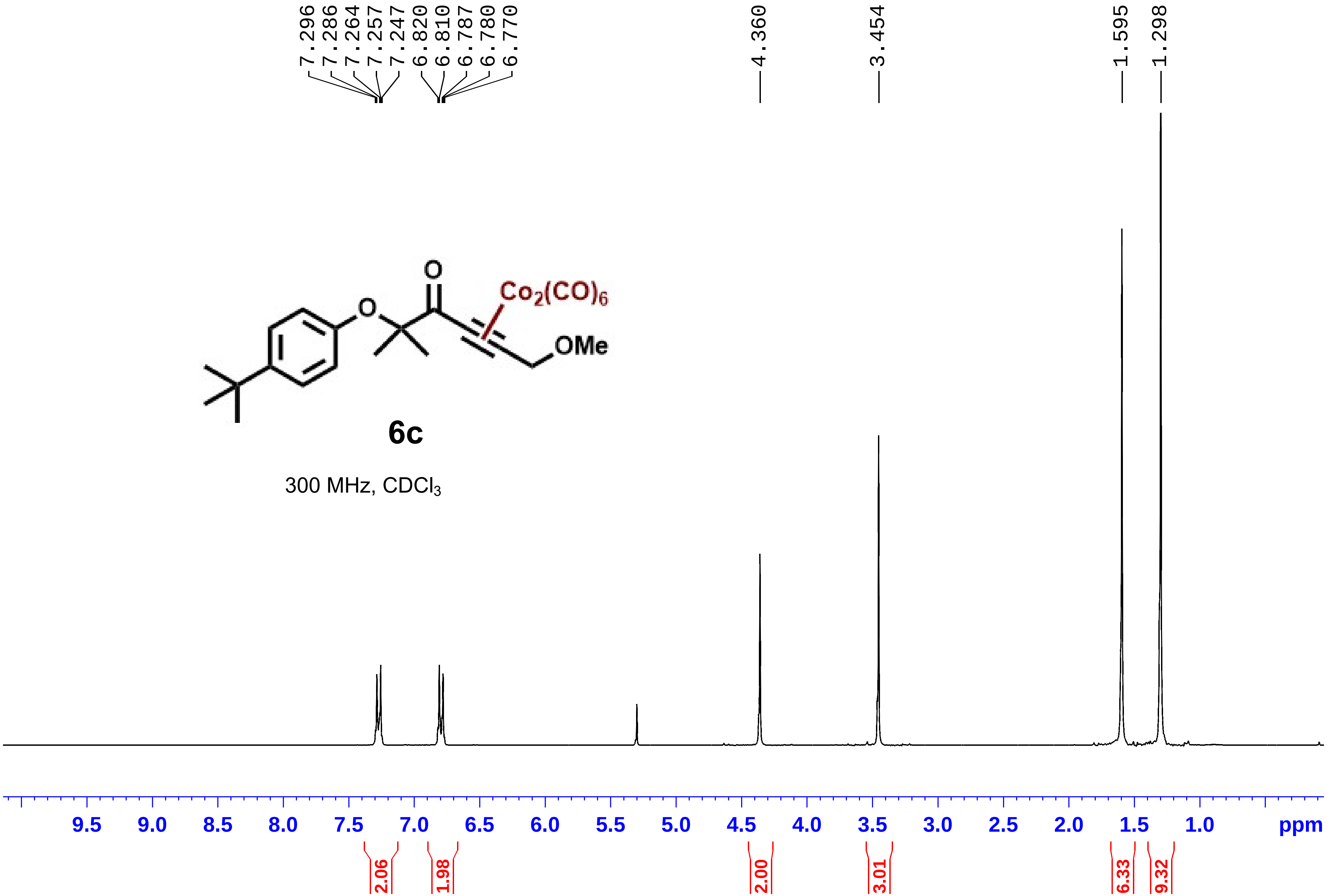

7.371
7.366
7.360
7.359
7.354
7.347
7.345
7.343
7.334
7.329
7.325
7.323
7.315
7.314
7.305
7.301
7.298
7.293
7.154
7.152
7.150
7.137
7.125
7.123
7.121
6.933
6.931
6.927
6.918
6.916
6.914
6.909
4.780
4.767
4.759
4.755
4.743
4.735
4.691
4.668
1.640
1.608
1.597
1.584
$Co_2(CO)_6$
OBn
O
6aa
500 MHz, $CDCl_3$
9.5
9.0
8.5
8.0
7.5
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
ppm
7.08
1.00
1.97
3.08
9.58

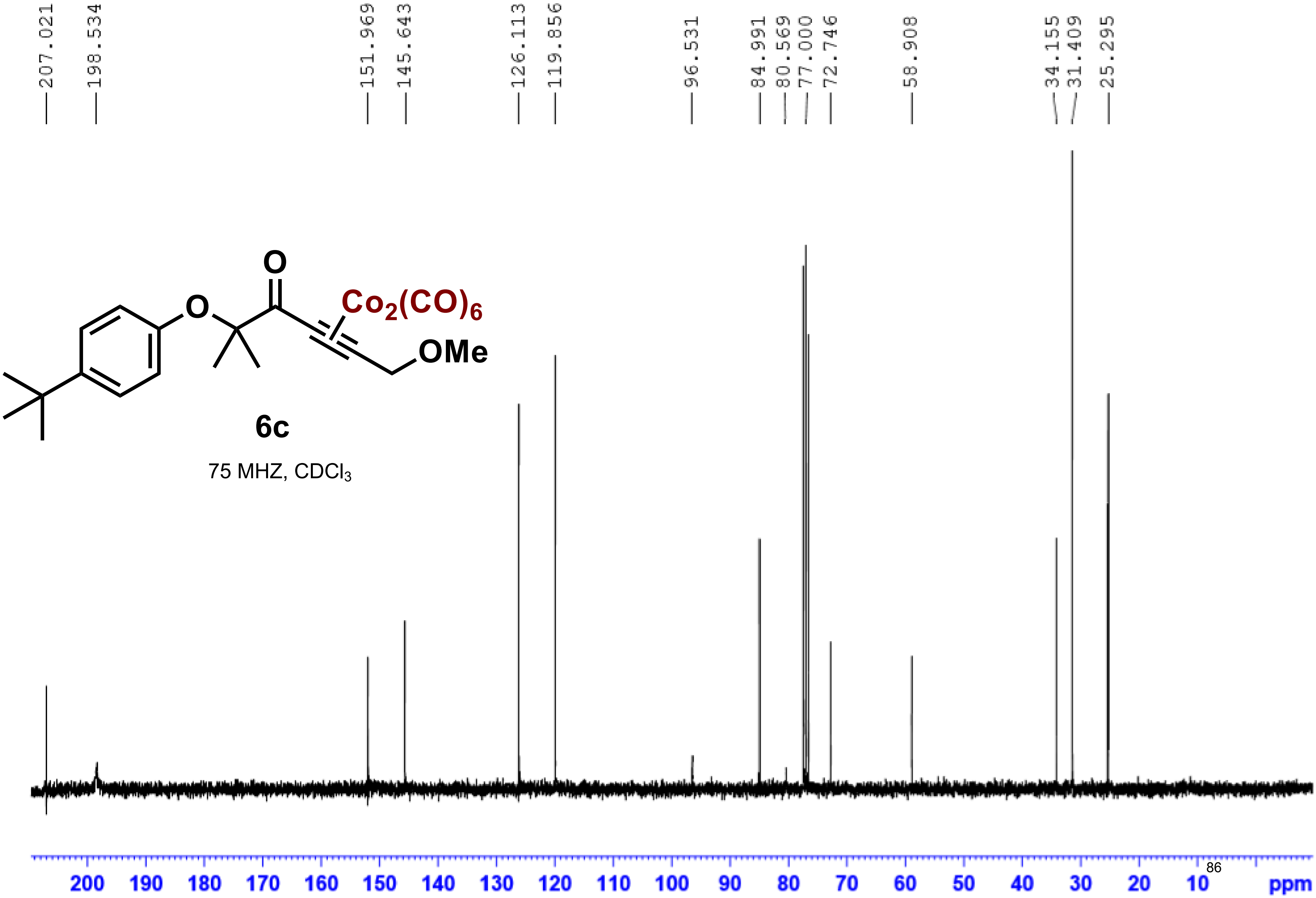

207.117
198.591
153.916
138.072
129.268
128.267
127.533
127.510
123.413
121.829
104.300
85.733
81.878
77.254
77.000
76.746
74.595
71.022
25.675
25.067
22.618
O
O
$Co_2(CO)_6$
OBn
6aa
125 MHz, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

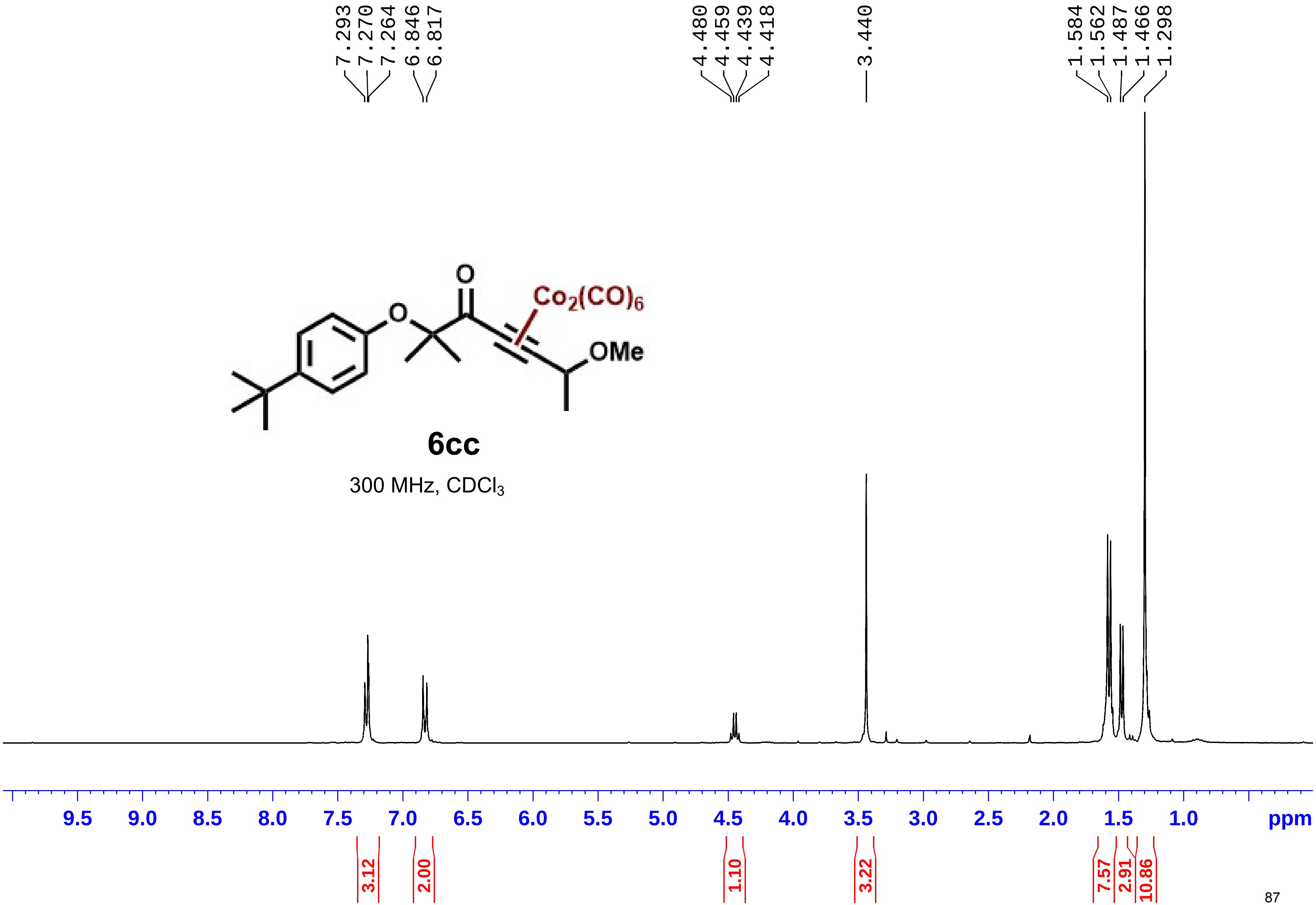

O
O
Co2(CO)6
OMe
6b
300 MHz, CDCl3
7.270
7.087
7.060
6.799
6.771
4.457
3.476
2.306
1.559
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.94
1.94
2.00
3.03
3.02
6.10



206.588
198.522
151.948
132.686
129.781
121.162
96.274
85.341
80.576
77.423
77.000
76.576
72.896
58.940
25.209
20.554
O
O
$Co_2(CO)_6$
OMe
6b
75 MHZ, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

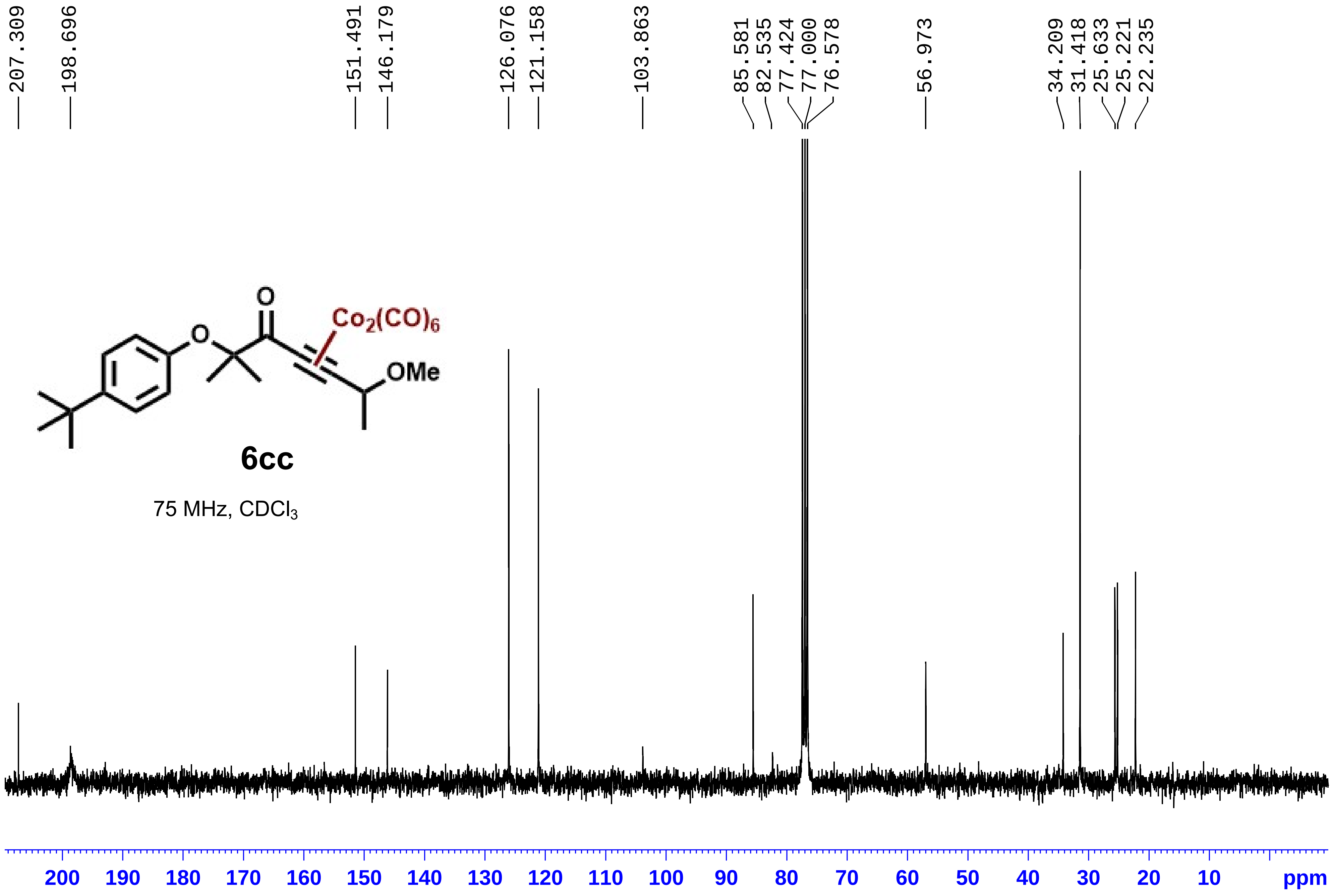

7.296
7.286
7.264
7.257
7.247
6.820
6.810
6.787
6.780
6.770
4.360
3.454
1.595
1.298
O
Co2(CO)6
O
OMe
6c
300 MHz, CDCl3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.06
1.98
2.00
3.01
6.33
9.32

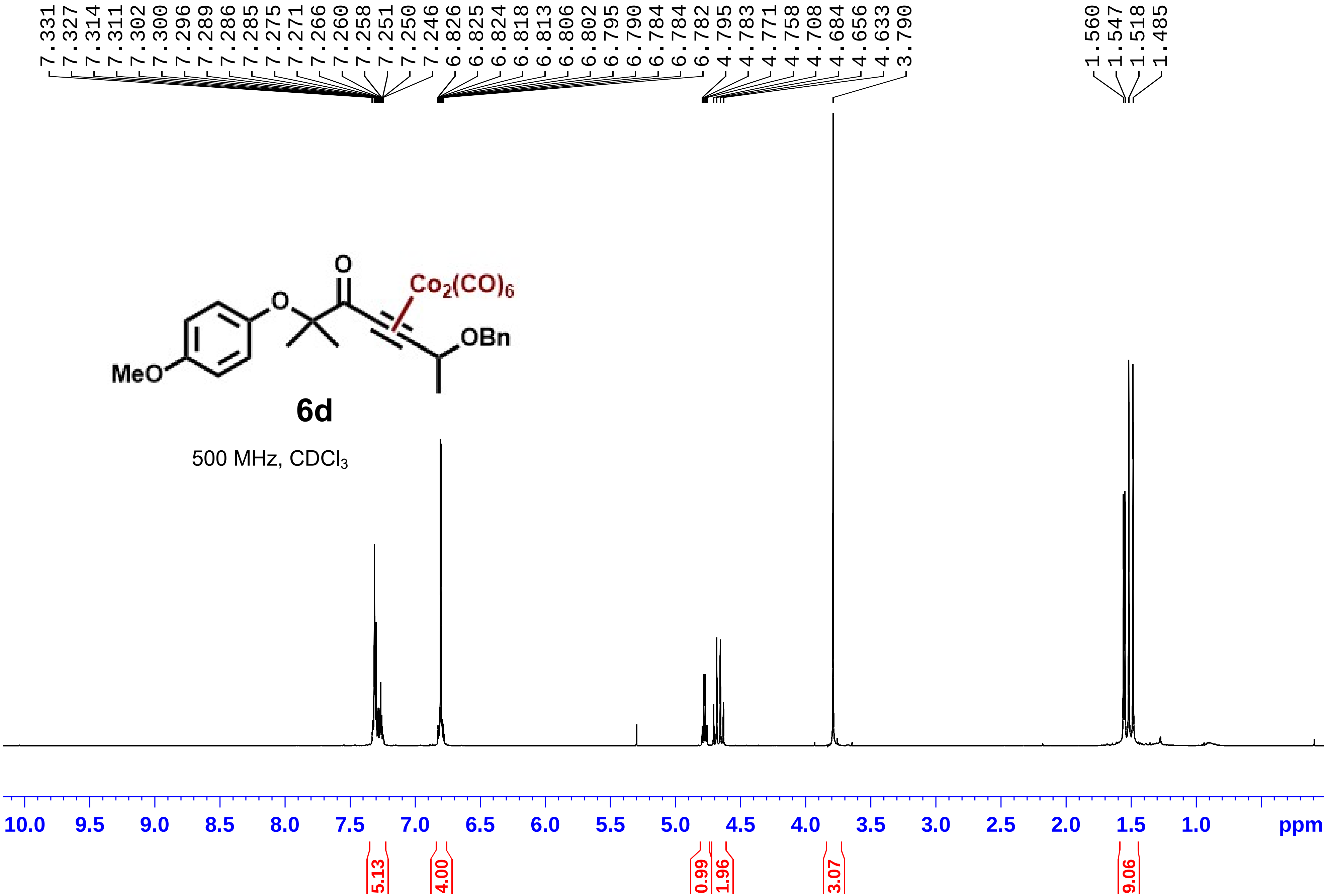

207.021
198.534
151.969
145.643
126.113
119.856
96.531
84.991
80.569
77.000
72.746
58.908
34.155
31.409
25.295
O
O
$Co_2(CO)_6$
OMe
6c
75 MHZ, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

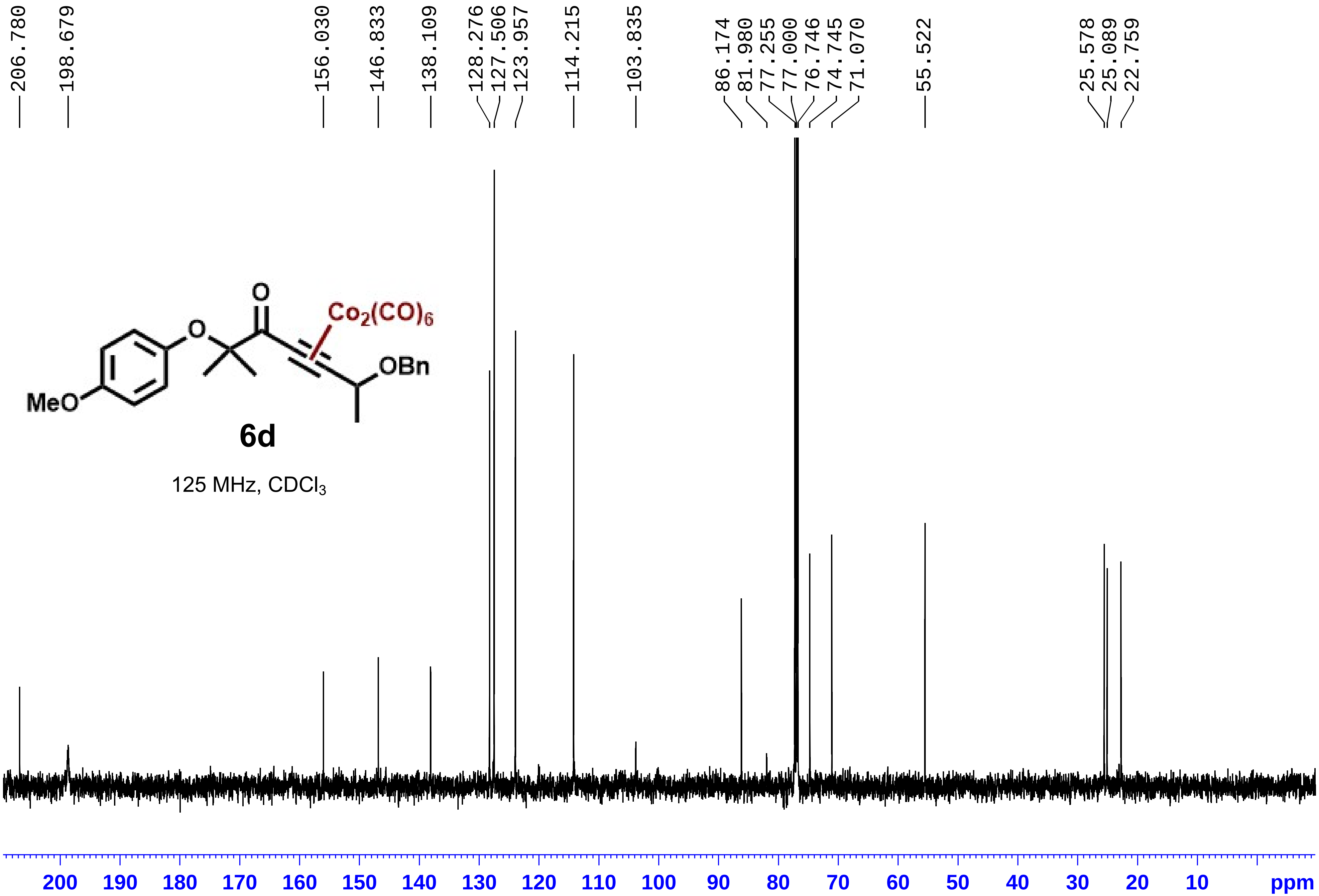


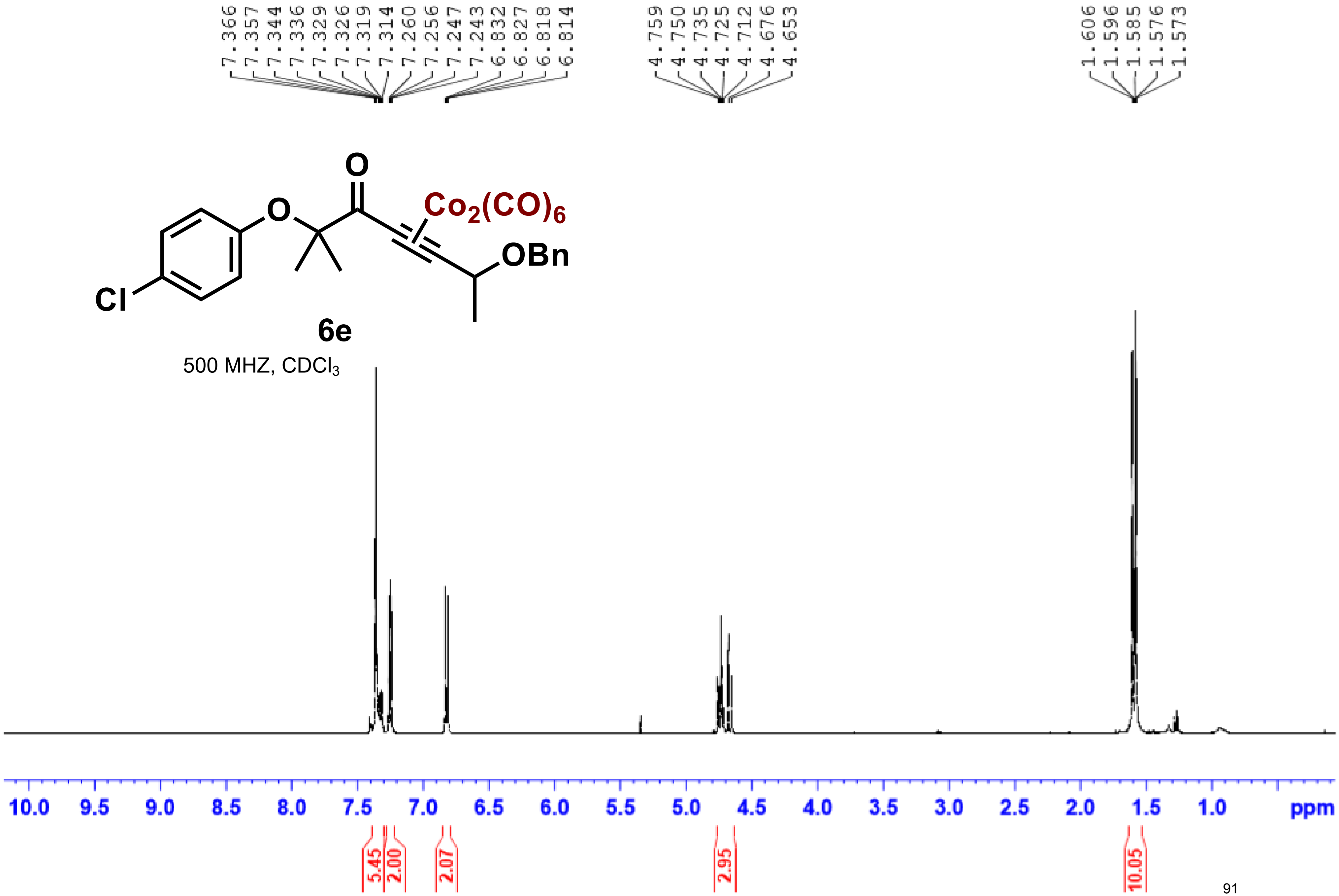
6cc

300 MHz, $CDCl_3$


207.309
198.696
151.491
146.179
126.076
121.158
103.863
85.581
82.535
77.424
77.000
76.578
56.973
34.209
31.418
25.633
25.221
22.235
O
O
Co2(CO)6
OMe
6cc
75 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

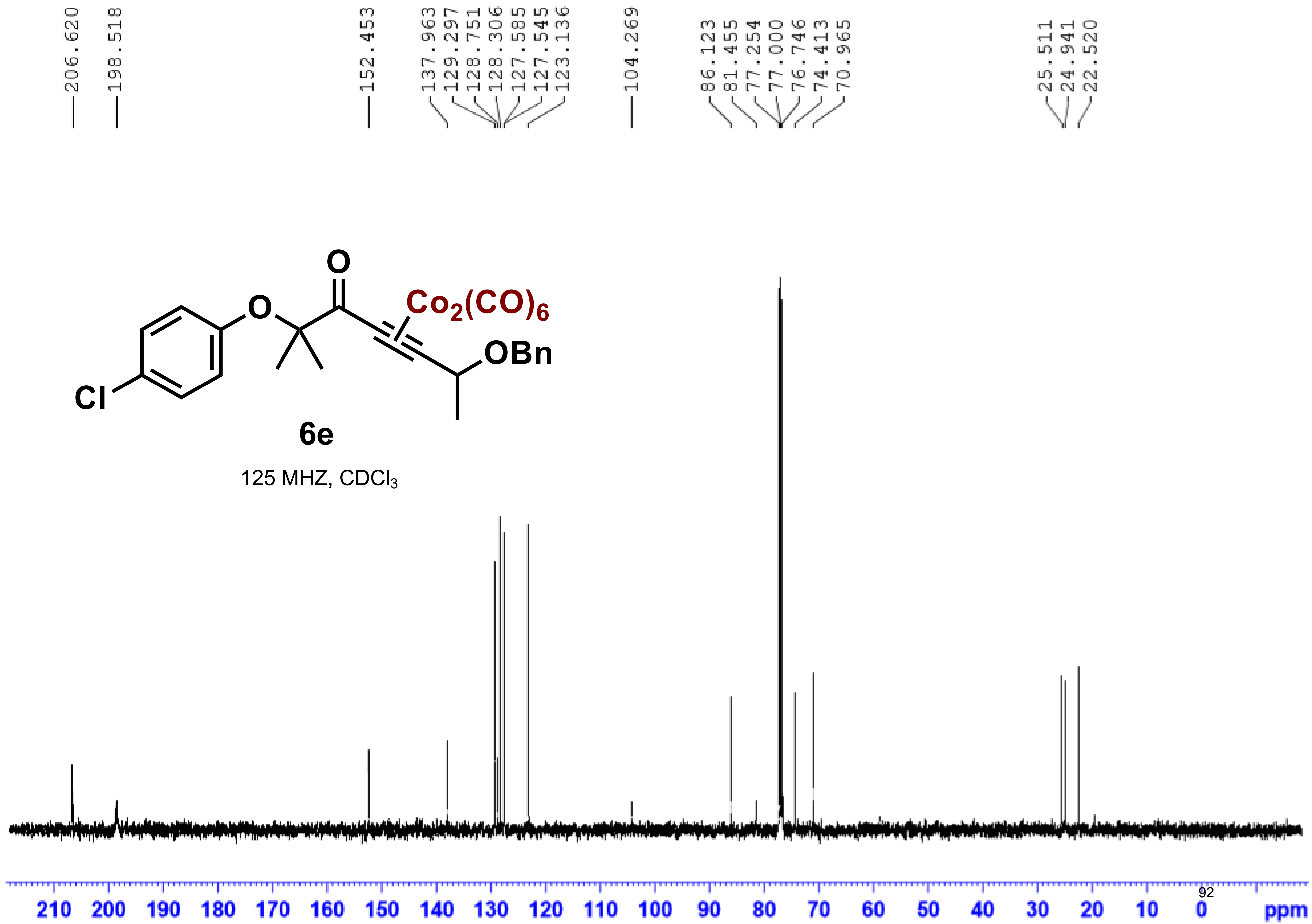

7.331
7.327
7.314
7.311
7.302
7.300
7.296
7.289
7.286
7.285
7.275
7.271
7.266
7.260
7.258
7.251
7.250
7.246
6.826
6.825
6.824
6.818
6.813
6.806
6.802
6.795
6.790
6.784
6.784
6.782
4.795
4.783
4.771
4.758
4.708
4.684
4.656
4.633
3.790
1.560
1.547
1.518
1.485
O
O
$Co_2(CO)_6$
OBn
MeO
6d
500 MHz, $CDCl_3$
10.0
9.5
9.0
8.5
8.0
7.5
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
ppm
5.13
4.00
0.99
1.96
3.07
9.06


206.780
198.679
156.030
146.833
138.109
128.276
127.506
123.957
114.215
103.835
86.174
81.980
77.255
77.000
76.746
74.745
71.070
55.522
25.578
25.089
22.759
O
Co2(CO)6
OBn
MeO
6d
125 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

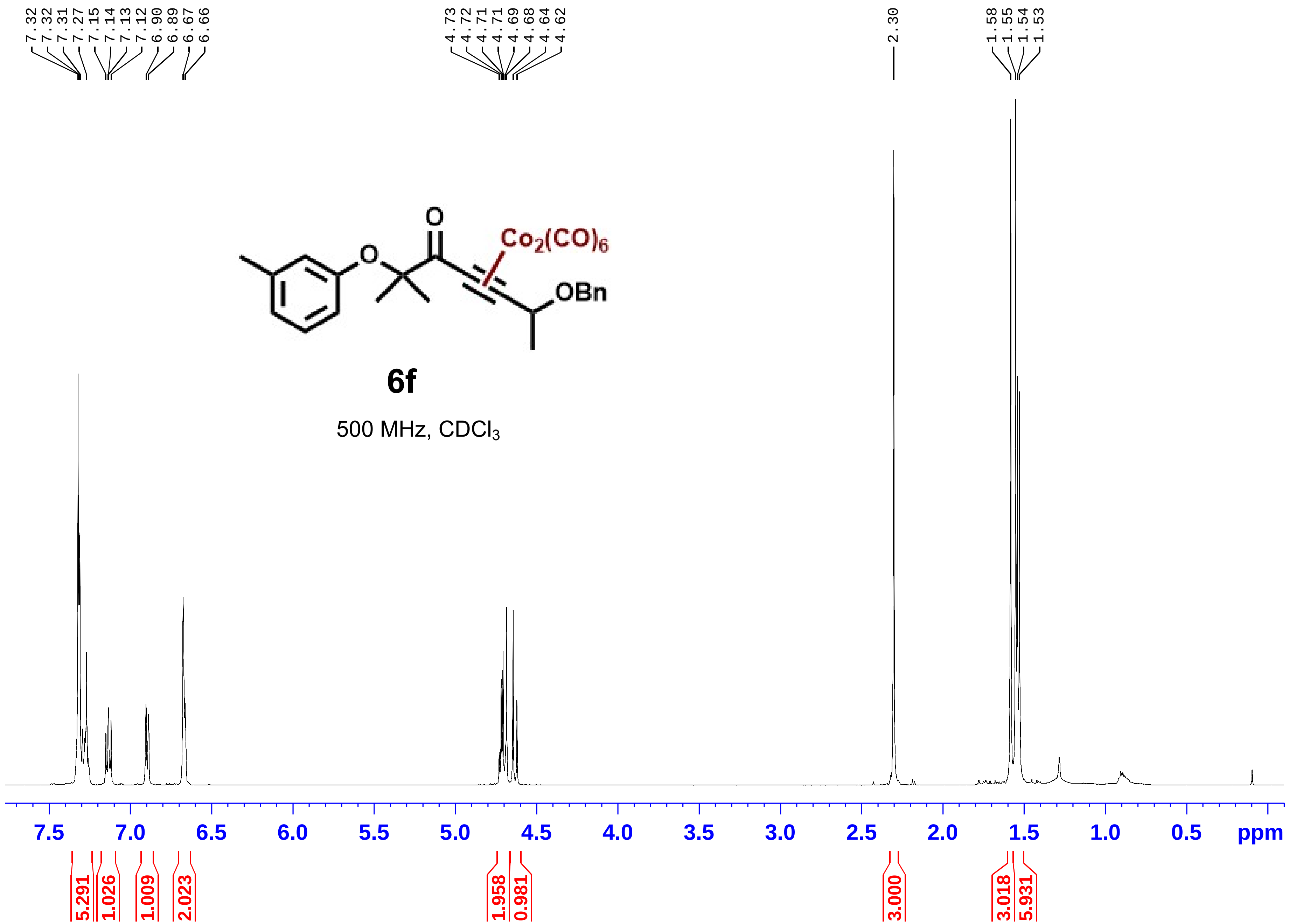


7.366
7.357
7.344
7.336
7.329
7.326
7.319
7.314
7.260
7.256
7.247
7.243
6.832
6.827
6.818
6.814
4.759
4.750
4.735
4.725
4.712
4.676
4.653
1.606
1.596
1.585
1.576
1.573
O
O
Co2(CO)6
OBn
Cl
500 MHZ, CDCl3
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
5.45
2.00
2.07
2.95
10.05

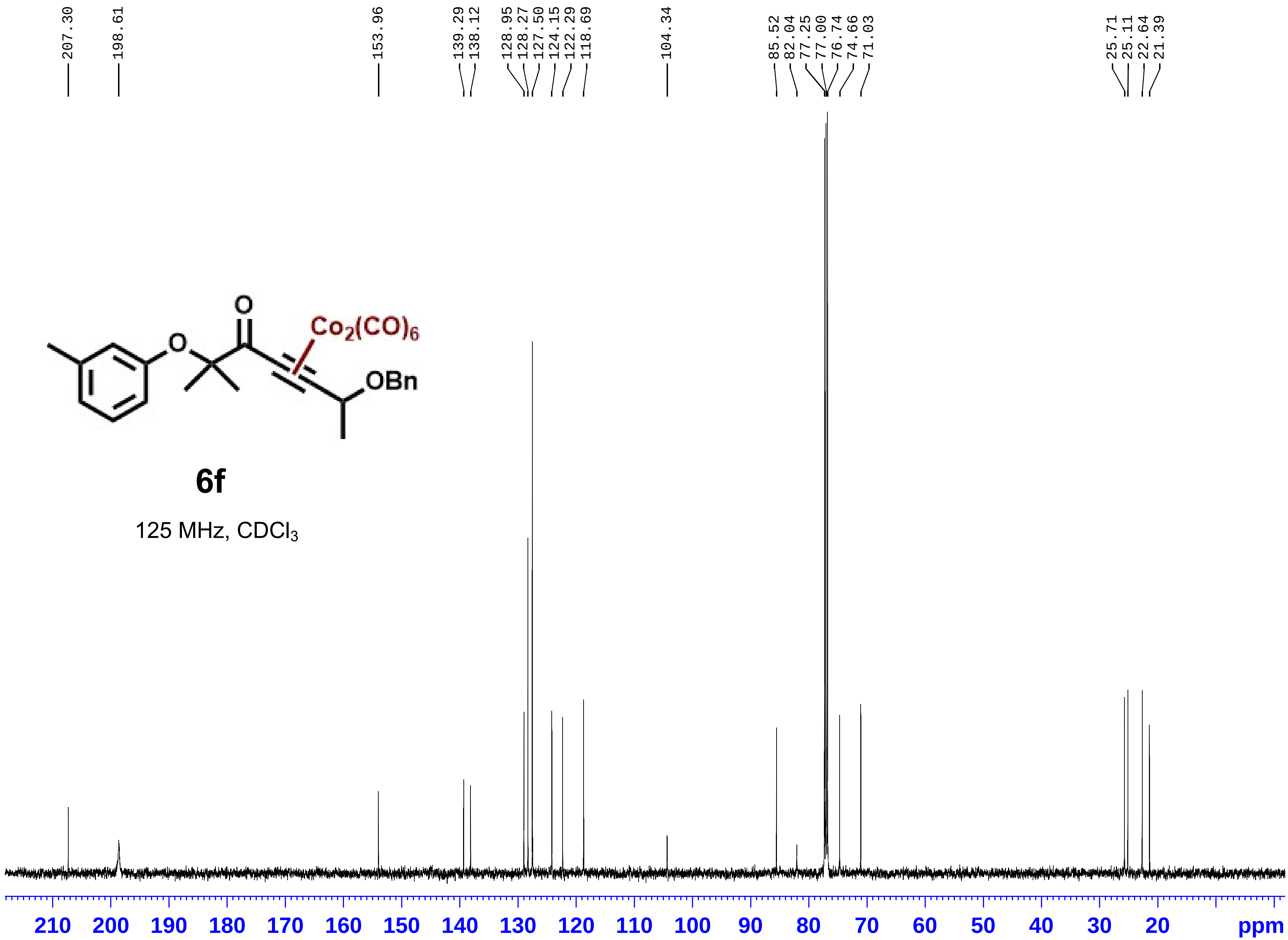
6e


206.620
198.518
152.453
137.963
129.297
128.751
128.306
127.585
127.545
123.136
104.269
86.123
81.455
77.254
77.000
76.746
74.413
70.965
25.511
24.941
22.520
O
O
Co$_2$(CO)$_6$
OBn
Cl
6e
125 MHZ, CDCl$_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

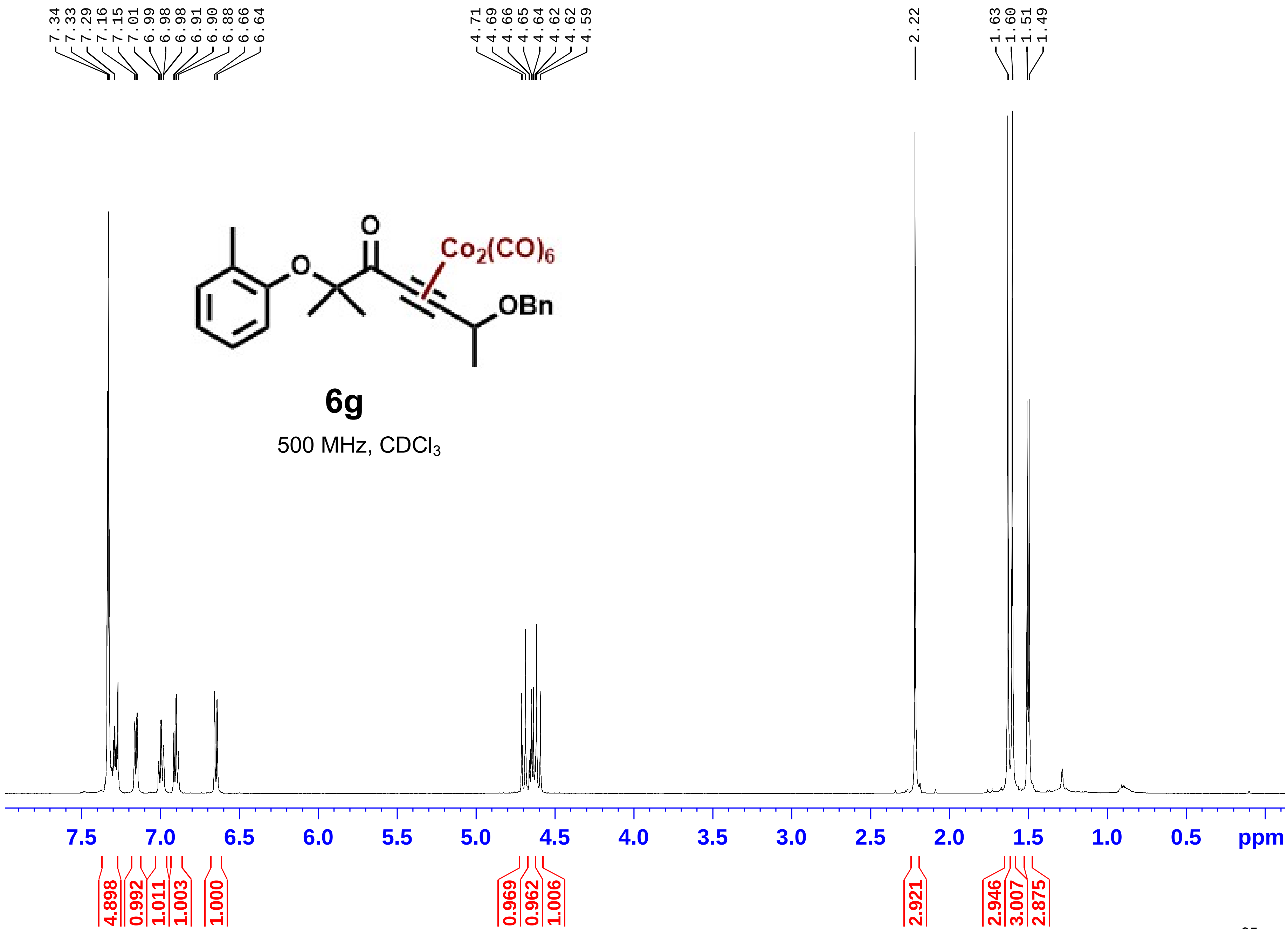
bso.0608 1 m-Me propargyl Me SM complex, 6/8/21



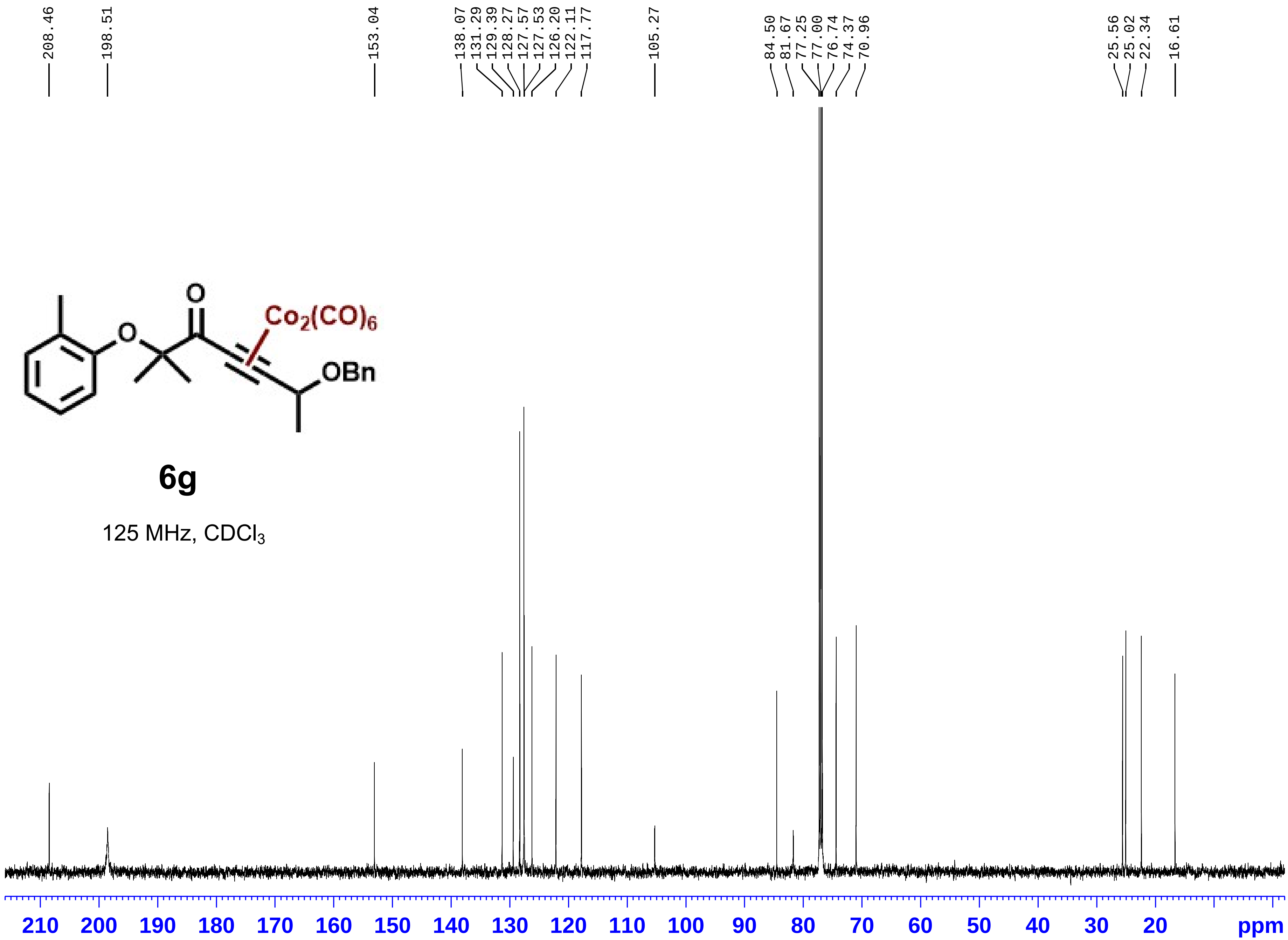
bso.0608 2 13C m-Me proprg Me SM complex, 125 MHz, 6/8/21



bso.0609 1 o-Me propargyl Me SM complex, 6/9/21

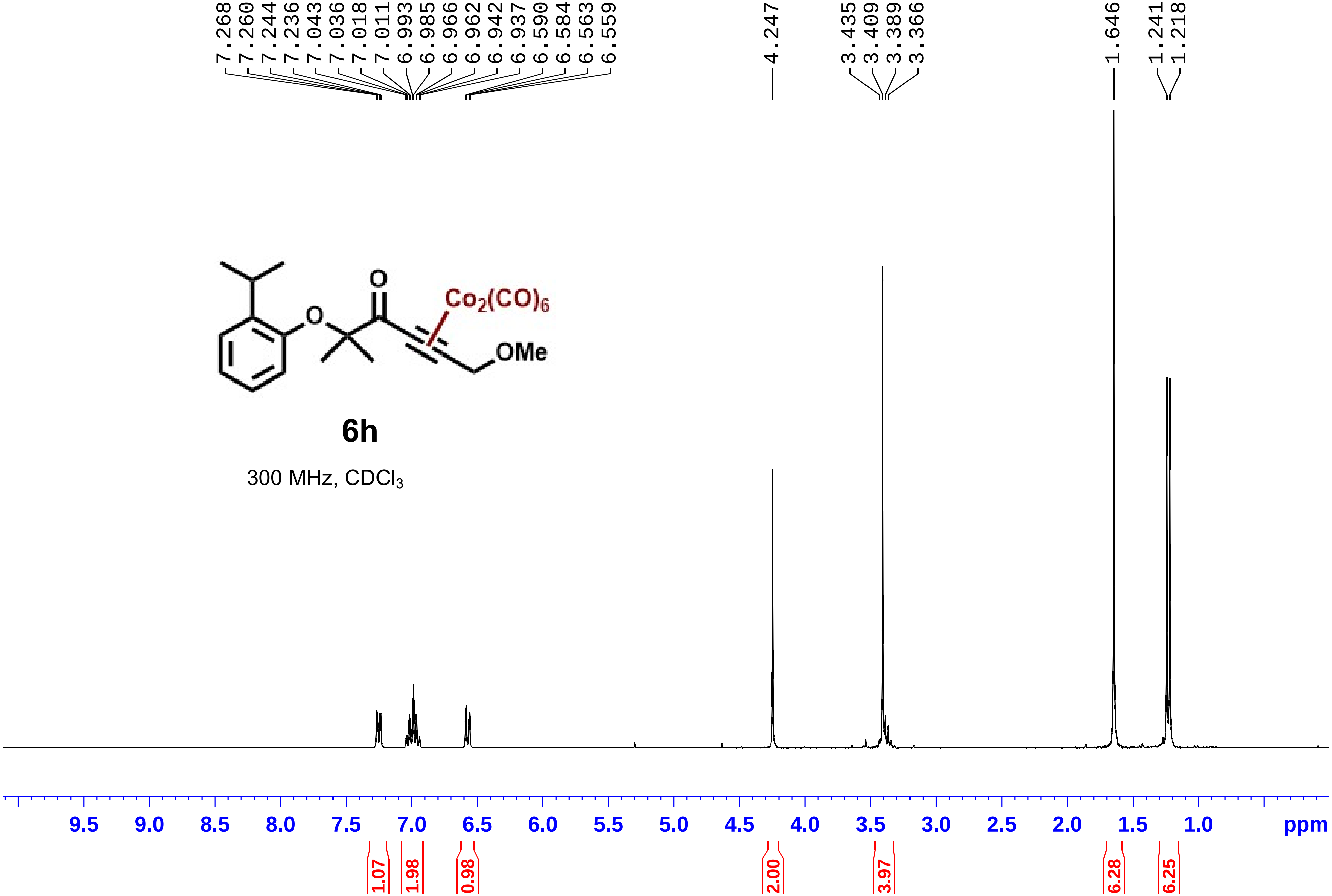


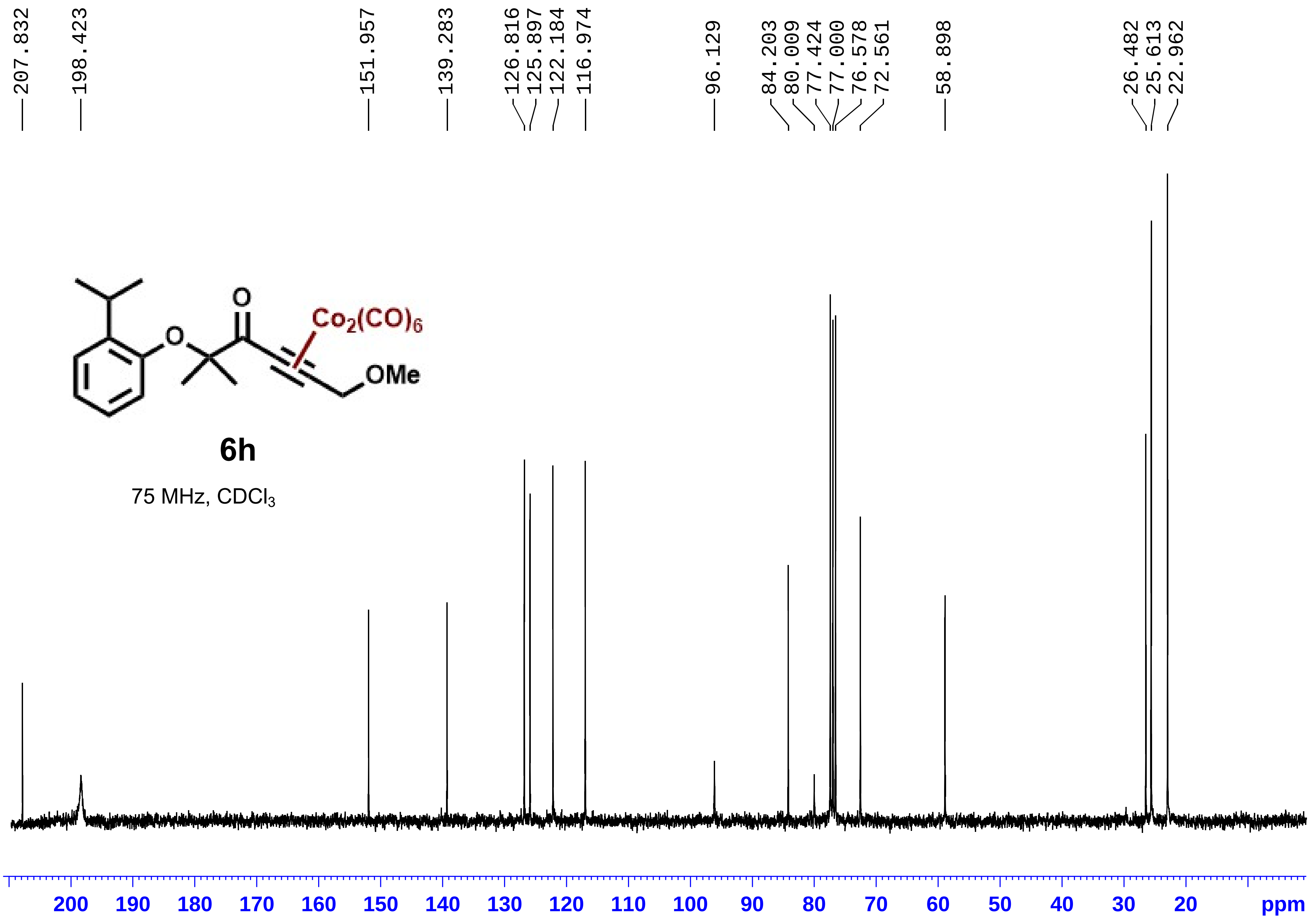
bso.0609 2 13C o-Me proparg Me SM complex, 125 MHz, 6/9/21



6g

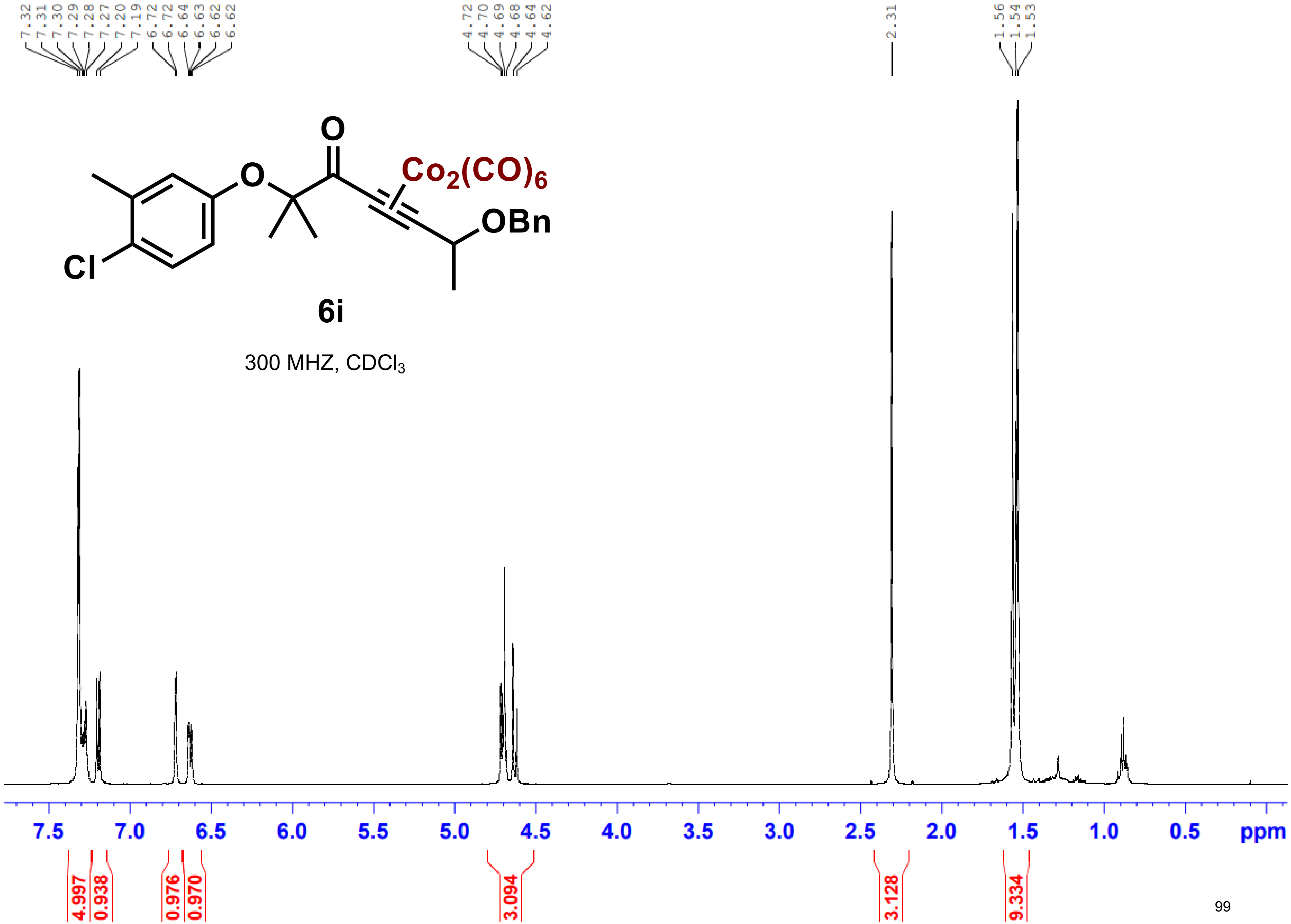
125 MHz, $CDCl_3$

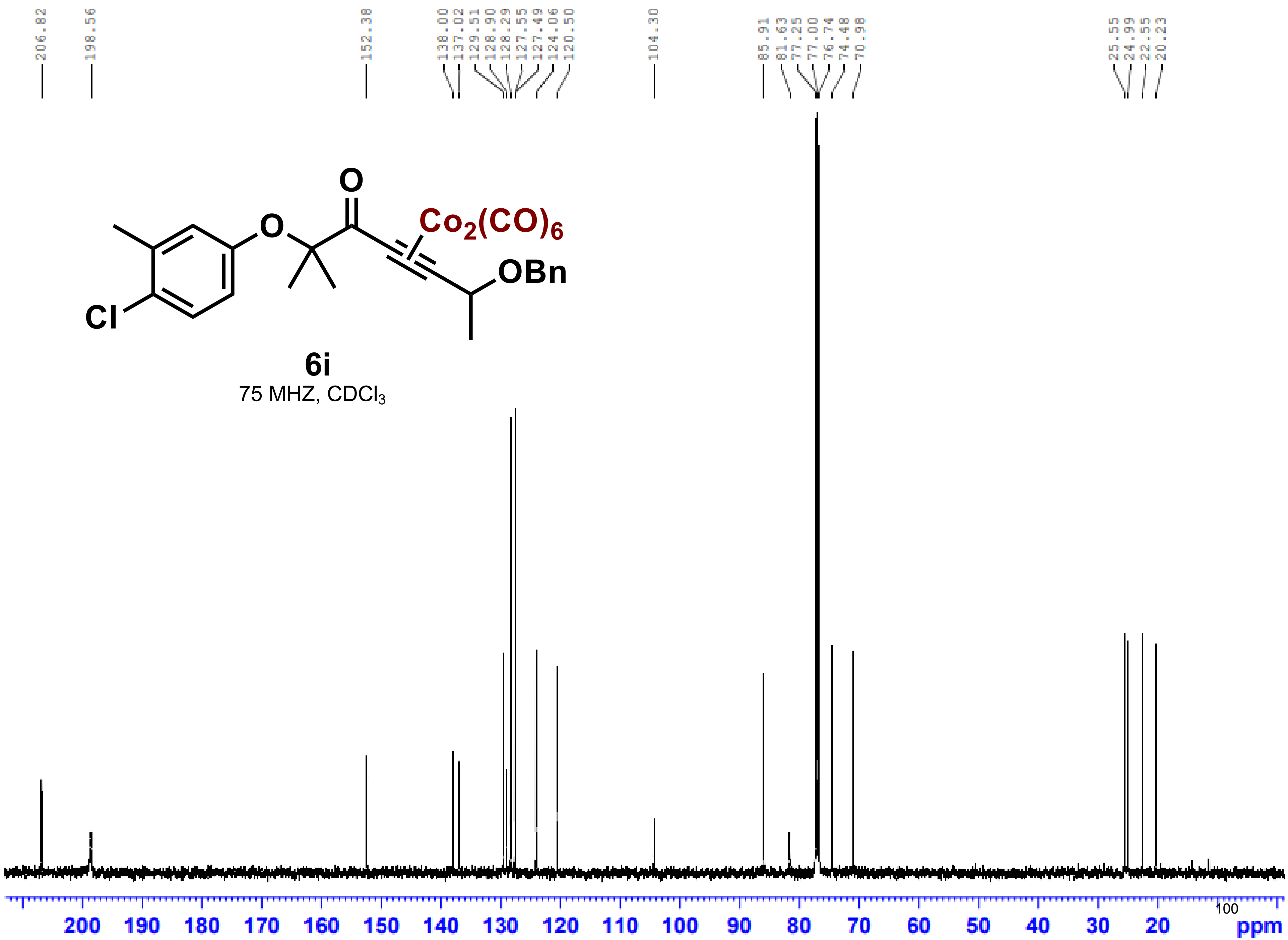

7.268
7.260
7.244
7.236
7.043
7.036
7.018
7.011
6.993
6.985
6.966
6.962
6.942
6.937
6.590
6.584
6.563
6.559
4.247
3.435
3.409
3.389
3.366
1.646
1.241
1.218
O
Co2(CO)6
OMe
6h
300 MHz, CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.07
1.98
0.98
2.00
3.97
6.28
6.25



6h

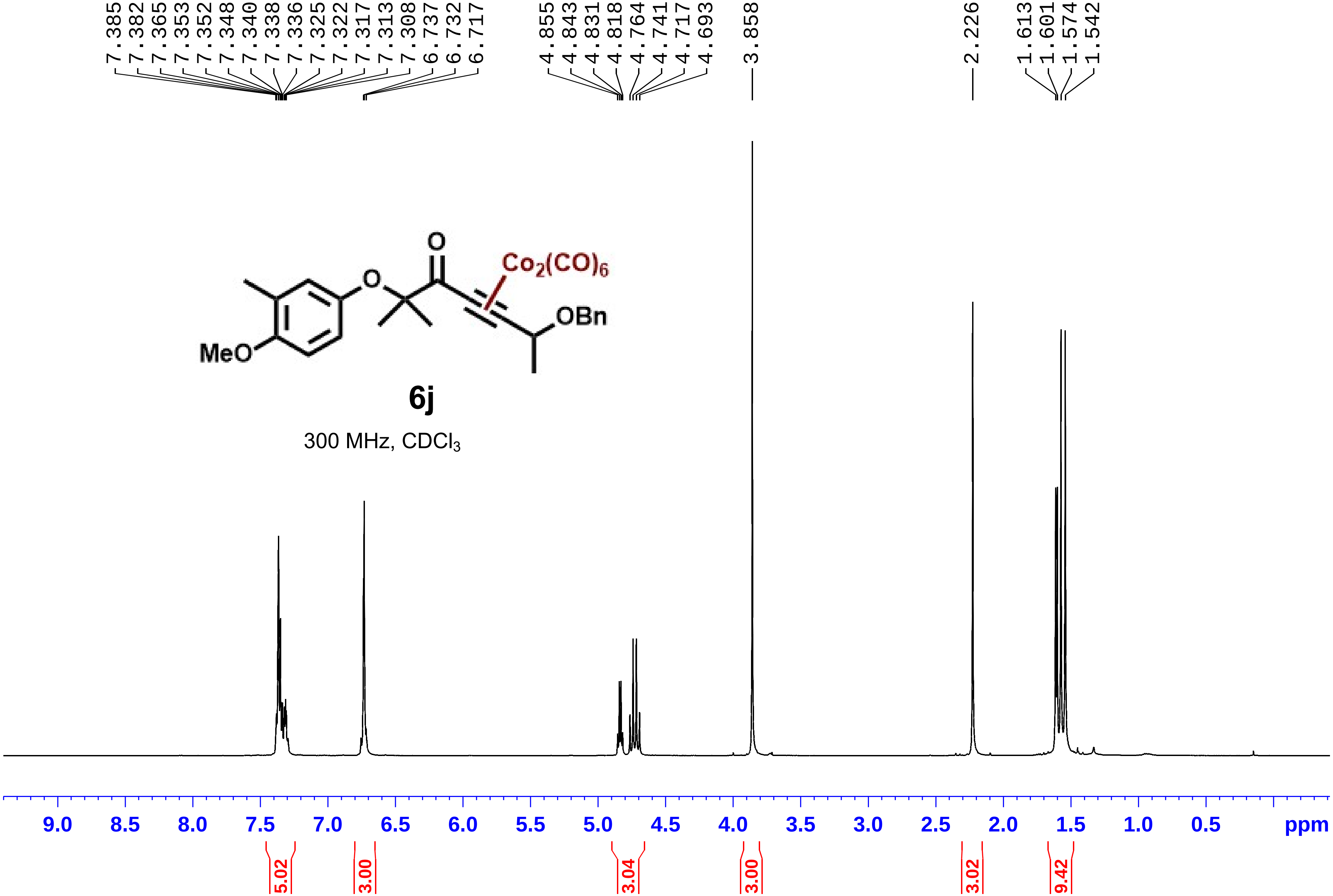
75 MHz, $CDCl_3$

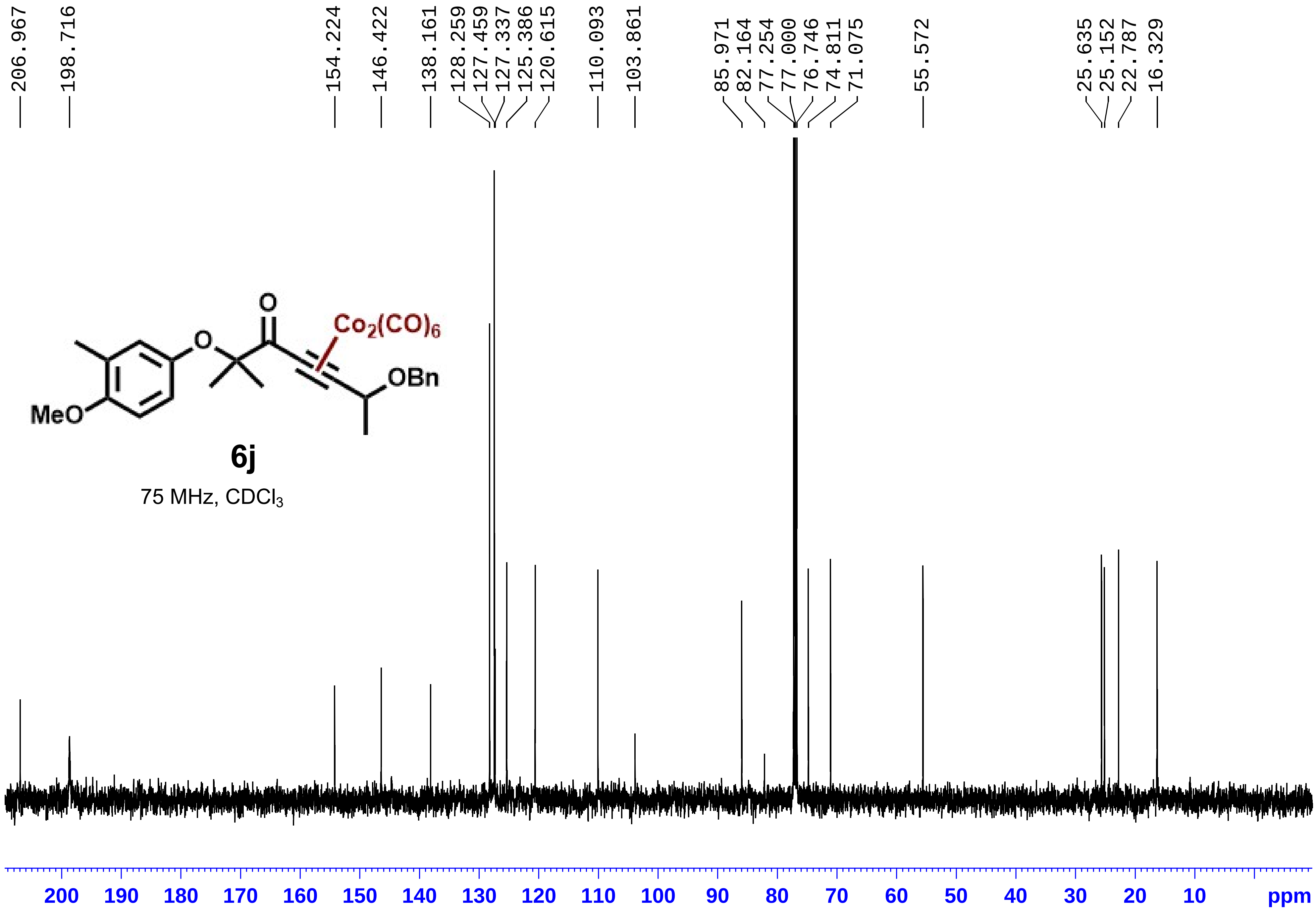

7.32
7.31
7.30
7.29
7.28
7.27
7.20
7.19
6.72
6.72
6.64
6.63
6.62
6.62
4.72
4.70
4.69
4.68
4.64
4.62
2.31
1.56
1.54
1.53
O
O
Co2(CO)6
OBn
Cl
6i
300 MHZ, CDCl3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.997
0.938
0.976
0.970
3.094
3.128
9.334



6i

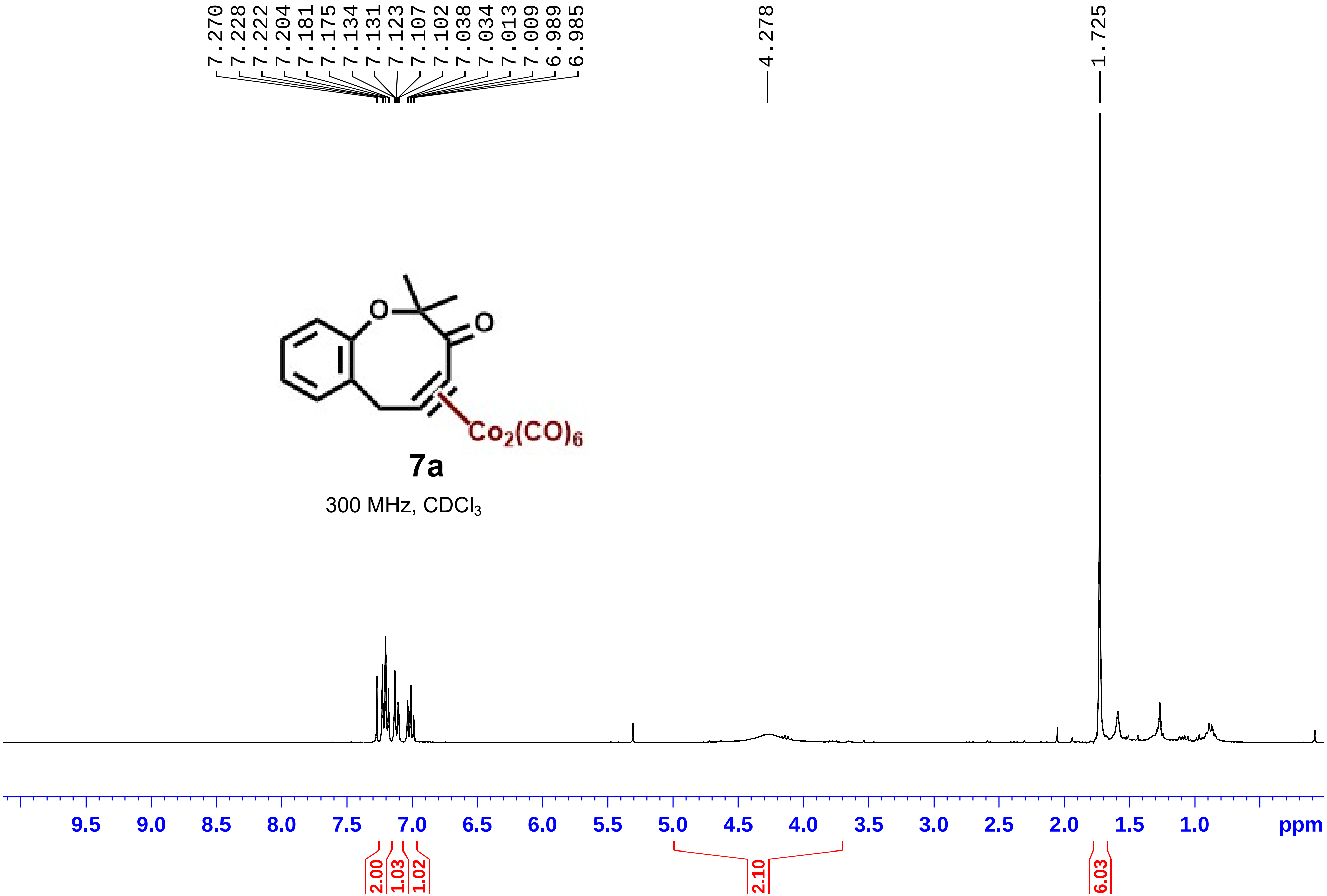
75 MHZ, $CDCl_3$


7.385
7.382
7.365
7.353
7.352
7.348
7.340
7.338
7.336
7.325
7.322
7.317
7.313
7.308
6.737
6.732
6.717
4.855
4.843
4.831
4.818
4.764
4.741
4.717
4.693
3.858
2.226
1.613
1.601
1.574
1.542
MeO
O
O
$Co_2(CO)_6$
OBn
6j
300 MHz, $CDCl_3$
9.0 8.5 8.0 7.5 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
5.02
3.00
3.04
3.00
3.02
9.42

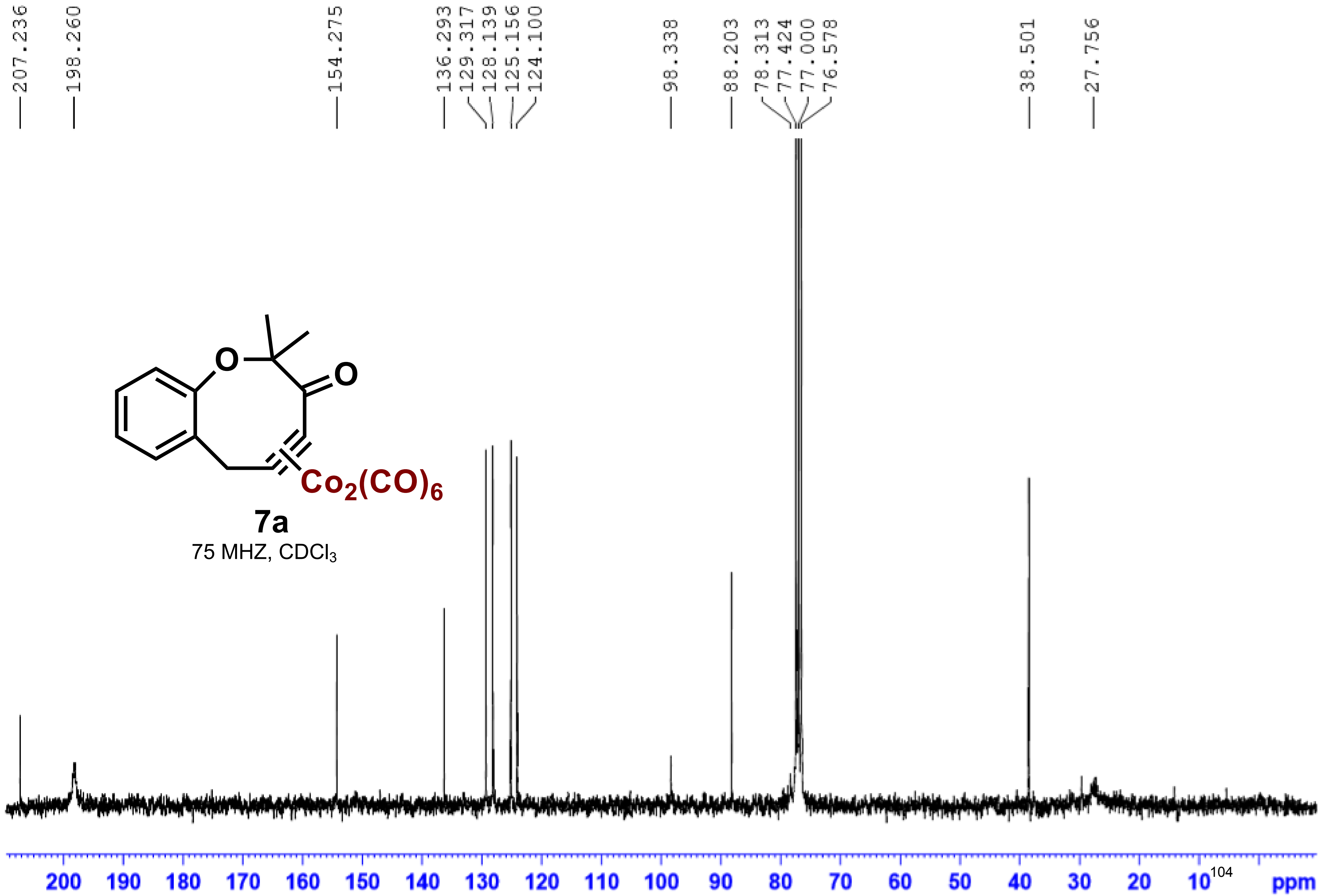


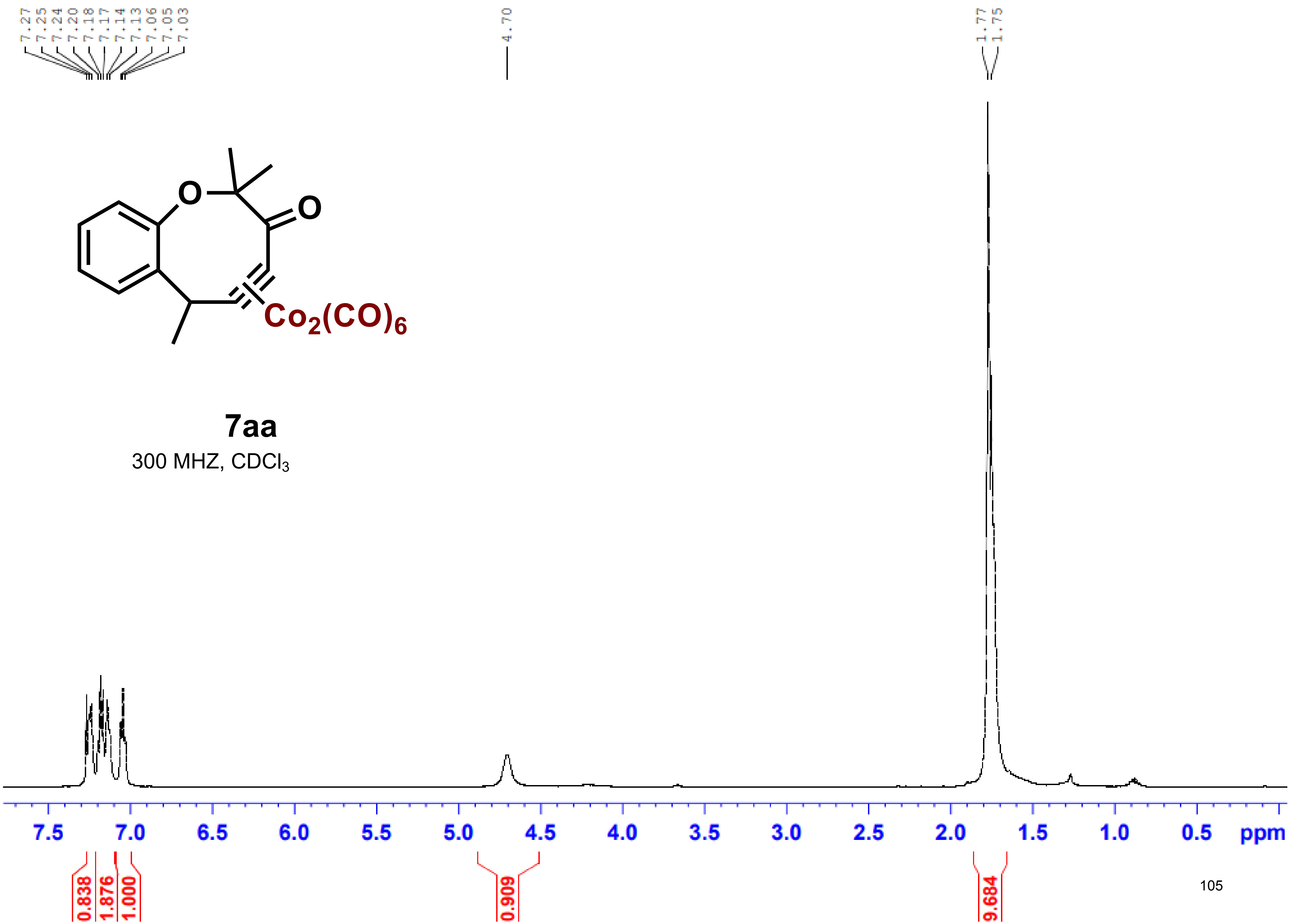
6j

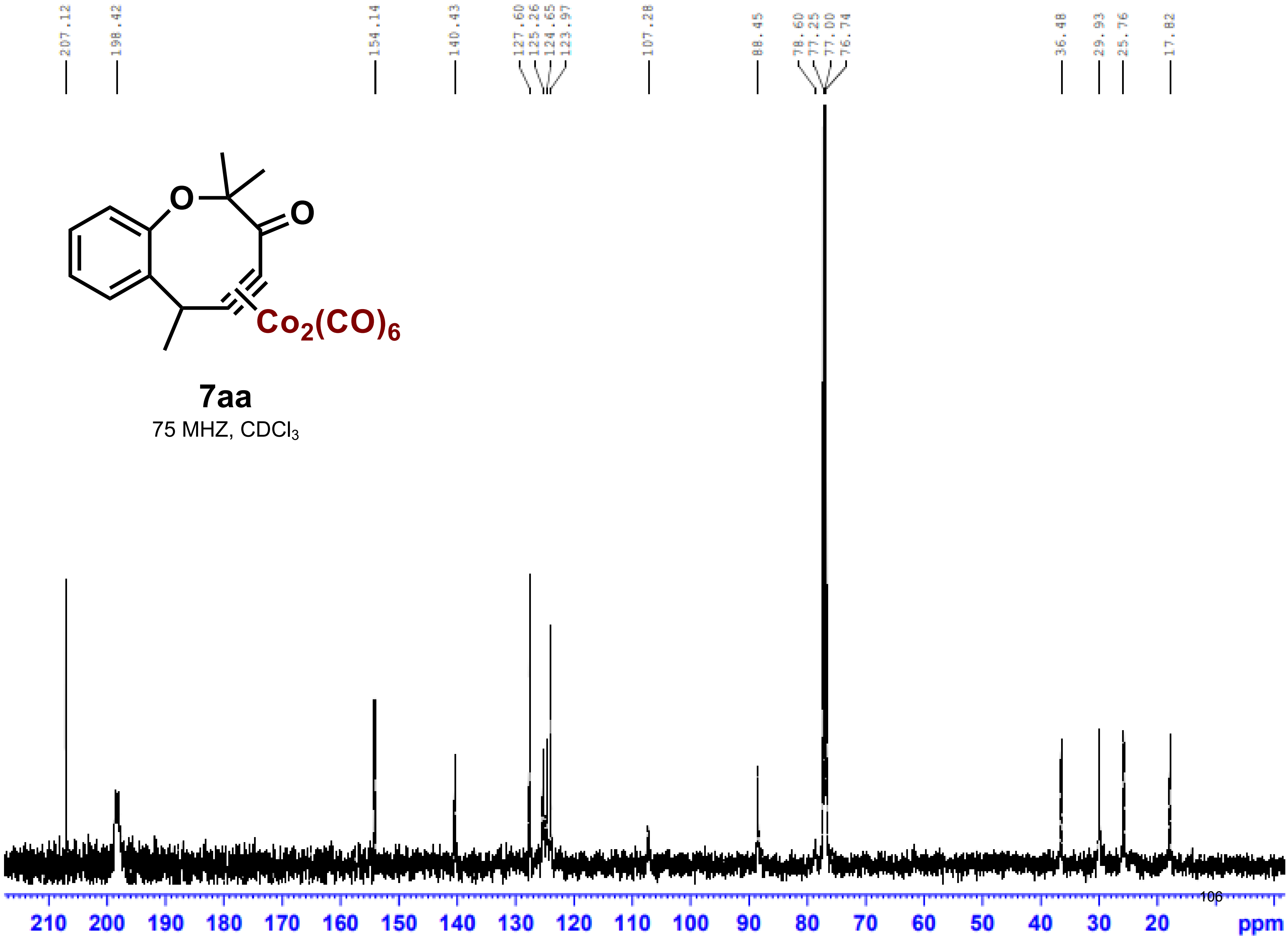
75 MHz, $CDCl_3$



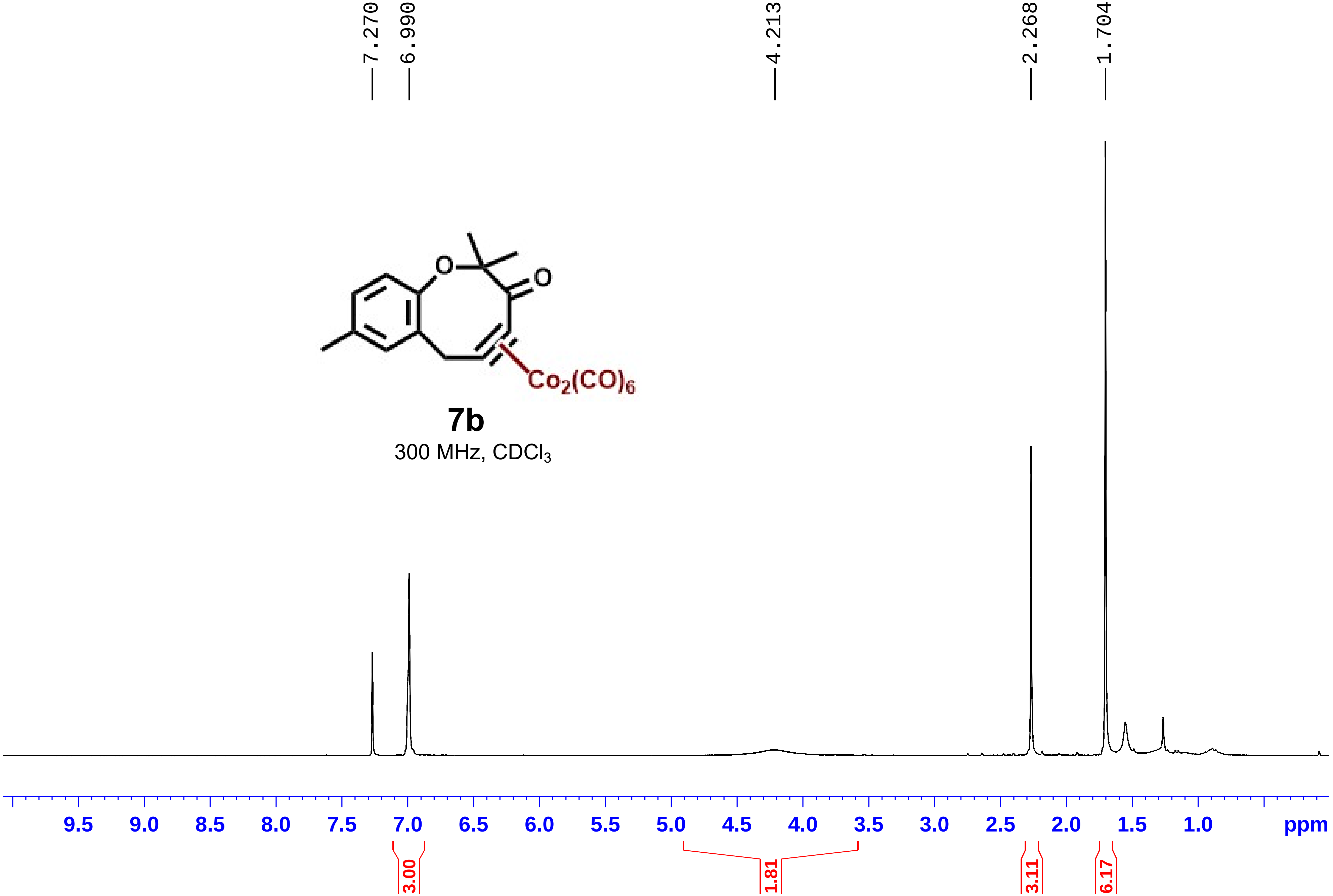
7a
300 MHz, CDCl3
7.270
7.228
7.222
7.204
7.181
7.175
7.134
7.131
7.123
7.107
7.102
7.038
7.034
7.013
7.009
6.989
6.985
4.278
1.725
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
1.03
1.02
2.10
6.03

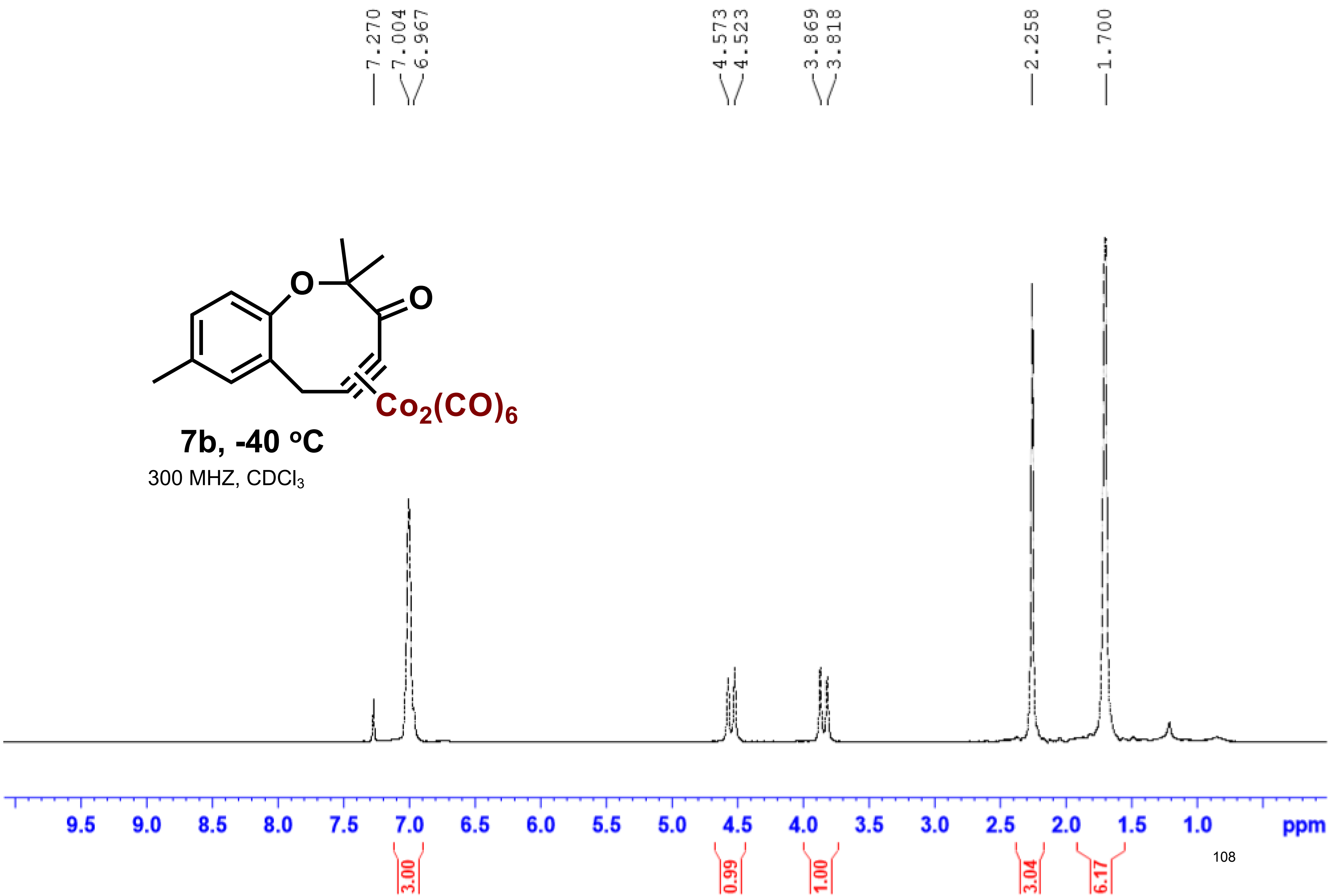

207.236
198.260
154.275
136.293
129.317
128.139
125.156
124.100
98.338
88.203
78.313
77.424
77.000
76.578
38.501
27.756
O
O
$Co_2(CO)_6$
7a
75 MHZ, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

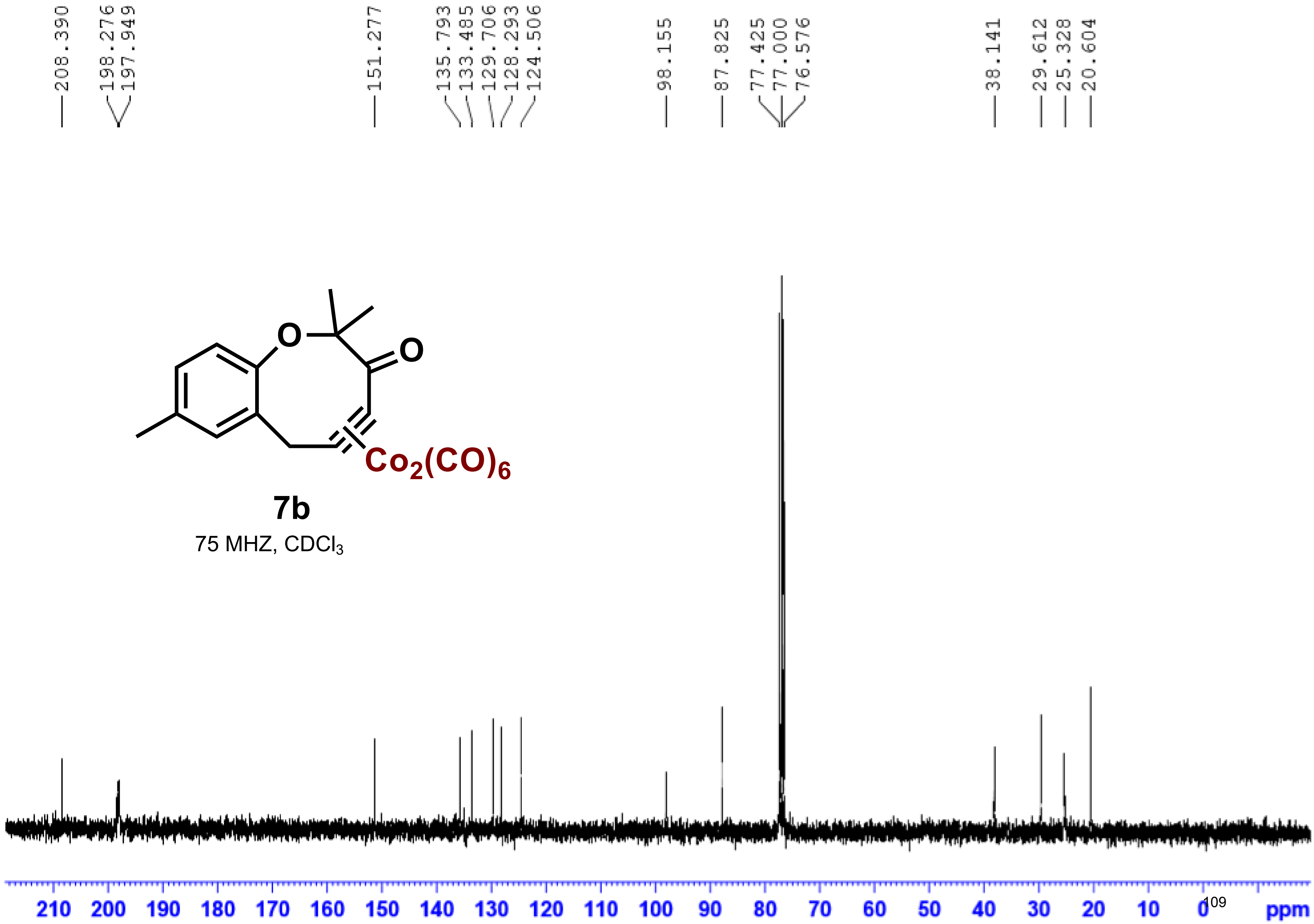

7.27
7.25
7.24
7.20
7.18
7.17
7.14
7.13
7.06
7.05
7.03
4.70
1.77
1.75
O
O
Co2(CO)6
7aa
300 MHZ, CDCl3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.838
1.876
1.000
0.909
9.684



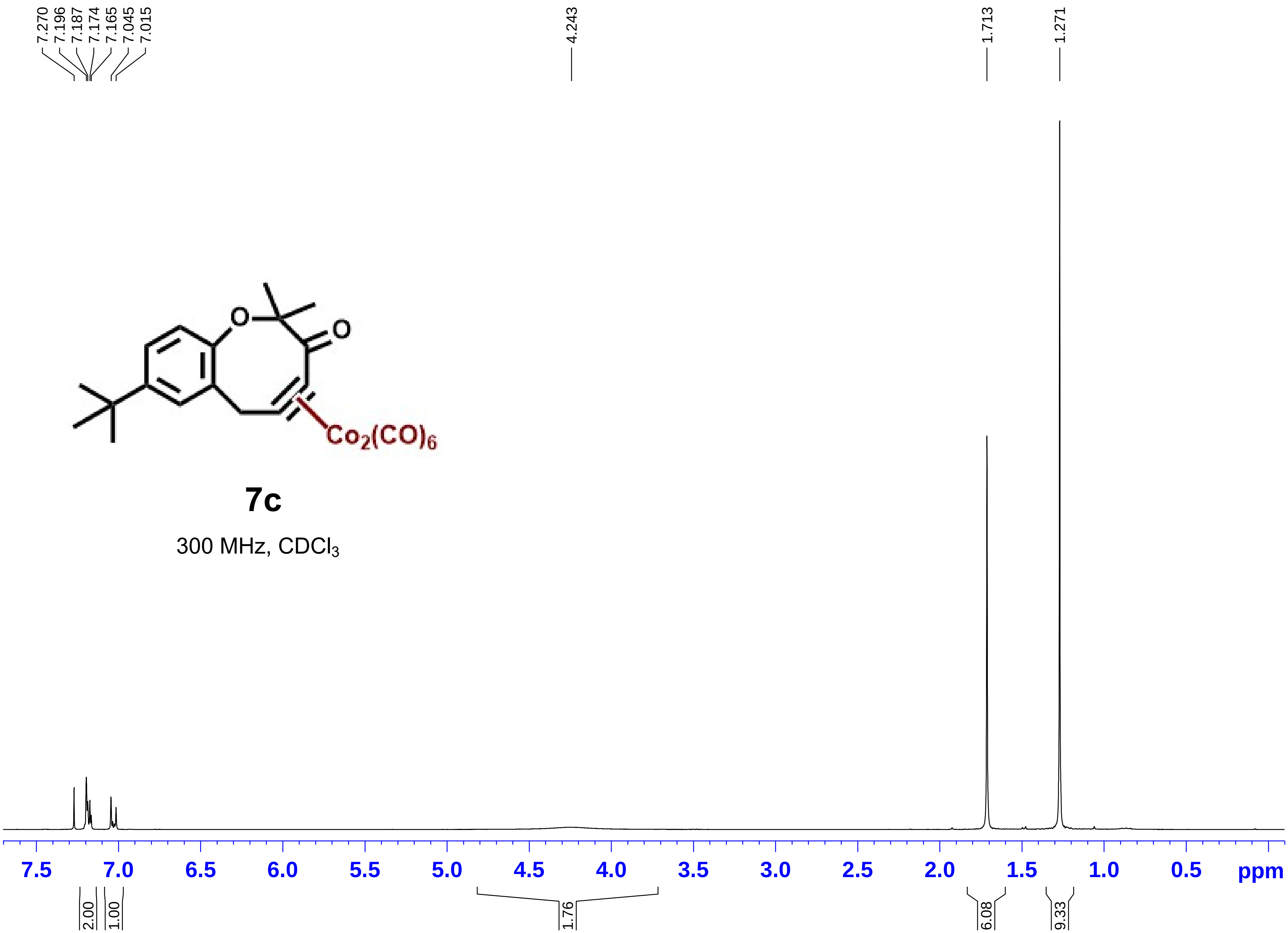
O
O
$Co_2(CO)_6$
7aa
75 MHZ, $CDCl_3$
207.12
198.42
154.14
140.43
127.60
125.26
124.65
123.97
107.28
88.45
78.60
77.25
77.00
76.74
36.48
29.93
25.76
17.82
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.270
6.990
4.213
2.268
1.704
Co2(CO)6
7b
300 MHz, CDCl3
9.5
9.0
8.5
8.0
7.5
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
ppm
3.00
1.81
3.11
6.17


7b, -40 °C
300 MHZ, $CDCl_3$
$Co_2(CO)_6$
O
O
7.270
7.004
6.967
4.573
4.523
3.869
3.818
2.258
1.700
9.5 9.0 8.5 8.0 7.5 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 ppm
3.00
0.99
1.00
3.04
6.17

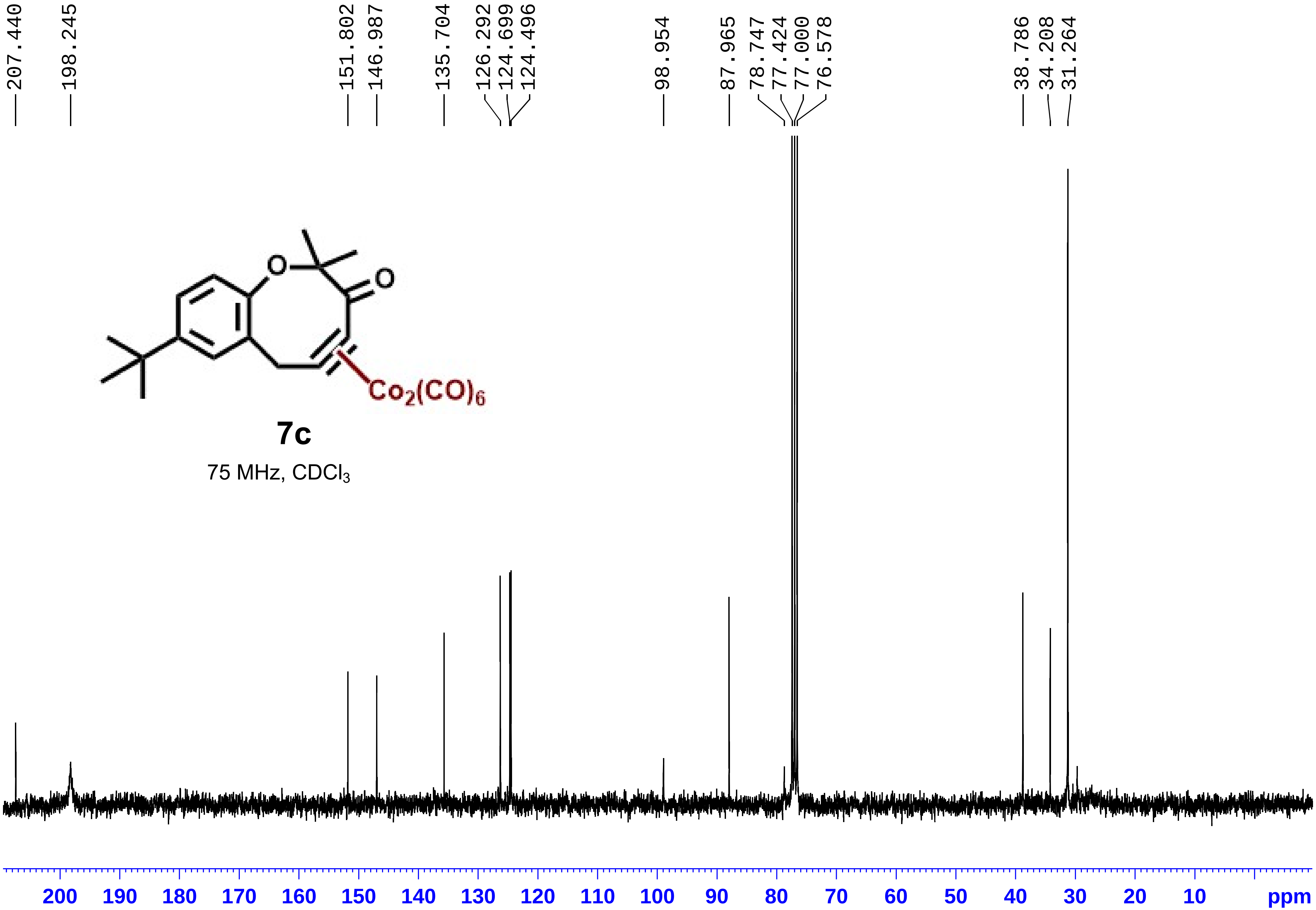

208.390
198.276
197.949
151.277
135.793
133.485
129.706
128.293
124.506
98.155
87.825
77.425
77.000
76.576
38.141
29.612
25.328
20.604
O
O
Co2(CO)6
7b
75 MHZ, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

bso.0607 1, p-tBu-propargyl cycliz prod, 6/7/21

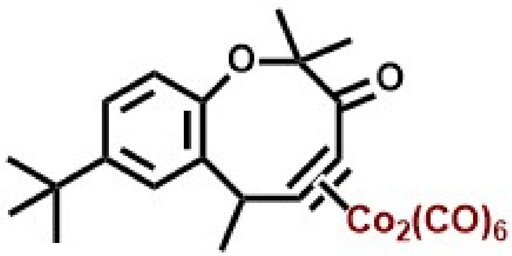


7c

300 MHz, $CDCl_3$

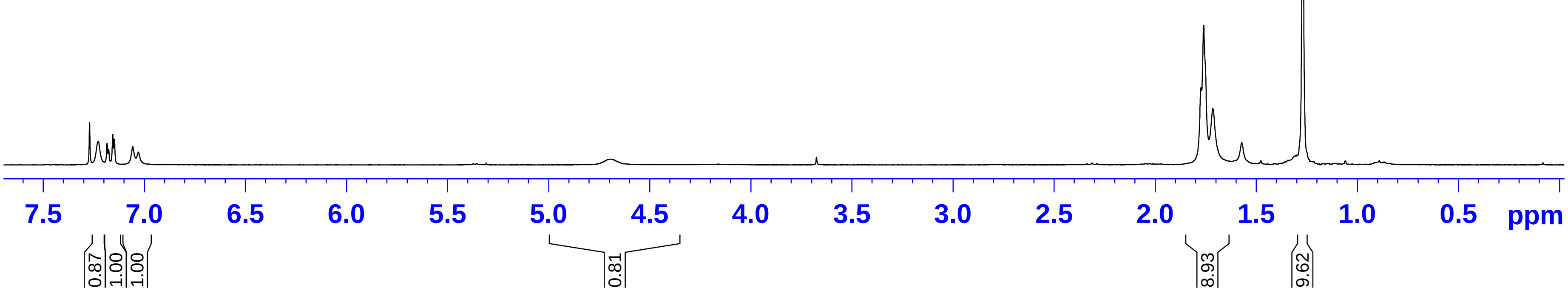

207.440
198.245
151.802
146.987
135.704
126.292
124.699
124.496
98.954
87.965
78.747
77.424
77.000
76.578
38.786
34.208
31.264
O
O
$Co_2(CO)_6$
7c
75 MHz, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

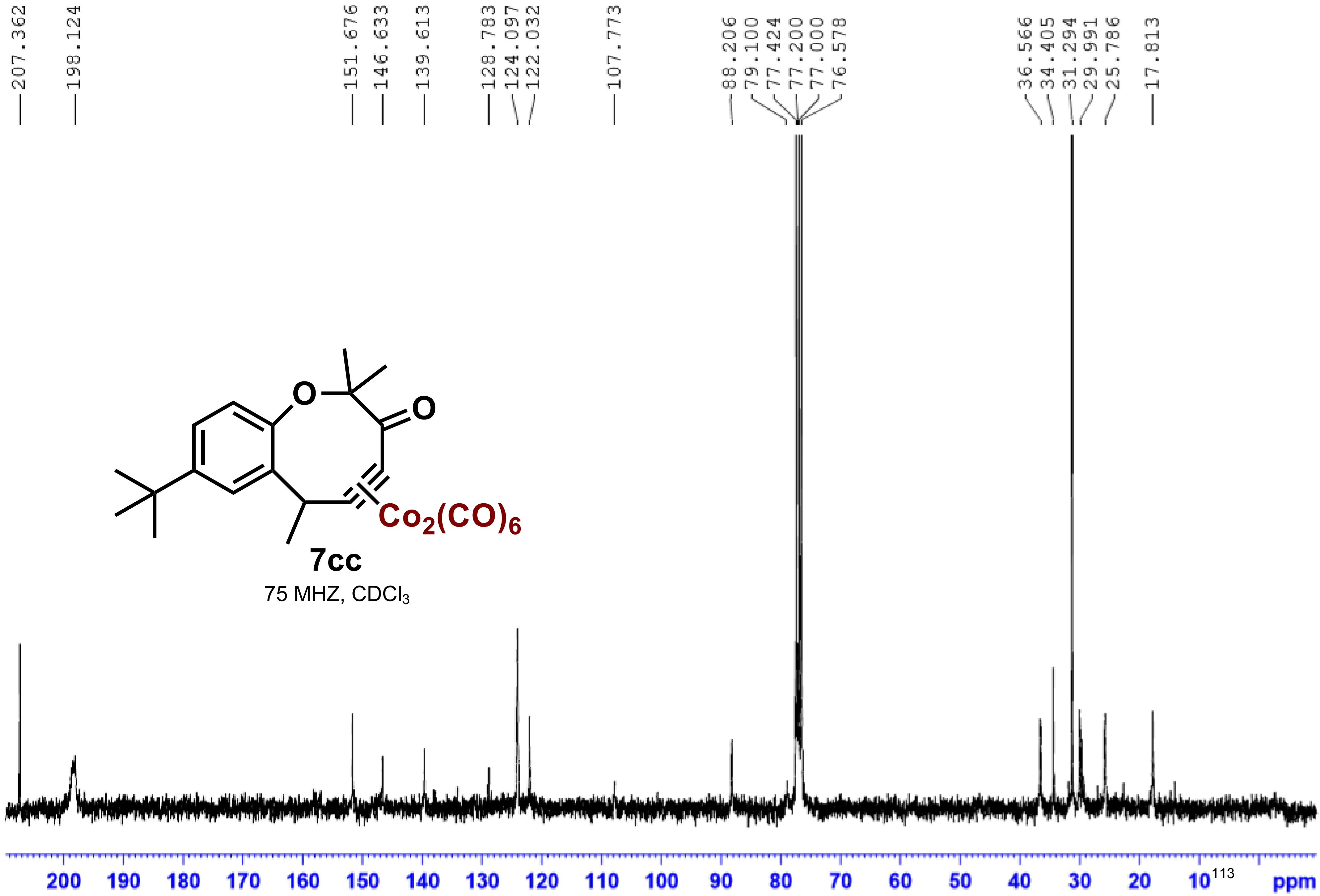
bso.0601 1,

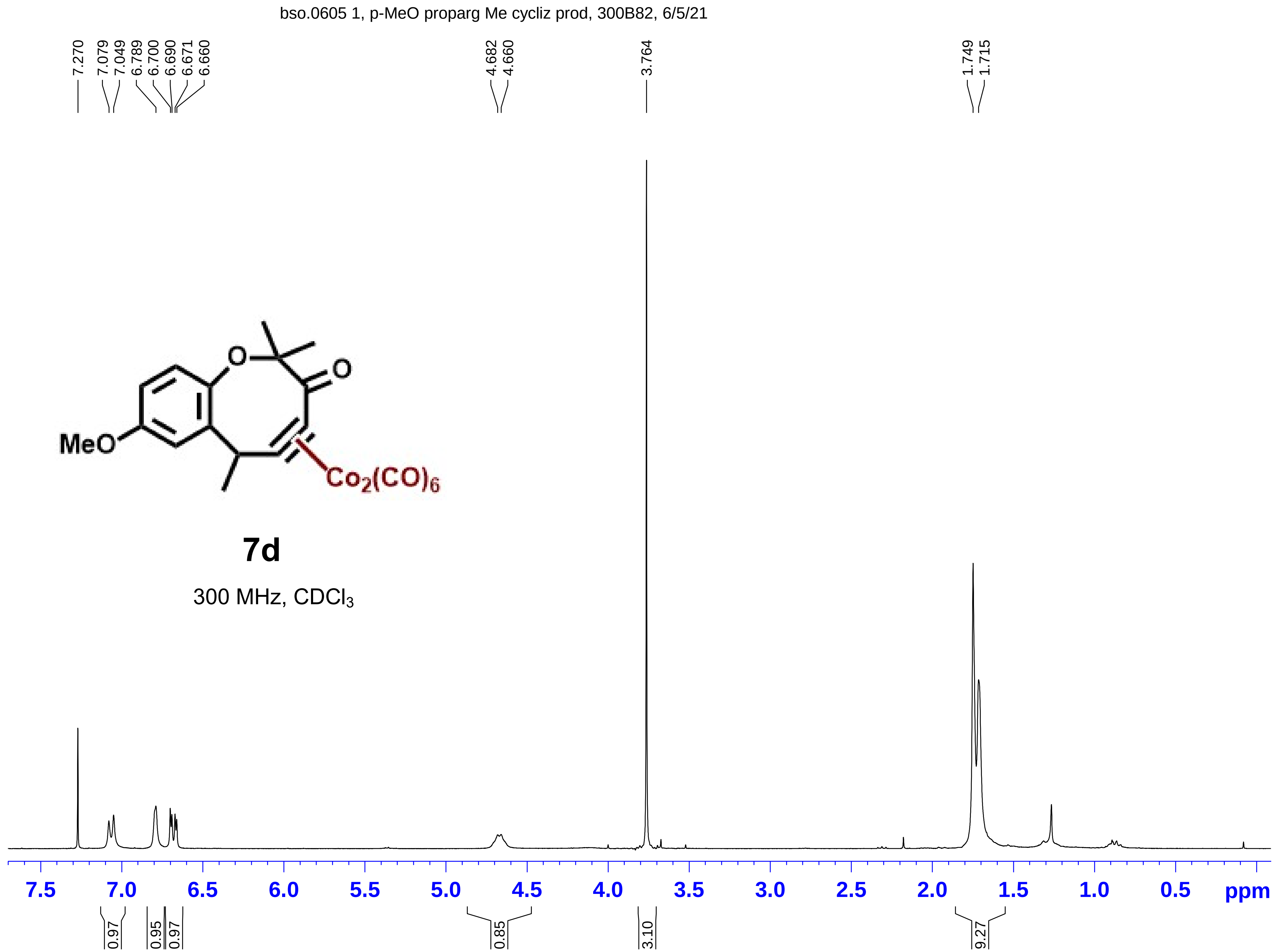


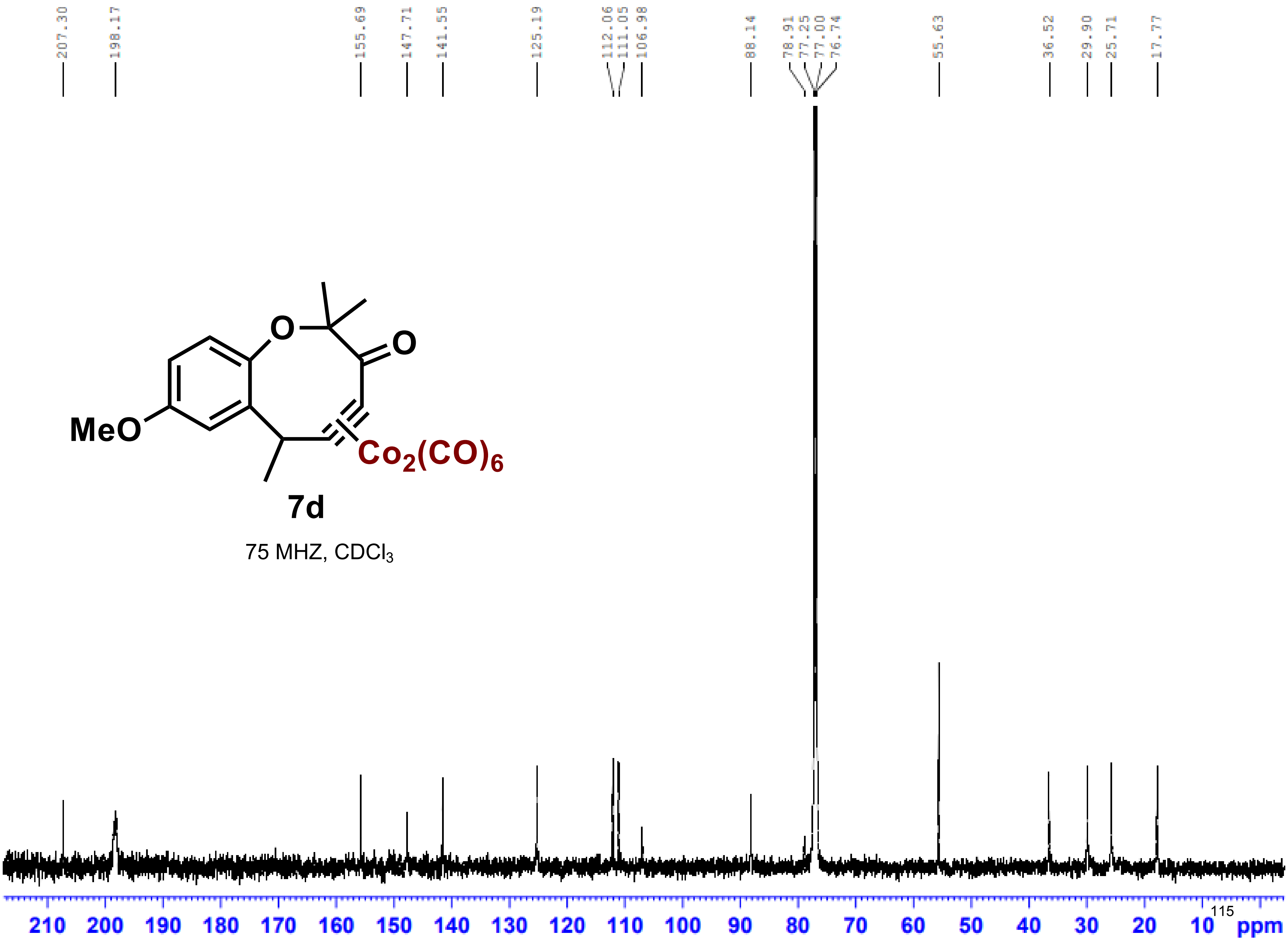
7cc

300 MHz, $CDCl_3$

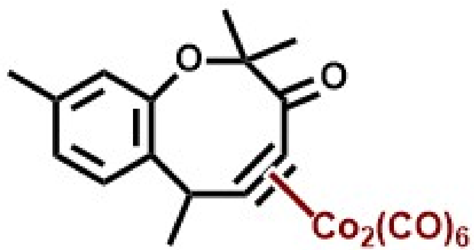



207.362
198.124
151.676
146.633
139.613
128.783
124.097
122.032
107.773
88.206
79.100
77.424
77.200
77.000
76.578
36.566
34.405
31.294
29.991
25.786
17.813
O
O
Co2(CO)6
7cc
75 MHZ, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


bso.0605 1, p-MeO proparg Me cycliz prod, 300B82, 6/5/21
7.270
7.079
7.049
6.789
6.700
6.690
6.671
6.660
4.682
4.660
3.764
1.749
1.715
MeO
O
O
$Co_2(CO)_6$
7d
300 MHz, $CDCl_3$
7.5
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
0.95
0.97
0.85
3.10
9.27

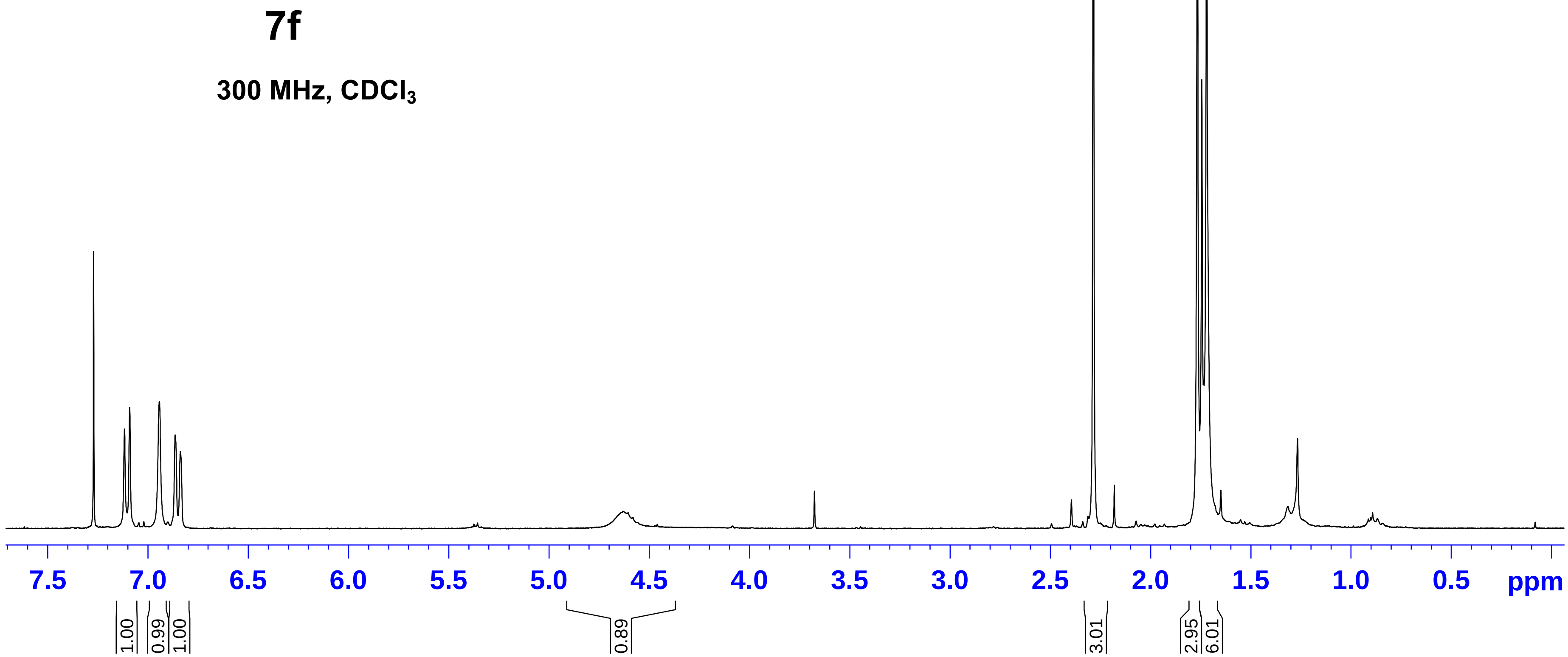

207.30
198.17
155.69
147.71
141.55
125.19
112.06
111.05
106.98
88.14
78.91
77.25
77.00
76.74
55.63
36.52
29.90
25.71
17.77
MeO
O
$Co_2(CO)_6$
7d
75 MHZ, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

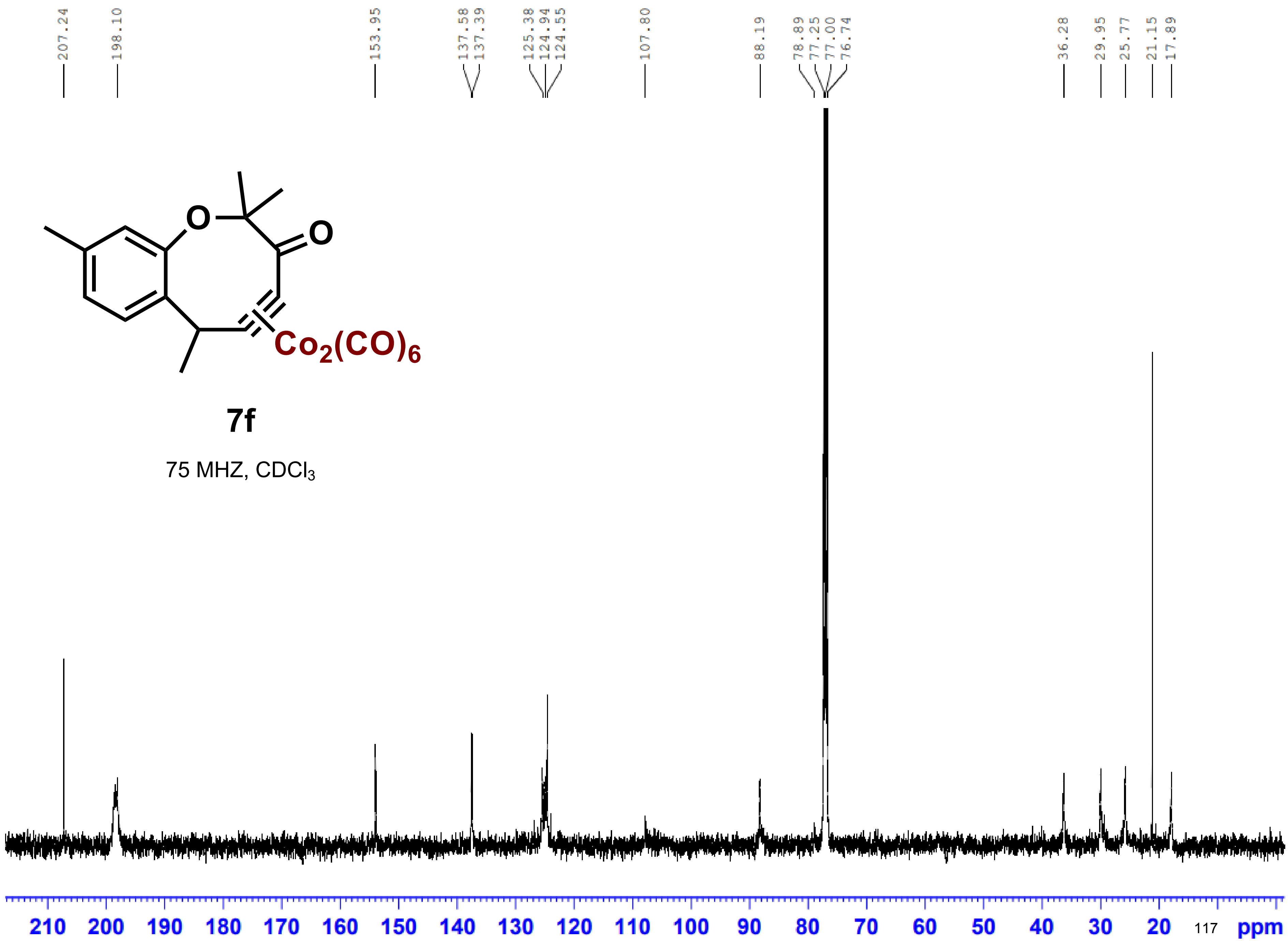
bso.0603 3, m-Me-propargyl Me cycliz prod, again 6/6/21

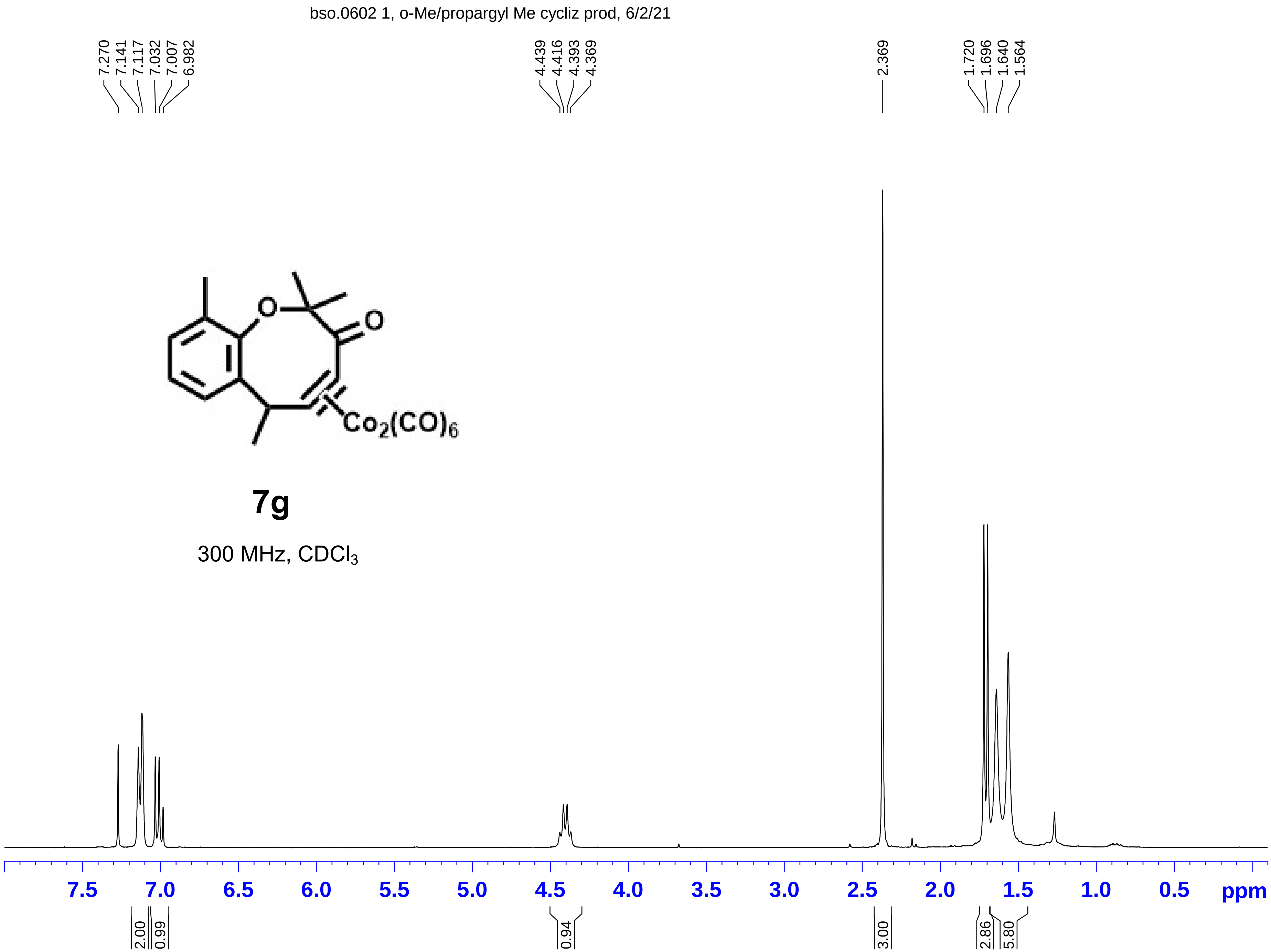


7f

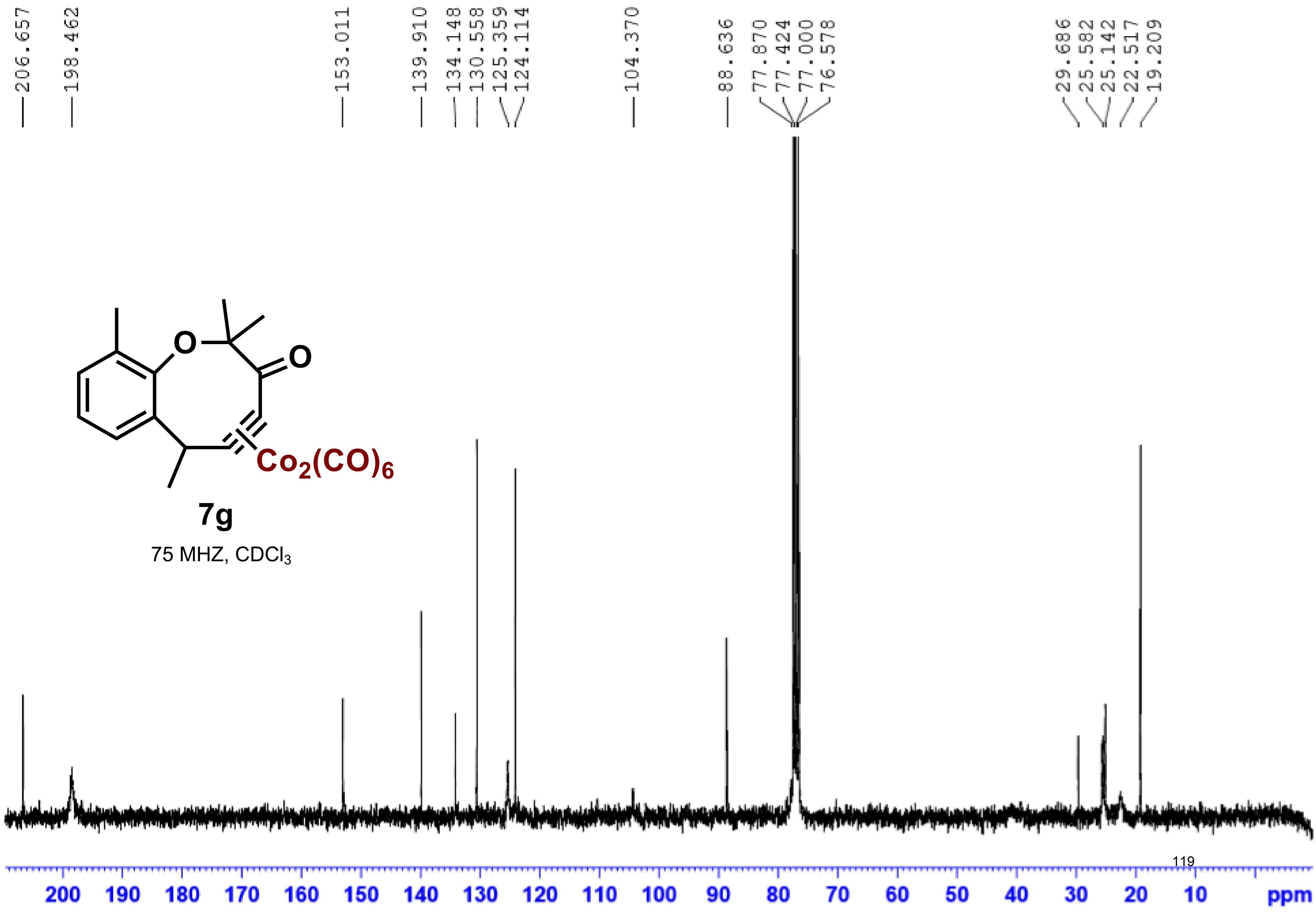
300 MHz, $CDCl_3$




207.24
198.10
153.95
137.58
137.39
125.38
124.94
124.55
107.80
88.19
78.89
77.25
77.00
76.74
36.28
29.95
25.77
21.15
17.89
O
O
$Co_2(CO)_6$
7f
75 MHZ, $CDCl_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

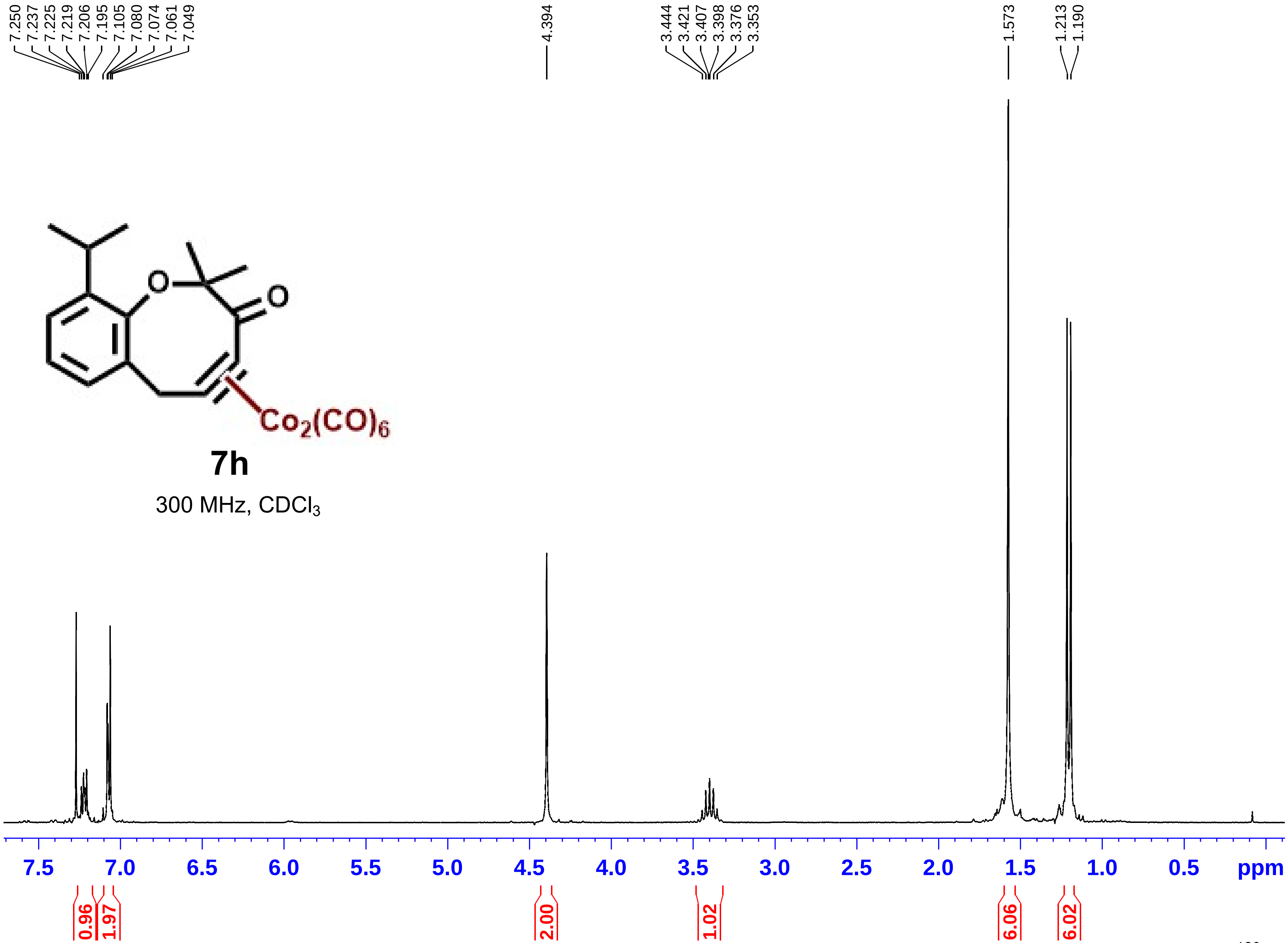


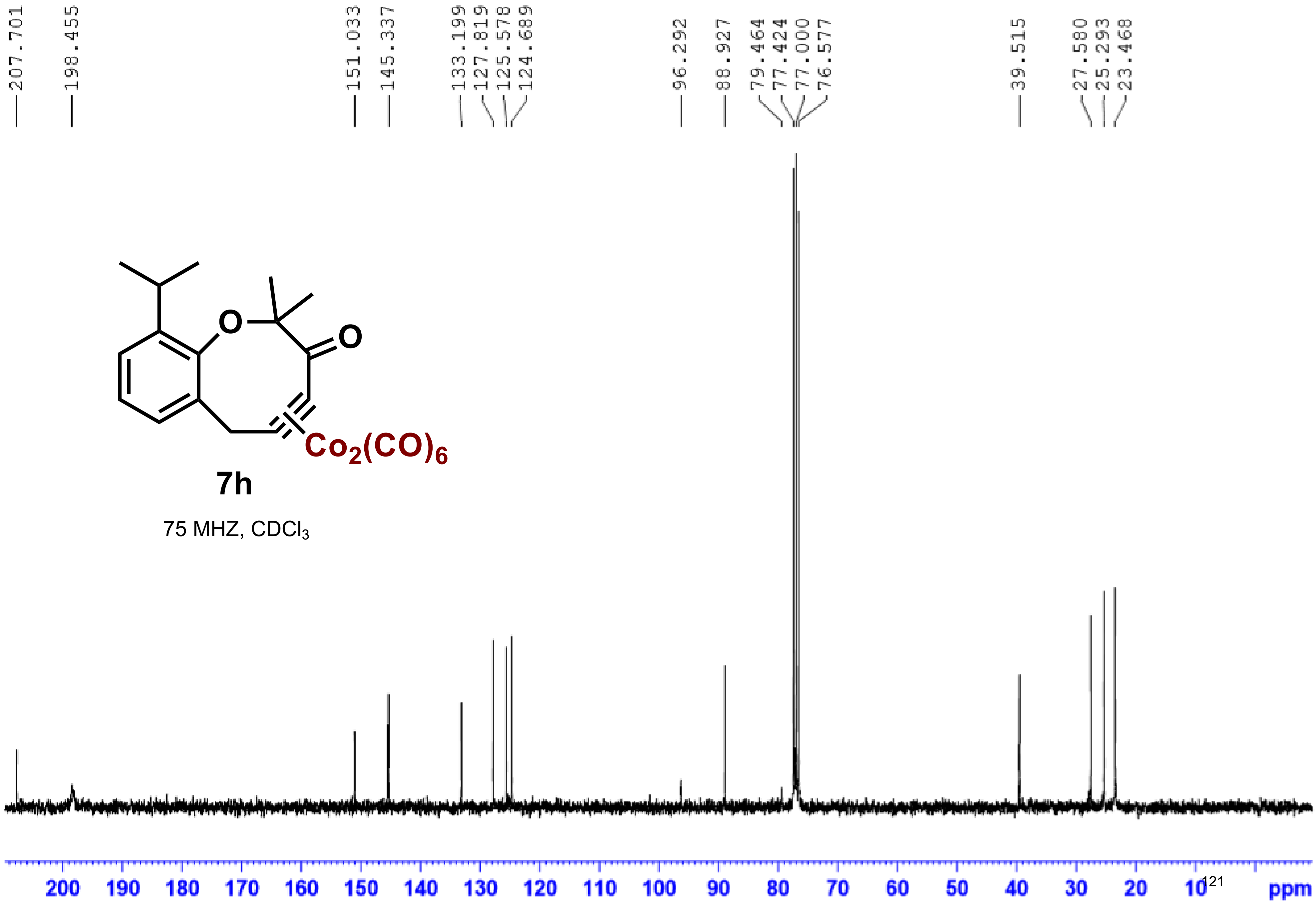
bso.0602 1, o-Me/propargyl Me cycliz prod, 6/2/21
7.270
7.141
7.117
7.032
7.007
6.982
4.439
4.416
4.393
4.369
2.369
1.720
1.696
1.640
1.564
Co2(CO)6
7g
300 MHz, CDCl3
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
0.99
0.94
3.00
2.86
5.80

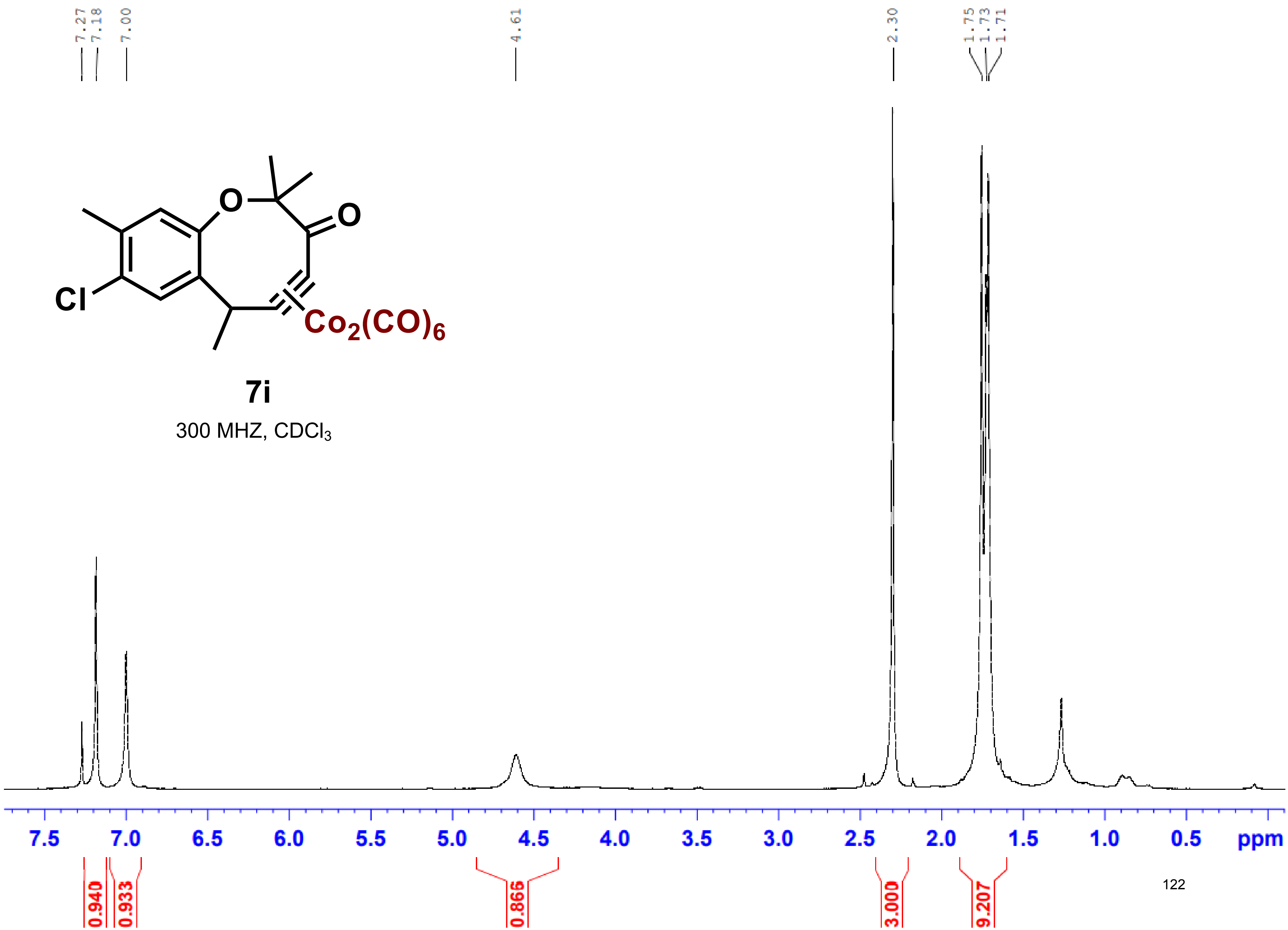


206.657
198.462
153.011
139.910
134.148
130.558
125.359
124.114
104.370
88.636
77.870
77.424
77.000
76.578
29.686
25.582
25.142
22.517
19.209
O
O
$Co_2(CO)_6$
7g
75 MHZ, $CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

bso.161M-1 2-isopropyl

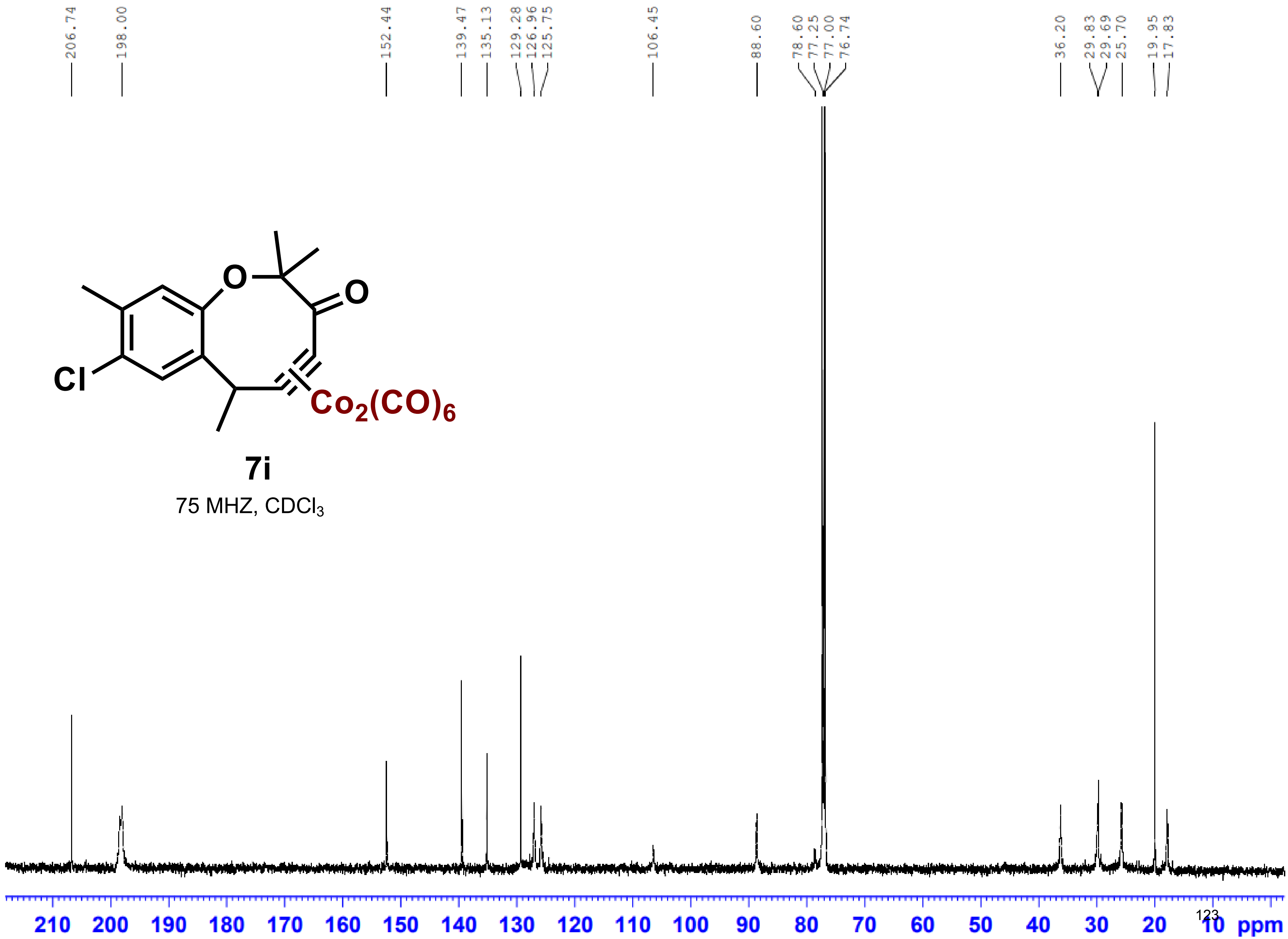


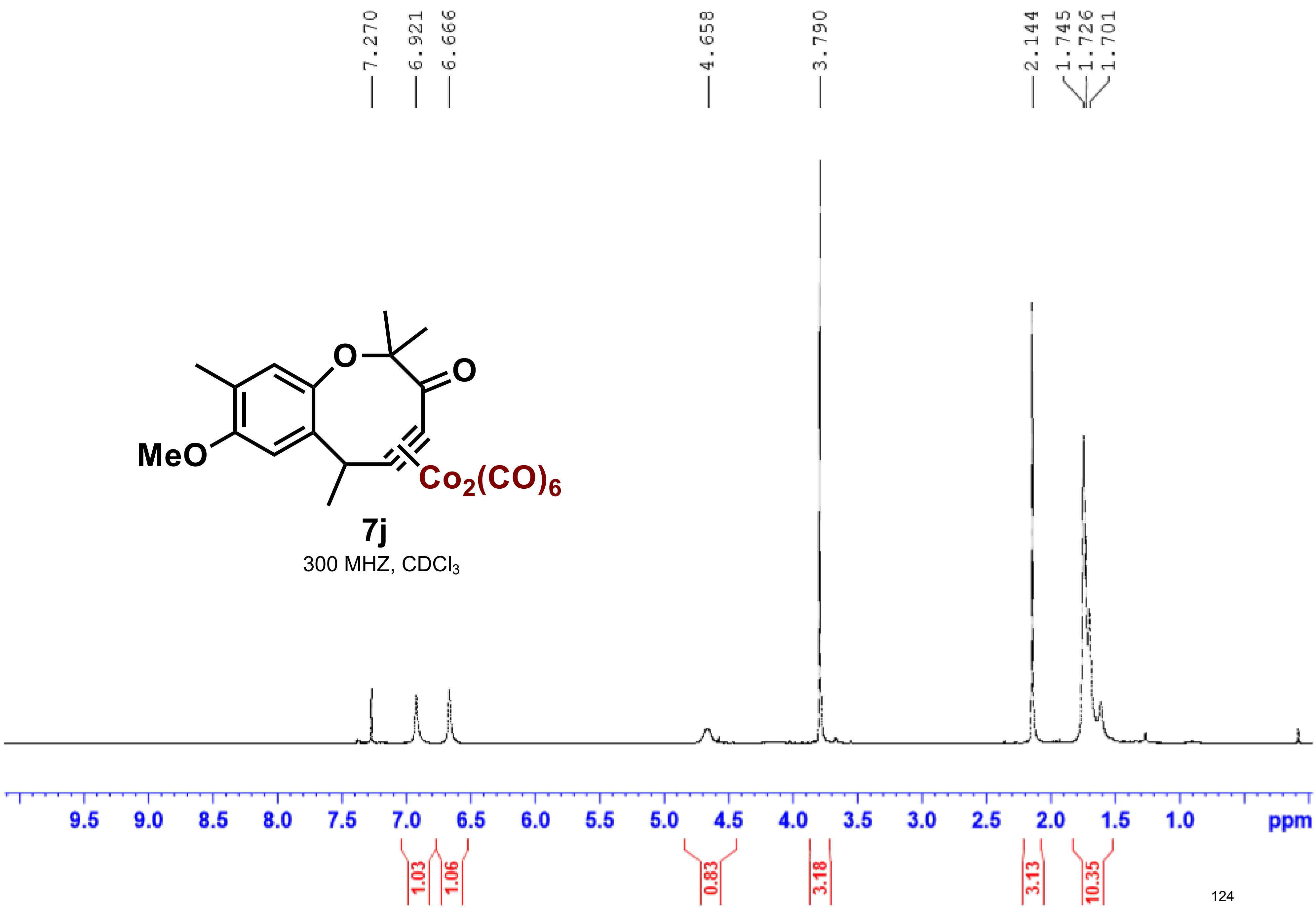

207.701
198.455
151.033
145.337
133.199
127.819
125.578
124.689
96.292
88.927
79.464
77.424
77.000
76.577
39.515
27.580
25.293
23.468
O
O
$Co_2(CO)_6$
7h
75 MHZ, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

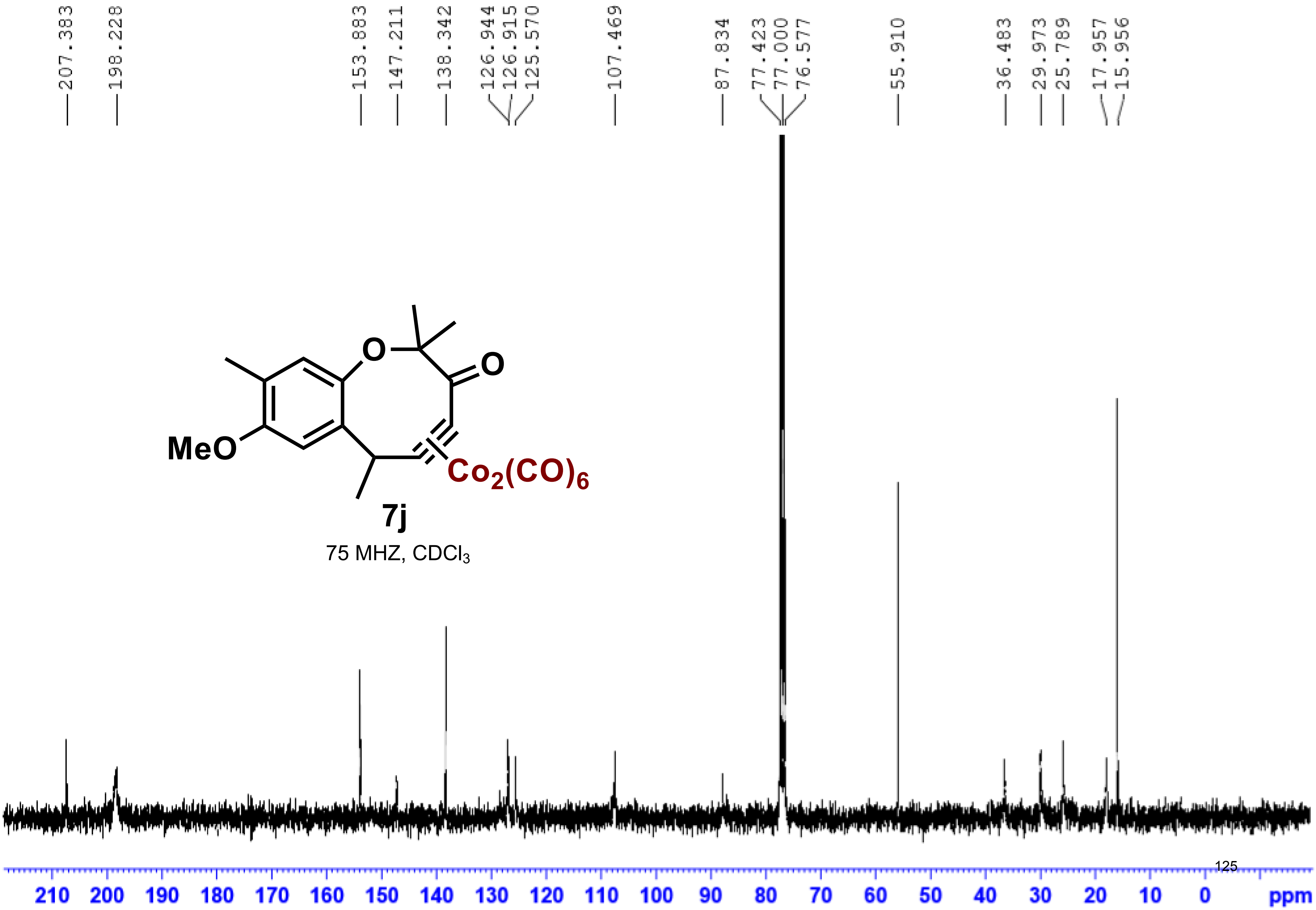


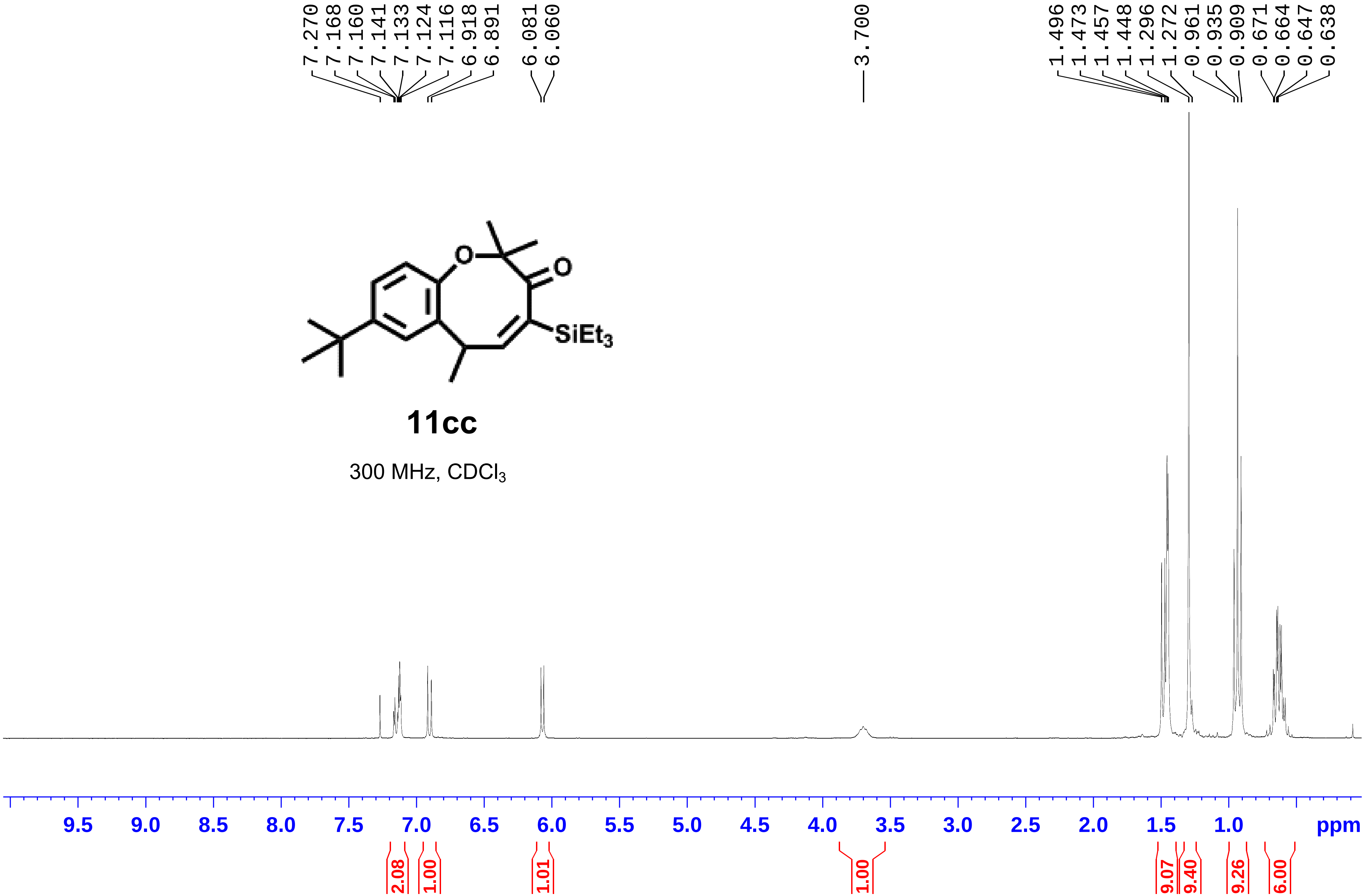
7i

300 MHZ, $CDCl_3$

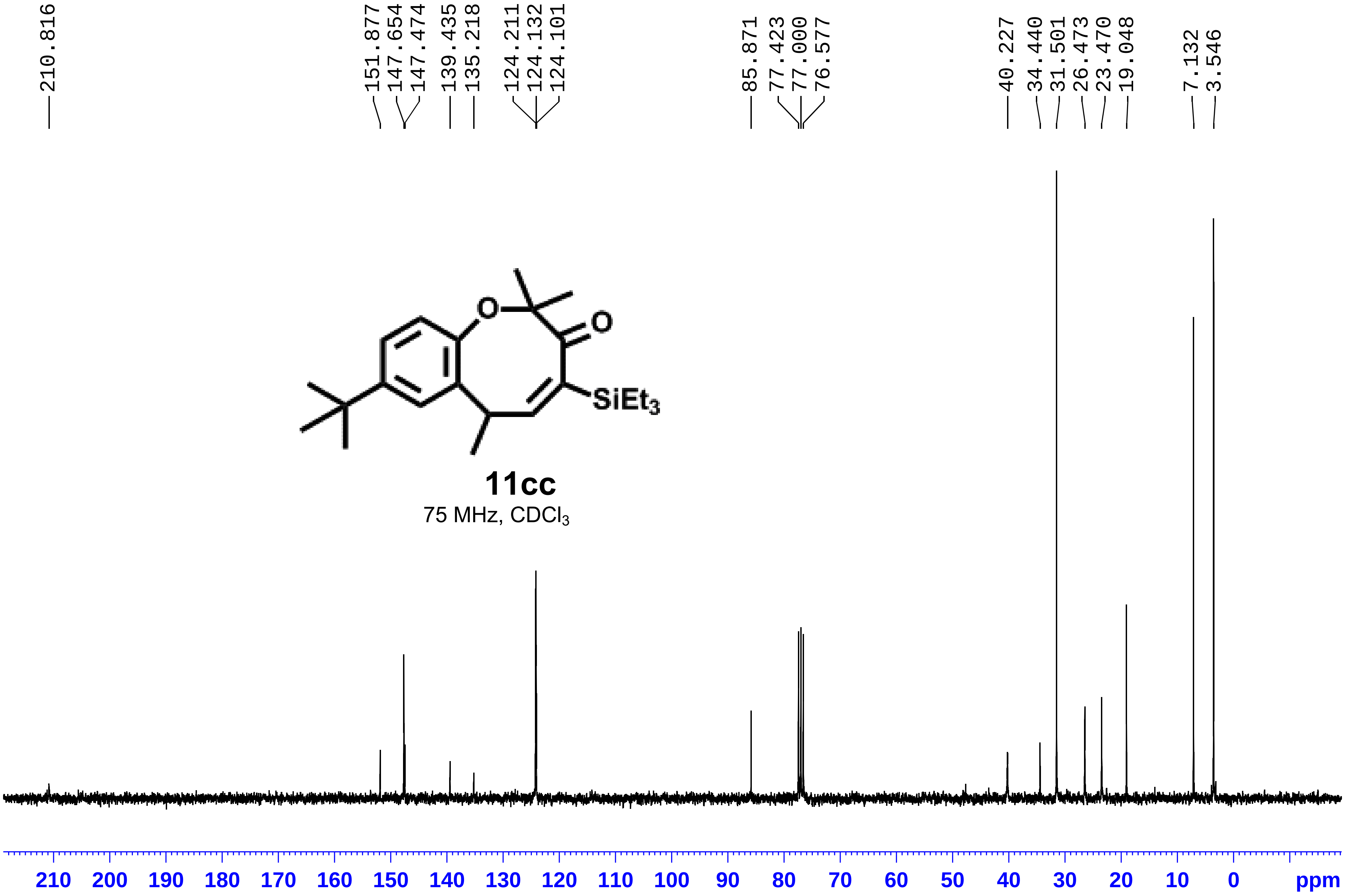

206.74
198.00
152.44
139.47
135.13
129.28
126.96
125.75
106.45
88.60
78.60
77.25
77.00
76.74
36.20
29.83
29.69
25.70
19.95
17.83
O
O
Cl
$Co_2(CO)_6$
7i
75 MHZ, $CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

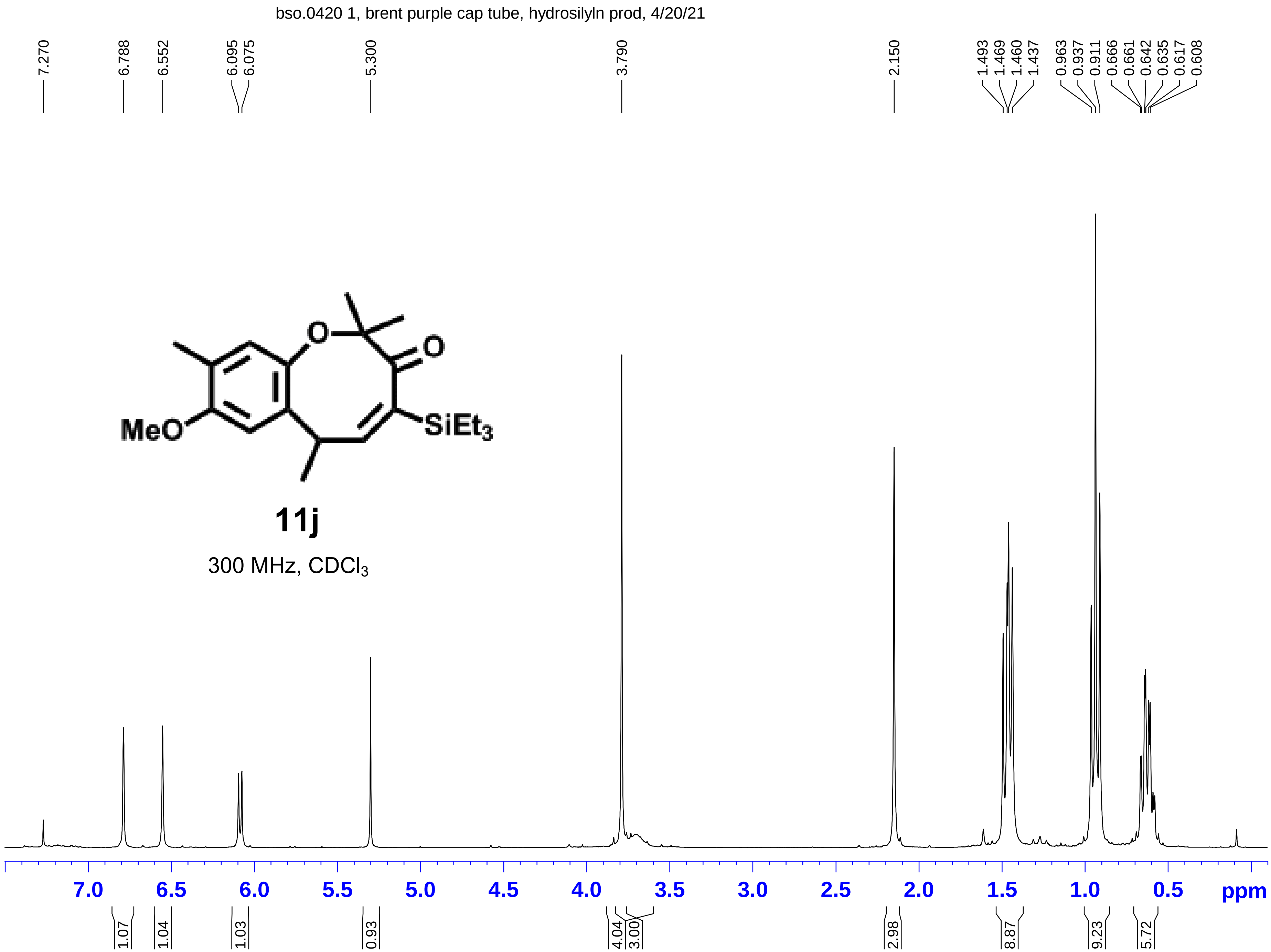

7.270
6.921
6.666
4.658
3.790
2.144
1.745
1.726
1.701
MeO
O
O
Co2(CO)6
7j
300 MHZ, CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.03
1.06
0.83
3.18
3.13
10.35

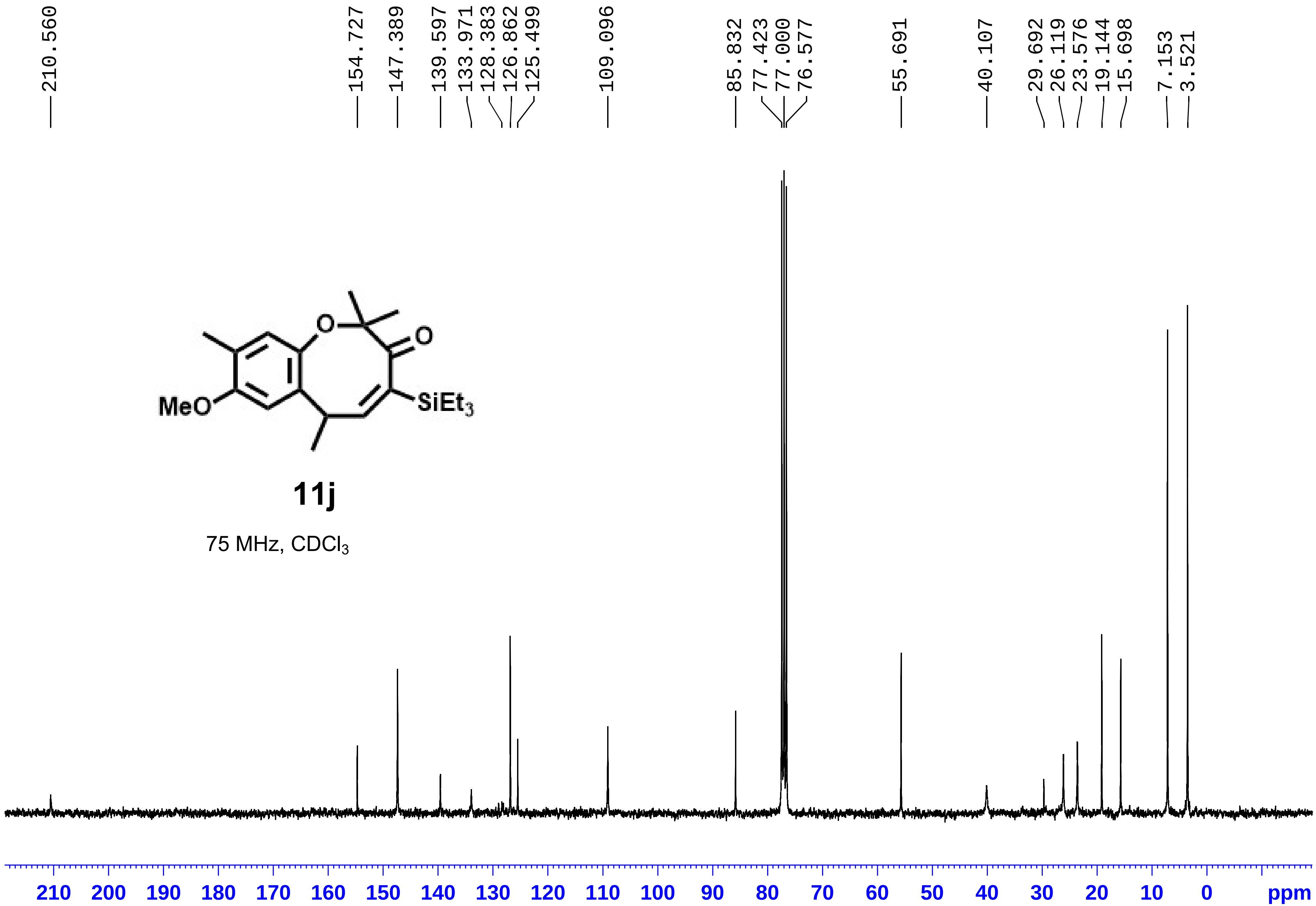

207.383
198.228
153.883
147.211
138.342
126.944
126.915
125.570
107.469
87.834
77.423
77.000
76.577
55.910
36.483
29.973
25.789
17.957
15.956
MeO
O
O
Co2(CO)6
7j
75 MHZ, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



7.270 7.168 7.160 7.141 7.133 7.124 7.116 6.918 6.891
6.081 6.060
3.700
1.496 1.473 1.457 1.448 1.296 1.272 0.961 0.935 0.909 0.671 0.664 0.647 0.638
O
SiEt3
11cc
300 MHz, CDCl3
9.5 9.0 8.5 8.0 7.5 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 ppm
2.08 1.00 1.01 1.00 9.07 9.40 9.26 6.00

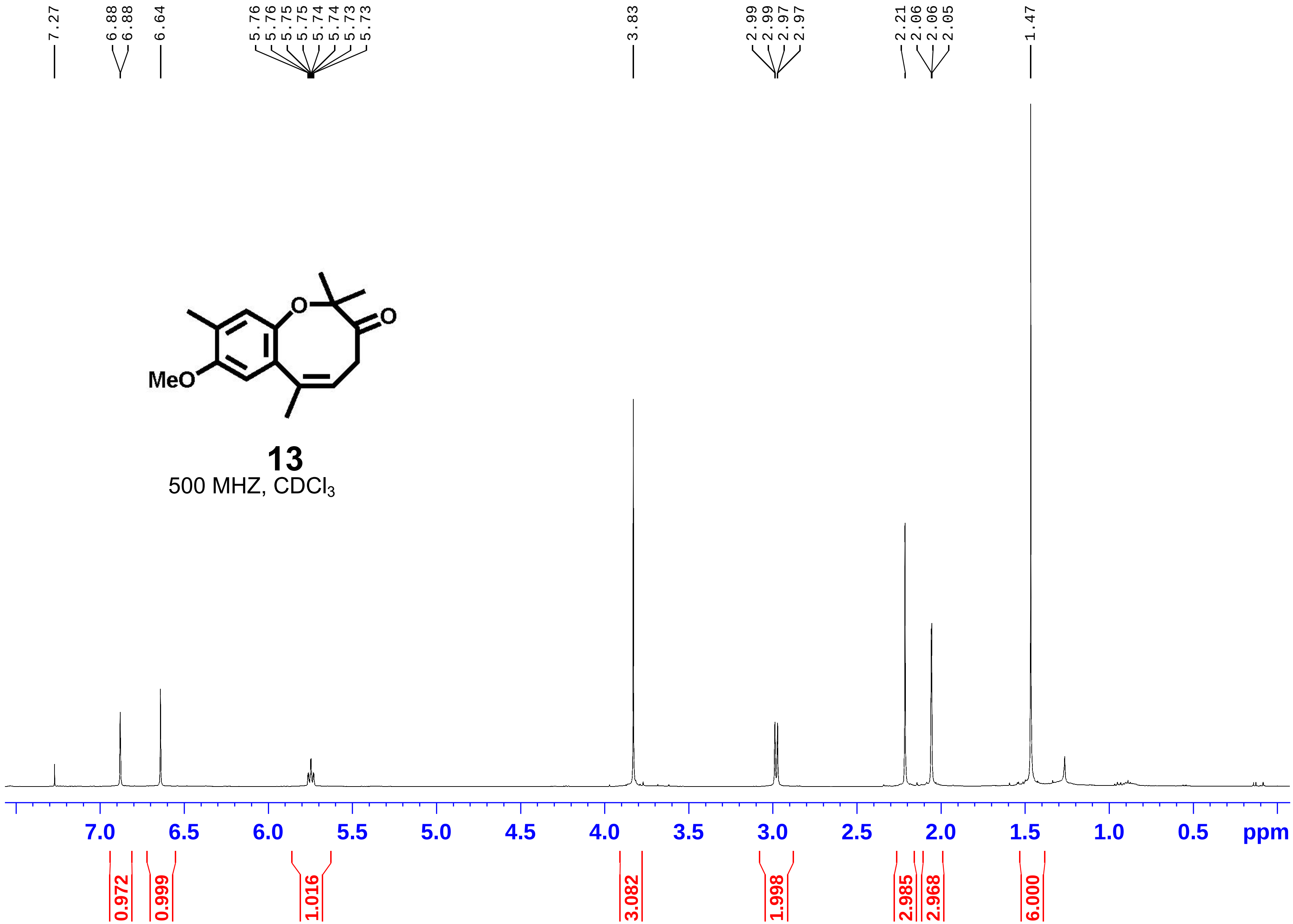

210.816
151.877
147.654
147.474
139.435
135.218
124.211
124.132
124.101
85.871
77.423
77.000
76.577
40.227
34.440
31.501
26.473
23.470
19.048
7.132
3.546
SiEt3
11cc
75 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


bso.0420 1, brent purple cap tube, hydrosilyln prod, 4/20/21
7.270
6.788
6.552
6.095
6.075
5.300
3.790
2.150
1.493
1.469
1.460
1.437
0.963
0.937
0.911
0.666
0.661
0.642
0.635
0.617
0.608
MeO
O
O
SiEt3
11j
300 MHz, CDCl3
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
1.07
1.04
1.03
0.93
4.04
3.00
2.98
8.87
9.23
5.72



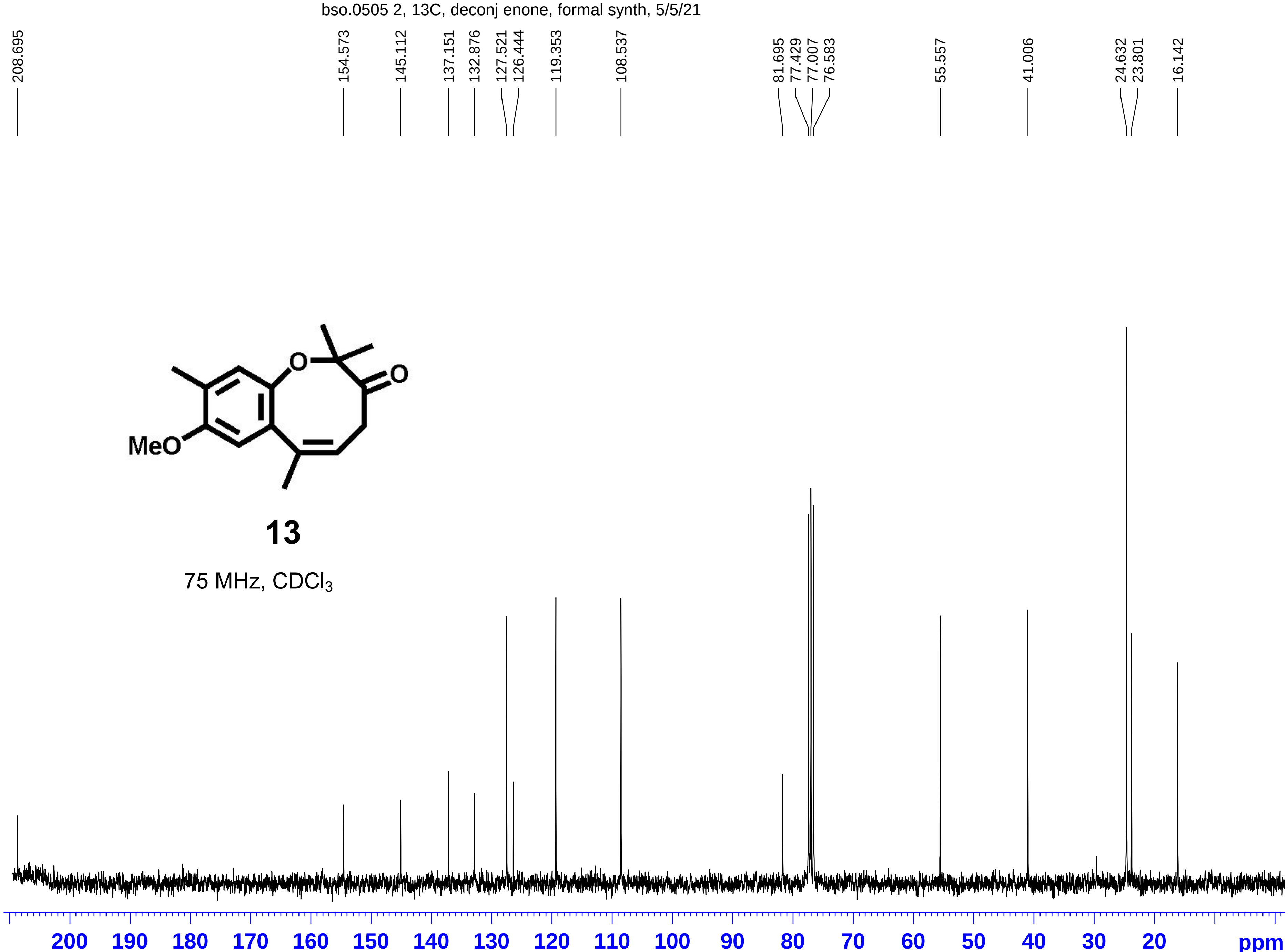
210.560
154.727
147.389
139.597
133.971
128.383
126.862
125.499
109.096
85.832
77.423
77.000
76.577
55.691
40.107
29.692
26.119
23.576
19.144
15.698
7.153
3.521
MeO
O
O
SiEt3
11j
75 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

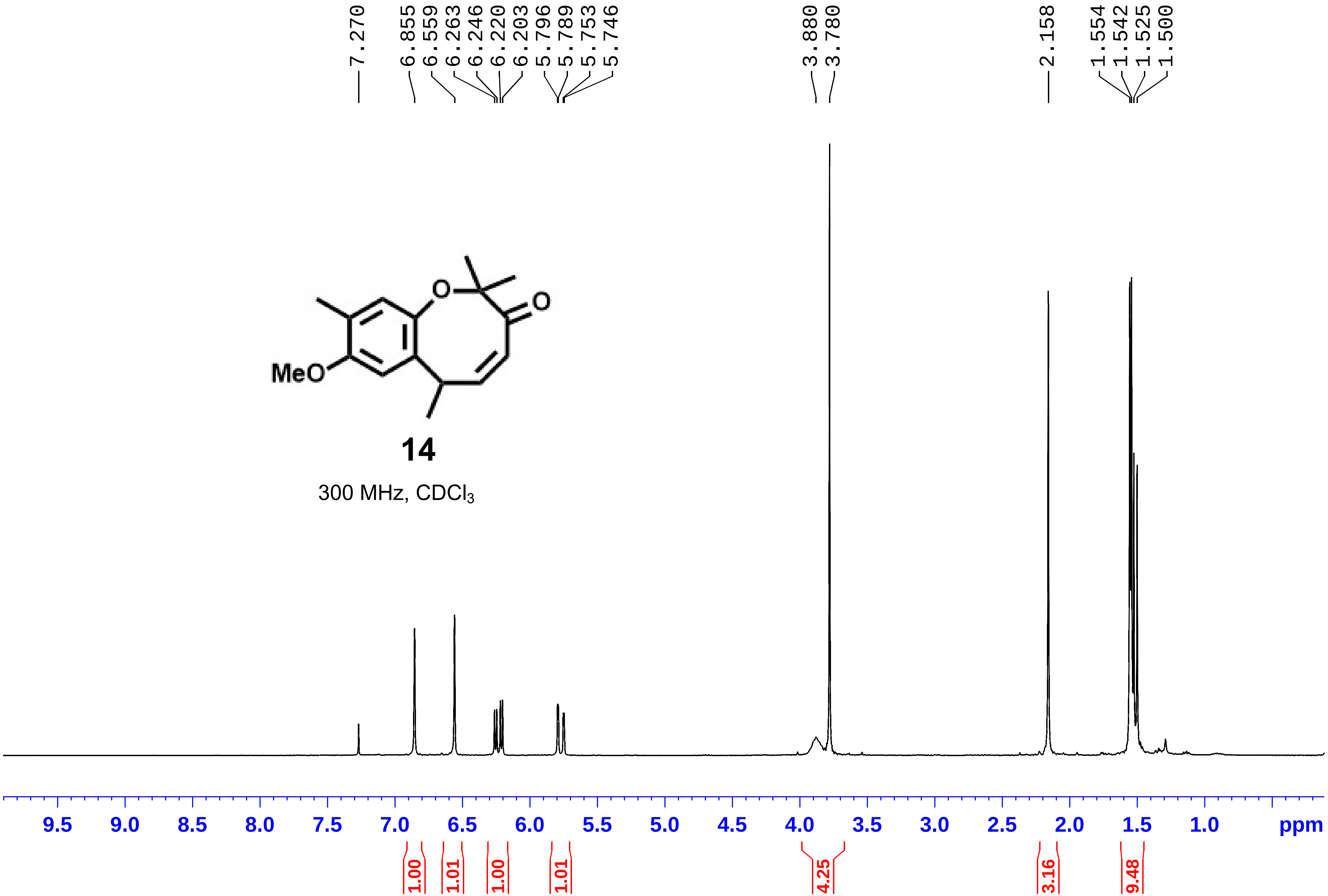
bso.0510 5, deconj ketone formal synth, 1H, 5/10/21

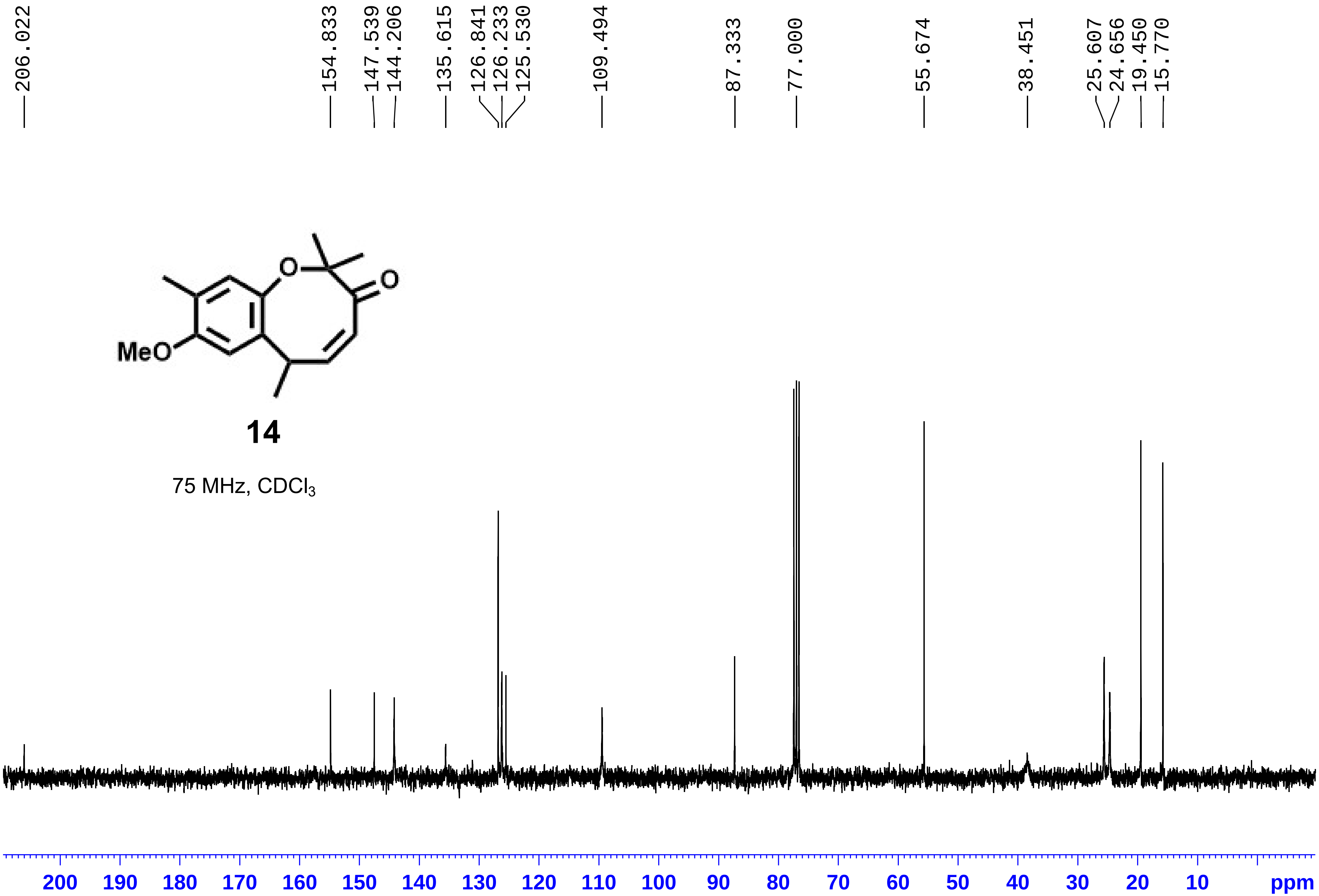


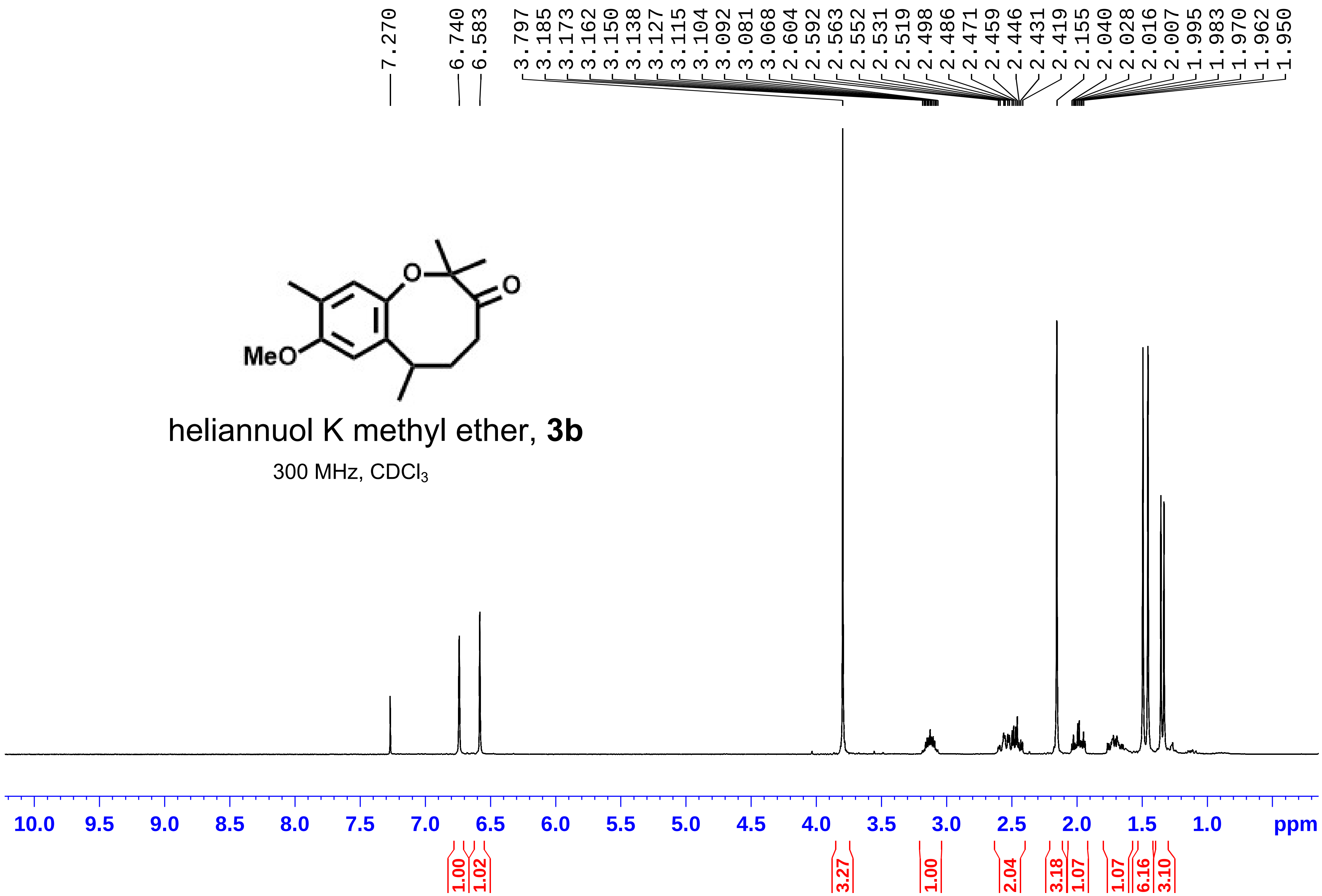
13

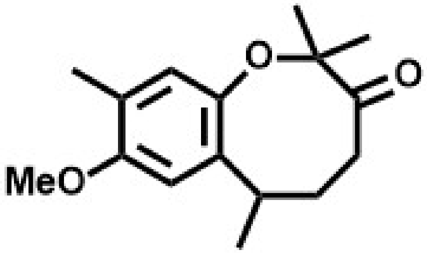
500 MHZ, $CDCl_3$


bso.0505 2, 13C, deconj enone, formal synth, 5/5/21
208.695
154.573
145.112
137.151
132.876
127.521
126.444
119.353
108.537
81.695
77.429
77.007
76.583
55.557
41.006
24.632
23.801
16.142
MeO
O
13
75 MHz, $CDCl_3$
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm


7.270
6.855
6.559
6.263
6.246
6.220
6.203
5.796
5.789
5.753
5.746
3.880
3.780
2.158
1.554
1.542
1.525
1.500
MeO
O
O
14
300 MHz, $CDCl_3$
9.5
9.0
8.5
8.0
7.5
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
ppm
1.00
1.01
1.00
1.01
4.25
3.16
9.48


206.022
154.833
147.539
144.206
135.615
126.841
126.233
125.530
109.494
87.333
77.000
55.674
38.451
25.607
24.656
19.450
15.770
MeO
O
14
75 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


heliannuol K methyl ether, **3b**
300 MHz, $CDCl_3$
MeO
O
7.270
6.740
6.583
3.797
3.185
3.173
3.162
3.150
3.138
3.127
3.115
3.104
3.092
3.081
3.068
2.604
2.592
2.563
2.552
2.531
2.519
2.498
2.486
2.471
2.459
2.446
2.431
2.419
2.155
2.040
2.028
2.016
2.007
1.995
1.983
1.970
1.962
1.950
10.0 9.5 9.0 8.5 8.0 7.5 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 ppm
1.00
1.02
3.27
1.00
2.04
3.18
1.07
1.07
6.16
3.10



heliannuol K methyl ether, **3b**

75 MHz, $CDCl_3$