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Supporting Information

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Total Synthesis of (+)-Machaeriol D via Regio- and Stereoselectivity S_N2' Reaction

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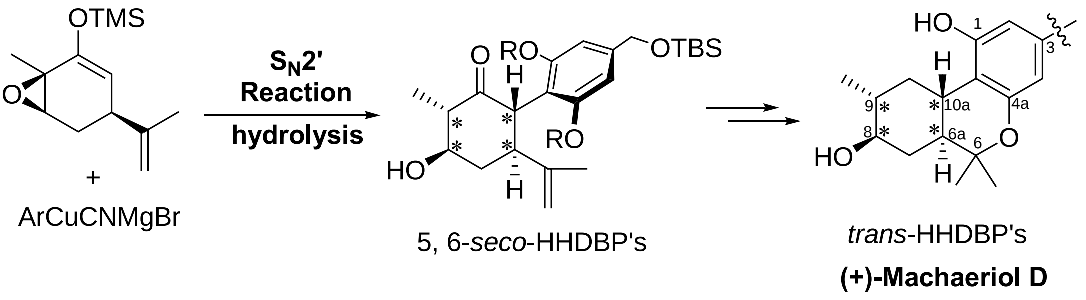
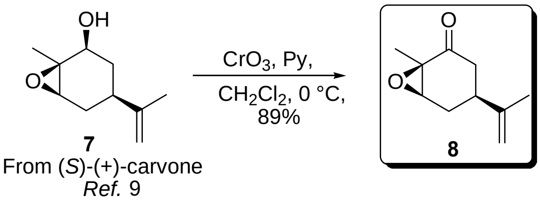


Experimental Procedures and Spectroscopic and Analytical Data of the Products

Note: ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solution on Varian Mercury-300 or 400 MHz. Optical rotations were determined on a JASCO J-20C polarimeter with 0.2 dm tube. IR spectra were recorded on a Nicolet Mx-1 spectrometer. The MS data were obtained with EI (70 eV), and the relative intensity (%) is given in brackets. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker ApexII by means of the SIMS or ESI technique.

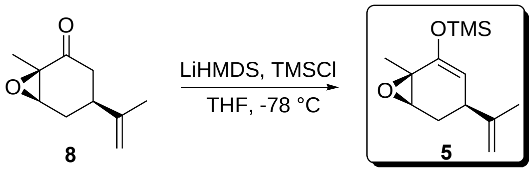
Synthesis of α,β-epoxycyclohexanone 8



4 mL (50 mmol) of dry pyridine was dissolved in 40 mL CH_2Cl_2 and the solution cooled to 0 °C . At this point, 2.5 g (25 mmol) of CrO_3 was added, and the mixture was stirred at 0 °C for 15 min. The epoxy alcohol **7** (840 mg, 5.00 mmol) was dissolved in 2 mL of CH_2Cl_2 and slowly added to the oxidizing mixture, which was stirred for 5 additional h at 0 °C. The reaction was quenched by addition of Et_2O (50 mL) and allowed to stir for another 0.5 h. Then, the reaction mixture was filtered through a neutral Al_2O_3 column, and washed with ether (50 mL). The combined organic solution was concentrated *in vacuo* and the residue was purified through column chromatography on silica gel (petroleum/EtOAc 50:1) to give the ketone **8** (739 mg, 89%). $[\alpha]_D^{25}$ = 23.7 (*c* 4.5, $CHCl_3$)

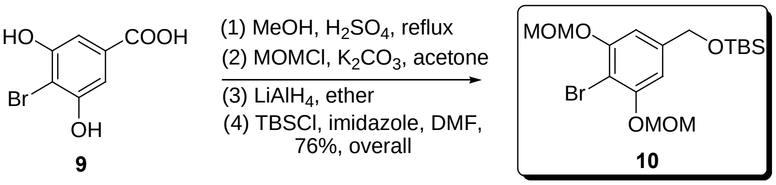
^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.71 (s, 1H), 4.68 (s, 1H), 3.41-3.42(m, 1H), 2.73-2.82 (t, *J* = 14.1, 12.3 Hz, 1H), 2.26-2.63 (m, 1H), 2.07-2.20 (m, 2H), 1.94-2.03 (m, 1H), 1.66 (s, 3H), 1.36 ppm (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 207.9, 145.9, 110.5, 64.6, 59.1, 44.7, 40.3, 28.8, 19.5, 14.6 ppm; **MS** (70 eV): *m*/*z* (%): 166 (M^+), 151, 135, 109, 67, 43 (100).

Preparation of enol silyl ether 5



Dry $(Me_3Si)_2NH$ (2.2 mL, 10.60 mmol) was dissolved in 25 mL of dry THF and cooled to 0 °C under nitrogen. The cooled solution was slowly added 4.3 mL of *n*-BuLi (2.0 M, 8.50 mmol). After being stirred at 0 °C for 30 min, the solution was cooled to –78 °C, and 706 mg (4.25 mmol) of **8**, dissolved in 1 mL THF, was slowly added dropwise. About 30 min was allowed for enolate formation, and then 1.1 mL (8.50 mmol) of neat trimethylsilyl chloride was added. The reaction mixture was allowed to warm up from –78 °C to room temperature over 30 min. Workup consisted of removing the solvent under reduced pressure taking the residue up into ether, filtering the salts through a short neutral Al_2O_3 column. Evaporation of the filtrate gave **5** as a slightly yellowish oil, sufficiently pure for the next step.

Synthesis of TBS ether 10



(1) To a solution of 4-bromo-3,5-dihydroxybenzoic acid (2.90 g, 12.50 mmol) in MeOH (50 mL), H_2SO_4 (catalytic amount) was added. The mixture was refluxed for 12 h. Then 10% NaOH (10 mL) was added, and the mixture was extracted with EtOAc (3×100 mL). The organic phase was washed with 10% NaOH (3×10 mL), brine and dried with anhydrous Na_2SO_4 giving methyl-4-bromo-3,5-dihydroxybenzoate as white solid (2.95 g, 96%): **^{1}H NMR** (400 MHz, acetone-*d*$_6$): δ = 9.42 (s, Ar-OH), 7.14 (s, 2H), 3.82 ppm (s, 3H); **^{13}C NMR** (100 MHz, acetone-*d*$_6$): δ = 166.7, 156.2, 131.0, 108.5, 104.4, 52.4 ppm; **MS** (70 eV): *m*/*z* (%): 246 (M^+), 217(100), 187, 108, 79, 51, 43.

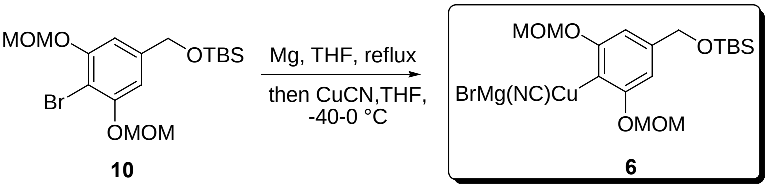
(2) Methyl-4-bromo-3,5-dihydroxybenzoate (2.70 g, 10.98 mmol), K_2CO_3(15.150 g, 110 mmol) and MOMCl (2.0 mL, 26.3 mmol) were taken in 50 mL of acetone and stirred at 0 °C for 30 min. It was filtered through a büchner funnel and concentrated in vacuo. The residue was washed with water and extracted twice with EtOAc. The combined organic layers was washed with brine and dried with anhydrous Na_2SO_4 and evaporated. The residue was purified by silica gel column by eluting with petroleum ether and EtOAc (10: 1, v/v) to afford 3.23 g (88%) of methyl 4-bromo-3,5-bis(methoxymethoxyl)benzoate as a white solid. **^{1}H NMR** (400 MHz, CDCl3):7.47 (s, 2H), 5.29 (s, 4H), 3.89 (s, 3H), 3.51 ppm (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.1, 154.8, 130.3, 109.9, 95.0, 56.5, 52.4 ppm; **MS** (70 eV): *m*/*z* (%): 334 (M^+), 305, 274, 143, 45 (100).

(3) To a solution of the compound from (2) (3.20 g, 9.58 mmol) in ether (100 mL) was added $LiAlH_4$ (437 mg, 11.50 mmol), and the mixture was stirred for 10 min. Then water was added, the mixture was extracted with EtOAc, and the combined organic layer was washed with dil. HCl , brine and then dried with anhydrous Na_2SO_4 and evaporated. The residue was purified by silica gel column by eluting with petroleum ether and EtOAc (5: 1, v/v) to afford 2.79 g (95%) of the alcohol as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.76 (s, 2H), 5.18 (s, 4H), 4.51 (s, 2H), 3.45 (s, 6H), 3.00 ppm (br s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 154.6, 141.8, 107.3, 102.1, 94.7, 64.3, 56.2 ppm; **MS** (70 eV): *m*/*z* (%): 306 (M^+), 246, 151, 45 (100).

(4) To a solution of the alcohol (2.70 g, 8.82 mmol) in DMF (5 mL) was added imidazole (1.50 g, 22.5 mmol), TBSCl 1.59 g, 10.59 mmol), and the mixture was stirred for 30 min at room temperature. Then EtOAc (100 mL) was added, the organic layers was washed with water (5×5 mL) and dried with anhydrous Na_2SO_4 and evaporated. The residue was

purified by silica gel column by eluting with petroleum ether and EtOAc (50: 1, v/v) to afford 3.52 g (95%) of TBS ether **10** as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.83 (s, 2H), 5.23 (s, 4H), 4.67 (s, 2H), 3.50 (s, 4H), 0.93 (s, 9H), 0.81 ppm (s, 6H), **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 154.7, 142.5, 106.9, 101.5, 95.0, 64.3, 56.2, 25.8, 25.6, 18.3, -5.4 ppm; **MS** (70 eV): *m*/*z* (%): 420 (M^+), 363, 333, 89, 45(100).

preparetion arylcyanocuprate reagent 6



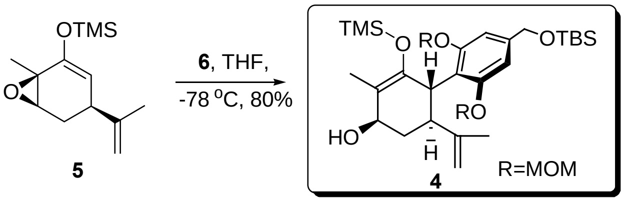
(1) Formation of ArMgBr.

With a magnetic stirring bar, reflux condenser, with a stopcock, and a 25-mL addition funnel is charged with 205 mg (8.54 mmol) of magnesium dust. The system is evacuated and placed under argon. 0.01 mL 1,2-dibromoethane is added via syringe to the magnesium suspension in 1 mL dry THF to initiate Grignard formation, then a solution of **10** (3.50 g, 8.33 mmol) in THF (17 mL) was added dropwise via addition funnel to the refluxing mixture. Afer addition the solution was refluxed for 45 min, by which time all the Mg had dissolved.

(2) Formation of the Cuprate.

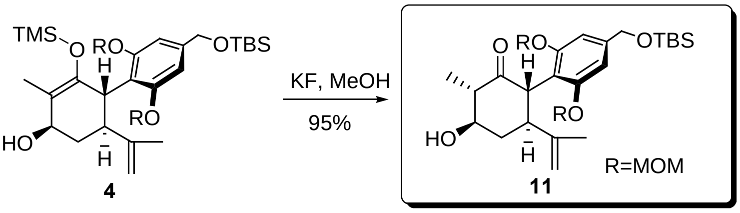
The arylmagnesium bromide solution was added to a stirred and cooled (- 40 °C) mixture of CuCN (750 mg, 8.33 mmol) in dry THF (8 mL) under nitrogen. The reaction mixture was allowed to warm up to 0 °C until no CuCN remained visible (1 h).

Synthesis of silyl enol ether 4



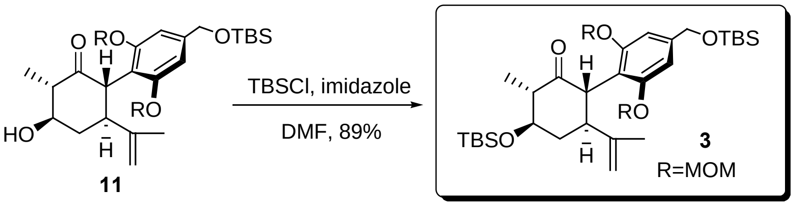
A solution of **5** (1.01 g, 4.25 mmol) in dry THF (2 mL) was added by cannula to a stirred and cooled (-78 °C) solution of arylcyanocuprate reagent **6** (ca. 30 mL, ca. 8.33 mmol in THF) under nitrogen.The reaction mixture was allowed to warm up to –10 °C–0 °C over 3 h. Ether (100 mL) was added, and the organic phase was washed with saturated aqueous NH_4Cl (30 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel, using first 30:1 petroleum ether–EtOAc and then 10:1 petroleum ether–EtOAc, gave **4** (1.97 g, 80%) as a pure, colorless oil: $[\alpha]^{25}_{D}$ = 96 (*c* 3.3, $CHCl_3$); IR (film): υ_{max} 3353 (-OH), 2954, 1672, 1251, 1045, 951, 841, 776 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 6.75 (s, 1H), 6.66 (s, 1H), 4.94-5.08 (m, 4H), 4.65 (s, 2H), 4.44 (s, 1H), 4.38 (m, 1H), 4.29 (s, 1H), 3.95-3.98 (d, *J* = 10.8 Hz, 1H) 3.39-3.43 (s, 6H) 2.79-2.88 (t, *J* = 12.9, 10.5 Hz, 1H), 2.03-2.10 (m,1H), 1.58-1.70 (m, 7H), 0.90 (s, 9H), 0.04 (s, 6H), - 0.07 ppm (s, 9H); ^{13}**C NMR** (75 MHz, $CDCl_3$): δ = 157.1, 156.3, 147.1, 146.7, 141.2, 118.1, 114.0, 111.3, 106.3, 105.2, 95.1, 94.7, 71.2, 64.9, 55.7, 44.7, 40.6, 38.8, 25.8, 18.9, 18.3, 12.3, 0.1, -5.3 ppm; **MS** (70 eV): *m*/*z* (%): 580 (M^+), 535, 408, 363, 341, 73, 45 (100%); **HRMS** (SIMS): *m*/*z* calcd for $C_{30}H_{52}O_7Si_2Na$: 603.3144; found: 603.3147 $[M+Na]^+$.

Synthesis of β-hydroxy ketone 11



To a solution of silyl enol ether **4** (1.90 g, 3.28 mmol) in MeOH (10 mL) was added KF (285 mg, 14.91 mmol), and the mixture was stirred at room temperature for 1 h. The methanol was removed in vacuo, water (10 mL) was added, and the resulting mixture was extracted with EtOAc (3×20 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the residue through column chromatography on silica gel (petroleum/EtOAc 5:1) afforded **11** (1.58 g, 95%). $[\alpha]_D^{25}$ = – 46 (*c* 0.6, $CHCl_3$); IR (film): υ_{max} 3473 (-OH), 2932, 1709, 1589, 1434, 1035, 840, 778 cm^{-1};
^{1}**H NMR** (400 MHz, $CDCl_3$): δ = 6.76(s, 2H), 5.01-5.08 (m, 4H), 4.66 (s, 2H), 4.51 (s,1H), 4.48 (s, 1H), 4.03-4.06 (d, *J* = 12.0 Hz, 1H), 3.67-3.69 (m, 1H), 3.40 (s, 6H), 3.07-3.14 (t, *J* = 12.0, 12.8 Hz, 1H), 2.34-2.39 (m, 1H), 2.15-2.20 (m, 1H, -OH), 2.06-2.10 (m, 1H), 1.92-2.01 (dt, *J* = 12.8, 11.8 Hz, 1H), 1.65 (s, 3H), 1.23-1.27 (d, *J* = 6.8, 3H), 0.92 (s, 9H), 0.07 ppm (s, 6H); short distances identified by NOE: 6a-H to 8-H, 10a-H to 9-H, 10a-H to 6-CH_3,
^{13}**C NMR** (100 MHz, $CDCl_3$): δ = 207.1, 156.2, 155.6, 145.6, 142.1, 115.1, 112.0, 105.8, 105.6, 95.1, 94.7, 73.9, 64.8, 55.9, 53.3, 49.6, 43.9, 40.2, 25.8, 18.4, 18.3, 11.2, -5.3 ppm; **HRMS** (SIMS): *m*/*z* calcd for $C_{27}H_{48}NO_7Si$: 526.3195; found: 526.3185 $[M+NH_4]^+$.

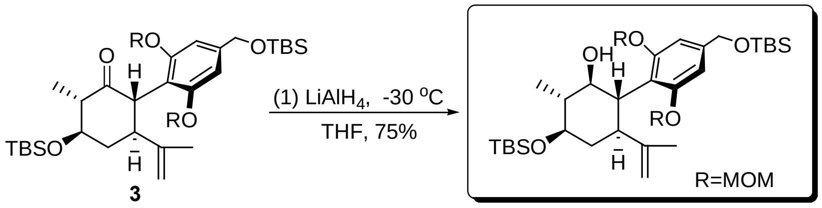
Synthesis of ketone 3



A solution of **11** (1.52 g, 3.00 mmol) and imidazole (510 mg, 7.50 mmol) in dry DMF (2 mL) was treated with TBSCl (542 mg,3.60 mmol) and stirred for 3 h at room temperature. The reaction was then diluted with ether, washed with water and brine, dried with anhydrous Na_2SO_4, and concenerated. Purification of the residue through column chromatography on silica gel (petroleum/EtOAc 50:1) afforded **3** (1.66 g, 89%). $[\alpha]^{25}_{D}$ = – 22 (*c* 1.0, $CHCl_3$); IR (film): υ_{max} 2932, 1715, 1589, 1467, 1254, 1040, 838, 776 cm^{-1};

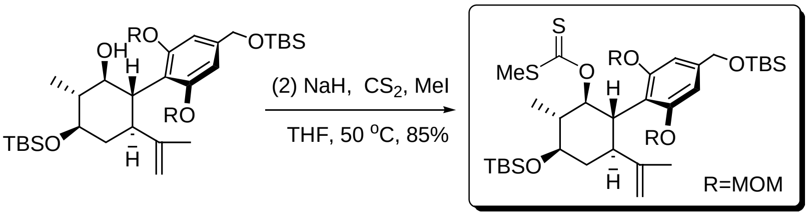
^{1}H NMR (400 MHz, $CDCl_3$): δ =6.76 (s, 2H), 5.01-5.09 (m, 4H), 4.67 (s, 2H), 4.49-4.50 (m, 2H), 4.05-4.08 (d, *J* = 11.6 Hz, 1H), 3.62-3.68 (ddd, *J* = 4, 10.4, 10.2 Hz, 1H), 3.40-3.43 (d, 6H), 3.04-3.11 ((ddd, *J* = 3.6, 12.4, 12.0 Hz, 1H), 2.40-2.44 (m, 1H), 2.04-2.09 (m, 1H), 1.93-2.02 (dt, *J* = 10.8, 11.8 Hz, 1H), 1.66 (s, 3H), 1.15-1.17 (d, *J* = 6.8 Hz, 3H), 0.93 (s, 18H), 0.11 (s, 6H), 0.07 ppm (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 207.6, 156.1, 155.8, 146.0, 142.0, 115.2, 111.8, 105.9, 105.6, 95.1, 94.8, 74.6, 64.8, 56.0, 55.9, 53.8, 49.8, 44.0, 40.9, 25.9, 25.8, 18.4, 18.0, 11.7, -4.1, -4.7, -5.3 ppm; **HRMS** (SIMS): *m*/*z* calcd for $C_{33}H_{62}NO_7Si_2$: 640.4059; found: 640.4065 $[M+NH_4]^+$.

Synthesis of compound 12



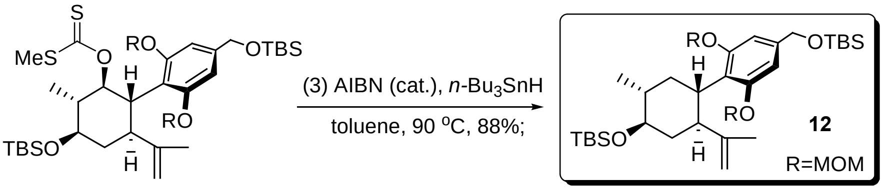
(1) The compound **3** (1.64 g, 2.64 mmol) dissolved in 20 mL of dry THF was added slowly to a slurry of $LiAlH_4$ (120 mg, 3.16 mmol) in THF at -30 °C. The reaction mixture was then stirred at this point for 1 h, at which point the reduction was complete according to TLC. H_2O (2 mL) was added carefully. The resulting slurry was filtered off and washed with EtOAc (100 mL). The combined filtrate was dried over Na_2SO_4 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel (petroleum/EtOAc 10:1) provided the alcohol (1.23 g, 75%). $[\alpha]^{25}_{D}$ = 5 (*c* 1.0, $CHCl_3$); IR (film): υ_{max} 3500 (-OH), 2930, 1586, 1440, 1041, 836, 776 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.77 (s, 1H), 6.75 (s, 1H), 5.09-5.18 (m, 4H), 4.65 (s, 2H), 4.52 (s, 1H), 4.41 (s, 1H), 3.68-3.74 (ddd, *J* = 4.4, 9.8, 10.8 Hz, 1H), 3.49 (s, 3H), 3.46 (s, 3H), 3.32-3.41 (m, 2H), 2.95-3.02 (t, *J* = 12.4, 12.4 Hz, 1H), 1.79-1.84 (m, 1H), 1.54 (s, 3H), 1.45-1.62 (m, 3H), 1.12-1.25 (d, *J* = 6.8 Hz, 3H), 0.91 (s, 18H), 0.07 ppm (m, 12, H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ =157.4, 157.0, 147.4, 142.0, 116.3, 110.5, 106.6, 106.0, 95.6, 94.6, 74.6, 74.4, 64.7, 56.2, 56.1, 48.1, 45.8, 42.8, 41.7, 25.9, 18.7, 18.3, 18.1, 15.2, -3.9, -4.6, -5.3 ppm; **HRMS** (SIMS): *m*/*z* calcd for $C_{33}H_{64}NO_7$ Si_2: 642.4216; found: 642.4225 $[M+NH_4]^+$.



(2) Under an argon atmosphere, alcohol (1.20 g, 1.92 mmol) was dissolved in dry THF (6 mL) and NaH (57% suspension in mineral oil, 243 mg, 5.77 mmol) was added at room temperature. The reaction mixture was stirred for 30 min before CS_2 (1.5 mL) was introduced into the flask and was heated to 50 °C for 2 h. Then, MeI (1.2 mL, 19.2 mmol) was added and stirring was continued for 5 h. After cooling to ambient temperature, the reaction mixture was filtered and concentrated and the resulting residue was purified by flash column chromatography on silica gel (petroleum/EtOAc 30:1) provided the xanthate ester (1.17 g, 85%). $[\alpha]_D^{25}$ = 29 (*c* 2.0, $CHCl_3$); IR (film): υ_{max} 2931, 1587, 1467, 1221, 1044, 839, 776 cm^{-1};

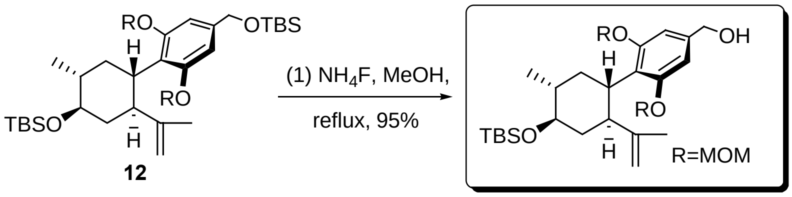
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.66(s, 2H), 6.19-6.24 (t, *J* = 10.8, 10.6 Hz, 1H), 5.09-5.17 (m, 4H), 4.61 (s, 3H), 4.47 (s, 1H), 3.63-3.68 (t, *J* = 10.4, 11.0 Hz, 1H), 3.55 (s, 3H), 3.51 (s, 3H), 3.47-3.53 (m, 1H), 3.12-3.18 (t, *J* = 12.8, 11.6 Hz, 1H), 2.32 (s, 3H), 1.84-1.90 (m, 2H), 1.60-1.66 (m, 1H), 1.58 (s, 3H), 1.01-1.03 (d, *J* = 6.8 Hz, 3H), 0.91 (s, 18H), 0.10 (s, 6H), 0.03 ppm (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 215.5, 157.4, 156.5, 146.6, 142.0, 114.4, 111.0, 105.6, 105.6, 95.3, 86.1, 74.0, 64.9, 56.1, 56.0, 47.1, 42.5, 42.4, 41.4, 25.8, 18.6, 18.5, 18.3, 18.0, 15.1, -4.0, -4.7, -5.3 ppm; **HRMS** (SIMS): *m*/*z* calcd for $C_{35}H_{66}NO_7S_2Si_2$: 732.3814; found: 732.3817 $[M+NH_4]^+$.



(3) AIBN (cat.) and *n*-Bu_3SnH (neat, 0.43 mL, 16.10 mmol) were sequentially added under an argon atmosphere at room temperature to a solution of the xanthate ester (1.15 g, 1.61 mmol) in dry toluene (2 mL). The mixture was carefully deoxygenated by bubbling argon through it for 30 min. The reaction flask was then immersed into a preheated oil bath (90 °C) and the mixture was stirred at this temperature for 30 min. After cooling to ambient temperature, the solvent was evaporated and the resulting residue was purified by flash column chromatography on silica gel (petroleum/EtOAc 30:1) provided **12** (862 mg, 88%). $[\alpha]_D^{25}$ = –2 (*c* 1.0, $CHCl_3$); IR (film): υ_{max} 2930, 1585, 1466, 1253, 1043, 837, 775 cm^{-1};

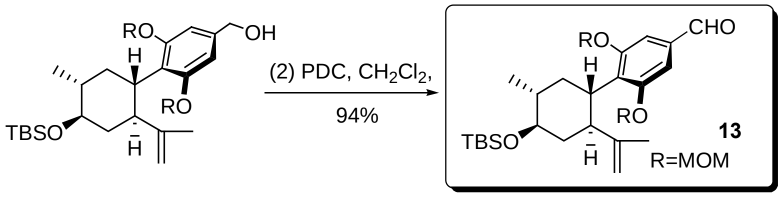
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.76 (s, 1H), 6.73 (s, 1H), 5.10-5.19 (m, 4H), 4.65 (s, 2H), 4.55 (s, 1H), 4.42 (s, 1H), 3.52 (s, 3H), 3.47 (s, 3H), 3.28-3.39 (m, 2H), 3.02-3.09 (t, *J* = 12.4, 11.6 Hz, 1H), 1.83-1.88 (m, 1H), 1.72-1.78 (dt, *J* = 12.4, 12.6 Hz, 1H), 1.49-1.61 (m, 6H), 0.92-0.99 (m, 21H), 0.09-0.10 ppm (m, 12H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ =157.1, 155.5, 148.6, 140.7, 120.6, 109.9, 106.1, 106.0, 95.3, 94.5, 77.1, 64.8, 55.9, 46.3, 42.3, 40.9, 37.8, 37.5, 25.9, 19.1, 18.9, 18.3, 18.1, -3.9, -4.6, -5.3 ppm; **HRMS** (SIMS): *m*/*z* calcd for $C_{33}H_{64}NO_6Si_2$: 626.4267; found: 626.4257 [M+NH_4]$^+$.

Synthesis of aldehyde 13



(1) To a solution of **12** (830 mg, 1.36 mmol) in MeOH (10 mL) was added NH_4F (76 mg, 2.04 mmol), and the mixture was heated under refluxing for 5 h. The methanol was removed in vacuo, water (10 mL) was added, and the resulting mixture was extracted with EtOAc (3×20 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the residue through column chromatography on silica gel (petroleum/EtOAc 5:1) afforded the primary alcohol (640 mg, 95%). $[\alpha]_D^{25}$ = – 5 (*c* 1.0, $CHCl_3$); IR (film): υ_{max} 3411 (-OH), 2930, 1584, 1437, 1252, 1043, 836, 774 cm^{-1};

^{1}**H NMR** (400 MHz, $CDCl_3$): δ = 6.76 (s, 1H), 6.74 (s, 1H), 5.10-5.21 (m, 4H), 4.54-4.57 (m, 3H), 4.42 (s, 1H), 3.52 (s, 3H), 3.46 (s, 3H), 3.27-3.40 (m, 2H), 3.02-3.08 (t, *J* = 12.0, 11.6 Hz, 1H), 2.00-2.03 (m, 1H, -OH), 1.82-1.86 (m, 1H), 1.71-1.80 (dt, *J* = 12.4, 12.4 Hz, 1H), 1.48-1.58 (m, 6H), 0.94-0.96 (d, *J* = 6.0 Hz, 3H), 0.91 (s, 9H), 0.09 ppm (s, 6H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ = 157.3, 155.6, 148.6, 140.1, 121.3, 109.9, 106.8, 106.7, 95.1, 94.4, 77.0, 65.3, 56.1, 46.3, 42.3, 40.8, 37.7, 37.3, 25.9, 19.1, 18.8, 18.1, -4.0, -4.6 ppm; **HRMS** (SIMS): *m*/*z* calcd for $C_{27}H_{50}NO_6Si$: 512.3402; found: 512.3406[M+NH_4]$^+$.

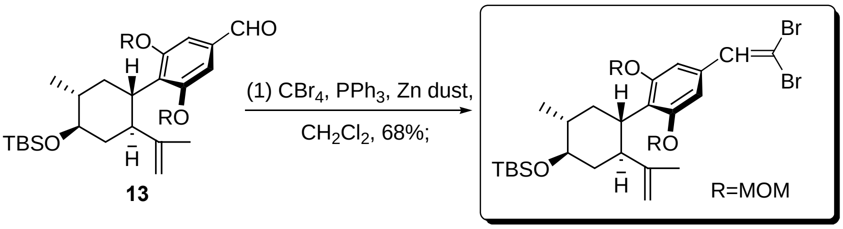


(2) To a a solution of the alcohol (610 mg, 1.23 mmol) in CH_2Cl_2 (10 mL) was added PDC (925 mg, 2.46 mmol) and neutral Al_2O_3 (1 g). The mixture was stirred for 3 h. Then, the reaction mixture was filtered through a neutral Al_2O_3 column, and washed with ether (100 mL). The combined organic solution was concentrated *in vacuo* and the residue was purified

through column chromatography on silica gel (petroleum/EtOAc 20:1) to give the aldehyde **13** (571 mg, 94%). [α]$^{25}_{D}$ = – 1 (*c* 0.9, $CHCl_3$); IR (film): υ_{max} 2929, 1699, 1582, 1438, 1290, 1043, 836, 774 cm^{-1};

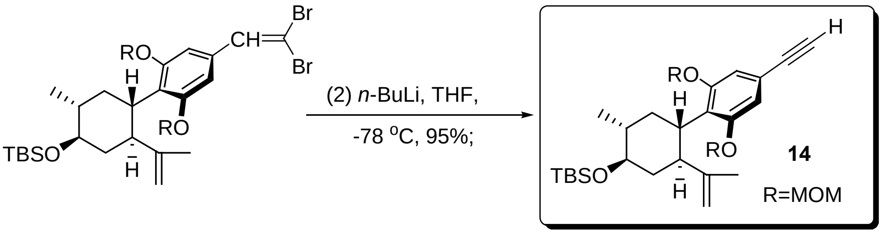
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.83 (s, 1H, -CHO), 7.26-7.28 (d, 2H), 5.18-5.28 (m, 4H), 4.53 (s, 1H), 4.42 (s, 1H), 3.54 (s, 3H), 3.49 (s, 3H), 3.42-3.49 (m, 1H), 3.28-3.34 (m, 1H), 3.05-3.12 (t, *J* = 12.4, 11.6 Hz, 1H), 1.84-1.89 (m, 1H), 1.74-1.83 (dt, *J* = 12.4, 12.4 Hz, 1H), 1.48-1.61 (m, 6H), 0.96-0.97 (d, *J* = 6.8 Hz, 3H), 0.93 (s, 9H), 0.09 ppm (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 191.6, 157.6, 156.0, 148.0, 135.6, 129.5, 110.2, 109.2, 109.1, 95.1, 94.6, 76.8, 56.3, 56.3, 46.1, 42.1, 40.7, 38.4, 36.7, 25.9, 19.0, 18.8, 18.1, -4.0, -4.6 ppm; **HRMS** (SIMS): *m*/*z* calcd for $C_{27}H_{48}NO_6Si$: 510.3245; found: 510.3238 $[M+NH_4]^+$.

Synthesis of alkyne 14



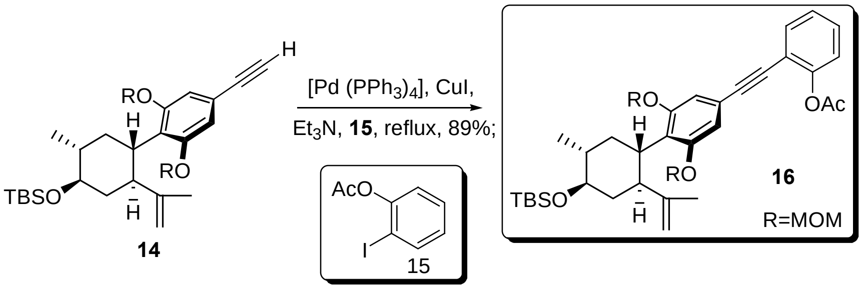
(1) Zinc dust (428 mg, 6.59 mmol) and PPh_3 (1.73 g, 6.59 mmol) were added to CH_2Cl_2 (10 mL) at 0 °C. The mixture was stirred for 5 min followed by the addition of CBr_4 (2.18 g, 6.59 mmol). The reaction mixture was then stirred for 3 h at room temperature followed by addition of aldehyde **13** (540 mg, 1.10 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred for 5 min and then quenched with saturated aqueous $NaHCO_3$ (10 mL). This was diluted with saturated aqueous $NaHCO_3$ (100 mL) and extracted with CH_2Cl_2 (3×50 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the residue through column chromatography on silica gel (petroleum/EtOAc 50:1) afforded the homologated dibromoalkene (482 mg, 68%). [α]$^{25}_{D}$ = – 1 (*c* 0.9, $CHCl_3$)
IR (film): υ_{max} 2929, 1568, 1251, 1082, 1042, 835, 773 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (s, 1H), 7.02 (s, 1H), 7.00 (s, 1H), 5.11-5.20 (m, 4H), 4.54 (s, 1H), 4.44 (s, 1H), 3.53 (s, 3H), 3.47 (s, 3H), 3.28-3.40 (m, 2H), 3.04-3.47 (t, *J* = 12.4, 11.2 Hz, 1H), 1.83-1.87 (m, 1H), 1.73-1.77 (dt, *J* = 12.0, 12.0 Hz, 1H), 1.51-1.60 (m, 6H), 0.95-0.96 (d, *J* = 6.8 Hz, 3H), 0.91 (s, 9H), 0.10 ppm (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 157.0, 155.5, 148.4, 136.7, 133.9, 123.2, 110.0, 108.6, 95.4, 94.7, 88.7, 77.2, 56.1, 46.3, 42.3, 40.8, 38.1, 37.2, 25.9, 19.1, 18.9, 18.1, -3.9, -4.6 ppm; **HRMS** (SIMS): *m*/*z* calcd for $C_{28}H_{45}Br_2O_5Si$: 647.1398; found: 647.1383 $[M+H]^+$.



(2) To a a solution of the dibromoalkene (450 mg, 0.70 mmol) in THF (10 mL) was added sequentially *n*-BuLi (2.0 *M* in hexane, 1.1 mL, 2.09 mmol) at –78 °C. The mixture was stirred for 1 h at this point and then stirred for another 1 h at room temperature, quenched with H_2O, diluted with ether (100 mL), washed with aqueous NH_4Cl and NaCl, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the residue through column chromatography on silica gel (petroleum/EtOAc 50:1) afforded the alkene **14** (323 mg, 95%). $[\alpha]_D^{25}$ = 5 (*c* 0.8, $CHCl_3$); IR (film): υ_{max} 3307, 2929, 1566, 1252, 1083, 1043, 835, 774 cm^{-1}; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ = 6.92 (s, 1H), 6.89 (s, 1H), 5.09-5.19 (m, 4H), 4.52 (s, 1H), 4.13 (s, 1H), 3.52 (s, 3H), 3.46 (s, 3H), 3.26-3.41 (m, 2H), 2.99-3.05 (m, 2H), 1.82-1.87 (m, 1H), 1.69-1.79 (dt, *J* = 12.4, 12.4 Hz, 1H), 1.47-1.58 (m, 6H), 0.94-0.96 (d, *J* = 6.0 Hz, 3H), 0.91 (s, 9H), 0.08 ppm (s, 6H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ = 156.9, 155.4, 148.3, 124.1, 120.4, 112.2, 112.1, 110.1, 95.3, 94.7, 83.7, 76.4, 56.1, 46.3, 42.3, 40.8, 38.0, 37.1, 25.9, 19.1, 18.9, 18.1, -3.9, -4.6 ppm; **HRMS** (SIMS): *m*/*z* calcd for $C_{28}H_{45}O_5Si$: 489.3031; found: 489.3025 $[M+H]^+$.

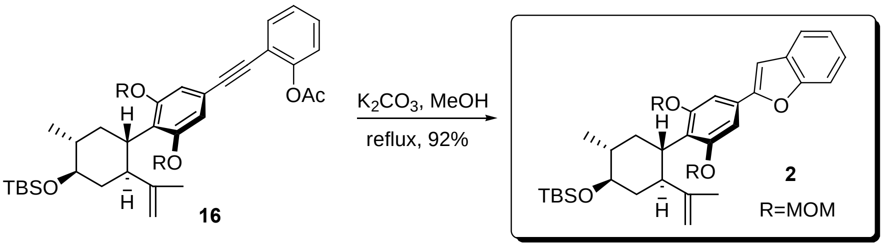
Synthesis of 16



A mixture of alkene **14** (300 mg, 0.61 mmol), Ac-protected *o*-iodophenol **15** (245 mg, 0.92 mmol), $Pd(PPh_3)_4$ (13 mg, 0.01 mmol), CuI (3 mg, 0.01 mmol), and Et_3N (4 mL) was degassed via five freeze-thaw cycles, warmed to refluxing , and stirred for 10 h. After removal of the solvent in vacuo. Purification of the residue through column chromatography on silica gel (petroleum/EtOAc 20:1) afforded **16** (340 mg, 89%). $[\alpha]_D^{25}$ = 4 (*c* 0.5, $CHCl_3$); IR (film): υ_{max} 2929, 1786, 1564, 1370, 1247, 1082, 1041, 836, 774 cm^{-1};

^{1}**H NMR** (400 MHz, $CDCl_3$): δ = 7.52-7.55 (d, 1H), 7.31-7.36 (t, 1H), 7.19-7.25 (t, 1H), 7.09-7.11 (d, 1H), 6.91-6.94 (d, 2H), 5.11-5.20 (m, 4H), 4.54 (s, 1H), 4.44 (s, 1H), 3.52 (s, 3H), 3.47 (s, 3H), 3.27-3.41 (m, 2H), 3.00-3.06 (t, *J* = 12.0, 13.2 Hz, 1H), 1H), 2.38 (s, 3H), 1.82-1.87 (m, 1H), 1.70-1.80(dt, *J* = 12.4, 12.6 Hz, 1H), 1.48-1.62 (m, 6H), 0.95-0.97 (d, *J* = 5.6 Hz, 3H), 0.91 (s, 9H), 0.09 ppm (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.9, 157.1, 155.5, 151.6, 148.3, 132.8, 129.3, 125.9, 123.8, 122.2, 121.3, 117.5, 111.6, 110.1, 95.3, 94.7, 94.5, 83.6, 77.0, 56.1, 46.4, 42.3, 40.8, 38.0, 37.2, 25.9, 20.7, 19.1, 18.9, 18.1, -3.9, -4.6 ppm; **HRMS** (SIMS): *m*/*z* calcd for $C_{36}H_{54}NO_7Si$: 640.3664; found: 640.3657 $[M{+}NH_4]^+$.

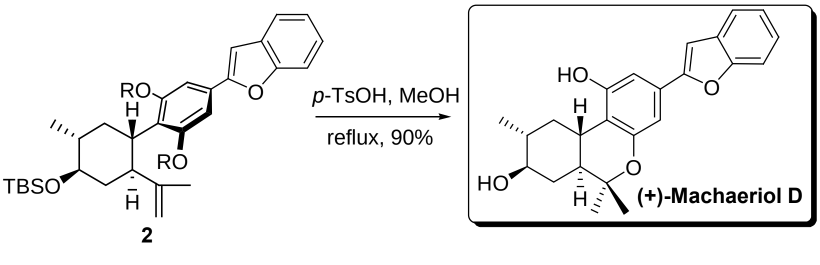
Synthesis of 5,6-*seco*-HHDBP's benzofuran 2



To a solution of **16** (300 mg, 0.48 mmol) in MeOH (5 mL) was added K_2CO_3 (133 mg, 0.96 mmol), and the mixture was heated under refluxing for 12 h. The methanol was removed in vacuo, water (10 mL) was added, and the resulting mixture was extracted with EtOAc (3×20 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the residue through column chromatography on silica gel (petroleum/EtOAc 50:1) afforded **2** (257 mg, 92%). $[\alpha]_D^{25} = -1$ (*c* 1.4, $CHCl_3$); IR (film): υ_{max} 3433, 2927, 1561, 1453, 1252, 1079, 1035, 858, 772 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51-7.56 (m, 2H), 7.19-7.29 (m, 4H), 7.00 (s, 1H), 5.22-5.33 (m, 4H), 4.59 (s, 1H), 4.47 (s, 1H), 3.59 (s, 3H), 3.54 (s, 3H), 3.40-3.50 (t, *J* = 11.6, 12.0 Hz, 1H), 3.31-3.37 (ddd, *J* = 4.0, 10.0, 10.0 Hz, 1H), 3.06-3.13 (t, *J* = 12.4, 13.4 Hz, 1H), 1.87-1.91 (m, 1H), 1.77-1.86 (dt, *J* = 12.8, 13.6 Hz, 1H), 1.52-1.65 (m, 6H), 0.98-1.00 (d, *J* = 6.0 Hz, 3H), 0.94 (s, 9H), 0.12 ppm (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 157.5, 155.9, 155.8, 154.7, 148.4, 129.4, 129.2, 124.1, 122.8, 120.7, 111.2, 110.1, 104.9, 101.3, 95.3, 94.7, 77.0, 56.2, 46.4, 42.3, 40.8, 38.0, 37.3, 25.9, 19.1, 18.9, 18.1, -3.9, -4.6 ppm; **HRMS** (SIMS): *m*/*z* calcd for $C_{34}H_{48}O_6SiNa$:603.3112; found: 603.3123 $[M{+}Na]^+$.

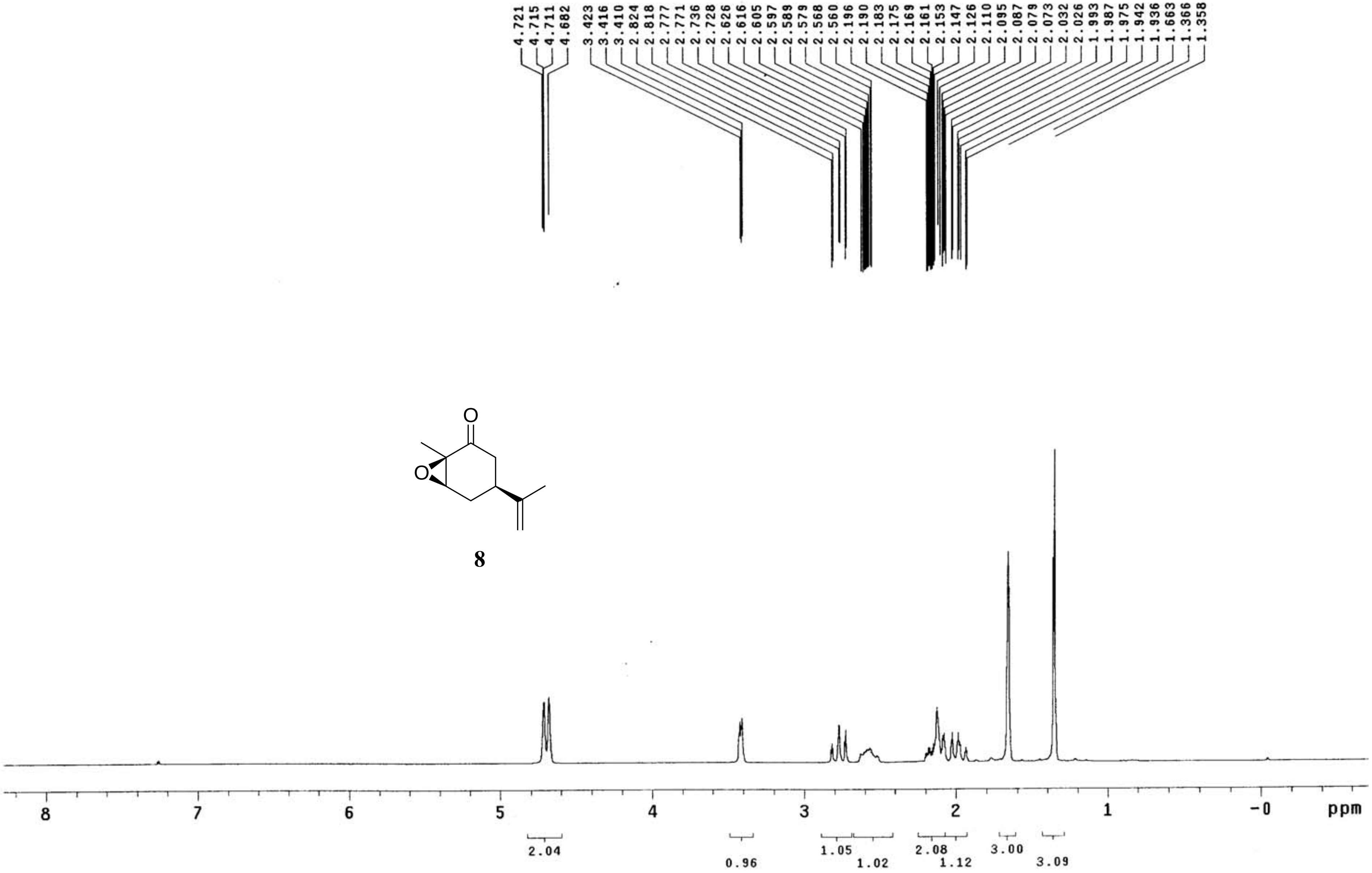
Synthesis of (+)-Macheriol D



To a solution of **2** (100 mg, 0.17 mmol) in MeOH (5 mL) was added *p*-TsOH (59 mg, 0.34 mmol), and the mixture was heated under refluxing for 12 h. The methanol was removed in vacuo, water (10 mL) was added, and the resulting mixture was extracted with EtOAc (3×20 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the residue through column chromatography on silica gel (petroleum/EtOAc 3:1) afforded (+)-Macheriol D (59 mg, 90%). $[\alpha]_D^{25}$ = 107 (*c* 0.4, MeOH) {lit.[1b] $[\alpha]_D^{25}$ = 80.2 (*c* 0.347, MeOH)}; IR (KBr): υ_{max} 3523, 3258, 2924, 2865, 1621, 1564, 1452, 1248, 1133, 965, 749 cm^{-1};

^{1}H NMR (400 MHz, DMSO-d_6): δ =9.78 (s, 1H, Ar-OH), 7.58-7.63 (m, 2H), 7.23-7.32 (m, 3H), 6.90 (s, 1H), 6.77 (s, 1H), 4.66-4.67 (d, *J* = 3.6 Hz, 1H, -OH), 3.10-3.17 (m, 2H), 2.37-2.43 (t, *J* = 11.2, 10.4 Hz, 1H), 1.96-1.99 (m, 1H), 1.43-1.52 (m, 2H), 1.35 (s, 3H), 1.10 (s, 3H), 0.98-0.99 (d, *J* = 6.0 Hz, 3H), 0.66-0.75 ppm (dt, *J* = 12.0, 12.6 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 157.3, 155.3, 154.9, 154.0, 128.8, 128.5, 124.2, 123.1, 120.9, 113.2, 110.9, 104.6, 103.4, 101.2, 76.5, 74.7, 47.0, 39.7, 37.0, 36.1, 35.0, 27.4, 18.9, 18.8 ppm; **MS** (70 eV): *m*/*z* (%): 378 (M^+), 345, 317, 279, 239,165, 43(100); **HRMS** (SIMS): *m*/*z* calcd for $C_{24}H_{27}O_4$: 379.1904; found: 379.1899 $[M+H]^+$.

2. Copies of NMR Spectra of the Products



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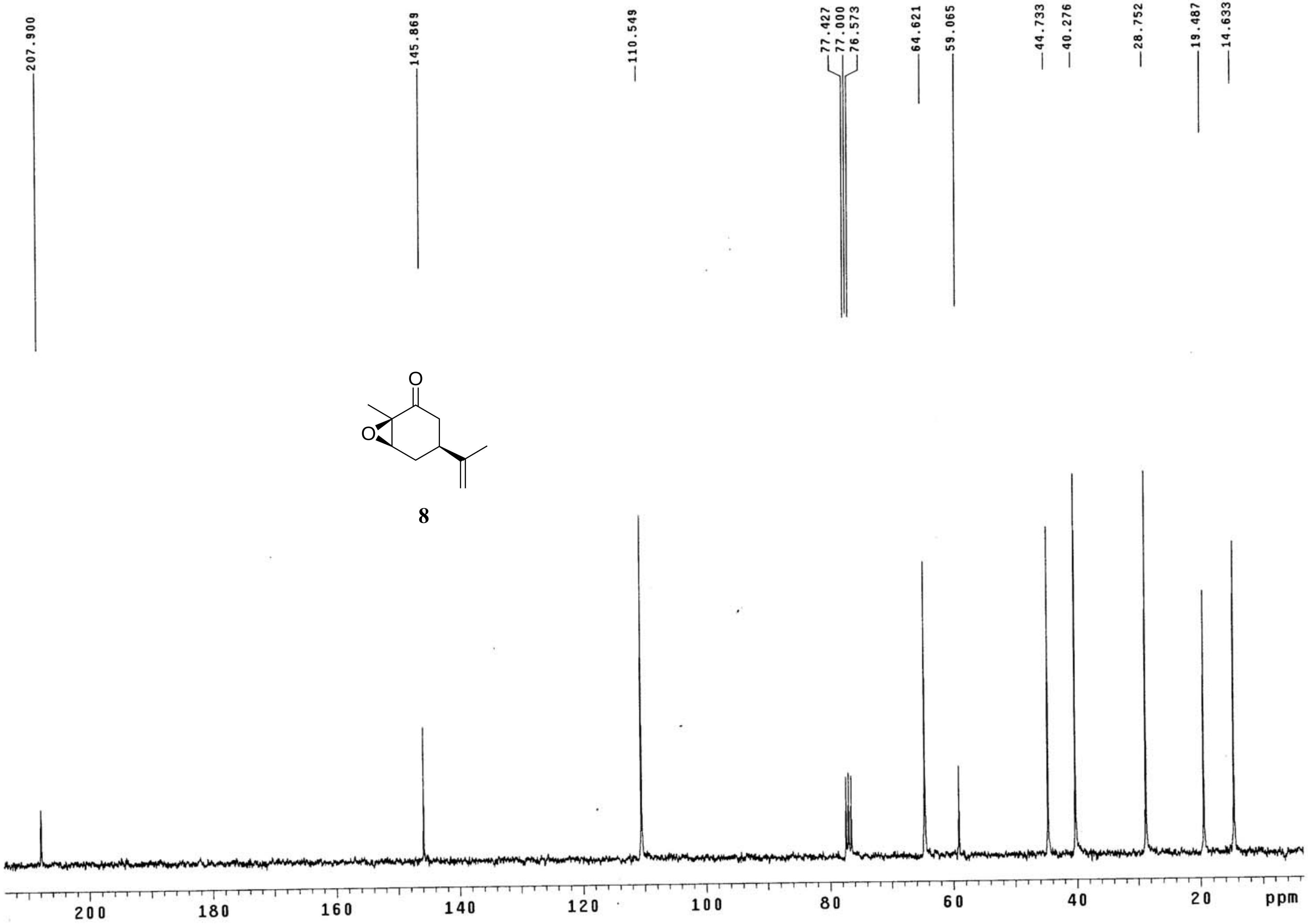
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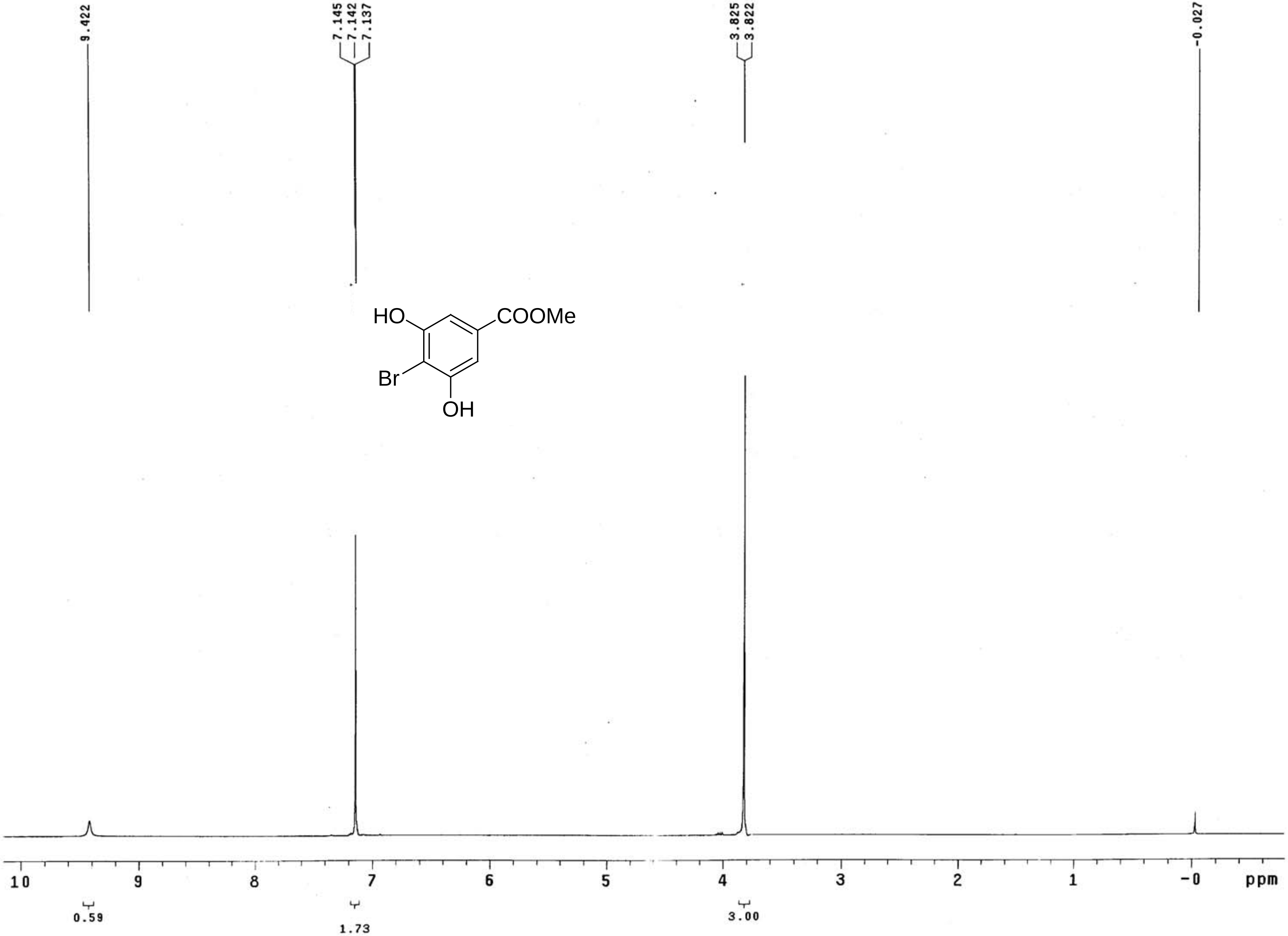
8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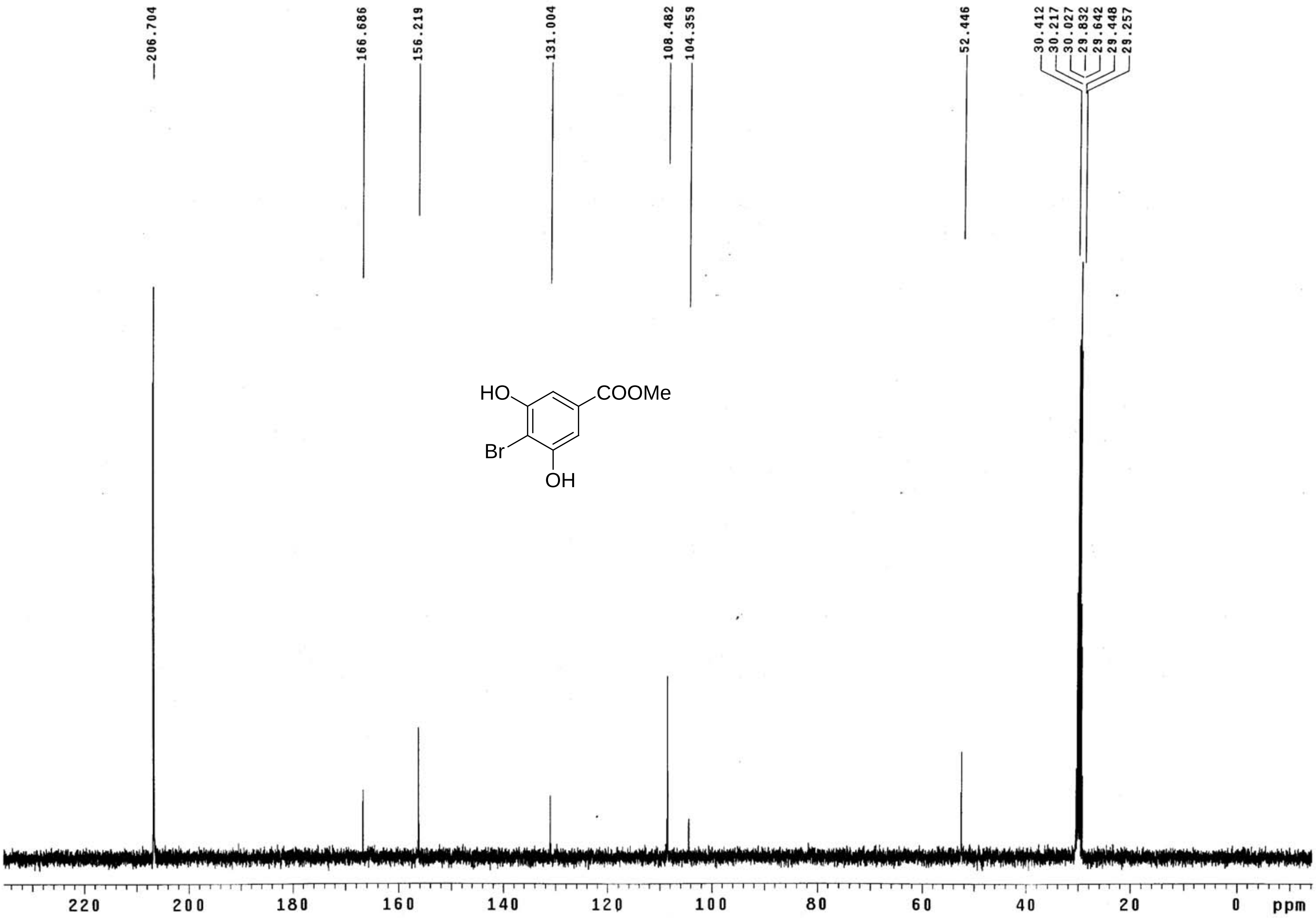
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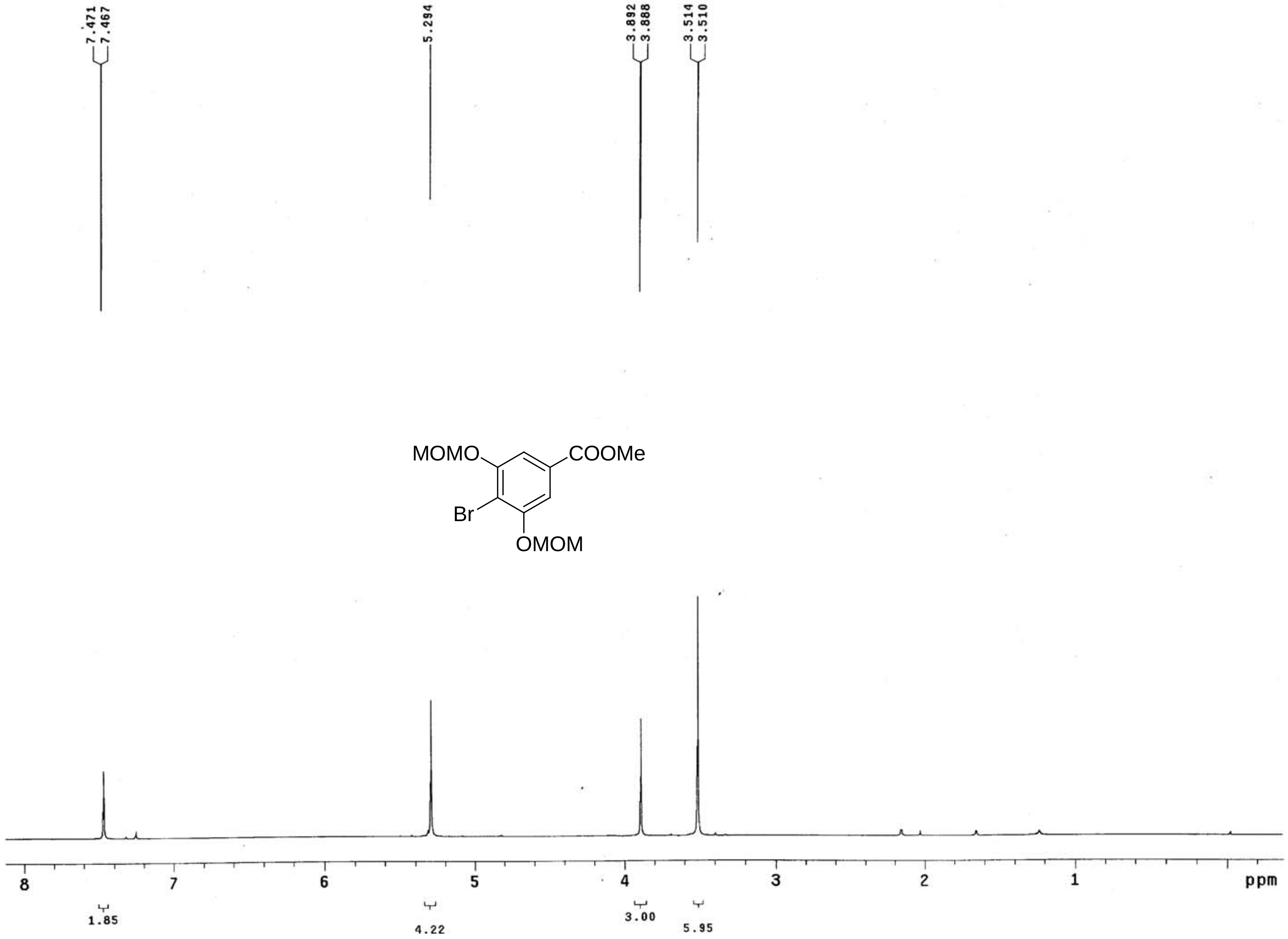
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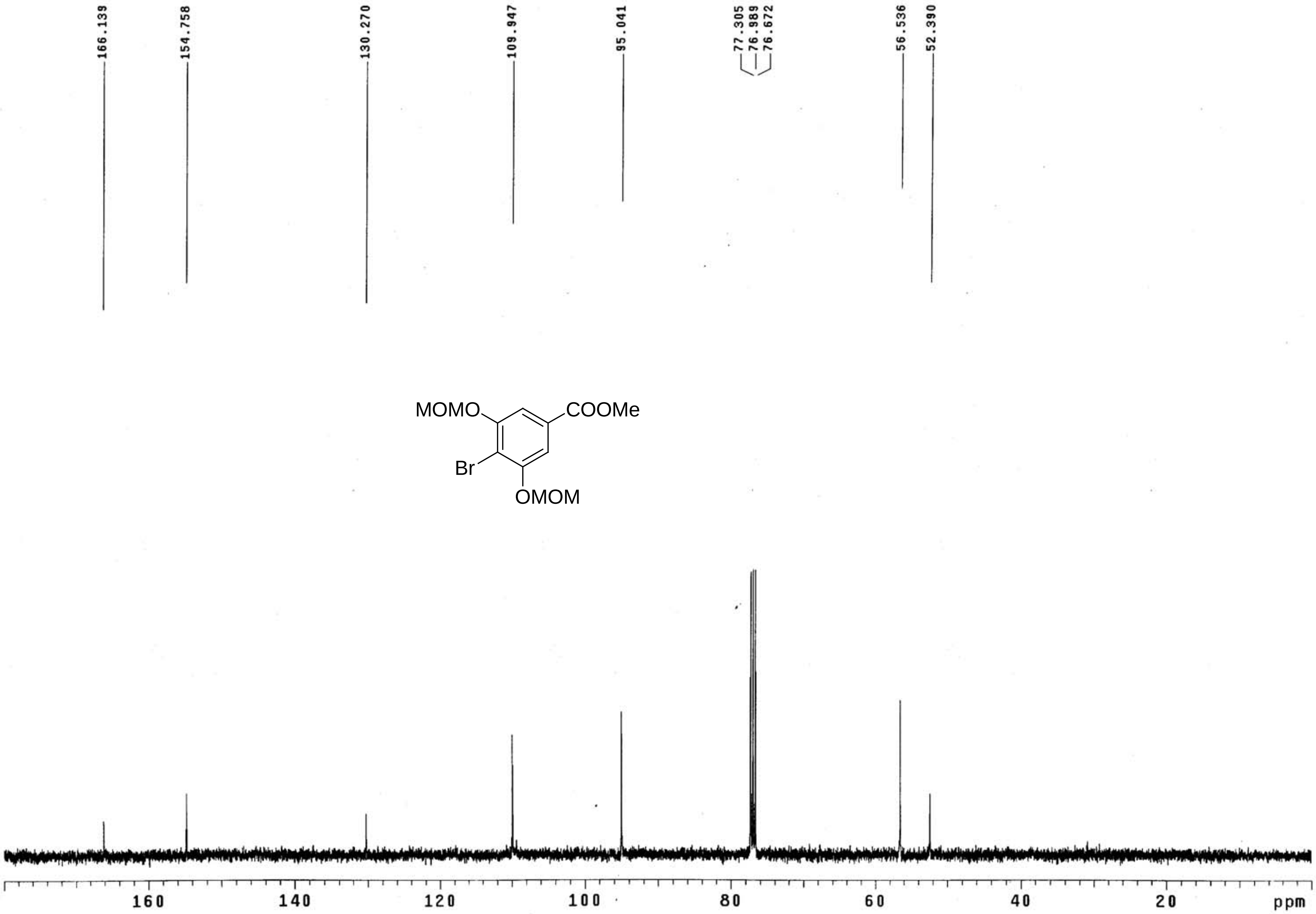
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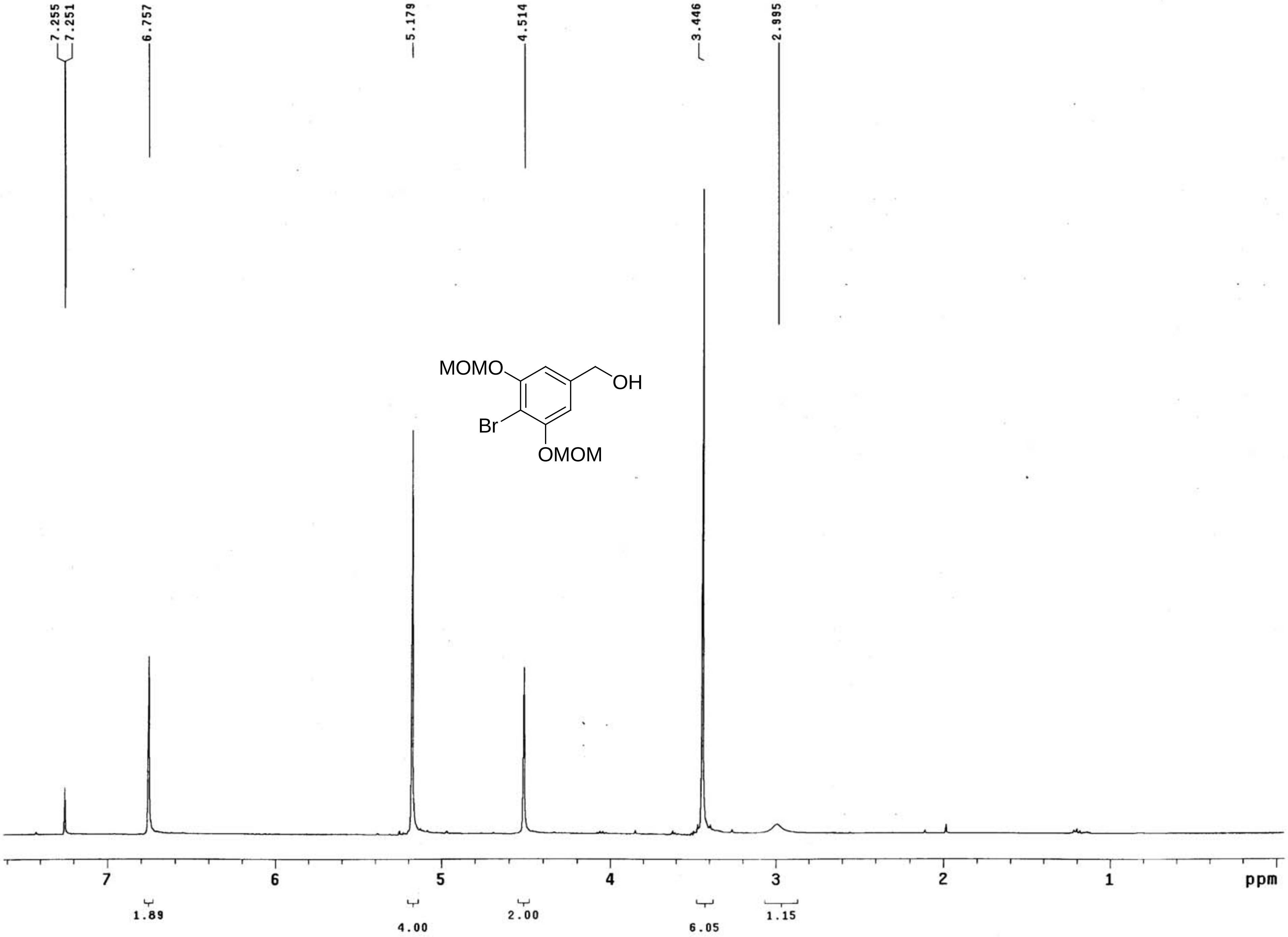
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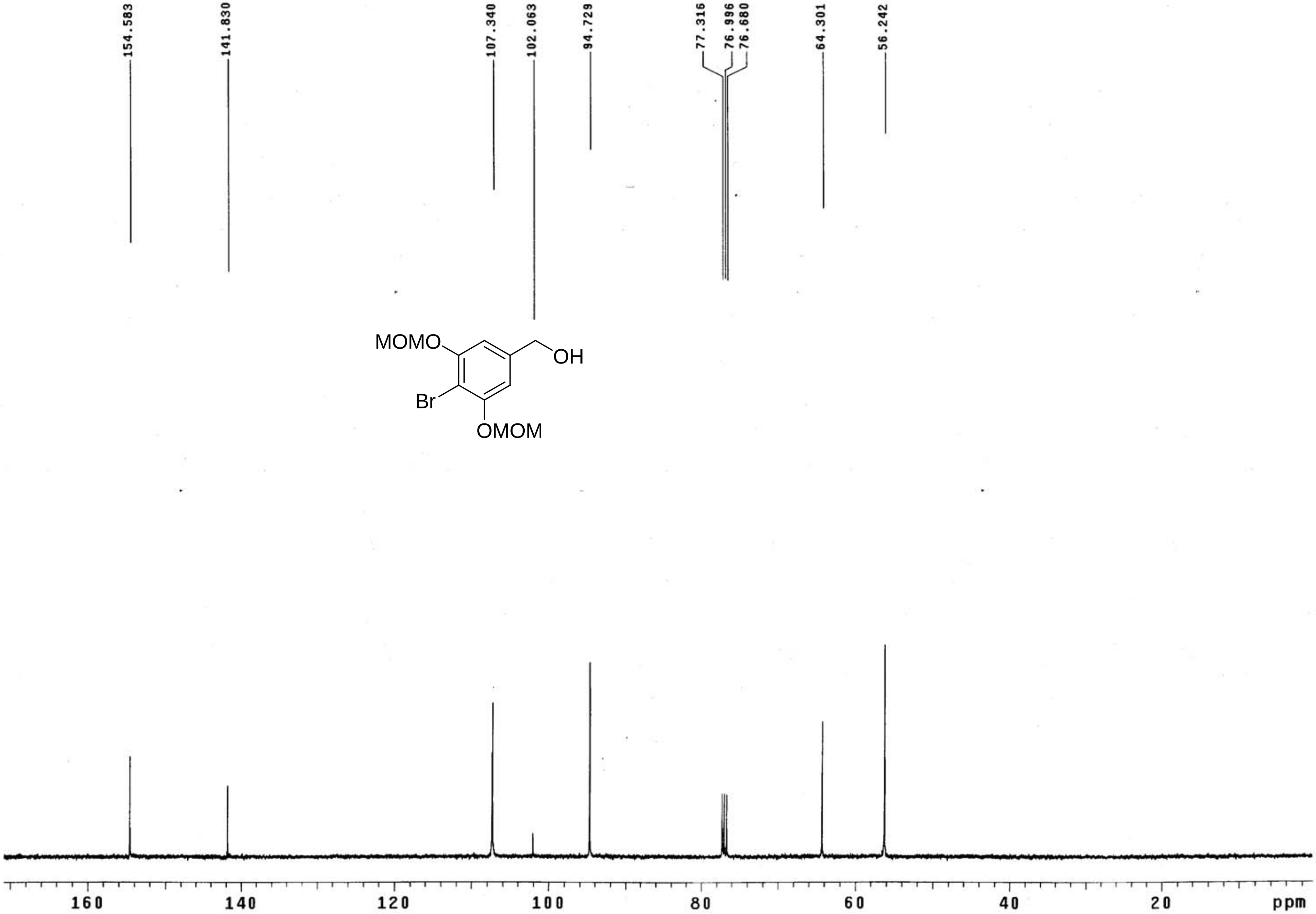
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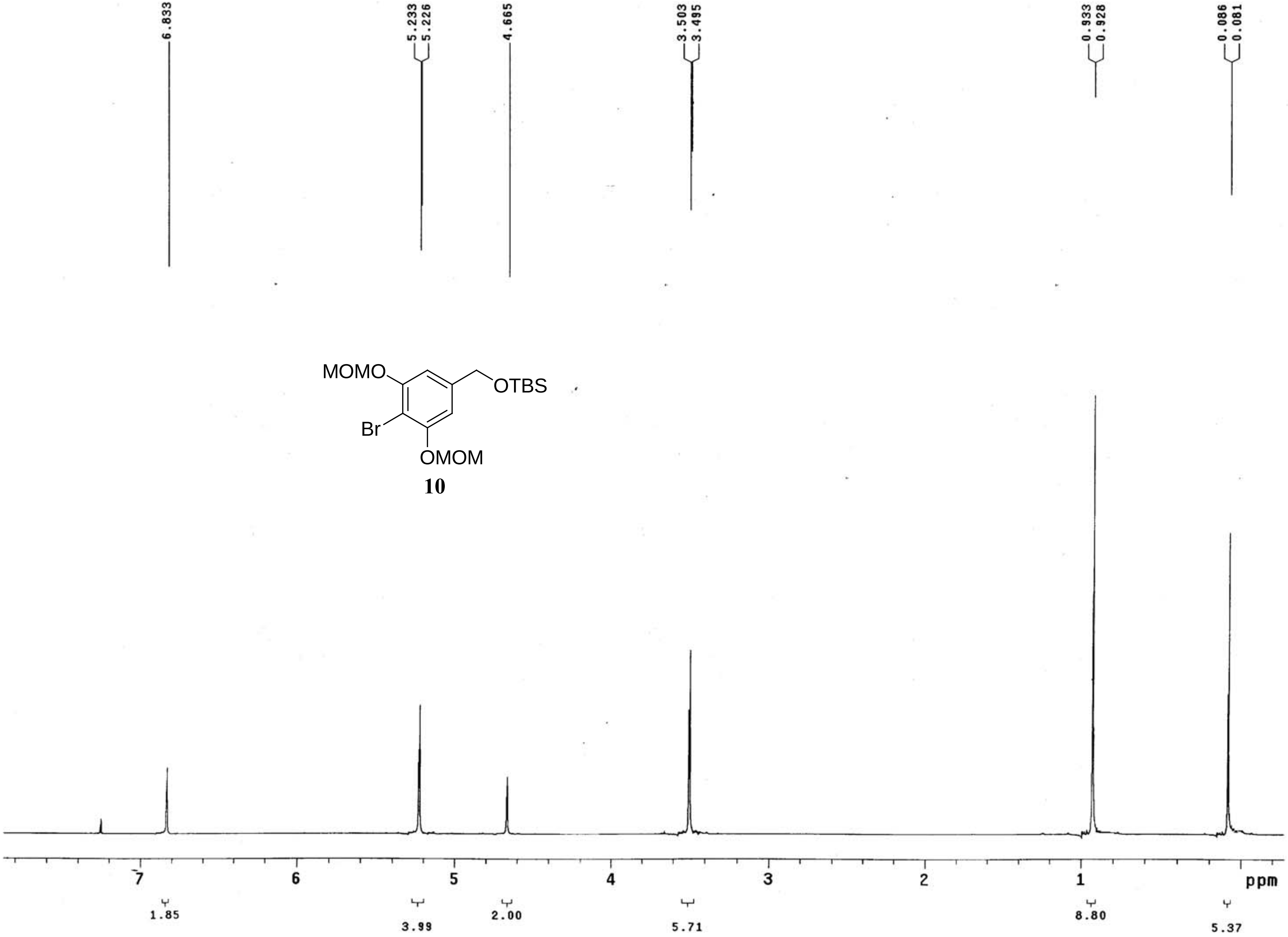
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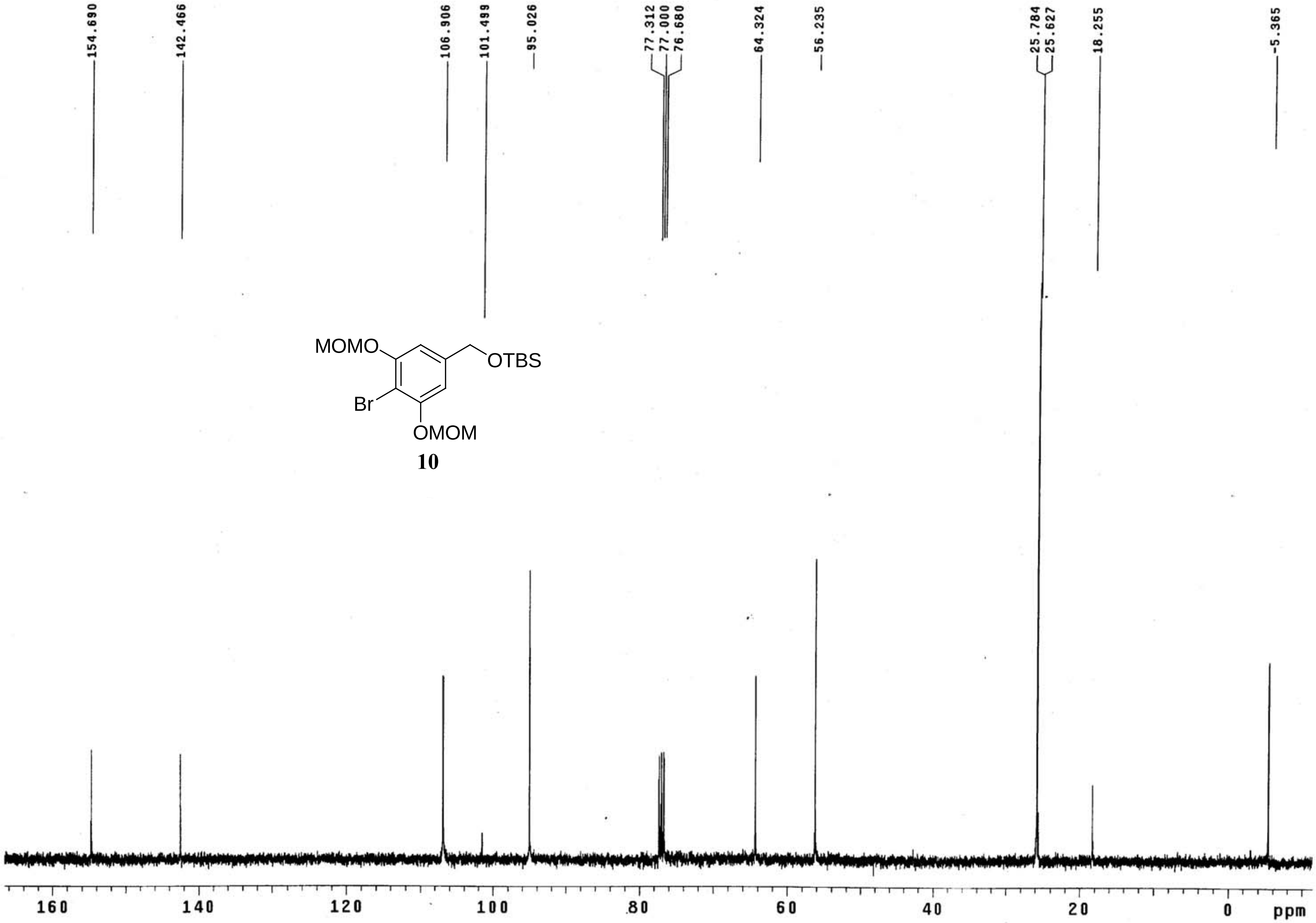
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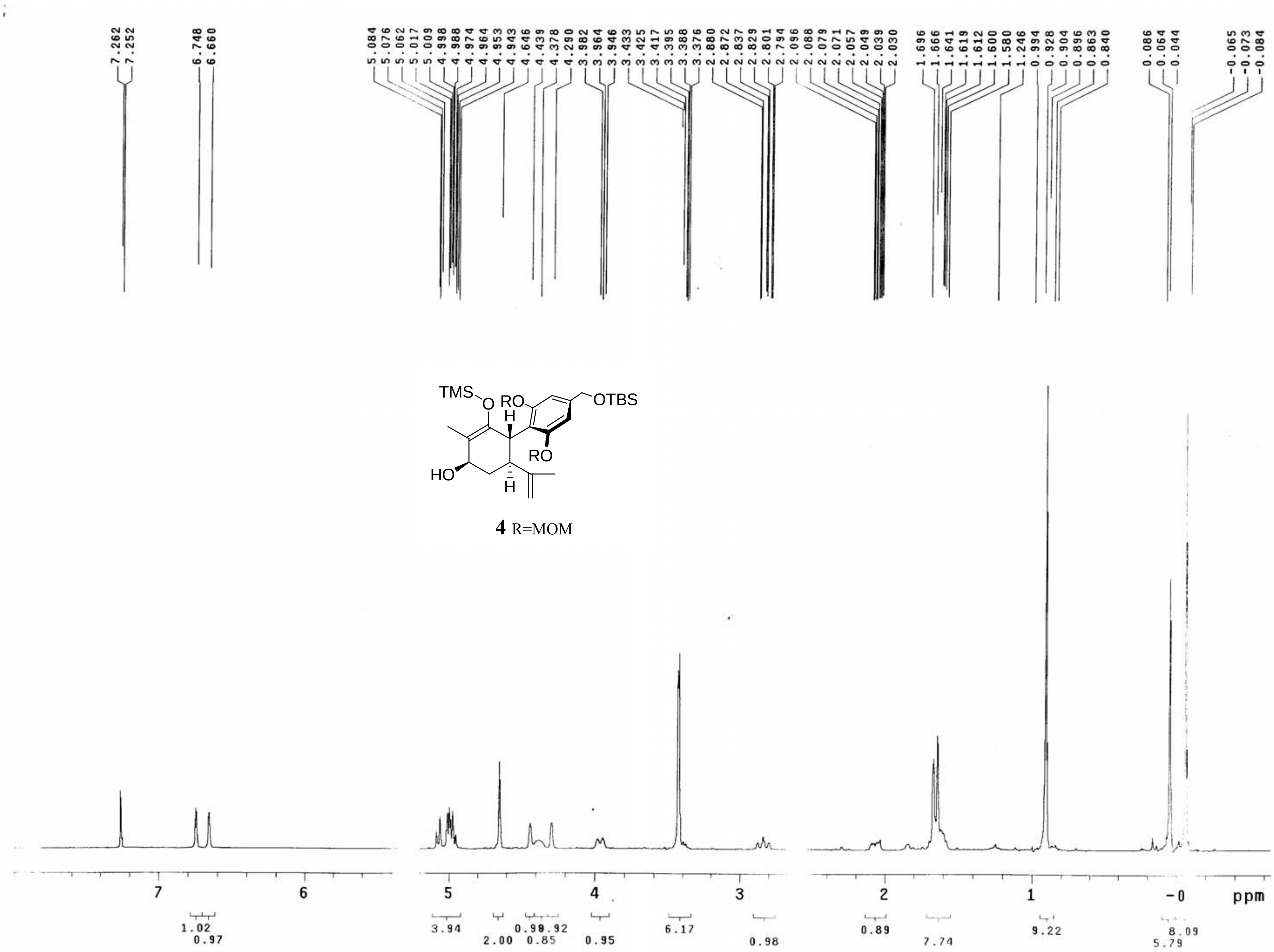

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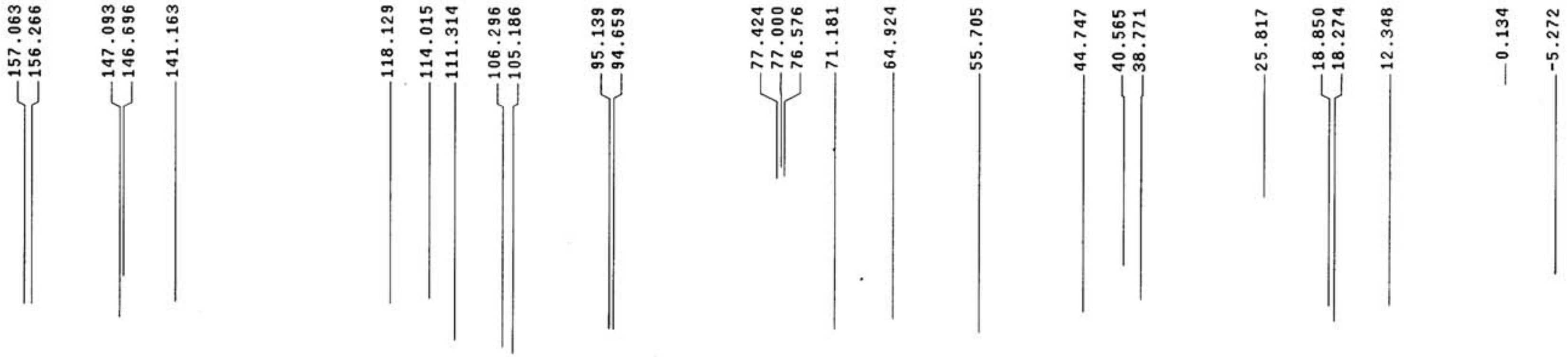
0.95
6.17
0.98
0.89
7.74
9.22
8.09
5.79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156.266
147.093
146.696
141.163
118.129
114.015
111.314
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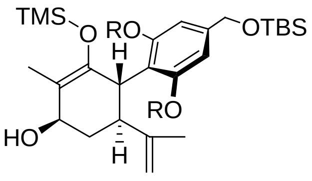
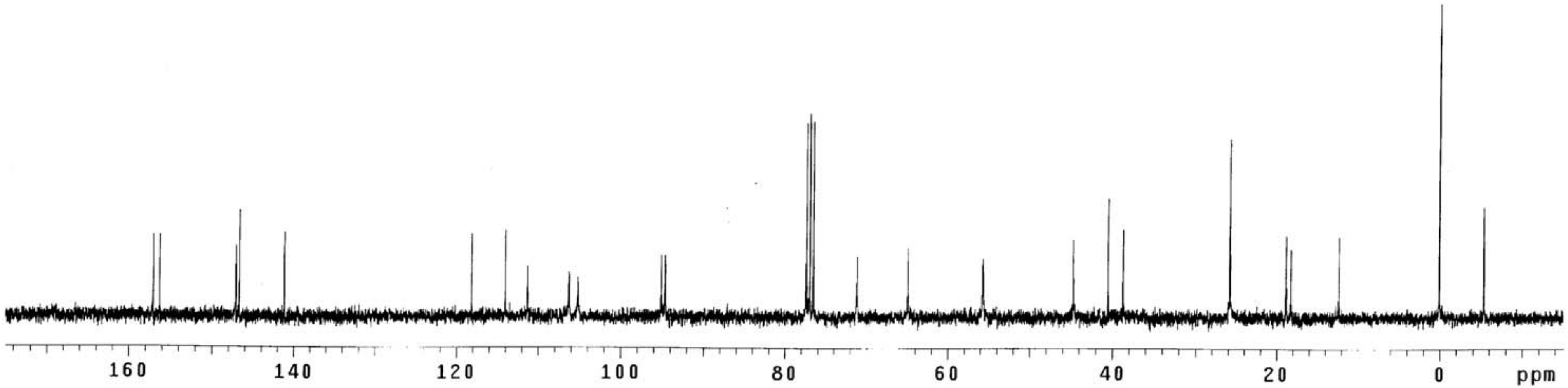
105.186
95.139
94.659
77.424
77.000
76.576
71.181
64.924
55.705
44.747
40.565
38.771
25.817
18.850
18.274
12.348
0.134
-5.272


TMS
O
RO
H
OTBS
RO
HO
H

4 R=MOM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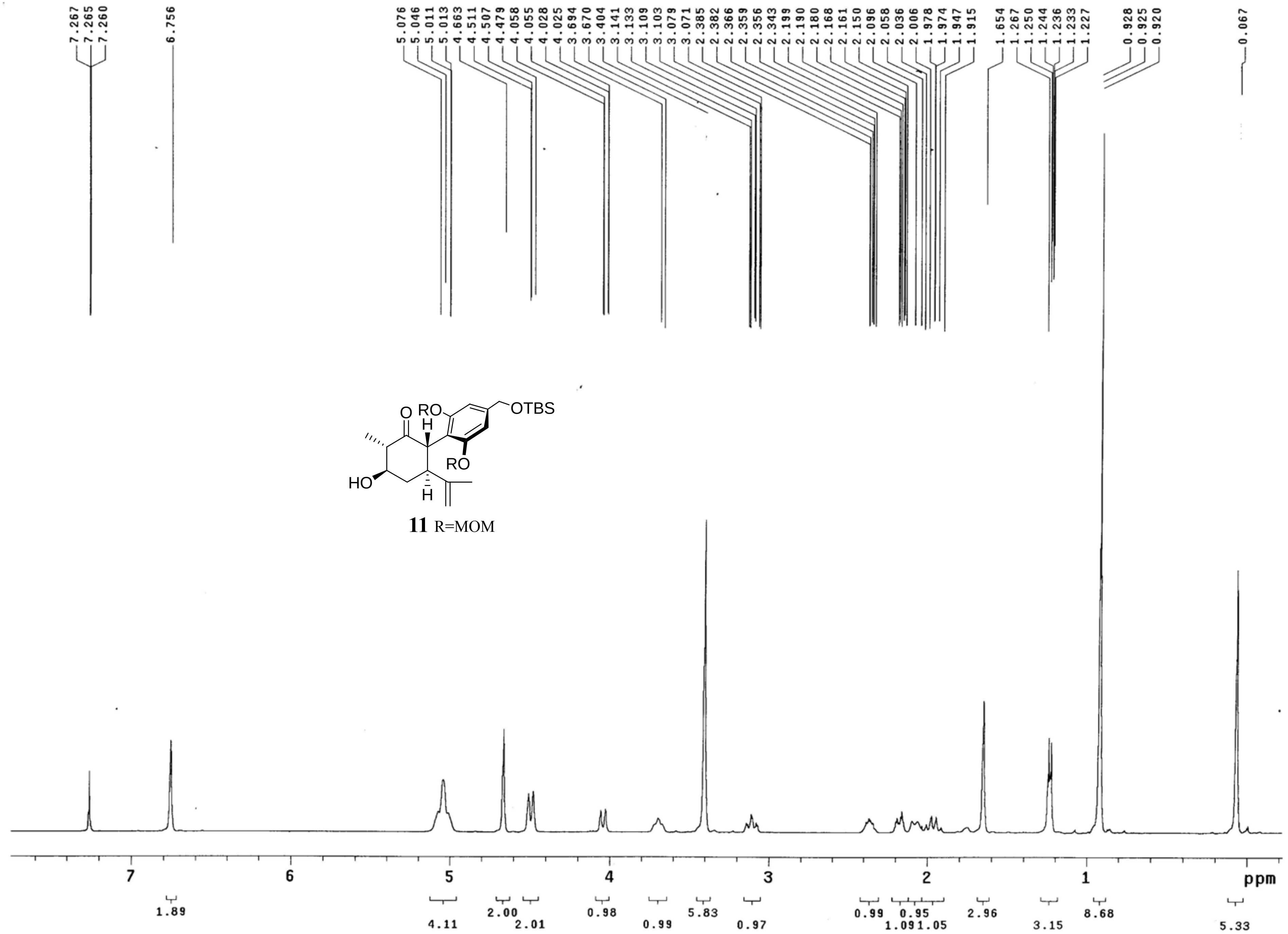
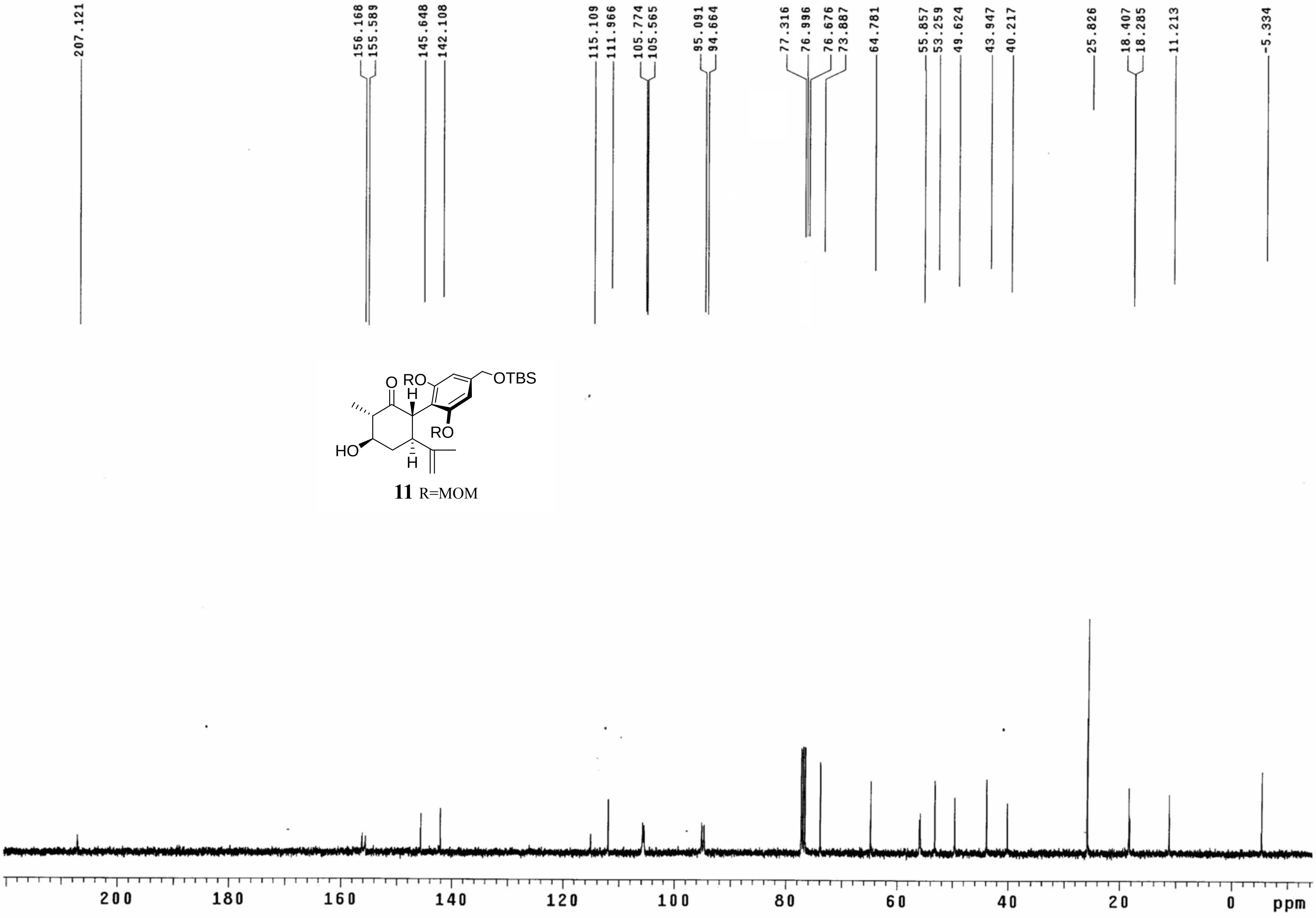
140
120
100
80
60
40
20
0
ppm



11 R=MOM

7.267
7.265
7.260
6.756
5.076
5.046
5.011
5.013
4.663
4.511
4.507
4.479
4.058
4.055
4.028
4.025
3.694
3.670
3.404
3.141
3.133
3.109
3.103
3.079
3.071
2.385
2.382
2.366
2.359
2.356
2.343
2.199
2.190
2.180
2.168
2.161
2.150
2.096
2.058
2.036
2.006
1.978
1.974
1.947
1.915
1.654
1.267
1.250
1.244
1.236
1.233
1.227
0.928
0.925
0.920
0.067
O
RO
H
OTBS
RO
HO
H
7
6
5
4
3
2
1
ppm
1.89
4.11
2.00
2.01
0.98
0.99
5.83
0.97
0.99
1.09
0.95
1.05
2.96
3.15
8.68
5.33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156.168
155.589
145.648
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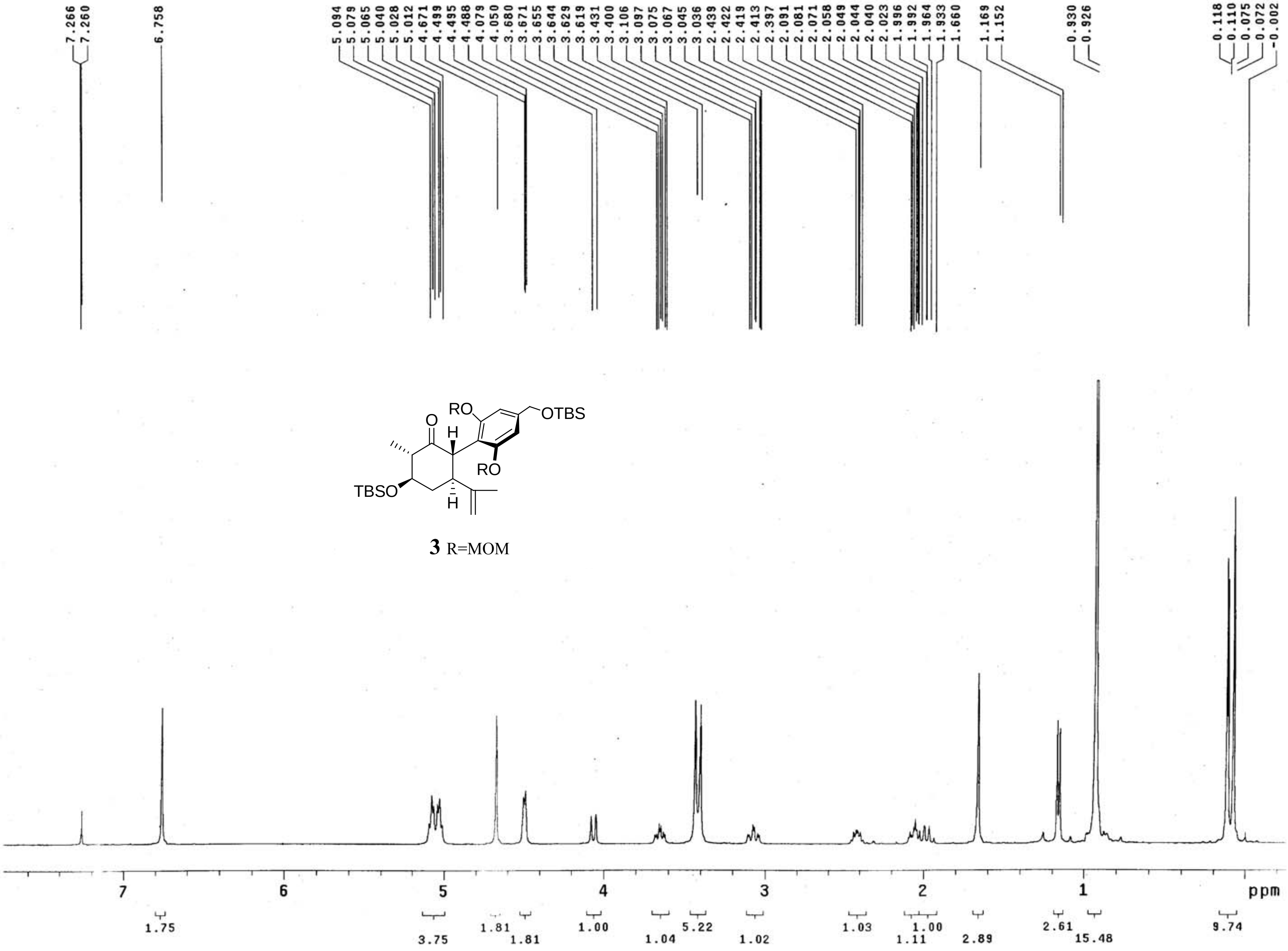
115.109
111.966
105.774
105.565
95.091
94.664
77.316
76.996
76.676
73.887
64.781
55.857
53.259
49.624
43.947
40.217
25.826
18.407
18.285
11.213
-5.334
RO
OTBS
O
H
RO
HO
H
200
180
160
140
120
100
80
60
40
20
0
ppm

11 R=MOM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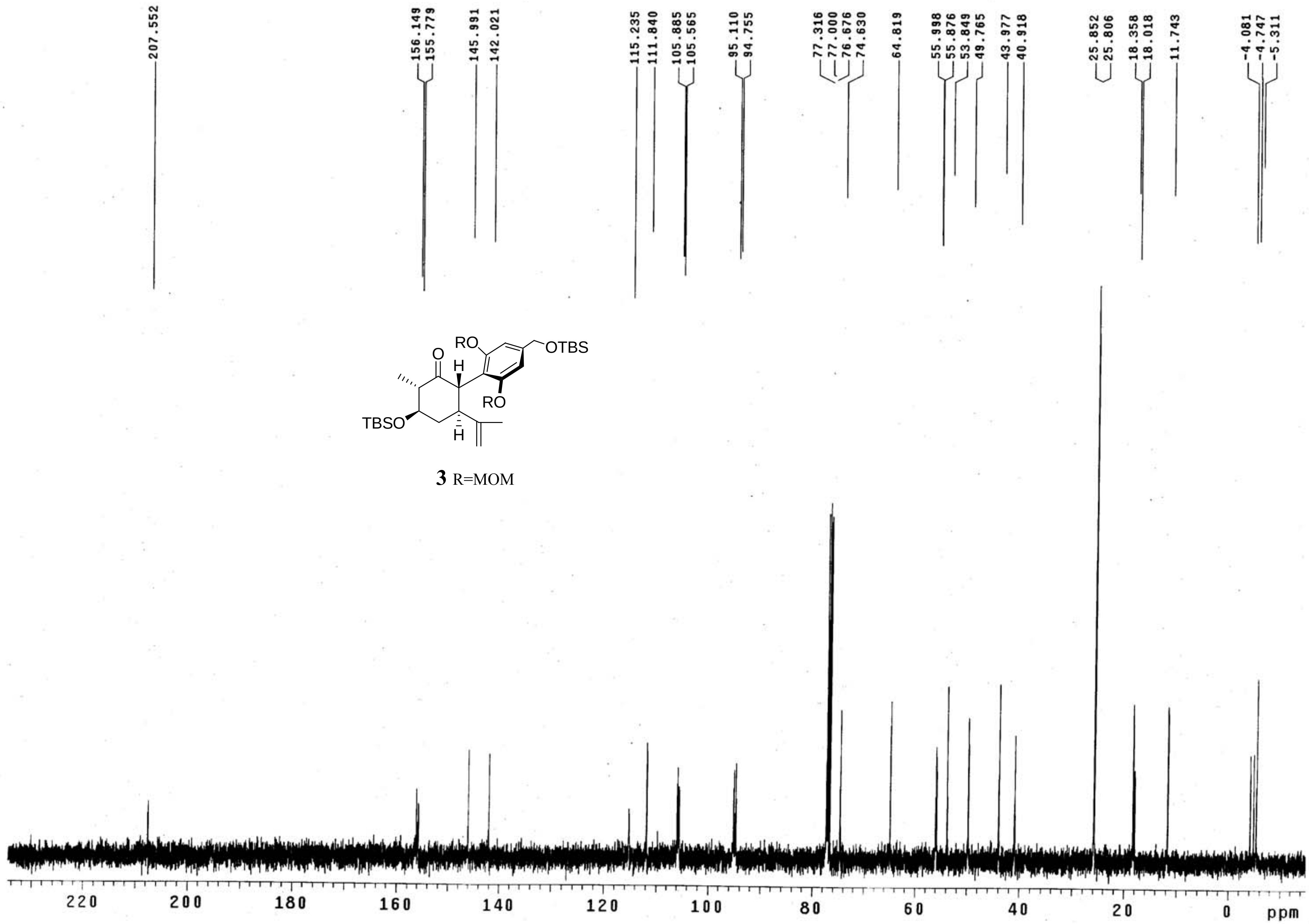
7.260
6.758
5.094
5.079
5.065
5.040
5.028
5.012
4.671
4.499
4.495
4.488
4.079
4.050
3.680
3.671
3.655
3.644
3.629
3.619
3.431
3.400
3.106
3.097
3.075
3.067
3.045
3.036
2.439
2.422
2.419
2.413
2.397
2.091
2.081
2.071
2.058
2.049
2.044
2.040
2.023
1.996
1.992
1.964
1.933
1.660
1.169
1.152
0.930
0.926
0.118
0.110
0.075
0.072
-0.002
RO
OTBS
O
H
RO
TBSO
H
7
6
5
4
3
2
1
ppm
1.75
3.75
1.81
1.81
1.00
1.04
5.22
1.02
1.03
1.11
1.00
2.89
2.61
15.48
9.74

3 R=MOM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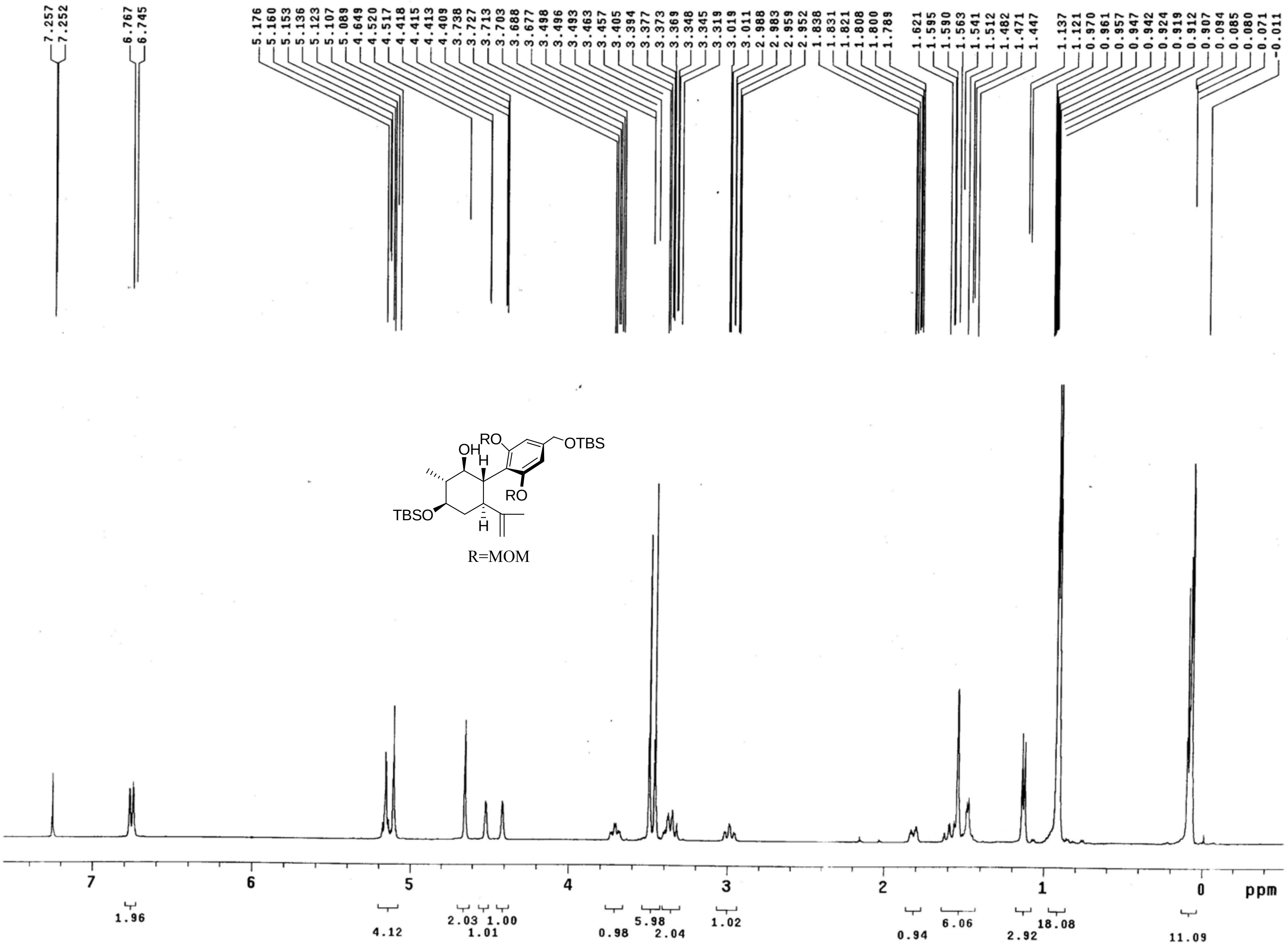
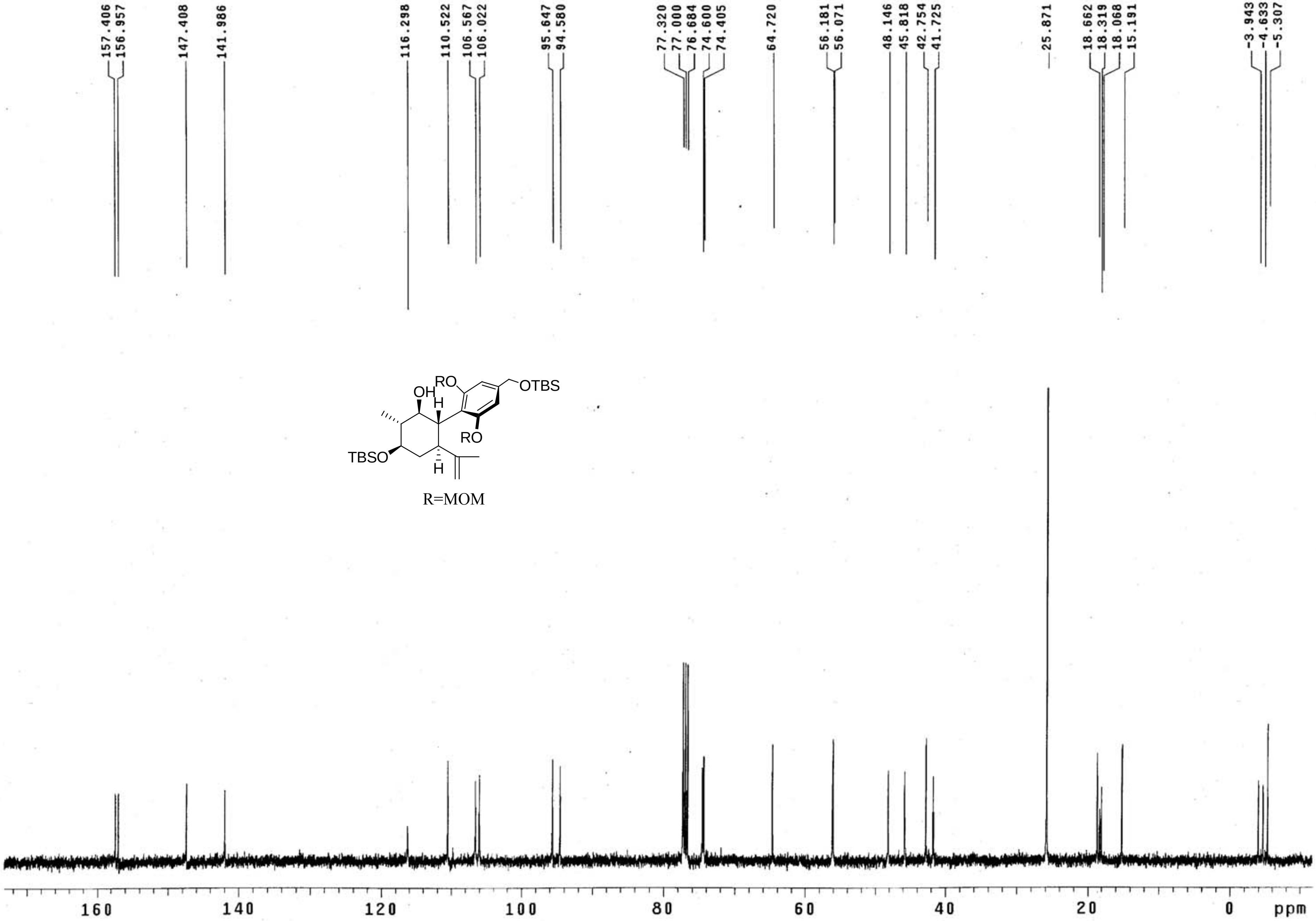
155.779
145.991
142.021
115.235
111.840
105.885
105.565
95.110
94.755
77.316
77.000
76.676
74.630
64.819
55.998
55.876
53.849
49.765
43.977
40.918
25.852
25.806
18.358
18.018
11.743
-4.081
-4.747
-5.311
RO
OTBS
O
H
RO
TBSO
H
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3 R=MOM


7.257
7.252
6.767
6.745
5.176
5.160
5.153
5.136
5.123
5.107
5.089
4.649
4.520
4.517
4.418
4.415
4.413
4.409
3.738
3.727
3.713
3.703
3.688
3.677
3.498
3.496
3.493
3.463
3.457
3.405
3.394
3.377
3.373
3.369
3.348
3.345
3.319
3.019
3.011
2.988
2.983
2.959
2.952
1.838
1.831
1.821
1.808
1.800
1.789
1.621
1.595
1.590
1.563
1.541
1.512
1.482
1.471
1.447
1.137
1.121
0.970
0.961
0.957
0.947
0.942
0.924
0.919
0.912
0.907
0.094
0.085
0.080
0.071
-0.011
RO
OH
H
OTBS
RO
TBSO
H
R=MOM
7
6
5
4
3
2
1
0
ppm
1.96
4.12
2.03
1.01
1.00
0.98
5.98
2.04
1.02
0.94
6.06
2.92
18.08
11.09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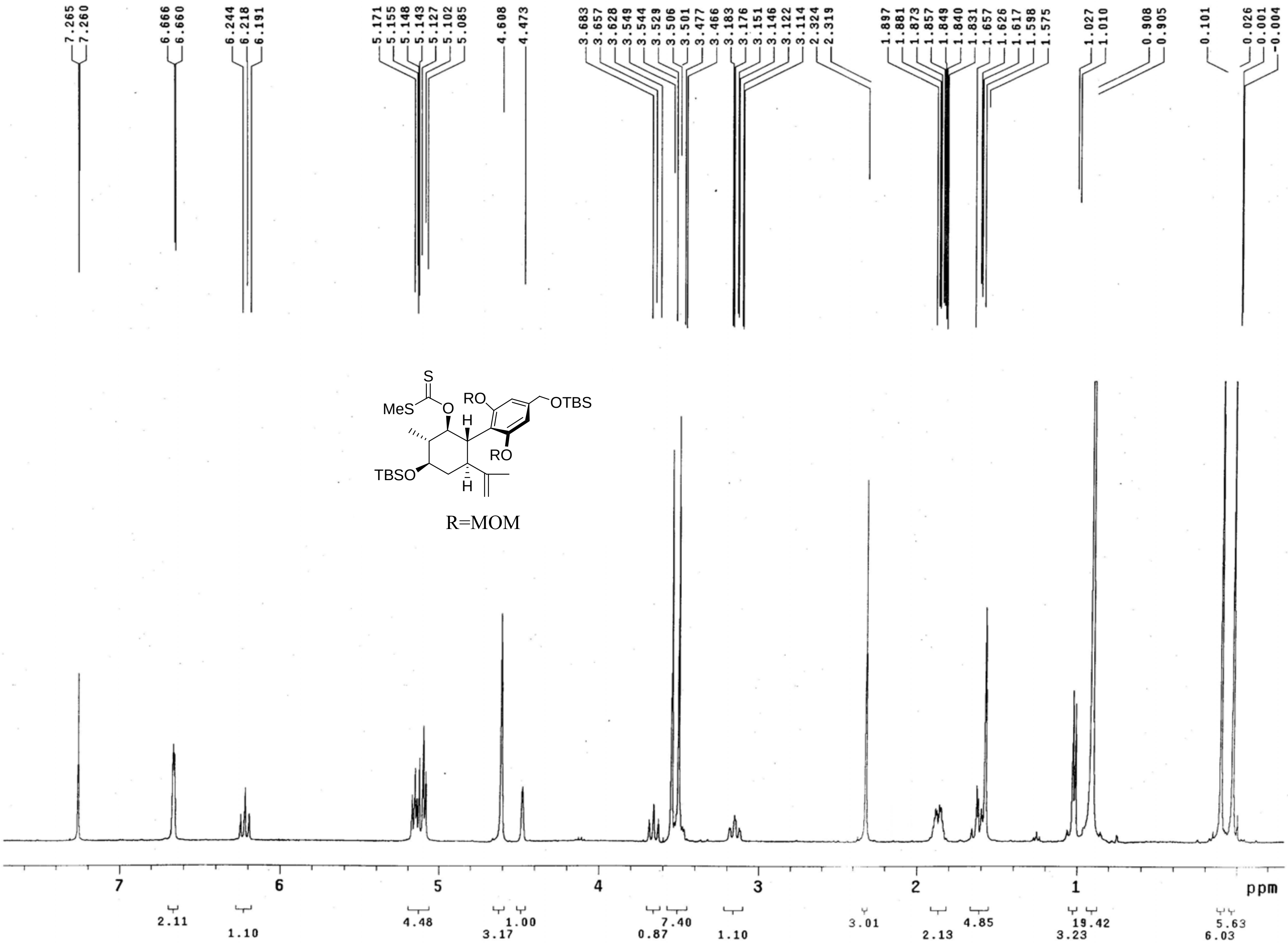
110.522
106.567
106.022
95.647
94.580
77.320
77.000
76.684
74.600
74.405
64.720
56.181
56.071
48.146
45.818
42.754
41.725
25.871
18.662
18.319
18.068
15.191
-3.943
-4.633
-5.307
RO
OTBS
OH
H
RO
TBSO
H
R=MOM
160
140
120
100
80
60
40
20
0
ppm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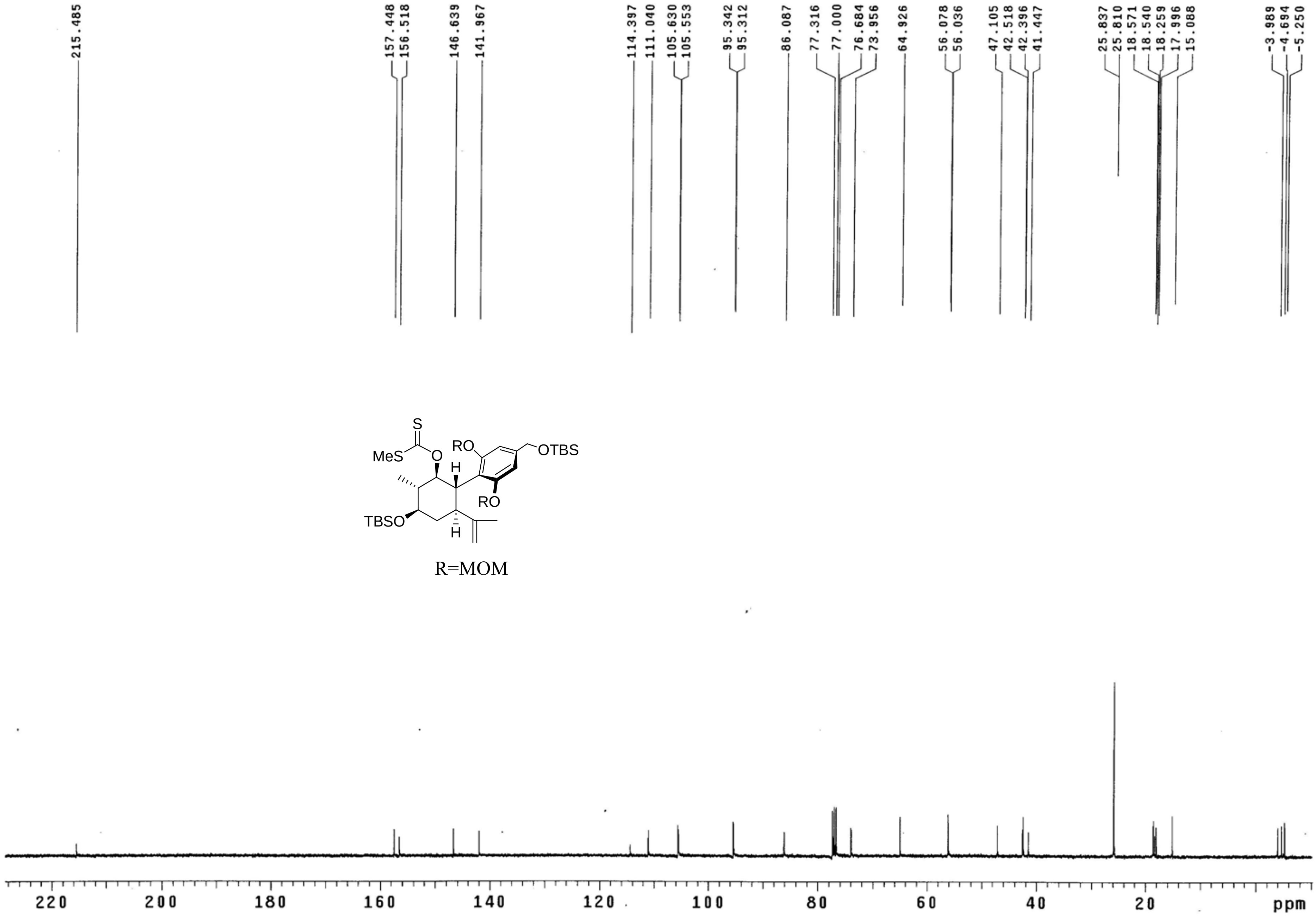
7.260
6.666
6.660
6.244
6.218
6.191
5.171
5.155
5.148
5.143
5.127
5.102
5.085
4.608
4.473
3.683
3.657
3.628
3.549
3.544
3.529
3.506
3.501
3.477
3.466
3.183
3.176
3.151
3.146
3.122
3.114
2.324
2.319
1.897
1.881
1.873
1.857
1.849
1.840
1.831
1.657
1.626
1.617
1.598
1.575
1.027
1.010
0.908
0.905
0.101
0.026
0.001
-0.004
S
MeS
O
RO
OTBS
H
RO
TBSO
H
R=MOM
7
6
5
4
3
2
1
ppm
2.11
1.10
4.48
3.17
1.00
0.87
7.40
1.10
3.01
2.13
4.85
3.23
19.42
6.03
5.63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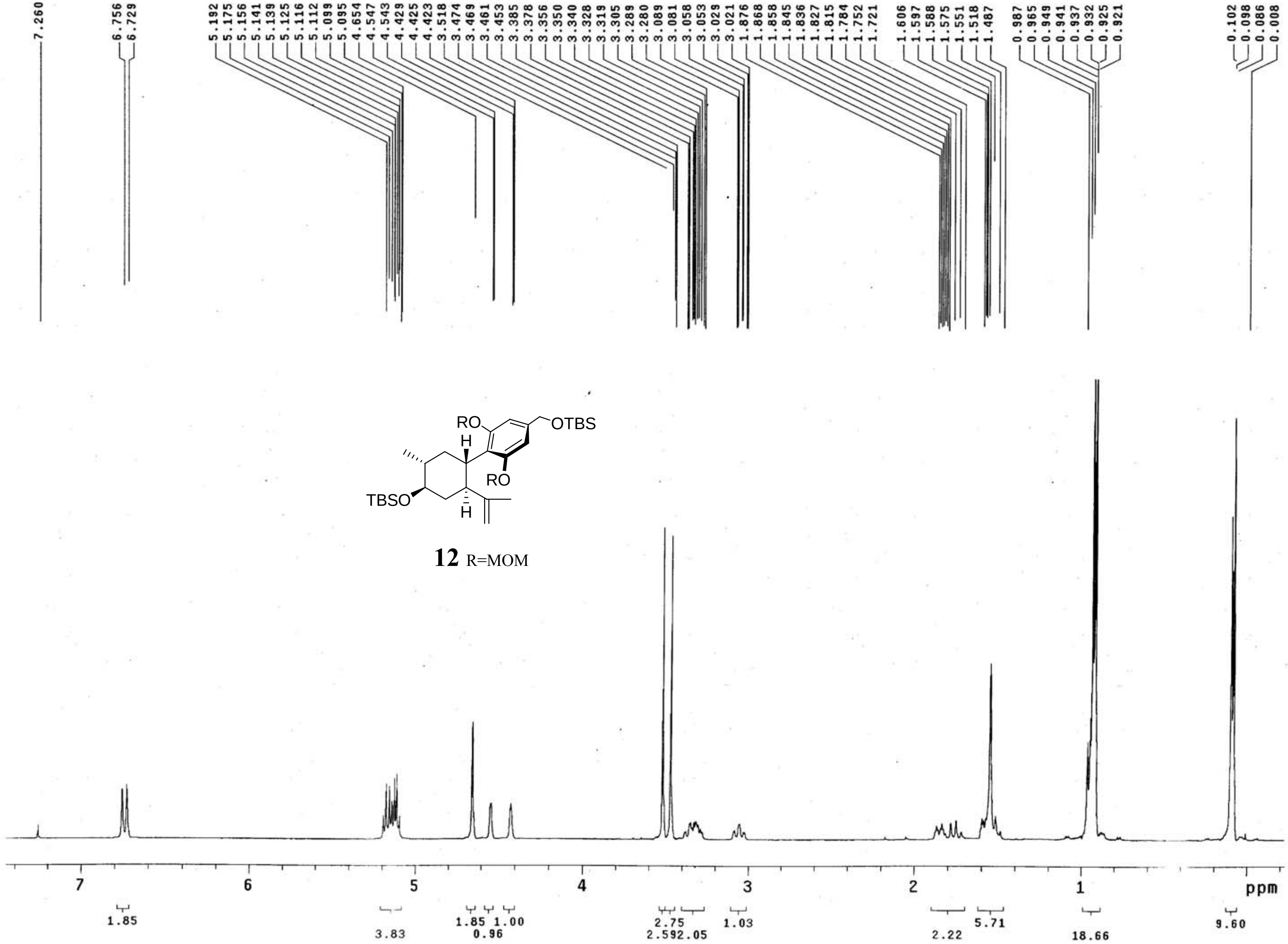
141.967
114.397
111.040
105.630
105.553
95.342
95.312
86.087
77.316
77.000
76.684
73.956
64.926
56.078
56.036
47.105
42.518
42.396
41.447
25.837
25.810
18.571
18.540
18.259
17.996
15.088
-3.989
-4.694
-5.250
S
MeS
O
RO
OTBS
H
RO
TBSO
H
R=MOM
220
200
180
160
140
120
100
80
60
40
20
ppm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6.729
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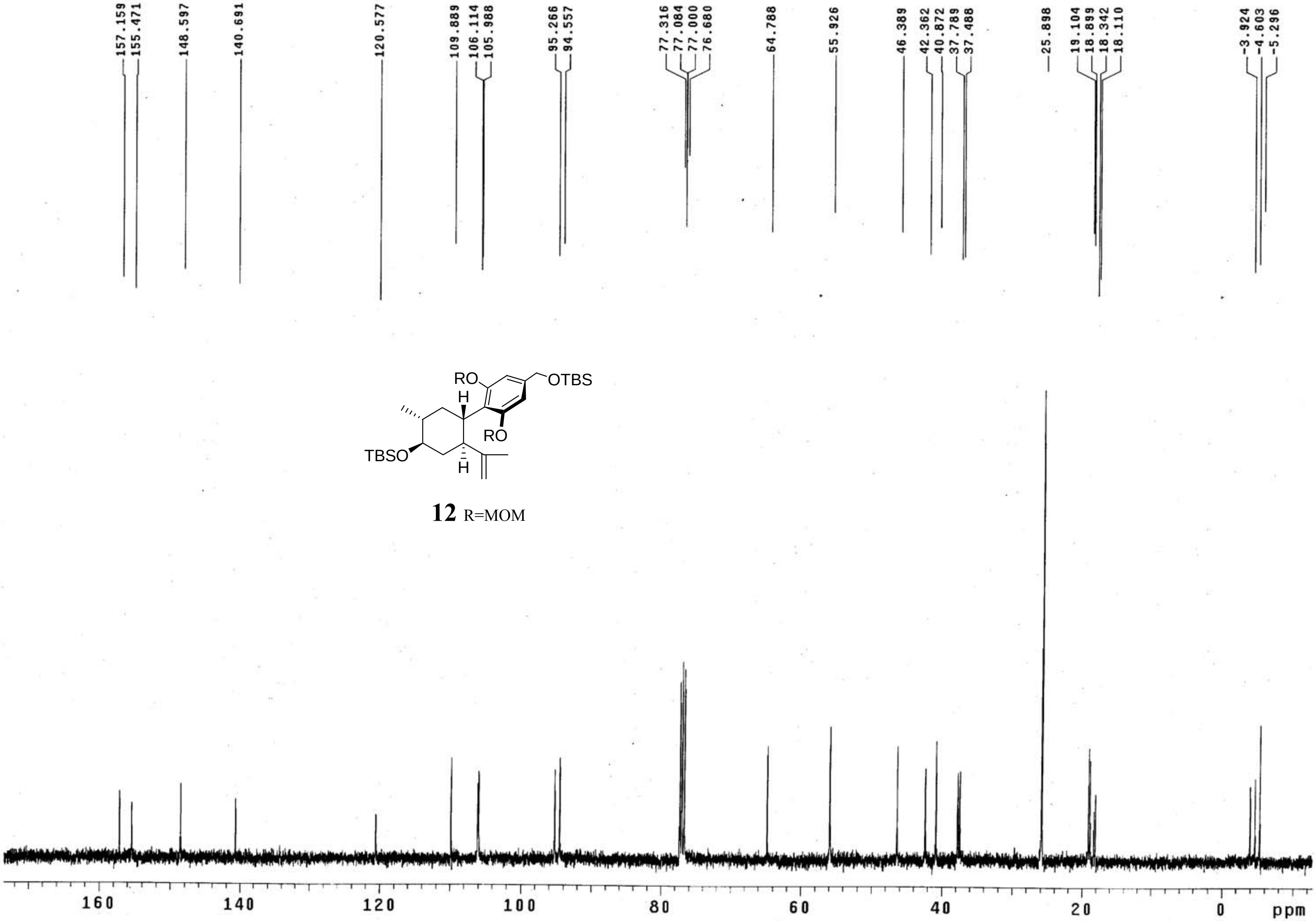
5.175
5.156
5.141
5.139
5.125
5.116
5.112
5.099
5.095
4.654
4.547
4.543
4.429
4.425
4.423
3.518
3.474
3.469
3.461
3.453
3.385
3.378
3.356
3.350
3.340
3.328
3.319
3.305
3.289
3.280
3.089
3.081
3.058
3.053
3.029
3.021
1.876
1.868
1.858
1.845
1.836
1.827
1.815
1.784
1.752
1.721
1.606
1.597
1.588
1.575
1.551
1.518
1.487
0.987
0.965
0.949
0.941
0.937
0.932
0.925
0.921
0.102
0.098
0.086
0.008
RO
OTBS
H
RO
TBSO
H
12 R=MOM
7
6
5
4
3
2
1
ppm
1.85
3.83
1.85
0.96
1.00
2.75
2.59
2.05
1.03
2.22
5.71
18.66
9.60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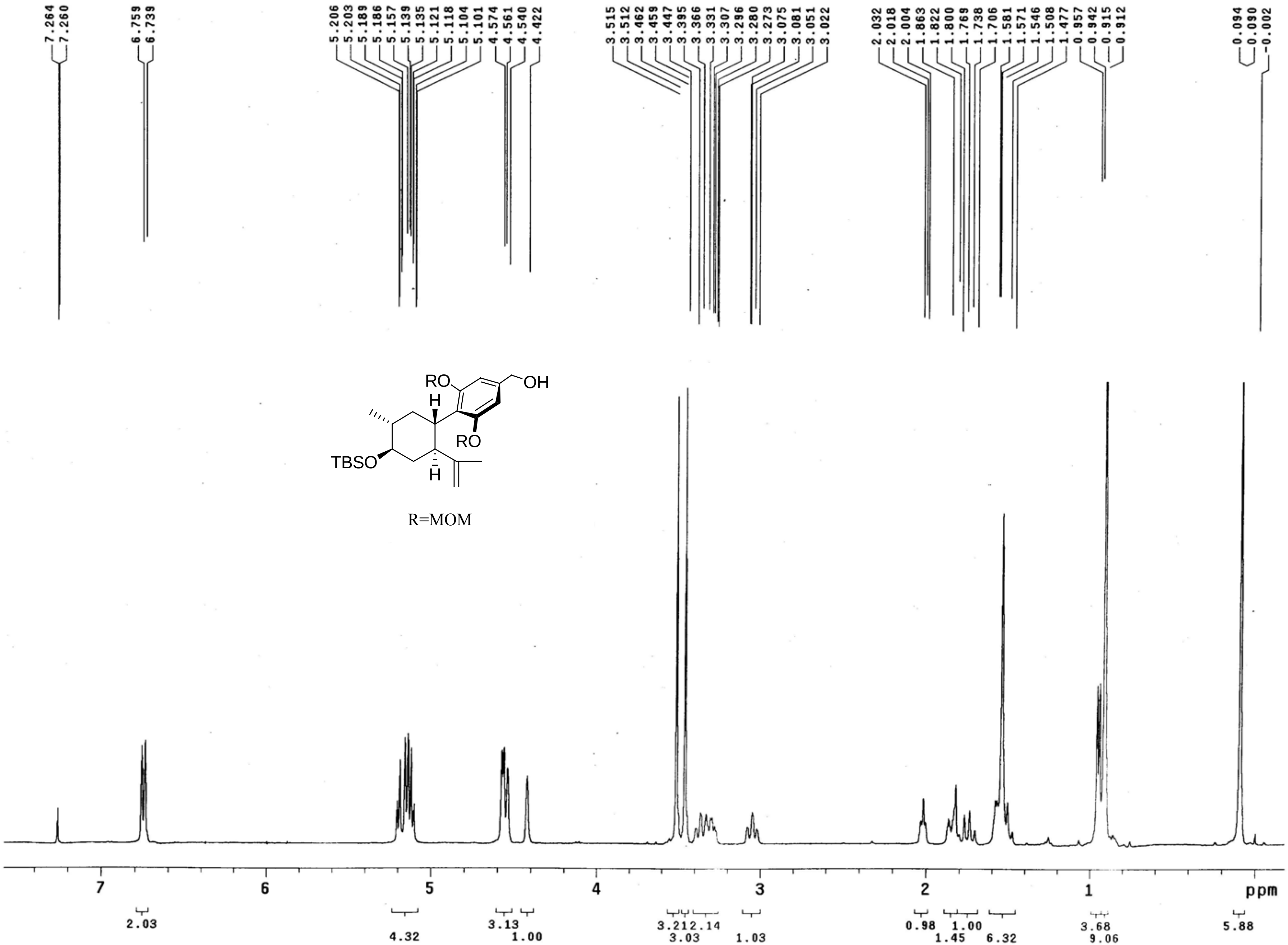
105.988
95.266
94.557
77.316
77.084
77.000
76.680
64.788
55.926
46.389
42.362
40.872
37.789
37.488
25.898
19.104
18.899
18.342
18.110
-3.924
-4.603
-5.296
RO
OTBS
H
RO
TBSO
H
160
140
120
100
80
60
40
20
0
ppm

12 R=MOM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7.260
6.759
6.739
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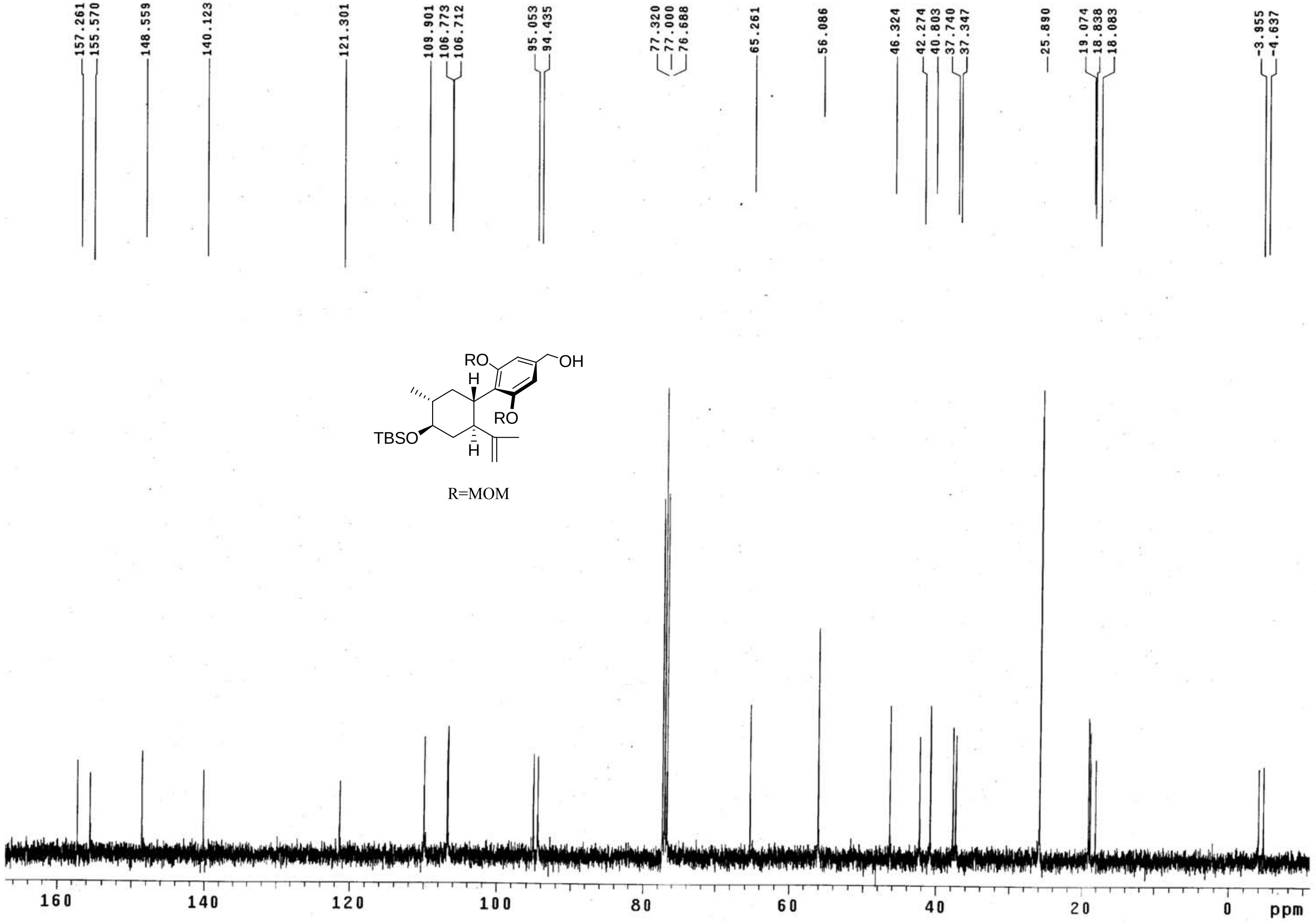
5.203
5.189
5.186
5.157
5.139
5.135
5.121
5.118
5.104
5.101
4.574
4.561
4.540
4.422
3.515
3.512
3.462
3.459
3.447
3.395
3.366
3.331
3.307
3.296
3.280
3.273
3.075
3.081
3.051
3.022
2.032
2.018
2.004
1.863
1.822
1.800
1.769
1.738
1.706
1.581
1.571
1.546
1.508
1.477
0.957
0.942
0.915
0.912
0.094
0.090
-0.002
RO
OH
H
RO
TBSO
H
R=MOM
7
6
5
4
3
2
1
ppm
2.03
4.32
3.13
1.00
3.21
2.14
3.03
1.03
0.98
1.00
1.45
6.32
3.68
9.06
5.88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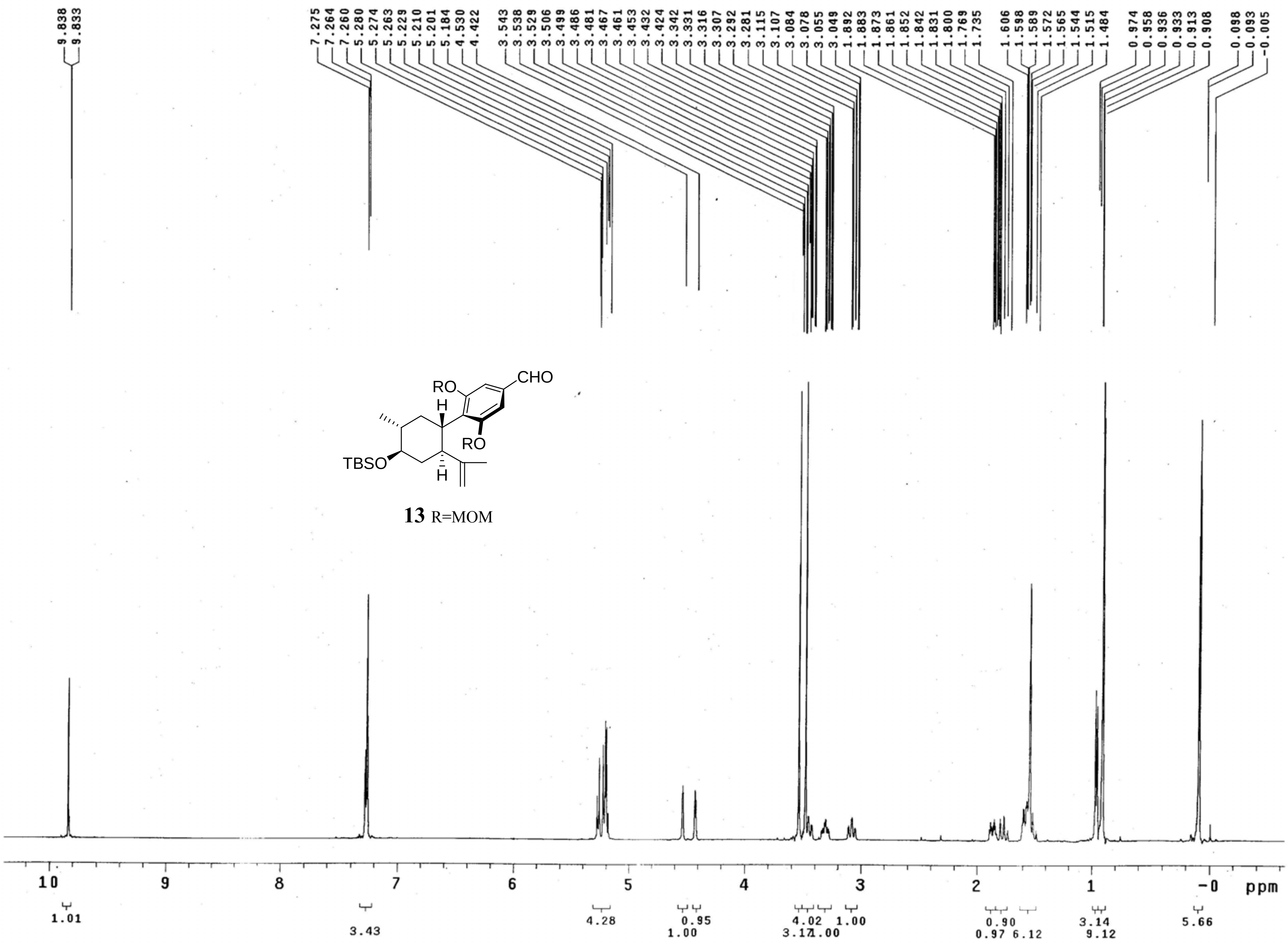
155.570
148.559
140.123
121.301
109.901
106.773
106.712
95.053
94.435
77.320
77.000
76.688
65.261
56.086
46.324
42.274
40.803
37.740
37.347
25.890
19.074
18.838
18.083
-3.955
-4.637
RO
OH
H
RO
TBSO
H
R=MOM
160
140
120
100
80
60
40
20
0
ppm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9.833
7.275
7.264
7.260
5.280
5.274
5.263
5.229
5.210
5.201
5.184
4.530
4.422
3.543
3.538
3.529
3.506
3.499
3.486
3.481
3.467
3.461
3.453
3.432
3.424
3.342
3.331
3.316
3.307
3.292
3.281
3.115
3.107
3.084
3.078
3.055
3.049
1.892
1.883
1.873
1.861
1.852
1.842
1.831
1.800
1.769
1.735
1.606
1.598
1.589
1.572
1.565
1.544
1.515
1.484
0.974
0.958
0.936
0.933
0.913
0.908
0.098
0.093
-0.005
RO
CHO
H
RO
TBSO
H
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.01
3.43
4.28
1.00
0.95
4.02
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1.00
1.00
0.90
0.97
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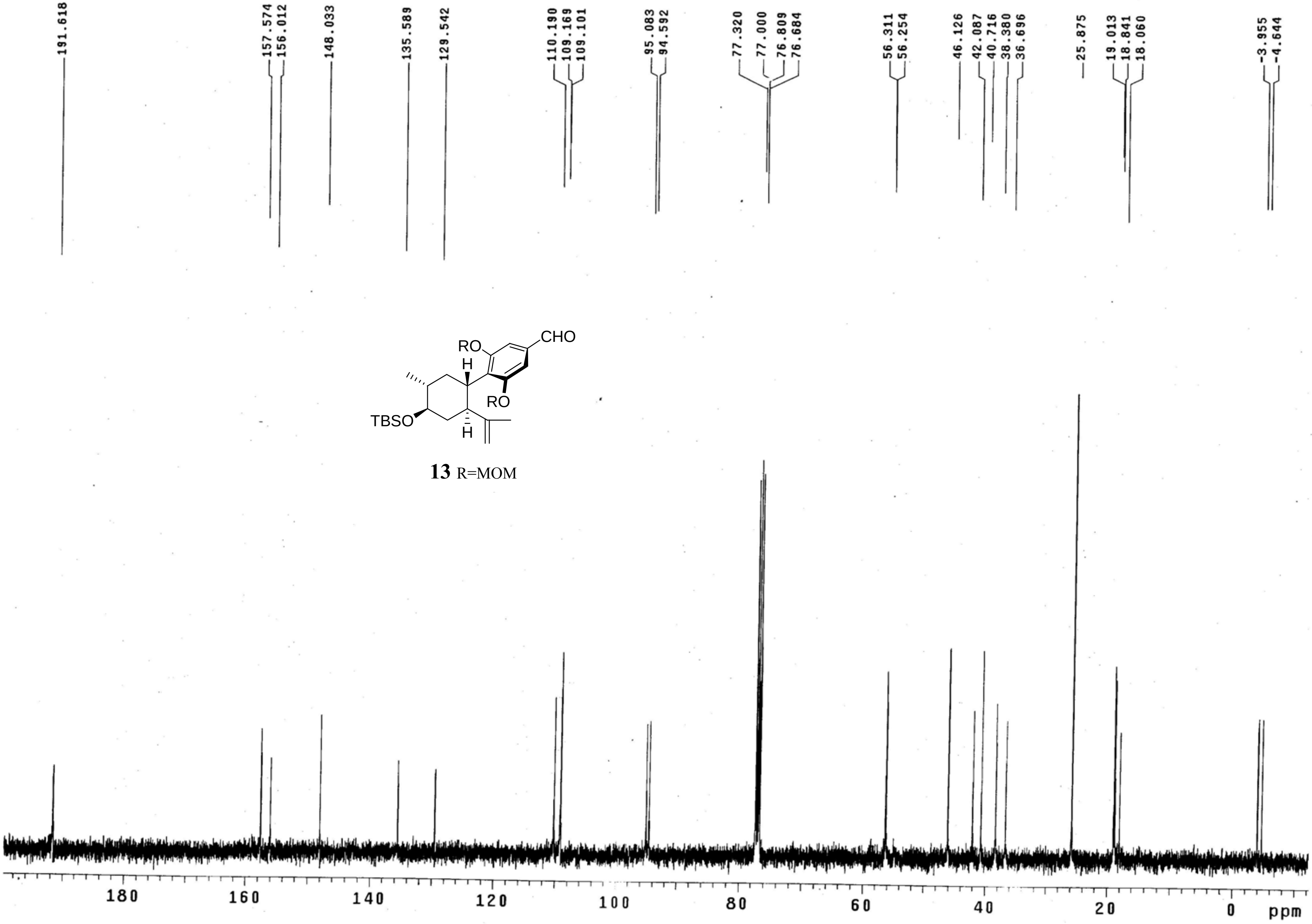
3.14
9.12
5.66

13 R=MOM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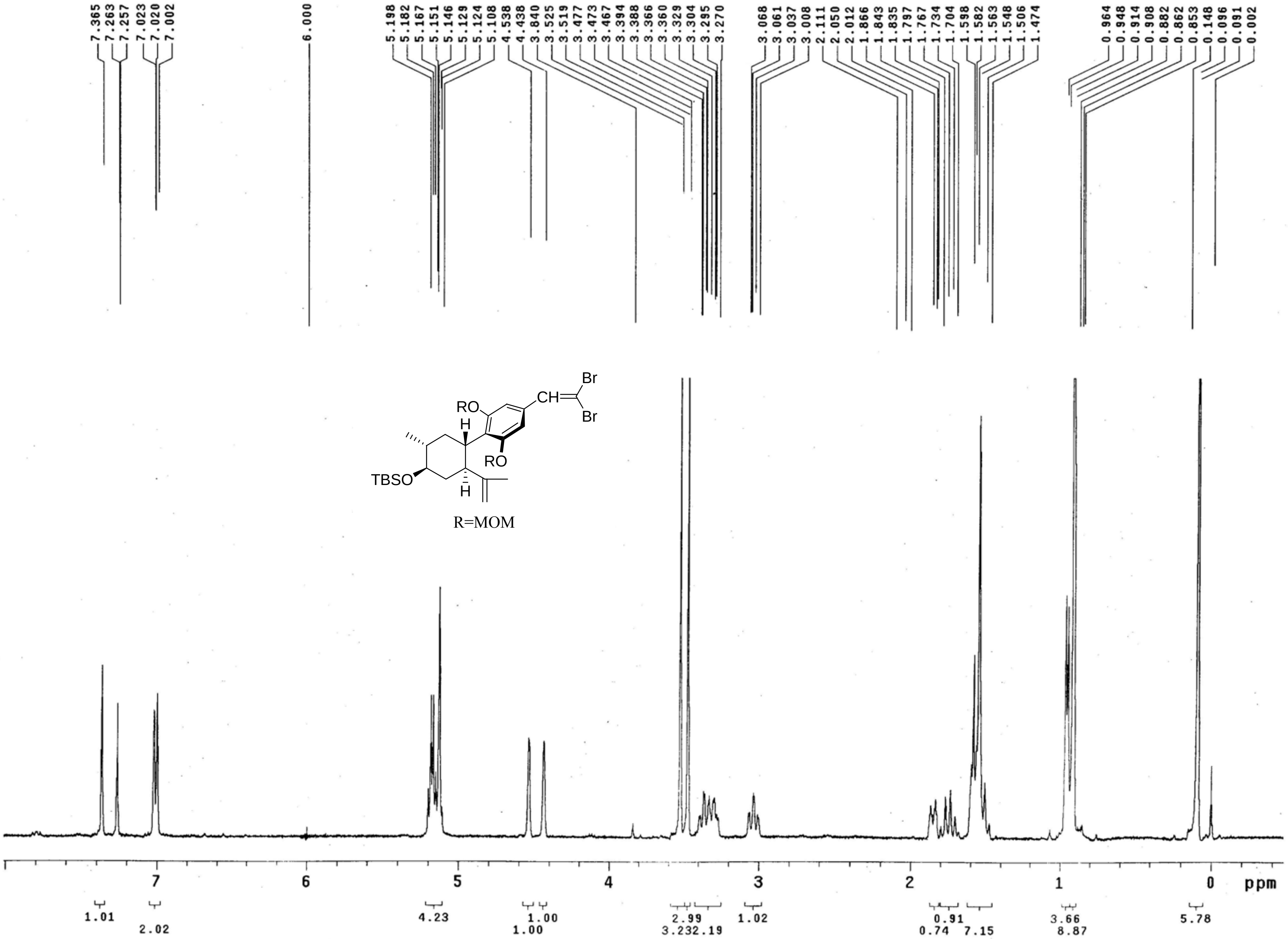
156.012
148.033
135.589
129.542
110.190
109.169
109.101
95.083
94.592
77.320
77.000
76.809
76.684
56.311
56.254
46.126
42.087
40.716
38.380
36.696
25.875
19.013
18.841
18.060
-3.955
-4.644
RO
CHO
H
RO
TBSO
H
180
160
140
120
100
80
60
40
20
0
ppm

13 R=MOM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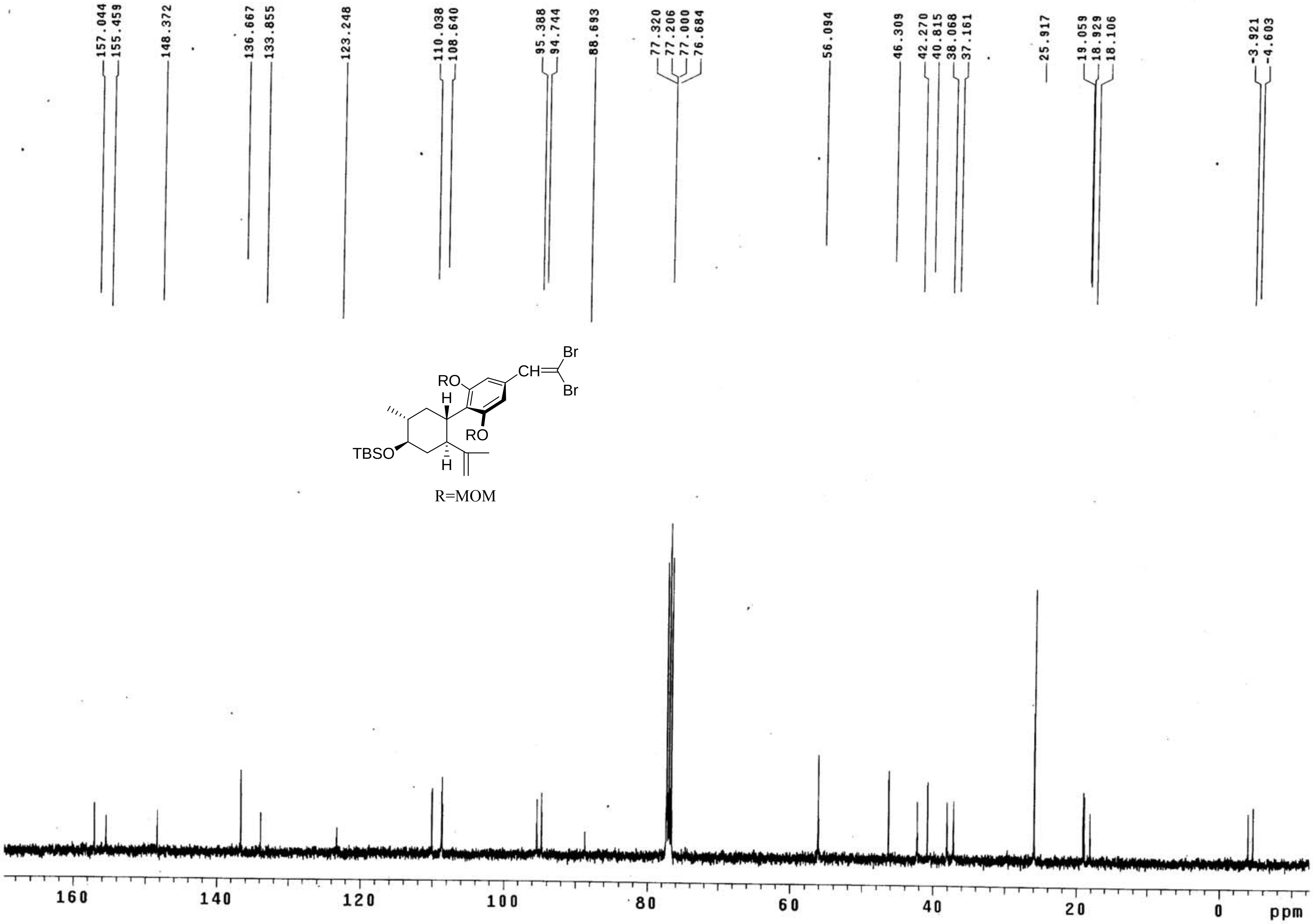
7.020
7.002
6.000
5.198
5.182
5.167
5.151
5.146
5.129
5.124
5.108
4.538
4.438
3.840
3.525
3.519
3.477
3.473
3.467
3.394
3.388
3.366
3.360
3.329
3.304
3.295
3.270
3.068
3.061
3.037
3.008
2.111
2.050
2.012
1.866
1.843
1.835
1.797
1.767
1.734
1.704
1.598
1.582
1.563
1.548
1.506
1.474
0.964
0.948
0.914
0.908
0.882
0.862
0.853
0.148
0.096
0.091
0.002
Br
CH
Br
RO
H
RO
TBSO
H
R=MOM
7
6
5
4
3
2
1
0
ppm
1.01
2.02
4.23
1.00
1.00
2.99
3.23
2.19
1.02
0.91
0.74
7.15
3.66
8.87
5.78


157.044
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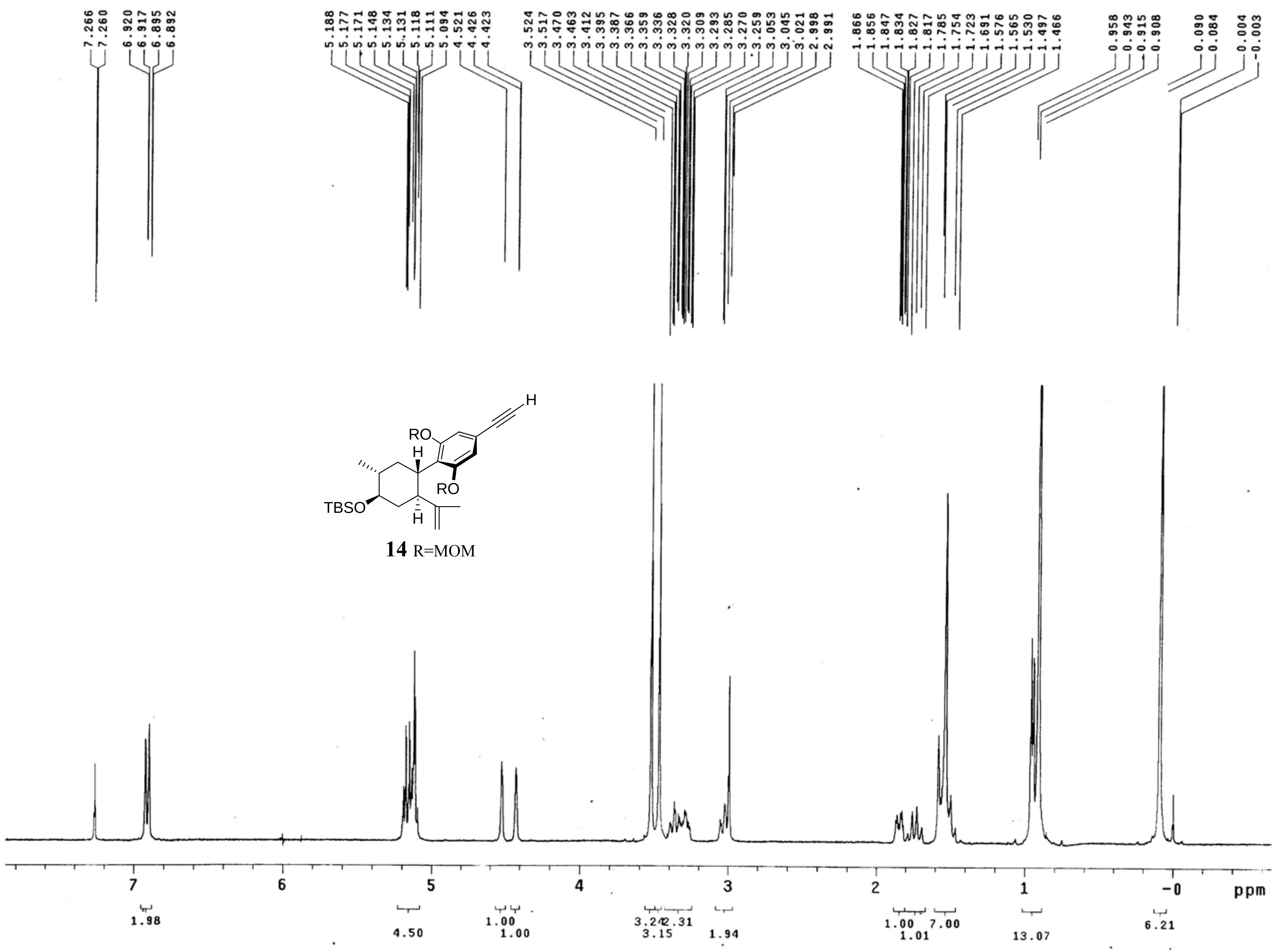
148.372
136.667
133.855
123.248
110.038
108.640
95.388
94.744
88.693
77.320
77.206
77.000
76.684
56.094
46.309
42.270
40.815
38.068
37.161
25.917
19.059
18.929
18.106
-3.921
-4.603
Br
RO
CH
Br
H
RO
TBSO
H
R=MOM
160
140
120
100
80
60
40
20
0
ppm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7.260
6.920
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6.892
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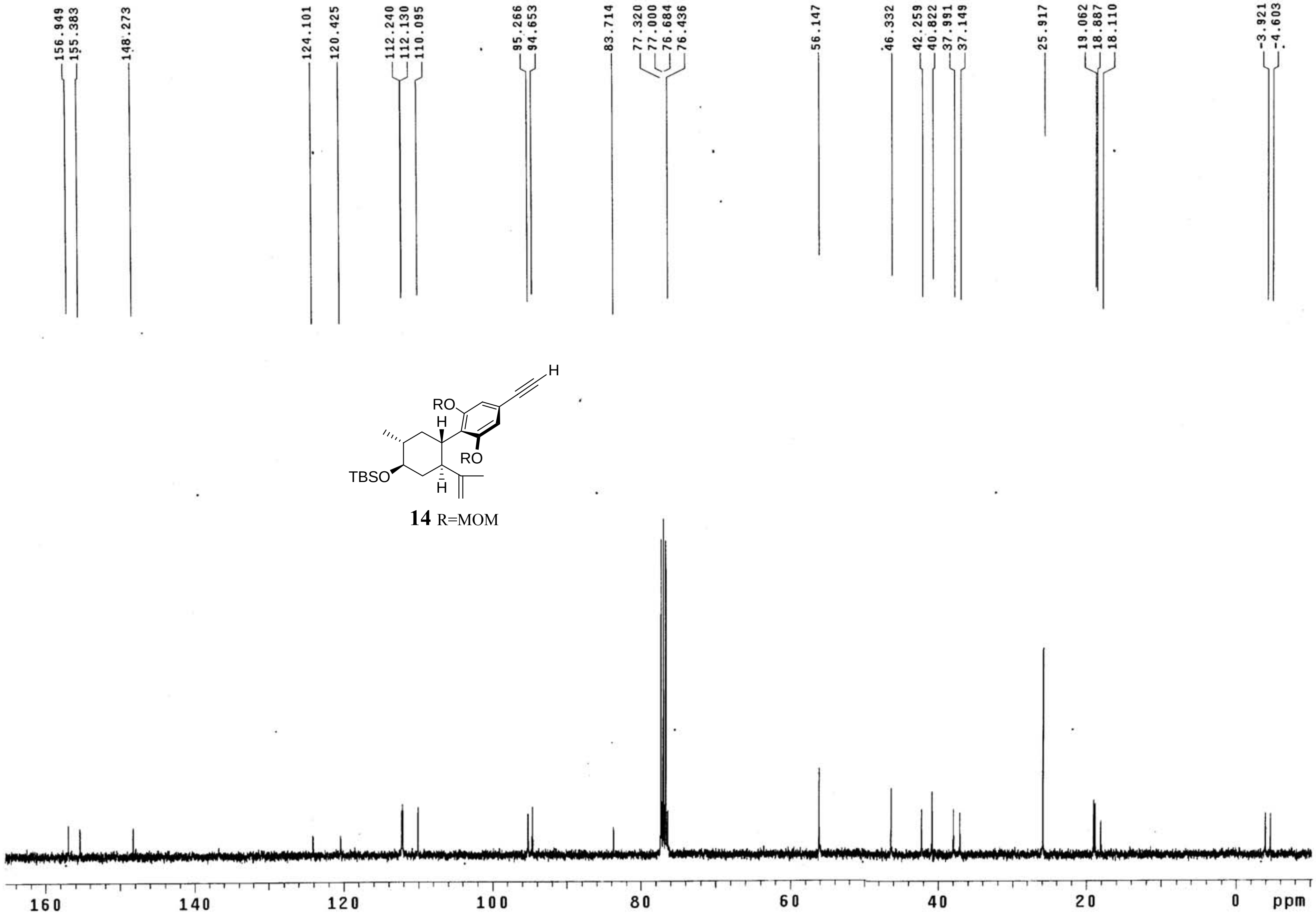
5.177
5.171
5.148
5.134
5.131
5.118
5.111
5.094
4.521
4.426
4.423
3.524
3.517
3.470
3.463
3.412
3.395
3.387
3.366
3.359
3.336
3.328
3.320
3.309
3.293
3.285
3.270
3.259
3.053
3.045
3.021
2.998
2.991
1.866
1.856
1.847
1.834
1.827
1.817
1.785
1.754
1.723
1.691
1.576
1.565
1.530
1.497
1.466
0.958
0.943
0.915
0.908
0.090
0.084
0.004
-0.003
H
RO
H
RO
TBSO
H
7
6
5
4
3
2
1
-0
ppm
1.98
4.50
1.00
1.00
3.24
2.31
3.15
1.94
1.00
1.01
7.00
13.07
6.21

14 R=MOM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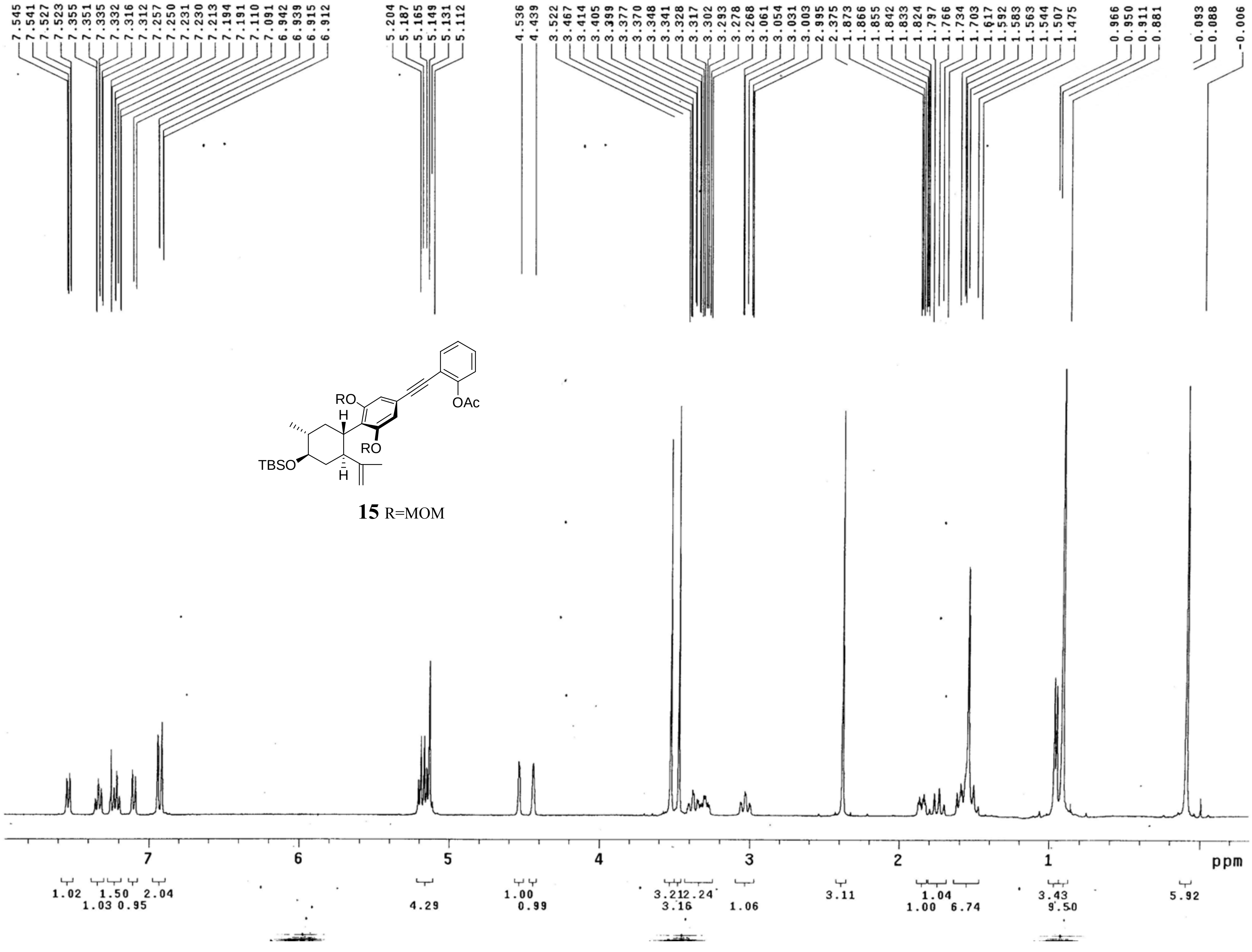
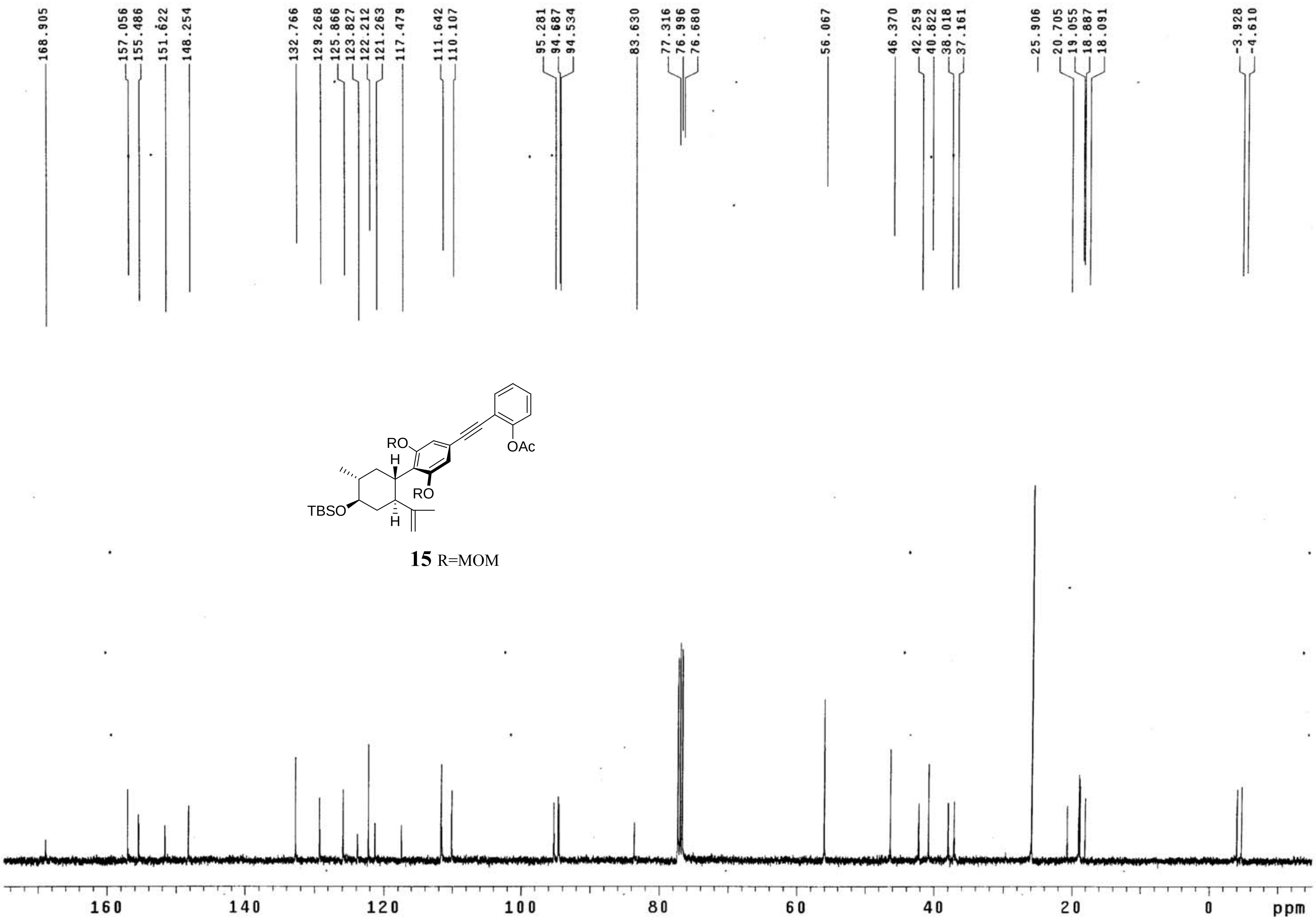
155.383
148.273
124.101
120.425
112.240
112.130
110.095
95.266
94.653
83.714
77.320
77.000
76.684
76.436
56.147
46.332
42.259
40.822
37.991
37.149
25.917
19.062
18.887
18.110
-3.921
-4.603
RO
H
TBSO
RO
H
H
160
140
120
100
80
60
40
20
0
ppm

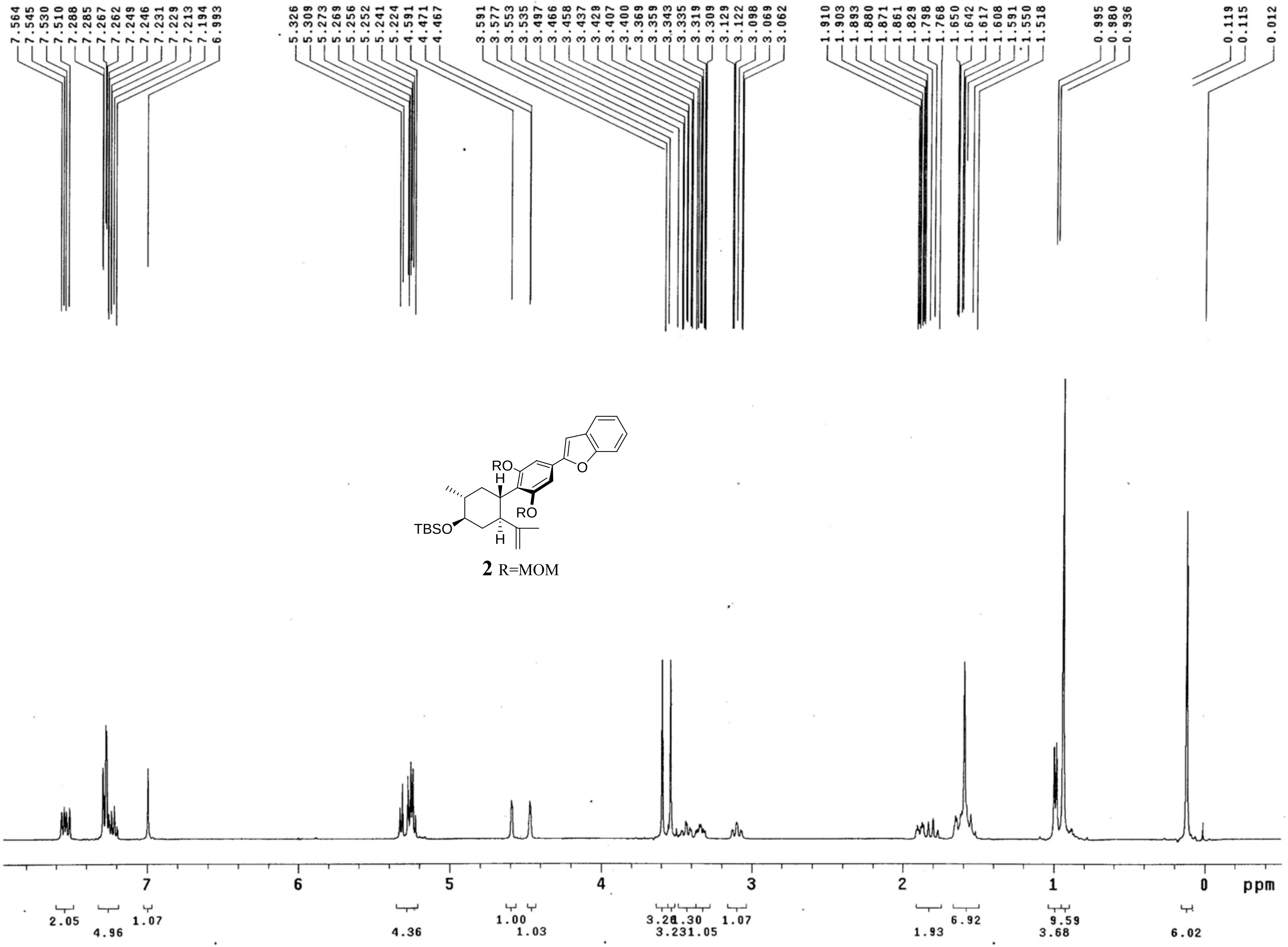
14 R=MOM


7.545
7.541
7.527
7.523
7.355
7.351
7.335
7.332
7.316
7.312
7.257
7.250
7.231
7.230
7.213
7.194
7.191
7.110
7.091
6.942
6.939
6.915
6.912
5.204
5.187
5.165
5.149
5.131
5.112
4.536
4.439
3.522
3.467
3.414
3.405
3.399
3.377
3.370
3.348
3.341
3.328
3.317
3.302
3.293
3.278
3.268
3.061
3.054
3.031
3.003
2.995
2.375
1.873
1.866
1.855
1.842
1.833
1.824
1.797
1.766
1.734
1.703
1.617
1.592
1.583
1.563
1.544
1.507
1.475
0.966
0.950
0.911
0.881
0.093
0.088
-0.006
RO
H
RO
TBSO
H
OAc
7
6
5
4
3
2
1
ppm
1.02
1.03
1.50
0.95
2.04
4.29
1.00
0.99
3.21
3.16
12.24
1.06
3.11
1.04
1.00
6.74
3.43
9.50
5.92

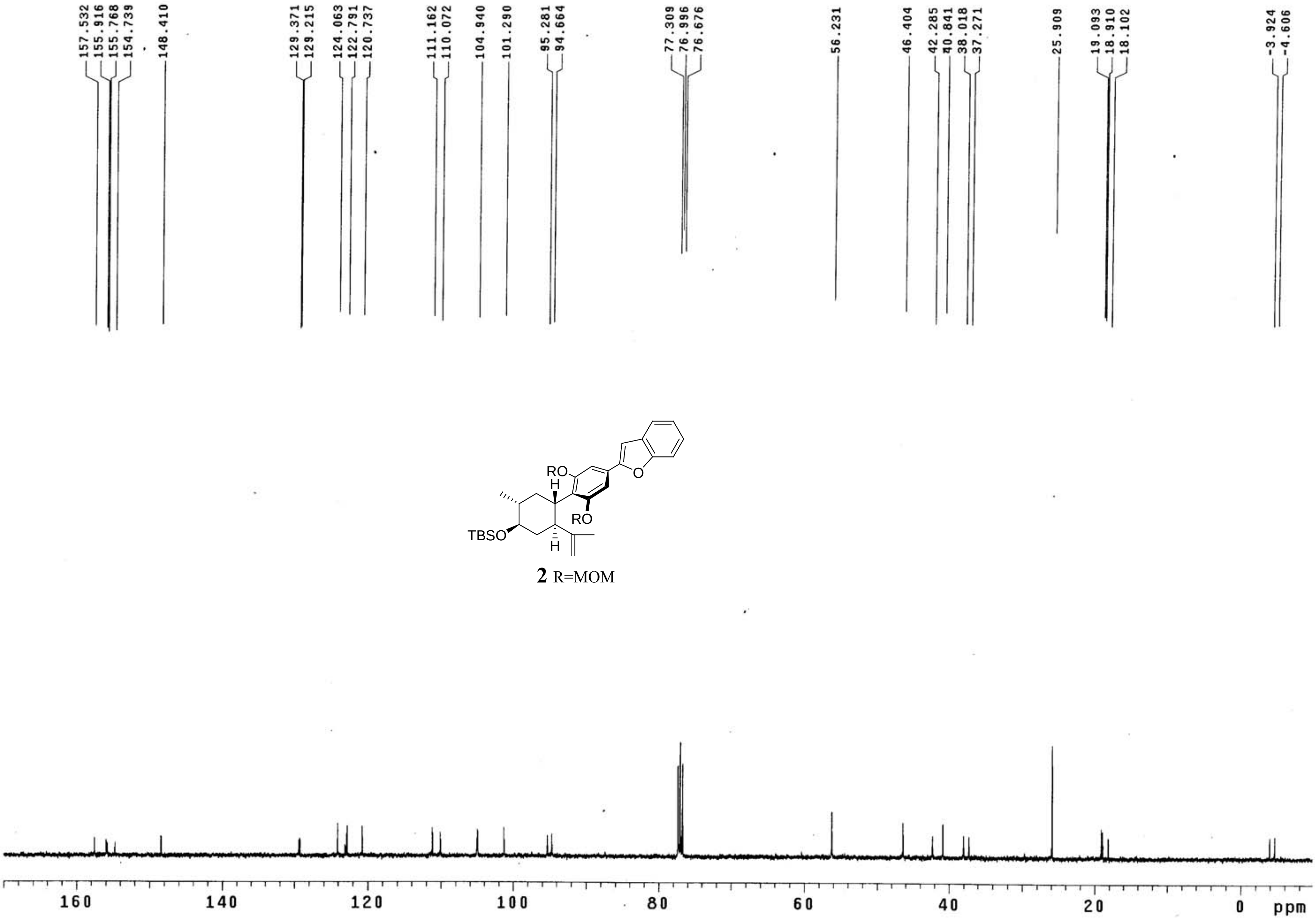
15 R=MOM


168.905
157.056
155.486
151.622
148.254
132.766
129.268
125.866
123.827
122.212
121.263
117.479
111.642
110.107
95.281
94.687
94.534
83.630
77.316
76.996
76.680
56.067
46.370
42.259
40.822
38.018
37.161
25.906
20.705
19.055
18.887
18.091
-3.928
-4.610
RO
OAc
H
RO
TBSO
H
160
140
120
100
80
60
40
20
0
ppm

15 R=MOM


7.564
7.545
7.530
7.510
7.288
7.285
7.267
7.262
7.249
7.246
7.231
7.229
7.213
7.194
6.993
5.326
5.309
5.273
5.269
5.256
5.252
5.241
5.224
4.591
4.471
4.467
3.591
3.577
3.553
3.535
3.497
3.466
3.458
3.437
3.429
3.407
3.400
3.369
3.359
3.343
3.335
3.319
3.309
3.129
3.122
3.098
3.069
3.062
1.910
1.903
1.893
1.880
1.871
1.861
1.829
1.798
1.768
1.650
1.642
1.617
1.608
1.591
1.550
1.518
0.995
0.980
0.936
0.119
0.115
0.012
RO
H
O
RO
TBSO
H
7
6
5
4
3
2
1
0
ppm
2.05
4.96
1.07
4.36
1.00
1.03
3.26
3.23
1.30
1.05
1.07
1.93
6.92
9.59
3.68
6.02

2 R=MOM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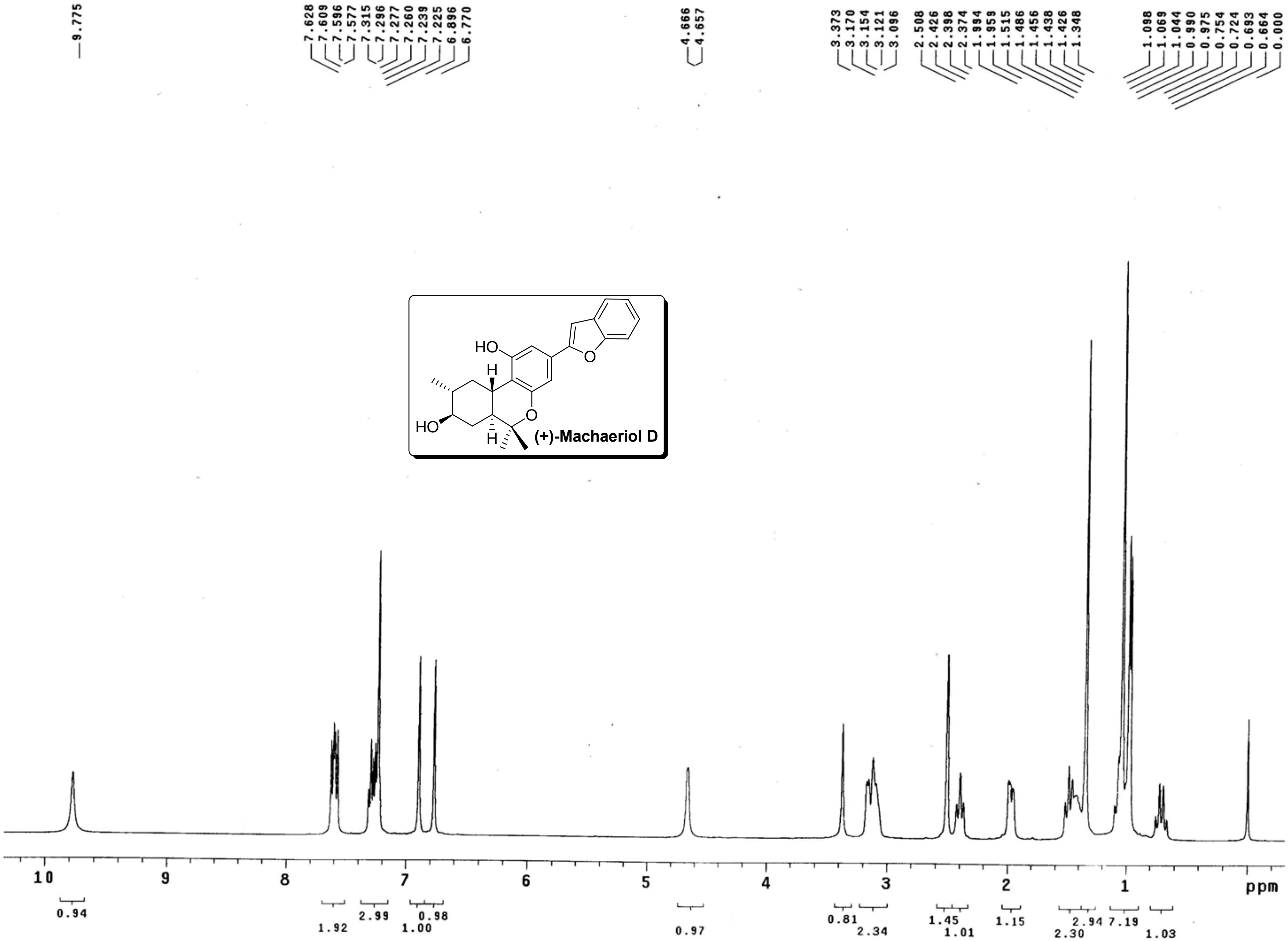
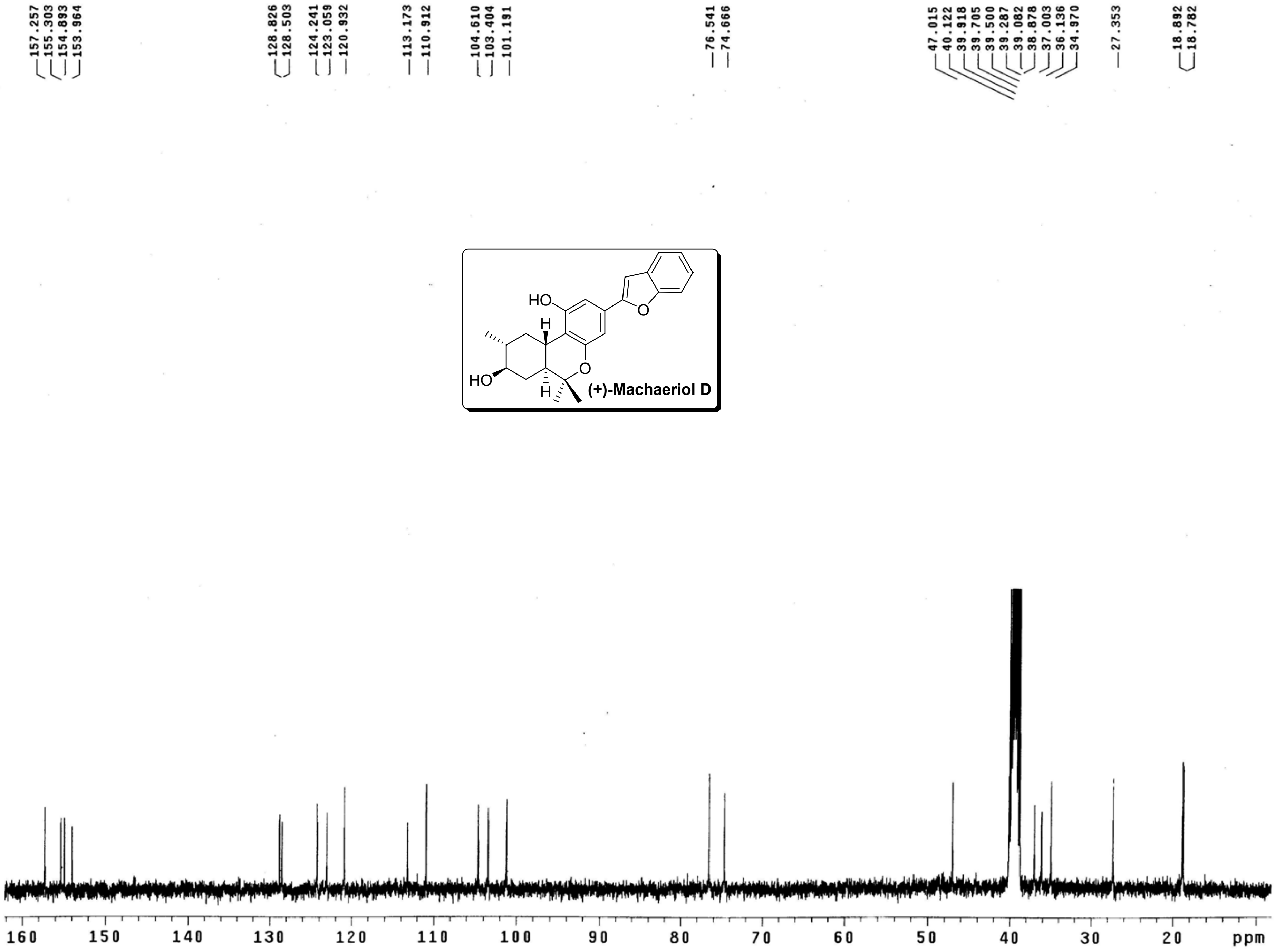
155.916
155.768
154.739
148.410
129.371
129.215
124.063
122.791
120.737
111.162
110.072
104.940
101.290
95.281
94.664
77.309
76.996
76.676
56.231
46.404
42.285
40.841
38.018
37.271
25.909
19.093
18.910
18.102
-3.924
-4.606
RO
H
RO
TBSO
H
160
140
120
100
80
60
40
20
0
ppm

2 R=MOM


(+)-Machaeriol D


157.257
155.303
154.893
153.964
128.826
128.503
124.241
123.059
120.932
113.173
110.912
104.610
103.404
101.191
76.541
74.666
47.015
40.122
39.918
39.705
39.500
39.287
39.082
38.878
37.003
36.136
34.970
27.353
18.892
18.782
HO
H
HO
O
H
O
(+)-Machaeriol D
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm