A rapid synthesis of iminosugars using ring closing metathesis

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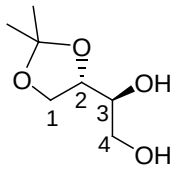
Supporting Information

General information

IR spectra were recorded as solutions using a Perkin-Elmer 1600 series FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AV400 or DRX500 FT spectrometer. ^{1}H NMR data are expressed as chemical shift in ppm followed by number of proton(s), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet) and coupling constant(s) *J* (Hz). ^{13}C NMR chemical shifts are expressed in ppm. Low resolution mass spectra (LRMS) and high resolution mass spectra (HRMS) were obtained using a VG LCT spectrometer using electrospray ionisation (ESI). Microanalysis was performed by the microanalysis section of the School of Chemistry, University of Nottingham, using an Exeter Analytical Inc. CE-440 elemental analyser. Optical rotations were obtained using a Jasco DIP 370 digital polarimeter. $[\alpha]_D$ Values were measured at the concentration (in g/100 mL) and temperature shown.

Diol 12



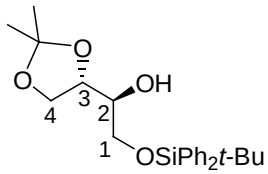
12

Ethyl-(2*R*)-[(4*S*)-2,2-dimethyl-1,3-dioxolan-4-yl](hydroxy)acetate (1.61 g, 7.89 mmol, 1.0 eq) prepared from L-ascorbic acid[1] was dissolved in anhydrous THF (25 mL). $LiAlH_4$ (1.0 M in THF, 10.3 mL, 10.3 mmol, 1.3 eq) was added dropwise at 0 °C (ice bath). The resulting

[1] Andre, C.; Bolte, J.; Demuynck, C. *Tetrahedron: Asym.* **1998**, *9*, 1359-1367; Abushanab, E.; Vemishetti, P.; Leiby, R.W.; Singh, H.K.; Mikkilineni, A.B.; Wu, D.C.J.; Saibaba, R.; Panzica, R. P. *J. Org. Chem.* **1988**, *53*, 2598-602; Abushanab, E.; Bessodes, M.; Antonakis, K. *Tetrahedron Lett.* **1984**, *25*, 3841-4.

yellow solution was stirred at 20 °C for 16 h. H_2O (3 mL) was then carefully added, and the mixture was filtered through a pad of celite and washed with ethyl acetate (50 mL). The filtrate was concentrated *in vacuo* to yield the title compound as a colourless oil (1.28 g, 100%). R_f 0.30 (ethyl acetate). ν_{max} ($CHCl_3$)/cm^{-1} 3580, 1374, 1063. δ_H (400 MHz, $CDCl_3$) 4.16 (1 H, td, *J* 6.6 and 4.6 Hz, 2-C**H**), 4.04 (1 H, dd, *J* 8.1 and 6.6 Hz, 1-C**H**H), 3.84 (1 H, dd, *J* 8.2 and 6.7 Hz, 1-CH**H**), 3.70-3.60 (3 H, m, 4-C$\mathbf{H}_2$OH, 3-C**H**OH), 2.88 (1 H, bs, O**H**), 2.72 (1 H, bs, O**H**), 1.43 (3 H, s, C(C$\mathbf{H}_3$)), 1.36 (3 H, s, C(C$\mathbf{H}_3$)). δ_C (100 MHz, $CDCl_3$) 109.7 (**C**$(CH_3)_2$), 76.7 (2-CH), 71.8 (3-CH), 65.9 (1-CH_2), 64.2 (4-CH_2), 26.5 (C(**C**$H_3)_2$), 25.3 (C(**C**$H_3)_2$). LRMS (ESI) 227 (26%), 185 (100). HRMS (ESI) required for $C_7H_{14}NaO_4$ 185.0790, found 185.0794. $[\alpha]_D$ (c 0.62, $CHCl_3$) +4.7 at 26 °C (lit.[2] $[\alpha]_D$ (c 1.8, CH_3OH) +4.3).

Alcohol 13



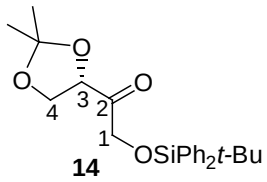
13

Diol **12** (1.28 g, 7.89 mmol, 1.0 eq) was dissolved in dry DMF (30 mL). Imidazole (1.07 g, 15.78 mmol, 2.0 eq) was added at 20 °C, followed by *tert*-butyldiphenylsilyl chloride (2.05 mL, 7.89 mmol, 1.0 eq). The resulting pale yellow solution was stirred at 20 °C for 16 h. H_2O (30 mL) and Et_2O (50 mL) were then added, the layers separated, and the aqueous layer extracted with Et_2O (3 × 50 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude oil was purified by column chromatography (petroleum ether (40-60)/diethyl ether, 2:1). The title compound was obtained as a colourless oil (2.31 g, 73%). R_f 0.25 (petroleum ether (40-60)/diethyl ether, 2:1). ν_{max} ($CHCl_3$)/cm^{-1} 3568, 2932, 2889, 2859, 1382, 1373, 1112, 1066. δ_H (400 MHz, $CDCl_3$) 7.35-7.75 (10 H, m, Ar**H**), 4.24 (1 H, ddd, *J* 7.1, 6.5 and 4.3 Hz, 3-C**H**), 4.02 (1 H, dd, *J* 8.2 and 6.5 Hz, 4-C**H**H), 3.84 (1 H, dd, *J* 8.2 and 7.1 Hz, 4-CH**H**), 3.67-3.76 (3 H, m, 1-C$\mathbf{H}_2$, 2-C**H**OH), 2.48 (1 H, bs, O**H**), 1.43 (3 H, s, C(C$\mathbf{H}_3)_2$), 1.39 (3 H, s, C(C$\mathbf{H}_3)_2$), 1.09 (9 H, s, SiC(C$\mathbf{H}_3)_3$). δ_C (100 MHz, $CDCl_3$) 135.8 (CH Ar), 133.1 (C Ar), 129.9, 127.8 (CH Ar), 109.2 (**C**$(CH_3)_2$), 76.5 (3-CH), 72.0 (2-CH), 66.1 (4-CH_2), 65.1 (1-CH_2), 26.9 (C(**C**$H_3)_3$), 26.6 (C(**C**$H_3)_2$), 25.4 (C(**C**$H_3)_2$), 19.3

[2] Neuß, O.; Furman, B.; Kaluza, Z.; Chmielewski, M. *Heterocycles* **1997**, *45*, 265-270.

(Si**C**$(CH_3)_3$). LRMS (ESI) 423 (100%), 343 (9), 187 (8). HRMS (ESI) required for $C_{23}H_{32}NaO_4Si$ 423.1968, found 423.1952. $[\alpha]_D$ (c 1.11, $CHCl_3$) +4.3 at 24 °C (lit.[3] $[\alpha]_D$ (c 2.1, $CHCl_3$) +4.4 at 22 °C).

Ketone 14

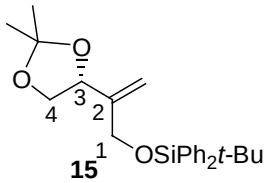


14

Oxalyl chloride (1.01 mL, 11.56 mmol, 2.0 eq) was dissolved in CH_2Cl_2 (pre-dried on 3Å MS, 25 mL). DMSO (pre-dried on 3Å MS, 1.64 mL, 23.12 mmol, 4.0 eq) was added at -60 °C. The resulting colourless solution was stirred at -60 °C for 5 min. Alcohol **5** (2.31 g, 5.78 mmol, 1.0 eq) in CH_2Cl_2 (pre-dried on 3Å MS, 50 mL) was added at -60 °C. The resulting white suspension was stirred at -60 °C for 15 min. Et_3N (3.22 mL, 23.12 mmol, 4.0 eq) was then added, and the pale yellow suspension was allowed to warm to 0 °C over 1.5 h. The reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography (petroleum ether (40-60)/diethyl ether, 2:1). The title compound was obtained as a colourless oil (2.06 g, 90%). R_f 0.45 (petroleum ether (40-60)/diethyl ether, 2:1). ν_{max} ($CHCl_3$)/cm^{-1} 2932, 2893, 2859, 1736, 1384, 1375, 1113, 1082. δ_H (400 MHz, $CDCl_3$) 7.30-7.75 (10 H, m, Ar**H**), 4.61 (1 H, dd, *J* 7.9 and 5.6 Hz, 3-CH), 4.53 (2 H, s, 1-CH_2), 4.21 (1 H, dd, *J* 8.8 and 7.9 Hz, 4-C**H**H), 3.87 (1 H, dd, *J* 8.8 and 5.6 Hz, 4-CH**H**), 1.34 (3 H, s, C(C**H**$_3)_2$), 1.31 (3 H, s, C(C**H**$_3)_2$), 1.12 (9 H, s, SiC(C**H**$_3)_3$). δ_C (100 MHz, $CDCl_3$) 207.2 (2-CO), 135.6 (CH Ar), 132.7 (C Ar), 130.1, 127.9 (CH Ar), 111.0 (**C**$(CH_3)_2$), 79.0 (3-**C**HOC$(CH_3)_2$), 68.0 (1-**C**H_2), 66.4 (4-**C**H_2), 26.8 (SiC(**C**$H_3)_3$), 25.8 (C(**C**$H_3)_2$), 25.1 (C(**C**$H_3)_2$), 19.3 (**C**$(CH_3)_3$). LRMS (ESI) 453 (69%), 421 (100), 321 (43), 263 (29). HRMS (ESI) required for $C_{23}H_{30}NaO_4Si$ 421.1811, found 421.1802. $[\alpha]_D$ (c 4.96, $CHCl_3$) -21.0 at 28 °C (lit.[3] $[\alpha]_D$ (c 2.5, $CHCl_3$) -19.5 at 22 °C).

[3] Marco, J. A.; Carda, M.; Gonzalez, F.; Rodriguez, S.; Murga, J. *Liebigs Ann*. **1996**, 1801-1810.

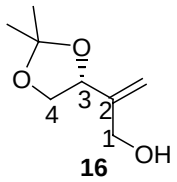
Alkene 15



15

Ph_3PCH_3Br (2.59 g, 7.25 mmol, 1.4 eq) was suspended in anhydrous THF (50 mL). *n*-BuLi (3.56 mL, 1.6 M in THF, 5.69 mmol, 1.1 eq) was added dropwise at 0 °C. The resulting bright yellow suspension was stirred at 20 °C for 3 h. Ketone **14** (2.06 g, 5.18 mmol, 1.0 eq) in anhydrous THF (20 mL) was then added at -78 °C. The resulting orange suspension was stirred at -78 °C for 45 min, then at 20 °C for 2 h. The reaction was quenched by careful addition of MeOH (10 mL) at 0 °C. Et_2O (100 mL) was added and the organic phase was successively washed with saturated aqueous NH_4Cl (3×100 mL) and saturated aqueous NaCl (3×100 mL). The combined aqueous layers were back-extracted with diethyl ether (3×200 mL). The combined organic extracts were dried (Mg SO_4), filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography (*n*-hexane/diethyl ether, 10:1). The title compound was obtained as a colourless oil (1.70 g, 83%). R_f 0.30 (*n*-hexane/diethyl ether, 10:1). ν_{max} ($CHCl_3$)/cm^{-1} 2932, 2859, 1382, 1372, 1112, 1062. δ_H (400 MHz, $CDCl_3$) 7.35-7.75 (10 H, m, Ar**H**), 5.28 (2 H, m, 2-C=C**H**$_2$), 4.61 (1 H, m, 3-C**H**), 4.21 (2 H, d, *J* 0.8 Hz, 1-C**H**$_2$), 4.14 (1 H, dd, *J* 8.2 and 6.5 Hz, 4-C**H**H), 3.65 (1 H, app. t, *J* 8.0 Hz, 4-CH**H**), 1.40 (6 H, s, C(C**H**$_3$)$_2$), 1.08 (9 H, s, SiC(C**H**$_3$)$_3$). δ_C (100 MHz, $CDCl_3$) 145.8 (2-**C**=CH_2), 135.6 (**C**H Ar meta), 133.4 (**C** Ar), 129.8 (**C**H Ar para), 127.8 (**C**H Ar ortho), 111.0 (2-C=**C**H_2), 109.1 (**C**(CH$_3$)$_2$), 76.9 (3-CH), 69.6 (4-CH_2), 64.4 (1-CH_2), 26.9 (C(**C**H$_3$)$_3$), 26.3 (SiC(**C**H$_3$)$_2$), 25.8 (C(**C**H$_3$)$_2$), 19.3 (Si**C**(CH$_3$)$_3$). LRMS (ESI) 419 (100%), 279 (41). HRMS (ESI) required for $C_{24}H_{32}NaO_3Si$ 419.2018, found 419.1991. $[\alpha]_D$ (c 1.29, $CHCl_3$) -21.8 at 29 °C.

Alcohol 16

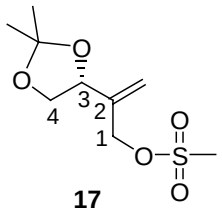


16

Alkene **15** (396 mg, 1.0 mmol, 1.0 eq) was dissolved in anhydrous THF (8 mL). TBAF (2 mL, 1.0 M in THF, 2.0 mmol, 2.0 eq) was added dropwise and the resulting yellow solution was stirred at 20 °C for 24 h. Saturated aqueous NH_4Cl (12 mL) was added, the layers were

separated and the aqueous layer extracted with diethyl ether (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude oil was purified by column chromatography (diethyl ether) and the title compound obtained as a colourless oil (155 mg, 98%). R_f 0.67 (diethyl ether). ν_{max} ($CHCl_3$)/cm^{-1} 3611, 3541, 2987, 2935, 2879, 1382, 1373, 1063. δ_H (400 MHz, $CDCl_3$) 5.17-5.19 (2 H, m, 2-C=C**H**$_2$), 4.64 (1 H, dd, *J* 7.2 and 7.0 Hz, 3-CH), 4.18 (1 H, d, *J* 13.4 Hz, 1-C**H**H), 4.13 (1 H, dd, *J* 8.2 and 6.5 Hz, 4-C**H**H), 4.09 (1 H, d, *J* 13.4 Hz, 1-CH**H**), 3.69 (1 H, dd, *J* 8.2 and 7.7 Hz, 4-CH**H**), 2.50 (1 H, bs, 1-O**H**), 1.43 (3 H, s, CH_3), 1.37 (3 H, s, CH_3). δ_C (100 MHz, $CDCl_3$) 145.8 (2-**C**=CH_2), 113.1 (2-C=**C**H_2), 109.4 (**C**(CH_3)$_2$), 77.6 (3-CH), 69.0 (4-CH_2), 63.2 (1-CH_2OH), 26.3 (C(**C**H_3)$_2$), 25.5 (C(**C**H_3)$_2$). LRMS (ESI) 222 (62%), 181 (100). HRMS (ESI) required for $C_8H_{14}NaO_3$ 181.0841, found 181.0855. $[\alpha]_D$ (c 1.20, $CHCl_3$) -51.4 at 29 °C (lit.[4] $[\alpha]_D$ (c 20, $CHCl_3$) -45.5 at 20 °C).

Mesylate 17



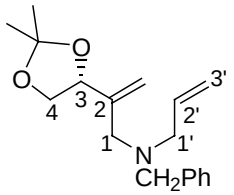
17

Alcohol **16** (131 mg, 0.83 mmol, 1.0 eq) was dissolved in CH_2Cl_2 (10 mL). Et_3N (0.17 mL, 1.24 mmol, 1.5 eq) was added at 0 °C, followed by methanesulfonyl chloride (0.10 mL, 1.24 mmol, 1.5 eq). The resulting colourless solution was stirred at 0 °C for 1 h. H_2O (10 mL) was added, the layers separated and the organic layer successively washed with 1M HCl (10 mL), saturated aqueous $NaHCO_3$ (10 mL) and H_2O (10 mL). The organic layer was then dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield a colourless oil which was used without any purification. A sample was further purified by column chromatography (*n*-hexane/diethyl ether, 1:1). R_f 0.13 (*n*-hexane/diethyl ether, 1:1). ν_{max} ($CHCl_3$)/cm^{-1} 2986, 2938, 2887, 1456, 1360, 1153, 1066, 993, 971, 912, 864. δ_H (400 MHz, $CDCl_3$) 5.46 (1 H, bs, 2-C=C**H**H), 5.39 (1 H, bs, 2-C=CH**H**), 4.72-4.79 (2 H, m, 1-C**H**$_2$OMs), 4.65 (1 H, dd, *J* 7.0 and 6.9 Hz, 3-C**H**), 4.18 (1 H, dd, *J* 8.4 and 6.5 Hz, 4-C**H**H), 3.73 (1 H, dd, *J* 8.4 and 7.4 Hz, 4-CH**H**), 3.04 (3 H, s, SO_2C**H**$_3$), 1.46 (3 H, s, C(C**H**$_3$)$_2$), 1.40 (3 H, s, C(C**H**$_3$)$_2$). δ_C (100 MHz, $CDCl_3$) 140.0 (2-**C**=CH_2), 117.7 (2-C=**C**H_2), 109.7 (3-**C**(CH_3)$_2$), 76.5 (**C**HOC(CH_3)$_2$), 69.1 (1-**C**H_2OMs), 68.9

[4] Van der Eycken, E.; De Wilde, H.; Deprez, L.; Vandewalle, M. *Tetrahedron Lett.* **1987**, *28*, 4759-60.

(4-**C**H_2OC(CH_3)$_2$), 38.0 (SO_2**C**H_3), 26.3 (C(**C**H_3)$_2$), 25.5 (C(**C**H_3)$_2$). LRMS (ESI) 300 (57%), 259 (100), 237 (5). HRMS (ESI) required for $C_9H_{16}NaO_5S$ 259.0616, found 259.0615. $[\alpha]_D$ (c 2.34, $CHCl_3$) -36.0 at 27 °C.

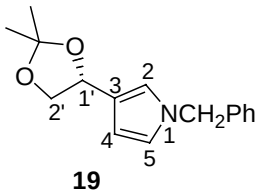
Diene 18



18

NaH (24 mg, 60% dispersion in oil, 0.59 mmol, 1.5 eq) was suspended in dry THF (4 mL). *N*-Benzylallylamine (57 mg, 0.39 mmol, 1.0 eq) in dry THF (1 mL) was added dropwise at 0 °C, and the resulting orange suspension was stirred at 20 °C for 2 h. The mixture was then cooled to 0 °C, and a solution of mesylate **17** (92 mg, 0.39 mmol, 1.0 eq) in dry THF (4 mL) was added dropwise. The orange suspension was stirred at 20 °C for 1 d, then under reflux for 5 d. The reaction was quenched by the addition of H_2O (8 mL). The layers were separated, and the aqueous layer extacted with Et_2O (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a crude oil which was purified by column chromatography (petroleum ether (40-60)/diethyl ether, 4:1). The title compound was obtained as a yellow oil (62 mg, 55%). R_f 0.55 (petroleum ether (40-60)/diethyl ether, 4:1). ν_{max} ($CHCl_3$)/cm^{-1} 2929, 2881, 2804, 1454, 1382, 1372, 1120, 1065, 994. δ_H (400 MHz, $CDCl_3$) 7.20-7.40 (5 H, m, Ar**H**), 5.87 (1 H, ddt, *J* 16.6, 10.2 and 6.3 Hz, 2'-C**H**=CH_2), 5.36 (1 H, bs, 2-C=C**H**H), 5.15-5.24 (3 H, m, 2'-CH=C**H**$_2$ and 2-C=CH**H**), 4.58 (1 H, dd, *J* 7.3 and 7.0 Hz, 3-CH), 4.13 (1 H, dd, *J* 8.0 and 6.4 Hz, 4-C**H**H), 3.58 (1 H, d, *J* 13.6 Hz, NC**H**HPh), 3.56 (1 H, t, *J* 8.0 Hz, 4-CH**H**), 3.49 (1 H, d, *J* 13.6 Hz, NCH**H**Ph), 2.96-3.08 (4 H, m, 1- and 1'-NCH_2), 1.43 (3 H, s, CH_3), 1.42 (3 H, s, CH_3). δ_C (100 MHz, $CDCl_3$) 144.7 (2-**C**=CH_2), 139.4 (**C** Ar), 135.6 (2'- **C**H=CH_2), 128.9, 128.3, 127.0 (CH Ar), 117.7 (2'-CH=**C**H_2), 113.2 (2-C=**C**H_2), 108.9 (**C**(CH_3)$_2$), 77.3 (3-CH), 69.6 (4-CH_2), 58.1 (N**C**H_2Ph), 56.9, 56.4 (1- and 1'-CH_2N), 26.4 (C(**C**H_3)$_2$), 26.0 (C(**C**H_3)$_2$). LRMS (ESI) 288 (100%), 230 (23). HRMS (ESI) required for $C_{18}H_{26}NO_2$ 288.1964 found 288.1955. $[\alpha]_D$ (c 2.14, $CHCl_3$) +46.8 at 26 °C.

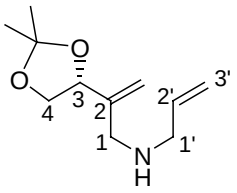
Pyrrole 19



19

Diene **18** (18 mg, 0.06 mmol, 1.0 eq) was dissolved in dry toluene (2 mL). Ruthenium complex **2** (<10 mg, cat.) was added in 2 portions at 20 °C. The resulting purple solution turned brown after 10 min. The reaction mixture was stirred under reflux for 2 h, and then concentrated *in vacuo* and the residue purified by column chromatography (silica, petroleum ether (40-60)/diethyl ether, 6:1). The title compound was obtained as a yellow liquid (16 mg, 99%). R_f 0.23 (petroleum ether (40-60)/diethyl ether, 6:1). ν_{max} ($CHCl_3$)/cm^{-1} 2927, 2855, 2360, 1710, 1455, 1372, 1157, 1057, 866. δ_H (400 MHz, $CDCl_3$) 7.28-7.35 (3 H, m, Ar**H**), 7.13-7.15 (2 H, m, Ar**H**), 6.73, 6.66 (1 H, t, *J* 2.0 Hz, 2-CH and 5-CH), 6.22 (1 H, dd, *J* 2.7 and 1.8 Hz, 4-CH), 5.04 (1 H, dd, *J* 8.6 and 5.9 Hz, 1'-CH), 5.02 (2 H, s, C**H**$_2$Ph), 4.19 (1 H, dd, *J* 8.0 and 5.9 Hz, 2'-C**H**H), 3.81 (1 H, dd, *J* 8.6 and 8.0 Hz, 2'-CH**H**), 1.50 and 1.45 (3 H, s, CH_3). δ_C (100 MHz, $CDCl_3$) 137.8 (C**,** Ar), 128.8, 127.8, 127.3 (CH, Ar), 122.0 (2-CH or 5-CH), 121.4 (3-C), 120.0 (2-CH or 5-CH), 108.9 (**C**(CH_3)$_2$), 107.2 (4-CH), 72.9 (1'-CH), 70.8 (2-CH_2), 53.6 (CH_2Ph), 27.0 (C(CH_3)$_2$), 26.3 (C(CH_3)$_2$). LRMS (ESI) 280 (62%), 200 (100). HRMS (ESI) required for $C_{16}H_{19}NNaO_2$ 280.1320 found 280.1313. $[\alpha]_D$ (c 0.92, $CHCl_3$) -17.0 at 30 °C.

Amine 20

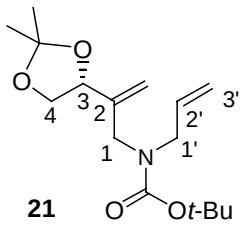


20

Mesylate **17** (791 mg, 3.35 mmol, 1.0 eq) in CH_2Cl_2 (10 mL) was slowly added to a stirred solution of allylamine (1.25 mL, 16.8 mmol, 5.0 eq) in CH_2Cl_2 (20 mL). The resulting colourless solution was stirred at 20 °C for 24 h. The mixture was then concentrated *in vacuo*

and the residue purified by column chromatography (petroleum ether (40-60)/diethyl ether, 1:2, 0.5% NH_3). The title compound was obtained as a yellow liquid (607 mg, 92%). R_f 0.41 (petroleum ether (40-60)/diethyl ether, 1:2, 0.5% NH_3). ν_{max} ($CHCl_3$)/cm^{-1} 2985, 2934, 2884, 1455, 1382, 1372, 1154, 1063, 994, 863. δ_H (400 MHz, $CDCl_3$) 5.89 (1 H, ddt, *J* 17.2, 10.2 and 6.0 Hz, 2'-C**H**=CH_2), 5.23 (1 H, bs, 2-C=C**H**H), 5.17 (1 H, dq, *J* 17.2 and 1.7 Hz, 2'-CH=C**H**$_2$ *trans*), 5.07-5.11 (2 H, m, 2'-CH=C**H**$_2$ *cis* and 2-C=CH**H**), 4.61 (1 H, dd, *J* 7.1 Hz, 1-CH), 4.15 (1 H, dd, *J* 8.1 and 6.6 Hz, 4-C**H**H), 3.66 (1 H, dd, *J* 8.0 Hz, 4-CH**H**), 3.19-3.30 (4 H, m, 1- and 1'-C**H**$_2$NH), 1.44 (3 H, 2 × s, CH_3), 1.39 (3 H, 2 × s, CH_3). δ_C (100 MHz, $CDCl_3$) 145.0 (2-**C**=CH_2), 136.8 (2'-**C**H=CH_2), 116.0 (2'-CH=**C**H_2), 112.5 (2-C=**C**H_2), 109.2 (**C**$(CH_3)_2$), 78.0 (3-CH), 69.3 (4-CH_2), 51.8 ,50.6 (1- and 1'-CH_2), 26.4 (C(**C**$H_3)_2$), 26.0 (C(**C**$H_3)_2$). LRMS 198 (67%), 140 (100). HRMS (ESI) required for $C_{11}H_{20}NO_2$ 198.1494 found 198.1497. $[\alpha]_D$ (c 1.19, $CHCl_3$) -47.8 at 30 °C.

Diene 21

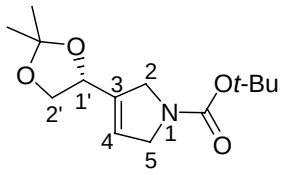


21

Amine **20** (214 mg, 1.09 mmol, 1.0 eq) was dissolved in *n*-hexane (10 mL). A solution of Boc_2O (237 mg, 1.09 mmol, 1.0 eq) in *n*-hexane (5 mL) was then added dropwise at 0 °C, and the resulting colourless solution was stirred at 20 °C for 1 h. A solution of 0.01 N HCl (20 mL) was then added, the layers separated and the organic layer washed with saturated aqueous $NaHCO_3$ (20 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a crude oil. The residue was purified by column chromatography (*n*-hexane/diethyl ether, 3:1) and the title compound was obtained as a yellow oil (319 mg, 98%). R_f 0.38 (*n*-hexane/diethyl ether, 3:1). ν_{max} ($CHCl_3$)/cm^{-1} 2982, 2933, 1683, 1456, 1368, 1065. δ_H (400 MHz, $CDCl_3$) 5.72 (1 H, m, 2'-C**H**=CH_2), 5.06-5.27 (3 H, m, 2-C=C**H**H and 2'-C**H**$_2$=CH), 4.92 (1 H, bs, 2-C=CH**H**), 4.52 (1 H, app. t, *J* 7.0 Hz, 3-CH), 4.11 (1 H, m, C4-C**H**H), 3.69-3.89 (4 H, m, 1- and 1'-C**H**$_2$), 3.61 (1 H, app. t, *J* 7.8 Hz, 4-CH**H**), 1.42 (9 H, s, $NO_2C(CH_3)_3$), 1.41 (3 H, s, C(C**H**$_3)_2$), 1.36 (3 H, s, C(C**H**$_3)_2$). δ_C (100 MHz, $CDCl_3$) 155.5 (NCO), 142.7 (2-C=CH_2), 133.5 (2'-**C**H=CH_2), 116.9 and 116.5 (2'-CH=**C**H_2), 112.3 and 111.2 (2-C=**C**H_2), 109.2

(NO_2**C**(CH_3)$_2$), 79.8 (**C**(CH_3)$_3$), 76.9 (3-**C**HCH_2), 69.0 (4-CH_2), 48.7, 47.3 (1- and 1'-CH_2NH and NH**C**H$_2$), 28.3 (NO_2C(**C**H_3)$_3$), 26.3 (C(**C**H_3)$_2$), 25.5 (C(**C**H_3)$_2$). LRMS (ESI) 320 (100%), 264 (16), 184 (21). HRMS (ESI) required for $C_{16}H_{27}NNaO_4$ 320.1838 found 320.1851. $[\alpha]_D$ (c 1.04, $CHCl_3$) -11.6 at 29 °C. Anal. calc. for $C_{16}H_{27}NO_4$ C, 64.62%; H, 9.15%; N, 4.71%; found C, 64.49%; H, 9.13%; N, 4.99%.

Pyrroline 22

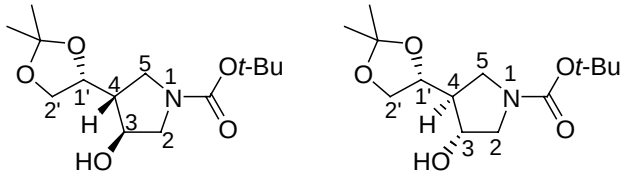


22

Diene **21** (319 mg, 1.07 mmol, 1.0 eq) was dissolved in dry CH_2Cl_2 (40 mL). Ruthenium complex **2** (10 mg, 1 mol%) was added in 3 portions at 20 °C. The resulting purple solution turned brown after 10 min. The reaction mixture was stirred at 20 °C for 36 h, and then concentrated *in vacuo*. The residue was purified by column chromatography (Florisil, *n*-hexane/diethyl ether, 2:1). The title compound was obtained as a yellow oil (271 mg, 94%). R_f 0.22 (*n*-hexane/diethyl ether, 2:1). ν_{max} ($CHCl_3$)/cm^{-1} 2980, 2866, 1693, 1660, 1392, 1368, 1123, 1062, 874. δ_H (400 MHz, $CDCl_3$) 5.71 (1 H, bd, *J* 11.8 Hz, 4-CH), 4.68 (1 H, t, *J* 6.8 Hz, 1'-CH), 4.09-4.19 (5 H, m, 2-,5-CH_2 and 2'-CH**H**), 3.71 (1 H, m, 2'-CH**H**), 1.45 (9 H, s, NO_2C(C**H**$_3$)$_3$), 1.40 (3 H, s, C(C**H**$_3$)$_2$), 1.36 (3 H, s, C(C**H**$_3$)$_2$). δ_C (100 MHz, $CDCl_3$) 154.3 (NCO), 137.7 (3-C), 122.2 (4-CH), 109.6 (**C**(CH_3)$_2$), 79.5 (**C**(CH_3)$_3$), 73.2 (1'-**C**H), 67.9 (2'-CH_2), 53.3 and 53.0 (2- and 5- CH_2), 52.0 and 51.7 (2- and 5- CH_2),* 28.5 (C(**C**H_3)$_3$), 26.3 (C(**C**H_3)$_2$), 25.6 and 25.5 (C(**C**H_3)$_2$). LRMS (ESI) *m/z* 561 (74%), 333 (85), 324 (92), 292 (100), 170 (98). HRMS (ESI) required for $C_{14}H_{23}NNaO_4$ 292.1525 found 292.1510. $[\alpha]_D$ (c 1.09, $CHCl_3$) -24.8 at 27 °C. Anal. calc. for $C_{14}H_{23}NO_4$ C, 62.43%; H, 8.61%; N, 5.20%; found C, 62.79%; H, 8.64%; N, 4.89%.

* rotamers

Alcohols 23 and 24



Pyrroline **22** (269 mg, 1.0 mmol, 1.0 eq) was dissolved in anhydrous THF (10 mL). BH_3.THF (1.1 mL, ~1.0 M in THF, 1.1 mmol, 1.1 eq) was added dropwise at 20 °C. The resulting colourless solution was stirred at 20 °C for 2 h. The reaction mixture was then added to a solution of H_2O_2 (10 mL, ~30%) and aqueous NaOH (2 M, 10 mL). The suspension was stirred at 20 °C for 16 h and extracted with diethyl ether (4 × 40 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude oil was purified by column chromatography (silica, petroleum ether 40-60/ethyl acetate, 1:1).

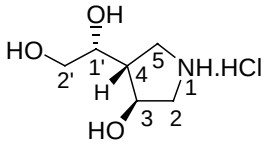
23: colourless oil that crystallised on standing, 113 mg, 40%. R_f 0.48 (ethyl acetate). ν_{max} ($CHCl_3$)/cm^{-1} 3561, 2980, 2935, 2882, 1682, 1455, 1368, 1143, 1095, 1061, 880. δ_H (400 MHz, $CDCl_3$) 4.34 (1 H, q, *J* 6.6 Hz, 1'-CH), 4.07 (1 H, dd, *J* 7.9 and 6.2 Hz, 2-C**H**H), 4.00 (1 H, m, 3-C**H**OH), 3.73 (1 H, m, 2'-C**H**H), 3.65 (1 H, m, 2-CH**H**), 3.53 (1 H, m, 5-C**H**H), 3.21 (1 H, m, 2'-CH**H**), 2.98 (1 H, app. dt, *J* 10.8 and 8.0 Hz, 5-CH**H**), 2.77 (1 H, bs, O**H**), 2.19 (1 H, m, 4-CH), 1.45 (9 H, s, $NO_2C(CH_3)_3$), 1.44 ($C(CH_3)_2$), 1.36 ($C(CH_3)_2$). δ_C (100 MHz, $CDCl_3$) 154.6 and 154.3 (NCO), 109.7 (**C**$(CH_3)_2$), 79.7 (**C**$(CH_3)_3$), 77.7 and 77.3 (3-CHOH), 73.8 and 72.9 (1'-CH), 68.5 and 68.4 (2-CH_2),* 52.1 and 51.8 (2'-CH_2),* 49.5 and 48.9 (4-CH), 46.3 and 45.8 (5-CH_2),* 28.5 ($NO_2C(CH_3)_3$), 26.8 ($C(CH_3)_2$), 25.5 ($C(CH_3)_2$). LRMS (ESI) *m/z* 597 (5%), 351 (21), 310 (100), 188 (24), 130 (11). HRMS (ESI) required for $C_{14}H_{25}NNaO_5$ 310.1630 found 310.1653. $[\alpha]_D$ (c 1.63, $CHCl_3$) -29.3 at 27 °C.

24: colourless oil, 67 mg, 24%. R_f 0.34 (ethyl acetate). ν_{max} ($CHCl_3$)/cm^{-1} 3614, 2981, 2932, 2885, 1682, 1455, 1368, 1132, 1058, 881. δ_H (400 MHz, $CDCl_3$) 4.25-4.00 (3 H, m, 3-C**H**OH, 1'-C**H**, 2'-C**H**H or 2-C**H**), 3.72 (2 H, m, 2-C**H**H and 2'-C**H**H), 3.63 (1 H, dd, *J* 10.2 and 8.8 Hz, 5-C**H**H), 3.29 (1 H, dd, *J* 10.2 and 8.0 Hz, 5-CH**H**), 3.21 (1 H, m, 2'-CH**H** or 2-CH**H**), 2.80 and 2.69 (1 H, bs, O**H**), 2.26 (1 H, m, 4-CH), 1.46 (9 H, s, $NO_2C(CH_3)_3$), 1.41 ($C(CH_3)_2$), 1.36 (3-$C(CH_3)_2$). δ_C (100 MHz, $CDCl_3$) 154.6 (NCO), 109.1 (**C**$(CH_3)_2$), 79.7 (**C**$(CH_3)_3$), 76.1 and 75.3 (3-**C**HOH or 1'-**C**H), 72.3 and 71.7 (1'-CH or 3-CHOH), 67.9 and 67.6 (2-CH_2 or 2'-CH_2), 53.1 and 52.8 (2'-CH_2 or 2-CH_2), 49.2 and 48.0 (4-CH),* 46.5 and

45.5 (5-CH_2),* 28.6 ($NO_2C(\mathbf{C}H_3)_3$), 26.6 ($C(\mathbf{C}H_3)_2$), 25.5 ($C(\mathbf{C}H_3)_2$). LRMS (ESI) *m/z* 597 (40%), 351 (24), 310 (100), 188 (36), 130 (5). HRMS (ESI) required for $C_{14}H_{25}NNaO_5$ 310.1630 found 310.1636. $[\alpha]_D$ (c 1.63, $CHCl_3$) +25.5 at 22 °C.

* rotamers

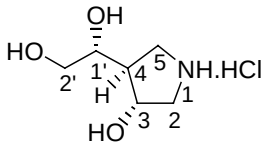
Iminosugar 25



25

Alcohol **23** (31 mg, 0.11 mmol, 1.0 eq) was stirred in 1 M HCl (2 mL) at 20 °C for 16 h. The resulting pale yellow solution was then concentrated *in vacuo* and the residue purified by reverse-phase column chromatography (20% MeOH in water). The title compound was obtained as a colourless oil (20 mg, 100%). δ_H (400 MHz, D_2O) 4.55 (1 H, app. dt, *J* 5.8 and 3.1 Hz, 3-C**H**OH), 3.88 (1 H, dd, *J* 6.5 and 3.8 Hz, 1'-CH), 3.61 (1 H, m, 2'-C**H**HOH), 3.59 (1 H, dd, *J* 12.3 and 8.3 Hz, 5-C**H**H), 3.53 (1 H, dd, *J* 11.6 and 6.6 Hz, 2'-CH**H**OH), 3.39 (1 H, dd, *J* 12.6 and 5.4 Hz, 2-C**H**H), 3.23 (1 H, dd, *J* 12.6 and 2.8 Hz, 2-CH**H**), 3.13 (1 H, dd, *J* 12.3 and 6.9 Hz, 5-CH**H**), 2.37 (1 H, m, 4-CH). δ_C (100 MHz, D_2O) 70.8 (1'-CH), 70.3 (3-CHOH), 63.8 (2'-CH_2OH), 52.3 (2-CH_2), 47.8 (4-CH), 46.5 (5-$\mathbf{C}H_2$). LRMS (ESI) 148 (100%). HRMS (ESI) required for $C_6H_{14}NO_3$ 148.0974, found 148.0987. $[\alpha]_D$ (c 1.00, MeOH) +6.7 at 25 °C.

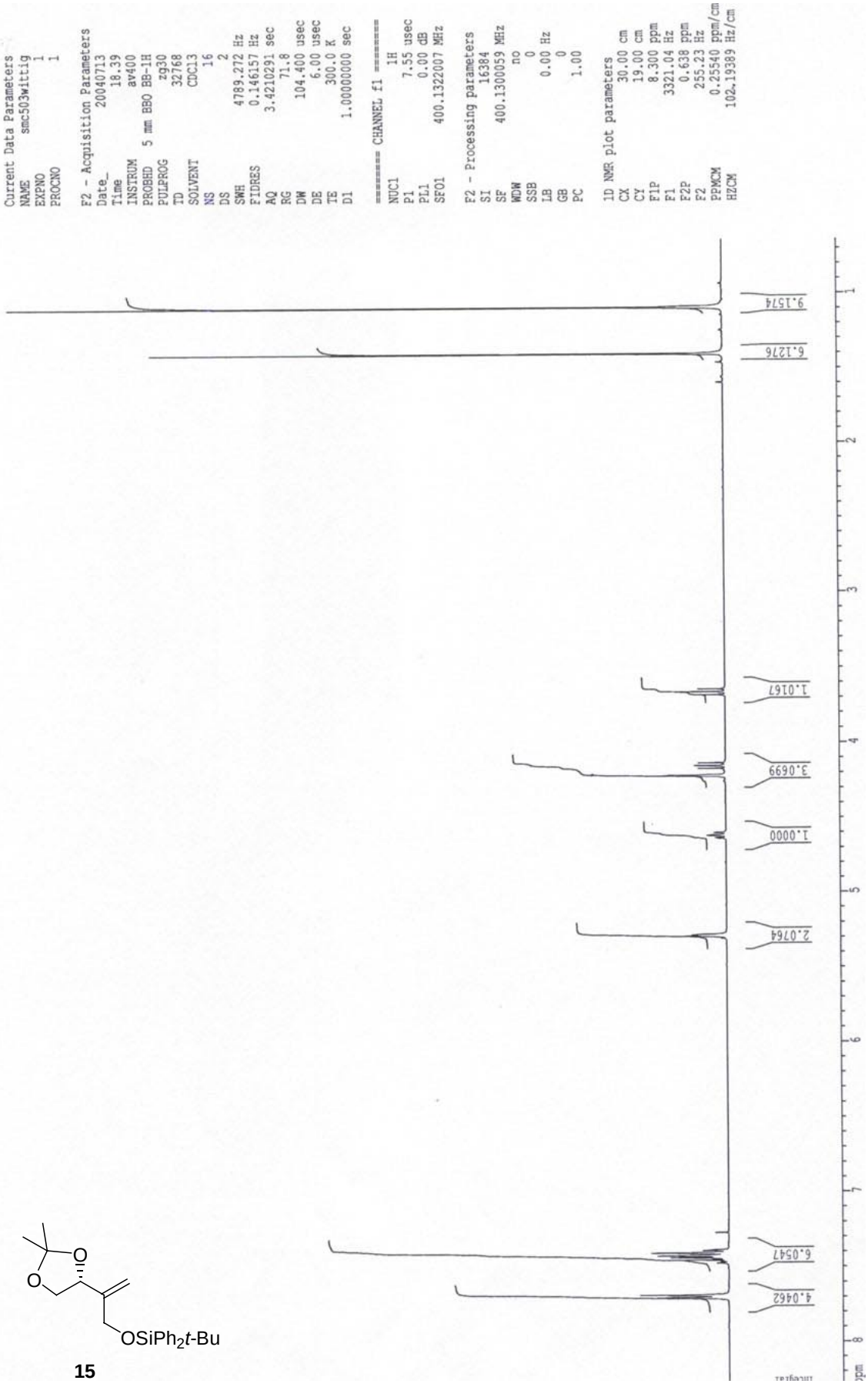
Iminosugar 3



3

Alcohol **24** (35 mg, 0.12 mmol, 1.0 eq) was stirred in 1 M HCl (2 mL) at 20 °C for 16 h. The resulting pale yellow solution was then concentrated *in vacuo* and the residue purified by

reverse-phase column chromatography (20% MeOH in water). The title compound was obtained as a colourless oil (20 mg, 91%). δ_H (400 MHz, D_2O) 4.39 (1 H, dt, *J* 5.6 and 4.1 Hz, 3-C**H**OH), 3.78 (1 H, ddd, *J* 9.6, 6.7 and 4.4 Hz, 1'-CH), 3.59 (1 H, dd, *J* 11.9 and 4.2 Hz, 2'-C**H**HOH), 3.52 (1 H, dd, *J* 12.2 and 8.2 Hz, 5-C**H**H), 3.49 (1 H, dd, *J* 11.9 and 6.9 Hz, 2'-CH**H**OH), 3.43 (1 H, dd, *J* 12.5 and 5.8 Hz, 2-C**H**H), 3.28 (1 H, dd, *J* 12.2 and 7.3 Hz, 5-CH**H**), 3.19 (1 H, dd, *J* 12.5 and 3.7 Hz, 2-CH**H**), 2.34 (1 H, m,2'- CH). δ_C (100 MHz, D_2O) 71.9 (3-CHOH), 70.2 (4'-CH), 64.1 (2-CH_2OH), 51.6 (2-**C**H_2), 47.7 (4-CH), 44.8 (5-CH_2). LRMS (ESI) 148 (100%). HRMS (ESI) required for $C_6H_{14}NO_3$ 148.0974, found 148.0983. $[\alpha]_D$ (c 1.00, MeOH) +31.6 at 28 °C.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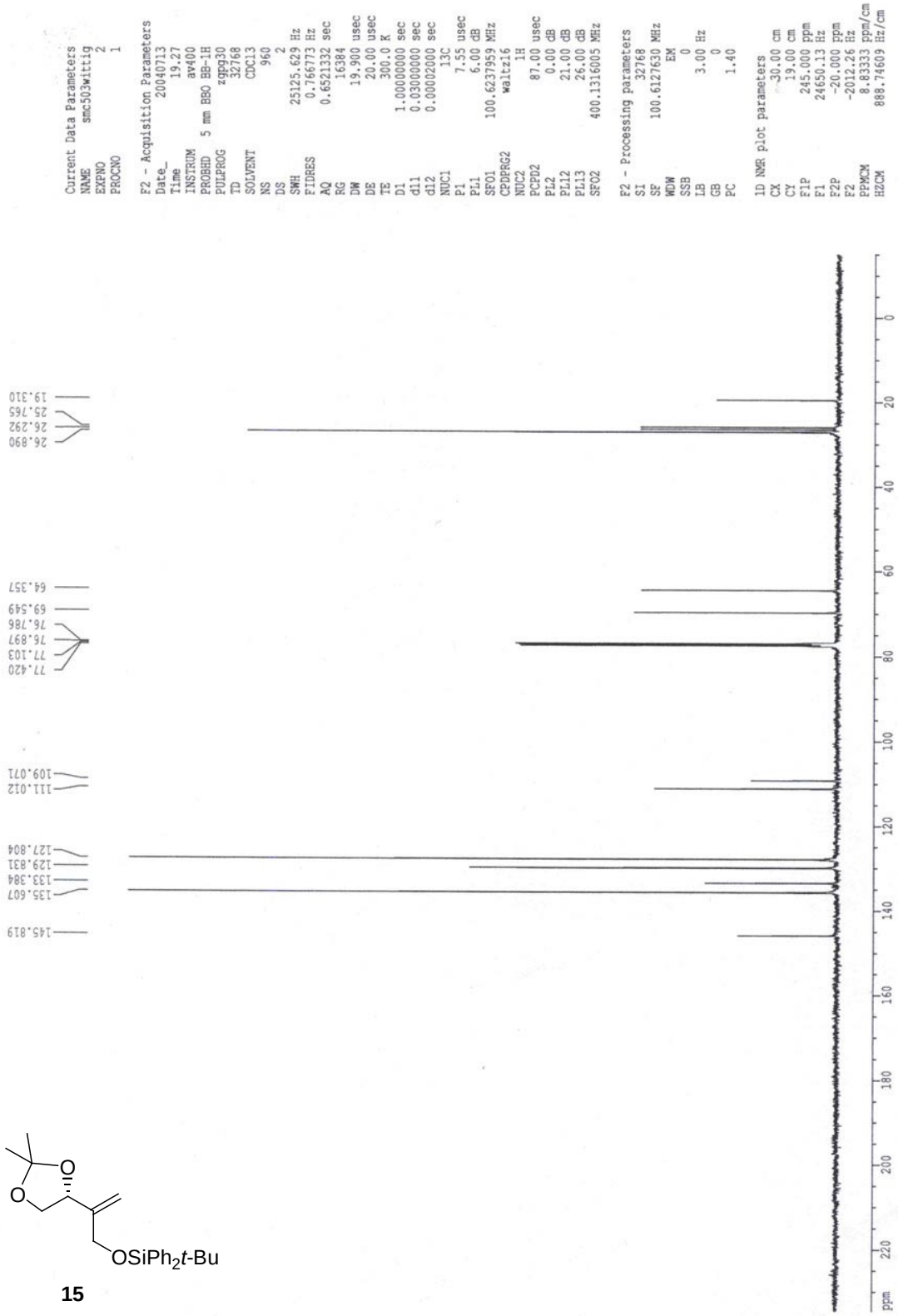
15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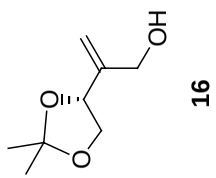

16

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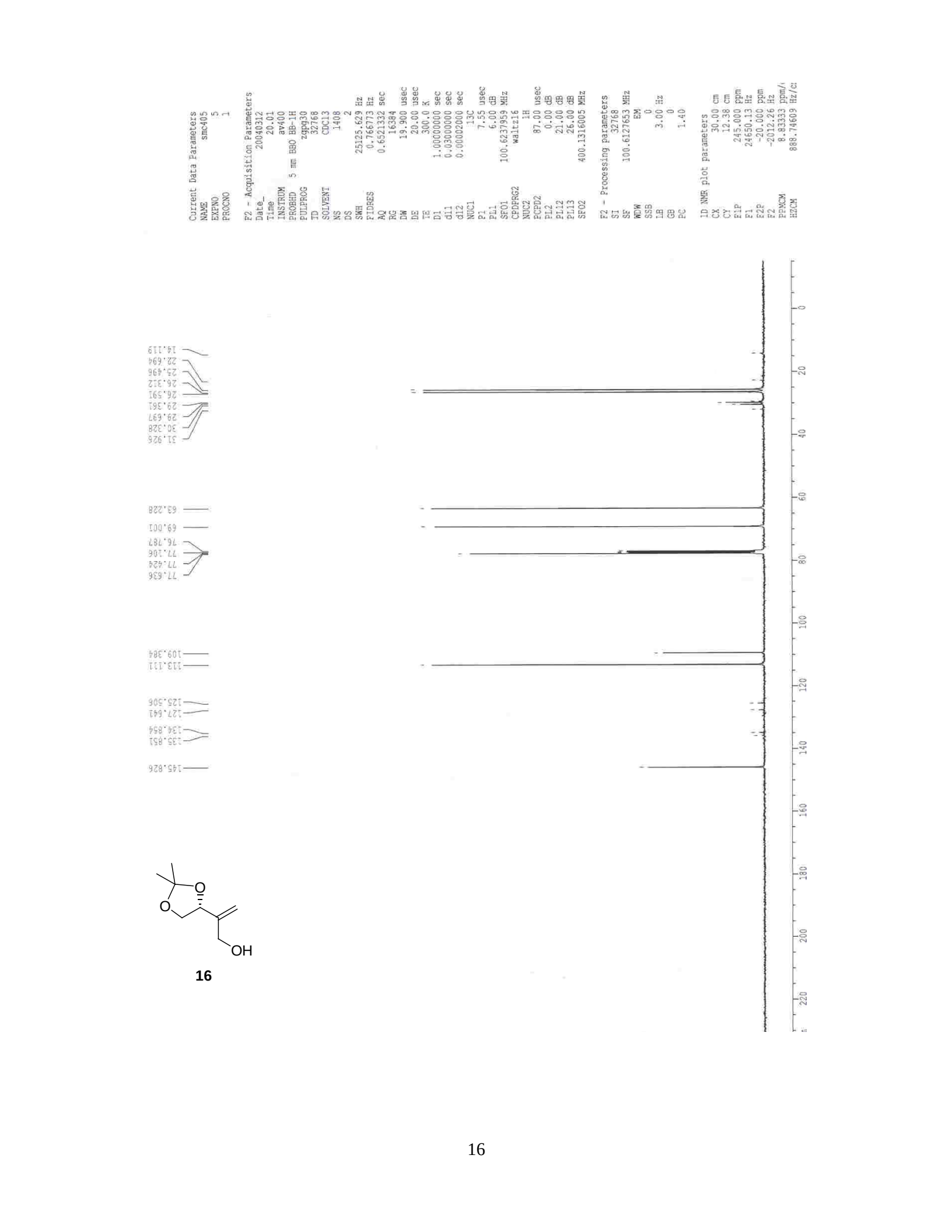
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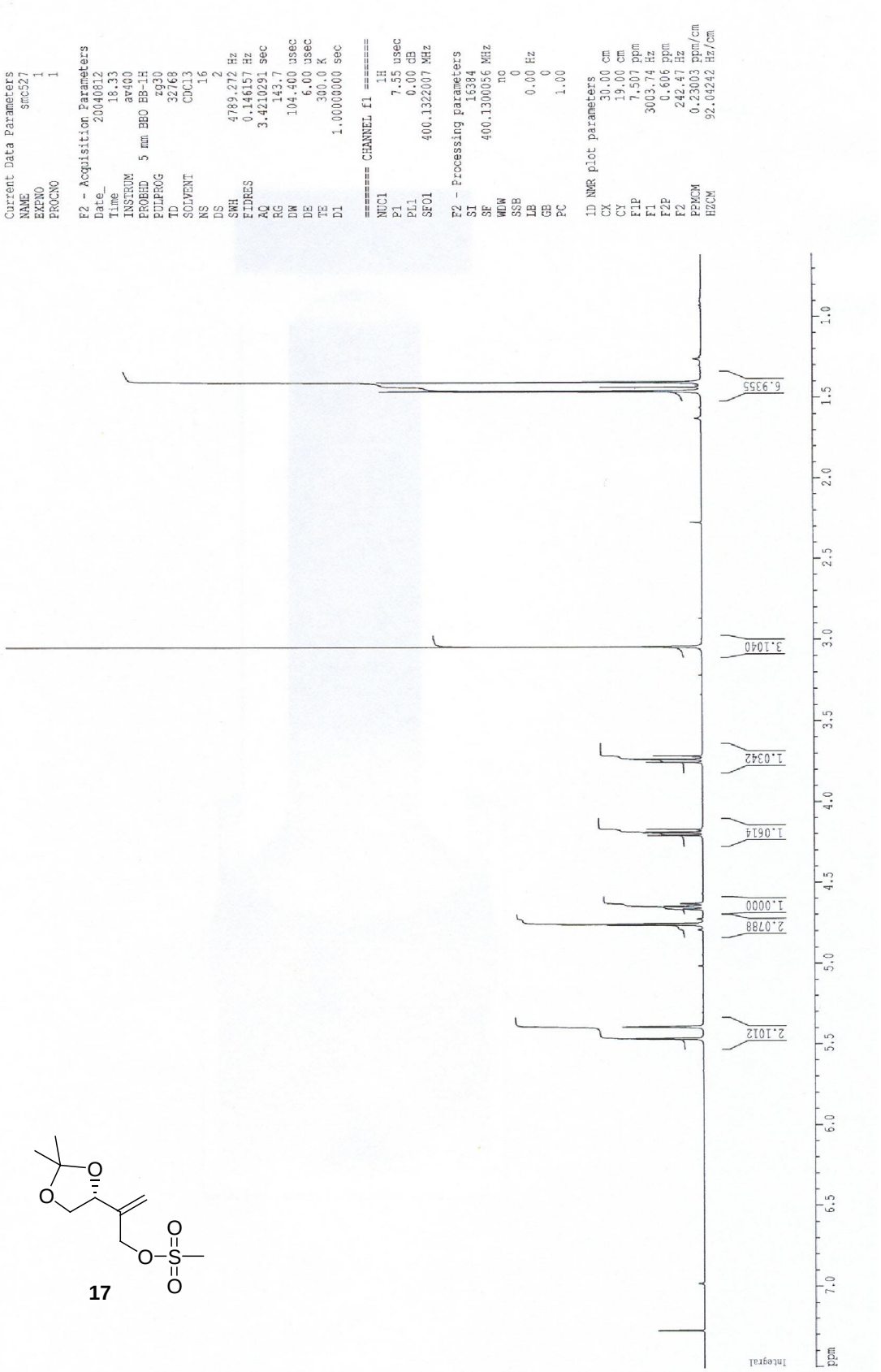
16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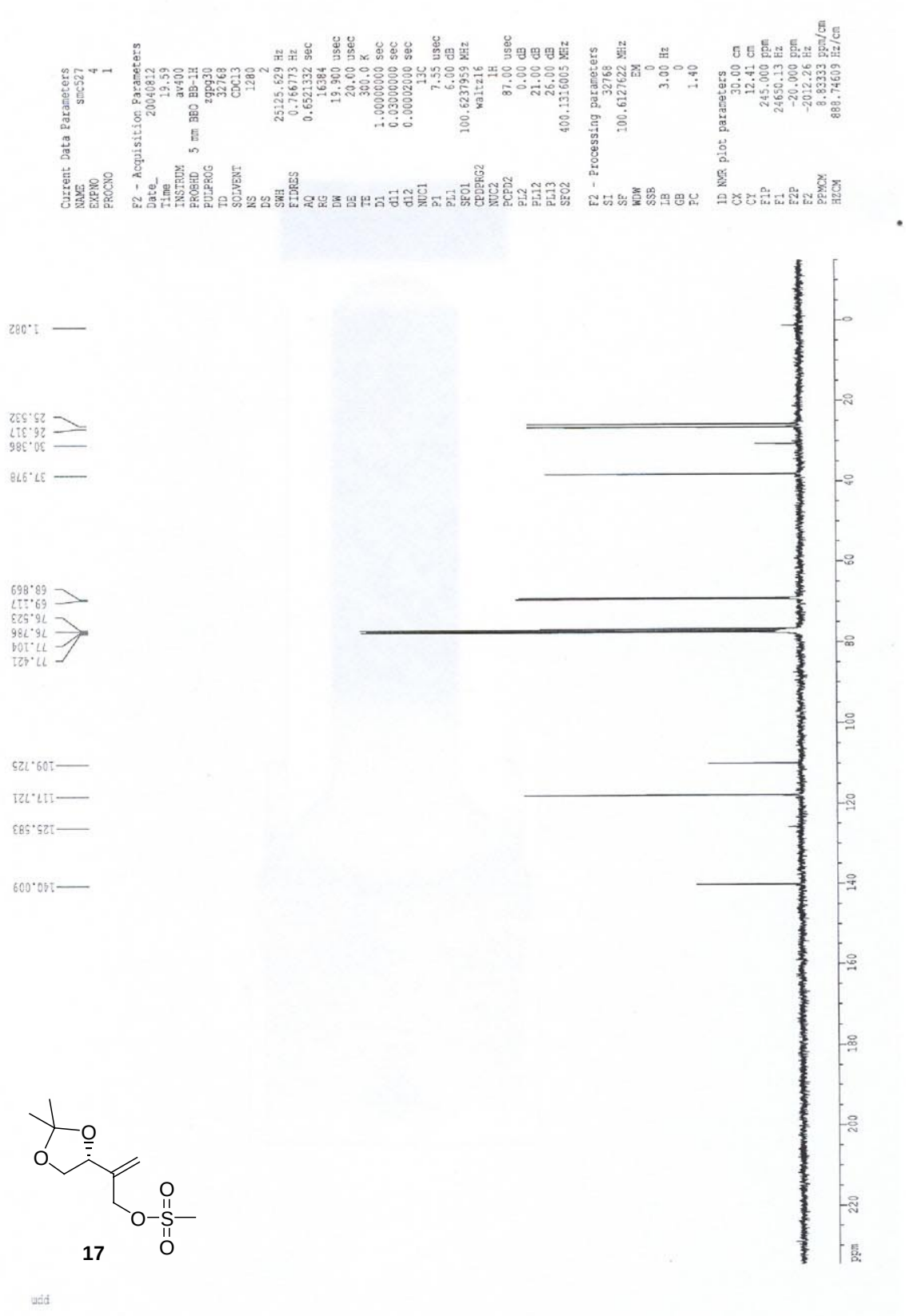
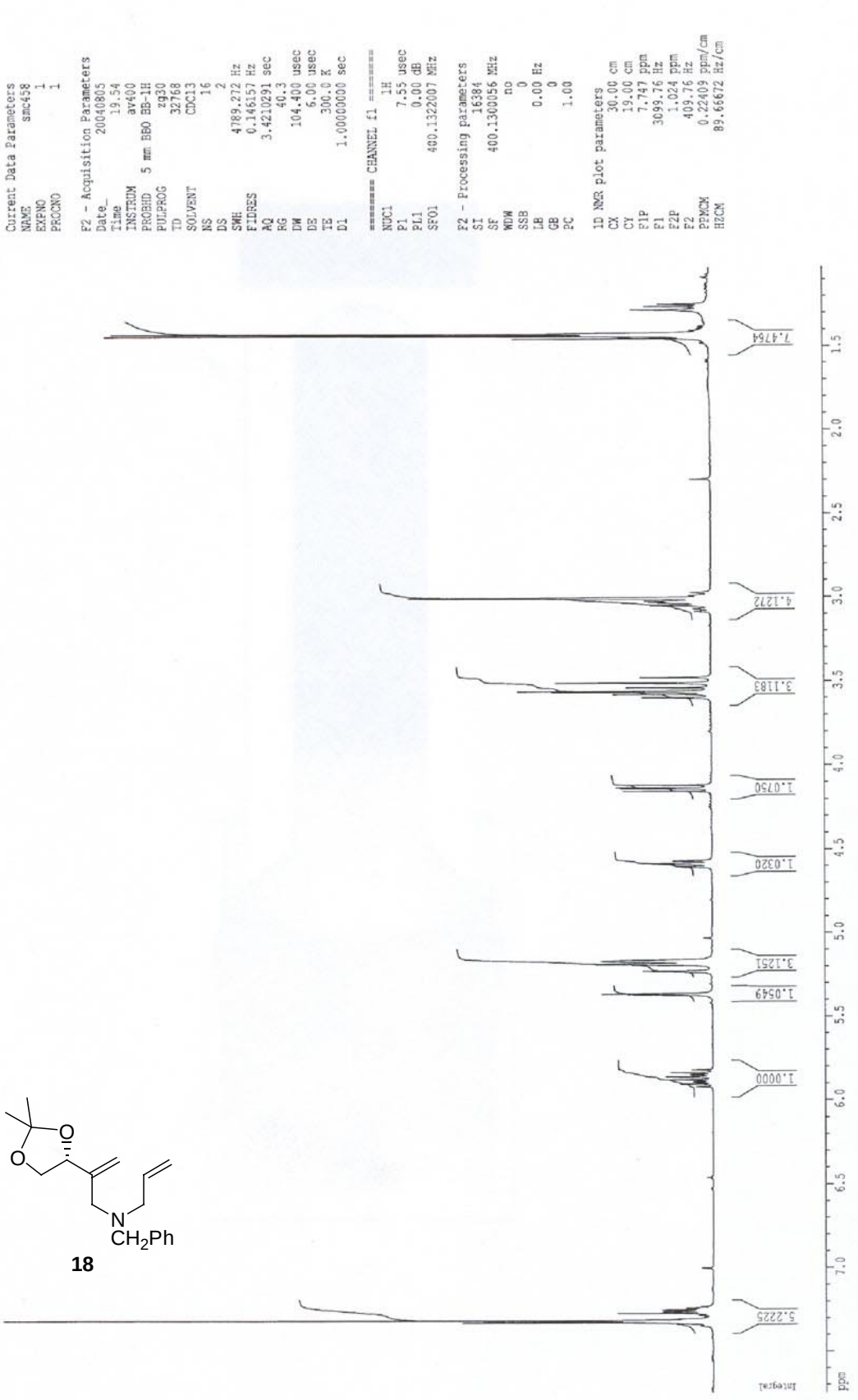
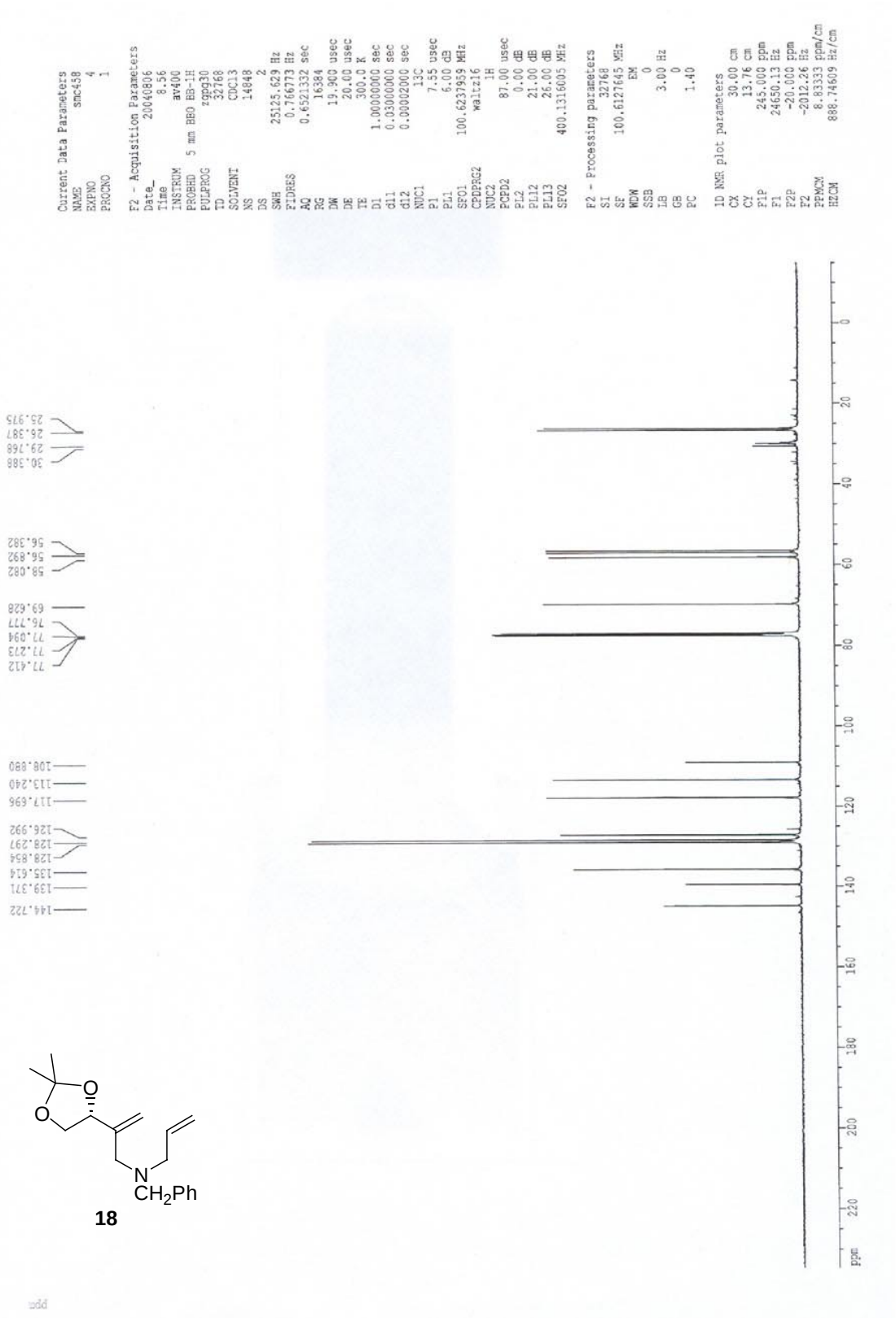
O

17


Current Data Parameters
NAME smc527
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20040812
Time 19.59
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1280
DS 2
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 16384
DW 19.900 usec
DE 20.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
NUC1 13C
P1 7.55 usec
PL1 6.00 dB
SFO1 100.6237959 MHz
CPDPRG2 waltz16
NUC2 1H
PCPD2 87.00 usec
PL2 0.00 dB
PL12 21.00 dB
PL13 26.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127622 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 30.00 cm
CY 12.41 cm
F1P 245.000 ppm
F1 24650.13 Hz
F2P -20.000 ppm
F2 -2012.26 Hz
PPMCM 8.93333 ppm/cm
HZCM 888.74609 Hz/cm
1.082
25.532
26.317
30.386
37.978
68.869
69.117
76.523
76.786
77.104
77.421
109.725
117.721
125.583
140.009
ppm
0
20
40
60
80
100
120
140
160
180
200
220
O
O
O
O
O
S
O
17

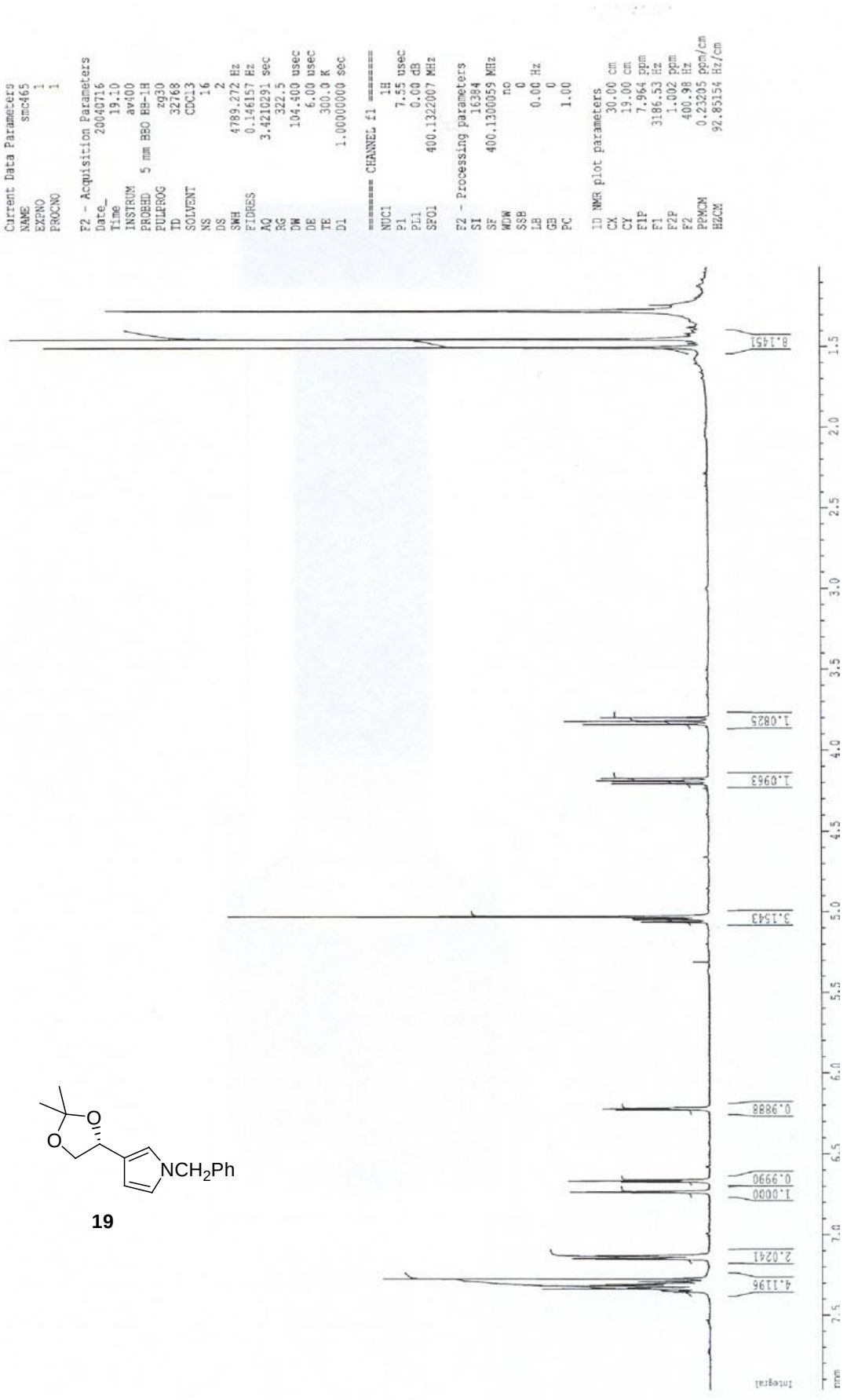

Current Data Parameters
NAME smc458
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20040805
Time 19.54
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 40.3
DW 104.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.55 usec
PL1 0.00 dB
SFO1 400.1322007 MHz
F2 - Processing parameters
SI 16384
SF 400.1300056 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 30.00 cm
CY 19.00 cm
F1P 7.747 ppm
F1 3099.76 Hz
F2P 1.024 ppm
F2 409.76 Hz
PPMCM 0.22409 ppm/cm
HZCM 89.66672 Hz/cm
7.4764
4.1272
3.1183
1.0750
1.0320
3.1251
1.0549
1.0000
5.2225
Integral
ppm
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
O
O
N
CH2Ph

18

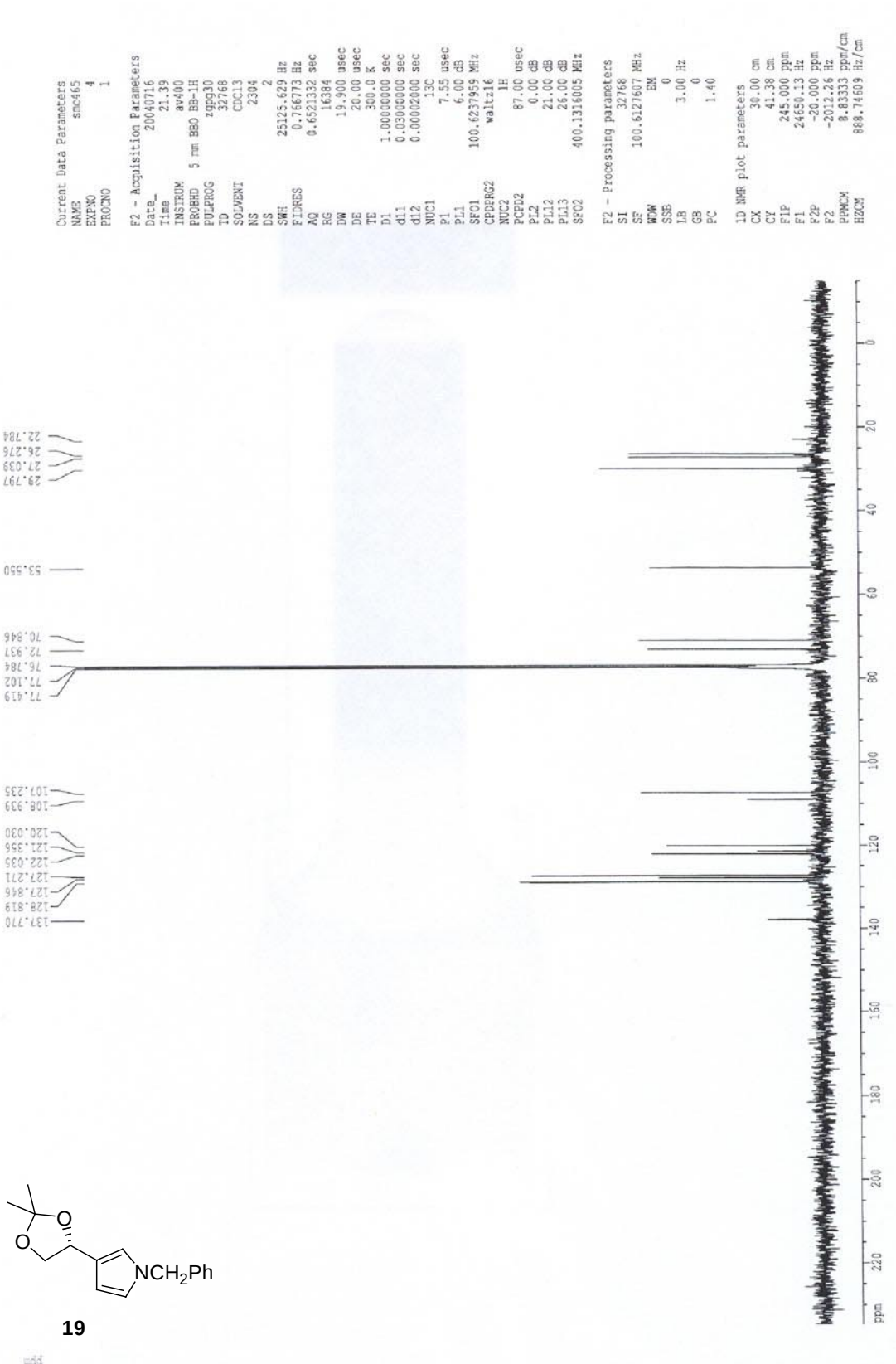

Current Data Parameters
NAME smc458
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20040806
Time 8.56
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1404
DS 2
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 16384
DW 19.900 usec
DE 20.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
NUC1 13C
P1 7.55 usec
PL1 6.00 dB
SFO1 100.6237959 MHz
CPDPRG2 waltz16
NUC2 1H
PCPD2 87.00 usec
PL2 0.00 dB
PL12 21.00 dB
PL13 26.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127645 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 30.00 cm
CY 13.76 cm
F1P 245.000 ppm
F1 24650.13 Hz
F2P -20.000 ppm
F2 -2012.26 Hz
PPMCM 8.83333 ppm/cm
HZCM 888.74609 Hz/cm
25.975
26.387
29.768
30.388
56.382
56.892
58.082
69.628
76.777
77.094
77.213
77.412
108.880
113.240
117.696
126.992
128.297
128.854
135.614
139.371
144.722
0
20
40
60
80
100
120
140
160
180
200
220
ppm

O
O
N
CH2Ph

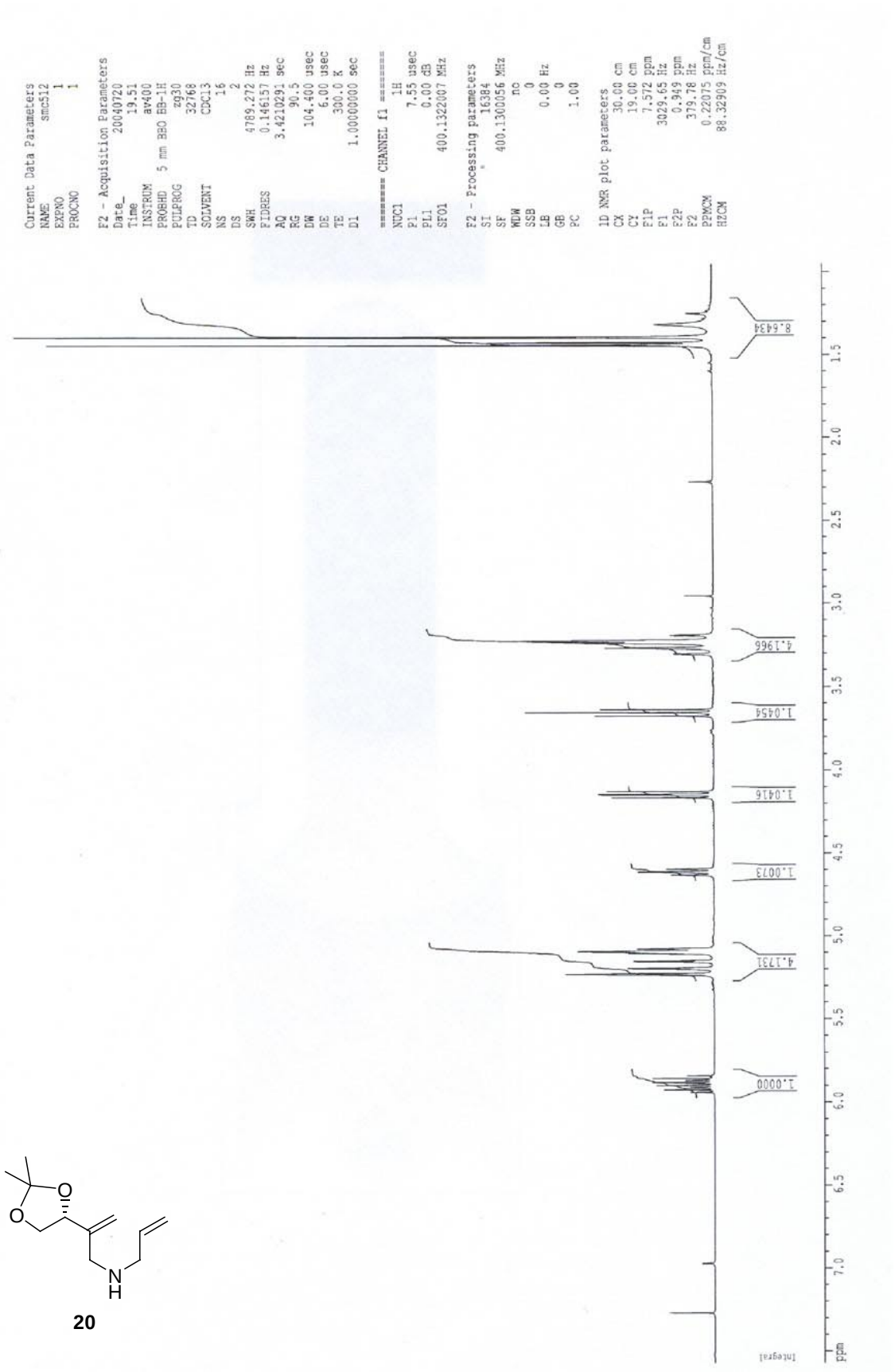
18


Current Data Parameters
NAME smc465
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20040716
Time 19.10
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 322.5
DW 104.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.55 usec
PL1 0.00 dB
SFO1 400.1322007 MHz
F2 - Processing parameters
SI 16384
SF 400.1300059 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 30.00 cm
CY 19.00 cm
F1P 7.964 ppm
F1 3186.53 Hz
F2P 1.002 ppm
F2 400.98 Hz
PPMCM 0.23205 ppm/cm
HZCM 92.85154 Hz/cm
8.1451
1.0825
1.0963
3.1543
0.9888
0.9990
1.0000
2.0241
4.1196
Integral
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
O
O
NCH2Ph

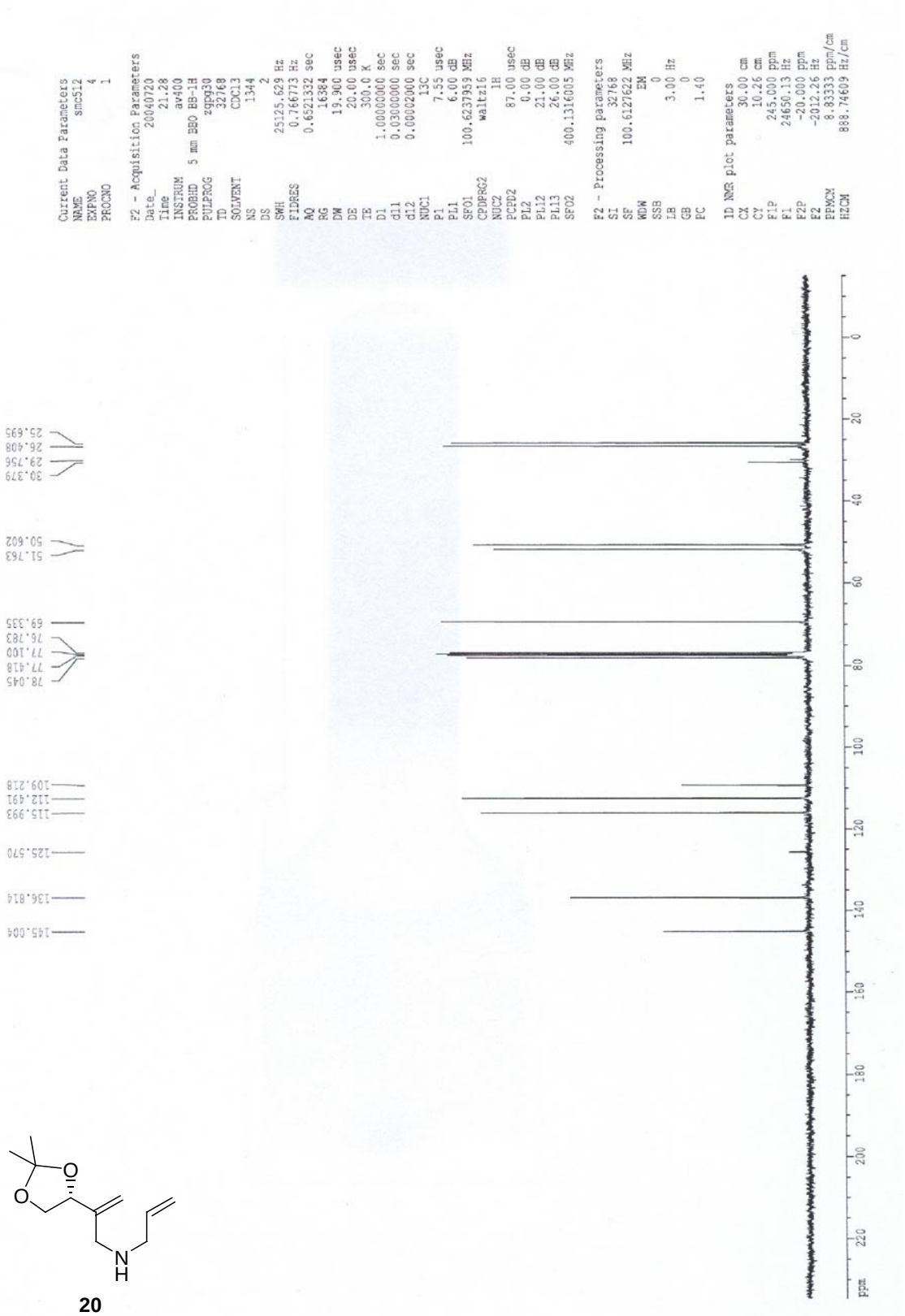
19


Current Data Parameters
NAME smc465
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20040716
Time 21.39
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 2
DS 2
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 16384
DW 19.900 usec
DE 20.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
NUC1 13C
P1 7.55 usec
PL1 6.00 dB
SFO1 100.6237959 MHz
CPDPRG2 waltz16
NUC2 1H
PCPD2 87.00 usec
PL2 0.00 dB
PL12 21.00 dB
PL13 26.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127607 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 30.00 cm
CY 41.38 cm
F1P 245.000 ppm
F1 24650.13 Hz
F2P -20.000 ppm
F2 -2012.26 Hz
PPMCM 8.83333 ppm/cm
HZCM 888.74609 Hz/cm
22.784
26.276
27.039
29.797
53.550
70.846
72.937
76.784
77.102
77.419
107.235
108.939
120.030
121.356
122.035
127.271
127.846
128.819
137.770
ppm
220
200
180
160
140
120
100
80
60
40
20
0
O
O
NCH2Ph

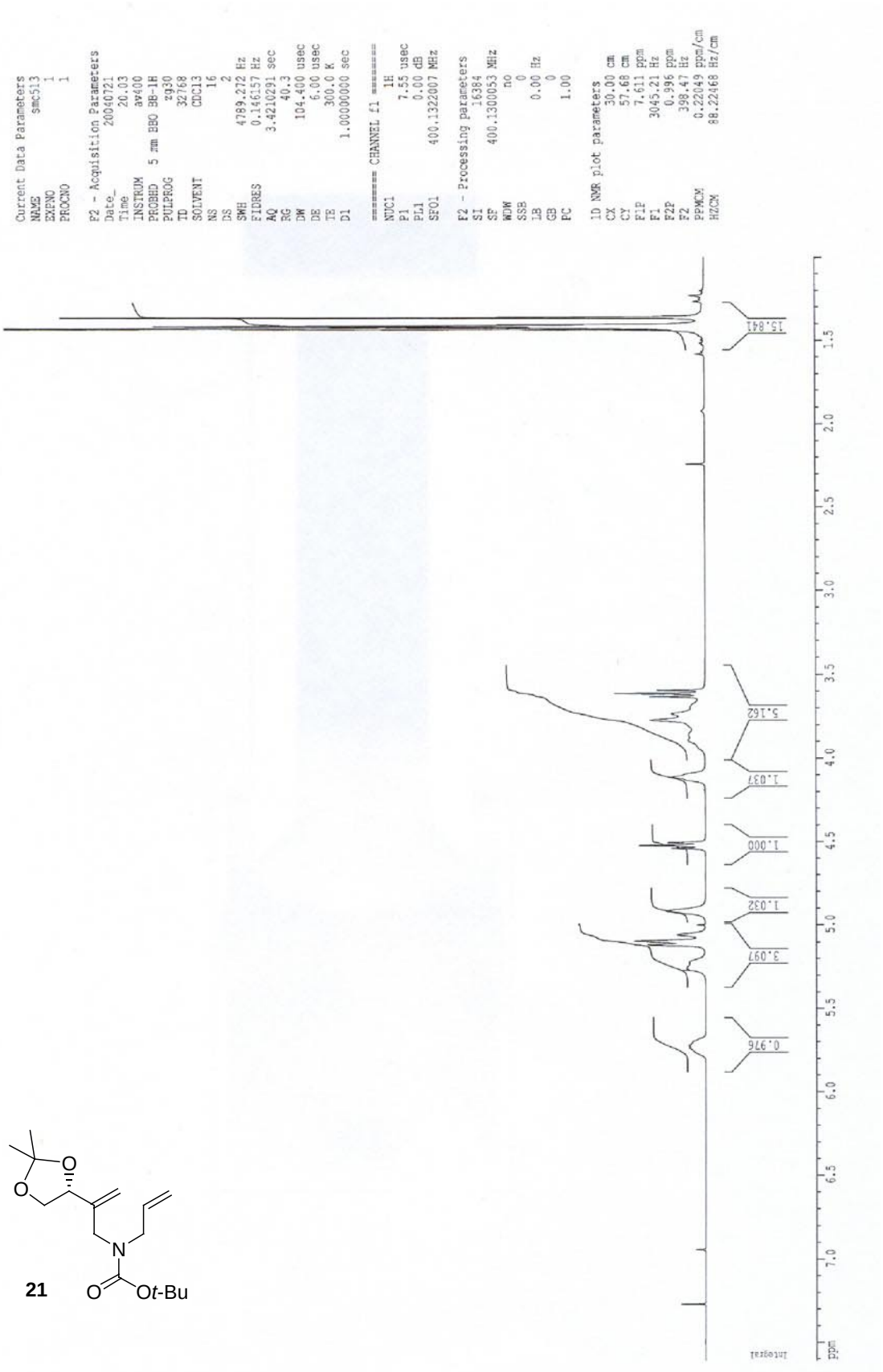
19


Current Data Parameters
NAME smc512
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20040720
Time 19.51
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 90.5
DW 104.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.55 usec
PL1 0.00 dB
SFO1 400.1322007 MHz
F2 - Processing parameters
SI 16384
SF 400.1300056 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 30.00 cm
CY 19.00 cm
F1P 7.572 ppm
F1 3029.65 Hz
F2P 0.949 ppm
F2 379.78 Hz
PPMCM 0.22075 ppm/cm
HZCM 88.32909 Hz/cm
8.6434
4.1966
1.0454
1.0416
1.0073
4.1731
1.0000
Integral
ppm
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

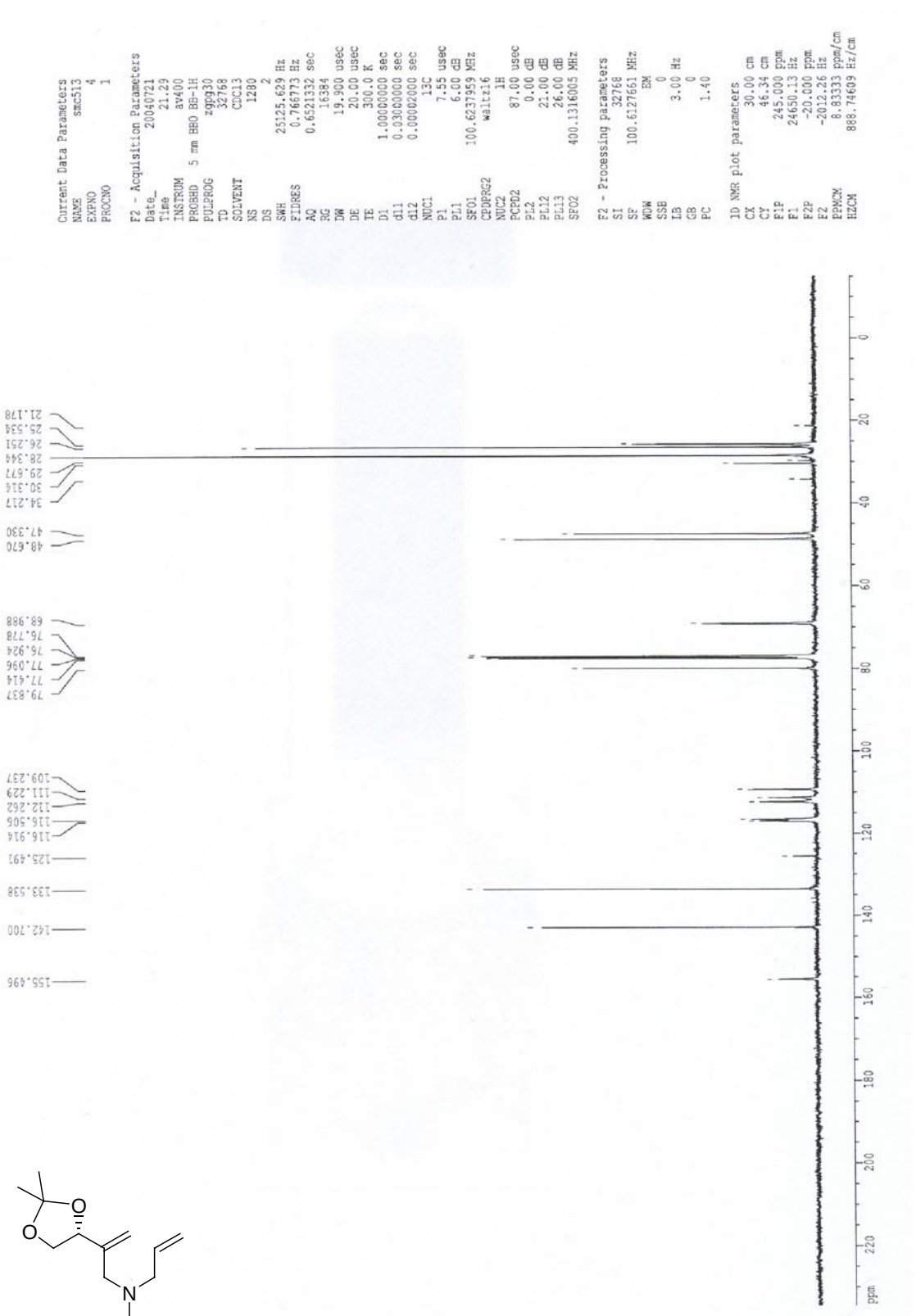
20


Current Data Parameters
NAME smc512
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20040720
Time 21.28
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1344
DS 2
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 16384
DW 19.900 usec
DE 20.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
NUC1 13C
P1 7.55 usec
PL1 6.00 dB
SFO1 100.6237959 MHz
CPDPRG2 waltz16
NUC2 1H
PCPD2 87.00 usec
PL2 0.00 dB
PL12 21.00 dB
PL13 26.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127622 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 30.00 cm
CY 10.26 cm
F1P 245.000 ppm
F1 24650.13 Hz
F2P -20.000 ppm
F2 -2012.26 Hz
PPMCM 8.83333 ppm/cm
HZCM 888.74609 Hz/cm
25.695
26.408
28.756
30.379
50.602
51.763
69.335
76.783
77.100
77.418
78.045
109.218
112.491
115.993
125.570
136.814
145.004
ppm
0
20
40
60
80
100
120
140
160
180
200
220

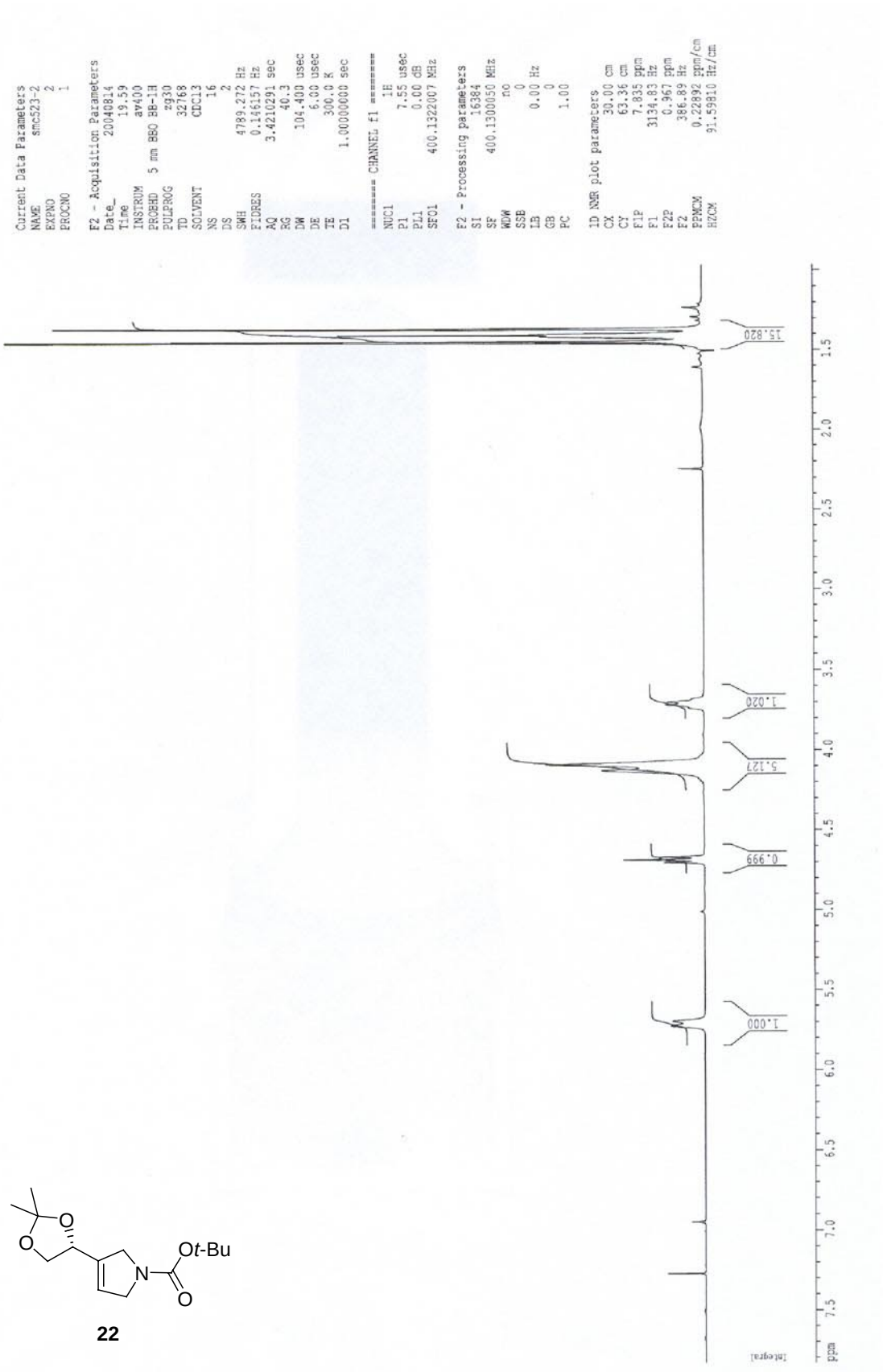
20


Current Data Parameters
NAME smc513
EXPNO 1
PROCNO 1
P2 - Acquisition Parameters
Date_ 20040721
Time 20.03
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 40.3
DW 104.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.55 usec
PL1 0.00 dB
SFO1 400.1322007 MHz
F2 - Processing parameters
SI 16384
SF 400.1300053 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 30.00 cm
CY 57.68 cm
F1P 7.611 ppm
F1 3045.21 Hz
F2P 0.996 ppm
F2 398.47 Hz
PPMCM 0.22049 ppm/cm
HZCM 88.22468 Hz/cm
15.841
5.162
1.037
1.000
1.032
3.097
0.976
Integral
ppm
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

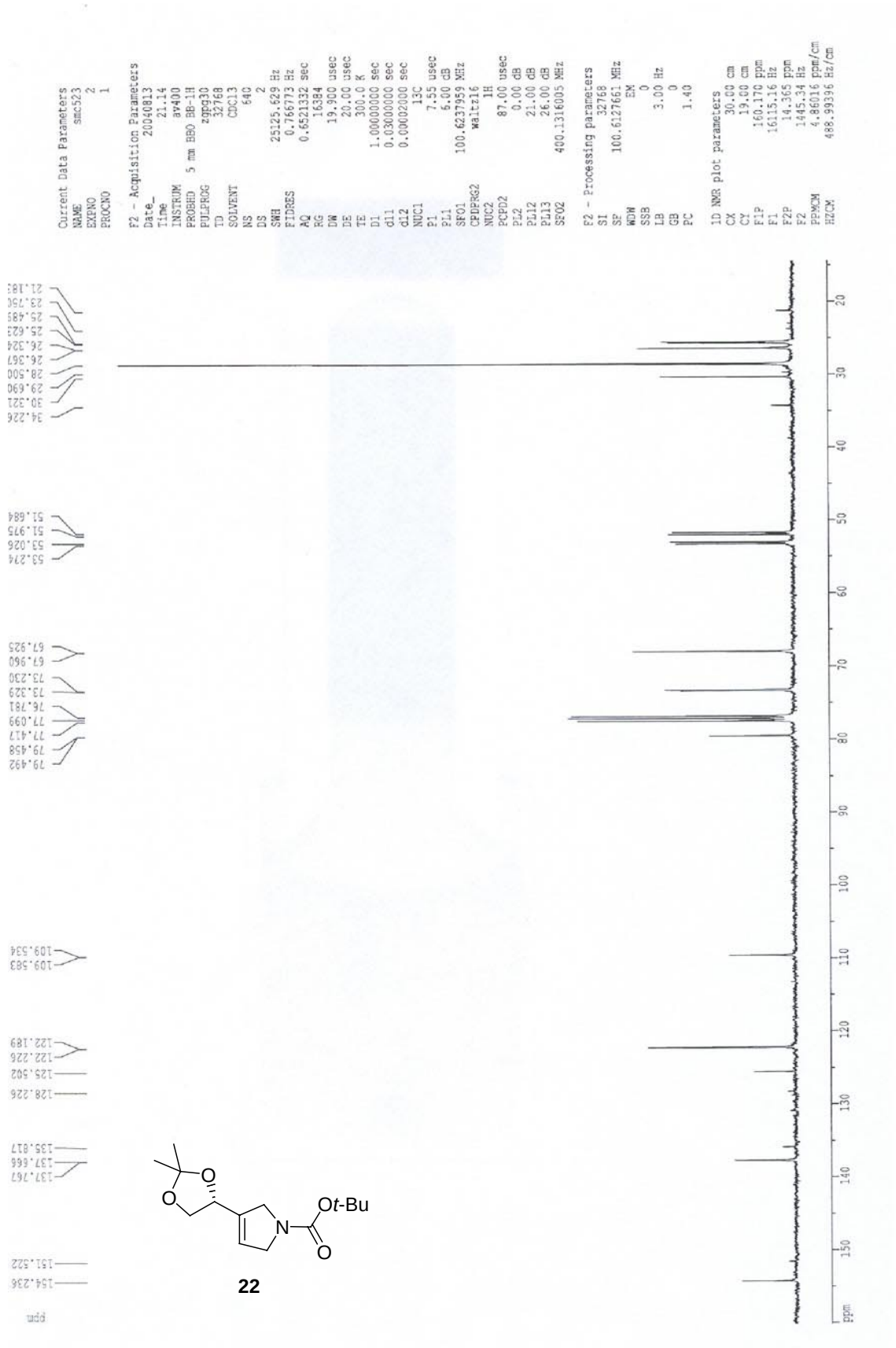
21


Current Data Parameters
NAME smc513
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20040721
Time 21.29
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1280
DS 2
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 16384
DW 19.900 usec
DE 20.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
NUC1 13C
P1 7.55 usec
PL1 6.00 dB
SFO1 100.6237959 MHz
CPDPRG2 waltz16
NUC2 1H
PCPD2 87.00 usec
PL2 0.00 dB
PL12 21.00 dB
PL13 26.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127651 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 30.00 cm
CY 46.34 cm
F1P 245.000 ppm
F1 24650.13 Hz
F2P -20.000 ppm
F2 -2012.26 Hz
PPMCM 8.83333 ppm/cm
HZCM 888.74609 Hz/cm
21.178
25.534
26.251
28.344
29.677
30.314
34.217
47.330
48.670
68.988
76.778
76.924
77.096
77.414
79.837
109.237
111.229
112.262
116.506
116.914
125.491
133.598
142.700
155.496
ppm
0
20
40
60
80
100
120
140
160
180
200
220
O
O
N
O
Ot-Bu

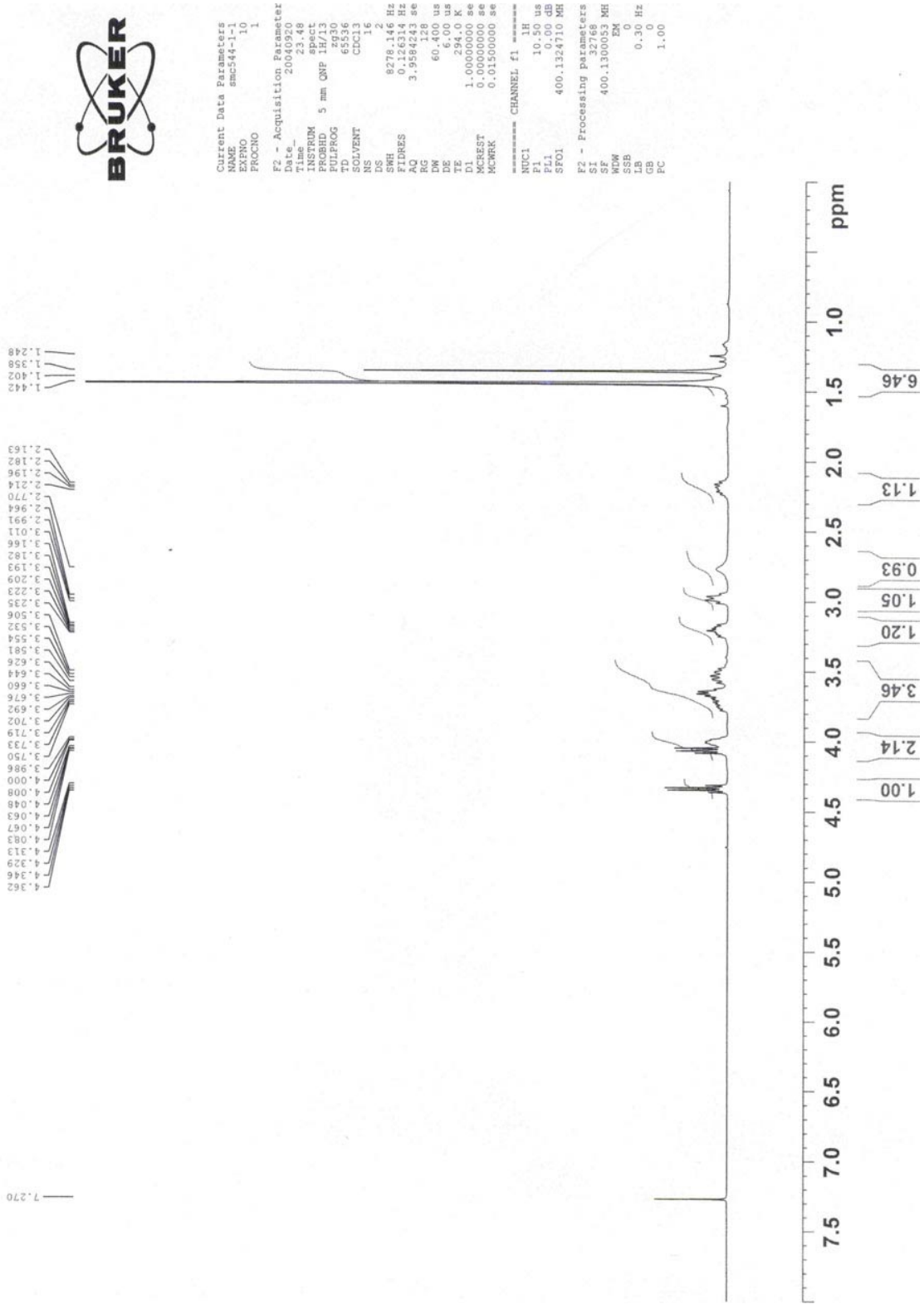
21

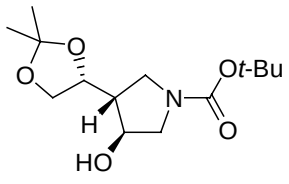

Current Data Parameters
NAME smc523-2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20040814
Time 19.59
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 40.3
DW 104.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.55 usec
PL1 0.00 dB
SFO1 400.1322007 MHz
F2 - Processing parameters
SI 16384
SF 400.1300050 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 30.00 cm
CY 63.36 cm
F1P 7.835 ppm
F1 3134.83 Hz
F2P 0.967 ppm
F2 386.89 Hz
PPMCM 0.22892 ppm/cm
HZCM 91.59810 Hz/cm
15.820
1.020
5.127
0.999
1.000
Integral
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
O
O
N
O
Ot-Bu

22

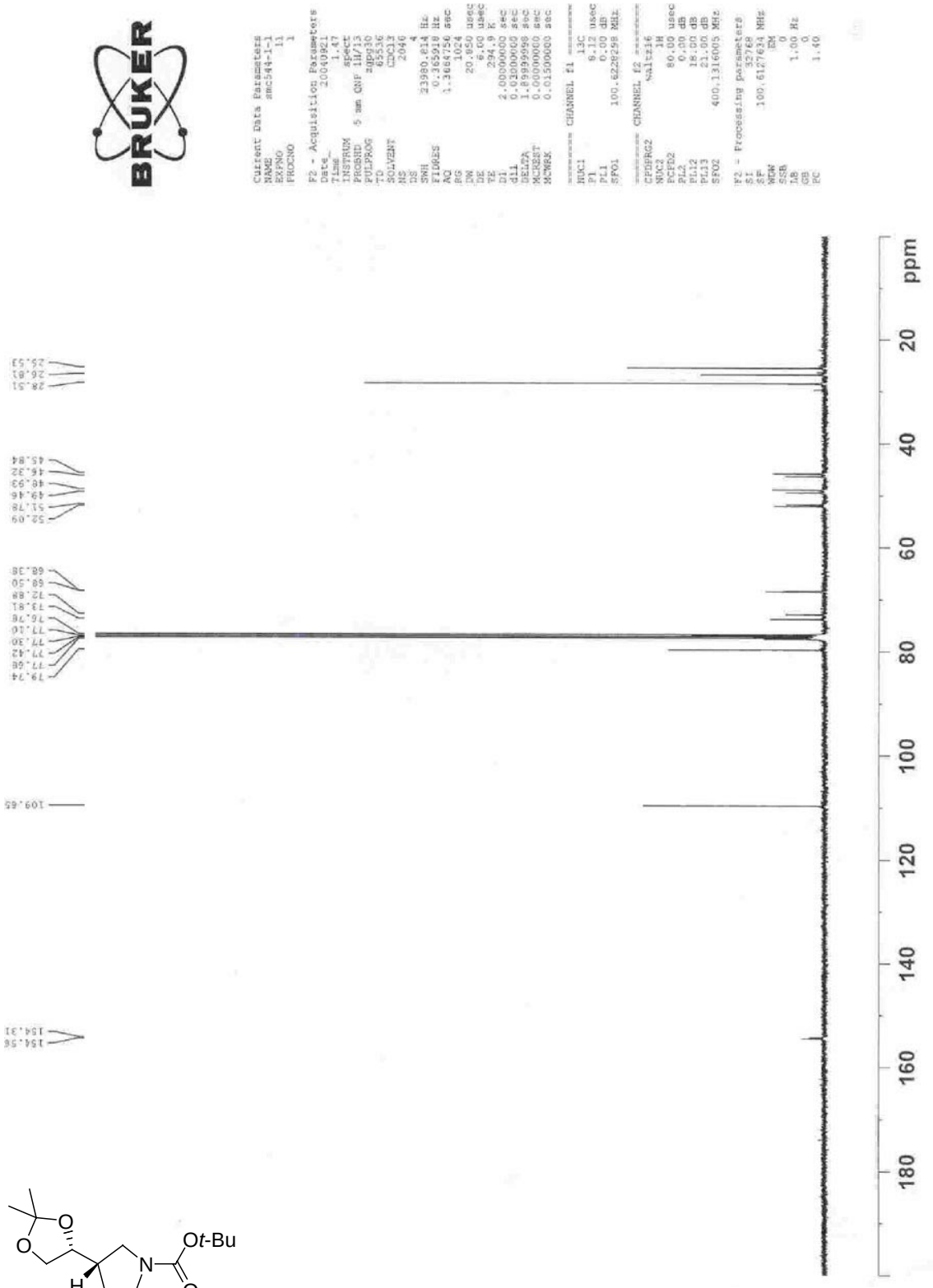

Current Data Parameters
NAME smc523
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20040813
Time 21.14
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 640
DS 2
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 16384
DW 19.900 usec
DE 20.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
NUC1 13C
P1 7.55 usec
PL1 6.00 dB
SFO1 100.6237959 MHz
CPDPRG2 waltz16
NUC2 1H
PCPD2 87.00 usec
PL2 0.00 dB
PL12 21.00 dB
PL13 26.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127661 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 30.00 cm
CY 19.00 cm
F1P 160.170 ppm
F1 16115.16 Hz
F2P 14.365 ppm
F2 1445.34 Hz
PPMCM 4.86016 ppm/cm
HZCM 488.99396 Hz/cm
21.181
23.756
25.485
25.623
26.324
26.367
28.500
29.690
30.321
34.226
51.684
51.975
53.026
53.274
67.925
67.960
73.230
73.329
76.781
77.099
77.417
79.458
79.492
109.534
109.583
122.189
122.226
125.502
128.226
135.817
137.666
137.767
151.522
154.236
ppm
O
O
N
O
Ot-Bu

22

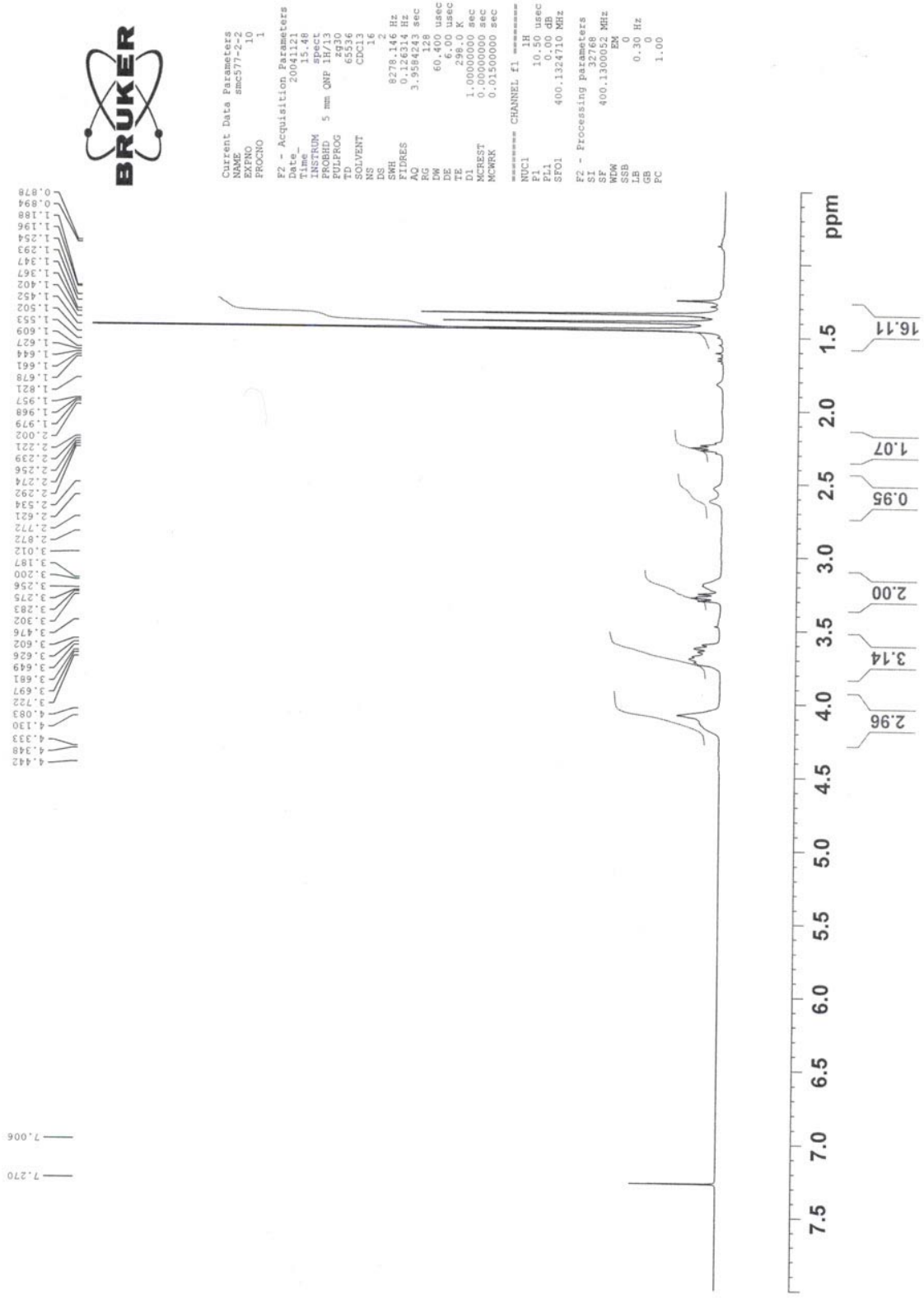

BRUKER
Current Data Parameters
NAME smc544-1-1
EXPNO 10
PROCNO 1
F2 - Acquisition Parameter
Date_ 20040920
Time 23.48
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 se
RG 128
DW 60.400 us
DE 6.00 us
TE 294.0 K
D1 1.00000000 se
MCREST 0.00000000 se
MCWRK 0.01500000 se
======== CHANNEL f1 ========
NUC1 1H
P1 10.50 us
PL1 0.00 dB
SFO1 400.1324710 MH
F2 - Processing parameters
SI 32768
SF 400.1300053 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm
6.46
1.13
0.93
1.05
1.20
3.46
2.14
1.00

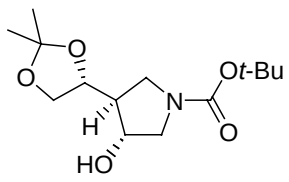

O
O
H
HO
N
O
Ot-Bu

23

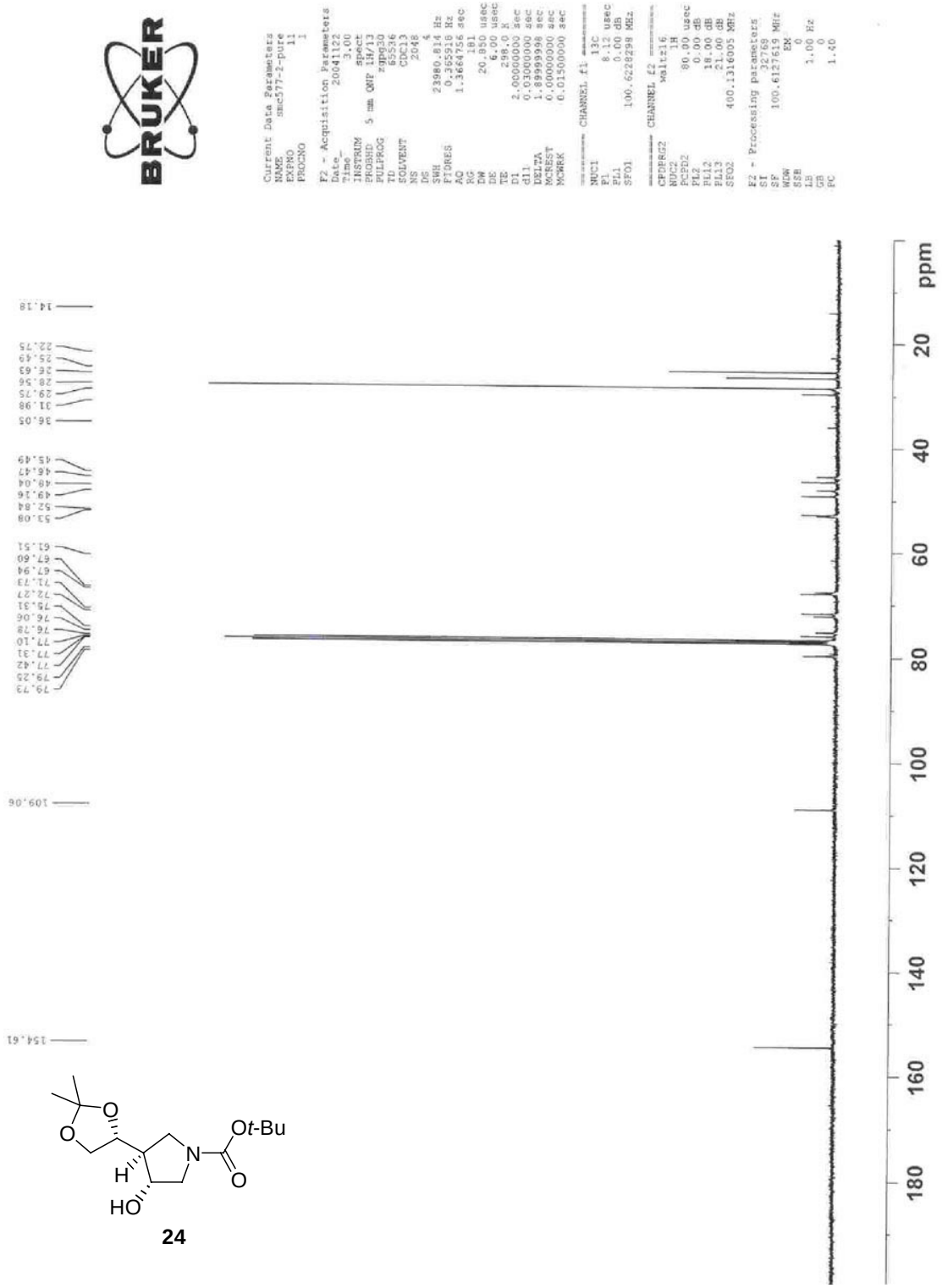

BRUKER
Current Data Parameters
NAME amc544-1-1
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20040921
Time 1.47
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2046
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664736 sec
RG 1024
DW 20.850 usec
DE 6.00 usec
TE 294.0 K
D1 2.0000000 sec
d11 0.0300000 sec
DELTA 1.8999999 sec
MCREST 0.0000000 sec
MCWRK 0.0150000 sec
CHANNEL f1
NUC1 13C
P1 9.12 usec
PL1 0.00 dB
SFO1 100.6229259 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 18.00 dB
PL13 21.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127634 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
ppm
20
40
60
80
100
120
140
160
180
25.53
26.81
28.51
45.84
46.32
48.93
49.46
51.78
52.09
68.38
69.50
72.88
73.81
76.78
77.10
77.30
77.42
77.68
79.74
109.65
154.31
154.56
O
O
H
HO
N
O
Ot-Bu

23

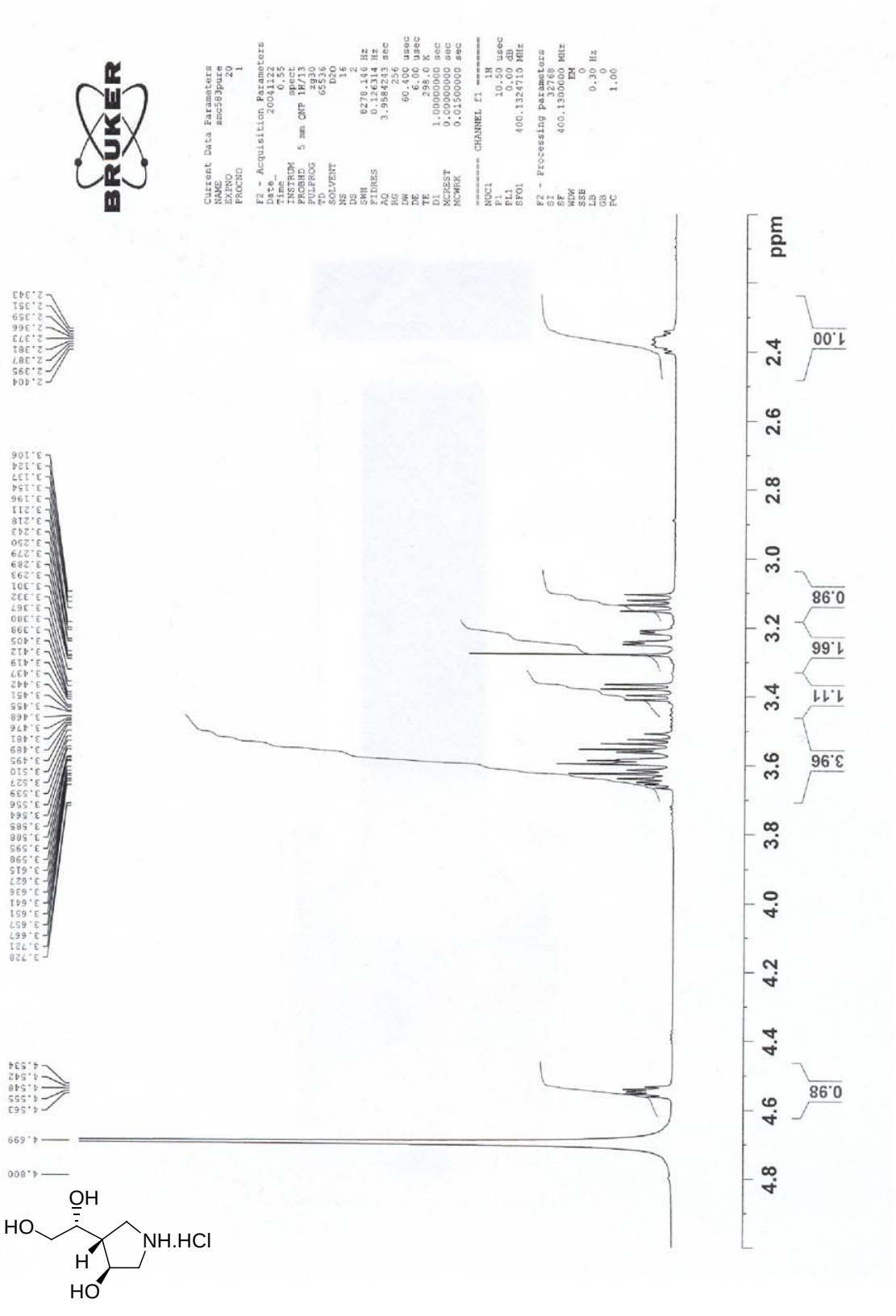

BRUKER
Current Data Parameters
NAME smc577-2-2
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20041121
Time 15.48
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 128
DW 60.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 10.50 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300052 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm
16.11
1.07
0.95
2.00
3.14
2.96
7.270
7.006


O
O
Ot-Bu
N
O
H
HO

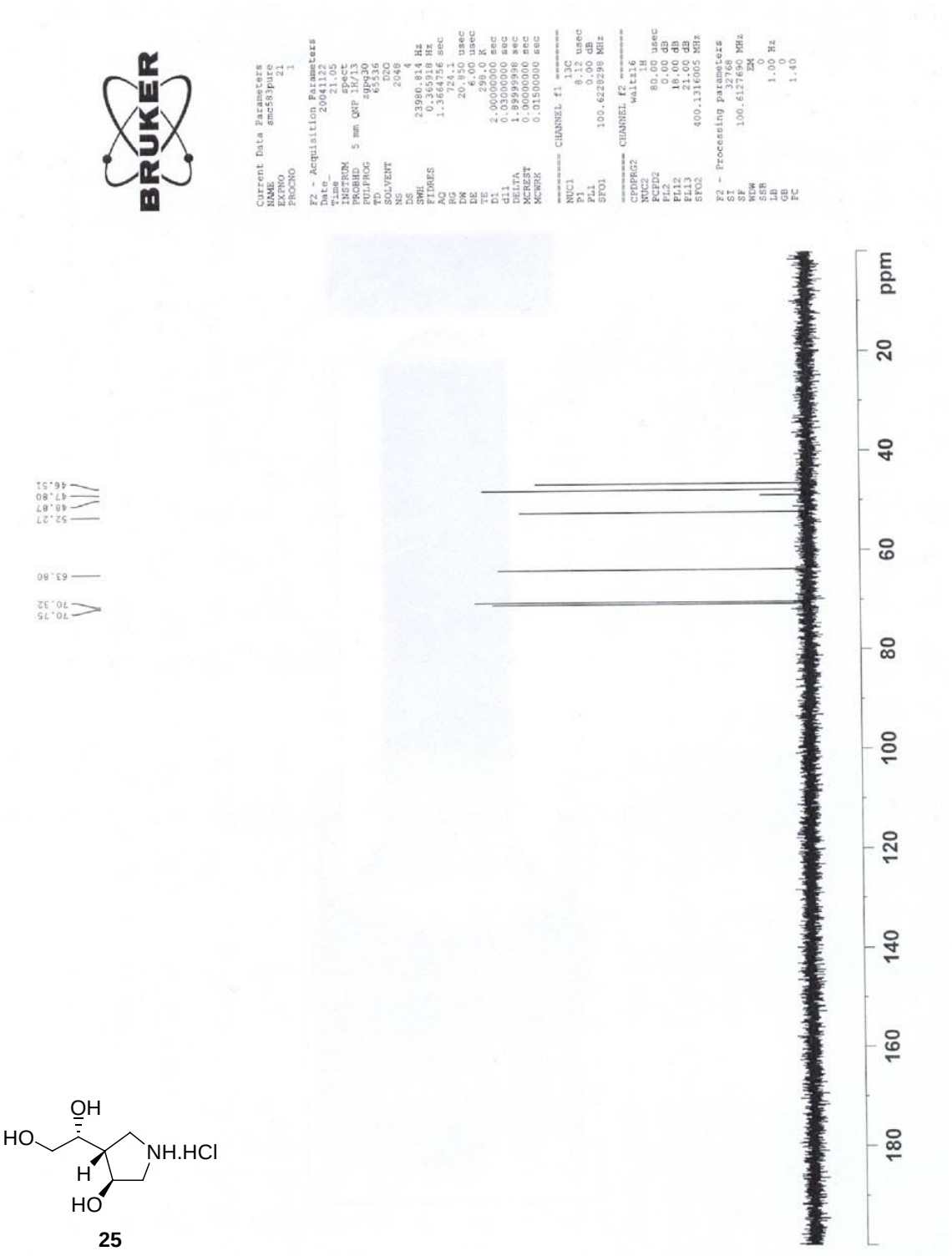
24


Current Data Parameters
NAME sme577-2-pure
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20041122
Time 3.00
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2048
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 101
DW 20.850 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
CHANNEL f1
NUC1 13C
P1 8.12 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 18.00 dB
PL13 21.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127619 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
14.18
22.75
25.49
26.63
28.56
29.75
31.98
36.05
45.49
46.47
48.04
49.16
52.84
53.08
61.51
67.60
67.94
71.73
72.27
75.31
76.06
76.78
77.10
77.31
77.42
79.25
79.73
109.06
154.61
O
O
O
Ot-Bu
N
H
HO
ppm
20
40
60
80
100
120
140
160
180

24

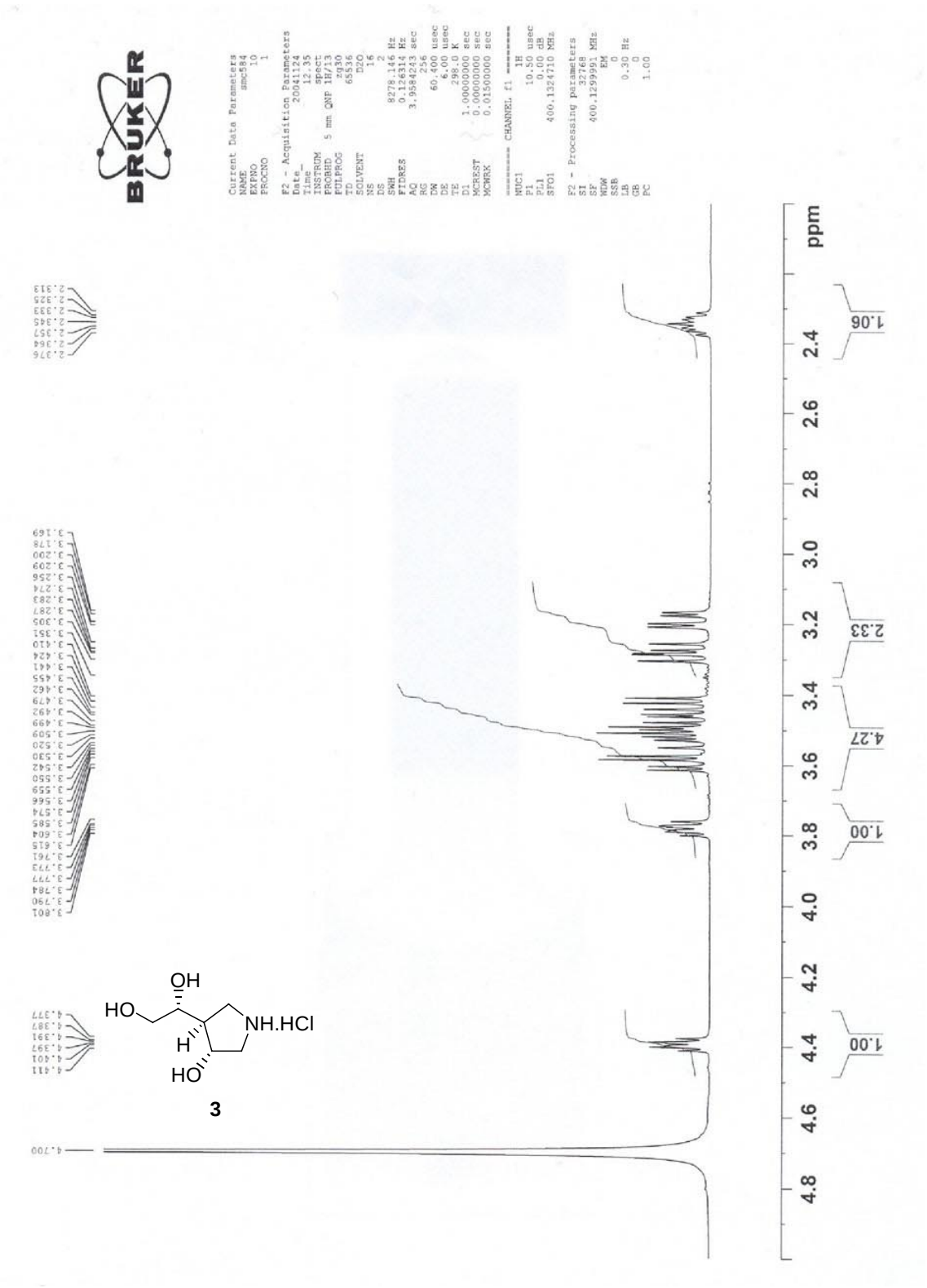

BRUKER
ppm
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
0.98
3.96
1.11
1.66
0.98
1.00
OH
HO
NH.HCl
H
HO

25


BRUKER
Current Data Parameters
NAME smc583pure
EXPNO 21
PROCNO 1
F2 - Acquisition Parameters
Date_ 20041122
Time 21.05
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT D2O
NS 2048
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 724.1
DW 20.850 usec
DE 6.00 usec
TE 299.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.12 usec
PL1 0.00 dB
SFO1 100.6229299 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 18.00 dB
PL13 21.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
70.75
70.32
63.80
52.27
48.87
47.80
46.51
ppm
180
160
140
120
100
80
60
40
20

OH
HO
NH.HCl
H
HO

25


OH
HO
NH.HCl
H
HO
3
ppm
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
1.00
1.00
4.27
2.33
1.06

BRUKER
Current Data Parameters
NAME smc504
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20041124
Time 21.45
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT D2O
NS 2048
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 362
DW 20.850 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.12 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 18.00 dB
PL13 21.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
44.79
47.69
51.59
64.06
70.24
71.87
180
160
140
120
100
80
60
40
20
ppm

OH
HO
NH.HCl
H
HO

3