Supporting Information

Synthesis of the C17-C30 Fragment of Amphidinol 3.

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General Methods

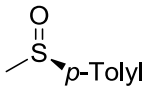
Experimental Procedures and Spectroscopic and Analytical Data of the Products

Note:

Reagents and solvents were purchased as reagent grade and used without further purification. THF was distilled over sodium benzophenone ketyl. Dichloromethane was distilled over CaH_2 and acetonitrile over P_2O_5. Flash column chromatography (FC) was performed using silica gel 60 for preparative column chromatography (40–63 mm), unless specifically noted otherwise. Demetalled silica gel was prepared according to published procedure. [1]Thin Layer Chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} (otherwise stated), visualization by UV light or through staining with phosphomolybdic acid, $KMnO_4$ or Vanillin. Optical rotations were measured on a polarimeter with a sodium lamp and are reported as follows: α_D (*c* g/100 mL, solvent). NMR spectra (^1H and ^{13}C) were recorded on a 300 MHz or 400 MHz. Chemical shifts are reported in ppm with the solvent ($CDCl_3$) resonance as the δ 7.26 ppm (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, s ap=apparent singlet, mc=multiplet center, coupling constants Hz, integration). Carbon NMR (^{13}C NMR) spectra were also run at various field strengths as indicated. Spectra were recorded in $CDCl_3$ using residual undeuterated solvent (77 ppm) as an internal reference. Infra red (IR) spectra were recorded on a diamond ATR spectrometer using neat simples. Infra red frequencies are reported in wavenumbers (cm^{-1}), intensities were determined qualitatively and are reported as strong (s), medium (m) or weak (w). Solid Lewis acids were flamed-dried in the reaction flask under vacuum and under Argon before use.

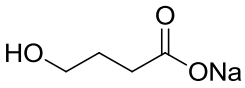
[1]Hubbard, J.S.; Harris, T.M.; *J. Org. Chem.* **1981**, *46*, 2566.

Synthesis of (+)-(*R*)-1-methyl-4-(methylsulfinyl)benzene[2]



A solution of methyl iodide (4.17 g, 29.4 mmol) in 26 mL of Et_2O was added slowly at room temperature to magnesium (650 mg, 26.7 mmol) and stirred at room temperature for 2 h. The resulting mixture was transferred *via* transfer syringe to a solution of (-)-(1*R*,2*S*,3*R*,S_S)-menthyl-*p*-tolyl-sulfinate[2] (6.56 g, 22.3 mmol) in 26 mL of toluene at 0 °C. After the addition, the mixture is stirred at room temperature for 3 h and then hydrolyzed with aqueous saturated solution of NH_4Cl (30 mL). The aqueous phase is extracted with Et_2O (3x30 mL) and the combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was crystallized in hot petroleum ether and overnight storage at -10 °C. After filtration, the mother liquid was subsequently purified by flash chromatography on silica gel (Et_2O → EtOAc) giving the (+)-(*R*)-1-methyl-4-(methylsulfinyl)benzene as white crystals (2.84 g, 18.41 mmol, 83%): m.p. 72 - 74 °C; $[\alpha]^{25}_D$ +197.2° (c = 1.03 in $CHCl_3$); R_f: 0.36 (EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (A_2B_2, J_{AB} = 8.1 Hz, $\Delta\nu$ = 62.9 Hz, 4H), 2.68 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4, 141.4, 129.9, 123.4, 43.9, 21.3; IR 3052, 3020, 2997, 2907, 1595, 1494, 1455, 1422, 1398, 1387, 1299, 1209, 1178, 1104, 1087, 1046, 1013, 970, 947, 848, 815, 707, 686 cm^{-1}.

Synthesis of sodium 4-hydroxybutanoate 3[3]



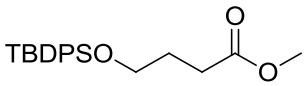
Sodium hydroxide (7.57 g, 0.19 mol) was dissolved in 112 mL of EtOH at room temperature and stirred for 30 min, prior to the addition of δ-butyrolactone (16.0 g, 0.19 mol). The resulting mixture was stirred for 2 h at room temperature, while a white precipitate has been formed. The solution was concentrated under reduced pressure and the resultant white solid was suspended in 300 mL of benzene and heated for 2 h using a Dean Stark device to remove traces of water. After evaporation of the solvent the white solid was dried under reduced pressure. Recrystallization of the crude product in EtOH furnished sodium salt **3** (22.2 g, 0.176 mol, 95%) as white crystals: ^{1}H NMR (300 MHz, D_2O) δ 3.58 (t, J = 6.7 Hz, 2H), 2.22 (t, J = 7.6 Hz, 2H), 1.78 (q, J = 7.0 Hz, 2H); ^{13}C NMR (75 MHz) (D_2O) δ 183.7, 62.1, 34.7,

[2] Solladié, G.; Hutt, J.; Girardin, A.; *Synthesis*, **1987**, 173.

[3] Weber, A.E.; Halgren, T.A.; Doyle, J.J.; Lynch, R.J.; Siegl, P.K.S.; Parsons, W.H.; Greenlee, W.J.; Patchett, A.A.; *Journal of Medicinal Chemistry*, **1991**, *34*, 2692.

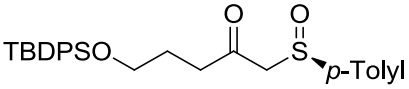
29.0; IR 3318, 2960, 2944, 2878, 1555, 1475, 1450, 1437, 1407, 1361, 1329, 1248, 1273, 1228, 1173, 1157, 1066, 1052, 1015, 946, 920, 881, 869, 775, 751, 697cm^{-1}.

Synthesis of methyl 4-(*tert*-butyldiphenylsilyloxy) butanoate 4[4]



Iodomethane (6.5 mL, 104.13 mmol) in 12 mL of dry DMF was added to a stirred solution of sodium 4-hydroxybutanoate **3** (2.02 g, 16.02 mmol) in 44 mL of DMF. The resulting solution was stirred for 24 h prior to the addition of imidazole (2.40 g, 35.2 mmol) and *tert*-butyldiphenylchlorosilane (5.28 g, 19.2 mmol). Stirring was continued for 16 h, and the mixture was diluted with 100 mL of EtOAc, washed subsequently with distilled water, aqueous saturated $Na_2S_2O_3$ and brine (40 mL each), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/10) to afford the protected ester **4** as a colorless oil (5.18 g, 14.52 mmol, 91%): R_f 0.60 (EtOAc/Cyclohexane: 1/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-7.71 (m, 4H), 7.37-7.47 (m, 6H), 3.71 (t, *J* = 6.1 Hz, 2H), 3.67 (s, 3H), 2.49 (t, *J* = 7.5 Hz, 2H), 1.87-1.96 (m, 2H), 1.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 135.5, 133.7, 129.6, 127.6, 62.8, 51.4, 30.6, 27.76, 26.8, 19.2; IR 3072, 3051, 2953, 2932, 2858, 1738, 1590, 1473, 1463, 1428, 1390, 1362, 1256, 1192, 1168, 1105, 998, 967, 822, 738, 700, 688cm^{-1}.

Synthesis of (*R*)-5-(*tert*-butyldiphenylsilyloxy)-1-(*p*-tolylsulfinyl)pentan-2-one 5

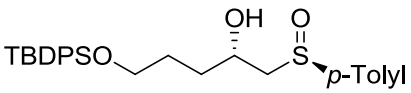


To a solution of diisopropylamine (1.59 mL, 11.35 mmol) in 15 mL of THF cooled at -78 °C was added dropwise *n*-BuLi (6.48 mL, 1.60 M in hexane, 10.37 mmol). The resulting solution was stirred for 1 h at -78 °C, prior to the addition of a solution of (+)-(*R*)-1-methyl-4-(methylsulfinyl)benzene (1.52 g, 9.87 mmol) in 12 mL of THF at -78 °C. After stirring for 1 h at -78 °C, the anion solution was transferred *via* transfer syringe to a -78 °C cold solution of the ester **4** (1.76 g, 4.94 mmol) in 18 mL of THF and stirred for 1 h. The reaction mixture was then diluted with 20 mL of Et_2O, hydrolyzed with aqueous saturated NH_4Cl (20 mL) and washed with brine (20 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on demetalled silica gel (Et_2O) to furnish the ß-ketosulfoxyde **5** as a colorless

[4]Clive, D.L.J.; Zhang, J.; *Tetrahedron*, **1999**, *55*, 12059.

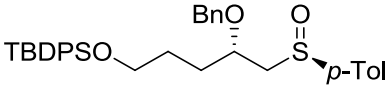
oil (2.34 g, 4.89 mmol, 99%): $[\alpha]^{25}_{D}$ +90.6° (c = 1.43 in $CHCl_3$) and recovered 40% of the excess of (+)-(*R*)-1-methyl-4-(methylsulfinyl)benzene, R_f 0.63 (Et_2O), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.64 (m, 4H), 7.52 (B of A_2B_2, J_{AB} = 8.1 Hz, Δ*v* = 63.3 Hz, 2H), 7.35-7.45 (m, 6H), 7.31 (A of A_2B_2, J_{AB} = 8.1 Hz, Δ*v* = 63.3 Hz, 2H), 3.79 (AB, J_{AB} = 13.5 Hz, Δ*v* = 34.7 Hz, 2H), 3.63 (t, *J* = 6.1 Hz, 2H), 2.49-2.68 (m, 2H), 2.40 (s, 3H), 1.74-1.83 (m, 2H), 1.04 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.4, 142.1, 139.8, 135.5, 133.6, 130.0, 129.6, 127.7, 124.01, 68.2, 62.7, 41.5, 26.9, 26.1, 21.5, 19.2; IR 2931, 2858, 1712, 1590, 1494, 1472, 1428, 1390, 1362, 1110, 1056, 963, 823, 810, 741, 705, 688cm^{-1}; HRMS ES *m/z* $(M+Li)^+$Calcd for $C_{28}H_{34}LiO_3SSi$ 485.2152, found 485.2100.

Synthesis of (*S*)-5-(*tert*-butyldiphenylsilyloxy)-1-((*R*)-*p*-tolylsulfinyl)pentan-2-ol 6



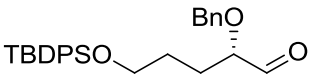
To a solution of ß-ketosulfoxyde **5** (614 mg, 1.28 mmol) in 10 mL of THF cooled at -78 °C was added dropwise DIBAL-H (1.60 mL, 1.0 M in toluene, 1.60 mmol). The resulting solution was stirred for 5 h at -78 °C, quenched with 2 mL of MeOH, diluted with 10 mL of EtOAc, hydrolyzed with an aqueous saturated solution of sodium-potassium tartrate (10 mL) and stirred overnight until a clear phase-separation occurred. The aqueous phase was extracted with EtOAc (3x20 mL) and the combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on demetalled silica gel (EtOAc/cyclohexane: 1/1) gave the ß-hydroxysulfoxyde **6** as a colorless oil (611 mg, 1.27 mmol, 99%): $[\alpha]^{25}_{D}$: +120.0° (c = 1.15 in $CHCl_3$); R_f 0.37 (EtOAc/Cyclohexane: 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.66 (m, 4H), 7.51-7.53 (m, 2H), 7.32-7.45 (m, 8H), 4.17-4.24 (m, 1H), 3.61-3.69 (m, 2H), 2.85 (AB of ABX, J_{AB} = 13.4 Hz, J_{AX} = 9.8 Hz, J_{BX} = 2.0 Hz, Δ*v* = 102.9 Hz, 2H), 2.42 (s, 3H), 1.54 - 1.68 (m, 4H), 1.03 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 139.9, 135.55, 135.5, 133.65, 133.6, 130.1, 130.0, 129.6, 127.6, 124.0, 124.0, 66.6, 63.8, 61.7, 34.0, 28.3, 26.8, 21.4, 19.2; IR 3365, 2930, 2858, 1472, 1428, 1390, 1110, 1085, 1027, 1010, 908, 823, 807, 729, 700, 687 cm^{-1}; HRMS ES *m/z* $(M+Li)^+$ Calcd for $C_{28}H_{36}LiO_3SSi$ 487.2310, found 487.2274.

Synthesis of ((*S*)-4-(benzyloxy)-5-((*R*)-*p*-tolylsulfinyl)pentyloxy)(*tert*-butyl)diphenylsilane 7



A solution of alcohol **6** (958 mg, 1.99 mmol) in 5 mL of THF was added dropwise at 0 °C to a solution of (96 mg, 3.99 mmol) oil-free sodium hydride in 20 mL of THF. The reaction mixture was stirred for 30 min, prior to the addition of (592 µl, 4.98 mmol) benzyl bromide. After 30 min at 0 °C and 3 h at room temperature the resulting solution was carefully hydrolyzed by adding 5 mL of an aqueous saturated solution of NH_4Cl. The aqueous layer was extracted with EtOAc (3x20 mL) and the combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 2/5) to give the benzylether **7** (854 mg, 1.49 mmol, 75%) as a colorless oil: $[\alpha]^{25}_D$ +91.2° (c = 1.43 in $CHCl_3$); R_f 0.60 (EtOAc/Cyclohexane: 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.67 (m, 4H), 7.46-7.47 (m, 2H), 7.27-7.43 (m, 13H), 4.67 (AB, J_{AB} = 11.0 Hz, Δν = 11.5 Hz, 2H), 4.07-4.14 (X of ABX, m, 1H), 3.65 (t, *J* = 6.1 Hz, 2H), 2.82-2.91 (AB of ABX, m, 2H), 2.42 (s, 3 H), 1.52-1.85 (m, 4 H), 1.04 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.6, 141.3, 138.0, 135.5, 133.8, 130.0, 129.6, 128.4, 128.1, 127.8, 127.6, 123.8, 73.2, 72.3, 64.6, 63.6, 30.2, 27.6, 26.9, 21.4, 19.2; IR 2930, 2857 , 1494, 1472, 1455, 1428, 1105, 1086, 1045, 1016, 998, 938, 822, 807, 738, 699cm^{-1}; HRMS ES *m/z* $(M+Na)^+$ Calcd for $C_{35}H_{42}NaO_3SSi$ 593.2516, found 593.2472.

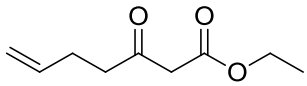
Synthesis of (*S*)-2-(benzyloxy)-5-(*tert*-butyldiphenylsilyloxy)pentanal 8



To a solution of sulfoxyde **7** (850 mg, 1.49mmol) in 12 mL of MeCN cooled at 0 °C was added dropwise subsequently 2,4,6-collidine (595 µl, 4.47 mmol) and trifluoroacetic anhydride (1.04 mL, 7.45 mmol). The reaction mixture was stirred 30 min, prior to the addition of 12 mL of an aqueous saturated solution of $NaHCO_3$, warmed to room temperature and stirred for 1 h at this temperature. The aqueous layer was extracted with EtOAc (3x15 mL) and the combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/9) gave the aldehyde **8** (585 mg, 1.31 mmol, 88%) as a colorless oil: $[\alpha]^{25}_D$ –30.6° (c = 1.03 in $CHCl_3$); R_f 0.46 (EtOAc/Cyclohexane: 1/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.65 (d, *J* = 2.0 Hz, 1H); 7.65-7.68 (m, 4H), 7.29-7.47 (m, 11H), 4.59 (AB, J_{AB} = 11.7 Hz, Δν = 41.7 Hz, 2H), 3.78 (ddd, *J* = 7.4 Hz, *J* = 5.2 Hz, *J* = 2.0 Hz, 1H), 3.64 (t, *J* = 6.0 Hz, 2H), 1.57-1.93 (m, 4H), 1.06 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.5, 137.3, 135.5, 133.8, 129.6, 128.5, 128.0, 128.0, 127.6, 83.2, 72.4, 63.2, 27.7, 26.9, 26.419, 19.209; IR 2858, 1733, 1472, 1455, 1428, 1106, 1090,

1028, 1007, 998, 937, 823, 794, 738, 699 cm^{-1}, Anal. Calcd for $C_{28}H_{34}O_3Si$ C, 75.29; H, 7.67; Found: C, 75.23; H, 7.598.

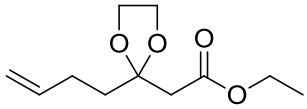
Synthesis of ethyl-3-oxohept-6-enoate[5]



To a stirred solution of 4 pentenoic acid **9** (6.0 g, 59.3 mmol) in THF (60 mL) was added portion wise carbonyldiimidazole (9.62 g, 59.3 mmol). The mixture was stirred 1 h at room temperature.

A solution of diisopropylamine (33.5 mL, 237.2 mmol) in THF (30 mL) was cooled to –78 °C and was subsequently treated with a solution of *n*-butyllithium (148.3 mL, 1.60 M in hexane, 237.2 mmol). After 30 min at –78 °C a solution of EtOAc (11.61 mL, 118.6 mmol) in 30 mL of THF was added dropwise. After 30 min at –78 °C this solution was added to the imidazolide solution cooled at -78 °C. After 15 min at -78 °C the reaction was warmed to room temperature and stirred 3 h. The reaction mixture was quenched with 300 mL of aqueous saturated solution of NH_4Cl. The mixture was extracted with Et_2O (2x200 mL) and the combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/9 → 2/8) yielding the *ß*-keto ester as a colorless oil (7.4 g, 43.68 mmol, 74%): R_f 0.47 (EtOAc/Cyclohexane: 1/3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.42-5.89 (m, 1 H), 5.04 (d, *J* = 17.1 Hz, 1 H), 5.00 (d, *J* = 9.3 Hz, 1 H), 4.21 (q, *J* = 7.2 Hz, 2 H), 3.44 (s, 2 H), 2.65 (d, *J* = 7.2 Hz, 2 H), 2.30-2.40 (m, 2 H), 1.28 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.8, 167.0, 136.4, 115.4, 61.2, 49.2, 41.9, 27.3, 14.0.

Synthesis of ethyl 3,3-ethylenedioxy-hept-6-enoate 10[6]

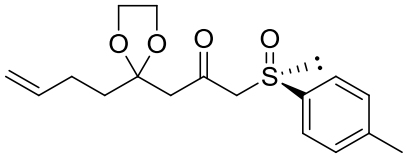


ß-keto ester (*vide supra*) (6.23 g, 36.6 mmol) was diluted in ethylene glycol (26.5 mL, 475.8 mmol) and treated subsequently at room temperature with triethyl orthoformate (15 mL, 91.5 mmol) and (±)-10-camphorsulfonic acid (860 mg, 3.7 mmol). The resulting mixture was stirred for 24 h, prior to addition of a $NaHCO_3$ saturated solution (100 mL). The aqueous layer was extracted with EtOAc (3x100 mL) and the combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel

[5] Vlattas, I.; Harrison, I.T.; Tokes, L.; Fried, J.H.; Cross, A.D.; *J. Org. Chem.*, **1968**, *33*, 4176.
[6] Baldwin, S.W.; Wilson, J.D.; Aube, J.; *J. Org. Chem.*, **1985**, *50*, 4432.

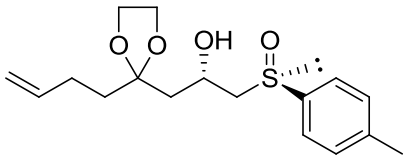
(EtOAc/Cyclohexane: 1/9) afforded acetal **10** as a colorless oil (7.56 g, 35.46 mmol, 97%): R_f 0.26 (EtOAc/Cyclohexane: 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.75-3.91 (m, 1H), 5.03 (dq, *J* = 18.0, *J* = 1.8 Hz, 1H), 4.95 (dq, *J* = 9.0, *J* = 1.5 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.93-4.05 (m, 4H), 2.66 (s, 2H), 2.12-2.23 (m, 2H), 1.88-1.96 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4, 138.1, 114.4, 109.0, 65.1, 60.5, 42.7, 36.8, 27.7, 14.1

Synthesis of 1-(2-but-3-enyl-1,3-dioxolan-2-yl)-3-((*R*)-p-tolylsulfinyl)propan-2-one



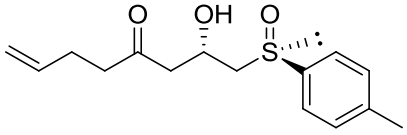
To a solution of diisopropylamine (6.4 mL, 45.4 mmol) in 50 mL of THF cooled at -78 °C was added dropwise *n*-BuLi (28.4 mL, 1.60 M in hexane, 45.4 mmol). The resulting solution was stirred for 1 h at -78 °C, prior to the addition of a solution of (+)-(*R*)-1-methyl-4-(methylsulfinyl)benzene (7.0 g, 45.4 mmol) in 40 mL of THF at -78 °C. After stirring for 1 h at -78 °C, a solution of ester **10** (4.31 g, 20.17 mmol) in 40 mL of THF was added dropwise. The reaction mixture was stirred for 5 h at –78 °C, hydrolyzed with an aqueous saturated solution of NH_4Cl (150 mL) and warmed to room temperature. The aqueous layer was extracted with EtOAc (3x100 mL) and the combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification of the crude by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/1→7/3) afforded the sulfoxide as a yellow oil (4.61g, 14.25 mmol, 72%): $[\alpha]^{25}_D$ +135.7° (c = 0.79 in $CHCl_3$); R_f 0.25 (EtOAc/Cyclohexane: 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.31 d, *J* = 7.8 Hz, 2H), 5.65-5.82 (m, 1H), 4.97 (dq, *J* = 17.1 Hz, *J* = 2.4 Hz, 1H), 4.91 (dq, *J* = 10.2 Hz, *J* = 2.7 Hz, 1H), 3.90-3.98 (m, 6H), 2.84 (AB, J_{AB} = 13.5 Hz, Δ*v* = 29.7 Hz, 2H), 2.40 (s, 3 H), 2.00-2.12 (m, 2 H), 1.63-1.72 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.2, 142.0, 139.7, 137.8, 130.0, 124.1, 114.6, 109.1, 69.0, 64.9, 51.8, 37.0, 27.5, 21.4; IR 2922, 1708, 1641, 1494, 1359, 1306, 1085, 1035, 950, 911, 809 cm^{-1}; HRMS ES *m/z* $(M+Li)^+$ Calcd for $C_{17}H_{22}LiO_4S$ 329.1394, found 329.1385

Synthesis of (S)-1-(2-but-3-enyl-1,3-dioxolan-2-yl)-3-((*R*)-p-tolylsulfinyl)propan-2-ol 11



Dibal-H (17 mL, 1.0 M in toluene, 17 mmol) was added dropwise to ß-ketosulfoxide (*vide supra*) (2.2 g, 6.83 mmol) dissolved in 100 mL of THF cooled at -78 °C. The resulting solution was stirred for 2 h at -78 °C, quenched with 20 mL of MeOH, diluted with 65 mL of EtOAc, hydrolyzed with a saturated sodium-potassium tartrate solution (65 mL) and stirred overnight. The aqueous phase was extracted with EtOAc (3x100 mL) and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/1→6/4) affording the ß-hydroxysulfoxyde **11** as a white solid (2.19 g, 6.75 mmol, 99%): $[\alpha]^{25}_D$ +206.7° (c = 1.00 in $CHCl_3$); R_f 0.46 (EtOAc/Cyclohexane: 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.69-5.85 (m, 1H), 4.99 (d, *J* = 18.3, 1H), 4.94 (d, *J* = 10.2, 1H), 4.42- 4.53, (m, 1H), 3.89-3.99 (m, 4H), 2.77-2.93 (m, 2 H), 2.41 (s, 3 H), 2.01-2.13 (m, 2 H), 1.82-1.89 (m, 2 H), 1.61-1.73 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 140.5, 137.8, 129.8, 123.7, 114.4, 110.7, 64.6, 64.5, 62.7, 42.6, 36.3, 27.7, 21.2; IR 3359, 2927, 1710, 1641, 1492, 1398, 1305, 1085, 1030, 911, 810cm^{-1}; HRMS ES *m/z* $(M+Na)^+$ Calcd for $C_{17}H_{24}NaO_4S$ 347.1288, found 347.1247.

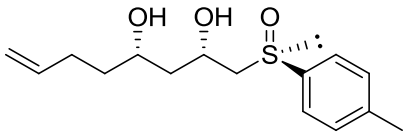
Synthesis of (2*S*)-2-Hydroxy-1((*R*)-p-tolylsulfinyl)-oct-7-en-4-one



Acetal **11** (1.09 g, 3.36 mmol) in 35 mL of acetone was treated with (±)-10-camphorsulfonic acid (170 mg, 0.73 mmol). The reaction was stirred 24 h and diluted with 20 mL of CH_2Cl_2. The organic phase was washed with a saturated $NaHCO_3$ solution (2x10 mL). The aqueous phase was extracted with CH_2Cl_2 (3x20 mL) and the combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure affording hydroxyketone as a solid, which was directly used for the next step without further purification. For analysis, a sample was recrystallized in ether to give a white solid: m.p. 73 - 75 °C; $[\alpha]^{25}_D$ +228.6° (c = 0.61 in $CHCl_3$); R_f 0.45 ((EtOAc/Cyclohexane: 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 5.69-5.86 (m, 1H), 5.01 (d, *J* = 17.1, 1H), 4.98 (d, *J* = 10.2, 1H), 4.57-4.68 (m, 1H), 2.90 (AB of ABX, J_{AB} = 13.5, J_{AX} = 9.5 Hz, J_{BX} = 2.7 Hz, Δν = 86.24 Hz, 2H), 2.64-2.70 (m, 2H), 2.45-2.56 (m, 2 H), 2.43 (s, 3 H), 2.26-2.36 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.0, 141.6, 136.6,

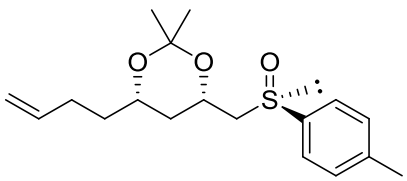
130.1, 123.9, 123.9, 115.5, 65.8, 63.4, 48.6, 42.6, 27.3, 21.4; IR 3361, 2907, 1710, 1641, 1494, 1376, 1049, 1038, 905, 808cm^{-1}; HRMS ES *m/z* $(M+Na)^+$ Calcd for $C_{15}H_{20}NaO_3S$ 303.1025, found 303.0989.

Synthesis of (2*S*,4*S*)-7-(4-methoxybenzyloxy)-1-((*R*)-p-tolylsulfinyl)octane-2,4-diol 12



Diethylmethoxy borane (4 mL, 1.0 M in THF, 4 mmol) was added dropwise to crude hydroxyketone (*vide supra*) (874 mg, 3.12 mmol) in 40 mL of THF/MeOH (4/1) at –78 °C. The resulting mixture was stirred for 20 min, prior to the addition of sodium borohydride (138 mg, 4.06 mmol). The reaction was stirred 4 h at –78 °C and was quenched with 38 mL of acetic acid, warmed up to room temperature, diluted with EtOAc (50 mL) and treated with an saturated $NaHCO_3$ solution up to pH = 6. The aqueous phase was extracted with EtOAc (3x100 mL) and the combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was taken up in MeOH, heated and concentrated *in vacuo*. This procedure was repeated four times. The residue was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane : 6/4) affording the diol **12** as a white solid (704 mg, 2.49 mmol, 80% over two steps): m.p. 110-114°C; $[\alpha]^{25}_D$ +230.3° (c = 1.00 in $CHCl_3$), R_f 0.33 (EtOAc/Cyclohexane: 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 5.71-5.88 (m, 1H), 5.01 (dd, *J* = 17.3, *J* = 1.7, 1H), 4.95 (d, *J* = 10.7 Hz, 1H), 4.38-4.55 (m, 1H), 3.81-3.97 (m, 1H), 3.61 (s broad, 2 H), 2.87 (ABX, J_{AB} = 13.4 Hz, J_{AX} = 9.8 Hz, J_{BX} = 2.0 Hz, Δν = 126.3 Hz, 2H), 2.42 (s, 3 H), 2.02-2.24 (m, 2 H), 1.41-1.75 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.7, 139.4, 138.3, 130.1, 124.0, 114.9, 71.3, 67.4, 62.2, 42.7, 36.9, 29.6, 21.4; IR 3284, 2907, 1641, 1494, 1450, 1318, 1105, 1084, 1034, 910, 810cm^{-1}; HRMS ES *m/z* $(M+Li)^+$ Calcd for $C_{15}H_{22}LiO_3S$ 289.1445, found 289.1407.

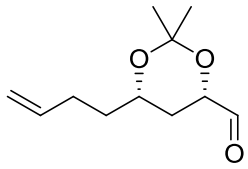
Synthesis of (4*S*,6*S*)-4-(3-(4-methoxybenzyloxy)butyl-2,2-dimethyl-6((*R*)-p-tolylsulfinylmethyl)-1,3-dioxane



Dimethoxypropane (4.5 mL, 36,7 mmol) and PPTS (109 mg, 433 µmol) were added to diol **12** (608 mg, 1.45 mmol) in 14 mL of acetone at room temperature. The reaction was

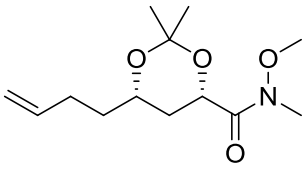
stirred for 16 h, hydrolyzed with 10 mL of a saturated $NaHCO_3$ solution and poured in 30 mL of EtOAc. The aqueous layer was extracted with EtOAc (3x20 mL) and the combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (EtOAc/Cyclohexane: 2/1) gave the acetal as a solid (351.8 mg, 1.09 mmol, 95%): m.p. 59 - 61 °C; $[\alpha]^{25}_D$ +204.7° (c = 0.51 in $CHCl_3$); R_f 0.76 ((EtOAc/Cyclohexane: 4/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.72-5.87 (m, 1H), 4.93-5.06 (m, 2 H), 4.42- 4.57 (m, 1H), 3.85-3.97 (m, 1H), 2.70-2.86 (m, 2 H), 2.41 (s, 3 H), 2.01-2.25 (m, 2 H), 1.52 (s, 3 H), 1.45-1.70 (m, 2 H), 1.44 (s, 3 H), 1.17-1.38 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 138.0, 130.0, 123.8, 114.8, 99.2, 67.9, 65.0, 63.5, 36.4, 35.2, 30.0, 29.0, 21.3, 21.3, 19.8; IR 2993, 2937, 1638, 1494, 1436, 1376, 1263, 1195, 1170, 1053, 1033, 807cm^{-1}; HRMS ES *m/z* $(M+Li)^+$:Calcd for $C_{18}H_{16}LiO_3S$ 329.1758, found 329.1711.

Synthesis of (4*S*,6*S*)-6-(3-(4-methoxybenzyloxy)butyl)-2,2-dimethyl-1,3-dioxane-4-carbaldehyde 13



2,4,6-collidine (0.72 mL, 5.54 mmol) and trifluoroacetic anhydride (1.2 mL, 8.63 mmol) were added dropwise subsequently to a solution of sulfoxide (*vide supra*) (568 mg, 1.76 mmol) in 20 mL of MeCN cooled at 0 °C. The reaction mixture was stirred 45 min, prior to the addition of 20 mL of a saturated $NaHCO_3$ solution, warmed to room temperature and stirred for 1 h 30. The aqueous layer was extracted with EtOAc (3x100 mL) and the combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (EtOAc/Cyclohexane: 5/95→20/80) gave the aldehyde **13** as a colorless oil (325 mg, 1.58 mmol, 90%): $[\alpha]^{25}_D$ -37.9° (c = 0.33 in $CHCl_3$); R_f 0.37 (EtOAc/Cyclohexane: 1/3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 5.72-5.88 (m, 1H), 4.93-5.09 (m, 2H), 4.28 (dd, *J* = 12.3 Hz, 3.0 Hz, 1H), 3.53-4.00 (m, 1H), 2.03-2.25 (m, 2H), 1.49-1.68 (m, 2H), 1.47 (s, 3H), 1.46 (s, 3H), 1.31 (q, *J* = 12.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.3, 137.9, 115.0, 99.1, 74.1, 67.5, 35.2, 31.0, 29.8, 28.9, 19.5; IR: 2993, 2927, 1739, 1641, 1435, 1380, 1267, 1201, 1111, 911cm^{-1}; HRMS ES *m/z* $(M+Li)^+$ Calcd for $C_{11}H_{18}LiO_3$ 205.1411, found 205.1395.

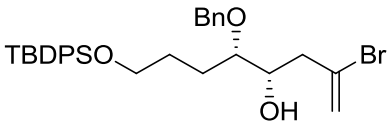
Synthesis of (4*S*,6*S*)-6-(but-3-enyl)-*N*-methoxy-N,2,2-trimethyl-1,3-dioxane-4-carboxamide 14



To aldehyde **13** (148 mg, 0.75 mmol) in 14 mL of *t*-BuOH and 14 mL of water was added subsequently KH_2PO_4 (605 mg, 4.45 mmol), 2-methyl-2-butene (6.4 mL, 56.0 mmol) and $NaClO_2$ (227 mg, 2.51 mmol). The reaction mixture was stirred 5 h 30 min and organic solvents were removed under reduced pressure. The aqueous layer was extracted 3 times with EtOAc and the combined organic layers were washed with brine dried over Na_2SO_4, filtered and concentrated under reduced pressure to give the crude acid, which was used for the next step without purification.

To a solution of the crude acid in 4 mL of CH_2Cl_2 was added portionwise carbonyldiimidazole (184 mg, 1.14 mmol). The reaction mixture was stirred 1 h at room temperature, prior to the addition of N,O-dimethylhydroxylamine hydrochloride (110 mg, 1.13 mmol). The reaction mixture was stirred overnight at room temperature filtered to remove insoluble materials and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (EtOAc/Cyclohexane: 20/80) gave the amide **14** as a colorless oil (146.7 mg, 0.57 mmol, 76%): $[\alpha]^{25}_D$ -24.1° (c = 0.86 in $CHCl_3$); R_f 0.4 (EtOAc/Cyclohexane: 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.71-5.88 (m, 1H), 4.91-5.07 (m, 2H), 4.82 (d, *J* = 10.2 Hz, 1 H), 3.84-3.97 (m, 1H), 3.73 (s, 3H), 3.19 (s, 3 H), 2.03-2.24 (m, 2 H), 1.49-1.87 (m, 4H), 1.47 (s, 3 H), 1.44 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 138.0, 114.8, 99.2, 67.8, 67.0, 61.6, 35.2, 32.3, 32.0, 30.0, 29.0, 19.4; IR 2992, 2937, 1671, 1642, 1440, 1380, 1258, 1199, 1165, 1115, 972, 912cm^{-1}; HRMS ES *m/z* $(M+Li)^+$ Calcd for $C_{13}H_{23}LiO_4$ 264.1782, found 264.1768.

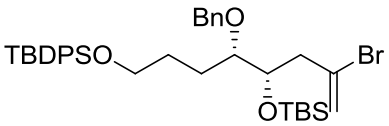
Synthesis of (4*S*,5*S*)-5-(benzyloxy)-2-8-(*tert*-butyldiphenylsilyloxy)oct-1-en-4-ol 15



To a solution of aldehyde **8** (460 mg, 1.03 mmol) in 8 mL of CH_2Cl_2 was added dropwise at –78 °C a solution of $TiCl_4$ (1.03 mL, 1.0 M in CH_2Cl_2, 1.03 mmol), followed by the dropwise addition of 2-bromo-3-(trimethylsilyl)propene (199 mg, 1.03 mmol). The reaction mixture was stirred for 2 h 30 min at –78°C, 30 min at 0 °C and hydrolyzed with an aqueous saturated solution of NH_4Cl (8 mL). The aqueous layer was extracted with CH_2Cl_2 (3x10 mL) and the combined organic layers were washed with brine (10 mL), dried over

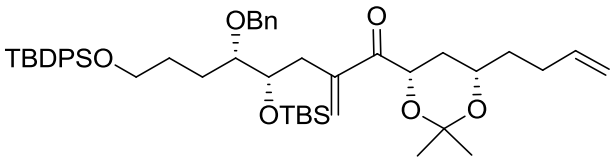
Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/6) to give the alcohol **15** (495 mg, 0.87 mmol, 85%) as a colourless oil as the favoured diastereomer (8.5/1): $[\alpha]^{25}_D$ +7.6° (c = 1.10 in $CHCl_3$); R_f 0.48 (EtOAc/Cyclohexane: 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.71 (m, 4H), 7.28-7.47 (m, 11H), 5.63 (d, *J* = 1.6 Hz, 1H), 5.50 (d, *J* = 1.6 Hz, 1H), 4.57 (AB, J_{AB} = 11.4 Hz, Δν = 47.7 Hz, 2H), 3.93-3.98 (X of ABX, m, 1H), 3.71 (t, *J* = 5.9 Hz, 2H), 3.39 (dt as q, *J* = *J* = 5.2 Hz, 1H), 2.51-2.68 (AB of ABX, m, 2H), 2.09 (s, br., 1H), 1.59-1.87 (m, 4H), 1.08 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.1, 135.6, 133.9, 130.7, 129.6, 128.5, 127.9, 127.8, 127.6, 119.2, 80.2, 72.0, 70.1, 63.8, 45.5, 28.2, 26.9, 26.2, 19.2; IR 3461, 2931, 2858, 1472, 1455, 1428, 1390, 1207, 1105, 1088, 1070, 1028, 998, 938, 889, 797, 738, 699 cm^{-1}; ; HRMS ES *m/z* $(M+Li)^+$ Calcd for $C_{31}H_{39}BrLiO_3Si$ 573.2007, found 573.1943.

Synthesis of (5*S*,6*S*)-6-(benzyloxy)-5-(2-bromoallyl)-2,2,3,312,12-hexamethyl-11,11-diphenyl-4,10-dioxa-3,11-disilatridecane 16



A solution of alcohol **15** (300 mg, 532 μmol) in 3 mL of DMF was treated subsequently with imidazole (72 mg, 1.06 mmol), *N*,*N*-dimethylaminopyridine (2 mg, 16.4 □mol) and TBSCl (120 mg, 798 mmol) at room temperature. After 16 h the reaction mixture was poured on diethylether/ H_2O (1:1) (20 mL). The organic layer was washed with distilled water (3x10 mL). The aqueous layer was extracted with Et_2O (3x20 mL) and the combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/40) afforded the silylether **16** (347 mg, 0.51 mmol, 96%) as a colorless oil: $[\alpha]^{25}_D$ –16.5° (c = 1.00 in $CHCl_3$); R_f 0.46 (EtOAc/Cyclohexane: 1/40); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.70 (m, 4H), 7.67-7.70 (m, 4H), 7.27-7.46 (m, 11H), 5.61 (s, 1H), 5.45 (d, *J* = 1.2 Hz, 1H), 4.57 (AB, J_{AB} = 11.5 Hz, Δν = 44.4 Hz, 2H), 4.18 - 4.23 (X of ABX, m, 1H), 3.62-3.76 (m, 2H), 3.34-3.39 (m, 1H), 2.29-2.75 (AB of ABX, m, 2H), 1.26-1.88 (m, 4H), 1.07 (s, 9H), 0.87 (s, 9H), 0.07 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 135.6, 134.1, 132.5, 129.5, 128.3, 128.0, 127.6, 127.6, 119.2, 81.3, 72.1, 69.3, 64.2, 43.7, 29.9, 26.9, 25.8, 25.1, 19.2, 18.0, -4.5, -4.5; IR 2954, 2929, 2893, 2857, 1472, 1463, 1428, 1389, 1361, 1251, 1091, 1028, 1006, 957, 936, 885, 826, 810, 776, 738, 699 cm^{-1}; HRMS ES *m/z* $(M+Li)^+$ Calcd for $C_{37}H_{53}BrLiO_3Si_2$ 687.2871, found 687.2845.

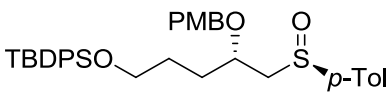
Synthesis of (4*S*,5*S*)-5-(benzyloxy)-1-((4*S*,6*S*)-6-(but-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)-4-((tert-butyldimethylsilyl)oxy)-8-((tert-butyldiphenylsilyl)oxy)-2-methyleneoctan-1-one 17



3

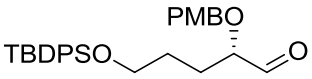
To a solution of vinylbromide **16** (243 mg, 0.36 mmol) in 3.5 mL of Et_2O cooled at -78 °C was added dropwise *t*-BuLi (0.46 mL, 1.7 M in pentane, 0.78 mmol). The reaction mixture was stirred 40 min at -78 °C and a solution of amide **14** (50 mg, 0.19 mmol) in 2.5 mL of Et_2O was added *via* cannula. The temperature was gradually increased until 0 °C during 3 h and the reaction mixture was quenched with aqueous saturated solution of NH_4Cl. The mixture was extracted 3 times with Et_2O and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/30) yielding the coupling compound **17** (106 mg, 0.133 mmol ,70 %) as a colourless oil: $[\alpha]^{25}_D$ -21.6° (c = 1.0 in $CHCl_3$); R_f 0.65 ((EtOAc/Cyclohexane: 1/6); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-7.69 (m, 5H), 7.28-7.44 (m, 10H), 6,25 (d, *J* = 0.6 Hz, 1H), 5.90 (s, 1H), 5.71-5.89 (m, 1H), 4.94-5.08 (m, 2H), 4.87 (dd, *J* = 10.8 Hz, *J* = 3.6 Hz, 1H), 4.59 (AB, J_{AB} = 11.4 Hz, Δν = 79.6 Hz, 2H), 3.98-4.06 (m, 1H), 3.82-3.97. (m, 1H), 3.55-3.76 (m, 2H), 3.28-3.36 (m, 1H), 2.83 (dd, *J* = 12.9 Hz, *J* = 2.7 Hz, 1H), 2.05-2.24 (m, 3H), 1.75-1.87 (m, 2H), 1.50-1.71 (m, 6H), 1.49 (s, 3H), 1.45 (s, 3H), 1.05 (s, 9H), 0.83 (s, 9H), -0,07 (s, 3H), -0,09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.1, 143.2, 138.8, 138.1, 135.6, 134.1, 129.6, 129.5, 128.3, 128.0, 127.55, 127.5, 114.9, 99.2, 81.5, 71.6, 71.5, 70.3, 67.9, 64.3, 35.3, 34.2, 33.1, 30.0, 29.99, 29.0, 26.9, 25.9, 24.7, 19.3, 19.2, 17.9, -4.4; IR 2929, 2856, 1683, 1641, 1380, 1255, 1201, 1106, 1085, 936, 826, 775, 738, 700 cm^{-1}; HRMS ES *m/z* $(M+Li)^+$ Calcd for $C_{48}H_{70}LiO_6Si_2$ 805.4866, found 805.4823.

Synthesis of tert-butyl((*S*)-4-(4-methoxybenzyloxy)-5-((*R*)-p-tolylsulfinyl)pentyloxy)-diphenylsilane 19



To a solution of β-hydroxysulfoxide **6** (1.84 g, 3.83 mmol) in 20 mL of THF at room temperature was added methoxybenzyl-trichloracetimidate[7] (1.53 g, 5.74 mmol) and $Yb(OTf)_3{*}H_2O$ (124 mg, 0.20 mmol). The resulting mixture was stirred for 16 h at room temperature and hydrolyzed with 15 mL of distilled water. The aqueous layer was extracted with EtOAc (3x 15 mL) and the combined organic layers were washed with brine (15 mL) dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/1) gave the protected alcohol **22** as a yellow oil (2.01 g, 3.41 mmol, 80%): $[\alpha]^{25}_D$ +55.73° (c = 1.50 in $CHCl_3$); R_f 0.29 (EtOAc/Cyclohexane: 1/2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.7-7.6 (m,18H), 4.52 (AB, J_{AB} = 8.7 Hz, $\Delta\nu$ = 8.95 Hz, 2H), 3.97 (m, 1H), 3.71 (s, 3H), 3.56 (t, J = 6.3 Hz, 2H), 2.76 (m, 2H), 2.32 (s, 3H), 1.40-1.70 (m, 4H), 0.95 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 141.6, 141.3, 135.5, 133.9, 130.2, 130.0, 129.7, 129.6, 127.6, 123.8, 113.9, 72.9, 72.0, 64.6, 63.6, 55.3, 30.2, 27.7, 26.9, 21.4, 19.20; IR 2931, 2857, 1726, 1612, 1587, 1513, 1494, 1463, 1427, 1390, 1359, 1302, 1246, 1174, 1109, 1085, 1033, 1013, 937, 821, 808, 741, 701, 687 cm^{-1}; HRMS ES *m/z* $(M+Na)^+$ Calcd for $C_{36}H_{44}NaO_4SSi$ 623.262, found 623.262.

Synthesis of (*S*)-5-(*tert*-butyldiphenylsilyloxy)-2-(4-methoxybenzyloxy)-pentanal 20

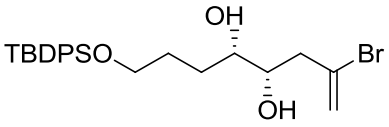


To a solution of sulfoxide **19** (950 mg, 1.62 mmol) in 16 mL of MeCN cooled at 0 °C was added dropwise subsequently 2,4,6-collidine (0.60 mL, 4.88 mmol) and trifluoroacetic anhydride (1.20 mL, 8.1 mmol). The reaction mixture was stirred for 30 min, prior to the addition of 65 mL of saturated solution of $NaHCO_3$, warmed to room temperature and stirred for 1 h. The aqueous layer was extracted with EtOAc (3x50 mL) and the combined organic layers were washed with brine (50mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/9) to give the aldehyde **20** (683 mg, 1.42 mmol, 88%) as a brown oil: $[\alpha]^{25}_D$ -19.6° (c = 1.00 in $CHCl_3$), R_f 0.21 (EtOAc/Cyclohexane: 1/3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.65 (d, J=2.1 Hz, 1H), 6.8-7.7 (m, 14H), 4.50 (AB, J_{AB} = 9 Hz; $\Delta\nu$ = 34.15 Hz, 2H), 3.80 (s, 3H), 3.70 (m, 1H), 3.64 (t, J = 6 Hz, 2H), 1.57-1.98 (m, 4H), 1.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.7, 159.5, 135.6, 133.8, 129.7, 129.6, 129.4, 127.5, 113.9, 82.9, 72.1, 63.2, 55.3, 27.7, 26.9, 26.4, 19.2; IR: 3071, 2931, 2857, 1732, 1612, 1587, 1513, 1471,

[7] Audis, J.E.; Boisvert, L.; Patten, A. D.; Villalobos, A.; Danishefsky, S. J. *J. Org. Chem.*, **1989**, *54*, 3738.

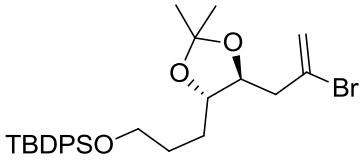
1463, 1427, 1389, 1373, 1361, 1302, 1246, 1173, 1106, 1088, 1034, 1007, 997, 937, 821, 741, 700, 687 cm^{-1}; HRMS ES *m/z* $(M+Na)^+$ Calcd for $C_{29}H_{36}NaO_4Si$ 499.228, found 499.225.

Synthesis of (4*S*,5*S*)-2-bromo-8-(*tert*-butyldiphenylsilyloxy)oct-1-ene-4,5-diol 21



To a solution of aldehyde **20** (253 mg, 0.53 mmol) in 4 mL of CH_2Cl_2 was added dropwise at -78 °C a solution of $TiCl_4$ (0.5 mL, 1.0 M in CH_2Cl_2, 0.53 mmol), followed by the dropwise addition of 2-bromo-3-(trimethylsilyl)propene (100 mg, 0.53 mmol). The reaction mixture was stirred for 3 h at -78 °C and hydrolyzed with a saturated solution of NH_4Cl (4 mL). The aqueous layer was extracted with CH_2Cl_2 (3x5 mL) and the combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/6) giving the diol **21** as a colorless oil as the only *syn* diastereomer (215 mg, 0.45 mmol, 85%): $[\alpha]^{25}_D$ -3.23° (c = 1.07, $CHCl_3$); R_f 0.53 (EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25-7.55 (m, 10H); 5.59 (d, *J* = 1.08 Hz, 1H), 5.40 (d, *J* = 1.59 Hz, 1H), 3.66 (m, 1H), 3.59 (t, *J* = 3.27 Hz, 2H), 3.40 (m, 1H), 2.87 (m, 1H), 2.51 (m, 2H), 2.25 (m, 1H, OH), 1.45-1.68 (m, 4H), 0.93 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 133.5, 130.6, 129.8, 127.7, 119.6, 72.9, 71.7, 64.2, 46.0, 31.0, 28.7, 26.9, 19.2; IR 3397, 2930, 2856, 1738, 1631, 1472, 1427, 1389, 1245, 1106, 889, 822, 739, 700, 687 cm^{-1}; HRMS ES *m/z* $(M+Na)^+$ Calcd for $C_{24}H_{33}BrNaO_3Si$ 499.127, found 499.128.

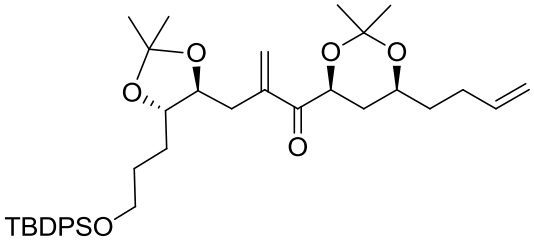
Synthesis of (3-((4*S*,5*S*)-5-(2-bromoallyl)-2,2-dimethyl-1,3-dioxolan-4-yl)propoxy)(*tert*-butyl)diphenylsilane 22



To a solution of diol **21** (120 mg, 0.25 mmol) in 3 mL of acetone and 0.9 mL of dimethoxypropane was added PPTS (22 mg, 0.093 mmol) at room temperature. The reaction mixture was stirred for 16 h, hydrolyzed with 2 mL of a saturated solution of $NaHCO_3$ and poured on 30 mL of EtOAc. The aqueous layer was extracted with EtOAc (3x6 mL) and the combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification of the residue by flash column chromatography on silica gel (EtOAc/ Cyclohexane: 2/98) gave the acetal **22** (127 mg, 0.25 mmol, 98%) as a colorless oil: $[\alpha]^{25}_D$ -12.37° (c = 1.03 , $CHCl_3$); R_f 0.81 (EtOAc/Cyclohexane: 1/4); ^{1}H NMR (300

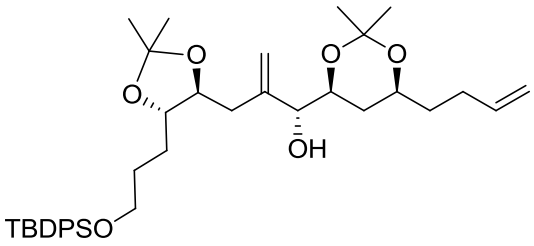
MHz, $CDCl_3$) δ 7.26-7.68 (m, 10H), 5.72 (d, *J* = 0.9 Hz, 1H), 5.50 (d, *J* = 1.5 Hz, 1H), 3.95 (td, *J* = 7.68 Hz, *J* = 4.68 Hz, 1H), 3.7 (m, 3H), 2.65 (AB (ABX), J_{AB} = 15 Hz, J_{AX} = 7.5 Hz, J_{BX} = 4.5 Hz, Δ*v* = 43.88 Hz, 2H), 1.5-1.8 (m, 4H), 1.39 (s, 3H), 1.37 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 134.0, 129.6, 129.4, 127.6, 119.1, 108.5, 80.4, 78.1, 63.6, 45.3, 29.3, 29.0, 27.3, 27.2, 26.9, 19.2; HRMS ES *m/z* $(M+Na)^+$ Calcd for $C_{27}H_{37}BrNaO_3Si$ 539.159, found 539.159.

Synthesis of 1-((4*S*,6*S*)-6-(but-3-enyl)-2,2-dimethyl-1,3-dioxan-4-yl)-2-(((4*R*,5*R*)-5-(3-(tert-butyldiphenylsilyloxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)prop-2-en-1-one 23



To a solution of vinylbromide **22** (600 mg, 1.16 mmol) in 15 mL of Et_2O cooled at -78 °C was added dropwise *t*-BuLi (1.36 mL, 1.7 M in pentane, 2.32 mmol). The reaction mixture was stirred 40 min at -78 °C and a solution of amide **14** (150 mg, 0.58 mmol) in 15 mL of Et_2O was added *via* cannula. The temperature was gradually increased until 0°C during 3 h and the reaction mixture was quenched with aqueous saturated solution of NH_4Cl. The mixture was extracted 3 times with Et_2O and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (EtOAc/cyclohexane: 1/30) yielding the coupling compound **23** (246 mg, 0.40 mmol, 70%) as a colorless oil: $[\alpha]^{25}_D$ -9.41° (c = 0.505 in $CHCl_3$); R_f 0.65 (EtOAc/cyclohexane: 1/6); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3-7.7 (m, 10H), 6.24 (s, 1H), 6.01 (s, 1H), 5.79 (ddt, J_{trans} = 16.86 Hz, J_{cis} = 10.05 Hz, ^3J = 6.6 Hz, 1H), 4.97 (m, 2H), 4.91 (dd, *J* = 11.64 Hz, *J* = 2.79 Hz, 1H), 3.75 (m, 1H), 3.45-3.7 (m, 4H), 2.45 (AB (ABX), J_{AB} = 22.5 Hz, J_{AX} = 2.7 Hz, J_{BX} = 8.1 Hz; Δ*v* = 88.95 Hz, 2H), 2.1 (m, 2H), 1.49 (s, 3H), 1.44 (s, 3H), 1.35 (s, 3H), 1.34 (s 3H), 1.05 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.1, 142.5, 138.1, 135.6, 134.0, 129.5, 128.4, 127.6, 115.0, 108.1, 99.2, 80.6, 78.9, 71.4, 67.9, 63.7, 35.3, 35.1, 32.9, 30.2, 30.0, 29.0, 27.3, 27.3, 26.9, 26.9, 19.4, 19.2; IR 3072, 2986, 2931, 2858, 1731, 1684, 1641, 1589, 1428, 1378, 1252, 1200, 1164, 1109, 1088, 996, 962, 938, 912, 865, 822, 740 710, 687cm^{-1}; HRMS ES *m/z* $(M+Na)^+$ Calcd for $C_{38}H_{54}NaO_6Si$ 657.358, found 657.360.

Synthesis of (*R*)-1-((4*S*,6*S*)-6-(but-3-enyl)-2,2-dimethyl-1,3-dioxan-4-yl)-2-(((4*R*,5*R*)-5-(3-(tert-butyldiphenylsilyloxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)prop-2-en-1-ol 24



<u>Way A:</u> Stereoselective reduction of enone 23

To a solution of enone **23** (173 mg, 0.27 mmol) in 10 mL of Et_2O cooled at 0 °C was added $CeCl_3$ (20 mg, 0.08 mmol) and dropwise a freshly prepared[8] solution of $Zn(BH_4)_2$ (1.15 mL. 0.183 M in Et_2O, 0.210 mmol). The mixture was stirred 20 minutes at 0 °C and quenched with 10 mL of NH_4Cl saturated solution. The mixture was extracted 3 times with Et_2O and the combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (EtOAc/Cyclohexane: 1/15 then 1/6) giving the alcohol (69 mg, 0.11 mmol, 40%) as a colorless oil as the only *trans* diastereomer **24**.

<u>Way B:</u> Stereoselective addition of vinyl bromide 22 to aldehyde 13 in the presence of magnesium bromide.

Dibromomethane (1.25 g, 6.65 mmol) in 1.7 mL of distillated toluene was added dropwise over 30 minutes in a solution of magnesium (173 mg, 7.11 mmol) in 5 mL of distillated Et_2O at RT. The reaction was stirred 30 minutes at RT and was clarified for 1 h 30 (solution supposed at 1 M).

t-BuLi (1.7 M in hexane, 270 µl, 0.457 mmol) wad added dropwise in a solution of vinyl bromide **22** (107.5 mg, 0.21 mmol) in 3 mL of THF at -78 °C. The reaction was stirred 30 minutes at -78°C and turned into deep yellow. $MgBr_2$ solution (1 M, 210 µl, 0.210 mmol) was added at -78 °C, and the reaction was stirred 30 minutes at -78 °C. Aldehyde **13** (33 mg, 0.166 mmol) in 2 mL of dichloromethane was added *via* cannula. The reaction was stirred 1 h 30 at -78 °C and allowed to warm to RT.

The reaction was hydrolyzed with NH_4Cl solution, aqueous phase extracted three times with DCM. Organic phases were washed with brine, dried over Na_2SO_4, filtrated and

[8] *J. Am. Chem. Soc.* **1960,** *82* (23), 6074-6081

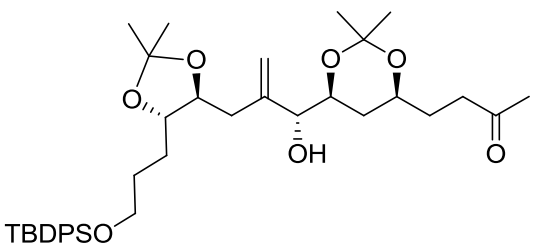
evaporated. Diastereoisomers (5.5/1) were separated by flash chromatography (EtOAc/ Cyclohexane 1/6), giving the alcohol **24** (58 mg, 0.091 mmol, 55%) as a colorless oil.

Way C: Stereoselective addition of vinyl bromide 22 to aldehyde 13

t-BuLi (1.7M in hexane, 173 µl, 0.29 mmol) was added dropwise in a solution of vinyl bromide **22** (70 mg, 0.14 mmol) in 2 mL of distillated Et_2O at -78°C. The reaction was stirred 45 minutes -78°C, the solution turned to deep yellow. Aldehyde **13** (14 mg, 0.067 mmol) in 2 mL of Et_2O was added *via* cannula to the reaction, and the reaction was stirred 2h at -78°C. The reaction was allowed to warm to RT and was hydrolyzed with NH_4Cl solution. The aqueous phase was extracted three times with Et_2O, organic phases were washed with brine, dried over Na_2SO_4, filtrated, evaporated. The two diastereoisomers (6/1) were separated by flash chromatography (EtOAc/cyclohexane 1/6), giving the alcohol **26** (27 mg, 0.042 mmol, 62%) as a colorless oil: $[\alpha]^{25}_D$ -22.71° (c = 1.035 in $CHCl_3$), R_f 0.28 (EtOAc/Cyclohexane: 1/6); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.70 (m, 10H), 5.79 (ddt, J_{trans} = 17.01 Hz, J_{cis} = 10.17 Hz, ^3J = 6.75 Hz, 1H), 5.21 (s, 1H), 5.07 (s, 1H), 4.97 (m, 2H), 4.05 (m, 1H), 3.95 (m, 1H), 3.80 (m, 1H), 3.6-3.75 (m, 4H), 3.15 (m, 1H), 2.27 (d, *J* = 5.7 Hz, 2H), 2.12 (m, 2H), 1.1-18 (m, 20H), 1.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1, 138.3, 135.6, 134.0, 129.6, 127.6, 115.5, 114.7, 108.3, 98.6, 81.0, 80.7, 76.6, 70.64, 68.0, 63.6, 35.8, 35.5, 31.1, 30.1, 29.2, 29.0, 28.8, 27.7, 27.2, 26.9, 19.8, 19.2; IR 3473, 3072, 2988, 2930, 2857, 1741, 1641, 1472, 1462, 1428, 1378, 1239, 1199, 1165, 1109, 1089, 1047, 990, 909, 823, 740, 701, 687 cm^{-1}; HRMS ES *m/z* $(M+Na)^+$ Calcd for $C_{38}H_{56}NaO_6Si$ 659.374, found 659.378.

Minor diastereoisomer: R_f 0.24 ((EtOAc/Cyclohexane: 1/6); ^{1}H NMR (300 MHz, CDCl3) δ 7.30-7.70 (m, 10H), 5.79 (m, 1H), 5.10 (s, 1H), 5.03 (s, 1H), 4.97 (m, 2H), 4.25 (m, 1H), 3.6-3.95 (m, 6H), 3.15 (m, 1H), 2.10-2.32 (m, 4H), 1.1-18 (m, 20H), 1.05 (s, 3H).

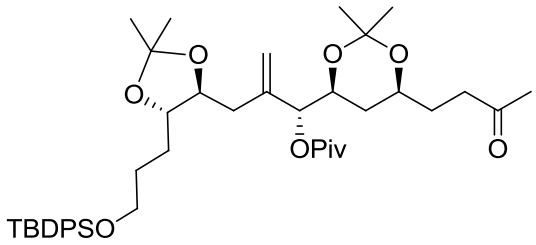
Synthesis of 4-((4*S*,6*S*)-6-((*R*)-2-(((4*R*,5*R*)-5-(3-(tert-butyldiphenylsilyloxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-1-hydroxyallyl)-2,2-dimethyl-1,3-dioxan-4-yl)butan-2-one 26



To a solution of alcohol **24** (20 mg, 0.03 mmol) in a mixture of 2 mL of dimethylacetamide and 0.7 mL of water was added $Cu(OAc)_2$ (13 mg, 0.065 mmol) and $PdCl_2$ (3 mg, 0.016 mmol). The flask was connected with a balloon of O_2 and the reaction mixture

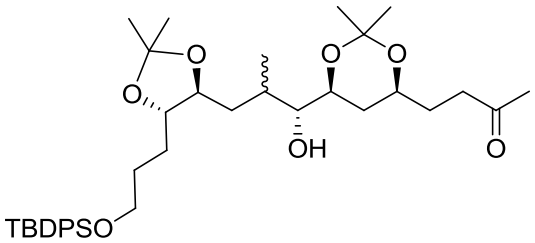
was stirred 3 days at room temperature. The reaction mixture was extracted 3 times with ethyl acetate and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by flash column chromatography on silica gel (EtOAc/Hexane 1/4), giving the methyl ketone **26** (16.6 mg, 0.025mmol, 85%) as a colorless oil: $[\alpha]^{25}_D$ -21.03° (c = 0.98, $CHCl_3$); R_f 0.25 (EtOAc/Cyclohexane 1/4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.68 (m, 10H), 5.21 (s, 1H, 17), 5.07 (s, 1H), 4.05 (d, *J* = 5.01 Hz, 1H), 3.95 (m, 1H), 3.80 (m, 1H), 3.6-3.75 (m, 4H), 2.52 (t , *J* = 2.47 Hz, 2H), 2.26 (d , *J* = 5.7 Hz, 2H), 2.13 (s, 3H), 1.5-1.9 (m, 6H), 1.2-1.45 (m, 14H), 1.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.6, 144.1, 135.6, 133.9, 129.6, 127.6, 115.6, 108.3, 98.6, 81.0, 80.7, 76.6, 70.6, 67.9, 63.6, 39.1, 35.8, 31.1, 30.3, 30.0, 29.9, 29.0, 28.8, 27.3, 27.2, 26.9, 19.8, 19.2; HRMS ES *m/z* $(M+Na)^+$ Calcd for $C_{38}H_{56}NaO_6Si$ 659.374, found 659.378.

Synthesis of (*R*)-2-(((4*S*,5*S*)-5-(3-((tert-butyldiphenylsilyl)oxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-1-((4*S*,6*S*)-2,2-dimethyl-6-(3-oxobutyl)-1,3-dioxan-4-yl)allyl pivalate



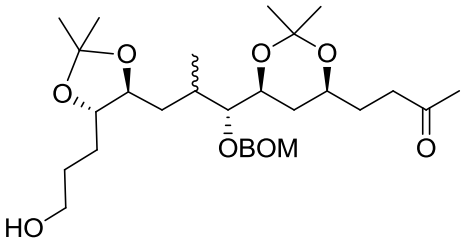
To a solution of **26** (16 mg, 0.025 mmol) and DMAP (1 mg, 0.009 mmol) in pyridine (2 mL) was added pivaloyl chloride (5 µl, 0.038 mmol) at 0°C. The reaction was stirred at 70°C for 24 hours, and then cooled down to RT and MeOH (200 µl), was added. The reaction was stirred 1 h at RT and then concentrated under reduced pressure and diluted with EtOAc. The solution was washed respectively with 1 N HCl, saturated solution of $NaHCO_3$, and water. The organic layer was dried over Na_2SO_4, filtrated and evaporated. The crude was purified by flash chromatography (EtOAc/Hexane 1/6) affording the corresponding pivalate (16.5 mg, 0.022 mmol, 88%); $[\alpha]^{25}_D$ -14.72° (c = 1.03, $CHCl_3$); R_f 0.72 (EtOAc/ Cyclohexane 2/3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.61 (m, 10H), 5.10 (d, *J* = 4.8 Hz, 1H), 5.05 (d, *J* = 3.3 Hz, 2H), 4.01 (m, 1H), 3.55-3.76 (m, 5H), 2.41-2.47 (m, 2H), 2.15-2.25 (m, 2H), 2.07 (s, 3H), 1.4 (m, 8H), 1.05-1.35 (m, 21H), 0.97 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.6, 177.0, 141.9, 135.5, 133.9, 129.5, 127.6, 114.3, 108.1, 98.6, 80.8, 79.3, 76.9, 69.3, 67.7, 63.7, 39.0, 38.7, 36.4, 31.9, 30.0, 29.9, 29.7, 29.1, 27.4, 27.3, 27.2, 26.9, 19.6, 19.2; HRMS ES *m/z* $(M+Na)^+$ Calcd for $C_{43}H_{64}NaO_8Si$ 759.424, found 759.426.

Synthesis of 4-((4*S*,6*S*)-6-((1*R*)-3-((4*R*,5*R*)-5-(3-((tert-butyldiphenylsilyl)oxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-1-hydroxy-2-methylpropyl)-2,2-dimethyl-1,3-dioxan-4-yl)butan-2-one 28



Pd/C (4 mg, 10% WT) was added to a solution of **26** (32 mg, 0.05 mmol) in 5mL of MeOH in an autoclave. The autoclave was purged three times with H_2 and the reaction was stirred overnight over 80 bars of H_2 at RT. The reaction was filtrated over celite, concentrated and purified by flash chromatography (EtOAc/Hexane 1/4) affording the hydrogenated compound as a mixture of two diastereoisomers **28** and **28'** (31 mg, 0.048 mmol, 99%): R_f 0.41-0.44 (EtOAc/ Cyclohexane 2/3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.68 (m, 10H), 3.5-3.95 (m), 3.31 (t, *J* = 6.16 Hz), 2.95 (m), 2.54 (m), 2.15 (s, 3H), 1.97 (m), 1.45-1.90 (m), 1.30-1.45 (m, 12H), 1.05 (s, 9H), 1.10 (d, *J* = 7.04 Hz, 3H), 0.91 (d, *J* = 6.76 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.6, 208.6, 135.5, 133.9, 129.5, 127.6, 108.1, 108.2, 98.4, 98.4, 81.0, 81.3, 78.3, 79.5, 77.2, 77.2, 69.1, 69.9, 67.9, 68.1, 63.5, 63.6, 39.1, 39.1, 34.8, 31.9, 32.3, 31.7, 30.3, 30.3, 30.1, 29.9, 29.0, 28.8, 28.9, 27.2, 27.3, 26.8, 19.6, 19.7, 19.2, 14.0, 16.2; HRMS ES *m/z* $(M+Na)^+$ Calcd for $C_{38}H_{58}NaO_7Si$ 677.391, found 677.384.

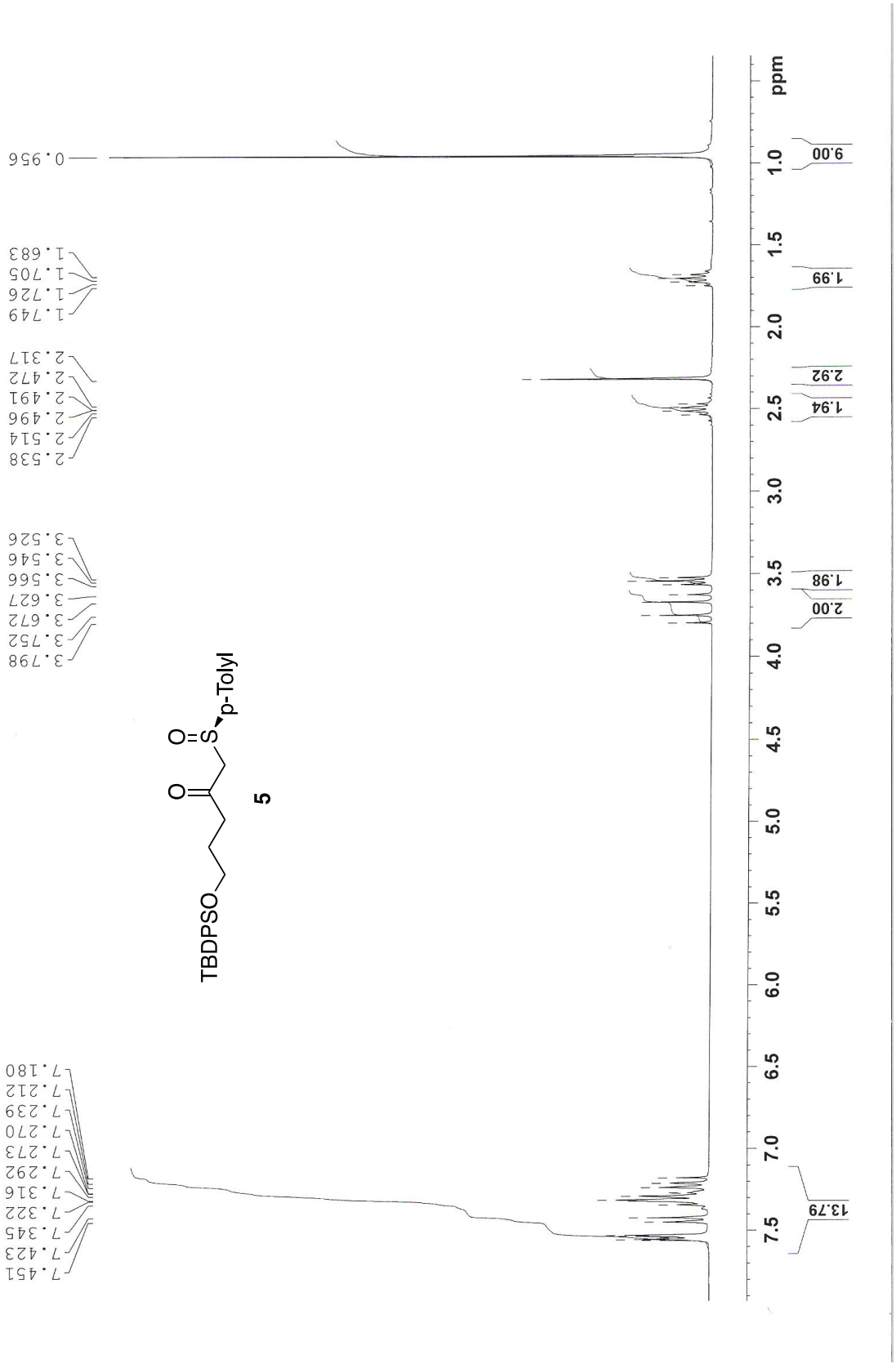
Synthesis of 4-((4*S*,6*S*)-6-((1R)-1-((benzyloxy)methoxy)-3-((4*S*,5*S*)-5-(3-hydroxypropyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-2-methylpropyl)-2,2-dimethyl-1,3-dioxan-4-yl)butan-2-one

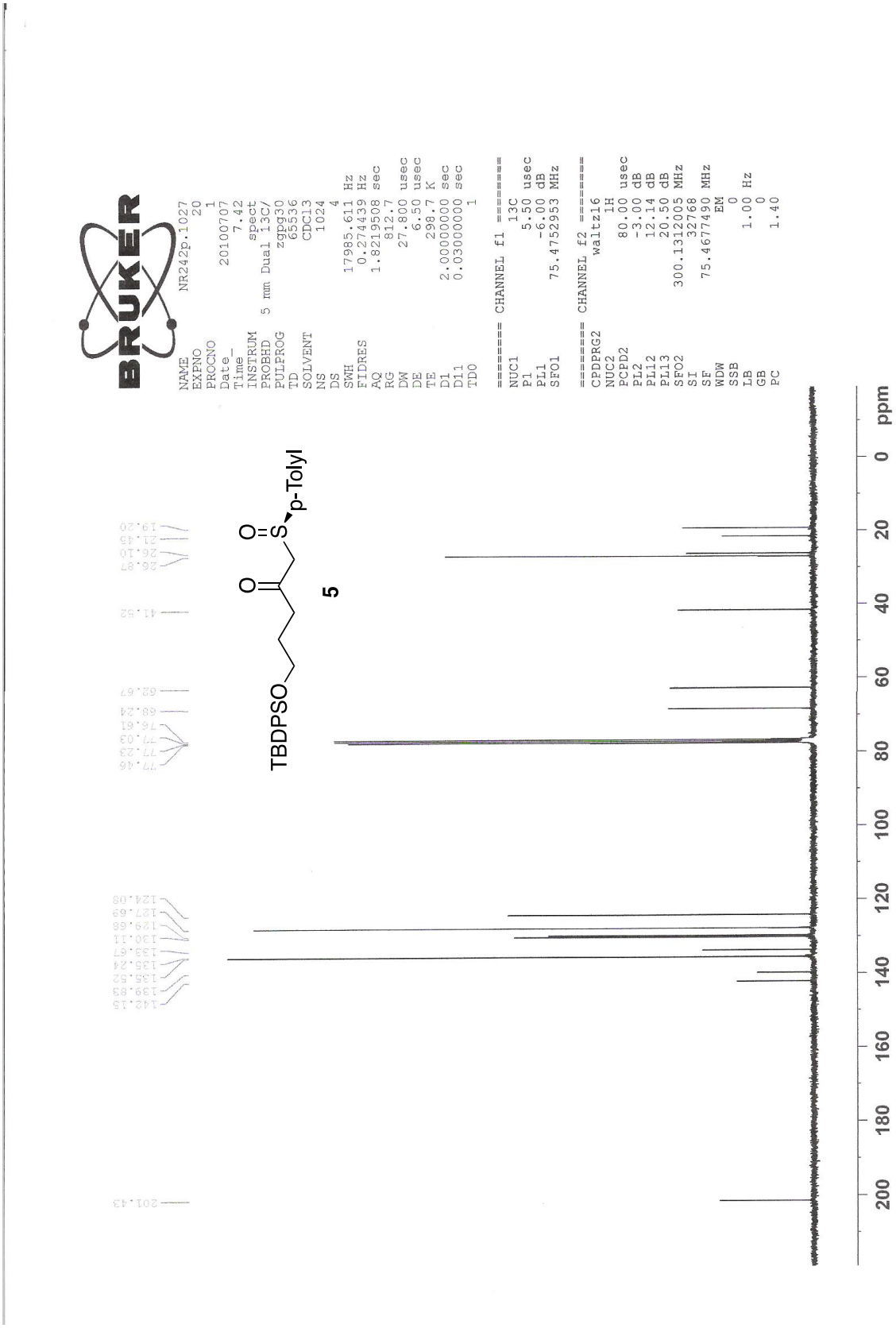


BOMCl (75%, 25 µl, 0.132 mmol) was added to a solution of **32** (28 mg, 0.044 mmol), DIPEA (50 µl, 0.27 mmol) and Bn_4NI (2 mg, 4.4 µmol) in CH_2Cl_2 (2 mL). The reaction was stirred four days at RT and then quenched with water (2 mL). The aqueous phase was extracted three times with CH_2Cl_2; the organic phases were washed with brine, dried over Na_2SO_4, evaporated giving **33**, which was directly used for the next step without further purification.

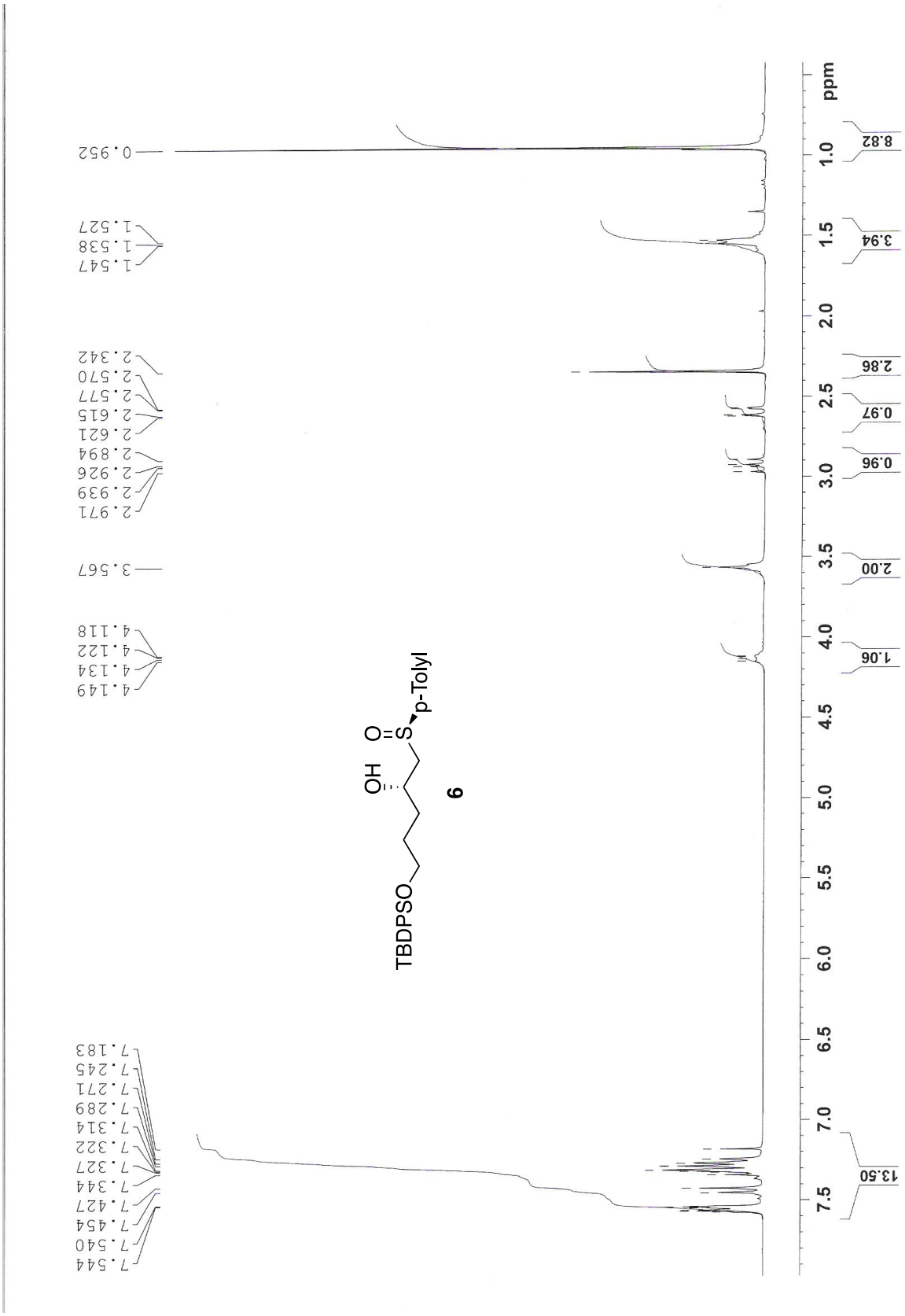
TBAF (40 µl, 1 M, 0.040 mmol) was added to a solution of **33** (14 mg, 0.019 mmol) in THF (1 mL). The reaction was stirred 6 hours at RT and quenched with brine. The aqueous phase was extracted three times with EtOAc, and the organic phases were dried over Na_2SO_4, filtrated, concentrated and purified by flash chromatography (EtOAc/Hexane 1/6) affording the Paquette's *et al.* fragment (15.3 mg, 0.028 mmol , 65%).

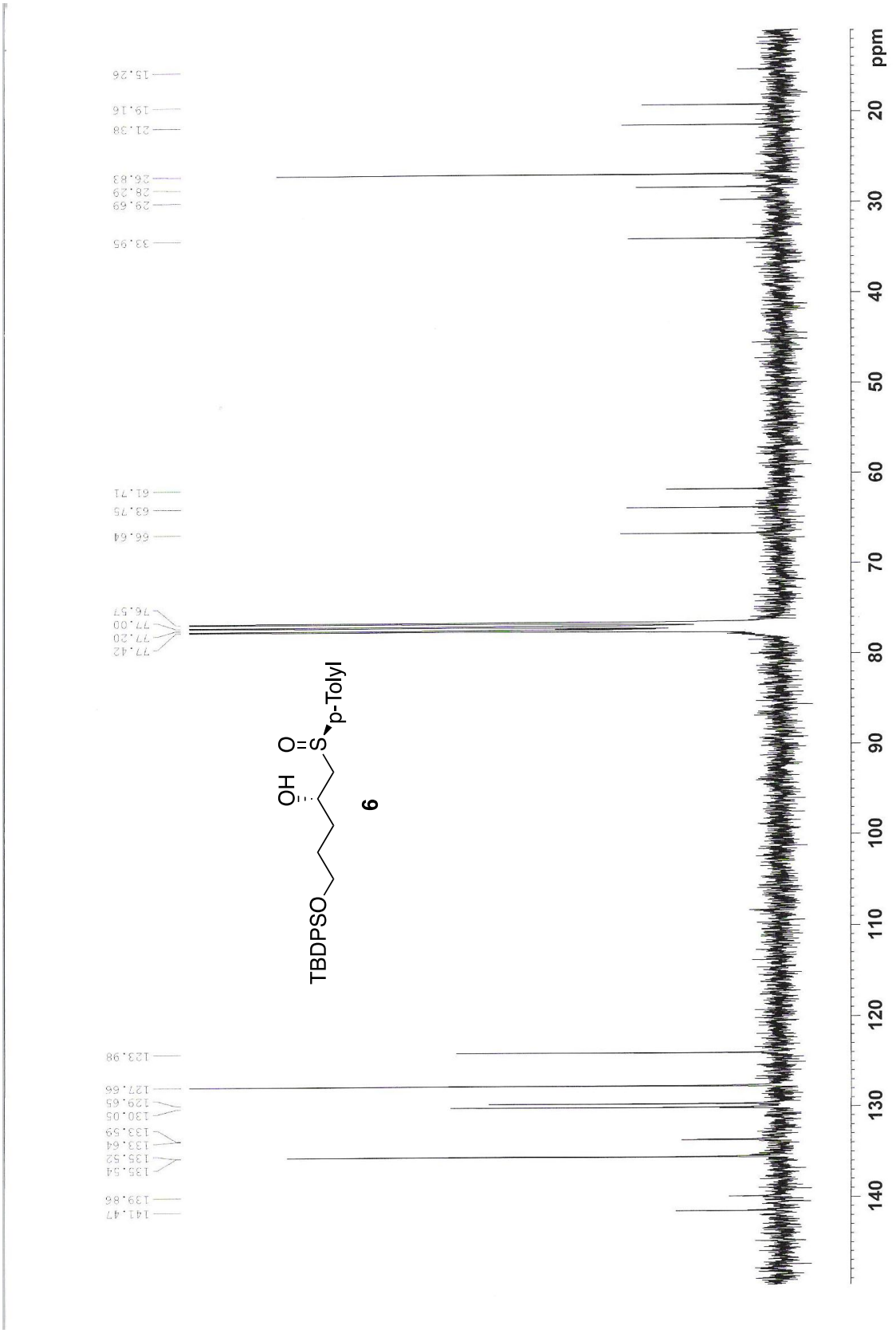
(*R*)-5-(*tert*-butyldiphenylsilyloxy)-1-(*p*-tolylsulfinyl)pentan-2-one 5



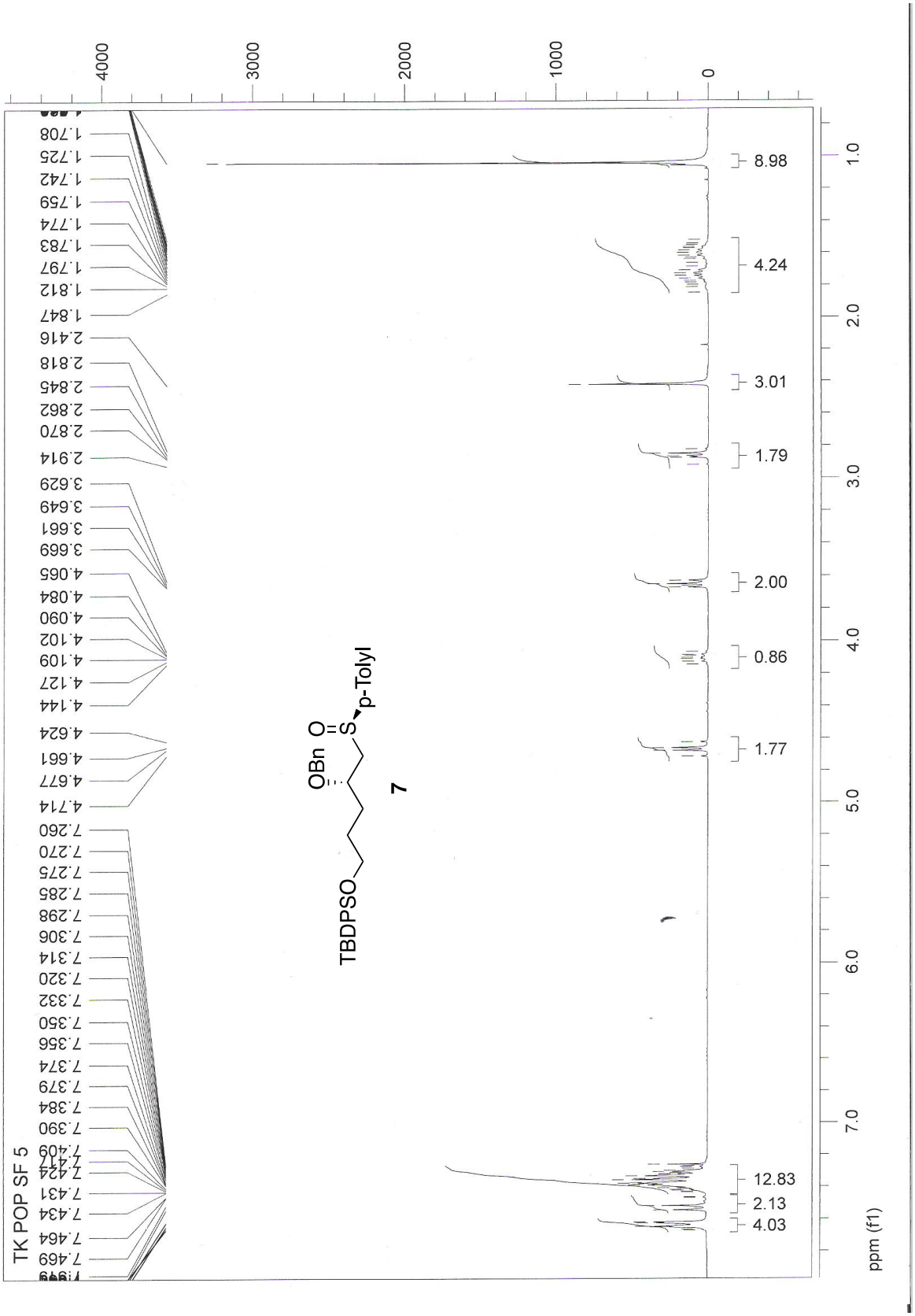


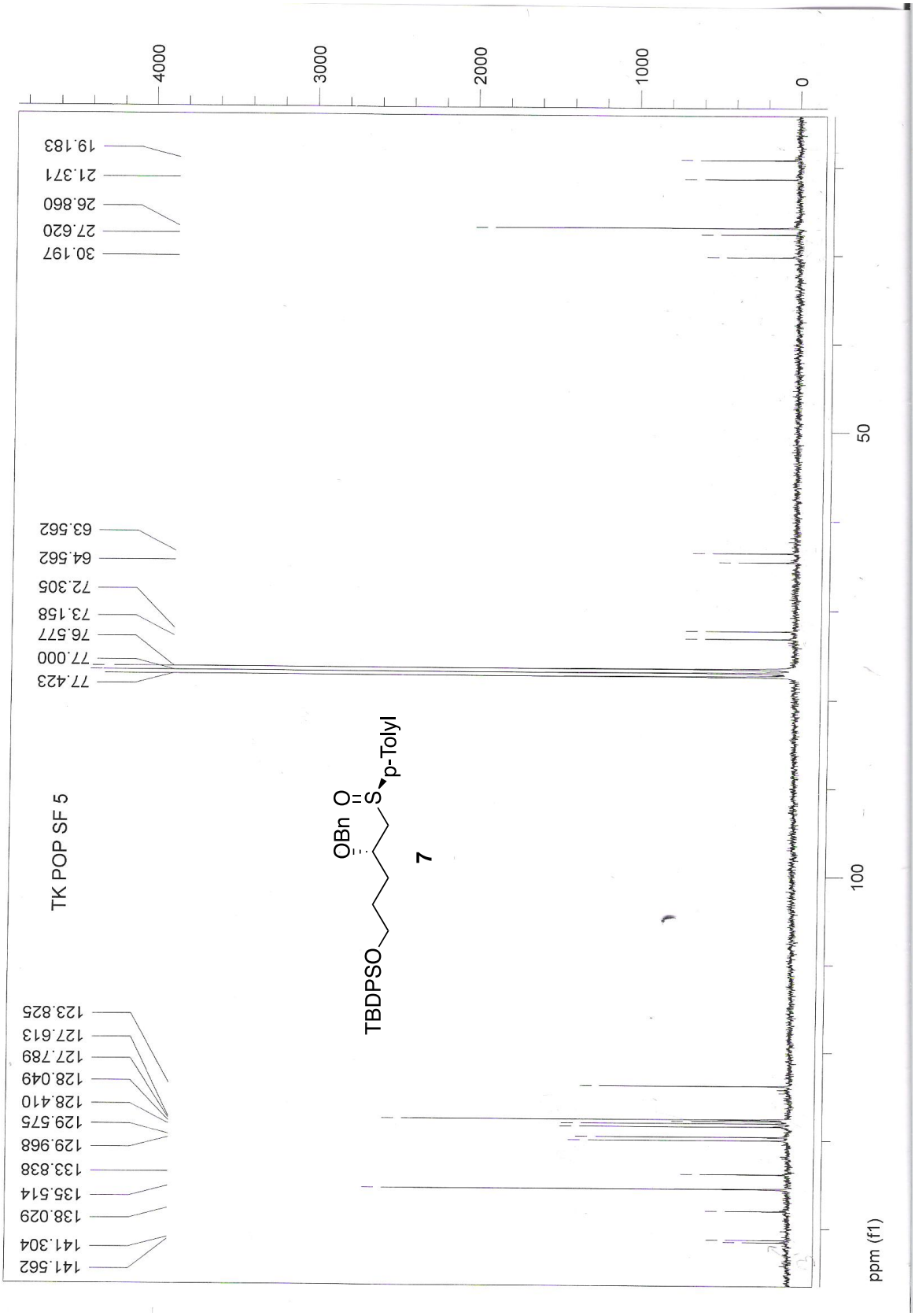
(*S*)-5-(*tert*-butyldiphenylsilyloxy)-1-((*R*)-*p*-tolylsulfinyl)pentan-2-ol 6



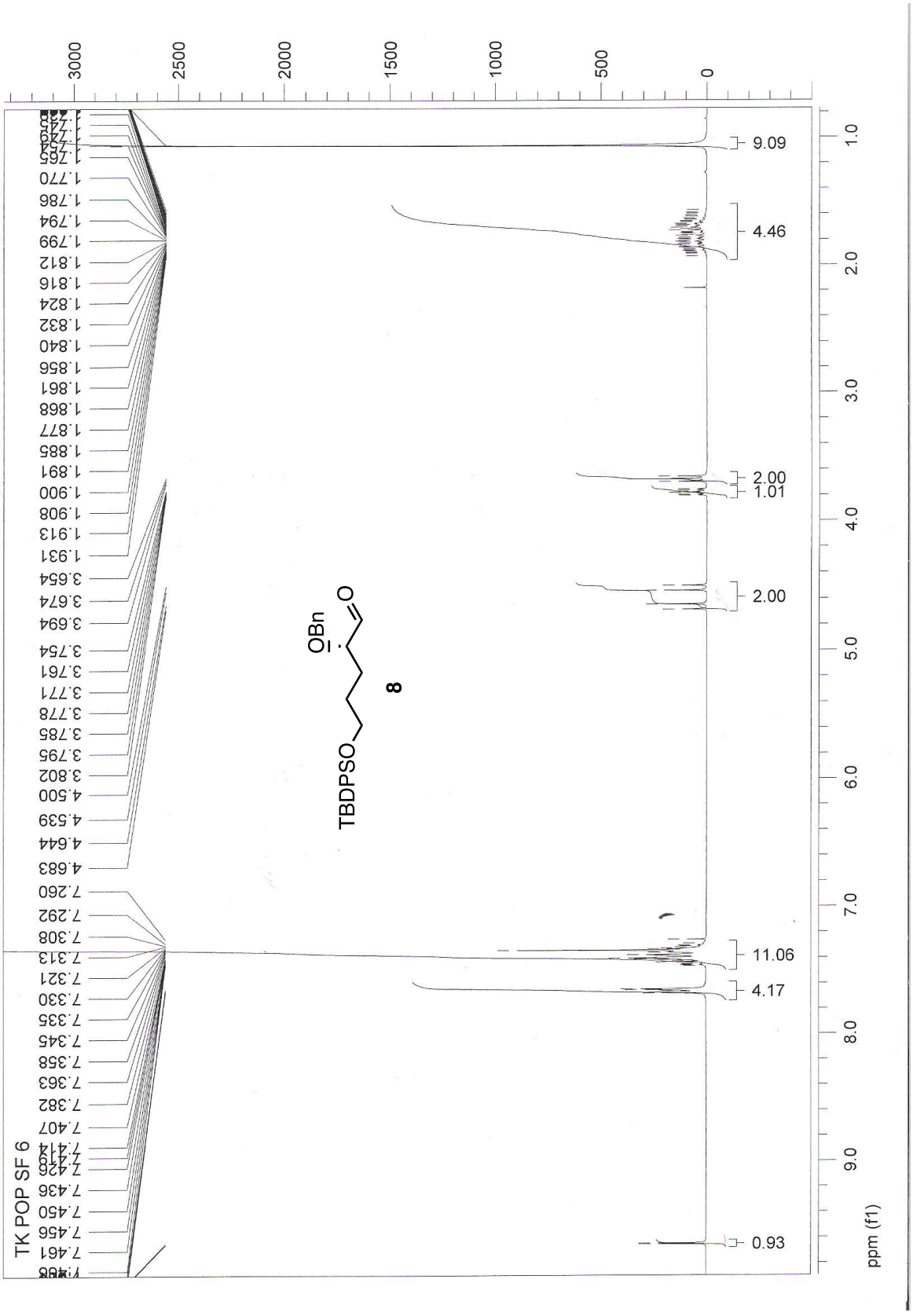


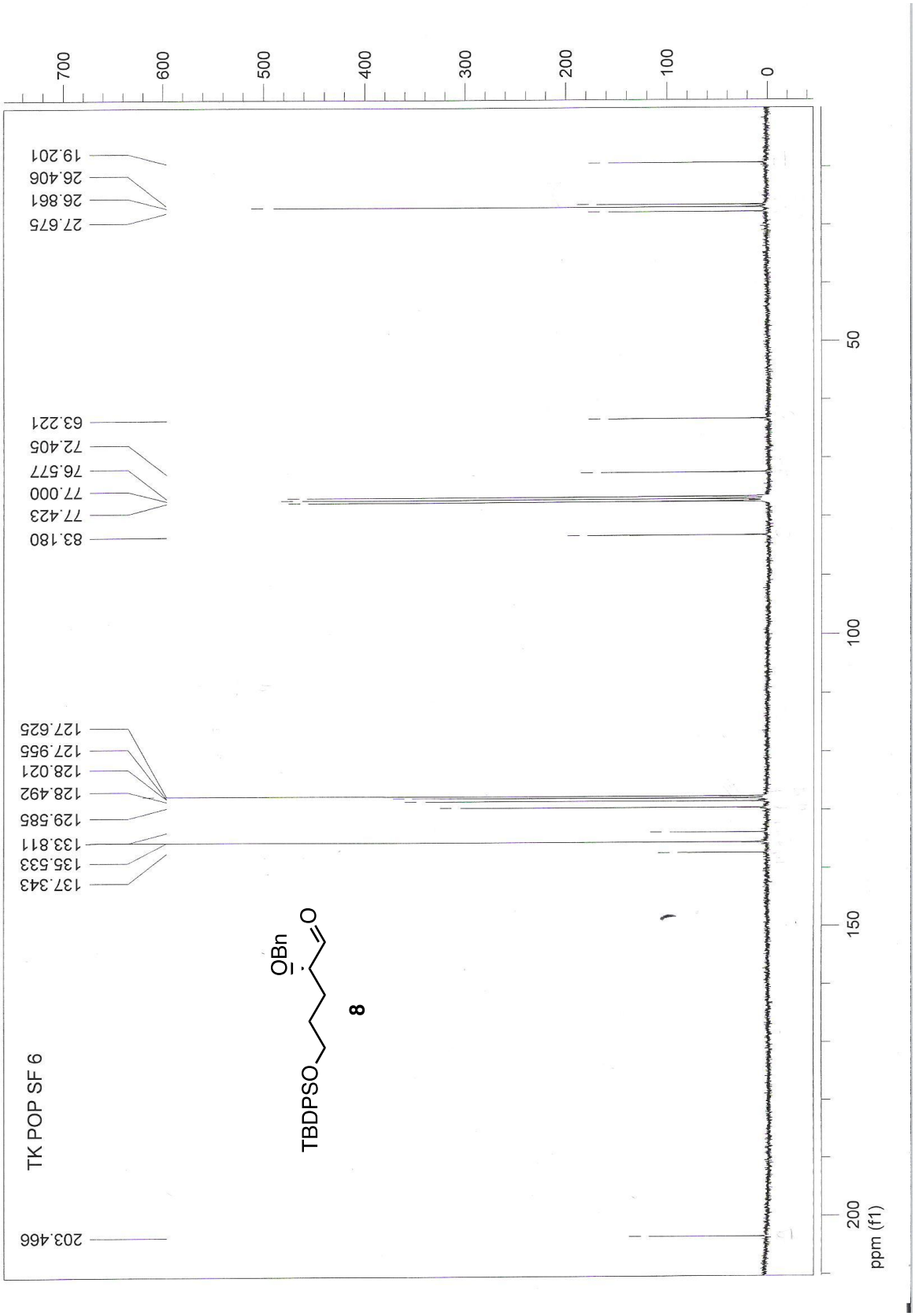
((*S*)-4-(benzyloxy)-5-((*R*)-*p*-tolylsulfinyl)pentyloxy)(*tert*-butyl)diphenylsilane 7



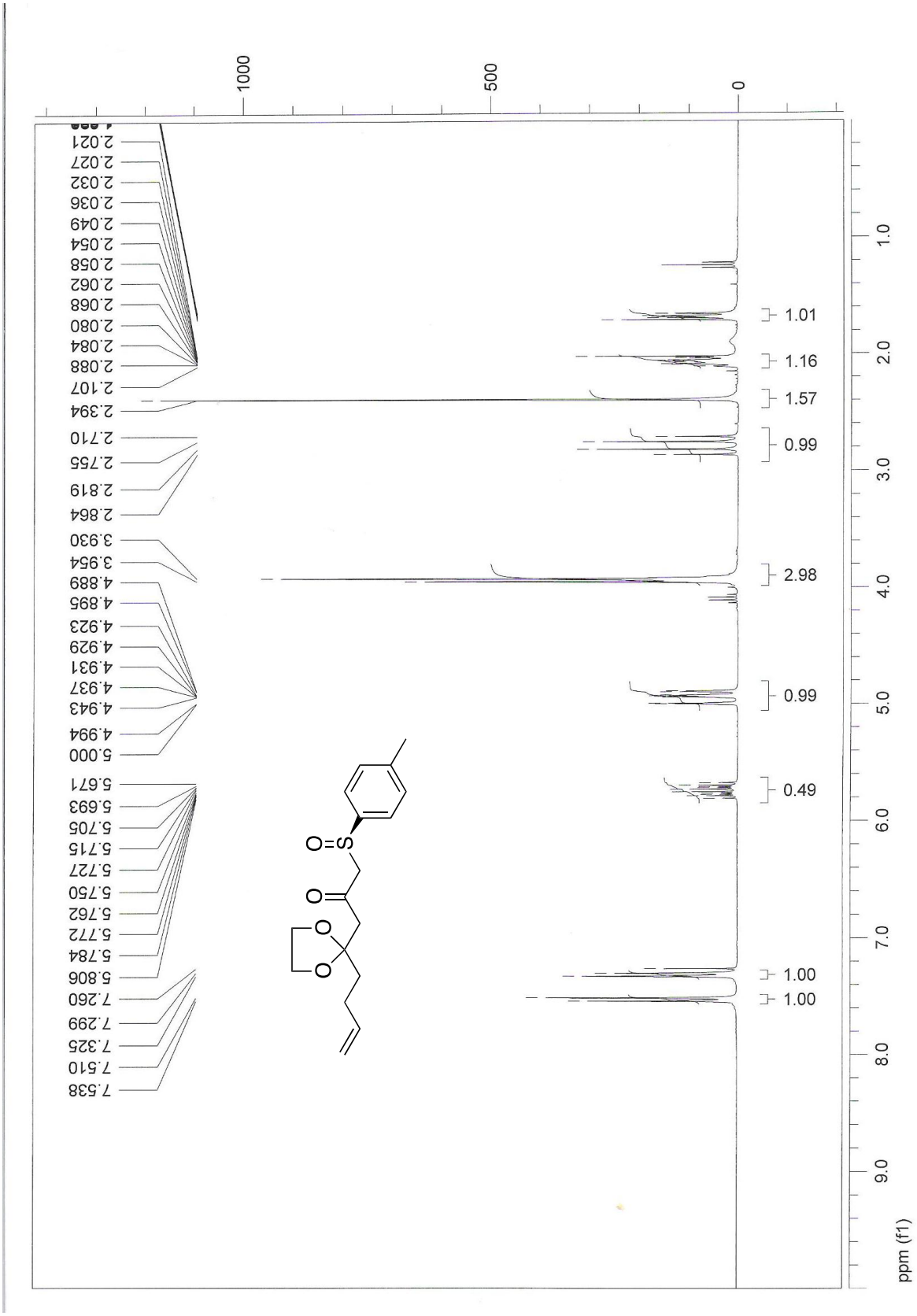


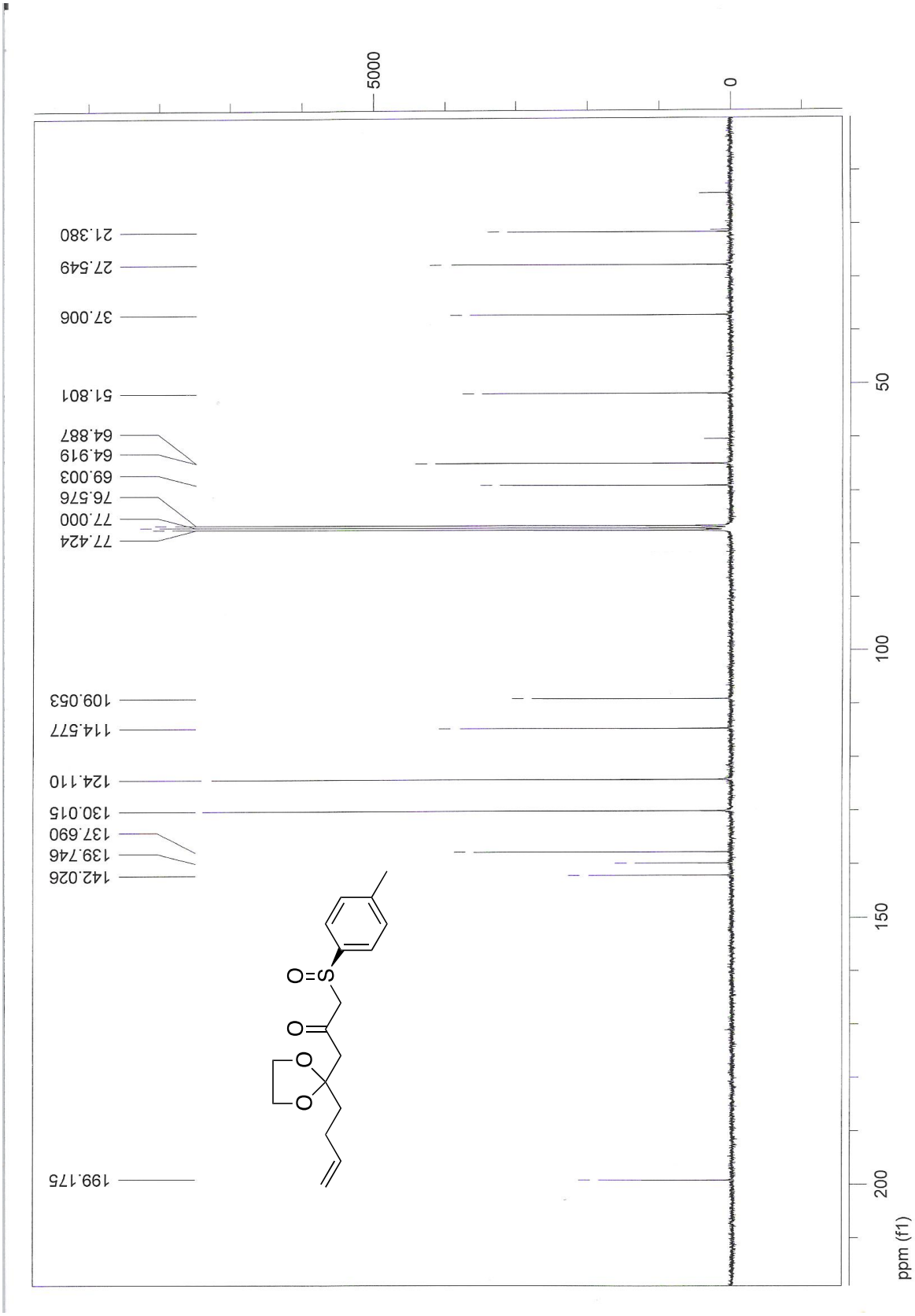
(*S*)-2-(benzyloxy)-5-(*tert*-butyldiphenylsilyloxy)pentanal 8



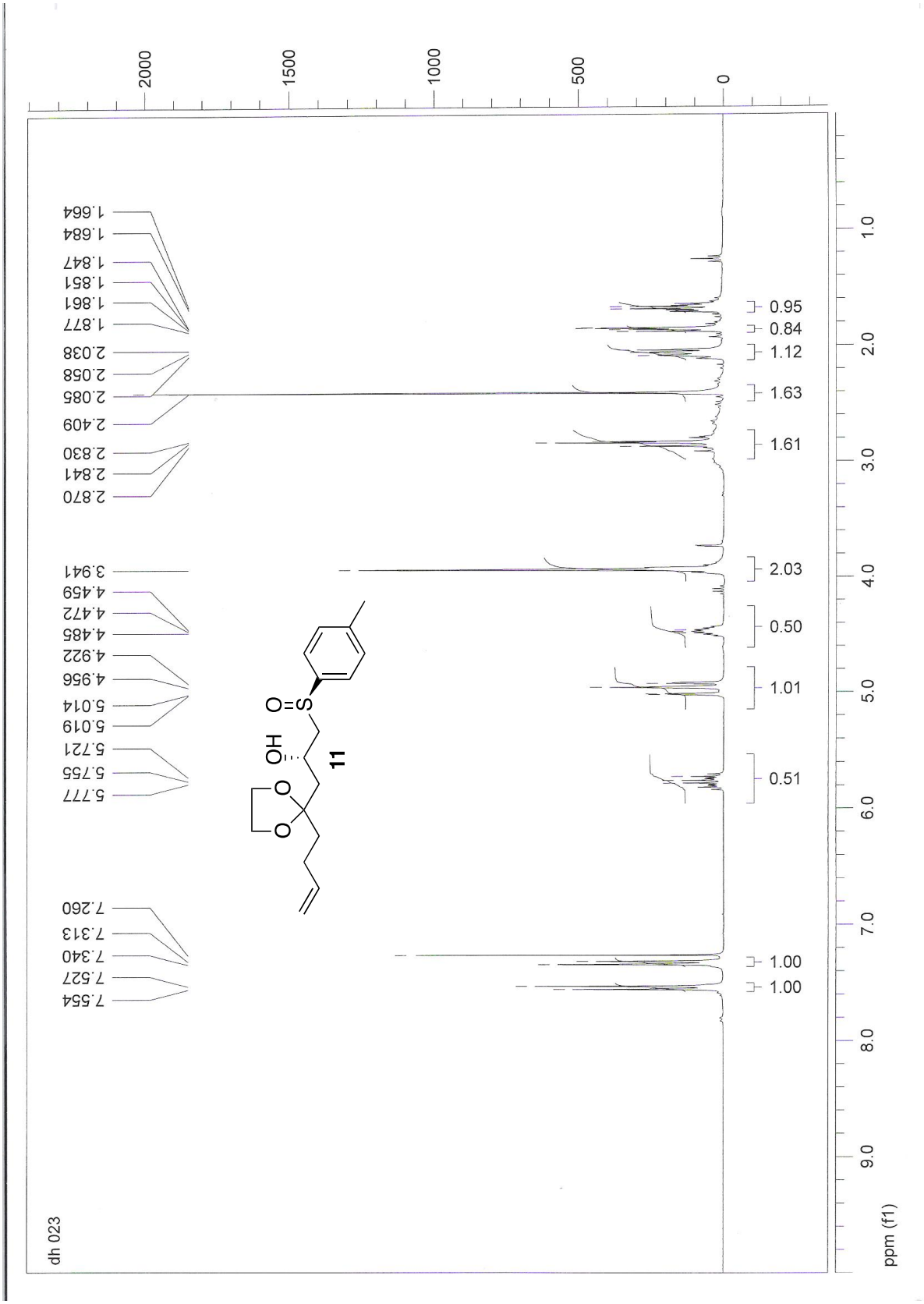


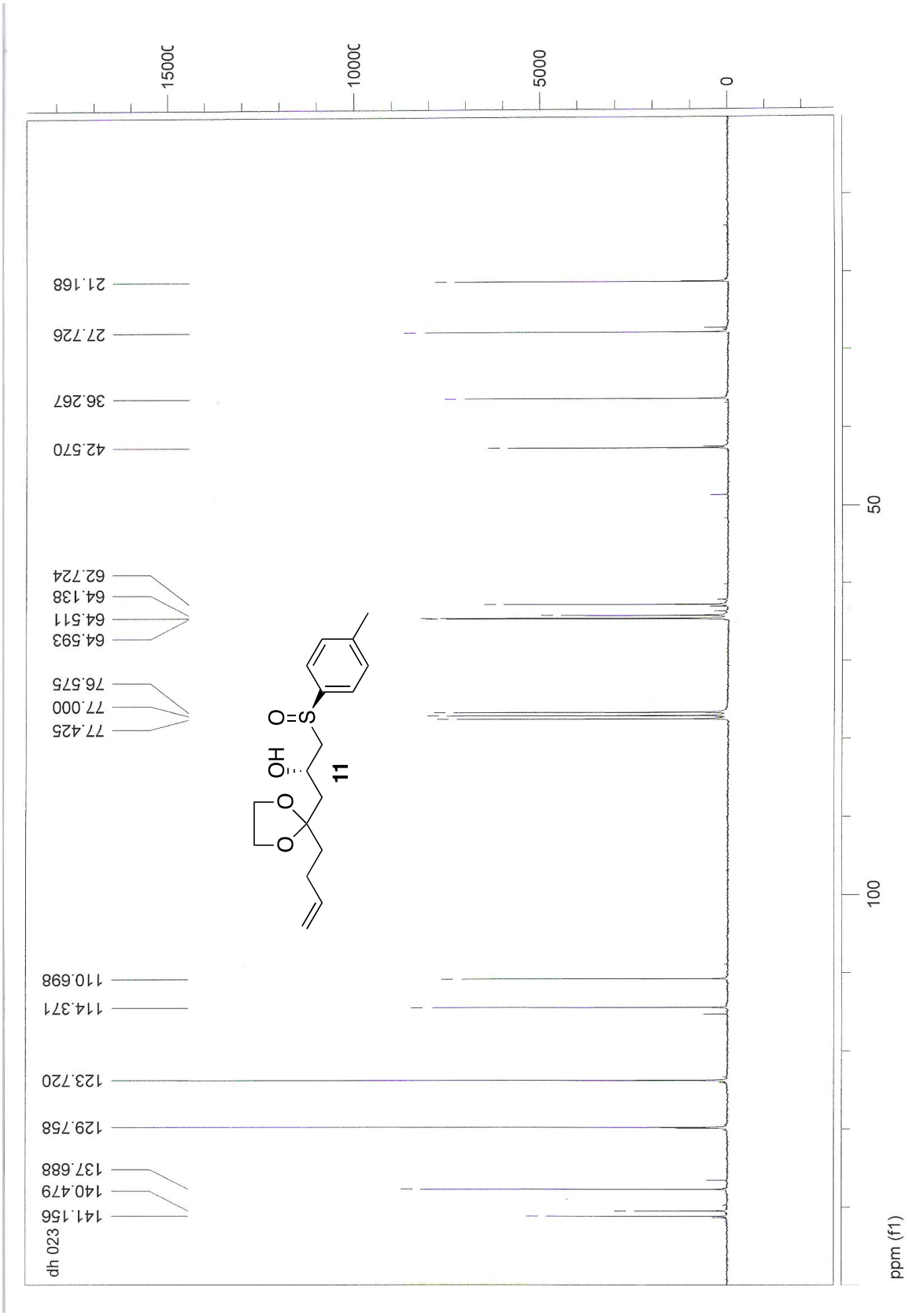
1-(2-but-3-enyl-1,3-dioxolan-2-yl)-3-((R)-p-tolylsulfinyl)propan-2-one



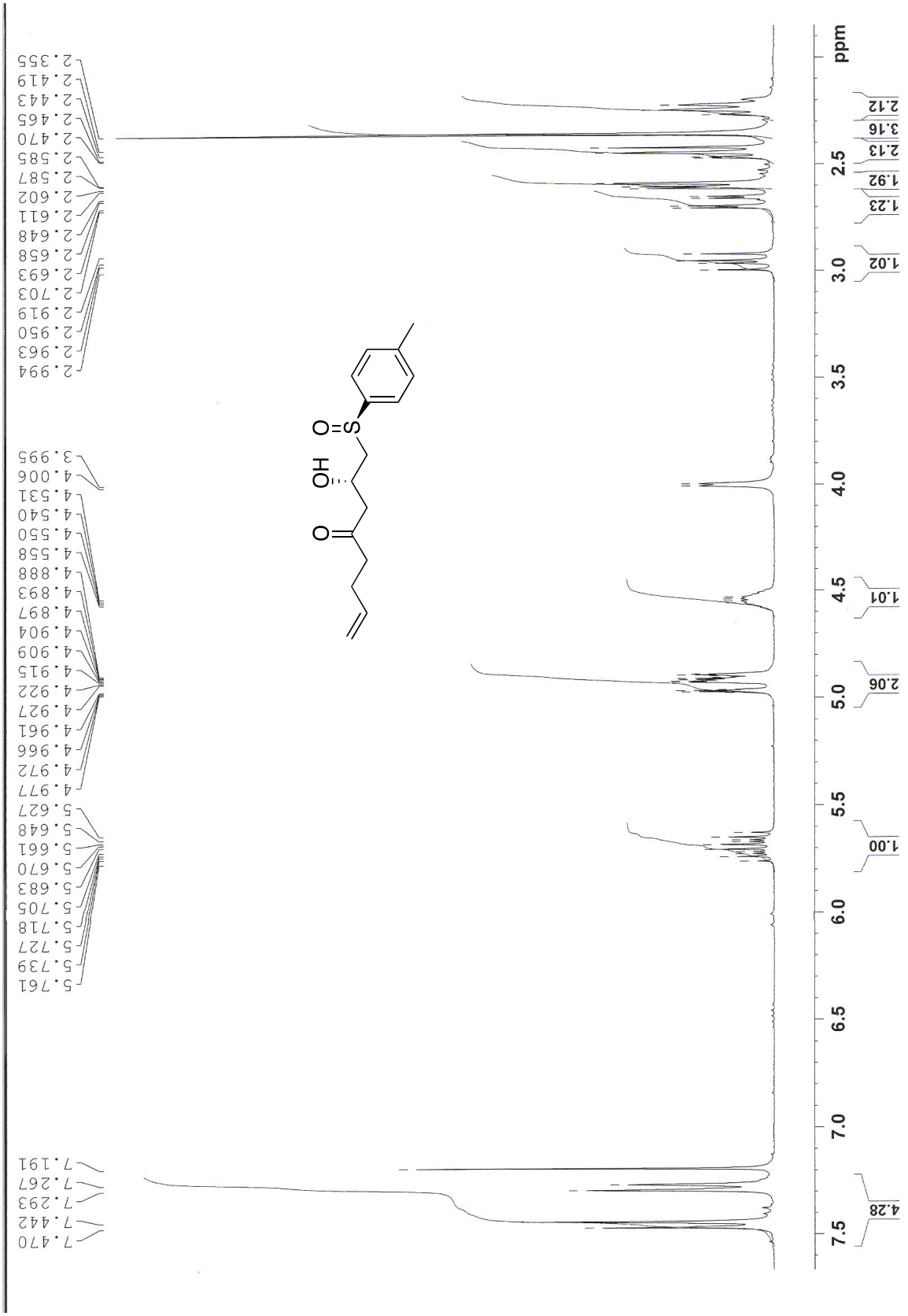


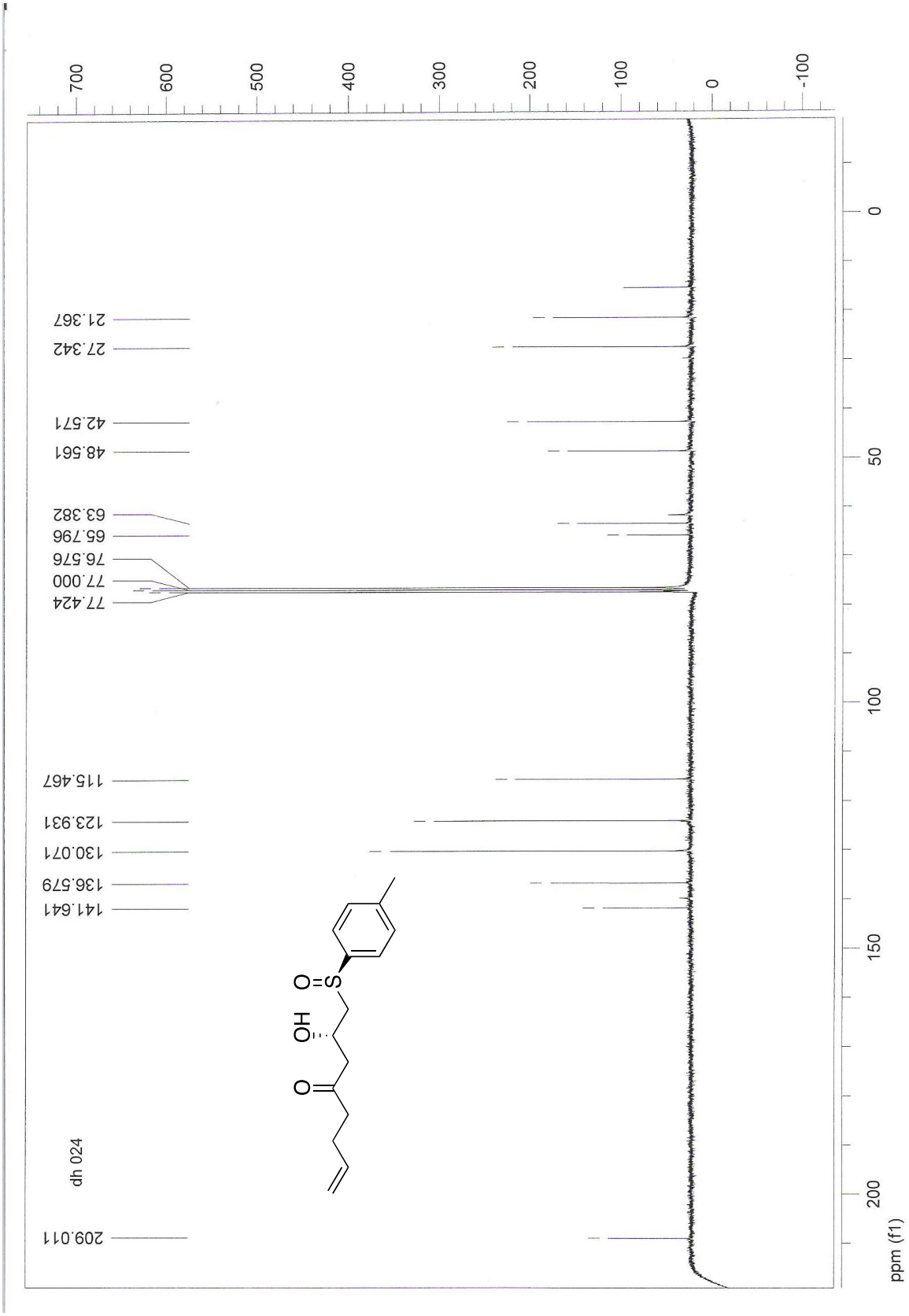
(S)-1-(2-but-3-enyl-1,3-dioxolan-2-yl)-3-((R)-p-tolylsulfinyl)propan-2-ol 11



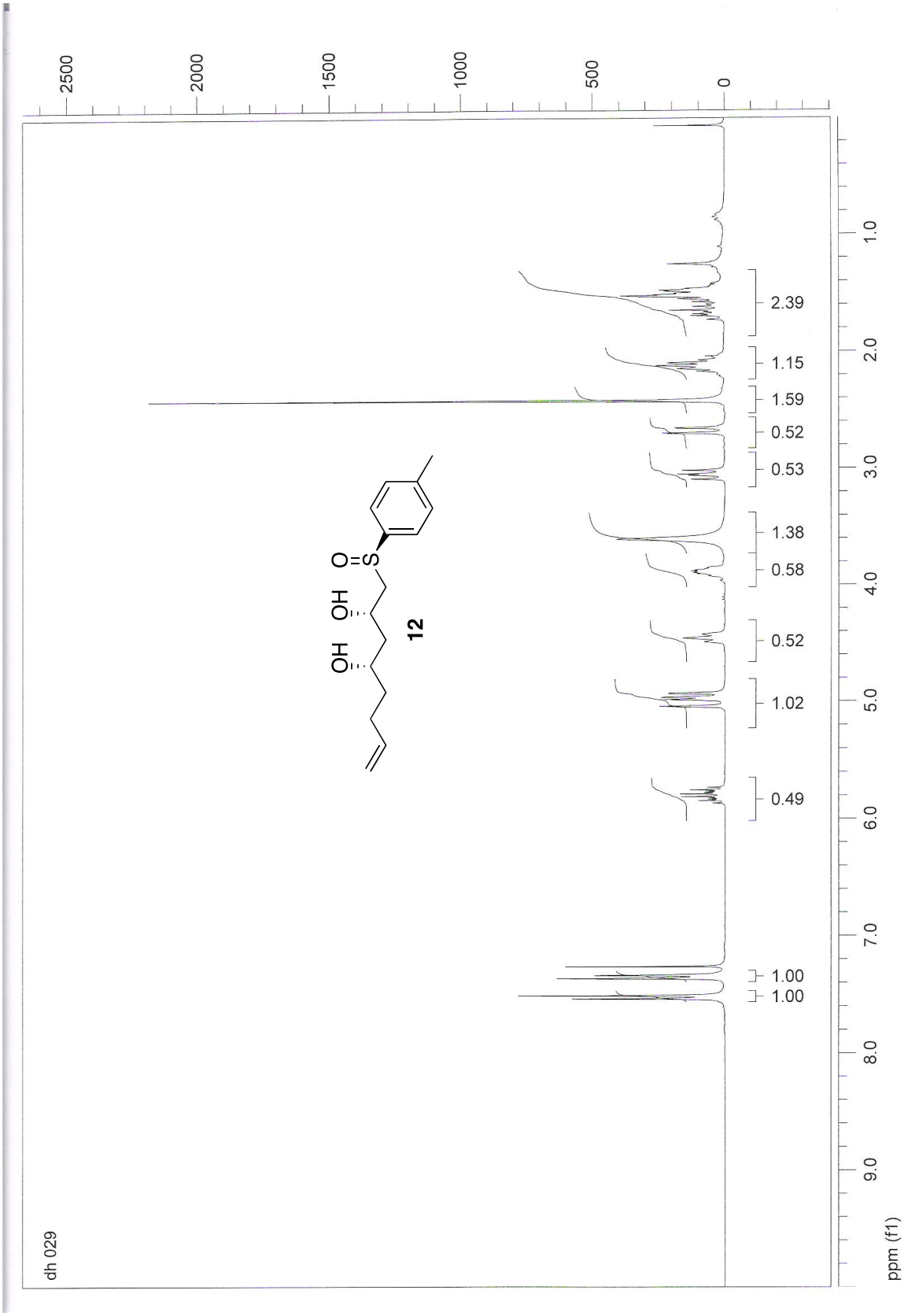


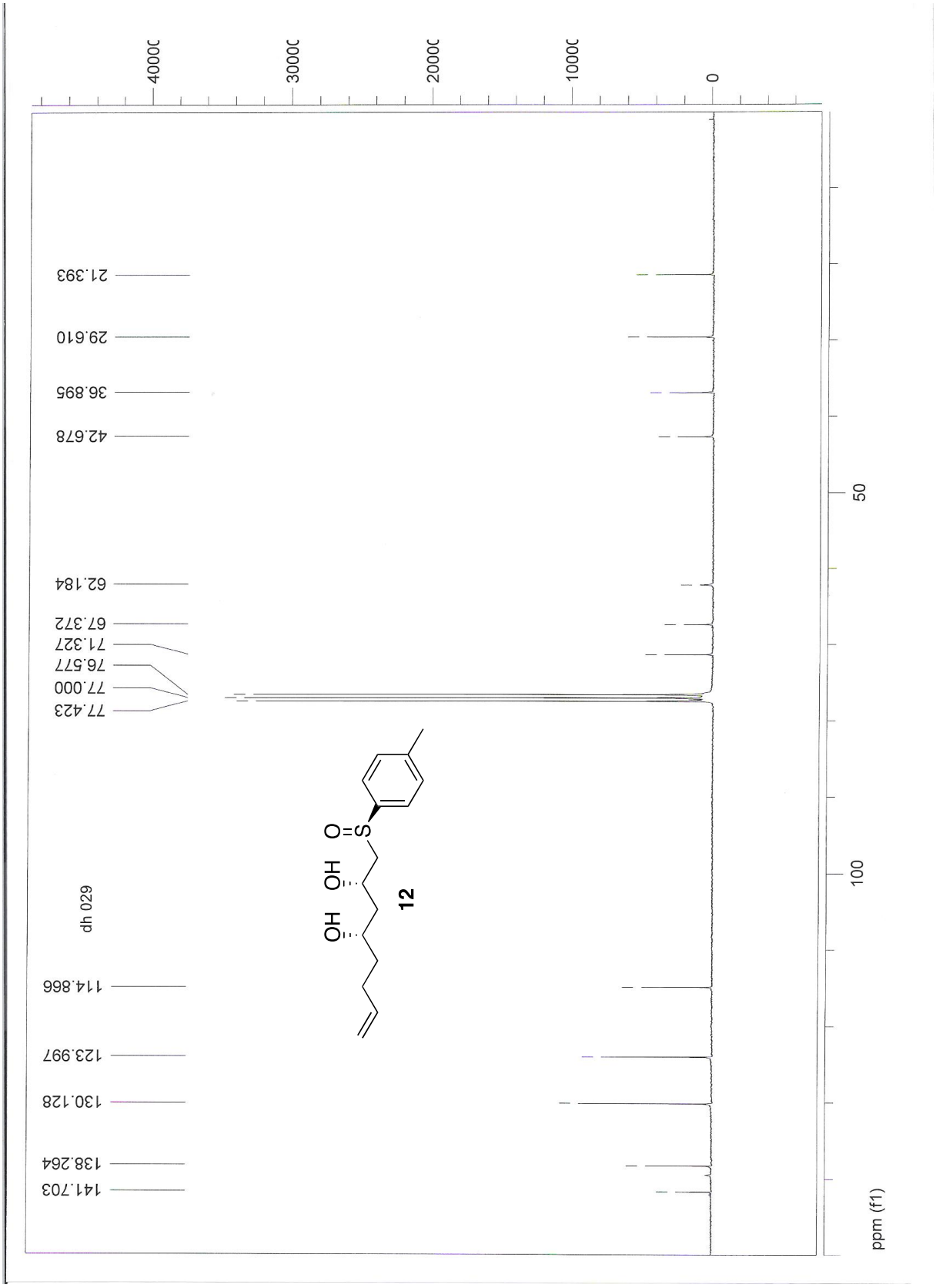
(2S)-2-Hydroxy-1((R)-p-tolylsulfinyl)-oct-7-en-4-one



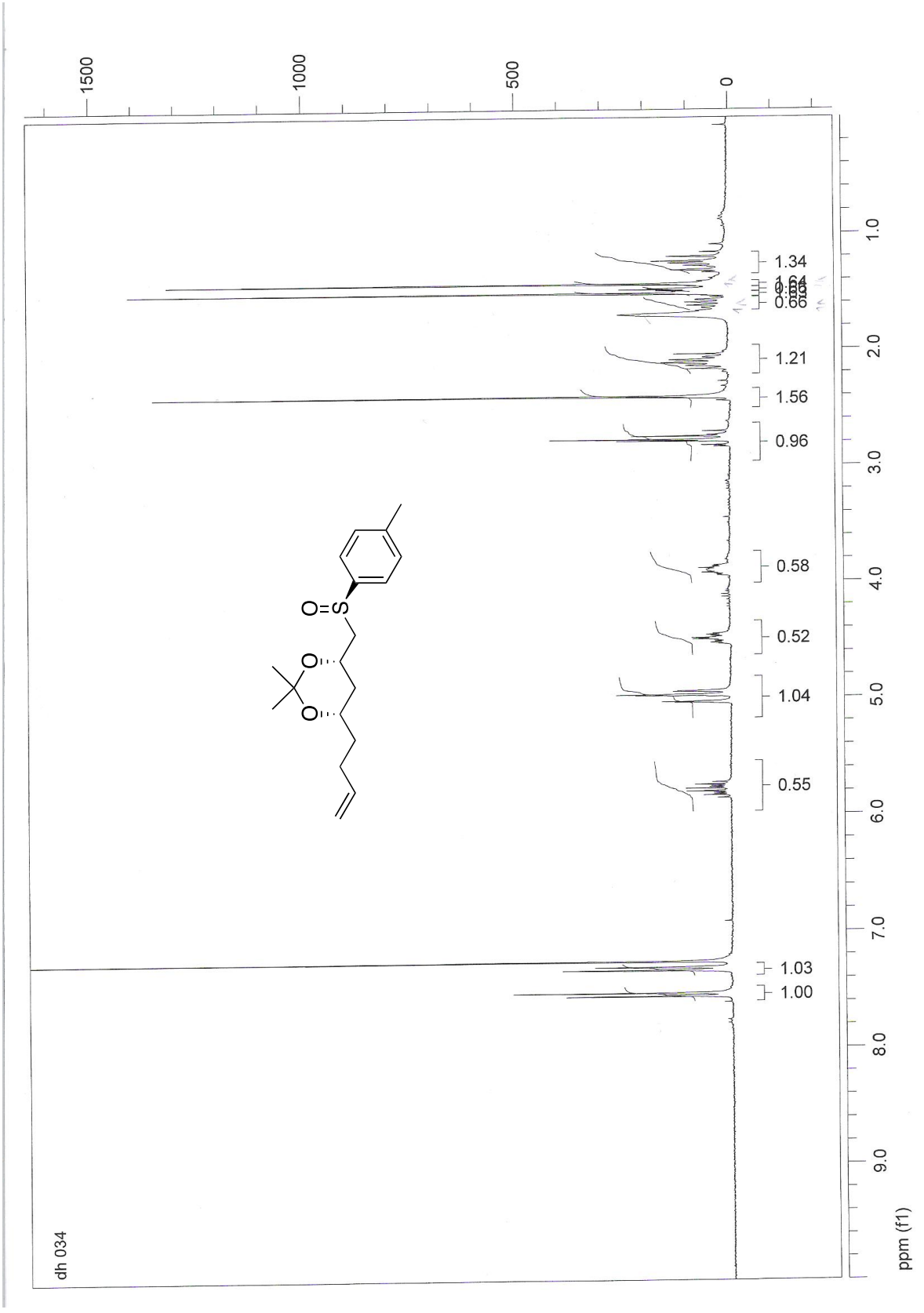


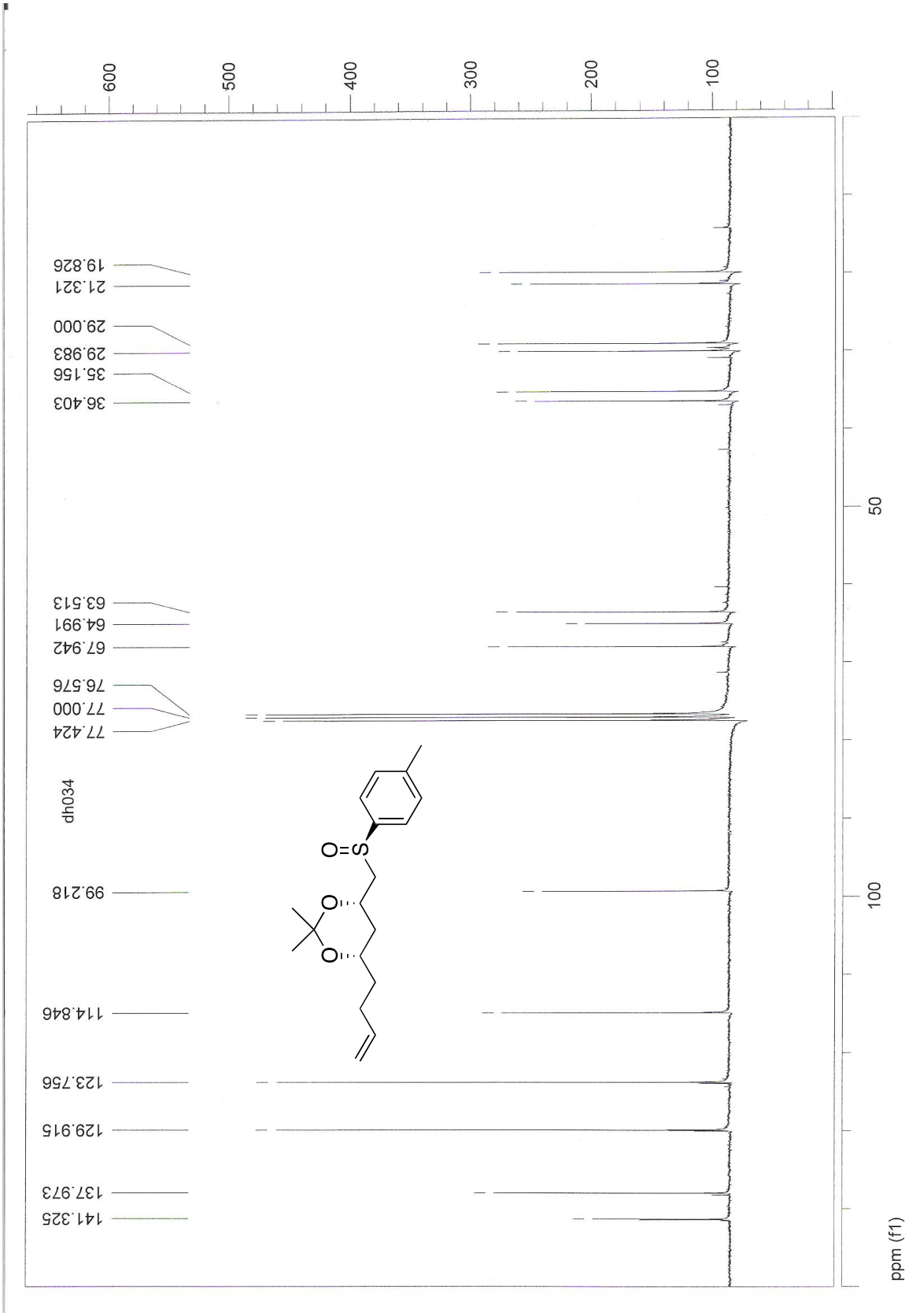
(2S,4S)-7-(4-methoxybenzyloxy)-1-((R)-p-tolylsulfinyl)octane-2,4-diol 12



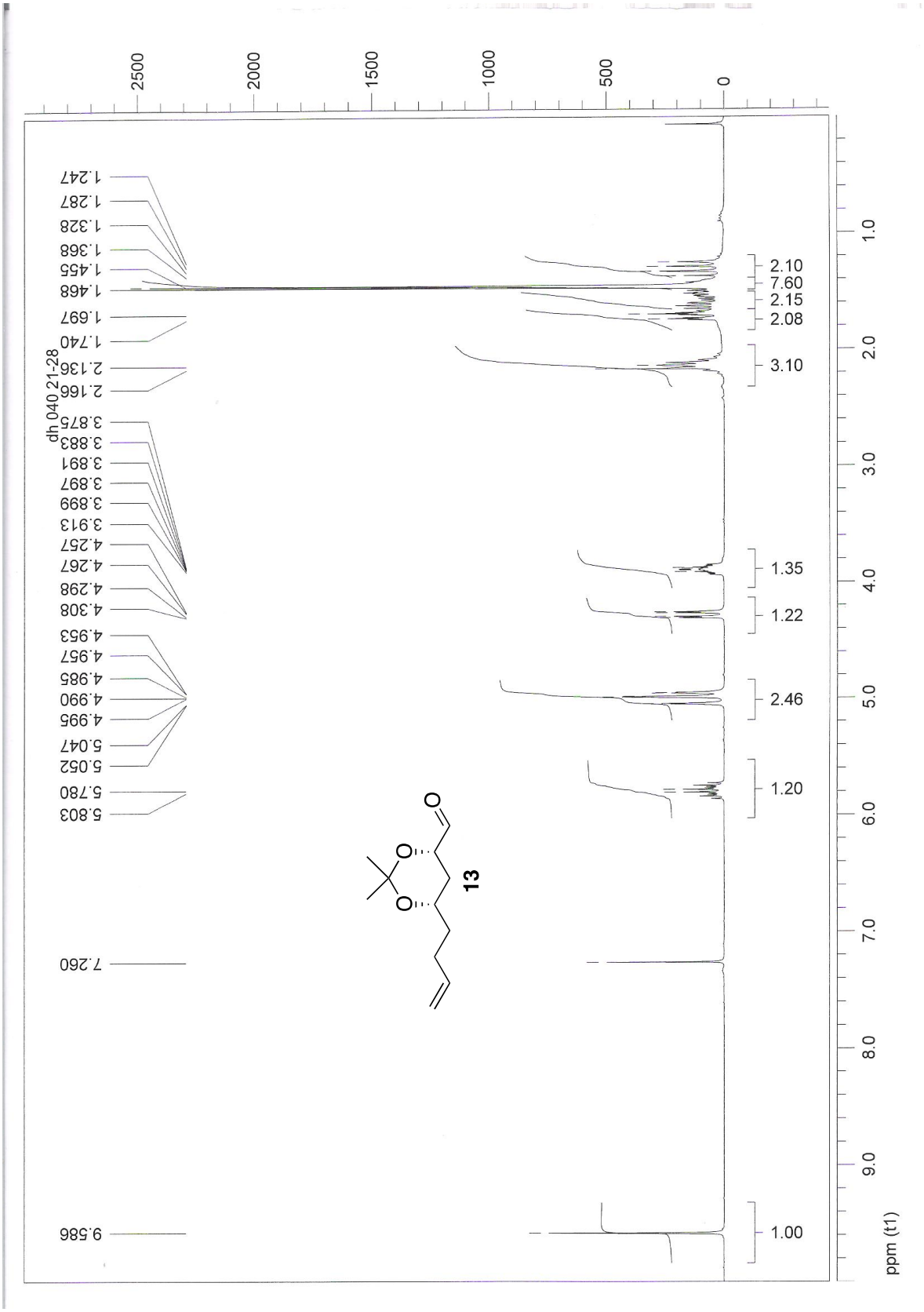


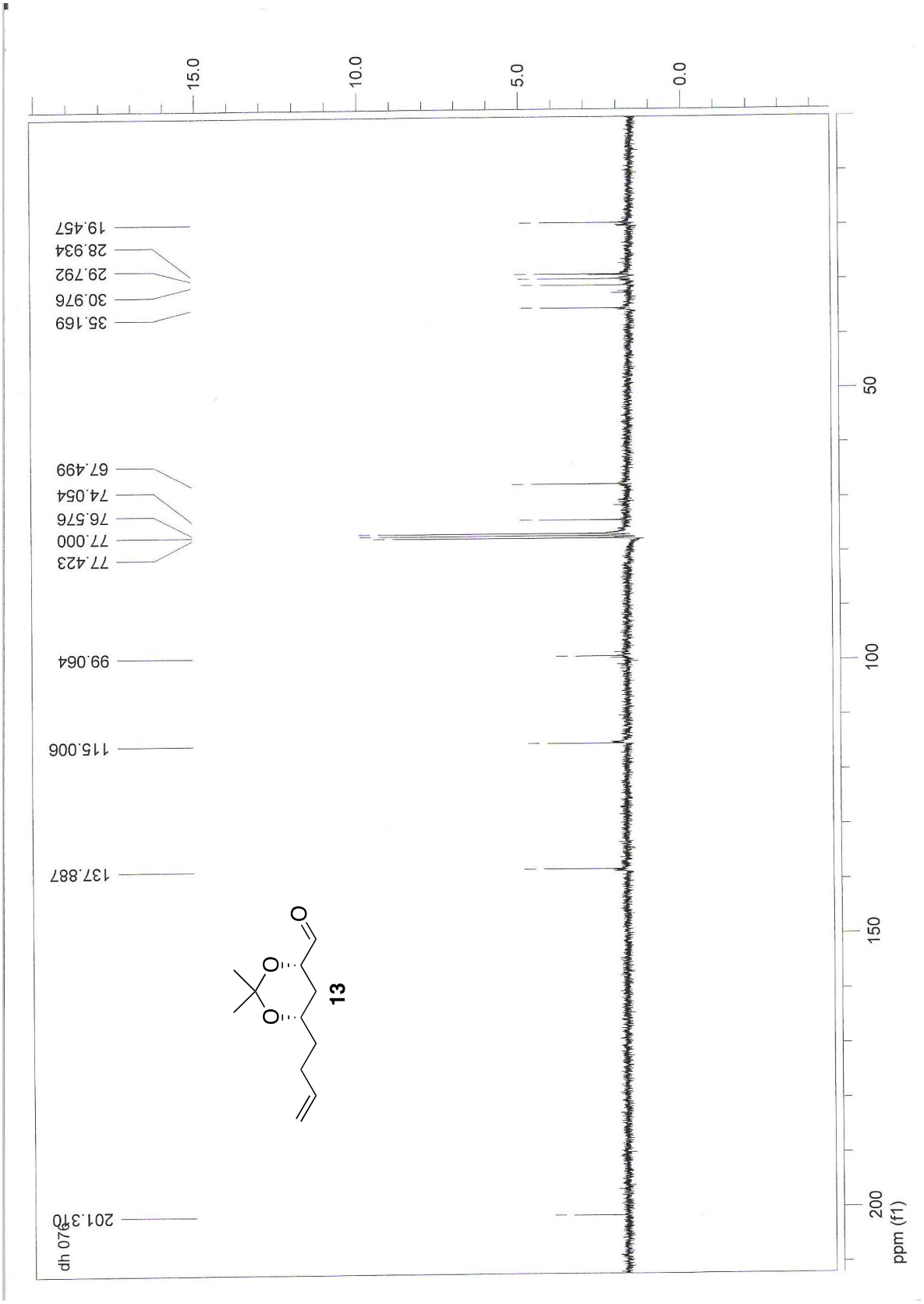
(4S,6S)-4-(3-(4-methoxybenzyloxy)butyl-2,2-dimethyl-6((R)-p-tolylsulfinylmethyl)-1,3-dioxane



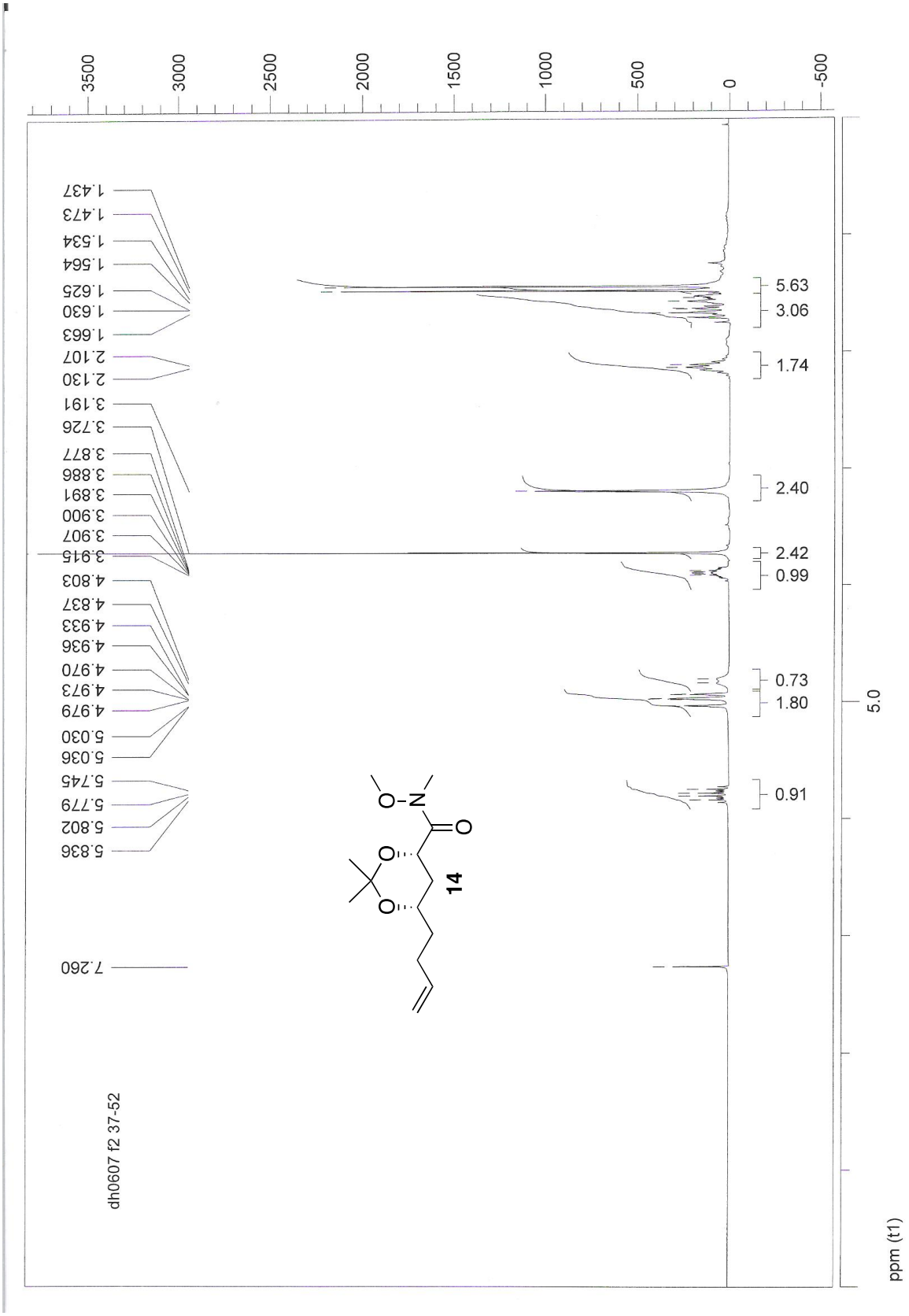


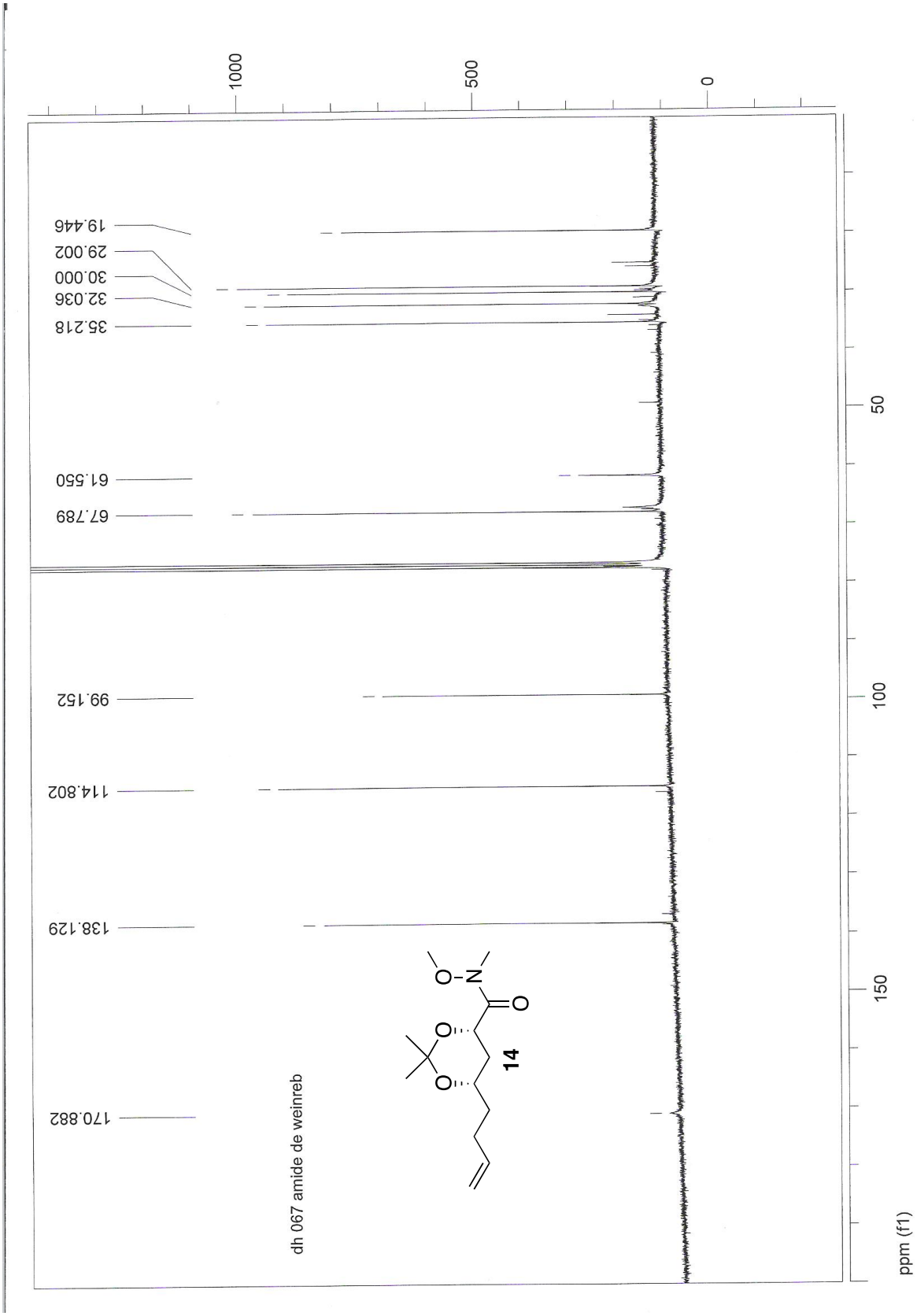
(4S,6S)-6-(3-(4-methoxybenzyloxy)butyl)-2,2-dimethyl-1,3-dioxane-4-carbaldehyde 13



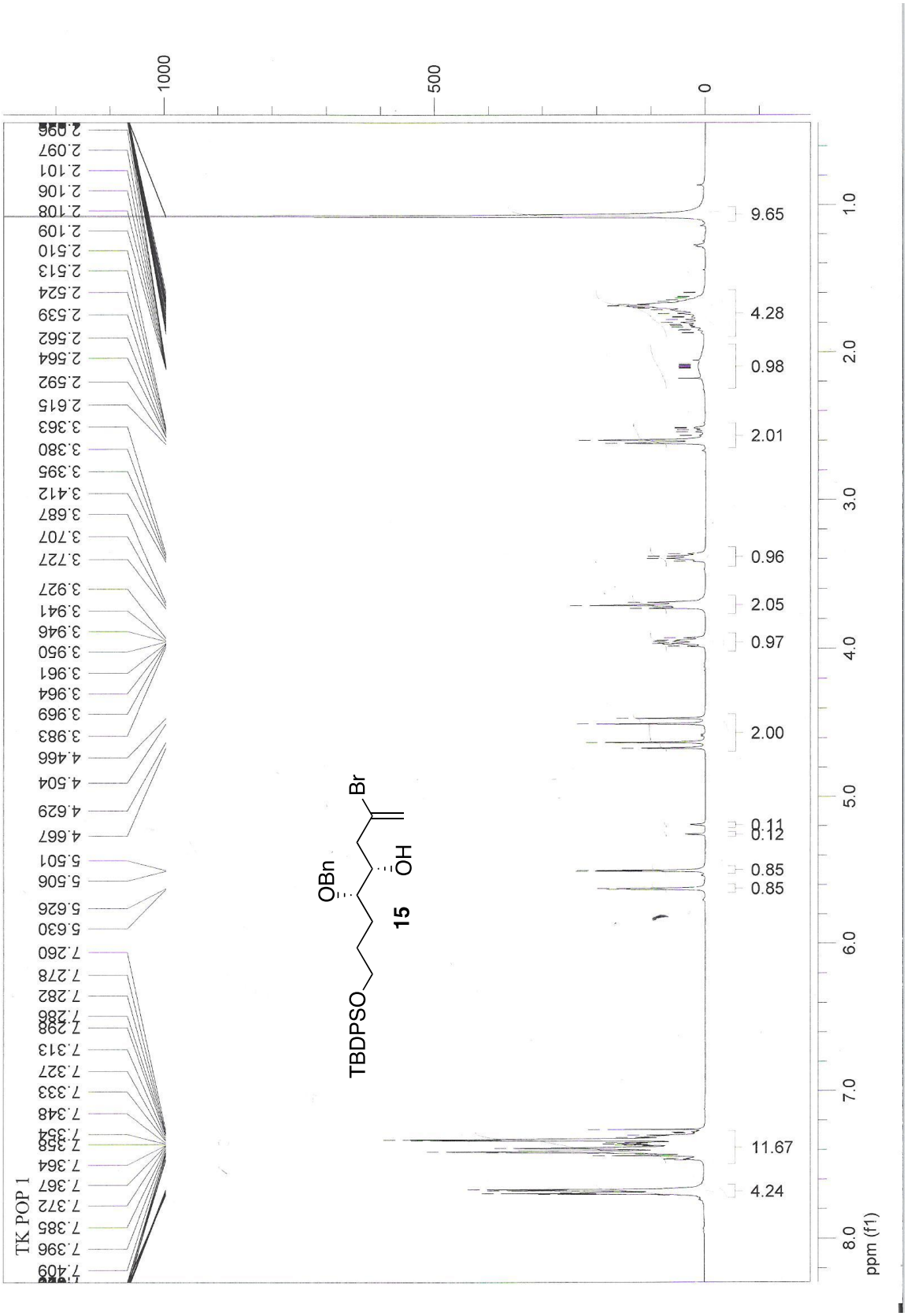


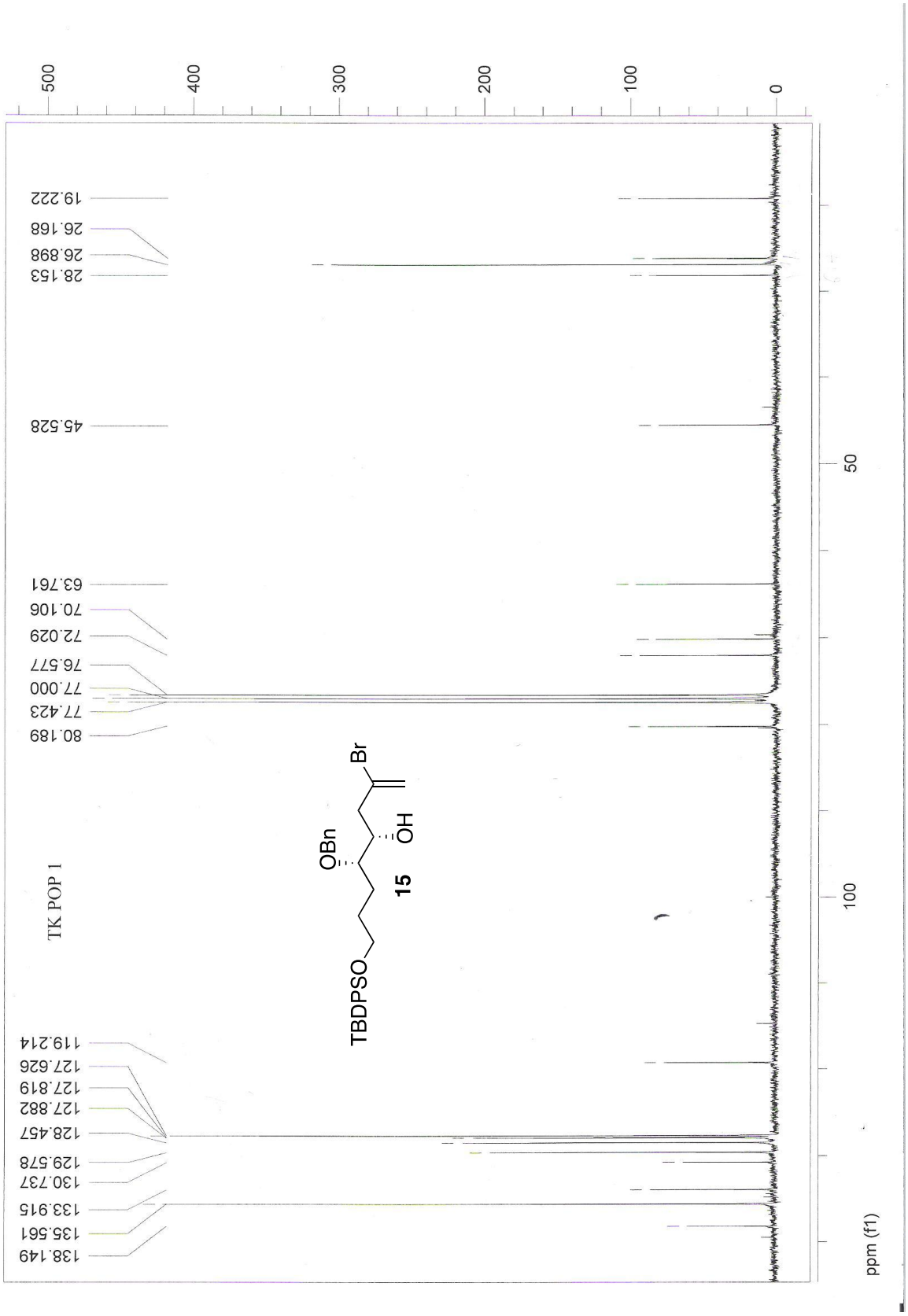
(4S,6S)-6-(but-3-enyl)-N-methoxy-N,2,2-trimethyl-1,3-dioxane-4-carboxamide 14



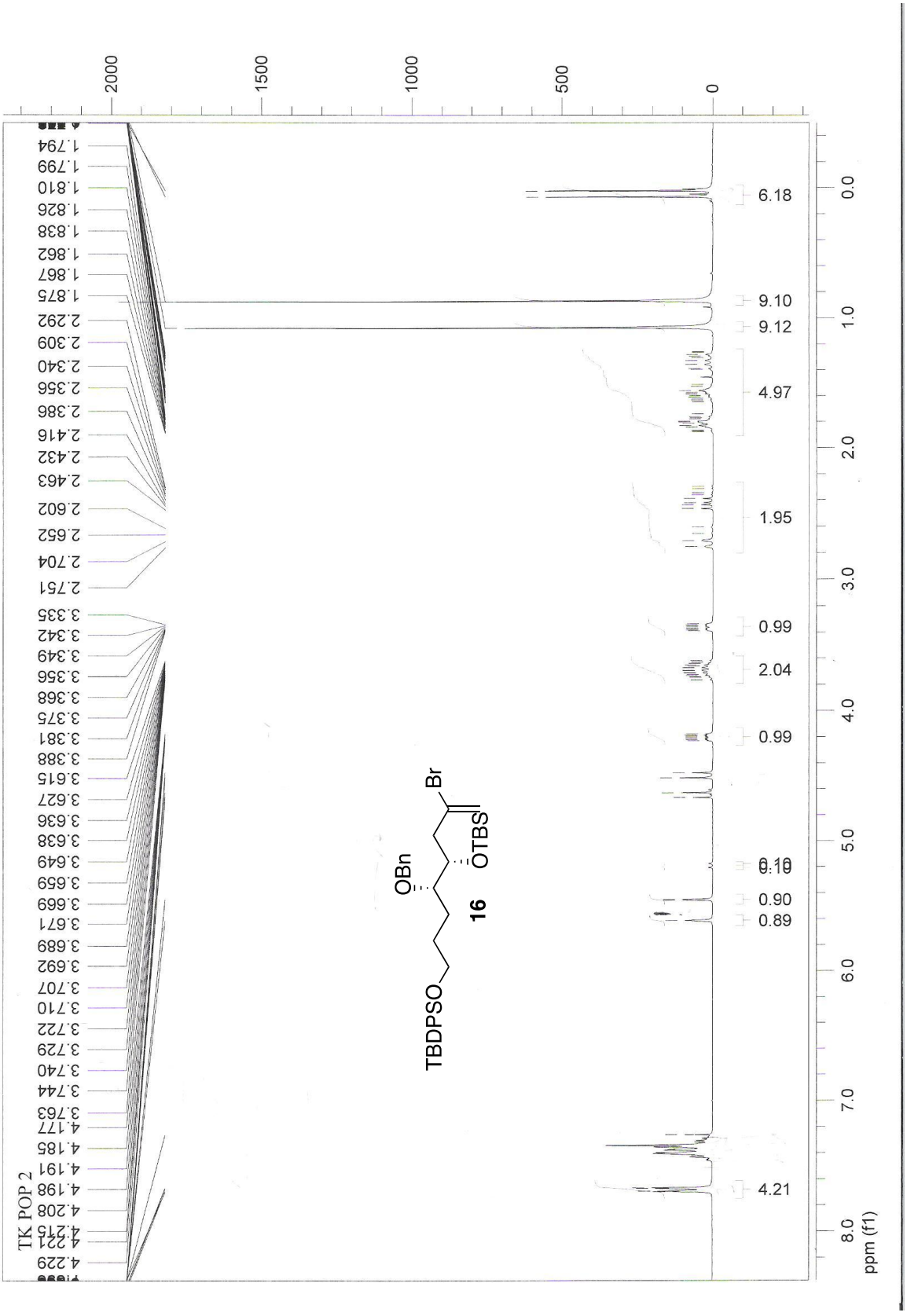


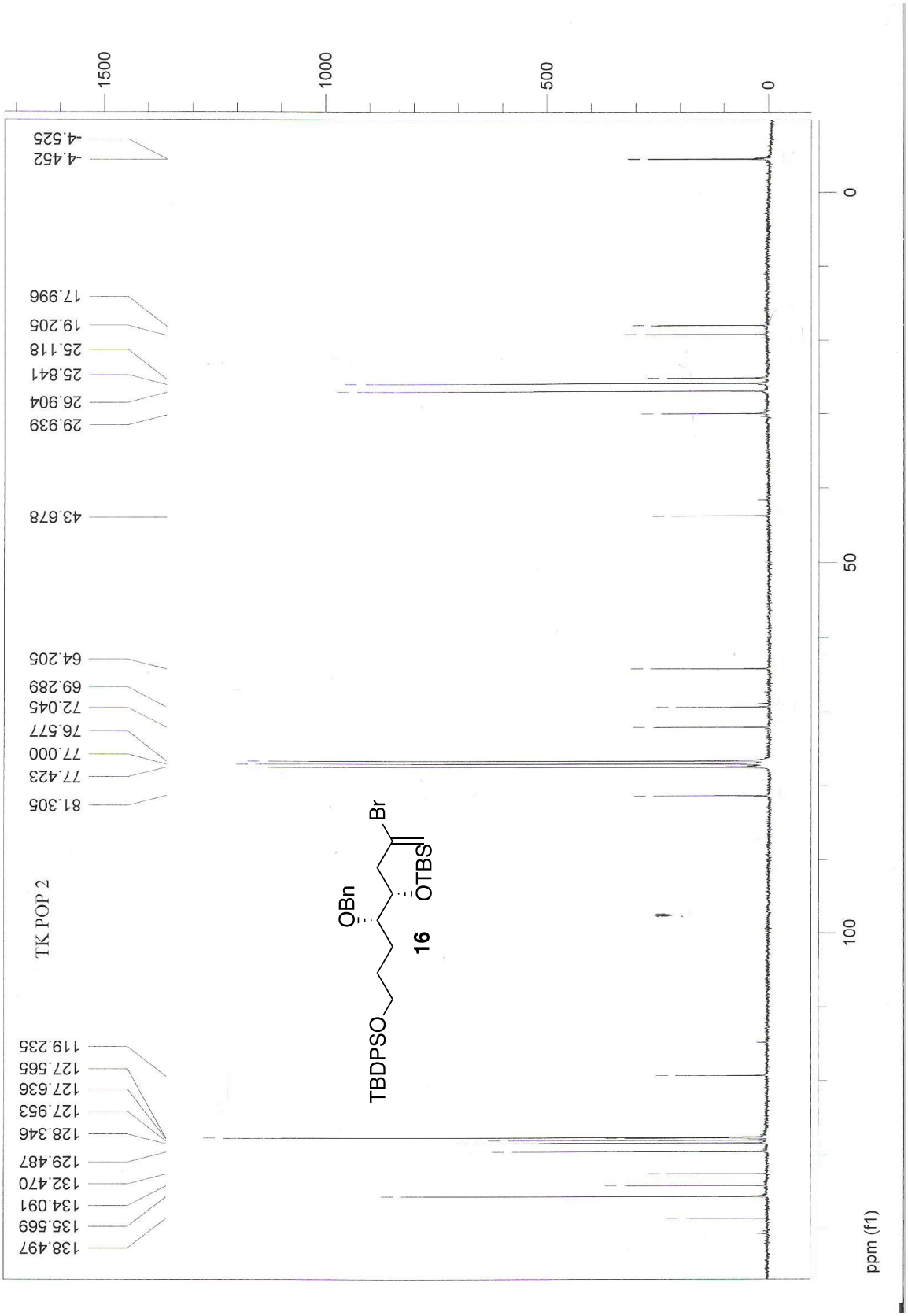
(4*S*,5*S*)-5-(benzyloxy)-2-8-(*tert*-butyldiphenylsilyloxy)oct-1-en-4-ol 15



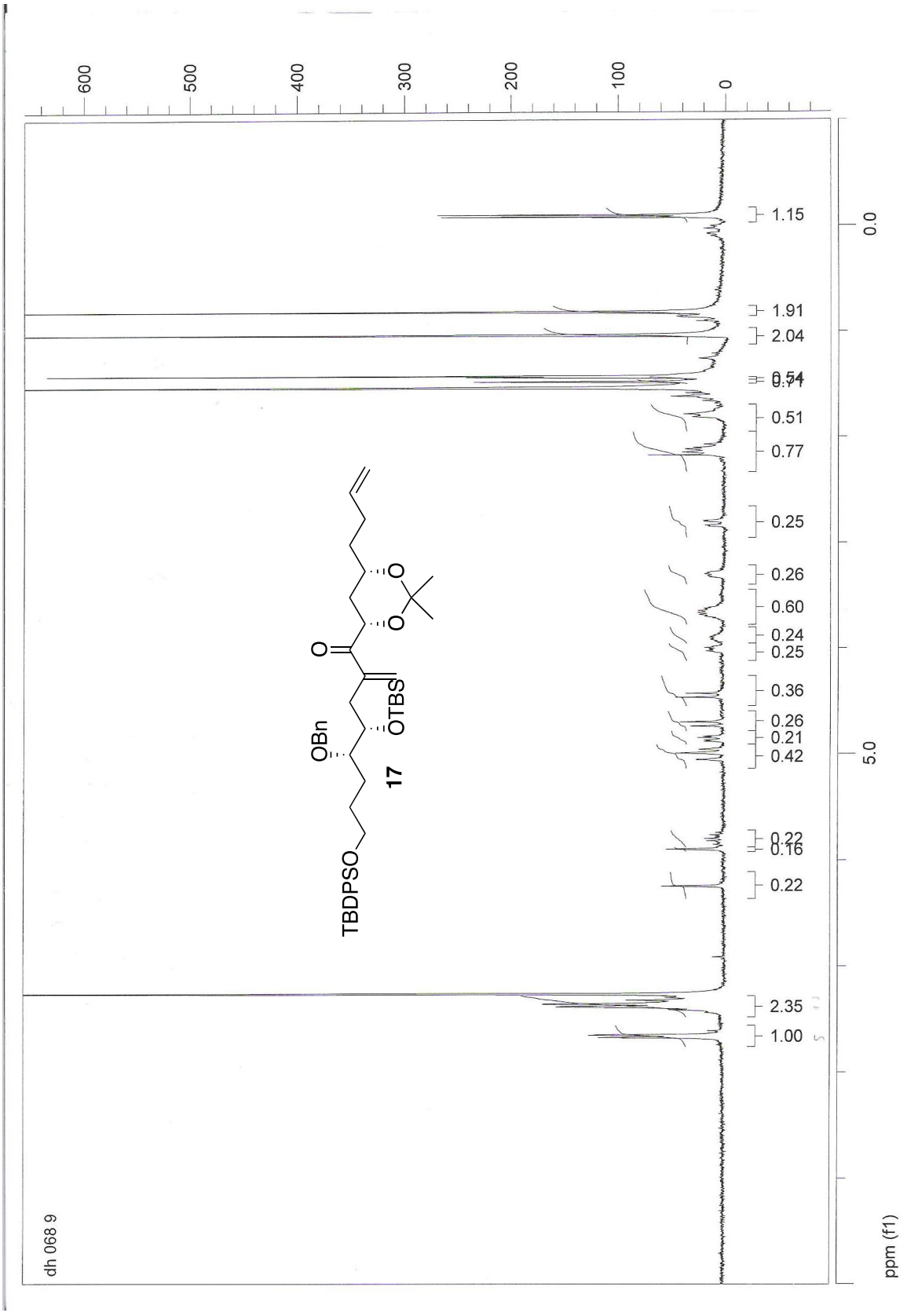


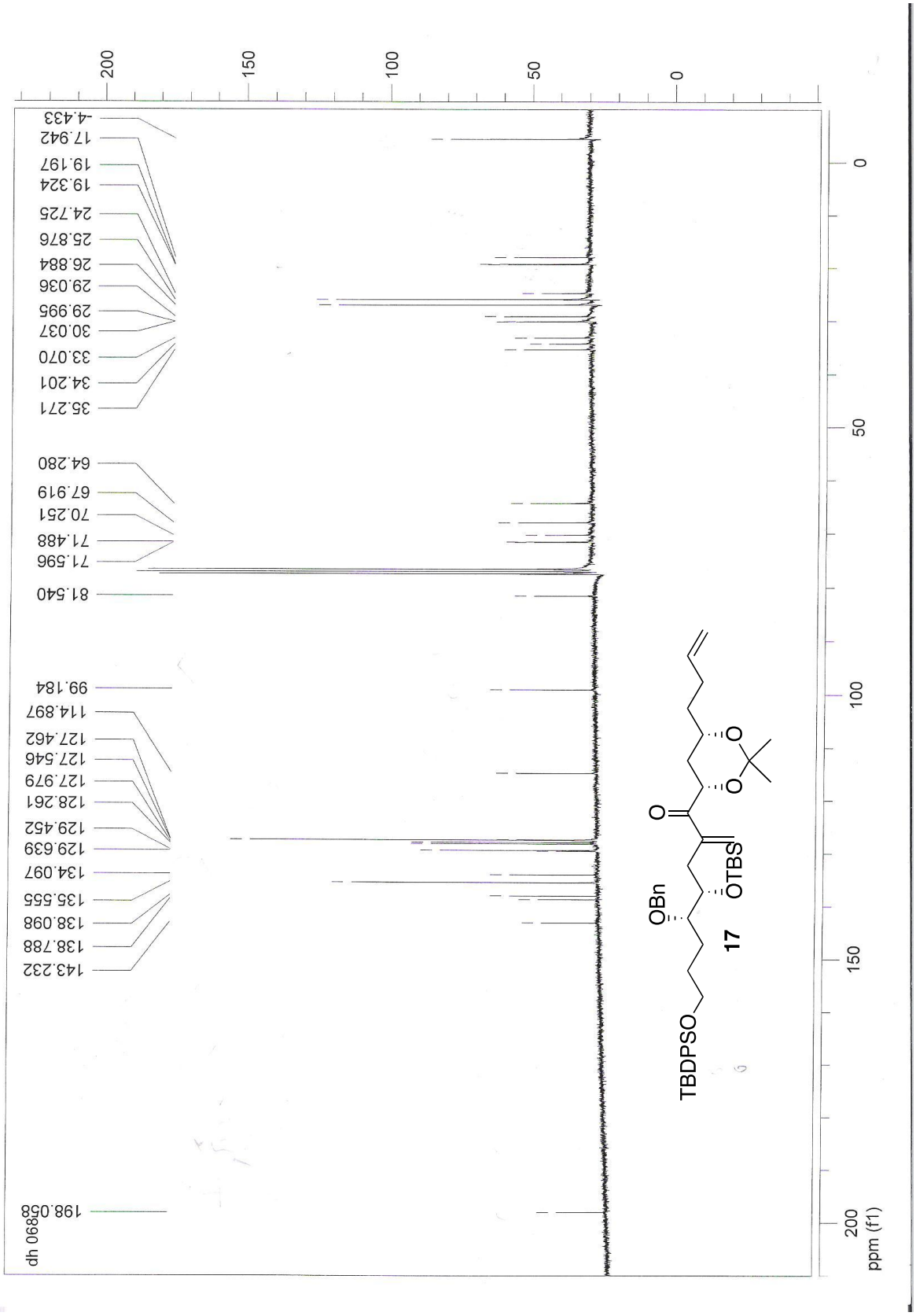
(5*S*,6*S*)-6-(benzyloxy)-5-(2-bromoallyl)-2,2,3,312,12-hexamethyl-11,11-diphenyl-4,10-dioxa-3,11-disilatridecane 16



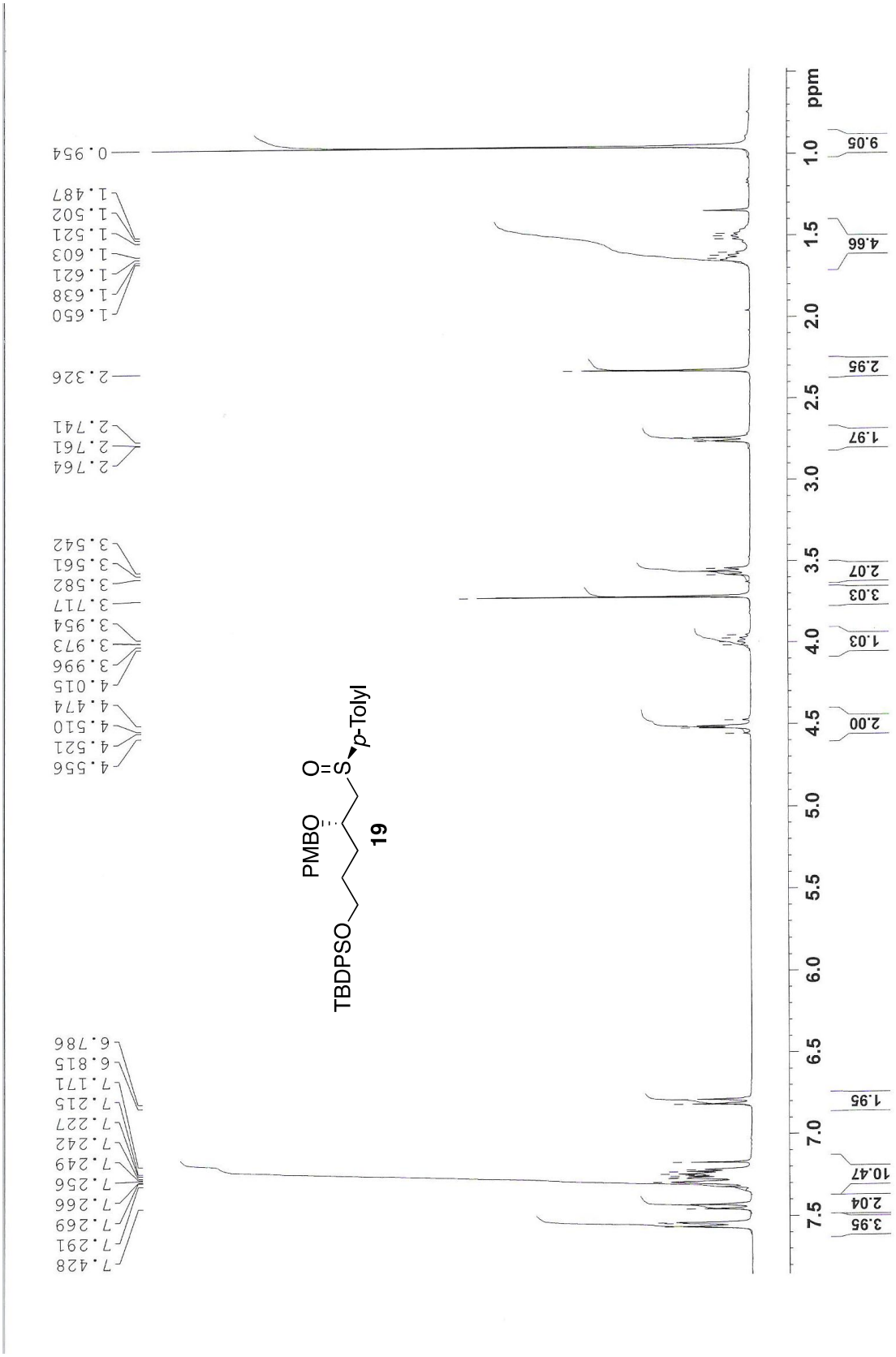


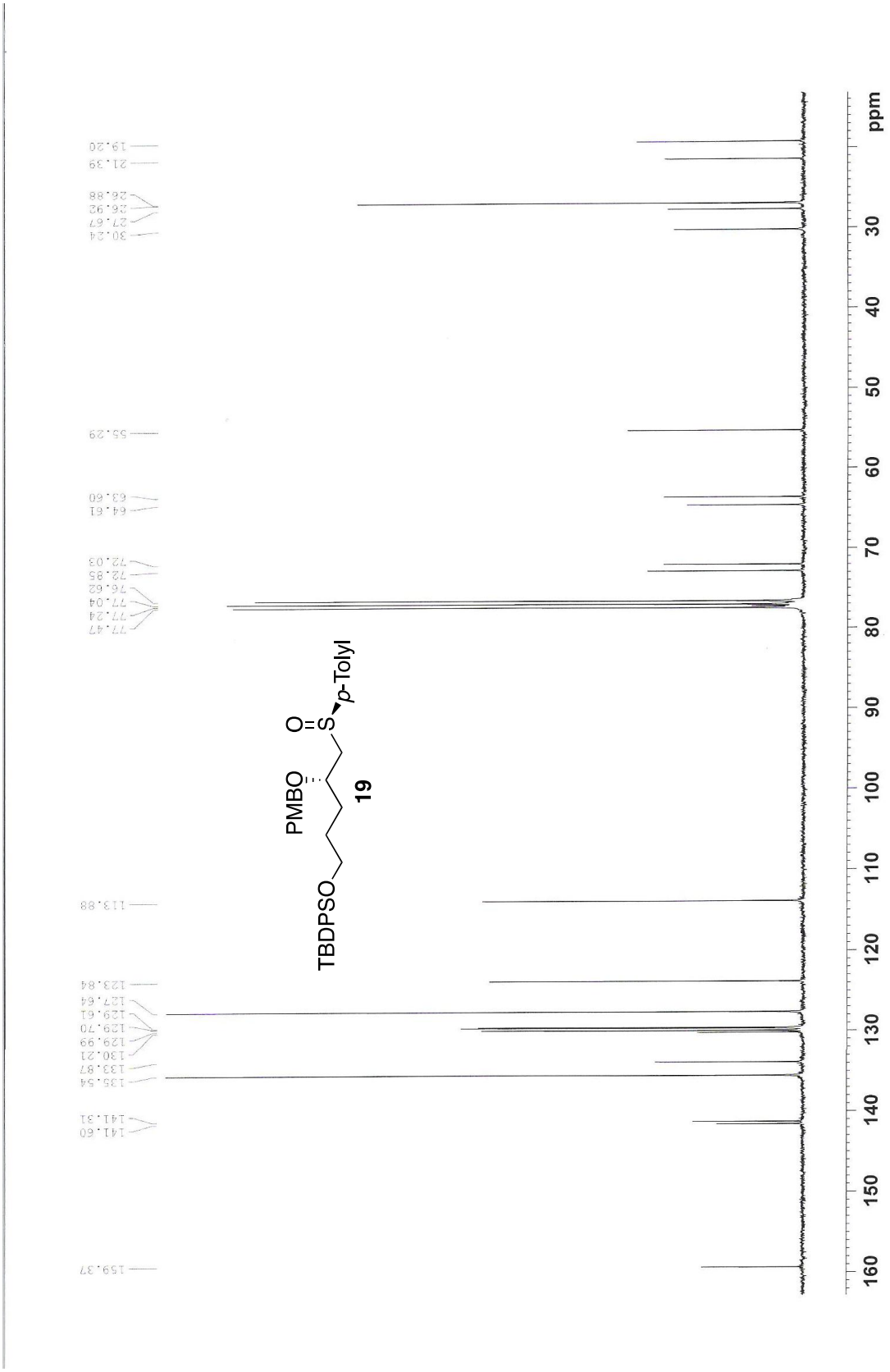
(4S,5S)-5-(benzyloxy)-1-((4S,6S)-6-(but-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)-4-((tert-butyldimethylsilyl)oxy)-8-((tert-butyldiphenylsilyl)oxy)-2-methyleneoctan-1-one 17



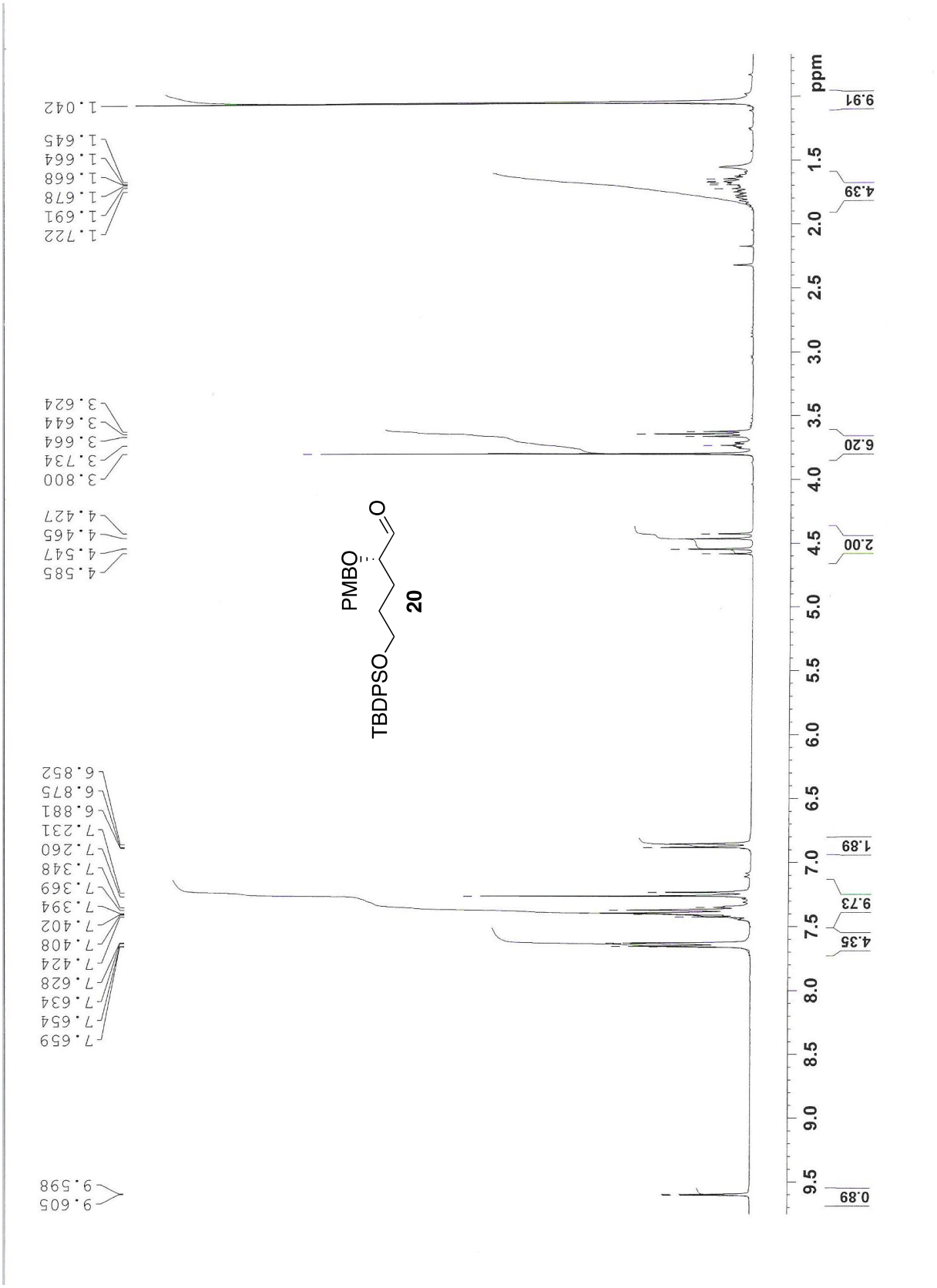


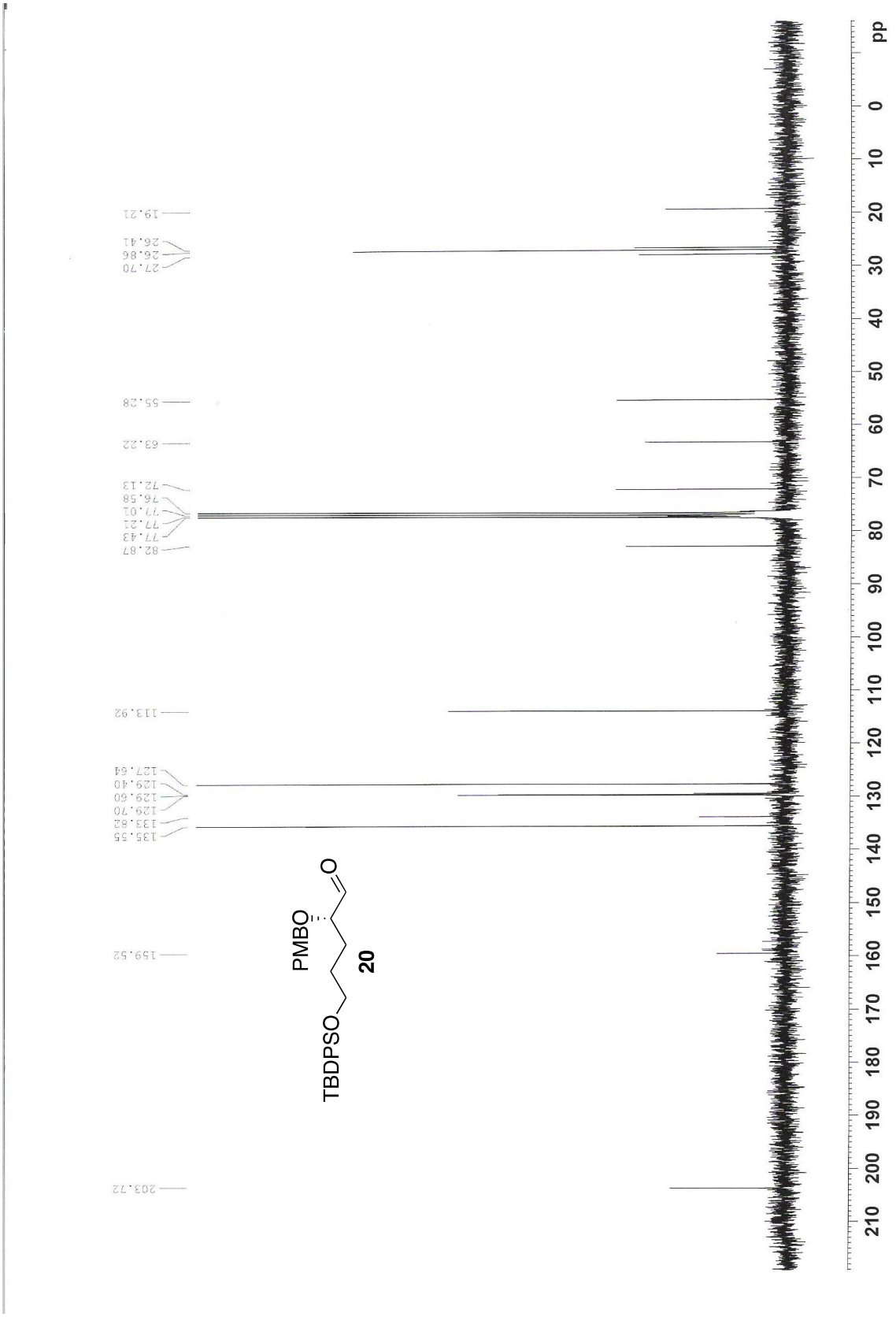
tert-butyl((S)-4-(4-methoxybenzyloxy)-5-((R)-p-tolylsulfinyl)pentyloxy)diphenylsilane 19



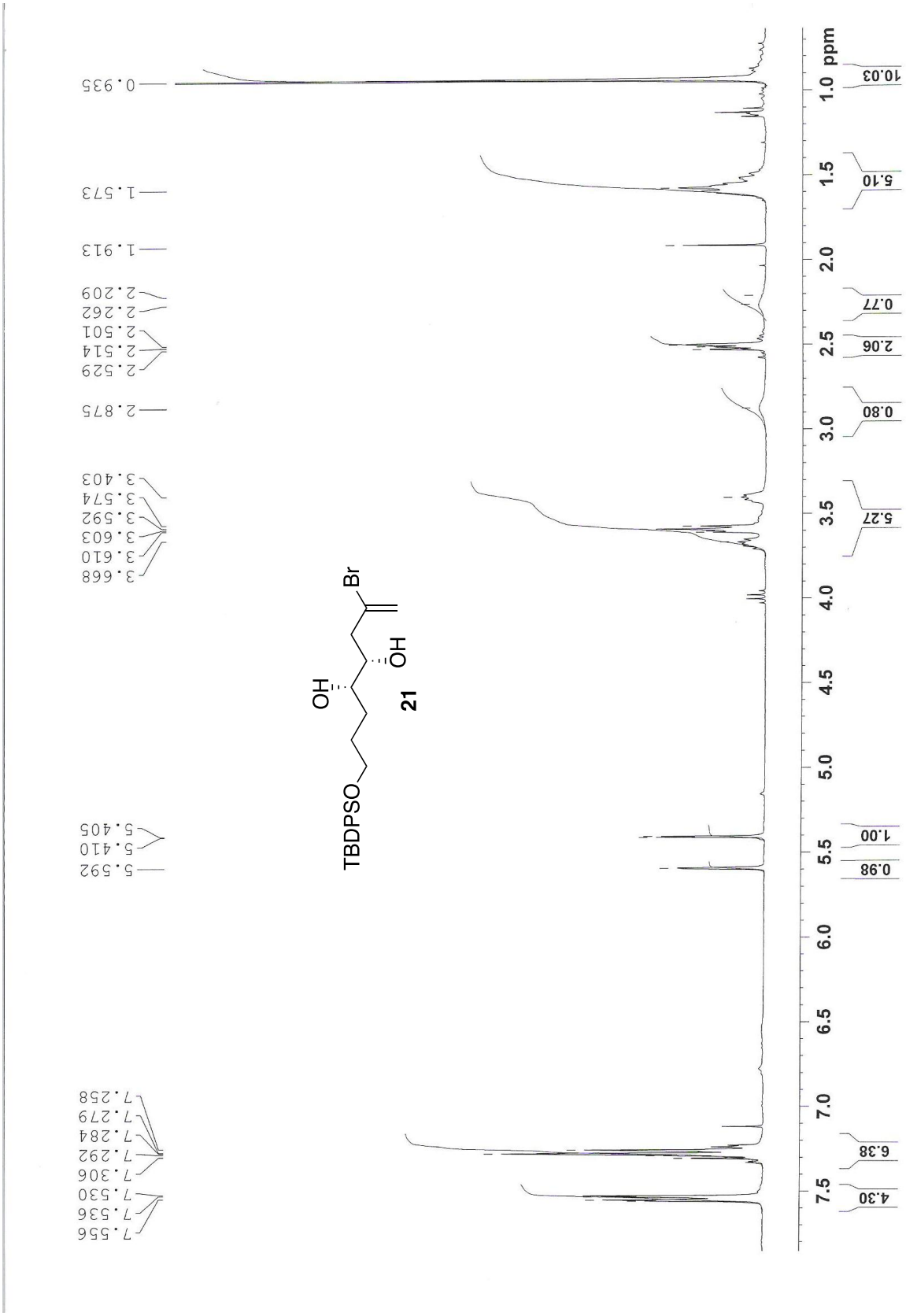


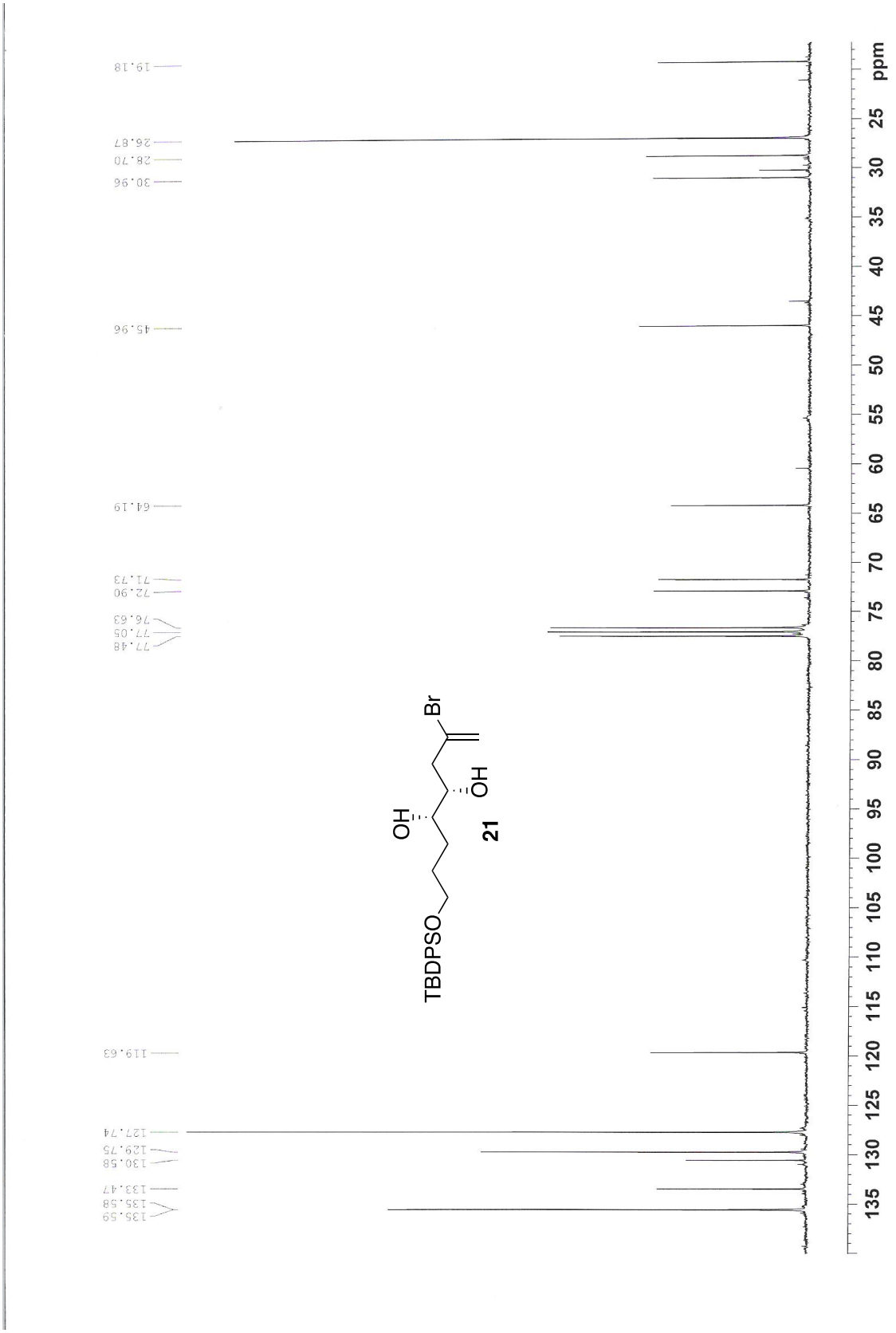
(*S*)-5-(*tert*-butyldiphenylsilyloxy)-2-(4-methoxybenzyloxy)pentanal 20



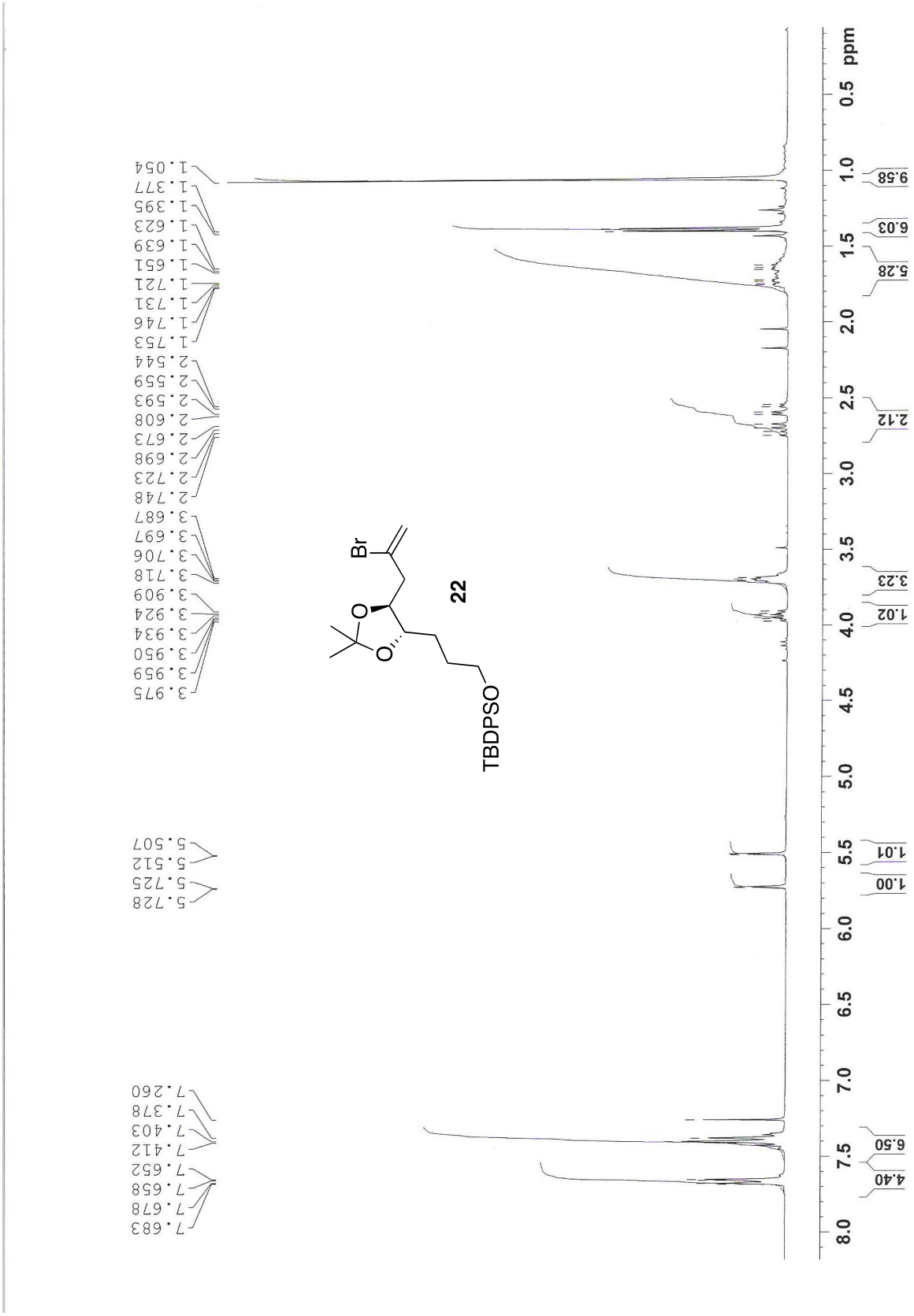


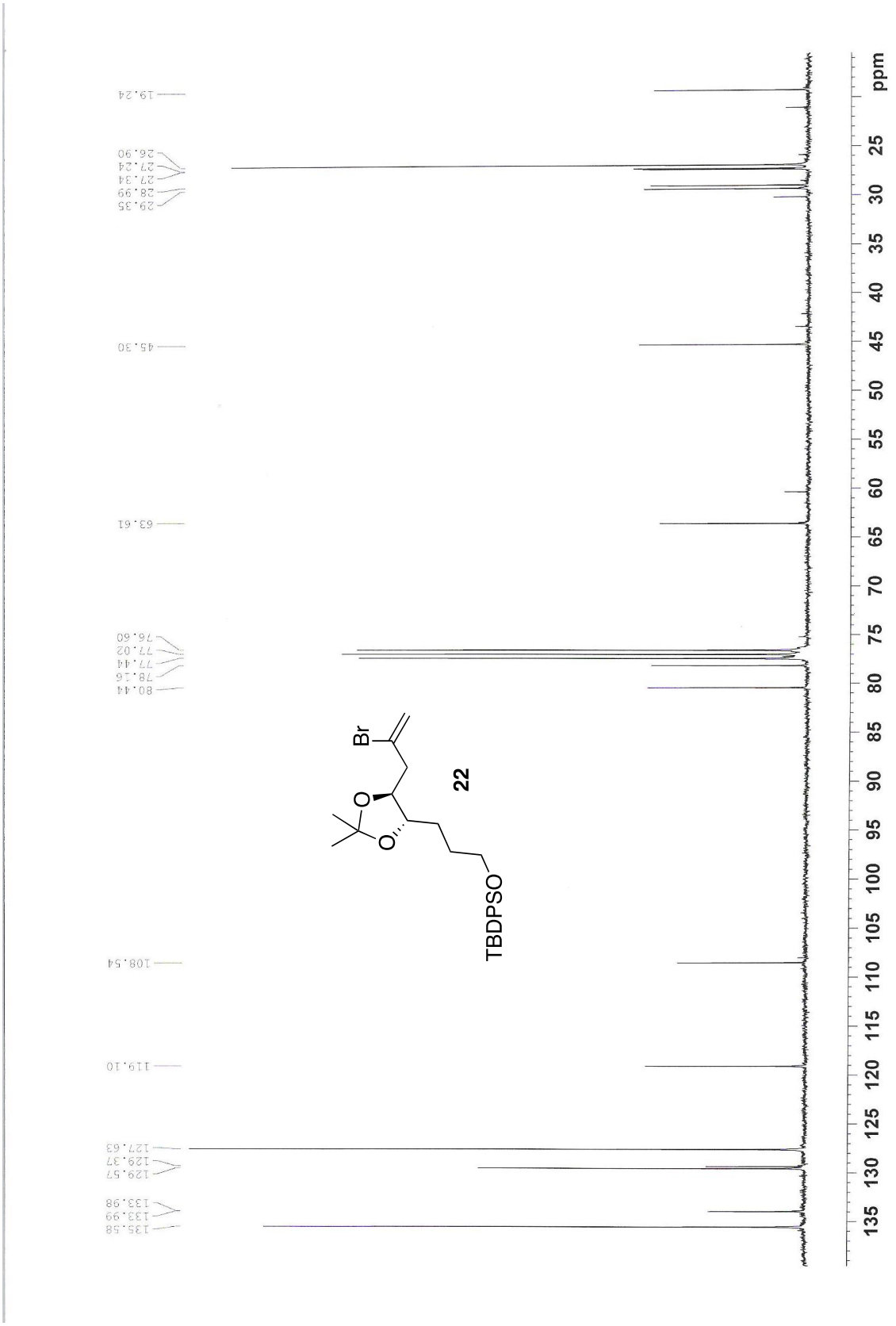
(4*S*,5*S*)-2-bromo-8-(*tert*-butyldiphenylsilyloxy)oct-1-ene-4,5-diol 21



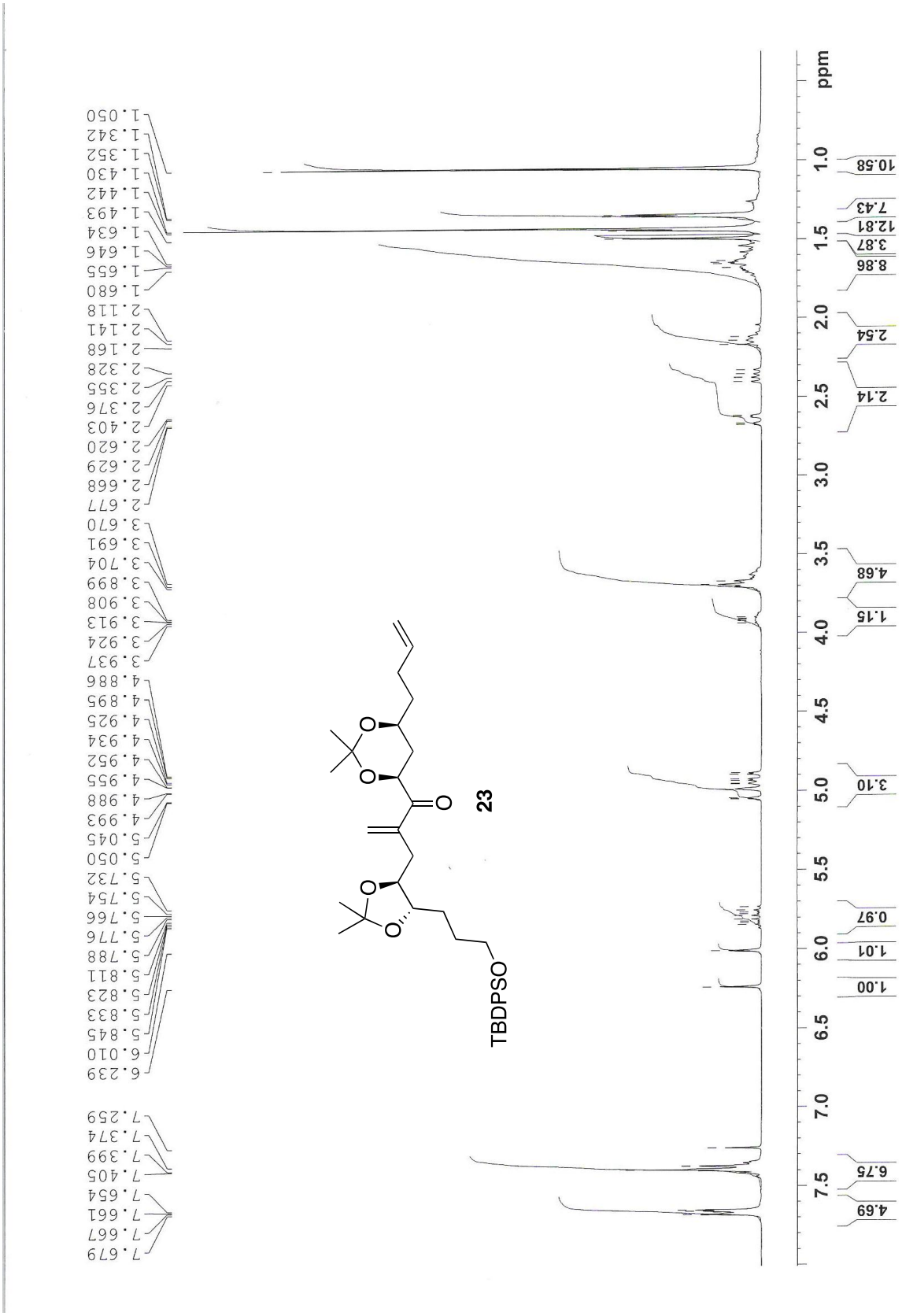


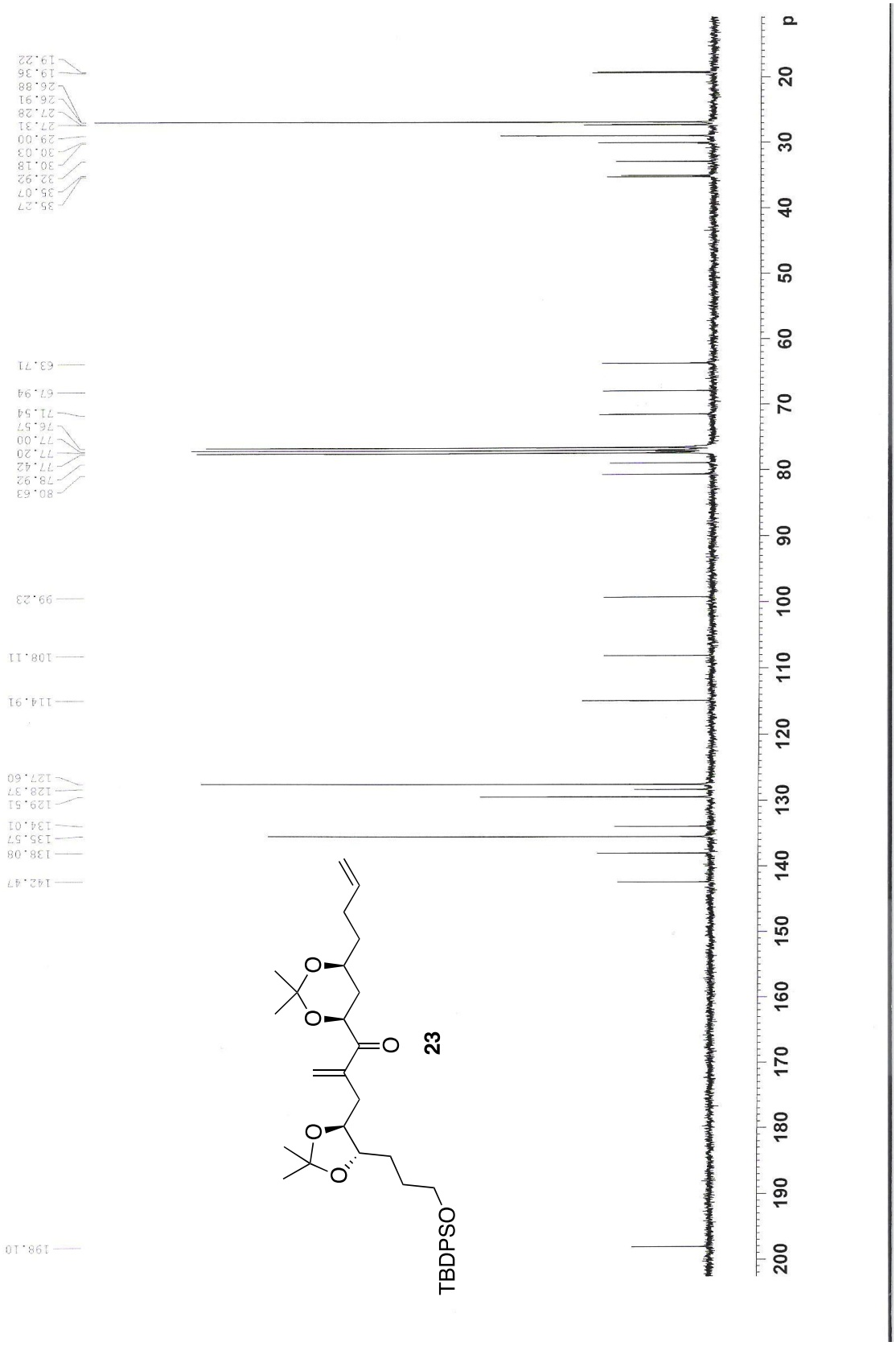
(3-((4*S*,5*S*)-5-(2-bromoallyl)-2,2-dimethyl-1,3-dioxolan-4-yl)propoxy)(*tert*-butyl)diphenylsilane 22



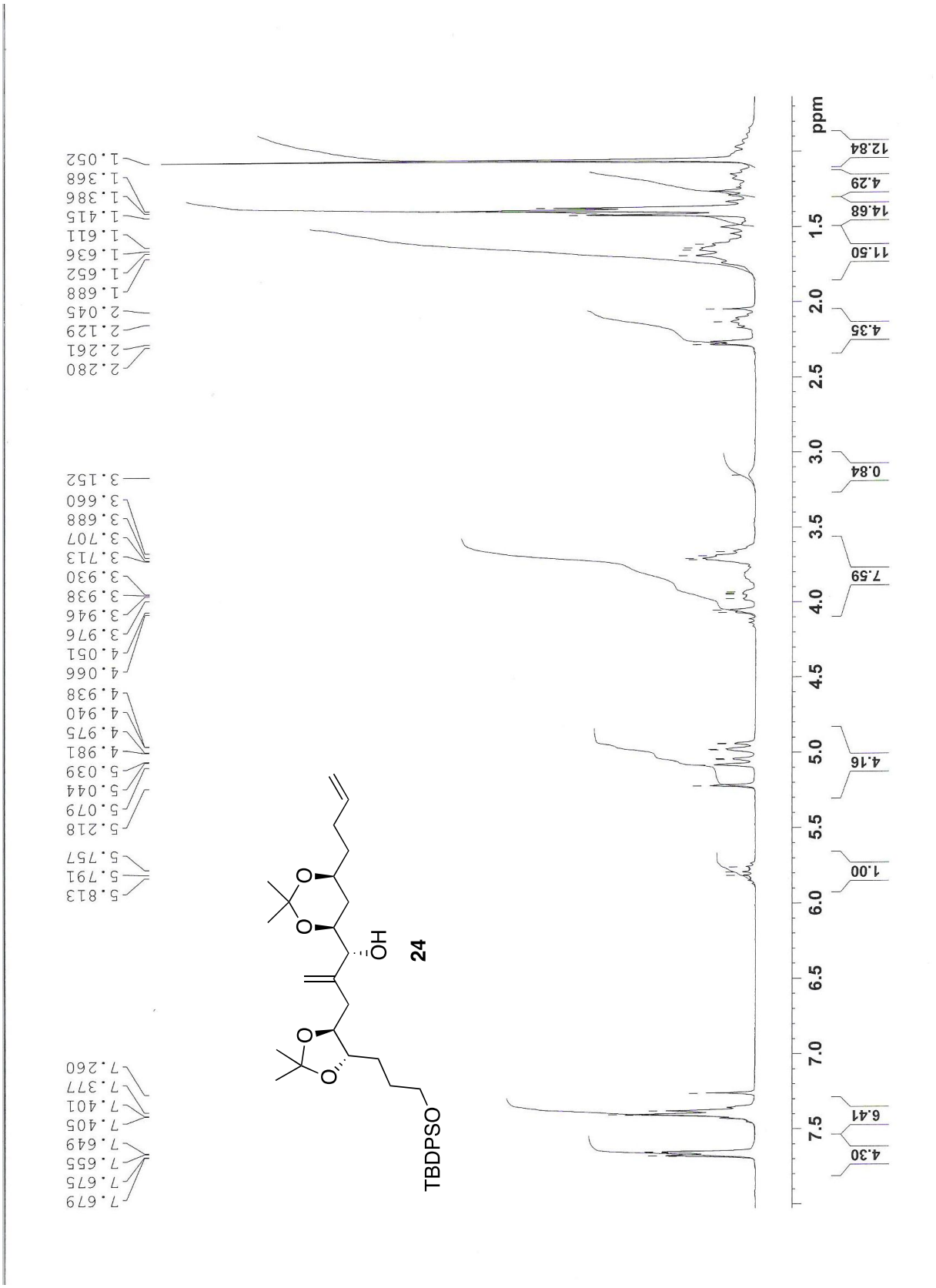


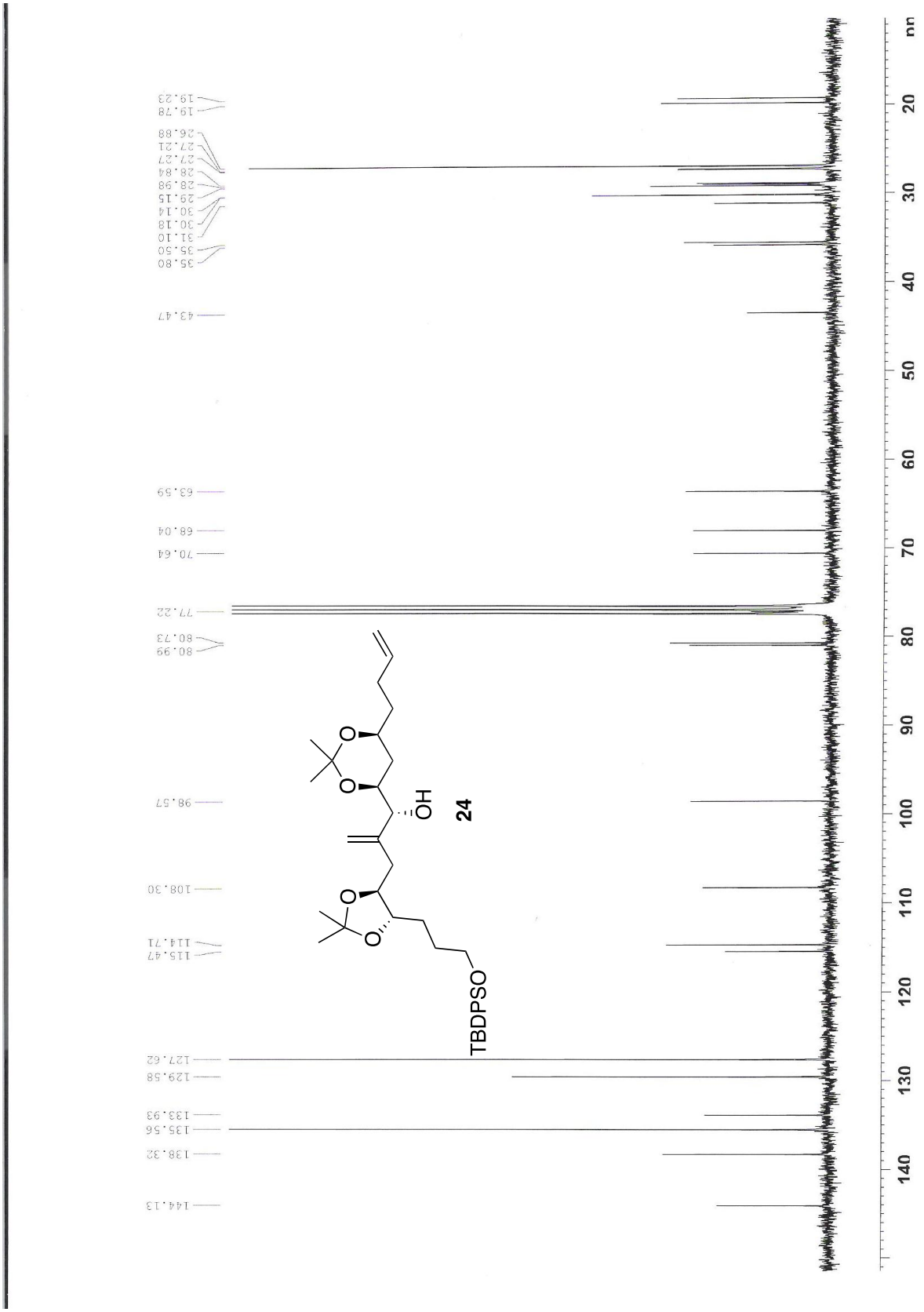
1-((4S,6S)-6-(but-3-enyl)-2,2-dimethyl-1,3-dioxan-4-yl)-2-(((4R,5R)-5-(3-(tert-butyldiphenylsilyloxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)prop-2-en-1-one 23



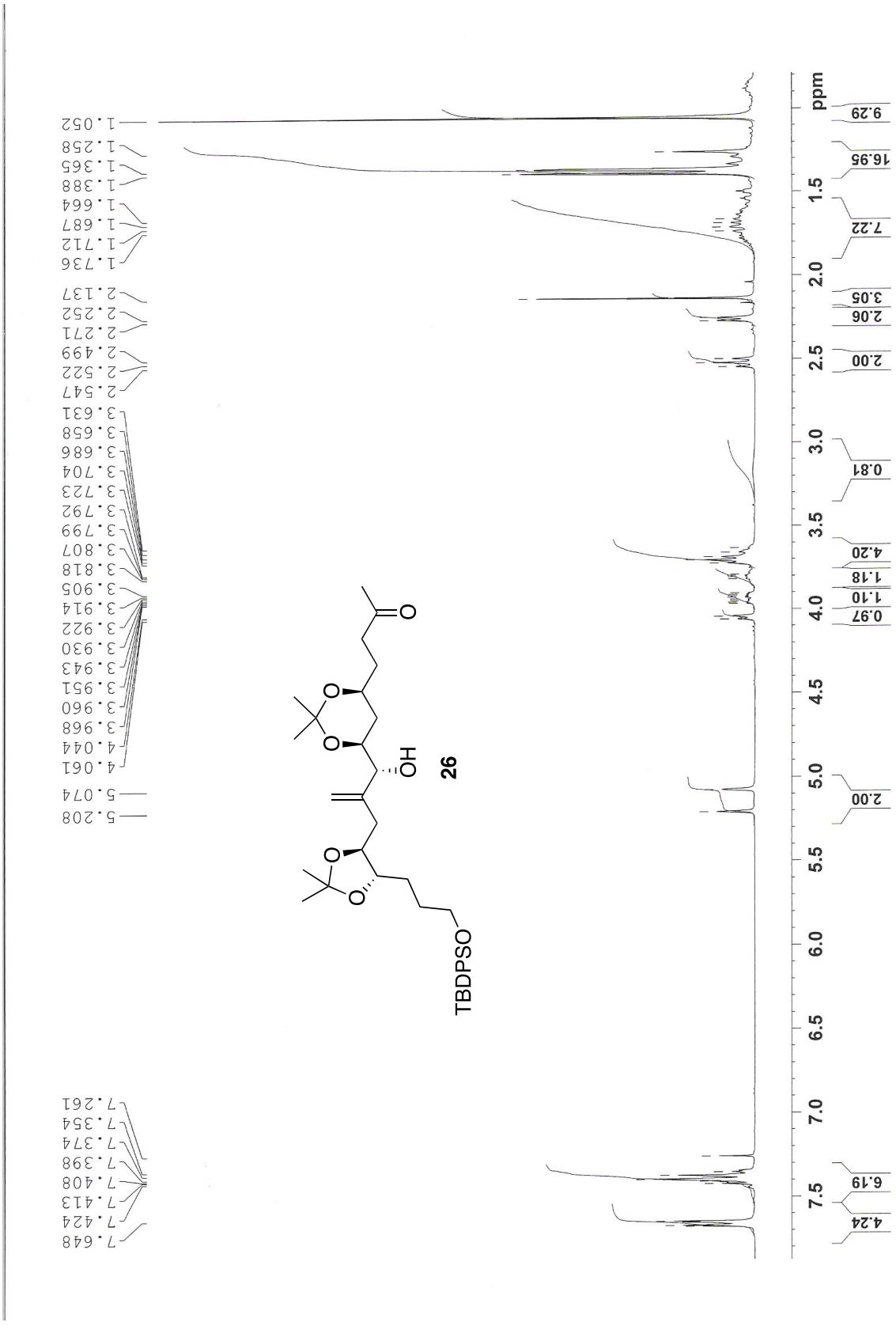


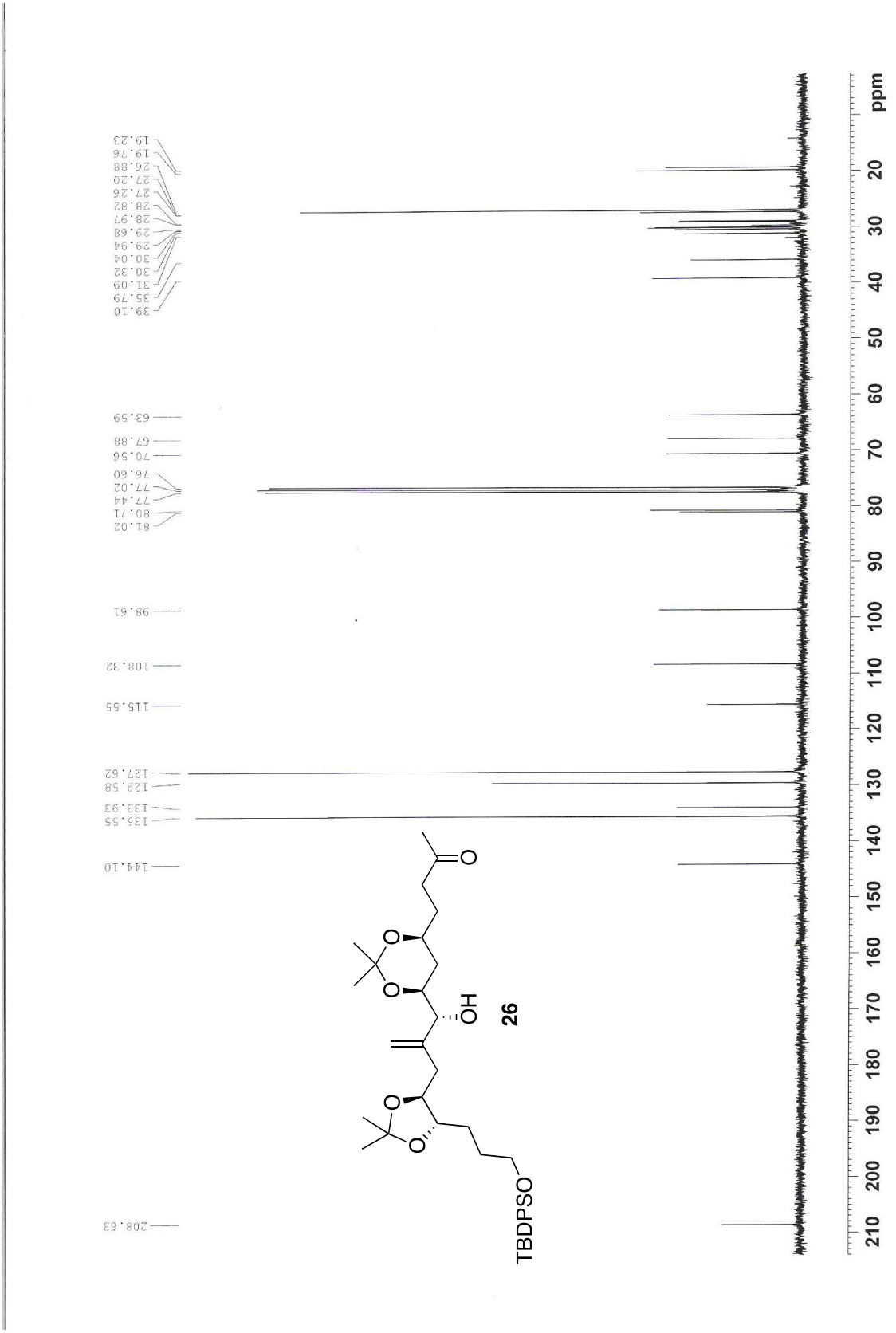
(R)-1-((4S,6S)-6-(but-3-enyl)-2,2-dimethyl-1,3-dioxan-4-yl)-2-(((4R,5R)-5-(3-(tert-butyldiphenylsilyloxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)prop-2-en-1-ol 24



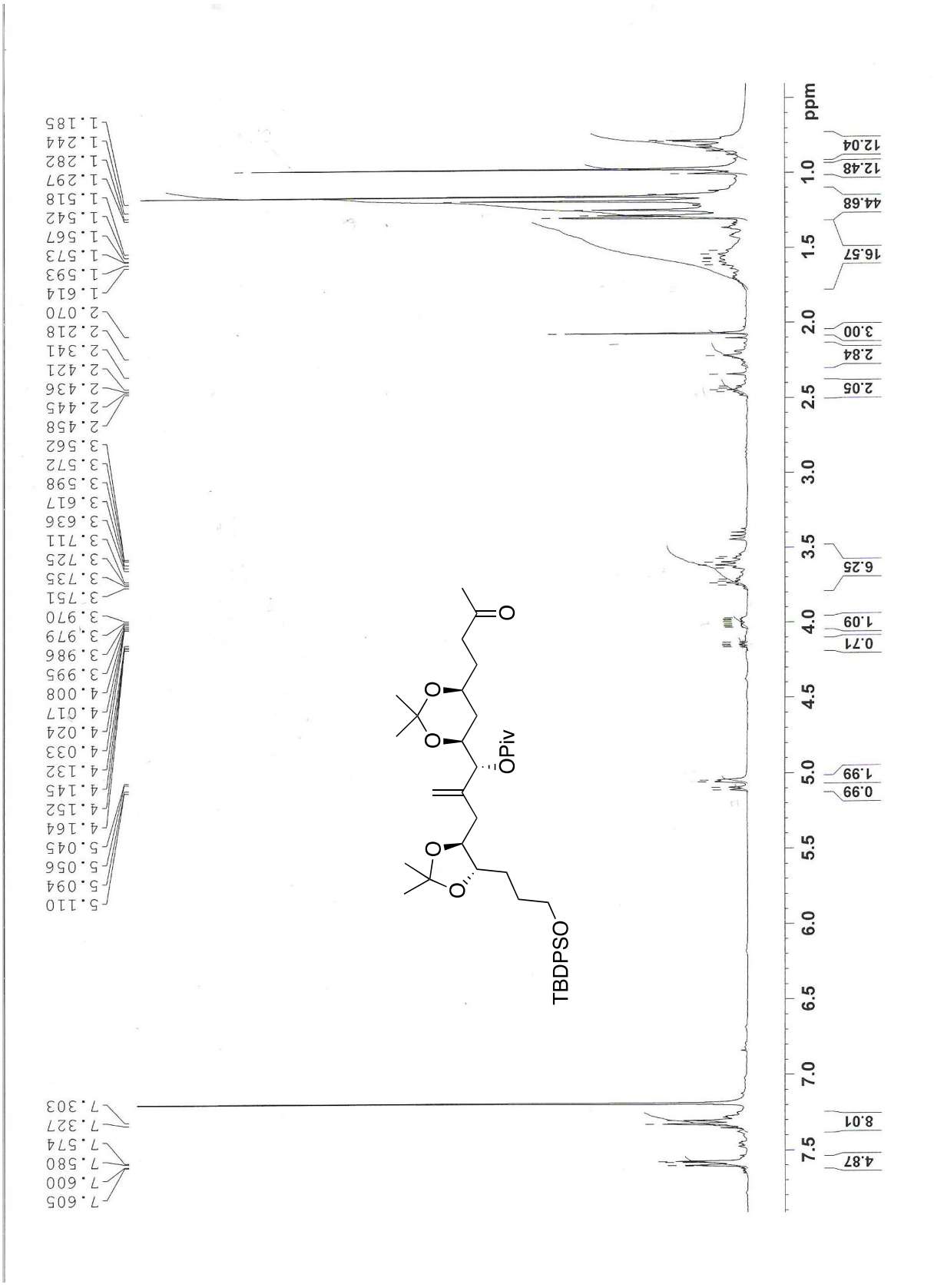


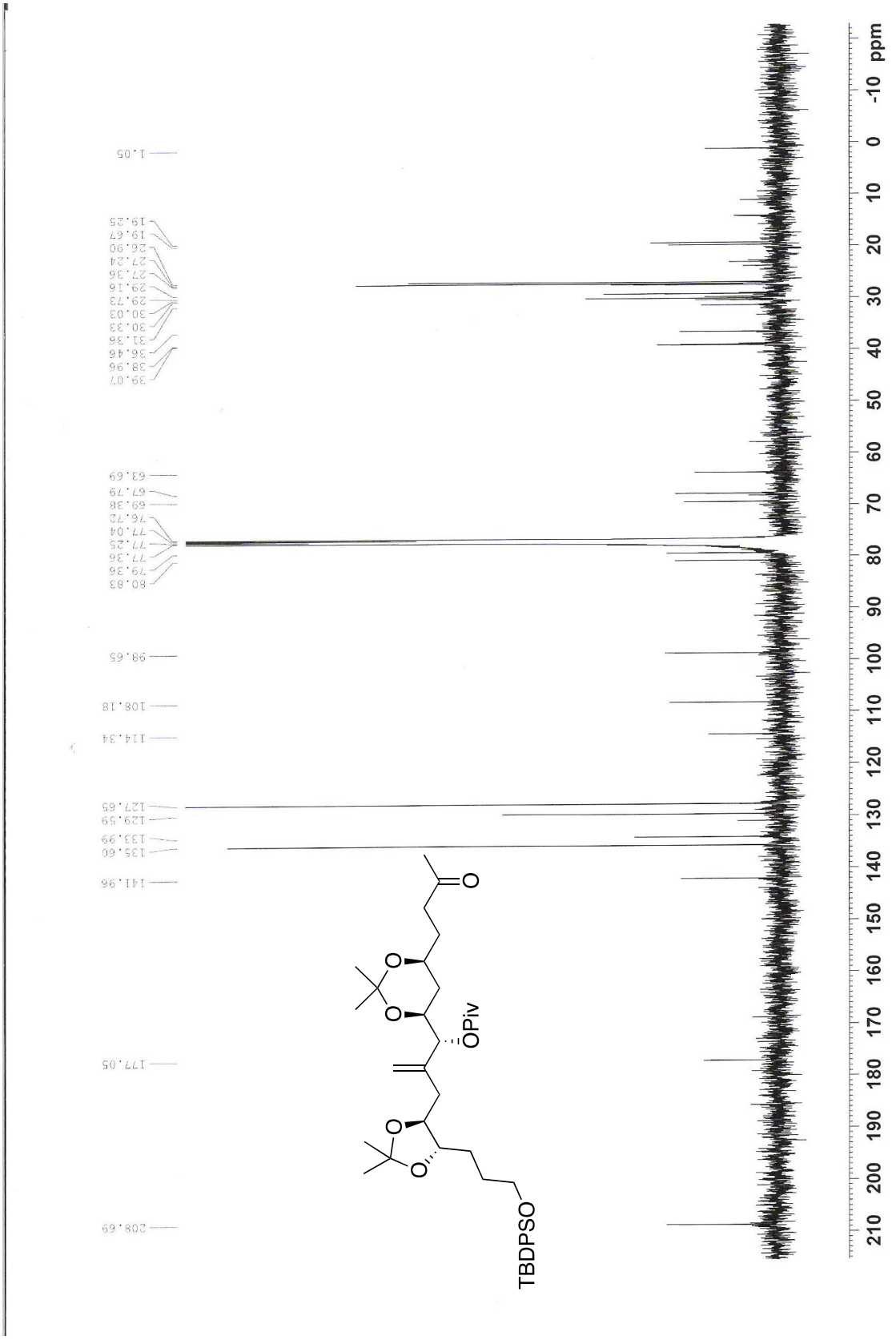
4-((4S,6S)-6-((R)-2-(((4R,5R)-5-(3-(tert-butyldiphenylsilyloxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-1-hydroxyallyl)-2,2-dimethyl-1,3-dioxan-4-yl)butan-2-one 26





(R)-2-(((4S,5S)-5-(3-((tert-butyldiphenylsilyl)oxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-1-((4S,6S)-2,2-dimethyl-6-(3-oxobutyl)-1,3-dioxan-4-yl)allyl pivalate





4-((4S,6S)-6-((1R)-3-((4R,5R)-5-(3-((tert-butyldiphenylsilyl)oxy)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-1-hydroxy-2-methylpropyl)-2,2-dimethyl-1,3-dioxan-4-yl)butan-2-one

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