Diastereoselective Brook Rearrangement-Mediated [3 + 4] Annulation : Application to a Formal Synthesis of (+)-Laurallene

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Supporting Information

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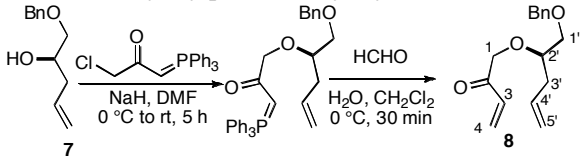
General. Infrared spectra were recorded on an FT-IR spectrometer. Melting points were uncorrected. ^{1}H NMR spectra were taken on either 500 MHz spectrometer in $CDCl_3$ with reference to $CHCl_3$ (δ 7.26) or in C_6D_6 with reference to C_6H_6 (δ 7.20). ^{13}C NMR spectra were measured with either 125 MHz spectrometers in $CDCl_3$ with reference to the $CDCl_3$ triplet (δ 77.2) or in C_6D_6 with reference to the C_6H_6 triplet (δ 128.0). Resonance patterns were described as s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad. The assignment of ^{1}H and ^{13}C NMR spectra is based on H-H decoupling and HMQC experiments. Mass spectra were obtained either in EI mode or in FAB mode using NBA as the matrix or without any matrix. Liquid chromatography under medium pressures (MPLC) was carried out using prepacked columns (22 mm x 100 mm (5 μ silica gel) or 22 mm x 300 mm (10 μ silica gel)). For routine chromatography, the following adsorbents were used: silica gel 60N of particle size 63-210 μm for column chromatography; precoated silica gel 60 F-254 plates for analytical thin-layer chromatography. All moisture sensitive reactions were performed under a positive pressure of nitrogen. Anhydrous $MgSO_4$ was used for drying all organic solvent extracts in workup, and the removal of the solvents was performed with a rotary evaporator. Dry solvents and reagents were obtained by using standard procedures.

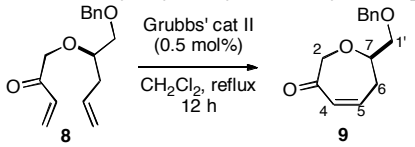
(*R*)-1-(1-(Benzyloxy)pent-4-en-2-yloxy)but-3-en-2-one (8)



To a cooled (ice-water) solution of (*R*)-1-(benzyloxy)pent-4-en-2-ol (2.63g, 13.6 mmol) and $ClCH_2C(O)CH{=}PPh_3$ (4.80g, 13.6 mmol) in DMF was added NaH (60% purity, 657 mg, 16.4 mmol). After the cooling bath was removed, the reaction mixture was stirred at room temperature for 4 hr. The mixture was diluted with saturated brine (60 mL) and extracted with AcOEt (25 mL x 3). Combined Organic phases were washed with saturated brine (30 mL x 2), dried and concentrated. The residual oil (8.38 g) was used in the following step without further purification.

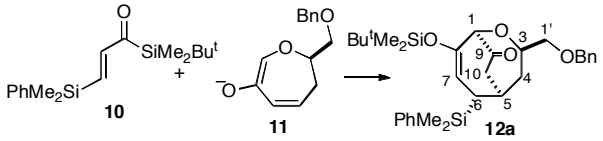
To a cooled (ice-water) solution of the above compound in CH_2Cl_2 was added formaldehyde (37% aqueous solution, 10.2 mL). After being stirred at the same temperature for 30 min, the mixture was diluted with H_2O (80 mL) and separated, and the aqueous phase was extracted with Et_2O (30 mL x 2). Combined organic phases were washed with saturated brine (50 mL), dried and concentrated. The residue was triturated with Et_2O and the insoluble material was filtrated, and then the filtrate was concentrated. The residual oil was subjected to column chromatography (silica gel 180 g; elution with hexane:Et_2O = 3:2) to give **8** (2.59 g, 73%), a pale yellow oil. R_f = 0.37 (hexane:Et_2O = 3:2). $[\alpha]^{28}_D$ +8.65 (*c* 1.08, $CHCl_3$). IR (film) = 1700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.31-2.41 (2H, m, H-3'), 3.55 (2H, d, *J* = 5.3 Hz, H-1'), 3.60-3.66 (1H, m, H-2'), 4.38 and 4.43 (each 1H, d *J* = 17.0 Hz, PhC*H*$_2$), 4.51 (2H, s, H-1), 5.06 (1H, dm, *J* = 10.3 Hz, H-5'), 5.09 (1H, dm, *J* = 17.0 Hz, H-5'), 5.77 (1H, dd, *J* = 10.8, 0.7 Hz, H-4), 5.81 (1H, ddt, *J* = 17.0, 10.3, 7.1 Hz, H-4'), 6.31 (1H, dd, *J* = 17.6, 0.7 Hz, H-4), 6.58 (1H, dd, *J* = 17.6, 10.8 Hz, H-3), 7.26-7.35 (5H, m, Ph). ^{13}C NMR δ 36.3 (C-3'), 72.7 (C-1'), 73.5 (C-1), 74.6 (*C*H$_2$Ph), 79.5 (C-2'), 117.6 (C-5'), 127.7, 128.5, 128.9, and 132.6 (Ph, C-4, C-4', and C5'), 134.2 (C-3), 197.7 (C-2). HRFAB MS calcd for $C_{16}H_{20}O_3$ (M^+ + 1) 261.1491, found 261.1518.

(*R*)-7-(Benzyloxymethyl)-6,7-dihydrooxepin-3(2*H*)-one (9)



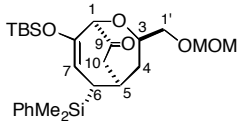
To a solution of **8** (2.58 g, 9.9 mmol) in CH_2Cl_2 (200 mL) was added Grubbs' cat. II (25 mg, 0.3 mol%). After being refluxed for 12 hr, the reaction mixture was concentrated. The residue was subjected to column chromatography (silica gel 80 g; elution with hexane:AcOEt = 2:1) and bulb-to-bulb distillation under reduced pressure to give **9** (1.74 g, 75%), bp 300 °C/0.75 mmHg, a pale yellow oil. R_f = 0.22 (hexane:Et_2O = 1:1). $[\alpha]^{27}_D$ +133.8 (*c* 0.93, $CHCl_3$). IR (film) = 1666 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.56-2.68 (2H, m, H-6), 3.48 (1H, dd, *J* = 10.1, 4.8 Hz, H-1'), 3.56 (1H, dd, *J* = 10.1, 5.7 Hz, H-1'), 3.83-3.88 (1H, m, H-7), 4.23 (1H, d, *J* = 18.3 Hz, H-2), 4.43 (1H, d, *J* = 18.3 Hz, H-2), 4.55 and 4.57 (each 1H, d, *J* = 12.1 Hz, C*H*$_2$Ph), 6.02 (1H, dt, *J* = 12.3, 1.1 Hz, H-4), 6.51 (1H, ddd, *J* = 12.3, 5.5, 3.9 Hz, H-5), 7.25-7.35 (5H, m, Ph). ^{13}C NMR δ 36.7 (C-6), 72.7 (C-1'), 73.6 (*C*H$_2$Ph), 77.8 (C-2), 78.8 (C-7), 127.7, 127.9, 128.5, and 138.1 (Ph), 130.3 (C-4), 144.3 (C-5), 204.0 (C-3). HRMS calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1093.

(1*R,3*R**,5*R**,6*S**)-3-(Benzyloxymethyl)-8-(*tert*-butyldimethylsiloxy)-6-(dimethyl(phenyl)silyl)-2-oxabicyclo[3.3.2]dec-7-en-9-one (12a)**



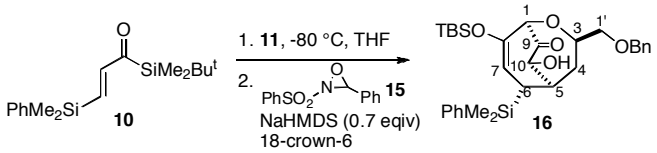
To a cooled (-80 °C) solution of lithium diisopropylamide (LDA), prepared from *i*-Pr_2NH (60 μL, 0.426 mmoL) and *n*-BuLi (2.19 M in hexane, 187 μL, 0.410 mmol) in THF (2.4 mL), was added dropwise a solution of **9** (91.5 mg, 0.394 mmol) in THF (2.4 mL) and then the solution was stirred at the same temperature for 20 min. To this solution was added a solution of **10** (99 mg, 0.328 mmol) in THF (1.6 mL) over a period of 5 min and the mixture was allowed to warm to room temperature over 40 min before addition of AcOH (1.0 M in THF, 0.43 mL). The resulting mixture was filtered through a pad of Celite and concentrated. The residue was purified by column chromatography (silica gel 12 g; elution with hexane:AcOEt = 8:1) to give **12a** (139.4 mg, 76%), a pale yellow oil. R_f = 0.31 (hexane:AcOEt = 8:1). IR (film) = 1707 cm^{-1}. ^1H NMR (C_6D_6) δ 0.14 and 0.15 (each 3H, s, $SiMe_2$), 0.21 and 0.22 (each 3H, s, $SiMe_2$), 0.93 (9H, s, *t*-Bu), 1.52 (1H, dd, *J* = 12.1, 12.1 Hz, H-4), 1.85-1.90 (1H, m, H-4), 1.92 (1H, br m, H-6), 2.00-2.06 (1H, br m, H-5), 2.15 (1H, dd, *J* = 19.2, 4.1 Hz, H-10), 2.53 (1H, dd, *J* = 19.2, 3.4 Hz, H-10), 3.31 (1H, dd, *J* = 9.6, 5.5 Hz, H-1'), 3.45 (1H, dd, *J* = 9.6, 4.8 Hz, H-1'), 3.71-3.77 (1H, m, H-3), 4.34 and 4.37 (each 1H, d, *J* = 12.1 Hz, C*H*$_2$Ph), 4.95 (1H, d, *J* = 1.6 Hz, H-1), 5.21 (1H, dd, *J* = 4.8, 1.6 Hz, H-7), 7.10-7.20 (6H, m, Ph), 7.30 (2H, m, Ph), 7.35 (2H, m, Ph). ^{13}C NMR δ -4.6, -4.4, -4.0 and -3.5 ($SiMe_2$), 17.9 (($CH_3)_3C$), 25.6 (($CH_3)_3$C), 26.9 (C-5), 36.4 (C-6), 38.8 (C-4), 43.6 (C-10), 72.4 (*C*H_2Ph), 73.3 (C-3), 73.7 (C-1'), 88.7 (C-1), 111.6 (C-7), 127.5, 128.1, 129.4, 133.8, 137.3 and 138.9 (Ph), 147.2 (C-8), 205.8 (C-9). HRFAB MS calcd for $C_{31}H_{44}O_4Si_2$ 536.2778, found 536.2797.

(1*R,3*R**,5*R**,6*S**)-8-(*tert*-butyldimethylsilyloxy)-6-(dimethyl(phenyl)silyl)-3-((methoxymethoxy)methyl)-2-oxabicyclo[3.3.2]-dec-7-en-9-one (12b)**



colorless platelets (hexane), mp 93-93.5 °C. R_f = 0.29 (hexane:AcOEt = 1:3). IR (film) = 1705 cm^{-1}. ^1H NMR (C_6D_6) δ 0.14 and 0.15 (each 3H, s, $SiMe_2$), 0.21 and 0.22 (each 3H, s, $SiMe_2$), 0.93 (9H, s, *t*-Bu), 1.50 (1H, dd, *J* = 14.4, 14.4 Hz, H-4), 1.76 (1H, ddd, *J* = 14.4, 10.0, 2.7 Hz, H-4), 1.94 (1H, dd, *J* = 3.7, 3.7 Hz, H-6), 2.00-2.06 (1H, br m, H-5), 2.16 (1H, dd, *J* = 19.2, 4.1 Hz, H-10), 2.55 (1H, dd, *J* = 19.2, 3.7 Hz, H-10), 3.18 (3H, s, OMe), 3.41 (1H, dd, *J* = 10.3, 5.0 Hz, H-1'), 3.57 (1H, dd, *J* = 10.3, 5.3 Hz, H-1'), 3.68-3.74 (1H, m, H-3), 4.50 and 4.52 (each 1H, d, *J* = 6.4 Hz, OC*H*$_2$OMe), 4.95 (1H, d, *J* = 1.8 Hz, H-1), 5.21 (1H, dd, *J* = 5.0, 1.8 Hz, H-7), 7.15-7.20 (3H, m, Ph), 7.38 (2H, m, Ph). ^{13}C NMR δ -4.7, -4.4, -4.1 and -3.6 ($SiMe_2$), 17.9 (($CH_3)_3C$), 25.6 (($CH_3)_3$C), 26.9 (C-5), 36.3 (C-6), 38.7 (C-4), 43.5 (C-10), 54.7 (OMe), 71.1 (C-1'), 72.4 (C-3), 88.8 (C-1), 96.7 (OCH_2OMe), 111.4 (C-7), 128.1, 129.4, 133.8, and 137.3 (Ph), 147.3 (C-8), 202.6 (C-9). HRFAB MS calcd for $C_{26}H_{42}O_5Si_2$ 490.2571, found 490.2549.

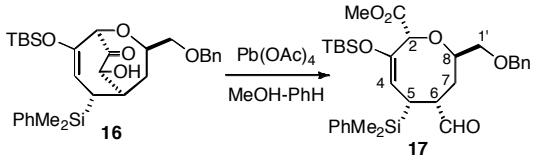
(1*R*,3*R*,5*R*,6*S*,10*R*)-3-(Benzyloxymethyl)-8-(*tert*-butyldimethylsiloxy)-6-(dimethyl(phenyl)silyl)-10-hydroxy-2-oxabicyclo[3.3.2]dec-7-en-9-one (16)



To a cooled (-80 °C) solution of NaHMDS (1.0 M in THF, 2.13 mL, 2.13 mmol) in THF (11 mL) was added dropwise a solution of **9** (495 mg, 2.13 mmol) in THF (11 mL), and then the solution was stirred at the same temperature for 20 min. To this solution was added a cooled (-80 °) solution of **10** (500 mg, 1.64 mmol) in THF (11 mL) rapidly, and the reaction mixture was allowed to warm to -15 °C over a period of 20 min, and stirred at the same temperature for 5 min. The solution was recooled to -80 °C before successive addition of NaHMDS (1.0 M in THF, 1.15 mL, 1.15 mmol) and a cooled (-80 °C) solution of **15** (560 mg, 2.13 mmol) and 18-crown-6 (130 mg, 0.49 mmol) in THF (5 mL) and stirred at -70 °C for 40 min. The reaction mixture was diluted with 10 % aqueous NH_4Cl solution (60 mL), phases were separated, and the aqueous phase was extracted with Et_2O (25 mL x 3). Combined organic phases were washed with saturated brine (60 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 120 g, elution with hexane/AcOEt = 4:1) to give **16** (579 mg, 64%), colorless needles (hexane-AcOEt), mp 95.5-96 °C. R_f = 0.29 (hexane:AcOEt = 9:2). $[\alpha]^{28}_D$ +240.2 (*c* 0.99, $CHCl_3$). IR (film) = 3436, 1716 cm^{-1}. ^1H NMR (C_6D_6) δ 0.01 and 0.04 (each 3H, s, $SiMe_2$), 0.21 and 0.23 (each 3H, s, $SiMe_2$), 0.87 (9H, s, *t*-Bu), 1.42 (1H, dd, *J* = 14.2, 13.1 Hz, H-4), 2.18 (1H, d, *J* = 2.5 Hz, H-6), 1.92 (1H, br m, H-6), 2.28 (1H, ddd, *J* = 14.2, 7.3, 4.1 Hz, H-4), 2.73 (1H, br dd, *J* = 7.3, 3.2 Hz, H-5), 2.93 (1H, s, OH), 3.22 (1H, dd, *J* = 10.3, 3.9 Hz, H-1'), 3.35 (1H, dd, *J* = 10.3, 5.7 Hz, H-1'), 3.88-3.95 (1H, m, H-3), 4.18 (1H, d, *J* = 2.6 Hz, H-10), 4.34 (2H, s, C*H*$_2$Ph), 4.96 (1H, d, *J* = 1.6 Hz, H-1), 5.16 (1H, dd, *J* = 2.8, 1.6 Hz, H-7), 7.05-7.10 (1H, m, Ph), 7.10-7.20

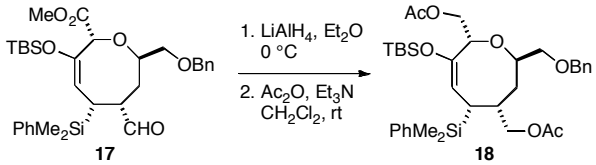
(5H, m, Ph), 7.20-7.25 (2H, m, Ph), 7.40 (2H, m, Ph). ^{13}C NMR δ -5.0, -4.7, -4.5 and -4.5 ($SiMe_2$), 17.8 ($(CH_3)_3C$), 25.5 ($(CH_3)_3C$), 32.0 (C-6), 32.7 (C-5), 37.3 (C-4), 71.7 (CH_2Ph), 73.2 (C-1'), 73.5 (C-3), 75.1 (C-10), 86.6 (C-1), 109.7 (C-7), 127.4, 128.1, 128.3, 129.5, 133.9, and 136.8 (Ph), 148.2 (C-8), 207.2 (C-9). HRFAB MS calcd for $C_{31}H_{44}O_5Si_2$ 552.2727, found 552.2720. Anal. calcd for $C_{31}H_{44}O_5Si_2$: C, 67.35; H 8.02. Found: C, 67.24; H, 8.26.

(2*R*,5*R*,6*R*,8*R*)-Methyl 8-(Benzyloxymethyl)-3-(*tert*-butyldimethylsiloxy)-5-(dimethyl(phenyl)silyl)-6-formyl-5,6,7,8-tetrahydro-2*H*-oxocine-2-carboxylate (17)



To a cooled (ice-water) solution of **16** (1.60 g, 2.89 mmol) in MeOH-benzene (1:1, 168 mL) was added $Pb(OAc)_4$ (80% purity, 3.73 g, 6.7 mmol). The mixture was stirred at the same temperature for 1 hr, diluted with hexane (160 mL) and filtered through a short pad of silica gel. The filtrate was concentrated and subjected to column chromatography (silica gel, 120 g, elution with hexane:AcOEt = 5:1) to give **17** (1.61 g, 95%), a yellow oil. R_f = 0.39 (hexane:AcOEt = 4:1). $[\alpha]^{30}_D$ +46.9 (*c* 0.96, $CHCl_3$). IR (film) = 1748, 1725 cm^{-1}. ^{1}H NMR (C_6D_6) δ 0.16 and 0.19 (each 3H, s, $SiMe_2$), 0.35 and 0.39 (each 3H, s, $SiMe_2$), 0.90 (9H, s, *t*-Bu), 1.50-1.57 (1H, m, H-7), 2.48 (1H, dd, *J* = 14.4, 3.2 Hz, H-7), 2.53-2.58 (2H, m, H-5 and H-6), 3.42 (3H, s, OMe), 3.55 (1H, dd, *J* = 9.6, 6.6 Hz, H-1'), 3.73 (1H, dd, *J* = 9.6, 4.1 Hz, H-1'), 4.42 and 4.46 (each 1H, d, *J* = 12.1 Hz, CH_2Ph), 4.60 (1H, m, H-8), 5.21 (1H, d, *J* = 1.6 Hz, H-2), 5.35 (1H, dd, *J* = 10.3, 1.6 Hz, H-4), 7.19 (1H, m, Ph), 7.18-7.25 (5H, Ph), 7.32 (2H, m, Ph), 7.48 (2H, m, Ph), 9.43 (1H, s, CHO). ^{13}C NMR (C_6D_6) δ -4.8, -4.5, -4.0 and –3.4 ($SiMe_2$), 17.9 ($(CH_3)_3C$), 24.3 (C-5), 25.5 ($(CH_3)_3C$), 32.5 (C-7), 51.0 (C-6), 51.0 (OMe), 72.8 (C-8), 73.0 (CH_2Ph), 73.5 (C-1'), 76.6 (C-2), 107.0 (C-4), 127.3, 127.7, 128.1, 128.2, 129.4, 134.0, 137.4, and 139.0 (Ph), 148.8 (C-3), 169.3 (CO_2Me), 202.5 (CHO). HRFAB MS calcd for $C_{32}H_{46}O_6Si_2$ (M^+ + 1) 583.2911, found 583.2891.

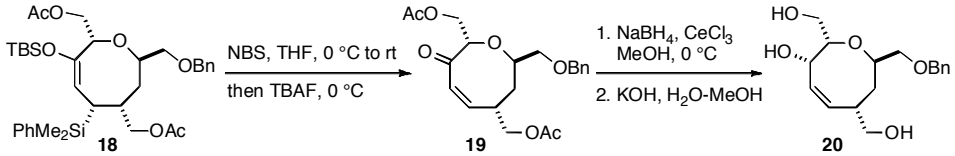
((2*S*,5*S*,6*R*,8*R*,*Z*)-8-(benzyloxymethyl)-3-(*tert*-butyldimethylsilyloxy)-5-(dimethyl(phenyl)silyl)-5,6,7,8-tetrahydro-2*H*-oxocine-2,6-diyl)bis-(methylene) diacetate (18)



To a cooled (ice-water) solution of **17** (3.86 g, 6.62 mmol) in Et_2O (66 mL) was added $LiAlH_4$ (253 mg, 6.67 mmol). After being stirred at the same temperature for 30 min, an extra amount (250 mg, 6.59 mmol) of $LiAlH_4$ was added. After being stirred at the same temperature for another 30 min, the reaction mixture was diluted with Et_2O (60 mL) and a few drops of saturated aqueous Na_2SO_4 was added. The mixture was filtered through a pad of Celite and concentrated. The residual oil was filtered through a short pad of silica gel to give diol derivative (2.85 g), and this was used in the following step without further purification.

To a cooled (ice-water) solution of the above compound, NEt_3 (1.75 mL, 12.6 mmol) and 4-dimethylaminopyridine (246 mg, 2.01 mmol) in CH_2Cl_2 (50 mL) was added acetic anhydride (1.05 mL, 11.0 mmol). After being stirred at the same temperature for 1.5 h, the mixture was diluted with CH_2Cl_2 (50 mL) and 10% aqueous NH_4Cl solution (90 mL), separated, and the aqueous phase was extracted with CH_2Cl_2 (30 mL x 3). Combined organic phases were washed with saturated brine (30 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 90 g, elution with hexane/AcOEt = 4:1) to give **18** (2.75 g, 65% from **17**), a colorless oil. R_f = 0.35 (hexane:AcOEt = 4:1). $[\alpha]^{21}_D$ +2.3° (*c* 0.91, $CHCl_3$). IR (film) = 1741 cm^{-1}. ^{1}H NMR (C_6D_6) δ 0.14 and 0.18 (each 3H, s, $SiMe_2$), 0.40 and 0.41 (each 3H, s, $SiMe_2$), 0.96 (9H, s, *t*-Bu), 1.61-1.67 (1H, m, H-7), 1.65 (3H, s, Ac), 1.76 (3H, s, Ac), 2.20 (1H, dd, *J* = 14.8, 4.1 Hz, H-7), 2.44-2.47 (1H, m, H-6), 2.64 (1H, dd, *J* = 10.5, 1.8 Hz, H-5), 3.41 (1H, dd, *J* = 9.6, 6.6 Hz, H-1'), 3.63 (1H, dd, *J* = 9.6, 4.8 Hz, H-1"'), 4.17 (1H, t, *J* = 10.7 Hz, H-1"), 4.34-4.39 (2H, m, H-1" and H-8), 4.40 (2H, s, CH_2Ph), 4.57 (1H, dd, *J* = 7.1, 11.5 Hz, H-1'), 4.68 (1H, dd, *J* = 11.5, 4.8 Hz, H-1'), 4.93 (1H, br ddd, *J* = 7.1, 4.8, 1.1 Hz, H-2), 5.06 (1H, dd, *J* = 10.5, 1.1 Hz, H-4), 7.10-7.13 (1H, m, Ph), 7.20-7.25 (3H, m, Ph), 7.28 (2H, m, Ph), 7.31 (2H, m, Ph), 7.60 (2H, m, Ph). ^{13}C NMR (C_6D_6) δ-4.6, –4.0, -3.6 and -3.4 ($SiMe_2$), 18.2 ($(CH_3)_3C$), 20.4 (C(O)CH_3), 20.5 (C(O)CH_3), 25.8 ($(CH_3)_3C$), 26.8 (C-5), 34.9 (C-7), 37.1 (C-6), 64.2 (C-1), 64.6 (C-1"), 70.0 (C-8), 72.5 (CH_2Ph), 73.3 (C-2), 74.2 (C-1"'), 106.7 (C-4), 127.7, 128.2, 129.4, 134.3, 138.1, and 139.2 (Ph), 150.8 (C-3), 169.9 (C(O)Me)170.1 (C(O)Me). HRMS calcd for $C_{35}H_{52}O_7Si_2$ 640.3252, found 640.3246.

((*2S,3S,6S,8R,Z*)-8-(benzyloxymethyl)-3-hydroxy-3,6,7,8-tetrahydro-*2H*-oxocine-2,6-diyl)dimethanol (20)

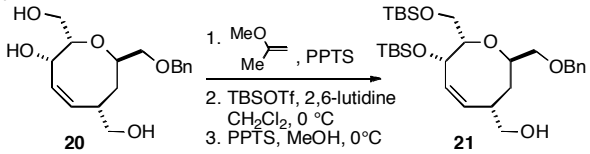


To a cooled (ice-water) solution of **18** (500 mg, 0.78 mmol) in THF (8 mL) was added *N*-bromosuccinimide (181 mg, 1.02 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 15 min. The mixture was recooled to 0 °C before addition of tetra-*n*-butylammonium fluoride (TBAF) (1.0 M in THF, 1.01 mL, 1.01 mmol). After being stirred at the same temperature for 20 min, the mixture was diluted with Et_2O (20 mL) and 10% aqueous NH_4Cl solution (50 mL), separated and the organic phase was washed with H_2O (10 mL). Combined the aqueous phases were extracted with Et_2O (20 mL x 3). Combined organic phases were washed with saturated brine (20 mL), dried and concentrated. The residual oil was filtered through a short pad silica gel. The filtrate was concentrated. The residual oil (230 mg) was used in following step without further purification.

To a cooled (ice-water) solution of the above compound and $CeCl_3{\cdot}7H_2O$ (210 mg, 0.56 mmol) in MeOH (3 mL) was added $NaBH_4$ (28 mg, 0.74 mmol). After being stirred at the same temperature for 1 h, the reaction mixture was diluted with Et_2O (10 mL) and 10% aqueous NH_4Cl solution (5 mL), separated, and the aqueous phase was extracted with Et_2O (3 mL x 3). Combined organic phases were washed with saturated brine (5 mL), dried, and concentrated. The residual oil was filtered through a short pad silica gel. The filtrate was concentrated. The residual oil (232 mg) was used in following step without further purification.

To a cooled (ice-water) solution of the above compound (232 mg) in MeOH (0.1 mL) was added 1% solution of KOH in MeOH (0.8 mL). After removing the cooling bath, the mixture was stirred at room temperature fon 1 h. The mixture was then cooled to 0 °C (ice-water), added drops of 1N aqueous HCl to be neutralized, and the solvent was evaporated. The residual oil was diluted with AcOEt (10 mL) and saturated brine (2 mL), separated, and the aqueous phase was extracted with AcOEt (2 mL x 4). Combined organic phases were washed with saturated brine (3 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 5 g, elution with $CHCl_3$/MeOH = 9:1) to give **20** (150 mg, 62% from **18**), a coloreless oil. R_f = 0.30 ($CHCl_3$:MeOH = 9:1). $[\alpha]^{21}_D$ +12.7° (*c* 1.56, $CHCl_3$). IR (film) = 3428, 3397, 3369 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.24 (1H, ddd, *J* = 13.1, 12.6, 3.3 Hz, H-7"), 1.68 (1H, ddd, *J* = 13.1, 11.9, 5.5 Hz, H-7"), 2.88 (1H, brm, H-6"), 3.32 (1H, dd, *J* = 9.6, 1.8 Hz, H-1"'), 3.38 (1H, dd, *J* = 9.6, 9.2 Hz, H-1"'), 3.52 (1H, dd, *J* = 10.5, 7.6 Hz, H-1'), 3.58 (1H, dd, *J* = 10.5, 5.0 Hz, H-1'), 3.77 (1H, dd, *J* = 13.3, 3.0 Hz, H-1), 3.91 (1H, dd, *J* = 13.3, 10.8 Hz, H-1), 4.12 (1H, brt, *J* = 8.9 Hz, H-8"), 4.19 (1H, ddd, *J* = 10.8, 4.4, 3.4, H-2"), 4.50 and 4.60 (each 1H, d, *J* = 11.9 Hz, CH_2Ph), 4.80 (1H, ddd, *J* = 6.6, 4.8, 1.8 Hz, H-3"), 5.48 (1H, ddd, *J* = 11.0, 9.2, 1.8 Hz, H-5"), 5.74 (1H, dd, *J* = 11.0, 6.6 Hz, H-4"), 7.28-7.40 (5H, m, Ph). ^{13}C NMR ($CDCl_3$) δ 36.1 (C-7"), 37.8 (C-6"), 56.2 (C-1), 66.4 (C-1'), 67.8 (C-8"), 70.5 (C-3"), 73.8 (*C*H_2Ph), 74.6 (C-1"'), 83.1 (C-2"), 132.0 (C-5"), 134.8 (C-4"), 128.3, 128.4, 128.8, and 136.8 (Ph). HRMS calcd for $C_{17}H_{24}O_5$ 308.1624, found 308.1617.

((*2R,4S,7S,8S,Z*)-2-(benzyloxymethyl)-7-(*tert*-butyldimethylsilyloxy)-8-((*tert*-butyldimethylsilyloxy)methyl)-3,4,7,8-tetrahydro-*2H*-oxocin-4-yl)methanol (21)



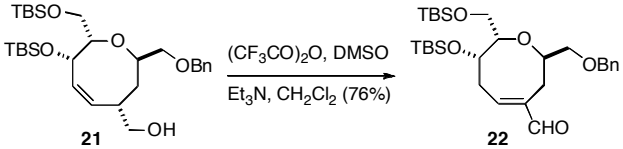
To a cooled (ice-water) solution of **20** (580 mg, 1.88 mmol) and pyridinium *p*-toluensulfonate (47 mg, 0.188 mmol) in THF (31 mL) was added dropwise 2-methoxyprop-1-ene (270 μL, 2.82 mmol). After being stirred at the same temperature for 50 min, the mixture was diluted with saturated aqueous $NaHCO_3$ solution (5 mL) and saturated brine (40 mL). The aqueous phases were extracted with Et_2O (30 mL x 4). Combined organic phases were washed with saturated brine (50 mL), dried and concentrated. The residual oil (910 mg) was used in the following step without further purification.

To a cooled (ice-water) solution of the above compound and 2,6-lutidine (1.31 mL, 11.2 mmol) in CH_2Cl_2 (15 mL) was added dropwise a solution of TBSOTf (864 μL, 3.76 mmol) in CH_2Cl_2 (1 mL). After being stirred at the same temperature for 20 min, the mixture was diluted with Et_2O (50 mL) and saturated aqueous $NaHCO_3$ solution (50 mL), separated, the aqueous phases were extracted with Et_2O (20 mL x 3). Combined organic phases were washed with 1N aqueous HCl (10 mL) and saturated brine (30 mL) successfully, dried and concentrated. The residual oil was filtered through a short pad column of silica gel and the filtrate was concentrated. The residual oil (938 mg) was used in the following step without further purification.

To a cooled (ice-water) solution of the above compound in MeOH (12 mL) was added pyridinium *p*-toluensulfonate (47 mg, 0.188 mmol). After being stirred at the same temperature for 30 min, the mixture was diluted with Et_2O (50 mL), saturated aqueous $NaHCO_3$ solution (10 mL) and saturated brine (30 mL), separated, and the aqueous phases were extracted with Et_2O (15 mL x 4). Combined organic phases were washed with saturated brine (30 mL), dried and concentrated. The residual oil was subjected by column chromatography (silica gel, 25 g, elution with hexane/EtOAc = 3:1) to give **21** (640

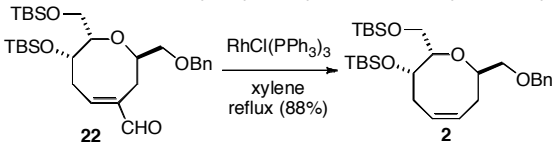
mg, 63 % from **20**), a colorless platelets. mp 68.5-69 °C. R_f = 0.25 (hexane:AcOEt = 3:1). $[\alpha]^{15}_D$ +6.6 (*c* 0.80, CH_2Cl_2). IR (film) = 3501 cm^{-1}. ^1H NMR δ 0.07, 0.08, 0.16 and 0.17 (each 3H, s, $SiMe_2$), 0.98 and 1.05 (each 9H, s, *t*-Bu), 1.61 (1H, ddd, *J* = 13.5, 13.5, 3.7 Hz, H-3'), 1.94 (1H, ddd, *J* =13.5, 11.5, 5.7 Hz, H-3'), 2.91-2.99 (1H, m, H-4'), 3.28-3.37 (2H, m, H-1), 3.57 (1H, dd, *J* = 8.9, 7.1 Hz, H-1'), 3.87 (1H, dd, *J* = 8.9, 4.6 Hz, H-1"), 4.15-4.22 (2H, m, H-1'"), 4.27 (1H, app br q, *J* = ca. 5 Hz, H-8'), 4.37-4.42 (1H, m, H-2'), 4.51 and 4.54 (each 1H, d, *J* = 11.9 Hz, CH_2Ph), 4.89 (1H, ddd, *J* = 6.2, 4.6, 2.1 Hz, H-7'), 5.31 (1H, ddd, *J* = 11.0, 9.6, 2.1 Hz, H-5'), 5.78 (1H, ddd, *J* = 11.0, 6.2, 1,1 Hz, H-6'), 7.12-7.15 (1H, m, Ph), 7.22-7.24 (2H, m, Ph), 7.37-7.39 (2H, m, Ph). ^{13}C NMR (C_6D_6) δ -5.2, –5.0, and -4.7 ($SiMe_2$), 18.2 and 18.4 (($CH_3)_3C$), 25.9 and 26.2 (($CH_3)_3C$), 37.7 (C-3'), 38.5 (C-4'), 59.5 (C-1'"), 66.5 (C-1), 68.3 (C-2'), 71.9 (C-7'), 73.7 (CH_2Ph), 74.9 (C-1"), 82.6 (C-8'), 127.6 (Ph), 128.3 (Ph), 128.5 (Ph), 131.4 (C-5'), 135.9 (C-6'), 139.3 (Ph). HRMS calcd for $C_{29}H_{52}O_5Si_2$ 536.3353, found 536.3362. Anal. calcd for $C_{29}H_{52}O_5Si_2$: C, 64.88; H 9.76. Found: C, 65.24; H, 10.04.

(*2R,7S,8S,E*)-2-(benzyloxymethyl)-7-(*tert*-butyldimethylsilyloxy)-8-((*tert*-butyldimethylsilyloxy)methyl)-3,6,7,8-tetrahydro-*2H*-oxocine-4-carbaldehyde (22)



To a cooled (-70 °C) solution of trifluoroacetic anhydride (23 μL, 0.17 mmol) in CH_2Cl_2 (1.0 mL) was added dropwise a solution of DMSO (22 μL, 0.33mmol) in CH_2Cl_2 (0.5 mL). After being stirred at the same temperature for 10 min, the mixture was added a solution of **21** (50 mg, 0.093 mmol) in CH_2Cl_2 (0.5 mL) nd the reaction mixture was allowed to warm to -35 °C over a period of 30 min before addition of NEt_3 (91 μL, 0.65 mmol). The mixture was allowed to warm to -20 °C and diluted with half-saturated aqueous $NaHCO_3$ (4 mL). Phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 mL x 3). Combined organic phases were washed with brine (2 mL x 2), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 2 g, elution with hexane/AcOEt = 6:1) to give **22** (38 mg, 76%), colorless oil. R_f = 0.33 (hexane:AcOEt = 6:1). $[\alpha]^{22}_D$ +334.9 (*c* 0.64, CH_2Cl_2). IR (film) = 1685 cm^{-1}. ^1H NMR δ 0.08, 0.09, 0.17 and 0.19 (each 3H, s, $SiMe_2$), 1.00 and 1.03 (each 9H, s, *t*-Bu), 2.07 (1H, ddd, *J* = 12.6, 7.8, 2.7 Hz, H-6), 2.38 (1H, dd, *J* =13.5, 9.4 Hz, H-3), 2.56 (1H, ddd, *J* = 12.6, 7.8, 7.8 Hz, H-6), 2.67 (1H, dd, *J* = 13.5, 3.9 Hz, H-3), 3.38 (1H, dd, *J* = 10.8, 3.9 Hz, H-1'), 3.45 (1H, dd, *J* = 10.8, 6.6 Hz, H-1'), 3.72-3.84 (3H, m, H-1"and H-8), 4.00-4.05 (1H, m, H-2), 4.35 (1H, brm, H-7), 4.24 and 4.37 (each 1H, d, *J* = 11.9 Hz, CH_2Ph), 6.39 (1H, dd, *J* = 7.8, 7.8 Hz, H-5), 7.14 (1H, dd, *J* = 7.3, 7.3 Hz, Ph), 7.24 (2H, dd, *J* = 7.8, 7.3 Hz, Ph), 7.34 (2H, d, *J* = 7.8 Hz, Ph), 9.33 (1H, s, CHO). ^{13}C NMR (C_6D_6) δ -5.2, –5.0, -4.7 and -4.2 ($SiMe_2$), 18.4 and 18.4 (($CH_3)_3C$), 25.8 (C-3), 26.0 and 26.2 (($CH_3)_3C$), 35.3 (C-6), 62.9 (C-1"), 72.0 (C-7), 72.4 (C-1'), 73.1 (CH_2Ph), 74.3 (C-2), 75.4 (C-8), 127.7 (Ph), 127.7 (Ph), 128.3 (Ph), 128.6 (Ph),138.8 (Ph), 143.7 (C-4), 151.8 (C-5), 192.6 (CHO). HRMS calcd for $C_{29}H_{51}O_5Si_2$ (M^+ + 1) 535.3275, found 535.3273.

((2*S*,3*S*,8*R*)-8-(Benzyloxymethyl)-2-((*tert*-butyldimethylsiloxy)methyl)-3,4,7,8-tetrahydro-*2H*-oxocin-3-yloxy)(*tert*-butyl)dimethylsilane (2)



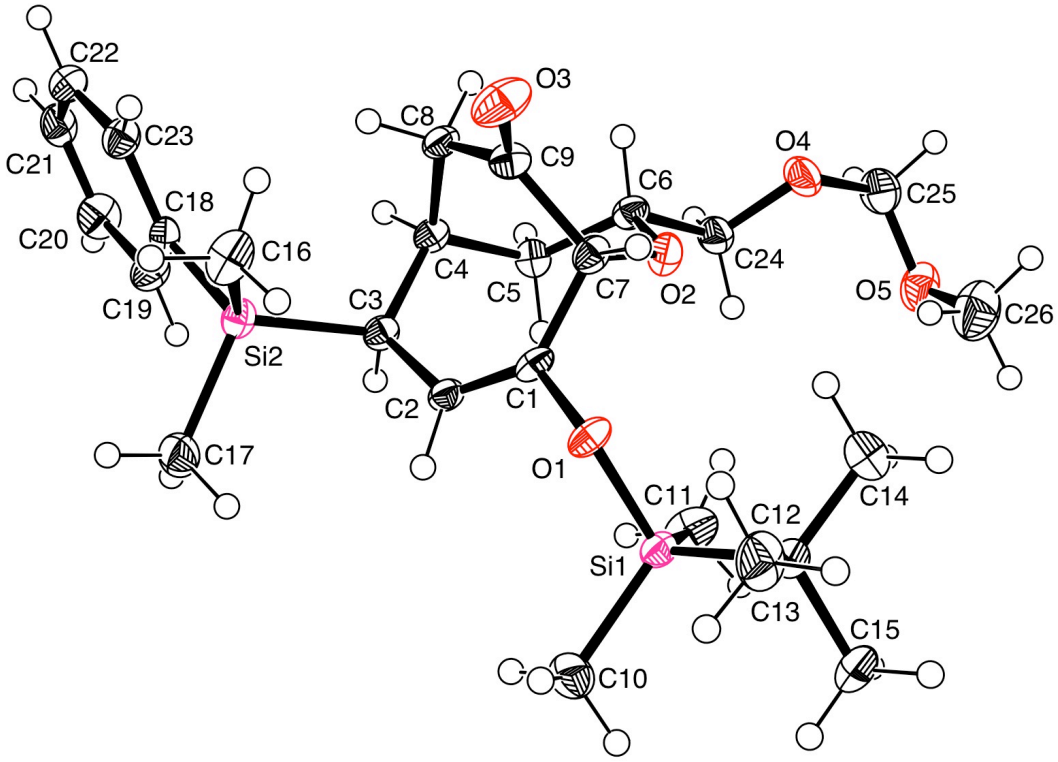
To a solution of **22** (33 mg, 0.062 mmol) in xylene (6.2 mL) was added $RhCl(PPh_3)_3$ (86 mg, 0.093 mmol) and degassed by a freeze-thaw method[1] (repeated 4 times). The reaction mixture was heated at 140 °C for 1 hr, cooled to room temperature, diluted with EtOH (10 mL) and filtered. The filtrate was concentrated and the residual oil was subjected to column chromatography (silica gel, 3 g, elution with hexane/EtOAc = 7:1) to give **2** (27.7 mg, 89%), a colorless oil. R_f = 0.23 (hexane:Et_2O = 9:1). $[\alpha]^{18}_D$ +74.0 (*c* 0.93, CH_2Cl_2). IR (film) = 3027, 2954, 2930, 2888, 2857, 1465, 1362, 1253, 1097, 1067, 945, 917, 835, 775, 734, 397, 374 cm^{-1}. H NMR ($CDCl_3$) δ 0.01 and 0.01 (each 3H, s, $SiMe_2$), 0.07 and 0.09 (each 3H, s, $SiMe_2$), 0.87 (9H, s, *t*-Bu), 0.90 (9H, s, *t*-Bu), 2.16-2.22 (1H, m, H-4), 2.25-2.33 (1H, m, H-7), 2.42-2.48 (1H, m, H-7), 2.52-2.58 (1H, m, H-4), 3.49 (1H, dd, *J* = 9.6, 6.6 Hz, H-1'), 3.55-3.60 (2H, m, H-1"), 3.60-3.66 (1H, m, H-2), 3.70 (1H, dd, *J* = 9.6, 6.0 Hz, H-1'), 3.98-4.10 (1H, m, H-3), 4.08-4.15 (1H, m H-8), 4.50 and 4.55 (each 1H, d, 12.0 Hz, CH_2Ph), 5.73-5.82 (2H, m, H-5 and H-6), 7.20-7.38 (5H, m, Ph). ^{13}C NMR ($CDCl_3$) δ -5.3, -5.2, -4.7, and -4.2 ($SiMe_2$), 18.4 (($CH_3)_3C$), 26.1 (($CH_3)_3C$), 26.1 (($CH_3)_3C$), 29.8 (C-7), 33.4 (C-4), 63.7 (C-1"), 70.8 (C-1'), 73.1 (C-3), 73.2 (CH_2Ph), 74.9 (C-8), 75.1 (C-2), 127.6 (Ph), 127.7 (Ph), 128.4 (Ph), 128.6, and 129.9 (C-5 and C-6), 138.4 (Ph). HRMS calcd for $C_{28}H_{50}O_4Si_2$ 506.3248, found 506.3231.

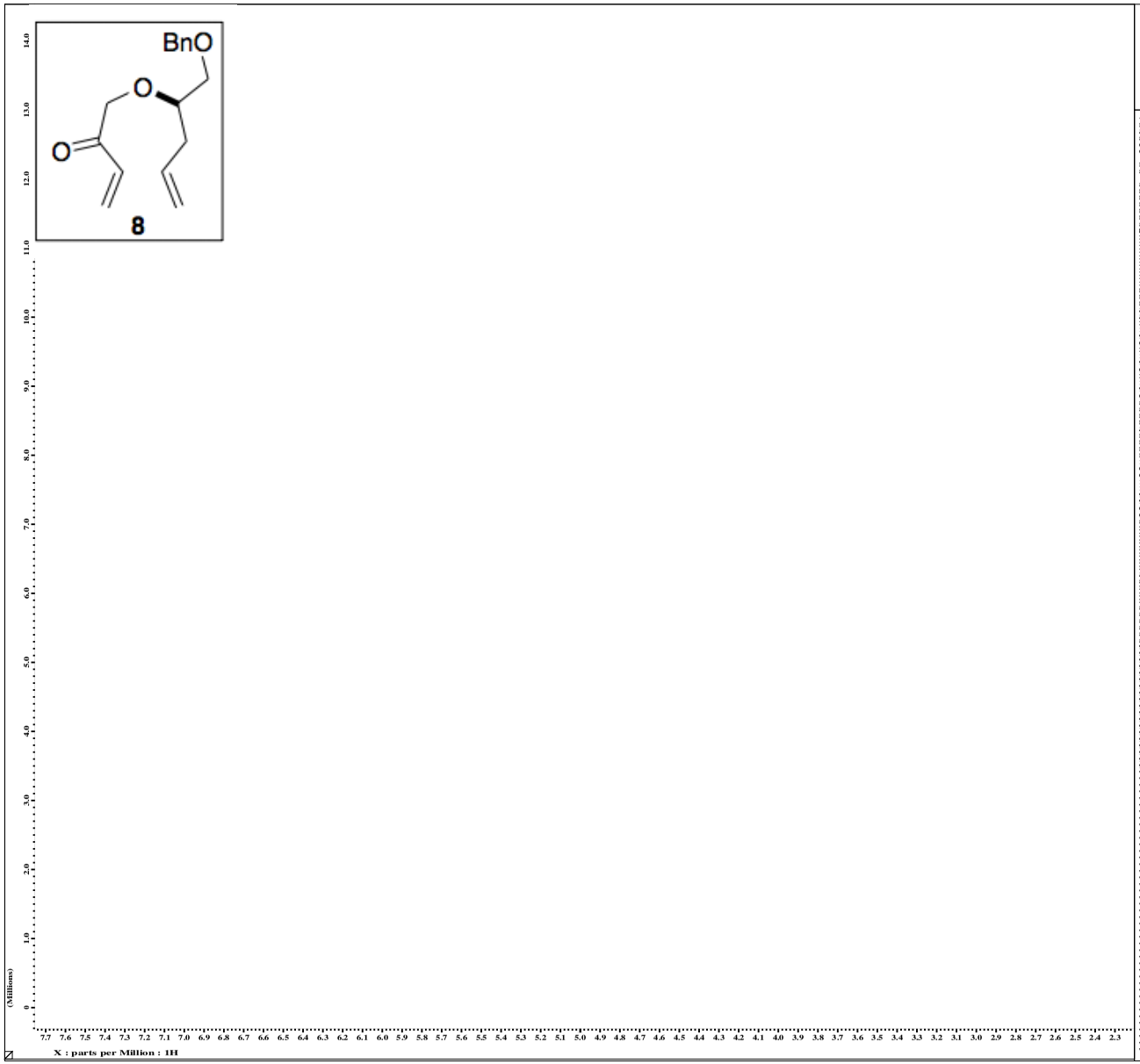
(1) Ciganek, E. *Org. React.*, **1984**, *32*, 97.

Crystal data and structure refinement for 12b

Formula weight	490.78	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.0993(17) Å	α = 90°.
	b = 16.560(2) Å	β = 104.882(2)°.
	c = 12.0918(15) Å	γ = 90°.
Volume	2728.6(6) $Å^3$	
Z	4	
Density (calculated)	1.195 Mg/m^3	
Absorption coefficient	0.162 mm^{-1}	
F(000)	1064	
Crystal size	0.50 x 0.50 x 0.10 mm^3	
Theta range for data collection	1.49 to 27.56°.	
Index ranges	-18<=h<=17, -21<=k<=21, -15<=l<=11	
Reflections collected	16180	
Independent reflections	6222 [R(int) = 0.0532]	
Completeness to theta = 27.56°	98.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6222 / 0 / 306	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0487, wR2 = 0.1157	
R indices (all data)	R1 = 0.0812, wR2 = 0.1310	
Largest diff. peak and hole	0.345 and -0.284 e.$Å^{-3}$	

ORTEP Drawing of 12b





JEOL

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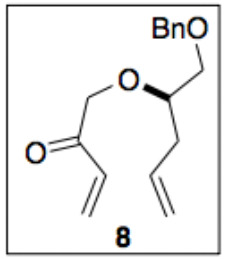
Vt_pid_long_60_h_hc      = 2.5
Vt_pid_long_60_h_hl      = 70
Vt_pid_long_60_m_pb      = 1.5
Vt_pid_long_60_m_ti      = 30
Vt_pid_long_60_m_td      = 5
Vt_pid_long_60_m_chl     = 9.9
Vt_pid_long_60_m_chb     = 2.3
Vt_pid_long_60_m_hc      = 2.5
Vt_pid_long_60_m_hl      = 70
Sample_action            = LOADED
Sample_state             = LOAD
Sample_status            = LOADED
Changer_sample           = 5
N2_level                 = 81[%]
He_level                 = 75[%]
Autoshim_mode            = AUTOSHIM OFF
Autoshim_delay           = 3.6[hr]
Autoshim_track           = AUTOSHIM OFF
Shim_max_recall          = MAX FOUND
Shim_names               = SHIM_50
Shim_z0                  = -16.07[kHz]
Shim_z1                  = -102.27[Hz]
Shim_z2                  = -294.14[Hz]
Shim_z3                  = -212.17[Hz]
Shim_z4                  = 15.64[Hz]
Shim_z5                  = 10.5[Hz]
Shim_z6                  = 2.96[Hz]
Shim_z7                  = 0[Hz]
Shim_z8                  = 0[Hz]
Shim_x                   = -302[Hz]
Shim_xz                  = 54.5[Hz]
Shim_xz2                 = -346.5[Hz]
Shim_xz3                 = -9.1[Hz]
Shim_xz4                 = 4.5[Hz]
Shim_xz5                 = 9.8[Hz]
Shim_x2                  = 171.2[Hz]
Shim_x2z                 = 113.6[Hz]
Shim_x2z2                = 52.8[Hz]
Shim_x2z3                = 19.1[Hz]
Shim_x2z4                = -0.8[Hz]
Shim_x3                  = 127.3[Hz]
Shim_x3z                 = -55[Hz]
Shim_x3z2                = -28[Hz]
Shim_x3z3                = 3.3[Hz]
Shim_x4                  = -45.5[Hz]
Shim_x4z                 = 49[Hz]
Shim_x4z2                = -4[Hz]
Shim_y                   = 118.5[Hz]
Shim_yz                  = 71.2[Hz]
Shim_yz2                 = 830.1[Hz]
Shim_yz3                 = 0.7[Hz]
Shim_yz4                 = -17[Hz]
Shim_yz5                 = -8.3[Hz]
Shim_y2                  = 382.4[Hz]
Shim_y2z                 = -225.9[Hz]
Shim_y2z2                = 7.8[Hz]
Shim_y2z3                = 12[Hz]
Shim_y2z4                = 0.4[Hz]
Shim_y3                  = -365.9[Hz]
Shim_y3z                 = 131.4[Hz]
Shim_y3z2                = 7.5[Hz]
Shim_y3z3                = -5.4[Hz]
Shim_y4                  = -59[Hz]
Shim_y4z                 = 11.8[Hz]
Shim_y4z2                = 5.5[Hz]
Num_scans                = 0
Iterations               = 0
End_time                 = 21-AUG-2007 10:10
Local_time               = 21-AUG-2007 10:10
Probe_atn                = 0
Probe_tune               = 0
Probe_match              = 2625
Probe_coarse             = A
Probe_id                 = 3204
Lf_tune_dial             = 0
Lf_match_dial            = 0
Hf_tune_dial             = 0
Hf_match_dial            = 0
Experiment               = single_pulse.exp
Transition_ratio         = 0.9
Pass_ripple              = 10[mdB]
Stop_ripple              = 60[dB]
Orders                   =
Factors                  =
Probe_recovery           = 0[us]
X_acq_time               = 4.3646976[s]
X_angle                  = 45[deg]
X_90_width               = 7.4[us]
X_pulse                  = 3.7[us]
Dead_time                = 0[us]
Delay                    = 0[us]
Phase_preset             = 2[us]
Relaxation_delay         = 4[s]
Initial_wait             = 1[s]
```

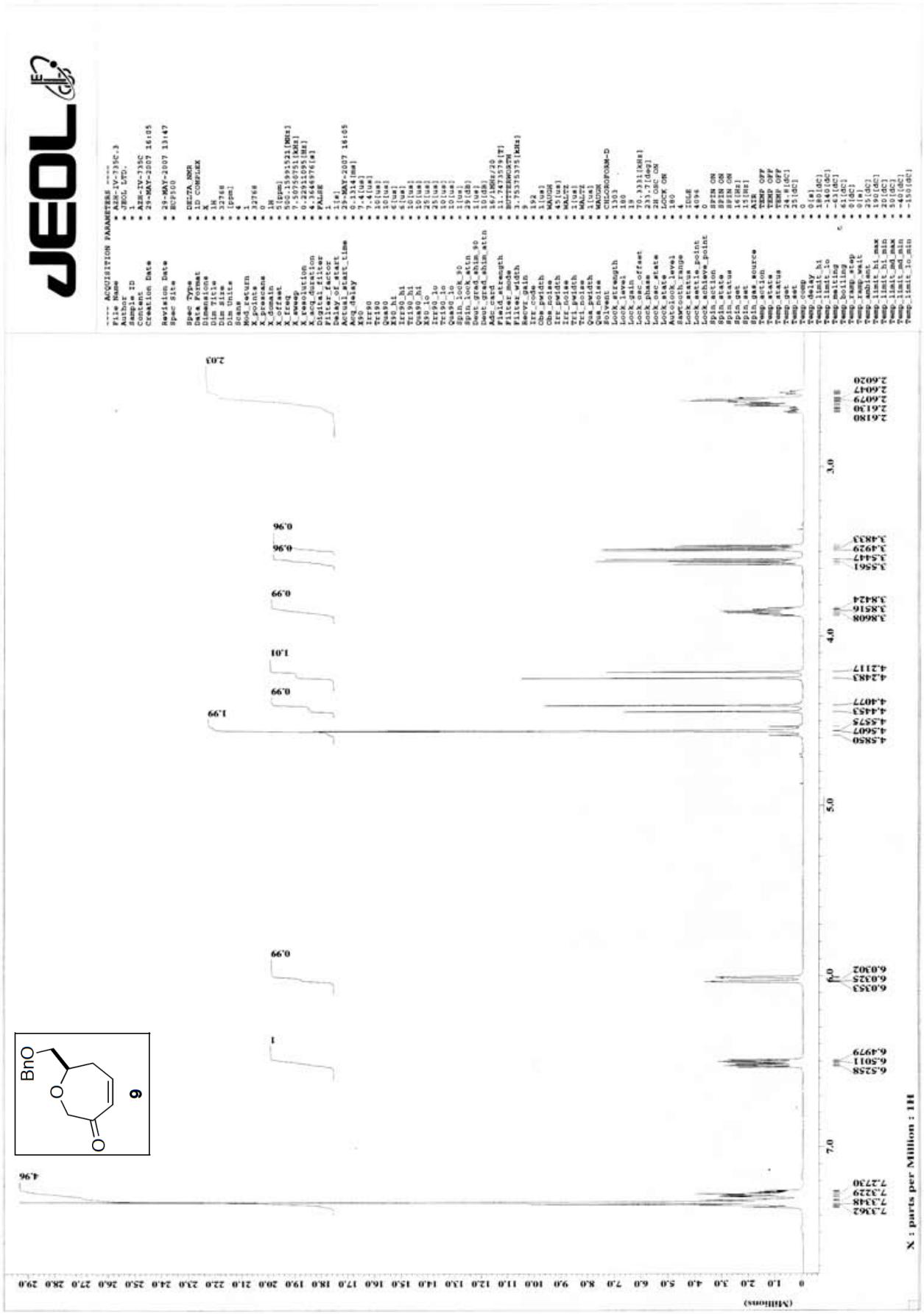


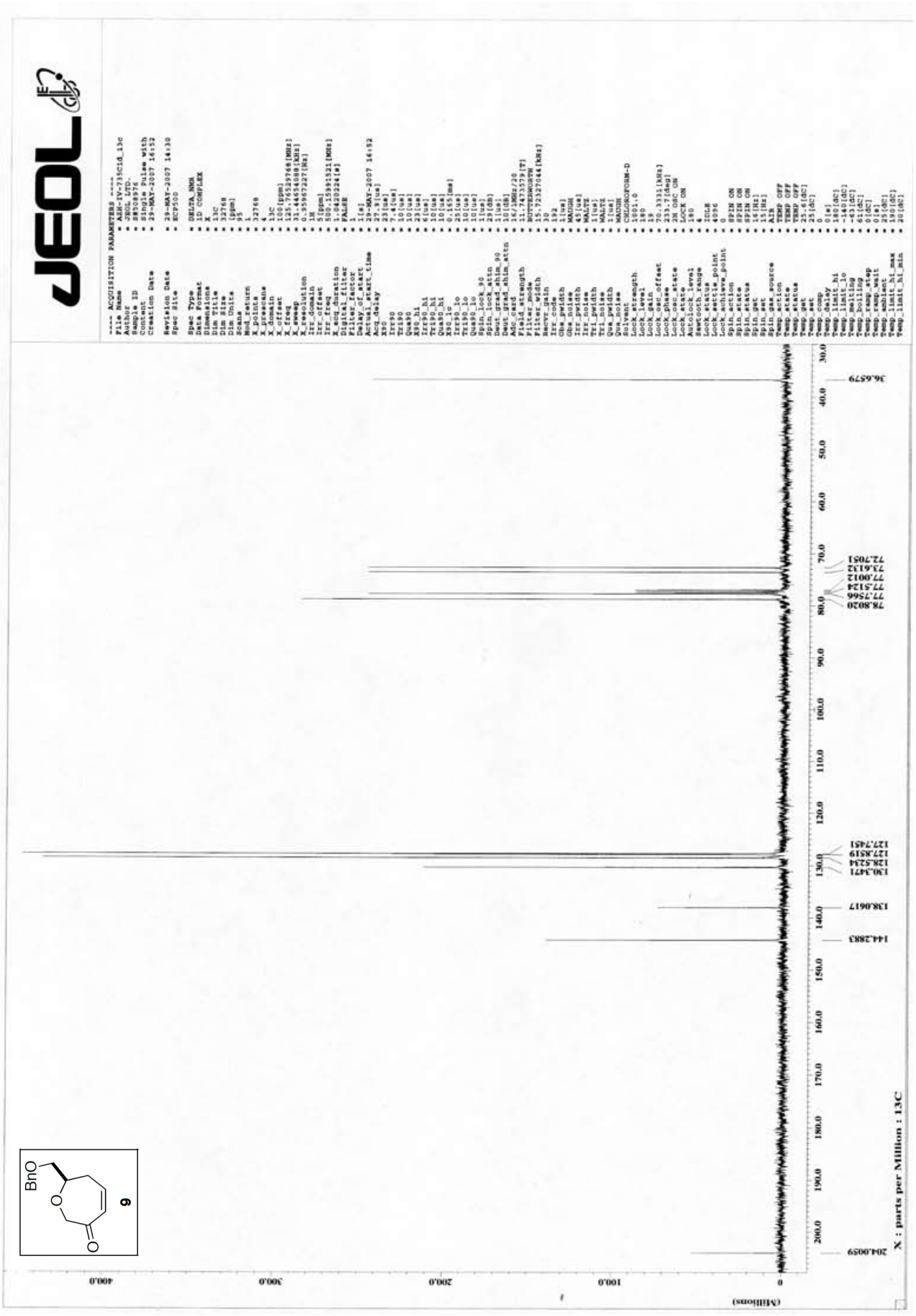
JEOL

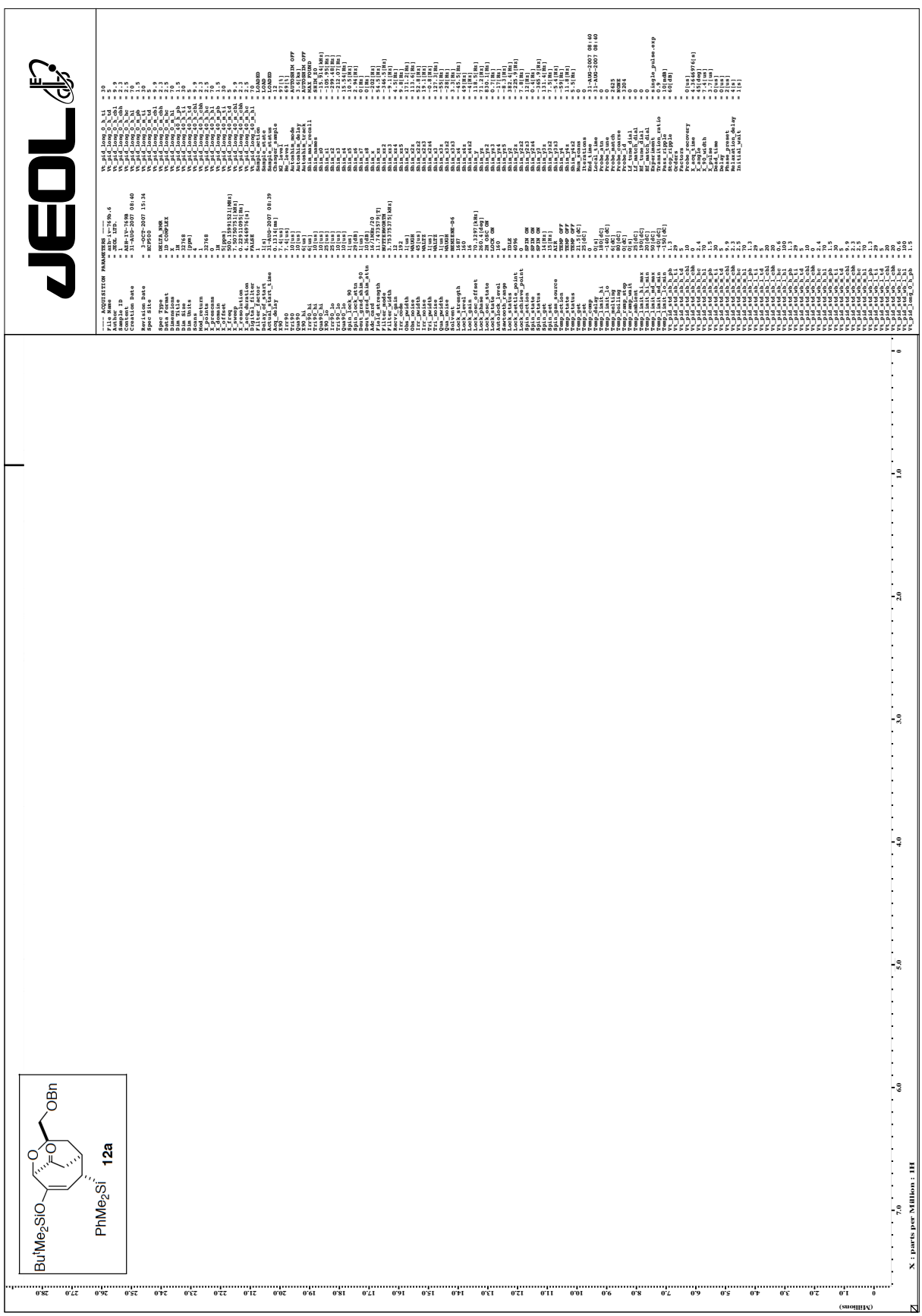
```
=== ACQUISITION PARAMETERS ===
File Name               = ash-iv-803b.9
Author                  = JEOL LTD.
Sample ID               = 1
Content                 = ASH-IV-803B
Creation Date           = 22-AUG-2007 09:12

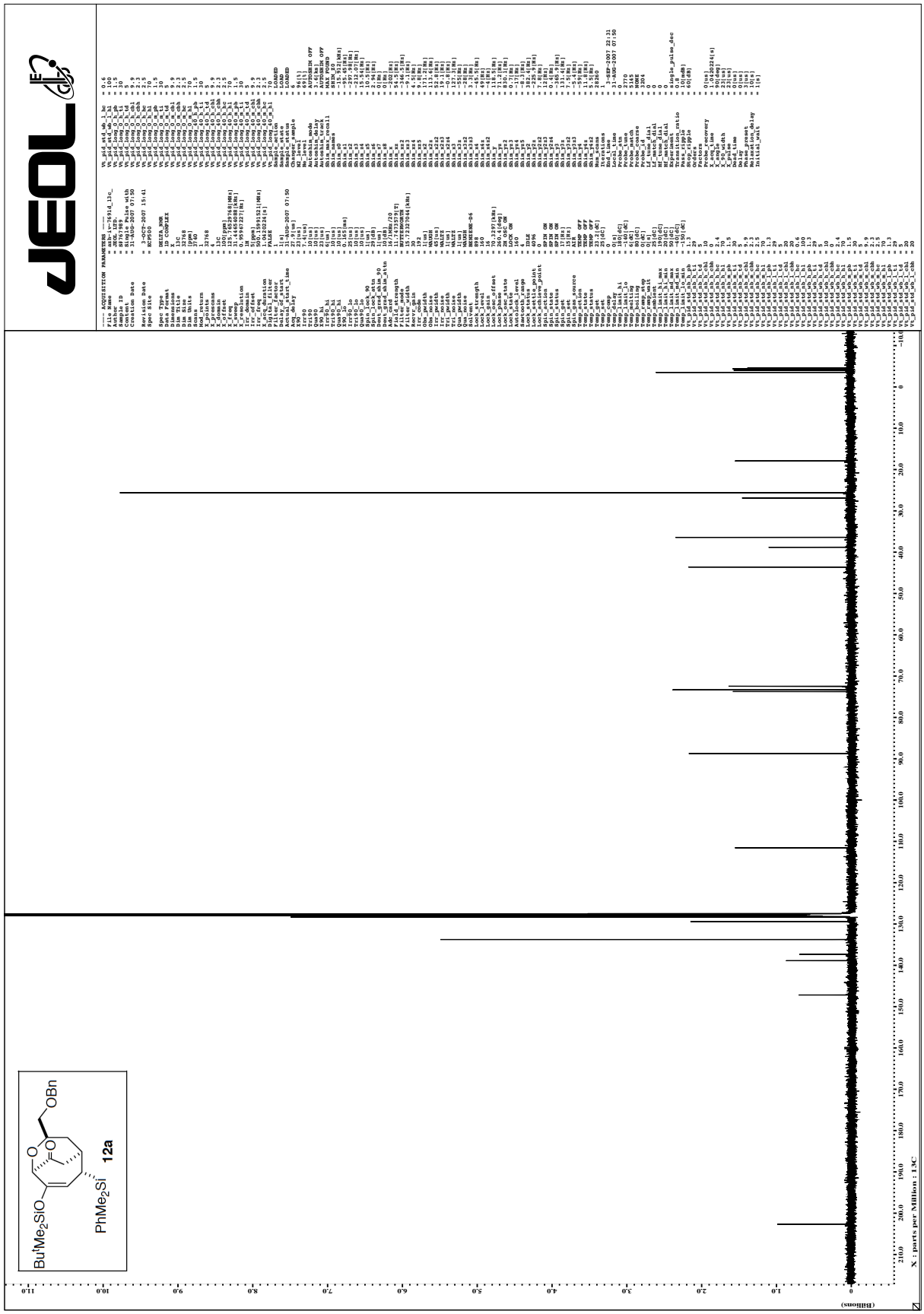
Revision Date           =  3-OCT-2007 16:53
Spec Site               = ECP500

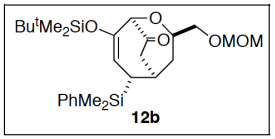
Spec Type               = DELTA_NMR
Data Format             = 1D COMPLEX
Dimensions              = X
Dim Title               = 13C
Dim Size                = 32768
Dim Units               = [ppm]
Scans                   = 608
Mod_return              = 1
X_points                = 32768
X_prescans              = 4
X_domain                = 13C
X_offset                = 100[ppm]
X_freq                  = 125.76529768[MHz]
X_sweep                 = 31.44654088[kHz]
X_resolution            = 0.95967227[Hz]
Irr_domain              = 1H
Irr_offset              = 5[ppm]
Irr_freq                = 500.15991521[MHz]
X_acq_duration          = 1.0420224[s]
Digital_filter          = FALSE
Filter_factor           = 1
Delay_of_start          = 1[s]
Actual_start_time       = 22-AUG-2007 09:12
Acq_delay               = 27.9[us]
X90                     = 23[us]
Irr90                   = 7.4[us]
Tri90                   = 10[us]
Qua90                   = 10[us]
X90_hi                  = 23[us]
Irr90_hi                = 6[us]
Tri90_hi                = 10[us]
Qua90_hi                = 10[us]
X90_lo                  = 0.165[ms]
Irr90_lo                = 25[us]
Tri90_lo                = 10[us]
Qua90_lo                = 10[us]
Spin_lock_90            = 1[us]
Spin_lock_attn          = 29[dB]
Deut_grad_shim_90       = 1[us]
Deut_grad_shim_attn     = 10[dB]
Ade_card                = 16/16Hz/20
Field_strength          = 11.7473579[T]
Filter_mode             = BUTTERWORTH
Filter_width            = 15.72327044[kHz]
Recvr_gain              = 20
Irr_code                = 192
Obs_pwidth              = 1[us]
Obs_noise               = WALTZ
Irr_pwidth              = 45[us]
Irr_noise               = WALTZ
Tri_pwidth              = 1[us]
Tri_noise               = WALTZ
Qua_pwidth              = 1[us]
Qua_noise               = WALTZ
Solvent                 = CHLOROFORM-D
Lock_strength           = 1194
Lock_level              = 180
Lock_gain               = 19
Lock_osc_offset         = 70.3331[kHz]
Lock_phase              = 260.4[deg]
Lock_osc_state          = 2H OSC ON
Lock_state              = LOCK ON
Autolock_level          = 180
Sawtooth_range          = 4
Lock_status             = IDLE
Lock_settle_point       = 4096
Lock_achieve_point      = 0
Spin_action             = SPIN ON
Spin_state              = SPIN ON
Spin_status             = SPIN ON
Spin_set                = 16[Hz]
Spin_act                = 15[Hz]
Spin_sss_source         = AIR
Temp_action             = TEMP OFF
Temp_state              = TEMP OFF
Temp_status             = TEMP OFF
Temp_set                = 25[dC]
Temp_act                = 24.6[dC]
Temp_comp               = 0
Temp_delay              = 0[s]
Temp_limit_hi           = 180[dC]
Temp_limit_lo           = -10[dC]
Temp_melting            = -63[dC]
Temp_boiling            = 61[dC]
Temp_ramp_step          = 0[dC]
Temp_ramp_wait          = 0[s]
Temp_ambient            = 25[dC]
Temp_limit_hi_max       = 190[dC]
Temp_limit_hi_min       = 20[dC]
Temp_limit_md_max       = 50[dC]
Temp_limit_md_min       = -40[dC]
Temp_limit_lo_min       = -150[dC]
Vt_pid_std_nb_h_ph      = 1.3
Vt_pid_std_nb_h_ti      = 29
Vt_pid_std_nb_h_td      = 5
Vt_pid_std_nb_h_chl     = 10
Vt_pid_std_nb_h_chh     = 0
Vt_pid_std_nb_h_hc      = 2.4
Vt_pid_std_nb_h_hl      = 70
Vt_pid_std_nb_m_ph      = 1.5
Vt_pid_std_nb_m_ti      = 30
Vt_pid_std_nb_m_td      = 5
Vt_pid_std_nb_m_chl     = 9.9
Vt_pid_std_nb_m_chh     = 2.3
Vt_pid_std_nb_m_hc      = 2.5
Vt_pid_std_nb_m_hl      = 70
Vt_pid_std_nb_l_ph      = 1.3
Vt_pid_std_nb_l_ti      = 29
Vt_pid_std_nb_l_td      = 5
Vt_pid_std_nb_l_chl     = 20
Vt_pid_std_nb_l_chh     = 20
Vt_pid_std_nb_l_hc      = 0.6
Vt_pid_std_nb_l_hl      = 100
Vt_pid_std_wb_h_ph      = 1.3
Vt_pid_std_wb_h_ti      = 29
Vt_pid_std_wb_h_td      = 5
Vt_pid_std_wb_h_chl     = 10
Vt_pid_std_wb_h_chh     = 0
Vt_pid_std_wb_h_hc      = 2.4
Vt_pid_std_wb_h_hl      = 70
Vt_pid_std_wb_m_ph      = 1.5
Vt_pid_std_wb_m_ti      = 30
Vt_pid_std_wb_m_td      = 5
Vt_pid_std_wb_m_chl     = 9.9
Vt_pid_std_wb_m_chh     = 2.3
Vt_pid_std_wb_m_hc      = 2.5
Vt_pid_std_wb_m_hl      = 70
Vt_pid_std_wb_l_ph      = 1.3
Vt_pid_std_wb_l_ti      = 29
Vt_pid_std_wb_l_td      = 5
Vt_pid_std_wb_l_chl     = 20
Vt_pid_std_wb_l_chh     = 20
Vt_pid_std_wb_l_hc      = 0.6
Vt_pid_std_wb_l_hl      = 100
Vt_pid_long_0_h_ph      = 1.5
Vt_pid_long_0_h_ti      = 30
Vt_pid_long_0_h_td      = 5
Vt_pid_long_0_h_chl     = 9.9
Vt_pid_long_0_h_chh     = 2.3
Vt_pid_long_0_h_hc      = 2.5
Vt_pid_long_0_h_hl      = 70
Vt_pid_long_0_m_ph      = 1.5
Vt_pid_long_0_m_ti      = 30
Vt_pid_long_0_m_td      = 5
Vt_pid_long_0_m_chl     = 9.9
Vt_pid_long_0_m_chh     = 2.3
Vt_pid_long_0_m_hc      = 2.5
Vt_pid_long_0_m_hl      = 70
Vt_pid_long_40_h_ph     = 1.5
Vt_pid_long_40_h_ti     = 30
Vt_pid_long_40_h_td     = 5
Vt_pid_long_40_h_chl    = 9.9
Vt_pid_long_40_h_chh    = 2.3
Vt_pid_long_40_h_hc     = 2.5
Vt_pid_long_40_h_hl     = 70
Vt_pid_long_40_m_ph     = 1.5
Vt_pid_long_40_m_ti     = 30
Vt_pid_long_40_m_td     = 5
Vt_pid_long_40_m_chl    = 9.9
Vt_pid_long_40_m_chh    = 2.3
Vt_pid_long_40_m_hc     = 2.5
Vt_pid_long_40_m_hl     = 70
Sample_action           = LOADED
Sample_state            = LOAD
Sample_status           = LOADED
Changer_sample          = 1
H2_level                = 99[%]
He_level                = 75[%]
Autoshim_mode           = AUTOSHIM OFF
Autoshim_delay          = 3.6[hr]
Autoshim_track          = AUTOSHIM OFF
Shim_max_recall         = MAX FOUND
Shim_names              = SHIM_ZO
Shim_z0                 = -16.363[kHz]
Shim_z1                 = -97.67[Hz]
Shim_z2                 = -296.34[Hz]
Shim_z3                 = -212.07[Hz]
Shim_z4                 = 15.54[Hz]
Shim_z5                 = 10.5[Hz]
Shim_z6                 = 2.94[Hz]
Shim_z7                 = 0[Hz]
Shim_z8                 = 0[Hz]
Shim_x                  = -202[Hz]
Shim_xx                 = 54.5[Hz]
Shim_xx2                = -346.5[Hz]
Shim_xx3                = -9.1[Hz]
Shim_xx4                = 4.5[Hz]
Shim_xx5                = 9.8[Hz]
Shim_x2                 = 171.2[Hz]
Shim_x2x                = 113.6[Hz]
Shim_x2x2               = 52.8[Hz]
Shim_x2x3               = 19.1[Hz]
Shim_x2x4               = -0.8[Hz]
Shim_x3                 = 127.3[Hz]
Shim_x3x                = -55[Hz]
Shim_x3x2               = -28[Hz]
Shim_x3x3               = 3.3[Hz]
Shim_x4                 = -45.5[Hz]
Shim_x4x                = 49[Hz]
Shim_x4x2               = -4[Hz]
Shim_y                  = 118.5[Hz]
Shim_yy                 = 71.2[Hz]
Shim_yy2                = 830.1[Hz]
Shim_yy3                = 0.7[Hz]
Shim_yy4                = -17[Hz]
Shim_yy5                = -8.3[Hz]
Shim_y2                 = 382.4[Hz]
Shim_y2x                = -225.9[Hz]
Shim_y2x2               = 7.8[Hz]
Shim_y2x3               = 12[Hz]
Shim_y2x4               = 0.4[Hz]
Shim_y3                 = -365.9[Hz]
Shim_y3x                = 131.4[Hz]
Shim_y3x2               = 7.5[Hz]
Shim_y3x3               = -5.4[Hz]
Shim_y4                 = -59[Hz]
Shim_y4x                = 11.8[Hz]
Shim_y4x2               = 5.5[Hz]
Num_scans               = 31393
Iterations              = 1
End_time                = 23-AUG-2007 11:44
Local_time              = 22-AUG-2007 09:12
Probe_atn               = 0
Probe_tune              = 2770
Probe_match             = 5165
Probe_coarse            = NONE
Probe_id                = 3204
Lf_tune_dial            = 0
Lf_match_dial           = 0
Hf_tune_dial            = 0
Hf_match_dial           = 0
Experiment              = single_pulse_dec
Transition_ratio        = 0.8
Pass_ripple             = 10[mdB]
Stop_ripple             = 60[dB]
Orders                  =
Factors                 =
Probe_recovery          = 0[us]
X_acq_time              = 1.0420224[s]
X_angle                 = 90[deg]
X_90_width              = 23[us]
X_pulse                 = 23[us]
Dead_time               = 0[us]
Delay                   = 0[us]
Phase_preset            = 3[us]
Relaxation_delay        = 2[s]
Initial_wait            = 1[s]
```


JEOL
BnO
O
O
9
X : parts per Million : 1H
(Millions)


JEOL
BnO
O
O
9
36.6579
72.7051
73.6132
77.0012
77.5124
77.7566
78.8020
127.7451
127.8519
128.5234
130.3471
138.0617
144.2883
204.0059
X : parts per Million : 13C
(Millions)


JEOL
OBn
PhMe2Si
12a
X : parts per Million : 1H


JEOL
OBn
PhMe2Si
12a
X : parts per Million : 13C



12b

JEOL

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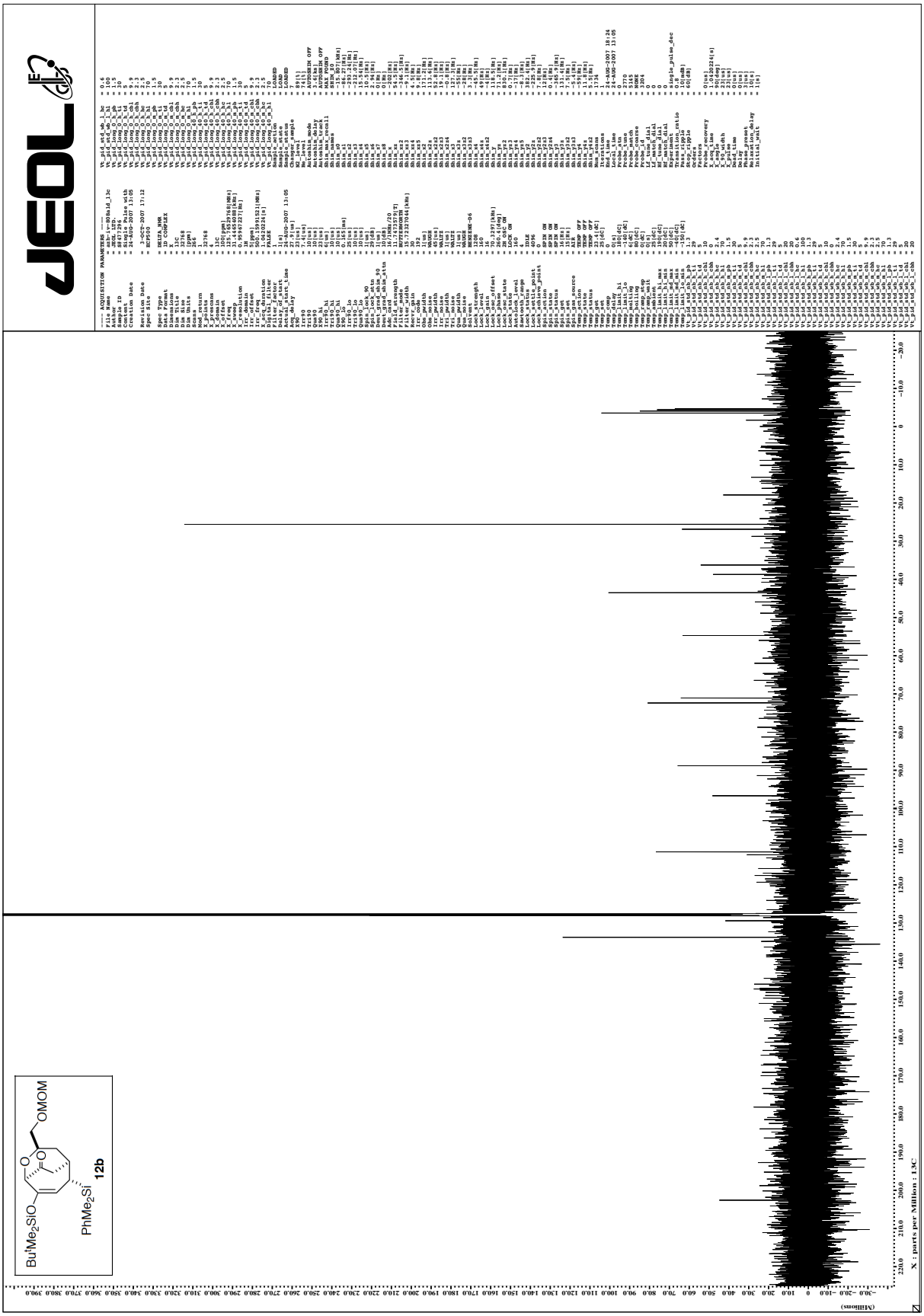
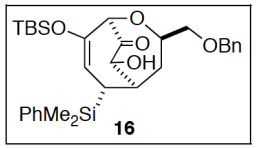
=== ACQUISITION PARAMETERS ===
File Name              = ash-iv-808a.4
Author                 = JEOL LTD.
Sample ID              = 1
Content                = ASH-IV-808A
Creation Date          = 24-AUG-2007 10:43
Revision Date          =  3-OCT-2007 17:09
Spec Site              = ECP500

Spec Type              = DELTA_NMR
Data Format            = 1D COMPLEX
Dimensions             = X
Dim Title              = 1H
Dim Size               = 32768
Dim Units              = [ppm]
Scans                  = 4
Mod_return             = 1
X_points               = 32768
X_prescans             = 0
X_domain               = 1H
X_offset               = 5[ppm]
X_freq                 = 500.15991521[MHz]
X_sweep                = 7.50750751[kHz]
X_resolution           = 0.22911095[Hz]
X_acq_duration         = 4.3646976[s]
Digital_filter         = FALSE
Filter_factor          = 1
Delay_of_start         = 1[s]
Actual_start_time      = 24-AUG-2007 10:43
Acq_delay              = 0.1314[ms]
X90                    = 7.4[us]
Irr90                  = 7.4[us]
Tri90                  = 10[us]
Qua90                  = 10[us]
X90_hi                 = 6[us]
Irr90_hi               = 6[us]
Tri90_hi               = 10[us]
Qua90_hi               = 10[us]
X90_lo                 = 25[us]
Irr90_lo               = 25[us]
Tri90_lo               = 10[us]
Qua90_lo               = 10[us]
Spin_lock_90           = 1[us]
Spin_lock_attn         = 29[dB]
Deut_grad_shim_90      = 1[us]
Deut_grad_shim_attn    = 10[dB]
Adc_card               = 16/1MHz/20
Field_strength         = 11.7473579[T]
Filter_mode            = BUTTERWORTH
Filter_width           = 3.75375375[kHz]
Recvr_gain             = 16
Irr_code               = 192
Obs_pwidth             = 1[us]
Obs_noise              = WALTZ16
Irr_pwidth             = 0.165[ms]
Irr_noise              = WALTZ16
Tri_pwidth             = 1[us]
Tri_noise              = WALTZ16
Qua_pwidth             = 1[us]
Qua_noise              = WALTZ16
Solvent                = BENZENE-D6
Lock_strength          = 2099
Lock_level             = 160
Lock_gain              = 16
Lock_osc_offset        = 70.3297[kHz]
Lock_phase             = 260.4[deg]
Lock_osc_state         = 2H OSC ON
Lock_state             = LOCK ON
Autolock_level         = 160
Sawtooth_range         = 4
Lock_status            = IDLE
Lock_settle_point      = 4096
Lock_achieve_point     = 0
Spin_action            = SPIN ON
Spin_state             = SPIN ON
Spin_status            = SPIN ON
Spin_get               = 17[Hz]
Spin_set               = 15[Hz]
Spin_gas_source        = AIR
Temp_action            = TEMP OFF
Temp_state             = TEMP OFF
Temp_status            = TEMP OFF
Temp_get               = 21[dC]
Temp_set               = 25[dC]
Temp_comp              = 0
Temp_delay             = 0[s]
Temp_limit_hi          = 180[dC]
Temp_limit_lo          = -140[dC]
Temp_heating           = 6[dC]
Temp_boiling           = 80[dC]
Temp_ramp_step         = 0[dC]
Temp_ramp_wait         = 0[s]
Temp_ambient           = 25[dC]
Temp_limit_hi_max      = 190[dC]
Temp_limit_hi_min      = 20[dC]
Temp_limit_md_max      = 50[dC]
Temp_limit_md_min      = -40[dC]
Temp_limit_lo_min      = -150[dC]
Vt_pid_std_nb_h_pb     = 1.3
Vt_pid_std_nb_h_ti     = 29
Vt_pid_std_nb_h_td     = 5
Vt_pid_std_nb_h_chl    = 10
Vt_pid_std_nb_h_chb    = 0
Vt_pid_std_nb_h_hc     = 2.4
Vt_pid_std_nb_h_hl     = 70
Vt_pid_std_nb_m_pb     = 1.5
Vt_pid_std_nb_m_ti     = 30
Vt_pid_std_nb_m_td     = 5
Vt_pid_std_nb_m_chl    = 9.9
Vt_pid_std_nb_m_chb    = 2.3
Vt_pid_std_nb_m_hc     = 2.5
Vt_pid_std_nb_m_hl     = 70
Vt_pid_std_nb_l_pb     = 1.3
Vt_pid_std_nb_l_ti     = 29
Vt_pid_std_nb_l_td     = 5
Vt_pid_std_nb_l_chl    = 20
Vt_pid_std_nb_l_chb    = 20
Vt_pid_std_nb_l_hc     = 0.6
Vt_pid_std_nb_l_hl     = 100
Vt_pid_std_wb_h_pb     = 1.3
Vt_pid_std_wb_h_ti     = 29
Vt_pid_std_wb_h_td     = 5
Vt_pid_std_wb_h_chl    = 10
Vt_pid_std_wb_h_chb    = 0
Vt_pid_std_wb_h_hc     = 2.4
Vt_pid_std_wb_h_hl     = 70
Vt_pid_std_wb_m_pb     = 1.5
Vt_pid_std_wb_m_ti     = 30
Vt_pid_std_wb_m_td     = 5
Vt_pid_std_wb_m_chl    = 9.9
Vt_pid_std_wb_m_chb    = 2.3
Vt_pid_std_wb_m_hc     = 2.5
Vt_pid_std_wb_m_hl     = 70
Vt_pid_std_wb_l_pb     = 1.3
Vt_pid_std_wb_l_ti     = 29
Vt_pid_std_wb_l_td     = 5
Vt_pid_std_wb_l_chl    = 20
Vt_pid_std_wb_l_chb    = 20
Vt_pid_std_wb_l_hc     = 0.6
Vt_pid_std_wb_l_hl     = 100
Vt_pid_long_0_h_pb     = 1.5
Vt_pid_long_0_h_ti     = 30
Vt_pid_long_0_h_td     = 5
Vt_pid_long_0_h_chl    = 9.9
Vt_pid_long_0_h_chb    = 2.3
Vt_pid_long_0_h_hc     = 2.5
Vt_pid_long_0_h_hl     = 70
Vt_pid_long_0_m_pb     = 1.5
Vt_pid_long_0_m_ti     = 30
Vt_pid_long_0_m_td     = 5
Vt_pid_long_0_m_chl    = 9.9
Vt_pid_long_0_m_chb    = 2.3
Vt_pid_long_0_m_hc     = 2.5
Vt_pid_long_0_m_hl     = 70
Vt_pid_long_40_h_pb    = 1.5
Vt_pid_long_40_h_ti    = 30
Vt_pid_long_40_h_td    = 5
Vt_pid_long_40_h_chl   = 9.9
Vt_pid_long_40_h_chb   = 2.3
Vt_pid_long_40_h_hc    = 2.5
Vt_pid_long_40_h_hl    = 70
Vt_pid_long_40_m_pb    = 1.5
Vt_pid_long_40_m_ti    = 30
Vt_pid_long_40_m_td    = 5
Vt_pid_long_40_m_chl   = 9.9
Vt_pid_long_40_m_chb   = 2.3
Vt_pid_long_40_m_hc    = 2.5
Vt_pid_long_40_m_hl    = 70
Sample_action          = LOADED
Sample_state           = LOAD
Sample_status          = LOADED
Changer_sample         = 1
N2_level               = 89[%]
He_level               = 76[%]
Autoshim_mode          = AUTOSHIM OFF
Autoshim_delay         = 3.6[hr]
Autoshim_track         = AUTOSHIM OFF
Shim_max_recall        = MAX FOUND
Shim_names             = 8SHM_20
Shim_z0                = -15.937[mHz]
Shim_z1                = -98.67[Hz]
Shim_z2                = -287.04[Hz]
Shim_z3                = -212.07[Hz]
Shim_z4                = 15.54[Hz]
Shim_z5                = 10.5[Hz]
Shim_z6                = 2.96[Hz]
Shim_x7                = 0[Hz]
Shim_z8                = 0[Hz]
Shim_x                 = -202[Hz]
Shim_xz                = 54.5[Hz]
Shim_xz2               = -346.5[Hz]
Shim_xz3               = -9.1[Hz]
Shim_xz4               = 4.5[Hz]
Shim_xz5               = 9.8[Hz]
Shim_x2                = 171.2[Hz]
Shim_x2z               = 113.6[Hz]
Shim_x2z2              = 52.8[Hz]
Shim_x2z3              = 19.1[Hz]
Shim_x2z4              = -0.8[Hz]
Shim_x3                = 127.3[Hz]
Shim_x3z               = -55[Hz]
Shim_x3z2              = -28[Hz]
Shim_x3z3              = 3.5[Hz]
Shim_x4                = -65.5[Hz]
Shim_x4z               = 49[Hz]
Shim_x4z2              = -4[Hz]
Shim_y                 = 118.5[Hz]
Shim_yz                = 71.2[Hz]
Shim_yz2               = 830.1[Hz]
Shim_yz3               = 0.7[Hz]
Shim_yz4               = -17[Hz]
Shim_yz5               = -8.3[Hz]
Shim_y2                = 382.4[Hz]
Shim_y2z               = -225.9[Hz]
Shim_y2z2              = 7.8[Hz]
Shim_y2z3              = 12[Hz]
Shim_y2z4              = 0.4[Hz]
Shim_y3                = -365.9[Hz]
Shim_y3z               = 131.4[Hz]
Shim_y3z2              = 7.5[Hz]
Shim_y3z3              = -5.4[Hz]
Shim_y4                = -59[Hz]
Shim_y4z               = 11.8[Hz]
Shim_y4z2              = 5.5[Hz]
Num_scans              = 0
Iterations             = 0
End_time               = 24-AUG-2007 10:43
Local_time             = 24-AUG-2007 10:43
Probe_atn              = 0
Probe_tune             = 0
Probe_match            = 2625
Probe_coarse           = NONE
Probe_id               = 3204
Lf_tune_dial           = 0
Lf_match_dial          = 0
Hf_tune_dial           = 0
Hf_match_dial          = 0
Experiment             = single_pulse.exp
Transition_ratio       = 0.9
Pass_ripple            = 10[mdB]
Stop_ripple            = 60[dB]
Orders                 =
Factors                =
Probe_recovery         = 0[us]
X_acq_time             = 4.3646976[s]
X_angle                = 45[deg]
X_90_width             = 7.4[us]
X_pulse                = 3.7[us]
Dead_time              = 0[us]
Delay                  = 0[us]
Phase_preset           = 2[us]
Relaxation_delay       = 4[s]
Initial_wait           = 1[s]
```


JEOL
OMOM
O
O
O
Bu^tMe_2SiO
$PhMe_2Si$
12b
X : parts per Million : 13C
(Hz/cm)

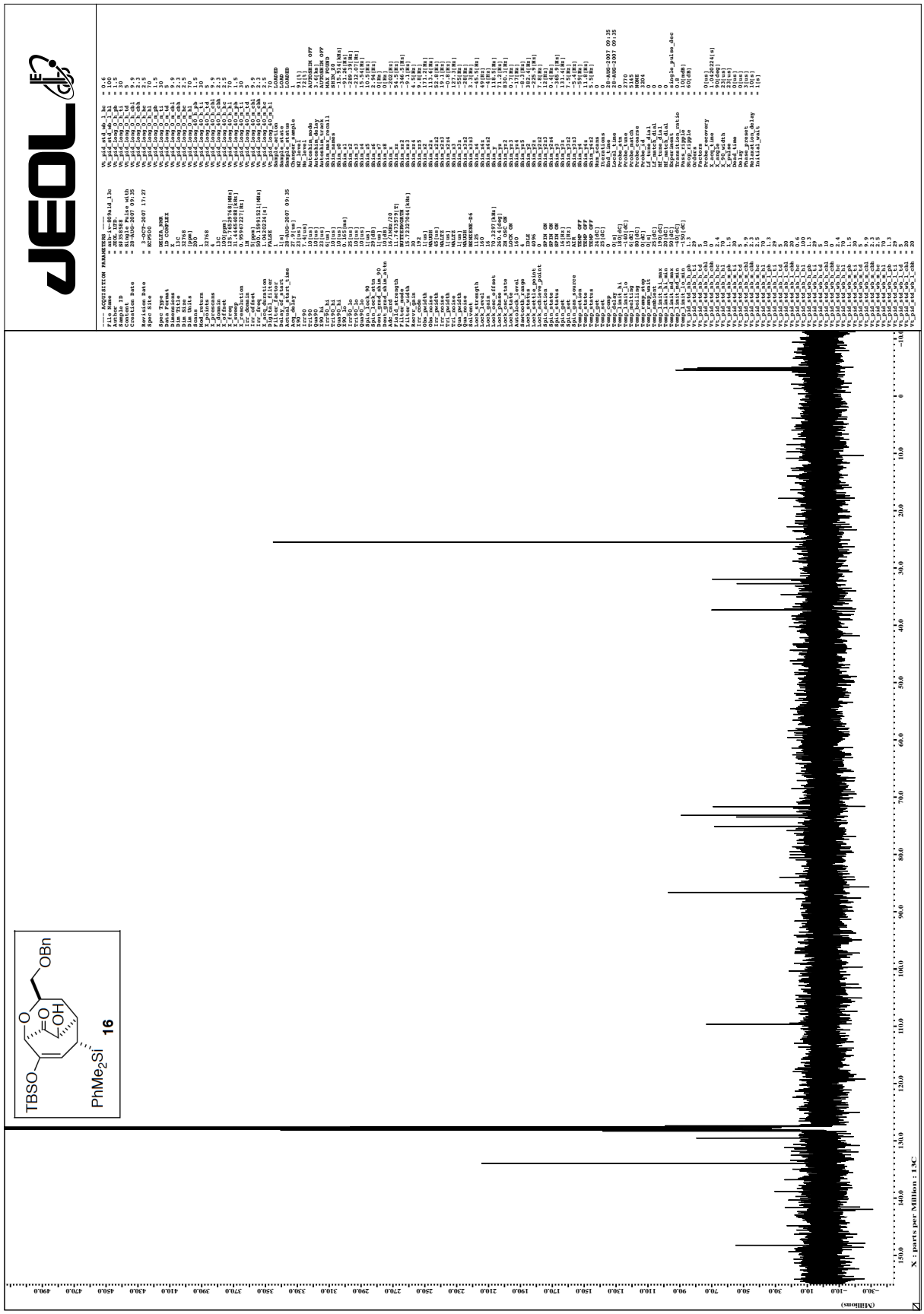


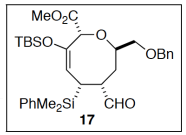
JEOL

```
=== ACQUISITION PARAMETERS ===
File Name          = ash-iv-809a.4
Author             = JEOL LTD.
Sample ID          = 1
Content            = ASH-IV-809A
Creation Date      = 28-AUG-2007 08:31

Revision Date      =  3-OCT-2007 17:15
Spec Site          = ECP500

Spec Type          = DELTA_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 1H
Dim Size           = 32768
Dim Units          = [ppm]
Scans              = 4
Mod_return         = 1
X_points           = 32768
X_prescans         = 0
X_domain           = 1H
X_offset           = 5[ppm]
X_freq             = 500.15991521[MHz]
X_sweep            = 7.50750751[kHz]
X_resolution       = 0.22911095[Hz]
X_acq_duration     = 4.3646976[s]
Digital_filter     = FALSE
Filter_factor      = 1
Delay_of_start     = 1[s]
Actual_start_time  = 28-AUG-2007 08:30
Acq_delay          = 0.1314[ms]
X90                = 7.4[us]
Irr90              = 10[us]
Tri90              = 10[us]
Qua90              = 10[us]
X90_hi             = 6[us]
Irr90_hi           = 10[us]
Tri90_hi           = 10[us]
Qua90_hi           = 10[us]
X90_lo             = 25[us]
Irr90_lo           = 50[us]
Tri90_lo           = 10[us]
Qua90_lo           = 10[us]
Spin_lock_90       = 1[us]
Spin_lock_attn     = 29[dB]
Deut_grad_shim_90  = 1[us]
Deut_grad_shim_attn = 10[dB]
Adc_card           = 16/18Hz/20
Field_strength     = 11.7473579[T]
Filter_mode        = BUTTERWORTH
Filter_width       = 3.75375375[kHz]
Recvr_gain         = 13
Irr_code           = 192
Obs_pwidth         = 1[us]
Obs_noise          = WALTZ16
Irr_pwidth         = 0.165[ms]
Irr_noise          = WALTZ
Tri_pwidth         = 1[us]
Tri_noise          = WALTZ
Qua_pwidth         = 1[us]
Qua_noise          = WALTZ
Solvent            = BENZENE-D6
Lock_strength      = 1798
Lock_level         = 160
Lock_gain          = 16
Lock_osc_offset    = 70.3297[kHz]
Lock_phase         = 260.4[deg]
Lock_osc_state     = 2H OSC ON
Lock_state         = LOCK ON
Autolock_level     = 160
Sawtooth_range     = 4
Lock_status        = IDLE
Lock_settle_point  = 4096
Lock_achieve_point = 0
Spin_action        = SPIN ON
Spin_state         = SPIN ON
Spin_status        = SPIN ON
Spin_get           = 15[Hz]
Spin_set           = 15[Hz]
Spin_gas_source    = AIR
Temp_action        = TEMP OFF
Temp_state         = TEMP OFF
Temp_status        = TEMP OFF
Temp_get           = 22.4[dC]
Temp_set           = 25[dC]
Temp_comp          = 0
Temp_delay         = 0[s]
Temp_limit_hi      = 180[dC]
Temp_limit_lo      = -140[dC]
Temp_melting       = 6[dC]
Temp_boiling       = 80[dC]
Temp_ramp_step     = 0[dC]
Temp_ramp_wait     = 0[s]
Temp_ambient       = 25[dC]
Temp_limit_hi_max  = 190[dC]
Temp_limit_hi_min  = 20[dC]
Temp_limit_md_max  = 50[dC]
Temp_limit_md_min  = -40[dC]
Temp_limit_lo_min  = -150[dC]
Vt_pid_std_nb_h_pb = 1.3
Vt_pid_std_nb_h_ti = 29
Vt_pid_std_nb_h_td = 5
Vt_pid_std_nb_h_chl = 10
Vt_pid_std_nb_h_chh = 0
Vt_pid_std_nb_h_hc = 2.4
Vt_pid_std_nb_h_hl = 70
Vt_pid_std_nb_m_pb = 1.5
Vt_pid_std_nb_m_ti = 30
Vt_pid_std_nb_m_td = 5
Vt_pid_std_nb_m_chl = 9.9
Vt_pid_std_nb_m_chh = 2.3
Vt_pid_std_nb_m_hc = 2.5
Vt_pid_std_nb_m_hl = 70
Vt_pid_std_nb_l_pb = 1.3
Vt_pid_std_nb_l_ti = 29
Vt_pid_std_nb_l_td = 5
Vt_pid_std_nb_l_chl = 20
Vt_pid_std_nb_l_chh = 20
Vt_pid_std_nb_l_hc = 0.6
Vt_pid_std_nb_l_hl = 100
Vt_pid_std_wb_h_pb = 1.3
Vt_pid_std_wb_h_ti = 29
Vt_pid_std_wb_h_td = 5
Vt_pid_std_wb_h_chl = 10
Vt_pid_std_wb_h_chh = 0
Vt_pid_std_wb_h_hc = 2.4
Vt_pid_std_wb_h_hl = 70
Vt_pid_std_wb_m_pb = 1.5
Vt_pid_std_wb_m_ti = 30
Vt_pid_std_wb_m_td = 5
Vt_pid_std_wb_m_chl = 9.9
Vt_pid_std_wb_m_chh = 2.3
Vt_pid_std_wb_m_hc = 2.5
Vt_pid_std_wb_m_hl = 70
Vt_pid_std_wb_l_pb = 1.3
Vt_pid_std_wb_l_ti = 29
Vt_pid_std_wb_l_td = 5
Vt_pid_std_wb_l_chl = 20
Vt_pid_std_wb_l_chh = 20
Vt_pid_std_wb_l_hc = 0.6
Vt_pid_std_wb_l_hl = 100
Vt_pid_long_0_h_pb = 1.5
Vt_pid_long_0_h_ti = 30
Vt_pid_long_0_h_td = 5
Vt_pid_long_0_h_chl = 9.9
Vt_pid_long_0_h_chh = 2.3
Vt_pid_long_0_h_hc = 2.5
Vt_pid_long_0_h_hl = 70
Vt_pid_long_0_m_pb = 1.5
Vt_pid_long_0_m_ti = 30
Vt_pid_long_0_m_td = 5
Vt_pid_long_0_m_chl = 9.9
Vt_pid_long_0_m_chh = 2.3
Vt_pid_long_0_m_hc = 2.5
Vt_pid_long_0_m_hl = 70
Vt_pid_long_40_h_pb = 1.5
Vt_pid_long_40_h_ti = 30
Vt_pid_long_40_h_td = 5
Vt_pid_long_40_h_chl = 9.9
Vt_pid_long_40_h_chh = 2.3
Vt_pid_long_40_h_hc = 2.5
Vt_pid_long_40_h_hl = 70
Sample_action      = LOADED
Sample_state       = LOAD
Sample_status      = LOADED
Changer_sample     = 1
N2_level           = 92[%]
He_level           = 72[%]
Autoshim_mode      = AUTOSHIM OFF
Autoshim_delay     = 3.6[hs]
Autoshim_track     = AUTOSHIM OFF
Shim_max_recall    = MAX FOUND
Shim_names         = SHIM 20
Shim_z0            = -15.914[mHz]
Shim_z1            = -91.26[Hz]
Shim_z2            = -289.39[Hz]
Shim_z3            = -212.07[Hz]
Shim_z4            = 15.54[Hz]
Shim_z5            = 10.5[Hz]
Shim_z6            = 2.96[Hz]
Shim_z7            = 0[Hz]
Shim_z8            = 0[Hz]
Shim_x             = -202[Hz]
Shim_xz            = 54.5[Hz]
Shim_xz2           = -346.5[Hz]
Shim_xz3           = -9.1[Hz]
Shim_xz4           = 4.5[Hz]
Shim_xz5           = 9.8[Hz]
Shim_x2            = 171.2[Hz]
Shim_x2z           = 113.6[Hz]
Shim_x2z2          = 52.8[Hz]
Shim_x2z3          = 19.1[Hz]
Shim_x2z4          = -0.8[Hz]
Shim_x3            = 127.3[Hz]
Shim_x3z           = -55[Hz]
Shim_x3z2          = -28[Hz]
Shim_x3z3          = 3.5[Hz]
Shim_x4            = -65.5[Hz]
Shim_x4z           = 49[Hz]
Shim_x4z2          = -4[Hz]
Shim_y             = 118.5[Hz]
Shim_yz            = 71.2[Hz]
Shim_yz2           = 830.1[Hz]
Shim_yz3           = 0.7[Hz]
Shim_yz4           = -17[Hz]
Shim_yz5           = -8.3[Hz]
Shim_y2            = 382.4[Hz]
Shim_y2z           = -225.9[Hz]
Shim_y2z2          = 7.8[Hz]
Shim_y2z3          = 12[Hz]
Shim_y2z4          = 0.4[Hz]
Shim_y3            = -365.9[Hz]
Shim_y3z           = 131.4[Hz]
Shim_y3z2          = 7.5[Hz]
Shim_y3z3          = -5.4[Hz]
Shim_y4            = -59[Hz]
Shim_y4z           = 11.8[Hz]
Shim_y4z2          = 5.5[Hz]
Num_scans          = 0
Iterations         = 0
End_time           = 28-AUG-2007 08:31
Local_time         = 28-AUG-2007 08:31
Probe_atn          = 0
Probe_tune         = 0
Probe_match        = 2625
Probe_coarse       = NONE
Probe_id           = 3204
Lf_tune_dial       = 0
Lf_match_dial      = 0
Hf_tune_dial       = 0
Hf_match_dial      = 0
Experiment         = single_pulse.exp
Transition_ratio   = 0.9
Pass_ripple        = 10[mdB]
Stop_ripple        = 60[dB]
Orders             =
Factors            =
Probe_recovery     = 0[us]
X_acq_time         = 4.3646976[s]
X_angle            = 45[deg]
X_90_width         = 7.4[us]
X_pulse            = 3.7[us]
Dead_time          = 0[us]
Delay              = 0[us]
Phase_preset       = 2[us]
Relaxation_delay   = 4[s]
Initial_wait       = 1[s]
```


TBSO
OBn
OH
PhMe2Si
16
JEOL
X : parts per Million : 13C



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JEOL

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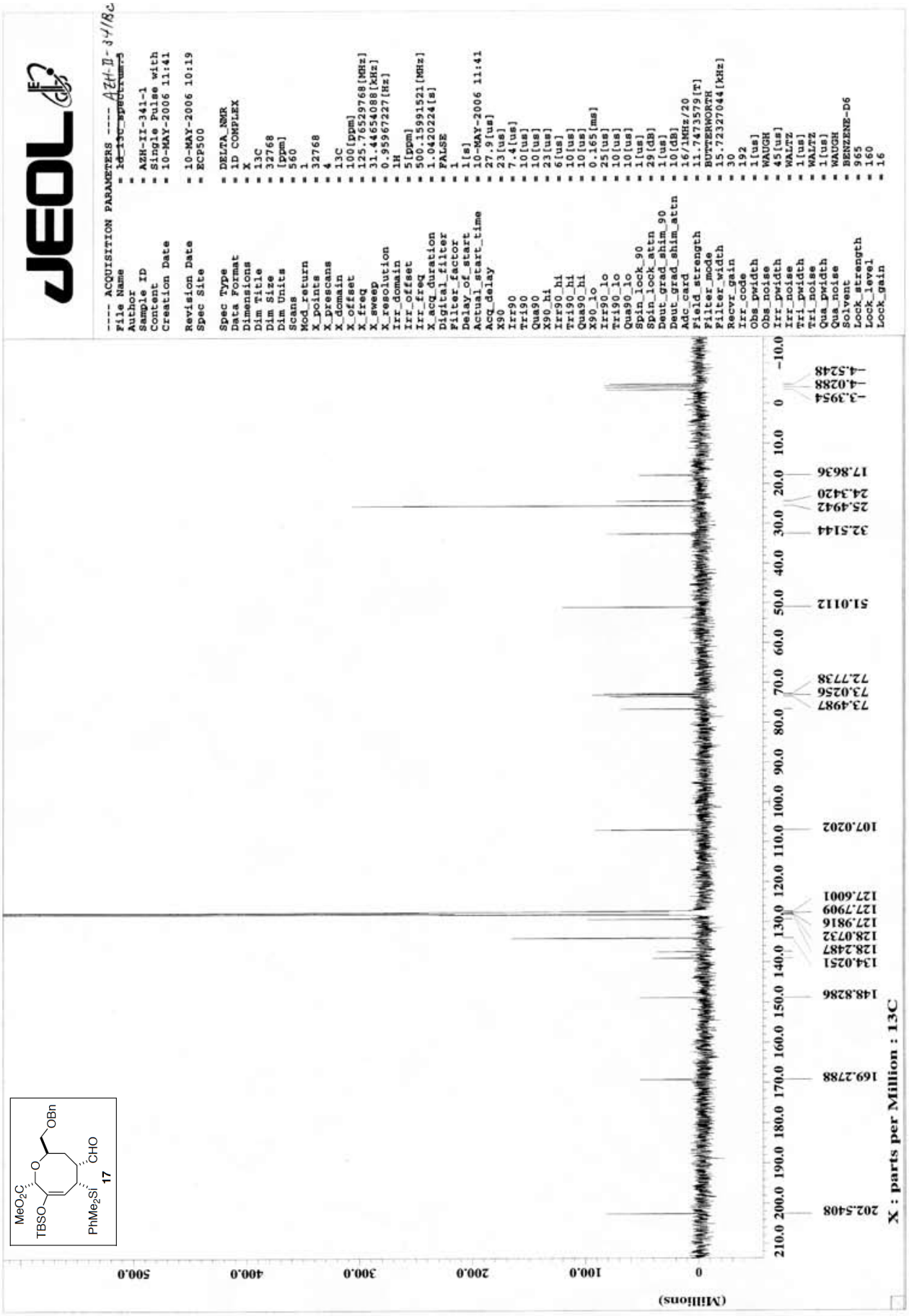
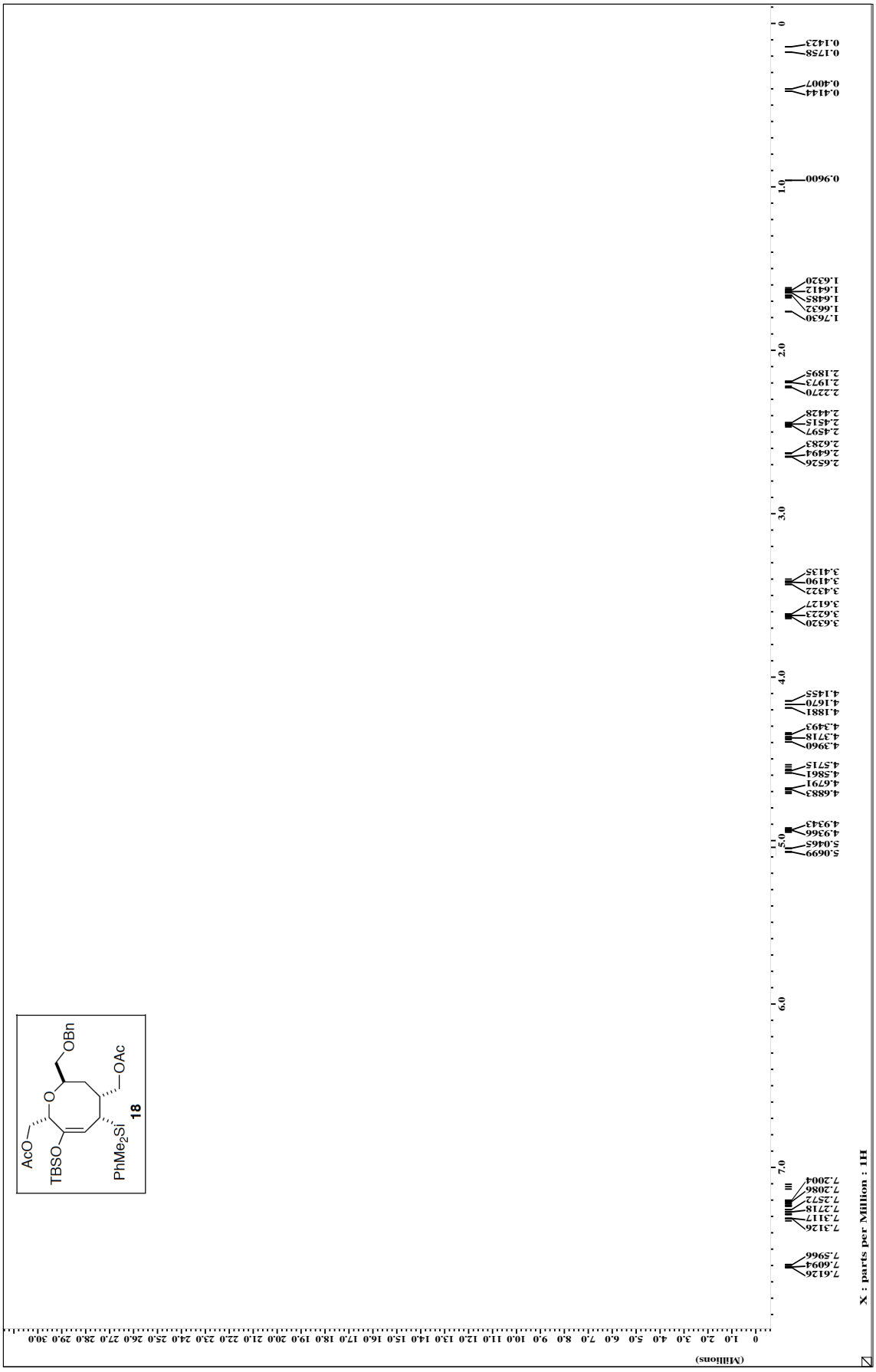
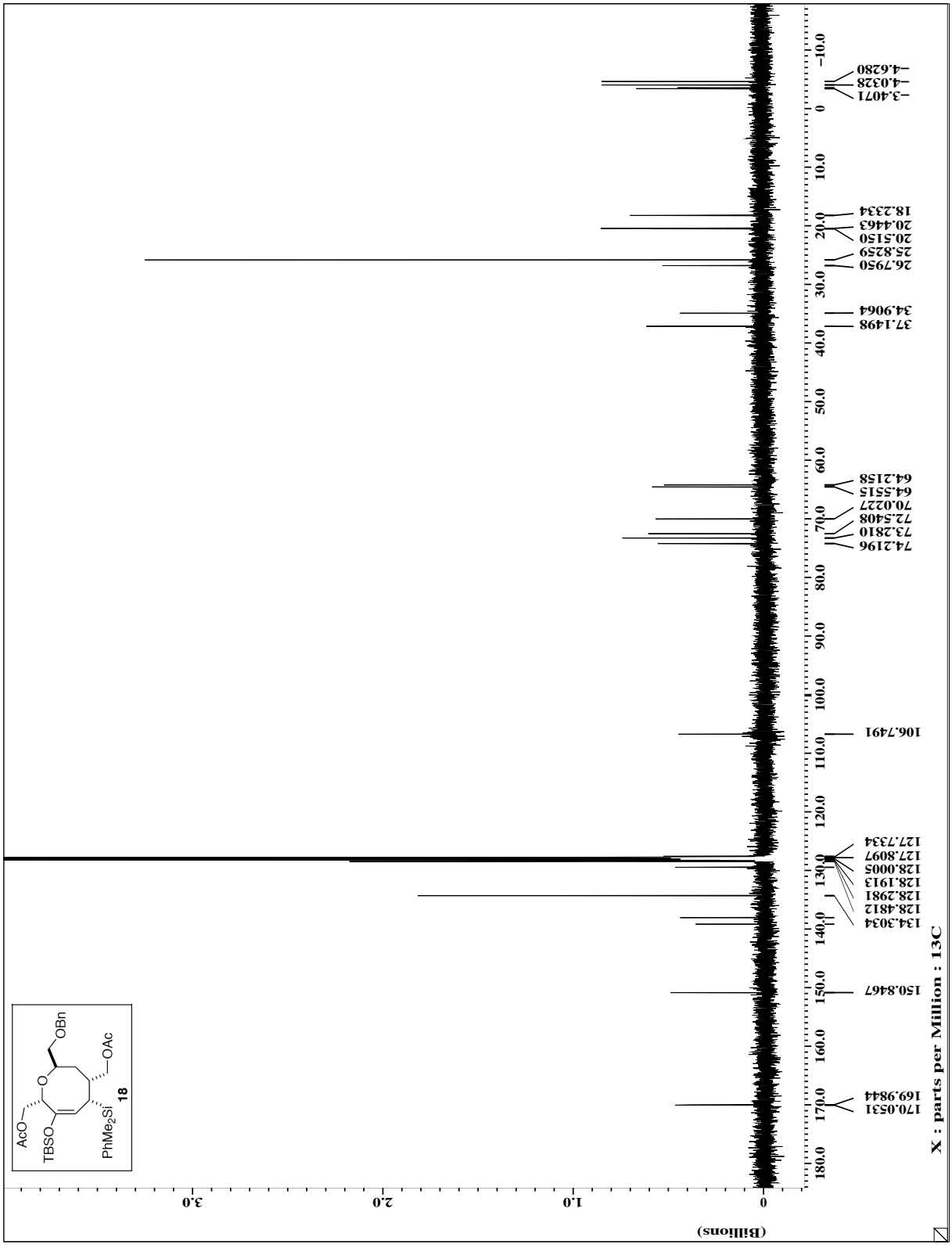
--- ACQUISITION PARAMETERS ---
File Name              = ash-iv-806b.3
Author                 = JEOL LTD.
Sample ID              = 1
Content                = ASH-IV-806B
Creation Date          = 20-AUG-2007 18:26

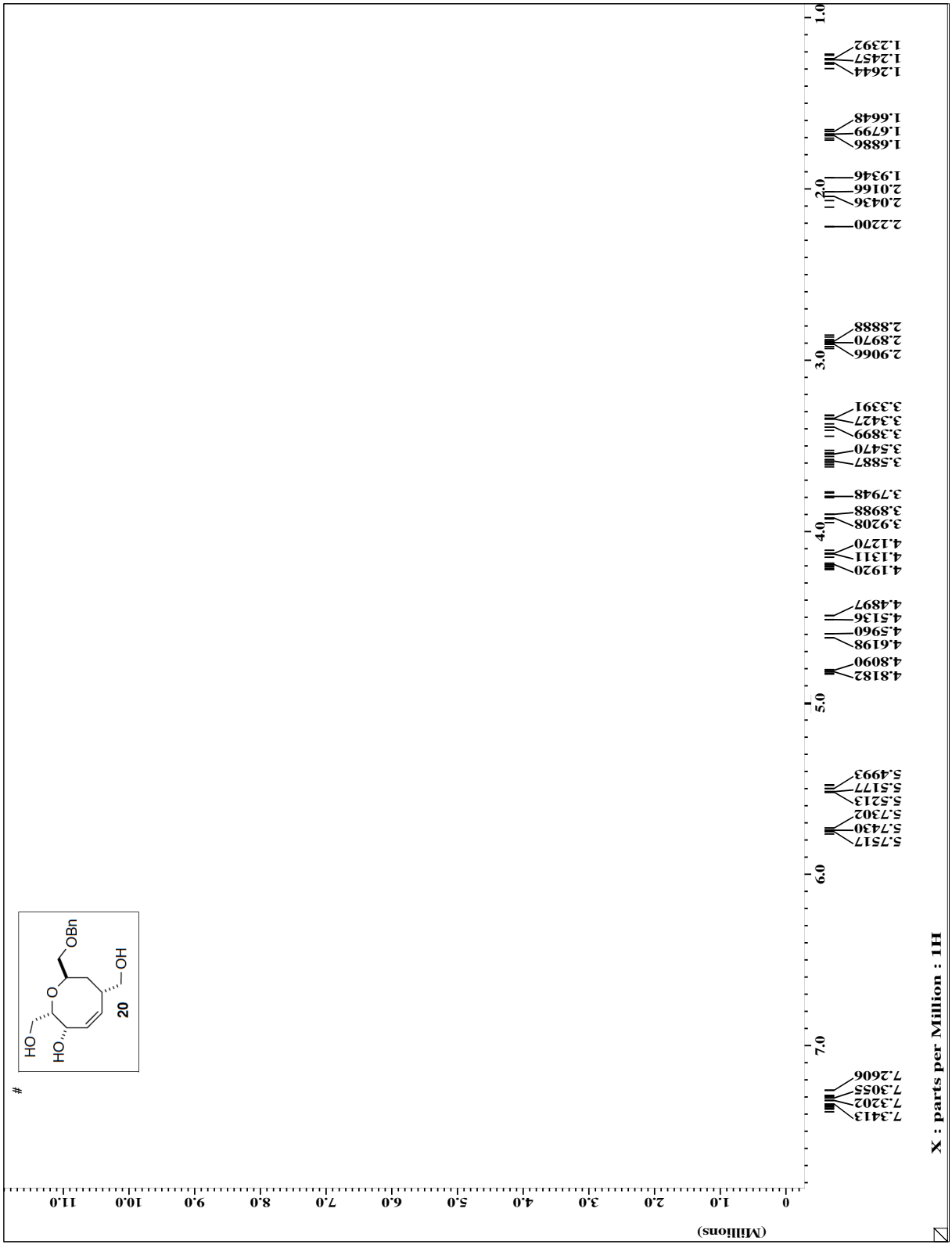
Revision Date          =  3-OCT-2007 16:57
Spec Site              = ECP500

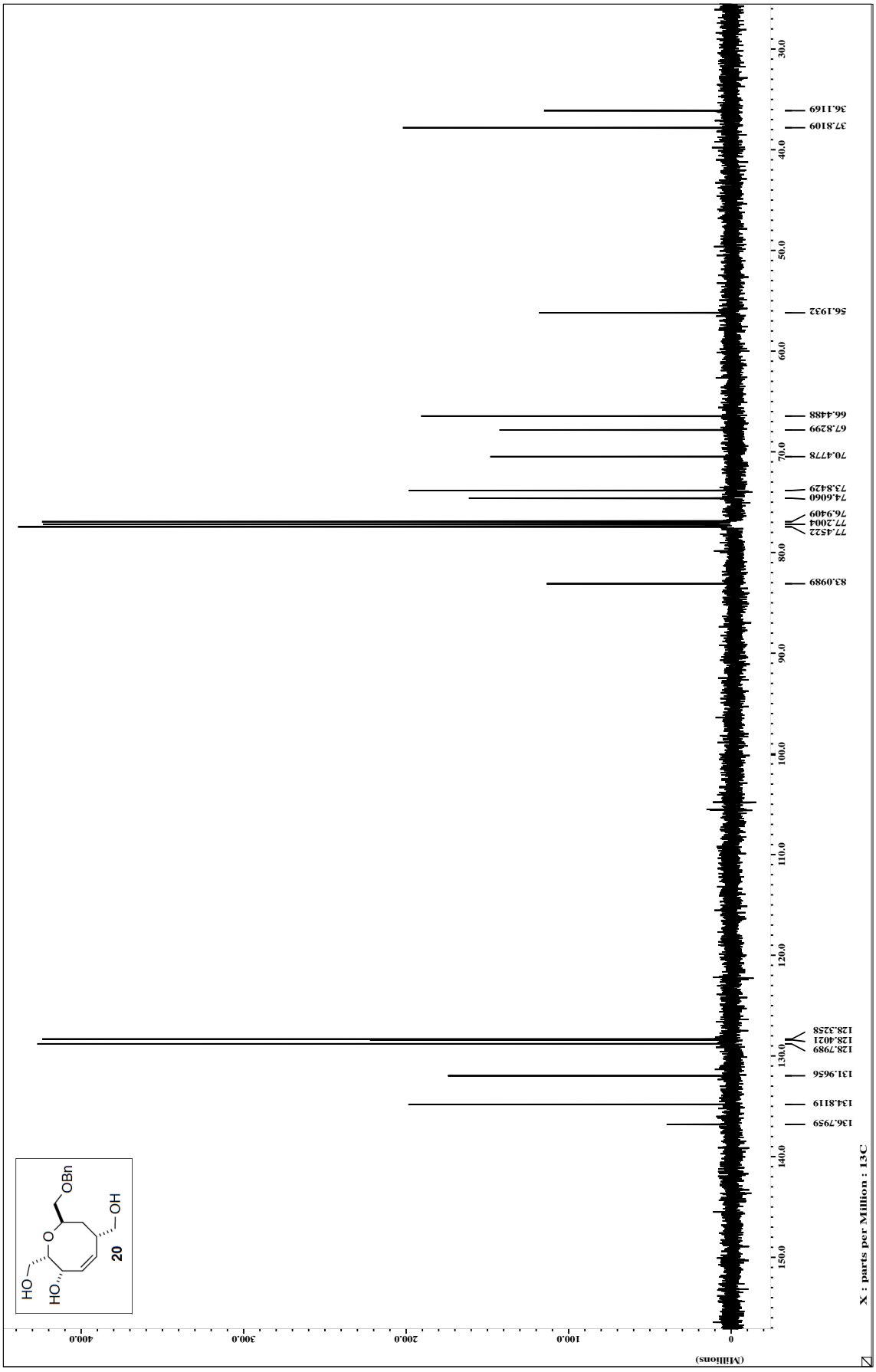
Spec Type              = DELTA_NMR
Data Format            = 1D COMPLEX
Dimensions             = X
Dim Title              = 1H
Dim Size               = 32768
Dim Units              = [ppm]
Scans                  = 4
Mod_return             = 1
X_points               = 32768
X_prescans             = 0
X_domain               = 1H
X_offset               = 5[ppm]
X_freq                 = 500.15991521[MHz]
X_sweep                = 7.50750751[kHz]
X_resolution           = 0.22911095[Hz]
X_acq_duration         = 4.3646976[s]
Digital_filter         = FALSE
Filter_factor          = 1
Delay_of_start         = 1[s]
Actual_start_time      = 20-AUG-2007 18:26
Acq_delay              = 0.1314[ms]
X90                    = 7.4[us]
Irr90                  = 10[us]
Tri90                  = 10[us]
Qua90                  = 10[us]
X90_hi                 = 6[us]
Irr90_hi               = 10[us]
Tri90_hi               = 10[us]
Qua90_hi               = 10[us]
X90_lo                 = 25[us]
Irr90_lo               = 50[us]
Tri90_lo               = 10[us]
Qua90_lo               = 10[us]
Spin_lock_90           = 1[us]
Spin_lock_attn         = 29[dB]
Deut_grad_shim_90      = 1[us]
Deut_grad_shim_attn    = 10[dB]
Adc_card               = 16/1MHz/20
Field_strength         = 11.7473579[T]
Filter_mode            = BUTTERWORTH
Filter_width           = 3.75375375[kHz]
Recvr_gain             = 22
Irr_code               = 192
Obs_pwidth             = 1[us]
Obs_noise              = WALTZ16
Irr_pwidth             = 1[us]
Irr_noise              = WALTZ16
Tri_pwidth             = 1[us]
Tri_noise              = WALTZ16
Qua_pwidth             = 1[us]
Qua_noise              = WALTZ16
Solvent                = BENZENE-D6
Lock_strength          = 1253
Lock_level             = 160
Lock_gain              = 15
Lock_osc_offset        = 70.3297[kHz]
Lock_phase             = 260.4[deg]
Lock_osc_state         = 2H OSC ON
Lock_state             = LOCK ON
Autolock_level         = 160
Sawtooth_range         = 4
Lock_status            = IDLE
Lock_settle_point      = 4096
Lock_achieve_point     = 0
Spin_action            = SPIN ON
Spin_state             = SPIN ON
Spin_status            = SPIN ON
Spin_get               = 17[Hz]
Spin_set               = 15[Hz]
Spin_gas_source        = AIR
Temp_action            = TEMP OFF
Temp_state             = TEMP OFF
Temp_status            = TEMP OFF
Temp_get               = 23.8[dC]
Temp_set               = 25[dC]
Temp_comp              = 0
Temp_delay             = 0[s]
Temp_limit_hi          = 180[dC]
Temp_limit_lo          = -140[dC]
Temp_melting           = 6[dC]
Temp_boiling           = 80[dC]
Temp_ramp_step         = 0[dC]
Temp_ramp_wait         = 0[s]
Temp_ambient           = 25[dC]
Temp_limit_hi_max      = 190[dC]
Temp_limit_hi_min      = 20[dC]
Temp_limit_md_max      = 50[dC]
Temp_limit_md_min      = -40[dC]
Temp_limit_lo_min      = -150[dC]
Vt_pid_std_nb_h_pb     = 1.3
Vt_pid_std_nb_h_ti     = 29
Vt_pid_std_nb_h_td     = 5
Vt_pid_std_nb_h_chl    = 10
Vt_pid_std_nb_h_chb    = 0
Vt_pid_std_nb_h_hc     = 2.4
Vt_pid_std_nb_h_hl     = 70
Vt_pid_std_nb_m_pb     = 1.5
Vt_pid_std_nb_m_ti     = 30
Vt_pid_std_nb_m_td     = 5
Vt_pid_std_nb_m_chl    = 9.9
Vt_pid_std_nb_m_chb    = 2.3
Vt_pid_std_nb_m_hc     = 2.5
Vt_pid_std_nb_m_hl     = 70
Vt_pid_std_nb_l_pb     = 1.3
Vt_pid_std_nb_l_ti     = 29
Vt_pid_std_nb_l_td     = 5
Vt_pid_std_nb_l_chl    = 20
Vt_pid_std_nb_l_chb    = 20
Vt_pid_std_nb_l_hc     = 0.6
Vt_pid_std_nb_l_hl     = 100
Vt_pid_std_wb_h_pb     = 1.3
Vt_pid_std_wb_h_ti     = 29
Vt_pid_std_wb_h_td     = 5
Vt_pid_std_wb_h_chl    = 10
Vt_pid_std_wb_h_chb    = 0
Vt_pid_std_wb_h_hc     = 2.4
Vt_pid_std_wb_h_hl     = 70
Vt_pid_std_wb_m_pb     = 1.5
Vt_pid_std_wb_m_ti     = 30
Vt_pid_std_wb_m_td     = 5
Vt_pid_std_wb_m_chl    = 9.9
Vt_pid_std_wb_m_chb    = 2.3
Vt_pid_std_wb_m_hc     = 2.5
Vt_pid_std_wb_m_hl     = 70
Vt_pid_std_wb_l_pb     = 1.3
Vt_pid_std_wb_l_ti     = 29
Vt_pid_std_wb_l_td     = 5
Vt_pid_std_wb_l_chl    = 20
Vt_pid_std_wb_l_chb    = 20
Vt_pid_std_wb_l_hc     = 0.6
Vt_pid_std_wb_l_hl     = 100
Vt_pid_long_0_h_pb     = 1.5
Vt_pid_long_0_h_ti     = 30
Vt_pid_long_0_h_td     = 5
Vt_pid_long_0_h_chl    = 9.9
Vt_pid_long_0_h_chb    = 2.3
Vt_pid_long_0_h_hc     = 2.5
Vt_pid_long_0_h_hl     = 70
Vt_pid_long_0_m_pb     = 1.5
Vt_pid_long_0_m_ti     = 30
Vt_pid_long_0_m_td     = 5
Vt_pid_long_0_m_chl    = 9.9
Vt_pid_long_0_m_chb    = 2.3
Vt_pid_long_0_m_hc     = 2.5
Vt_pid_long_0_m_hl     = 70
Vt_pid_long_40_h_pb    = 1.5
Vt_pid_long_40_h_ti    = 30
Vt_pid_long_40_h_td    = 5
Vt_pid_long_40_h_chl   = 9.9
Vt_pid_long_40_h_chb   = 2.3
Vt_pid_long_40_h_hc    = 2.5
Vt_pid_long_40_h_hl    = 70
Vt_pid_long_40_m_pb    = 1.5
Vt_pid_long_40_m_ti    = 30
Vt_pid_long_40_m_td    = 5
Vt_pid_long_40_m_chl   = 9.9
Vt_pid_long_40_m_chb   = 2.3
Vt_pid_long_40_m_hc    = 2.5
Vt_pid_long_40_m_hl    = 70
Sample_action          = LOADED
Sample_state           = LOAD
Sample_status          = LOADED
Changer_sample         = 14
N2_level               = 84[%]
He_level               = 75[%]
Autoshim_mode          = AUTOSHIM OFF
Autoshim_delay         = 3.6[hr]
Autoshim_track         = AUTOSHIM OFF
Shim_max_recall        = MAX FOUND
Shim_names             = SHIM 20
Shim_z0                = -15.971[kHz]
Shim_z1                = -96.47[Hz]
Shim_z2                = -285.64[Hz]
Shim_z3                = -212.17[Hz]
Shim_z4                = 15.44[Hz]
Shim_z5                = 10.5[Hz]
Shim_z6                = 2.96[Hz]
Shim_z7                = 0[Hz]
Shim_z8                = 0[Hz]
Shim_x                 = -202[Hz]
Shim_xz                = 54.5[Hz]
Shim_xz2               = -346.5[Hz]
Shim_xz3               = -9.1[Hz]
Shim_xz4               = 4.5[Hz]
Shim_xz5               = 9.8[Hz]
Shim_x2                = 171.2[Hz]
Shim_x2z               = 113.6[Hz]
Shim_x2z2              = 52.8[Hz]
Shim_x2z3              = 19.1[Hz]
Shim_x2z4              = -0.8[Hz]
Shim_x3                = 127.3[Hz]
Shim_x3z               = -55[Hz]
Shim_x3z2              = -28[Hz]
Shim_x3z3              = 3.3[Hz]
Shim_x4                = -65.5[Hz]
Shim_x4z               = 49[Hz]
Shim_x4z2              = -4[Hz]
Shim_y                 = 118.5[Hz]
Shim_yz                = 71.2[Hz]
Shim_yz2               = 830.1[Hz]
Shim_yz3               = 0.7[Hz]
Shim_yz4               = -17[Hz]
Shim_yz5               = -8.3[Hz]
Shim_y2                = 382.4[Hz]
Shim_y2z               = -225.9[Hz]
Shim_y2z2              = 7.8[Hz]
Shim_y2z3              = 12[Hz]
Shim_y2z4              = 0.4[Hz]
Shim_y3                = -365.9[Hz]
Shim_y3z               = 131.4[Hz]
Shim_y3z2              = 7.5[Hz]
Shim_y3z3              = -5.4[Hz]
Shim_y4                = -59[Hz]
Shim_y4z               = 11.8[Hz]
Shim_y4z2              = 5.5[Hz]
Num_scans              = 0
Iterations             = 0
End_time               = 20-AUG-2007 18:26
Local_time             = 20-AUG-2007 18:26
Probe_atn              = 0
Probe_tune             = 0
Probe_match            = 2625
Probe_coarse           = A
Probe_id               = 3204
Lf_tune_dial           = 0
Lf_match_dial          = 0
Hf_tune_dial           = 0
Hf_match_dial          = 0
Experiment             = single_pulse.exp
Transition_ratio       = 0.9
Pass_ripple            = 10[mdB]
Stop_ripple            = 60[dB]
Orders                 =
Factors                =
Probe_recovery         = 0[us]
X_acq_time             = 4.3646976[s]
X_angle                = 45[deg]
X_90_width             = 7.4[us]
X_pulse                = 3.7[us]
Dead_time              = 0[us]
Delay                  = 0[us]
Phase_preset           = 2[us]
Relaxation_delay       = 4[s]
Initial_wait           = 1[s]
```

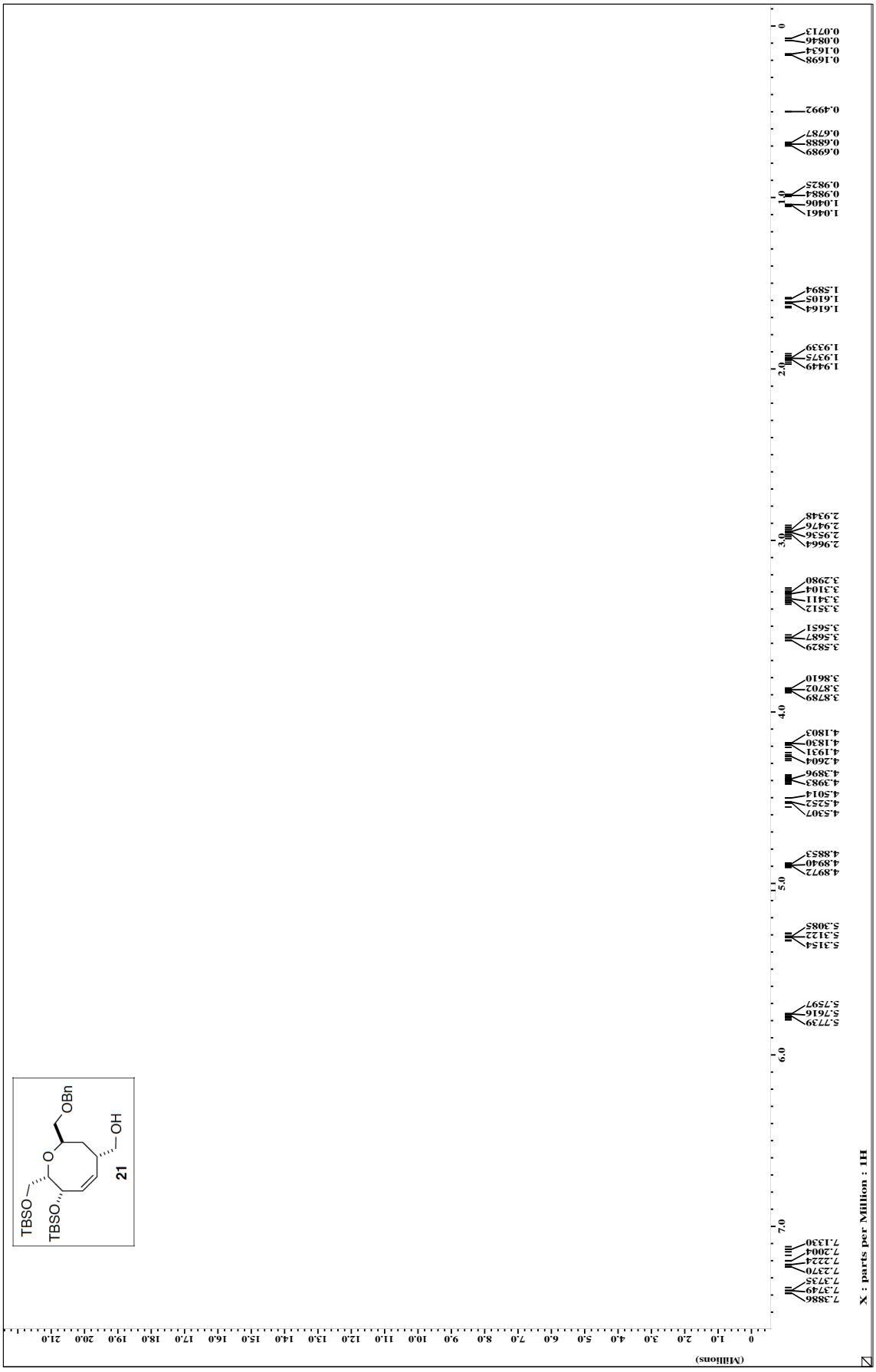

JEOL
---- ACQUISTION PARAMETERS ---- AZH-II-34/8c
File Name = 1d_13c_spectrum.3
Author =
Sample ID = AZH-II-341-1
Content = Single Pulse with
Creation Date = 10-MAY-2006 11:41
Revision Date = 10-MAY-2006 10:19
Spec Site = ECP500
Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Dim Title = 13C
Dim Size = 32768
Dim Units = [ppm]
Scans = 560
Mod_return = 1
X_points = 32768
X_prescans = 4
X_domain = 13C
X_offset = 100[ppm]
X_freq = 125.76529768[MHz]
X_sweep = 31.44654088[kHz]
X_resolution = 0.95967227[Hz]
Irr_domain = 1H
Irr_offset = 5[ppm]
Irr_freq = 500.15991521[MHz]
X_acq_duration = 1.04202224[s]
Digital_filter = FALSE
Filter_factor = 1
Delay_of_start = 1[s]
Actual_start_time = 10-MAY-2006 11:41
Acq_delay = 27.9[us]
X90 = 23[us]
Irr90 = 7.4[us]
Tri90 = 10[us]
Qua90 = 10[us]
X90_hi = 23[us]
Irr90_hi = 6[us]
Tri90_hi = 10[us]
Qua90_hi = 10[us]
X90_lo = 0.165[ms]
Irr90_lo = 25[us]
Tri90_lo = 10[us]
Qua90_lo = 10[us]
Spin_lock_90 = 1[us]
Spin_lock_attn = 29[dB]
Deut_grad_shim_90 = 1[us]
Deut_grad_shim_attn = 10[dB]
Adc_card = 16/1MHz/20
Field_strength = 11.7473579[T]
Filter_mode = BUTTERWORTH
Filter_width = 15.723270441[KHz]
Recvr_gain = 30
Irr_code = 192
Obs_pwidth = 1[us]
Obs_noise = WAUGH
Irr_pwidth = 45[us]
Irr_noise = WALTZ
Tri_pwidth = 1[us]
Tri_noise = WALTZ
Qua_pwidth = 1[us]
Qua_noise = WAUGH
Solvent = BENZENE-D6
Lock_strength = 965
Lock_level = 160
Lock_gain = 16
-3.3954
-4.0288
-4.5248
17.8636
24.3420
25.4942
32.5144
51.0112
72.7738
73.0256
73.4987
107.0202
127.6001
127.7909
127.9816
128.0732
128.2487
134.0251
148.8286
169.2788
202.5408
X : parts per Million : 13C
(Millions)
MeO2C
TBSO
OBn
PhMe2Si
CHO
17

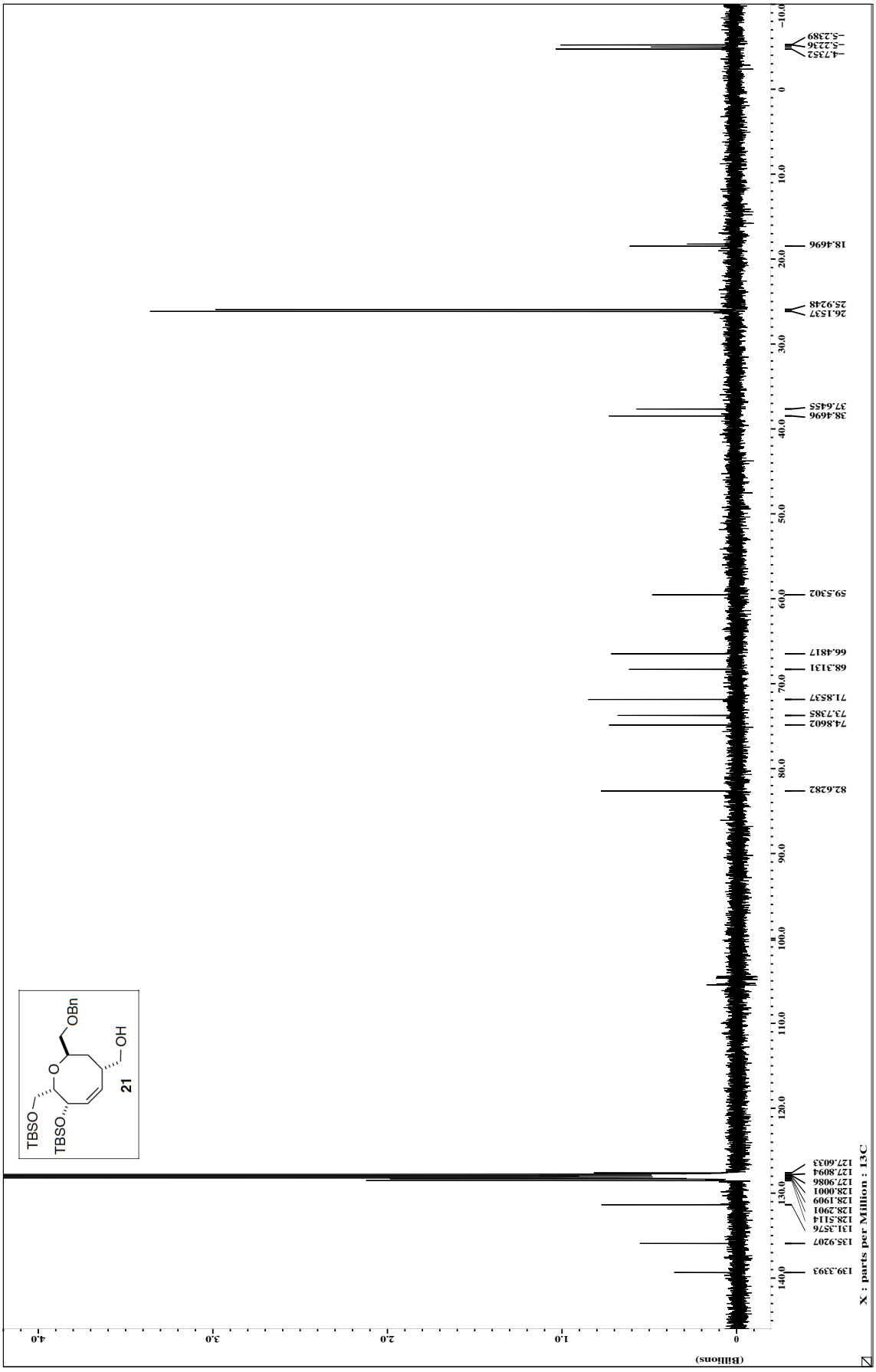

AcO
TBSO
O
OBn
OAc
PhMe2Si
18
X : parts per Million : 1H
7.6126
7.6094
7.5966
7.3126
7.3117
7.2718
7.2572
7.2086
7.2004
5.0699
5.0465
4.9366
4.9343
4.6883
4.6791
4.5861
4.5715
4.3960
4.3718
4.3493
4.1881
4.1670
4.1455
3.6320
3.6223
3.6127
3.4322
3.4190
3.4135
2.6526
2.6494
2.6283
2.4597
2.4515
2.4428
2.2270
2.1973
2.1895
1.7630
1.6632
1.6485
1.6412
1.6320
0.9600
0.4144
0.4007
0.1758
0.1423

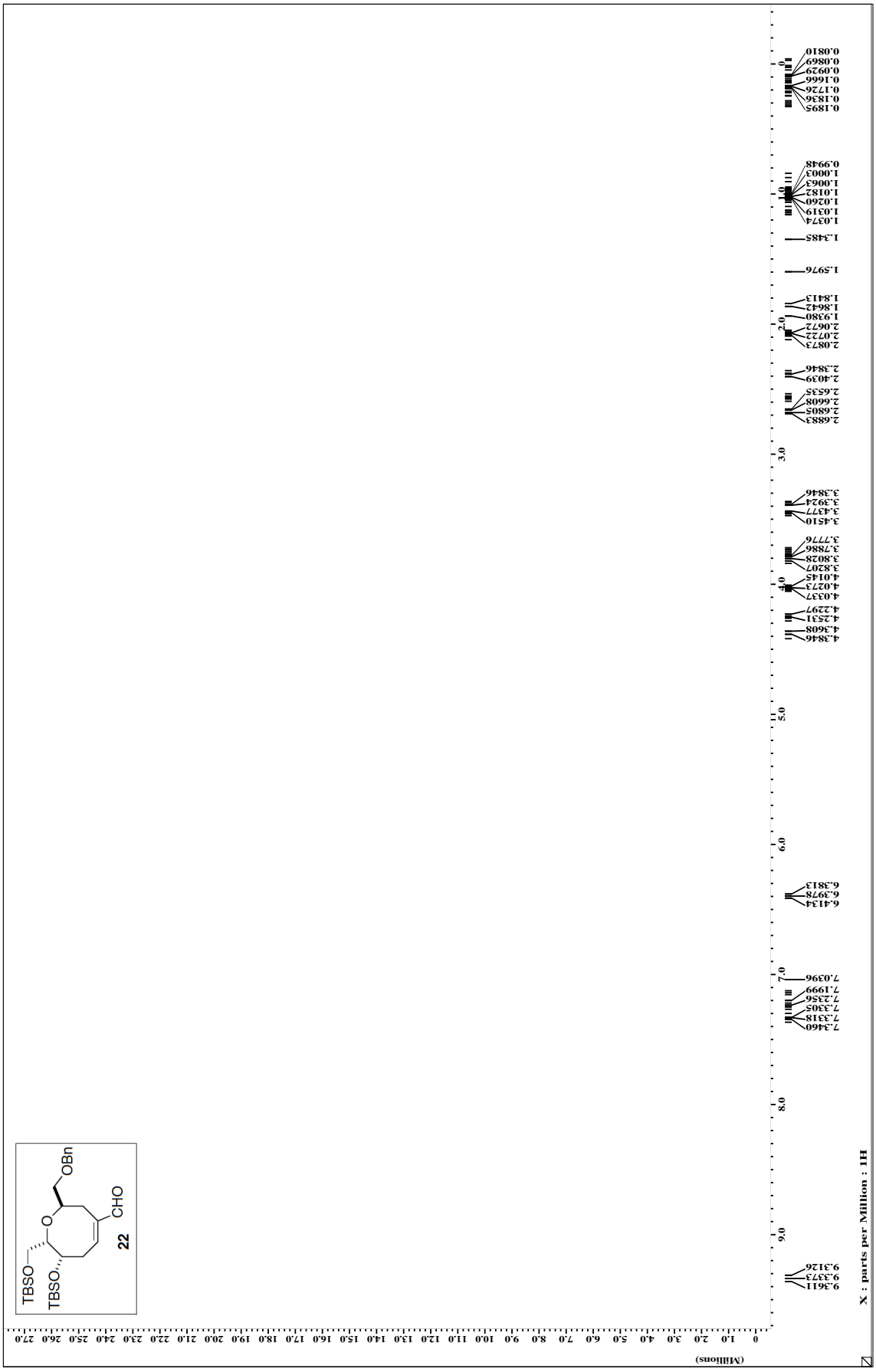

AcO
TBSO
OBn
OAc
PhMe2Si
18
X : parts per Million : 13C
(Billions)
170.0531
169.9844
150.8467
134.3034
128.4812
128.2981
128.1913
128.0005
127.8097
127.7334
106.7491
74.2196
73.2810
72.5408
70.0227
64.5515
64.2158
37.1498
34.9064
26.7950
25.8259
20.5150
20.4463
18.2334
-3.4071
-4.0328
-4.6280

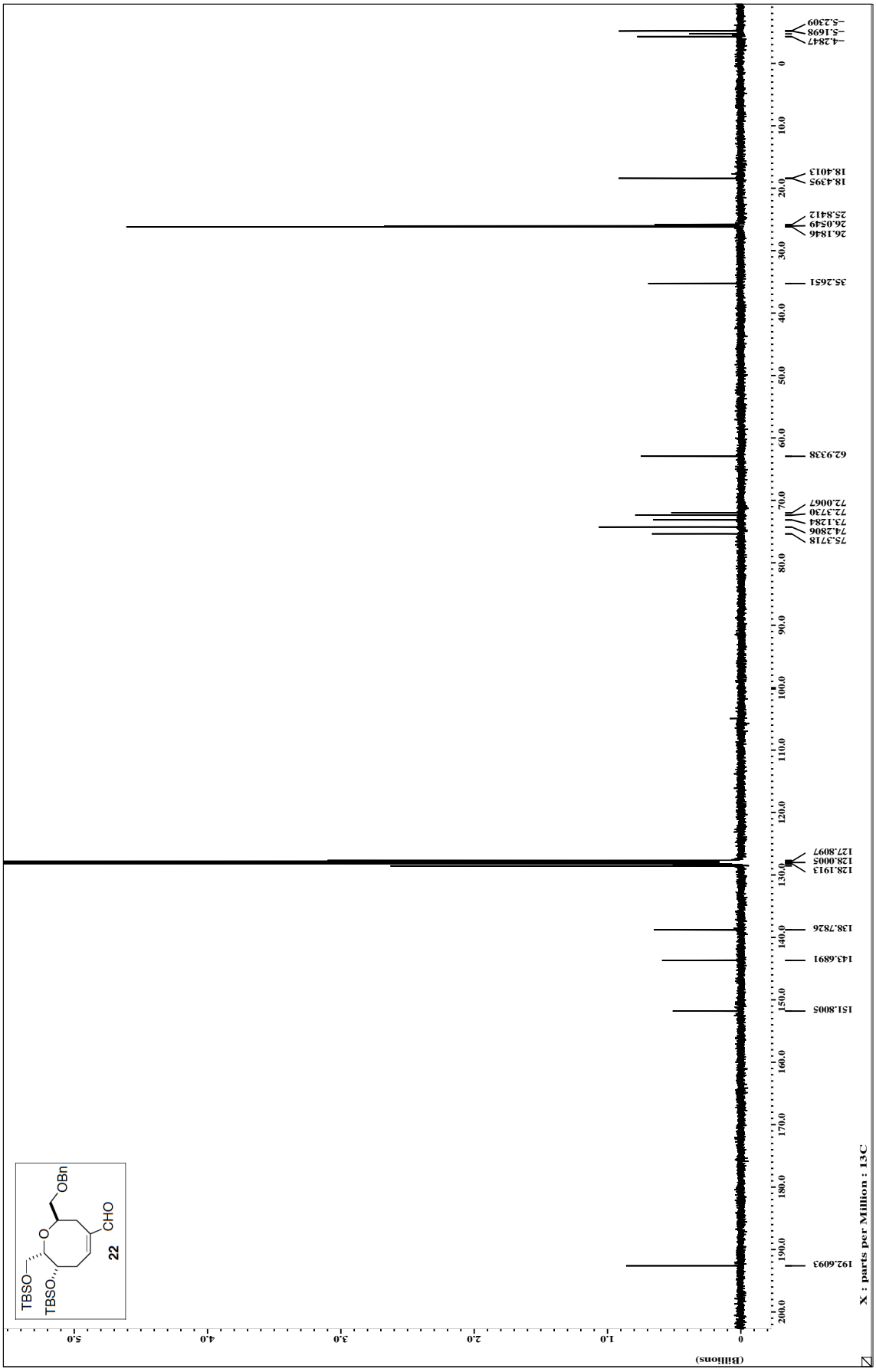

(Millions)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
X : parts per Million : 1H
7.3413
7.3202
7.3055
7.2606
5.7517
5.7430
5.7302
5.5213
5.5177
5.4993
4.8182
4.8090
4.6198
4.5960
4.5136
4.4897
4.1920
4.1311
4.1270
3.9208
3.8988
3.7948
3.5887
3.5470
3.3899
3.3427
3.3391
2.9066
2.8970
2.8888
2.2200
2.0436
2.0166
1.9346
1.6886
1.6799
1.6648
1.2644
1.2457
1.2392
#
HO
HO
O
OBn
OH
20

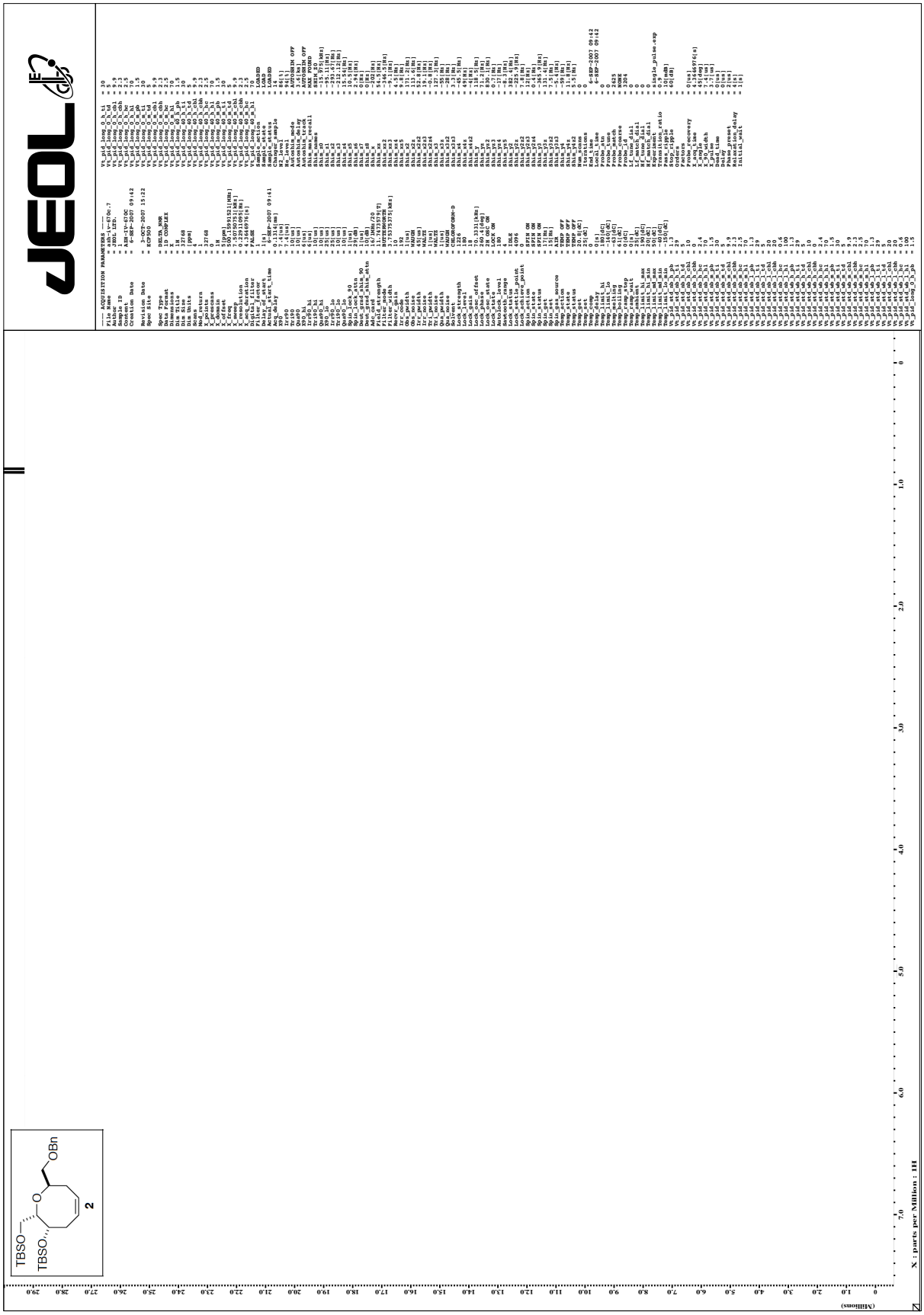

36.1169
37.8109
56.1932
66.4488
67.8299
70.4778
73.8429
74.6060
76.9409
77.2004
77.4522
83.0989
128.3258
128.4021
128.7989
131.9656
134.8119
136.7959
X : parts per Million : 13C
(Millions)
OBn
OH
HO
HO
O
20

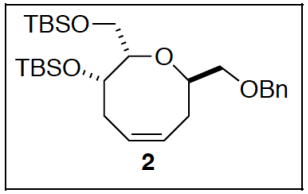

TBSO
TBSO
O
OBn
OH
21
X : parts per Million : 1H
7.3886
7.3749
7.3735
7.2370
7.2224
7.2004
7.1330
5.7739
5.7616
5.7597
5.3154
5.3122
5.3085
4.8972
4.8940
4.8853
4.5307
4.5252
4.5014
4.3983
4.3896
4.2604
4.1931
4.1830
4.1803
3.8789
3.8702
3.8610
3.5829
3.5687
3.5651
3.3512
3.3411
3.3104
3.2980
2.9664
2.9536
2.9476
2.9348
1.9449
1.9375
1.9339
1.6164
1.6105
1.5894
1.0461
1.0406
0.9884
0.9825
0.6989
0.6888
0.6787
0.4992
0.1698
0.1634
0.0846
0.0713


TBSO
TBSO
O
OBn
OH
21
X : parts per Million : 13C
(Billions)
139.3393
135.9207
131.3576
128.5114
128.2901
128.1909
128.0001
127.9086
127.8094
127.6033
82.6282
74.8602
73.7385
71.8537
68.3131
66.4817
59.5302
38.4696
37.6455
26.1537
25.9248
18.4696
-4.7352
-5.2236
-5.2389


TBSO
TBSO
O
OBn
CHO
22
X : parts per Million : 1H
(Millions)


TBSO
TBSO
O
OBn
CHO
22
X : parts per Million : 13C
(Billions)
192.6093
151.8005
143.6891
138.7826
128.1913
128.0005
127.8097
75.3718
74.2806
73.1284
72.3730
72.0067
62.9338
35.2651
26.1846
26.0549
25.8412
18.4395
18.4013
-4.2847
-5.1698
-5.2309


TBSO
TBSO
O
OBn
2
JEOL
X : parts per Million : 1H
(Millions)



JEOL

```
---- ACQUISITION PARAMETERS ----
File Name             = azh-iv-67Oc_copy.
Author                = JEOL LTD.
Sample ID             = 1
Content               = AZH-IV-67OC
Creation Date         =  6-SEP-2007 10:18

Revision Date         =  3-OCT-2007 15:37
Spec Site             = ECP500

Spec Type             = DELTA_NMR
Data Format           = 1D COMPLEX
Dimensions            = X
Dim Title             = 13C
Dim Size              = 32768
Dim Units             = [ppm]
Scans                 = 357
Mod_return            = 1
X_points              = 32768
X_prescans            = 4
X_domain              = 13C
X_offset              = 100[ppm]
X_freq                = 125.76529768[MHz]
X_sweep               = 31.44654088[kHz]
X_resolution          = 0.95967227[Hz]
Irr_domain            = 1H
Irr_offset            = 5[ppm]
Irr_freq              = 500.15991521[MHz]
X_acq_duration        = 1.0420224[s]
Digital_filter        = FALSE
Filter_factor         = 1
Delay_of_start        = 1[s]
Actual_start_time     =  6-SEP-2007 10:00
Acq_delay             = 27.9[us]
X90                   = 23[us]
Irr90                 = 7.4[us]
Tri90                 = 10[us]
Qua90                 = 10[us]
X90_hi                = 23[us]
Irr90_hi              = 6[us]
Tri90_hi              = 10[us]
Qua90_hi              = 10[us]
X90_lo                = 0.165[ms]
Irr90_lo              = 25[us]
Tri90_lo              = 10[us]
Qua90_lo              = 10[us]
Spin_lock_90          = 1[us]
Spin_lock_attn        = 29[dB]
Deut_grad_shim_90     = 1[us]
Deut_grad_shim_attn   = 10[dB]
Adc_card              = 16/1MHz/20
Field_strength        = 11.7473579[T]
Filter_mode           = BUTTERWORTH
Filter_width          = 15.72327044[kHz]
Recvr_gain            = 20
Irr_code              = 192
Obs_pwidth            = 1[us]
Obs_noise             = WAUGH
Irr_pwidth            = 45[us]
Irr_noise             = WALTZ
Tri_pwidth            = 1[us]
Tri_noise             = WALTZ
Qua_pwidth            = 1[us]
Qua_noise             = WAUGH
Solvent               = CHLOROFORM-D
Lock_strength         = 920.0
Lock_level            = 180
Lock_gain             = 18
Lock_osc_offset       = 70.3331[kHz]
Lock_phase            = 260.4[deg]
Lock_osc_state        = 2H OSC ON
Lock_state            = LOCK ON
Autolock_level        = 180
Sawtooth_range        = 4
Lock_status           = IDLE
Lock_settle_point     = 4096
Lock_achieve_point    = 0
Spin_action           = SPIN ON
Spin_state            = SPIN ON
Spin_status           = SPIN ON
Spin_get              = 14[Hz]
Spin_set              = 15[Hz]
Spin_gas_source       = AIR
Temp_action           = TEMP OFF
Temp_state            = TEMP OFF
Temp_status           = TEMP OFF
Temp_get              = 21.9[dC]
Temp_set              = 25[dC]
Temp_comp             = 0
Temp_delay            = 0[s]
Temp_limit_hi         = 180[dC]
Temp_limit_lo         = -140[dC]
Temp_melting          = -63[dC]
Temp_boiling          = 61[dC]
Temp_ramp_step        = 0[dC]
Temp_ramp_wait        = 0[s]
Temp_ambient          = 25[dC]
Temp_limit_hi_max     = 190[dC]
Temp_limit_hi_min     = 20[dC]
Temp_limit_md_max     = 50[dC]
Temp_limit_md_min     = -40[dC]
Temp_limit_lo_min     = -150[dC]
Vt_pid_std_nb_h_pb    = 1.3
Vt_pid_std_nb_h_ti    = 29
Vt_pid_std_nb_h_td    = 5
Vt_pid_std_nb_h_cbl   = 10
Vt_pid_std_nb_h_cbh   = 0
Vt_pid_std_nb_h_hc    = 2.4
Vt_pid_std_nb_h_hl    = 70
Vt_pid_std_nb_m_pb    = 1.5
Vt_pid_std_nb_m_ti    = 30
Vt_pid_std_nb_m_td    = 5
Vt_pid_std_nb_m_cbl   = 9.9
Vt_pid_std_nb_m_cbh   = 2.3
Vt_pid_std_nb_m_hc    = 2.5
Vt_pid_std_nb_m_hl    = 70
Vt_pid_std_nb_l_pb    = 1.3
Vt_pid_std_nb_l_ti    = 29
Vt_pid_std_nb_l_td    = 5
Vt_pid_std_nb_l_cbl   = 20
Vt_pid_std_nb_l_cbh   = 20
Vt_pid_std_nb_l_hc    = 0.6
Vt_pid_std_nb_l_hl    = 100
Vt_pid_std_wb_h_pb    = 1.3
Vt_pid_std_wb_h_ti    = 29
Vt_pid_std_wb_h_td    = 5
Vt_pid_std_wb_h_cbl   = 10
Vt_pid_std_wb_h_cbh   = 0
Vt_pid_std_wb_h_hc    = 2.4
Vt_pid_std_wb_h_hl    = 70
Vt_pid_std_wb_m_pb    = 1.5
Vt_pid_std_wb_m_ti    = 30
Vt_pid_std_wb_m_td    = 5
Vt_pid_std_wb_m_cbl   = 9.9
Vt_pid_std_wb_m_cbh   = 2.3
Vt_pid_std_wb_m_hc    = 2.5
Vt_pid_std_wb_m_hl    = 70
Vt_pid_std_wb_l_pb    = 1.3
Vt_pid_std_wb_l_ti    = 29
Vt_pid_std_wb_l_td    = 5
Vt_pid_std_wb_l_cbl   = 20
Vt_pid_std_wb_l_cbh   = 20
Vt_pid_std_wb_l_hc    = 0.6
Vt_pid_std_wb_l_hl    = 100
Vt_pid_long_0_h_pb    = 1.5
Vt_pid_long_0_h_ti    = 30
Vt_pid_long_0_h_td    = 5
Vt_pid_long_0_h_cbl   = 9.9
Vt_pid_long_0_h_cbh   = 2.3
Vt_pid_long_0_h_hc    = 2.5
Vt_pid_long_0_h_hl    = 70
Vt_pid_long_0_m_pb    = 1.5
Vt_pid_long_0_m_ti    = 30
Vt_pid_long_0_m_td    = 5
Vt_pid_long_0_m_cbl   = 9.9
Vt_pid_long_0_m_cbh   = 2.3
Vt_pid_long_0_m_hc    = 2.5
Vt_pid_long_0_m_hl    = 70
Vt_pid_long_40_h_pb   = 1.5
Vt_pid_long_40_h_ti   = 30
Vt_pid_long_40_h_td   = 5
Vt_pid_long_40_h_cbl  = 9.9
Vt_pid_long_40_h_cbh  = 2.3
Vt_pid_long_40_h_hc   = 2.5
Vt_pid_long_40_h_hl   = 70
Vt_pid_long_40_m_pb   = 1.5
Vt_pid_long_40_m_ti   = 30
Vt_pid_long_40_m_td   = 5
Vt_pid_long_40_m_cbl  = 9.9
Vt_pid_long_40_m_cbh  = 2.3
Vt_pid_long_40_m_hc   = 2.5
Vt_pid_long_40_m_hl   = 70
Sample_action         = LOADED
Sample_state          = LOAD
Sample_status         = LOADED
Changer_sample        = 14
N2_level              = 85[%]
He_level              = 94[%]
Autoshim_mode         = AUTOSHIM OFF
Autoshim_delay        = 3.6[Hz]
Autoshim_track        = AUTOSHIM OFF
Shim_max_recall       = MAX FOUND
Shim_names            = SHIM_ZO
Shim_z0               = -15.975[kHz]
Shim_z1               = -95.11[Hz]
Shim_z2               = -293.67[Hz]
Shim_z3               = -212.12[Hz]
Shim_z4               = 15.54[Hz]
Shim_z5               = 10.5[Hz]
Shim_z6               = 2.94[Hz]
Shim_z7               = 0[Hz]
Shim_z8               = 0[Hz]
Shim_x                = -202[Hz]
Shim_xz               = 54.5[Hz]
Shim_xz2              = -346.5[Hz]
Shim_xz3              = -9.1[Hz]
Shim_xz4              = 4.5[Hz]
Shim_xz5              = 9.8[Hz]
Shim_x2               = 171.2[Hz]
Shim_x2z              = 113.6[Hz]
Shim_x2z2             = 52.8[Hz]
Shim_x2z3             = 19.1[Hz]
Shim_x2z4             = -0.8[Hz]
Shim_x3               = 127.3[Hz]
Shim_x3z              = -55[Hz]
Shim_x3z2             = -28[Hz]
Shim_x3z3             = 3.3[Hz]
Shim_x4               = -45.5[Hz]
Shim_x4z              = 49[Hz]
Shim_x4z2             = -4[Hz]
Shim_y                = 118.5[Hz]
Shim_yz               = 71.2[Hz]
Shim_yz2              = 830.1[Hz]
Shim_yz3              = 0.7[Hz]
Shim_yz4              = -17[Hz]
Shim_yz5              = -8.3[Hz]
Shim_y2               = 382.4[Hz]
Shim_y2z              = -225.9[Hz]
Shim_y2z2             = 7.8[Hz]
Shim_y2z3             = 12[Hz]
Shim_y2z4             = 0.4[Hz]
Shim_y3               = -365.9[Hz]
Shim_y3z              = 131.4[Hz]
Shim_y3z2             = 7.5[Hz]
Shim_y3z3             = -5.4[Hz]
Shim_y4               = -59[Hz]
Shim_y4z              = 11.8[Hz]
Shim_y4z2             = 5.5[Hz]
Num_scans             = 19644
Iterations            = 1
End_time              =  7-SEP-2007 02:54
Local_time            =  6-SEP-2007 10:18
Probe_atn             = 0
Probe_tune            = 2770
Probe_match           = 5145
Probe_coarse          = NONE
Probe_id              = 3204
Lf_tune_dial          = 0
Lf_match_dial         = 0
Hf_tune_dial          = 0
Hf_match_dial         = 0
Experiment            = single_pulse_dec
Transition_ratio      = 0.8
Pass_ripple           = 10[mdB]
Stop_ripple           = 60[dB]
Orders                =
Factors               =
Probe_recovery        = 0[us]
X_acq_time            = 1.0420224[s]
X_angle               = 90[deg]
X_90_width            = 23[us]
X_pulse               = 23[us]
Dead_time             = 0[us]
Delay                 = 0[us]
Phase_preset          = 3[us]
Relaxation_delay      = 2[s]
Initial_wait          = 1[s]
```