Formal Total Syntheses of (+)-Prelaureatin and (+)-laurallene by Diastereoselective Brook Rearrangement-Mediated [3 + 4] Annulation

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Supporting Information

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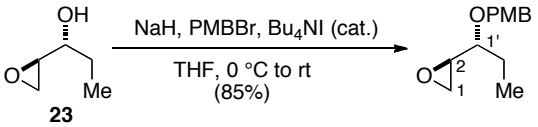
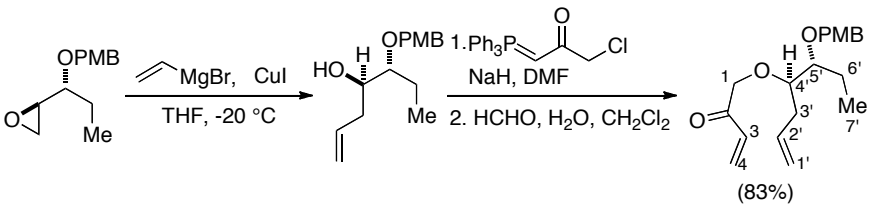
General. Infrared spectra were recorded on an FT-IR spectrometer. Melting points were uncorrected. ^{1}H NMR spectra were taken on either 500 MHz spectrometer in $CDCl_3$ with reference to $CHCl_3$ (δ 7.26) or in C_6D_6 with reference to C_6H_6 (δ 7.20). ^{13}C NMR spectra were measured with either 125 MHz spectrometers in $CDCl_3$ with reference to the $CDCl_3$ triplet (δ 77.2) or in C_6D_6 with reference to the C_6H_6 triplet (δ 128.0). Resonance patterns were described as s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad. The assignment of ^{1}H and ^{13}C NMR spectra is based on H-H decoupling and HMQC experiments. Mass spectra were obtained either in EI mode or in ESI mode. Liquid chromatography under medium pressures (MPLC) was carried out using prepacked columns (22 mm x 100 mm (5 μ silica gel) or 22 mm x 300 mm (10 μ silica gel)). For routine chromatography, the following adsorbents were used: silica gel 60N of particle size 63-210 μm for column chromatography; precoated silica gel 60 F-254 plates for analytical thin-layer chromatography. All moisture sensitive reactions were performed under a positive pressure of nitrogen. Anhydrous $MgSO_4$ was used for drying all organic solvent extracts in workup, and the removal of the solvents was performed with a rotary evaporator. Dry solvents and reagents were obtained by using standard procedures.

(*R*)-2-((*R*)-1-(4-Methoxybenzyloxy)propyl)oxirane



To a cooled (0 °C) suspension of NaH (60%, 90 mg, 2.24 mmol) in THF (2 mL) were added a solution of **22** (191 mg, 1.87 mmol) in THF (0.5 mL), *n*-Bu_4NI (83 mg, 0.224 mmol) and a solution of *p*-methoxybenzyl bromide (326 μL, 2.24 mmol) in THF (0.5 mL). After being stirred at room temperature for 1 h, the mixture was poured into water (1.5 mL) and extracted with AcOEt (5 mL x3). Combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 50 g, elution with hexane/Et_2O = 4:1) to give the title compound (351 mg, 85%), colorless oil, R_f = 0.26 (hexane/Et_2O = 4:1), $[\alpha]^{25}_D$ 32.1 (*c* 1.00, $CHCl_3$). IR (film) = 1612, 1514, 1248 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.97 (3H, t, *J* = 7.6 Hz, H-3'), 1.55-1.72 (2H, m, H-2'), 2.50 (1H, dd, *J* = 4.8, 2.7 Hz, H-1), 2.78 (1H, dd, *J* = 4.8, 4.1 Hz, H-1), 2.95 (1H, ddd, *J* = 7.3, 7.3, 5.3 Hz, H-1'), 3.02 (1H, ddd, *J* = 7.3, 4.1, 2.7 Hz, H-2), 3.80 (3H, s, OMe), 4.53 and 4.76 (each 1H, d, *J* = 11.4 Hz, $CH_2OC_6H_4OMe$), 6.88 (2H, d, *J* = 8.7 Hz, Ar-H), 7.31 (2H, d, *J* = 8.7 Hz, Ar-H). ^{13}C NMR ($CDCl_3$) δ 10.3 (C-3'), 25.6 (C-2'), 43.3 (C-1), 55.1 (C-2), 55.4 (OMe), 71.5 ($CH_2C_6H_4OMe$), 81.6 (C-1'), 113.9 (Ar), 129.6 (Ar), 131.0 (Ar), 159.3 (Ar). HRMS calcd for $C_{13}H_{18}O_3$ 222.1256, found 222.1257. This reaction can be performed on a multigram scale.

1-(((4*R*,5*R*)-5-((4-Methoxybenzyl)oxy)hept-1-en-4-yl)oxy)but-3-en-2-one



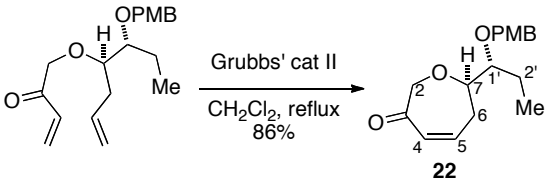
To a cooled (–78 °C) solution of CuI (860 mg, 4.50 mmol) in THF (30 mL) was added allyl magnesium chloride (1.46 M in THF, 23 mL, 33.7 mmol). The mixture was stirred at –50 °C for 10 min before addition of a solution of (*R*)-2-((*R*)-1-((4-methoxybenzyl)oxy)propyl)oxirane (5.00 g, 22.5 mmol) in THF (15 mL). After being stirred at the same temperature for 10 min, the mixture was warmed to room temperature and then saturated aqueous NH_4Cl solution (50 mL) was added. The resulting suspension was filtered through a pad of Celite. The solid was washed with Et_2O, and the filtrate was separated. The aqueous phase was

extracted with Et_2O (30 mL x 2). Combined organic phases were washed with saturated brine, dried, and concentrated. The residual oil was used for next step without further purification.

To a cooled (0 °C) solution of the above crude material (5.60 g) and 1-chloro-3-(triphenylphosphoranylidene)propan-2-one (7.94 g, 22.5 mmol) in DMF (75 mL) was added NaH (60%, 1.35 g, 33.7 mmol). The reaction mixture was warmed to room temperature and stirred for 6 h before addition of ice-water (5 mL). The mixture was partitioned between AcOEt (10 mL) and saturated brine (20 mL), and the aqueous phase was extracted with AcOEt (10 mL). Combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was used for next step without further purification.

To a cooled (0 °C) solution of the above crude material (14.70 g) in CH_2Cl_2 (450 mL) was added aqueous HCHO (37%, 16.8 mL, 22.5 mmol). The mixture was stirred at the same temperature for 1 h before addition of H_2O (60 mL). Phases were separated and the aqueous phase was extracted with CH_2Cl_2 (60 mL x 2). Combined organic phases were washed with saturated brine (50 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 300 g, elution with hexane/CH_2Cl_2/Et_2O = 8:5:1) to give the title compound (5.93 g, 83%), colorless oil, R_f = 0.46 (hexane/CH_2Cl_2/Et_2O = 3:5:1), $[\alpha]^{22}_D$ –41.4 (*c* 1.00, $CHCl_3$). IR (film) = 1703 cm^{-1}. ^1H NMR δ 0.95 (3H, t, *J* = 7.3 Hz, H-7'), 1.43-1.53 (1H, m, H-6'), 1.62-1.71 (1H, m, H-6'), 2.24-2.31 (1H, m, H-3), 2.39-2.45 (1H, m, H-3), 3.39-3.47 (2H, m, H-4' and H-5'), 3.79 (3H, s, OMe), 4.35 and 4.51 (each 2H, s, CH_2OAr and C-1), 5.05 (1H, dm, *J* = 10.0 Hz, H-1'), 5.09 (1H, dd, *J* = 17.6, 1.8 Hz, H-1'), 5.77 (1H, d, *J* = 10.7 Hz, H-4), 5.82-5.90 (1H, m, H-2'), 6.30 (1H, dd, *J* = 17.6, 1.4 Hz, H-4), 6.56 (1H, dd, *J* = 17.6, 10.7 Hz, H-3), 6.86 (2H, d, *J* = 8.7 Hz, Ar-H), 7.25 (2H, d, *J* = 8.7 Hz, Ar-H). ^{13}C NMR δ 10.2 (C-7'), 23.1 (C-6'), 35.0 (C-3'), 55.4 (OMe), 75.3 (*C*$H_2OC_6H_4OMe$), 76.9 (C-1), 81.7 and 81.9 (C-4' and C-5'), 113.9 (Ar), 117.2 (C-1'), 129 (C-3), 131.0 (Ar), 131.0 (Ar), 132.7 (C-2'), 135.3 (C-5), 159.3 (Ar), 197.6 (C-2). HRMS calcd for $C_{19}H_{26}O_4Na$ $(M + Na)^+$ 341.1723, found 341.1719.

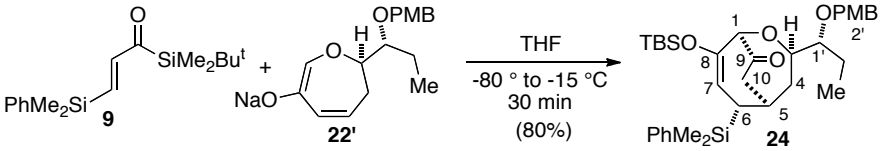
(*R*)-7-((*R*)-1-(4-Methoxybenzyloxy)propyl)-6,7-dihydrooxepin-3(2*H*)-one (22)



22

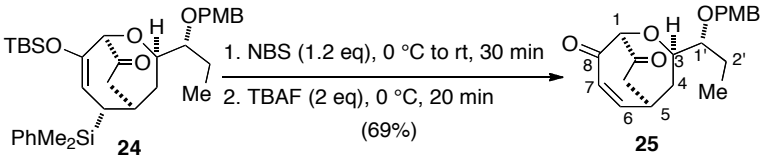
A solution of 1-(((4*R*,5*R*)-5-((4-methoxybenzyl)oxy)hept-1-en-4-yl)oxy)but-3-en-2-one (7.04 g, 22.1 mmol) and the Grubbs' second generation catalysis (94 mg, 0.111mmol) in CH_2Cl_2 (440 mL) was refluxed for 13 h at which time the solution was concentrated, and the residue was subjected to column chromatography (silica gel, 200 g; elution with hexane/AcOEt = 3:1) to give **22** (5.53 g, 86%), colorless oil, R_f = 0.27 (hexane/CH_2Cl_2/Et_2O = 3:5:1), $[\alpha]^{21}_D$ 104.8 (*c* 1.01, $CHCl_3$). IR (film) = 1666, 1248 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.96 (1H, t, *J* = 7.3 Hz, H-3'), 1.51-1.60 (1H, m, H-2'), 1.62-1.71 (1H, m, H-2'), 2.45 (1H, ddd, *J* = 19.7, 5.5, 2.3 Hz, H-6), 2.77 (1H, dddd, *J* = 19.7, 10.5, 3.4, 3.4 Hz, H-6), 3.30-3.33 (1H, m, H-1'), 3.71-3.74 (1H, m, H-7), 3.8 (3H, s, OMe), 4.21 (1H, d, *J* = 18.3 Hz, H-2), 4.45 (1H, d, *J* = 18.3 Hz, H-2), 4.52 (1H, d, *J* = 11.2 Hz, C*H*$_2C_6H_4OMe$), 4.57 (1H, d, *J* = 11.2 Hz, C*H*$_2C_6H_4OMe$), 6.02 (1H, dd, *J* = 12.4, 2.3 Hz, H-4), 6.56 (1H, ddd, *J* = 12.4, 3.4, 3.4 Hz, H-5), 6.87 (2H, d, *J* = 8.5 Hz, Ar-H), 7.26 (2H, d, *J* = 8.5 Hz, Ar-H). ^{13}C NMR ($CDCl_3$) δ 10.4 (C-3'), 23.0 (C-2'), 35.8 (C-6), 55.4 (OMe), 72.7 (*C*$H_2OC_6H_4OMe$), 78.1 (C-2), 80.8 (C-7), 81.9 (C-1'), 113.9 (C-5), 113.9 (Ar), 129.7 (Ar), 130.0 (C-4), 130.7 (Ar), 159.4 (Ar), 204.4 (C-3). HRMS calcd for $C_{17}H_{22}O_4Na$ $(M + Na)^+$ 313.1410, found 313.1407.

(1*R*,3*R*,5*R*,6*S*)-8-(*tert*-Butyldimethylsilyloxy)-6-(dimethyl(phenyl)silyl)-3-((*R*)-1-(4-methoxybenzyloxy)propyl)-2-oxabicyclo[3.3.2]-dec-7-en-9-one (24)



To a cooled (–80 °C) solution of NaHMDS (1.66 M in THF, 1.37 mL, 2.27 mmol) in THF (30 mL) was added a solution of **9** (692 mg, 2.27 mmol) in THF (8 mL) over 8 min and then the solution was stirred at the same temperature for 15 min. To this solution was added a solution of **22** (600mg, 2.27 mmol) in THF (8 mL) over 5 min and the mixture was allowed to warm to –15 °C over 30 min. The reaction mixture was poured into 10% aqueous NH_4Cl solution (30 mL) and extracted with Et_2O (20 mL x 3). Combined organic phases were washed with saturated brine (30 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 50 g, elution with hexane/AcOEt = 4:1) to give **24** (982 mg, 80%), pale yellow oil, R_f = 0.39 (hexane/AcOEt = 5:1), $[\alpha]^{25}_D$ 107.2 (*c* 1.00, $CHCl_3$). IR (film) =1707, 1252 cm^{-1}. ^1H NMR (C_6D_6) δ 0.19 and 0.19 (each 3H, s, Si*Me*$_2$Bu^t), 0.27 (6H, s, Si*Me*$_2$Ph), 0.98 (9H, s, *t*-Bu), 1.03 (3H, t, *J* = 7.3 Hz, H-3'), 1.50-1.58 (1H, m, H-2'), 1.69 (1H, dd, *J* = 12.8, 12.8 Hz, H-4), 1.73-1.78 (1H, m, H-2'), 1.92-1.97 (1H, m, H-4), 2.04-2.06 (1H, br m, H-6), 2.16-2.18 (1H, br m, H-5), 2.25 (1H, dd, *J* = 19.5, 4.1 Hz, H-10), 2.63 (1H, dd, *J* = 19.5, 3.4 Hz, H-10), 3.35 (3H, s, OMe), 3.38-3.42 (1H, m, H-1'), 3.79-3.83 (1H, m, H-3), 4.46 (1H, d, *J* = 11.5 Hz, C*H*$_2$C$_6$H$_4$OMe), 4.51 (1H, d, *J* = 11.5 Hz, C*H*$_2$C$_6$H$_4$OMe), 5.02 (1H, s, H-1), 5.24 (1H, dd, *J* = 4.6, 1.4 Hz, H-7), 6.85 (2H, d, *J* = 8.5 Hz, Ar-H), 7.24-7.25 (m), 7.29 (2H, d, *J* = 8.5 Hz, Ar-H), 7.42-7.44 (m). ^{13}C NMR (C_6D_6) δ –4.4, –4.2, –3.8, and –3.5 (SiMe$_2$Ph, SiMe$_2$Bu^t), 10.9 (C-3'), 18.1 (*C*Me$_3$), 23.2 (C-2'), 25.8 (C*Me$_3$*), 26.9 (C-5), 36.3 (C-6), 36.8 (C-4), 43.5 (C-10), 54.7 (OMe), 72.8 (*C*H$_2$OC$_6$H$_4$OMe), 74.3 (C-3), 83.0 (C-1'), 89.3 (C-1), 111.3 (C-7), 114.0, 128.3, 129.4, 129.6, 131.8, 134.0, 137.5, 147.6 and 159.7 (Ph and C-8), 203.0 (C-9). HRMS calcd for $C_{34}H_{50}O_5Si_2$ 594.3197, found 594.3186. This reaction can be performed on a multigram scale.

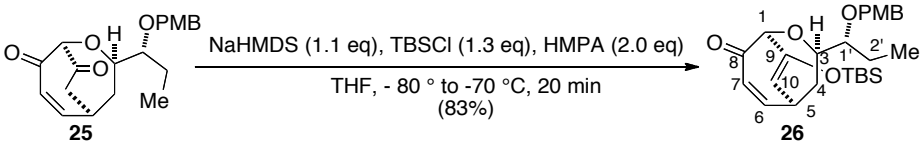
(1*S*,3*R*,5*R*)-3-((*R*)-1-(4-Methoxybenzyloxy)propyl)-2-oxabicyclo[3.3.2]dec-6-ene-8,9-dione (25)



To a cooled (0 °C) solution of NBS (682 mg, 3.83 mmol) in THF (70 mL) was added **24** (1.90 g, 3.19 mmol) in THF (8 mL) and the solution was stirred at room temperature for 20 min. The reaction mixture was recooled to 0 °C before addition of TBAF (1.0 M in THF, 3.83 mL, 3.83 mmol) and stirred for 20 min at the same temperature. The reaction mixture was poured into 10% aqueous NH_4Cl solution (40 mL) and Et_2O (40 mL), phases were separated and the aqueous phase was extracted with Et_2O (40 mL x 2). Combined organic phases were successively washed with water and saturated brine (40 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 50 g, elution with hexane/AcOEt = 2:1) to give **25** (758 mg, 69%), pale yellow oil, R_f = 0.42 (hexane/AcOEt = 1:1), $[\alpha]^{25}_D$ 228.8 (*c* 0.995, $CHCl_3$). IR (film) = 1720, 1680, 1250 cm^{-1}. ^1H NMR (C_6D_6) δ0.91 (3H, t, *J* = 7.3 Hz, H-3'), 1.04-1.48 (1H, m, H-2'), 1.18 (1H, ddd, *J* = 13.5, 7.8, 3.4 Hz, H-4), 1.28-1.37 (m), 1.65 (1H, dd, *J* = 13.5, 13.5 Hz, H-4), 1.98-2.03 (1H, m, H-5), 2.12 (1H, dd, *J* = 19.5, 3.0 Hz, H-10), 2.24 (1H, dd, *J* = 19.5, 3.2 Hz, H-10), 3.11-3.15 (1H, m, H-1'), 3.36 (3H, s, OMe), 3.94 (1H, ddd, *J* = 13.5, 4.5, 3.4 Hz, H-3), 4.39 (2H, s, C*H*$_2$C$_6$H$_4$OMe), 5.05 (1H, s, H-1), 5.76 (dd), 6.18 (1H, dd, *J* = 11.7, 11.7 Hz, H-6), 6.83 (2H, d, *J* = 8.7 Hz,

Ar-H), 7.28 (2H, d, *J* = 8.7 Hz, Ar-H). ^{13}C NMR (C_6D_6) δ 10.3 (C-3'), 23.0 (C-2'), 30.3 (C-4), 30.8 (C-5), 42.5 (C-10), 54.8 (OMe), 73.1 ($CH_2OC_6H_4OMe$), 80.4 (C-3), 82.5 (C-1'), 96.6 (C-1), 114.0 (Ar), 127.1 (C-7), 129.5 (Ar), 131.4 (Ar), 150.4 (C-6), 150.8 (Ar), 194.1 and 203.0 (C=O). HRMS calcd for $C_{20}H_{24}O_5$ 344.1624, found 344.1619.

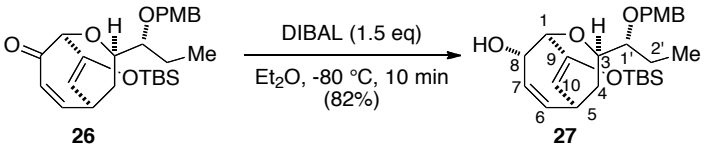
(3*R*)-9-(*tert*-Butyldimethylsilyloxy)-3-((*R*)-1-(4-methoxybenzyloxy)propyl)-2-oxabicyclo[3.3.2]deca-6,9-dien-8-one (26)



25 **26**

To a cooled (–80 °C) solution of NaHMDS (1.66 M in THF, 1.03 mL, 1.71 mmol) in THF (20 mL) were successively added a solution of **25** (534 mg, 1.55 mmol) in THF (2.5 mL), TBSCl (314 mg, 2.02 mmol) in THF (2.5 mL) and HMPA (539 mL, 3.10 mmol) in THF (1.5 mL). After being stirred at the same temperature for 20 min, the mixture was poured into 10% aqueous NH_4Cl solution (15 mL) and extracted with Et_2O (15 mL x 2). Combined organic phases were washed with water (15 mL) and saturated brine (15 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 30 g, elution with hexane/AcOEt = 6:1 to 5:1) to give **26** (591 mg, 83%), colorless oil, R_f = 0.48 (hexane/AcOEt = 4:1), $[\alpha]^{25}_D$ -103.3 (*c* 1.00, $CHCl_3$). IR (film) = 1684, 1254 cm^{-1}. ^{1}H NMR (C_6D_6) δ 0.15 and 0.16 (each 3H, s, $SiMe_2$), 0.95 (9H, s, *t*-Bu), 0.98 (3H, t, *J* = 7.3 Hz, H-3'), 1.38-1.47 (1H, m, H-4 and H-2'), 1.53-1.59 (1H, m, H-4), 1.60-1.63 (1H, m, H-2'), 2.51 (1H, ddd, *J* = 8.9, 8.5, 8.5 Hz, H-5), 3.31-3.35 (1H, m, H-1'), 3.36 (3H, s, OMe), 4.45 (1H, d, *J* = 11.5 Hz, CH_2C$_6$H$_4$OMe), 4.50 (1H, ddd, *J* = 10.3, 5.5, 4.4 Hz, H-3), 4.56 (1H, d, *J* = 11.5 Hz, CH_2C$_6$H$_4$OMe), 4.83 (1H, dd, *J* = 2.1, 2.1 Hz, H-1), 5.37 (1H, dd, *J* = 8.5, 2.1 Hz, H-10), 5.78 (1H, dd, *J* = 11.7, 2.1 Hz, H-7), 6.25 (1H, dd, *J* = 11.7, 8.9 Hz, H-6), 6.83 (2H, d, *J* = 8.7 Hz, Ar-H), 7.26 (2H, d, *J* = 8.7 Hz, Ar-H). ^{13}C NMR (C_6D_6) δ –4.7 and –4.3 ($SiMe_2$), 10.5 (C-3'), 18.1 (*C*Me$_3$), 23.3 (C-2'), 25.7 (C*Me$_3$*), 28.5 (C-4), 32.5 (C-5), 54.8 (OMe), 72.9 ($CH_2OC_6H_4OMe$), 77.0 (C-3), 82.6 (C-1'), 89.7 (C-1), 111.0 (C-10), 113.9 (Ar), 125.1 (C-7), 129.4 (Ar), 131.9, 149.9 and 159.6 (Ar and C-9), 149.9 (C-6), 193.4 (C-8). HRMS calcd for $C_{26}H_{38}O_5Si$ 458.2489, found 458.2490.

(3*R*,8*S*)-9-(*tert*-Butyldimethylsilyloxy)-3-((*R*)-1-(4-methoxybenzyloxy)propyl)-2-oxabicyclo[3.3.2]deca-6,9-dien-8-ol (27)

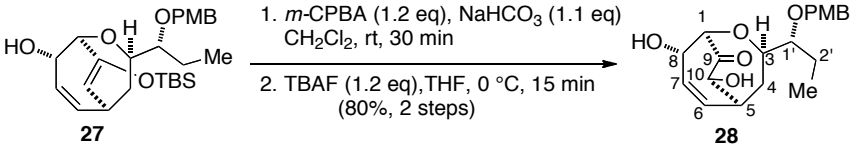


26 **27**

To a cooled (–80 °C) solution of **26** (107 mg, 0.233 mmol) in Et_2O (4 mL) was added DIBAL (1.0 M in hexane, 350 μL, 0.350mmol). After being stirred at the same temperature for 10 min, the mixture was poured into 10% aqueous NH_4Cl solution (5 mL) and Et_2O (5 mL). The mixture was warmed to room temperature, filtered through a pad of Celite, and washed with Et_2O. The filtrate was extracted with Et_2O (5 ml x 2). The combined organic phases were washed with water (5 mL) and brine (5 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 5 g, elution with hexane/AcOEt = 7:1 to 5:1) to give **27** (87.5 mg, 82%), colorless oil, R_f = 0.38 (hexane/AcOEt = 4:1), $[\alpha]^{25}_D$ 145.4 (*c* 1.010, $CHCl_3$). IR (film) = 3444, 1250 cm^{-1}. ^{1}H NMR (C_6D_6) δ 0.23s, 0.24s, 1.01s, 1.02 (3H, t, *J* = 7.3 Hz, H-3'), 1.43-1.50 (1H, m, OH), 1.43-1.50 (1H, m, H-2'), 1.43-1.50 (1H, m, H-4), 1.52-1.60 (1H, m, H-4), 1.62-1.70 (1H, m, H-2'), 2.45 (1H, ddd, *J* = 8.7, 8.7, 8.7 Hz, H-5), 3.36s, 3.37-3.41 (1H, m, H-1'), 4.18-4.22 (1H, br m, H-8), 4.39 (1H, ddd, *J* = 9.4, 5.7, 3.9 Hz, H-3), 4.53-4.54 (1H, m, H-1), 4.53 (1H, d, *J* = 11.2 Hz, CH_2OC$_6$H$_4$OMe), 4.70 (1H, d, *J* = 11.2 Hz, CH_2OC$_6$H$_4$OMe), 5.34 (1H, dd, *J* = 8.9, 2.5 Hz, H-10), 5.58 (1H, ddd, *J* = 11.5, 5.0, 1.4 Hz, H-7), 5.90 (1H, dd, *J* = 11.5, 9.2 Hz, H-6), 6.85 (1H, d, *J* = 8.7 Hz, Ar-H), 7.32 (1H, d, *J* = 8.7 Hz, Ar-H). ^{13}C NMR (C_6D_6) δ –4.2 and –4.0 ($SiMe_2$), 10.5 (C-3'), 18.1 (*C*Me$_3$), 23.6

(C-2'), 25.8 (C*Me*$_3$), 30.0 (C-5), 31.0 (C-4), 54.7 (OMe), 67.8 (C-8), 72.9 (*C*H$_2$OC$_6$H$_4$OMe), 76.2 (C-3), 82.9 (C-1'), 83.2 (C-1), 110.2 (C-10), 113.9 (Ar), 128.3 (C-7), 129.4 (Ar), 132.2, 150.4 and 159.5 (Ar and C-9), 135.6 (C-6). HRMS calcd for $C_{26}H_{40}O_5Si$ 460.2645, found 460.2635.

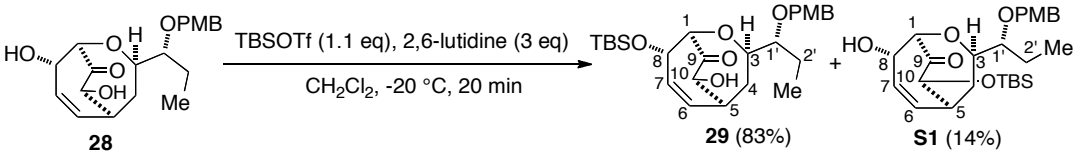
(1*R*,3*R*,5*S*,8*S*,10*S*)-8,10-Dihydroxy-3-((*R*)-1-(4-methoxybenzyloxy)propyl)-2-oxabicyclo[3.3.2]dec-6-en-9-one (28)



27 **28**

To a solution of **27** (436 mg, 0.915 mmol) were added $NaHCO_3$ (83 mg, 1.00 mmol) and mCPBA (77%, 224 mg, 1.00 mmol). After being stirred at room temperature for 30 min, the mixture was poured into 10% K_2CO_3 (10 mL) and Et_2O (20 mL). Phases were separated and the aqueous phase was extracted with Et_2O (10 mL x 2). Combined organic phases were successively washed with 10% K_2CO_3 (10 mL) and saturated brine (10 mL), dried, and concentrated. The residual oil was dissolved in THF (17 mL), and *n*-Bu_4NF (TBAF)(1.0 M in THF, 1.1 mL, 1.10 mmol) was added at room temperature. After being stirred for 12 min, the mixture was poured into water (15 mL) and Et_2O (15 mL). Phases were separated and the aqueous phase was extracted with Et_2O (10 mL x 2). Combined organic phases were washed with saturated brine (15 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 20 g, elution with hexane/AcOEt = 1:8) to give **28** (265 mg, 80%), colorless oil, R_f = 0.46 (AcOEt), $[\alpha]^{26}_D$ 145.0 (*c* 1.04, $CHCl_3$). IR (film) = 3410, 1710, 1248 cm^{-1}. ^{1}H NMR (C_6D_6) δ 0.93 (3H, t, *J* = 7.3 Hz, H-3'), 1.27-1.35 (1H, m, H-2'), 1.37-1.47 (1H, m, H-2'), 1.37-1.47m, 1.54 (1H, dd, *J* = 13.1, 13.1 Hz, H-4), 2.68 (1H, ddd, *J* = 8.5, 8.5, 3.2 Hz, H-5), 3.11 (1H, ddd, *J* = 8.5, 5.5, 4.1 Hz, H-1'), 3.36 (3H, s, OMe), 3.71 (1H, ddd, *J* = 12.1, 5.5, 3.2 Hz, H-3), 3.87-3.91 (1H, m, H-10), 4.30 (1H, br dd, *J* = 4.4, 4.4 Hz, H-8), 4.43 (1H, d, *J* = 11.2 Hz, C*H*$_2$OC$_6$H$_4$OMe), 4.50, 4.69 (1H, d, *J* = 5.7 Hz, H-1), 5.53 (1H, ddd, *J* = 12.1, 4.4, 1.4 Hz, H-7), 5.67 (1H, dd, *J* = 12.1, 9.2 Hz, H-6), 6.86 (2H, d, *J* = 8.7 Hz, Ar-H), 7.27 (1H, d, *J* = 8.7 Hz, Ar-H). ^{13}C NMR (C_6D_6) δ 10.3 (C-3'), 23.3 (C-2'), 31.8 (C-4), 35.4 (C-5), 54.8 (OMe), 70.7 (C-8), 73.2 (*C*H$_2$OC$_6$H$_4$OMe), 78.8 (C-10), 78.9 (C-3), 83.1 (C-1'), 88.7 (C-1), 114.1 (Ar), 129.6 (Ar), 210.8 (C-9), 128.3, 129.3, 131.6 and 132.0 (Ar,C-6 and C-7). HRMS calcd for $C_{20}H_{26}O_6$ 362.1729, found 362.1733.

(1*R*,3*R*,5*S*,8*S*,10*S*)-8-(*tert*-Butyldimethylsilyloxy)-10-hydroxy-3-((*R*)-1-(4-methoxybenzyloxy)propyl)-2-oxabicyclo[3.3.2]dec-6-en-9-one (29)

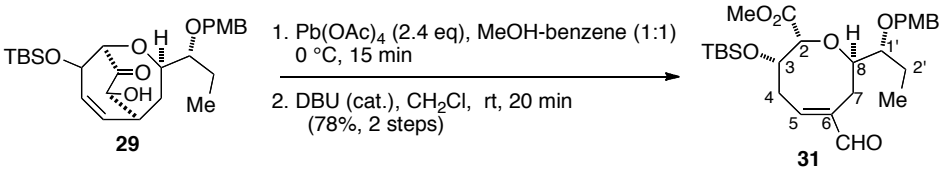


28 **29** (83%) **S1** (14%)

To a cooled (-40 °C) solution of **28** (264 mg, 0.728 mmol) were successively added 2,6-lutidine (254 μL, 2.18 mmol) and TBSOTf (184 μL, 0.801 mmol). After being stirred at the same temperature for 15 min, the mixture was poured into water (10 mL) and Et_2O (15 mL). Phases were separated and the aqueous phase was extracted with Et_2O (10 mL x 2). Combined organic phases were successively washed with 1*N* HCl (10 mL), water (10 mL) and, $NaHCO_3$ (10 mL) and saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 30 g, elution with hexane/Et_2O = 1:1) to give **29** (290 mg, 83%) and **S1** (49 mg, 14%).
29: pale yellow oil, R_f = 0.31 (hexane/Et_2O = 1:1), $[\alpha]^{23}_D$ 153.7 (*c* 1.04, $CHCl_3$). IR (film) = 3477, 1716, 1250 cm^{-1}. ^{1}H NMR (C_6D_6) δ –0.01 and 0.04 (each 3H, s, $SiMe_2$), 0.94 (9H, s, *t*-Bu), 0.94 (3H, t, *J* = 7.4 Hz, H-3'), 1.35-1.46 (2H, m, H-4 and H-2'), 1.49-1.57 (1H, m, H-2'), 1.73 (1H, dd, *J* = 12.8, 12.8 Hz, H-4), 2.76 (1H, ddd, *J* = 8.2, 8.2, 3.7 Hz, H-5), 3.17 (1H, ddd, *J* = 8.2, 4.4, 3.7 Hz, H-1'), 3.33

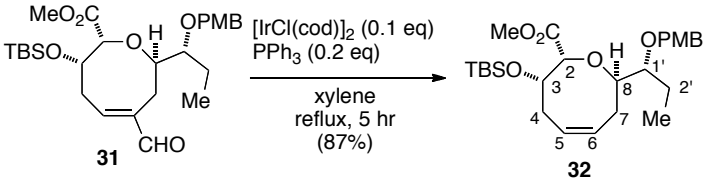
(1H, br s, OH), 3.37 (3H, s, OMe), 3.81 (1H, ddd, *J* = 12.4, 5.3, 3.7 Hz, H-3), 3.95 (1H, br s, H-10), 4.42 (1H, dd, *J* = 5.5, 5.5 Hz, H-8), 4.46 (1H, d, *J* = 11.5 Hz, C*H*$_2$OC$_6$H$_4$OMe), 4.49 (1H, d, *J* = 11.5 Hz, C*H*$_2$OC$_6$H$_4$OMe), 4.69 (1H, ddd, *J* = 6.2, 1.4, 1.4 Hz, H-1), 5.56 (1H, ddd, *J* = 11.9, 5.0, 1.4 Hz, H-7), 5.75 (1H, dd, *J* = 11.9, 8.2 Hz, H-6), 6.85 (2H, d, *J* = 8.7 Hz, Ar-H), 7.27 (2H, d, *J* = 8.7 Hz, Ar-H). ^{13}C NMR (C$_6$D$_6$) δ –5.0 and –4.8 (SiMe$_2$), 10.4 (C-3'), 18.2 (*C*Me$_3$), 23.1 C-2'), 25.8 (C*Me$_3$*), 31.2 (C-4), 35.9 (C-5), 54.8 (OMe), 70.7 (C-8), 73.0 (*C*H$_2$OC$_6$H$_4$OMe), 78.0 (C-10), 78.6 (C-3), 83.0 (C-1'), 88.4 (C-1), 114 (Ar), 128.8 (C-7), 129.4 (Ar), 131.6, 132.0 (C-6), 159.7 (Ar), 208.1 (C-9). HRMS calcd for C$_{26}$H$_{40}$O$_6$SiNa (M$^+$ + Na) 499.2492, found, 499.2505. **S1**: colorless oil, R_f = 0.40 (hexane/Et$_2$O = 1:1), [α]$^{23}_D$ 169.4 (*c* 0.825, CHCl$_3$). IR (film) = 3483, 1720, 1250 cm^{-1}. ^{1}H NMR (C$_6$D$_6$) δ 0.13 and 0.22 (each 3H, s, SiMe$_2$), 0.94 (9H, s, *t*-Bu), 0.95 (3H, t, *J* = 7.6 Hz, H-3'), 1.37-1.54 (3H, m, H-4 and H-2'), 1.76 (1H, dd, *J* = 12.8, 12.8 Hz, H-4), 2.51-2.55 (1H, m, H-5), 3.18 (1H, ddd, *J* = 8.7, 4.1, 3.9 Hz, H-1'), 3.37 (3H, s, OMe), 3.87 (1H, ddd, *J* = 12.4, 5.0, 3.9 Hz, H-3), 4.03 (1H, d, *J* = 4.4 Hz, H-10), 4.34-4.38 (1H, m H-8), 4.46 (2H, s, C*H*$_2$OC$_6$H$_4$OMe), 4.80 (1H, d, *J* = 6.4 Hz, H-1), 5.63 (1H, dd, *J* = 11.5, 8.7 Hz, H-6), 5.72 (1H, ddd, *J* = 11.5, 5.5, 0.9 Hz, H-7), 6.84 (2H, d, *J* = 8.7 Hz, Ar-H), 7.25 (2H, d, *J* = 8.7 Hz, Ar-H). HRMS calcd for C$_{26}$H$_{39}$O$_6$Si (M$^+$ – H) 475.2516, found 475.2516.

(2*R*,3*S*,8*R*,*E*)-Methyl 3-((*tert*-Butyldimethylsilyl)oxy)-6-formyl-8-((*R*)-1-((4-methoxybenzyl)oxy)propyl)-3,4,7,8-tetrahydro-2*H*-oxocine-2-carboxylate (31)



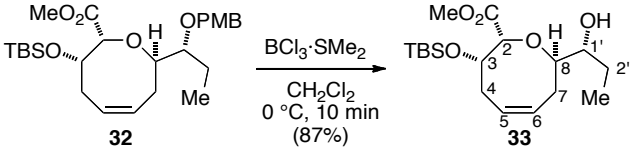
To a cooled (0 °C) solution of **29** (515 mg, 1.08 mmol) in benzene-MeOH (1:1, 30 ml) was added Pb(OAc)$_4$ (80%, 1.2 g, 2.16 mmol). After being stirred at the same temperature for 15 min, the mixture was diluted with hexane (20 mL). The mixture was filtered through a short pad of silica gel (silica gel, 40 g, elution with hexane/AcOEt = 1:1) and the filtrate was concentrated. This crude **30** was dissolved in CH_2Cl_2 (40 mL), and DBU (808 μL, 5.40 mmol) was added. The reaction mixture was stirred at room temperature for 20 min, and poured into 10% aqueous NH_4Cl solution and Et_2O (30 mL). Phases were separated and the aqueous phase was extracted with Et_2O (20 mL x 2). Combined organic phases were successively washed with water (15 mL x 2) and saturated brine (15 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 20 g, elution with hexane/Et2O = 1:1) to give **31** (435 mg, 80%), colorless oil, R_f = 0.49 (hexane/Et_2O= 2:3), [α]$^{20}_D$ 129.4 (*c* 1.15, CHCl$_3$). IR (film) = ^{1}H NMR (C$_6$D$_6$) δ 0.04 and 0.06 (each 3H, s, SiMe$_2$), 0.84 (3H, t, *J* = 7.3 Hz, H-3'), 0.95 (9H, s, *t*-Bu), 1.66-1.76 (1H, m, H-2'), 1.80-1.90 (1H, m, H-2'), 2.04-2.10 (1H, m, H-4), 2.48-2.56 (1H, m, H-4), 2.62-2.68 (2H, m, H-7), 3.10-3.14 (1H, m, H-1'), 3.35 (3H, s, C$_6$H$_4$O*Me*), 3.44 (3H, s, CO$_2$Me), 3.85-3.90 (1H, m, H-8), 4.08 (1H, d, *J* = 11.0 Hz, C*H*$_2$OC$_6$H$_4$OMe), 4.39 (1H, d, *J* = 11.0 Hz, C*H*$_2$OC$_6$H$_4$OMe), 4.40-4.42 (1H, m, H-3), 4.96 (1H, d, *J* = 1.6 Hz, H-2), 6.29 (1H, t, *J* = 8.0 Hz, H-5), 6.86 (2H, d, *J* = 8.7 Hz, Ar-H), 7.23 (2H, d, *J* = 8.7 Hz, Ar-H), 9.31 (1H, s, CHO). ^{13}C NMR (C$_6$D$_6$) δ –5.01 and –4.58 (SiMe$_2$), 10.2 (C-3'), 18.2 (*C*Me$_3$), 23.3 (C-2'), 25.8 (C*Me$_3$*), 26.6 (C-7), 35.1 (C-2'), 51.1 (CO$_2$*Me*), 54.8 (C$_6$H$_4$O*Me*), 71.5 (*C*H$_2$OC$_6$H$_4$OMe), 75.3 (C-3), 75.8 (C-8), 77.8 (C-2), 84.5 (C-1'), 114.0 (Ar), 129.1 (Ar), 131.4 (Ar), 144.0 (C-6), 150.6 (C-5), 159.7 (Ar), 171.6 (*C*O$_2$Me), 192.7 (CHO). HRMS calcd for C$_{27}$H$_{42}$O$_7$SiNa (M + Na)$^+$ 529.2597, found 529.2587.

(2*R*,3*S*,8*R*,*Z*)-Methyl 3-(*tert*-Butyldimethylsilyloxy)-8-((*R*)-1-(4-methoxybenzyloxy)propyl)-3,4,7,8-tetrahydro-2*H*-oxocine-2-carboxylate (32)



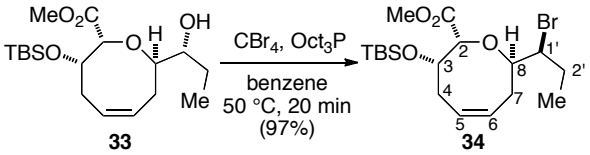
31 (422 mg, 0.833 mmol) was dissolved in xylene (4.2 mL) and $[IrCl(cod)]_2$ (114 mg, 0.017 mmol) was added. The solution was degassed by a freeze-thaw method (repeated three times). After being heated at 140 °C for 5 h, the mixture was poured into Et_2O (15 mL) and water (15 mL), and filtered through a pad of Celite. The filtrated was washed with saturated brine (15 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 40 g, hexane/Et_2O = 6:4) to give **32** (348 mg, 87%), colorless oil, R_f = 0.58 (hexane/Et_2O= 2:3), $[\alpha]^{19}_D$ 63.1 (*c* 1.10, $CHCl_3$). IR (film) = 1763, 1724, 1252 cm^{-1}. ^1H NMR (C_6D_6) δ 0.08 and 0.10 (each 3H, s, $SiMe_2$), 0.90 (3H, t, *J* = 7.3 Hz, H-3'), 0.99 (9H, s, *t*-Bu), 1.57-1.65 (1H, m, H-2'), 1.77-1.86 (1H, m, H-2'), 2.07 (1H, ddd, *J* = 14.7, 6.9, 3.4 Hz, H-7), 2.22 (1H, ddd, *J* = 13.3, 6.6, 3.2 Hz, H-4), 2.34 (1H, ddd, *J* = 14.7, 8.2, 8.2 Hz, H-7), 2.58 (1H, *J* = 13.3, 8.2. 8.2 Hz, H-4), 3.15-3.19 (1H, m, H-1'), 3.35 (3H, s, C_6H_4O*Me*), 3.45 (3H, s, CO_2Me), 3.88-3.94 (1H, m, H-8), 4.15 (1H, d, *J* = 11.2 Hz, C*H*$_2$OC$_6$H$_4$OMe), 4.42-4.45 (1H, m, H-3), 4.46 (1H, d, *J* = 11.2 Hz, C*H*$_2$OC$_6$H$_4$OMe), 4.93 (1H, d, *J* = 1.8 Hz, H-2), 5.68-5.83 (2H, m, H-5 and H-6), 6.86 (2H, d, *J* = 8.7 Hz, Ar-H), 7.27 (2H, d, *J* = 8.7 Hz, Ar-H). HRMS calcd for $C_{26}H_{42}O_6SiNa$ $(M + Na)^+$ 501.2652, found 501.2648.

(2*R*,3*S*,8*R*,*Z*)-Methyl 3-((*tert*-Butyldimethylsilyl)oxy)-8-((*R*)-1-hydroxypropyl)-3,4,7,8-tetrahydro-2*H*-oxocine-2-carboxylate (33)



To a cooled (0 °C) solution of **32** (150 mg, 0.313 mmol) in CH_2Cl_2 (10 mL) was added BCl_3·SMe_2 (2.0 M in CH_2Cl_2, 313 μL, 0.626 mmol)). After being stirred at the same temperature for 10 min, the mixture was poured into saturated aqueous $NaHCO_3$ solution (10 mL) and CH_2Cl_2 (10 mL). Phases were separated and the aqueous phase was extracted with CH_2Cl_2 (10 mL x 2). Combined organic phases were successively washed with water (10 mL) and saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 10 g, elution with hexane/Et_2O = 5:3) to give **33** (95 mg, 85 %), colorless oil, R_f = 0.26 (hexane/Et_2O= 1:1), $[\alpha]^{17}_D$ 97.0 (*c* 1.06, $CHCl_3$). IR (film) = 3483, 1738, 1255 cm^{-1}. ^1H NMR (C_6D_6) δ 0.06 and 0.12 (each 3H, s, $SiMe_2$), 0.98 (9H, s, *t*-Bu), 1.11 (3H, t, *J* = 7.3 Hz, H-3'), 1.20-1.32 (1H, m, H-2'), 1.32-1.42 (1H, m, H-2'), 1.68-1.78 (1H, m, H-7), 2.04-2.17 (2H, m, H-4 and H-7), 2.53 (1H, ddd, *J* = 13.1, 8.7, 8.7 Hz, H-4), 3.38 (3H, s, OMe), 3.43 (1H, ddd, *J* = 8.7, 8.7, 2.7 Hz, H-1'), 3.72-3.78 (1H, m, H-8), 4.25 (1H, br s, H-2), 4.30 (1H, s, OH), 4.47 (1H, ddd, *J* = 8.7, 3.7, 1.4 Hz, H-3), 5.52-5.58 (1H, app br q, H-6), 5.66-5.74 (1H, app br q, H-5). ^{13}C NMR (C_6D_6) δ –5.0 and –4.1 ($SiMe_2$), 9.9 (C-3'), 18.2 (*C*Me_3), 25.9 (C*Me*$_3$), 26.3 (C-2'), 28.6 (C-7), 33.2 (C-4), 51.8 (OMe), 70.3 (C-1'), 74.2 (C-2), 74.7 (C-3), 128.9 (C-6), 129.4 (C-5), 173.3 (*C*O_2Me). HRMS calcd for $C_{18}H_{35}O_5Si$ $(M^+ + 1)$ 359.2254, found 359.2256.

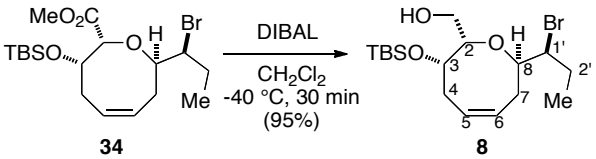
(2*R*,3*S*,8*R*,*Z*)-Methyl 8-((*S*)-1-Bromopropyl)-3-((*tert*-butyldimethylsilyl)oxy)-3,4,7,8-tetrahydro-2*H*-oxocine-2-carboxylate (34)



33 **34**

To a solution of **33** (94 mg, 0.262 mmol) in benzene (32 mL) were successively added CBr_4 (173 mg, 0.524 mmol) and tri-*n*-octylphosphine (552 μL, 1.05 mmol). After being stirred at 50 °C for 20 min, the solution was cooled and concentrated. The residual oil was subjected to column chromatography (10g, elution with hexane/AcOEt = 4:1) to give **34** (107 mg, 97%), colorless oil, R_f = 0.34 (hexane/Et_2O = 5:1), $[\alpha]^{19}_D$ 84.8 (*c* 1.10, $CHCl_3$). IR (film) = 1763, 1728, 1259 cm^{-1}. ^1H NMR (C_6D_6) δ 0.06 and 0.09 (each 3H, s, $SiMe_2$), 0.98 (9H, s, *t*-Bu), 1.01 (3H, s, *J* = 7.3 Hz, H-3'), 1.63-1.73 (1H, m, H-2'), 2.08-2.17 (2H, m, H-2' and H-4), 2.37-2.45 (1H, m, H-7), 2.49-2.56 (1H, m, H-4), 2.56-2.63 (1H, m, H-7), 3.44 (3H, s, OMe), 3.81 (1H, ddd, *J* = 8.7, 8.7, 2.7 Hz, H-1'), 4.02 (1H, ddd, *J* = 9.2, 7.8, 3.4 Hz, H-8), 4.22 (2H, d, *J* = 1.6 Hz, H-2), 4.38 (1H, ddd, *J* = 8.7, 3.9, 1.6 Hz, H-3), 5.65-5.74 (2H, m, H-5 and H-6). ^{13}C NMR (C_6D_6) δ –5.0 and –4.2 ($SiMe_2$), 11.3 (C-3'), 18.2 (*C*Me_3), 25.9 (C*Me*$_3$), 29.3 (C-2'), 30.8 (C-7), 33.3 (C-4), 51.2 (C-OMe), 58.4 (C-1'), 75.2 and 75.5 (C-2 and C-3), 79.0 (C-8), 128.3 and 129.1 (C-5 and C-6), 171.5 (*C*O_2Me). HRMS calcd for $C_{18}H_{33}BrO_4Si$ 420.1410 (M^+ + 1), found 421.1395.

(((2*S*,3*S*,8*R*,*Z*)-8-((*S*)-1-Bromopropyl)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-3,4,7,8-tetrahydro-2*H*-oxocin-3-yl)oxy)(*tert*-butyl)-dimethylsilane (8)



34 **8**

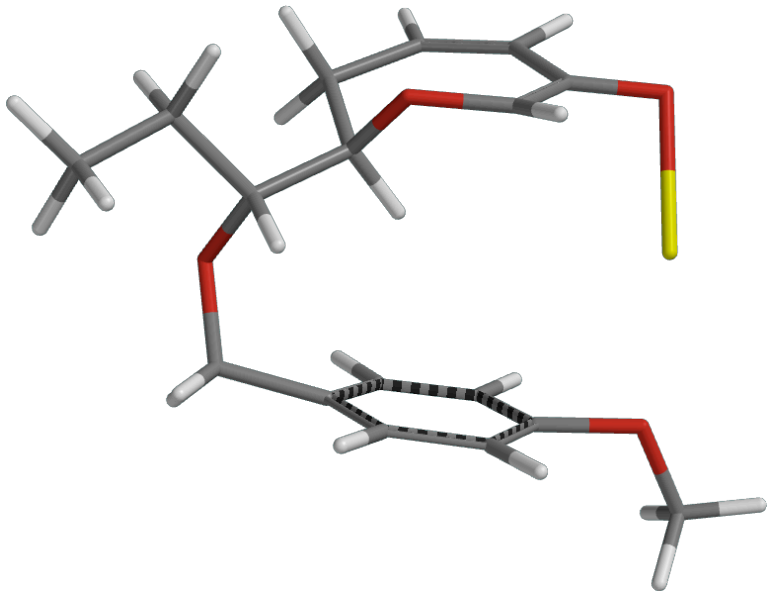
To a cooled (–40 °C) solution of **34** (30 mg, 0.071 mmol) in CH_2Cl_2 (1,7 mL) was added DIBAL (1.0M in hexane, 178 mL, 0.178 mmol). The solution was stirred at the same temperature for 30 min, and MeOH (few drops) was added and warmed to room temperature. Saturated 10% aqueous NH4Cl solution (5 mL) and Et_2O (5 mL) were added, and then the resulting solid was filtered through a pad of Celite. The filtrated was extracted with Et_2O (5 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 5 g, elution with hexane/AcOEt = 2:1) to give **8** (26.4 mg, 95%), colorless oil, R_f = 0.33 (hexane/Et_2O = 2:1), $[\alpha]^{17}_D$ 17.0 (*c* 1.10, CH_2Cl_2, lit. 17.3, *c* 1.17, CH_2Cl_2). IR (film) = 3500, 3024, 2952, 2860, 1462, 1373, 1253, 1084, 935, 838, 777, 742, 681 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.05 and 0.07 (each 3H, s, $SiMe_2$), 0.89 (9H, s, *t*-Bu), 1.07 (3H, t, *J* = 7.3 Hz, H-3'), 1.70-1.83 (1H, m, H-2), 1.91-2.02 (1H, m, H-2), 2.22 (1H, ddd, *J* = 13.3, 8.2, 4.4 Hz, H-4), 2.33 (1H, br d, *J* = 8.0 Hz, OH), 2.48 (1H, br dd, *J* = 16.7, 6.0 Hz, H-7), 2.51-2.66 (2H, m, H-4 and H-7), 5.60-5.68 (1H, m, H-5), 5.72-5.79 (1H, m, H-6). ^{13}C NMR ($CDCl_3$) δ –4.7 and –4.1 ($SiMe_2$), 12.6 (C-3'), 18.4 (*C*Me_3), 26.1 (C*Me*$_3$), 29.4 (C-2'), 31.1 (C-7), 33.3 (C-4), 64.0 (C-1'), 64.5 (CH_2OH), 73.5 (C-3), 76.2 (C-2), 77.8 (C-8), 126.1 (C-5), 129.9 (C-6). HRMS calcd for $C_{17}H_{33}BrO_3SiNa$ (M^+ + Na) 415.1275, found 415.1275.

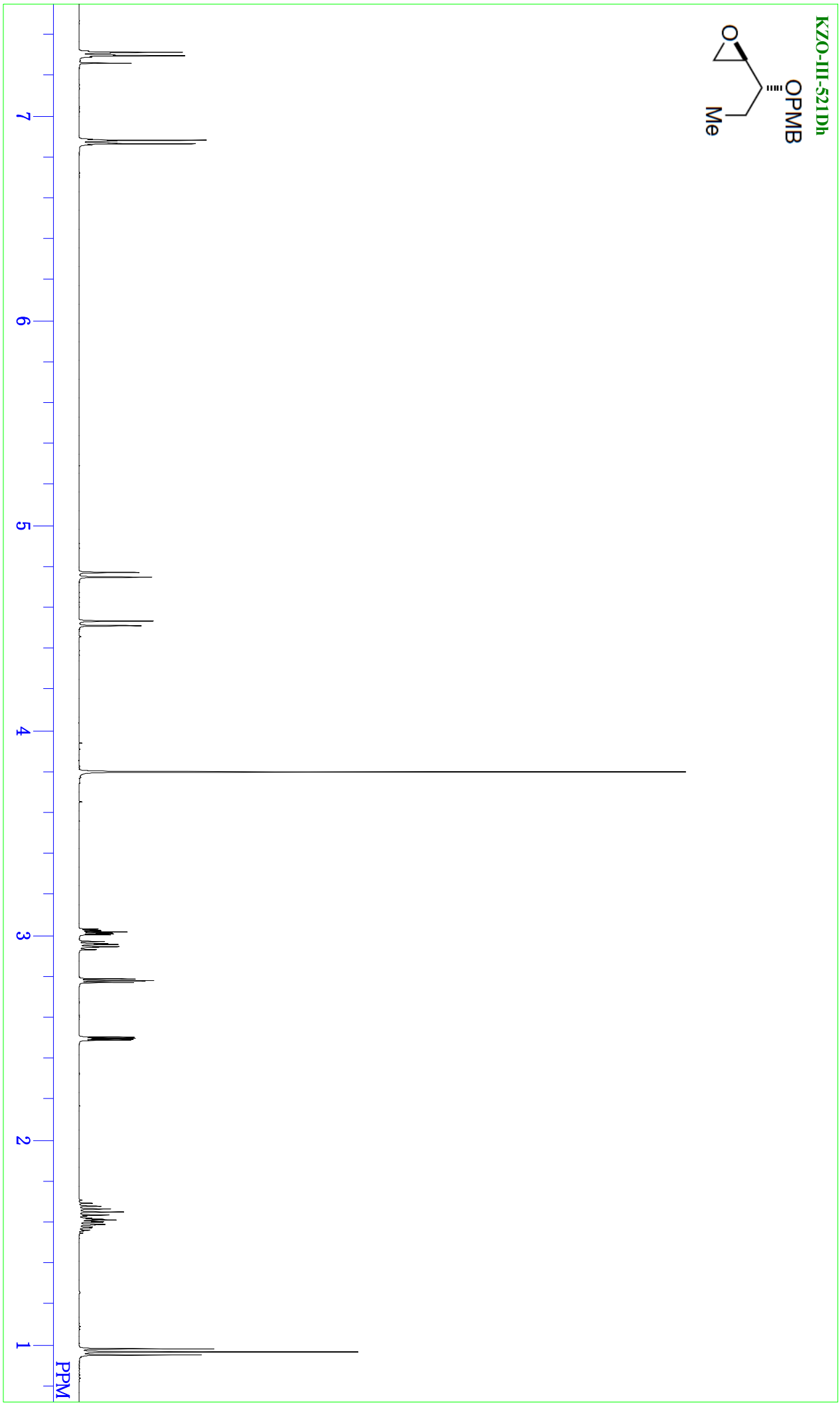
Representation of energy minimized structure, cartesian coordinates and computed total energy for compound 22'

All calculations were performed using Spartan '06 (Ver. 1.0.1 for Mac) on a quad-core Intel Xeon (2 x 3.2 GHz) running Mac OS 10.5.4. Equilibrium geometry of **22'** was calculated by subjection of conformers that were located MMFF94s to geometry optimization at HF/6-31+G* and then refinement at RI-MP2/6-31+G*. Computed total energy was –1120.2123796 au where 1 au = 2625 kJ/mol = 627.5 kcal/mol = 27.21 eV.

Table S1. Cartesian coordinates for (*E*)-**22'**

No.	ATOM	X	Y	Z	No.	ATOM	X	Y	Z
1	O	1.298043	–1.512316	1.070151	23	H	4.627778	2.049404	0.543243
2	C	0.011733	–2.045113	1.230587	24	H	5.647511	0.887952	1.405446
3	H	–0.313579	–2.041164	2.271233	25	O	2.431581	1.390206	–0.828633
4	C	–0.653830	–2.790023	0.274346	26	C	1.687675	2.592476	–0.600561
5	C	–0.067422	–3.100364	–1.053966	27	H	1.866865	3.206304	–1.489428
6	H	–0.647812	–3.870838	–1.563160	28	H	2.082750	3.124614	0.278713
7	C	1.021509	–2.618141	–1.699755	29	C	0.218988	2.305083	–0.415206
8	H	1.238226	–3.059979	–2.674798	30	C	–2.382436	1.386544	–0.009277
9	C	1.985088	–1.554277	–1.259793	31	C	–0.378346	2.402493	0.847899
10	H	2.934721	–2.023245	–0.966339	32	C	–0.523733	1.776279	–1.483844
11	H	2.213632	–0.887163	–2.104695	33	C	–1.823338	1.306116	–1.289122
12	C	1.464891	–0.713081	–0.108214	34	C	–1.685424	1.950615	1.058564
13	H	0.484409	–0.301952	–0.380679	35	H	0.186939	2.811702	1.684179
14	O	–1.872741	–3.272577	0.478101	36	H	–0.054293	1.671537	–2.461141
15	Na	–2.744270	–1.349458	0.926376	37	H	–2.378584	0.842299	–2.102433
16	C	2.387626	0.447548	0.273193	38	H	–2.151868	2.003008	2.040793
17	H	1.946136	0.936119	1.156448	39	O	–3.628824	0.784693	0.255250
18	C	3.814355	0.038895	0.596046	40	C	–4.761856	1.559531	–0.209121
19	H	3.777874	–0.821072	1.276399	41	H	–4.770837	2.530728	0.294194
20	H	4.300210	–0.290206	–0.330265	42	H	–5.649978	0.985506	0.054760
21	C	4.610802	1.185060	1.214889	43	H	–4.707842	1.696714	–1.292343
22	H	4.172546	1.495869	2.170777					

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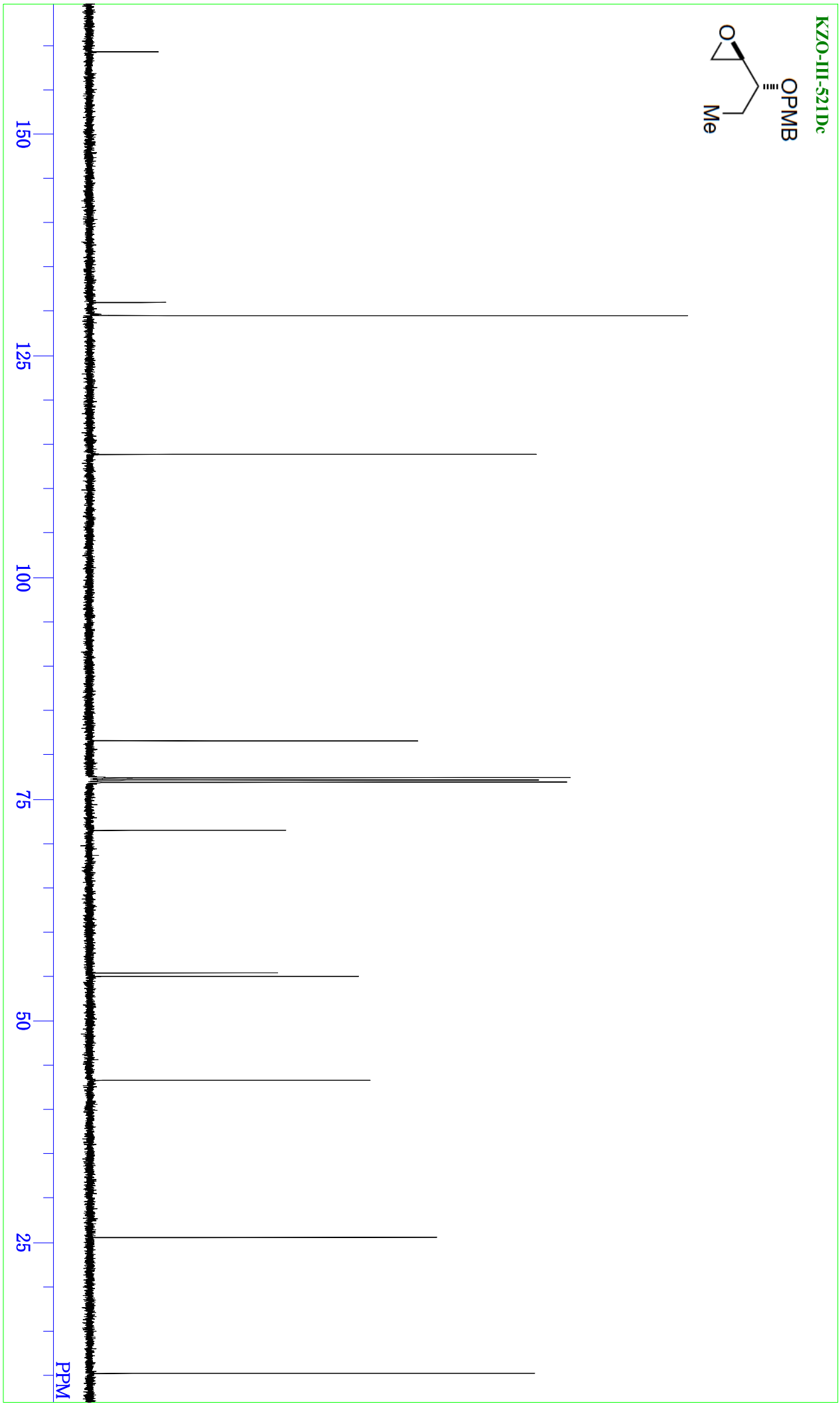
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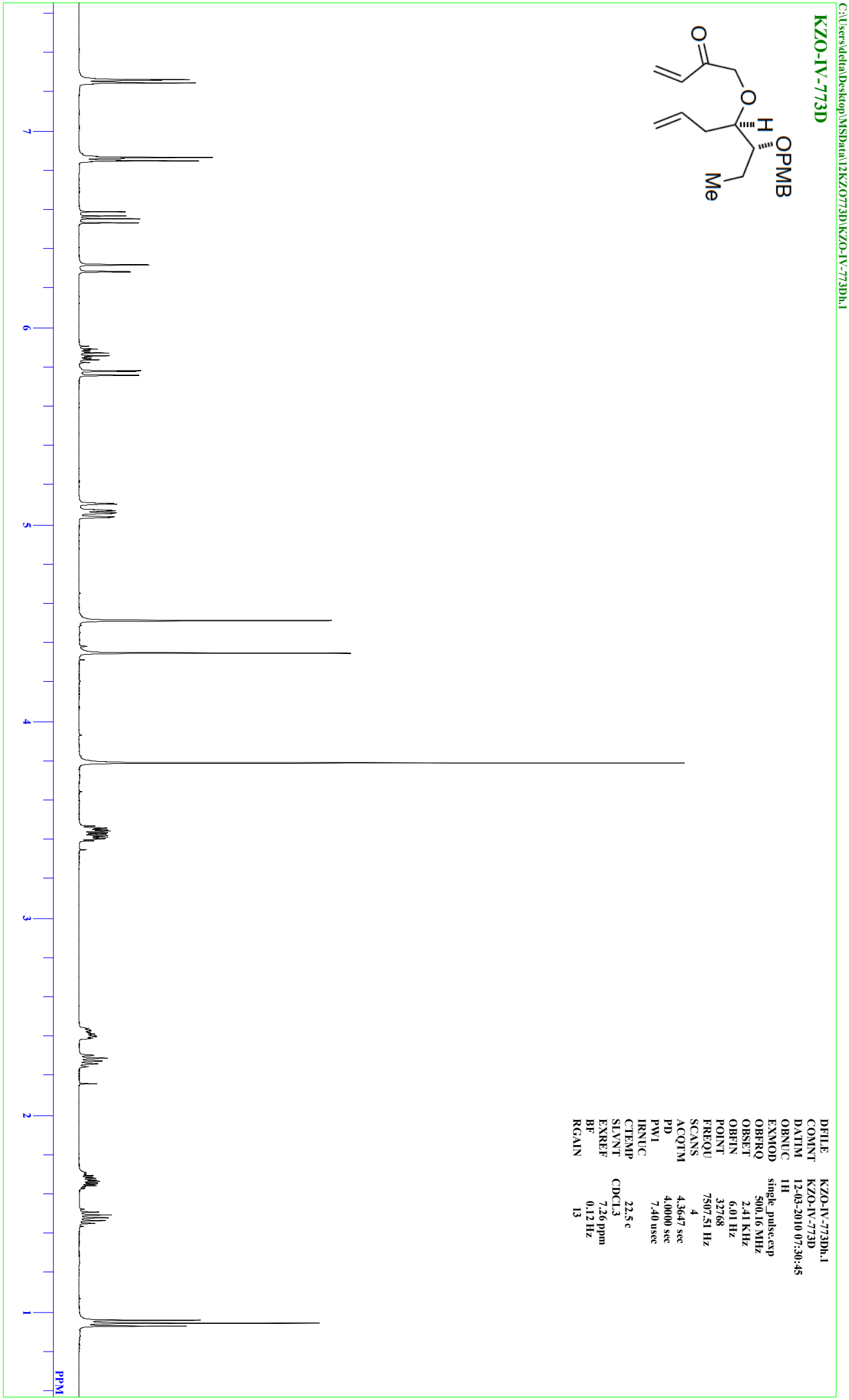
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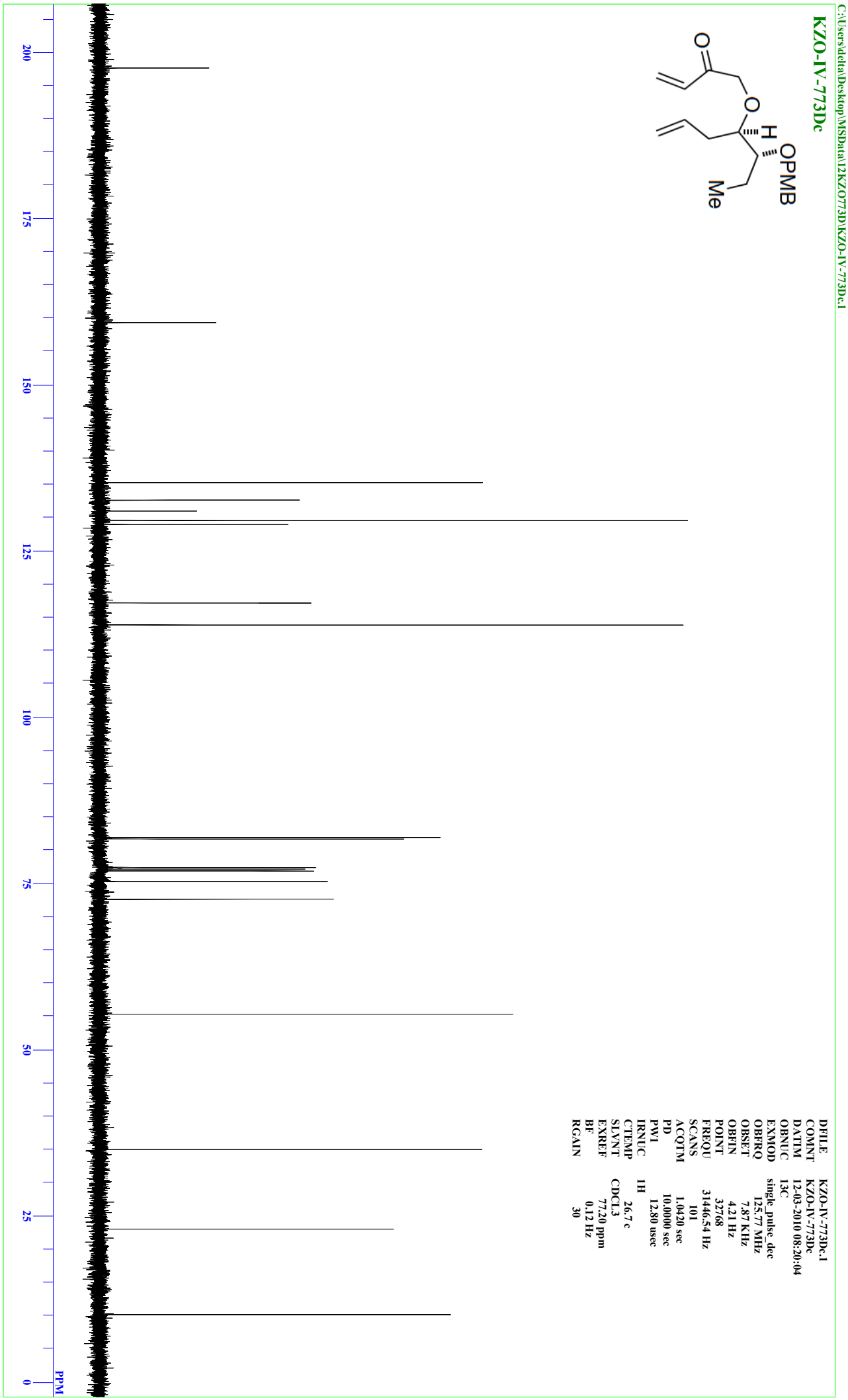
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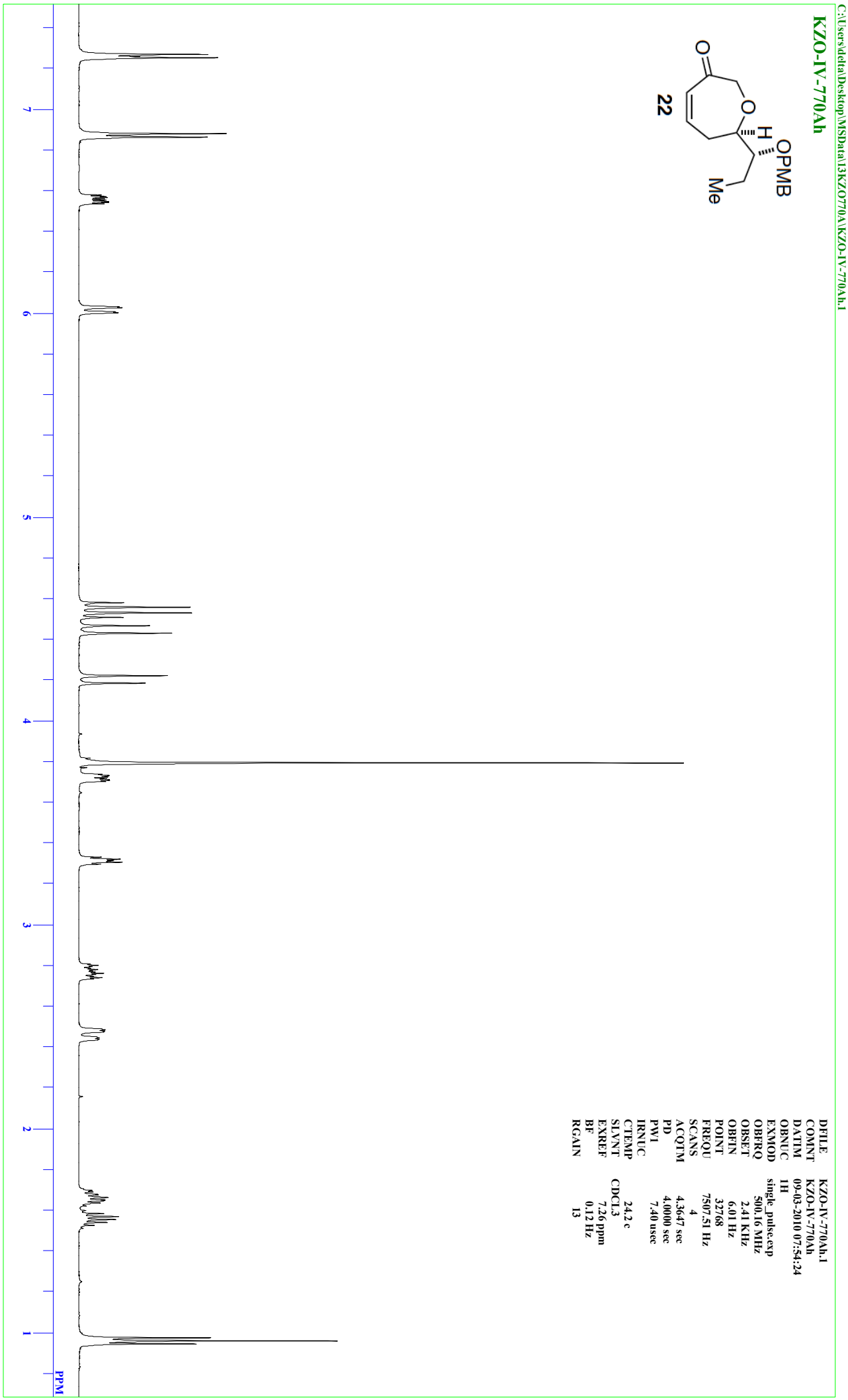
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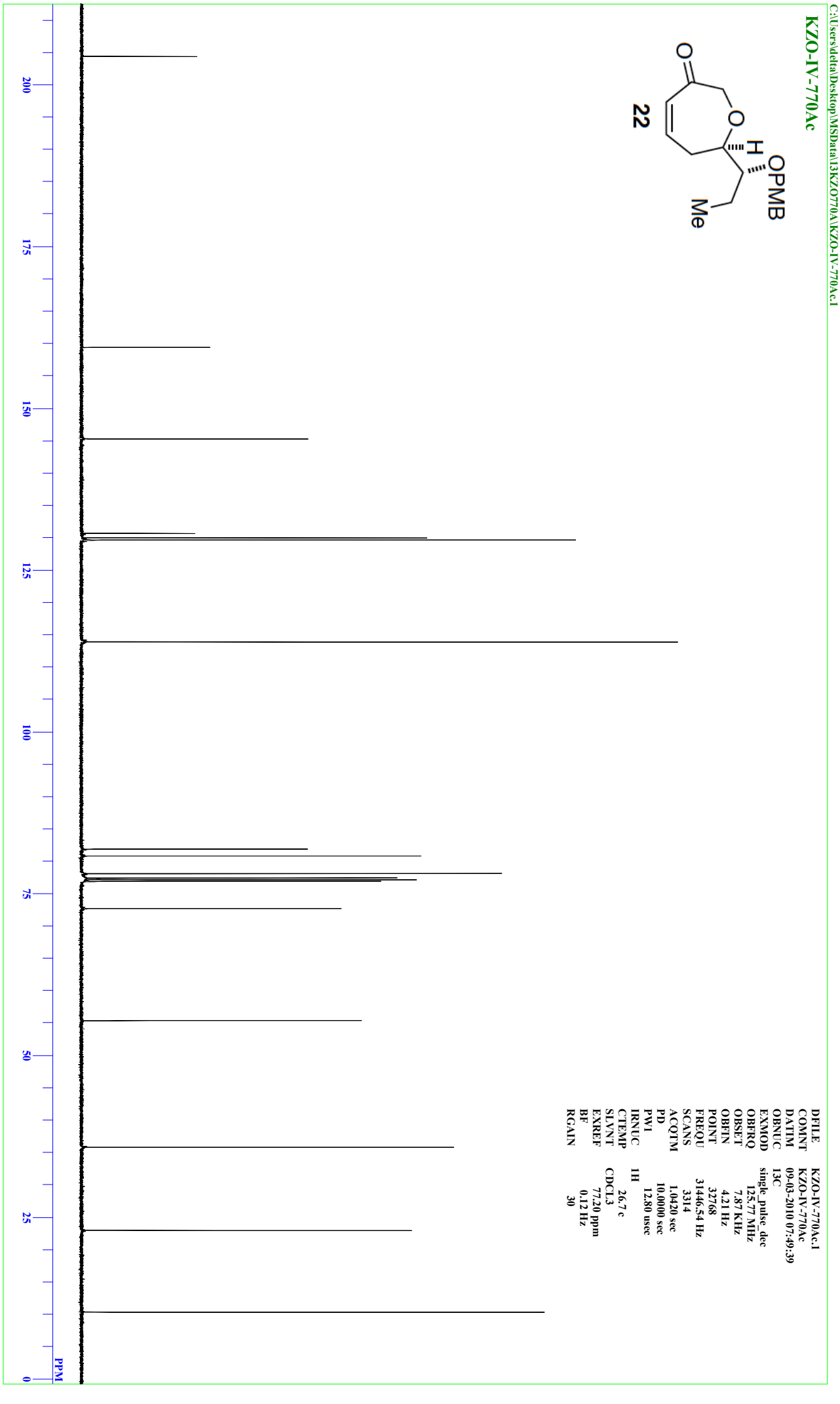
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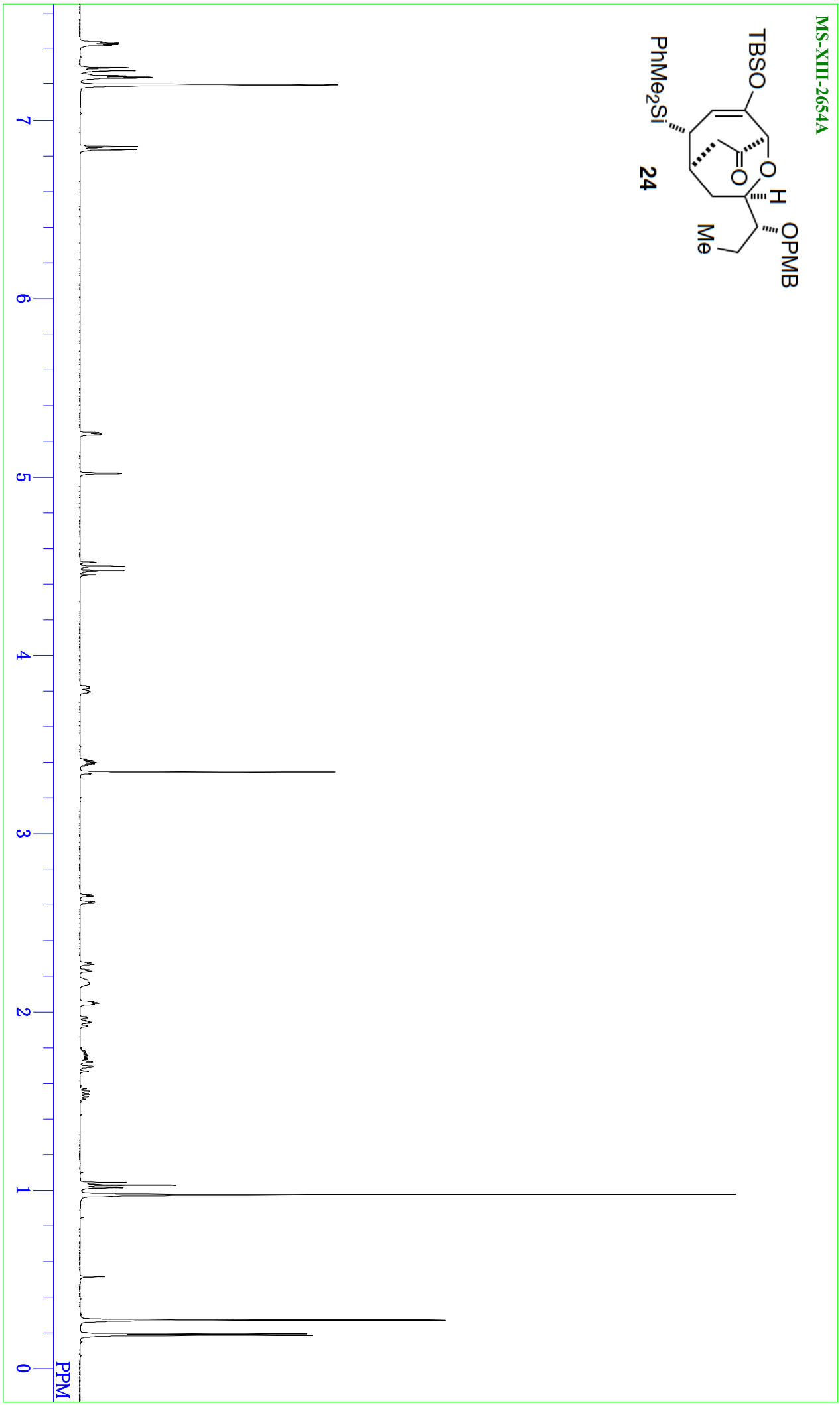
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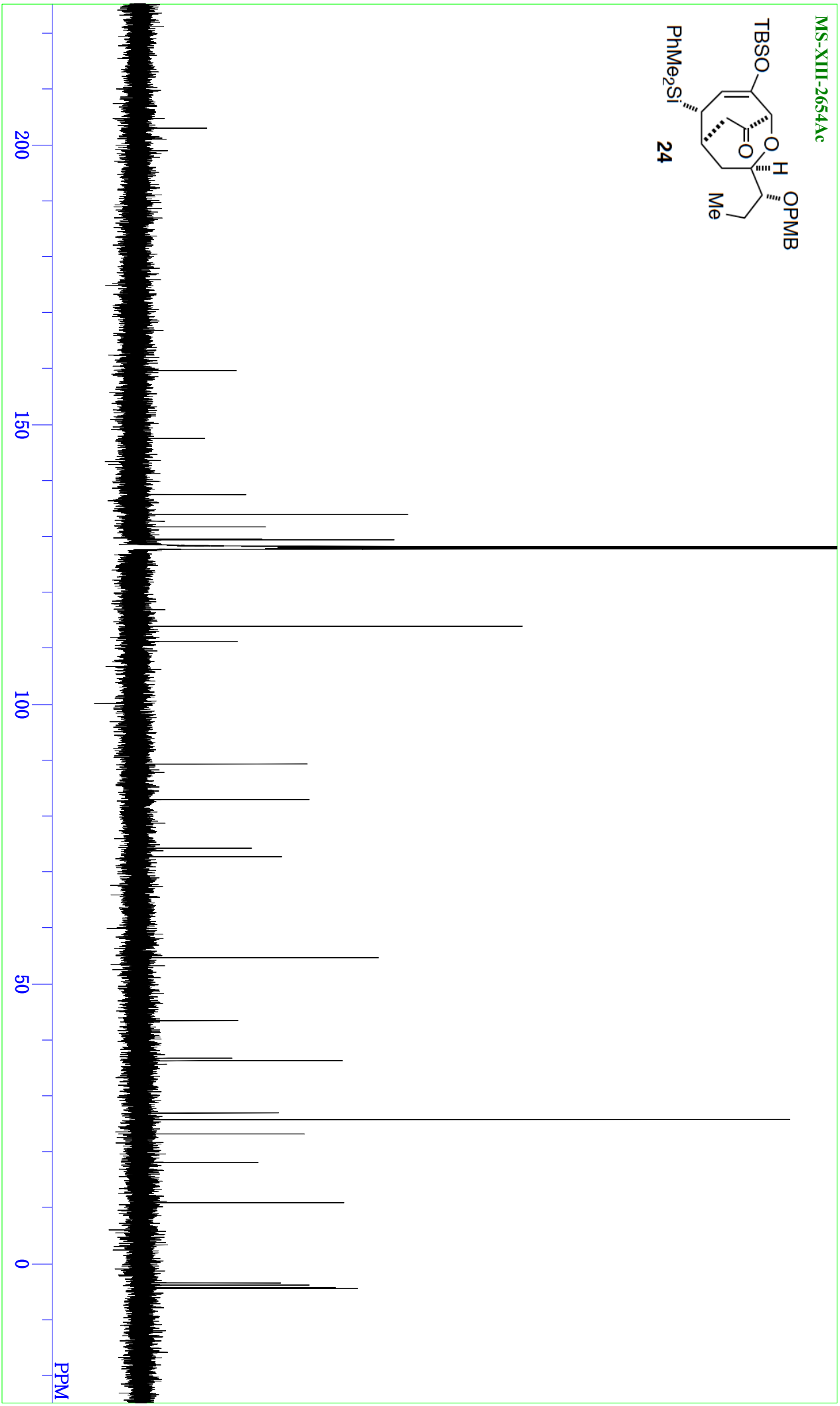
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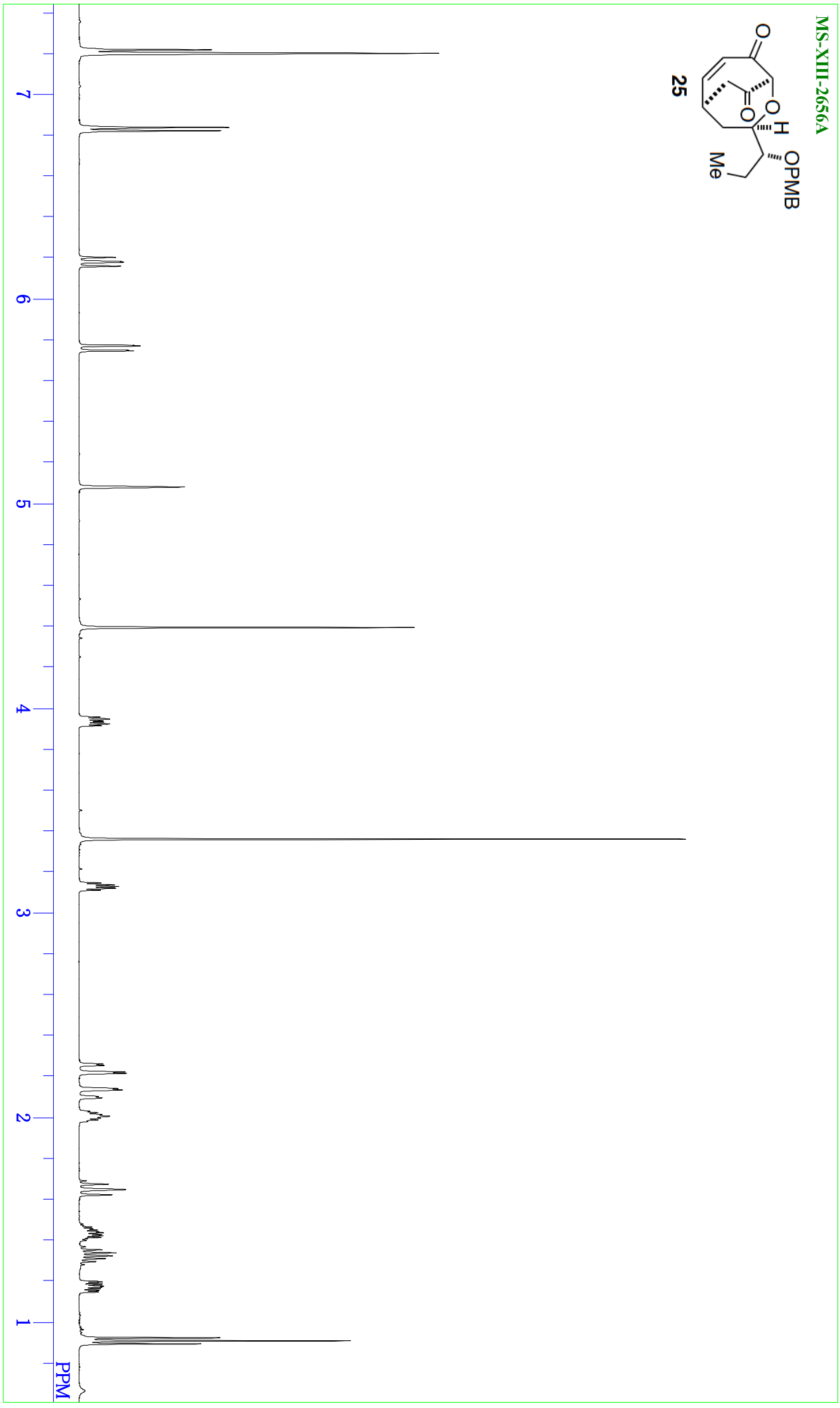
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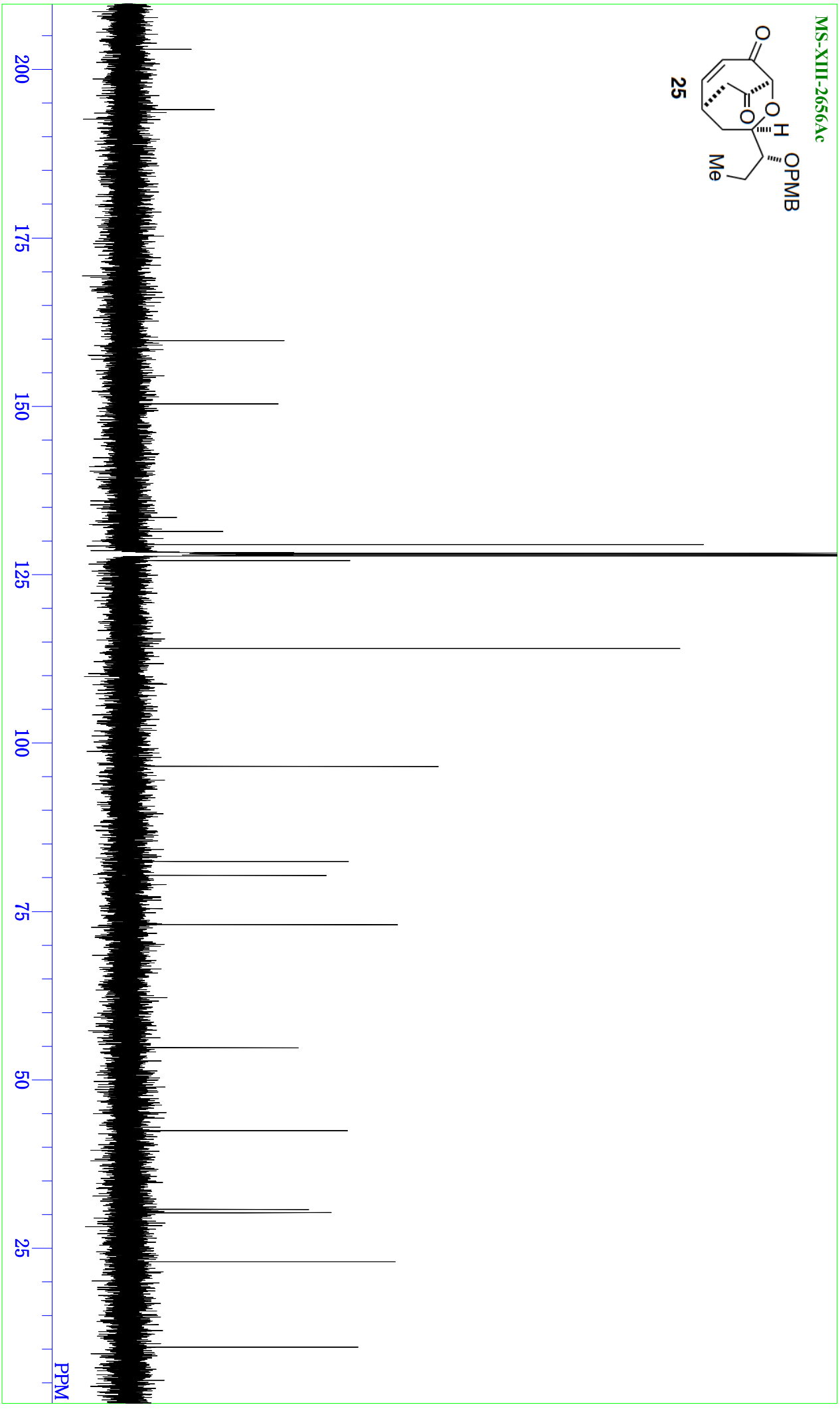
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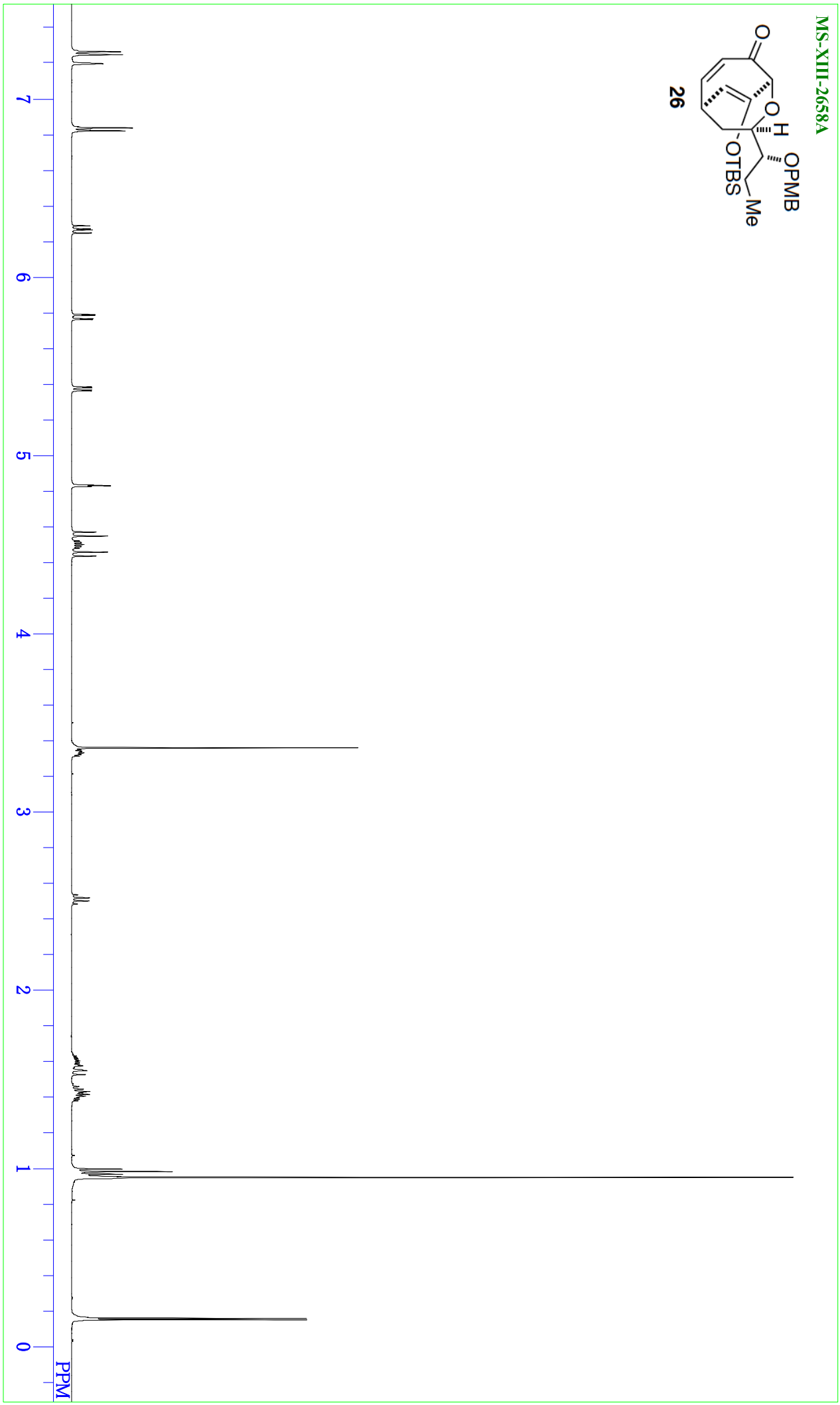
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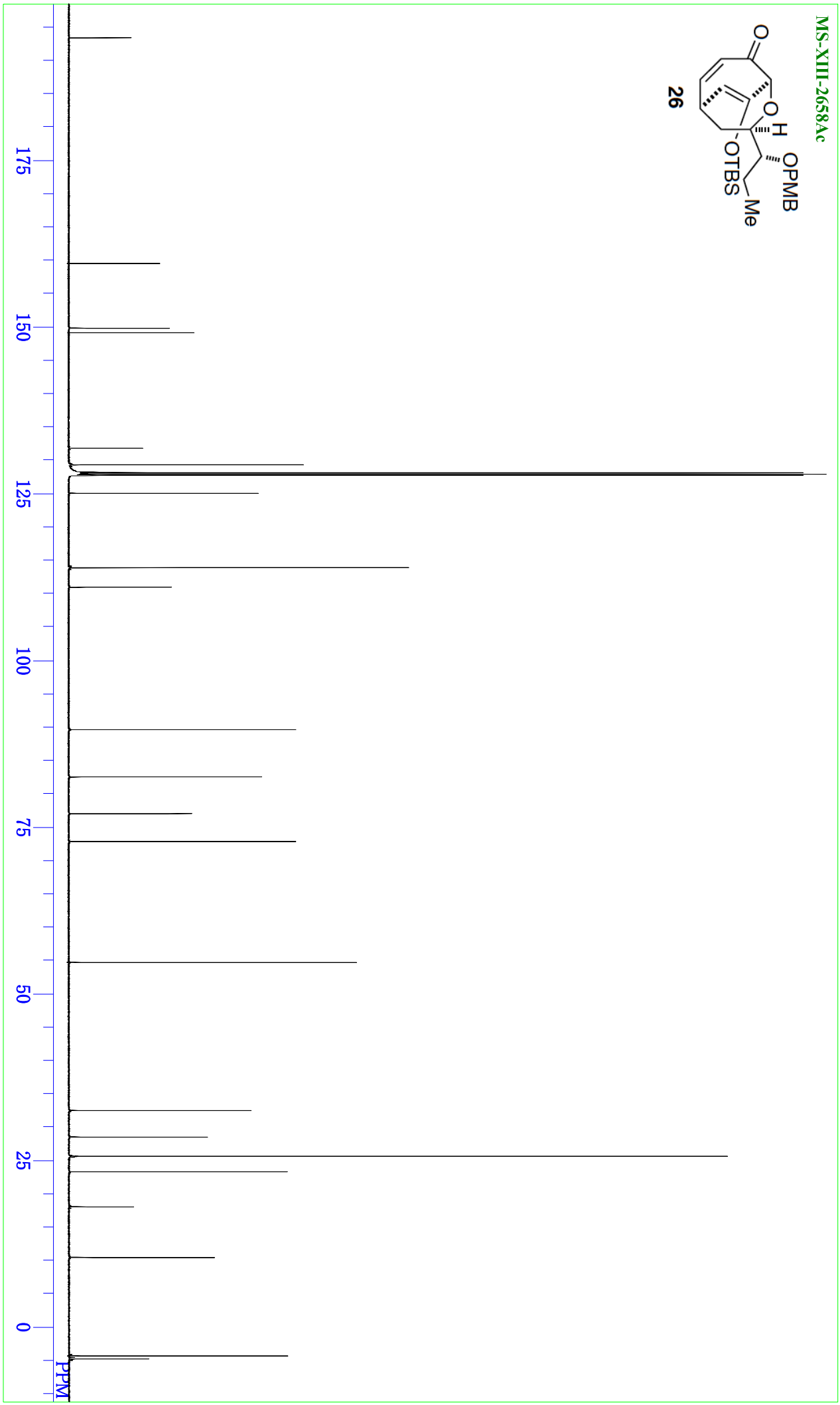
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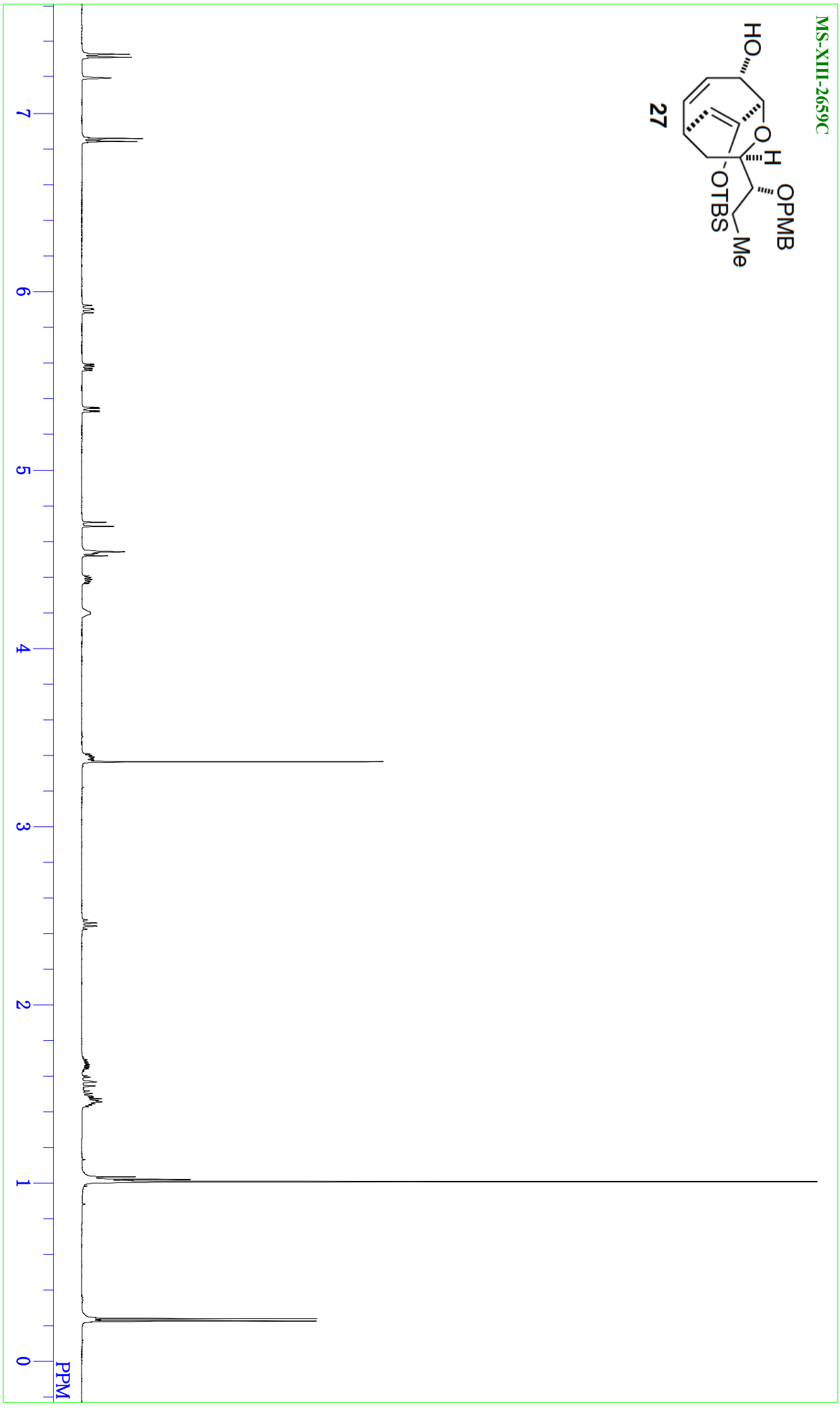
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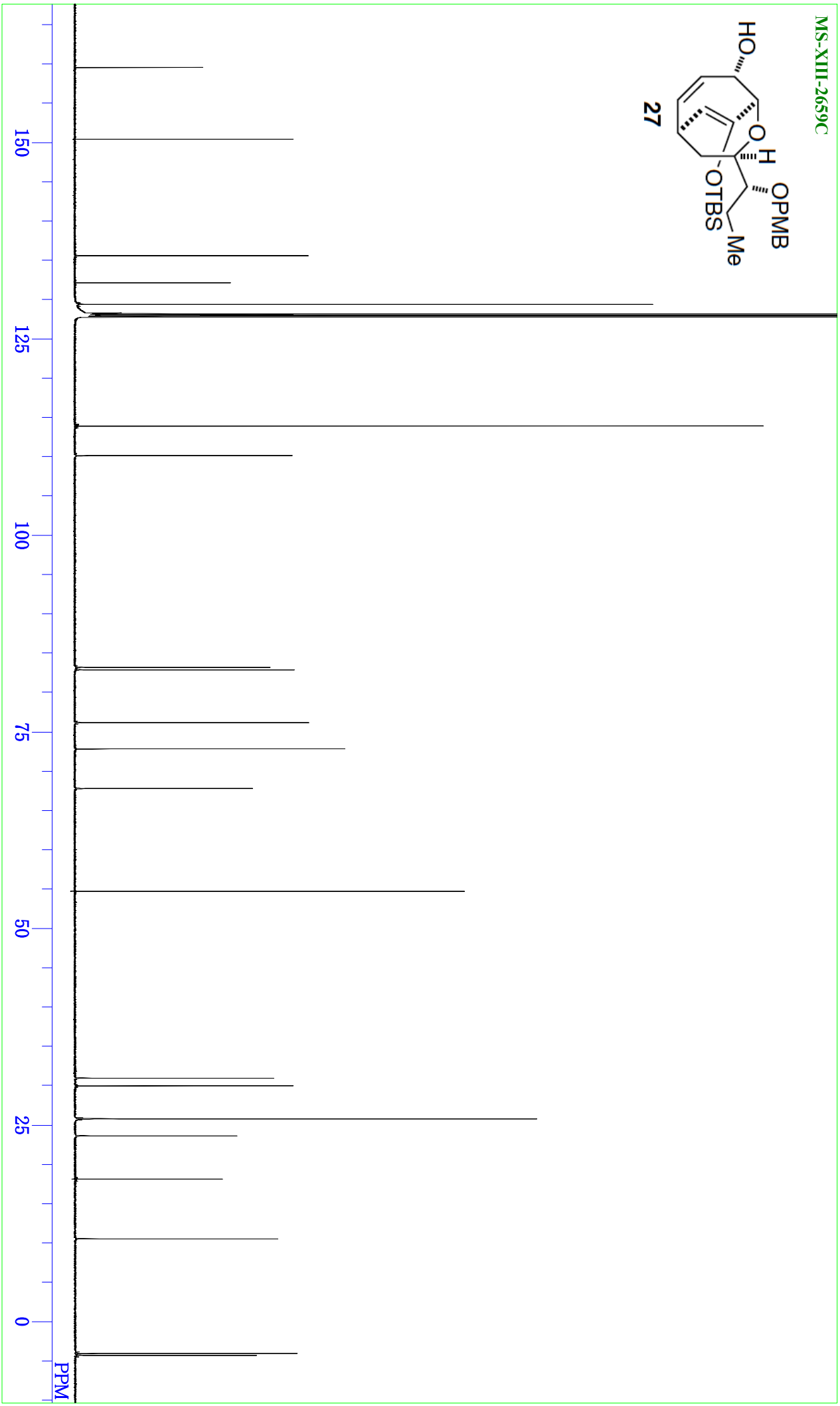
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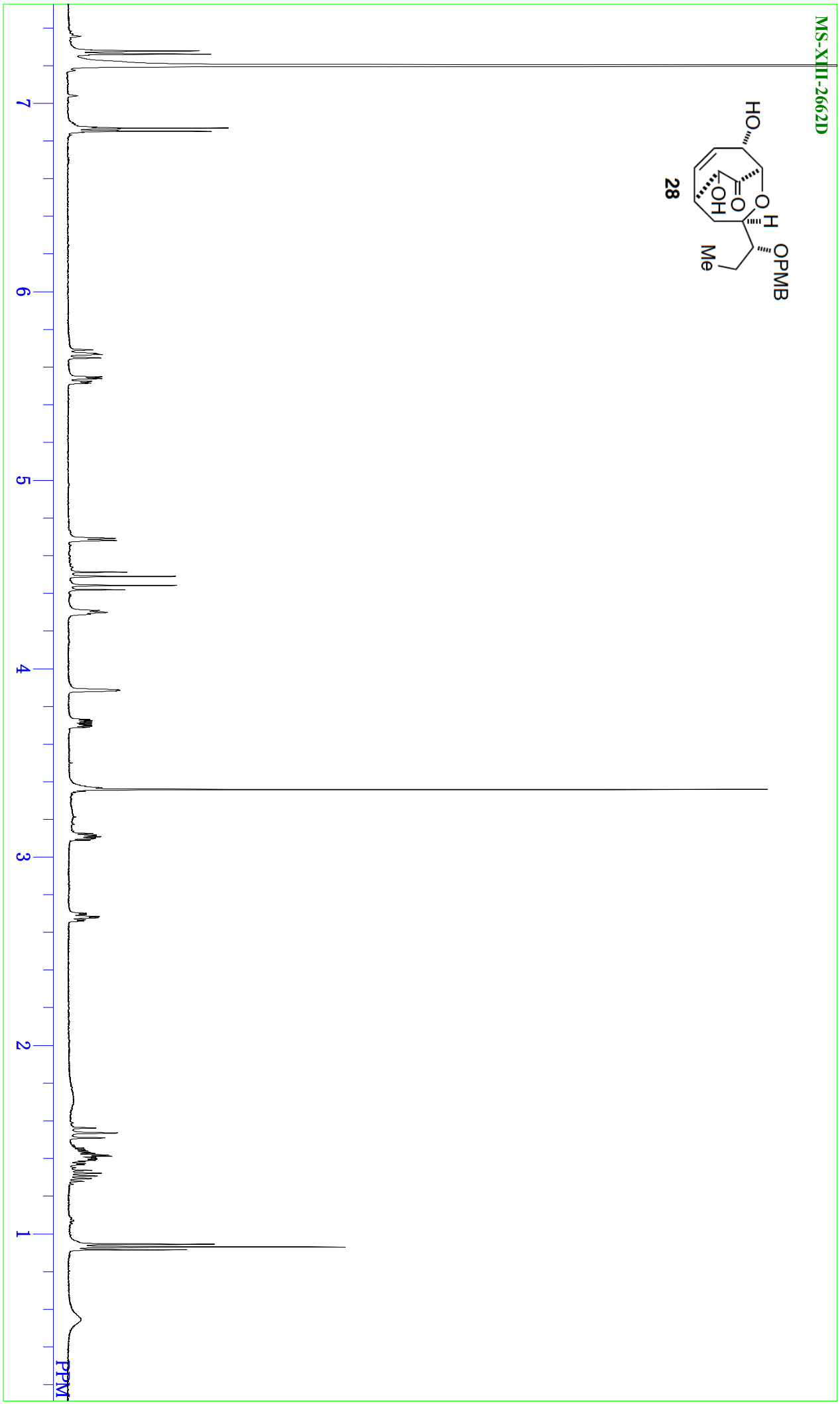
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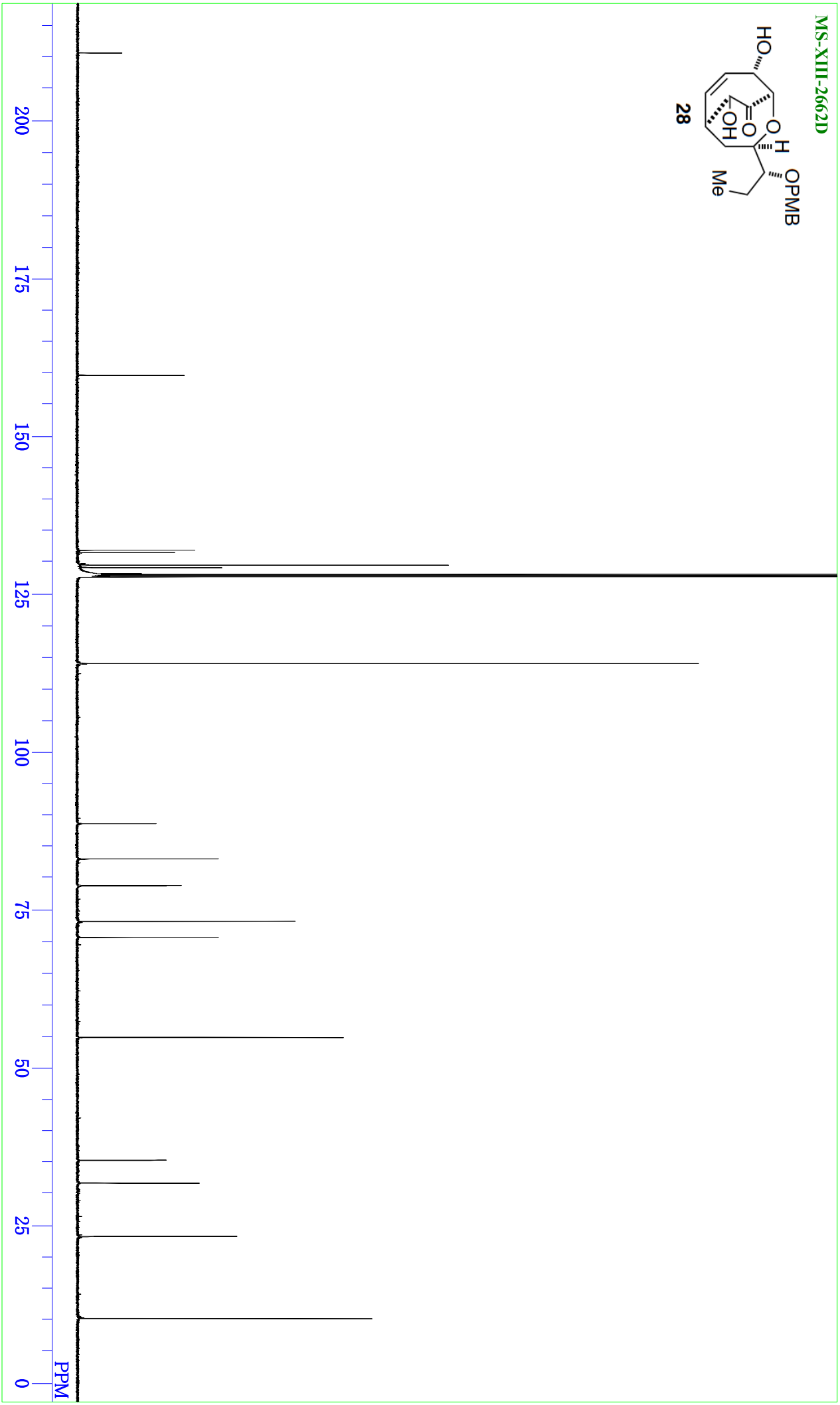
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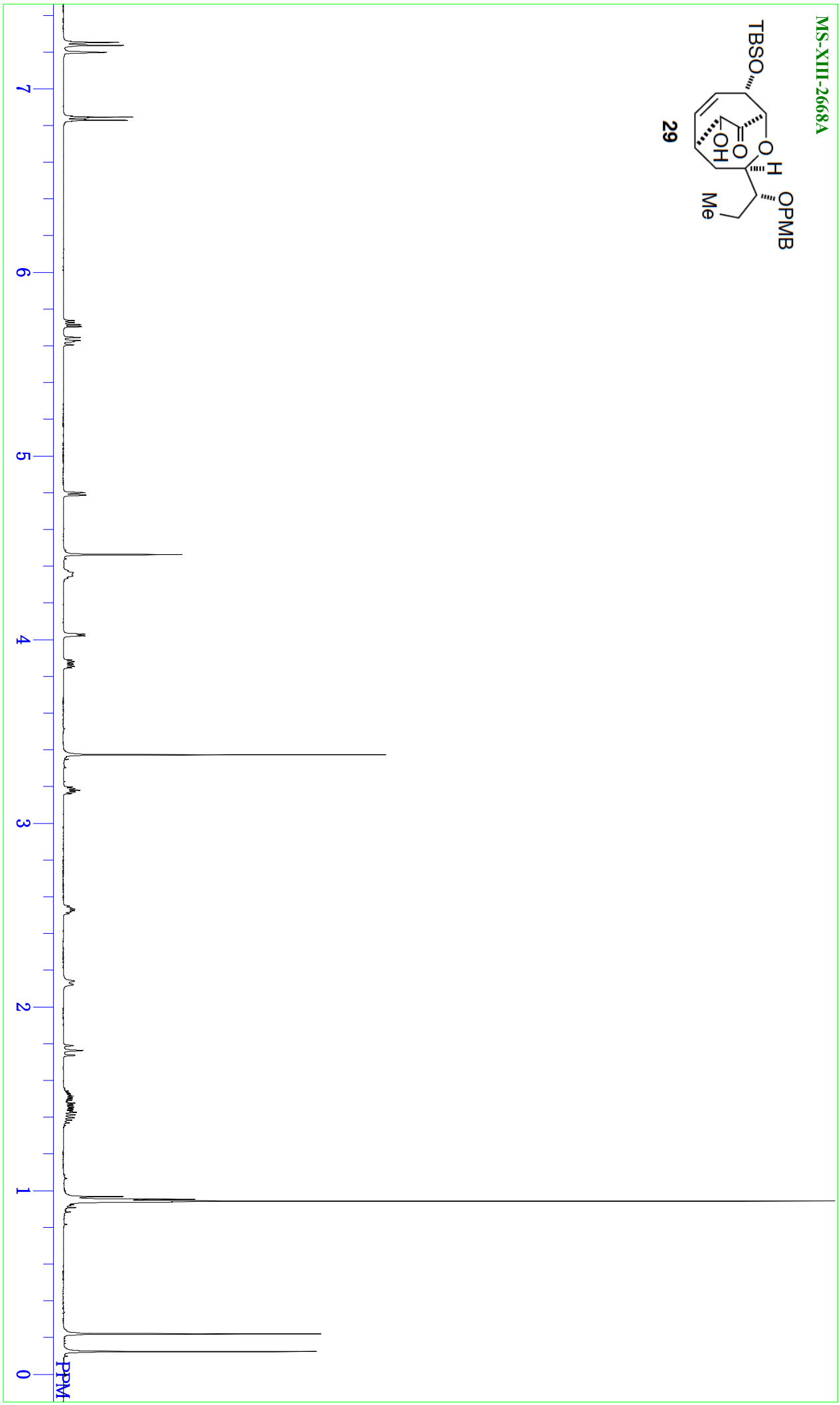
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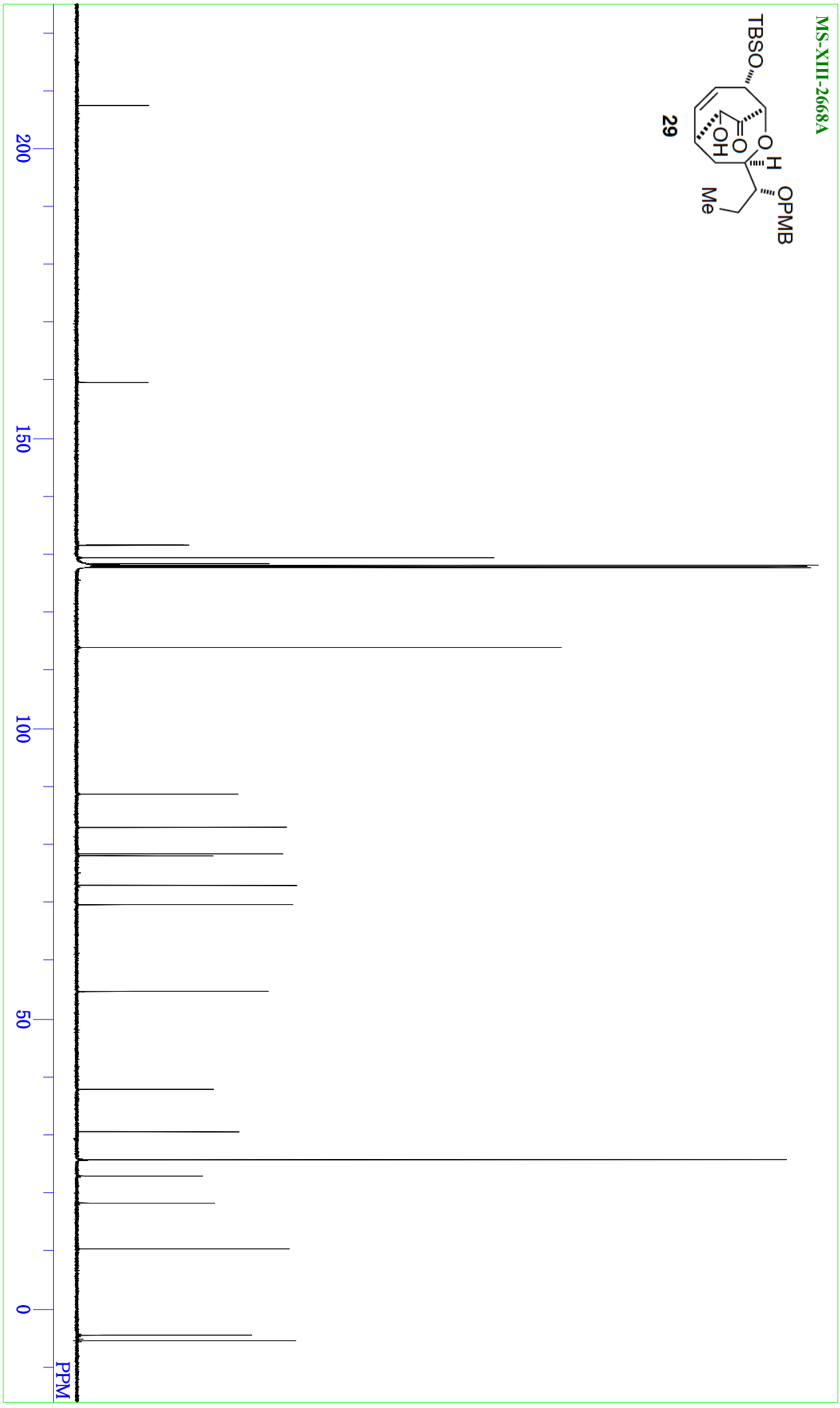
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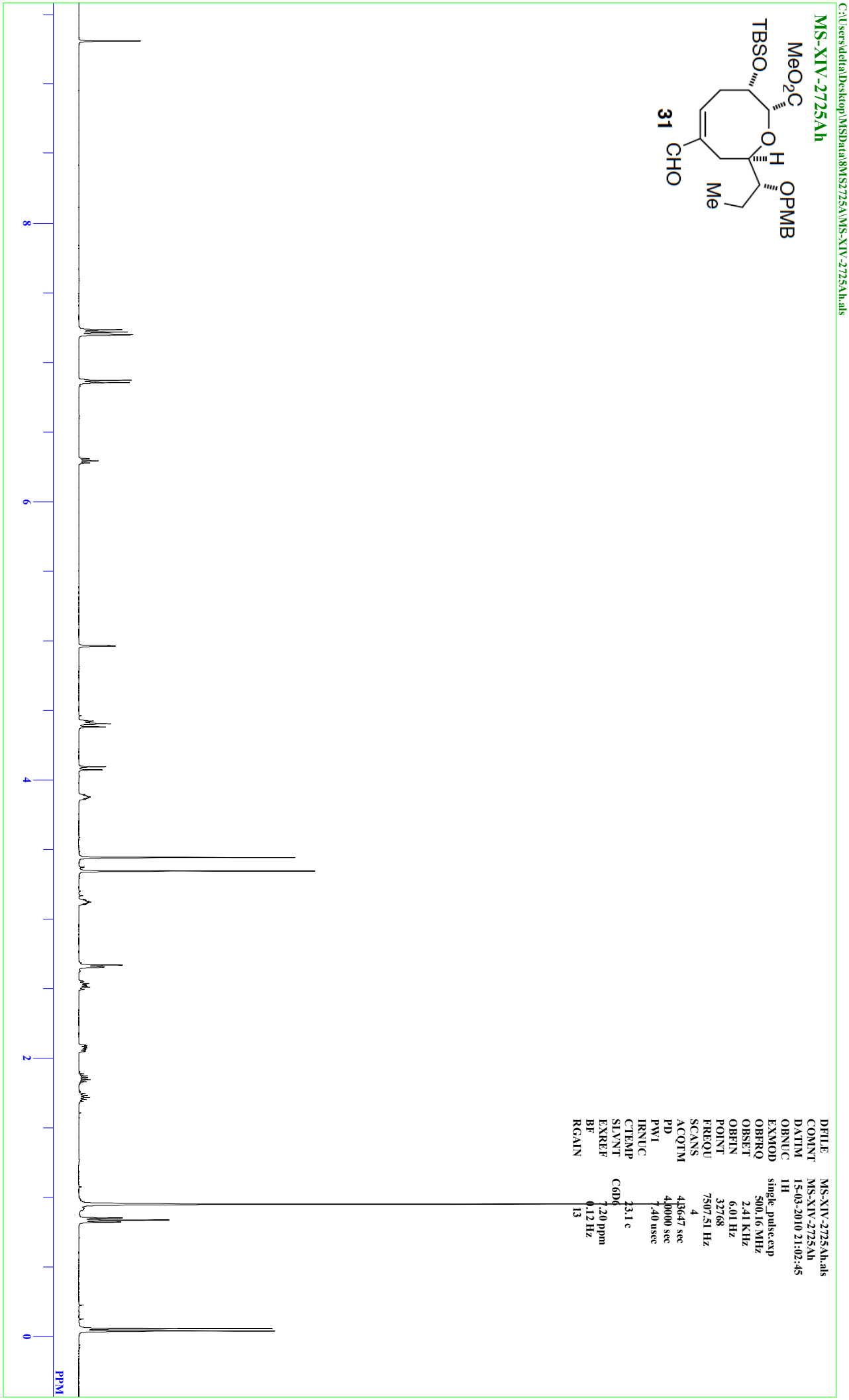
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OPMB
Me
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4
2
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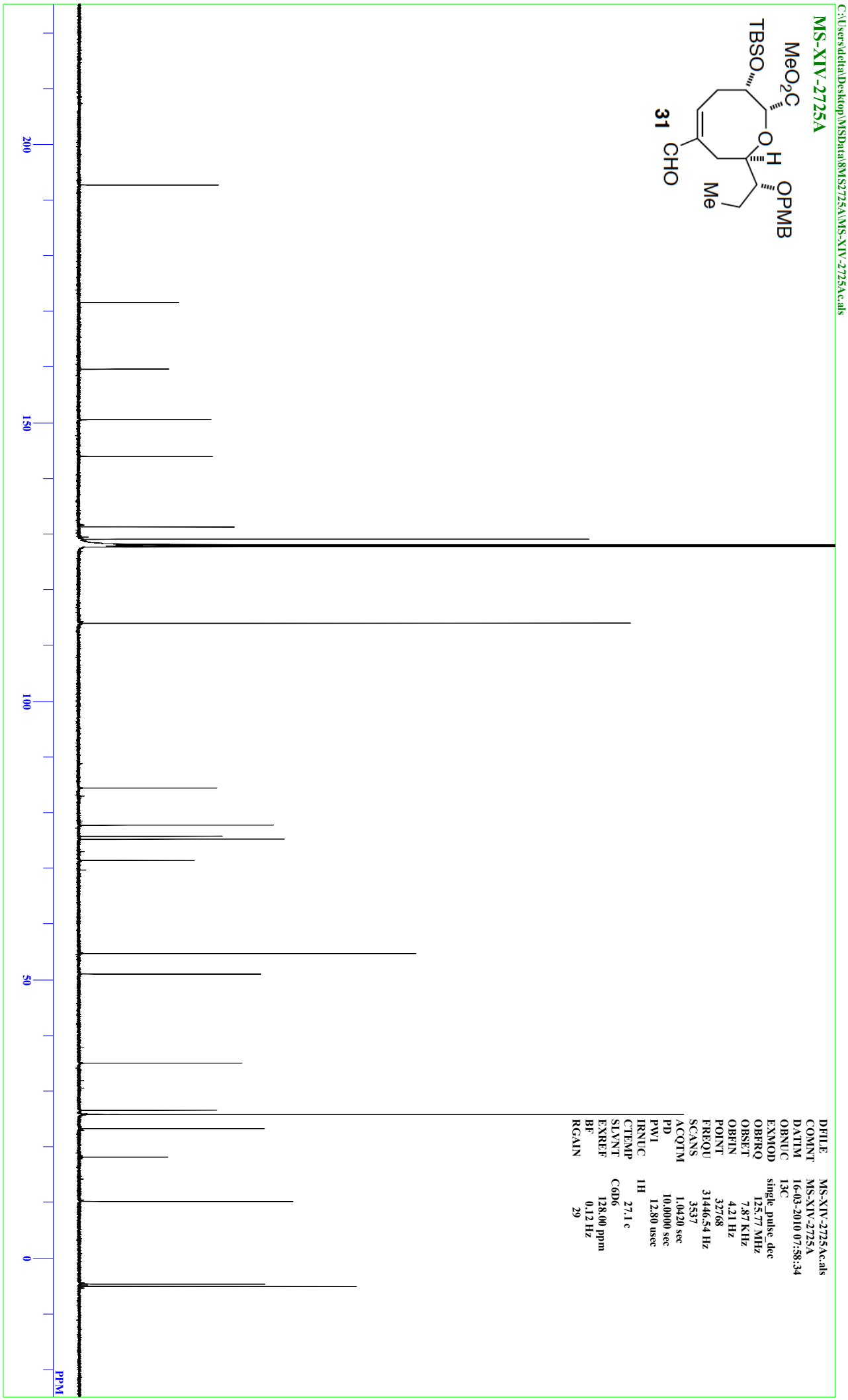
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100
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CTEMP 27.1 c
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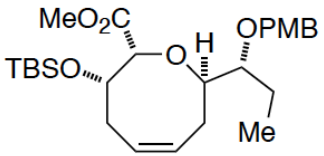
MS-XIV-2727Eh



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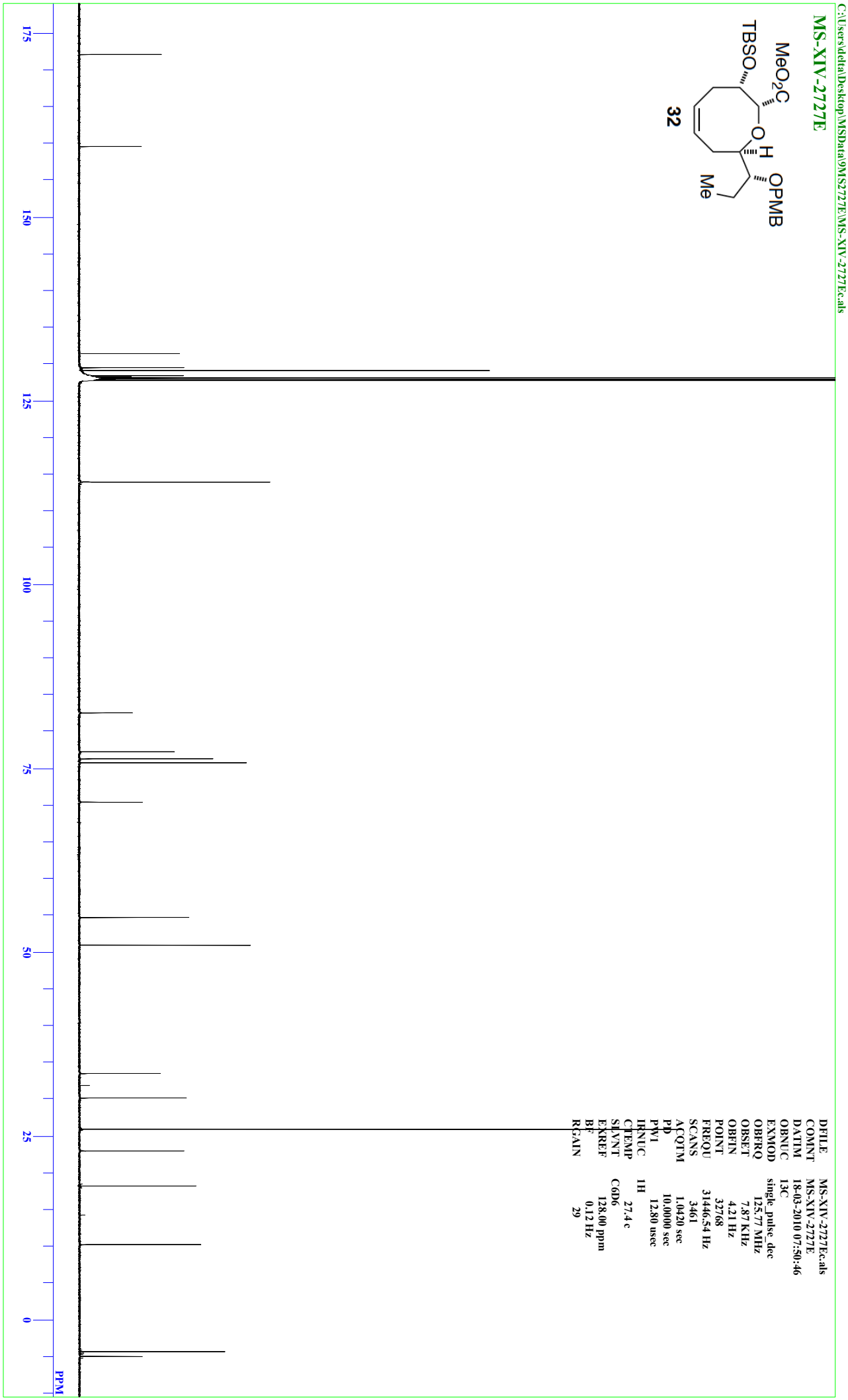
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OPMB
Me
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PD 10.0000 sec
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CTEMP 27.4 c
SLVNT C6D6
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BF 0.12 Hz
RGAIN 29
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150
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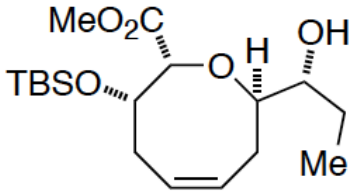
PPM

C:\Users\delta\Desktop\MSData\10MS2728C\MS-XIV-2728Ch.als

MS-XIV-2728Ch



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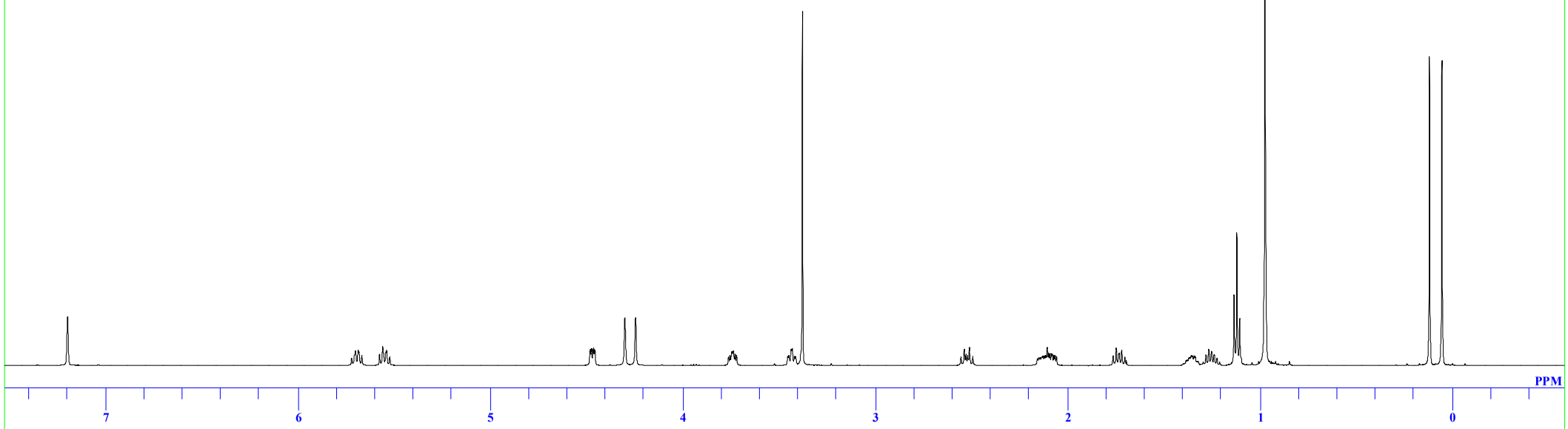
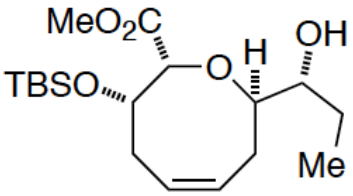
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	32768
FREQU	7507.51 Hz
SCANS	4
ACQTM	4.3647 sec
PD	4.0000 sec
PW1	7.40 usec
IRNUC	
CTEMP	23.3 c
SLVNT	C6D6
EXREF	7.20 ppm
BF	0.12 Hz
RGAIN	12



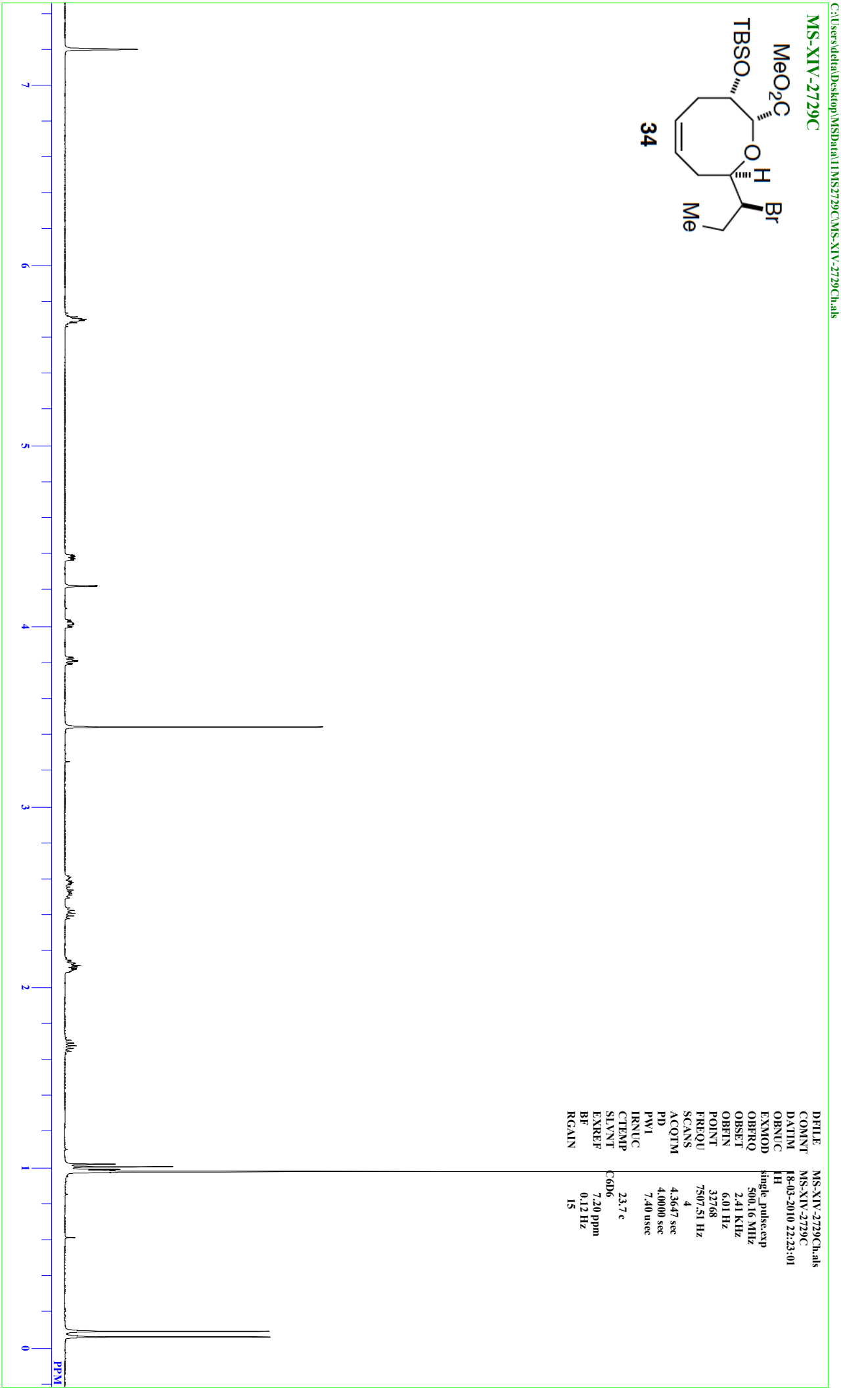
C:\Users\delta\Desktop\MSData\10MS2728C\MS-XIV-2728Cc.als

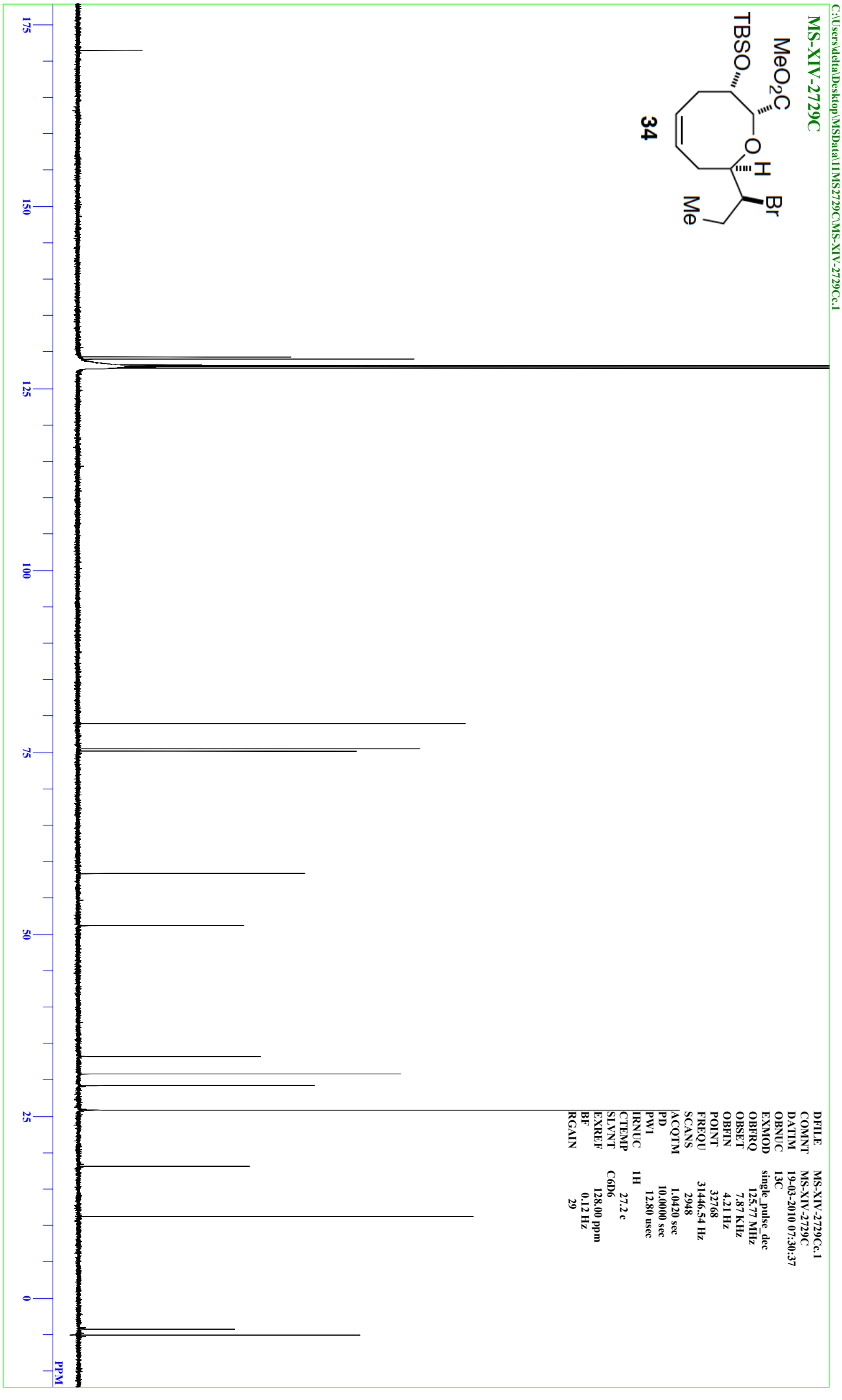
MS-XIV-2728Cc

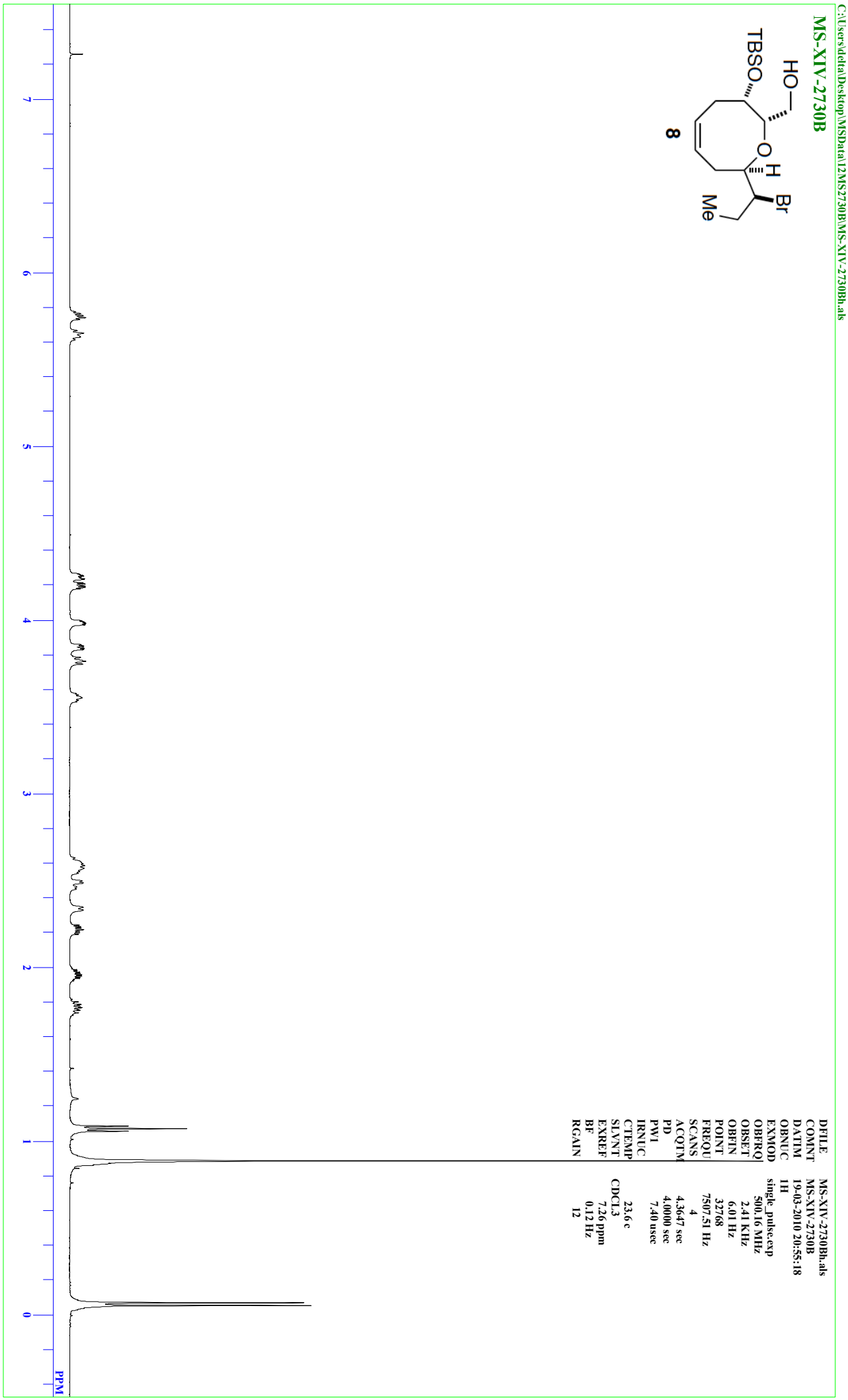


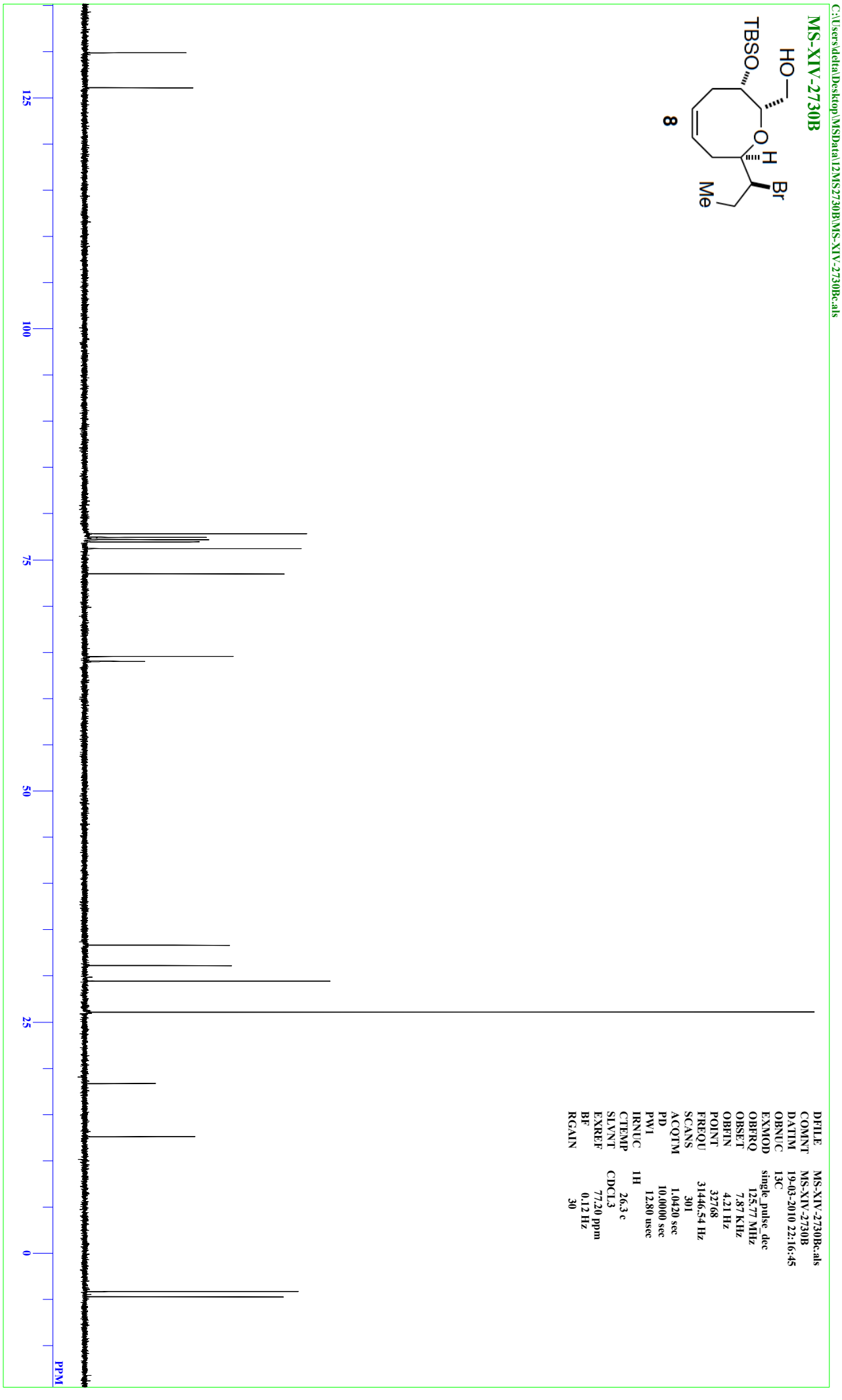
33

DFILE	MS-XIV-2728Cc.als
COMNT	MS-XIV-2728Cc
DATIM	18-03-2010 22:03:40
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	32768
FREQU	31446.54 Hz
SCANS	134
ACQTM	1.0420 sec
PD	10.0000 sec
PW1	12.80 usec
IRNUC	1H
CTEMP	27.2 c
SLVNT	C6D6
EXREF	128.00 ppm
BF	0.12 Hz
RGAIN	29


C:\Users\delfat\Desktop\MSData\11MS2729C\MS-XIV-2729Ch.als
MS-XIV-2729C
MeO2C
TBSO
O
H
Br
Me
34
DFILE MS-XIV-2729Ch.als
COMNT MS-XIV-2729C
DATIM 18-03-2010 22:23:01
OBNUC 1H
EXMOD single_pulse.exp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 32768
FREQU 7507.51 Hz
SCANS 4
ACQTM 4.3647 sec
PD 4.0000 sec
PW1 7.40 usec
IRNUC
CTEMP 23.7 c
SLVNT C6D6
EXREF 7.20 ppm
BF 0.12 Hz
RGAIN 15
7
6
5
4
3
2
1
0
PPM


C:\Users\delfat\Desktop\MSData\11MS2729C\MS-XIV-2729Cc.1
MS-XIV-2729C
MeO2C
TBSO
O
H
Br
Me
34
DFILE MS-XIV-2729Cc.1
COMNT MS-XIV-2729C
DATIM 19-03-2010 07:30:37
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 32768
FREQU 31446.54 Hz
SCANS 2948
ACQTM 1.0420 sec
PD 10.0000 sec
PW1 12.80 usec
IRNUC 1H
CTEMP 27.2 c
SLVNT C6D6
EXREF 128.00 ppm
BF 0.12 Hz
RGAIN 29
175
150
125
100
75
50
25
0
PPM


C:\Users\delfa\Desktop\MSData\12MS2730B\MS-XIV-2730Bh.als
MS-XIV-2730B
HO
TBSO
O
H
Br
Me
8
DFILE MS-XIV-2730Bh.als
COMNT MS-XIV-2730B
DATIM 19-03-2010 20:55:18
OBNUC 1H
EXMOD single_pulse.exp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 32768
FREQU 7507.51 Hz
SCANS 4
ACQTM 4.3647 sec
PD 4.0000 sec
PW1 7.40 usec
IRNUC
CTEMP 23.6 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 12
7
6
5
4
3
2
1
0
PPM


C:\Users\delfa\Desktop\MSData\12MS2730B\MS-XIV-2730Bc.als
MS-XIV-2730B
HO
TBSO
O
H
Br
Me
8
DFILE MS-XIV-2730Bc.als
COMNT MS-XIV-2730B
DATIM 19-03-2010 22:16:45
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 32768
FREQU 31446.54 Hz
SCANS 301
ACQTM 1.0420 sec
PD 10.0000 sec
PW1 12.80 usec
IRNUC 1H
CTEMP 26.3 c
SLVNT CDCL3
EXREF 77.20 ppm
BF 0.12 Hz
RGAIN 30
125
100
75
50
25
0
PPM