

# Supporting Information

for

## Peptoids and polyamines going sweet: Modular synthesis of glycosylated peptoids and polyamines using click chemistry

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### Methods and NMR spectra

#### General methods

All chemicals were obtained from commercial suppliers (Merck, Sigma-Aldrich, Fluka, Acros, ABCR, Alfa Aesar, KMF), the azidosugars, 1-azido-1-deoxy- $\beta$ -D-glucopyranoside and 1-azido-1-deoxy- $\beta$ -D-lactopyranoside as well as AZT were purchased from Sigma Aldrich. The solvents were anhydrous and of reagent grade. Merrifield resin was purchased from Polymer Laboratories (PL-CMS resin,

0.97 mmol/g, 1% crosslink, 75–150  $\mu\text{m}$  mesh). 2-Chlorotrityl chloride resin was purchased from Agilent (PL-Cl-Trt-Cl resin, 2.06 mmol/g, 1% crosslink, 150–300  $\mu\text{m}$  mesh). Rink amide resin was purchased from Novabiochem (0.64 mmol/g, 1% crosslink, 100–200  $\mu\text{m}$  mesh). All solid-phase reactions were typically carried out in glass frits under argon atmosphere and, if not mentioned otherwise, at ambient temperature. All solution-phase reactions were carried out in flasks with magnetic stirring. Reactions under inert gas were carried out in flasks equipped with septa under argon (supplied by using a standard manifold with vacuum and argon lines). NMR spectra were recorded at 25 °C by using Bruker AM 400 (400 ( $^1\text{H}$ ) and 100 MHz ( $^{13}\text{C}$ )), Bruker DP300 (300 ( $^1\text{H}$ ) and 75 MHz ( $^{13}\text{C}$ )), and DP400 (400 ( $^1\text{H}$ ) and 100 MHz ( $^{13}\text{C}$ )) spectrometers. Due to rotamers, NMR spectra of peptoids were not recorded. All spectra are referenced to tetramethylsilane as the internal standard ( $\delta = 0$  ppm) by using the signals of the residual protons of  $\text{CHCl}_3$  (7.26 ppm ( $^1\text{H}$ ) or 77.0 ppm ( $^{13}\text{C}$ )) in  $\text{CDCl}_3$ , or  $\text{CHD}_2\text{OD}$  (3.31 ppm ( $^1\text{H}$ ) or 49.1 ppm ( $^{13}\text{C}$ )) in  $\text{CD}_3\text{OD}$ . Multiplicities of signals are described as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants ( $J$ ) are given in hertz (Hz). Multiplicities in the  $^{13}\text{C}$  NMR spectra were determined by DEPT (distortionless enhancement by polarization transfer) measurements. Mass spectra (ESI) were obtained by using an Agilent 6230 TOF LC/MS. QToF electrospray-ionisation (ESI) MS was performed with a Micromass QToF2 spectrometer. MALDI-TOF mass spectra were obtained by using either a Bruker Biflex IV spectrometer with a pulsed ultraviolet nitrogen laser, 200  $\mu\text{J}$  at 337 nm and a time-of-flight mass analyzer with a 125 cm linear flight path, or a Micromass TOFSpecE spectrometer in reflectron mode. 2,5-Dihydroxybenzoic acid and  $\alpha$ -cyano-4-hydroxy cinnamic acid were used as the matrix. HPLC was performed on a Jasco HPLC system, with a C18 column (30  $\times$  190 mm). Flow rate: 15 mL/min; solvent A: 0.1% TFA in water; solvent B: 0.1%

TFA in MeCN. Analytical TLC was performed on MERCK ready-to-use plates with silica gel 60 (F254). Column chromatography: MERCK silica gel 60, 0.04–0.063 mm. The analytical data of resin-bound substrates were taken from the unpurified free product after test cleavage from the resin.

### **General procedures for solid-phase synthesis**

**General washing procedure for resin.** Procedure A: the resin was washed three times each with 10% H<sub>2</sub>O in THF, THF/Et<sub>2</sub>O and Et<sub>2</sub>O. Procedure B: the resin was washed three times each with DMF, 0.1 M EDTA solution in H<sub>2</sub>O, 10% H<sub>2</sub>O in THF, THF/Et<sub>2</sub>O and Et<sub>2</sub>O. In the steps with two solvents they were used alternatingly. Per 1 g of the resin, 50 mL solvent was used.

**Nosyl (Ns) deprotection.** For cleavage of the Ns protecting group the resin was swelled in DMF for 15 min. Then, 20.0 equiv of β-mercaptoethanol and 20.0 equiv of DBU were added. After agitation overnight the reaction mixture was removed and the resin was washed according to procedure A.

**Cleavage from the resin.** The product was cleaved from the resin by adding 1% TFA in CH<sub>2</sub>Cl<sub>2</sub>. Meanwhile the color of the resin turned to red. After 5–10 min the product was washed off with CH<sub>2</sub>Cl<sub>2</sub> and MeOH, followed by evaporation of the solvent in high vacuum.

**Synthesis of azidosugars 1–3:** To a solution of D-mannosamine/ D-glucosamine/ D-galactosamine hydrochloride (1.00 g; 4.64 mmol) in methanol (50 mL), sodium methanolate (30% w/w NaOMe in MeOH, 1.66 mL, 4.64 mmol, 1.00 equiv) was added and the mixture was stirred at room temperature for 30 min until complete dissolution. NEt<sub>3</sub> (0.47 g; 4.64 mmol, 1.00 equiv) and chloroacetic anhydride (871 mg; 5.10 mmol, 1.10 equiv) were added to the solution, and stirred at room

temperature overnight. The solvent was evaporated and the crude product was used in subsequent reaction without further purification. Comment: *If necessary, sodium bicarbonate was added to neutralize the solution.*

To a solution of *N*-chloroacetylmannosamine/ *N*-chloroacetylglucosamine/ *N*-chloroacetylgalactosamine in MeOH/H<sub>2</sub>O (10:1, (20 mL /2 mL)) sodium azide NaN<sub>3</sub> (1.06 g; 16.24 mmol, 3.50 equiv) was added. The mixture was stirred for 5 h at 65 °C. Subsequently, the reaction mixture was concentrated and dried in vacuo. The residue was then suspended in pyridine (20 mL) and acetic anhydride (20 mL) was added to the solution. The reaction was stirred at room temperature overnight. After concentration in vacuo, the residue was dissolved in EtOAc (50 mL) and washed with 1N HCl, NaHCO<sub>3</sub> and brine (each 50 mL) (*CAUTION: extraction with sodium bicarbonate causes gas formation and excess pressure in the separating funnel*). After drying over MgSO<sub>4</sub> the crude product was purified by column chromatography (cyclohexane/ethyl acetate 1:1) to afford the desired product (mixture of α/β anomers) as a white-yellowish oil that solidified upon *lyophilization*. The yield for all azides is about 55% overall yield.

**1,3,4,6-Tetra-O-acetyl-N-azidoacetyl-D-glucosamine (1)**; mixture of anomers: α/β : 65/35; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 6.49 (d, 1H, *J* = 9.3 Hz, NH-β), 6.43 (d, 1H, *J* = 9.3 Hz, NH-α), 6.19 (d, 1H, *J* = 3.7 Hz, H-1α) 5.80 (d, 1H, *J* = 8.7 Hz, H-1β), 5.32–5.18 (m, 3H), 5.13 (t, 1H, *J* = 9.6 Hz, *J* = 9.6 Hz), 4.44 (ddd, 1H, *J* = 3.7 Hz, *J* = 8.9 Hz, *J* = 10.8 Hz), 4.29–4.17 (m, 3H), 4.14 (d, 1H, *J* = 2.2 Hz), 4.10 (d, 1H, *J* = 2.2 Hz), 3.93 (s, 2H), 3.91 (s, 2H), 3.83 (ddd, 1H, *J* = 2.3 Hz, *J* = 4.6 Hz, *J* = 9.8 Hz), 2.20 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 171.5, 170.8, 170.6, 170.6, 169.3, 169.2, 169.1, 168.7, 168.0, 166.8, 92.2 (C-1β), 90.2 (C-1α), 72.9, 72.1, 70.3, 69.8, 67.7, 67.4, 61.6,

61.5, 53.2, 52.6, 52.4, 51.2, 20.9, 20.8, 20.7, 20.6, 20.6, 20.5; MS (ESI),  $[M + Na]^+$   
 $C_{16}H_{22}N_4NaO_{10}$ : calcd. 453.1234; found 453.1471.

**1,3,4,6-Tetra-O-acetyl-N-azidoacetyl-D-galactosamine (2)**; mixture of anomers:  $\alpha/\beta$   
: 65/35;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 6.39 (d, 1H,  $J$  = 9.4 Hz, NH- $\beta$ ), 6.29 (d, 1H,  $J$   
= 9.1 Hz, NH- $\alpha$ ), 6.23 (d, 1H,  $J$  = 3.5 Hz, H-1 $\alpha$ ), 5.79 (d, 1H,  $J$  = 8.8 Hz, H-1 $\beta$ ), 5.45  
(d, 1H,  $J$  = 2.0 Hz), 5.39 (d, 1H,  $J$  = 3.2 Hz), 5.26 (ddd, 1H,  $J$  = 3.2 Hz,  $J$  = 11.5 Hz,  $J$   
= 23.1 Hz), 4.74–4.69 (m, 1H), 4.67 (d, 1H,  $J$  = 3.6 Hz), 4.38 (td, 1H,  $J$  = 9.2 Hz,  $J$  =  
11.2 Hz), 3.95 (s, 2H), 3.92 (s, 2H), 2.18 (s, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 2.05 (s,  
3H), 2.04 (s, 3H), 2.03 (s, 3H);  $^{13}C$  NMR (100.6 MHz,  $CDCl_3$ ):  $\delta$  = 170.9, 170.8,  
170.4, 170.4, 170.4, 170.3, 170.1, 169.9, 169.3, 169.0, 168.8, 167.2, 166.9, 166.9,  
93.8, 92.6, 90.9, 73.9, 71.8, 70.2, 69.9, 68.7, 67.6, 66.6, 66.6, 62.1, 61.2, 56.2, 52.6,  
52.5, 49.9, 47.0, 21.0, 20.9, 20.8, 20.8, 20.7, 20.6, 20.6; MS (ESI),  $[M + Na]^+$   
 $C_{16}H_{22}N_4NaO_{10}$ : calcd. 453.1234; found. 453.1451.

**1,3,4,6-Tetra-O-acetyl-N-azidoacetyl-D-mannosamine (3)**; mixture of anomers:  $\alpha/\beta$   
: 54/46;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) = 6.67 (d, 1H,  $J$  = 9.0 Hz); 6.63 (d, 1H,  $J$   
= 9.3 Hz); 6.03 (d, 1H,  $J$  = 1.8 Hz); 5.88 (d, 1H,  $J$  = 1.6 Hz); 5.33 (dd, 1H,  $J$  =  
10.2 Hz,  $J$  = 4.3 Hz); 5.21 (t, 1H,  $J$  = 10.0 Hz); 5.15 (t, 1H,  $J$  = 9.8 Hz); 5.05 (dd, 1H,  
 $J$  = 9.9 Hz,  $J$  = 3.9 Hz); 4.72 (ddd, 1H,  $J$  = 9.0 Hz,  $J$  = 3.8 Hz,  $J$  = 1.6 Hz); 4.61 (ddd,  
1H,  $J$  = 9.3 Hz,  $J$  = 4.2 Hz,  $J$  = 1.9 Hz); 4.27–4.19 (m, 2H); 4.16–3.99 (m, 7H); 3.81  
(ddd, 1H,  $J$  = 9.6 Hz,  $J$  = 4.6 Hz,  $J$  = 2.5 Hz); 2.17 (s, 3H); 2.10 (s, 3H); 2.10 (s, 6H);  
2.05 (s, 6H); 1.99 (s, 3H); 1.99 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) = 170.5;  
170.1; 170.1; 169.6; 168.3; 168.1; 167.4; 166.8; 91.3; 90.3; 73.4; 71.4; 70.3; 68.8;  
65.1; 65.0; 61.8; 61.7; 52.6; 52.4; 49.7; 49.3; 20.8; 20.7; 20.7; 20.6; 20.6; MS (ESI),  
 $[M + Na]^+$   $C_{16}H_{22}N_4NaO_{10}$ : calcd. 453.1234; found 453.1481.

**Sperminyl-*N*-[(*N*',*N*'',*N*'''-trinosyl)-*N*'''-pent-4-ynyl]*p*-hydroxytrityl resin 9.** To a suspension of 2.43 g (1.00 equiv) resin **8** and 2.09 mL (12.0 equiv) of 2,4,6-collidine in 15 mL CH<sub>2</sub>Cl<sub>2</sub> was added 1.80 g (6.00 equiv) of 2-nitrobenzenesulfonylchloride. The resin was agitated for 16 h, then washed according to procedure A and dried under reduced pressure. After drying, 1.94 g (1.00 equiv) resin and 1.45 g (15.0 equiv) K<sub>2</sub>CO<sub>3</sub> were suspended together in 20 mL DMF. Then, 1.0 mL (10.0 equiv) of 5-chloropent-1-yne was added and the mixture was agitated at 60 °C for 16 h. After cooling down, the solvent was removed and the resin was washed following procedure A until all K<sub>2</sub>CO<sub>3</sub> was removed. An orange resin was obtained after drying under reduced pressure. NMR data and MS were obtained after cleavage from the resin according to the general procedures for solid-phase synthesis.

<sup>1</sup>H NMR (400 MHz, [D<sub>4</sub>]-MeOH): δ (ppm) = 1.53 (m, 4 H, CH<sub>2</sub>); 1.71 (m, 3H, CH<sub>2</sub>); 1.96 (m, 4H, CH<sub>2</sub>); 2.15 (m, 2H, CH<sub>2</sub>); 3.05 (m, 4H, CH<sub>2</sub>); 3.32–3.49 (m, 10H, CH<sub>2</sub>); 7.72–7.89 (m, 9H, CH<sub>ar</sub>); 7.97–8.10 (m, 3H, CH<sub>ar</sub>); MS (MALDI) *m/z*: 824.15 [M + H]<sup>+</sup>.

**Sperminyl-*N*-(*N*'''-1-β-D-glucopyranosyl-4-propyl-1*H*-1,2,3-triazole) 13.** A suspension of 200 mg (1.00 equiv) resin **9** in 2 mL DMF reacted with 12.3 mg (0.500 equiv) CuSO<sub>4</sub>·5H<sub>2</sub>O in 1 mL DMF, 97.72 mg (5.00 equiv) sodium ascorbate in 0.5 mL aqua dest. and 40.08 mg (2.00 equiv) 1-azido-1-deoxy-β-D-glucopyranosid or 71.75 mg (2.00 equiv). After agitating for 2 d the reaction mixture was removed and the resin was washed according to procedure B. After deprotection of the nosyl group and washing of the resin according to procedure A the products were cleaved from the resin according to general procedures.

<sup>1</sup>H NMR (400 MHz, [D<sub>4</sub>]-MeOH): δ (ppm) = 1.71–1.81 (m, 6H, CH<sub>2</sub>); 2.01–2.15 (m, 6H, CH<sub>2</sub>); 3.05–3.15 (m, 14H, CH<sub>2</sub>); 3.35 (m, 2H, CH); 3.45–3.60 (m, 1H, CH); 3.72 (dd, 1H, CH<sub>2</sub>, *J*<sub>1</sub> = 12.15 Hz, *J*<sub>2</sub> = 5.22 Hz); 3.88 (m, 1H, CH<sub>2</sub>); 5.58 (d, 1H, CH, *J* =

9.19 Hz); 8.02 (s, 1H,  $CH_{ar}$ , (Triazole-H));  $^{13}C$  NMR (100 MHz,  $[D_4]$ -MeOH):  $\delta$  (ppm) = 24.17; 24.90; 25.33; 27.46; 29.94; 33.72; 37.80; 39.33; 45.83; 62.26; 70.84; 73.96; 78.35; 81.00; 89.70, 122.78, 147.36; MS (ESI)  $m/z$ : 474.34  $[M + H]^+$ ; HRMS (EI,  $C_{21}H_{44}O_5N_7$ ): calc. 474.3404; found 474.3401.

**Sperminyl- $N$ -( $N''$ -1- $\beta$ -D-lactopyranosyl-4-propyl-1H-1,2,3-triazole) 14.** A suspension of 200 mg (1.00 equiv) resin **9** in 2 mL DMF reacted with 12.3 mg (0.500 equiv)  $CuSO_4 \cdot 5H_2O$  in 1 mL DMF, 97.72 mg (5.00 equiv) sodium ascorbate in 0.5 mL aqua dest. and 71.75 mg (2.00 equiv) 1-azido-1-deoxy- $\beta$ -D-lactopyranoside. After agitating for 2 d the reaction mixture was removed and the resin was washed according to procedure B. After deprotection of the nosyl group and washing of the resin according to procedure A the products were cleaved from the resin according to general procedures.

$^1H$  NMR (400 MHz,  $[D_4]$ -MeOH):  $\delta$  (ppm) = 1.69–1.81 (m, 6H,  $CH_2$ ); 2.01–2.15 (m, 6H,  $CH_2$ ); 3.04–3.16 (m, 14H,  $CH_2$ ); 3.33–3.36 (m, 2H,  $CH$ ); 3.50–3.65 (m, 5H,  $CH_2+CH$ ); 3.72–3.90 (m, 5H,  $CH_2+CH$ ); 4.00 (m, 1H,  $CH$ ); 4.43 (d, 1H,  $CH$ ,  $J = 7.55$  Hz); 5.63 (d, 1H,  $CH$ ,  $J = 9.32$  Hz); 8.03 (s, 1H,  $CH_{ar}$ , (triazole-H));  $^{13}C$  NMR (100 MHz,  $[D_4]$ -MeOH):  $\delta$  (ppm) = 24.18; 24.91; 25.33; 27.46; 29.95; 33.72; 37.81; 39.34; 45.83; 61.65; 62.71; 70.47; 72.68; 73.85; 74.94; 76.96; 77.30; 79.66; 79.94; 89.41, 105.27; 123.04; 147.26; MS (ESI)  $m/z$ : 636.40  $[M + H]^+$ ; HRMS (EI,  $C_{27}H_{54}O_{10}N_7$ ): calc. 636.3932; found 636.3935.

**Sperminyl- $N$ -( $N''$ -1-2',3'-deoxythymidine-4-propyl-1H-1,2,3-triazole) 15.** 402.5 mg (1.00 equiv) of resin **9** was suspended in 2 mL DMF. Then, 25.2 mg (0.500 equiv)  $CuSO_4 \cdot 5H_2O$  in 1 mL DMF and 201.9 mg (5.00 equiv) sodium ascorbate in 0.5 mL distilled water were added, followed by 100 mg (1.86 equiv) AZT.

The suspension was agitated for 2.5 d, then the reaction mixture was removed from the resin. After that, the orange resin was washed according to procedure B, deprotected from the Nosyl group and dried under vacuum.

$^1\text{H}$  NMR (400 MHz,  $[\text{D}_4]\text{-MeOH}$ ):  $\delta$  (ppm) = 1.71 (m, 2H,  $\text{CH}_2$ ); 1.81 (m, 4H,  $\text{CH}_2$ ); 1.90 (d, 3H,  $\text{CH}_3$ ,  $J = 1.14$  Hz); 2.10 (m, 6H,  $\text{CH}_2$ ); 2.13 (m, 2H,  $\text{CH}_2$ ); 2.85 (m, 2H,  $\text{CH}_2$ ); 3.03–3.15 (m, 12H,  $\text{CH}_2$ ); 3.77 (dd, 1H,  $\text{CH}_2$ ,  $J_1 = 12.18$  Hz,  $J_2 = 3.22$  Hz); 3.89 (dd, 1H,  $\text{CH}_2$ ,  $J_1 = 12.13$  Hz,  $J_2 = 3.03$  Hz); 4.35 (m, 1H, CH); 5.39 (dt, 1H, CH,  $J_1 = 8.67$  Hz,  $J_2 = 4.93$  Hz); 6.49 (t, 1H, CH,  $J = 6.57$  Hz); 7.90 (d, 1H,  $\text{CH}_{ar}$ ,  $J = 1.01$  Hz); 7.94 (s, 1H,  $\text{CH}_{ar}$ , (triazole-H)); MS (ESI)  $m/z$ : 536.36  $[\text{M} + \text{H}]^+$ .

### Synthesis of 20

In a vial 0.180 mmol of alkyne resin **16** was swollen in 6 mL abs. THF. 0.360 mmol of azidosugar **1**, 0.360 mmol of copper(I) iodide and 9.00 mmol DIPEA were added. The vial was sealed and shaken for 16 h at room temperature. Afterwards, the solvent was removed and the resin was washed with THF, saturated aqueous sodium ascorbate solution, water, THF/MeOH/THF/MeOH/THF, MeOH/ $\text{CH}_2\text{Cl}_2$ /MeOH/ $\text{CH}_2\text{Cl}_2$ /MeOH, and three times with  $\text{CH}_2\text{Cl}_2$ . The resin was dried in vacuo. After cleavage from the resin with 5% TFA in dichloromethane, the product was obtained.

MS (MALDI-TOF):  $m/z = 838.9$   $[\text{M} + \text{H}]^+$ .

### Synthesis of hexaalkyne 27 on 2-chloro tritylchloride resin

For the synthesis, 50 mg (0.103 mmol, 1.00 equiv) of 2-chlorotriyl chloride resin and washed in a fritted plastic syringe (Multisyntech) with 1 mL of dichloromethane, followed by swelling in 1 mL of dichloromethane for 5 min. The first submonomer was added by reacting 77.2 mg of bromoacetic acid (0.555 mmol, 5.40 equiv) and 99  $\mu\text{L}$  of DIPEA (71.8 mg, 0.555 mmol, 5.00 equiv) in 1 mL of dichloromethane on a shaker



platform for 40 min at room temperature, followed by washing with dichloromethane (three times with 2 mL) and DMF (three times with 2 mL). The bromoacetylated resin was incubated with 1 mL of 47.0 mg propargylamine (0.855 mmol, 8.30 equiv) in 1 mL DMF on a shaker platform at room temperature, followed by washing with DMF (three times with 3 mL). The displacement reaction times were 30 min for propargylamine. The following bromoacetylations were carried out by reacting the resin with 143 mg bromoacetic acid (1.03 mmol, 10.0 equiv) and 160  $\mu$ L DIC (130 mg, 1.03 mmol, 10.0 equiv) in 1 mL DMF for 30 min. Coupling steps were continued until the desired peptoid length was achieved. After the last displacement step, the resin was washed with DMF/dichloromethane/DMF (two times with 3 mL for each solvent).

For the coupling of rhodamine B, the resin was incubated for 18 h with a solution of 144 mg rhodamine B (0.309 mmol, 3.00 equiv), 40.5 mg HOBt (0.309 mmol, 3.00 equiv) and 76.4  $\mu$ L DIC (61.9 mg, 0.309 mmol, 3.00 equiv) in 2 mL DMF on a shaker platform. After the reaction the resin was washed with DMF and dichloromethane until the washing solution was colorless.

Mass spectrum (MALDI): calc.: 1013.46 g/mol, found: 1013.3 [M]<sup>+</sup>.

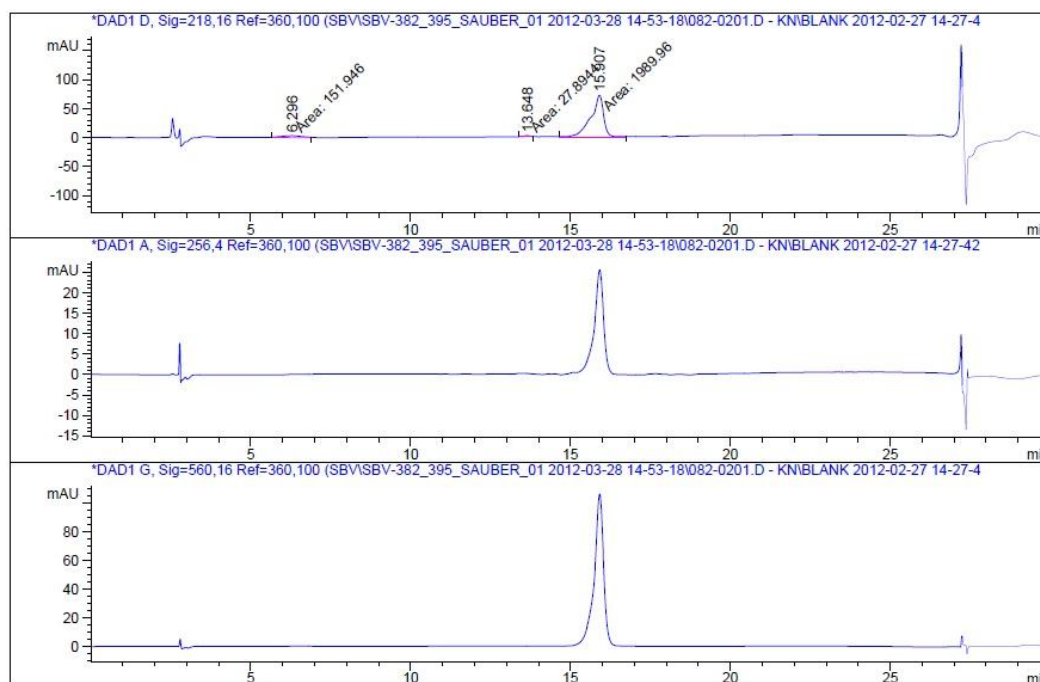
### **Cu-catalyzed alkyne azide cycloaddition on resin **27** and cleavage from the resin**

For the reaction with the sugar, the resin **27** was swollen in THF, and 70 mg Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> (0.188 mmol, 1.83 equiv) was directly weighed into the plastic syringe containing the resin. In 2 mL dry THF, 310 mg of Ac<sub>4</sub>GalNAz (**2**, 0.721 mmol, 7.00 equiv) and 100  $\mu$ L 2,6-lutidine (92.0 mg, 0.859 mmol, 8.34 equiv) were dissolved and added to the resin. The resin was shaken for 18 h at rt.

After the reaction, the resin was washed with saturated aqueous sodium ascorbate solution, water, THF and dichloromethane (three times 2 mL each).

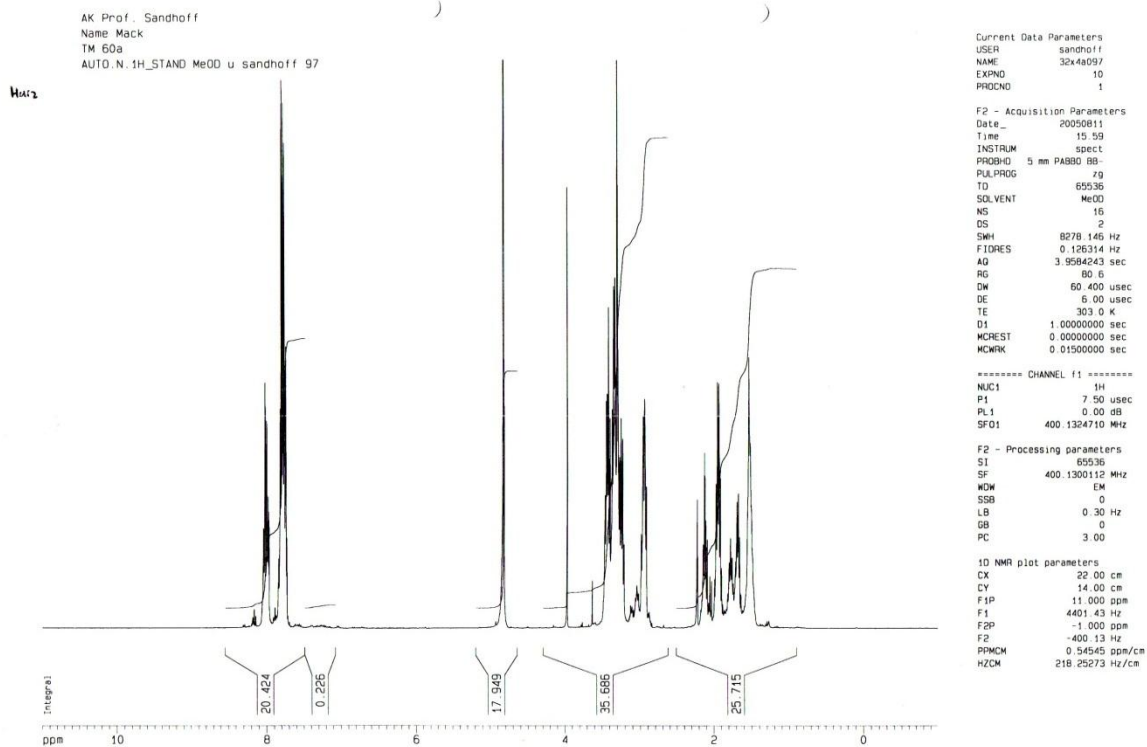
The peptoid was cleaved from the resin using 3 mL 33% HFIP in dichloromethane (v/v) at room temperature for 30 min. After collecting the cleavage solution, the resin was washed with 3 mL dichloromethane twice. The elution and washing solutions were combined. The solvent was evaporated under a stream of argon gas. After cleavage, HPLC purification and lyophilization, 70 mg (0.019 mmol, 19% yield) of a purple solid (**28**) were obtained.

Mass spectrum (MALDI, *Matrix*: DHB): calc.: 3594 g/mol, found: 3593 [M]<sup>+</sup>; Analytical HPLC (5–95% Acetonitrile +0.1% TFA in 30 min,  $t_{Ret}$  = 15.9 min, Detection at 218 nm), Purity: 92%.

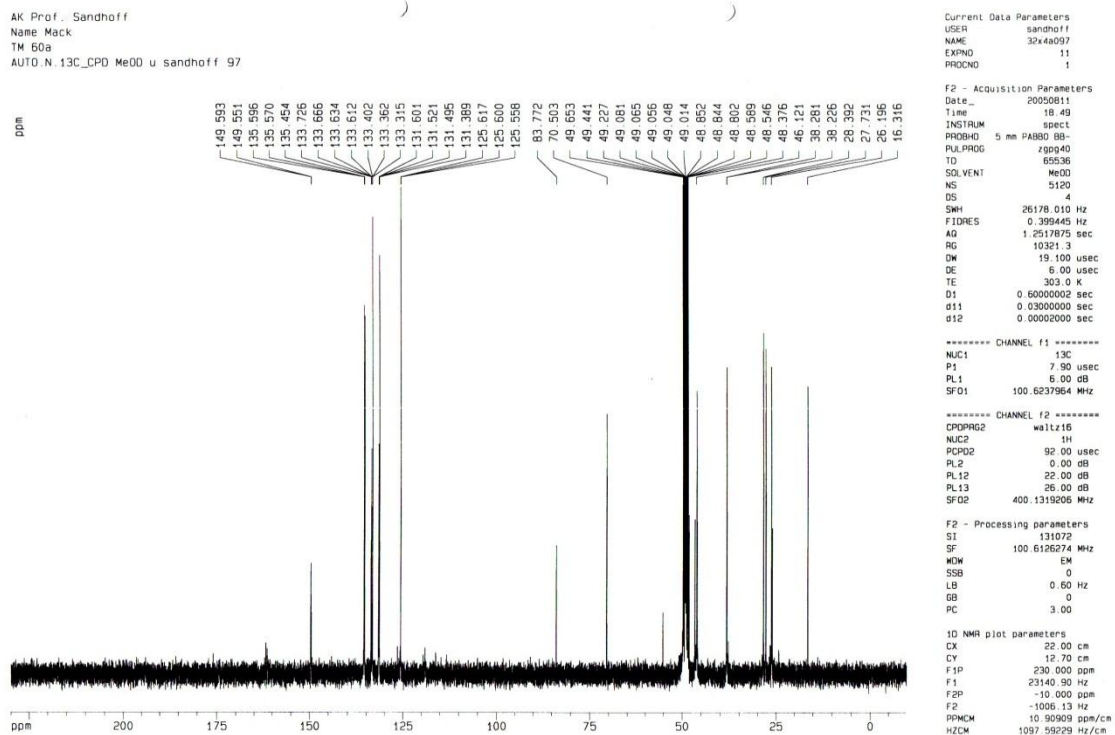


## NMR spectra:

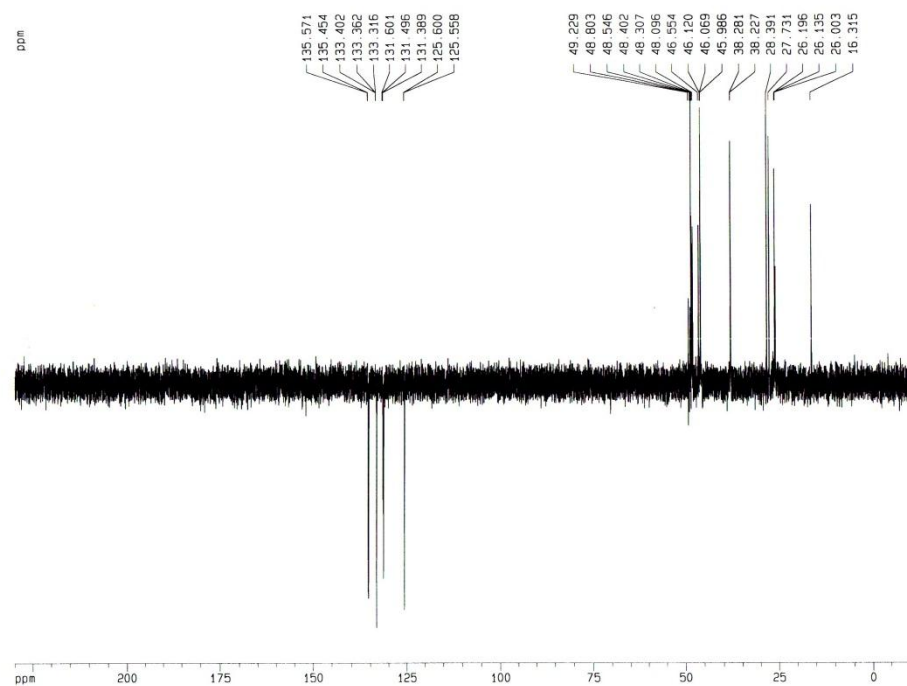
### <sup>1</sup>H NMR of compound 9 (after cleavage from resin):



### <sup>13</sup>C NMR of compound 9 (after cleavage from resin)



AK Prof. Sandhoff  
 Name Mack  
 TM 60a  
 AUTO.N.13C\_D135 Me00 u sandhoff 97



Current Data Parameters  
 USER sandhoff  
 NAME 3x4a057  
 EXPNO 12  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20050811  
 Time 19.24  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB-  
 PULPROG dept135  
 TD 65536  
 SOLVENT Me00  
 NS 1024  
 DS 4  
 SWH 26178.010 Hz  
 FIDRES 0.399448 Hz  
 AQ 1.2517875 sec  
 RG 18390.4  
 DW 19.100 usec  
 DE 6.00 usec  
 TE 303.0 K  
 CNST2 145.000000  
 D1 0.6000002 sec  
 D2 0.00344828 sec  
 d12 0.00002000 sec  
 DELTA 0.00001006 sec  
 MCREST 0.00000000 sec  
 MCWRR 0.01500000 sec

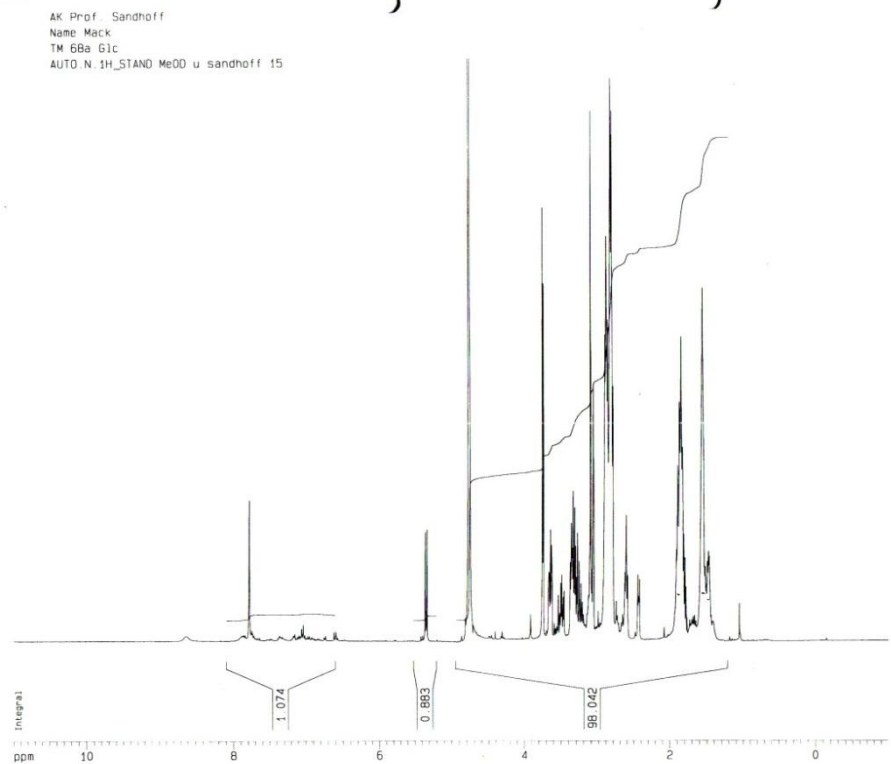
\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 13C  
 P1 7.90 usec  
 PL1 15.00 dB  
 PL1 6.00 dB  
 SF01 100.6237964 MHz

\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CPDPRG2 waltz16  
 NUC2 1H  
 P3 7.70 usec  
 PL4 15.40 usec  
 PL4 82.00 usec  
 PL2 0.00 dB  
 PL12 22.00 dB  
 SF02 400.1319208 MHz

F2 - Processing parameters  
 SI 131072  
 SF 100.6126274 MHz  
 MDW EM  
 SSB 0  
 LB 0.60 Hz  
 GB 0  
 PC 3.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 7.00 cm  
 F1P 230.000 ppm  
 F1 23140.90 Hz  
 F2P -10.000 ppm  
 F2 -1006.13 Hz  
 PPMCM 10.90993 ppm/cm  
 HZCM 1097.55229 Hz/cm

# <sup>1</sup>H NMR of compound 13:



Current Data Parameters  
 USER sandhoff  
 NAME 3x4a015  
 EXPNO 10  
 PROCNO 1

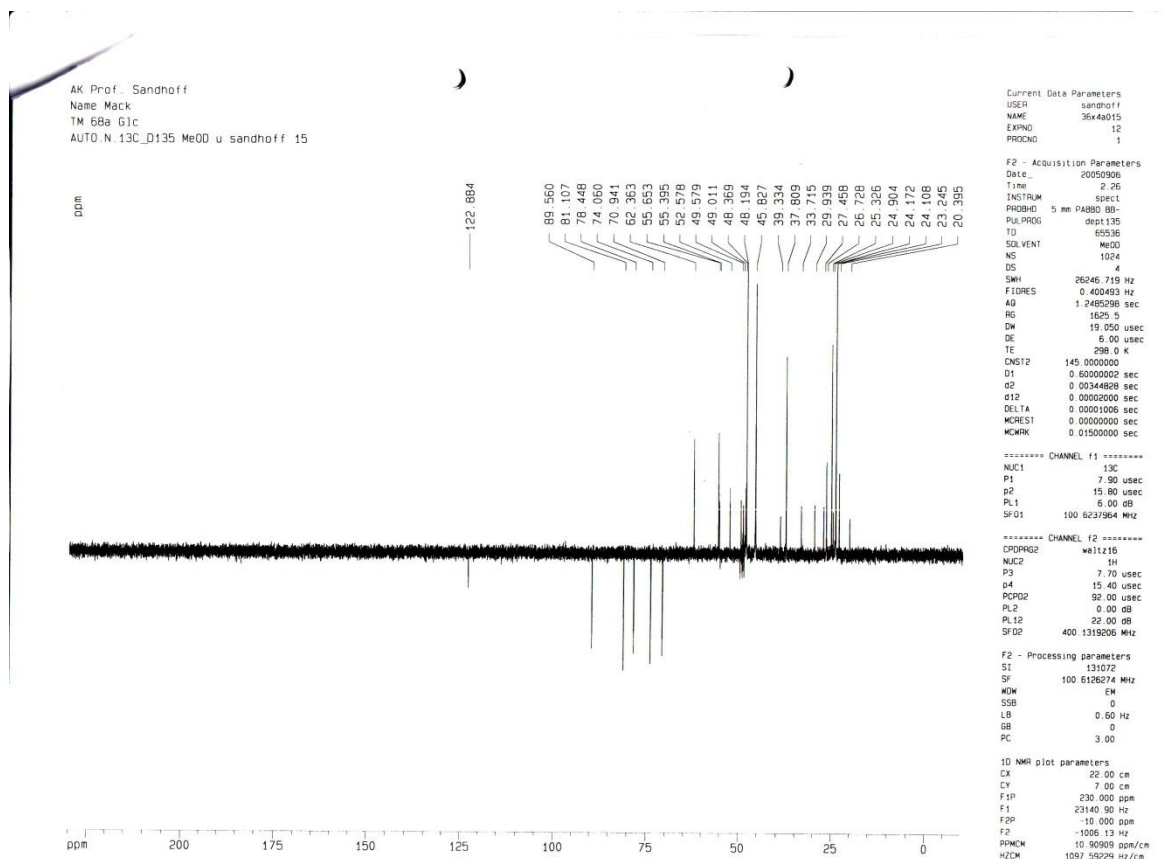
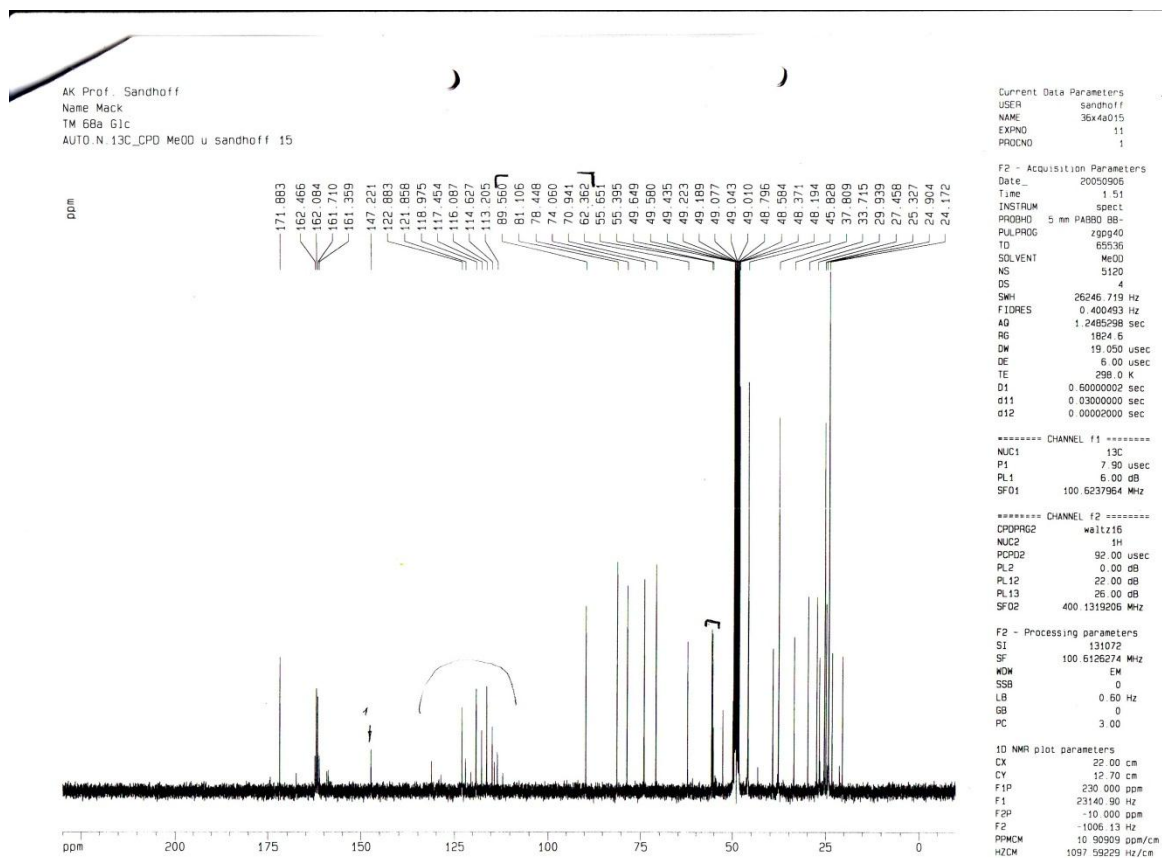
F2 - Acquisition Parameters  
 Date\_ 20050905  
 Time 23.02  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB-  
 PULPROG zg  
 TD 65536  
 SOLVENT Me00  
 NS 16  
 DS 2  
 SWH 8290.825 Hz  
 FIDRES 0.125898 Hz  
 AQ 3.9715922 sec  
 RG 45.3  
 DW 60.600 usec  
 DE 6.00 usec  
 TE 299.0 K  
 D1 1.00000000 sec  
 MCREST 0.00000000 sec  
 MCWRR 0.01500000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 1H  
 P1 7.50 usec  
 PL1 0.00 dB  
 SF01 400.1324710 MHz

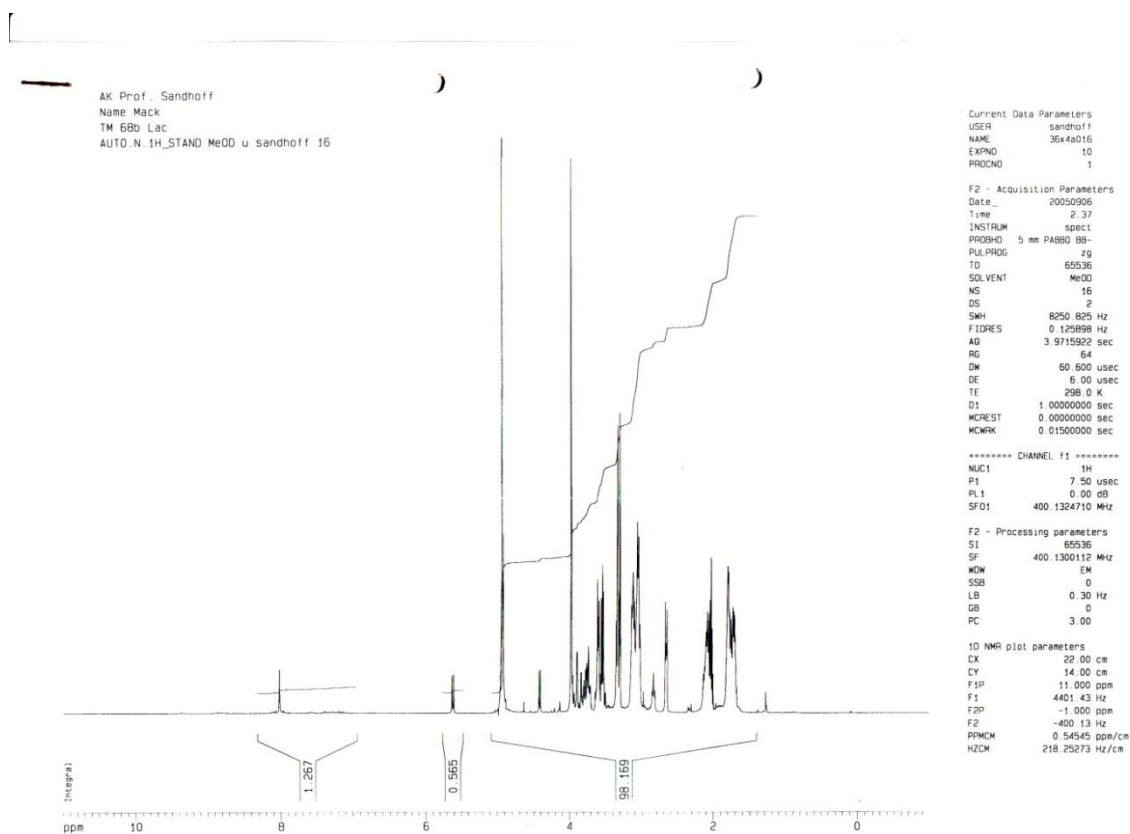
F2 - Processing parameters  
 SI 65536  
 SF 400.1301035 MHz  
 MDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 3.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 14.00 cm  
 F1P 11.000 ppm  
 F1 4401.43 Hz  
 F2P -1.000 ppm  
 F2 -400.13 Hz  
 PPMCM 0.54545 ppm/cm  
 HZCM 219.25278 Hz/cm

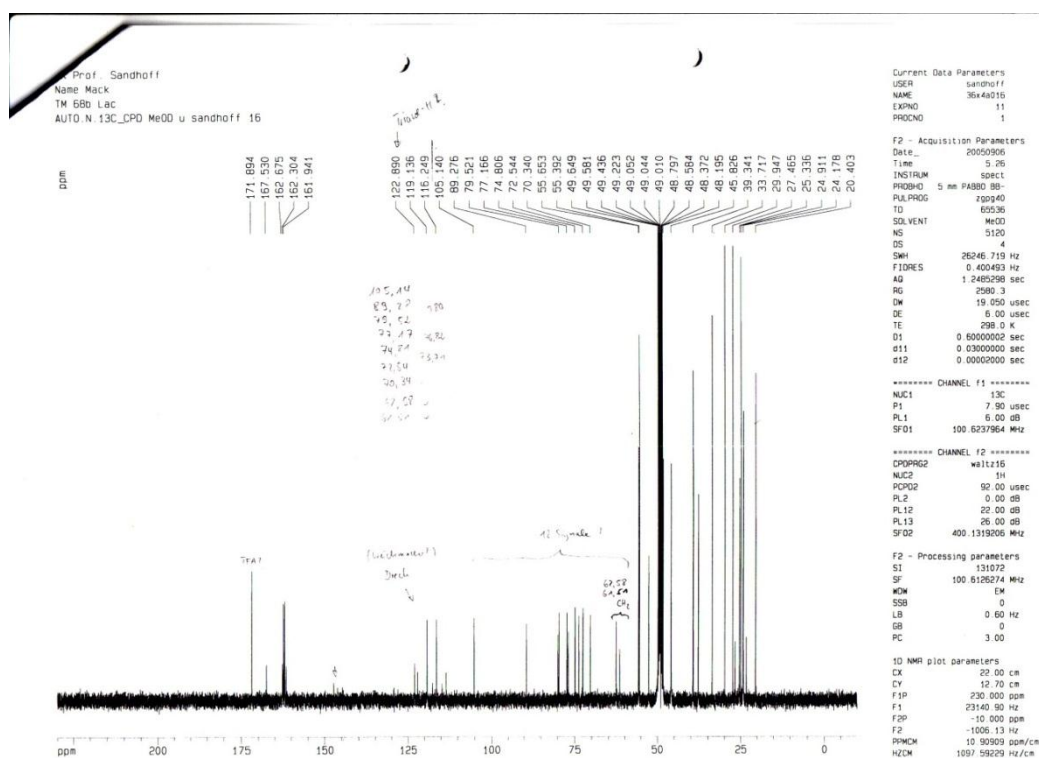
# <sup>13</sup>C NMR of compound 13:



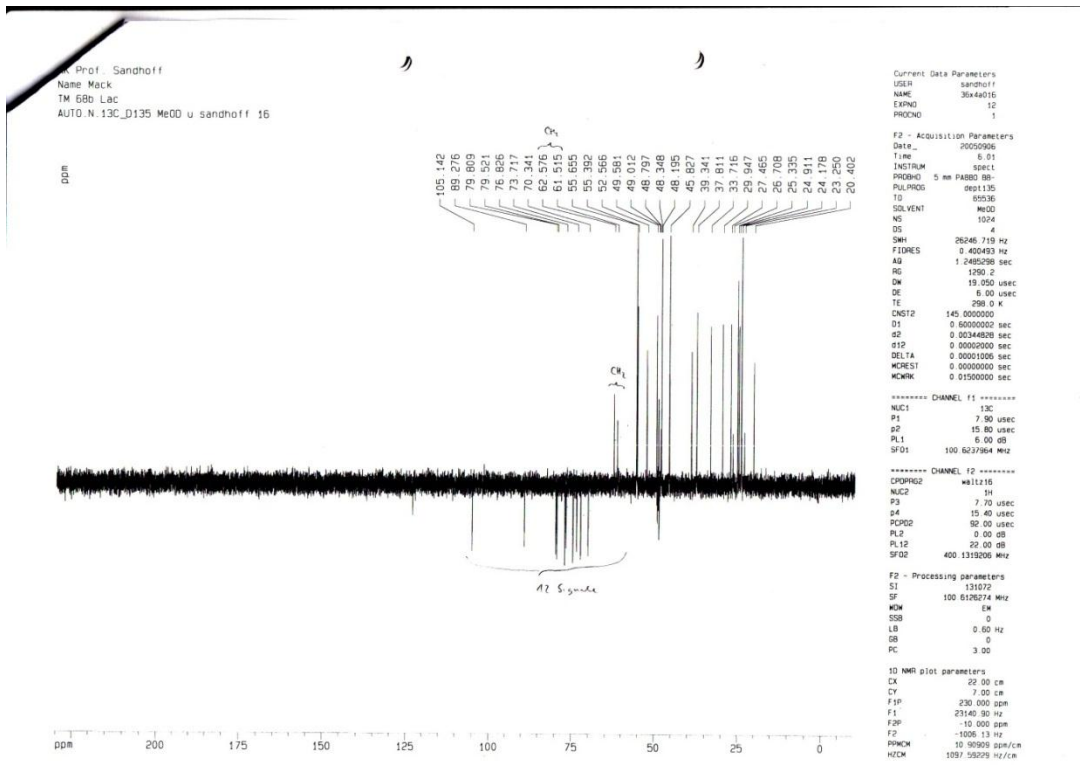
# <sup>1</sup>H NMR of compound 14:



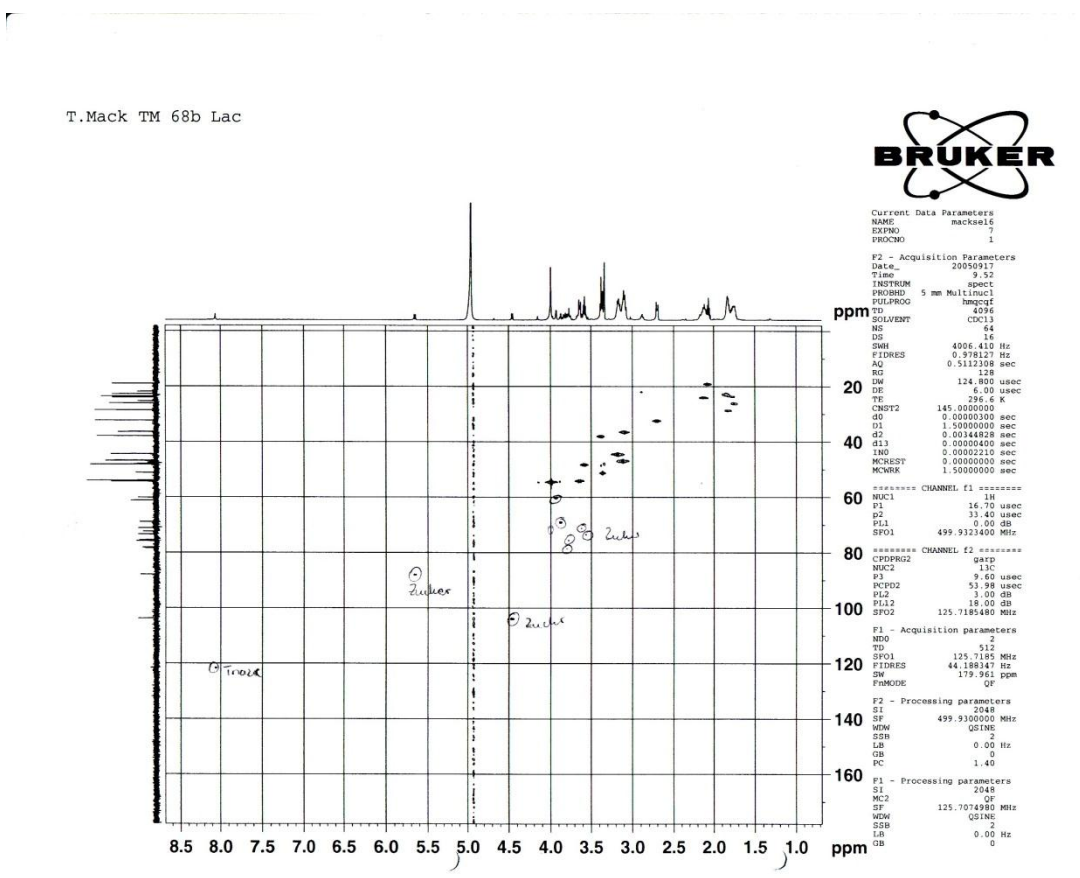
# <sup>13</sup>C NMR of compound 14



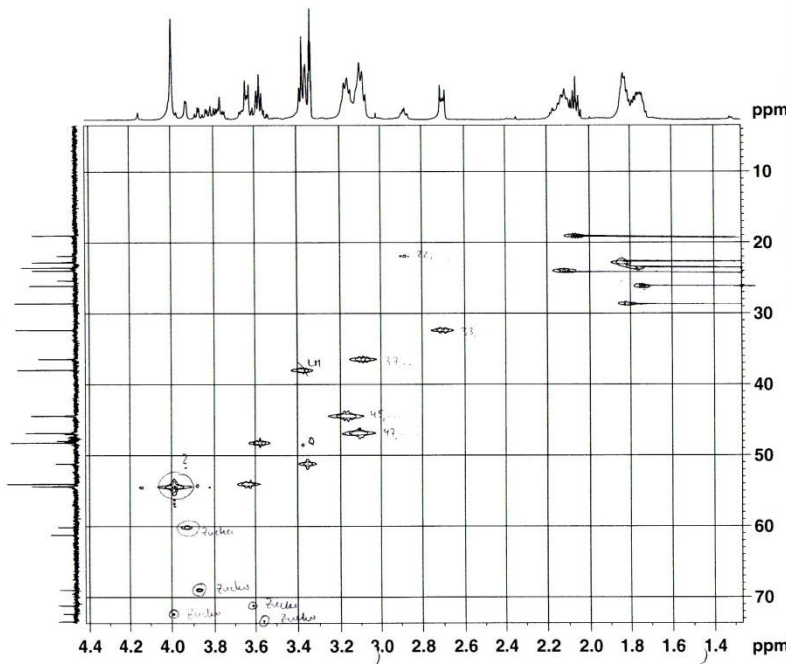




## 2D- NMR of compound 14



T.Mack TM 68b Lac



```
Current Data Parameters
NAME      mackse16
EXPRO    7
PROCNO   1

F2 - Acquisition Parameters
Date_    20050917
Time     4.23
INSTRUM  spect
PROBHD   5 mm Multinuc1
PULPROG  hmgcf
TD       4096
SOLVENT  CDCl3
NS       64
DS       16
SWH      4006.410 Hz
FIDRES   0.978127 Hz
AQ       0.5112308 sec
RG       128
DE       6.00 usec
TE       296.6 K
CNSF2    145.000000
d0       0.00000300 sec
d1       1.50000000 sec
d2       0.00344828 sec
d3       0.00000490 sec
TMO     0.00002210 sec
MCREST   0.00000000 sec
MCWRR    1.50000000 sec

***** CHANNEL f1 *****
NUC1     1H
P1       16.70 usec
P2       33.40 usec
PL1      0.00 dB
SFO1    499.9323400 MHz

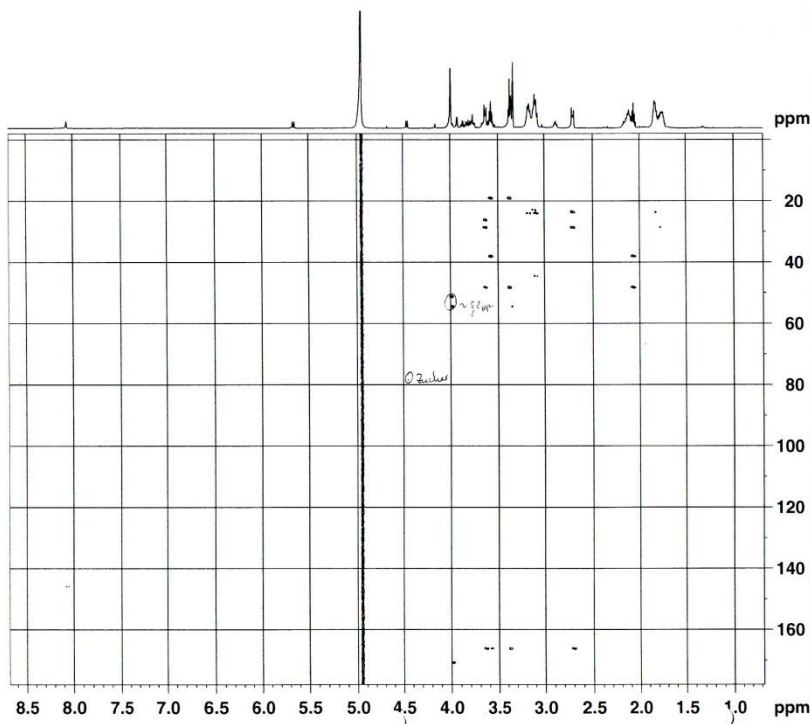
***** CHANNEL f2 *****
CPDPRG2  garp
NUC2     13C
P3       9.60 usec
PCPD2    53.98 usec
PL2      3.00 dB
PL12     18.00 dB
SFO2    125.7185480 MHz

F1 - Acquisition parameters
ND0      2
TD       512
SFO1    125.7185 MHz
FIDRES   44.188347 Hz
SW       179.961 ppm
F2MODE   QF

F2 - Processing parameters
S1       2048
SF       499.9300000 MHz
WDW      SINC
SSB      0
GB       0
PC       1.40

F1 - Processing parameters
S1       2048
MC2      QF
SF       125.7074990 MHz
WDW      SINC
SSB      0
GB       0
```

T.Mack TM 68b Lac



```
Current Data Parameters
NAME      mackse16
EXPRO    8
PROCNO   1

F2 - Acquisition Parameters
Date_    20050918
Time     4.23
INSTRUM  spect
PROBHD   5 mm Multinuc1
PULPROG  hbhcfgp2
TD       4096
SOLVENT  cmcl3
NS       64
DS       16
SWH      4006.410 Hz
FIDRES   0.978127 Hz
AQ       0.5112308 sec
RG       128
DE       6.00 usec
TE       296.7 K
CNSF2    145.000000
d0       0.00000300 sec
d1       1.50000000 sec
d2       0.00344828 sec
d3       0.06250000 sec
TMO     0.00002210 sec
MCREST   0.00000000 sec
MCWRR    1.50000000 sec

***** CHANNEL f1 *****
NUC1     1H
P1       16.70 usec
P2       33.40 usec
PL1      0.00 dB
SFO1    499.9323400 MHz

***** CHANNEL f2 *****
NUC2     13C
P3       9.60 usec
PL2      3.00 dB
SFO2    125.7185480 MHz

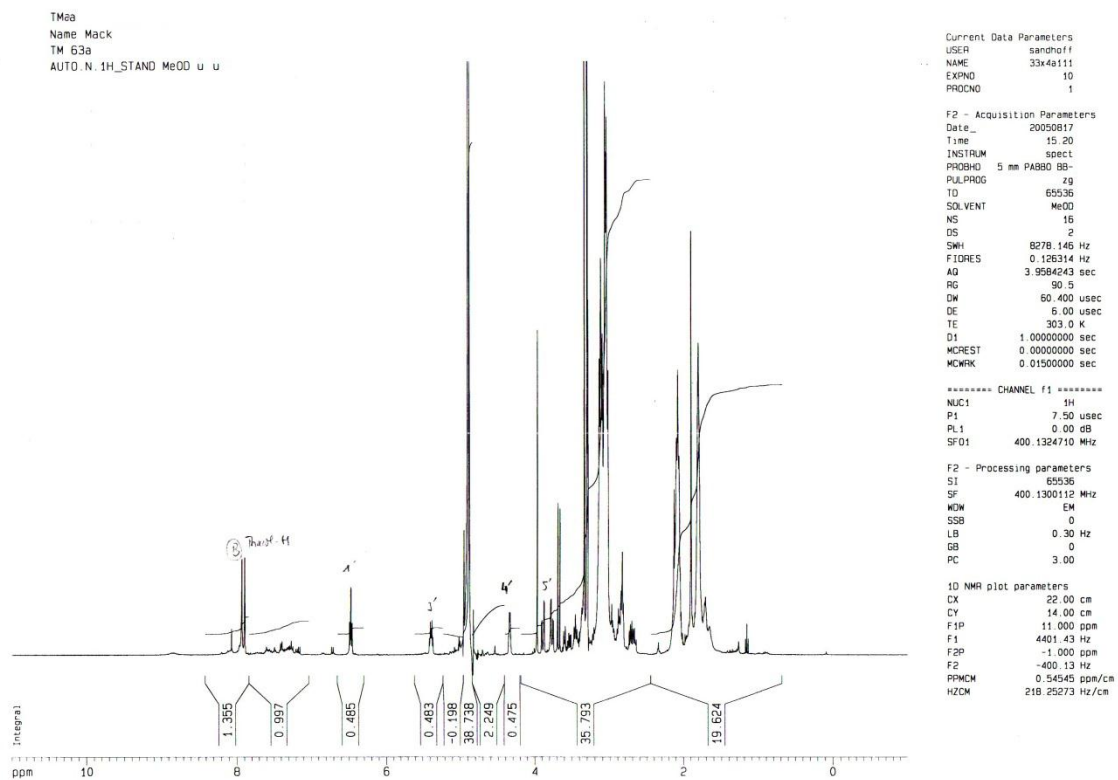
F1 - Acquisition parameters
ND0      2
TD       512
SFO1    125.7185 MHz
FIDRES   44.188347 Hz
SW       179.961 ppm
F2MODE   QF

F2 - Processing parameters
S1       2048
SF       499.9300000 MHz
WDW      SINC
SSB      0
GB       0
PC       1.40

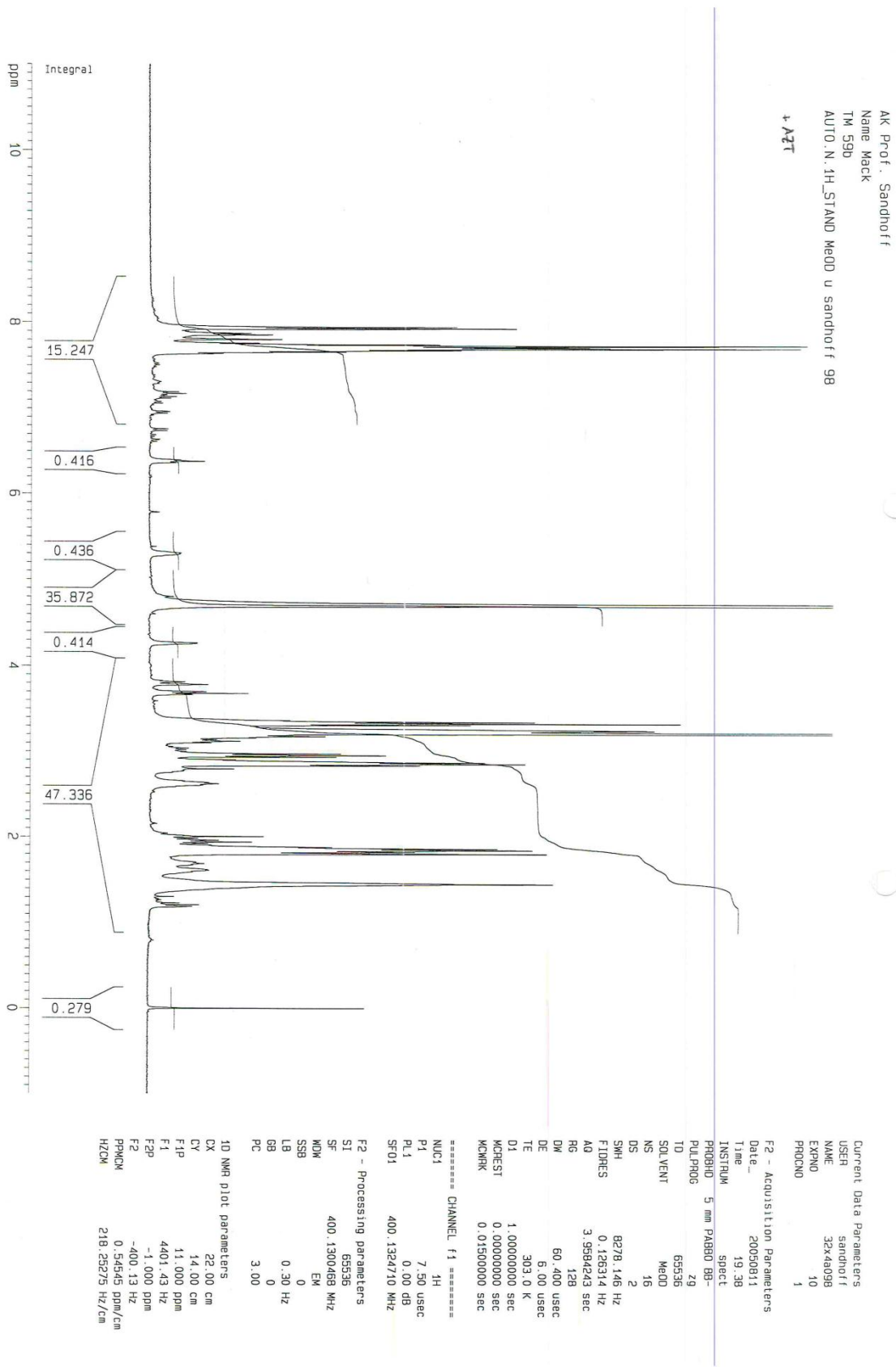
F1 - Processing parameters
S1       2048
MC2      QF
SF       125.7074990 MHz
WDW      SINC
SSB      0
GB       0
```



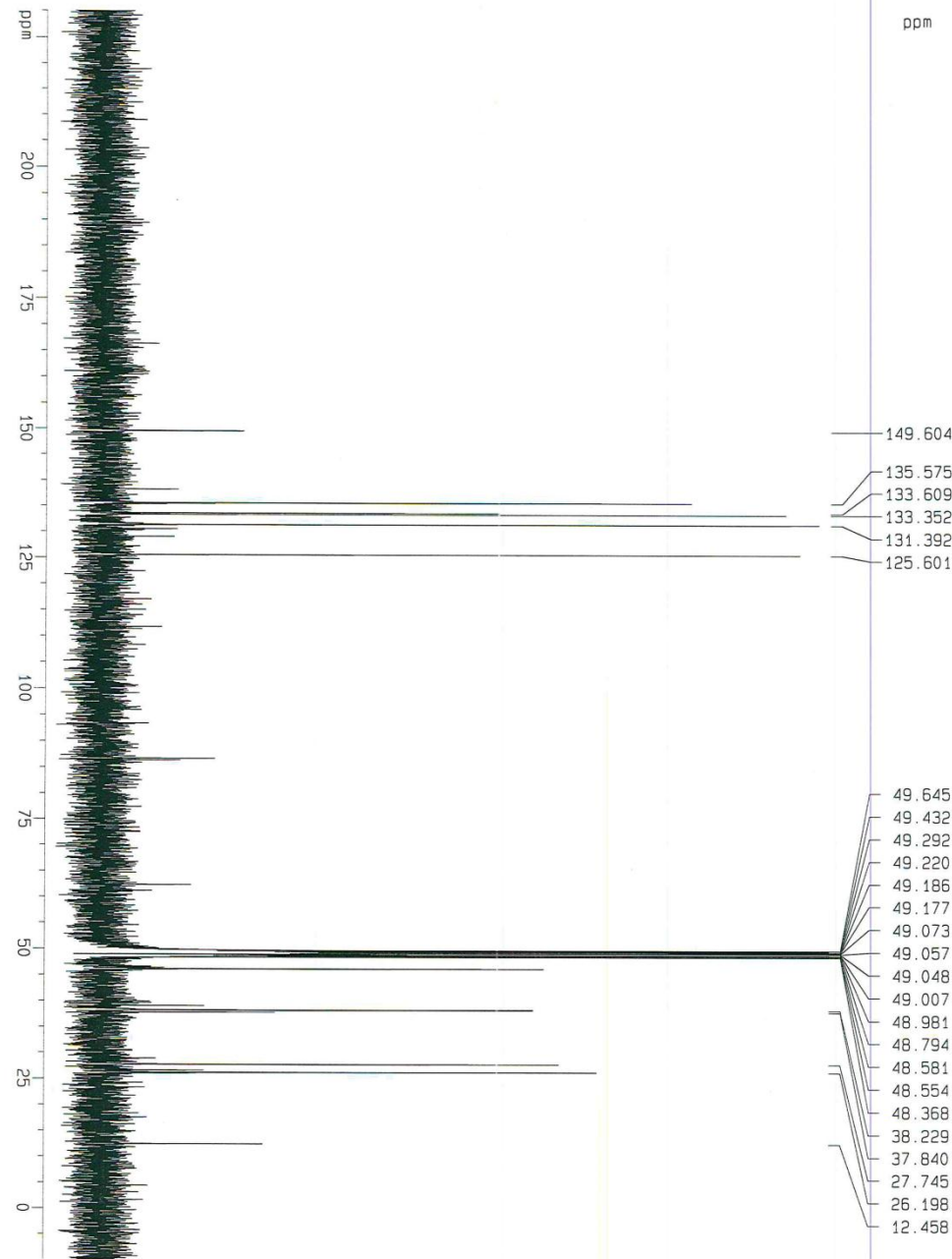
# Compound 15:



Compound 21, 24 and 28:



AK Prof. Sandhoff  
 Name Mack  
 TM 590  
 AUTO\_N.13C\_CPD MeOD u sandhoff 98



Current Data Parameters  
 USER sandhoff  
 NAME 32x4a098  
 EXPNO 11  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20050811  
 Time 22.27  
 INSTRUM spect  
 PROBRD 5 mm PABBO BB-  
 PULPROG zgpg30

TD 65536  
 SOLVENT MeOD  
 NS 5120  
 DS 4  
 SMH 26178.010 Hz  
 FIDRES 0.399445 Hz  
 AQ 1.2517875 sec  
 RG 5160.6  
 DW 19.100 usec  
 DE 6.00 usec  
 TE 303.0 K  
 D1 0.60000002 sec  
 d11 0.03000000 sec  
 d12 0.00002000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 13C  
 P1 7.90 usec  
 PL1 6.00 dB  
 SFO1 100.6237984 MHz

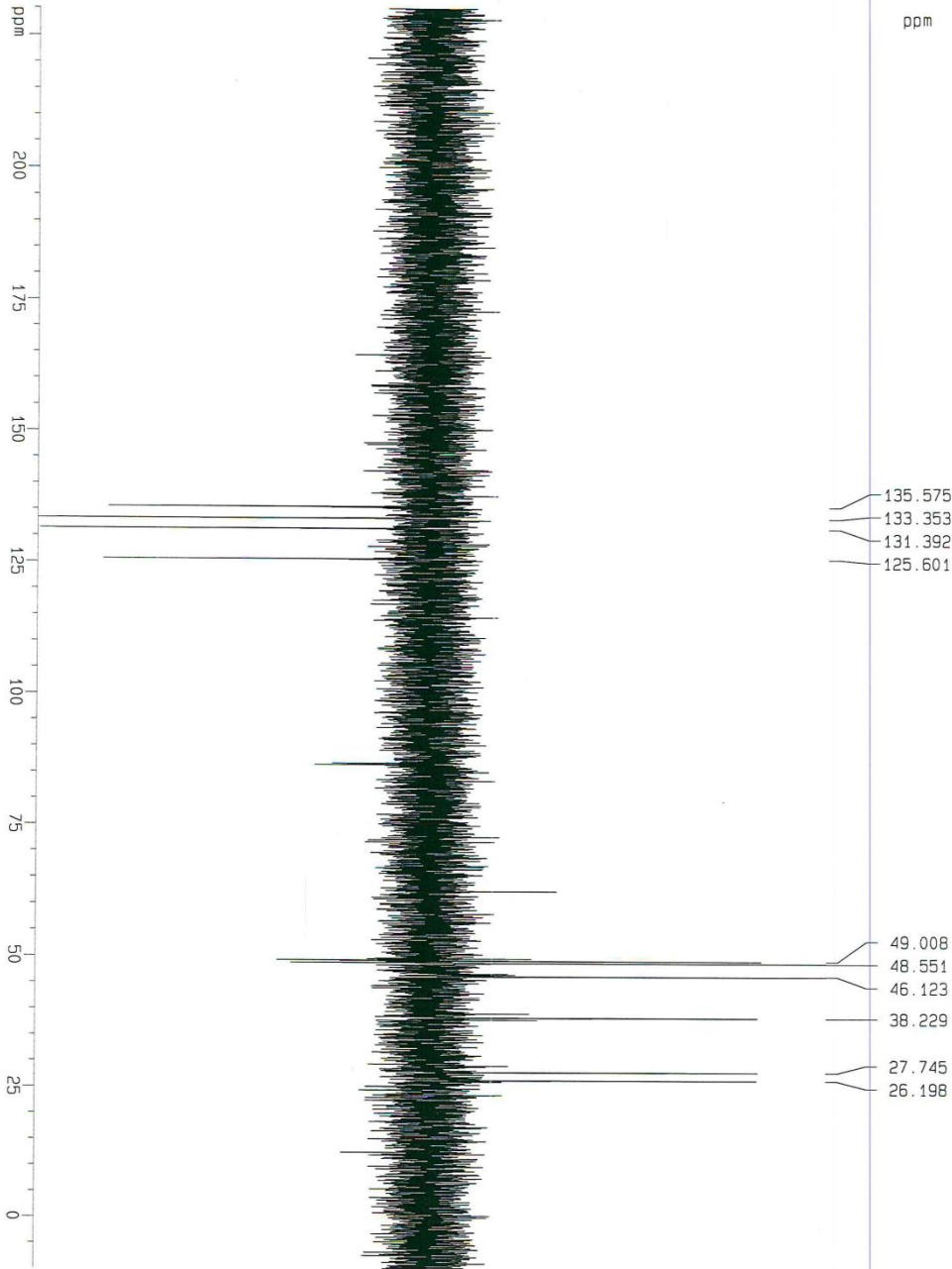
\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 92.00 usec  
 PL2 0.00 dB  
 PL12 22.00 dB  
 PL13 26.00 dB  
 SF02 400.1319206 MHz

F2 - Processing parameters  
 SI 131072  
 SF 100.6126274 MHz  
 WDW EM  
 SSB 0  
 LB 0.60 Hz  
 GB 0  
 PC 3.00

10 NMR plot parameters  
 CX 22.00 cm  
 CY 12.70 cm  
 F1P 230.000 ppm  
 F1 23140.90 Hz  
 F2P -10.000 ppm  
 F2 -1006.13 Hz  
 PPKCM 10.90909 ppm/cm  
 HZCM 1097.59229 Hz/cm

AK Prof. Sandhoff  
 Name Mack  
 TM 590  
 AUTO.N.13C\_D135 Me00 u sandhoff 98

ppm  
 135.575  
 133.353  
 131.392  
 125.601



Current Data Parameters  
 USER sandhoff  
 NAME 32x4d98  
 EXPNO 12  
 PROCNO 1

Date\_ 20050811  
 Time 23.02  
 INSTRUM spect  
 PROBRD 5 mm PABBO BB-  
 PULPROG zgpg30  
 DELTA135  
 10  
 65536

SOLVENT Me00  
 NS 1024  
 DS 4

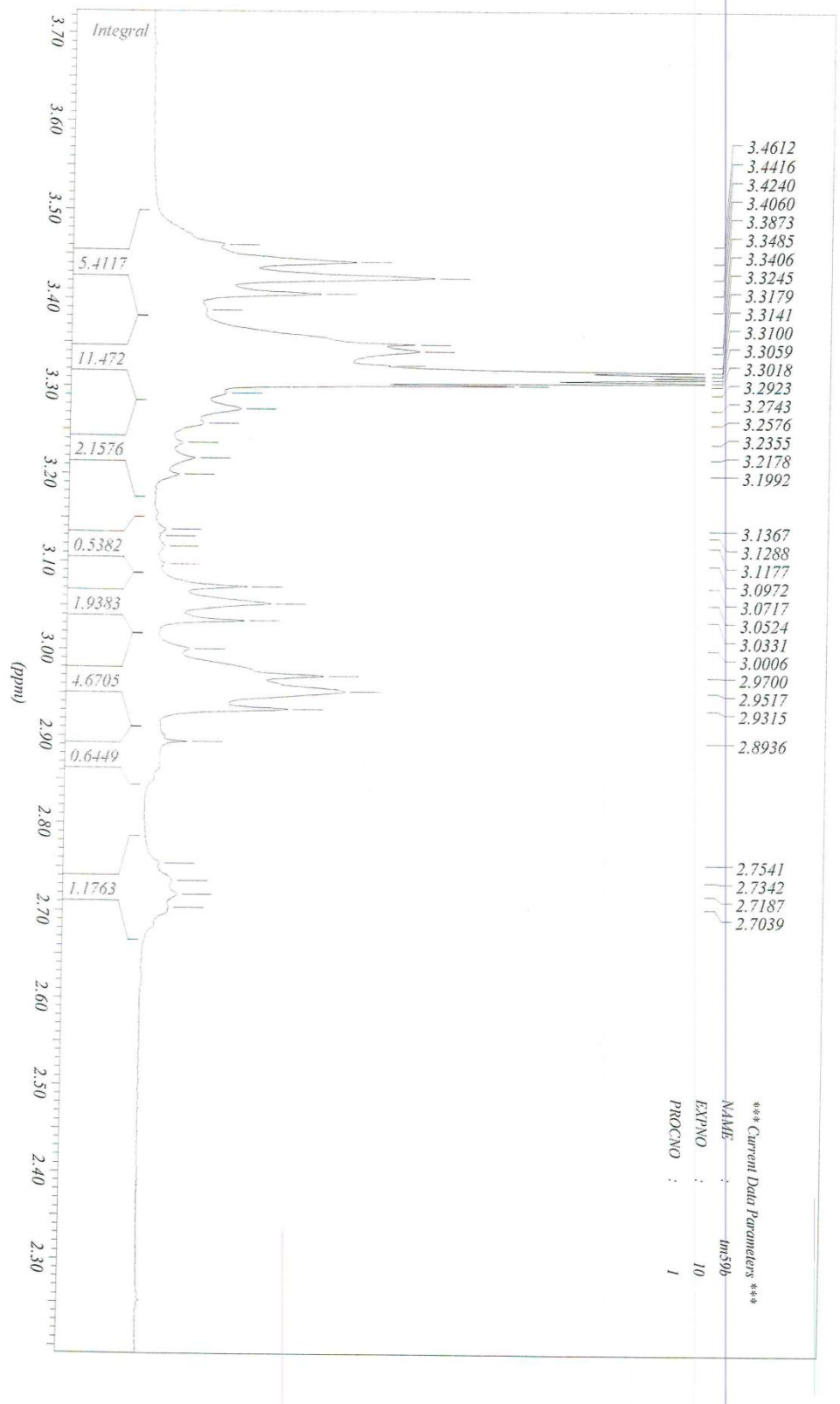
SMH 26178.010 Hz  
 FIDRES 0.399445 Hz  
 AQ 1.25177875 sec  
 RG 20642.5  
 DW 19.100 usec  
 DE 5.00 usec  
 TE 303.0 K  
 CNST2 145.0000000  
 D1 0.60000002 sec  
 d2 0.00344828 sec  
 d12 0.0002200 sec  
 DELTA 0.0001006 sec  
 KCRCST 0.0000000 sec  
 KCMKRC 0.01500000 sec

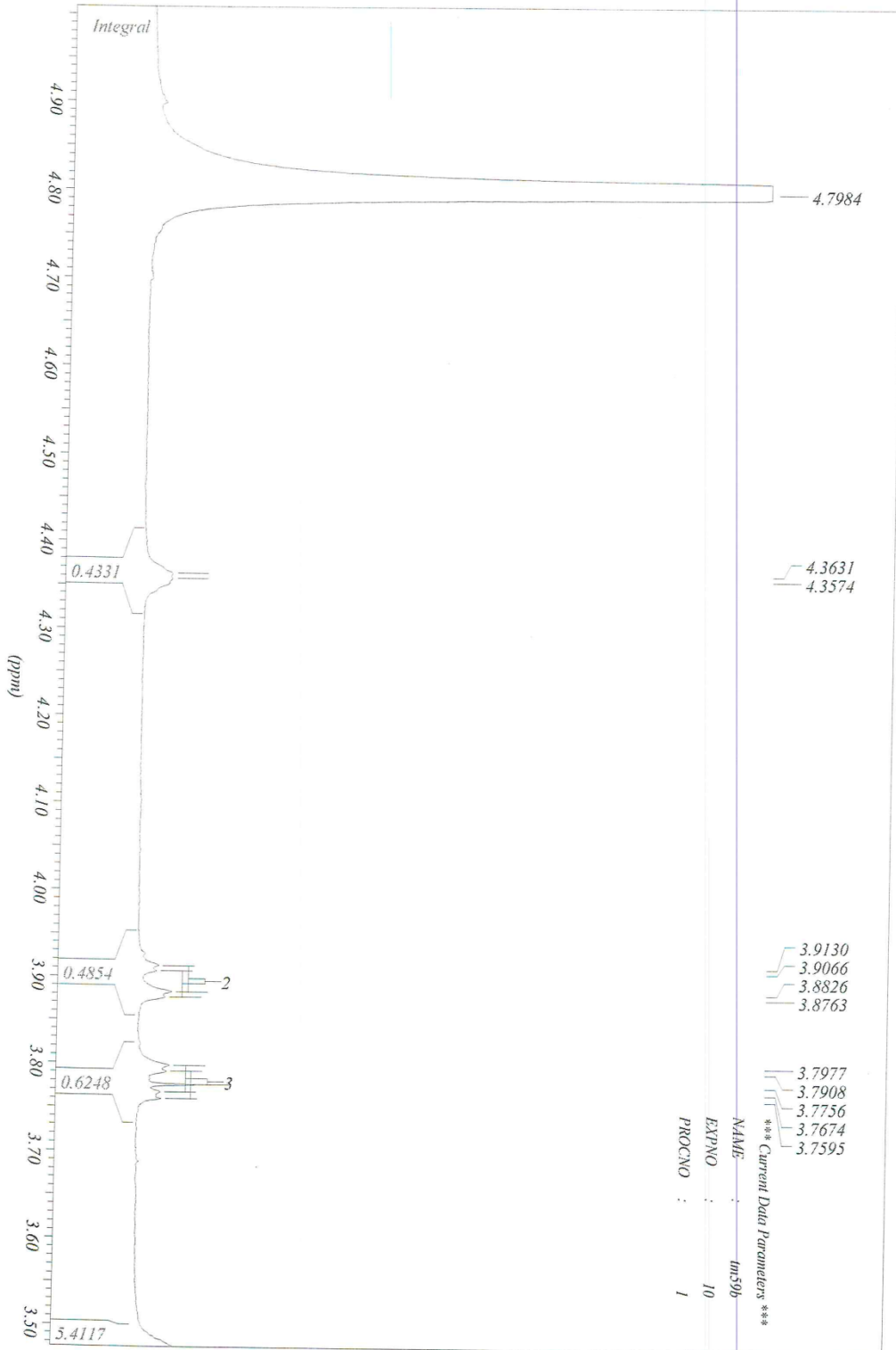
\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 13C  
 P1 7.90 usec  
 P2 15.80 usec  
 PL1 6.00 dB  
 SF01 100.6237954 MHz

\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CPOPRG2 waltz16  
 NUC2 1H  
 P3 7.70 usec  
 P4 15.40 usec  
 PCPO2 92.00 usec  
 PL2 0.00 dB  
 PL12 22.00 dB  
 SF02 400.1319206 MHz

F2 - Processing parameters  
 SI 131072  
 SF 100.6126274 MHz  
 MDW EM  
 SSB 0  
 LB 0.60 Hz  
 GB 0  
 PC 3.00

10 NMR plot parameters  
 CX 22.00 cm  
 CY 7.00 cm  
 F1P 230.000 ppm  
 F1 23140.90 Hz  
 F2P -10.000 ppm  
 F2 -1006.13 Hz  
 PPMCKM 10.90609 ppm/cm  
 HZCM 1097.59229 Hz/cm





\*\*\* Current Data Parameters \*\*\*

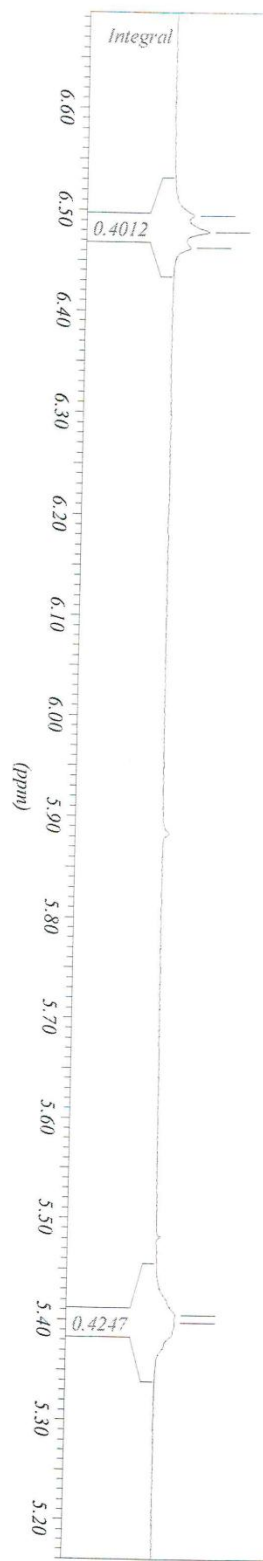
NAME : tm50b  
 EXPNO : 10

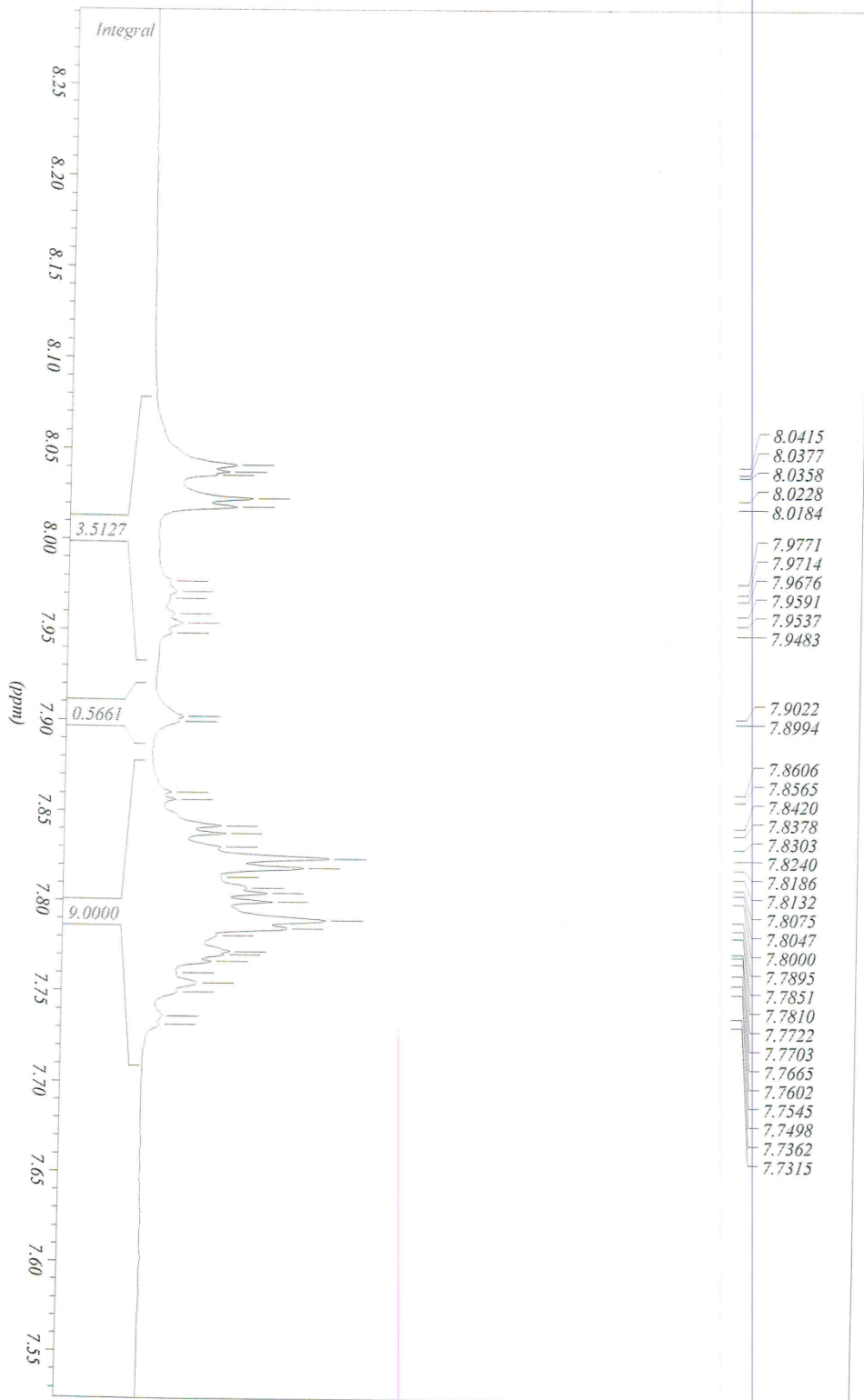
PROCNO : 1

6.4949  
 6.4788  
 6.4630

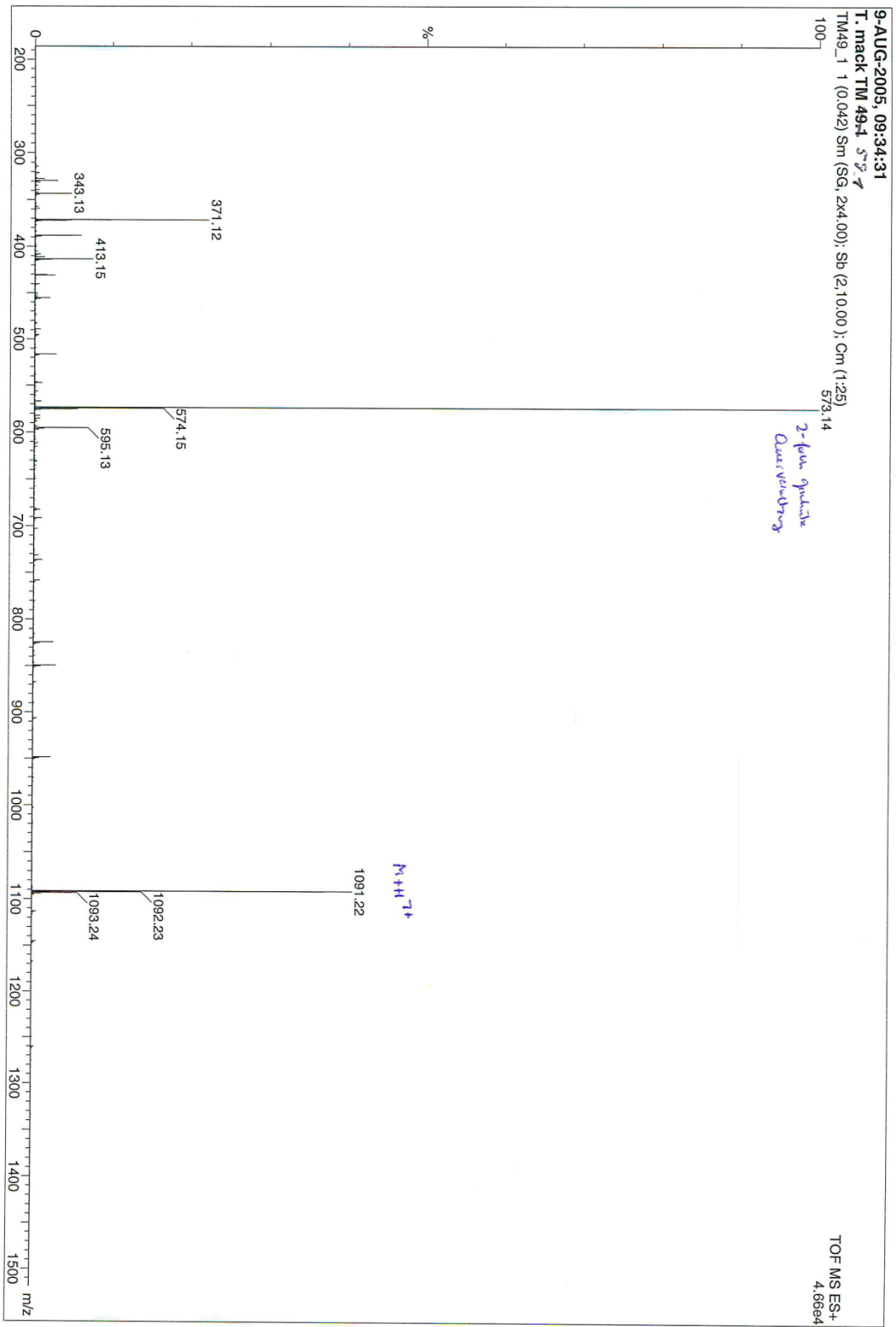
5.4046  
 5.3973

Identifier	Chem. Shift [ppm]	J [Hz]
1	6.4786	6.3789
		6.3789
2	3.8946	2.5263
		12.1262
3	3.7789	2.9684
		12.3157









AK Prof. Sandhoff  
 Name Mack  
 TM 59a  
 AUTO N. 1H\_STAND DMSO u sandhoff 20



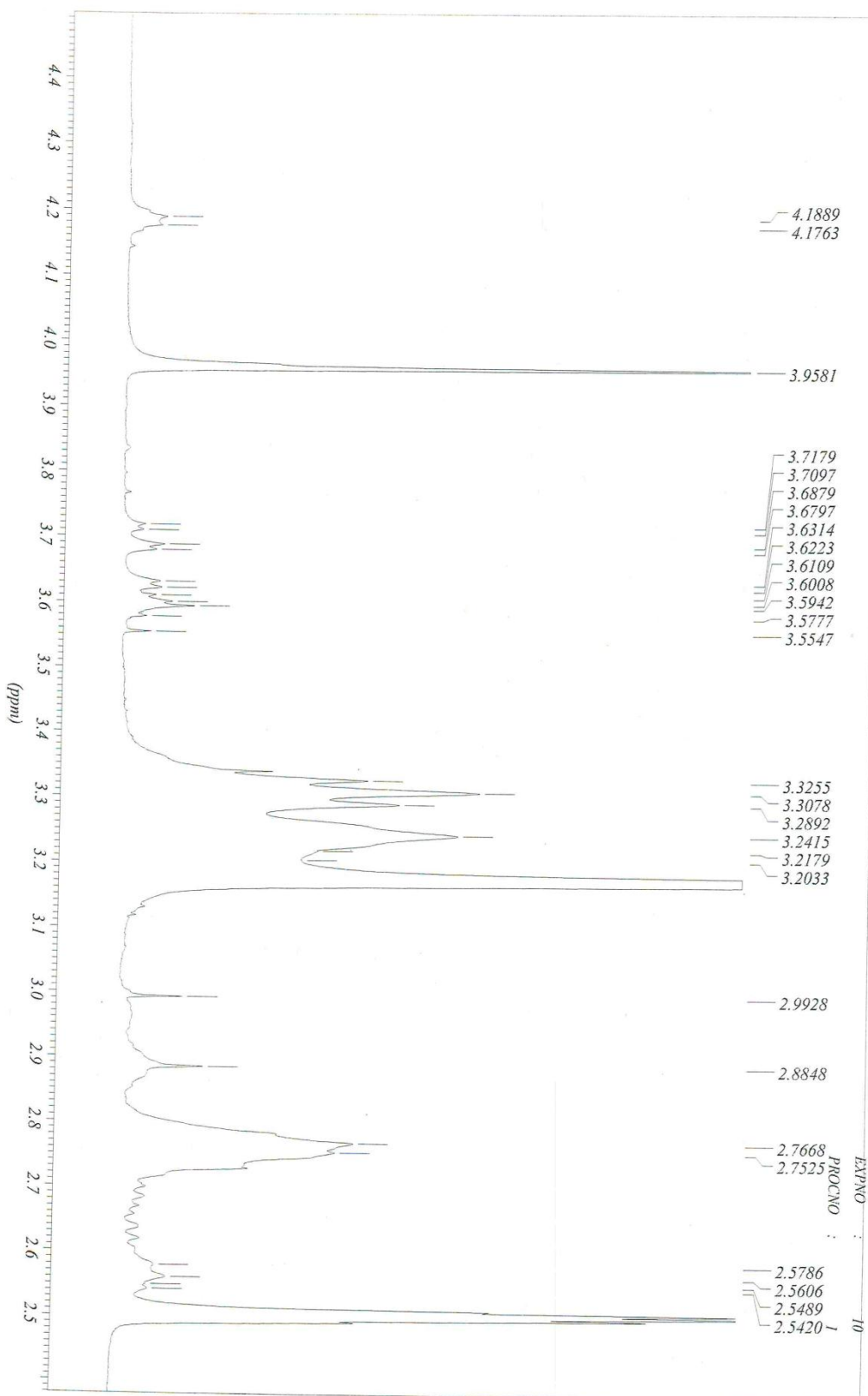
Current Data Parameters  
 USER sandhoff  
 NAME 32x48020  
 EXPNO 10  
 PROCNO 1

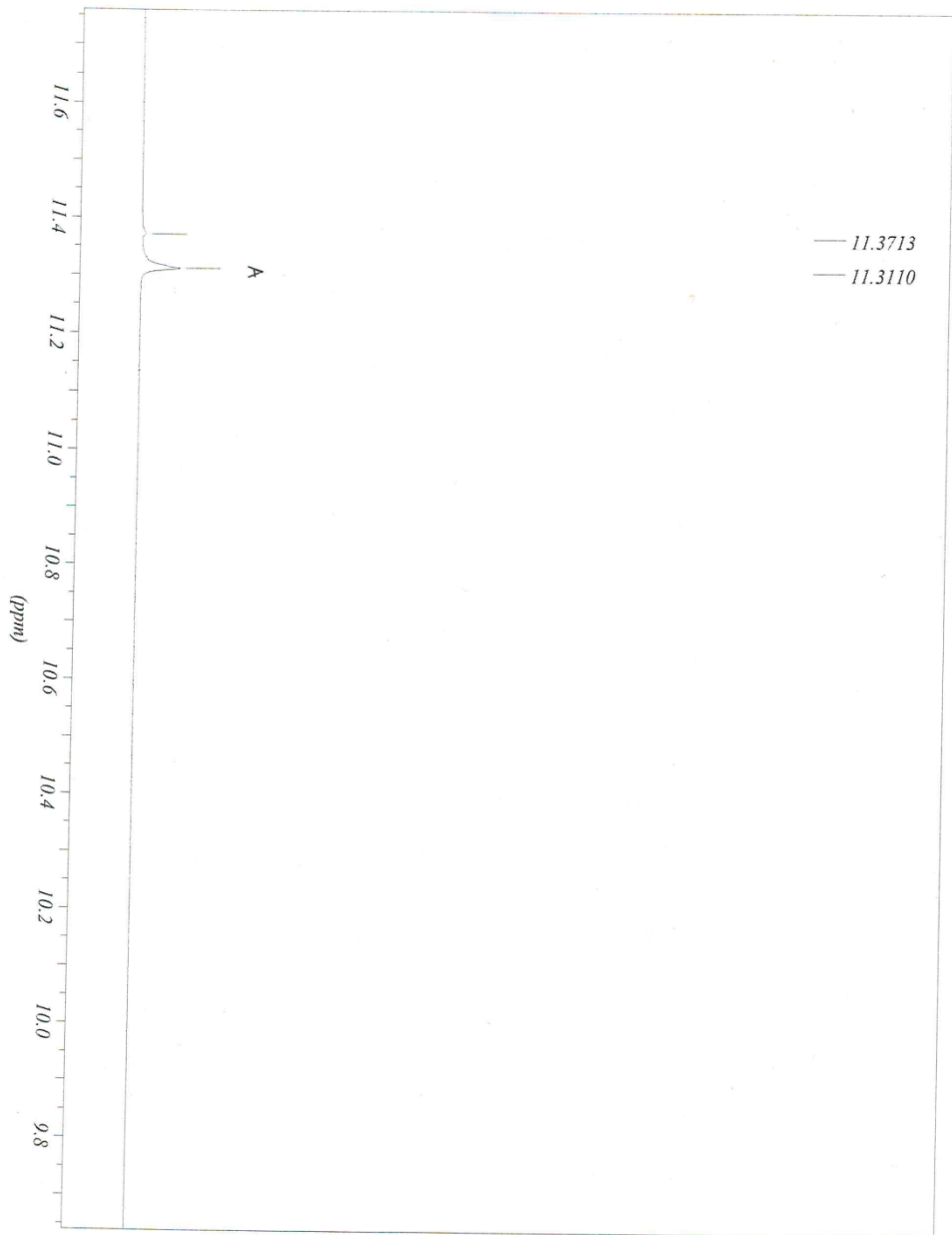
F2 - Acquisition Parameters  
 Date\_ 20050808  
 Time\_ 16:25  
 INSTAUM spect  
 PROBHD 5 mm PABBO BB-  
 PULPROG zg  
 TD 65536  
 SOLVENT DMSO  
 NS 16  
 DS 2  
 SMH 8278.146 Hz  
 FIDRES 0.125314 Hz  
 AQ 3.9584243 sec  
 RG 71.8  
 DM 60.400 usec  
 DE 5.00 usec  
 TE 303.0 K  
 D1 1.00000000 sec  
 MCOREST 0.00000000 sec  
 MCORR 0.01500000 sec

==== CHANNEL f1 =====  
 NUC1 1H  
 P1 7.50 usec  
 PL1 0.00 dB  
 SF01 400.1324710 MHz

F2 - Processing parameters  
 SI 65536  
 SF 400.1300050 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 3.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 14.00 cm  
 F1P 11.000 ppm  
 F1 4401.43 Hz  
 F2P -1.000 ppm  
 F2 -400.13 Hz  
 PPGCM 0.54545 ppm/cm  
 HZCM 218.29273 Hz/cm





\*\*\* Current Data Parameters \*\*\*  
NAME : 32x4d120  
EXPNO : 10  
PROCNO : 1