Supporting Information

Enantio- and stereoselective route to the phoslactomycin family of antibiotics: formal synthesis of (+)-fostriecin and (+)-phoslactomycin B

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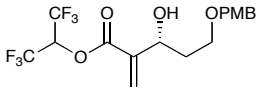
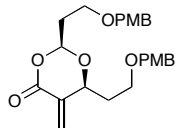
General. Where appropriate, reactions were performed in flame-dried glassware under argon atmosphere. All extracts were dried over $MgSO_4$ and concentrated by rotary evaporation below 30 °C at 25 Torr unless otherwise noted. Commercial reagents and solvents were used as supplied with following exceptions. *N*,*N*-Dimethyformamide (DMF), dichloromethane (CH_2Cl_2), acetonitrile (MeCN), and pyridine were distilled from CaH_2. Methanol (MeOH) was distilled from sodium. Thin-layer chromatography (TLC) was performed using glass-packed silica gel plates (0.2 or 0.5 mm thickness). Column chromatography was performed using silica gel (particle size 100-210 μm (regular), 40-50 μm (flush)). Optical rotations were recorded on a digital polarimeter at ambient temperature. IR spectra were measured on a Fourier transform infrared spectrometer. ^{1}H NMR and ^{13}C NMR spectra were measured using $CDCl_3$ as solvent, and chemical shifts are reported as δ values in ppm based on internal TMS (0.00 ppm, ^{1}H) or $CHCl_3$ (7.26 ppm, ^{1}H; 77.0 ppm, ^{13}C). HRMS spectra were taken in EI or FAB mode.

Baylis-Hillman Reaction of 3-(4-Methoxybenzyloxy)propanal (9): β-ICD·H_2O·MeOH[1] (0.90 g, 2.50 mmol) was dissolved into THF (5 mL) and the solution was evaporated by rotary evaporation at room temperature. After repeating this operation three times, the resulting amorphous solid was dried under vacuum at room temperature for 10 min, and dissolved in DMF (24 mL). To this solution were added a solution of **9**[2] (5.26 g, 27.1 mmol) in DMF (5 mL) and HFIPA (6.3 mL, 37.8 mmol) at –55 ˚C. After stirring at –55 ˚C for 23 h, the reaction was quenched with 0.1 M HCl (25 mL). The reaction mixture was extracted with EtOAc, washed with saturated $NaHCO_3$ and brine, dried ($MgSO_4$), concentrated and chromatographed (hexane:EtOAc = 5:1 to 2:1) to give **10** (6.14 g, 58 %) and **11** (1.52 g, 14 %) each as a pale yellow oil.

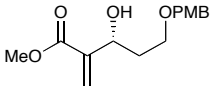


(*R*)-1,1,1,3,3,3-Hexafluoropropan-2-yl 5-(4-Methoxybenzyloxy)-3-hydroxy-2-methylenepentanoate (10): $[\alpha]_D^{24}$ +21.1 (*c* 1.01, $CHCl_3$) (99% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.8 Hz, 2 H), 6.88 (d, *J* = 8.0 Hz, 2 H), 6.52 (s, 1 H), 6.25 (s, 1 H), 5.83-5.80 (m, 1 H), 4.74-4.71 (m, 1H), 4.48 (d, *J* = 11.2 Hz, 1H), 4.43 (d, *J* = 11.2 Hz, 1H), 3.81 (s, 4 H), 3.67 (t, *J* = 5.4 Hz, 2 H), 2.06-2.01 (m, 1 H), 1.86-1.77 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4, 159.4, 140.2, 129.4, 129.0, 113.8, 72.9, 69.6, 68.0, 66.5, 55.0, 35.4; IR (neat) 3473, 1752, 1613, 1513, 1385, 1361, 1248, 1204, 1110, 1038 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{18}F_6O_5$ (M^+) 416.1058, found 416.1053.

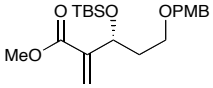


(2*S*,6*S*)-2,6-Bis(2-(4-methoxybenzyloxy)ethyl)-5-methylene-1,3-dioxan-4-one (11): $[\alpha]_D^{24}$ –48.1 (*c* 1.10, $CHCl_3$) (38% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.8 Hz, 4 H), 6.87 (d, *J* = 8.3 Hz, 4 H), 6.48 (d, *J* = 2.4 Hz, 1 H),

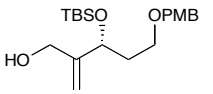
5.59 (dd, *J* = 2.0, 5.4 Hz, 1 H), 5.50 (t, *J* = 5.4 Hz, 1 H), 4.75 (m, 1 H), 4.42 (m, 4 H), 3.80 (s, 6 H), 3.63-3.53 (m, 4 H), 2.2.11-2.03 (m, 3 H), 1.96-1.91 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 159.25, 136.7, 130.1, 129.2, 125.6, 113.7, 99.6, 74.6, 72.8, 65.0, 64.2, 55.2, 35.2, 34.8; IR (neat) 1732, 1610, 1508, 1236, 1176, 1082 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{30}O_7$ (M^+) 442.1991, found 442.1984.



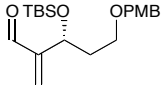
(*R*)-Methyl 5-(4-Methoxybenzyloxy)-3-hydroxy-2-methylene-pentanoate (12): A mixture of **10** (5.63 g, 13.52 mmol) and Et_3N (6.8 mL) in MeOH (68 mL) was stirred at room temperature for 30 min. The reaction mixture was neutralized with Dowex 50 (H^+ form), filtered, concentrated and chromatographed (hexane:EtOAc = 3:1) to give **12** (3.73 g, 98 %,) as a pale yellow oil: $[\alpha]_D^{23}$ +21.5 (*c* 0.95, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 6.27 (s, 1H), 5.92 (s, 1H), 4.69-4.65 (m, 1H), 4.44 (s, 2H), 3.80 (s, 3H), 3.75 (s, 3H), 3.66-3.64 (m, 3H), 2.07-2.01 (m, 1H), 1.87-1.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 159.2, 142.2, 129.3, 124.9, 113.8, 72.8, 69.9, 68.1, 66.5, 55.1, 51.7, 35.6; IR (neat) 3466, 1714, 1613, 1514, 1443, 1299, 1252, 1152, 1088, 1037 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{20}O_5$ (M^+) 280.1311, found 280.1305.



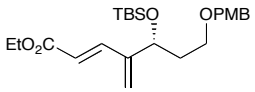
(*R*)-Methyl 5-(4-Methoxybenzyloxy)-3-(*tert*-butyldimethylsilyl)-oxy-2-methylenepen-tanoate: To a stirred solution of **12** (3.72 g, 13.3 mmol) and 2,6-lutidine (4.0 mL, 34.5 mmol) in CH_2Cl_2 (133 mL) at –78 ˚C was added TBSOTf (4.0 mL, 17.3 mmol). After stirring at –78 ˚C for 30 min, the reaction was quenched with saturated $NaHCO_3$, and the mixture stirred at room temperature for 20 min. The reaction mixture was extracted with EtOAc, washed with brine, dried, concentrated and chromatographed (hexane:EtOAc = 10:1) to give the corresponding TBS-ether (5.22 g, quant) as a pale yellow oil: $[\alpha]_D^{24}$ +28.0 (*c* 0.86, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.22 (s, 1H), 5.90 (s, 1H), 4.73-4.70 (m, 1H), 4.39 (s, 2H), 3.80 (s, 3H), 3.74 (s, 3H), 3.54-3.52 (m, 1H), 3.50-3.47 (m 1H), 2.0-1.96 (m, 1H), 1.78-1.73 (m, 1H), 0.89 (s, 9H), 0.04 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 158.9, 143.8, 130.5, 129.0, 124.1, 113.5, 72.2, 67.7, 66.1, 55.0, 51.5, 37.5, 25.6, 17.9; IR (neat) 1722, 1613, 1513, 1465, 1251, 1098, 1038 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{34}O_5Si$ (M^+) 394.2176, found 394.2178.



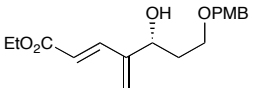
(*R*)-5-(4-Methoxybenzyloxy)-3-(*tert*-butyldimethylsilyl)oxy-2-methylene-pentan-1-ol (13): To a stirred solution of the TBS-ether (5.11 g, 13.0 mmol) in CH_2Cl_2 (65 mL) at –78 ˚C was added DIBAH (0.98 M in hexane, 30.4 mL, 29.8 mmol). After stirring at –78 ˚C for 30 min, saturated Rochelle's salt (35 mL) and Et_2O (60 mL) were added, the mixture was allowed to warm to room temperature over 1 h. The reaction mixture was extracted with EtOAc, washed with brine, dried, concentrated and chromatographed (hexane:EtOAc = 5:1) to give **13** (4.36 g, 99 %) as a clear oil: $[\alpha]_D^{23}$ +15.7 (*c* 1.13, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 5.04 (d, *J* = 9.2 Hz, 2H), 4.43-4.34 (m, 3H), 4.23 (dd, *J* = 5.4 Hz, 4.9 Hz, 1H), 4.14 (dd, *J* = 6.8, 6.8 Hz, 1H), 3.80 (s, 3H), 3.49-3.43 (m, 2H), 2.27 (t, *J* = 5.9, 1H), 1.93-1.85 (m, 2H), 0.88 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 150.2, 130.3, 129.3, 113.7,111.2, 72.6, 72.4, 66.3, 62.8, 55.1, 37.0, 25.8, 18.0, -4.8, -5.2; IR (neat) 3433, 1612, 1513, 1465, 1360, 1300, 1248, 1176, 1088, 1036 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{34}O_4Si$ (M^+) 309.1522, found 309.1506.



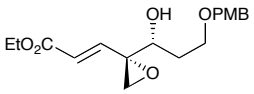
(*R*)-5-(4-Methoxybenzyloxy)-3-(*tert*-butyldimethylsilyl)oxy-2-methylene-pentanal: To a solution of **13** (4.23 g, 11.54 mmol) in CH_2Cl_2 (150 mL) was added Dess-Martin periodinane (7.33 g, 17.31 mmol) at 0 ˚C, and the mixture was stirred at room temperature for 30 min. After addition of saturated $NaHCO_3$ (30 mL) and 10 % $Na_2S_2O_3$ (15 mL), the mixture was stirred at room temperature for 30 min. The reaction mixture was extracted with Et_2O, washed with saturated $NaHCO_3$ and brine, dried and chromatographed (hexane:EtOAc = 20:1) to give the aldehyde (4.20 g, quant) as a colorless oil: $[\alpha]_D^{23}$ +12.0 (*c* 0.63, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.24 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.51 (s, 1H), 6.05 (s, 1H), 4.75-4.72 (m, 1H), 4.39 (s, 2H), 3.80 (s, 3H), 3.55-3.45 (m, 2H), 1.96-1.92 (m, 1H), 1.76-1.54 (m, 1H), 0.88 (s, 9H), 0.03 (s, 3H), -0.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.0, 159.0, 153.4, 133.5, 130.5, 129.1, 113.6, 65.9, 65.8, 55.0, 37.2, 25.7, 18.0, -4.9, -5.3; IR (neat) 1691, 1613, 1513, 1465, 1360, 1301, 1251, 1176, 1105, 1037, 1008 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{32}O_4$ (M^+) 364.2070, found 364.2065.



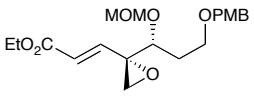
(*R*,*E*)-Ethyl 7-(4-Methoxybenzyloxy)-5-(*tert*-butyldimethyl-silyl)oxy-4-methylene-hept-2-enoate: To a suspension of NaH (60 % dispersion in mineral oil, 673 mg, 16.83 mmol) in THF (100 mL) was added triethyl phosphonoacetate (4.5 mL, 22.44 mmol) at 0 ˚C. The mixture was stirred at 0 °C for 45 min and cooled to –78 ˚C, and a solution of the aldehyde (4.08 g, 11.19 mmol) in THF (12 mL) was added. After stirring at –78 ˚C for 11 h, the reaction was quenched with saturated NH_4Cl (40 mL). The reaction mixture was extracted with Et_2O, washed with water and brine, dried, concentrated and chromatographed (hexane:EtOAc = 15:1) to give the unsaturated ester (3.72 g, 77 %) as a colorless oil: $[\alpha]_D^{22}$ +32.2 (*c* 1.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 16.0 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.12 (d, *J* = 16.0 Hz, 1 H), 5.54 (s, 1H), 5.42 (s, 1H), 4.58-4.45 (m, 1H), 4.43 (d, *J* = 11.2 Hz, 1H), 4.37 (d, *J* = 11.2 Hz, 1H), 4.23 (q, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 3.58-3.53 (m, 1H), 3.47-3.43 (m, 1H), 1.90-1.87 (m, 1H), 1.81-1.77 (m, 1H), 1.30 (t, *J* = 7.3 Hz, 3H), 0.88 (s, 9H), 0.03 (s, 3H), -0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 159.0, 147.8, 143.4, 130.5, 129.1, 121.7, 118.9, 113.6, 72.6, 69.5, 66.4, 60.3, 55.2, 37.9, 25.7, 18.0, 14.2, -4.7, -5.2; IR (neat) 1716, 1611, 1513, 1465, 1305, 1250, 1175, 1097, 1039 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{38}O_5Si$ (M^+) 434.2489, found 434.2483.



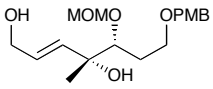
(*R*,*E*)-Ethyl 7-(4-Methoxybenzyloxy)-5-hydroxy-4-methylene-hept-2-enoate (14): To a solution of the unsaturated ester (3.54 g, 8.54 mmol) in THF (17 mL) was added TBAF (1.0 M in THF, 12.8 mL, 12.81 mmol) at 0 ˚C, and the mixture was stirred at room temperature for 30 min. The reaction mixture was diluted with EtOAc, washed with water and brine, dried, concentrated and chromatographed (hexane: EtOAc = 3:1) to give **14** (2.62 g, 90 %) as a pale yellow viscous oil: $[\alpha]_D^{22}$ +18.0 (*c* 1.08, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 16.1 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 5.96 (d, *J* = 16.0 Hz, 1H), 5.66 (s, 1H), 5.50 (s, 1H), 4.64-4.61 (m, 1H), 4.45 (s, 2H), 4.20 (q, *J* = 6.8 Hz, 2H), 3.80 (s, 3H), 3.69-3.61 (m, 2H), 3.44 (s, 1H), 1.99-1.94 (m, 1H), 1.86-1.81 (m, 1H), 1.29 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 159.3, 146.5, 143.8, 129.7, 129.3, 121.7, 118.4, 113.8, 73.0, 70.5, 68.4, 60.4, 55.2, 35.7, 14.2; IR (neat) 3470, 1711, 1611, 1513, 1462, 1366, 1303, 1248, 1179, 1095, 1035 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{24}O_5$ (M^+) 320.1623, found 320.1612.



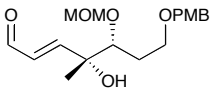
(*E*)-Ethyl 3-((*S*)-2-((*R*)-3-(4-Methoxybenzyloxy)-1-hydroxypropyl)-oxiran-2-yl)acrylate (15): To a solution of **14** (900 mg, 2.81 mmol) and V(O)(acac)$_2$ (149 mg, 0.56 mmol) in CH_2Cl_2 (28 mL) at –20 ˚C was added *tert*-butyl hydroperoxide (2.97 M in CH_2Cl_2, 2.0 mL, 5.62 mmol) over 5 min. The mixture was gradually warmed to room temperature over 1 h, diluted with EtOAc (50 mL) and stirred vigorously with saturated $Na_2S_2O_3$ (20 mL) until the layers were separated. The reaction mixture was filtered through Celite, extracted with EtOAc, washed with brine, dried and concentrated. The residue was chromatographed (hexane:EtOAc = 3:1) to give **15** (799 mg, 87 %) as a clear viscous oil: $[\alpha]_D^{23}$ +71.7 (*c* 1.56, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 15.6 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.10 (d, *J* = 15.6 Hz, 1H), 4.45 (s, 2H), 4.21 (q, *J* = 7.8 Hz, 2H), 3.80 (s, 3H), 3.72-3.70 (m, 2H), 3.65-3.62 (m, 1H), 3.34 (brs, 1H), 3.02 (d, *J* = 5.8 Hz, 1H), 2.69 (d, *J* = 5.8 Hz, 1H), 1.86-1.81 (m, 2H), 1.28 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 159.2, 142.6, 129.6, 129.31, 122.4, 113.8, 72.9, 72.4, 68.1, 60.5, 59.5, 55.2, 55.1, 32.7, 14.1; IR (neat) 3474, 1719, 1655, 1612, 1513, 1463, 1367, 1251, 1177, 1096, 1036 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{24}O_6$ (M^+) 336.1573, found 336.1569.



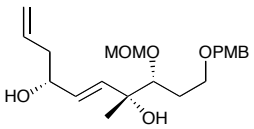
(*E*)-Ethyl 3-((*S*)-2-((*R*)-3-(4-Methoxybenzyloxy)-1-(methoxy-methoxy)propyl)oxiran-2-yl)acrylate (16): To a solution of **15** (699 mg, 2.05 mmol) and *i*-Pr$_2$EtN (1.43 mL, 8.32 mmol) in CH_2Cl_2 (20 mL) was added methoxymethyl chloride (0.32 mL, 4.16 mmol) at 0 ˚C. After being heated at reflux for 12 h, the reaction mixture was diluted with EtOAc, washed with brine (10 mL), dried, concentrated and chromatographed (hexane:EtOAc = 6:1) to give **16** (689 mg, 93 %) as a clear oil: $[\alpha]_D^{25}$ +68.8 (*c* 1.12, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 15.6 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.11 (d, *J* = 16.0 Hz, 1H), 4.71 (d, *J* = 6.8 Hz, 1H), 4.61 (d, *J* = 6.8 Hz, 1H), 4.44 (d, *J* = 11.7 Hz, 1H), 4.41 (d, *J* = 11.7 Hz, 1H), 4.21 (q, *J* = 6.8 Hz, 2H), 3.80 (s, 3 H), 3.57-3.53 (m, 2H), 3.47-3.44 (m, 1H), 3.34 (s, 3H), 3.01 (d, *J* = 5.8 Hz, 1H), 2.71 (d, *J* = 5.8 Hz, 1H), 1.99-1.94 (m, 1H), 1.81-1.76 (m, 1H), 1.28 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 159.0, 142.6, 130.3 129.1, 122.3, 113.6, 96.1, 76.2, 72.4, 65.5, 60.4, 58.0, 56.8, 55.5, 55.1, 32.5, 14.0; IR (neat) 1719, 1655, 1610, 1513, 1463, 1366, 1306, 1251, 1213, 1170, 1102, 1035 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{28}O_7$ (M^+) 380.1836, found 380.1830.



(*E*,4*R*,5*R*)-7-(4-Methoxybenzyloxy)-5-(methoxymethoxy)-4-methylhept-2-ene-1,4-diol (18): To a solution of **16** (315 mg, 0.82 mmol) in THF (8 mL) was added LiEt$_3$BH (1.0 M in THF, 3.4 mL, 3.4 mmol) at –78 ˚C. After being stirred at –78 ˚C for 30 min, the mixture was warmed to 0 ˚C over 45 min. Water (8 mL) was added and the reaction mixture was extracted with EtOAc, washed with brine, dried, concentrated and chromatographed (hexane:EtOAc = 1:1) to give **18** (282 mg, 98 %) as a clear oil: $[\alpha]_D^{24}$ –17.3 (*c* 1.61, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 5.95 (dt, *J* = 15.6, 10.7 Hz, 1H), 5.74 (d, *J* = 15.6 Hz, 1H), 4.67 (d, *J* = 6.3 Hz, 1H), 4.62 (d, *J* = 6.3 Hz, 1H), 4.44 (d, *J* = 11.2 Hz, 1H), 4.38 (d, *J* = 11.2 Hz, 1H), 4.17-4.14 (m, 2H), 3.80 (s, 4H), 3.54-3.48 (m, 3H), 3.40 (s, 3H), 1.91-1.85 (m, 1H), 1.67-1.62 (m, 1H), 1.35 (t, *J* = 6.3 Hz, 1H), 1.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 135.2, 130.2, 129.5, 129.1, 113.8, 98.5, 85.1, 73.9, 72.7, 66.6, 63.1, 56.1, 55.3, 31.4, 32.7, 22.7; IR (neat) 3415, 1612, 1513, 1460, 1368, 1301, 1248, 1151, 1098, 1034 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{28}O_6$ (M^+) 340.1886, found 340.1869.



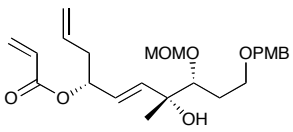
(*E*,4*R*,5*R*)-7-(4-methoxybenzyloxy)-4-hydroxy-5-(methoxymeth-oxy)-4-methylhept-2-enal (19): To a solution of **18** (50 mg, 0.15 mmol) in CH_2Cl_2 (3 mL) was added Dess-Martin periodinane (97.5 mg, 0.23 mmol) at 0 ˚C, and the mixture was stirred at room temperature for 30 min. After addition of saturated $NaHCO_3$ (4 mL) and 10 % $Na_2S_2O_3$ (2 mL), the reaction mixture was stirred at room temperature for 30 min and then extracted with Et_2O. The extract was washed with saturated $NaHCO_3$ and brine, dried, concentrated and chromatographed (hexane:EtOAc = 3:1) to give **19** (51 mg, quant) as a colorless oil: $[\alpha]_D^{25}$ –13.2 (*c* 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (d, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 15.6 Hz, 1H), 6.42 (dd, *J* = 8.2, 15.6 Hz, 1H), 4.67 (s, 2H), 4.48 (d, *J* = 11.2 Hz, 1H), 4.42 (d, *J* = 11.2 Hz, 1H), 4.25 (s, 1H), 3.84 (s, 3H), 3.67-3.54 (m, 3H), 3.42 (s, 3H), 1.92-1.87 (m, 1H), 1.81-1.78 (m, 1H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 161.0, 131.2, 129.7, 129.5, 113.9, 97.8, 83.7, 74.7, 72.9, 66.2, 56.2, 55.3, 31.4, 23.6; IR (neat) 3439, 1689, 1612, 1513, 1460, 1366, 1300, 1248, 1150, 1102, 1032 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{26}O_6$ (M^+) 338.1763, found 338.1713.



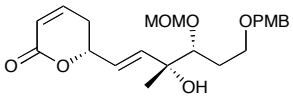
(*E*,4*R*,7*R*,8*R*)-10-(4-methoxybenzyloxy)-8-(methoxymethoxy)-7-methyldeca-1,5-diene-4,7-diol (20).

Brown's Method: To a stirred solution of (+)-*B*-methoxydiisopinocampheylborane (674 mg, 2.13 mmol) in Et_2O (8.5 mL) was added allylmagnesium bromide (1.0 M in Et_2O; 2.1 mL, 2.1 mmol) at -78 ˚C. After 30 min, the mixture was allowed to warm to room temperature and stirred for 16 h. The resulting solution was added to a mixture of **19** (288 mg, 0.85 mmol) in Et_2O (4 mL) via cannula at –78 °C. After stirring for 1 h at –78 °C, 30% NaOH (3 mL) and 30% H_2O_2 (3 mL) were added at 0 °C. After being stirred at room temperature overnight, the reaction mixture was diluted with water (10 ml), extracted with Et_2O, washed water and saturated NaCl, dried, and concentrated. The residue was purified by flush chromatography (benzene:EtOAc = 2:1) to give **20** (256 mg, 79%) as a pale yellow oil.

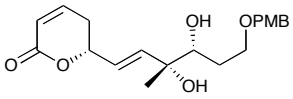
Yamamoto's Method: A mixture of AgF (11.5 mg, 0.0914 mmol) and (*R*)-*p*-Tol-BINAP[3] (62 mg, 0.0914 mmol) in MeOH (2 mL) was stirred at 20 ˚C for 10 min with exclusion of direct light. To the resulting solution were added dropwise a solution of **19** (155 mg, 0.457 mmol) in MeOH (1.5 mL) and allyltrimethoxysilane (115 μL, 0.685 mmol) successively at –20 ˚C. After stirring at –20 °C for 5 h, the reaction was quenched by the addition of a mixture of 1 M HCl (2.2 mL) and KF (220 mg), and the mixture was stirred at room temperature for 30 min. The resulting precipitates were filtered off through Celite and silica gel. The filtrate was dried, concentrated and chromatographed (hnexane:EtOAc = 2:1) to give **20** (141 mg, 81%) as a colorless oil. The absolute configuration and diastereomeric ratio (dr = 94:6) of the newly formed asymmetric center were determined by ^{1}H NMR analysis of the corresponding (*R*)- and (*S*)-MTPA ester: $[\alpha]_D^{24}$ –16.9 (*c* 1.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.2 Hz, 2H), 5.86-5.72 (m, 3H), 5.14 (d, *J* = 17.0 Hz, 1H), 5.13 (d, *J* = 10.5 Hz, 1H), 4.68 (d, *J* = 6.3 Hz, 1H), 4.62 (d, *J* = 6.3 Hz, 1H), 4.48 (d, *J* = 11.2 Hz, 1H), 4.42 (d, *J* = 11.2 Hz, 1H), 4.20-4.19 (m, 1H), 3.81 (s, 3H), 3.57 (s, 1H), 3.57-3.48 (m, 3H), 3.41 (s, 3H), 2.33-2.28 (m, 2H), 1.92-1.89 (m, 1H), 1.68-1.61 (m, 2H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 134.8, 134.2, 131.8, 129.4, 118.2, 113.8, 98.4, 85.2, 73.8, 72.6, 71.1, 66.5, 56.0, 55.2, 4.8, 31.4, 22.9; IR (neat) 3422, 1611, 1513, 1459, 1368, 1301, 1248, 1150, 1098 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{32}O_6$ (M^+) 380.2199, found 380.2172.



(*E*,4*R*,7*R*,8*R*)-10-(4-Methoxybenzyloxy)-7-hydroxy-8-(methoxymethoxy)-7-methyldeca-1,5-dien-4-yl Acrylate: To a solution of **20** (1 g, 2.63 mmol) and *i*-Pr_2EtN (0.99 mL, 5.79 mmol) in CH_2Cl_2 (25 mL) was added acryloyl chloride (0.43 mL, 5.26 mmol) at 0 ˚C, and the mixture was stirred at 0 ˚C for 15 min. After addition of saturated $NaHCO_3$ (7.0 mL), the mixture was stirred at 0 ˚C for 1 h. The reaction mixture was extracted with EtOAc, washed with brine, dried, concentrated and chromatographed (hexane:EtOAc = 4:1) to afford the acrylate (891 mg, 78 %) as a colorless oil: $[\alpha]_D^{24}$ –2.2 (*c* 1.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.3 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 6.36 (d, *J* = 17.0 Hz, 1H), 6.12 (dd, *J* = 10.7, 17.0 Hz, 1H), 5.83-5.71 (m, 4H), 5.44-5.40 (m, 1H), 5.11-5.05 (m, 2H), 4.66 (d, *J* = 6.8 Hz, 1H), 4.62 (d, *J* = 6.8 Hz, 1H), 4.46 (d, *J* = 11.2 Hz, 1H), 4.40 (d, *J* = 11.2 Hz, 1H), 3.84 (s, 1H), 3.81 (s, 3H), 3.56-3.46 (s, 3H), 3.40 (s, 3H), 2.43 (t, *J* = 5.8 Hz, 2H), 1.88-1.85 (m, 1H), 1.67-1.62 (m, 1H), 1.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 159.2, 137.1, 133.1, 130.5, 129.3, 128.7, 127.3, 117.9, 113.8, 98.3, 85.0, 73.9, 73.4, 72.5, 66.5, 56.0, 55.2, 39.0, 31.2, 23.0; IR (neat) 3445, 1724, 1614, 1513, 1460, 1405, 1367, 1296, 1249, 1193, 1100, 1040 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{34}O_7$ (M^+) 434.2305, found 434.2299.

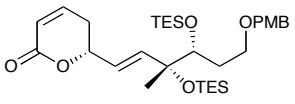


(*R*)-6-((*E*,3*R*,4*R*)-6-(4-Methoxybenzyloxy)-3-hydroxy-4-(methoxymethoxy)-3-methylhex-1-enyl)-5,6-dihydropyran-2-one (21): To a solution of the acrylate (880 mg, 2.02 mmol) in CH_2Cl_2 (30 mL) was added Grubbs second generation catalyst (172 mg, 0.202 mmol), and the mixture was heated at reflux for 45 min. After addition of saturated $NaHCO_3$ (6 mL) at 0 °C, the reaction mixture was extracted with EtOAc, washed with brine, dried and concentrated. The residue was then chromatographed (hexane:EtOAc = 2:1) to give **21** (700 mg, 85%.) as a pale brown oil: $[\alpha]_D^{25}$ +10.3 (*c* 0.33, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.8 Hz, 2 H), 6.88 (d, *J* = 8.7 Hz, 3H), 6.03 (d, *J* = 2.4 Hz, 1H), 5.90 (d, *J* = 2.4 Hz, 2H), 4.93 (m, 1H), 4.67 (d, *J* = 6.9 Hz, 1H), 4.63 (d, *J* = 6.9 Hz, 1H), 4.46 (d, *J* = 11.4 Hz, 1H), 4.40 (d, *J* = 11.4 Hz, 1H), 3.97 (s, 1H), 3.80 (s, 3H), 3.53-3.08 (m, 3H), 3.40 (s, 3H), 2.44-2.39 (m, 2H), 1.90-1.86 (m, 1H), 1.68-1.56 (m, 1H), 1.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 159.2, 144.2, 137.9, 137.8, 137.7, 130.1, 129.6, 129.4, 126.3, 121.5, 113.8, 98.2, 84.8, 73.8, 72.6, 66.3, 56.0, 55.2, 31.3, 29.7, 23.0; IR (neat) 3442, 1718, 1612, 1512, 1456, 1378, 1299, 1246, 1152, 1092, 1028 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{30}O_7$ (M^+) 406.1991, found 406.1982.

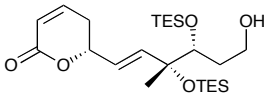


(6*R*)-6-[(3*R*,4*R*,1*E*)-6-(4-Methoxybenzyloxy)-3-methyl-3,4-dihydroxyhexen-1-yl]-5,6-dihydropyran-2-one (22): To a solution of **21** (51 mg, 0.125 mmol) in *i*-PrOH (1.5 mL) was added $ZrCl_4$ (23 mg, 0.1 mmol), and the mixture was stirred at room temperature for 24 h.[4] The solvent was evaporated and the residue was extracted with EtOAc, washed with brine, dried and concentrated. The residue was chromatographed (hexane:EtOAc = 1:2) gave **22** (31 mg, 67%) as a pale yellow oil. This compound was shown to be enantiomerically pure by ^{1}H NMR (500 MHz) analysis of the corresponding (*R*)- and (*S*)-MTPA esters: $[\alpha]_D^{20}$ +34.7 (*c* 0.99, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.86 (m, 1H), 6.02 (dt, *J* = 9.9, 1.2 Hz, 1H), 5.95 (d, *J* = 15.6 Hz, 1H), 5.87 (dd, *J* = 5.1, 15.6 Hz, 1H), 4.93 (dt, *J* = 9.9, 5.1 Hz, 1H), 4.44 (s, 2H), 3.79 (s, 3H), 3.72-3.64 (m 3H), 3.48 (brs, 1H), 2.78 (brs, 1H), 2.46-2.42 (m, 2H), 1.78-1.75 (m, 2H), 1.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 159.4, 144.9, 138.5, 129.7,

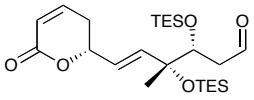
129.5, 126.1, 121.5, 113.9, 76.9, 74.3, 73.1, 69.0, 55.3, 30.5, 29.9, 22.8; IR (neat) 3446, 1722, 1612, 1513, 1460, 1381, 1299, 1249, 1151, 1096, 1034 cm^{-1}; MS (FAB, NBA) *m/z* 363 ($M+H^+$).



(6*R*)-6-[(3*R*,4*R*,1*E*)-6-(4-Methoxybenzyloxy)-3-methyl-3,4-di(triethylsilanyloxy)hex-en-1-yl]-5,6-dihydropyran-2-one (23): To a solution of **22** (851 mg, 2.35 mmol) and 2,6-litidine (0.82 mL, 7.04 mmol) in CH_2Cl_2 (17 mL) was added TESOTf (1.3 mL, 5.75 mmol) at –78 °C. After stirring at –78 °C for 30 min, the reaction was quenched with saturated $NaHCO_3$ (100 mL). The reaction mixture was extracted with CH_2Cl_2, dried, concentrated and chromatographed (hexane:EtOAc = 6:1) gave **23** (1.26 g, 91%) as a colorless oil: $[\alpha]_D^{18}$ +36.5 (*c* 1.04, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.86 (m, 1H), 6.04 (dt, *J* = 9.6, 1.7 Hz, 1H), 5.92 (d, *J* = 15.9 Hz, 1H), 5.76 (dd, *J* = 6.6, 15.9 Hz, 1H), 4.92 (q, *J* = 7.2 Hz, 1H), 4.40 (s, 2H), 3.80 (s, 3H), 3.58 (dd, *J* = 3.6, 7.8 Hz, 1H), 3.45 (dd, *J* = 6.3, 7.8 Hz, 2H), 2.40 (m, 2H), 1.94 (ddt, *J* = 3.6, , 14.1, 7.8 Hz, 1H), 1.41 (ddt, *J* = 7.8, 14.1 6.3 Hz, 1H), 1.33 (s, 3H), 0.94 (t, *J* = 7.8 Hz, 9H), 0.94 (t, *J* = 7.8 Hz, 9H), 0.59 (q, *J* = 7.8 Hz, 6H), 0.58 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 159.1, 144.8, 138.3, 129.3, 125.6, 121.7, 113.7, 78.1, 77.8, 76.9, 72.5, 67.5, 55.3, 33.4, 29.9, 25.6, 7.2, 7.1, 6.9, 5.4; IR (neat) 1730 , 1514, 1246, 1105, 1007 cm^{-1}; MS (FAB, NBA) *m/z* 363 ($M+H^+$).



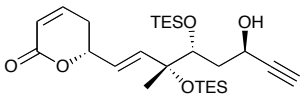
(6*R*)-6-[(3*R*,4*R*,1*E*)-6-Hydroxy-3-methyl-3,4-di(triethylsilan-yloxy)-hexen-1-yl]-5,6-dihydropyran-2-one: To an ice-cooled solution of **23** (356 mg, 0.603 mmol) in CH_2Cl_2-H_2O (20:1, 27 mL) was added DDQ (344 mg, 0.731 mmol). After being stirred at room temperature for 1 h, the reaction mixture was diluted with saturated $NaHCO_3$ (50 mL), extracted with CH_2Cl_2, washed with water and brine, dried, and concentrated. The residue was chromatographed (hexane:EtOAc = 4:1 to 2:1) gave the alcohol (282.4 mg, 99%) as a colorless oil: $[\alpha]_D^{23}$ +42.8 (*c* 1.01, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 6.88 (dt, *J* = 3.9, 9.6 Hz, 1H), 6.05 (dt, *J* = 1.5, 9.9 Hz, 1H), 5.93 (dd, *J* = 0.9, 15.9 Hz, 1H), 5.77 (dd, *J* = 6.3, 15.9 Hz, 1H), 4.96 (q, *J* = 6.3 Hz, 1H), 3.67 (brquint, *J* = 5.1 Hz, 2H), 2.45 (m, 2H), 1.95 (brt, *J* = 5.1 Hz, 2H), 1.86 (m, 1H), 1.58 (d, *J* = 2.4 Hz, 3H), 1.53 (m, 1H), 0.97 (t, *J* = 8.1 Hz, 9H), 0.96 (t, *J* = 8.1 Hz, 9H), 0.63 (q, *J* = 8.1 Hz, 6H), 0.62 (q, *J* = 8.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 144.7, 138.0, 125.8, 121.59, 78.0, 77.9, 77.7, 60.2, 36.4, 29.8, 25.4, 7.1, 7.0, 6.8, 5.2; IR (neat) 3448, 1724, 1459, 1381, 1244, 1105, 1012 cm^{-1}; MS (FAB, NBA) *m/z* 493 ($M+Na^+$).



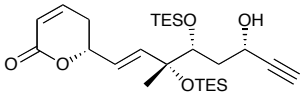
(3*R*,4*R*,5*E*)-4-Methyl-6-[(2*R*)-6-oxo-3,6-dihydro-2*H*-pyran-2-yl]-3,4-di(triethylsilan-yloxy)-hex-5-enal (24): To an ice-cooled solution of the alcohol (997 mg, 2.121 mmol) in CH_2Cl_2 (20 mL) Dess-Martin periodinane (2.70 g, 6.378 mmol). After stirring at 0 °C for 1 h, the reaction was quenched with saturated $NaHCO_3$ (50 mL) and 10% $Na_2S_2O_3$ (50 mL). The reaction mixture was extracted with AcOEt, washed with saturated $NaHCO_3$ and brine, dried, and concentrated. The residue was chromatographed (hexane:EtOAc = 2:1) gave **24** (996 mg, quant) as a colorless oil: $[\alpha]_D^{24}$ +42.5 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 9.70 (t, *J* = 2.1 Hz, 1H), 6.89 (ddd, *J* = 4.5, 5.1, 9.6 Hz, 1H), 6.05 (dt, *J* = 2.1, 9.9 Hz, 1H), 5.93 (d, *J* = 15.6 Hz, 1H), 5.78 (dd, *J* = 6.3, 15.6 Hz, 1H), 4.97 (dt, *J* = 6.3, 8.7 Hz, 1H), 4.03 (dd, *J* = 5.1, 6.0 Hz, 1H), 2.62 (ddd, *J* = 2.1, 6.0, 16.5 Hz, 1H), 2.45 (m, 2H), 2.36 (ddd, *J* = 2.1, 5.1, 16.5 Hz, 1H), 1.40 (s, 3H), 0.95 (t, *J* = 7.8 Hz, 9H), 0.94 (t, *J* = 7.8 Hz, 9H), 0.62 (q, *J* = 7.8 Hz, 6H), 0.59 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 200.5, 164.1, 144.7, 137.0, 128.3, 126.8, 121.1, 77.6, 75.2, 47.9, 29.8, 25.6, 6.9, 4.99; IR (neat) 1728, 1240, 1107, 1011 cm^{-1}; MS (FAB, NBA) *m/z* 491 [$(M+Na)^+$].

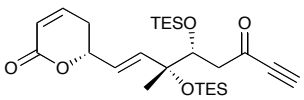
Ethynylation of 24: A suspension of anhydrous $CeCl_3$ (609 mg, 2.47 mmol) in THF (6 mL) was stirred at room temperature for 12 h. To this suspension was added ethynylmagnesium bromide (0.5 M in THF, 4.9 mL, 2.45 mmol) at –78 °C over 5 min. After stirring at –78 °C for 1 h, a solution of **24** (366 mg, 0.781 mmol) in THF (5 mL) was added to the mixture at –78 °C over 7 min. After 10 min, the reaction mixture was allowed to warm to –50 °C, and stirred for 50 min. The reaction was quenched with water (15 mL) and the reaction mixture was filtered through Celite. The filtrate was extracted with Et_2O, washed with water, dried, concentrated and chromatographed (hexane:AcOEt = 4:1 to 2:1) gave an epimeric mixture of the ethynylated compounds (379 mg, 98%) (11*R*:11*S* = 36:64) as a colorless oil. The following data were collected after separation of the epimers by flash column chromatography.



(*R*)-isomer: $[\alpha]_D^{24}$ +46.0 (*c* 1.03, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 6.89 (ddd, *J* = 4.2, 5.1, 9.9 Hz, 1H), 6.05 (dt, *J* = 9.9, 1.5 Hz, 1H), 5.93 (dd, *J* = 0.6, 15.6 Hz, 1H), 5.78 (dd, *J* = 6.3, 15.6 Hz, 1H), 4.97 (ddt, *J* = 0.6, 6.0, 8.1 Hz, 1H), 4.48 (brd, *J* = 9.6 Hz, 1H), 3.75 (dd, *J* = 4.8, 6.9 Hz, 1H), 2.46 (m, 2H), 2.40 (brs, 1H), 2.02 (ddd, *J* = 4.8, 9.6, 14.1 Hz, 1H), 1.62 (ddd, *J* = 3.6, 6.9, 14.1 Hz, 1H), 1.38 (s, 3H), 1.25 (s, 1H), 0.97 (t, *J* = 8.1 Hz, 9H), 0.96 (t, *J* = 8.1 Hz, 9H), 0.65 (q, *J* = 8.1 Hz, 6H), 0.63 (q, *J* = 8.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 144.7, 137.7, 126.3, 121.8, 85.4, 77.9, 72.6, 59.6, 41.7, 29.9, 25.5, 7.2, 7.1, 6.9, 5.4; IR (neat) 3440, 3309, 1722, 1382, 1242, 1103, 1009 cm^{-1}; MS (FAB, NBA) *m/z* 517 [$(M+Na)^+$].

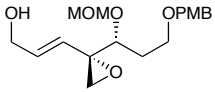


(*S*)-isomer: $[\alpha]_D^{17}$ +25.8 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 6.88 (dt, *J* = 3.6, 9.9 Hz, 1H), 6.05 (dt, *J* = 9.9, 1.5 Hz, 1H), 5.94 (dd, *J* = 0.6, 15.9 Hz, 1H), 5.77 (dd, *J* = 6.3, 15.9 Hz, 1H), 4.96 (ddt, *J* = 0.6, 7.8, 6.3 Hz, 1H), 4.45 (brq, *J* = 4.2 Hz, 1H), 3.79 (dd, *J* = 5.1, 6.3 Hz, 1H), 2.46 (m, 3H), 2.02 (ddd, *J* = 5.1, 6.9, 14.1 Hz, 1H), 1.70 (dt, *J* = 14.1, 6.3 Hz, 1H), 1.40 (s, 3H), 1.25 (s, 1H), 0.97 (t, *J* = 8.1 Hz, 18H), 0.65 (q, *J* = 8.1 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 144.7, 137.6, 126.3, 121.7, 84.9, 78.1, 77.8, 76.8, 73.5, 60.3, 41.6, 30.0, 25.5, 7.2, 7.1, 6.9, 5.4; IR (neat) 3429, 3309, 1724, 1382, 1242, 1105 cm^{-1}; MS (FAB, NBA) *m/z* 517 [$(M+Na)^+$].

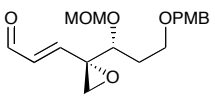


(6*R*)-6-[(3*R*,1*E*)-3-Methyl-6-oxo-3,4-di(triethylsilanyloxy)-oct-1-en-7-ynyl]-5,6-dihyd-ropyran-2-one (3): To an ice-cooled solution of the above-mentioned epimeric mixture (887 mg, 1.80 mmol) in CH_2Cl_2 (40 mL) was added Dess-Martin periodinane (3.78 g, 8.90 mmol). After stirring at 0 °C for 4 h, the reaction was quenched with saturated $NaHCO_3$ (120 mL) and 10% $Na_2S_2O_3$ (60 mL). The reaction mixture was extracted with AcOEt, washed with saturated $NaHCO_3$ and saturated NaCl, dried, concentrated and chromatographed (hexane:EtOAc = 4:1) to give **3** (841 mg, 95%) as a colorless oil. $[\alpha]_D^{24}$ +56.2 (*c* 1.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 6.88 (ddd, *J* = 3.6, 4.8, 9.6 Hz, 1H), 6.03 (ddd, *J* = 1.5, 2.1, 9.6 Hz), 5.88 (1H, d, *J* = 15.6 Hz), 5.78 (1H, dd, *J* = 5.7, 15.6 Hz), 4.96 (1H, dt, *J* = 5.7, 9.3 Hz, 1H), 4.17 (dd, *J* = 4.8, 6.6 Hz, 1H), 3.22 (s, 1H), 2.89 (dd, *J* = 4.8, 16.5 Hz, 1H), 2.45 (m, 2H), 2.40 (dd, *J* = 6.6, 16.5 Hz, 1H), 1.38 (s, 3H), 0.92 (t, *J* = 8.1 Hz, 9H), 0.93 (t, *J* = 8.1 Hz, 9H), 0.59 (q, *J* =8.1 Hz, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.3, 164.2, 144.7, 136.9, 126.6, 121.7, 81.9, 78.6, 77.6, 77.3, 75.2, 50.0, 29.9, 25.6, 7.2, 7.0, 6.8, 5.1;

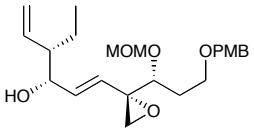
IR (neat) 1730, 1682, 1460, 1383, 1244, 1111, 1007 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{44}O_5Si_2$ (M^+): 492.2727, found: 492.2776.



(*E*)-3-((*S*)-2-((*R*)-3-(4-Methoxybenzyloxy)-1-(methoxymethoxy)propyl)-oxiran-2-yl)prop-2-en-1-ol (17): To a solution of **16** (2.0 g, 5.26 mmol) in THF (25 mL) was added DIBAH (1.03 M in hexane, 17.2 mL, 18.2 mmol) at –78 ˚C. After stirring at –78 ˚C for 1 h, the mixture was treated with saturated Rochelle's salt (10 mL), diluted with EtOAc (20 mL) and allowed to warm to room temperature over 1 h. The reaction mixture was extracted with EtOAc, washed with brine, dried, concentrated and chromatographed (hexane:EtOAc = 3:1) to give **17** (1.5 g, 85 %) as a clear oil: $[\alpha]_D^{26}$ +68.9 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.99 (s, 2H), 4.71 (d, *J* = 6.8 Hz, 1H), 4.59 (d, *J* = 6.8 Hz, 1H), 4.44 (d, *J* = 11.6 Hz, 1H), 4.40 (d, *J* = 11.2 Hz, 1H), 4.17-4.15 (m, 2H), 3.80 (s, 3H), 3.58-3.53 (m, 2H), 3.46 (dd, *J* = 3.4, 9.3 Hz, 1H), 3.34 (s, 3H), 2.93 (d, *J* = 5.8 Hz, 1H), 2.69 (d, *J* = 5.3 Hz, 1H), 1.99-1.96 (m, 1H), 1.82-1.79 (m, 1H), 1.39 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 131.8, 130.7, 129.1, 125.1, 113.5, 95.9, 76.0, 72.3, 65.8, 62.3, 58.1, 55.5, 55.4, 55.0, 32.3; IR (neat) 3437, 1612, 1513, 1462, 1363, 1300, 1247, 1153, 1100, 1035 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{26}O_6$ (M^+) 338.1663, found 338.1729.

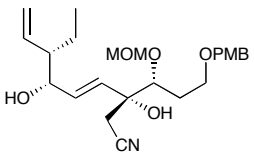


(*E*)-3-((*S*)-2-((*R*)-3-(4-Methoxybenzyloxy)-1-(methoxymethoxy)propyl)-oxiran-2-yl)acrylaldehyde (25): To a solution of **17** (1.4 g, 4.1 mmol) in CH_2Cl_2 (20 mL) was added Dess-Martin periodinane (2.6 g, 6.2 mmol) at 0 ˚C, and the mixture was stirred at room temperature for 2 h. After addition of saturated $NaHCO_3$ (8 mL) and 10 % $Na_2S_2O_3$ (4 mL), the mixture was stirred at room temperature for 30 min and then extracted with EtOAc. The extract was washed with saturated $NaHCO_3$ and brine, dried and concentrated. The residue was purified by flash column chromatography (hexane:EtOAc = 3:1) to give **25** (1.18 g, 86%.) as a pale yellow oil: $[\alpha]_D^{23}$ +77.4 (*c* 1.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 15.6 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 2H), 6.38 (dd, 7.8, 15.6 Hz, 1H), 4.73 (d, *J* = 6.8 Hz, 1H), 4.64 (d, *J* = 6.8 Hz, 1H), 4.44 (d, *J* = 11.2 Hz, 1H), 4.40 (d, *J* = 11.2 Hz, 1H), 3.80 (s, 3H), 3.58-3.50 (m, 3H), 3.36 (s, 3H), 3.10 (d, *J* = 5.8 Hz, 1H), 2.78 (d, *J* = 5.8 Hz, 1H), 2.05-1.94 (m, 1H), 1.82-1.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.8, 159.1, 151.3, 132.4, 130.2, 129.2, 127.3, 113.6, 96.3, 76.2, 72.5, 65.3, 58.2, 57.29, 55.6, 55.1, 32.6; IR (neat) 1691, 1613, 1513, 1462, 1363, 1301, 1248, 1116, 1039 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{24}O_6$ (M^+) 336.1577, found 336.1581.

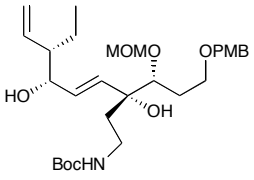


(*E*,3*S*,4*S*)-1-((*S*)-2-((*R*)-3-(4-Methoxybenzyloxy)-1-(methoxymethoxy)-propyl)oxiran-2-yl)-4-ethylhexa-1,5-dien-3-ol (26): To a stirred suspension of *t*-BuOK (1.2 g, 10.7 mmol) in THF (15 mL) at –78 °C were added (*Z*)-2-pentene (1.7 mL, 16 mmol) and *n*-BuLi (1.65 M in hexane, 6.4 mL, 10.7 mmol), and the mixture was stirred at –50 °C for 20 min. The mixture was cooled to –78 °C and a solution of (+)-*B*-methoxydiisopinocampheylborane (4.46 g, 13.3 mmol) in Et_2O (12 mL), $BF_3{\cdot}Et_2O$ (2.1 mL, 21.3 mmol) and **25** (0.90 g, 2.67 mmol) were sequentially added. After being stirred at –78 °C for 3 h, 1 M NaOH (30 mL) was added, and the mixture was stirred at room temperature for 8 h. The reaction mixture was filtered through Celite, extracted with AcOEt, washed with water and brine, dried and concentrated. Purification of the residue by flash chromatography (hexane:AcOEt = 5:1 to 2:1 to 1:1) gave **26** (0.90 g, 83%) as a pale colorless oil:

$[\alpha]_D^{24}$ +63.2 (*c* 1.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.96 (d, *J* = 15.2 Hz, 1H), 5.93 (dd, *J* = 6.3 Hz, 15.6 Hz, 1H), 5.50 (ddd, *J* = 7.8, 10.2, 17.0 Hz, 1H), 5.15 (d, *J* = 10.2 Hz, 1H), 5.09 (d, *J* = 17.0 Hz, 2H), 4.71 (d, *J* = 6.8 Hz, 1H), 4.58 (d, *J* = 6.8 Hz, 1H), 4.44 (d, *J* = 11.7 Hz, 1H), 4.40 (d, *J* = 11.7 Hz, 1H), 4.11-4.06 (m, 1H), 3.79 (s, 3H), 3.56-3.52 (m, 2H), 3.44 (dd, *J* = 3.4, 9.2 Hz, 1H), 3.33 (s, 3H), 2.92 (d, *J* = 5.8 Hz, 1H), 2.65 (d, *J* = 5.8 Hz, 1H), 2.11-2.08 (m, 1H), 1.98-1.90 (m, 1H), 1.80-1.75 (m, 2H), 1.55-1.45 (m, 1H), 1.9-1.20 (m, 1H), 1.85 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 137.8, 132.5, 130.4, 129.2, 126.1, 118.2, 113.6, 95.9, 76.3, 73.9, 72.4, 65.9, 58.2, 56.2, 55.5, 55.2, 52.4, 32.5, 23.1, 11.7; IR (neat) 3461, 1612, 1512, 1460, 1364, 1300, 1247, 1154, 1104, 1037 cm^{-1}; HRMS (FAB) calcd for $C_{23}H_{34}O_6$ (M^+) 406.2314, found 406.2355.

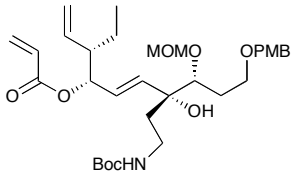


(*E*,3*R*,6*S*,7*S*)-3-((*R*)-3-(4-methoxybenzyloxy)-1-(methoxyme-thoxy)propyl)-7-ethyl-3,6-dihydroxynona-4,8-dienenitrile (27): To a degassed solution of **26** (390 mg, 0.96 mmol) in THF (15 mL) was added LiCN.acetone[5] (349 mg, 3.84 mmol), and the mixture was heated at 45 ˚C for 20 h. The reaction mixture was cooled to room temperature, diluted with EtOAc, washed with brine, dried and concentrated. The residue was chromatographed (hexane:EtOAc = 3:1 to 1:1) to give **27** (333 mg, 80%) as a pale yellow oil: $[\alpha]_D^{24}$ +26.0 (*c* 1.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.99 (dd, *J* = 5.8, 15.6 Hz, 1H), 5.71 (d, *J* = 17.1 Hz, 1H), 5.51 (dt, *J* = 17.1, 10.2 Hz, 1H), 5.15 (d, *J* = 10.2 Hz, 1H), 5.09 (d, *J* = 17.1 Hz, 1H), 4.89 (s, 1H), 4.67 (d, *J* = 6.8 Hz, 1H), 4.63 (d, *J* = 6.8 Hz, 1H), 4.41 (s, 2H), 4.12 (t, *J* = 5.4 Hz, 1H), 4.11 (s, 3H), 3.63 (t, *J* = 5.8 Hz, 1H), 3.57-3.50 (m, 2H), 3.40 (s, 3H), 2.73 (d, *J* = 16.6 Hz, 1H), 2.58 (d, *J* = 16.6 Hz, 1H), 2.14-2.09 (m, 1H), 1.99-1.94 (m, 1H), 1.86 (s, 1H), 1.72-1.68 (m, 1H), 1.52-1.48 (m, 1H), 1.27-1.21 (m, 1H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 137.9, 133.2, 130.1, 129.4, 129.2, 118.3, 117.5, 113.8, 97.6, 83.6, 74.1, 73.6, 72.8, 66.5, 56.1, 55.1, 52.4, 31.2, 27.5, 23.1, 11.8; IR (neat) 3423, 2253, 1612, 1513, 1459, 1419, 1363, 1300, 1247, 1090, 1028 cm^{-1}; HRMS (FAB) calcd for $C_{24}H_{35}NO_6$ (M^+) 433.2473, found 433.2464.

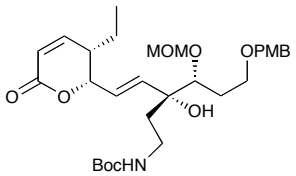


(*E*,3*S*,4*S*,7*R*,8*R*)-10-(4-Methoxybenzyloxy)-7-(2-(butoxycarbonyl-aminoethyl)-3-ethyl-8-(methoxymethoxy)deca-1,5-diene-4,7-diol (28): To a solution of **27** (370 mg, 0.85 mmol) in Et_2O (15 mL) was added $LiAlH_4$ (129 mg, 3.41 mmol) at 0 ˚C, and the mixture was stirred at room temperature for 4 h. The reaction was quenched with water (2.5 mL) at 0 ˚C, and the reaction mixture was filtered through Celite which was washed with MeOH (5 mL). The filtrate and washings were combined. To this solution were added $NaHCO_3$ (573 mg, 6.9 mmol) and $(Boc)_2O$ (0.4 mL, 1.70 mmol), and the mixture was stirred at room temperature for 2 h. Most of the MeOH was evaporated and the residue was extracted with EtOAc. The extract was concentrated, dried and chromatographed (hexane:EtOAc = 2:1 to 1:1) to give **28** (379 mg, 83%) as a colorless oil: $[\alpha]_D^{22}$ +13.8 (*c* 1.00, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 5.85 (dd, *J* = 5.8, 15.6 Hz, 1H), 5.60 (d, *J* = 15.1 Hz, 1H), 5.51 (d, *J* = 9.8 Hz, 1H), 5.47 (d, *J* = 9.8 Hz, 1H) 5.17 (brs, 1H), 5.12 (d, *J* = 13.1 Hz, 1H), 5.08 (d, *J* = 17.6 Hz, 1H), 4.63 (d, *J* = 6.8 Hz, 1H), 4.60 (d, *J* = 6.8 Hz, 1H), 4.43 (d, *J* = 11.2 Hz, 1H), 4.38 (d, *J* = 11.2 Hz, 1H), 4.16 (s, 1H), 4.08 (t, *J* = 6.3 Hz, 1H), 3.80 (s, 3H), 3.55-3.41 (m, 3H), 3.38 (s, 3H), 3.29-3.21 (m, 1H), 3.16-3.11 (m, 1H), 2.13-2.08 (m, 2H), 1.93-1.88 (m, 1H), 1.78-1.61 (m, 4H), 1.58-1.52 (m, 1H), 1.42 (s, 9H), 0.86 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

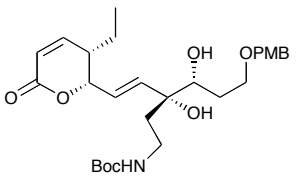
159.2, 155.9, 138.2, 133.1, 131.4, 129.8, 129.3, 117.8, 113.7, 98.0, 85.4, 78.7, 76.3, 74.1, 72.5, 66.6, 55.9, 55.1, 52.4, 36.2, 35.1, 31.1, 28.3, 23.1, 11.78; IR (neat) 3411, 1694, 1613, 1513, 1456, 1366, 1249, 1170, 1097, 1033 cm^{-1}; HRMS (FAB) calcd for $C_{29}H_{47}NO_8$ (M^+) 537.3297, found 537.3302.



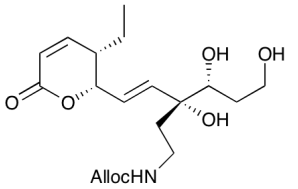
(*E*,3*S*,4*S*,7*R*,8*R*)-10-(4-methoxybenzyloxy)-7-(2-(butoxy-carbonyl)-aminoethyl)-3-ethyl-7-hydroxy-8-(methoxy-methoxy)deca-1,5-dien-4-yl acrylate: To a solution of **28** (537 mg, 0.32 mmol) and *i*-Pr_2EtN (92 μL, 0.71 mmol) in CH_2Cl_2 (3 mL) was added acryloyl chloride (51 μL, 0.65 mmol) at 0 ˚C, and the mixture was stirred at 0 ˚C for 2 h. After addition of saturated $NaHCO_3$ (1 mL), the reaction mixture was stirred at 0 °C for 15 min and then extracted with EtOAc. The extract was washed with brine, dried and concentrated. The residue was chromatographed on florisil (hexane:EtOAc = 4:1) to give the acrylate (155 mg, 81 %) as a colorless oil: $[\alpha]_D^{22}$ +34.7 (*c* 1.00, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.41 (d, *J* = 17.6 Hz, 1H), 6.12 (dd, *J* = 10.2 Hz, 17.1 Hz, 1H), 5.83 (d, *J* = 4.4 Hz, 1H), 5.79 (d, *J* = 4.4 Hz, 1H), 5.63 (d, *J* = 15.1 Hz, 1H), 5.52 (ddd, *J* = 9.2, 10.2, 17.1 Hz, 1H), 5.31 (t, *J* = 6.3 Hz, 1H), 5.23 (brs, 1H), 5.09 (d, *J* = 10.2 Hz, 1H), 5.03 (d, *J* = 17.6 Hz, 2H), 4.59 (s, 2H), 4.43 (d, *J* = 11.7 Hz, 1H), 4.38 (d, *J* = 11.7 Hz, 1H), 4.23 (s, 1H), 3.80 (s, 3H), 3.57-3.47 (m, 2H), 3.42-3.39 (m, 1H), 3.37 (s, 3H), 3.25-3.22 (m, 1H), 3.13-3.10 (m, 1H), 2.26-2.22 (m, 1H), 1.86-1.82 (m, 1H), 1.76-1.61 (m, 3H), 1.52-1.48 (m, 1H), 1.2 (s, 9H), 1.30-1.25 (m, 1H), 0.86 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 159.1, 155.9, 137.3, 135.1, 130.5, 129.8, 129.2, 128.6, 127.3, 117.5, 113.7, 97.9, 85.2, 76.3, 72.4, 66.5, 55.9, 55.1, 49.6, 35.3, 31.0, 28.3, 23.0, 11.4; IR (neat) 3398, 1715, 1614, 1512, 1458, 1403, 1365, 1250, 1176, 1096, 1034 cm^{-1}; HRMS (FAB) calcd for $C_{32}H_{49}NO_9$ (M^+) 591.3427, found 591.3408.



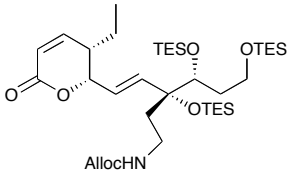
(5*S*,6*S*)-6-((*E*,3*R*,4*R*)-6-(4-Methoxybenzyloxy)-3-(2-(butoxycarbo-nyl)aminoethyl)-3-hydroxy-4-(methoxy-methoxy)hex-1-enyl)-5-ethyl-5,6-dihydropyran-2-one (29): To a solution of the acrylate (140 mg, 0.236 mmol) in CH_2Cl_2 (10 mL) was added Grubbs second generation catalyst (20 mg, 0.0236 mmol), and the mixture was heated at reflux for 12 h. The reaction mixture was cooled to 0 ˚C, treated with saturated $NaHCO_3$ (5 mL) and extracted with EtOAc. The extract was washed with brine, dried, concentrated and purified by flash chromatography (hexane:EtOAc = 1:1.5) to give **29** (101 mg, 76 %.) as a pale yellow oil: $[\alpha]_D^{24}$ +80.7 (*c* 1.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.8 Hz, 2H), 6.93 (dd, *J* = 5.4, 9.7 Hz, 1H), 6.87 (s, *J* = 8.7 Hz, 2H), 6.03 (d, *J* = 9.7 Hz, 1H), 5.88 (s, 2H), 5.17 (brs, 1H), 5.01 (t, *J* = 3.9 Hz, 1H), 4.62 (d, *J* = 6.8 Hz, 1H), 4.59 (d, *J* = 6.3 Hz, 1H), 4.42 (d, *J* = 11.6 Hz, 1H), 4.37 (d, *J* = 11.7 Hz, 1H), 3.80 (s, 3H), 3.55-3.44 (m, 3H), 3.41 (s, 3H), 3.25-3.21 (m, 1H), 3.12-3.07 (m, 1H), 2.41-2.38 (m, 1H), 1.94-1.55 (m, 5H), 1.46 (s, 10H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 159.1, 155.8, 149.8, 129.7, 129.3, 125.5, 120.6, 113.6, 97.9, 85.2, 79.7, 76.3, 72.5, 66.3, 55.9, 55.1, 39.1, 35.1, 31.0, 28.3, 21.4, 10.9; IR (neat) 3394, 1716, 1612, 1513, 1463, 1365, 1249, 1172, 1097, 1031 cm^{-1}; HRMS (FAB) calcd for $C_{30}H_{46}NO_9$ [$(M+1)^+$] 564.3145, found 564.3117.



(5*S*,6*S*)-6-((*E*,3*R*,4*R*)-6-(4-Methoxybenzyloxy)-3-(2-(butoxycarbonyl)aminoethyl)-3,4-dihydroxyhex-1-enyl)-5-ethyl-5,6-dihydropyran-2-one (30): To a solution of **29** (50 mg, 0.08 mmol) in *i*-PrOH (1.5 mL) was added $ZrCl_4$ (16.5 mg, 0.071 mmol) at room temperature, and the mixture was stirred at 50 ˚C for 12 h. The solvent was evaporated, and the residue was extracted with EtOAc. The extract was washed brine, dried and concentrated. Purification of the residue by preparative TLC (hex:EtOAc = 1:2.5) gave **30** (30 mg, 72%) as a pale yellow oil: $[\alpha]_D^{26}$ +83.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.5 Hz, 2H), 6.95 (dd, *J* = 9.8, 5.4 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.04 (d, *J* = 9.8 Hz, 1H), 5.91-5.89 (m, 2H), 5.10-4.95 (m, 2H), 4.44 (s, 2H), 3.80 (s, 3H), 3.70-3.60 (m, 3H), 3.48-3.40 (m, 1H), 3.30-3.09 (m, 2H), 3.09 (s, 1H), 2.44-2.40 (m, 1H), 1.86-1.65 (m, 4H), 1.65-1.54 (m,1H), 1.43 (s, 9H), 1.59-1.39 (m, 1H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 159.2, 156.1, 150.1, 135.7, 129.6, 129.2, 125.0, 120.6, 113.7, 100.5, 79.9, 79.0, 76.5, 72.8, 68.8, 55.1, 39.1, 36.0, 35.3, 30.5, 28.3, 21.4, 10.9; IR (neat) 3417, 1730, 1612, 1520, 1260, 1180 cm^{-1}; HRMS (EI) calcd for $C_{28}H_{41}NO_8$ (M+) 519.2833, found 519.2841.

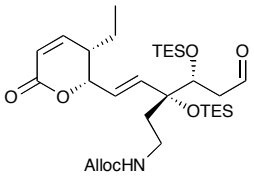


(5*S*,6*S*)-6-((*E*,3*R*,4*R*)-(2-(Allyloxycarbonylamino)ethyl)-3,4,6-trihydroxy-3-hex-1-enyl)-5-ethyl-5,6-dihydropyran-2-one. To an ice-cooled solution of **30** (720 mg, 1.39 mmol) in THF (9.8 ml) was added 5 M HCl (4.2 mL), and the mixture was stirred at room temperature for 2.5 days. The mixture was cooled to 0 °C and $NaHCO_3$ (2.0 g, 28.8 mmol) and allyl chloroformate (0.3 mL, 2.78 mmol) were added. After being stirred at room temperature for 3 h, the reaction mixture was diluted with saturated $NaHCO_3$ (10 mL), extracted with EtOAc, dried, concentrated and chromatographed (EtOAc) to give the triol (520 mg, 98%) as an amorphous solid: $[\alpha]_D^{24}$ +90.6 (*c* 0.53, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (dd, *J* = 9.8 Hz, 5.4 Hz, 1H), 6.05 (d, *J* = 9.8 Hz, 1H), 5.97-5.89 (m, 3H), 5.30 (d, *J* = 17.1 Hz, 1H), 5.20 (d, *J* = 10.5 Hz, 1H), 5.28-5.19 (brs, 1H), 5.08-5.01 (m, 1H), 4.56 (d, *J* = 5.6 Hz, 2H), 3.95-3.80 (m, 2H), 3.75-3.65 (m, 1H), 3.58-3.43 (m, 1H), 3.38-3.28 (m, 2H), 3.28-3.14 (m, 2H), 2.49-2.41 (m, 1H), 2.45-2.27 (m, 1H), 1.97-1.84 (m, 1H), 1.80-1.63 (m, 3H), 1.55-1.40 (m, 1H), 0.96 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 156.5, 150.4, 135.3, 132.7, 125.0, 120.3, 117.4, 80.1, 75.8, 74.6, 65.4, 60.5, 39.1, 36.6, 35.3, 32.7, 21.5, 11.0; IR (neat) 3390, 1714, 1533, 1385, 1257, 1061 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{29}NO_7$ (M^+) 383.1944, found 383.1930.

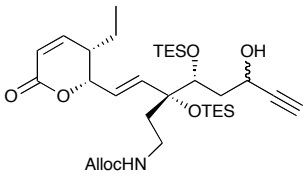


(5*S*,6*S*)-6-((*E*,3*R*,4*R*)-3-(2-(Allyloxycarbonylamino)ethyl)-3,4,6-tris(triethylsilyloxy)-3-hex-1-enyl)-5-ethyl-5,6-dihydropyran-2-one (31): To a solution of the triol (500 mg, 1.3 mmol) and 2,6-litidine (1.5 mL, 13 mmol) in CH_2Cl_2 (13 ml) was added TESOTf (2.1 mL, 9.1 mmol) at –78 °C. After stirring at –78 °C for 3 h, the reaction was quenched with brine (15 mL), and the mixture was stirred at room temperature for 10 h. The reaction mixture was extracted with Et_2O, washed with brine, dried, concentrated and chromatographed (hexane:EtOAc = 10:1 to 5:1) gave **31** (700 mg, 74%) as a colorless oil: $[\alpha]_D^{23}$ +52.2 (*c* 0.65, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (dd, *J* = 9.8 Hz, 5.1 Hz, 1H), 6.05 (d, *J* = 9.8 Hz, 1H), 5.97-5.74 (m, 3H), 5.29 (d, *J* = 17.3 Hz, 1H), 5.19 (d, *J* = 10.2 Hz, 1H), 5.03-5.00 (m, 1H), 4.96-4.82 (brs, 1H), 4.55 (d, *J* = 4.9 Hz, 2H), 3.77-3.52 (m, 3H), 3.38-3.06 (m, 2H), 2.46-2.38 (m, 1H), 2.08-1.99 (m, 1H), 1.92-1.70 (m, 2H), 1.70-1.48 (m, 2H), 1.38-1.24 (m, 1H),

1.00-0.87 (m, 30H), 0.72-0.50 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 155.8, 149.5, 136.5, 132.8, 124.4, 120.7, 117.0, 80.3, 79.8, 75.0, 65.1, 59.4, 39.5, 37.6, 36.5, 35.6, 21.5, 10.9, 7.1, 7.0, 6.8, 6.7, 5.4, 4.3; IR (neat) 3350, 1727, 1520, 1461, 1382, 1244, 1104, 1011 cm^{-1}; HRMS (FAB) calcd for $C_{37}H_{71}NO_7Si_3Na$ [(M + Na)$^+$] 748.4439, found 748.4422.



(3*R*,4*R*,5*E*)-4-(2-(Allyloxycarbonylamino)ethyl)-6-((2*S*,3*S*)-3-ethyl-3,6-dihydro-6-oxo-2*H*-pyran-2-yl)-3,4-bis(triethylsilyloxy)hex-5-enal (32). To a stirred solution of oxalyl chloride (0.68 ml, 7.82 mmol) in CH_2Cl_2 (5 mL) at –78 °C were added DMSO (1.11 mL, 15.6 mmol) a solution of **31** (1.29 g, 1.78 mmol) in CH_2Cl_2 (8 mL), and stirring was kept at –78 °C for 20 min and at –40 °C for 20 min. The mixture was cooled to –78 °C and triethylamine (3.72 ml, 26.7 mmol) was added, and the mixture was stirred at 0 °C for 20 min. The reaction mixture was diluted with Et_2O, washed with 1 M HCl, water, and saturated $NaHCO_3$, dried, concentrated and chromatographed on Florisil (hexane:EtOAc = 5:1) to give **32** (909 mg, 84%) as a pale yellow oil: $[\alpha]_D^{25}$ +24.8 (*c* 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 6.95 (dd, *J* = 9.8, 5.4 Hz, 1H), 6.06 (d, *J* = 9.8 Hz, 1H), 5.98-5.89 (m, 2H), 5.83 (dd, *J* = 15.6, 5.2 Hz, 1H), 5.30 (d, *J* = 17.1 Hz, 1H), 5.20 (d, *J* = 10.2 Hz, 1H), 5.03 (t, *J* = 5.2 Hz, 1H), 4.88-4.75 (brs, 1H), 4.65-4.55 (m, 2H), 4.15 (t, *J* = 3.9 Hz, 1H), 3.41-3.07 (m, 2H), 2.64 (dd, *J*=18.0, 3.9 Hz, 1h), 2.49-2.37 (m, 2H), 2.15-2.05 (m, 1H), 1.85-1.71 (m, 1H), 1.65-1.45 (m, 2H), 1.10-0.80 (m, 21H), 0.64 (q, *J* = 7.5 Hz, 6H), 0.62 (q, *J* = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 163.8, 156.0, 149.7, 135.3, 133.0, 125.9, 121.0, 117.5, 80.1, 79.8, 73.0, 65.5, 47.7, 39.5, 37.8, 36.8, 21.8, 11.2, 7.3, 7.1, 6.9, 5.2; IR (neat) 3346, 1718, 1525, 1460, 1242, 1107, 1005 cm^{-1}; HRMS (EI) calcd for $C_{31}H_{55}NO_7Si_2$ (M$^+$) 609.3517, found 609.3515.

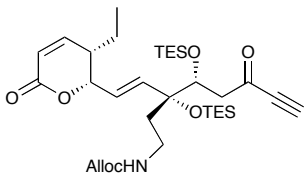


Ethynylation of Aldehyde 32: Commercially available anhydrous $CeCl_3$ (1.07 g, 4.33 mmol) was heated under vacuum at 140 °C for 2 h. THF (4.9 mL) was added and the resulting suspension was stirred at room temperature for 35 h. Ethynylmagnesium bromide (1.07 M in THF, 4.0 mL, 4.33 mmol) was added at –78 °C, and stirring was kept at the same temperature for 1.5 h. To this mixture at –78 °C was added a solution of **32** (909 mg, 1.49 mmol) in THF (10 ml), and the mixture was stirred at –50 °C for 4 h. The reaction was quenched with water (20 ml) and the reaction mixture was filtered through Celite. The filtrate was extracted with Et_2O, washed with water and brine, dried, and concentrated. The residue was chromatographed (hexane:EtOAc = 5:1 to 2:1) to give the corresponding ethynylated compound (698 mg, 74%), a colorless oil, as a 1:1 epimeric mixture.

Less Polar Epimer: $[\alpha]_D^{26}$ +46.9 (*c* 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (dd, *J* = 9.8, 4.9 Hz, 1H), 6.06 (d, *J* = 9.8 Hz, 1H), 5.96-5.85 (m, 2H), 5.83 (dd, *J* = 15.6, 5.6 Hz, 1H), 5.29 (d, *J* = 17.5 Hz, 1H), 5.19 (d, *J* = 10.2 Hz, 1H), 5.04 (t, *J* = 5.6 Hz, 1H), 5.00-4.91 (brs, 1H), 4.64-4.50 (m, 2H), 4.49-4.39 (br, 1H), 3.85 (d, *J* =7.8 Hz, 1H), 3.31-3.11 (m, 2H), 2.48-2.39 (m, 2H), 2.18-2.10 (br, 1H), 2.08-1.96 (m, 2H), 1.92-1.70 (m, 1H), 1.70-1.44 (m, 3H), 0.99-0.84 (m, 21H), 0.72-0.58 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 155.9, 149.5, 136.3, 132.9, 125.1, 120.8, 117.3, 85.2, 80.2, 79.6, 74.6, 72.4, 65.3, 58.6, 41.0, 39.5, 37.4, 36.5, 21.6, 11.1, 7.2, 7.0, 6.9, 5.4; IR (neat) 3408, 1714, 1520, 1456, 1244, 1103, 1007 cm^{-1}; HRMS (EI) calcd for $C_{33}H_{57}NO_7Si_2$ (M$^+$) 635.3673, found 635.3672.

More Polar Epimer: $[\alpha]_D^{26}$ +27.3 (*c* 0.81, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (dd, *J* = 9.8, 5.4 Hz, 1H), 6.06 (d, *J* = 9.8 Hz, 1H), 5.98-5.85 (m, 2H), 5.82 (dd, *J* = 15.6, 5.6 Hz, 1H),

5.30 (d, *J* = 17.0 Hz, 1H), 5.20 (d, *J* = 10.7 Hz, 1H), 5.03 (t, *J* = 5.6 Hz, 1H), 5.03-4.94 (brs, 1H), 4.62-4.50 (m, 2H), 4.49-4.40 (m, 1H), 3.79 (d, *J* = 6.4 Hz, 1H), 3.36-3.10 (m, 2H), 2.53 (s, 1H), 2.50-2.40 (m, 1H), 2.08-1.90 (m, 2H), 1.90-1.74 (m, 2H), 1.74-1.58 (m, 2H), 1.55-1.44 (m, 1H), 1.00-0.88 (m, 21H), 0.72-0.64 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 156.0, 149.5, 136.2, 132.9, 125.2, 120.8, 117.3, 84.6, 80.2, 79.7, 75.6, 74.1, 65.4, 60.5, 41.0, 39.4, 37.4, 36.6, 21.7, 11.1, 7.2, 7.1, 6.9, 5.5; IR (neat) 3305, 1712, 1522, 1456, 1242, 1107, 1009 cm^{-1}; HRMS (EI) calcd for $C_{33}H_{57}NO_7Si_2$ (M^+) 635.3673, found 635.3669.



(5*S*,6*S*)-6-((*E*,3*R*,4*R*)-3-(2-(Allyloxycarbonylamino)ethyl)-6-oxo-3,4-bis(triethylsilyloxy)oct-1-en-7-ynyl)-5-ethyl-5,6-dihydropyran-2-one (4). To an ice-cooled solution of the above-mentioned epimeric mixture (698 mg, 1.10 mmol) in CH_2Cl_2 (11 mL) were added Dess-Martin periodinane (1.42 g, 3.29 mmol) and $NaHCO_3$ (924 mg, 11.0 mmol). After being stirred at 0 °C for 4 h, the reaction mixture was diluted with Et_2O, washed with 10% $Na_2S_2O_3$, water, saturated $NaHCO_3$, dried, and concentrated. The residue was chromatographed (hexane:EtOAc = 5:1) to give **4** (666 mg, 96%) as a colorless oil: $[\alpha]_D^{26}$ +38.6 ° (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (dd, *J* = 9.8, 5.4 Hz, 1H), 6.07 (d, *J* = 9.8 Hz, 1H), 5.97-5.85 (m, 2H), 5.82 (dd, *J* = 15.6, 5.9 Hz, 1H), 5.30 (d, *J* = 17.3 Hz, 1H), 5.20 (d, *J* = 10.2 Hz, 1H), 5.06 (t, *J* = 5.9 Hz, 1H), 4.84-4.75 (brs, 1H), 4.62-4.45 (m, 2H), 4.25 (d, *J* = 5.8 Hz, 1H), 3.26 (s, 1H), 3.35-3.11 (m, 2H), 2.88 (dd, *J* = 17.6, 2.5 Hz, 1H), 2.54 (dd, *J* = 17.6, 5.8 Hz, 1H), 2.49-2.40 (m,1H), 2.13-2.05 (m, 1H), 1.82-1.70 (m, 1H), 1.70-1.45 (m, 2H), 1.01-0.92 (m, 21H), 0.71-0.56 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1, 163.7, 156.0, 149.5, 135.3, 133.0, 125.5, 120.9, 117.5, 81.7, 80.1, 79.5, 79.1, 73.0, 65.5, 49.9, 39.6, 37.6, 36.7, 21.8, 11.2, 7.3, 7.1, 6.9, 5.2; IR (neat) 3350, 1720, 1523, 1460, 1242, 1105, 1009 cm^{-1}; HRMS (EI) calcd for $C_{33}H_{55}NO_7Si_2$ (M^+) 633.3517, found 633.3509.

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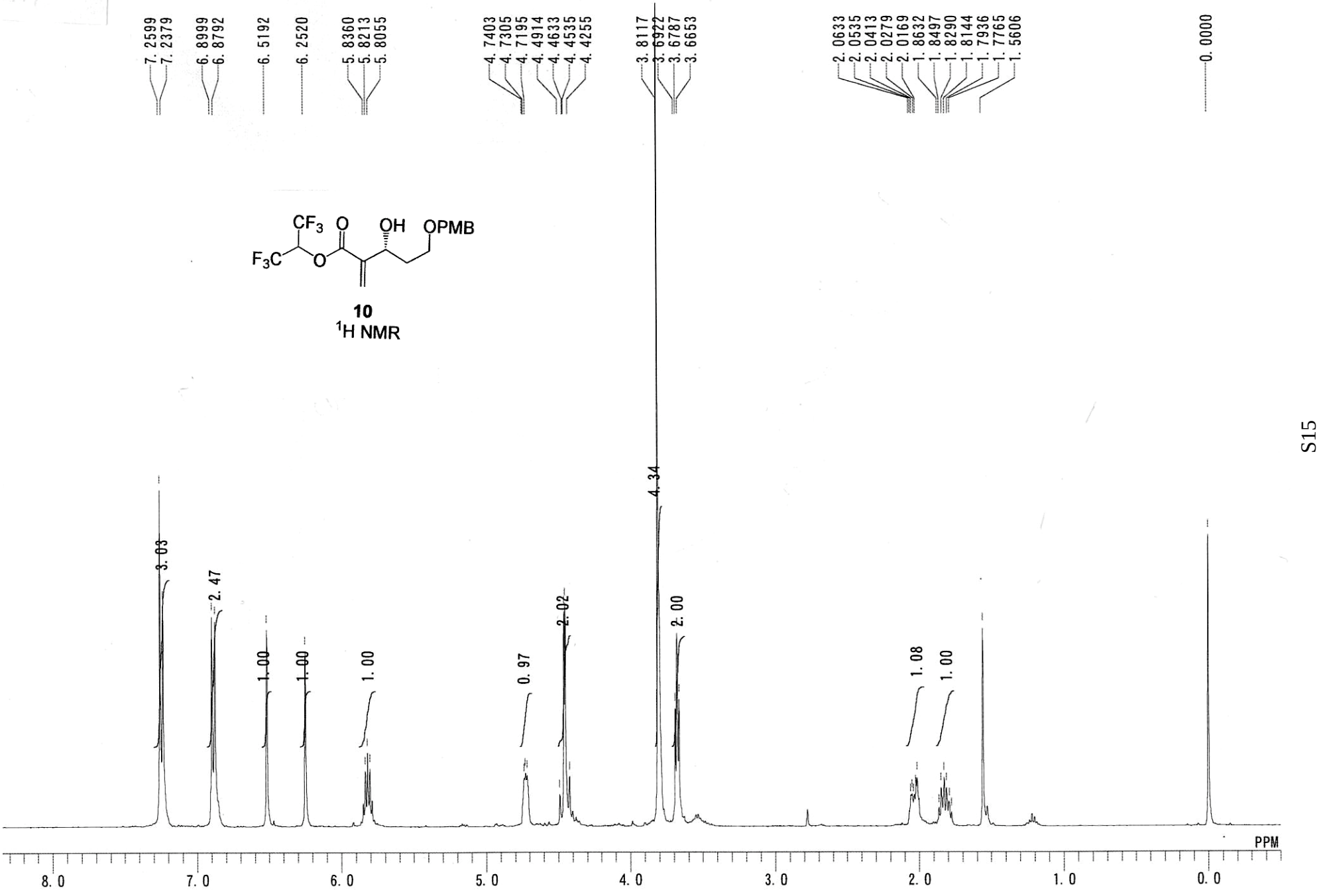
(2) S. Shibahara, M. Fujino, Y. Tashiro, K. Takahashi, J. Ishihara and S. Hatakeyama, *Org. Lett.,* 2008, **10**, 2139.
(3) A. Yanagisawa, H. Kageyama, Y. Nakatsuka, K. Asakawa, Y. Matsumoto and H. Yamamoto, *Angew. Chem. Int. Ed*., 1999, **38**, 3701.
(4) G. V. M. Sharma, K. L. Reddy, P. S. Lakshmi and P. R. Krishna, *Tetrahedron Lett.,* 2004, **45**, 9229.
(5) J. A. Ciaccio, M. Smrtka, W. A. Maio and D. Rucando, *Tetrahedron Lett*., 2004, **45**, 7201.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4.7195
4.4914
4.4633
4.4535
4.4255
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3.6787
3.6653
2.0633
2.0535
2.0413
2.0279
2.0169
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1.8497
1.8290
1.8144
1.7936
1.7765
1.5606
0.0000
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OH
OPMB
F3C
O
10
1H NMR
3.03
2.47
1.00
1.00
1.00
0.97
2.02
4.34
2.00
1.08
1.00
PPM
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4.0
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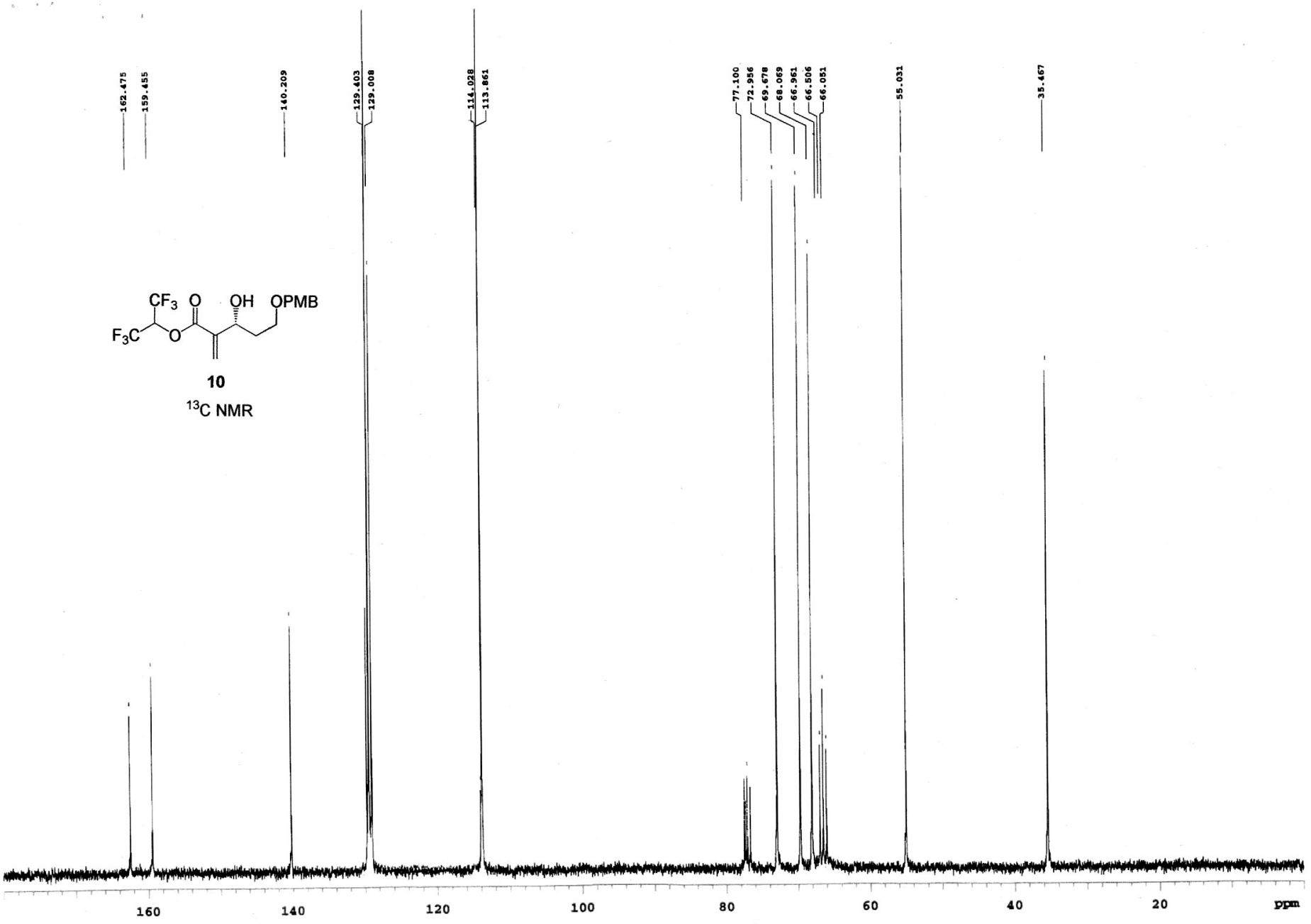
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66.506
66.051
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F3C O
10
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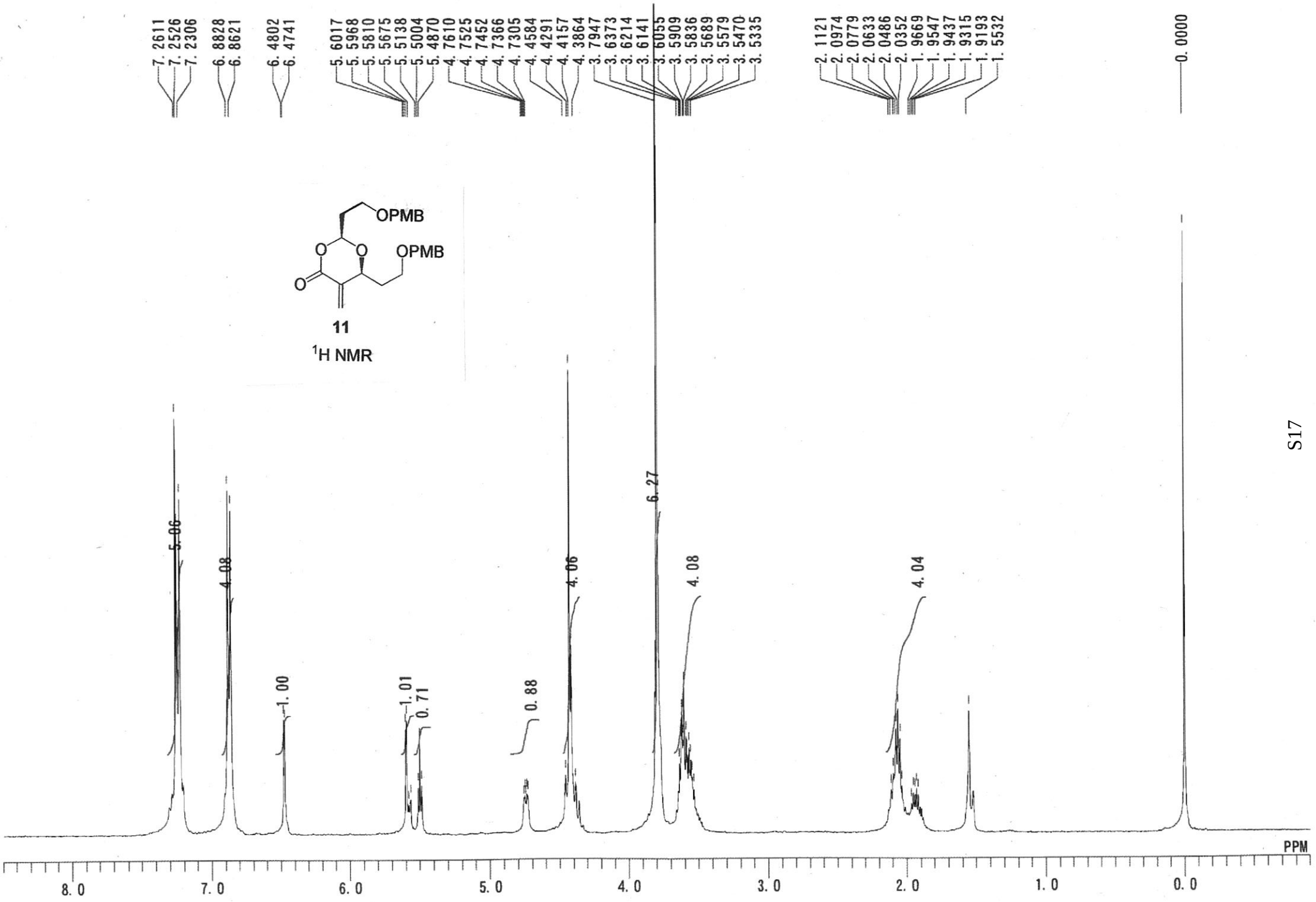
140
120
100
80
60
40
20
ppm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4.7305
4.4584
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3.7947
3.6373
3.6214
3.6141
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2.0633
2.0486
2.0352
1.9669
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1.9437
1.9315
1.9193
1.5532
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OPMB
OPMB
O
O
O
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4.08
1.00
1.01
0.71
0.88
4.06
6.27
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PPM
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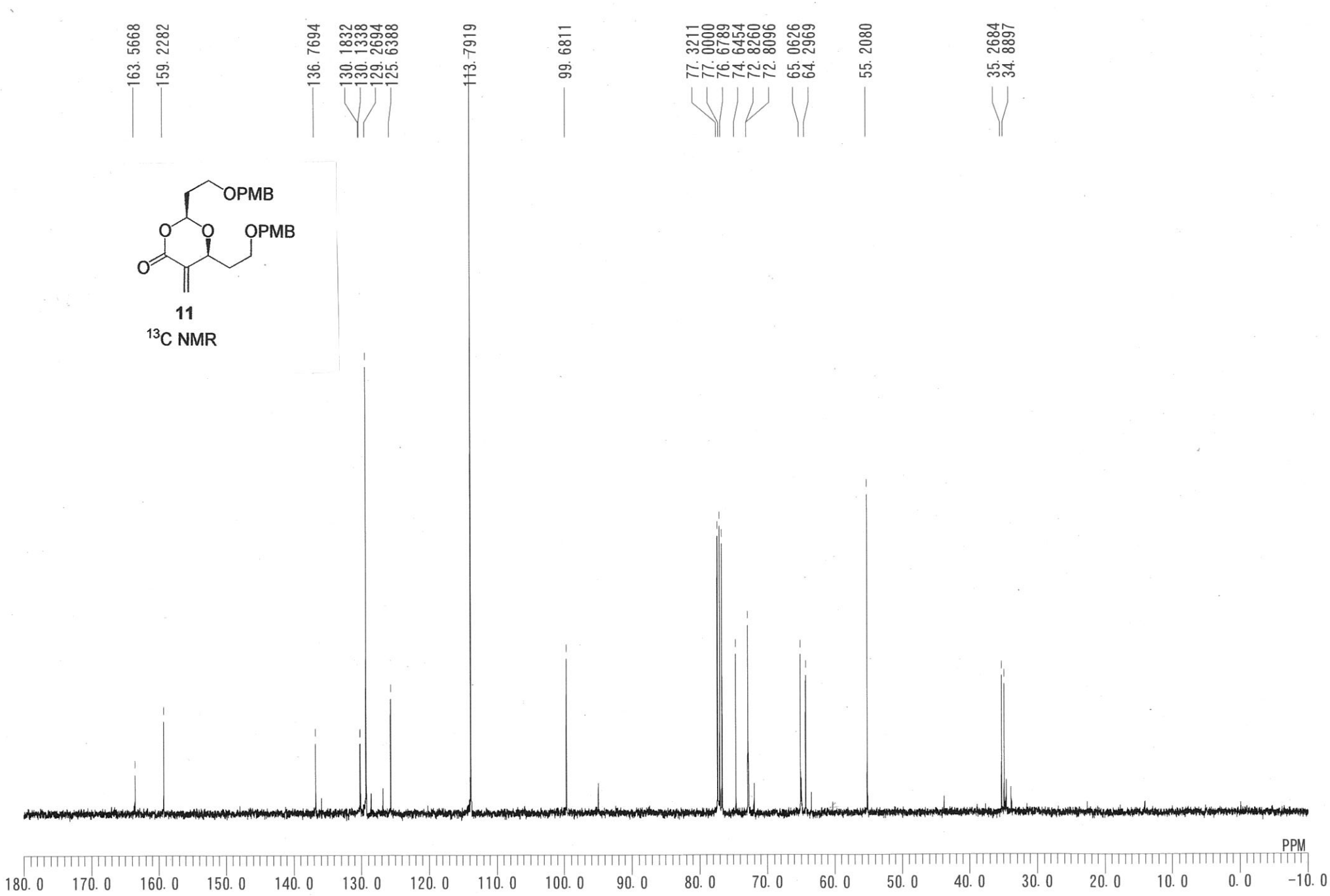
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64.2969
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35.2684
34.8897
OPMB
OPMB
O
O
O
11
13C NMR
PPM
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170.0
160.0
150.0
140.0
130.0
120.0
110.0
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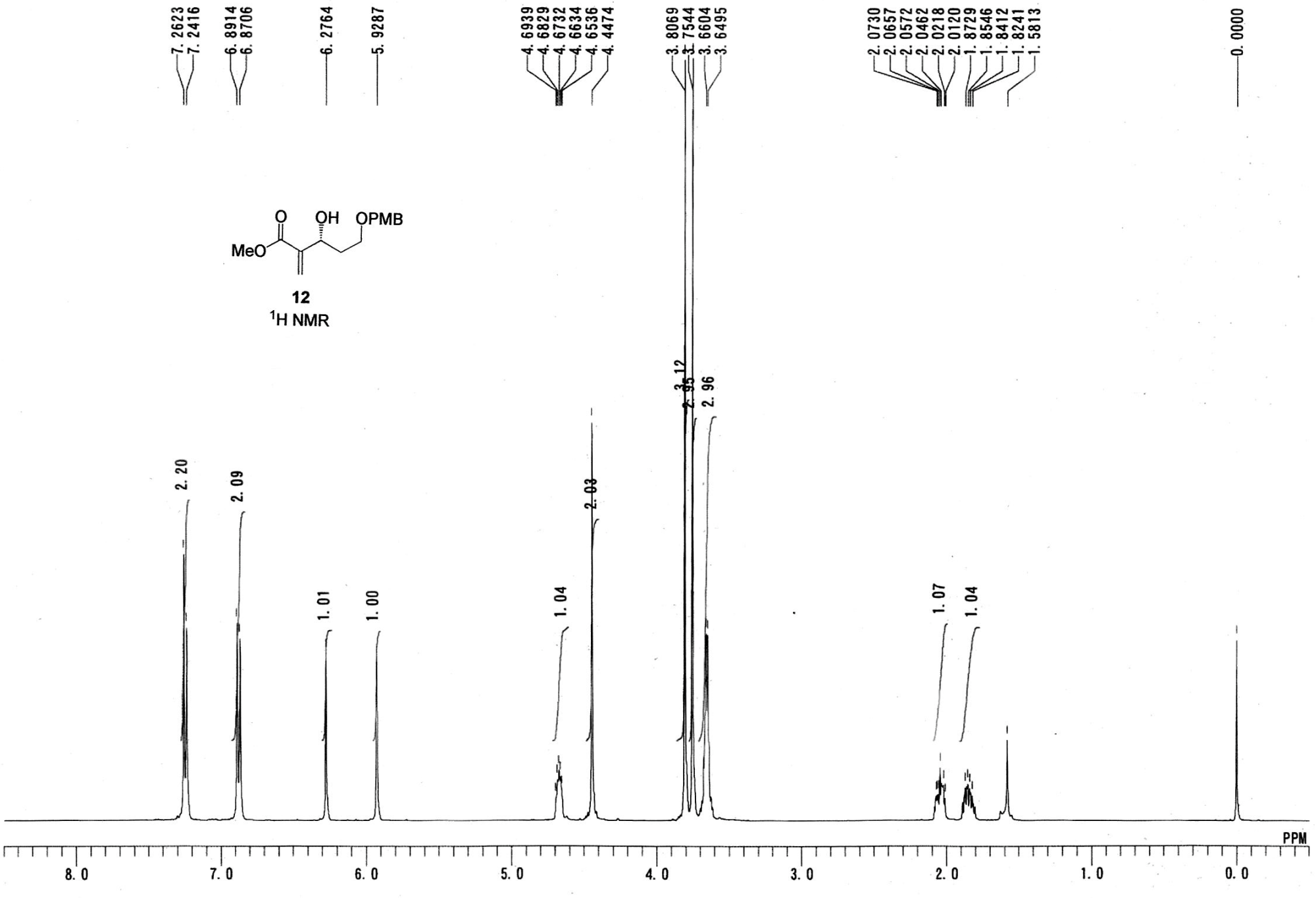
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3.7544
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3.6495
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2.0572
2.0462
2.0218
2.0120
1.8729
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1.8412
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1.5813
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O
OH
OPMB
MeO
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1H NMR
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2.09
1.01
1.00
1.04
2.03
3.12
2.95
2.96
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PPM
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5.0
4.0
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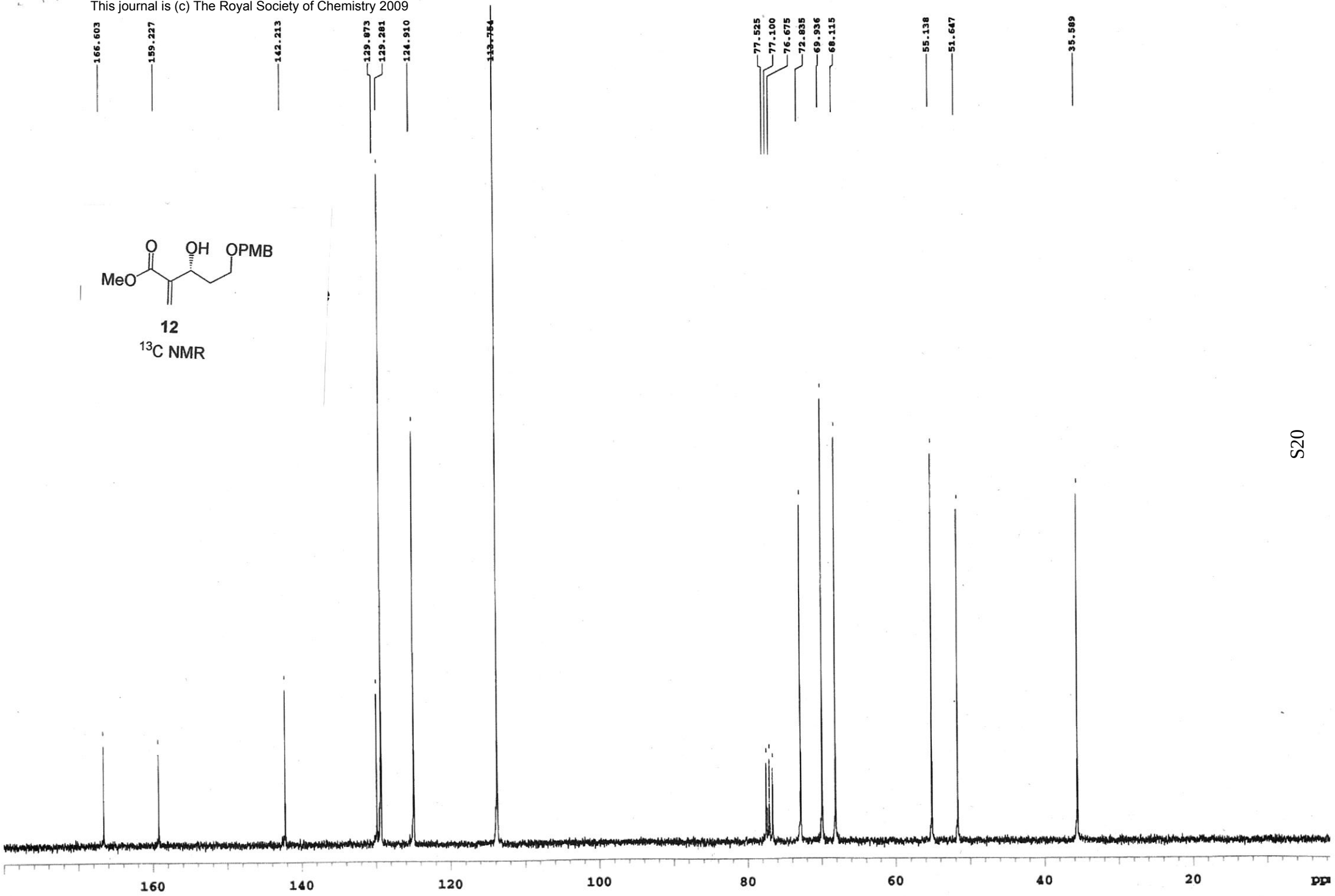
0.0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55.138
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O
OH
OPMB
MeO
12
13C NMR
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140
120
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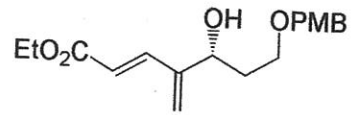
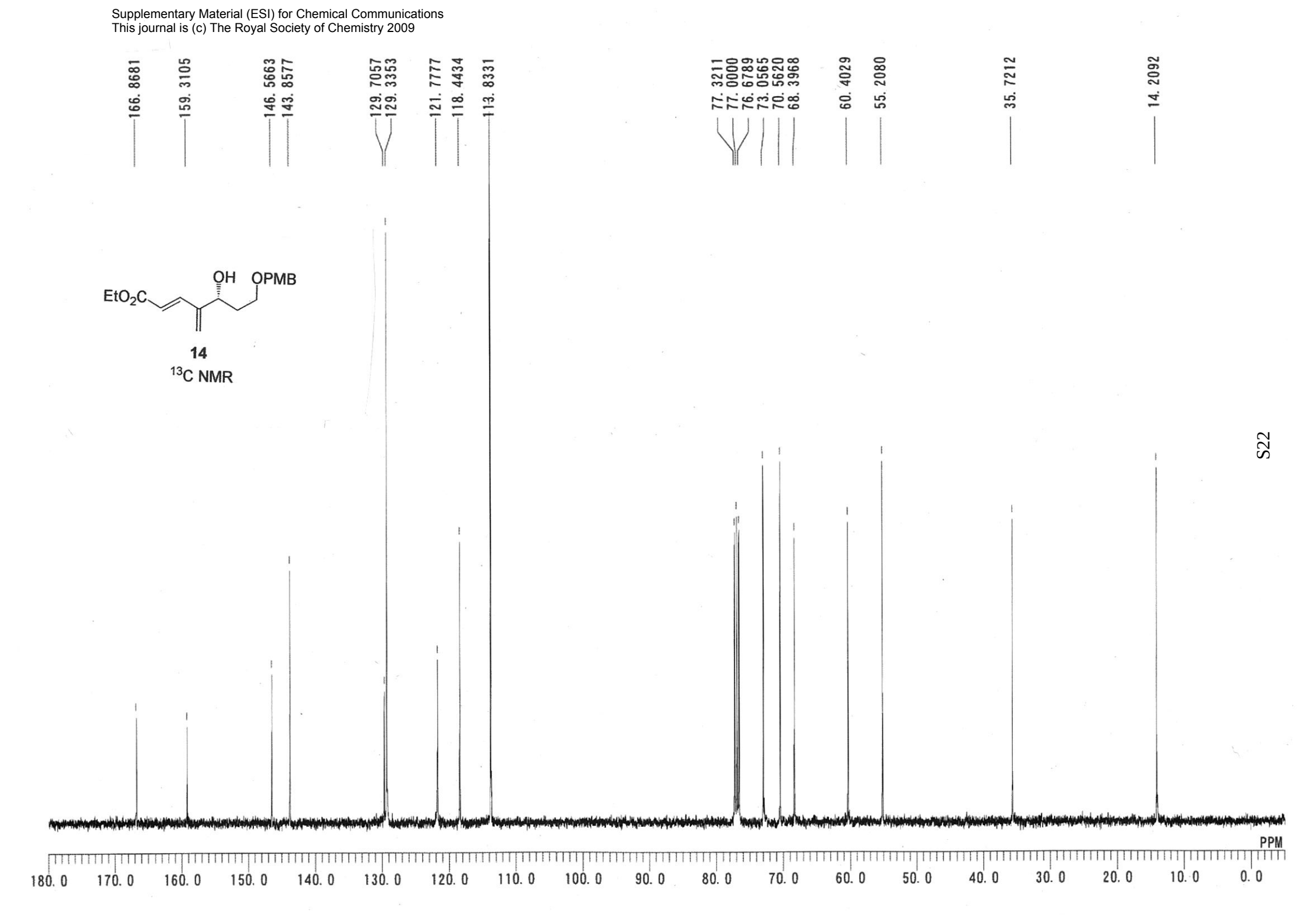
80
60
40
20
ppm



14

^{1}H NMR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121. 7777
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77. 0000
76. 6789
73. 0565
70. 5620
68. 3968
60. 4029
55. 2080
35. 7212
14. 2092
OH
OPMB
EtO2C
14
13C NMR
PPM
180. 0
170. 0
160. 0
150. 0
140. 0
130. 0
120. 0
110. 0
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90. 0
80. 0
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50. 0
40. 0
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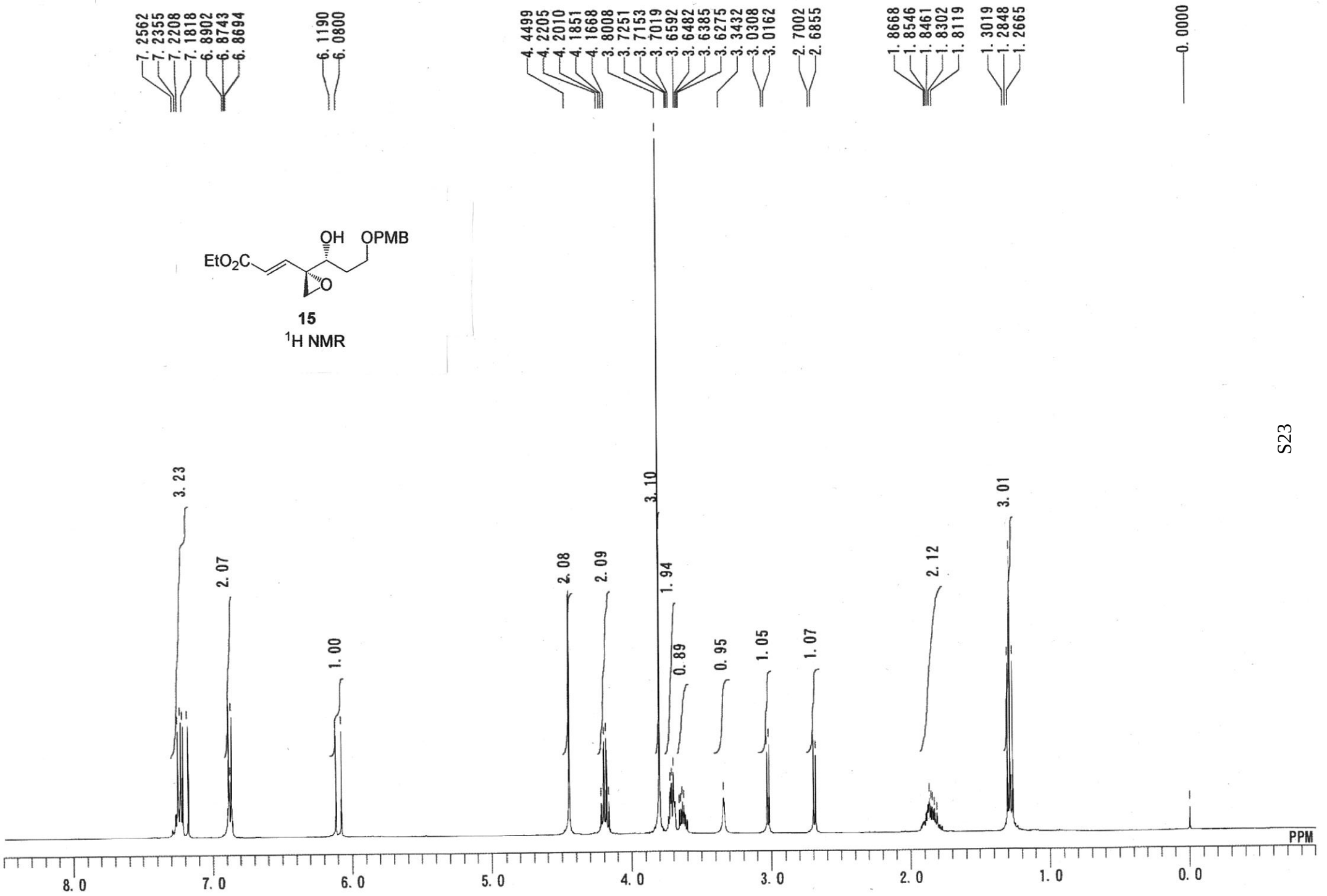
0. 0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6.8694
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6.0800
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4.2205
4.2010
4.1851
4.1668
3.8008
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3.6592
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3.6385
3.6275
3.3432
3.0308
3.0162
2.7002
2.6855
1.8668
1.8546
1.8461
1.8302
1.8119
1.3019
1.2848
1.2665
0.0000
OH
OPMB
EtO2C
O
15
1H NMR
3.23
2.07
1.00
2.08
2.09
3.10
1.94
0.89
0.95
1.05
1.07
2.12
3.01
PPM
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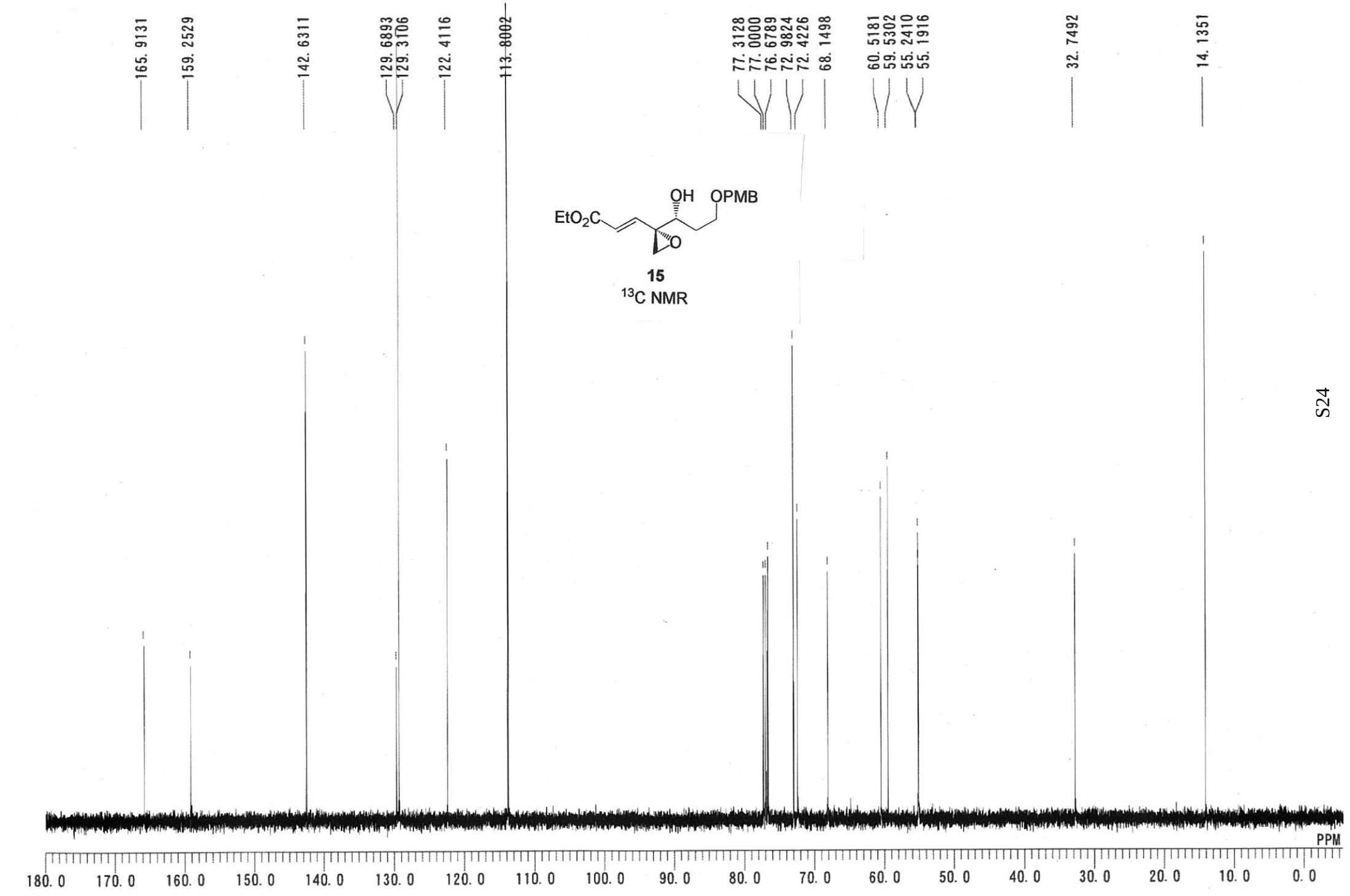
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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77. 0000
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72. 4226
68. 1498
60. 5181
59. 5302
55. 2410
55. 1916
32. 7492
14. 1351
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OPMB
EtO2C
O
15
13C NMR
PPM
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170. 0
160. 0
150. 0
140. 0
130. 0
120. 0
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80. 0
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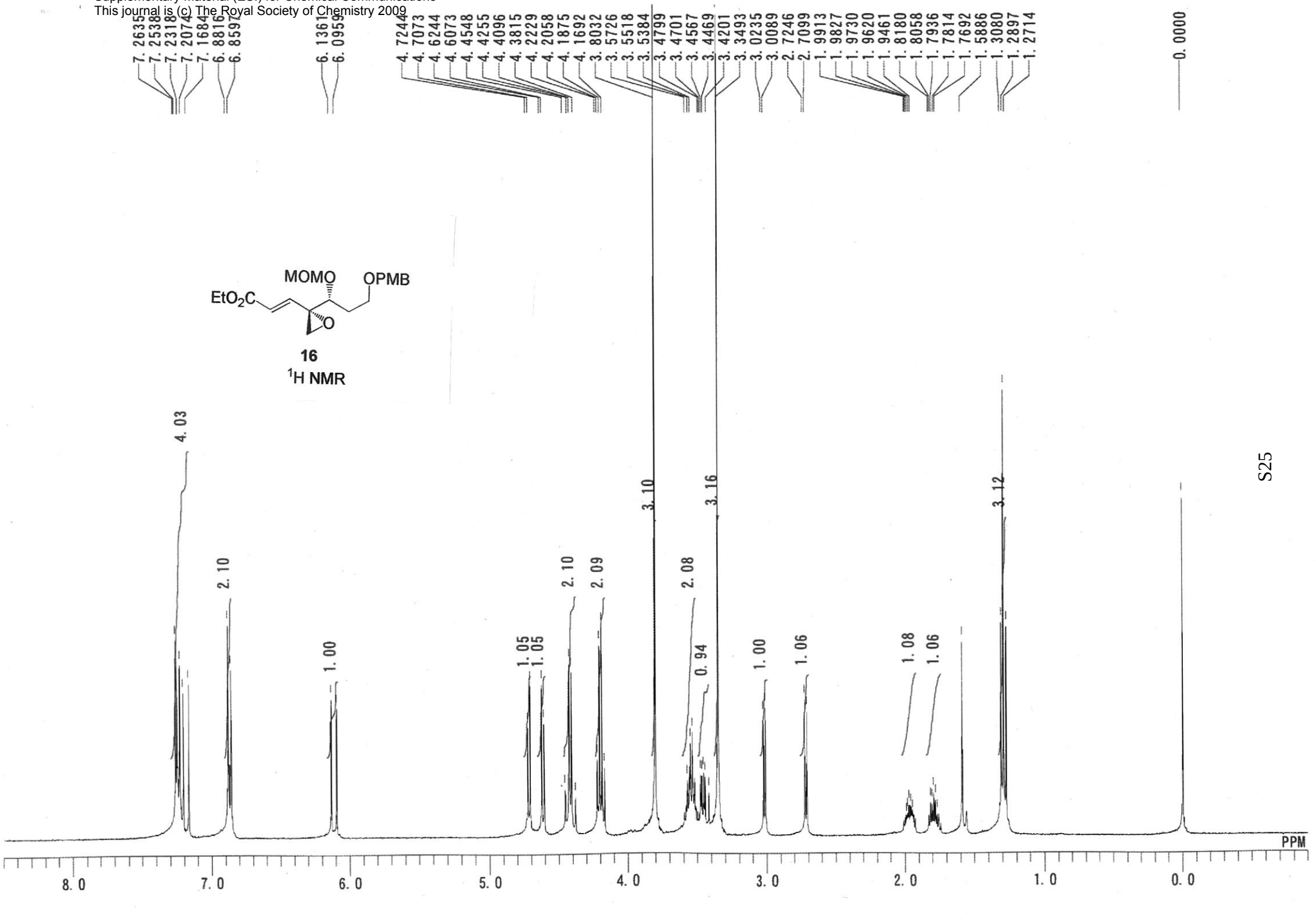
0. 0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OPMB
EtO2C
O
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4.0
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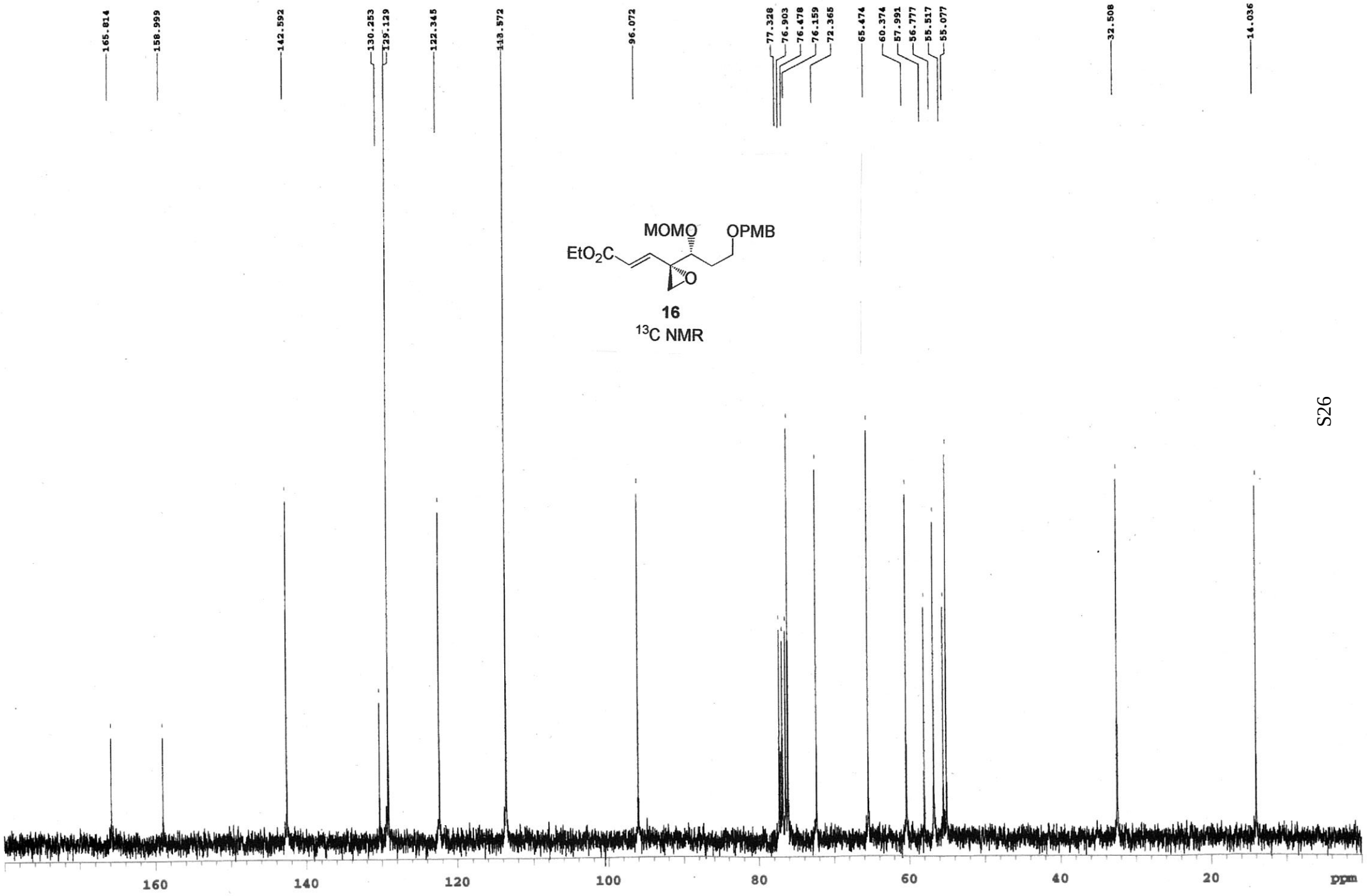
2.0
1.0
0.0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72.365
65.474
60.374
57.991
56.777
55.517
55.077
32.508
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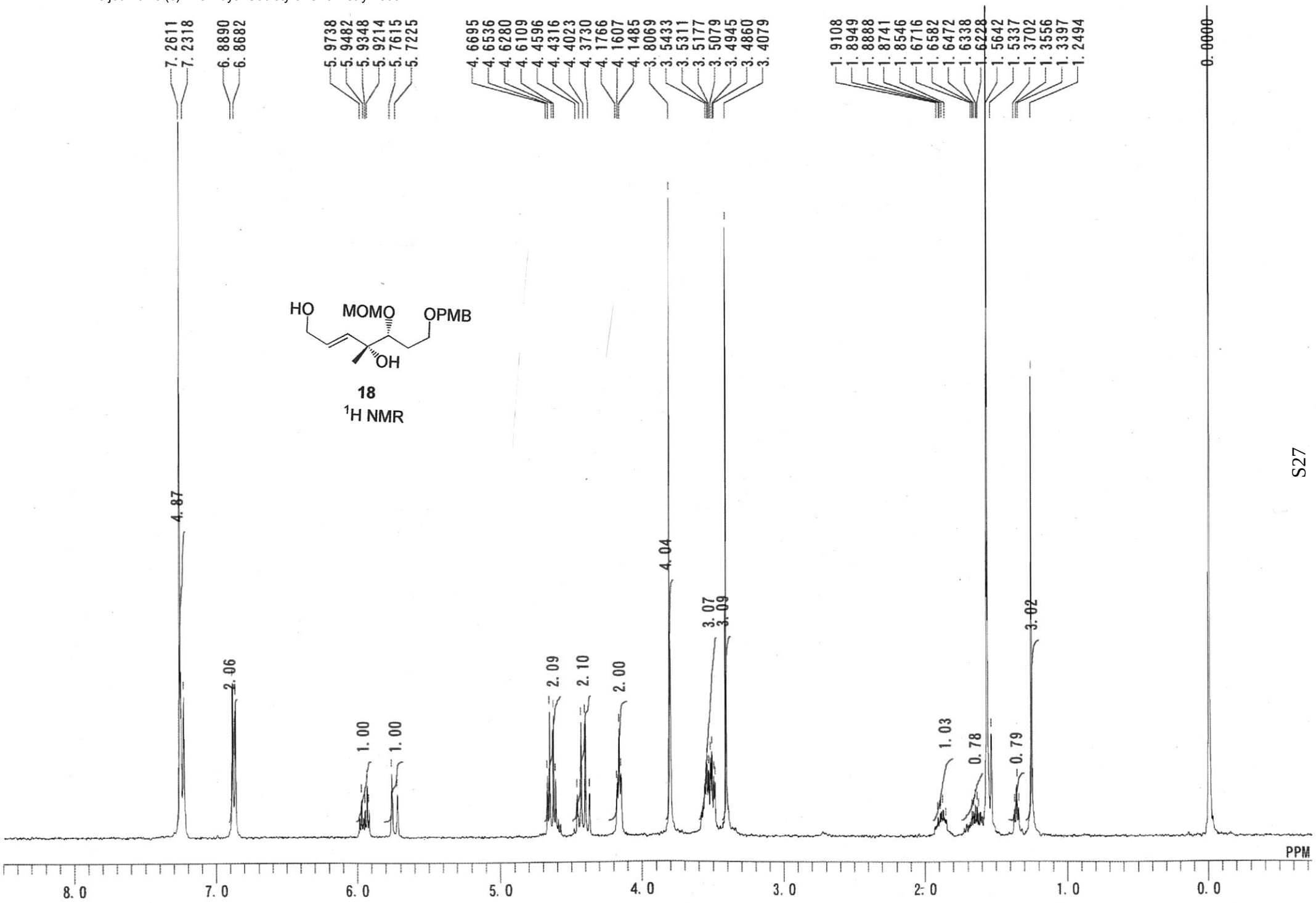
MOMO
OPMB
EtO2C
O
160
140
120
100
80
60
40
20
ppm

16

^{13}C NMR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OPMB
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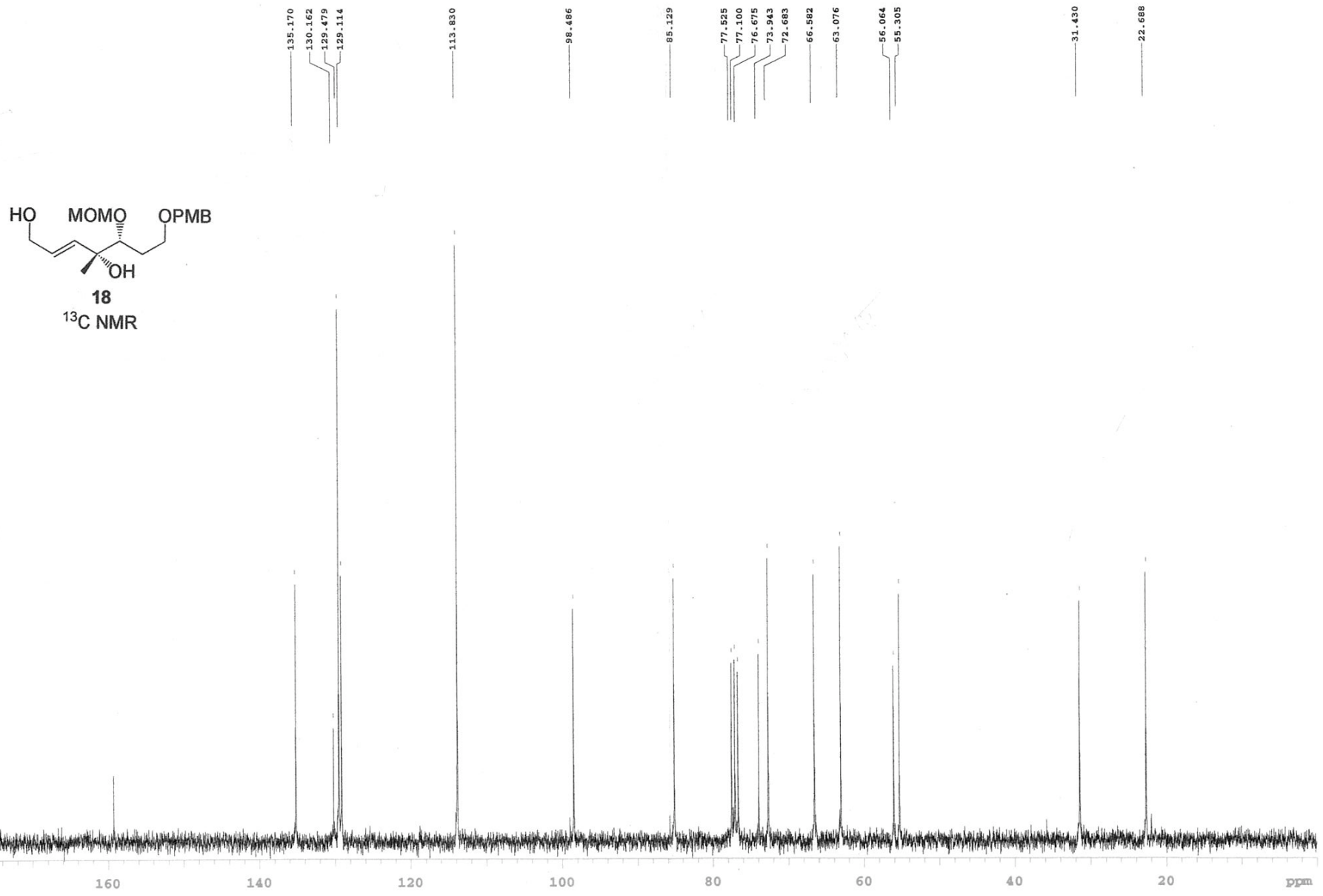
0.0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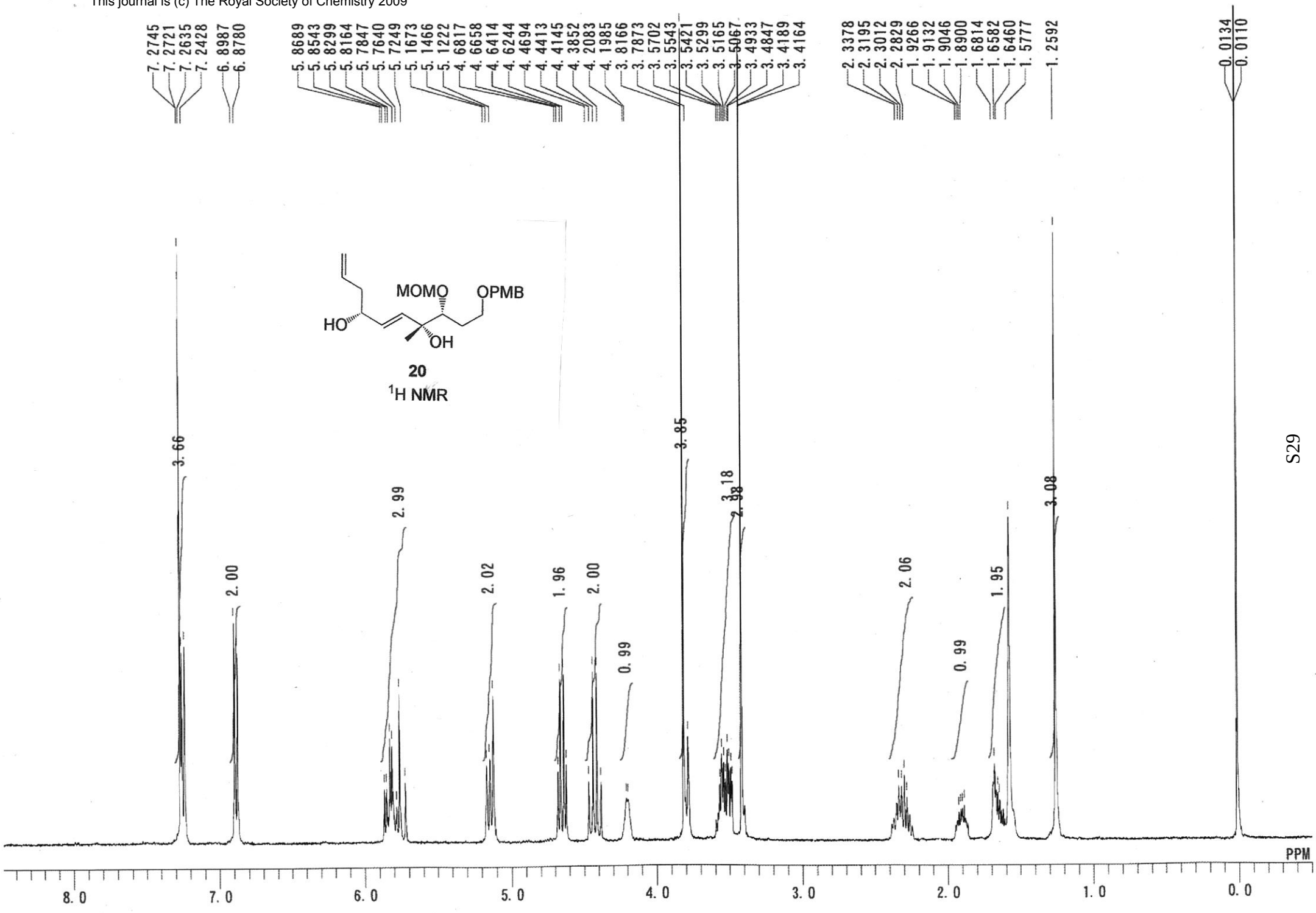
80
60
40
20
ppm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OH
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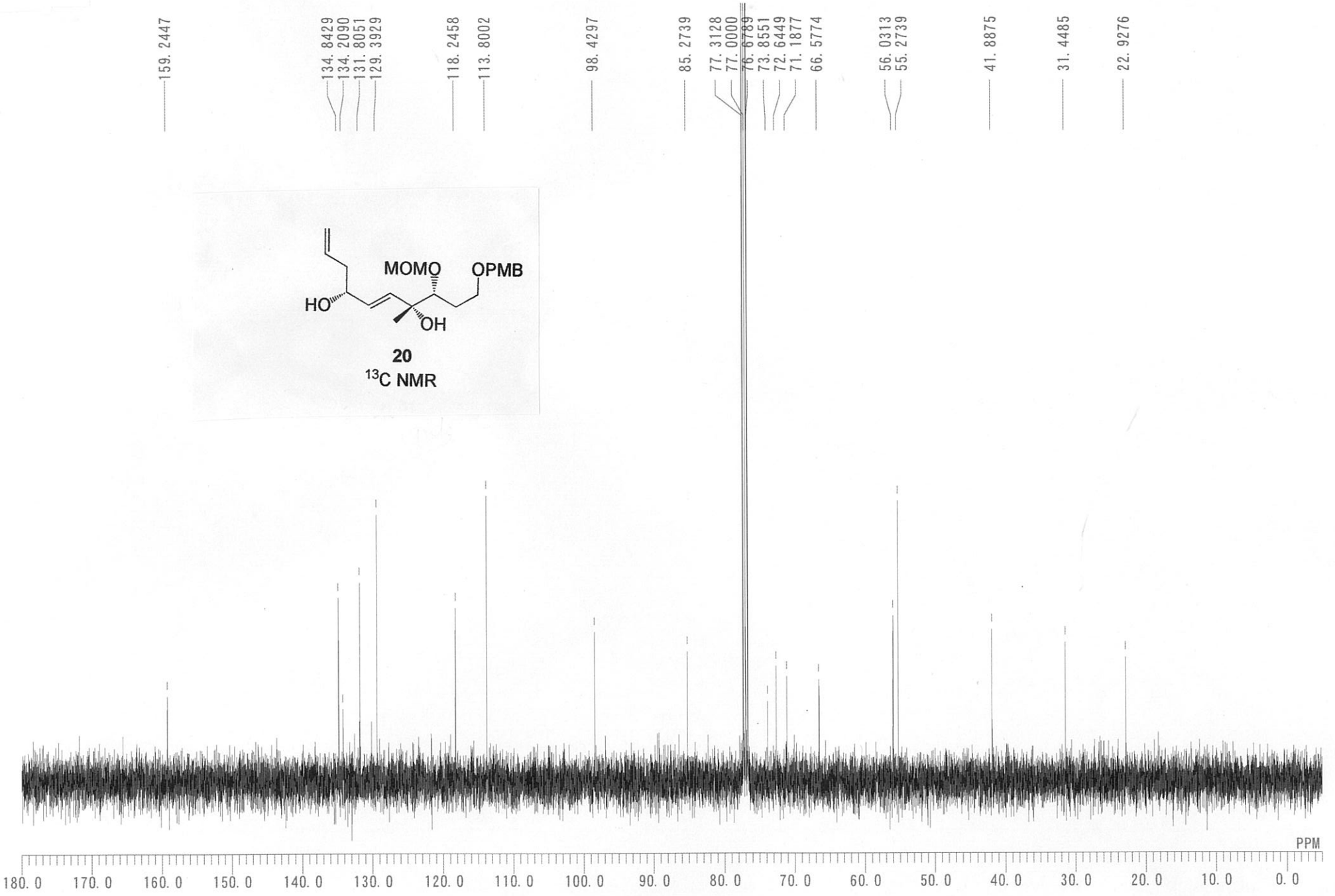
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77. 0000
76. 6789
73. 8551
72. 6449
71. 1877
66. 5774
56. 0313
55. 2739
41. 8875
31. 4485
22. 9276
MOMO
OPMB
HO
OH
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13C NMR
PPM
180. 0
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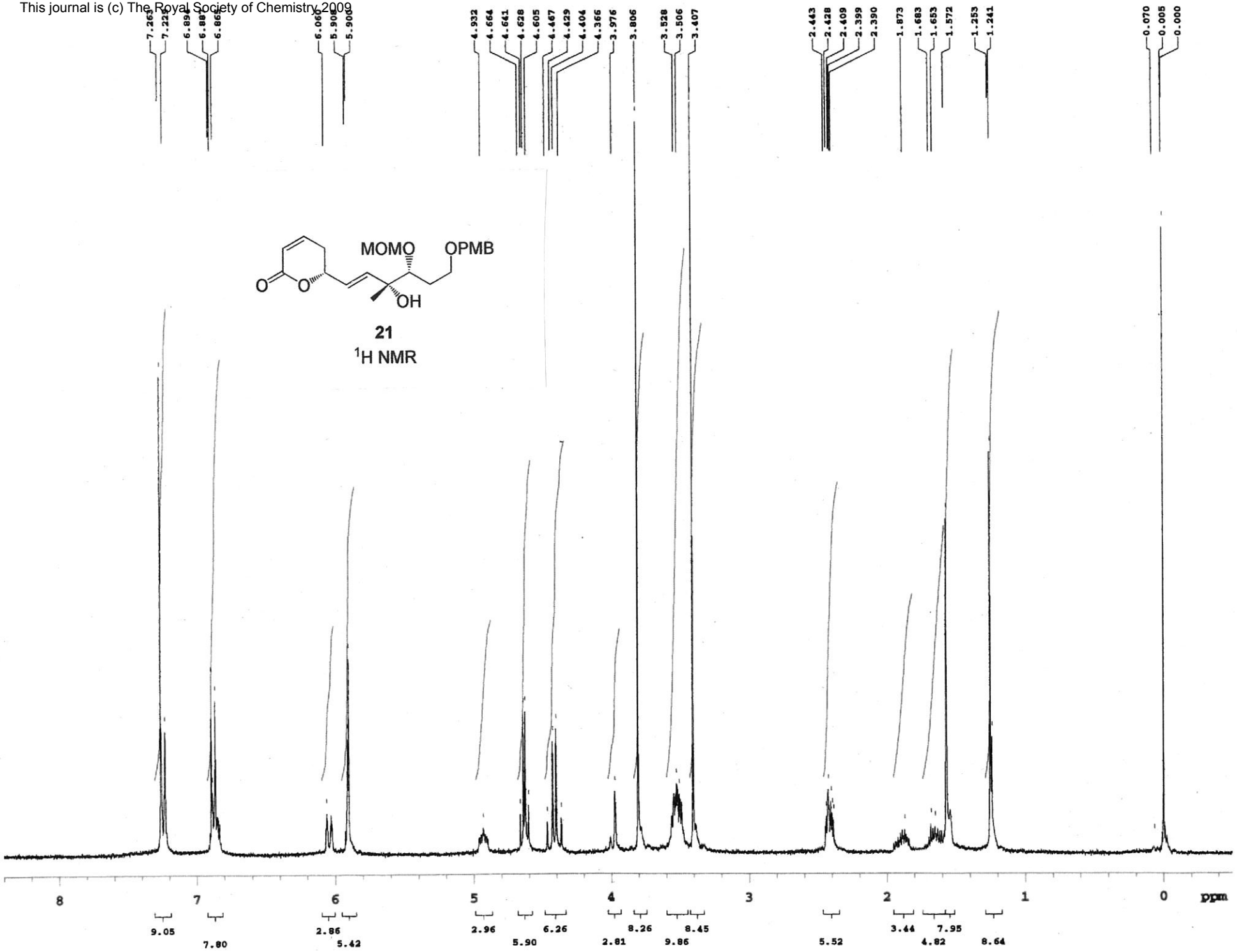
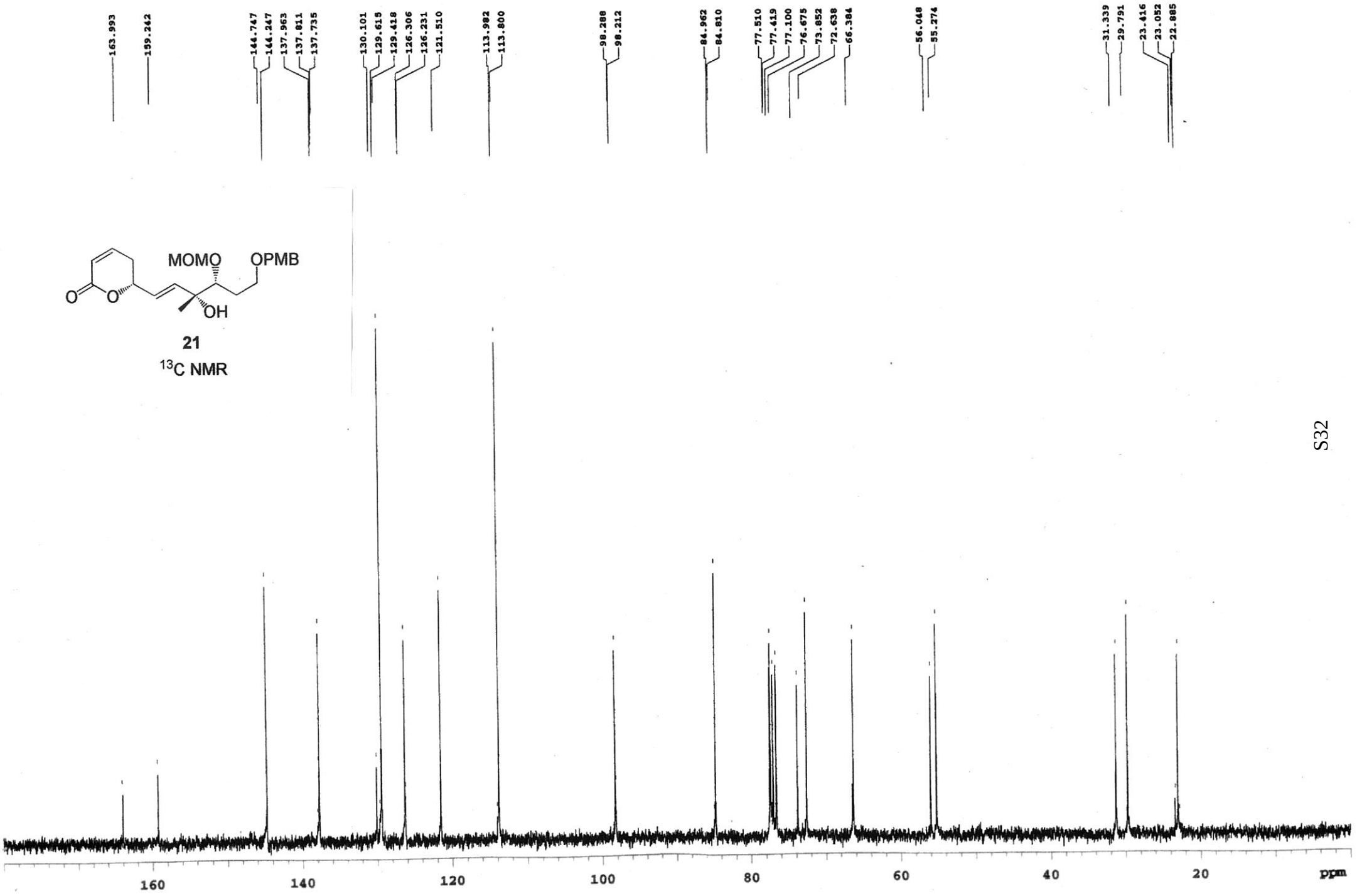
0. 0

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126.231
121.510
113.982
113.800
98.288
98.212
84.962
84.810
77.510
77.419
77.100
76.675
73.852
72.638
66.384
56.048
55.274
31.339
29.791
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OPMB
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OH
21
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140
120
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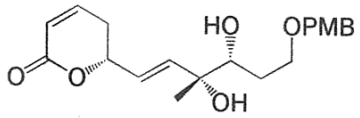
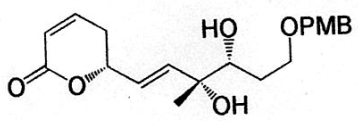
80
60
40
20
ppm



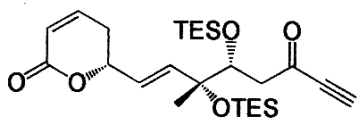
22

^{1}H NMR



22

^{13}C NMR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O
O
O
OTES

3

^{1}H NMR

8
7
6
5
4
3
2
1
0
ppm
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2.32
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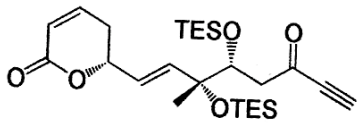
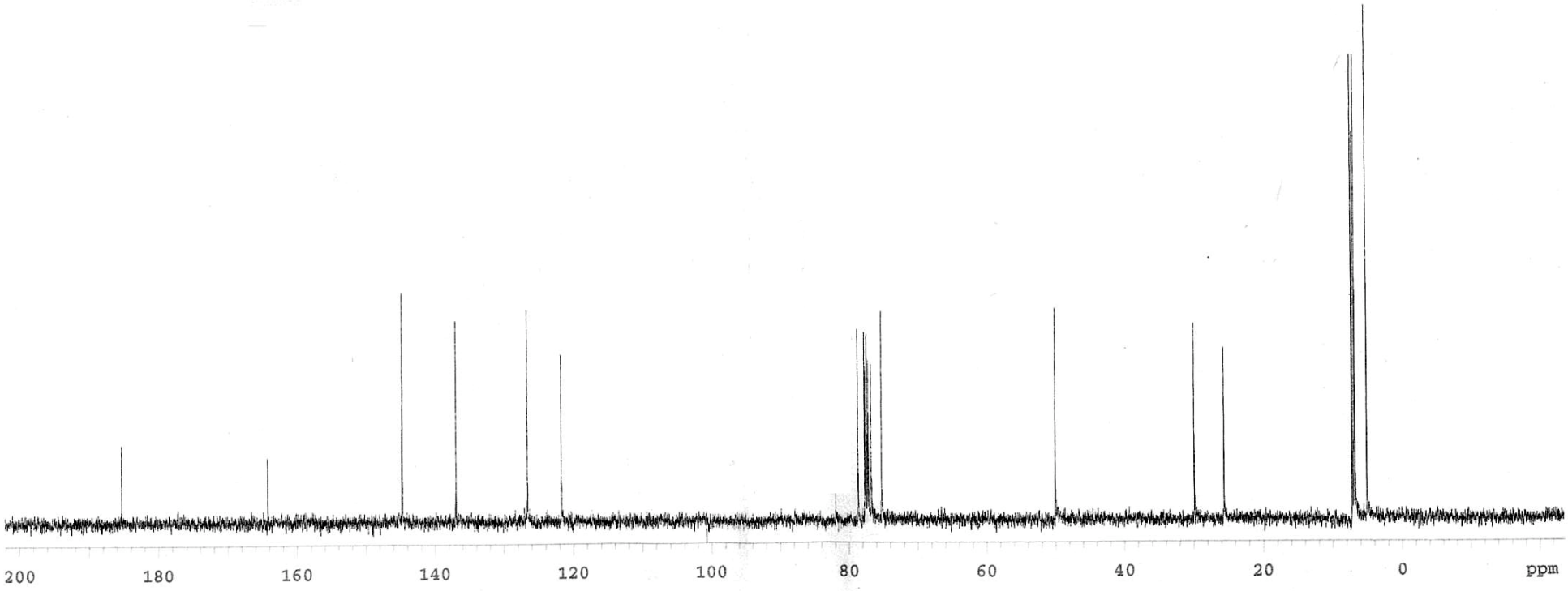
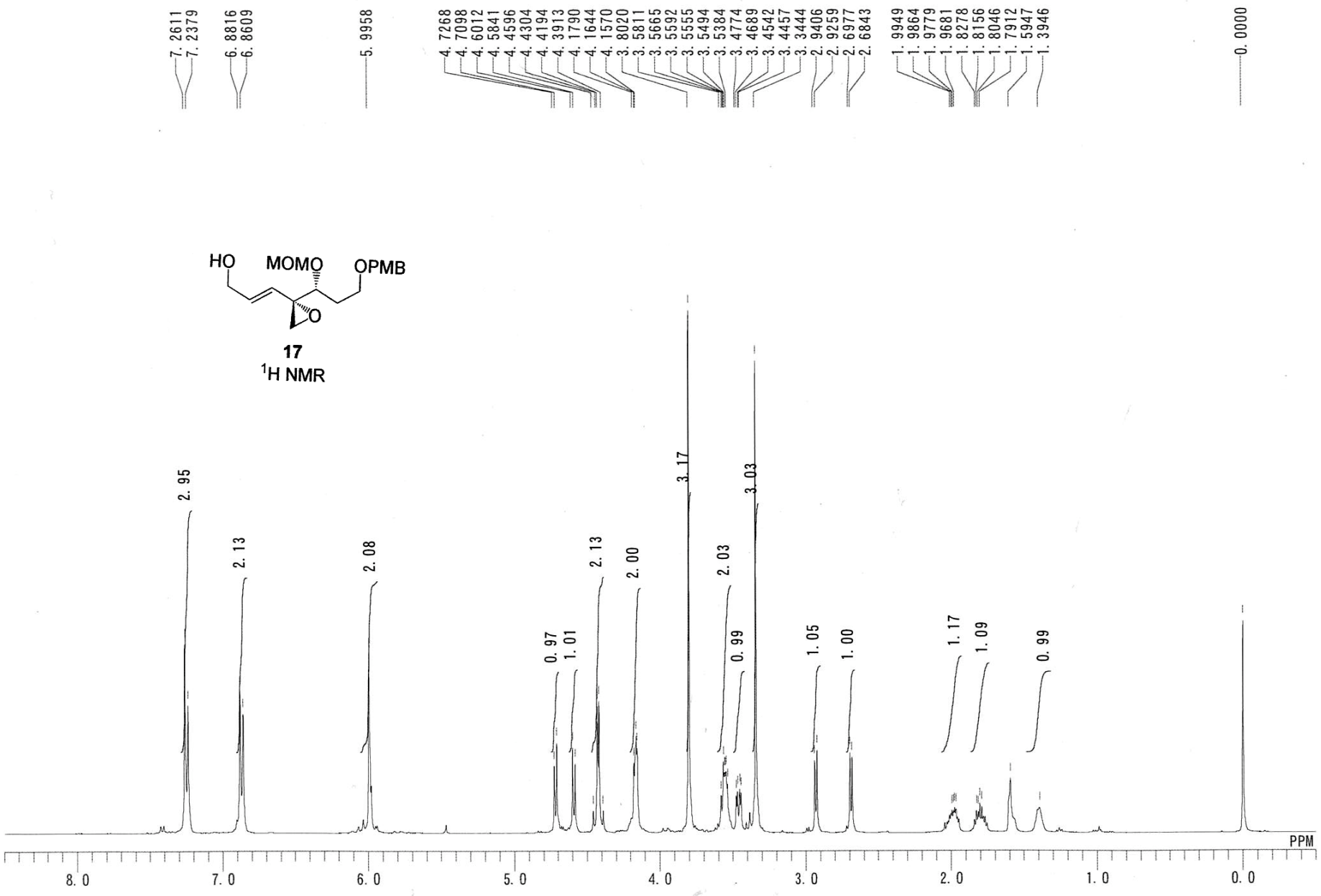
27.48



3

^{13}C NMR

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3.5494
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OPMB
O
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2.00
3.17
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3.03
1.05
1.00
1.17
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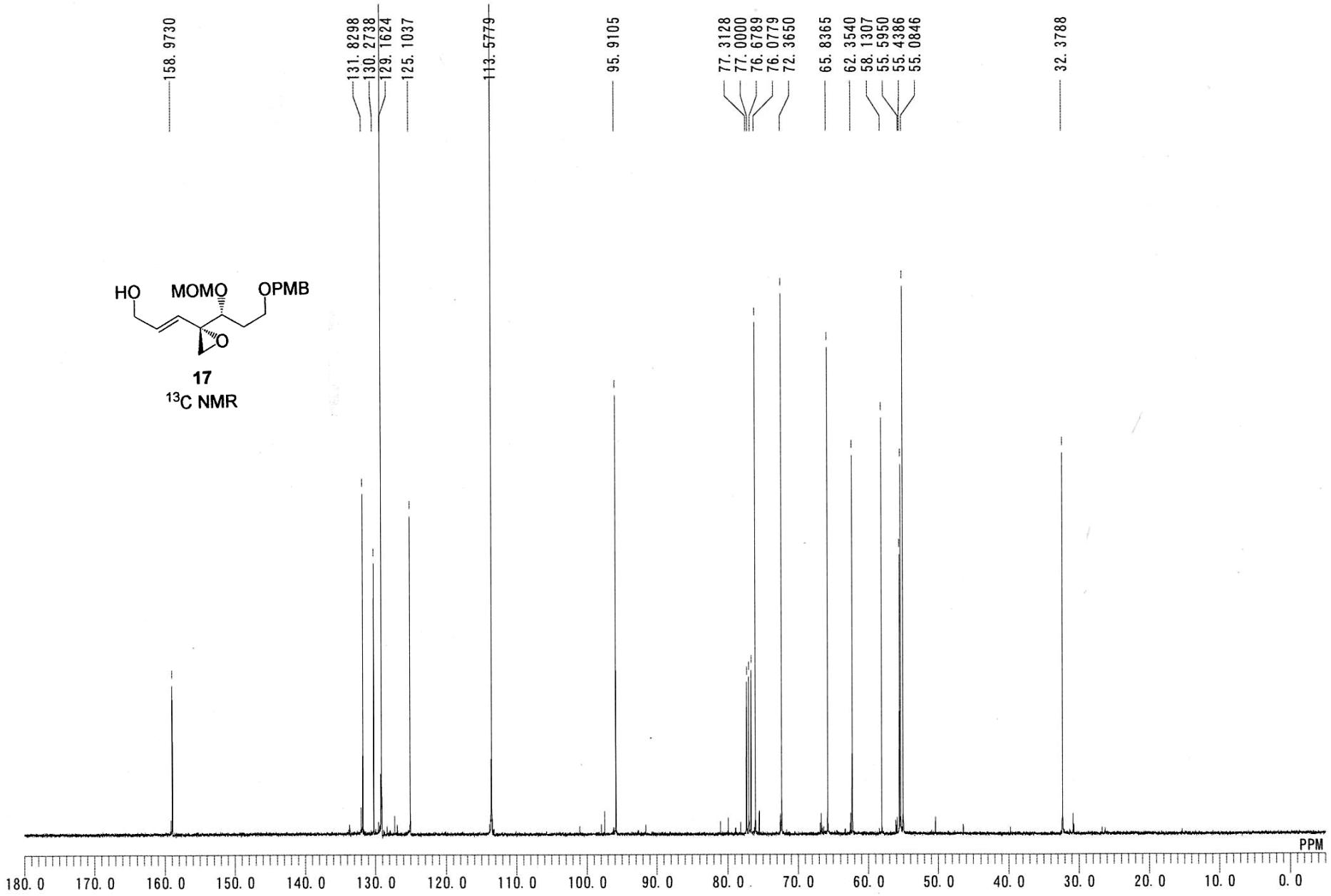
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55.5950
55.4386
55.0846
32.3788
HO
MOMO
OPMB
O
17
13C NMR
PPM
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120.0
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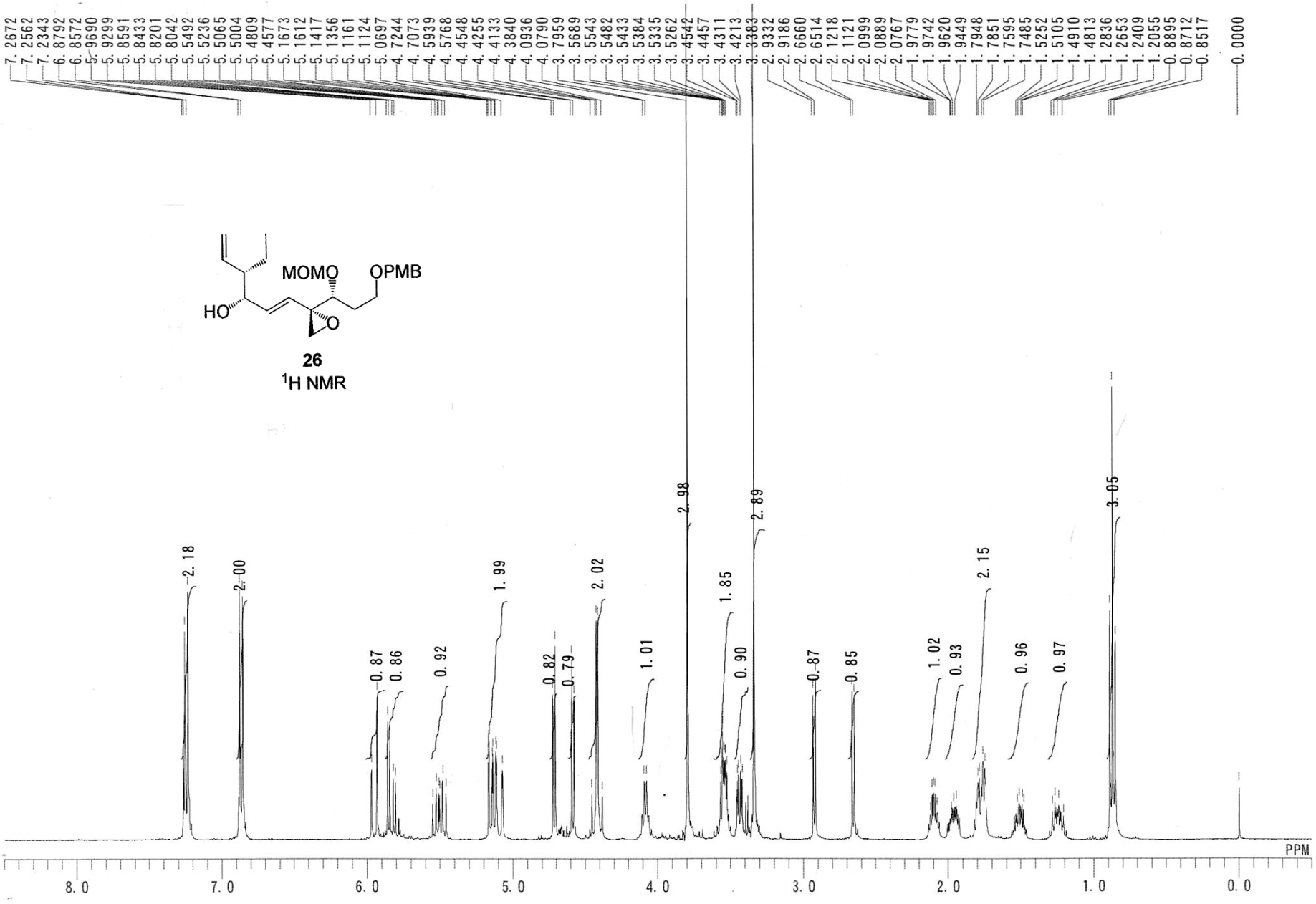
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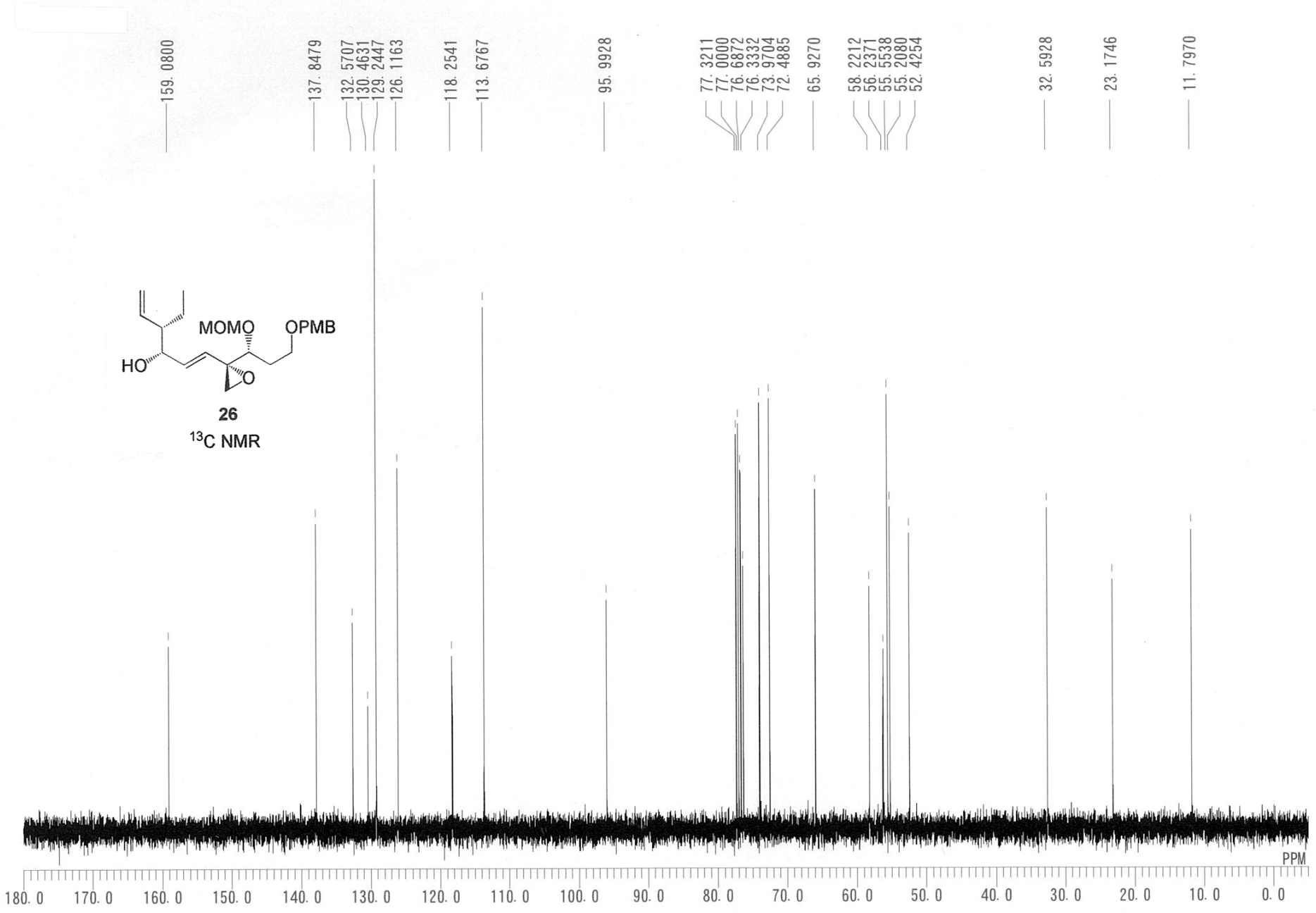
1.0
0.0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23. 1746
11. 7970
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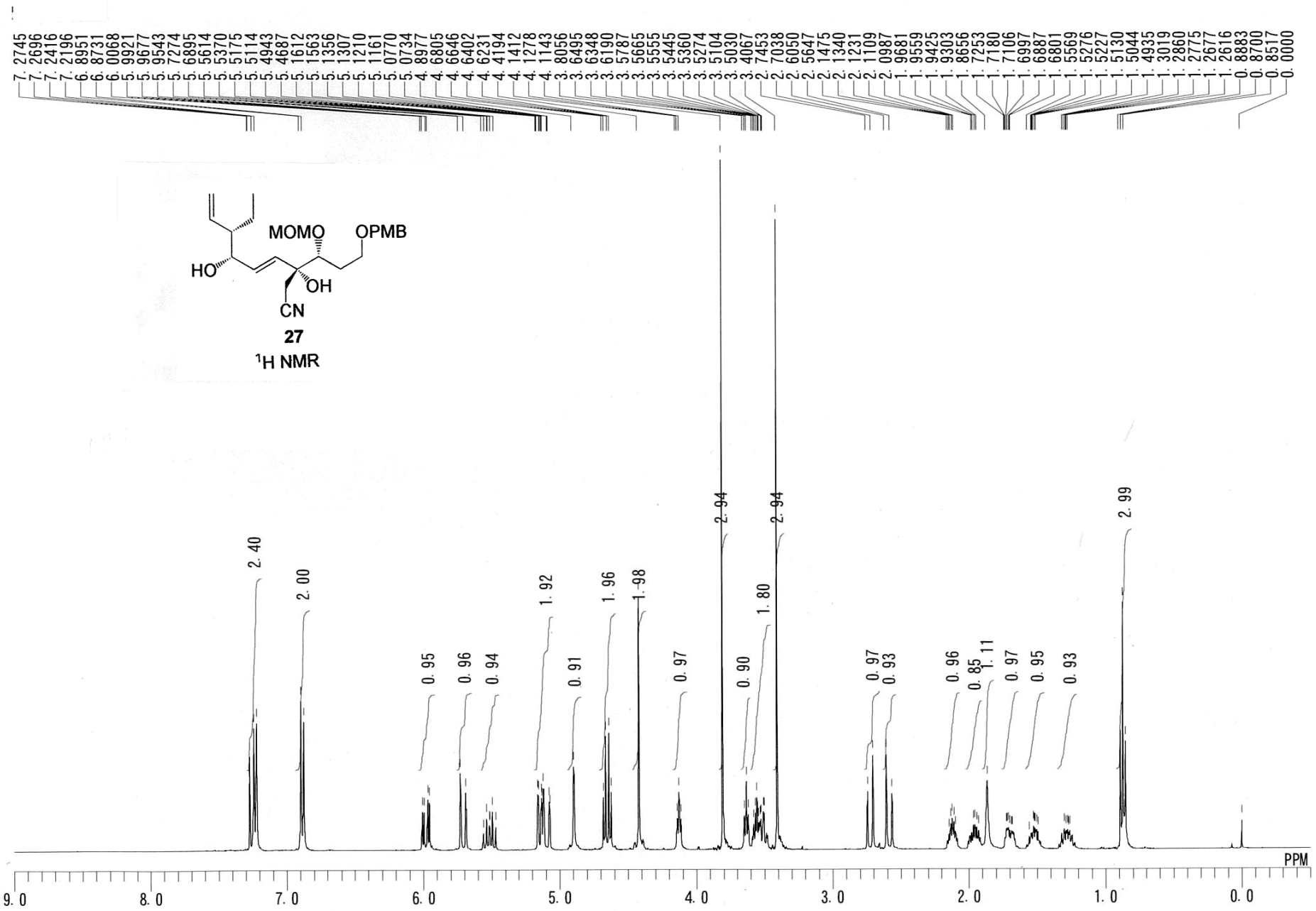
26
13C NMR
PPM
180. 0
170. 0
160. 0
150. 0
140. 0
130. 0
120. 0
110. 0
100. 0
90. 0
80. 0
70. 0
60. 0
50. 0
40. 0
30. 0
20. 0
10. 0
0. 0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OPMB
HO
OH
CN
27
^{1}H NMR
PPM
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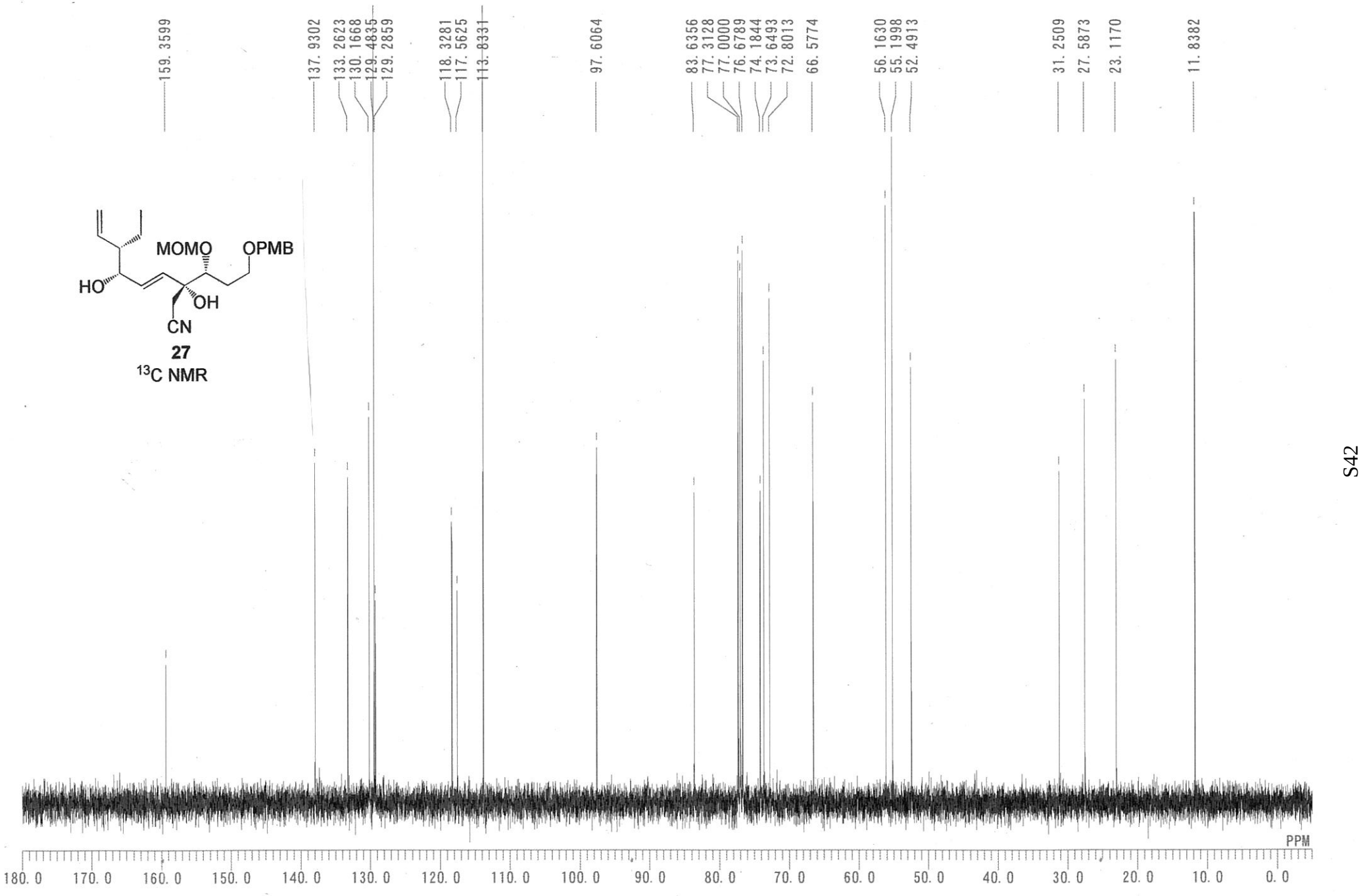
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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137.9302
133.2623
130.1668
129.4835
129.2859
118.3281
117.5625
113.8331
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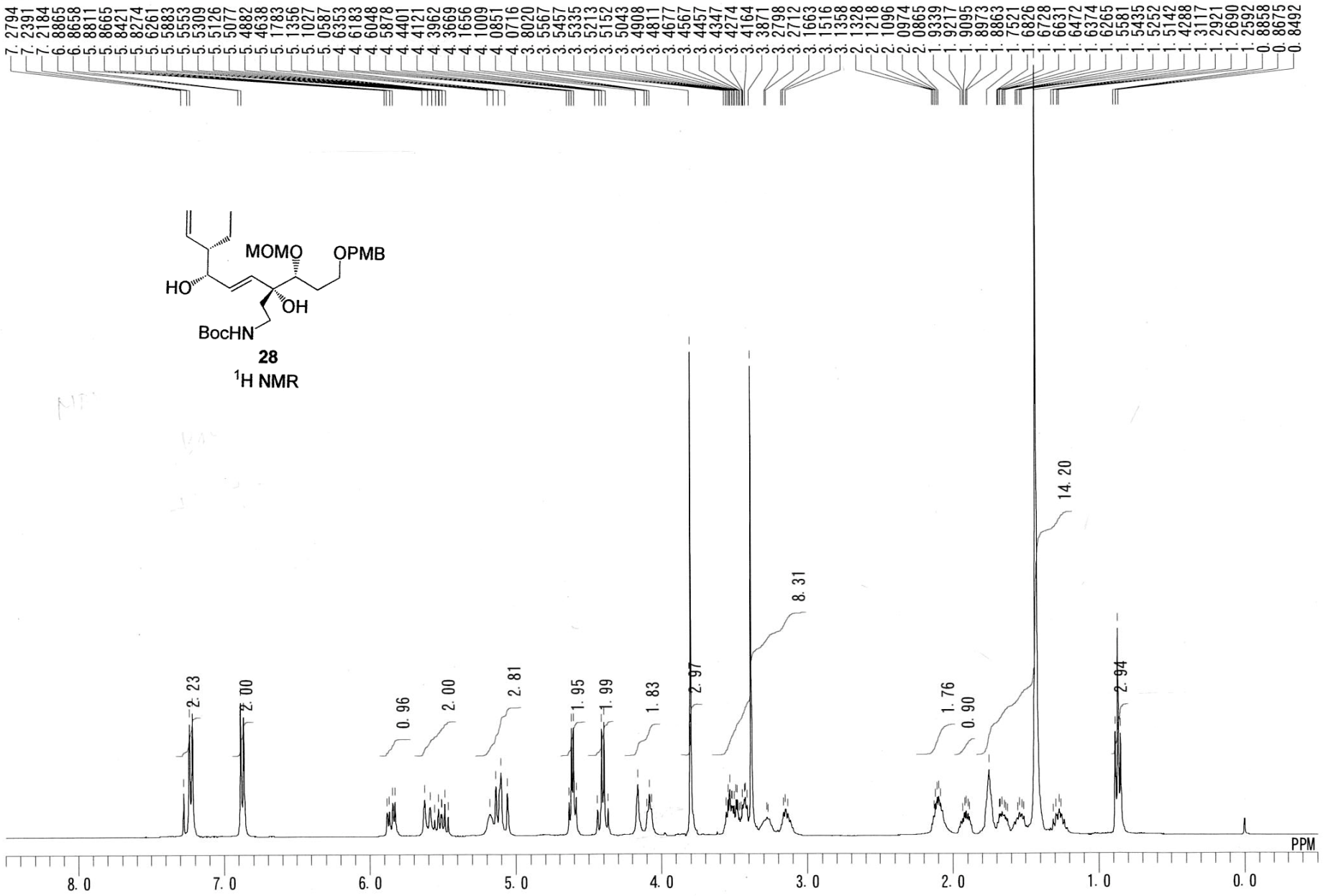
83.6356
77.3128
77.0000
76.6789
74.1844
73.6493
72.8013
66.5774
56.1630
55.1998
52.4913
31.2509
27.5873
23.1170
11.8382
MOMO
OPMB
HO
OH
CN
27
13C NMR
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0


MOMO
OPMB
HO
OH
BocHN
28
1H NMR
PPM
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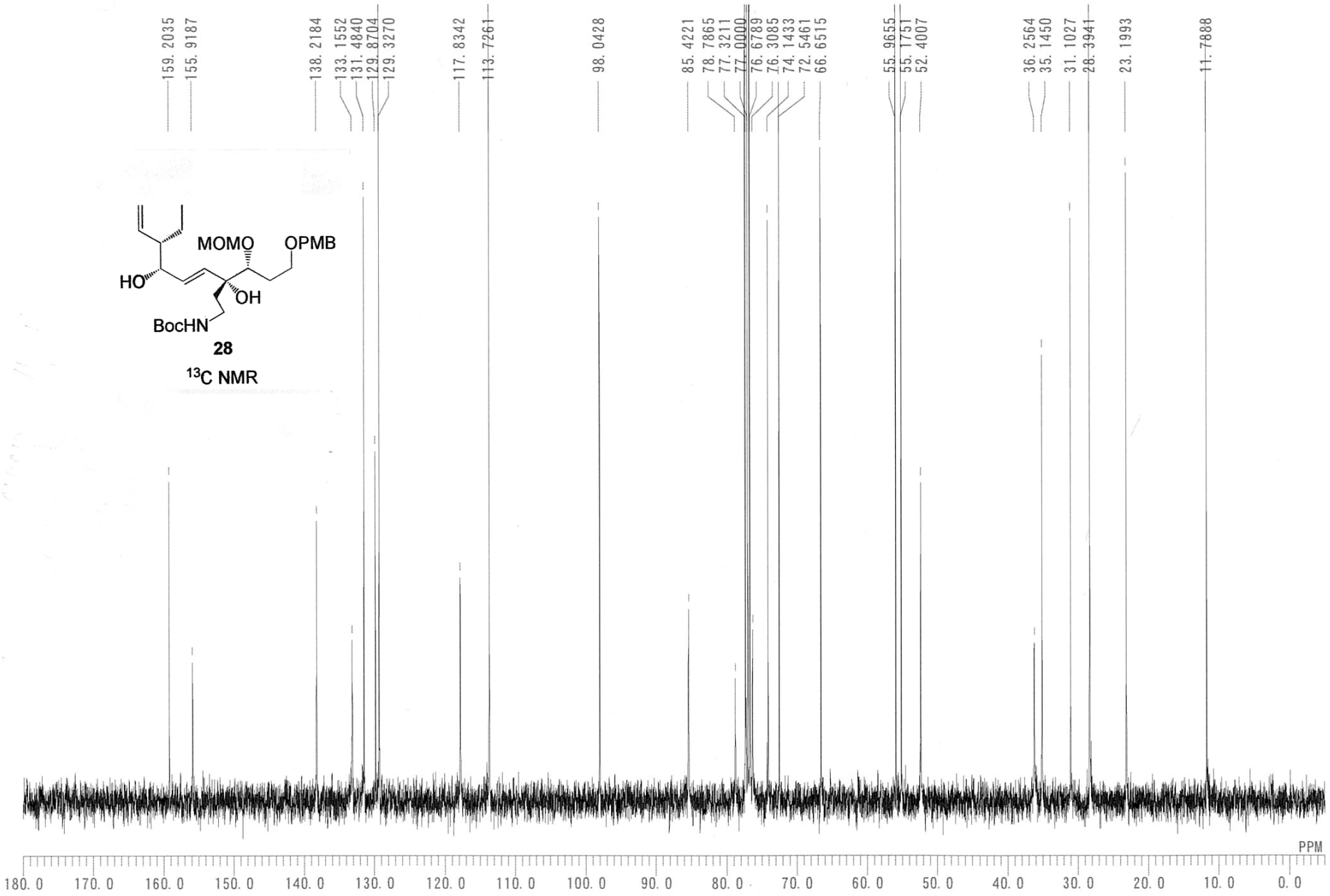
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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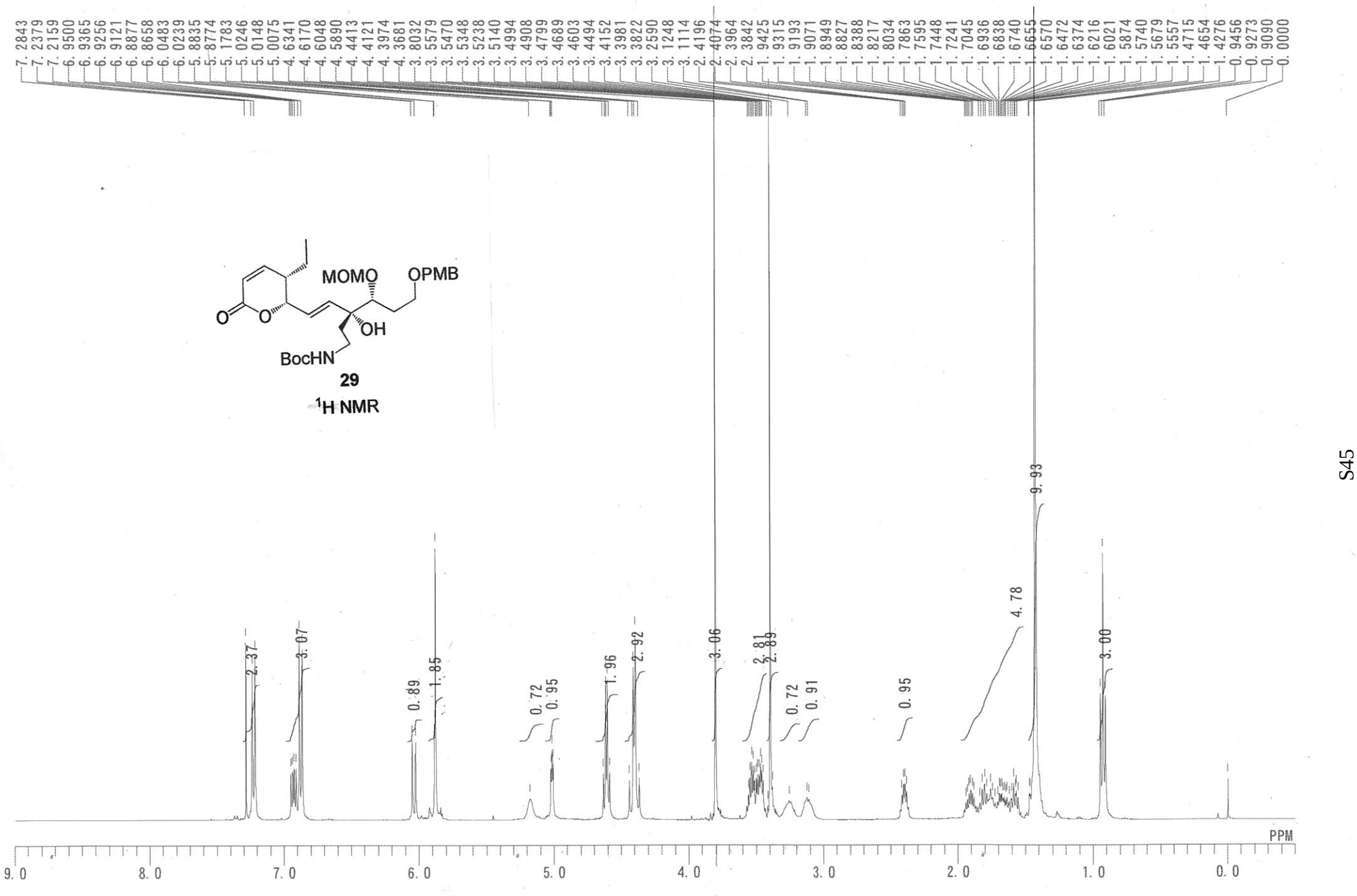
138.2184
133.1552
131.4840
129.8704
129.3270
117.8342
113.7261
98.0428
85.4221
78.7865
77.3211
77.0000
76.6789
76.3085
74.1433
72.5461
66.6515
55.9655
55.1751
52.4007
36.2564
35.1450
31.1027
28.3941
23.1993
11.7888
MOMO
OPMB
HO
OH
BocHN
28
13C NMR
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0


MOMO
OPMB
OH
BocHN
29
^{1}H NMR
PPM
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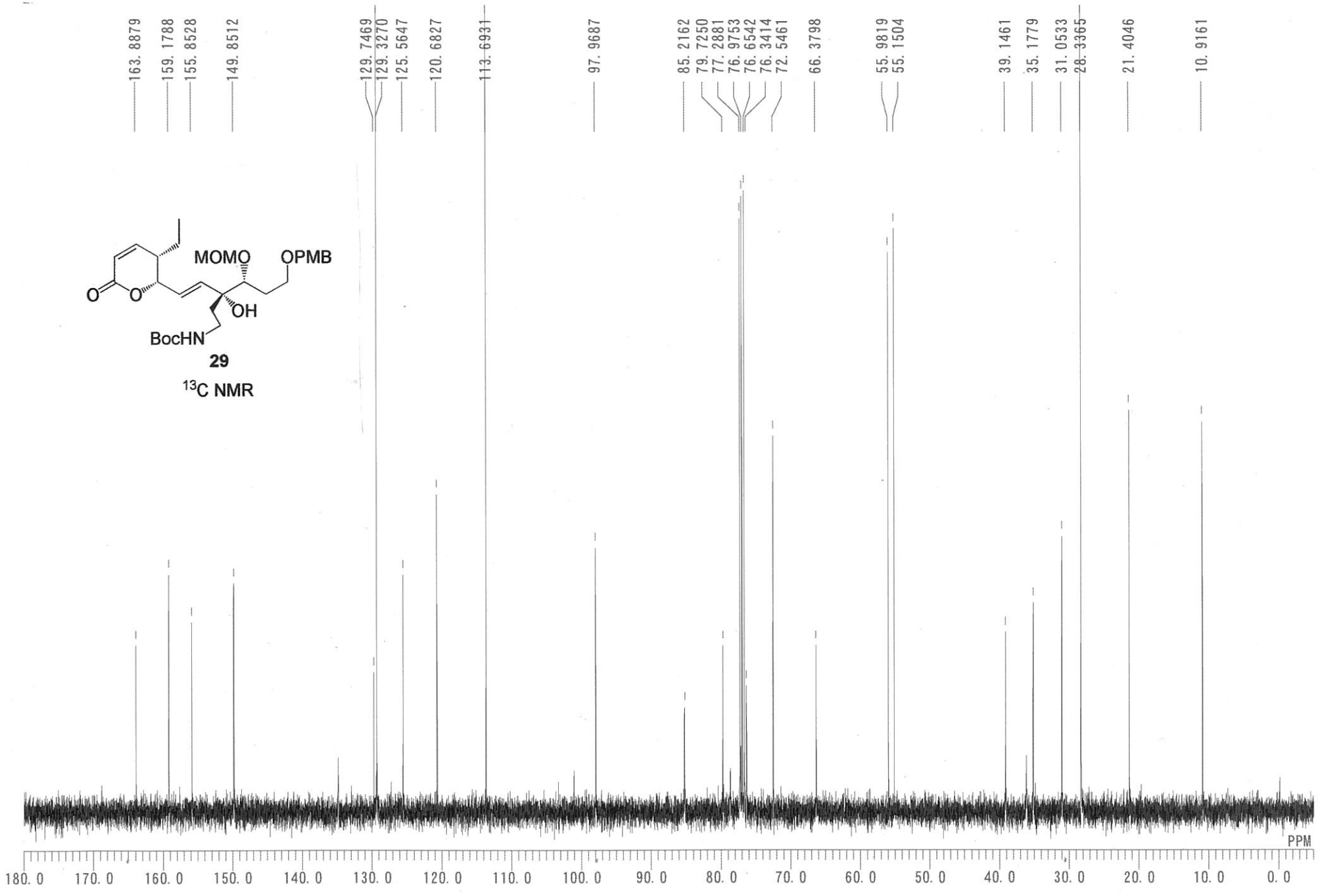
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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149.8512
129.7469
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120.6827
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97.9687
85.2162
79.7250
77.2881
76.9753
76.6542
76.3414
72.5461
66.3798
55.9819
55.1504
39.1461
35.1779
31.0533
28.3365
21.4046
10.9161
MOMO
OPMB
OH
BocHN
29
13C NMR
PPM
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
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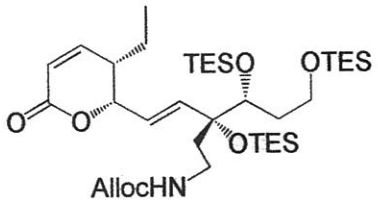
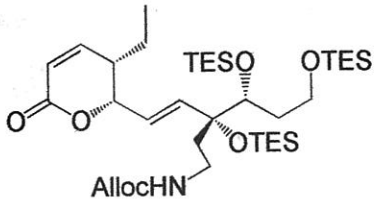

TESO
OTES
OTES
AllocHN

31

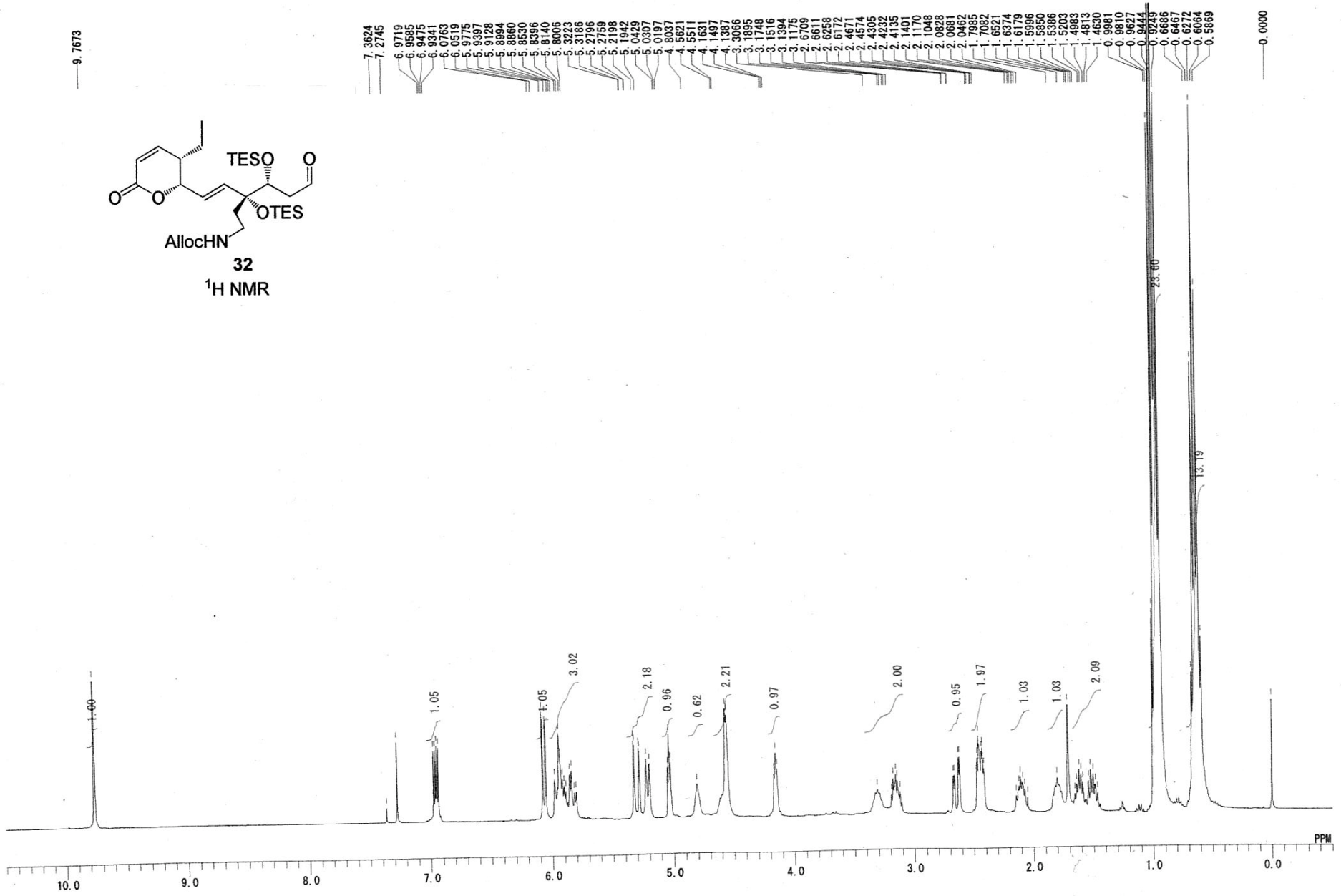
^{1}H NMR

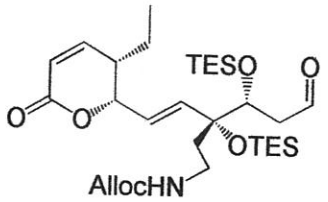
0.93
3.00
1.01
1.04
1.75
2.37
3.38
2.08
1.05
0.99
1.60
9.45
1.07
PPM
8
6
4
2
0



31

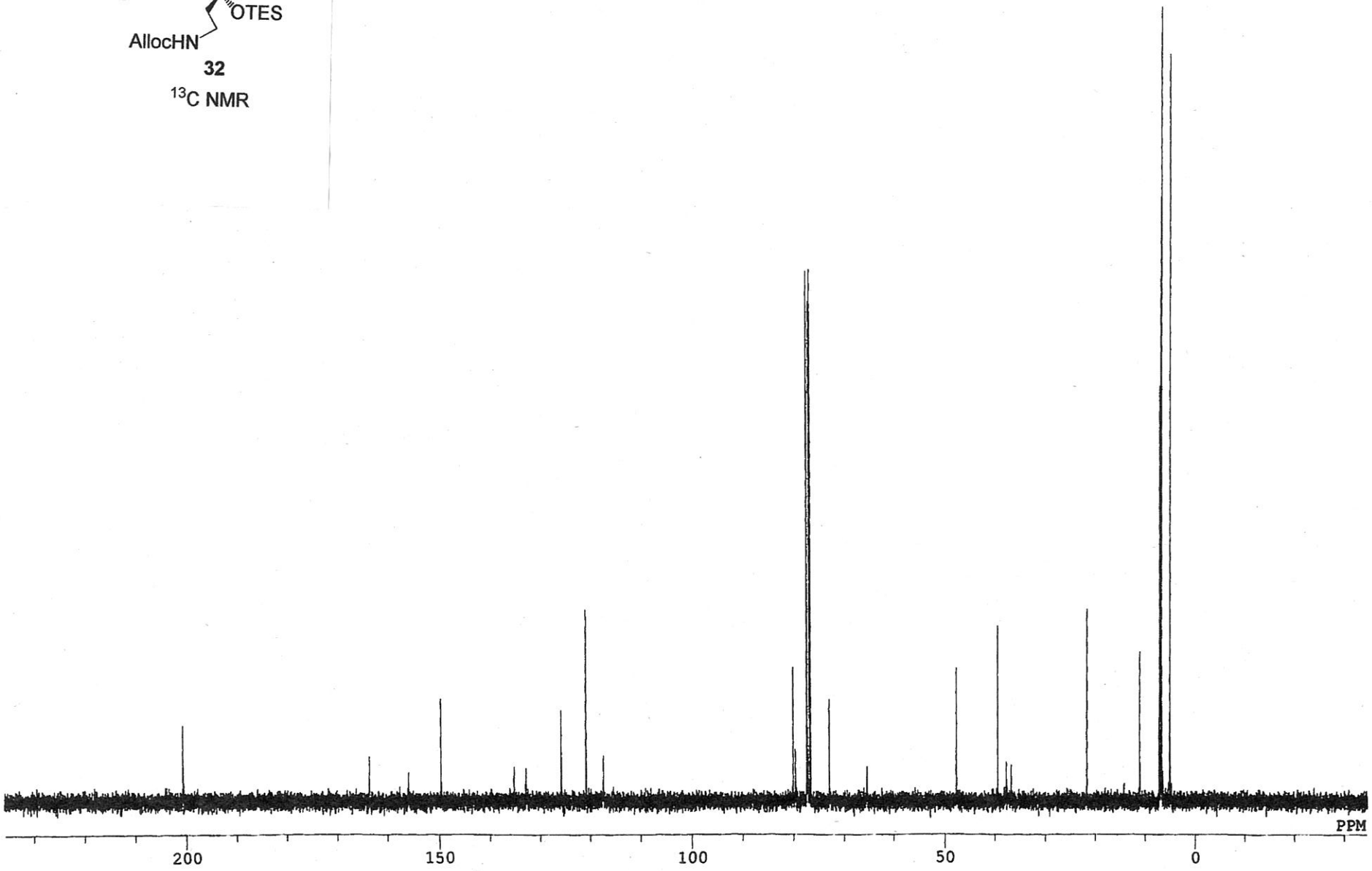
^{13}C NMR

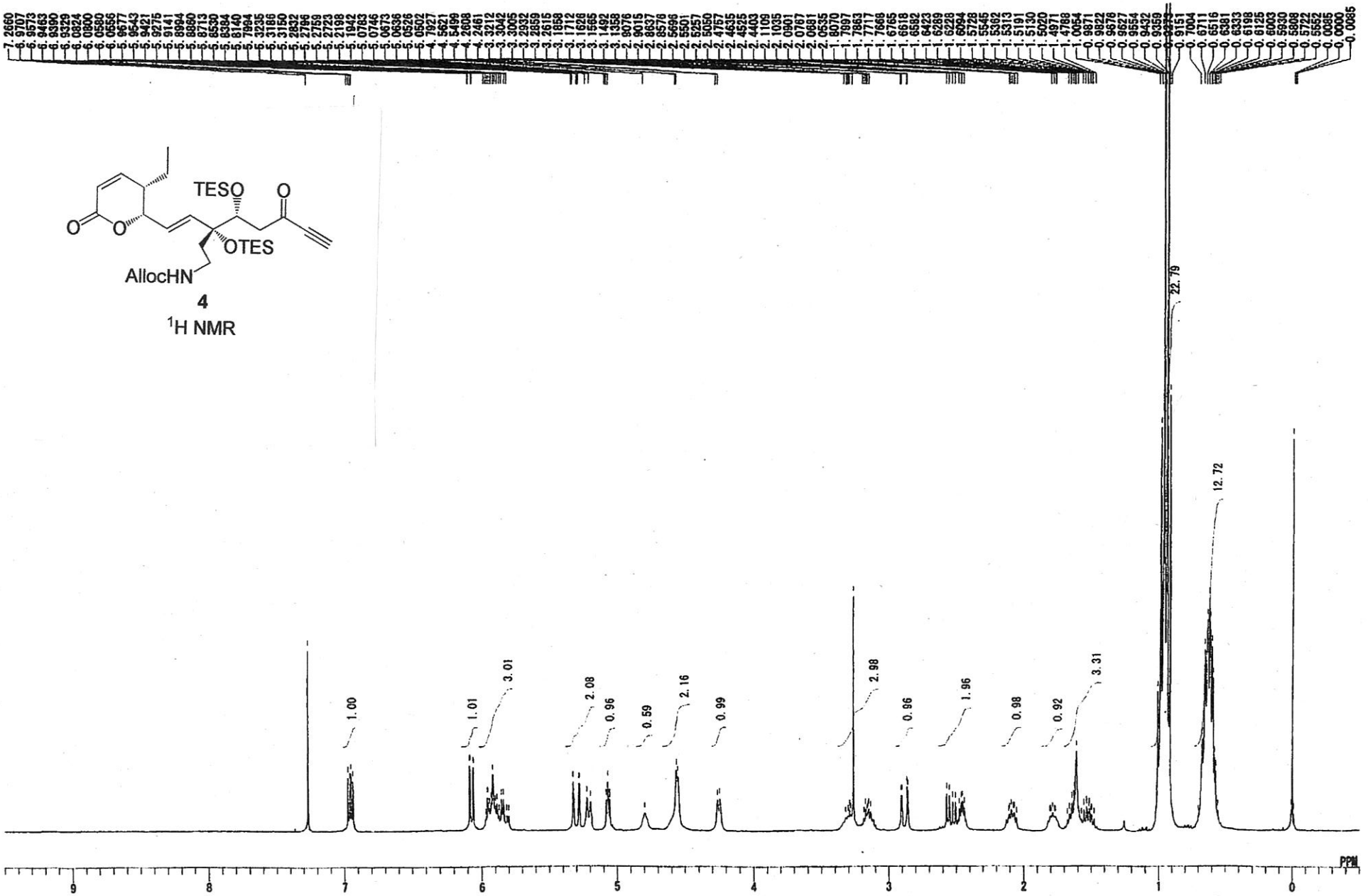

TESO
O
O
O
OTES
AllocHN
32
^{1}H NMR
PPM

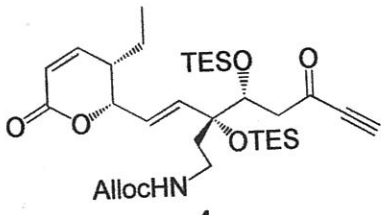


32

^{13}C NMR




TESO
O
O
O
OTES
AllocHN
4
^{1}H NMR
1.00
1.01
3.01
2.08
0.96
0.59
2.16
0.99
2.98
0.96
1.96
0.98
0.92
3.31
22.79
12.72
PPM
9
8
7
6
5
4
3
2
1
0



4

^{13}C NMR