Electronic supplementary information for:

Palladium-Catalyzed Cascade Carbonylative Annulation between Alkene-tethered Aryl Iodides and Carbon Monoxide

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1. General Information:

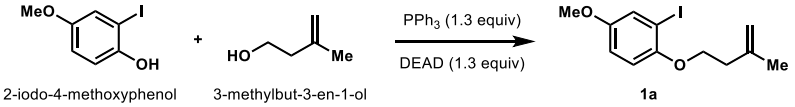
Unless otherwise stated, all reactions were performed in oven-dried or flame-dried glassware under an atmosphere of dry nitrogen. Anhydrous dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), N,N-dimethyl formamide (DMF), toluene, hexane, and acetonitrile were obtained by passing these previously degassed solvents through activated alumina columns. Dry N,N-dimethylacetamide (DMA) was purchased from Energy Chemical (water ≤ 50 ppm by K.F.) All other solvents and reagents were used as received without further purification.

Reactions were monitored by thin layer chromatography (TLC) (250 μm thickness, F-254 indicator) and visualized by UV irradiation and staining with phosphomolybdic acid as developing agent. Volatile solvents were removed under reduced pressure using a rotary evaporator. Flash column chromatography was performed over silica gel (230-400 mesh) purchased from Yantai Xinnuo Co., China.

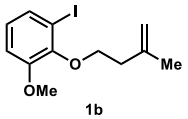
Proton nuclear magnetic resonance (^{1}H-NMR) and carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on a Bruker AV 600 MHz spectrometer using residue solvent peaks as an internal standard (^{1}H-NMR: $CDCl_3$ = 7.26, Benzene-d_6 = 7.16; ^{13}C-NMR: $CDCl_3$ = 77.16, Benzene-d_6 = 128.06). Chemical shifts are reported in parts per million (ppm) with respect to the residual solvent signal. Peak multiplicities are reported as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, m = multiplet. IR spectra were recorded on a Bruker Tensor27 FT-IR spectrometer. High-resolution mass spectra (HRMS) were collected on a Bruker Maxis System. X-ray crystallographic analyses were performed on Bruker D8 Quest or Bruker D8 Venture. HPLC analysis was performed on Thermo UltiMate3000. CHIRALCEL OD-3 column was purchased from Daicel Chemical Industries, LTD.

2. Synthesis of the Substrates:

Synthesis of 1a:

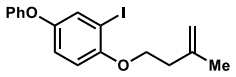


To a solution of 2-iodo-4-methoxyphenol[1] (1 g, 4.00 mmol, 1.0 equiv) in CH_2Cl_2 (40 mL) was added PPh_3 (1.36 g, 5.20 mmol, 1.3 equiv) and 3-methyl-3-buten-1-ol (448 mg, 5.20 mmol, 1.3 equiv) at room temperature. The reaction mixture was cooled to 0 °C and DEAD (10.4 mL, 5.20 mmol, 1.3 equiv, 0.5 M in CH_2Cl_2) was added dropwise via syringe over the course of 20 min. After stirring for 4 h at this temperature, the reaction mixture was quenched with water (40 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with brine (40 mL), dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **1a** (0.89 g, 71%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.33 (d, J = 2.8 Hz, 1H), 6.84 (dd, J = 8.8 and 2.8 Hz, 1H), 6.75 (d, J = 8.8 Hz, 1H), 4.85 (s, 1H), 4.83 (s, 1H), 4.05 (t, J = 6.8 Hz, 2H), 3.75 (s, 3H), 2.54 (t, J = 6.8 Hz, 2H), 1.83 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 154.5, 152.3, 142.3, 124.8, 114.9, 113.5, 112.4, 87.2, 69.2, 56.1, 37.5, 23.1; IR (KBr, cm^{-1}) 3056, 2957, 1729, 1486, 1279, 1137, 1075, 849, 661; HRMS (ESI) calcd. for $[C_{12}H_{15}IO_2Na]^+$ $(M+Na)^+$: *m/z* 341.0009, found 340.9998.



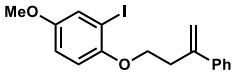
1b

1b was prepared from 2-iodo-6-methoxyphenol[2] and 3-methyl-3-buten-1-ol following the same procedure that was used for preparation of **1a**. The reaction mixture was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **1b** (in 73% yield) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.34 (d, J = 7.8 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 6.78 (dd, J = 8.8 and 7.8 Hz, 1H), 4.84 (s, 1H), 4.83 (s, 1H), 4.08 (t, J = 7.0 Hz, 2H), 3.84 (s, 3H), 2.60 (t, J = 7.0 Hz, 2H), 1.83 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 153.1, 148.3, 142.5, 130.8, 125.9, 112.8, 112.0, 93.2, 71.5, 56.1, 38.4, 23.0; IR (KBr, cm^{-1}) 3075, 2941, 1575, 1468, 1260, 1032, 889, 765, 636; HRMS (ESI) calcd. for $[C_{12}H_{15}IO_2Na]^+$ $(M+Na)^+$: *m/z* 341.0009, found 341.0000.



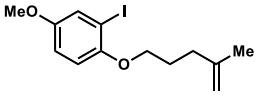
1c

1c was prepared from 2-iodo-4-phenoxyphenol[3] and 3-methyl-3-buten-1-ol following the same procedure that was used for preparation of **1a**. The reaction mixture was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **1c** (in 68% yield) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.37 (d, J = 2.8 Hz, 1H), 7.23-7.18 (m, 2H), 6.97 (dd, J = 7.4 and 7.4 Hz, 1H), 6.88 (dd, J = 8.8 and 2.8 Hz, 1H), 6.86-6.82 (m, 2H), 6.67 (d, J = 8.8 Hz, 1H), 4.77 (s, 1H), 4.75 (s, 1H), 3.00 (t, J = 6.8 Hz, 2H), 2.47 (t, J = 6.8 Hz, 2H), 1.75 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 158.0, 154.2, 150.9, 142.1, 130.6, 129.8, 129.8, 123.1, 120.3, 118.0, 118.0, 112.8, 112.6, 86.8, 68.8, 37.3, 23.1; IR (KBr, cm^{-1}) 3072, 2928, 1586, 1481, 1264, 1217, 1043, 884; HRMS (ESI) calcd. for $[C_{17}H_{17}IO_2Na]^+$ $(M+Na)^+$: *m/z* 403.0165, found 403.0157.



1d

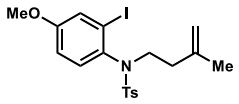
1d was prepared from 2-iodo-4-methoxyphenol and 3-phenylbut-3-en-1-ol[4] following the same procedure that was used for preparation of **1a**. The reaction mixture was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **1d** (in 65% yield) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.45 (d, J = 7.8 Hz, 2H), 7.33 (dd, J = 7.8 and 7.4 Hz, 2H), 7.31 (d, J = 3.0 Hz, 1H), 7.27 (dd, J = 7.4 and 7.4 Hz, 1H), 6.78 (dd, J = 8.8 and 3.0 Hz, 1H), 6.66 (d, J = 8.8 Hz, 1H), 5.41 (s, 1H), 5.23 (s, 1H), 4.03 (t, J = 7.0 Hz, 2H), 3.72 (s, 3H), 3.04 (t, J = 6.8 Hz, 2H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 154.5, 152.1, 144.5, 140.7, 128.5, 128.5, 127.7, 126.3, 126.3, 124.8, 114.9, 114.9, 113.6, 87.3, 69.2, 56.0, 35.3; IR (KBr, cm^{-1}) 3026, 2954, 1627, 1571, 1489, 1217, 1112, 1040, 901; HRMS (ESI) calcd. for $[C_{17}H_{17}IO_2Na]^+$ $(M+Na)^+$: *m/z* 403.0165, found 403.0159.



1e

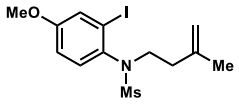
1e was prepared from 2-iodo-4-methoxyphenol and 4-methylpent-4-en-1-ol following the same procedure that was used for preparation of **1a**. The reaction mixture was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **1e** (in 72% yield) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.32 (d, J = 2.8 Hz, 1H), 6.84 (dd, J = 8.8 and 2.8 Hz, 1H), 6.74 (d, J = 8.8

Hz, 1H), 4.78-4.71 (m, 2H), 3.95 (t, *J* = 6.2 Hz, 2H), 3.75 (s, 3H), 2.26 (t, *J* = 7.6 Hz, 2H), 1.99-1.92 (m, 2H), 1.76 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 154.4, 152.4, 145.1, 124.8, 115.0, 113.3, 110.6, 87.2, 69.7, 56.1, 34.3, 27.4, 22.6; IR (KBr, cm^{-1}) 3647, 2939, 1570, 1489, 1216, 1147, 1041, 845, 766; HRMS (ESI) calcd. for $[C_{13}H_{17}IO_2Na]^+$ $(M+Na)^+$: *m/z* 355.0165, found 355.0165.



1j

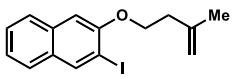
1j was prepared from N-(2-iodo-4-methoxyphenyl)-4-methyl benzenesulfonamide[5] and 3-methyl-3-buten-1-ol following the same procedure that was used for preparation of **1a**. The reaction mixture was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **1j** (in 75% yield) as a white solid; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.63 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 2.8 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.81 (dd, *J* = 8.8 and 2.8 Hz, 1H), 4.72 (s, 1H), 4.61 (s, 1H), 3.79 (s, 3H), 3.72 (ddd, *J* = 13.2, 11.4 and 5.4 Hz, 1H), 2.48 (ddd, *J* = 13.2, 11.4 and 5.4 Hz, 1H), 2.44 (s, 3H), 2.31 (ddd, *J* = 14.8, 11.4 and 5.2 Hz, 1H), 2.12 (ddd, *J* = 14.8, 11.4 and 5.2 Hz, 1H), 1.65 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 159.5, 143.7, 142.4, 136.4, 134.2, 130.6, 130.6, 129.6, 129.6, 128.3, 125.2, 114.8, 112.0, 103.7, 55.8, 50.6, 36.5, 22.8, 21.7; IR (KBr, cm^{-1}) 3559, 3073, 1648, 1592, 1486, 1349, 1161, 685, 554; HRMS (ESI) calcd. for $[C_{19}H_{22}INO_3SNa]^+$ $(M+Na)^+$: *m/z* 494.0257, found 494.0249.



1k

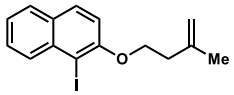
1k was prepared from N-(2-iodo-4-methoxyphenyl) methanesulfonamide[6] and 3-methyl-3-buten-1-ol following the same procedure that was used for preparation of **1a**. The reaction mixture was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **1k** (in 73% yield) as a white solid; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.43 (d, *J* = 3.0 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 6.92 (dd, *J* = 8.8 and 3.0 Hz, 1H), 4.77 (s, 1H), 4.69 (s, 1H), 3.86-3.82 (m, 1H), 3.80 (s, 3H), 3.62-3.55 (m, 1H), 3.05 (s, 3H), 2.29 (t, *J* = 8.0 Hz, 2H), 1.69 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 159.8, 142.3, 133.7, 132.7, 125.4, 115.0, 112.2, 101.8, 55.9, 50.1, 40.8, 36.9, 22.7; IR (KBr, cm^{-1}) 3077, 1591, 1486,

1338, 1151, 1028, 961, 766, 524; HRMS (ESI) calcd. for $[C_{13}H_{18}INO_3SNa]^+$ $(M+Na)^+$: *m/z* 417.9944, found 417.9936.



1m

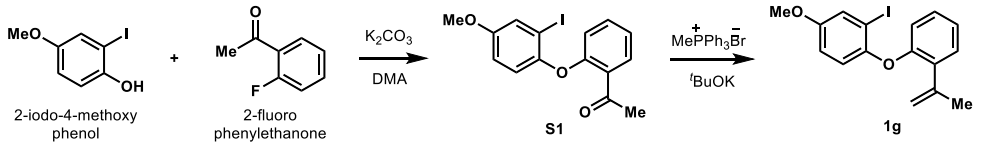
1m was prepared from 3-iodo-2-naphthalenol[7] and 3-methyl-3-buten-1-ol following the same procedure that was used for preparation of **1a**. The reaction mixture was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **1m** (in 78% yield) as a white solid; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 8.20 (s, 1H), 7.56 (d, J = 8.2 Hz, 1H), 7.52 (d, J = 8.2 Hz, 1H), 7.32 (ddd, J = 8.0, 8.0 and 1.0 Hz, 1H), 7.21 (ddd, J = 8.0, 8.0 and 1.0 Hz, 1H), 6.92 (s, 1H), 4.79 (d, J = 1.2 Hz, 1H), 4.78 (d, J = 1.2 Hz, 1H), 4.09 (t, J = 6.8 Hz, 2H), 2.52 (t, J = 6.8 Hz, 2H), 1.77 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 154.5, 142.2, 139.3, 134.3, 130.4, 126.9, 126.7, 126.7, 124.3, 112.6, 106.4, 88.9, 68.1, 37.1, 23.2; IR (KBr, cm^{-1}) 3054, 5843, 1664, 1590, 1456, 1246, 1022, 743, 605; HRMS (ESI) calcd. for $[C_{15}H_{16}IO]^+$ $(M+H)^+$: *m/z* 339.0246, found 339.0240.



1n

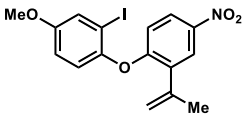
1n was prepared from 1-iodo-2-naphthalenol[8] and 3-methyl-3-buten-1-ol following the same procedure that was used for preparation of **1a**. The reaction mixture was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **1n** (in 76% yield) as a white solid; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 8.15 (d, J = 8.2 Hz, 1H), 7.80 (d, J = 9.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.53 (dd, J = 8.2 and 8.2 Hz, 1H), 7.38 (dd, J = 8.0 and 8.0 Hz, 1H), 7.19 (d, J = 9.0 Hz, 1H), 4.89 (s, 1H), 4.88 (s, 1H), 4.29 (t, J = 6.8 Hz, 2H), 2.64 (t, J = 6.8 Hz, 2H), 1.87 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 156.3, 142.2, 135.9, 131.5, 130.4, 130.2, 128.3, 128.2, 124.5, 114.5, 112.6, 89.0, 69.3, 37.6, 23.1; IR (KBr, cm^{-1}) 3074, 2314, 1677, 1553, 1456, 1239, 1028, 802, 641; HRMS (ESI) calcd. for $[C_{15}H_{15}IONa]^+$ $(M+Na)^+$: *m/z* 361.0060, found 361.0054.

Synthesis of 1g:



To a solution of 2-iodo-4-methoxyphenol (600 mg, 2.40 mmol, 1.2 equiv) in dry DMA (10 mL) was added K_2CO_3 (330 mg, 2.40 mmol, 1.2 equiv) and 2-fluorophenylethanone (0.24 mL, 2.0 mmol, 1.0 equiv) in sequence. The reaction mixture was heated to 100 °C and stirred for 10 h at the same temperature. Then the reaction mixture was cooled to room temperature and quenched with water (6 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were washed with water (2 x 30 mL), dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **S1** (348 mg, 47%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.86 (d, J = 7.8 Hz, 1H), 7.41 (s, 1H), 7.36 (dd, J = 7.8 and 7.6 Hz, 1H), 7.11 (dd, J = 7.6 and 7.6 Hz, 1H), 6.95-6.89 (m, 2H), 6.62 (d, J = 8.2 Hz, 1H), 3.82 (s, 3H), 2.77 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 199.2, 157.2, 157.1, 148.8, 133.7, 130.8, 129.2, 124.7, 122.8, 121.4, 116.4, 116.0, 90.0, 56.1, 32.4; IR (KBr, cm^{-1}) 3060, 1713, 1678, 1574, 1473, 1258, 1215, 1028, 812; HRMS (ESI) calcd. for $[C_{15}H_{13}IO_3Na]^+$ $(M+Na)^+$: *m/z* 390.9802, found 390.9803.

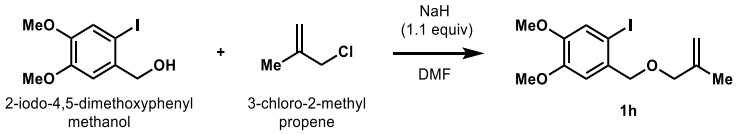
To a solution of methyltriphenylphosphonium bromide (312 mg, 0.87 mmol, 3.0 equiv) in dry toluene (6 mL) was added ^{t}BuOK (99 mg, 0.87 mmol, 3.0 equiv) at room temperature. After 1 h, **S1** (6 mL, 0.30 mmol, 1.0 equiv, 0.05 M in toluene) was added dropwise via syringe. The reaction mixture was warmed to 50 °C and stirred for 4 h. Then the reaction mixture was quenched with brine (6 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 x 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **1g** (99 mg, 91%) as a white solid; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.36 (d, J = 2.8 Hz, 1H), 7.31 (dd, J = 7.6 and 1.6 Hz, 1H), 7.17 (ddd, J = 8.0, 8.0 and 1.6 Hz, 1H), 7.06 (ddd, J = 8.0, 7.6 and 1.0 Hz, 1H), 6.83 (dd, J = 8.8 and 2.8 Hz, 1H), 6.73 (d, J = 8.8 Hz, 1H), 6.66 (dd, J = 8.0 and 1.0 Hz, 1H), 5.17 (s, 2H), 3.78 (s, 3H), 2.19 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 156.1, 154.3, 150.5, 143.0, 134.5, 130.0, 128.4, 124.4, 123.3, 119.7, 117.5, 116.1, 115.6, 88.9, 56.0, 23.7; IR (KBr, cm^{-1}) 3075, 2923, 1598, 1479, 1440, 1216, 1038, 903; HRMS (ESI) calcd. for $[C_{16}H_{15}IO_2Na]^+$ $(M+Na)^+$: *m/z* 389.0009, found 389.0009.



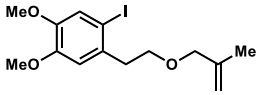
1f

1f was prepared from 1-(2-chloro-5-nitrophenyl) ethenone and 2-iodo-4-methoxyphenol using a modified procedure for preparation of **1g** (KOH/CH_3CN/80 °C instead of K_2CO_3/DMA/100 °C). The reaction mixture was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **1f** (in 42% overall yield) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 8.20 (d, J = 2.8 Hz, 1H), 8.00 (dd, J = 9.0 and 2.8 Hz, 1H), 7.40 (d, J = 2.4 Hz, 1H), 6.97-6.92 (m, 2H), 6.55 (d, J = 9.0 Hz, 1H), 5.33 (s, 1H), 5.32 (s, 1H), 3.82 (s, 3H), 2.26 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 160.0, 157.6, 148.1, 142.6, 141.2, 133.9, 125.7, 124.9, 124.2, 122.1, 118.0, 116.1, 114.7, 90.1, 56.0, 23.3; IR (KBr, cm^{-1}) 3084, 1519, 1476, 1344, 1252, 1221, 1031, 743, 610; HRMS (ESI) calcd. for $[C_{16}H_{14}INO_4Na]^+$ $(M+Na)^+$: *m/z* 433.9860, found 433.9853.

Synthesis of 1h:

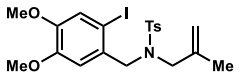


To a suspension of NaH (30 mg, 0.75 mmol, 1.1 equiv, 60% w/w in mineral oil) in dry DMF (2 mL) was added 2-iodo-4,5-dimethoxyphenyl methanol[9] (1.36 mL, 0.68 mmol, 1.0 equiv, 0.5 M in DMF) at 0 °C. After stirring for 20 min at the same temperature, 3-chloro-2-methyl propene (2.7 mL, 1.36 mmol, 2.0 equiv, 0.5 M in DMF) was added dropwise via syringe and the reaction mixture was heated to 80 °C for 10 h. After cooling the reaction flask to room temperature, the reaction mixture was carefully quenched with water (5 mL) and extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with water (3 x 5 mL), dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **1h** (142 mg, 60%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.22 (s, 1H), 7.01 (s, 1H), 5.03 (s, 1H), 4.94 (s, 1H), 4.42 (s, 2H), 3.98 (s, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 1.79 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 149.6, 149.0, 142.2, 133.4, 121.6, 112.6, 111.9, 85.8, 75.6, 74.6, 56.3, 56.0, 19.8; IR (KBr, cm^{-1}) 3065, 2843, 1664, 1590, 1456, 1246, 1022, 743, 605; HRMS (ESI) calcd. for $[C_{13}H_{17}IO_3Na]^+$ $(M+Na)^+$: *m/z* 371.0115, found 371.0114.



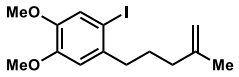
1i

1i was prepared from 2-(2-iodo-4,5-dimethoxyphenyl)ethan-1-ol[10] and 3-chloro-2-methyl propene following the same procedure that was used for preparation of **1h**. The reaction mixture was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **1i** (in 50% yield) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.18 (s, 1H), 6.80 (s, 1H), 4.93 (s, 1H), 4.85 (s, 1H), 3.87 (s, 2H), 3.82 (s, 3H), 3.81 (s, 3H), 3.56 (t, J = 6.8 Hz, 2H), 2.94 (t, J = 6.8 Hz, 2H), 1.69 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 149.2, 148.1, 142.3, 134.2, 121.6, 113.1, 111.9, 88.2, 74.8, 69.6, 56.2, 55.9, 40.7, 19.5; IR (KBr, cm^{-1}) 3076, 2845, 1505, 1441, 1255, 1162, 855, 741, 661; HRMS (ESI) calcd. for $[C_{14}H_{19}IO_3Na]^+$ $(M+Na)^+$: *m/z* 385.0271, found 385.0260.



1l

1l was prepared from N-(2-iodo-4,5-dimethoxybenzyl)-4-methyl benzenesulfonamide,[11] 3-chloro-2-methyl propene, and NaI (0.2 equiv) following the same procedure that was used for the preparation of **1h**. The crude mixture was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **1l** (in 80% yield) as a white solid; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.74 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.12 (s, 1H), 6.99 (s, 1H), 4.75 (s, 1H), 4.69 (s, 1H), 4.32 (s, 2H), 3.83 (s, 3H), 3.77 (s, 3H), 3.70 (s, 2H), 2.43 (s, 3H), 1.56 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 149.7, 149.0, 143.5, 139.6, 137.2, 130.9, 129.9, 127.4, 127.4, 121.3, 121.3, 114.9, 112.1, 86.7, 56.3, 56.1, 55.9, 54.7, 21.6, 20.1; IR (KBr, cm^{-1}) 3666, 3159, 2919, 1574, 1503, 1340, 1210, 1159, 909; HRMS (ESI) calcd. for $[C_{20}H_{24}INO_4SNa]^+$ $(M+Na)^+$: *m/z* 524.0363, found 524.0350.



1o

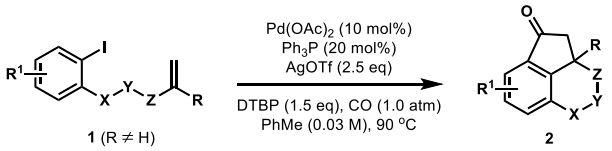
1o was prepared according to the know literature procedure[12]; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.20 (s, 1H), 6.72 (s, 1H), 4.74 (s, 1H), 4.72 (s, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 2.65-2.60 (m, 2H), 2.10 (t, J = 7.6 Hz, 2H), 1.75 (s, 3H), 1.74-1.68 (m, 2H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 149.4, 147.8, 145.6, 137.7, 121.8, 112.3, 110.3, 88.0, 56.3, 56.0, 40.2, 37.5, 28.5, 22.6; IR (KBr, cm^{-1}) 2935, 1504,

1441, 1252, 1215, 1161, 1029, 584, 788; HRMS (ESI) calcd. for $[C_{14}H_{19}IO_2Na]^+$ $(M+Na)^+$: *m/z* 369.0322, found 369.0312.

3. Pd-catalyzed Cascade Cyclization for Rapid Polycycle Assembly

3.1 General Procedure

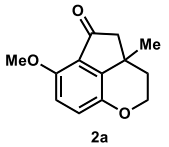
Caution! Carbon monoxide is highly toxic. The operation must be carried out in a good hood with an adequate shield.



1 (R ≠ H) **2**

In a nitrogen-filled glovebox, a 25 mL flame-dried reaction tube with a stirring bar was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), Ph_3P (10.5 mg, 0.04 mmol, 0.2 equiv), AgOTf (128 mg, 0.50 mmol, 2.5 equiv) , DTBP (57 mg, 0.30 mmol, 1.5 equiv) and degassed dry toluene (1 mL). The reaction tube was sealed with a rubber septum and taken out of the glovebox. The reaction mixture was stirred for 3 h at room temperature and then substrate **1** (0.20 mmol, 1.0 equiv, 0.035 M in toluene) was added in one portion. The reaction tube was purged with carbon monoxide (CO balloon) for a while (3-5 seconds) and immediately placed into a preheated 90 °C oil bath where it was stirred vigorously for 4 h under carbon monoxide atmosphere (CO balloon). The reaction mixture was cooled to room temperature and filtered through a pad of silica and eluted with ethyl acetate (10 mL). The eluent was concentrated in *vacuo* and the residue was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford product **2**.

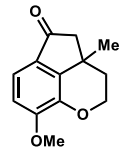
3.2 Substrates Extension



2a

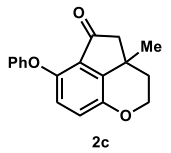
Prepared according to the general procedure using **1a** (64 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2a** (36 mg, 83%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 6.92 (d, J = 8.8 Hz, 1H), 6.69 (d, J = 8.8 Hz, 1H), 4.47-4.43 (m, 2H), 3.88 (s, 3H), 2.69 (d, J = 16.4 Hz, 1H), 2.55 (d, J = 16.4 Hz, 1H), 2.06-2.01 (m, 1H), 1.98-1.92 (m, 1H), 1.40 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 201.6, 150.8, 145.7, 145.6, 122.5, 121.8,

111.7, 64.4, 56.3, 55.7, 34.2, 33.8, 28.7; IR (KBr, cm^{-1}) 3462, 2960, 1711, 1598, 1494, 1299, 1262, 1052, 811; HRMS (ESI) calcd. for $[C_{13}H_{14}O_3Na]^+$ $(M+Na)^+$: *m/z* 241.0835, found 241.0830.



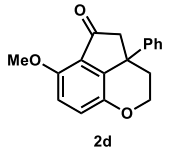
2b

Prepared according to the general procedure using **1b** (64 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2b** (29 mg, 66%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.25 (d, *J* = 8.2 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 4.62 (ddd, *J* = 11.8, 5.4 and 1.2 Hz, 1H), 4.58-4.52 (m, 1H), 3.94 (s, 3H), 2.70 (d, *J* = 16.6 Hz, 1H), 2.54 (d, *J* = 16.6 Hz, 1H), 2.11-2.06 (m, 1H), 1.98 (ddd, *J* = 13.2, 13.2 and 5.4 Hz, 1H), 1.41 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 202.7, 151.9, 145.2, 140.8, 128.1, 116.4, 111.9, 65.1, 56.5, 55.4, 34.0, 33.6, 28.9; IR (KBr, cm^{-1}) 2960, 1708, 1607, 1504, 1258, 1350, 1075, 803; HRMS (ESI) calcd. for $[C_{13}H_{14}O_3Na]^+$ $(M+Na)^+$: *m/z* 241.0835, found 241.0832.



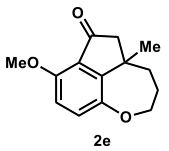
2c

Prepared according to the general procedure using **1c** (76 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2c** (24 mg, 43%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.35-7.29 (m, 2H), 7.10 (dd, *J* = 7.4 and 7.4 Hz, 1H), 7.04-6.99 (m, 2H), 6.87 (d, *J* = 8.8 Hz, 1H), 6.65 (d, *J* = 8.8 Hz, 1H), 4.53-4.46 (m, 2H), 2.71 (d, *J* = 16.6 Hz, 1H), 2.59 (d, *J* = 16.6 Hz, 1H), 2.10-2.05 (m, 1H), 2.03-1.97 (m, 1H), 1.44 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 200.6, 157.3, 147.8, 147.3, 145.2, 129.8, 129.8, 125.0, 123.7, 121.6, 119.2, 119.1, 119.1, 64.6, 55.8, 34.3, 33.7, 28.9; IR (KBr, cm^{-1}) 3462, 1718, 1645, 1480, 1384, 1230, 753, 695; HRMS (ESI) calcd. for $[C_{18}H_{16}O_3Na]^+$ $(M+Na)^+$: *m/z* 303.0992, found 303.0988.



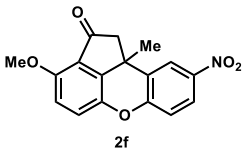
2d

Prepared according to the general procedure using **1d** (76 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2d** (34 mg, 61%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.26 (d, J = 7.4 Hz, 1H), 7.27-7.24 (m, 1H), 7.21-7.16 (m, 1H), 7.04 (d, J = 8.8 Hz, 1H), 6.96 (d, J = 7.4 Hz, 1H), 6.95 (d, J = 7.4 Hz, 1H), 6.84 (d, J = 8.8 Hz, 1H), 4.30 (ddd, J = 11.4, 4.4 and 1.2 Hz, 1H), 3.93 (s, 3H), 3.83 (ddd, J = 13.8, 11.6 and 2.6 Hz, 1H), 3.08 (d, J = 16.6 Hz, 1H), 2.94 (d, J = 16.6 Hz, 1H), 2.55-2.51 (m, 1H), 2.21 (ddd, J = 13.4, 13.4 and 4.6 Hz, 1H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 200.7, 151.0, 146.9, 146.4, 141.9, 128.8, 128.8, 127.4, 127.4, 127.0, 123.9, 122.0, 112.6, 64.7, 56.5, 56.4, 43.7, 35.4; IR (KBr, cm^{-1}) 3521, 2959, 1712, 1599, 1493, 1257, 1049, 767, 703; HRMS (ESI) calcd. for $[C_{18}H_{16}O_3Na]^+$ $(M+Na)^+$: *m/z* 303.0992, found 303.0984.



2e

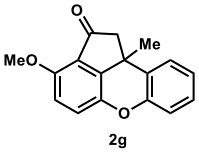
Prepared according to the general procedure using **1e** (66 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2e** (18 mg, 39%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.16 (d, J = 8.6 Hz, 1H), 6.69 (d, J = 8.6 Hz, 1H), 4.48 (d, J = 12.2 Hz, 1H), 3.91 (s, 3H), 3.55 (dd, J = 12.2 and 12.2 Hz, 1H), 2.58 (d, J = 19.2 Hz, 1H), 2.55 (d, J = 19.2 Hz, 1H), 2.39-2.30 (m, 1H), 2.04 (d, J = 13.6 Hz, 1H), 1.82 (dd, J = 15.2 and 3.0 Hz, 1H), 1.66 (dd, J = 13.6 and 3.0 Hz, 1H), 1.37 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 203.3, 154.7, 153.9, 151.5, 128.7, 124.8, 110.4, 74.7, 56.1, 54.5, 41.9, 38.6, 28.3, 25.8; IR (KBr, cm^{-1}) 3474, 2967, 1622, 1491, 1252, 1177, 1032, 641; HRMS (ESI) calcd. for $[C_{14}H_{16}O_3Na]^+$ $(M+Na)^+$: *m/z* 255.0992, found 255.0990.



2f

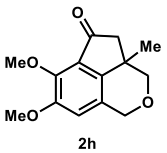
Prepared according to the general procedure using **1f** (82 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2f** (33 mg, 53%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 8.18 (dd, J = 8.8 and 2.6 Hz, 1H), 8.17 (d, J = 2.6 Hz, 1H), 7.35 (d, J = 8.8 Hz, 1H), 7.31 (d, J = 8.8 Hz, 1H), 6.86 (d, J = 8.8 Hz, 1H), 3.97 (s, 3H), 3.16 (d, J = 16.4 Hz, 1H), 3.12

(d, *J* = 16.4 Hz, 1H), 1.48 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 198.7, 157.7, 154.1, 145.4, 144.3, 143.7, 131.5, 124.0, 122.7, 122.4, 121.7, 118.3, 111.7, 56.5, 52.8, 38.2, 33.9; IR (KBr, cm^{-1}) 3461, 2313, 1718,1603, 1520,1344, 1244,1041, 803; HRMS (ESI) calcd. for $[C_{17}H_{13}NO_5Na]^+$ $(M+Na)^+$: *m/z* 334.0686, found 334.0678.



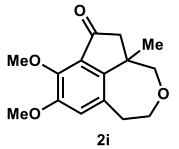
2g

Prepared according to the general procedure using **1g** (73 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2g** (20 mg, 37%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.30 (d, *J* = 8.8 Hz, 1H), 7.27-7.23 (m, 2H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.16 (dd, *J* = 7.6 and 7.4 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 3.95 (s, 3H), 3.14 (d, *J* = 16.8 Hz, 1H), 3.05 (d, *J* = 16.8 Hz, 1H), 1.44 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 200.6, 153.3, 153.2, 147.3, 145.1, 130.6, 128.0, 126.1, 124.5, 122.5, 121.7, 117.5, 111.0, 56.5, 53.2, 38.2, 33.7; IR (KBr, cm^{-1}) 3433, 2925, 1717, 1632, 1384, 1249, 1154, 1043, 757; HRMS (ESI) calcd. for $[C_{17}H_{14}O_3Na]^+$ $(M+Na)^+$: *m/z* 289.0835, found 289.0834.



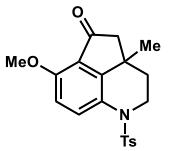
2h

Prepared according to the general procedure using **1h** (70 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2h** (27 mg, 55%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 6.78 (s, 1H), 5.01 (d, *J* = 15.4 Hz, 1H), 4.72 (d, *J* = 15.4 Hz, 1H), 4.11 (s, 3H), 4.02 (d, *J* = 10.2 Hz, 1H), 3.85 (s, 3H), 3.50 (d, *J* = 10.2 Hz, 1H), 2.54 (d, *J* = 16.8 Hz, 1H), 2.49 (d, *J* = 16.8 Hz, 1H), 1.43 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 200.5, 152.1, 149.1, 146.3, 125.9, 125.4, 114.2, 72.9, 65.8, 63.0, 57.2, 51.7, 37.4, 27.8; IR (KBr, cm^{-1}) 3449, 1713, 1633, 1491, 1340, 1268, 1074, 1054, 724; HRMS (ESI) calcd. for $[C_{14}H_{16}O_4Na]^+$ $(M+Na)^+$: *m/z* 271.0941, found 271.0934.



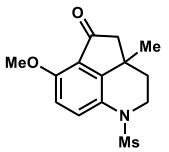
2i

Prepared according to the general procedure using **1i** (72 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2i** (18 mg, 34%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 6.91 (s, 1H), 4.33-4.27 (m, 1H), 3.96 (s, 3H), 3.91 (d, J = 11.6 Hz, 1H), 3.86 (s, 3H), 3.53-3.43 (m, 3H), 2.64 (dd, J = 15.4 and 3.4 Hz, 1H), 2.42 (d, J = 18.0 Hz, 1H), 2.38 (d, J = 18.0 Hz, 1H), 1.44 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 202.4, 152.8, 151.4, 145.4, 134.2, 128.7, 121.5, 78.6, 72.0, 61.9, 57.0, 49.9, 44.8, 38.2, 24.7; IR (KBr, cm^{-1}) 3309, 2922, 1711, 1675, 1494, 1273, 1012, 744, 667, 642; HRMS (ESI) calcd. for $[C_{15}H_{18}O_4Na]^+$ $(M+Na)^+$: *m/z* 285.1097, found 285.1092.



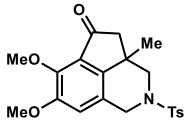
2j

Prepared according to the general procedure using **1j** (94 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2j** (50 mg, 67%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 8.15 (d, J = 9.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 9.0 Hz, 1H), 4.02 (dd, J = 13.2 and 5.0 Hz, 1H), 3.94 (s, 3H), 3.55 (ddd, J = 13.2, 13.2 and 5.0 Hz, 1H), 2.51 (d, J = 17.2 Hz, 1H), 2.45 (d, J = 17.2 Hz, 1H), 2.37 (s, 3H), 2.09 (dd, J = 13.2 and 5.6 Hz, 1H), 1.71 (ddd, J = 13.2, 13.2 and 5.8 Hz, 1H), 0.60 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 201.4, 153.9, 152.6, 144.4, 134.4, 129.8, 129.8, 127.4, 127.3, 127.3, 122.2, 111.2, 56.2, 54.5, 44.1, 35.7, 34.8, 25.6, 21.7; IR (KBr, cm^{-1}) 3432, 1712, 1591, 1493, 1302, 1165, 1058, 815, 558; HRMS (ESI) calcd. for $[C_{20}H_{21}NO_4SNa]^+$ $(M+Na)^+$: *m/z* 394.1083, found 394.1076.



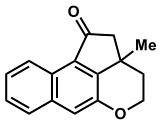
2k

Prepared according to the general procedure using **1k** (79 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2k** (41 mg, 70%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.90 (d, J = 9.0 Hz, 1H), 6.78 (d, J = 9.0 Hz, 1H), 4.02 (ddd, J = 12.4, 6.2 and 1.6 Hz, 1H), 3.92 (s, 3H), 3.78 (ddd, J = 13.2, 12.6 and 5.2 Hz, 1H), 2.97 (s, 3H), 2.68 (d, J = 17.2 Hz, 1H), 2.53 (d, J = 17.2 Hz, 1H), 2.26 (ddd, J = 13.2, 5.2 and 1.4 Hz, 1H), 1.84 (ddd, J = 13.2, 13.2 and 6.2 Hz, 1H), 1.34 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 201.2, 153.4, 151.4, 127.2, 126.9, 122.4, 111.2, 56.1, 54.3, 44.2, 36.7, 35.7, 34.3, 26.4; IR (KBr, cm^{-1}) 3473, 2929, 1711, 1494, 1342, 1275, 1155, 1057, 732; HRMS (ESI) calcd. for $[C_{14}H_{17}NO_4SNa]^+$ $(M+Na)^+$: *m/z* 318.0770, found 318.0763.



2l

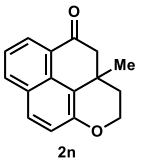
Prepared according to the general procedure using **1l** (100 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2l** (41 mg, 51%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.73 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 6.82 (s, 1H), 4.83 (dd, J = 15.4 and 0.6 Hz, 1H), 4.09 (d, J = 11.0 Hz, 1H), 4.07 (s, 3H), 3.91 (d, J = 15.8 Hz, 1H), 3.82 (s, 3H), 2.61 (d, J = 11.6 Hz, 1H), 2.60 (d, J = 16.6 Hz, 1H), 2.49 (d, J = 16.6 Hz, 1H), 2.42 (s, 3H), 1.40 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 200.0, 152.2, 148.3, 146.5, 143.9, 134.2, 129.9, 129.9, 127.4, 127.4, 125.3, 123.2, 115.9, 62.9, 57.1, 52.9, 52.2, 45.4, 38.1, 28.1, 21.6; IR (KBr, cm^{-1}) 3443, 2925, 1712, 1638, 1493, 1344, 1269, 1162, 943; HRMS (ESI) calcd. for $[C_{21}H_{23}NO_5SNa]^+$ $(M+Na)^+$: *m/z* 424.1189, found 424.1180.



2m

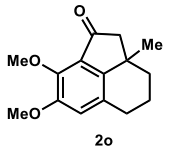
Prepared according to the general procedure using **1m** (68 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2m** (30 mg, 62%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 8.85-8.79 (m, 1H), 7.79-7.72 (m, 1H), 7.51-7.44 (m, 2H), 7.34 (s, 1H), 4.64-4.56 (m, 2H), 2.86 (d, J = 16.8 Hz, 1H), 2.70 (d, J = 16.8 Hz, 1H), 2.20-2.16 (m, 1H), 2.08 (ddd, J = 13.2, 12.8 and 6.0 Hz, 1H), 1.50 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 204.0, 151.8,

150.0, 135.4, 129.4, 127.2, 126.8, 126.1, 124.8, 124.0, 116.4, 64.8, 55.4, 34.7, 33.9, 28.4; IR (KBr, cm^{-1}) 3433, 2927, 1704, 1517, 1465, 1288, 1155, 1065, 1021, 576; HRMS (ESI) calcd. for $[C_{16}H_{14}O_2Na]^+$ $(M+Na)^+$: *m/z* 261.0886, found 261.0886.



2n

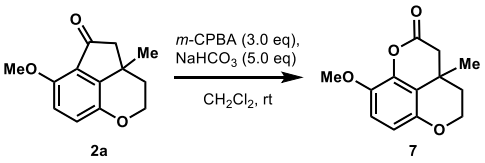
Prepared according to the general procedure using **1n** (68 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2n** (41 mg, 85%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 8.16 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.41 (dd, *J* = 7.6 and 7.6 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 1H), 4.54-4.44 (m, 2H), 2.83 (d, *J* = 14.6 Hz, 1H), 2.75 (d, *J* = 14.6 Hz, 1H), 2.24 (ddd, *J* = 13.4, 13.0 and 5.2 Hz, 1H), 1.94 (ddd, *J* = 13.4, 1.8 and 1.8 Hz, 1H), 1.37 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 197.5, 151.7, 134.3, 131.5, 128.9, 128.7, 128.2, 125.8, 123.1, 119.5, 117.4, 63.1, 52.2, 35.7, 32.1, 27.3; IR (KBr, cm^{-1}) 3064, 2962, 1757, 1684, 1585, 1253, 1240, 833, 776; HRMS (ESI) calcd. for $[C_{16}H_{14}O_2Na]^+$ $(M+Na)^+$: *m/z* 261.0886, found 261.0880.



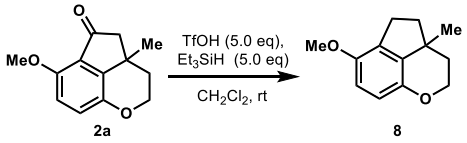
2o

Prepared according to the general procedure using **1o** (69 mg, 0.20 mmol). Purification by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2o** (36 mg, 72%) as a yellowish oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 6.87 (s, 1H), 4.03 (s, 3H), 3.84 (s, 3H), 2.87 (dd, *J* = 17.2 and 7.8 Hz, 1H), 2.71-2.65 (m, 1H), 2.61 (d, *J* = 16.6 Hz, 1H), 2.51 (d, *J* = 16.6 Hz, 1H), 2.15-2.06 (m, 1H), 2.01-1.92 (m, 2H), 1.60-1.53 (m, 1H), 1.26 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 202.5, 152.3, 151.6, 145.2, 128.9, 126.0, 118.9, 62.5, 57.1, 56.7, 37.2, 34.1, 29.4, 25.0, 18.8; IR (KBr, cm^{-1}) 3482, 2936, 1711, 1491, 1347, 1268, 1029, 743, 582; HRMS (ESI) calcd. for $[C_{15}H_{18}O_3Na]^+$ $(M+Na)^+$: *m/z* 269.1148, found 269.1143.

4. Synthetic Transformations of Tricyclic 2a



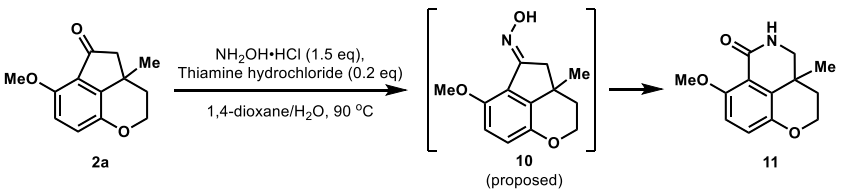
Lactone 7: To a solution of **2a** (15 mg, 0.07 mmol, 1.0 eq) in CH_2Cl_2 (1.5 mL) was added $NaHCO_3$ (29 mg, 0.34 mmol, 5.0 eq), followed by *m*-CPBA (42 mg, 0.21 mmol, 3.0 eq) at rt. The reaction was stirred for 2 h. The reaction mixture was quenched with a mixture of saturated aqueous $NaHCO_3$ solution (2 mL) and saturated aqueous $Na_2S_2O_3$ solution (2 mL). The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford lactone **7** (10.5 mg, 65%) as a yellow oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.80 (d, J = 9.0 Hz, 1H), 6.58 (d, J = 9.0 Hz, 1H), 4,37 (ddd, J = 11.6, 4.4 and 2.2 Hz, 1H), 4.29-4.24 (m, 1H), 3.83 (s, 3H), 2.78 (d, J = 15.2 Hz, 1H), 2.46 (d, J = 15.2 Hz, 1H), 1.88 (ddd, J = 13.4, 13.4 and 4.2 Hz, 1H), 1.82 (ddd, J = 13.4, 2.2 and 2.2 Hz, 1H), 1.36 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ 167.0, 146.1, 141.2, 140.1, 114.3, 113.5, 111.5, 62.6, 57.1, 43.1, 34.1, 29.4, 25.7; IR (KBr, cm^{-1}) 2961, 2838, 1769, 1495, 1254, 1231, 1152, 892; HRMS (ESI) calcd. for $[C_{13}H_{14}O_4Na]^+$ $(M+Na)^+$: *m/z* 257.0784, found 257.0781.



Ether 8: To a solution of **2a** (15 mg, 0.07 mmol, 1.0 eq) in CH_2Cl_2 (1.5 mL) was added TfOH (31 uL, 0.34 mmol, 5.0 eq) and Et_3SiH (55 uL, 0.34 mmol, 5.0 eq) at rt. After stirring for 5 h at this temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford ether **8** (10.6 mg, 75%) as a yellow oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.60 (d, J = 8.6 Hz, 1H), 6.54 (d, J = 8.6 Hz, 1H), 4,36 (ddd, J = 11.6, 5.2 and 1.6 Hz, 1H), 4.32-4.26 (m, 1H), 3.78 (s, 3H), 3.03-2.96 (m,

1H), 2.78 (dd, *J* = 15.8 and 8.2 Hz, 1H), 2.13 (dd, *J* = 11.6 and 6.0 Hz, 1H), 1.92 (ddd, *J* = 13.2, 2.8 and 1.6 Hz, 1H), 1.83 (ddd, *J* = 19.6, 11.4 and 8.4 Hz, 1H), 1.76 (ddd, *J* = 13.2, 13.2 and 5.2 Hz, 1H), 1.26 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ 149.6, 146.4, 134.9, 130.6, 112.8, 111.5, 64.1, 56.2, 43.7, 39.3, 35.6, 27.4, 24.2; IR (KBr, cm^{-1}) 2949, 2852, 1492, 1245, 1195, 1060, 797; HRMS (ESI) calcd. for $[C_{13}H_{16}O_2Na]^+$ $(M+Na)^+$: *m/z* 227.1043, found 227.1041.

Ketone 9: To a solution of **2a** (15 mg, 0.07 mmol, 1.0 eq) in CH_2Cl_2 (1.5 mL) was added B $F_3{\cdot}Et_2O$ (17 uL, 0.14 mmol, 2.0 eq) at -78 °C. After 15 min, $TMSCHN_2$ (69 uL, 0.14 mmol, 2.0 eq) was added at the same temperature. After stirring for 3 h at this temperature, the react ion mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to affo rd ketone **9** (9.8 mg, 60%) as a yellow oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.96 (d, *J* = 9.0 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 1H), 4.32-4.28 (m, 2H), 3.84 (s, 3H), 2.84 (ddd, *J* = 19.4, 12. 8 and 7.0 Hz, 1H), 2.67 (ddd, *J* = 19.4, 6.8 and 1.2 Hz, 1H), 1.98-1.93 (m, 1H), 1.93-1.86 (m, 2H),1.76 (ddd, *J* = 13.6, 2.2 and 2.2 Hz, 1H), 1.32 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ 197.3, 153.5, 145.8, 133.2, 122.4, 120.9 112.1, 62.2, 56.5, 36.2, 35.9, 35.5, 30.4, 26.4; IR (KBr, cm^{-1}) 3330, 2935, 1679, 1585, 1475, 1254, 1056, 906; HRMS (ESI) calcd. for $[C_{14}H_{16}O_3Na]^+$ $(M+Na)^+$: *m/z* 255.0992 , found 255.0987.

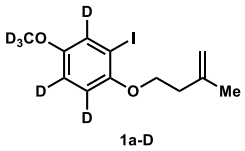


Lactam 11: To a solution of **2a** (15 mg, 0.07 mmol, 1.0 eq) in 1,4-dioxane/H_2O (1.8 mL/0.2 mL) was added $NH_2OH{\cdot}HCl$ (7.2 mg, 0.10 mmol, 1.5 eq) and Thiamine hydrochloride (4.7 mg, 0.01 mmol, 0.2 eq) at 90 °C. After 12 h, the reaction mixture was cooled to rt and quenched with saturated aqueous

$NaHCO_3$ solution (2 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford lactam **11** (13.4 mg, 84%) as a yellow solid; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.72 (d, J = 8.6 Hz, 1H), 6.68 (d, J = 8.6 Hz, 1H), 4.45-4.35 (m, 2H), 3.88 (s, 3H), 3.30 (d, J = 16.4 Hz, 1H), 2.57 (d, J = 16.4 Hz, 1H), 2.05-1.99 (m, 1H), 1.91 (ddd, J = 12.8, 12.8 and 5.8 Hz, 1H), 1.33 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ 159.9, 149.7, 145.9, 139.1, 121.9, 116.6, 111.4, 64.5, 56.0, 44.3, 36.8, 34.1, 28.1; IR (KBr, cm^{-1}) 2692, 2837, 1496, 1232, 1058, 927, 802; HRMS (ESI) calcd. for $[C_{13}H_{15}NO_3H]^+$ $(M+H)^+$: *m/z* 234.1125, found 234.1123.

5. Mechanistic Investigation of the Pd-catalyzed Cascade Cyclization

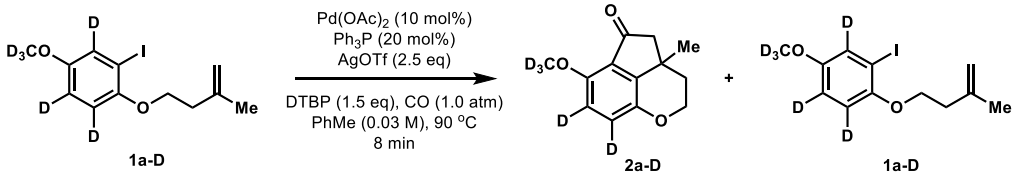
5.1. Synthesis of Deuterated 1a-D



1a-D

1a-D was prepared from 2-iodo-4-(methoxy-d_3)phen-3,5,6-d_3-ol[13] following the same procedure that was used for preparation of **1a**, and the reaction mixture was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **1a-D** as a yellowish oil. ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 4.85 (s, 1H), 4.83 (s, 1H), 4.05 (t, J = 6.8 Hz, 2H), 2.54 (t, J = 6.8 Hz, 2H), 1.84 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 154.5, 152.3, 142.3, 124.4, 114.5, 112.9, 112.4, 87.0, 69.0, 55.1, 37.4, 23.1;IR (KBr, cm^{-1}) 3433, 2924, 1632, 1424, 1383, 1149, 911, 741; HRMS (ESI) calcd. for $[C_{12}H_{10}D_6IO_2]^+$ $(M+H)^+$: *m/z* 325.0572, found 325.0566.

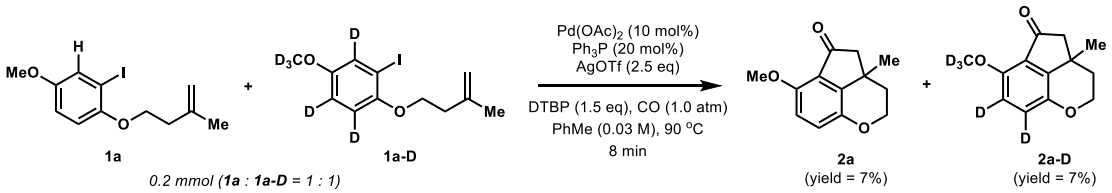
5.2. H/D Exchange Experiment



The reaction was performed according to the general procedure of Pd-catalyzed cascade using **1a-D** (89 mg, 0.20 mmol) at low conversion (run 8 min). The reaction mixture was directly concentrated and purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2a-D** (9.6 mg, 16%) as a yellowish oil and substrate **1a-D** (33 mg, 37%).

2a-D: ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 4.50-4.41 (m, 2H), 2.70 (d, J = 16.4 Hz, 1H), 2.56 (d, J = 16.4 Hz, 1H), 2.06-2.01 (m, 1H), 2.00-1.92 (m, 1H), 1.40 (s, 3H); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm) 201.6, 150.8, 145.7, 145.6, 122.5, 121.5, 111.3, 64.4, 55.7, 34.2, 33.8, 28.8; IR (KBr, cm^{-1}) 3449, 1711, 1633, 1434, 1325, 1081,850 , 708; HRMS (ESI) calcd. for $[C_{13}H_{10}D_5O_3]^+$ $(M+H)^+$: *m/z* 224.1335, found 224.1333.

5.3. Intermolecular KIE Experiment

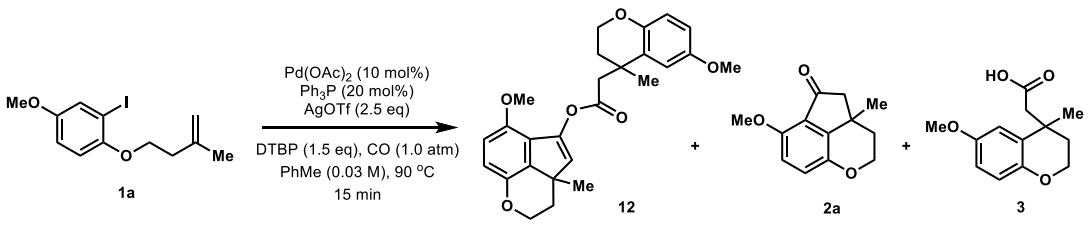


The reaction was performed according to the general procedure using a 1:1 mixture of **1a** (32 mg, 0.10 mmol) and **1a-D** (32 mg, 0.10 mmol) at low conversion (run 8 min). The reaction mixture was directly concentrated and purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2a** (1.5 mg, 7%), **2a-D** (1.6 mg, 7%), **1a** (12.4 mg, 39%), and **1a-D** (12.6 mg, 39%).

1a/1a-D: ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 7.33 (d, J = 2.9 Hz, 0.5H), 6.84 (dd, J = 8.9 and 2.9 Hz, 0.5H), 6.75 (d, J = 8.9 Hz, 0.5H), 4.85 (s, 1H), 4.83 (s, 1H), 4.05 (t, J = 6.8 Hz, 2H), 3.75 (s, 1.5H), 2.54 (t, J = 6.8 Hz, 2H), 1.83 (s, 3H).

2a/2a-D: ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm) 6.93 (d, J = 8.8 Hz, 0.5H), 6.69 (d, J = 8.8 Hz, 0.5H), 4.50-4.41 (m, 2H), 3.89 (s, 1.5H), 2.70 (d, J = 16.4 Hz, 1H), 2.56 (d, J = 16.4 Hz, 1H), 2.06-2.01 (m, 1H), 2.00-1.92 (m, 1H), 1.40 (s, 3H).

5.4. Isolation of the Reaction Intermediates

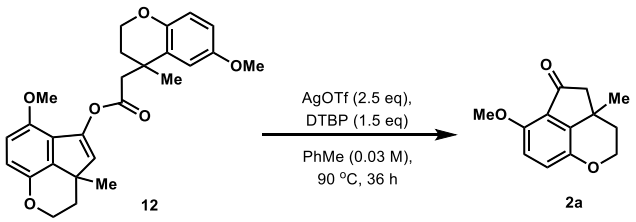


The reaction was performed according to the general procedure using **1a** (30 mg, 0.09 mmol) at low conversion (run 15 min). The reaction mixture was directly concentrated and purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **12**, **2a**, and **3**.

12: ^{1}H-NMR (600 MHz, C_6D_6) δ (ppm) 6.97 (d, J = 9.0 Hz, 1H), 6.92 (dd, J = 2.6 and 2.6 Hz, 1H), 6.80 (d, J = 8.8 Hz, 1H), 6.63 (ddd, J = 9.0, 2.6 and 1.0 Hz, 1H), 6.43 (dd, J = 8.8 and 2.8 Hz, 1H), 5.95 (d, J = 5.6 Hz, 1H), 4.14-4.07 (m, 1H), 4.06-3.99 (m, 2H), 3.93-3.88 (m, 1H), 3.36 (d, J = 2.8 Hz, 3H), 3.30 (d, J = 3.4 Hz, 3H), 2.84 (dd, J = 15.0 and 1.2 Hz, 1H), 2.78 (dd, J = 15.0 and 5.2 Hz, 1H), 2.31-2.25 (m, 1H), 1.81-1.73 (m, 1H), 1.45 (s, 3H), 1,35 (dd, J = 12.8 and 4.0 Hz, 1H), 1.18-1.14 (m, 1H), 1.22 (d, J = 9.2 Hz, 3H); ^{13}C-NMR (151 MHz, C_6D_6) δ (ppm) 168.6, 154.2, 149.3, 148.6, 148.0, 146.9, 135.8, 130.7, 127.6, 125.2, 118.4, 114.6, 114.0, 113.0, 112.5, 65.3, 62.7, 55.9, 55.3, 46.5, 42.1,

34.6, 33.6, 30.4, 28.2, 21.9.; HRMS (ESI) calcd. for $[C_{26}H_{28}O_6Na]^+$ $(M+Na)^+$: *m/z* 459.1778, found 459.1777.

5.5. Transformation of 12 to 2a



To a solution of **12** (10.3 mg, 0.024 mmol, 1.0 equiv) in degassed dry toluene (1 mL) was added AgOTf (15.2 mg, 0.059 mmol, 2.5 equiv) and DTBP (6.8 mg, 0.035 mmol, 1.5 equiv) at room temperature. The reaction mixture was heated to 90 °C and stirred for 36 h. Then the reaction mixture was purified by flash column chromatography (SiO_2, ethyl acetate/hexane) to afford **2a** (9.3 mg, 90%) as a yellowish oil.

6. References

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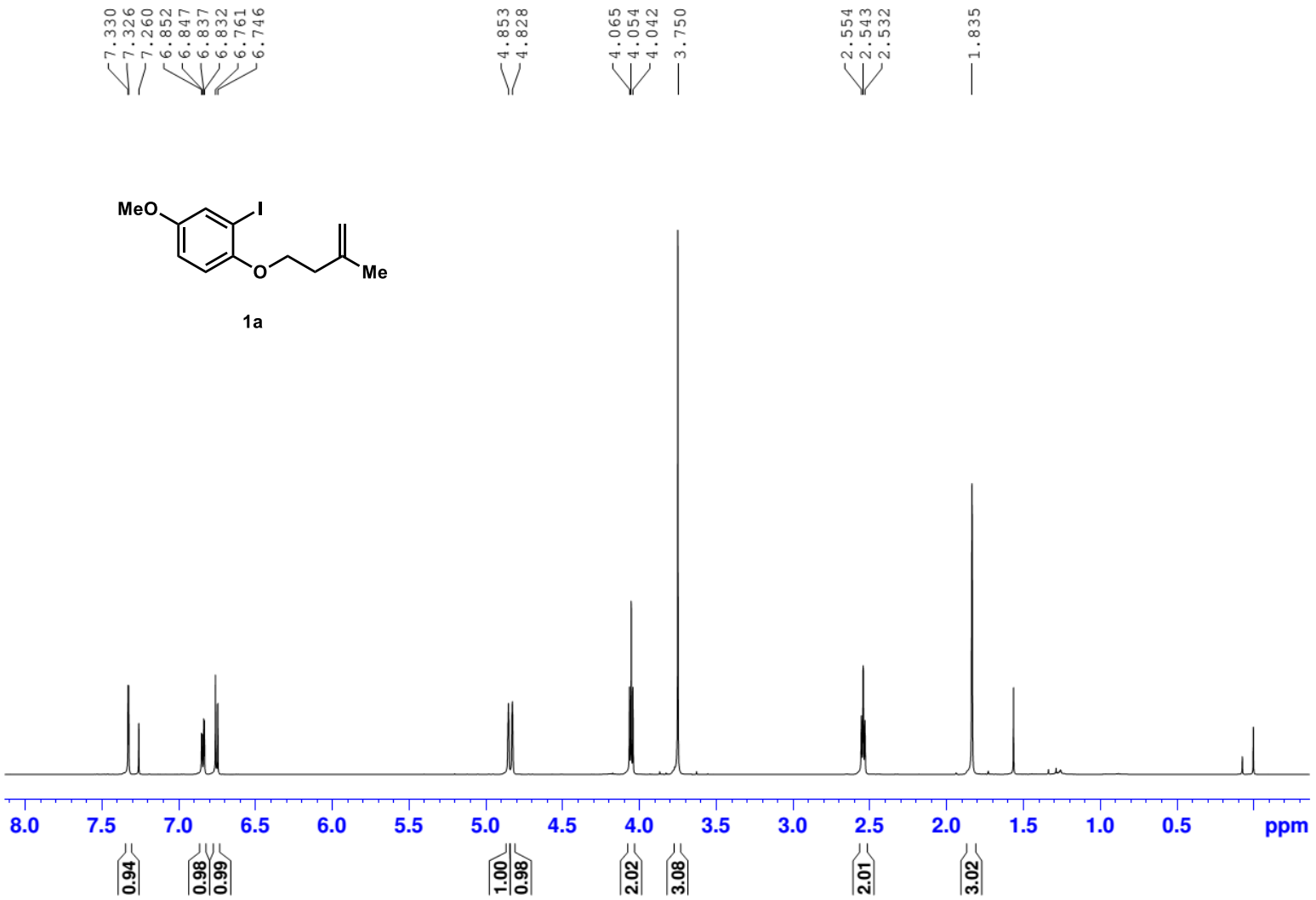
7. Copies of ^{1}H and ^{13}C-NMR Spectra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6.0
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4.5
4.0
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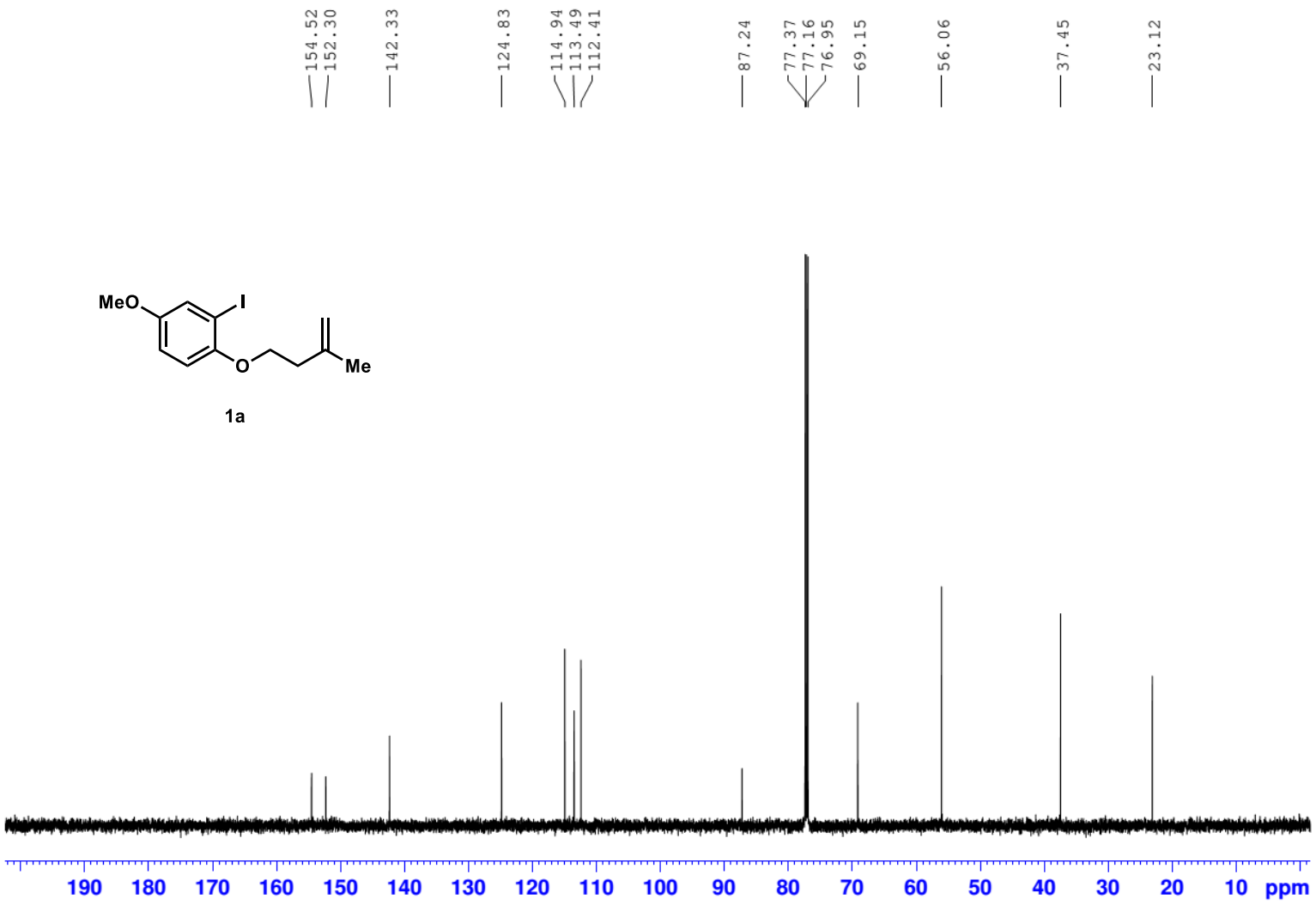
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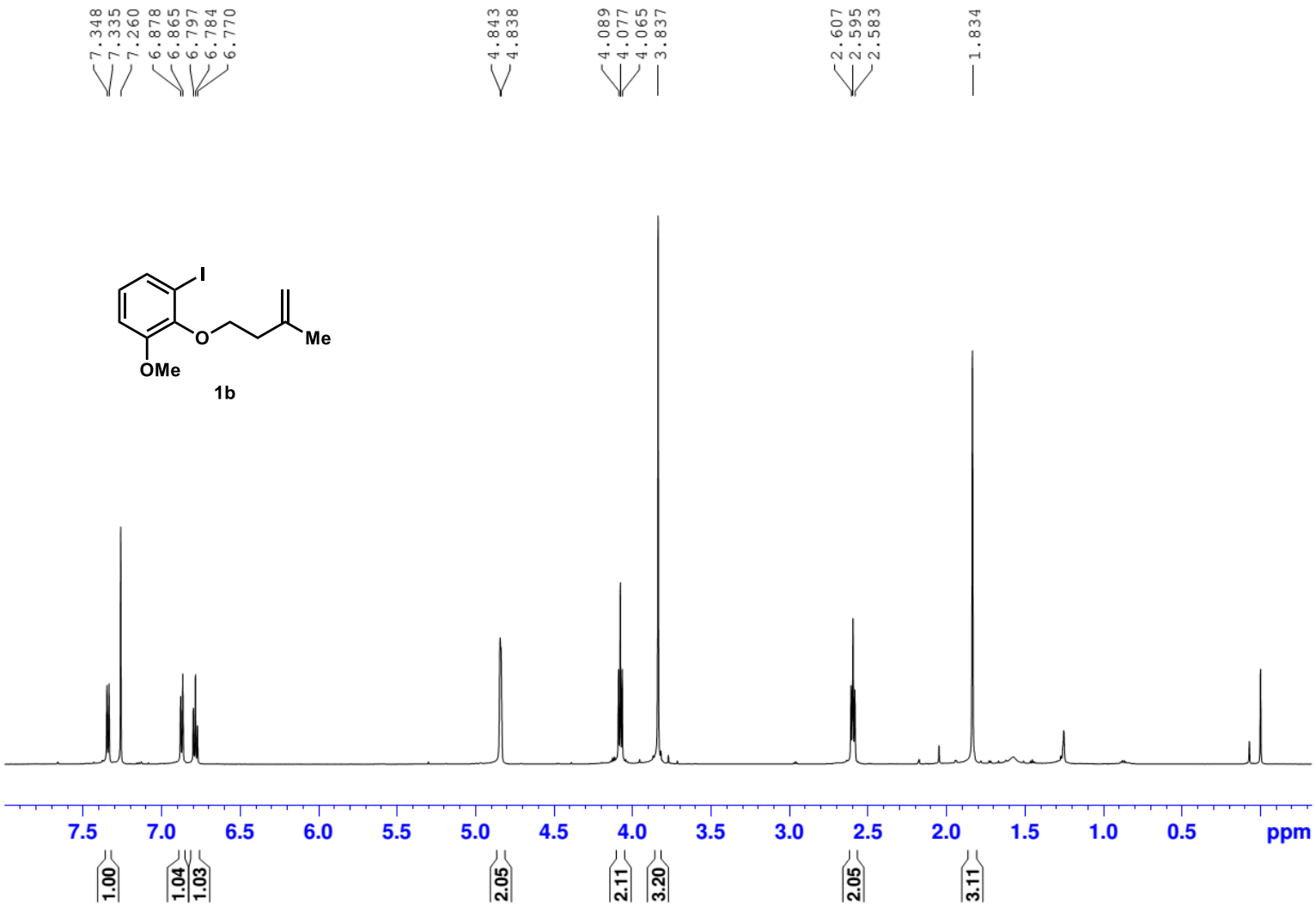
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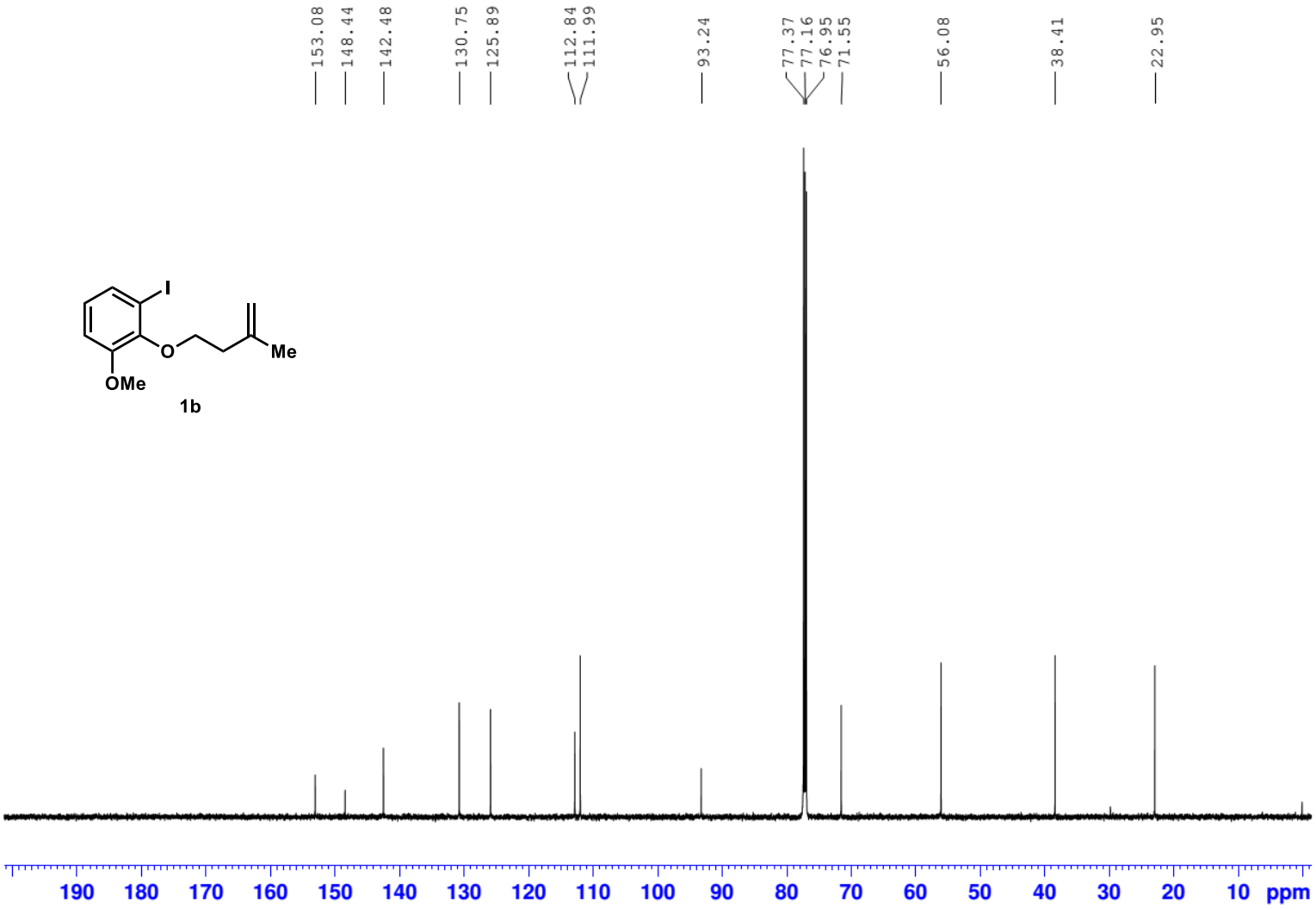
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OMe
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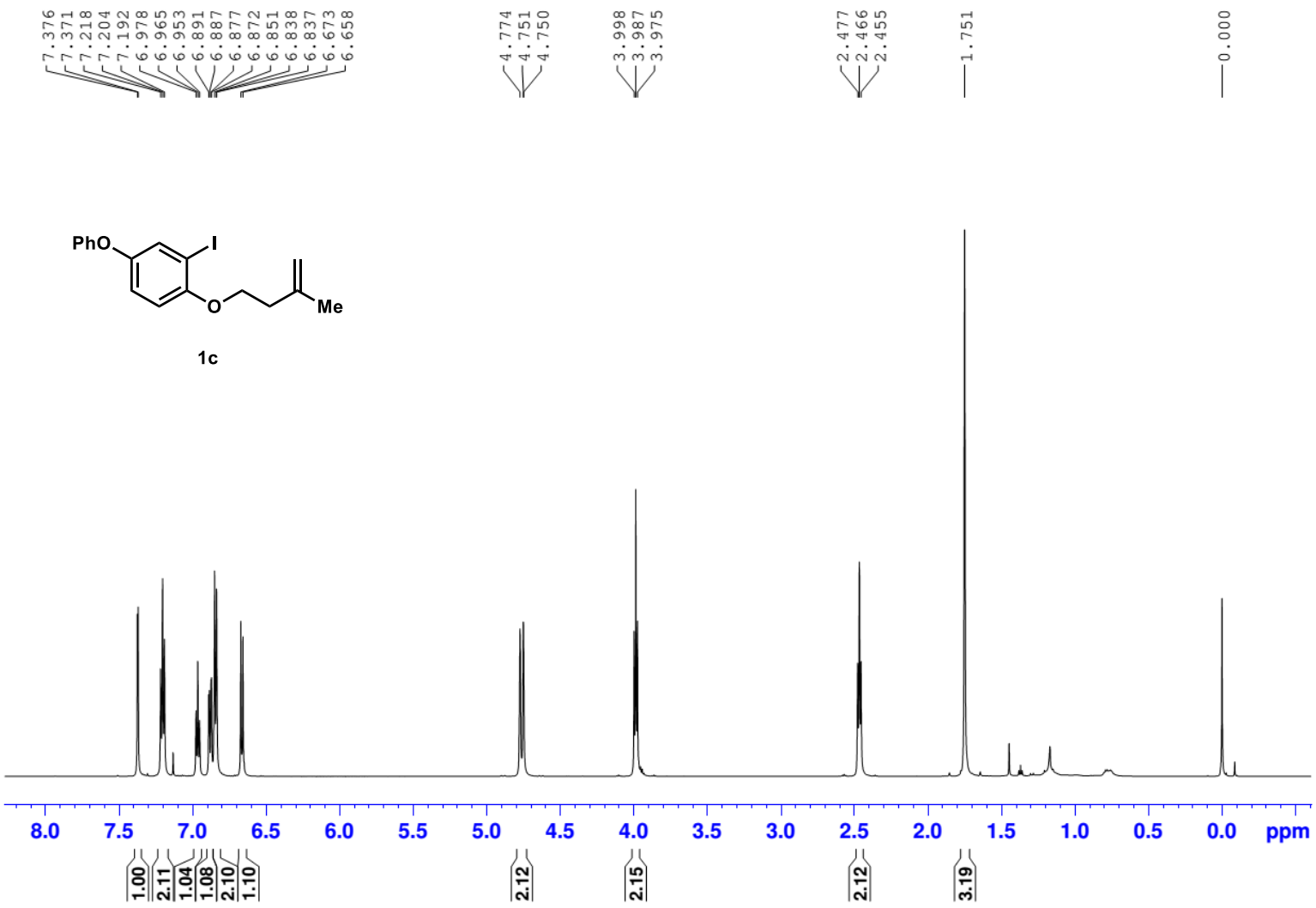
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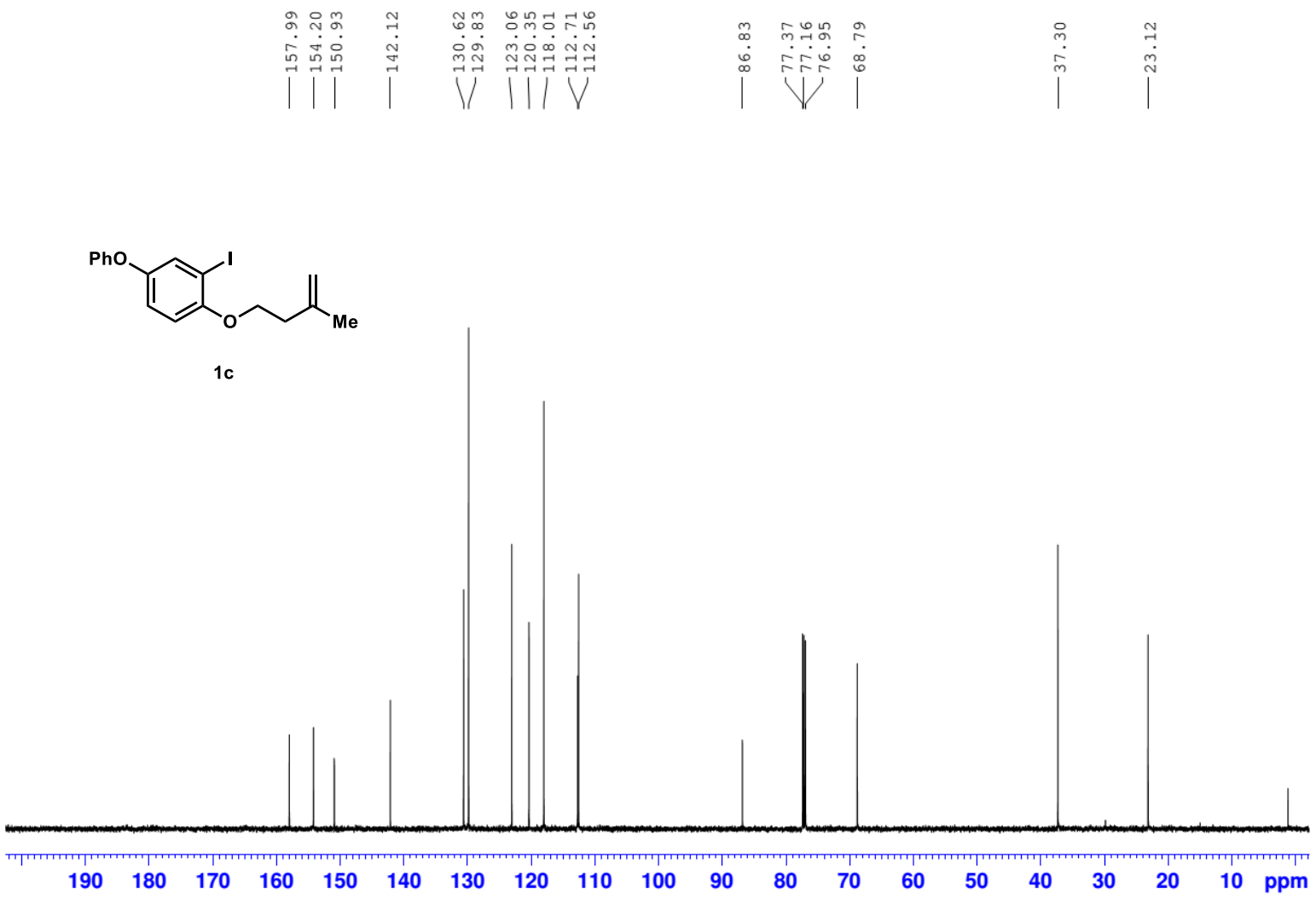
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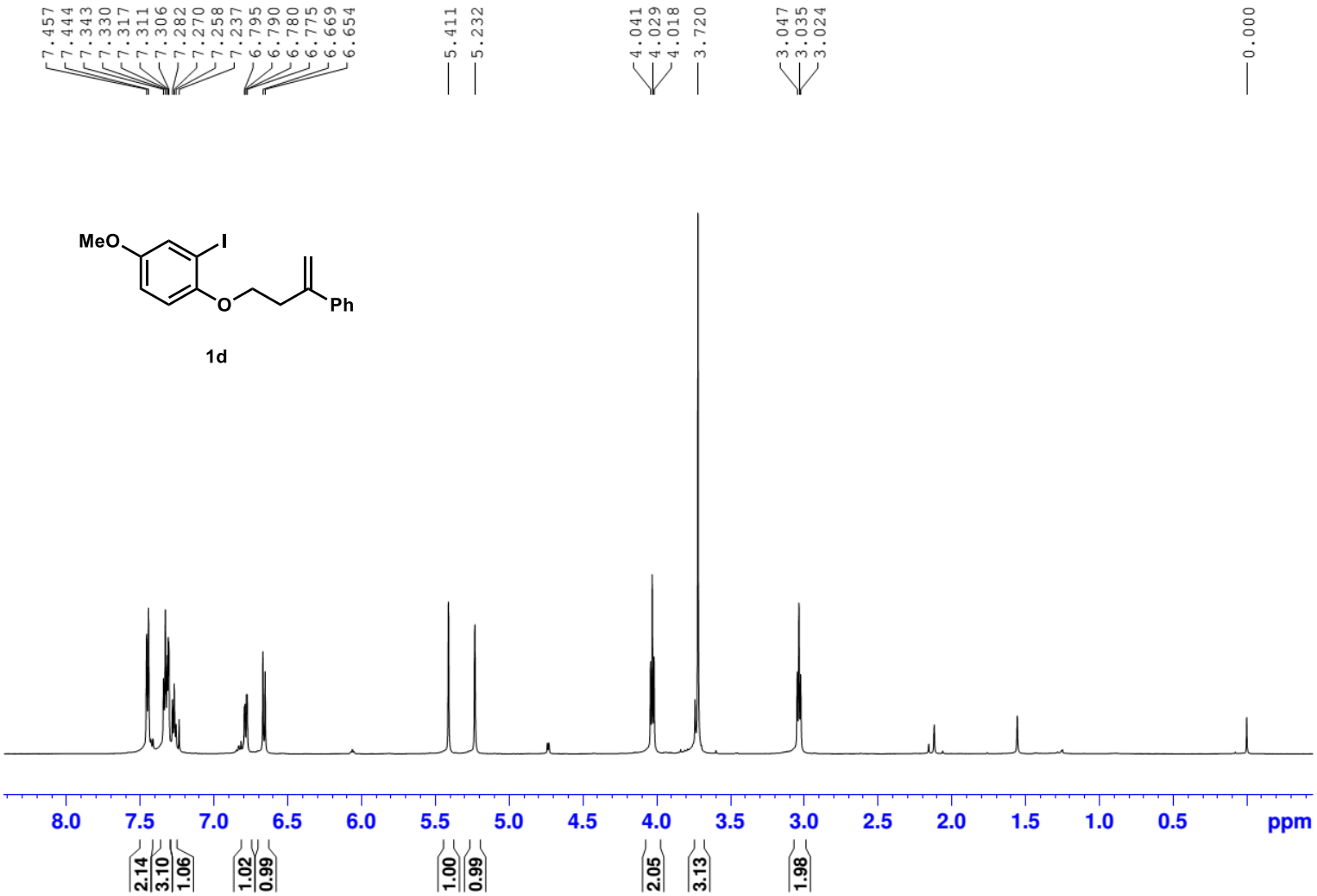
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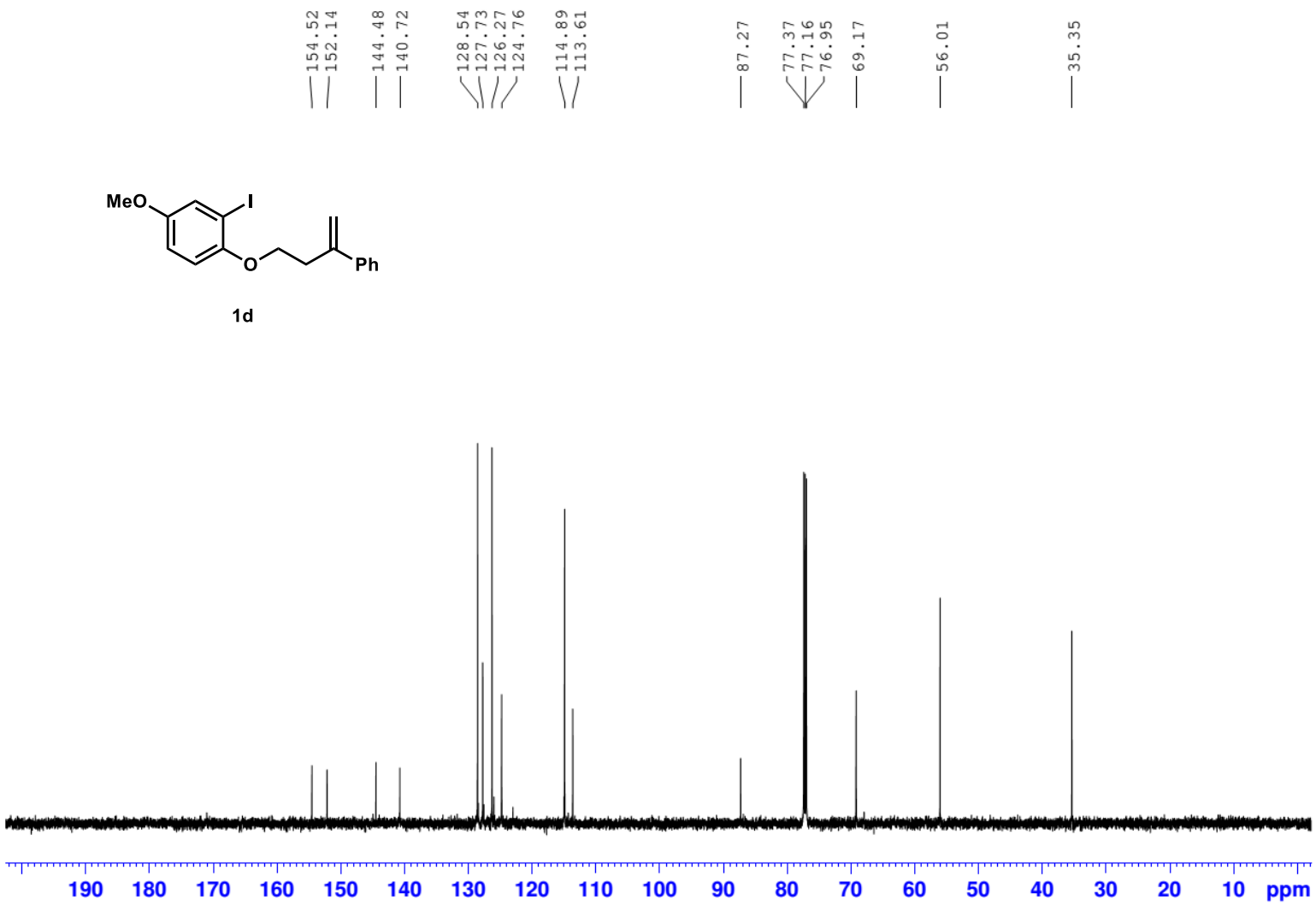
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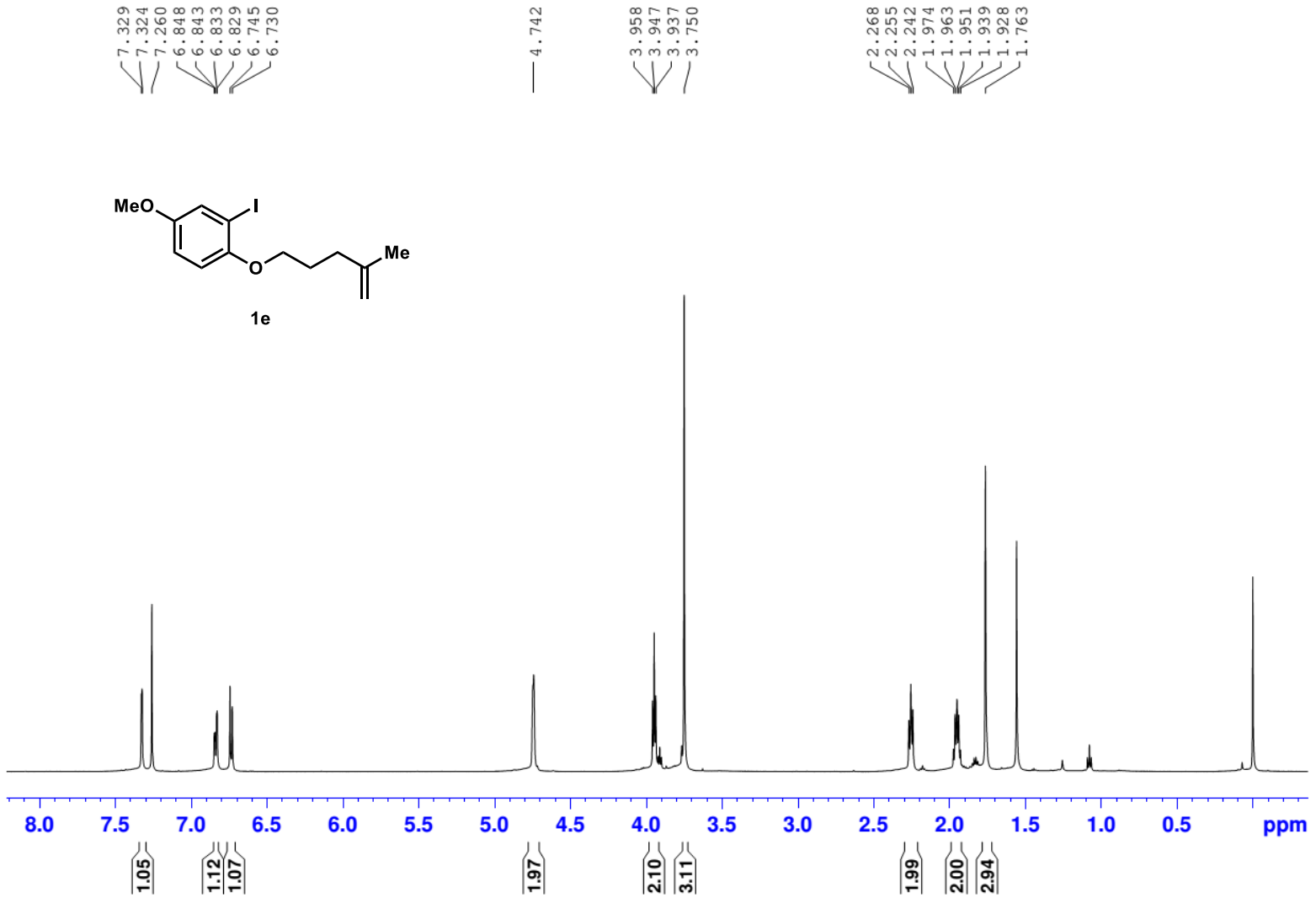
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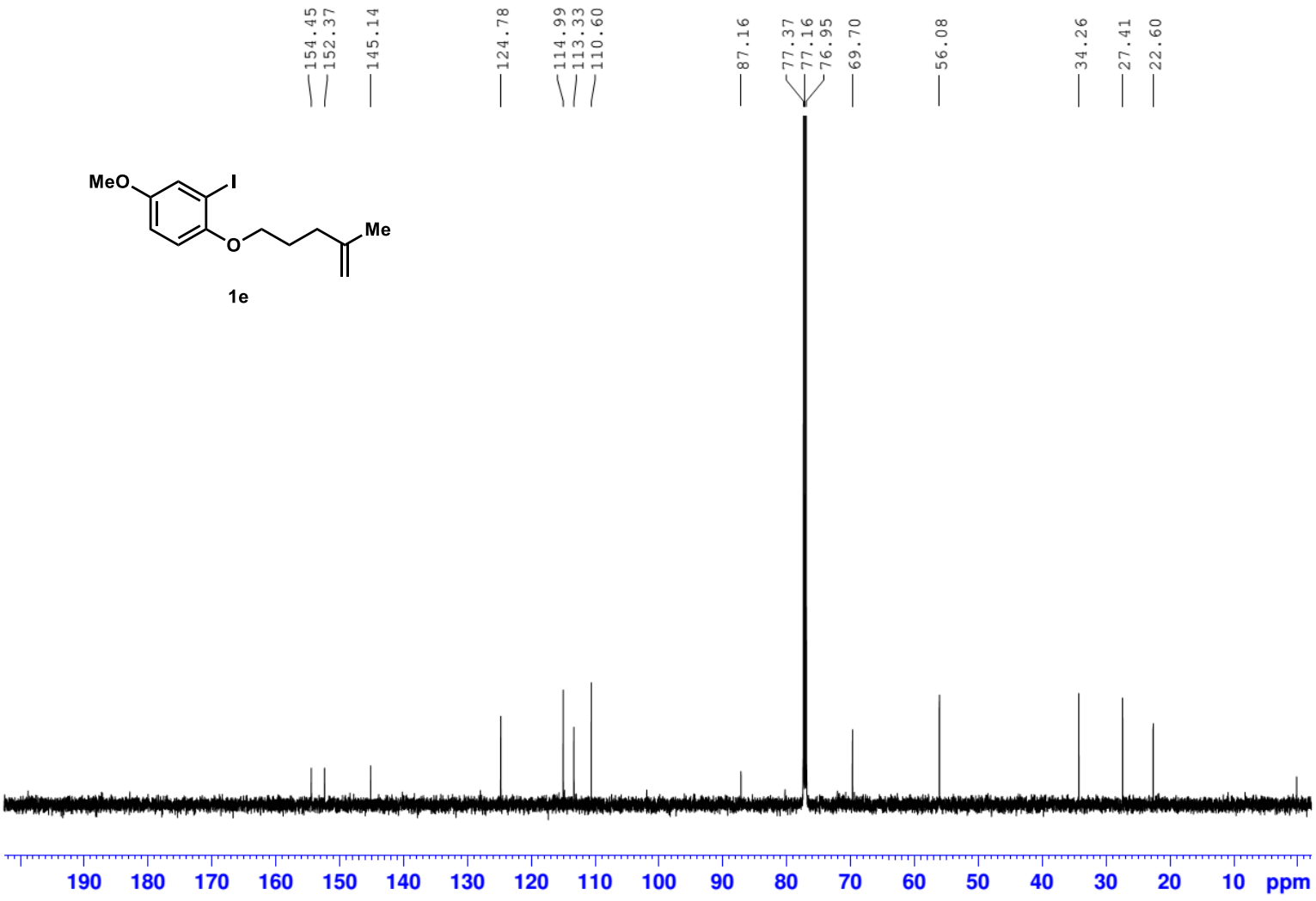
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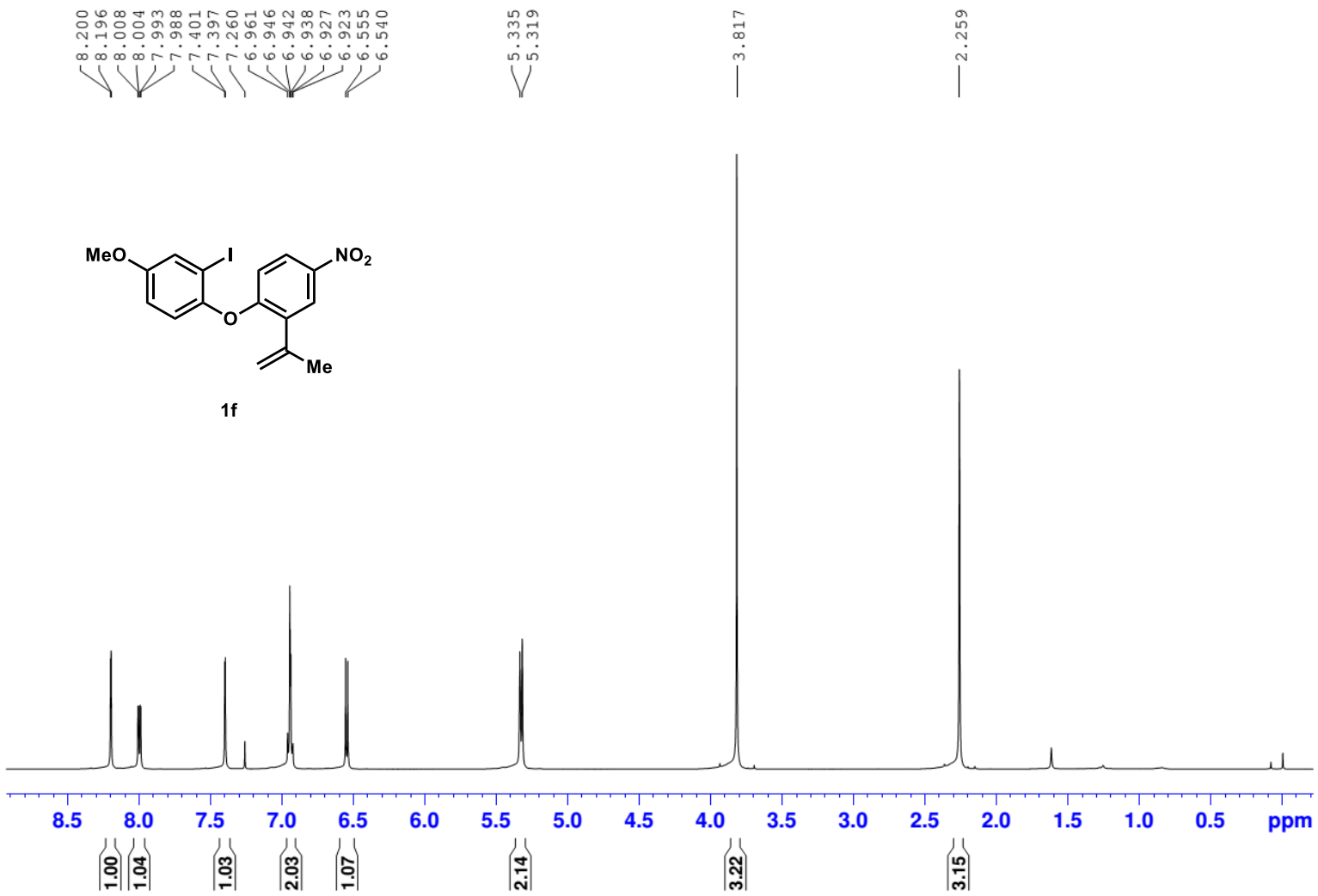
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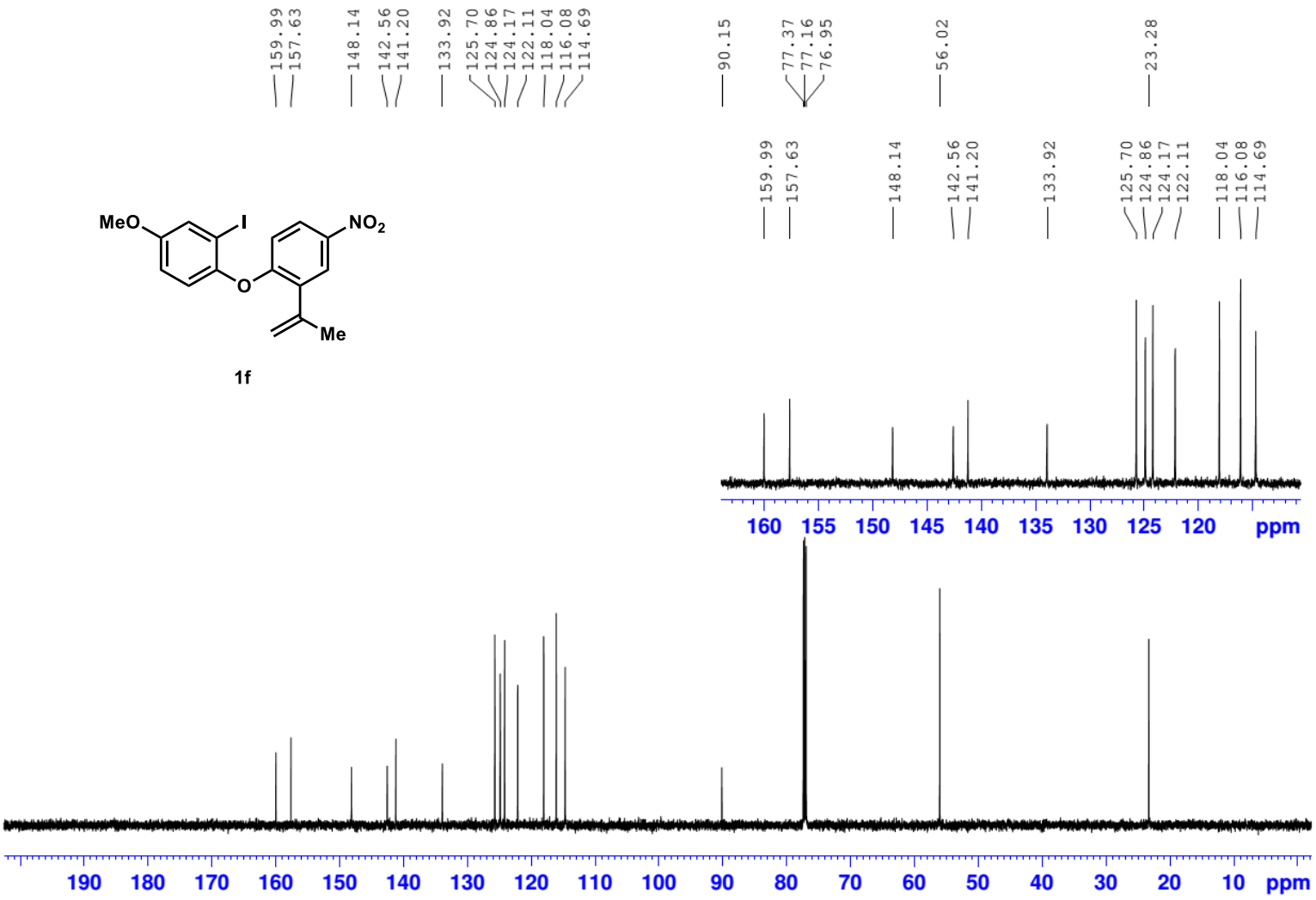
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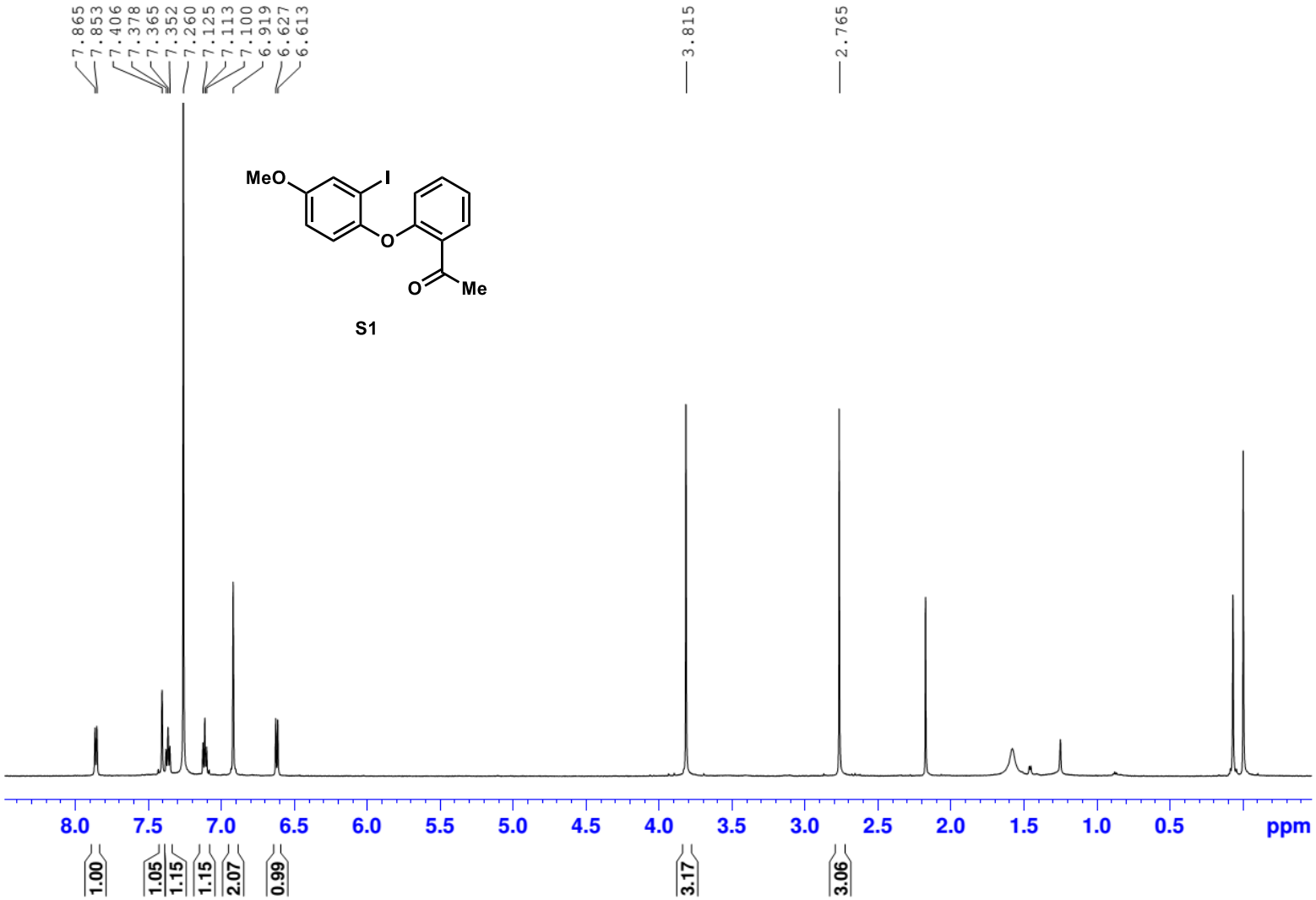
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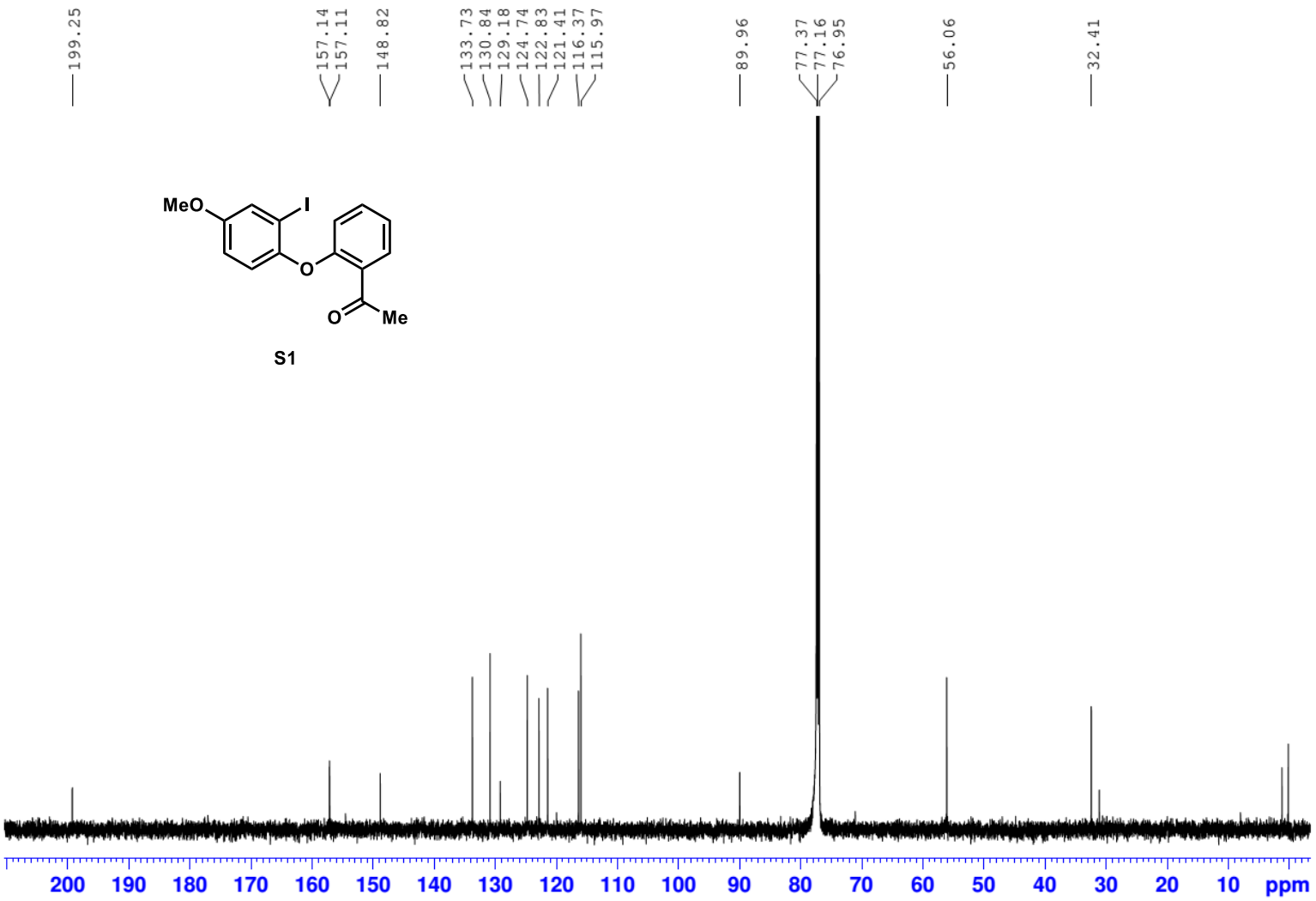
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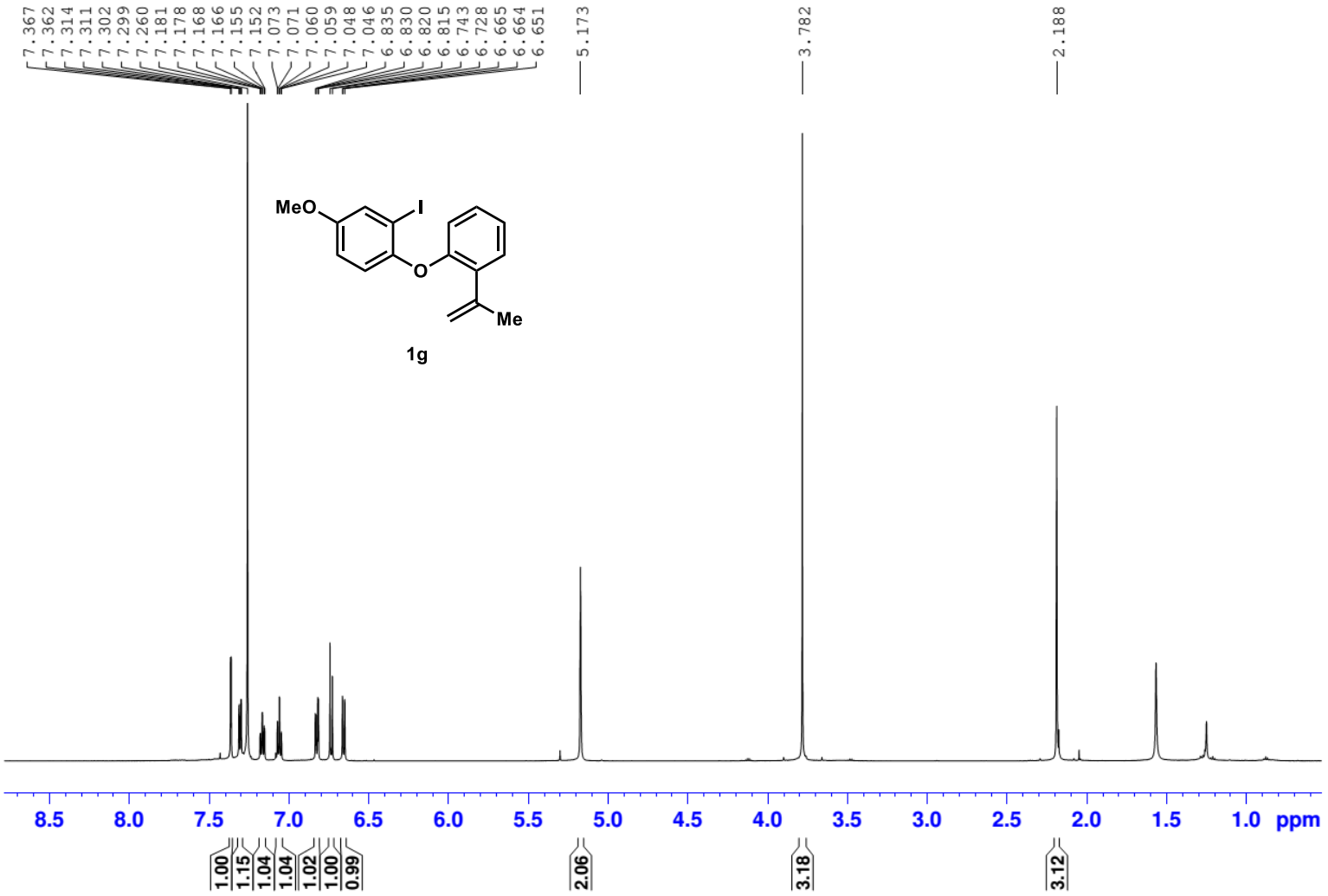
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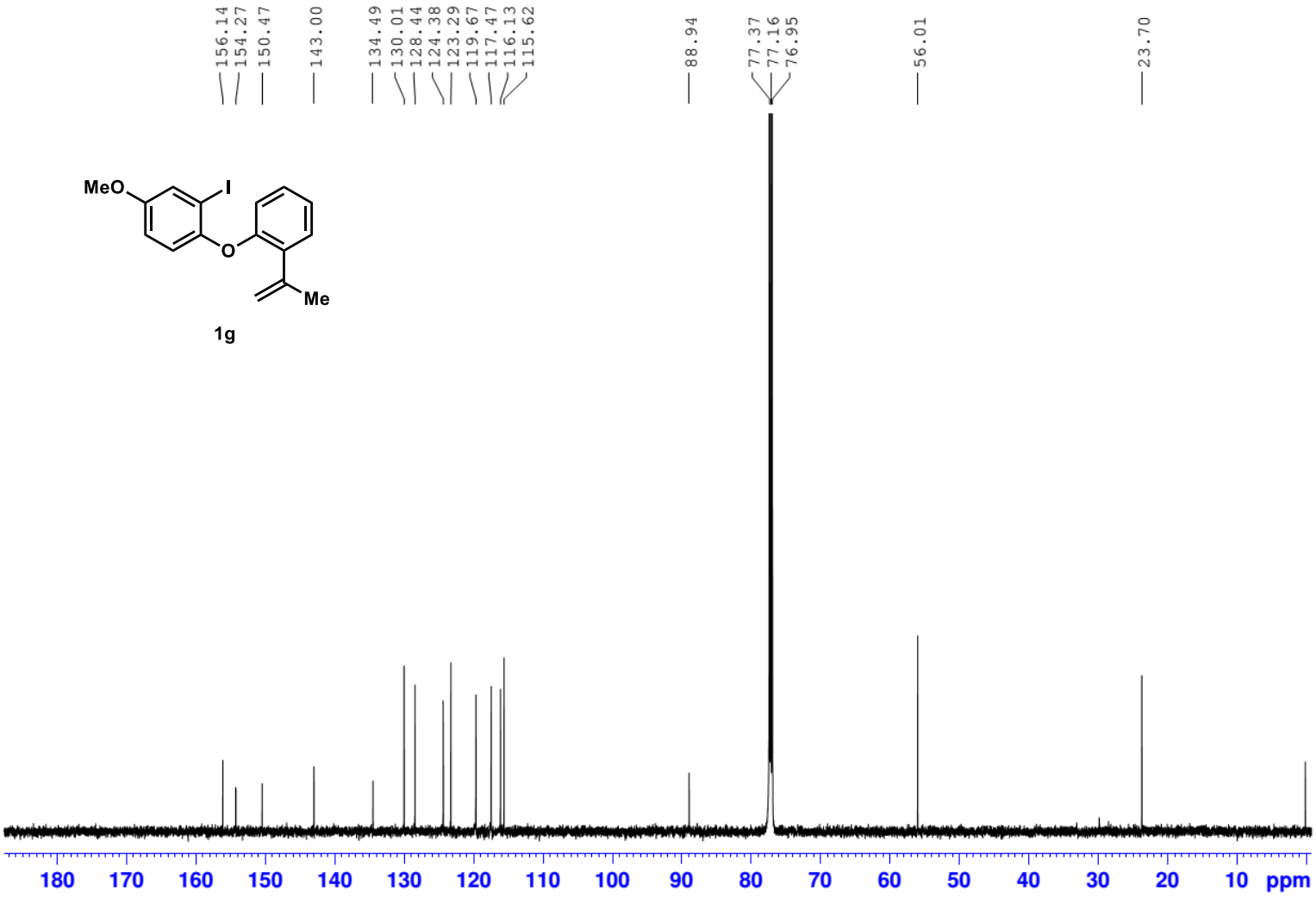
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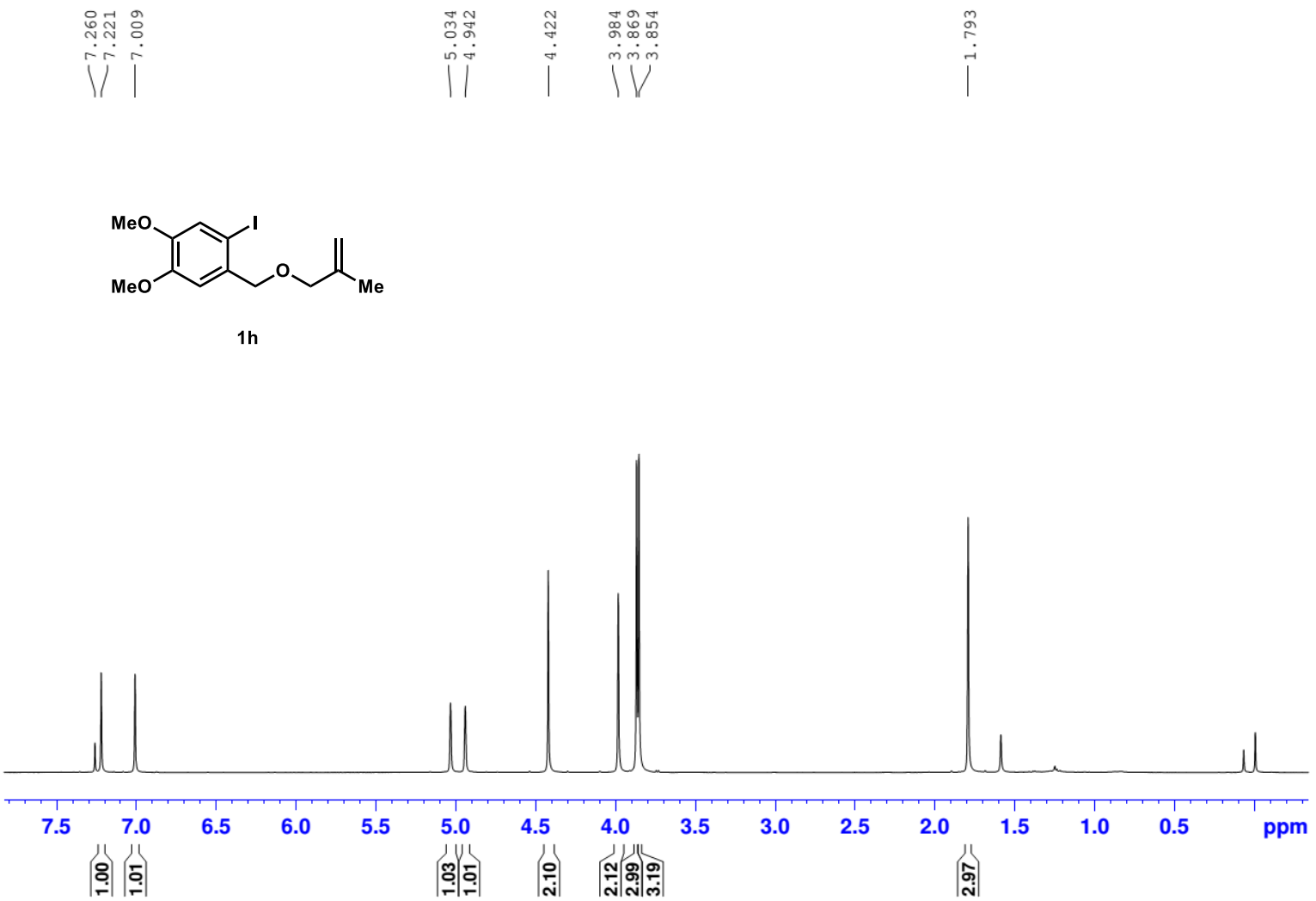
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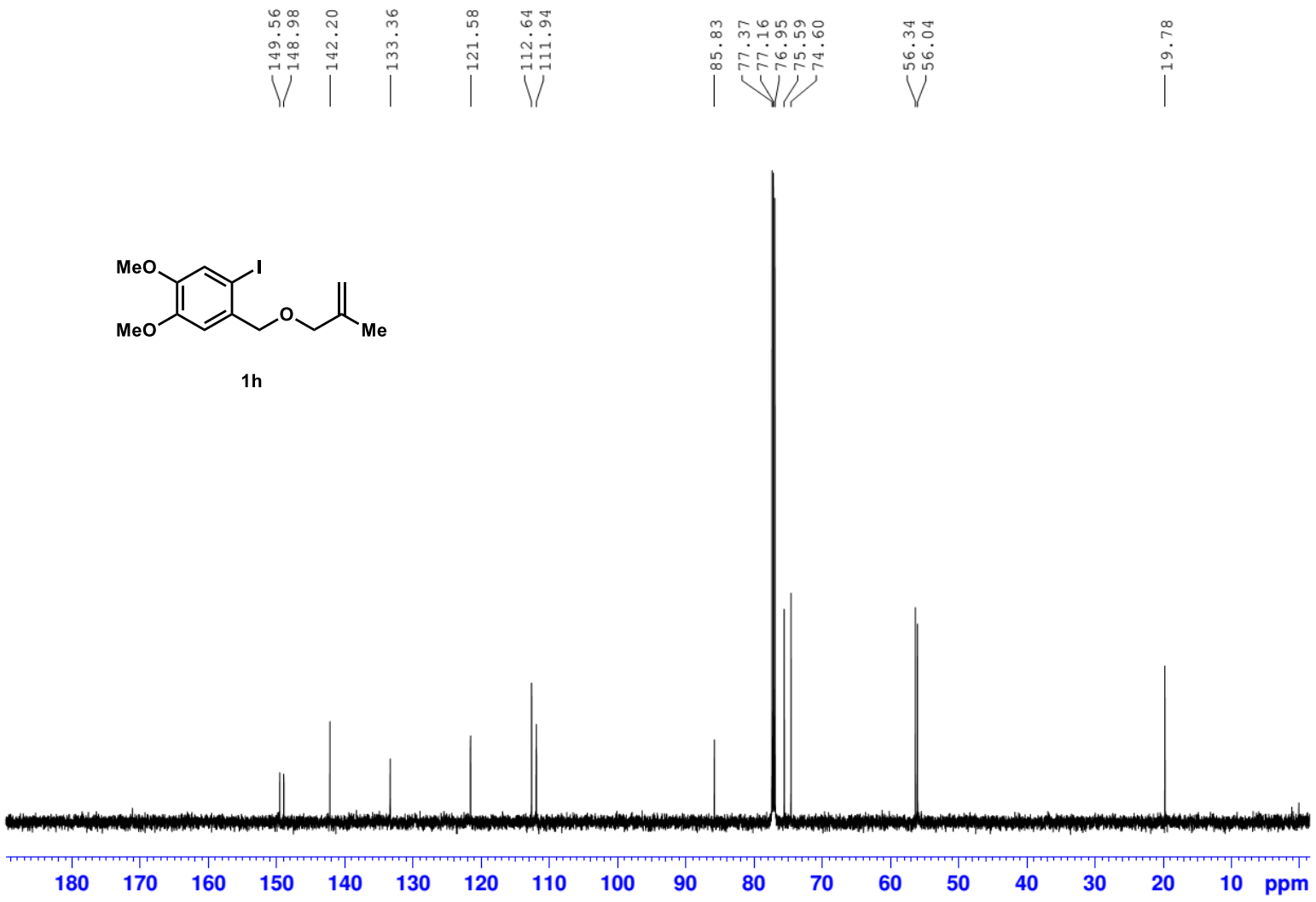
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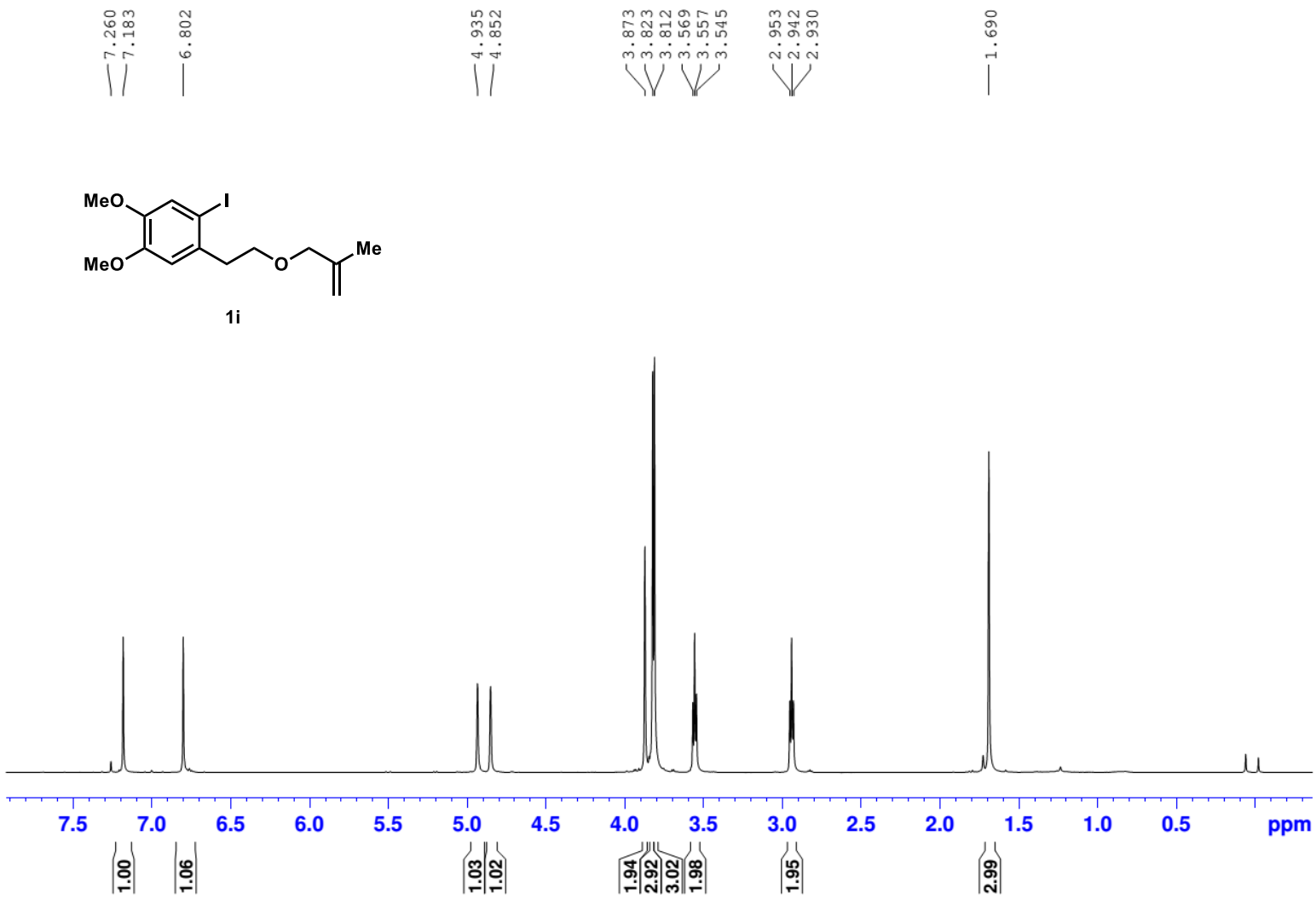
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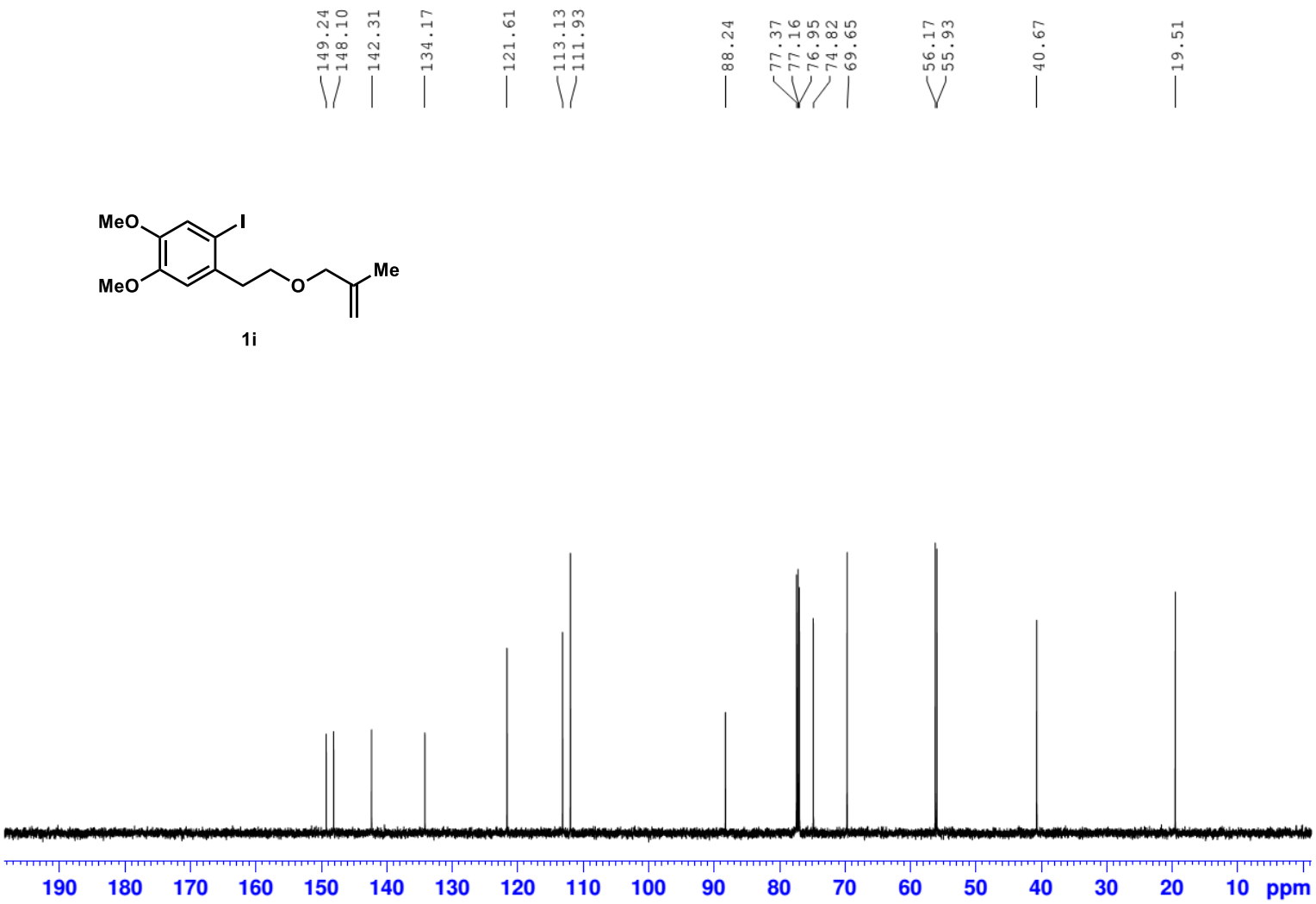
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MeO
I
O
Me
1i
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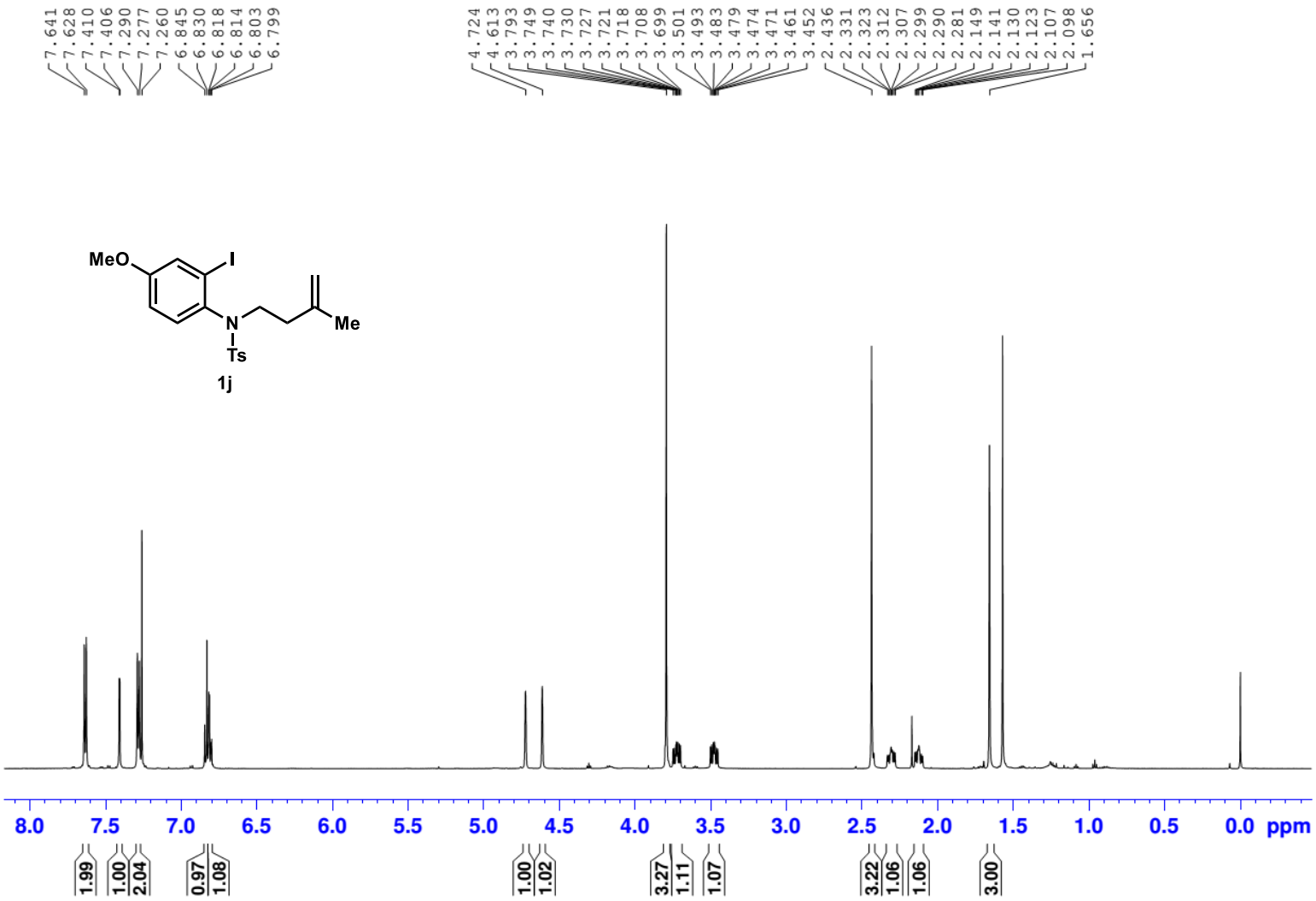
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3.452
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2.290
2.281
2.149
2.141
2.130
2.123
2.107
2.098
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MeO
I
N
Ts
Me
1j
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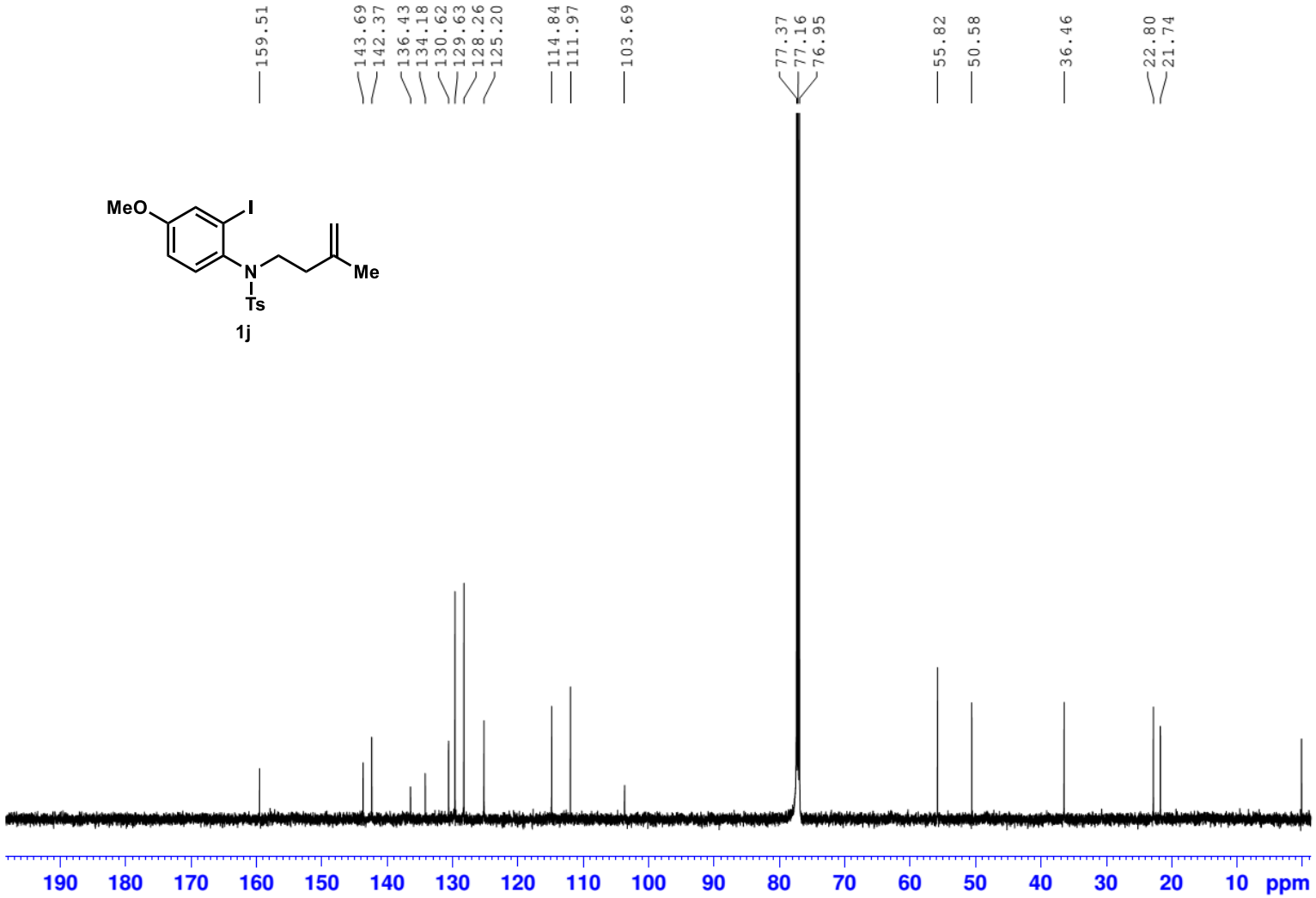
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22.80
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MeO
I
N
Ts
Me
1j
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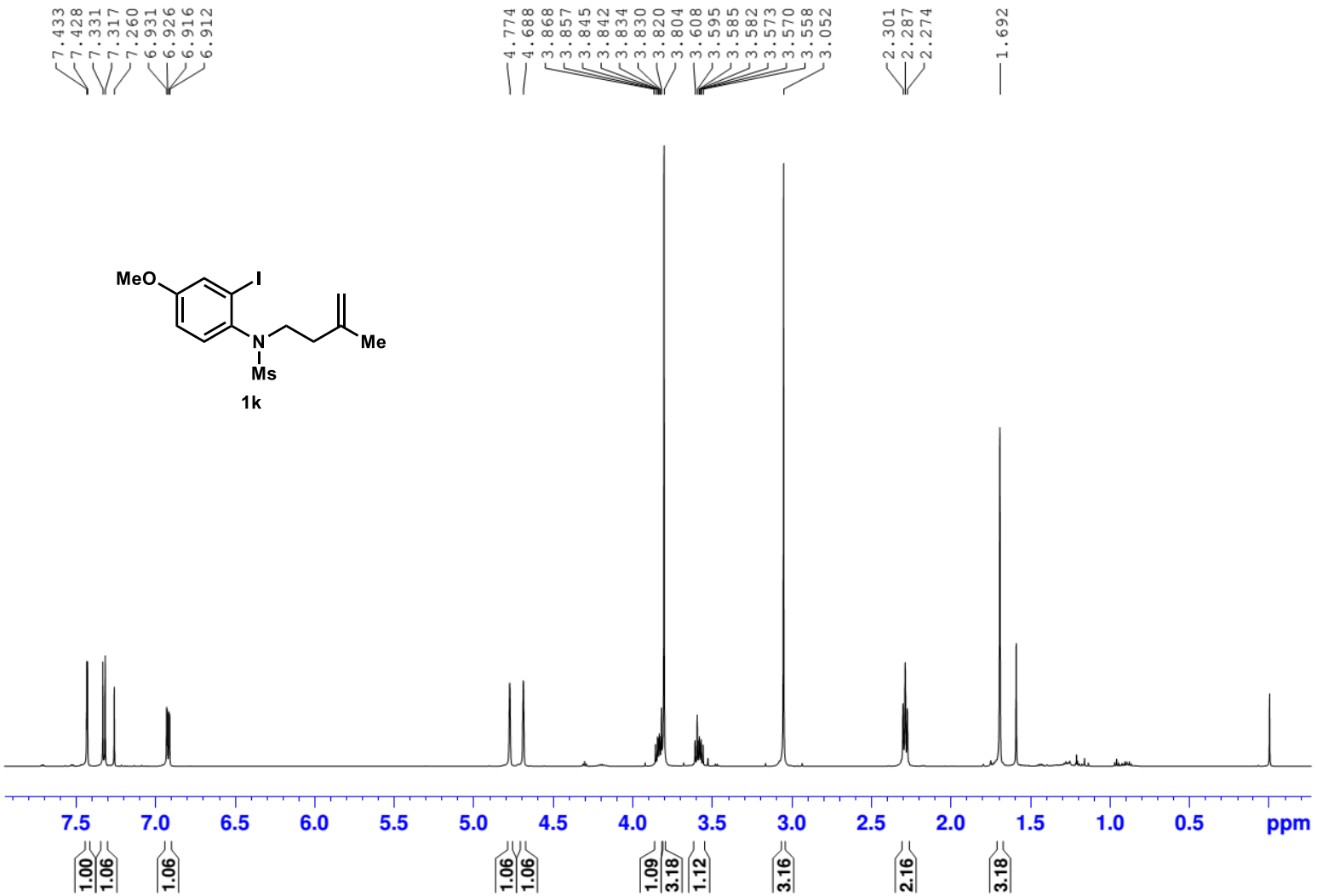
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3.582
3.573
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3.558
3.052
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2.287
2.274
1.692
MeO
I
N
Ms
Me
1k
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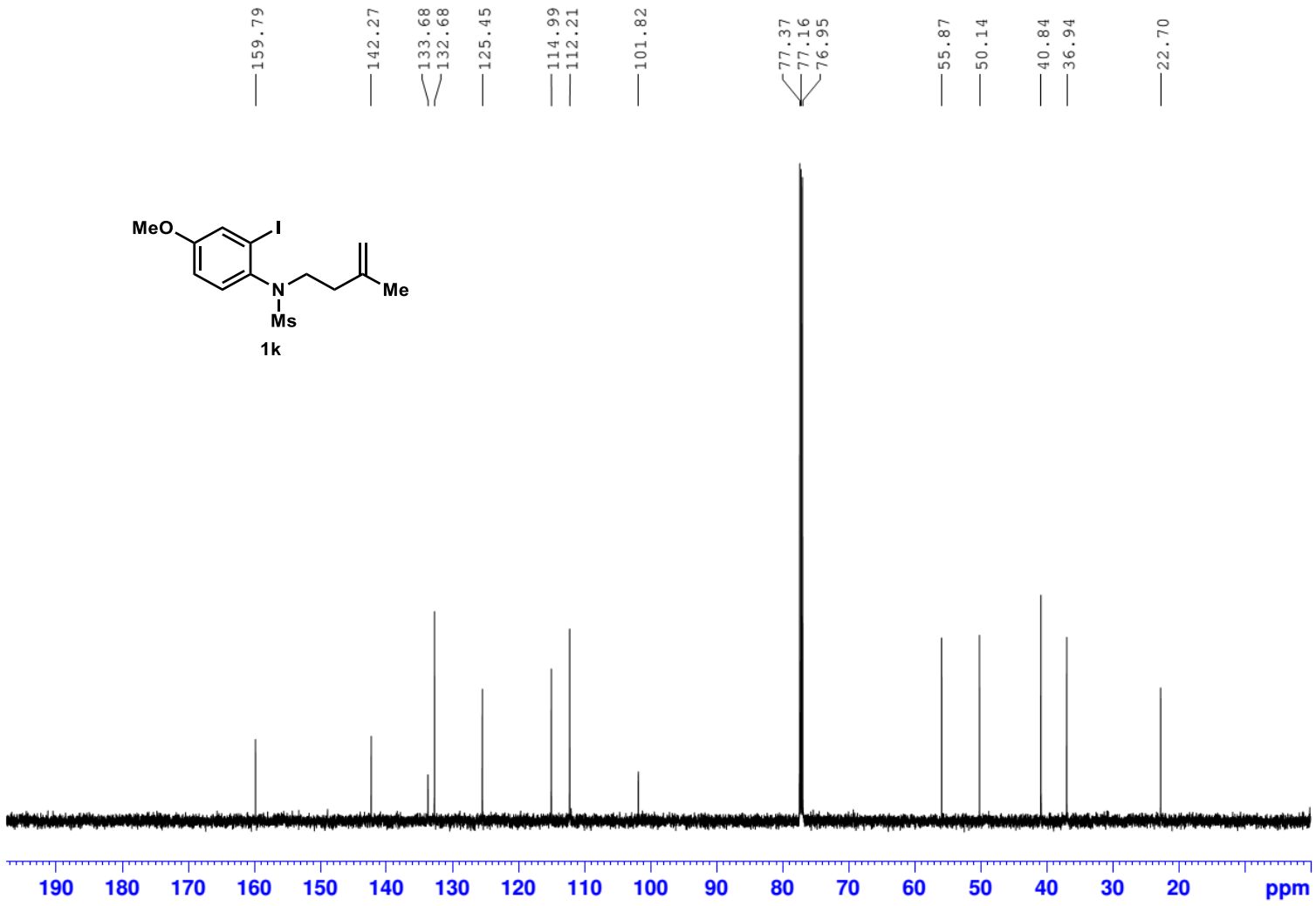
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50.14
40.84
36.94
22.70
MeO
I
N
Ms
Me
1k
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150
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80
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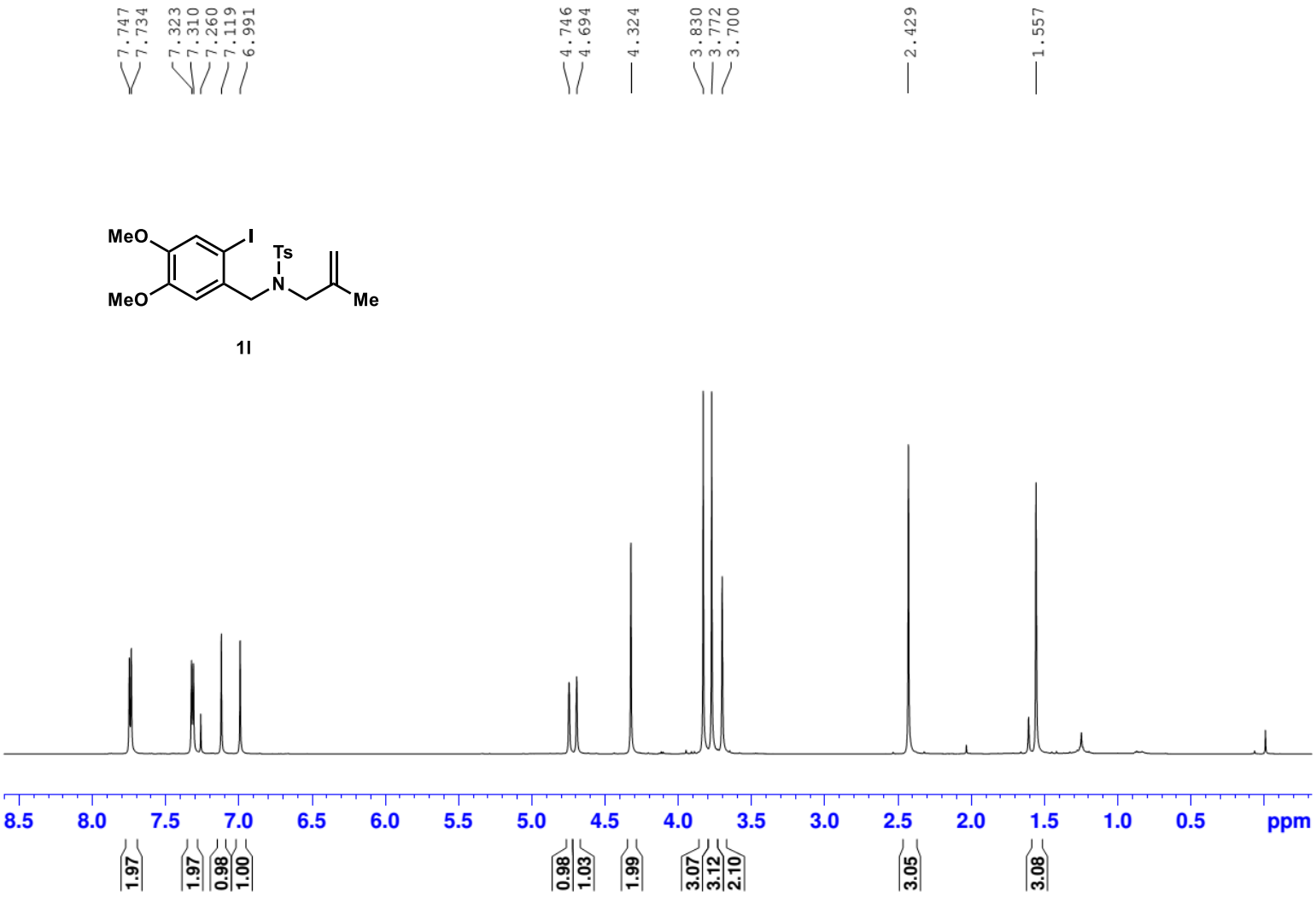
20
ppm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2.429
1.557
MeO
MeO
I
Ts
N
Me
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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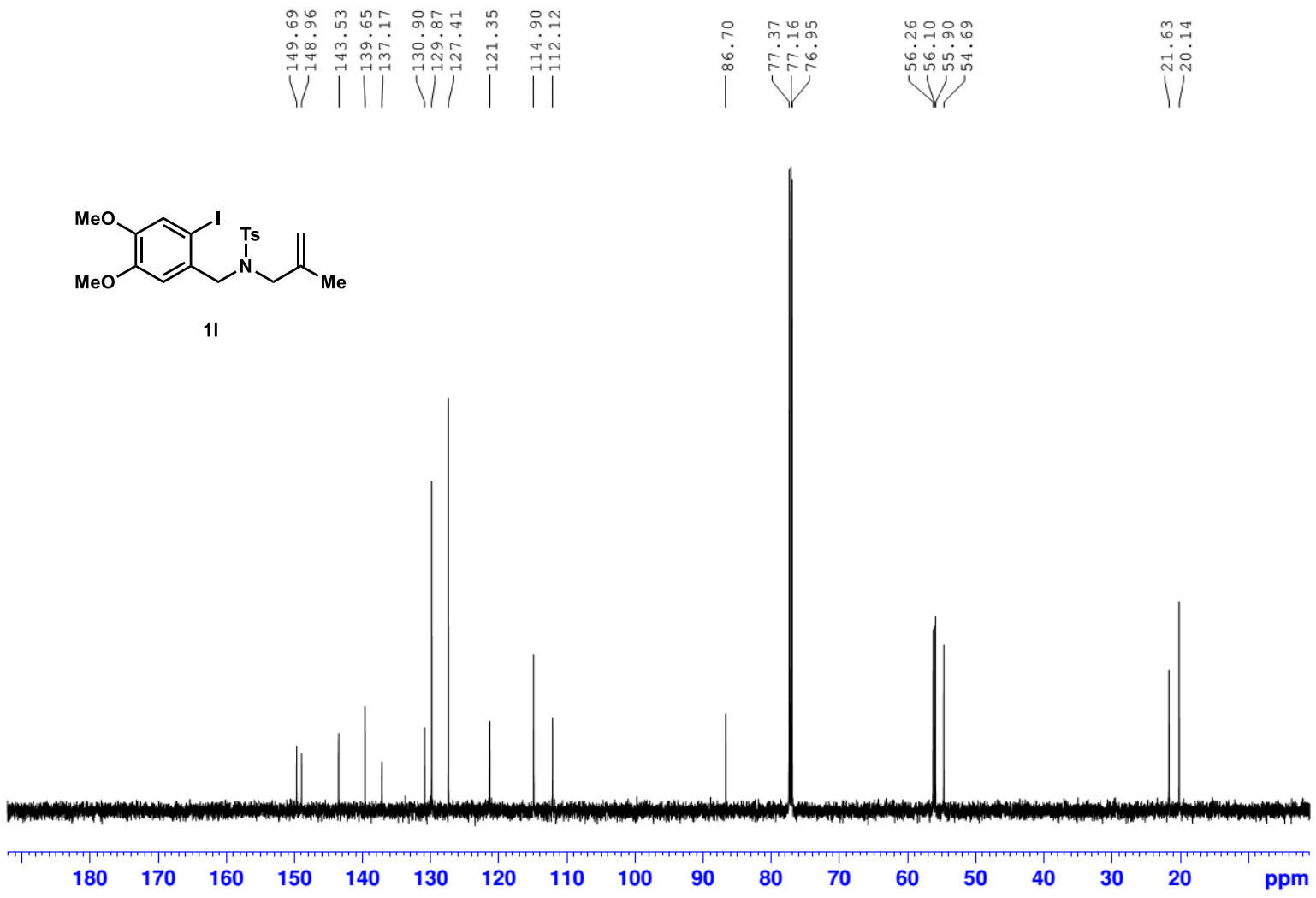
3.08

1l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77.16
76.95
56.26
56.10
55.90
54.69
21.63
20.14
MeO
MeO
I
Ts
N
Me
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150
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80
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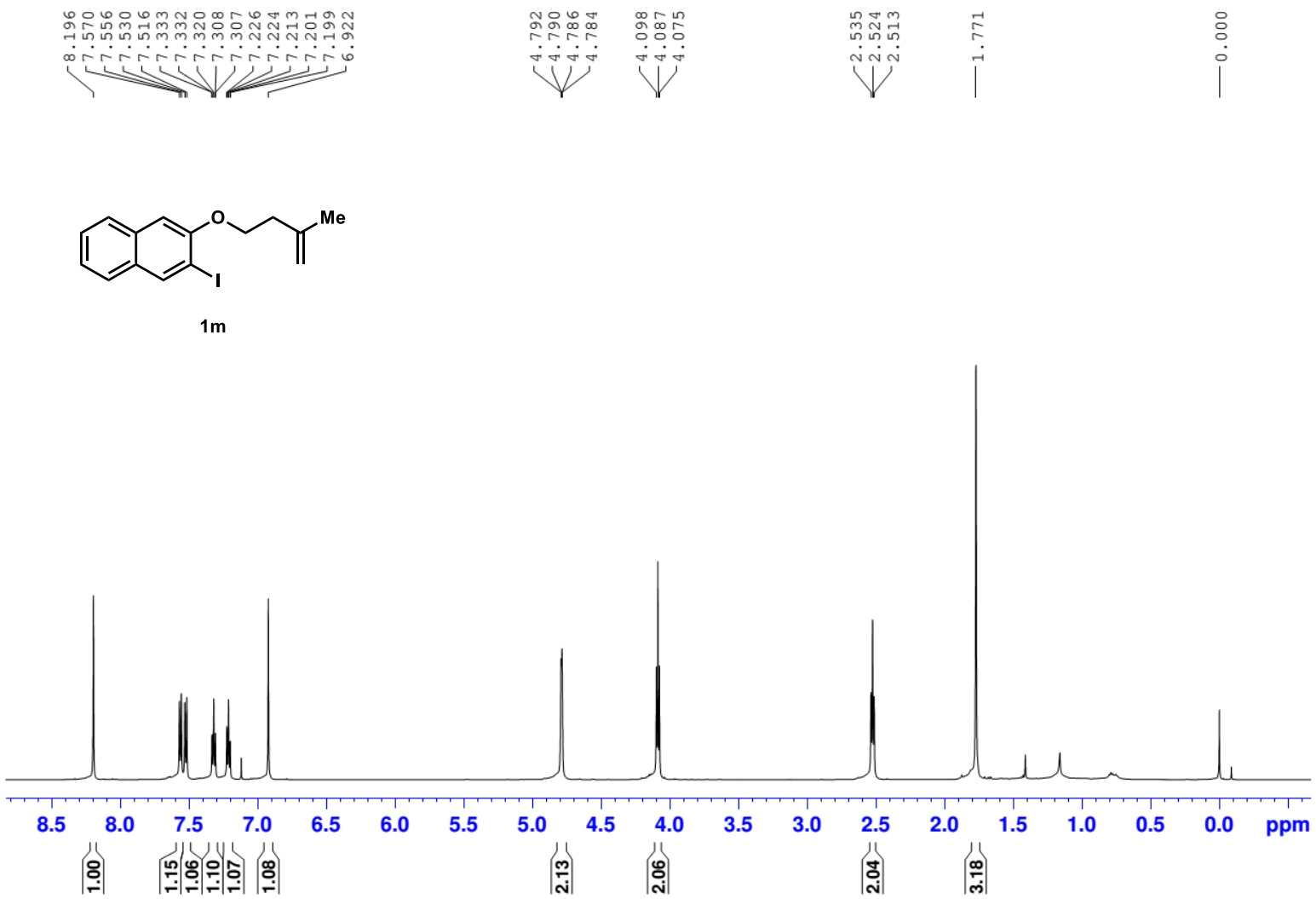
50
40
30
20
ppm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7.224
7.213
7.201
7.199
6.922
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4.790
4.786
4.784
4.098
4.087
4.075
2.535
2.524
2.513
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0.000
O
Me
I
1m
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7.5
7.0
6.5
6.0
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4.5
4.0
3.5
3.0
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1.08
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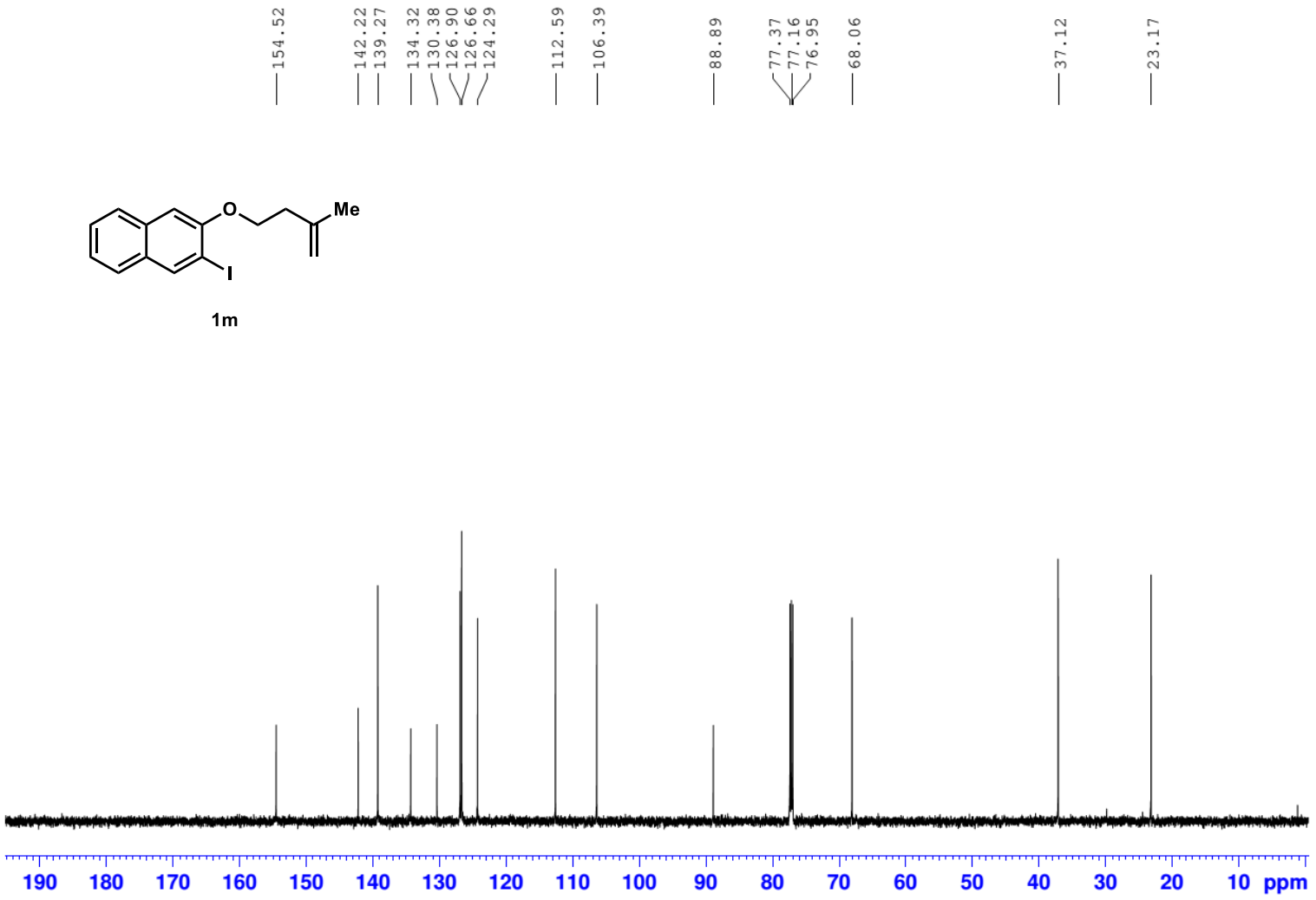
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77.37
77.16
76.95
68.06
37.12
23.17
O
Me
I
1m
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150
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30
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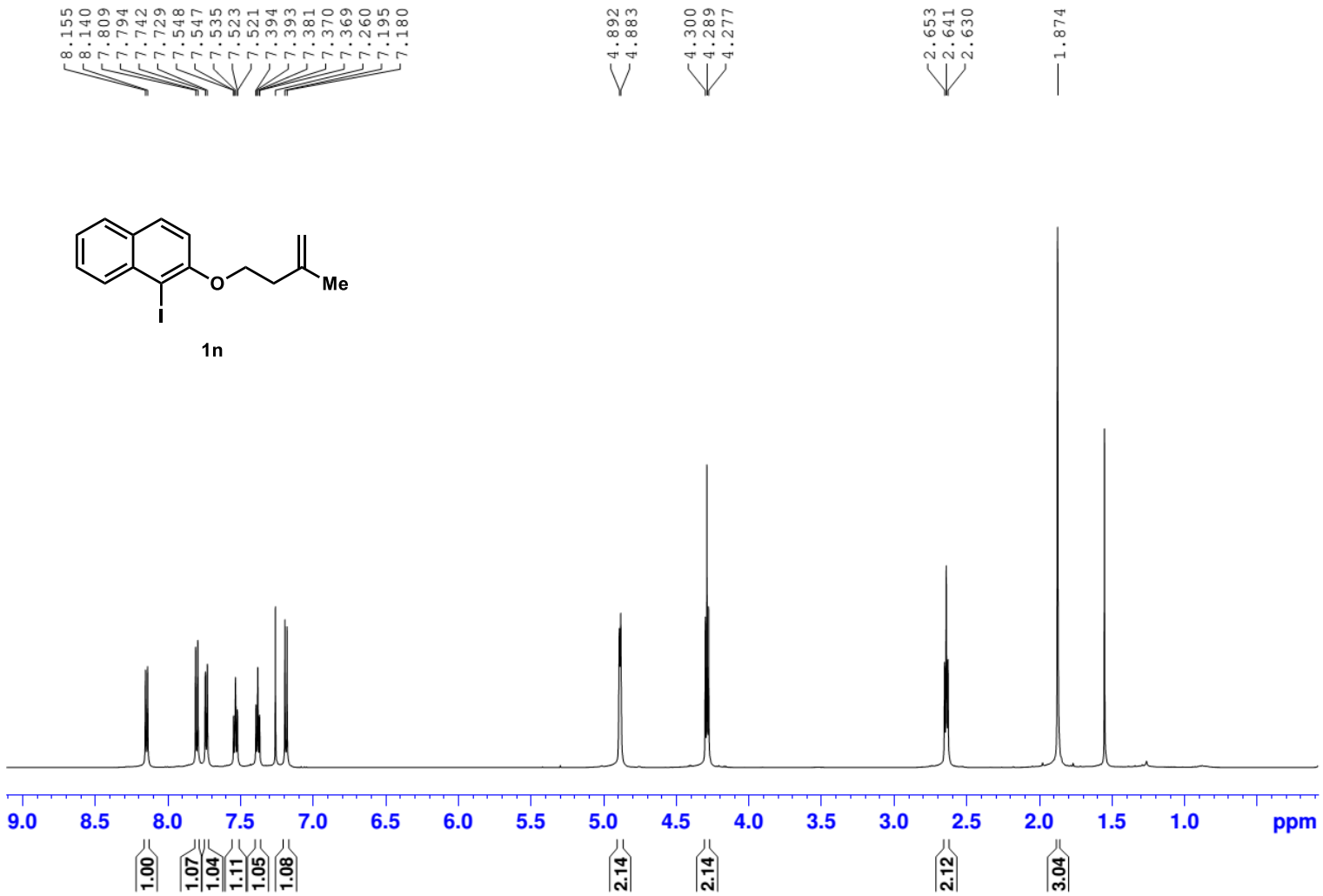
10
ppm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7.393
7.381
7.370
7.369
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O
Me
I
1n
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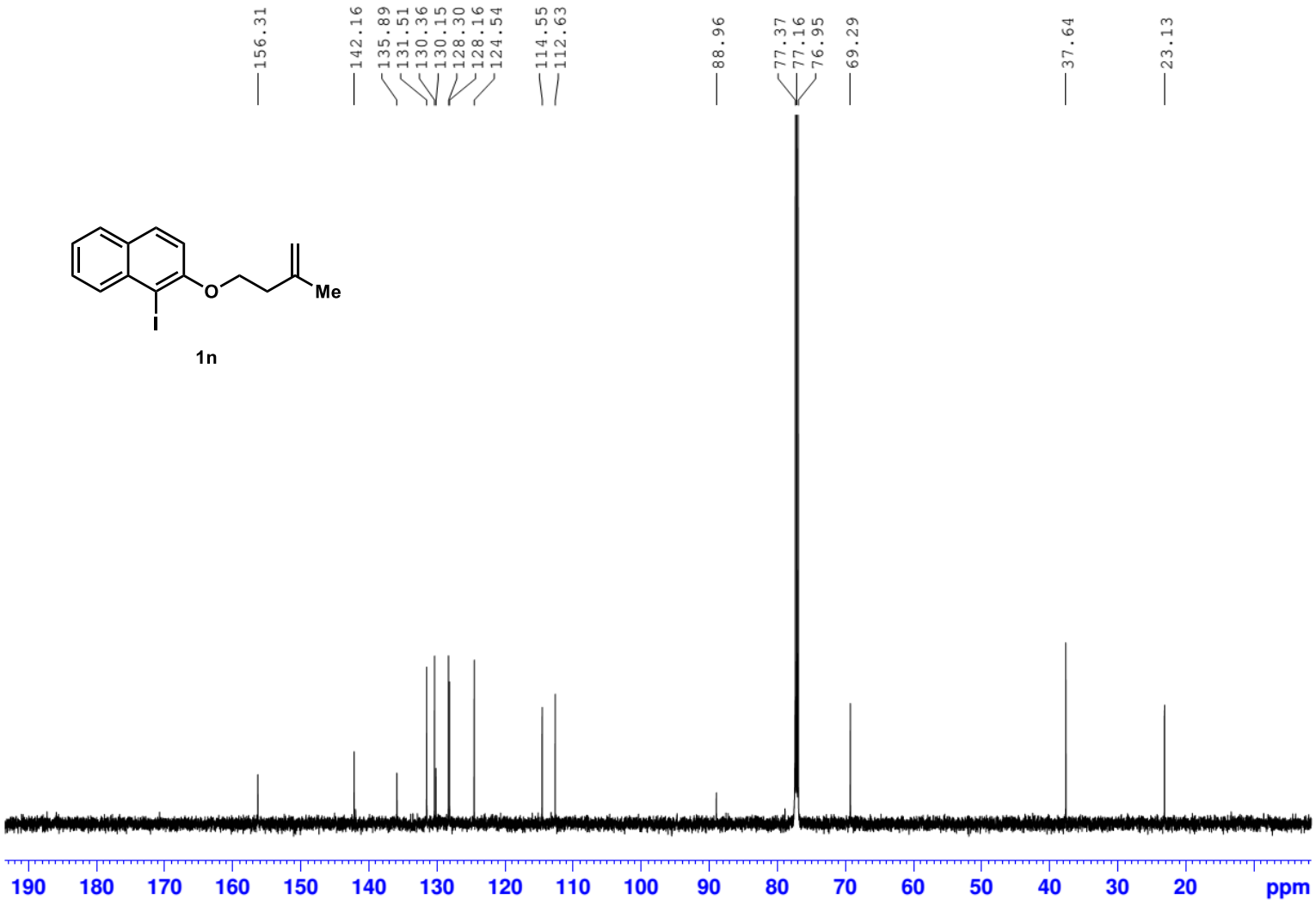
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77.16
76.95
69.29
37.64
23.13
O
Me
I
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150
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120
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80
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40
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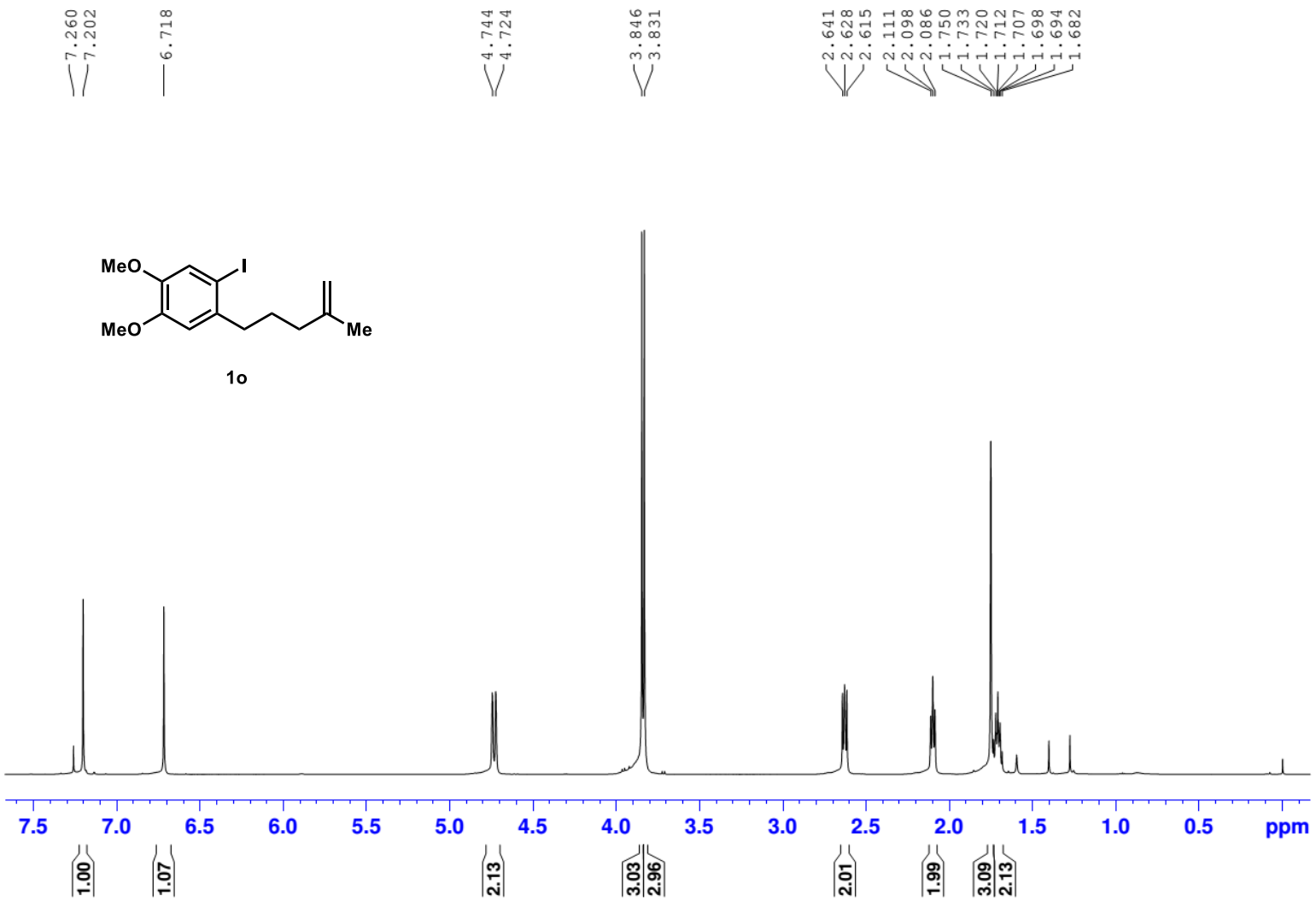
20
ppm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MeO
I
MeO
Me
1o
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6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
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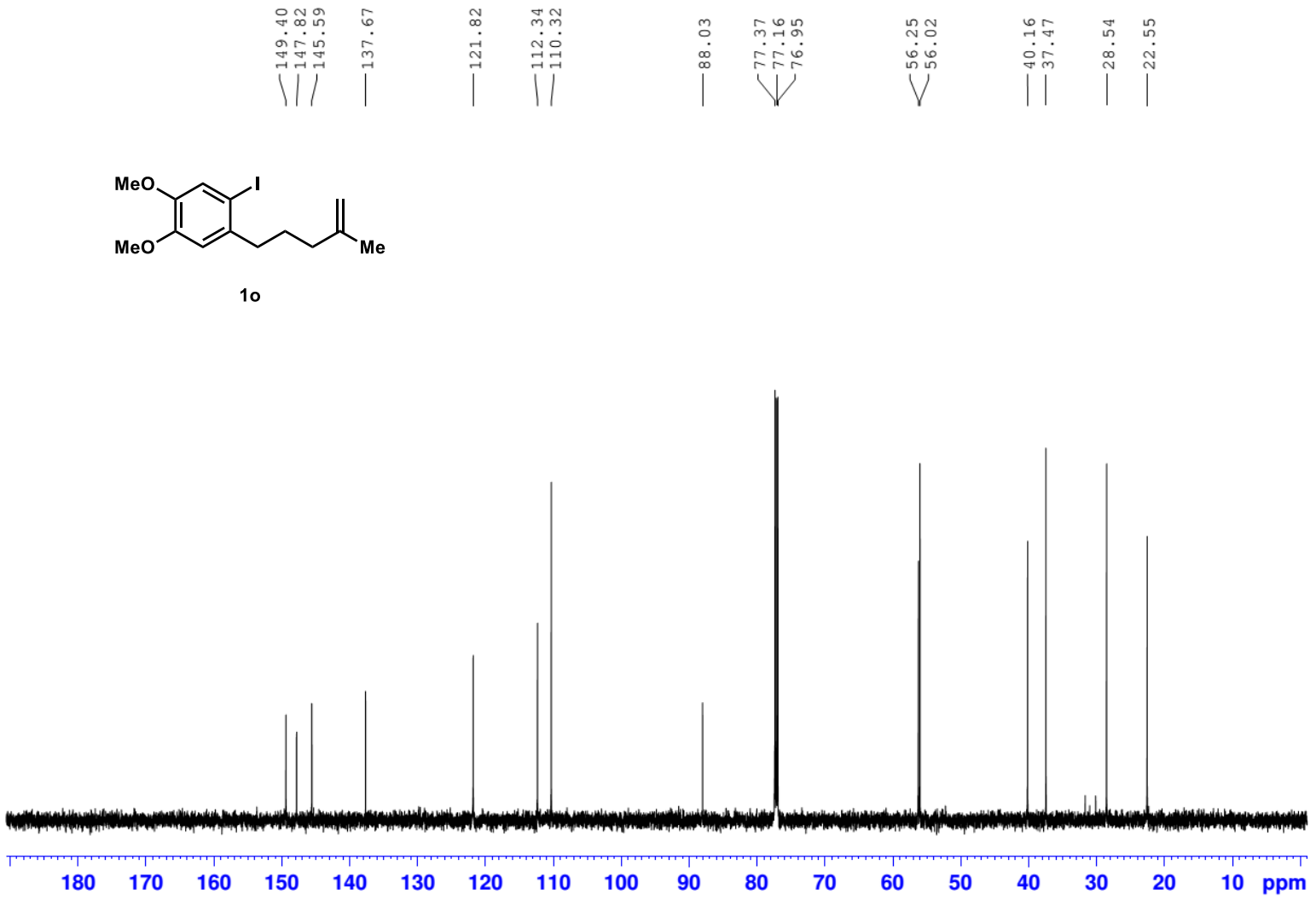
2.13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77.16
76.95
56.25
56.02
40.16
37.47
28.54
22.55
MeO
I
MeO
Me
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120
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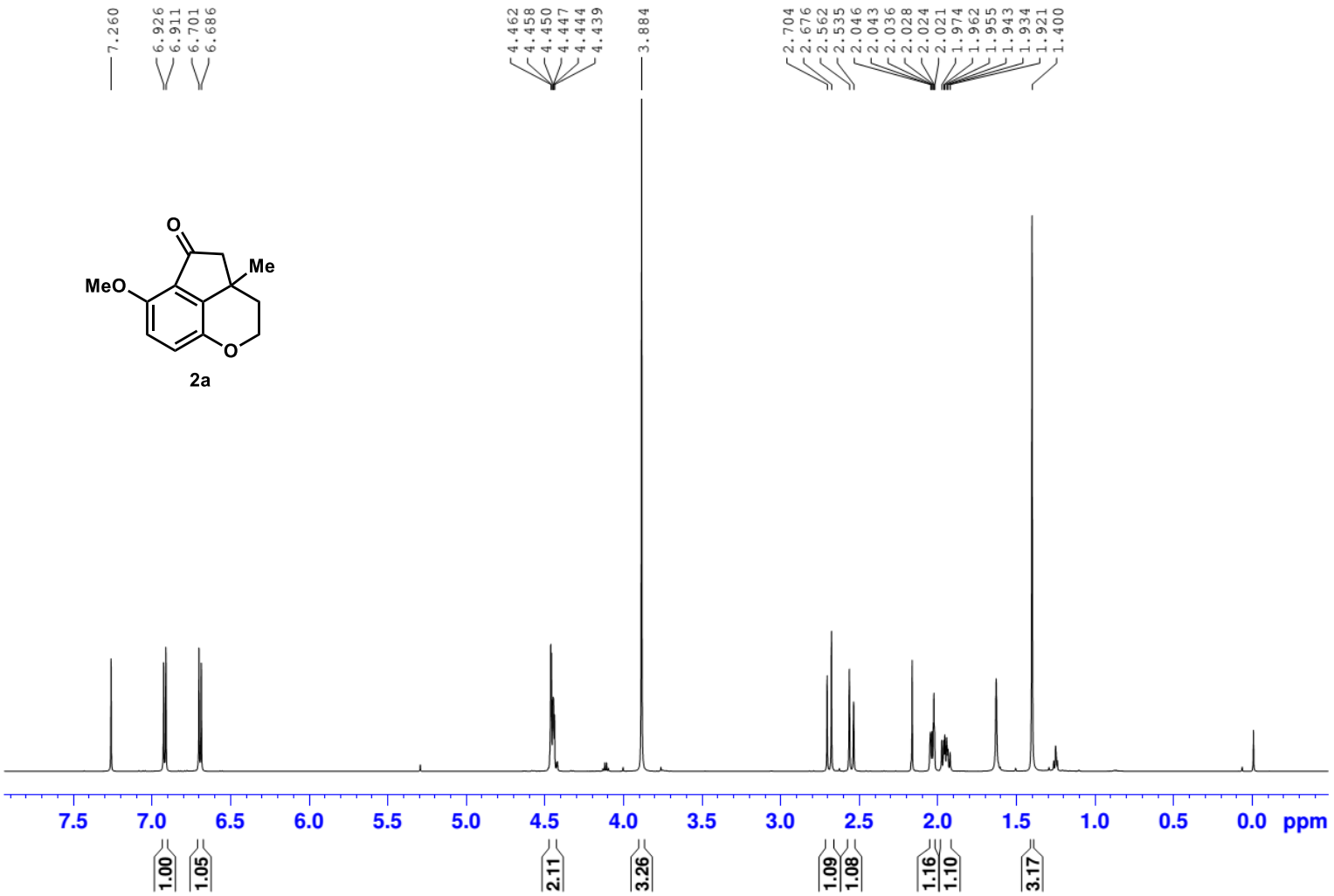
ppm

1o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2.043
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2.021
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Me
MeO
O
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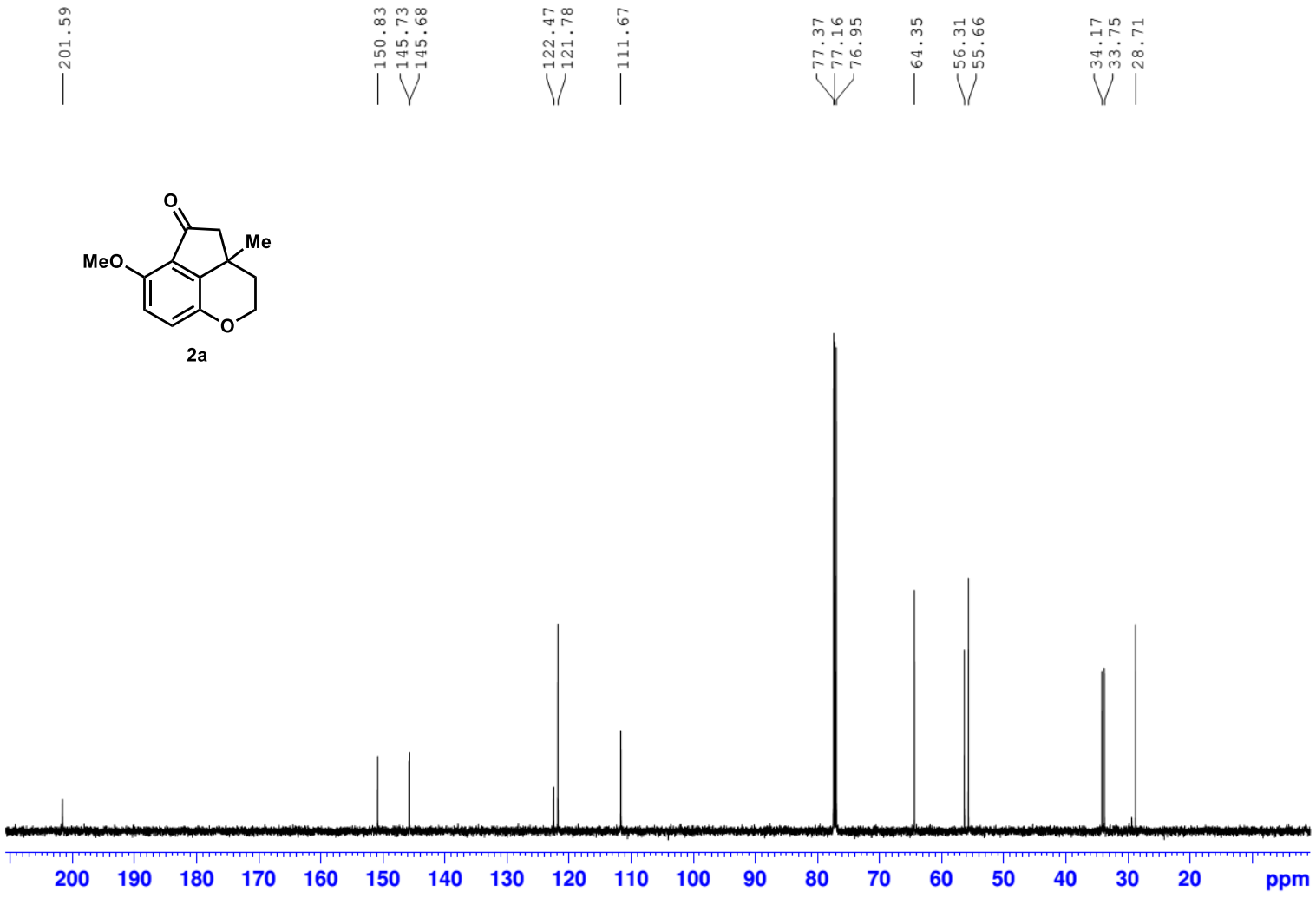
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34.17
33.75
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O
Me
MeO
O
2a
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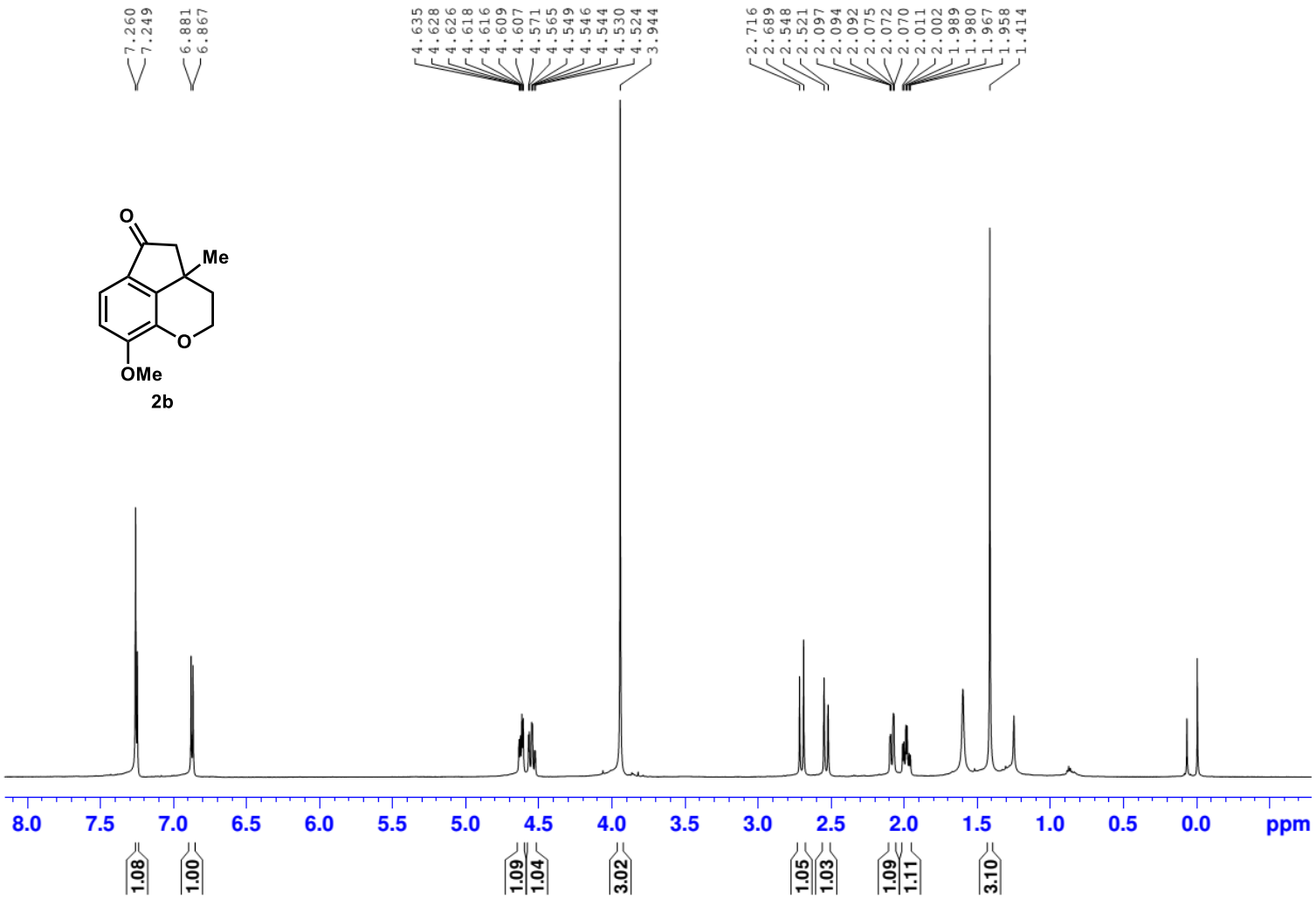
20
ppm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4.544
4.530
4.524
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2.521
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2.094
2.092
2.075
2.072
2.070
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2.002
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1.980
1.967
1.958
1.414
O
Me
O
OMe
2b
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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1.09
1.04
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1.05
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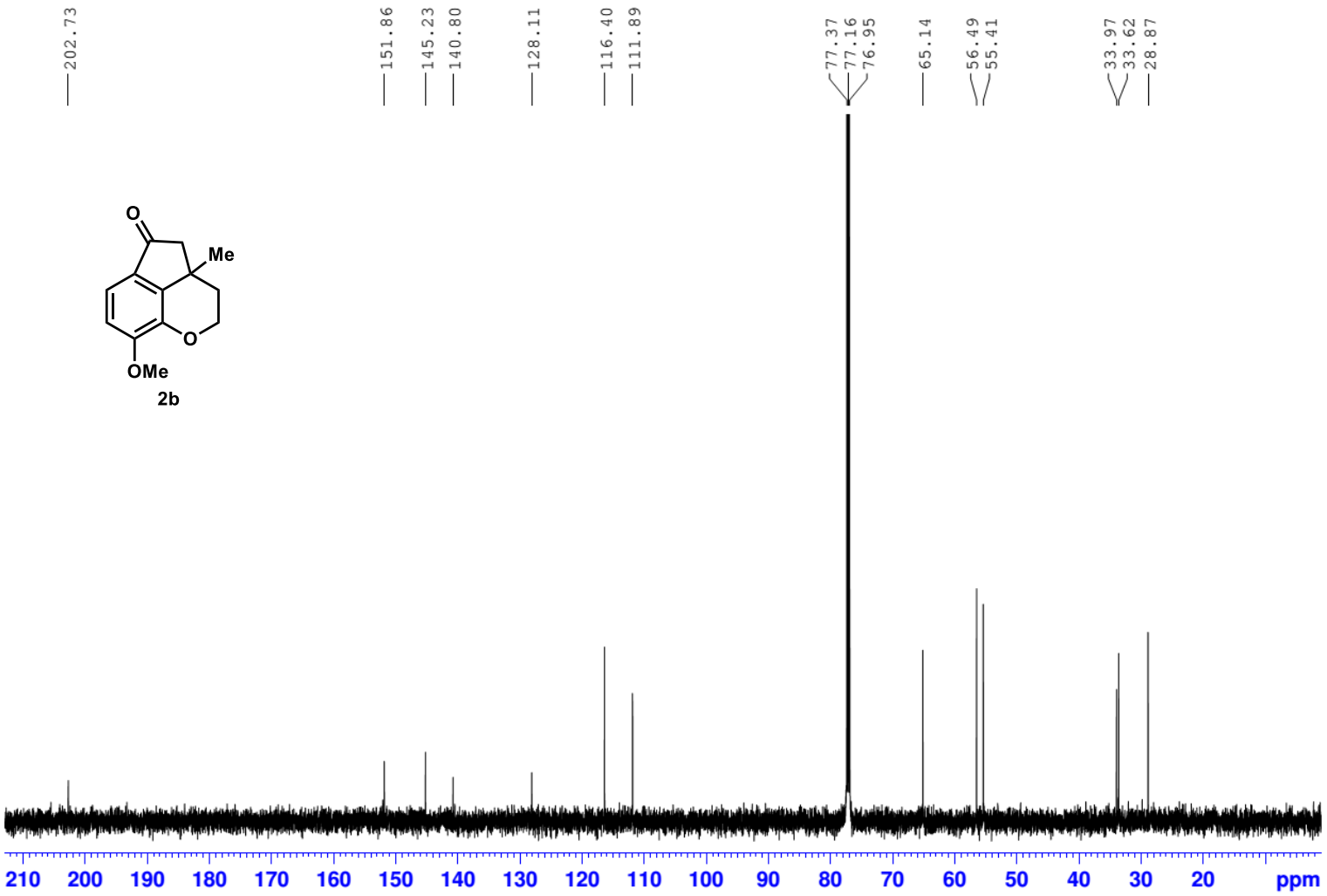
1.09
1.11
3.10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33.97
33.62
28.87
O
Me
O
OMe
2b
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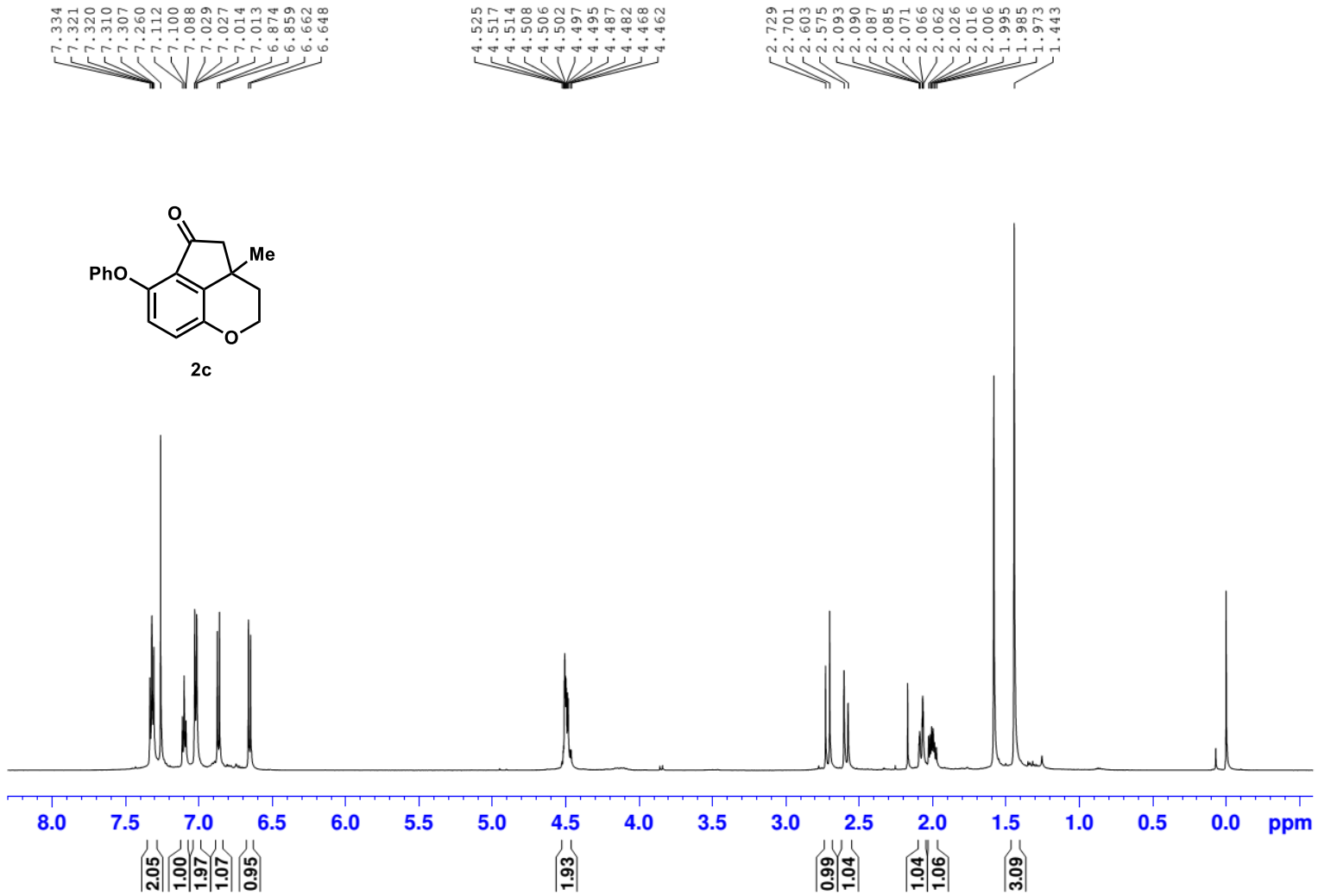
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4.506
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4.495
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4.462
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2.090
2.087
2.085
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Me
PhO
O
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6.0
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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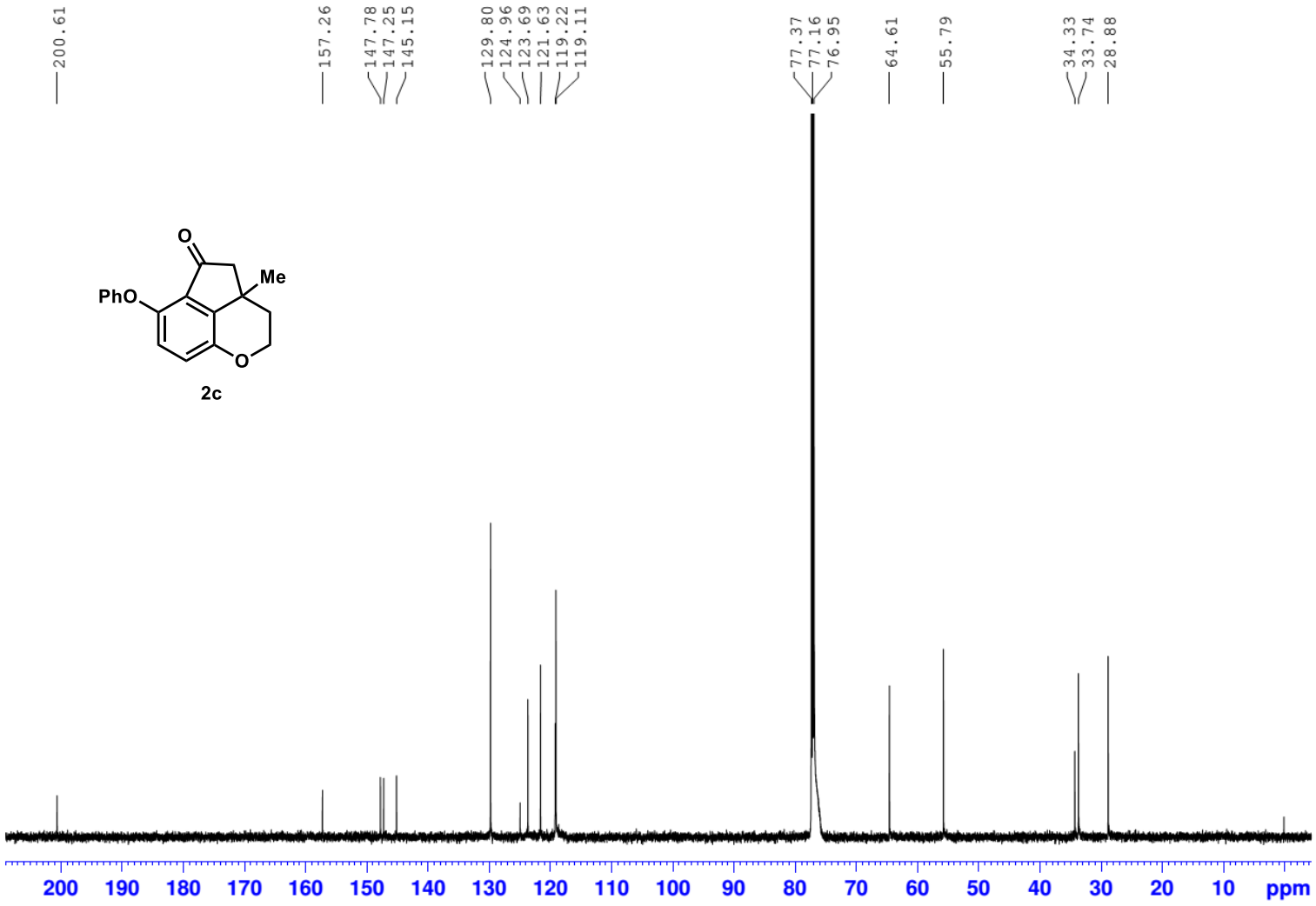
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55.79
34.33
33.74
28.88
O
Me
PhO
O
2c
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70
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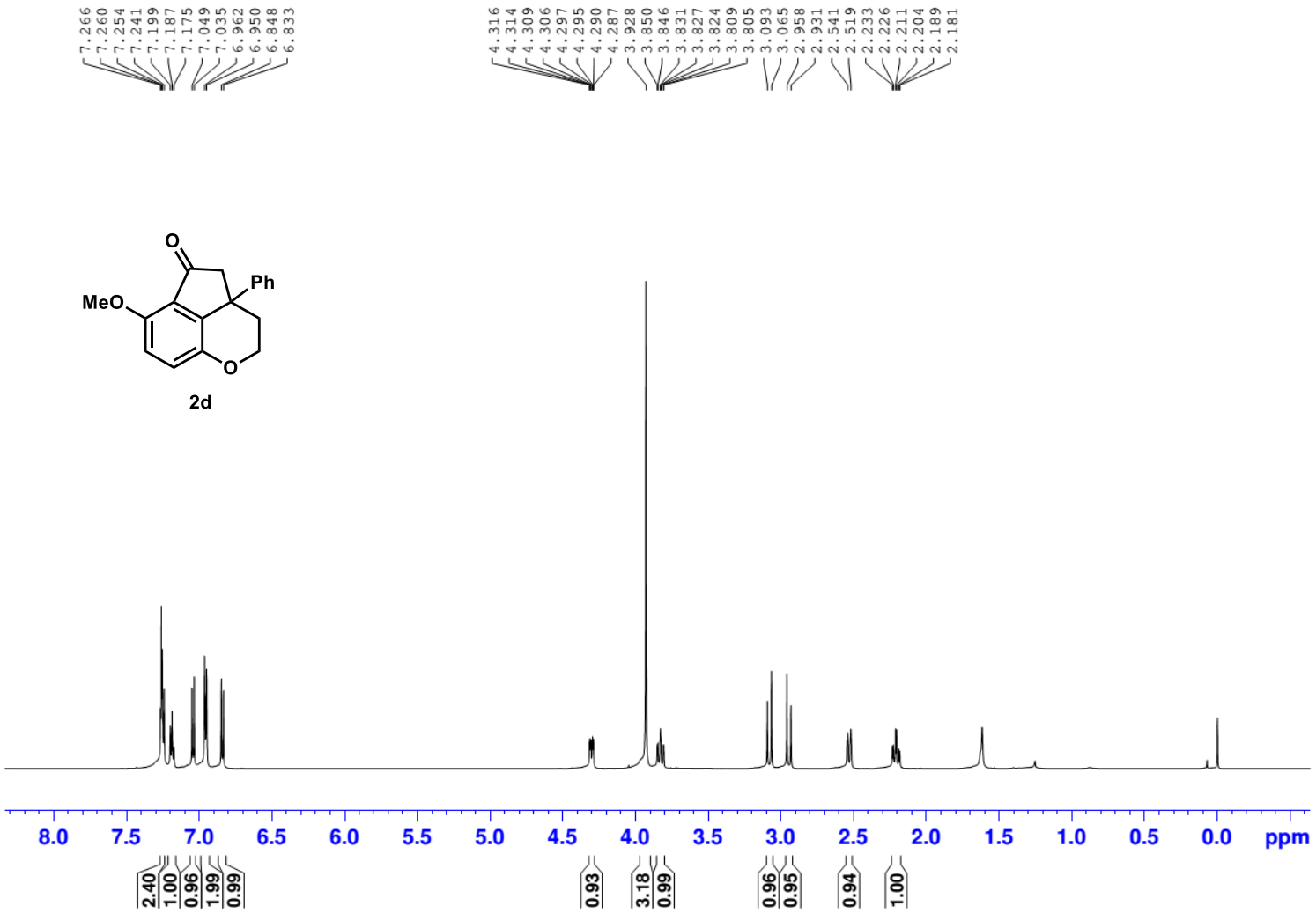
10
ppm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6.833
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4.314
4.309
4.306
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4.295
4.290
4.287
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3.850
3.846
3.831
3.827
3.824
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3.805
3.093
3.065
2.958
2.931
2.541
2.519
2.233
2.226
2.211
2.204
2.189
2.181
O
Ph
MeO
O
2d
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7.0
6.5
6.0
5.5
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4.0
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3.0
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2.0
1.5
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0.5
0.0
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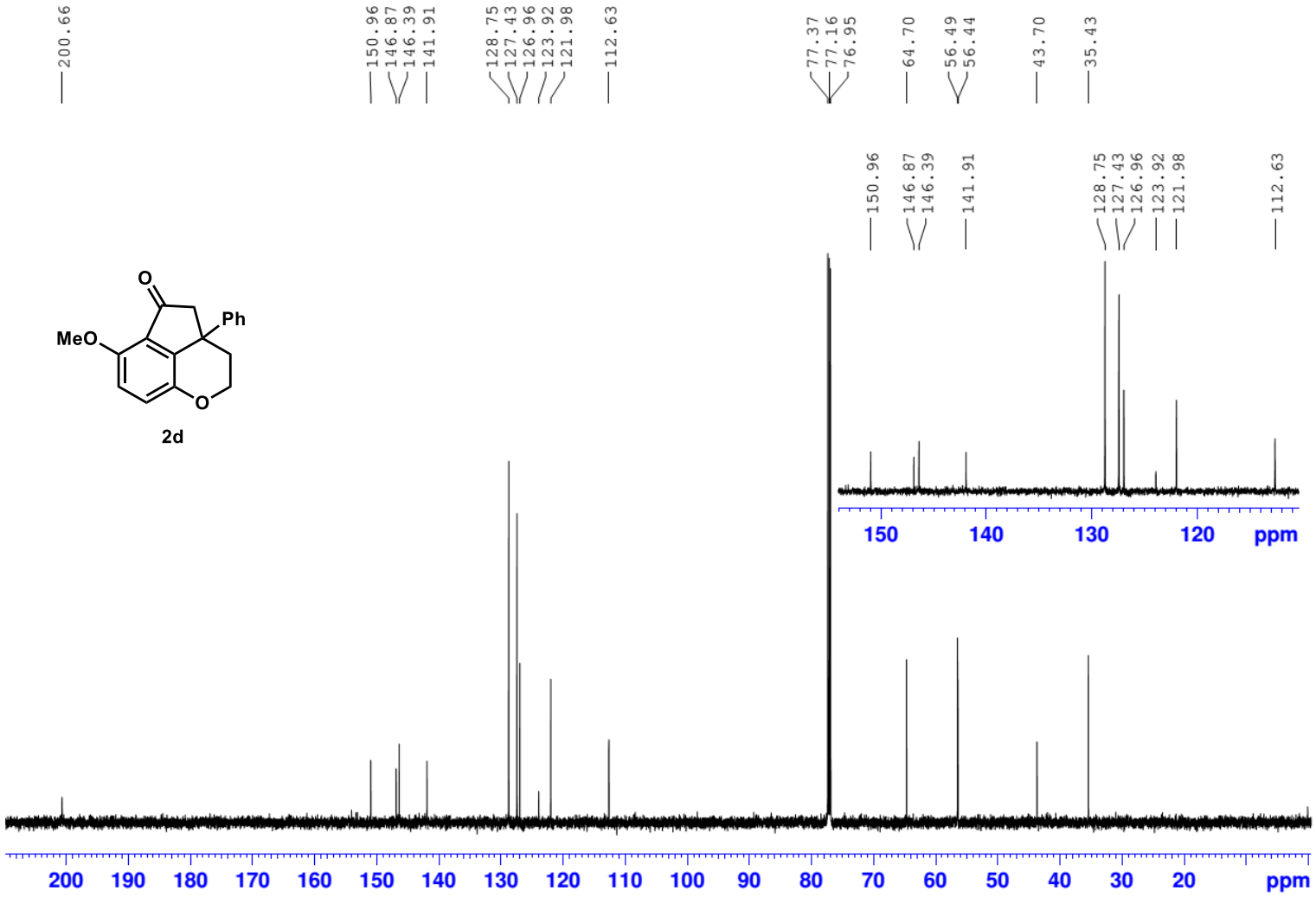
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77.16
76.95
64.70
56.49
56.44
43.70
35.43
O
Ph
MeO
O
2d
150
140
130
120
ppm
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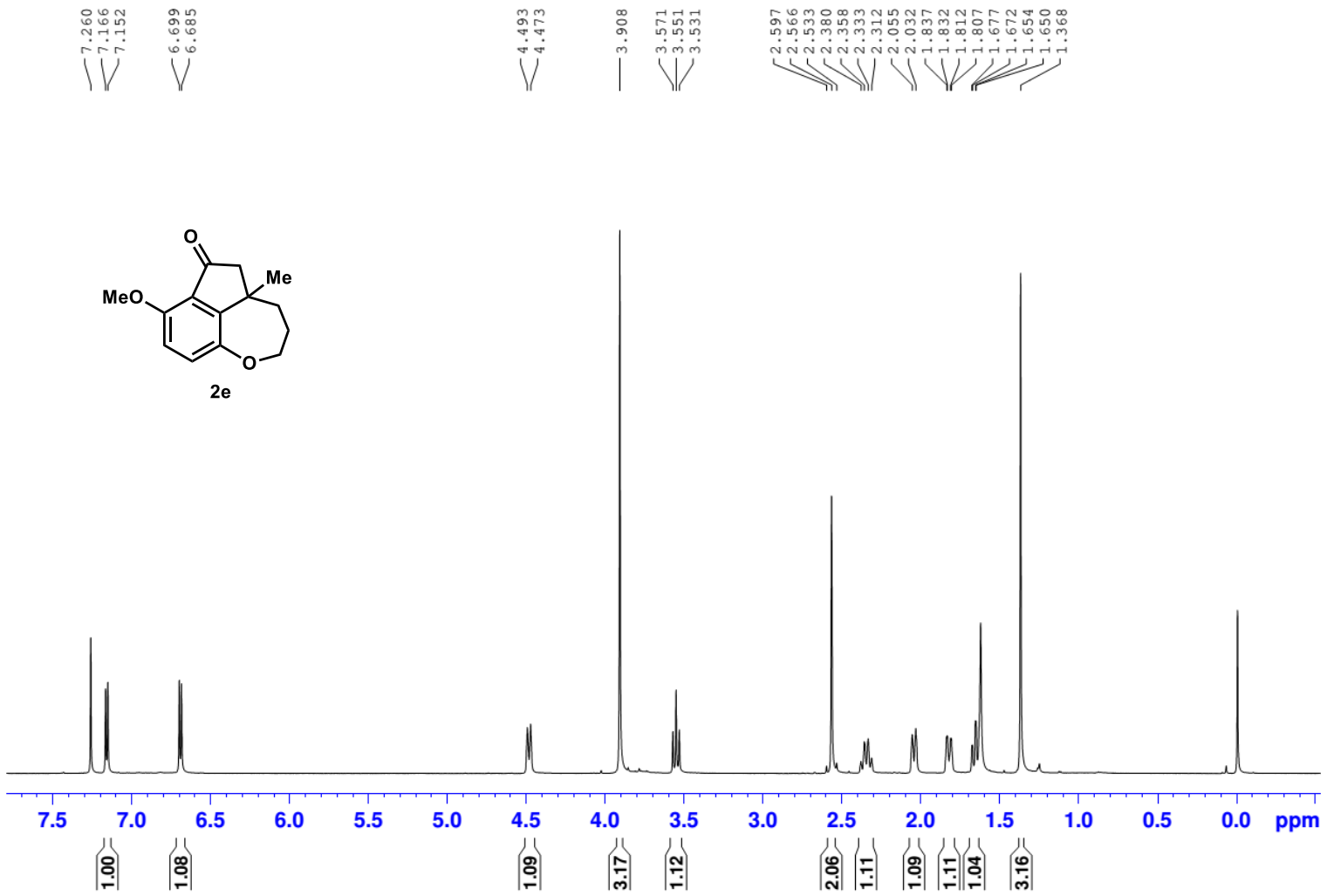
20
ppm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2.358
2.333
2.312
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2.032
1.837
1.832
1.812
1.807
1.677
1.672
1.654
1.650
1.368
O
Me
MeO
O
2e
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6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
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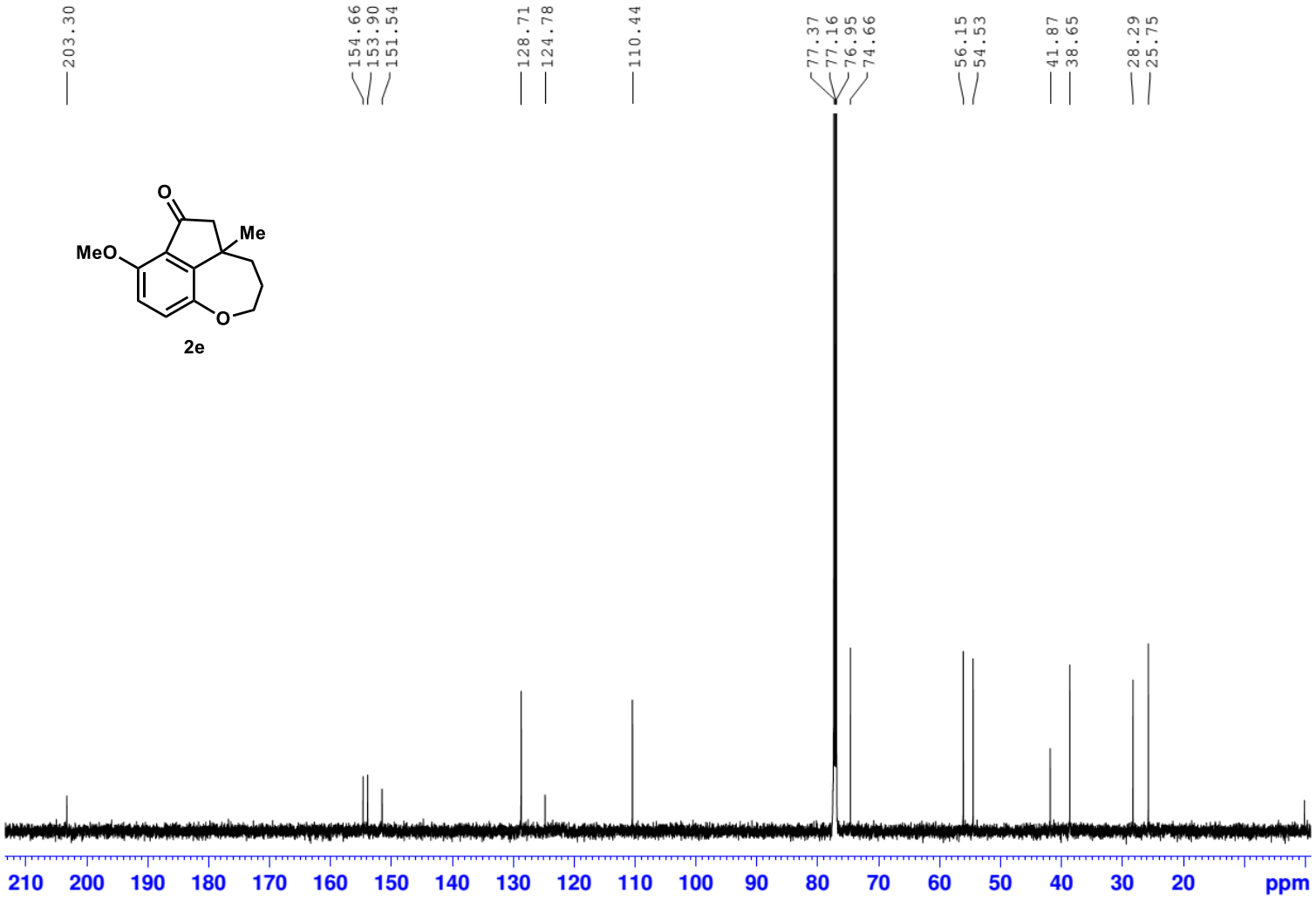
1.04
3.16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124.78
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77.37
77.16
76.95
74.66
56.15
54.53
41.87
38.65
28.29
25.75
O
Me
MeO
O
2e
210
200
190
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160
150
140
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120
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80
70
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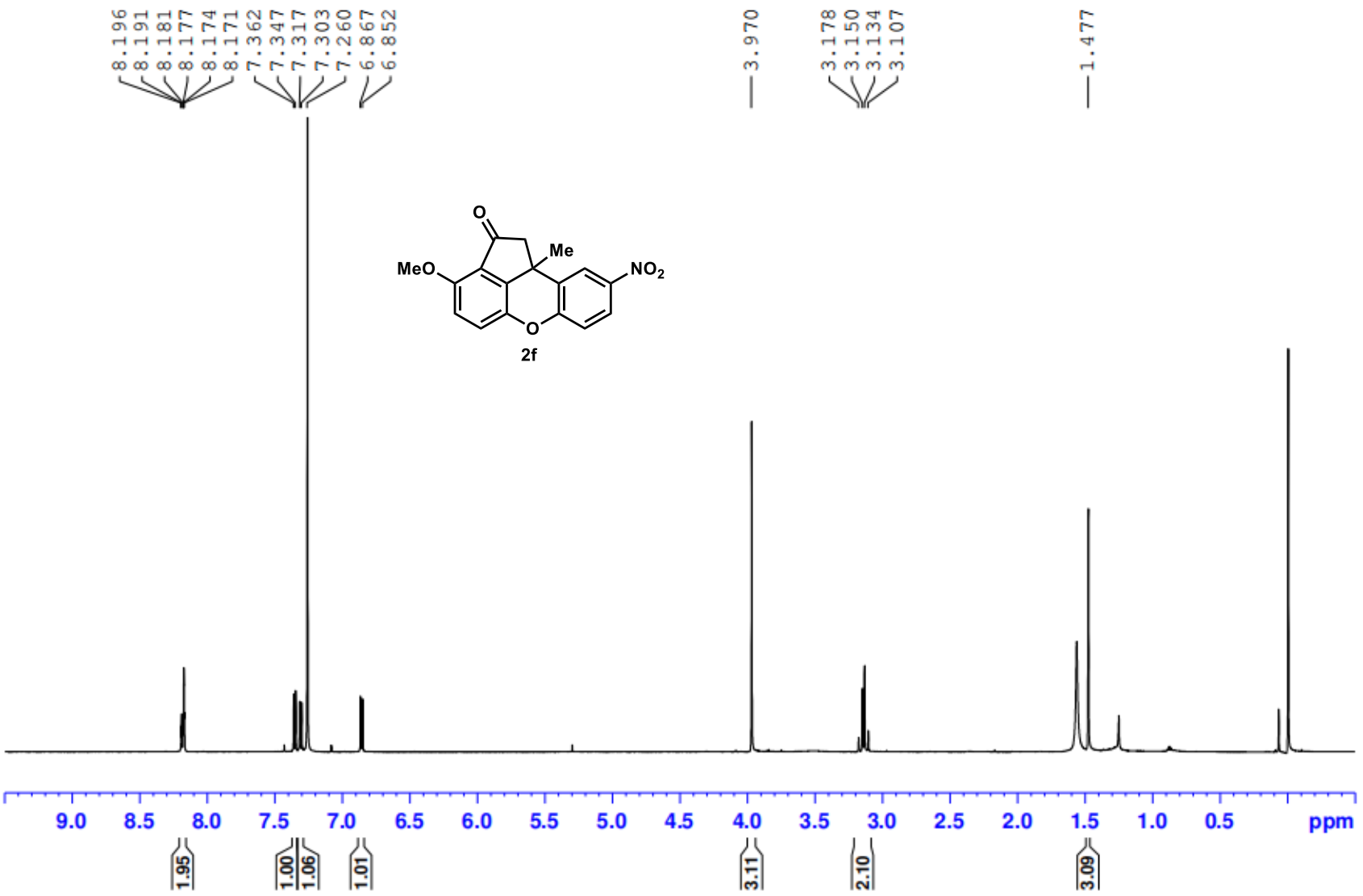
40
30
20
ppm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7.362
7.347
7.317
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7.260
6.867
6.852
3.970
3.178
3.150
3.134
3.107
1.477
O
Me
MeO
NO2
O
2f
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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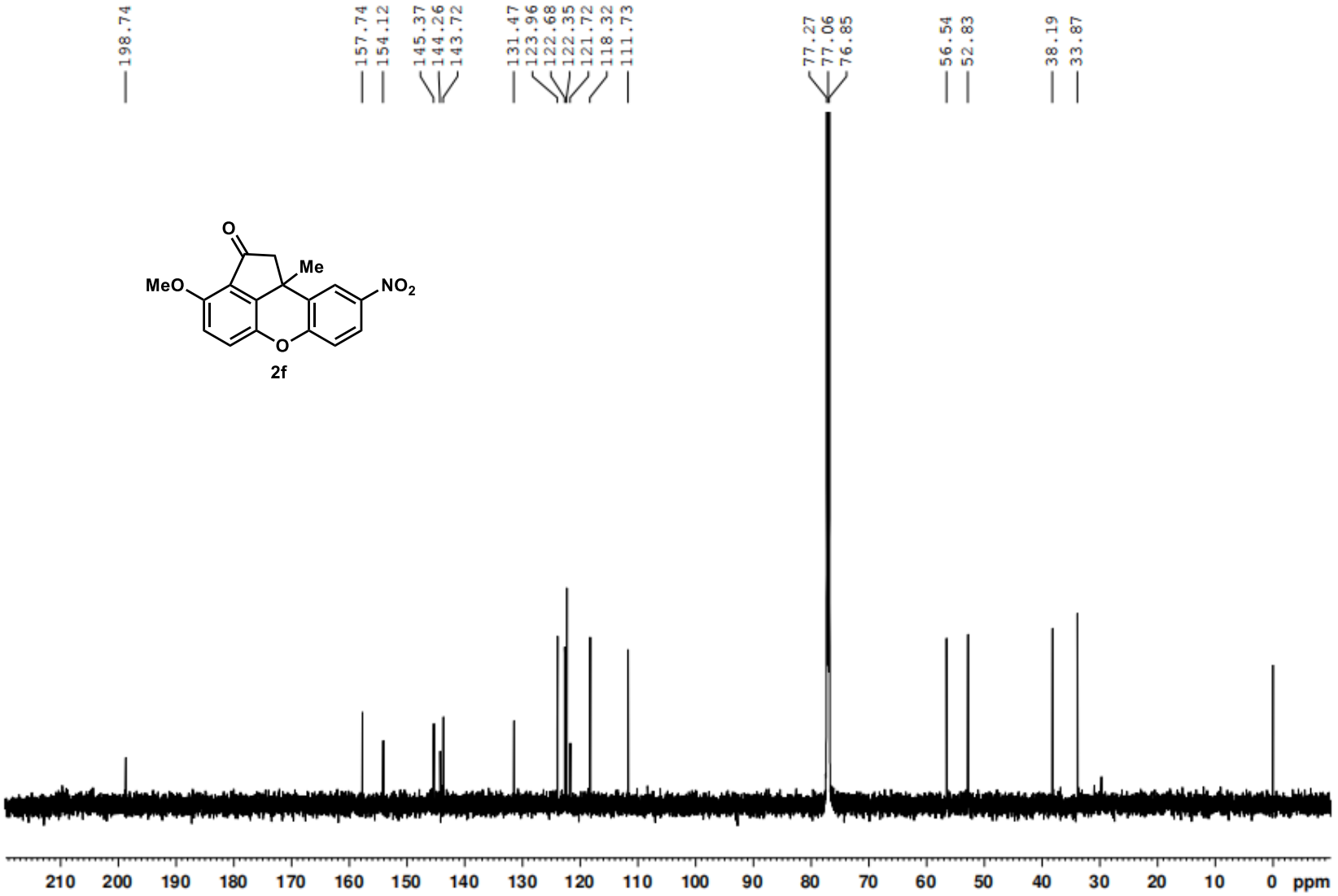
3.09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143.72
131.47
123.96
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122.35
121.72
118.32
111.73
77.27
77.06
76.85
56.54
52.83
38.19
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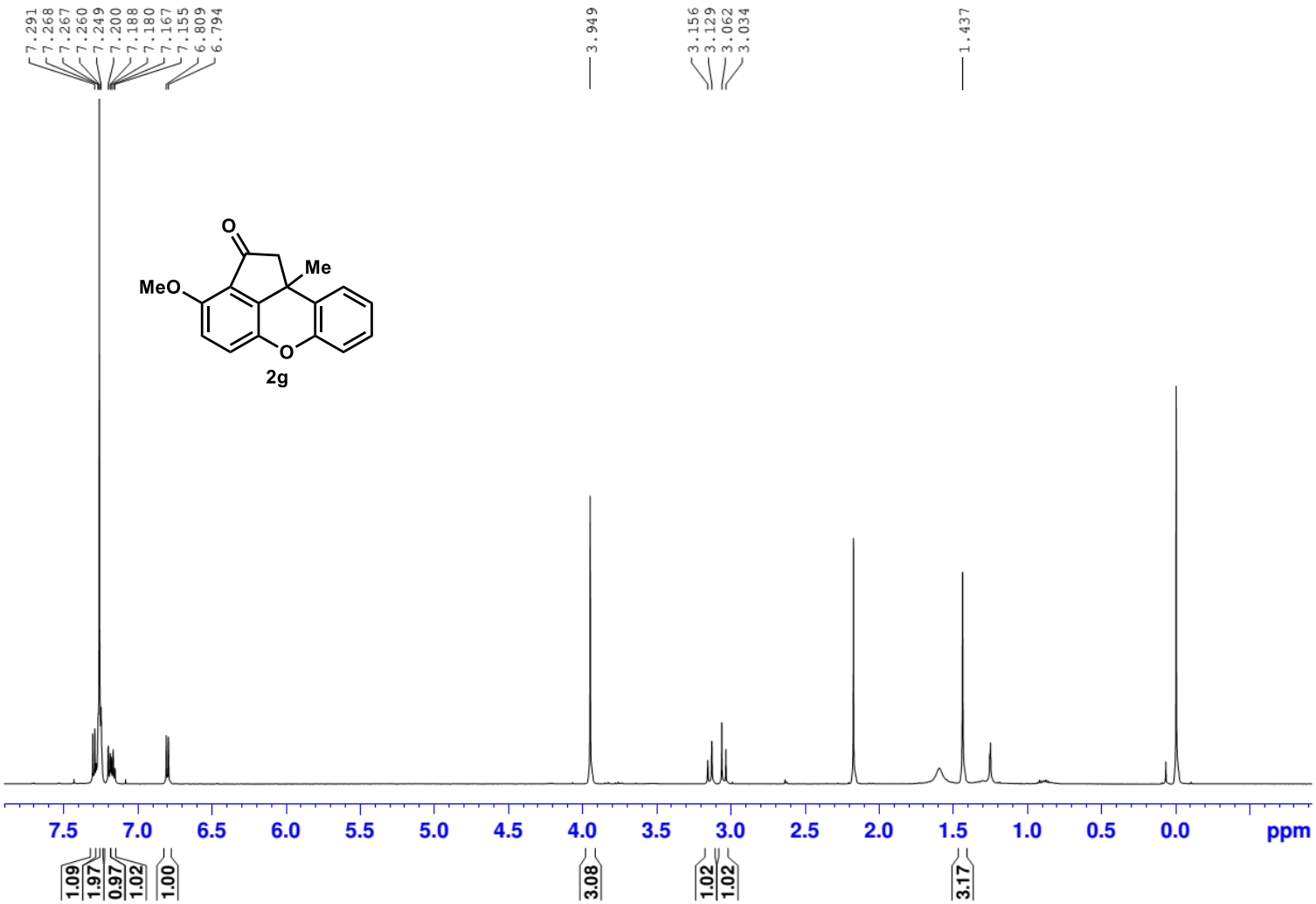
O
Me
MeO
NO2
O
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.267
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7.180
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7.155
6.809
6.794
3.949
3.156
3.129
3.062
3.034
1.437
O
Me
MeO
O
2g
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
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1.00
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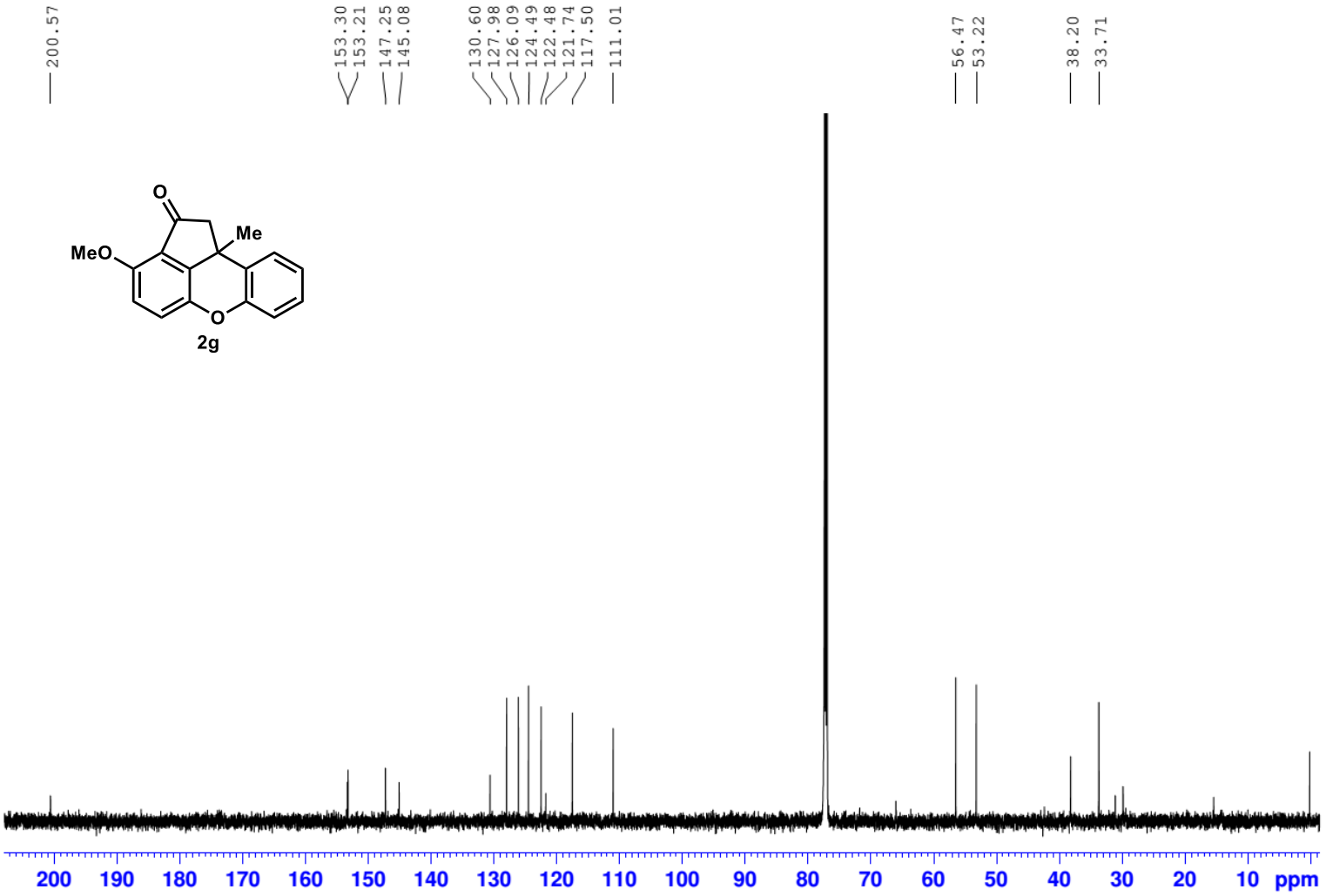
3.17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147.25
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130.60
127.98
126.09
124.49
122.48
121.74
117.50
111.01
56.47
53.22
38.20
33.71
O
Me
MeO
O
2g
200
190
180
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150
140
130
120
110
100
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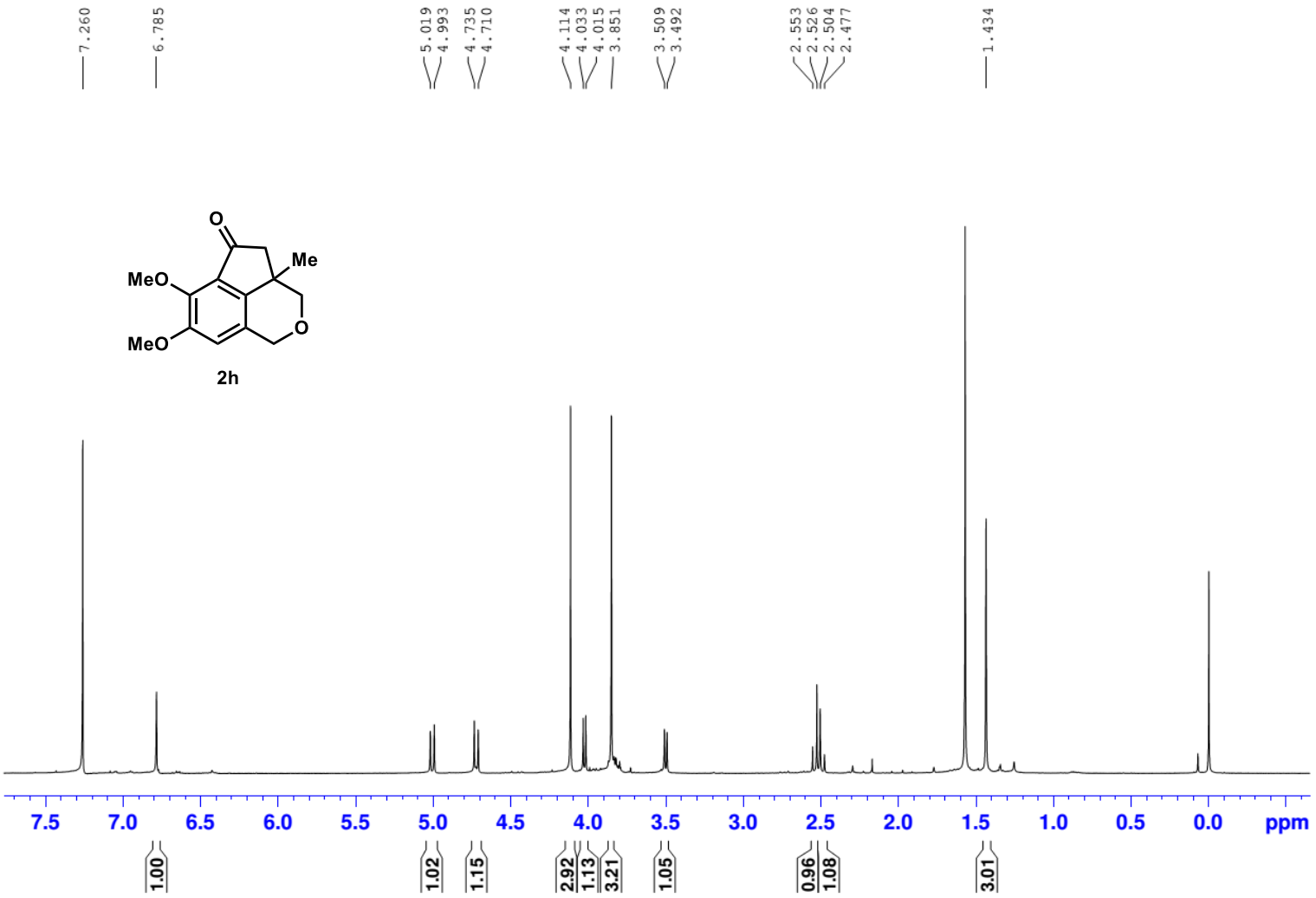
80
70
60
50
40
30
20
10
ppm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4.710
4.114
4.033
4.015
3.851
3.509
3.492
2.553
2.526
2.504
2.477
1.434
O
Me
MeO
MeO
O
2h
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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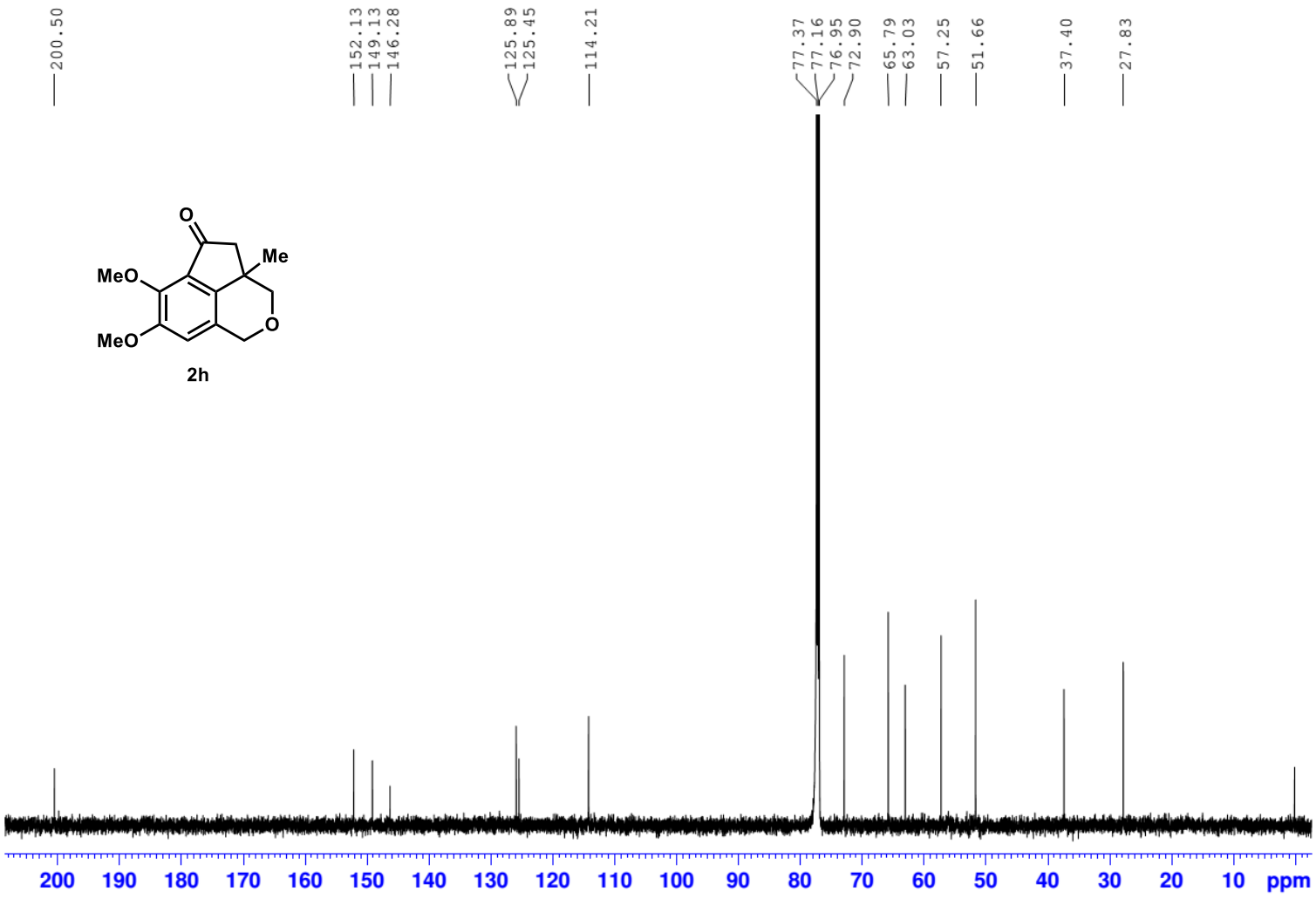
3.01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149.13
146.28
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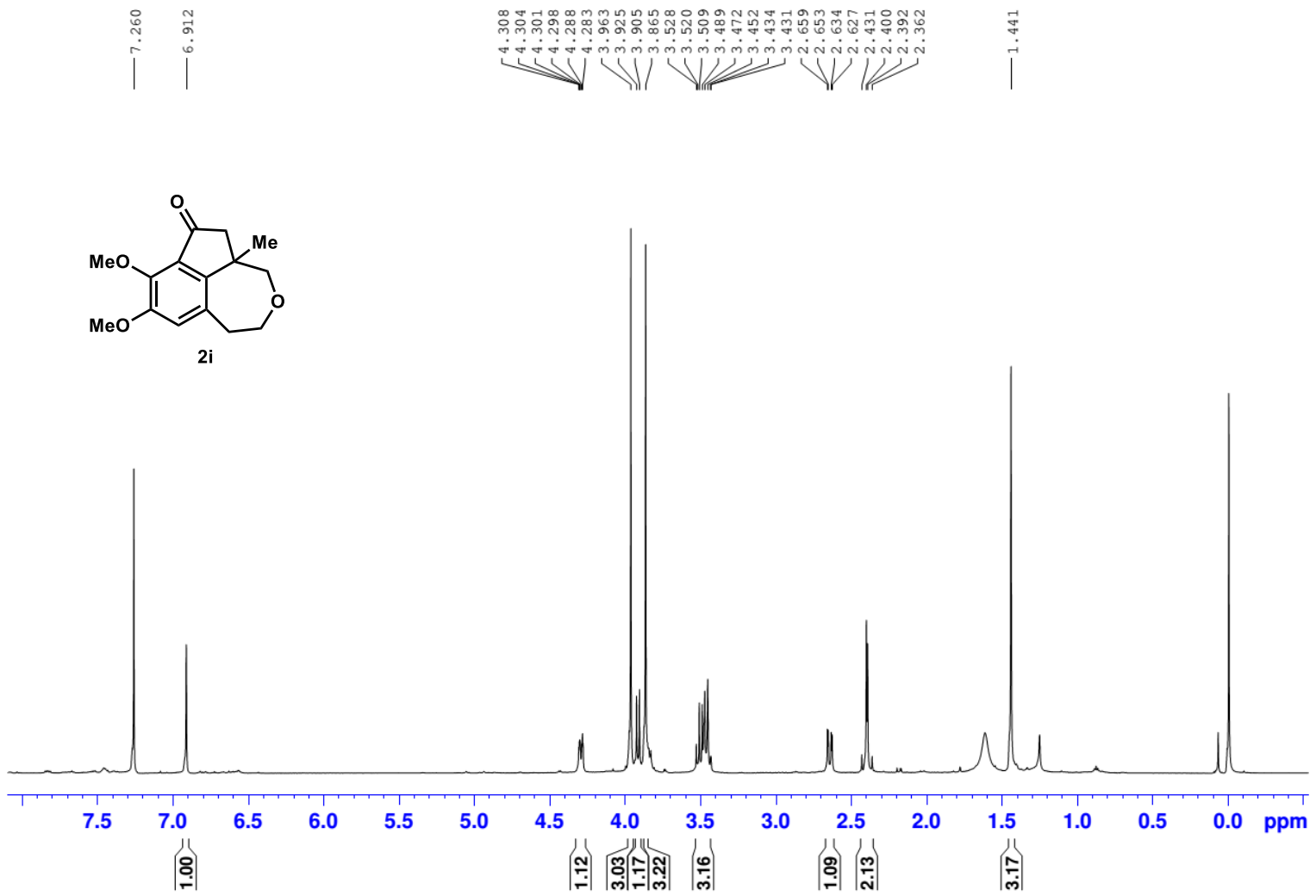
125.45
114.21
77.37
77.16
76.95
72.90
65.79
63.03
57.25
51.66
37.40
27.83
O
Me
MeO
MeO
O
2h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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4.288
4.283
3.963
3.925
3.905
3.865
3.528
3.520
3.509
3.489
3.472
3.452
3.434
3.431
2.659
2.653
2.634
2.627
2.431
2.400
2.392
2.362
1.441
O
Me
MeO
MeO
O
2i
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
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ppm
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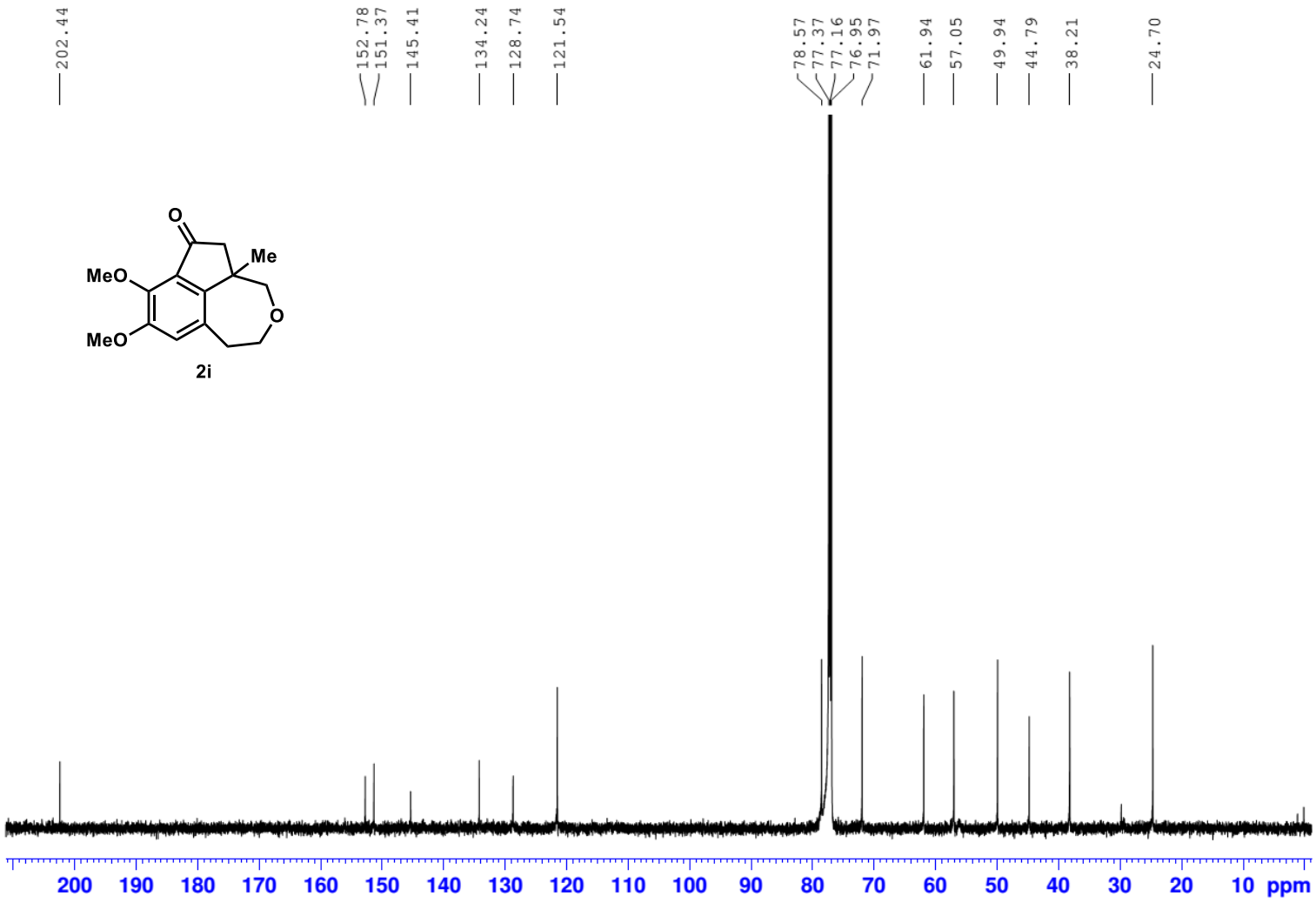
3.03
1.17
3.22
3.16
1.09
2.13
3.17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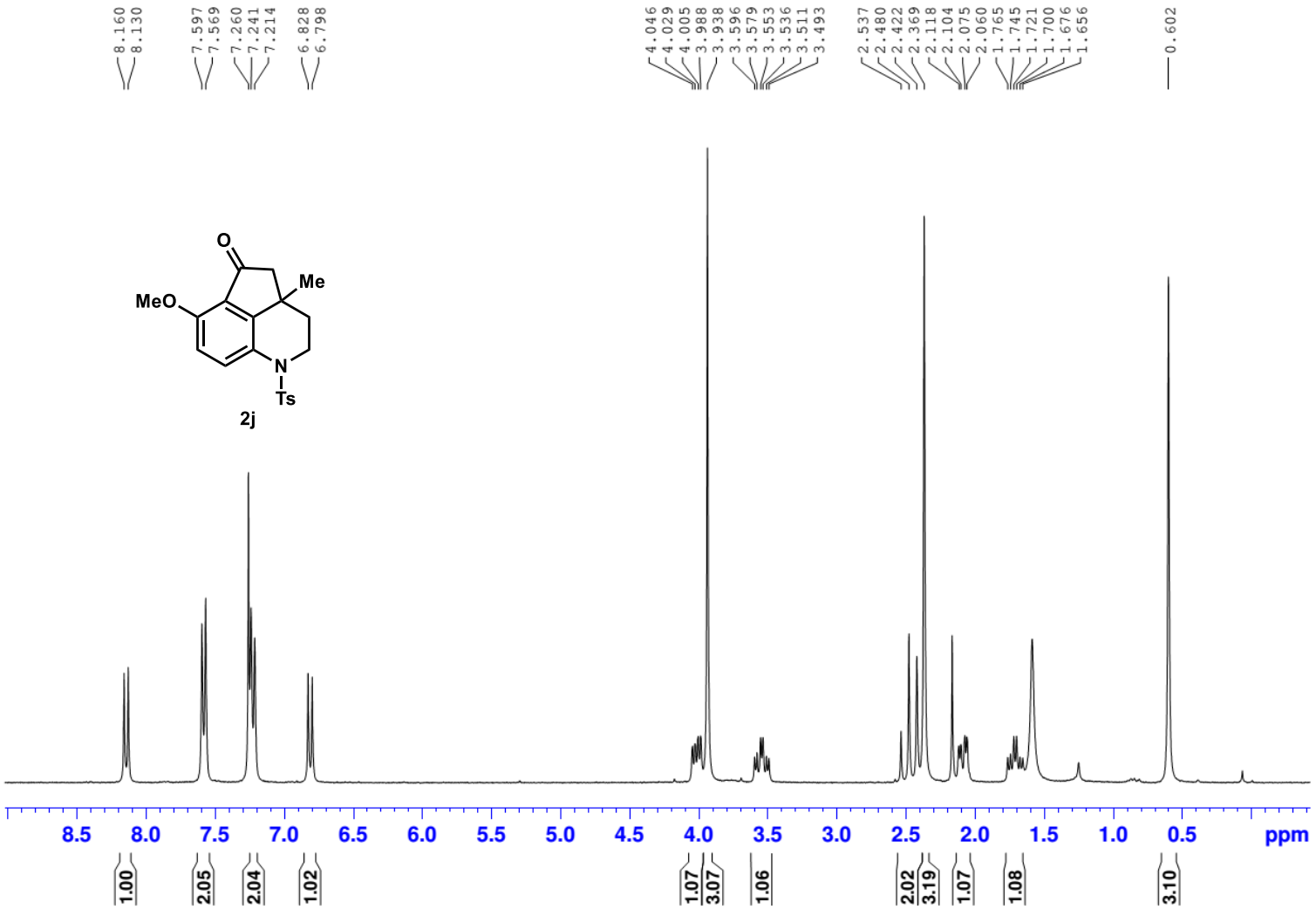
145.41
134.24
128.74
121.54
78.57
77.37
77.16
76.95
71.97
61.94
57.05
49.94
44.79
38.21
24.70
O
Me
MeO
MeO
O
2i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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8.130
7.597
7.569
7.260
7.241
7.214
6.828
6.798
4.046
4.029
4.005
3.988
3.938
3.596
3.579
3.553
3.536
3.511
3.493
2.537
2.480
2.422
2.369
2.118
2.104
2.075
2.060
1.765
1.745
1.721
1.700
1.676
1.656
0.602
O
Me
MeO
N
Ts
2j
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
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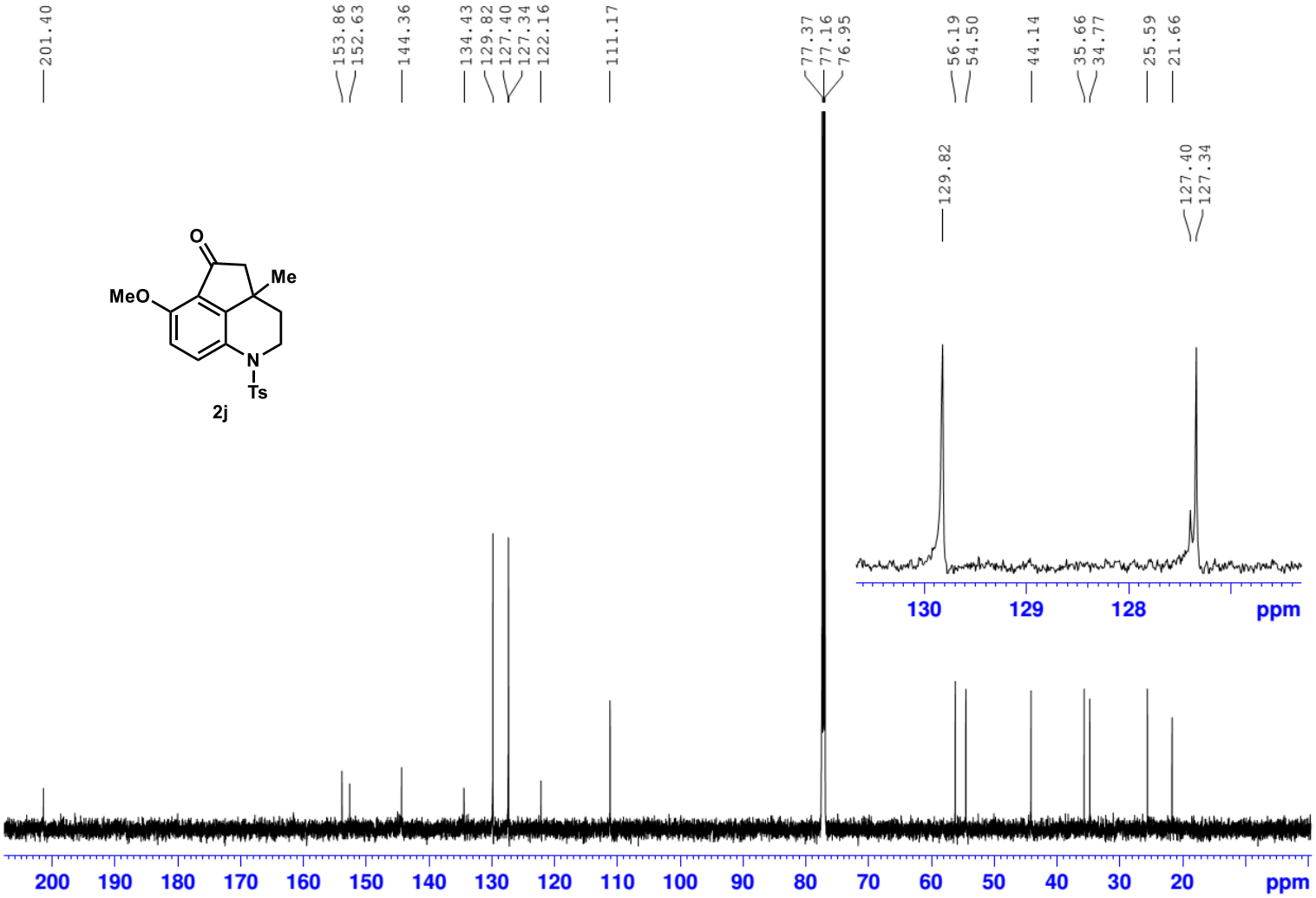
2.04
1.02
1.07
3.07
1.06
2.02
3.19
1.07
1.08
3.10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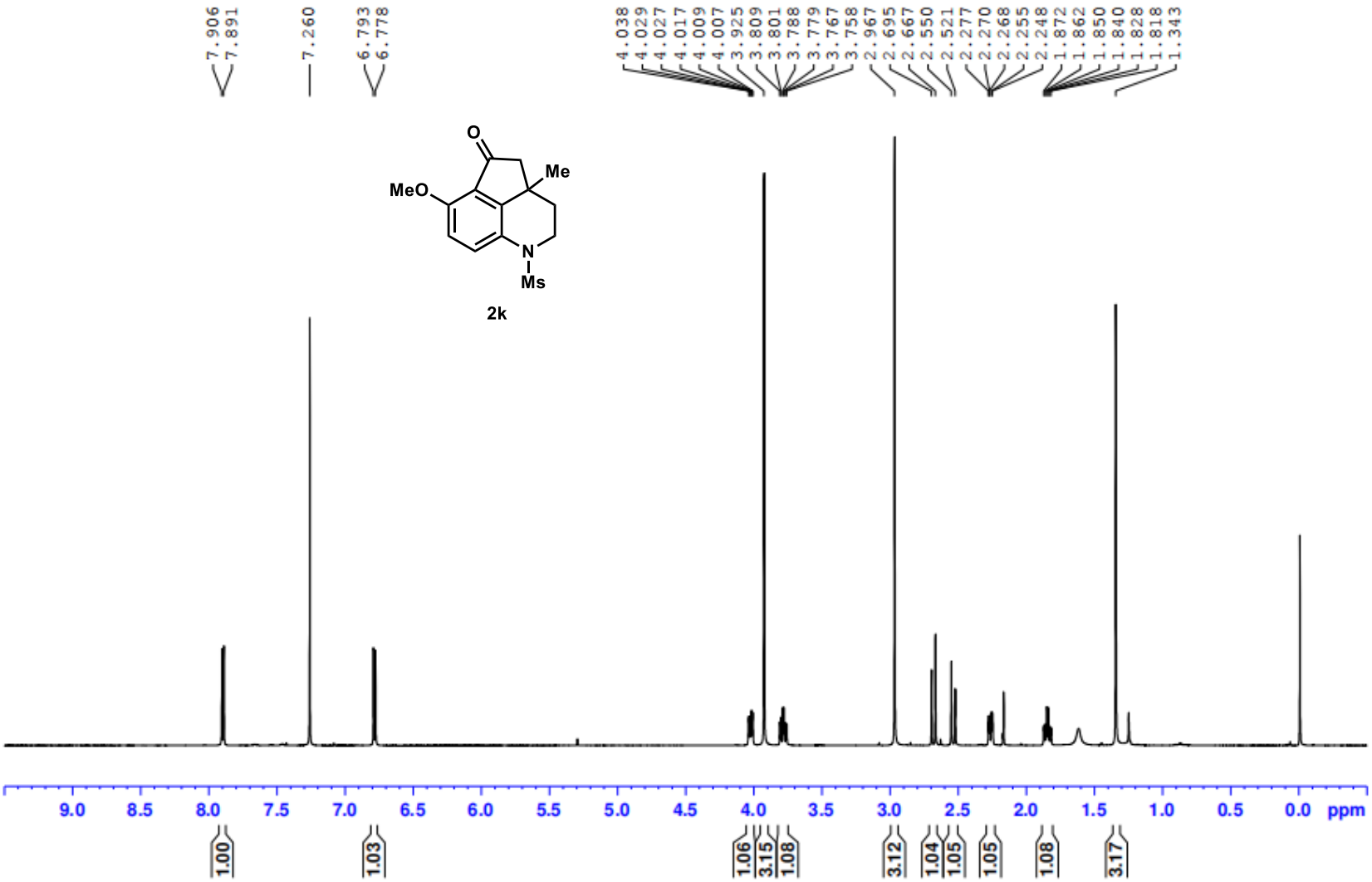
129.82
127.40
127.34
122.16
111.17
77.37
77.16
76.95
56.19
54.50
44.14
35.66
34.77
25.59
21.66
129.82
127.40
127.34
O
Me
MeO
N
Ts
2j
130
129
128
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.891
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6.778
4.038
4.029
4.027
4.017
4.009
4.007
3.925
3.809
3.801
3.788
3.779
3.767
3.758
2.967
2.695
2.667
2.550
2.521
2.277
2.270
2.268
2.255
2.248
1.872
1.862
1.850
1.840
1.828
1.818
1.343
O
Me
MeO
N
Ms
2k
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
0.0
ppm
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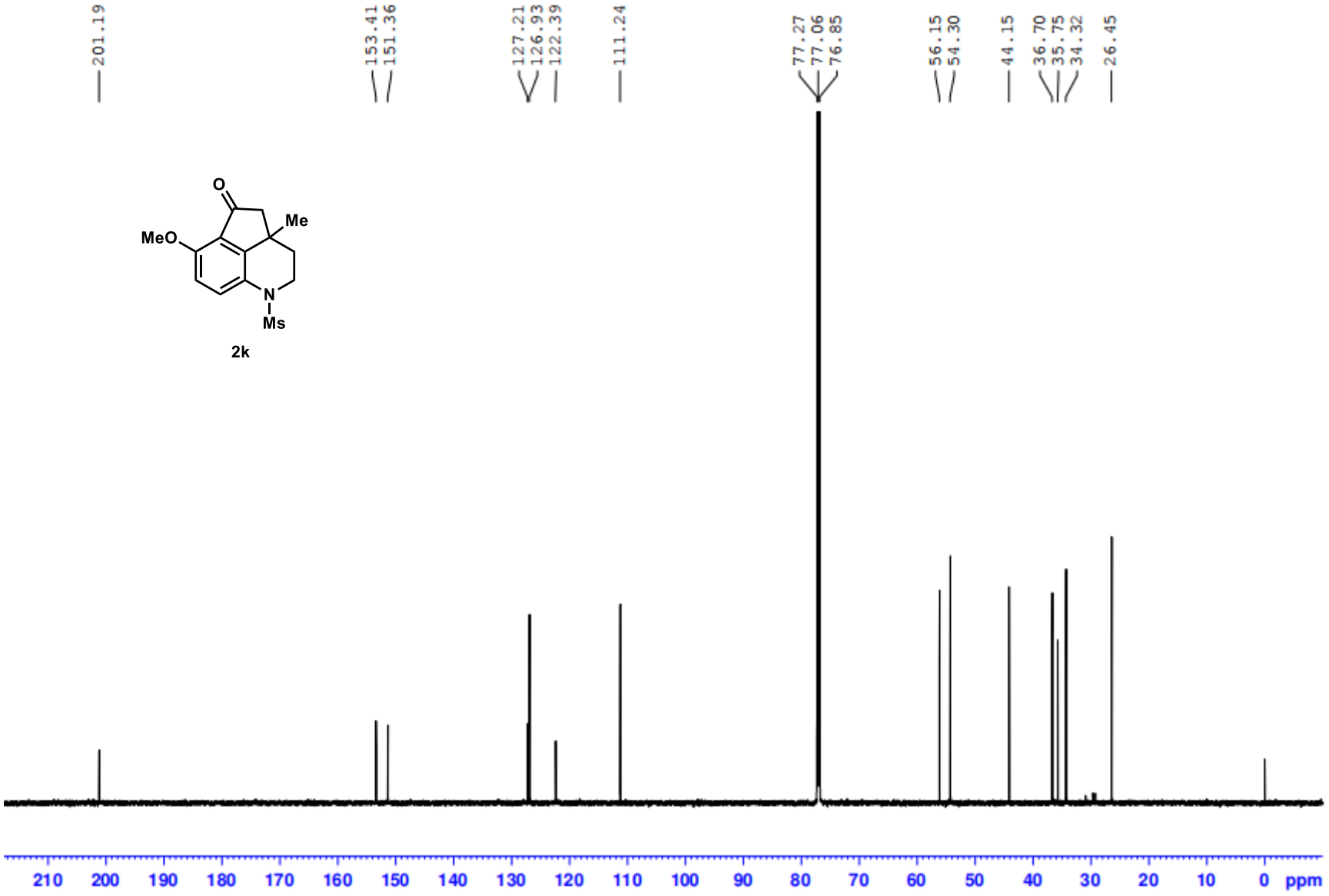
1.03
1.06
3.15
1.08
3.12
1.04
1.05
1.05
1.08
3.17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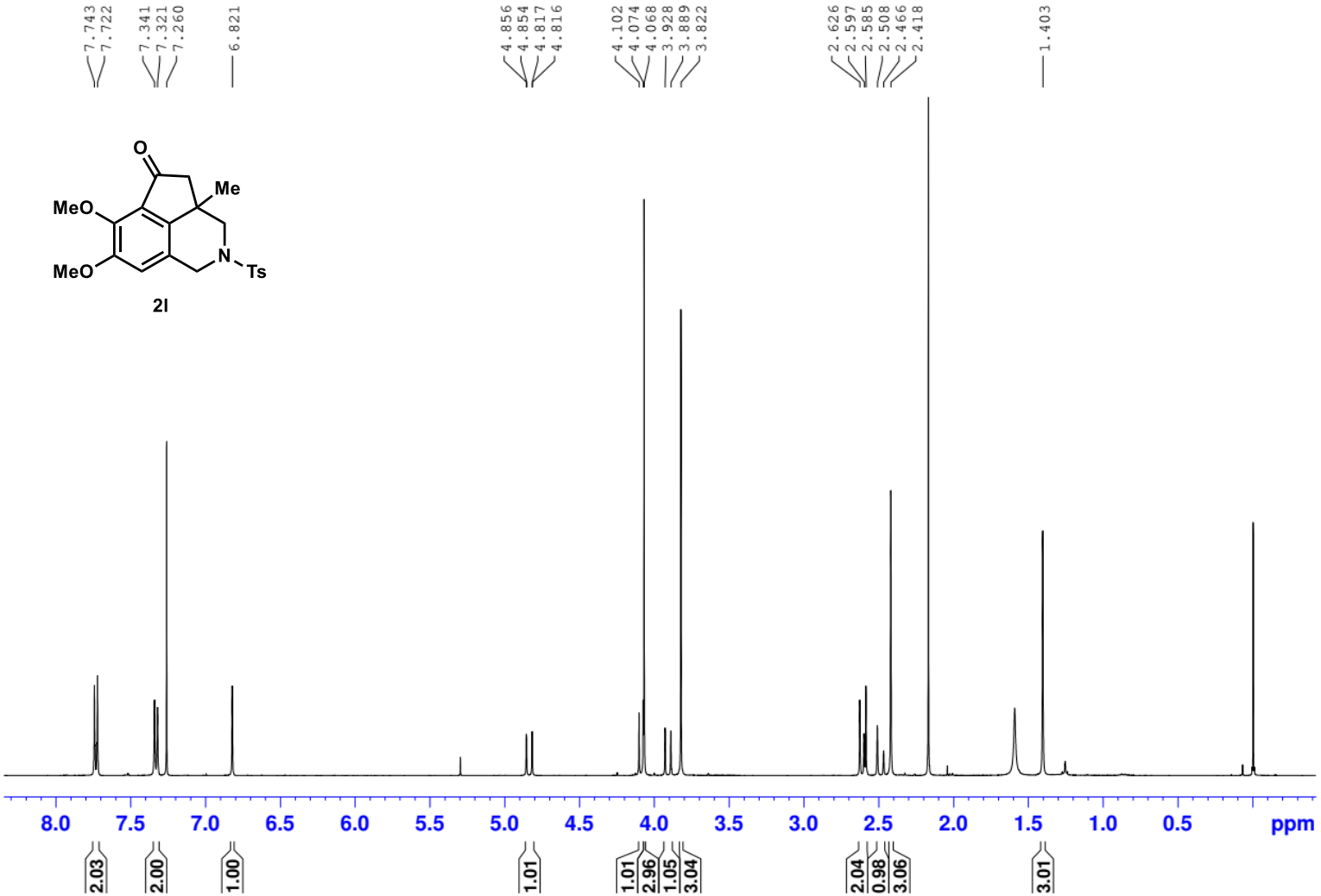
122.39
111.24
77.27
77.06
76.85
56.15
54.30
44.15
36.70
35.75
34.32
26.45
O
Me
MeO
N
Ms
2k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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4.854
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4.074
4.068
3.928
3.889
3.822
2.626
2.597
2.585
2.508
2.466
2.418
1.403
O
Me
MeO
MeO
N
Ts
2l
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
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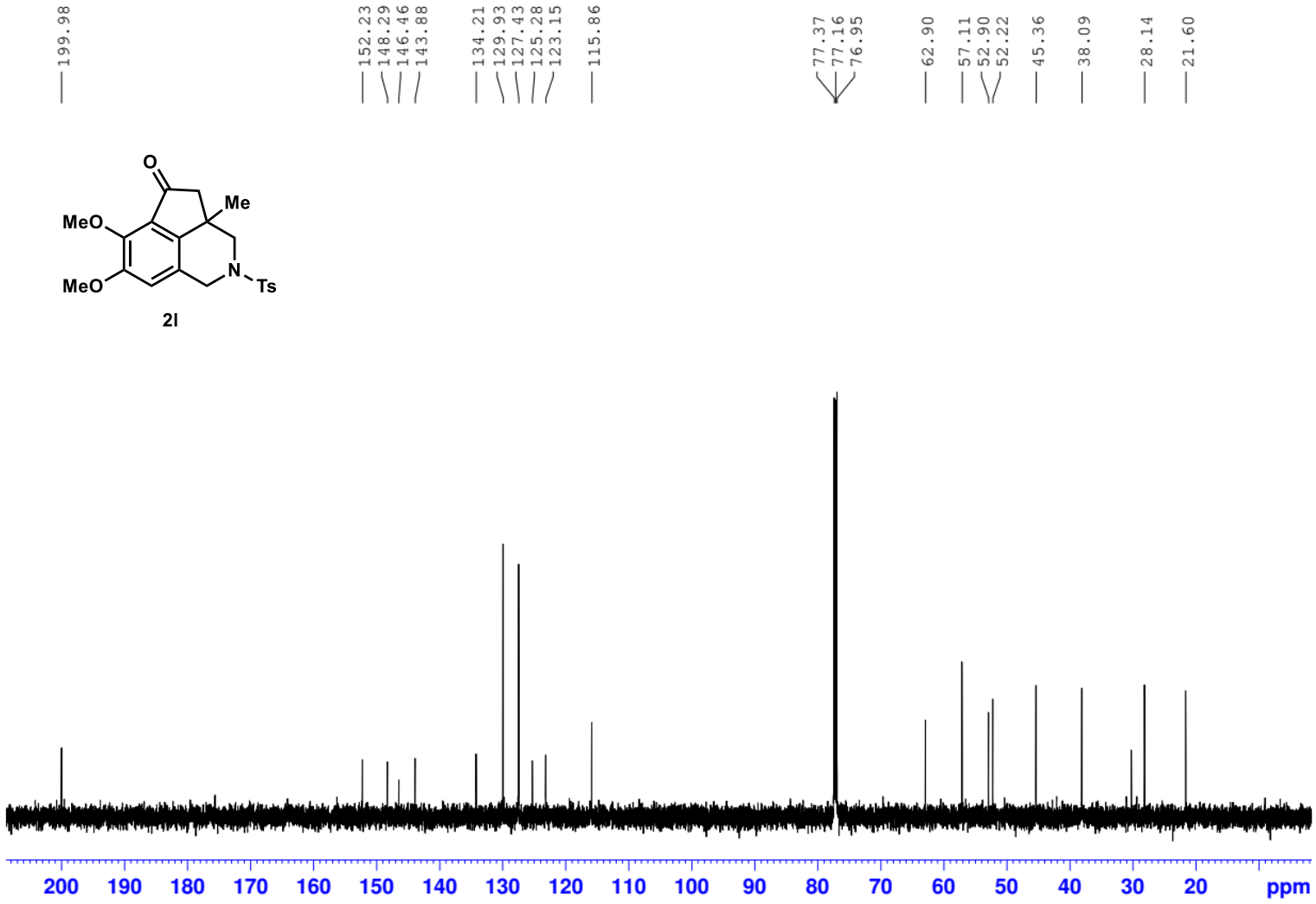
3.01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127.43
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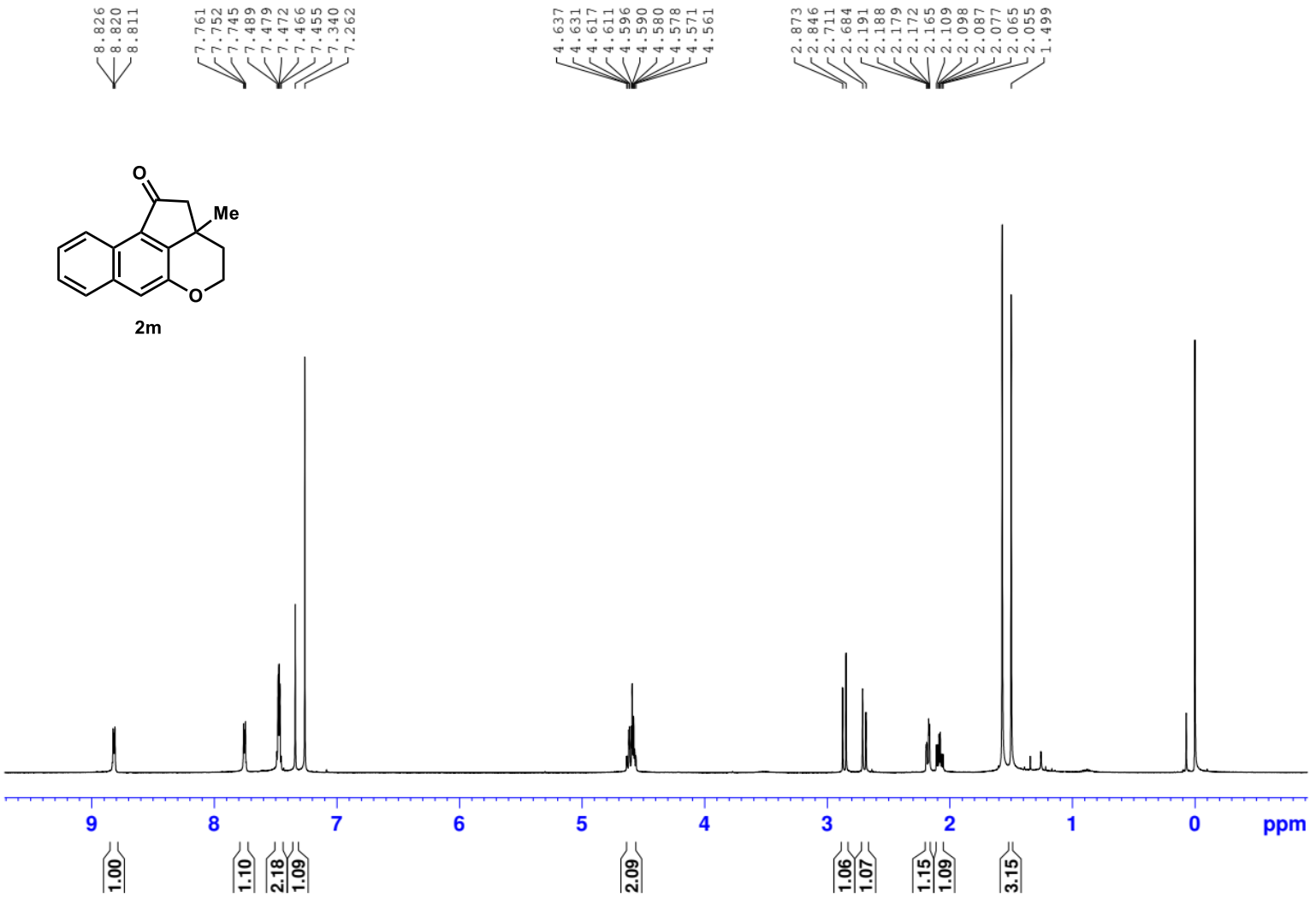
123.15
115.86
77.37
77.16
76.95
62.90
57.11
52.90
52.22
45.36
38.09
28.14
21.60
O
Me
MeO
MeO
N
Ts
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

2l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7.752
7.745
7.489
7.479
7.472
7.466
7.455
7.340
7.262
4.637
4.631
4.617
4.611
4.596
4.590
4.580
4.578
4.571
4.561
2.873
2.846
2.711
2.684
2.191
2.188
2.179
2.172
2.165
2.109
2.098
2.087
2.077
2.065
2.055
1.499
O
Me
O
2m
9
8
7
6
5
4
3
2
1
0
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1.09
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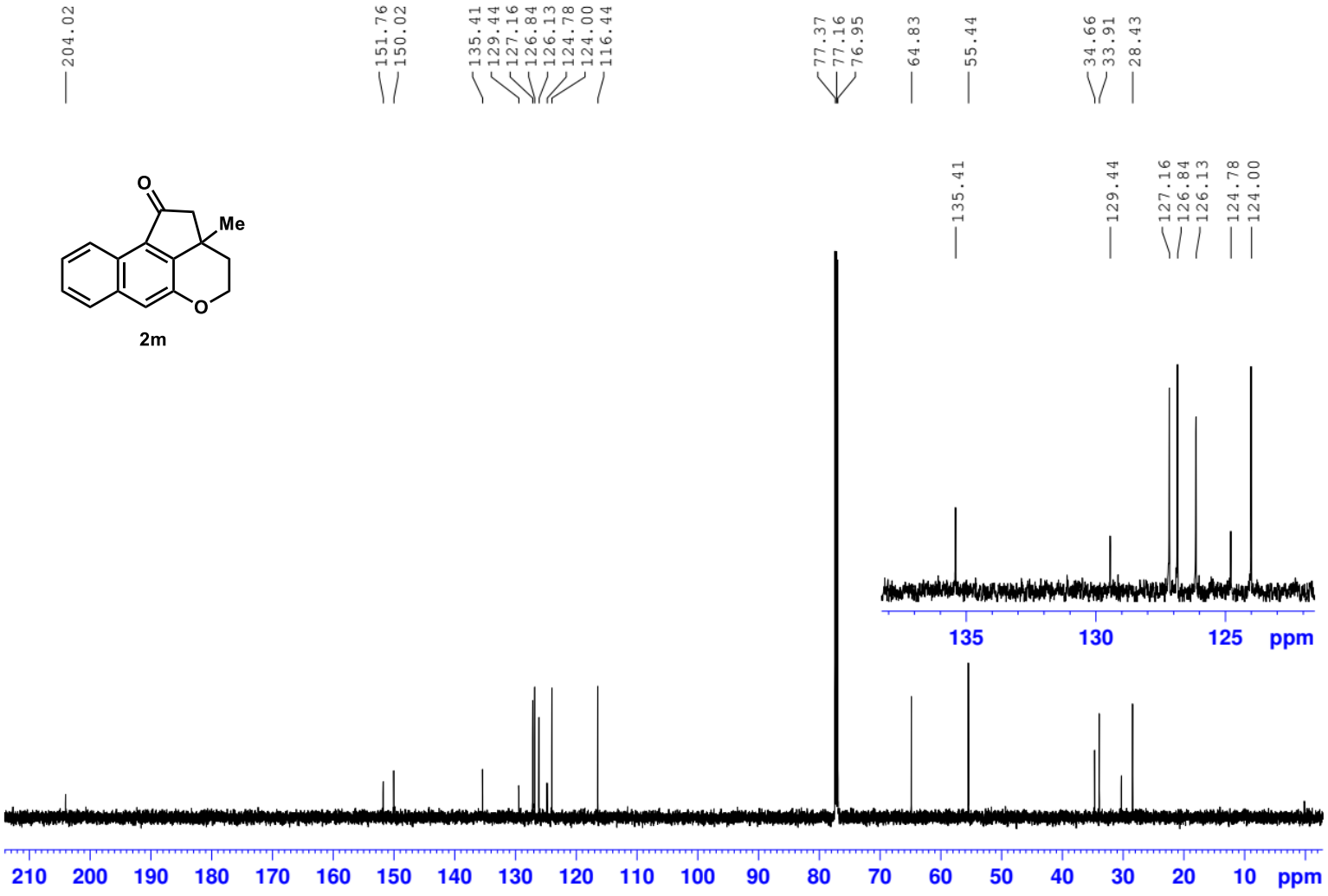
1.06
1.07
1.15
1.09
3.15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127.16
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126.13
124.78
124.00
116.44
77.37
77.16
76.95
64.83
55.44
34.66
33.91
28.43
O
Me
O
2m
135.41
129.44
127.16
126.84
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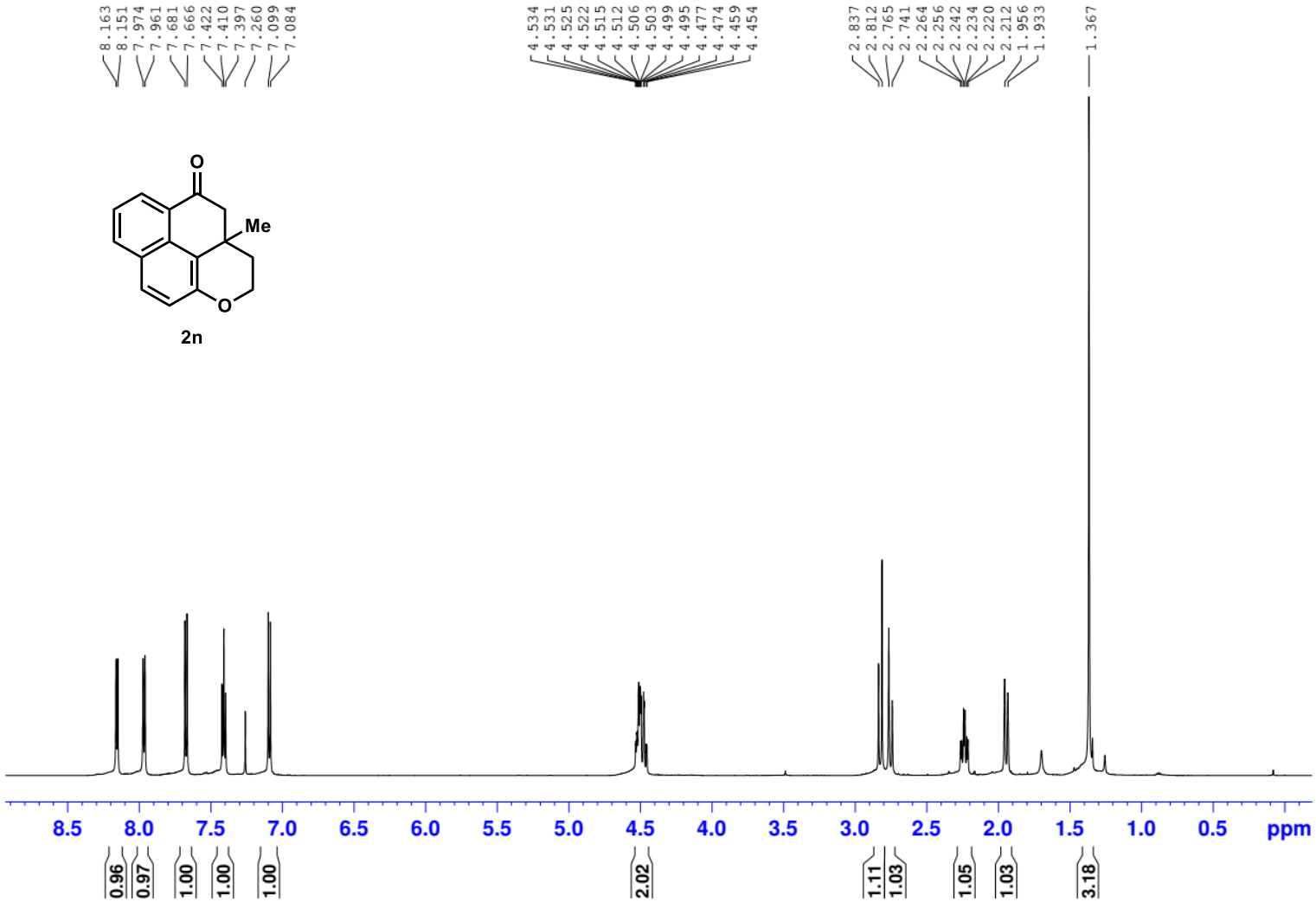
124.78
124.00
135
130
125
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.410
7.397
7.260
7.099
7.084
4.534
4.531
4.525
4.522
4.515
4.512
4.506
4.503
4.499
4.495
4.477
4.474
4.459
4.454
2.837
2.812
2.765
2.741
2.264
2.256
2.242
2.234
2.220
2.212
1.956
1.933
1.367
O
Me
O
2n
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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
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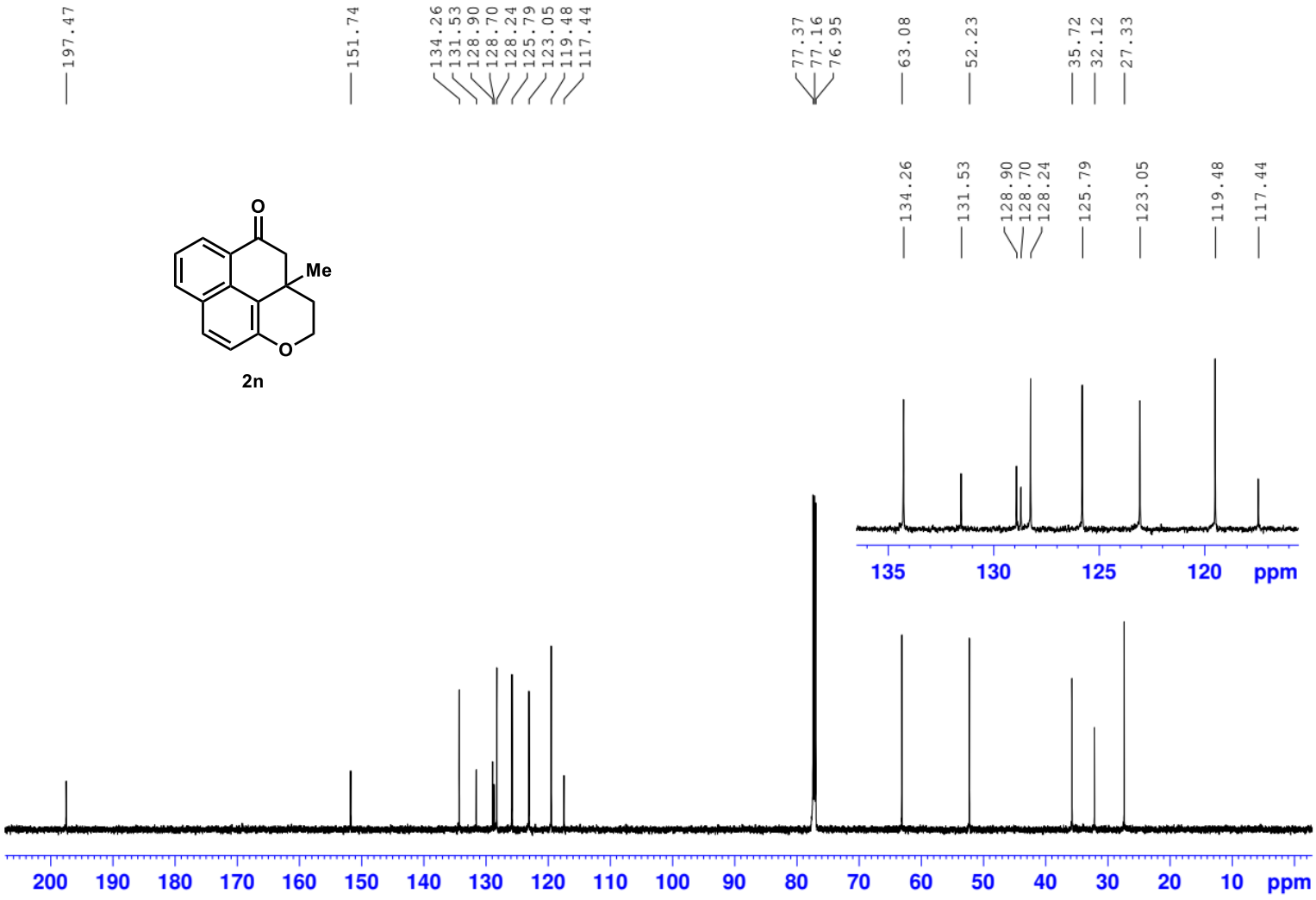
1.05
1.03
3.18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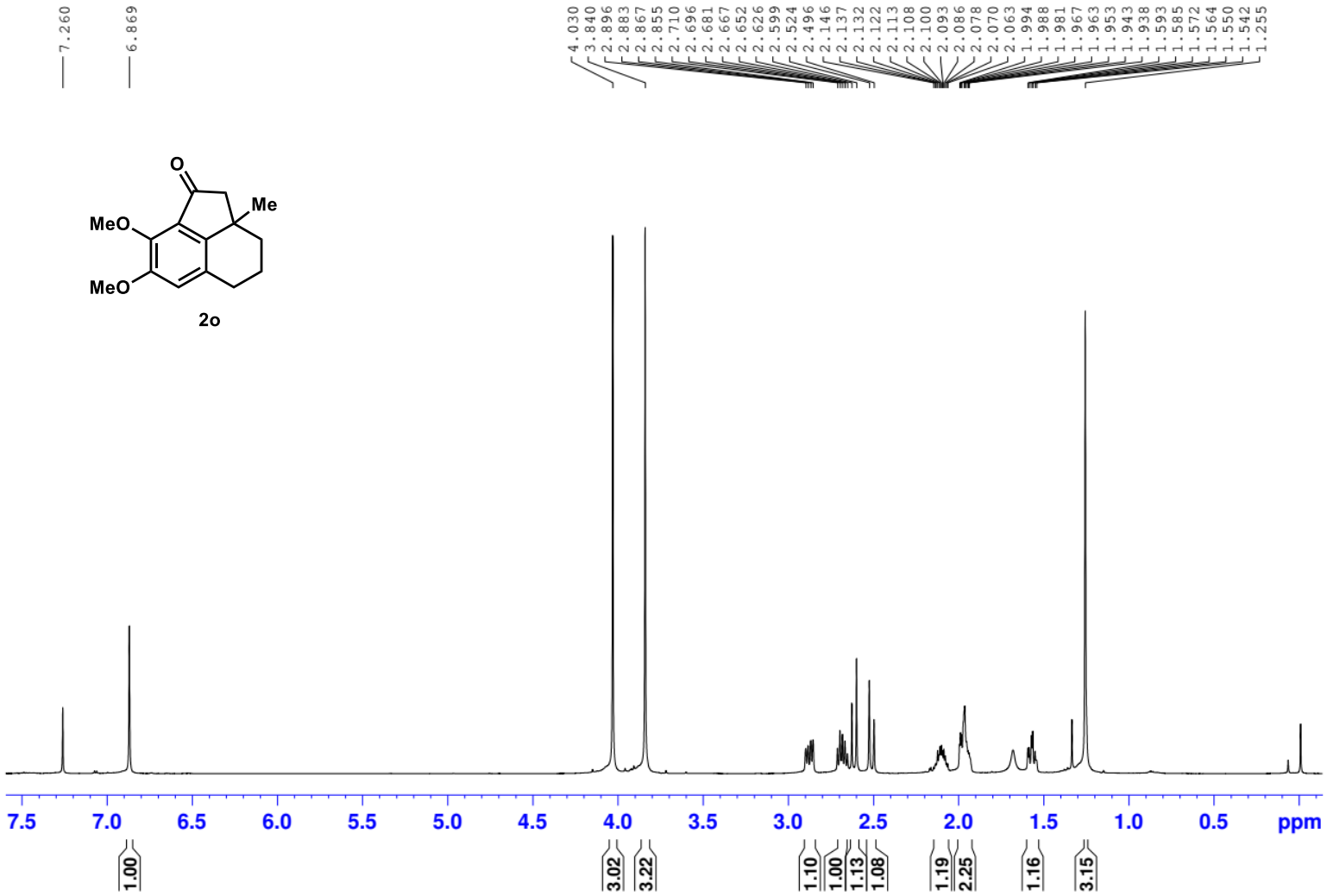
131.53
128.90
128.70
128.24
125.79
123.05
119.48
117.44
77.37
77.16
76.95
63.08
52.23
35.72
32.12
27.33
O
Me
O
2n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
135 130 125 120 ppm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2.855
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2.696
2.681
2.667
2.652
2.626
2.599
2.524
2.496
2.146
2.137
2.132
2.122
2.113
2.108
2.100
2.093
2.086
2.078
2.070
2.063
1.994
1.988
1.981
1.967
1.963
1.953
1.943
1.938
1.593
1.585
1.572
1.564
1.550
1.542
1.255
O
Me
MeO
MeO
2o
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
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3.22
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1.00
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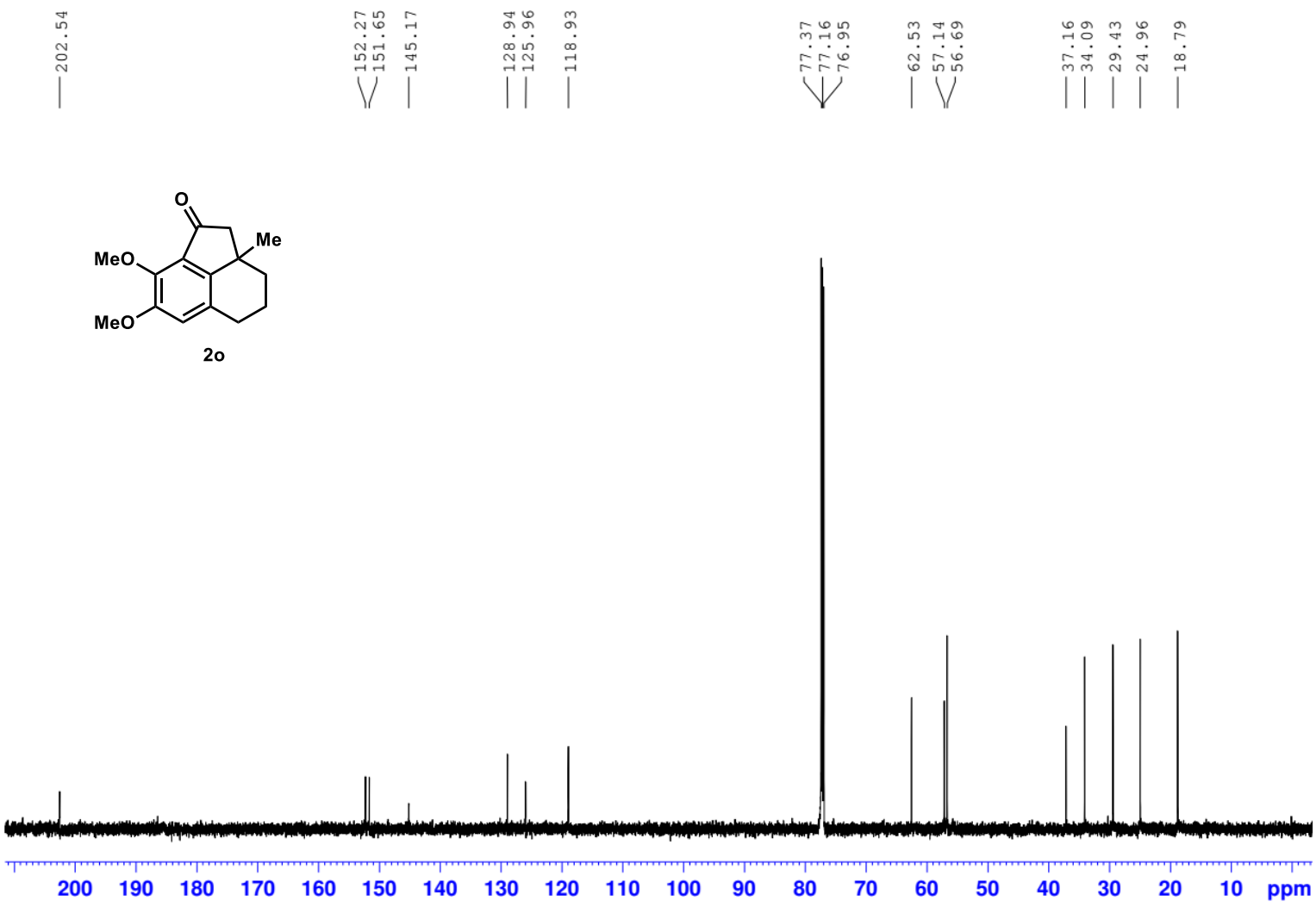
1.08
1.19
2.25
1.16
3.15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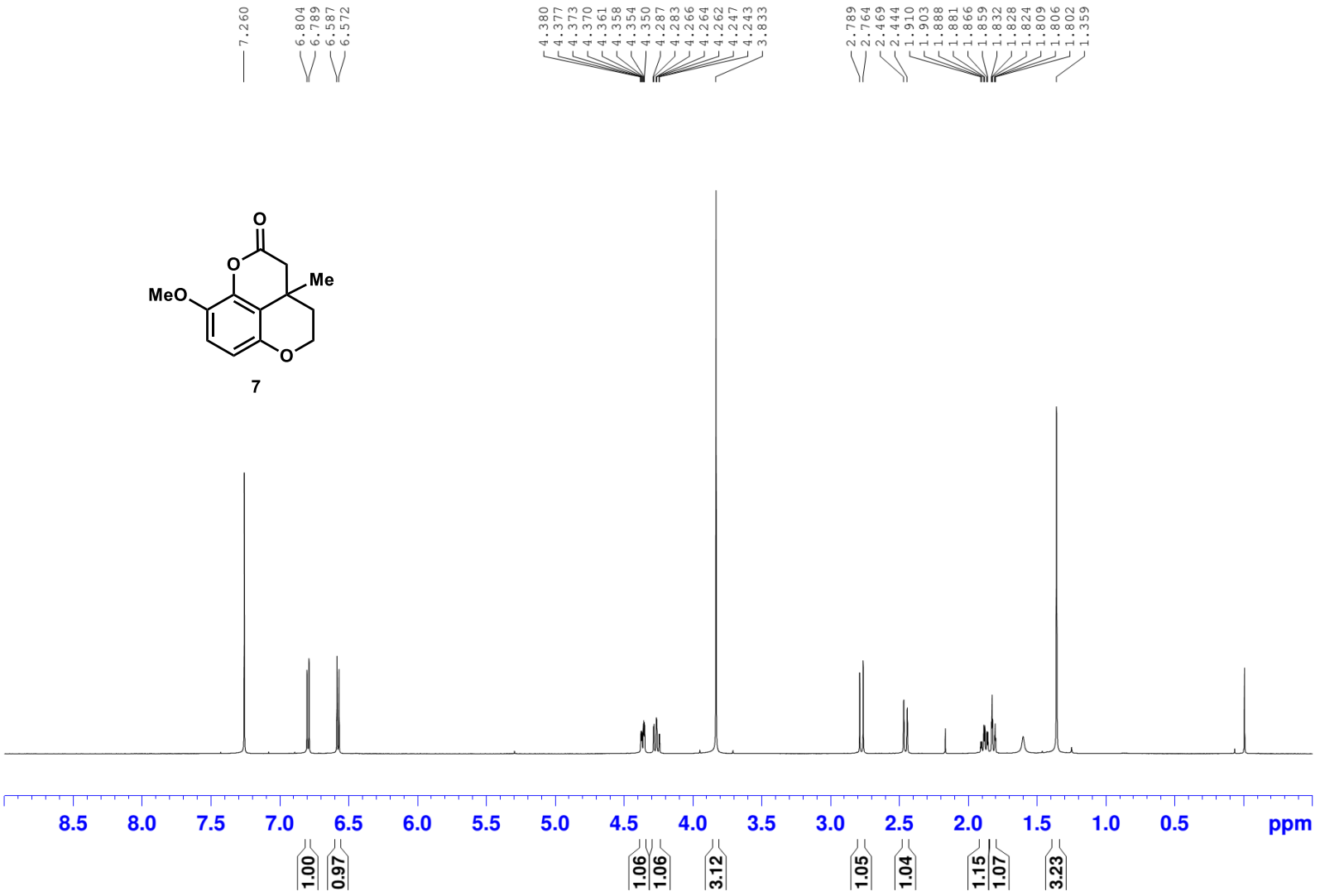
125.96
118.93
77.37
77.16
76.95
62.53
57.14
56.69
37.16
34.09
29.43
24.96
18.79
O
Me
MeO
MeO
2o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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4.287
4.283
4.266
4.264
4.262
4.247
4.243
3.833
2.789
2.764
2.469
2.444
1.910
1.903
1.888
1.881
1.866
1.859
1.832
1.828
1.824
1.809
1.806
1.802
1.359
O
O
Me
MeO
O
7
8.5
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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
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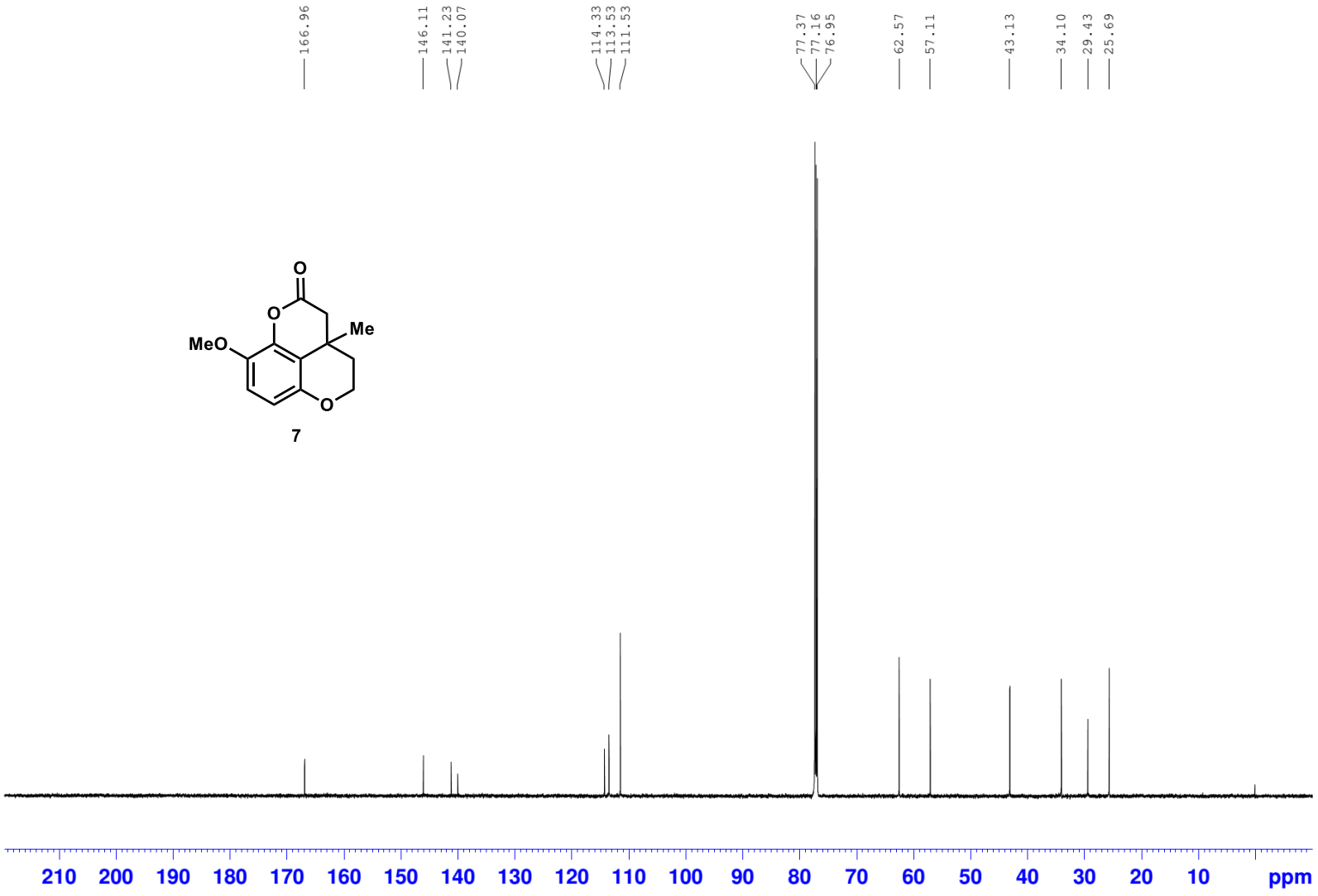
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77.37
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34.10
29.43
25.69
O
O
Me
MeO
O
7
210
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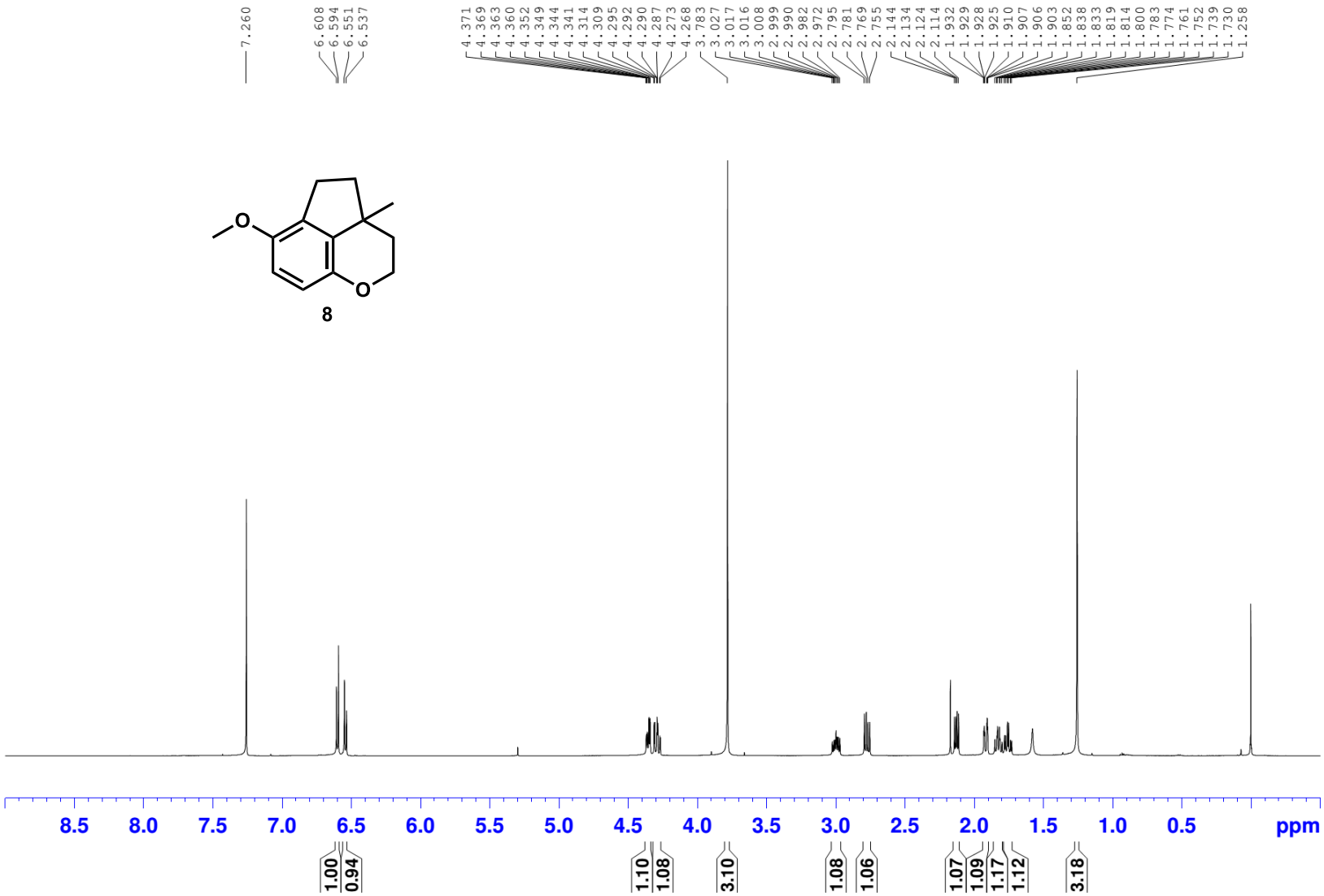
ppm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4.344
4.341
4.314
4.309
4.295
4.292
4.290
4.287
4.273
4.268
3.783
3.027
3.017
3.016
3.008
2.999
2.990
2.982
2.972
2.795
2.781
2.769
2.755
2.144
2.134
2.124
2.114
1.932
1.929
1.928
1.925
1.910
1.907
1.906
1.903
1.852
1.838
1.833
1.819
1.814
1.800
1.783
1.774
1.761
1.752
1.739
1.730
1.258
O
O
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8.5
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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
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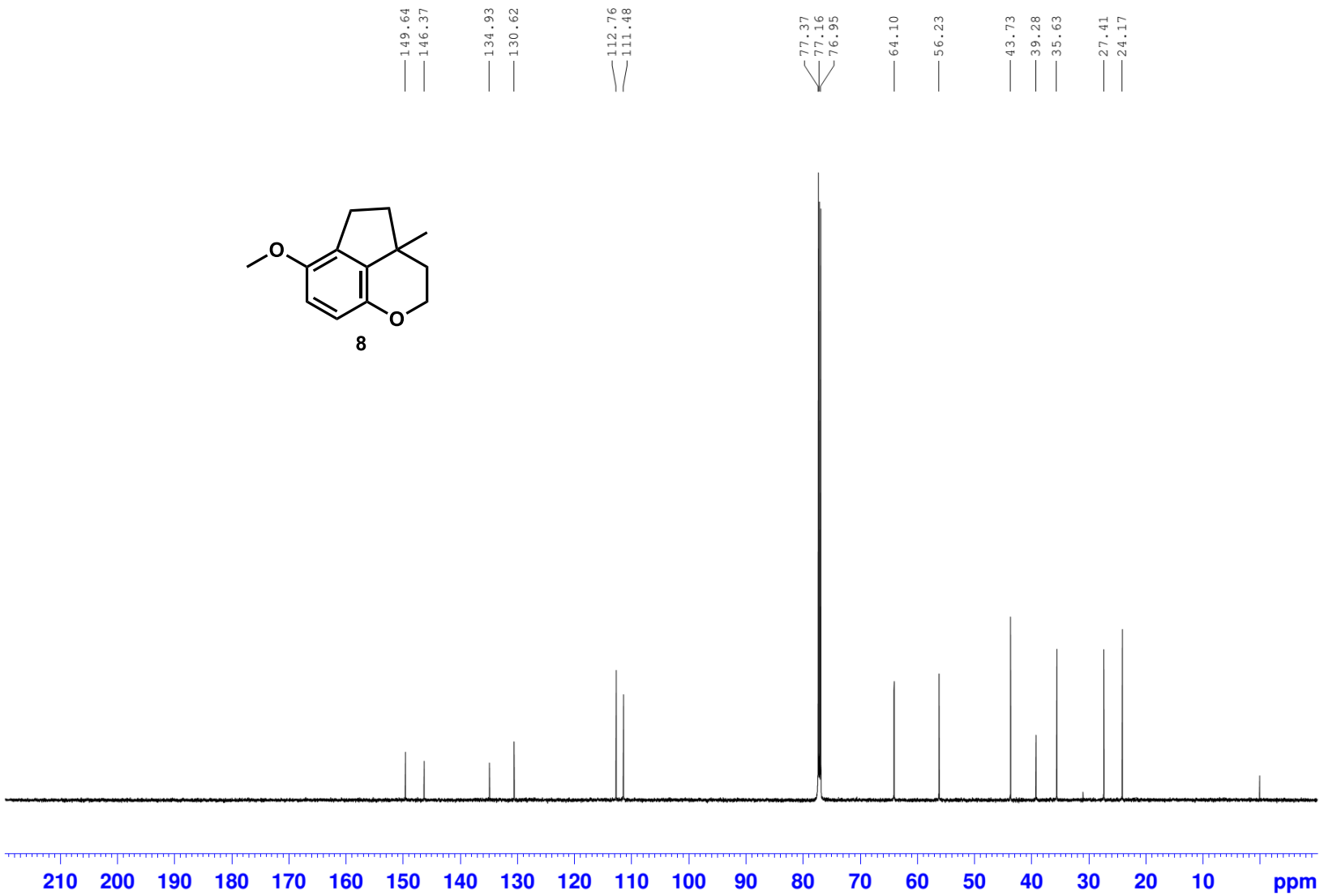
3.18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77.37
77.16
76.95
64.10
56.23
43.73
39.28
35.63
27.41
24.17
O
O
8
210
200
190
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150
140
130
120
110
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90
80
70
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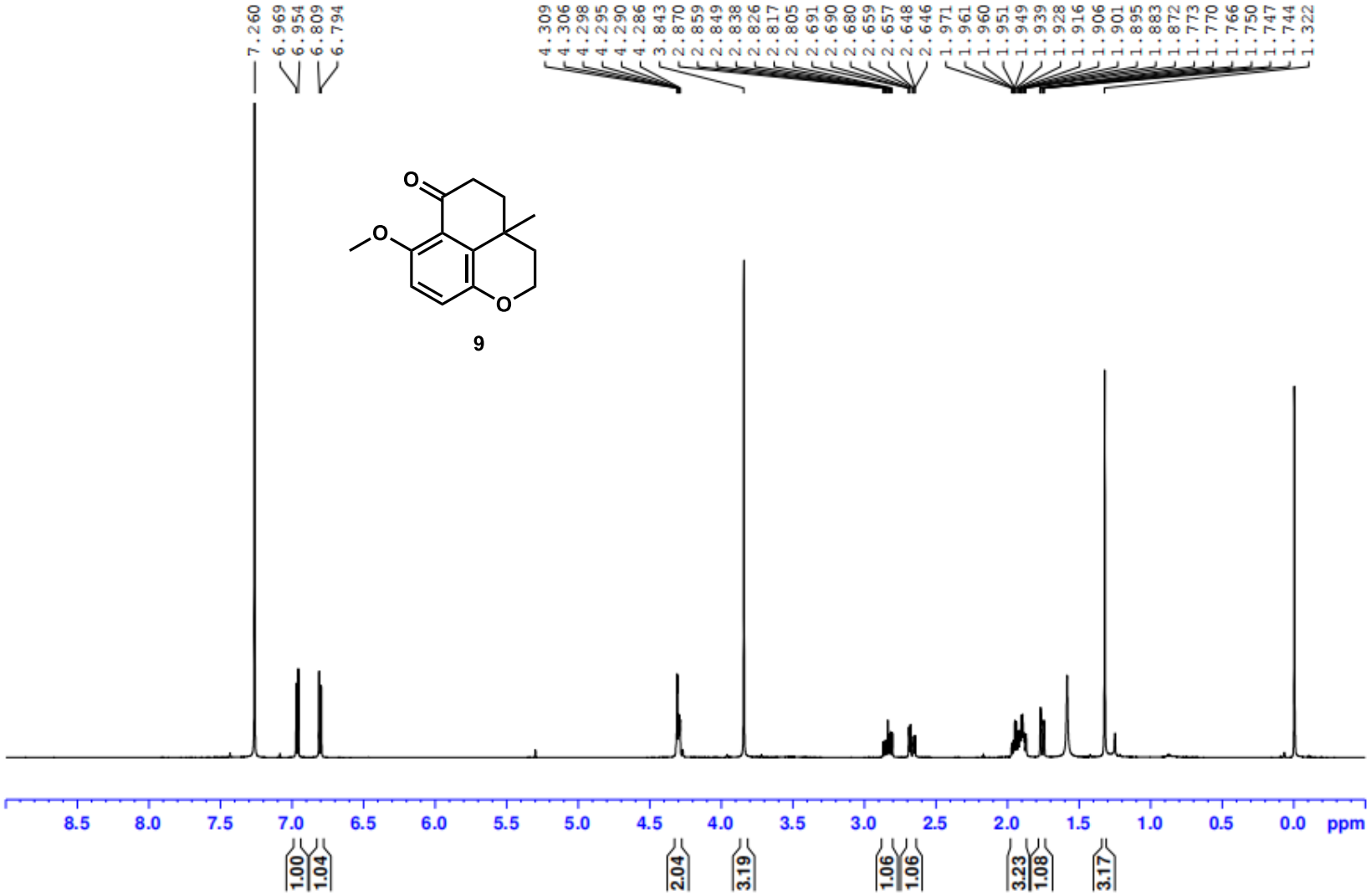
40
30
20
10
ppm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6.809
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4.306
4.298
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4.286
3.843
2.870
2.859
2.849
2.838
2.826
2.817
2.805
2.691
2.690
2.680
2.659
2.657
2.648
2.646
1.971
1.961
1.960
1.951
1.949
1.939
1.928
1.916
1.906
1.901
1.895
1.883
1.872
1.773
1.770
1.766
1.750
1.747
1.744
1.322
O
O
O
9
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
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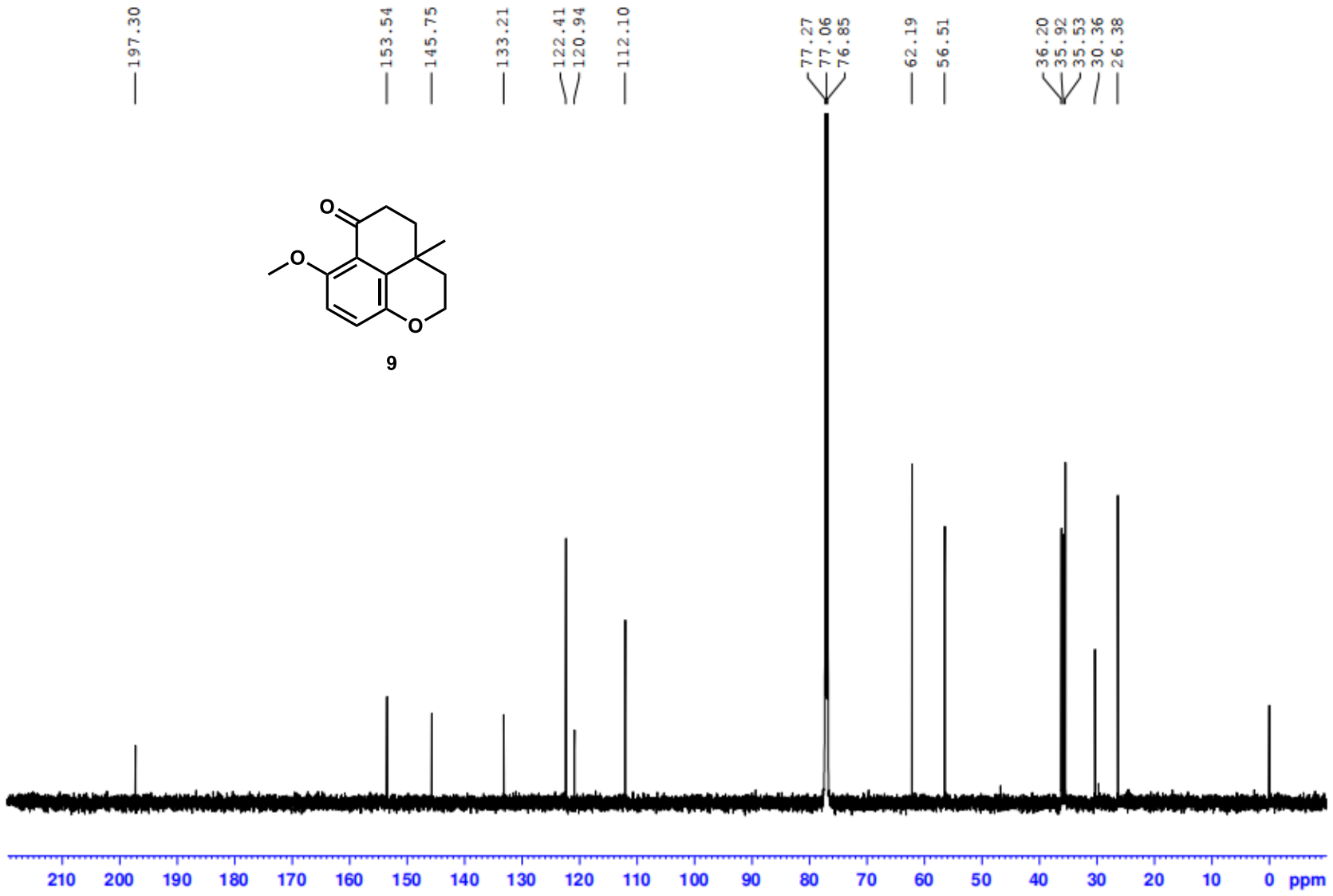
2.04
3.19
1.06
1.06
3.23
1.08
3.17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153.54
145.75
133.21
122.41
120.94
112.10
77.27
77.06
76.85
62.19
56.51
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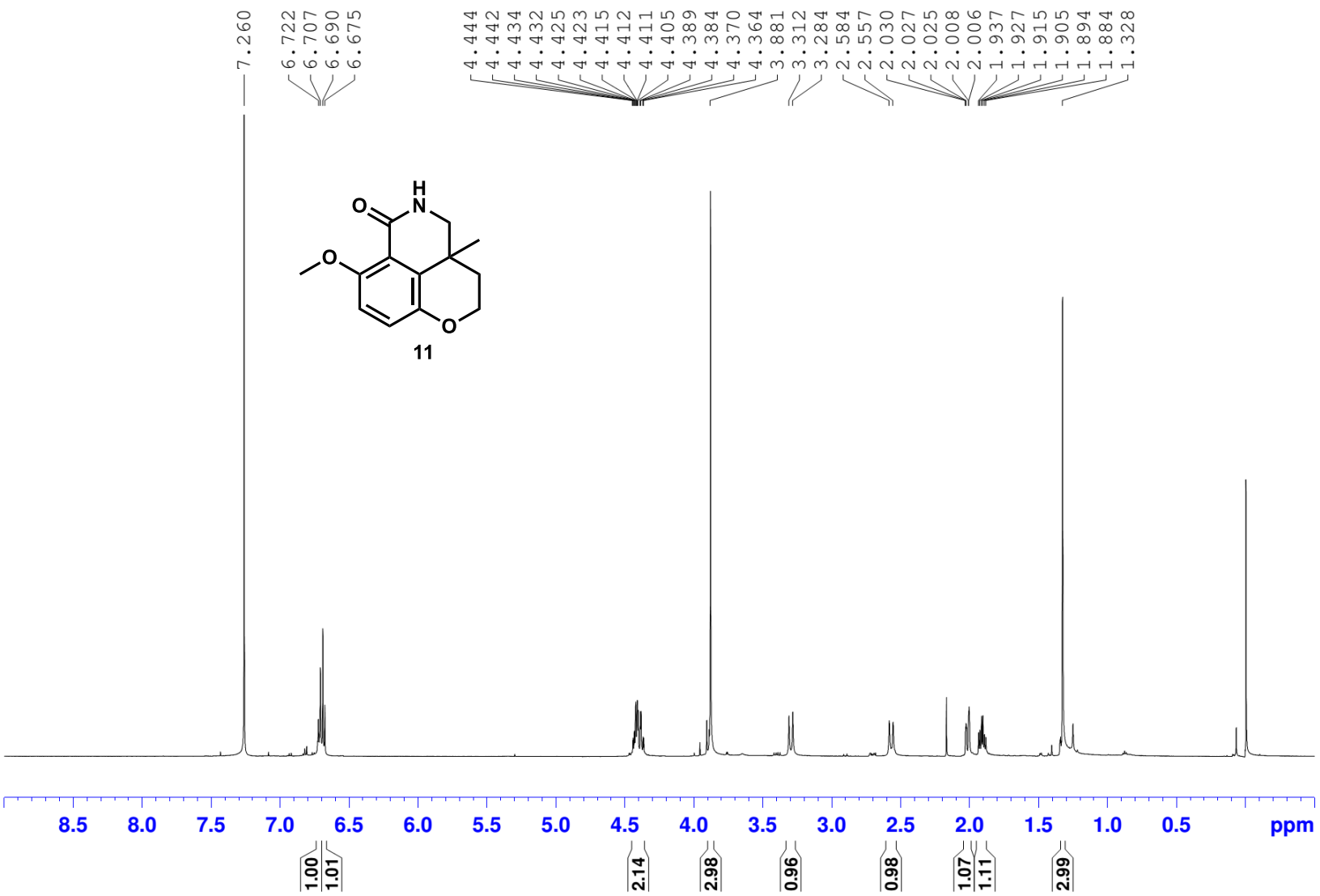
35.53
30.36
26.38
O
O
O
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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6.707
6.690
6.675
4.444
4.442
4.434
4.432
4.425
4.423
4.415
4.412
4.411
4.405
4.389
4.384
4.370
4.364
3.881
3.312
3.284
2.584
2.557
2.030
2.027
2.025
2.008
2.006
1.937
1.927
1.915
1.905
1.894
1.884
1.328
H
N
O
O
O
11
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
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ppm
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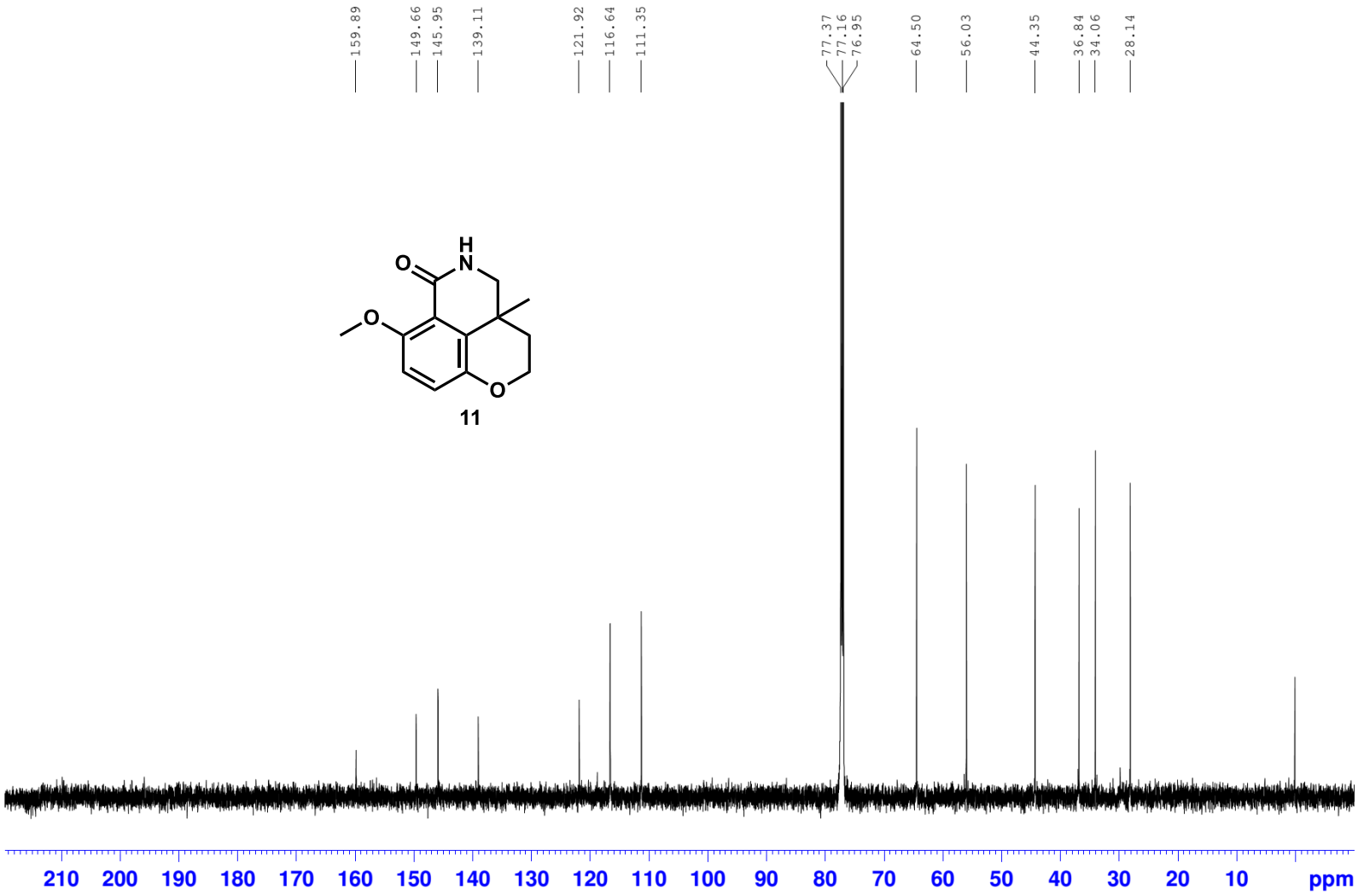
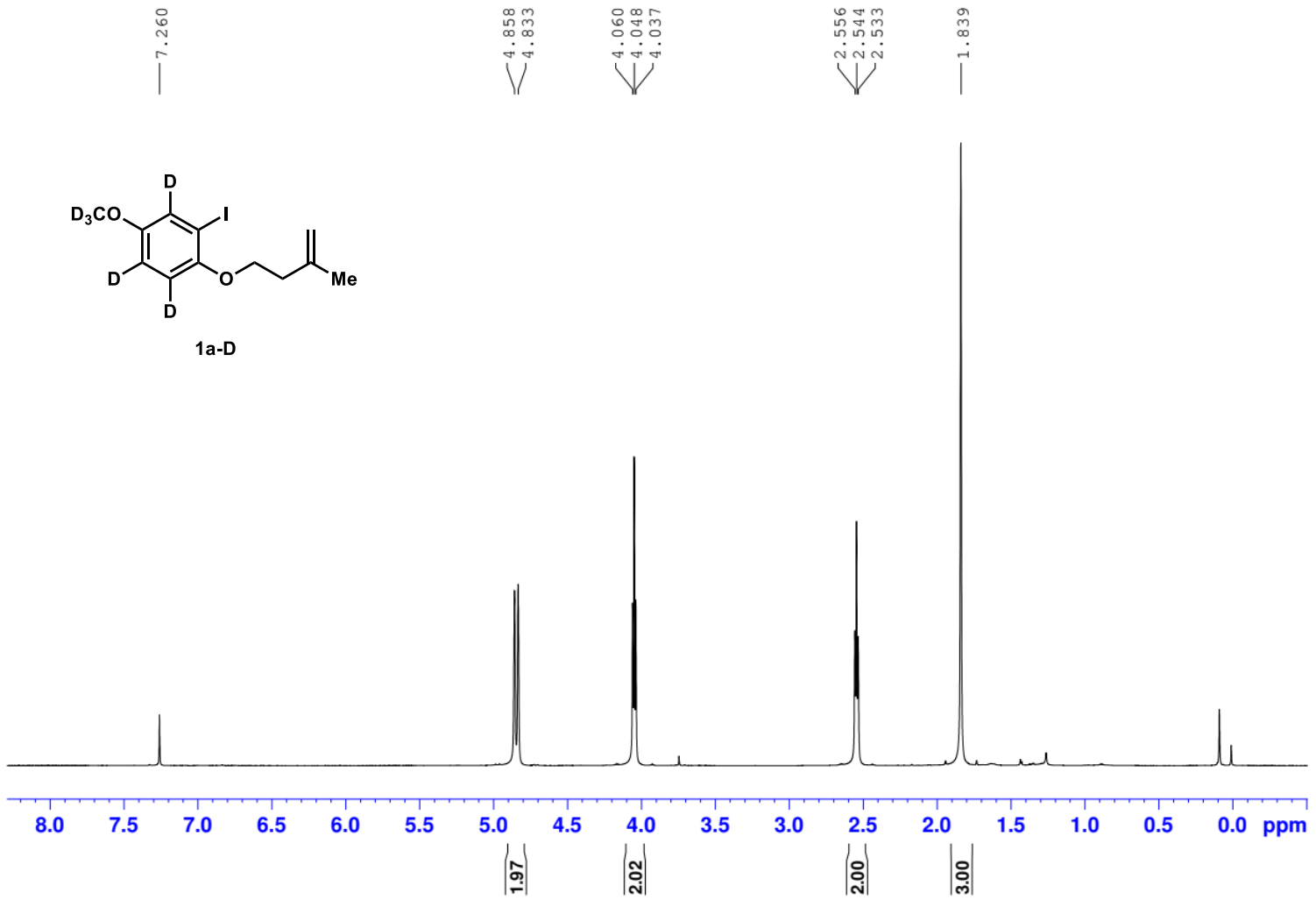
0.96
0.98
1.07
1.11
2.99


159.89
149.66
145.95
139.11
121.92
116.64
111.35
77.37
77.16
76.95
64.50
56.03
44.35
36.84
34.06
28.14
H
N
O
O
O
11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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4.833
4.060
4.048
4.037
2.556
2.544
2.533
1.839
D
D3CO
I
D
O
Me
D
1a-D
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
0.0
ppm
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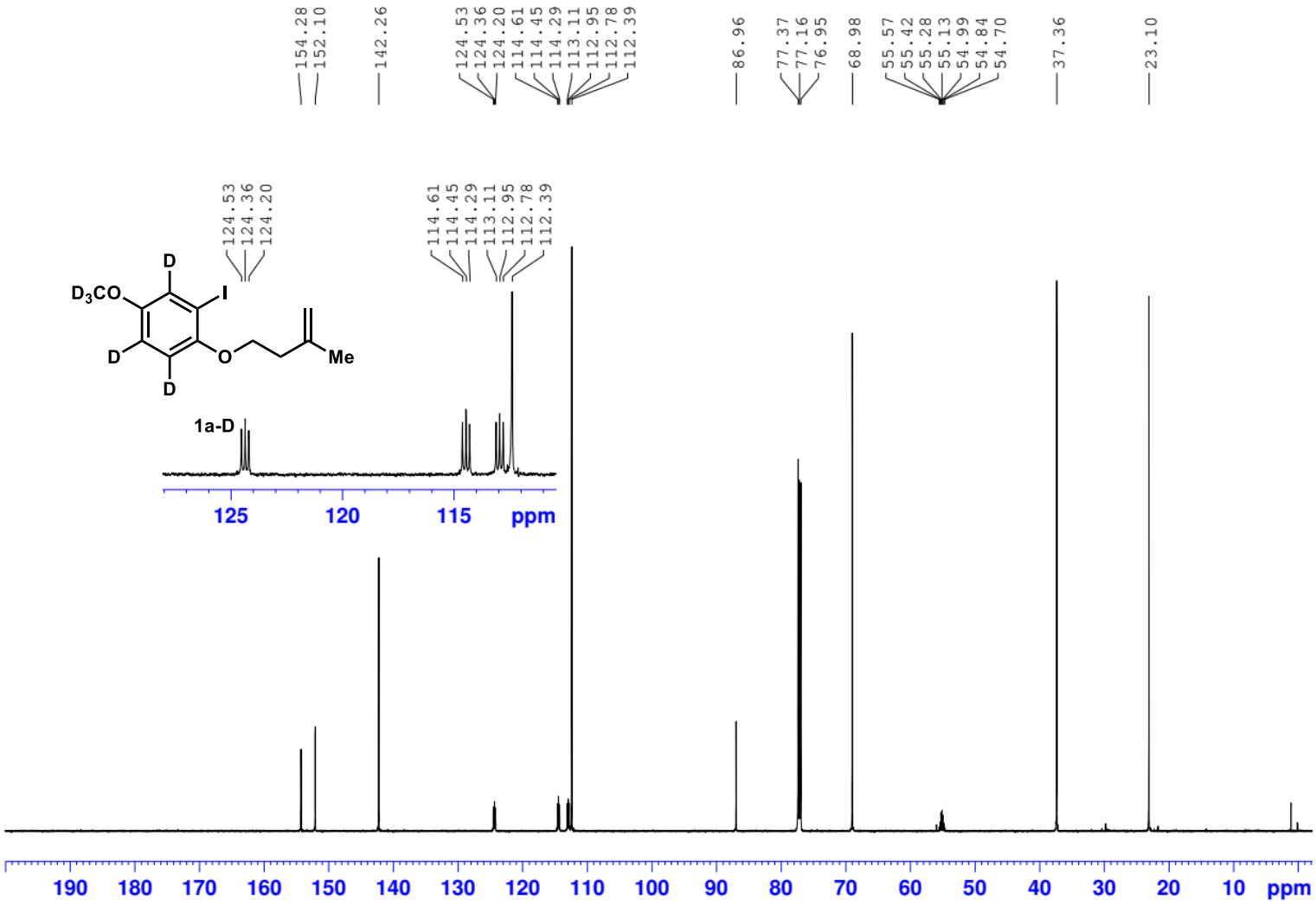
2.02
2.00
3.00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152.10
142.26
124.53
124.36
124.20
114.61
114.45
114.29
113.11
112.95
112.78
112.39
86.96
77.37
77.16
76.95
68.98
55.57
55.42
55.28
55.13
54.99
54.84
54.70
37.36
23.10
D
D3CO
I
D
O
Me
D
1a-D
125
120
115
ppm
190
180
170
160
150
140
130
120
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90
80
70
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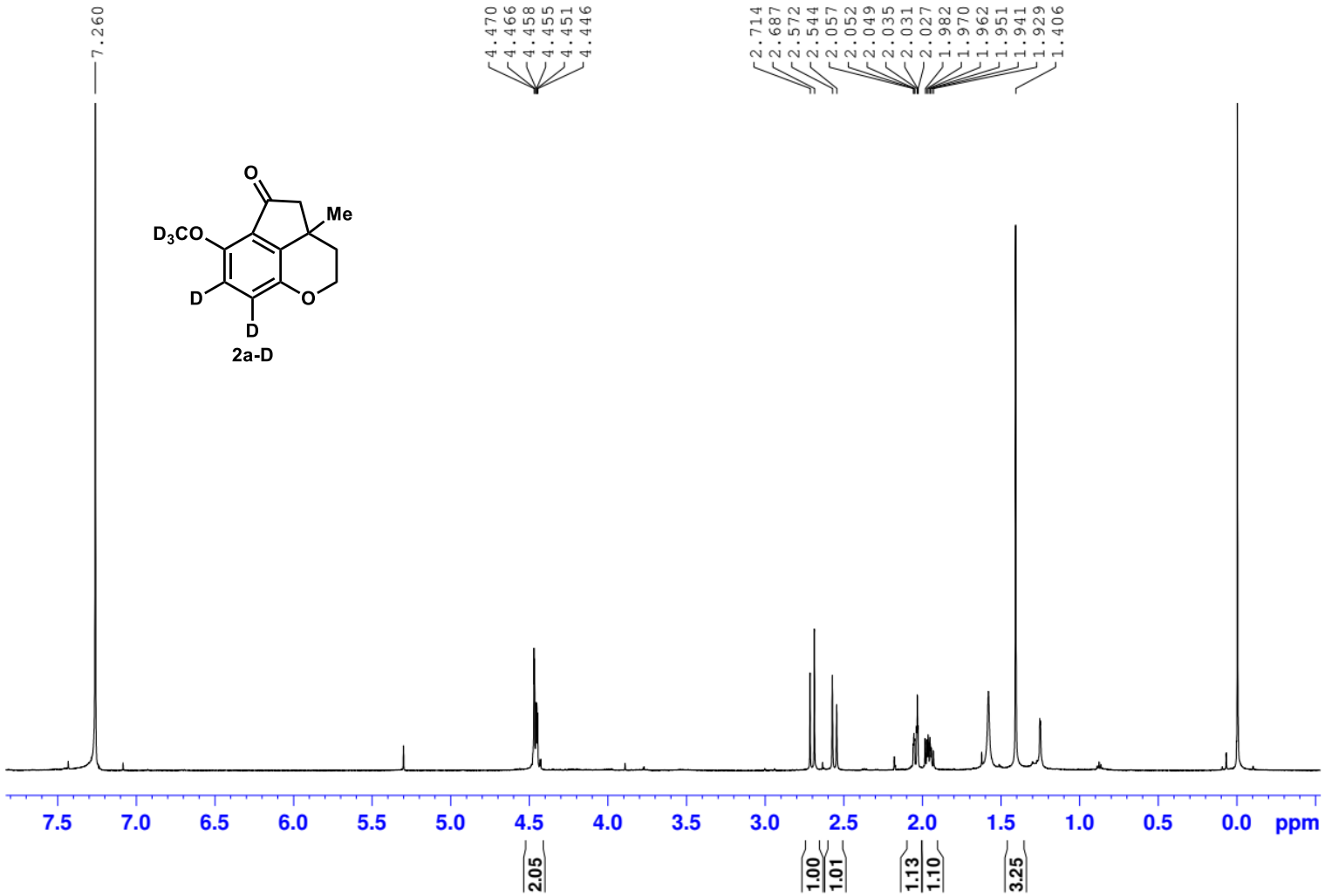
40
30
20
10
ppm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2.544
2.057
2.052
2.049
2.035
2.031
2.027
1.982
1.970
1.962
1.951
1.941
1.929
1.406
O
Me
D3CO
D
O
D
2a-D
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
0.5
0.0
ppm
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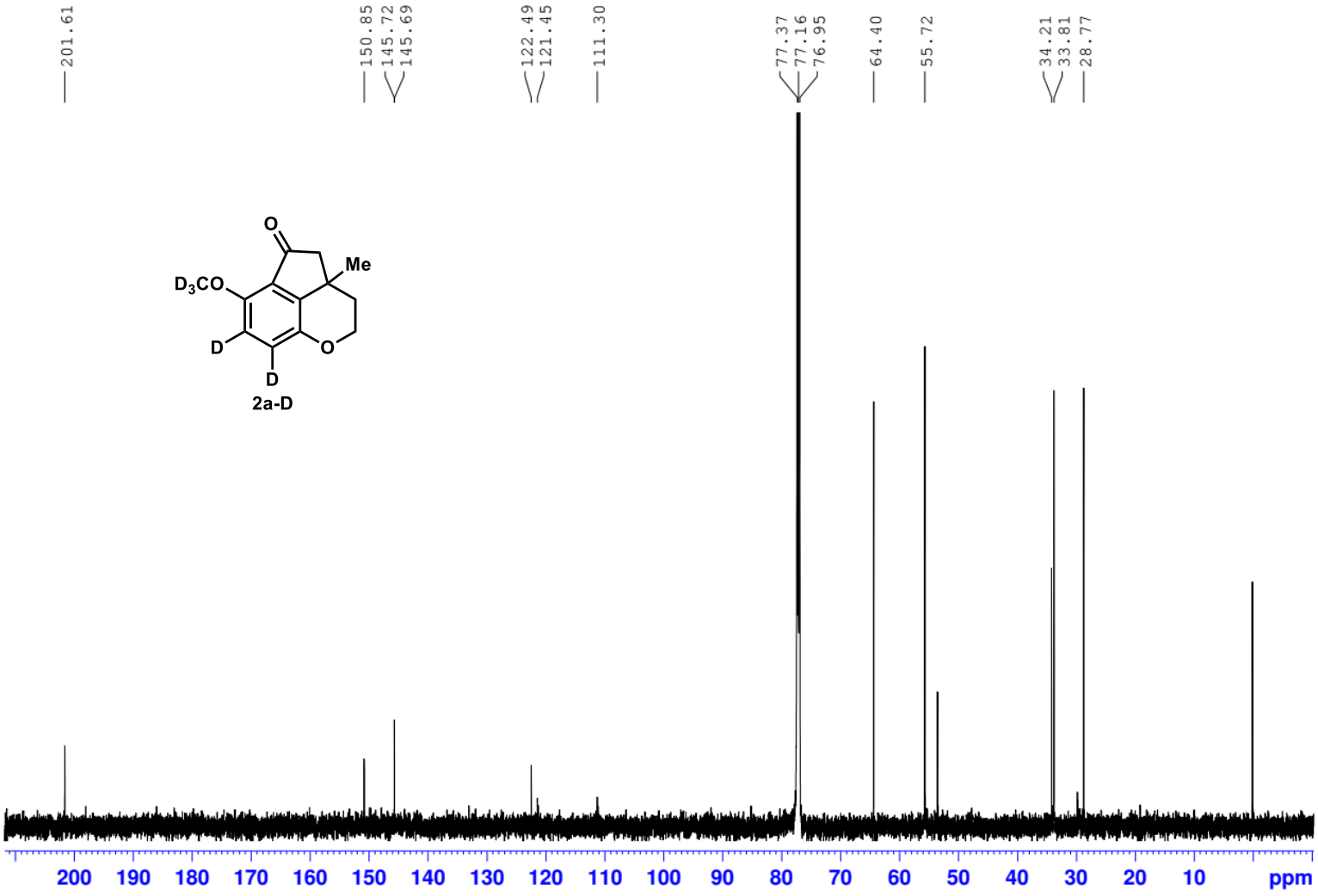
1.00
1.01
1.13
1.10
3.25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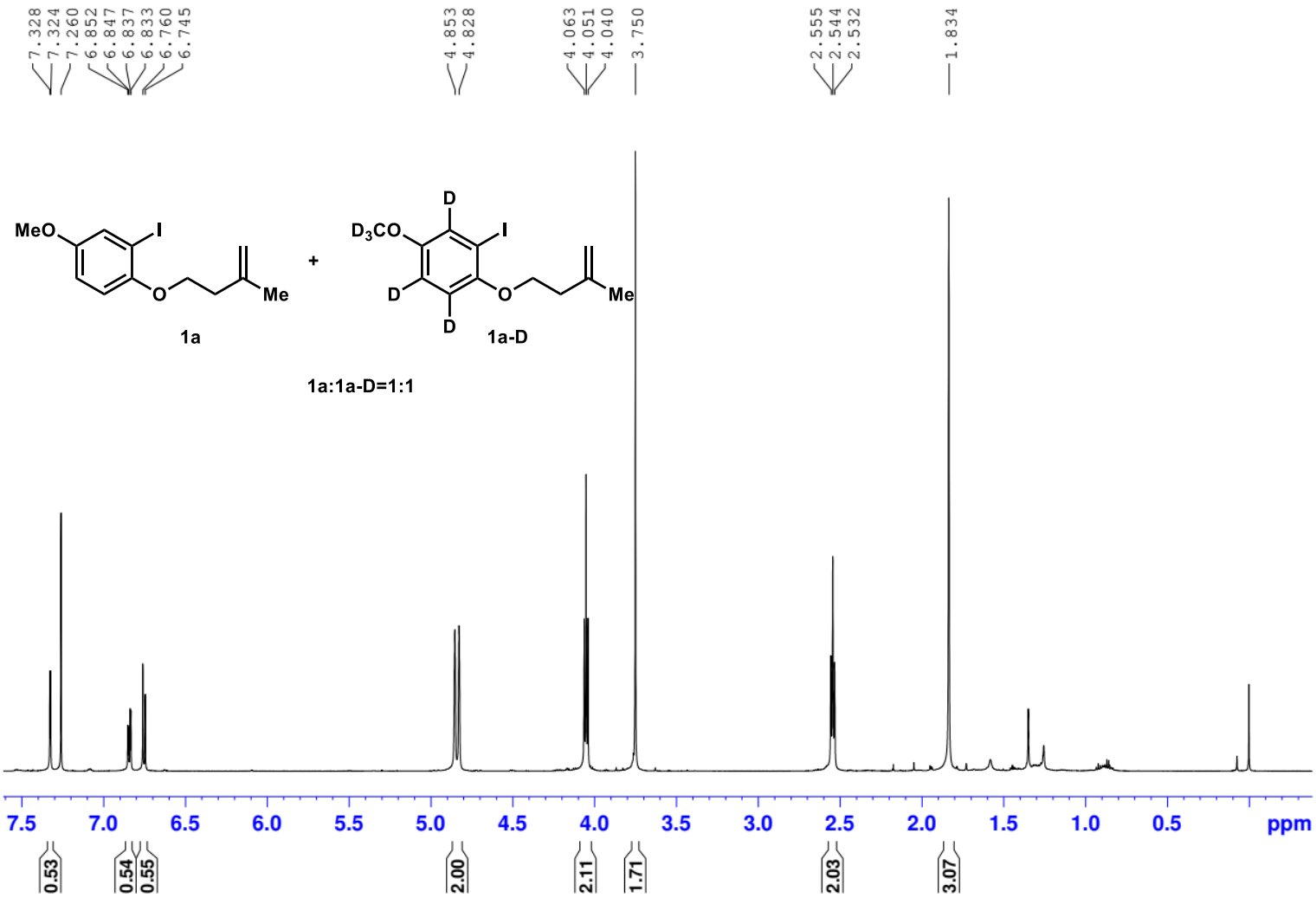
150.85
145.72
145.69
122.49
121.45
111.30
77.37
77.16
76.95
64.40
55.72
34.21
33.81
28.77
O
Me
D3CO
D
O
D
2a-D
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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6.760
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4.828
4.063
4.051
4.040
3.750
2.555
2.544
2.532
1.834
MeO
I
O
Me
1a
+
D
D3CO
I
D
O
Me
D
1a-D
1a:1a-D=1:1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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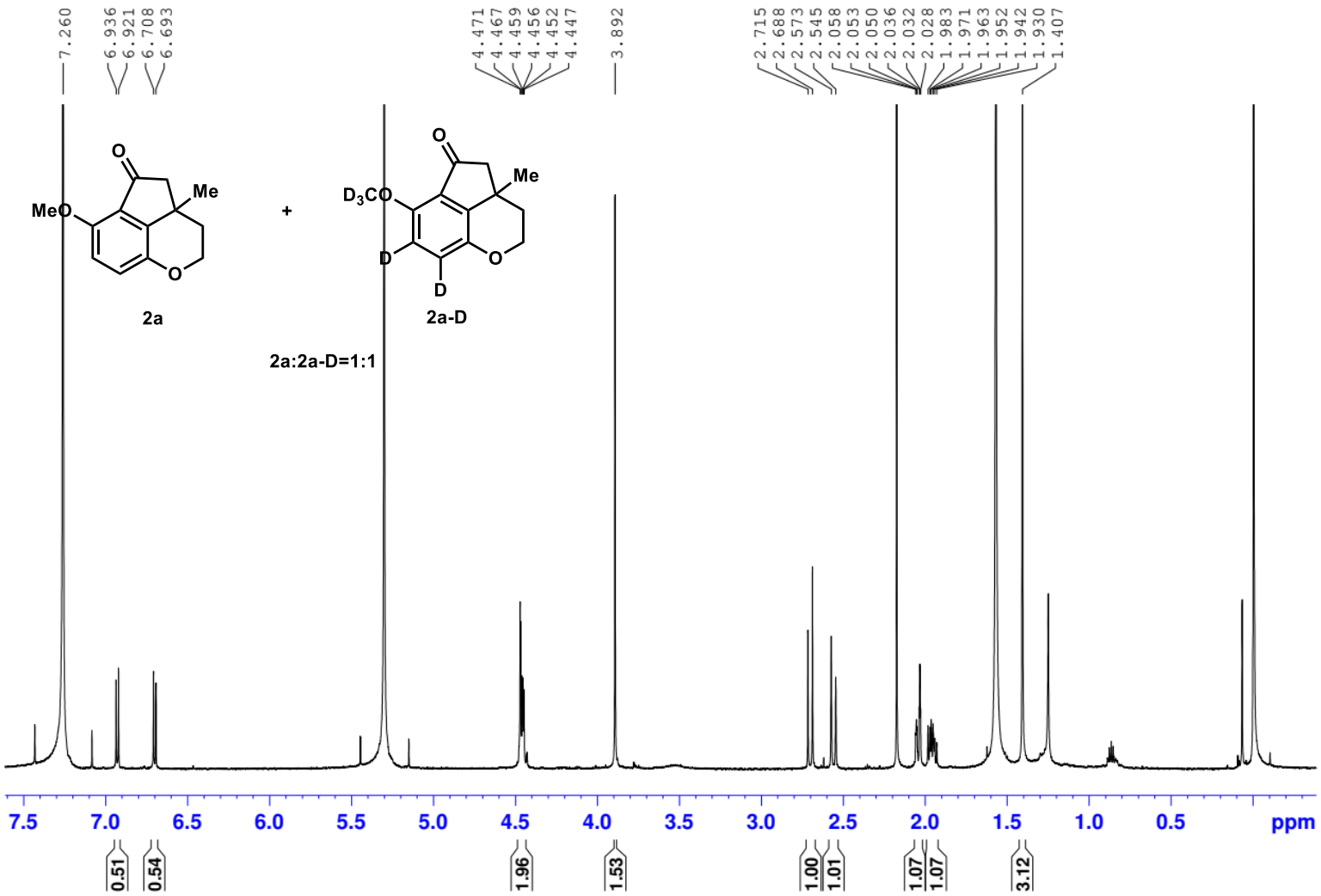
3.07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4.452
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2.688
2.573
2.545
2.058
2.053
2.050
2.036
2.032
2.028
1.983
1.971
1.963
1.952
1.942
1.930
1.407
MeO
Me
O
O
2a
+
D3CO
Me
O
D
D
O
2a-D
2a:2a-D=1:1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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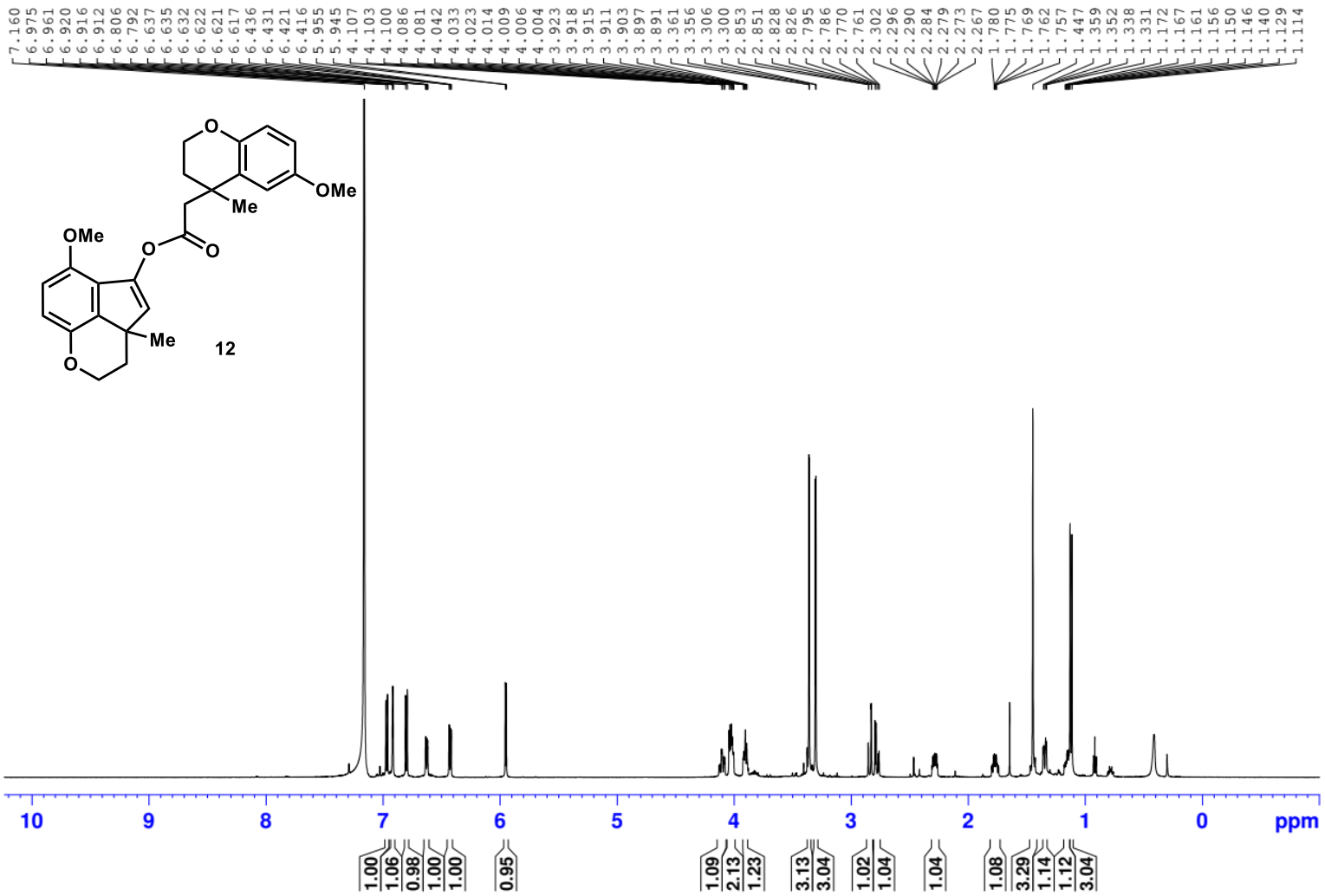
1.07
3.12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6.622
6.621
6.617
6.436
6.431
6.421
6.416
5.955
5.945
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4.100
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4.004
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1.769
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1.757
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1.352
1.338
1.331
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1.161
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1.146
1.140
1.129
1.114
OMe
Me
OMe
O
O
Me
O
O
12
10
9
8
7
6
5
4
3
2
1
0
ppm
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1.06
0.98
1.00
1.00
0.95
1.09
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3.04
1.02
1.04
1.04
1.08
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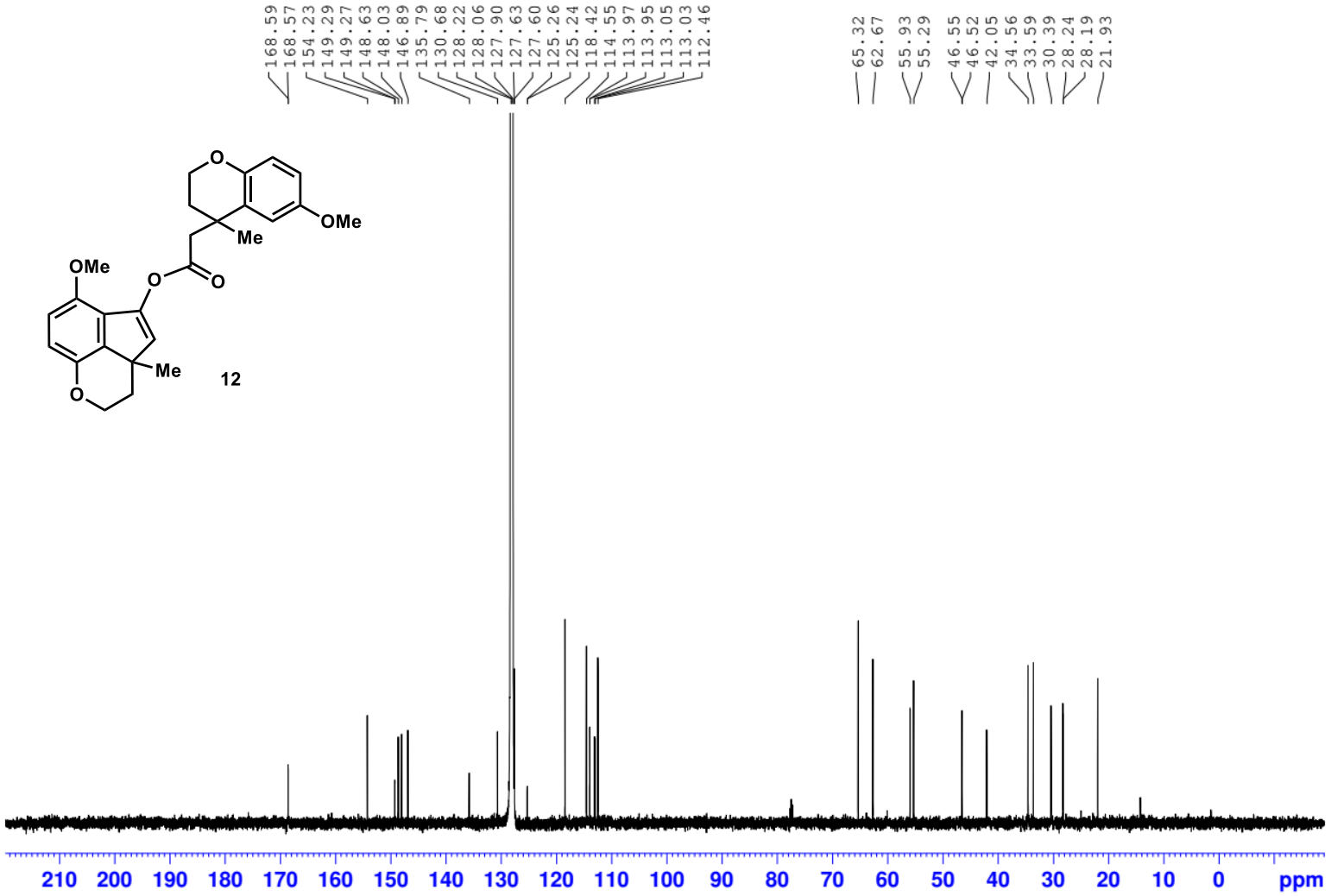
3.04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127.63
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125.26
125.24
118.42
114.55
113.97
113.95
113.05
113.03
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65.32
62.67
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55.29
46.55
46.52
42.05
34.56
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28.24
28.19
21.93
OMe
Me
OMe
O
O
Me
O
O
12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm