Synthesis of the Monomeric Counterpart of Marinomycin A

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General

TLC was performed on Merck $60F_{254}$ silica gel plates and visualized either with a UV lamp (254 nm), or by using a solution of *p*-anisaldehyde/sulfuric acid/acetic acid in EtOH followed by heating. Flash chromatography was performed with Merck Geduran Si60 silica gel (40-63 UM). Infrared (IR) spectra were recorded on a Perkin-Elmer 298 or on a Bruker TENSOR^{TM} 27 (IRFT), wavenumbers are indicated in cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker AVANCE 400 at 400 MHz and data are reported as follows: chemical shift in ppm from tetramethylsilane as an internal standard, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, m = multiplet or overlap of non equivalent resonances), integration. ^{13}C NMR spectra were recorded on a Bruker AC 300 at 75 MHz or on a Bruker AVANCE 400 at 100 MHz and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator ($CDCl_3$ δ 77.0 ppm), multiplicity with respect to proton (deduced from DEPT experiments, s = quaternary C, d = CH, t = CH_2, q = CH_3). Mass spectra with electronic impact (MS) were recorded from a Hewlett-Packard tandem 5890A GC (12 m capillary column) – 5971 MS (70 eV). High resolution mass spectra (HRMS) were performed by the Groupe de Spectrométrie de Masse de l'Université Pierre et Marie Curie (Paris). All the reactions were performed under an argon atmosphere.

I- Experimental Section

(*E*)-3-(2,2-Dimethyl-4-oxo-4H-benzo[1,3]dioxin-5-yl)-propenal (6). To a solution of aryl triflate **4**[1] **(**100 mg, 0.307 mmol, 1.0 equiv) and boronic acid **5** (40 mg, 0.398 mmol, 1.3 equiv) in 1,4-dioxane (3 mL), within a microwave vial, were successively added K_3PO_4 (97 mg, 0,459 mmol, 1,5 equiv) and $Pd(PPh_3)_4$ (34 mg, 0.031 mmol, 0.1 equiv). The vial was flushed with argon and sealed. After 15 min of stirring at 130 °C in the microwave, the reaction mixture was concentrated under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether/EtOAc : 95/5 to 80/20) furnished α,β-unsaturated aldehyde **6** (52 mg, 73%) as a yellow solid: $R_f \approx 0.35$ (petroleum ether/EtOAc : 80/20); IR (neat) 3072, 2998, 2943, 2815, 2735, 1722, 1678, 1624, 1594, 1577, 1476, 1390, 1380, 1319, 1272, 1204, 1118, 1080, 1046, 1024, 968, 924, 799,780, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.80 (d, 1H, J = 7.6 Hz), 8.65 (d, 1H, J = 16.0 Hz), 7.57 (t, 1H, J = 7.9 Hz), 7.34 (d, 1H, J = 7.7 Hz), 7.07 (dd, 1H, J = 8.5, 0.8 Hz), 6.62 (dd, 1H, J = 16.0, 7.9 Hz), 1.75 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1 (d), 160.1 (s), 157.2 (s), 150.3 (d), 138.0 (s), 135.7 (d), 132.0 (d), 122.3 (d), 119.6 (d), 111.5 (s), 106.0 (s), 25.6 (2q); MS (EI, 70 eV): *m/z* (%): 232 ($M^{+\bullet}$, 1), 204 (13), 203 (100), 174 (46), 147 (12), 146 (58), 118 (78), 90 (17), 89 (25), 63 (11).

5-[(1*E*,3*E*)-Hexa-1,3-dien-5-ynyl]-2,2-dimethylbenzo[1,3]dioxine-4-one (8). To a solution of 3-trimethylsilyl-2-propynyl phosphonium bromide (1.5 g, 3.27 mmol, 1.3 equiv) in THF (45 mL) was added *n*-BuLi (2 M in THF, 1.49 mL, 2.98 mmol, 1.18 equiv) at -78 °C. After 1 h of stirring in the dark, a solution of aldehyde **6** (585 mg, 2.52 mmol, 1.0 equiv) in THF (5 mL) was added dropwise. The reaction mixture was slowly warmed to 0 °C and after 1 h of stirring at this temperature, the reaction mixture was hydrolyzed by adding H_2O (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic layers were washed with brine (20 mL) dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of the residue by flash

[1] Arylic triflate **4** was synthesized in two steps from commercially available 2,6-dihydroxybenzoic acid according to: (a) Hadfield, A.; Schweitzer, H.; Trova, M. P.; Green, K. *Synth. Commun.* **1994**, *24*, 1025–1028; (b) Dushin, R. G.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1992**, *114*, 655–659.

chromatography on silica gel (petroleum ether/EtOAc : 98/2 to 95/5) furnished enyne **7** (480 mg, 58%) as a mixture of diastereoisomers (*E*/*Z* = 75/25).

To a solution of 3-trimethylsilyl-2-propynyl phosphonium bromide (147 mg, 0.325 mmol, 1.2 equiv) in THF (5 mL) was added sodium bis-trimethylsilylamide (2 M in THF, 160 μL, 0.320 mmol, 1.18 equiv) at rt. After 1 h of stirring in the dark, a solution of aldehyde **6** (63 mg, 0.271 mmol, 1.0 equiv) in THF (1 mL) was added dropwise. After 1.5 h, the reaction mixture was hydrolyzed by adding H_2O (5 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers were washed with brine (5 mL) dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of the residue by flash chromatography on silica gel (petroleum ether/EtOAc : 98/2 to 95/5) furnished enyne **7** (58 mg, 65%) as a mixture of diastereoisomers (*E*/*Z* = 82/18).

To a solution of trimethylsilylalkyne **7** (33 mg, 0.10 mmol, 1.0 equiv) in THF (1 mL) at 0 °C was added tetra-*n*-butylammonium fluoride (1 M in THF, 120 μL, 0.12 mmol, 1.2 equiv). After 10 min, the reaction mixture was hydrolyzed by adding a saturated aqueous solution of NH_4Cl (3 mL) and the resulting solution was diluted with ether (3 mL). The aqueous phase was extracted with Et_2O (3 x 5 mL) and the combined organic layers were washed with brine (5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of the residue by flash chromatography on silica gel (petroleum ether/EtOAc : 98/2 to 95/5) furnished terminal alkyne **8** (25 mg, 97%) as a yellow oil: $R_f \approx 0.55$ (petroleum ether/EtOAc : 80/20); IR (neat) 3312, 2955, 2918, 2846, 2097, 1694, 1552, 1462, 1376, 1181, 1072, 996, 636 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, 1H, *J* = 15.4 Hz), 7.45 (t, 1H, *J* = 8.0 Hz), 7.30 (d, 1H, *J* = 7.4 Hz), 6.92 (dd, 1H, *J* = 15.6, 10.8 Hz), 6.87 (dd, 1H, *J* = 8.1, 1.0 Hz), 6.77 (dd, 1H, *J* = 15.4, 11.0 Hz), 5.73 (dd, 1H, *J* = 15.5, 2.4 Hz), 3.13 (d, 1H, *J* = 2.4 Hz), 1.71 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3 (s), 157.0 (s), 140.8 (s), 135.2 (d), 133.1 (d), 131.6 (d), 121.0 (d), 116.9 (d), 111.8 (d), 110.9 (s), 105.4 (s), 84.5 (s), 82.9 (d), 81.0 (s), 25.6 (2q); MS (EI, 70 eV): *m/z (*%): 254 ($M^{+\bullet}$, 6), 197 (15), 196 (100), 168 (38), 140 (9), 139 (24), 58 (6); HRMS (ESI) calcd for $C_{16}H_{14}O_3 + Na^+$ 277.0835, found 277.0834.

5-[(*E*)-3-Hydroxypropenyl]-2,2-dimethylbenzo[1,3]dioxin-4-one (11). To a flame dried flask containing aryl triflate **4**[1] (2.0 g, 6.13 mmol, 1.0 equiv), $Pd_2(dba)_3$ (113 mg,

0.12 mmol, 0.02 equiv), tri-(2-furyl)phosphine (230 mg, 0.98 mmol, 0.16 equiv) and LiCl (780 mg, 18.4 mmol, 3.0 equiv), was added anhydrous DMF (15 mL). The resulting mixture was stirred at rt for 30 min before addition of a solution of vinyl stannane **10** (2.77 g, 7.97 mmol, 1.3 equiv) in DMF (10 mL). The mixture was stirred for 2 h at 60 °C, cooled to rt and quenched with a saturated aqueous KF solution (25 mL). The mixture was stirred for 30 min and the aqueous layer was extracted with 20% EtOAc in hexanes (3 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of the residue by flash chromatography on silica gel (hexanes/EtOAc: 80/20 to 50/50) provided the desired allylic alcohol **11** (1.17 g, 82%) as a light yellow solid. Physical and spectral data matched those previously reported:[2] mp = 98-100 °C; R_f = 0.2 (petroleum ether/EtOAc : 60/40); IR (neat) 3301, 2954, 2920, 2851, 1720, 1648, 1597, 1573, 1474, 1378, 1316, 1267, 1205, 1079, 1040, 966, 831, 781, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, 1H, J = 15.8 Hz), 7.43 (t, 1H, J = 8.0 Hz), 7.23 (d, 1H, J = 8.0 Hz), 6.85 (d, 1H, J = 8.0 Hz), 3.33 (dt, 1H, J = 15.8, 5.6 Hz), 4.36 (br t, 2H, J = 5.6 Hz), 3.55 (br m, 1H, OH), 1.70 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5 (s), 157.0 (s), 141.8 (s), 135.4 (d), 133.5 (d), 128.6 (d), 121.8 (d), 116.2 (d), 111.0 (s), 105.2 (s), 63.2 (t), 25.7 (2q); MS (EI, 70 eV): *m/z* (%): 234 (23), 203 (49), 177 (12), 176 (100), 163 (10), 149 (12), 148 (40), 147 (99), 146 (30), 131 (13), 121 (74), 120 (41), 119 (21), 118 (29), 105 (13), 103 (15), 102 (15), 92 (18), 91 (36), 89 (18), 77 (15), 65 (13), 63 (14); HRMS (ESI) calcd for $C_{13}H_{14}O_4$ + Na^+ 257.0789, found 257.0784.

5-[(*E*)-3-Bromopropenyl]-2,2-dimethylbenzo[1,3]dioxin-4-one. To a stirred solution of **11** (1.03 g, 4.40 mmol, 1.0 equiv) in Et_2O (30 mL) at rt was added phosphorus tribromide (165 μL, 1.76 mmol, 0.4 equiv) dropwise. The resulting mixture was refluxed for 1 h, cooled to rt and poured into a cold saturated aqueous solution of $NaHCO_3$ (15 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of the residue by flash chromatography on silica gel (petroleum ether/Et_2O: 90/10) afforded the title allylic bromide (1.29 g, 99%) as a

[2] Wang, X.; Bowman, E. J.; Bowman, B. J.; Porco, J. A. Jr. *Angew. Chem. Int. Ed.* **2004**, *43*, 3601–3605.

viscous yellow oil which crystallized upon standing at –20 °C: R_f = 0.8 (petroleum ether/EtOAc : 60/40); IR (neat) 3066, 2996, 2942, 2863, 1724, 1598, 1576, 1475, 1316, 1270, 1257, 1200, 1043, 965, 925, 801, 776, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, 1H, J = 15.6 Hz), 7.48 (t, 1H, J = 8.0 Hz), 7.27 (d, 1H, J = 8.0 Hz), 6.90 (d, 1H, J = 8.0 Hz), 6.36 (dt, 1H, J = 15.6 and J = 7.9 Hz), 4.19 (d, 2H, J = 7.9 Hz), 1.71 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2 (s), 156.9 (s), 140.1 (s), 135.3 (d), 132.2 (d), 129.2 (d), 121.7 (d), 117.1 (d), 111.0 (s), 105.4 (s,), 33.0 (t), 25.6 (2q); MS (EI, 70 eV): *m/z* (%): 298 ($M^{+\bullet}$ ^{81}Br, 3), 296 ($M^{+\bullet}$ ^{79}Br, 3), 240 (27), 238 (28), 217 (26), 160 (14), 159 (100), 131 (13), 103 (31), 102 (11), 77 (13); HRMS (ESI) calcd for $C_{13}H_{13}{}^{79}BrO_3 + Na^+$ 318.9946, found 318.9943, calcd for $C_{13}H_{13}{}^{81}BrO_3 + Na^+$ 320.9915, found 320.9921.

[(*E*)-3-(2,2-Dimethyl-4-oxo-4*H*-benzo[1,3]dioxin-5-yl)-allyl]-phosphonic acid diethyl ester (12). To a stirred solution of 5-[(*E*)-3-bromopropenyl]-2,2-dimethylbenzo[1,3]dioxin-4-one (1.29 g, 4.34 mmol, 1.0 equiv) in anhydrous toluene (10 mL) at rt was added triethyl phosphite (10 mL, 61.2 mmol, 14 equiv) dropwise. The resulting mixture was refluxed for 2 h, allowed to cool to rt and directly transferred on top of a silica gel column. Flash chromatography (hexanes/EtOAc: 80/20 to 0/100) furnished the desired diethylallyl phosphonate **12** (1.49 g, 96%) as a viscous colorless oil which crystallized upon standing (white solid): mp = 94-95 °C; R_f = 0.1 (petroleum ether/EtOAc : 40/60); IR (neat) 2986, 2941, 2907, 1726, 1643, 1599, 1576, 1475, 1390, 1317, 1251, 1206, 1023, 961, 925, 779, 727 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, 1H, J = 15.7 and $J_{H\text{-}P}$ = 5.1 Hz), 7.45 (t, 1H, J = 8.0 Hz), 7.24 (d, 1H, J = 8.0 Hz), 6.87 (d, 1H, J = 8.0 Hz), 6.17 (m, 1H), 4.15 (m, 4H), 2.85 (ddd, 2H, $J_{H\text{-}P}$ = 22.0, J = 7.6 and J = 1.4 Hz), 1.71 (s, 6H), 1.34 (t, 6H, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3 (s), 156.8 (s), 141.3 (s), 135.3 (d), 132.8 (d, $J_{C\text{-}P}$ = 15.0 Hz), 123.4 (d, $J_{C\text{-}P}$ = 12.0 Hz), 121.6 (d), 116.4 (d), 110.7 (s), 105.3 (s), 62.1 (2t), 32.3 (t, $J_{C\text{-}P}$ = 137.0 Hz), 25.6 (2q), 16.5 (2t); MS (EI, 70 eV): *m/z* (%): 354 (27), 297 (16), 296 (100), 268 (19), 240 (47), 222 (17), 212 (35), 160 (94), 159 (25), 132 (19), 131 (17), 103 (30), 77 (15); HRMS (ESI) calcd for $C_{17}H_{23}O_6P + H^+$ 355.1311, found 355.1308.

(*E*)-4-Iodo-3-methylbut-3-en-1-ol. To a stirred solution of zirconocene dichloride (4.15 g, 14.2 mmol, 0.22 equiv) in CH_2Cl_2 (250 mL) at -20 °C was added trimethylaluminum (2 M in hexanes, 100 mL, 200 mmol, 3.1 equiv) dropwise *via* cannula. After stirring the resulting yellow mixture for 10 min at -20 °C, water (1.8 mL, 100 mmol, 1.55 equiv) was cautiously added dropwise (Caution: exothermic reaction!). After an additional 10 min stirring, commercially available 3-butyn-1-ol **15** (4.9 mL, 64.5 mmol, 1.0 equiv), pretreated with trimethylaluminum (2 M in hexanes, 10 mL, 20 mmol, 0.31 equiv) in anhydrous CH_2Cl_2 (50 mL) at 0 °C, was added dropwise *via* cannula. The reaction mixture was allowed to warm to rt and the resulting yellow thick slurry was stirred for 2.5 h. The reaction mixture was then cooled to -20 °C and a solution of I_2 (20 g, 77.5 mmol, 1.2 equiv) in anhydrous ether (130 mL) was added dropwise *via* cannula. The mixture was allowed to warm to rt and was stirred for an additional 2 h. The reaction mixture was slowly poured into a well-stirred mixture of a saturated aqueous solution of sodium potassium tartrate (500 mL) and Et_2O (500 mL), and the resulting biphasic mixture was stirred for 2 h. The slurry was filtered through Celite®, the layers were separated and the aqueous layer was extracted with Et_2O (3 x 500 mL). The combined organic layers were washed with $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (pentane/Et_2O : 90/10 to 70/30) provided the title compound (10.5 g, 77%) as a light yellow oil. Physical and spectral data match those previously reported:[3] R_f = 0.3 (petroleum ether/EtOAc : 80/20); IR (neat) 3313, 2936, 2910, 2880, 1616, 1428, 1375, 1271, 1141, 1038, 764, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.01 (br s, 1H), 3.7 (br t, 2H, J = 6.0 Hz), 2.47 (br t, 2H, J = 6.0 Hz), 1.98 (br s, 1H, OH), 1.87 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4 (s), 76.8 (d), 60.1 (t), 42.4 (t) 23.8 (q); MS (EI, 70 eV): *m/z* (%): 212 (47), 182 (8), 181 (16), 127 (8), 85 (100), 67 (31), 57 (19), 55 (36), 54 (23), 53 (36); Elemental analysis calcd for C_5H_9IO : C, 28.32; H, 4.28. Found : C, 28.56; H, 4.47.

(*E*)-4-iodo-3-methylbut-3-enal (16). To a stirred solution of (*E*)-4-iodo-3-methylbut-3-en-1-ol (4.0 g, 18.9 mmol, 1.0 equiv) in CH_2Cl_2 (35 mL) at 0 °C was added dropwise a

[3] Marshall, J. A.; Eidam, P. *Org. Lett.* **2004**, *6*, 445–448.

solution of Dess-Martin periodinane (8.8 g, 20.8 mmol, 1.1 equiv) in CH_2Cl_2 (65 mL). The solution was allowed to warm to rt and stirred until complete conversion of the starting material by TLC (approximately 1.5 h). The reaction mixture was diluted with Et_2O (200 mL) and poured into a saturated aqueous solution of $NaHCO_3$ (150 mL) containing solid $Na_2S_2O_3$ (24 g). The resulting slurry was stirred for 10 min until two clear layers separated. The aqueous layer was extracted with Et_2O (3 x 200 mL). The combined organic layers were washed with brine (200 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude aldehyde **16** (3.9 g, 98%) was obtained as a light yellow oil and was used in the next step without further purification.

(*E*)-(*R*)-1-Iodo-2-methylhepta-1,6-dien-4-ol. To a stirred solution of cyclopentadienyl[(4*S*,*trans*)-2,2-dimethyl-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethanolato-*O*,*O*']titanium chloride (15 g, 24.5 mmol, 1.3 equiv) in anhydrous Et_2O (150 mL) at 0 °C, was added dropwise allylmagnesium chloride (2 M in THF, 10.4 mL, 20.8 mmol, 1.1 equiv). After 2 h at 0 °C, the reaction mixture was cooled to –78 °C and a solution of crude (*E*)-4-iodo-3-methylbut-3-enal **16** (3.9 g, 18.9 mmol, 1.0 equiv) in Et_2O (40 mL) was added dropwise *via* cannula. After 4 h at -78 °C, the reaction was quenched by addition of a 45% aqueous NH_4F solution (100 mL). The reaction mixture was stirred overnight at rt and then filtered over Celite®. The layers were separated and the aqueous phase was extracted with ether (3 x 200 mL). The combined organic extracts were washed with brine (200 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was then diluted with pentane (150 mL) and filtered to remove (4*S*,*trans*)-2,2-dimethyl-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethanol. After removal of pentane under reduced pressure, purification of the residue by flash chromatography on silica gel (toluene/Et_2O: 99/1) provided the title enantiopure homoallylic alcohol (4.02 g, 84%, 2 steps) as a colorless oil: $R_f \approx 0.2$ (petroleum ether/Et_2O : 80/20); $[\alpha]^{20}_D$ – 13.3 (*c* 1.32, $CHCl_3$); IR (neat) 3383, 3074, 2976, 2909, 1640, 1615, 1433, 1377, 1272, 1143, 1053, 994, 915, 764, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.03 (br s, 1H), 5.83 (m, 1H), 5.17 (m, 1H), 5.13 (m, 1H), 3.81 (m, 1H), 2.39-2.35 (m, 2H), 2.29 (m, 1H), 2.18 (m, 1H), 1.88 (br s, 3H), 1.69 (d, 1H, J = 3.2 Hz, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7 (s), 134.3 (d), 118.4 (t), 77.5 (d), 68.3 (d), 46.8 (t), 41.6 (t), 24.2 (d); MS (EI, 70 eV):

m/z (%): 252 (1), 237 (M-Me^+, 1), 211 (5), 183 (16), 182 (100), 167 (4), 107 (28), 83 (28), 71 (35), 55 (83); HRMS (ESI) calcd for $C_8H_{13}IO + Na^+$ 274.9909, found 274.9904.

(*E*)-(*R*)-1-[(1-Iodo-2-methylhepta-1,6-dien-4-yloxy)methyl]-4-methoxybenzene (17). To a solution of (*E*)-(*R*)-1-iodo-2-methylhepta-1,6-dien-4-ol (3.3 g, 13 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (60 mL), were successively added *p*-methoxybenzyltrichloroacetimidate (7.4 g, 26 mmol, 2 equiv) and camphorsulfonic acid (453 mg, 1.95 mmol, 0.15 equiv) at rt. After 12 h of stirring, the reaction mixture was quenched by addition of a saturated aqueous solution of $NaHCO_3$ (30 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (petroleum ether/EtOAc: 98/2 to 95/5) provided the desired protected alcohol **17** (3.06 g, 63%) as a colorless oil: $R_f \approx 0.5$ (petroleum ether/EtOAc : 90/10); $[\alpha]^{20}_D$ – 14.6 (*c* 1.09, $CHCl_3$); IR (neat) 3071, 2932, 2907, 2834, 1639, 1612, 1585, 1510, 1462, 1439, 1244, 1172, 1069, 1034, 914, 819, 809 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, 2H, J = 8.6 Hz), 6.87 (d, 2H, J = 8.6 Hz), 5.96 (br s, 1H), 5.82 (m, 1H), 5.10 (m, 1H), 5.07 (br s, 1H,), 4.50 (d, 1H, $J_{syst\ AB}$ = 11.2 Hz), 4.39 (d, 1H, $J_{syst\ AB}$ = 11.2 Hz), 3.79 (s, 3H), 3.55 (m, 1H), 2.44 (dd, 1H, $J_{syst\ AB}$ = 14.1, 7.5 Hz), 3.36 (dd, 1H, J = 14.1, 5.0 Hz), 2.31-2.25 (m, 2H), 1.79 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (s), 145.0 (s), 134.5 (d), 130.5 (s), 129.8 (2d), 117.5 (t), 113.8 (2d), 77.3 (d), 75.9 (d), 70.9 (t), 55.3 (q), 44.1 (t), 38.3 (t), 24.4 (q); MS (EI, 70 eV): *m/z* (%): 372 (1), 331 (1), 245 (3), 175 (5), 121 (100), 91 (3), 77 (4); HRMS (ESI) calcd for $C_{16}H_{21}IO_2 + Na^+$ 395.0484, found 395.0480.

(*S*,*E*)-6-Iodo-3-(4-methoxybenzyloxy)-5-methylhex-5-enal (18). To a stirred solution of alkene **17** (3.0 g, 8.06 mmol, 1.0 equiv) in a *tert*-BuOH/THF/water mixture (5/5/1, 80 mL) at 0 °C, were added *N*-methylmorpholine *N*-oxide (1.04 g, 8.86 mmol, 1.1 equiv) and osmium tetroxide (2.5 wt% in *tert*-BuOH, 1.0 mL, 0.08 mmol, 0.01 equiv). After 18 h of stirring at rt, the reaction mixture was quenched by addition of a saturated aqueous solution of $Na_2S_2O_3$ (50 mL) and the resulting mixture was allowed to stir for 1 h. The

aqueous layer was extracted with Et_2O (3 x 100 mL) and the combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The obtained crude 1,2-diol was used in the next step without further purification.

To a stirred solution of the obtained 1,2-diol in a MeOH/H_2O mixture (2/1, 135 mL) was added sodium periodate in one portion (10.4 g, 48.6 mmol, 6.0 equiv) at rt. The resulting white slurry was stirred for 45 min and was subsequently quenched by addition of water (50 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 80 mL) and the combined organic layers were washed with brine (80 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting crude aldehyde **18** was used in the next step without further purification.

(4*R*,6*R*)-6-(*tert*-Butyldimethylsilyloxy)-hept-1-en-4-ol. To a stirred solution of commercially available ethyl (*R*)-(–)-3-hydroxybutyrate **19** (2.5 g, 18.9 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (30 mL) was added imidazole (2.58 g, 37.8 mmol, 2.0 equiv) at 0 °C. After stirring for 5 min, TBSCl (3.4 g, 22.7 mmol, 1.2 equiv) was added in one portion and stirring was carried on for 30 min at 0 °C. The solution was then allowed to warm to rt, and after 20 h of stirring the reaction mixture was hydrolyzed by adding water (20 mL). The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* which provided ethyl (*R*)-3-(*tert*-butyldimethylsilyloxy)butyrate (4.3 g, quantitative) as a colorless oil. Physical and spectral data match those previously reported.[4]

To a stirred solution of the previously obtained ethyl (*R*)-3-(*tert*-butyldimethylsilyloxy)butyrate (2.5 g, 10.85 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (100 mL) was added DIBAL-H (1 M in hexanes, 12 mL, 12 mmol, 1.1 equiv) at -78 °C. After stirring for 45 min at -78 °C, the mixture was warmed to -30 °C and methanol (11 mL) was added. The mixture was allowed to warm to 0 °C and then poured into a well-stirred saturated aqueous solution of sodium potassium tartrate (100 mL). The resulting biphasic mixture was stirred for 2 h until two clear layers separated. The layers were separated and

[4] Brimble, M. A.; Nairn, M. R.; Park, J. S. O. *J. Chem. Soc. Perkin. Trans. 1*, **2000**, 697–709.

the aqueous phase was extracted with ether (3 x 100 mL). The combined organic extracts were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting crude (*R*)-3-(*tert*-butyldimethylsilyloxy)butyraldehyde was used in the next step without further purification.

To a stirred solution of cyclopentadienyl[(4*S*,*trans*)-2,2-dimethyl-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethanolato-*O*,*O*']titanium chloride (8.6 g, 14.1 mmol, 1.3 equiv) in anhydrous Et_2O (150 mL) at 0 °C, was added dropwise allylmagnesium chloride (2 M in THF, 6.0 mL, 11.9 mmol, 1.1 equiv). After 2 h at 0 °C, the reaction mixture was cooled to –78 °C and a solution of (*R*)-3-(*tert*-butyldimethylsilyloxy)butyraldehyde (10.85 mmol, 1.0 equiv) in Et_2O (50 mL) was added dropwise *via* cannula. After 2 h at -78 °C, the reaction was quenched by addition of water (60 mL). The reaction mixture was stirred for 48 h at rt and then filtered over Celite. The layers were separated and the aqueous phase was extracted with ether (3 x 100 mL). The combined organic extracts were washed with brine (150 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was then diluted with pentane (50 mL) and filtered to remove (4*S*,*trans*)-2,2-dimethyl-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethanol. After removal of pentane under reduced pressure, purification of the residue by flash chromatography on silica gel (petroleum ether/EtOAc: 99/1 to 95/5) provided the desired enantiopure homoallylic alcohol (1.88 g, 71% over two steps) as a colorless oil: $R_f \approx 0.2$ (petroleum ether/EtOAc : 95/5); $[\alpha]^{20}_D$ – 17.0 (*c* 1.05, $CHCl_3$); IR (neat) 3447, 2930, 2857, 1641, 1472, 1445, 1376, 1254, 1070, 1002, 913, 834, 774 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.74 (ddt, 1H, J = 17.2, 10.4, 7.1 Hz), 5.03-4.97 (m, 2H), 4.11 (m, 1H), 3.92 (m, 1H), 3.23 (d, 1H, J = 2.2 Hz, OH), 2.19-2.05 (m, 2H), 1.53 (ddd, 1H, J = 14.3, 9.8, 3.8 Hz), 1.43 (ddd, 1H, J = 14.3, 5.5, 2.4 Hz), 1.12 (d, 3H, J = 6.4 Hz), 0.80 (s, 9H), 0.00 (s, 3H), -0.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1 (d), 117.2 (t), 67.6 (d), 67.4 (d), 43.8 (t), 42.3 (t), 25.8 (3q), 22.9 (q), 17.9 (s), -4.5 (q), -5.0 (s); MS (EI, 70 eV): *m/z* (%): 229 (M-Me^+, 4), 205 (3), 203 (6), 187 (M-*t*Bu^+), 159 (40), 145 (19), 119 (100), 115 (11), 101 (17), 95 (40), 75 (84), 73 (33), 59 (11); HRMS (ESI) calcd for $C_{13}H_{28}O_2Si + Na^+$ 267.1756, found 267.1751.

(4*R*,6*R*)-6-(*tert*-Butyldimethylsilyloxy)-4-triethylsilyloxyhept-1-ene (20). To a stirred solution of (4*R*,6*R*)-6-(*tert*-butyldimethylsilyloxy)heptan-1-en-4-ol (1.39 g, 5.68 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (20 mL) was added 4-dimethylaminopyridine (70 mg, 0.57 mmol, 0.1 equiv) at rt. The solution was cooled to 0 °C and Et_3N (1.58 mL, 11.36 mmol, 2.0 equiv) was added dropwise. After stirring for 5 min at 0 °C, triethylsilyl chloride (1.43 mL, 8.53 mmol, 1.5 equiv) was added dropwise and the reaction mixture was allowed to warm to rt and stirred for 2 h. The resulting cloudy mixture was hydrolyzed by addition of water (10 mL) and neutralized by adding a 1 M solution of HCl (2 mL). The layers were separated and the aqueous phase was extracted with Et_2O (3 x 40 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of the residue by flash chromatography on silica gel (petroleum ether/AcOEt: 99/1) provided the desired protected 1,3-diol **20** (1.93 g, 95%) as a colorless oil: *Rf* ≈ 0.9 (petroleum ether/EtOAc : 95/5); $[\alpha]^{20}_D$ +10.5 (*c* 1.26, $CHCl_3$); IR (neat) 2954, 2877, 1641, 1461, 1414, 1375, 1253, 1069, 1003, 913, 834, 772, 724 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.76 (m, 1H), 4.98 (br d, 1H, J = 16.0 Hz), 4.98 (br d, 1H, J = 11.0 Hz), 3.85 (br sext, 1H, J = 6.2 Hz), 3.77 (br quint, 1H, J = 5.8 Hz), 2.17 (m, 2H), 1.60 (ddd, 1H, J = 13.8, 7.4, 5.2 Hz), 1.41 (ddd, 1H, J = 13.8, 7.0, 5.2 Hz), 1.08 (d, 3H, J = 6.1 Hz), 0.90 (t, 9H, J = 8.0 Hz), 0.82 (s, 9H), 0.54 (q, 6H, J = 8.0 Hz), 0.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0 (d), 116.9 (t), 69.6 (d), 66.3 (d), 47.6 (t), 42.6 (t), 25.9 (3q), 24.5 (q), 18.1 (s), 7.0 (3q), 5.3 (3t), -3.8 (q), -4.5 (q); MS (EI, 70 eV): *m/z* (%): 343 (M-Et, 1), 301 (M-*t*Bu, 1), 288 (10), 287 (38), 259 (10), 234 (12), 233 (57), 190 (14), 189 (70), 175 (12), 161 (71), 159 (100), 147 (13), 133 (15), 115 (24), 103 (25), 101 (15), 95 (40), 87 (16), 75 (20), 73 (32), 59 (15); HRMS (ESI) calcd for $C_{19}H_{42}O_2Si_2 + Na^+$ 381.2621, found 381.2617.

(*R*)-2-[(2*R*,4*R*)-4-(*tert*-Butyldimethylsilyloxy)-2-triethylsilyloxypentyl]-oxirane (22). To a suspension of AD-mix-β (4.64 g, 1.4 g/mmol of olefin) in a *tert*-BuOH/H_2O mixture (1/1, 32 mL) vigorously stirred at 0 °C was added olefin **20** (1.6 g, 3.31 mmol). After 20 h of stirring at 0 °C, the reaction mixture was concentrated under reduced pressure and was then diluted with Et_2O (30 mL). The aqueous phase was extracted with Et_2O (3 x 30 mL) and the combined organic layers were washed with brine (30 mL), dried over

$MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (petroleum ether/EtOAc : 85/15) furnished 1,2-diol **21** (960 mg, 56%) as a 75/25 inseparable mixture of diastereoisomers.

To a suspension of NaH (60% in oil, 425 mg, 10.63 mmol, 4.2 equiv) in THF (35 mL) at 0 °C was added a solution of 1,2-diol **21** (994 mg, 2.53 mmol, 1.0 equiv) in THF (15 mL) dropwise *via* cannula. After 30 min of stirring at 0 °C, the reaction mixture was cooled to -78 °C and a solution of tosylimidazole (645 mg, 2.91 mmol, 1.15 equiv) in THF (15 mL) was added to the previous mixture *via* cannula. The solution was warmed to 0 °C and after 2 h of stirring at this temperature, the reaction mixture was hydrolyzed by adding a saturated aqueous solution of NH_4Cl (20 mL). The aqueous phase was extracted with Et_2O (3 x 30 mL) and the combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (petroleum ether/EtOAc : 99/1) furnished epoxide **22** (780 mg, 83%) as a 75/25 inseparable mixture of diastereoisomers: $R_f \approx 0.15$ (petroleum ether/EtOAc : 98/2); IR (neat) 2954, 2878, 1461, 1413, 1375, 1253, 1117, 1071, 1004, 833, 772, 724, 673 cm^{-1}; *Major isomer:* ^1H NMR (400 MHz, $CDCl_3$) δ 4.02-3.83 (m, 2H), 3.03 (m, 1H), 2.76 (br dd, 1H, J = 5.0, 4.1 Hz), 2.45 (dd, 1H, J = 5.1, 2.8 Hz), 1.78-1.56 (m, 4H), 1.15 (d, 3H, J = 6.2 Hz), 0.96 (t, 9H, J = 7.8 Hz), 0.88 (s, 9H), 0.61 (q, 6H, J = 8.1 Hz), 0.06 (s, 3H), 0.07-0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.1 (d, C_6), 66.2 (d, C_4), 49.3 (d, C_2), 48.0 (t, C_1), 46.8 (t, C_5), 40.9 (t, C_3), 25.9 (3q, C_{10}), 24.5 (q, C_7), 18.1 (s, C_9), 6.9 (3q, C_{12}), 5.2 (3t, C_{11}), -3.8 (q, C_8), -4.5 (q, C_8); MS (EI, 70 eV): *m/z* (%): 345 (M-Et^+,1), 317 (M-*t*Bu^+, 1), 233 (6), 189 (15), 185 (14), 161 (17), 160 (14), 159 (100), 143 (18), 119 (8), 117 (30), 115 (41), 103 (28), 101 (10), 87 (17), 75 (21), 73 (35), 59 (14). *Minor isomer:* ^1H NMR (400 MHz, $CDCl_3$) δ 4.02-3.83 (m, 2H), 3.03 (m, 1H), 2.78 (dd, 1H, J = 5.0, 4.1 Hz), 2.49 (dd, 1H, J = 5.1, 2.7 Hz), 1.78-1.56 (m, 4H), 1.15 (d, 3H, J = 6.2 Hz), 0.97 (t, 9H, J = 8.0 Hz), 0.87 (s, 9H), 0.63 (q, 6H, J = 7.6 Hz), 0.07-0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.2 (d), 66.3 (d), 49.6 (d), 48.7 (t), 47.5 (t), 41.1 (t), 25.9 (3q), 24.4 (q), 18.1 (s), 6.9 (3q), 5.2 (3t), -3.9 (q), -4.5 (q); MS (EI, 70 eV): *m/z* (%): 345 (M-Et^+,1), 317 (M-*t*Bu^+, 1), 233 (6), 189 (15), 185 (14), 161 (17), 160 (14), 159 (100), 143 (18), 119 (8), 117 (30), 115 (41),

103 (28), 101 (10), 87 (17), 75 (21), 73 (35), 59 (14); HRMS (ESI) calcd $C_{19}H_{42}O_3Si_2$ + Na^+ 397.2565, found 397.2568.

(4*S*,6*R*,8*R*)-8-(*tert*-Butyldimethylsilyloxy)-4-hydroxy-6-triethylsilyloxy-1-trimethylsilylnon-1-yne (23). To a solution of trimethylsilylacetylene (76 µL, 0.534 mmol, 4.0 equiv) in THF (2 mL) was added *n*-BuLi (2.5 M in hexanes, 207 µL, 0.519 mmol, 3.9 equiv) dropwise at -78 °C. The resulting solution was slowly warmed to 0 °C and stirring was carried on at this temperature for 1 h. The reaction mixture was then cooled to -78 °C and $BF_3{\cdot}Et_2O$ (37 µL, 0.292 mmol, 2.2 equiv) was added dropwise. After 20 min at -78 °C, a solution of epoxide **22** (50 mg, 0.133 mmol, 1.0 equiv) in THF (2 mL) was added *via* cannula. After 1 h of stirring at this temperature, the reaction mixture was hydrolyzed by adding brine (3 mL). The aqueous phase was extracted with Et_2O (3 x 5 mL) and the combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (petroleum ether/EtOAc : 98/2 furnished homopropargylic alcohol **23** (49 mg, 77%) as yellow oil, along with its epimer at C4 in a 75/25 ratio in favour of the desired compound **23**: $R_f \approx 0.8$ (petroleum ether/EtOAc : 90/10); IR (neat) 3460, 2955, 2879, 2857, 2175, 1462, 1414, 1377, 1250, 1064, 1003, 908, 836, 731, 647 cm^{-1}; *Major isomer:* ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12-4.05 (m, 1H), 3.91-3.81 (m, 2H), 3.30 (br s, 1H, OH), 2.45 (dd, 1H, J = 16.8, 5.4 Hz), 2.37 (dd, 1H, J = 16.8, 7.0 Hz), 1.86 (m, 1H), 1.78-1.51 (m, 3H), 1.14 (d, 3H, J = 6.1 Hz), 0.97 (t, 9H, J = 8.2 Hz), 0.88 (s, 9H), 0.64 (q, 6H, J = 8.0 Hz), 0.14 (s, 9H), -0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.4 (s), 86.9 (s), 70.7 (d), 69.2 (d), 66.1 (d), 48.5 (t), 42.6 (t), 28.6 (t), 25.8 (3q), 23.8 (q), 18.0 (s), 6.8 (3q), 5.2 (3t), 0.0 (3q), -4.3 (q), -4.6 (q). *Minor isomer :* ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99-3.91 (m, 2H), 3.91-3.81 (m, 1H), 3.71 (br d, 1H, J = 2.1 Hz, OH), 2.46 (dd, 1H, J = 16.7, 5.5 Hz), 2.37 (dd, 1H, J = 16.7, 7.1 Hz), 1.89 (dd, 1H, J = 4.4, 2.7 Hz), 1.81 (dd, 1H, J = 7.5, 6.3 Hz), 1.78-1.51 (m, 2H), 1.15 (d, 3H, J = 6.1 Hz), 0.96 (t, 9H, J = 7.6 Hz), 0.87 (s, 9H), 0.63 (q, 6H, J = 8.0 Hz), 0.14 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.4 (s), 86.8 (s), 70.7 (d), 69.2 (d), 67.2 (d), 46.6 (t), 40.8 (t), 28.8 (t), 25.8 (3q), 23.8 (q), 18.0 (s), 6.8 (3q), 4.8 (3t), 0.0 (3q), -4.1 (q), -4.5 (q).

(4*S*,6*S*,8*R*)-4,8-Bis-(*tert*-butyldimethylsilyloxy)-6-triethylsilyloxynon-1-yne (24). To a solution of alcohol **23** (27 mg, 0.057 mmol, 1.0 equiv) in anhydrous DMF (1 mL) was added imidazole (20 mg, 0.285 mmol, 5.0 equiv) at 0 °C. After 5 min, *tert*-butyldimethylsilyl chloride (18 mg, 0.114 mmol, 2.0 equiv) was added in one portion and the mixture was stirred for 5 h at rt. The reaction mixture was then hydrolyzed by adding water (2 mL) and Et_2O (5 mL) was added. The aqueous phase was extracted with Et_2O (3 x 5 mL) and the combined organic layers were washed with brine (2 x 5 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (petroleum ether/EtOAc : 99/1 furnished the fully protected 1,3,5-triol (26 mg, 78%) as a colorless oil.

To a solution of the previously obtained trimethylsilylalkyne (5.7 mg, 0.01 mmol, 1.0 equiv) in MeOH (1 mL) was added potassium carbonate (2 mg, 0.015 mmol, 1.5 equiv). After 12 h of stirring at rt, the reaction mixture was hydrolyzed by adding a saturated aqueous solution of NH_4Cl (2 mL) and Et_2O (5 mL) was added. The aqueous phase was extracted with Et_2O (3 x 5 mL) and the combined organic layers were washed with brine (5 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (petroleum ether/EtOAc : 99/1) furnished terminal alkyne **24** (3.8 mg, 74%) as a colorless oil: $R_f \approx 0.7$ (petroleum ether/EtOAc : 99/1); $[\alpha]^{20}_D$ +7.8 (*c* 0.94, $CHCl_3$); IR (neat) 3315, 2953, 2929, 2878, 2857, 1472, 1462, 1377, 1361, 1253, 1085, 1004, 833, 773, 724, 637 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.93-3.80 (m, 3H), 2.34 (m, 2H), 1.97 (t, 1H, J = 2.6 Hz), 1.77 (ddd, 1H, J = 12.4, 7.2, 5.0 Hz), 1.69-1.50 (m, 3H), 1.14 (d, 3H, J = 6.1 Hz), 0.96 (t, 9H, J = 8.0 Hz), 0.89 (s, 9H), 0.88 (s, 9H), 0.61 (q, 6H, J = 8.1 Hz), 0.1 (s, 3H), 0.09 (s, 3H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.3 (s), 70.1 (d), 68.3 (d), 67.6 (d), 66.0 (d), 48.6 (t), 45.4 (t), 27.8 (t), 25.9 (6q), 24.2 (q), 18.1 (2s), 6.9 (3t), 5.7 (3q), -4.1, -4.2, -4.4, -4.5 (4q); MS (EI, 70 eV): *m/z* (%): 457 (M-*t*Bu^+, 1), 325 (7), 285 (12), 233 (33), 189 (26), 183 (21), 161 (17), 160 (91), 159 (100), 147 (8), 133 (18), 119 (15), 115 (17), 103 (11), 75 (14), 73 (45); HRMS (ESI) calcd for $C_{27}H_{58}O_3Si_3 + Na^+$ 537.3586, found 537.3581.

***S*-*tert*-Butyl (3*S*,5*R*)-5-(*tert*-butyldimethylsilyloxy)-3-hydroxyhexanethioate (26).** To a solution of the previously obtained aldehyde derived from ester **19** (1.06 g, 5.22 mmol,

1.0 equiv) in CH_2Cl_2 (50 mL) at -78 °C was added $MeAlCl_2$ (1 M in THF, 13.0 mL, 13.0 mmol, 2.5 equiv) dropwise. After 15 min of stirring at this temperature, the reaction mixture was cooled to -100 °C ($EtOH/N_{2liq}$ bath) and a solution of silyl ketene actetal of *tert*-butylthioacetate **25** (1.28 g, 6.26 mmol, 1.2 equiv) in CH_2Cl_2 (5 mL) was added dropwise. After 30 min of stirring at -100 °C, the reaction mixture was hydrolyzed by adding a saturated aqueous solution of NH_4Cl (15 mL). The resulting mixture was then poured into water (20 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Analysis of the crude ^1H NMR showed the presence of two diastereoisomers *anti* and *syn* in a 80:20 *anti*/*syn* ratio. Purification of the residue by flash chromatography on silica gel (petroleum ether/EtOAc : 98/2 to 95/5) furnished β-hydroxythioester **26** (1.44 g, 82%) as a 80:20 mixture of diastereoisomers: $R_f \approx 0.3$ (petroleum ether/EtOAc : 90/10); IR (neat) 3481, 2957, 2928, 2857, 1680, 1472, 1461, 1364, 1254, 1144, 1002, 834, 774, 722, 658 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{34}O_3SSi_2 + Na^+$ 357.1890, found 357.1893. *Major anti isomer:* ^1H NMR (400 MHz, $CDCl_3$) δ 4.33 (ddd, 1H, J = 7.5, 4.7, 2.5 Hz), 4.16 (m, 1H), 3.52 (br s, 1H, OH), 2.64 (dd, 1H, J = 15.2, 7.8 Hz), 2.55 (dd, 1H, J = 15.2, 4.7 Hz), 1.66-1.56 (m, 1H), 1.50 (ddd, 1H, J = 14.2, 6.5, 2.6 Hz), 1.45 (s, 9H), 1.18 (d, 3H, J = 5.5 Hz), 0.87 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5 (s), 66.7 (d), 65.6 (d), 51.8 (t), 48.3 (s), 44.2 (t), 29.8 (3q), 25.8 (3q), 23.2 (q), 18.0 (s), -4.5 (q), -5.0 (q); MS (EI, 70 eV): *m/z* (%): 277 (M-*t*Bu^+, 1), 259 (1), 245 (5), 203 (6), 187 (14), 159 (16), 146 (12), 145 (100), 143 (11), 115 (15), 101 (48), 75 (66), 73 (21), 59 (12), 57 (25), 56 (10). *Minor syn isomer:* ^1H NMR (400 MHz, $CDCl_3$) δ 4.19-4.11 (m, 1H), 4.06 (m, 1H), 3.52 (br s, OH), 2.64 (dd, 1H, J = 15.2, 7.8 Hz), 2.57 (dd, 1H, J = 15.2, 5.4 Hz), 1.66-1.56 (m, 1H), 1.50-1.43 (m, 1H), 1.45 (s, 9H), 1.16 (d, 3H, J = 6.0 Hz), 0.87 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4 (s), 68.6 (d), 67.8 (d), 51.4 (t), 48.3 (s), 45.3 (t), 29.8 (3q), 25.8 (3q), 24.2 (q), 17.9 (s), -4.0 (q), -4.8 (q); MS (EI, 70 eV): *m/z* (%): 277 (M-*t*Bu^+, 1), 259 (2), 203 (6), 187 (11), 159 (16), 146 (12), 145 (100), 143 (15), 115 (15), 101 (52), 75 (70), 73 (22), 59 (12), 57 (27), 56 (11).

***S*-*tert*-Butyl (3*S*,5*R*)-5-(*tert*-butyldimethylsilyloxy)-3-triethylsilyloxyhexanethioate (27).** To a solution of alcohol **26** (1.34 g, 4.0 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added 4-dimethylaminopyridine (50 mg, 0,40 mmol, 0,1 equiv) at rt. The solution was cooled to 0 °C and triethylamine (1.12 mL, 8.0 mmol, 2.0 equiv) was added dropwise. After 5 min of stirring at this temperature, triethylsilyl chloride (905 µL, 8.53 mmol, 1.5 equiv) was added dropwise and the reaction mixture was stirred for 2 h at rt. The resulting cloudy mixture was then hydrolyzed by adding water (10 mL) and was neutralized by the use of an aqueous solution of HCl 1 M (5 mL). The aqueous phase was extracted with Et_2O (3 x 50 mL) and the combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (petroleum ether/EtOAc : 99/1) furnished the protected 1,3-diol **27** (1.78 g, 93%) as a colorless oil: $R_f \approx 0.5$ (petroleum ether/EtOAc : 98/2); IR (neat) 2954, 2928, 2877, 2857, 1683, 1460, 1364, 1253, 1108, 1081, 1002, 834, 773, 739, 725, 664 cm^{-1}. *Major isomer*: ^1H NMR (400 MHz, $CDCl_3$) δ 4.20 ($quint_{app}$, 1H, J = 5.3 Hz), 3.86 ($sext_{app}$, 1H, J = 6.1 Hz), 2.67-2.55 (m_{systAB}, 2H), 1.68 (ddd, 1H, J = 13.8, 6.8, 6.4 Hz), 1.55 (ddd, 1H, J = 11.6, 6.0, 5.7 Hz), 1.43 (s, 9H), 1.15 (d, 3H, J = 6.1 Hz), 0.95 (t, 9H, J = 7.8 Hz), 0.87 (s, 9H, H_9), 0.60 (q, 6H, J = 7.7 Hz), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0 (s), 67.4 (d), 66.2 (d), 53.2 (t), 48.2 (t), 48.0 (s), 29.8 (3q), 25.9 (3q), 24.4 (q), 18.1 (s), 6.9 (3q), 5.1 (3t), -3.9 (s), -4.5 (s). *Minor isomer:* ^1H NMR (400 MHz, $CDCl_3$) δ 4.28-4.20 (m, 1H), 3.86 ($sext_{app}$, 1H, J = 6.1 Hz), 2.65-2.55 (m_{systAB}, 2H), 1.69 (ddd, 1H, J = 12.8, 7.0, 5.8 Hz), 1.54 (ddd, 1H, J = 13.7, 6.8, 5.5 Hz), 1.43 (s, 9H), 1.14 (d, 3H, J = 6.0 Hz), 0.95 (t, 9H, J = 7.8 Hz), 0.88 (s, 9H), 0.59 (q, 6H, J = 8.0 Hz), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1 (s), 66.8 (d), 65.6 (d), 52.3 (t), 48.0 (s), 47.6 (t), 29.8 (3q), 25.9 (3q), 24.0 (q), 18.0 (s), 6.9 (3q), 5.1 (3t), -4.3 (s), -4.7 (s).

(3*S*,5*R*)-5-(*tert*-Butyldimethylsilyloxy)-3-triethylsilyloxyhexanal (28).

- By reduction of thioester **27**: To a solution of thioester **27** (1.59 g, 2.45 mmol, 1.0 equiv) in toluene (25 mL) at -78 °C was added DIBAL-H (1 M in toluene, 2.94 mmol, 1.2 equiv) dropwise. After 30 min of stirring at this temperature, the reaction mixture was poured into an aqueous saturated solution of Rochelle's salt (25 mL) and

was diluted with Et_2O (50 mL). The resulting biphasic mixture was stirred for 1 h and the layers were separated. The aqueous phase was extracted with Et_2O (3 x 30 mL) and the combined organic layers were washed with brine (3 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (petroleum ether/EtOAc : 99/1) allowed the separation of the two diastereoisomers *anti*/*syn* and permitted to isolate the *anti* 1,3-dihydroxyaldehyde **28** (618 mg, 70%), along with the corresponding *syn* diastereoisomer (262 mg, 29%): $R_f \approx 0.5$ (petroleum ether/EtOAc : 98/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (br t, 1H, J = 2.5 Hz), 4.28 (br quint$_{app}$, 1H, J = 6.2 Hz), 3.90 (sext$_{app}$, 1H, J = 6.2 Hz), 2.60 (dd$_{systAB}$, 1H, J = 15.7, 5.0, 2.2 Hz), 2.52 (dd$_{systAB}$, 1H, J = 15.6, 6.3, 2.9 Hz, H_2), 1.68 (m, 2H), 1.16 (d, 3H, J = 6.1 Hz), 0.95 (t, 9H, J = 7.9 Hz), 0.88 (s, 9H), 0.61 (q, 6H, J = 8.0 Hz), 0.06 (br s, 6H).

- By oxidative cleavage of alkene **20:** To a stirred solution of alkene **20** (1.4 g, 3.90 mmol, 1.0 equiv) in a 1,4-dioxane/water mixture (3/1, 40 mL) at rt, were successively added 2,6-lutidine (910 µL, 7.80 mmol, 2.0 equiv), sodium periodate (3.34 g, 15.6 mmol, 4.0 equiv) and OsO_4 (2.5 wt% in *tert*-BuOH, 975 µL, 0.08 mmol, 0.02 equiv). After 3 h of stirring at rt, the resulting white slurry was quenched by addition of a saturated aqueous solution of $Na_2S_2O_3$ (20 mL) and the resulting mixture was allowed to stir for 1 h. The aqueous layer was extracted with CH_2Cl_2 (3 x 40 mL) and the combined organic layers were washed with brine (40 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting crude aldehyde **28** was used in the next step without further purification.

(4*S*,6*R*,8*R*)-8-*tert*-Butyldimethylsilyloxy-6-triethylsilyloxynon-1-en-4-ol. To a stirred solution of cyclopentadienyl[(4*R*,*trans*)-2,2-dimethyl-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethanolato-*O*,*O*']titanium chloride (3.1 g, 5.70 mmol, 1.3 equiv) in anhydrous Et_2O (60 mL) at 0 °C, was added dropwise allylmagnesium chloride (2 M in THF, 2.15 mL, 4.29 mmol, 1.1 equiv). After 2 h at 0 °C, the reaction mixture was cooled to –78 °C and a solution of crude aldehyde **28** (3.90 mmol, 1.0 equiv) in Et_2O (20 mL) was added dropwise *via* cannula. After 5 h at -78 °C, the reaction was quenched by addition of water (20 mL). The reaction mixture was stirred for 48 h at rt and then filtered

over Celite. The layers were separated and the aqueous phase was extracted with ether (3 x 80 mL). The combined organic extracts were washed with brine (80 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was then diluted with pentane (20 mL) and filtered to remove (4*R*,*trans*)-2,2-dimethyl-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethanol. After removal of pentane under reduced pressure, purification of the residue by flash chromatography on silica gel (Toluene/EtOAc: 99/1) provided the desired enantiopure title compound (1.19 g, 75%, 2 steps) as a colorless oil: $R_f \approx 0.2$ (petroleum ether/EtOAc : 98/2); $[\alpha]^{20}_D$ – 21.5 (*c* 1.02, $CHCl_3$); IR (neat) 3470, 2954, 2930, 2878, 2857, 1642, 1462, 1414, 1377, 1253, 1064, 1003, 834, 773, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.77 (ddt, 1H, J = 17.0, J = 10.2, 7.1 Hz), 5.07-5.01 (m, 2H), 4.03-3.92 (m, 2H), 3.74 ($sext_{app}$, 1H, J = 6.5 Hz), 3.45 (d, 1H, J = 1.8 Hz, OH), 2.24-2.08 (m, 2H), 1.79 (ddd, 1H, J = 13.7, J = 7.7, 6.5 Hz), 1.65-1.55 (m, 2H), 1.50 (ddd, 1H, J = 14.4, 4.5, 2.4 Hz), 1.08 (d, 3H, J = 6.1 Hz), 0.91 (t, 9H, J = 8.1 Hz), 0.82 (s, 9H), 0.56 (q, 6H, J = 8.1 Hz), 0.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0 (d), 117.3 (t), 69.5 (d), 67.9 (d), 66.4 (d), 46.7 (t), 42.4 (t), 41.5 (t), 25.9 (3q), 24.1 (q), 18.1 (s), 6.9 (3q), 4.9 (3t), -4.1 (q), -4.5 (q); MS (EI, 70 eV): *m/z* (%): 373 (M-Et^+, 4), 345 (M-*t*Bu^+, 1), 241 (7), 233 (21), 213 (35), 199 (38), 189 (31), 173 (33), 159 (100), 145 (25), 119 (51), 115 (39), 103 (43), 75 (55), 155, 73 (48); HRMS (ESI) calcd for $C_{21}H_{46}O_3Si_2$ + Na^+ 425.2883, found 425.2887.

(4*S*,6*S*,8*R*)-4,8-Bis-(*tert*-butyldimethylsilyloxy)-6-triethylsilyloxynon-1-en-4-ol (29). To a stirred solution of alcohol (4*S*,6*R*,8*R*)-8-*tert*-butyldimethylsilyloxy-6-triethylsilyloxynon-1-en-4-ol (210 mg, 0.519 mmol, 1.0 equiv) in anhydrous DMF (5 mL) was added imidazole (177 mg, 2.59 mmol, 5.0 equiv) at 0 °C. After stirring for 5 min, TBSCl (156 mg, 1.04 mmol, 2.0 equiv) was added in one portion and the reaction mixture was allowed to warm to rt and stirred for 4 h. The reaction was stopped by addition of water (5 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with brine (2 x 15 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of the residue by flash chromatography on silica gel (petroleum ether/AcOEt: 99/1) provided the protected triol **29** (234 mg, 87%) as a colorless oil: $R_f \approx 0.9$ (petroleum ether/EtOAc : 98/2); $[\alpha]^{20}_D$

– 0.2 (*c* 1.19 $CHCl_3$); IR (neat) 2954, 2929, 2878, 2857, 1641, 1462, 1377, 1253, 1071, 1004, 833, 772, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.76 (m, 1H), 5.02-4.95 (m, 2H), 3.83 (sext, 1H, J = 6.0 Hz), 3.79-3.71 (m, 2H), 2.23-2.08 (m, 2H), 1.59-1.52 (m, 2H), 1.49-1.39 (m, 2H), 1.08 (d, 3H, J = 6.1 Hz), 0.87 (t, 9H, J = 8.0 Hz), 0.82-0.80 (m, 18H), 0.45 (q, 6H, J = 8.0 Hz), 0.00, -0.04 (2s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0 (d), 116.9 (t), 69.4 (s), 67.7 (d), 66.0 (d), 48.5 (t), 45.7 (t), 42.1 (t), 25.8 (6t), 24.4 (q), 18.2 (2s), 6.8 (3q), 6.4 (3t), -2.66 – -4.31 (4q); MS (EI, 70 eV): *m/z* (%): 459 (M-*t*Bu^+, 1), 343 (5), 327 (4), 259 (27), 233 (27), 189 (22), 185 (55), 161 (15), 160 (14), 159 (100), 115 (17), 103 (11), 75 (11), 73 (44); HRMS (ESI) calcd for $C_{27}H_{60}O_3Si_3 + Na^+$ 539.3748, found 539.3737.

(4*S*,6*S*,8*R*)-1,1-Dibromo-4,8-bis-(*tert*-butyldimethylsilyloxy)-6-triethylsilyloxynon-1-ene. To a solution of alkene **29** (822 mg, 1.59 mmol, 1.0 equiv) in a dioxane/H_2O mixture (3/1, 16 mL) were successively added 2,6-lutidine (370 µL, 3.18 mmol, 2.0 equiv), osmium tetroxide (2.5 wt% in 2-methyl-2-propanol, 400 µL, 0.032 mmol, 0.02 equiv) and sodium periodate (1.36 g, 6.36 mmol, 4.0 equiv). After 4 h of stirring at rt, the reaction mixture was hydrolyzed by adding a saturated aqueous solution of $Na_2S_2O_3$ (15 mL) and stirred for 1 h. The mixture was then diluted with CH_2Cl_2 (50 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude aldehyde was not purified but directly used in the next step.

To a solution of triphenylphosphine (1.25 g, 4.77 mmol, 3.0 equiv), zinc powder (312 mg, 4.77 mmol, 3.0 equiv) and pyridine (384 µL, 4.77 mmol, 3.0 equiv) in CH_2Cl_2 (15 mL) was added carbon tetrabromide (1.58 g, 4.77 mmol, 3.0 equiv) portionwise at rt. After 30 min of stirring, a solution of the previously obtained crude aldehyde (1.59 mmol, 1.0 equiv) diluted with CH_2Cl_2 (5 mL) was slowly added dropwise *via* syringe. After 15 min of stirring ar rt, the reaction mixture was hydrolyzed by adding water (10 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was then diluted in a CH_2Cl_2/pentane mixture (1/5, 12

mL) and the precipitate of triphenylphosphine oxide was eliminated upon filtration over Celite®. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc : 99/1) to give the title *gem*-dibromo olefin (905 mg, 84% over two steps) as a colorless oil: $R_f \approx 0.8$ (petroleum ether/EtOAc : 99/1); $[\alpha]^{20}_D$ +1.8 (*c* 0.56, $CHCl_3$); IR (neat) 2953, 2928, 2878, 2856, 1624, 1471, 1462, 1413, 1376, 1361, 1253, 1114, 1066, 1004, 833, 772, 724, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.47 (dd, 1H, *J* = 7.4, 6.7 Hz), 3.93-3.83 (m, 2H), 3.80 (quint, 1H, *J* = 6.4 Hz), 2.28-2.23 (m, 2H), 1.66-1.53 (m, 3H), 1.50 (ddd, 1H, *J* = 12.5, 7.0, 5.4 Hz), 1.15 (d, 3H, *J* = 6.1 Hz), 0.96 (t, 9H, *J* = 7.8 Hz), 0.89 (s, 9H), 0.88 (s, 9H), 0.61 (q, 6H, *J* = 7.8 Hz), 0.07 (br s, 6H), 0.06 (br s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4 (d), 89.9 (s), 68.1 (2d), 67.5 (d), 48.5 (t, C_7), 46.1 (t), 41.0 (t), 25.9 (6t), 24.4 (q), 18.1, 18.0 (2s), 6.9 (3q), 5.7 (3t), -4.0 (2q), -4.5 (2q); MS (EI, 70 eV): *m/z* (%): 527 (1), 419 (7), 417 (13), 345 (20), 343 (42), 341 (19), 234 (9), 233 (42), 189 (35), 161 (19), 160 (14), 159 (100), 115 (21), 103 (12), 75 (12), 73 (47).

To a solution of (4*S*,6*S*,8*R*)-1,1-dibromo-4,8-bis-(*tert*-butyldimethylsilyloxy)-6-triethylsilyloxynon-1-ene (955 mg, 1.42 mmol, 1.0 equiv) in THF (20 mL) at -78 °C was added *n*-butyllithium (2.5 M in hexanes, 1.25 mL, 3.12 mmol, 2.2 equiv) dropwise. After 30 min of stirring at -78 °C, the reaction mixture was warmed to -40 °C and stirring was carried on for 30 min. The reaction mixture was hydrolyzed by adding a saturated aqueous solution of NH_4Cl (10 mL). The aqueous phase was extracted with Et_2O (3 x 20 mL) and the combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (petroleum ether/EtOAc : 99/1) furnished terminal alkyne **24** (639 mg, 87%) as a colorless oil.

(*E*)-(*S*)-5-(4-Methoxybenzyloxy)-8-iodo-7-methylocta-1,7-dien-3-one (32). To a stirred solution of the previously obtained crude aldehyde **18** (8.06 mmol, 1.0 equiv) in anhydrous THF (90 mL) at -78 °C was added vinylmagnesium chloride (1.6 M in THF, 15 mL, 24.2 mmol, 3.0 equiv) dropwise. After 2 h stirring, the reaction mixture was quenched by adding a saturated aqueous solution of NH_4Cl (40 mL). The layers were

separated and the aqueous phase was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* affording the crude allylic alcohol as a 1:1 mixture of diastereomers which was used in the next step without further purification.

To a stirred solution of the obtained crude allylic alcohol in CH_2Cl_2 (90 mL) were successively added 4Å molecular sieves (5 g) and pyridinium chlorochromate (2.6 g, 12.1 mmol, 1.5 equiv) at rt. The resulting black mixture was stirred for 1 h and a large amount of Et_2O (500 mL) was added. After stirring for 1 h, the resulting mixture was filtered through Celite® and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (petroleum ether/EtOAc: 95/5 to 80/20) provided the desired vinyl ketone **32** (1.52 g, 56%, 2 steps) as a colorless oil: R_f = 0.5 (petroleum ether/EtOAc : 70/30); $[\alpha]^{20}_D$ + 1.5 (*c* 1.0, $CHCl_3$); IR (neat) 2906, 2835, 1678, 1611, 1511, 1245, 1172, 1066, 1032, 819 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, 2H, *J* = 8.7 Hz), 6.88 (d, 2H, *J* = 8.7 Hz), 6.38 (dd, 1H, *J* = 17.6, 10.5 Hz), 6.23 (dd, 1H, *J* = 17.6, 1.0 Hz), 6.01 (br s, 1H), 5.88 (dd, 1H, *J* = 10.5, 1.0 Hz), 4.48 (d, 1H, J_{systAB} = 10.8 Hz), 4.43 (d, 1H, J_{systAB} = 10.8 Hz), 4.14 (m, 1H), 3.81 (s, 3H), 2.95 (dd, 1H, *J* = 16.4, 6.9 Hz), 2.63 (dd, 1H, *J* = 16.4, 5.4 Hz), 2.53 (ddd, 1H, *J* = 13.7, 6.9, 1.0 Hz), 2.40 (ddd, 1H, *J* = 13.7 Hz, 5.5, 1.0 Hz), 1.85 (d, 3H, *J* = 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9 (s), 159.3 (s), 144.6 (s), 136.9 (d), 130.2 (s), 129.6 (2d), 128.8 (t), 113.8 (2d), 78.0 (d), 73.2 (d), 71.8 (t), 55.3 (q), 44.7 (t), 44.2 (t), 24.4 (q); HRMS (ESI) calcd for $C_{17}H_{21}O_3I + Na^+$ 423.0433, found 423.0428.

Methyl 2-hydroxy-6-[(1*E*,3*E*,5*E*,7*E*,13*E*)-(10*S*,12*S*,16*S*,18*S*,20*R*)-10,12,16,20-tetrakis-(*tert*-butyldimethylsilyloxy)-8-methyl-18-triethylsilyloxyhenicosa-1,3,5,7,13-pentaenyl]benzoate (37). To a solution of acetonide **36** (37 mg, 0.0328 mmol, 1.0 equiv) in methanol (3 mL) was added sodium methanolate (9 mg, 0.164 mmol, 5.0 equiv). After 1 hour of stirring at 40 °C, the reaction mixture was hydrolyzed by adding an aqueous solution of 1M HCl (3 mL). The aqueous phase was extracted with EtOAc (5 mL) and the combined organic layers were washed with brine (5 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash

chromatography on silica gel (petroleum ether/EtOAc : 99/1) furnished phenol **37** (31 mg, 86%) as a yellow wax. *Rf* ≈ 0.65 (petroleum ether/EtOAc : 90/10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.09 (s, 1H, OH), 7.35 (t, 1H, *J* = 8.0 Hz), 7.14 (d, 1H, *J* = 15.2 Hz), 7.03 (d, 1H, *J* = 7.6 Hz), 6.88 (dd, 1H, *J* = 8.3, 1.0 Hz), 6.63 (dd, 1H, *J* = 15.2, 10.0 Hz), 6.52-6.39 (m, 3H), 6.21 (dd, 1H, *J* = 14.8, 10.4 Hz), 5.93 (d, 1H, *J* = 10.9 Hz), 5.56 (dt, 1H, *J* = 15.5, 6.7 Hz), 5.42 (dd, 1H, *J* = 15.4, 6.8 Hz), 4.16 (br q, 1H, *J* = 6.2 Hz), 3.97 (s, 3H), 3.92-3.80 (m, 3H), 3.75 (m, 1H), 2.29 (br dd, 1H, *J* = 13.4, 4.8 Hz), 2.24-2.14 (m, 3H), 1.84 (m, 1H), 1.80 (s, 3H), 1.75-1.45 (m, 5H), 1.13 (d, 3H, *J* = 6.1 Hz) 0.95 (t, 9H, *J* = 7.8 Hz), 0.90-0.86 (m, 36H), 0.60 (q, 6H, *J* = 8.0 Hz), 0.07 (s, 3H), 0.06 (s, 9H), 0.03 (2s, 2x3H), 0.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7 (s), 162.3 (s), 140.9 (s), 137.7 (s), 135.9 (d), 135.0 (d), 134.2 (d), 132.1 (d), 132.0 (d), 131.9 (d), 130.8 (d), 130.5 (d), 128.3 (d), 126.4 (d), 119.1 (d), 116.6 (d), 110.7 (s), 71.0 (d), 69.4 (d), 68.2 (d), 67.7 (d), 66.0 (d), 52.4 (q), 48.6 (t), 48.1 (t), 46.6 (t), 45.6 (t), 40.6 (t), 25.9 (12q), 24.1 (q), 18.1 (4s), 17.8 (q), 7.1 (3q), 5.7 (3t), -3.8, -3.9, -4.0, -4.3, -4.4, -4.5, -4.7 (8q).

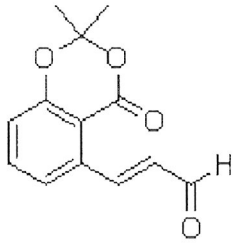
Methyl 2-[(1*E*,3*E*,5*E*,7*E*,13*E*)-(10*S*,12*S*,16*S*,18*S*,20*R*)-10,12,16,20-tetrakis-(*tert*-butyldimethylsilyloxy)-8-methyl-18-triethylsilyloxyhenicosa-1,3,5,7,13-pentaenyl]-6-triisopropylsilyloxybenzoate (38). To a solution of phenol **37** (31 mg, 0.028 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) at 0 °C were successively added 2,6-lutidine (195 µL, 1.68 mmol, 60 equiv) and triisopropylsilyl trifluoromethanesulfonate (200 µL, 0.84 mmol, 30 equiv) dropwise. After 1 h of stirring at rt, the reaction mixture was hydrolyzed by adding a saturated aqueous solution of NH_4Cl (2 mL). The aqueous layer was extracted with Et_2O (3 x 5 mL) and the combined organic layers were washed with brine (5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of the residue by flash chromatography on silica gel (petroleum ether/EtOAc : 99/1) furnished phenyl silyl ether **38** (37 mg, 100%) as a pale yellow oil. *Rf* ≈ 0.6 (petroleum ether/EtOAc : 95/5); $[\alpha]^{20}_{D}$ – 1.3 (*c* = 0.61, $CHCl_3$); IR (neat) 2928, 2856, 1731, 1577, 1464, 1378, 1361, 1290, 1252, 1066, 1002, 834, 808, 774, 737 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.14 (m, 2H), 6.80 (dd, 1H, *J* = 15.4, 10.2 Hz), 6.70 (m, 1H), 6.52-6.28 (m, 4H), 6.19 (dd, 1H, *J* = 14.6, 10.4 Hz), 5.92 (d, 1H, *J* = 11.1 Hz), 5.56 (dt, 1H, *J* = 15.3, 6.7 Hz), 5.42 (br dd, 1H, *J* = 15.4, 6.7 Hz), 4.16 (br q, 1H, *J* = 6.0 Hz), 3.92-3.80 (m, 4H), 3.89 (s, 3H),

2.28 (br dd, 1H, J = 13.5, 5.3 Hz), 2.24-2.15 (m, 7H), 1.79 (s, 3H), 1.76-1.45 (m, 5H), 1.09 (d, 3H, J = 7.3 Hz), 1.07-0.93 (m, 27H), 0.91-0.85 (m, 36H), 0.60 (q, 6H, J = 8.0 Hz), 0.07 (s, 3H), 0.06 (s, 12H), 0.03 (2s, 2 x 3H), 0.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7 (s), 151.9 (s), 136.6 (s), 135.3 (s), 134.9 (d), 134.2 (d), 131.0 (d), 130.8 (d), 129.8 (d), 129.4 (d), 128.9 (d), 127.3 (d), 126.7 (d), 125.4 (d), 124.5 (d), 124.0 (d), 116.2 (s), 69.9 (d), 68.4 (d), 67.2 (d), 66.7 (d), 65.0 (d), 51.0 (q), 47.6 (t), 47.1 (t), 45.6 (t), 44.5 (t), 39.6 (t), 29.3 (q), 24.9 (12q), 23.1 (q), 17.2-16.5 (6q+4s), 12.8-11.8 (3d), 6.1 (3q), 4.7 (3t), -4.8, -4.9, -5.1, -5.3, -5.39, -5.42, -5.5, -5.7 (8q).

II- Spectra

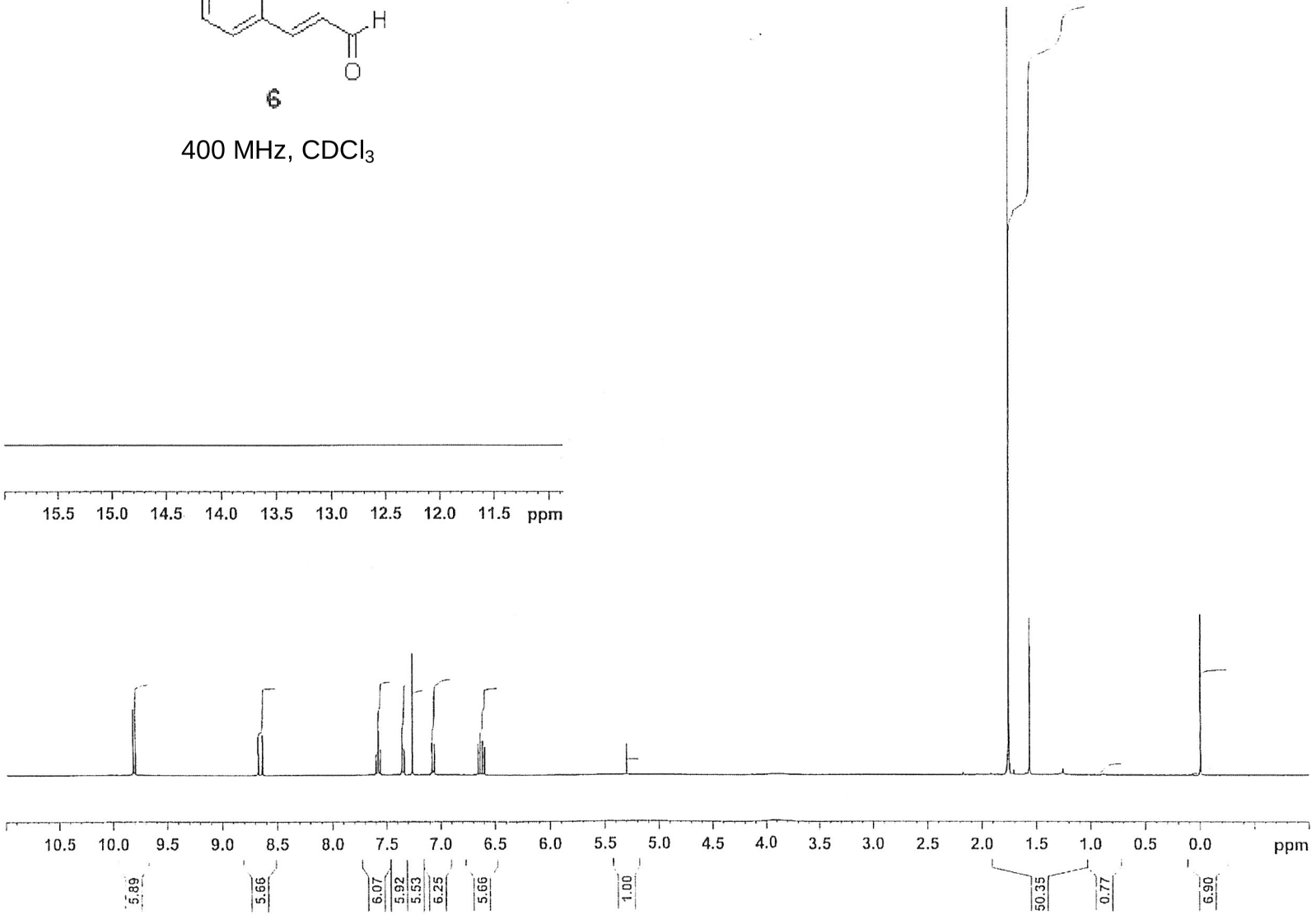
^{1}H and ^{13}C spectra for compounds **6**, **8**, **11**, **12**, **14**, **17**, **20**, **22**-**24**, **26**-**29** and **31**-**38**

DA 474-2



6

400 MHz, $CDCl_3$



BRUKER

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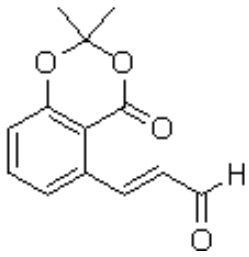
DA-474



6

100 MHz, $CDCl_3$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NUC2                 1H
PCPD2            100.00 usec
PL2               -4.00 dB
PL12              14.00 dB
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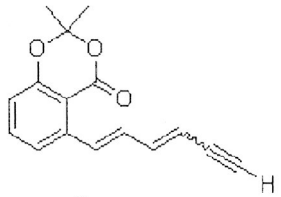
DA-515



8

400 MHz, $CDCl_3$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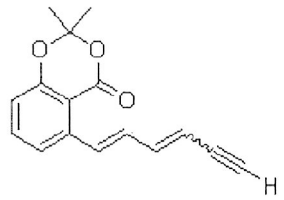

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100 MHz, $CDCl_3$


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TD0                           1

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PL1                       -4.00 dB
SFO1                100.6228292 MHz

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PL12                      14.00 dB
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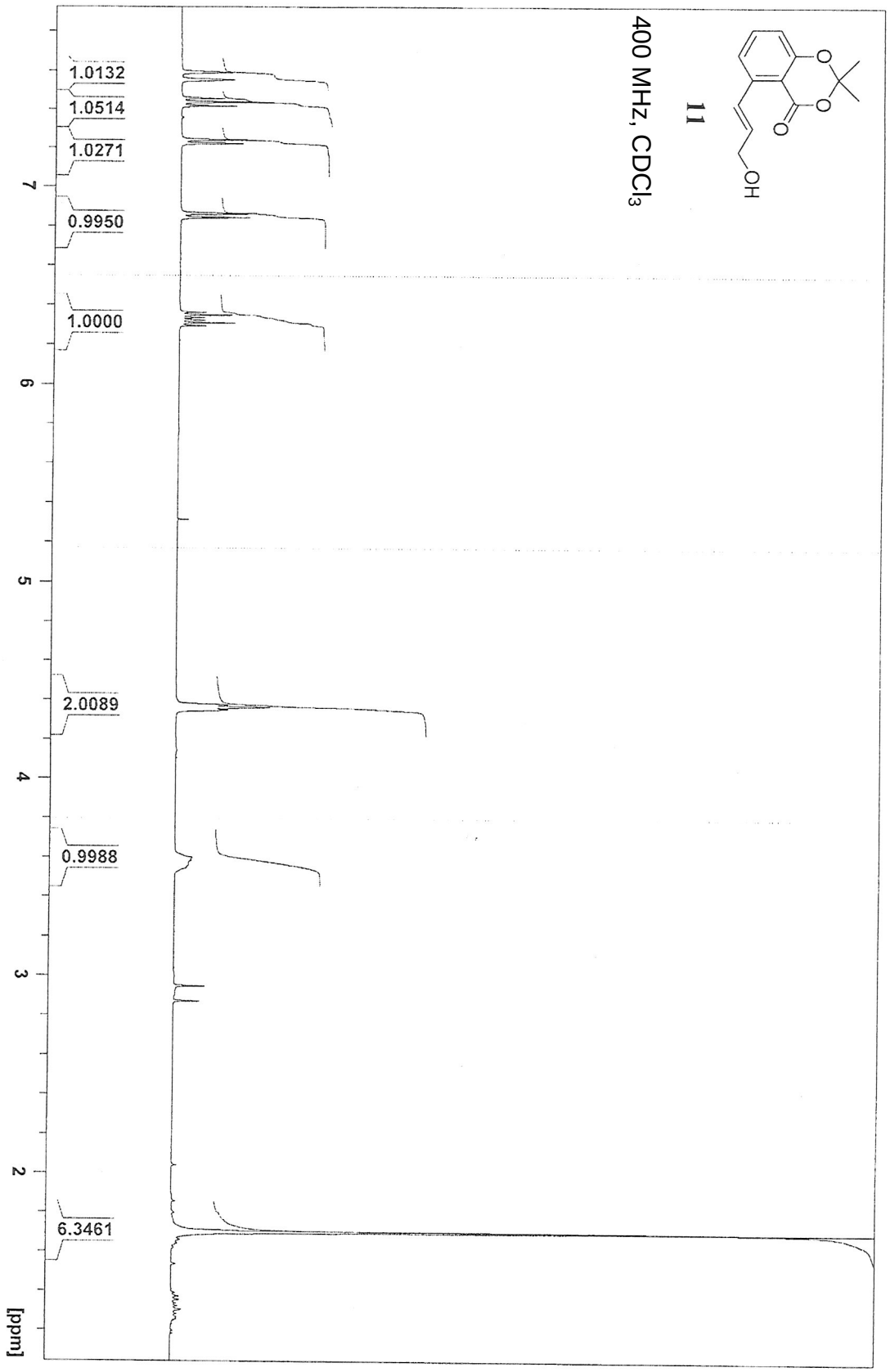
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O
O
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7
6
5
4
3
2
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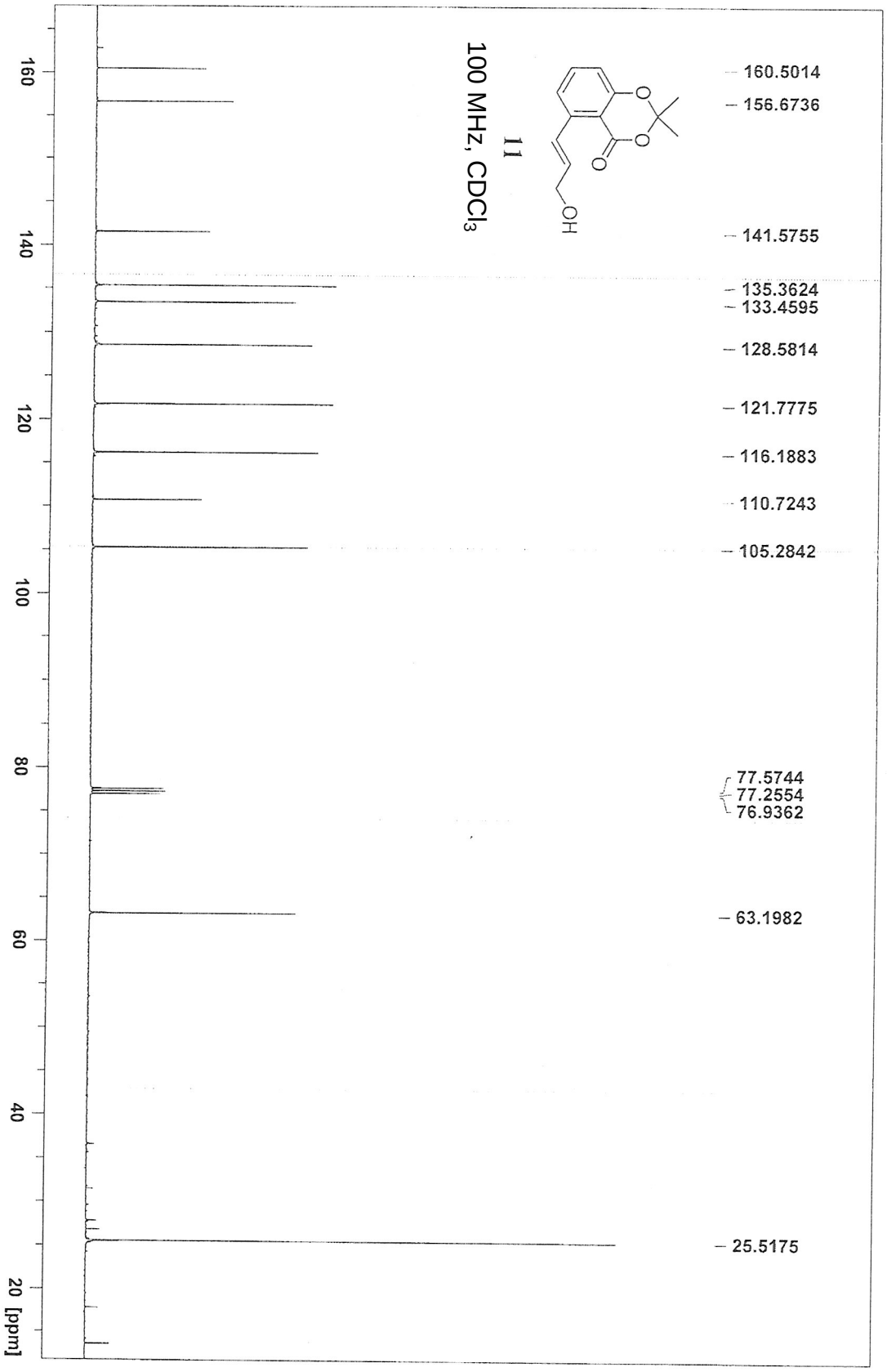
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60
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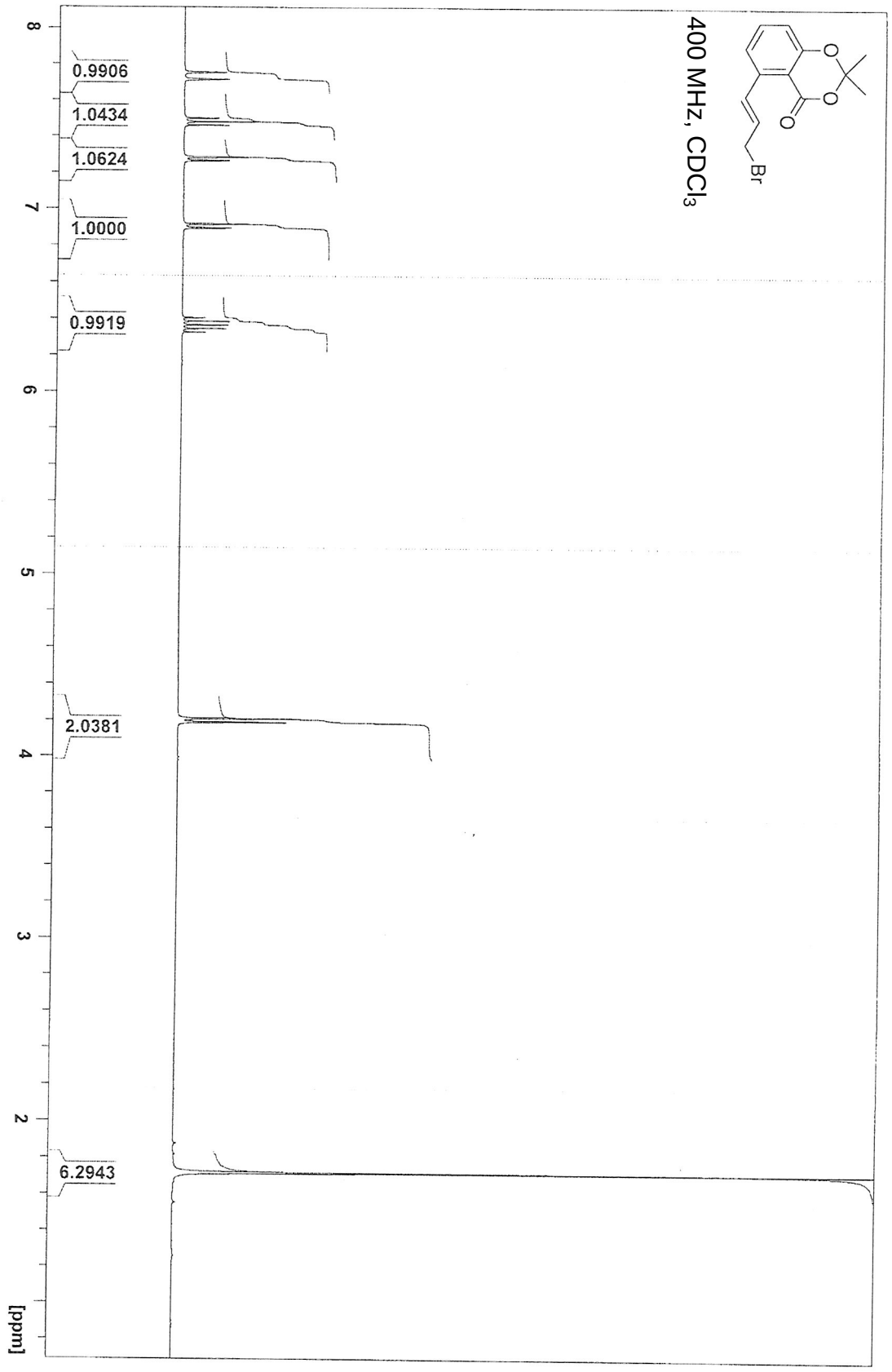
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O
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3
2
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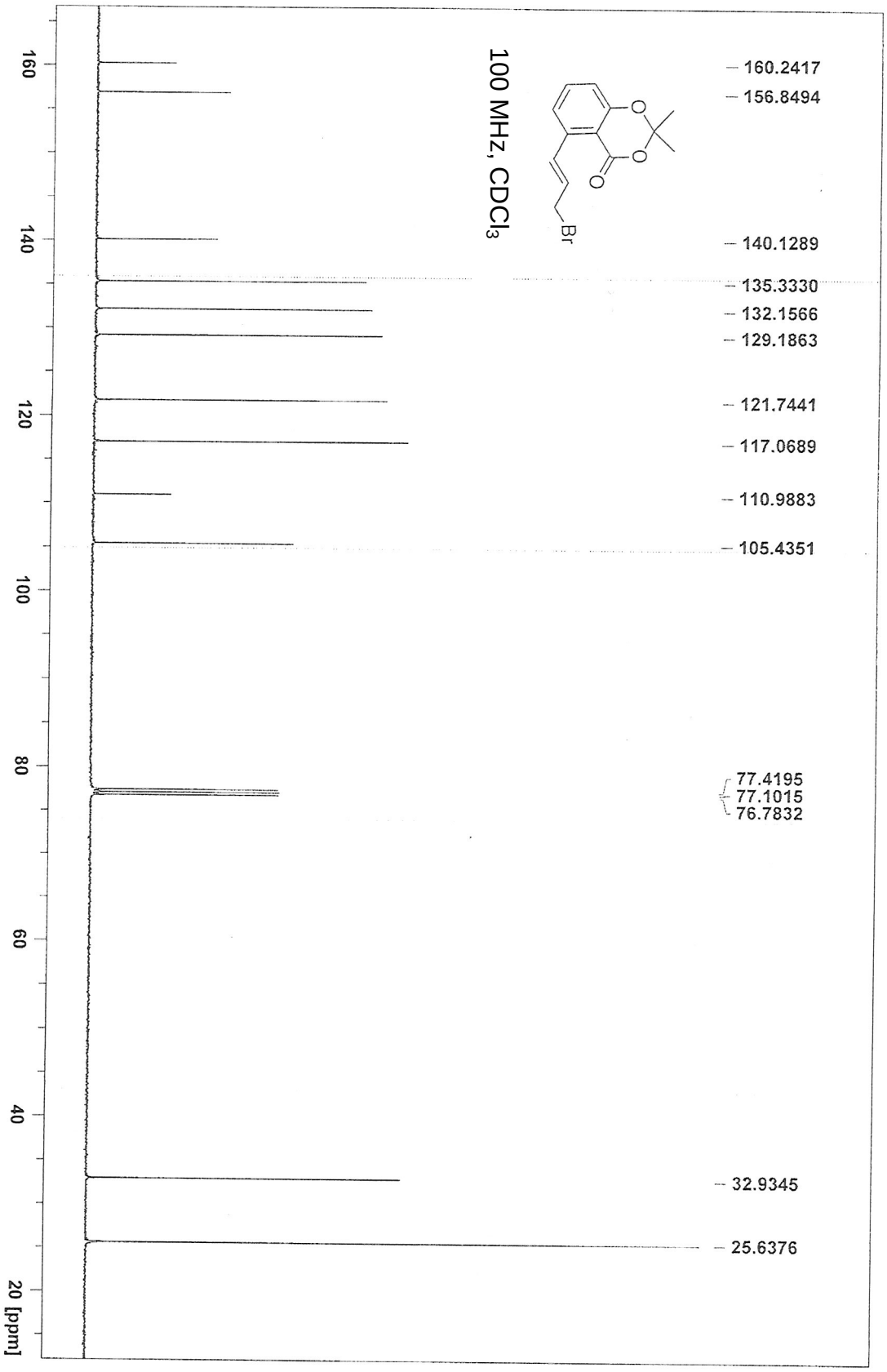
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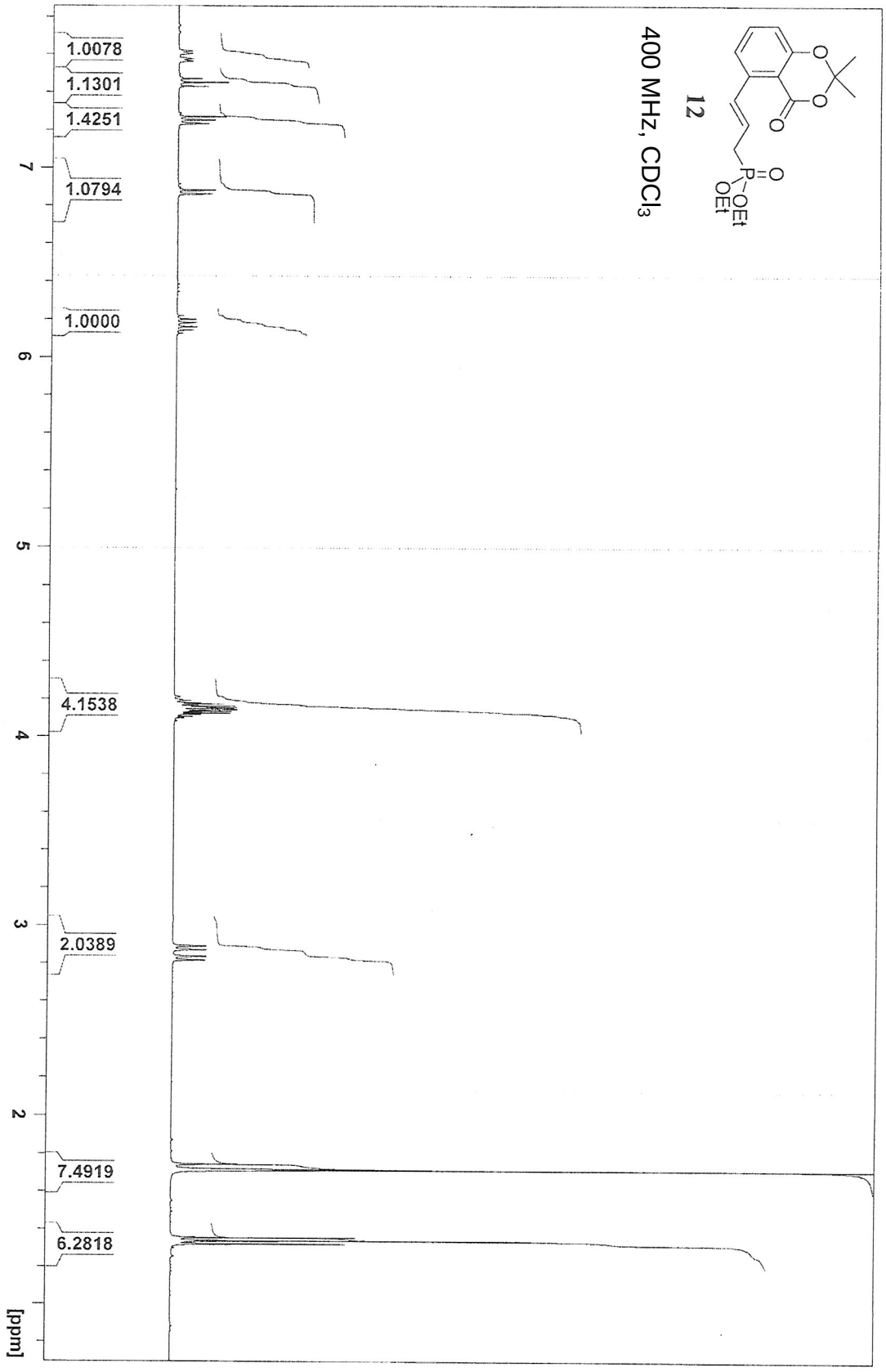
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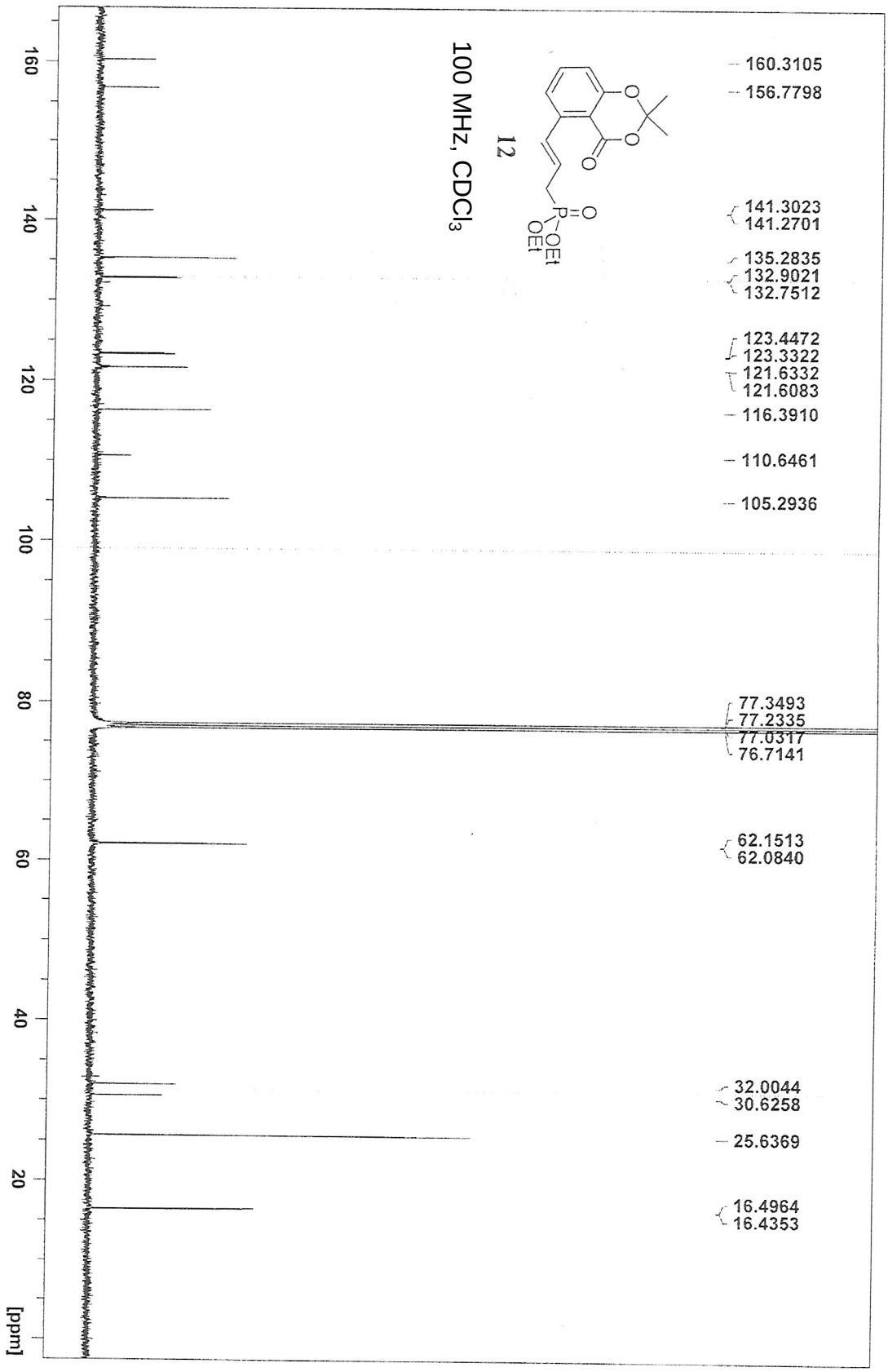
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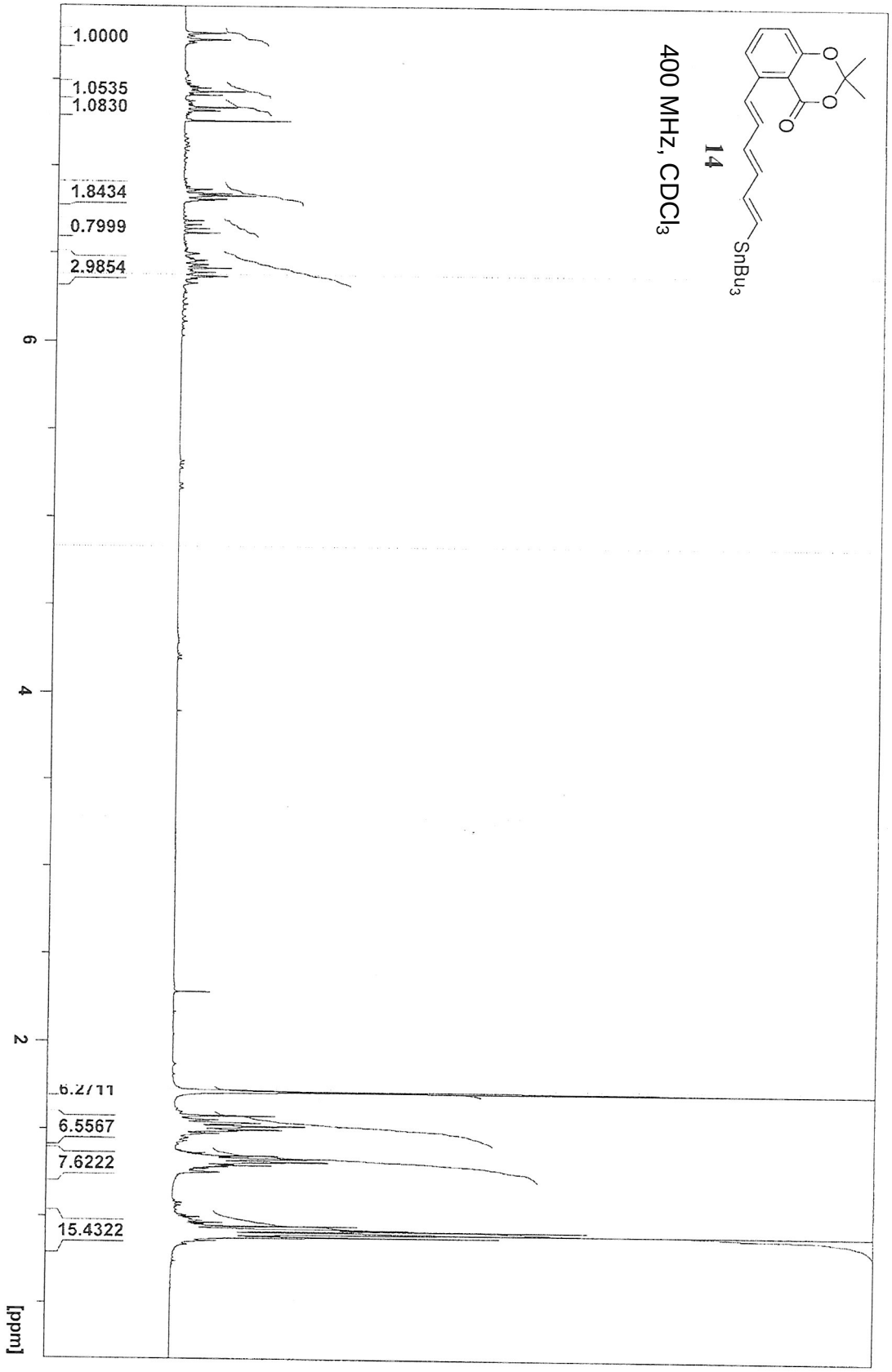
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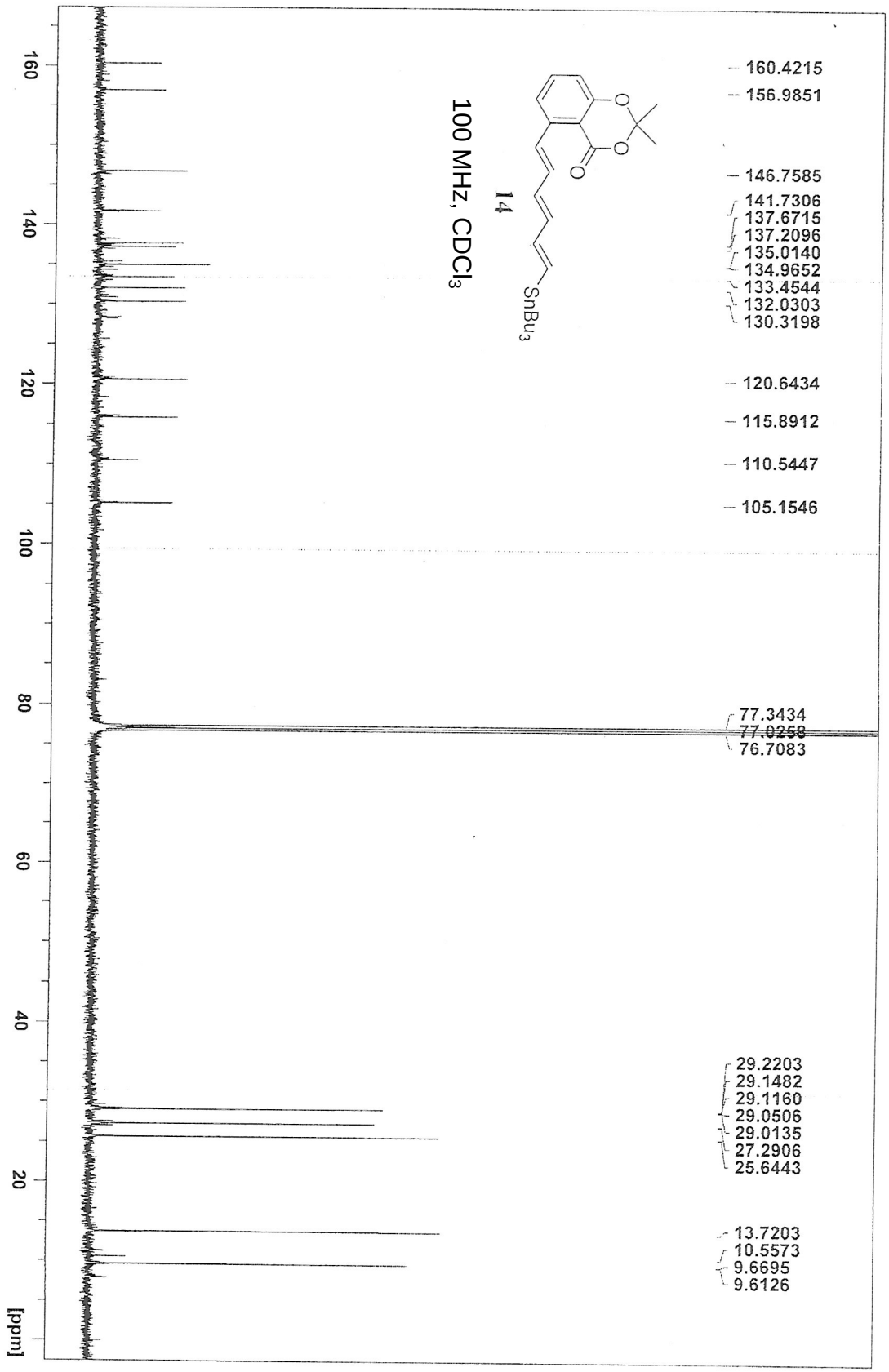
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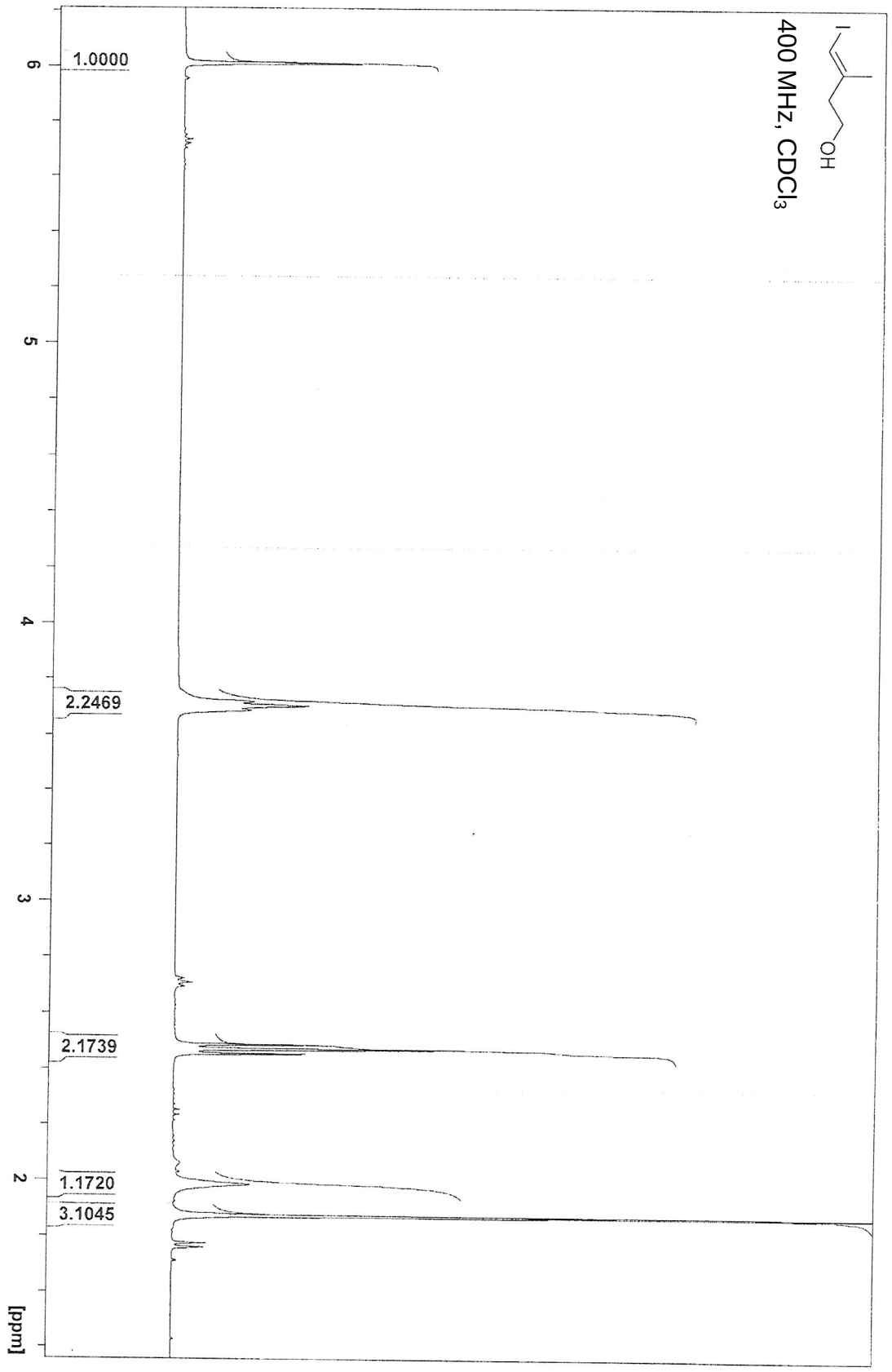
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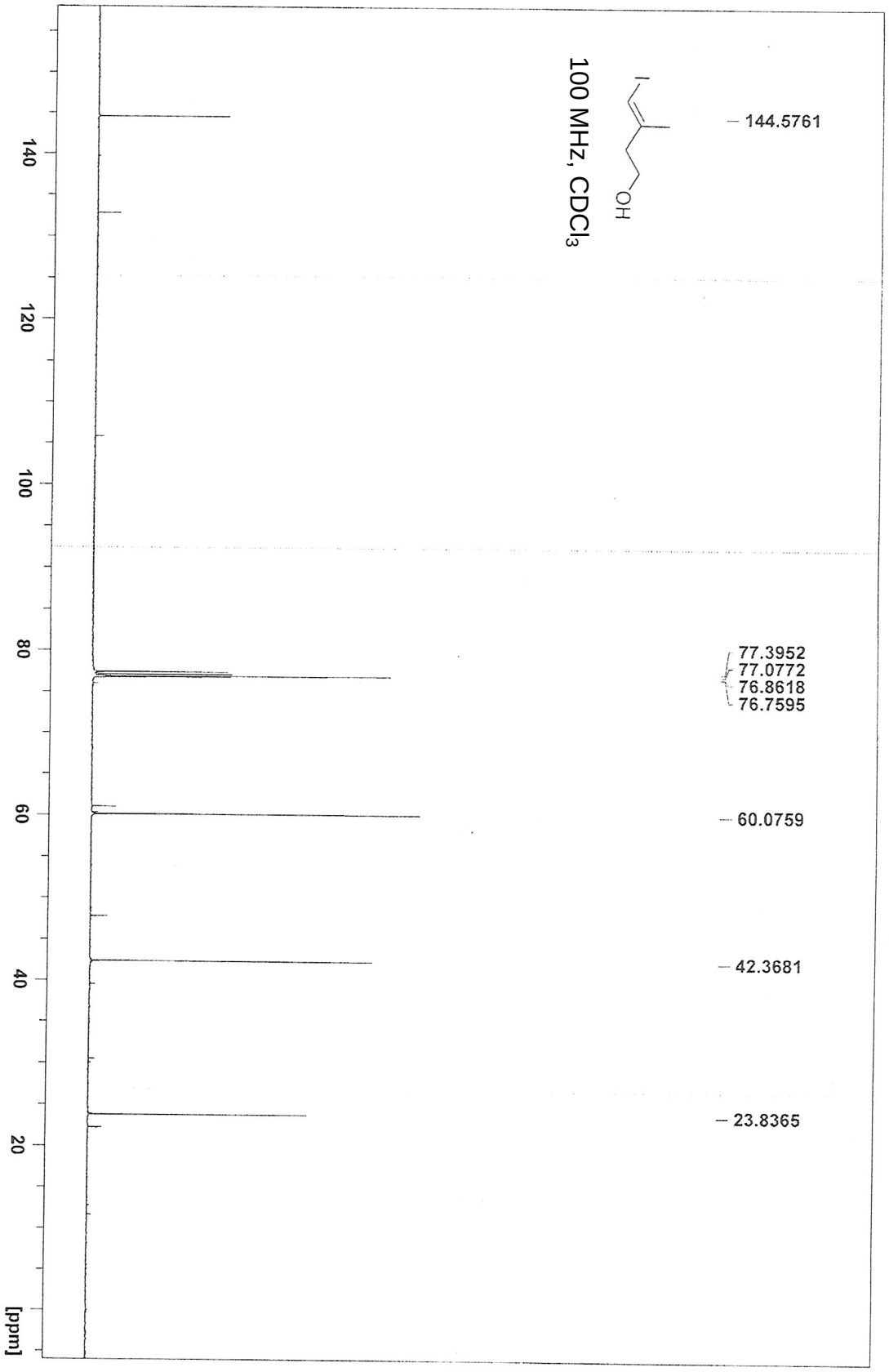
2
[ppm]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120
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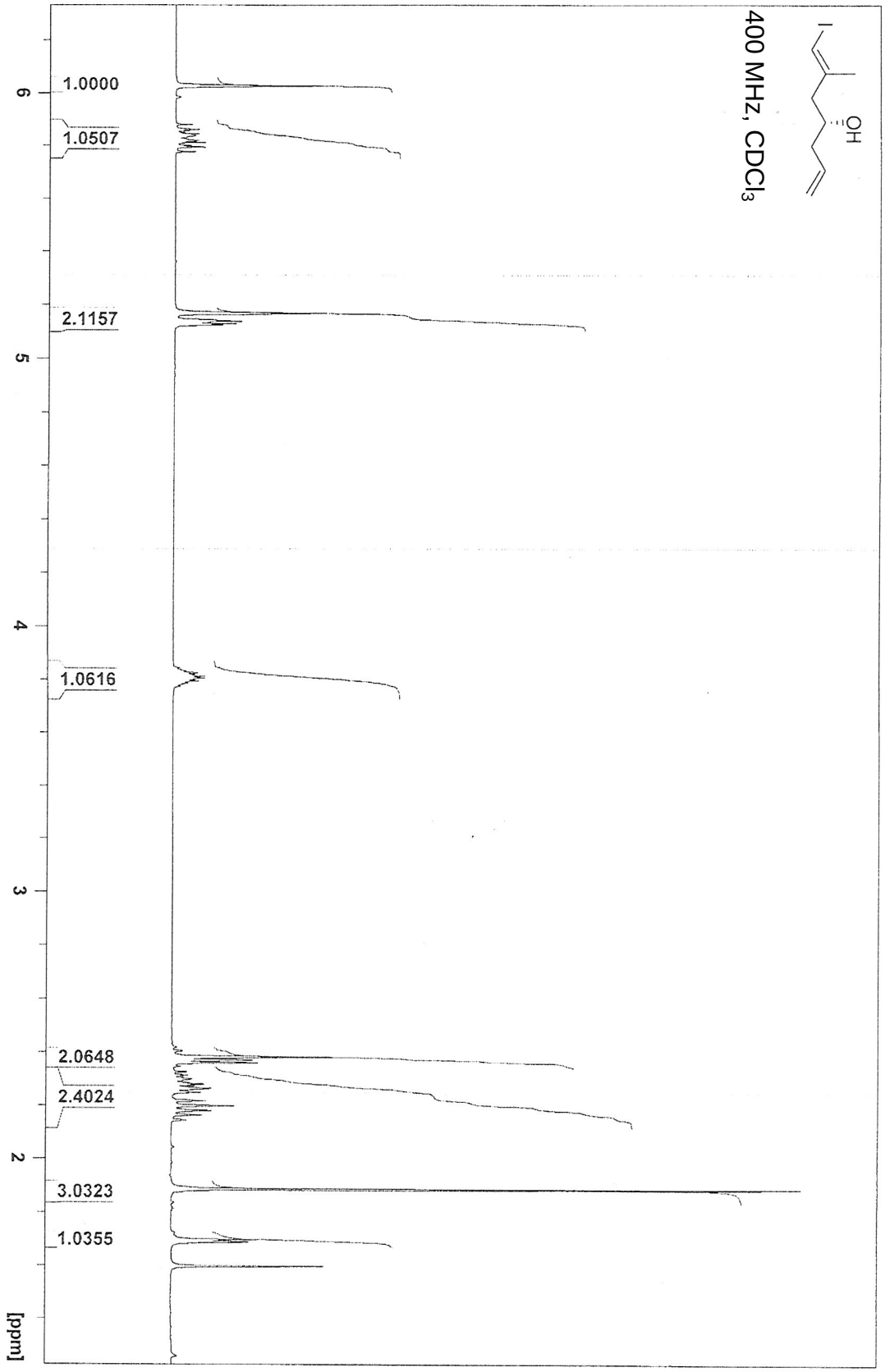
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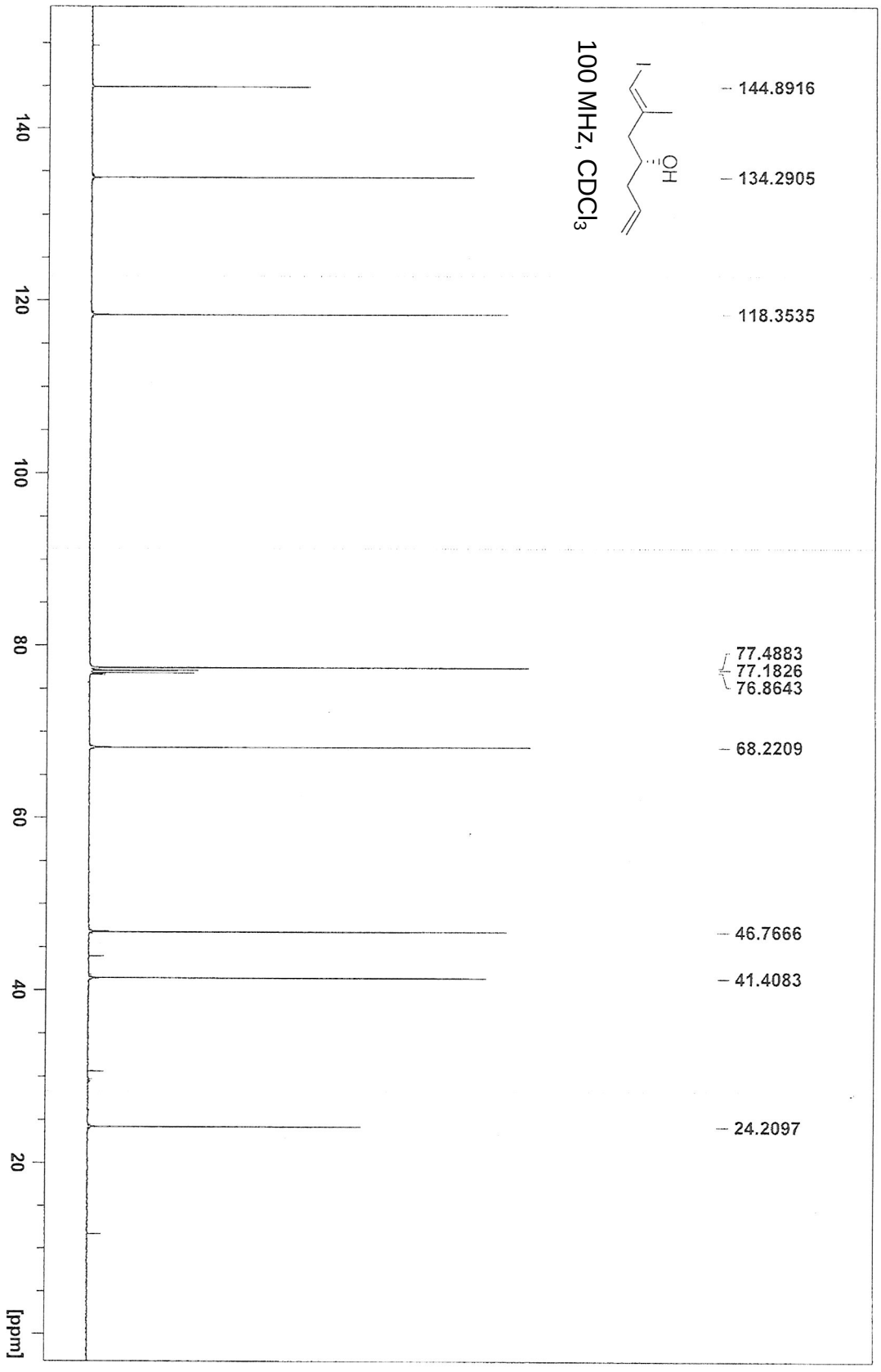
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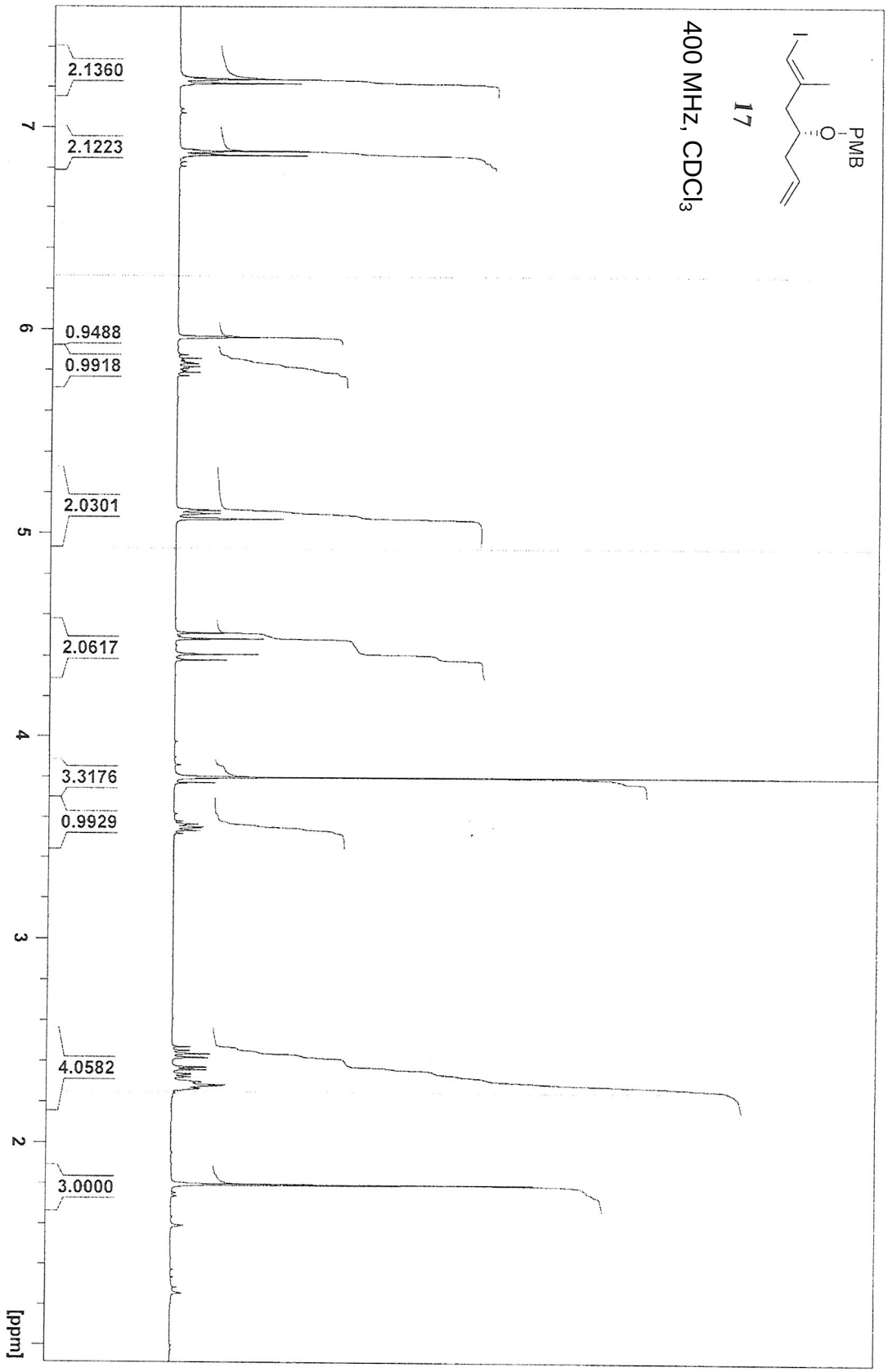
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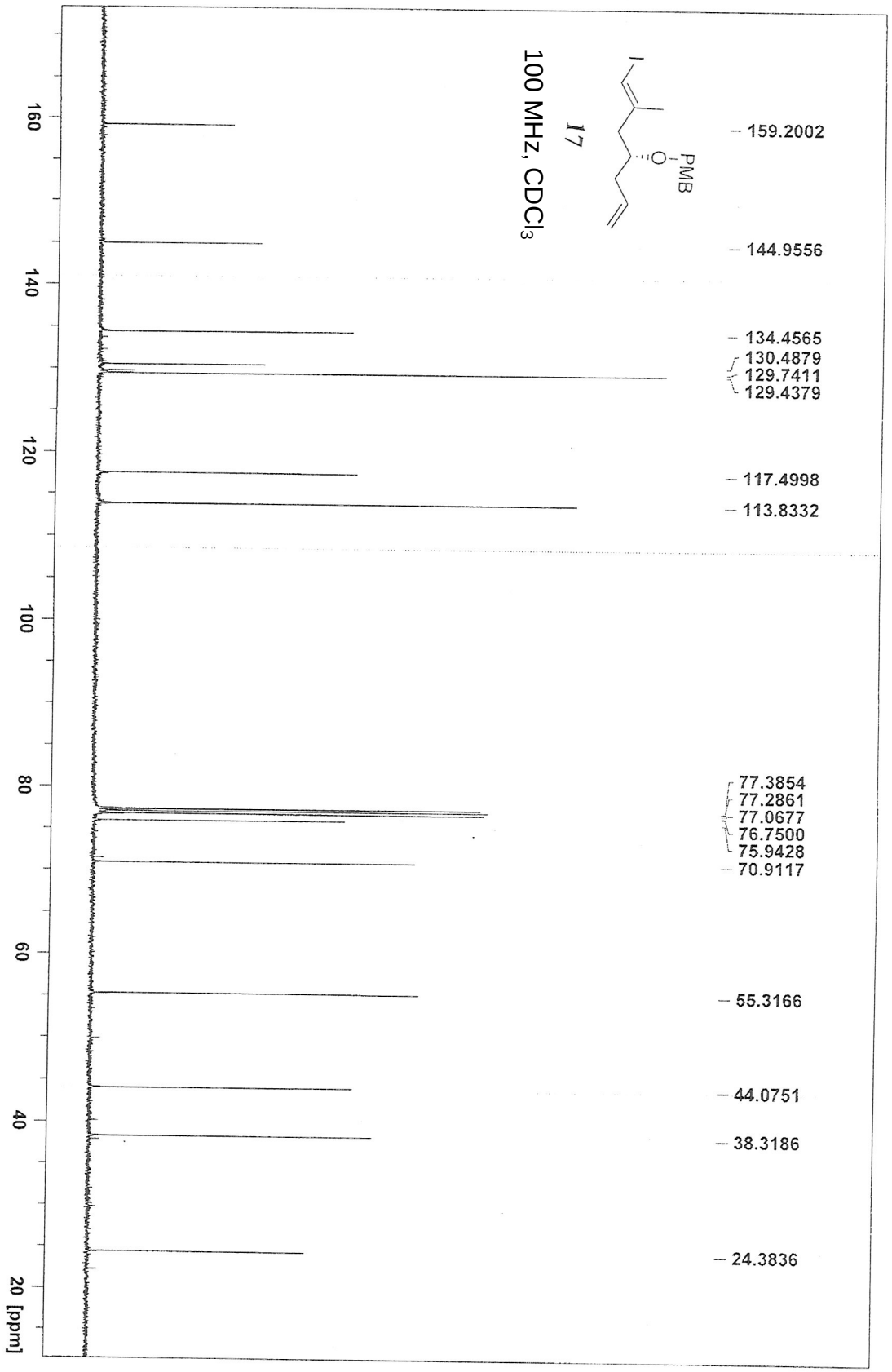
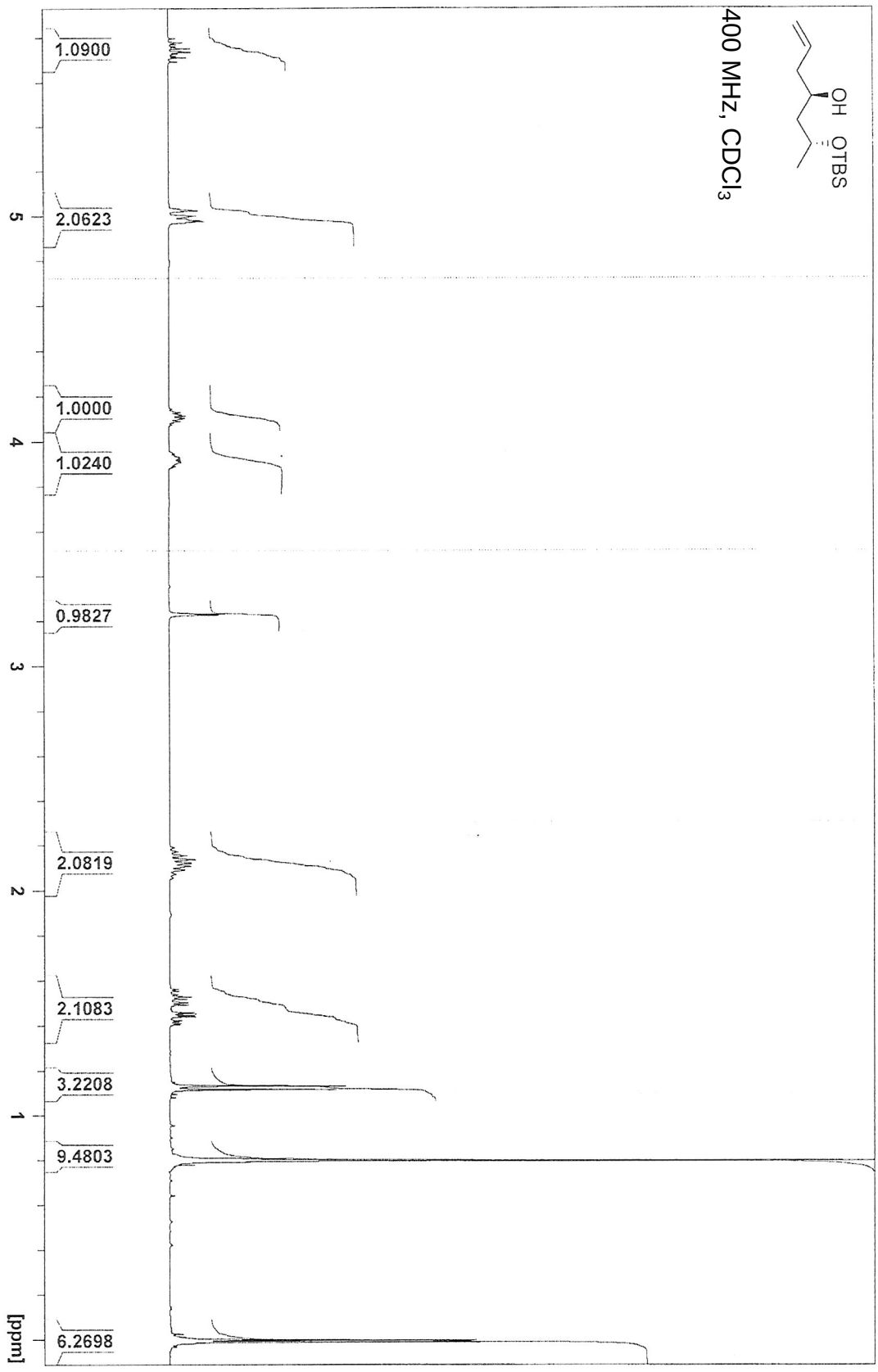
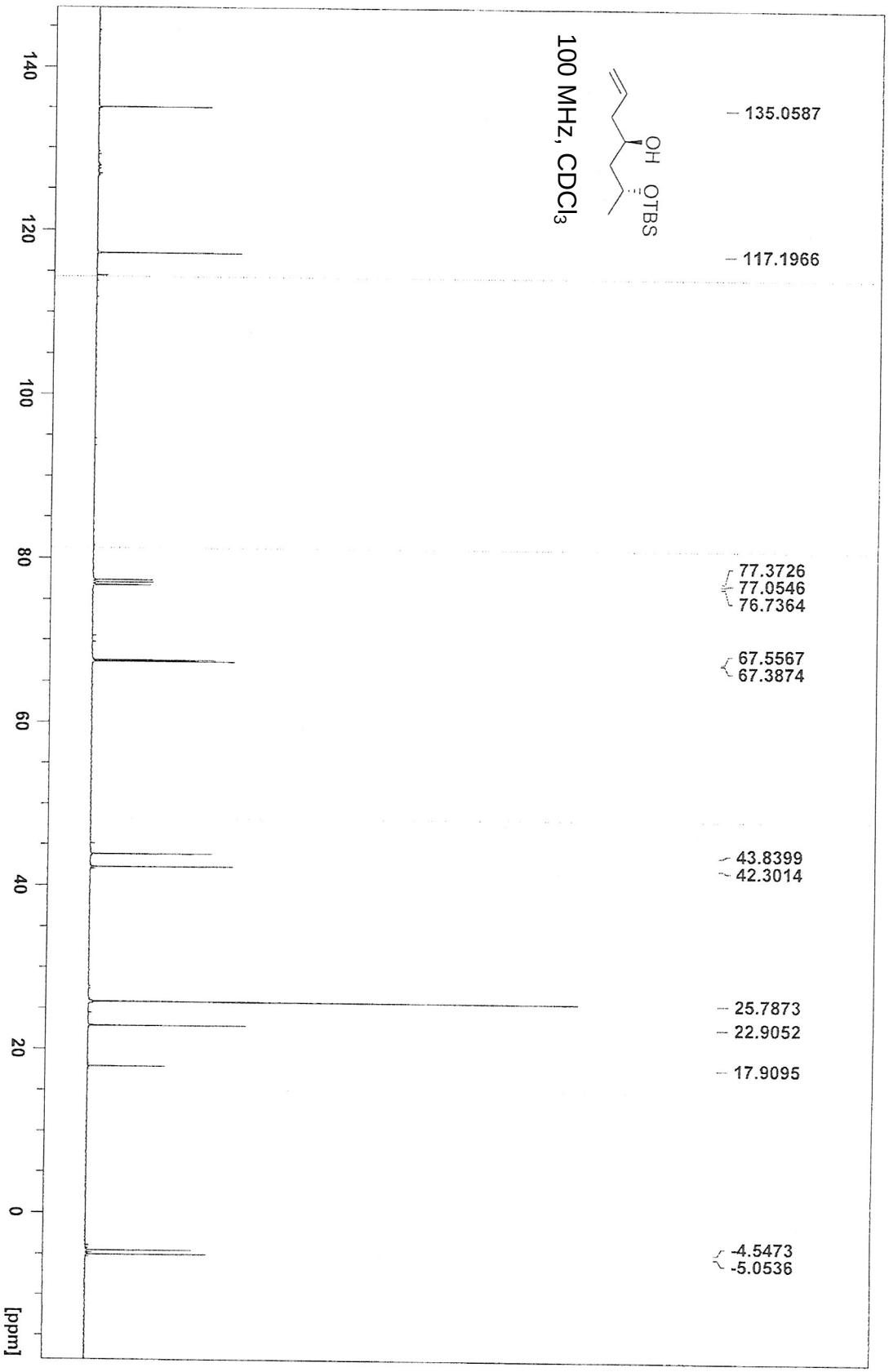
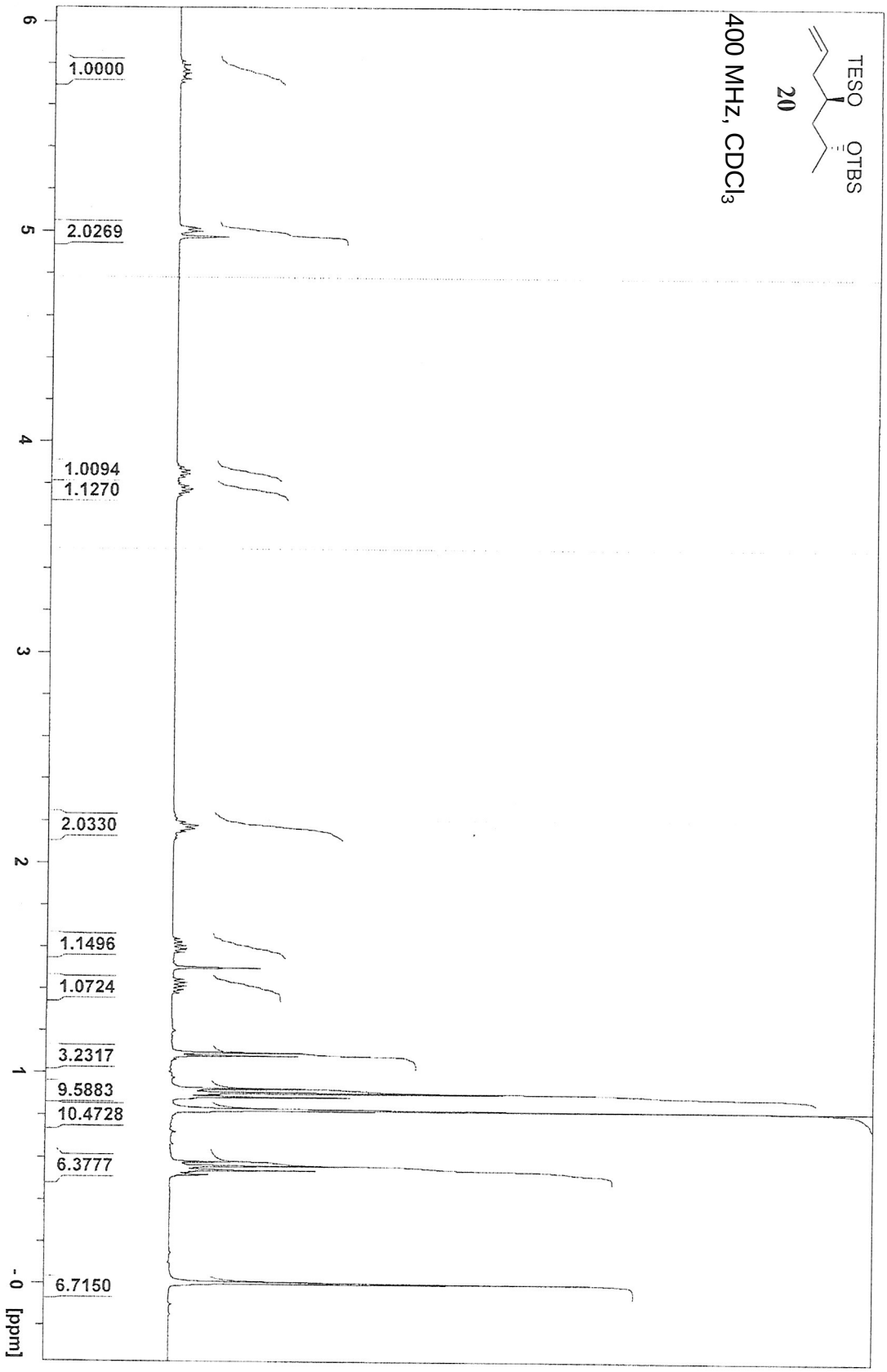
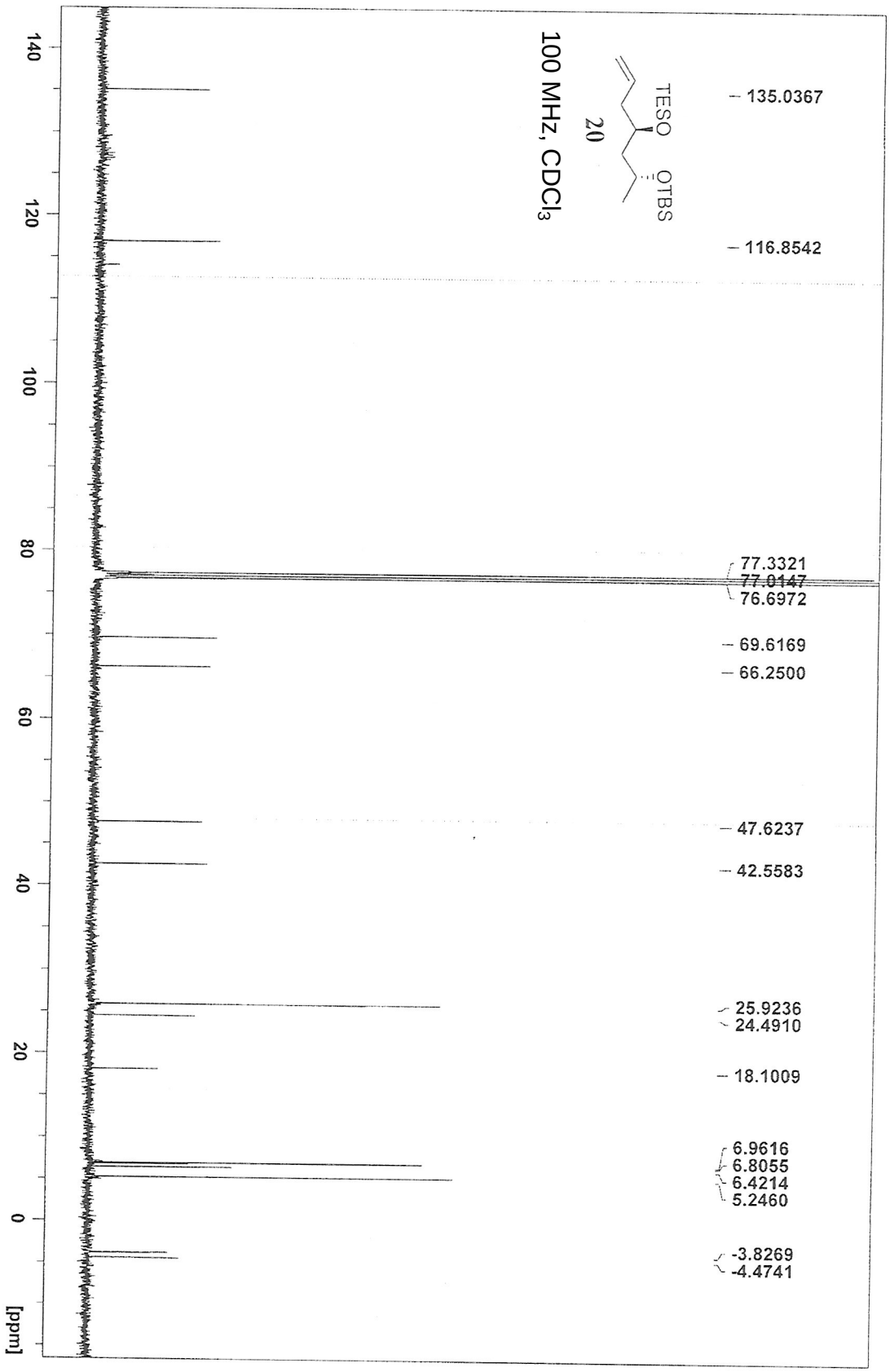
3.0000
[ppm]

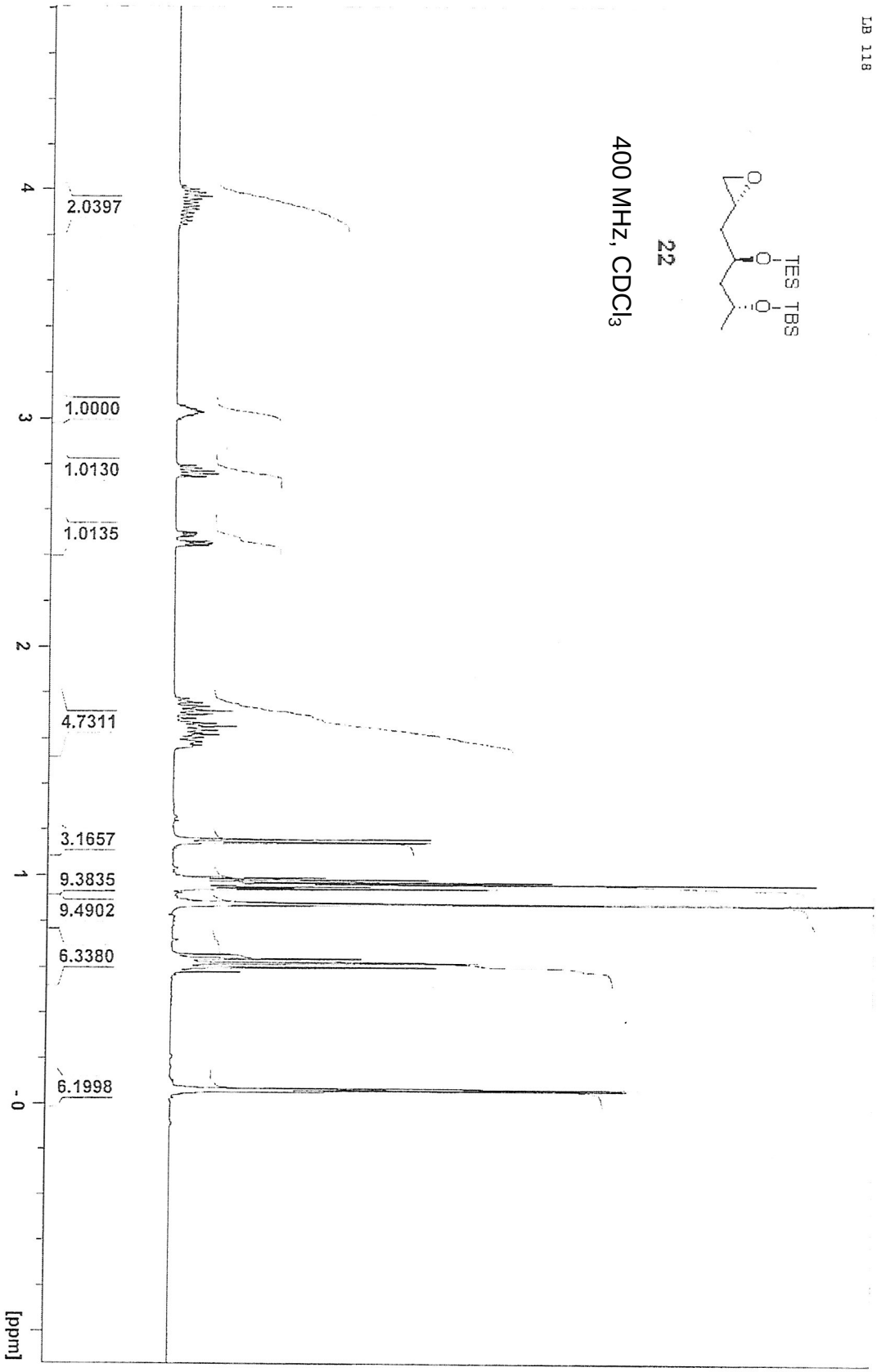

17
100 MHz, CDCl3
PMB
159.2002
144.9556
134.4565
130.4879
129.7411
129.4379
117.4998
113.8332
77.3854
77.2861
77.0677
76.7500
75.9428
70.9117
55.3166
44.0751
38.3186
24.3836
160
140
120
100
80
60
40
20 [ppm]


400 MHz, CDCl3
OH OTBS
1.0900
2.0623
1.0000
1.0240
0.9827
2.0819
2.1083
3.2208
9.4803
6.2698
[ppm]

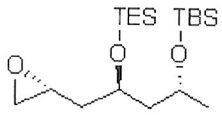

100 MHz, CDCl3
OH
OTBS
135.0587
117.1966
77.3726
77.0546
76.7364
67.5567
67.3874
43.8399
42.3014
25.7873
22.9052
17.9095
-4.5473
-5.0536
140
120
100
80
60
40
20
0
[ppm]


TESO
OTBS
20
400 MHz, CDCl3
1.0000
2.0269
1.0094
1.1270
2.0330
1.1496
1.0724
3.2317
9.5883
10.4728
6.3777
6.7150
6
5
4
3
2
1
0
[ppm]


100 MHz, CDCl3
TESO
OTBS
20
135.0367
116.8542
77.3321
77.0147
76.6972
69.6169
66.2500
47.6237
42.5583
25.9236
24.4910
18.1009
6.9616
6.8055
6.4214
5.2460
-3.8269
-4.4741
140
120
100
80
60
40
20
0
[ppm]


20060724 380 1 Z: Cossy
LB 118
TES TBS
22
400 MHz, CDCl3
2.0397
1.0000
1.0130
1.0135
4.7311
3.1657
9.3835
9.4902
6.3380
6.1998
4
3
2
1
- 0
[ppm]

LB 118

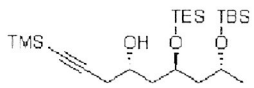


22

100 MHz, $CDCl_3$


```
Current Data Parameters
NAME                  20060724
EXPNO                      383
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20060724
Time                     20.02
INSTRUM                  spect
PROBHD    5 mm DUL 13C-1
PULPROG                zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                          512
DS                            4
SWH                26178.010 Hz
FIDRES             0.399445 Hz
AQ                 1.2517875 sec
RG                        29193
DW                    19.100 usec
DE                    10.00 usec
TE                    299.4 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                      13C
P1                     6.80 usec
PL1                   -4.00 dB
SFO1              100.6228292 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                100.00 usec
PL2                   -4.00 dB
PL12                  14.00 dB
PL13                  16.75 dB
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                100.6127690 MHz
WDW                          EM
SSB                           0
LB                     1.00 Hz
GB                            0
PC                         1.40
```

DA 760

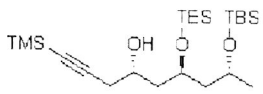


23

400 MHz, $CDCl_3$

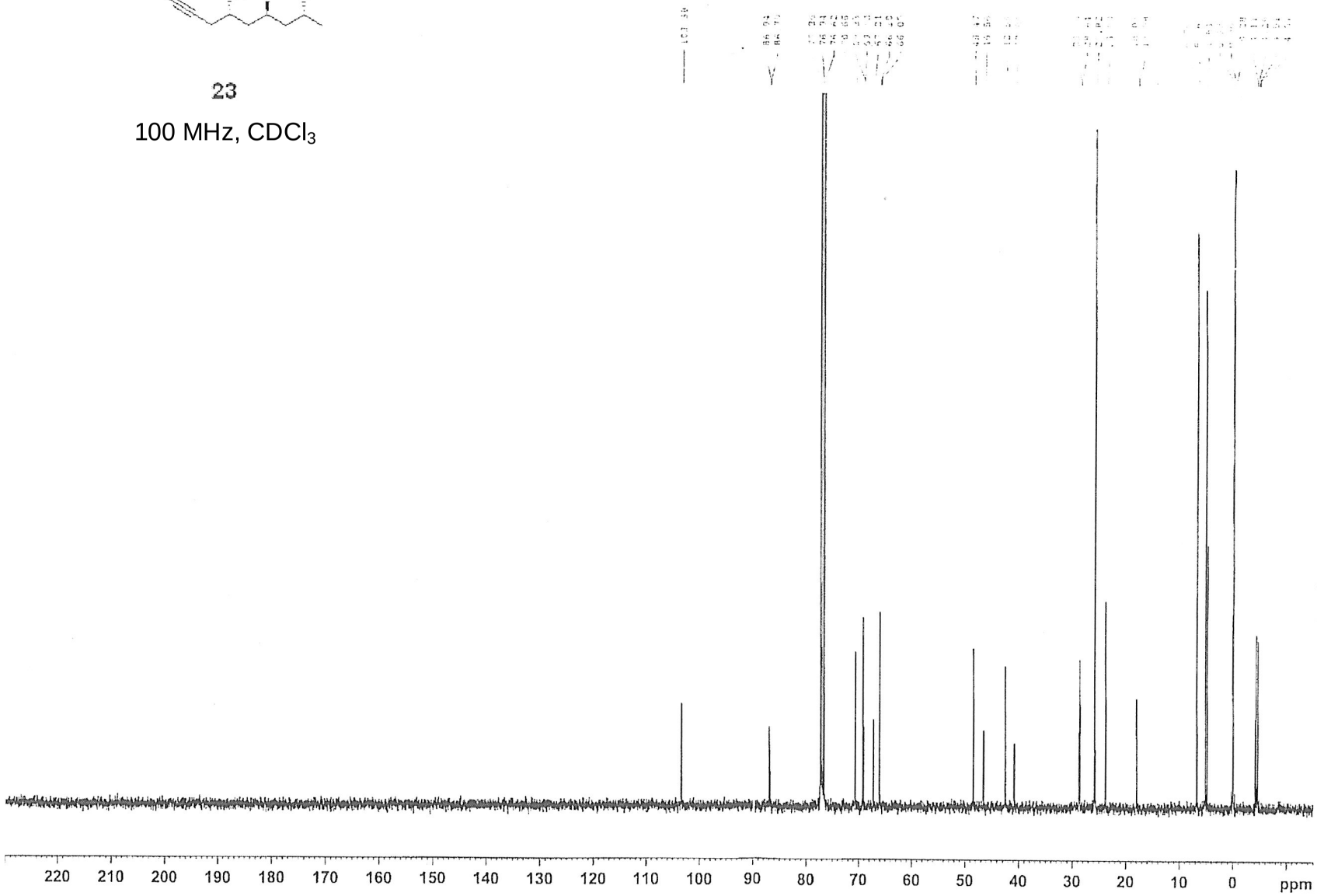

```
Current Data Parameters
NAME                 20070207
EXPNO                     620
PROCNO                      1
USER                    Cossy

F2 - Acquisition Parameters
Date_                20070208
Time                     8.00
INSTRUM                 spect
PROBHD    5 mm DUL 13C-1
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                       80.6
DW                     60.800 usec
DE                     10.00 usec
TE                     296.3 K
D1                  1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     10.70 usec
PL1                    -4.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF                 400.1300665 MHz
WDW                        EM
SSB                         0
LB                       0.00 Hz
GB                          0
PC                       1.00
```

DA 760



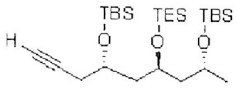
23

100 MHz, $CDCl_3$



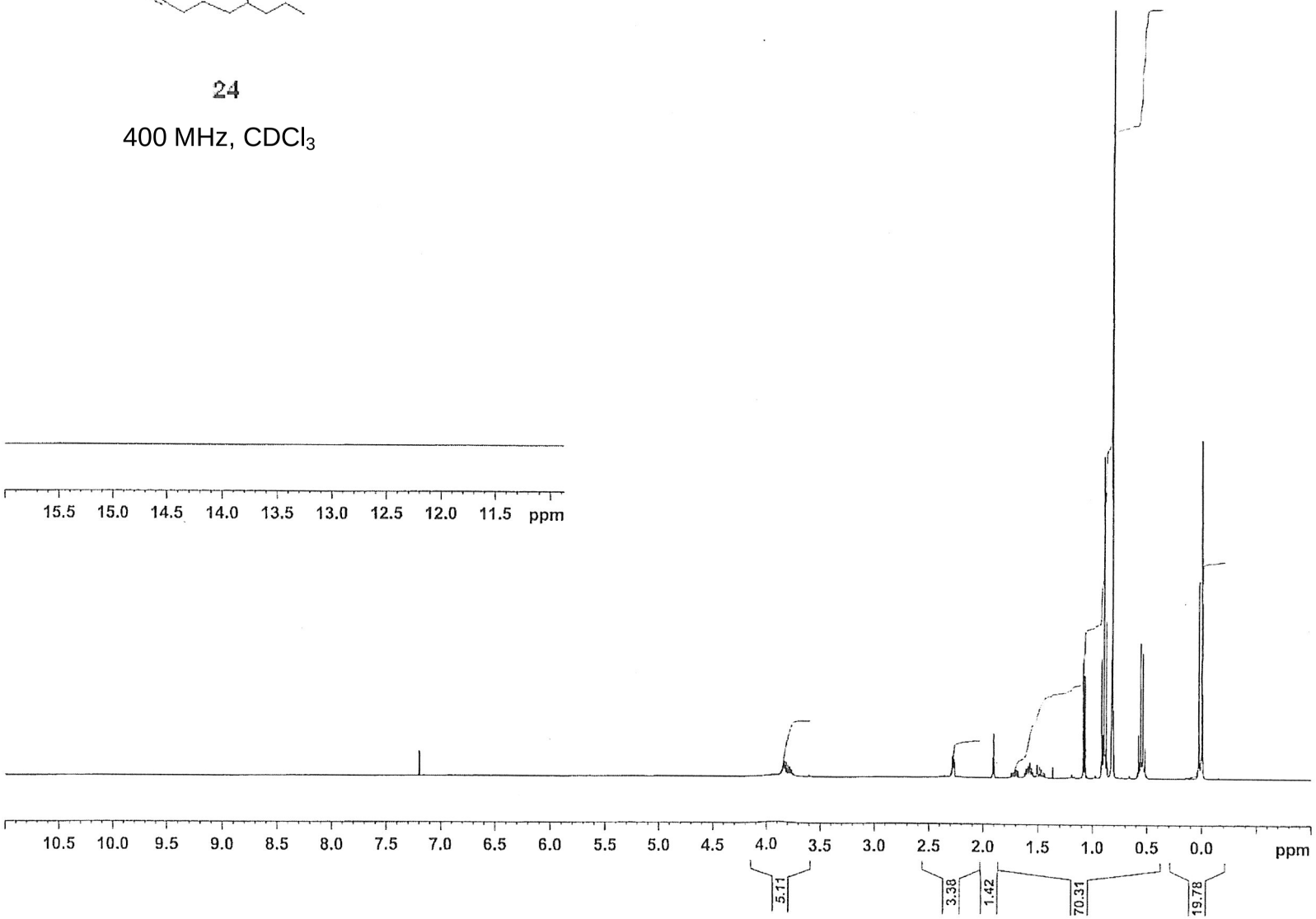

```
Current Data Parameters
NAME                 20070207
EXPNO                     621
PROCNO                      1
USER                    Cosby

F2 - Acquisition Parameters
Date_               20070208
Time                    8.29
INSTRUM                 spect
PROBHD   5 mm DUL 13C-1
PULPROG                 zgpg30
TD                       65536
SOLVENT                 CDCl3
NS                        512
DS                          4
SWH                 26178.010 Hz
FIDRES                0.399445 Hz
AQ                  1.2517875 sec
RG                       16008
DW                   19.100 usec
DE                   10.00 usec
TE                       296.8 K
D1                  2.00000000 sec
d11                 0.03000000 sec
DELTA               1.89999998 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                      6.80 usec
PL1                     -4.00 dB
SFO1              100.6228292 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                 100.00 usec
PL2                     -4.00 dB
PL12                    14.00 dB
PL13                    18.75 dB
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF                100.6127769 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```

DA 756



24

400 MHz, $CDCl_3$



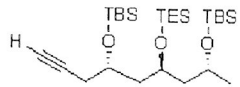
Current Data Parameters
NAME 20070205
EXPNO 655
PROCNO 1
USER Cossy

F2 - Acquisition Parameters
Date_ 20070205
Time 21.43
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 71.8
DW 60.800 usec
DE 10.00 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 10.70 usec
PL1 -4.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300347 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

DA 756

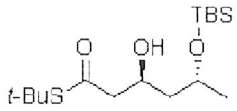


24

100 MHz, $CDCl_3$

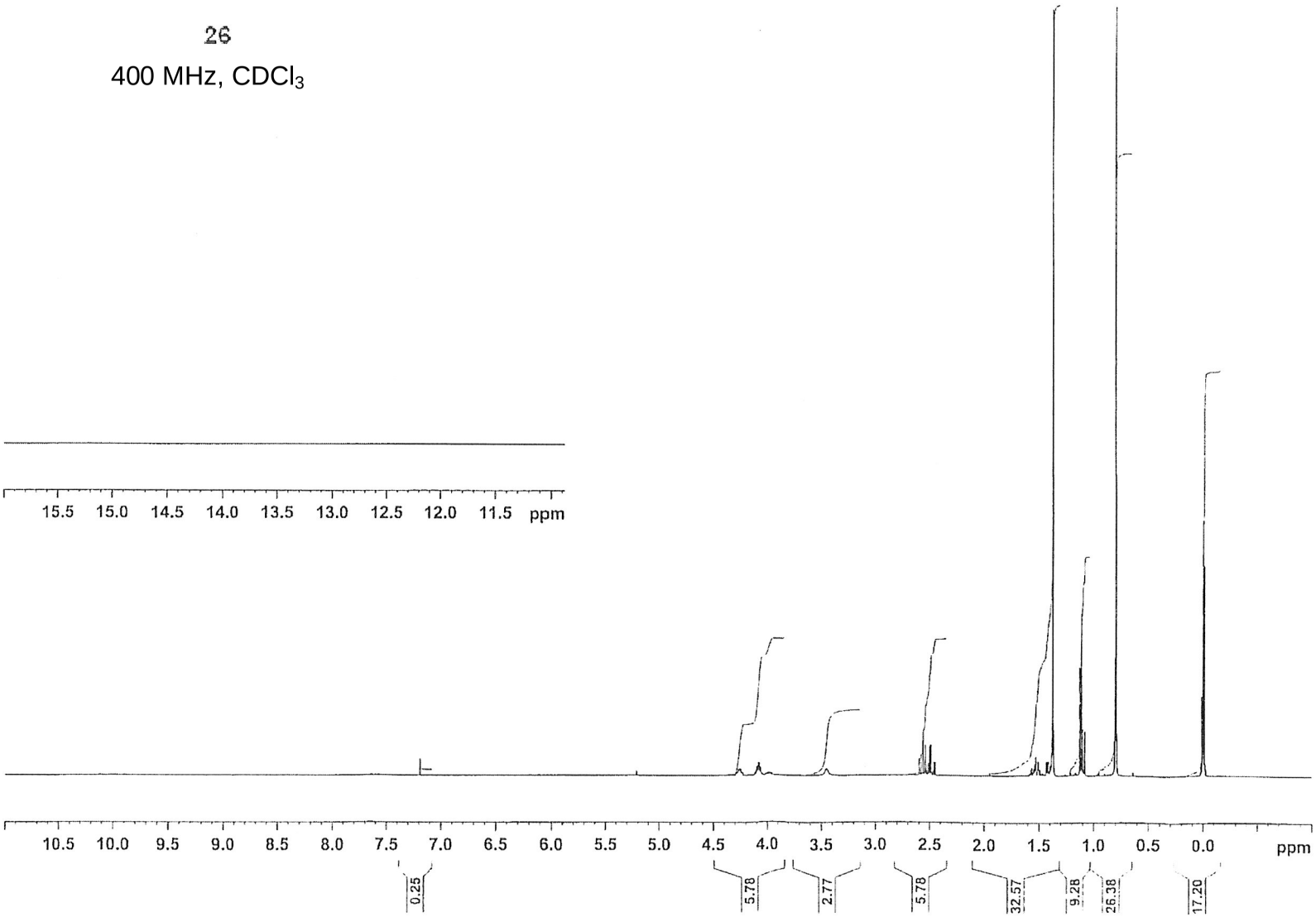

```
Current Data Parameters
NAME                  20070205
EXPNO                      652
PROCNO                       1
USER                     Cossy

F2 - Acquisition Parameters
Date_                 20070205
Time                     21.28
INSTRUM                  spect
PROBHD    5 mm DUL 13C-1
PULPROG                zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                          128
DS                            4
SWH                26178.010 Hz
FIDRES                 0.399445 Hz
AQ                     1.2517675 sec
RG                        26008
DW                     19.100 usec
DE                     10.00 usec
TE                     296.9 K
D1                     2.00000000 sec
d11                    0.03000000 sec
DELTA                  1.89999998 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P1                     6.80 usec
PL1                    -4.00 dB
SFO1               100.6228292 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                 100.00 usec
PL2                    -4.00 dB
PL12                   14.00 dB
PL13                   18.75 dB
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                 100.6127690 MHz
WDW                          EM
SSB                           0
LB                     1.00 Hz
GB                            0
PC                     1.40
```

DA 652

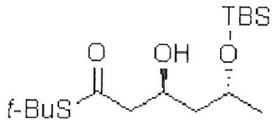


26

400 MHz, $CDCl_3$

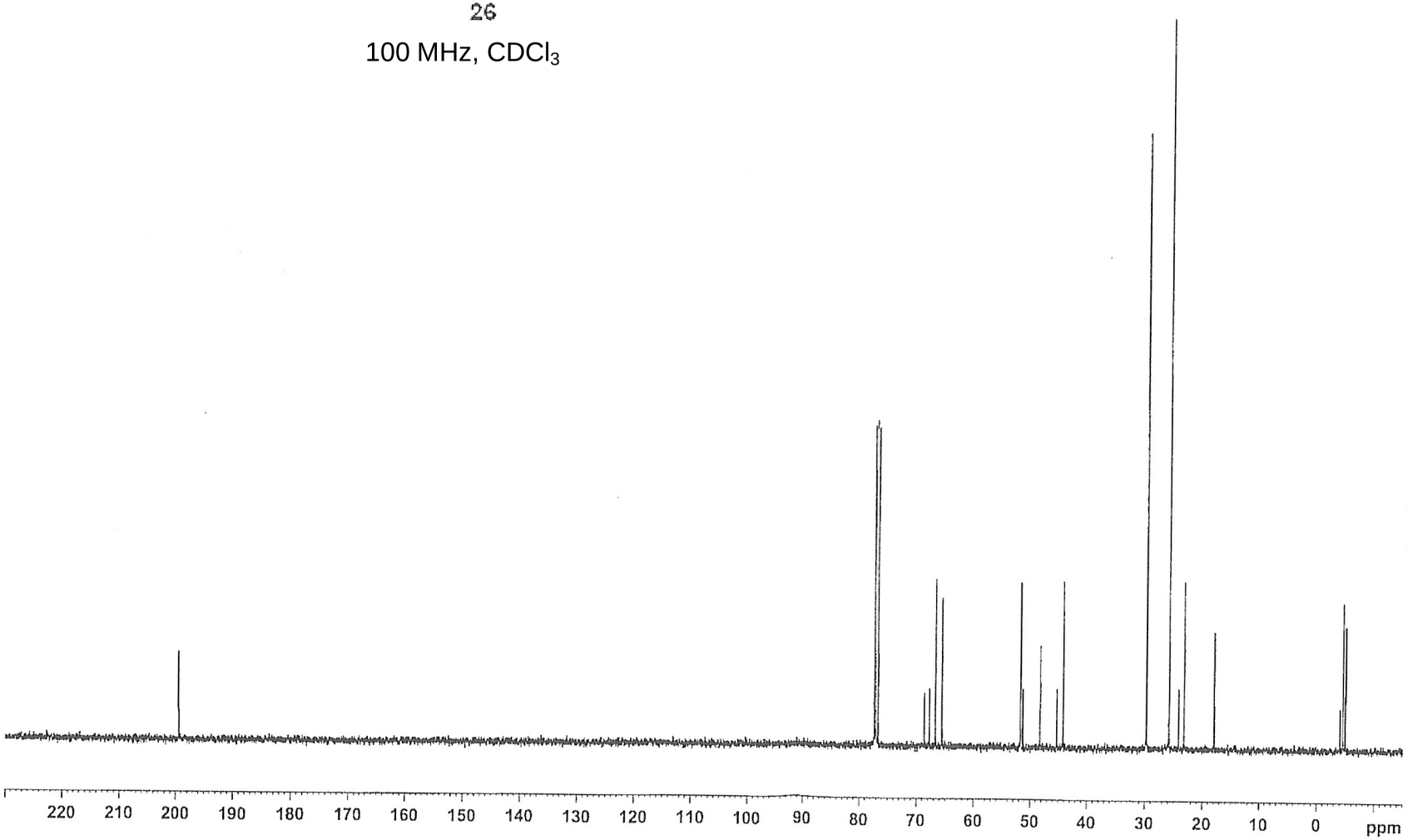



```
Current Data Parameters
NAME                 20070523
EXPNO                     135
PROCNO                      1
USER                    Cossy

F2 - Acquisition Parameters
Date_                20070523
Time                    12.59
INSTRUM                 spect
PROBHD    5 mm DUL 13C-1
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                        57
DW                    60.800 usec
DE                    10.00 usec
TE                    296.8 K
D1                  1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                    10.70 usec
PL1                   -4.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                     32768
SF                400.1300389 MHz
WDW                       EM
SSB                        0
LB                    0.00 Hz
GB                         0
PC                      1.00
```



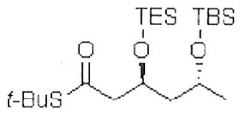
26

100 MHz, $CDCl_3$



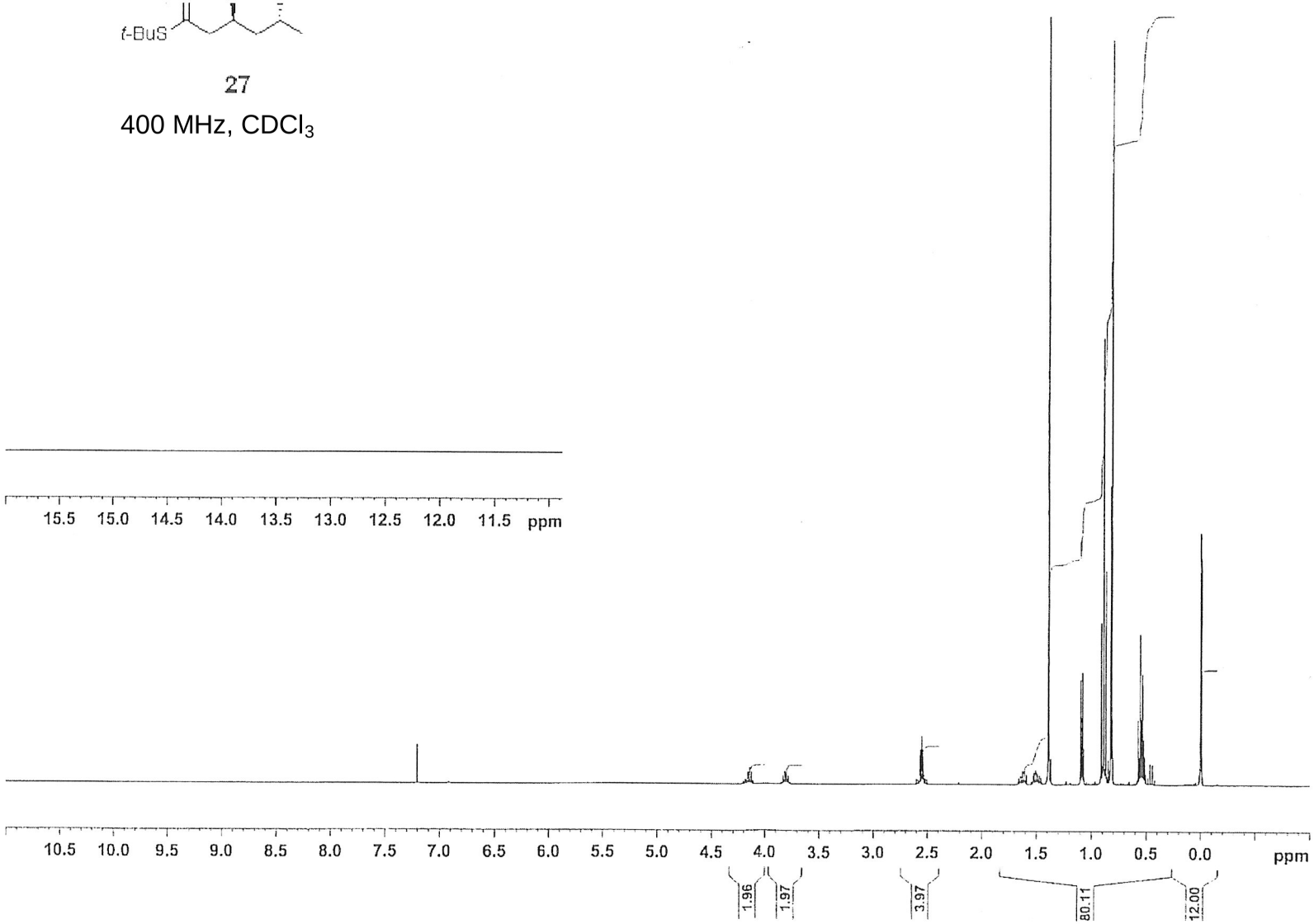

```
Current Data Parameters
NAME                  20070523
EXPNO                      132
PROCNO                       1
USER                     Cossy

F2 - Acquisition Parameters
Date_                 20070523
Time                     12.45
INSTRUM                  spect
PROBHD    5 mm DUL 13C-1
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         128
DS                           4
SWH                  26178.010 Hz
FIDRES                0.399445 Hz
AQ                    1.2517075 sec
RG                       29193
DW                    19.100 usec
DE                    10.00 usec
TE                       297.2 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                    6.80 usec
PL1                     -4.00 dB
SFO1               100.6228292 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                100.00 usec
PL2                     -4.00 dB
PL12                    14.00 dB
PL13                    18.75 dB
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF                 100.6127690 MHz
WDW                         EM
SSB                          0
LB                      1.00 Hz
GB                           0
PC                        1.40
```

DA 657

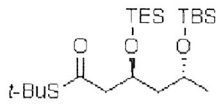


27

400 MHz, $CDCl_3$

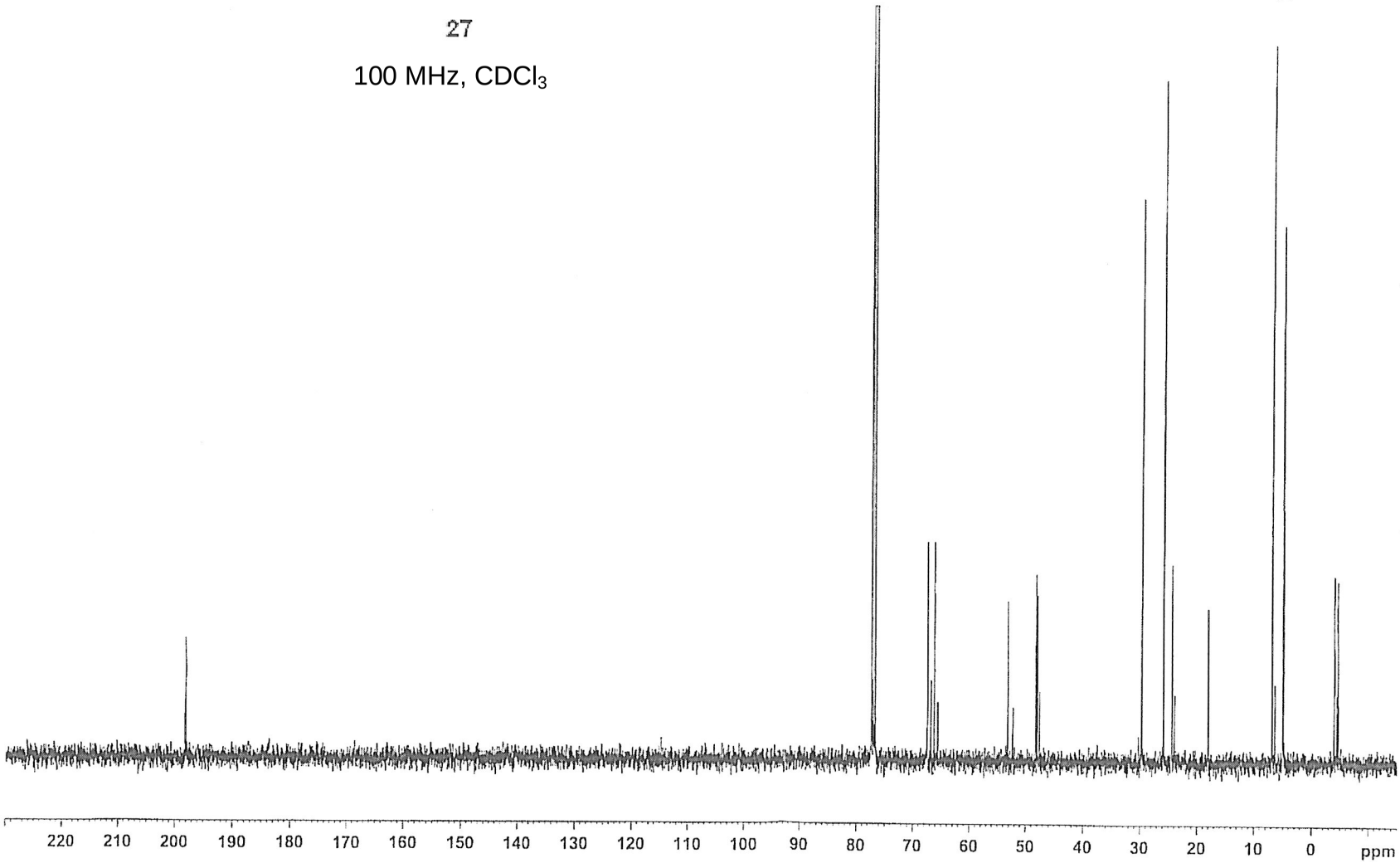



```
Current Data Parameters
NAME                  20070523
EXPNO                      190
PROCNO                       1
USER                     Cossy

F2 - Acquisition Parameters
Date_                 20070523
Time                     15.57
INSTRUM                  spect
PROBHD    5 mm DUL 13C-1
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                       80.6
DW                    60.800 usec
DE                    10.00 usec
TE                    296.7 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                    10.70 usec
PL1                   -4.00 dB
SFO1             400.1324710 MHz

F2 - Processing parameters
SI                      32768
SF                400.1300324 MHz
WDW                        EM
SSB                         0
LB                    0.00 Hz
GB                          0
PC                       1.00
```

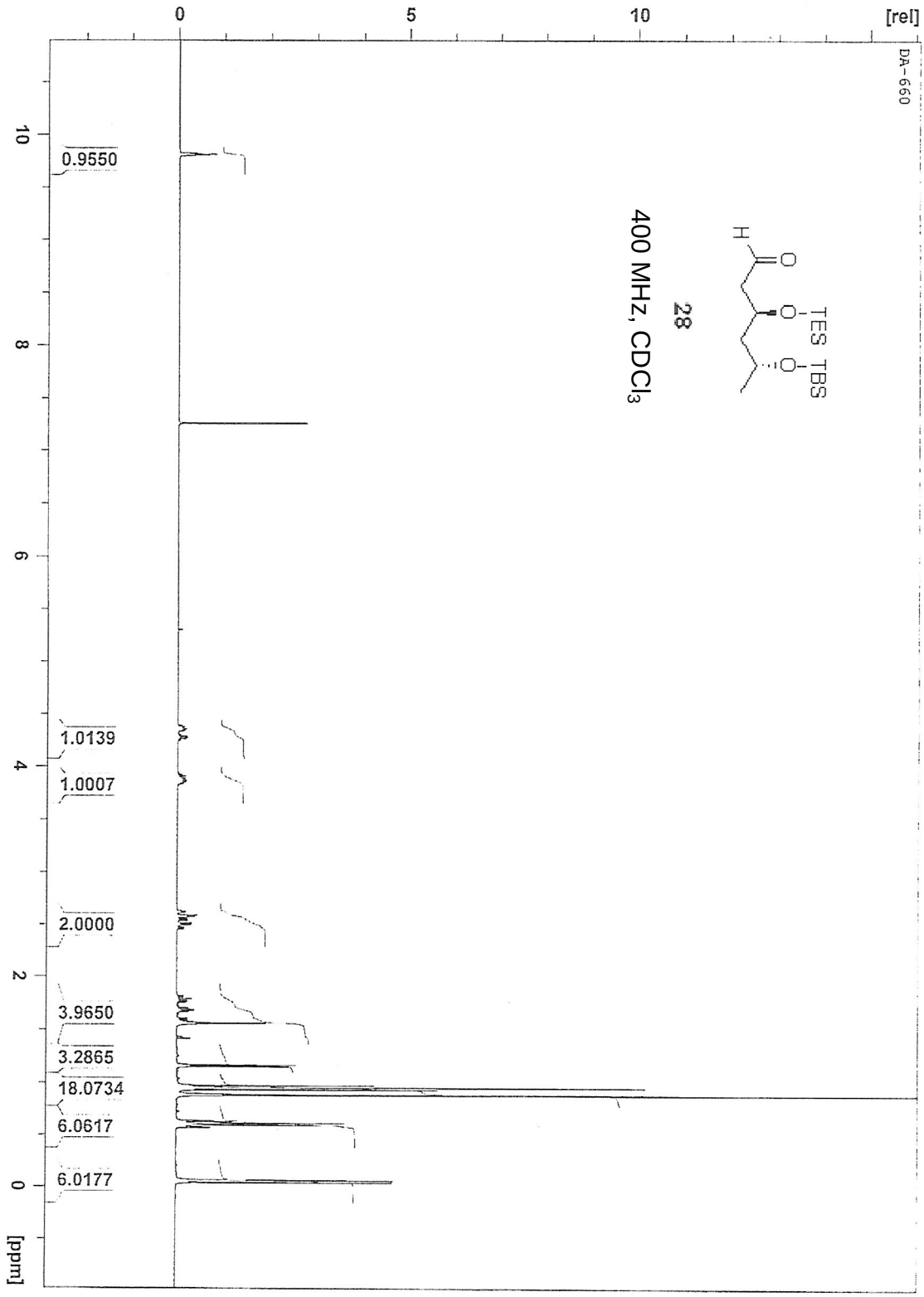


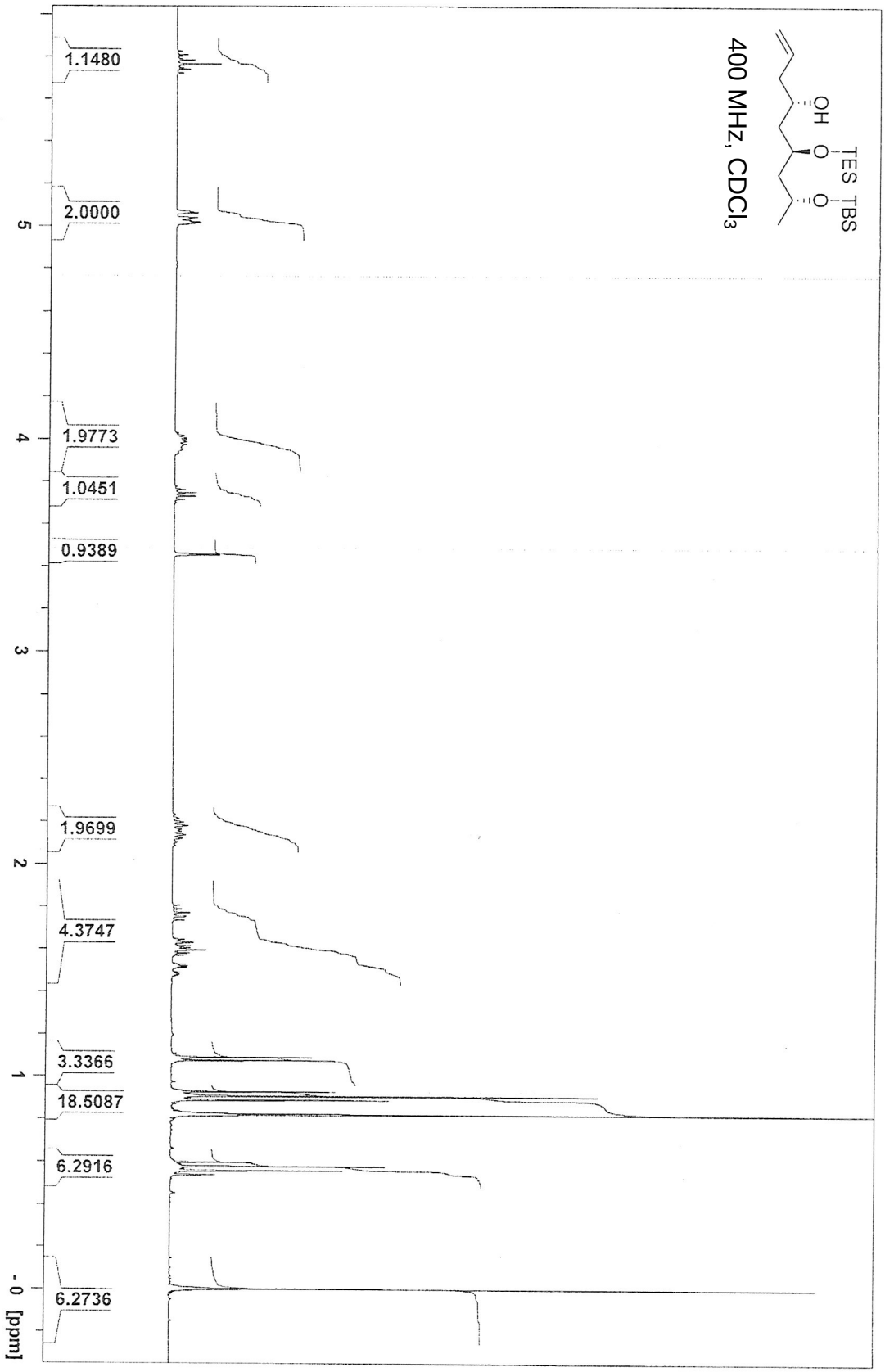
27

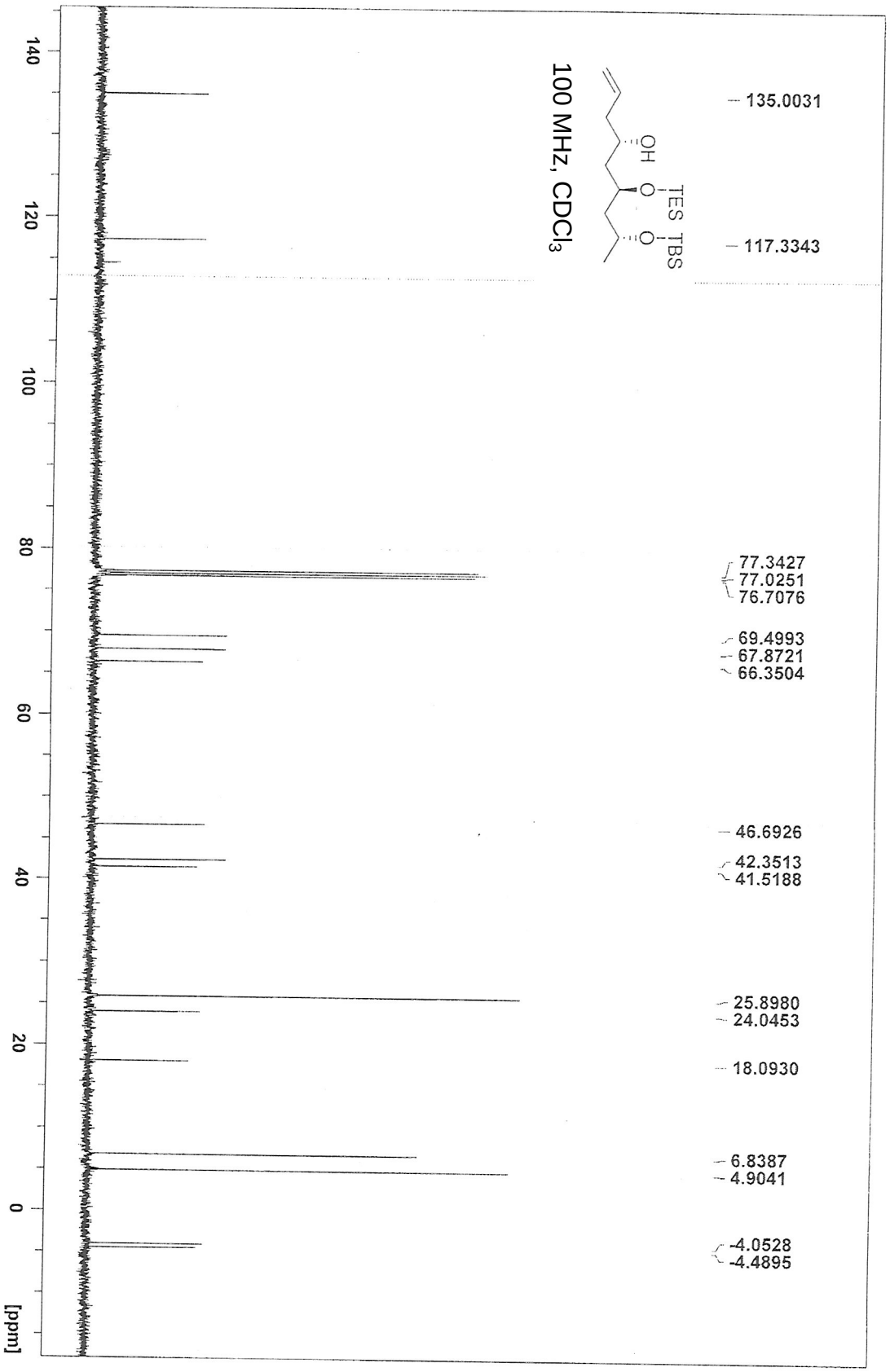
100 MHz, $CDCl_3$

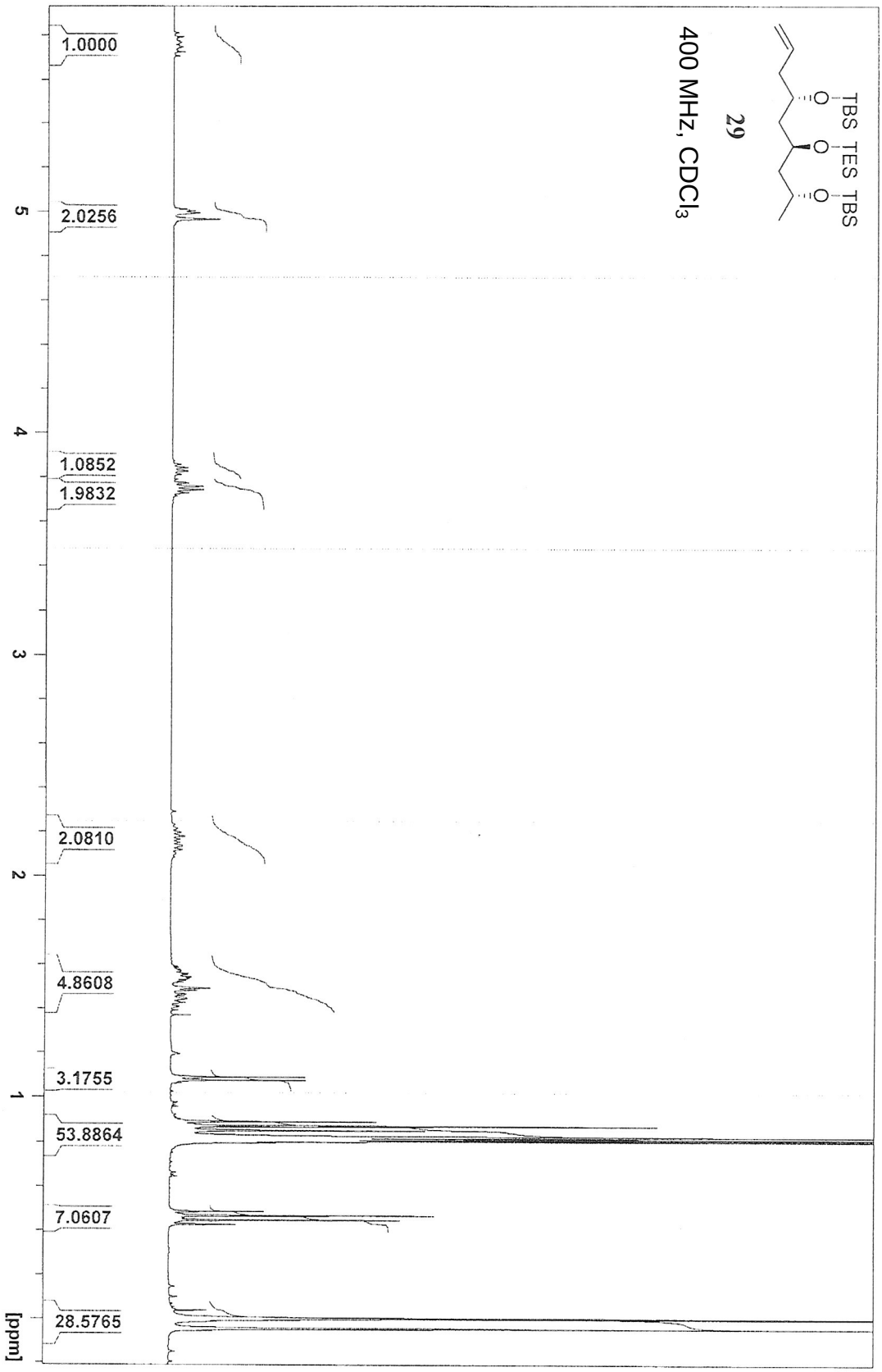


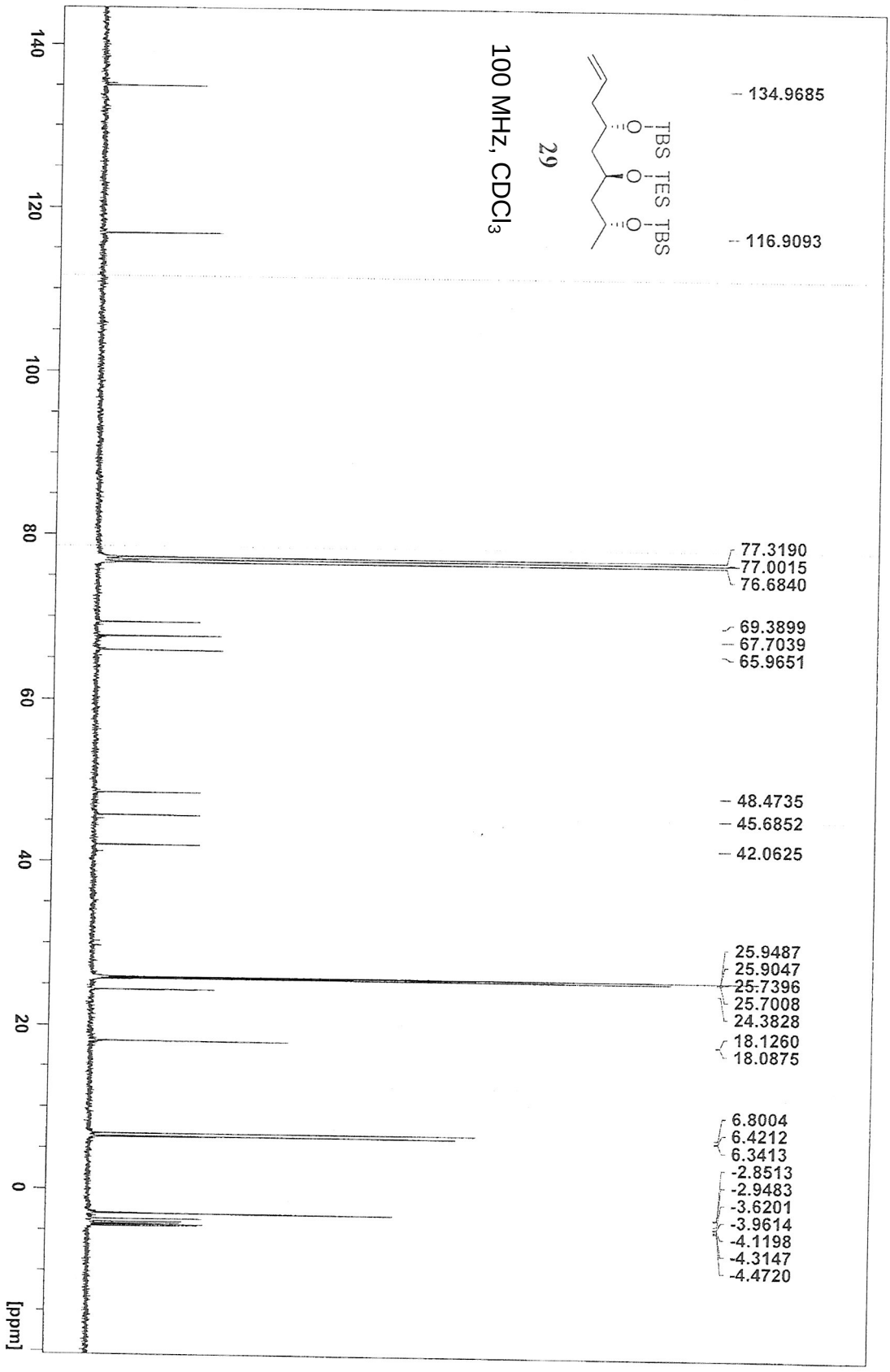

```
Current Data Parameters
NAME                  20070523
EXPNO                      162
PROCNO                       1
USER                     Cossy

F2 - Acquisition Parameters
Date_                 20070523
Time                     19.14
INSTRUM                  spect
PROBHD    5 mm DUL 13C-1
PULPROG                zgpg30
TD                        65536
SOLVENT                  CDCl3
NS                         128
DS                           4
SWH                  26170.010 Hz
FIDRES               0.399445 Hz
AQ                   1.2517875 sec
RG                       29193
DW                      19.100 usec
DE                      10.00 usec
TE                      297.3 K
D1                   2.00000000 sec
d11                  0.03000000 sec
DELTA                1.89999998 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                        6.80 usec
PL1                      -4.00 dB
SFO1                100.6228292 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   100.00 usec
PL2                      -4.00 dB
PL12                     14.00 dB
PL13                     18.75 dB
SFO2                400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                  100.6127690 MHz
WDW                           EM
SSB                            0
LB                        1.00 Hz
GB                             0
PC                         1.40
```

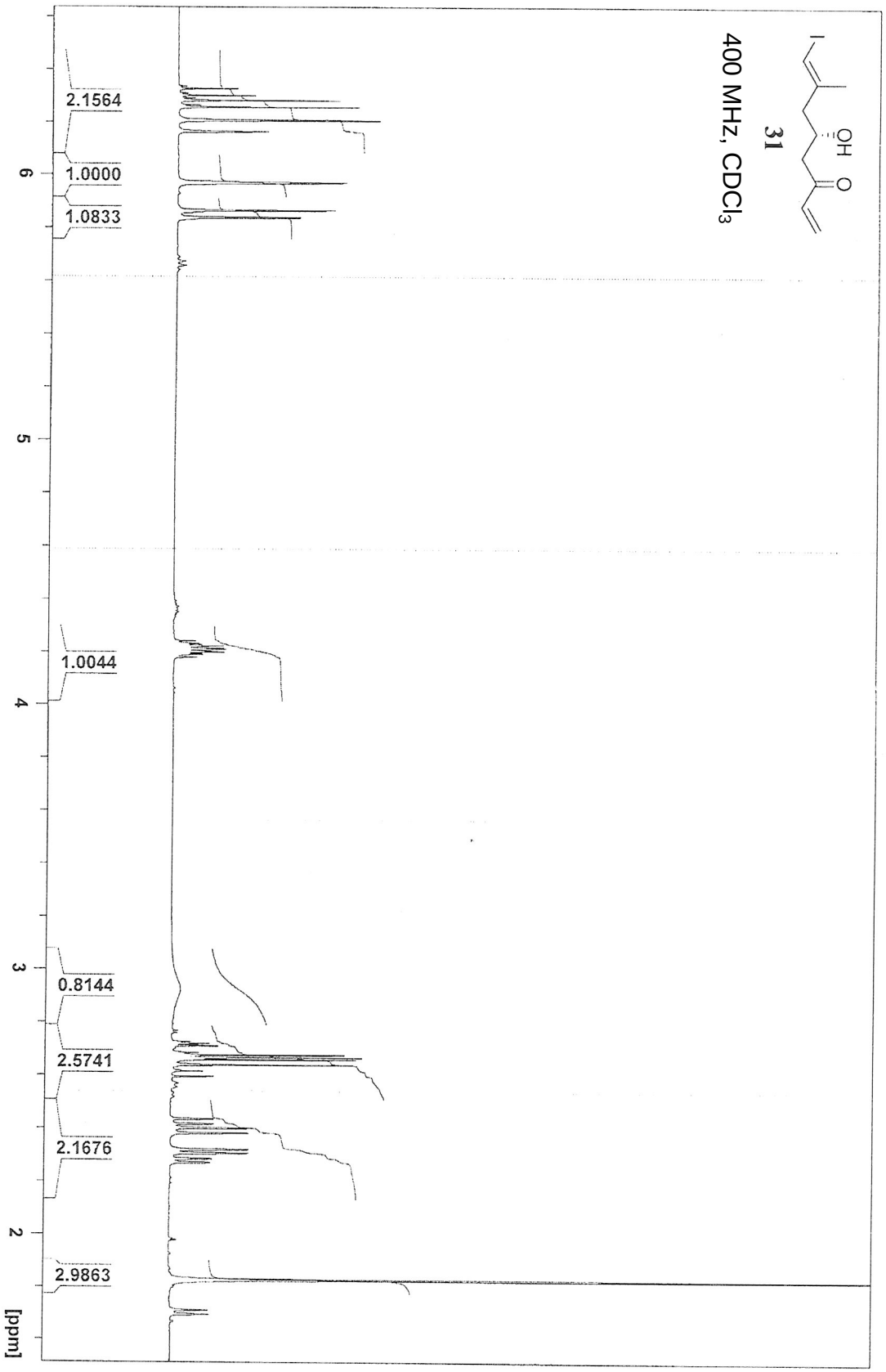

20061021 10 1 D: Cossy
DA-660
[rel]
0
5
10
TES TBS
28
400 MHz, CDCl3
0.9550
1.0139
1.0007
2.0000
3.9650
3.2865
18.0734
6.0617
6.0177
[ppm]

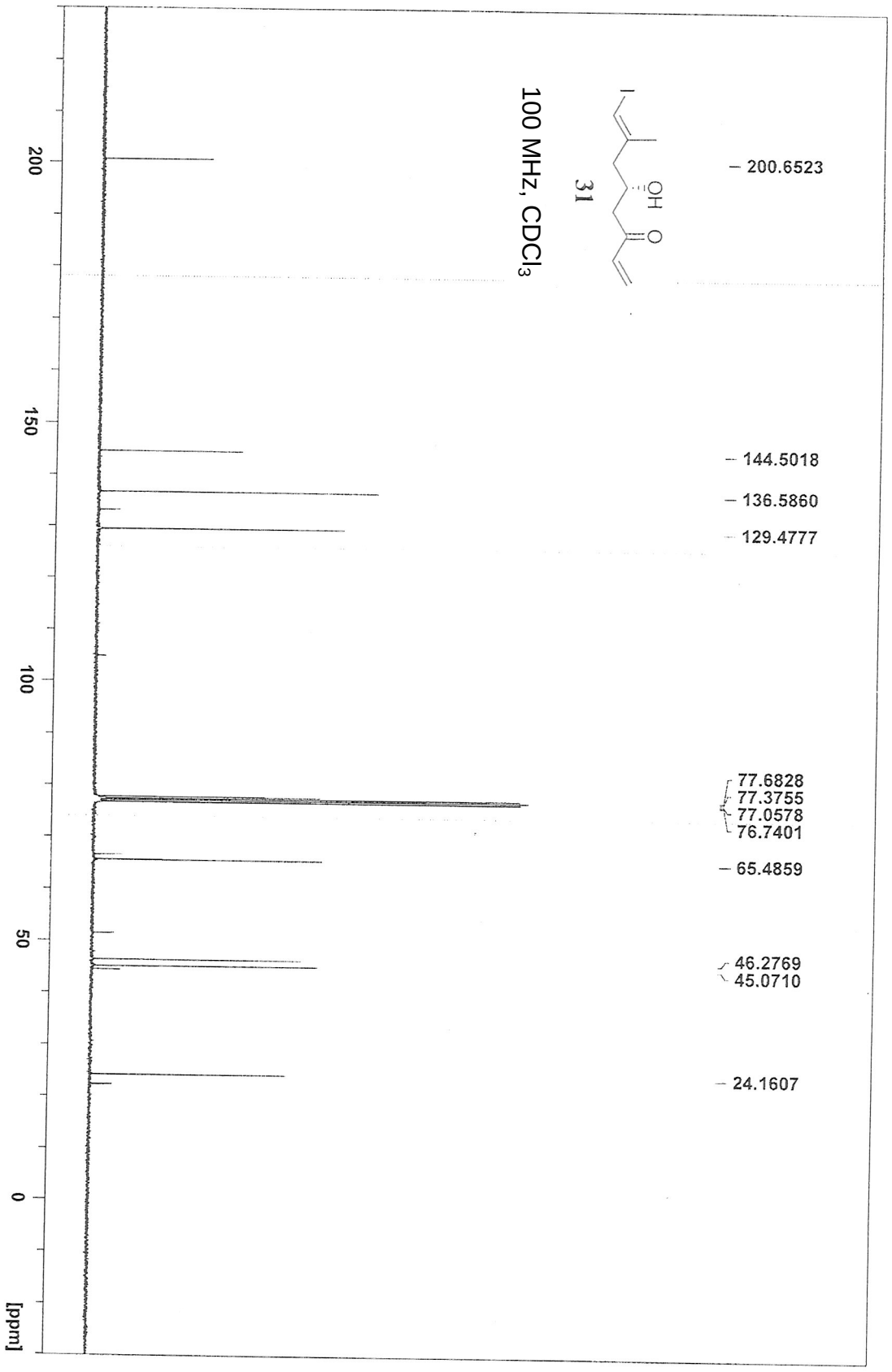

400 MHz, CDCl3
TES TBS
OH
1.1480
2.0000
1.9773
1.0451
0.9389
1.9699
4.3747
3.3366
18.5087
6.2916
6.2736
5
4
3
2
1
- 0 [ppm]

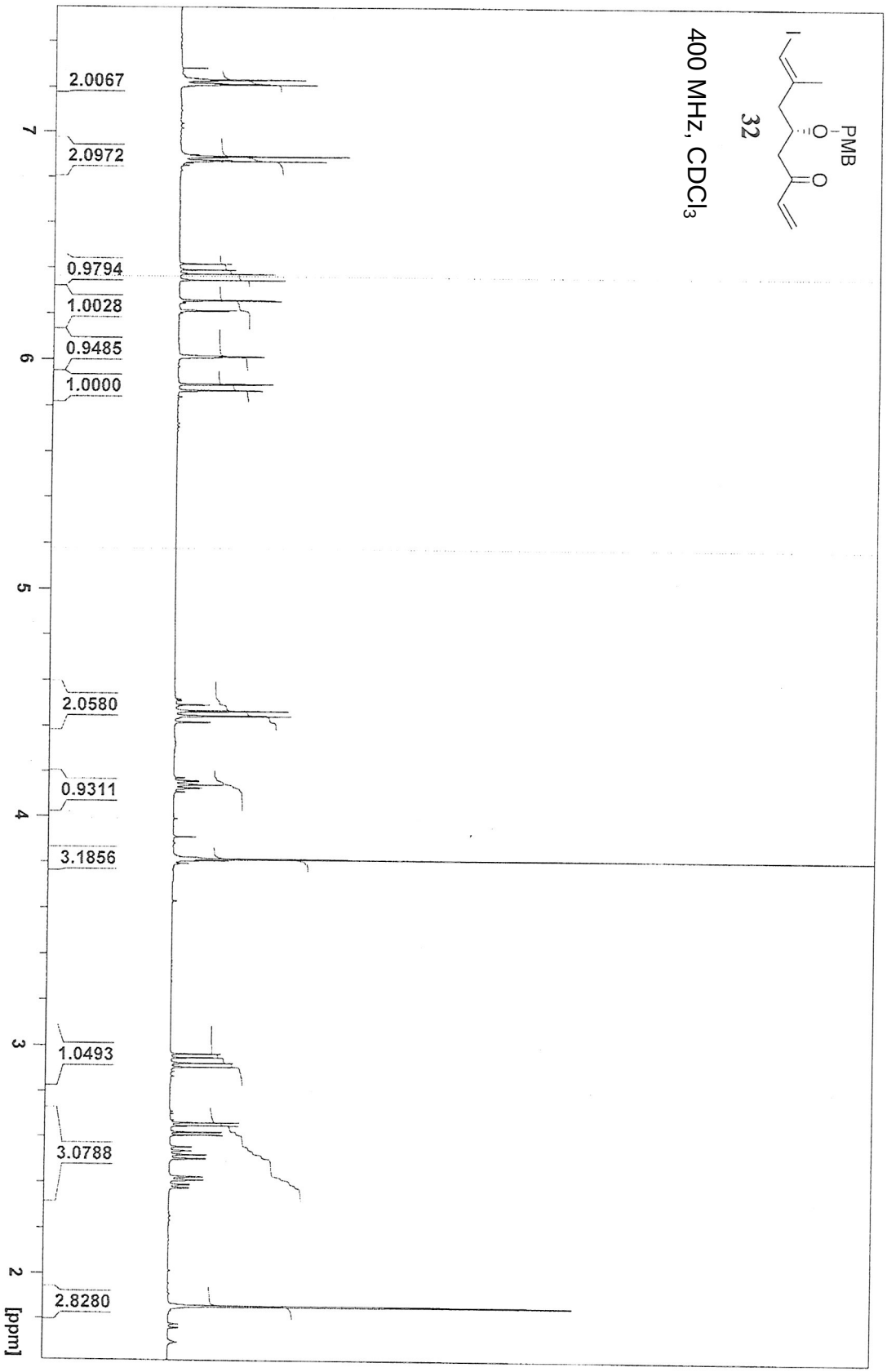

100 MHz, CDCl3
OH
TES
TBS
135.0031
117.3343
77.3427
77.0251
76.7076
69.4993
67.8721
66.3504
46.6926
42.3513
41.5188
25.8980
24.0453
18.0930
6.8387
4.9041
-4.0528
-4.4895
140
120
100
80
60
40
20
0
[ppm]

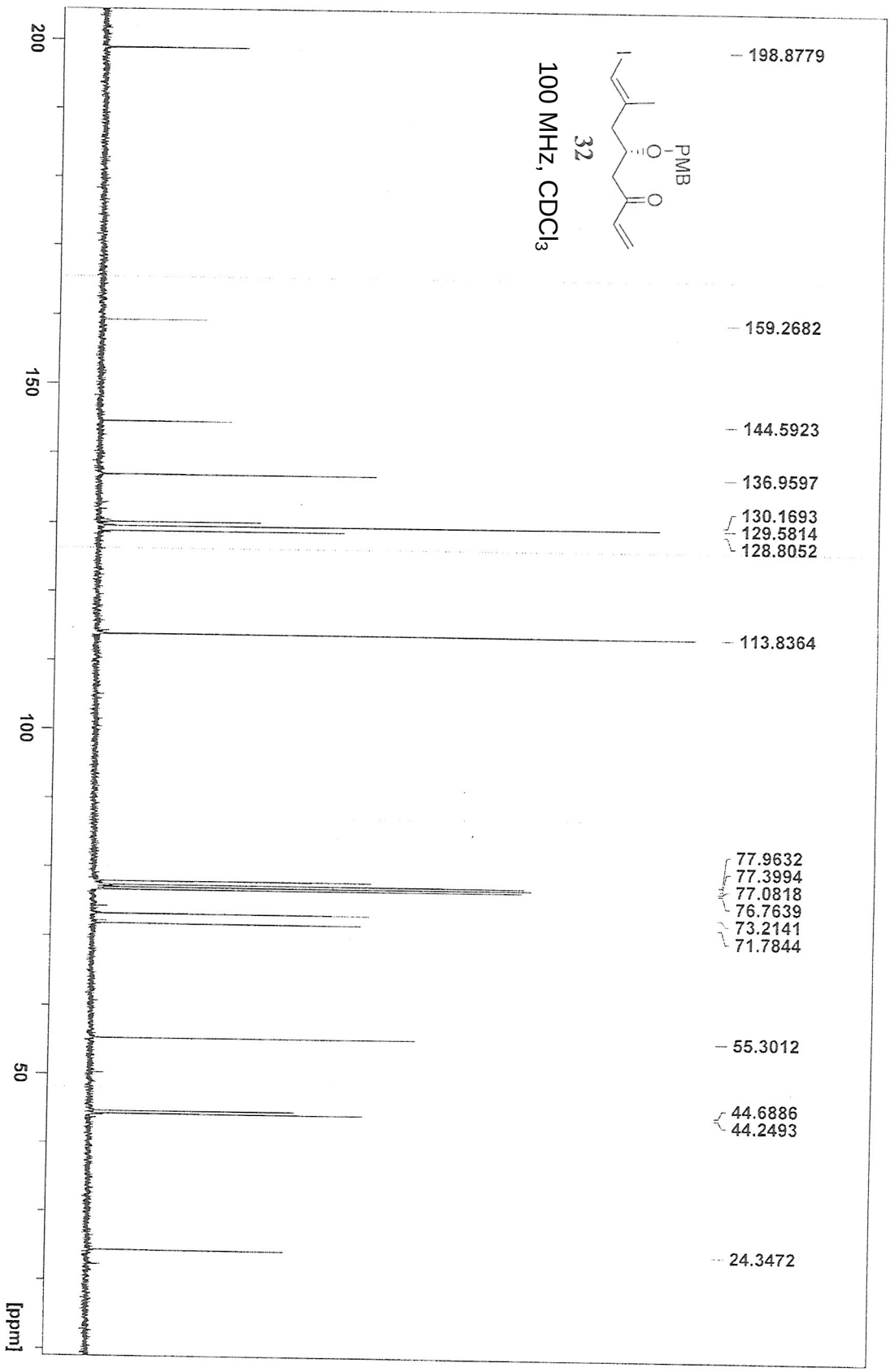

TBS TES TBS
29
400 MHz, CDCl3
1.0000
2.0256
1.0852
1.9832
2.0810
4.8608
3.1755
53.8864
7.0607
28.5765
[ppm]

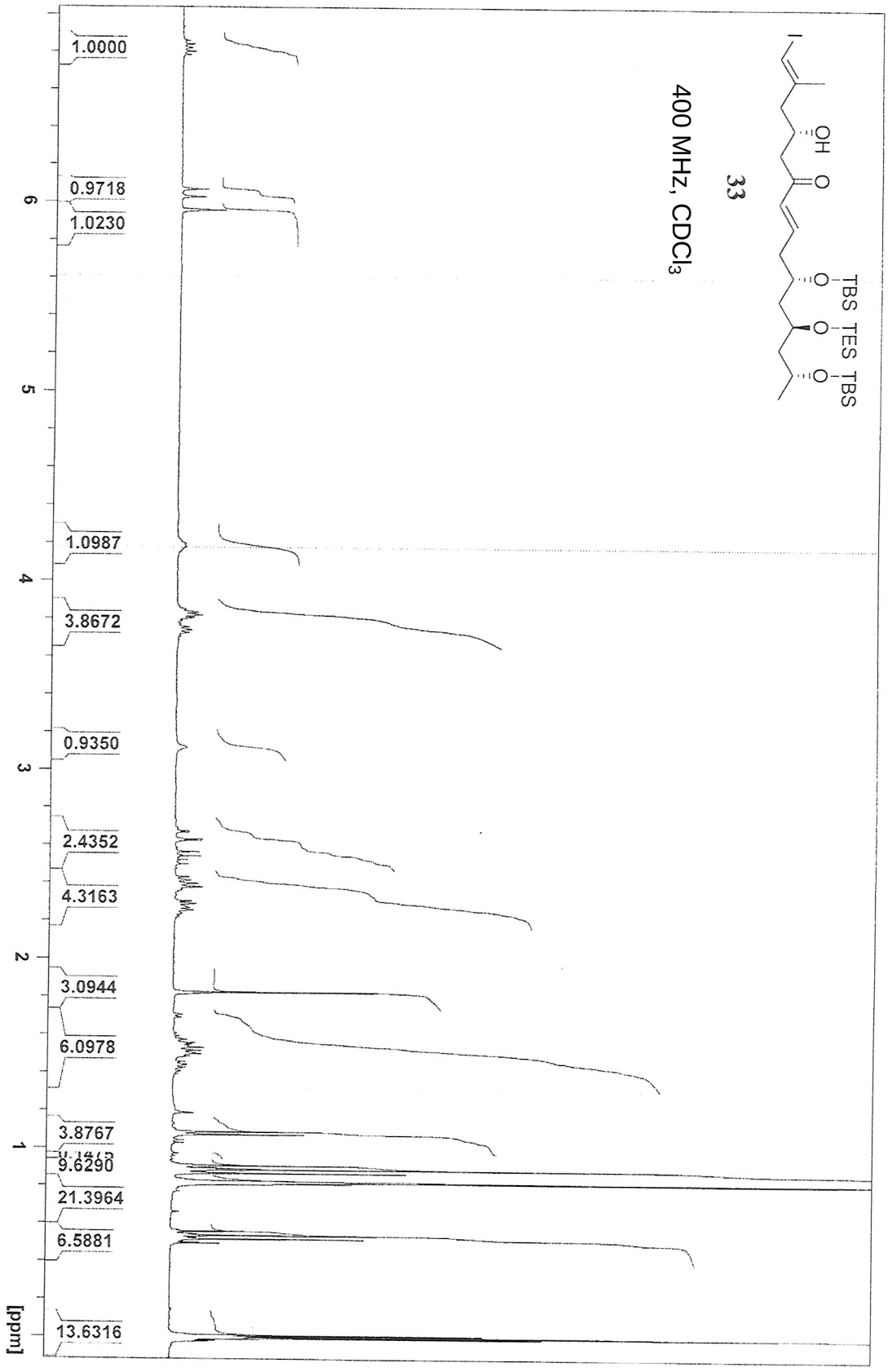

29
100 MHz, CDCl3
TBS TES TBS
134.9685
116.9093
77.3190
77.0015
76.6840
69.3899
67.7039
65.9651
48.4735
45.6852
42.0625
25.9487
25.9047
25.7396
25.7008
24.3828
18.1260
18.0875
6.8004
6.4212
6.3413
-2.8513
-2.9483
-3.6201
-3.9614
-4.1198
-4.3147
-4.4720
140
120
100
80
60
40
20
0
[ppm]

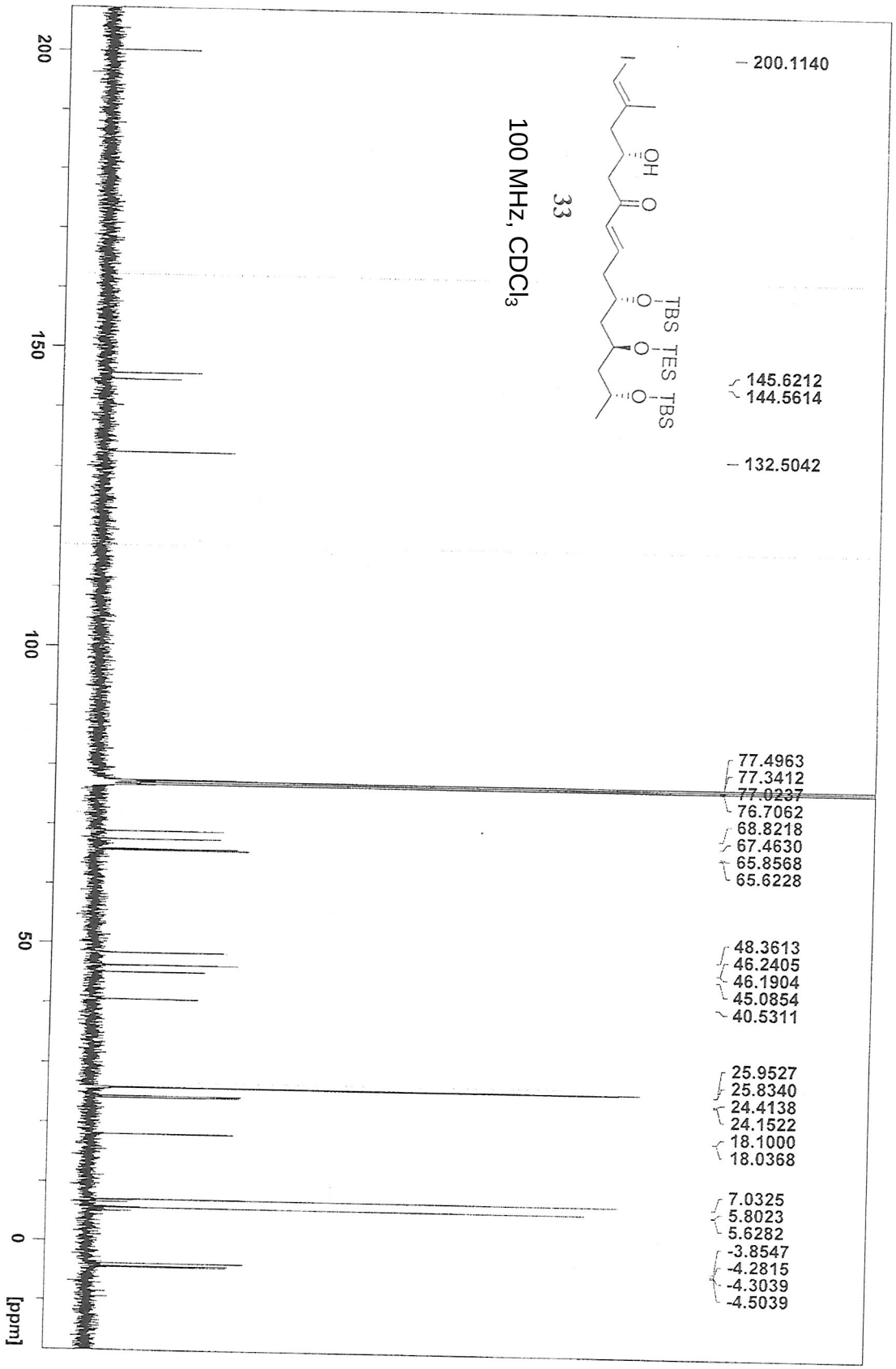

31
400 MHz, CDCl3
2.1564
1.0000
1.0833
1.0044
0.8144
2.5741
2.1676
2.9863
6
5
4
3
2
[ppm]

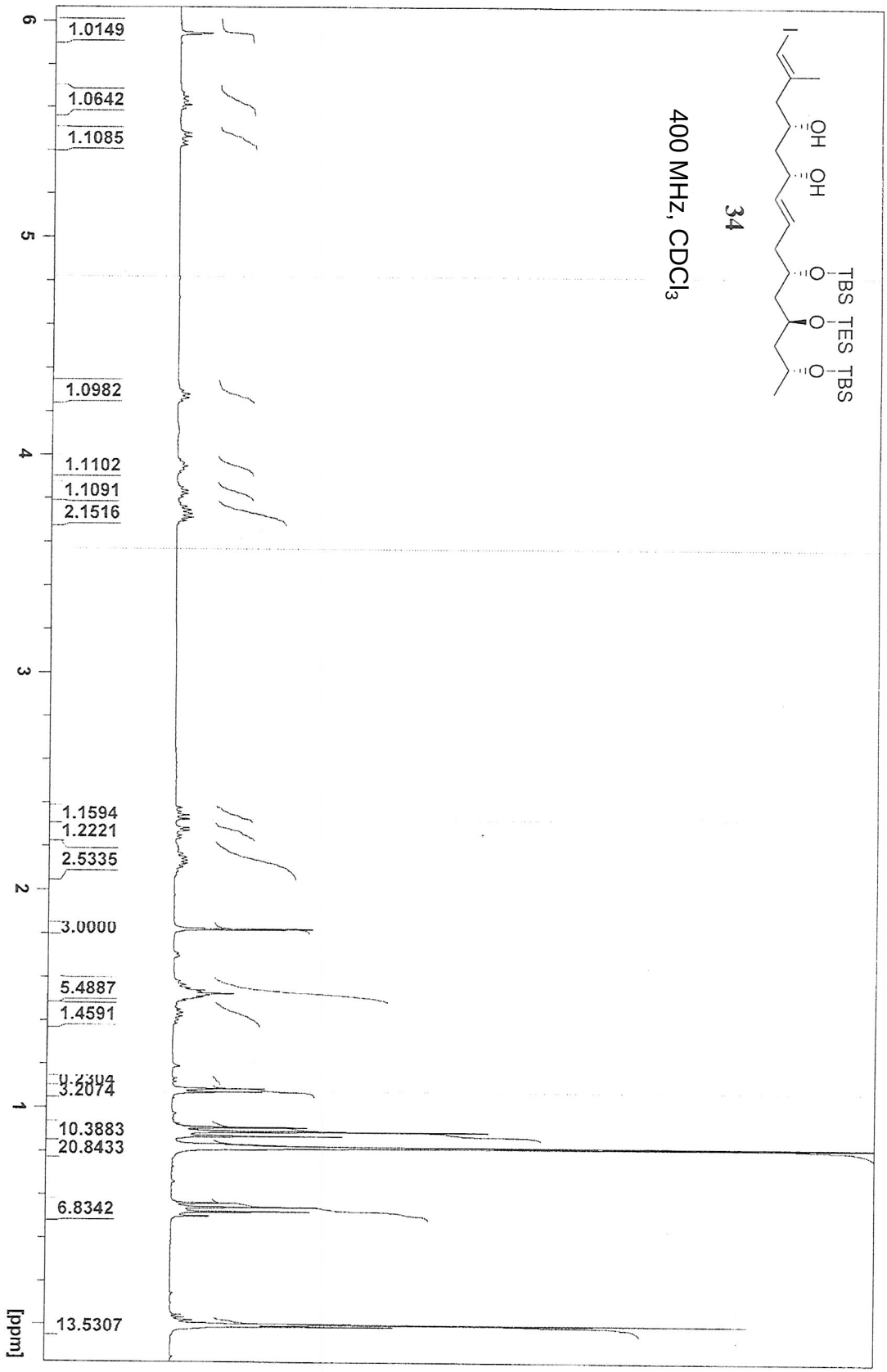

100 MHz, CDCl3
31
OH
O
200.6523
144.5018
136.5860
129.4777
77.6828
77.3755
77.0578
76.7401
65.4859
46.2769
45.0710
24.1607
200
150
100
50
0
[ppm]

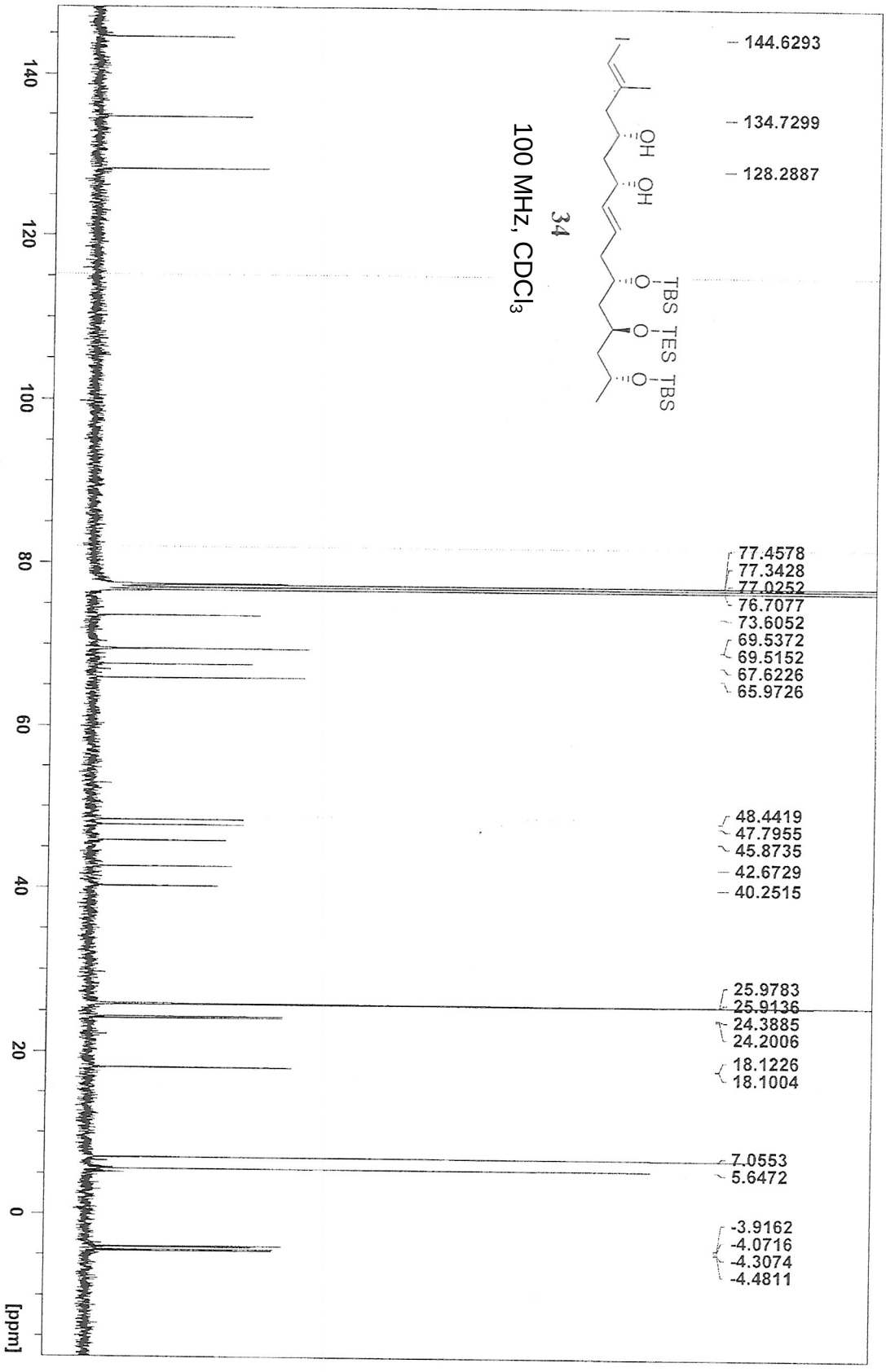

PMB
O
O
O
I
32
400 MHz, CDCl3
2.0067
2.0972
0.9794
1.0028
0.9485
1.0000
2.0580
0.9311
3.1856
1.0493
3.0788
2.8280
7
6
5
4
3
2
[ppm]

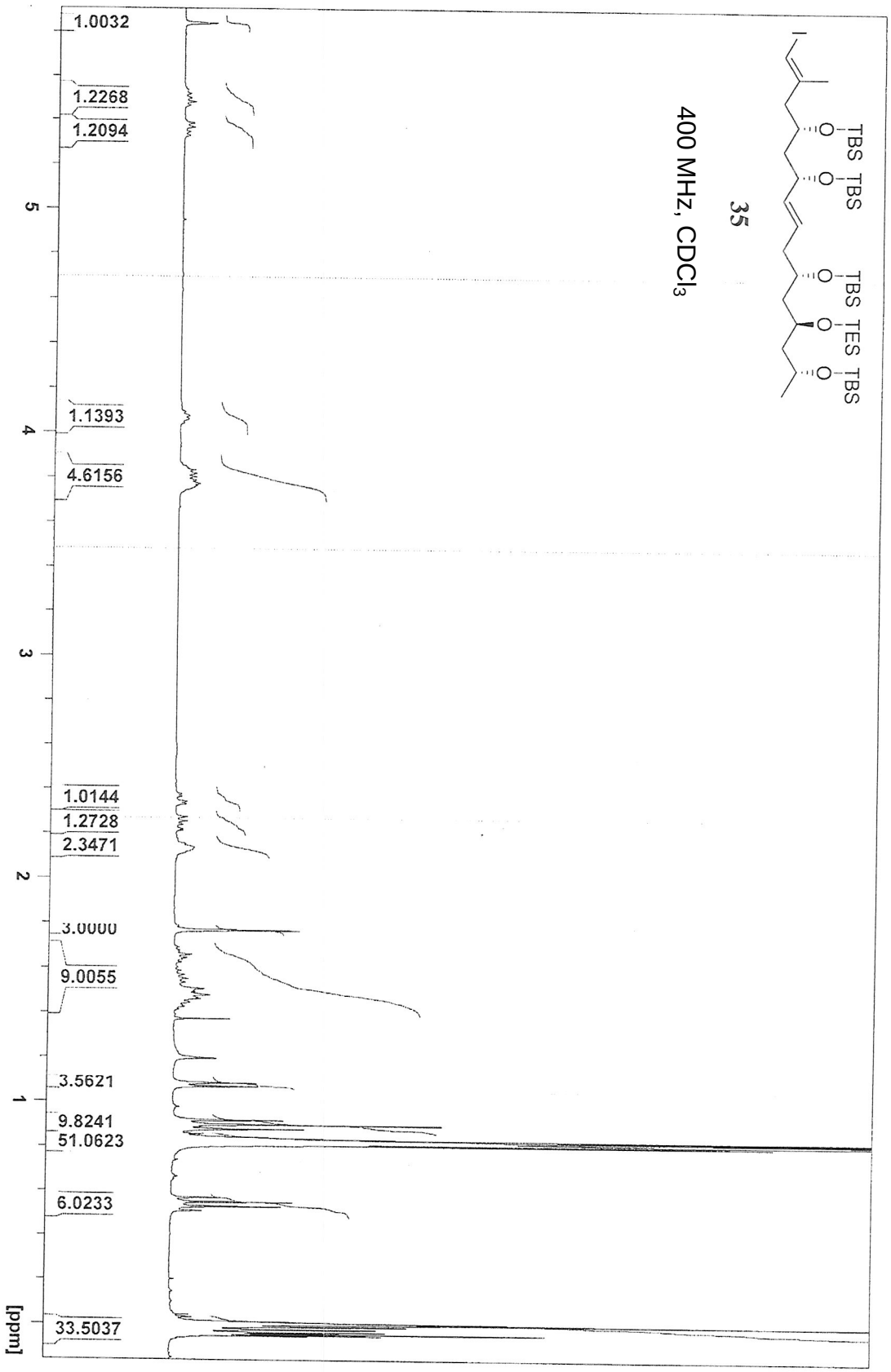

32
100 MHz, CDCl3
PMB
O
O
O
198.8779
159.2682
144.5923
136.9597
130.1693
129.5814
128.8052
113.8364
77.9632
77.3994
77.0818
76.7639
73.2141
71.7844
55.3012
44.6886
44.2493
24.3472
200
150
100
50
[ppm]

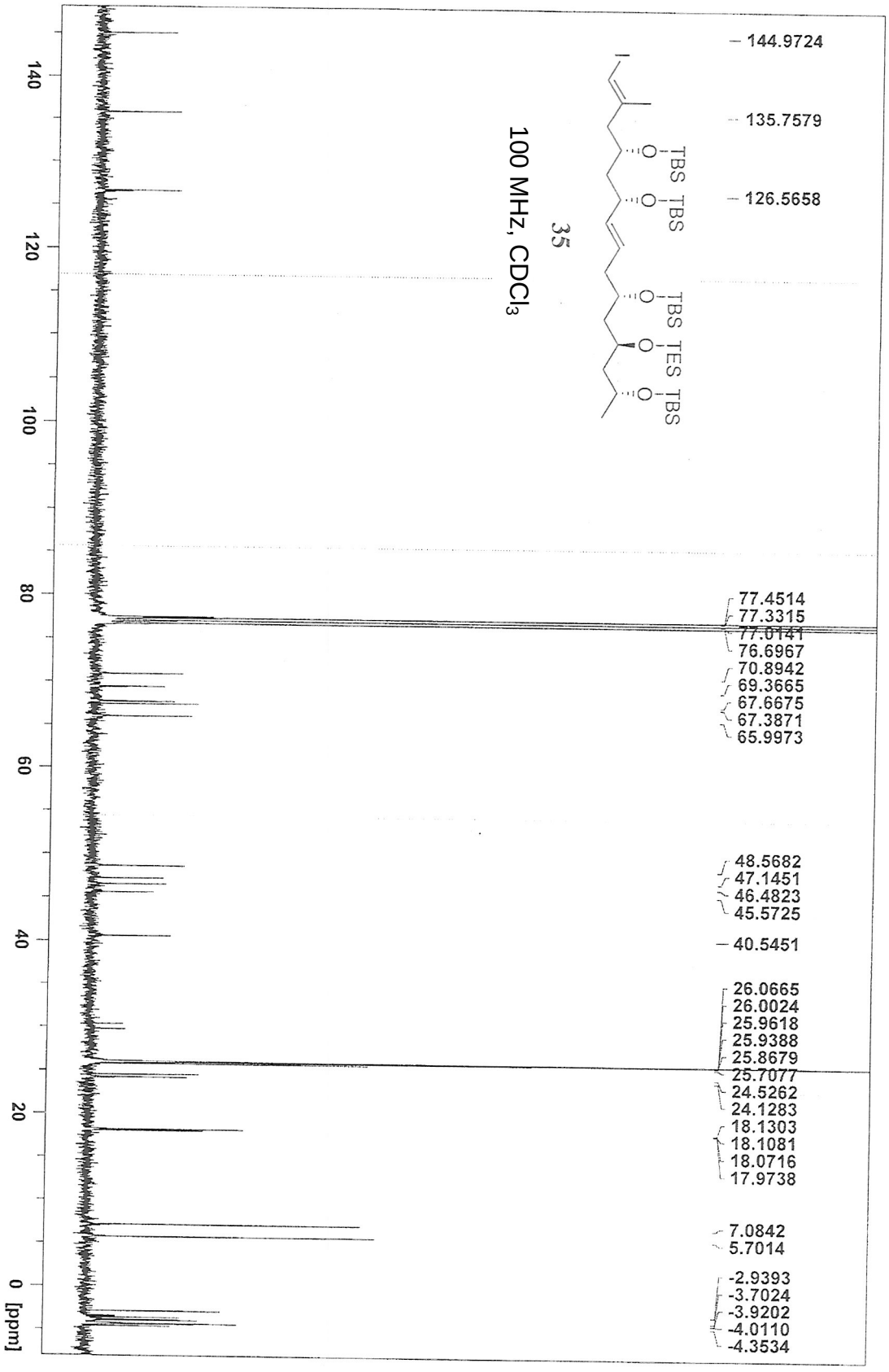

33
400 MHz, CDCl3
TBS TES TBS
OH O
I
1.0000
0.9718
1.0230
1.0987
3.8672
0.9350
2.4352
4.3163
3.0944
6.0978
3.8767
9.6290
21.3964
6.5881
13.6316
[ppm]

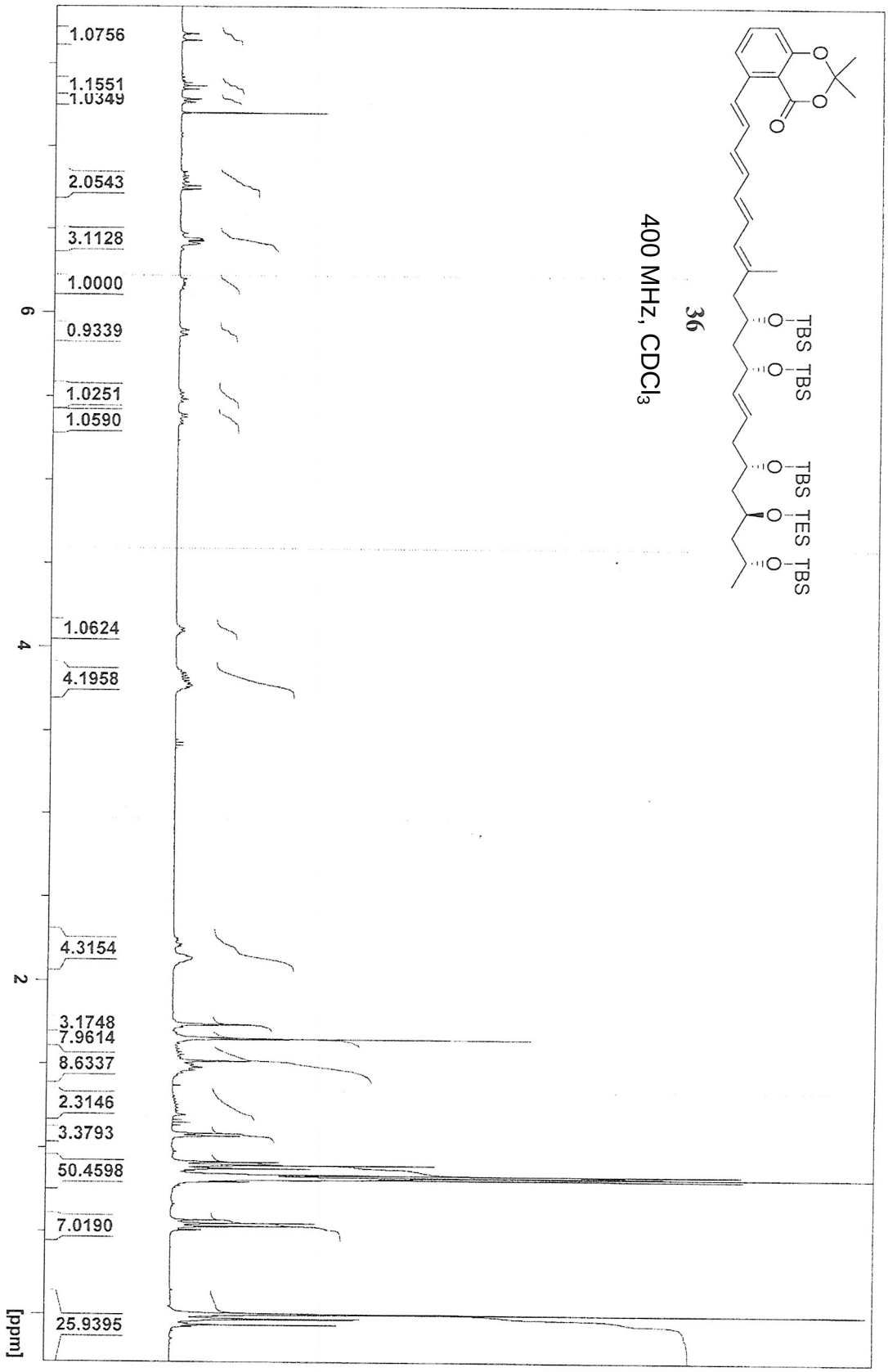

33
100 MHz, $CDCl_3$
200.1140
145.6212
144.5614
132.5042
77.4963
77.3412
77.0237
76.7062
68.8218
67.4630
65.8568
65.6228
48.3613
46.2405
46.1904
45.0854
40.5311
25.9527
25.8340
24.4138
24.1522
18.1000
18.0368
7.0325
5.8023
5.6282
-3.8547
-4.2815
-4.3039
-4.5039
200
150
100
50
0
[ppm]

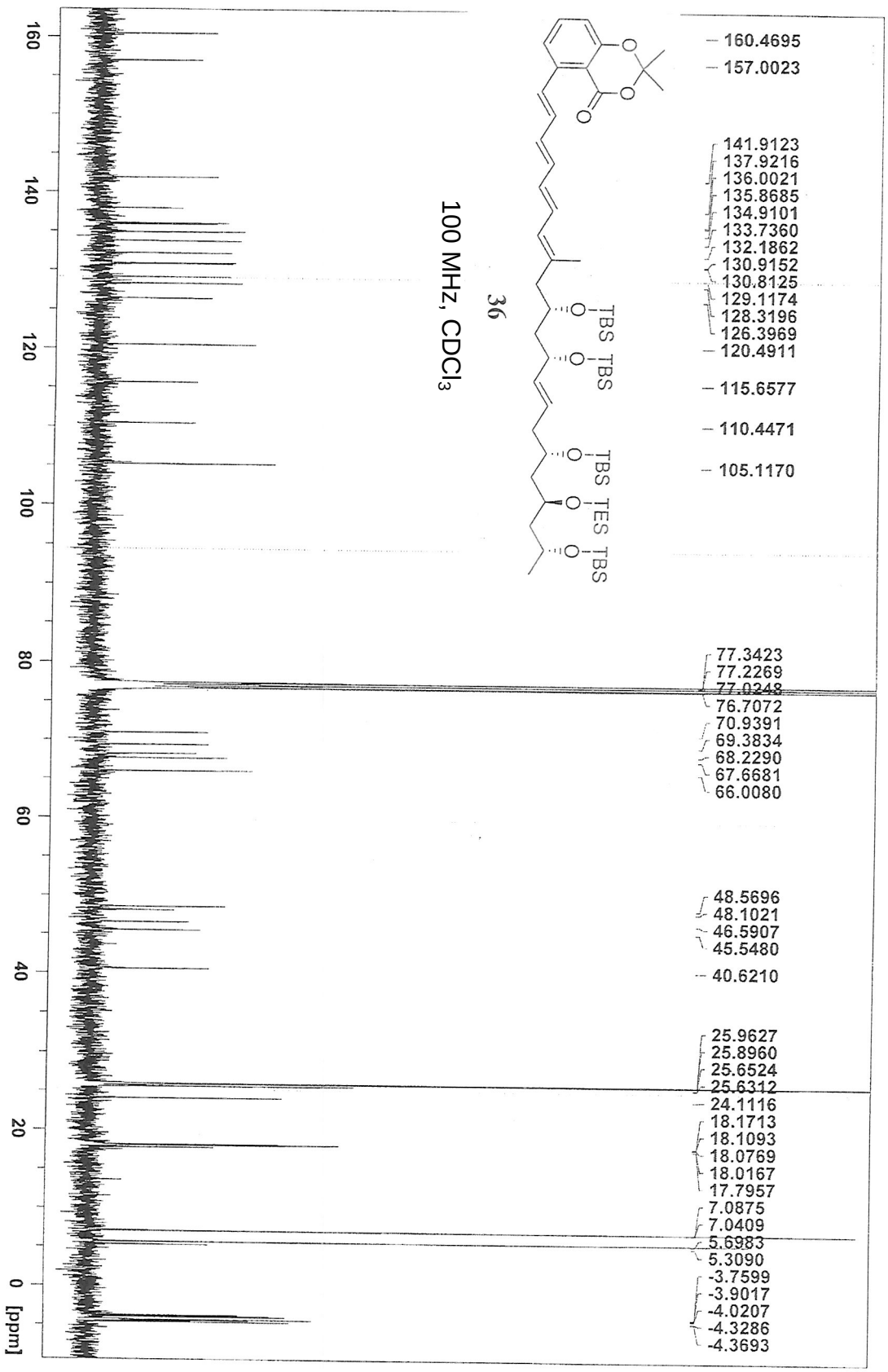

34
400 MHz, CDCl3
TBS TES TBS
OH OH
I
1.0149
1.0642
1.1085
1.0982
1.1102
1.1091
2.1516
1.1594
1.2221
2.5335
3.0000
5.4887
1.4591
3.2074
10.3883
20.8433
6.8342
13.5307
[ppm]


34
100 MHz, CDCl3
OH
OH
TBS
TES
TBS
144.6293
134.7299
128.2887
77.4578
77.3428
77.0252
76.7077
73.6052
69.5372
69.5152
67.6226
65.9726
48.4419
47.7955
45.8735
42.6729
40.2515
25.9783
25.9136
24.3885
24.2006
18.1226
18.1004
7.0553
5.6472
-3.9162
-4.0716
-4.3074
-4.4811
140
120
100
80
60
40
20
0
[ppm]


35
400 MHz, CDCl3
TBS TBS
TBS TES TBS
1.0032
1.2268
1.2094
1.1393
4.6156
1.0144
1.2728
2.3471
3.0000
9.0055
3.5621
9.8241
51.0623
6.0233
33.5037
[ppm]


35
100 MHz, CDCl3
TBS
TBS
TBS
TES
TBS
144.9724
135.7579
126.5658
77.4514
77.3315
77.0141
76.6967
70.8942
69.3665
67.6675
67.3871
65.9973
48.5682
47.1451
46.4823
45.5725
40.5451
26.0665
26.0024
25.9618
25.9388
25.8679
25.7077
24.5262
24.1283
18.1303
18.1081
18.0716
17.9738
7.0842
5.7014
-2.9393
-3.7024
-3.9202
-4.0110
-4.3534
140
120
100
80
60
40
20
0
[ppm]

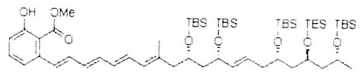

1.0756
1.1551
1.0349
2.0543
3.1128
1.0000
0.9339
1.0251
1.0590
1.0624
4.1958
4.3154
3.1748
7.9614
8.6337
2.3146
3.3793
50.4598
7.0190
25.9395
6
4
2
[ppm]
TBS TBS
TBS TES TBS
36
400 MHz, CDCl3



36

100 MHz, $CDCl_3$

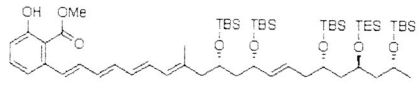
DA-mono-2



37

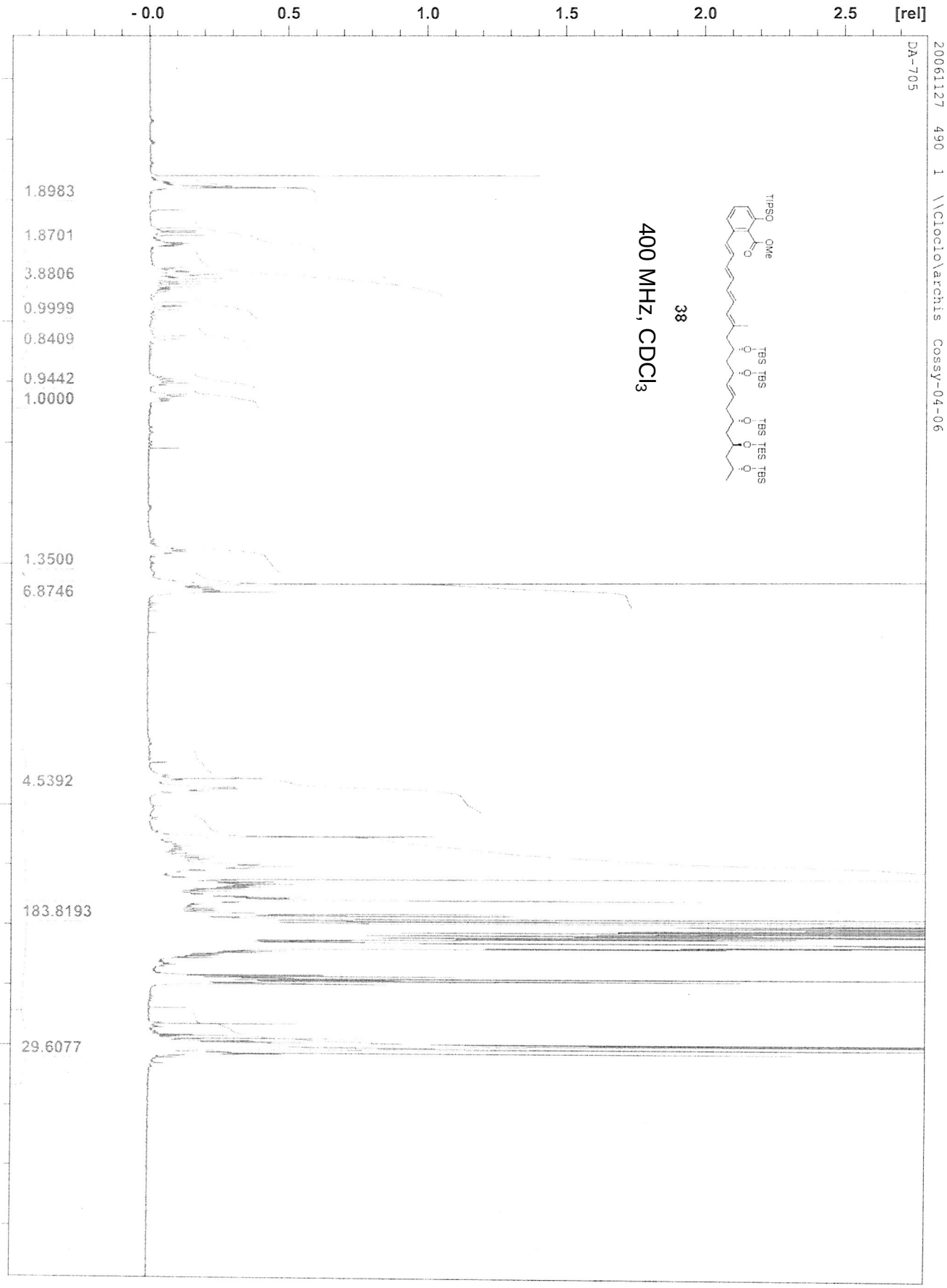
400 MHz, $CDCl_3$

DA-mono-2

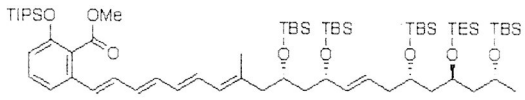


37

100 MHz, $CDCl_3$


- 0.0
0.5
1.0
1.5
2.0
2.5
[rel]
DA-705
20061127 490 1 \\Cloclo\archis Cossy-04-06
1.8983
1.8701
3.8806
0.9999
0.8409
0.9442
1.0000
1.3500
6.8746
4.5392
183.8193
29.6077
8
6
4
2
0
[ppm]
38
400 MHz, CDCl3
TIPSO
OMe
TBS
TBS
TBS
TES
TBS

DA-705



38

100 MHz, $CDCl_3$